

## Supporting Information

# Transition Metal Free Carboamination of Internal Alkynes – an Easy Access to Polysubstituted Quinolines

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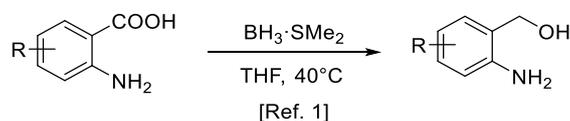
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## General Experimental

Reactions, if not otherwise mentioned, were performed in standard glassware with no special precautions taken for the exclusion of moisture or air. 1,2-Dichloroethane (DCE) was filtered through basic alumina before used. Products were purified by flash chromatography on basic alumina (eluents given in brackets, EtOAc refers to ethyl acetate) or by semi-preparative HPLC received from Knauer containing a Hibar<sup>®</sup>250-25 HPLC-column, a Smartline Pump 1000 and a Smartline UV Detector 2500 (eluents given in brackets, EtOAc refers to ethyl acetate). Yields refer to analytically pure samples. NMR: Varian Mercury 300, Agilent VNMRS 400, Agilent VNMRS 600. <sup>1</sup>H-NMR: CDCl<sub>3</sub> (7.26 ppm) as internal standard in the same solvent; <sup>13</sup>C-NMR: CDCl<sub>3</sub> (77.16 ppm) as internal standard in the same solvent; integrals in accordance with assignments, coupling constants are measured in Hz and always constitute J<sub>H,H</sub> coupling constants, if not otherwise noted. IR spectra: Perkin-Elmer 1760 series FT-IR as neat films on KBr plates. Low-resolution and high resolution mass spectra were obtained using electron impact ionisation (EI) and chemical ionisation (CI) techniques, or positive and/or negative electrospray ionisation (ES) on Finnigan SSQ or 7000 Thermo Deca XP mass spectrometers. The signal around 83.5 ppm in some <sup>13</sup>C-NMR spectra is an artifact peak, originates from the 600 MHz spectrometer and is not an impurity from the submitted sample.

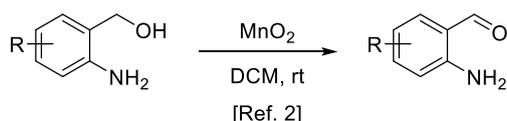
## Synthesis of Starting Materials

### General Procedure for the Reduction of Carboxylic Acids to Benzylic Alcohols (GP1)<sup>1</sup>



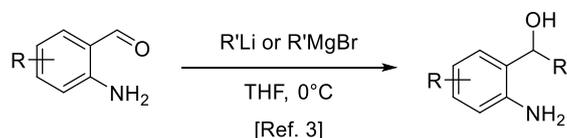
To the anthranilic acid derivative (1.0 equiv.) dissolved in dry THF in a flame-dried schlenk flask was added BH<sub>3</sub>·SMe<sub>2</sub> (2M in THF, 3.0 equiv.) at 0°C under an argon atmosphere. After complete addition the reaction mixture was heated to 40°C and stirred at this temperature for 24h. The mixture was quenched by water addition and the aqueous phase was saturated with potassium carbonate. The phases were separated and the aqueous phase was extracted with Et<sub>2</sub>O. The combined organic layers were dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure. The corresponding benzylic alcohols were used without further purification.

## General Procedure for the Oxidation of Benzylic Alcohols (GP2)<sup>2</sup>



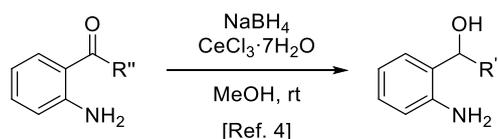
The respective 2-aminobenzyl alcohol (1.0 equiv) was dissolved in DCM when MnO<sub>2</sub> (4.0 equiv) was added. The mixture was stirred at room temperature for 20 h, filtered through a short plug of celite and the solvent removed under reduced pressure. The residue was purified by column chromatography to obtain the corresponding benzaldehyde.

## General Procedure for the Addition of Organolithium- or Grignard-Reagents to 2-Aminobenzaldehyde (GP3)<sup>3</sup>



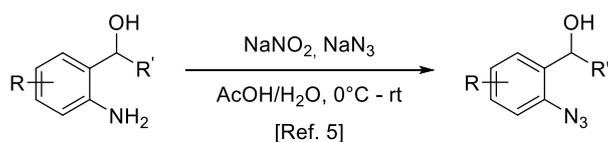
To the benzaldehyde derivative (1.0 equiv.) dissolved in dry THF in a flame-dried schlenk flask was added dropwise the respective organometallic reagent (3.0 equiv.) at 0°C under an argon atmosphere. After full consumption of the starting material (monitored by TLC) the reaction was quenched by addition of sat. aqueous NH<sub>4</sub>Cl. The mixture was extracted with Et<sub>2</sub>O, the combined organic layers dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure. The residue was purified by column chromatography.

## General Procedure for the Reduction of Ketones to Alcohols (GP4)<sup>4</sup>



The respective acetophenone derivative (1.0 equiv) and CeCl<sub>3</sub>·7H<sub>2</sub>O (1.1 equiv) were dissolved in MeOH and NaBH<sub>4</sub> (3.0 equiv) was added portionwise at room temperature. After full consumption of the starting material (~ 15-30 min, monitored by TLC), the reaction was quenched by careful addition of water. The mixture was extracted with Et<sub>2</sub>O, the combined organic layers were dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The residue was purified by column chromatography.

## General Procedure for the Azidation of Anilines (GP5)<sup>5</sup>

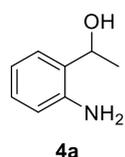


The respective 2-amino alcohol (1.0 equiv) was suspended in a HOAc/H<sub>2</sub>O mixture (2:1) and the flask, coated with aluminum foil, placed in an ice-bath. NaNO<sub>2</sub> (1.4 equiv) was added slowly and the reaction mixture was stirred at 0°C for 1 h. After addition of NaN<sub>3</sub> (1.5 equiv) the ice-bath was removed and the solution stirred for 30 min. The reaction mixture was diluted with H<sub>2</sub>O and DCM and solid K<sub>2</sub>CO<sub>3</sub> was added until no further gas evolution occurred. The phases were separated and the aqueous phase extracted with DCM. The combined organic layers were washed with brine, dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure. The residue was purified by column chromatography to obtain the corresponding azide.

## Synthesis of Compounds 1a and 1f

Compounds **1a** and **1f** were synthesized in two steps following literature procedures.<sup>4,5</sup>

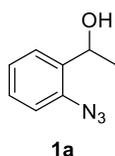
### 1-(2-Aminophenyl)ethan-1-ol (**4a**)<sup>6</sup>



Following the general procedure GP4 using 2-aminoacetophenone (1.35 g, 10.0 mmol, 1.0 equiv.), CeCl<sub>3</sub>·7H<sub>2</sub>O (4.10 g, 11.0 mmol, 1.1 equiv.) and NaBH<sub>4</sub> (1.13 g, 30.0 mmol, 3.0 equiv.) in MeOH (40 mL) afforded the corresponding alcohol **4a** after purification by column chromatography (pentane/EtOAc = 5:1) as a yellow solid (1.32 g, 9.6 mmol, 96% yield). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.13 – 7.06 (m, 2H), 6.73 (td, *J* = 7.5, 1.2 Hz, 1H), 6.69 – 6.64 (m, 1H), 4.92 (q, *J* = 6.6 Hz, 1H), 1.59 (d, *J* = 6.6 Hz, 3H). <sup>13</sup>C-NMR (150 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ = 145.6, 129.7, 127.4, 126.0, 116.3, 115.4, 66.3, 22.9; *m/z* (EI) (%): 137.1 (100), 122.1 (36), 120.1 (26), 119.1 (85), 118.1 (60), 94.1 (43), 93.1 (17), 91.1 (18), 77.2 (25); IR (KBr): ν = 3427, 2938, 2869, 2212, 1718, 1670, 1591, 1452, 1351, 1319, 1072, 964, 843 cm<sup>-1</sup>.

