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Note

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Study of the Reactivity of [Hydroxy(tosyloxy)iodo]benzene Toward Enol Esters to Access α-Tosyloxy Ketones

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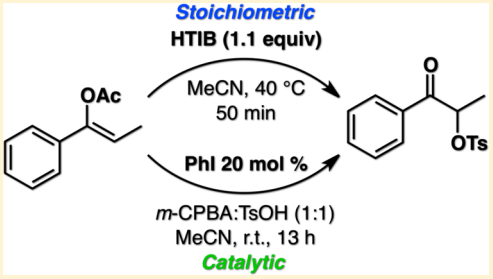
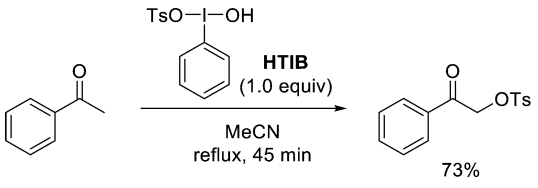
Supporting Information

ABSTRACT: The reactivity of enol esters toward [hydroxy(tosyloxy)iodo]-benzene (HTIB) was assessed. These substrates were found to be rapidly converted in high yields to their corresponding α-tosyloxy ketones. This transformation demonstrates that these substrates can act as ketone surrogates. The scope of the method was investigated and aromatic, aliphatic, and cyclic enol esters were found to be suitable substrates for the reaction. The relative reactivity of a model substrate toward HTIB and *m*-CPBA was investigated, and it was found that the reaction could be performed under catalytic conditions.

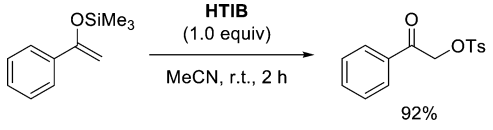


Hypervalent iodine compounds have proven to be proficient reagents in synthetic chemistry and have been an alternative to toxic transition metals in numerous oxidation reactions.[1] For this reason, hypervalent iodine chemistry has received increasing attention over the past three decades. Important advances are periodically made in either the development of new hypervalent iodine reagents or the application of known reagents to new transformations. Another area of active research is the development of catalytic[2] and enantioselective systems for a broad range of applications in organic chemistry.[3] Our group has studied the functionalization of ketones,[4] in particular, the α-tosyloxylation reaction, which was initially reported by Koser et al. using [hydroxy-(tosyloxy)iodo]benzene (HTIB)[5] (eq 1).[6]



(1)

Pioneering work by Wirth et al. has demonstrated that the process could be rendered catalytic and enantioselective.[7] Despite the work of numerous groups[7,8] and as well as our own,[9] the enantioselectivities attained for this transformation have remained low (<60% ee). Access to these enantiopure products would be of great interest as they are polyvalent chiral percursors that could serve as building blocks in synthesis. In an attempt to surpass this current limitation, we have initiated the study of substrates that would effectively lead to the same α-tosyloxy ketone products. Enol analogues would be convenient substrates to access such products using Koser's methodology. Moriarty et al. have, for example, demonstrated the rapid conversion of silyl enol ethers to their corresponding α-tosyloxy ketones using HTIB (eq 2).[10]



(2)

Unfortunately, such derivatives are too reactive to be used in the conditions of the currently developed catalytic methodologies. Surprisingly, the investigation of enol analogues toward HTIB is scarce. We envisioned, in the hope of achieving access to catalytic systems, exploiting enol analogues bearing electron-withdrawing groups on the oxygen atom, such as enol esters. These substrates, having lower nucleophilicity, could possibly be used under catalytic conditions without degradation. Moreover, enol esters can be obtained through numerous other methodologies, such as the addition of carboxylic acids to alkynes.[11] This would effectively increase the available paths to access α-substituted ketones from nonketonic substrates. Herein, we evaluate the reactivity of various enol ester derivatives toward HTIB. We reveal that enol esters can be cleanly converted to their corresponding α-tosyloxy ketone products. Additionally, we demonstrate that they can serve as substrates in iodine(III)-mediated catalytic systems.

The selected enol analogue candidates were easily obtained from the corresponding ketone under basic conditions. The evaluation of substrate reactivity is presented in Table 1 using enol analogues derived from propiophenone as a reference.

The substrates were allowed to react with a slight excess of HTIB at room temperature. Reaction completion was monitored by the disappearance of the HTIB suspension, as its solubility in the reaction conditions is very low. It is important to note that under these conditions HTIB is almost unreactive toward propiophenone (<5% conversion in 12 h). Simple methyl enol ether **1a** led to major degradation under the

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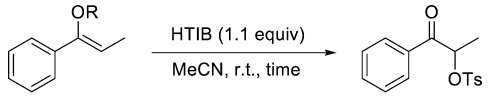
Table 1. Evaluation of Enol Analogues 1a–d Reactivity Toward HTIB



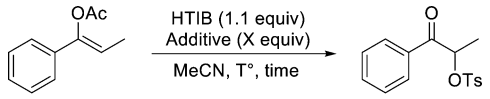
1a-d **2**

entry	R	time (h)	yield (%)[a]
1	Me (**1a**)	4	<5
2	MeCO (**1b**)	7	92
3	*t*-BuCO (**1c**)	13	91
4	*p*-TolSO$_2$ (**1d**)	48	90

