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Photoaddition Reactions of Acetylpyridines with Silyl Ketene Acetals: SET vs [2 + 2]-Cycloaddition Pathways

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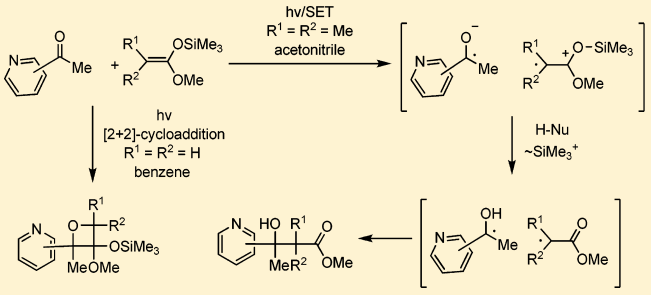
Supporting Information

ABSTRACT: Photoaddition reactions of silyl ketene acetals with 2-, 3- and 4-acetylpyridine have been explored. The results show that the acetylpyridines react with an electron rich, dimethyl-substituted silyl ketene acetal via a pathway in which excited state single electron transfer (SET) takes place to produce β-hydroxyesters in high yields. In contrast, photochemical reactions of the acetylpyridines with an electron deficient, nonmethyl-substituted silyl ketene acetal generate oxetanes as major products, which arise via a route involving excited state [2 + 2]-cycloaddition. In addition, an increase in solvent polarity significantly enhances the relative efficiencies of the SET processes versus [2 + 2]-cycloaddition reactions. Importantly, the carbonyl groups rather than the pyridine moieties in the acetylpyridine substrates participate in both types of addition reactions. Finally, the results demonstrate that photoinduced electron transfer (PET)-promoted chemical reactions between acetylpyridines and electron rich silyl ketene acetals in polar solvent serve as useful methods to promote β-hydroxyester forming, Claisen or Mukaiyama condensation reactions under mild conditions.

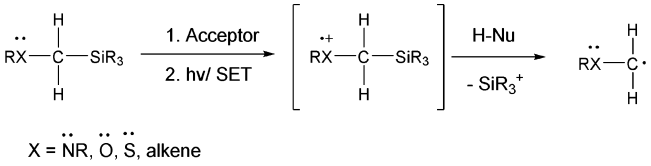


INTRODUCTION

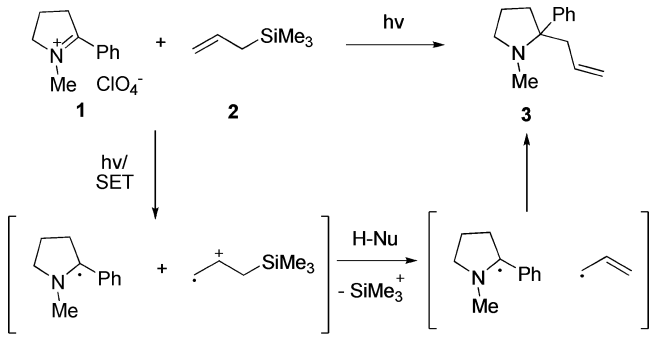
Earlier investigations in the area of single electron transfer (SET) photochemistry have led to the development of new synthetic methodologies[1−3] and to the elucidation of mechanisms involved in novel excited state reactions.[4] In one phase of this work, we showed that sequential SET-desilylation reactions of α-trialkylsilyl substituted electron donors serve as highly efficient and regioselective methods to generate carbon-centered free radicals.[5] The high efficiencies of these reactions are a consequence of the fact that trialkylsilyl transfer from α-trialkylsilyl cation radicals, generated by SET oxidation, to silophiles takes place more rapidly than other possible radical cation fragmentation processes (Scheme 1).[1−6] A pertinent example of a photochemical reaction that follows this pathway is the SET-promoted addition of allyltrimethylsilane (**2**) to the 1-pyrrolinium perchlorate (**1**) (Scheme 2).

Studies in this and related areas have shown that a number of α-trialkylsilyl substituted electron donors, including benzylsilanes,[7,8] allylsilanes,[9−11] silyl ketene acetals,[12−14] and silyl enol ethers,[15,16] serve as substrates for a wide variety of synthetically

Scheme 1



Scheme 2



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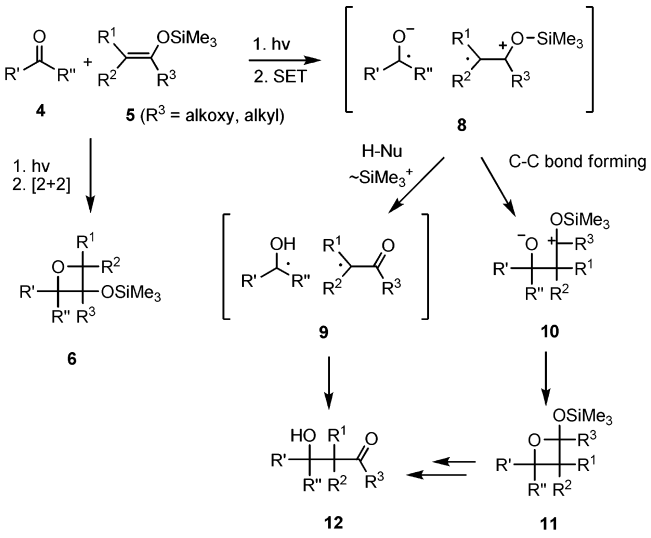
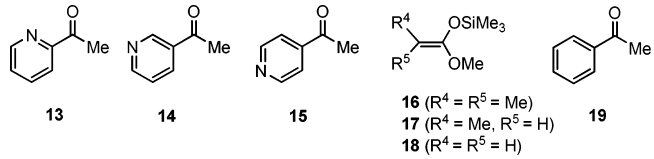
important ground and excited state organic transformations. Of special relevance to the studies described below are Lewis acid catalyzed Claisen or Mukaiyama reactions of carbonyl compounds with silyl ketene acetals and silyl enol ethers.[12−16] Recently, we explored photoinduced Mukaiyama type addition reactions that take place between aromatic carbonyl compounds and silyl ketene acetals,[14b] *N*-methylphthalimide and silyl enol ether,[17] and 1,2-diketones and silyl ketene acetal.[3b] The results of these efforts revealed that diverse excited state photochemical reaction pathways are operable in these systems and that competition between the pathways is governed by the structural nature and redox properties of the excited state of the carbonyl reactant and ground state of the α-trialkylsiloxy substituted alkenes, along with solvent polarity.[3b,5c,12a,c,14b,17] For instance, we observed that irradiation of solutions containing aromatic carbonyl compounds **4** and silyl ketene acetals **5** promotes two competitive excited state reactions that lead to formation of 3-silyloxyoxetanes **6** and β-hydroxyesters **12** (Scheme 3). Oxetanes were formed in these processes

Scheme 3



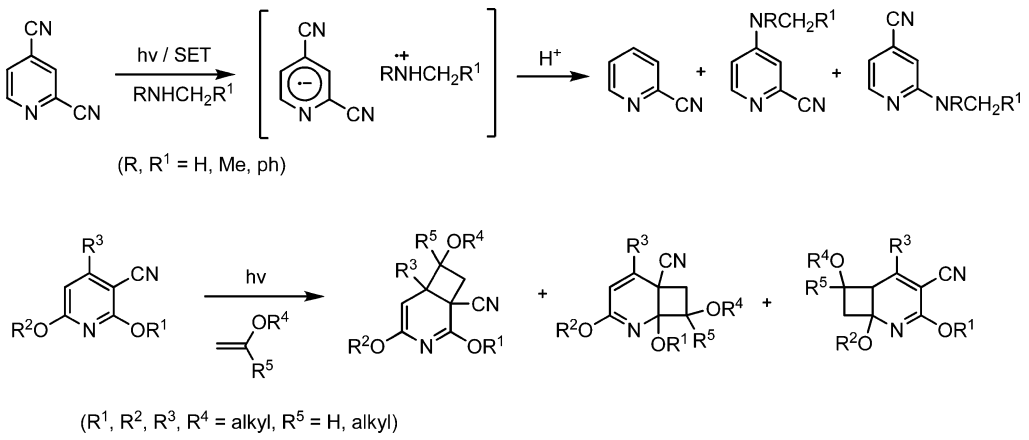
through classical Paterno−Buchi type [2 + 2]-cycloadditions[18] taking place between the triplet excited states of **4** and ground state of **5**. A competitive route involving SET from **5** (or silyl enol ethers) to the triplet excited states of **4** generated radical



ion pairs **8**,[14b] which undergo desilylation to furnish radical pairs **9** or zwitterions **10** that are converted to the respective 2-silyloxyoxetanes **11** or β-hydroxyesters **12**. Interestingly, in photoreactions of electron rich, dimethyl-substituted silyl ketene acetals, the SET-desilylation process producing **11** and **12** predominated. In contrast, photochemical processes of electron deficient, nonmethyl-substituted silyl ketene acetals gave rise to the formation of **6** by way of [2 + 2]-cycloaddition. In addition, when solvents of high polarity were employed, the SET pathway was favored.[3b,14b] These observations show that the relative efficiencies of the competitive SET vs [2 + 2]-cycloaddition reactions are strongly governed by the oxidation potentials of silyl ketene acetals and polarity of the medium.[5c,12c,3b,14b]

