

Transition Metal-Free Addition of Ketones or Nitriles to 1,3-Dienes

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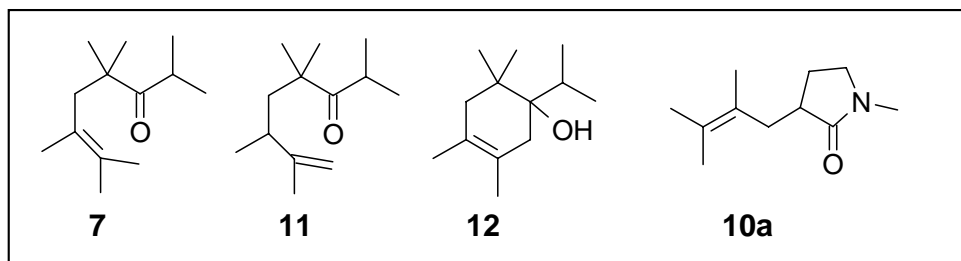
Supplementary Data

General. All reactions were performed under N₂. GLC and prep GLC: *Hewlett Packard* 6890 instrument equipped with a flame ionization detector (250°C) coupled to a *Hewlett Packard* Chemstation 6.03; capillary columns *Chrompack*. *DB-Wax* (15 m, 0.25 mm), and *DB-1* (15 m, 0.25 mm). Silica gel for flash chromatography is a 60 Å quality in prepacked cartridges from *Interchim*. Bulb-to-bulb distillation: *Büchi GKR-50* oven; b.p. correspond to the air temp. NMR: *Bruker WH-400*, *Bruker AMX-360*; ¹H at 400 and ¹³C at 90 MHz in CDCl₃; chemical shifts in ppm rel. to TMS. MS: *Varian MAT-112* spectrometer (*ca.* 70 eV); intensities in % rel to the base peak (100%).

Large scale procedure for the production of 7.

A 5 L plastic coated pyrex reactor with screw cap (7 bars max.) is charged with 2,4-dimethyl-3-pentanone (864 g), 2,3-dimethyl-1,3-butadiene (520 g), *t*BuOK (400g), DMF (1.6 L) and heated at 80°C during 72 h (internal pressure less than 1 bar). Then the reaction mixture (4 litres) was cooled down and poured into 6 litres of water and 3 litres of cyclohexane. The organic layer was washed two times with 2 litres of water. After solvent evaporation, 1.29 kg of crude product was obtained and distilled with 100 g of *Primol* as ballast (7mbar, Eb 85°C) affording 1.03 kg of pure (99.8 GC %) **7** (83% yield).

Typical procedure for the hydrogenation. Molar solutions of olefins in ethylacetate in the presence of 10% weight of Pd/C 5% humid - *Degussa* were shaken in a *Parr* apparatus under 3 bar of hydrogen. The mixtures were filtered and the filtrates evaporated, affording the reduced compound in nearly quantitative yields (95–100%).



7 2,4,4,6,7-PENTAMETHYL-6-OCTEN-3-ONE

MS: *m/z* (%): 196 [M⁺] (15), 178 (1), 153 (5), 135 (7), 125 (16), 114 (100), 99 (22), 83 (78), 71 (20), 69 (57), 55 (33), 43 (26), 41 (27). ¹³C-NMR: δ = 20.3 (*q*, 2C), 20.9 (*q*), 21.0 (*q*), 21.5 (*q*), 24.3 (*q*, 2C), 34.4 (*d*), 42.3 (*t*), 49.5 (*s*), 124.5 (*s*), 128.3 (*s*), 220.3 ppm (*s*). ¹H-NMR: δ = 1.05 (*d*, J=6Hz, 6H), 1.13 (*s*, 6H), 1.61 (*s*, 3H), 1.66 (*s*, 6H), 2.34 (*s*, 2H), 3.16 ppm (*m*, 1H).

