Palladium-Catalysed Cross-Coupling of Iodovinylic Acids with Organometallic Reagents. Selective Synthesis of 3,3-Disubstituted Prop-2-enoic Acids

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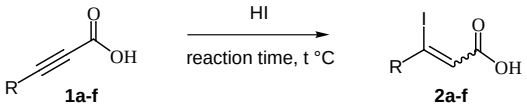
Abstract: 3,3-Disubstituted prop-2-enoic acids were selectively prepared in good yields under mild experimental conditions via palladium-catalysed cross-coupling of 3-substituted 3-iodobut-2-enoic acids with miscellaneous organometallic reagents using dichlorobis(acetonitrile)palladium(II) as catalyst and DMF as solvent.

Key words: coupling reactions, carboxylic acids, organozinc reagents, organotin reagents, palladium catalyst

The transition metal-catalysed sp^2-sp^2 or sp-sp^2 carbon-carbon bond formation has attracted much attention over the last fifteen years.[1–3] For example, palladium catalysed cross-coupling of vinyl bromides, iodides[4] or triflates[5] with vinyl or acetylide organometallic reagents[6] permits the easy preparation of enyne or diene compounds. These classes of important synthetic intermediates[7] are present in numerous natural products.[8] Intermediates bearing two electrophilic centers have been widely used over the past few years as the key step in total synthesis, and some di-electrophiles containing a carboxylic function have been applied in the synthesis of natural products.[9] Thus a new method of synthesis of pure double bond isomers, especially those of the thermodynamically unfavourable *Z* configuration, would be significant. 3-Iodobut-2-enoic acid and its derivatives have proved to be valuable intermediates in organic synthesis owing to the presence of three functional groups,[10] the C–I bond, the conjugated double bond and the carboxylic function. Pursuing our interest in the selective synthesis of dienoic or enynoic acids with defined configuration, we report herein a general study for the coupling of 3-substituted 3-iodobut-2-enoic acids with different organometallic reagents.[11]

Synthesis of β-Iodovinylic Acids (Reaction of Hydroiodic Acid with α,β-Acetylenic Acids)

To explore the different aspects of the cross-coupling reactions of the above mentioned iodo acids, we first focused our attention on their preparation. The procedure developed by Chalcat et al.[12] was extended to numerous α,β-acetylenic acids which are commercially available or prepared using known procedures (Scheme 1). While the hydroiodation reaction mainly yielded *Z*-isomers, it was found that both stereoselectivity and yields were dependent on the reaction temperature and time.



Scheme 1

The hydroiodation of but-3-ynoic acid with hydroiodic acid regioselectively and stereoselectively yielded (*Z*)-3-iodobut-2-enoic acid (**2a**) at 90 °C. Slightly increasing the temperature and reaction time resulted in a mixture of the *E* and *Z* isomers of 3-iodobut-3-enoic acid. Finally, an equimolar mixture was obtained by heating at 130 °C for 12 hours (Table 1, entries 1–5). It should be noted that the use of the lithium iodide–acetic acid couple,[13] yielded identical products with approximately identical selectivity but resulted in lower yields.[14]

The hydroiodation reaction was extended to other alk-2-ynoic acids. The ratio of *Z*- and *E*-isomers was in most cases up to 90% in favour of the *Z*-configuration. Fortunately, pure *Z*-isomers were obtained after crystallization.

Reactivity of 3-Iodoprop-2-enoic Acid Derivatives 2a–2e

Substitution with Organozinc Reagents

The reactivity of iodovinylic acid (*Z*)-**2a** was then studied through the substitution reaction of the iodine atom using various organometallic reagents. We first performed the substitution on **2a** with organocuprate reagents, which were found to promote the reaction. Nevertheless, although the chemical yields were acceptable, a mixture of *Z*- and *E*-isomers was obtained in each case (Scheme 2, Table 2). Grignard reagents or alkyl organocuprates in various solvents (such as ether, THF, HMPA) did not achieve the expected substitution

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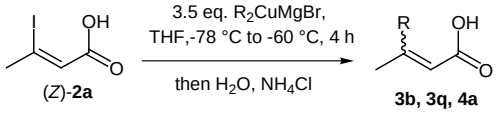
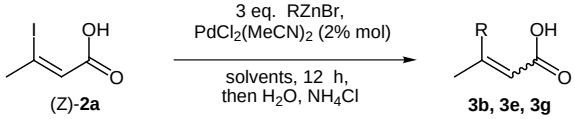
Table 1 Hydroiodation of α,β-Acetylenic Acids

Entry	R	Acid	Time (h)	T (°C)	*Z*:*E*	**2**	Yield (%)
1	Me	**1a**	24	100	77:23	(*Z*)-**2a**:(*E*)-**2a**	78
2[a]	″	**1a**	12	130	50:50	″	69[b]
3[a]	″	″	18	″	″	″	66
4[a]	″	″	24	″	″	″	55
5	″	**1a**	12	90	100:0	(*Z*)-**2a**	82
6	Pr	**1b**	12	90	95:5	(*Z*)-**2b**:(*E*)-**2b**	79[c]
7	Pent	**1c**	6	100	70:30	(*Z*)-**2c**:(*E*)-**2c**	40[c]
8	″	**1c**	4	60	95:5	″	86[c]
9	$MeO-CH_2$	**1d**	1	0	96:4	(*Z*)-**2d**:(*E*)-**2d**	80[b]
10	Ph	**1e**	12	100	polymers	-	0
11	Ph	**1e**	16	75	100:0	(*Z*)-**2e**	70
12	Me_3Si	**1f**	3	100	92:8	(*Z*)-**2f**:(*E*)-**2f**	62

[a] Sealed tube.
[b] 15 % yield of pure (*E*)-**2a** was obtained after four crystallizations.
[c] Pure *Z*-isomer was obtained by crystallization.

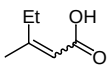
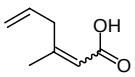
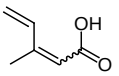


Scheme 2



Scheme 3

Table 2 Substitution of 3-Iodobut-2-enoic acid (*Z*)-**2a** with Organocuprates

Entry	R	Products	*Z*:*E*	**3 or 4**	Yield (%)
1	Et		80:20	(*Z*)-**3b**:(*E*)-**3b**	65
2	Allyl		94:6	(*Z*)-**3p**:(*E*)-**3p**	60
3	Vinyl		55:45	(*Z*)-**4a**:(*E*)-**4a**	52

On the basis of Negishi's work and our previous studies, we decided to use organozinc reagents under palladium (II) catalysis[15] in a mixture of ether−THF solvents (entry 1, Table 3) or THF alone (entries 2, 3, Table 3); this provided fairly good yields of a mixture of *Z*- or *E*-3-substituted acids (Scheme 3). The problem was solved by addition of a polar aprotic solvent such as DMF and the reaction occurred with complete retention of stereochemistry and yielded only the *Z*- or *E*-isomer.