In a recent effort, described below, we explored photochemical reactions occurring between silyl ketene acetals and 2-, 3- and 4-acetylpyridines (**13**−**15**) and silyl ketene acetals **16**−**18**, along with those involving the model aryl-ketone acetophenone (**19**).[14b] As a consequence of the presence of carbonyl and pyridine moieties in **13**−**15**, a manifold of different SET-promoted reactions can take place. For example, it is well-known that the ketones serve as electron acceptors in photochemical C−C bond forming processes as well as participants in Paterno−Buchi reactions that generate oxetanes. In addition, pyridines, especially those possessing electron-withdrawing groups (e.g., cyano) have been observed to participate in both the SET and [2 + 2]-cycloaddition reactions[19,20] (Scheme 4). The results of the current studies show that acetylpyridines react with an electron rich, dimethyl-substituted silyl ketene acetal via a pathway promoted by excited state SET that produces β-hydroxyesters in high yields. In contrast, photochemical reactions of the acetylpyridines with an electron deficient, nonmethyl-substituted silyl ketene acetal generate oxetanes along with β-hydroxyesters as major products, the former of which arise via a route involving [2 + 2]-cycloaddition. In addition, an increase in solvent polarity significantly enhances the relative efficiencies of the SET vs [2 + 2]-cycloaddition reactions. Importantly, the carbonyl groups rather than the pyridine moieties in the acetylpyridine

Scheme 4



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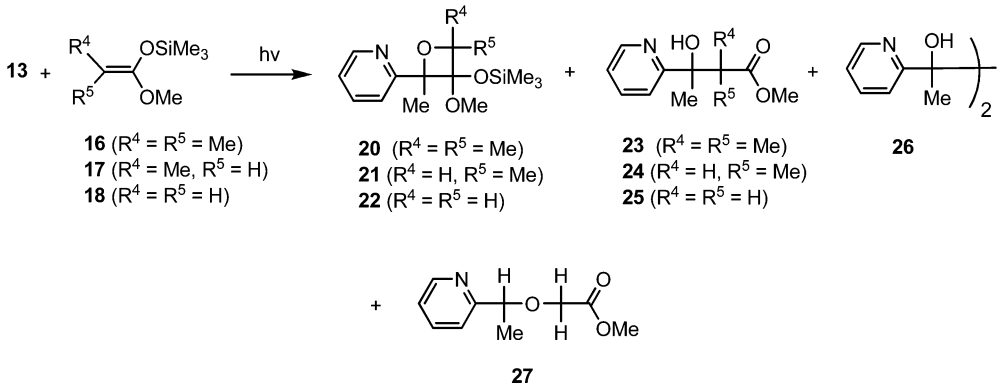
Scheme 5



substrates participate in both of the observed addition reactions.

RESULTS AND DISCUSSION

Photochemical reactions were performed by using Pyrex filtered-light ($\alpha > 290$ nm) in benzene or acetonitrile solutions containing acetylpyridines **13**–**15** (20 mM) and silyl ketene acetals **16**–**18** (40 mM) for time periods that bring about 45–100% conversion of the acetylpyridines. In each case, the photolysate was concentrated and the residue was subjected to silica gel chromatography to obtain the photoproducts.

Photochemistry of 2-Acetylpyridine (13). As can be seen by viewing the results (Scheme 5 and Table 1), irradiation of a benzene solution containing **13** and electron rich, silyl ketene acetal **16** resulted in formation of a mixture of products containing predominantly β-hydroxyester **23**, which arises by a sequential SET-desilylation pathway. Minor components of the product mixture (**23**:**20a,b** = ca. 6:1) were the diasteromeric oxetanes **20a** and **20b**, formed by a [2 + 2]-cycloaddition process (Scheme 5 and Table 1). When more polar acetonitrile was used as the solvent, the SET pathway became more favorable, and as a result, β-hydroxyester **23** was produced nearly exclusively (90%, **23**:**20a,b** = ca. 23:1).

Irradiation of a benzene solution containing **13** and the monomethyl substituted silyl ketene acetal **17** promoted formation of near equal amounts of β-hydroxyester **24** and oxetane **21**, both as mixtures of diastereomers, along with the pinacol-type dimer **26**.[21] Interestingly, photoreaction of **13** with **17** in acetonitrile generated 3:1 ratio of **24** and **21**.

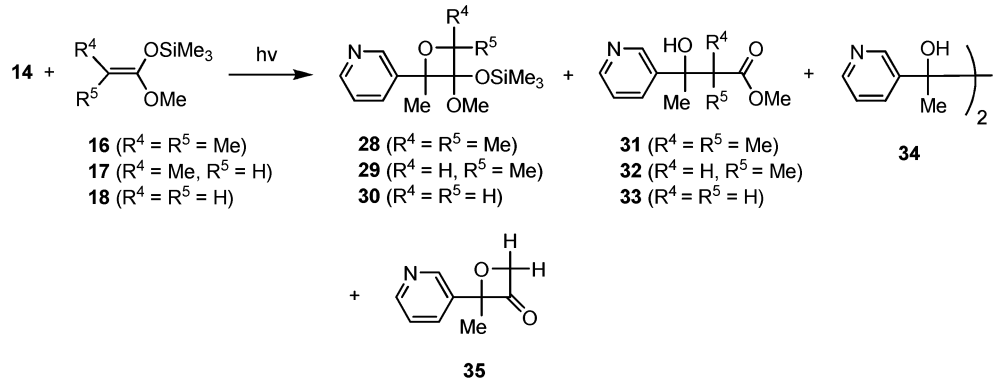
In contrast to the photoreaction of **13** with **16**, reaction with the relatively electron poor, nonmethyl substituted, silyl ketene acetal **18** in benzene yielded the diastereomeric oxetanes **22a** and **22b** (36%), β-hydroxyester **25** (14%), and α-alkoxyacetate **27** as the major product (50%). On the basis of the proposal that ester **27** arose by hydrolytic ring-opening of oxetanes **22**, it appears that excited state reaction of **13** with **18** predominantly follows a [2 + 2]-cycloaddition pathway. Although the yield of **25** increased, the [2 + 2]-cycloaddition process was still favored when acetonitrile was employed as the solvent. Another observation is that, compared to the photoreactions occurring between **13** and acetals **16** and **17**, photoreaction between **13** and **18** required a longer time to bring about high conversion (82–94%). In addition, it is important to note that careful ^{1}H NMR analysis of product mixtures generated in the reactions

Table 1. Photoreactions of 2-Acetylpyridine (13) and Silyl Ketene Acetals 16–18[a]

reactants	solvent	reaction time (h)	% conversion	product (% yield)[b]
13 + **16**	Benzene	2.5	100	**20a** (7), **20b** (6), **23** (75)
13 + **16**	CH_3CN	2.5	100	**20a** (2), **20b** (2), **23** (90)
13 + **17**	Benzene	4	77	**21a** (10), **21b** (20), **24a** (12), **24b** (22), **26** (trace)
13 + **17**	CH_3CN	4.5	96	**21a** (6), **21b** (14), **24a** (13), **24b** (49), **26** (2)
13 + **18**	Benzene	16	94	**22a** (36), **22b** (trace), **25** (14), **27** (50)
13 + **18**	CH_3CN	16	82	**22a** (23), **22b** (10), **25** (23), **27** (15)

[a]Concentrations of reactants, **13**/**16**–**18** are 20/40 (mM). [b]Yields are based on consumed **13**.

Scheme 6



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described failed to reveal the presence of substances that would have been generated by reactions of the pyridine moieties in **13** as exemplified by those depicted in Scheme 4.

The results described above show that photochemical reactions of **13** with silyl ketene acetals **16**–**18** generate β-hydroxyesters as well as oxetanes in ratios that depend on the degree of methyl substitution on the acetals and the polarity of the solvent. The relative yields of β-hydroxyesters and oxetanes appear to be governed by the relative efficiencies of competitive SET-desilylation vs [2 + 2]-cycloaddition open to the reactive triplet excited state of 2-acetylpyridine, which are controlled by both the electron donating abilities (i.e., oxidation potentials) of the silyl ketene acetals and solvent stabilization of radical ion intermediates. For example, when the electron rich acetal **16** with a relatively low oxidation potential (0.90 V vs SCE)[12c] is the substrate and the more polar acetonitrile is the solvent, SET from **16** to excited **13** takes place rapidly to form a radical ion pair (ΔG_{SET} ca. −0.26 V)[22] Desilylation of the radical cation of the silyl ketene acetal then occurs to form the radical pair precursor of the β-hydroxyester product **21**. However, classical Paterno–Buchi [2 + 2]-cycloaddition reaction of the ketone moiety in the excited state of **13** predominates when the SET is slow because of the higher oxidation potentials (ca. 1.28 V vs SCE, ΔG_{SET} ca. 0.12 V)[12c,22,23] of less methyl substituted silyl ketene acetals (e.g., **18**) and less solvent stabilization of the resulting ion radicals. It is important to note that the patterns observed for reactions of **13** with **16**–**18** match well trends seen in previous studies with a number of substrates.[3b,14b,17]

Photochemistry of 3-Acetylpyridine (14). The results arising from studies of the photoreactions of 3-acetylpyridine (**14**) with **16**–**18**, summarized in Scheme 6 and Table 2, parallel those of the reactions of **13** with the same acetals. Specifically, irradiation of a benzene solution containing **14** and **16** produced β-hyroxyester **31** predominantly (77%) along with lesser amounts of the diastereomeric oxetanes **28** (12%) and dimer **34**[24] (9%). Exclusive formation of **31** (92%) was observed to take place when an acetonitrile solution of **14** and **16** was irradiated. Reaction of **14** with **17** in benzene competitively generated diasteromeric β-hydroxyesters **32** (30%) and diasteromeric oxetanes **29a,b** (22%, trace), and the yield of **32** was dramatically enhanced (81%) when acetonitrile was the solvent. Lastly, irradiation of a benzene solution of **14** containing **18** generated of oxetane **30a,b** (22%, trace), oxacyclobutanone **35** (50%) and β-hydroxyester **33** (29%). On the basis of the plausible assumption that oxacyclobutanone **35** results from hydrolysis of **30**, the product profiles show that [2 + 2]-cycloaddition reactions of 3-acetylpyridine, which occur in competition with those promoted by SET, become more competitive when the silyl ketene acetals are less electron rich and less polar benzene is utilized as solvent. The substrate and solvent dependent differences in preferred reaction pathways are also reflected in reaction quantum efficiencies, which are qualitatively echoed in irradiation time vs percent conversion data given in Table 2.