10a 3-(2,3-DIMETHYLBUT-2-ENYL)-1-METHYLPYRROLIDIN-2-ONE

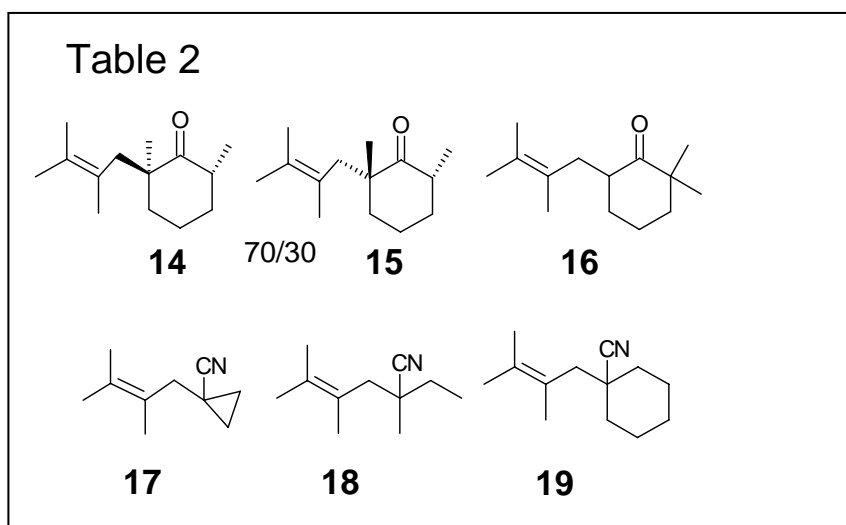
MS: m/z (%): 181 [M^+] (19), 166 (3), 152 (1), 138 (1), 112 (6), 99 (100), 98 (67), 67 (5), 55 (11), 41 (12). $^{13}\text{C-NMR}$: δ = 18.0 (*q*), 20.5 (*q*), 20.7 (*q*), 24.3 (*t*), 29.8 (*q*), 35.3 (*t*), 41.0 (*d*), 47.7 (*t*), 125.3 (*s*), 126.1 (*s*), 176.9 ppm (*s*). $^1\text{H-NMR}$: δ = 1.63 (*s*, 3H), 1.66 (*s*, 3H), 1.67 (*s*, 3H), 2.04 (*m*, 1H), 2.23 (*dd*, $J=14$, 10Hz, 1H), 2.43–2.57 (*m*, 2H), 2.85 (*s*, 3H), 3.25–3.33 ppm (*m*, 2H).

11 (\pm)-2,4,4,6,7-PENTAMETHYL-7-OCTEN-3-ONE

MS: m/z (%): 196 [M^+] (1), 178 (1), 153 (2), 135 (4), 125 (4), 114 (51), 99 (7), 83 (21), 71 (20), 69 (100), 55 (10), 43 (31), 41 (35). $^{13}\text{C-NMR}$: δ = 18.6 (*q*), 20.0 (*q*), 20.3 (*q*), 22.1 (*q*), 24.3 (*q*), 24.9 (*q*), 34.3 (*d*), 38.2 (*d*), 44.0 (*t*), 48.2 (*s*), 109.9 (*t*), 150.9 (*s*), 219.8 ppm (*s*). $^1\text{H-NMR}$: δ = 0.98 (*d*, $J=7\text{Hz}$, 3H), 1.03 (*d*, $J=7\text{Hz}$, 6H), 1.16 (*d*, $J=7\text{Hz}$, 6H), 1.49 (*dd*, $J=14$, 6Hz, 1H), 1.65 (*s*, 3H), 1.76 (*dd*, $J=14$, 7Hz, 1H), 2.22 (*m*, 1H), 3.09 (*sept*, $J=7\text{Hz}$, 1H), 4.63 (*brs*, 1H), 4.70 ppm (*brs*, 1H).

12 (\pm)-1-ISOPROPYL-3,4,6,6-TETRAMETHYL-3-CYCLOHEXEN-1-OL

MS: m/z (%): 196 [M^+] (4), 178 (16), 153 (33), 135 (100), 121 (35), 119 (15), 114 (62), 109 (19), 99 (21), 91 (11), 71 (16), 69 (11), 55 (9), 43 (37), 41 (18). $^{13}\text{C-NMR}$: δ = 18.8 (*q*), 18.9 (*q*), 19.5 (*q*), 20.0 (*q*), 23.9 (*q*), 25.3 (*q*), 32.8 (*d*), 37.8 (*t*), 38.1 (*s*), 47.4 (*t*), 76.5 (*s*), 122.3 (*s*), 124.8 ppm (*s*). $^1\text{H-NMR}$: δ = 0.94 (*s*, 3H), 0.97 (*s*, 3H), 0.97 (*d*, $J=7\text{Hz}$, 3H), 1.01 (*d*, $J=7\text{Hz}$, 3H), 1.46 (*d*, $J=7\text{Hz}$, 1H), 1.54 (*brs*, 1H), 1.61 (*brs*, 6H), 1.81 (*d*, $J=7\text{Hz}$, 1H), 2.03 (*sept*, $J=7\text{Hz}$, 1H), 2.19 (*d*, $J=7\text{Hz}$, 1H), 2.23 ppm (*d*, $J=7\text{Hz}$, 1H).



