



Supporting Information

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## Copper(I)-Mediated Oxidative Cross-Coupling Between Functionalized Alkynyllithium and Arylmagnesium Reagents

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**General** All reactions were carried out under argon atmosphere in dried glassware. All starting materials were purchased from commercial suppliers and used without further purification unless otherwise stated. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. (*i*-Pr)<sub>2</sub>NH was distilled from CaH<sub>2</sub> under nitrogen atmosphere. Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by <sup>1</sup>H NMR and capillary GC.

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

Magnesium turnings (110 mmol) and anhydrous LiCl (100 mmol) were placed in an argon-flushed flask, and THF (50 mL) was added. A solution of *i*-PrCl (100 mmol) in THF (50 mL) was slowly added at room temperature. The reaction starts within few minutes. After the addition was finished, the reaction mixture was stirred for 12 h at room temperature. The grey solution of *i*-PrMgCl·LiCl was cannulated to a different flask under argon and removed in this way from excess of magnesium. A yield of ca. 95-98% of *i*-PrMgCl·LiCl was obtained. The reagent was titrated prior to use by the method of Paquette,<sup>1</sup> or the method developed by our laboratory.<sup>2</sup>

### Preparation of the reagent TMPMgCl·LiCl:

A dry and nitrogen-flushed 250 mL Schlenk-flask, equipped with a magnetic stirring bar and a septum, was charged with freshly titrated *i*-PrMgCl·LiCl (1.2 M in THF) (100 mL, 120 mmol). 2,2,6,6-Tetramethylpiperidine (TMPH) (19.8 g, 126 mmol, 1.05 equiv) was added dropwise at room temperature. The reaction mixture was stirred at room temperature until gas

evolution was completed (ca. 24 h). The reagent was titrated prior to use (benzoic acid and 4-(phenylazo)diphenylamine as indicator).<sup>3,4</sup>

**Preparation of Grignard reagents like 1e-f and 1j:**

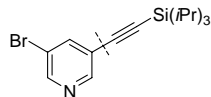
Magnesium turnings (150 mmol) and anhydrous LiCl (100 mmol) were placed in an argon-flushed three-necked round-bottom flask, equipped with a magnetic stirrer, a condenser and an addition funnel, and THF (50 mL) was added. A solution of the corresponding bromoarene (100 mmol) in dry THF (50 mL) was added dropwise at 50-60 °C through the addition funnel. If the reaction did not start spontaneously, 1,2-dibromoethane (10 mmol) or DIBAH (10 % solution in hexane, 10 mmol) was added to the reaction mixture. After 2 h of vigorous stirring the desired Grignard reagent was formed, as determined by GC analysis after the iodolysis of a reaction aliquot. The grey solution of the Grignard reagent was cannulated from the excess of magnesium under argon to a Schlenk-flask. The reagent was titrated prior to use by the method developed in our laboratory.<sup>2</sup>

**Preparation of the reagent CuCl·2LiCl (1 M in THF):**

A dry and argon-flushed 50 mL Schlenk-flask, equipped with a magnetic stirrer and a glass stopper, was charged with LiCl (1.7 g, 40 mmol) and heated up to 130 °C under high vacuum for 1 h. After cooling to room temperature under argon, CuCl (1.98 g, 20 mmol, 99.5% Cu) was added under inert atmosphere inside a glove-box. The Schlenk-flask was further heated to 130 °C for 5 h under high vacuum, cooled to room temperature, charged with freshly distilled THF (20 mL) under argon and wrapped in aluminium foil to protect it from light. The mixture was vigorously stirred until all solid goes in solution (ca. 6 h.). The reagent CuCl·2LiCl (1 M in THF) appears as a colourless or slightly pink/yellow solution (colour depends on purity of CuCl).

## TYPICAL PROCEDURE (TP1):

### Synthesis of 3-bromo-5-[(triisopropylsilyl)-ethynyl]-pyridine (**6a**) (Scheme 2):



A dry and argon-flushed Schlenk-flask, equipped with a magnetic stirring bar and a septum, was charged with 3,5-dibromopyridine (**7**) (237 mg, 1.0 mmol). After cooling to 0 °C, *i*PrMgCl·LiCl (0.92 mL, 1.20 M in THF, 1.1 mmol) was added dropwise and stirred for 0.5 h and then at 25 °C for further 0.5 h affording the 5-bromo-3-pyridylmagnesium chloride (**1a**). CuCl·2LiCl (1.2 mL, 1.0 M in THF, 1.2 mmol) was added dropwise to (**1a**) at -50 °C under argon and the mixture was stirred for 25 min. 1-Triisopropylsilylethynyllithium (**3a**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of triisopropylsilylacetylene in THF (365 mg, 2 mmol) at 0 °C and stirring for 30 min) was added dropwise to the resulting cuprate **2a**, and the mixture was stirred for 1 h at -50 °C. The reaction mixture was cooled to -78 °C, then a solution of **5** (320 mg, 1.3 mmol) in dry THF (7 mL) was added slowly over a period of 45 min. The reaction mixture was then warmed to -50 °C and stirred for 3 h. Et<sub>2</sub>O (10 mL) was poured into the crude reaction mixture and the reaction mixture was then filtered through celite and the residue washed with Et<sub>2</sub>O (ca. 100 mL). The organic phase was washed with 2 x 10 mL portions of aqueous NH<sub>4</sub>OH (2.0 M) and extracted with Et<sub>2</sub>O. The combined organic layers were dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. Purification by flash chromatography (pentane/Et<sub>2</sub>O; 20:1) yielded the alkyne **6a** (281 mg, 83 %) as a pale yellow viscous oil.

**IR (neat):**  $\nu_{\text{max}}$  (cm<sup>-1</sup>) = 2941, 2863, 2160, 1571, 1536, 1461, 1424, 1403, 1304, 1230, 1158, 1093, 1018, 995, 875, 695, 675, 660, 631.

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.58 (*br. s*, 2H, ArH), 7.87 (dd, <sup>4</sup>*J*(H,H) = 1.8 Hz, <sup>4</sup>*J*(H,H) = 2.2 Hz 1H, ArH), 1.12 (*br. s*, 21H, Si(*i*Pr)<sub>3</sub>).

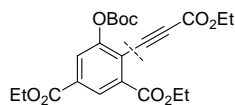
**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 150.7, 149.7, 141.1, 122.0, 120.0, 101.7, 96.8, 18.6, 11.2.

**MS (70 eV, EI):** *m/z* (%) = 339 [M + 2]<sup>+</sup>(17), 337 [M]<sup>+</sup>(16), , 297 (17), 296 (100), 294 (97), 267 (21), 265 (21), 253 (17), 251 (17), 239 (31), 237 (30), 225 (27), 223 (27).

**HRMS (EI):** *m/z* calc. for [C<sub>16</sub>H<sub>24</sub>N<sup>79</sup>Br<sup>28</sup>Si] 337.0861, found: 337.0869.

## TYPICAL PROCEDURE (TP2):

### Synthesis of diethyl 5-[(*tert*-butoxycarbonyloxy]-4-(3-ethoxy-3-oxoprop-1-yn-1-yl)isophthalate (**6h**) (Scheme 2):



A dry and argon-flushed Schlenk-flask, equipped with a magnetic stirrer and a septum, was charged with a solution of 5-*tert*-butoxycarbonyloxy-isophthalic acid diethyl ester **8** (338 mg, 1.0 mmol) in dry THF (3 mL). After cooling to 0 °C, TMPMgCl·LiCl (1.20 M in THF; 0.92 mL, 1.1 mmol) was added dropwise and stirred for 1 h to afford the corresponding Grignard reagent. CuCl·2LiCl (1.2 mL, 1.0 M in THF, 1.2 mmol) was added dropwise to this Grignard reagent at -50 °C under argon and the mixture was stirred for 20 min. The corresponding ethynyllithium (**3h**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of 1-ethylpropiolate in THF (196 mg, 2 mmol) at -78 °C and stirring for 60 min) was added dropwise to the resulting cuprate **2b**, and the mixture was further stirred for 1 h at -78 °C (the mixture was usually stirred at -50 °C for 60 min). Then a solution of chloranil (**5**, 320 mg, 1.3 mmol) in dry THF (7 mL) was added slowly over a period of 45 min at -78 °C. The reaction mixture was then stirred for additional 3 h. Et<sub>2</sub>O (10 mL) was poured into the crude reaction mixture and the reaction mixture was then filtered through celite and the residue washed with Et<sub>2</sub>O (ca. 100 mL). The organic phase was washed with 2 x 10 mL portions of aqueous NH<sub>4</sub>OH (2.0 M) and extracted with Et<sub>2</sub>O. The combined organic layers were dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. Purification by flash chromatography (pentane/Et<sub>2</sub>O; 7:1) yielded **6h** (316 mg, 73 %) as yellow solid.

**mp.:** 77.6–78.4 °C.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 3437, 3388, 3091, 2980, 2939, 2908, 2875, 2221, 1760, 1724, 1704, 1616, 1592, 1468, 1420, 1395, 1365, 1328, 1286, 1245, 1199, 1177, 1147, 1099, 1052, 1023, 956, 936, 917, 862, 816, 796, 763, 744, 703.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.55 (d, <sup>4</sup>*J*(H,H) = 1.8 Hz, 1H, ArH), 8.00 (d, <sup>4</sup>*J*(H,H) = 1.8 Hz, 1H, ArH), 4.44 (q, <sup>3</sup>*J*(H,H) = 7.1 Hz, 2H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.41 (q, <sup>3</sup>*J*(H,H) = 7.1 Hz, 2H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.30 (q, <sup>3</sup>*J*(H,H) = 7.1 Hz, 2H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.57 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.43 (t, <sup>3</sup>*J*(H,H) = 7.1, 3H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.40 (t, <sup>3</sup>*J*(H,H) = 7.1, 3H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.34 (t, <sup>3</sup>*J*(H,H) = 7.1, 3H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

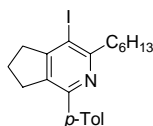
$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 164.3, 154.1, 153.4, 150.8, 135.4, 133.0, 129.3, 126.8, 119.4, 92.0, 85.2, 77.9, 62.5, 62.4, 62.2, 27.8, 14.5, 14.3.