Table 2. Photoreactions of 3-Acetylpyridine (14) and Silyl Ketene Acetals 16–18[a]

reactants	solvent	reaction time (h)	% conversion	product (% yield)[b]
14 + **16**	Benzene	7	90	**28a** (6), **28b** (6), **31** (77), **34** (9)
14 + **16**	CH_3CN	7	60	**28a** (trace), **28b** (trace), **31** (92), **34** (trace)
14 + **17**	Benzene	8.5	71	**29a** (22), **29b** (trace), **32a** (7), **32b** (23), **34** (8)
14 + **17**	CH_3CN	8.5	45	**29a** (11), **29b** (6), **32a** (26), **32b** (55), **34** (trace)
14 + **18**	Benzene	15	93	**30a** (22), **30b** (trace), **33** (29), **35** (50)
14 + **18**	CH_3CN	15	81	**30a** (12), **30b** (trace), **33** (41), **35** (35)

[a]Concentrations of reactants, **14**/**16**–**18** are 20/40 (mM). [b]Yields are based on consumed **14**.

Photochemistry of 4-Acetylpyridine (15). Irradiation of 4-acetylpyridine (**15**) in benzene and acetonitrile solutions containing **16**–**18** led to formation of product mixtures containing the corresponding β-hydroxyesters **39**–**41**, oxetanes **36**–**38** and, in certain cases, the pyridylethanol **42** and α-alkoxy acetate **43** (Table 3, Scheme 7). In a manner that is similar to those of the 2- and 3-acetylpyridine analogues, photoreaction of **15** with **16** yielded β-hydroxyester **39**, diastereomeric oxetanes **36**, and alcohol **42** in relative yields that depend upon the solvent used (**39**:**36a,b** = 5:1 in benzene and >80:1 in acetonitrile). In addition, nearly equal amounts of **40** and **37** were produced in the photoreaction of **15** with **17** in benzene, whereas the process in acetonitrile formed **40** and **37** in a 5:1 ratio. In both of these cases, alcohol **42** was a minor product. Moreover, irradiation of benzene and acetonitrile solutions of **15** containing **18** led to generation of **38** and **43** as major products along with minor amounts of **41**. Finally, as is observed with the other pyridine derivatives, a correlation appears to exist between the nature of the major reaction pathway followed by **15** and the irradiation time vs percent conversion (i.e., longer times lower conversions for reactions in which the [2 + 2]-cycloaddition process becomes more predominate).

Table 3. Photoreactions of 4-Acetylpyridine (15) and Silyl Ketene Acetals 16–18[a]

reactants	solvent	reaction time (h)	% conversion	product (% yield)[b]
15 + **16**	Benzene	3.5	79	**36a** (7), **36b** (7), **39** (68), **42** (12)
15 + **16**	CH_3CN	6	78	**36a** (trace), **36b** (trace), **39** (82), **42** (4)
15 + **17**	Benzene	4.5	64	**37a** (30), **37b** (4), **40a** (10), **40b** (33),**42** (8)
15 + **17**	CH_3CN	4	63	**37a** (14), **37b** (trace), **40a** (24), **40b** (48), **42** (8)
15 + **18**	Benzene	16	96	**38a** (25), **38b** (4), **41** (17), **43** (52)
15 + **18**	CH_3CN	16	89	**38a** (21), **38b** (2), **41** (26), **43** (37)

[a]Concentrations of reactants, **15**/**16**–**18** are 20/40 (mM). [b]Yields are based on consumed **15**.

Comparison of Photoreaction of the Acetylpyridines vs the Nonheterocyclic Analogue Acetophenone. A comparison of the photochemical reaction profile of the nonheterocyclic analogue acetophenone (**19**) with those of the acetylpyridines was made to determine if differences exist in the relative contributions of the SET vs [2 + 2]-cycloaddition reaction pathways. The results of photoreactions of **19** with **16**–**18**, observed in our previous study,[14b] are displayed Scheme 8 and Table 4. Unfortunately, because of the fact that different conditions (e.g., reactant concentrations and photochemical apparatus) were employed in the earlier study, it is

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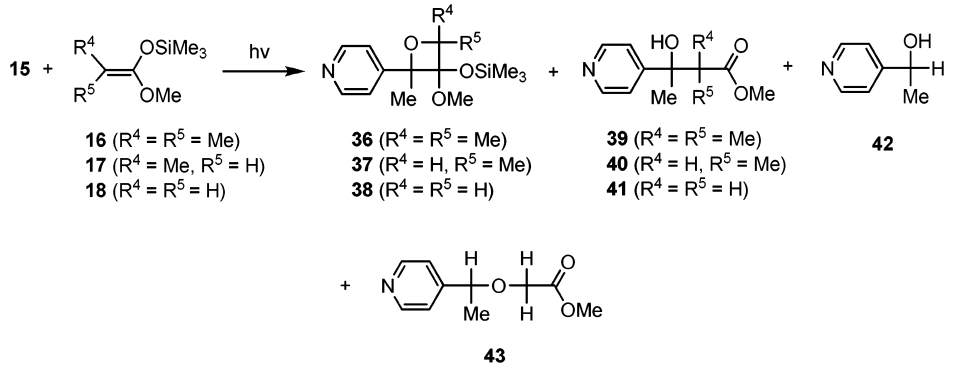
Scheme 7



Scheme 8

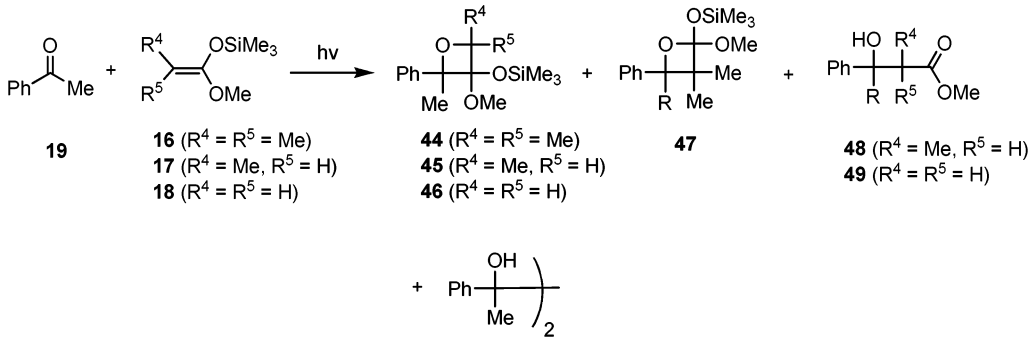


Table 4. Photoreactions of Acetophenone (19) and Silyl Ketene Acetals 16−18[a]

reactants	solvent	reaction time (h)	% conversion	product (% yield)[b]
19 + **16**	Benzene	33	77	**44a** (11), **44b** (7), **47** (64), **50** (3)
19 + **16**	CH_3CN	16	100	**44a** (5), **44b** (6), **47** (83), **50** (5)
19 + **17**	Benzene	14	47	**45a** (21), **45b** (34), **48a** (15), **48b** (25)
19 + **17**	CH_3CN	12	72	**45a** (8), **45b** (16), **48a** (19), **48b** (24), **50** (16)
19 + **18**	Benzene	16	65	**46a** (21), **46b** (32), **49** (22)
19 + **18**	CH_3CN	20	49	**46a** (16), **46b** (30), **49** (25)

[a]Concentrations of reactants, **19**/**16**−**18** are 36/72 (mM). [b]Yields are based on consumed **19**.

Table 5. Reduction Potentials and Triplet Excited State Energies of Acetylpyridines 13−15 and Acetophenone 19

		triplet energy (kcal/mol)	
ketone	$E_{1/2}$ (V)	hydrocarbon[a]	alcohol[b]
19	−2.09	73.6	74.1
13	−1.91	70.0	70.9
14	−1.94	71.1	73.0
15	−1.86	69.5	70.3

[a]Methylcyclohexane/isopentane (4:1). [b]Ethanol/methanol (4:1).

not possible to make a qualitative estimate of the relative quantum efficiencies of the photoreactions of **13**−**15** with those of **19**. However, a comparison of the product composition data shows that approximately the same ratios of oxetane and *β*-hydroxyester products are generated in photoreactions of the acetals with both **19** and **13**−**15** in benzene and acetonitrile. This observation is interesting in light of the fact that the **13**−**15** and **19** have nearly equivalent triplet excited state energies and ground state reduction potentials ($E_{1/2}$) (Table 5) (i.e., nearly equivalent triplet excited state reduction potentials).[22] Thus, the propensity of the triplet excited state of **19** and **13**−**15** to accept an electron from **16**−**18** appears to be the singular most important factor governing the nature of the reaction pathways followed in these processes.

