Pseudocine Substitution of 4-(Mesyloxy)-2-cyclopentenones: An Efficient Route to 2,4-Disubstituted 2-Cyclopentenones[1]

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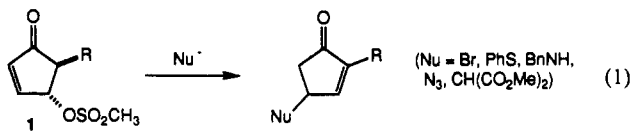
Readily available mesylates **1a–d** were found to undergo a novel substitution reaction. In the presence of a variety of nucleophiles, **1a–d** underwent a net substitution in which the nucleophile was introduced vicinally (C-3) to the departing mesylate (C-4) and the double bond migrated to C-4/C-5. Lithium bromide, thiophenol, benzylamine, sodium azide, and the potassium salt of dimethyl malonate all led to substitution products in good yield. The reaction is thought to proceed by way of initial conjugate addition of the nucleophile, followed by enolate equilibration and β-elimination of mesylate.

Introduction

The biological importance and ubiquity of cyclopentanoid natural products have stimulated the development of numerous approaches to the preparation and derivatization of the cyclopentenone ring system.[2] Considerable attention has been paid to 2-substituted cyclopent-2-en-1-ones[3] since they can be further elaborated to 2,3-disubstituted cyclopentanones,[4] including the prostaglandins.[5] While many elegant ring-forming approaches to cyclopentenones have been developed, modification of simple cyclopentanoid precursors may lend itself more easily to scale-up.

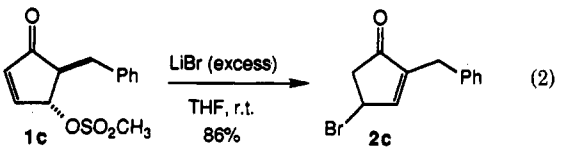
We report here a novel and general method to synthesize 2-substituted cyclopentenones with concomitant introduction of various functional groups to the allylic (C-4) position starting from readily available 5-substituted 4-(mesyloxy)-2-cyclopentenones 1. This procedure constitutes overall displacement of the mesyloxy group with vicinal introduction of the nucleophile, accompanied by transposition of alkene to afford the more substituted enone moiety (eq 1).



(1)

Results

4-(Mesyloxy)-5-alkylcyclopent-2-en-1-ones 1 could be prepared by mesylation of the corresponding hydroxycyclopentenones, prepared in two steps from furan and a variety of aldehydes via the method of Piancatelli (Scheme I).[6] Our intention had been to carry out direct displacement with bromide to yield the corresponding 4-bromo-5-alkylcyclopent-2-en-1-ones. However, when **1c** was stirred with excess LiBr a single product **2c** was isolated in good yield (eq 2), while none of the simple S_N2 substitution product was observed. In light of this surprising result, we sought to examine the generality of the reaction.



(2)

Treatment of **1a,b,d** with LiBr furnished bromides **2a,b,d** in moderate to good yields (Table I, entries 1–4). Success with bromide displacement prompted examination of other nucleophiles. In the event, thiolate, primary amine, and azide[7] all reacted with **1c** analogously to bromide (entries 5–7), furnishing substitution products **3–5c**. We also examined the suitability of stabilized carbon nucleophiles in this transformation. Thus, the anion of dimethyl malonate reacted cleanly with **1a–d** to give the adducts **6a–d** (entries 8–11) in moderate to excellent yields.

Cine substitution typically involves displacement of a leaving group attached to an sp^2 carbon with introduction of the nucleophile at a vicinal sp^2 carbon and often involves a transient intermediate such as benzyne.[8] The examples reported herein are similar in that the nucleophile is introduced at a (formerly) sp^2 carbon adjacent to the carbon bearing the leaving group. However, since the leaving group and the newly introduced nucleophile reside

(1) Presented in preliminary form at the 203rd National Meeting of the American Chemical Society, April 1992; ORGN 433.

(2) For reviews, see: (a) Ellison, R. A. *Synthesis* **1973**, 397. (b) Ho, T.-L. *Synth. Commun.* **1974**, *4*, 265; **1977**, *7*, 351. (c) Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1. (d) Trost, B. M. *Chem. Soc. Rev.* **1982**, 141. (e) Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820. (f) Piancatelli, G. *Heterocycles* **1982**, *19*, 1775. (g) Ramaiah, M. *Synthesis* **1984**, 529. (h) Yoshikoshi, A.; Miyashita, M. *Acc. Chem. Res.* **1985**, *18*, 284. (i) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1735.

(3) For recent developments in the preparation of 2-substituted 2-cycloalkenones, see: (a) Ono, N.; Miyake, H.; Kaji, A. *Synthesis* **1981**, 1003. (b) Miller, D. D.; Moorthy, K.; Hamada, A. *Tetrahedron Lett.* **1983**, *24*, 555. (c) Baraldi, P. G.; Barco, A.; Bennetti, S.; Pollini, G. P.; Zanirato, V. *Tetrahedron Lett.* **1984**, *25*, 4291. (d) Boga, C.; Savoia, D.; Trombini, C.; Umani-Ronchi, A. *Synthesis* **1986**, 212. (e) Dalcanale, E.; Foa, M. *Synthesis* **1986**, 492. (f) Kusuda, S.; Watanabe, Y.; Ueno, Y.; Toru, T. *J. Org. Chem.* **1992**, *57*, 3145.

(4) For selected examples, see: (a) Dygos, J. H.; Adamek, J. P.; Babiak, K. A.; Behling, J. R.; Medich, J. R.; Ng, J. S.; Wieczorek, J. J. *J. Org. Chem.* **1991**, *56*, 2549. (b) Sih, C. J.; Heather, J. B.; Sood, R.; Price, P.; Peruzzotti, G. P.; Hsu Lee, L. F.; Lee, S. S. *J. Am. Chem. Soc.* **1975**, *97*, 865. (c) Sih, C. J.; Price, P.; Sood, R.; Salomon, R. G.; Peruzzotti, G.; Hsu Lee, L.-F.; Casey, M. *Ibid.* **1972**, *94*, 3643. (d) Kluge, A. F.; Untch, K. G.; Fried, J. H. *Ibid.* **1972**, *94*, 7827.

