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Supporting Information

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Efficient Direct Synthesis of Functionalized Organozinc Compounds**

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General All reactions were carried out under a nitrogen 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.

Typical procedure (TP):
Anhydrous LiCl (5 mmol) was placed in an Ar-flushed flask and dried 20 min at 150-170 °C on high vacuum (1 mbar). Zinc powder (7.5 mmol, 1.5 equiv, (150 mesh, Chemetall, 99.9 % or 325 mesh, Strem, 99.9 %); in the case of active sensitive substrates 1.4 equiv) was added under Ar and heterogeneous mixture of Zn and LiCl was dried again 10-20 min at 150-170 °C on high vacuum (1 mbar). The reaction flask was evacuated and refilled with argon three times. THF (5 mL) was added and Zn was activated by $BrCH_2CH_2Br$ (5 mol %) and Me_3SiCl (1 mol %) (in the case of the insertion into C_{sp3}-Br bonds following addition of 5 drops of 1 M solution of I_2 in THF further accelerates the reaction).[1] The substrate (5 mmol) was added neat at the room temperature. The reaction mixture was stirred at temperature T_1. The completion of the insertion reaction was checked by GC analysis of reaction aliquots quenched with a solution of NH_4Cl in water (the conversion was more than 96%). An aliquot of organozinc reagent (1 mL) was titrated using iodine.[2] The titrated organozinc solution in THF (3 mmol) were carefully separated from the remaining zinc powder using a syringe and transferred to another dry and Ar-flushed flask. The electrophile or its solution in THF was added at the temperature T_2. After the completion of the reaction (checked by GC analysis of reaction aliquots quenched with sat. aqueous NH_4Cl solution) the reaction mixture was quenched with sat. aqueous NH_4Cl solution (5 mL). The aqueous phase was extracted

with ethyl acetate (3 x 5 mL) and concentrated *in vacuo*. The crude residue was purified by flash chromatography.

2,2-Dimethyl-1-phenylpropan-1-one (1c): According to **TP** – *insertion*: 6 h, T_1 = 50 °C. Reaction *with an electrophile:* transmetallation with CuCN·2LiCl (20 mol %) 5 min at 0°C, followed by addition of pivaloyl chloride at T_2 = –20 °C. The reaction mixture was stirred afterwards for 1 h at 25°C. The crude residue was purified by column chromatography yielding 2,2-dimethyl-1-phenylpropan-1-one (**1c**; 90%). The analytical data was found to match the literature data.[3]

2-(Trifluoromethyl)phenyl dimethyldithiocarbamate (2c): According to **TP** – *insertion*: 18 h, T_1 = 25 °C. Reaction *with an electrophile:* tetramethyl thiuram disulfide (1.1 equiv.) was dissolved in dichloromethane and added dropwise at T_2 = 0 °C. The reaction mixture was stirred afterwards for 1 h at 25°C. The crude residue was purified by recrystallization from heptane yielding 2-(trifluoromethyl)phenyl dimethyl-dithiocarbamate (**2c**; 91%). The analytical data was found to match the literature data.[4]

Ethyl 4-allylbenzoate (3c): According to **TP** – *insertion*: 24 h, T_1 = 25 °C. Reaction *with an electrophile:* allyl bromide (1.1 equiv) was added, followed by the addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, ca. 0.4 mol %) at –20°C. The reaction mixture was stirred afterwards for 1 h at 0°C. The crude residue was purified by column chromatography yielding ethyl 4-allylbenzoate (**3c**; 94%). The analytical data was found to match the literature data.[5]

1-Allyl-4-methoxybenzene (4b): According to **TP** – *insertion*: 90 h, T_1 = 50 °C. Reaction *with an electrophile:* allyl bromide (1.1 equiv) was added, followed by the addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, ca. 0.4 mol %) at –20°C. The reaction mixture was stirred afterwards for 1 h at 0°C. The crude residue was purified by column chromatography yielding 1-allyl-4-methoxybenzene (**4b**; 94%). The analytical data was found to match the literature data.[6]

