Microwave-assisted dry oxidation of 3-trialkylsilyl(germyl)prop-2-yn-1-ols to propynals and the direct conversion of acetylenic alcohols to ynimines and enynes

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The efficient solvent-free microwave-assisted oxidation of 3-trialkylsilyl(germyl)prop-2-yn-1-ols with manganese dioxide or pyridinium chlorochromate to propynals and the direct conversion of acetylenic alcohols to the corresponding imines and Knövenagel adducts have been carried out.

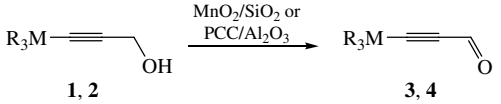
Trialkylsilyl(germyl) propynals hold a special place among propynals in organic synthesis.[1] Silicon and germanium heteroatoms inhibit the triple bond in the uncatalysed addition of S-, N- and C-nucleophiles and promote the orbital controlled cycloaddition of 1,3-dipols. The α-silicon- or germanium-containing groups stabilise the adducts on the carbonyl centre and products of their transformations, while subsequent heterolysis of the M–Csp bond leads to analogues with a terminal triple bond.

The oxidation of corresponding alcohols with activated manganese dioxide or pyridinium chlorochromate (PCC) has advantages over another oxidants for the synthesis of the aldehydes $R_3MC{\equiv}CCHO$ (M = Si or Ge).[2] The oxidation with MnO_2 is slow and requires a large excess of the oxidant. Oxidation with PCC is more rapid but 3-trimethylsilylprop-2-yn-1-al **1** prepared by this method is unstable and polymerises on storage.

The extensive development of aldehyde chemistry in recent years is considerably caused by using microwave irradiation.[3] This technique can be used to carry out a wide range of reactions in short times, with high conversions and selectivity without solvents. It is also of special interest as an example of green chemistry.[4] Synthetic use of propynals is made difficult by problems in isolation owing to volatility, toxicity or high reactivity (*e.g.*, to polymerisation). Propynal is highly mutagenic.[5] The elaboration of a rich synthetic potential of this class of compounds requires a new approach to the synthesis and use of propynals generated *in situ*.

The microwave-assisted solvent-free synthesis of propynals was carried out by the oxidation of 3-organosilyl- or 3-organogermylprop-2-yn-1-ols (**1** or **2**, respectively)† with MnO_2/SiO_2 and PCC/Al_2O_3. The use of 3-organosilyl- or 3-organogermylprop-2-yn-1-als (**3** or **4**, respectively) generated *in situ* in the one pot synthesis of ynimines and Knövenagel adducts from corresponding alcohols was studied. Silica[6] or bentonite[7] supported manganese dioxide provides a rapid and high-yield route to aromatic carbonyl compounds under microwave conditions. Chromium trioxide immobilised on moistened alumina was used for the microwave-assisted oxidation of benzyl alcohols to carbonyl compounds[8] or for the preparation of acyclic α-nitroketones by the oxidation of nitroalkanols[9] under solvent-free conditions. To the best of our knowledge, MnO_2/SiO_2 and PCC/Al_2O_3 have not been used for the oxidation of acetylenic alcohols and for their direct conversion into imines or Knövenagel adducts under microwave irradiation.

The oxidation of alcohols **1**, **2** was performed with 5 equiv. of activated MnO_2 on silica by irradiation in a domestic microwave oven (LG MS-1904H, 700 W) in an ampoule or a screw-capped pressure vial (Scheme 1). This method has considerable advantages over the classical one in shortening the reaction time by a factor of 500 or more, increasing propynal yields (Table 1) and simplicity of isolation. A comparison of propynal yields under microwave with conventional heating (oil bath) shows a specific microwave effect (non-pure thermal effect).[3(c),10] For 3-triethylgermylprop-2-yn-1-al **4**, this effect is greater than that with silicon analogue **3**. The oxidation of alcohol **2** into **4** proceeds more slowly than that of silicon analogue **1** (Table 1, entries 2, 5).