(5) (a) Mitra, A. *The Synthesis of Prostaglandins*; John Wiley: New York, 1977. (b) *Prostaglandins and Thromboxanes*; Roberts, S. M., Newton, R. F., Eds.; Butterworth Scientific: London, 1982.

(6) (a) Piancatelli, G.; Scettri, A.; Barbadoro, S. *Tetrahedron Lett.* **1976**, 3555. (b) Piancatelli, G.; Scettri, A. *Ibid.* **1977**, 1131. (c) Piancatelli, G.; Scettri, A. *Tetrahedron* **1977**, *33*, 69.

(7) A dramatic solvent effect was observed with azide nucleophile. When **1c** was treated with NaN_3 in acetonitrile at room temperature, the direct substitution product **9c** was formed in 80% isolated yield.

(8) (a) Review: Dyall, L. K. *Rev. Pure Appl. Chem.* **1958**, *8*, 33. (b) For a recent Pd-catalyzed example, see: Stork, G.; Isaacs, R. C. A. *J. Am. Chem. Soc.* **1990**, *112*, 7399.

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Scheme I

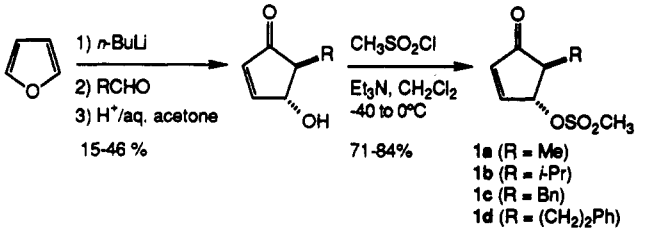


Table I. Reactions of 5-Substituted 4-(Mesyloxy)-2-cyclopentenones with Nucleophiles

entry	substrate	R	Nu	condns[a]	product[b]	yield[c] (%)
1	1a	Me	Br	A	2a	37
2	1b	*i*-Pr	Br	A	2b	86
3	1c	Bn	Br	A	2c	86
4	1d	$Ph(CH_2)_2$	Br	A	2d	81
5	1c	Bn	PhS	B	3c	71
6	1c	Bn	BnNH	C	4c	59[d]
7	1c	Bn	N_3	D	5c	81
8	1a	Me	$CH(CO_2Me)_2$	E	6a	43
9	1b	*i*-Pr	$CH(CO_2Me)_2$	E	6b	79
10	1c	Bn	$CH(CO_2Me)_2$	E	6c	93
11	1d	$Ph(CH_2)_2$	$CH(CO_2Me)_2$	E	6d	95

[a] Reaction conditions: (A) A 0.01–0.015 M solution of mesylate in dry acetone was stirred with 10 equiv of dry LiBr at rt. (B) A 0.3 M solution of mesylate in dry acetone was cooled to 0 °C. Thiophenol (1.05 equiv) and Et_3N (0.25 equiv) were added. The solution was stirred at 0 °C for 5 min and then continued at rt. (C) Benzylamine (1 equiv) was added dropwise to a 0.3 M solution of mesylate in dry MeOH, and the solution was stirred at rt. (D) A 0.1–0.15 M solution of mesylate in dry acetone was stirred with 10 equiv of NaN_3 and 1.05 equiv Bu_4NHSO_4 at rt. (E) A 0.16 M solution of mesylate in *t*-BuOH was added dropwise to a 0.1 M solution of the potassium salt of dimethyl malonate (1.05 equiv) and the solution was stirred at rt for 3 h. [b] Satisfactory IR, ^1H NMR, ^{13}C NMR, and combustion analysis or HRMS were obtained for all products. [c] Isolated yield after flash chromatography. [d] A Diels–Alder dimer of 2-benzylcyclopentadienone was also isolated (25%).

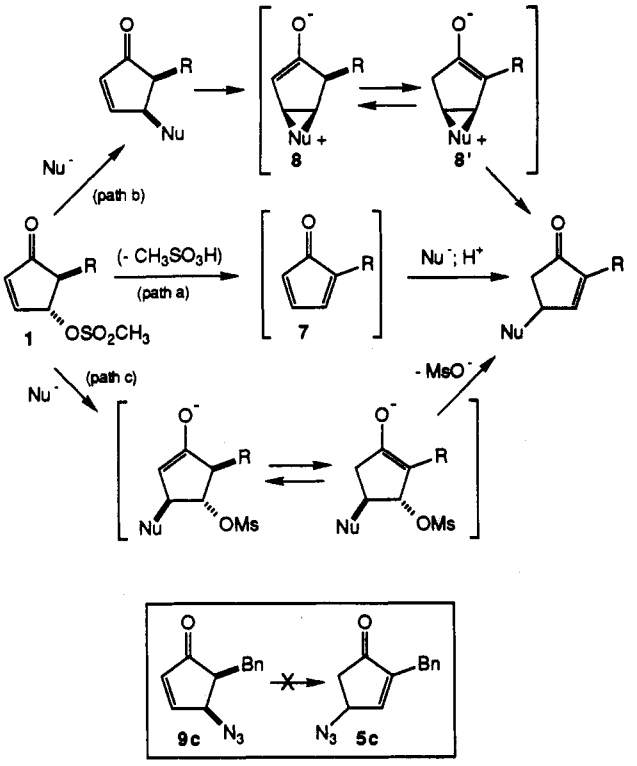
at sp^3 carbons and this process involves a double-bond migration concomitant with substitution, we refer to it as a "pseudocine substitution."

Discussion

Three mechanistic possibilities were considered (Scheme II). The intermediacy of a cyclopentadienone (path a) is formally possible,[9] with subsequent conjugate addition of the nucleophile to the less substituted double bond. However, if **7** were involed some Diels–Alder dimer formation would be expected, yet dimers were detected in only one instance (entry 6).[10] A pathway involving equilibrating bicyclic zwitterionic intermediates **8** and **8'** (path b) might apply to the reactions with bromide, thiolate, or amine, but it is arguable whether the linear azido group is capable of forming such a bridge. Importantly, when independently prepared[7] **9c** was stirred in acetone at room temperature, **5c** was not detected and **9c** remained largely unreacted.

