A New Method for the Synthesis of Cyclopentenones via the Tandem Michael Addition–Carbene Insertion Reaction of β-Ketoethynyl(phenyl)iodonium Salts†

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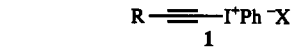
Abstract: A variety of substituted 2-cyclopentenones are obtained in good yields (53–82%) via intramolecular 1,5-carbon–hydrogen insertion reactions of [β-(*p*-toluenesulfonyl)alkylidene]carbenes derived from Michael addition of sodium *p*-toluenesulfinate to β-ketoethynyl(phenyl)iodonium triflates. An extension of the methodology using β-amidoethynyl(phenyl)iodonium triflates provides a facile synthesis of γ-lactams including fused bicyclic systems. The isomerization of a substituted cyclopentenone on silica gel is also reported.

The development of new synthetic methods for the preparation of substituted cyclopentenones continues to be an area of intense interest[1] as a result of the ubiquity of the cyclopentenone nucleus in nature. Prostaglandins,[2] ambrosin,[3] dicranenones,[4] jasmonoids,[5] and aromatin[6] are but a few of the natural products incorporating this structural unit. Among the current, extensively employed synthetic methods for the construction of cyclopentenones are the Nazarov[7] and related cationic cyclizations and the Pauson–Khand[8,9] $Co_2(CO)_8$-mediated cyclizations of alkynes with olefins. However, each of these methods has limitations.[7-9]

Intramolecular carbon–hydrogen insertion reactions of carbenes have been widely used for the construction of a large variety of five-membered ring systems.[10] For example, gas-phase thermolysis at 550–740 °C of α-acetylenic ketones has been employed for the preparation of 2-cyclopentenones, but some functional groups are incompatible with the extreme reaction conditions, giving rise to product mixtures and decreased yields.[11] In addition to requiring specialized equipment, flash-vacuum pyrolysis has limited value as a preparative procedure due to the small sample throughput.

Alkynyl(phenyl)iodonium salts[12] **1** have recently emerged as valuable reagents for organic synthesis. These compounds have



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been utilized in alkynylations,[13] cycloadditions,[14,15] and alkynyl ester formation.[16] We envisioned that an annulation sequence could be developed for the preparation of cyclopentenones by using readily available β-ketoethynyl(phenyl)iodonium salts[14] as precursors.

In this paper we report a new, mild, and general method for the synthesis of 2-cyclopentenones via alkynyliodonium triflates, as well as an extension of this methodology for accessing the basic skeleton of various classes of fused bicyclic alkaloids.

Results and Discussion

Preparation and Characterization of 6–16. Reaction of β-ketoethynyl(phenyl)iodonium triflates **2a–f** with anhydrous sodium *p*-toluenesulfinate in CH_2Cl_2 at 20 °C produces a reactive

† Dedicated to Professor Jerome A. Berson on the occasion of his 70th birthday.

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Scheme I

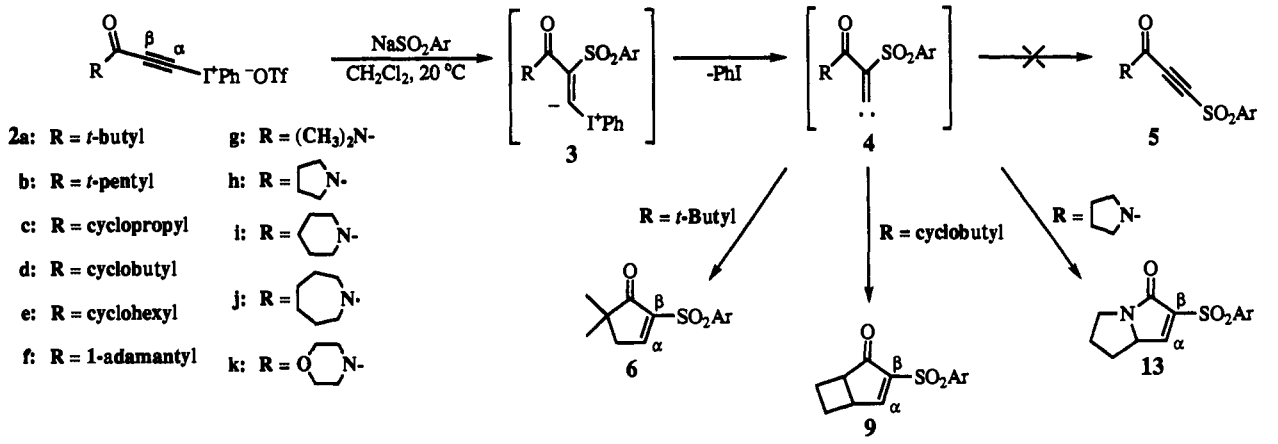


Table I. Cyclopentenones and γ-Lactams via the Reaction of β-Ketoethynyliodonium Triflates with $NaSO_2Ar$[a]

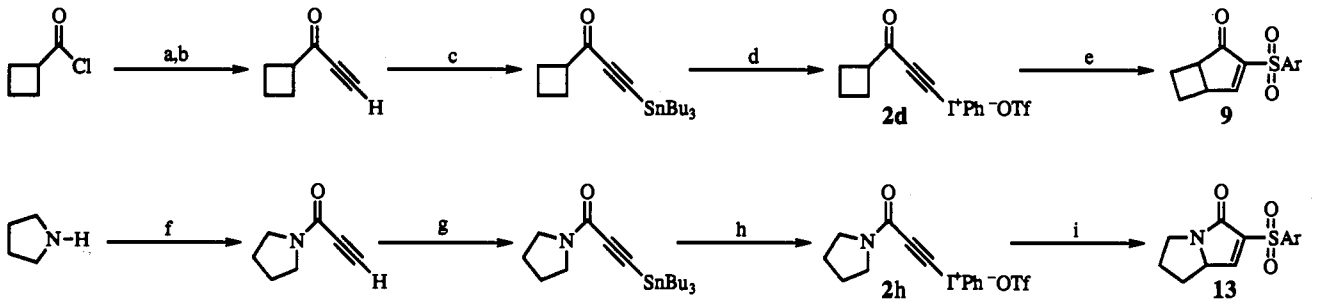
entry	iodonium salt	product	yield, %[b]	entry	iodonium salt	product	yield, %[b]
1	2a	6	72	7	2g	12	63
2	2b	7a + 7b	60[c]	8	2h	13	63
3	2c	8	53	9	2i	14	69
4	2d	9	75	10	2j	15	44
5	2e	10	57	11	2k	16	53
6	2f	11	82				

