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General Preparation of Functionalized *o*-Nitroarylmagnesium Halides via an Iodine Magnesium Exchange

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Typical procedure (**TP**) for the iodine-magnesium exchange of *o*-iodonitrobenzene derivatives.

A dry and argon flushed 25 mL flask, equipped with a magnetic stirrer and a septum, was charged with 2-iodonitrobenzene derivative (2.0 mmol). Dry THF (8 mL) was added and the mixture cooled to –40 °C. PhMgCl (1.1 mL, 2.2 mmol, 2 M in THF) was added dropwise. The I/Mg-exchange was complete after 5 min (checked by GC analysis of reaction aliquots) and the electrophile (2.4 mmol) was added to the magnesiated benzene (**2a**). If the reactivity of the electrophile required a transmetallation to the copper derivative, a solution of CuCN·2LiCl (2.2 mL, 1 M in THF) was added slowly before the addition of the electrophile. After 0.5 h of stirring at –40 °C, the reaction mixture was quenched with sat. NH_4Cl solution (2 mL) and poured into water (25 mL). The aqueous phase was extracted with ethyl acetate (2 x 40 mL). The organic fractions were washed with brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography on silica gel furnished the product.

Preparation of (2-nitrophenyl)-(phenyl)-methanol (**3a**):
Prepared according to **TP** from 2-iodonitrobenzene (**1a**) (498 mg, 2.0 mmol) PhMgCl (1.1 mL, 2.2 mmol, 2 M in THF) and benzaldehyde (255 mg, 2.4 mmol). Reaction time: 0.5 h. Purification by flash chromatography (pentane/diethyl ether = 4:1) yielded the benzylic alcohol (**3a**) as a red oil (400 mg, 87 %).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.84 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.3 Hz, 1 H), 7.65 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.3 Hz, 1 H), 7.54 (dt, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.3 Hz, 1 H), 7.36 (dt, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.3 Hz, 1 H), 7.25-7.17 (m, 5 H), 6.34 (br, 1 H), 2.83 (br, 1 H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 148.8, 141.9, 138.9, 133.8, 129.8, 129.0, 128.4, 127.3, 126.9, 125.1, 71.9.
MS (70 eV, EI): m/z (%): 229 (0.1)[M^+], 211 (5), 194 (46), 181 (21), 167 (100), 152 (57), 39 (10), 127 (5), 115 (5), 105 (17), 92 (2), 77 (46), 65 (4), 51 (12).
IR (KBr): $\tilde{\nu}$ = 3412 (m, br), 3064 (m), 1955 (w), 1740 (w), 1667 (w), 1598 (m), 1578 (m), 1525 (vs), 1452 (s), 1349 (vs), 1260 (s), 1178 (s), 1022 (s), 861 (m), 787 (m), 760 (s), 736 (s), 701 (vs), 647 (w), 601 (w).

HRMS for **$C_{13}H_{11}NO_3$** (229.0739): calc.: 229.0582 $[M]^+$
found: 229.0518 $[M]^+$.

Preparation of 1-allyl-2-nitrobenzene (**3b**):
Prepared according to **TP** from 2-iodonitrobenzene (**1a**) (498 mg, 2.0 mmol), PhMgCl (1.1 mL, 2.2 mmol, 2.0 M in THF) CuCN·2LiCl (2.2 mL, 2.2 mmol, 1 M in THF) and allyl bromide (290 mg, 2.4 mmol). Reaction time: 1 h. Purification by flash chromatography (pentane/dichloromethane = 4:1) yielded 1-allyl-2-nitrobenzene (**3b**) (244 mg, 1.5 mmol, 75 %) as a red oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.81$ (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.3 Hz, 1 H), 7.45 (dt, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.3 Hz, 1 H), 7.30-7.25 (m, 2 H), 5.95-5.82 (m, 1 H), 5.05-4.96 (m, 2 H), 3.60 (d, ^3J(H,H) = 8 Hz, 2 H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 149.7, 135.4, 135.2, 133.4, 132.3, 127.7, 125.0, 117.5, 34.3.
MS (70 eV, EI): *m/z* (%) 162 (22) ([M^+], 146 (68), 134 (56), 129 (23), 115 (100), 104 (19), 91 (51), 77 (39), 65 (28), 51 (18).
IR (KBr): $\tilde{\nu}$ = 3081 (w), 1610 (m), 1526 (vs), 1435 (m), 1349 (s), 1147 (w), 995 (w), 921 (m), 857 (m), 786 (m), 741 (m), 705 (w), 672 (w), 643 (w).
HRMS for $C_9H_9NO_2$ (163.0633): calc.: 163.0633 $[M]^+$
found: 163.0642 $[M]^+$.