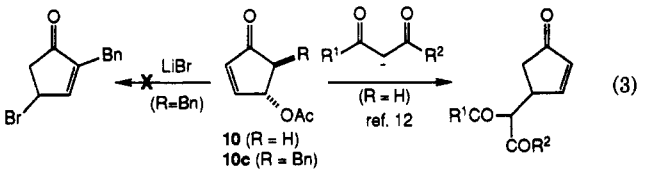
We presently favor a mechanism consisting of initial 1,4-addition of the nucleophile to the enone, equilibration of the resultant enolate to the more substituted isomer,

Scheme II



and subsequent elimination of mesylate to form the new enone moiety (path c). Addition of the relatively weakly nucleophilic mesylate ion to regenerate starting material would be unlikely in the presence of excess Nu^-. In contrast to the experiment described above, **9c** was cleanly converted to **5c** when stirred *in the presence of excess NaN_3*, suggestive of an addition/elimination sequence. It appears that formation of the more highly substituted double bond is sufficient driving force to effect the substitution reaction.[11] Regardless of which mechanism is operant, one may envision mesylates **1** as synthetic equivalents of the corresponding intractable cyclopentadienones with respect to conjugate addition.

Use of mesylate as the leaving group deserves comment. Winterfeldt has described substitution reactions (eq 3) of



(3)

acetate **10** with carbon nucleophiles for which a similar mechanism was proposed.[12] The choice of acetate was based on the assumption that better leaving groups would eliminate prematurely to generate cyclopentadienone. Successful substitution of **1** with malonate nucleophiles indicates that use of leaving groups such as mesylate is not precluded. However, treatment of acetate **10c** with LiBr under identical conditions to those used with mesylate **1c** gave no reaction, in contrast to the efficient conversion

(9) For a report of thermal generation of cyclopentadienone from 4-bromo-2-cyclopentenones, see: Baraldi, P. G.; Barco, A.; Benetti, S.; Pollini, G. P.; Polo, E.; Simoni, D. *J. Chem. Soc., Chem. Commun.* **1984**, 1049.

(10) Observation of dimers in the case of benzylamine displacement presumably arises from its basicity. Mesylates **1**, when treated with a weak base, gave mixtures of Diels–Alder dimers of the corresponding cyclopentadienones at temperatures as low as −78 °C.

(11) A similar sequence has been described as an undesirable side reaction during organocuprate addition to a 4-alkoxycyclopent-2-en-1-one in an attempted conjugate addition/alkylation approach to prostaglandins. For a discussion of this observation, see: (a) Davis, R.; Untch, K. G. *J. Org. Chem.* **1979**, *44*, 3755. See also: (b) Reference 5a, p 268. (c) Scheinmann, F. In ref 5b, pp 79–80.

(12) Harre, M.; Raddatz, P.; Walenta, R.; Winterfeldt, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 480 and references cited therein.

of 1c to 2c. Thus, 4-(mesyloxy)-2-cyclopentenones are suitable substrates for displacement with active methylene compounds, yet they also react with a greatly broadened range of nucleophiles in the substitution reaction.

Summary

In summary, we have reported a straightforward and versatile method for the preparation of a variety of 2,4-disubstituted 2-cyclopentenones from simple precursors. 4-(Mesyloxy)-5-alkylcyclopent-2-en-1-ones can be easily prepared in three steps from furan and the appropriate aldehydes. A variety of heteronucleophiles and the anion of dimethyl malonate cleanly displace the mesylate in a pseudocine sense, with vicinal substitution and double-bond migration. Reactions of mesylates 1 with more complex nucleophiles are currently under investigation in our laboratories and will be reported in due course.

Experimental Section

General. Solvents were distilled before use: dichloromethane from calcium hydride and diethyl ether from sodium benzophenone ketyl. Reagents purchased from Aldrich Chemical Co. were used without further purification. Thin-layer chromatography (TLC) was performed on plates of silica precoated with 0.25-mm Kieselgel 60 F_{254} (Merck). Flash chromatography columns were packed with 230–400-mesh silica gel (Merck or Baxter). Melting points were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected.

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded at 300 MHz, and chemical shifts are reported on the δ scale (ppm) downfield from tetramethylsilane. Carbon nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 75 MHz and are reported (ppm) relative to the center line of a triplet at 77.0 ppm for deuteriochloroform.

Representative Procedure for Preparation of Mesylate 1: *trans*-4-[(Methanesulfonyl)oxy]-5-methylcyclopent-2-en-1-one (1a). Furan (2.7 mL, 37 mmol, 2 equiv) was measured into a dry round-bottom flask equipped with a magnetic stirrer and containing freshly distilled ether (20 mL) under nitrogen atmosphere. The flask was cooled to −25 °C, and *n*-BuLi in hexanes (7.9 mL, 2.3M, 18 mmol) was added dropwise from a syringe. The flask was allowed to warm to 0 °C, the cold bath was removed, and the reaction mixture was stirred 4 h at room temperature. The reaction mixture was cooled back to −25 °C, and acetaldehyde (4.0 mL, 73 mmol, 4 equiv) was added dropwise via a syringe. After being allowed to warm to room temperature over a period of 3 h, the reaction mixture was neutralized with cold saturated NH_4Cl solution (5 mL). The organic layer was separated, and the aqueous layer was extracted with ether (2 × 5 mL). The combined organic phase was dried (Na_2SO_4) and passed through a silica gel plug to remove polar impurities, after which TLC analysis showed the presence of a single component. The solution was concentrated and dried in vacuo to give 1.7 g (84%) of 2-furylmethylcarbinol as an orange liquid (used without further purification); R_f 0.26 (Et_2O/CH_2Cl_2/hexanes (2:1:5)); IR (neat) 3367, 3150, 1601, 1555 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (1 H, dd, J = 1.8, 0.9 Hz), 6.30 (1 H, dd, J = 3.3, 1.8 Hz), 6.21–6.19 (1 H, m), 4.85 (1 H, q, J = 6.6 Hz), 2.09 (1 H, br s), 1.52 (3 H, d, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.50, 141.79, 110.05, 105.03, 63.58, 21.27.

