Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Preparation of Functionalized Benzylic Magnesium Reagents Using a New Sulfur-Magnesium Exchange Reaction **

Supporting Information

Armin H. Stoll, Arkady Krasovskiy and Paul Knochel*

Ludwig Maximilians-Universität München, Department Chemie
Butenandtstrasse 5-13, Haus F, 81377 München (Germany)
Fax: (+49) 089 2180 77680
e-mail: paul.knochel@cup.uni-muenchen.de

General All reactions were carried out under an argon atmosphere in dried glassware. All starting materials were purchased from commercial sources and used without further purification. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by ^{1}H-NMR and capillary GC.

Preparation of the reagent *i*PrMgCl·LiCl:

Magnesium turnings (2.67 g, 110 mmol) and anhydrous LiCl (4.24 g, 100 mmol) were placed in an Ar-flushed flask and THF (50 mL) was added. A solution of *i*PrCl (7.85 g, 100 mmol) in THF (50 mL) was slowly added at rt. The exothermic reaction starts within a few min after the addition of ca. 10 % of *i*PrI. The remaining 90 % of *i*PrI were added dropwise to keep THF boiling. After complete addition, the reaction mixture was stirred for 12 h at rt. The grey solution of *i*PrMgCl·LiCl was cannulated to another flask under Ar and removed in this way from excess of magnesium. A yield of ca. 95-98% of *i*PrMgCl·LiCl is obtained and titrated prior to use by the method of Paquette.[1]

Typical procedure for the preparation of thiosulfonates of type 2 from benzylic halides[2] (TP1)

A dry and argon-flushed 500 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with $PhSO_2SNa$[3] (6.86 g, 35.0 mmol) and DMF (200 mL). After addition of the benzylic halide (1.0 equiv) the reaction mixture was stirred for 40 to 94 h at rt. The completion of the reaction was checked by TLC and the mixture was quenched with water (400 mL). After extraction with Et_2O or CH_2Cl_2 (3 x 100 mL) the combined organic phases were washed with saturated $NaHCO_3$ solution (100 mL) and water (200 mL). The organic phase was then dried over Na_2SO_4 and concentrated *in vacuo* to lead to the desired compounds (**2b-2d, 2g, 2h**). In some cases additional recrystallization from heptane was necessary to obtain analytically pure compounds.

Typical procedure for the preparation of thioethers of type 1 from thiosulfonates(TP2)

A dry and argon flushed 250 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with 2,2´-diiodobiphenyl (1.0 equiv) and THF. The clear solution was cooled to –50 °C followed by the slow addition of *i*PrMgCl·LiCl (1.0 – 1.1 equiv, solution in THF). The reaction mixture was stirred for 1.5 h at –40 °C and the conversion to the magnesium reagent of type **3** was checked by GC-analysis, using tetradecane as internal standard. After full conversion a solution of **2a-d, g, h** (1.0 equiv) in THF was added at –50 °C and the temperature was increased. When no further conversion to the desired product of type **1** could be observed, the mixture was quenched with saturated NH_4Cl solution, and extracted with Et_2O. The organic layer was separated and washed with water (3x). The aqueous solution was also extracted with Et_2O (2x). The combined ether phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by recrystallization or column chromatography.

Typical procedure for the preparation of thioethers of type 1 from arylcopper derivatives (TP3)

A dry and argon flushed 100 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with 2-chloromethylsulfanyl-2´-iodobiphenyl (**5**) (1.0 equiv) and THF. The clear solution was cooled to –40 °C followed by the addition of Bu_4NI (1.0 equiv). The reaction mixture was stirred for 30 min at –40 °C. Then the corresponding arylcopper derivate (1.5 equiv) was cannulated to **5** at –40 °C and the reaction temperature was slowly increased to room temperature by turning off the cooling device. All used arylcopper derivatives were obtained from the reaction of aryl bromides with *i*PrMgCl·LiCl followed by transmetalation with CuCN·2LiCl (1.0 M solution in THF, 1.0 equiv) at -30 °C in 30 min. When no further conversion to the desired product of type **1** could be observed (20 h), the mixture was quenched with a saturated NH_4Cl/NH_3 solution and extracted with Et_2O. The organic layer was separated and washed with saturated NH_4Cl (3x). The aqueous solutions were then extracted with Et_2O (2x). The combined ether phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by column chromatography.

Typical procedure for the preparation of benzylic magnesium reagents of type 8a (TP4)

A dry and argon flushed 50 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with **1a** (0.402 g, 1.0 mmol) and THF (1.0 mL). The resulting solution was cooled to –50 °C followed by the slow addition of *i*PrMgCl (1.3 mL, 1.1 mmol, 0.85 M in THF). The reaction mixture was stirred for 1.5 h at –15 °C and then evaporated (10^{-1} mm Hg, 25 °C, 1 h). The white precipitate was dissolved with THF (2.0 mL) and evaporated again as described before. THF (1.0 – 1.9 mL) was used to dissolve the residue a second time and conversion of I/Mg-exchange was checked by GC-analysis, using tetradecane as internal standard. After full conversion, a solution of LiO*t*Bu (0.1 – 1.0 equiv, 1.0 M in THF) was added at –20 °C and the mixture was stirred for 20 – 46 h. After the addition of an electrophile, the reaction mixture was quenched with water(50 mL), extracted with Et_2O (3 x 50 mL) and dryed over Na_2SO_4. Concentration *in vacuo* afforded a crude residue which was purified by flash-chromatography.

Typical procedure for the preparation of benzylic magnesium reagents of type 8b (TP5)

A dry and argon flushed 50 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with **1b** (0.481 g, 1.0 mmol) and THF (1.0 mL). The solution was cooled to –50 °C followed by the slow addition of *i*PrMgCl (1.3 mL, 1.1 mmol, 0.85 M in THF). The reaction mixture was stirred for 1.5 h at –15 °C and then evaporated (10^{-1} mm Hg, 25 °C, 1 h). The resulting white precipitate was dissolved with THF (2.0 mL) and evaporated again as described before. THF (1.5 mL) was used to dissolve the residue a second time and the completion of S/Mg-exchange was checked by GC-analysis, using tetradecane as internal standard. After full conversion, the benzylic magnesium reagent **8b** was treated with various electrophiles, leading to the expected products. Quenching with water (50 mL), extraction with Et_2O (3 x 150 mL), drying over Na_2SO_4 and concentration *in vacuo* afforded a crude reaction mixture which was purified by flash-chromatography.

Typical procedure for the preparation of benzylic magnesium reagents of type 8c or 8d-f (TP6)

The procedure is the same as **TP5**, but evaporation was started after 45 min (for **8c**) or immediately (for **8d-f**) after addition of *i*PrMgCl. The benzylic magnesium reagents **8d-f** were only prepared on 0.50 mmol scale.

Typical procedure for the preparation of benzylic magnesium reagents of type 8g (TP7)

A dry and argon flushed 50 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with **1g** (0.216 g, 0.50 mmol) and THF (1.0 mL). The clear solution was cooled to –50 °C followed by the slowly addition of *i*PrMgCl (0.58 mL, 0.55 mmol, 0.95 M in THF). The reaction mixture was immediately evaporated (10^{-1} mm Hg, 25 °C, 1 h). The white precipitate was dissolved with THF (2.0 mL) and evaporated again as described before. THF (1.5 mL) was used to dissolve the residue a second time and conversion of I/Mg-exchange was checked by GC-analysis, using tetradecane as internal standard. After full conversion a solution of LiO*t*Bu (0.50 mL. 0.50 mmol, 1.0 M in THF) was added at -15 °C and the mixture was stirred for 18 h at –5 °C. The addition of various electrophiles leads to the expected products. Quenching with water (100 mL), extraction with Et_2O (3 x 150 mL), drying over Na_2SO_4 and concentration *in vacuo* afforded a crude product which was purified by flash-chromatography.

Typical Procedure for transmetalation of magnesium reagents (TP8)

The freshly prepared benzylic magnesium reagent was cooled to -30 °C and $ZnCl_2$ (1.0 M solution in THF, 1.0 equiv) was added drop by drop. After stirring 30 min at this temperature CuCN·2LiCl (1.0 M solution in THF, 1.0 equiv) was added in the same way. After 30 min, the mixture was ready for a reaction with acid chlorides.

2-Benzylsulfanyl-2'-iodo-biphenyl (1a)

The reaction was performed according to **TP2** with 2,2´-diiodobiphenyl (4.06 g, 10.0 mmol), THF (10 mL) and *i*PrMgCl·LiCl (9.09 mL, 10.0 mmol, 1.10 M in THF). After full conversion to the magnesium reagent (1.5 h) a solution of **2a** (2.64 g, 10.0 mmol) in THF (10 mL) was added at -40 °C and the temperature was increased to –15 °C. After a reaction time of 45 min the mixture was worked up. The crude residue was recrystallized from heptane yielding 2-benzylsulfanyl-2'-iodo-biphenyl (**1a**) (2.82 g, 70%) as white crystals.

Alternatively **1a** can be prepared according to **TP3** with **5** (721 mg, 2.00 mmol), THF (2.0 mL), Bu_4NI (739 mg, 2.00 mmol), PhMgCl (2.08 mL, 3.00 mmol, 1.44 M in THF) and CuCN·LiCl (3.00 mL, 3.00 mmol, 1.00 M in THF). After a reaction time of 20 h the mixture was worked up. The crude residue was purified by flash-chromatography (pentane/CH_2Cl_2 = 5/1) yielding 2-benzylsulfanyl-2'-iodo-biphenyl (**1a**) (0.61 g, 75%) as white crystals.

mp: 55.9 – 56.4 °C.