Ethyl 2-acetylbenzoate (5b): According to **TP** – *insertion*: 1 h, T_1 = 25 °C. Reaction *with an electrophile:* allyl bromide (1.1 equiv) was added, followed by the addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, ca. 0.4 mol %) at –20°C. The reaction mixture was stirred afterwards for 1 h at 0°C. The crude residue was purified by column chromatography yielding ethyl 2-acetylbenzoate (**5b**; 90%). The analytical data was found to match the literature data.[7]

4-Cyanophenyl dimethyldithiocarbamate (6b): According to **TP** – *insertion*: 3 h, T_1 = 50 °C. Reaction *with an electrophile:* tetramethyl thiuram disulfide (1.0 equiv.) was dissolved in dichloromethane and added dropwise at T_2 = 0 °C. The reaction mixture was stirred afterwards for 1 h at 25°C. The crude residue was purified by recristallization from heptane yielding 4-cyanophenyl dimethyldithiocarbamate (**6b**; 89%). The analytical data was found to match the literature data.[4]

3-Benzoylbenzonitrile (7b): According to **TP** – *insertion*: 6 h, T_1 = 50 °C. Reaction *with an electrophile:* transmetallation with CuCN·2LiCl (20 mol %) 5 min at 0°C, followed by addition of benzoyl chloride at T_2 = –20 °C. The reaction mixture was stirred afterwards for 1 h at 25°C. The crude residue was purified by column chromatography yielding 3-benzoylbenzonitrile (**7b**; 88%). The analytical data was found to match the literature data.[8]

1-(4-Allylbenzoyl)piperidine (8b): According to **TP** – *insertion*: 24 h, T_1 = 25 °C. Reaction *with an electrophile:* allyl bromide (1.1 equiv) was added, followed by the addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, ca. 0.4 mol %) at –20°C. The reaction mixture was stirred afterwards for 1 h at 0°C. The crude residue was purified by column chromatography yielding 1-(4-allylbenzoyl)piperidine (**8b**; 96%). The analytical data was found to match the literature data.[9]

1-(4-Benzoylphenyl)ethanone (9b): According to **TP** – *insertion*: 3 h, T_1 = 25 °C (**Caution:** freshly purified white 1-(4-iodophenyl)ethanone has to be used and the resulting organozinc reagent has to be reacted with an electrophile immediately after preparation since this reagent is not stable). Reaction *with an electrophile:* transmetallation with CuCN·2LiCl (20 mol %) 5 min at 0°C, followed by addition of benzoyl chloride at T_2 = –20 °C. The reaction mixture was stirred afterwards for 1 h at 25°C. The crude residue was purified by column chromatography yielding 1-(4-benzoylphenyl)ethanone (**9b**; 88%). The analytical data was found to match the literature data.[10]

Ethyl 5'-formyl-2',3'-dimethoxybiphenyl-4-carboxylate (10b): According to **TP** – *insertion*: 12 h, T_1 = 25 °C (**Caution:** A THF solution of the zinc reagent has to be removed from the remaining of zinc powder immediately after the preparation. this reagent is not stable over Zn powder). Reaction *with an electrophile:* 1 mol % of $Pd(PPh_3)_4$ was added at room temperature, followed by the addition of ethyl 4-iodobenzoate at T_2 = 25 °C. The reaction mixture was stirred afterwards for 6 h at 25°C. The crude residue was purified by column

chromatography yielding ethyl 5'-formyl-2',3'-dimethoxybiphenyl-4-carboxylate (**10b**; 85%) as white crystals (mp = 62 – 63 °C).
^{1}H-NMR ($CDCl_3$, 200 MHz): d = 9.98 (s, 1 H); 8.16 (d, *J* = 8.6 Hz, 2 H); 7.65 (d, *J* = 8.6 Hz, 2 H); 7.52 (brs, 2 H); 4.44 (q, *J* = 7.2 Hz, 2 H); 4.02 (s, 3 H); 3.73 (s, 3 H); 1.45 (t, *J* = 7.2 Hz, 3 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 191.2; 166.6; 154.1; 152.2; 141.8; 135.4; 132.7; 130.0; 129.8; 129.4; 127.1; 110.5; 61.3; 61.2; 56.4; 14.6.
MS (EI, 70 eV): m/z (%) = 314 (M^+, 100); 286 (9); 270 (9); 269 (42); 226 (8); 199 (12).
HR-MS: **($C_{18}H_{18}O_5$) calculated 314,1154 found 314,1143**

