(CH_3CN, 92). Anal. Calcd for $C_7H_7NO_2S_2$: C, 41.77; H, 3.51; N, 6.96. Found: C, 41.65; H, 3.44; N, 6.76.

4-(2,5-Dithiacyclopentylidene)-3-phenylisoxazol-5(4*H*)-one (3) was obtained analogously from 3-phenylisoxazol-5(4*H*)-one: yield 65%; mp 270-272 °C, ^{1}H NMR (DMSO-d_6) δ 7.53-7.49 (m, 5 H), 3.72-3.70 (m, 4 H); IR (KBr) 1722, 1527, 1385, 883 cm^{-1}. MS (Varian Mat, 150 °C), m/z 263 (M^+, 100), 235 (5), 205 (12), 167 (12), 159 (7), 145 (35), 143 (53), 103 (PhCN, 5), 92 (25), 88 (C_2S_2, 9), 77 (18), 64 (S_2, 2), 60 (10), 44 (CO_2, 5); MS (Varian Mat, 885 °C), m/z 263 (M^+, 0), 235 (0), 205 (0), 167 (0), 159 (12), 145 (0), 143 (0), 103 (PhCN, 100), 92 (0), 88 (C_2S_2, 23), 77 (32), 64 (S_2, 17), 60 (7), 44 (CO_2, 53). Anal. Calcd for $C_{12}H_9NO_2S_2$: C, 54.73; H, 3.45; N, 5.32. Found: C, 54.66; H, 3.28; N, 5.22.

2,5-Dithiacyclopentylideneketene (4). FVP of **1** at temperatures between 450 and 675 °C with Ar matrix isolation of the products at 12 K gave a ketene band at 2078, 2094 (shoulder) cm^{-1}, increasing in intensity with the temperature. Bands due to CO_2 (2340 cm^{-1}) and acetone were formed at the same time, and bands due to unreacted **1** decreased in intensity and had virtually disappeared at 700 °C.

FVP of **1** at 675 °C (10^{-4} mbar) with neat isolation of the product at 77 K gave rise to a very strong ketene absorption at 2080 cm^{-1} together with bands due to acetone (Figure 2) [IR (**4**, 77 K) 2080 (vs), 1625, 1420, 1293, 1054, 917, 854 cm^{-1}]. This material was stable on warming to -60 °C and disappeared on further warming to -10 °C. At -50 °C the half-life of the ketene was ca. 20 min.

In an analogous experiment, **1** was pyrolyzed at 650 °C, and the product was collected at 77 K on a cold finger. CO_2 and the majority of acetone were pumped away at -60 °C, the cold finger was recooled, and CD_2Cl_2 was distilled onto the sample. Warming to -50 °C allowed the CD_2Cl_2 solution to flow into an NMR tube [^{1}H NMR (CD_2Cl_2, -45 °C) δ 3.70 (s)]. The IR spectrum of this solution confirmed the presence of the strong C=C=O stretch at 2080 cm^{-1}, surviving brief exposure to room temperature.

The mass spectrum of **4** was obtained on both Kratos MS25RFA and Varian Mat 311 spectrometers with on-line FVP appliances. The temperature profiles of m/z 246 (**1**) and 144 (**4**) are shown in Figure 1. CAMS of m/z 144 (Variant Mat 311), m/z 116 (M^+ - CO, 75%), 88 (41), 84 (36), 60 (100).

Ethenedithione (5). Mass spectra of C_2S_2 (m/z 88) were obtained on the Kratos MS25RFA and Varian Mat 311 spectrometers with on-line FVP appliances. The temperature profile for C_2S_2 production from **1** is given in Figure 1 and from **2** and **3** in Figure 3. The CAMS of **5** (Varian Mat) produced by FVP of **1** at 590 °C, **2** at 778 °C, and **3** at 797 °C are shown in Figure 3. IR spectra (Ar, 12 K) were obtained on FVP of **1** at 700-1000 °C and of **2** and **3** at 600-1000 °C. Representative spectra are given in Figure 5: C_2S_2, 1180 cm^{-1}; ^{34}SCCS, 1176 cm (ca. 10%); S^{13}CCS, 1163 cm^{-1} (ca. 2.5%). The UV spectrum similarly obtained by FVP of **3** at 700 °C is shown in Figure 6. Identical spectra of the 350-400-nm region were obtained by FVP of **1** (900 °C) and **2** (800 °C). λ_{max} 361, 363, 369, 370, 377, 378, 384, 385 (sh), 392 nm.

The IR and UV bands ascribed to **5** disappeared on broad-band photolysis (1000 W high pressure Hg lamp) in 9 min. An increased but complex band at 1280 cm^{-1} developed during the irradiation and is ascribed to CS. Neat isolation of **5** at 12 K gave an IR band at 1170 cm^{-1}, which disappeared on warming to 60 K. The use of an insert of quartz rods in the pyrolysis tube had hardly any effet on the strength of the IR signal observed for **5** at 1180 cm^{-1} as long as the pressure was 10^{-4} mbar. Use of a higher partial pressure created by fast sublimation of **1**, **2**, or **3** or pyrolysis temperatures above 1000 °C caused increased formation of CS and CS_2 (1274 and 1527 cm^{-1}, respectively) and partial or complete disappearance of **5** (1180 cm^{-1}).

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Generation of [β-(Phenylsulfonyl)alkylidene]carbenes from Hypervalent Alkenyl- and Alkynyliodonium Tetrafluoroborates and Synthesis of 1-(Phenylsulfonyl)cyclopentenes

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Abstract: Michael-type addition of benzenesulfinic acid to alkynyl(phenyl)iodonium tetrafluoroborates in methanol gives stereoselectively (*Z*)-(β-(phenylsulfonyl)alkenyl)iodonium tetrafluoroborates in high yields. [β-(Phenylsulfonyl)alkylidene]carbenes derived from the (*Z*)-(β-(phenylsulfonyl)alkenyl)iodonium tetrafluoroborates by base treatment predominantly undergo intramolecular 1,5-carbon-hydrogen insertions to give 1-(phenylsulfonyl)cyclopentenes along with a small amount of rearranged alkynes, which is in a marked contrast with the facile 1,2-migration of β-(phenylsulfenyl) and β-(phenylsulfinyl) groups of alkylidenecarbenes. Reaction of alkynyl(phenyl)iodonium tetrafluoroborates with benzenesulfinates directly affords 1-(phenylsulfonyl)cyclopentenes via tandem Michael-carbene insertion reactions. The mechanism of 1,2-migration of [β-(phenylsulfonyl)alkylidene]carbenes is also discussed.

α-Elimination of vinyl halides[1] and vinyl triflates[2] constitutes the most general method for generation of alkylidenecarbenes.[3] Recently we reported that base treatment of vinyl(phenyl)iodonium tetrafluoroborates leads to α-elimination under mild conditions to give alkylidenecarbenes.[4] While the reactive intermediates resulting from base-induced α-elimination of vinyl halides are believed to be carbenoids,[5] the species generated from vinyl triflates and vinyliodonium salts are free carbenes. Alkylidenecarbenes are singlets with a fairly sizable singlet-triplet energy difference and electrophilic species, as are most carbenes,[3,6] They readily

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(1) (a) Erickson, K. L.; Wolinsky, J. *J. Am. Chem. Soc.* **1965**, *87*, 1142. (b) Köbrich, G.; Drischel, W. *Tetrahedron* **1966**, *22*, 2621. (c) Walsh, R. A.; Bottini, A. T. *J. Org. Chem.* **1970**, *35*, 1086. (d) Fischer, R. H.; Baumann, M.; Köbrich, G. *Tetrahedron Lett.* **1974**, 1207. (e) Baumann, M.; Köbrich, G. *Tetrahedron Lett.* **1974**, 1217. (f) Wolinsky, J.; Clark, G. W.; Thorstenson, P. C. *J. Org. Chem.* **1976**, *41*, 745. (g) Cunico, R. F.; Han, Y. K. *J. Organomet. Chem.* **1976**, *105*, C29. (h) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5035. (i) Iyoda, M.; Sakaitani, M.; Miyazaki, T.; Oda, M. *Chem. Lett.* **1984**, 2005. (j) Harada, T.; Nozaki, Y.; Yamaura, Y.; Oku, A. *J. Am. Chem. Soc.* **1985**, *107*, 2189. (k) Barluenga, J.; Rodriguez, M. A.; Campos, P. J.; Asensio, G. *J. Am. Chem. Soc.* **1988**, *110*, 5567.

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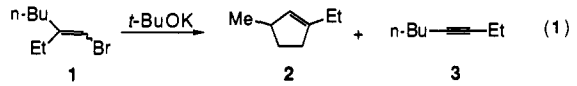
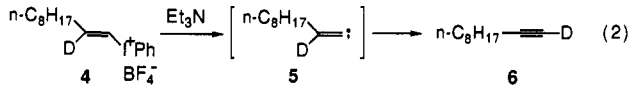
insert into various types of σ bonds like carbon–hydrogen, oxygen–hydrogen, and silicon–hydrogen bonds.

Intramolecular C–H insertions of alkylidenecarbenes are highly regioselective and afford substituted cyclopentenes via 1,5-C–H insertions,[1,7,8] which is in marked contrast to the results of the saturated relatives.[6,9] For example, Wolinski and Erickson have reported that α-elimination of the terminal vinyl bromide **1** with *t*-BuOK at 240 °C afforded the 1,5-C–H insertion product **2** and the rearranged alkyne **3**.[1a,f] They also found that 1,5-C–H insertions of alkylidenecarbenes into an unactivated primary C–H bond is a slow process and relative reactivities of the C–H bonds at C-5 are in the order of tertiary > secondary (benzylic) > secondary ≫ primary.