^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.96 (dd, *J* = 7.8 Hz, *J* = 1.2 Hz, 1 H); 7.44 – 7.35 (m, 3 H); 7.33 – 7.23 (m, 6 H); 7.17 –7.05 (m, 3 H); 4.07 (d, *J* = 13.0 Hz, 1 H); 4.02 (d, *J* = 13.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 75 MHz): d = 145.8; 145.3; 139.3; 137.5; 136.1; 130.7; 130.4; 129.5; 129.5; 129.4; 128.9; 128.8; 128.2; 127.5; 126.3; 100.8; 38.9.

IR (KBr; cm^{-1}): $\tilde{n}$ **=** 3060 (m); 3026 (m); 2919 (m); 1578 (w); 1494 (m); 1453 (vs); 1438 (m); 1428 (m); 1018 (m); 1000 (m); 756 (vs); 734 (w); 719 (s); 699 (m); 687 (w); 648 (w); 488 (w).

HRMS (EI, 70 eV): m/z (%) = 275 (6); 197 (3); 184 (62); 158 (1); 152 (7); 139 (9); 91 (100); 79 (3); 65 (8).

HRMS: calc.: 401.9939, found.: 401.9890 (M^+).

2-(3-Bromo-benzylsulfanyl)-2'-iodo-biphenyl (1b)

The reaction was performed according to **TP2** with 2,2´-diiodobiphenyl (5.55 g, 13.7 mmol), THF (25 mL) and *i*PrMgCl·LiCl (12.4 mL, 13.7 mmol, 1.10 M in THF). After full conversion to the magnesium reagent (1.5 h) a solution of **2b**

(5.17 g, 15.1 mmol) in THF (15 mL) was added at -40 °C and the temperature was increased to –15 °C. After a reaction time of 1.5 h the mixture was worked up. The crude residue was purified by flash-chromatography (pentane/CH_2Cl_2 = 5/1) yielding 2-(3-bromo-benzylsulfanyl)-2'-iodo-biphenyl (**1b**) (4.02 g, 61%) as a colourless viscous oil.

^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.97 (dd, *J* = 7.7 Hz, *J* = 1.1 Hz, 1 H); 7.43 – 7-28 (m, 6 H); 7.16 – 7.06 (m, 5 H); 3.99 (d, *J* = 13.5 Hz, 1 H); 3.94 (d, *J* = 13.5 Hz, 1 H).
^{13}C NMR ($CDCl_3$, 75 MHz): d = 145.8; 145.7; 140.0; 139.3; 135.2; 132.3; 130.6; 130.6; 130.3; 130.1; 129.5; 129.0; 128.3; 127.9; 126.8; 122.8; 114.1; 100.8; 38.1.

IR (film; cm^{-1}): $\tilde{n}$ = 3051 (w); 1590 (m); 1578 (m); 1568 (m); 1474 (m); 1453 (s); 1428 (s); 1233 (w); 1070 (m); 1018 (m); 1000 (s); 786 (m); 752 (vs); 733 (m); 722 (m); 681 (m); 648 (w).
HRMS (EI, 70 eV): m/z (%) = 355 ([M-I]$^+$, 14); 274 (2); 197 (24); 184 (69); 169 (100); 152 (17); 139 (21); 113 (2); 90 (18); 75 (2); 63 (5); 51 (2).
HRMS (FAB, NBA, 20 kV): calc.: 480.9123, found.: 480.9111 ([M+H]$^+$).

2-(2-Bromo-benzylsulfanyl)-2'-iodo-biphenyl (1c)

The reaction was performed according to **TP2** with 2,2´-diiodobiphenyl (5.68 g, 14.0 mmol), THF (30 mL) and *i*PrMgCl·LiCl (12.7 mL, 14.0 mmol, 1.10 M in THF). After full conversion to the magnesium reagent (1.5 h) a solution of **2c** (5.29 g, 15.4 mmol) in THF (20 mL) was added at -40 °C and the temperature was increased to –20 °C. After a reaction time of 45 min the mixture was worked up. The crude residue was purified by flash-chromatography (pentane/CH_2Cl_2 = 5/1) yielding 2-(2-bromo-benzylsulfanyl)-2'-iodo-biphenyl (**1c**) (4.92 g, 73%) as fine white crystals.

mp: 75.5 – 76.6 °C.

^{1}H NMR (CDCl$_3$, 300 MHz): d = 7.96 (dd, *J* = 8.0 Hz, *J* = 1.3, 1 H); 7.54 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1 H); 7.42 – 7.25 (m, 5 H); 7.21 – 7.05 (m, 5 H); 4.12 (s, 2 H).

^{13}C NMR (CDCl$_3$, 75 MHz): d = 145.9; 145.8; 139.3; 136.9; 135.4; 133.3; 131.3; 130.6; 130.5; 129.5; 129.1; 128.9; 128.2; 127.8; 126.7; 125.1; 114.1; 100.8; 39.5.

IR (KBr; cm^{-1}): $\tilde{n}$ = 3050 (m); 2926 (m); 2846 (m); 1586 (m); 1572 (w); 1470 (m); 1453 (s); 1444 (m); 1428 (s); 1233 (w); 1018 (m); 1000 (m); 756 (vs); 746 (s); 648 (w).

MS (EI, 70 eV): m/z (%) = 355 ([M-I]$^+$, 18); 273 (4); 239 (2); 197 (7); 184 (64); 169 (100); 152 (16); 139 (20); 90 (13); 63 (4).

HRMS (FAB, NBA, 20 kV): calc.: 480.9123, found.: 480.9102 ([M+H]$^+$).

2-(4-Bromo-3-methyl-benzylsulfanyl)-2'-iodo-biphenyl (1d)

The reaction was performed according to **TP2** with 2,2´-diiodobiphenyl (6.42 g, 15.8 mmol), THF (30 mL) and *i*PrMgCl·LiCl (13.2 mL, 15.8 mmol, 1.20 M in THF). After full conversion to the magnesium reagent (1.5 h) a solution of **2d** (6.20 g, 17.4 mmol) in THF(20 mL) was added at –50 °C and the temperature was increased to –30 °C. After a reaction time of 1.5 h the mixture was worked up. The crude residue was purified by flash-chromatography (pentane/CH$_2$Cl$_2$ = 5/1) yielding 2-(4-bromo-3-methyl-benzylsulfanyl)-2'-iodo-biphenyl (**1d**) (7.03 g, 81%) as a colourless viscous oil.

^{1}H NMR (CDCl$_3$, 300 MHz): d = 7.96 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1 H); 7.42 – 7.27 (m, 5 H); 7.16 – 7.05 (m, 4 H); 6.91 (dd, *J* = 8.4 Hz, *J* = 2.2 Hz, 1H); 3.96 (d, *J* = 13.3 Hz, 1 H); 3.91 (d, *J* = 13.3 Hz, 1 H); 2.35 (s, 3 H).

^{13}C NMR (CDCl$_3$, 75 MHz): d = 145.8; 145.5; 139.3; 138.3; 136.8; 135.6; 132.6; 131.8; 130.7; 130.5; 129.8; 129.5; 128.5; 128.3; 128.2; 126.6; 123.9; 100.8; 38.4; 23.2.

IR (film; cm^{-1}): $\tilde{n}$ **=** 3050 (m); 2922 (m); 1579 (m); 1474 (s); 1453 (vs); 1430 (s); 1028 (vs); 1019 (s); 1000 (s); 820 (m); 751 (vs); 732 (s); 722 (m); 648 (m).

HRMS (EI, 70 eV): m/z (%) = 367 ([M-I]$^+$, 2); 197 (2); 186 (11); 185 (100); 139 (12); 104 (9); 77 (6); 63 (2); 51 (2).

HRMS: calc.: 493.9200, found.: 493.9190 (M$^+$).

2-(3-Chloro-benzylsulfanyl)-2'-iodo-biphenyl (1e)

The reaction was performed according to **TP3** with **5** (2.16 g, 6.00 mmol), THF (6.0 mL) and Bu$_4$NI (2.21 g, 6.00 mmol). Another dry and argon flushed 50 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (8.57 mL, 9.00 mmol, 1.05 M in THF). 1-Bromo-3-chloro-benzene (1.72 g, 9.00 mmol) was added at rt and stirred for 15 h to give the aryl magnesium derivative. After transmetalation with CuCN·LiCl (9.00 mL, 9.00 mmol, 1.00 M in THF) the arylcopper derivative was cannulated slowly to **5** at –40 °C. After a reaction time of 20 h the mixture was worked up. The crude residue was purified by flash-chromatography (pentane/CH$_2$Cl$_2$ = 10/1) yielding 2-(3-chloro-benzylsulfanyl)-2'-iodo-biphenyl (**1e**) (1.78 g, 68%) as a yellow oil.

^{1}H NMR (CDCl$_3$, 300 MHz): d = 7.97 (dd, *J* = 7.8 Hz, J = 1.1 Hz, 1 H); 7.43 – 7.37 (m, 2 H); 7.36 – 7.27 (m, 2 H); 7.25 – 7.17 (m, 3 H); 7.17 – 7.05 (m, 4 H); 4.00 (d, *J* = 13.3 Hz, 1 H); 3.95 (d, *J* = 13.3 Hz, 1 H).