Preparation of [hydroxy(phenyl)methyl]-4-nitrobenzonitrile (**3c**):
Prepared according to **TP** from 4-iodo-3-nitrobenzonitrile (**1b**) (274 mg, 1.0 mmol), PhMgCl (0.55 mL, 1.1 mmol, 2.0 M in THF) and benzaldehyde (128 mg, 1.2 mmol). Reaction time: 0.5 h. Purification by flash chromatography (dichloromethane) yielded [hydroxy(phenyl)methyl]-4-nitrobenzonitrile (**3c**) (240 mg, 0.94 mmol, 94 %) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 8.10$ (d, ^4J(H,H) = 1.8 Hz, 1 H), 7.87 (d, ^3J(H,H) = 8 Hz, 1 H), 7.66 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.8 Hz, 1 H), 7.31-7.18 (m, 5 H), 6.36 (d, ^3J(H,H) = 3 Hz, 1 H), 2.7 (d, ^3J(H,H) = 3 Hz, 1 H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 149.1, 139.4, 138.8, 132.1, 131.0, 128.6, 128.0, 127.5, 126.1, 124.2, 116.0, 69.9.
MS (70 eV, EI): *m/z* (%) 236 (11), 219 (73), 206 (25), 192 (100), 177 (23), 165 (15), 151 (27), 129 (7), 105 (20), 77 (59), 63 (5), 51 (11).
IR (KBr): $\tilde{\nu}$ = 3468 (br, s), 3085 (s), 2238 (s), 1673 (w), 1601 (m), 1584 (vs), 1454 (s), 1350 (vs), 1299 (s), 1146 (m), 1077 (m), 1023 (s), 917 (w), 846 (vs), 759 (s), 701 (vs), 592 (w), 554 (w).
HRMS for **$C_{14}H_{10}N_2O_3$** (254.0691): calc.: 252.0535 $[M\text{-}2H]^+$
found: 252.0546 $[M\text{-}2H]^+$.

Preparation of (4-methoxy-2-nitrophenyl)(phenyl)methanol (**3d**):
Prepared according to **TP** from 1-iodo-4-methoxy-2-nitrobenzene (**1c**) (418 mg, 1.5 mmol), PhMgCl (1 mL, 1.7 mmol, 1.7 M in THF) and benzaldehyde (190 mg,

1.8 mmol). Reaction time: 0.5 h. Purification by flash chromatography (dichloromethane) yielded (4-methoxy-2-nitrophenyl)(phenyl)methanol (**3d**) (279 mg, 72 %) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.48 (d, ^3J(H,H) = 8.5 Hz, 1 H), 7.35(d, ^4J(H,H) = 2.8 Hz, 1 H), 7.26-7.18 (m, 5 H), 7.05 (dd, ^3J(H,H) = 8.5 Hz and ^4J(H,H) = 2.8 Hz, 1 H), 6.25 (s, 1 H), 3.78 (s, 3 H), 2.61 (br s, 1 H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 159.6, 149.4, 142.2, 131.1, 131.0, 128.9, 128.2, 127.2, 120.1, 109.8, 71.6,56.3.
MS (70 eV, EI): *m/z* (%) 241 (26) [M-H_2O], 224 (48), 211 (27), 196 (32), 182 (100), 168 (50), 154 (87), 140 (22), 135 (26), 127 (11), 115 (18), 105 (22), 92 (12), 77 (80), 63 (18), 51 (17).
IR (KBr): $\tilde{\nu}$ = 3400 (m), 2840 (w), 1621 (m), 1530 (vs), 1352 (s), 1244 (s), 1181 (m), 1066 (m), 1033 (s), 759 (m), 700 (s), 549 (w).
$C_{14}H_{13}NO_4$: calc.: C: 64.86, H: 5.40, N: 5.40
found: C: 65.22, H: 5.13, N: 5.23.

