



SUPPLEMENTARY MATERIAL TO
**Synthesis of five- and six-membered 1,3,3-trimethyl-2-
-(trimethylsilyl)cycloalkenes: a novel preparation of
alkyl/alkenyl/aryl 2,5,5-trimethyl-1-cyclopentenyl ketones**

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SPECTRAL DATA OF THE PRODUCTS

1,3,3-Trimethyl-2-(trimethylsilyl)cyclopentene (I).¹ Light yellow oil; yield: 81–83 %; b.p.: 65–70 °C/4 mm. IR (film, cm⁻¹): 2958, 2866, 1647, 1458, 1377, 1261, 1095, 1016, 802. ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.08 (9H, s, –SiMe₃), 0.98 (6H, s, [–CH₃]₂), 1.48–1.51 (2H, t, J = 7.2 Hz, –CH₂–), 1.70 (3H, s, –CH₃), 2.17–2.21 (2H, t, J = 7.2 Hz, –CH₂–). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 1.5 (–SiMe₃), 17.9, 28.7, 28.8, 39.0, 41.8, 51.7, 142.7 [C (sp²)], 149.6 [C (sp²)]. GC–MS (*m/z* (relative intensity)): 182 (13, M⁺), 167 (72), 108 (28), 93 (25), 73 (100 %, base peak), 74 (46), 59 (58), 45 (62).

1,3,3-Trimethyl-2-(trimethylsilyl)cyclohexene (2). New compound. Light yellow oil; yield: 75–77 %; b.p.: 77–80 °C/2 mm; Anal. Calcd. for C₁₂H₂₄Si: C, 73.38; H, 12.32 %. Found: C, 73.58; H, 12.42 %; IR (film, cm⁻¹): 2950, 2866, 1649, 1581, 1452, 1456, 1255, 1095, 1051, 840, 808, 761; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.22 (9H, s, –SiMe₃), 1.05 (6H, s, [–CH₃]₂), 1.33–1.36 (2H, m, –CH₂–), 1.53–1.59 (2H, m, –CH₂–), 1.75 (3H, s, –CH₃), 1.90–1.94 (2H, t, J = 8 Hz, –CH₂–). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 3.8, 19.3, 24.7, 29.5, 34.6, 35.5, 41.3, 139.1 [C (sp²)], 142.8 [C (sp²)]. GC–MS (*m/z* (relative intensity)): 196 (3, M⁺), 181(8), 123 (10), 122 (31), 107 (25), 73 (100 %, base peak), 59 (15), 45 (24), 43 (15).

2,2,5-Trimethylcyclopentanone hydrazone (II). New compound. White needles; yield: 75 %; Anal. Calcd. for C₈H₁₆N₂: C, 68.52; H, 11.5; N, 19.98 %. Found: C, 68.34; H, 11.65; N, 20.30 %; IR (film, cm⁻¹): 3357, 3211, 2962, 2871, 1737, 1461, 1380, 1361, 1255, 1080, 1006. ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.07 (3H, s, –CH₃), 1.13 (3H, s, –CH₃), 1.16–1.18 (3H, d, J = 8 Hz, –CH₃), 1.46–

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-1.56 (2H, *m*, -CH-), 1.68-1.75 (1H, *m*), 1.93-2.00 (1H, *m*), 2.76-2.81 (1H, *m*), 4.8 (2H, *s*, -NH₂). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 15.9, 27.2, 27.6, 30.2, 32.8, 38.2, 42.1, 168.6 [C (sp²)]. GC-MS (*m/z* (relative intensity)): 140 (35, M⁺), 125 (46), 124 (54), 109 (10), 108 (17), 95 (21), 81 (26), 69 (28), 67 (29), 55 (63), 41 (100 %, base peak).