[a]Isolated yields after flash chromatography. Values reported are the average of a minimum of two experiments.

described conditions. Gratifyingly, acetyl enol ester **1b** was converted cleanly to desired product **2** in excellent yields (Table 1, entry 2). The pivaloyl enol ester **1c** showed slightly lower reactivity with complete conversion in 13 h (Table 1, entry 3). The steric hindrance of the acyl group thus has a noticeable effect on reactivity. We also tested the *p*-toluenesulfonyl enol ester **1d** to evaluate the effect of a stronger electron-withdrawing group on the enol oxygen. Whereas **1d** was found to be much less reactive than enol esters **1b** or **1c**, it was converted cleanly to **2** in 48 h. Acetyl enol ester **1b** was selected as the ideal substrate for further optimization due the size and cost of its acyl group. The effect of temperature and additives on the reaction of **1b** with HTIB was next investigated. The results are illustrated in Table 2.

Table 2. Evaluation of Reaction Conditions on the Conversion of 1b to 2



1b **2**

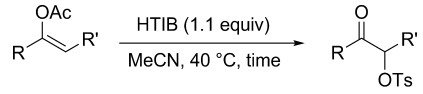
entry	*T* (°C)	additive	*X* (equiv)	time (min)	yield (%)[a]
1	25			420	92
2	40			50	94
3	25	TsOH·H$_2$O	1.0	10	92
4	25	TsOH·H$_2$O	0.1	60	91
5	40	TsOH·H$_2$O	0.1	13	95
6	25	AcOH	0.1	180	89
7	25	BF_3·OEt$_2$	1.0	1	43

[a]Isolated yields after flash chromatography. Results reported are the average of a minimum of two experiments.

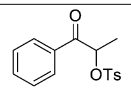
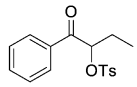
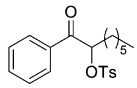
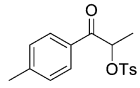
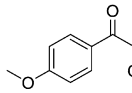
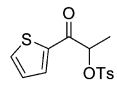
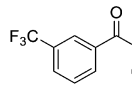
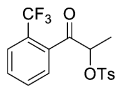
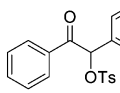
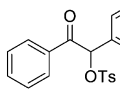
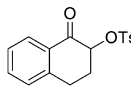
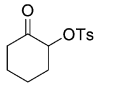
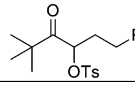
A slight elevation in temperature (+15 °C) increases the reaction rate significantly, enabling complete conversion of **1b** within 50 min without any loss in yield (Table 2, entry 2). The effect of acid additives was investigated next. The addition of a stoichiometric quantity of TsOH·H$_2$O led to a drastic increase in the reaction rate, affording **2** in 92% yield within 10 min (Table 2, entry 3). Even a catalytic quantity of TsOH·H$_2$O (0.1 equiv) increased the reaction rate drastically (Table 2, entry 4). Using the same catalytic quantity of TsOH·H$_2$O and increasing the temperature to 40 °C enabled complete conversion of **1b** within 13 min, affording **2** in 95% yield (Table 2, entry 5). The addition of AcOH also resulted in a noticeable, albeit smaller, rate enhancement (Table 2, entry 6). Finally, we evaluated the use of trifluoroborane etherate, a commonly used Lewis acid in iodine(III)-mediated processes.[12] Disappearance of the HTIB suspension and conversion of **1b** was almost instantaneous (~1 min), but the reaction conditions led to numerous side products, resulting in only 43% yield of **2** (Table 2, entry 7).

Whereas the addition of an acid catalyst does lead to rate enhancement, for the sake of simplicity and atom economy, the scope of the reaction was evaluated using only HTIB at 40 °C (Table 2, conditions from entry 2). The results are presented in Table 3.

Table 3. Study of the Reaction Scope of the Conversion of Acetyl Enol Esters to α-Tosyloxy Ketones



1b, 3a-k **2, 4a-k**

Entry	Product	Time (min)	Yield (%)[a]
1	 **2**	50	94
2	 **4a**	45	91
3	 **4b**	45	88
4	 **4c**	50	94
5	 **4d**	17	93
6	 **4e**	20	92
7	 **4f**	600	81
8[b]	 **4g**	4300	80
9	 **4h**	150	34
10[c]	 **4h**	150	84
11	 **4i**	5	25[d]
12	 **4j**	10	74
13	 **4k**	150	93

[a]Isolated yield after flash chromatography. Results reported are the average of a minimum of two experiments. [b]Substrate **3g** is a mixture of both *Z* and *E* isomers. [c]Reaction performed in dichloromethane instead of acetonitrile. [d]1,4-Naphthoquinone is obtained as the major side product.