Ethyl 2-[(5-formyl-2-furyl)methyl]acrylate (11b): According to **TP** – *insertion*: 2.5 h, T_1 = 25 °C (**Caution:** THF solution of the zinc reagent has to be removed from the remaining of zinc powder immediately after preparation, since this reagent is not stable over Zn powder). Reaction *with an electrophile:* ethyl 2-(bromomethyl)acrylate (1.1 equiv) was added, followed by the addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, ca. 0.4 mol %) at –20°C. The reaction mixture was stirred afterwards for 1 h at 0°C. The crude residue was purified by column chromatography yielding ethyl 2-[(5-formyl-2-furyl)methyl]acrylate (**11b**; 81%) as colourless oil.
^{1}H-NMR ($CDCl_3$, 200 MHz): d = 9.31 (s, 1 H); 6.75 (d, *J* = 3.5 Hz, 1 H); 6.21 (s, 1 H); 6.00 (d, *J* = 3.5 Hz, 1 H); 5.40 (s, 1 H); 4.01 (q, *J* = 7.2 Hz, 2 H); 3.53 (s, 2 H); 1.07 (t, *J* = 7.2 Hz, 3 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 176.9; 165.9; 159.7; 152.5; 136.0; 127.8; 122.3; 110.0; 61.0; 31.2; 14.1.
MS (EI, 70 eV): m/z (%) = 208 (M^+, 11); 163 (16); 162 (36); 135 (14); 134 (100); 105 (19); 79 (17); 78 (13); 77 (27); 51 (12).
HR-MS: **($C_{11}H_{12}O_4$) calculated 208,0736 found 208,0733**

1-Allyl-4-bromobenzene (12b): According to **TP** – *insertion*: 6 h, T_1 = 50 °C. Reaction *with an electrophile:* allyl bromide (1.1 equiv) was added, followed by the addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, ca. 0.4 mol %) at –20°C. The reaction mixture was stirred afterwards for 1 h at 0°C. The crude residue was purified by column chromatography yielding ethyl 1-allyl-4-bromobenzene (**12b**; 96%). The analytical data was found to match the literature data.[11]

1-Allyl-4-iodo-2,5-dimethoxybenzene (13b): According to **TP** – *insertion*: 120 h, T_1 = 50 °C. Reaction *with an electrophile:* allyl bromide (1.1 equiv) was added, followed by the addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, ca. 0.4 mol %) at –20°C. The reaction mixture

was stirred afterwards for 1 h at 0°C. The crude residue was purified by column chromatography yielding ethyl 1-allyl-4-iodo-2,5-dimethoxybenzene (**13b**; 90%). The analytical data was found to match the literature data.[11]

(5-Iodo-2-thienyl)(phenyl)methanone (14b): According to **TP** – *insertion*: 10 min, T_1 = 25 °C (**Caution:** freshly purified white 2,5-diiodothiophene has to be used). Reaction *with an electrophile:* transmetallation with CuCN·2LiCl (20 mol %) 5 min at 0°C, followed by addition of benzoyl chloride at T_2 = –20 °C. The reaction mixture was stirred afterwards for 1 h at 25°C. The crude residue was purified by column chromatography yielding (5-iodo-2-thienyl)(phenyl)methanone (**14b**; 94%) as white crystals (mp = 132-133 °C).
^{1}H-NMR ($CDCl_3$, 200 MHz): d = 7.84 (m, 2 H); 7.62 (m, 1 H); 7.51 (m, 1 H); 7.35 (d, *J* = 4.0 Hz, 1 H); 7.28 (d, *J* = 4.0 Hz, 1 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 187.0; 149.8; 138.4; 137.9; 136.0; 132.9; 129.4; 128.9; 86.3.
MS (EI, 70 eV): m/z (%) = 313 (M^+, 100); 237 (57); 187 (12); 105 (35); 82 (11); 77 (24); 51 (8).
HR-MS: **($C_{11}H_7IOS$) calculated 313,9262 found 313,9240**