2,2,6-Trimethylcyclohexanone hydrazone (12).² White needles; yield: 78 %; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.12 (6H, *s*, [-CH₃]₂), 1.16 (3H, *d*, *J* = 8 Hz, -CH₃), 1.53-1.58 (2H, *m*, -CH₂-), 1.59-1.63 (2H, *m*, -CH₂-), 1.72-1.77 (2H, *m*, -CH₂-), 2.95-2.99 (1H, *m*, -CH-), 4.69 (2H, *s*, -NH₂). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 17.6, 17.8, 26.9, 29.3, 29.9, 32.1, 38.06, 40.8, 163.02 [C (sp²)]. GC-MS (*m/z* (relative intensity)): 154 (5, M⁺), 139 (3), 122 (5), 109 (4), 95 (5), 81 (10), 67 (14), 56 (31), 41 (100 %, base peak).

1,1-Dichloro-2,2,5-trimethylcyclopentane (13). New compound. Yellow oil; yield: 33 %; b.p.: 60-63 °C/4 mm. Anal. Calcd. for C₈H₁₄Cl₂: C, 53.06; H, 7.79 %. Found: C, 53.47; H, 7.29 %; IR (film, cm⁻¹): 2966, 2939, 2875, 1506, 1455, 1371, 1217, 1105, 1002, 973, 914, 848, 784, and 761. ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.17 (3H, *s*, -CH₃), 1.22-1.24 (3H, *d*, *J* = 8 Hz, -CH₃), 1.27 (3H, *s*, -CH₃), 1.36-1.43 (1H, *m*), 1.55-1.62 (1H, *m*), 1.73-1.78 (1H, *m*), 1.81-1.93 (1H, *m*), 2.65-2.71 (1H, *m*, -CH-). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 15.0, 24.0, 27.0, 27.3, 35.0, 46.8, 50.5, 106.9 (-CCl₂). GC-MS (*m/z* (relative intensity)): 184 (1, M+4), 182 (3, M+2), 180 (1, M⁺), 144 (1), 131 (2), 129 (7), 109 (29), 104 (16), 97 (22), 77 (9), 70 (23), 69 (100 %, base peak), 56 (19), 55 (9), 42 (14), 41 (30).

1,1-Dichloro-2,2,6-trimethylcyclohexane (14). New compound. Yellow oil; yield: 42 %; b.p.: 72-75 °C/4 mm; Anal. Calcd. for C₉H₁₆Cl₂: C, 55.40; H, 8.26 %. Found: C, 55.12; H, 8.45 %; IR (film, cm⁻¹): 2987, 2937, 2864, 1456, 1373, 1326, 1278, 1242, 1215, 1175, 1122, 1058, 989; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.21-1.23 (3H, *d*, *J* = 8 Hz, -CH₃), 1.24 (3H, *s*, -CH₃), 1.28 (3H, *s*, -CH₃), 1.36-1.41 (1H, *m*), 1.46-1.61 (4H, *m*), 1.82-1.85 (1H, *m*), 2.36-2.37 (1H, *m*, -CH-) ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 18.0, 20.6, 24.8, 27.3, 32.0, 36.5, 42.6, 44.8, 108.6 (-CCl₂). GC-MS (*m/z* (relative intensity)): 198 (1, M+4), 196 (3, M+2), 194 (1, M⁺), 145 (4), 143 (2), 123 (20), 109 (6), 107 (21), 93 (6), 91 (16), 81 (32), 69 (34), 53 (39), 41 (100, base peak).

2-Chloro-1,3,3-trimethylcyclopentene (17). New compound. Yellow oil; yield: 31 %; b.p.: 60-63 °C/4 mm. Anal. Calcd. for C₈H₁₃Cl: C, 66.43; H, 9.06 %. Found: C, 66.23; H, 9.27 %; IR (film, cm⁻¹): 2960, 2867, 1664, 1461, 1363, 1259, 1006, 939; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.04 (6H, *s*, [-CH₃]₂), 1.69 (3H, *s*, -CH₃), 1.76 (2H, *t*, *J* = 4.4 Hz, -CH₂-), 2.26 (2H, *t*, *J* = 6 Hz, -CH₂-). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 14.2, 24.9, 26.4, 33.0, 34.8, 37.3, 130.9 [C (sp²)], 134.9 [C (sp²)]. GC-MS (*m/z* (relative intensity)): 146 (5, M+2), 144

(17, M⁺), 131 (31), 129 (100 %, base peak), 93 (59), 91 (31), 78 (43), 63 (67), 53 (14), 45 (30), 41 (22).

