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Acid-Catalyzed Synthesis of α,β-Disubstituted Conjugated Enones by a Meyer–Schuster-Type Rearrangement in Allenols

Benito Alcaide,[a,*] Pedro Almendros,[b,*] Sara Cembellín,[a] and Teresa Martínez del Campo[a]

[a] Grupo de Lactamas y Heterociclos Bioactivos, Departamento de Química Orgánica I, Unidad Asociada al CSIC, Facultad de Química, Universidad Complutense de Madrid, 28040 Madrid, Spain
Fax: (+34)-91-394-4103; e-mail: alcaideb@quim.ucm.es

[b] Instituto de Química Orgánica General, Consejo Superior de Investigaciones Científicas, IQOG-CSIC, Juan de la Cierva 3, 28006 Madrid, Spain
Fax: (+34)-91-564-4853; e-mail: Palmendros@iqog.csic.es

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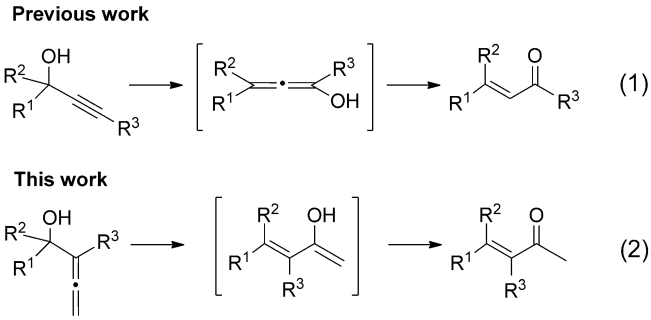
Abstract: A novel, direct and simple methodology to gain access to α,β-disubstituted conjugated enones from α-allenols in a sustainable metal catalysis context, considering the inexpensiveness and environmentally friendliness of iron(III) species and protons, has been developed.

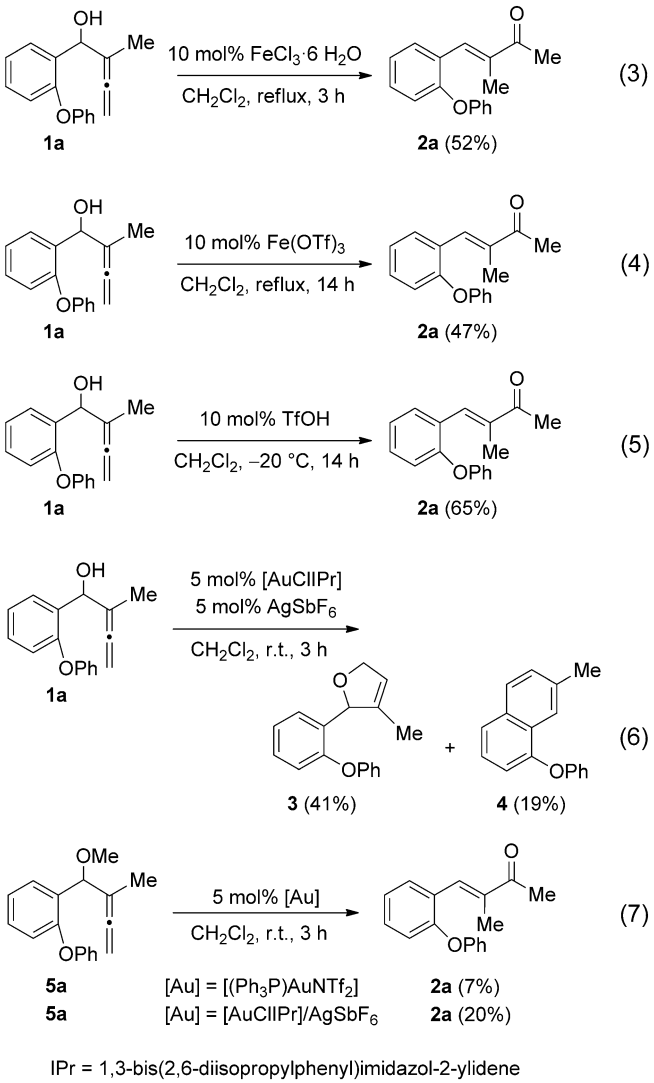
Keywords: alcohols; allenes; Brønsted acids; homogeneous catalysis; Lewis acids



Scheme 1. Alkynol *versus* allenol isomerization.

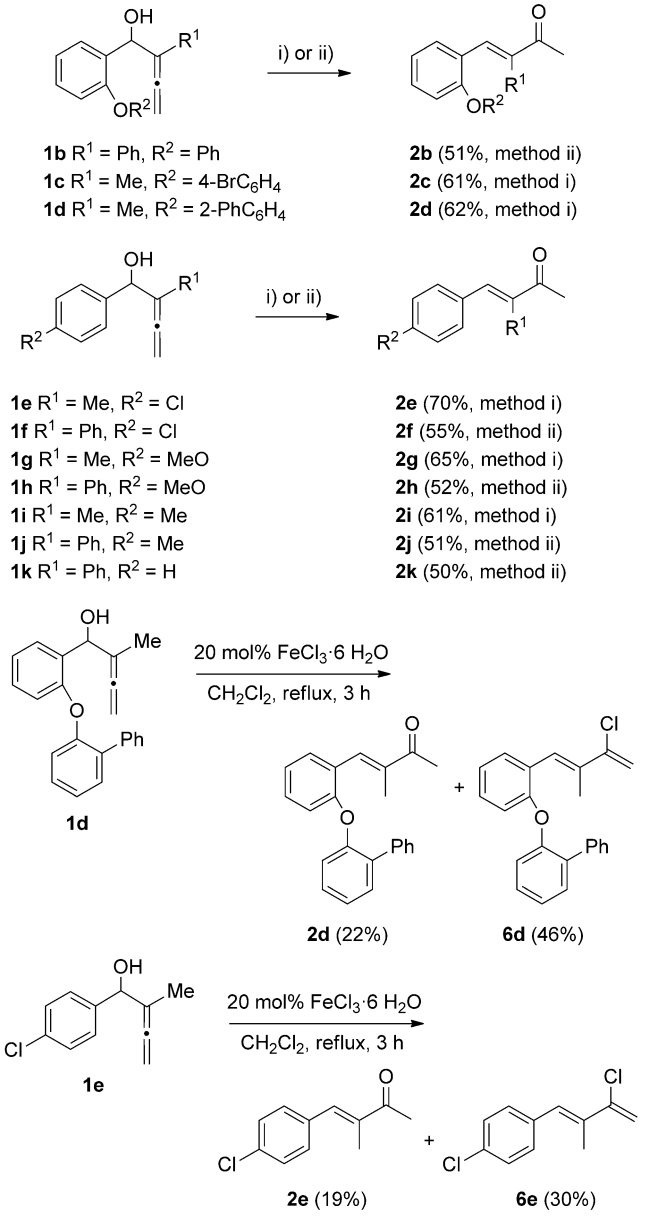
The use of α,β-unsaturated ketones as starting materials to prepare a variety of compounds, as well as the presence of this structural unit in a large number of biologically active natural products have led to increased recent interest in methods for preparing such compounds.[1] Classical methods such as aldol condensation and olefination strategies present serious drawbacks. Thus, harsh conditions and modest yields are usually encountered in the aldol condensation, while the generation of noxius waste by-products coupled with low atom economy are disadvantages of Wittig-type reactions. Besides, these traditional protocols usually require strong basic conditions, which may be incompatible with selectivity control as well as sensitive functional groups. An alternative method for the synthesis of α,β-unsaturated ketones is the Meyer–Schuster rearrangement [Scheme 1, Eq. (1)], which starts from propargylic alcohols and consists in a formal 1,3-hydroxy shift followed by tautomerization.[2] In this regard, the rearrangement of allenic alcohols may be a possible solution to produce α,β-unsaturated ketones with high reaction efficiency; although this achievement has not yet been fully accomplished.[3] Besides, the allenol rearrangement could provide competitive advantages, because in contrast with the alkynol rearrangement, the allenic version could afford internally substituted conjugated enones. On the other hand, iron-catalyzed processes have attracted recent attention because iron is one of the most inexpensive and environmentally benign metals on earth.[4] Following up on our combined interest in the area of allenes and metals,[5] and considering the economic attractiveness and the environmentally friendliness of iron species, we chose to study the iron-catalyzed reaction of α-allenols as a sustainable metal-catalyzed route to access α,β-disubstituted conjugated enones [Scheme 1, Eq. (2)].

