Electronic supplementary materials *Mendeleev Commun.*, 2018, **28**, 47–48

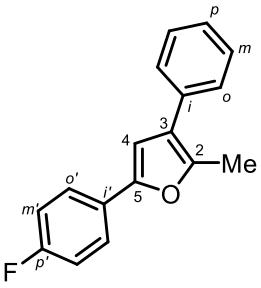
Acetylene as driving and organizing molecule in the assembling reactions with chalcones in the NaOBu^t/DMSO superbase system

Elena Yu. Schmidt, Ivan A. Bidusenko, Natalia A. Cherimichkina and Boris A. Trofimov

2-Methyl-3,5-diphenylfuran **2a**. Yield 0.316 g (27%); light yellow oil. Physical-chemical characteristics of compound **2a** were identical to the literature data.[1]

7-Methylidene-1,3,5-triphenyl-6,8-dioxabicyclo[3.2.1]octane **3a**. Yield 0.106 g (12%); colourless crystals; mp 78 °C (lit.[2] 77-78 °C). The spectral data of compound **3f** were identical to the literature data.[2]

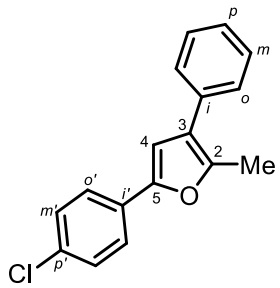
5-(4-Fluorophenyl)-2-methyl-3-phenylfuran **2b**.



Yield 0.769 g (61%); light yellow crystals; mp 87 °C. Found (%): C, 80.82; H, 5.28; F, 7.46. Calcd for $C_{17}H_{13}FO$ (252.283) (%): C, 80.93; H, 5.19; F, 7.53. IR (film, ν/cm^{-1}): 3054, 2955, 2921, 2856, 1648, 1603, 1561, 1499, 1450, 1396, 1310, 1228, 1136, 1061, 838, 810, 762, 697. ^{1}H NMR, δ: 7.61 – 7.53 (m, 2H, H$_{o'}$), 7.39 – 7.31 (m, 4H, H$_{o,m}$), 7.25 – 7.19 (m, 1H, H$_p$), 7.05 – 6.94 (m, 2H, H$_{m'}$), 6.64 (s, 1H, H^4), 2.45 (s, 3H, *Me*). ^{13}C NMR, δ: 162.1 (d, ^1J = 246.7 Hz, C$_{p'}$), 151.0 (C^5), 147.7 (C^2), 134.1 (C$_i$), 128.8 (C$_m$), 127.7 (C$_o$), 127.4 (d, ^4J = 2.8 Hz, C$_{i'}$), 126.7 (C$_p$), 125.3 (d, ^3J = 7.9 Hz, C$_{o'}$), 123.2 (C^3), 115.8 (d, ^2J = 21.9 Hz, C$_{m'}$), 106.3 (C^4), 13.3 (*Me*).

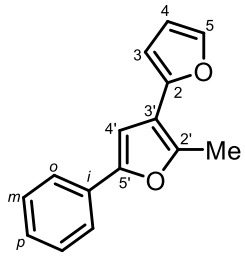
1. I. A. Bidusenko, N. A. Cherimichkina, E. Yu. Schmidt and B. A. Trofimov, *Russ. J. Org. Chem*., 2017, **53**, 470 (*Zh. Org. Khim*., 2017, **53**, 459).
2. E. Yu. Schmidt, I. A. Bidusenko, N. I. Protsuk, I. A. Ushakov and B. A. Trofimov *Eur. J. Org. Chem.*, 2013, 2453.

5-(4-Chlorophenyl)-2-methyl-3-phenylfuran **2c**.