^{13}C NMR (CDCl$_3$, 75 MHz): d = 145.7; 145.7; 139.7; 139.3; 135.3; 134.6; 130.6; 130.6; 130.0; 130.0; 129.5; 129.4; 129.0; 128.3; 127.7; 127.5; 126.7; 100.7; 38.5.

IR (UATR; cm^{-1}): $\tilde{n}$ **=** 3049 (w); 1585 (m); 1573 (m); 1556 (m); 1475 (m); 1452 (s); 1427 (s); 1231 (m); 1076 (m); 1017 (m); 999 (s); 785 (m); 747 (vs); 721 (s); 680 (s).
MS (EI, 70 eV): m/z (%) = 309 (11); 197 (14); 184 (48); 183 (5); 152 (12); 139 (15); 127 (33); 125 (100); 99 (3); 89 (9); 63 (4).
HRMS (ESI): calc.: 434.9471, found.: 434.9488 ([M-H]$^{+}$).

2'-Iodo-2-(3-trifluoromethyl-benzylsulfanyl)-biphenyl (**1f**) The reaction was performed according to **TP3** with **5** (2.16 g, 6.00 mmol), THF (6.0 mL) and Bu_4NI (2.21 g, 6.00 mmol). Another dry and argon flushed 50 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (8.57 mL, 9.00 mmol, 1.05 M in THF). 1-Bromo-3-trifluoromethyl-benzene (2.03 g, 9.00 mmol) was added at rt and stirred for 2 h to give the aryl magnesium derivative. After transmetalation with CuCN·LiCl (9.00 mL, 9.00 mmol, 1.00 M in THF) the arylcopper derivative was cannulated slowly to **5** at –40 °C. After a reaction time of 20 h the mixture was worked up. The crude residue was purified by flash-chromatography (pentane/ether = 10/1) yielding 2'-iodo-2-(3-trifluoromethyl-benzylsulfanyl)-biphenyl (**1f**) (3.02 g, 71%) as a colourless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): d = 8.00 – 7.93 (m, 1H); 7.53 – 7.43 (m, 2 H); 7.42 – 7.27 (m, 6 H); 7.18 – 7.04 (m, 3 H); 4.06 (d, *J* = 13.2 Hz, 1 H); 4.00 (d, *J* = 13.2 Hz, 1 H).
^{13}C NMR ($CDCl_3$, 75 MHz): d = 146.1; 145.7; 139.3; 138.8; 134.9; 132.6; 131.1 (d, *J* = 32.3 Hz); 130.6; 130.6; 130.5; 129.5; 129.2; 129.0; 128.2; 127.0; 126.1 (q, *J* = 3.5 Hz); 124.4 (q, *J* = 3.5 Hz); 120.8 (d, *J* = 274.0 Hz); 100.7; 38.7.

IR (UATR, cm^{-1}): $\tilde{n}$ **=** 3050 (w); 1579 (w); 1557 (w); 1490 (w); 1450 (m); 1428 (m); 1232 (m); 1162 (s); 1119 (vs); 1090 (m); 1071 (s); 1018 (m); 1000 (m); 748 (vs); 698 (vs); 658 (s).

MS (EI, 70 eV): m/z (%) = 343 (36); 323 (1); 197 (10); 184 (58); 159 (100); 152 (11); 139 (14); 109 (6); 89 (2); 69 (1).
HRMS (ESI): calc.: 468.9735, found.: 468.9754 ($[M-H]^+$).

2'-Iodo-2-(2-methoxy-benzylsulfanyl)-biphenyl (1g)

The reaction was performed according to **TP2** with 2,2´-diiodobiphenyl (7.38 g, 18.2 mmol), THF (20 mL) and *i*PrMgCl·LiCl (8.86 mL, 18.2 mmol, 2.05 M in THF). After full conversion to the magnesium reagent (1.5 h) a solution of **2g** (5.88 g, 20.0 mmol) in THF (15 mL) was added at -50 °C and the temperature was increased to –30 °C. After a reaction time of 1 h the mixture was worked up. The crude residue was purified by flash-chromatography (pentane/CH_2Cl_2 = 5/1) yielding 2'-iodo-2-(2-methoxy-benzylsulfanyl)-biphenyl (**1g**) (6.99 g, 81%) as white crystals.

mp: 76.1 – 78.5 °C.
^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.84 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1 H); 7.35 – 6.72 (m, 11 H); 3.97 (s, 2 H); 3.69 (s, 3 H).
^{13}C NMR ($CDCl_3$, 75 MHz): d = 157.8; 146.0; 145.3; 139.2; 136.6 130.7; 130.7; 130.3; 129.7; 129.3; 128.8; 128.1; 126.0; 125.9; 120.8; 110.9; 100.8; 89.3; 55.9; 33.2.

IR (KBr; cm^{-1}): $\tilde{n}$ **=** 3061 (m); 2922 (m); 2836 (m); 1600 (m); 1587 (m); 1494 (vs); 1462 (s); 1454 (vs); 1437 (s); 1426 (s); 1289 (m); 1249 (vs); 1175 (m); 1095 (m); 1048 (m); 1022 (s); 1000 (m); 758 (vs).
HRMS (EI, 70 eV): m/z (%) = 305 ($[M-I]^+$, 1); 197 (2); 184 (37); 152 (5); 139 (6); 121 (100); 91 (27); 78 (2); 65 (3); 51(1).
HRMS: calc.: 432.0044, found.: 432.0080 (M^+).

1-Bromo-2-(2'-iodo-biphenyl-2-ylsulfanylmethyl)-naphthalene (1h)

The reaction was performed according to **TP2** with 2,2´-diiodobiphenyl (5.17 g, 12.7 mmol), THF (20 mL) and *i*PrMgCl·LiCl (11.6 mL, 12.7 mmol, 1.10 M in THF). After full conversion to the magnesium reagent (1.5 h) a solution of **2h** (5.50 g, 14.0 mmol) in THF (15 mL) was added at -50 °C and the temperature was increased to –30 °C. After a reaction time of 1 h the mixture was worked up. The crude residue was purified by flash-chromatography (pentane/CH$_2$Cl$_2$ = 7/1) yielding 1-bromo-2-(2'-iodo-biphenyl-2-ylsulfanylmethyl)-naphthalene (**1h**) (5.40 g, 80%) as white crystals.

mp: 94.1 – 95.1 °C.
^{1}H NMR (CDCl$_3$, 300 MHz): d = 8.30 (brd, *J* = 8.7 Hz, 1 H); 7.95 (brd, *J* = 8.4 Hz, 1 H); 7.80 (brd, *J* = 7.7 Hz, 1 H); 7.69 (d, *J* = 8.4 Hz, 1 H); 7.63 - 7.43 (m, 3H); 7.38 – 7.25 (m, 4 H); 7.18 – 7.02 (m, 3 H); 4.39 (d, *J* = 13.1 Hz, 1 H); 4.35 (d, *J* = 13.1 Hz, 1 H).
^{13}C NMR (CDCl$_3$, 75 MHz): d = 146.1; 145.8; 139.2; 135.4; 135.1; 134.1; 132.9; 130.9; 130.6; 130.5; 129.4; 129.0; 128.4; 128.3; 128.1; 128.0; 127.8; 127.8; 126.9; 126.8; 125.0; 100.9; 40.8.

IR (KBr; cm^{-1}): $\tilde{n}$ **=** 3051 (m); 1621 (w); 1588 (w); 1578 (w); 1556 (m); 1501 (m); 1542 (s); 1434 (m); 1329 (m); 1019 (m); 1000 (m); 817 (s); 758 (vs); 648 (m).
HRMS (FAB, NBA, 8 kV): m/z (%) = 532 ([M+H]$^+$, 16); 405 (5); 221 (60); 219 (61); 77 (10); 41 (5).
HRMS (FAB, NBA, 8 kV): calc.: 530.9279, found.: 530.9267 ([M+H]$^+$).

2-Benzylsulfanyl-2'-bromo-biphenyl (1i)

2,2´-Dibromo-biphenyl was prepared in one step from 1,2-dibromo-benzene.[4]

A dry and argon flushed 50 mL flask, equipped with a magnetic stirrer and a septum, was charged with 2,2´-dibromo-biphenyl (1.87 g, 6.00 mmol) and THF (15 mL). The clear solution was cooled to –90 °C followed by the very slow addition of *n*BuLi (3.75 mL, 6.00 mmol, 1.60 M in hexane). After five minutes the Br/Li-exchange was complete and a solution of **2a** (1.59 g, 6.00 mmol) in THF (6.0 mL) was added at -90 °C. After 15 min the mixture was quenched with water (50 mL) and extracted with Et_2O (100 mL). The organic layer was separated and washed with water (2x 50 mL). The aqueous solutions were then extracted with Et_2O (2x 50 mL). The combined ether phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash-chromatography (pentane/CH_2Cl_2 = 10/1) yielding 2-benzylsulfanyl-2'-bromo-biphenyl (**1i**) (1.86 g, 87%) as a white solid.

mp: 50.3 – 50.8 °C.
^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.69 (dd, *J* = 8.0 Hz, J = 1.3 Hz, 1 H); 7.45 – 7.40 (m, 1 H); 7.38 – 7.27 (m, 4 H); 7.27 – 7.15 (m, 7 H); 4.03 (d, *J* = 12.8 Hz, 1 H); 3.99 (d, *J* = 12.8 Hz, 1 H).
^{13}C NMR ($CDCl_3$, 75 MHz): d = 142.4; 141.8; 137.5; 136.1; 132.9; 131.8; 130.5; 129.8; 129.5; 129.3; 128.8; 128.8; 127.5; 127.4; 126.4; 124.4; 39.1.