1, **2** **3**, **4**

1, **3** $R_3M = Me_3Si$
2, **4** $R_3M = Et_3Ge$

Scheme 1

The oxidation of alcohols **1** and **2** with PCC/Al_2O_3 at 25 °C proceeds more rapidly than that with MnO_2/SiO_2 (entries 1, 7 and 4, 10 respectively). Note that MnO_2 shows a high thermal effect under microwave exposure.[3(c)] In the oxidation of alcohols **1**, **2**, the thermal effect of PCC/Al_2O_3 on microwave heating is greater than that with MnO_2/SiO_2. The microwave-assisted oxidation of 3-trimethylsilylprop-2-yn-1-ol **1** was performed in mild regime of irradiation [*P* = 280 W (40% power), 50 °C, 2 min]. The oxidation of alcohol **1** by PCC/Al_2O_3 proceeds in a short time (2 min against 2 h at 25 °C) to give propynal **3** in

Table 1 Oxidation of alcohols **1**, **2** to propynals **3**, **4** under variuos conditions.

Entry	R_3M	Oxidant	Reaction time	*T*/°C	Microwave irradiation/ W	Yield (%)
1	Me_3Si	MnO_2/SiO_2	70 h	25	—	95
2	Me_3Si	MnO_2/SiO_2	1 min	70–80	—	50
3	Me_3Si	MnO_2/SiO_2	1 min	70–80	420	70
4	Et_3Ge	MnO_2/SiO_2	16 h	25	—	34
5	Et_3Ge	MnO_2/SiO_2	2 min	125–130	—	25
6	Et_3Ge	MnO_2/SiO_2	2 min	125–130	700	95
7	Me_3Si	PCC/Al_2O_3	2 h	25	—	70
8	Me_3Si	PCC/Al_2O_3	2 min	50	—	70
9	Me_3Si	PCC/Al_2O_3	2 min	50	280	70
10	Et_3Ge	PCC/Al_2O_3	2 h	25	—	82
11	Et_3Ge	PCC/Al_2O_3	2 min	90	—	55
12	Et_3Ge	PCC/Al_2O_3	2 min	50	280	50
13	Et_3Ge	PCC/Al_2O_3	2 min	90–95	700	55

† IR spectra were recorded on a Specord IR-75 spectrometer. NMR spectra were recorded on a Bruker DPX-400 spectrometer. ^1H (400.13 MHz) and ^{13}C NMR (101.61 MHz), tetramethylsilane (TMS) was used as an internal standard.

MnO_2 was prepared by a published method.[23] MnO_2/SiO_2 was obtained by trituration of manganese dioxide (10 g) and LS 5/40 Chemapol silica (18.57 g) for 10–15 min. PCC/Al_2O_3 was prepared by a published method.[24]

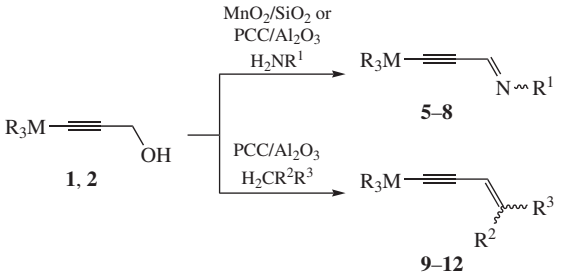
General procedure for the microwave-assisted oxidation of acetylenic alcohols **1**, **2**. Caution! The volume of the reaction mixture should not occupy more than 1/10–1/12 part of the ampoule or vessel volume. The acetylenic alcohol (1.5 mmol) and an oxidant (1.86 g, 5 equiv. MnO_2/SiO_2 or 2.25 g, 1.5 equiv. PCC/Al_2O_3) were mixed thoroughly and the mixture was placed in an ampoule. The ampoule was sealed and dipped into the alumina bath placed into the screw capped vial and irradiated in the domestic microwave oven, with cooling after each impulse (1 min). The temperature was measured by placing a glass thermometer into the alumina bath immediately after stopping the irradiation. The reaction mixture was extracted with CH_2Cl_2 or benzene in the cases of MnO_2/SiO_2 and PCC/Al_2O_3, respectively. The solvent was removed by distillation, and the residue was analysed by ^1H NMR spectroscopy. The yields of propynals **3**, **4** are presented in Table 1.

70% yield (entries 7, 9). Propynal **4** was prepared under various reaction conditions with microwave irradiation in a yield no higher than 55%. Probably, PCC/Al_2O_3 at the heating of the reaction mixture promotes the heterolysis of the Ge–Csp bond in **4**. The cleavage of this bond in germanium-containing acetylenes by acids[11] and the acidic character of PCC[12] were described.

Thus, despite the efficiency of both oxidants in the oxidation of alcohol **1**, MnO_2/SiO_2 is best suitable for the microwave-assisted synthesis of propynals **3**, **4**.

