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2,5-Dimethoxy-2,5-dihydrofuran chemistry: a new approach to 2(5*H*)-furanone derivatives

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Abstract

2,5-Dimethoxy-2,5-dihydrofuran is a synthetic equivalent of 2(5*H*)-furanone or 2-trimethylsilyloxyfuran, useful C_4 synthons in the preparation of 5-substituted-2(5*H*)-furanone derivatives. The reaction conditions adopted allow to obtain different classes of complex and biologically interesting compounds, in only one step, with high yields.

Keywords: 2,5-Dimethoxy-2,5-dihydrofuran; Mukaiyama-aldol reaction; 2(5*H*)-Furanones

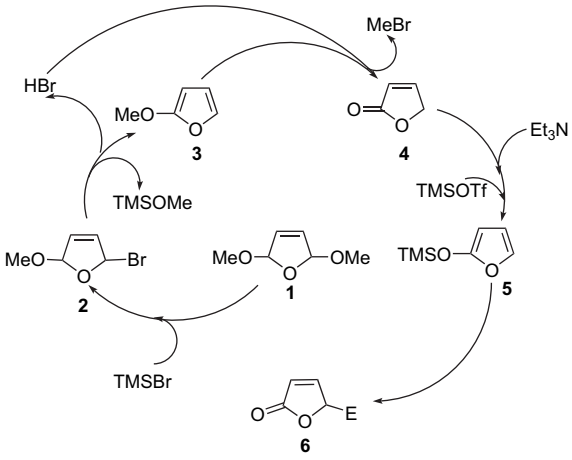
1. Introduction

Our recent studies on the reactivity of 2,5-dimethoxy-2,5-dihydrofuran[1] (**1**) as C_4 building block in the syntheses of many furofuran[1a] and 2-alkylfuran[1b–d] moieties of biological interest,[2] encouraged us to investigate the reactivity of the allylic diacetal functional group of **1**, towards trimethylsilyl halides.

Only few examples[3] of this approach are described but no general interpretation has ever been proposed.

It was noted that the treatment of **1** with an equimolar amount of trimethylsilyl bromide, in CH_2Cl_2 at room temperature, afforded a yellow solution containing the more expensive 2(5*H*)-furanone (**4**) in quantitative yield (Scheme 1). Compound **4** could be employed in the following reactions without further purification. Under particular reaction conditions, the one-pot reaction with an equimolar amount of trimethylsilyl triflate (TMSOTf), in the presence of triethylamine, allowed the conversion of **4** into 2-trimethylsilyloxyfuran **5** (Scheme 1).

Compound **5**, which is a key intermediate in the Mukaiyama-aldol synthetic sequence,[4a] could be reacted one-pot with suitable electrophiles to give the corresponding products in high yields.



Scheme 1. Transformation of 2,5-dimethoxy-2,5-dihydrofuran.

It is noteworthy that no Lewis acid catalyst was necessary.[4]

2. Results and discussion

A rationale of the described transformations is outlined in Scheme 1.

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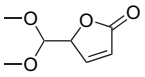
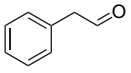
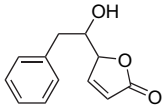
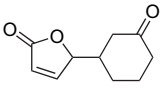
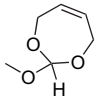
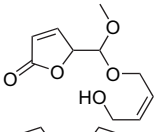
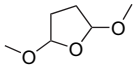
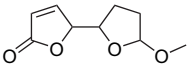
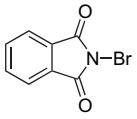
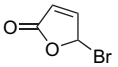
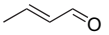
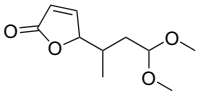
Trimethylsilyl bromide reacts with **1** (Scheme 1) affording 2-methoxy-5-bromo-2,5-dihydrofuran (**2**) as an elusive yet detectable intermediate (GLC–MS), which decomposes into 2-methoxylfuran (**3**) (GLC–MS, NMR) in the same reaction conditions.

The transformation of **1** into **3** represents a novel approach towards the formation of key intermediates **4** and **5**.

