Synthesis of Functionalized Nitroarylmagnesium Halides *via* an Iodine-Magnesium Exchange

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General All reactions were carried out under an argon atmosphere in oven dried glassware. Elemental analyses were carried out on a Heraeus CHN-Rapid-Elementanalyzer. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Preparative flash chromatography was performed on silicagel 60 (0.040-0.063 mm) from Merck. Yields refer to isolated yields of compounds estimated to be > 95% pure as determined by ¹H-NMR, capillary GC and combustion analysis (new compounds).

Typical procedures (TP)

Typical procedure for the nitration of arenes (TP 1)

A cold mixture of 1.9 mL nitric acid (HNO₃, 100%) and 2.7 mL sulfuric acid (H₂SO₄, 100%) was added slowly to a solution of the corresponding arene (10 mmol) dissolved in 5 mL sulphuric acid (H₂SO₄, 100%) within 30 min with vigorous stirring. Upon completion of the addition the solution was allowed to warm to ambient temperature and stirring was continued for 5 h and the reaction mixture was poured onto crushed ice (100 g). The solid was filtrated, taken up in ethyl acetate (100 mL) and washed with saturated NaHCO_{3(aq.)} (100 mL), dried over Na₂SO₄, filtered and concentrated *in vacuo*. Recrystallization from ethanol yielded the pure product.

Typical procedure for the iodination of arenes using silver sulfate (TP 2)¹

A 250 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with iodine (5.08 g, 20.0 mmol) and silver sulfate (6.23 g, 20.0 mmol) in ethanol (100 mL). The aromatic compound (20 mmol) was then added and the mixture was stirred vigorously at rt until tlc analysis indicated complete conversion (typically 30min-2 h). The reaction mixture was filtered through a glass sinter, the solids on the sinter were washed with ethyl acetate (2 x 100 mL) and the filtrate was concentrated *in vacuo*. The residue was taken up in CH₂Cl₂ (100 mL), washed with 2 M NaOH (100 mL), water (100 mL), dried over Na₂SO₄ and concentrated *in vacuo*. Flash chromatography on silica gel furnished the product.

Typical procedure for the performance of an iodine-magnesium exchange reaction on functionalised *o*-iodonitroarenes (TP 3)

A dry and argon flushed 25 mL flask, equipped with a magnetic stirrer and a septum, was charged with the *o*-iodo-nitrobenzene (2 mmol). Dry THF (5 mL) was added, the mixture cooled to -40 °C and PhMgCl (2.2 mmol, solution in THF) was then added dropwise. The I/Mg exchange was usually complete after 5 min (checked by GC analysis of reaction aliquots) and, if necessary, CuCN·2LiCl (2 mL, 1.0 M in THF) was added prior to the addition of the electrophile. The reaction mixture was stirred for 30 min at -40 °C, the cooling bath was removed and the mixture stirred for additional 30 min at room temperature. The reaction

mixture was quenched with saturated $\text{NH}_4\text{Cl}_{(\text{aq})}$ (2 mL) and poured into water (25 mL). The aqueous phase was extracted with ethyl acetate (2 x 40 mL), the collected organic phases were washed with brine (30 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography furnished the product.

Typical procedure for the preparation of nitro-substituted polyfunctional biphenyls by Negishi cross-coupling of *o*-nitroarylzinc reagents (TP 4)

A dry and argon flushed 25 mL flask, equipped with a magnetic stirrer and a septum, was charged with the 2-iodonitroarene (1.00 mmol). Dry THF (5 mL) was added, the mixture cooled to $-40\text{ }^\circ\text{C}$ and mesitylmagnesium bromide (1.6 mL, 1.1 mmol, 0.70 M in THF) was added dropwise. The I/Mg exchange was complete after 15 min (checked by GC analysis of reaction aliquots) and zinc bromide (1.1 mL, 1.1 mmol, 1.0 M in THF) was added to the magnesiated nitroarene. Another dry two-necked flask equipped with a magnetic stirrer and a septum was charged with *bis*-(dibenzylideneacetone)palladium(0) ($\text{Pd}(\text{dba})_2$) (29 mg, 5 mol %) and *tris-o*-furylphosphine (tfp) (25 mg, 10 mol %) followed by THF (2 mL). The initial red colour disappeared after 2 min leading to a yellow solution and haloarene (1.5 mmol) was added. This solution was added *via cannula* after 10 min of stirring to the reaction mixture at $-40\text{ }^\circ\text{C}$ and the cooling bath was removed. The reaction was stirred for 5 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 over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography furnished the product.

Typical procedure for the performance of an iodine-magnesium exchange reaction on functionalised *m*- and *p*-iodonitroarenes (TP 5)

A dry and argon flushed 25 mL flask, equipped with a magnetic stirrer and a septum, was charged with the *m*- or *p*-iodo-nitrobenzene (1 mmol). Dry THF (3 mL) was added, the mixture cooled to $-78\text{ }^\circ\text{C}$ and PhMgCl (1.1 mmol, solution in THF) was then added dropwise. The I/Mg exchange was usually complete after 30 min (checked by GC analysis of reaction aliquots) and, if necessary, $\text{CuCN}\cdot 2\text{LiCl}$ (2 mL, 1.0 M in THF) was added prior to the addition of the electrophile. The reaction mixture was stirred for 30 min at $-78\text{ }^\circ\text{C}$, the cooling bath was removed and the reaction mixture stirred for additional 30 min at ambient temperature. The reaction mixture was quenched with saturated $\text{NH}_4\text{Cl}_{(\text{aq})}$ (2 mL) and poured into water (25 mL). The aqueous phase was extracted with ethyl acetate (2 x 40 mL), the collected organic phases were washed with brine (30 mL), dried over Na_2SO_4 , filtered and concentrated *in vacuo*. Purification by flash chromatography furnished the product.

Typical procedure for the preparation of nitro-substituted polyfunctional biphenyls by Negishi cross-coupling of *m*- and *p*-nitroarylzinc reagents (TP 6)

A dry and argon flushed 25 mL flask, equipped with a magnetic stirrer and a septum, was charged with *m*- or *p*-iodonitrobenzene (1.0 mmol). Dry THF (5 mL) was added, the mixture cooled to $-78\text{ }^\circ\text{C}$ and PhMgCl (0.65 mL, 1.05 mmol, solution in THF) was added dropwise. The I/Mg exchange was complete after 10 min (checked by GC analysis of reaction aliquots) and zinc bromide (1.1 mL, 1.1 mmol, 1.0 M in THF) was added to the magnesiated benzoate

at $-78\text{ }^{\circ}\text{C}$. Another dry two-necked flask equipped with a magnetic stirrer and a septum was charged with *bis*-(dibenzylideneacetone)palladium(0) ($\text{Pd}(\text{dba})_2$) (29 mg, 5 mol %) and *tris*-*o*-furylphosphine (tfp) (25 mg, 10 mol %) followed by THF (2 mL). The initial red colour disappeared after 2 min leading to a yellow solution and the iodobenzene (2 mmol) was added. This solution was added *via cannula* after 10 min of stirring to the reaction mixture at $-78\text{ }^{\circ}\text{C}$ and the cooling bath was removed. The reaction mixture was stirred for 2 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 over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography furnished the product.

Typical procedure for the formation of alkyl- and aryl-sulfonates from the corresponding phenols (TP 7)

A 100 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with the corresponding phenol (10.0 mmol) and dry pyridine (20 mL) was added. The solution was cooled to $0\text{ }^{\circ}\text{C}$ and the aryl or alkyl sulfonyl chloride (12.0 mmol) was added portionwise. On completion of the addition, the reaction mixture was stirred for additional 15 min at $0\text{ }^{\circ}\text{C}$ and was then allowed to warm to room temperature and was stirred overnight. The reaction mixture was poured onto ice (50 g) and ethyl acetate (100 mL), 2M HCl (30 mL) was added and the phases were separated. The organic phase was washed with 2M HCl (30 mL), saturated $\text{NaHCO}_{3(\text{aq})}$ (50 mL), brine (50 mL), dried over Na_2SO_4 , filtered and concentrated *in vacuo*. Flash chromatography on silica gel furnished the product.

Synthesis of starting materials 1

Synthesis of ethyl 4-iodo-3-nitrobenzoate (**1f**)²

Prepared according to **TP 1** from HNO₃ (100%, 1.9 mL), H₂SO₄ (100%, 2.7 mL) and ethyl 4-iodobenzoate (5.52 g, 20.0 mmol). Recrystallization from ethanol gave title compound **1f** as yellow solid (5.48 g, 86%).

mp.: 89-90 °C (Lit.: 89.5 °C). **¹H-NMR** (CDCl₃, 300 MHz, 25 °C): δ = 8.36 (d, ⁴J(H,H) = 2.2 Hz, 1 H), 8.06 (d, ³J(H,H) = 8.9 Hz, 1 H), 7.80 (dd, ³J(H,H) = 8.9 Hz, ⁴J(H,H) = 2.2 Hz, 1 H), 4.35 (q, ³J(H,H) = 7.1 Hz, 2 H), 1.34 (t, ³J(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (CDCl₃, 75 MHz, 25 °C): δ = 164.0, 153.2, 142.3, 133.4, 131.9, 125.9, 91.9, 62.1, 14.2. **MS** (70 eV, EI), *m/z* (%): 321 (88) [M⁺], 293 (100), 276 (99), 260 (12), 247 (26), 230 (37), 219 (4), 201 (12), 191 (11), 176 (2), 149 (1), 136 (8), 119 (5), 103 (34), 92 (13), 75 (40), 63 (5), 53 (2). **IR** (KBr): $\tilde{\nu}$ = 2982 (m), 1708 (vs), 1600 (s), 1561 (m), 1532 (vs), 1469 (s), 1385 (m), 1366 (m), 1341 (vs), 1285 (vs), 1238 (vs), 1158 (s), 1136 (m), 1116 (m), 1018 (s), 916 (w), 864 (w), 854 (m), 834 (m), 768 (m), 743 (s), 727 (m), 658 (w). **C₉H₈INO₄**: required: C: 33.67; H: 2.51; N: 4.36; found: C: 33.76; H: 2.35; N: 4.33.

Synthesis of 4-iodo-3-nitrobenzonitrile (**1g**)

Prepared according to **TP 1** from HNO₃ (100%, 0.96 mL), H₂SO₄ (100%, 1.4 mL) and 4-iodobenzonitrile (2.30 g, 10.0 mmol). Recrystallization from ethanol gave title compound **1g** as yellow solid (1.84 g, 67%).

mp.: 132-133 °C. **¹H-NMR** (CDCl₃, 300 MHz, 25 °C): δ = 8.16 (d, ³J(H,H) = 8.4 Hz, 1 H), 8.05 (d, ⁴J(H,H) = 1.8 Hz, 1 H), 7.45 (dd, ³J(H,H) = 8.4 Hz, ⁴J(H,H) = 1.8 Hz, 1 H). **¹³C-NMR** (CDCl₃, 75 MHz, 25 °C): δ = 151.0, 143.7, 135.8, 128.8, 116.4, 114.0, 93.1. **MS** (70 eV, EI), *m/z* (%): 274 (100) [M⁺], 258 (2), 228 (50), 216 (6), 127 (5), 117 (12), 101 (31), 75 (7), 50 (10). **IR** (KBr): $\tilde{\nu}$ = 3091 (w), 3066 (w), 2236 (s), 1597 (m), 1548 (s), 1530 (vs), 1464 (m), 1352 (s), 1264 (w), 1024 (w), 843 (w), 788 (w), 671 (w), 55 (w). **HRMS** for **C₇H₃IN₂O₂** (273.9239): found: 273.9245.

Synthesis of pyperidino-4-iodo-3-nitro-benzamide (1h)

Prepared according to **TP 1** from HNO₃ (100%, 1.9 mL), H₂SO₄ (100%, 2.7 mL) pyperidino-4-iodo-benzamide (4.73 g, 15.0 mmol). Recrystallization from ethanol furnished title compound **1h** as colourless solid (4.50 g, 83%).

mp.: 155.5-156.5 °C. **¹H-NMR** (400 MHz, CDCl₃, 25 °C): δ = 8.06 (d, ³*J*(H,H) = 8.0 Hz, 1 H), 7.86 (d, ⁴*J*(H,H) = 1.9 Hz, 1 H), 7.27 (dd, ³*J*(H,H) = 8.0 Hz, ⁴*J*(H,H) = 1.9 Hz, 1 H), 3.67 (s_br, 2 H), 3.31 (s_br, 2 H), 1.72-1.42 (m, 6 H). **¹³C-NMR** (100 MHz, CDCl₃, 25 °C): δ = 166.7, 152.8, 142.1, 137.7, 131.5, 123.9, 87.2, 48.8, 43.4, 26.5, 25.4, 24.3. **MS** (70 eV, EI), *m/z* (%): 359 (100) [M⁺], 34 (31), 325 (15), 313 (10), 275 (95), 229 (36), 186 (30), 158 (4), 127 (23), 103 (63), 84 (16), 75 (44). **IR** (KBr): $\tilde{\nu}$ = 2952 (m), 1608 (vs), 1598 (vs), 1527 (vs), 1443 (m), 1341 (s), 1248 (m), 1021 (m), 1010 (m), 844 (m), 742 (m). **HRMS** for C₁₂H₁₃IN₂O₃ (359.9971): found: 359.9954.

Synthesis of ethyl 2-iodo-5-nitrobenzoate (1i)

Prepared according to **TP 1** from HNO₃ (100%, 3.8 mL), H₂SO₄ (100%, 5.2 mL) ethyl 2-iodobenzoate (11.0 g, 40.0 mmol) at 75 °C. Reaction time: 12 h. Recrystallization from ethanol furnished product **1i** as pale yellow needles (10.8 g, 84%).

mp.: 100-101.3 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.52 (d, ³*J*(H,H) = 8.7 Hz, 1 H), 8.14 (d, ⁴*J*(H,H) = 2.7 Hz, 1 H), 7.90 (dd, ³*J*(H,H) = 8.7 Hz, ⁴*J*(H,H) = 2.7 Hz, 1 H), 4.39 (q, ³*J*(H,H) = 7.1 Hz, 2 H), 1.38 (t, ³*J*(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 165.0, 148.1, 143.1, 137.1, 126.6, 125.8, 102.9, 63.0, 14.6. **MS** (70 eV, EI), *m/z* (%): 321 (84) [M⁺], 293 (79), 276 (100), 260 (10), 247 (11), 230 (31), 202 (14), 176 (2), 136 (2), 120 (5), 103 (5), 92 (9), 75 (23), 63 (3). **IR** (KBr): $\tilde{\nu}$ = 1731 (vs), 1601 (s), 1565 (m), 1526 (vs), 1474 (m), 1459 (m), 1445 (m), 1384 (m), 1341 (vs), 1303 (vs), 1253 (vs), 1150 (s), 1127 (s), 1112 (m), 1091 (s), 1021 (vs), 969 (w), 919 (s), 869 (m), 837 (s), 781 (m), 734 (s). **C₉H₈INO₄**: required: C: 33.67; H: 2.51; N: 4.36; I: 39.53; found: C: 33.57; H: 2.44; N: 4.29; I: 39.52.

Synthesis of *N,N*-diethyl-2-iodo-5-nitro-benzamide (**1j**)

Prepared according to **TP 1** from HNO₃ (100%, 3.8 mL), H₂SO₄ (100%, 5.2 mL) *N,N*-diethyl-2-iodobenzamide (11.2 g, 37.0 mmol) at 75 °C. Reaction time: 12 h. Purification by flash-chromatography (pentane/diethyl ether = 1:1) yielded product **1j** as pale yellow solid (6.30 g, 49%).

mp.: 87-88 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.04-8.00 (m, 2 H), 7.87 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 2.6 Hz, 1 H), 3.92-3.70 (m, 1 H), 4.42-3.98 (m, 3 H), 1.30 (t, ³*J*(H,H) = 7.1 Hz, 3 H), 1.10 (t, ³*J*(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 169.9, 148.0, 144.4, 140.6, 124.1, 121.5, 101.3, 43.0, 39.3, 14.0, 12.4. **MS** (70 eV, EI), *m/z* (%): 347 (36) [*M*⁺], 331 (21), 319 (2), 305 (6), 276 (100), 260 (5), 248 (2), 230 (34), 218 (4), 202 (15), 175 (15), 150 (6), 131 (1), 118 (1), 104 (5), 90 (1), 75 (15), 56 (3). **IR** (KBr): $\tilde{\nu}$ = 3280 (s), 1642 (vs), 1602 (m), 1550 (s), 1522 (vs), 1450 (m), 1341 (vs), 1309 (s), 1253 (w), 1160 (w), 1150 (w), 1125 (w), 1099 (w), 1047 (w), 1019 (m), 843 (m), 827 (w), 778 (w), 735 (m). **HRMS** for C₁₁H₁₃IN₂O₃ (347.9971): found: 347.9985.

Synthesis of 2-iodo-4,6-dimethyl-nitrobenzene (**1k**) and 5-iodo-1,3-dimethyl-2-nitrobenzene (**1l**)

A 25 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with HNO₃ (65%, 15 mL), cooled to 0 °C and 3,5-dimethyl-iodobenzene (4.64 g, 20.0 mmol) was added dropwise. On completion of the addition, the cooling bath was removed and the mixture was heated to 50 °C for 4 h. The reaction mixture was poured onto ice (20 g), neutralized with saturated NaHCO_{3(aq)}-solution and extracted with diethyl ether (3 x 50 mL). The combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated *in vacuo*. Purification by flash chromatography (pentane/diethyl ether = 99:1) yielded **1k** and **1l** as a pale yellow solids (**1k**, 2.4 g, 44%) and (**1l**, 2.3 g, 41%).

Compound **1k**

mp.: 46.2-47.2 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 7.46 (s, 1 H), 6.97 (s, 1 H), 2.23 (s, 3 H), 2.21 (s, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 153.9, 142.2, 138.4,

132.2, 131.2, 85.2, 21.1, 18.3. **MS** (70 eV, EI), m/z (%): 277 (93) [M^+], 260 (100), 184 (7), 133 (63), 104 (55), 91 (17), 78 (25), 63 (10), 51 (8), 43 (10). **IR** (KBr): $\tilde{\nu}$ = 2924 (m), 1599 (s), 1580 (m), 1565 (s), 1529 (vs), 1448 (s), 1368 (vs), 1282 (m), 1225 (m), 1084 (m), 1039 (m), 844 (vs), 792 (s), 735 (m), 728 (m), 604 (m), 588 (m). **HRMS** for $C_8H_8INO_2$ (276.9600): found: 276.9588. $C_8H_8INO_2$: required: C: 34.68; H: 2.91; N: 5.06; found: C: 34.74; H: 3.04; N: 5.05.

Compound 1l

mp.: 73-73.5 °C. **1H -NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.43 (s, 2 H), 2.19 (s, 6 H). **^{13}C -NMR** (75 MHz, $CDCl_3$, 25 °C): δ = 151.9, 138.0, 131.9, 96.4, 17.5. **MS** (70 eV, EI), m/z (%): 277 (82) [M^+], 260 (100), 197 (13), 184 (16), 133 (65), 104 (64), 91 (20), 78 (34), 63 (15), 50 (16), 43 (17). **IR** (KBr): $\tilde{\nu}$ = 1594 (s), 1563 (s), 1520 (vs), 1470 (s), 1459 (s), 1438 (s), 1409 (m), 1399 (m), 1382 (s), 1365 (vs), 1280 (s), 1260 (s), 1245 (m), 1133 (s), 1084 (m), 1035 (m), 855 (vs), 712 (m), 589 (m), 582 (m). **HRMS** for $C_8H_8INO_2$ (276.9600): found: 276.9622. $C_8H_8INO_2$: required: C: 34.68; H: 2.91; N: 5.06; found: C: 34.44; H: 2.56; N: 4.91.