14 (\pm)-*R*-2-(2,3-DIMETHYL-2-BUTENYL)-2,6-DIMETHYLCYCLOHEXANONE
MS: m/z (%): 208 [M^+] (4), 193 (2), 126 (100), 111 (25), 83 (35), 55 (25), 41 (13).

15 (\pm)-*R*-2-(2,3-DIMETHYL-2-BUTENYL)-2,6-DIMETHYLCYCLOHEXANONE
MS: m/z (%): 208 [M^+] (8), 190 (6), 126 (100), 111 (28), 83 (37), 55 (35), 41 (13).

16 (\pm)-6-(2,3-DIMETHYL-2-BUTENYL)-2,2-DIMETHYLCYCLOHEXANONE
MS: m/z (%): 208 [M^+] (62), 193 (20), 190 (20), 175 (5), 165 (28), 137 (19), 126 (100), 111 (95), 95 (37), 83 (45), 70 (45), 55 (64), 41 (48). $^{13}\text{C-NMR}$: δ = 18.4 (*q*), 20.6 (*q*), 20.7 (*q*), 21.7 (*t*), 25.4 (*q*), 25.8 (*q*), 33.7 (*t*), 33.8 (*t*), 41.9 (*t*), 44.9 (*d*), 45.5 (*s*), 125.5 (*s*), 125.8 (*s*), 217.1 ppm (*s*). $^1\text{H-NMR}$: δ = 1.05 (*s*, 3H), 1.18 (*s*, 3H), 1.21 (*m*, 1H), 1.52 (*m*,

1H), 1.57 (*s*, 3H), 1.61 (*s*, 3H), 1.63 (*s*, 3H), 1.66 (*m*, 1H), 1.76 (*m*, 1H), 1.81 (*m*, 1H), 2.03 (*m*, 1H), 2.12 (*dd*, *J*=14, 8Hz, 1H), 2.35 (*dd*, *J*=14, 1Hz, 1H), 2.64 ppm (*m*, 1H).

17 1-(2,3-DIMETHYL-2-BUTENYL)CYCLOPROPANECARBONITRILE

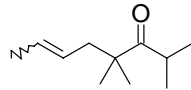
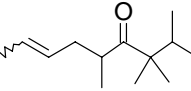
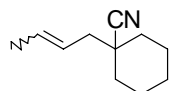
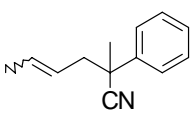
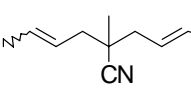
MS: *m/z* (%): 149 [M^+] (48), 134 (100), 119 (28), 106 (25), 83 (65), 55 (77), 41 (58). ^{13}C -NMR: δ = 9.0 (*s*), 13.7 (*t*, 2C), 18.8 (*q*), 20.7 (*q*, 2C), 38.4 (*t*), 123.4 (*s*), 123.8 (*s*), 128.7 ppm (*s*). ^1H -NMR: δ = 1.15 (*m*, 1H), 1.25 (*m*, 2H), 1.62 (*m*, 2H), 1.68 (*s*, 3H), 1.70 (*s*, 3H), 1.70 (*m*, 3H), 1.82 (*s*, 3H), 1.95 (*d*, *J*=13Hz, 2H), 2.35 ppm (*s*, 2H).

18 (\pm)-2-ETHYL-2,4,5-TRIMETHYL-4-HEXENENITRILE

MS: *m/z* (%): 165 [M^+] (10), 83 (100), 55 (50), 41 (19). ^{13}C -NMR: δ = 9.4 (*s*), 20.4 (*q*), 20.9 (*q*), 21.4 (*q*), 23.8 (*q*), 33.3 (*t*), 37.6 (*s*), 43.6 (*t*), 123.1 (*s*), 125.0 (*s*), 130.1 ppm (*s*). ^1H -NMR: δ = 1.09 (*t*, *J*=7Hz, 3H), 1.27 (*s*, 3H), 1.50 (*dq*, *J*=14, 7Hz, 1H), 1.70 (*s*, 6H), 1.70 (*m*, 1H), 1.82 (*s*, 3H), 2.28 (*d*, *J*=14Hz, 1H), 2.40 ppm (*d*, *J*=14Hz, 1H).