(5-Allyl-2-thienyl)(phenyl)methanone (14c): According to **TP** – *insertion*: 10 min, T_1 = 25 °C. Reaction *with an electrophile:* allyl bromide (1.1 equiv) was added, followed by the addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, ca. 0.4 mol %) at –20°C. The reaction mixture was stirred afterwards for 1 h at 0°C. The crude residue was purified by column chromatography yielding ethyl (5-allyl-2-thienyl)(phenyl)methanone (14c; 87%) as colourless oil.
^{1}H-NMR ($CDCl_3$, 200 MHz): d = 7.86 (m, 2 H); 7.60 (m, 1 H); 7.50 (m, 3 H); 6.90 (dt, *J* = 3.7 Hz, *J* = 0.9 Hz, 1 H); 6.03 (m, 1 H); 5.22 (m, 2 H); 3.60 (dq, *J* = 6.6 Hz, *J* = 1.2 Hz, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 188.4; 153.7; 142.2; 138.6; 135.8; 135.4; 132.4; 129.4; 128.7; 126.4; 117.8; 35.2.
MS (EI, 70 eV): m/z (%) = 228 (M^+, 100); 152 (9); 151 (84); 123 (17); 105 (70); 79 (12); 77 (42).
HR-MS: **($C_{14}H_{12}OS$) calculated 228,0609 found 228,0601**

2,2'-Diallylbiphenyl (15b): According to **TP** – *insertion*: 5 equiv of Zn powder, 24 h, T_1 = 25 °C. Reaction *with an electrophile:* allyl bromide (2.4 equiv) was added, followed by the addition of one two drops of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.04 mmol, ca. 0.4 mol %) at –20°C. The reaction mixture was stirred afterwards for 1 h at 0°C. The crude residue was purified by column chromatography yielding ethyl 2,2'-diallylbiphenyl (**15b**; 77%).
^{1}H-NMR ($CDCl_3$, 200 MHz): d = 7.29 (m, 8 H); 5.81 (m, 2 H); 4.88 (m, 4 H); 3.11 (brd, 4 H).

^{13}C-NMR ($CDCl_3$, 75 MHz): d = 141.2; 138.2; 137.6; 130.3; 129.5; 127.8; 126.2; 116.1; 38.0.
MS (EI, 70 eV): m/z (%) = 234 (M^+, 40); 219 (42); 205 (52); 204 (15); 203 (23); 193 (43); 192 (23); 191 (38); 190 (17); 189 (19); 179 (33); 178 (100); 165 (47).
HR-MS: **($C_{18}H_{18}$) calculated 234,1409 found 234,1406**

Ethyl 4-pyridin-3-ylbenzoate (16b): According to **TP** – *insertion*: 8 h, T_1 = 25 °C (**Note:** organozinc reagent has yellow colour). Reaction *with an electrophile:* 1 mol % of $Pd(PPh_3)_4$ was added at room tepmerature, followed by the addition of ethyl 4-iodobenzoate at T_2 = 25 °C. The reaction was exothermic and finished after 5 min. The crude residue was purified by column chromatography yielding ethyl 4-pyridin-3-ylbenzoate (**16b**; 87%). The analytical data was found to match the literature data.[12]