Starting allenols **1** were readily prepared in good overall yield from the appropriate carbaldehyde through a regioselective indium-mediated Barbier-type carbonyl-allenylation reaction in aqueous media using our methodology.[6] Initially, we were attempting the iron-catalyzed cycloisomerization reaction of allenol **1a**. Unexpectedly, the alkenone **2a** was obtained using either iron(III) chloride hexahydrate or iron(III) triflate. Considering the abundance and non-

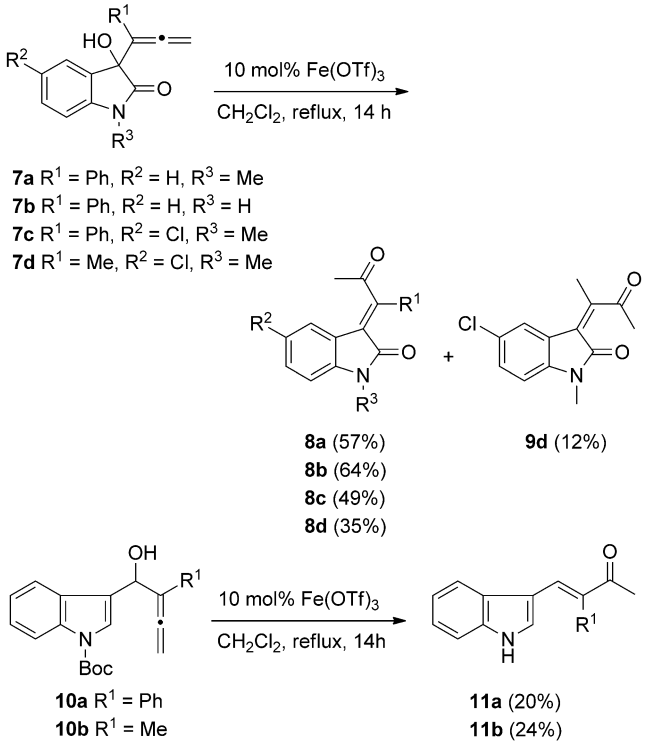


Scheme 2. Divergent metal-catalyzed rearrangement of allenol derivatives **1a** and **5a**.

toxicity of iron(III) species, we became interested in developing an allenol-based Meyer–Schuster rearrangement methodology for the preparation of functionalized α,β-unsaturated ketones. The reaction was next optimized by screening solvent and temperature. A 52% yield of α,β-unsaturated ketone **2a** was obtained through the use of $FeCl_3{\cdot}6H_2O$ (10 mol%) and dichloromethane as the solvent at 40 °C [Scheme 2, Eq. (3)]. A similar result was encountered through the use of catalytic amounts of $Fe(OTf)_3$ [Scheme 2, Eq. (4)]. This reaction could also be catalyzed by $Bi(OTf)_3$ and $In(OTf)_3$, but with diminished effectiveness. Different Lewis acid catalysts such as $InCl_3$, $ZnCl_2$, and AgOTf were found to be completely ineffective in carrying out any reorganization of the allenol. A Brønsted acid such as the super acid TfOH was shown to efficiently transform **1a** into **2a** at low temperature [Scheme 2, Eq. (5)]. To check whether gold complexes are good catalysts for this rearrangement, a reaction of allenol **1a** in the presence of $[(Ph_3P)AuNTf_2]$ was also carried out.[7] The reaction does take a different course, with a separable mixture of oxycyclization and carbocyclization adducts **3** and **4** being obtained [Scheme 2, Eq. (6)].[8] It was interesting at this point to test the reactivity of a protected allenol moiety under gold-catalyzed conditions. When the hydroxy functionality in **1a** was protected in the form of a methyl ether as in **5a**, the gold-catalyzed Meyer–Schuster type rearrangement occurred,[9] but in low yield [Scheme 2, Eq. (7)].



Scheme 3. Acid-catalyzed rearrangement of allenols **1**. *Reagents and conditions:* i) 10 mol% TfOH, CH_2Cl_2, –20 °C, 14 h; ii) 10 mol% $Fe(OTf)_3$, CH_2Cl_2, reflux, 14 h.

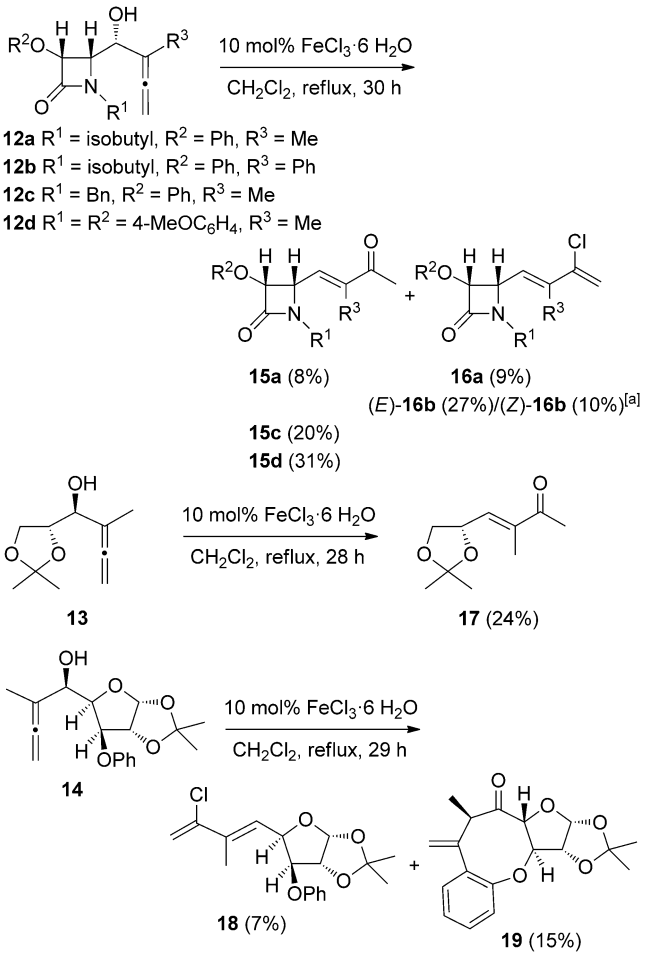


Scheme 4. $Fe(OTf)_3$-catalyzed rearrangement of indole-linked allenols **7** and **10**.

With the optimized conditions in hand, we then examined the generality of this acid-catalyzed rearrangement protocol in α-allenols **1**. When allenols **1c–1e**, **1g**, and **1i** were tested as precursors using triflic acid catalysis, they furnished the corresponding reorganization products **2c–2e**, **2g**, and **2i** (Scheme 3). Complete conversion was observed for phenyl-substituted allenes **1b**, **1f**, **1h**, **1j**, and **1k** but complicated reaction mixtures were obtained. Competing reactions lead to the exclusion of the above allenols as efficient substrates for the TfOH-promoted reaction. Fortunately, $Fe(OTf)_3$ did afford the corresponding α,β-unsaturated ketones **2b**, **2f**, **2h**, **2j**, and **2k** in fair yields (Scheme 3). The reactions were selective and only Meyer–Schuster adducts were formed, with no trace of isomeric oxycyclization products. Electron-withdrawing and electron-donating substituents on the aryl ring were tolerated with only little influence on the reactivity (Scheme 3). Chlorodienes **6** were often obtained as important components during the $FeCl_3{\cdot}6H_2O$-catalyzed reaction of α-allenols **1** (Scheme 3).