MS (70 eV, ESI):  $m/z$  (%) = 333 [ $\text{M} - \text{Boc}$ ] $^+$ (100).

HRMS (ESI):  $m/z$  calc. for  $[\text{C}_{22}\text{H}_{26}\text{O}_9 + \text{NH}_4]$  452.1912, found: 452.1917.

### TYPICAL PROCEDURE (TP3):

#### Synthesis of 3-hexyl-4-iodo-1-(4-methylphenyl)-6,7-dihydro-5H-cyclopenta[*c*]pyridine (Scheme 3, 19b)



A dry and argon-flushed Schlenk-flask, equipped with a magnetic stirring bar and a septum, was charged with **14b** (127 mg, 0.5 mmol) in 3 mL  $\text{Et}_2\text{O}$ . After cooling to  $-78^\circ\text{C}$ ,  $t\text{BuLi}$  (1.0 mmol, 1.6 M in pentane) was added dropwise and stirred for 1 h to afford compound **15**, which was monitored by GC analysis or by TLC. Then, *p*-tolunitrile (76 mg, 0.65 mmol), dissolved in 1 mL of  $\text{Et}_2\text{O}$ , was added dropwise and the mixture was stirred for 1 h at  $-78^\circ\text{C}$  to afford compound **17**, which was also monitored by GC analysis or by TLC.  $\text{I}_2$  (253 mg, 1 mmol) in 2 mL  $\text{Et}_2\text{O}$  was added at  $-78^\circ\text{C}$  and the mixture was allowed to reach  $25^\circ\text{C}$  within 6 h.  $\text{Et}_2\text{O}$  (10 mL) was poured into the crude reaction mixture, the reaction mixture was washed with 2 x 5 mL portions of  $\text{Na}_2\text{S}_2\text{O}_3$  solution and extracted with  $\text{Et}_2\text{O}$ . The combined organic layers were dried ( $\text{MgSO}_4$ ), filtered, and concentrated under reduced pressure. Purification by flash chromatography (pentane/ $\text{Et}_2\text{O}$  30:1 (0.5%  $\text{Et}_3\text{N}$ )) yielded **19b** (126 mg, 60 %) as a brown viscous oil.

IR (neat):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2954, 2925, 2855, 1664, 1610, 1560, 1539, 1511, 1456, 1431, 1394, 1351, 1307, 1180, 1103, 1020, 824, 749.

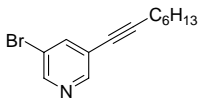
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.65 (d,  $^3J(\text{H,H}) = 8.2$  Hz, 2H, ArH), 7.24 (d,  $^3J(\text{H,H}) = 8.2$  Hz, 2H, ArH), 3.22 (t,  $^3J(\text{H,H}) = 7.4$  Hz, 2H), 3.02 (br.t,  $^3J(\text{H,H}) = 7.9$  Hz, 2H), 2.96 (t,  $^3J(\text{H,H}) = 7.4$  Hz, 2H), 2.39 (s, 3H,  $\text{CH}_3$ ), 2.07 (quin.,  $^3J(\text{H,H}) = 7.4$  Hz, 2H), 1.76 (br.quin.,  $^3J(\text{H,H}) = 7.9$  Hz, 2H), 1.46-1.32 (m, 6H), 0.90 (t,  $^3J(\text{H,H}) = 7.1$  Hz, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 161.0, 160.2, 152.7, 138.3, 136.9, 134.8, 129.2, 128.6, 94.3, 40.9, 40.1, 34.4, 32.0, 29.5, 29.4, 24.0, 22.9, 21.5, 14.4.

MS (70 eV, EI):  $m/z$  (%) = 419 [ $\text{M}^+$ ] (6), 376 (10), 350 (19), 349 (100), 292 (11), 248 (7), 236 (10), 223 (48).

HRMS (EI):  $m/z$  calc. for  $[\text{C}_{21}\text{H}_{26}\text{N}^{127}\text{I}]$  419.1110, found: 419.1115

### Synthesis of 3-bromo-5-oct-1-ynyl-pyridine (**6b**) (Table 1, entry 1)



Prepared according to **TP1** from 3,5-dibromopyridine (**7**) (237 mg, 1.0 mmol) and 1-hexylethynyllithium (**3b**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of 1-octyne in THF (220 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane/Et<sub>2</sub>O; 20:1) yielded **6b** (200 mg, 75 %) as a light green oil.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2953, 2927, 2856, 2360, 2229, 1573, 1536, 1466, 1428, 1404, 1162, 1095, 1019, 880, 695.

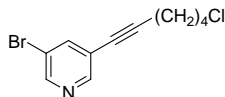
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.52 (d, <sup>4</sup>*J*(H,H) = 2.2 Hz, 1H, ArH), 8.50 (d, <sup>4</sup>*J*(H,H) = 1.8 Hz, 1H, ArH), 7.80 (dd, <sup>4</sup>*J*(H,H) = 1.8 Hz, <sup>4</sup>*J*(H,H) = 2.2 Hz, 1H, ArH), 2.40 (t, <sup>3</sup>*J*(H,H) = 7.1 Hz, 2H), 1.59 (quin., <sup>3</sup>*J*(H,H) = 7.3 Hz, 2H), 1.42 (m, 2H), 1.31 (m, 4H), 0.89 (t, <sup>3</sup>*J*(H,H) = 7.1 Hz, 3H, CH<sub>3</sub>).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 150.3, 149.0, 140.7, 122.6, 119.9, 95.8, 76.1, 31.3, 28.6, 28.4, 22.5, 19.4, 14.0.

**MS (70 eV, EI):** *m/z* (%) = 267 [M + 2]<sup>+</sup>(76), 265 [M]<sup>+</sup>(79), 238 (94), 236 (100), 224 (90), 222 (88), 210 (60), 208 (61), 198 (32), 197 (35), 196 (58), 157 (47), 143 (87), 130 (66), 117 (41), 116 (55), 115 (49), 95 (32), 88 (40), 68 (31), 43 (42), 41 (52).

**HRMS (EI):** *m/z* calc. for [C<sub>13</sub>H<sub>16</sub>N<sup>79</sup>Br] 265.0466, found: 265.0478.

### Synthesis of 3-bromo-5-(6-chloro-hex-1-ynyl)-pyridine (**6c**) (Table 1, entry 2)



Prepared according to **TP1** from 3,5-dibromopyridine (**7**) (237 mg, 1.0 mmol) and 6-chlorobutylethynyllithium (**3c**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of 6-chloro-1-hexyne in THF (233 mg, 2 mmol) at -50 °C and stirring for 40 min). Purification by flash chromatography (pentane/Et<sub>2</sub>O; 15:1) yielded **6c** (191 mg, 70 %) as a colourless viscous oil.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2931, 2232, 1573, 1536, 1428, 1405, 1310, 1162, 1096, 1018, 882, 695, 650.

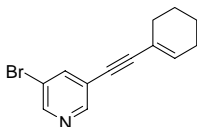
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.55 (d, <sup>4</sup>J(H,H) = 2.2 Hz, 1H, ArH), 8.50 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, ArH), 7.81 (dd, <sup>4</sup>J(H,H) = 1.8 Hz, <sup>4</sup>J(H,H) = 2.2 Hz, 1H, ArH), 3.59 (t, <sup>3</sup>J(H,H) = 6.8 Hz, 2H), 2.47 (t, <sup>3</sup>J(H,H) = 6.8 Hz, 2H), 1.94 (quin, <sup>3</sup>J(H,H) = 6.8 Hz, 2H), 1.76 (quin, <sup>3</sup>J(H,H) = 6.8 Hz, 2H).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 150.3, 149.2, 140.8, 122.3, 119.9, 94.5, 76.7, 44.3, 31.6, 25.6, 18.8.

**MS (70 eV, EI):** *m/z* (%) = 275 [M + 2]<sup>+</sup>(20), 273 [M<sup>+</sup>](87), 271 (65), 238 (34), 237 (33), 236 (45), 235 (27), 234 (15), 224 (40), 222 (37), 210 (34), 208 (36), 198 (59), 196 (100), 194 (45), 156 (22), 143 (57), 130 (27), 115 (28), 102 (17), 88 (31), 87 (17), 63 (17), 62 (15), 51 (12).

**HRMS (EI):** *m/z* calc. for [C<sub>11</sub>H<sub>11</sub>N<sup>79</sup>Br<sup>35</sup>Cl] 270.9763, found: 270.9755.

### Synthesis of 3-bromo-5-cyclohex-1-enylethynyl-pyridine (6d) (Table 1, entry 3)



Prepared according to **TP1** from 3,5-dibromopyridine (**7**) (237 mg, 1.0 mmol) and corresponding ethynyllithium (**3d**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of 1-ethynyl-cyclohexene in THF (212 mg, 2 mmol) at -50 °C and stirring for 40 min). Purification by flash chromatography (pentane/Et<sub>2</sub>O; 9:1) yielded **6d** (183 mg, 70 %) as a light green solid.

**mp.:** 47.9–49.5 °C.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 3025, 2924, 2857, 2200, 2206, 1672, 1567, 1532, 1429, 1402, 1166, 1132, 1097, 1012, 945, 916, 880, 873, 841, 830, 798, 745, 694, 670.

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.52 (br.s, 2H, ArH), 7.83 (dd, <sup>4</sup>J(H,H) = 2.2 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, ArH), 6.26 (m, 1H), 2.18 (m, 4H), 1.64 (s, 4H).

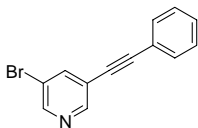
**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 150.1, 149.1, 140.4, 137.2, 122.4, 120.1, 120.0, 96.0, 82.0, 28.9, 25.8, 22.2, 21.4.