IR (KBr; cm^{-1}): $\tilde{n}$ **=** 3050 (w); 2916 (w); 1580 (w); 1493 (w); 1452 (m); 1422 (m); 1056 (m); 1026 (m); 1001 (m); 750 (vs); 733 (s); 710 (s); 696 (s); 675 (s).
MS (EI, 70 eV): m/z (%) = 275 (12); 197 (3); 184 (21); 158 (1); 152 (6); 139 (7); 91 (100); 79 (1); 65 (7).
HRMS (EI, 70 eV): calc.: 354.0078, found.: 354.0086 (M^+).

Preparation of thiosulfonate (2a) from the corresponding disulfide[5]

Benzenethiosulfonic acid S-benzyl ester (2a)

A dry 500 mL flask, equipped with a magnetic stirring bar and a septum, was charged with dibenzyl disulfide (9.85 g, 40.0 mmol) and CH_2Cl_2 (100 mL). After adding iodine (20.3 g, 80.0 mmol) and $PhSO_2Na$ (21.0 g, 128 mmol) the mixture was stirred 22 h at rt. Saturated $Na_2S_2O_3$ solution was added until the reaction mixture was completely decolourized. After separation and extraction of the organic layer with water (3 x 100 mL) the organic phase was dried over Na_2SO_4. Concentration *in vacuo* afforded an orange oil. Recrystallization from heptane gave analytically pure benzenethiosulfonic acid S-benzyl ester (**2a**) (16.5 g, 95%) as a white crystalline product.

mp: 43.5 – 44.5 °C.
^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.88 –7.84 (m,2 H); 7.64 – 7.58 (m, 1 H); 7.53 – 7.47 (m, 2 H); 7.28 – 7.17 (m, 5 H); 4.29 (s, 2 H).
^{13}C NMR ($CDCl_3$, 75 MHz): d = 145.3; 134.0; 133.9; 129.5; 129.5; 129.2; 128.4; 127.3; 40.8.

IR (KBr; cm^{-1}): $\tilde{n}$ **=** 3069 (s); 1495 (s); 1480 (m); 1447 (w); 1161 (m); 1081 (w); 1066 (m); 776 (m); 756 (w); 682 (w).
MS (FAB, NBA, 8 kV): m/z (%) = 287 ([M+Na]$^+$, 14); 265 ([M+H]$^+$, 64); 260 (7); 181 (4); 165 (4); 125 (6); 123 (22); 122 (13); 107 (11); 91 (100).
HRMS (FAB, NBA, 8 kV): calc.: 265.0357, found.: 265.0342 ([M+H]$^+$).

Benzenethiosulfonic acid S-(3-bromo-benzyl) ester (2b)

According to **TP1**, $PhSO_2SNa$ (5.96 g, 30.4 mmol), DMF, 1-bromo-3-bromomethyl-benzene (7.59 g, 30.4 mmol) were stirred for 40 h at rt. After workup, benzenethiosulfonic acid S-(3-bromo-benzyl) ester (**2b**) (9.48 g, 91%) was obtained as a viscous colourless oil.
^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.84 – 7.80 (m, 2 H); 7.63 – 7.57 (m, 1 H); 7.52 – 7.46 (m, 2 H); 7.36 – 7.27 (m, 2 H); 7.15 – 7.07 (m, 2 H); 4.25 (s, 2 H).
^{13}C NMR ($CDCl_3$, 75 MHz): d = 145.2; 136.5; 134.1; 132.3; 131.5; 130.6; 129.6; 128.0; 127.2; 123.0; 40.0.

IR (film; cm^{-1}): $\tilde{n}$ = 3063 (m); 1570 (s); 1474 (s); 1447 (s); 1429 (s); 1324 (s); 1309 (s); 1292 (s); 1143 (vs); 1077 (s); 753 (m); 715 (s); 683 (s); 596 (vs); 536 (s).

MS (EI, 70eV): m/z (%) = 202 (85); 200 (72); 199 (14); 171 (71); 169 (71); 143 (37); 122 (69); 121 (41); 90 (33); 89 (25); 77 (100); 51 (41).

HRMS (FAB, NBA, 8 kV): calc.: 342.9462, found.: 342.9464 ([M+H]$^+$).

Benzenethiosulfonic acid S-(2-bromo-benzyl) ester (2c)

According to **TP1**, PhSO$_2$SNa (4.91 g, 25.0 mmol), DMF, 1-bromo-2-bromomethyl-benzene (6.25 g, 25.0 mmol) were stirred for 64 h at rt. After workup, benzenethiosulfonic acid S-(2-bromo-benzyl) ester (**2c**) (8.32 g, 97%) was obtained as a white crystalline powder.

mp: 68.5 – 70.0 °C.

^{1}H NMR (CDCl$_3$, 300 MHz): d = 7.85 – 7.81 (m, 2 H); 7.55 – 7.38 (m, 4 H); 7.19 – 6.99 (m, 3 H); 4.30 (s, 2 H).

^{13}C NMR (CDCl$_3$, 75 MHz): d = 145.1; 134.1; 134.0; 133.5; 131.6; 130.1; 129.6; 128.1; 127.4; 125.0; 41.1.

IR (KBr; cm^{-1}): $\tilde{n}$ **=** 2997 (m); 2902 (m); 2838 (w); 1692 vs); 1600 (m); 1497 (s); 1462 (s); 1450 (s); 1333 (s); 1292 (m); 1247 (vs); 1218 (s); 1113 (m); 1027 (s); 992 (m); 761 (vs); 753 (m); 692 (m).

MS (EI, 70eV): m/z (%) = 202 (100); 201 (24); 200 (90); 171 (71); 169 (74); 122 (56); 121 (50); 90 (25); 89 (20); 77 (65); 51 (35).

HRMS (FAB, NBA, 8 kV): calc.: 342.9462, found.: 342.9434 ([M+H]$^+$).

Benzenethiosulfonic acid S-(4-bromo-3-methyl-benzyl) ester (2d)

1-Bromo-4-bromomethyl-2-methyl-benzene was obtained in two steps from 4-bromo-3-methyl-benzoic acid[6] and used without any further purification in the next step.
According to **TP1**, $PhSO_2SNa$ (4.01 g, 20.4 mmol), DMF, 1-bromo-4-bromomethyl-2-methylbenzene (5.39 g, 20.4 mmol) were stirred for 70 h at rt. After workup, benzenethiosulfonic acid S-(4-bromo-3-methyl-benzyl) ester (**2d**) (6.23 g, 85%) was obtained as white crystals.

^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.88 – 7.79 (m, 2 H); 7.64 – 7.58 (m, 1 H); 7.53 – 7.46 (m, 2 H); 7.36 (d, *J* = 8.0 Hz, 1 H); 7.05 – 6.97 (m, 1 H); 6.87 (dd, *J* = 8.0 Hz, *J* = 2.2 Hz, 1 H); 4.21 (s, 2 H); 2.28 (s, 3 H).
^{13}C NMR ($CDCl_3$, 75 MHz): d = 145.3; 138.7; 133.9; 133.4; 133.0; 131.8; 129.5; 128.3; 127.2; 124.9; 40.1; 23.1.

IR (KBr; cm^{-1}): $\tilde{n}$ = 3065 (m); 2923 (m); 1637 (w); 1589 (w); 1475 (m); 1447 (m); 1324 (s); 1308 (m); 1143 (vs); 1078 (m); 1028 (s); 716 (s); 685 (m); 598 (vs); 536 (s).

Benzenethiosulfonic acid S-(2-methoxy-benzyl) ester (2g)

1-Bromomethyl-2-methoxy-benzene was obtained from (2-methoxy-phenyl)-methanol[6] as described for (**2d**) and used without any further purification in the next step.
According to **TP1**, $PhSO_2SNa$ (4.91 g, 25.0 mmol), DMF, 1-bromomethyl-2-methoxy-benzene (5.03 g, 25.0 mmol) were stirred for 70 h at rt. After workup, benzenethiosulfonic acid S-(2-methoxy-benzyl) ester (**2g**) (6.74 g, 92%) was obtained as white crystals.

mp: 75.8 – 76.9 °C.
^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.91 (brd, *J* = 6.9 Hz, 2 H); 7.64 – 7.58 (m, 1 H); 7.54 – 7.48 (m, 2 H); 7.29 – 7.20 (m, 1 H); 7.11 (dd, *J* = 7.5 Hz, *J* = 1.8 Hz, 1 H); 6.85 – 6.77 (m, 2 H); 4.29 (s, 2 H); 3.75 (s, 3 H).

^{13}C NMR ($CDCl_3$, 75 MHz): d = 157.7; 145.5; 133.7; 130.9; 130.0; 129.4; 127.3; 122.7; 120.9; 110.9; 55.8; 35.9.