[a] Ar = p-$CH_3C_6H_4$. [b] Isolated yield of pure compound. [c] 13:8 ratio of 7a:7b by ^1H NMR spectroscopy.

alkylidenecarbene intermediate which undergoes a subsequent intramolecular 1,5-carbon–hydrogen insertion reaction to yield the corresponding cyclopentenones as crystalline solids in 53–82% isolated yields, as illustrated in Scheme I and summarized in Table I. The generality and versatility of the methodology is demonstrated by the formation of not only simple cyclopentenones **6** and **7** (entries 1 and 2) but also fused bicyclic (entries 3–5) and polycyclic (entry 6) products **8–10** and **11**. Moreover, the methodology is applicable to the formation of a γ-lactam (**12**), as illustrated by entry 7. In an attempt to extend the scope of this reaction, we investigated the synthesis of fused bicyclic alkaloids by using as precursors β-amidoethynyl(phenyl)iodonium salts **2h–k** in which the amide nitrogen is incorporated in a ring. Insertion of the intermediate alkylidenecarbene into a secondary carbon–hydrogen bond adjacent to the nitrogen atom affords the corresponding alkaloids **13–16** as crystalline solids in 44–69% isolated yields (entries 8–11).

Cyclopentenones **6–11** and γ-lactams **12–16** were fully characterized by multinuclear NMR, IR, elemental analysis, and/or high-resolution mass spectrometry. The infrared spectra display characteristic α,β-unsaturated carbonyl absorptions between 1738 and 1702 cm^{-1} for cyclopentenones **6–11** and between 1695 and 1681 cm^{-1} for γ-lactams **12–16**. All products exhibit conjugated C=C absorptions just below 1600 cm^{-1} in the infrared spectra as well as asymmetric and symmetric SO_2-stretching absorption bands due to the p-toluenesulfonyl group at 1320–1300 and at 1160–1145 cm^{-1}, respectively. In the ^1H NMR spectra, the vinylic proton resonances between 8.44 and 8.20 ppm for **6–11** and between 7.95 and 7.73 ppm for **12–16**. All other proton signals are consistent with the proposed structures. The carbonyl carbon

Scheme II[a]



[a] Reagents and conditions: (a) bis(trimethylsilyl)acetylene, $AlCl_3$, CH_2Cl_2, 0 °C, 3 h, 99%; (b) KF, CH_3OH, −70 to −40 °C, 2 h, 74%; (c) $(Bu_3Sn)_2O$, Et_2O, $MgSO_4$, 20 °C, 24 h, 98%; (d) PhI^+CN^-OTf, CH_2Cl_2, −42 °C, 45 min, 58%; (e) $NaSO_2Ar$ (Ar = *p*-$CH_3C_6H_4$), CH_2Cl_2, 20 °C, 15 min, 75%; (f) ethyl propiolate, CH_3OH, −78 °C, 9 h, 71%; (g) $(Bu_3Sn)_2O$, Et_2O, $MgSO_4$, 20 °C, 19 h, 99%; (h) PhI^+CN^-OTf, CH_2Cl_2, −42 °C, 45 min, 45%; (i) $NaSO_2Ar$ (Ar = *p*-$CH_3C_6H_4$), CH_2Cl_2, 20 °C, 15 min, 63%.

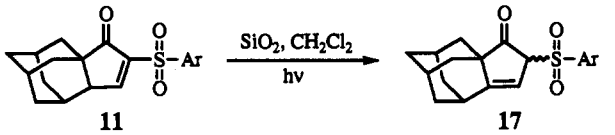
in the ^{13}C NMR spectra resonates between 204 and 195 ppm for cyclopentenones **6–11** and between 167 and 160 ppm for the more electron-rich γ-lactams **12–16**, in accord with expectations.[17] Similarly, the β-olefinic carbon signal appears between 172 and 166 ppm for **6–11** and between 155 and 147 ppm for **12–16**, whereas the α-olefinic carbon resonances between 148 and 140 ppm for cyclopentenones **6–11** and between 143 and 139 ppm for γ-lactams **12–16**.

The mechanism of the reaction[18] is outlined in Scheme I. Michael addition of the nucleophile, $NaSO_2Ar$, to **2** produces the unstable iodonium ylide **3**, which reductively eliminates PhI to generate alkylidenecarbene[19] **4**. The low migratory aptitude of the β-sulfonyl and β-carbonyl moieties precludes the usual rearrangement of carbene **4** to alkyne **5**. Instead, the carbene regioselectively undergoes an intramolecular 1,5-carbon–hydrogen insertion reaction, resulting in the desired cyclopentenone products. Preferential 1,5- rather than 1,6-cyclization is illustrated by the absence of any cyclohexenone-derived product in the reaction of **2b** and is consistent with the known[19–21] behavior of alkylidenecarbenes **4**. Specifically, Gilbert and co-workers established that alkylidenecarbenes preferentially insert into 1,5-carbon–hydrogen bonds with regio- and stereospecificity, resulting in cyclopentenes with retained configurations.[21] Furthermore, the generation of alkylidenecarbenes from alkynyl(phenyl)-iodonium salts has been utilized in efficient cyclopentene annulations.[22]

Entry 2 of Table I illustrates a limitation of this methodology. When two different types of 1,5-carbon–hydrogen bonds are present, a mixture of products is observed. The ratio of products observed in entry 2 favoring insertion of carbene **4** into the secondary carbon–hydrogen bond (product **7a**) over insertion into the primary carbon–hydrogen bond (product **7b**) is consistent with the data of Gilbert and co-workers on the carbon–hydrogen insertion behavior of alkylidenecarbenes (3° > 2° benzylic > 2° aliphatic > 1°).[23] The presently studied cyclization reaction also has its advantages. Since the cyclization is intramolecular in nature, the regioselectivity problems often encountered when using intermolecular methods for cyclopentenone formation are avoided. Additionally, the tandem Michael addition–carbene insertion reaction of β-ketoethynyl(phenyl)iodonium salt **2e** proved to be an efficient process for synthesizing the hexahydro-1-indenone system **10**. In contrast, cyclohexene is reported[8] to react sluggishly in the Pauson–Khand reaction to afford poor yields of hexahydro-1-indenones.

