Gold(III)-Catalyzed Intramolecular Furanylation and Cyclopropanation of Acyclic Conjugated Enynones

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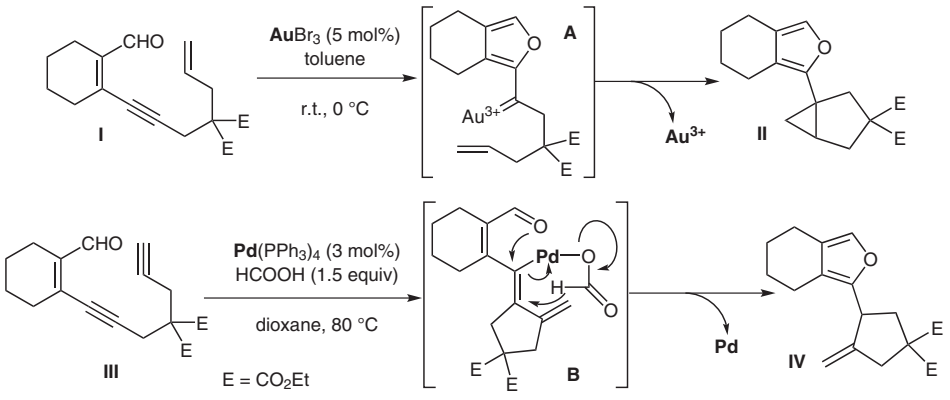
Abstract: We have developed an efficient cascade gold-catalyzed furanylation–cyclopropanation of acyclic (*E*)-deca-2,9-dien-4-yn-1-ones and an (*E*)-undeca-2,10-dien-4-yn-1-one to give 1-(2-furyl)bicyclo[3.1.0]hexanes and a 1-(2-furyl)bicyclo[4.1.0]heptane, respectively. This requires a configurational change from the *E*-isomer to the *Z*-isomer prior to furan formation. The intermediate was proposed to be a gold–carbene, which would undergo cyclopropanation to furnish the product.

Key words: cyclization, gold catalyst, furanylation, cyclopropanation, enynone

Among many new synthetic transformations, transition-metal-catalyzed reactions are very attractive since these reactions can directly construct complicated molecules from readily accessible starting materials under mild conditions.[1] Platinum- or gold-catalyzed electrophilic activation of alkynes has attracted much attention as an efficient method to facilitate atom-economical construction of complex molecules.[2] The use of gold compounds as homogeneous catalysts for the conversion of many organic substrates is a fast growing area in organic chemistry.[3] Gold catalysis is emerging as an extraordinary tool to create molecular complexity due to the unique ability of gold(I) and gold(III) complexes to activate C–C π-systems.[4] Electrophilic activation of the alkyne occurs by alkynophilic gold compounds and hence substrates containing both an acetylene moiety and an oxygen or nitrogen atom can be transformed into zwitterionic intermediates that undergo cycloaddition reactions with additional alkynes or alkenes.[5]

Many diynals, enynals, and enynones have been transformed to novel bifunctional metal-containing carbonyl ylides, dipolar species, with alkynophilic metal cations and successively reacted with an unsaturated bond to provide polycycles via cycloaddition.[6] Recently we extensively studied various platinum-catalyzed Husigen-type [3+2]-cycloadditions of enynal substrates.[7] In general, the platinum–pyrylium intermediate, formed in situ in a 6-*endo-dig* manner, reacts with a double bond to form the platinum–carbene complex which, depending on the reaction conditions, undergoes deprotonation, hydration, or insertion to give various [m,7,n] tricyclic compounds. In contrast to platinum catalysts, gold catalysts have exhibited a somewhat different behavior toward enynals. Gold compounds react with substrate **I** to form the furanyl intermediate **A** in a 5-*exo-dig* manner in which the resulting gold–carbene would undergo cyclopropanation with the pendant double bond to give the product **II**.[8] It is worth noting that we have found a similar transformation but with a different mechanistic pathway from enediynal **III** to the furan **IV** under palladium-catalyzed cycloreduction conditions. The hydropalladation would occur at the terminal triple bond of **III** to form vinylpalladium which underwent carbopalladation with the internal alkyne unit to form the intermediate **B**,[9] and then subsequent carbonyl oxygen attack to the carbon attached to the palladium could result in the formation of the product **IV** and palladium species for next catalytic cycles (Scheme 1).[10]



Scheme 1 Furan formation from enynals under gold and palladium catalysis

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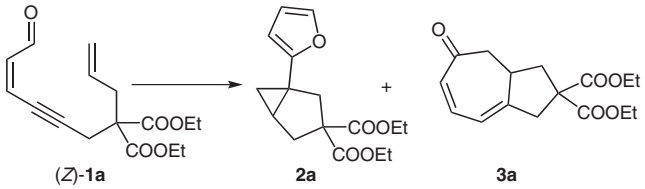
The furan nucleus is of immense interest because it is widely found in numerous natural products and biologically active compounds and can be utilized to access other useful compounds.[11] Furan syntheses in a *5-exo-dig* manner from alkynones or alkenones have been reported using a variety of catalysts containing mercury,[12] palladium,[13] gold,[14] and indium.[15] In an extension to work on gold-catalyzed furanylation–cyclopropanation,[16] we wish to report our recent results using acyclic enynals and enynones with gold catalysis. Compared to the previous substrates anchored by rigid aromatics or cycloalkenes, the present work using acyclic substrates is of interest to us because of their relatively flexible configurations. For metal-catalyzed reactions of acyclic ynones with an alkene, the Echavarren group reported cyclization of acyclic enynes bearing a carbonyl group at the alkenyl side chain to give oxatricyclic derivatives by using gold(I) catalyst.[17] The Iwasawa group also reported in 2008 that acyclic γ,δ-ynones using a catalytic amount of platinum(II) chloride in the presence of electron-rich alkenes gave oxabicyclic derivatives through the novel bifunctional platinum-containing carbonyl ylides and developed its asymmetric version in 2010.[18]