1-[6-(4-Methoxyphenoxy)pyridin-3-yl]ethanone (17b): According to **TP** – *insertion*: 24 h, T_1 = 25 °C (**Note:** organozinc reagent has brown colour). Reaction *with an electrophile:* transmetallation with CuCN·2LiCl (20 mol %) 5 min at 0°C, followed by addition of acyl chloride at T_2 = –20 °C. The reaction mixture was stirred afterwards for 1 h at 25°C. The crude residue was purified by column chromatography yielding 1-[6-(4-methoxyphenoxy)pyridin-3-yl]ethanone (**17b**; 83%) as white crystals (mp ~36-40 C)
^{1}H-NMR ($CDCl_3$, 200 MHz): d = 8.78 (dd, J_2 = 2.5 Hz, J_2 = 0.6 Hz, 1 H); 8.26 (dd, J_2 = 8.6 Hz, J_2 = 2.4 Hz, 1 H); 7.10 (d, J_1 = 9.3 Hz, 2 H); 6.97 (m, 3 H); 3.85 (s, 3 H); 2.59 (s, 3 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 195.6; 167.1; 157.3; 150.0; 146.8; 139.4; 128.3; 122.7; 115.1; 111.2; 55.9; 26.7.
MS (EI, 70 eV): m/z (%) = 243 (M^+, 100); 242 (14); 228 (45); 200 (46); 173 (9); 172 (10); 77 (9); 43 (30).
HR-MS: **($C_{14}H_{13}NO_3$) calculated 243,0895 found 243,0876**

2-Allylpyridin-3-yl benzoate (18b): According to **TP** – *insertion*: 12 h, T_1 = 25 °C (**Note:** the resulting organozinc reagent has a brown colour). Reaction *with an electrophile:* allyl bromide (1.1 equiv) was added, followed by the addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, ca. 0.4 mol %) at –20°C. The reaction mixture was stirred afterwards for 1 h at 0°C. The crude residue was purified by column chromatography yielding ethyl 2-allylpyridin-3-yl benzoate (**18b**; 85%) as colourless oil.
^{1}H-NMR ($CDCl_3$, 200 MHz): d = 8.52 (dd, *J* = 4.8 Hz, *J* = 1.4 Hz, 1 H); 8.24 (m, 2 H); 7.71 (m, 1 H); 7.58 (m, 3 H); 7.30 (dd, *J* = 4.8 Hz, *J* = 8.0 Hz, 1 H); 6.06 (m, 1 H); 5.13 (m, 2 H); 3.65 (brd, *J* = 6.7 Hz, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 164.7; 153.0; 147.1; 146.0; 134.3; 132.9; 130.7; 130.5; 129.1; 129.0; 122.7; 116.1; 37.8.

MS (EI, 70 eV): m/z (%) = 239 (M^+, 18); 238 (9); 134 (8); 106 (8); 105 (100); 77 (44).
HR-MS: **($C_{15}H_{13}NO_2$) calculated 239,0946 found 239,0926**

Isoquinolin-1-yl(phenyl)methanone (19b): According to **TP** – *insertion*: 12 h, T_1 = 25 °C (**Note:** the resulting organozinc reagent has brown colour). Reaction *with an electrophile:* transmetallation with CuCN·2LiCl (20 mol %) 5 min at 0°C, followed by addition of benzoyl chloride at T_2 = –20 °C. The reaction mixture was stirred afterwards for 1 h at 25°C. The crude residue was purified by column chromatography yielding isoquinolin-1-yl(phenyl)methanone (**19b**; 90%). The analytical data was found to match the literature data.[13]

Diethyl 4-allylisophthalate (20c): According to **TP** – *insertion*: 12 h, T_1 = 25 °C (**Note:** the resulting organozinc reagent has a deep red colour). Reaction *with an electrophile:* allyl bromide (1.1 equiv) was added, followed by the addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, ca. 0.4 mol %) at –20°C. The reaction mixture was stirred afterwards for 1 h at 0°C. The crude residue was purified by column chromatography yielding ethyl diethyl 4-allylisophthalate (**20c**; 90%) as colourless oil.
^{1}H-NMR ($CDCl_3$, 200 MHz): d = 8.54 (d, *J* = 1.8 Hz, 1 H); 8.11 (dd, J_1 = 1.8 Hz, J_2 = 8.0 Hz, 1 H); 7.38 (d, *J* = 8.0 Hz, 1 H); 6.02 (m, 1 H); 5.07 (m, 2 H); 4.42 (m, 4 H); 3.83 (brd, *J* = 6.5 Hz, 2 H); 1.43 (m, 6 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 167.2; 166.1; 146.6; 136.8; 133.9; 132.8; 132.0; 131.3; 129.0; 116.5; 61.5; 61.4; 38.6; 14.6; 14.5.
MS (EI, 70 eV): m/z (%) = 262 (M^+, 63); 247 (62); 234 (12); 220 (14); 219 (100); 218 (18); 217 (90); 206 (13); 191 (14); 189 (28); 188 (16); 171 (32); 145 (11); 144 (11); 143 (14); 117 (43); 116 (20); 115 (64)
HR-MS: **($C_{15}H_{18}O_4$) calculated 262,1205 found 262,1185**