2-Furylmethylcarbinol (0.10 g, 0.89 mmol) was dissolved in a mixture of distilled water (85 mL) and acetone (106 mL) in a round-bottom flask equipped with a condenser and a magnetic stirrer. Concd. H_2SO_4 (0.2 mL) was added, and the solution was stirred vigorously at 50 °C for 35 h. The reaction mixture was cooled to room temperature and added to water (100 mL). The aqueous mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried (Na_2SO_4), concentrated, and purified by flash chromatography (silica gel; 1.5-cm × 6-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:1)) to give 0.018 g (18%) of *trans*-4-hydroxy-5-methylcyclopent-2-en-1-one as a yellow oil: R_f 0.16 (Et_2O/CH_2Cl_2/hexanes (2:1:1)); spectral data are in agreement with those reported.[13]

trans-4-Hydroxy-5-methylcyclopent-2-en-1-one (0.13 g, 1.2 mmol) was dissolved in freshly distilled CH_2Cl_2 (20 mL) in a dry round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere. The solution was cooled to −42 °C, and methanesulfonyl chloride (0.14 mL, 1.8 mmol, 1.5 equiv) was added. Triethylamine (0.28 mL, 2.0 mmol, 1.7 equiv) was then added dropwise via a syringe. The reaction mixture was allowed to warm to 0 °C slowly and quenched with 5% aqueous HCl solution (3 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were dried (Na_2SO_4) and passed through a silica gel plug to remove polar impurities to give 0.16 g (71%) of 1a as a greenish oil, which was chromatographically and spectroscopically pure: R_f 0.37 (Et_2O/CH_2Cl_2/hexanes (2:1:1)); IR (neat) 1650, 1340, 1160 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (1 H, dd, J = 5.7, 2.4 Hz), 6.37 (1 H, d, J = 5.7 Hz), 5.37 (1 H, br s), 3.10 (3 H, s), 2.54 (1 H, qd, J = 7.6, 2.6 Hz), 1.30 (3 H, d, J = 7.5 Hz); ^{13}NMR (75 MHz, $CDCl_3$) δ 204.91, 155.73, 136.83, 83.71, 47.14, 38.61, 12.71; HRMS calcd for $C_7H_{10}O_4S$ m/e 190.0299, found m/e 190.0294.

***trans*-4-[(Methanesulfonyl)oxy]-5-isopropylcyclopent-2-en-1-one (1b).** Furan (2.7 mL, 37 mmol, 2 equiv), *n*-BuLi in hexanes (7.3 mL, 2.5M, 18 mmol), and isobutyraldehyde (3.3 mL, 37 mmol, 2 equiv) were subjected to the standard conditions, and 2.4 g (93%) of 2-furylisopropylcarbinol was obtained as a yellow liquid (used without further purification): R_f 0.27 (Et_2O/CH_2Cl_2/hexanes (2:1:5)); IR (neat) 3396, 2963 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.34 (1 H, m), 6.31 (1 H, dd, J = 3.0, 2.1 Hz), 6.21 (1 H, d, J = 2.7 Hz), 4.36 (1 H, dd, J = 6.8, 5.3 Hz), 2.15–2.03 (1 H, m), 1.85 (1 H, d, J = 5.1 Hz), 1.00 (3 H, d, J = 6.6 Hz), 0.85 (3 H, d, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.04, 125.13, 110.41, 106.84, 73.95, 33.79, 19.16, 18.68.

2-Furylisopropylcarbinol (0.10 g, 0.73 mmol) was subjected to the standard conditions, and the crude product was purified by flash chromatography (silica gel; 1.5-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (4:2:1)) to give 0.039 g (39%) of *trans*-4-hydroxy-5-isopropylcyclopent-2-en-1-one as a pale yellow liquid: R_f 0.29 (Et_2O/CH_2Cl_2/hexanes (4:2:1)); IR (neat) 3390, 1680, 1580 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (1 H, dd, J = 5.7, 2.4 Hz), 6.17 (1 H, dd, J = 5.7, 1.4 Hz), 4.8 (1 H, br s), 2.34–2.23 (1 H, m), 2.19 (1 H, dd, J = 4.5, 2.4 Hz), 1.9 (1 H, br s), 1.1 (3 H, d, J = 6.9 Hz), 0.84 (3 H, d, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.69, 161.73, 135.01, 72.91, 60.88, 27.14, 20.78, 18.27; HRMS calcd for $C_8H_{12}O_2$ m/e 140.0837, found m/e 140.0826.

trans-4-Hydroxy-5-isopropylcyclopent-2-en-1-one (0.13 g, 0.90 mmol) was subjected to the standard conditions, and the crude product was purified by flash chromatography (silica gel; 2-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:2)) to give 0.14 g (72%) of 1b as a green liquid: R_f 0.45 (Et_2O/CH_2Cl_2/hexanes (2:1:2)); IR (neat) 1710, 1585, 1330, 1160 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (1 H, dd, J = 5.9, 2.4 Hz), 6.33 (1 H, dd, J = 5.9, 1.1 Hz), 5.61–5.59 (1 H, m), 3.10 (3 H, s), 2.44 (1 H, dd, J = 4.2, 2.4 Hz), 2.37–2.27 (1 H, m), 1.06 (3 H, d, J = 6.9 Hz), 0.87 (3 H, d, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.68, 156.63, 137.87, 79.36, 56.76, 38.88, 27.33, 20.08, 18.20; HRMS calcd for $C_9H_{14}O_4S$ m/e 218.0613, found m/e 218.0610.

***trans*-4-[(Methanesulfonyl)oxy]-5-benzylcyclopent-2-en-1-one (1c).** Furan (2.7 mL, 37 mmol, 2 equiv), *n*-BuLi in hexanes (7.7 mL, 2.4 M, 18 mmol), and phenylacetaldehyde (4.3 mL, containing unknown amount of polystyrene oxide as supplied by Aldrich Chemical Co.) were subjected to the standard condtions, and the crude product was purified by flash chromatography (silica gel; 4-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:4)) to give 2.5 g (73%) of 2-furylbenzylcarbinol as a colorless liquid: R_f 0.54 (Et_2O/CH_2Cl_2/hexanes (2:1:4)); IR (neat) 3390, 3020, 1600 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (1 H, dd, J = 1.8, 1.0 Hz), 7.25–7.10 (5 H, m), 6.25 (1 H, dd, J = 3.3, 1.8 Hz), 6.14 (1 H, dd, J = 3.2, 1.0 Hz), 4.85 (1 H, ddd, J = 8.0, 5.0, 4.9 Hz), 3.09 (1 H, dd, J = 13.8 5.4 Hz), 3.08 (1 H, dd, J = 13.5, 8.1 Hz), 1.9 (1 H, d, J = 4.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.64, 141.92, 137.27, 129.36, 128.46, 126.66, 110.18, 106.37, 68.77, 42.22.