Table 1 Furanylative Cyclopropanations of Enynal (*Z*)-**1a**



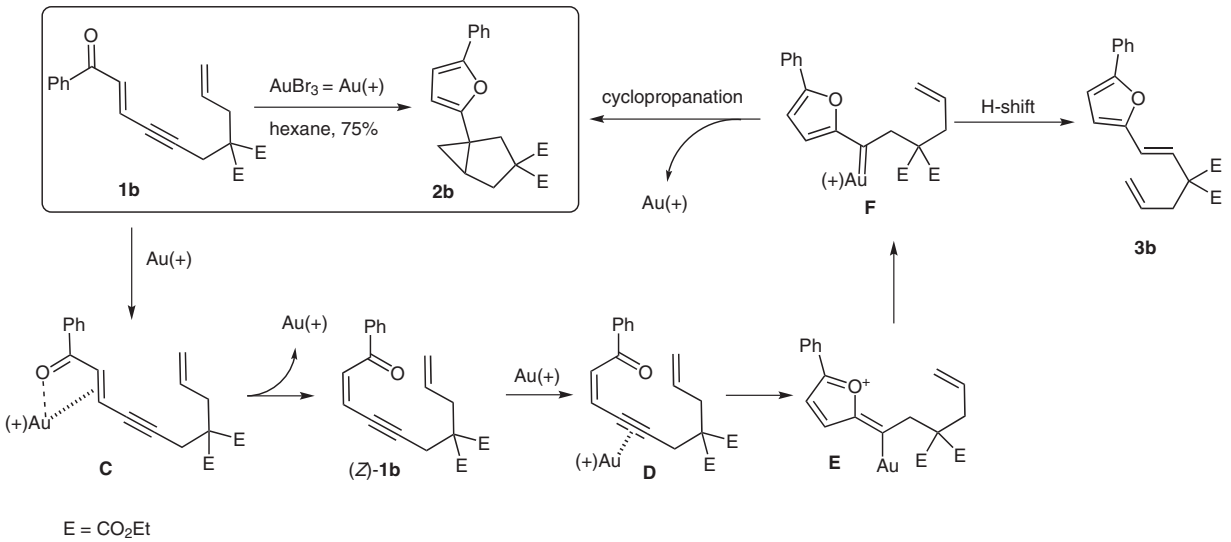
	Catalyst[a]	Solvent	Temp (°C)	Time (h)	Yield (%)
1	$AuBr_3$	toluene	r.t.	1	65 (**2a**)
2	$PtCl_2$	toluene	60	6	61 (**2a**)
3	AgOTf	toluene	80	2	40 (**2a**)
4[b]	$PtCl_2(PPh_3)_2$	toluene	120	1	19 (**2a**), 31 (**3a**)
5	$PtCl_2/AgSbF_6$	toluene	r.t.	2	26 (**3a**)
6	$PtCl_2/AgSbF_6$	CH_2Cl_2	r.t.	1	57 (**3a**)
7	$PtCl_2/AgBF_4$	CH_2Cl_2	r.t.	1	21 (**3a**)
8	$AuBr_3$	CH_2Cl_2	r.t.	2	45 (**2a**)
9	$AuBr_3$	hexane	r.t.	1	86 (**2a**)

[a] Catalyst (5 mol%) was used.
[b] Substrate (*Z*)-**1a** (40%) was recovered.

Thus, we synthesized acyclic enynal (*Z*)-**1a**, with *Z* configuration, and screened its reaction with several transition-metal catalysts (Table 1). First, gold(III) bromide was chosen based on our previous work.[8] Thus, the catalytic activity of gold(III) bromide, platinum(II) chloride, silver(I) triflate were examined in the furanylative cyclopropanations of (*Z*)-**1a** in toluene, which gave the corresponding product **2a** in 65%, 61%, and 40% yields, respectively (entries 1–3). Since platinum(II) chloride was found to catalyze the present reaction well, we further examined other platinum(II) chloride based catalytic systems. Thus $PtCl_2(PPh_3)_2$ in refluxing toluene was found to catalyze the reaction of (*Z*)-**1a** to give **2a** together with **3a** (entry 4). Cationic platinum, generated in situ from platinum(II) chloride/silver(I) hexafluoroantimonate, reacted with (*Z*)-**1a** in toluene to afford solely the cyclized product **3a** in 26% yield (entry 5); in dichloromethane, this cationic platinum afforded **3a** as the major product (entry 6).[7] Platinum(II) chloride/silver(I) tetrafluoroborate in dichloromethane, however, afforded **3a** in only 21% yield (entry 7). Assuming that solvent polarity is important in the present reaction, we examined gold(III) bromide as a catalyst in different solvents. The reaction of (*Z*)-**1a** using gold(III) bromide catalysis with dichloromethane or hexane as the solvent in resulted in the formation of **2a** in 45% and 86% yields, respectively (entries 8 and 9).

With this encouraging result in hand, a new acyclic enynone **1b** was examined. Since the *Z*-configuration was required in order to form the furan ring, we expected that **1b** could be isomerized into (*Z*)-**1b** under our conditions. Fortunately, when we treated **1b** with a gold(III) bromide solution in hexane for four hours, the corresponding product **2b** was isolated in 75% yield as the major product along with two byproducts. When we ran this reaction in dichloromethane, the H-shift product, **3b**, was obtained along with **2b** in 27% and 54% yields, respectively. Yet, such a dramatic solvent dependency is still unknown. A possible pathway for this reaction is proposed in Scheme 2.