IR (KBr; cm^{-1}): $\tilde{n}$ **=** 3059 (m); 3009 (m); 2838 (m); 1600 (s); 1493 (vs); 1465 (s); 1319 (vs); 1251 (vs); 1142 (vs); 1079 (vs); 1027 (s); 759 (vs); 717 (vs); 688 (vs); 599 (vs); 538 (vs).

HRMS (EI, 70 eV): m/z (%) = 153 (19); 152 (50); 138 (23); 122 (10); 121 (100); 119 (16); 110 (7), 107 (8); 91 (82); 78 (37); 77 (48); 65 (16).

HRMS (FAB, NBA, 8 kV): calc.: 295.0463, found.: 295.0440 ([M+H]$^+$).

Benzenethiosulfonic acid S-(1-bromo-naphthalen-2-ylmethyl) ester (2h)

1-Bromo-2-bromomethyl-naphthalene was obtained by the radical bromination of 1-bromo-2-methyl-naphthalene[7] and used without any further purification in the next step.

According to **TP1**, $PhSO_2SNa$ (4.32 g, 22.0 mmol), DMF, 1-bromo-2-bromomethyl-naphthalene (6.60 g, 22.0 mmol) were stirred for 94 h at rt. After workup, the yellow oil was recrystallized from heptane to afford benzenethiosulfonic acid S-(1-bromo-naphthalen-2-ylmethyl) ester (**2h**) (7.11 g, 82%) as white crystals.

mp: 110.3 – 111.0 °C.

^{1}H NMR ($CDCl_3$, 300 MHz): d = 8.16 (brd, *J* = 8.4 Hz, 1 H); 7.93 – 7.89 (m, 2 H); 7.75 (dd, *J* = 7.8 Hz, *J* = 1.3 Hz, 1 H); 7.65 (brd, *J* = 8.4 Hz, 1 H); 7.60 – 7.41 (m, 5 H); 7.26 (d, *J* = 8.4 Hz, 1 H); 4.60 (s, 2 H).

^{13}C NMR ($CDCl_3$, 75 MHz): d = 145.1; 134.3; 133.9; 132.7; 132.1; 129.5; 128.5; 128.5; 128.2; 128.0; 127.7; 127.5; 127.4; 125.6; 42.3.

IR (KBr; cm^{-1}): $\tilde{n}$ = 3058 (m); 1597 (w); 1500 (m); 1449 (s); 1334 (s); 1323 (vs); 1310 (vs); 1144 (vs); 1078 (s); 819 (s); 753 (s); 717 (vs); 682 (s); 595 (vs); 537 (vs).
MS (FAB, NBA, 8kV): m/z (%) = 788 ([2M+Na]$^+$, 5); 417 ([M+Na]$^+$, 14); 393 ([M+H]$^+$, 30); 252 (44); 250 (42); 221 (100); 219 (99); 138 (20); 137 (34); 89 (13).
HRMS (FAB, NBA, 8 kV): calc.: 392.9619, found.: 392.9603 ([M+H]$^+$).

2-Chloromethylsulfanyl-2´-iodobiphenyl (5)

Benzenethiosulfonic acid S-methyl ester (**a**) was prepared according to **TP 1**. $PhSO_2SNa$ (7.90 g, 40.3 mmol), DMF, methyl iodide (5.72 g, 40.3 mmol) were stirred for 72 h at rt. After workup, benzenethiosulfonic acid S-metylester (**a**)(6.82 g, 90%) was obtained as a colourless oil.
Analytical data were found to match literature data.[5]
2'-Iodo-2-methylsulfanyl-biphenyl(**b**) was prepared according to **TP 2** with 2,2´-diiodobiphenyl (11.1 g, 27.3 mmol), THF (40 mL) and *i*PrMgCl·LiCl (30.3 mL, 27.3 mmol, 0.90 M in THF). After full conversion to the magnesium reagent (1.5 h) a solution of (**a**) (5.14 g, 27.3 mmol) in THF (15 mL) was added at -40 °C and the temperature was increased to –15 °C. After a reaction time of 1 h the mixture was worked up. The crude residue was recrystallized from heptane yielding 2'-iodo-2-methylsulfanyl-biphenyl(**b**) (7.65 g, 86%) as white crystals.

mp: 89.3 – 90.5 °C.
^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.98 (dd, *J* = 7.9 Hz, J = 1.3 Hz, 1 H); 7.47 – 7.39 (m, 2 H); 7.35 – 7.22 (m, 3 H); 7.14 – 7.07 (m, 2 H); 2.42 (s, 3 H).
^{13}C NMR ($CDCl_3$, 75 MHz): d = 145.6; 143.5; 139.4; 138.0; 130.6; 130.1; 129.6; 129.0; 128.4; 125.6; 125.0; 100.6; 16.3.

IR (KBr; cm^{-1}): $\tilde{n}$ = 3044 (m); 2919 (m); 1634 (m); 1587 (m); 1578 (m); 1454 (vs); 1434 (s); 1320 (w); 1272 (w); 1254 (w); 1017 (m); 1000 (m); 765 (m); 757 (vs).
HRMS (EI, 70 eV): m/z (%) = 326 (M$^+$, 1); 200 (11); 199 (96); 185 (11); 184 (100); 152 (9); 151 (3); 139 (9).
HRMS (EI, 70 eV): calc.: 325.9626, found.: 325.9627 (M$^+$).

2-Chloromethylsulfanyl-2´-iodobiphenyl (**5**)
5 was obtained by radical chlorination reaction.[8] A dry 100 mL flask, equipped with a magnetic stirring bar and a septum, was charged with 2'-iodo-2-methylsulfanyl-biphenyl(**b**) (6.52 g, 20.0 mmol) and CCl$_4$ (20 mL). After adding N-chlorosuccinimide (2.94 g, 22.0 mmol) the mixture was stirred 11 h at rt and then filtered. Concentration *in vacuo* afforded 2-chloromethylsulfanyl-2´-iodobiphenyl (**5**) (6.08 g, 84%) as a yellow oil.

^{1}H NMR (CDCl$_3$, 300 MHz): d = 7.97 (dd, *J* = 8.0 Hz, J = 1.0 Hz, 1 H); 7.75 (dd, *J* = 8.0 Hz, J = 1.0, 1 H); 7.52 – 7.38 (m, 3 H); 7.31 – 7.26 (m, 1 H); 7.22 (dd, *J* = 7.8 Hz, J = 1.5 Hz, 1 H); 7.15 – 7.07 (m, 1 H); 4.92 (d, *J* = 12.0 Hz, 1 H); 4.82 (d, *J* = 12.0 Hz, 1 H).
^{13}C NMR (CDCl$_3$, 75 MHz): d = 145.9; 145.3; 139.4; 130.0; 130.8; 130.8; 130.3; 129.8; 129.3; 128.3; 127.9; 100.6; 50.2.

IR (KBr; cm^{-1}): $\tilde{n}$ = 3052 (m); 3012 (m); 1922 (w); 1807(w); 1731 (w); 1579 (m); 1557 (m); 1454 (vs); 1430 (s); 1226 (s); 1018 (s); 1000 (s); 752 (vs); 733 (s); 648 (s).
HRMS (EI, 70 eV): m/z (%) = 325 ([M-Cl]$^+$, 6); 311 (8); 199 (6); 198 (35); 187 (19); 186 (5); 185 (18); 184 (100); 152 (9); 151 (3); 139 (10).
HRMS (EI, 70 eV): calc.: 324.9548, found.: 324.9522 ([M-Cl]$^+$).

1,2-Diphenyl-ethanol (9a)

The reaction was performed according to **TP4**. After the second evaporation THF (1.5 mL), LiO*t*Bu (0.50 mL, 0.50 mmol, 1.0 M in THF) was added followed by stirring for 20 h. Benzaldehyde (85 mg, 0.80 mmol) was added at –20 °C and temperature was increased to –10 °C. The mixture was quenched after a reaction time of 45 min. The crude residue was purified by flash-chromatography (pentane/ether = 5/1) yielding 1,2-diphenyl-ethanol (**9a**) (131 mg, 75%) as a white solid. Analytical data were found to match literature data.[9]

3,3-Dimethyl-1-phenyl-butan-2-ol (9b)

The reaction was performed according to **TP4**. After the second evaporation THF (1.0 mL), LiO*t*Bu (1.0 mL, 1.0 mmol, 1.0 M in THF) was added followed by stirring for 20 h. Pivaldehyde (79 mg, 0.90 mmol) was added at –20 °C and the temperature was increased to –10 °C. The mixture was quenched after a reaction time of 45 min. The crude residue was purified by flash-chromatography (pentane/ether = 10/1) yielding 3,3-dimethyl-1-phenyl-butan-2-ol (**9b**) (137 mg, 85%) as a colourless oil.

^{1}H NMR (CDCl$_3$, 300 MHz): d = 7.26 – 7.21 (m, 2 H); 7.16 – 7.11 (m, 3 H); 3.34 (brd, *J* = 10.6 Hz, 1 H); 2.83 (dd, *J* = 13.7 Hz, *J* = 1.8 Hz, 1 H); 2.38 (dd, *J* = 13.7 Hz, *J* = 10.6 Hz, 1 H); 1.40 (s, 1 H); 0.92 (s, 9 H).

^{13}C NMR (CDCl$_3$, 75 MHz): d = 140.3; 129.7; 129.0; 126.7; 81.0; 38.8; 35.2; 26.3.

