Magnesiated Unsaturated Silylated Cyanohydrins as Synthetic Equivalents of Aromatic and Heterocyclic Grignard Reagents Bearing a Ketone or an Aldehyde

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Supporting Information

General considerations

Unless otherwise indicated, all reactions were carried out with magnetic stirring and, if air or moisture sensitive, in flame-dried glassware under argon. Syringes used to transfer reagents and solvent were purged with argon prior to use. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC).

Preparation of the reagent *i*-PrMgCl·LiCl:

Magnesium turnings (110 mmol) and anhydrous LiCl (100 mmol) were placed in an Ar-flushed flask and THF (25 mL) was added. A solution of *i*-PrCl (100 mmol) in THF (25 mL) was slowly added at rt. The reaction starts within a few minutes. After addition, the reaction mixture was stirred for 12 h at rt. The grey solution of *i*-PrMgCl·LiCl was transferred to another flask under Ar and removed in this way from excess of magnesium. A yield of ca. 95-98 % of *i*-PrMgCl·LiCl is obtained.

1-[3-(Pyrrolidin-1-ylazo)-phenyl]-ethanone was prepared from the commercially available 3-aminoacetophenone. A solution of 3-aminoacetophenone (6.8 g, 50.0 mmol) in 25 mL of conc. HCl was cooled in an ice bath while a solution of NaNO₂ (5.2 g, 75.0 mmol) in 100 mL of cold water was added dropwise. The resulting solution of the diazonium salt was stirred at 0 °C for 30 min and then added at once to a solution of pyrrolidine (23.8 g, 250 mmol) and K₂CO₃ (34.5 g, 250 mmol) in 1:2 acetonitrile/water (150 mL). The reaction mixture was stirred for 30 min at 0 °C and was

extracted with CH_2Cl_2 (3×150 mL). The organic layer was washed twice with brine, dried (MgSO_4), filtered, and concentrated by evaporation. The crude product was purified by flash chromatography over silica gel giving the pure product (10.1 g, 93 %) as a dark brown liquid. ^1H NMR (CDCl_3 , 300 MHz): 7.94 (t, $J = 1.8$ Hz, 1 H), 7.69 (d, $J = 8.0$ Hz, 1 H), 7.58 (d, $J = 8.0$ Hz, 1 H), 7.37 (t, $J = 8.0$ Hz, 1 H), 3.77 (br s, 4 H, CH_2N), 2.58 (s, 3 H), 2.00 (br, 4 H, CH_2); ^{13}C NMR (CDCl_3 , 75 MHz): 198.3, 151.7, 137.8, 128.9, 124.8, 124.6, 120.3, 26.7, 23.7; IR (film): 3066, 2974, 2874, 1683, 1586, 1408, 1356, 1316, 1272, 1211 cm^{-1} ; MS (EI, 70 ev), m/z (%): 2217 (M^+ , 26 %), 147 ($\text{M}-\text{C}_4\text{H}_8\text{N}$, 60 %), 119 ($\text{M}-\text{C}_4\text{H}_8\text{N}-\text{N}_2$, 100 %), 91 (70 %); HRMS (EI): calcd. for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}$: 217.1215, found: 217.1218.

3-Iodoacetophenone. 1-[3-(Pyrrolidin-1-ylazo)-phenyl]-ethanone (1.1 g, 5.0 mmol) was dissolved in freshly distilled iodomethane (15 mL) and heated in a sealed tube at 120 °C for 24 h. The reaction mixture was cooled, diluted with dichloromethane, and filtered through a pad of Celite and silica gel. Concentration and purification of the crude product by column chromatography (pentane:ether = 1:1) provided the product (1.0 g, 83 %) as a dark brown liquid. ^1H NMR (CDCl_3 , 300 MHz): 8.26 (t, $J = 1.8$ Hz, 1 H), 7.84-7.91 (m, 2 H), 7.19 (t, $J = 8.0$ Hz, 1 H), 2.56 (s, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 196.5, 141.8, 138.8, 137.3, 130.3, 127.4, 94.4, 26.5; IR (film): 3059, 3003, 2922, 1684, 1562, 1415, 1357, 1251, 1058 cm^{-1} ; MS (EI, 70 ev): 246 (M^+ , 64 %), 231 (100 %), 203 (42 %), 76 (25 %); HRMS (EI): calcd. for $\text{C}_8\text{H}_7\text{IO}$: 245.9542, found: 245.9525.

General Procedure A for the Preparation of 2-(3-iodo-phenyl)-2-trimethylsilyloxy-propionitrile (2b).

To a stirred solution of 3-iodoacetophenone (246 mg, 1.00 mmol) and CsF (30.4 mg, 0.20 mmol) in dry CH_3CN (1.5 mL) was added TMSCN (150 mg, 1.50 mmol) dropwise. The resulting reaction mixture was continuously stirred at room temperature and the reaction progress was followed by TLC. After 2 h, the reaction mixture was diluted with water (10 mL) and extracted with ether (2×15 mL). The organic layer was washed twice with brine, dried (MgSO_4), filtered, and concentrated by evaporation. The crude product **2b** (338 mg, 98 %) was obtained as colorless oil and used directly in the next step. ^1H NMR (CDCl_3 , 300 MHz): 7.85 (s, 1 H), 7.67 (d, $J = 8.2$ Hz, 1 H), 7.48 (d, $J = 8.2$ Hz, 1 H), 7.11 (t, $J = 8.2$ Hz, 1 H), 1.81 (s, 3 H), 0.19 (s, 9 H); ^{13}C NMR (CDCl_3 , 75 MHz): 144.3, 137.8, 133.7, 130.3, 123.9, 121.1, 94.3, 70.8, 33.5, 1.1; IR (film): 3341, 3060, 2963,

2228, 1682, 1562, 1415, 1357, 1252, 1059, 995 cm^{-1} ; MS (EI, 70 eV): 345 (M^+ , 32 %), 330 (100 %), 303 (58 %), 231 (47 %), 176 (74 %), 161 (21 %), 75 (42 %); HRMS (EI): calcd. for $\text{C}_{12}\text{H}_{16}\text{INO}_2\text{Si}$: 345.0046, found: 345.0036.

General Procedure B for the Preparation of 1-[3-(naphthalene-1-carbonyl)-phenyl]-ethanone (5c).