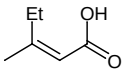
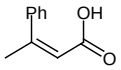
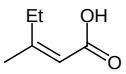
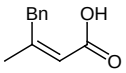
The results are shown in Table 3. The use of THF as a co-solvent was compatible with the reaction (THF facilitated the formation of organozinc reagents by exchange between zinc bromide and organomagnesium reagents)

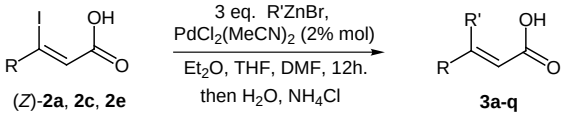
As seen in Table 2, the best arrangement was: 3 equivalents of organozinc, solvents: ether−THF−DMF (2:1:1) and 2 mol% of dichlorobis(acetonitrile)palladium(II). As shown in Scheme 4 and Table 4, substitution reactions with alkyl, phenyl, alkynyl and benzyl groups occurred in good yields, affording 3-substituted but-2-enoic acids **3a**−**q**. No isomerisation product was obtained, giving the procedure general significance.

The introduction of the allyl group (see entry 16, Table 4) to (*Z*)-**2a** through the allylzinc reagent again provided a mixture of the desired product (*Z*)-**3p** (3-methylhex-2,5-dienoic acid, 15%) and product **3q** (68%), derived from dimerisation of the allylzinc reagent and substitution of iodovinylic acid (*Z*)-**2a**.[16,17]

Furthermore, introduction of the allyl unit was possible by a cross-coupling reaction of allyltribuyltin and (*Z*)-**2a** in the presence of tetrakis(triphenylphosphine)palladium(0), with fair yield (70%) (Scheme 5).

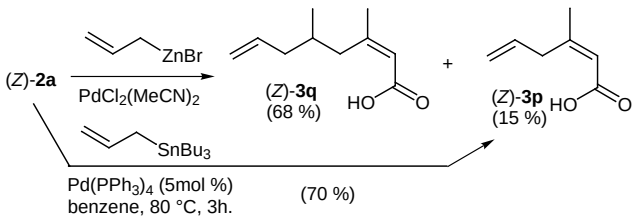
Table 3 Substitution of 3-Iodobut-2-enoic Acid (*Z*)-**2a** in Various Solvents

Entry	R	Solvent	Product	**3**	*Z* :*E*	Yield %
1	Et	Et_2O–THF (1:1)		(*Z*)-**3b**:(*E*)-**3b**	92:8	67
2	Ph	THF		(*Z*)-**3e**:(*E*)-**3e**	90:10	70
3	Et	Et_2O–DMF (1:1)		(*Z*)-**3b**:(*E*)-**3b**	100:0	98
4	Et	Et_2O–THF–DMF (2:1:1)	″	(*Z*)-**3b**:(*E*)-**3b**	100:0	96
3	Bn	THF		(*Z*)-**3g**:(*E*)-**3g**	80:20	72
6	Bn	THF–DMF (1:1)	″	(*Z*)-**3g**:(*E*)-**3g**	100:0	76



(*Z*)-**2a**, **2c**, **2e** **3a-q**

Scheme 4



Scheme 5

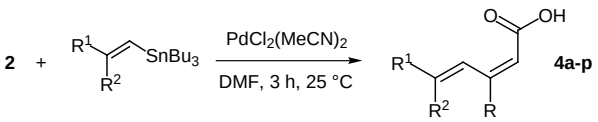
Introduction of Vinyl Units with Organotin Reagents

The introduction of vinyl groups on vinyl iodide (**2**) required the use of organozinc reagents in solutions of THF or HMPA (generated from organolithium or organomagnesium compounds in THF or HMPA solutions), neither of which are appropriate in this reaction. To introduce the vinyl group, the reaction was therefore performed with 1.1 equivalents of vinyltin reagents, which did not affect the carboxylic function under Stille conditions.[18,19] Thus the cross-coupling reaction provided extensive access to dienoic acids with defined stereochemistry, and the configuration of the trisubstituted double bond was firmly established by NOESY NMR experiment (Scheme 6, Table 5).

Table 4 Preparation of 3-Substituted Alk-2-enoic Acids **3a**–**q**

Entry	R	R’	Yield[a](%)	**3**
1	(*Z*)-**2a**	Me	95	**3a**
2	″	Et	98	**3b**
3	″	Bu	80	**3c**
4	″	Me_3SiCH_2	58	**3d**
5	″	Ph	83	**3e**
6	″	*p*-Tol	78	**3f**
7	″	Bn	77	**3g**
8	″		85	**3h**
9	″	*n*-Bu—≡	70	**3i**
10	(*Z*)-**2a**	Me_3Si—≡	78	**3j**
11	(*Z*)-**2c**:(*E*)-**2c**	Me	85b	**3k**
12	″	Bn	82b	**3l**
13	(*Z*)-**2e**	Me	90	**3m**c
14	″	Bn	77	**3n**c
15	(*Z*)-**2e**	*p*-Tol	92	**3o**
16	(*Z*)-**2a**	Allyl	83	**3p**:**3q** (68:15)

[a] Yields obtained after purification on silica gel or crystallization.
[b] Mixture of *E*/*Z*: 95/5 as from the starting material.
[c] *E*-isomer was obtained.



Scheme 6

In summary, 3-iodoalk-2-enoic acids were prepared by the hydroiodation reaction between alk-2-ynoic acids and hydroiodic acid. The stereoselectivity of the reaction was found to be dependent on the reaction time and temperature. The palladium-catalysed cross-coupling reaction of vinyl iodides with organometallic reagents such as copper, zinc or tin reagents yielded 3-substituted alk-2-enoic acids in fair to good yields, without requiring protection of the carboxylic acid functionality.

