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Cationic Palladium Complex-catalyzed Carbonylation of 2,3-Dien-1-ols to 1,3-Diene-2-carboxylic Acids and Esters under Mild Conditions

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A cationic palladium complex, $[Pd(PPh_3)_2(MeCN)_2](BF_4)_2$, catalyzed the carbonylation of 2,3-dien-1-ols under mild conditions. The dienols bearing two or more alkyl substituents on the diene part afforded 1,3-diene-2-carboxylic acids successfully in tetrahydrofuran (THF), while those possessing one or no alkyl substituent gave polymers of the products exclusively. The former afforded the corresponding methyl esters in good yields when the reactions were carried out in methanol, while the latter afforded mainly the Diels–Alder reaction products of the resulting esters. An alkylidene group-substituted π-allylpalladium species has been presumed to be an intermediate.

Keywords: cationic palladium complex; carbonylation; dienol; dienecarboxylic acid

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INTRODUCTION

Palladium(0) complexes catalyze the dimerization of propa-1,2-diene (allene) with addition of nucleophiles to give 1,3-diene derivatives.[1] Palladium(0) complexes also mediate the carbopalladation of allenes with aryl and vinylic halides or triflates followed by addition of various nucleophiles to give products containing all three moieties.[2] Several intramolecular versions of this chemistry have also been developed. π-Allylpalladium intermediates are estimated to play a crucial role in these reactions. On the other hand, derivatives of 2,3-dien-1-ol (α-allenic alcohol) such as carboxylates, phosphates and carbonates are reported to undergo palladium-catalyzed reactions, including alkylation[3] and carbonylation,[4] under mild conditions. Palladium-catalyzed alkylation of carboxylates and phosphates with hard carbonucleophiles (alkylmagnesium and - zinc compounds) affords 1,3-dienes while with soft ones (malonates) it affords 2,3-dienes.[5] Carbonylation of 2,3-dienyl carbonates catalyzed by a palladium(0) complex proceeds smoothly to give 1,3-diene-2-carboxylates.[4] In these reactions, a somewhat different intermediate is expected where an alkylidene group is directly attached to the π-allyl group. However, the palladium chemistry of 2,3-dienol itself is far less studied in spite of the ready availability of the substrate. In 1994, a cationic palladium complex / *p*-toluenesulfonic acid system was developed for the regioselective carbonylation of 2,3-dienols to α-vinylacrylic acids.[6] This catalytic system can be applied to the buta-2,3-dien-1-ols having alkyl substituents on the C-4 position, whereas those bearing no substituents on that position give some uncharacterized polymeric materials possessing carbonyl groups.

In this paper, we present a cationic palladium complex that is active enough for the carbonylation of 2,3-dien-1-ols under mild conditions even in the absence of a co-catalyst (*p*-toluenesulfonic acid).

RESULTS AND DISCUSSIONS

The carbonylation of 2,3-dien-1-ols **1** was carried out in tetrahydrofuran (THF) or methanol at

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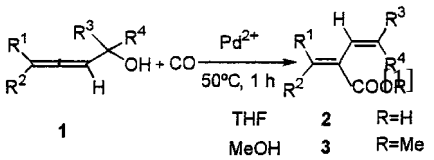


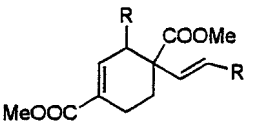
50 °C for 1 h under carbon monoxide (10 atm) in the presence of 2 mol% of the cationic palladium complex $[Pd(PPh_3)_2(MeCN)_2](BF_4)_2$. This procedure afforded 1,3-diene-2-carboxylic acids 2 or their methyl esters **3** (Eqn [1]). Neutral palladium(II) and palladium(0) complexes such as $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ did not show the catalytic activity. The results are given in Table 1.