IR (film; cm^{-1}): $\tilde{n}$ = 3468 (m); 3028 (m); 2956 (vs); 2870 (s); 1495 (m); 1480 (m); 1467 (m); 1455 (m); 1364 (m); 1238 (m); 1219 (m); 1192 (m); 1171 (m); 1077 (s); 1069 (s); 1031 (m); 1009 (s); 736 (s); 699 (s).

HRMS (EI, 70 eV): m/z (%) = 178 (M^+, 1); 121 ($[M-C_4H_9]^+$, 30); 103 (15); 92 (100); 87 (13); 77 (3); 69 (8); 65 (4); 57 (4); 51 (1); 45 (3); 41 (6).

HRMS: **calc.: 178.1358, found.: 178.1365 (M^+).**

(2-Methoxy-cyclohex-2-enylmethyl)-benzene (9c)

The reaction was performed according to **TP4**. After the second evaporation THF (1.5 mL), LiO*t*Bu (0.50 mL, 0.50 mmol, 1.0 M in THF) was added followed by stirring for 20 h. 6-Bromo-1-methoxycyclohexene (153 mg, 0.80 mmol) was added at –40 °C and the temperature was increased to 0 °C. The mixture was quenched after a reaction time of 1 h. The crude residue was purified by flash-chromatography (pentane) yielding (2-methoxy-cyclohex-2-enylmethyl)-benzene (**9c**) (132 mg, 82%) as a colourless oil.

^{1}H NMR (CDCl$_3$, 300 MHz): d = 7.32 – 7.05 (m, 5 H); 4.57 (t, *J* = 4.0 Hz, 1 H); 3.45 (s, 3 H), 3.15 – 3.04 (m, 1 H); 2.42 – 2.28 (m, 2 H); 2.01 – 1.90 (m, 2 H); 1.62 – 1.30 (m, 4 H).
^{13}C NMR (CDCl$_3$, 75 MHz): d = 158.0; 141.6; 129.7; 128.5; 126.1; 94.3; 54.3; 39.6; 39.0; 27.2; 24.3; 20.1.

IR (film; cm^{-1}): $\tilde{n}$ = 3062 (m); 3026 (m); 2932 (vs); 2860 (s); 2838 (s); 1662 (s); 1495 (s); 1462 (m); 1453 (s); 1377 (m); 1221 (s); 1210 (vs); 1183 (m); 1159 (vs); 1028 (s); 791 (m); 780 (m); 739 (s); 700 (vs).
HRMS (EI, 70 eV): m/z (%) = 202 (M$^+$, (88); 187 (3); 170 (5); 141(8); 129 (7); 111 (100); 91 (31); 79 (22); 65 (6); 55 (3); 45 (9).
HRMS: calc.: 202.1358, found.: 202.1354 (M$^+$).

1,2-diphenyl-ethanone (9d)

The reaction was performed according to **TP4**. After the second evaporation THF (1.5 mL), LiO*t*Bu (0.50 mL, 0.05 mmol, 1.0 M in THF) was added followed by stirring for 20 h. Benzoyl chloride (112 mg, 0.80 mmol) was added after transmetalation (**TP8**) at –30 °C and the temperature was increased to –20 °C. The mixture was quenched after a reaction time of 1.5 h. The crude residue was purified by flash-chromatography (pentane/ether = 10/1) yielding 1,2-diphenyl-ethanone (**9d**) (141 mg, 90%) as a white solid. Analytical data were found to match literature data.[9]

1-cyclohexyl-2-phenyl-ethanone (9e)

The reaction was performed according to **TP4**. After the second evaporation THF (1.9 mL), LiO*t*Bu (0.10 mL, 0.10 mmol, 1.0 M in THF) was added followed by stirring for 46 h. Cyclohexanecarbonyl chloride (117 mg, 0.80 mmol) was added after transmetalation (**TP8**) at –30 °C and the temperature was increased to –20 °C. The mixture was quenched after a reaction time of 1.5 h. The crude residue was purified by flash-chromatography (pentane/ether = 10/1) yielding 1-cyclohexyl-2-phenyl-ethanone (**9e**) (126 mg, 78%) as a light yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.27 – 7.08 (m, 5 H); 3.64 (s, 2 H); 2.38 (tt, *J* = 11.2 Hz, *J* = 3.3 Hz, 1 H); 1.79 – 1.53 (m, 5 H); 1.36 – 1.03 (m, 5 H).
^{13}C NMR ($CDCl_3$, 75 MHz): d = 211.6; 134.8; 129.8; 129.0; 127.2; 50.5; 48.2; 28.9; 26.2; 26.0.

IR (film; cm^{-1}): $\tilde{n}$ = 3029 (m); 2930 (vs); 2854 (s); 1709 (vs); 1496 (m); 1451 (s); 1370 (m); 1328 (m); 1313 (m); 1142 (m); 1064 (m); 1030 (m); 1007 (m); 1000 (m); 703 (s).
HRMS (EI, 70 eV): m/z (%) = 203 ($[M+H]^+$; 5); 202 (M^+, 2); 111 (85); 91 (33); 83 (100); 65 (6); 55 (38); 41 (12).
HRMS: calc.: 202.1357, found.: 202.1374 (M^+).

2-(3-Bromo-phenyl)-1-phenyl-ethanol (9f)

The reaction was performed according to **TP5**. Benzaldehyde (85 mg, 0.80 mmol) was added at -30 °C and the temperature was increased to –20 °C. The mixture was quenched after a reaction time of 2 h. The crude residue was purified by flash-chromatography (pentane/ether = 2/1) yielding 2-(3-bromo-phenyl)-1-phenyl-ethanol (**9f**) (197 mg, 89%) as a colourless oil.

^{1}H NMR (CDCl$_3$, 300 MHz): d = 7.34 – 7.18 (m, 7 H); 7.10 – 7.00 (m, 2 H); 4.80 (t, *J* = 6.7 Hz, 1 H); 2.90 (d, *J* = 6.7 Hz, 2 H); 1.82 (s, 1 H).
^{13}C NMR (CDCl$_3$, 75 MHz): d = 143.9; 140.9; 132.9; 130.3; 130.0; 128.9; 128.6; 128.2; 126.2; 122.9; 75.5; 45.9.

IR (film; cm^{-1}): $\tilde{n}$ = 3392 (s); 3062 (m); 3031 (m); 2922 (m); 1596 (m); 1568 (s); 1475 (s); 1454 (m); 1426 (m); 1044 (s); 1028 (s); 775 (s); 697 (vs); 671 (m).
HRMS (EI, 70 eV): m/z (%) = 258 ([M-H$_2$O]$^+$; 3); 178 (7); 170 (16); 107 (100); 90 (6); 79 (31); 63 (1); 51 (1).
HRMS: **calc.: 275.0072, found.: 275.0030 ([M-H]$^+$)**.

2-(3-Bromo-phenyl)-1-phenyl-ethanone (9g)

The reaction was performed according to **TP5**. Benzoyl chloride (112 mg, 0.80 mmol) was added after transmetalation (**TP8**) at –30 °C and the temperature was increased to –10 °C. The mixture was quenched after a reaction time of 1 h. The crude residue was purified by flash-chromatography (pentane/ether = 10/1) yielding 2-(3-bromo-phenyl)-1-phenyl-ethanone (**9g**) (185 mg, 82%) as a white solid.

mp: 63.2 –63.5 °C.
^{1}H NMR (CDCl$_3$, 300 MHz):d = 7.95 –7.91 (m, 2 H); 7.54 – 7.48 (m, 1 H); 7.43 – 7.28 (m, 4 H); 7.18 – 7.10 (m, 2 H); 4.18 (s, 2 H).
^{13}C NMR (CDCl$_3$, 75 MHz): d = 197.2; 137.1; 136.8; 133.8; 132.9; 130.5; 130.5; 129.1; 128.9; 128.6; 123.0; 45.2.

IR (KBr; cm^{-1}): $\tilde{n}$ = 3054 (m); 2902 (m); 1686 (vs); 1597 (m); 1568 (m); 1446 (m); 1337 (m); 1218 (s); 1072 (m); 998 (m); 755 (m); 691 (s).
HRMS (EI, 70 eV): m/z (%) = 170 ([M-C$_7$H$_5$O]$^+$, 1); 165 (1); 106 (7); 105 (100); 90 (4); 78 (2); 77 (21); 63 (2); 51 (4).
HRMS: calc.: 273.9993, found.: 273.9980 (M$^+$).

2-(3-Bromo-phenyl)-1-cyclohexyl-ethanone (9h)

The reaction was performed according to **TP5**. Cyclohexanecarbonyl chloride (117 mg, 0.80 mmol) was added after transmetalation (**TP8**) at –30 °C and the temperature was increased to –20 °C. The mixture was quenched after a reaction time of 2 h. The crude residue was purified by flash-chromatography (pentane/ether = 10/1) yielding 2-(3-bromo-phenyl)-1-cyclohexyl-ethanone (**9h**) (180 mg, 80%) as a white solid.

mp: 51.6 – 52.3 °C

^{1}H NMR (CDCl$_3$, 300 MHz): d = 7.33 – 7.26 (m, 2 H); 7.14 – 7.02 (m, 2 H); 3.62 (s, 2 H); 2.37 (tt, *J* = 11.2 Hz, *J* = 3.3 Hz, 1 H); 1.80 – 1.56 (m, 5 H); 1.36 – 1.05 (m, 5 H).