The use of sodium *p*-toluenesulfinate as the nucleophile in the tandem Michael addition–carbene insertion reaction of β-ketoethynyl(phenyl)iodonium salts is important not only for the generation of an alkylidenecarbene intermediate, which preferentially undergoes an intramolecular 1,5-carbon–hydrogen insertion reaction rather than rearrangement to an alkyne, but also for further synthetic manipulation and regiocontrolled elaboration of the products. Cyclopentenones **6–11** and α,β-unsaturated γ-lactams **12–16** all possess a *p*-toluenesulfonyl group at the 2-position. Thus, these compounds are expected to readily undergo conjugate addition reactions[24] followed by a regiospecifically-directed[25] alkylation of the resulting enolate at the 2-position. Furthermore, vinyl sulfones are themselves regarded as useful intermediates in organic synthesis. They serve as both Michael acceptors and activated vinyl equivalents in cycloaddition reactions.[26] In addition, the *p*-toluenesulfonyl group can be reductively removed with the use of aluminum amalgam to produce the desulfurized product in excellent yield.[27]

Scheme III



Typical conditions for transforming an acid chloride and amine to the corresponding cyclopentenone and α,β-unsaturated γ-lactam are outlined in Scheme II. The overall reaction sequence can be used to prepare a diverse array of products since numerous acyclic, cyclic, and polycyclic acid chlorides and amines are readily available.

Isomerization of Cyclopentenone 11. In the course of our present investigation, we initially attempted to isolate cyclopentenone **11** via radial chromatography rather than crystallization. We found that 2-cyclopentenone **11** readily isomerized to the corresponding 3-cyclopentenone upon being exposed to silica gel and UV irradiation using CH_2Cl_2 as eluent (Scheme III). Compound **17**[28] was isolated as the sole product and, like its

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(28) The structure of compound **17** has been confirmed by a single-crystal X-ray analysis.

progenitor, has 18 distinct signals in the proton-decoupled ^{13}C NMR spectrum. Its ^1H NMR spectrum possesses a vinylic resonance at 5.64 ppm as opposed to the vinylic resonance observed at 8.30 ppm for cyclopentenone **11**. Furthermore, the infrared spectrum of **17** displays a carbonyl absorption at 1745 cm^{-1} in contrast to the carbonyl absorption at 1717 cm^{-1} of α,β-unsaturated cyclopentenone **11**. Cyclopentenones **8-10**, however, were found to be stable under similar conditions. Their attempted isomerization on silica gel under UV irradiation with CH_2Cl_2 as eluent led only to recovered starting material. Additionally, it was discovered that α,β-unsaturated γ-lactams **13-16** cleanly isomerize in $CDCl_3$ at room temperature over the course of several hours, whereas cyclopentenones **6-11** and γ-lactam **12** are stable in solution.

The isomerization of 2-cyclopentenone **11** to 3-cyclopentenone **17** upon exposure to silica gel is somewhat unusual since it involves removing the double bond from conjugation with both carbonyl and sulfonyl functionalities. However, it has been reported that β,γ-unsaturated sulfones are more thermodynamically stable than the corresponding α,β-unsaturated isomers.[29] Additionally, the conversion of a variety of vinyl sulfones to the corresponding allyl isomers using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) has been demonstrated.[30] β,γ-Unsaturated sulfones such as **17** are themselves useful synthetic intermediates since the *p*-toluenesulfonyl group can serve to stabilize an adjacent carbanion[31] and act as a leaving group in substitution[32] or elimination reactions.[26]

Conclusions. The tandem Michael addition-carbene insertion reaction of β-ketoethynyl(phenyl)iodonium triflates with sodium *p*-toluenesulfinate constitutes a general method for the synthesis of a variety of substituted 2-cyclopentenones under mild conditions. Furthermore, using β-amidoethynyl(phenyl)iodonium salts in which the amide-nitrogen is incorporated in a ring permits the synthesis of fused bicyclic alkaloids. Both the cyclopentenones and the α,β-unsaturated γ-lactams prepared via this methodology possess a synthetically versatile *p*-toluenesulfonyl group at the 2-position making further regiocontrolled elaboration of the products possible.

Experimental Section

General Methods. Melting points were obtained with a Mel-Temp capillary melting point apparatus and are uncorrected. Radial chromatography was performed with a Harrison Research Chromatotron, Model 7924T. Ultraviolet irradiation (254 nm) was provided by a Mineralight lamp, Model UVGL-25. 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, acetonitrile at δ 1.93, nitromethane at δ 4.33, or methylene chloride at δ 5.32; ^{13}C chemical shifts are expressed relative to $CDCl_3$ at δ 77.0, CD_3CN at δ 1.3, CD_3NO_2 at δ 62.8, or CD_2Cl_2 at δ 53.8. 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 or under electron impact (EI) conditions at 70 eV. 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. Elemental analyses were performed by Atlantic Microlab, Inc., of Norcross, GA.

Materials. Reagent grade methylene chloride was distilled from calcium hydride prior to use. Bis(tributyltin) oxide was purchased from Lancaster and used as received. Sodium *p*-toluenesulfinate hydrate was purchased from Lancaster and dried by heating in vacuo at 200 °C for 24 h. The preparation of alkynyl(phenyl)iodonium triflates **2a**, **c**, **f**, and **g** has been reported previously.[14] Alkynylstannanes used for the preparation of alkynyl(phenyl)iodonium triflates **2b**, **d**, **e**, **h–k** were obtained via reaction of the appropriate terminal acetylene with bis(tributyltin) oxide. The acetylenic ketones were made by the Friedel–Crafts acylation[33] of bis(trimethylsilyl)acetylene followed by fluoride ion-promoted removal of the remaining trimethylsilyl group at low temperature.[34] *N,N*-Tetramethylenepropiolamide, *N,N*-pentamethylenepropiolamide, and the propiolamide derived from morpholine were prepared from methyl or ethyl propiolate and the requisite amine at low temperature.[35] *N,N*-Hexamethylenepropiolamide was synthesized by coupling the amine to propiolic acid using 1,3-dicyclohexylcarbodiimide.[36] Reaction flasks were flame-dried and flushed with nitrogen prior to use.