Selectivity for Reactions at the Ketone Rather than Pyridine Ring Center. An interesting feature of photoreactions of **13**−**15** with **16**−**18** is that both the SET and [2 + 2]-cycloaddition processes take place at the ketone carbonyl rather than pyridine ring center. The highly regioselective nature of these excited state processes is somewhat surprising because electron withdrawing group substituted pyridines were known to participate in [2 + 2]-cycloaddition and SET-promoted reactions, which occur in the pyridine ring centers (Scheme 4).[19,20] One possible reason for the high selectivity of photochemical reactions of acetylpyridines could be associated with the magnitudes of charge coefficients in the $n-\pi$ triplet excited states of these substrates (T_1), which could govern the sites of energetically most favored interactions with **16**−**18**. To gain information about this proposal, density functional theory (DFT) calculations using a B3LYP hybrid exchange correlation function employing 6-31G** (for ground states (S_0) and anion radicals of acetylpyridines) and CIS (for triplet states of acetylpyridines T_1) were carried out. The results, depicted in Table 6, show that charge coefficients of **13**−**15** are both heavily localized on the ketone carbonyl moieties, while a large extent of charge coefficients are located on C_2 and C_6 in pyridine ring (Table 7). If in fact [2 + 2]-photocyloaddition

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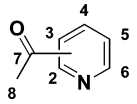
Table 6. Calculated Charge Coefficients of Ground States (S_0), Triplet Excited States (T_1) and Anion Radicals of the Acetylpyridines 13−15



	2-acetylpyridine (**13**)			3-acetylpyridine (**14**)			4-acetylpyridine (**15**)		
atom	S_0	T_1	radical anion	S_0	T_1	radical anion	S_0	T_1	radical anion
N	−0.490	−0.562	−0.553	−0.439	−0.512	−0.483	−0.420	−0.502	−0.532
C_2	0.210	0.167	0.182	0.169	0.279	0.046	0.185	0.242	0.074
C_3	0.043	0.077	−0.058	0.034	−0.098	0.057	−0.009	0.033	−0.103
C_4	0.048	0.030	−0.069	0.069	0.094	−0.069	0.067	−0.054	0.080
C_5	0.010	−0.101	−0.150	0.003	−0.015	−0.082	−0.009	0.033	−0.103
C_6	0.198	0.263	0.097	0.212	0.253	0.024	0.185	0.242	0.074
C_7	0.399	0.319	0.303	0.393	0.292	0.282	0.402	0.297	0.292
C_8	0.031	0.107	−0.134	0.012	0.094	−0.157	0.013	0.094	−0.154
O	−0.450	−0.391	−0.616	−0.450	−0.387	−0.618	−0.440	−0.385	−0.609

Table 7. Calculated Charge Coefficients of the Ground State (S_0) and Excited State (S_1, T_1) of Pyridine

	charge coefficient		
atom	S_0	S_1	T_1
N	−0.428	−0.584	−0.471
C_2	0.094	0.314	0.247
C_3	−0.093	−0.056	−0.001
C_4	−0.058	−0.068	−0.020
C_5	−0.093	−0.056	−0.001
C_6	0.094	0.314	0.247

reactions are governed by interactions between the ground state of silyl ketene acetals **16−18** and triplet states of the acetylpyridines **13−15** (T_1) and if odd electron densities in the acetylpyridine radical anions, which are reflected in charge densities, control the regioselectivity of radical coupling steps in the SET-promoted processes, the DFT and CIS calculation results are in accord with the regioselectivities in both types of photochemical reactions observed to take place between these substrates.

CONCLUSION

The combined results arising from our previous studies and those described above demonstrate that photoaddition reactions of acetylpyridines **13−15** with silyl ketene acetals **16−18** serve as a highly efficient and extremely mild methods for the preparation of *β*-hydroxyesters. In contrast to typical Claisen or Mukaiyama reactions that are used for this purpose, the photochemical processes are promoted using mild conditions that do not require the presence of strong acids or bases and, as a result, are environmentally benign. The *β*-hydroxyester forming reactions, following a sequential SET-desilylation pathway, take place with high levels of chemoselectivity when the electron rich silyl ketene acetals and relatively polar solvents are used.

EXPERIMENTAL SECTION

General Procedure. ^{1}H and ^{13}C NMR (200 MHz) spectra were recorded on $CDCl_3$ solutions, and chemical shifts are reported in parts per million relative to $CHCl_3$ peak (7.24 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR) as an internal standard. IR spectral bands are reported in cm^{-1}. Preparative photochemical reactions were conducted with an apparatus consisting of a 450 W Hanovia medium vapor pressure mercury lamp surrounded by a Pyrex glass filter in a water-cooled quartz immersion well surrounded by the solution being irradiated. The photolysis solutions were purged with nitrogen before and during irradiations. The photolyzates were concentrated under reduced pressure giving residues, which were subjected to silica gel column chromatography. High resolution (HRMS) mass spectra were obtained by use of quadrupole mass analyzer, electron impact ionization unless otherwise noted. All starting materials used in the photoreactions were derived from commercial sources. All new compounds described were isolated as oils in >90% purity (by NMR analysis) unless noted otherwise.

Irradiation of 2-Acetylpyridine (13) and 1-Methoxy-2-methyl-1-(trimethylsilyloxy)propene (16). *In Benzene.* A 150 mL solution of **13** (364 mg, 3.00 mmol) and **16** (1.04 g, 6.00 mmol) was irradiated for 2.5 h (ca. 100% conversion of **13**). Concentration of photolysate gave a residue, which was subjected to silica gel column chromatography (ethyl acetate:*n*-hexane = 1:3) giving **20** (**20a**, 62 mg, 7% and **20b**, 53 mg, 6%) and 502 mg (75%) of **23**.

In Acetonitrile. A 150 mL solution of **13** (100 mg, 0.83 mmol) and **16** (290 mg, 1.65 mmol) was irradiated for 2.5 h (ca. 100% conversion of **13**). Workup and column chromatography (ethyl acetate:*n*-hexane = 1:3) gave **20** (**20a**, 5 mg, 2% and **20b**, 5 mg, 2%) and 166 mg (90%) of **23**.

20a *(liq).* ^{1}H NMR ($CDCl_3$) −0.10 (s, 9H), 1.31 and 1.50 (s, 6H), 1.78 (s, 3H), 3.47 (s, 3H), 7.09 (m, 1H), 7.64 (m, 2H), 8.54 (d, 1H, J = 4.7 Hz); ^{13}C NMR ($CDCl_3$) 1.0, 24.3, 25.1, 25.9, 52.0, 89.8, 93.3, 103.2, 120.1, 121.2, 135.6, 148.1, 163.6; MS (CI) m/z (rel. intensity) 296 (M^+ + H, 1), 280 (M^+−CH_3, 7), 264 (M^+ − OCH_3, 3), 222 (M^+-$SiMe_3$, 25), 206 (M^+ − $OSiMe_3$, 3), 194 (8), 174 (100), 132 (16), 105 (16), 73 (37); HRMS (CI) m/z 296.1684 (M + H, $C_{15}H_{26}NO_3Si$ requires 296.1682).

20b *(liq).* ^{1}H NMR ($CDCl_3$) 0.25 (s, 9H), 1.43 and 1.49 (s, 6H), 1.77 (s, 3H), 2.80 (s, 3H), 7.11 (m, 1H), 7.66 (t, 1H, J = 8.0 Hz), 7.82 (d, 1H, J = 8.0 Hz), 8.52 (d, 1H, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 1.4, 24.3, 24.5, 26.7, 51.4, 90.3, 92.9, 103.2, 121.4, 121.6, 135.8, 147.9, 163.0; MS (CI) m/z (rel. intensity) 296 (M^+ + H, 5), 280 (M^+ − CH_3, 3), 264 (M^+ − OCH_3, 3), 222 (M^+-$SiMe_3$, 32), 206 (M^+ − $OSiMe_3$, 6), 194 (13), 174 (100), 132 (25), 105 (41), 73 (82); HRMS (CI) m/z 296.1667 (M + H, $C_{15}H_{26}NO_3Si$ requires 296.1682).

23 *(liq).* ^{1}H NMR ($CDCl_3$) 1.17 and 1.19 (s, 3H), 1.64 (s, 3H), 3.58 (s, 3H), 5.50 (s, 1H), 7.18 (t, 1H, J = 6.1 Hz), 7.34 (d, 1H, J = 8.1 Hz), 7.66 (t, 1H, J = 7.6 Hz), 8.49 (d, 2H, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 21.2, 21.6, 23.4, 50.9, 51.5, 76.4, 120.9, 122.1, 136.0, 146.9, 162.4, 177.1; IR (neat) 3100−3500 (br, OH stretching), 1730 (C═O stretching); MS (CI) m/z (rel. intensity) 224 (M^+ + H, 5), 192 (M^+ − OCH_3, 4), 176 (2), 146 (6), 123 (92), 122 (M^+ − $C(CH_3)_2CO_2CH_3$, 100), 104 (22), 79 (23); HRMS (CI) m/z 224.1288 (M + H, $C_{12}H_{18}NO_3$ requires 224.1287).