The analytic data matched with that reported previously.<sup>6</sup>

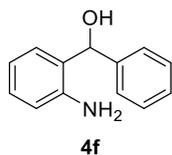
### 1-(2-Azidophenyl)ethan-1-ol (**1a**)<sup>7</sup>



Following the general procedure GP5 using **4a** (772 mg, 5.6 mmol, 1.0 equiv.), NaNO<sub>2</sub> (544 mg, 7.9 mmol, 1.4 equiv.) and NaN<sub>3</sub> (549 mg, 8.5 mmol, 1.5 equiv.) in AcOH (38 mL) and water (19 mL) afforded the corresponding azide **1a** after column chromatography (pentane/EE = 10:1) as an orange oil (898 mg, 5.5 mmol, 98%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.51 – 7.43 (m, 1H), 7.31 (td, *J* = 7.7, 1.6 Hz, 1H), 7.19 – 7.12 (m, 2H), 5.08 (q, *J* = 6.3 Hz, 1H), 2.24 (s, 1H), 1.47 (d, *J* = 6.5 Hz, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 136.8, 136.6, 128.6, 126.7, 125.2, 118.2, 66.1, 23.8. *m/z* (EI) (%): 119.8 (95), 117.7 (100), 105.8 (55), 92.9 (37), 91.9 (76), 90.8 (33), 78.9 (32), 76.8 (27), 64.9 (71), 63.9 (21), 62.9 (26); IR (KBr): ν = 3346, 2109, 1583, 1483, 1283, 1069, 1009, 898, 750, 669 cm<sup>-1</sup>.

The analytic data matched with that reported previously.<sup>7</sup>

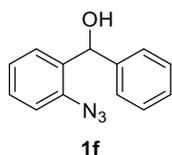
### (2-aminophenyl)phenylmethanol (**4f**)<sup>8</sup>



Following the general procedure GP4 using 2-aminobenzophenone (1.61 g, 8.0 mmol, 1.0 equiv.), CeCl<sub>3</sub>·7H<sub>2</sub>O (3.28 g, 8.8 mmol, 1.1 equiv.) and NaBH<sub>4</sub> (0.91 g, 24.0 mmol, 3.0 equiv.) in MeOH (30 mL) afforded the corresponding alcohol **4f** after purification by column chromatography (pentane/EtOAc = 6:1 → 3:1) as a yellow solid (1.49 g, 7.5 mmol, 94%). <sup>1</sup>H-NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ = 7.37 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.97 – 6.91 (m, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.51 (t, *J* = 7.4 Hz, 1H), 5.84 (d, *J* = 4.3 Hz, 1H), 5.72 (d, *J* = 4.2 Hz, 1H), 4.95 (s, 2H). <sup>13</sup>C-NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ = 145.8, 144.2, 127.9, 127.8, 127.6, 127.5, 126.53, 126.47, 115.7, 115.2, 71.9. *m/z* (EI) (%): 199.0 (29), 181.0 (19), 180.0 (100); IR (KBr): ν = 3200, 1615, 1465, 1280, 1009, 871, 736 cm<sup>-1</sup>.

The analytic data matched with that reported previously.<sup>8</sup>

### (2-Azidophenyl)(phenyl)methanol (**1f**)<sup>8</sup>



Following the general procedure GP5 using **4f** (500 mg, 2.5 mmol, 1.0 equiv.), NaNO<sub>2</sub> (242 mg, 3.5 mmol, 1.4 equiv.) and NaN<sub>3</sub> (249 mg, 3.8 mmol, 1.5 equiv.) in AcOH (17 mL) and water (9 mL) afforded the corresponding azide **1f** after column chromatography (pentane/EE = 10:1) as a yellow solid (542 mg, 2.4 mmol, 96%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.46 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.38 – 7.36 (m, 2H), 7.34 – 7.30 (m, 3H), 7.28 – 7.24 (m, 1H), 7.15 (td, *J* = 8.2, 1.1 Hz, 2H), 6.02 (d, *J* = 4.1 Hz, 1H), 2.58 – 2.56 (m, 1H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ = 142.9, 137.1, 134.8, 129.0, 128.5,

128.1, 127.7, 126.7, 125.2, 118.3, 71.7.  $m/z$  (EI) (%): 196.0 (64), 180.0 (44), 168.0 (100), 167.0 (32), 77.0 (26); IR (KBr):  $\nu = 3285, 2120, 1483, 1448, 1289, 1186, 1019, 849, 752, 687$ . The analytic data matched with that reported previously.<sup>8</sup>

## Synthesis of Compounds **1b**, **1c**, **1d**, **1e**

Compounds **1b** and **1c** were synthesized in four steps following literature procedures.<sup>1-3,5</sup> Compounds **1d** and **1e** were prepared in three steps starting from the corresponding benzylic alcohols.<sup>2,3,5</sup> Yields are not optimized.

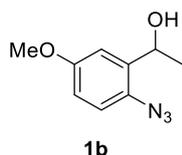
### 2-Amino-5-methoxybenzaldehyde (**4b**)<sup>9</sup>



Following the general procedure GP1 using 2-amino-5-methoxybenzoic acid (1.76 g, 10.5 mmol, 1.0 equiv.) and  $\text{BH}_3\cdot\text{SMe}_2$  (15.8 mL, 31.5 mmol, 3.0 equiv., 2M in THF) in THF (17 mL) afforded the corresponding benzylic alcohol which was used without further purification. The crude benzylic alcohol (1.32 g, 8.6 mmol, 1.0 equiv.) was reacted together with  $\text{MnO}_2$  (2.99 g, 34.4 mmol, 4.0 equiv.) in DCM (28 mL) following GP2 afforded the corresponding benzaldehyde **4b** after purification by column chromatography (pentane/EtOAc = 3:1) as a red oil (1.00 g, 6.6 mmol, 63% overall yield).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.85$  (s, 1H), 7.00 (dd,  $J = 8.8, 3.0$  Hz, 1H), 6.96 (d,  $J = 2.9$  Hz, 1H), 6.62 (d,  $J = 8.8$  Hz, 1H), 5.83 (s, 2H), 3.79 (s, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 193.6, 150.9, 144.9, 124.8, 118.6, 117.8, 116.9, 56.1$ .  $m/z$  (EI) (%): 151.2 (27), 108.2 (44), 90.2 (21), 80.2 (38), 65.2 (22), 63.2 (40), 53.2 (71), 52.2 (100), 51.2 (25); IR (KBr):  $\nu = 3460, 3347, 2938, 2837, 1660, 1590, 1558, 1485, 1365, 1240, 1155, 1033, 932, 814, 763, 670, 540$   $\text{cm}^{-1}$ .