**MS (70 eV, EI):** *m/z* (%) = 263 [M + 2]<sup>+</sup>(95), 261 [M<sup>+</sup>](100), 260 (38), 248 (16), 246 (17), 235 (13), 233 (13), 167 (29), 154 (11), 127 (11).

**HRMS (EI):** *m/z* calc. for [C<sub>13</sub>H<sub>12</sub>N<sup>79</sup>Br] 261.0153, found: 261.0148.



### Synthesis of 3-bromo-5-phenylethynyl-pyridine (**6e**) (Table 1, entry 4)



Prepared according to **TP1** from 3,5-dibromopyridine (**7**) (237 mg, 1.0 mmol) and corresponding phenylethynyllithium (**3e**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of phenyl acetylene in THF (204 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane/Et<sub>2</sub>O; 9:1) yielded **6e** (186 mg, 72 %) as a white solid.

**mp.:** 99.1-100.2 °C.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 3032, 2213, 1597, 1572, 1489, 1428, 1405, 1101, 1013, 941, 916, 879, 756, 687, 659, 558, 538.

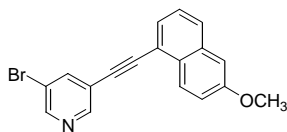
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.65 (d, 1H, <sup>4</sup>*J*(H,H) = 1.8 Hz, ArH), 8.6d (d, 1H, <sup>4</sup>*J*(H,H) = 2.2 Hz, ArH), 7.95 (dd, <sup>4</sup>*J*(H,H) = 1.8 Hz, <sup>4</sup>*J*(H,H) = 2.2 Hz, 1H, ArH), 7.53 (m, 2H, ArH). 7.37 (m, 3H, ArH).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 150.2, 149.7, 140.6, 131.7, 129.1, 128.5, 122.0, 121.9, 120.1, 94.0, 84.4.

**MS (70 eV, EI):** *m/z* (%) = 259 [M + 2]<sup>+</sup>(97), 257 [M<sup>+</sup>](100), 152 (14), 151 (26), 150 (12), 75 (5).

**HRMS (EI):** *m/z* calc. for [C<sub>13</sub>H<sub>8</sub>N<sup>79</sup>Br] 256.9840, found: 256.9850.

### Synthesis of 3-bromo-5-(6-methoxy-naphthalen-1-ylethynyl)-pyridine (**6f**) (Table 1, entry 5)



Prepared according to **TP1** from 3,5-dibromopyridine (**7**) (237 mg, 1.0 mmol) and corresponding 6-methoxynaphthylethynyllithium (**3f**, 2.0 mmol; prepared by adding *n*-BuLi (2 mmol) to a 0.3 M solution of 6-methoxynaphthyl acetylene in THF (364 mg, 2 mmol) at 0

°C and stirring for 30 min). Purification by flash chromatography (pentane/CH<sub>2</sub>Cl<sub>2</sub> 1:1) yielded **6f** (230 mg, 72 %) as a white solid.

**mp.:** 177.7-179.8 °C.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 3016, 2209, 1623, 1599, 1572, 1538, 1480, 1457, 1427, 1405, 1384, 1257, 1213, 1162, 1098, 1027, 1013, 936, 900, 876, 857, 820, 803, 741, 692, 679, 665, 654, 583, 575, 550, 532.

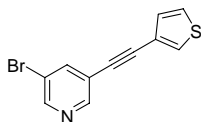
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.66 (d, <sup>4</sup>*J*(H,H) = 1.7 Hz, 1H, ArH), 8.60 (d, <sup>4</sup>*J*(H,H) = 2.2 Hz, 1H, ArH), 7.98 (br.s, 1H, ArH), 7.97 (dd, <sup>4</sup>*J*(H,H) = 1.7 Hz, <sup>4</sup>*J*(H,H) = 2.2 Hz, 1H, ArH), 7.71 (m, 2H, ArH), 7.52 (dd, <sup>3</sup>*J*(H,H) = 8.5 Hz, <sup>4</sup>*J*(H,H) = 1.8 Hz, 1H, ArH), 7.17 (dd, <sup>3</sup>*J*(H,H) = 9.0 Hz, <sup>4</sup>*J*(H,H) = 2.4 Hz, 1H, ArH), 7.12 (m, 1H, ArH), 3.93 (s, 3H, OCH<sub>3</sub>).

**<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):**  $\delta$  = 158.9, 150.4, 149.7, 140.3, 134.8, 132.1, 129.7, 128.9, 128.6, 127.3, 122.4, 120.4, 119.9, 117.0, 106.1, 95.0, 84.4, 55.6.

**MS (70 eV, EI):** *m/z* (%) = 339 [M + 2]<sup>+</sup>(100), 338 [M<sup>+</sup>](22), 337 (99), 324 (7), 322 (5), 295 (28), 294 (28), 213 (10), 188 (11), 187 (19), 169 (10), 168 (10), 115 (6), 94 (3).

**HRMS (EI):** *m/z* calc. for [C<sub>18</sub>H<sub>12</sub>N<sup>79</sup>BrO] 337.0102, found: 337.0098.

### Synthesis of 3-bromo-5-thiophen-3-ylethynyl-pyridine (**6g**) (Table 1, entry 6)



Prepared according to **TP1** from 3,5-dibromopyridine (**7**) (237 mg, 1.0 mmol) and corresponding 3-thiopheneethynyllithium (**3g**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of 3-ethynylthiophene in THF (216 mg, 2 mmol) at -50 °C and stirring for 45 min). Purification by flash chromatography (pentane/Et<sub>2</sub>O; 15:1) yielded **6g** (172 mg, 65 %) as a light green solid.

**mp.:** 100.7-101.6 °C (decomposition).

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 3094, 3021, 2206, 1575, 1536, 1434, 1406, 1355, 1207, 1167, 1099, 1078, 1012, 943, 879, 870, 807, 776, 692, 678, 621, 561, 532.

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.63 (d, 1H, <sup>4</sup>*J*(H,H) = 1.8 Hz, ArH), 8.59 (d, 1H, <sup>4</sup>*J*(H,H) = 2.2 Hz, ArH), 7.93 (dd, <sup>4</sup>*J*(H,H) = 2.2 Hz, <sup>4</sup>*J*(H,H) = 1.8 Hz, 1H, ArH), 7.57 (dd, <sup>4</sup>*J*(H,H) = 3.1 Hz, <sup>4</sup>*J*(H,H) = 1.1 Hz, 1H, ArH), 7.32 (dd, <sup>3</sup>*J*(H,H) = 5.1 Hz, <sup>4</sup>*J*(H,H) = 3.1 Hz, 1H, ArH), 7.19 (dd, <sup>3</sup>*J*(H,H) = 5.1 Hz, <sup>4</sup>*J*(H,H) = 1.1 Hz, 1H, ArH).

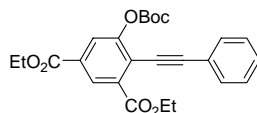
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.1, 149.6, 140.5, 130.0, 129.7, 125.8, 121.9, 121.1, 120.1, 89.2, 84.1.

MS (70 eV, EI):  $m/z$  (%) = 265 [ $\text{M} + 2$ ] $^+$ (100), 2563 [ $\text{M}^+$ ](99), 184 (16), 157 (18), 140 (15), 113 (11), 78 (10).

HRMS (EI):  $m/z$  calc. for [ $\text{C}_{11}\text{H}_6^{79}\text{Br}^{32}\text{S}$ ] 262.9404, found: 262.9417.

### Synthesis of diethyl 5-[(*tert*-butoxycarbonyl)oxy]-4-(phenylethynyl)isophthalate (**6i**)

(Table 2, entry 1)



Prepared according to **TP2** from ethyl 5-*tert*-butoxycarbonyloxy-isophthalic acid diethyl ester **8** (338 mg, 1.0 mmol)<sup>5</sup> [reaction conditions: deprotonation with  $\text{TMPMgCl}\cdot\text{LiCl}$  at  $T = 0\text{ }^\circ\text{C}$  for 1 h] and corresponding phenylethynyllithium (**3f**, 2.0 mmol; prepared by adding  $n\text{BuLi}$  (2 mmol) to a 0.5 M solution of phenyl acetylene in THF (204 mg, 2 mmol) at  $0\text{ }^\circ\text{C}$  and stirring for 30 min). Purification by flash gradient chromatography (pentane/ $\text{Et}_2\text{O}$ ; 9:1 $\rightarrow$ 4:1) yielded **6i** (285 mg, 65 %) as yellowish solid.

mp.: 103.7-105.1  $^\circ\text{C}$

IR (neat):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2978, 2929, 2217, 1755, 1720, 1610, 1495, 1463, 1443, 1394, 1369, 1327, 1291, 1234, 1178, 1143, 1093, 1050, 1031, 953, 914, 858, 818, 761, 694.

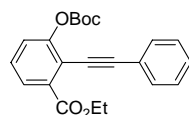
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.52 (d,  $^4J(\text{H,H}) = 1.8\text{ Hz}$ , 1 H, ArH), 7.98 (d,  $^4J(\text{H,H}) = 1.8\text{ Hz}$ , 1 H, ArH), 7.59 (m, 2H, ArH), 7.36 (m, 3H, ArH), 4.43 (q,  $^3J(\text{H,H}) = 7.1\text{ Hz}$ , 2 H), 4.39 (q,  $^3J(\text{H,H}) = 7.1\text{ Hz}$ , 2 H), 1.47 (s, 9 H,  $\text{C}(\text{CH}_3)_3$ ), 1.41 (t,  $^3J(\text{H,H}) = 7.1\text{ Hz}$ , 3 H,  $\text{CH}_3$ ), 1.40 (t,  $^3J(\text{H,H}) = 7.1\text{ Hz}$ , 3 H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 164.8, 164.5, 152.7, 150.9, 133.7, 131.9, 130.4, 129.2, 129.0, 128.3, 126.1, 122.6, 122.5, 103.0, 84.3, 82.4, 61.7, 27.6, 14.3, 14.2.