The rapid and quantitative interconversion of the methyl ketene acetal (**3**) into α,β-unsaturated-γ-lactone (**4**) could be reasonably ascribed to the hydrogen bromide, produced in the first step of the reaction. Compound **1**, a synthetic equivalent of **4**, is an important intermediate in the preparation of 3-substituted furan-2-ones[5] or 2(5*H*)-furanones **6**, useful building blocks in the preparation of more complex biological organic structures (Table 1, entry 5).[6]

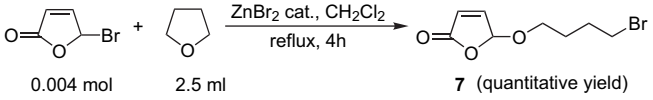
Table 1
Reactivity of **1** with electrophiles in the presence of TMSBr/Et_3N, TMSOTf

Entry	Electrophile	Product[a]		Yield[b,c] (%)
1	$CH(OMe)_3$		**6a**	95
2			**6b**	90
3			**6c**	85
4			**6d**	90
5			**6e**	75
6			**6f**	90
7			**6g**	70

[a] Mixtures of diastereomers in a ca. 1:1 ratio (^1H, ^{13}C NMR, GLC, GLC–MS).
[b] Evaluated on the isolated products.
[c] IR, NMR, mass spectroscopies and elemental analyses are in agreement with the structures proposed for products **6**.

In particular, entry 6 (Table 1), represents a new approach to the synthesis of compound **6f**,[7] where *N*-bromosuccinimide is used as electrophilic bromine source.

Compound **6f** acts as a vinylogous organic acid halide[8] as shown by its peculiar reactivity. In fact, in the presence of a catalytic amount of $ZnBr_2$, **6f** reacts with THF and causes its ring opening giving 5-(4-bromobutoxy)-5*H*-furan-2-one (**7**, Scheme 2), useful precursor in the synthesis of furopyrans by well known free radical cyclization reaction.[9]



Scheme 2. Furan ring opening.

It seems possible to rationalize this last step as a S_N2 concerted reaction[8d] with a possible transition state showed in Figure 1.

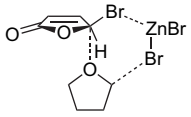


Figure 1. Proposed adduct for the tetrahydrofuran ring opening reaction.

3. Conclusions

In conclusion, a new one-pot electrophilic derivatization of 2(5*H*)-furanone, starting from the cheaper 2,5-dimethoxy-2,5-dihydrofuran (**1**) has been reported. The products can be obtained by a simple work-up procedure and promise to give valuable intermediates in the preparation of natural and biologically active products.

Further studies are in progress to apply these new synthetic approaches to various other electrophiles.

4. Experimental section

4.1. Materials and methods

Dichloromethane was refluxed and distilled over P_2O_5. Et_3N was refluxed and distilled over KOH. TMSBr and TMSOTf (Aldrich) were used as-received. $ZnBr_2$ (Fluka) was used as-received. GLC analyses were performed on a Perkin–Elmer 8500 instrument [ZB_1 capillary column (15 m×0.25 mm), film 0.25 mm] equipped with a flame ionization detector and a split–splitless injector, with N_2 as carrier gas. ^1H and ^{13}C NMR (200 and 50 MHz, respectively) spectra were recorded on a Varian Geminy 200 spectrometer; all NMR data were obtained using $CDCl_3$ solutions. Chemical shifts (δ, ppm) are referred to tetramethylsilane (TMS) (^1H NMR) or $CDCl_3$ (^{13}C NMR) as internal standard. Mass spectra (*m*/*z*, *I*%) were taken on a 5980 Hewlett–Packard GC instrument, equipped with an HP-5MS column (30 m×0.25 mm, film 0.25 mm) interfaced with a Hewlett–Packard 5995A instrument, with He as carrier gas. Indicated yields are reported on the isolated chemically pure products.

4.2. General procedure

A solution of trimethylsilyl bromide (1.32 ml, 0.013 mol) in 20 ml of anhydrous CH_2Cl_2 was slowly added to a solution of **1** (1.30 g, 0.010 mol) dissolved in 30 ml of anhydrous CH_2Cl_2, at room temperature.

The resulting yellow solution of **4** was stirred at room temperature for 24 h and then cooled to −80 °C. After the addition of freshly distilled triethylamine (1.80 ml, 0.013 mol, in 20 ml

of CH_2Cl_2), the yellow-brown solution is stirred at room temperature for 10 min and then cooled to −80 °C. The following slow addition of a TMSOTf solution (2.35 ml, 0.013 mol, in 20 ml of CH_2Cl_2) under stirring, afforded a pink solution containing compound **5** as the sole product.