General Procedure for the Preparation of Alkynyl(phenyl)iodonium Triflates 2b, d, e, h–k. A solution of the appropriate functionalized alkynylstannane (3.15–10.5 mmol, a 5% molar excess) in CH_2Cl_2 (10 mL) was added dropwise to a stirred 0.08 M suspension of cyano(phenyl)-iodonium triflate[37] (3.00–10.0 mmol) in CH_2Cl_2 at –42 °C (CH_3CN/dry ice slush bath) under nitrogen. Stirring was maintained at –42 °C for 45 min followed by slow addition of twice the volume of pentane to precipitate the product. The microcrystalline solid was filtered from the cold solution under a nitrogen atmosphere, washed with pentane (3 × 30 mL), immediately recrystallized from CH_2Cl_2/Et_2O/pentane, and dried in vacuo.

Note: While we have experienced no difficulties in the preparation and handling of any of the alkynyl(phenyl)iodonium triflates, due caution should be exercised when working with β-amidoethynyl(phenyl)iodonium triflate derivatives 2g–k, as these microcrystalline solids detonate when heated to 70–90 °C.

(2,2-Dimethylbutyryl)[phenyl[[(trifluoromethyl)sulfonyl]oxy]-iodo]acetylene (2b). Reaction of (2,2-dimethylbutyryl)(tributylstannyl)-acetylene (2.02 g, 5.25 mmol) with cyano(phenyl)iodonium triflate (1.90 g, 5.00 mmol) afforded 1.79 g (75%) of **2b** as a white microcrystalline solid, mp 100–101 °C dec: IR (CCl_4) 3093, 3086, 3063, 2972, 2934, 2881, 2156 (C≡C), 1675 (CO), 1563, 1472, 1447, 1394, 1291, 1235, 1218, 1166, 1086, 1041, 1024, 987, 636 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.09 (d, 2 H), 7.67 (t, 1 H), 7.52 (t, 2 H), 1.58 (q, 2 H), 1.10 (s, 6 H), 0.76 (t, 3 H); ^{19}F NMR ($CDCl_3$) δ –78.37 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 191.00 (CO), 134.67, 132.97, 132.48, 119.47 (q, J = 319 Hz, $CF_3SO_3^-$), 116.69, 101.19 (*C*≡CI$^+$), 48.90, 39.53 (C≡*C*I$^+$), 31.56 (CH_2), 22.64 (CH_3), 8.72 (CH_3); FAB HRMS m/z 327.026 139 (M – $CF_3SO_3^-$)$^+$, calcd for $C_{14}H_{16}OI$ 327.024 467. Anal. Calcd for $C_{15}H_{16}O_4SF_3I$: C, 37.83; H, 3.39; S, 6.73. Found: C, 37.56; H, 3.45; S, 6.67.

Cyclobutyryl[phenyl[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (2d). Reaction of cyclobutyryl(tributylstannyl)acetylene (2.92 g, 7.35 mmol) with cyano(phenyl)iodonium triflate (2.65 g, 7.00 mmol) afforded 1.86 g (58%) of **2d** as a white needles, mp 70 °C dec: IR (CCl_4) 3083, 3062, 2998, 2943, 2865, 2157 (C≡C), 1666 (CO), 1563, 1474, 1444, 1296, 1234, 1217, 1178, 1133, 1015, 988, 631 cm^{-1}; ^1H NMR ($CDCl_3$, –30 °C) δ 8.06 (d, 2 H), 7.64 (t, 1 H), 7.48 (t, 2 H), 3.39–3.28 (m, 1 H), 2.28–2.05 (m, 4 H), 1.96–1.83 (m, 1 H), 1.78–1.68 (m, 1 H); ^{19}F NMR ($CDCl_3$, –30 °C) δ –78.51 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$, –30 °C) δ 186.58 (CO), 134.63, 132.95, 132.33, 119.10 (q, J = 319 Hz, $CF_3SO_3^-$), 115.95, 100.18 (*C*≡CI$^+$), 46.74 (CH), 40.14 (C≡*C*I$^+$), 23.88 (CH_2), 17.51 (CH_2); FAB HRMS m/z 310.994 654 (M – $CF_3SO_3^-$)$^+$, calcd for $C_{13}H_{12}OI$ 310.993 167. Anal. Calcd for $C_{14}H_{12}O_4SF_3I$: C, 36.54; H, 2.63; S, 6.97. Found: C, 36.28; H, 2.71; S, 6.87.

Cyclohexanoyl[phenyl[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (2e). Reaction of cyclohexanoyl(tributylstannyl)acetylene (4.46 g, 10.5 mmol) with cyano(phenyl)iodonium triflate (3.79 g, 10.0 mmol) afforded 2.29 g (47%) of **2e** as a white microcrystalline solid, mp 71 °C dec: IR (CCl_4) 3085, 3061, 2934, 2855, 2157 (C≡C), 1665 (CO), 1560, 1474, 1445, 1297, 1234, 1217, 1179, 1017, 635 cm^{-1}; ^1H NMR ($CDCl_3$, –30 °C) δ 8.06 (d, 2 H), 7.67 (t, 1 H), 7.59 (t, 2 H), 2.48–2.41 (m, 1 H), 1.93–1.89 (m, 2 H), 1.72–1.68 (m, 2 H), 1.61–1.57 (m, 1 H), 1.30–1.11 (m, 5 H); ^{19}F NMR ($CDCl_3$, –30 °C) δ –78.55 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$, –30 °C) δ 188.54 (CO), 134.66, 132.99, 132.40, 119.13 (q, J = 319 Hz, $CF_3SO_3^-$), 115.85, 100.97 (*C*≡CI$^+$), 51.75 (CH), 39.48 (C≡*C*I$^+$), 27.25 (CH_2), 25.21 (CH_2), 24.86 (CH_2); FAB HRMS m/z 339.024 125 (M

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– $CF_3SO_3^-)^+$, calcd for $C_{15}H_{16}OI$ 339.024 467. Anal. Calcd for $C_{16}H_{16}O_4SF_3I$: C, 39.36; H, 3.30; S, 6.57. Found: C, 39.10; H, 3.27; S, 6.44.