Preparation of ethyl 2-(4-methoxy-2-nitrobenzyl)acrylate (**3e**):
Prepared according to **TP** from 1-iodo-4-methoxy-2-nitrobenzene (**1c**) (558 mg, 2 mmol), PhMgCl (1.3 mL, 2.2 mmol, 1.7 M in THF), CuCN·2LiCl (2.2 mL, 2.2 mmol, 1 M in THF) and ethyl 2-(brommethyl)acrylate (463 mg, 2.4 mmol). Reaction time: 45 min. Purification by flash chromatography (pentane/diethyl ether = 9:1) furnished ethyl 2-(4-methoxy-2-nitrobenzyl)acrylate (**3e**) (381 mg, 72 %) as an orange liquid.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.38(d, ^4J(H,H) = 2.8 Hz, 1 H), 7.17 (d, ^3J(H,H) = 8 Hz, 1 H), 7.01 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 2.8 Hz, 1 H), 6.17-6.14 (m, 1 H), 5.29-5.27 (m, 1 H), 4.12 (q, ^3J(H,H) = 7 Hz, 2 H), 3.82 (s, 2 H), 3.77 (s, 3 H), 1.18 (t, ^3J(H,H) = 7 Hz, 3 H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.4, 157.6, 148.8, 137.7, 132.3, 124.4, 118.6, 108.4,59.9, 54.8, 33.2, 13.1.
MS (70 eV, EI): *m/z* (%) 265 (2) $[M]^+$, 248 (23), 236 (100), 220 (52),202 (20), 190 (60), 174 (63), 164 (37), 146 (56), 132 (28), 103 (32), 91 (24), 77 (42), 63 (15), 51 (18).
IR (KBr): $\tilde{\nu}$ = 2982 (m), 1715 (s), 1625 (m), 1531 (vs), 1410 (m), 1352 (s), 1252 (s), 1150 (s), 1034 (s), 945 (w), 814 (m), 757 (w).
HRMS for $C_{13}H_{15}NO_5$ (265.0950): calc.: 264.0872 $[M-H]^+$
found: 264.0888 $[M-H]^+$.

Preparation of ethyl 4-[hydroxy(phenyl)methyl]-3-nitro-benzoate (**3f**):
Prepared according to **TP** from ethyl 4-iodo-3-nitrobenzoate (**1d**) (642 mg, 2.0 mmol), PhMgCl (1.10 mL, 2.2 mmol, 2.0 M in THF) and benzaldehyde (254 mg, 2.4 mmol). Reaction time: 0.5 h. Purification by flash chromatography (pentane/dichloromethane = 4:1) yielded ethyl 4-[hydroxy(phenyl)methyl]-3-nitro-benzoate (**3f**) (564 mg, 1.86 mmol, 94 %) as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.45 (d, ^4J(H,H) = 1.8 Hz, 1 H), 8.19 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.8 Hz, 1 H), 7.84 (d, ^3J(H,H) = 8 Hz 1 H), 7.25-7.18 (m,