Synthesis of 1,4-diiodo-2 nitrobenzene (1m)

A 50 mL round-bottom flask, equipped with a magnetic stirring bar and a dropping funnel was charged with water (3.8 mL) and H_2SO_4 (100%, 3.5 mL), glacial acetic acid (3.5 mL) and 4-iodo-2 nitroaniline¹ (1.32 g, 5.00 mmol) were added at 0 °C. Afterwards, a solution of $NaNO_2$ (380 mg, 5.5 mmol, in 1.5 mL H_2O) was added dropwise over a period of 1 h. On completion of the addition the mixture was stirred for 30 min and a solution of KI (1.0 g, 6 mmol, in 1.5 mL H_2O) was added dropwise with a strong evolution of gas (N_2). On completion of addition the sticky mixture was heated to 60 °C for 1 h, cooled again to 0 °C and diethyl ether was added until all precipitate was dissolved and the reaction mixture was poured into saturated $NaHCO_{3(aq)}$ solution (30 mL) in a separatory funnel. After extraction with diethyl ether (2 x 30 ml) the organic phases were washed with brine, dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was recrystallized from ethanol to give compound **1m** as a yellow-orange powder (1.27 g, 95%).

mp.: 106.5-107.2 °C. **1H -NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 8.07 (d, $^4J(H,H)$ = 1.8 Hz, 1 H), 7.67 (d, $^3J(H,H)$ = 8.4 Hz, 1 H), 7.47 (dd, $^3J(H,H)$ = 8.4 Hz, $^4J(H,H)$ = 1.8 Hz, 1 H). **^{13}C -NMR** (750 MHz, $CDCl_3$, 25 °C): δ = 143.4, 142.7, 134.4, 100.0, 93.2, 85.9. **MS** (70 eV, EI), m/z (%): 375 (100) [M^+], 329 (31), 317 (4), 218 (7), 202 (21), 127 (3), 75 (39). **IR** (KBr): $\tilde{\nu}$ = 1567 (w), 1544 (w), 1525 (vs), 1451 (w), 1350 (s), 1252 (w), 1081 (w), 1016 (s), 888 (w), 865 (w), 817 (m), 750 (w), 724 (w). $C_6H_3I_2NO_2$: required: C: 19.22; H: 0.81; I: 67.70; N: 3.74; found: C: 19.27; H: 0.79; I: 67.66; N: 3.72.

Synthesis of 2-iodo-5-nitrobenzophenone (**1n**)

Prepared according to the procedure of Baik and Wong³ from 2-amino-5-nitrobenzophenone (726 mg, 3.00 mmol), NaNO₂ (417 mg, 6.00 mmol), HI (2.8 mL, 15 mmol, 50%_(aq)), CuI (570 mg, 3.00 mmol) and DMSO (20 mL) at 60 °C. Recrystallization from ethanol yielded compound **1n** as yellow solid (650 mg, 62%).

mp.: 141.5-143 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.14 (d, ³*J*(H,H) = 8.8 Hz, 1 H), 8.10 (d, ⁴*J*(H,H) = 2.7 Hz, 1 H), 8.00 (d, ³*J*(H,H) = 8.8 Hz, ⁴*J*(H,H) = 2.7 Hz, 1 H), 7.81-7.76 (m, 2 H), 7.69-7.63 (m, 1 H), 7.53-7.46 (m, 2 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 194.9, 147.7, 145.9, 141.1, 134.5, 134.5, 130.4, 129.0, 125.1, 122.8, 100.6. **MS** (70 eV, EI), *m/z* (%): 353 (60) [M⁺], 275 (9), 229 (5), 201 (3), 180 (3), 151 (6), 105 (100), 77 (43), 51 (9). **IR** (KBr): $\tilde{\nu}$ = 1662 (vs), 1593 (s), 1523 (vs), 1449 (m), 1350 (vs), 1315 (m), 1279 (vs), 1160 (m), 1023 (m), 967 (m), 858 (m), 850 (m), 798 (m), 761 (m), 740 (m), 728 (m), 705 (m), 688 (m), 638 (m). **HRMS** for C₁₃H₈INO₃ (352.9549): found: 352.9579. C₁₃H₈INO₃: required: C: 44.22; H: 2.28; N: 3.97; found: C: 44.70; H: 2.32; N: 4.03.

Synthesis of 4-iodo-3-nitrobenzophenone (**1o**)

Prepared according to the procedure reported of Baik and Wong³ from 4-amino-3-nitrobenzophenone (726 mg, 3.00 mmol), KNO₂ (510 mg, 6.00 mmol), HI (2.8 mL, 15 mmol, 50%_(aq)), CuI (570 mg, 3.00 mmol) and DMSO (20 mL) at 60 °C. Recrystallization from ethanol yielded compound **1o** as yellow solid (750 mg, 73%).

mp.: 116.7-117.3 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.21-8.17 (m, 2 H), 7.79-7.75 (m, 2 H), 7.68-7.62 (m, 2 H), 7.55-7.49 (m, 2 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 193.3, 153.0, 142.2, 138.6, 135.9, 133.6, 133.5, 129.9, 128.8, 126.2, 91.3. **MS** (70 eV, EI), *m/z* (%): 353 (55) [M⁺], 275 (12), 229 (5), 180 (3), 152 (4), 127 (2), 105 (100), 77 (42), 51 (8). **IR** (KBr): $\tilde{\nu}$ = 1651 (vs), 1590 (vs), 1534 (vs), 1340 (m), 1280 (vs), 1245 (s), 1021 (m), 975 (m), 795 (w), 719 (vs), 697 (m), 672 (m). **HRMS** for C₁₃H₈INO₃ (352.9549): found: 352.9521.

Synthesis of 2-iodo-4-nitrophenol (**1p**) and 2,6-diiodo-4-nitrophenol (**1e**)

Prepared according to **TP 2** from 4-nitrophenol (1.39 g, 10.0 mmol), iodine (2.79 g, 11.0 mmol) and Ag₂SO₄ (3.43 g, 11.0 mmol) in ethanol (100 mL). Purification by flash-chromatography furnished products **69** and **70** as light yellow solids; **1p** (1.33 g, 50%) and **1e** (858 mg, 22%).

Compound **1p**

mp.: 78-79 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.57 (d, ⁴*J*(H,H) = 2.7 Hz, 1 H), 8.15 (dd, ³*J*(H,H) = 8.8 Hz, ⁴*J*(H,H) = 2.7 Hz, 1 H), 7.05 (d, ⁴*J*(H,H) = 2.7 Hz, 1 H), 6.00 (s_{br}, 1 OH). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 136.4, 134.4, 126.1, 115.7, 114.6, 84.4. **MS** (70 eV, EI), *m/z* (%): 265 (100) [M⁺], 235 (61), 92 (44), 42 (37), 63 (23), 64 (21), 53 (17). **IR** (KBr): $\tilde{\nu}$ = 3550 (w), 1581 (s), 1510 (vs), 1487 (s), 1414 (w), 1342 (vs), 1290 (vs), 1212 (w), 1130 (w), 1117 (s), 747 (s), 683 (m), 638 (w), 552 (w), 521 (w), 466 (w), 435 (w). **HRMS** for C₆H₄INO₃ (264.9236): found: 264.9243. C₆H₄INO₃: required: C: 27.19; H: 1.52; N: 5.29; found: C: 27.53; H: 1.82; N: 5.22.

Compound **1e**

mp.: 155-156 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.42 (s, 2 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 160.9, 141.2, 134.5, 82.2. **MS** (70 eV, EI), *m/z* (%): 391 (100), 361 (22), 345 (3), 218 (24), 127 (11), 91 (14).

Spectral data matches that of the commercially available sample.

Synthesis of 2-iodo-4-nitrophenyl 4-methylbenzenesulfonate (**1q**)

Prepared according to **TP 7** from 2-iodo-4-nitrophenol (**1p**) (2.85 g, 10.0 mmol) and *p*-toluenesulfonic acid chloride (2.52 g, 12.0 mmol). Recrystallization from ethanol furnished title compound **1q** as light yellow solid (3.85 g, 92%).

mp.: 101-101.5 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.60 (d, ⁴*J*(H,H) = 2.7 Hz, 1 H), 8.21 (dd, ³*J*(H,H) = 9.3 Hz, ⁴*J*(H,H) = 2.7 Hz, 1 H), 7.81 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 7.51 (d, ³*J*(H,H) = 9.3 Hz, 1 H), 7.36 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 2.46 (s, 3 H). **¹³C-NMR** (100 MHz, CDCl₃, 25 °C): δ = 154.6, 146.6, 145.9, 135.3, 132.3, 130.1, 128.8, 124.8, 122.8, 90.1, 21.8.

MS (70 eV, EI), m/z (%): 418 (21) [M^+], 264 (3), 1881 (2), 155 (100), 91 (47), 63 (23). **IR** (KBr): $\tilde{\nu}$ = 3073 (m), 1595 (m), 1530 (vs), 1459 (s), 1381 (vs), 1348 (vs), 1291 (m), 1208 (m), 1178 (vs), 1188 (vs), 1129 (m), 1088 (m), 1035 (m), 920 (m), 877 (s), 844 (vs), 830 (m), 815 (s), 754 (vs), 733 (vs), 709 (m), 673 (vs), 650 (m), 571 (vs), 552 (m), 543 (m). **HRMS** for $C_{13}H_{10}INO_5S$ (418.9324): found: 418.9285. $C_{13}H_{10}INO_5S$: required: C: 37.25; H: 2.40; N: 3.34; S: 7.65; found: C: 37.25; H: 2.38; N: 3.37; S: 7.51.

Synthesis of 2,6-diiodo-4-nitrophenyl 4-methylbenzenesulfonate (**1r**)

Prepared according to **TP 7** from 2,6-diiodo-4-nitrophenol (**1e**) (3.91 g, 10.0 mmol) and *p*-toluenesulfonic acid chloride (2.15 g, 11.0 mmol). Recrystallization from ethanol furnished title compound **1r** as light yellow solid (4.76 g, 90%).

mp.: 189.5-190 °C. **1H -NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 8.57 (s, 2 H), 7.90 (d, $^3J(H,H)$ = 8.4 Hz, 2 H), 7.41 (d, $^3J(H,H)$ = 8.4 Hz, 2 H), 2.42 (s, 3 H). **^{13}C -NMR** (75 MHz, $CDCl_3$, 25 °C): δ = 156.9, 147.0, 146.1, 136.0, 135.1, 130.6, 129.5, 129.2, 90.7, 22.3. **MS** (70 eV, EI), m/z (%): 544 (10) [M^+], 390 (11), 216 (4), 188 (9), 155 (100), 91 (43), 65 (8). **IR** (KBr): $\tilde{\nu}$ = 3088 (w), 1595 (m), 1522 (vs), 1450 (w), 1405 (m), 1381 (vs), 1339 (vs), 1306 (m), 1271 (w), 1216 (s), 1189 (s), 1175 (vs), 1090 (s), 1047 (m), 892 (vs), 839 (vs), 816 (s), 751 (vs), 736 (m), 723 (vs), 707 (m), 668 (vs), 631 (s), 567 (s), 544 (vs). **HRMS** for $C_{13}H_9I_2NO_5S$ (544.8291): found: 544.8316. $C_{13}H_9I_2NO_5S$: required: C: 28.64; H: 1.66; N: 2.57; found: C: 28.55; H: 1.65; N: 2.61.

Synthesis of 3,5-diiodo-2,6-dimethyl-nitrobenzene (**1s**)

A suspension of Ag_2SO_4 (3.12 g, 10.0 mmol) in H_2SO_4 (50 mL, 90%_(aq)) was stirred at rt for 15 min, ICl (3.25 g, 20.0 mmol) was added and stirring was continued at rt for 1 h. The precipitated $AgCl$ was removed by filtration and the resulting dark brown solution was added over a period of 1 h to a solution of 1,3-dimethyl-2-nitrobenzene (1.41 g, 9.00 mmol), dissolved in H_2SO_4 (10 mL, 90%_(aq)) at 0 °C. On completion of the addition, the reaction mixture was stirred for 1 h at rt and the mixture was poured into H_2O (100 mL). Filtration and subsequent recrystallization from ethanol furnished compound **1s** as white solid (2.73 g, 68%).

mp.: 137.5-139 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.31 (s, 2 H), 2.24 (s, 6 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 148.5, 138.1, 130.4, 97.1, 21.3. **MS** (70 eV, EI), *m/z* (%): 402 (74) [M⁺], 385 (95), 357 (21), 293 (9), 258 (28), 230 (36), 132 (19), 103 (100). **IR** (KBr): $\tilde{\nu}$ = 1528 (vs), 1422 (m), 1381 (s), 1346 (m), 942 (w), 879 (m), 739 (s). **HRMS** for C₈H₇I₂NO₂ (402.8566): found: 402.8575.

Synthesis of di(*tert*-butyl) 2-iodo-4-nitrophenylimidodicarbonate (**1t**)⁴

A dry and nitrogen flushed 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with 2-iodo-4-nitroaniline (**1d**) (2.64 g, 10.0 mmol) and acetonitrile (25 mL), cooled to 0 °C and DMAP (125 mg, 1.00 mmol) was added. Subsequently, a solution of Boc₂O (5.23 g, 24.0 mmol) dissolved in acetonitrile (15 mL) was added dropwise. On completion of addition, the cooling bath was removed, the reaction mixture stirred for 24 h at 60 °C and poured into water. After extraction with ethyl acetate (3 x 30 mL), the combined organic fractions were washed with KHSO_{4(aq)} (30 mL, 1 M), brine (30 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. Purification by flash chromatography (pentane/diethyl ether = 9:1) furnished title compound **1t** as colourless oil (3.41 g, 70%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.68 (d, ⁴*J*(H,H) = 2.7 Hz, 1 H), 8.22 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 2.7 Hz, 1 H), 7.36 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 1.40 (s, 18 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 149.2, 148.0, 146.7, 134.1, 129.4, 123.9, 99.7, 84.0, 41.8, 27.9. **MS** (FAB, NBA): *m/z* (%): 487 [M+Na]⁺. **MS** (70 eV, EI), *m/z* (%): 363 (11) [M-Boc]⁺, 307 (17), 263 (6), 233 (4), 181 (4), 91 (3.6, 57 (100). **IR** (KBr): $\tilde{\nu}$ = 3435 (m), 1797 (m), 1756 (vs), 1725 (s), 1524 (vs), 1372 (m), 1346 (vs), 1315 (m), 1280 (vs), 1252 (s), 1153 (s), 1115 (vs), 860 (w), 772 (w). **HRMS** for C₁₆H₂₁I₂N₂O₆ (487.0342 [M+Na]⁺): found: 487.0351 [M+Na]⁺. C₁₆H₂₁I₂N₂O₆: required: C: 41.39; H: 4.56; N: 6.03; found: C: 41.17; H: 4.58; N: 6.01.

Synthesis of 1-[(*E*)-(2-iodo-4-nitrophenyl)diazenyl]pyrrolidine (**1u**)

A 50 mL round-bottom flask, equipped with a magnetic stirring bar and a dropping funnel was charged with water (5 mL), conc. HCl (0.6 mL) and 2-iodo-4-nitroaniline (**1d**) (2.64 g, 10.0 mmol) were added at 0 °C. Afterwards, a solution of NaNO₂ (825 mg, 12.0 mmol, in 10 mL H₂O) was added dropwise over a period of 30 min. On completion of the addition the mixture was stirred for 30 min and was poured into a solution of pyrrolidine (1.06 g, 15.0 mmol, in 9 mL H₂O) and K₂CO₃ (2.49 g, 18.0 mmol) with a strong evolution of gas. On completion of addition the sticky mixture was stirred for an additional 1 h at rt and the reaction mixture was poured into saturated NaHCO_{3(aq)} solution (30 mL) in a separatory funnel. After extraction with ethyl acetate (2x 30 mL) the organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was recrystallized from ethanol furnishing compound **1u** as an orange powder (2.69 g, 78%).

mp.: 156-157 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.69 (d, ⁴J(H,H) = 2.7 Hz, 1 H), 8.12 (dd, ³J(H,H) = 8.9 Hz, ⁴J(H,H) = 2.7 Hz, 1 H), 7.38 (d, ⁴J(H,H) = 8.9 Hz, 1 H), 4.00 (br_t, ³J(H,H) = 6.6 Hz, 2 H), 3.79 (br_t, ³J(H,H) = 6.6 Hz, 2 H), 2.14-2.05 (m, 4 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 155.4, 144.5, 134.9, 124.2, 116.2, 94.8, 51.7, 48.0, 24.0, 23.4. **MS** (70 eV, EI), *m/z* (%): 346 (24) [M⁺], 275 (64), 247 (100), 217 (11), 201 (15), 75 (37), 70 (15). **IR** (KBr): $\tilde{\nu}$ = 1505 (s), 1406 (m), 1375 (m), 1331 (vs), 1299 (vs), 1270 (vs), 1245 (m), 1112 (m), 866 (w), 854 (w), 826 (w), 748 (w). **HRMS** for C₁₀H₁₁IN₄O₂ (345.9927): found: 345.9892. C₁₀H₁₁IN₄O₂: required: C: 34.70; H: 3.20; N: 16.19; found: C: 34.59; H: 3.22; N: 16.09.

Synthesis of heterocyclic iodines 5

Synthesis of 2-iodo-3-nitropyridine (**5a**)

Prepared according to the procedure reported of Baik and Wong³ from 2-amino-3-nitropyridine (696 mg, 5.00 mmol), KNO₂ (850 mg, 10.0 mmol), HI (3.8 mL, 25 mmol, 50%_(aq)), CuI (475 mg, 2.50 mmol) and DMSO (45 mL) at 60 °C. Purification by flash chromatography (pentane/diethyl ether = 2:1) yielded compound **5a** as yellow solid (784 mg, 63%).

mp.: 130.2-131.8 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.55 (dd, ³J(H,H) = 4.9 Hz, ⁴J(H,H) = 1.8 Hz, 1 H), 8.05 (dd, ³J(H,H) = 8.0 Hz, ⁴J(H,H) = 1.8 Hz, 1 H), 7.50 (dd, ³J(H,H) = 8.0 Hz, ³J(H,H) = 4.9 Hz, 1 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 153.4, 151.0, 132.8, 123.4, 110.4. **MS** (70 eV, EI), *m/z* (%): 249 (100) [M⁺], 203 (34), 126 (8), 77 (22), 53 (22). **IR** (KBr): $\tilde{\nu}$ = 3037 (m), 1574 (vs), 1555 (vs), 1526 (vs), 1447 (w), 1401 (vs), 1347 (vs), 1245 (m), 1221 (m), 1053 (m), 1039 (s), 854 (s), 827 (s), 740 (s), 720 (s), 633 (m), 565 (w). **HRMS** for C₁₂H₁₀N₂O₂ (249.9239): found: 249.9208. C₅H₃IN₂O₂: required: C: 24.02; H: 1.21; N: 11.21; found: C: 24.13; H: 1.08; N: 11.18.

