Supplementary Information

General Methods. ^{1}H and ^{13}C NMR spectra were measured with 200 MHz (50 MHz) using tetramethylsilane as the internal standard. $CDCl_3$ is the solvent for all NMR experiments. All solvents used were of reagent grade and were further dried. Reactions were monitored by TLC on silica gel 60_{P254} and detected either by UV-absorption or by staining with H_2SO_4/ 4-methoxybenzaldehyde in ethanol. Were necessary, flash column chromatography was performed on silica gel 60 (230-400 mesh). Except for alcohols **12** and **13** all starting compounds are commercially available. The general procedures for the preparation of functionalized polymers **1** and their use in 1,2-cohalogenations of alkenes is described in reference 15 and references cited therein. The structures of aldehydes **6**, **15 - 18** and of ketones **30 - 35** as well as **37** have been elucidated before or were compared with commercial material.

General Procedure for the Preparation of Polymer-Bound Reagent 1: A suspension of polymer bound halide (available from Fluka; 3.5 g/mmol bromide) and $PhI(OAc)_2$ (1.8 eq.) in dry CH_2Cl_2 (2.5 mL/mmol halide anion) under nitrogen was shaken at 300 rpm for 24 h at room temperature. The yellowish suspension was protected from light. Filtration and washing of the resin with CH_2Cl_2 (3x) and drying in vacuo afforded the light yellow reagent.

General Procedure for the Oxidation of Alcohols: A mixture of the alcohol (1 eq.) resin (6 equiv.) in dry CH_2Cl_2 (2.5 mL/mmol bromide) with optional (refer to tables) 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) under nitrogen were shaken at 300 rpm. The reaction temperature (rt, 40 °C or 90 °C) varied according to the choice of alcohol. Completion of the reaction was monitored by TLC. Filtration terminated the reaction. The resin was washed with CH_2Cl_2 , cyclohexane or *n*-hexane (3x), and combined organic washings and filtrate were concentrated under reduced pressure. Typically, further purification steps were unnecessary (>95% purity) and the carbonyl compounds could directly be subjected for the next step. Still, for generating analytically pure samples and in order to remove oligomeric resin impurities purification by flash column chromatography was carried out in some cases. Finally, the polymer was recycled to the halide form by treatment with concentrated aqueous HBr for 1 h at room temperature.

Dichloromethane may be substituted by dry toluene. For reactive alcohols addition of TEMPO is not necessary. For use in automated synthesis, however, the addition of TEMPO is recommended in all cases in order to guarantee equal reaction conditions.

Acetophenone **(6)**: By treatment of 1-phenyl-ethanol (**5**) (61 mg, 0.5 mmol) with reagent **1** in CH_2Cl_2 at 40°C for 24h the title compound (**7**) (49 mg, 0.41 mmol, 81.6 %) was prepared. Under these conditions, conversion of **5** was quantitative. Final purification was achieved by flash column chromatography (petroleum ether/ethyl acetate 10:1).

Acetic acid 1-bromo-2-oxo-2-phenyl-ethyl ester **(7)**: By treatment of 1-phenyl-ethanol (**5**) (61.1 mg, 0.5 mmol) with reagent **1** in toluene at 90°C for 24h the title compound **7** (123 mg, 0.48 mmol, 95.2 %) was prepared. Under these conditions, conversion of **5** was quantitative. Final purification was achieved by flash column chromatography (petroleum ether/ethyl acetate 7:1).

7: colourless crystals: Mp. 50°C. **-** IR (KBr): ν = 694, 773, 899, 957, 1017, 1053, 1103, 1201, 1229, 1381, 1452, 1597, 1710, 1748, 1765, 2953 (cm^{-1}); ^{1}H NMR ($CDCl_3$): δ 8.25–7.25 (m, 5H), 7.6 (s, 1H), 2.18 (s, 3H). **-** ^{13}C NMR ($CDCl_3$): δ 188.7 (s), 168.6 (s), 134.2 (d), 133.1 (s), 128.8 (d), 128.7 (d), 86.2 (d), 20.6 (q). – $C_{10}H_9BrO_3$: (257.08): calcd. C 46.72, H 3.53, Br 31.08; found: C 46.55, H 3.57, Br 30.78.

Likewise, acetophenone **5** (60 mg, 0.5 mmol) was used to prepare the title compound **7** (114 mg, 0.44 mmol, 88.7 %) by the procedure described above.

Benzaldehyde **(15)**: By treatment of benzyl alcohol (**8**) (32.4 mg, 0.3 mmol) with reagent **1** and TEMPO in toluene at rt for 24h the title compound **15** (29 mg, 0.28 mmol, 94 %) was prepared. The conversion was quantitative as judged by GC.

4-Methoxybenzaldehyde **(16)**: By treatment of 4-methoxybenzyl alcohol (**9**) (41.4 mg, 0.3 mmol) with reagent **1** and TEMPO in CH_2Cl_2 at 40°C for 24h the title compound **16** (32 mg, 0.234 mmol, 78.1 %) was prepared. The conversion was quantitative as judged by GC. Final purification was achieved by flash column chromatography (petroleum ether/ethyl acetate 6.5:1).