MS (70 eV, EI):  $m/z$  (%) = 438 (4), 339 (19), 338 (100), 310 (53), 293 (17), 265 (27), 237 (6), 219 (4), 209 (6), 163 (7), 152 (7), 105 (4), 57 (33).

HRMS (EI): calc. for [ $\text{C}_{25}\text{H}_{26}\text{O}_7$ ] 438.1679, found 438.1682.

**Synthesis of ethyl 3-[(*tert*-butoxycarbonyl)oxy]-2-(phenylethynyl)benzoate (**6j**) (Table 2, entry 2)**



Prepared according to **TP2** from ethyl 3-*tert*-butoxycarbonyloxy-benzoate (266 mg, 1.0 mmol) [reaction conditions: deprotonation with TMPMgCl·LiCl at T = 0 °C for 3 h]<sup>5</sup> and corresponding phenylethynyllithium (**3f**, 2.0 mmol; prepared by adding *n*-BuLi (2 mmol) to a 0.5 M solution of phenyl acetylene in THF (204 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane/Et<sub>2</sub>O; 9:1) yielded **6j** (256 mg, 70 %) as a light yellowish viscous oil.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2979, 2217, 1757, 1724, 1595, 1493, 1452, 1394, 1368, 1250, 1227, 1135, 1050, 1030, 942, 877, 754, 690.

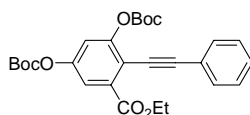
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.89 (dd, <sup>3</sup>*J*(H,H) = 7.5 Hz, <sup>4</sup>*J*(H,H) = 1.5 Hz, 1 H, ArH), 7.57 (m, 2 H, ArH), 7.40-7.33 (m, 5 H, ArH), 4.41 (q, <sup>3</sup>*J*(H,H) = 7.1 Hz, 2 H, CH<sub>2</sub>), 1.47 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.39 (t, <sup>3</sup>*J*(H,H) = 7.2 Hz, 3 H, CH<sub>3</sub>).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 165.5, 152.7, 151.2, 133.6, 131.8, 128.7, 128.4, 128.3, 128.1, 125.6, 123.1, 118.2, 100.0, 84.0, 82.5, 61.4, 27.6, 14.3.

**MS (70 eV, EI):** *m/z* (%) = 366 (8), 267 (15), 266 (100), 239 (14), 238 (100), 237 (38), 221 (19), 193 (7), 165 (13), 139 (7), 138 (4), 105 (4), 57 (51).

**HRMS (EI):** calc. for [C<sub>22</sub>H<sub>22</sub>O<sub>5</sub>] 366.1467, found 366.1480.

**Synthesis of ethyl 3,5-bis[(*tert*-butoxycarbonyl)oxy]-2-(phenylethynyl)benzoate (**6k**) (Table 2, entry 3).**



Prepared according to **TP2** from ethyl 3,5-bis-*tert*-butoxycarbonyloxy-benzoate (382 mg, 1.0 mmol) [reaction conditions: deprotonation with TMPMgCl·LiCl at T = 0 °C for 3 h]<sup>5</sup> and corresponding phenylethynyllithium (**3f**, 2.0 mmol; prepared by adding *n*-BuLi (2 mmol) to a 0.5 M solution of phenyl acetylene in THF (204 mg, 2 mmol) at 0 °C and stirring for 30 min).

Purification by flash gradient chromatography (pentane/Et<sub>2</sub>O; 4:1) yielded **6k** (304 mg, 63 %) as yellowish viscous oil.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2980, 2216, 1761, 1731, 1496, 1596, 1496, 1465, 1370, 1243, 1140, 1117, 1054, 860, 757, 691.

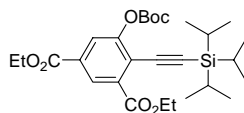
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.73 (d, <sup>4</sup>J(H,H) = 2.6 Hz, 1 H, ArH), 7.56 (m, 2 H, ArH), 7.34 (m, 3 H, ArH), 7.30 (d, <sup>4</sup>J(H,H) = 2.6 Hz, 1 H, ArH), 4.41 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 1.55 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.46 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.38 (t, <sup>3</sup>J(H,H) = 7.1 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>).

**<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):**  $\delta$  = 164.7, 153.1, 150.7, 150.6, 150.2, 140.0, 131.8, 128.7, 128.3, 123.1, 120.9, 119.1, 115.7, 99.8, 84.4, 84.3, 82.1, 61.6, 27.7, 27.6, 14.3.

**MS (70 eV, EI) m/z (%)** = 482 (4), 382 (8), 282 (100), 254 (70), 253 (34), 237(8), 209 (4), 181 (3), 152 (7), 139 (3), 105 (5), 57 (61), 40 (14).

**HRMS (ES):** calc. for [C<sub>27</sub>H<sub>30</sub>O<sub>8</sub>] 482.1941 found 482.1953

#### Synthesis of diethyl 5-[(*tert*-butoxycarbonyl)oxy]-4 [(triisopropylsilyl)ethynyl] isophthalate (**6l**) (Table 2, entry 4).



Prepared according to **TP2** from ethyl 5-*tert*-butoxycarbonyloxy-isophthalic acid diethyl ester **8** (338 mg, 1.0 mmol) [reaction conditions: deprotonation with TMPMgCl·LiCl at T = 0 °C for 1 h]<sup>5</sup> and 1-triisopropylsilylethynyllithium (**3a**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of triisopropylsilylacetylene in THF (365 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane/Et<sub>2</sub>O; 7:1) yielded **6l** (384 mg, 74 %) as yellowish solid.

**mp.:** 53.3-55.6 °C

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2941, 2864, 2356, 1761, 1723, 1609, 1462, 1369, 1243, 1145, 1096, 1056, 1023, 868, 763, 705, 677.

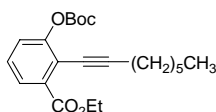
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.34 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1 H, ArH), 7.94 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1 H, ArH), 44.39 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 4 H, CH<sub>2</sub>), 1.53 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.39 (t, <sup>3</sup>J(H,H) = 7.1 Hz, 3 H, CH<sub>3</sub>), 1.39 (t, <sup>3</sup>J(H,H) = 7.1 Hz, 3 H, CH<sub>3</sub>), 1.15 (*br. s.*, 21H, Si(*i*Pr)<sub>3</sub>).

**<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):**  $\delta$  = 164.9, 164.4, 152.8, 150.8, 135.2, 130.0, 127.8, 125.8, 121.2, 106.2, 97.8, 83.9, 61.5, 61.5, 27.4, 18.5, 14.1 (2 x CH<sub>3</sub>), 11.1.

**MS (70 eV, EI):**  $m/z$  (%) = 475 (32), 419 (85), 375 (100), 343 (16), 328 (23), 57 (16).

**HRMS (EI):** calc. for  $[C_{28}H_{43}O_7^{28}Si]$   $[M + H]^+$  519.2778, found 519.2794.

**Synthesis of ethyl 3-[(*tert*-butoxycarbonyl)oxy]-2-oct-1-yn-1-ylbenzoate (**6m**) (Table 2, entry 5)**



Prepared according to **TP2** from ethyl 3-*tert*-butoxycarbonyloxy-benzoate (266 mg, 1.0 mmol) [reaction conditions: deprotonation with  $TMPMgCl \cdot LiCl$  at  $T = 0$  °C for 3 h]<sup>5</sup> and corresponding hexylethynyllithium (**3b**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of 1-octyne in THF (220 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane/Et<sub>2</sub>O; 9:1) yielded **6m** (257 mg, 69 %) as colourless oil.

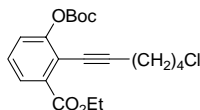
**IR (neat):**  $\nu_{max}$  (cm<sup>-1</sup>) = 2933, 2860, 2227, 1763, 1731, 1460, 1369, 1298, 1250, 1231, 1185, 1152, 1053, 1032, 878.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.79 (dd, <sup>3</sup> $J(H,H) = 7.5$  Hz, <sup>4</sup> $J(H,H) = 1.8$  Hz, 1H, ArH), 7.33-7.27 (m, 2H, ArH), 4.37 (q, <sup>3</sup> $J(H,H) = 7.1$  Hz, 2H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.47 (t, <sup>3</sup> $J(H,H) = 7.1$  Hz, 2H), 1.68-1.61 (m, 2H), 1.55 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.49-1.42 (m, 2H), 1.39 (t, <sup>3</sup> $J(H,H) = 7.5$  Hz, 3H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.36-1.28 (m, 2H), 0.90 (t, <sup>3</sup> $J(H,H) = 7.1$  Hz, 3H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

**<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):**  $\delta$  = 166.0, 153.1, 151.4, 134.3, 128.0, 127.8, 125.6, 119.0, 102.1, 83.9, 73.5, 61.4, 31.6, 28.9, 28.8, 27.9, 22.8, 20.4, 14.5, 14.3.

**HRMS (ESI):**  $m/z$  calc. for  $[C_{22}H_{30}O_5 + NH_4]$  392.2437, found: 392.2437.

**Synthesis of ethyl 3-[(*tert*-butoxycarbonyl)oxy]-2-(6-chlorohex-1-yn-1-yl)benzoate (**6n**) (Table 2, entry 6)**



Prepared according to **TP2** from ethyl 3-*tert*-butoxycarbonyloxy-benzoate (266 mg, 1.0 mmol) [reaction conditions: deprotonation with  $TMPMgCl \cdot LiCl$  at  $T = 0$  °C for 3 h]<sup>5</sup> and

corresponding 6-chlorobutylethynyllithium (**3c**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of 6-chloro-1-hexyne in THF (233 mg, 2 mmol) at -40 °C and stirring for 1 h). Purification by flash chromatography (pentane/Et<sub>2</sub>O; 9:1) yielded **6n** (265 mg, 70 %) as colourless oil.