Initially, the *E*-configuration of **1b** should be isomerized to the *Z*-configuration. We proposed that the gold cation would coordinate with the carbonyl oxygen to form **C** which could make isomerization into (*Z*)-**1b** possible. The intermediate (*Z*)-**1b** would be activated by alkynophilic gold cation to **D** followed by cyclization to yield ylide **F** through **E**.[19] The carbenoid **F** would react with the pendant double bond to form the cyclopropane **2b** as the major route. When this reaction was carried out in relatively polar dichloromethane, the carbenoid **F** could undergo H-transfer to afford the product **3b**. We also wish to report the scope of the furanylative cyclopropanations of enynones catalyzed by gold(III) bromide in hexane. We prepared various acyclic enynones **1c**–**m** by known methods.[20] Then, we tested the substrates under our optimized conditions [$AuBr_3$ (5 mol%), dry hexane, 25–60 °C] and the results are summarized Table 2.



Scheme 2 Proposed mechanism furanylative cyclopropanation

Table 2 Gold-Catalyzed Furanylative Cyclopropanation of Enynones

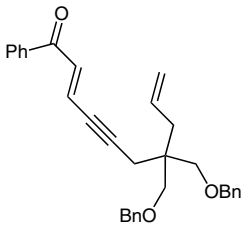
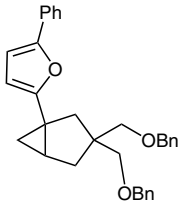
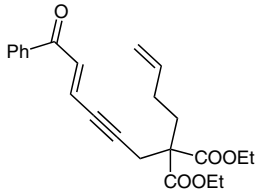
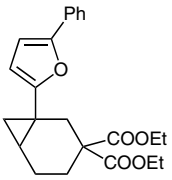
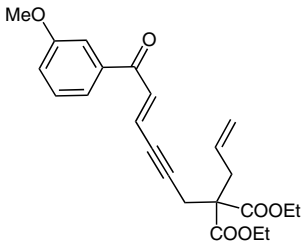
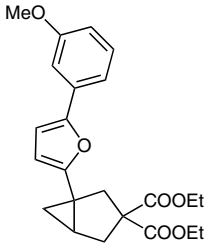
Entry	Substrate	Temp, time	Products	Yield (%)
1	 **1c**	60 °C, 12 h	 **2c**	89
2	 **1d**	25 °C, 15 h	 **2d**	72
3	 **1e**	60 °C, 10 h	 **2e**	64

Table 2 Gold-Catalyzed Furanylative Cyclopropanation of Enynones (continued)

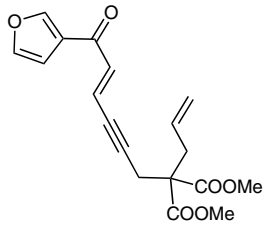
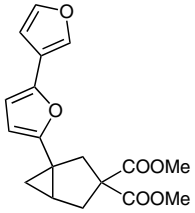
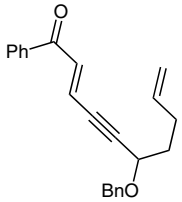
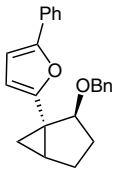
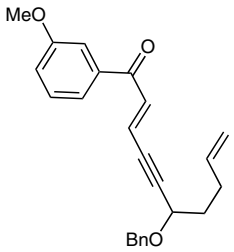
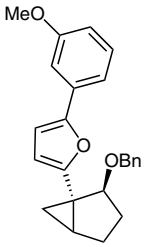
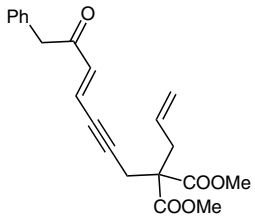
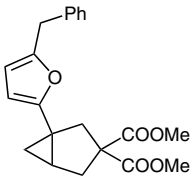
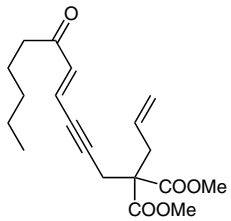
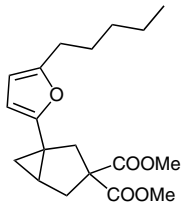
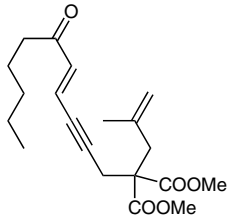
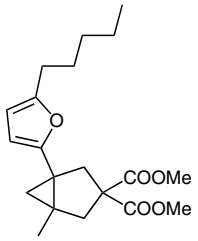
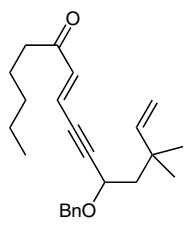
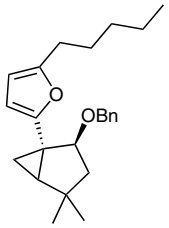
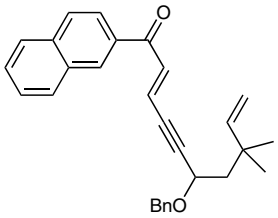
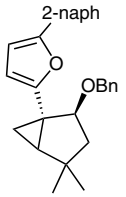
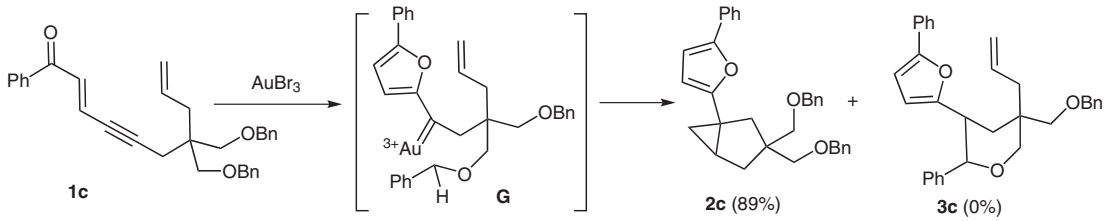
Entry	Substrate	Temp, time	Products	Yield (%)
4	 **1f**	60, °C12 h	 **2f**	52
5	 **1g**	60 °C, 1 h	 **2g**	87
6	 **1h**	60 °C, 2 h	 **2h**	90
7	 **1i**	60 °C, 10 h	 **2i**	73
8	 **1j**	60 °C, 6 h	 **2j**	86
9	 **1k**	60 °C, 20 h	 **2k**	61

Table 2 Gold-Catalyzed Furanylative Cyclopropanation of Enynones (continued)

Entry	Substrate	Temp, time	Products	Yield (%)
10	 **1l**	60 °C, 15 h	 **2l**	65
11	 **1m**	60 °C, 2 h	 **2m**	72

[a] General conditions: 0.1 to 1.0 mmol scale, $AuBr_3$ (5 mol%), hexane (1–2 mL).