All reactions were carried out under inert atmosphere (Ar or N_2). THF and Et_2O were dried and freshly distilled from sodium/benzophenone. DMF was dried by distillation over CaH_2. Flash chromatography was carried out with Merck silica gel (silica gel, 230–400 mesh). ^1H NMR spectra were recorded on a Bruker AC 200 (200 MHz) or a Bruker ARX 400 (400 MHz) NMR spectrometer, using $CDCl_3$ as solvent. Data reported using the residual solvent proton resonance of $CDCl_3$ (δ_H = 7.25 ppm) as internal reference,

Table 5 Cross-coupling of (*Z*)-**2a**, (*Z*)-**2d**, (*Z*)-**2e**, (*Z*)-**2f** and (*E*)-**2a** with Vinyltins

Entry	**2**	R^1	R^2	Yield (%)	**4**
1	(*Z*)-**2a**	H	H	75	**4a**
2	″	Me	Me	65	**4b**
3	″	Ph	H	75	**4c**
4	″	$(EtO)_2CH-CH_2$	H	63	**4d**
5	″	Me_3Si	H	64	**4e**
6	(*Z*)-**2d**	H	H	72	**4f**
7	″	Me	Me	68	**4g**
8	″	Ph	H	75	**4h**
9	(*Z*)-2**d**	Me_3Si	H	71	**4i**
10	(*Z*)-**2e**	H	H	72	**4j**
11	(*Z*)-**2f**	H	H	68	**4k**
12	(*Z*)-**2f**	Ph	H	71	**4l**
13	(*Z*)-**2f**	Me_3Si	H	74	**4m**
11	(*E*)-**2a**	H	H	74	**4n**
12	(*E*)-**2a**	Ph	H	68	**4o**
13	(*E*)-**2a**	Me_3Si	H	65	**4p**

were as follows (in order): chemical shift (δ in ppm relative to Me_4Si), multiplicity (s, d, t, q, m, br for singlet, doublet, triplet, quartet, multiplet, broad) and coupling constants (*J* in Hz). ^{13}C NMR was recorded at 50 MHz on the same instruments, using the $CDCl_3$ solvent peak at $\delta_C = 77.0$ ppm as reference. Mass spectra were obtained on a Hewlett Packard (engine 5989A) in direct introduction mode (70eV). IR spectra were recorded on a Nicolet 250 FT-IR spectrophotometer and are reported in cm^{-1}. Melting points were uncorrected. Tetrolic acid, hexynoic acid, octynoic acid, phenylpropiolic acid and 3-trimethylsilylpropenoic acid were commercially available or were prepared by known procedures and 4-methoxybut-3-ynoic acid was prepared by carbonation of 3-methoxypropynylmagnesium bromide. Vinyltributyltin and isobutenyltributyltin were prepared from vinylmagnesium bromide and isobutenylmagnesium bromide and bis(tributyltin)oxide respectively.[20] (*E*)-1-Trimethylsilyl-2-*n*-tributylstannylethylene[21] was prepared by hydrostannation of trimethylsilylacetylene; other vinyltin reagents were prepared by hydrostannation of the corresponding terminal alkynes under radical conditions (AIBN) and used as a thermodynamic mixture of (*E*) and (*Z*)-isomers.[22] Petroleum ether has been abbreviated as PE.

(*Z*)-3-Iodobut-2-enoic Acid [(*Z*)-2a]

In a 100 mL flask, an aq soln of hydroiodic acid (57%, 14.6 mL, 65 mmol) was added dropwise to **1a** (4.2 g, 50 mmol). After stirring for 2 h at 90 °C, a 5% soln of $Na_2S_2O_3$ was added and the reaction mixture was then washed with brine and extracted with Et_2O. The organic phases were dried over $MgSO_4$ and concentrated, yielding 8.5 g (40 mmol, 80%) of **2**. The pure acid (*Z*)-**2a** was obtained by crystallization (PE−Et_2O, 9:1).

Mp: 111 °C.

IR (KBr): 3421, 1693, 1616, 1229, 1082 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.84 (3 H, s), 6.43 (1 H, s), 11.6 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 37, 116.8, 125.2, 169.2.

MS (70 eV): *m/z* (%) = 212 (M^+, 74), 127 (19), 85 (97), 45 (25), 43 (43), 41 (43), 39 (100), 38 (17), 18 (17).

Anal. Calcd for $C_4H_5IO_2$: C, 22.66; H, 2.38; I, 59.86. Found: C, 22.84; H, 2.50; I, 59.62.

(*E*)-3-Iodobut-2-enoic Acid [(*E*)-2a][23]

Mp: 106 °C.

IR (KBr): 3425, 3074, 2921, 2858, 2724, 1696, 1614, 1420, 1330, 1075 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.98 (3 H, s), 6.65 (1 H, s), 10.6 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.5, 124.4, 130.9, 169.6.

MS (70 eV): *m/z* (%) = 212 (M^+, 10), 85 (63), 45 (10), 43 (12), 41 (17), 39 (49), 18 (100), 17 (24).

(*Z*)-3-Iodohex-2-enoic Acid [(*Z*)-2b]

After stirring for 12 h at 90 °C, hex-2-ynoic acid (11.2 g, 0.1 mol) (**1b**) yielded 18.9 g (79% yield) of a 95:5 mixture of *Z* and *E* stereoisomers of 3-iodohex-2-enoic acid. The pure acid (*Z*)-**2b** was obtained by crystallization (PE−Et_2O, 9:1).

Mp: 56 °C.

IR (KBr): 3084, 2964, 2872, 1709, 1616 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.96 (3 H, t, *J* = 7.3 Hz), 1.68 (2 H, sext, *J* = 7.3 Hz), 2.74 (2 H, t, *J* = 7.2 Hz), 6.43 (1 H, s), 9.5 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.6, 22.4, 50.1, 124.4, 124.9, 169.5.

MS (70 eV): *m/z* (%) = 240 (M^+, 23), 113 (33), 95 (31), 67 (53), 65 (11), 57 (50), 45 (35), 43 (46), 41 (100), 39 (80).

Anal. Calcd for $C_6H_9IO_2$: C, 30.02; H, 3.78; I, 52.87. Found: C, 30.12; H, 3.79, I, 52.72.

3-Iodooct-2-enoic Acid [(*Z*)-2c] [(*E*)-2c]

After stirring for 6 h at 60 °C, oct-2-ynoic acid (14 g, 0.1 mol) (**1c**) yielded 22.8 g (85% yield) of a 95:5 mixture of (*Z*)-**2c**:(*E*)-**2c**.

IR (KBr): 3087, 2960, 1712 cm^{-1}.

MS (70 eV): *m/z* = 268 (M, 29), 232 (17), 158 (21), 129 (18), 127 (17), 95 (98), 85 (34), 81(42), 57(35), 55 (69), 45 (24), 43 (69), 41 (100), 39 (85), 29 (86), 28 (63).

E-Isomer:

^1H NMR (200 MHz, $CDCl_3$): δ = 0.86 (3 H, t, *J* = 6.6 Hz), 1.24−1.34 (4 H, m), 1.53−1.64 (2 H, m), 3.07 (2 H, t, *J* = 7.3 Hz), 6.64 (1 H, s), 11.57 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.6, 22, 27, 30.8, 49.2, 130.5, 134.5, 171.4.

Z-Isomer:

^1H NMR (200 MHz, $CDCl_3$): δ = 0.86 (3 H, t, *J* = 6.6 Hz), 1.24−1.34 (4 H, m), 1.53−1.64 (2 H, m), 2.68 (2 H, t, *J* = 7.2 Hz), 6.36 (1 H, s), 11.57 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8, 22.2, 28.8, 30.2, 48.2, 124.2, 125.2, 169.7.