Carbonylation in THF: synthesis of carboxylic acids

The carbonylation of the parent substrate buta-2,3-dien-1-ol (**1a**) and the methyl-substituted substrate penta-3,4-dien-2-ol (**1b**) afforded products that polymerized quite easily. The IR spectra of the crude samples before polymerization exhibited broad peaks at 3500–2500 cm^{-1} and strong ones around 1700 cm^{-1} indicating the formation of carboxylic acids. 1,1-Disubstituted buta-2,3-dien-1-ols (**1c–1e**) underwent smooth carbonylation to afford the corresponding 1,3-diene-2-carboxylic acids **2c–2e** respectively, in good yields. These types of carboxylic acids were not obtained from the reactions using *p*-toluenesulfonic acid as the co-catalyst because of the polymerization of the products. [6] Modest to fair yields (27–72%) resulted when poly-substituted buta-2,3-dien-1-ols (**1f–1i**) were employed as the substrates. The *E/Z* ratios in the products **2d, 2f** and **2g** were, 67:33, 80:20 and 100:0, respectively. It is noted that this type of product is an efficient substrate for nickel-catalyzed carbonylation to α-ketolactone.[7]

Carbonylation in methanol: synthesis of esters

The carbonylation of the parent substrate **1a** in methanol did not give the expected methyl ester. Instead, Diels–Alder reaction product **4a** of the anticipated product **3a** was obtained in 45% yield. Methyl-substituted substrate **1b** gave the anticipated ester **3b** in a modest yield of 15% together with a Diels–Alder product **4b** in 78% yield. The yield of **3b** was slightly improved to 26% when the reaction was carried out at room temperature for 1 h, although the main product was still **4b** (54%). The stereochemistry around the double bond in **3b** was confirmed to be *Z* by the ^1H NMR coupling constant (11.58 Hz). One possibility of the *Z* isomer being able to survive is that the *E* isomer undergoes faster Diels–Alder reaction than the *Z* isomer. Actually, the stereochemistry around the double bond in **4b** was *E*.



4a R=H
4b R=Me

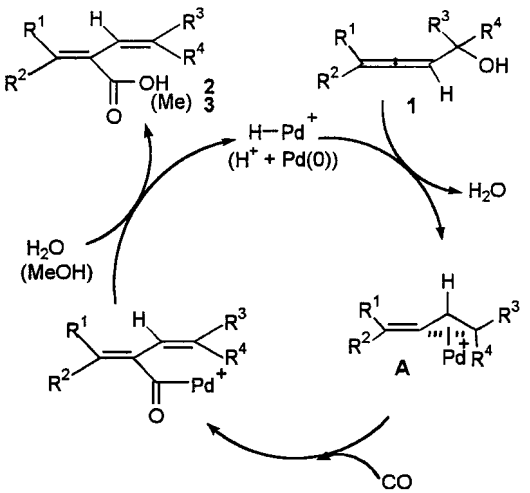
Smooth carbonylation occurred with the substrates **1c–1i** to produce the corresponding methyl 1,3-diene-2-carboxylates **3c–3i**. Diels–Alder-type products were scarcely observed in these cases. The *E/Z* ratios in the products **3d, 3f** and **3g** were 67:33, 85:15 and 100:0, respectively. 1,3-Diene-2-carboxylates **3** were reported to be obtained from the

Table 1 Carbonylation of **1** catalyzed by $[Pd(PPh_3)_2(MeCN)_2](BF_4)_2$ (Eqn [1])

	1							
1	R^1	R^2	R^3	R^4	**2**	Yield (%)	**3**	Yield (%)
1a	H	H	H	H	2a	(Polymer)	3a	0 (**4a** 45)
1b	H	H	Me	H	2b	(Polymer)	3b	13(*Z*) (**4b** 78)
1c	H	H	Me	Me	2c	61	3c	75
1d	H	H	Me	Et	2d	95(*E*/*Z* = 67:33)	3d	96(*E*/*Z* = 67:33)
1e	H	H	-$(CH_2)_5$		2e	40	3e	54
1f	Me	H	Me	Me	2f	72(*E*/*Z* = 80:20)	3f	82(*E*/*Z* = 85:15)
1g	Ph	H	Me	Me	2g	48(*E*)	3g	45(*E*)
1h	Me	Me	Me	Me	2h	38	3h	75
1i	Me	Me	H	H	2i	27	3i	78

carbonylation of 2,3-dienyl carbonates in the presence of a palladium catalyst.[4] Since 2,3-dienyl carbonates are usually prepared from 2,3-dienols and alkyl chloroformate, the carbonylation reaction mentioned above has the advantage of being able to employ 2,3-dienols as substrates directly.