5 H), 6.40 (d, ^3J(H,H) = 3.5 Hz, 1 H), 4.34 (q, ^3J(H,H) = 7 Hz, 2 H), 2.85 (d, ^3J(H,H) = 3.5 Hz, 1 H), 1.33 (t, ^3J(H,H) = 7 Hz, 3 H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 164.7, 148.5, 143.1, 141.4, 134.2, 131.4, 129.8, 129.1, 128.8, 127.4, 126.1, 71.8, 62.3, 14.6.
MS (70 eV, EI): *m/z* (%) 283 (14), 266 (26), 256 (16), 238 (41), 222 (20), 211 (14), 194 (100), 180 (23), 167 (72), 152 (69), 139 (8), 127 (5), 115 (6), 105 (41), 77 (54), 65 (4), 51 (9).
IR (KBr): $\tilde{\nu}$ = 3478 (br, s), 2984 (m), 1728 (vs), 1620 (s), 1538 (vs), 1493 (s), 1454 (s), 1355 (s), 1288(br, s), 1152 (s), 1021 (s), 919 (m), 838 (m), 764 (vs), 749 (vs), 701 (vs), 665 (w), 557 (w).
HRMS for $C_{16}H_{15}NO_5$ (301.0950): calc.: 302.1028 $[M+H]^+$
found: 302.1031 $[M+H]^+$.

Preparation of ethyl 4-[cyclohexyl(hydroxy)methyl]-3-nitro-benzoate (**3g**):
Prepared according to **TP** from ethyl 4-iodo-3-nitro-benzoate (**1d**) (583 mg, 1.8 mmol), PhMgCl (1.0 mL, 2.0 mmol, 2.0 M in THF) and cyclohexanecarbaldehyde (249 mg, 2.2 mmol). Reaction time: 1 h. Purification by flash chromatography (pentane/dichloromethane = 7:3) yielded ethyl 4-[cyclohexyl(hydroxy)methyl]-3-nitro-benzoate (**3g**) (355 mg, 64 %) as an orange-yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): 8.41 (d, ^4J(H,H) = 1.8 Hz, 1 H), 8.16 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.8 Hz, 1 H), 7.76 (d, ^3J(H,H) = 8 Hz 1 H), 5.06 (d, ^3J(H,H) = 5.5 Hz, 1 H), 4.35 (q, ^3J(H,H) = 7 Hz, 2 H), 2.15 (br, 1 H), 1.68-1.58 (m, 6 H), 1.34 (t, ^3J(H,H) = 7 Hz, 3 H), 1.11-1.05 (m, 5 H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): 183.8, 164.9, 148.7, 143.6, 133.6, 130.9, 129.8, 125.7, 73.6, 62.2, 44.6, 30.2, 27.7, 26.6, 26.3, 14.6.
MS (70 eV, EI): *m/z* (%) 288 (5), 272 (18), 262 (18), 244 (13), 224 (11), 207 (100), 191 (27), 179 (56), 162 (30), 151 (30), 135 (8), 123 (36), 118 (6), 105 (12), 83 (20), 77 (15), 65 (10), 55 (46).
IR (KBr): $\tilde{\nu}$ = 3497 (br, m), 2929 (vs), 2854 (vs), 1726 (vs), 1619 (m), 1535 (vs), 1450 (m), 1355 (s), 1285 (br, vs), 1189 (m), 1096 (m), 1020 (s), 919 (w), 863 (m), 838 (m), 759 (vs), 718 (w), 705 (w).
HRMS for $C_{16}H_{21}NO_5$ (307.1420): calc.: 308.1498 $[M+H]^+$
found: 308.1485 $[M+H]^+$.