The final addition of the electrophile solution (0.010 mol in 25 ml of CH_2Cl_2) was carried out at −80 °C, afforded **6** in a few minutes.

The reaction mixture was allowed to warm up to room temperature and washed with a 5% $NaHCO_3$ solution and extracted with diethyl ether. The organic layers were dried over Na_2SO_4 and the solvent removed in vacuo to give a dark oil that was dissolved in benzene. The solution was filtered to remove the triethylammonium triflate. The resulting yellow oil residue was repeatedly extracted with hot pentane, and, after the elimination of the solvent, gave the final product **6**.

4.3. Spectroscopic characterization of the products

4.3.1. 2(5H)-Furanone (**4**)

^{1}H NMR: 7.65 (dt, 1H, J_1=1.7 Hz, J_2=5.8 Hz, O=C−CH=C*H*−), 6.18 (dt, 1H, J_3=2.2 Hz, J_2=5.8 Hz, O=C−C*H*=CH−), 4.95 (dd, 2H, J_1=1.7 Hz, J_3=2.2 Hz, CH=CH−CH_2−O).

^{13}C NMR: 173.6, 153.0, 121.2, 72.1.

4.3.2. 5-(Dimethoxymethyl)furan-2(5H)-one (**6a**)

^{1}H NMR: 7.38 (dd, 1H, J_1=1.4 Hz, J_2=5.8 Hz, O=C−CH=C*H*−), 6.05 (dd, 1H, J_3=2.0 Hz, J_2=5.8 Hz, O=C−C*H*=CH−), 4.91 (ddd, 1H, J_1=1.4 Hz, J_4=1.2 Hz, J_5=5.1 Hz, CH=CH−C*H*<), 4.23 (d, 1H, J_5=5.1 Hz, >CH−C*H*(OMe)$_2$), 3.36, 3.31 (2s, 6H, OCH_3).

^{13}C NMR: 172.3, 152.7, 122.4, 103.7, 82.4, 56.5, 56.2.

FTIR liquid film (ν, cm^{-1}): 3103, 2940, 2838, 1786, 1757, 1446, 1356, 1335, 1303, 1264, 1192, 1160, 1103, 1066, 976, 917, 890, 824, 733.

EIMS (*m*/*z* (%)): 127 (M^+−MeO, 2.27), 99 (M^+−MeO−CO, 9.44), 83 (M^+−HC(OMe)$_2$, 3.63), 75 (100), 71 (9.01), 55 (8.21), 47 (16.2).

Elemental analysis: Found: C, 53.26; H, 6.31%; Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37; O, 40.47%.

4.3.3. 5-(1-Hydroxy-2-phenylethyl)furan-2(5H)-one (**6b**)

^{1}H NMR: 7.60−7.64 (m, 1H, O=C−CH=C*H*−), 7.22−7.27 (m, 5H, −Ph), 6.12−6.17 (m, 1H, O=C−C*H*=CH−), 5.00−4.80 (m, 2H, CH=CH−C*H*< and >CH−CH(O*H*)−), 4.00−4.08 (m, 1H, >CH−C*H*(OH)−), 3.12−3.17 (m, 2H, >CH−CH(OH)−CH_2−Ph).

^{13}C NMR: 173.4, (154.7, 154.3), 136.6, 129.4, 129.3, 128.6, 128.4, 126.7, (122.5, 122.3), (85.0, 84.6), (72.4, 71.9), (39.8, 39.6).

FTIR liquid film (ν, cm^{-1}): 3449, 3086, 3064, 2925, 1939, 1741, 1597, 1496, 1448, 1399, 1341, 1287, 1245, 1223, 1164, 1090, 1031, 945, 881, 812, 752.

EIMS (*m*/*z* (%)): 203 (M^+−H, 0.32), 191 (0.61), 175 (1.19), 161 (1.41), 149 (3.57), 136 (6.45), 121 (Ph−CH_2−CHOH, 10.31), 107 (8.70), 95 (21.70), 81 (80.37), 69 (100), 55 (5.49).

Elemental analysis: Found: C, 70.63; H, 6.02%; Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92; O, 23.50%.