2-Chloro-1,3,3-trimethylcyclohexene (18).³ Yellow oil; yield: 40 %; b.p.: 72–75 °C/4 mm; Anal. Calcd. for C₉H₁₅Cl: C, 68.13; H, 9.53 %. Found: C, 68.23; H, 9.27 %; IR (film, cm⁻¹): 2964, 2933, 2870, 1654, 1458, 1361, 1161, 964. ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.06 (6H, s, [-CH₃]₂), 1.55–1.58 (4H, m), 1.70 (3H, s, -CH₃), 2.03–2.04 (2H, m, -CH₂-). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 18.5, 20.4, 27.8, 32.5, 36.9, 38.8, 128.9 [C(sp²)], 135.1 [C(sp²)]. GC-MS (*m/z* (relative intensity)): 160 (4, M+2), 158 (12, M⁺), 145 (12), 143 (41), 123 (12), 109 (10), 107 (100, base peak), 91 (41), 81 (25), 79 (34), 77 (28), 53 (23), 41 (51).

2-Bromo-1,3,3-trimethylcyclopentene (19). New compound. Brown oil; yield: 64 %; b.p.: 69–71 °C/4 mm; Anal. Calcd. for C₈H₁₃Br: C, 50.81; H, 6.93 %. Found: C, 51.2; H, 7.23 %; IR (film, cm⁻¹): 2956, 2925, 2854, 1656, 1504, 1467, 1441, 1375, 1259, 1080, 1020, 860, 796. ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.06 (6H, s, [-CH₃]₂), 1.70 (3H, s, -CH₃), 1.79–1.82 (2H, m, -CH₂-), 2.23–2.27 (2H, m, -CH₂-). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 16.1, 27.1, 28.2, 34.1, 37.3, 128.3 [C(sp²)], 139.3 [C(sp²)]. GC-MS (*m/z* (relative intensity)): 190 (18, M+2), 188 (18, M⁺), 175 (83), 173 (86), 94 (100 %, base peak), 79 (44), 64 (14), 53 (16), 41 (20).

2-Bromo-1,3,3-trimethylcyclohexene (20). New compound. Brown oil; yield: 69 %; b.p.: 76–78 °C/4 mm; Anal. Calcd. for C₉H₁₅Br: C, 53.22; H, 7.44 %. Found: C, 53.42; H, 7.13 %; IR (film, cm⁻¹): 2960, 2927, 2866, 1650, 1456, 1361, 1338, 1280, 1211, 1049, 939, 803, 815, 761; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.05 (6H, s, [-CH₃]₂), 1.53–1.58 (4H, m), 1.72 (3H, s, -CH₃), 1.98–2.01 (2H, m, -CH₂-). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 19.2, 24.4, 29.3, 29.7, 33.8, 39.5, 131.8 [C(sp²)], 131.9 [C(sp²)]. GC-MS (*m/z* (relative intensity)): 204 (26, M+2), 202 (24, M⁺), 188 (79), 186 (77), 123 (53), 107 (100), 91 (49), 81 (42), 67 (21), 52 (25), 41 (44).

2-Iodo-1,3,3-trimethylcyclopentene (21). New compound. Brown oil; yield: 79 %; b.p.: 82–85 °C/4 mm. Anal. Calcd. for C₈H₁₃I: C, 40.70; H, 5.55 %. Found: C, 40.31; H, 5.71 %; IR (film, cm⁻¹): 2954, 2923, 2866, 1677, 1589, 1446, 1308, 1261, 1018, 802; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.99 (6H, s, [-CH₃]₂), 1.75 (3H, s, -CH₃), 1.85 (2H, t, *J* = 6.96 Hz, -CH₂-), 2.35 (2H, t, *J* = 7.44 Hz, -CH₂-). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 19.5, 28.1, 35.6, 36.7, 49.3, 51.8, 109.4 [C(sp²)], 141.7 [C(sp²)]. GC-MS (*m/z* (relative intensity)): 236 (31, M⁺), 221 (100, base peak), 127(20), 109 (5), 94 (87), 79 (70), 65 (19), 53 (24), 41 (31).