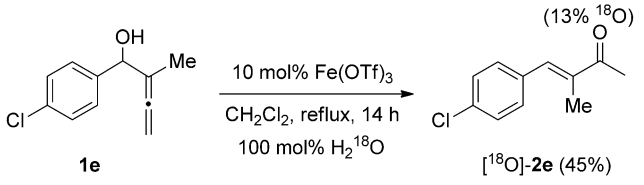
3-Methyleneindolin-2-ones are not only recognized as versatile intermediates in organic synthesis,[10] but also exhibit interesting biological activities.[11] Consequently, the iron-catalyzed stereoselective synthesis of 3-alkenyloxindole **8a** from 2-indolinone-tethered allenol **7a** under similar conditions is noteworthy (Scheme 4). Allenic *NH*-indolinone **7b** smoothly provided the 3-alkenyloxindole rearranged adduct **8b** as sole product (Scheme 4), it was thus apparent that substitution at the nitrogen atom of the heterocycle should have little effect upon the reactivity of the allenol moiety. Allenic 5-chloroindolinone **7c** smoothly provided the rearranged adduct **8c** in reasonable yield (Scheme 4). The major product for the methyl-substituted allenol **7d** was assigned to be the *E* form, α,β-unsaturated ketone **8d**, the unexpected *Z* isomer **9d** being the minor component (Scheme 4).[12] The iron-catalyzed rearrangement reaction of (indol-3-yl)-α-allenols **10a** and **10b** afforded *N*-Boc deprotected α,β-unsaturated ketones **11a** and **11b** in modest yields (Scheme 4).[13]

Unfortunately, enantiopure allenols **12–14** derived from aliphatic aldehydes were not as rewarding as their aromatic counterparts. Neither $Fe(OTf)_3$ nor TfOH reacted well, because decomposition adducts were detected. Interestingly, the use of $FeCl_3{\cdot}6H_2O$ afforded identifiable products. However, this variation led to less efficiency in terms of chemical yields of the ketone derivatives **15** and **17** (Scheme 5). Chloro-

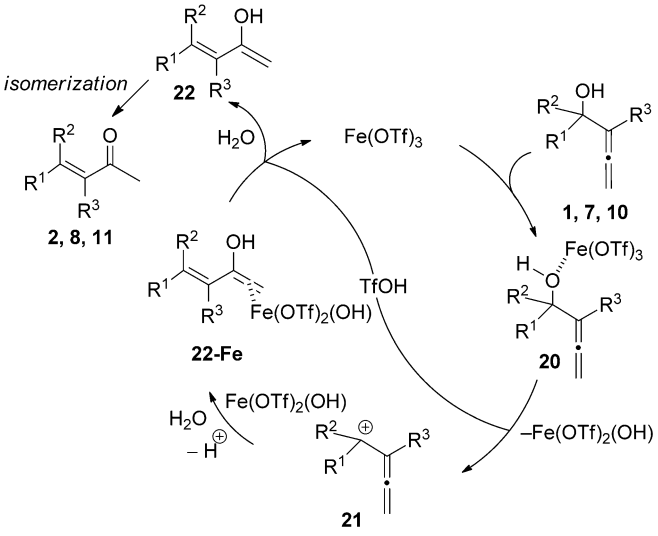


[a] The reaction was carried out using 20 mol% $FeCl_3$.

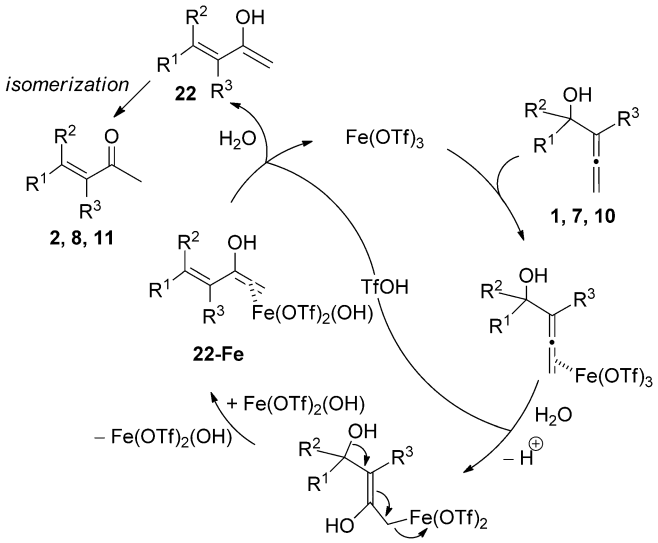
Scheme 5. $FeCl_3$-catalyzed rearrangement of allenols **12–14**.



Scheme 6. Labelling experiment.



Scheme 7. Mechanistic explanation for the iron-catalyzed rearrangement of allenols through elimination–addition.



Scheme 8. Mechanistic explanation for the iron-catalyzed rearrangement of allenols through addition–elimination.

dienes **16a**, **16b**, and **18** were obtained in appreciable amounts. Surprisingly, tricycle **19** was obtained as major component from allene sugar derivative **14** (Scheme 5). Importantly, no erosion of the stereochemical integrity was observed in enantiopure products **15**–**19**.

In order to interpret the rearrangement reaction outcome in a more useful manner, an ^{18}O-labelling experiment was planned. ^{18}O-incorporation was monitored as an indicator of a mechanistic scenario that involves an indirect intermolecular 1,3-shift of the OH group. Mass spectrometric analysis of the product of reaction of allenol **1e** under $Fe(OTf)_3$ catalysis in presence of 100 mol% $H_2{}^{18}O$ showed that the α,β-unsaturated ketone **2e** was partially ^{18}O-labelled (Scheme 6), revealing that the carbonylic oxygen atom may arise from external H_2O.

The high stereoselectivity of the rearrangement which occurs by (*E*)-alkene formation, is independent of the stereochemistry of the starting α-allenol (racemic or enantiopure). This fact and the labelling experiment may indicate a stepwise path with the participation of carbocationic species. A possible reaction pathway leading to α,β-unsaturated ketones from α-allenols was proposed as shown in Scheme 7. $Fe(OTf)_3$ acts as a Lewis acid interacting with the alcohol group in the allenol moiety. Initial σ-coordination of the metal to the hydroxy group of allenols **1**, **7**, and **10**, leads to complexes **20**. Separation of the alcohol group by $Fe(OTf)_3$ generates allenic cation **21**, which would facilitate the nucleophilic addition of water to the carbenium ion, thus leading to a metallated intermediate **22-Fe**. Next, demetallation yields neutral dienol species **22** and regenerates the iron catalyst. Finally, isomerization could generate α,β-unsaturated ketones **2**, **8**, and **11** (Scheme 7). However, taking all the experiments into account, an alternative addition–elimination mechanism scenario as sketched in Scheme 8 cannot be completely ruled out.

In conclusion, a novel, direct and simple methodology to gain access to α,β-disubstituted conjugated enones from α-allenols in a sustainable metal catalysis context, considering the inexpensiveness and environmentally friendliness of iron(III) species and protons, has been developed.

Experimental Section

General Methods

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance-300 or Bruker AMX-500. NMR spectra were recorded in $CDCl_3$ solutions unless otherwise stated. Chemical shifts are given in ppm relative to TMS (^1H, 0.0 ppm), or $CDCl_3$ (^{13}C, 77.0 ppm). Coupling constants *J* are expressed in Hertz (multiplicity: s = singulet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quadruplet, quint = quintuplet, sext = sextuplet, sept = septuplet, m = multiplet). Low and high resolution mass spectra were taken on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electrospray mode (ES) unless otherwise

stated. IR spectra were recorded on a Bruker Tensor 27 spectrometer. Specific rotations $[\alpha]_D$ are given in 10^{-1} deg $cm^2 g^{-1}$ at 20 °C, and the concentration (c) is expressed in g per 100 mL. All commercially available compounds were used without further purification.