4.3.4. 5-(3-Oxocyclohexyl)furan-2(5H)-one (**6c**)

^{1}H NMR: 7.75−7.25 (m, 1H, O=C−CH=C*H*−), 6.40−6.00 (m, 1H, O=C−C*H*=CH−), 5.25−4.85 (m, 1H, CH=CH−C*H*<), 3.50−3.00 (m, 4H, CH_2−CO−CH_2), 3.00−1.50 (m, 5H, CO−CH_2−CH_2−CH_2−C*H*<).

^{13}C NMR: 209.3, 173.8, 154.1, 122.1, 86.3, (41.5, 41.4), (41.2, 41.1), (27.3, 27.5), 25.5, 24.5.

FTIR liquid film (ν, cm^{-1}): 3090, 3035, 2940, 2869, 1760, 1713, 1600, 1479, 1449, 1266, 1223, 1154, 1095, 1031, 967, 924, 897, 817, 758.

EIMS (*m*/*z* (%)): 180 (M^+, 12.98), 152 (9.91), 137 (4.15), 123 (19.69), 111 (47.63), 97 (C_6H_9O, 31.25), 82 (M^+−$C_6H_{10}O$, 32.69), 69 (25.99), 55 (100).

Elemental analysis: Found: C, 66.75; H, 6.65%; Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; O, 26.64%.

4.3.5. 5-(((Z)-4-Hydroxybut-2-enyloxy)(methoxy)methyl)-furan-2(5H)-one (**6d**)

^{1}H NMR: 7.77−7.17 (m, 1H, O=C−CH=C*H*−), 6.40−6.00 (m, 1H, O=C−C*H*=CH−), 5.95−5.45 (m, 2H, O−CH_2−C*H*=C*H*−CH_2), 5.25−4.85 (m, 1H, CH=CH−C*H*<), 4.65−4.45 (m, 1H, >CH−C*H*(O)−OCH_3), 4.35−4.15 (m, 4H, O−CH_2−CH=CH−CH_2), 3.50, 3.45 (2s, 3H, >CH−CH(O)−OCH_3), 2.70 (br s, 1H, CH=CH−CH_2−O*H*).

^{13}C NMR: 173.5, 152.9, (132.7, 132.6), 128.3, (126.7, 126.4), 122.6, (102.3, 102.0), (83.0, 82.5), (64.6, 64.4), (58.2, 58.1).

FTIR liquid film (ν, cm^{-1}): 3468, 3102, 2939, 2882, 2840, 1773, 1752, 1447, 1330, 1276, 1255, 1218, 1164, 1095, 1057, 1031, 913, 892, 822, 732.

EIMS (*m*/*z* (%)): 143 (M^+−CH_2CH=CHCH_2OH, 44.51), 137 (25.39), 127 (17.89), 113 (7.94), 101 (6.96), 83 ($C_4H_3O_2^+$, 1.68), 73 ($C_4H_9O^+$, 100), 59 (9.70), 53 (7.43), 45 (7.80).

Elemental analysis: Found: C, 55.95; H, 6.65%; Anal. Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59; O, 37.34%.

4.3.6. 5-(5-Methoxy-tetrahydrofuran-2-yl)furan-2(5H)-one (**6e**)

^{1}H NMR: 7.80−7.40 (m, 1H, O=C−CH=C*H*−), 6.40−6.00 (m, 1H, O=C−C*H*=CH−), 5.20−4.80 (m, 1H, CH=CH−C*H*<), 4.20−3.80 (m, 1H, CH=CH−(O)CH−C*H*(O)−CH_2−CH_2), 3.33 (br s, 3H, CH_2−(O)CH−OCH_3), 2.20−1.80 (m, 4H, CH−CH_2−CH_2−CH(O)−OCH_3).

^{13}C NMR: 174.0, (153.2, 153.0, 152.8), (122.6, 122.3, 122.0), (105.6, 105.4), (85.5, 85.1), (84.3, 84.2), 55.7, (32.5, 32.4), (25.0, 24.9, 24.7).

FTIR liquid film (ν, cm^{-1}): 3096, 2951, 2833, 1752, 1600, 1444, 1349, 1311, 1205, 1161, 1097, 1039, 952, 891, 820, 700.