Dodecanal **(17)**: By treatment of dodecanol (**10**) (37 mg, 0.2 mmol) with reagent **1** and TEMPO in CH_2Cl_2 at rt for 3.5h the title compound **17** (35 mg, 0.19 mmol, 93 %) was prepared. The conversion was quantitative as judged by GC.

2,2-Dimethylpropanal **(18):** By treatment of 2,2-dimethyl-1-propanol (**11**) (44 mg, 0.5 mmol) with reagent **1** and TEMPO in $CDCl_3$ at rt for 3.5h the title compound **18** was prepared. The conversion was quantitative as judged by ^{1}H NMR-spectroscopy. ^{1}H NMR ($CDCl_3$): δ 9.48 (s, 1H), 1.09 (s, 9H). **-** ^{13}C NMR ($CDCl_3$): δ 206.3 (d), 42.5 (s), 23.3 (3q).

(2R)-3-(tert.-Butyldiphenylsiloxy)-2-methyl-1-propanal **(19):** By treatment of (2*S*)-3-(*tert*.-butyldiphenylsiloxy)-2-methyl-1-propanol (**12**)[1] (65.6 mg, 0.2 mmol) with reagent **1** and TEMPO in CH_2Cl_2 at rt for 1.5h the title compound **19** (65 mg, 0.2 mmol, 99 %) was prepared.

19: oil. **-** $[\alpha]_D^{23}$= -24° (*c*= 1, $CHCl_3$). **-** IR (film): ν = 428, 613, 702, 740, 823, 937, 1035, 1112, 1391, 1427, 1472, 1736, 2858, 2932, 3071, 3384. **-** ^{1}H NMR ($CDCl_3$): δ 9.76 (d, 1H, *J*= 1.6), 7.7–7.35 (m, 10H), 3.90 (dd, 2H, *J*= 5.2, 10.4), 3.85 (dd, 1H, *J*= 6.2, 10.4), 2.57 (dddq, 1H, *J*= 1.6, 5.2, 6.2, 7.0), 1.10 (d, 3H, *J*= 7.0), 1.04 (s, 9H). - ^{13}C NMR ($CDCl_3$): δ 204.5 (d), 135.5 (d), 133.1 (s), 129.7 (d), 127.7 (d) 64.0 (t), 48.7 (d), 26.7 (q), 19.1 (s), 10.2 (q). – $C_{20}H_{26}O_2Si$: (326.50): calcd. C 73.57, H 8.03; found: C 73.76, H 8.07.

(2S, 3R)-4-(tert.-Butyldiphenylsiloxy)-2-(methoxymethoxyl)-3-methyl-1-butanal **(20):** By treatment of (2*S*, 3*R*)-4-(*tert*.-butyldiphenylsiloxy)-2-(methoxymethoxyl)-3-methyl-1-butanol (**13**)[2] (40.2 mg, 0.1 mmol) with reagent **1** and TEMPO in CH_2Cl_2 at rt for 2h the title compound **20** (40 mg, 0.1 mmol, 99 %) was prepared.

20: oil. - $[\alpha]_D^{23}$= -6° (*c*= 1, $CHCl_3$). - IR (film): ν = 449, 613, 703, 741, 823, 919, 1036, 1111, 1154, 1215, 1390, 1428, 1472, 1732, 2932. - ^{1}H NMR ($CDCl_3$): δ 9.74 (d, 1H, *J*= 1.6), 7.70–7.33 (m, 10H), 4.72 and 4.70 (2d, 2H), 4.22 (dd, 1H, *J*= 1.2, 3.8), 3.64 (ddd, 1H, *J*= 5.6, 10.0), 3.60 (dd, 1H, *J*= 7.8, 10.0), 3.40 (s, 3H), 2.22 (m, 1H), 1.05 (s, 9H), 0.86 (d, 1H, *J*= 7.0). - ^{13}C NMR ($CDCl_3$): □ 203.7 (d), 135.5 (d), 133.3 (s), 129.7 (d), 127.6 (d), 97.1 (t), 82.6 (d), 64.4 (t), 55.9 (q), 37.9 (d), 26.7 (q), 19.1 (s), 10.9 (q). – $C_{23}H_{32}O_4Si$: (400.58): calcd. C 68.96, H 8.05; found: C 68.77, H 8.11.

1,2:3,4-Di-O-isopropylidene-6-oxo-α-D-galactopyranose **(21):** By treatment of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**14**) (130 mg, 0.5 mmol) with reagent **1** and TEMPO in CH_2Cl_2 at 40°C for 24h the title compound (**16**) (129 mg, 0.49 mmol, 99 %) was prepared.