2-Iodo-1,3,3-trimethylcyclohexene (22).² Brown oil; yield: 82 %; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.02 (6H, s, [-CH₃]₂), 1.54–1.67 (m, 4H), 1.79 (3H, s, -CH₃), 2.07–2.11 (2H, t, *J* = 7.76 Hz, -CH₂-). ¹³C-NMR (100, MHz, CDCl₃, δ /

/ ppm): 19.4, 31.0, 31.5, 33.7, 37.9, 39.5, 117.3 [C (sp²)], 137.7 [C (sp²)]. GC-MS (*m/z* (relative intensity)): 250 (52, M⁺), 235 (21), 123(86), 108 (41), 93 (58), 81 (100), 67 (28), 53 (26), 41 (56).

1-(2,5,5-Trimethylcyclopent-1-enyl)-1-ethanone (23a).⁴ Light yellow oil; yield: 65 %; 53–57 °C/1 mm; GC-MS (*m/z* (relative intensity)): 152 (27, M⁺), 109 (100 %, base peak), 91 (15), 81(28), 67 (82), 55 (17), 40 (92).

1-(2,5,5-Trimethylcyclopent-1-enyl)-1-propanone (23b). New compound. Light yellow oil; yield: 71 %; b.p.: 64–67 °C/1 mm; Anal. Calcd. for C₁₁H₁₈O: C, 79.46; H, 10.91 %. Found: C, 78.98; H, 10.67 %; IR (film, cm⁻¹): 2881, 2857, 2830, 1718, 1450, 1360, 1248, 1017; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.96 (3H, *t*, *J* = 3.08 Hz, -CH₃), 0.96 (3H, *s*, -CH₃), 1.27 (3H, *s*, -CH₃), 1.26–1.38 (2H, *m*, -CH₂-), 1.54–1.59 (2H, *m*, -CH₂-), 1.67 (3H, *s*, -CH₃), 2.09–2.13 (2H, *m*, -CH₂-), 2.14–2.35 (2H, *m*, -CH₂-). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 15.2, 23.9, 28.8, 31.0, 35.6, 42.2, 46.6, 71.3, 126.5 [C (sp²)], 137.0 [C (sp²)], 212.0 (C=O). GC-MS (*m/z* (relative intensity)): 166 (22, M⁺), 151 (2), 137 (4), 123 (10), 109 (100 %, base peak), 95 (7), 91 (14), 81 (20), 67 (59), 57 (43), 55 (19), 40 (73).

(*E*)-*1-(2,5,5-Trimethylcyclopent-1-enyl)but-2-en-1-one (23c)*. New compound. Light yellow oil; yield: 78 %; b.p.: 69–73 °C/1 mm; Anal. Calcd. for C₁₂H₁₈O: C, 80.85; H, 10.18 %. Found: C, 80.36; H, 10.43 %; IR (film, cm⁻¹): 2950, 2890, 1755, 1708, 1635, 1442, 1301, 1075, 950; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.08 (6H, *s*, [-CH₃]₂), 1.48 (3H, *s*, -CH₃), 1.75–1.85 (5H, *m*), 1.95–2.15 (2H, *m*, -CH₂-), 6.18–6.23 (1H, *m*, =CH-), 6.84–6.93 (1H, *m*, =CH-). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 15.2, 17.2, 24.2, 31.1, 42.2, 46.9, 126.5, 130.2, 137.2, 138.6 [C (sp²)], 141.6 [C (sp²)], 200.2 (C=O). GC-MS (*m/z* (relative intensity)): 178 (9, M⁺), 163 (6), 135 (3), 122 (4), 109 (33), 91 (9), 79 (14), 69 (100, base peak), 55 (12), 41 (55).