1 **2** **3**

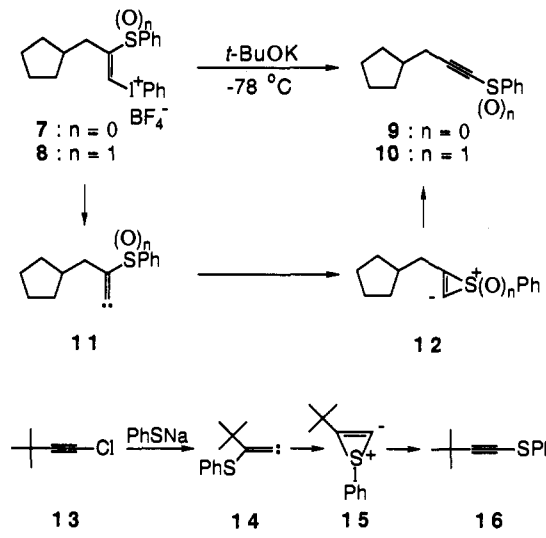
The high regio- and chemoselectivity makes insertions of alkylidenecarbenes a useful route to the synthesis of cyclopentenes. However, when alkylidenecarbenes have hydrogens or aryl groups at the β-position, the intramolecular C–H insertion can no longer compete with an alternative 1,2-shift of these groups, which yields the rearranged alkynes.[4,7a,10] Thus, the alkylidenecarbene **5**, generated from (*E*)-(β-deuteriovinyl)iodonium salt **4** via the reductive α-elimination by the reaction with triethylamine readily rearranges to the deuterioalkyne **6**.



4 **5** **6**

Similarly, the considerable migratory aptitude of β-(phenylsulfenyl) and β-(phenylsulfinyl) groups was demonstrated by the reaction of the substituted vinyliodonium salts **7** and **8** with *t*-BuOK at −78 °C. The isolated products from the reaction were the alkynyl sulfide **9** and the alkynyl sulfoxide **10**, respectively, and the corresponding 1,5-C–H insertion products were not detected.[4] The intermediacy of sulfur ylides **12** produced by nucleophilic attack of lone pair electrons on the sulfur atoms to the electron-deficient carbenic center of the resulting alkylidenecarbenes **11** would reasonably explain the formation of these rearranged alkynes. In the formal nucleophilic substitution at the acetylene triple bond of **13** by thiophenolate yielding the sulfide **16**, a similar mechanism involving the formation of sulfur ylide **15**, the so-called Viehe onium mechanism, has been proposed[11,12]

Scheme I



Scheme II

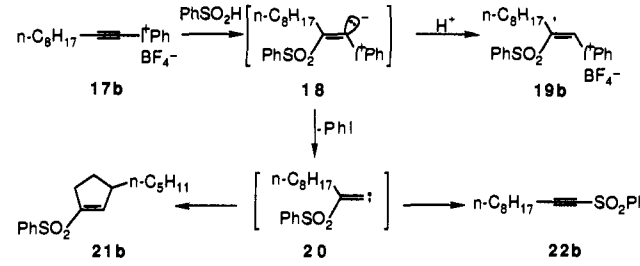


Table I. Solvent Effect on Product Ratios in the Reaction of **17b** with Benzenesulfinic Acid

entry	solvent	temp, °C	yield,[a] %	product ratio 19b:(21b + 22b)	product ratio 21b:22b
1	benzene	25	94	60:40	71:29
2	Et_2O	0	72	38:62	76:24[b]
3	dioxane	25	87	43:57	80:20
4	CH_2Cl_2	0	64	38:62	55:45[b]
5	MeOH	0	100	100:0	
6	MeOH[c]	0	100	51:49	78:22
7	H_2O	0	83	40:60	72:28
8	H_2O[d]	25	72	61:39	68:32[b]
9	H_2O[e]	0	96	66:34	76:24[b]

[a] Isolated yields. [b] Determined by NMR. [c] 10 equiv of BF_3–Et_2O was used as an additive. [d] 2 equiv of BF_3–Et_2O was used as an additive. [e] 10 equiv of HBF_4 was used as an additive.

(Scheme I).

If the intermediacy of sulfur ylides **12** in the alkyne-forming reaction is valid, it seems reasonable to assume that decreasing nucleophilicity of the β-sulfur atoms of the alkylidenecarbenes **11** by the conversion to the corresponding sulfone would greatly retard the rate of 1,2-shift of the β-substituent, and thereby the 1,5-C–H insertion of carbenes providing the desired 1-(phenylsulfonyl)cyclopentenes becomes important. The present contribution addresses the above working hypothesis.

Results and Discussion

Synthesis of (*Z*)-(β-Sulfonylalkenyl)(phenyl)iodonium Tetrafluoroborates. All the attempts to oxidize **7** and **8** to the corre-

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(8) Intramolecular insertions of alkylidenecarbenes into C–H bonds at C-4 or C-6 have not been observed. It is uncertain whether or not the formation of methylenecyclopropanes from α-elimination of vinyl bromides involves 1,3-C–H insertions of alkylidenecarbenes.[1f]

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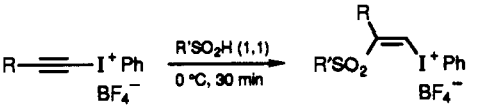
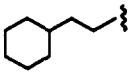
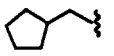
Table II. Synthesis of (*Z*)-(β-Sulfonylalkenyl)iodonium Tetrafluoroborates **19** and **25–27** in Methanol



17 **19**

entry	17	R	R′	product	yield,[a] %	NOE,[b] %
1	**17a**	Me	Ph	**19a**	77	7.3
2	**17b**	*n*-C_8H_{17}	Ph	**19b**	100	7.0
3	**17c**		Ph	**19c**	88	6.5
4	**17d**		Ph	**19d**	99	6.5
5	**17e**	$Ph(CH_2)_3$	Ph	**19e**	93	4.7
6	**17f**	$HO(CH_2)_2$	Ph	**19f**	64	*c*
7	**17b**	*n*-C_8H_{17}	*p*-$NO_2C_6H_4$	**25**	90	*c*
8	**17b**	*n*-C_8H_{17}	*p*-$MeOC_6H_4$	**26**	91	2.7
9	**17a**	Me	*n*-Bu	**27**	89	

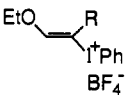
[a] Isolated yields. [b] NOE enhancement between the vinylic and allylic protons. [c] Not determined.

sponding sulfone **19d** led to disappointing results. For the synthesis of (β-sulfonylalkenyl)iodonium salts, we turned our attention to the reaction of alkynyl(phenyl)iodonium salts with benzenesulfinic acid (BSA), because it has been well established that the electron-deficient alkynyl(phenyl)iodonium salts[13] serve as powerful Michael acceptors toward a variety of nucleophiles.[14] Furthermore, BSA, which is a strong acid with pK_a of 1.84[15] and a good *S* nucleophile, acts as a useful Michael donor toward the activated olefins and acetylenes.[16]

In dichloromethane, reaction of 1-decynyl(phenyl)iodonium tetrafluoroborate (**17b**) with BSA at 0 °C afforded only a 24% yield of (*Z*)-(β-(phenylsulfonyl)vinyl)iodonium tetrafluoroborate (**19b**), along with the alkylidenecarbene-derived products, the cyclopentene **21b** (22%) and the alkyne **22b** (18%). Conjugate addition of BSA may lead to the formation of the (*Z*)-alkenyliodonium ylide intermediate **18**, which can be trapped stereoselectively by a proton to give (*Z*)-**19b**. Similar trans addition of azides to alkynyliodonium salts has been reported to give (*Z*)-(β-azidovinyl)iodonium salts.[14g,i] Alternatively, the ylide **18** can lose iodobenzene by a competing reductive elimination to give the alkylidenecarbene **20**, which further undergoes intramolecular 1,5-C–H insertion or 1,2-rearrangement yielding **21b** or **22b**, respectively (Scheme II).

To obtain (*Z*)-**19b** selectively, the reaction was carried out in a variety of protic and aprotic solvents and the results are summarized in Table I. Methanol as a solvent gave (*Z*)-**19b** in quantitative yield (Table I, entry 5), while all the other solvents gave a mixture of products. These observations probably reflect the low basicity of the iodonium ylide **18**, which makes the subsequent protonation step of **18** a slow process. The low basicity of **18** might be attributed to the considerable stabilization of the ylide carbanion by both α-(phenyliodonio) and β-(phenylsulfonyl) groups. Thus, the effective concentration of protons in methanol, which is higher than that in the other solvents, leads to facile protonation of **18** and thereby exclusive formation of (*Z*)-**19b**. Since BSA is sparingly soluble in water, the effective concentration of protons in the solvent would be low. In fact, the 40:60 ratio of the addition product (*Z*)-**19b** to the carbene-derived products **21b** and **22b** in water was reversed by the addition of acids such as BF_3 and HBF_4 (Table I, entries 7–9). Surprisingly, a 1:1 ratio of products was obtained by the addition of BF_3 in methanol.