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We first studied substrates bearing both an aromatic group and an aliphatic chain. The length of the alkyl chain on the enol ester did not significantly influence the rate of the reaction (Table 3, entries 1−3). In contrast, modulation of the electronic properties of the aromatic moiety has a drastic effect on the substrate reactivity toward HTIB. The presence of an electron-rich aromatic moiety resulted in a roughly 3-fold rate acceleration (Table 3, entries 5 and 6). The effect of electron-withdrawing groups was more noticeable. For example, introduction of a trifluoromethyl (CF_3) group at the meta position of the aromatic group caused a decrease in reactivity by a factor of more than 10 (Table 3, entry 7). Moving the CF_3 group to the ortho position thus caused deactivation for both electronic and steric reasons, resulting in an almost 100-fold decrease in reactivity (Table 3, entry 8). The reaction of substrate **3h**, bearing two phenyl groups, led to a modest yield (34%) of desired product **4h** (Table 3, entry 9). The lower yield with this specific substrate can be attributed to a side reaction with acetonitrile, as 4,5-diphenyl-2-methyloxazole (28%) was also isolated under these conditions. Product **4h** was obtained in a very good yield (84%) by performing the reaction in dichloromethane to prevent this side reaction (Table 3, entry 10). Substrate **3i**, derived from tetralone, also resulted in a modest yield of the desired compound (Table 3, entry 10). It was found by analysis of the ^{1}H NMR spectrum of the crude mixture that product **4i** is not stable under the reaction conditions. It undergoes rapid elimination of TsOH, followed by aromatization to yield 1-naphthol. The latter is then further oxidized by HTIB to produce 1,4-naphthoquinone. To favor formation of the latter, substrate **3i** was reacted with an excess of HTIB (2 equiv). Under these conditions, 1,4-naphthoquinone was isolated in very good yield (86%). Finally, we investigated the reactivity of enol esters bearing two aliphatic groups. Reaction of enol ester **3j**, derived from cyclohexanone, with HTIB afforded desired compound **4j** in 74% yield (Table 3, entry 12). The lower yield in comparison to other substrates is attributed to partial elimination of TsOH and formation of cyclohexenone, as found by analysis of the ^{1}H NMR spectrum of the crude mixture. Attempts to change the reaction conditions did not lead to an increase in the isolated yield of **4j**. The reaction of **3k**, an acyclic substrate bearing two aliphatic groups, led to the formation of **4k** in excellent yield (Table 3, entry 13). The slight decrease in reactivity is attributable to steric hindrance of the *t*-butyl group.

The potential of acetyl enol esters to be used as substrates in catalytic systems was investigated last. Classical catalytic conditions involve in situ generation of HTIB from PhI and an excess of TsOH·H_2O and *m*-chloroperbenzoic acid (*m*-CPBA). We evaluated the stability and relative reactivity of enol ester **1b** toward these reagents to determine if selective reaction with HTIB was possible under catalytic conditions. The conversion rates of **1b** are illustrated in Figure 1.

This substrate was found to be stable in the presence of TsOH·H_2O, showing no noticeable degradation (e.g., hydrolysis) over a period of 6 h. Without the presence of TsOH·H_2O, compound **1b** showed a similar kinetic profile toward both *m*-CPBA and HTIB. However, in the presence of TsOH·H_2O, more representative of the actual catalytic conditions, a great increase in reactivity with HTIB was observed, whereas reactivity with *m*-CPBA remained mostly unaffected. These kinetic profiles supported the feasibility of selective reaction with HTIB in the presence of an excess of *m*-CPBA and TsOH·H_2O. As expected, the α-tosyloxy ketone product **2** was obtained in 74% yield under catalytic conditions by slow addition of **1b** to a mixture of 20 mol % of phenyl iodide and a stoichiometric quantity of *m*-CPBA and TsOH·H_2O in acetonitrile at room temperature (eq 3).

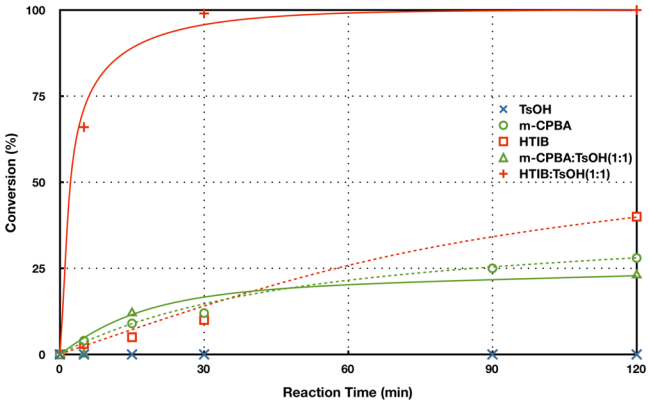

Figure 1. Kinetic profiles of **1b** with TsOH, *m*-CPBA, and HTIB.

In summary, we have demonstrated that enol esters are proficient substrates to access α-tosyloxy ketones by reaction with HTIB. Despite the presence of an electron-withdrawing group on the enol oxygen, they react rapidly under mild conditions, similarly to silyl enol ethers.[10] In contrast to the latter, they are more stable in acidic and oxidative conditions. This has permitted us to develop catalytic conditions for this transformation. Additionally, the acyl enol esters are accessible through numerous methodologies even from nonketonic precursors.[11] The described transformation can thus serve to devise novel synthetic strategies to access α-substituted ketone intermediates.