Preparation of ethyl 4-[2-(ethoxycarbonyl)-2-propenyl]-3-nitro-benzoate (**3h**):
Prepared according to **TP** from ethyl 4-iodo-3-nitro-benzoate (**1d**) (642 mg, 2.0 mmol), PhMgCl (1.1 mL, 2.2 mmol, 2.0 M in THF), CuCN·2LiCl (2.2 mL, 2.2 mmol, 1 M in THF) and ethyl 2-(brommethyl)acrylate (463 mg, 2.4 mmol). Reaction time: 1 h. Purification by flash chromatography (pentane/diethyl ether = 85:15) yielded ethyl 4-[2-(ethoxycarbonyl)-2-propenyl]-3-nitro-benzoate (**3h**) (461 mg, 1.5 mmol, 75 %) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.47 (d, ^4J(H,H) = 1.8 Hz, 1 H), 8.10 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.8 Hz, 1 H), 7.39 (d, ^3J(H,H) = 8 Hz 1 H), 6.24 (d, ^2J(H,H) = 1 Hz, 1 H), 5.40 (d, ^2J(H,H) = 1 Hz, 1 H), 4.34 (q, ^3J(H,H) = 7 Hz, 2 H), 4.09

(q, ^3J(H,H) = 7 Hz, 2 H), 3.95 (s, 2 H), 1.34 (t, ^3J(H,H) = 7 Hz, 3 H), 1.17 (t, ^3J(H,H) = 7 Hz, 3 H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.4, 164.8, 149.8, 138.7, 138.0, 133.7, 132.8, 130.8, 127.8, 126.2, 62.1, 61.5, 35.2, 14.6, 14.4.
MS (70 eV, EI): *m/z* (%) 306 (2)[$(M-H)^+$], 278 (16), 261 (100), 244 (7), 233 (67), 217 (24), 206 (21), 188 (29), 172 (15), 160 (29), 144 (24), 134 (13), 115 (33), 103 (13), 89 (14), 77 (14), 63 (7), 55 (5).
IR (KBr): $\tilde{\nu}$ = 3429 (br, w), 2984 (m), 1724 (vs), 1620 (m), 1536 (vs), 1494 (w), 1446 (w), 1408 (w), 1367 (s), 1281 (vs), 1263 (vs), 1152 (s), 1113 (s), 1023 (m), 935 (w), 863 (w), 822 (w), 772 (w), 757 (w), 725 (w).
HRMS for $C_{15}H_{17}NO_6$ (307.1056): calc.: 306.0978$[M-H]^+$
found: 306.0957$[M-H]^+$.

Preparation of ethyl 4-benzoyl-3-nitrobenzoate (**3i**):
Prepared according to **TP** from ethyl 4-iodo-3-nitrobenzoate (**1d**) (642 mg, 2.0 mmol), PhMgCl (1.16 mL, 2.2 mmol, 1.9 M in THF) and benzoyl bromide (481 mg, 2.6 mmol). Reaction time: 0.5 h. Purification by flash chromatography (pentane/diethyl ether = 4:1) yielded ethyl 4-benzoyl-3-nitrobenzoate (**3i**) (454 mg, 76 %) as a yellow solid.

mp.: 94 °C
^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.79 (d, ^4J(H,H) = 1.8 Hz, 1 H), 8.35 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.8 Hz, 1 H), 7.68-7.64 (m, 2 H), 7.56- 7.48 (m, 2 H), 7.41-7.36 (m, 2 H), 4.42 (q, ^3J(H,H) = 7 Hz, 2 H), 1.38 (t, ^3J(H,H) = 7 Hz, 3 H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 193.0, 164.2, 147.1, 140.1, 135.9, 135.1, 134.5, 133.5, 129.6, 129.5, 129.3, 126.0, 62.7, 14.7.
MS (70 eV, EI): *m/z* (%) 299 (6) [M^+], 270 (2), 254 (21), 222 (18), 206 (100), 194 (4), 176 (23), 152 (21), 126 (3), 105 (98), 77 (37), 51 (6).
IR (KBr): $\tilde{\nu}$ = 3422 (br, w), 2986 (m), 1721 (vs), 1674 (vs), 1597 (w), 1534 (vs), 1492 (m), 1449 (m), 1352 (vs), 1287 (s), 1236 (s), 1163 (s), 1020 (m), 941 (m), 920 (s), 858 (m), 837 (m), 766 (s), 742 (m), 715 (s), 701 (m), 685 (m).
HRMS for $\mathbf{C_{16}H_{13}NO_5}$ (299.0794): calc.: 299.0794$[M]^+$
found: 299.0802$[M]^+$.