The analytic data matched with that reported previously.<sup>9</sup>

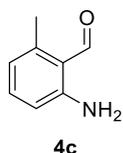
### 1-(2-Azido-5-methoxyphenyl)ethan-1-ol (**1b**)



Following the general procedure GP3 reacting **4b** (1.00 g, 6.6 mmol, 1.0 equiv.) in THF (30 mL) together with  $\text{MeMgI}$  (6.6 mL, 19.9 mmol, 3.0 equiv., 3M in  $\text{Et}_2\text{O}$ ) afforded the corresponding alcohol which was used directly for the next step without further purification. Following the general procedure GP5 using the crude alcohol (1.00g, 6.6 mmol, 1.0 equiv.),  $\text{NaNO}_2$  (638 mg, 9.2 mmol, 1.4 equiv.) and  $\text{NaN}_3$  (646 mg, 9.9 mmol, 1.5 equiv.) in AcOH (43 mL) and water (20 mL) afforded the corresponding azide **1b** after column chromatography (pentane/EE = 10:1  $\rightarrow$  7:1) as a red oil (256 mg, 1.3 mmol, 20% overall yield).  $^1\text{H-NMR}$  (600 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta = 7.15$  (d,  $J = 8.7$

Hz, 1H), 7.08 (d,  $J = 3.0$  Hz, 1H), 6.89 (dd,  $J = 8.7, 3.0$  Hz, 1H), 5.18 (d,  $J = 4.4$  Hz, 1H), 4.88 – 4.80 (m, 1H), 3.75 (s, 3H), 1.25 (d,  $J = 6.4$  Hz, 3H).  $^{13}\text{C}$ -NMR (150 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta = 156.8, 140.0, 127.4, 119.3, 113.2, 111.7, 63.2, 55.3, 24.8$ .  $m/z$  (EI) (%): 150.0 (100), 136.0 (33), 122.0 (71), 104.0 (35), 94.1 (24), 84.8 (51), 83.0 (64), 80.1 (34), 79.2 (32), 78.2 (26), 77.1 (46), 66.2 (26), 65.2 (22), 63.1 (21), 53.2 (30), 52.2 (56), 51.2 (29), 47.0 (32); HRMS-EI calcd. for  $\text{C}_9\text{H}_{11}\text{O}_2\text{N}_3$ : 193.0846, found: 193.0845 ( $[\text{M}]^+$ ); IR (KBr):  $\nu = 3368, 2116, 1486, 1283, 1233, 1162, 1020, 876, 809$   $\text{cm}^{-1}$ .

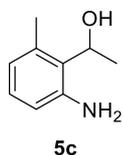
## 2-Amino-6-methylbenzaldehyde (**4c**)<sup>2</sup>



Following the general procedure GP1 using 2-amino-6-methylbenzoic acid (1.8 g, 11.8 mmol, 1.0 equiv.) and  $\text{BH}_3\cdot\text{SMe}_2$  (17.7 mL, 35.4 mmol, 3.0 equiv.) in THF (40 mL) afforded the corresponding benzylic alcohol which was used without further purification. The crude benzylic alcohol (417 mg, 3.0 mmol, 1.0 equiv.) was reacted together with  $\text{MnO}_2$  (1057 mg, 12.0 mmol, 4.0 equiv.) in DCM (10 mL) following GP2 afforded the corresponding benzaldehyde **4c** after purification by column chromatography (pentane/EtOAc = 10:1) as a yellow liquid (411 mg, 3.0 mmol, 26% overall yield).  $^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 10.36$  (s, 1H), 7.16 (t,  $J = 7.8$  Hz, 1H), 6.49 (d,  $J = 8.4$  Hz, 1H), 6.44 (d,  $J = 7.2$  Hz, 1H), 6.40 (bs, 2H), 2.56 (s, 3H).  $^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta = 192.6, 151.1, 142.9, 135.6, 118.9, 116.5, 115.2, 19.2$ .  $m/z$  (EI) (%): 135.1 (59), 118.1 (18), 107.1 (74), 106.1 (100), 91.1 (63), 90.1 (53), 89.1 (43), 79.2 (40), 78.2 (28), 77.2 (80), 65.2 (53), 64.2 (21), 63.2 (37), 57.2 (19), 55.2 (23), 54.2 (18), 53.2 (40), 52.2 (46), 51.2 (59), 50.2 (28); IR (KBr):  $\nu = 3428, 3323, 1606, 1455, 1197, 1028, 965, 779, 719$   $\text{cm}^{-1}$ .

The analytic data matched with that reported previously.<sup>2</sup>

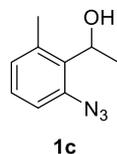
## 1-(2-Amino-6-methylphenyl)ethan-1-ol (**5c**)



Following the general procedure GP3 reacting **4c** (411 mg, 3.0 mmol, 1.0 equiv.) in THF (13 mL) together with  $\text{MeMgI}$  (3 mL, 9.1 mmol, 3.0 equiv., 3M in  $\text{Et}_2\text{O}$ ) afforded the corresponding alcohol **5c** after purification by column chromatography (pentane/EE = 5:1  $\rightarrow$  2:1) as a yellow solid (164 mg, 1.1 mmol, 36%).  $^1\text{H}$ -NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta = 6.77$  (t,  $J = 7.7$  Hz, 1H), 6.43 (d,  $J = 8.0$  Hz, 1H), 6.30 (d,  $J = 7.4$  Hz, 1H), 5.36 (d,  $J = 2.0$  Hz, 1H), 5.22 (s, 2H), 5.10 (q,  $J = 6.5$  Hz, 1H), 2.15 (s, 3H), 1.35 (d,  $J = 6.6$  Hz, 3H).  $^{13}\text{C}$ -NMR (100 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta = 146.9, 133.8, 126.7, 126.2, 118.4, 114.3, 65.5, 20.1, 19.7$ .  $m/z$  (EI) (%): 151.1 (100), 136.0 (41), 134.0 (32), 133.1 (55), 132.0 (49), 116.0 (19), 106.1 (17), 93.1 (18), 91.1 (15); HRMS-ESI calcd. for

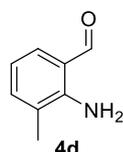
C<sub>9</sub>H<sub>13</sub>ONNa: 174.0889, found: 174.0892 ([M + Na]<sup>+</sup>); IR (KBr):  $\nu$  = 3357, 3290, 2953, 1591, 1454, 1286, 1070, 829, 677 cm<sup>-1</sup>.

### 1-(2-Azido-6-methylphenyl)ethan-1-ol (**1c**)



Following the general procedure GP5 using **5c** (164 mg, 1.1 mmol, 1.0 equiv.), NaNO<sub>2</sub> (90 mg, 1.3 mmol, 1.4 equiv.) and NaN<sub>3</sub> (92 mg, 1.4 mmol, 1.5 equiv.) in AcOH (7 mL) and water (3 mL) afforded the corresponding azide **1c** after column chromatography (pentane/EE = 20:1) as a yellow oil (176 mg, 1.0 mmol, 90%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.18 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 5.11 (dq, *J* = 10.5, 6.8 Hz, 1H), 3.41 (d, *J* = 10.5 Hz, 1H), 2.35 (s, 3H), 1.54 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 137.0, 136.8, 134.1, 128.0, 127.8, 116.8, 67.1, 23.4, 19.9. *m/z* (EI) (%): 134.0 (67), 132.0 (69), 120.0 (34), 117.0 (23), 106.0 (80), 104.0 (27), 91.0 (29), 80.2 (27), 79.1 (90), 78.2 (38), 77.1 (100), 65.1 (31), 63.1 (30), 53.2 (22), 52.2 (31), 51.2 (50); HRMS-EI calcd. for C<sub>9</sub>H<sub>11</sub>ON<sub>3</sub>: 177.0897, found: 177.0895 ([M]<sup>+</sup>); IR (KBr):  $\nu$  = 3396, 2974, 2110, 1581, 1459, 1288, 1072, 1013, 899, 775, 738 cm<sup>-1</sup>.

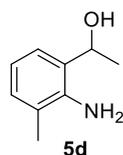
### 2-Amino-3-methylbenzaldehyde (**4d**)<sup>2</sup>



Following the general procedure GP2 reacting 2-amino-3-methylbenzyl alcohol (2.06 g, 15.0 mmol, 1.0 equiv.) together with MnO<sub>2</sub> (5.22 g, 60.0 mmol, 4.0 equiv.) in DCM (40 mL) afforded the corresponding benzaldehyde **4d** after purification by column chromatography (pentane/EtOAc = 5:1) as a yellow liquid (0.86 g, 6.4 mmol, 42%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.88 (s, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.21 (s, 2H), 2.17 (s, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 194.4, 148.5, 135.9, 134.0, 122.7, 118.4, 116.1, 16.7. *m/z* (EI) (%): 134.9 (100), 106.9 (54), 105.9 (99), 76.8 (22); IR (KBr):  $\nu$  = 3465, 3344, 1609, 1451, 1380, 1216, 916, 751 cm<sup>-1</sup>.