The addition of BSA was stereoselective and no formation of the *E* isomer of **19b** was detected in all of the reactions.[17] The *Z* stereochemistry of **19b** was established by the observation of a large nuclear Overhauser effect (NOE) enhancement (7%) between the vinylic and allylic protons. This result is in good agreement with the well-known anti stereoselectivity of nucleophilic additions to activated and unactivated acetylenes.[18] Therefore, as a possible structure of the intermediate alkenyliodonium ylide generated in the BSA addition reaction, the bent structure **18** seems to be more attractive than the linear alternative. Experiments in support of such a bent structure of vinyliodonium ylides have been reported: deuterium exchange of the vinylic protons of **23** with base and the fluoride ion induced or base-induced protodesilylation of **24** proceed with retention of the stereochemistry via iodonium ylide intermediates.[19]



23 : R = H
24 : R = $SiMe_3$

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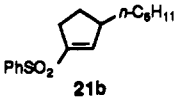
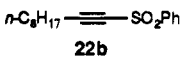
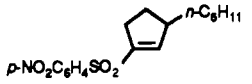
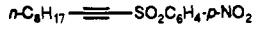
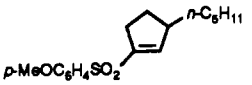
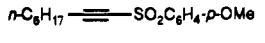
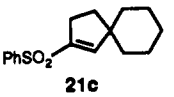
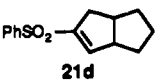
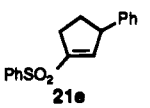
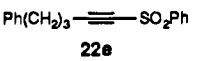
(19) Ochiai, M.; Kunishima, M.; Fuji, K.; Shiro, M.; Nagao, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1076.

Table III. Reaction of (*Z*)-(β-Sulfonylalkenyl)iodonium Salts with Et_3N in Benzene

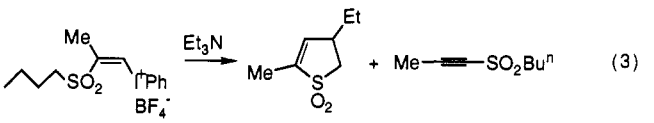
entry	salt	temp, °C (time, h)	product(s) cyclopentene	product(s) alkyne	yield,[a] % (ratio[b])
			 **21b**	 **22b**	
1	**19b**	25 (0,5)	**21b**	**22b**	97 (77:23)
2	**19b**	25 (0.5)[c]	**21b**	**22b**	86 (78:22)
3	**19b**	0 (0.5)[d]	**21b**	**22b**	95 (75:25)
4	**25**	25 (0.5)			100 (72:28)
5	**26**	25 (0.5)			98 (79:21)
6	**19c**	25 (0.5)	 **21c**	 **22c**	92 (70:30)
7	**19d**	25 (0.5)	 **21d**	 **22d**	89 (80:20)
8	**19e**	25 (0.5)	 **21e**	 **22e**	97 (74:26)

[a] Isolated yields. [b] Ratios of cyclopentenes to alkynes. [c] In dioxane. [d] In water.

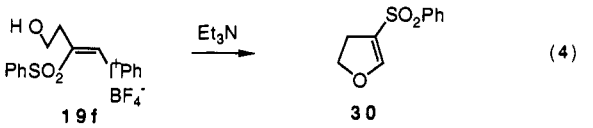
The results of Michael-type additions of arene- and alkanesulfinic acids to **17** in methanol are summarized in Table II. In general, the reactions are very rapid, complete within 30 min at 0 °C, and afford (*Z*)-(β-sulfonylalkenyl)iodonium tetrafluoroborates **19** and **25–27** in high yields.

Generation of Alkylidenecarbenes from (*Z*)-(β-Sulfonylalkenyl)iodonium Tetrafluoroborates by Base-Induced α-Elimination. Exposure of **19b** to *t*-BuOK, which was used as a base to undergo reductive α-elimination of **7** and **8**, gave a complex mixture of products; however, triethylamine afforded clean carbene-derived products (Table III). As we expected, the reaction predominantly afforded the alkylidenecarbene-derived 1,5-C–H insertion product **21b**. Thus, with triethylamine in benzene, **21b** and the rearranged alkyne **22b** were obtained in a ratio of 77:23 (97%) (Table III, entry 1). Note that the reaction proceeds even in water, which dissolves the iodonium salt **19b**, yielding a similar ratio of products (Table III, entry 3). These results show that the migratory aptitude of the β-(phenylsulfonyl) group to the electron-deficient carbenic center is much lower than that of the β-(phenylsulfenyl) and -sulfinyl) groups. To gain further insight into the migratory aptitude of β-(arylsulfonyl) groups, α-elimination of the sulfones, **25** and **26**, having electron-withdrawing and -donating groups at the para position was carried out in benzene. The ratio of insertion to migration obtained from these compounds was found to be nearly the same as that of **19b**, which suggests that the electronic effect of these para substituents on product distribution might not be important (Table III, entries 4 and 5).

1-(Phenylsulfonyl)cyclopentenes have been shown to be useful intermediates for the synthesis of complex natural products.[20] Thus, the spiro and bicyclic cyclopentenes **21c** and **21d** were synthesized from the alkenyliodonium tetrafluoroborates **19c** and **19d** in 64 and 71% yields, respectively. The reaction provides a useful route to the synthesis of not only 1-(phenylsulfonyl)-cyclopentenes but also five-membered heterocycles. Exposure of **27** to triethylamine in dichloromethane gave raise to a 53% yield of the disubstituted 2-sulfolene **28** along with a 28% rearranged alkyne **29** (eq 3). (2-(Phenylsulfonyl)-4-hydroxy-1-butenyl)-iodonium tetrafluoroborate **19f** underwent an intramolecular 1,5-O–H insertion selectively without competing with the 1,2-rearrangement and provided the 2,3-dihydrofuran **30** in 61% yield; no rearranged alkyne could be detected (eq 4). The high selectivity for insertion observed with **19f** would be attributed to the more facile 1,5-O–H insertions of alkylidenecarbenes than the 1,5-C–H insertions. A similar preference for O–H insertions has been observed in the tandem Michael–carbene insertion (MCI) reactions of alkynyliodonium tetrafluoroborates with enolate anions of β-keto sulfones and β-keto nitriles.[14d]



27 **28** **29** (3)



19f **30** (4)

Tandem MCI Reactions of 17 with Benzenesulfinates. Formation of the carbene-derived product **21b** in the reaction of **17b** with BSA, albeit in low yield (Table I), encouraged us to explore for a more efficient method for the synthesis of 1-(phenylsulfonyl)cyclopentenes by tandem MCI reactions. The idea of generating the alkylidenecarbene **20** selectively from the intermediate alkenyliodonium ylide **18** is based on decreasing the rate of protonation toward **18** compared to that of reductive elimination. To realize this, it seems reasonable to carry out the reaction under nonacidic conditions. In fact, when **17b** was treated with sodium benzenesulfinate in water, only the carbene-derived products **21b** and **22b** were isolated in a total 89% yield, and the formation of **19b** could not be detected. The ratio of **21b** to **22b** was 74:26, almost the same as that obtained by the base-induced

(20) (a) Donaldson, R. E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1981**, *103*, 2108. (b) Saddler, J. C.; Donaldson, R. E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1981**, *103*, 2110. (c) Saddler, J. C.; Fuchs, P. L. *J. Am. Chem. Soc.* **1981**, *103*, 2112. (d) Paquette, L. A.; Lin, H.-S.; Gunn, B. P.; Coghlan, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 5818.

Table IV. Tandem MCI Reaction of **17b** with Benzenesulfinates

$$\mathbf{17b} \xrightarrow[0\ ^\circ C,\ 30\ min]{PhSO_2M} \mathbf{21b} + \mathbf{22b}$$

entry	M	$PhSO_2M$, equiv	solvent	yield,[a] % (ratio[b])
1	Li^+	1.1	H_2O	89 (74:26)
2	Na^+	1.1	H_2O	88 (74:26)
3	K^+	1.1	H_2O	79 (79:21)
4	Cs^+	1.1	H_2O	83 (76:24)
5	Bu_4N^+	1.1	H_2O	86 (76:24)
6	Li^+	1.1	THF	29 (88:12)
7	Na^+	1.1	THF	36 (91:9)
8	K^+	1.1	THF	57 (89:11)
9	Cs^+	1.2	THF	69 (89:11)
10	Bu_4N^+	1.1	THF	65 (94:6)
11	Bu_4N^+	1.9	THF	74 (98:2)

[a] Isolated yields. [b] Ratios of **21b** to **22b**.

α-elimination of **19b** (Table III). In order to investigate the effect of countercations of benzenesulfinates on product distribution and also to gain some insight into the freeness of the carbenic species generated, **17b** was treated with a variety of benzenesulfinates in water and tetrahydrofuran (THF), and the results are summarized in Table IV.

In water, however, the ratios of **21b** to **22b** obtained by the reactions with alkaline-metal salts of BSA and tetrabutylammonium benzenesulfinate were essentially constant within the range of 74–79:21–26. On the other hand, changing the solvent from water to THF increased the ratios for C–H insertions, as shown in entries 6–11 of Table IV. Tetrabutylammonium benzenesulfinate (1.9 equiv) in THF led to the highest selectivity for the C–H insertion and the cyclopentene **21b** was obtained with more than 98% selectivity. The low yields of the products in the reaction with lithium and sodium benzenesulfinates in THF may be interpreted in terms of their poor solubility toward the solvent.

High selectivity for the C–H insertions was also demonstrated by the reactions shown in eq 5. With 2 equiv of tetrabutylammonium benzenesulfinate in THF, the reactions of **17c–e** gave moderate yields of the cyclopentenes **21c–e** in >96% selectivity.