2-Furylbenzylcarbinol (0.11 g, 0.61 mmol) was subjected to the standard conditions, and the crude product was purified by flash chromatography (silica gel; 1.5-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (4:2:1)) to give 0.047 g (41%) of *trans*-4-hydroxy-

(13) Shono, T.; Hamaguchi, H.; Aoki, K. *Chem. Lett.* **1977**, 1053.

5-benzylcyclopent-2-en-1-one as a yellow liquid: R_f 0.49 (Et_2O/CH_2Cl_2/hexanes (4:2:1)); IR (neat) 3400, 3040, 1710, 1610 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (1 H, dd, J = 5.9, 2.3 Hz), 7.35–7.19 (6 H, m), 6.21 (1 H, dd, J = 5.9, 1.4 Hz), 4.72 (1 H, d, J = 1.2 Hz), 3.29 (1 H, dd, J = 14, 4.1 Hz), 2.74–2.57 (2 H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.55, 161.54, 138.86, 134.00, 128.78, 128.76, 126.61, 75.62, 56.98, 34.05.

trans-4-Hydroxy-5-benzylcyclopent-2-en-1-one (0.16 g, 0.82 mmol) was subjected to the standard conditions, and the crude product was purified by flash chromatography (silica gel; 2-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:2)) to give 0.19 g (87%) of **1c** as a pale yellow liquid: R_f 0.46 (Et_2O/CH_2Cl_2/hexanes (2:1:2)); IR (neat) 3020, 1715, 1595, 1355, 1165 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (1 H, dd, J = 5.7, 2.4 Hz), 7.34–7.22 (5 H, m), 6.37 (1 H, dd, J = 5.9, 1.1 Hz), 5.44–5.42 (1 H, m), 3.34 (1 H, dt, J = 13.2, 3.8 Hz), 2.89–2.75 (2 H, m), 2.53 (3 H, s); ^{13}NMR (75 MHz, $CDCl_3$) δ 203.75, 157.02, 137.56, 136.79, 129.28, 128.84, 126.98, 81.72, 52.74, 37.59, 33.72; HRMS calcd for $C_{13}H_{14}O_4S$ m/e 266.0613, found m/e 266.0622.

***trans*-4-[(Methanesulfonyl)oxy]-5-(2-phenylethyl)cyclopent-2-en-1-one (1d).** Furan (2.7 mL, 37 mmol, 2 equiv), *n*-BuLi in hexanes (7.3 mL, 2.5 mL, 18 mmol, 1.1 equiv), and hydrocinnamaldehyde (2.4 mL, 17 mmol) were subjected to the standard conditions, and 3.5 g (99%) of 2-furyl-(2-phenylethyl)carbinol was obtained as an orange oil (used without further purification): R_f 0.56 (Et_2O/CH_2Cl_2/hexanes (2:1:4)); IR (neat) 3360, 3030, 1600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38–7.37 (1 H, m), 7.24–7.09 (5 H, m), 6.26 (1 H, dd, J = 3.3, 1.8 Hz), 6.17 (1 H, d, J = 3.3 Hz), 4.71–4.66 (1 H, m), 2.75–2.57 (2 H, m), 2.14–2.07 (2 H, m), 1.89 (1 H, d, J = 4.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.44, 141.95, 141.40, 128.43, 128.37, 125.89, 110.12, 105.97, 66.99, 37.00, 31.77.

2-Furyl-(2-phenylethyl)carbinol (0.11 g, 0.53 mmol) was subjected to the standard conditions, and the crude product was purified by flash chromatography (silica gel; 1.5-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:1)) to give 0.048 g (45%) of *trans*-4-hydroxy-5-(2-phenylethyl)cyclopent-2-en-1-one as a yellow liquid: R_f 0.25 (Et_2O/CH_2Cl_2 hexanes (2:1:1)); IR ($CDCl_3$) 3400, 3020, 1690, 1600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (1 H, dd, J = 5.9, 2.3 Hz), 7.30–7.16 (5 H, m), 6.18 (1 H, dd, J = 5.9, 1.4 Hz), 4.89 (1 H, br s), 4.63 (1 H, br s), 2.83–2.75 (2 H, m), 2.55–2.51 (1 H, m), 2.32–2.21 (2 H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.99, 162.03, 141.24, 131.89, 128.37, 128.29, 126.03, 76.78, 54.72, 33.43, 30.31; HRMS calcd for $C_{13}H_{14}O_2$ m/e 202.0994, found m/e 202.0967.

trans-4-Hydroxy-5-(2-phenylethyl)cyclopent-2-en-1-one (0.18 g, 0.88 mmol) was subjected to the standard conditions, and the crude product was purified by flash chromatography (silica gel; 2-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:1)) to give 0.21 g (84%) of **1d** as a yellow liquid: R_f 0.5 (Et_2O/CH_2Cl_2/hexanes (2:1:1)); IR ($CDCl_3$) 1700, 1580, 1330, 1155 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (1 H, dd, J = 5.9, 2.3 Hz), 7.33–7.18 (5 H, m), 6.39 (1 H, dd, J = 5.7, 1.2 Hz), 5.58 (1 H, br s), 3.06 (3 H, s), 2.93–2.72 (2 H, m), 2.55 (1 H, ddd, J = 8.0, 5.6, 2.4 Hz), 2.25–2.13 (1 H, m), 2.00–1.88 (1 H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.42, 156.07, 140.57, 137.11, 128.37 (2 C), 126.12, 82.01, 50.72, 38.63, 32.50, 29.90; HRMS calcd for $C_{14}H_{16}O_4S$ m/e 280.0769, found m/e 280.0770.