Typical Procedure for the TfOH-Catalyzed Rearrangement Reaction of α-Allenols 1

To a cooled solution of the appropriate allenol **1** (1.0 mmol) in dichloromethane (10 mL) at −20 °C, TfOH (0.10 mmol) was added. The reaction mixture was stirred at −20 °C until the starting material disappeared as indicated by TLC. Water (1 mL) was added, and the mixture was allowed to warm to room temperature before being partitioned between dichloromethane and water. The organic extract was concentrated under vacuum, and purified by flash column chromatography eluting with ethyl acetate/hexanes mixtures. Spectroscopic and analytical data for pure forms of compounds **2** are given below.[14]

α,β-Unsaturated ketone 2a: From 134 mg (0.53 mmol) of α-allenol **1a**, chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound **2a** as a colorless oil; yield: 88 mg (65%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.66 (s, 1H, =CH), 7.45 (dd, 1H, J = 7.7, 1.3 Hz, Ar), 7.34 (t, 2H, J = 7.6 Hz, Ar), 7.31 (td, 1H, J = 7.4, 1.6 Hz, Ar), 7.18 (t, 1H, J = 7.9 Hz, Ar), 7.11 (t, 1H, J = 7.4 Hz, Ar), 6.97 (m, 3H, Ar), 2.36 (s, 3H, COMe), 2.01 (t, 3H, J = 1.2 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 202.2 (CO), 157.2, 155.0, 138.6, 134.9 (=CH), 130.6 (Ar, CH), 130.0 (Ar, CH), 129.8 (Ar, 2CH), 127.7, 123.3 (Ar, CH), 123.3 (Ar, CH), 119.1 (Ar, CH), 118.1 (Ar, 2CH), 25.7 (Me), 12.3 (Me); IR ($CHCl_3$): ν = 3066, 1668 (CO), 1484, 1238, 753 cm^{-1}; HR-MS (ES): m/z = 252.1142, calcd. for $C_{17}H_{16}O_2$ $[M]^+$: 252.1150.

α,β-Unsaturated ketone 2c: From 108 mg (0.33 mmol) of α-allenol **1c**, chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **2c** as a colorless oil; yield: 67 mg (61%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.60 (s, 1H, =CH), 7.44 (m, 1H, Ar), 7.43 (d, 2H, J = 9.0 Hz, Ar), 7.34 (td, 1H, J = 7.7, 1.7 Hz, Ar), 7.20 (td, 1H, J = 7.9, 1.0 Hz, Ar), 6.96 (dd, 1H, J = 8.1, 1.1 Hz, Ar), 6.84 (d, 2H, J = 9.0 Hz, Ar), 2.37 (s, 3H, COMe), 1.99 (t, 3H, J = 1.4 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 198.6 (CO), 159.1, 157.8, 138.9, 134.4 (=CH), 132.8 (Ar, 2CH), 130.8 (Ar, CH), 130.2 (Ar, CH), 128.7, 123.9 (Ar, CH), 119.8 (Ar, 2CH), 119.2 (Ar, CH), 116.4, 25.8 (Me), 13.0 (Me); IR ($CHCl_3$): ν = 3066, 1667 (CO), 1477, 1234, 756 cm^{-1}; HR-MS (ES): m/z = 330.0245, calcd. for $C_{17}H_{15}BrO_2$ $[M]^+$: 330.0255.

α,β-Unsaturated ketone 2d: From 238 mg (0.73 mmol) of allenol **1d**, chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **2d** as a colorless oil; yield: 147 mg (62%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.60 (s, 1H, =CH), 7.49 (m, 3H, Ar), 7.32 (m, 4H, Ar), 7.24 (t, 3H, J = 7.6 Hz, Ar), 7.07 (t, 1H, J = 7.5 Hz, Ar), 6.90 (dd, 1H, J = 8.0, 1.2 Hz, Ar), 6.85 (d, 1H, J = 7.3 Hz, Ar), 2.36 (s, 3H, COMe), 1.94 (d, 3H, J = 1.3 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 200.4 (CO), 155.4, 153.4, 153.2, 137.6, 136.8, 135.2 (Ar, CH), 133.4, 131.4 (Ar, CH), 130.4 (Ar, CH), 129.8 (Ar, CH), 129.1 (Ar, 2CH), 128.7 (Ar, CH), 128.0 (Ar, 2CH), 127.3 (Ar, CH), 124.3 (Ar, CH), 122.5 (Ar, CH), 119.7 (Ar, CH), 117,3 (=CH), 25.7 (Me), 12.9 (Me); IR ($CHCl_3$): ν = 3061, 1666 (CO), 1476, 1223, 745, 695 cm^{-1}; HR-MS (ES): m/z = 328.1473, calcd. for $C_{23}H_{20}O_2$ $[M]^+$: 328.1463.

α,β-Unsaturated ketone 2e: From 340 mg (1.75 mmol) of allenol **1e**, chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent gave compound **2e** as a colorless oil; yield: 239 mg (70%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.38 (d, 1H, J = 0.9 Hz), 7.32 (d, 2H, J = 8.9 Hz), 7.28 (d, 2H, J = 8.8 Hz), 2.39 (s, 3H), 1.96 (d, 3H, J = 1.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 200.0, 138.1, 134.4, 130.9 (2C), 129.5, 128.8 (2C), 128.7, 25.9, 13.0; IR ($CHCl_3$): ν = 3070, 1668 (CO), 751, 696 cm^{-1}; HR-MS (ES): m/z = 194.0497, calcd. for $C_{11}H_{11}ClO$ $[M]^+$: 194.0498.

α,β-Unsaturated ketone 2g: From 40 mg (0.21 mmol) of α-allenol **1g**, chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound **2g** as a colorless oil; yield: 26 mg (65%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.40 (s, 1H), 7.34 (d, 2H, J = 8.8 Hz), 6.88 (d, 2H, J = 8.9 Hz), 3.78 (s, 3H), 2.38 (s, 3H), 2.00 (d, 3H, J = 1.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 200.3, 139.6, 135.9, 131.6 (2C), 129.8, 128.5, 113.9 (2C), 55.4, 28.5, 12.9; IR ($CHCl_3$): ν = 3069, 1670 (CO), 1481, 1236, 751, 696 cm^{-1}; HR-MS (ES): m/z = 190.0998, calcd. for $C_{12}H_{14}O_2$ $[M]^+$: 190.0994.

α,β-Unsaturated ketone 2i: From 100 mg (0.57 mmol) of α-allenol **1i**, chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent gave compound **2i** as a colorless oil; yield: 61 mg (61%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.42 (s, 1H), 7.27 (d, 2H, J = 8.0 Hz), 7.15 (d, 2H, J = 8.0 Hz), 2.38 (s, 3H), 2.32 (s, 3H), 1.99 (d, 3H, J = 1.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 200.0, 140.3, 139.1, 137.2, 133.2, 130.2 (2C), 129.6 (2C), 26.3, 22.0, 13.4; IR ($CHCl_3$): ν = 3074, 1672 (CO), 1482, 1233, 752, 697 cm^{-1}; HR-MS (ES): m/z = 174.1047, calcd. for $C_{12}H_{14}O$ $[M]^+$: 174.1045.

Typical Procedure for the $Fe(OTf)_3$-Catalyzed Rearrangement Reaction of α-Allenols 1, 7, and 10

To a solution of the appropriate allenol **1** (1.0 mmol) in dichloromethane (10 mL), $Fe(OTf)_3$ (0.10 mmol) was added. The reaction mixture was stirred at reflux temperature until the starting material disappeared as indicated by TLC. After filtration through a pad of Celite, the mixture was concentrated under vacuum, and purified by flash column chromatography eluting with ethyl acetate/hexanes mixtures. Spectroscopic and analytical data for pure forms of compounds **2**, **8**, **9**, and **11** are given below.