The analytic data matched with that reported previously.<sup>2</sup>

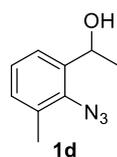
### 1-(2-Amino-3-methylphenyl)ethan-1-ol (**5d**)



Following the general procedure GP3 reacting **4d** (591 mg, 4.4 mmol, 1.0 equiv.) in THF (20 mL) together with MeMgI (4.4 mL, 13.2 mmol, 3.0 equiv., 3M in Et<sub>2</sub>O) afforded the corresponding alcohol **5d** after purification by column chromatography (pentane/EE = 5:1) as a pale yellow solid (512 mg, 3.4 mmol, 77%). <sup>1</sup>H-NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  = 6.93 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.46

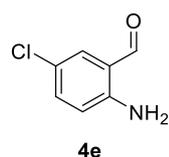
(t,  $J = 7.4$  Hz, 1H), 5.18 – 5.15 (m, 1H), 4.83 – 4.72 (m, 3H), 2.07 (s, 3H), 1.34 (dd,  $J = 6.4$ , 0.8 Hz, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta = 143.4, 128.8, 128.4, 123.9, 121.5, 115.7, 66.9, 22.7, 17.7$ .  $m/z$  (EI) (%): 151.1 (90), 136.1 (21), 134.1 (21), 133.1 (100), 132.0 (72), 117.1 (16), 108.1 (26), 106.1 (20), 93.1 (21), 91.2 (16); HRMS-ESI calcd. for  $\text{C}_9\text{H}_{13}\text{ONNa}$ : 174.0889, found: 174.0892 ( $[\text{M} + \text{Na}]^+$ ); IR (KBr):  $\nu = 3329, 2970, 1739, 1617, 1445, 1369, 1226, 1048, 913, 771 \text{ cm}^{-1}$ .

### 1-(2-Azido-3-methylphenyl)ethan-1-ol (**1d**)



Following the general procedure GP5 using **5d** (545 mg, 3.6 mmol, 1.0 equiv.),  $\text{NaNO}_2$  (348 mg, 5.0 mmol, 1.4 equiv.) and  $\text{NaN}_3$  (351 mg, 5.4 mmol, 1.5 equiv.) in AcOH (24 mL) and water (12 mL) afforded the corresponding azide **1d** after column chromatography (pentane/EE = 10:1  $\rightarrow$  3:1) as a yellow oil (536 mg, 3.0 mmol, 84%).  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.35$  (ddd,  $J = 7.6, 1.1, 0.5$  Hz, 1H), 7.14 (t,  $J = 7.6$  Hz, 1H), 7.10 (dd,  $J = 7.5, 0.9$  Hz, 1H), 5.21 (q,  $J = 6.5$  Hz, 1H), 2.44 (s, 3H), 1.49 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta = 139.3, 135.1, 132.9, 130.6, 126.5, 124.1, 66.6, 24.2, 18.1$ .  $m/z$  (EI) (%): 134.0 (100), 132.0 (30), 120.0 (24), 106.0 (39), 79.0 (19), 77.0 (19); HRMS-ESI calcd. for  $\text{C}_9\text{H}_{11}\text{ON}_3\text{Na}$ : 200.0794, found: 200.0793 ( $[\text{M} + \text{Na}]^+$ ); IR (KBr):  $\nu = 3350, 2116, 1460, 1427, 1285, 1240, 1109, 1069, 1012, 864, 783, 753 \text{ cm}^{-1}$ .

### 2-Amino-5-chlorobenzaldehyde (**4e**)<sup>10</sup>

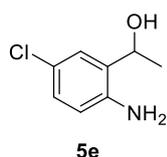


Following the general procedure GP2 reacting 2-amino-5-chlorobenzyl alcohol (2.36 g, 15.0 mmol, 1.0 equiv.) together with  $\text{MnO}_2$  (5.22 g, 60.0 mmol, 4.0 equiv.) in DCM (40 mL) afforded the corresponding benzaldehyde **4e** after purification by column chromatography (pentane/EtOAc = 5:1) as a yellow solid (1.65 g, 10.6 mmol, 70%).  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.80$  (s, 1H), 7.44 (d,  $J = 2.5$  Hz, 1H), 7.25 (dd,  $J = 8.8, 2.5$  Hz, 1H), 6.61 (d,  $J = 8.8$  Hz, 1H), 6.13 (s, 2H).  $^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta = 193.0, 148.5, 135.4, 134.4, 120.9, 119.4, 117.8$ .  $m/z$  (EI) (%): 157.0 (28), 155.0 (81), 129.0 (332), 127.0 (100), 92.1 (21); IR (KBr):  $\nu = 3327, 1659, 1551, 1472, 1159, 889, 711 \text{ cm}^{-1}$ .

The analytic data matched with that reported previously.<sup>10</sup>

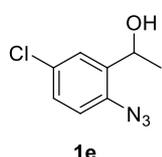
### 1-(2-Amino-5-chlorophenyl)ethan-1-ol (**5e**)

Following the general procedure GP3 reacting **4e** (562 mg, 3.6 mmol, 1.0 equiv.) in THF (15 mL) together with  $\text{MeMgI}$  (3.6 mL, 10.8 mmol, 3.0 equiv., 3M in  $\text{Et}_2\text{O}$ ) afforded the



corresponding alcohol **5e** after purification by column chromatography (pentane/EE = 6:1 → 2:1) as a white solid (347 mg, 2.0 mmol, 56%). <sup>1</sup>H-NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ = 7.10 (d, *J* = 2.6 Hz, 1H), 6.92 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 5.18 (d, *J* = 4.2 Hz, 1H), 5.08 (s, 2H), 4.79 – 4.69 (m, 1H), 1.28 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C-NMR (150 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): δ = 144.1, 131.8, 126.5, 125.1, 119.3, 116.3, 64.9, 22.8. *m/z* (EI) (%): 173.1 (29), 171.1 (100), 156.1 (22), 155.1 (31), 154.1 (30), 153.1 (83), 152.2 (34), 117.1 (24), 93.2 (27); HRMS-EI calcd. for C<sub>8</sub>H<sub>10</sub>ClNO: 171.0445, found: 171.0446 ([M]<sup>+</sup>); IR (KBr): ν = 3377, 1613, 1481, 1258, 1183, 1095, 885, 813, 733 cm<sup>-1</sup>.

### 1-(2-Azido-5-chlorophenyl)ethan-1-ol (**1e**)

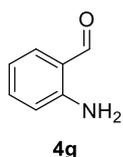


Following the general procedure GP5 using **5e** (294 mg, 1.7 mmol, 1.0 equiv.), NaNO<sub>2</sub> (166 mg, 2.4 mmol, 1.4 equiv.) and NaN<sub>3</sub> (167 mg, 2.6 mmol, 1.5 equiv.) in AcOH (12 mL) and water (6 mL) afforded the corresponding azide **1e** after column chromatography (pentane/EE = 10:1) as a yellow oil (208 mg, 1.1 mmol, 62%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.48 (d, *J* = 2.4 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 5.04 (q, *J* = 6.5 Hz, 1H), 1.45 (d, *J* = 6.5 Hz, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ = 138.6, 135.1, 130.7, 128.5, 126.9, 119.4, 65.7, 23.8. *m/z* (EI) (%): 197.1 (33), 155.9 (25), 154.0 (100), 125.9 (26); HRMS-EI calcd. for C<sub>8</sub>H<sub>8</sub><sup>35</sup>ClON<sub>3</sub>: 197.0350, found: 197.0354 ([M]<sup>+</sup>); IR (KBr): ν = 3232, 2974, 2118, 2081, 1472, 1403, 1346, 1294, 1187, 1100, 1074, 1018, 911, 810, 690 cm<sup>-1</sup>.