Preparation of (2,4-dinitrophenyl)(phenyl)methanol (**3j**):
Prepared according to **TP** from 2,4-dinitro-iodobenzene (**1e**) (588 mg, 2.0 mmol), PhMgCl (1,05 mL, 2,1 mmol, 2 M in THF) and benzaldehyde (424 mg, 4 mmol). Reaction time: 0.5 h. Purification by flash chromatography (dichloromethane) yielded (2,4-dinitrophenyl)(phenyl)methanol (**3j**) (442 mg, 81 %) as an orange oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.66 (d, ^4J(H,H) = 2.1 Hz, 1 H), 8.39 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 2.1 Hz, 1 H), 8.07 (d, ^3J(H,H) = 8 Hz, 1 H), 7.30-7.18 (m, 5 H), 6.47 (s, 1 H), 2,46 (br s, 1 H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 146.9, 146.1, 143.9, 139.3, 129.4, 128.0, 127.8, 126.2, 126.1, 119.2, 70.3.
MS (70 eV, EI): *m/z* (%) 256 (11) $[M-H_2O]^+$, 239 (100), 210 (17), 193 (15), 180 (25), 166 (85), 152 (68), 139 (32), 127 (11), 105 (31), 77 (76), 63 (8), 51 (14).

IR (KBr): $\tilde{\nu}$ = 3542 (br, s), 3111 (s), 1605 (s), 1538 (vs), 1454 (s), 1348 (vs), 1176 (m), 1036 (s), 919 (m), 836 (s), 758 (s), 740 (s), 701 (s).

HRMS for **$C_{13}H_{10}N_2O_5$** (274.0590): calc.: 272.0433[M-2H]$^+$
found: 272.0432[M-2H]$^+$.

$C_{13}H_{10}N_2O_5$: calc.: C: 56.94, H: 3.68, N: 10.22
found: C: 57.13, H: 3.71, N: 10.01.

Preparation of cyclohexyl(2,4-dinitrophenyl)methanol (**3k**):

Prepared according to **TP** from 2,4-dinitro-iodobenzene (**1e**) (588 mg, 2.0 mmol), PhMgCl (1,05 mL, 2,1 mmol, 2 M in THF) and cyclohexanecarbaldehyde (560 mg, 5 mmol). Reaction time: 0.5 h. Purification by flash chromatography (dichloromethane/pentane = 4:1) yielded cyclohexyl(2,4-dinitrophenyl)methanol (**3k**) (416 mg, 74 %) as an orange oil

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.67 (d, ^4J(H,H) = 2.1 Hz, 1 H), 8.37 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 2.1 Hz, 1 H), 7.61 (d, ^3J(H,H) = 8 Hz, 1 H), 5.19 (d, ^3J(H,H) = 5 Hz, 1 H), 2.18 (br s, 1 H), 1.69-157 (m, 5 H), 1.44-1.41 (m, 1 H), 1.18-1.03 (m, 5 H).

^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 148.3, 147.1, 146.1, 131.1, 127.1, 120.2, 73.3, 44.8, 30.2, 27.2, 26.5, 26.4, 26.2.

MS (70 eV, EI): *m/z* (%) 261 (2) [M-H_2O]$^+$, 245 (5), 217 (4), 198 (90), 180 (100), 164 (8), 151 (14), 134 (31), 124 (5), 103 (9), 83 (50), 77 (13), 67 (7), 55 (75).

IR (KBr): $\tilde{\nu}$ = 3562 (br, s), 3111 (m), 2926 (vs), 1605 (m), 1538 (vs), 1450 (s), 1353 (vs), 1262 (m), 1188 (m), 1083 (s), 1024 (m), 916 (m), 836 (s), 745 (s), 720 (s).