To a solution of **2b** (1035 mg, 3.00 mmol) in THF (2.0 mL) was slowly added *i*-PrMgCl·LiCl (2.2 mL, 3.30 mmol, 1.5 M in THF) at $-20\text{ }^{\circ}\text{C}$. The reaction mixture was continuously stirred at $-20\text{ }^{\circ}\text{C}$ for 1 h. A complete conversion to the Grignard reagent was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. $\text{CuCN}\cdot 2\text{LiCl}$ (3.00 mmol, 3.0 mL, 1.0 M in THF) was added dropwise at $-40\text{ }^{\circ}\text{C}$ and then the reaction mixture was slowly warmed to $-30\text{ }^{\circ}\text{C}$ over 40 min. 1-Naphthoyl chloride (860 mg, 4.50 mmol) in THF (0.7 mL) was added and the mixture was stirred at $-30\text{ }^{\circ}\text{C}$ for 1 h and then warmed to rt and stirred again for 0.5 h. TBAF (4.5 mL, 1.0 M in THF) was added. After 30 min, HCl (3.0 mL, 2.0 M) was added and the reaction mixture was stirred for another 2 h before the addition of aq. NH_3 (12 mL). The aqueous phase was extracted with diethyl ether ($2 \times 60\text{ mL}$). The combined organic layers were washed with brine (60 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 7:3) yielded the pure product **5c** (592 mg, 72 %) as a yellow solid; m.p.: $117.0\text{--}119.0\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 300 MHz): 8.44 (s, 1 H), 8.17 (d, $J = 8.0\text{ Hz}$, 1 H), 8.12 (d, $J = 8.0\text{ Hz}$, 1 H), 8.00 (t, $J = 8.0\text{ Hz}$, 2 H), 7.92 (d, $J = 8.0\text{ Hz}$, 1 H), 7.49–7.59 (m, 5 H), 2.60 (s, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 197.2, 197.0, 138.8, 137.3, 135.5, 134.7, 133.8, 132.4, 131.9, 130.9, 129.8, 128.8, 128.5, 128.2, 127.5, 126.6, 125.5, 124.3, 26.7; IR (KBr): 3055, 1690, 1655, 1597, 1508, 1356, 1285, 1239, 1200, 1149 cm^{-1} ; MS (EI, 70 eV): 274 (M^+ , 91 %), 259 (17 %), 231 (34 %), 202 (13 %), 155 (100 %), 127 (78 %); HRMS (EI): calcd. for $\text{C}_{19}\text{H}_{14}\text{IO}_2$: 274.0994, found: 274.0981.

2-(4-Iodo-phenyl)-2-trimethylsilanyloxy-propionitrile (2a) was prepared from the commercially available product 3-iodoacetophenone (246 mg, 1.00 mmol) according to the general procedure A and yielding the pure product **2a** (328 mg, 95 %) as colorless oil and used directly in the next step.

^1H NMR (CDCl_3 , 300 MHz): 7.66 (d, J = 8.4 Hz, 2 H), 7.22 (d, J = 8.4 Hz, 2 H), 1.75 (s, 3 H), 0.12 (s, 9 H); ^{13}C NMR (CDCl_3 , 75 MHz): 142.0, 137.8, 126.5, 121.1, 94.4, 71.2, 33.5, 1.1; IR (film): 2991, 2960, 2233, 1587, 1485, 1392, 1254, 1119, 995 cm^{-1} ; MS (EI, 70 eV): 345 (M^+ , 24 %), 330 (94 %), 303 (45 %), 231 (85 %), 176 (52 %), 161 (17 %), 129 (18 %), 102 (18 %), 75 (100 %); HRMS (EI): calcd. for $\text{C}_{12}\text{H}_{16}\text{INO}$: 345.0046, found: 345.0051.

General Procedure C for the Preparation of 3-(4-acetyl-phenyl)-cyclohex-2-enone (5a).

To a solution of **2a** (518 mg, 1.50 mmol) in THF (1.0 mL) was slowly added *i*-PrMgCl·LiCl (0.8 mL, 1.65 mmol, 2.0 M in THF) at $-20\text{ }^{\circ}\text{C}$. The reaction mixture was continuously stirred at $-20\text{ }^{\circ}\text{C}$ for 60 min. A complete conversion to the Grignard reagent was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. $\text{CuCN}\cdot 2\text{LiCl}$ (1.50 mmol, 1.5 mL, 1.0 M in THF) was added dropwise at $-40\text{ }^{\circ}\text{C}$ and then the reaction mixture was slowly warmed to $-30\text{ }^{\circ}\text{C}$ over 40 min. 3-Iodo-cyclohex-2-enone (333 mg, 1.50 mmol) in THF (0.7 mL) was added and the reaction mixture was stirred at $-30\text{ }^{\circ}\text{C}$ for 2.5 h. The reaction mixture was then gradually warmed to rt and stirred again for 1 h. TBAF (2.3 mL, 1.0 M in THF) was added. After 30 min, HCl (1.5 mL, 2.0 M) was added and the reaction mixture was stirred for 2 h before the addition of aq. NH_3 (6 mL). The aqueous phase was extracted with diethyl ether ($2 \times 30\text{ mL}$). The combined organic layers were washed with brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 3:7) yielded the pure product **5a** (266 mg, 83 %) as a yellow powder; m.p.: $94.5\text{--}96.0\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 300 MHz): 7.96 (d, J = 8.4 Hz, 2 H), 7.58 (d, J = 8.4 Hz, 2 H), 6.42 (s, 1 H), 2.72–2.80 (m, 2 H), 2.60 (s, 3 H), 2.44–2.52 (m, 2 H), 2.10–2.21 (m, 2 H); ^{13}C NMR (CDCl_3 , 75 MHz): 199.5, 197.3, 158.2, 143.3, 137.8, 128.7, 126.8, 126.3, 37.2, 28.0, 26.7, 22.7; IR (KBr): 3045, 2949, 1680, 1667, 1604, 1407, 1351, 1330, 1272, 1189, 965 cm^{-1} ; MS (EI, 70 eV): 214 (M^+ , 100 %), 199 (31 %), 186 (25 %), 171 (69 %), 144 (72 %), 128 (16 %), 115 (38 %); HRMS (EI): calcd. for $\text{C}_{14}\text{H}_{14}\text{O}_2$: 214.0994, found: 214.0986.