We tentatively propose a following reaction pathway where an H–Pd^+ species is involved as an active species (Scheme 1). Thus, an H–Pd^+ species [or $H^+ + Pd(0)$] generated *in situ* would react with 2,3-dienol **1** to give the π-allylic species **A** with elimination of water, where an alkylidene group is directly attached to the π-allyl group.[6] Insertion of carbon monoxide followed by hydrolysis (or methanolysis) of the resulting acylpalladium species would give rise to the observed product.



Scheme 1 Presumed reaction pathway.

This reaction affords a ready access to 1,3-diene-2-caboxylic acids and esters which cannot be obtained easily by other methods. The key to the reaction is the employment of the cationic palladium(II) complex, $[Pd(PPh_3)_2(MeCN)_2](BF_4)$, as a catalyst precursor which has weakly ligated ligands (MeCN) and shows a propensity to promote the heterolytic cleavage[8] of the carbon–oxygen bond of 2,3-dienols.

EXPERIMENTAL

2,3-Dienols **1**[9] and the cationic palladium(II) complex[10] $[Pd(PPh_3)_2(MeCN)_2](BF_4)_2$ were prepared according to the published methods. The ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Bruker DPX-400 spectrometer with HMQC and (in certain cases) nuclear overhances (NOE) experiments. The IR and mass spectra were recorded on a Jasco FT/IR 350 spectrometer and a Shimadzu GCMS QP2000A apparatus, respectively.

Carbonylation of 1 in THF: synthesis of 2

A mixture of **1** (2 mmol), $[Pd(PPh_3)_2(MeCN)_2](BF_4)_2$ (0.04 mmol) and THF (4 ml) was placed in an autoclave and heated at 50 °C under carbon monoxide pressure (10 atm). After 1 h, the reaction mixture was taken up in diethyl ether and passed through a short Florisil® column to remove palladium complexes. Then the acidic product was extracted with 0.5 mol dm^{-3} NaOH (3×15 ml). After acidification with 1 mol dm^{-3} HCl, the product was extracted with diethyl ether, dried ($MgSO_4$) and concentrated to give **2**. In certain cases, the products were further purified by column chromatography over silica gel using hexane/ethyl acetate (3:1).

2-Methylenebut-3-enoic acid (2a)
This compound underwent facile polymerization into white solids during isolation. IR of the polymer (KBr): 3500–2500, 1694, 1654 cm^{-1}.

2-Methylenepent-3-enoic acid (2b)
Mass spectrum: *m/z* 41 (100), 67 (85), 97 (17), 112 (48, M^+). This compound underwent facile polymerization into white solids during isolation. Found: C, 63.35; H, 7.25; calcd for $(C_6H_8O_2)_n$: C, 64.24; H, 7.19%.

4-Methyl-2-methylenepent-3-enoic acid (2c)
IR (neat): 3500–2500, 1697, 1607, 1284 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.78 (s, 3 H, one of Me_2), 1.86 (s, 3 H, one of Me_2), 5.66 (s, 1 H, =CH (*trans* to the carbonyl group)), 6.45 [s, 1 H, =CH (*cis* to the carbonyl group)], 10.23 (br, 1 H, OH). ^{13}C NMR ($CDCl_3$): δ 19.53, 26.64, 119.64, 128.20, 136.44, 138.91, 172.62. Mass spectrum: *m/z* 39 (95), 53 (55), 79 (100), 126 (72, M^+). This compound underwent polymerization on standing. Found: C, 66.59; H, 8.03; calcd for $(C_7H_{10}O_2)_n$: C, 66.64; H, 7.99%.