EXPERIMENTAL SECTION

General Remarks. All nonaqueous reactions involving air or moisture-sensitive compounds were run under an inert atmosphere (nitrogen or argon) with rigid exclusion of moisture from reagents and glassware using standard techniques.[13] All glassware was stored in the oven and/or was flame-dried prior to use under an inert atmosphere of gas. Anhydrous solvents were obtained either by distillation over sodium (THF, ether, toluene) or over calcium hydride (CH_2Cl_2, Et_3N). Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gels (Merck 60 F_{254}). Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, iodine, or aqueous potassium permanganate. Flash column chromatography was performed using 230−400 mesh silica (EM Science or Silicycle) of the indicated solvent system according to standard techniques.[14] Melting points were obtained on a Buchi melting point apparatus and are uncorrected. Infrared spectra were taken on an FTIR instrument and are reported in reciprocal centimeters (cm^{-1}). Nuclear magnetic resonance spectra (^{1}H, ^{13}C, DEPT, COSY, HMQC) were recorded on either a 300 or 400 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.27 ppm, acetonitrile, δ 1.94 ppm). Data are reported as follows: chemical shift multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sext = sextuplet, m = multiplet and br = broad) and the

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coupling constant is in Hz for integration. Chemical shifts for ^{13}C NMR spectra are recorded in ppm from tetramethylsilane using the central peak of deuterochloroform (77.23 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. When ambiguous, proton and carbon assignments were established using COSY, NOESY, HMQC, and DEPT experiments. High resolution mass spectra were performed using an UPLC-Q-TOF (ESI) mass spectrometer.

*(1-Methoxyprop-1-en-1-yl)benzene (**1a**).* Propiophenone (4.47 mmol) was mixed with trimethylorthoformate (4.92 mmol) and *p*-toluenesulfonic acid (0.022 mmol). The mixture was stirred for 24 h, and then the MeOH formed was distilled. The product was purified by distillation under reduced pressure (20 Torr, 80 °C) to provide 144 mg (36% yield) (1.7:1 *Z*:*E*) of **1a** as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53−7.26 (m, 5H), 5.44 (q, J = 6.9 Hz, 1H, *Z*), 4.86 (q, J = 7.0 Hz, 1H, *E*), 3.68 (s, 3H, *E*), 3.60 (s, 3H, *Z*), 1.86 (d, J = 6.9 Hz, 3H, *Z*), 1.75 (d, J = 7.0 Hz, 3H, *E*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 155.3, 136.2, 136.0, 128.7, 128.3, 127.9, 127.90, 127.6, 125.7, 108.9, 94.1, 58.4, 55.0, 12.8, 11.0; IR (neat) 2935, 2832, 1656, 1445, 1224, 1073, 771, 698 cm^{-1}; HRMS ESI (m/z) calcd for $C_{10}H_{12}NaO$ $[MNa]^+$ 171.0780, found 171.0790.

*(Z)-1-Phenylprop-1-en-1-yl Acetate (**1b**).*[15] *General Vinyl Acetate Formation Procedure.* *n*-Butyllithium (9.6 mmol) was added to a solution of diisopropylamine (9.6 mmol) in THF (40 mL) in a flame-dried round-bottom flask under an argon atmosphere at −78 °C. The mixture was stirred for 30 min, and then propiophenone (8 mmol) was added. The resulting mixture was stirred for 45 min, and then acetic anhydride (16 mmol) was added. The reaction was stirred 30 min at −78 °C and another 30 min at room temperature. The mixture was poured into saturated $NaHCO_3$ (100 mL), and extracted thrice with EtOAc (60 mL). The combined organic layers were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced atmosphere. The crude mixture was purified by column chromatography on silica gel with EtOAc:hexanes (5:95 to 20:80) to provide 1.35 g (96% yield) of **1b** as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51−7.41 (m, 2H), 7.41−7.24 (m, 3H), 5.93 (q, J = 6.9 Hz, 1H), 2.27 (s, 3H), 1.74 (d, J = 6.9 Hz, 3H); HRMS ESI (m/z) calcd for $C_{11}H_{12}NaO_2$ $[MNa]^+$ 199.0730, found 199.0729.

*(Z)-1-Phenylprop-1-en-1-yl Pivalate (**1c**).* *n*-Butyllithium (3.9 mmol) was added to a solution of diisopropylamine (3.9 mmol) in THF (17 mL) in a flame-dried round-bottom flask under an argon atmosphere at −78 °C. The mixture was stirred for 30 min, and then propiophenone (3.25 mmol) was added. The resulting mixture was stirred for 45 min, and pivaloyl chloride (6.5 mmol) was added. The reaction was stirred 30 min at −78 °C and another 30 min at room temperature. The mixture was poured into saturated $NaHCO_3$ (50 mL) and extracted thrice with EtOAc (60 mL). The combined organic layers were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced atmosphere. The crude mixture was purified by column chromatography on silica gel with EtOAc:hexanes (5:95 to 20:80) to provide 647 mg (91% yield) of **1c** as a colorless oil; R_f = 0.52 (EtOAc:hexanes, 10:80); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.23 (m, 5H), 5.89 (q, J = 7.0 Hz, 1H), 1.71 (d, J = 7.0 Hz, 3H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.9, 147.0, 135.5, 128.4, 127.9, 124.3, 112.4, 39.2, 27.3, 11.3; IR (neat) 2975, 2872, 1750, 1494, 1479, 1264, 1126, 1112, 1031, 753, 692 cm^{-1}; HRMS ESI (m/z) calcd for $C_{14}H_{18}NaO_2$ $[MNa]^+$ 241.1199, found 241.1199.