1-[4-(Furan-2-carbonyl)-phenyl]-ethanone (5b) was prepared from **2a** (518 mg, 1.50 mmol) according to the general procedure **B** and yielding the pure product **5b** (273 mg, 85 %). A white solid; m.p.: 90.2-91.0 °C. ¹H NMR (CDCl₃, 300 MHz): 8.05 (d, *J* = 8.4 Hz, 2 H), 8.01 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 1.8 Hz, 1 H), 7.25 (d, *J* = 4.0 Hz, 1 H), 6.60 (dd, *J* = 1.8, 4.0 Hz, 1 H), 2.64 (s, 3 H); ¹³C NMR (CDCl₃, 75 MHz): 197.4, 193.8, 152.1, 147.5, 140.8, 139.7, 129.4, 128.2, 121.0, 112.5, 26.8; IR (KBr): 3156, 3138, 3066, 1687, 1636, 1568, 1466, 1298, 1269, 1017, 964 cm⁻¹; MS (EI, 70 ev): 214 (M⁺, 47 %), 199 (100 %), 171 (13 %), 147 (7 %), 115 (16 %), 95 (21 %); HRMS (EI): calcd. for C₁₃H₁₀O₃: 214.0630, found: 214.0646.

2-(5-Iodo-furan-2-yl)-2-trimethylsilanyloxy-butynitrile (2c) was prepared from 1-(5-iodo-furan-2-yl)-propan-1-one (1.25 g, 5.0 mmol) according to the general procedure **A** and yielding the pure product **2c** (1.11 g, 89 %) as a colorless oil and used directly in the next step. ¹H NMR (CDCl₃, 300 MHz): 6.52 (d, *J* = 3.5 Hz, 1 H), 6.42 (d, *J* = 3.5 Hz, 1 H), 2.01-2.22 (m, 2 H), 1.00 (t, *J* = 7.5 Hz, 3 H), 0.07 (s, 9 H); ¹³C NMR (CDCl₃, 75 MHz): 156.3, 121.1, 118.9, 111.8, 89.0, 70.6, 34.6, 8.4, 0.5; IR (KBr): 1461, 1478, 1254, 1100 cm⁻¹; MS (EI, 70 ev): 349 (M⁺, 14 %), 334 (10 %), 320 (89 %), 221 (100 %), 185 (15 %); HRMS (EI): calcd. for C₁₁H₁₆INO₂Si: 348.9995, found: 349.0006.

General Procedure D for the Preparation of 1-[5-(furan-2-carbonyl)-furan-2-yl]-propan-1-one (5d).

To a solution of **2c** (125 mg, 0.5 mmol) in THF (0.5 mL) was slowly added *i*-PrMgCl·LiCl (0.35 mL, 0.55 mmol, 1.55 M in THF) at -78 °C. The reaction mixture was stirred at -78 °C for 45 min. A complete conversion to the Grignard reagent was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. THF (1.0 mL) and the solution of CuCN·2LiCl (0.55 mmol, 0.55 mL, 1.0 M in THF) were added dropwise at -78 °C and then the reaction mixture was stirred for 30 min. 2-Furoyl chloride (0.75 mmol) in THF (0.5 mL) was added and the mixture was stirred at -30 °C for 1 h and then warmed to rt and stirred again for 1 h. TBAF (0.7 mL, 1.0 M in THF) was added. After 30 min, HCl (0.45 mL, 2.0 M) was added and the reaction mixture was stirred for another 2 h.

before the addition of aq. NH_3 (2 mL). The aqueous phase was extracted with diethyl ether (2×10 mL). The combined organic layers were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 1:1) yielded the pure product **5d** (78 mg, 72 %) as a white solid, mp: 119.9-120.5 °C. ^1H NMR (CDCl_3 , 300 MHz): 7.67 (d, $J = 1.7$ Hz, 1 H), 7.62 (d, $J = 3.5$ Hz, 1 H), 7.45 (d, $J = 3.5$ Hz, 1 H), 7.20 (d, $J = 3.5$ Hz, 1 H), 6.59 (dd, $J_1 = 3.5$ Hz, $J_2 = 1.7$ Hz, 1 H), 2.92 (q, $J = 7.1$ Hz, 2 H), 1.18 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 190.5, 168.5, 153.7, 152.2, 150.9, 147.6, 121.0, 119.5, 116.7, 112.7, 32.2, 7.6; IR (KBr): 1690, 1632, 1563, 1254 cm^{-1} ; MS (EI, 70 eV): 218 (M^+ , 61 %), 189 (100 %), 105 (7 %), 95 (73 %); HRMS (EI): calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_4$: 218.0579, found: 218.0588.

1-(5-Benzoyl-furan-2-yl)-propan-1-one (5e) was prepared from **2c** (125 mg, 0.5 mmol) according to the general procedure **E** and yielding the pure **5e** (81 mg, 71 %) as a white solid; mp: 71.5-72.0 °C. ^1H NMR (CDCl_3 , 300 MHz): 7.90-8.00 (m, 2 H), 7.52-7.59 (m, 1 H), 7.42-7.48 (m, 2 H), 7.17-7.23 (m, 2 H), 2.91 (qd, $J_1 = 7.1$ Hz, $J_2 = 1.3$ Hz, 2 H), 1.15 (td, $J_1 = 7.1$ Hz, $J_2 = 1.3$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 190.9, 182.4, 154.0, 153.0, 136.4, 133.2, 129.5, 128.6, 120.3, 116.3, 32.1, 7.5; IR (KBr): 1685, 1646, 1291, 1213 cm^{-1} ; MS (EI, 70 eV): 228 (M^+ , 51 %), 199 (100 %), 105 (67 %), 77 (43 %); HRMS (EI): calcd. for $\text{C}_{14}\text{H}_{12}\text{O}_3$: 228.0786, found: 228.0765.