EIMS (*m*/*z* (%)): 152 (M^+−MeOH, 32.51), 123 (M^+−MeOH−CHO, 100), 109 (15.93), 96 (45.60), 82 (78.34), 68 (32.93), 55 (44.99).

Elemental analysis: Found: C, 58.73; H, 6.67%; Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57; O, 34.74%.

*4.3.7. 5-Bromofuran-2(5H)-one (**6f**)*

^{1}H NMR: 7.65 (dd, 1H, J_1=1.5 Hz, J_2=5.5 Hz, O=C–CH=C*H*–), 7.20–6.80 (m, 1H, O=C–C*H*=CH–), 6.24 (dd, 1H, J_2=5.5 Hz, J_3=1.0 Hz CH=CH–C*H*<).

^{13}C NMR: 168.3, 154.9, 120.7, 75.5.

FTIR liquid film (ν, cm^{-1}): 3096, 3000, 1784, 1747, 1715, 1597, 1437, 1325, 1314, 1186, 1143, 1090, 1036, 967, 865, 828, 737.

EIMS (*m*/*z* (%)): 83 (M^+– Br, 100), 55 (M^+–Br–CO, 9.00).

Elemental analysis: Found: C, 29.38; H, 1.85; Br, 49.13%; Anal. Calcd for $C_4H_3BrO_2$: C, 29.48; H, 1.86; Br, 49.03; O, 19.63%.

*4.3.8. 5-(4,4-Dimethoxybutan-2-yl)furan-2(5H)-one (**6g**)*

^{1}H NMR: 7.70–7.30 (m, 1H, O=C–CH=C*H*–), 6.18 (dd, 1H, J_1=2.0 Hz, J_2=5.7 Hz, O=C–C*H*=CH–), 5.20–4.80 (m, 1H, O=C–CH=CH–C*H*<), 4.48 (dd, 1H, J_3=5 Hz, J_4=4.5 Hz, CH_2–C*H*(OCH_3)$_2$), 3.45, 3.31 (2s, 6H, CH_2–CH(OC*H*$_3$)$_2$), 2.70–2.30 (m, 2H, CH–C*H*$_2$–CH(OCH_3)$_2$), 2.30–1.90 (m, 1H, (O)CH–C*H*(CH_3)–CH_2), 1.10, 1.00 (2s, 3H, (O)CH–CH(C*H*$_3$)–CH_2).

^{13}C NMR: 174.2, 154.6, (122.3, 122.2), 102.7, (86.6, 86.0), (52.9, 52.8), 34.7, (32.4, 31.0), (16.3, 15.2).

FTIR liquid film (ν, cm^{-1}): 3090, 2939, 2833, 2733, 1753, 1676, 1602, 1458, 1386, 1273, 1164, 1097, 1063, 1030, 992, 896, 821.

EIMS (*m*/*z* (%)): 126 (M^+–$CH_2CH(OCH_3)_2$, 0.37), 111 (M^+–$CH_2CH(OCH_3)_2$–CH_3, 8.93), 97 (17.44), 84 ($C_4H_4O_2^+$, 100), 71 (8.89), 55 (14.87).

Elemental analysis: Found: C, 60.01; H, 7.98%; Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05; O, 31.96%.

*4.3.9. 5-(4-Bromobutoxy)furan-2(5H)-one (**7**)*

^{1}H NMR: 7.24 (dd, 1H, J_1=1.0 Hz, J_2=5.8 Hz, O=C–CH=C*H*–), 6.26 (dd, 1H, J_1=1.0 Hz, J_2=5.8 Hz, O=C–C*H*=CH–), 6.15–5.75 (m, 1H, O=C–CH=CH–C*H*<), 3.70–3.40 (m, 4H, O–C*H*$_2$–CH_2–CH_2–C*H*$_2$–Br), 2.00–1.50 (m, 4H, O–CH_2–C*H*$_2$–C*H*$_2$–CH_2–Br).

^{13}C NMR: 170.6, 150.3, 124.9, 103.3, 69.3, 33.2, 29.1, 27.9.

FTIR liquid film (ν, cm^{-1}): 3105, 2947, 2875, 1787, 1760, 1432, 1353, 1255, 1157, 1130, 1091, 1039, 1006, 960, 927, 901, 822, 724, 685.