(*Z*)-3-Iodo-4-methoxybut-2-enoic Acid [(*Z*)-2d]

After stirring for 1 h at 0 °C, 4-methoxybut-2-ynoic acid (11.4 g, 0.1 mol) (**1d**) yielded 19.4 g (80% yield) of a 96:4 mixture of (*Z*)-

2d:(*E*)-**2d**. The pure acid (*Z*)-**2d** was obtained by crystallization (PE−Et_2O, 9:1).

Mp: 96 °C.

IR (KBr): 3084, 2930, 2820, 1700, 1626, 1112 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 3.46 (3 H, s), 4.23 (2 H, d, *J* = 1.8 Hz), 6.85 (1 H, t, *J* = 1.8 Hz), 10.5 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 58.5, 81.7, 119.0, 122.9, 169.2.

MS (70 eV): *m/z* (%) = 242 (M^+, 100), 127 (17), 115 (99), 83 (40), 69 (32), 45 (45), 39 (30).

Anal. Calcd for $C_5H_7IO_2$: C, 24.81; H, 2.92; I, 52.44. Found: C, 24.72; H, 2.91; I, 52.21.

(*Z*)-3-Iodo-3-phenylpropenoic Acid [(*Z*)-2e]
After stirring for 16 h at 75 °C, 3-phenylpropynoic acid (14.6 g, 0.1 mol) (**1e**) yielded 19.2 g (70% yield) of (*Z*)-3-iodo-3-phenylpropenoic acid.

Mp: 140 °C.

IR (KBr): 3456, 3063, 1690, 1599, 750 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 6.84 (1 H, s), 7.4−7.85 (5 H, m), 10.05 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 115.9, 128.3, 129.3, 129.5, 130.8, 144.1, 165.7.

MS (70 eV): *m/z* (%) = 147 (M^+–127, 73), 103 (25), 102 (48), 77 (54), 69 (86), 51 (24), 45 (13), 18 (100), 17 (25).

Anal. Calcd for $C_9H_7IO_2$: C, 39.44; H, 2.57; I, 46.31. Found: C, 39.26; H, 2.58; I, 46.42.

(*Z*)-3-Iodo-3-trimethylsilylpropenoic Acid [(*Z*)-2f]
After stirring for 3 h at 100 °C, 14.2 g (0.1 mol) of 3-trimethylsilylpro-2-ynoic acid **1f** yielded 16.7 g (62% yield) of a 92/8 mixture of *Z* and *E* stereoisomers of 3-iodo-3-trimethylsilylpropenoic acid. The pure acid (*Z*)-**2f** was obtained by crystallisation (PE−Et_2O, 9:1).

Mp: 100 °C.

IR (KBr): 3077, 2783, 2573, 1698, 1207 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.30 (9 H, s), 7.04 (1 H, s), 10.50 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = −1.67 (3C), 129.9, 133.8, 169.1.

MS (70 eV): *m/z* (%) = 270 (M^+, 29), 255 (28), 185 (23), 127 (16), 83 (50), 75 (100), 73 (63), 53 (49), 45 (46), 43 (77).

Anal. Calcd for $C_6H_{11}ISiO_2$: C, 26.68; H, 4.1; I, 46.98. Found: C, 26.74; H, 4.08; I, 46.82.

Preparation of Compound (3f); Typical Procedure
ZnBr (7 g, 31 mmol) was added to an ethereal soln of benzylmagnesium bromide, made from magnesium (0.729 g, 30 mmol) and BnBr (5.13 g, 32 mmol) in anhyd Et_2O (30 mL). The soln was stirred overnight at r.t. THF (15 mL) and DMF (15 mL) were added to the newly prepared organozinc until a homogeneous soln was obtained. Next, (*Z*)-**2a** (1.27 g, 10 mmol) diluted in DMF (5 mL) was added dropwise. At the end of the addition, $PdCl_2$(MeCN) (0.52 mg, 0.2 mmol) was added. The mixture was stirred for 12 h at 25 °C, hydrolysed with a cold soln of HCl (1 N) and washed with a sat. soln of NH_4Cl. The organic phase was treated at 0 °C with a soln of NaOH (1 N). The aq soln obtained was acidified and extracted with Et_2O. The solvent was removed and crude **3f** purified using column chromatography on silica gel (PE−Et_2O, 70:30 as an eluent).

(*Z*)-3-Methylpent-2-enoic Acid (3b)
IR: 3071, 2980, 2692, 2578, 1688, 1635, 1173 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.08 (3 H, t, *J* = 7.6 Hz), 1.92 (3 H, d, *J* = 1.3 Hz), 2.64 (2 H, q, *J* = 7.6 Hz), 5.65 (1 H, br q, *J* = 1.3 Hz), 10.65 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.4, 24.7, 26.6, 115.3, 166.2, 172.3.

MS (70 eV): *m/z* (%) = 114 (M^+, 46), 99 (41), 81 (19),71 (22), 69 (40), 68 (23), 67 (28), 55 (24), 53 (37), 45 (27), 43 (56), 41 (97), 39 (100), 38 (21), 29 (30), 27 (53), 18 (34), 17 (21)

Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 62.92; H, 8.76.

(*Z*)-3,5-Dimethylhex-2-enoic Acid (3c)
IR: 3050, 2956, 2876, 2674, 1688, 1636, 1171, 1105 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.9 (6 H, d, *J* = 6.6 Hz), 1.76−1.93 (1 H, m), 1.88 (3 H, s), 2.56 (2 H, d, *J* = 7.5 Hz), 5.71 (1 H, s), 12.2 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.4, 25.7, 27.5, 41.8, 116.8, 162.8, 172.3.

MS (70 eV): *m/z* (%) = 142 (M^+, 24), 127 (23), 100 (89), 85 (47), 83 (38), 82 (64), 71 (80), 57 (19), 55 (32), 45 (25), 43 (100), 42 (17), 41 (78), 39 (53), 29 (27), 27 (43), 18 (84).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67. 45; H, 9.89.

(*Z*)-3-Trimethylsilylmethylbut-2-enoic Acid (3d)
IR: 3167, 2955, 2899, 1677, 1614, 1140 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.06 (9 H, s), 1.83 (3 H, s), 2.37 (2 H, s), 5.50 (1 H, s), 12.33 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.4, 27.9, 28.5, 111.6, 163.8, 172.8.

MS (70 eV): *m/z* (%) = 172 (M^+, 4), 157 (56), 156 (24), 155 (48), 83 (31), 82 (100), 75 (98), 73 (84), 54 (25), 53 (15), 47 (19), 45 (55), 43 (30).