α,β-Unsaturated ketone 2b: From 68 mg (0.22 mmol) of α-allenol **1b**, chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent gave compound **2b** as a colorless oil; yield: 36 mg (51%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.94 (s, 1H, =CH), 7.37 (m, 6H, Ar), 7.15 (m, 3H, Ar), 7.01 (d, 2H, J = 8.6 Hz, Ar), 6.87 (d, 1H, J = 8.1 Hz, Ar), 6.76 (d, J = 4.1 Hz, Ar), 2.33 (s, 3H, COMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 199.4 (CO), 157.4, 156.1, 156.0, 142.0, 133.6 (=CH), 130.9 (Ar, CH), 130.3 (Ar, CH), 129.9 (Ar, 2CH), 129.8 (Ar, 2CH), 128.7 (Ar, 2CH), 127.8 (Ar, CH), 126.6, 123.4 (Ar, CH), 123.0 (Ar, CH), 118.9 (Ar, CH), 118.6 (Ar, 2CH), 27.4(Me); IR ($CHCl_3$): ν = 3061, 1675

(CO), 1482, 1233, 752, 695 cm^{-1}; HR-MS (ES): m/z = 314.1306, calcd. for $C_{22}H_{18}O_2$ $[M]^+$: 314.1307.

α,β-Unsaturated ketone 2f: From 200 mg (0.78 mmol) of α-allenol **1f**, chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent gave compound **2f** as a colorless oil; yield: 110 mg (55%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.59 (s, 1H, =CH), 7.42 (m, 3H, Ar), 7.16 (m, 2H, Ar), 7.14 (d, 2H, J = 8.6 Hz, Ar), 6.96 (d, 2H, J = 8.5 Hz, Ar), 2.30 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 199.1 (CO), 141.3, 137.2 (=CH), 136.6, 135.1, 133.1, 132.0 (Ar, 2CH), 129.4 (Ar, 2CH), 129.2 (Ar, 2CH), 128.5 (Ar, 2CH), 128.1 (Ar, CH), 28.0 (Me); IR ($CHCl_3$): ν = 2930, 1662 (CO), 1457, 1090, 810 cm^{-1}; HR-MS (ES): m/z = 256.0659, calcd. for $C_{16}H_{13}OCl$ $[M]^+$: 256.0655.

α,β-Unsaturated ketone 2h: From 95 mg (0.38 mmol) of allenol **1h**, chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound **2h** as a colorless oil; yield: 49 mg (52%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.55 (s, 1H), 7.34 (m, 3H), 7.11 (dd, 2H, J = 8.0, 1.9 Hz), 6.90 (d, 2H, J = 8.9 Hz), 6.61 (d, 2H, J = 8.9 Hz), 3.68 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 199.2, 160.5, 138.8, 138.7, 137.5, 132.7 (2C), 129.6 (2C), 129.2 (2C), 128.5, 127.2, 113.8 (2C), 55.2, 27.9; IR ($CHCl_3$): ν = 3075, 1670 (CO), 1471, 1225, 742, 692 cm^{-1}; HR-MS (ES): m/z = 252.1157, calcd. for $C_{17}H_{16}O_2$ $[M]^+$: 252.1150.

α,β-Unsaturated ketone 2j: From 220 mg (0.93 mmol) of α-allenol **1j**, chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound **2j** as a colorless oil; yield. 112 mg (51%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.64 (s, 1H, =CH), 7.40 (m, 3H, Ar), 7.19 (dd, 2H, J = 7.8, 2.0 Hz, Ar), 6.99 (d, 2H, J = 8.3 Hz, Ar), 6.93 (d, 2H, J = 8.3 Hz, Ar), 2.32 (s, 3H, Me), 2.28 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 199.3 (CO), 140.0, 139.6, 139.0 (=CH), 137.2, 131.7, 130.9 (Ar, 2CH), 129.5 (Ar, 2CH), 129.0 (Ar, 4CH), 127.8 (Ar, CH), 27.9 (Me), 21.3 (Me); IR ($CHCl_3$): ν = 2900, 1653 (CO), 1434, 815 cm^{-1}; HR-MS (ES): m/z = 236.1199, calcd. for $C_{17}H_{16}O$ $[M]^+$: 236.1201.

α,β-Unsaturated ketone 2k: From 161 mg (0.72 mmol) of α-allenol **1k**, chromatography of the residue using hexanes/ethyl acetate (30:1) as eluent gave compound **2k** as a colorless oil; yield: 80 mg (50%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.66 (s, 1H, =CH), 7.42 (m, 3H, Ar), 7.18 (m, 5H, Ar), 7.05 (d, 2H, J = 7.7 Hz, Ar), 2.33 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 199.3 (CO), 140.9, 138.8 (=CH), 136.9, 134.6, 130.8 (Ar, 2CH), 129.5 (Ar, 2CH), 129.2 (Ar, CH), 129.0 (Ar, 2CH), 128.2 (Ar, 2CH), 127.9 (Ar, CH), 27.9 (Me); IR ($CHCl_3$): ν = 2915, 1660 (CO), 1426, 1024 cm^{-1}; HR-MS (ES): m/z = 222.1041, calcd. for $C_{16}H_{14}O$ $[M]^+$: 222.1045.

α,β-Unsaturated ketone 8a: From 140 mg (0.50 mmol) of α-allenol **7a**, chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **8a** as a colorless oil; yield: 79 mg (57%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.43 (m, 5H), 7.16 (m, 1H), 6.72 (d, 1H, J = 7.7 Hz), 6.68 (m, 2H), 3.17 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 204.4, 167.1, 151.8, 145.0, 133.4, 130.5, 130.2, 129.7 (2C), 128.7, 128.3 (2C), 123.6, 122.4, 121.1, 108.7, 29.5, 26.4; IR ($CHCl_3$): ν = 2932, 1705 (CO), 1610 (CO), 1482, 754, 696 cm^{-1}; HR-MS (ES): m/z = 277.1093, calcd. for $C_{18}H_{15}NO_2$ $[M]^+$: 277.1103.

α,β-Unsaturated ketone 8b: From 60 mg (0.23 mmol) of α-allenol **7b**, chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **8b** as a colorless oil; yield: 38 mg (62%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.44 (m, 5H), 7.10 (m, 1H), 6.75 (d, 1H, J = 7.7 Hz), 6.66 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 167.7, 150.4, 147.9, 141.7, 132.9, 131.1, 130.2, 129.9, 129.4 (2C), 127.8 (2C), 123.7, 122.0, 121.5, 109.9, 29.0; IR ($CHCl_3$): ν = 2936, 1706 (CO), 1606 (CO), 1482, 755, 695 cm^{-1}; HR-MS (ES): m/z = 263.0956, calcd. for $C_{17}H_{13}NO_2$ $[M]^+$: 263.0946.

α,β-Unsaturated ketone 8c: From 125 mg (0.38 mmol) of allenol **7c**, chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound **8c** as a colorless oil; yield: 63 mg (49%); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.50 (m, 4H, Ar), 7.20 (m, 2H, Ar), 6.73 (d, 1H, J = 8.3 Hz, Ar), 6.70 (d, 1H, J = 2.1 Hz, Ar), 3.24 (s, 3H, NMe), 2.48 (s, 3H, COMe); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 203.4 (CO), 166.4 (CO), 153.0, 143.0, 132.4, 130.3 (Ar, CH), 129.7 (Ar, CH), 129.5 (Ar, 2CH), 128.3 (Ar, CH), 127.7 (Ar, 2CH), 127.4, 123.3 (Ar, CH), 123.0, 122.0, 109.1 (Ar, CH), 28.9 (Me), 26.1 (NMe); IR ($CHCl_3$): ν = 2924, 1707 (CO), 1608 (CO), 1485, 755, 698 cm^{-1}; HR-MS (ES): m/z = 311.0724, calcd. for $C_{18}H_{14}ClNO_2$ $[M]^+$: 311.0713.