*(Z)-1-Phenylprop-1-en-1-yl 4-Methylbenzenesulfonate (**1d**).* *n*-Butyllithium (3.9 mmol) was added to a solution of diisopropylamine (3.9 mmol) in THF (17 mL) in a flame-dried round-bottom flask under an argon atmosphere at −78 °C. The mixture was stirred for 30 min, and then propiophenone (3.25 mmol) was added. The resulting mixture was stirred for 45 min, and *p*-toluenesulfonic anhydride (6.5 mmol) was added. The reaction was stirred 30 min at −78 °C and another 30 min at room temperature. The mixture was poured into saturated $NaHCO_3$ (50 mL), extracted thrice with EtOAc (60 mL). The combined organic layers were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced atmosphere. The crude mixture was purified by column chromatography on silica gel with EtOAc:hexanes (5:95 to 20:80) to provide 824 mg (82% yield) of **1e** as a white solid; T_{fus} 64−68 °C; R_f = 0.43 (EtOAc:hexanes, 10:90); ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.36−7.11 (m, 8H), 5.82 (q, J = 7.0 Hz, 1H), 2.42 (s, 3H), 1.75 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 144.8, 141.2, 134.9, 134.0, 129.4, 128.1 125.5, 117.3, 107.0, 21.6, 12.2; IR (neat) 3061, 2924, 1597, 1370, 1177, 1093, 984, 827, 727 cm^{-1}; HRMS ESI (m/z) calcd for $C_{16}H_{16}NaO_3S$ $[MNa]^+$ 311.0712, found 311.0711.

*(Z)-1-Phenylbut-1-en-1-yl Acetate (**3a**).* The title compound was obtained as a colorless oil (78% yield) according to the general vinyl acetate formation procedure; R_f = 0.48 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.47−7.28 (m, 5H), 5.84 (t, J = 7.4 Hz, 1H), 2.32 (s, 3H), 2.17 (qn J = 7.5 Hz, 2H), 1.09 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 145.6, 128.5, 128.0, 124.3, 119.8, 64.5, 20.6, 19.7, 13.5; IR (neat) 2967, 2935, 1759, 1666, 1494, 1370 1209, 1034, 749 cm^{-1}; HRMS ESI (m/z) calcd for $C_{12}H_{14}NaO_2$ $[MNa]^+$ 213.0886, found 213.0889.

*(Z)-1-Phenyloct-1-en-1-yl Acetate (**3b**).* The title compound was obtained as a colorless oil (78% yield) according to the general vinyl acetate formation procedure; R_f = 0.73 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.46−7.20 (m, 1H), 5.85 (t, J = 7.4 Hz, 1H), 2.32 (s, 1H), 2.15 (q, J = 7.2 Hz, 1H), 1.54−1.19 (m, 2H), 0.93 (t, J = 6.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 146.0, 135.1, 128.5, 128.0, 124.3, 118.4, 38.6, 31.7, 29.1, 26.3, 22.6, 20.7, 14.1; IR (neat) 2928, 2856, 1761, 1369, 1205, 1183, 1021, 757, 692 cm^{-1}; HRMS ESI (m/z) calcd for $C_{16}H_{22}NaO_2$ $[MNa]^+$ 269.1512, found 269.1519.

*(Z)-1-(p-Tolyl)prop-1-en-1-yl Acetate (**3c**).* The title compound was obtained as a colorless oil (84% yield) according to the general vinyl acetate formation procedure; R_f = 0.39 (10% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.24 (m, 3H), 7.13 (d, J = 7.9 Hz, 2H), 5.84 (dd, J = 13.9, 7.0 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 1.70 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 147.0, 137.9, 132.3, 129.2, 124.2, 111.6, 21.1, 20.6, 11.5; IR (neat) 2920, 1760, 1670, 1513, 1369, 1207, 1184, 1030, 798 cm^{-1}; HRMS ESI (m/z) calcd for $C_{12}H_{14}NaO_2$ $[MNa]^+$ 213.0886, found 213.0886.

*(Z)-1-(4-Methoxyphenyl)prop-1-en-1-yl Acetate (**3d**).* The title compound was obtained as a colorless oil (88% yield) according to the general vinyl acetate formation procedure; R_f = 0.41 (10% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 5.75 (q, J = 7.0 Hz, 1H), 3.78 (d, J = 1.2 Hz, 3H), 2.28 (d, J = 1.2 Hz, 3H), 1.67 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 159.5, 146.7, 127.8, 125.7, 113.9, 110.7, 55.3, 20.7, 11.5; IR (neat) 3029, 2919, 1760, 1512, 1368, 1207, 1184, 1030, 798 cm^{-1}; HRMS ESI (m/z) calcd for $C_{12}H_{14}NaO_3$ $[MNa]^+$ 229.0835, found 229.0846.