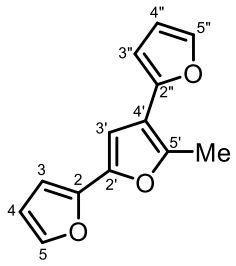
Yield 0.457 g (34%); light yellow crystals; mp 87 °C. Found (%): C, 75.82; H, 4.73; Cl, 13.11. Calcd for $C_{17}H_{13}ClO$ (268.738) (%): C, 75.98; H, 4.88; Cl, 13.19. IR (film, ν/cm^{-1}): 3051, 2920, 2855, 1892, 1743, 1684, 1647, 1620, 1550, 1485, 1446, 1396, 1313, 1223, 1139, 1092, 1006, 930, 815, 762, 697. ^{1}H NMR, δ: 7.60 – 7.56 (m, 2H, H_o), 7.42 – 7.38 (m, 4H, $H_{o,m}$), 7.34 – 7.31 (m, 2H, $H_{m'}$), 7.30 – 7.24 (m, 1H, H_p), 6.75 (s, 1H, H^4), 2.49 (s, 3H, *Me*). ^{13}C NMR, δ: 150.7 (C^5), 148.1 (C^2), 134.0 (C_i), 132.7 ($C_{p'}$), 129.5 ($C_{i'}$), 129.0 ($C_{m'}$), 128.8 (C_m), 127.6 (C_o), 126.7 (C_p), 124.8 ($C_{o'}$), 123.4 (C^3), 107.1 (C^4), 13.3 (*Me*).

2'-Methyl-5'-phenyl-2,3'-bifuran **2d**.



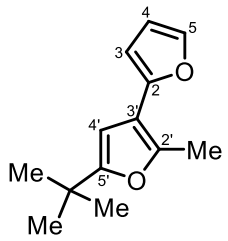
Yield 0.314 g (28%); yellow oil. Found (%): C, 80.12; H, 5.69. Calcd for $C_{15}H_{12}O_2$ (224.255) (%): C, 80.34; H, 5.39. IR (film, ν/cm^{-1}): 3401, 3300, 3146, 3118, 3060, 2922, 2856, 1709, 1648, 1600, 1574, 1489, 1447, 1388, 1357, 1293, 1224, 1144, 1069, 1020, 891, 799, 758, 734, 695. ^{1}H NMR, δ: 7.67 – 7.62 (m, 2H, H_o), 7.40 (d, ^3J = 1.5 Hz, 1H, H^5), 7.36 – 7.32 (m, 2H, H_m), 7.23 – 7.19 (m, 1H, H_p), 6.77 (s, 1H, H$^{4'}$), 6.43 (dd, ^3J = 3.0 Hz, ^3J = 1.5 Hz, 1H, H4), 6.31 (d, ^3J = 3.0 Hz, 1H, H3), 2.55 (s, 3H, Me). ^{13}C NMR, δ: 151.9 (C$^{5'}$), 148.8 (C^2), 147.6 (C$^{2'}$), 141.0 (C^5), 130.6 (C_i), 128.6 (C_m), 127.2 (C_p), 123.5 (C_o), 114.4 (C$^{3'}$), 111.1 (C^4), 104.9 (C^3), 104.1 (C$^{4'}$), 13.4 (*Me*).

5'-Methyl-2,2':4',2''-terfuran **2e**.