19 1-(2,3-DIMETHYL-2-BUTENYL)CYCLOHEXANECARBONITRILE

MS: *m/z* (%): 191 [M^+] (10), 109 (15), 83 (100), 55 (29), 41 (15). ^{13}C -NMR: δ = 20.8 (*q*), 20.9 (*q*), 21.6 (*q*), 23.1 (*t*, 2C), 25.4 (*t*), 36.2 (*t*, 2C), 39.5 (*s*), 45.0 (*t*), 122.7 (*s*), 124.2 (*d*), 130.0 ppm (*s*). ^1H -NMR: δ = 0.85 (*m*, 2H), 1.20 (*m*, 2H), 1.70 (*s*, 3H), 1.72 (*s*, 3H), 1.76 (*s*, 3H), 2.30 ppm (*s*, 2H).

20		<i>E/Z</i> =50/50
21		<i>E/Z</i> =75/25
22		<i>E/Z</i> =88/12
23		<i>E/Z</i> =75/25
24		<i>EE/ EZ</i> =70/30

20E/20Z 2,4,4-TRIMETHYL-6-OCTEN-3-ONE

Two identical MS spectra: *m/z* (%): 168 [M^+] (5), 153 (2), 139 (1), 125 (52), 97 (85), 81 (11), 71 (27), 69 (27), 55 (100), 43 (46).

Minor isomer with a double bond in terminal position MS: *m/z* (%): 168 [M^+] (0.2), 125 (3), 114 (76), 97 (52), 81 (12), 71 (28), 55 (100), 43 (46).

Hydrogenation of this mixture gives the single following compound: 2,4,4-TRIMETHYL-3-OCTANONE

MS: *m/z* (%): 114 (20), 99 (29), 71 (17), 57 (100), 43 (35), 41 (20). ^{13}C -NMR: δ = 14.0 (*q*), 20.2 (*q*, 2C), 23.4 (*t*), 24.0 (*q*, 2C), 27.1 (*t*), 33.9 (*d*), 39.3 (*t*), 48.2 (*s*), 220.1 ppm (*s*).

$^1\text{H-NMR}$: δ = 0.88 (*t*, $J=8\text{Hz}$, 3H), 1.02 (*d*, $J=7\text{Hz}$, 3H), 1.12 (*s*, 3H), 1.12 (*m*, 2H), 1.28 (*m*, 2H), 1.50 (*m*, 2H), 3.11 ppm (*sept*, $J=7\text{Hz}$, 1H).

21E/21Z (\pm)-2,3,3,5-TETRAMETHYL-7-NONEN-4-ONE

Two identical MS spectra: m/z (%): 196 [M^+] (3), 154 (1), 113 (19), 111 (22), 85 (100), 83 (73), 55 (37), 43 (47). E major, based on the $^{13}\text{C-NMR}$ shift of the methyl on the double bond (17.8 ppm for the *E* isomer and 12.8 ppm for the *Z* isomer).

Hydrogenation of this mixture gives the single following compound: (\pm)-2,3,3,5-TETRAMETHYL-4-NONANONE

MS: m/z (%): 198 (2), 142 (3), 113 (12), 85 (100), 57 (8), 43 (32). $^{13}\text{C-NMR}$: δ = 14.0 (*q*), 17.7 (*q*), 17.8 (*q*), 17.9 (*q*), 20.1 (*q*), 20.5 (*q*), 22.8 (*t*), 29.6 (*t*), 32.7 (*d*), 34.0 (*t*), 39.7 (*d*), 51.2 (*s*), 220.1 ppm (*s*). $^1\text{H-NMR}$: δ = 0.81 (*d*, $J=7\text{Hz}$, 3H), 0.82 (*d*, $J=7\text{Hz}$, 3H), 0.88 (*t*, $J=8\text{Hz}$, 3H), 1.01 (*s*, 3H), 1.02 (*d*, $J=7\text{Hz}$, 3H), 1.06 (*s*, 3H), 1.19 (*m*, 1H), 1.30 (*m*, 3H), 1.52 (*m*, 1H), 2.05 (*sept*, $J=7\text{Hz}$, 1H), 2.95 ppm (*m*, 1H).