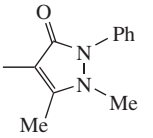
Previously, we studied the one-pot synthesis of acetylenic hydroxyimines from primary-tertiary acetylenic γ-diols and primary amines by oxidation with manganese dioxide.[13] This approach was developed for propargylic alcohols, which were subjected to *in situ* oxidation and imine formation in high yields.[14] Imines are widely applied as analytical, medicinal, polymer and liquid crystalline materials[15] and as synthons in organic synthesis.[16] The conjugation of the triple bond and the imino group in 1,3-aza-enynes provides further synthetic possibilities.[17] The successful use of α,β-acetylenic silicon-containing aldimines as key compounds in the synthesis of thienomycines stimulates the search for synthetic methods and new application of organometal aza-enynes in organic synthesis.[18]

Synthesis of 1,3-aza-enynes **5**–**8** by tandem oxidation-amination of alcohols **1**, **2** with MnO_2/SiO_2 under microwave irradiation for 3–4 min (P = 700 W) was carried out with a yield of 75–96% (Scheme 2).‡ Note that the synthesis of ynimines according to ref. 14 requires 10 equiv. of MnO_2. Our method requires no more than 5 equiv. of oxidant.



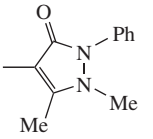
5 $R_3M = Me_3Si$, $R^1 = CH_2Ph$

6 $R_3M = Me_3Si$, R^1 =



7 $R_3M = Et_3Ge$, $R^1 = CH_2Ph$

8 $R_3M = Et_3Ge$, R^1 =



9 $R_3M = Me_3Si$, R^2 = MeCO, R^3 = COOMe

10 $R_3M = Me_3Si$, $R^2 = R^3$ = CN

11 $R_3M = Et_3Ge$, R^2 = MeCO, R^3 = COOMe

12 $R_3M = Et_3Ge$, $R^2 = R^3$ = CN

Scheme 2

1,3-Aza-enynes **6**, **8** were obtained from alcohols **1**, **2** at 25 °C for 2 h in 50 and 62% yields, respectively (Table 2). Imines **5**, **7** were obtained in low yields (20–30%); however, benzylamine was not detected in the reaction mixture (^{1}H NMR). Since the oxidation of starting alcohols **1**, **2** to propynals **3**, **4** with PCC/Al_2O_3 proceeds effectively at room temperature (Table 1), low yields of ynimines **5**, **7** are probably caused by complexing of amine with oxidant. Sufficient yields of imines **6**, **8** compare to **5**, **7** were possibly achieved due to the lower basicity of 4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one than that of benzylamine. Taking into account the obtained results, we have not used a microwave technique for the preparation of ynimines with PCC/Al_2O_3.

Imines **6**, **8** were isolated only as the *E*-isomers independent of the oxidant. In imines **5**, **7**, the ratio of *E*/*Z* depends on the type of the oxidant. Thus, the *E*-configuration isomer domi-

Table 2 One-pot synthesis of acetylenic imines (**5**–**8**) and enynes (**9**–**12**) under various conditions.

Entry	R_3M	Product	Method[a]	Reaction time	Yield (%)
1	Me_3Si	**5**	A	3 min	89
2			B	2 h	30
3		**6**	A	4 min	87
4			B	2 h	50
5	Et_3Ge	**7**	A	3 min	75
6			B	2 h	20
7		**8**	A	4 min	96
8			B	2 h	62
9	Me_3Si	**9**	C	2 h	56
10			D	2 min	54
11			B	2 h	60
12			A*	4 min	4
13		**10**	C	2 h	70
14			D	2 min	2
15			A*	4 min	traces
16	Et_3Ge	**11**	C	2 h	40
17			B	2 h	60
18		**12**	C	2 h	80

[a]A, MnO_2/SiO_2 (5 equiv.), microwave irradiation (700 W); B, PCC/Al_2O_3 (3 equiv.), 25 °C; C, PCC/Al_2O_3 (1.5 equiv.), 25 °C; D, PCC/Al_2O_3 (1.5 equiv.), microwave irradiation (280 W), 45–50 °C; A*, MnO_2/SiO_2 (5 equiv.), microwave irradiation (700 W), 85–90 °C.

‡ *General procedure for microwave-assisted solvent-free tandem oxidation–amination of alcohols* **1**, **2** *to imines* **5**–**8**. A mixture of an acetylenic alcohol (1.5 mmol), an amine (1.5 mmol) and MnO_2/SiO_2 (1.86 g, 5 equiv.) was placed in a 20 cm^3 screw-capped pressure vial and irradiated in the domestic microwave oven. The reaction times are presented in Table 2. The reaction mixture was extracted with $CHCl_3$:MeOH (10:1), and the solvents were removed *in vacuo*. The residue was analysed by ^{1}H NMR and IR spectroscopy. Compounds **5**[25] and **7**[26] are known.