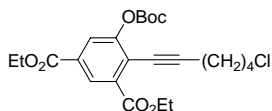
**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2982, 2937, 2872, 2233, 1759, 1728, 1601, 1456, 1395, 1369, 1296, 1248, 1228, 1180, 1144, 1079, 1052, 1031, 942, 876, 823, 773, 749.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.79 (dd, <sup>3</sup>*J*(H,H) = 7.5 Hz, <sup>4</sup>*J*(H,H) = 1.3 Hz, 1 H, ArH), 7.34-7.28 (m, 2H), 4.37 (q, <sup>3</sup>*J*(H,H) = 7.1 Hz, 2H), 3.61 (t, <sup>3</sup>*J*(H,H) = 7.2 Hz, 2H), 2.54 (t, <sup>3</sup>*J*(H,H) = 7.1 Hz, 2H), 2.03-1.97 (m, 2H), 1.84-1.78 (m, 2H), 1.55 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.39 (t, <sup>3</sup>*J*(H,H) = 7.1 Hz, 3H) ppm.

**<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):**  $\delta$  = 165.8, 153.1, 151.4, 134.2, 128.0, 127.9, 125.6, 118.7, 100.8, 84.0, 61.5, 44.8, 31.7, 27.9, 25.9, 19.5, 14.5.

**HRMS (ESI):** *m/z* calc. for [C<sub>20</sub>H<sub>25</sub><sup>35</sup>ClO<sub>5</sub> + NH<sub>4</sub>] 398.1734, found: 398.1727.

### Synthesis of diethyl 5-[(*tert*-butoxycarbonyl)oxy]-4-(6-chlorohex-1-yn-1-yl)isophthalate (**6o**) (Table 2, entry 7)



Prepared according to **TP2** from ethyl 5-*tert*-butoxycarbonyloxy-isophthalic acid diethyl ester **8** (338 mg, 1.0 mmol) [reaction conditions: deprotonation with TMPMgCl·LiCl at T = 0 °C for 1 h]<sup>5</sup> and 6-chlorobutylethynyllithium (**3c**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of 6-chloro-1-hexyne in THF (233 mg, 2 mmol) at -40 °C and stirring for 1 h). Purification by flash chromatography (pentane/Et<sub>2</sub>O; 7:1) yielded **6o** (306 mg, 68 %) as colourless oil.

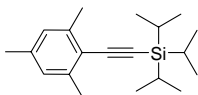
**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2977, 2930, 2217, 1760, 1724, 1610, 1476, 1463, 1367, 1323, 1241, 1176, 1148, 1101, 1057, 1026, 954, 866, 765.

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.46 (d, <sup>4</sup>*J*(H,H) = 1.8 Hz, 1H, ArH), 7.95 (d, <sup>4</sup>*J*(H,H) = 1.8 Hz, 1H, ArH), 4.42 (q, <sup>3</sup>*J*(H,H) = 7.1 Hz, 2H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.41 (q, <sup>3</sup>*J*(H,H) = 7.1 Hz, 2H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.63 (t, <sup>3</sup>*J*(H,H) = 6.4 Hz, 2H, CH<sub>2</sub>Cl), 2.59 (t, <sup>3</sup>*J*(H,H) = 7.1 Hz, 2H, CCH<sub>2</sub>), 2.07-1.96 (m, 2H, CH<sub>2</sub>), 1.90-1.78 (m, 2H, CH<sub>2</sub>), 1.58 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.43 (t, <sup>3</sup>*J*(H,H) = 7.1, 3H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.42 (t, <sup>3</sup>*J*(H,H) = 7.1, 3H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.2, 164.8, 153.1, 151.1, 134.4, 130.2, 128.9, 126.2, 104.3, 84.4, 74.3, 61.9, 61.8, 44.8, 31.7, 27.9, 25.8, 19.7, 14.5.

HRMS (ESI):  $m/z$  calc. for  $[\text{C}_{23}\text{H}_{29}\text{ClO}_7+\text{NH}_4]$  470.1946, found: 470.1937.

#### Synthesis of triisopropyl(mesitylethynyl)silane (**6p**) (Table 2, entry 8).



Prepared according to **TP1** from corresponding mesitylmagnesium bromide (**1e**, 1.0 mmol) and 1-triisopropylsilylethynyllithium (**3a**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of triisopropylsilylacetylene in THF (365 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane) yielded **6p** (219 mg, 73 %) as a colourless oil.

IR (neat):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2941, 2863, 2144, 1609, 1462, 1381, 1223, 1145, 1067, 995, 881, 850, 796, 726, 675, 609.

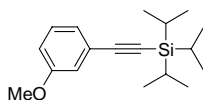
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.87 (br.s, 2H, ArH), 2.44 (s, 6H, 2  $\times$   $\text{CH}_3$ ), 2.28 (s, 3H,  $\text{CH}_3$ ), 1.15 (br. s, 21H, Si(*i*Pr) $_3$ ).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 140.6 (2  $\times$  C), 137.6, 127.5, 120.5, 104.6, 98.1, 21.3, 21.1, 18.7, 11.4.

MS (70 eV, EI):  $m/z$  (%) = 300  $[\text{M}]^+$  (32), 258 (20), 257 (100), 215 (21), 201 (22), 187 (40), 173 (12), 100 (13), 59 (7).

HRMS (EI):  $m/z$  calc. for  $[\text{C}_{20}\text{H}_{32}^{28}\text{Si}]$  300.2273, found: 300.2280.

#### Synthesis of triisopropyl[(3-methoxyphenyl)ethynyl]silane (**6q**) (Table 2, entry 9)



Prepared according to **TP1** from 3-methoxyphenylmagnesium bromide (**1f**) (1.0 ml, 1 M in THF, 1.0 mmol) and 1-triisopropylsilylethynyllithium (**3a**, 2.0 mmol; prepared by adding *n*-BuLi (2 mmol) to a 0.5 M solution of triisopropylsilylacetylene in THF (365 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane) yielded **6q** (195 mg, 68 %) as a yellow oil.



**IR (neat):**  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 2941, 2889, 2863, 2155, 1602, 1592, 1574, 1478, 1460, 1421, 1315, 1282, 1266, 1192, 1150, 1047, 993, 933, 915, 882, 851, 783, 776, 750, 680, 662.

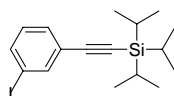
**$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.23 (t,  $^3J(\text{H,H}) = 7.9$  Hz, 1H, ArH), 7.10 (d,  $^3J(\text{H,H}) = 7.5$  Hz, 1H, ArH), 7.01 (s, 1H, ArH), 6.89 (dd,  $^3J(\text{H,H}) = 8.4$  Hz,  $^4J(\text{H,H}) = 1.5$  Hz, 1H, ArH), 3.83 (s, 3H,  $\text{OCH}_3$ ), 1.15 (s, 21H,  $\text{Si}(i\text{Pr})_3$ ).

**$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 159.5, 129.5, 124.9, 124.8, 117.1, 115.1, 107.2, 90.6, 55.5, 18.9, 11.6.

**MS (70 eV, EI):**  $m/z$  (%) = 288 (22)  $[M]^+$ , 246 (17), 245 (100), 217 (20), 203 (31), 189 (33), 175 (55), 95 (27).

**HRMS (EI):**  $m/z$  calc. for  $[\text{C}_{18}\text{H}_{28}\text{O}^{28}\text{Si}]$  288.1909, found: 288.1902.

### Synthesis of [(3-iodophenyl)ethynyl](triisopropyl)silane (**6r**) (Table 2, entry 10)



Prepared according to **TP1** from 1,3-diiodobenzene (330 mg, 1.0 mmol) [reaction conditions: I/Mg-exchange with  $i\text{PrMgCl}\cdot\text{LiCl}$  at  $T = 0$  °C for 15 min] and 1-triisopropylsilylethynyllithium (**3a**, 2.0 mmol; prepared by adding  $n\text{BuLi}$  (2 mmol) to a 0.5 M solution of triisopropylsilylacetylene in THF (365 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane) yielded **6r** (295 mg, 77 %) as a colourless oil.

**IR (neat):**  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 2941, 2889, 2858, 2159, 1582, 1552, 1467, 1397, 1382, 1295, 1218, 1070, 1063, 992, 918, 882, 851, 780, 679, 637.

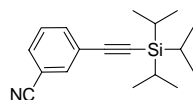
**$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 7.84 (t,  $^4J(\text{H,H}) = 1.8$  Hz, 1H, ArH), 7.68-7.64 (m, 1H, ArH), 7.45 (dt,  $^3J(\text{H,H}) = 7.7$  Hz,  $^4J(\text{H,H}) = 1.1$  Hz, 1H, ArH), 7.05 (t,  $^4J(\text{H,H}) = 7.9$  Hz, 1H, ArH), 1.14 (s, 21H,  $\text{Si}(i\text{Pr})_3$ ).

**$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):**  $\delta$  = 140.7, 137.6, 131.4, 129.9, 125.8, 105.4, 93.8, 92.6, 18.9, 11.5.

**MS (70 eV, EI):**  $m/z$  (%) = 384 (18)  $[M]^+$ , 342 (17), 341 (100), 312 (19), 299 (21), 285 (27), 271 (36), 142 (14).

**HRMS (EI):**  $m/z$  calc. for  $[\text{C}_{17}\text{H}_{25}^{127}\text{I}^{28}\text{Si}]$  384.0770, found: 384.0751.

### Synthesis of 3-[(triisopropylsilyl)ethynyl]benzonitrile (**6s**) (Table 2, entry 11)



Prepared according to **TP1** from 3-bromobenzonitrile (182 mg, 1.0 mmol) [reaction conditions: Br/Mg-exchange with *i*PrMgCl·LiCl at T = 0 °C for 3 h] and 1-triisopropylsilylethynyllithium (**3a**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of triisopropylsilylacetylene in THF (365 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane/Et<sub>2</sub>O; 30:1) yielded **6s** (204 mg, 72 %) as a light yellow oil.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2942, 2889, 2864, 2232, 2150, 1595, 1572, 1476, 1457, 1413, 1250, 996, 922, 882, 797, 734, 680, 663, 643.