4-Methyl-2-methylenehex-3-enoic acid (2d)
Mixture of E and Z isomers
IR (neat): 3500–2500, 1696, 1285 cm^{-1}. Mass

spectrum: *m/z* 39 (86), 55 (76), 79 (100), 95 (46), 125 (100), 140 (52, M^+). Found: C, 67.94; H, 9.05%; calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63%.

E isomer
^{1}H NMR ($CDCl_3$): δ 1.07 (t, 3 H, J = 7.28 Hz, —CH_2CH_3), 1.78 (s, 3 H, =C—CH_3), 2.17 (q, 2 H, J = 7.28 Hz, —CH_2CH_3), 5.67 [s, 1H, =CH (*trans* to the carbonyl group)], 5.96 (d, 1 H, J = 1.40 Hz, =CH), 6.46 [d, 1 H, J = 1.40 Hz (*cis* to the carbonyl group)], 11.15 (br 1 H, OH). ^{13}C NMR ($CDCl_3$): δ 12.37, 17.88, 25.71, 117.98, 128.08, 136.45, 144.10, 172.79.

Z isomer
^{1}H NMR ($CDCl_3$): δ 1.04 (t, 3 H, J = 7.57 Hz, —CH_2CH_3), 1.84 (s, 3 H, =C—CH_3), 2.18 (q, 2 H, J = 7.57 Hz, —CH_2CH_3), 5.65 [s, 1 H, =CH (*trans* to the carbonyl group)], 5.92 (d, 1 H, J = 1.40 Hz, =CH), 6.42 [d, 1 H, J = 1.40 Hz (*cis* to the carbonyl group)], 11.15 (br. 1 H, OH). ^{13}C NMR ($CDCl_3$): δ 12.75, 23.32, 25.55, 119.23, 127.65, 136.21, 144.28, 172.71.

2-Cyclohexylidenemethyl-2-propenoic acid (2e)
IR (neat): 3500–2500, 1696, 1609, 1288 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.56–1.62 (m, 6 H, CH_2), 2.20–2.35 (m, 4 H, =C—CH_2), 5.64 [s, 1 H, =CH (*trans* to the carbonyl group)], 5.87 (s, 1 H, =CH), 6.42 [s, 1 H, =CH (*cis* to the carbonyl group)], 10.00 (br. 1 H, OH). ^{13}C NMR ($CDCl_3$): δ 26.54, 27.74, 28.38, 29.64, 37.51, 116.51, 128.32, 136.01, 146.46, 172.71. Mass spectrum: *m/z* 39 (23), 81 (100), 121 (12), 166 (16, M^+). Found: C, 71.32; H, 8.72; calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%.

2-Ethylidene-4-methylpent-3-enoic acid (2f)
Mixture of E and Z isomers
IR (neat): 3500–2500, 1687, 1628, 1281 cm^{-1}. Mass spectrum: *m/z* 39 (81), 41 (69), 55 (55), 67 (52), 79 (100), 95 (38), 125 (32), 140 (64, M^+). Found: C, 68.51; H, 8.77; calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63%.

E isomer
^{1}H NMR ($CDCl_3$): δ 1.57 (s, 3 H, one of Me_2), 1.74 (d, 3 H, J = 7.13 Hz, =C—CH_3), 1.85 (s, 3 H, one of Me_2), 5.74 (s, 1 H, =CH), 7.02 (q, 1 H, J = 7.13 Hz, =C*H*CH_3), 10.25 (br. 1 H, OH). ^{13}C NMR ($CDCl_3$): δ 15.70, 19.67, 25.33, 117.45, 130.46, 138.21, 141.16, 172.92.