3-(3-Cyano-3-trimethylsilyloxy-cyclohex-1-enyl)-4-iodo-benzoic acid ethyl ester (2d) was prepared from 4-iodo-3-(3-oxo-cyclohex-1-enyl)-benzoic acid ethyl ester¹ (370 mg, 1.00 mmol) according to the general procedure **A** and yielding the pure product **2d** (436 mg, 93 %) as a colorless oil and used directly in the next step. ^1H NMR (CDCl_3 , 300 MHz): 7.90 (d, $J = 8.4$ Hz, 1 H), 7.73 (s, 1 H), 7.60 (d, $J = 8.4$ Hz, 1 H), 5.62 (s, 1 H), 4.35 (q, $J = 7.1$ Hz, 2 H), 1.90-2.36 (m, 6 H), 1.38 (t, $J = 7.1$ Hz, 3 H), 0.25 (s, 9 H); ^{13}C NMR (CDCl_3 , 75 MHz): 165.8, 146.5, 146.2, 139.6, 130.7, 129.7, 128.7, 127.5, 121.3, 103.4, 67.1, 61.3, 36.6, 29.4, 18.9, 14.2, 1.6; IR (film): 2958, 2870, 2231, 1722, 1589, 1454, 1367, 1296, 1252, 1109, 1015, 906 cm^{-1} ; MS (EI, 70 eV): 469 (M^+ , 69 %), 454 (100 %), 441 (39 %), 427 (67 %), 408 (40 %), 379 (40 %), 334 (38 %), 296 (14 %), 215

(17 %), 187 (22 %), 152 (17 %), 75 (28 %); HRMS (EI): calcd. for $C_{19}H_{24}INO_3Si$: 469.0570, found: 469.0595.

4-(Furan-2-carbonyl)-3-(3-oxo-cyclohex-1-enyl)-benzoic acid ethyl ester (5f) was prepared from **2d** (235 mg, 0.50 mmol) according to the general procedure **B** and yielding the pure product **5f** (294 mg, 87 %) as a pale yellow solid; m.p.: 79.8-80.4 °C. 1H NMR ($CDCl_3$, 300 MHz): 8.08 (dd, J = 1.3, 8.0 Hz, 1 H), 7.98 (d, J = 1.8 Hz, 1 H), 7.61-7.66 (m, 2 H), 7.06 (d, J = 3.5 Hz, 1 H), 6.55 (dd, J = 1.8, 3.5 Hz, 1 H), 5.92 (s, 1 H), 4.39 (q, J = 7.0 Hz, 2 H), 2.55-2.62 (m, 2 H), 2.31-2.38 (m, 2 H), 1.94-2.04 (m, 2 H), 1.39 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 198.7, 183.2, 165.2, 160.9, 152.1, 147.9, 140.9, 140.0, 132.7, 129.3, 129.2, 129.0, 128.9, 121.0, 112.7, 61.6, 37.0, 31.1, 22.9, 14.2; IR (KBr): 3133, 3177, 2939, 1721, 1662, 1646, 1563, 1464, 1394, 1296, 1255, 1222, 1188, 1103 cm^{-1} ; MS (EI, 70 ev): 338 (M^+ , 13 %), 309 (50 %), 293 (28 %), 282 (100 %), 253 (25 %), 237 (98 %), 225 (30 %), 209 (28 %), 181 (50 %), 152 (50 %), 95 (43 %); HRMS (EI): calcd. for $C_{20}H_{18}O_5$: 338.1154, found: 338.1164.

3-(3-Cyano-3-trimethylsilyloxy-cyclohex-1-enyl)-4-iodo-benzonitrile (2e) was prepared from 4-iodo-3-(3-oxo-cyclohex-1-enyl)-benzonitrile¹ (323 mg, 1.00 mmol) according to the general procedure **A** and yielding the pure product **2e** (405 mg, 96 %) as colorless oil and used directly in the next step. 1H NMR ($CDCl_3$, 300 MHz): 7.96 (d, J = 8.2 Hz, 1 H), 7.37 (s, 1 H), 7.22 (d, J = 8.2 Hz, 1 H), 5.62 (s, 1 H), 1.90-2.30 (m, 6 H), 0.25 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 147.3, 145.5, 140.4, 131.8, 130.9, 128.4, 120.9, 117.8, 112.5, 103.6, 66.9, 36.5, 29.2, 18.9, 1.5; IR (film): 3060, 2958, 2232, 1658, 1585, 1456, 1254, 1188, 1112, 1032, 958 cm^{-1} ; MS (EI, 70 ev): 422 (M^+ , 22 %), 407 (72 %), 380 (100 %), 366 (8 %), 332 (14 %), 280 (11 %), 168 (11 %), 140 (19 %), 75 (31 %); HRMS (EI): calcd. for $C_{17}H_{19}IN_2OSi$: 422.0311, found: 422.0316.

4-(Furan-2-carbonyl)-3-(3-oxo-cyclohex-1-enyl)-benzonitrile (5g) was prepared from **2e** (211 mg, 0.50 mmol) according to the general procedure **B** and yielding the pure product **5g** (118 mg, 81 %) as a yellow solid; m.p.: 134.2-136.0 °C. ^1H NMR (CDCl_3 , 300 MHz): 7.60-7.76 (m, 4 H), 7.12 (d, $J = 1.8$ Hz, 1 H), 6.58 (dd, $J = 1.8, 3.5$ Hz, 1 H), 5.88 (s, 1 H), 2.52-2.62 (m, 2 H), 2.30-2.40 (m, 2 H), 1.94-2.06 (m, 2 H); ^{13}C NMR (CDCl_3 , 75 MHz): 198.2, 182.1, 159.0, 151.8, 148.1, 141.7, 140.1, 131.7, 131.3, 129.7, 129.5, 121.2, 117.4, 114.9, 113.0, 37.0, 30.9, 22.9; IR (KBr): 3131, 3036, 2946, 2236, 1670, 1646, 1563, 1464, 1390, 1309, 1190, 1031, 953 cm^{-1} ; MS (EI, 70 eV): 291 (M^+ , 8 %), 262 (94 %), 235 (100 %), 206 (83 %), 190 (17 %), 178 (39 %); HRMS (EI): calcd. for $\text{C}_{18}\text{H}_{13}\text{NO}_3$: 291.0895, found: 291.0900.