For **5**: a dark red oil (89%). ^{1}H NMR ($CDCl_3$) δ: (*E*)-isomer 0.26 (s, 9H, Me_3Si), 4.71 (d, 2H, CH_2), 7.26–7.39 (m, 5H, Ph), 7.59 (t, 1H, CH=N); (*Z*)-isomer 0.30 (s, 9H, Me_3Si), 4.89 (d, 2H, CH_2), 7.26–7.39 (m, 5H, Ph), 7.63 (t, 1H, CH=N). ^{13}C NMR, δ: (*E*)-isomer –0.60 (Me_3Si), 65.53 (CH_2), 98.21 (≡*C*–CH=), 101.40 (Si–C≡), 127.22 (CH, Ph), 128.19 (CH, Ph), 128.49 (CH, Ph), 138.90 (C, Ph), 145.59 (HC=N); (*Z*)-isomer –0.57 (Me_3Si), 59.97 (CH_2), 96.48 (≡*C*–CH=), 105.11 (Si–C≡), 126.93 (CH, Ph), 128.05 (CH, Ph), 128.40 (CH, Ph), 137.72 (C, Ph), 143.48 (HC=N). IR (film, ν/cm^{-1}): 1590, 1600 (C=N, Ph), 2165 (C≡C).

For **6**: yellow crystals (87%), mp 186–187 °C (benzene). ^{1}H NMR ($CDCl_3$) δ: 0.23 (s, 9H, Me_3Si), 2.42 (s, 3H, Me), 3.16 (s, 3H, Me–N), 7.10–7.58 (m, 5H, Ph), 8.95 (s, 1H, CH=N). ^{13}C NMR δ: –0.38 (Me_3Si), 10.10 (Me), 35.22 (Me–N), 100.60 (≡*C*–CH=), 103.87 (Si–C≡), 118.14 (=*C*–Me), 124.97 (CH, Ph), 127.39 (CH, Ph), 128.97 (C, Ph), 129.27 (CH, Ph), 134.25 (N–C=), 140.68 (CH=N), 151.66 (C=O). IR (KBr, ν/cm^{-1}): 1510 (C=C), 1580, 1590 (C=N, Ph), 1650 (C=O), 2170 (C≡C). Found (%): C, 65.40; H, 6.76; N, 13.38; Si, 9.11. Calc. for $C_{17}H_{21}N_3OSi$ (%): C, 65.55; H, 6.79; N, 13.48; Si, 9.01.

For **7**: a dark red oil (75%). ^{1}H NMR, δ: (*E*)-isomer 0.80–0.95 [m, 6H, (MeCH_2)$_3$Ge], 1.00–1.20 [m, 9H, (*Me*CH_2)$_3$Ge], 4.84 (d, 2H, CH_2), 7.19–7.33 (m, 5H, Ph), 7.57 (t, 1H, CH=N); (*Z*)-isomer 0.80–0.95 [m, 6H, (MeCH_2)$_3$Ge], 1.00–1.20 [m, 9H, (*Me*CH_2)$_3$Ge], 4.64 (d, 2H, CH_2), 7.19–7.33 (m, 5H, Ph), 7.55 (t, 1H, CH=N). ^{13}C NMR, δ: (*E*)-isomer 5.58 [(MeCH_2)$_3$Ge], 8.88 [(*Me*CH_2)$_3$Ge], 65.39 (CH_2), 97.93 (≡*C*–CH=), 104.59 (Ge–C≡), 127.13 (CH, Ph), 128.19 (CH, Ph), 128.44 (CH, Ph), 139.07 (C, Ph), 145.77 (HC=N); (*Z*)-isomer 5.48 [(MeCH_2)$_3$Ge], 8.81 [(*Me*CH_2)$_3$Ge], 59.84 (CH_2), 97.71 (≡*C*–CH=), 102.57 (Ge–C≡), 126.84 (CH, Ph), 128.04 (CH, Ph), 128.35 (CH, Ph), 137.91 (C, Ph), 143.72 (CH=N). IR (film, ν/cm^{-1}): 1590, 1600 (C=N, Ph), 2165 (C≡C).