Anal. Calcd for $C_8H_{16}O_2Si$: C, 55.77; H, 9.36. Found: C, 55.61; H, 9.32.

(*Z*)-3-Phenylbut-2-enoic Acid (3e)
Mp: 131 °C.

IR (KBr): 3420, 3063, 2980, 1691, 1635, 1597, 780 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.17 (3 H, d, *J* = 1.5 Hz), 5.87 (1 H, br q, *J* = 1.5 Hz), 7.11−7.39 (5 H, m), 9.67 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.7, 117.1, 126.6, 128 (3C), 140.4, 158.3, 171.2.

MS (70 eV): *m/z* (%) = 162 (M^+, 77), 161 (60), 144 (49), 116 (48), 115 (100), 103 (12),102 (20), 91 (42), 78 (34), 77 (40), 51 (69), 45 (60), 39 (74), 18 (16).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.11; H, 6.18.

(*Z*)-3-*p*-Tolylbut-2-enoic Acid (3f)
Mp: 114 °C.

IR (KBr): 3427, 2962, 2927, 1695, 1621, 1595, 1192, 862 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.16 (3 H, s), 2.34 (3 H, s), 5.84 (1 H, s), 7.11 (4 H, m), 9.1 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.2, 27.5, 116.6, 126.9 (2 C), 128.6 (2C), 137.1, 137.9, 157.9, 171.

MS (70 eV): *m/z* (%) = 176 (M^+, 100), 161 (24), 158 (49), 129 (31), 116 (23), 115 (67), 92 (21), 91 (47), 77 (15), 65 (17), 51 (15), 39 (20).

Anal. Calcd for C $_{11}$ H$_{12}$ O$_2$: C, 74.98; H, 6.86. Found: C, 75.10; H, 6.84.

(*Z*)-3-Benzylbut-2-enoic Acid (3g)
Mp: 72 °C.

IR (KBr): 3029, 2671, 2592, 1683, 1635, 1601, 1192 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.80 (3 H, d, *J* = 1.3 Hz), 4.03 (2 H, s), 5.8 (1 H, br q, *J* = 1.3 Hz), 7.23 (5 H, br s), 10.65 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25, 39.2, 116.8, 126.6, 128.7 (2 C),129.1 (2 C), 138.7, 161.1, 172.3.

MS (70 eV): *m/z* (%) = 176 (M$^+$, 69), 158 (65), 131 (70), 129 (73), 116 (28), 115 (97), 92 (12), 91 (100), 89 (23), 77 (31), 65 (65), 51 (51), 45 (29), 41 (21), 39 (87), 29 (13), 27 (29), 18 (32), 17 (24).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.88; H, 6.89.

(*Z*)-3,7-Dimethyloct-2,6-dienoic Acid (3h)
IR: 3300, 2967, 2920, 1690, 1636, 1181 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.55 (3 H, s), 1.62 (3 H, s), 1.85 (3 H, s), 2.11 (2 H, m), 2.58 (2 H, t, *J* = 7 Hz), 5.05 (1 H, t, *J* = 6.8 Hz), 5.59 (1 H, s), 10.23 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.6, 25, 25.7, 27, 33.8, 116.1, 123.7, 132.5, 163.4, 172.1.

MS (70 eV): *m/z* (%) = 168 (M$^+$, 5), 123 (14), 100 (19), 69 (100), 67 (11), 41 (95), 39 (32), 29 (12), 27 (22).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.42; H, 9.57.

(*Z*)-3-Methylnon-2-en-4-ynoic Acid (3i)
IR: 3350, 2957, 2931, 2873, 2215, 1682, 1610, 1195 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (3 H, t, *J* = 7.2 Hz), 1.21 (2 H, m), 1.56−1.71 (2 H, m), 2.13 (3 H, s), 2.46 (2 H, t, *J* = 7.3 Hz), 5.95 (1 H, s), 11 (1 H, s).

^{13}C NMR (50 MHz, CDCl3): δ = 13.8, 21.5, 22.2, 29, 33.4, 105.8, 110.6, 119, 156.5, 165.1.

MS (70 eV): *m/z* (%) = 166 (M$^+$, 34), 138 (28), 109 (87), 96 (33), 95 (83), 53 (100), 51 (10), 41(23), 29 (18), 27 (37).

(*Z*)-3-Methyl-5-trimethylsilylpent-2-en-4-ynoic Acid (3j)
IR: 3326, 2957, 2149, 1695, 1612 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.23 (9 H, s), 2.13 (3 H, s), 5.98 (1 H, s), 10.55 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.4, 25.3, 109.9, 117.4, 125.1, 154.2, 169.7.

MS (70 eV): *m/z* (%) = 182 (M$^+$, 2), 168 (11), 167 (76), 149 (13), 101 (17), 99 (100), 75 (66), 45 (25), 43 (13).

Anal. Calcd for $C_9H_{14}O_2Si$: C, 59.30; H, 7.74. Found: C, 59.27; H, 7.72.

(*E*)-3-Methyloct-2-enoic Acid (3k)
IR: 3039, 2959, 2931, 2867, 1682, 1637, 1169 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.8 (3 H, t, *J* = 6.4 Hz), 1.03−1.24 (4 H, m), 1.28−1.4 (2 H, m), 2.16 (3 H, d, *J* = 1.5 Hz), 2.35 (2 H, t, *J* = 7 Hz), 5.69 (1 H, br q, *J* = 1.5 Hz), 11 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7, 18.7, 22.3, 26.9, 31.2, 41, 114.8, 163.6, 172.6.

MS (70 eV): *m/z* (%) = 156 (M$^+$, 5), 141 (13), 139 (95), 113 (26), 100 (56), 97 (11), 96 (40), 95 (36), 82 (27), 81 (21), 71 (11), 69 (22), 67 (29), 59 (11), 57 (18), 56 (17), 55 (45), 45 (14), 43 (50), 41 (100), 39 (75), 29 (81), 28 (12), 27 (67).

(*Z*)-3-Benzyloct-2-enoic Acid (3l)
IR: 3469, 3414, 2958, 2931, 1692, 1635, 1602, 1190 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85 (3 H, t, *J* = 6.4 Hz), 1.23−1.25 (4 H, m), 1.37−1.48 (2 H, m), 2.08 (2 H, t, *J* = 7.4 Hz), 4.06 (2 H, s), 5.82 (1 H, s), 7.24−7.27 (5 H, m), 11 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9, 22.4, 27.2, 31.3, 37.3, 37.5, 115.9, 126.3, 128.4, 128.9, 138.6, 164.9, 172.

MS (70 eV): *m/z* (%) = 232 (M$^+$, 63), 176 (17), 158 (83), 131 (45), 130 (35), 129 (64), 128 (35), 127 (12), 117 (45), 115 (51), 92 (13), 91 (91), 77 (16), 65 (30), 55 (19), 43 (18), 41 (32), 39 (25), 29 (31), 28 (100), 27 (20).