22E 1-[(2*E*)-2-BUTENYL]CYCLOHEXANECARBONITRILE

MS: m/z (%): 163 [M^+] (6), 109 (100), 82 (20), 67 (15), 55 (42), 41 (9). $^{13}\text{C-NMR}$: δ = 18.0 (*q*), 23.0 (*t*, 2C), 25.4 (*t*), 35.4 (*t*, 2C), 39.2 (*s*), 43.5 (*t*), 123.6 (*s*), 124.5 (*d*), 130.3 ppm (*d*). $^1\text{H-NMR}$: δ = 1.20 (*m*, 4H), 1.62 (*m*, 2H), 1.70 (*d*, $J=6\text{Hz}$, 3H), 1.73 (*m*, 2H), 1.93 (*m*, 2H), 2.20 (*d*, $J=7\text{Hz}$, 2H), 5.55 ppm (*m*, 2H).

23 (\pm)-2-METHYL-2-PHENYL-4-HEXENENITRILE

23E MS: m/z (%): 185 [M^+] (3), 131 (100), 116 (5), 103 (17), 77 (10), 55 (27).

23Z MS: m/z (%): 185 [M^+] (2), 131 (100), 116 (5), 103 (17), 77 (11), 55 (23).

Minor isomer MS: m/z (%): 185 [M^+] (56), 170 (84), 156 (53), 143 (100), 129 (61), 115 (47), 103 (28), 91 (13), 77 (32).

Hydrogenation of this mixture gives the single following compound: (\pm)-2-METHYL-2-PHENYLHEXANENITRILE

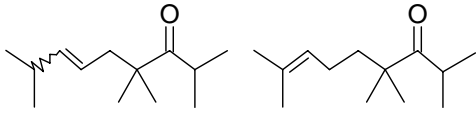
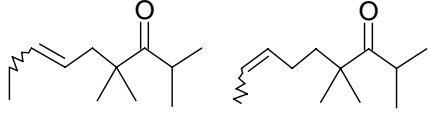

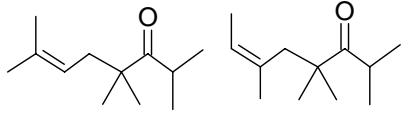
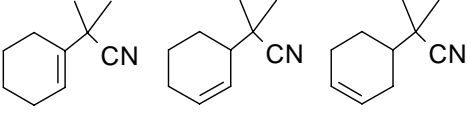
MS: m/z (%): 187 [M^+] (15), 131 (100), 116 (8), 103 (18), 91 (5), 77 (9). $^{13}\text{C-NMR}$: δ = 13.8 (*q*), 22.5 (*t*), 27.6 (*q*), 27.8 (*t*), 41.9 (*t*), 42.5 (*s*), 123.6 (*s*), 125.4 (*d*, 2C), 127.6 (*d*), 128.9 (*d*, 2C), 140.4 ppm (*s*). $^1\text{H-NMR}$: δ = 0.86 (*t*, $J=7\text{Hz}$, 3H), 1.14–1.34 (*m*, 3H), 1.35–1.49 (*m*, 1H), 1.70 (*s*, 3H), 1.89 (*m*, 2H), 7.29 (*m*, 1H), 7.35–7.40 (*m*, 2H), 7.42–7.45 ppm (*m*, 2H).

24EE (4*E*)-2-[(2*E*)-2-BUTENYL]-2-METHYL-4-HEXENENITRILE

MS: m/z (%): 163 [M^+] (4), 148 (6), 135 (7), 108 (22), 106 (15), 94 (33), 82 (19), 68 (13), 55 (100), 53 (11). $^{13}\text{C-NMR}$: δ = 18.0 (*q*, 2C), 23.4 (*q*), 37.0 (*s*), 41.9 (*t*, 2C), 124.1 (*s*), 124.6 (*d*, 2C), 130.7 ppm (*d*, 2C). $^1\text{H-NMR}$: δ = 1.24 (*s*, 3H), 1.72 (*d*, $J=6\text{Hz}$, 6H), 2.12 (*dd*, $J=14$, 7Hz, 1H), 2.27 (*dd*, $J=14$, 7Hz, 1H), 5.43–5.52 (*m*, 1H), 5.59 ppm (*dd*, $J=15$, 6Hz, 1H).