(*N,N*-Tetramethylenecarbamoyl)[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (2h). Reaction of (*N,N*-tetramethylenecarbamoyl)(tributylstannyl)acetylene (2.16 g, 5.25 mmol) with cyano(phenyl)iodonium triflate (1.90 g, 5.00 mmol) afforded 1.07 g (45%) of **2h** as an off-white microcrystalline solid, mp 70 °C explodes: IR (CCl_4) 3087, 2991, 2987, 2967, 2879, 2171 (C≡C), 1636 (CO), 1559, 1472, 1456, 1443, 1420, 1291, 1259, 1237, 1172, 1017, 987, 675, 632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.15 (d, 2 H), 7.65 (t, 1 H), 7.51 (t, 2 H), 3.55 (t, 2 H), 3.37 (t, 2 H), 1.91–1.82 (m, 4 H); ^{19}F NMR ($CDCl_3$) δ –78.36 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 149.56 (CO), 134.85, 132.88, 132.43, 119.86 (q, J = 319 Hz, $CF_3SO_3^-$), 116.92, 96.00 (*C*≡CI$^+$), 48.34 (CH_2), 46.13 (CH_2), 40.59 (C≡*C*I$^+$), 25.12 (CH_2), 24.33 (CH_2); FAB HRMS m/z 326.004 665 (M – $CF_3SO_3^-)^+$, calcd for $C_{13}H_{13}ONI$ 326.004 066.

(*N,N*-Pentamethylenecarbamoyl)[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (2i). Reaction of (*N,N*-pentamethylenecarbamoyl)(tributylstannyl)acetylene (2.24 g, 5.25 mmol) with cyano(phenyl)iodonium triflate (1.90 g, 5.00 mmol) afforded 1.93 g (79%) of **2i** as white needles, mp 88–89 °C explodes: IR (CCl_4) 3086, 3062, 2990, 2962, 2939, 2856, 2167 (C≡C), 1637 (CO), 1562, 1473, 1451, 1437, 1293, 1264, 1235, 1219, 1179, 1020, 987, 634 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.10 (d, 2 H), 7.66 (t, 1 H), 7.52 (t, 2 H), 3.61 (t, 2 H), 3.50 (t, 2 H), 1.68–1.49 (br m, 6 H); ^{19}F NMR ($CDCl_3$) δ –78.36 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 149.43 (CO), 134.64, 132.90, 132.53, 119.64 (q, J = 319 Hz, $CF_3SO_3^-$), 116.53, 96.96 (*C*≡CI$^+$), 48.34 (CH_2), 42.90 (CH_2), 38.82 (C≡*C*I$^+$), 26.24 (CH_2), 25.26 (CH_2), 24.22 (CH_2); FAB HRMS m/z 340.018 247 (M – $CF_3SO_3^-)^+$, calcd for $C_{14}H_{15}ONI$ 340.019 716. Anal. Calcd for $C_{15}H_{15}O_4NSF_3I$: C, 36.82; H, 3.09; S, 6.55; N, 2.86. Found: 36.89; H, 3.15; S, 6.64; N, 2.93.

(*N,N*-Hexamethylenecarbamoyl)[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (2j). Reaction of (*N,N*-hexamethylenecarbamoyl)(tributylstannyl)acetylene (2.31 g, 5.25 mmol) with cyano(phenyl)iodonium triflate (1.90 g, 5.00 mmol) afforded 1.38 g (55%) of **2j** as an off-white microcrystalline solid, mp 90 °C explodes: IR (CCl_4) 3083, 3061, 2930, 2887, 2852, 2175 (C≡C), 1609 (CO), 1564, 1473, 1442, 1430, 1303, 1234, 1216, 1164, 1024, 636 cm^{-1}; ^1H NMR (CD_3NO_2) δ 8.32 (d, 2 H), 7.84 (t, 1 H), 7.69 (t, 2 H), 3.60 (t, 2 H), 3.46 (t, 2 H), 1.69–1.58 (br m, 4 H), 1.58–1.46 (br m, 4 H); ^{19}F NMR (CD_3NO_2) δ –78.54 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3NO_2) δ 152.85 (CO), 136.54, 134.87, 134.17, 121.66 (q, J = 319 Hz, $CF_3SO_3^-$), 119.02, 97.67 (*C*≡CI$^+$), 50.44 (CH_2), 47.10 (CH_2), 40.75 (C≡*C*I$^+$), 30.05 (CH_2), 28.06 (CH_2), 27.80 (CH_2), 27.60 (CH_2); FAB HRMS m/z 354.035 497 (M – $CF_3SO_3^-)^+$, calcd for $C_{15}H_{17}ONI$ 354.035 366. Anal. Calcd for $C_{16}H_{17}O_4NSF_3I$: C, 38.19; H, 3.40; S, 6.37; N, 2.78. Found: C, 38.25; H, 3.45; S, 6.43; N, 2.74.

(Morpholinocarbonyl)[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene (2k). Reaction of (morpholinocarbonyl)(tributylstannyl)acetylene (1.35 g, 3.15 mmol) with cyano(phenyl)iodonium triflate (1.14 g, 3.00 mmol) afforded 1.21 g (82%) of **2k** as white needles, mp 96 °C explodes: IR (CCl_4) 3093, 3053, 2976, 2928, 2861, 2167 (C≡C), 1644 (CO), 1593, 1474, 1455, 1443, 1432, 1289, 1277, 1235, 1219, 1177, 1108, 1021, 636 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.07 (d, 2 H), 7.68 (t, 1 H), 7.53 (t, 2 H), 3.75–3.58 (br m, 8 H); ^{19}F NMR ($CDCl_3$) δ –78.40 (s, $CF_3SO_3^-$); ^{13}C NMR ($CDCl_3$) δ 149.65 (CO), 134.72, 133.04, 132.59, 119.56 (q, J = 319 Hz, $CF_3SO_3^-$), 115.94, 96.36 (*C*≡CI$^+$), 66.81 (CH_2), 66.14 (CH_2), 47.23 (CH_2), 47.32 (CH_2), 38.72 (C≡*C*I$^+$); FAB HRMS m/z 341.998019 (M – $CF_3SO_3^-)^+$, calcd for $C_{13}H_{13}O_2NI$ 341.998981. Anal. Calcd for $C_{14}H_{13}O_5NSF_3I$: C, 34.23; H, 2.67; S, 6.53; N, 2.85. Found: C, 34.30; H, 2.66; S, 6.61; N, 2.86.