α,β-Unsaturated ketones 8d and 9d: From 111 mg (0.45 mmol) of α-allenol **7d**, chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave the less polar compound **8d** (yield: 32 mg, 35%) and the more polar compound **9d** '(yield: 11 mg, 12%). *α,β-Unsaturated ketone* **8d:** Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.26 (dd, 1H, J = 8.3, 1.9 Hz, Ar), 7.14 (d, 1H, J = 2.0 Hz, Ar), 6.74 (d, 1H, J = 8.3 Hz, Ar), 3.23 (s, 3H, NMe), 2.62 (s, 3H, Me), 2.50 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 205.2 (CO), 167.3 (CO), 151.6, 141.1, 129.2 (Ar, CH), 127.6, 122.6 (Ar, CH), 121.5, 120.8, 108.9 (Ar, CH), 28.4 (NMe), 25.9 (Me), 15.7 (Me); IR ($CHCl_3$): ν = 2925, 1715 (CO), 1604 (CO), 1475, 756 cm^{-1}; HR-MS (ES): m/z = 249.0567, calcd. for $C_{13}H_{12}ClNO_2$ $[M]^+$: 249.0557. *α,β-Unsaturated ketone* **9d:** Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.50 (d, 1H, J = 2.0 Hz, Ar), 7.30 (dd, 1H, J = 8.3, 1.9 Hz, Ar), 6.77 (d, 1H, J = 8.3 Hz, Ar), 3.20 (s, 3H, NMe), 2.49 (s, 3H, Me), 2.36 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 206.3 (CO), 170.3 (CO), 165.9, 142.7, 129.1 (Ar, CH), 127.6, 123.9 (Ar, CH), 123.0, 109.1 (Ar, CH), 28.6 (NMe), 25.9 (Me), 17.4 (Me); IR ($CHCl_3$): ν = 2920, 1706 (CO), 1600 (CO), 1461, 736 cm^{-1}; HR-MS (ES): m/z = 249.0564, calcd. for $C_{13}H_{12}ClNO_2$ $[M]^+$: 249.0557.

α,β-Unsaturated Ketone 11a: From 94 mg (0.26 mmol) of α-allenol **10a**, chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound **11a** as a colorless oil; yield: 18 mg (20%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.30 (s, 1H, NH), 8.12 (m, 2H, Ar), 7.97 (s, 1H, Ar), 7.72 (m, 3H, Ar), 7.49 (m, 3H, Ar + =CH), 7.35 (m, 2H, Ar), 2.36 (s, 3H, COMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 172.8 (CO), 171.3, 129.5 (=CH), 129.1, 128.9 (Ar, 2CH), 128.7 (Ar, CH), 128.1 (Ar, CH), 127.4 (2C), 127.3 (Ar, CH), 125.1 (Ar, CH), 123.2 (Ar, CH), 118.4 (Ar, CH), 115.2 (Ar, CH), 110.7 (Ar, CH), 28.0 (Me); IR ($CHCl_3$): ν = 3370 (NH), 3057, 1734 (CO) 1457, 1152, 754 cm^{-1}; HR-MS (ES): m/z = 261.1166, calcd. for $C_{18}H_{15}NO$ $[M]^+$: 261.1154.

α,β-Unsaturated Ketone 11b: From 82 mg (0.27 mmol) of α-allenol **10b**, chromatography of the residue using hexanes/

ethyl acetate (6:1) as eluent gave compound **11b** as a colorless oil; yield: 19 mg (26%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.64 (s, 1H, NH), 7.91 (s, 1H, =CH), 7.82 (d, 1H, J = 7.1 Hz, Ar), 7.59 (d, 1H, J = 2.8 Hz, Ar), 7.46 (d, 1H, J = 7.1 Hz, Ar), 7.29 (m, 2H, Ar), 2.55 (s, 3H, COMe); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 172.6 (CO), 135.4, 132.8, 131.1 (Ar, CH), 129.4, 126.1 (Ar, CH), 124.5, 123.3 (Ar, CH), 120.9 (Ar, CH), 118.5 (Ar, CH), 111.4 (Ar, CH), 25.5 (Me), 19.6 (Me); IR ($CHCl_3$): ν = 3314 (NH), 1708 (CO) 1460, 1245, 748 cm^{-1}; HR-MS (ES): m/z = 199.1005, calcd. for $C_{13}H_{13}NO$ $[M]^+$: 199.0997.

Typical Procedure for the Iron-Catalyzed Rearrangement Reaction of α-Allenols 1 and 12–14

To a solution of the appropriate allenol **1** or **12–14** (1.0 mmol) in dichloromethane (10 mL), $FeCl_3{\cdot}6H_2O$ (0.10 mmol or 0.20 mmol) was added. The reaction mixture was stirred at reflux temperature until the starting material disappeared as indicated by TLC. After filtration through a pad of Celite, the mixture was concentrated under vacuum, and purified by flash column chromatography eluting with ethyl acetate/hexanes mixtures. Spectroscopic and analytical data for pure forms of compounds **2**, **6**, and **15–19** are given below.

α,β-Unsaturated ketone 2d and chlorodiene 6d: From 238 mg (0.73 mmol) of allenol **1d**, chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave the less polar compound **6d** (yield: 114 mg, 46%) and the more polar compound **2d** (yield: 52 mg (22%). *Chlorodiene* **6d:** colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.48 (dd, 2H, J = 7.0, 1.5 Hz, Ar), 7.36 (td, 2H, J = 7.6, 1.6 Hz, Ar), 7.28 (t, 1H, J = 7.0 Hz, Ar), 7.15 (m, 3H, Ar), 7.02 (td, 1H, J = 7.8, 1.6 Hz, Ar), 6.88 (td, 1H, J = 7.6, 1.0 Hz, Ar), 6.81 (dd, 1H, J = 8.0, 1.2 Hz, Ar), 6.67 (dd, 1H, J = 8.2, 1.0 Hz, Ar), 6.34 (s, 1H, =CH), 5.08 (d, 1H, J = 1.1 Hz, =C*H*H), 4.91 (d, 1H, J = 1.1 Hz, =CH*H*), 1.92 (d, 3H, J = 1.4 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.9, 153.8, 139.8, 137.8, 136.2, 133.2, 131.2 (Ar, CH), 130.3 (Ar, CH), 129.7, 129.3 (Ar, 2CH), 128.6 (Ar, CH), 128.3 (Ar, CH), 128.1 (Ar, 2CH), 127.2 (Ar, CH), 124.7 (Ar, CH), 123.7 (Ar, CH), 122.7 (Ar, CH), 119.3 (Ar, CH), 117.7 (=CH), 115.3 (=CH_2), 23.3 (Me); IR ($CHCl_3$): ν = 3060, 1477, 1430, 1228, 744, 694 cm^{-1}; HR-MS (ES): m/z = 346.1138, calcd. for $C_{23}H_{19}ClO$ $[M]^+$: 346.1124.

α,β-Unsaturated ketone 2e and chlorodiene 6e: From 340 mg (1.75 mmol) of allenol **1e**, chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent gave the less polar compound **6e** (yield: 112 mg, 30%) and the more polar compound **2e** (yield: 65 mg, 19%). *Chlorodiene* **6e:** colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.22 (d, 2H, J = 8.6 Hz), 7.17 (d, 2H, J = 8.8 Hz), 6.21 (d, 1H, J = 1.2 Hz), 5.21 (d, 1H, J = 1.3 Hz), 5.05 (d, 1H, J = 1.3 Hz), 1.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 139.6, 136.3, 135.0, 132.8, 130.0 (2C), 128.3 (2C), 128.1, 115.5, 23.7; IR ($CHCl_3$): ν = 3060, 1478, 745, 692 cm^{-1}; HR-MS (ES): m/z = 212.0143, calcd for $C_{11}H_{10}Cl_2$ $[M]^+$: 212.0160.