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Irradiation of 2-Acetylpyridine (13) and 1-Methoxy-1-(trimethylsilyloxy)propene (17). *In Benzene.* A 150 mL solution of **13** (357 mg, 2.85 mmol) and **17** (1.13 g, 7.10 mmol) was irradiated for 4 h (ca. 77% conversion of **13**). Workup and column chromatography (ethyl acetate:*n*-hexane = 1:3) giving **21** (**21a**, 62 mg, 10% and **21b**, 124 mg, 20%), **24** (**24a**, 55 mg, 12% and **24b**, 101 mg, 22%) and trace of **26**.[21]

In Acetonitrile. A 150 mL solution of **13** (372 mg, 3.10 mmol) and **17** (1.08 g, 6.89 mmol) was irradiated for 4.5 h (ca. 96% conversion of **13**). Workup and column chromatography (ethyl acetate:*n*-hexane = 1:3) gave **21** (**21a**, 50 mg, 6% and **21b**, 118 mg, 14%), **24** (**24a**, 82 mg, 13% and **24b**, 305 mg, 49%) and 14 mg (2%) of **26**.

21a *(liq).* ^{1}H NMR ($CDCl_3$) −0.19 (s, 9H), 1.31 (d, 3H, J = 6.2 Hz), 1.78 (s, 3H), 3.34 (s, 3H), 4.91 (q, 1H, J = 6.3 Hz), 7.13 (t, 1H, J = 5.6 Hz), 7.67 (m, 2H), 8.53 (d, 1H, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 1.0, 16.9, 22.2, 51.1, 83.1, 94.5, 102.7, 121.5, 121.7, 135.6, 148.1, 162.4; MS (EI) m/z (rel. intensity) 281 (M^+, 0.1), 266 ($M^+ - CH_3$, 2), 250 ($M^+ - OCH_3$, 1), 222 (19), 208 (M^+-$SiMe_3$, 5), 192 ($M^+ - OSiMe_3$, 4), 179 (17), 160 (100), 132 (16), 100 (58), 81 (53), 73 (82), 59 (72); HRMS (EI) m/z 281.1475 ($C_{14}H_{23}NO_3Si$ requires 281.1448).

21b *(liq).* ^{1}H NMR ($CDCl_3$) 0.20 (s, 9H), 1.41 (d, 3H, J = 6.4 Hz), 1.81 (s, 3H), 2.63 (s, 3H), 4.90 (q, 1H, J = 6.4 Hz), 7.17 (t, 1H, J = 4.9 Hz), 7.71 (t, 1H, J = 7.4 Hz), 7.85 (d, 1H, J = 8.0 Hz), 8.55 (d, 1H, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 1.1, 15.8, 22.5, 49.9, 85.5, 94.9, 100.8, 122.5, 122.6, 136.0, 148.0, 161.9; MS (EI) m/z (rel. intensity) 281 (M^+, 1), 266 ($M^+ - CH_3$, 0.6), 222 (21), 208 (M^+-$SiMe_3$, 4), 192 ($M^+ - OSiMe_3$, 5), 160 (100), 132 (15), 100 (62), 73 (96), 59 (73); HRMS (EI) m/z 281.1463 ($C_{14}H_{23}NO_3Si$ requires 281.1448).

24a *(liq).* ^{1}H NMR ($CDCl_3$) 0.94 (d, 3H, J = 7.1 Hz), 1.56 (s, 3H), 3.06 (q, 1H, J = 7.2 Hz), 3.69 (s, 3H), 4.75 (s, 1H), 7.17 (t, 1H, J = 4.9 Hz), 7.51 (d, 1H, J = 7.9 Hz), 7.69 (t, 1H, J = 5.9 Hz), 8.51 (d, 1H, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 12.4, 27.4, 48.8, 51.6, 75.0, 119.7, 121.9, 136.6, 147.9, 163.4, 176.4; IR (neat) 3100−3600 (br, OH stretching), 1730 (C═O stretching); MS (EI) m/z (rel. intensity) 209 (M^+, 0.4), 194 ($M^+ - CH_3$, 5), 162 ($M^+ - CO_2CH_3$, 8), 122 (100), 102 (21), 77 (24), 56 (11); HRMS (EI) m/z 209.1039 ($C_{11}H_{15}NO_3$ requires 209.1053).

24b *(liq).* ^{1}H NMR ($CDCl_3$) 1.24 (d, 3H, J = 7.3 Hz), 1.45 (s, 3H), 3.20 (q, 1H, J = 7.3 Hz), 3.44 (s, 3H), 4.76 (s, 1H), 7.10 (t, 1H, J = 4.8 Hz), 7.53 (d, 1H, J = 6.8 Hz), 7.62 (t, 1H, J = 7.3 Hz), 8.44 (d, 1H, J = 5.1 Hz); ^{13}C NMR ($CDCl_3$) 11.9, 25.5, 47.7, 51.3, 75.3, 119.5, 121.7, 136.5, 147.5, 165.2, 176.5; IR (neat) 3100−3500 (br, OH stretching), 1730 (C═O stretching); MS (EI) m/z (rel. intensity) 209 (M^+, 0.3), 162 ($M^+ - CO_2CH_3$, 5), 194 ($M^+ - CH_3$, 3), 178 ($M^+ - OCH_3$, 5), 149 (7), 122 (100), 99 (14), 78 (22); HRMS (EI) m/z 209.1053 ($C_{11}H_{15}NO_3$ requires 209.1053).

Irradiation of 2-Acetylpyridine (13) and 1-Methoxy-1-(trimethylsilyloxy)ethene (18). *In Benzene.* A 150 mL solution of **13** (374 mg, 3.10 mmol) and **18** (1.00 g, 7.00 mmol) was irradiated for 16 h (ca. 94% conversion of **13**). Workup and column chromatography (ethyl acetate:CH_2Cl_2:*n*-hexane = 1:1:6) giving **22** (**22a**, 280 mg, 36% and **22b**, trace), 81 mg (14%) of **25** and 284 mg (50%) of **27**.

In Acetonitrile. A 150 mL solution of **13** (375 mg, 3.10 mmol) and **18** (1.00 g, 7.00 mmol) was irradiated for 16 h (ca. 82% conversion of **13**). Workup and column chromatography (ethyl acetate:CH_2Cl_2:*n*-hexane = 1:1:3) gave **22** (**22a**, 156 mg, 23% and **22b**, 67 mg, 10%), 112 mg (23%) of **25** and 74 mg (15%) of **27**.

22a *(liq).* ^{1}H NMR ($CDCl_3$) −0.11 (s, 9H), 1.80 (s, 3H), 3.37 (s, 3H), 4.52 (d, 1H, J = 6.6 Hz), 4.67 (d, 1H, J = 7.0 Hz), 7.15 (m, 1H), 7.68 (m, 2H), 8.58 (d, 1H, J = 4.7 Hz); ^{13}C NMR ($CDCl_3$) 0.7, 21.9, 50.9, 79.0, 98.1, 101.0, 120.3, 121.5, 135.7, 148.4, 161.9; MS (CI) m/z (rel. intensity) 268 (M^+ + H, 11), 252 ($M^+ - CH_3$, 13), 194 (M^+-$SiMe_3$, 41), 179 (59), 146 (100), 131 (65), 104 (90), 89 (82), 74 (98); HRMS (CI) m/z 268.1378 (M + H, $C_{13}H_{22}NO_3Si$ requires 268.1368).

22b *(liq).* ^{1}H NMR ($CDCl_3$) 0.19 (s, 9H), 1.83 (s, 3H), 2.79 (s, 3H), 4.61 (d, 1H, J = 6.8 Hz), 4.70 (d, 1H, J = 6.7 Hz), 7.18 (m, 1H), 7.75 (m, 2H), 8.56 (d, 1H, J = 5.9 Hz); ^{13}C NMR ($CDCl_3$) 1.0, 22.3, 50.1, 79.6, 97.6, 101.2, 121.6, 122.0, 136.1, 148.2, 161.3; MS (EI) m/z (rel. intensity) 267 (M^+, 2), 252 ($M^+ - CH_3$, 1), 222 (9), 194 (M^+-$SiMe_3$, 7), 146 (74), 99 (44), 73 (100); HRMS (EI) m/z 267.1267 ($C_{13}H_{21}NO_3Si$ requires 267.1291).

25 *(liq).* ^{1}H NMR ($CDCl_3$) 1.54 (s, 3H), 2.82 (d, 1H, J = 15.8 Hz), 3.19 (d, 1H, J = 15.8 Hz), 3.58 (s, 3H), 4.94 (s, 1H), 7.16 (t, 1H, J = 6.2 Hz), 7.64 (m, 2H), 8.48 (d, 1H, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 29.2, 45.4, 51.5, 73.6, 119.2, 121.9, 136.8, 147.9, 164.9, 172.9; IR (neat) 3100−3600 (br, OH stretching), 1730 (C═O stretching); MS (EI) m/z (rel. intensity) 195 (M^+, 5), 180 ($M^+ - CH_3$, 67), 148 (66), 136 (77), 122 ($M^+ - CH_2CO_2CH_3$, 100), 106 (67), 79 (97), 51 (47); HRMS (EI) m/z 180.0671 ($M^+ - CH_3$, $C_9H_{10}NO_3$ requires 180.0666).