(*E*)-3-Phenylbut-2-enoic Acid (3m)
Mp: 91−92 °C.

IR (KBr): 3450, 2933, 1675, 1620, 1595, 868 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.61 (3 H, d, *J* = 4.5 Hz), 6.20 (1 H, q, *J* = 4.5 Hz), 7.35−7.57 (5 H, m), 11.3 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.3, 116.5, 126.4 (2 C), 128.6 (2 C), 129.3, 142, 158.5, 172.6.

MS (70 eV): *m/z* (%) = 162 (M$^+$, 81), 161 (74), 145 (55), 116 (54), 115 (100), 105 (18), 78 (30), 77 (28), 65 (15), 51 (12), 39 (30), 28 (14).

(*E*)-3,4-Diphenylbut-2-enoic Acid (3n)
Mp: 138−139 °C.

IR (KBr): 3080, 1683, 1612, 1598 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.52 (2 H, s), 6.27 (1 H, s), 7.05−7.55 (10 H, m), 11.5 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 36.5, 118, 126.1, 127, 128.4, 128.5, 128.6, 129.3, 138.3, 140.6, 160.2, 172.1.

MS (70 eV): *m/z* (%) = 238 (M$^+$, 100), 221 (17), 220 (46), 193 (56), 192 (74), 91 (50), 178 (26), 147 (21), 115 (72), 91 (47), 77 (31), 65 (27), 51 (23), 39 (18).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.42; H, 5.90.

(*Z*)-3-Phenyl-3-(*p*-tolyl)propenoic Acid (3o)
Mp: 174 °C.

IR (KBr): 3448, 1700, 1612, 1595, 1209, 860 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.37 (3 H, s), 6.26 (1 H, s), 7.05−7.45 (9 H, m), 10.15 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4, 116.2, 128.3, 128.5, 128.6, 129.4, 129.6, 135.4, 138.5, 141.2, 159.2, 171.4.

MS (70 eV): *m/z* (%) = 238 (M$^+$, 100), 237 (44), 193 (25), 179 (17), 178 (43), 165 (16), 115 (18), 77 (8), 51 (9), 39 (8).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.55; H, 5.94.

(*Z*)-3-Methylhex-2,5-dienoic Acid (3p)
(*Z*)-3-iodobut-2-enoic acid (*Z*)-**2a** (2.12 g, 10 mmol) diluted in benzene (20 mL) was added dropwise to a benzene soln of allyltributyltin (4.3 g, 13 mmol). Pd(PPh$_3$)$_4$ (577 mg, 0.5 mmol) was added at the end of the addition. The mixture was stirred for 3 h at 80 °C and then hydrolysed with a sat. soln of KF (25 mL) and acetone (25 mL) after cooling. After vigorous stirring for 2 h, the reaction mixture was filtered, washed with NH_4Cl soln and extracted with Et_2O. The organic layer was then treated with 1N NaOH soln and washed with Et_2O, the aq layer was acidified with 1N HCl soln and extracted with Et_2O. The etheral soln was dried over $MgSO_4$. The solvent was removed and crude **3p** was purified using column chromatography

on silica gel (PE–Et_2O, 85:15 as an eluent) which yielded (*Z*)-3-methylhexa-2,5-dienoic acid (**3p**) (0.88 g, 70%).

IR: 3070, 2974, 2902, 1688, 1638, 1160 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.89 (3 H, d, *J* = 1.2 Hz), 3.36 (2 H, d, *J* = 6.9 Hz), 5.02 (1 H, dd, *J* = 9.9, 1.5 Hz), 5.06 (1 H, dd, *J* = 17, 1.5 Hz), 5.66–5.86 (1 H, m), 5.69 (1 H, br q, *J* = 1.2 Hz), 11.5 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.5, 38.5, 116.7, 117.1, 135, 160.9, 172.3.

MS (70 eV): *m/z* (%) = 126 (M^+, 6), 111 (79), 109 (50), 81 (100), 80 (20), 67 (14), 65 (13), 55 (21), 53 (25), 45 (13), 43 (17), 41 (37), 39 (81), 29 (12), 28 (23), 27 (28).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.57; H, 7.94.

(*Z*)-3,5-Dimethyloct-2,7-dienoic Acid (3q)
IR: 3462, 2980, 1692, 1645, 1633 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.90 (3 H, d, *J* = 6 Hz), 1.79–1.89 (1 H, m), 1.93 (3 H, s), 1.96–2.02 (1 H, m), 2.07–2.14 (1 H, m), 2.6 (1 H, d, *J* = 6.2 Hz), 2.68 (1 H, d, *J* = 7.5 Hz), 5.02–5.04 (1 H, m), 5.02–5.06 (1 H, m), 5.77 (1 H, s), 5.75–5.86 (1 H, m), 10 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.5, 26.1, 32.5, 40.2, 41.8, 116.4, 117.2, 137.6, 163, 172.3.

MS (70 eV): *m/z* (%) = 168 (M^+, 2), 151 (29), 125 (24), 111 (18), 109 (42), 81 (40), 69 (40), 68 (20), 67 (24), 55 (19), 41 (37), 39 (94), 38 (100), 18 (19).

Preparation of Dienoic Acids; General Procedure
(*Z*)-3-Iodobut-2-enoic acid [(*Z*)-**2a**] (2.12 g, 10 mmol) diluted in DMF (5 mL) was added dropwise to a DMF soln of vinyltin reagent (12 mmol). At the end of the addition, $PdCl_2$(MeCN) (129 mg, 0.5 mmol) was added. The mixture was stirred for 3 h at 25 °C then hydrolyzed with a sat. soln of NH_4Cl. The organic layer was then treated with 1N NaOH soln. After washing with Et_2O, the aq layer was acidified with 1N HCl soln and extracted with Et_2O. The etheral soln was dried over $MgSO_4$. The solvent was removed and the crude products were purified using column chromatography on silica gel (PE–Et_2O, 70:30 as an eluent).

(*Z*)-3-Methylpent-2,4-dienoic Acid (4a)
IR: 3140, 1686, 1610, 1190 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.04 (3 H, s), 5.49 (1 H, d, *J* = 10.8 Hz), 5.64 (1 H, d, *J* = 17.5 Hz), 5.76 (1 H, s), 7.8 (1 H, dd, *J* = 17.5, 10.8 Hz), 11.67 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.6, 117.6, 121.5, 134, 153.4, 172.

MS (70 eV): *m/z* (%) = 112 (M^+, 8), 41 (18), 39 (18), 18 (100), 17 (38).

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.31; H, 7.22.