General Procedure for the Preparation of Cyclopentenones and γ-Lactams via β-Functionalized Alkynyl(phenyl)iodonium Salts 2. The appropriate salt **2a–k** (1.00 mmol) was reacted with anhydrous sodium *p*-toluenesulfinate (1.01 mmol) in CH_2Cl_2 (15 mL) at 20 °C under nitrogen for 15 min, after which time H_2O (10 mL) was added and the phases were separated. The aqueous layer was extracted with additional CH_2Cl_2 (2 × 5 mL), and the combined organic extracts were dried over anhydrous $MgSO_4$. The solution was filtered, hexanes (30 mL) were added, and the majority of the solvents were removed by rotary evaporation, precipitating the product. The microcrystalline solid was collected by filtration, washed with pentane (3 × 10 mL), and dried in vacuo. Further purification of cyclopentenones **6–10** was effected by radial chromatography (silica gel, 200–400 mesh) using CH_2Cl_2/hexanes (1:1) as eluent.

Cyclopentenone 6. Reaction of iodonium salt **2a** (0.462 g, 1.00 mmol) with anhydrous sodium *p*-toluenesulfinate (0.180 g, 1.01 mmol) in CH_2Cl_2 for 15 min according to the general procedure afforded 0.190 g (72%) of **6** as a white microcrystalline solid, mp 124–125 °C: IR (CCl_4) 3087, 3070, 2964, 2930, 2870, 1722 (CO), 1706, 1596, 1463, 1422, 1314, 1285, 1150, 1120, 1086, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.33 (t, 1 H, =CH), 7.89 (d, 2 H, ArH), 7.29 (d, 2 H, ArH), 2.61 (d, 2 H, CH_2), 2.38 (s, 3 H, $ArCH_3$), 1.04 (s, 6 H, 2 CH_3); ^{13}C NMR ($CDCl_3$) δ 203.67 (CO), 167.28 (C=*C*H), 145.03 (Ar), 144.61 (*C*=CH), 136.00 (Ar), 129.66 (Ar), 128.51 (Ar), 45.85, 43.07 (CH_2), 24.62 (CH_3), 21.63 ($ArCH_3$); EI HRMS (70 eV) m/z 264.082 67 (M^+), calcd for $C_{14}H_{16}O_3S$ 264.082 02. Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10, S, 12.13. Found: C, 63.44; H, 6.13; S, 12.21.

Cyclopentenones 7a and 7b. Reaction of iodonium salt **2b** (0.476 g, 1.00 mmol) with anhydrous sodium *p*-toluenesulfinate (0.180 g, 1.01 mmol) in CH_2Cl_2 for 15 min according to the general procedure afforded 0.167 g (60%) of an inseparable mixture of **7a** and **7b** as colorless needles, mp not determined: IR (CCl_4) 3069, 2966, 2931, 2872, 1738 (CO), 1716 (CO), 1596, 1456, 1319, 1292, 1283, 1154, 1122, 1087, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.38 (t, =CH), 8.21 (d, =CH), 7.91 (d, ArH), 7.31 (d, ArH), 2.76–2.67 (m), 2.58 (dd), 2.40 (s, $ArCH_3$), 1.53–1.36 (m), 1.15 (s, CH_3), 1.12 (s, CH_3), 1.04 (s, CH_3), 0.92 (s, CH_3), 0.62 (t, CH_3); ^{13}C NMR ($CDCl_3$) δ 203.80 (CO), 203.73 (CO), 171.38 (C=*C*H), 167.67 (C=*C*H), 145.69 (*C*=CH), 144.97 (Ar), 143.46 (C=CH), 136.06 (Ar), 129.66 (Ar), 128.53 (Ar), 49.84, 49.59, 45.61, 40.22, 30.90, 24.63, 23.01, 21.74, 20.49, 13.92, 8.60; EI HRMS (70 eV) m/z 278.096 34 (M^+), calcd for $C_{15}H_{18}O_3S$ 278.097 67. Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52; S, 11.52. Found: C, 64.44; H, 6.46; S, 11.43.

Cyclopentenone 8. Reaction of iodonium salt **2c** (0.446 g, 1.00 mmol) with anhydrous sodium *p*-toluenesulfinate (0.180 g, 1.01 mmol) in CH_2Cl_2 for 15 min according to the general procedure afforded 0.132 g (53%) of **8** as a white microcrystalline solid, mp 135–137 °C dec: IR (CCl_4) 3090, 3066, 3052, 2928, 2920, 1720 (CO), 1594, 1577, 1320, 1311, 1295, 1174, 1151, 673 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.37 (d, 1 H, =CH), 7.83 (d, 2 H, ArH), 7.28 (d, 2 H, ArH), 2.65–2.59 (m, 1 H), 2.43–2.33 (overlapping m, 1 H), 2.38 (s, 3 H, $ArCH_3$), 1.64–1.57 (m, 1 H), 1.43–1.38 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 195.21 (CO), 169.27 (C=*C*H), 144.87 (Ar), 140.20 (*C*=CH), 136.13 (Ar), 129.58 (Ar), 128.30 (Ar), 35.05 (CH_2), 27.14 (CH), 21.63 ($ArCH_3$), 20.96 (CH); EI HRMS (70 eV) m/z 248.050 21 (M^+), calcd for $C_{13}H_{12}O_3S$ 248.050 72.

Cyclopentenone 9. Reaction of iodonium salt **2d** (0.460 g, 1.00 mmol) with anhydrous sodium *p*-toluenesulfinate (0.180 g, 1.01 mmol) in CH_2Cl_2 for 15 min according to the general procedure afforded 0.197 g (75%) of **9** as a white microcrystalline solid, mp 164–165 °C dec: IR (CCl_4) 3091, 3065, 3053, 2999, 2988, 2961, 2952, 1702 (CO), 1595, 1574, 1323, 1309, 1285, 1151, 1094, 1023, 707, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.44 (d, 1 H, =CH), 7.92 (d, 2 H, ArH), 7.30 (d, 2 H, ArH), 3.49–3.42 (m, 1 H), 3.13–3.06 (m, 1 H), 2.61–2.45 (m, 2 H), 2.40 (s, 3 H, $ArCH_3$), 1.86–1.71 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 201.16 (CO), 170.91 (C=*C*H), 147.69 (*C*=CH), 145.00 (Ar), 135.96 (Ar), 129.62 (Ar), 128.51 (Ar), 45.34 (CH), 38.00 (CH), 23.34 (CH_2), 21.65 ($ArCH_3$), 19.82 (CH_2); EI HRMS (70 eV) m/z 262.067 23 (M^+), calcd for $C_{14}H_{14}O_3S$ 262.066 37.