Ethyl 5-(4-cyanophenyl)-2-furoate (21c): According to **TP** – *insertion*: 12 h, T_1 = 25 °C (**Note:** the resulting organozinc reagent has a deep red colour). Reaction *with an electrophile:* 1 mol % of $Pd(PPh_3)_4$ was added at room temperature, followed by the addition of 4-iodobenzonitrile at T_2 = 25 °C. The reaction was stirred afterwards for 6 h at 25°C. The crude residue was purified by column chromatography yielding ethyl 5-(4-cyanophenyl)-2-furoate (**21c**; 89%) as white crystals (mp = 143-144 °C).
^{1}H-NMR ($CDCl_3$, 200 MHz): d = 7.89 (brd, *J* = 8.4 Hz, 2 H); 7.72 (brd, *J* = 8.4 Hz, 2 H); 7.27 (d, *J* = 3.7 Hz, 1 H); 6.90 (d, *J* = 3.7 Hz, 1 H); 4.42 (q, *J* = 7.2 Hz, 2 H); 1.43 (t, *J* = 7.2 Hz, 3 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 158.7; 155.2; 145.5; 133.6; 132.9; 125.3; 119.8; 118.8; 112.2; 109.7; 61.5; 14.6.

MS (EI, 70 eV): m/z (%) = 241 (M^+, 100); 213 (93); 197 (20); 196 (55); 169 (48); 141 (11); 140 (76); 113 (13).
HR-MS: **($C_{14}H_{11}NO_3$) calculated 241,0739 found 241,0717**

1-Phenylnonan-1-one (22b): According to **TP** – *insertion*: 24 h, T_1 = 50 °C. Reaction *with an electrophile:* 0.1 mol % of $Pd(dba)_2$ and 0.2 mol % of S-Phos was added at room temperature, followed by the addition benzoyl chloride at T_2 = 25 °C. The reaction mixture was stirred afterwards for 30 min at 25°C. The crude residue was purified by column chromatography yielding 1-phenylnonan-1-one (**22b**; 89%). The analytical data was found to match the literature data.[14]

6-Chloro-1-phenylhexan-1-one (23b): According to **TP** – *insertion*: 12 h, T_1 = 50 °C. Reaction *with an electrophile:* 0.1 mol % of $Pd(dba)_2$ and 0.2 mol % of S-Phos was added at room temperature, followed by the addition benzoyl chloride at T_2 = 25 °C. The reaction mixture was stirred afterwards for 30 min at 25°C. The crude residue was purified by column chromatography yielding 6-chloro-1-phenylhexan-1-one (**23b**; 89%). The analytical data was found to match the literature data.[15]

Ethyl 2-(2-cyclobutylethyl)acrylate (24b): According to **TP** – *insertion*: 50 h, T_1 = 50 °C. Reaction *with an electrophile:* ethyl 2-(bromomethyl)acrylate (1.0 equiv) (**Note**: no excess of ethyl 2-(bromomethyl)acrylate has to be used) was added, followed by the addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, ca. 0.4 mol %) at –20°C. The reaction mixture was stirred afterwards for 1 h at 0°C. The crude residue was purified by column chromatography yielding ethyl 2-(2-cyclobutylethyl)acrylate (**24b**; 82%) as a colourless oil.
^{1}H-NMR ($CDCl_3$, 200 MHz): d = 6.09 (brs, 1 H); 5.47 (q, *J* = 1.4 Hz, 1 H); 4.19 (q, *J* = 7.1 Hz, 2 H); 2.26 (m, 1 H); 2.18 (m, 2 H); 2.03 (m, 2 H); 1.80 (m, 2 H); 1.56 (m, 4 H); 1.29 (t, *J* = 7.1 Hz, 3 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 167.6; 141.3; 124.3; 60.7; 35.9; 35.8; 29.7; 28.4; 18.6; 14.4.
MS (EI, 70 eV): m/z (%) = 182 (M^+, 14); 154 (28); 153 (25); 139 (54); 137 (21); 126 (41); 125 (29); 111 (77); 109 (50); 108 (19); 108 (31); 86 (25); 81 (100); 80 (52); 79 (58); 67 (41); 41 (52).
HR-MS: **($C_{11}H_{18}O_2$) calculated 182,1307 found 182,1319**