Synthesis of 5-iodo-6-nitroquinoline (5b)

Prepared according to the procedure reported of Baik and Wong³ from 5-amino-6-nitroquinoline (946 mg, 5.00 mmol), KNO₂ (935 mg, 11.0 mmol), HI (3.9 mL, 27 mmol, 50%_(aq)) CuI (950 mg, 5.00 mmol) and DMSO (45 mL) at 60 °C. Purification by flash chromatography (pentane/diethyl ether = 2:1) yielded compound **5b** as green-yellow solid (1.26 g, 84%).

mp.: 159.7-161.9 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 9.01 (s_{br}, 1 H), 8.66 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 8.21 (d, ³*J*(H,H) = 9.3 Hz, 1 H), 8.91 (d, ³*J*(H,H) = 8.9 Hz, 1 H), 7.50 (dd, ³*J*(H,H) = 8.9 Hz, ³*J*(H,H) = 4.5 Hz, 1 H). **¹³C-NMR** (150 MHz, CDCl₃, 25 °C): δ = 153.3, 153.2, 148.5, 142.9, 131.9, 129.8, 124.5, 124.2, 92.8. **MS** (70 eV, EI), *m/z* (%): 300 (100) [M]⁺, 254 (31), 242 (15), 145 (18), 127 (44), 115 (14), 101 (11), 74 (7). **IR** (KBr): $\tilde{\nu}$ = 1597 (w), 1561 (vs), 1524 (vs), 1488 (s), 1335 (s), 1325 (s), 1307 (m), 1299 (m), 963 (m), 838 (m), 806 (s), 772 (m), 731 (w). **HRMS** for C₉H₅IN₂O₂ (299.9396): found: 299.9409.

Synthesis of compounds 9

Synthesis of (2-nitrophenyl)(phenyl)methanol (9a)

Prepared according to **TP 3** from 2-iodonitrobenzene (**1a**) (498 mg, 2.00 mmol) PhMgCl (1.1 mL, 2.2 mmol, 2.0 M in THF) and benzaldehyde (255 mg, 2.40 mmol). Reaction time: 0.5 h. Purification by flash chromatography (pentane/diethyl ether = 4:1) yielded the benzylic alcohol **9a** as a red oil (400 mg, 87%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.84 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 1.4 Hz, 1 H), 7.65 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 1.4 Hz, 1 H), 7.54 (dt, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 1.3 Hz, 1 H), 7.36 (dt, ³*J*(H,H) = 8.6 Hz, ⁴*J*(H,H) = 1.3 Hz, 1 H), 7.25-7.17 (m, 5 H), 6.34 (s_{br}, 1 H), 2.83 (s_{br}, 1 OH). **¹³C-NMR** (75 MHz, CDCl₃, 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 C₁₃H₁₁NO₃ (229.0739): found: 229.0518.

Synthesis of (2,4-dinitrophenyl)(phenyl)methanol (**9b**)

Prepared according to **TP 3** from 2,4-dinitro-iodobenzene (**1b**) (588 mg, 2.00 mmol), PhMgCl (1.1 mL, 2.1 mmol, 2.0 M in THF) and benzaldehyde (424 mg, 4.00 mmol). Reaction time: 0.5 h. Purification by flash chromatography (CH₂Cl₂) yielded compound **9b** (442 mg, 81%) as an orange oil.

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.66 (d, ⁴*J*(H,H) = 2.1 Hz, 1 H), 8.39 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 2.1 Hz, 1 H), 8.07 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 7.30-7.18 (m, 5 H), 6.47 (s, 1 H), 2.46 (s_br, 1 OH). **¹³C-NMR** (75 MHz, CDCl₃, 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-H₂O]⁺, 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 (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 C₁₃H₁₀N₂O₅ (274.0590): found: 272.0432 [M-2H]⁺. C₁₃H₁₀N₂O₅: required: C: 56.94, H: 3.68, N: 10.22; found: C: 57.13, H: 3.71, N: 10.01.

Synthesis of cyclohexyl(2,4-dinitrophenyl)methanol (**9c**)

Prepared according to **TP 3** from 2,4-dinitro-iodobenzene (**1b**) (588 mg, 2.00 mmol), PhMgCl (1.1 mL, 2.1 mmol, 2 M in THF) and cyclohexanecarbaldehyde (560 mg, 5.00 mmol). Reaction time: 0.5 h. Purification by flash chromatography (CH₂Cl₂/pentane = 4:1) yielded product **9c** (416 mg, 74%) as an orange oil

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.67 (d, ⁴*J*(H,H) = 2.1 Hz, 1 H), 8.37 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 2.1 Hz, 1 H), 7.61 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 5.19 (d, ³*J*(H,H) = 5 Hz, 1 H), 2.18 (s_br, 1 OH), 1.69-1.57 (m, 5 H), 1.44-1.41 (m, 1 H), 1.18-1.03 (m, 5 H). **¹³C-NMR** (75 MHz, CDCl₃, 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-H₂O]⁺, 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 C₁₃H₁₆N₂O₅ (280.1059): found: 263.0999[M-OH]⁺. C₁₃H₁₆N₂O₅: required: C: 55.71, H: 5.75, N: 9.99; found: C: 55.60, H: 5.78, N: 9.62.

Synthesis of (4-methoxy-2-nitrophenyl)(phenyl)methanol (**9d**)

Prepared according to **TP 3** from 1-iodo-4-methoxy-2-nitrobenzene (**1c**) (418 mg, 1.50 mmol), PhMgCl (1.0 mL, 1.7 mmol, 1.7 M in THF) and benzaldehyde (190 mg, 1.80 mmol). Reaction time: 0.5 h. Purification by flash chromatography (CH₂Cl₂) yielded (4-methoxy-2-nitrophenyl)(phenyl)methanol (**9d**) (279 mg, 72%) as a yellow oil.

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.48 (d, ³*J*(H,H) = 8.5 Hz, 1 H), 7.35(d, ⁴*J*(H,H) = 1.9 Hz, 1 H), 7.26-7.18 (m, 5 H), 7.05 (dd, ³*J*(H,H) = 8.5 Hz, ⁴*J*(H,H) = 1.9 Hz, 1 H), 6.25 (s, 1 H), 3.78 (s, 3 H), 2.61 (s_br, 1 OH). **¹³C-NMR** (75 MHz, CDCl₃, 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-H₂O]⁺, 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). **C₁₄H₁₃NO₄**: required: C: 64.86, H: 5.40, N: 5.40; found: C: 65.22, H: 5.13, N: 5.23.

Synthesis of 1-(4-methoxy-2-nitrophenyl)-1-hexanol (**9e**)

Prepared according to **TP 3** from 3-iodo-4-nitroanisole (**1c**) (418 mg, 1.50 mmol), PhMgCl (0.85 mL, 1.6 mmol, 1.9 M in THF) and hexanal (201 mg, 2.00 mmol). Reaction time: 2 h. Purification by flash chromatography (pentane/diethyl ether = 7:1) yielded product **9e** (270 mg, 71%) as a colourless oil.

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.60 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 7.29 (d, ⁴*J*(H,H) = 1.9 Hz, 1 H), 7.06 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 1.9 Hz, 1 H), 5.07-5.03 (m, 1 H), 3.78 (s, 3 H), 2.37 (s_br, 1 OH), 1.68-1.21 (m, 8 H), 0.83-0.78 (m, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 159.2, 148.9, 132.6, 129.5, 120.4, 109.1, 69.4, 56.2, 38.4, 31.9, 26.2, 22.9, 14.4. **MS** (70 eV, EI), *m/z* (%): 253 (0.1) [M⁺], 235 (32), 213 (14), 197 (39), 183 (100), 170 (28), 153 (81), 140 (14), 135 (13), 126 (22), 115 (25), 77 (5), 63 (3) (43 (26)). **IR** (KBr): $\tilde{\nu}$ = 3401 (m), 2956 (s), 1621 (m), 1530 (vs), 1498 (m), 1463 (m), 1351 (s), 1297 (m), 1242 (s), 1184 (m), 1119 (w), 1066 (m), 1037 (s), 929 (w), 854 (w), 832 (w), 761 (w). **HRMS** for **C₁₃H₁₉NO₄** (253.1314): found: 254.1136 [M+H]⁺.

Synthesis of ethyl 4-[hydroxy(phenyl)methyl]-3-nitro-benzoate (**9f**)

Prepared according to **TP 3** from ethyl 4-iodo-3-nitrobenzoate (**1f**) (642 mg, 2.00 mmol), PhMgCl (1.1 mL, 2.2 mmol, 2.0 M in THF) and benzaldehyde (254 mg, 2.40 mmol). Reaction time: 0.5 h. Purification by flash chromatography (pentane/CH₂Cl₂ = 4:1) yielded title compound **9f** (564 mg, 94%) as a pale yellow oil.

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.45 (d, ⁴*J*(H,H) = 1.8 Hz, 1 H), 8.19 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.84 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 7.25-7.18 (m, 5 H), 6.40 (d, ³*J*(H,H) = 3.5 Hz, 1 H), 4.34 (q, ³*J*(H,H) = 7.1 Hz, 2 H), 2.85 (d, ³*J*(H,H) = 3.5 Hz, 1 OH), 1.33 (t, ³*J*(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 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) [M-H₂O]⁺, 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 (s), 2984 (m), 1728 (vs), 1620 (s), 1538 (vs), 1493 (s), 1454 (s), 1355 (s), 1288 (s), 1152 (s), 1021 (s), 919 (m), 838 (m), 764 (vs), 749 (vs), 701 (vs), 665 (w), 557 (w). **HRMS** for C₁₆H₁₅NO₅ (301.0950): found: 302.1031 [M+H]⁺.

Synthesis of ethyl 4-(1-hydroxyhexyl)-3-nitrobenzoate (**9g**)

Prepared according to **TP 3** from ethyl 4-iodo-3-nitrobenzoate (**1f**) (483 mg, 1.50 mmol), PhMgCl (0.85 mL, 1.6 mmol, 1.9 M in THF) and hexanal (201 mg, 2.00 mmol). Reaction time: 2 h. Purification by flash chromatography (pentane/diethyl ether = 5:1) yielded title compound **9g** (383 mg, 87%) as a colourless oil.

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.43 (d, ⁴*J*(H,H) = 1.8 Hz, 1 H), 8.18 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.82 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 5.21-5.17 (m, 1 H), 4.36 (q, ³*J*(H,H) = 7.1 Hz, 2 H), 2.41 (s_br, 1 OH), 1.85-1.29 (m, 8 H), 0.92-0.85 (m, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 164.5, 147.6, 144.9, 133.8, 130.5, 128.4, 125.4, 69.3, 61.8, 38.3, 32.7, 25.6, 22.9, 14.2, 14.0. **MS** (70 eV, EI), *m/z* (%): 295 (4) [M⁺], 278 (9), 250 (12), 224 (100), 207 (26), 176 (58), 162 (14), 149 (17), 121 (11), 105 (14), 77 (7), 65 (13), 43 (31). **IR** (KBr): $\tilde{\nu}$ = 3440 (m), 2957 (s), 1727 (vs), 1620 (m), 1534 (vs), 1466 (m), 1354 (s), 1286 (vs), 1113 (s), 1020 (m), 920 (w), 862 (w), 772 (m), 759 (m), 717 (w). **HRMS** for C₁₅H₂₁NO₅ (295.1420): found: 296.1490 [M+H]⁺.

Synthesis of [hydroxy(phenyl)methyl]-4-nitrobenzonitrile (**9h**)

Prepared according to **TP 3** from 4-iodo-3-nitrobenzonitrile (**1g**) (274 mg, 1.00 mmol), PhMgCl (0.55 mL, 1.1 mmol, 2.0 M in THF) and benzaldehyde (128 mg, 1.20 mmol). Reaction time: 0.5 h. Purification by flash chromatography (CH₂Cl₂) yielded compound **9h** (240 mg, 94%) as a yellow oil.

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.10 (d, ⁴J(H,H) = 1.8 Hz, 1 H), 7.87 (d, ³J(H,H) = 8.4 Hz, 1 H), 7.66 (dd, ³J(H,H) = 8.4 Hz, ⁴J(H,H) = 1.8 Hz, 1 H), 7.31-7.18 (m, 5 H), 6.36 (d, ³J(H,H) = 3.6 Hz, 1 H), 2.7 (d, ³J(H,H) = 3.6 Hz, 1 OH). **¹³C-NMR** (75 MHz, CDCl₃, 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) [M-H₂O]⁺, 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 C₁₄H₁₀N₂O₃ (254.0691): found: 252.0546 [M-2H]⁺.

Synthesis of 1-(4-cyano-2-nitrophenyl)-1-hexanol (**9i**)

Prepared according to **TP 3** from 3-iodo-4-nitrobenzonitrile (**1g**) (411 mg, 1.50 mmol), PhMgCl (0.85 mL, 1.6 mmol, 1.9 M in THF) and hexanal (225 mg, 2.30 mmol). Reaction time: 2 h. Purification by flash chromatography (pentane/diethyl ether = 4:1) yielded title compound **9i** (234 mg, 63%) as a pale yellow oil.

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.17 (d, ⁴J(H,H) = 1.8 Hz, 1 H), 8.00 (d, ³J(H,H) = 8.4 Hz, 1 H), 7.87 (dd, ³J(H,H) = 8.4 Hz, ⁴J(H,H) = 1.8 Hz, 1 H), 5.33-5.29 (m, 1 H), 2.47 (s_{br}, 1H), 1.81-1.25 (m, 8 H), 1.33-1.26 (m, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 149.3, 147.7, 137.9, 131.4, 129.8, 118.3, 113.9, 70.9, 40.3, 33.1, 27.4, 24.3, 15.7. **MS** (70 eV, EI), *m/z* (%) 249 (1) [M+H]⁺, 177 (100), 160 (51), 145 (9), 129 (27), 117 (11), 104 (11), 77 (3). **IR** (KBr): $\tilde{\nu}$ = 3438 (m), 2956 (m), 2930 (m), 2238 (s), 1617 (w), 1537 (vs), 1466 (m), 1356 (s), 1055 (m), 849 (m), 818 (w). **HRMS** for C₁₃H₁₆N₂O₃ (248.1161): found: 249.1262 [M+H]⁺.

Synthesis of [2-nitro-4-(1-piperidinylcarbonyl)phenyl](phenyl)methanol (**9j**)

Prepared according to **TP 3** from 1-(4-iodo-3-nitrobenzoyl)piperidine (**1h**) (360 mg, 1.00 mmol), PhMgCl (0.63 mL, 1.1 mmol, 1.8 M in THF) and benzaldehyde (212 mg, 2.00 mmol). Reaction time: 1 h. Purification by flash chromatography (pentane/diethyl ether = 2:1) yielded title compound **9j** as a colourless oil (285 mg, 84%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.89 (d, ⁴J(H,H) = 1.8 Hz, 1 H), 7.81 (d, ³J(H,H) = 8.4 Hz, 1 H), 7.58 (dd, ³J(H,H) = 8.4 Hz, ⁴J(H,H) = 1.8 Hz, 1 H), 7.26-7.18 (m, 5 H), 6.41 (d, ²J(H,H) = 3.8 Hz, 1 H), 3.68 (s_{br}, 2 H), 3.50 (d, ²J(H,H) = 3.8 Hz, 1 OH), 3.31 (s_{br}, 2 H), 1.70-1.45 (m, 6 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 167.5, 147.9, 141.4, 140.0, 136.5, 131.5, 129.6, 128.6, 128.1, 127.0, 123.2, 70.9, 48.9, 43.4, 26.5, 25.5, 24.4. **MS** (70 eV, EI), *m/z* (%): 337 (100) [M-2H]⁺, 321 (23), 311 (9), 290 (24), 254 (54), 224 (10), 207 (9), 197 (13), 180 (43), 152 (40), 105 (23), 77 (17). **IR** (KBr): $\tilde{\nu}$ = 3392 (m), 2939 (w), 1616 (vs), 1532 (vs), 1495 (m), 1445 (m), 1353 (m), 1287 (m), 1180 (w), 1117 (s), 1041 (w), 1026 (m), 1010 (w), 906 (w), 854 (w), 752 (m), 700 (m). **HRMS** for C₁₉H₂₀N₂O₄ (340.1423): found: 338.1263 [M-2H]⁺. C₁₉H₂₀N₂O₄: required: C: 67.05; H: 5.92; N: 8.23; found: C: 66.73; H: 5.89; N: 8.18.

Synthesis of (3,5-dimethyl-2-nitrophenyl)(phenyl)methanol (**9k**)

Prepared according to **TP 3** from 2-iodo-4,6-dimethyl-nitrobenzene (**1k**) (277 mg, 1.00 mmol), PhMgCl (0.63 mL, 1.1 mmol, 1.75 M in THF) and benzaldehyde (212 mg, 2.00 mmol). Reaction time: 2 h. Purification by flash chromatography (pentane/diethyl ether = 29:1) yielded benzylic alcohol **9k** as a colourless oil (189 mg, 74%).

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ = 7.34-7.28 (m, 5 H), 7.14 (s_{br}, 1 H), 7.02 (s_{br}, 1 H), 5.92 (s, 1 H), 2.31 (s, 3 H), 2.28 (s, 3 H). **¹³C-NMR** (100 MHz, CDCl₃, 25 °C): δ = 147.8, 141.5, 141.0, 135.5, 131.4, 129.9, 128.5, 127.9, 126.7, 126.5, 71.4, 21.3, 17.6. **MS** (70 eV, EI), *m/z* (%): 257 (not detectable), 239 (12) [M-H₂O]⁺, 222 (23), 194 (100), 180 (79), 165 (36), 105 (20), 77 (37). **IR** (KBr): $\tilde{\nu}$ = 3411 (w), 1599 (w), 1524 (vs), 1495 (m), 1451

(w), 1365 (s), 1175 (w), 1051 (m), 842 (m), 759 (w), 701 (s). **C₁₅H₁₅NO₃**: required: C: 70.02; H: 5.88; N: 5.44; found: C: 70.33; H: 5.76; N: 5.24.

Synthesis of (4-iodo-2-nitrophenyl)(phenyl)methanol (**9l**)

Prepared according to **TP 3** from 2,5-diiodo-nitrobenzene (**1m**) (563 mg, 1.50 mmol), PhMgCl (0.80 mL, 1.6 mmol, 2.0 M in THF) and benzaldehyde (190 mg, 1.80 mmol). Reaction time: 0.5 h. Purification by flash chromatography (pentane/diethyl ether = 4:1) yielded title compound **9l** (458 mg, 86%) as a yellow oil.

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.15 (d, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.86 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.42 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 7.28-7.18 (m, 5 H), 6.30 (s, 1 H), 2.45 (s_br, 1 H). **¹³C-NMR** (75 MHz, CDCl₃, 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 (br), 1530 (vs), 1469 (s), 1347 (vs), 1275 (m), 1179 (m), 1034 (s), 871 (m), 808 (m), 763 (s), 700 (s). **HRMS** for **C₁₃H₁₀INO₃** (354.9705): found: 352.9544 [M-2H]⁺.