HRMS for **$C_{13}H_{16}N_2O_5$** (280.1059): calc.: 263.1032[M-OH]$^+$
found: 263.0999[M-OH]$^+$.

$C_{13}H_{16}N_2O_5$: calc.: C: 55.71, H: 5.75, N: 9.99
found: C: 55.60, H: 5.78, N: 9.62.

Preparation of (4-iodo-2-nitrophenyl)(phenyl)methanol (**3l**):

Prepared according to **TP** from 2,5-diiodo-nitrobenzene (**1f**) (563 mg, 1.5 mmol), PhMgCl (0.97 mL, 1.65 mmol, 2 M in THF) and benzaldehyde (190 mg, 1,8 mmol). Reaction time: 0.5 h. Purification by flash chromatography (pentane/diethyl ether = 4:1) yielded (4-iodo-2-nitrophenyl)(phenyl)methanol (**3l**) (458 mg, 86 %) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.15 (d, ^4J(H,H) = 1.8 Hz, 1 H), 7.86 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.8 Hz, 1 H), 7.42 (d, ^3J(H,H) = 8 Hz, 1 H), 7.28-7.18 (m, 5 H), 6.30 (s, 1 H), 2,45 (br s, 1 H).

^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 141.5, 141.2, 140.0, 137.1, 132.1, 129.8, 127.7, 127.2, 125.9, 91.2, 70.2.

MS (70 eV, EI): *m/z* (%) 353 (3) [M$^+$], 337 (18), 320 (82), 308 (6), 293 (38), 260 (8), 231 (13), 182(22), 166 (100), 152 (73), 139 (25), 109 (22), 77 (58), 63 (10), 51 (14).

IR (KBr): $\tilde{\nu}$ = 3369 (s, br), 1530 (vs), 1469 (s), 1347 (vs), 1275 (m), 1179 (m), 1034 (s), 871 (m), 808 (m), 763 (s), 700 (s).

HRMS for **$C_{13}H_{10}INO_3$** (354.9705): calc.: 352.9549 [M-2H]$^+$
found: 352.9544 [M-2H]$^+$.

Preparation of ethyl 2-(4-iodo-2-nitrobenzyl)acrylate (**3m**):
Prepared according to **TP** from 2,5-diiodo-nitrobenzene (**2f**) (563 mg, 1.5 mmol), PhMgCl (0.97 mL, 1.65 mmol, 2 M in THF), CuCN·LiCl (1.65 mL, 1.65 mmol, 1 M in THF) and ethyl (2-bromomethyl)acrylate (345 mg, 1.8 mmol). Reaction time: 45 min. Purification by flash chromatography (pentane/dichloromethane = 2:1) yielded ethyl 2-(4-iodo-2-nitrobenzyl)acrylate (**3m**) (401 mg, 74 %) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.16 (d, ^4J(H,H) = 1.8 Hz, 1 H), 7.77 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.8 Hz, 1 H), 7.04 (d, ^3J(H,H) = 8 Hz, 1 H), 6.21 (d, ^2J(H,H) = 1 Hz, 1 H), 5.38 (d, ^2J(H,H) = 1 Hz, 1 H), 4.10 (q, ^3J(H,H) = 7 Hz, 2 H), 3.84 (s, 2 H), 1.18 (t, ^3J(H,H) = 7 Hz, 3 H).
^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 165.1, 148.8, 140.7, 136.7, 132.8, 132.3, 132.3, 126.2, 89.8, 60.1, 33.4, 13.1.
MS (70 eV, EI): *m/z* (%) 360 (7) [M$^+$], 344 (10), 332 (100), 316 (100), 304 (12), 298 (28), 287 (78), 270 (78), 261 (58), 230 (19), 205 (32), 177 (11), 161 (72), 145 (21), 133 (66), 117 (22), 102 (29), 89 (58), 77 (34), 63 (41).
IR (KBr): $\tilde{\nu}$ = 2981 (w), 1714 (vs), 1529 (vs), 1475 (m), 1349 (vs), 1299 (m), 1137 (s), 1025 (m), 953(m), 810 (m), 727 (w), 701 (w).
HRMS for **$C_{12}H_{12}INO_4$** (360.9811): calc.: 359.9733 [M-H]$^+$
found: 359.9765 [M-H]$^+$
$C_{12}H_{12}INO_4$: calc.: C:39.91, H: 3.35, N: 3,88
found: C:39.90, H: 3.10, N: 3.86.