(*Z*)-3,5-Dimethylhex-2,4-dienoic Acid (4b)
Mp: 62–63 °C.

IR (KBr): 3327, 1685, 1628 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.8 (3 H, d, *J* = 0.7 Hz), 1.9 (3 H, d, *J* = 1 Hz), 2.07 (3 H, d, *J* = 1 Hz), 5.7 (1 H, br s), 6.48 (1 H, br s), 10.33 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.4, 25.6, 27.4, 116.6, 123.8, 140, 156, 171.4.

MS (70 eV): *m/z* (%) = 140 (M^+, 11), 125 (100), 79 (43), 39 (36), 27 (19).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.51; H, 8.65.

(2*Z*, 4*E*)-3-Methyl-5-phenylpent-2,4-dienoic Acid (4c)
Mp: 152 °C.

IR (KBr): 3160, 1675, 1615, 1595, 1090 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.11 (3 H, s), 5.75 (1 H, br s), 6.89 (1 H, d, *J* = 17 Hz), 7.15–7.39 (3 H, m), 7.42–7.44 (2 H, m), 8.29 (1 H, d, *J* = 17 Hz), 11.46 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.2, 117.3, 126, 127.6 (2C), 128.8 (2C), 128.9, 136.3, 136.7, 153.2, 171.8.

MS (70 eV): *m/z* (%) = 188 (M^+, 24), 144 (14), 143 (100), 142 (37), 141 (30), 129 (23), 128 (71), 127 (19), 77 (24), 51 (18), 43 (49), 39 (19), 18 (21).

Anal. Calcd for C_{12} $H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.61; H, 6.39.

(2*Z*, 4*E*)-7,7-Diethoxy-3-methylhept-2,4-dienoic Acid (4d)
Mp: 51 °C.

IR (KBr): 3452, 2976, 2927, 1679, 1636, 1601, 1122, 1060 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.21 (6 H, t, *J* = 7 Hz), 2.06 (3 H, s), 2.57 (2 H, br t, *J* = 6.4 Hz), 3.43–3.76 (4 H, qd, *J* = 7, 9.3 Hz), 4.57 (1 H, t, *J* = 5.7 Hz), 5.66 (1 H, s), 6.16 (1 H, dt, *J* = 15.8 , 7.1 Hz), 7.62 (1 H, d, *J* = 15.8 Hz), 9.91(1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.3 (2 C), 21.3, 38, 61.5 (2 C), 102.2, 115.8, 129.9, 134.2, 153.4, 171.6.

MS (70 eV): *m/z* (%) = 137 (15), 111 (17), 103 (89), 81 (13), 79 (15), 75 (77), 47 (100), 43 (11), 41 (14), 39 (11), 29 (32).

Anal. Calcd for C_{12} $H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 62.98; H, 8.79.

(2*Z*, 5*E*)-5-Trimethylsilyl-3-methylpent-2,4-dienoic Acid (4e)
IR: 3427, 3061, 2962, 2760, 1685, 1662, 1614, 871 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.18 (9 H, s), 2.08 (3 H, d, *J* = 1 Hz), 5.81 (1 H, s), 6.43 (1 H, d, *J* = 19.2 Hz), 8.02 (1 H, d, *J* = 19.2 Hz), 9.56 (1 H, s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = −1.6, 20.7, 116.7, 139.1, 140.1, 153.9, 171.5.

MS (70 eV): *m/z* (%) = 184 (M^+, 2), 111 (47), 75 (45), 73 (10), 71 (12), 46 (25), 45 (60), 43 (27), 31 (100).

Anal. Calcd for $C_9H_{16}O_2Si$: C, 58.65; H, 8.75. Found: C, 58.67; H, 8.73.

(*Z*)-3-Methoxymethylpent-2,4-dienoic Acid (4f)
Mp: 98 °C.

IR (KBr): 1689, 1650, 1248 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 3.45 (3 H, s), 4.28 (2 H, d, *J* = 1.3 Hz), 5.50 (1 H, ddd, *J* = 11.3 , 1.2, 1.2 Hz), 5.63 (1 H, ddd, *J* = 18.2, 0.7, 0.7 Hz), 6.06 (1 H, br s), 7.68 (1 H, dd, *J* = 18.2, 11.3 Hz), 9.50 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 58.5, 71.7, 115.8, 120.4, 131.3, 151.4, 171.3.

MS (70 eV): *m/z* (%) = 142 (M^+, 4), 111 (20), 110 (24), 97 (17), 65 (14), 55 (26), 53 (37), 45 (100), 43 (15), 41 (36), 39 (61).

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.10; H, 7.12.

(*Z*)-3-Methoxymethyl-5-methylhex-2,4-dienoic Acid (4g)
IR (KBr): 3400–2500, 1690, 1627, 1181, 1120 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.71 (3 H, s), 1.87 (3 H, s), 3.41 (3 H, s), 4.03 (2 H, s), 6.02 (1 H, br s), 6.08 (1 H, br s), 10.80 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.0, 26.5, 58.3, 74.6, 115.1, 119.8, 140.3, 154.7, 171.5.

MS (70 eV): *m/z* (%) = 155 (M^+–15, 22), 96 (12), 95 (62), 67 (16), 45 (37), 43 (100), 41 (28), 39 (36).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.48; H, 8.31.

(2*Z*,4*E*)-3-Methoxymethyl-5-phenylpent-2,4-dienoic Acid (4h)
Mp: 118 °C.

IR (KBr): 3400−2500, 3082, 3024, 1683, 1622, 1601, 1253 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.50 (3 H, s), 4.43 (2 H, s), 6.13 (1 H, s), 7.04 (1 H, d, *J* = 16.8 Hz), 7.30−7.45 (m, 3 H), 7.55−7.65 (m, 2 H), 8.30 (1 H, d, *J* = 16.8 Hz), 10.80 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 58.4, 72.4, 115.8, 123.0, 127.4, 128.7, 128.9, 135.3, 136.3,151, 171.5.

MS (70 eV): *m/z* (%) = 218 (M^+, 45), 173 (30), 155 (14), 143 (11), 142 (43), 141 (95), 130 (14), 129 (69), 128 (72), 127 (63), 115 (40), 91 (22), 85 (15), 83 (20), 77 (30), 63 (16), 51 (28), 45 (100), 39 (23).

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.51; H, 6.49.

(2*Z*,4*E*)-3-Methoxymethyl-5-trimethylsilylpent-2,4-dienoic Acid (4i)
Mp: 83 °C.

IR (KBr): 3400−2500, 1685, 1663, 1622 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.17 (9 H, s), 3.45 (3 H, s), 4.29 (2 H, s), 6.05 (1 H, s), 6.34 (1 H, d, *J* = 19.7 Hz), 7.87 (1 H, d, *J* = 19.7 Hz), 9.80 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = −1.7, 58.5, 71.7, 115.2, 137.8 (2 C), 152, 171.5.