3-Iodo-1-trimethylsilanyloxy-cyclohex-2-enecarbonitrile (2f) was prepared from 3-iodo-cyclohex-2-enone (222 mg, 1.0 mmol) according to the general procedure **A** and yielding the pure product **2f** (282 mg, 88 %) as a colorless oil and used directly in the next step. ^1H NMR (CDCl_3 , 300 MHz): 6.39 (t, $J = 2.0$ Hz, 1 H), 2.54 (dt, $J_1 = 6.2$ Hz, $J_2 = 2.0$, 2 H), 2.11-2.19 (m, 1 H), 1.75-1.98 (m, 3 H), 0.22 (s, 9 H); ^{13}C NMR (CDCl_3 , 75 MHz): 136.3, 120.5, 104.4, 68.3, 38.6, 35.7, 20.8, 1.3; IR (film): 2231, 1629, 1254 cm^{-1} ; MS (EI, 70 eV): 321 (M^+ , 21%), 306 (30%), 279 (100 %), 231 (19 %), 194 (86 %); HRMS (EI): calcd. for $\text{C}_{10}\text{H}_{16}\text{INOSi}$: 321.0046; found: 321.002.

General Procedure E for the Preparation of Bicyclohexyl-1,1'-diene-3,3'-dione (5h).²

To a solution of **2f** (161 mg, 0.5 mmol) in THF (0.2 mL) was slowly added *i*-PrMgCl·LiCl (0.55 mmol, 2.00 M in THF) at -40°C . After 2 h, a complete conversion to the Grignard reagent was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. THF (1.0 mL) and $\text{CuCN}\cdot 2\text{LiCl}$ (0.55 mL, 1.0 M in THF) was added at this temperature and stirred for 15 min. 3-Iodo-cyclohex-2-enone (0.55 mmol in 0.5 mL of THF) was added and the reaction mixture was stirred continuously 4 h at -30°C . The reaction mixture was warmed up to 25°C and TBAF (0.5 mL, 1.0

M in THF) was added. After 30 min, HCl (0.5 mL, 2 M in H₂O) was added and the mixture was stirred for another 2 h before the addition of aq. NH₃ (2 mL). The aqueous phase was extracted with diethyl ether (3 × 10 mL). The organic fractions were washed with brine (10 mL), dried over Na₂SO₄ and concentrated *in vacuo*. Purification by flash chromatography (ether) yielded the pure product **5h** (71 mg, 74 %) as a white solid, mp: 100.5-101.0 °C. ¹H NMR (CDCl₃, 300 MHz): 6.27 (s, 1 H), 2.50 (dt, *J*₁ = 6.2 Hz, *J*₂ = 1.3 Hz, 2 H), 2.42 (t, *J* = 6.2 Hz, 2 H), 2.01-2.10 (m, 2 H); ¹³C NMR (CDCl₃, 75 MHz): 199.6, 156.5, 128.0, 37.4, 25.8, 22.2; IR (KBr): 1663, 1576, 1263 cm⁻¹; MS (EI, 70 ev): 190 (M⁺, 95 %), 162 (45 %), 134 (100 %), 119 (45 %), 106 (49 %).

3-Benzoyl-cyclohex-2-enone (5i)³ was prepared from **2f** (161 mg, 0.5 mmol) according to the general procedure **F** and yielding the pure **5i** (71 mg, 74 %) as a yellow oil. ¹H NMR (CDCl₃, 300 MHz): 7.70-7.77 (m, 2 H), 7.53-7.60 (m, 1 H), 7.40-7.47 (m, 2 H), 6.22 (t, *J* = 1.8 Hz, 1 H), 2.66 (dt, *J*₁ = 6.2 Hz, *J*₂ = 1.8 Hz, 2 H), 2.51 (t, *J* = 6.6 Hz, 2 H), 2.07-2.18 (m, 2 H); ¹³C NMR (CDCl₃, 75 MHz): 200.0, 197.0, 155.8, 135.5, 133.4, 132.3, 129.5, 128.6, 37.8, 25.5, 22.2; IR (film): 1680, 1658, 1448, 1255 cm⁻¹; MS (EI, 70 ev): 200 (M⁺, 40 %), 183 (15 %), 171 (8 %), 144 (10%), 105 (100 %).

4-Benzoyl-3-(3-cyano-3-trimethylsilyloxy-cyclohex-1-enyl)-benzonitrile (**6**).

To a solution of **2e** (1266 mg, 3.00 mmol) in THF (2.0 mL) was slowly added *i*-PrMgCl·LiCl (2.2 mL, 3.30 mmol, 1.5 M in THF) at -40 °C. The reaction mixture was continuously stirred at -40 °C for 60 min. A complete conversion to the Grignard reagent was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. CuCN·2LiCl (3.00 mmol, 3.0 mL, 1.0 M in THF) was added dropwise at -40 °C and then the reaction mixture was slowly warmed to -30 °C over 40 min. Benzoyl chloride (635 mg, 4.50 mmol) in THF (0.7 mL) was added and the mixture was stirred at -30 °C for 1 h and then warmed to rt and stirred for another 1 h before the addition of aq. NH₃ (5 mL). The aqueous phase was extracted with diethyl ether (2 × 30 mL). The combined organic layers were washed with brine (30 mL), dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 7:3) yielded the pure product **6** (973 mg, 81 %) as a white powder; m.p.: 122.5-123.6 °C. ¹H NMR (CDCl₃, 300 MHz): 7.70 (d, *J* = 8.0 Hz, 1 H), 7.54-7.66

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(m, 5 H), 7.38-7.48 (m, 2 H), 5.53 (s, 1 H), 2.00-2.60 (m, 2 H), 1.50-1.84 (m, 4 H), 0.14 (s, 9 H); ^{13}C NMR (CDCl_3 , 75 MHz): 196.4, 142.4, 141.3, 140.7, 136.7, 133.8, 131.5, 131.2, 129.7, 129.6, 129.4, 128.7, 120.5, 117.7, 114.2, 66.6, 36.0, 29.1, 18.5, 1.3; IR (KBr): 2967, 2233, 1673, 1598, 1449, 1280, 1254, 1100, 1032, 848 cm^{-1} ; MS (EI, 70 eV): 400 (M^+ , 9 %), 385 (7 %), 371 (98 %), 258 (100 %), 245 (31 %), 232 (13 %), 215 (18 %), 105 (18 %), 75 (49 %); HRMS (EI): calcd. for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_2\text{Si}$: 400.1607, found: 400.1591.