Cyclopentenone 10. Reaction of iodonium salt **2e** (0.488 g, 1.00 mmol) with anhydrous sodium *p*-toluenesulfinate (0.180 g, 1.01 mmol) in CH_2Cl_2 for 15 min according to the general procedure afforded 0.166 g (57%) of **10** as a white microcrystalline solid, mp 112 °C: IR (CCl_4) 3065, 2948, 2862, 1733, 1719 (CO), 1594, 1566, 1446, 1316, 1258, 1173, 1153, 1084, 670, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.20 (d, 1 H, =CH), 7.90 (d, 2 H, ArH), 7.30 (d, 2 H, ArH), 2.43–2.38 (overlapping m, 1 H), 2.40 (s, 3 H, $ArCH_3$), 2.15–2.03 (m, 3 H), 1.91–1.84 (m, 2 H), 1.44–1.20 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 197.11 (CO), 166.84 (C=*C*H), 145.49 (*C*=CH), 144.96 (Ar), 136.20 (Ar), 129.64 (Ar), 128.57 (Ar), 58.04 (CH), 46.03 (CH), 29.26 (CH_2), 26.51 (CH_2), 25.65 (CH_2), 23.79 (CH_2), 21.71 ($ArCH_3$); EI HRMS (70 eV) m/z 290.097 41 (M^+), calcd for $C_{16}H_{18}O_3S$ 290.097 67.

Cyclopentenone 11. Reaction of iodonium salt **2f** (0.540 g, 1.00 mmol) with anhydrous sodium *p*-toluenesulfinate (0.180 g, 1.01 mmol) in CH_2Cl_2 for 15 min according to the general procedure afforded 0.281 g (82%) of **11** as a white microcrystalline solid, mp 97–98 °C: IR (CCl_4) 3053, 2930, 2904, 2854, 1717 (CO), 1595, 1570, 1451, 1320, 1296, 1256, 1153, 1091, 715, 656 cm^{-1}; ^1H NMR ($CDCl_3$, –30 °C) δ 8.30 (d, 1 H, =CH), 7.86 (d, 2 H, ArH), 7.28 (d, 2 H, ArH), 2.87 (s, 1 H), 2.36 (br s, 4 H, CH and $ArCH_3$), 2.05–1.42 (m, 12 H); ^{13}C NMR ($CDCl_3$, –30 °C) δ 201.61 (CO), 168.00 (C=*C*H), 144.93 (Ar), 143.56 (*C*=CH), 135.45 (Ar), 129.60 (Ar), 128.17 (Ar), 52.10, 51.26, 38.14, 38.00, 35.98, 34.43, 32.34, 29.56, 27.35, 26.77, 21.65 ($ArCH_3$); EI HRMS (70 eV) m/z 342.129 60 (M^+), calcd for $C_{20}H_{22}O_3S$ 342.128 97.

γ-Lactam 12. Reaction of iodonium salt **2g** (0.449 g, 1.00 mmol) with anhydrous sodium *p*-toluenesulfinate (0.180 g, 1.01 mmol) in CH_2Cl_2 for 15 min according to the general procedure afforded 0.158 g (63%) of **12** as colorless needles, mp 135–136 °C: IR (CCl_4) 3098, 2961, 2935, 1681 (CO), 1651, 1596, 1437, 1410, 1396, 1314, 1299, 1184, 1155, 1131, 710, 664 cm^{-1}; ^1H NMR (CD_3CN) δ 7.89 (d, 2 H, ArH), 7.88 (s, 1 H, =CH), 7.39 (d, 2 H, ArH), 4.05 (s, 2 H, CH_2), 2.86 (s, 3 H, NCH_3), 2.41 (s, 3 H, $ArCH_3$); ^{13}C NMR (CD_3CN) δ 164.12 (CO), 151.79 (C=CH), 146.35 (Ar), 140.97 (*C*=CH), 137.05 (Ar), 130.53 (Ar), 129.35 (Ar), 53.40 (CH_2), 29.38 (NCH_3), 21.61 ($ArCH_3$); EI HRMS (70 eV) *m/z* 251.060 88 (M^+), calcd for $C_{12}H_{13}O_3NS$ 251.061 62. Anal. Calcd for $C_{12}H_{13}O_3NS$: C, 57.35; H, 5.21; S, 12.76; N, 5.57. Found: C, 57.09; H, 5.26; S, 12.66; N, 5.56.

γ-Lactam 13. Reaction of iodonium salt **2h** (0.475 g, 1.00 mmol) with anhydrous sodium *p*-toluenesulfinate (0.180 g, 1.01 mmol) in CH_2Cl_2 for 15 min according to the general procedure afforded 0.175 g (63%) of **13** as a white microcrystalline solid, mp 132–133 °C dec: IR (CCl_4) 3069, 2979, 2955, 2893, 1693 (CO), 1650, 1594, 1449, 1321, 1161, 1145, 710, 669 cm^{-1}; ^1H NMR ($CDCl_3$, −30 °C) δ 7.95 (s, 1 H, =CH), 7.92 (d, 2 H, ArH), 7.28 (d, 2 H, ArH), 4.30–4.24 (m, 1 H), 3.41–3.32 (m, 1 H), 3.21–3.16 (m, 1 H), 2.40–2.11 (overlapping m, 3 H), 2.36 (s, 3 H, $ArCH_3$), 1.20–1.14 (m, 1 H); ^{13}C NMR ($CDCl_3$, −30 °C) δ 166.23 (CO), 153.63 (C=CH), 145.24 (Ar), 140.62 (*C*=CH), 134.67 (Ar), 129.52 (Ar), 128.50 (Ar), 64.85 (CH), 42.02 (CH_2), 29.22 (CH_2), 28.23 (CH_2), 21.69 ($ArCH_3$); EI HRMS (70 eV) *m/z* 277.078 06 (M^+), calcd for $C_{14}H_{15}O_3NS$ 277.077 27. Anal. Calcd for $C_{14}H_{15}O_3NS$: C, 60.63; H, 5.45; S, 11.56; N, 5.05. Found: C, 60.41; H, 5.51; S, 11.69; N, 5.03.