Scheme 3 Cyclopropanation to give **2c** vs C–H insertion to give **3c** of gold–carbene **G**

All substrates (*Z*)-**1a** and **1b**–**m** were successfully transformed into the furanyl-substituted bicyclo[n.1.0]alkane derivatives **2a**–**m** with good to excellent yields. Substrate **1c** was designed in order to see if there was any possibility of benzylic C–H insertion into the gold–carbene species **G** to form **3c**, but this resulted in failure (Scheme 3).

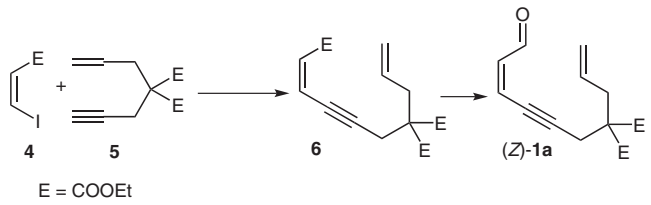
Substrate **1d**, a homologue of **1b**, gave bicyclo[4.1.0]heptane derivative **2d** in 72% yield. Substrates **1e**, with a methoxy group on the phenyl ring, also gave corresponding products **2e** in good yield (64%). Substrate **1f** with a furanyl group also worked well to give the product **2f** in 52% yield. Even substrates **1g** and **1h** containing a stereogenic center resulted in exclusive formation of **2g** (87%) and **2h** (90%), respectively, under these conditions. Replacing the aryl group by an alkyl group did not affect this reaction in terms of efficiency. Substrates **1i** with a benzyl group and substrates, **1j**–**l** with a pentyl group on the carbonyl group underwent these reactions smoothly to give the products **2i**–**l** in 73%, 86%, 61%, and 65% yields, respectively. Finally, substrate **1m** with a 2-naphthyl substituent underwent the reaction to afford **2m** in 72% yield. Note that the bulkiness at the alkenyl position of **1l** and **1m** did not diminish its scope. Based on ^1H and ^{13}C NMR data, **2g**,**h**,**l**,**m** were obtained as a single diastereomer with a *trans* relationship between the furanyl group and benzyloxy group.[21]

In summary, we have found that the gold-catalyzed reaction of acyclic enynones **1** provide the furanyl-substituted bicyclo[n.1.0]alkanes **2** in good to excellent yields. Further studies to extend the practical application are in progress in our group.

^1H and ^{13}C NMR spectra were recorded with a Varian Mercury 400 instrument and chemical shifts were measured relative to the residual solvent signal or TMS as an internal standard. All reagents were reagent grade and used without further purification. All solvents including hexane were used after distillation unless specified otherwise. Technical grade EtOAc and *n*-hexane used for column chromatography were distilled prior to use. Column chromatography was carried out using silica gel (60–120 mesh) packed in glass columns. All reactions were performed under argon atmosphere in oven-dried glassware with magnetic stirring. General routes for the synthesis of (*Z*)-**1a** and **1b** are given in Schemes 4 and 5, respectively. All other substrates **1c**–**m** were prepared by using the corresponding iodoacrylate (instead of **8**) and enyne (instead of **5**).

Methyl 3-Iodoacrylate (4)[22]

NaI (8.4 g, 56.1 mmol) was dried under vacuum for 30 min and dissolved in AcOH (20 mL) under an argon atmosphere. To this soln



Scheme 4 Preparation of substrate (*Z*)-**1a**

was added ethyl propiolate (5.01 g, 51.0 mmol) at r.t. The resulting mixture was stirred for 6 h at 70 °C. When the reaction was complete (TLC analysis), the mixture was cooled to r.t. and diluted with sat. NaCl soln. The organic layer was extracted with Et_2O (2 × 50 mL), and the combined organic layers were washed with sat. NaCl soln, dried (anhyd $MgSO_4$), filtered, and concentrated using a rotary evaporator. The residue was column chromatographed (silica gel, hexane–EtOAc, 10:1, R_f = 0.4) to afford compound **4** (8.3 g, 72%) as a yellow oil.

Diethyl 2-Allyl-2-(prop-2-ynyl)malonate (5)[23]
Diethyl allylmalonate (3.0 g, 15 mmol) was dissolved in anhyd DMF (25 mL). The mixture was cooled to 0 °C and NaH (0.72 g, 18.0 mmol) was slowly added. After 10min of stirring at 0 °C, propargyl bromide (2.15 g, 18.0 mmol) was added. The mixture was stirred for 30 min at 0 °C, and then it was allowed to warm up to r.t. and stirred for an additional 30 min. When the reaction was complete (TLC analysis), it was quenched with sat. NH_4Cl soln at 0 °C. The organic layer was extracted with Et_2O (2 × 50 mL) and the combined organic layers were washed with sat. NaCl soln, dried (anhyd $MgSO_4$), filtered, and concentrated using a rotary evaporator. The residues were column chromatographed (silica gel, hexane–EtOAc, 10:1, R_f = 0.4) to afford compound **5** (3.3 g, 92%) as a colorless oil.