3-(3-Oxo-cyclohex-1-enyl)-4-(1-phenyl-vinyl)-benzonitrile (7).

To a solution of triphenylmethylphosphonium bromide (393 mg, 1.10 mmol) in THF (1.5 mL) was slowly added *n*-BuLi (0.77 mL, 1.20 mmol, 1.55 M in hexane) at -78°C . The reaction mixture was continuously stirred at -78°C for 15 min and then warmed to rt and stirred for 1 h. 3-(3-Cyano-3-trimethylsilanyloxy-cyclohex-1-enyl)-4-iodobenzoic acid ethyl ester **6** (400 mg, 1.00 mmol) in THF (1.5 mL) was added dropwise at -78°C and the reaction mixture was stirred at the same temperature for 30 min and then warmed to rt and stirred again for 3 h. TBAF (1.5 mL, 1.0 M in THF) was added. After 30 min, HCl (1.0 mL, 2.0 M) was added and the reaction mixture was stirred for 1 h before the addition of aq. NH_3 (2 mL). The aqueous phase was extracted with diethyl ether (2×15 mL). The combined organic layers were washed with brine (15 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 1:1) yielded the pure product **7** (248 mg, 83 %) as a colorless liquid. ^1H NMR (CDCl_3 , 300 MHz): 7.62 (d, $J = 8.0$ Hz, 1 H), 7.40-7.50 (m, 2 H), 7.18-7.24 (m, 3 H), 7.00-7.08 (m, 2 H), 5.87 (s, 1 H), 5.66 (d, $J = 1.0$ Hz, 1 H), 5.34 (d, $J = 1.0$ Hz, 1 H), 2.15-2.23 (m, 2 H), 2.05-2.13 (m, 2 H), 1.55-1.67 (m, 2 H); ^{13}C NMR (CDCl_3 , 75 MHz): 193.7, 159.7, 148.2, 144.7, 141.0, 140.1, 131.95, 131.91, 131.2, 130.4, 128.5, 128.3, 127.3, 118.1, 118.0, 112.1, 36.8, 30.0, 22.5; IR (film): 2946, 2229, 1669, 1493, 1447, 1346, 1325, 1252, 1189, 1133, 963 cm^{-1} ; MS (EI, 70 eV): 299 (M^+ , 33 %), 281 (53 %), 271 (40 %), 255 (33 %), 242 (100 %), 228 (53 %), 215 (18 %), 166 (15 %), 120 (18 %), 91 (15 %); HRMS (EI): calcd. for $\text{C}_{21}\text{H}_{17}\text{NO}$: 299.1310, found: 299.1304.

6-Cyano-3'-oxo-3-phenyl-spiro[cyclohexane-1, 1'-[H]-indene] (8).

3-(3-Oxo-cyclohex-1-enyl)-4-(1-phenyl-vinyl)-benzonitrile **7** (67 mg, 0.22 mmol) was dissolved in CHCl_3 (3.0 mL) at 0 °C. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (190 mg, 1.34 mmol) was slowly added and the resulting solution was stirred at 40 °C for 7 h. The reaction mixture was then quenched with H_2O (2 mL) and CH_2Cl_2 (5 mL), and the aqueous phase was extracted with CH_2Cl_2 (5 mL). Combined organic phases were dried (MgSO_4) and evaporated to yield a crude product. Purification by flash chromatography (pentane:ether = 2:3) yielded **8** (57 mg, 86 %) as a white powder; m.p.: 156.8-158.5 °C. ^1H NMR (CDCl_3 , 300 MHz): 7.30-7.70 (m, 8 H), 6.67 (s, 1 H), 2.48-2.92 (m, 3 H), 1.88-2.40 (m, 4 H), 1.56-1.84 (m, 1 H), ^{13}C NMR (CDCl_3 , 75 MHz): 209.7, 151.4, 146.1, 142.8, 141.0, 133.9, 132.0, 128.8, 128.5, 127.6, 125.4, 121.7, 119.4, 109.1, 55.9, 48.0, 33.0, 24.9; IR (KBr): 3062, 2956, 2222, 1706, 1606, 1492, 1470, 1445, 1414, 1350, 1229, 1073, 950 cm^{-1} ; MS (EI, 70 ev): 299 (M^+ , 90 %), 281 (80 %), 271 (10%), 256 (15 %), 243 (100 %), 227 (69 %), 215 (15 %), 201 (19 %), 193 (19 %), 120 (13 %), 100 (13 %), 91 (10 %); HRMS (EI): calcd. for $\text{C}_{21}\text{H}_{17}\text{NO}$: 299.1310, found: 299.1287.

4-(1-Methoxycarbonyl-vinyl)-3-(3-oxo-cyclohex-1-enyl)-benzoic acid ethyl ester (9).

To a solution of **2d** (600 mg, 1.28 mmol) in THF (0.85 mL) was slowly added *i*-PrMgCl·LiCl (0.9 mL, 1.41 mmol, 1.55 M in THF) at -40 °C. The reaction mixture was continuously stirred at -40 °C for 1 h. A complete conversion to the Grignard reagent (**3d**) was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. ZnBr_2 (1.28 mmol, 1.3 mL, 1.0 M in THF) was added at -20 °C and the reaction mixture was slowly warmed to -5 °C. After 1 h, the zinc reagent was transferred to a solution of tetrakis(triphenylphosphine)palladium (74 mg, 0.06 mmol) and 2-iodoacrylic acid methyl ester² (300 mg, 1.41 mmol) in THF (2.0 mL). The reaction mixture was heated under reflux for 2 h. The mixture was cooled and then TBAF (2.0 mL, 1.0 M in THF) was added. After 30 min, HCl (1.3 mL, 2.0 M) was added and the reaction mixture was stirred for 2 h before the addition of aq. NH_3 (5 mL). The aqueous phase was extracted with diethyl ether (2 × 15 mL). The combined organic layers were washed with brine (15 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (pentane:ether = 2:3) yielded the pure product **9** (340 mg, 81 %) as a colorless liquid. ^1H NMR (CDCl_3 , 300 MHz): 7.99 (d, J = 8.0 Hz, 1 H), 7.90 (s, 1 H), 7.34 (d, J = 8.0 Hz, 1 H), 6.43 (s, 1 H), 5.93 (d, J = 1.0 Hz, 1 H), 5.88 (d, J = 1.0 Hz, 1 H), 4.37 (q, J = 7.2 Hz, 2 H), 3.68 (s, 1 H), 2.56-2.66 (m, 2 H), 2.36-2.45 (m, 2 H), 2.00-2.12 (m, 2 H), 1.38 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 199.0, 166.3, 165.7, 161.5, 140.7, 140.0, 139.2,