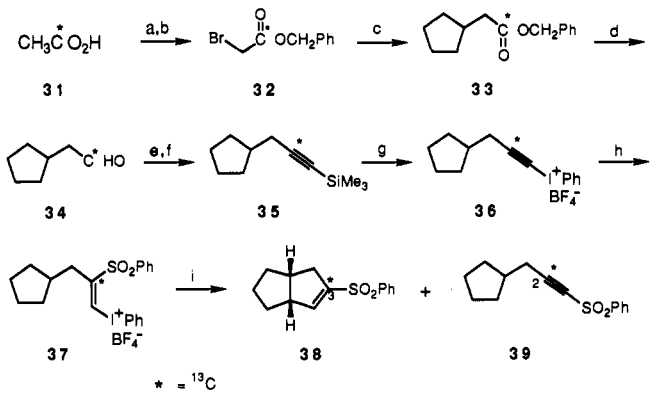
$$\mathbf{17c\text{-}e} \xrightarrow[THF,\ 0^\circ C,\ 30\ min]{PhSO_2NBu_4\ (2)} \mathbf{21c\text{-}e} + \mathbf{22c\text{-}e} \qquad (5)$$

17c	yield 55%	ratio 98 : 2
17d	55%	96 : 4
17e	43%	96 : 4

Discussion. As noted above, the experimental results clearly show that, in contrast to the considerable migratory aptitude of β-(phenylsulfenyl) and -sulfinyl) groups in alkylidenecarbenes, [β-(phenylsulfonyl)alkylidene]carbenes predominantly undergo intramolecular 1,5-C–H insertions yielding synthetically useful 1-(phenylsulfonyl)cyclopentenes. These results can be rationalized in terms of the participation of lone pair electrons on the sulfur atoms; 1,2-rearrangements of β-organosulfur substituents in alkylidenecarbenes probably involve the formation of sulfur ylides like **12**, produced by nucleophilic attack of a lone pair on the sulfur atoms on the empty 2p orbital of the singlet carbenic center, while for [β-(phenylsulfonyl)alkylidene]carbenes, participation of a similar sulfur ylide intermediate seems to be impossible and thus the 1,5-C–H insertions take place as a major pathway.

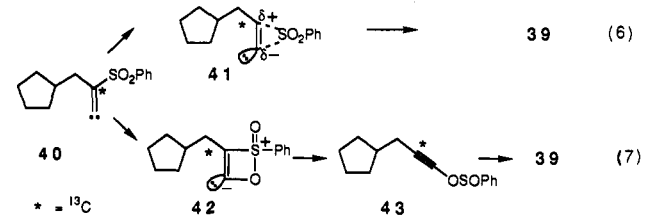
However, it was found by a ^{13}C NMR experiment that in the formation of the rearranged alkynyl phenyl sulfone **39** from the intermediate [β-(phenylsulfonyl)alkylidene]carbene **40**, the β-(phenylsulfonyl) group itself does migrate to the carbenic center. As shown in Scheme III, the required (β-(phenylsulfonyl)alkenyl)iodonium tetrafluoroborate **37**, which was enriched in carbon-13 (99%) at the β-vinylic position, was prepared from acetic-*1*-^{13}C acid (**31**). All of the isotopic enrichment of the 1,5-C–H insertion product **38**, obtained from the ^{13}C-enriched **37** by the reaction with triethylamine via the intermediate formation of **40**, was contained at C-3, while that of the rearranged alkyne **39** was at C-2 (see under Experimental Section). The latter shows, for the first time, that the migratory aptitude of a β-phenylsulfonyl group in 1,2-shifts of alkylidenecarbenes is much greater than that of an alkyl group like a cyclopentylmethyl group.

Scheme III[a]



[a] Reagents; (a) P (red), Br_2, 100 °C, 24 h; (b) $PhCH_2OH$, 25 °C, 12 h; (c) cyclopentene, 9-BBN, THF, 25 °C, 1.5 h and then addition of 2,6-di-*tert*-butylphenol, *t*-BuOK in *t*-BuOH, and **32**, 25 °C, 1.5 h; (d) DIBAL, Et_2O, −78 °C, 2 h; (e) Ph_3P, CBr_4, CH_2Cl_2, 0 °C, 1 h; (f) *n*-BuLi, THF, −78 °C (1 h), 25 °C (2.5 h) and then addition of Me_3SiCl, −78 °C, 25 °C, 12 h; (g) $(PhIO)_n$, BF_3–Et_2O, CH_2Cl_2, 25 °C, 12 h; (h) BSA, MeOH, 0 °C, 1 h; (i) Et_3N, PhH, 25 °C, 0.5 h.

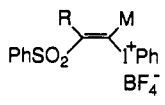
Gilbert and Blackburn observed a large solvent effect in the formation of 2-butynamides by the reaction of *N*,*N*-disubstituted-2-oxopropanamides with diethyl (diazomethyl)phosphonate under basic conditions and proposed an ionic mechanism for 1,2-migration of the intermediate alkylidenecarbenes.[7d] A similar ionic mechanism involving heterolytic cleavage of the β-carbon–sulfur σ bond of β-(phenylsulfonyl)alkylidenecarbenes and reunion of the resulting ion pair seems to be unlikely, since the data in Tables III and IV show only a small solvent effect on the product ratios of **21b** to **22b**. The small solvent effect may suggest that the transition state for 1,2-migration of the β-(phenylsulfonyl) group of **20** is slightly more ionic than that for 1,5-C–H insertion. A possible transition state **41** for 1,2-migration of the phenylsulfonyl group of **40**, which involves participation of the C–S σ bond to the carbenic center, may account for the formation of **39** (eq 6). An alternative mechanism involving an initial formation of the alkynyl sulfinate **43** via an interaction between the sulfonyl oxygen and the carbenic center, which then undergoes an oxygen → sulfur rearrangement to give **39**,[21] should be considered (eq 7). The latter mechanism, however, may not be compatible with the fact that the electronic effect of *p*-MeO and *p*-NO_2 groups of **25** and **26** on product distribution is negligibly small (Table III).



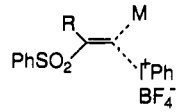
In α-eliminations of alkenyliodonium tetrafluoroborates by base treatment, the involvement of free alkylidenecarbenes rather than alkylidenecarbenoids has been suggested.[4] However, the freeness of the carbenic species generated by tandem MCI reactions of alkynyliodonium tetrafluoroborates with enolate anions is virtually unknown. It seems reasonable to assume that, if the tandem MCI reactions of **17** with benzenesulfinates involve the generation of

(21) The rearrangement of arenesulfinate esters to the corresponding sulfones has been reported: (a) Arcus, C. L.; Balfe, M. P.; Kenyon, J. *J. Chem. Soc.* **1983**, 485. (b) Cope, A. C.; Morrison, D. E.; Field, L. *J. Am. Chem. Soc.* **1950**, *72*, 59. (c) Wragg, A. H.; McFadyen, J. S.; Stevens, T. S. *J. Chem. Soc.* **1958**, 3603. (d) Darwish, D.; McLaren, R. A. *Tetrahedron Lett.* **1962**, 1231. (e) Darwish, D.; Preston, E. A. *Tetrahedron Lett.* **1964**, 113. (f) Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1967**, 131 and ref 16.

an alkylidenecarbenoid like **45**, changing the countercation of the benzenesulfinate anion from lithium cation to highly ionic cesium and tetrabutylammonium cations would have an influence on the ratios of the 1,5-C–H insertion to the 1,2-shift to some extent.[22] The finding that, in the tandem MCI reaction of **17b** with benzenesulfinates, the ratios of the insertion product **21b** to the rearranged alkyne **22b** did not depend on the counterions employed, as shown in Table IV, indicates that the loss of counterions from the Michael adduct **44** (R = n-C_8H_{17}) precedes the 1,5-C–H insertion and the 1,2-shift. Thus, the involvement of the alkylidenecarbenoid **45** (R = n-C_8H_{17}) in the reaction seems to be unlikely. The species involved is probably a free alkylidenecarbene, which may be coordinated with solvents such as THF and water, and it simply partitions between two unimolecular processes, insertion and migration.[7d] However, the intermediacy of a counterion-free alkylidenecarbenoid cannot be ruled out.



44



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Conclusions. In Michael-type additions of benzenesulfinic acid and the derivatives to the alkynyliodonium tetrafluoroborates, we developed a new method for controlling both possible reaction pathways of alkenyliodonium ylide intermediates, that is, protonation yielding the (*Z*)-(β-(phenylsulfonyl)alkenyl)iodonium tetrafluoroborates and reductive elimination of iodobenzene generating the [β-(phenylsulfonyl)alkylidene]carbenes. In contrast to the facile 1,2-migration of β-(phenylsulfenyl)- and β-(phenylsulfinyl)-substituted alkylidenecarbenes, the alkylidenecarbenes derived from α-elimination of (*Z*)-(β-(phenylsulfonyl)alkenyl)-iodonium tetrafluoroborates or conjugate addition of benzenesulfinates to alkynyliodonium tetrafluoroborates undergo predominantly intramolecular 1,5-C–H insertions; this offers an efficient procedure for the synthesis of 1-(phenylsulfonyl)cyclopentenes.

Experimental Section

NMR spectra were recorded on either a JOEL JNM-FX 100, Varian VXR 200, JOEL JNM-GX 400, or Bruker 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from internal tetramethylsilane. IR spectra were recorded on either a Jasco A-202, Jasco IR-810, and Hitachi 260-30 spectrophotometer. Mass spectra (MS) were taken on a JOEL JMS-DX 300 mass spectrometer. Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254). Kieselgel 60 (Merck, 230–400 mesh) was used for flash chromatography.