1-(2,5,5-Trimethylcyclopent-1-enyl)-1-pentanone (23d). New compound. Light yellow oil; yield: 83 %; b.p.: 68–72 °C/1 mm. Anal. Calcd. for C₁₃H₂₂O: C, 80.35; H, 11.41 %. Found: C, 80.56; H, 11.13 %; IR (film, cm⁻¹): 2880, 2855, 2830, 1720, 1450, 1340, 1250, 1020; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.93(3H, *t*, *J* = 3.08 Hz, -CH₃), 0.99 (3H, *s*, -CH₃), 1.28 (3H, *s*, -CH₃), 1.29–1.36 (4H, *m*), 1.51–1.58 (2H, *m*, -CH₂-), 1.65 (3H, *s*, -CH₃), 2.07–2.11 (2H, *m*), 2.1–2.39 (3H, *m*). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 12.9, 15.3, 21.4, 24.36, 24.5, 31.0, 42.3, 46.7, 71.3, 126.4 [C (sp²)], 137.1 [C (sp²)], 211.5 (C=O). GC-MS (*m/z* (relative intensity)): 194 (26, M⁺), 179 (1), 151 (4), 137 (4), 109 (100 %, base peak), 91 (10), 85 (74), 67 (52), 57 (70), 41 (43).

1-(2,5,5-Trimethylcyclopent-1-enyl)-1-hexanone (23e). New compound. Light yellow oil; yield: 87 %; b.p.: 71–74 °C/1 mm; Anal. Calcd. for C₁₄H₂₄O: C, 80.71; H, 11.61 %. Found: C, 80.34; H, 11.45 %; IR (film, cm⁻¹): 2958, 2931, 1710, 1465, 1335, 1265, 1073; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 0.87 (3H,

m, -CH₃), 0.97 (3H, *s*, -CH₃), 1.25 (3H, *s*, -CH₃), 1.28–1.35 (6H, *m*), 1.53–1.68 (5H, *m*), 2.11–2.38 (4H, *m*). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 13.9, 16.3, 22.5, 23.1, 25.0, 29.7, 31.5, 32.1, 43.5, 47.7, 72.3, 127.4 [C (sp²)], 138.1 [C (sp²)]. GC-MS (*m/z* (relative intensity)): 208 (24, M⁺), 193 (2), 165 (2), 137 (4), 109 (100 %, base peak), 99 (68), 81 (20), 71 (56), 67 (49), 55 (19), 43 (73).

(2,5,5-Trimethylcyclopent-1-enyl)phenylmethanone (**23f**). New compound. Yellow oil; yield: 86 %; b.p.: 82–84 °C /1 mm; Anal. Calcd. for C₁₅H₁₈O: C, 84.07; H, 8.47 %. Found: C, 84.74; H, 8.45 %; IR (film, cm⁻¹): 2846, 1681, 1600, 1454, 1415, 1323, 1026; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 1.22 (6H, *s*, [-CH₃]₂), 1.48 (3H, *s*, -CH₃), 1.80 (2H, *t*, *J* = 6.8 Hz, -CH₂-), 2.41–2.48 (2H, *m*, -CH₂-), 7.41–7.45 (3H, *m*, aromatic), 7.80–7.87 (2H, *m*, aromatic). ¹³C-NMR (100, MHz, CDCl₃, δ / ppm): 16.0, 26.1, 29.3, 35.7, 39.1, 48.3, 124.4, 127.0, 127.2, 131.1, 138.5, 142.3, 143.5, 197.6 (C=O). GC-MS (*m/z* (relative intensity)): 214 (16, M⁺), 199 (38), 158 (9), 137 (1), 105 (100 %, base peak), 91 (7), 77 (52), 67 (6), 51 (12), 41 (9).

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