130.7, 130.6, 129.6, 129.5, 128.0, 65.8, 61.3, 52.3, 37.1, 30.4, 23.0, 14.3; IR (film): 2952, 1722, 1668, 1616, 1437, 1409, 1294, 1243, 1218, 1111, 1023, 962 cm^{-1} ; MS (EI, 70 ev): 328 (M^+ , 9 %), 310 (13 %), 300 (35 %), 283 (18 %), 272 (45 %), 240 (47 %), 227 (25 %), 213 (100 %), 195 (45 %), 185 (35 %), 168 (27 %), 152 (24 %), 139 (44 %), 128 (16 %), 115 (20 %); HRMS (EI): calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_5$: 328.1311, found: 328.1293.

8-Oxo-5,6,7,8,9,10-hexahydro-phenanthrene-3,10-dicarboxylic acid 3-ethyl ester 10-methyl ester (10).

Dienic ketone **9** (115 mg, 0.35 mmol) was dissolved in mesitylene (5 mL) and heated in a sealed tube at 220 °C for 72 h. The reaction mixture was cooled and then the mesitylene was evaporated. Purification of the crude product by column chromatography (pentane:ether = 2:3) provided **10** (98 mg, 85 %) as an orange solid; m.p.: 109.8-112.2 °C. ^1H NMR (CDCl_3 , 300 MHz): 8.10 (s, 1 H), 7.98 (d, $J = 8.0$ Hz, 1 H), 7.30 (d, $J = 8.0$ Hz, 1 H), 4.36 (q, $J = 7.2$ Hz, 2 H), 3.62 (s, 3 H), 3.12-3.26 (m, 1 H), 2.74-2.86 (m, 2 H), 2.44-2.66 (m, 3 H), 2.02-2.20 (m, 2 H), 1.37 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 198.0, 172.6, 165.9, 148.1, 139.0, 134.2, 131.0, 130.6, 130.2, 128.6, 125.9, 61.1, 52.2, 43.4, 37.3, 25.9, 22.7, 22.0, 14.3; IR (KBr): 2958, 2930, 2869, 1728, 1709, 1657, 1616, 1385, 1332, 1280, 1104, 1019, 957 cm^{-1} ; MS (EI, 70 ev): 328 (M^+ , 6 %), 283 (6 %), 269 (100 %), 241 (5 %), 223 (6 %), 213 (8 %), 167 (8 %), 153 (7 %), 139 (8 %); HRMS (EI): calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_5$: 328.1311, found: 328.1323.

(2-Iodo-phenyl)-trimethylsilanyloxy-acetonitrile (11a) was prepared from 2-iodo-benzaldehyde (646 mg, 3.0 mmol) according to the general procedure **A** and yielding the pure product **11a** (894 mg, 90 %) as a colorless oil and used directly in the next step. ^1H NMR (CDCl_3 , 300 MHz): 7.83 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.3$ Hz, 1 H), 7.68 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.8$ Hz, 1 H), 7.42 (dt, $J_1 = 7.5$ Hz, $J_2 = 1.3$ Hz, 1 H), 7.07 (dt, $J = 7.5$ Hz, $J_2 = 1.8$ Hz, 1 H), 5.63 (s, 1 H), 0.25 (s, 9 H); ^{13}C NMR (CDCl_3 , 75 MHz): 139.7, 138.5, 131.0, 129.0, 128.4, 118.4, 95.6, 68.1, -0.2; IR (film): 2239, 1585, 1568, 1439, 1463, 1256, 1096 cm^{-1} ; MS (EI, 70 ev): 331 (4 %), 316 (100 %), 242 (12 %), 189 (19 %), 115 (18 %); HRMS (EI): calcd. for $\text{C}_{11}\text{H}_9\text{INO}_2\text{Si}$: 330.9889, found: 330.9911.

General Procedure F for the Preparation of 2-Allyl-benzaldehyde (**12a**).

A dry and argon-flushed 10 ml flask, equipped with a magnetic stirrer and a septum, was charged with a solution of **11a** (166 mg, 0.5 mmol) in dry THF (0.5 mL). *i*-PrMgCl·LiCl (2.0 M in THF, 0.55 mmol) was added slowly at -78 °C, and the resulting reaction mixture was stirred at this temperature for 0.5 h. A complete conversion to the Grignard reagent was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. Allyl bromide (91 mg, 0.75 mmol) and the solution of CuCN·2LiCl (one drop) were added at this temperature and stirred for 1 h, then warmed to rt and stirred for 1 h before it was quenched with aq.NH₄Cl (2 mL). The aqueous phase was extracted with diethyl ether (3 × 20 mL). The organic fractions were washed with brine (10 mL), dried (Na₂SO₄) and concentrated *in vacuo*. The concentrated organic fraction is dissolved in ethanol (2 mL). An aqueous solution of NaOH (1M, 1 mL) and CuSO₄·5 H₂O (0.5 mmol, 125 mg) were added to the ethanolic solution and the reaction mixture was stirred at room temperature for 2 h. The aqueous phase was extracted with diethyl ether (3 × 20 mL). The organic fractions were washed with brine (10 mL), dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash chromatography (eluent: pentane: ether = 10: 1) yielded the pure product **12a** (64 mg, 88 %) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz): 10.23 (s, 1 H), 7.82 (d, *J*₁ = 7.5 Hz, *J*₂ = 1.3 Hz, 1 H), 7.51 (dt, *J*₁ = 7.5 Hz, *J*₂ = 1.8 Hz, 1 H), 7.37 (t, *J*₁ = 7.5 Hz, *J*₂ = 1.3 Hz, 1 H), 7.27 (d, *J* = 7.5 Hz, 1 H), 5.95-6.08 (m, 1 H), 4.92-5.09 (m, 2 H), 3.80 (d, *J* = 6.2 Hz, 2 H); ¹³C NMR (CDCl₃, 75 MHz): 192.3, 142.2, 136.9, 133.9, 133.8, 131.6, 131.0, 126.9, 116.4, 36.5; IR (film): 1697, 1599, 755 cm⁻¹; MS (EI, 70 ev): 146 (32 %), 145 (38 %), 131 (100 %), 115 (83 %), 103 (29 %).