### Synthesis of Compound **1g**

Compound **1g** was synthesized in three steps following literature procedures.<sup>2,3,5</sup> Yields refer to the whole synthetic route and are not optimized.

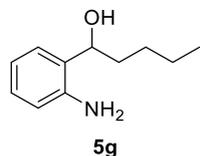
### 2-Aminobenzaldehyde (**4g**)<sup>11</sup>



Following the general procedure GP2 reacting 2-aminobenzyl alcohol (2.46 g, 20.0 mmol, 1.0 equiv.) together with MnO<sub>2</sub> (6.96 g, 80.0 mmol, 4.0 equiv.) in DCM (50 mL) afforded the corresponding benzaldehyde **4g** after purification by column chromatography (pentane/EtOAc = 10:1) as a yellow solid (1.65 g, 13.6 mmol, 68%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.88 – 9.87 (m, 1H), 7.48 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.34 – 7.28 (m, 1H), 6.75 (ddd, *J* = 7.8, 7.2, 1.0 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 6.11 (s, 2H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ = 194.2, 150.0, 135.9, 135.3, 119.0, 116.5, 116.1. *m/z* (EI)

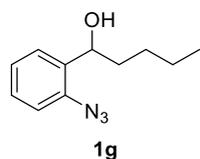
(%): 121.0 (100), 93.1 (94), 92.1 (33), 66.8 (36), 66.0 (27), 46.0 (73); IR (KBr):  $\nu = 3461, 3321, 1659, 1584, 1472, 1396, 1321, 1141, 1011, 869, 745 \text{ cm}^{-1}$ .

### 1-(2-Aminophenyl)pentan-1-ol (**5g**)<sup>12</sup>



Following the general procedure GP3 reacting **4g** (848 mg, 7.0 mmol, 1.0 equiv.) in THF (30 mL) together with BuLi (13 mL, 21.0 mmol, 3.0 equiv., 1.6 M in THF) afforded the corresponding alcohol **5g** after purification by column chromatography (pentane/EE = 20:1  $\rightarrow$  5:1) as a yellow solid (515 mg, 2.9 mmol, 41%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 7.08$  (td,  $J = 7.6, 1.5$  Hz, 1H),  $7.01$  (dd,  $J = 7.6, 1.3$  Hz, 1H),  $6.72$  (td,  $J = 7.4, 1.0$  Hz, 1H),  $6.63$  (dd,  $J = 7.9, 0.9$  Hz, 1H),  $4.60$  (t,  $J = 7.0$  Hz, 1H),  $4.17$  (s, 2H),  $2.63$  (s, 1H),  $1.93 - 1.79$  (m, 2H),  $1.46 - 1.32$  (m, 3H),  $1.30 - 1.20$  (m, 1H),  $0.92$  (t,  $J = 7.3$  Hz, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>):  $\delta = 145.0, 128.4, 127.9, 127.6, 118.1, 116.9, 74.5, 34.9, 28.5, 22.7, 14.1$ .  $m/z$  (EI) (%): 179.1 (50), 132.1 (20), 122.1 (100), 94.1 (33); IR (KBr):  $\nu = 3277, 2938, 1740, 1451, 1366, 1221, 1047, 766 \text{ cm}^{-1}$ .

### 1-(2-Azidophenyl)pentan-1-ol (**1g**)



Following the general procedure GP5 using **5g** (515 mg, 2.9 mmol, 1.0 equiv.), NaNO<sub>2</sub> (302 mg, 4.4 mmol, 1.4 equiv.) and NaN<sub>3</sub> (305 mg, 4.7 mmol, 1.5 equiv.) in AcOH (22 mL) and water (11 mL) afforded the corresponding azide **1g** after column chromatography (pentane/EE = 10:1) as a yellow oil (442 mg, 2.2 mmol, 74%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.46 - 7.40$  (m, 1H),  $7.33 - 7.29$  (m, 1H),  $7.17 - 7.13$  (m, 2H),  $4.88$  (t,  $J = 6.5$  Hz, 1H),  $2.15$  (s, 1H),  $1.81 - 1.67$  (m, 2H),  $1.50 - 1.21$  (m, 4H),  $0.90$  (t,  $J = 7.0$  Hz, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 136.7, 136.1, 128.6, 127.4, 125.1, 118.2, 70.2, 37.7, 28.2, 22.7, 14.2$ .  $m/z$  (EI) (%): 160.0 (59), 147.9 (22), 133.9 (52), 129.9 (74), 119.9 (90), 117.9 (26), 105.9 (46), 92.9 (62), 91.9 (100), 90.9 (24), 79.0 (22), 76.9 (34), 66.0 (22), 65.0 (78), 57.1 (20); HRMS-EI calcd. for C<sub>11</sub>H<sub>15</sub>ON<sub>3</sub>: 205.1210, found: 205.1209 ([M]<sup>+</sup>); IR (KBr):  $\nu = 3358, 2937, 2865, 2114, 1483, 1285, 1044, 749, 677 \text{ cm}^{-1}$ .

## General Procedure for the Quinoline Synthesis

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### Procedure A:

The alcohol (0.25 mmol) and the alkyne (0.75 mmol) were dissolved in 2.5 mL of 1,2-dichloroethane. HNTf<sub>2</sub> (5 mol%) and *p*-toluenesulfonic acid (0.375 mmol.) were added and the reaction was stirred at 60 °C for the indicated time until complete conversion of the alcohol (monitored by TLC). For the isolation of the product sat. NaHCO<sub>3</sub>-solution is added, the aqueous phase extracted with dichloromethane, the combined organic phases dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The crude product is purified by column chromatography or by semi-preparative HPLC.

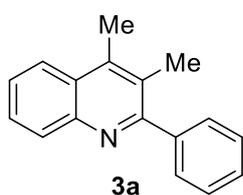
### Procedure B:

The alcohol (0.25 mmol) and the alkyne (0.75 mmol) were dissolved in 2.5 mL of 1,2-dichloroethane. BF<sub>3</sub>·OEt<sub>2</sub> (0.30 mmol) was added and the reaction was stirred at 40 °C for the indicated time until complete conversion of the alcohol (monitored by TLC). For the isolation of the product sat. NaHCO<sub>3</sub>-solution is added, the aqueous phase extracted with dichloromethane, the combined organic phases dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The crude product is purified by column chromatography.

## Analytical Data of Products

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### 3,4-Dimethyl-2-phenylquinoline (3a)<sup>13</sup>

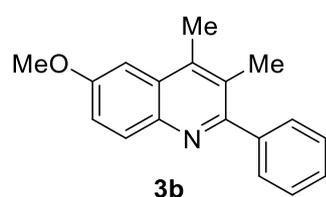


According to the general procedure A 1-(2-azidophenyl)ethan-1-ol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), 1-phenyl-1-propyne **2a** (87.1 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 8:1 → 5:1) afforded product **3a** as a pale yellow solid (51.9 mg, 0.22 mmol, 89%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.16 – 8.00 (m, 2H), 7.70 – 7.61 (m, 1H), 7.58 – 7.52 (m, 3H), 7.51 – 7.46 (m, 2H), 7.45 – 7.41 (m, 1H), 2.70 (d, *J* = 2.6 Hz, 3H), 2.40 (d, *J* = 2.6 Hz, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ = 160.7, 146.1, 142.4, 142.0, 130.3, 129.1, 128.40, 128.38, 128.1, 127.4, 127.2, 126.3, 123.5, 17.7, 15.0. *m/z* (EI) (%): 234.1 (38), 233.1 (64), 232.1 (100), 217.1 (16); HRMS-ESI calcd. for C<sub>17</sub>H<sub>16</sub>N: 234.1277, found: 234.1277 ([M + H]<sup>+</sup>); IR (KBr): ν = 3059,

2112, 1575, 1493, 1444, 1381, 1350, 1274, 1234, 1186, 1138, 1073, 1004, 917, 861, 792, 758, 702 cm<sup>-1</sup>.