Alkynyl(phenyl)iodonium tetrafluoroborates **17** were prepared from the corresponding alkynyltrimethylsilanes by the reaction with iodosylbenzene and boron trifluoride–diethyl ether in dichloromethane.[13d] Benzenesulfinic acid was obtained by acidification of an aqueous solution of the commercially available sodium salt with HCl.[23] The other sulfinic acids were prepared by reduction of the corresponding sulfonyl chloride with Na_2SO_3.[24]

General Procedure for the Reaction of 1-Decynyl(phenyl)iodonium Tetrafluoroborate (17b) with Benzenesulfinic Acid. A Typical Example (Table I, entry 1): To a solution of benzenesulfinic acid (16 mg, 0.11 mmol) in 0.5 mL of benzene was added a solution of **17b** (43 mg, 0.1 mmol) in 0.7 mL of benzene at 25 °C under nitrogen and the mixture was stirred for 0.5 h. After addition of a saturated aqueous sodium tetrafluoroborate solution to the mixture, extraction with dichloromethane and then concentration in vacuo afforded a crude oil (58.7 mg), which was washed several times with hexane and diethyl ether by decantation to give 31.7 mg (56%) of **19b**: colorless powder; mp 126.5–132.5 °C; IR (film) 3080, 2950, 2880, 1585, 1470, 1450, 1305, 1140, 1060, 730, 685, 665, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, J = 7.3 Hz, 3 H), 1.09–1.32 (m, 10 H), 1.42 (m, 2 H), 2.35 (t, J = 7.5 Hz, 2 H), 6.94 (s, 1 H), 7.55 (t, J = 7.8 Hz, 2 H), 7.65–7.73 (m, 3 H), 7.73–7.80 (m, 1 H), 7.98–8.04 (m, 2 H), 8.25 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 14.0 (q), 22.5 (t), 28.2 (t), 28.8 (t), 31.7 (t), 32.4 (t), 107.5 (d), 113.1 (s), 128.8 (d), 130.3 (d), 132.5 (d), 133.5 (d), 135.3 (s), 135.8 (d), 136.5 (d), 149.3 (s); MS, m/z 482 [(M – HBF_4)$^+$]; FAB MS m/z 483 [(M – BF_4)$^+$]; HRMS calcd for $C_{22}H_{27}IO_2S$ [(M – HBF_4)$^+$] 482.0779, found 482.0779. Anal. Calcd for $C_{22}H_{28}BF_4IO_2S$: C, 46.33; H, 4.95; I, 22.26. Found: C, 46.63; H, 4.90; I, 22.10. Concentration of the combined hexane and diethyl ether solution and purification by preparative TLC (hexane-chloroform 4:6) gave the cyclopentene **21b** (7.4 mg, 27%) and the alkyne **22b** (3 mg, 11%). **21b**: colorless oil; IR ($CHCl_3$) 2975, 2950, 2875, 1615, 1450, 1310, 1150, 1090, 690, 610, 570 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3 H), 1.18–1.51 (m, 8 H), 1.55–1.66 (m, 1 H), 2.14–2.24 (m, 1 H), 2.40–2.60 (m, 2 H), 2.78–2.88 (m, 1 H), 6.70 (q, J = 2.0 Hz, 1 H), 7.51–7.57 (m, 2 H), 7.59–7.65 (m, 1 H), 7.87–7.92 (m, 2 H); MS, m/z 278 (M$^+$); HRMS calcd for $C_{16}H_{22}O_2S$ (M$^+$) 278.1340, found 278.1338. Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.02; H, 7.97. Found: C, 68.77; H, 7.95. **22b**: colorless oil; IR ($CHCl_3$) 2930, 2860, 2200, 1450, 1330, 1165, 1090, 685, 630, 575 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 3 H), 1.18–1.36 (m, 10 H), 1.55 (quintet, J = 7.3 Hz, 2 H), 2.36 (t, J = 7.3 Hz, 2 H), 7.55–7.60 (m, 2 H), 7.64–7.69 (m, 1 H), 7.99–8.03 (m, 2 H); MS, m/z 278 (M$^+$); HRMS calcd for $C_{16}H_{22}O_2S$ (M$^+$) 278.1340, found 278.1330.

General Procedure for the Synthesis of (*Z*)-(β-Sulfonylvinyl)iodonium Tetrafluoroborates 19 and 25–27 in Methanol. To a solution of benzenesulfinic acid (39 mg, 0.28 mmol) in 1 mL of methanol was added a solution of an alkynyl(phenyl)iodonium tetrafluoroborate **17** (0.25 mmol) at 0 °C under nitrogen and the mixture was stirred for 0.5 h. After addition of a saturated aqueous sodium tetrafluoroborate solution to the mixture, methanol was removed in vacuo and the mixture was extracted with dichloromethane. Concentration in vacuo afforded a crude oil, which was washed several times with hexane and diethyl ether by decantation to give a (*Z*)-(β-sulfonylvinyl)iodonium tetrafluoroborate. The yields of pure products are given in Table II.

(*Z*)-Phenyl(2-(phenylsulfonyl)-1-propenyl)iodonium Tetrafluoroborate (19a). Colorless powder; IR (KBr) 3050, 1600, 1585, 1470, 1440, 1290, 1220, 1040, 730, 680, 620, 575 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.13 (d, J = 1.5 Hz, 3 H), 7.07 (q, J = 1.5 Hz, 1 H), 7.52–7.58 (m, 2 H), 7.67–7.73 (m, 3 H), 7.76–7.81 (m, 1 H), 8.00–8.03 (m, 2 H), 8.21–8.25 (m, 2 H); FAB MS, m/z 385 [(M – BF_4)$^+$].

(*Z*)-Phenyl(4-cyclohexyl-2-(phenylsulfonyl)-1-butenyl)iodonium Tetrafluoroborate (19c). Colorless powder; IR (KBr) 3050, 2910, 2860, 1580, 1570, 1445, 1290, 1040, 730, 680, 610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.69–0.80 (m, 2 H), 1.01–1.17 (m, 4 H), 1.24–1.34 (m, 2 H), 1.45–1.53 (m, 2 H), 1.53–1.70 (m, 3 H), 2.37 (ddd, J = 9.8, 7.0, 1.5 Hz, 2 H), 6.94 (t, J = 1.5 Hz, 1 H), 7.52–7.59 (m, 2 H), 7.66–7.73 (m, 3 H), 7.75–7.80 (m, 1 H), 7.99–8.03 (m, 2 H), 8.23–8.27 (m, 2 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 26.0 (t), 26.3 (t), 30.1 (t), 32.7 (t), 35.7 (t), 37.2 (d), 107.2 (d), 113.0 (s), 128.9 (d), 130.3 (d), 132.5 (d), 133.5 (d), 135.3 (s), 135.7 (d), 136.5 (d), 149.7 (s); FAB MS, m/z 481 [(M – BF_4)$^+$].

(*Z*)-Phenyl(3-cyclopentyl-2-(phenylsulfonyl)-1-propenyl)iodonium Tetrafluoroborate (19d). Colorless powder; IR (KBr) 3040, 2930, 2870, 1590, 1440, 1290, 1040, 730, 680, 610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90–1.00 (m, 2 H), 1.40–1.56 (m, 4 H), 1.56–1.70 (m, 2 H), 2.00 (septet, J = 7.5 Hz, 1 H), 2.37 (dd, J = 7.5, 1.8 Hz, 2 H), 6.96 (t, J = 1.8 Hz, 1 H), 7.54–7.60 (m, 2 H), 7.66–7.74 (m, 3 H), 7.75–7.80 (m, 1 H), 7.99–8.03 (m, 2 H), 8.23–8.28 (m, 2 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 24.7 (t), 31.9 (t), 38.1 (d), 38.1 (t), 107.6 (d), 112.8 (s), 128.6 (d), 130.3 (d), 132.4 (d), 133.4 (d), 135.0 (s), 135.9 (d), 136.3 (d), 148.7 (s); FAB MS, m/s 453 [(M – BF_4)$^+$]. Anal. Calcd for $C_{20}H_{22}BF_4IO_2S$: C, 44.47; H, 4.11; I, 23.50. Found: C, 44.74; H, 4.05; I, 23.75.

(*Z*)-Phenyl(5-phenyl-2-(phenylsulfonyl)-1-pentenyl)iodonium Tetrafluoroborate (19e). Colorless powder; IR (KBr) 3040, 2940, 1580, 1570, 1440, 1285, 1030, 725, 680, 610 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.78 (quintet, J = 7.5 Hz, 2 H), 2.37 (dt, J = 1.5, 7.5 Hz, 2 H), 2.51 (t, J = 7.5 Hz, 2 H), 6.93 (t, J = 1.5 Hz, 1 H), 6.98–7.02 (m, 2 H), 7.12–7.22 (m, 3 H), 7.50–7.56 (m, 2 H), 7.60–7.76 (m, 4 H), 7.89–7.93 (m, 2 H), 8.20–8.25 (m, 2 H); FAB MS, m/z 489 [(M – BF_4)$^+$]. Anal. Calcd for $C_{23}H_{22}BF_4IO_2S$: C, 47.94; H, 3.85. Found: C, 48.09; H, 3.61.

(*Z*)-Phenyl(4-hydroxy-2-(phenylsulfonyl)-1-butenyl)iodonium Tetrafluoroborate (19f). Colorless powder; IR (KBr) 3370, 3050, 2950, 2890, 1585, 1470, 1440, 1290, 1040, 730, 680, 610 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 2.59 (dt, J = 1.3, 6.0 Hz, 2 H), 3.55 (t, J = 6.0 Hz, 2 H), 7.62–7.68 (m, 3 H), 7.73–7.91 (m, 4 H), 8.04–8.07 (m, 2 H), 8.27–8.31 (m, 2 H); FAB MS, m/z 415 [(M – BF_4)$^+$].

(*Z*)-Phenyl(2-((4-nitrophenyl)sulfonyl)-1-decenyl)iodonium Tetrafluoroborate (25). Colorless needles; mp 150–153 °C; IR (KBr) 3120, 3060, 2930, 2870, 1595, 1535, 1445, 1350, 1300, 1135, 1075, 990, 855,

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810, 735, 720, 680, 650 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ 0.86 (t, J = 7.3 Hz, 3 H), 1.12–1.36 (m, 10 H), 1.40–1.50 (m, 2 H), 2.45 (t, J = 7.8 Hz, 2 H), 7.65–7.71 (m, 2 H), 7.80–7.89 (m, 2 H), 8.28–8.37 (m, 4 H), 8.55–8.60 (m, 2 H); FAB MS, m/z 528 [(M − BF_4)$^+$]. Anal. Calcd for $C_{22}H_{27}BF_4INO_4S$: C, 42.95; H, 4.42; N, 2.28; I, 20.63. Found: C, 43.05; H, 4.26; N, 2.18; I, 20.43.