EIMS (*m*/*z* (%)): 151 (M^+–HBr, 0.90), 137 (M^+–HBr–CH_2, 21.14), 83 ($C_4H_3O_2^+$, 100), 71 (13.88), 55 (32.43).

Elemental analysis: Found: C, 40.73; H, 4.81; Br, 34.05%; Anal. Calcd for $C_8H_{11}BrO_3$: C, 40.88; H, 4.72; Br, 33.99; O, 20.42%.

References and notes

1. (a) Malanga, C.; Mannucci, S.; Lardicci, L. *J. Chem. Res., Synop.* **2001**, 97–99; (b) Malanga, C.; Mannucci, S. *Tetrahedron Lett.* **2001**, *42*, 2023–2025; (c) Malanga, C.; Mannucci, S.; Lardicci, L. *Tetrahedron Lett.* **1998**, *39*, 5615–5616; (d) Malanga, C.; Mannucci, S.; Lardicci, L. *Synth. Commun.* **1996**, *26*, 2317–2327.
2. (a) Rao, S. Y. *Chem. Rev.* **1964**, *64*, 353–388; (b) Rao, S. Y. *Chem. Rev.* **1975**, *75*, 625–693; (c) Chiacchio, U.; Pipern, A.; Rescifina, A.; Romeo, A.; Uccella, N. *Tetrahedron* **1988**, *54*, 5695–5708.
3. Feringa, B. L. *Synth. Commun.* **1985**, *15*, 87–89; (b) Feringa, B. L.; Dannnberg, W. *Synth. Commun.* **1983**, *13*, 509–514; (c) Chan, T. H.; Lee, S. D. *Tetrahedron Lett.* **1983**, *24*, 1225–1228; (d) Vankar, Y. D.; Shah, K. *Tetrahedron Lett.* **1991**, *32*, 1081–1084; (e) Guindon, Y.; Bernstein, M. A.; Anderson, P. C. *Tetrahedron Lett.* **1987**, *28*, 2225–2228; (f) Jung, M. E.; Andrus, M. A.; Ornstein, P. L. *Tetrahedron Lett.* **1977**, *48*, 4175–4178; (g) Kricheldorf, H. R.; Morber, G.; Regel, W. *Synthesis* **1981**, *81*, 383–384; (h) Gil, G. *Tetrahedron Lett.* **1984**, *25*, 3805–3808.
4. (a) Casiraghi, G.; Zanardi, F.; Appendino, G.; Rassu, G. *Chem. Rev.* **2000**, *100*, 1929–1972; (b) Rassu, G.; Zanardi, F.; Battistini, L.; Casiraghi, G. *Synlett* **1999**, 1333–1350.
5. Busque, F.; De March, P.; Figueredo, M.; Font, J.; Gonzalez, L. *Eur. J. Org. Chem.* **2004**, 1492–1499 and references therein.
6. (a) Zanardi, F.; Battistini, L.; Rassu, G.; Auzzas, L.; Pinna, L.; Marzocchi, L.; Acquotti, D.; Casiraghi, G. *J. Org. Chem.* **2000**, *65*, 2048–2064; (b) Li, P.; Yang, J.; Zhao, K. *J. Org. Chem.* **1999**, *64*, 2259–2263; (c) Hoyle, T. R.; Hanson, P. R. *Tetrahedron Lett.* **1993**, *34*, 5043–5046.
7. Chapleo, C. B.; Svanholt, K. L.; Martin, R.; Dreiding, A. S. *Helv. Chim. Acta* **1976**, *59*, 100–107.
8. (a) Mimero, P.; Saluzzo, C.; Amouroux, R. *Synth. Commun.* **1995**, *25*, 613–627; (b) Node, M.; Kajimoto, T.; Nishide, K.; Fujita, E.; Fuji, K. *Tetrahedron Lett.* **1984**, *25*, 219–222; (c) Pri-Bar, I.; Stille, J. K. *J. Org. Chem.* **1982**, *47*, 1215–1220; (d) Goldshmith, D.; Kennedy, E.; Campbell, R. G. *J. Org. Chem.* **1975**, *40*, 3571–3574; (e) Yadav, V. K.; Fallis, A. G. *J. Org. Chem.* **1986**, *51*, 3372–3374.
9. (a) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073–3100; (b) Hart, D. J. *Science* **1984**, *223*, 883–887; (c) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 553–565; Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon: Oxford, 1986.