Trimethyl Nona-1,8-dien-3-yne-1,6,6-tricarboxylate (6)
To a DMF (15 mL) soln of compound **4** (2.01 g, 8.4 mmol) was added $PdCl_2(PPh_3)_2$ (118.4 mg, 0.17 mmol, 2 mol%) and CuI (80.3 mg, 0.42 mmol) at 0 °C. The mixture was stirred for 5 min, and then additional **5** (2.41 g, 10.1 mmol) and Et_3N (4.7 mL, 33.8 mmol) in DMF (5 mL) were added. The resulting mixture was stirred for 4 h at 60 °C. When the reaction was complete (TLC analysis), it was quenched with sat. NH_4Cl soln. The organic layer was extracted with Et_2O (2 × 50 mL), and the combined organic layers were washed with sat. NaCl soln, dried (anhyd $MgSO_4$), filtered, and concentrated. The residues were column chromatographed (silica gel, hexane–EtOAc, 10:1, R_f = 0.2) to afford compound **6** (1.98 g, 70%) as a yellow oil.

Diethyl 2-Allyl-2-(6-oxohex-4-en-2-ynyl)malonate [(*Z*)-1a]
A 1.0 M DIBAL-H in THF soln (1.4 mL, 1.4 mmol) was added dropwise to a soln of **6** (401.1 mg, 1.2 mmol) in CH_2Cl_2 (10 mL) at –78 °C, on completion of the addition, the mixture was stirred for 30 min. When the reaction was complete (TLC analysis), it was quenched with 1.0 M HCl soln. The organic layer was extracted with Et_2O (2 × 50 mL), and the combined organic layers were washed with sat. NaCl soln, dried (anhyd $MgSO_4$), and concentrated by rotary evaporation. The residues were column chromatographed (silica gel, hexane–EtOAc, 10:1, R_f = 0.3) to afford (*Z*)-**1a** (250.7 mg, 72%) as a yellow oil.

3-Iodo-1-phenylprop-2-en-1-one (8)[20a]
NaI (1.56 g, 15.5 mmol) was dried under vacuum for 30 min and dissolved in AcOH (20 mL) under an argon atmosphere. To this soln was added the compound **7** (1.20 g, 17 mmol) at r.t. The resulting mixture was stirred for 12 h at 60 °C. When the reaction was complete (TLC analysis), it was quenched with sat. NaCl soln. The organic layer was extracted with Et_2O (2 × 50 mL), and the combined organic layers were washed with sat. NaCl soln, dried (anhyd $MgSO_4$), and concentrated by rotary evaporation. The residues were column chromatographed (silica gel, hexane–EtOAc, 10:1, R_f = 0.3) to afford compound **8** (1.26 g, 64%) as a yellow oil.

Dimethyl 2-Allyl-2-(6-oxo-6-phenylhex-4-en-2-ynyl)malonate (1b)
To a soln of compound **8** (1.26 g, 4.88 mmol) in DMF (15 mL) was added $PdCl_2(PPh_3)_2$ (68.5 mg, 0.098 mmol) and CuI (46.5 mg, 0.24 mmol) at 0 °C. The mixture was stirred for 5 min, and then **5** (1.40 g, 5.86 mmol) and Et_3N (2.7 mL, 19.5 mmol) were added. The resulting mixture was stirred for 1 h at r.t. When the reaction was complete (TLC analysis), it was quenched with sat. NH_4Cl soln. The organic layer was extracted with Et_2O (2 × 50 mL), washed with sat. NaCl soln, dried (anhyd $MgSO_4$), and concentrated by rotary evaporation. The residues were column chromatographed (silica gel, hexane–EtOAc, 10:1, R_f = 0.2) to afford compound **1b** (1.27 g, 71%) as a yellow oil.

Diethyl 1-(5-Phenylfuran-2-yl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (2b); Typical Procedure
Enynone **1b** (37.0 mg, 0.1 mmol), $AuBr_3$ (2 mg, 0.005 mmol), and dry hexane (1.0 ml) were placed in a new 5-mL test tube at 0 °C. The mixture was purged with a stream of dry argon gas and stirred at r.t. for 4 h (TLC monitoring). Upon completion, a drop of Et_3N was added to quench the reaction and the solvent was removed under vacuum. The residue was purified by flash column chromatography (silica gel, hexane–EtOAc, 20:1) to give the product **2b** (27.8 mg, 75%) as a colorless oil.

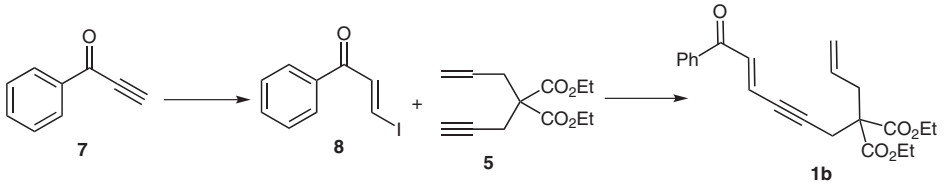
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 7.6 Hz, 2 H), 7.36–7.33 (m, 2 H), 7.22–7.19 (m, 1 H), 6.55 (d, *J* = 2.8 Hz, 1 H), 6.11 (d, *J* = 3.6 Hz, 1 H), 4.25–4.16 (m, 4 H), 2.98–2.85 (m, 2 H), 2.69–2.59 (m, 2 H), 1.85–1.80 (m, 1 H), 1.30–1.20 (m, 7 H), 0.75–0.72 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.57, 171.49, 156.51, 151.71, 130.94, 128.56, 126.79, 123.29, 106.01, 105.88, 61.88, 61.74, 59.54, 37.95, 35.90, 27.26, 26.73, 16.95, 14.02.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{22}H_{24}O_5$: 368.1624; found: 368.1624.