Synthesis of 1-(4-iodo-2-nitrophenyl)-1-hexanol (**9m**)

Prepared according to **TP 3** from 2,5-diiodonitrobenzol (**1m**) (562 mg, 1.50 mmol), PhMgCl (0.80 mL, 1.6 mmol, 2.0 M in THF) and hexanealdehyde (201 mg, 2.00 mmol). Reaction time: 2 h. Purification by flash chromatography (pentane/diethyl ether = 9:1) yielded title compound **9m** (480 mg, 86%) as a pale yellow oil.

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.21 (d, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.96 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.55 (d, ³*J*(H,H) = 8.4 Hz 1 H), 5.22-5.18 (m, 1 H), 2.47 (s_br, 1 OH), 1.83-1.27 (m, 8 H), 0.92-0.88 (m, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 148.1, 142.3, 140.0, 132.7, 129.8, 91.4, 69.1, 38.1, 31.4, 25.7, 22.5, 14.0. **MS** (70 eV, EI, *m/z* (%): 349 (not detectable), 332 (2) [M-OH]⁺, 278 (100), 261 (16), 229 (24), 203 (4), 76 (3). **IR** (KBr): $\tilde{\nu}$ = 3418 (w), 2928 (m), 1529 (vs), 1466 (m), 1347 (vs), 1054 (m), 869 (w), 832 (w), 761 (w). **HRMS** for **C₁₂H₁₆INO₃** (332.0148 [M-OH]⁺): found: 332.0169 [M-OH]⁺. **C₁₂H₁₆INO₃**: required: C: 41.28; H: 4.62; I: 36.35; N: 4.01; found: C: 41.69, H: 4.32; I: 36.76; N: 4.00.

Synthesis of {3-[hydroxy(phenyl)methyl]-4-nitrophenyl}(phenyl)methanone (**9n**)

Prepared according to **TP 3** from 4-iodo-3-nitrobenzophenone (**1o**) (353 mg, 1.00 mmol), PhMgCl (0.63 mL, 1.1 mmol, 1.75 M in THF) and benzaldehyde (212 mg, 2.00 mmol). Reaction time: 1 h. Purification by flash chromatography (pentane/diethyl ether = 4:1) yielded ketone **9n** as a yellow oil (309 mg, 93%).

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ = 8.29 (d, $^4J(\text{H,H})$ = 1.7 Hz, 1 H), 8.04 (dd, $^3J(\text{H,H})$ = 8.2 Hz, $^4J(\text{H,H})$ = 1.7 Hz, 1 H), 7.96 (d, $^3J(\text{H,H})$ = 8.2 Hz, 1 H), 7.79-7.76 (m, 2 H), 7.63 (dt, $^3J(\text{H,H})$ = 7.5 Hz, $^4J(\text{H,H})$ = 1.4 Hz, 1 H), 7.54-7.48 (m, 2 H), 7.35-7.31 (m, 5 H), 6.51 (s, 1 H). **¹³C-NMR** (100 MHz, CDCl₃, 25 °C): δ = 193.8, 148.0, 142.2, 141.0, 137.8, 136.3, 133.9, 133.3, 129.9, 129.4, 128.8, 128.7, 128.4, 127.1, 125.9, 70.4. **MS** (70 eV, EI), m/z (%): 331(0.5) [M-2H]⁺, 315 (15), 300 (38), 270 (6), 238 (24), 224 (9), 194 (56), 166 (11), 152 (11), 105 (100), 77 (45). **IR** (KBr): $\tilde{\nu}$ = 3437 (m), 3063 (w), 1661 (vs), 1615 (s), 1598 (s), 1577 (m), 1532 (vs), 1493 (m), 1448 (s), 1350 (vs), 1319 (vs), 1281 (vs), 1180 (s), 1074 (m), 1037 (m), 1024 (m), 978 (m), 878 (w), 758 (m), 718 (s), 699 (s), 676 (s). **HRMS** for C₂₀H₁₅NO₄ (333.1001): found: 331.0826 [M-2H]⁺.

Synthesis of compounds 12

Synthesis of (3-nitro-2-pyridinyl)(phenyl)methanol (**12a**)

Prepared according to **TP 3** from 2-iodo-3-nitropyridine (**5a**) (125 mg, 0.50 mmol), PhMgCl (0.35 mL, 0.55 mmol, 1.5 M in THF) and benzaldehyde (106 mg, 1.00 mmol) at -78 °C. Reaction time: 2 h. Purification by flash chromatography (pentane/diethyl ether = 1:1) yielded benzylic alcohol **12a** as a pale yellow oil (64 mg, 55%).

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ = 8.90 (dd, $^3J(\text{H,H})$ = 4.9 Hz, $^4J(\text{H,H})$ = 1.7 Hz, 1 H), 8.36 (dd, $^3J(\text{H,H})$ = 8.4 Hz, $^4J(\text{H,H})$ = 1.7 Hz, 1 H), 7.50 (dd, $^3J(\text{H,H})$ = 8.1 Hz, $^3J(\text{H,H})$ = 4.9 Hz, 1 H), 7.31-7.21 (m, 5 H), 6.50 (d, $^3J(\text{H,H})$ = 6.6 Hz, 1 H), 5.38 (d, $^3J(\text{H,H})$ = 6.6 Hz, 1 H). **¹³C-NMR** (100 MHz, CDCl₃, 25 °C): δ = 156.3, 152.3, 144.2, 141.7, 134.0, 129.0, 128.5, 128.0, 123.8, 72.5. **MS** (70 eV, EI), m/z (%): 230 (5) [M⁺], 213 (15), 196 (43), 182 (60), 168 (91), 155 (87), 137 (44), 127 (29), 105 (66), 94 (9), 77 (100), 63 (7). **IR** (KBr): $\tilde{\nu}$ = 3396 (w), 1597 (m), 1567 (m), 1529 (vs), 1453 (m), 1349 (vs), 1188 (m), 1041

(m), 835 (m), 767 (m), 745 (s), 700 (s), 606 (s). **HRMS** for $C_{12}H_{10}N_2O_3$ (230.0691): found: 230.0693.

Synthesis of (6-nitro-5-quinolinyl)(phenyl)methanol (**12b**)

Prepared according to **TP 3** from 5-iodo-6-nitroquinoline (**5b**) (300 mg, 1.00 mmol), PhMgCl (0.63 mL, 1.1 mmol, 1.75 M in THF) and benzaldehyde (212 mg, 2.00 mmol). Reaction time: 1 h. Purification by flash chromatography (pentane/diethyl ether = 1:1) yielded quinoline derivative **12b** as a pale yellow solid (218 mg, 78%).

mp.: 138.2-139.5 °C. **¹H-NMR** (600 MHz, CDCl₃, 25 °C): δ = 8.79 (dd, $^3J_{(H,H)} = 4.9$ Hz, $^4J_{(H,H)} = 1.7$ Hz, 1 H), 8.64 (d, $^3J_{(H,H)} = 8.1$ Hz, 1 H), 8.04 (d, $^3J_{(H,H)} = 9.0$ Hz, 1 H), 7.84 (d, $^3J_{(H,H)} = 9.0$ Hz, 1 H), 7.29 (d, $^3J_{(H,H)} = 7.3$ Hz, 2 H), 7.17-7.14 (m, 2 H), 7.08 (t, $^3J_{(H,H)} = 7.3$ Hz, 1 H), 6.42 (s, 1 H), 6.11 (s_{br}, 1 OH), 5.38 (d, $^3J_{(H,H)} = 6.6$ Hz, 1 H). **¹³C-NMR** (150 MHz, CDCl₃, 25 °C): δ = 151.7, 149.0, 147.6, 142.5, 137.3, 135.1, 130.8, 127.9, 126.7, 126.3, 125.5, 122.5, 121.3, 68.8. **MS** (70 eV, EI), m/z (%): 278 (0.2) [M-2H]⁺, 246 (23), 232 (12), 218 (100), 206 (17), 176 (8), 151 (4), 128 (4), 105 (15), 77 (23). **IR** (KBr): $\tilde{\nu}$ = 3272 (m), 1597 (w), 1530 (vs), 1499 (s), 1450 (m), 1359 (s), 1260 (w), 1045 (m), 1026 (w), 908 (w), 836 (s), 808 (s), 778 (m), 759 (m), 736 (m), 709 (s), 581(w). **HRMS** for $C_{16}H_{12}N_2O_3$ (280.0848): found: 278.0686 [M-2H]⁺.

Synthesis of compounds 14

Synthesis of 1-allyl-2-nitrobenzene (**14a**)

Prepared according to **TP 3** from 2-iodo-nitrobenzene (**1a**) (498 mg, 2.00 mmol), PhMgCl (1.3 mL, 2.2 mmol, 1.7 M in THF), CuCN·2LiCl (2.2 mL, 2.2 mmol, 1.0 M in THF) and allyl bromide (290 mg, 2.40 mmol). Reaction time: 45 min. Purification by flash chromatography (pentane/CH₂Cl₂ = 4:1) furnished title compound **14a** (244 mg, 75%) as a red liquid.

¹H-NMR (CDCl₃, 300 MHz): δ = 7.81 (dd, $^3J_{H-H} = 8.0$ Hz, $^4J_{H-H} = 1.3$ Hz, 1 H), 7.45 (dt, $^3J_{H-H} = 8.0$ Hz, $^4J_{H-H} = 1.3$ 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, $^3J_{H-H} = 8.0$ Hz, 2 H). **¹³C-NMR** (CDCl₃, 75 MHz): 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 (M⁺, 22), 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 $\text{C}_9\text{H}_9\text{NO}_2$ (163.0633): found: 163.0642.

Synthesis of ethyl 2-(4-methoxy-2-nitrobenzyl)acrylate (**14b**)

Prepared according to **TP 3** from 1-iodo-4-methoxy-2-nitrobenzene (**1c**) (558 mg, 2.00 mmol), PhMgCl (1.3 mL, 2.2 mmol, 1.7 M in THF), $\text{CuCN}\cdot 2\text{LiCl}$ (2.2 mL, 2.2 mmol, 1.0 M in THF) and ethyl (2-bromomethyl)acrylate (463 mg, 2.40 mmol). Reaction time: 45 min. Purification by flash chromatography (pentane/diethyl ether = 9:1) furnished title compound **14b** (381 mg, 72%) as an orange liquid.

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25 °C): δ = 7.38 (d, $^4J(\text{H,H})$ = 1.8 Hz, 1 H), 7.17 (d, $^3J(\text{H,H})$ = 8.5 Hz, 1 H), 7.01 (dd, $^3J(\text{H,H})$ = 8.5 Hz, $^4J(\text{H,H})$ = 1.8 Hz, 1 H), 6.17-6.14 (m, 1 H), 5.29-5.27 (m, 1 H), 4.12 (q, $^3J(\text{H,H})$ = 7.1 Hz, 2 H), 3.82 (s, 2 H), 3.77 (s, 3 H), 1.18 (t, $^3J(\text{H,H})$ = 7.1 Hz, 3 H). **$^{13}\text{C-NMR}$** (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 $\text{C}_{13}\text{H}_{15}\text{NO}_5$ (265.0950): found: 264.0888 [M-H] $^+$.

Synthesis of ethyl 4-[2-(ethoxycarbonyl)-2-propenyl]-3-nitro-benzoate (**14c**)

Prepared according to **TP 3** from ethyl 4-iodo-3-nitrobenzoate (**1f**) (642 mg, 2.00 mmol), PhMgCl (1.1 mL, 2.2 mmol, 2.0 M in THF), $\text{CuCN}\cdot 2\text{LiCl}$ (2.2 mL, 2.2 mmol, 1.0 M in THF) and ethyl (2-bromomethyl)acrylate (463 mg, 2.4 mmol). Reaction time: 1 h. Purification by flash chromatography (pentane/diethyl ether = 85:15) yielded the title compound **14c** (461 mg, 75%) as a yellow oil.

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25 °C): δ = 8.47 (d, $^4J(\text{H,H})$ = 1.8 Hz, 1 H), 8.10 (dd, $^3J(\text{H,H})$ = 8.4 Hz, $^4J(\text{H,H})$ = 1.8 Hz, 1 H), 7.39 (d, $^3J(\text{H,H})$ = 8.4 Hz, 1 H), 6.24 (d, $^2J(\text{H,H})$ = 0.9 Hz, 1 H), 5.40 (d, $^2J(\text{H,H})$ = 0.9 Hz, 1 H), 4.34 (q, $^3J(\text{H,H})$ = 7.1 Hz, 2 H), 4.09 (q, $^3J(\text{H,H})$ = 7.1 Hz, 2 H), 3.95 (s, 2 H), 1.34 (t, $^3J(\text{H,H})$ = 7.1 Hz, 3 H), 1.17 (t, $^3J(\text{H,H})$ = 7.1 Hz, 3 H). **$^{13}\text{C-NMR}$** (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): found: 306.0957 $[M-H]^+$.

Synthesis of ethyl 4-benzoyl-3-nitrobenzoate (**14d**)

Prepared according to **TP 3** from ethyl 4-iodo-3-nitrobenzoate (**1f**) (642 mg, 2.00 mmol), $PhMgCl$ (1.2 mL, 2.2 mmol, 1.9 M in THF), $CuCN \cdot 2LiCl$ (2.2 mL, 2.2 mmol, 1.0 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 title compound **14d** (454 mg, 76%) as a yellow solid.

mp.: 93-94 °C. **1H -NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 8.79 (d, $^4J(H,H)$ = 1.8 Hz, 1 H), 8.35 (dd, $^3J(H,H)$ = 8.4 Hz, $^4J(H,H)$ = 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, $^3J(H,H)$ = 7.1 Hz, 2 H), 1.38 (t, $^3J(H,H)$ = 7.1 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 $C_{16}H_{13}NO_5$ (299.0794): found: 299.0802.

Synthesis of ethyl 3-nitro-4-propionyl-benzoate (**14e**)

Prepared according to **TP 3** from ethyl 4-iodo-3-nitrobenzoate (**1f**) (482 mg, 1.50 mmol), $PhMgCl$ (0.97 mL, 1.6 mmol, 1.7 M in THF), $CuCN \cdot 2LiCl$ (1.6 mL, 1.6 mmol, 1.0 M in THF) and propionyl chloride (223 mg, 2.25 mmol). Reaction time: 4 h. Purification by flash chromatography (pentane/ethyl acetate = 9:1) furnished title compound **14e** (231 mg, 61%) as a yellow oil.

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.68 (d, ⁴J(H,H) = 1.8 Hz, 1 H), 8.29 (dd, ³J(H,H) = 8.4 Hz, ⁴J(H,H) = 1.8 Hz, 1 H), 7.38 (d, ³J(H,H) = 8.4 Hz, 1 H), 4.38 (q, ³J(H,H) = 7.1 Hz, 2 H), 2.74 (q, ³J(H,H) = 7.1 Hz, 2 H), 1.37 (t, ³J(H,H) = 7.1, 3 H), 1.20 (t, ³J(H,H) = 7.1, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 201.5, 162.8, 144.7, 140.6, 134.0, 131.9, 126.6, 124.5, 61.2, 35.4, 13.2, 7.0. **MS** (70 eV, EI), *m/z* (%): 251 (1) [M⁺], 222 (100), 206 (9), 193 (5), 176 (2), 165 (8), 148 (1), 136 (1), 120 (2), 103 (5). **IR** (KBr): $\tilde{\nu}$ = 3094 (w), 2984 (s), 2942 (m), 2907 (w), 2880 (w), 1726 (vs), 1622 (m), 1566 (m), 1538 (vs), 1491 (s), 1461 (m), 1403 (m), 1351 (vs), 1311 (vs), 1287 (vs), 1256 (vs), 1211 (vs), 1175 (m), 1155 (s), 1125 (s), 1092 (s), 1069 (w), 1018 (s), 955 (s), 920 (m), 861 (m), 839 (m), 803 (w), 768 (s), 750 (s), 696 (w), 564 (w). **HRMS** for C₁₂H₁₃NO₅ (251.0794): found: 251.0768.

Synthesis of ethyl 4-(2-methyl-3-oxo-1-cyclopentenyl)-3-nitro-benzoate (**14f**)

Prepared according to **TP 3** from ethyl 4-iodo-3-nitrobenzoate (**1f**) (482 mg, 1.50 mmol), PhMgCl (0.97 mL, 1.6 mmol, 1.7 M in THF), CuCN·2LiCl (1.6 mL, 1.6 mmol, 1.0 M in THF) and 3-iodo-2-methyl-2-pentenone (500 mg, 2.25 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/diethyl ether = 1:2) yielded compound **14f** (266 mg, 61%) as a yellow solid.

mp.: 80-81 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.69 (d, ⁴J(H,H) = 1.8 Hz, 1 H), 8.29 (dd, ³J(H,H) = 8.2 Hz, ⁴J(H,H) = 1.8 Hz, 1 H), 7.32 (d, ³J(H,H) = 8.2 Hz, 1 H), 4.40 (q, ³J(H,H) = 7.1 Hz, 2 H), 2.79-2.75 (m, 2 H), 2.55-2.52 (m, 2 H), 1.52 (s, 3 H), 1.37 (t, ³J(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (300 MHz, CDCl₃, 25 °C): δ = 208.4, 165.1, 164.4, 147.6, 139.3, 137.5, 134.6, 132.5, 130.0, 126.4, 62.5, 34.7, 31.1, 14.6, 9.0. **MS** (70 eV, EI), *m/z* (%): 290 (32) [M+H]⁺, 244 (74), 234 (57), 218 (100), 204 (73), 192 (83), 176 (50), 144 (24), 141 (36), 128 (37), 115 (60). **IR** (KBr): $\tilde{\nu}$ = 3432 (m), 1708 (vs) 1721 (vs), 1652 (w), 1619 (m), 1533 (s), 1440 (w), 1398 (w), 1388 (w), 1345 (m), 1289 (s), 1252 (s), 1219 (w), 1160 (w), 1112 (m), 1058 (w), 1021 (m), 865 (w), 837 (w), 774 (w), 729 (m), 664 (w). **HRMS** for C₁₅H₁₅NO₅ (289.0950): found: 290.1026 [M+H]⁺. C₁₅H₁₅NO₅: required: C: 62.28; H: 5.23; N: 4.84; found: C: 61.99; H: 5.37; N: 4.74.

Synthesis of ethyl 2-(4-cyano-2-nitrobenzyl)acrylate (**14g**)

Prepared according to **TP 3** from 4-iodo-3-nitrobenzonitrile (**1g**) (548 mg, 2.00 mmol), PhMgCl (1.1 mL, 2.1 mmol, 2.0 M in THF), CuCN·2LiCl (2.0 mL, 2.0 mmol, 1.0 M in THF)

and ethyl (2-bromomethyl) acrylate (463 mg, 2.40 mmol). Reaction time: 30 min. Purification by flash chromatography (pentane/CH₂Cl₂ = 4:6) furnished title compound **14g** (300 mg, 58%) as a yellow solid.

mp.: 62-63 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.23 (d, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.81 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.56 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 6.31 (s, 1 H), 5.38 (m, 1 H), 4.13 (q, ³*J*(H,H) = 7.1 Hz, 2 H), 3.95 (s, 2 H), 1.17 (t, ³*J*(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 165.8, 149.5, 139.1, 137.0, 135.6, 133.4, 128.4, 128.2, 116.5, 112.1, 61.3, 34.9, 14.0. **MS** (70 eV, EI), *m/z* (%): 261 (0.1) [M⁺], 215 (100), 186 (77), 169 (40), 159 (47), 142 (39), 129 (27), 115 (28), 104 (23), 90 (18), 77 (14), 63 (17). **IR** (KBr): $\tilde{\nu}$ = 3065 (m), 1703 (s), 1703 (vs), 1536 (vs), 1361 (s), 1331 (s), 1310 (s), 1211 (m), 1197 (s), 1159 (m), 1027 (m), 965 (m), 928 (m), 849 (m), 826 (m). **HRMS** for C₁₃H₁₂N₂O₄ (260.0797): found: 261.0887 [M+H]⁺.