21: ^{1}H NMR ($CDCl_3$): δ 9.63 (s, 1H) 5.67 (d, 1H, *J* = 5.0), 4.65 (2dd, 2H, *J*= 2.2, 8.0), 4.39 (dd, 1H *J*= 2.2, 4.8), 4.2 (d, 1H, *J* = 2.2), 1.52, 1.44, 1.36, 1.32 (3s, 12H). - ^{13}C NMR ($CDCl_3$): δ 200.3 (d), 110.0 (s), 109,0 (s) 96.2 (d), 73.2 (d), 71.7 (d), 70.4 (d), 70.3 (d), 25.9 (q), 25.8 (q), 24.8 (q), 24.2 (q).

Indanon (30): By treatment of indanol (**24**) (40 mg, 0.3 mmol) with reagent **1** and TEMPO in CH_2Cl_2 at 40°C for 24h the title compound **30** (32 mg, 0.24 mmol, 81 %) was prepared. The conversion was quantitative as judged by GC. Final purification was achieved by flash column chromatography (petroleum ether/ethyl acetate 6.5:1).

Cyclohexanone (31): By treatment of cyclohexanol (**25**) (20 mg, 0.2 mmol) with reagent **1** and TEMPO in CH_2Cl_2 at rt for 24h the title compound **31** (19 mg, 0.19 mmol, 96 %) was prepared. The conversion was quantitative as judged by GC.

Cyclooctanone (32): By treatment of cyclooctanol (**26**) (38.4 mg, 0.3 mmol) with reagent **1** and TEMPO in CH_2Cl_2 at 40°C for 24h the title compound **32** (30.3 mg, 0.24 mmol, 80.1 %) was prepared. The conversion was quantitative as judged by GC.

1,2,3,4-Tetrahydro-1-naphthanone (33): By treatment of tetralole (**27**) (59.3 mg, 0.4 mmol) with reagent **1** and TEMPO in CH_2Cl_2 at 40°C for 24h the title compound **33** (55 mg, 0.38 mmol, 94 %) was prepared. The conversion was quantitative as judged from the crude ^{1}H NMR-spectrum. Final purification was achieved by flash column chromatography (petroleum ether/ethyl acetate 15:1). The conversion was quantitative as judged from the crude ^{1}H NMR-spectrum.

33: oil. - ^{1}H NMR ($CDCl_3$): δ 8.1-7.2 (m, 4H), 2.97 (t, 2H, *J*= 6.0), 2.66 (dd, 2H, *J* = 6.0, 7.2), 2.14 (q, 2H, *J*= 6.0). - ^{13}C NMR ($CDCl_3$): δ 198.4 (s), 144.4 (s), 133.3 (d), 132.5 (s), 128.7 (d), 127.1 (d), 126.6 (d), 39.1 (t), 29.6 (t), 23.2 (t).

1-(2-Methoxyphenyl)-ethanone (34): By treatment of 1-(2-methoxyphenyl)ethanol (**28**) (84 mg, 0.5 mmol) with reagent **1** and TEMPO in CH_2Cl_2 at 40°C for 24h the title compound **34** (80 mg, 0.48 mmol, 96 %) was prepared. The conversion was quantitative as judged from the crude ^{1}H NMR-spectrum. Final purification was achieved by flash column chromatography (petroleum ether/ethyl acetate 10:1).

34: oil. - ^{1}H NMR ($CDCl_3$): δ 7.80 – 6.9 (m, 4H), 3.90 (s, 3H), 2.62 (s, 3H). - ^{13}C NMR ($CDCl_3$): δ 199.9 (s), 158.8 (s), 133.6 (d), 130.3 (d), 128.2 (s),120.5 (d), 111.5 (d), 55.4 (q), 31.8 (q).

2-Hydroxy-1-phenyl-ethanone (35): By treatment of 1-phenyl-1,2-ethandiol (**29**) (69.1 mg, 0.5 mmol) with reagent **1** and TEMPO in CH_2Cl_2 at rt for 24h the title compound **35**. The conversion was quantitative as judged from the crude ^{1}H NMR-spectrum. Final purification was achieved by flash column chromatography (petroleum ether/ethyl acetate 10:1) but the yield was reduced in the purification step (30 mg, 0.22 mmol, 44 %).

35: colourless crystals: Mp. 82°C. - ^{1}H NMR ($CDCl_3$): δ 8.0 - 7.4 (m, 5H), 4.88 (d, 2H, *J*= 4.4). - ^{13}C NMR ($CDCl_3$): δ 198.8 (s), 134.7 (s), 133.7 (d), 2x 129.4 (d) 2x 128.1 (d) 65.8 (t).

References:

(1) Alcohol **12** was prepared from commercial (2*R*)-3-hydroxy-2-methyl-propionic methyl ester by silylation and dibal-promoted reduction of the ester functionality under standard conditions.

(2) Alcohol **13** was prepared from alcohol **23** by methoxymethylation (MOMCl, CH_2Cl_2, Et_3N) and dibal-promoted reduction of the ester functionality.