α,β-Unsaturated ketone 15a and chlorodiene 16a: From 101 mg (0.33 mmol) of allenol **12a**, chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave the less polar compound **16a** (yield: 10 mg, 9%) and the more polar compound **15a** (yield: 8 mg 8%). *α,β-Unsaturated ketone* **15a:** colorless oil; $[\alpha]_D$: +32.0 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.27 (t, 2H, J = 7.3 Hz, Ar), 7.00 (t, 1H, J = 7.4 Hz, Ar), 6.92 (d, 2H, J = 7.9 Hz, Ar), 6.55 (dd, 1H, J = 9.4, 1.3 Hz, =CH), 5.45 (d, 1H, J = 4.4 Hz, H3), 4.79 (dd, 1H, J = 9.4, 4.4 Hz, H4), 3.23 (dd, 1H, J = 14.0, 7.7 Hz, NCH*H*), 2.88 (dd, 1H, J = 14.0, 6.7 Hz, NC*H*H), 2.23 (s, 3H, COMe), 1.86 (m, 1H, CH isobut), 1.85 (d, 3H, J = 1.3 Hz, Me), 0.98 (d, 3H, J = 7.4 Hz, Me), 0.95 (d, 3H, J = 6.8 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 198.5 (CO), 165.4 (CO), 156.5, 142.8, 134.6 (=CH), 130.7 (Ar, 2CH), 122.5 (Ar, CH) 115.2 (Ar, 2CH), 81.1 (CH), 56.8 (CH), 48.7 (NCH_2), 26.5 (CH isobut), 24.6 (Me), 19.3 (Me), 19.3 (Me); IR ($CHCl_3$): ν = 1757 (CO), 1673 (CO), 1232, 754 cm^{-1}; HR-MS (ES): m/z = 301.1682, calcd. for $C_{18}H_{23}NO_3$ $[M]^+$: 301.1678. *Chlorodiene* **16a:** colorless oil; $[\alpha]_D$: +7.8 (c 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.28 (t, 2H, J = 7.3 Hz, Ar), 7.01 (t, 1H, J = 7.3 Hz, Ar), 6.98 (dd, 2H, J = 8.8, 1.1 Hz, Ar), 5.47 (dd, 1H, J = 9.8, 1.5 Hz, =CH), 5.45 (d, 1H, J = 1.3 Hz, =C*H*H), 5.29 (d, 1H, J = 4.4 Hz, H3), 5.14 (d, 1H, J = 1.2 Hz, =CH*H*), 4.76 (dd, 1H, J = 9.9, 4.5 Hz, H4), 3.16 (dd, 1H, J = 14.0, 7.9 Hz, NCH*H*), 2.88 (dd, 1H, J = 14.0, 6.7 Hz, NC*H*H), 1.92 (d, 3H, J = 1.5 Hz, Me),.1.88 (m, 1H, CH isobut), 0.95 (d, 3H, J = 6.9 Hz, Me), 0.92 (d, 3H, J = 6.7 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.8 (CO), 157.3, 142.5, 138.1, 129.5 (Ar, 2CH), 123.8 (Ar, CH), 122.2 (=CH), 115.7 (Ar, 2CH), 115.3 (=CH_2), 81.7 (CH), 57.3 (CH), 48.2 (NCH_2), 27.5 (CH isobut), 22. 6 (Me), 20.3 (Me), 20.3 (Me); IR ($CHCl_3$): ν = 3342 (OH), 1758 (CO), 1236, 756 cm^{-1}; HR-MS (ES): m/z = 319.1324, calcd. for $C_{18}H_{22}ClNO_2$ $[M]^+$: 319.1339.

Chlorodiene (*E*)-16b and chlorodiene (*Z*)-16b: From 140 mg (0.38 mmol) of allenol **12b**, chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave the less polar compound (*E*)-**16b** (yield: 41 mg, 27%) and the more polar compound (*Z*)-**16b** (yield: 15 mg, 10%). *Enol* (*E*)-**16b:** colorless oil; $[\alpha]_D$: +23.3 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.22 (m, 4H, Ar), 7.18 (m, 3H, Ar), 6.91 (d, 2H, J = 7.7 Hz, Ar), 6.90 (m, 1H, Ar), 5.96 (d, 1H, J = 10.1 Hz, =CH), 5.69 (d, 1H, J = 1.0 Hz, =C*H*H), 5.33 (d, 1H, J = 4.4 Hz, H-3), 5.29 (d, 1H, J = 1.2 Hz, =CH*H*), 4.85 (dd, 1H, J = 9.9, 4.4 Hz, H-4), 3.12 (dd, 1H, J = 13.9, 7.6 Hz, NCH*H*), 2.89 (dd, 1H, J = 13.9, 6.9 Hz, NC*H*H), 1.86 (sept, 1H, J = 6.7 Hz, CH isobut), 0.89 (d, 3H, J = 6.7 Hz, Me), 0.86 (d, 3H, J = 6.6 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.6 (CO), 157.1, 145.9, 136.6, 135.9, 129.5 (Ar, 2CH), 128.8 (Ar, CH), 128.6 (Ar, 2CH), 126.7 (Ar, 2CH), 124.5 (=CH), 122.3 (Ar, CH), 118.6 (=CH_2), 115.5 (Ar, 2CH), 81.8 (CH), 58.0 (CH), 48.6 (NCH_2), 27.6 (CH isobut), 20.3 (Me), 20.3 (Me); IR ($CHCl_3$): ν = 3405 (OH), 3061, 1761 (CO), 1235, 757, 694 cm^{-1}; HR-MS (ES): m/z = 381.1508, calcd. for $C_{23}H_{24}ClNO_2$ $[M]^+$: 381.1496. *Enol* (*Z*)-**16b:** colorless oil; $[\alpha]_D$: +15.4 (c 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.42 (m, 4H, Ar), 7.26 (m, 3H, Ar), 7.14 (d, 2H, J = 7.4 Hz, Ar), 7.00 (m, 1H, Ar), 6.30 (d, 1H, J = 2.8 Hz, =CH), 5.69 (d, 1H, J = 1.6 Hz, =C*H*H), 5.26 (d, 1H, J = 1.6 Hz, =CH*H*), 5.08 (d, 1H, J = 4.2 Hz, H-3), 4.78 (dd, 1H, J = 4.1, 2.8 Hz, H-4), 3.33 (dd, 1H, J = 13.9, 8.0 Hz, NCH*H*), 3.12 (dd, 1H, J = 14.0, 6.6 Hz, NC*H*H), 2.00 (m, 1H, CH isobut), 1.04 (d, 3H, J = 6.7 Hz, Me), 0.99 (d, 3H, J = 6.7 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.1 (CO), 156.2, 145.3, 137.1, 132.2, 130.7 (Ar, CH), 129.5 (Ar, CH), 128.8 (Ar, CH), 128.5 (Ar,

2 CH), 128.0 (Ar, CH), 127.4 (Ar, CH), 125.6 (Ar, 2 CH), 124.9 (=CH), 121.7 (Ar, CH), 120.4 (=CH_2), 88.1 (CH), 60.7 (CH), 48.6 (NCH_2), 27.4 (CH isobut), 20.5 (Me), 20.5 (Me); IR ($CHCl_3$): ν = 3396 (OH), 3062, 1758 (CO), 1231, 760, 699 cm^{-1}; HR-MS (ES): m/z = 381.1481, calcd. for $C_{23}H_{24}ClNO_2$ $[M]^+$: 381.1496.