Synthesis of ethyl 2-[2-nitro-4-(1-piperidinylcarbonyl)benzyl]acrylate (**14h**)

Prepared according to **TP 3** from 1-(4-iodo-3-nitrobenzoyl)piperidine (**1h**) (360 mg, 1.00 mmol), PhMgCl (0.63 mL, 1.1 mmol, 1.8 M in THF), CuCN·2LiCl (1.1 mL, 1.1 mmol, 1.0 M in THF) and ethyl (2-bromomethyl) acrylate (386 mg, 2.00 mmol). Reaction time: 2 h. Purification by flash chromatography (pentane/diethyl ether = 1:2) yielded compound **14h** as a pale yellow oil (270 mg, 78%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 7.94 (d, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.55 (dd, ³*J*(H,H) = 8.0 Hz, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.40 (d, ³*J*(H,H) = 8.0 Hz, 1 H), 6.27 (m, 1 H), 5.44 (m, 1 H), 6.05-5.94 (m, 1 H), 4.16 (q, ³*J*(H,H) = 7.1 Hz, 2 H), 3.97 (s, 2 H), 3.7 (s_{br}, 2 H), 3.50 (s_{br}, 2 H), 1.70-1.45 (m, 6 H), 1.23 (t, ³*J*(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 167.5, 166.2, 149.2, 137.9, 136.2, 134.9, 132.6, 131.2, 127.2, 123.5, 112.5, 61.1, 48.9, 43.4, 34.6, 25.5, 24.4, 14.1. **MS** (70 eV, EI), *m/z* (%): 345 (100) [M⁺], 329 (18), 311 (19), 301 (19), 283 (6), 262 (12), 254 (7), 239 (10), 226 (14), 216 (9), 200 (3), 189 (8), 172 (10), 160 (16), 143 (15), 130 (8), 115 (23), 103 (7), 89 (10), 84 (11), 77 (7), 69 (6), 56 (5). **IR** (KBr): $\tilde{\nu}$ = 2939 (s), 1715 (vs), 1633 (vs), 1532 (vs), 1498 (s), 1441 (vs), 1351 (vs), 1276 (vs), 1191 (s), 1135 (s), 1124 (m), 1026 (s), 1010 (s), 955 (m), 906 (w), 854 (m), 822 (m), 756 (w), 732 (w), 668 (w). **HRMS** for C₁₈H₂₂N₂O₅ (346.1529): found: 345.1453 [M-H]⁺.

Synthesis of ethyl 2-(3,5-dimethyl-2-nitrobenzyl)acrylate (**14i**)

Prepared according to **TP 3** from 2-iodo-4,6-dimethyl-nitrobenzene (**1k**) (277 mg, 1.00 mmol), PhMgCl (0.73 mL, 1.1 mmol, 1.5 M in THF), CuCN·2LiCl (1.1 mL, 1.1 mmol, 1.0 M in THF) and ethyl (2-bromomethyl) acrylate (288 mg, 1.50 mmol). Reaction time: 1 h. Purification by flash chromatography (pentane/diethyl ether = 9:1) yielded title compound **14i** as a yellow oil (200 mg, 76%).

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ = 6.96 (s, 1 H), 6.92 (s, 1 H), 6.27 (d, ²J(H,H) = 1.0 Hz, 1 H), 5.43 (d, ²J(H,H) = 1.0 Hz, 1 H), 4.16 (q, ³J(H,H) = 7.1 Hz, 2 H), 3.60 (s, 2 H), 2.31 (s, 3 H), 2.27 (s, 3 H), 1.24 (t, ³J(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (100 MHz, CDCl₃, 25 °C): δ = 166.3, 140.4, 138.1, 130.4, 130.3, 129.9, 129.1, 127.1, 60.9, 36.0, 33.5, 21.1, 17.6, 14.1. **MS** (70 eV, EI), *m/z* (%): 262 (0.2) [M-H]⁺, 217 (100), 200 (26), 189 (58), 172 (53), 160 (15), 144 (23), 128 (18), 115 (15), 91 (13), 77 (8). **IR** (KBr): $\tilde{\nu}$ = 2982 (w), 1717 (vs), 1603 (m), 1525 (vs), 1443 (m), 1366 (s), 1301 (m), 1255 (m), 1194 (m), 1143 (s), 1026 (m), 953 (w), 860 (m), 835 (m), 817 (w). **HRMS** for C₁₄H₁₇NO₄ (263.1158): found: 262.1094 [M-H]⁺.

Synthesis of 2-allyl-4,6-dimethyl-1-nitrobenzene (**14j**)

Prepared according to **TP 3** from 2-iodo-4,6-dimethyl-nitrobenzene (**1k**) (277 mg, 1.00 mmol), PhMgCl (0.73 mL, 1.1 mmol, 1.5 M in THF), CuCN·2LiCl (1.1 mL, 1.1 mmol, 1.0 M in THF) and allyl bromide (242 mg, 2.00 mmol). Reaction time: 2 h. Purification by flash chromatography (pentane/diethyl ether = 49:1) yielded compound **14j** as a yellow oil (149 mg, 78%).

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ = 6.95-6.92 (m, 2 H), 5.92-5.82 (m, 1 H), 5.11-5.05 (m, 2 H), 3.32 (d, ³J(H,H) = 6.7 Hz, 2 H), 2.32 (s, 3 H), 2.27 (s, 3 H). **¹³C-NMR** (100 MHz, CDCl₃, 25 °C): δ = 140.5, 135.0, 131.5, 130.0, 129.7, 128.7, 117.1, 113.0, 35.6, 21.1, 17.5. **MS** (70 eV, EI), *m/z* (%): 191 (1) [M⁺], 174 (100), 159 (7), 144 (17), 131 (29), 115 (23), 105 (9), 91 (21), 77 (14), 65 (5), 55 (28). **IR** (KBr): $\tilde{\nu}$ = 2925 (m), 1603 (w), 1524 (vs), 1441 (w), 1366 (vs), 1296 (w), 1180 (w), 994 (m), 918 (m), 856 (m), 834 (s), 604 (w). **HRMS** for C₁₁H₁₃NO₂ (191.0946): found: 191.0949.

Synthesis of ethyl 2-(4-iodo-2-nitrobenzyl)acrylate (**14k**)

Prepared according to **TP 3** from 2,5-diiodo-nitrobenzene (**1m**) (563 mg, 1.50 mmol), PhMgCl (0.85 mL, 1.7 mmol, 2.0 M in THF), CuCN·2LiCl (1.7 mL, 1.7 mmol, 1.0 M in THF) and ethyl (2-bromomethyl) acrylate (345 mg, 1.80 mmol). Reaction time: 45 min. Purification by flash chromatography (pentane/CH₂Cl₂ = 2:1) yielded compound **14k** (401 mg, 74%) as a yellow oil.

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.16 (d, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.77 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.04 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 6.21 (d, ²*J*(H,H) = 0.9 Hz, 1 H), 5.38 (d, ²*J*(H,H) = 0.9 Hz, 1 H), 4.10 (q, ³*J*(H,H) = 7.1 Hz, 2 H), 3.84 (s, 2 H), 1.18 (t, ³*J*(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 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 C₁₂H₁₂INO₄ (360.9811): found: 359.9765 [M-H]⁺. C₁₂H₁₂INO₄: required: C: 39.91; H: 3.35; N: 3.88; found: C: 39.90; H: 3.10; N: 3.86.

Synthesis of ethyl 2-(4-benzoyl-2-nitrobenzyl)acrylate (**14l**)

Prepared according to **TP 3** from 4-iodo-3-nitrobenzophenone (**1o**) (353 mg, 1.00 mmol), PhMgCl (0.73 mL, 1.1 mmol, 1.5 M in THF), CuCN·2LiCl (1.1 mL, 1.1 mmol, 1.0 M in THF) and ethyl (2-bromomethyl) acrylate (288 mg, 1.50 mmol). Reaction time: 1 h. Purification by flash chromatography (pentane/diethyl ether = 9:1) yielded title compound **14l** as a yellow oil (329 mg, 97%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.34 (d, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.99 (dd, ³*J*(H,H) = 8.0 Hz, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.84-7.78 (m, 2 H), 7.69-7.63 (m, 1 H), 7.57-7.51 (m, 3 H), 6.85 (d, ²*J*(H,H) = 0.9 Hz, 1 H), 5.54 (d, ²*J*(H,H) = 0.9 Hz, 1 H), 4.21 (q, ³*J*(H,H) = 7.1 Hz, 2 H), 4.07 (s, 2 H), 1.28 (t, ³*J*(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 194.2, 166.4, 149.7, 138.2, 138.0, 137.5, 136.8, 134.0, 133.6, 132.9, 130.3, 129.1, 127.9, 126.6, 61.5, 35.2, 14.6. **MS** (70 eV, EI), *m/z* (%): 338 (1) [M-H]⁺, 310

(8), 293 (27), 265 (14), 248 (8), 189 (5), 160 (4), 144 (5), 115 (8), 105 (100), 77 (55). **IR** (KBr): $\tilde{\nu}$ = 1715 (vs), 1665 (vs), 1616 (s), 1534 (vs), 147 (s), 1353 (s), 1318 (s), 1301 (s), 1278 (vs), 1191 (s), 1180 (s), 1151 (s), 721 (m), 700 (m). **HRMS** for $\text{C}_{14}\text{H}_{17}\text{NO}_4$ (339.1107): found: 338.1025 $[\text{M}-\text{H}]^+$. $\text{C}_{19}\text{H}_{17}\text{NO}_5$: required: C: 67.25; H: 5.05; N: 4.13; found: C: 67.25; H: 5.30; N: 4.00.

Synthesis of compounds 22

Synthesis of ethyl 2-nitro[1,1'-biphenyl]-4-carboxylate (**22a**)

Prepared according to **TP 4** from ethyl 4-iodo-3-nitrobenzoate (**1f**) (482 mg, 1.50 mmol), PhMgCl (0.89 mL, 1.7 mmol, 1.9 M in THF), ZnBr_2 (1.7 mL, 1.7 mmol, 1.0 M in THF), $\text{Pd}(\text{dba})_2$ (44.0 mg, 0.075 mmol) and tfp (35 mg, 0.15 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/diethyl ether = 9:1) yielded biphenyl **22a** as a yellow oil (317 mg, 78%).

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25 °C): δ = 8.47 (d, $^4J(\text{H,H})$ = 1.8 Hz, 1H), 8.25 (dd, $^3J(\text{H,H})$ = 8.0 Hz, $^4J(\text{H,H})$ = 1.8 Hz, 1H), 7.53 (d, $^3J(\text{H,H})$ = 8.0 Hz, 1 H), 7.46-7.40 (m, 3 H), 7.34-7.31 (m, 2 H), 4.44 (q, $^3J(\text{H,H})$ = 7.1 Hz, 2 H), 1.43 (t, $^3J(\text{H,H})$ = 7.1 Hz, 3 H). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3 , 25 °C): δ = 164.3, 149.2, 140.2, 136.8, 132.8, 132.1, 130.7, 128.8, 127.7, 125.1, 113.2, 61.8, 14.3. **MS** (70 eV, EI), m/z (%): 271 (23) $[\text{M}^+]$, 254 (49), 243 (100), 226 (61), 214 (22), 198 (38), 187 (45), 182 (12), 170 (51), 151 (91), 142 (30), 126 (9), 115 (26), 75 (5). **IR** (KBr): $\tilde{\nu}$ = 2984 (m), 1723 (vs), 1618 (m), 1535 (vs), 1447 (m), 1360 (s), 1303 (s), 1285 (vs), 1236 (s), 1153 (m), 1113 (s), 1008 (m), 918 (w), 860 (m), 836 (w), 770 (m), 752 (s), 699 (s), 677 (w). **HRMS** for $\text{C}_{15}\text{H}_{13}\text{NO}_4$ (271.0845): found: 271.0846.

Synthesis of 4'-nitro-2,4-dinitro-biphenyl (**22b**)

Prepared according to **TP 4** from 1-iodo-2,4-dinitrobenzene (**1b**) (441 mg, 1.50 mmol), mesitylmagnesium bromide (2.5 mL, 1.7 mmol, 0.72 M in THF), ZnBr_2 (1.7 mL, 1.7 mmol, 1.0 M in THF), $\text{Pd}(\text{dba})_2$ (39.5 mg, 0.075 mmol), tfp (35 mg, 0.15 mmol) and ethyl 4-iodo-nitrobenzene (560 mg, 2.25 mmol). Reaction time: 4 h. Purification by flash chromatography (pentane/ethyl acetate = 5:1) yielded biphenyl **22b** as a yellow solid (240 mg, 55%).

mp.: 177-178°C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.79 (d, ⁴*J*(H,H) = 2.2 Hz, 1 H), 8.49 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 2.4 Hz, 1 H), 8.28 (d, ³*J*(H,H) = 8.8 Hz, 2 H), 7.63 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 7.46 (d, ³*J*(H,H) = 8.8 Hz, 2 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 147.6, 147.4, 146.8, 140.9, 139.2, 132.1, 127.9, 126.1, 123.2, 119.2. **MS** (70 eV, EI), *m/z* (%): 298 (12) [M⁺], 272 (36), 242 (47), 215 (70), 169 (92), 150 (100), 139 (68). **IR** (KBr): $\tilde{\nu}$ = 3436 (m), 3099 (m), 3052 (w), 1598 (s), 1532 (vs), 1476 (w), 1349 (vs), 1291 (w), 1110 (w), 1078 (w), 1006 (w), 917 (w), 858 (s), 836 (m), 760 (m), 745 (m), 723 (w), 700 (m), 537 (w). **HRMS** for C₁₂H₇N₃O₆ (289.0335): found: 289.0339.

Synthesis of ethyl 2',4'-dinitro-biphenyl-4-carboxylate (**22c**)

Prepared according to **TP 4** from 1-iodo-2,4-dinitrobenzene (**1b**) (441 mg, 1.50 mmol), mesitylmagnesium bromide (2.5 mL, 1.7 mmol, 0.72 M in THF), ZnBr₂ (1.7 mL, 1.7 mmol, 1.0 M in THF), Pd(dba)₂ (39.5 mg, 0.075 mmol), tfp (35 mg, 0.15 mmol) and ethyl 4-iodobenzoate (455 mg, 1.65 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/diethyl ether = 4:1) yielded biphenyl **22c** as a yellow solid (320 mg, 68%).

mp.: 121-122°C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.70 (d, ⁴*J*(H,H) = 2.4 Hz, 1 H), 8.43 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 2.4 Hz, 1 H), 8.08 (d, ³*J*(H,H) = 8.2 Hz, 2 H), 7.61 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 7.34 (d, ³*J*(H,H) = 8.2 Hz, 2 H), 4.41 (q, ³*J*(H,H) = 7.1 Hz, 2 H), 1.39 (t, ³*J*(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 164.7, 147.9, 146.3, 140.4, 138.6, 132.1, 130.5, 129.2, 126.8, 125.7, 118.9, 60.4, 13.3. **MS** (70 eV, EI), *m/z* (%): 316 (2) [M⁺], 288 (50), 271 (100), 260 (22), 242 (12), 225 (32), 215 (20), 179 (53), 169 (16), 151 (33), 139 (20). **IR** (KBr): $\tilde{\nu}$ = 3106 (w), 2988 (w), 1717 (vs), 1602 (m), 1530 (vs), 1416 (w), 1352 (s), 1298 (m), 1286 (s), 1189 (w), 1134 (w), 1106 (m), 1077 (w), 1025 (w), 1007 (w), 910 (w), 846 (w), 836 (w), 776 (w), 763 (w), 741 (m), 705 (w). **HRMS** for C₁₅H₁₂N₂O₆ (316.0695): found: 316.0685. C₁₅H₁₂N₂O₆: required: C: 56.96; H: 3.82; N: 8.86; found: C: 56.66; H: 3.92; N: 8.69.

Synthesis of 4'-chlor-2,4-dinitro-biphenyl (**22d**)

Prepared according to **TP 4** from 1-iodo-2,4-dinitrobenzene (**1b**) (441 mg, 1.50 mmol), mesitylmagnesium bromide (2.5 mL, 1.7 mmol, 0.72 M in THF), ZnBr₂ (1.7 mL, 1.7 mmol, 1.0 M in THF), Pd(dba)₂ (39.5 mg, 0.075 mmol), tfp (35 mg, 0.15 mmol) and 4-chloro-

iodobenzene (536 mg, 2.25 mmol). Reaction time: 5 h. Purification by flash chromatography (pentane/diethyl ether = 9:1) yielded biphenyl **22d** as a pale yellow solid (228 mg, 55%).

mp.: 80-81 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.65 (d, ⁴*J*(H,H) = 2.2 Hz, 1 H), 8.40 (dd, ³*J*(H,H) = 8.3 Hz, ⁴*J*(H,H) = 2.2 Hz, 1 H), 7.58 (d, ³*J*(H,H) = 8.3 Hz, 1 H), 7.59-7.33 (m, 2 H), 7.22-7.18 (m, 2 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 147.9, 146.1, 140.1, 135.0, 132.1, 128.6, 128.0, 127.4, 125.6, 118.9. **MS** (70 eV, EI), *m/z* (%): 278 (74) [M⁺], 250 (29), 243 (57), 233 (27), 215 (41), 186 (37), 169 (61), 151 (100), 139 (60). **IR** (KBr): $\tilde{\nu}$ = 3103 (w), 1651 (w), 1603 (s), 1541 (vs), 1528 (vs), 1472 (m), 1351 (vs), 1192 (w), 1150 (w), 1092 (m), 1074 (m), 984 (w), 1006 (m), 909 (m), 853 (w), 834 (s), 768 (w), 747 (m), 728 (m), 716 (m), 693 (w), 549 (w), 416 (w). **HRMS** for C₁₂H₇ClN₂O₄ (278.0094): found: 278.0068.