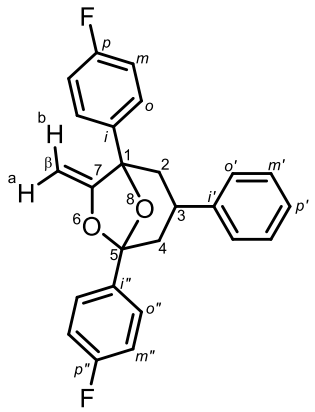
Yield 0.311 g (29%); light yellow oil. Found (%): C, 72.93; H, 4.78. Calcd for $C_{13}H_{10}O_3$ (214.217) (%): C, 72.89; H, 4.71. IR (film, ν/cm^{-1}): 3127, 2922, 2855, 1711, 1656, 1573, 1550, 1502, 1464, 1218, 1157, 1134, 1077, 1006, 965, 891, 796, 730. ^{1}H NMR, δ: 7.41 (d, ^3J = 0.9 Hz, 1H, H^5), 7.38 (d, ^3J = 1.0 Hz, 1H, H$^{5''}$), 6.67 (s, 1H, H$^{3'}$), 6.51 (d, ^3J = 3.2 Hz, 1H, H$^{3''}$), 6.44 – 6.42 (m, 2H, H^4, H$^{4''}$), 6.31 (d, ^3J = 3.2 Hz, 1H, H^3), 2.54 (s, 3H, *Me)*. ^{13}C NMR, δ: 148.7, 147.6, 146.4 (C$^{2',5',2''}$), 144.7 (C^2), 141.8 (C^5), 141.3 (C$^{5''}$), 114.3 (C$^{4'}$), 111.5, 111.3, 105.3 (C$^{3,4,4''}$), 105.0 (C$^{3''}$), 104.4 (C$^{3'}$), 13.5 (*Me*).

5'-(tert-Butyl)-2'-methyl-2,3'-bifuran **2f**.



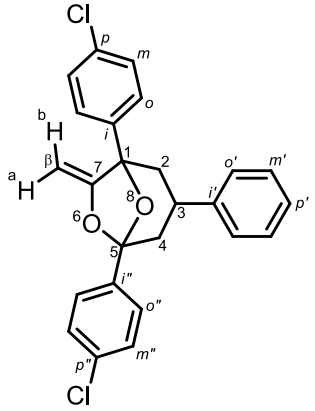
Yield 0.633 g (62%); light yellow oil. Found (%): C, 76.58; H, 7.81; H, 4.78. Calcd for $C_{13}H_{16}O_2$ (204.265) (%): C, 76.44; H, 7.90. IR (film, ν/cm^{-1}): 3119, 2965, 2928, 2869, 1648, 1587, 1500, 1459, 1386, 1362, 1291, 1224, 1139, 1024, 1003, 945, 892, 796, 729. ^{1}H NMR, δ: 7.36 (d, ^3J = 1.5 Hz, 1H, H^5), 6.39 (dd, ^3J = 3.0 Hz, ^3J = 1.5 Hz, 1H, H^4), 6.22 (d, ^3J = 3.0 Hz, 1H, H^3), 6.08 (s, 1H, H$^{4'}$), 2.45 (s, 3H, 2'-*Me*), 1.26 (s, 9H, 5'-C*Me*$_3$). ^{13}C NMR, δ: 162.4 (C$^{5'}$), 149.7 (C^2), 146.0 (C$^{2'}$), 140.8 (C^5), 112.6 (C$^{3'}$), 111.1 (C^4), 104.4 (C^3), 101.4 (C$^{4'}$), 32.5 (5'-*C*Me$_3$), 29.2 (5'-C*Me*$_3$), 13.4 (2'-*Me*).

1,5-Bis(4-fluorophenyl)-7-methylidene-3-phenyl-6,8-dioxabicyclo[3.2.1]octane **3b**.