Representative Procedure for Conversion of Mesylate 1 to Bromide 2: 2-Methyl-4-bromocyclopent-2-en-1-one (2a). Mesylate **1a** (0.094 g, 0.49 mmol) was dissolved in dry acetone (4 mL) in a dry round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere. Anhydrous lithium bromide (0.44 g, 5.0 mmol, 10 equiv) was added, and the solution was vigorously stirred at room temperature. After the substrate was consumed (3 h), acetone was removed by rotary evaporation and the residue was taken up in CH_2Cl_2 (5 mL). The suspension was filtered through a Celite plug, concentrated, and purified by flash chromatography (silica gel; 1.5-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:5)) to give 0.032 g (37%) of **2a** as a pale yellow liquid: R_f 0.46 (Et_2O/CH_2Cl_2/hexanes (2:1:5)); IR ($CDCl_3$) 1710, 1635 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (1 H, qd, J = 2.7, 1.4 Hz), 5.09–5.04 (1 H, m), 3.02 (1 H, dd, J = 19.6, 6.2 Hz), 2.73 (1 H, dd, J = 19.6, 1.6 Hz), 1.83 (3 H, dd, J = 1.7, 1.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.52, 156.16, 143.67, 45.17, 42.15, 10.05. Anal. Calcd for C_6H_7OBr: C, 41.18; H, 4.03. Found: C, 41.26; H, 4.07.

2-Isopropyl-4-bromocyclopent-2-en-1-one (2b). Mesylate **1b** (0.13 g, 0.60 mmol) was subjected to the standard conditions, and the crude product was purified by flash chromatography (silica gel; 1.5-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:6)) to give 0.11 g (86%) of **2b** as a pale yellow oil: R_f 0.39 (Et_2O/CH_2Cl_2/hexanes (2:1:6)); IR (neat) 1700, 1610 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (1 H, dd, J = 2.7, 1.3 Hz), 5.08–5.04 (1 H, m), 3.02 (1 H, dd, J = 19.6, 6.2 Hz), 2.74 (1 H, dd, J = 19.6, 1.7 Hz), 2.69–2.61 (1 H, m), 1.12 (3 H, d, J = 7.1 Hz), 1.09 (3 H, d, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.84, 153.77, 153.65, 45.97, 42.19, 24.73, 20.92 (2 C). Anal. Calcd for $C_8H_{11}OBr$: C, 47.32; H, 5.46. Found: C, 47.48; H, 5.47.

2-Benzyl-4-bromocyclopent-2-en-1-one (2c). Mesylate **1c** (0.16 g, 0.59 mmol) was subjected to the standard conditions, and the crude product was purified by flash chromatography (silica gel; 1.5-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:6)) to give 0.13 g (86%) of **2c** as a pale yellow liquid: R_f 0.39 (Et_2O/CH_2Cl_2/hexanes (2:1:6)); IR (neat) 3050, 3020, 1705, 1640 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27–7.10 (5 H, m), 7.01 (1 H, dd, J = 2.9, 1.4 Hz), 5.00–4.95 (1 H, m), 3.48 (1 H, d, J_{AB} = 16.5 Hz), 3.45 (1 H, d, J_{AB} = 16.2 Hz), 3.00 (1 H, ddd, J = 19.8, 6.3, 1.2 Hz), 2.73 (1 H, dt, J = 19.6, 1.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.59, 156.58, 147.41, 137.30, 128.86, 128.68, 126.65, 45.60, 41.87, 3.09. Anal. Calcd for $C_{12}H_{11}OBr$: C, 57.40; H, 4.42. Found: C, 57.18; H, 4.37.

2-(2-Phenylethyl)-4-bromocyclopent-2-en-1-one (2d). Mesylate **1d** (0.11 g, 0.39 mmol) was subjected to the standard conditions, and the crude product was purified by flash chromatography (silica gel; 1.5-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:5)) to give 0.084 g (81%) of **2d** as a yellow liquid: R_f 0.34 (Et_2O/CH_2Cl_2/hexanes (2:1:5)); IR (neat) 3030, 1690, 1610 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24–7.08 (6 H, m), 4.99–4.94 (1 H, m), 2.95 (1 H, dd, J = 19.7, 1.6 Hz), 2.78–2.67 (2 H, m), 2.68 (1 H, dd, J = 19.7, 1.6 Hz), 2.52–2.45 (2 H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.12, 156.08, 146.78, 140.50, 128.39, 128.31, 126.15, 45.43, 42.04, 33.35, 26.22. Anal. Calcd for $C_{13}H_{13}OBr$: C, 58.89; H, 4.94. Found: C, 58.94; H, 4.98.

2-Benzyl-4-(thiophenoxy)cyclopent-2-en-1-one (3c). Mesylate **1c** (0.088 g, 0.33 mmol) was dissolved in dry acetone (1 mL) in a dry round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere. The solution was cooled to 0 °C, and thiophenol (0.035 mL, 0.33 mmol, 1 equiv) was added. Triethylamine (0.12 mL, 0.083 mmol, 0.25 equiv) was then added dropwise. The reaction mixture was stirred 5 min at 0 °C, the ice bath was removed, and stirring was continued at room temperature. After the substrate was consumed (6 h), acetone was removed by rotary evaporation. The residue was taken up in CH_2Cl_2 (1 mL) and washed with water (1 mL). The organic layer was dried (Na_2SO_4), concentrated, and purified by flash chromatography (silica gel; 1.5-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:5)) to give 0.66 g (71%) of **3c** as a pale yellow liquid: R_f 0.42 (Et_2O/CH_2Cl_2/hexanes (2:1:5)); IR (neat) 1707, 1626 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28–6.92 (11 H, m), 4.16 (1 H, ddd, J = 6.5, 4.5, 2.1 Hz), 3.38 (1 H, d, J_{AB} = 16.5 Hz), 3.35 (1 H, d, J_{AB} = 16.2 Hz), 2.82 (1 H, dd, J = 19.4, 6.5 Hz), 2.40 (1 H, dd, J = 19.2, 2.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.31, 156.73, 146.40, 137.49, 133.03, 131.56, 128.60, 128.41, 128.12, 127.74, 126.01, 44.12, 42.21, 30.74. Anal. Calcd for $C_{18}H_{16}OS$: C, 77.11; H, 5.75. Found: C, 77.30; H, 5.74.