Z isomer
^{1}H NMR ($CDCl_3$): δ 1.70 (s, 3 H, one of Me_2), 1.80 (s, 3 H, one of Me_2), 2.08 (d, 3 H, J = 7.35 Hz, =CCH_3), 5.86 (s, 1 H, =CH), 6.10 (q, 1 H, J = 7.35 Hz, =$CHCH_3$), 10.25 (br 1 H, OH). ^{13}C NMR ($CDCl_3$): δ 15.75, 19.00, 25.47, 122.14, 130.14, 135.76, 140.73, 173.29.

2-Benzylidene-4-methyl-3-pentenoic acid (2g)
M.p. 82–83 °C. IR (KBr): 3500–2500, 1684, 1604, 1273 cm^{-1}. ^{1}H NMR ([D_6]DMSO): δ 1.36 (s, 3 H, one of Me_2), 1.82 (s, 3 H, one of Me_2), 5.92 (s, 1 H, =CH), 7.32–7.42 (m, 3 H, Ph), 7.49 (s, 1 H, =C*H*Ph), 7.57 (d, 2 H, J = 7.30 Hz, Ph), 12.47 (br. 1 H, OH). ^{13}C NMR ($CDCl_3$): δ 19.97, 25.57, 118.39, 128.35, 129.11, 130.29, 135.55, 139.33, 140.96, 173.38. Mass spectrum: *m/z* 39 (46), 79 (41), 91 (41), 115 (51), 128 (69), 143 (79), 157 (100), 187 (44), 202 (25, M^+). Found: C, 77.53; H, 7.36; calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.

2-Isopropylidene-4-methyl-3-pentenoic acid (2h)
IR (neat): 3500–2500, 1683, 1613, 1276 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.55 (s, 3 H, one of Me_4), 1.79 (s, 3 H, one of Me_4), 1.81 (s, 3 H, one of Me_4), 2.12 (s, 3 H, one of Me_4), 5.78 (s, 1 H, =CH), 11.85 (br, 1 H, OH). ^{13}C NMR ($CDCl_3$): δ 19.35, 22.51, 23.84, 25.31, 120.80, 125.13, 136.95, 148.96, 174.08. Mass spectrum: *m/z* 41 (100), 59 (90), 67 (82), 93 (79), 139 (33), 154 (64, M^+). Found: C, 70.01; H, 9.04; calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15%.

2-Ethenyl-3-methyl-2-butenoic acid (2i)[6]
IR (neat): 3500–2500, 1694, 1637, 1243 cm^{-1}. ^{1}H NMR ([D_6]DMSO): δ 1.79 (s, 3 H, one of Me_2), 1.80 (s, 3 H, one of Me_2), 5.05 [d, 1 H, J = 17.30 Hz, HC=CH*H* (*trans*)], 5.11 (d, 1 H, J = 11.00 Hz, HC=C*H*H (*cis*)), 6.60 (dd, J = 17.30, 11.00 Hz, *H*C=CHH), 12.60 (br, 1 H, OH). ^{13}C NMR ([D_6]DMSO): δ 19.63, 23.14, 114.94, 131.33, 131.58, 135.36, 170.53. Mass spectrum: *m/z* 39 (100), 53 (49), 59 (35), 79 (74), 81 (66), 111 (17), 126 (52, M^+). Found: C, 65.96; H, 7.86. calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99%.

Carbonylation of 1 in methanol: synthesis of 3

A mixture of **1** (2 mmol), [$Pd(PPh_3)_2(MeCN)_2$](BF_4)$_2$ (0.04 mmol) and methanol (4 ml) was placed in an autoclave and heated at 50 °C under carbon monoxide pressure (10 atm). After 1 h, the reaction mixture was taken up in diethyl ether and passed through a short Florisil® column to remove palladium complexes. The products were isolated

by column chromatography over silica gel using hexane/ethyl acetate (10:1).

Methyl 2-methylene-3-butenoate (3a)
This afforded the Diels–Alder reaction product **4a** exclusively.