(*Z*)-Phenyl(2-((4-methoxyphenyl)sulfonyl)-1-decenyl)iodonium Tetrafluoroborate (26). Colorless powder; mp 88.5–91.5 °C; IR (KBr) 2900, 2850, 1565, 1430, 1245, 1020, 800, 675, 595 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, J = 7.3 Hz, 3 H), 1.10–1.28 (m, 10 H), 1.39–1.48 (m, 2 H), 2.37 (t, J = 7.5 Hz, 2 H), 3.91 (s, 3 H), 6.83 (s, 1 H), 7.13 (d, J = 9.0 Hz, 2 H), 7.54–7.60 (m, 2 H), 7.69–7.75 (m, 1 H), 7.91–7.96 (d, J = 9.0 Hz, 2 H), 8.23–8.27 (m, 2 H); FAB MS, m/z 513 [(M − BF_4)$^+$]. Anal. Calcd for $C_{23}H_{30}BF_4IO_3S$: C, 46.02; H, 5.04; I, 21.14. Found: C, 45.74; H, 5.07; I, 21.14.

(*Z*)-Phenyl(2-(butylsulfonyl)-1-propenyl)iodonium Tetrafluoroborate (27). Colorless needles; mp 106–114 °C; IR (KBr) 2970, 2880, 1605, 1450, 1320, 1280, 1085, 740, 640, 550 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, J = 7.3 Hz, 3 H), 1.51 (sextet, J = 7.3 Hz, 2 H), 1.81–1.90 (m, 2 H), 2.40 (d, J = 1.5 Hz, 3 H), 3.32–3.37 (m, 2 H), 7.02 (q, J = 1.5 Hz, 1 H), 7.52–7.58 (m, 2 H), 7.70–7.75 (m, 1 H), 8.15–8.19 (m, 2 H); FAB MS, m/z 365 [(M − BF_4)$^+$].

General Procedure for the Reaction of (*Z*)-(β-Sulfonylalkenyl)-Iodonium Tetrafluoroborates with Triethylamine. To a solution of (*Z*)-(β-sulfonylalkenyl)iodonium tetrafluoroborate (0.19 mmol) in 3 mL of benzene was added triethylamine (0.23 mmol) at room temperature under nitrogen and the mixture was stirred for 0.5 h. The mixture was poured into water and extracted with diethyl ether. Drying of the extract with $MgSO_4$ and then concentration in vacuo afforded a crude product, which was purified by preparative TLC (hexane–chloroform) to give a (phenylsulfonyl)cyclopentene and an alkynyl phenyl sulfone. The yields of pure products are given in Table III.

2-(Phenylsulfonyl)spiro[4.5]-1-decene (21c). Colorless prisms; mp 52–56.5 °C; IR (KBr) 2930, 2860, 1610, 1450, 1305, 1295, 1150, 1120, 1090, 940, 765, 720, 695, 605, 570 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35–1.60 (m, 10 H), 1.83 (t, J = 7.3 Hz, 2 H), 2.50 (m, 2 H), 6.70 (s, 1 H), 7.51–7.56 (m, 2 H), 7.60–7.65 (m, 1 H), 7.87–7.90 (m, 2 H); MS, m/z 276 (M$^+$); HRMS calcd for $C_{16}H_{20}O_2S$ (M$^+$) 276.1183, found 276.1160. Anal. Calcd for $C_{16}H_{20}O_2S \cdot {}^1/_4H_2O$: C, 68.41; H, 7.36. Found: C, 68.64; H, 7.15.

4-Cyclohexyl-1-butynyl Phenyl Sulfone (22c). Colorless prisms; mp 59–63 °C; IR (KBr) 2935, 2850, 2195, 1450, 1330, 1160, 1090, 990, 760, 725, 690, 635, 575, 560 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77–0.89 (m, 2 H), 1.05–1.30 (m, 4 H), 1.44 (q, J = 7.3 Hz, 2 H), 1.54–1.70 (m, 5 H), 2.37 (t, J = 7.3 Hz, 2 H), 7.55–7.60 (m, 2 H), 7.64–7.69 (m, 1 H), 7.99–8.02 (m, 2 H); MS, m/z 276 (M$^+$); HRMS calcd for $C_{16}H_{20}O_2S$ (M$^+$) 276.1183, found 276.1194. Anal. Calcd for $C_{16}H_{20}O_2S \cdot {}^1/_4H_2O$: C, 68.41; H, 7.36. Found: C, 68.74; H, 7.63.

3-(Phenylsulfonyl)bicyclo[3.3.0]-2-octene (21d). Colorless oil; IR ($CHCl_3$) 2950, 2870, 1620, 1450, 1305, 1150, 1090, 1020, 605, 565 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24–1.33 (m, 1 H), 1.37–1.56 (m, 3 H), 1.68–1.81 (m, 2 H), 2.22 (br d, J = 15.8 Hz, 1 H), 2.70–2.86 (m, 2 H), 3.30 (m, 1 H), 6.56 (q, J = 2.1 Hz, 1 H), 7.51–7.57 (m, 2 H), 7.59–7.65 (m, 1 H), 7.86–7.90 (m, 2 H); MS, m/z 248 (M$^+$); HRMS calcd for $C_{14}H_{16}O_2S$ (M$^+$) 248.0870, found 248.0862.

3-Cyclopentyl-1-propynyl Phenyl Sulfone (22d). Colorless oil; IR ($CHCl_3$) 2945, 2860, 2200, 1445, 1325, 1155, 1090, 570 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14–1.25 (m, 2 H), 1.49–1.64 (m, 4 H), 1.72–1.81 (m, 2 H), 2.07 (septet, J = 7.4 Hz, 1 H), 2.37 (d, J = 7.4 Hz, 2 H), 7.55–7.60 (m, 2 H), 7.64–7.69 (m, 1 H), 7.98–8.02 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7 (t), 25.1 (t), 32.0 (t), 37.8 (d), 78.3 (s), 97.7 (s), 127.1 (d), 129.2 (d), 133.8 (d), 142.2 (s); MS, m/z 248 (M$^+$); HRMS calcd for $C_{14}H_{16}O_2S$ (M$^+$) 248.0871, found 248.0876. Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49. Found: C, 67.52; H, 6.52.

1-(Phenylsulfonyl)-3-phenylcyclopentene (21e). Colorless plates; mp 56–59 °C; IR (KBr) 2940, 1615, 1600, 1495, 1450, 1310, 1150, 1095, 755, 725, 705, 690, 610, 565 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91–2.20 (m, 1 H), 2.52–2.76 (m, 3 H), 4.04–4.11 (m, 1 H), 6.74 (q, J = 2.0 Hz, 1 H), 7.08–7.11 (m, 2 H), 7.21–7.33 (m, 3 H), 7.55–7.60 (m, 2 H), 7.63–7.68 (m, 1 H), 7.94–7.97 (m, 2 H); MS, m/z 284 (M$^+$); HRMS calcd for $C_{17}H_{16}O_2S$ (M$^+$) 284.0870, found 284.0851. Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.27; H, 5.55.

Phenyl 5-Phenyl-1-pentynyl Sulfone (22e). Colorless oil; IR ($CHCl_3$) 2950, 2200, 1330, 1160, 1090 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (quintet, J = 7.4 Hz, 2 H), 2.35 (t, J = 7.4 Hz, 2 H), 2.65 (t, J = 7.4 Hz, 2 H), 7.07–7.11 (m, 2 H), 7.17–7.22 (m, 1 H), 7.24–7.29 (m, 2 H), 7.56–7.61 (m, 2 H), 7.65–7.70 (m, 1 H), 8.00–8.03 (m, 2 H); MS, m/z 284 (M$^+$); HRMS calcd for $C_{17}H_{16}O_2S$ (M$^+$) 284.0870, found 284.0862.

1-((4-Nitrophenyl)sulfonyl)-3-pentylcyclopentene. Colorless prisms; mp 70–72 °C; IR ($CHCl_3$) 2975, 2950, 2870, 1605, 1540, 1350, 1330, 1310, 1155, 1100, 855, 620, 575 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 3 H), 1.15–1.50 (m, 8 H), 1.58–1.73 (m, 1 H), 2.12–2.32 (m, 1 H), 2.35–2.62 (m, 2 H), 2.86 (m, 1 H), 6.84 (q, J = 1.8 Hz, 1 H), 8.08 (m, 2 H), 8.38 (m, 2 H); MS, m/z 323 (M$^+$); HRMS calcd for $C_{16}H_{21}NO_4S$ (M$^+$) 323.1192, found 323.1200. Anal. Calcd for $C_{16}H_{21}NO_4S \cdot {}^1/_3H_2O$: C, 58.34; H, 6.63; N, 4.25. Found: C, 58.67; H, 6.39; N, 4.35.

1-Decynyl 4-Nitrophenyl Sulfone. Colorless prisms; mp 53–54 °C; IR ($CHCl_3$) 2940, 2860, 2210, 1605, 1540, 1460, 1400, 1345, 1310, 1165, 1090, 855, 640, 590 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, J = 6.7 Hz, 3 H), 1.10–1.40 (m, 10 H), 1.48–1.65 (m, 2 H), 2.39 (t, J = 7.0 Hz, 2 H), 8.16–8.24 (m, 2 H), 8.38–8.46 (m, 2 H); MS, m/z 323 (M$^+$); HRMS calcd for $C_{16}H_{21}NO_4S$ (M$^+$) 323.1192, found 323.1227. Anal. Calcd for $C_{16}H_{21}NO_4S$: C, 59.42; H, 6.55; N, 4.33. Found: C, 59.34; H, 6.42; N, 4.31.