α,β-Unsaturated ketone 15c: From 28 mg (0.08 mmol) of α-allenol **12c**, chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound **15c** as a colorless oil; yield: 5 mg (20%); $[\alpha]_D$ =: +25.3 (*c* 0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.30 (m, 6 H, Ar), 7.03 (m, 2 H, Ar), 6.90 (d, 2 H, *J* = 7.9 Hz, Ar), 6.34 (dd, 1 H, *J* = 9.5, 1.3 Hz, =CH), 5.41 (d, 1 H, *J* = 4.5 Hz, H3), 4.65 (dd, 1 H, *J* = 9.5, 4.5 Hz, H4), 4.57 (d, 1 H, *J* = 14.8 Hz, NC*H*H), 4.29 (d, 1 H, *J* = 14.9 Hz, NCH*H*), 2.06 (s, 3 H, COMe), 1.64 (d, 3 H, *J* = 1.3 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 198.9 (CO), 164.7 (CO), 156.9, 142.4, 134.8, 134.5 (=CH), 129.6 (Ar, 2 CH), 129.0 (Ar, 2 CH), 128.7 (Ar, 2 CH), 128.3 (Ar, CH), 122.5 (Ar, CH), 115.2 (Ar, 2 CH), 81.8 (CH), 55.9 (CH), 45.2 (NCH_2), 25.5 (Me), 11.4 (Me); IR ($CHCl_3$): ν = 3063, 1760 (CO), 1682 (CO), 1234, 754, 699 cm^{-1}; HR-MS (ES): m/z = 335.1526, calcd. for $C_{21}H_{21}NO_3$ $[M]^+$: 335.1521.

α,β-Unsaturated ketone 15d: From 12 mg (0.03 mmol) of α-allenol **12d**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **15d** as a colorless oil; yield: 4 mg (31%); $[\alpha]_D$: +18.3 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.31 (d, 2 H, *J* = 9.1 Hz, Ar), 6.92 (d, 2 H, *J* = 9.2 Hz, Ar), 6.89 (d, 2 H, *J* = 9.1 Hz, Ar), 6.82 (d, 2 H, *J* = 9.1 Hz, Ar), 6.65 (dd, 1 H, *J* = 9.2, 1,3 Hz, =CH), 5.47 (d, 1 H, *J* = 4.8 Hz, H3), 5.17 (dd, 1 H, *J* = 9.2, 4.8 Hz, H4), 3.81 (s, 3 H, OMe), 3.77 (s, 3 H, OMe), 2.26 (s, 3 H, Me), 1.97 (d, 3 H, *J* = 1.5 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 197.2 (CO), 161.9 (CO), 156.8, 155.1, 151.1, 142.7, 135.3 (=CH), 130.4, 118.3 (Ar, 2 CH), 116.5 (Ar, 2 CH), 114.7 (Ar, 2 CH), 114.6 (Ar, 2 CH), 82.0 (CH), 56.4 (CH), 55.6 (OMe), 55. 5. (OMe), 25.7 (Me), 11.9 (Me); IR ($CHCl_3$): ν = 2924, 1755 (CO), 1675 (CO), 1508, 1247, 628 cm^{-1}; HR-MS (ES): m/z = 381.1578, calcd for $C_{22}H_{23}NO_5$ $[M]^+$: 381.1576.

α,β-Unsaturated ketone 17: From 158 mg (0.86 mmol) of α-allenol **13**, chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound **17** as a colorless oil; yield: 38 mg (24%); $[\alpha]_D$: +13.0 (*c* 0.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.56 (dd, 1 H, *J* = 7.4, 1,3 Hz, =CH), 4.94 (q, 1 H, *J* = 7.5 Hz, OCH), 4.21 (dd, 1 H, *J* = 8.2, 6.3 Hz, C*H*H), 3.64 (dd, 1 H, *J* = 8.0, 7.6 Hz, CH*H*), 2.35 (s, 3 H, COMe), 1.82 (d, 3 H, *J* = 1.3 Hz, Me), 1.49 (s, 3 H, Me), 1.43 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 199.4 (CO), 139.4 (=CH), 109.9 (2 C), 73.1 (OCH_2), 68.7 (OCH), 26.6 (Me), 25.7 (Me), 25.5 (Me), 11.8 (Me); IR ($CHCl_3$): ν = 2927, 1720 (CO), 1257, 1098 cm^{-1}; HR-MS (ES): m/z = 184.1104, calcd. for $C_{10}H_{16}O_3$ $[M]^+$: 184.1099.

Chlorodiene 18 and tricycle 19: From 133 mg (0.42 mmol) of allenol **14**, chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave the less polar compound **19** (yield: 20 mg, 15%) and the more polar compound **18** (yield: 11 mg, 7%). *Chlorodiene* **18:** colorless oil; $[\alpha]_D$: −17.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.31 (t, 2 H, *J* = 7.5 Hz, Ar), 7.00 (t, 1 H, *J* = 7.5 Hz, Ar), 6.96 (d, 2 H, *J* = 7.7 Hz, Ar), 6.41 (d, 1 H, *J* = 7.3 Hz, =CH), 6.03 (d, 1 H, *J* = 3.8 Hz, H1), 5.46 (d, 1 H, *J* = 1.5 Hz, = C*H*H), 5.41 (d, 1 H, *J* = 1.5 Hz, =CH*H*), 5.14 (dd, 1 H, *J* = 8.0, 3.1 Hz, H4), 4.71 (d, 1 H, *J* = 4.0 Hz, H2), 4.64 (d, 1 H, *J* = 3.2 Hz, H3), 1.98 (d, 3 H, *J* = 1.0 Hz, Me), 1.60 (s, 3 H, Me), 1.35 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 157.1, 141.4, 135.8, 129.7 (Ar, 2 CH), 124.8 (=CH), 121.7 (Ar, CH), 115.3 (Ar, 2 CH), 113.6 (=CH_2), 111.8, 104.8 (CH), 82.7 (CH), 81.5 (CH), 75.9 (CH), 26.8 (Me), 26.2 (Me), 15.0 (Me); IR ($CHCl_3$): ν = 3475 (OH), 1726, 1492, 1231, 1076, 1020, 756 cm^{-1}; HR-MS (ES): m/z = 336.1141, calcd. for $C_{18}H_{21}ClO_4$ $[M]^+$: 336.1128. *Tricycle* **19:** colorless oil; $[\alpha]_D$: +38.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.22 (dt, 1 H, *J* = 7.6, 1.5 Hz, Ar), 7.14 (t, 1 H, *J* = 8.0 Hz, Ar), 6.93 (td, 1 H, *J* = 7.5, 1.1 Hz, Ar), 6.80 (dd, 1 H, *J* = 8.2, 1.2 Hz, Ar), 5.93 (d, 1 H, *J* = 3.6 Hz, H1), 4.72 (m, 1 H, H2), 4.71 (m, 2 H, =CH_2), 4.65 (dd, 1 H, *J* = 3.9, 2.0 Hz, H4), 4.51 (d, 1 H, *J* = 1.6 Hz, H3), 3.85 (d, 1 H, *J* = 3.8 Hz, CH), 1.79 (t, 3 H, *J* = 3.1 Hz, Me), 1.57 (s, 3 H, Me), 1.36 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 209.0 (CO), 152.9, 128.9 (Ar, CH), 127.9 (Ar, CH), 121.1 (Ar, CH), 119.8, 116.3 (Ar, CH), 111.9, 105.2 (CH), 97.0, 83.3 (CH), 78.8 (CH), 75.7 (CH), 74.1 (=CH_2), 40.3 (CH), 26.6 (Me), 26.2 (Me), 16.5 (Me); IR ($CHCl_3$): ν = 2927, 1738 (CO), 1216, 1078, 1015, 757 cm^{-1}; HR-MS (ES): m/z = 316.1298, calcd. for $C_{18}H_{20}O_5$ $[M]^+$: 316.1311.

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