Diels–Alder reaction product of 3a (4a)
IR (neat): 1731, 1715, 1654, 1635, 1437, 1258, 1088 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.81–1.85 (m, 1 H, one H of $=CCH_2CH_2$), 2.08–2.12 (m, 1 H, the other H of $=CCH_2CH_2$), 2.32 (s, 2 H, $=CCH_2CH_2$), 2.79 (d, 1 H, J = 19.46 Hz, one H of $=CHCH_2$), 2.81 (d, 1 H, J = 19.46 Hz, the other H of $=CHCH_2$), 3.69 [s, 3 H, one of $(OMe)_2$], 3.72 [s, 3 H, one of $(OMe)_2$], 5.11 [d, 1 H, J = 17.35 Hz, CH=C*H*H (*trans*)], 5.16 [d, 1 H, J = 10.55 Hz, CH=CH*H* (*cis*)], 5.87 (dd, 1 H, J = 10.55, 17.35 Hz, C*H*=CHH), 6.96 (s, 1 H, =CH. ^{13}C NMR ($CDCl_3$): δ 21.61, 29.35, 32.04, 47.12, 51.45, 52.14, 115.07, 129.25, 136.88, 139.26, 167.16, 174.65. Mass spectrum: *m/z* 45 (100), 59 (69), 83 (62), 105 (53), 123 (49), 142 (60), 165 (46), 182 (37), 224 (4, M^+).

Methyl (*Z*)-2-methylene-3-pentenoate (3b)
IR (neat): 1725, 1652, 1260, 1094 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.77 (dd, 3 H, J = 7.10, 1.74 Hz, $=CCH_3$) 3.77 (s, 3 H, OCH_3), 5.65 [d, 1 H, J = 1.36 Hz, =CH (*trans* to the carbonyl group)], 5.83 (dq, 1 H, J = 11.58, 7.10 Hz, $=CHCH_3$), 6.17 (dq, 1 H, J = 11.58, 1.74 Hz, =CH), 6.39 [d, 1 H, J = 1.36 Hz, =CH (*cis* to the carbonyl group)]. ^{13}C NMR ($CDCl_3$): δ 14.45, 51.94, 124.87, 126.88, 129.26, 135.85, 167.34. Mass spectrum: *m/z* 41 (100), 67 (93), 111 (28), 126 (27, M^+).

Diels–Alder reaction product of 3b (4b)
IR (neat): 1731, 1714, 1651, 1259 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.98 (d, 3 H, J = 7.26 Hz, —CHC*H*$_3$), 1.71 (d, 3 H, J = 6.34 Hz, $=CCH_3$), 1.74–1.78 (m, 1 H, one H of $=CCH_2CH_2$), 2.13–2.17 (m, 1 H, the other H of $=CCH_2CH_2$), 2.24–2.40 (m, 2 H, $=CCH_2$), 2.99–3.02 (m, 1 H, C*H*CH$_3$), 3.65 [s, 3 H, one of $(OMe)_2$], 3.70 [s, 3 H, one of $(OMe)_2$], 5.41 (d, 1 H, J = 15.80 Hz, —C*H*=CHCH$_3$), 5.54 (dq, 1 H, J = 15.80, 6.34 Hz, —CH=C*H*CH$_3$), 6.92 (d, 1 H, J = 4.55 Hz, C=CH). ^{13}C NMR ($CDCl_3$): δ 16.00, 18.07, 21.99, 24.58, 35.42, 49.99, 51.34, 51.89, 126.24, 127.84, 131.28, 143.48, 167.37, 175.18. Mass spectrum: *m/z* 41 (97), 67 (80), 126 (84), 161 ((100), 193 (94), 252 (13, M^+). Found: C, 66.52; H, 8.07; calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99%.