Synthesis of ethyl 2,4'-dinitro[1,1'-biphenyl]-4-carboxylate (**22e**)

Prepared according to **TP 4** from ethyl 4-iodo-3-nitrobenzoate (**1f**) (321 mg, 1.00 mmol), mesitylmagnesium bromide (1.3 mL, 1.1 mmol, 0.85 M in THF), ZnBr₂ (1.1 mL, 1.1 mmol, 1.0 M in THF), Pd(dba)₂ (29 mg, 0.05 mmol), tfp (23 mg, 0.10 mmol) and 4-iodo-1-nitrobenzene (374 mg, 1.50 mmol). Reaction time: 5 h at rt. Purification by flash chromatography (pentane/diethyl ether = 3:1) yielded biphenyl **22e** as a pale yellow solid (269 mg, 85%).

mp.: 124.5-125 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.61 (d, ⁴*J*(H,H) = 2.0 Hz, 1 H), 8.34-8.28 (m, 3 H), 7.54-7.47 (m, 3 H), 4.44 (q, ³*J*(H,H) = 7.1 Hz, 2 H), 1.43 (t, ³*J*(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 163.9, 148.6, 147.9, 143.3, 138.1, 133.4, 132.1, 131.9, 128.9, 125.6, 123.9, 62.1, 14.2. **MS** (70 eV, EI), *m/z* (%): 316 (51) [M⁺], 299 (50), 271 (88), 255 (9), 242 (53), 225 (46), 214 (72), 195 (36), 179 (72), 168 (26), 150 (100), 139 (67), 125 (13), 115 (21), 99 (9), 75 (24), 63 (10). **IR** (KBr): $\tilde{\nu}$ = 1722 (vs), 1530 (s), 1517 (s), 1353 (vs), 1307 (s), 1286 (s), 1242 (m), 1126 (m), 1110 (m), 857 (m), 850 (m), 749 (m). **HRMS** for C₁₅H₁₂N₂O₆ (316.0695): found: 316.0686. C₁₅H₁₂N₂O₆: required: C: 56.96; H: 3.82; N: 8.86; found: C: 56.69; H: 3.74; N: 8.78.

Synthesis of ethyl 3'-methoxy-2-nitro[1,1'-biphenyl]-4-carboxylate (**22f**)

Prepared according to **TP 4** from ethyl 4-iodo-3-nitrobenzoate (**1f**) (321 mg, 1.00 mmol), mesitylmagnesium bromide (1.3 mL, 1.1 mmol, 0.85 M in THF), ZnBr₂ (1.1 mL, 1.1 mmol, 1.0 M in THF), Pd(dba)₂ (29 mg, 0.05 mmol), tfp (23 mg, 0.10 mmol) and 3-iodoanisole (468 mg, 2.00 mmol). Reaction time: 4 h. Purification by flash chromatography (pentane/diethyl ether = 9:1) yielded biphenyl **22f** as a colorless liquid (240 mg, 80%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.49 (d, ⁴J(H,H) = 1.8 Hz, 1 H), 8.27 (dd, ³J(H,H) = 8.4 Hz, ⁴J(H,H) = 1.8 Hz, 1 H), 7.56 (d, ³J(H,H) = 8.4 Hz, 1 H), 7.37 (t, ³J(H,H) = 8.4 Hz, 1 H), 6.98 (dd, ³J(H,H) = 8.0 Hz, ⁴J(H,H) = 1.8 Hz, 1 H), 6.93-6.87 (m, 2 H), 4.46 (q, ³J(H,H) = 7.1 Hz, 2 H), 3.84 (s, 3 H), 1.45 (t, ³J(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 164.3, 159.8, 149.3, 140.0, 132.7, 132.0, 130.8, 129.9, 128.9, 125.0, 120.1, 114.3, 113.5, 61.8, 55.3, 14.3. **MS** (70 eV, EI), *m/z* (%): 301 (100) [M⁺], 284 (8), 273 (55), 256 (51), 242 (23), 230 (27), 214 (23), 202 (21), 196 (14), 183 (20), 170 (28), 152 (26), 139 (66), 127 (17), 115 (10), 101 (4), 89 (7), 76 (8), 63 (7), 55 (12). **IR** (KBr): $\tilde{\nu}$ = 1728 (vs), 1663 (m), 1538 (vs), 1355 (s), 1318 (m), 1279 (vs), 1239 (vs), 1133 (m), 828 (m), 716 (m). **HRMS** for C₁₆H₁₅NO₅ (301.0950): found: 301.0954.

Synthesis of ethyl 4'-methoxy-2-nitro[1,1'-biphenyl]-4-carboxylate (**22g**)

Prepared according to **TP 4** from ethyl 4-iodo-3-nitrobenzoate (**1f**) (482 mg, 1.50 mmol), mesitylmagnesium bromide (2.3 mL, 1.6 mmol, 0.70 M in THF), ZnBr₂ (1.6 mL, 1.6 mmol, 1.0 M in THF), Pd(dba)₂ (44.0 mg, 0.075 mmol), tfp (35 mg, 0.15 mmol) and 4-iodoanisole (523 mg, 2.25 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/ethyl acetate = 9:1) yielded biphenyl **22g** as a yellow oil (220 mg, 49%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.32 (d, ⁴J(H,H) = 1.8 Hz, 1H), 8.22 (dd, ³J(H,H) = 8.0 Hz, ⁴J(H,H) = 1.8 Hz, 1H), 7.51 (d, ³J(H,H) = 8.0 Hz, 1 H), 7.26 (d, ³J(H,H) = 8.8 Hz, 2 H), 6.95 (d, ³J(H,H) = 8.8 Hz, 2 H), 4.41 (q, ³J(H,H) = 7.1 Hz, 2 H), 3.83 (s, 3 H), 1.42 (t, ³J(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 164.4, 160.2, 149.2, 139.7, 132.6, 131.9, 130.2, 129.1, 128.4, 125.1, 114.4, 61.8, 55.3, 14.3. **MS** (70 eV, EI), *m/z* (%): 301 (100) [M⁺], 284 (9), 271 (3), 256 (32), 241 (5), 228 (6), 218 (17), 190 (9), 182 (14), 167 (12), 156 (5), 139 (57), 127 (4), 113 (4), 89 (4). **IR** (KBr): $\tilde{\nu}$ = 1722 (vs), 1675 (s), 1534 (s), 1352 (s), 1315 (m), 1287 (vs), 1237 (vs), 1164 (m), 764 (w), 716 (m), 687 (m). **HRMS** for C₁₆H₁₅NO₅ (301.0950): found: 301.0939.

Synthesis of ethyl 4'-cyano-2-nitro[1,1'-biphenyl]-4-carboxylate (**22h**)

Prepared according to **TP 4** from ethyl 4-iodo-3-nitrobenzoate (**1f**) (482 mg, 1.50 mmol), mesitylmagnesium bromide (2.3 mL, 1.6 mmol, 0.70 M in THF), ZnBr₂ (1.6 mL, 1.6 mmol, 1.0 M in THF), Pd(dba)₂ (43.0 mg, 0.075 mmol), tfp (35 mg, 0.15 mmol) and 4-iodoanisole (458 mg, 2.00 mmol). Reaction time: 4 h. Purification by flash chromatography (pentane/ethyl acetate = 6:1) yielded biphenyl **22h** as a yellow oil (235 mg, 53%).

mp.: 143-144 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.79 (d, ⁴*J*(H,H) = 1.8 Hz, 1 H), 8.35 (dd, ³*J*(H,H) = 8.0 Hz, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.67-7.64 (m, 2 H), 7.53-7.48 (m, 1 H), 7.41-7.35 (m, 2 H), 4.41 (q, ³*J*(H,H) = 7.1 Hz, 2 H), 1.38 (t, ³*J*(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 191.6, 162.8, 145.8, 138.7, 134.5, 133.7, 133.1, 132.1, 128.2, 128.2, 127.9, 124.5, 61.3, 13.3. **MS** (70 eV, EI), *m/z* (%): 296 (25) [M⁺], 279 (17), 268 (81), 251 (81), 223 (32), 207 (49), 195 (80), 177 (100), 167 (21), 150 (35). **IR** (KBr): $\tilde{\nu}$ = 3435 (s), 2229 (m), 1721 (vs), 1619 (m), 1534 (s), 139 (w), 1369 (m), 1354 (m), 1306 (s), 1289 (s), 1241 (m), 1161 (w), 1127 (m), 1111 (m), 1022 (w), 1006 (w), 863 (w), 839 (m), 763 (m), 740 (w), 575 (m). **C₁₆H₁₂N₂O₄**: required: C: 64.86; H: 4.08; N: 9.46; found: C: 64.50; H: 4.19; N: 9.27.

Synthesis of ethyl 3-nitro-4-(1,3-thiazol-2-yl)benzoate (**22i**)

Prepared according to **TP 4** from ethyl 4-iodo-3-nitrobenzoate (**1f**) (321 mg, 1.00 mmol), mesitylmagnesium bromide (1.6 mL, 1.1 mmol, 0.70 M in THF), ZnBr₂ (1.1 mL, 1.1 mmol, 1.0 M in THF), Pd(dba)₂ (29 mg, 0.05 mmol), tfp (23 mg, 0.10 mmol) and 2-bromothiazole (328 mg, 2.00 mmol). Reaction time: 6 h. Purification by flash chromatography (pentane/diethyl ether = 4:1) furnished title compound **22i** as a yellow solid (133 mg, 48%).

mp.: 140.5-143 °C. **¹H-NMR** (400 MHz, CDCl₃, 25 °C): δ = 8.40 (d, ⁴*J*(H,H) = 1.7 Hz, 1 H), 8.25 (dd, ³*J*(H,H) = 8.1 Hz, ⁴*J*(H,H) = 1.7 Hz, 1 H), 7.95 (d, ³*J*(H,H) = 3.2 Hz, 1 H), 7.84 (d, ³*J*(H,H) = 8.1 Hz, 1 H), 7.52 (d, ³*J*(H,H) = 3.2 Hz, 1 H), 4.44 (q, ³*J*(H,H) = 7.1 Hz, 2 H), 1.42 (t, ³*J*(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (100 MHz, CDCl₃, 25 °C): δ = 163.9, 160.9, 148.7, 144.5, 134.1, 132.6, 131.4, 130.7, 125.2, 121.7, 62.1, 14.2. **MS** (70 eV, EI), *m/z* (%): 278 (9) [M⁺], 233 (34), 206 (14), 180 (40), 176 (100), 161 (97), 152 (11), 148 (22), 135 (42), 120 (15), 103 (20), 89 (4), 75 (15), 58 (31). **IR** (KBr): $\tilde{\nu}$ = 2963 (m), 1712 (s), 1546 (s), 1366

(m), 1288 (m), 1263 (vs), 1238 (m), 1097 (vs), 1020 (vs), 801 (vs), 766 (s). **HRMS** for $C_{16}H_{15}NO_5$ (278.0402): found: 278.0368.

Synthesis of ethyl 4'-cyano-2'-nitro[1,1'-biphenyl]-4-carboxylate (**22j**)

Prepared according to **TP 4** from 4-iodo-3-nitro-benzonitrile (**1g**) (411 mg, 1.50 mmol), mesitylmagnesium bromide (2.3 mL, 1.6 mmol, 0.70 M in THF), $ZnBr_2$ (1.6 mL, 1.6 mmol, 1.0 M in THF), $Pd(dba)_2$ (39.5 mg, 0.075 mmol), tfp (35 mg, 0.15 mmol) and ethyl 4-iodobenzoate (621 mg, 2.50 mmol). Purification by flash chromatography (pentane/ethyl acetate = 6:1) yielded biphenyl **22j** as a pale yellow solid (325 mg, 73%).

mp.: 166-167 °C. **1H -NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 8.21 (d, $^4J(H,H)$ = 1.8 Hz, 1 H), 8.13 (d, $^3J(H,H)$ = 8.5 Hz, 2 H), 7.93 (dd, $^3J(H,H)$ = 8.5 Hz, $^4J(H,H)$ = 1.8 Hz, 1 H), 7.60 (d, $^3J(H,H)$ = 8.4 Hz, 1 H), 7.38 (d, $^3J(H,H)$ = 8.5 Hz, 2 H), 4.40 (q, $^3J(H,H)$ = 7.2 Hz, 2 H), 1.41 (t, $^3J(H,H)$ = 7.2 Hz, 3 H). **^{13}C -NMR** (100 MHz, $CDCl_3$, 25 °C): δ = 165.7, 149.1, 139.9, 135.5, 132.9, 131.4, 130.8, 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 (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): found: 296.0779. $C_{16}H_{12}N_2O_4$: required: C: 64.86; H: 4.08; N: 9.46; found: C: 64.62, H: 3.64; N: 9.40.

Synthesis of 2,4'-dinitro[1,1'-biphenyl]-4-carbonitrile (**22k**)

Prepared according to **TP 4** from 4-iodo-3-nitro-benzonitrile (**1g**) (411 mg, 1.50 mmol), mesitylmagnesium bromide (2.3 mL, 1.65 mmol, 0.70 M in THF), $ZnBr_2$ (1.6 mL, 1.6 mmol, 1.0 M in THF), $Pd(dba)_2$ (39.5 mg, 0.075 mmol), tfp (35 mg, 0.15 mmol) and ethyl-4-iodobenzoate (621 mg, 2.50 mmol). Purification by flash chromatography (pentane/ethyl acetate = 6:1) yielded biphenyl **22k** as a pale yellow solid (325 mg, 73%).

mp.: 142-143 °C. **1H -NMR** (300 MHz, $DMSO-d_6$, 25 °C): δ = 8.71 (d, $^4J(H,H)$ = 1.8 Hz, 1 H), 8.36-8.30 (m, 3 H), 7.83 (d, $^3J(H,H)$ = 8.4 Hz, 1 H), 7.71 (d, $^3J(H,H)$ = 8.9 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** (75 MHz, $DMSO-d_6$, 25 °C): δ = 148.7, 148.1, 142.8, 138.1, 137.1, 133.5, 129.8, 129.0, 124.2, 117.0, 113.1. **MS**

(70 eV, EI), m/z (%): 269 (31) [M^+], 252 (26), 239 (5), 222 (28), 206 (7), 195 (100), 177 (39), 164 (73), 150 (42), 140 (75), 126 (8), 114 (9), 99 (9), 87 (8), 75 (14), 63 (9), 51 (5). **IR** (KBr): $\tilde{\nu}$ = 2237 (m), 1618 (w), 1600 (m), 1527 (vs), 1509 (s), 1352 (vs), 1300 (w), 1112 (w), 858 (w), 845 (m), 755 (w), 711 (w). **HRMS** for $C_{16}H_{12}N_2O_4$ (269.0437): found: 269.0425. $C_{13}H_7N_3O_4$: required: C: 58.00, H: 2.62, N: 15.61; found: C: 57.94, H: 2.31, N: 15.39.

Synthesis of 3'-methoxy-2-nitro[1,1'-biphenyl]-4-carbonitrile (**22l**)

Prepared according to **TP 4** from 4-iodo-3-nitrobenzonitrile (**1g**) (273 mg, 1.00 mmol), mesitylmagnesium bromide (1.3 mL, 1.1 mmol, 0.85 M in THF), $ZnBr_2$ (1.1 mL, 1.1 mmol, 1.0 M in THF), $Pd(dba)_2$ (29 mg, 0.05 mmol), tfp (23 mg, 0.10 mmol) and 3-iodoanisole (468 mg, 2.00 mmol). Reaction time: 5 h. Purification by flash chromatography (pentane/diethyl ether = 4:1) yielded biphenyl **22l** as a yellow solid (190 mg, 75%).

mp.: 115-115.5 °C. **1H -NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 8.10 (d, $^4J(H,H)$ = 1.8 Hz, 1 H), 7.87 (dd, $^3J(H,H)$ = 8.0 Hz, $^4J(H,H)$ = 1.8 Hz, 1 H), 7.60 (d, $^3J(H,H)$ = 8.0 Hz, 1 H), 7.36 (t, $^3J(H,H)$ = 8.0 Hz, 1 H), 6.99 (dd, $^3J(H,H)$ = 8.5 Hz, $^4J(H,H)$ = 1.8 Hz, 1 H), 6.88-6.82 (m, 2 H), 3.82 (s, 3 H). **^{13}C -NMR** (75 MHz, $CDCl_3$, 25 °C): δ = 159.9, 149.4, 140.5, 136.7, 135.1, 133.0, 130.2, 127.6, 119.9, 116.5, 114.7, 113.5, 112.5, 55.4. **MS** (70 eV, EI), m/z (%): 254 (100) [M^+], 237 (11), 226 (40), 209 (32), 195 (46), 183 (31), 177 (30), 164 (90), 153 (44), 140 (36), 127 (17), 114 (9), 101 (9), 87 (8), 75 (11), 63 (12), 55 (15). **IR** (KBr): $\tilde{\nu}$ = 2234 (s), 1604 (m), 1527 (vs), 1442 (w), 1354 (vs), 1238 (vs), 1112 (m), 842 (m), 789 (w), 771 (m), 714 (m), 632 (w). **HRMS** for $C_{14}H_{10}N_2O_3$ (254.0691): found: 254.0705. $C_{14}H_{10}N_2O_3$: required: C: 66.14; H: 3.96; N: 11.02; found: C: 65.97; H: 3.96; N: 11.03.

Synthesis of 1-[(3'-methoxy-2-nitro[1,1'-biphenyl]-4-yl)carbonyl]piperidine (**22m**)

Prepared according to **TP 4** from 1-(4-iodo-3-nitrobenzoyl)piperidine (**1h**) (360 mg, 1.00 mmol), mesitylmagnesium bromide (1.3 mL, 1.1 mmol, 0.85 M in THF), $ZnBr_2$ (1.1 mL, 1.1 mmol, 1.0 M in THF), $Pd(dba)_2$ (29 mg, 0.05 mmol), tfp (23 mg, 0.10 mmol) and 3-

iodoanisole (351 mg, 1.50 mmol). Reaction time: 4 h. Purification by flash chromatography (pentane/diethyl ether = 1:1) yielded biphenyl **22m** as a light yellow solid (228 mg, 67%).

mp.: 90-91 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 7.86 (d, ⁴*J*(H,H) = 1.8 Hz, 2 H), 7.61 (dd, ³*J*(H,H) = 7.8 Hz, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.47 (d, ³*J*(H,H) = 7.8 Hz, 1 H), 7.32 (t, ³*J*(H,H) = 7.9 Hz, 1 H), 6.95-6.92 (m, 1 H), 6.88-6.83 (m, 2 H), 3.80 (s, 3 H), 3.72 (s_br, 2 H), 3.40 (s_br, 2 H), 1.84-1.50 (m, 6 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 167.3, 159.7, 149.0, 137.9, 137.0, 126.7, 132.1, 130.5, 129.8, 122.6, 120.1, 114.0, 113.6, 55.3, 48.8, 43.4, 26.5, 25.5, 24.4. **MS** (70 eV, EI), *m/z* (%): 339 (100) [M⁺], 323 (10), 306 (13), 294 (21), 256 (54), 228 (10), 209 (44), 180 (19), 152 (19), 139 (27), 127 (4), 84 (5). **IR** (KBr): $\tilde{\nu}$ = 2857 (m), 1631 (vs), 1601 (s), 1530 (s), 1445 (s), 1350 (s), 1321 (m), 1286 (s), 1260 (m), 1220 (s), 1179 (m), 1022 (m), 855 (m), 847 (m), 795 (m). **HRMS** for C₁₉H₂₀N₂O₄ (340.1423): found: 340.1428.