2-Benzoyl-benzaldehyde (12b)⁴ was prepared from **11a** (166 mg, 0.5 mmol) according to the general procedure **G** and yielding the pure **12b** (75 mg, 71 %) as a white solid; mp: 62.1-63.2 °C. ¹H NMR (CDCl₃, 300 MHz): 10.00 (s, 1 H), 7.97-8.03 (m, 1 H), 7.75-7.79 (m, 2 H), 7.63-7.69 (m, 2 H), 7.54-7.60 (m, 1 H), 7.36-7.51 (m, 3 H); ¹³C NMR (CDCl₃, 75 MHz): 196.5, 190.5, 141.3, 137.0, 135.4, 133.6, 133.3, 130.6, 130.0, 129.9, 128.8, 128.6; IR (KBr): 1699, 1685, 1667, 1596, 1569, 1280 cm⁻¹; MS (EI, 70 ev): 210 (100 %), 181 (97 %), 152 (31 %), 105 (31 %), 77 (41 %).

(3-Iodo-4,5-dimethoxy-phenyl)-trimethylsilanyloxy-acetonitrile (11b) was prepared from 3-iodo-4,5-dimethoxy-benzaldehyde (876 mg, 3.0 mmol) according to the general procedure A and yielding the pure product **11b** (1.07 g, 91 %) as a yellow oil and used directly in the next step. ^1H NMR (CDCl_3 , 300 MHz): 7.37 (d, $J = 1.8$ Hz, 1 H), 6.96 (d, $J = 1.8$ Hz, 1 H), 5.36 (s, 1 H), 3.85 (s, 3 H), 3.81 (s, 3 H), 0.22 (s, 9 H); ^{13}C NMR (CDCl_3 , 75 MHz): 152.8, 149.7, 133.9, 128.2, 118.7, 110.6, 92.3, 62.4, 60.4, 56.0, -0.3; IR (film): 1592, 1568, 1464, 1481, 1256 cm^{-1} ; MS (EI, 70 ev): 391 (100 %), 376 (59 %), 302 (100 %), 277 (5 %), 165 (61 %); HRMS (EI): calcd. for $\text{C}_{13}\text{H}_{18}\text{INO}_3\text{Si}$: 391.0101, found: 391.0100.

General Procedure G for the Preparation of 3-(furan-2-carbonyl)-4,5-dimethoxybenzaldehyde (12c).

A dry and argon-flushed 10 ml flask, equipped with a magnetic stirrer and a septum, was charged with a solution of **11b** (196 mg, 0.5 mmol) in dry THF (0.5 ml). $i\text{-PrMgCl}\cdot\text{LiCl}$ (2.0 M in THF, 0.55 mmol) was added slowly at -78°C , and the resulting reaction mixture was stirred at this temperature for 0.5 h. A complete conversion to the Grignard reagent was observed as indicated by GC-analysis of hydrolyzed reaction aliquots. THF (1.0 mL) and the solution of $\text{CuCN}\cdot 2\text{LiCl}$ (0.55 mmol, 0.55 mL, 1.0 M in THF) were added at this temperature and stirred for 15 min. 2-Furoyl chloride (0.75 mmol in 0.5 mL of THF) was added and the reaction mixture was stirred at -78°C for 1 h, then warmed to rt and stirred for 1 h before it was quenched with aq. ammonia (2 mL). The aqueous phase was extracted with diethyl ether (3×20 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The concentrated organic fraction is dissolved in ethanol (2 mL). An aqueous solution of NaOH (1M, 1 mL) and $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (0.5 mmol, 125 mg) were added to the ethanolic solution and the reaction mixture was stirred at room temperature for 2 h. The aqueous phase was extracted with diethyl ether (3×20 mL). The organic fractions were washed with brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash chromatography (eluent: pentane: ether = 3: 1) yielded the pure product **12c** (108 mg, 83 %) as a white solid; mp: $103.6\text{--}104.0^\circ\text{C}$. ^1H NMR (CDCl_3 , 300 MHz): 9.87 (s, 1 H), 7.63–7.65 (m, 1 H), 7.54 (d, $J = 2.0$ Hz, 1 H), 7.48 (d, $J = 2.0$ Hz, 1 H), 7.07 (d, $J = 3.2$ Hz, 1 H), 6.54 (dd, $J_1 = 3.2$ Hz,

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$J_2 = 1.3$ Hz, 1 H), 3.94 (s, 3 H), 3.87 (s, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 190.2, 181.4, 153.3, 152.5, 152.3, 147.7, 132.9, 131.9, 124.8, 120.9, 112.5, 112.3, 62.0, 56.1; IR (KBr): 1696, 1647, 1565, 1464, 1269, 1143, 1024 cm^{-1} ; MS (EI, 70 eV): 260 (100 %), 243 (29 %), 231 (42 %), 179 (87 %), 95 (47 %); HRMS (EI): calcd. for $\text{C}_{14}\text{H}_{12}\text{O}_5$: 260.0685, found: 260.0678.

3-Benzoyl-4,5-dimethoxy-benzaldehyde (12d) was prepared from **11b** (196 mg, 0.5 mmol) according to the general procedure **H** and yielding the pure **12d** (106 mg, 79 %) as an oil. ^1H NMR (CDCl_3 , 300 MHz): 9.86 (s, 1 H), 7.75-7.80 (m, 2 H), 7.52-7.58 (m, 2 H), 7.39-7.45 (m, 3 H), 3.94 (s, 3 H), 3.76 (s, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz): 194.8, 190.3, 153.2, 152.2, 136.9, 133.7, 133.5, 132.0, 129.7, 128.4, 124.9, 111.9, 61.6, 56.1; IR (film): 1694, 1672, 1596, 1139, 996 cm^{-1} ; MS (EI, 70 eV): 270 (M^+ , 94 %), 255 (12 %), 193 (51 %), 179 (100 %), 105 (52 %); HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{14}\text{O}_4$: 270.0892, found: 270.0880.

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