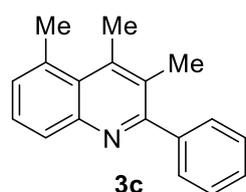
The analytic data matched with that reported previously.<sup>13</sup>

### 6-Methoxy-3,4-dimethyl-2-phenylquinoline (3b)



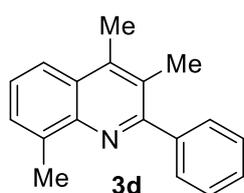
According to the general procedure A 1-(2-azido-5-methoxyphenyl)ethan-1-ol **1b** (38.6 mg, 0.25 mmol, 1.0 equiv.), 1-phenyl-1-propyne **2a** (87.1 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 2 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 5:1 → 2:1) afforded product **3b** as a yellow solid (46.7mg, 0.18 mmol, 71%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.02 (d, *J* = 9.1 Hz, 1H), 7.55 - 7.50 (m, 2H), 7.48 - 7.45 (m, 2H), 7.43 - 7.39 (m, 1H), 7.32 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.25 (d, *J* = 2.7 Hz, 1H), 3.98 (s, 3H), 2.65 (s, 3H), 2.38 (s, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ = 158.3, 157.8, 142.11, 142.07, 140.9, 131.8, 129.2, 128.4, 128.2, 127.9, 127.4, 120.6, 102.0, 55.7, 17.8, 15.1. *m/z* (EI) (%): 263.0 (65), 262.0 (100), 219.0 (43), 204.0 (19), 115.0 (20); HRMS-ESI calcd. for C<sub>18</sub>H<sub>18</sub>NO: 264.1383, found: 264.1379 ([M + H]<sup>+</sup>); IR (KBr): ν = 2937, 2114, 1738, 1615, 1486, 1363, 1251, 1028, 929, 824, 761, 707 cm<sup>-1</sup>.

### 3,4,5-Trimethyl-2-phenylquinoline (3c)



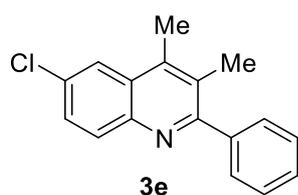
According to the general procedure A 1-(2-azido-6-methylphenyl)ethan-1-ol **1c** (35.4 mg, 0.25 mmol, 1.0 equiv.), 1-phenyl-1-propyne **2a** (87.1 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 6:1) afforded product **3c** as a pale yellow oil (43.5 mg, 0.18 mmol, 70%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.95 (dd, *J* = 8.3, 0.6 Hz, 1H), 7.55 - 7.51 (m, 2H), 7.50 - 7.45 (m, 3H), 7.44 - 7.39 (m, 1H), 7.31 (d, *J* = 7.0 Hz, 1H), 2.94 (s, 3H), 2.85 (s, 3H), 2.36 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.9, 147.7, 144.0, 142.0, 134.5, 130.0, 129.3, 129.1, 128.4, 128.13, 128.06, 127.99, 127.8, 26.4, 20.2, 18.2; *m/z* (EI) (%): 249.0 (31), 248.0 (100), 247.0 (77), 246.0 (93), 231.0 (19), 230.0 (16); HRMS-ESI calcd. for C<sub>18</sub>H<sub>18</sub>N: 248.1434, found: 248.1433 ([M + H]<sup>+</sup>); IR (KBr): ν = 2946, 1567, 1459, 1372, 1239, 1149, 1011, 914, 772, 704 cm<sup>-1</sup>.

### 3,4,8-Trimethyl-2-phenylquinoline (3d)



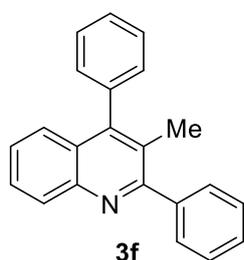
According to the general procedure A 1-(2-azido-3-methylphenyl)ethan-1-ol **1a** (35.4 mg, 0.25 mmol, 1.0 equiv.), 1-phenyl-1-propyne **2d** (87.1 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 25:1) afforded product **3d** as a pale yellow oil (29.6 mg, 0.12 mmol, 48%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.89 (d, *J* = 8.4 Hz, 1H), 7.65 – 7.62 (m, 2H), 7.49 (m, 3H), 7.45 – 7.41 (m, 2H), 2.80 (s, 3H), 2.68 (s, 3H), 2.43 (s, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ = 158.9, 145.2, 142.4, 142.3, 138.1, 129.7, 128.5, 128.1, 127.9, 127.1, 126.6, 125.9, 121.4, 18.4, 17.9, 15.2; *m/z* (EI) (%): 248.0 (18), 247.0 (89), 246.0 (100), 115.0 (23), 77.1 (27); HRMS-ESI calcd. for C<sub>18</sub>H<sub>18</sub>N: 248.1434, found: 248.1430 ([M + H]<sup>+</sup>); IR (KBr): ν = 2931, 2103, 1596, 1451, 1363, 1220, 1003, 942, 865, 758, 699 cm<sup>-1</sup>.

### 6-Chloro-3,4-dimethyl-2-phenylquinoline (3e)



According to the general procedure A 1-(2-azido-5-chlorophenyl)ethan-1-ol **1e** (49.4 mg, 0.25 mmol, 1.0 equiv.), 1-phenyl-1-propyne **2a** (87.1 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 7:1 → 5:1) afforded product **3e** as a white solid (42.1 mg, 0.16 mmol, 63%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.04 (d, *J* = 8.9 Hz, 1H), 8.00 (d, *J* = 2.2 Hz, 1H), 7.58 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.50 – 7.47 (m, 2H), 7.45 – 7.41 (m, 1H), 2.64 (s, 3H), 2.39 (s, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ = 161.0, 144.5, 141.60, 141.55, 132.1, 131.9, 129.2, 129.0, 128.4, 128.2, 128.1, 122.7, 17.8, 15.0.; *m/z* (EI) (%): 268.1 (47), 267.1 (53), 266.0 (100); HRMS-ESI calcd. for C<sub>17</sub>H<sub>15</sub>NCl: 268.0888, found: 268.0890 ([M + H]<sup>+</sup>); IR (KBr): ν = 2916, 2195, 1690, 1614, 1482, 1420, 1350, 1226, 1131, 1097, 1073, 997, 958, 881, 825, 758, 719, 694 cm<sup>-1</sup>.

### 3-Methyl-2,4-diphenylquinoline (3f)<sup>14</sup>

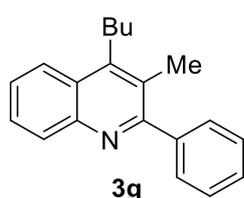


According to the general procedure A (2-azidophenyl)(phenyl)methanol **1f** (56.3 mg, 0.25 mmol, 1.0 equiv.), 1-phenyl-1-propyne **2a** (87.1 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in

DCE at 60 °C for 3 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 10:1 → 5:1) afforded product **3f** as a brownish solid (63.0 mg, 0.21 mmol, 85%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.19 – 8.16 (m, 1H), 7.68 – 7.61 (m, 3H), 7.59 – 7.42 (m, 6H), 7.40 (dd, *J* = 4.5, 0.9 Hz, 2H), 7.34 – 7.30 (m, 2H), 2.16 (s, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ = 161.0, 147.9, 146.4, 141.7, 137.9, 129.6, 129.5, 129.1, 128.8, 128.6, 128.4, 128.2, 128.0, 127.2, 126.8, 126.4, 126.1, 18.7. *m/z* (EI) (%): 296.1 (22), 295.1 (67), 294.1 (100); HRMS-ESI calcd. for C<sub>22</sub>H<sub>18</sub>N: 296.1434, found: 296.1434 ([M + H]<sup>+</sup>); IR (KBr): ν = 3054, 1568, 1483, 1368, 1223, 1011, 915, 758, 703 cm<sup>-1</sup>.