Synthesis of 1-[(2,4'-dinitro[1,1'-biphenyl]-4-yl)carbonyl]piperidine (**22n**)

Prepared according to **TP 4** from 1-(4-iodo-3-nitrobenzoyl)piperidine (**1h**) (360 mg, 1.00 mmol), mesitylmagnesium bromide (1.3 mL, 1.1 mmol, 0.85 M in THF), ZnBr₂ (1.1 mL, 1.1 mmol, 1.0 M in THF), Pd(dba)₂ (29 mg, 0.05 mmol), tfp (23 mg, 0.10 mmol) and 4-iodonitrobenzene (498 mg, 2.00 mmol). Reaction time: 3 h. Purification by flash chromatography (pentane/diethyl ether = 2:1) yielded biphenyl **22n** as a pale yellow solid (345 mg, 77%).

mp.: 152.5-153 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.27 (d, ³*J*(H,H) = 8.4 Hz, 2 H), 8.01 (d, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.70 (dd, ³*J*(H,H) = 7.9 Hz, ⁴*J*(H,H) = 1.8 Hz, 1 H), 7.49-7.44 (m, 3 H), 3.72 (s_br, 2 H), 3.40 (s_br, 2 H), 1.75-1.52 (m, 6 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 166.8, 148.3, 147.8, 143.6, 138.1, 135.2, 131.9, 131.1, 128.9, 123.9, 123.3, 48.9, 43.3, 26.5, 25.4, 24.3. **MS** (70 eV, EI), *m/z* (%): 354 (100) [M-H]⁺, 338 (19), 320 (9), 309 (17), 271 (54), 225 (26), 179 (47), 167 (3), 150 (28), 139 (11), 84 (8). **IR** (KBr): $\tilde{\nu}$ = 2940 (w), 1632 (vs), 1599 (m), 1523 (vs), 1466 (w), 1444 (s), 1348 (vs), 1284 (m), 1113 (w), 1006 (w), 911 (w), 854 (m), 847 (m), 744 (m), 694 (w). **HRMS** for C₁₈H₁₇N₃O₅ (355.1168): found: 355.1162. C₁₈H₁₇N₃O₅: required: C: 60.84; H: 4.82; N: 11.83; found: C: 60.47; H: 4.87; N: 11.71.

Synthesis of compounds 26

Synthesis of 6-nitro-3-phenyl-2-benzofuran-1(3H)-one (26a)

Prepared according to **TP 5** from ethyl 2-iodo-5-nitrobenzoate (**1i**) (321 mg, 1 mmol), PhMgCl (0.55 mL, 1.1 mmol, 2.0 M in THF) and benzaldehyde (212 mg, 2 mmol). Reaction time: 2 h at -78°C . Purification by flash chromatography (pentane/diethyl ether = 9:1) furnished title compound **26a** as a pale yellow oil (199 mg, 78%).

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25°C): δ = 8.75 (d, $^4J(\text{H,H}) = 2.2$ Hz, 1 H), 8.51 (dd, $^3J(\text{H,H}) = 8.4$ Hz, $^4J(\text{H,H}) = 2.2$ Hz, 1 H), 7.56 (d, $^3J(\text{H,H}) = 8.4$ Hz, 1 H), 7.45-7.37 (m, 5 H), 6.53 (s, 1 H). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3 , 25°C): δ = 167.9, 154.7, 149.0, 134.6, 129.7, 129.1, 129.0, 127.1, 126.8, 124.4, 121.0, 82.6. **MS** (70 eV, EI), m/z (%): 255 (100) [M^+], 226 (4), 180 (12), 165 (28), 149 (40), 139 (8), 132 (9), 105 (85), 87 (3), 77 (23). **IR** (KBr): $\tilde{\nu}$ = 1778 (vs), 1615 (m), 1537 (vs), 1455 (m), 1347 (vs), 1303 (m), 1254 (m), 1097 (vs), 797 (w), 763 (w), 739 (m), 700 (m), 620 (w). **HRMS** for $\text{C}_{14}\text{H}_9\text{NO}_4$ (255.0532): found: 255.0504.

Synthesis of ethyl 2-allyl-5-nitrobenzoate (26b)

Prepared according to **TP 5** from ethyl 2-iodo-5-nitrobenzoate (**1i**) (321 mg, 1.00 mmol), PhMgCl (0.66 mL, 1.1 mmol, 1.6 M in THF), $\text{CuCN}\cdot 2\text{LiCl}$ (1.1 mL, 1.1 mmol, 1.0 M in THF) and allyl bromide (240 mg, 2.00 mmol). Reaction time: 2 h at -78°C . Purification by flash chromatography (pentane/diethyl ether = 29:1) furnished title compound **26b** as a yellow oil (204 mg, 87%).

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25°C): δ = 8.70 (d, $^4J(\text{H,H}) = 2.7$ Hz, 1 H), 8.24 (dd, $^3J(\text{H,H}) = 8.9$ Hz, $^4J(\text{H,H}) = 2.7$ Hz, 1 H), 7.46 (d, $^3J(\text{H,H}) = 8.9$ Hz, 1 H), 6.03-5.89 (m, 1 H), 5.12-5.00 (m, 2 H), 4.39 (q, $^3J(\text{H,H}) = 7.1$ Hz, 2 H), 3.84 (d, $^3J(\text{H,H}) = 6.6$ Hz, 2 H), 1.40 (t, $^3J(\text{H,H}) = 7.1$ Hz, 3 H). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3 , 25°C): δ = 165.5, 148.9, 146.2, 135.6, 132.0, 131.2, 126.1, 125.7, 117.1, 61.8, 38.2, 14.2. **MS** (70 eV, EI), m/z (%): 235 (23) [M^+], 220 (35), 207 (34), 192 (100), 179 (11), 160 (12), 144 (8), 115 (42), 89 (5). **IR** (KBr): $\tilde{\nu}$ = 2983 (w), 1727 (vs), 1613 (m), 1525 (vs), 1479 (m), 1445 (m), 1350 (vs), 1252 (s), 1127 (s), 1067 (m), 1018 (m), 921 (m), 837 (w), 745 (w), 716 (w), 604 (w). **HRMS** for $\text{C}_{12}\text{H}_{13}\text{NO}_4$ (235.0845): found: 235.0845.

Synthesis of ethyl 2-benzoyl-5-nitrobenzoate (**26c**)

Prepared according to **TP 5** from ethyl 2-iodo-5-nitrobenzoate (**1i**) (642 mg, 2 mmol), PhMgCl (1.1 mL, 2.2 mmol, 2.0 M in THF), CuCN·2LiCl (2.2 mL, 2.2 mmol, 1.0 M in THF) and benzoyl bromide (648 mg, 3.50 mmol). Reaction time: 1 h at -78°C . Purification by flash chromatography (pentane/diethyl ether = 9:1) furnished title compound **26c** as a yellow solid (570 mg, 94%).

mp.: $88\text{--}89.5^{\circ}\text{C}$. **$^1\text{H-NMR}$** (300 MHz, CDCl_3 , 25°C): δ = 8.83 (d, $^4J(\text{H,H}) = 2.8$ Hz, 1 H), 8.40 (dd, $^3J(\text{H,H}) = 8.8$ Hz, $^4J(\text{H,H}) = 2.8$ Hz, 1 H), 7.67–7.64 (m, 2 H), 7.53–7.51 (m, 1 H), 7.51–7.49 (m, 2 H), 7.42–7.36 (m, 1 H), 4.10 (q, $^3J(\text{H,H}) = 7.1$ Hz, 2 H), 1.07–1.03 (m, $^3J(\text{H,H}) = 7.1$ Hz, 3 H). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3 , 25°C): δ = 194.8, 163.7, 148.2, 147.3, 136.1, 133.9, 130.9, 129.3, 128.9, 128.8, 126.9, 125.4, 62.4, 13.6. **MS** (70 eV, EI), m/z (%): 299 (22) [M^+], 270 (4), 254 (14), 222 (15), 194 (51), 180 (3), 152 (7), 105 (100), 77 (28). **IR** (KBr): $\tilde{\nu}$ = 1723 (vs), 1672 (vs), 1606 (s), 1596 (s), 1582 (m), 1528 (vs), 1450 (s), 1367 (m), 1353 (vs), 1313 (vs), 1278 (vs), 1250 (s), 1017 (m), 908 (m), 863 (w), 848 (m), 838 (w), 792 (w), 742 (m), 714 (s), 698 (s), 690 (m). **HRMS** for $\text{C}_{16}\text{H}_{13}\text{NO}_5$ (299.0794): found: 299.0801. $\text{C}_{16}\text{H}_{13}\text{NO}_5$: required: C: 64.21; H: 4.38; N: 4.68; found: C: 63.98; H: 4.76; N: 4.67.

Synthesis of ethyl 2-[2-(ethoxycarbonyl)-2-propenyl]-5-nitrobenzoate (**26d**)

Prepared according to **TP 5** from ethyl 2-iodo-5-nitrobenzoate (**1i**) (642 mg, 2.00 mmol), PhMgCl (1.1 mL, 2.2 mmol, 2.0 M in THF), CuCN·2LiCl (2.2 mL, 2.2 mmol, 1.0 M in THF) and ethyl (2-bromomethyl) acrylate (580 mg, 3.00 mmol). Reaction time: 1 h at -78°C . Purification by flash chromatography (pentane/diethyl ether = 4:1) furnished title compound **26d** as an orange oil (411 mg, 67%).

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25°C): δ = 8.66 (d, 1 H), 8.19 (dd, $^4J(\text{H,H}) = 2.7$ Hz, $^3J(\text{H,H}) = 8.6$ Hz, 1 H), 7.40 (d, 1 H), 6.20 (d, 1 H), 5.29–5.28 (m, 1 H), 4.30 (q, $^3J(\text{H,H}) = 7.1$ Hz, 2 H), 4.15–4.11 (m, 2 H), 4.08–4.06 (m, 2 H), 1.33 (t, $^3J(\text{H,H}) = 7.1$ Hz, 3 H), 1.21–1.13 (m, 3 H). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3 , 25°C): δ = 165.4, 164.4, 146.7, 145.4, 137.9, 131.4, 130.6, 125.8, 125.0, 124.8, 60.8, 60.0, 34.8, 13.2, 13.1. **MS** (70 eV, EI), m/z

(%): 307 (1) [M^+], 261 (41), 233 (100), 216 (3), 205 (43), 189 (24), 175 (11), 159 (9), 142 (6), 131 (12), 115 (29), 103 (4), 89 (3), 77 (4). **IR** (KBr): $\tilde{\nu}$ = 1722 (vs), 1526 (vs), 1367 (s), 1351 (vs), 1254 (vs), 1137 (s), 1070 (s), 1023 (m), 935 (w), 921 (w), 838 (w), 821 (w), 787 (w), 738 (w), 722 (w). **HRMS** for $C_{15}H_{17}NO_6$ (307.1056): found: 307.1058.

Synthesis of 2-benzoyl-*N,N*-diethyl-5-nitrobenzamide (**26e**)

Prepared according to **TP 5** from *N,N*-diethyl-2-iodo-5-nitrobenzamide (**1j**) (694 mg, 2.00 mmol), $PhMgCl$ (1.1 mL, 2.2 mmol, 2.0 M in THF), $CuCN \cdot 2LiCl$ (2.2 mL, 2.2 mmol, 1.0 M in THF) and benzoyl bromide (648 mg, 3.50 mmol). Reaction time: 1 h at $-78^\circ C$. Purification by flash chromatography (pentane/ethyl acetate = 9:1) furnished title compound **26e** as a yellow oil (313 mg, 68%).

1H -NMR (300 MHz, $CDCl_3$, $25^\circ C$): δ = 8.28 (dd, $^3J(H,H) = 8.4$ Hz, $^4J(H,H) = 2.2$ Hz, 1 H), 8.24-8.21 (m, 1 H), 7.77-7.72 (m, 2 H), 7.64 (d, $^3J(H,H) = 8.4$ Hz, 1 H), 7.62-7.56 (m, 1 H), 7.47-7.41 (m, 2 H), 3.40 (q, $^3J(H,H) = 7.1$ Hz, 2 H), 3.25 (q, $^3J(H,H) = 7.1$ Hz, 2 H), 1.15 (t, $^3J(H,H) = 7.1$ Hz, 3 H), 1.02 (t, $^3J(H,H) = 7.1$ Hz, 2 H). **^{13}C -NMR** (75 MHz, $CDCl_3$, $25^\circ C$): δ = 194.9, 167.3, 148.4, 143.0, 139.5, 136.0, 134.0, 130.3, 129.2, 128.6, 123.2, 121.7, 43.0, 39.2, 13.7, 12.1. **MS** (70 eV, EI), m/z (%): 325 (1) [M] $^+$, 254 (73), 238 (3), 208 (29), 196 (6), 180 (21), 152 (43), 105 (4), 72 (100). **IR** (KBr): $\tilde{\nu}$ = 1671 (s), 1634 (vs), 1528 (vs), 1448 (s), 1349 (vs), 1316 (s), 1278 (vs), 1218 (m), 1113 (m), 940 (m), 901 (m), 851 (m), 733 (m), 705 (m). **HRMS** for $C_{18}H_{18}N_2O_4$ (326.1267): found: 326.1277.

Synthesis of compounds **27**

Synthesis of 2-[hydroxy(phenyl)methyl]-4-nitrophenyl 4-methylbenzenesulfonate (**27a**)

Prepared according to **TP 5** from 2-iodo-4-nitrophenyl 4-methylbenzenesulfonate (**1q**) (439 mg, 1.00 mmol), $PhMgCl$ (0.65 mL, 1.1 mmol, 1.6 M in THF) and benzaldehyde

(127 mg, 1.20 mmol). Purification by flash chromatography (pentane/diethyl ether = 4:1) furnished title compound **27a** as a colourless oil (320mg, 77%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.27 (d, $^4J(\text{H,H})$ = 2.7 Hz, 1 H), 8.06 (dd, $^3J(\text{H,H})$ = 8.9 Hz, $^4J(\text{H,H})$ = 2.7 Hz, 1 H), 7.70 (d, $^3J(\text{H,H})$ = 8.4 Hz, 2 H), 7.36-7.26 (m, 7 H), 7.21 (d, $^3J(\text{H,H})$ = 8.9 Hz, 1 H), 6.01 (s, 1 H), 2.80 (s_{br}, 1 OH), 2.47 (s, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 150.7, 146.5, 146.2, 141.1, 138.9, 131.8, 130.2, 128.6, 128.3, 128.1, 126.5, 124.0, 123.8, 122.1, 69.6, 21.7. **MS** (70 eV, EI), m/z (%): 399 (0.1) [M⁺], 382 (14), 319 (23), 301 (13), 244 (100), 226 (34), 180 (11), 166 (22), 155 (10), 91 (61), 77 (13). **IR** (KBr): $\tilde{\nu}$ = 3541 (w), 1596 (m), 1530 (vs), 1475 (m), 1381 (s), 1350 (vs), 1209 (s), 1178 (vs), 1090 (s), 1038 (m), 856 (s), 766 (m), 717 (s), 700 (s), 670 (m), 565 (m), 550 (m). **HRMS** for C₂₀H₁₇NO₆S (399.0777): found: 399.0812.

Synthesis of 2-allyl-4-nitrophenyl 4-methylbenzenesulfonate (**27b**)

Prepared according to **TP 5** from 2-iodo-4-nitrophenyl 4-methylbenzenesulfonate (**1q**) (439 mg, 1.00 mmol), PhMgCl (0.65 mL, 1.1 mmol, 1.6 M in THF), CuCN·2LiCl (1.1 mL, 1.1 mmol, 1.0 M in THF) and allyl bromide (0.17 mL, 1.6 mmol). Purification by flash chromatography (pentane/diethyl ether = 19:1) furnished title compound **27b** as a colourless oil (311mg, 93%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.08-8.02 (m, 2 H), 7.77 (d, $^3J(\text{H,H})$ = 8.4 Hz, 2 H), 7.38-7.35 (m, 1 H), 7.27 (d, $^3J(\text{H,H})$ = 8.9 Hz, 1 H), 5.81-5.67 (m, 1 H), 5.13 (ddt, $^3J(\text{H,H})$ = 9.7 Hz, $^2J(\text{H,H})$, $^4J(\text{H,H})$ = 1.8 Hz, 1 H), 5.04 (ddt, $^3J(\text{H,H})$ = 16.8 Hz, $^2J(\text{H,H})$, $^4J(\text{H,H})$ = 1.8 Hz, 1 H), 3.27 (d, $^3J(\text{H,H})$ = 6.6 Hz, 1 H), 2.47 (s, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 152.0, 146.2, 146.0, 135.4, 133.7, 132.4, 130.1, 128.4, 125.9, 122.9, 118.4, 112.6, 33.8, 21.7. **MS** (70 eV, EI), m/z (%): 334 (17) [M+H]⁺, 317 (19), 178 (48), 155 (68), 132 (12), 103 (7), 91 (100), 77 (4), 65 (8). **IR** (KBr): $\tilde{\nu}$ = 3081 (w), 1596 (w), 1585 (w), 1528 (vs), 1479 (m), 1381 (vs), 1350 (vs), 1218 (s), 1191 (vs), 1179 (vs), 1159 (s), 1091 (s), 1074 (s), 922 (m), 850 (vs), 809 (s), 761 (s), 735 (s), 708 (s), 669 (m), 577 (m), 550 (m). **HRMS** for C₁₆H₁₅NO₅S (333.0671): found: 334.0751 [M+H]⁺.

Synthesis of 2-[hydroxy(phenyl)methyl]-6-iodo-4-nitrophenyl 4-methylbenzenesulfonate (**27c**)

Prepared according to **TP 5** from 2,6-diiodo-4-nitrophenyl 4-methylbenzenesulfonate (**1r**) (529 mg, 1.00 mmol), PhMgCl (0.65 mL, 1.1 mmol, 1.6 M in THF) and benzaldehyde (127 mg, 1.20 mmol). Purification by flash chromatography (pentane/diethyl ether = 4:1) furnished title compound **27c** as a light yellow solid (445 mg, 85%).

mp.: 156-158 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.51 (d, ³J(H,H) = 2.8 Hz, 1 H), 8.37 (d, ³J(H,H) = 2.8 Hz, 1 H), 7.94 (d, ³J(H,H) = 8.4 Hz, 2 H), 7.43 (d, ³J(H,H) = 8.4 Hz, 2 H), 7.38-7.27 (m, 5 H), 6.42 (s_{br}, 1 H), 3.12 (s_{br}, 1 OH), 2.50 (s, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 151.5, 146.8, 146.6, 142.3, 141.3, 134.3, 133.0, 130.2, 129.0, 128.7, 128.0, 126.1, 125.1, 91.1, 70.0, 21.9. **MS** (70 eV, EI), *m/z* (%): 525 (0.6) [M⁺], 508 (9), 443 (15), 428 (35), 415 (29), 370 (100), 369 (14), 352 (52), 321 (9), 305 (9), 292 (10), 155 (14), 139 (18), 105 (29), 91 (81), 77 (28). **IR** (KBr): $\tilde{\nu}$ = 3436 (m), 1526 (vs), 1367 (s), 1352 (vs), 1179 (s), 1088 (s), 846 (m), 728 (vs), 701 (m), 570 (m). **HRMS** for C₂₀H₁₆INO₆S (524.9743): found: 524.9745.