Diethyl 1-(Furan-2-yl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (2a)
Colorless oil; yield: 25.9 mg (86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (s, 1 H), 6.28 (t, *J* = 2.2 Hz, 1 H), 6.02 (d, *J* = 3.2 Hz, 1 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 4.17 (q, *J* = 7.2 Hz, 2 H), 2.83 (ABq, Δδ = 20.4 Hz, *J* = 17.6 Hz, 2 H), 2.63 (d, *J* = 14.0 Hz, 1 H), 2.58 (dd, *J* = 14.0, 4.8 Hz, 1 H), 1.73 (m, 1 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 1.23 (*J* = 7.2 Hz, 3 H), 1.13 (dd, *J* = 6.4, 6.4 Hz, 1 H), 0.67 (dd, *J* = 6.4, 6.4 Hz, 1 H).



Scheme 5 Preparation of substrate **1b**

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.71, 171.63, 156.92, 140.53, 110.46, 103.92, 61.98, 61.84, 59.69, 38.21, 36.03, 27.18, 26.36, 16.69, 14.14.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{16}H_{20}O_5$: 292.1311; found: 292.1320.

3,3-[Bis(benzyloxy)methyl]-1-(5-phenylfuran-2-yl)bicyclo[3.1.0]hexane (2c)
Yellow oil; yield: 40.2 mg (89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 6.8 Hz, 2 H), 7.60–7.39 (m, 12 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 6.67 (d, *J* = 3.0 Hz, 1 H), 6.16 (d, *J* = 3.0 Hz, 1 H), 4.69 (s, 2 H), 4.65 (s, 2 H), 3.61 (s, 2 H), 3.52 (s, 2 H), 2.46 (d, *J* = 13.6 Hz, 1 H), 2.19 (dd, *J* = 14.0, 6.4 Hz, 1 H), 2.06 (d, *J* = 13.6 Hz, 1 H), 1.91 (m, 1 H), 1.76 (d, *J* = 13.6 Hz, 1 H), 1.60 (dd, *J* = 8.4, 4.0 Hz, 1 H), 0.97 (dd, *J* = 5.0, 4.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.60, 151.53, 138.92, 131.27, 128.63, 128.37, 127.50, 127.48, 126.70, 123.31, 106.01, 105.26, 74.63, 74.58, 73.32, 73.30, 38.89, 36.31, 29.61, 29.47, 25.20.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{32}H_{32}O_3$: 464.2351; found: 464.2360.

Diethyl 1-(5-Phenylfuran-2-yl)bicyclo[4.1.0]heptane-3,3-dicarboxylate (2d)
Colorless oil; yield: 36.8 mg (72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 8.0 Hz, 2 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 6.56 (d, *J* = 3.2 Hz, 1 H), 6.23 (d, *J* = 3.2 Hz, 1 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 3.12 (d, *J* = 14.8 Hz, 1 H), 2.14 (d, *J* = 14.0 Hz, 1 H), 2.02 (d, *J* = 14.4 Hz, 1 H), 1.92 (m, 2 H), 1.66 (m, 1 H), 1.59 (m, 1 H), 1.37 (dd, *J* = 9.6, 4.0 Hz, 1 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 1.20 (t, *J* = 7.2 Hz, 3 H), 0.68 (dd, *J* = 5.6, 5.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.44, 171.03, 159.64, 151.25, 131.32, 128.64, 126.69, 123.32, 106.20, 105.73, 61.57, 61.39, 52.81, 33.34, 25.00, 20.34, 19.46, 17.14, 14.18.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{23}H_{26}O_5$: 382.1780; found: 382.1793.

Diethyl 1-[5-(3-Methoxyphenyl)furan-2-yl]bicyclo[3.1.0]hexane-3,3-dicarboxylate (2e)
Colorless oil; yield: 20.0 mg (64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (t, *J* = 8.4 Hz, 1 H), 7.18 (d, *J* = 8.0 Hz, 1 H), 7.12 (s, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 6.54 (d, *J* = 2.8 Hz, 1 H), 6.11 (d, *J* = 3.6 Hz, 1 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 3.85 (s, 3 H), 2.87 (ABq, Δδ = 18.6 Hz, *J* = 13.2 Hz, 2 H) , 2.67 (d, *J* = 13.2 Hz, 1 H), 2.61 (dd, *J* = 4.4, 4.8 Hz, 1 H), 1.83 (m, 1 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.20 (m, 1 H), 0.74 (dd, *J* = 5.2, 5.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.66 171.58, 159.95, 156.76, 151.67, 132.41, 129.75, 116.15, 112.42, 109.12, 106.38, 106.13, 61.98, 61.84, 59.79, 55.40, 38.14, 36.05, 27.41, 26.87, 17.23, 14.13.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{23}H_{26}O_6$: 398.1729; found: 398.1722.

Dimethyl 1-(2,3′-Bifuran-5-yl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (2f)
Colorless oil; yield: 18.7 mg (52%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 1 H), 7.40 (s, 1 H), 6.55 (s, 1 H), 6.26 (d, *J* = 3.2 Hz, 1 H), 6.05 (d, *J* = 2.8 Hz, 1 H), 3.76 (s, 3 H), 3.73 (s, 3 H), 2.86 (ABq, Δδ = 24.4 Hz, *J* = 13.6 Hz, 2 H), 2.67 (d, *J* = 13.6 Hz, 1 H), 2.62 (dd, *J* = 13.6, 4.4 Hz, 1 H), 1.77 (m, 1 H), 1.16 (dd, *J* = 6.8, 6.4 Hz, 1 H), 0.66 (dd, *J* = 5.6, 5.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.15, 172.07, 155.75, 145.94, 143.42, 137.81, 118.02, 107.82, 106.00, 59.64, 53.20, 53.08, 38.44, 36.19, 36.10, 29.84, 27.22, 26.55, 16.93.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{18}O_6$: 330.1103; found: 333.1096.