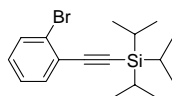
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.73 (br.s, 1H, ArH), 7.66 (d, <sup>3</sup>*J*(H,H) = 7.5 Hz, 1H, ArH), 7.56 (d, <sup>3</sup>*J*(H,H) = 7.5 Hz, 1H, ArH), 7.40 (t, <sup>3</sup>*J*(H,H) = 7.5 Hz, 1H, ArH), 1.12 (br. s, 21H, Si(*i*Pr)<sub>3</sub>).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 130.0, 135.3, 131.4, 129.1, 125.0, 118.0, 112.8, 104.3, 94.1, 18.6, 11.2.

**MS (70 eV, EI):** *m/z* (%) = 283 [M]<sup>+</sup>(15), 241 (20), 240 (100), 212 (27), 198 (27), 184 (50), 170 (51), 154 (10), 130(5).

**HRMS (EI):** *m/z* calc. for [C<sub>18</sub>H<sub>25</sub>N<sup>28</sup>Si] 283.1756, found: 283.1745.

### Synthesis of [(2-bromophenyl)ethynyl](triisopropyl)silane (**6t**) (Table 2, entry 12)



Prepared according to **TP1** from 1,2-dibromobenzene (236 mg, 1.0 mmol) [reaction conditions: Br/Mg-exchange with *i*PrMgCl·LiCl at T = -15 °C for 2 h or T = 0 °C for 1 h] and 1-triisopropylsilylethynyllithium (**3a**, 2.0 mmol; prepared by adding *n*-BuLi (2 mmol) to a 0.5 M solution of triisopropylsilylacetylene in THF (365 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane) yielded **6t** (228 mg, 68 %) as a colourless oil.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2941, 2889, 2863, 2159, 1552, 1467, 1432, 1382, 1256, 1218, 1044, 1024, 992, 882, 851, 750, 679, 637.

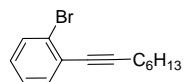
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.59 (dd, <sup>3</sup>*J*(H,H) = 7.9 Hz, <sup>4</sup>*J*(H,H) = 1.1 Hz, 1H, ArH), 7.53 (dd, <sup>3</sup>*J*(H,H) = 7.5 Hz, <sup>4</sup>*J*(H,H) = 1.8 Hz, 1H, ArH), 7.26 (ddd, <sup>3</sup>*J*(H,H) = 7.5 Hz, <sup>4</sup>*J*(H,H) = 1.3 Hz, 1H, ArH), 7.17 (ddd, <sup>3</sup>*J*(H,H) = 7.9 Hz, <sup>4</sup>*J*(H,H) = 1.8 Hz, 1H, ArH), 1.18 (s, 21 H, Si(*i*Pr)<sub>3</sub>).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 134.1, 132.6, 129.6, 127.1, 126.0, 125.9, 105.0, 96.4, 18.9, 11.6.

**MS (70 eV, EI):** *m/z* (%) = 338 (12) [*M*]<sup>+</sup>, 226 (12), 296 (19), 295 (100), 294 (20), 293 (98), 266 (24), 264 (22), 253 (16), 251 (18), 237 (23), 225 (33), 223 (34), 208 (13), 129 (20), 119 (12), 118 (12).

**HRMS (EI):** *m/z* calc. for [C<sub>17</sub>H<sub>25</sub><sup>79</sup>Br<sup>28</sup>Si] 336.0909, found: 336.0909.

### Synthesis of 1-bromo-2-oct-1-yn-1-ylbenzene (**6u**) (Table 2, entry 13)



Prepared according to **TP1** from 1,2-dibromobenzene (236 mg, 1.0 mmol) [reaction conditions: Br/Mg-exchange with *i*PrMgCl·LiCl at T = -15 °C for 2 h or T = 0 °C for 1 h] and 1-hexylethynyllithium (**3b**, 2.0 mmol; prepared by adding *n*-BuLi (2 mmol) to a 0.5 M solution of 1-octyne in THF (220 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane) yielded **6u** (180 mg, 68 %) as a light brown oil. Product is not UV active; KMNO<sub>4</sub> solution should be used for detection and also GC analysis.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2955, 2929, 2857, 2231, 1588, 1556, 1468, 1432, 1328, 1119, 1052, 1027, 941, 751.

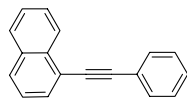
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.54 (dd, <sup>3</sup>*J*(H,H) = 7.5 Hz, <sup>4</sup>*J*(H,H) = 1.3 Hz 1H, ArH), 7.41 (dd, <sup>3</sup>*J*(H,H) = 7.5 Hz, <sup>4</sup>*J*(H,H) = 1.3 Hz 1H, ArH), 7.21 (td, <sup>3</sup>*J*(H,H) = 7.5 Hz, <sup>4</sup>*J*(H,H) = 1.3 Hz 1H, ArH), 7.10 (dd, <sup>3</sup>*J*(H,H) = 7.5 Hz, <sup>4</sup>*J*(H,H) = 1.3 Hz 1H, ArH), 2.45 (t, <sup>3</sup>*J*(H,H) = 7.1 Hz, 2H), 1.68-1.45 (m, 4H), 1.32 (m, 4H), 0.90 (t, <sup>3</sup>*J*(H,H) = 7.1 Hz, 3H, CH<sub>3</sub>).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 130.3, 132.2, 128.6, 126.8, 126.1, 125.4, 95.7, 79.3, 31.4, 28.6 (2 × CH<sub>2</sub>), 22.6, 19.6, 14.1.

**MS (70 eV, EI):** *m/z* (%) = 267 [*M* + 2]<sup>+</sup>(21), 266 [*M* + 1]<sup>+</sup>(92), 265 ([*M*]<sup>+</sup>(17), 264 (100), 237 (30), 223 (93), 221 (83), 195 (96), 193 (58), 182 (61), 180 (36), 171 (36), 169 (30), 156 (50), 143 (21), 142 (67), 129 (48), 116 (49), 115 (38), 114 (26).

**HRMS (EI):** *m/z* calc. for [C<sub>14</sub>H<sub>17</sub><sup>79</sup>Br] 264.0514, found: 264.0524

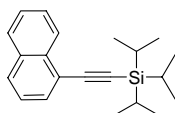
### Synthesis of 1-(phenylethynyl)naphthalene (**6v**) (Table 2, entry 14)



Prepared according to **TP1** from 1-naphthanylmagnesium bromide (**1j**, 1.0 mmol) and corresponding phenylethynyllithium (**3e**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of phenyl acetylene in THF (204 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane) yielded **6v** (160 mg, 70 %) as a colourless oil.<sup>6</sup>

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.46 (d, <sup>3</sup>*J*(H,H) = 7.5 Hz, 1H, ArH), 7.97-7.76 (m, 3H, ArH), 7.69-7.28 (m, 7H, ArH).

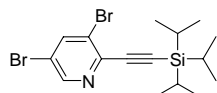
### Synthesis of triisopropyl(1-naphthylethynyl)silane (**6w**) (Table 2, entry 15)



Prepared according to **TP1** from 1-naphthanylmagnesium bromide (**1j**, 1.0 mmol) and 1-triisopropylsilylethynyllithium (**3a**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of triisopropylsilylacetylene in THF (365 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane) yielded **6w** (216 mg, 70 %) as a colourless oil.<sup>6</sup>

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.42 (d, <sup>3</sup>*J*(H,H) = 8.0 Hz, 1H, ArH), 7.88-7.72 (m, 2H, ArH), 7.63-7.38 (m, 4H, ArH), 1.12 (*br. s*, 21H, Si(*i*Pr)<sub>3</sub>).

### Synthesis of 3,5-dibromo-2-[(triisopropylsilyl)ethynyl]pyridine (**6p**) (Table 2, entry 16)



Prepared according to **TP2** from ethyl 3,5-dibromopyridine (237 mg, 1.0 mmol) [reaction conditions: deprotonation with TMPMgCl·LiCl at T = -25 °C for 30 min]<sup>3</sup> and 1-triisopropylsilylethynyllithium (**3a**, 2.0 mmol; prepared by adding *n*-BuLi (2 mmol) to a 0.5 M

solution of triisopropylsilylacetylene in THF (365 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash gradient chromatography (pentane/Et<sub>2</sub>O; 1:0→10:1) yielded **6x** (274 mg, 66 %) as yellowish oil.<sup>3</sup>

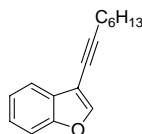
**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2941, 2864, 1547, 1520, 1462, 1420, 1363, 1261, 1094, 1036, 995, 883, 727, 678.

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.57 (d, <sup>4</sup>*J*(H,H) = 2.0 Hz, 1H, ArH), 8.08 (d, <sup>4</sup>*J*(H,H) = 2.0 Hz, 1H, ArH), 1.18 (s, 21H, Si(*i*Pr)<sub>3</sub>).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 149.5, 149.4, 142.0, 124.3, 119.5, 103.2, 99.4, 18.9, 11.4.

**HRMS (ESI):** *m/z* calc. for [C<sub>16</sub>H<sub>23</sub>Br<sub>2</sub>N<sup>28</sup>Si+H] 416.0045, found: 416.0035.

### Synthesis of 3-oct-1-yn-1-yl-1-benzofuran (**6y**) (Table 2, entry 17)



Prepared according to **TP1** from 3-bromobenzofuran (197 mg, 1.0 mmol) [reaction conditions: Br/Mg-exchange with *i*PrMgCl·LiCl at T = -55 °C for 24 h] and 1-hexylethynyllithium (**3b**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of 1-octyne in THF (220 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane) yielded **6y** (144 mg, 62 %) as a colourless oil.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 3061, 2956, 2917, 2858, 1813, 1592, 1452, 1337, 1287, 1201, 1132, 1108, 1088, 1007, 932, 856, 794, 768, 744.