1-((4-Methoxyphenyl)sulfonyl)-3-pentylcyclopentene. Colorless prisms; mp 43–45 °C; IR ($CHCl_3$) 2980, 2950, 2860, 1600, 1580, 1510, 1460, 1320, 1300, 1260, 1150, 1105, 1030, 835, 595, 560 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, J = 6.4 Hz, 3 H), 1.16–1.64 (m, 9 H), 2.07–2.26 (m, 1 H), 2.33–2.62 (m, 2 H), 2.80 (m, 1 H), 3.86 (s, 3 H), 6.61 (q, J = 2.0 Hz, 1 H), 6.94–7.02 (m, 2 H), 7.76–7.85 (m, 2 H); MS, m/z 308 (M$^+$); HRMS calcd for $C_{17}H_{24}O_3S$ (M$^+$) 308.1445, found 308.1443. Anal. Calcd for $C_{17}H_{24}O_3S$: C, 66.20; H, 7.84. Found: C, 66.49; H, 7.68.

1-Decynyl 4-Methoxyphenyl Sulfone. Colorless oil; IR ($CHCl_3$) 2950, 2875, 2210, 1600, 1585, 1510, 1465, 1335, 1265, 1160, 1100, 1030, 835, 680, 620, 560 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, J = 6.5 Hz, 3 H), 1.14–1.40 (m, 10 H), 1.42–1.63 (m, 2 H), 2.33 (t, J = 6.5 Hz, 2 H), 3.89 (s, 3 H), 6.97–7.05 (m, 2 H), 7.88–7.96 (m, 2 H); MS, m/z 308 (M$^+$); HRMS calcd for $C_{17}H_{24}O_3S$ (M$^+$) 308.1445, found 308.1427. Anal. Calcd for $C_{17}H_{24}O_3S$: C, 66.20; H, 7.84. Found: C, 66.35; H, 7.78.

Reaction of (*Z*)-Phenyl(2-(butylsulfonyl)-1-propenyl)iodonium Tetrafluoroborate (27) with Triethylamine. Iodonium tetrafluoroborate **27** (100 mg, 0.22 mmol) was treated with triethylamine (27 mg, 0.27 mmol) in 3 mL of dichloromethane at 0 °C for 1 h under nitrogen. Preparative TLC gave the 2-sulfolene **28** (18.8 mg, 53%) and the rearranged alkyne **29** (9.9 mg, 28%). **28**: colorless oil; IR ($CHCl_3$) 2970, 2930, 1440, 1300, 1155, 1110 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.4 Hz, 3 H), 1.50–1.61 (m, 1 H), 1.61–1.71 (m, 1 H), 2.04 (dd, J = 2.1, 1.7 Hz, 3 H), 2.87–3.00 (2 H), 3.41 (dd, J = 13.0, 7.7 Hz, 1 H), 6.21 (dq, J = 1.3, 1.5 Hz, 1 H); MS, m/z 160 (M$^+$); HRMS calcd for $C_7H_{12}O_2S$ (M$^+$) 160.0558, found 160.0549. **29**: colorless oil; IR ($CHCl_3$) 2970, 2880, 2220, 1460, 1330, 1140, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 3 H), 1.50 (sextet, J = 7.4 Hz, 2 H), 1.89 (m, 2 H), 2.10 (s, 3 H), 3.15 (m, 2 H); MS, M/z 161 [(M + 1)$^+$]; HRMS calcd for $C_7H_{13}O_2S$ [(M + 1)$^+$] 161.0636, found 161.0625.

Reaction of (*Z*)-Phenyl(4-hydroxy-2-(phenylsulfonyl)-1-butenyl)-Iodonium Tetrafluoroborate (19f) with Triethylamine. Iodonium tetrafluoroborate **19f** (58 mg, 0.12 mmol) was treated with triethylamine (14 mg, 0.14 mmol) in 1 mL of benzene at room temperature for 1 h under nitrogen. Preparative TLC gave the 2,3-dihydrofuran **30** (14.8 mg, 61%) as colorless prisms: mp 77–80 °C; IR (KBr) 3090, 2925, 1610, 1450, 1310, 1290, 1175, 1145, 1110, 755, 730, 685, 600, 570 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (dd, J = 9.6, 1.7 Hz, 2 H), 4.62 (t, J = 9.6 Hz, 2 H), 7.23 (t, J = 1.7 Hz, 1 H), 7.52–7.57 (m, 2 H), 7.59–7.64 (m, 1 H), 7.88–7.92 (m, 2 H); MS m/z 210 (M$^+$): HRMS calcd for $C_{10}H_{10}O_3S$ (M$^+$) 210.0351, found 210.0365.

General Procedure for the Reaction of 1-Decynyl(phenyl)iodonium Tetrafluoroborate (17b) with Benzenesulfinates. Lithium, potassium, and cesium benzenesulfinates were prepared in situ from benzenesulfinic acid by the reaction with lithium hydride, potassium hydride, and cesium carbonate, respectively. Tetrabutylammonium benzenesulfinate was synthesized by the reaction of benzenesulfinic acid with tetrabutylammonium hydroxide in water. The following is a typical example (Table IV, entry 9): To a mixture of cesium carbonate (23 mg, 0.07 mmol) in 0.5 mL of THF was added benzenesulfinic acid (20 mg, 0.14 mmol) at room temperature under nitrogen, and the mixture was stirred for 3 h. A solution of **17b** (50 mg, 0.12 mmol) in 1 mL of THF was added at 0 °C and the mixture was stirred for 0.5 h. After addition of water to the mixture, extraction with diethyl ether, drying of the extract with Na_2SO_4, and then concentration in vacuo afforded a crude oil, which was purified by preparative TLC (hexane–chloroform 4:6) to give **21b** (19.8 mg, 61%) and **22b** (2.5 mg, 8%).

Reaction of Phenyl(4-cyclohexyl-1-butynyl)iodonium Tetrafluoroborate (17c) with Tetrabutylammonium Benzenesulfinate. To a solution of **17c** (88 mg, 0.21 mmol) in 1.3 mL of THF was added a solution of tetrabutylammonium benzenesulfinate monohydrate (166 mg, 0.42 mmol) in 2.2 mL of THF at 0 °C under nitrogen. After being stirred for 0.5 h at 0 °C, the reaction mixture was poured into water and extracted with

diethyl ether. The extract was dried with Na_2SO_4 and concentrated in vacuo. Purification by preparative TLC (hexane–chloroform 2:8) gave **21c** (30.4 mg, 53%) and **22c** (0.6 mg, 1%).

Reaction of Phenyl(3-cyclopentyl-1-propynyl)iodonium Tetrafluoroborate (17d) with Tetrabutylammonium Benzenesulfinate. Reaction of **17d** (58 mg, 0.15 mmol) with tetrabutylammonium benzenesulfinate monohydrate (117 mg, 0.29 mmol) in 3 mL of THF at 0 °C for 0.5 h under nitrogen gave **21d** (19.1 mg, 53%) and **22d** (0.8 mg, 2%).

Reaction of Phenyl(5-phenyl-1-pentynyl)iodonium Tetrafluoroborate (17e) with Tetrabutylammonium Benzenesulfinate. Reaction of **17e** (105 mg, 0.24 mmol) with tetrabutylammonium benzenesulfinate monohydrate (195 mg, 0.49 mmol) in 4 mL of THF at 0 °C for 0.5 h under nitrogen gave **21e** (28.5 mg, 41%) and **22e** (1.1 mg, 2%).

Synthesis of Benzyl Bromoacetate-*1*-^{13}C (32).[25] To a mixture of 2.0 g (33 mmol) of acetic-*1*-^{13}C acid (99% enrichment) and 0.4 g (13 mmol) of red phosphorus was added 10.5 g (66 mmol) of bromine dropwise at room temperature over 1 h under nitrogen. The solution was warmed to 100 °C and stirred for 24 h. The unreacted bromine and hydrogen bromide were removed under reduced pressure. Benzyl alcohol (20 mL) was added to the mixture. After being stirred for 12 h, the mixture was poured into an aqueous $NaHCO_3$ solution and extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Flash column chromatography (6% ethyl acetate in hexane) afforded **32** (5.7 g, 75%): ^1H NMR (400 MHz, $CDCl_3$) δ 3.86 (d, $^2J(^{13}C-^1H)$ = 4.7 Hz, 2 H), 5.20 (d, $^3J(^{13}C-^1H)$ = 3.3 Hz, 2 H), 7.37 (m, 5 H).

Synthesis of Benzyl Cyclopentylacetate-*1*-^{13}C (33). The reaction was carried out according to the method developed by Brown.[26] Cyclopentene (1.55 g, 22.8 mmol) was added dropwise to a solutioin of 9-borabicyclo[3.3.1]nonane (9-BBN, 2.81 g, 11.5 mmol) in 26 mL of THF at room temperature under nitrogen and the solution was stirred for 1.5 h. A solution of 2,6-di-*tert*-butylphenol (4.71 g, 22.8 mmol) in 5 mL of THF and then *t*-BuOK (24.5 mL of a 0.93 M solution in *t*-BuOH, 22.8 mmol) were added at room temperature. After being stirred for 10 min, **32** (5.00 g, 21.7 mmol) was added dropwise to the mixture. The reaction mixture was stirred for 1.5 h, quenched with water, and extracted with diethyl ether. The extract was dried over Na_2SO_4 and concentrated in vacuo. Flash column chromatography (2% ethyl acetate in hexane) gave **33** (3.04 g, 64%): ^1H NMR (400 MHz, $CDCl_3$) δ 1.11–1.22 (m, 2 H), 1.49–1.68 (m, 4 H), 1.77–1.88 (m, 2 H), 2.25 (m, 1 H), 2.37 (t, J = 6.9 Hz, $^2J(^{13}C-^1H)$ = 6.9 Hz, 2 H), 5.11 (d, $^3J(^{13}C-^1H)$ = 3.3 Hz, 2 H), 7.37 (m, 5 H).