27 *(liq).* ^{1}H NMR ($CDCl_3$) 1.45 (d, 3H, J = 6.6 Hz), 3.64 (s, 3H), 3.97 (d of d, 2H, J = 16.5 Hz), 4.64 (q, 1H, J = 6.6 Hz), 7.18 (m, 1H), 7.45 (d, 1H, J = 7.8 Hz), 7.67 (t, 1H, J = 5.9 Hz), 8.52 (d, 1H, J = 4.1 Hz); ^{13}C NMR ($CDCl_3$) 21.9, 51.6, 66.1, 79.4, 120.0, 122.5 136.9, 148.7, 161.8, 170.4; IR (neat) 1770 (C═O stretching); MS (EI) m/z (rel. intensity) 195 (M^+, 0.1), 180 ($M^+ - CH_3$, 2), 149 (7), 136 (17), 122 ($M^+ - CH_2CO_2CH_3$, 77), 107 (100), 106 ($M^+ - OCH_2CO_2CH_3$, 97), 78 (48), 59 (27), 50 (19); HRMS (EI) m/z 195.0871 ($C_{10}H_{13}NO_3$ requires 195.0895).

Irradiation of 3-Acetylpyridine (14) and 1-Methoxy-2-methyl-1-(trimethylsilyloxy)propene (16). *In Benzene.* A 150 mL solution of **14** (364 mg, 3.00 mmol) and **16** (1.04 g, 6.00 mmol) was irradiated for 7 h (ca. 90% conversion of **14**). Workup and column chromatography (ethyl acetate:*n*-hexane = 1:3) giving **28** (**28a**, 47 mg, 6% and **28b**, 47 mg, 6%), 471 mg (77%) of **31** and 59 mg (9%) of **34**.[24]

In Acetonitrile. A 150 mL solution of **14** (364 mg, 3.00 mmol) and **16** (1.04 g, 6.00 mmol) was irradiated for 7 h (ca. 60% conversion of **14**). Workup and column chromatography (ethyl acetate:*n*-hexane = 1:3) gave **28** (**28a**, trace and **28b**, trace), 372 mg (92%) of **31** and trace of **34**.

28a *(liq).* ^{1}H NMR ($CDCl_3$) −0.03 (s, 9H), 1.25 and 1.48 (s, 6H), 1.66 (s, 3H), 3.45 (s, 3H), 7.25 (m, 1H), 7.70 (m, 1H), 8.46 (d, 1H, J = 3.2 Hz), 8.57 (s, 1H); ^{13}C NMR ($CDCl_3$) 1.2, 24.8, 26.0, 26.6, 51.6, 89.7, 91.0, 102.9, 122.4 133.1 147.5, 147.6, 139.9; MS (CI) m/z (rel. intensity) 296 (M^+ + H, 2), 280 ($M^+ - CH_3$, 1), 237 (12), 222 (M^+-$SiMe_3$, 4), 194 (24), 174 (83), 133 (55), 105 (29), 73 (100); HRMS (CI) m/z 296.1675 (M + H, $C_{15}H_{26}NO_3Si$ requires 296.1682).

28b *(liq).* ^{1}H NMR ($CDCl_3$) 0.28 (s, 9H), 1.39 and 1.46 (s, 6H), 1.66 (s, 3H), 2.92 (s, 3H), 7.24 (t, 1H, J = 4.8 Hz), 7.81 (d, 1H, J = 8.1 Hz), 8.48 (d, 1H, J = 1.8 Hz), 8.66 (s, 1H); ^{13}C NMR ($CDCl_3$) 1.6, 24.3, 26.3, 26.4, 51.3, 89.9, 90.3, 103.0, 122.5 133.7 147.7, 147.9, 139.3; MS (EI) m/z (rel. intensity) 295 (M^+, 0.3), 280 ($M^+ - CH_3$, 2), 237 (12), 222 (M^+-$SiMe_3$, 5), 194 (22), 174 (71), 133 (35), 73 (100); HRMS (EI) m/z 295.1613 ($C_{15}H_{25}NO_3Si$ requires 295.1605).

31 *(liq).* ^{1}H NMR ($CDCl_3$) 1.13 and 1.15 (s, 3H), 1.61 (s, 3H), 3.69 (s, 3H), 4.60 (s, 1H), 7.24 (m, 1H), 7.80 (d, 1H, J = 8.1 Hz), 8.48 (d, 1H, J = 4.8 Hz), 8.66 (s, 1H); ^{13}C NMR ($CDCl_3$) 21.3, 21.4, 24.7, 50.0, 51.9, 75.8, 122.1, 134.7, 139.1, 147.7, 148.2, 178.0; IR (neat) 3100−3500 (br, OH stretching), 1710 (C═O stretching); MS (CI) m/z (rel. intensity) 224 (M^+ + H, 3), 176 (0.5), 146 (0.5), 122 ($M^+ - C(CH_3)_2CO_2CH_3$, 100), 106 (12), 87 (10); HRMS (CI) m/z 224.1287 (M + H, $C_{12}H_{18}NO_3$ requires 224.1287).

Irradiation of 3-Acetylpyridine (14) and 1-Methoxy-1-(trimethylsilyloxy)propene (17). *In Benzene.* A 150 mL solution of **14** (363 mg, 3.00 mmol) and **17** (1.00 g, 6.30 mmol) was irradiated for 8.5 h (ca. 71% conversion of **14**). Workup and column chromatography (ethyl acetate:$CHCl_3$:*n*-hexane = 1:1:5) giving **29** (**29a**, 132 mg, 22% and **29b**, trace), **32** (**32a**, 32 mg, 7% and **32b**, 102 mg, 23%) and 42 mg (8%) of **34**.

In Acetonitrile. A 150 mL solution of **14** (368 mg, 3.10 mmol) and **17** (1.00 g, 6.26 mmol) was irradiated for 8.5 h (ca. 45% conversion of **14**). Workup and column chromatography (ethyl acetate:$CHCl_3$:*n*-hexane = 1:1:5) gave **29** (**29a**, 42 mg, 11% and **29b**, 23 mg, 6%), **32** (**32a**, 76 mg, 26% and **32b**, 162 mg, 55%) and trace of **34**.

29a *(liq).* ^{1}H NMR ($CDCl_3$) −0.18 (s, 9H), 1.34 (d, 3H, J = 6.2 Hz), 1.76 (s, 3H), 3.33 (s, 3H), 4.93 (q, 1H, J = 6.3 Hz), 7.27 (t, 1H, J = 6.7 Hz), 7.78 (d, 1H, J = 6.3 Hz), 8.50 (d, 1H, J = 6.4 Hz), 8.65 (s, 1H); ^{13}C NMR ($CDCl_3$) 1.0, 16.6, 22.9, 51.2, 82.7, 92.0, 102.9, 122.5,

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134.5, 138.3, 148.2, 148.3; MS (CI) m/z (rel. intensity) 282 ($M^+ + 1$, 0.6), 266 ($M^+ - CH_3$, 5), 224 (31), 194 (59), 192 ($M^+ - OSiMe_3$, 3), 160 (100), 133 (66), 105 (38), 74 (95), 56 (97); HRMS (CI) m/z 282.1526 (M + H, $C_{14}H_{24}NO_3Si$ requires 282.1525).

29b *(liq).* ^{1}H NMR ($CDCl_3$) 0.21 (s, 9H), 1.42 (d, 3H, J = 6.2 Hz), 1.77 (s, 3H), 2.60 (s, 3H), 4.89 (q, 1H, J = 6.2 Hz), 7.17 (t, 1H, J = 4.9 Hz), 7.71 (t, 1H, J = 7.4 Hz), 7.85 (d, 1H, J = 8.0 Hz), 8.55 (d, 1H, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 1.1, 15.8, 22.5, 49.9, 85.5, 94.9, 100.8, 122.5, 136.0, 138.3, 148.0, 148.1; MS (EI) m/z (rel. intensity) 281 (M^+, 1), 266 ($M^+ - CH_3$, 0.6), 222 (21), 208 (M^+-$SiMe_3$, 4), 192 ($M^+ - OSiMe_3$, 5), 160 (100), 132 (15), 100 (62), 73 (96), 59 (73); HRMS (EI) m/z 281.1463 ($C_{14}H_{23}NO_3Si$ requires 281.1448).

32a *(liq).* ^{1}H NMR ($CDCl_3$) 0.97 (d, 3H, J = 7.0 Hz), 1.58 (s, 3H), 2.85 (q, 1H, J = 7.0 Hz), 3.77 (s, 3H), 4.75 (s, 1H), 7.28 (t, 1H, J = 4.8 Hz), 7.81 (d, 1H, J = 6.1 Hz), 8.51 (d, 1H, J = 4.8 Hz), 8.65 (s, 1H); ^{13}C NMR ($CDCl_3$) 12.7, 29.6, 49.1, 52.0, 73.3, 123.0, 133.0, 140.5, 146.8, 148.0, 177.1; IR (neat) 3100−3300 (br, OH stretching), 1730 (C═O stretching); MS (CI) m/z (rel. intensity) 210 (M^+ + H, 5), 194 ($M^+ - CH_3$, 40), 162 ($M^+ - CO_2CH_3$, 21), 122 (100), 106 (17), 88 (65), 57 (48); HRMS (CI) m/z 210.1131(M + H, $C_{11}H_{16}NO_3$ requires 210.1130).