MS (70 eV): *m/z* (%) = 199 (M^+–15, 2), 141 (49), 111 (17), 110 (83), 75 (100), 73 (47), 65 (17), 61 (19), 59 (39), 53 (17), 45 (78), 43 (29).

Anal. Calcd for $C_{10}H_{18}O_3Si$: C, 56.04; H, 8.46. Found: C, 55.97; H, 8.43.

(2*E*)-3-Phenylpent-2,4-dienoic Acid (4j)
Mp: 76 °C.

IR (KBr): 3217, 3095, 2844, 2693, 1674, 1614, 1206 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.39 (1 H, dd, *J* = 17.5, 6 Hz), 5.69 (1 H, d, *J* = 10.9 Hz), 5.89 (1 H, dd, *J* = 0.6 Hz), 7.28−7.42 (5 H, m), 7.95 (1 H, dd, *J* = 17.5, 10.9 Hz), 11.2 (1 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 117.9, 126.2, 128.4, 129.2, 134, 139.4, 158, 171.9.

MS (70 eV): *m/z* (%) = 174 (M^+, 25), 130 (14), 129 (100), 128 (79), 127 (26), 102 (18), 77 (24), 51 (27), 39 (10), 27 (10).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.77; H, 5.80.

(*E*)-3-Trimethylsilylpent-2,4-dienoic Acid (4k)
Mp: 38 °C.

IR (KBr): 3094, 2959, 2875, 2555, 1691, 1570 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.28 (9 H, s), 5.47 (1 H, dd, *J* = 11.2 Hz), 5.53 (1 H, d, *J* = 18 Hz), 6.07 (1 H, s), 7.62 (1 H, dd, *J* = 18 Hz, 11.2 Hz), 9.80 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.1 (3 C), 122, 127.6, 137.3, 163.3, 172.1.

MS (70 eV): *m/z* = 170 (M, 20), 155 (21), 153 (22), 111 (29), 75 (57), 73 (100), 52 (38), 45 (39), 43 (23).

Anal. Calcd for $C_8H_{14}O_2Si$: C, 56.43; H, 8.29. Found: C, 56.47; H, 8.31.

(2*E*,4*E*)-3-Trimethylsilyl-5-phenylpent-2,4-dienoic Acid (4l)
Mp: 69 °C.

IR (KBr): 2960, 1684, 1563, 1553 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.4 (9 H, s), 6.1 (1 H, d, *J* = 18 Hz), 7.3−7.6 (5 H, m), 8.3 (1 H, d, *J* = 18 Hz), 10.7 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.4 (3 C), 126, 127.8, 128.9, 129.2, 129.3, 137.6, 138.2, 161.5, 171.6.

MS (70 eV): *m/z* (%) = 246 (M^+, 11), 231 (24), 157 (14), 149 (17), 128 (78), 77 (17), 75 (48), 73 (100), 45 (28), 43 (21).

Anal. Calcd for $C_{14}H_{18}O_2Si$: C, 68.25; H, 7.36. Found: C, 68.10; H, 7.30.

(2*E*,4*E*)-3,5-Bis(trimethylsilyl)pent-2,4-dienoic Acid (4m)
Mp: 52 °C.

IR (KBr): 3070, 2952, 1685, 1630 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.16 (9 H, s), 0.26 (9 H, s), 6.05 (1 H, dd, *J* = 1.2, 0.5 Hz), 6.17 (1 H, dd, *J* = 19.6, 0.5 Hz), 7.74 (1 H, dd, *J* = 19.6, 1.2 Hz), 9.50 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.9 (3 C), 0.1 (3 C), 125.2, 139.1, 143.5, 164.2, 171.5.

MS (70 eV): *m/z* (%) = 242 (M^+, 3), 170 (14), 169 (100), 152 (17), 147 (12), 133 (15), 75 (35), 73 (79), 45 (43), 43 (14).

Anal. Calcd for $C_{11}H_{22}O_2Si_2$: C, 54.49; H, 9.15. Found: C, 54.60; H, 9.23.

(*E*) -3-Methylpent-2,4-dienoic Acid (4n)
IR (KBr): 3198, 1685, 1624, 1603, 1254, 1182 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.19 (3 H, s), 5.34 (1 H, d, *J* = 10 Hz), 5.57 (1 H, d, *J* = 18 Hz), 5.73 (1 H, s), 6.34 (1 H, dd, *J* = 18, 10 Hz), 11.85 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.3, 119.4, 120.4, 140, 154.7, 173.

MS (70 eV): *m/z* (%) = 112 (M^+, 74), 111 (73), 97 (40), 95 (78), 83 (16), 69 (32), 67 (49), 66 (26), 65 (29), 56 (16), 51 (17), 50 (12), 45 (24), 43 (21), 41 (65), 39 (100), 38 (18), 29 (13), 27 (35).

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.05; H, 7.21.

(2*E*,4*E*)-3-Methyl-5-phenylpent-2,4-dienoic Acid (4o)
Mp: 148 °C.

IR (KBr): 3450, 3059, 3030, 1687, 1595, 1180 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.48 (3 H, s), 5.99 (1 H, s), 6.88 (1 H, d, *J* = 16.1 Hz), 7.05 (1 H, d, *J* = 16.1 Hz), 7.32−7.44 (3 H, m), 7.48−7.57 (2 H, m) 10.5 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9, 119, 127.1, 128.7, 131.6, 134.9, 136, 154.6, 172.3.

MS (70 eV): *m/z* (%) = 188 (M^+, 19), 144 (13), 143 (100), 142 (37), 141 (30), 129 (24), 128 (84), 127 (23), 115 (38), 91 (16), 77 (32), 65 (15), 51 (35), 45 (12), 39 (42).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.40; H, 6.40.

(2*E*,4*E*)-3-Methyl-5-trimethylsilylpent-2,4-dienoic Acid (4p)
IR (KBr): 3450, 3055, 1691, 1618, 1186 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.18 (9 H, s), 2.32 (3 H, s), 5.88 (1 H, s), 6.45 (1 H, d, *J* = 18.9 Hz), 6.63 (1 H, d, *J* = 18.9 Hz), 9.41 (1 H, br s).

^{13}C NMR (50 MHz, $CDCl_3$): δ = −1.6, 13.4, 119.2, 137.7, 146.2, 155.0, 172.7.

MS (70 eV): *m/z* (%) = 184 (M^+, 2), 169 (33), 111 (42), 77 (10), 75 (100), 73 (19), 45 (26), 43 (20), 39 (15).

Anal. Calcd for $C_9H_{16}O_2Si$: C, 58.65; H, 8.75. Found: C, 58.78; H, 8.77.

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