*(Z)-1-(Thiophen-2-yl)prop-1-en-1-yl Acetate (**3e**).* The title compound was obtained as a pale yellow oil (96% yield) according to the general vinyl acetate formation procedure; R_f = 0.52 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.18 (dd, J = 4.9, 1.3 Hz, 1H), 7.03−6.92 (m, 2H), 5.83 (q, J = 7.1 Hz, 1H), 2.32 (s, 3H), 1.70 (d, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 142.1, 139.1, 127.3, 124.5, 123.0, 112.4, 20.5, 11.4; IR (neat) 2938, 1764, 1667, 1435, 1370, 1201, 1025, 851, 805, 702 cm^{-1}; HRMS ESI (m/z) calcd for $C_9H_{10}NaO_2S$ $[MNa]^+$ 205.0294, found 205.0294.

*(Z)-1-(3-(Trifluoromethyl)phenyl)prop-1-en-1-yl Acetate (**3f**).* The title compound was obtained as a pale yellow oil (96% yield) according to the general vinyl acetate formation procedure; R_f = 0.42 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.69−7.39 (m, 4H), 6.00 (q, J = 7.0 Hz, 1H), 2.34 (s, 3H), 1.76 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8 (s), 136.0 (s), 131.0 (q, J = 32.3 Hz), 129.4 (s), 129.0 (s), 127.5 (s), 124.6 (q, J = 3.7 Hz), 124.0 (q, J = 272.4 Hz), 121.1 (q, J = 3.9 Hz), 114.6 (s), 20.5 (s), 11.6 (s); IR (neat) 2985, 1764, 1444, 1335, 1203, 1127, 797 cm^{-1}; HRMS ESI (m/z) calcd for $C_{12}H_{11}F_3NaO_2$ $[MNa]^+$ 267.0603, found 267.0602.

*1-(2-(Trifluoromethyl)phenyl)prop-1-en-1-yl Acetate (**3g**).* The title compound was obtained as a pale yellow oil (92% yield) (1:3 *Z*:*E*) according to the general vinyl acetate formation procedure; R_f = 0.44 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.79−7.39 (m, 4H), 5.69 (q, J = 7.2 Hz, 1H *Z*), 5.51 (q, J = 6.9 Hz, 1H *E*), 2.17 (s, 3H *E*), 2.09 (s, 3H *Z*), 1.76 (d, J = 6.9 Hz, 3H *Z*), 1.57 (d, J =

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7.2 Hz, 3H *E*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7 (s), 168.8 (s), 145.5 (s), 144.2 (s), 135.1 (q, J = 2.1 Hz), 133.5 (s), 132.0 (s), 131.7 (s), 131.5 (s), 128.9 (s), 128.5 (s), 127.8 (q, J = 30.9 Hz), 126.2 (q, J = 5.5 Hz), 123.9 (q, J = 273.5 Hz), 117.3 (s), 117.0 (s), 21.0 (s), 20.7 (s), 12.6 (s), 11.5 (s); IR (neat) 2984, 1759, 1375, 1315, 1211, 1169, 1131, 768 cm^{-1}; HRMS ESI (m/z) calcd for $C_{12}H_{11}F_3NaO_2$ $[MNa]^+$ 267.0603, found 267.0613

*(Z)-1,2-Diphenylvinyl Acetate (**3h**).*[16] The title compound was obtained as a pale yellow oil (90% yield) according to the general vinyl acetate formation procedure; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (dd, J = 11.4, 4.6 Hz, 1H), 7.47−7.24 (m, 2H), 6.73 (s, 1H), 2.34 (s, 3H). HRMS ESI (m/z) calcd for $C_{16}H_{14}NaO_2$ $[MNa]^+$ 261.0886, found 261.0885.

*3,4-Dihydronaphthalen-1-yl Acetate (**3i**).*[17] The title compound was obtained as a pale yellow oil (98% yield) according to the general vinyl acetate formation procedure; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24−7.06 (m, 1H), 5.73 (t, J = 4.7 Hz, 1H), 2.90 (t, J = 8.1 Hz, 1H), 2.48 (td, J = 8.1, 4.7 Hz, 1H), 2.33 (s, 1H); HRMS ESI (m/z) calcd for $C_{12}H_{12}NaO_2$ $[MNa]^+$ 211.0730, found 211.0743.

*Cyclohex-1-en-1-yl Acetate (**3j**).* Cyclohexanone (6.3 mmol) was mixed with acetic anhydride (12.6 mmol) and *p*-toluenesulfonic acid (0.6 mmol). The mixture was refluxed for 24 h, then cooled to room temperature, poured into saturated aqueous $NaHCO_3$ solution (150 mL), and extracted thrice with diethyl ether (75 mL). The combined organic layers were washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced atmosphere. The product was purified by distillation under reduced pressure (20 Torr, 80 °C) to provide 3.7 g (70% yield) of **3j** as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.38 (s, 1H), 2.14 (s, 7H), 1.79−1.69 (m, 2H), 1.61 (dd, J = 11.7, 6.2 Hz, 2H); HRMS ESI (m/z) calcd for $C_8H_{12}NaO_2$ $[MNa]^+$ 163.0730, found 163.0737.