Ethyl 3-[4-(acetyloxy)butyl]benzoate (25b): According to **TP** – *insertion*: 3 h, T_1 = 50 °C. Reaction *with an electrophile:* 0.1 mol % of $Pd(dba)_2$ and 0.2 mol % of S-Phos was added at room temperature, followed by the addition ethyl 4-iodobenzoate at T_2 = 25 °C. The reaction mixture was stirred afterwards for 6 h at 25 °C. The crude residue was purified by column

chromatography yielding ethyl 3-[4-(acetyloxy)butyl]benzoate (**25b**; 83%) as a colourless oil.

^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 7.93-7.85 (m, 2H), 7.22-7.10 (m, 2H), 4.40 (m, 2H), 4.06 (m, 2H), 2.66 (t, *J* = 7.0 Hz, 3H), 2.10 (s, 3H), 1.68-1.60 (m, 4H), 1.40 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 173.0, 166.8, 141.2, 133.3, 130.6, 129.1, 129.0, 127.3, 61.7, 60.7, 36.2, 30.1, 28.7, 20.4, 13.8.

IR (KBr): 2935 (w), 1719 (vs), 1279 (s), 1257(s), 1109 (w), 745 (s).

MS (EI, 70 eV): m/z (%) = 264 (12, M^+), 219 (40), 176 (43), 158 (37), 148 (41), 131 (47).

HR-MS: **($C_{15}H_{20}O_4$) calculated 264.1362 found: 264.1381.**

Ethyl 3-(4-ethoxy-4-oxobutyl)benzoate (26b): According to **TP** – *insertion*: 1 h, T_1 = 50 °C. Reaction *with an electrophile:* 0.1 mol % of $Pd(dba)_2$ and 0.2 mol % of S-Phos was added at room temperature, followed by the addition ethyl 4-iodobenzoate at T_2 = 25 °C. The reaction mixture was stirred afterwards for 6 h at 25 °C. The crude residue was purified by column chromatography yielding ethyl 3-(4-ethoxy-4-oxobutyl)benzoate (**26b**; 93%) as colourless oil.

^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 8.06-8.02 (m, 1H), 7.88-7.80 (m, 1H), 7.54-7.49 (m, 1H), 7.37-7.33 (m, 1H), 4.38 (td, J_1 = 14.5 Hz, J_2 = 7.1 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.00-1.93 (m, 2H), 1.39 (dt, J_1 = 8.5 Hz, J_2 = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 173.3, 166.7, 141.7, 140.4, 133.0, 129.5, 128.4, 127.3, 60.8, 60.3, 34.9, 33.5, 26.4, 14.3, 14.2.

IR (KBr): 2982 (w), 1721 (vs), 1280 (s), 1197(s), 749 (s).

MS (EI, 70 eV): m/z (%) = 219 (57), 218 (96), 190 (100), 177 (59), 149 (75), 117 (55), 105 (47), 90 (29).

HR-MS: **($C_{15}H_{20}O_4$) calculated 264.1362 found: 264.1333.**

Ethyl 4-(4-cyanobutyl)benzoate (27b): According to **TP** – *insertion*: 6 h, T_1 = 50 °C. Reaction *with an electrophile:* 0.1 mol % of $Pd(dba)_2$ and 0.2 mol % of S-Phos was added at room temperature, followed by the addition ethyl 4-iodobenzoate at T_2 = 25 °C. The reaction mixture was stirred afterwards for 6 h at 25 °C. The crude residue was purified by column chromatography yielding ethyl 4-(4-cyanobutyl)benzoate (**27b**; 88%) as colourless oil.