Synthesis of Cyclopentylacetaldehyde-*1*-^{13}C (34).[27] To a solution of **33** (2.88 g, 13.1 mmol) in 29 mL of diethyl ether was added diisobutylaluminum hydride (14.7 mL of a 0.94 M solution in hexane, 13.8 mmol) at −78 °C under nitrogen. After being stirred for 2 h, the solution was quenched with a saturated aqueous solution of ammonium chloride and extracted with pentane. Purification was carried out by using sodium hydrogen sulfite to give the aldehyde **34** (0.83 g, 56%): ^1H NMR (400 MHz, $CDCl_3$) δ 1.10–1.21 (m, 2 H), 1.51–1.70 (m, 4 H), 1.82–1.91 (m, 2 H), 2.27 (d of septet, J = 7.4 Hz, $^3J(^{13}C-^1H)$ = 3.3 Hz, 1 H), 2.44 (ddd, J = 6.3, 2.2 Hz, $^2J(^{13}C-^1H)$ = 7.1 Hz, 2 H), 9.75 (dt, J = 2.2 Hz, $^1J(^{13}C-^1H)$ = 169.3 Hz, 1 H).

Synthesis of Phenyl(3-cyclopentyl-1-propynyl)iodonium-*2*-^{13}C Tetrafluoroborate (36). According to the procedure of Corey and Fuchs,[28] 3-cyclopentyl-1,1-dibromo-1-propene-*2*-^{13}C (1.70 g, 86%) was prepared from **34** (0.83 g, 7.3 mmol) by the reaction with triphenylphosphine (8.43 g, 32.2 mmol) and carbon tetrabromide (5.33 g, 16.1 mmol) in 36 mL of dichloromethane (0 °C, 1 h). To a solution of the dibromoolefin (1.64 g, 6.1 mmol) in 3 mL of THF was added *n*-butyllithium (8.9 mL of a 1.51 M solution in hexane, 13.4 mmol) at −78 °C under nitrogen. After being stirred for 1 h, the reaction mixture was warmed to room temperature and maintained for 2.5 h at that temperature. Chlorotrimethylsilane (0.86 g, 7.9 mmol) was added at −78 °C and the mixture was warmed to room temperature. After being stirred for 12 h, the mixture was poured into water and extracted with diethyl ether. The extract was dried over Na_2SO_4 and concentrated in vacuo to give 3-cyclopentyl-1-(trimethylsilyl)propyne-*2*-^{13}C (**35**) quantitatively, which was used without further purification. To a suspension of **35** (0.50 g, 2.8 mmol) and iodosylbenzene (0.97 g, 4.4 mmol) in 35 mL of dichloromethane was added dropwise boron trifluoride–diethyl ether (0.63 g, 4.4 mmol) under nitrogen at 0 °C. The reaction mixture was stirred for 12 h at room temperature. A saturated aqueous sodium tetrafluoroborate solution was added and the mixture was stirred vigorously for 10 min. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was concentrated in vacuo to give an oil, which was washed several times with hexane and diethyl ether by decantation to give **36** (0.87 g, 79%): IR (KBr) 3060, 2960, 2870, 2125, 1475, 1445, 1085, 740, 680, 535, 520 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.16–1.26 (m, 2 H), 1.49–1.66 (m, 4 H), 1.75–1.84 (m, 2 H), 2.05–2.17 (m, 1 H), 2.65 (q, J = 6.9 Hz, $^2J(^{13}C-^1H)$ = 9.8 Hz, 2 H), 7.52–7.57 (m, 2 H), 7.64–7.69 (m, 1 H), 8.04–8.08 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6 (d, $^1J(^{13}C-^{13}C)$ = 171.6 Hz), 25.1, 26.6 (d, $^1J(^{13}C-^{13}C)$ = 171.6 Hz), 32.0 (d, $^3J(^{13}C-^{13}C)$ = 3.5 Hz), 38.3 (d, $^2J(^{13}C-^{13}C)$ = 2.9 Hz), 113.6, 114.5 (d, $^3J(^{13}C-^{13}C)$ = 1.4 Hz), 132.6, 132.8, 133.9; MS, m/z 311 [$(M - HBF_4)^+$]; FAB MS, m/z 312 [$(M - BF_4)^+$].

Synthesis of (*Z*)-Phenyl(3-cyclopentyl-2-(phenylsulfonyl)-1-propenyl)iodonium-*2*-^{13}C Tetrafluoroborate (37). Reaction of **36** (0.50 g, 1.3 mmol) with benzenesulfinic acid (0.20 g, 1.4 mmol) in 15 mL of methanol gave **37** (0.65 g, 96%): IR (KBr) 3070, 2950, 2860, 1450, 1310, 1085, 740, 690, 630 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89–1.00 (m, 2 H), 1.39–1.55 (m, 4 H), 1.59–1.70 (m, 2 H), 1.99 (d of septet, J = 7.4 Hz, $^3J(^{13}C-^1H)$ = 2.1 Hz, 1 H), 2.35 (dt, J = 7.4, 1.3 Hz, $^2J(^{13}C-^1H)$ = 7.4 Hz, 2 H), 6.96 (dt, J = 1.3 Hz, $^2J(^{13}C-^1H)$ = 5.4 Hz, 1 H), 7.52–7.58 (m, 2 H), 7.66–7.72 (m, 3 H), 7.74–7.79 (m, 1 H), 7.98–8.02 (m, 2 H), 8.22–8.27 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 32.1 (d, $^3J(^{13}C-^{13}C)$ = 2.9 Hz), 38.1 (d, $^2J(^{13}C-^{13}C)$ = 2.1 Hz), 38.4 (d, $^1J(^{13}C-^{13}C)$ = 38.7 Hz), 107.5 (d, $^1J(^{13}C-^{13}C)$ = 78.8 Hz), 113.0, 128.8, 130.2, 132.5, 133.5, 135.0 (d, $^2J(^{13}C-^{13}C)$ = 8.0 Hz), 135.8, 136.4, 148.7; FAB MS, m/z 454 [$(M - BF_4)^+$].

Reaction of 37 with Triethylamine. Reaction of **37** (0.5 g, 0.9 mmol) with triethylamine (0.11 g, 1.1 mmol) in 15 mL of benzene (25 °C, 0.5 h) gave **38** (0.15 g, 65%) and **39** (0.04 g, 18%). **38**: IR ($CHCl_3$) 2960, 2870, 1590, 1450, 1310, 1150, 1090, 610, 565 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24–1.33 (m, 1 H), 1.37–1.56 (m, 3 H), 1.68–1.81 (m, 2 H), 2.17–2.26 (m, 1 H), 2.69–2.86 (m, 2 H), 3.26–3.35 (m, 1 H), 6.56 (quintet, J = 2.0 Hz, $^2J(^{13}C-^1H)$ = 2.0 Hz, 1 H), 7.51–7.57 (m, 2 H), 7.59–7.65 (m, 1 H), 7.86–7.90 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 31.2 (d, $J(^{13}C-^{13}C)$ = 3.4 Hz), 35.1, 38.4 (d, $^1J(^{13}C-^{13}C)$ = 39.2 Hz, C-4), 41.5 (d, $J(^{13}C-^{13}C)$ = 2.7 Hz), 50.9 (d, $J(^{13}C-^{13}C)$ = 6.0 Hz), 127.8, 129.1, 133.2, 139.8 (d, $^2J(^{13}C-^{13}C)$ = 8.7 Hz), 142.8 (C-3), 145.9 (d, $^1J(^{13}C-^{13}C)$ = 69.4 Hz, C-2); MS, m/z 249 (M^+); HRMS calcd for $C_{13}{}^{13}CH_{16}O_2S$ (M^+) 249.0905, found 249.0916. **39**: IR ($CHCl_3$) 2950, 2865, 2160, 1450, 1330, 1160, 1090, 570 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14–1.24 (m, 2 H), 1.49–1.64 (m, 4 H), 1.72–1.81 (m, 2 H), 2.01–2.14 (m, 1 H), 2.37 (dd, J = 6.8 Hz, $^2J(^{13}C-^1H)$ = 10.2 Hz, 2 H), 7.55–7.60 (m, 2 H), 7.64–7.69 (m, 1 H), 7.98–8.02 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7 (d, $^1J(^{13}C-^{13}C)$ = 62.0 Hz, C-3), 25.1 (C-6, C-7), 32.0 (d, $^3J(^{13}C-^{13}C)$ = 3.4 Hz, C-5, C-8), 37.8 (d, $^2J(^{13}C-^{13}C)$ = 3.0 Hz), 78.3 (d, $^1J(^{13}C-^{13}C)$ = 169.6 Hz, C-1), 97.6 (C-2), 127.1, 129.2, 133.8, 142.3 (d, $^3J(^{13}C-^{13}C)$ = 2.0 Hz); MS, m/z 250 [$(M + 1)^+$]; HRMS calcd for $C_{13}{}^{13}CH_{17}O_2S$ [$(M + 1)^+$] 250.0983, found 250.1004. The ^{13}C enrichment at the β-acetylenic carbon of **39** was determined as 99% from the ^{13}C NMR spectrum.

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