32b *(liq).* ^{1}H NMR ($CDCl_3$) 1.34 (d, 3H, J = 7.3 Hz), 1.48 (s, 3H), 3.01 (q, 1H, J = 7.2 Hz), 3.49 (s, 3H), 7.20 (q, 1H, J = 4.1 Hz), 7.75 (d, 1H, J = 7.7 Hz), 8.40 (d, 1H, J = 2.9 Hz), 8.59 (s, 1H); ^{13}C NMR ($CDCl_3$) 12.2, 26.4, 48.4, 51.7, 73.5, 122.9, 132.7, 142.8, 146.5, 147.8, 176.5; IR (neat) 3100−3400 (br, OH stretching), 1730 (C═O stretching); MS (CI) m/z (rel. intensity) 210 (M^+ + H, 16), 194 ($M^+ - CH_3$, 5), 178 ($M^+ - OCH_3$, 11), 162 ($M^+ - CO_2CH_3$, 8), 149 (8), 122 (100), 106 (74), 88 (66), 78 (59), 57 (52); HRMS (CI) m/z 210.1130 ($C_{11}H_{16}NO_3$ requires 210.1130).

Irradiation of 3-Acetylpyridine (14) and 1-Methoxy-1-(trimethylsilyloxy)ethene (18). *In Benzene.* A 150 mL solution of **14** (372 mg, 3.10 mmol) and **18** (1.00 g, 7.00 mmol) was irradiated for 16 h (ca. 93% conversion of **14**). Workup and column chromatography (ethyl acetate:$CHCl_3$:*n*-hexane = 1:1:5) giving **30** (**30a**, 172 mg, 22% and **30b**, trace), 164 mg (29%) of **33** and 238 mg (50%) of **35**.

In Acetonitrile. A 150 mL solution of **14** (380 mg, 3.14 mmol) and **18** (1.00 g, 7.00 mmol) was irradiated for 16 h (ca. 81% conversion of **14**). Workup and column chromatography (ethyl acetate:$CHCl_3$:*n*-hexane = 1:1:5) gave **30** (**30a**, 80 mg, 12% and **30b**, trace), 195 mg (41%) of **33** and 146 mg (35%) of **35**.

30a *(liq).* ^{1}H NMR ($CDCl_3$) −0.11 (s, 9H), 1.71 (s, 3H), 3.36 (s, 3H), 4.49 (d, 1H, J = 7.0 Hz), 4.63 (d, 1H, J = 7.0 Hz), 7.26 (t, 1H, J = 6.6 Hz), 7.70 (d, 1H, J = 8.1 Hz), 8.45 (d, 1H, J = 4.8 Hz), 8.58 (s, 1H); ^{13}C NMR ($CDCl_3$) 0.7, 23.9, 50.5, 78.7, 95.9, 100.5, 122.6, 133.3, 138.3, 147.4, 147.9; MS (CI) m/z (rel. intensity) 268 (M^+ + H, 11), 252 ($M^+ - CH_3$, 13), 194 (M^+-$SiMe_3$, 41), 179 (59), 146 (100), 131 (65), 104 (90), 89 (82), 74 (98); HRMS (CI) m/z 268.1378 (M + H, $C_{13}H_{22}NO_3Si$ requires 268.1369).

30b *(liq).* ^{1}H NMR ($CDCl_3$) 0.23 (s, 9H), 1.78 (s, 3H), 2.80 (s, 3H), 4.63 (two d, 2H, J = 7.0 Hz and J = 11.0 Hz), 7.31 (m, 1H), 7.85 (d, 1H, J = 7.7 Hz), 8.51 (s, 1H), 8.68 (s, 1H); ^{13}C NMR ($CDCl_3$) 1.1, 23.9, 50.0, 79.1, 94.8, 101.3, 122.7, 134.2, 137.4, 147.7, 148.4; MS (EI) m/z (rel. intensity) 267 (M^+, 2), 252 ($M^+ - CH_3$, 1), 222 (9), 194 (M^+-$SiMe_3$, 7), 146 (74), 99 (44), 73 (100); HRMS (EI) m/z 267.1267 ($C_{13}H_{21}NO_3Si$ requires 267.1291).

33 *(liq).* ^{1}H NMR ($CDCl_3$) 1.56 (s, 3H), 2.91 (q, 2H, J = 16.6 Hz), 3.62 (s, 3H), 4.58 (s, 1H), 7.29 (t, 1H, J = 4.8 Hz), 7.83 (d, 1H, J = 8.0 Hz), 8.49 (d, 1H, J = 4.7 Hz), 8.65 (s, 1H); ^{13}C NMR ($CDCl_3$) 30.3, 45.9, 51.8, 71.4, 123.1, 132.5, 146.2, 148.0, 142.1, 172.6; IR(neat) 3100−3400 (br, OH stretching), 1730 (C═O stretching); MS (EI) m/z (rel. intensity) 195 (M^+, 2), 180 ($M^+ - CH_3$, 84), 148 (25), 136 (77), 122 ($M^+ - CH_2CO_2CH_3$, 100), 106 (88), 78 (51), 50 (30); HRMS (EI) m/z 180.0675 ($M^+ - CH_3$, $C_9H_{10}NO_3$ requires 180.0666).

35 *(liq).* ^{1}H NMR ($CDCl_3$) 1.83 (s, 3H), 5.39 (d of d, 2H, J = 15.2 Hz), 7.33 (q, 1H, J = 4.2 Hz), 7.76 (d, 1H, J = 7.8 Hz), 8.60 (d, 1H, J = 1.5 Hz), 8.74 (s, 1H); ^{13}C NMR ($CDCl_3$) 23.9, 86.9, 107.3, 123.4, 131.8, 134.3, 145.7, 149.5, 201.3 (C═O); IR (neat) 1730 (C═O stretching); MS (CI) m/z (rel. intensity) 164 (M^+ + H, 1), 149 (M^+ + 1 − CH_3, 10), 135 (6), 122 (100), 106 (98), 78 (29), 50 (19); HRMS (CI) m/z 164.0732 ($C_9H_{10}NO_2$ requires 164.0712).

Irradiation of 4-Acetylpyridine (15) and 1-Methoxy-2-methyl-1-(trimethylsilyloxy)propene (16). *In Benzene.* A 150 mL solution of **15** (363 mg, 3.00 mmol) and **16** (1.04 g, 6.00 mmol) was irradiated for 3.5 h (ca. 79% conversion of **15**). Workup and column chromatography (ethyl acetate:*n*-hexane = 1:3) giving **36** (**36a**, 50 mg, 7% and **36b**, 50 mg, 7%), 359 mg (68%) of **39** and 34 mg (12%) of **42**.[19,25]

In Acetonitrile. A 150 mL solution of **15** (364 mg, 3.00 mmol) and **16** (1.04 g, 6.00 mmol) was irradiated for 6 h (ca. 78% conversion of **15**). Workup and column chromatography (ethyl acetate:*n*-hexane = 1:3) gave **36** (**36a**, trace and **36b**, trace), 430 mg (82%) of **39** and 5 mg (4%) of **42**.

36a *(liq).* ^{1}H NMR ($CDCl_3$) −0.01 (s, 9H), 1.25 and 1.47 (s, 6H), 1.62 (s, 3H), 3.45 (s, 3H), 7.29 (d, 2H, J = 6.0 Hz), 8.54 (d, 2H, J = 5.8 Hz); ^{13}C NMR ($CDCl_3$) 1.1, 24.7, 26.0, 26.1, 51.6, 89.8, 91.6, 102.8, 120.7, 148.9, 153.6; MS (CI) m/z (rel. intensity) 295 (M^+, 0.1), 280 ($M^+ - CH_3$, 2), 237 (8), 222 (M^+-$SiMe_3$, 4), 194 (24), 174 (52), 133 (29), 106 (13), 73 (100); HRMS (EI) m/z 295.1595 ($C_{15}H_{25}NO_3Si$ requires 295.1605).

36b *(liq).* ^{1}H NMR ($CDCl_3$) 0.30 (s, 9H), 1.38 and 1.45 (s, 6H), 1.60 (s, 3H), 2.98 (s, 3H), 7.36 (d, 1H, J = 6.2 Hz), 8.48 (d, 2H, J = 5.8 Hz); ^{13}C NMR ($CDCl_3$) 1.6, 24.3, 26.3, 51.5, 90.4, 90.5, 103.1, 121.2, 149.0, 153.1; MS (CI) m/z (rel. intensity) 295 (M^+, 0.3), 280 ($M^+ - CH_3$, 2), 237 (12), 222 (M^+-$SiMe_3$, 5), 194 (22), 174 (71), 133 (35), 73 (100); HRMS (CI) m/z 296.1680 (M + H, $C_{15}H_{26}NO_3Si$ requires 296.1682).

39 *(liq).* ^{1}H NMR ($CDCl_3$) 1.13 and 1.17 (s, 6H), 1.58 (s, 3H), 3.67 (s, 3H), 4.64 (s, 1H), 7.34 (d, 2H, J = 6.2 Hz), 8.52 (d, 1H, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 21.3, 24.3, 49.8, 51.8, 76.2, 122.1, 148.5, 153.0, 177.6; IR (neat) 3100−3500 (br, OH stretching), 1710 (C═O stretching); MS (CI) m/z (rel. intensity) 224 (M^+ + H, 7), 206 (M^+−OH, 1), 176 (1), 122 ($M^+ - C(CH_3)_2CO_2CH_3$, 100), 102 (42), 87 (14); HRMS (CI) m/z 224.1283 (M + H, $C_{12}H_{18}NO_3$ requires 224.1287).

Irradiation of 4-Acetylpyridine (15) and 1-Methoxy-1-(trimethylsilyloxy)propene (17). *In Benzene.* A 150 mL solution of **15** (373 mg, 3.10 mmol) and **17** (1.20 g, 7.50 mmol) was irradiated for 4.5 h (ca. 64% conversion of **15**). Workup and column chromatography (ethyl acetate:CH_2Cl_2:*n*-hexane = 1:1:5) giving **37** (**37a**, 168 mg, 30% and **37b**, 21 mg, 4%), **40** (**40a**, 41 mg, 10% and **40b**, 137 mg, 33%) and 20 mg (8%) of **42**.