^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 7.96-7.92 (m, 2H), 7.22-7.19 (m, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.68 (t, *J* = 7.3 Hz, 2H), 2.35-2.30 (m, 2H), 1.82-1.74 (m, 2H), 1.70-1.62 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 166.4, 146.5, 129.7, 129.6, 128.2, 128.1, 119.3, 60.7, 34.9, 29.8, 24.7, 19.9, 14.2.
IR (KBr): 2937 (m), 1714 (vs), 1278 (vs), 1178(m), 1104 (s), 762 (m).
MS (EI, 70 eV): m/z (%) = 231 (12, M^+), 187 (13), 186 (100), 185 (44), 163 (22).
HR-MS: **($C_{14}H_{17}O_2N$) calculated** 231.1259 **found:** 231.1260.

Cyclohexyl(phenyl)methanone (28b): According to **TP** – *insertion*: 24 h, T_1 = 50 °C. Reaction *with an electrophile:* 0.1 mol % of $Pd(dba)_2$ and 0.2 mol % of S-Phos was added at room temperature, followed by the addition benzoyl chloride at T_2 = 25 °C. The reaction mixture was stirred afterwards for 30 min at 25°C. The crude residue was purified by column chromatography yielding cyclohexyl(phenyl)methanone (**27b**; 94%). The analytical data was found to match the literature data.[16]

2-Methyl-1-phenyloctan-1-one (29b): According to **TP** – *insertion*: 18 h, T_1 = 50 °C. Reaction *with an electrophile:* 0.1 mol % of $Pd(dba)_2$ and 0.2 mol % of S-Phos was added at room temperature, followed by the addition benzoyl chloride at T_2 = 25 °C. The reaction mixture was stirred afterwards for 30 min at 25°C. The crude residue was purified by column chromatography yielding 2-methyl-1-phenyloctan-1-one (**29b**; 90%). The analytical data was found to match the literature data.[17]

2-Adamantyl dimethyldithiocarbamate (30b): According to **TP** – *insertion*: 24 h, T_1 = 50 °C. Reaction *with an electrophile:* tetramethyl thiuram disulfide (1.0 equiv.) was dissolved in dichloromethane and added dropwise at T_2 = 0 °C. The reaction mixture was stirred afterwards for 1 h at 25°C. The crude residue was purified by recristallization from heptane yielding 2-adamantyl dimethyldithiocarbamate (**30b**; 79%) as white crystals (mp = 110.5-111 °C).
^{1}H-NMR ($CDCl_3$, 200 MHz): d = 4.31 (s, 1 H), 3.44 (d, *J* = 44.2 Hz, 6 H), 2.14 (s, 2 H), 2.00-1.82 (m, 8 H), 1.75-1.60 (m, 4 H).
^{13}C-NMR ($CDCl_3$, 75 MHz): d = 197.2, 58.9, 38.6, 37.5, 33.8, 33.1, 27.4, 27.1.
MS (EI, 70 eV): m/z (%) = 2912 (s), 2852 (m), 1494 (w), 1374 (m), 986 (m), 909 (vs), 733 (vs).
HR-MS: **($C_{13}H_{21}NS_2$) calculated 255.1115 found 255.1090**

1,2-Diphenylprop-2-en-1-one (31c): According to **TP** – *insertion*: 24 h, T_1 = 25 °C. Reaction *with an electrophile:* transmetallation with CuCN·2LiCl (20 mol %) 5 min at 0°C, followed by addition of benzoyl chloride at T_2 = –20 °C. The reaction mixture was stirred afterwards for 1 h at 25°C. The

crude residue was purified by column chromatography yielding 1,2-diphenylprop-2-en-1-one (**31c**; 81%). The analytical data was found to match the literature data.[18]

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