γ-Lactam 14. Reaction of iodonium salt **2i** (0.489 g, 1.00 mmol) with anhydrous sodium *p*-toluenesulfinate (0.180 g, 1.01 mmol) in CH_2Cl_2 for 15 min according to the general procedure afforded 0.202 g (69%) of **14** as a white microcrystalline solid, mp 123–124 °C dec: IR (CCl_4) 3100, 3062, 3048, 2980, 2952, 2930, 2856, 1684 (CO), 1595, 1454, 1415, 1315, 1305, 1286, 1159, 1142, 709, 690, 661 cm^{-1}; ^1H NMR ($CDCl_3$, −30 °C) δ 7.96 (d, 2 H, ArH), 7.82 (s, 1 H, =CH), 7.29 (d, 2 H, ArH), 4.14–4.08 (m, 1 H), 3.94–3.92 (m, 1 H), 2.78–2.70 (m, 1 H), 2.37 (s, 3 H, $ArCH_3$), 2.15–2.12 (m, 1 H), 1.92–1.88 (m, 1 H), 1.70–1.66 (m, 1 H), 1.54–1.40 (m, 1 H), 1.27–1.14 (m, 1 H), 1.09–0.96 (m, 1 H); ^{13}C NMR ($CDCl_3$, −30 °C) δ 160.72 (CO), 152.16 (C=CH), 145.22 (Ar), 139.98 (*C*=CH), 134.72 (Ar), 129.51 (Ar), 128.61 (Ar), 59.00 (CH), 39.41 (CH_2), 29.38 (CH_2), 24.48 (CH_2), 22.93 (CH_2), 21.73 ($ArCH_3$); EI HRMS (70 eV) *m/z* 291.092 07 (M^+), calcd for $C_{15}H_{17}O_3NS$ 291.092 92. Anal. Calcd for $C_{15}H_{17}O_3NS$: C, 61.83; H, 5.88; S, 11.00; N, 4.81. Found: C, 61.84; H, 5.92; S, 11.07; N, 4.85.

γ-Lactam 15. Reaction of iodonium salt **2j** (0.503 g, 1.00 mmol) with anhydrous sodium *p*-toluenesulfinate (0.180 g, 1.01 mmol) in CH_2Cl_2 for 15 min according to the general procedure afforded 0.135 g (44%) of **15** as pale yellow needles, mp 119–121 °C dec: IR (CCl_4) 3092, 2943, 2927, 2854, 1695 (CO), 1597, 1450, 1401, 1315, 1293, 1156, 1145, 1087, 663 cm^{-1}; ^1H NMR (CD_2Cl_2, −30 °C) δ 7.92 (d, 2 H, ArH), 7.73 (s, 1 H, =CH), 7.36 (d, 2 H, ArH), 4.28–4.23 (m, 1 H), 3.45–3.41 (m, 1 H), 3.30–3.25 (m, 1 H), 2.41 (s, 3 H, $ArCH_3$), 2.11–2.07 (m, 1 H), 1.79–1.73 (m, 2 H), 1.60–1.34 (br m, 5 H); ^{13}C NMR (CD_2Cl_2, −30 °C) δ 163.34 (CO), 154.35 (C=CH), 145.54 (Ar), 139.66 (*C*=CH), 135.59 (Ar), 129.67 (Ar), 128.77 (Ar), 61.97 (CH), 44.23 (CH_2), 31.65 (CH_2), 29.22 (CH_2), 27.28 (CH_2), 26.20 (CH_2), 21.73 ($ArCH_3$); EI HRMS (70 eV) *m/z* 305.108 76 (M^+), calcd for $C_{16}H_{19}O_3NS$ 305.108 57.

γ-Lactam 16. Reaction of iodonium salt **2k** (0.491 g, 1.00 mmol) with anhydrous sodium *p*-toluenesulfinate (0.180 g, 1.01 mmol) in CH_2Cl_2 for 15 min according to the general procedure afforded 0.156 g (53%) of **16** as a pale yellow microcrystalline solid, mp 128–130 °C dec: IR (CCl_4) 3097, 3076, 2919, 2857, 1692 (CO), 1596, 1456, 1438, 1412, 1308, 1292, 1155, 1092, 705, 661 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.96 (d, 2 H, ArH), 7.73 (s, 1 H, =CH), 7.31 (d, 2 H, ArH), 4.34–4.24 (m, 2 H), 4.04–3.99 (m, 1 H), 3.90–3.85 (m, 1 H), 3.19–3.06 (m, 2 H), 2.99–2.92 (m, 1 H), 2.39 (s, 3 H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 161.00 (CO), 147.48 (C=CH), 145.36 (Ar), 142.93 (*C*=CH), 135.19 (Ar), 129.64 (Ar), 128.87 (Ar), 70.01 (CH_2), 66.11 (CH_2), 57.87 (CH), 40.04 (CH_2), 21.67 ($ArCH_3$); EI HRMS (70 eV) *m/z* 293.071 56 (M^+), calcd for $C_{14}H_{15}O_4NS$ 293.072 18.

Isomerization of Cyclopentenone 11 on Silica Gel: Preparation of 17. Radial chromatography of cyclopentenone **11** (0.080 g, 0.234 mmol) on silica gel (200–400 mesh, 4-mm plate) with UV irradiation using CH_2Cl_2 as eluent afforded a clear, colorless oil as the sole product upon removal of the solvent. The oil was crystallized from Et_2O/pentane to yield 0.063 g (79%) of **17** as white needles, mp 136–137 °C: IR (CCl_4) 3097, 3079, 2915, 2883, 2854, 1745 (CO), 1597, 1450, 1312, 1301, 1291, 1171, 1133, 1084 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70 (d, 2 H, ArH), 7.31 (d, 2 H, ArH), 5.64 (d, 1 H, =CH), 4.44 (d, 1 H), 2.78 (d, 1 H), 2.42 (s, 3 H, $ArCH_3$), 2.04 (d, 1 H), 1.94–1.64 (m, 9 H), 1.45 (d, 1 H), 1.13 (d, 1 H), ^{13}C NMR ($CDCl_3$) δ 207.95 (CO), 161.00 (*C*=CH), 145.08 (Ar), 134.45 (Ar), 129.54 (Ar), 129.42 (Ar), 104.88 (C=CH), 75.52 (CH), 52.34 (C), 39.37, 38.68, 37.51, 37.41, 36.01, 34.47, 28.22 (CH), 28.18, 21.71 ($ArCH_3$); EI nominal MS (70 eV), *m/z* 342 (M^+), calcd for $C_{20}H_{22}O_3S$ 342. Anal. Calcd for $C_{40}H_{22}O_3S$: C, 70.15; H, 6.48; S, 9.36. Found: C, 70.20; H, 6.53; S, 9.46.

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