Yield 0.098 g (10%); light yellow oil. Found (%): C, 76.85; H, 5.11; F, 9.80. Calcd for $C_{25}H_{20}F_2O_2$ (390.422) (%): C, 76.91; H, 5.16; F, 9.73. IR (film, ν/cm^{-1}): 3030, 2925, 2849, 2808, 1686, 1603, 1513, 1455, 1411, 1380, 1350, 1311, 1273, 1231, 1160, 1143, 1090, 1076, 1033, 1013, 991, 957, 910, 833, 813, 764, 735, 700, 676, 598, 590, 576, 528. ^{1}H NMR, δ: 7.66 – 7.62 (m, 2H, H$_o$), 7.56 – 7.51 (m, 2H, H$_{o''}$), 7.37 – 7.28 (m, 4H, H$_{o',m'}$), 7.26 – 7.20 (m, 1H, H$_{p'}$), 7.13 – 7.02 (m, 4H, H$_{m,m''}$), 4.38 (d, ^2J = 2.4 Hz, 1H, H^b), 3.62 – 3.50 (m, 1H, H^a, H^3), 2.53 (dd, ^2J = 12.9 Hz, ^3J = 5.1 Hz, 1H, H^{4eq}), 2.46 (dd, ^2J = 13.6 Hz, ^3J = 5.4 Hz, 1H, H^{2eq}), 2.25 (dd, ^2J = 12.9 Hz, ^3J = 12.4 Hz, 1H, H^{4ax}), 2.14 (dd, ^2J = 13.6 Hz, ^3J = 12.1 Hz, 1H, H^{2ax}). ^{13}C NMR, δ: 163.3 (d, ^1J = 247.8 Hz, C$_p$), 162.9 (d, ^1J = 247.4 Hz, C$_{p''}$), 162.7 (C^7), 143.6 (C$_{i'}$), 135.5 (d, ^4J = 3.1 Hz), 135.3 (d, ^4J = 3.1 Hz) (C$_{i,i''}$), 129.0 (C$_{m'}$), 128.1 (d, ^3J = 8.2 Hz, C$_o$), 127.48 (C$_{o'}$), 127.48 (d, ^3J = 8.2 Hz, C$_{o''}$), 127.1 (C$_{p'}$), 115.43 (d, ^2J = 21.6 Hz, C$_m$), 115.4 (d, ^2J = 21.5 Hz, C$_{m''}$), 108.6 (C^5), 85.5 (C^1), 79.42 (C$^\beta$), 41.5 (C^4), 40.10 (C^2), 37.0 (C^3).

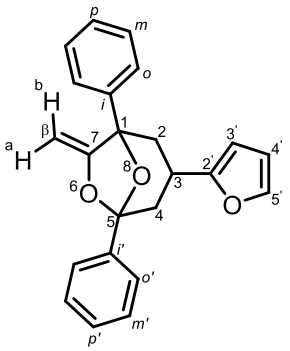
1,5-Bis(4-chlorophenyl)-7-methylidene-3-phenyl-6,8-dioxabicyclo[3.2.1]octane **3c**.



Yield 0.205 g (19%); yellow oil. Found (%): C, 71.12; H, 4.41; Cl, 16.52. Calcd for $C_{25}H_{20}Cl_2O_2$ (423.331) (%): C, 70.93; H, 4.76; Cl, 16.75. IR (film, ν/cm^{-1}): 3063, 3031, 2956, 2924, 2846, 1683, 1644, 1602, 1493, 1452, 1431, 1399, 1373, 1348, 1308, 1269, 1245, 1143, 1086, 990, 956, 909, 823, 734, 702. ^{1}H NMR, δ: 7.62 – 7.54 (m, 2H), 7.51 – 7.45 (m, 2H), 7.40 –

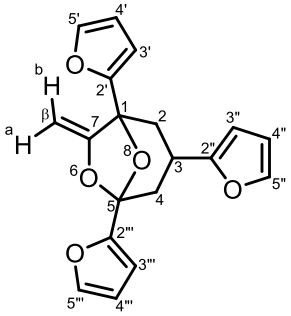
7.27 (m, 8H) (C_{Ar}), 7.25 – 7.21 (m, 1H, $H_{p'}$), 4.39 (d, ^2J = 2.3 Hz, 1H, H^a), 3.61 (d, ^2J = 2.3 Hz, 1H, H^b), 3.59 – 3.49 (m, 1H, H^3), 2.52 (dd, ^3J = 13.0 Hz, ^3J = 5.2 Hz, 1H, H^{2eq}), 2.42 (dd, ^3J = 13.6 Hz, ^3J = 5.5 Hz, 1H, H^{4eq}), 2.23 (dd, ^3J = 13.0 Hz, ^3J = 12.3 Hz, 1H, H^{2ax}), 2.12 (dd, ^3J = 13.6 Hz, ^3J = 12.3 Hz, 1H, H^{4ax}). ^{13}C NMR, δ: 162.1 (C^7), 143.3 ($C_{i'}$), 137.9, 137.6, 135.0, 134.3 ($C_{i,i'',p,p''}$), 128.8, 128.59, 128.57, 127.4, 127.3 (10C, C_{Ar}), 127.0 ($C_{p'}$), 126.8 ($C_{o''}$), 108.5 (C^5), 85.2 (C^1), 79.5 (C^β), 41.3, 39.8 ($C^{2,4}$), 36.8 (C^3).