Methyl 4-methyl-2-methylene-3-pentenoate (3c)
IR (neat): 1725, 1653, 1611, 1201, 1141 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.76 (s, 3 H, one of Me_2), 1.85 (s, 3 H, one of Me_2), 3.76 (s, 3 H, OCH_3), 5.54 [s, 1 H, =CH (*trans* to the carbonyl group)], 5.95 (s, 1 H, =CH), 6.31 [s, 1 H, =CH (*cis* to the carbonyl group)]. ^{13}C NMR ($CDCl_3$): δ 19.38, 26.52, 51.83, 120.24, 126.03, 136.96, 138.15, 167.66. Mass spectrum *m/z* 39 (100), 53 (73), 79 (100), 125 (49), 140 (50, M^+). Found: C, 68.83; H, 8.87; calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63%.

Methyl 4-methyl-2-methylene-3-hexenoate (3d)
Mixture of E and Z isomers
IR (neat): 1724, 1652, 1265, 1077 cm^{-1}. Mass spectrum: *m/z* 39 (77), 55 (60), 79 (100), 95 (46), 139 (56), 154 (35, M^+). Found: C, 70.34; H, 9.14; calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15%.

E isomer
^1H NMR ($CDCl_3$):δ 1.07 (t, 3 H, J = 7.48 Hz, —CH_2CH_3), 1.76 (s, 3 H, Me), 2.12–2.18 (m, 2 H, —CH_2CH_3), 3.76 (s, 3 H, OCH_3), 5.55 [d, 1 H, J = 1.66 Hz, =CH (*trans* to the carbonyl group)], 5.96 (t, 1 H, J = 1.37 Hz, =CH), 6.32 [d, 1 H, J = 1.66 Hz, =CH (*cis* to the carbonyl group)]. ^{13}C NMR ($CDCl_3$):δ 12.48, 17.90, 25.78, 51.97, 118.71, 126.12, 137.09, 143.59, 167.90.

Z isomer
^1H NMR ($CDCl_3$):δ 1.03 (t, 3 H, J = 7.57 Hz, —CH_2CH_3), 1.83 (s, 3 H, Me), 2.12–2.18 (m, 2 H, —CH_2CH_3), 3.76 (s, 3 H, OCH_3), 5.53 [d, 1 H, J = 1.71 Hz, =CH (*trans* to the carbonyl group)], 5.92 (s, 1 H, =CH), 6.27 [d, 1 H, J = 1.71 Hz, =CH (*cis* to the carbonyl group)]. ^{13}C NMR ($CDCl_3$):δ 12.86, 22.72, 26.98, 51.97, 119.97, 125.65, 136.85, 143.74, 167.82.

Methyl 2-cyclohexylidene-2-methylpropenoate (3e)
IR (neat): 1726, 1651, 1612, 1279, 1144 cm^{-1}. ^1H NMR ($CDCl_3$):δ 1.53–1.59 (m, 6 H, CH_2), 2.23 (d, 4 H, $=CCH_2$), 3.76 (s, 3 H, OCH_3), 5.51 [s, 1 H, =CH (*trans* to the carbonyl group)], 5.87 [s, 1 H, =CH), 6.27 (s, 1 H, =CH (*cis* to the carbonyl group)]. ^{13}C NMR ($CDCl_3$):δ 26.50, 27.68, 28.31, 29.54, 37.47, 51.82, 117.09, 126.11, 136.50, 145.76, 167.72. Mass spectrum: *m/z* 39 (62), 79 (70), 81 (100), 91 (67), 180 (40, M^+). Found: C, 73.36; H, 9.00; calcd for $C_{11}H_{16}O_2$: C, 73.29; H, 8.95%.

Methyl 2-ethylidene-4-methyl-3-pentenoate (3f)
Mixture of E and Z isomers
IR (neat): 1720, 1633, 1250, 1045 cm^{-1}. Mass spectrum: *m/z* 39 (62), 67 (66), 79 (100), 95 (54), 154 (46, M^+). Found: C, 70.22; H, 9.35; Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15%.