For **8**: yellow crystals (96%), mp 103–104 °C (hexane–benzene). ^{1}H NMR, δ: 0.91 [q, 6H, (MeCH_2)$_3$Ge], 1.10 [t, 9H, (*Me*CH_2)$_3$Ge], 2.40 (s, 3H, Me), 3.13 (s, 3H, Me–N), 7.10–7.50 (m, 5H, Ph), 8.97 (s, 1H, CH=N). ^{13}C NMR, δ: 5.76 [(MeCH_2)$_3$Ge], 9.03 [(*Me*CH_2)$_3$Ge], 11.27 (Me), 35.48 (Me–N), 100.42 (≡*C*–CH=), 105.18 (Ge–C≡), 118.42 (=*C*–Me), 125.04 (CH, Ph), 127.44 (CH, Ph), 129.14 (C, Ph), 129.40 (CH, Ph), 134.53 (N–C=), 141.48 (CH=N), 151.78 (C=O). IR (KBr, ν/cm^{-1}): 1520 (C=C), 1575, 1590 (C=N, Ph), 1650 (C=O), 2160 (C≡C). Found (%): C, 60.05; H, 7.07; N, 10.58; Ge, 18.15. Calc. for $C_{20}H_{27}N_3OGe$ (%): C, 60.04; H, 7.30; N, 10.50; Ge, 18.15.

nates in the case of MnO_2/SiO_2 (the ratios of *E*/*Z* isomers are 20:1 for **5** and 7:1 for **7**), but the use of PCC/Al_2O_3 leads to an increase in the *Z*-isomer content (*E*/*Z* = 2:3 for imine **5** and *E*/*Z* = 1:1 for **7**).

The Knövenagel reaction is a mild and effective method for the preparation of enynes from propynals. Silicon-containing enynes were prepared from trimethylsilylpropynal and CH acids in the presence of piperidine as a catalyst in 42–74% yield.[19] The Knövenagel condensation can be catalysed with bases[19] or acids, including Lewis acids,[20] K-10/$ZnCl_2$[21] and SiO_2.[22] However, the tandem oxidation/Knövenagel condensation is unknown.

Alcohols **1**, **2** are readily converted into 1,3-enynes **10**, **12** using PCC/Al_2O_3 (1.5 equiv.) and malonodinitrile at 25 °C for 2 h in 70–80% yield (Scheme 2),§ but Knövenagel adducts were not observed under microwave conditions. Probably, malonodinitrile undergoes an oxidative transformation under dielectric heating, as the conversion of **1** to aldehyde **3** without malonodinitrile proceeds in high yield (entry 9, Table 1). Compounds **9**, **11** were obtained in 60% yield using 3 equiv. of the oxidant at 25 °C for 2 h (Table 2). The microwave-assisted conversion of alcohol **1** to 1,3-enyne **9** with PCC/Al_2O_3 (1.5 equiv.) proceeds for 2 min in 55% yield. PCC/Al_2O_3 plays the role of an acid catalyst for Knövenagel condensation in the direct conversion of acetylenic alcohols to 1,3-enynes.

Manganese dioxide on silica is unsuitable for the direct conversion of acetylenic alcohols into 1,3-enynes at room temperature and conventional heating in an oil bath (85–90 °C) or under micriwave conditions. The ^{1}H NMR control of the reaction mixture from alcohol **1**, malonodinitrile and MnO_2/SiO_2 under microwave irradiation (700 W, 4 min) shows only 30% conversion of the alcohol and trace compound **9**. Since alcohol **1** is readily converted into propynal **3** under the same conditions (Table 1), the low activity of the oxidant may be ascribed to the adsorption of the CH acid by MnO_2/SiO_2.

In conclusion, the microwave-assisted solvent-free oxidation of α-silicon- and germanium-containing propargyl alcohols with manganese dioxide on silica or pyridinium chlorochromate on alumina gave corresponding propynals. The one-pot, solvent-free microwave-assisted syntheses of ynimines (using MnO_2/SiO_2) and 1,3-enynes (using PCC/Al_2O_3) from 3-organosilyl-(germyl)prop-2-yn-1-ols have been developed. The efficiency of an oxidant in these tandem processes depends on the nature of N- or C-nucleophiles.