3-(Furan-2-yl)-7-methylidene-1,5-diphenyl-6,8-dioxabicyclo[3.2.1]octane **3d**.



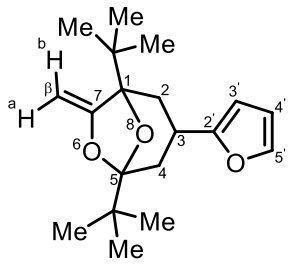
Yield 0.096 g (11%); yellow oil. Found (%): C, 80.43; H, 5.71. Calcd for $C_{23}H_{20}O_3$ (344.403) (%): C, 80.21; H, 5.85. IR (film, ν/cm^{-1}): 3062, 3034, 2959, 2927, 2854, 1717, 1682, 1654, 1596, 1540, 1499, 1447, 1352, 1336, 1280, 1244, 1180, 1145, 1105, 1066, 1011, 955, 912, 806, 754, 735, 698. ^{1}H NMR, δ: 7.69 – 7.65 (m, 2H, $H_{o'}$), 7.60 – 7.56 (m, 2H, H_o), 7.43 – 7.31 (m, 7H, $H^{5'}$, H_{Ph}), 6.29 (dd, ^3J = 2.5 Hz, ^3J = 1.2 Hz, 1H, $H^{4'}$), 6.06 (d, ^3J = 2.5 Hz, 1H, $H^{3'}$), 4.35 (d, ^2J = 2.1 Hz, 1H, H^a), 3.76 – 3.65 (m, 1H, H^3), 3.63 (d, ^2J = 2.1 Hz, 1H, H^b), 2.65 (dd, ^3J = 12.9 Hz, ^3J = 5.1 Hz, 1H, H^{2eq}), 2.54 (dd, ^3J = 13.4 Hz, ^3J = 5.4 Hz, 1H, H^{4eq}), 2.25 (dd, ^3J = 12.9 Hz, ^3J = 12.4 Hz, 1H, H^{2ax}), 2.18 (dd, ^3J = 13.4 Hz, ^3J = 12.5 Hz, 1H, H^{4ax}). ^{13}C NMR, δ: 162.6 (C^7), 157.3 ($C^{2'}$), 141.5 ($C^{5'}$), 139.6 ($C_{i'}$), 139.2 (C_i), 129.1 ($C_{p'}$), 128.5 ($C_{m,m'}$), 128.4 (C_p), 126.0 (C_o), 125.4 ($C_{o'}$), 110.3 ($C^{4'}$), 108.6 (C^5), 104.4 ($C^{3'}$), 85.2 (C^1), 79.3 (C^β), 38.9, 37.6 ($C^{2,4}$), 30.6 (C^3).

1,3,5-Tri(furan-2-yl)-7-methylidene-6,8-dioxabicyclo[3.2.1]octane **3e**.