E isomer
^{1}H NMR ($CDCl_3$):δ 1.52 (s, 3 H, one of Me_2), 1.68 (d, 3 H, J = 7.16 Hz, =CHCH_3), 1.85 (s, 3 H, one of Me_2), 3.72 (s, 3 H, OCH_3), 5.74 (s, 1 H, =CH), 6.88 [q, 1 H, J = 7.16 Hz, =CH (*cis* to the carbonyl group)]. ^{13}C NMR ($CDCl_3$):δ 15.29, 19.49, 25.22, 51.40, 117.95, 130.85, 137.12, 138.45, 167.93.

Z isomer
^{1}H NMR ($CDCl_3$):δ 1.67 (s, 3 H, one of Me_2), 1.79 (s, 3 H, one of Me_2), 1.99 (d, 3 H, J = 7.24 Hz, =CHCH_3), 3.75 (s, 3 H, OCH_3), 5.82 (s, 1 H, =CH), 5.93 [q, 1 H, J = 7.24 Hz, =CH (*trans* to the carbonyl group)]. ^{13}C NMR ($CDCl_3$):δ 13.86, 22.48, 31.43, 51.06, 122.42, 131.06, 134.99, 137.39, 167.93.

Methyl 2-benzylidene-4-methyl-3-pentenoate (3g)
IR (neat): 1714, 1615, 1253, 1048 cm^{-1}. ^{1}H NMR ($CDCl_3$):δ 1.39 (d, 3H, J = 1.15 Hz, one of Me_2), 1.83 (d, 3H, J = 1.16 Hz, one of Me_2), 3.77 (s, 3 H, OCH_3), 5.94 (s, 1 H, =CH), 7.22–7.31 (m, 3 H, Ph), 7.52 (d, 2 H, J = 7.24 Hz, Ph) 7.58 (s, 1 H, =C*H*Ph). ^{13}C NMR ($CDCl_3$):δ 19.62, 25.37, 51.80, 118.24, 128.07, 128.49, 128.90, 129.82, 135.63, 138.28, 168.59. Mass spectrum: *m/z* 115 (46), 141 (51), 142 (63), 157 (100), 201 (25), 216 (29, M^+). Found: C, 77.83; H, 7.52; calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

Methyl 2-isopropylidene-4-methyl-3-pentenoate (3h)
IR (neat): 1717, 1200, 1081 cm^{-1}. ^{1}H NMR ($CDCl_3$):δ 1.52 (s, 3 H, one of Me_4), 1.75 (s, 3 H, one of Me_4), 1.80 (s, 3 H, one of Me_4), 2.01 (s, 3 H, one of Me_4), 3.70 (s, 3 H, OCH_3), 5.77 (s, 1 H, =CH). ^{13}C NMR ($CDCl_3$):δ 18.97, 21.94, 22.53, 25.30, 51.05, 120.70, 125.96, 136.02, 143.85, 169.26. Mass spectrum: *m/z* 67(56), 73 (100), 93 (91), 168 (60, M^+). Found: C, 70.68; H, 9.69; calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%.

Methyl 2-ethenyl-3-methyl-2-butenoate (3i)
IR (neat): 1731, 1636, 1218, 1146 cm^{-1}. ^{1}H NMR ($CDCl_3$):δ 1.84 (s, 3 H, one of Me_2), 1.86 (s, 3 H, one of Me_2), 3.80 (s, 3 H, OCH_3), 5.07 [d, 1 H, J = 17.50 Hz, CH=CH*H* (*trans*)], 5.14 [d, 1 H, J = 11.00, CH=C*H*H (*cis*)], 6.57 (dd, J = 17.50, 11.00 Hz, =CH). ^{13}C NMR ($CDCl_3$): δ 19.81, 22.93, 51.52, 114.94, 129.83, 130.44, 137.72, 169.74. Mass spectrum: *m/z* 39 (79), 53 (52), 79 (100), 81 (67), 109 (36), 140 (44, M^+). Found: C, 68.34; H, 8.75; calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.59%.

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