Hydrogenation of the mixture **24EE/24EZ** gives the single following compound: 2-BUTYL-2-METHYLHEXANENITRILE

MS: m/z (%): 167 [M^+] (0.2), 166 (1), 152 (4), 138 (2), 124 (13), 111 (62), 110 (40), 96 (46), 83 (33), 68 (100), 57 (30), 55 (21), 41 (43). $^{13}\text{C-NMR}$: δ = 13.9 (*q*, 2C), 22.8 (*t*, 2C), 24.0 (*q*), 27.0 (*t*, 2C), 39.2 (*t*, 2C), 36.7 (*s*), 124.7 ppm (*s*). $^1\text{H-NMR}$: δ = 0.94 (*t*, $J=7\text{Hz}$, 6H), 1.29 (*s*, 3H), 1.31–1.40 (*m*, 4H), 1.40–1.48 (*m*, 6H), 1.54–1.63 ppm (*m*, 2H).

Table 4	
	25/26 40 / 10 / 50%
	27/28 30 / 50 / 7 / 13%
	29 70 / 30%
	30/31 58 / 33 / + oth.9%
	32/33/34 35 / 20 / 45%

25/26 2,4,4,8-TETRAMETHYL-6-NONEN-3-ONE/2,4,4,8-TETRAMETHYL-7-NONEN-3-ONE

25E (40% of the mixture) MS: m/z (%): 196 [M^+] (3), 153 (16), 125 (12), 114 (35), 83 (55), 69 (100), 55 (25), 43 (35), 41 (35).

25Z (10% of the mixture) MS: m/z (%): 196 [M^+] (1), 181 (1), 167 (1), 153 (8), 125 (15), 114 (64), 83 (58), 69 (100), 55 (25), 43 (37), 41 (37).

26 (50% of the mixture) MS: m/z (%): 114 (100), 99 (23), 69 (60), 43 (22), 41 (30).

Hydrogenation of this mixture gives the single following compound: 2,4,4,8-TETRAMETHYL-3-NONANONE

MS: m/z (%): 183 (1), 155 (1), 127 (27), 114 (38), 85 (36), 71 (100), 57 (53), 43 (65), 41 (32). $^{13}\text{C-NMR}$: δ = 20.2 (*q*), 22.6 (*q*, 2C), 22.7 (*t*), 24.0 (*q*, 2C), 27.8 (*d*), 33.9 (*d*), 39.7 (*t*), 39.8 (*t*), 48.3 (*s*), 220.2 ppm (*s*). $^1\text{H-NMR}$: δ = 0.85 (*d*, $J=7\text{Hz}$, 6H), 1.03 (*d*, $J=7\text{Hz}$, 6H), 1.05 (*m*, 1H), 1.12 (*s*, 6H), 1.14 (*m*, 4H), 1.49 (*m*, 2H), 3.11 ppm (*sept*, $J=7\text{Hz}$, 1H).

27/28 2,4,4-TRIMETHYL-6-NONEN-3-ONE/2,4,4-TRIMETHYL-7-NONEN-3-ONE

27Z (30% of the mixture) MS: m/z (%): 182 [M^+] (2), 139 (5), 111 (38), 95 (5), 71 (21), 69 (100), 55 (15), 43 (24), 41 (20).

27E (50% of the mixture) MS: m/z (%): 182 [M^+] (3), 139 (32), 111 (20), 95 (6), 71 (19), 69 (100), 55 (28), 43 (28), 41 (23).

Two identical spectra for **28E/28Z** (20% of the mixture) MS: m/z (%): 114 (100), 111 (14), 99 (19), 95 (9), 71 (21), 69 (63), 55 (60), 43 (33), 41 (20).

Hydrogenation of this mixture gives the single following compound: 2,4,4-TRIMETHYL-3-NONANONE

MS: m/z (%): 114 (32), 113 (28), 71 (100), 57 (82), 43 (55), 41 (30). $^{13}\text{C-NMR}$: δ = 14.0 (*q*), 20.2 (*q*, 2C), 22.6 (*t*), 24.0 (*q*, 2C), 24.6 (*t*), 32.5 (*t*), 33.9 (*d*), 39.6 (*t*), 48.3 (*s*), 220.2

ppm (s). $^1\text{H-NMR}$: δ = 0.87 (*t*, $J=7\text{Hz}$, 3H), 1.02 (*d*, $J=7\text{Hz}$, 6H), 1.12 (*s*, 6H), 1.15 (*m*, 2H), 1.26 (*m*, 4H), 1.50 (*m*, 2H), 3.11 ppm (*sept*, $J=7\text{Hz}$, 1H).