^{13}C NMR (CDCl$_3$, 75 MHz): d = 210.6; 137.0; 132.9; 130.4; 130.3; 128.6; 122.9; 50.8; 47.4; 28.9; 26.2; 26.0.

IR (KBr; cm^{-1}): $\tilde{n}$ = 3059 (m); 2931 (vs); 2853 (s); 2672 (m); 1712 (s); 1701 (s); 1567 (m); 1474 (m); 1448 (m); 1325 (m); 1067 (w); 1002 (w); 780 (m); 718 (w).

HRMS (EI, 70 eV): m/z (%) = 280 (M$^+$, 1); 171 (4); 169 (5); 111 (46); 90 (8); 84 (7); 83 (100); 63 (2); 55 (33); 41(10).

HRMS: **calc.: 280.0463, found.: 280.0464 (M$^+$).**

1-(2-Bromo-phenyl)-3,3-dimethyl-butan-2-ol (9i)

The reaction was performed according to **TP6**. Pivaldehyde (71 mg, 0.80 mmol) was added at –30 °C and the temperature was increased to –20 °C. The mixture was quenched after a reaction time of 45 min. The crude residue was purified by flash-chromatography (pentane/ether = 5/1) yielding 1-(2-bromo-phenyl)-3,3-dimethyl-butan-2-ol (**9i**) (167 mg, 81%) as a colourless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.48 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1 H); 7.24 – 7.15 (m, 2 H); 7.05 – 6.99 (m, 1 H); 3.47 (dd, *J* = 10.7 Hz; *J* = 2.0 Hz, 1 H); 3.08 (dd, *J* = 13.6 Hz, *J* = 2.0 Hz, 1 H); 2.51 (dd, *J* = 13.6 Hz, *J* = 10.7 Hz, 1 H); 1.36 (s, 1 H), 0.96 (s, 9 H).
^{13}C NMR ($CDCl_3$, 75 MHz): d = 139.7; 133.3; 132.4; 128.4; 127.7; 125.2; 79.0; 38.9; 35.7; 26.1.

IR (film; cm^{-1}): $\tilde{n}$ = 3468 (m); 2960 (vs); 2905 (m); 2870 (m); 1472 (s); 1440 (m); 1364 (m); 1065 (s); 1038 (s); 1024 (s); 1008 (m); 747 (vs); 660 (m).
HRMS (EI, 70 eV): m/z (%) = 241 ($[M-CH_3]^+$, 1); 199 (22); 172 (100);170 (97); 120 (36); 91 (43); 87 (42); 69 (20); 57 (9); 41 (17).
HRMS: calc.: 255.0385, found.: 255.0363($[M-H]^+$).

2-(4-Bromo-3-methyl-phenyl)-1-cyclohexyl-ethanone (9j)
The reaction was performed according to **TP6**. Cyclohexanecarbonyl chloride (59 mg, 0.40 mmol) was added after transmetalation (**TP8**) at –30 °C and the temperature was increased to –20 °C. The reaction mixture was quenched after a reaction time of 1 h. The crude residue was purified by flash-chromatography (pentane/ether = 10/1) yielding 2-(4-bromo-3-methyl-phenyl)-1-cyclohexyl-ethanone (**9j**)(97 mg, 81%) as a white solid.

mp: 45.9 – 47.7 °C.
^{1}H NMR ($CDCl_3$, 300 MHz): d = 7.38 (d, *J* = 8.1 Hz, 1 H); 6.97 (d, *J* = 2.1 Hz, 1 H); 6.79 (dd, *J* = 8.1 Hz, *J* = 2.1 Hz, 1 H); 3.58 (s, 2 H), 2.41 – 2.32 (m, 1 H); 2.30 (s, 3 H); 1.79 – 1.67 (m 4 H); 1.62 – 1.57 (m, 1 H); 1.35 – 1.08 (m, 5 H).
^{13}C NMR ($CDCl_3$, 75 MHz): d = 211.1; 138.4; 134.0; 132.8; 132.3; 128.8; 123.7; 50.7; 47.3; 28.9; 26.2; 26.0; 23.2.

IR (KBr; cm^{-1}): $\tilde{n}$ = 2925 (vs); 2855 (vs); 1706 (vs); 1476 (s); 1451 (s); 1406 (m); 1373 (m); 1326 (m); 1147 (m); 1070 (m); 1028 (s); 1006 (m); 826 (m); 792 (m); 717 (m).

HRMS (EI, 70 eV): m/z (%) 294 (M$^+$, 2); 183 (14); 111 (42); 103 (8); 83 (100); 77 (6); 55 (22); 41 (9).

HRMS: calc.: 294.0619, found.: 294.0604 (M$^+$).

2-(4-Bromo-3-methyl-phenyl)-1-phenyl-ethanone (9k)

The reaction was performed according to **TP6**. Benzoyl chloride (56 mg, 0.40 mmol) was added after transmetalation (**TP8**) at –30 °C and temperature was increased to –20 °C. The mixture was quenched after a reaction time of 1 h. The crude residue was purified by flash-chromatography (pentane/ether = 10/1) yielding 2-(4-bromo-3-methyl-phenyl)-1-phenyl-ethanone (**9k**) (101 mg, 86%) as a white solid.

mp: 89.9 –91.5 °C

^{1}H NMR (CDCl$_3$, 300 MHz): d = 8.02 (d, *J* = 6.9 Hz, 2 H); 7.63 – 7.57 (m, 1 H); 7.53 – 7.46 (m, 3 H); 7.16 (d, *J* = 1.8, 1 H); 6.97 (dd, *J* = 8.0 Hz, *J* = 1.8 Hz, 1 H); 4.23 (s, 2 H); 2.39 (s, 3 H).

^{13}C NMR (CDCl$_3$, 75 MHz): d = 197.6; 138.5; 136.8; 134.1; 133.7; 132.9; 132.4; 129.1; 129.0; 128.9; 123.8; 45.1; 23.3.

IR (KBr; cm^{-1}): $\tilde{n}$ **=** 2942 (m); 1691 (vs); 1593 (m); 1474 (s); 1448 (s); 1336 (s); 1207 (vs); 1023 (s); 1002 (m); 988 (m); 932 (m); 750 (s); 687 (s); 574 (m).

HRMS (EI, 70 eV): m/z (%) 183 ([M-C_7H_5O]$^+$, 2); 106 (7); 105 (100); 103 (6), 78 (5); 77 (30); 63 (2); 51 (11); 50(3).

HRMS: calc.: 288.0149, found.: 288.0161 (M$^+$).

1-(3-Chloro-phenyl)-3,3-dimethyl-butan-2-ol (9l)

The reaction was performed according to **TP6**. Pivaldehyde (35 mg, 0.40 mmol) was added at –30 °C and the mixture was quenched after stirring over night at –30 °C. The crude residue was purified by flash-chromatography (pentane/ether = 9/1) yielding 1-(3-chloro-phenyl)-3,3-dimethyl-butan-2-ol (**9l**) (60 mg, 71%) as a white solid.

mp: 41.1 –42.2 °C
^{1}H NMR (CDCl$_3$, 300 MHz): d = 7.20 – 7.11 (m, 3 H); 7.07 – 7.02 (m, 1H); 3.35 (dd, *J* = 10.6 Hz, *J* = 2.0 Hz, 1 H); 2.80 (dd, *J* = 13.7 Hz, *J* = 2.0 Hz, 1 H); 2.39 (dd, *J* = 13.7 Hz, *J* = 10.6 Hz, 1 H); 1.40 (s, 1 H); 0.92 (s, 9 H).
^{13}C NMR (CDCl$_3$, 75 MHz): d = 142.6; 134.7; 130.1; 129.8; 127.9; 126.8; 80.9; 38.4; 35.3; 26.2.

IR (KBr; cm^{-1}): $\tilde{n}$ **=** 3458 (w); 2955 (m); 1600 (m); 1574 (m); 1477 (m); 1360 (m); 1072 (s); 1011 (s); 765 (vs); 686 (vs).
MS (EI, 70 eV): m/z (%) = 197 (1); 179 (2); 155 (16); 126 (97); 125 (32); 87 (100); 69 (50); 57 (40).
HRMS (EI, 70 eV): calc.: 212.0968, found.: 212.0946 (M$^+$).

1-Phenyl-2-[3-(trifluoromethyl)phenyl]ethanone (**9m**)
The reaction was performed according to **TP6**. Benzoyl chloride (56 mg, 0.40 mmol) was added after transmetalation (**TP8**) at –30 °C and temperature was increased to –20 °C. The mixture was quenched after a reaction time of 1 h. The crude residue was purified by flash-chromatography (pentane/ether = 9/1) yielding 1-phenyl-2-[3-(trifluoromethyl)phenyl]ethanone (**9m**) (94 mg, 89%) as a white solid (mp: 36.0 – 36.6 °C). Analytical data were found to match literature data.[9]

1-(2-Methoxy-phenyl)-3,3-dimethyl-butan-2-ol (9n)
The reaction was performed according to **TP7**. Pivaldehyde (35 mg, 0.40 mmol) was added at –20 °C and the mixture was quenched after a reaction time of 40 min. The crude residue was purified by flash-chromatography (pentane/ether = 5/1) yielding 1-(2-methoxy-phenyl)-3,3-dimethyl-butan-2-ol (**9n**) (79 mg, 95%) as a colourless oil.