***trans*-2-(Benzyloxy)-1-(5-phenylfuran-2-yl)bicyclo[3.1.0]hexane (2g)**
Colorless oil; yield: 28.8 mg (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 7.2 Hz, 2 H), 7.34 (t, *J* = 7.6 Hz, 3 H), 7.29–7.23 (m, 5 H), 6.56 (d, *J* = 3.2 Hz, 1 H), 6.10 (d, *J* = 3.2 Hz, 1 H), 4.67 (t, *J* = 8.4 Hz, 1 H), 4.55 (s, 2 H), 2.06 (dt, *J* = 12.8, 8.0 Hz, 1 H), 1.93, (ddd, *J* = 12.0, 8.0, 4.0 Hz, 1 H), 1.82 (dd, *J* = 12.4, 8.4 Hz, 1 H), 1.65 (m, 1 H), 1.40 (m, 1 H), 1.31 (dd, *J* = 5.0, 4.8 Hz, 1 H), 1.23 (dd, *J* = 8.0, 5.0 Hz 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.05, 151.92, 138.88, 131.28, 128.68, 128.42, 127.93, 127.59, 126.86, 123.49, 106.58, 106.14, 81.93, 71.89, 30.50, 27.48, 27.40, 24.75, 12.05.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{23}H_{22}O_2$: 330.1620; found: 330.1620

***trans*-2-(Benzyloxy)-1-[5-(3-methoxyphenyl)furan-2-yl]bicyclo[3.1.0]hexane (2h)**
Colorless oil; yield: 37.0 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.17 (m, 7 H), 7.13 (d, *J* = 2.0 Hz, 1 H), 6.78 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.56 (d, *J* = 3.2 Hz, 1 H), 6.10 (d, *J* = 3.2 Hz, 1 H), 4.66 (t, *J* = 8.0 Hz, 1 H), 4.54 (s, 2 H), 3.82 (s, 3 H), 2.05 (dt, *J* = 13.2, 7.6 Hz, 1 H), 1.93, (ddd, *J* = 12.0, 8.0, 4.0 Hz, 1 H), 1.82 (dd, *J* = 12.4, 8.4 Hz, 1 H), 1.65 (m, 1 H), 1.40 (m, 1 H), 1.31 (dd, *J* = 5.0, 4.8 Hz, 1 H), 1.22 (dd, *J* = 8.0, 4.6 Hz 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.95, 157.06, 151.67, 138.81, 132.52, 129.73, 128.39, 127.88, 127.56, 116.15, 112.40, 109.04, 106.57, 106.49, 81.88, 71.85, 55.37, 30.46, 27.45, 27.34, 24.70, 12.03.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{24}H_{24}O_3$: 360.1725; found: 360.1726.

Dimethyl 1-(5-Benzylfuran-2-yl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (2i)
Colorless oil; yield: 23.9 mg (73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.22 (m, 5 H), 5.91 (d, *J* = 2.8 Hz, 1 H), 5.83 (d, *J* = 2.8 Hz, 1 H), 3.89 (s, 2 H), 3.74 (s, 3 H), 3.71 (s, 3 H), 2.81 (ABq, Δδ = 26.4 Hz, *J* = 18.4 Hz, 2 H), 2.63(d, *J* = 13.6 Hz, 1 H), 2.59 (dd, *J* = 13.6, 4.4 Hz, 1 H), 1.69 (m, 1 H), 1.08 (dd, *J* = 7.2, 7.2 Hz, 1 H), 0.59 (dd, *J* = 5.2, 4.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.15, 172.08, 155.60, 152.64, 138.41, 128.79, 128.53, 126.47, 107.06, 104.66, 59.57, 53.14, 53.01, 38.39, 36.17, 34.63, 27.17, 26.23, 16.63.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{21}H_{22}O_5$ 354.1467; found: 354.1458.

Dimethyl 1-(5-Pentylfuran-2-yl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (2j)
Colorless oil; yield: 36.4 mg (86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.89 (d, *J* = 3.0 Hz, 1 H), 5.84 (d, *J* = 3.0 Hz, 1 H), 3.75 (s, 3 H), 3.71 (s, 3 H), 2.81 (ABq, Δδ = 25.2 Hz, *J* = 14.0 Hz, 2 H), 2.64 (d, *J* = 13.2 Hz, 2 H), 2.59 (dd, *J* = 13.2, 4.4 Hz, 1 H), 2.53 (t, *J* = 8.0 Hz, 1 H), 1.69 (m, 1 H), 1.59 (quintet, *J* = 7.2 Hz, 2 H), 1.32 (m, 4 H), 1.08 (dd, *J* = 7.0, 6.8 Hz, 1 H), 0.89 (t, *J* = 6.8 Hz, 3 H), 0.59 (dd, *J* = 5.2, 5.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.22, 172.12, 154.75, 154.64, 105.18, 104.39, 59.43, 53.19, 53.06, 38.36, 36.14, 31.52, 28.10, 27.82, 27.13, 26.04, 22.53, 16.34, 14.15.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{19}H_{26}O_5$: 334.1780; found: 334.1768.

Dimethyl 5-Methyl-1-(5-pentylfuran-2-yl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (2k)
Colorless oil; yield: 28.5 mg (61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.92 (d, *J* = 2.8 Hz, 1 H), 5.86 (d, *J* = 2.8 Hz, 1 H), 3.75 (s, 3 H), 3.72 (s, 3 H), 2.84 (ABq, Δδ = 32.0 Hz, *J* = 14.0 Hz, 2 H), 2.72 (d, *J* = 13.8 Hz, 1 H), 2.55 (t, *J* = 8.0 Hz, 2 H), 2.42 (d, *J* = 13.8 Hz, 1 H), 1.61 (quintet, *J* = 6.8 Hz, 2 H), 1.31(m, 4 H), 1.07 (s, 3 H), 0.89 (t, *J* = 6.8 Hz, 3 H), 0.88 (d, *J* = 6.0 Hz, 1 H), 0.67 (d, *J* = 6.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.23, 172.29, 155.29, 153.21, 106.39, 105.14, 58.01, 53.17, 53.01, 42.27, 39.54, 31.46, 31.28, 31.05, 28.17, 27.79, 22.52, 20.22, 18.03, 14.15.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{20}H_{28}O_5$ 348.1937; found: 348.1952.