29E/29Z 2,2,5-TRIMETHYL-4-HEPTENENITRILE

29Z (30% of the mixture) MS: m/z (%): 151 [M^+] (32), 136 (38), 123 (26), 108 (30), 95 (48), 83 (44), 69 (100), 55 (100), 41 (74).

29E (70% of the mixture) MS: m/z (%): 151 [M^+] (6), 136 (2), 109 (2), 95 (3), 83 (80), 69 (13), 55 (100), 41 (25).

30 2,4,4,7-TETRAMETHYL-6-OCTEN-3-ONE

MS: m/z (%): 182 [M^+] (11), 167 (4), 139 (52), 114 (34), 111 (67), 69 (100), 55 (25), 43 (28), 41 (29). $^{13}\text{C-NMR}$: δ = 17.9 (*q*), 20.1 (*q*, 2C), 23.7 (*q*, 2C), 25.9 (*q*), 34.1 (*d*), 37.6 (*t*), 48.7 (*s*), 120.0 (*d*), 133.9 (*s*), 220.1 ppm (*s*). $^1\text{H-NMR}$: δ = 1.02 (*d*, $J=7\text{Hz}$, 6H), 1.12 (*s*, 6H), 1.60 (*s*, 3H), 1.69 (*s*, 3H), 2.21 (*d*, $J=7\text{Hz}$, 2H), 3.09 (*sept*, $J=7\text{Hz}$, 1H), 5.00 ppm (*m*, 1H).

31 2,4,4,6-TETRAMETHYL-6-OCTEN-3-ONE

MS: m/z (%): 182 [M^+] (8), 167 (3), 153 (3), 139 (18), 114 (23), 111 (77), 69 (100), 55 (28), 43 (31), 41 (28). $^{13}\text{C-NMR}$: δ = 13.5 (*q*), 17.9 (*q*), 20.2 (*q*, 2C), 24.0 (*q*), 24.6 (*q*), 34.5 (*d*), 37.7 (*t*), 48.6 (*s*), 123.1 (*d*), 132.4 (*s*), 220.0 ppm (*s*).

32/33/34 2-(1-CYCLOHEXEN-1-YL)-2-METHYLPROPANENITRILE/(\pm)-2-(2-CYCLOHEXEN-1-YL)-2-METHYLPROPANENITRILE/(\pm)-2-(3-CYCLOHEXEN-1-YL)-2-METHYLPROPANENITRILE

32 MS: m/z (%): 149 [M^+] (9), 134 (3), 120 (1), 107 (4), 91 (3), 81 (100), 79 (21), 77 (6), 69 (8), 53 (6). $^{13}\text{C-NMR}$: δ = 128.8 (*d*), 136.6 ppm (*s*).

33 MS: m/z (%): 149 [M^+] (3), 81 (100), 79 (22), 77 (6), 69 (9), 53 (7). $^{13}\text{C-NMR}$: δ = 125.7 (*d*), 131.1 ppm (*d*).

34 MS: m/z (%): 149 [M^+] (6), 134 (2), 117 (3), 107 (4), 91 (3), 81 (100), 79 (62), 71 (19), 69 (25), 56 (10), 54 (14), 53 (14). $^{13}\text{C-NMR}$: δ = 125.5 (*d*), 126.9 ppm (*d*).

Hydrogenation of this mixture gives the single following compound: 2-CYCLOHEXYL-2-METHYLPROPANENITRILE

MS: m/z (%): 83 (20), 69 (100), 55 (36), 41 (18). $^{13}\text{C-NMR}$: δ = 24.5 (*q*, 2C), 26.0 (*t*), 26.3 (*t*, 2C), 27.9 (*t*, 2C), 36.3 (*s*), 45.8 (*d*), 125.0 ppm (*s*). $^1\text{H-NMR}$: δ = 1.06–1.35 (*m*, 6H), 1.31 (*s*, 3H), 1.69 (*m*, 1H), 1.80–1.93 ppm (*m*, 4H).