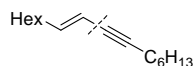
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.73 (s, 1H, ArH), 7.66 (d, <sup>3</sup>*J*(H,H) = 7.5 Hz, 1H, ArH), 7.47 (d, <sup>3</sup>*J*(H,H) = 7.9 Hz, 1H, ArH), 7.34-7.27 (m, 2H, ArH), 2.47 (t, <sup>3</sup>*J*(H,H) = 7.1 Hz, 2H), 1.68-1.62 (m, 2H), 1.53-1.46 (m, 2H), 1.39-1.30 (m, 4H), 0.92 (t, <sup>3</sup>*J*(H,H) = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):**  $\delta$  = 154.7, 147.0, 128.3, 125.1, 123.3, 120.6, 111.7, 105.3, 95.3, 69.8, 31.6, 29.0, 28.8, 22.8, 19.9, 14.3.

**MS (70 eV, EI):** *m/z* (%) = 226 (80), 197 (16), 183 (42), 169 (22), 157 (55), 155 (100), 131 (16), 129 (22), 128 (15), 127 (18), 126 (16), 115 (13).

**HRMS (EI):** *m/z* calc. for [C<sub>16</sub>H<sub>18</sub>O] 226.1358, found: 226.1359.

### Synthesis of (7E)-hexadec-7-en-9-yne (Scheme 3, 11a):



Prepared according to **TP1** from *E*-octenyl iodide (**9**)<sup>7</sup> (238 mg, 1.0 mmol) [reaction conditions: Br/Mg-exchange with *i*PrMgCl·LiCl at T = -40 °C for 7 h] and 1-hexylethynyllithium (**3b**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of 1-octyne in THF (220 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane) yielded **11a** (137 mg, 62 %) as a colourless viscous oil. The product is not UV active; KMNO<sub>4</sub> solution should be used for detection and also GC analysis.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2956, 2925, 2856, 2219, 1676, 1458, 1378, 1328, 1165, 1111, 952, 888, 723.

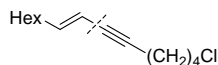
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 6.03 (dt, <sup>3</sup>*J*(H,H) = 15.9 Hz, <sup>3</sup>*J*(H,H) = 7.1 Hz, 1H), 5.43 (dm, <sup>3</sup>*J*(H,H) = 15.9 Hz, 1H), 2.26 (td, <sup>3</sup>*J*(H,H) = 6.8 Hz, <sup>4</sup>*J*(H,H) = 1.5 Hz, 2H), 2.06 (br.q, <sup>3</sup>*J*(H,H) = 6.8 Hz, 2H), 1.54-1.20 (m, 16H), 0.88 (tt, <sup>3</sup>*J*(H,H) = 6.8 Hz, 6H, CH<sub>3</sub>).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 143.4, 109.8, 88.7, 79.2, 33.0, 31.7, 31.4, 28.9, 28.8, 28.7, 28.6, 22.6, 22.5, 19.4, 14.1, 14.0.

**MS (70 eV, EI):** *m/z* (%) = 220 [M<sup>+</sup>] (25), 135 (19), 121 (21), 107 (37), 94 (20), 92 (52), 79 (61), 77 (30), 67 (71), 43 (64), 41 (100).

**HRMS (EI):** *m/z* calc. for [C<sub>16</sub>H<sub>28</sub>] 220.2191, found: 220.2189.

### Synthesis of (7E)-1-chlorotetradec-7-en-5-yne (Scheme 3, 11b)



Prepared according to **TP1** from *E*-octenyl iodide (**9**)<sup>7</sup> (238 mg, 1.0 mmol) [reaction conditions: Br/Mg-exchange with *i*PrMgCl·LiCl at T = -40 °C for 7 h] and 6-chlorobutylethynyllithium (**3c**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of 6-chloro-1-hexyne in THF (233 mg, 2 mmol) at -50 °C and stirring for 40 min). Purification by flash chromatography (pentane) yielded **11b** (136 mg, 60 %) as a colourless viscous oil. The product is not UV active; KMNO<sub>4</sub> solution should be used for detection and also GC analysis.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2955, 2926, 2856, 2216, 1765, 1632, 1455, 1433, 1378, 1331, 1315, 1300, 1275, 1166, 1051, 954, 725.

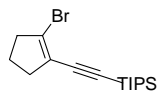
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 6.04 (dt, <sup>3</sup>*J*(H,H) = 15.9 Hz, <sup>3</sup>*J*(H,H) = 7.1 Hz, 1H), 5.41 (dm, <sup>3</sup>*J*(H,H) = 15.9 Hz, 1H), 3.56 (t, <sup>3</sup>*J*(H,H) = 6.5 Hz, 2H), 2.33 (dd, <sup>3</sup>*J*(H,H) = 6.8 Hz, <sup>4</sup>*J*(H,H) = 2.0 Hz, 2H), 2.06 (qd, <sup>3</sup>*J*(H,H) = 6.3 Hz, <sup>4</sup>*J*(H,H) = 1.3 Hz, 2H), 1.94-1.84 (m, 2H), 1.71-1.61 (m, 2H), 1.41-1.22 (m, 8H), 0.87 (t, <sup>3</sup>*J*(H,H) = 6.8 Hz, 3H, CH<sub>3</sub>).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 143.8, 109.6, 87.5, 79.9, 44.6, 33.0, 31.7, 31.6, 28.8 (2 × CH<sub>2</sub>), 26.6, 22.6, 18.7, 14.1.

**MS (70 eV, EI):** *m/z* (%) = 228 [M + 2]<sup>+</sup>(32), 226 [M<sup>+</sup>] (100), 155 (16), 142 (26), 135 (30), 119 (29), 107 (55), 93 (55), 91 (65), 79 (57), 67 (22).

**HRMS (EI):** *m/z* calc. for [C<sub>14</sub>H<sub>23</sub><sup>35</sup>Cl] 226.1488, found: 226.1478.

### Synthesis of [(2-bromocyclopent-1-en-1-yl)ethynyl](triisopropyl)silane (Scheme 3, 14a)



Prepared according to **TP1** from 1,2-dibromocyclopentene (**12**) (226 mg, 1.0 mmol) [reaction conditions: Br/Mg-exchange with *i*PrMgCl·LiCl at T = 25 °C for 48 h] and 1-triisopropylsilylethynyllithium (**3c**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of triisopropylsilylacetylene in THF (365 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane) yielded **14a** (200 mg, 61 %) as a colourless oil.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2943, 2892, 2866, 2147, 1763, 1717, 1608, 1581, 1463, 1384, 1367, 1311, 1291, 1244, 1230, 1092, 1072, 1016, 996, 935, 881, 730, 674.

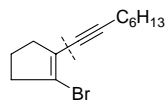
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  = 2.79-2.69 (m, 2H), 2.56-2.48 (m, 2H), 2.06-1.94 (m, 2H), 1.12 (s, 21H).

**<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):**  $\delta$  = 128.8, 124.9, 102.2, 97.6, 40.5, 36.1, 22.7, 18.8, 11.4.

**MS (70 eV, EI):** *m/z* (%) = 328 (15), 326 (14) [M]<sup>+</sup>, 286 (30), 285 (100), 284 (31), 283 (100), 257 (38), 255 (38), 243 (34), 241 (34), 229 (33), 227 (33), 215 (62), 213 (63), 199 (16), 175 (14), 173 (12), 161 (22), 159 (13), 147 (15), 139 (23), 137 (24), 133 (19), 117 (16), 109 (11), 107 (13), 91 (19).

**HRMS (EI):** *m/z* calc. for [C<sub>16</sub>H<sub>27</sub>BrSi] 326.1065, found: 326.1058.

### Synthesis of 1-bromo-2-oct-1-yn-1-ylcyclopentene (Scheme 3, 14b)



Prepared according to **TP1** from 1,2-dibromocyclopentene (**12**) (226 mg, 1.0 mmol) [reaction conditions: Br/Mg-exchange with *i*PrMgCl·LiCl at T = 25 °C for 48 h] and 1-hexylethynyllithium (**3b**, 2.0 mmol; prepared by adding *n*BuLi (2 mmol) to a 0.5 M solution of 1-octyne in THF (220 mg, 2 mmol) at 0 °C and stirring for 30 min). Purification by flash chromatography (pentane) yielded **14b** (158 mg, 62 %) as a colourless viscous oil, turns to brownish colour. The product is not UV active; KMNO<sub>4</sub> solution should be used for detection and also GC analysis.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2955, 2929, 2855, 2223, 1714, 1617, 1457, 1444, 1378, 1328, 1311, 1200, 1100, 941, 859, 724.

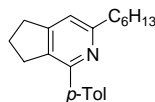
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 2.67 (m, 2H), 2.43 (m, 2H), 2.35 (t, <sup>3</sup>*J*(H,H) = 6.9 Hz, 2H), 1.95 (quin., <sup>3</sup>*J*(H,H) = 7.5 Hz, 2H), 1.55 (quin., <sup>3</sup>*J*(H,H) = 7.5 Hz, 2H), 1.48-1.22 (m, 6H), 0.88 (t, <sup>3</sup>*J*(H,H) = 6.9 Hz, 3H, CH<sub>3</sub>).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 125.4, 124.7, 97.0, 76.1, 40.0, 36.1, 31.3, 28.6, 28.5, 22.5, 22.4, 19.7, 14.0.

**MS (70 eV, EI):** *m/z* (%) = 256 [M + 2]<sup>+</sup>(93), 254 [M<sup>+</sup>] (100), 211 (29), 186 (27), 172 (25), 145 (26), 131 (29), 119 (41), 105 (52), 91 (65), 57 (30), 41 (48).

**HRMS (EI):** *m/z* calc. for [C<sub>13</sub>H<sub>19</sub><sup>79</sup>Br] 254.0670, found: 254.0666.

### Synthesis of 3-hexyl-1-(4-methylphenyl)-6,7-dihydro-5H-cyclopenta[c]pyridine (Scheme 4, 19a)



Prepared according to **TP3** from **14b** (0.5 mmol) and quenched with NH<sub>4</sub>Cl (or 1 M HCl). Purification by flash chromatography (pentane/Et<sub>2</sub>O 10:1 (0.5% Et<sub>3</sub>N)) yielded **19a** (94 mg, 64 %) as a colourless viscous oil.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2955, 2927, 2855, 1599, 1561, 1515, 1437, 1405, 1388, 1264, 1180, 1111, 1020, 824, 749, 722.