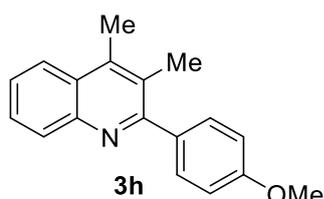
The analytic data matched with that reported previously.<sup>14</sup>

#### 4-Butyl-3-methyl-2-phenylquinoline (3g)



According to the general procedure A 1-(2-azidophenyl)pentan-1-ol **1g** (51.3 mg, 0.25 mmol, 1.0 equiv.), 1-phenyl-1-propyne **2a** (87.1 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 7:1) afforded product **3g** as a yellow oil (50.1 mg, 0.18 mmol, 73%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.12 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.03 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.64 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.57 – 7.39 (m, 6H), 3.20 – 3.06 (m, 2H), 2.39 (s, 3H), 1.73 – 1.50 (m, 4H), 1.03 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 161.0, 146.8, 146.4, 142.1, 130.4, 129.0, 128.4, 128.3, 128.0, 126.7, 126.5, 126.3, 123.5, 32.0, 28.7, 23.5, 17.1, 14.1.; *m/z* (EI) (%): 276.1 (50), 275.1 (100), 274.1 (76), 260.1 (25), 246.0 (63), 233.1 (42), 232.1 (73), 231.1 (28), 230.1 (29), 217.1 (20); HRMS-ESI calcd. for C<sub>20</sub>H<sub>22</sub>N: 276.1747, found: 276.1747 ([M + H]<sup>+</sup>); IR (KBr): ν = 3056, 2944, 1742, 1573, 1465, 1361, 1214, 1079, 1005, 759, 701 cm<sup>-1</sup>.

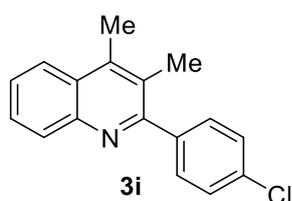
#### 2-(4-Methoxyphenyl)-3,4-dimethylquinoline (3h)



According to the general procedure A 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), 1-(4-methoxyphenyl)-1-propyne **2b** (109.6 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 5:1) afforded product **3h** as a pale yellow solid (44.1 mg, 0.17 mmol, 67%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.10 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4

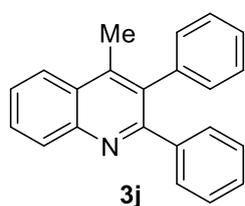
Hz, 1H), 7.67 – 7.62 (m, 1H), 7.56 – 7.49 (m, 3H), 7.02 (d,  $J = 8.4$  Hz, 2H), 3.88 (s, 3H), 2.68 (s, 3H), 2.42 (s, 3H).  $^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta = 160.3, 159.6, 146.1, 142.3, 134.5, 130.5, 130.2, 128.3, 127.3, 127.2, 126.1, 123.5, 113.8, 55.5, 17.8, 15.0$ ;  $m/z$  (EI) (%): 263.0 (63), 262.0 (100); HRMS-ESI calcd. for  $\text{C}_{18}\text{H}_{18}\text{NO}$ : 264.1383, found: 264.1384 ( $[\text{M} + \text{H}]^+$ ); IR (KBr):  $\nu = 3012, 2925, 2851, 1606, 1509, 1458, 1356, 1286, 1242, 1173, 1100, 1025, 823, 760 \text{ cm}^{-1}$ .

### 2-(4-Chlorophenyl)-3,4-dimethylquinoline (3i)



According to the general procedure A 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), 1-(4-chlorophenyl)-1-propyne **2c** (113.0 mg, 0.75 mmol, 3.0 equiv.),  $\text{HNTf}_2$  (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 10:1  $\rightarrow$  5:1) afforded product **3i** as a white solid (41.6 mg, 0.16 mmol, 62%).  $^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.09$  (dd,  $J = 8.4, 0.6$  Hz, 1H), 8.04 (dd,  $J = 8.5, 0.8$  Hz, 1H), 7.66 (ddd,  $J = 8.3, 6.8, 1.3$  Hz, 1H), 7.55 (ddd,  $J = 8.3, 6.8, 1.3$  Hz, 1H), 7.52 - 7.44 (m, 4H), 2.69 (s, 3H), 2.38 (s, 3H).  $^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta = 159.4, 146.1, 142.7, 140.4, 134.2, 130.6, 130.2, 128.6, 127.4, 127.0, 126.5, 123.5, 17.7, 15.0$ .  $m/z$  (EI) (%): 269.1 (20), 268.1 (54), 267.1 (64), 266.0 (100); HRMS-ESI calcd. for  $\text{C}_{17}\text{H}_{15}\text{ClN}$ : 268.0888, found: 268.0888 ( $[\text{M} + \text{H}]^+$ ); IR (KBr):  $\nu = 3055, 2929, 1580, 1477, 1377, 1084, 996, 829, 748 \text{ cm}^{-1}$ .

### 4-Methyl-2,3-diphenylquinoline (3j)<sup>15</sup>

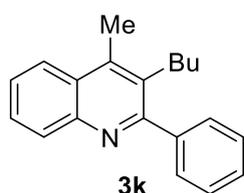


According to the general procedure A 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), diphenylacetylene **2d** (133.7 mg, 0.75 mmol, 3.0 equiv.),  $\text{HNTf}_2$  (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 10:1  $\rightarrow$  5:1) afforded product **3j** as yellow oil (41.3 mg, 0.14 mmol, 56%).  $^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.22$  (d,  $J = 8.4$  Hz, 1H), 8.09 (dd,  $J = 8.4, 0.8$  Hz, 1H), 7.75 (ddd,  $J = 8.3, 6.9, 1.3$  Hz, 1H), 7.61 (ddd,  $J = 8.3, 6.9, 1.2$  Hz, 1H), 7.33 – 7.24 (m, 5H), 7.21 – 7.18 (m, 3H), 7.13 - 7.10 (m, 2H), 2.55 (s, 3H).  $^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta = 159.0, 146.9, 142.4, 141.5, 139.2, 134.1, 130.9, 130.4, 129.9, 129.3, 128.1, 127.7, 127.5, 127.3, 127.1, 126.6, 124.3, 16.5$ ;  $m/z$  (EI) (%): 296.1 (22), 295.1 (60), 294.1 (100); HRMS-ESI calcd. for  $\text{C}_{22}\text{H}_{18}\text{N}$ : 296.1434,

found: 296.1433 ( $[M + H]^+$ ); IR (KBr):  $\nu = 3059, 1602, 1567, 1491, 1441, 1397, 1350, 1286, 1074, 1028, 1000, 908, 759, 728, 698 \text{ cm}^{-1}$ .