§ *General procedure for microwave-assisted solvent-free direct conversion of alcohols* **1**, **2** *into 1,3-enynes* **9**–**12**. A mixture of an acetylenic alcohol (1.5 mmol), a CH acid (1.5 mmol) and PCC/Al_2O_3 (2.25 g, 1.5 equiv.) was placed in an ampoule, which was dipped into the alumina bath and irradiated in the domestic microwave oven. The reaction times presented in Table 2. The reaction mixture was extracted with benzene, and the solvent was removed *in vacuo*. The residue was analysed by ^{1}H NMR spectroscopy. Compounds **9** and **10** are known.[17]

For **9**: ^{1}H NMR ($CDCl_3$) δ: (*E*)-isomer 0.19 (s, 9H, Me_3Si), 1.35 (t, 3H, *Me*CH_2O), 2.44 (s, 3H, Me), 4.33 (q, 2H, MeC*H*$_2$O), 6.74 (s, 1H, CH=C); (*Z*)-isomer 0.19 (s, 9H, Me_3Si), 1.28 (t, 3H, *Me*CH_2O), 2.33 (s, 3H, Me), 4.24 (q, 2H, MeC*H*$_2$O), 6.73 (s, 1H, CH=C). ^{13}C NMR, δ: (*E*)-isomer 2.62 (Me_3Si), 16.97 (OCH_2*Me*), 32.40 (*Me*–C=O), 64.71 (O*C*H$_2$Me), 93.04 (≡*C*–CH=), 102.46 (Si–*C*≡), 125.12 (*C*H=C), 155.64 (CH=*C*), 170.36 (*C*OOEt), 203.53 (C=O); (*Z*)-isomer 2.67 (Me_3Si), 17.06 (OCH_2*Me*), 33.69 (*Me*–C=O), 64.77 (O*C*H$_2$Me), 98.65 (≡*C*-CH=), 105.73 (Si–*C*≡), 126.63 (*C*H=C), 157.74 (CH=*C*), 170.60 (*C*OOEt), 204.87 (C=O).

For **10**: ^{1}H NMR ($CDCl_3$) δ: 0.28 (s, 9H, Me_3Si), 6.89 (s, 1H, CH=C). ^{13}C NMR, δ: 2.11 (Me_3Si), 99.19 (CH=*C*), 100.76 (≡*C*–CH=), 113.86 (CN), 115.11 (Si–C≡), 127.67 (CN), 144.18 (*C*H=C).

For **11**: ^{1}H NMR ($CDCl_3$) δ: (*E*)-isomer 0.91 [q, 6H, (MeC*H*$_2$)$_3$Ge], 1.09 [t, 9H, (*Me*CH_2)$_3$Ge], 1.33 (t, 3H, *Me*CH_2O), 2.44 (s, 3H, Me), 4.30 (q, 2H, MeC*H*$_2$O), 6.77 (s, 1H, CH=C); (*Z*)-isomer 0.90 [q, 6H, (MeC*H*$_2$)$_3$Ge], 1.08 [t, 9H, (*Me*CH_2)$_3$Ge], 1.27 (t, 3H, *Me*CH_2O), 2.31 (s, 3H, Me), 4.22 (q, 2H, MeC*H*$_2$O), 6.74 (s, 1H, CH=C). ^{13}C NMR, δ: (*E*)-isomer 5.68 [(Me*C*H$_2$)$_3$Ge], 8.93 [(*Me*CH_2)$_3$Ge], 14.10 (OCH_2*Me*), 30.40 (*Me*–C=O), 61.62 (O*C*H$_2$Me), 100.53 (≡*C*–CH=), 112.60 (Ge–*C*≡), 122.72 (*C*H=C), 142.36 (CH=*C*), 163.90 (*C*OOEt), 192.30 (C=O); (*Z*)-isomer 5.68 [(Me*C*H$_2$)$_3$Ge], 8.93 [(*Me*CH_2)$_3$Ge], 14.10 (OCH_2*Me*), 30.40 (*Me*–C=O), 61.62 (O*C*H$_2$Me), 100.66 (≡*C*–CH=), 113.86 (Ge–*C*≡), 124.05 (*C*H=C), 143.31 (CH=*C*), 165.56 (*C*OOEt), 193.90 (C=O).

For **12**: ^{1}H NMR ($CDCl_3$) δ: 0.98 [q, 6H, (MeC*H*$_2$)$_3$Ge], 1.12 [t, 9H, (*Me*CH_2)$_3$Ge], 6.90 (s, 1H, CH=C). ^{13}C NMR, δ: 5.71 [(Me*C*H$_2$)$_3$Ge], 8.94 [(*Me*CH_2)$_3$Ge], 95.48 (CH=*C*), 99.68 (≡*C*–CH=), 111.09 (CN), 112.34 (Ge–C≡), 126.43 (CN), 141.54 (*C*H=C).

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