Yield 0.097 g (12%); yellow oil. Found (%): C, 70.24; H, 4.81. Calcd for $C_{19}H_{16}O_5$ (324.327) (%): C, 70.36; H, 4.97. IR (film, ν/cm^{-1}): 3126, 2962, 2931, 2853, 1686, 1653, 1600, 1503, 1389, 1361, 1330, 1251, 1158, 1076, 1012, 950, 898, 819, 742 cm^{-1}. ^{1}H NMR, δ: 7.46 (d, ^3J = 0.8 Hz, 1H), 7.44 (d, ^3J = 0.7 Hz, 1H) ($H^{5',5'''}$), 7.33 (d, ^3J = 0.8 Hz, 1H, $H^{5''}$), 6.60 (d, ^3J = 3.3 Hz, 1H), 6.56 (d, ^3J = 3.2 Hz, 1H) ($H^{3',3'''}$), 6.39 – 6.36 (m, 2H, $H^{4',4'''}$), 6.30 (dd, ^3J = 3.1 Hz, ^3J = 0.8 Hz, 1H, $H^{4''}$), 6.09 (d, ^3J = 3.1 Hz, 1H, $H^{3''}$), 4.49 (d, ^2J = 2.4 Hz, 1H, H^a), 3.89 (d, ^2J = 2.4 Hz, 1H, H^b), 3.69 – 3.57 (m, 1H, H^3), 2.59 (dd, ^3J = 13.4 Hz, ^3J = 5.5 Hz, 1H, H^{2eq}), 2.49 (dd, ^3J = 13.0 Hz, ^3J = 12.3 Hz, 1H, H^{4ax}), 2.38 (dd, ^3J = 13.0 Hz, ^3J = 5.4 Hz, 1H, H^{4eq}), 2.31 (dd, ^3J = 13.4 Hz, ^3J = 12.1 Hz, 1H, H^{2ax}). ^{13}C NMR, δ: 158.7 (C^7), 156.6, 150.7, 149.9, 143.5 ($C^{1',1'',1''',5',5'''}$), 141.5 ($C^{5''}$), 110.2 ($C^{4''}$), 110.5, 109.7, 109.1, 104.6 ($C^{2',2''',3',3''',5}$), 104.3 ($C^{3''}$), 81.4 ($C^β$), 79.8 (C^1), 36.4, 35.7 ($C^{2,4}$), 29.3 (C^3).

1,5-Di-tert-butyl-3-(furan-2-yl)-7-methylidene-6,8-dioxabicyclo[3.2.1]octane **3f**.



Yield 0.079 g (10%); colourless oil. Found (%): C, 75.03; H, 9.41. Calcd for $C_{19}H_{28}O_3$ (304.424) (%): C, 74.96; H, 9.27. IR (film, ν/cm^{-1}): 3120, 2969, 2912, 2877, 1708, 1673, 1600, 1505, 1477, 1391, 1364, 1323, 1260, 1219, 1153, 1102, 1041, 1011, 963, 802, 732. ^{1}H NMR, δ: 7.30 (d, ^3J = 0.9 Hz, 1H, $H^{5'}$), 6.27 (dd, ^3J = 2.9 Hz, ^3J = 0.9 Hz, 1H, $H^{4'}$), 5.99 (d, ^3J = 2.9 Hz, 1H, $H^{3'}$), 4.29 (d, ^2J = 2.2 Hz, 1H, H^a), 3.91 (d, ^2J = 2.1 Hz, 1H, H^b), 3.39 – 3.27 (m, 1H, H^3), 2.09 (dd, ^3J = 12.9 Hz, ^3J = 5.5 Hz, 1H, H^{2eq}), 1.93 (dd, ^3J = 12.6 Hz, ^3J = 5.4 Hz, 1H**,** H^{4eq}), 1.84 (dd, ^3J = 12.6 Hz, ^3J = 11.9 Hz, 1H, H^{4ax}), 1.74 (dd, ^3J = 12.9 Hz, ^3J = 12.1 Hz, 1H, H^{2ax}), 1.08 (s, 9H), 1.00 (s, 9H) (C*Me*$_3$). ^{13}C NMR, δ: 161.3 (C^7), 158.7 ($C^{2'}$), 141.2 ($C^{5'}$), 111.2 (C^5), 110.1 ($C4^{'}$), 104.0 ($C^{3'}$), 88.5 (C^1), 77.6 ($C^β$), 37.0, 35.5 (*C*Me$_3$), 33.4, 32.0, 30.6 ($C^{2,3,4}$), 26.0, 25.0 (C*Me*$_3$).