In Acetonitrile. A 150 mL solution of **15** (373 mg, 3.10 mmol) and **17** (1.00 g, 6.26 mmol) was irradiated for 4 h (ca. 63% conversion of **15**). Workup and column chromatography (ethyl acetate:CH_2Cl_2:*n*-hexane = 1:1:5) gave **37** (**37a**, 77 mg, 14% and **37b**, trace), **40** (**40a**, 97 mg, 24% and **40b**, 198 mg, 48%) and 21 mg (8%) of **42**.

37a *(liq).* ^{1}H NMR ($CDCl_3$) −0.15 (s, 9H), 1.31 (d, 3H, J = 6.3 Hz), 1.70 (s, 3H), 3.34 (s, 3H), 4.91 (q, 1H, J = 6.4 Hz), 7.33 (d, 2H, J = 6.2 Hz), 8.57 (d, 2H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$) 1.0, 16.7, 22.8, 51.1, 82.9, 92.5, 102.6, 121.4, 149.0, 151.8; MS (EI) m/z (rel. intensity) 281 (M^+, 0.1), 266 ($M^+ - CH_3$, 0.7), 250 ($M^+ - OCH_3$, 2.0), 224 (27), 192 ($M^+ - OSiMe_3$, 2), 160 (99), 133 (57), 105 (70), 74 (100), 60 (93); HRMS (EI) m/z 281.1447 ($C_{14}H_{23}NO_3Si$ requires 281.1448).

37b *(liq).* ^{1}H NMR ($CDCl_3$) 0.22 (s, 9H), 1.42 (d, 3H, J = 6.2 Hz), 1.72 (s, 3H), 2.69 (s, 3H), 4.90 (q, 1H, J = 6.3 Hz), 7.45 (d, 2H, J = 5.9 Hz), 8.57 (d, 2H, J = 5.5 Hz); ^{13}C NMR ($CDCl_3$) 1.1, 15.5, 22.9, 49.6, 85.3, 92.3, 101.1, 121.6, 149.2, 151.2; MS (EI) m/z (rel. intensity) 281 (M^+, 0.1), 266 ($M^+ - CH_3$, 0.7), 250 ($M^+ - OCH_3$, 2.0), 224 (27), 192 ($M^+ - OSiMe_3$, 3), 160 (99), 133 (57), 105 (70), 74 (100), 60 (93); HRMS (EI) m/z 281.1447 ($C_{14}H_{23}NO_3Si$ requires 281.1448).

40a *(liq).* ^{1}H NMR ($CDCl_3$) 0.96 (d, 3H, J = 7.2 Hz), 1.53 (s, 3H), 2.83 (q, 1H, J = 7.1 Hz), 3.78 (s, 3H), 3.98 (s, 1H), 7.35 (d, 2H, J = 6.2 Hz), 8.58 (d, 2H, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$) 12.5, 29.0, 48.6, 51.9, 73.6, 120.1, 149.4, 154.3, 176.7; IR (neat) 3100−3500 (br, OH stretching), 1730 (C═O stretching); MS (EI) m/z (rel. intensity) 209

(M^+, 0.8), 194 ($M^+ - CH_3$, 31), 162 ($M^+ - CO_2CH_3$, 15), 122 (100), 105 (76), 88 (72), 57 (37); HRMS (CI) *m/z* 210.1131 (M + H, $C_{11}H_{16}NO_3$ requires 210.1130).

***40b** (liq).* ^{1}H NMR ($CDCl_3$) 1.35 (d, 3H, *J* = 7.3 Hz), 1.42 (s, 3H), 2.98 (q, 1H, *J* = 7.2 Hz), 3.47 (s, 3H), 4.25 (s, 1H), 7.33 (d, 2H, *J* = 6.3 Hz), 8.53 (d, 2H, *J* = 6.2 Hz); ^{13}C NMR ($CDCl_3$) 12.1, 26.0, 47.8, 51.6, 73.8, 119.9, 149.3, 156.5, 176.2; IR (neat) 3100−3400 (br, OH stretching), 1730 (C═O stretching); MS (EI) *m/z* (rel. intensity) 209 (M^+, 5), 194 ($M^+ - CH_3$, 4), 162 ($M^+ - CO_2CH_3$, 9), 122 (100), 106 (76), 88 (76), 88 (76), 61 (61); HRMS (EI) *m/z* 209.1052 ($C_{11}H_{15}NO_3$ requires 209.1053).

Irradiation of 4-Acetylpyridine (15) and 1-Methoxy-1-(trimethylsilyloxy)ethene (18). *In Benzene.* A 150 mL solution of **15** (367 mg, 3.00 mmol) and **18** (1.00 g, 7.00 mmol) was irradiated for 16 h (ca. 96% conversion of **15**). Workup and column chromatography (ethyl acetate:$CHCl_3$:*n*-hexane = 1:1:5) giving **38** (**38a**, 193 mg, 25% and **38b**, 32 mg, 4%), 292 mg (52%) of **41** and 285 mg (52%) of **43**.

In Acetonitrile. A 150 mL solution of **15** (372 mg, 3.10 mmol) and **18** (1.00 g, 7.00 mmol) was irradiated for 16 h (ca. 89% conversion of **15**). Workup and column chromatography (ethyl acetate:$CHCl_3$:*n*-hexane = 1:1:5) gave **38** (**38a**, 156 mg, 21% and **38b**, 16 mg, 2%), 140 mg (26%) of **41** and 190 mg (37%) of **43**.

***38a** (liq).* ^{1}H NMR ($CDCl_3$) −0.11 (s, 9H), 1.66 (s, 3H), 3.35 (s, 3H), 4.47 (d, 1H, *J* = 7.0 Hz), 4.60 (d, 1H, *J* = 7.0 Hz), 7.28 (d, 2H, *J* = 5.9 Hz), 8.57 (d, 2H, *J* = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 0.6, 23.6, 50.4, 78.6, 96.4, 100.3, 120.6, 149.1, 151.8; MS (CI) *m/z* (rel. intensity) 268 (M^+ + 1, 4), 252 ($M^+ - CH_3$, 13), 237 (47), 236 ($M^+ - OCH_3$, 16), 194 (M^+-$SiMe_3$, 48), 178 ($M^+ - OSiMe_3$, 59), 147 (59), 110 (79), 92 (84), 75 (97), 61 (100), 52 (74); HRMS (CI) *m/z* 268.1369 (M + H, $C_{13}H_{22}NO_3Si$ requires 268.1369).

***38b** (liq).* ^{1}H NMR ($CDCl_3$) 0.23 (s, 9H), 1.71 (s, 3H), 2.85 (s, 3H), 4.62 (s, 2H), 7.39 (d, 2H, *J* = 4.8 Hz), 8.59 (d, 2H, *J* = 5.1 Hz); ^{13}C NMR($CDCl_3$) 1.2, 23.2, 50.2, 79.0, 95.4, 101.3, 121.1, 149.3, 151.0; MS (EI) *m/z* (rel. intensity) 267 (M^+, 0.1), 252 ($M^+ - CH_3$, 3), 237 (6), 195 (M^+-$SiMe_3$, 56), 180 (26), 122 (80), 106 (100), 75 (70), 59 (74), 50 (90); HRMS (EI) *m/z* 267.1293 ($C_{13}H_{21}NO_3Si$ requires 267.1291).

***41** (liq).* ^{1}H NMR ($CDCl_3$) 1.52 (s, 3H), 2.89 (q, 2H, *J* = 16.2 Hz), 3.62 (s, 3H), 4.54 (s, 1H), 7.35 (d, 2H, *J* = 6.2 Hz), 8.56 (d, 2H, *J* = 6.2 Hz); ^{13}C NMR ($CDCl_3$) 30.0, 45.4, 51.9, 72.0, 119.7, 149.8, 155.8, 172.6; IR(neat) 3100−3400 (br, OH stretching), 1730 (C═O stretching); MS (EI) *m/z* (rel. intensity) 195 (M^+, 7), 180 ($M^+ - CH_3$, 100), 148 (36), 122 ($M^+ - CH_2CO_2CH_3$, 64), 106 (68), 78 (50); HRMS (EI) *m/z* 195.0892 ($C_{10}H_{13}NO_3$ requires 195.0896).

***43** (liq).* ^{1}H NMR ($CDCl_3$) 1.42 (d, 3H, *J* = 6.6 Hz), 3.66 (s, 3H), 3.93 (d of d, 2H, *J* = 16.4 Hz), 4.50 (q, 1H, *J* = 6.5 Hz), 7.20 (d, 2H, *J* = 5.6 Hz), 8.51 (d, 2H, *J* = 4.4 Hz); ^{13}C NMR ($CDCl_3$) 23.3, 52.3, 67.2, 78.0, 123.1, 149.6, 155.8, 174.1; IR(neat) 1750 (C═O stretching); MS (EI) *m/z* (rel. intensity) 195 (M^+, 2), 180 ($M^+ - CH_3$, 8), 149 (15), 122 ($M^+ - CH_2CO_2CH_3$, 100), 106 ($M^+ - OCH_2CO_2CH_3$, 93), 78 (16), 75 (20), 50 (13); HRMS (EI) *m/z* 180.0661 ($M^+ - CH_3$, $C_9H_{10}NO_3$ requires 180.0666).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all previously unidentified compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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