2-Benzyl-4-(*N*-benzylamino)cyclopent-2-en-1-one (4c). Mesylate **1c** (0.083 g, 0.31 mmol) was dissolved in methanol (1 mL) in a dry round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere. Benzylamine (0.034 mL, 0.31 mmol, 1 equiv) was added dropwise, and the reaction mixture was stirred at room temperature. After the substrate was consumed (4 h), methanol was removed by rotary evaporation. The resultant yellow solid was suspended in CH_2Cl_2 (2 mL), and 5% aqueous KOH solution was added dropwise until the solid completely dissolved. The organic layer was separated, washed with water (1 mL), dried (Na_2SO_4), concentrated, and purified by flash chromatography (silica gel; 1.5-cm × 15-cm column; gradient elution: Et_2O/CH_2Cl_2/hexanes (2:1:5) and Et_2O/CH_2Cl_2/hexanes (2:1:1)) to give 0.051 g (59%) of **4c** as a yellow liquid: R_f 0.32 (Et_2O/CH_2Cl_2/hexanes (2:1:1)); IR (neat) 3310, 3028, 1705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27–7.08 (10 H, m), 6.95–6.93 (1 H, m), 3.84 (1 H, ddd, J = 5.9, 3.9, 2.0 Hz), 3.75 (1 H, d, J_{AB} = 12.9 Hz), 3.73 (1 H, d, J_{AB} = 12.9 Hz), 3.43 (1 H, d, J_{AB} = 16.6

Hz), 3.40 (1 H, d, J_{AB} = 16.6 Hz), 2.67 (1 H, dd, J = 18.6, 6.0 Hz), 2.18 (1 H, dd, J = 18.6, 2.1 Hz), 1.42 (1 H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.35, 158.03, 146.79, 139.48, 138.15, 128.91, 128.52, 128.50, 128.11, 127.24, 126.36, 55.73, 52.03, 43.08, 31.22. Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.91; N, 5.05. Found: C, 82.04; H, 6.91; N, 4.94.

2-Benzyl-4-azidocyclopent-2-en-1-one (5c). Mesylate **1c** (0.10 g, 0.38 mmol) was dissolved in dry acetone (3 mL) in a dry round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere. Sodium azide (0.25 g, 3.8 mmol, 10 equiv), followed by tetrabutylammonium hydrogensulfate (0.14 g, 0.40 mmol, 1.05 equiv), was added, and the heterogeneous mixture was stirred vigorously at room temperature. After the substrate was consumed (4 h), acetone was removed by rotary evaporation. The residue was taken up in hexanes/CH_2Cl_2 (2:1; 3 mL) and filtered through a silica gel plus to remove polar impurities. The solution was concentrated and dried in vacuo to give 0.66 g (81%) of **5c** as a pale yellow liquid which was chromatographically and spectroscopically pure: R_f 0.5 (Et_2O/CH_2Cl_2/hexanes (2:1:3)); IR (neat) 3063, 3030, 2097, 1715, 1638, 1601 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27–7.10 (5 H, m), 6.88–6.87 (1 H, m), 4.46 (1 H, ddd, J = 6.5, 4.1, 2.1 Hz), 3.48 (1 H, d, J_{AB} = 18.6 Hz), 3.43 (1 H, d, J_{AB} = 18.6 Hz), 2.76 (1 H, dd, J = 18.9, 6.6 Hz), 2.34 (1 H, dd, J = 18.9, 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.72, 152.75, 149.15, 137.34, 128.86, 128.67, 126.64, 58.07, 41.11, 31.18. Anal. Calcd for $C_{12}H_{11}N_3O$: C, 67.59; H, 5.20; N, 19.71. Found: C, 67.68; H, 5.17; N, 19.61.

Representative Procedure for Conversion of Mesylate 1 to Malonate 6: Dimethyl 2-(3-Methyl-4-oxocyclopent-2-enyl)malonate (6a). Dimethyl malonate (0.081 mL, 0.71 mmol, 1.1 equiv) was dissolved in dry *t*-BuOH (6 mL) in a dry round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere. Potassium *tert*-butoxide (95%, 0.080 g, 0.68 mmol, 1.05 equiv) was added, and the resultant white suspension was stirred vigorously at room temperature for 15 min. Mesylate **1a** (0.12 g, 0.65 mmol) dissolved in dry *t*-BuOH (4 mL) was added dropwise via a cannula over 10 min, and the reaction mixture was stirred 3 h at room temperature. Aqueous HCl solution (5%, 1 mL) was added dropwise, and the solution was poured into distilled water (20 mL). The aqueous solution was extracted with CH_2Cl_2 (2 × 5 mL). Combined organic layers were washed with distilled water (5 mL), dried (Na_2SO_4), concentrated, and purified by flash chromatography (silica gel; 2-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:4)) to give 0.063 g (43%) of **6a** as a pale yellow liquid: R_f 0.27 (Et_2O/CH_2Cl_2/hexanes (2:1:4)); IR (neat) 1734, 1709, 1642 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23–7.20 (1 H, m), 3.74 (3 H, s), 3.72 (3 H, s), 3.51–3.44 (1 H, m), 3.38 (1 H, d, J = 8.7 Hz), 2.62 (1 H, dd, J = 19.1, 6.5 Hz), 2.21 (1 H, dd, J = 19.1, 2.6 Hz), 1.75 (3 H, t, J = 1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.30, 168.10, 167.98, 156.95, 143.44, 55.05, 52.76 (2 C), 39.05, 38.04, 10.17. Anal. Calcd for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24. Found: C, 58.18; H, 6.25.

Dimethyl 2-(3-Isopropyl-4-oxocyclopent-2-enyl)malonate (6b). Dimethyl malonate (0.090 mL, 0.79 mmol, 1.7 equiv), 95% potassium *tert*-butoxide (0.073 g, 0.62 mmol, 1.3 equiv), and mesylate **1b** (0.10 g, 0.48 mmol) were subjected to the standard conditions, and the crude product was purified by flash chromatography (silica gel neutralized with triethylamine; 1.5-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:3)) to give 0.10 g (79%) of **6b** as a yellow liquid: R_f 0.50 (et_2O/CH_2Cl_2/hexanes (2:1:3)); IR (neat) 1736, 1707 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (1 H, dd, J = 2.4, 1.2 Hz), 3.74 (3 H, s), 3.72 (3 H, s), 3.50–3.44 (1 H, m), 2.83 (1 H, d, J = 8.1 Hz), 2.64–2.53 (1 H, m), 2.62 (1 H, dd, J = 19.2, 6.3 Hz), 2.26 (1 H, dd, J = 19.1, 2.3 Hz), 1.07 (3 H, d, J = 6.0 Hz), 1.05 (3 H, d, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.64, 168.15, 167.98, 154.21, 135.18, 55.00, 52.71 (2C), 39.73, 37.73, 24.72, 21.36, 21.08. Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.41; H, 7.14. Found: C, 61.31; H, 7.17.