***trans*-2-(Benzyloxy)-4,4-dimethyl-1-(5-pentylfuran-2-yl)bicyclo[3.1.0]hexane (2l)**
Colorless oil; yield: 27.0 mg (65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.23 (m, 5 H), 5.89 (d, *J* = 3.0 Hz, 1 H), 5.85 (d, *J* = 3.0 Hz, 1 H), 4.59 (dd, *J* = 8.4, 8.4 Hz, 1 H), 4.48 (ABq, Δδ = 17.6 Hz, *J* = 12.0 Hz, 2 H), 2.55 (t, *J* = 7.2 Hz, 2 H), 1.76 (dd, *J* = 13.2, 7.2 Hz, 1 H), 1.61 (m, 2 H), 1.33 (m, 5 H), 1.19 (m, 2 H), 1.09 (s, 3 H), 1.04 (dd, *J* = 8.0, 6.0 Hz, 1 H), 1.00 (s, 3 H), 0.88 (t, *J* = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.34, 154.71, 139.03, 128.34, 127.80, 127.47, 105.21, 104.66, 81.29, 71.72, 41.71, 38.53, 37.33, 31.55, 30.44, 29.97, 28.19, 27.93, 26.33, 22.56, 14.18, 11.14.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{24}H_{32}O_2$: 352.2402; found: 352.2403.

***trans*-2-(Benzyloxy)-4,4-dimethyl-1-5-[5-(2-naphthyl)furan-2-yl]bicyclo[3.1.0]hexane (2m)**
Colorless oil; yield: 60.8 mg (72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (s, 1 H), 7.81 (m, 3 H), 7.70 (d, *J* = 8.4 Hz, 1 H), 7.44 (m, 2 H), 7.27 (m, 5 H), 6.68 (d, *J* = 3.2 Hz, 1 H), 6.14 (d, *J* = 3.2 Hz, 1 H), 4.74 (t, *J* = 8.0 Hz, 1 H), 4.55 (s, 2 H), 1.85 (dd, *J* = 12.8, 7.8 Hz, 1 H), 1.50 (dd, *J* = 8.4, 4.8 Hz, 1 H), 1.33 (dd, *J* = 4.8, 4.8 Hz, 1 H), 1.25 (m, 2 H), 1.15 (s, 3 H), 1.06(s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.48, 151.94, 138.78, 133.69, 132.48, 128.40, 128.33, 128.11, 127.83, 127.81, 127.55, 126.47, 125.67, 122.26, 121.34, 106.82, 106.57, 80.82, 71.77, 41.64, 39.22, 37.51, 30.70, 30.00, 26.31, 11.74.

HRMS (Cl): *m*/*z* calcd for $C_{29}H_{29}O_2$: 409.2168; found: 409.2190.

Diethyl 3-Oxobicyclo[5.3.0]deca-4,6-diene-9,9-dicarboxylate (3a)
Enynone **1a** (30.1 mg, 0.1 mmol), $PtCl_2$ (1.4 mg, 0.005 mmol), $AgSbF_6$ (1.8 mg, 0.005 mmol) and anhyd CH_2Cl_2 (1.0 mL) were placed in a new 5 mL test tube at 0 °C. The reaction mixture was purged with a stream of dry argon gas and stirred at r.t. for 1 h by monitoring the reaction periodically by TLC. Upon completion, a drop of Et_3N was added to quench the reaction and the solvent was removed under vacuum. The residue was purified by flash column chromatography (silica gel, hexane–EtOAc, 20:1) to give the product **3a** (17.2 mg, 57%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (m, 1 H), 6.25 (m, 1 H), 6.17 (m, 1 H), 4.20 (m, 4 H), 3.19 (dd, *J* = 17.6, 2.8 Hz, 1 H), 2.63 (m, 2 H), 2.45 (d, *J* = 17.2 Hz, 1 H), 2.35 (dt, *J* = 17.6, 6.4 Hz, 1 H), 2.04 (m, 1 H), 1.91(t, *J* = 13.0 Hz, 1 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.31, 170.55, 170.52, 135.07, 132.04, 131.71, 125.33, 62.11, 62.02, 53.78, 44.07, 34.76, 30.86, 30.19, 14.11.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{16}H_{20}O_5$: 292.1311; found: 292.1316.

(*E*)-Diethyl 2-Allyl-2-[2-(5-phenylfuran-2-yl)vinyl]malonate (3b)
Enynone **1b** (37.0 mg, 0.1 mmol), $AuBr_3$ (2 mg, 0.005 mmol), and anhyd CH_2Cl_2 (1.0 mL) were placed in a new 5 mL test tube at 0 °C. The reaction mixture was purged with a stream of dry argon gas and stirred at r.t. for 4 h by monitoring the reaction periodically by TLC. Upon completion, a drop of Et_3N was added to quench the reaction and the solvent was removed under vacuum. The residue was purified by flash column chromatography (silica gel, *n*-hexane–EtOAc, 20:1) to give the product **2b** (20.0 mg, 54%) and **3b** (10.0 mg, 27%) as colorless oils. Data for **3b** follow.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 7.2 Hz, 2 H), 7.42 (s, 2 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 7.30 (d, *J* = 7.2 Hz, 1 H), 6.68 (d, *J* = 3.6 Hz, 1 H), 6.66 (d, *J* = 3.6 Hz, 1 H), 5.75 (sext, *J* = 6.8 Hz, 1 H), 5.12 (d, *J* = 21.2 Hz, 1 H), 5.09 (d, *J* = 14.4 Hz, 1 H), 4.31–4.22 (m, 4 H), 3.10 (d, *J* = 7.6 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.26, 154.99, 150.71, 132.45, 130.24, 128.85, 128.10, 124.65, 124.21, 119.20, 113.23, 110.16, 106.97, 62.27, 60.30, 39.28, 14.22.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{22}H_{24}O_5$: 368.1624; found: 368.1625.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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