^{1}H NMR (CDCl$_3$, 300 MHz): d = 7.28 – 7.17 (m, 2 H); 6.97 – 6.88 (m, 2 H); 3.86 (s, 3 H); 3.45 (dd, *J* = 10.3 Hz, *J* = 1.9 Hz, 1 H); 2.94 (dd, *J* = 13.7, *J* = 1.9, 1 H); 2.59 (dd, *J* = 13.7, *J* = 10.3 Hz, 1 H); 2.03 (s, 1 H); 1.02 (s, 9 H).

^{13}C NMR (CDCl$_3$, 75 MHz): d = 157.9; 131.5; 129.0; 128.0; 121.2; 110.8; 80.5; 55.7; 35.4; 33.8; 26.1.

IR (film; cm^{-1}): $\tilde{n}$ **=** 3559 (m); 2955 (s); 2907 (m); 2870 (m); 1602 (m); 1494 (s); 1480 (m); 1465 (s); 1439 (m); 1363 (m); 1243 (vs); 1114 (s); 1066 (m); 1053 (s); 1040 (m); 1028 (m); 1009 (s); 753 (s).

HRMS (EI, 70 eV): m/z (%) 208 (M$^+$, 1); 175 (1); 151 (15); 133 (1); 122 (100); 121 (20); 107 (13); 91 (21); 77 (5); 65 (3); 51 (1); 41 (2).

HRMS: calc.: 208.1463, found.: 208.1476 (M$^+$).

2-(2-Methoxy-phenyl)-1-phenyl-ethanone (9o)

The reaction was performed according to **TP7**. Benzoyl chloride (56 mg, 0.40 mmol) was added after transmetalation (**TP8**) at –20 °C. The mixture was quenched after a reaction time of 1 h. The crude residue was purified by flash-chromatography (pentane/ether = 5/1) yielding 2-(2-methoxy-phenyl)-1-phenyl-ethanone (**9o**) (73 mg, 81%) as a white solid.

mp: 57.4 –59.0 °C.

^{1}H NMR (CDCl$_3$, 300 MHz): d = 7.98 – 7.94 (m, 2 H); 7.50 – 7.44 (m, 1H); 7.40 – 7.35 (m, 2 H); 7.21 – 7.15 (m, 1 H); 7.12 – 7.08(m, 1 H); 6.87 – 6.80 (m, 2 H); 4.20 (s, 2 H); 3.70 (s, 3 H).

^{13}C NMR (CDCl$_3$, 75 MHz): d = 189.4; 157.6; 137.4; 133.3; 131.4; 128.9; 128.8; 128.8; 124.1; 121.0; 111.0; 55.8; 40.4.

IR (KBr; cm^{-1}): $\tilde{n}$ **=** 2997 (m); 2902 (m); 1692 (vs); 1600 (m); 1497 (s); 1462 (m); 1450 (m); 1333 (m); 1247 (s); 1217 (s); 1112 (m); 1027 (m); 761 (s); 753 (m); 692 (m).

HRMS (EI, 70 eV): *m/z* (%) 226 (M$^+$, 61); 194 (1); 165 (4); 152 (2); 121 (10); 105 (100); 91 (17); 77 (21); 65 (4); 51 (5).
HRMS: calc.: 226.0994, found.: 226.0977 (M$^+$).

2-(1-Bromo-naphthalen-2-yl)-1-(4-bromo-phenyl)-ethanone (9p)

A dry and argon flushed 50 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with **1h** (265 mg, 0.50 mmol), 4-bromo-benzonitrile (82 mg, 0.45 mmol) and THF (1.0 mL). The clear solution was cooled to –50 °C followed by the slow addition of *i*PrMgCl (0.48 mL, 0.53 mmol, 1.10 M in THF). The reaction mixture was stirred for 3 h increasing slowly the temperature (1 h from –50 to –30 °C; 1h from –30 to 0 °C; 1h from 0 to +10 °C). After checking the conversion by GC-analysis, using tetradecane as internal standard, the reaction mixture was treated with HCl (6.0 mL; 2.0 M) and refluxed at 60 °C for 40 min. Water (50 mL) was added followed by the extraction with Et$_2$O (3 x 50 mL). The combined organic phases were dried over Na$_2$SO$_4$ and concentration *in vacuo.* The crude residue was purified by flash-chromatography (pentane/ether = 5/1) yielding 2-(1-bromo-naphthalen-2-yl)-1-(4-bromo-phenyl)-ethanone (**9p**) (143 mg, 79%) as a white solid.

mp: 146.8 – 147.6°C
^{1}H NMR (CDCl$_3$, 300 MHz): d = 8.31 (brd, *J* = 8.4 Hz, 1 H); 7.97 – 7.92 (m, 2 H); 7.85 – 7.77 (m, 2 H); 7.66 – 7.49(m, 4 H); 7.34 (d, *J* = 8.4 Hz, 1 H); 4.67 (s, 2 H).
^{13}C NMR (CDCl$_3$, 75 MHz): d = 195.9; 135.8; 134.1; 133.2; 133.0; 132.4; 130.3; 128.9; 128.7; 128.5; 128.2; 128.0; 127.8; 126.9; 125.4, 47.4.

IR (KBr; cm^{-1}): $\tilde{n}$ **=** 3054 (m); 2901 (m); 1954 (w); 1694 (vs); 1584 (vs); 1502 (m); 1397 (m); 1322 (s); 1207 (vs); 1072 (vs); 995 (vs); 975 (s); 814 (vs); 769 (s); 749 (vs).

HRMS (EI, 70 eV): *m/z* (%) 402 (M^+, 1); 326 (16); 325 (79); 323 (82); 295 (3); 221 (10); 219 (9); 216 (6); 185 (94); 183 (100); 157 (17); 155 (16); 140 (33), 139 (37); 104 (7); 76 (19).
HRMS: calc.: 401.9255, found.: 401.9258 (M^+).

1-Bromo-2-pentyl-naphthalene (9q)
A dry and argon flushed 50 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with **1h** (265 mg, 0.50 mmol), 1-iodobutane (0.12 mL, 1.0 mmol) and THF (1.0 mL). The clear solution was cooled to –50 °C followed by the slowly addition of *i*PrMgCl (0.48 mL, 0.53 mmol, 1.10 M in THF). The reaction mixture was stirred for 3 h increasing slowly the temperature (1 h from -50 to –30 °C; 1 h from –30 to 0 °C; 1 h from 0 to +10 °C). After checking the conversion by GC-analysis, using tetradecane as internal standard, the reaction mixture was quenched with water (50 mL). The mixture was extracted with Et_2O (3 x 100 mL). The combined organic phases were dried over Na_2SO_4 and concentration *in vacuo*. The crude residue was purified by flash-chromatography (pentane) yielding 1-bromo-2-pentyl-naphthalene (**9q**) (125 mg, 90%) as a colourless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): d = 8.33 (brd, *J* = 8.4 Hz, 1 H); 7.80 (brd, *J* = 8.0 Hz, 1 H); 7.73 (d, *J* = 8.4 Hz, 1 H); 7.60 – 7.55(m, 1 H); 7.50 – 7.45 (m, 1 H); 7.35 (d, *J* = 8.4 Hz, 1 H); 2.98 (t, *J* = 8.4 Hz, 2 H); 1.77 – 1.66 (m, 2 H); 1.48 – 1.33 (m, 4 H); 0.97 – 0.90 (m, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): d = 140.8; 135.5; 133.0; 128.6; 128.4; 127.8; 127.7; 127.6; 126.1; 123.9; 37.8; 32.1; 30.2; 22.9; 14.4.

IR (film; cm^{-1}): $\tilde{n}$ = 3052 (m); 2956 (vs); 2929 (vs); 2859 (vs); 1904 (w); 1556 (m); 1500 (s); 1465 (s); 1352 (m); 1331 (m); 1256 (s); 964 (m); 812 (vs); 747 (vs);530 (s).

HRMS (EI, 70 eV): *m/z* (%)276 (M^+, 50); 221 (75); 220 (10); 219 (75); 165 (6); 154 (5); 152 (10); 141 (100); 140 (37); 139 (23); 115 (6).
HRMS: calc.: 276.0514, found.: 276.0524 (M^+).

[1] H.-S.Sin, L. A. Paquette, *Synth. Commun.* **1994**, *24*, 2503.
[2] D. Scholz, *Liebigs Ann. Chem.* **1984**, 259.
[3] R. Sato, T. Goto, Y. Takikawa, S. Takizawa, *Synthesis*, **1980**, 615.
[4] G. P. M. van Klink, H. J. R. de Boer, G. Schat, O. S. Akkermann, F. Bickelhaupt, A. L. Spek, *Organometallics* **2002**, *21*, 2119.
[5] K. Fujiki, N. Tanifuji, Y. Sasaki, T. Yokoyama, *Synthesis* **2002**, 343.
[6] S. Hanessian, G. Papeo, M. Angiolini, K. Fettis, M. Beretta, A. Munro, *J. Org. Chem.* **2003**, *68*, 7204-7218.
[7] L. A. Carpino, Y.-Z. Lin, *J. Org. Chem.* **1990**, *55*, 247.
[8] P.G. Theobald, W. H. Okamura, *J. Org. Chem.* **1990**, *55*, 741.
[9] Y. Suh, J. Lee, S.-H. Kim, R. D. Rieke, *J. Organomet. Chem.* **2003**, *684*, 20.