Dimethyl 2-(3-Benzyl-4-oxocyclopent-2-enyl)malonate (6c). Mesylate **1c** (0.11 g, 0.40 mmol) was subjected to the standard conditions, and the crude product was filtered through a silica gel plug to remove polar impurities. Concentration and drying in vacuo gave 0.11 g (93%) of **6c** as a yellow oil which was chromatographically and spectroscopically pure: R_f 0.58 (Et_2O/CH_2Cl_2/hexanes (2:1:2)); IR (neat) 3028, 1734, 1709, 1633, 1602 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.09 (5 H, m), 7.03–7.02 (1 H, m), 3.62 (3 H, s), 3.61 (3 H, s), 3.46–3.39 (1 H, m), 3.43 (1 H, d, J_{Ab} = 17.7 Hz), 3.40 (1 H, d, J_{AB} = 17.7 Hz), 3.36 (1 H, d, J = 7.8 Hz), 2.61 (1 H, dd, J = 19.2, 6.3 Hz), 2.25 (1 H, dd, J = 19.1, 2.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.29, 167.99, 167.85, 157.46, 147.25, 138.19, 128.76, 128.48, 126.33, 54.67, 52.68, 52.66, 39.26, 38.03, 31.21. Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.41; H, 6.00.

Dimethyl 2-[3-(2-Phenylethyl)-4-oxocyclopent-2-enyl]malonate (6d). Mesylate **1d** (0.10 g, 0.37 mmol) dissolved in *t*-BuOH/THF (3 mL/1 mL) was subjected to the standard conditions, and the crude product was filtered through a silica gel plug to remove polar impurities. Concentration and drying in vacuo gave 0.11 g (95%) of **6d** as a pale yellow oil which was chromatographically and spectroscopically pure: R_f 0.41 (Et_2O/CH_2Cl_2/hexanes (2:1:3)); IR ($CDCl_3$) 3020, 1730, 1700, 1630, 1600 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.08 (6 H, m), 3.68 (6 H, s), 3.46–3.38 (1 H, m), 3.29 (1 H, d, J = 8.7 Hz), 2.76–2.70 (2 H, m), 2.59 (1 H, dd, J = 19.0, 6.6 Hz), 2.48–2.42 (2 H, m), 2.19 (1 H, dd, J = 19.0, 2.5 Hz); ^{13}C NMR (75 Hz, $CDCl_3$) δ 206.84, 168.07, 167.91, 156.97, 146.79, 140.97, 128.30 (2C), 125.99, 55.08, 52.78, 52.73, 39.35, 38.09, 33.67, 26.45. Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.19; H, 6.42.

***cis*-4-Azido-5-benzylcyclopent-2-en-1-one (9c).** Mesylate **1c** (0.16 g, 0.58 mmol) was dissolved in dry CH_3CN (4.5 mL) in a dry round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere. Sodium azide (0.19 g, 2.9 mmol, 5 equiv) was added, and the heterogeneous solution was stirred vigorously at room temperature. After the substrate was consumed (84 h), the solvent was removed by rotary evaporation. The residue was taken up in CH_2Cl_2 (4 mL), filtered, concentrated, and purified by flash chromatography (silica gel; 2-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:3)) to give 0.099 g (80%) of **9c** as a pale yellow liquid: R_f 0.51 (Et_2O/CH_2Cl_2/hexanes (2:1:3)); Ir (neat) 3063, 3028, 2100, 1719, 1603 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (1 H, dd, J = 5.9, 2.9 Hz), 7.29–7.11 (5 H, m), 6.35 (1 H, dd, J = 6.0, 1.2 Hz), 4.54 (1 H, ddd, J = 6.0, 2.6, 1.0 Hz), 3.18 (1 H, dd, J = 14.3, 3.5 Hz), 2.81 (1 H, ddd, J = 11.0, 6.1, 3.4 Hz), 2.68 (1 H, dd, J = 14.1, 11.1 Hz); ^{13}NMR (75 MHz, $CDCl_3$) δ 206.17, 157.14, 139.20, 135.49, 128.61, 128.58, 126.34, 62.59, 50.98, 31.61; HRMS calcd for $C_{12}H_{11}ON_3$ *m/e* 213.0902, found *m/e* 213.0882.

***trans*-4-Acetoxy-5-benzylcyclopent-2-en-1-one (10c).** *trans*-4-Hydroxy-5-benzylcyclopent-2-en-1-one (0.13 g, 0.68 mmol) was dissolved in dry CH_2Cl_2 (4 mL) in a dry round-bottom flask equipped with a magnetic stirrer under nitrogen atmosphere. To the stirred mixture were added acetic anhydride (0.10 mL, 1.0 mmol, 1.5 equiv), triethylamine (0.14 mL, 1.0 mmol, 1.5 equiv), and (dimethylamino)pyridine (0.0080 g, 0.068 mmol, 0.1 equiv) sequentially at room temperature. Stirring was continued overnight, 5% aqueous HCl solution (1 mL) was added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (1 × 2 mL). Combined organic layers were dried (Na_2SO_4), concentrated and purified by flash chromatography (silica gel; 2-cm × 15-cm column; Et_2O/CH_2Cl_2/hexanes (2:1:4)) to give 0.12 g (75%) of **10c** as a white crystalline solid: R_f 0.44 (Et_2O/CH_2Cl_2/hexanes (2:1:4)); mp 104–106 °C, IR ($CDCl_3$) 3065, 1736, 1721, 1655 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (1 H, dd, J = 5.7, 2.3 Hz), 7.18–7.10 (5 H, m), 6.19 (1 H, dd, J = 5.7, 1.2 Hz), 5.59 (1 H, ddd, J = 3.7, 2.4, 1.3 Hz), 3.12 (1 H, dd, J = 14.3 5.3 Hz), 2.86 (1 H, dd, J = 14.1, 7.8 Hz), 2.62 (1 H, ddd, J = 7.8, 5.1, 2.7 Hz), 1.86 (3 H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.62, 170.24, 158.19, 137.83, 135.93, 129.18, 128.40, 126.50, 76.15, 52.99, 33.77, 20.68; HRMS calcd for $C_{14}H_{14}O_3O_3$ *m/e* 230.0943, found *m/e* 230.0941.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for **1a–d**, **9c**, and **10c** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.