Synthesis of 2-allyl-6-iodo-4-nitrophenyl 4-methylbenzenesulfonate (**27d**)

Prepared according to **TP 5** from 2,6-diiodo-4-nitrophenyl 4-methylbenzenesulfonate (**1r**) (545 mg, 1.00 mmol), PhMgCl (0.65 mL, 1.1 mmol, 1.6 M in THF), CuCN·2LiCl (1.1 mL, 1.1 mmol, 1.0 M in THF) and allyl bromide (0.17 mL, 1.6 mmol). Purification by flash chromatography (pentane/diethyl ether = 19:1) furnished title compound **27d** as a colourless oil (401 mg, 87%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.50 (d, ⁴J(H,H) = 2.8 Hz, 1 H), 8.13 (d, ⁴J(H,H) = 2.8 Hz, 1 H), 7.92 (d, ³J(H,H) = 8.4 Hz, 2 H), 7.40 (d, ³J(H,H) = 8.4 Hz, 2 H), 5.92-5.79 (m, 1 H), 5.25-5.16 (m, 2 H), 3.60 (d, ³J(H,H) = 6.6 Hz, 1 H), 2.49 (s, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 153.4, 146.4, 146.1, 137.9, 134.0, 133.8, 133.3, 130.1, 128.4, 125.9, 119.0, 91.7, 35.8, 21.8. **MS** (70 eV, EI), *m/z* (%): 459 (6) [M⁺], 304 (31), 287 (31), 258 (9), 177 (1), 155 (100), 139 (4), 91 (99), 77 (11), 65 (14). **IR** (KBr): $\tilde{\nu}$ = 3081 (w), 1596 (w), 1528 (vs), 1425 (m), 1369 (s), 1345 (vs), 1311 (w), 1238 (w), 1200 (s), 1181 (s), 1178 (vs), 1145 (w), 1090 (m), 1076 (s), 924 (m), 841 (vs), 814 (w), 759 (s), 730 (vs), 669 (s), 573 (m), 545 (m). **HRMS** for C₁₆H₁₄I₂NO₅S (458.9637): found: 458.9626. C₁₆H₁₄I₂NO₅S: required: C: 41.84; H: 3.07; N: 3.05; found: C: 42.12; H: 3.42; N: 3.04.

Synthesis of di(*tert*-butyl) 2-allyl-4-nitrophenylimidodicarbonate (**27e**)

Prepared according to **TP 5** from di(*tert*-butyl) 2-iodo-4-nitrophenylimidodicarbonate (**1t**) (446 mg, 1.00 mmol), PhMgCl (0.65 mL, 1.1 mmol, 1.6 M in THF), CuCN·2LiCl (1.1 mL, 1.1 mmol, 1.0 M in THF) and allyl bromide (0.17 mL, 1.6 mmol). Purification by flash chromatography (pentane/diethyl ether = 9:1) furnished title compound **27e** as a colourless oil (220 mg, 61%).

¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 8.14 (d, $^4J(\text{H,H})$ = 2.7 Hz, 1 H), 8.08 (dd, $^3J(\text{H,H})$ = 8.4 Hz, $^4J(\text{H,H})$ = 2.7 Hz, 1 H), 7.25 (d, $^3J(\text{H,H})$ = 8.4 Hz, 1 H), 5.91-5.80 (m, 1 H), 5.22-5.14 (m, 2 H), 3.35 (d, $^3J(\text{H,H})$ = 6.6 Hz, 2 H), 1.39 (s, 18 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 150.8, 147.6, 144.1, 140.0, 134.3, 130.1, 125.2, 122.5, 118.7, 89.1, 84.0, 35.7, 28.3. **MS** (FAB, NBA): m/z (%): 401 (32) [M+Na]⁺, 379 (8) [M+H]⁺. **MS** (70 eV, EI), m/z (%): 278 (0.1) [M-Boc]⁺, 269 (1), 222 (11), 207 (8), 178 (7), 153 (14), 136 (20), 107 (21), 89 (30), 77 (63), 57 (100). **IR** (KBr): $\tilde{\nu}$ = 2981 (m), 1796 (vs), 1759 (s), 1723 (s), 1527 (vs), 1480 (m), 1394 (m), 1369 (vs), 1349 (vs), 1315 (s), 1276 (vs), 1251 (vs), 1154 (vs), 1116 (vs), 1099 (vs), 1006 (m), 869 (w), 851 (w), 832 (w), 812 (w), 778 (w). **HRMS** for C₁₉H₂₆N₂O₆ (401.1688 [M+Na]⁺): found: 401.1692 [M+Na]⁺.

Synthesis of {5-nitro-2-[(*E*)-1-pyrrolidinyldiazenyl]phenyl}(phenyl)methanol (**27f**)

Prepared according to **TP 5** from 1-[(*E*)-(2-iodo-4-nitrophenyl)diazenyl]pyrrolidine (**1u**) (346 mg, 1.00 mmol), PhMgCl (0.65 mL, 1.1 mmol, 1.6 M in THF), and benzaldehyde (168 mg, 1.50 mmol) in a THF/NMP-mixture 3:1 at -55 °C. Purification by flash chromatography (pentane/diethyl ether = 2:1) furnished title compound **27f** as a yellow solid (159 mg, 58%).

mp.: 171-171.5 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.22 (d, $^4J(\text{H,H})$ = 2.7 Hz, 1 H), 7.94 (dd, $^3J(\text{H,H})$ = 8.9 Hz, $^4J(\text{H,H})$ = 2.7 Hz, 1 H), 7.46 (d, $^4J(\text{H,H})$ = 8.9 Hz, 1 H), 7.29-7.08 (m, 5 H), 6.31 (s, 1 H), 3.86 (br_t, $^3J(\text{H,H})$ = 6.6 Hz, 2 H), 3.49 (br_t, $^3J(\text{H,H})$ = 6.6 Hz, 2 H), 2.00-1.91 (m, 4 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 152.4, 144.0, 143.4, 137.8,

127.9, 126.8, 126.4, 123.1, 123.0, 116.1, 72.5, 51.4, 47.1, 23.5, 23.1. **MS** (70 eV, EI), m/z (%): 326 (1) [M^+], 308 (8), 256 (7), 242 (41), 210 (56), 181 (544), 164 (44), 152 (30), 105 (8), 85 (100), 79 (12). **IR** (KBr): $\tilde{\nu}$ = 3400 (m), 1599 (w), 1581 (m), 1506 (vs), 1396 (vs), 1326 (vs), 1300 (vs), 1289 (vs), 1267 (vs), 1233 (s), 1084 (m), 1036 (m), 913 (w), 843 (m), 739 (w), 702 (w). **HRMS** for $C_{17}H_{18}N_4O_3$ (326.1379): found: 326.1397.

Synthesis of 1-[(*E*)-(2-allyl-4-nitrophenyl)diazenyl]pyrrolidine (**27g**)

Prepared according to **TP 5** from 1-[(*E*)-(2-allyl-4-nitrophenyl)diazenyl]pyrrolidine (**1u**) (346 mg, 1.00 mmol), PhMgCl (0.65 mL, 1.1 mmol, 1.6 M in THF), CuCN·2LiCl (1.1 mL, 1.1 mmol, 1.0 M in THF) and allyl bromide (0.17 mL, 1.6 mmol) in a THF/NMP-mixture 3:1 at $-55\text{ }^{\circ}\text{C}$. Purification by flash chromatography (pentane/diethyl ether = 4:1) furnished title compound **27g** as a yellow solid (159 mg, 61%).

mp.: 88.5-89 $^{\circ}\text{C}$. **$^1\text{H-NMR}$** (300 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): δ = 8.06 (d, $^4J(\text{H,H})$ = 2.7 Hz, 1 H), 8.00 (dd, $^3J(\text{H,H})$ = 8.9 Hz, $^4J(\text{H,H})$ = 2.7 Hz, 1 H), 7.49 (d, $^4J(\text{H,H})$ = 8.9 Hz, 1 H), 6.06-5.93 (m, 1 H), 5.13-5.04 (m, 2 H), 3.98 (br_t, 2 H), 3.69 (br_t, 2 H), 3.63 (d, $^3J(\text{H,H})$ = 6.6 Hz, 2 H), 2.10-2.03 (m, 4 H). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): δ = 153.7, 144.4, 136.4, 135.1, 125.3, 122.6, 116.3, 116.2, 51.4, 47.0, 35.5, 23.9, 23.4. **MS** (70 eV, EI), m/z (%): 259 (4) [M^+], 231 (3), 217 (3), 190 (18), 145 (12), 131 (7), 115 (100), 104 (7), 89 (7), 70 (7). **IR** (KBr): $\tilde{\nu}$ = 2975 (w), 1636 (w), 1582 (m), 1503 (vs), 1455 (m), 1389 (vs), 1325 (vs), 1305 (vs), 1268 (vs), 1231 (s), 1101 (m), 915 (m), 898 (m), 832 (w), 757 (w). **HRMS** for $C_{13}H_{16}N_4O_2$ (260.1273): found: 260.1297.

Synthesis of {5-nitro-2-[1-pyrrolidinyl diazenyl]phenyl}(phenyl)methanone (**27h**)

Prepared according to **TP 5** from 1-[(*E*)-(2-allyl-4-nitrophenyl)diazenyl]pyrrolidine (**1u**) (346 mg, 1.00 mmol), PhMgCl (0.65 mL, 1.1 mmol, 1.6 M in THF), CuCN·2LiCl (1.1 mL,

1.1 mmol, 1.0 M in THF) and benzoyl bromide (370 mg, 2.00 mmol) in a THF/NMP-mixture 3:1 at -55°C . Purification by flash chromatography (pentane/diethyl ether = 3:1) furnished title compound **27h** as a yellow solid (159 mg, 75%).

mp.: $172.5\text{--}173^{\circ}\text{C}$. **$^1\text{H-NMR}$** (400 MHz, CDCl_3 , 25°C): δ = 8.30–8.26 (m, 2 H), 7.73–7.69 (m, 2 H), 7.62 (d, $^3J(\text{H,H})$ = 8.9 Hz, 1 H), 7.51 (tt, $^3J(\text{H,H})$ = 7.5 Hz, $^4J(\text{H,H})$ = 2.0 Hz, 1 H), 7.40–7.36 (m, 2 H), 3.74 (br_t, 2 H), 3.09 (br_t, 2 H), 1.87–1.81 (m, 4 H). **$^{13}\text{C-NMR}$** (100 MHz, CDCl_3 , 25°C): δ = 195.9, 154.3, 144.2, 137.7, 133.5, 132.7, 129.3, 128.3, 125.9, 124.8, 119.1, 51.3, 46.9, 23.7, 23.1. **MS** (70 eV, EI), m/z (%): 324 (3) [M^+], 254 (36), 226 (12), 195 (7), 180 (100), 152 (37), 139 (6), 105 (41), 77 (40). **IR** (KBr): $\tilde{\nu}$ = 1667 (vs), 1597 (m), 1578 (w), 1511 (s), 1398 (vs), 1333 (vs), 1306 (vs), 1270 (vs), 1147 (m), 970 (m), 862 (w), 713 (m). **HRMS** for $\text{C}_{17}\text{H}_{16}\text{N}_4\text{O}_3$ (324.1222): found: 324.1226.

Synthesis of 1-allyl-5-nitrobenzophenone (**27i**)

Prepared according to **TP 5** from 3,5-diiodo-2,6-dimethyl-nitrobenzene (**1n**) (352 mg, 1.00 mmol), PhMgCl (0.65 mL, 1.1 mmol, 1.6 M in THF), $\text{CuCN}\cdot 2\text{LiCl}$ (1.1 mL, 1.1 mmol, 1.0 M in THF) and allyl bromide (0.17 mL, 1.50 mmol) at -78°C . Reaction time 1 h. Purification by flash chromatography (pentane/diethyl ether = 19:1) furnished title compound **27i** as a yellow oil (144 mg, 54%).

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25°C): δ = 8.25 (dd, $^3J(\text{H,H})$ = 8.4 Hz, $^4J(\text{H,H})$ = 2.2 Hz, 1 H), 8.15 (d, $^4J(\text{H,H})$ = 2.2 Hz, 1 H), 7.79–7.75 (m, 2 H), 7.51 (tt, $^3J(\text{H,H})$ = 7.5 Hz, $^4J(\text{H,H})$ = 1.4 Hz, 1 H), 7.54–7.46 (m, 3 H), 5.91–5.77 (m, 1 H), 5.07–4.96 (m, 2 H), 3.53–3.50 (m, 2 H). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3 , 25°C): δ = 196.1, 146.9, 146.3, 140.1, 136.9, 135.3, 134.5, 131.8, 130.5, 129.2, 125.2, 123.7, 118.3, 37.7. **MS** (70 eV, EI), m/z (%): 267 (30) [M^+], 252 (100), 237 (15), 220 (18), 206 (29), 202 (16), 189 (19), 165 (32), 115 (53), 105 (56), 77 (90), 51 (21). **IR** (KBr): $\tilde{\nu}$ = 1669 (vs), 1610 (w), 1596 (w), 1581 (w), 1525 (vs), 1449 (m), 1350 (vs), 1316 (m), 1261 (s), 1075 (w), 999 (w), 962 (w), 920 (m), 869 (m), 796 (m), 740 (m), 703 (m), 642 (m). **HRMS** for $\text{C}_{16}\text{H}_{13}\text{NO}_3$ (267.0895): found: 267.0899.

Synthesis of (5-iodo-2,4-dimethyl-3-nitrophenyl)(phenyl)methanol (**27j**)

Prepared according to **TP 5** from 3,5-diiodo-2,6-dimethyl-nitrobenzene (**1s**) (402 mg, 1.00 mmol), PhMgCl (0.65 mL, 1.1 mmol, 1.6 M in THF), and benzaldehyde (168 mg, 1.50 mmol) at $-40\text{ }^{\circ}\text{C}$. Exchange was finished after 30 min. Reaction time 1 h. Purification by flash chromatography (pentane/diethyl ether = 19:1) furnished title compound **27j** as a yellow oil (159 mg, 58%).

^1H -NMR (300 MHz, CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ = 8.15 (s, 1 H), 7.30-7.13 (m, 5 H), 5.75 (s, 1 H), 2.46 (s, 1 OH), 2.27 (s, 3 H), 1.88 (s, 3 H). **^{13}C -NMR** (75 MHz, CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ = 152.6, 142.2, 141.1, 138.0, 131.1, 128.9, 128.4, 127.1, 126.4, 98.7, 72.7, 23.2, 13.6. **MS** (70 eV, EI), m/z (%): 383 (81) [M^+], 348 (62), 303 (44), 288 (12), 221 (12), 193 (36), 165 (30), 127 (18), 105 (100), 77 (56). **IR** (KBr): $\tilde{\nu}$ = 3350 (m), 1531 (vs), 1454 (s), 1382 (s), 1359 (vs), 1164 (m), 1059 (m), 1016 (m), 891 (w), 767 (m), 742 (s), 700 (s). **HRMS** for $\text{C}_{15}\text{H}_{14}\text{INO}_3$ (383.0018): found: 383.0018.

Synthesis of compounds 29

Synthesis of ethyl 4-nitro[1,1'-biphenyl]-2-carboxylate (**29a**)

Prepared according to **TP 6** from ethyl 2-iodo-5-nitrobenzoate (**1i**) (321 mg, 1.00 mmol), PhMgCl (0.65 mL, 1.1 mmol, 1.7 M in THF), ZnBr_2 (1.1 mL, 1.1 mmol, 1.0 M in THF), $\text{Pd}(\text{dba})_2$ (29 mg, 0.05 mmol) and tfp (23 mg, 0.10 mmol). Reaction time: 4 h at $20\text{ }^{\circ}\text{C}$. Purification by flash chromatography (pentane/diethyl ether = 19:1) furnished biphenyl **29a** as a colourless solid (184 mg, 68%).

mp.: $64.8\text{--}66.0\text{ }^{\circ}\text{C}$. **^1H -NMR** (300 MHz, CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ = 8.60 (d, 1 H), 8.27 (dd, $^4J(\text{H,H}) = 2.7\text{ Hz}$, $^3J(\text{H,H}) = 8.7\text{ Hz}$, 1 H), 7.48 (d, 1 H), 7.37-7.36 (m, 2 H), 7.35-7.34 (m, 2 H), 7.26-7.23 (m, 1 H), 4.07 (q, $^3J(\text{H,H}) = 7.1\text{ Hz}$, 2 H), 0.97 (t, $^3J(\text{H,H}) = 7.1\text{ Hz}$, 3 H). **^{13}C -NMR** (75 MHz, CDCl_3 , $25\text{ }^{\circ}\text{C}$): δ = 165.6, 147.6, 145.8, 138.3, 131.6, 130.8, 127.4, 127.3, 127.1, 124.5, 124.0, 60.8, 12.6. **MS** (70 eV, EI), m/z (%): 271 (61) [M^+], 243 (18), 226 (100), 210 (3), 196 (2), 180 (39), 168 (2), 152 (37), 139 (12), 126 (4), 115 (3). **IR** (KBr): $\tilde{\nu}$ = 1720 (vs), 1609(w), 1575 (w), 1524 (s), 1349 (s), 1283 (s), 1236 (w), 1143 (m), 1115 (w), 777 (m), 759 (w), 742 (m), 699 (m). **$\text{C}_{15}\text{H}_{13}\text{NO}_4$** : required: C: 66.41; H: 4.83; N: 5.16; found: C: 66.57; H: 4.89; N: 5.24.

Synthesis of ethyl 4'-cyano-4-nitro[1,1'-biphenyl]-2-carboxylate (**29b**)

Prepared according to **TP 6** from ethyl 2-iodo-5-nitrobenzoate (**1i**) (321 mg, 1.00 mmol), PhMgCl (0.65 mL, 1.1 mmol, 1.7 M in THF), ZnBr₂ (1.1 mL, 1.1 mmol, 1.0 M in THF), Pd(dba)₂ (29 mg, 0.05 mmol), tfp (23 mg, 0.10 mmol) and 4-iodo-benzonitrile (**21h**) (458 mg, 2.00 mmol). Reaction time: 2 h at 20 °C. Purification by flash chromatography (pentane/diethyl ether = 2:1) yielded biphenyl **29b** as a pale yellow solid (245 mg, 83%).

mp.: 105-106 °C. **¹H-NMR** (300 MHz, CDCl₃, 25 °C): δ = 8.77 (d, ⁴*J*(H,H) = 2.8 Hz, 1 H), 8.40 (dd, ³*J*(H,H) = 8.4 Hz, ⁴*J*(H,H) = 2.8 Hz, 1 H), 7.72 (d, ³*J*(H,H) = 8.8 Hz, 2 H), 7.53 (d, ³*J*(H,H) = 8.4 Hz, 1 H), 7.40 (d, ³*J*(H,H) = 8.8 Hz, 2 H), 4.20 (q, ³*J*(H,H) = 7.1 Hz, 2 H), 1.12 (d, ³*J*(H,H) = 7.1 Hz, 3 H). **¹³C-NMR** (75 MHz, CDCl₃, 25 °C): δ = 165.3, 147.4, 146.8, 144.1, 132.0, 131.9, 131.8, 128.9, 126.0, 125.5, 118.3, 112.2, 62.0, 13.7. **MS** (70 eV, EI), *m/z* (%): 296 (51) [M⁺], 268 (53), 251 (100), 205 (32), 177 (28), 150 (12), 140 (8). **IR** (KBr): $\tilde{\nu}$ = 2228 (s), 1710 (vs), 1609 (s), 1525 (vs), 1474 (s), 1419 (m), 1353 (vs), 1304 (s), 1283 (vs), 1262 (m), 1153 (s), 1143 (s), 1006 (s), 837 (m), 733 (m). **HRMS** for C₁₆H₁₂N₂O₄ (296.0797): found: 296.0865. C₁₆H₁₂N₂O₄: required: C: 64.86; H: 4.08; N: 9.20; found: C: 65.14; H: 4.09; N: 9.20.

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