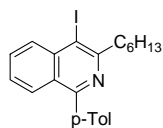
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.65 (d, <sup>3</sup>*J*(H,H) = 8.2 Hz, 2H, Ar*H*), 7.24 (d, <sup>3</sup>*J*(H,H) = 8.2 Hz, 2H, Ar*H*), 6.98 (s, 1H, Ar*H*), 3.03 (t, <sup>3</sup>*J*(H,H) = 7.4 Hz, 2H), 2.91 (t, <sup>3</sup>*J*(H,H) = 7.4 Hz, 2H), 2.79 (br.t, <sup>3</sup>*J*(H,H) = 7.9 Hz, 2H), 2.38 (s, 3H, CH<sub>3</sub>), 2.05 (quin., <sup>3</sup>*J*(H,H) = 7.4 Hz, 2H), 1.75 (br.quin., <sup>3</sup>*J*(H,H) = 7.9 Hz, 2H), 1.42-1.29 (m, 6H), 0.89 (t, <sup>3</sup>*J*(H,H) = 7.1 Hz, 3H, CH<sub>3</sub>).

**<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):**  $\delta$  = 160.4, 155.4, 153.5, 137.9, 137.8, 129.1, 128.6, 117.5, 38.6, 33.1, 32.5, 32.0, 30.3, 29.4, 25.7, 22.9, 21.5, 14.3.

**MS (70 eV, EI):** *m/z* (%) = 293 [M<sup>+</sup>] (6), 250 (11), 236 (15), 224 (18), 223 (100), 207 (3).

**HRMS (EI):** *m/z* calc. for [C<sub>21</sub>H<sub>27</sub>N] 293.2143, found: 293.2126.

### Synthesis of 3-hexyl-4-iodo-1-(4-methylphenyl)isoquinoline (Scheme 4, entry 20a)



Prepared according to **TP3** starting from **6u** (132 mg, 0.5 mmol). Purification by flash chromatography (pentane/Et<sub>2</sub>O 50:1 (2% Et<sub>3</sub>N)) yielded **20a** (133 mg, 62 %) as a colourless viscous oil turns to a greenish gum. Decomposes after several hours.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2954, 2925, 2855, 1615, 1597, 1494, 1455, 1439, 1407, 1348, 1323, 1183, 1123, 1019, 824, 763, 716, 691.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.86 (d, <sup>3</sup>*J*(H,H) = 7.7 Hz, Ar*H*), 7.95 (d, <sup>3</sup>*J*(H,H) = 7.9 Hz, 2H, Ar*H*), 7.84 (d, <sup>3</sup>*J*(H,H) = 7.7 Hz, 1H, Ar*H*), 7.50 (t, <sup>3</sup>*J*(H,H) = 7.7 Hz, 1H, Ar*H*), 7.46 (t, <sup>3</sup>*J*(H,H) = 7.7 Hz, 1H, Ar*H*), 7.32 (d, <sup>3</sup>*J*(H,H) = 7.9 Hz, 2H, Ar*H*), 3.65 (t, <sup>3</sup>*J*(H,H) = 7.5 Hz, 2H), 2.43 (s, 3H, CH<sub>3</sub>), 1.75 (quin., <sup>3</sup>*J*(H,H) = 7.5 Hz, 2H), 1.45-1.29 (m, 6H), 0.89 (t, <sup>3</sup>*J*(H,H) = 7.1 Hz, 3H, CH<sub>3</sub>).

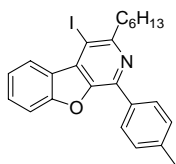
**<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):**  $\delta$  = 165.5, 153.7, 140.5, 140.3, 139.5, 131.5, 129.5, 128.5, 128.1, 128.0, 124.3, 122.3, 116.2, 43.3, 31.6, 30.5, 28.2, 22.6, 21.6, 14.1.

**MS (70 eV, EI):** *m/z* (%) = 429 [M<sup>+</sup>] (5), 386 (20), 359 (100), 302 (30), 258 (24), 233 (20), 217 (20), 140 (10), 115 (5).

**HRMS (EI):** *m/z* calc. for [C<sub>22</sub>H<sub>24</sub>N<sup>127</sup>I] 429.0953, found: 430.1015.

### Synthesis of 3-hexyl-4-iodo-1-(4-methylphenyl)[1]benzofuro[2,3-c]pyridine (Scheme 4, 23a)

Prepared according to **TP3** from 3-oct-1-yn-1-yl-1-benzofuran (**6y**) (93 mg, 0.41 mmol) [reaction conditions: deprotonation with *n*BuLi at  $t = -55$  °C for 4 h in THF and this lithiation was checked after iodolysis]. *p*-Tolunitrile (62 mg, 0.53 mmol), dissolved in 1 mL Et<sub>2</sub>O, was added at -40 °C and the mixture was stirred for 2 h at -40 °C. Then, I<sub>2</sub> (208 mg, 0.82 mmol) in 3 mL Et<sub>2</sub>O was added at -35 °C and stirred for 15 h. Purification by flash chromatography (pentane) yielded **23a** (120 mg, 62 %) as a pale yellow solid.



**mp.:** 108.1–108.9 °C.

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2952, 2916, 2851, 2359, 1624, 1556, 1513, 1460, 1397, 1354, 1197, 1187, 1063, 1023, 884, 826, 743.

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.90 (d, <sup>3</sup>*J*(H,H) = 7.7 Hz, 1H, ArH), 8.37 (d, <sup>3</sup>*J*(H,H) = 8.2 Hz, 2H, ArH), 7.73-7.61 (m, 2H, ArH), 7.54-7.45 (m, 1H, ArH), 7.39 (d, <sup>3</sup>*J*(H,H) = 8.2 Hz, 2H, ArH), 3.25 (t, <sup>3</sup>*J*(H,H) = 8.2 Hz, 2H, CH<sub>2</sub>), 2.48 (s, 3H, CH<sub>3</sub>), 1.97-1.84 (m, 2H, CH<sub>2</sub>), 1.62-1.27 (m, 6H), 0.95 (t, <sup>3</sup>*J*(H,H) = 7.1 Hz, 3H, CH<sub>3</sub>).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  = 157.1, 156.6, 148.2, 140.8, 139.7, 135.2, 133.2, 130.2, 129.6, 128.8, 124.1, 123.0, 122.6, 112.5, 85.2, 40.2, 32.1, 29.6, 29.4, 23.0, 21.7, 14.4.

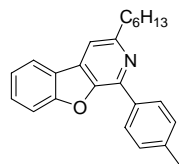
**MS (70 eV, EI):** *m/z* (%) = 426 (10), 400 (17), 399 (100), 342 (14), 273 (16).

**HRMS (EI):** *m/z* calc. for [C<sub>24</sub>H<sub>24</sub>INO] 469.0903, found: 469.0903.

### Synthesis of 3-hexyl-1-(4-methylphenyl)[1]benzofuro[2,3-c]pyridine (Scheme 4, 23b)

Iodo-compound **23a** (0.25 mmol) or corresponding bromo-compound (0.25 mmol) was placed in a dry flask and dissolved in dry THF (3 mL) and cooled to -78 °C. Then, *n*BuLi (0.275 mmol) was added dropwise and stirred for further 1h. The reaction mixture was diluted with ether and washed with aq. NH<sub>4</sub>Cl solution and extracted with Et<sub>2</sub>O. The combined organic

layers were dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. Purification by flash chromatography (pentane/Et<sub>2</sub>O 40:1) yielded **23b** (0.21 mmol, 83 %) as a white solid.



**mp:** 72.3-74.3 °C

**IR (neat):**  $\nu_{\max}$  (cm<sup>-1</sup>) = 2956, 2921, 2854, 1628, 1579, 1515, 1460, 1428, 1383, 1357, 1283, 1260, 1193, 1185, 1156, 1104, 1091, 1045, 1020, 879, 857, 823, 800, 744, 695, 620.

**<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.35 (d, <sup>3</sup>J(H,H) = 8.4 Hz, 2H, ArH), 8.00 (dt, <sup>3</sup>J(H,H) = 7.5 Hz, 1H, ArH), 7.66 (d, <sup>3</sup>J(H,H) = 8.4 Hz, 1H, ArH), 7.62 (s, 1H, ArH), 7.57 (t, <sup>3</sup>J(H,H) = 8.4 Hz, 1H, ArH), 7.38 (t, <sup>3</sup>J(H,H) = 7.9 Hz, 1H, ArH), 7.36 (d, <sup>3</sup>J(H,H) = 8.4 Hz, 2H, ArH), 2.99 (t, <sup>3</sup>J(H,H) = 7.9 Hz, 2H, CH<sub>2</sub>), 2.45 (s, 3H, CH<sub>3</sub>), 1.91-1.84 (m, 2H, CH<sub>2</sub>), 1.47-1.41 (m, 2H, CH<sub>2</sub>), 1.39-1.30 (m, 4H, 2 x CH<sub>2</sub>), 0.89 (t, <sup>3</sup>J(H,H) = 7.1 Hz, 3H, CH<sub>3</sub>).

**<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>):**  $\delta$  = 157.1, 155.8, 149.1, 141.6, 139.2, 134.0, 132.7, 129.7, 129.5, 128.8, 123.3, 122.9, 122.0, 112.7, 112.4, 38.6, 32.0, 30.5, 29.4, 22.9, 21.7, 14.3.

**MS (70 eV, EI):**  $m/z$  (%) = 343 (13), 314 (19), 301 (13), 300 (56), 287 (25), 286 (67), 274 (100), 273 (49), 272 (21), 257 (12).

**HRMS (EI):**  $m/z$  calc. for [C<sub>24</sub>H<sub>25</sub>NO] 343.1936, found: 343.1926.

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