*(Z)-2,2-Dimethyl-6-phenylhex-3-en-3-yl Acetate (**3k**).* The title compound was obtained as a pale yellow oil (72% yield) according to the general vinyl acetate formation procedure; R_f = 0.83 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.08 (m, 5H), 5.16 (t, J = 7.0 Hz, 1H), 2.84−2.59 (m, 1H), 2.19 (s, 3H), 2.18−2.11 (m, 2H), 1.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 155.1, 141.9, 128.4, 128.3, 125.8, 112.5, 36.0, 35.2, 28.0, 26.4, 20.6; IR (neat) 2969, 1758, 1454, 1369, 1208, 1098, 1048, 699 cm^{-1}; HRMS ESI (m/z) calcd for $C_{16}H_{22}NaO_2$ $[MNa]^+$ 269.1512, found 269.1518.

*1-Oxo-1-phenylpropan-2-yl 4-Methylbenzenesulfonate (**2**).*[7c] *General α-Tosyloxy Ketone Formation Procedure.* [Hydroxy(tosyloxy)iodo]benzene (0.33 mmol) was added to a solution of **1a** (0.3 mmol) in acetonitrile (1.5 mL). The mixture was stirred at 40 °C until disappearance of the suspension. The reaction mixture was poured into water (15 mL) and extracted thrice with dichloromethane (10 mL). The combined organics layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude mixture was purified by column chromatography on silica gel with EtOAc:hexanes (20:80) to provide 85.8 mg (92% yield) of **2** as a white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 7.0 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 5.78 (q, J = 7.0 Hz, 1H), 2.39 (s, 3H), 1.58 (d, J = 7.0 Hz, 3H); HRMS ESI (m/z) calcd for $C_{16}H_{16}NaO_4S$ $[MNa]^+$ 327.0661, found 327.0658.

*1-Oxo-1-phenylbutan-2-yl 4-Methylbenzenesulfonate (**4a**).*[7b] The title compound was obtained as a colorless solid (91% yield) according to the general α-tosyloxy ketone formation procedure; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 8.2, 1.0 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.25 (t, J = 7.0 Hz, 2H), 5.55 (dd, J = 7.9, 5.0 Hz, 1H), 2.39 (s, 3H), 2.05−1.83 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); HRMS ESI (m/z) calcd for $C_{17}H_{18}NaO_4S$ $[MNa]^+$ 341.0818, found 341.0810.

*1-Oxo-1-phenyloctan-2-yl 4-Methylbenzenesulfonate (**4b**).*[7b] The title compound was obtained as a light brown solid (89% yield) according to the general α-tosyloxy ketone formation procedure; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.78 (m, 2H), 7.77−7.68 (m, 2H), 7.62−7.52 (m, 1H), 7.44 (dd, J = 10.8, 4.8 Hz, 2H), 7.24 (t, J = 6.7 Hz, 2H), 5.58 (dd, J = 8.2, 4.9 Hz, 1H), 2.39 (s, 3H), 1.96−1.74 (m, 2H), 1.48−1.37 (m, 1H), 1.33 (ddd, J = 12.6, 9.2, 5.0 Hz, 1H), 1.27−1.11 (m, 6H), 0.83 (t, J = 6.9 Hz, 3H); HRMS ESI (m/z) calcd for $C_{21}H_{26}NaO_4S$ $[MNa]^+$ 397.1444, found 397.1444.

*1-Oxo-1-p-tolylpropan-2-yl 4-Methylbenzenesulfonate (**4c**).*[9b] The title compound was obtained as a light brown solid (95% yield) according to the general α-tosyloxy ketone formation procedure; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.66 (m, 4H), 7.34−7.18 (m, 4H), 5.82−5.69 (m, 1H), 2.40 (s, 3H), 2.39 (d, J = 5.9 Hz, 3H), 1.57 (dd, J = 6.9, 3.3 Hz, 3H); HRMS ESI (m/z) calcd for $C_{17}H_{18}NaO_4S$ $[MNa]^+$ 341.0818, found 341.0810.

*1-(4-Methoxyphenyl)-1-oxopropan-2-yl 4-Methylbenzenesulfonate (**4d**).* The title compound was obtained as a light brown solid (93% yield) according to the general α-tosyloxy ketone formation procedure; R_f = 0.08 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.82 (m, 2H), 7.75 (d, J = 8.3 Hz, 2H), 7.31−7.21 (m, 2H), 6.97−6.84 (m, 2H), 5.73 (q, J = 6.9 Hz, 1H), 3.87 (s, 3H), 2.40 (s, 3H), 1.57 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 164.1, 145.0, 133.5, 131.2, 129.7, 127.9, 126.4, 114.0, 77.5, 77.3, 77.1, 76.6, 55.5, 21.6, 18.8; IR (neat) 1689, 1359, 1175, 845, 758, 666 cm^{-1}; HRMS ESI (m/z) calcd for $C_{17}H_{18}NaO_5S$ $[MNa]^+$ 357.0767, found 357.0774.