Preparation of ethyl 4'-cyano-2'-nitro[1,1'-biphenyl]-4-carboxylate (**6**):
A dry and argon flushed 25 mL flask, equipped with a magnetic stirrer and a septum, was charged with 4-iodo-3-nitro-benzonitrile (**4**) (411 mg, 1.5 mmol). Dry THF (6 mL) was added and the mixture cooled to –40 °C. Mesitylmagnesium bromide (1.3 mL, 1.7 mmol, 0.7 M in THF) was added dropwise. The I/Mg-exchange was complete after 10 min (checked by GC analysis of reaction aliquots) and zinc bromide (1.7 mL, 1.7 mmol, 1 M in THF) was added to the magnesiated benzonitrile. Another dry two-necked flask equipped with a magnetic stirrer and a septum was charged with *bis*-(dibenzylideneacetone)palladium (0) ($Pd(dba)_2$) (43.5 mg, 5 mol %) and *tris-o*-furylphosphine (tfp) (37.0 mg, 10 mol %) followed by THF (2 mL). The initial red color disappeared after 2 min leading to a yellow solution and ethyl-4-iodo-benzoate (621 mg, 1.5 mmol) was added. This solution was added after 10 min of stirring to the reaction mixture at –40 °C and the cooling bath was removed. The reaction was stirred for 3 h at room temperature, treated with ethanol (2 mL) and poured into water (25 mL). The aqueous phase was extracted with ethyl acetate (3 x 40 mL), the collected organic phases were washed with brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane/ethyl acetate = 6:1) yielded ethyl 4'-cyano-2'-nitro[1,1'-biphenyl]-4-carboxylate (**6**) as a pale yellow solid (325 mg, 73 %).

mp.: 167 °C

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.21$ (d, ^4J(H,H) = 1.5 Hz, 1 H), 8.13 (d, ^3J(H,H) = 8.5 Hz, 2 H), 7.93 (dd, ^3J(H,H) = 8 Hz and ^4J(H,H) = 1.5 Hz, 1 H), 7.60 (d, ^3J(H,H) = 8 Hz, 1 H), 7.38 (d, ^3J(H,H) = 8.5 Hz, 2 H), 4.40 (q, ^3J(H,H) = 7.5 Hz, 2 H), 1.41 (t, ^3J(H,H) = 7.5 Hz, 3 H).

^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 165.7$, 149.1, 139.9, 135.5, 132.9, 131.4, 130.2, 127.9, 127.8, 116.3, 113.2, 61.3, 14.3.

MS (70 eV, EI): *m/z* (%) 296 (10) [M^+], 269 (52), 251 (100), 228 (16), 205 (40), 177 (63), 150 (23), 126 (8), 77 (14), 63 (6), 51 (4).

IR (KBr): $\tilde{\nu}$ = 3436 (br, m), 2235 (m), 1712 (vs), 1610 (w), 1528 (vs), 1358 (s), 1286 (vs), 1110 (m), 849 (m), 761 (w), 712 (w).

HRMS for **$C_{16}H_{12}N_2O_4$** (296.0797): calc.: 296.0797 $[M]^+$
found: 296.0779 $[M]^+$.

$C_{16}H_{12}N_2O_4$: calc.: C: 64.86, H: 4.08 , N: 9.46
found: C: 64.62, H: 3.64 , N: 9.40.