*1-(3-(Trifluoromethyl)phenyl)-1-oxopropan-2-yl 4-Methylbenzenesulfonate (**4e**).*[9b] The title compound was obtained as a colorless oil (93% yield) according to the general α-tosyloxy ketone formation procedure; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 8.3 Hz 2H), 7.60 (t, J = 7.7 Hz, 1H), 7.29−7.21 (m, 2H), 5.70 (q, J = 7.0 Hz, 1H), 2.40 (s, 3H), 1.61 (d, J = 7.0 Hz, 3H); HRMS ESI (m/z) calcd for $C_{17}H_{15}F_3NaO_4S$ $[MNa]^+$ 395.0535, found 395.0532.

*1-Oxo-1-(2-(trifluoromethyl)phenyl)propan-2-yl 4-Methylbenzenesulfonate (**4f**).*[9b] The title compound was obtained as a colorless oil (82% yield) according to the general α-tosyloxy ketone formation procedure; NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, J = 10.4, 6.1 Hz, 3H), 7.61−7.51 (m, 2H), 7.44 (dd, J = 5.1, 3.7 Hz, 1H), 7.25 (d, J = 8.1 Hz, 3H), 5.50 (q, J = 6.9 Hz, 1H), 2.41 (s, 3H), 1.53 (d, J = 6.9 Hz, 3H); HRMS ESI (m/z) calcd for $C_{17}H_{15}F_3NaO_4S$ $[MNa]^+$ 395.0535, found 395.0528.

*1-Oxo-1-(thiophen-2-yl)propan-2-yl 4-Methylbenzenesulfonate (**4g**).*[8] The title compound was obtained as a white solid (81% yield) according to the general α-tosyloxy ketone formation procedure; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J = 3.9 Hz, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 4.9 Hz, 1H), 7.30 (d, J = 8.8 Hz, 2H), 7.21−7.12 (m, 1H), 5.48 (q, J = 6.9 Hz, 1H), 2.44 (s, 3H), 1.62 (d, J = 6.9 Hz, 3H); HRMS ESI (m/z) calcd for $C_{14}H_{14}NaO_4S_2$ $[MNa]^+$ 333.0226, found 333.0229.

*2-Oxo-1,2-diphenylethyl 4-Methylbenzenesulfonate (**4h**).*[8] The title compound was obtained as a white solid (35% yield) according to the general α-tosyloxy ketone formation procedure; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 7.2 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.45−7.35 (m, 4H), 7.32 (q, J = 3.8 Hz, 3H), 7.24 (d, J = 8.3 Hz, 2H), 6.70 (s, 1H), 2.42 (s, 3H); HRMS ESI (m/z) calcd for $C_{21}H_{18}NaO_4S$ $[MNa]^+$ 389.0818, found 389.0825.

*1,2,3,4-Tetrahydro-1-oxonaphthalen-2-yl 4-Methylbenzenesulfonate (**4i**).*[8] The title compound was obtained as a brown solid (25% yield) according to the general α-tosyloxy ketone formation procedure; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (dd, J = 11.5, 8.1 Hz, 2H), 7.50 (td, J = 7.4, 1.1 Hz, 1H), 7.43−7.29 (m, 3H), 7.25 (t, J = 7.7 Hz, 1H), 5.16 (dd, J = 12.2, 5.0 Hz, 1H), 3.12 (dd, J = 6.2, 3.5 Hz, 2H), 2.55 (dt, J = 13.4, 4.5 Hz, 1H), 2.50−2.31 (m, 4H); HRMS ESI (m/z) calcd for $C_{17}H16NaO_4S$ $[MNa]^+$ 339.0662, found 339.0666.

*2-Oxocyclohexyl 4-Methylbenzenesulfonate (**4j**).*[18] The title compound was obtained as a white solid (74% yield) according to the general α-tosyloxy ketone formation procedure; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 4.89 (dd, J = 10.9, 5.9 Hz, 1H), 2.53 (d, J = 13.8 Hz, 2H), 2.43 (s, 3H), 2.37−2.21 (m, 2H), 2.02−1.82 (m, 2H), 1.77−1.57 (m, 2H); HRMS ESI (m/z) calcd for $C_{13}H_{16}NaO_4S$ $[MNa]^+$ 291.0662, found 291.0658.

*5,5-Dimethyl-4-oxo-1-phenylhexan-3-yl 4-Methylbenzenesulfonate (**4k**).* The title compound was obtained as a colorless oil (93% yield) according to the general α-tosyloxy ketone formation procedure; R_f = 0.25 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz,

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$CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.27 (dt, J = 14.9, 6.9 Hz, 3H), 7.12 (d, J = 6.9 Hz, 2H), 5.34 (dd, J = 7.2, 4.6 Hz, 1H), 2.89−2.70 (m, 1H), 2.68−2.53 (m, 1H), 2.48 (s, 3H), 2.02 (ddd, J = 12.3, 5.8, 2.0 Hz, 2H), 1.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 209.3, 145.0, 140.0, 133.7, 129.8, 128.6, 128.5, 128.0, 126.4, 78.0, 43.7, 34.0, 31.1, 26.7, 21.7; IR (neat) 2969, 1720, 1496, 1368, 1189, 1176, 932, 553 cm^{-1}; HRMS ESI (m/z) calcd for $C_{21}H_{26}NaO_4S$ $[MNa]^+$ 397.1444, found 397.1449.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra for all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00948.

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Notes

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