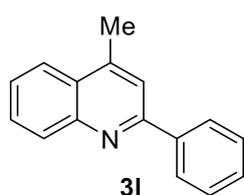
The analytic data matched with that reported previously.<sup>15</sup>

### 3-Butyl-4-methyl-2-phenylquinoline (3k)



According to the general procedure A 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), 1-phenyl-1-hexyne **2e** (118.7 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 8:1) afforded product **3k** as a pale yellow oil (53.2 mg, 0.19 mmol, 77%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.11$  (dd,  $J = 8.4, 0.7$  Hz, 1H), 8.04 (dd,  $J = 8.5, 0.8$  Hz, 1H), 7.65 (ddd,  $J = 8.3, 6.8, 1.4$  Hz, 1H), 7.55 (ddd,  $J = 8.3, 6.8, 1.3$  Hz, 1H), 7.50 – 7.38 (m, 5H), 2.79 – 2.74 (m, 2H), 2.73 (s, 3H), 1.42 (m, 2H), 1.29 – 1.17 (m, 2H), 0.78 (t,  $J = 7.3$  Hz, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 161.2, 145.8, 142.2, 141.8, 132.4, 130.2, 128.7, 128.5, 128.3, 127.9, 127.8, 126.3, 123.6, 32.7, 29.9, 22.9, 14.7, 13.8$ ;  $m/z$  (EI) (%): 277.1 (18), 276.0 (100); HRMS-ESI calcd. for C<sub>20</sub>H<sub>22</sub>N: 276.1747, found: 276.1746 ( $[M + H]^+$ ); IR (KBr):  $\nu = 3056, 2943, 1572, 1451, 1353, 1073, 1025, 938, 755, 702 \text{ cm}^{-1}$ .

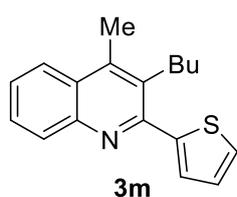
### 4-Methyl-2-phenylquinoline (3l)<sup>16</sup>



According to the general procedure A 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), phenylacetylene **2f** (76.6 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 8:1) afforded product **3l** as a yellow oil (41.5 mg, 0.19 mmol, 76%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.23 - 8.13$  (m, 3H), 8.00 (d,  $J = 8.3$  Hz, 1H), 7.76 – 7.68 (m, 2H), 7.58 – 7.50 (m, 3H), 7.49 – 7.43 (m, 1H), 2.77 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 157.2, 148.3, 144.9, 140.0, 130.4, 129.4, 129.3, 128.9, 127.7, 127.4, 126.1, 123.7, 119.9, 19.2$ .  $m/z$  (EI) (%): 220.1 (30), 219.0 (100), 218.0 (24), 204.0 (37); HRMS-ESI calcd. for C<sub>16</sub>H<sub>14</sub>N: 220.1121, found: 220.1123 ( $[M + H]^+$ ); IR (KBr):  $\nu = 3058, 2971, 1598, 1549, 1500, 1448, 1347, 1227, 1077, 1028, 864, 762, 690 \text{ cm}^{-1}$ .

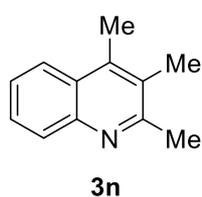
The analytic data matched with that reported previously.<sup>16</sup>

### 3-Butyl-4-methyl-2-(thiophen-2-yl)quinoline (3m)



According to the general procedure A 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), 1-thiophenyl-1-hexyne **2g** (123.2 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and semi-preparative HPLC (pentane/EtOAc = 8:1) afforded product **3m** as an orange-brownish oil (60.8 mg, 0.22 mmol, 86%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.08 (dd, *J* = 8.4, 0.7 Hz, 1H), 8.00 (dd, *J* = 8.5, 0.8 Hz, 1H), 7.64 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.45 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.38 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.14 (dd, *J* = 5.1, 3.6 Hz, 1H), 3.03 – 2.97 (m, 2H), 2.72 (s, 3H), 1.65 – 1.55 (m, 2H), 1.50 – 1.39 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.5, 146.0, 144.5, 142.2, 132.3, 130.2, 128.6, 127.6, 127.2, 127.19, 127.17, 126.5, 123.6, 32.8, 30.0, 23.0, 14.7, 14.0. *m/z* (EI) (%): 283.1 (19), 282.1 (69), 281.1 (100), 252.1 (35), 248.1 (26), 238.1 (58), 223.1 (22); HRMS-ESI calcd. for C<sub>18</sub>H<sub>20</sub>NS: 282.1311, found: 282.1310 ([M + H]<sup>+</sup>); IR (KBr): ν = 3069, 2955, 2926, 2865, 1570, 1491, 1432, 1344, 1236, 1185, 1058, 932, 900, 846, 755, 700 cm<sup>-1</sup>.

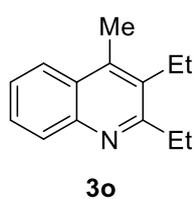
### 2,3,4-Trimethylquinoline (3n)<sup>17</sup>



According to the general procedure A 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), 2-butyne **2h** (40.6 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and purification via column chromatography (pentane/EtOAc = 20:1) afforded product **3n** as a pale brown solid (29.6 mg, 0.17 mmol, 69%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.95 (ddd, *J* = 13.8, 8.4, 0.9 Hz, 2H), 7.59 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.46 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 2.70 (s, 3H), 2.59 (s, 3H), 2.39 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 158.5, 146.0, 140.5, 129.2, 128.0, 127.9, 127.2, 125.5, 123.6, 25.0, 15.9, 14.5; *m/z* (EI) (%): 172.0 (74), 171.0 (100), 170.0 (56), 156.0 (32); HRMS-ESI calcd. for C<sub>12</sub>H<sub>14</sub>N: 172.1121, found: 172.1120 ([M + H]<sup>+</sup>); IR (KBr): ν = 2925, 1583, 1494, 1369, 1202, 1002, 748 cm<sup>-1</sup>.

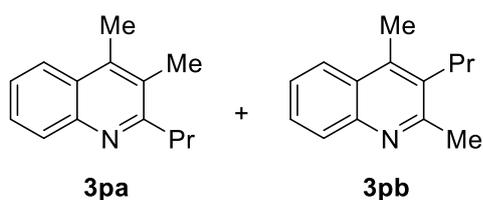
The analytic data matched with that reported previously.<sup>17</sup>

### 2,3-Diethyl-4-methylquinoline (3o)



According to the general procedure A 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), 3-hexyne **2i** (61.6 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and purification by column chromatography (pentane/EtOAc = 50:1) afforded product **3o** as a pale yellow solid (36.5 mg, 0.18 mmol, 73%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.02 – 7.94 (m, 2H), 7.60 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.47 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 3.04 (q, *J* = 7.5 Hz, 2H), 2.90 (q, *J* = 7.6 Hz, 2H), 2.65 (s, 3H), 1.39 (t, *J* = 7.5 Hz, 3H), 1.22 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ = 158.5, 146.5, 146.2, 133.0, 129.4, 128.1, 126.4, 125.6, 123.6, 24.1, 22.5, 21.2, 15.2, 14.6; *m/z* (EI) (%): 199.2 (95), 198.2 (100), 184.1 (24), 170.1 (47); HRMS-ESI calcd. for C<sub>14</sub>H<sub>18</sub>N: 200.1434, found: 200.1429 ([M + H]<sup>+</sup>); IR (KBr): ν = 2968, 2932, 1581, 1494, 1451, 1374, 1213, 1056, 1024, 955, 818, 754 cm<sup>-1</sup>.

### 3,4-Dimethyl-2-propylquinoline (3pa) + 2,4-Dimethyl-3-propylquinoline (3pb)



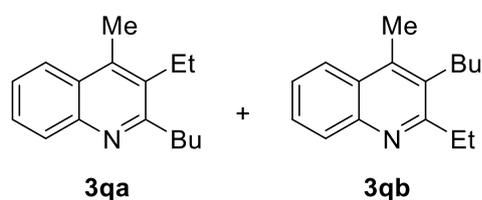
According to the general procedure A 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), 2-hexyne **2j** (61.6 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and purification by column chromatography (pentane/EtOAc = 50:1) afforded product **3pa/3pb** as a 1:3.6 mixture of regioisomers as a pale yellow oil (34.0 mg, 0.17 mmol, 68%).

**3pa**: <sup>1</sup>H-NMR (600-MHz, CDCl<sub>3</sub>): δ = 8.00 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.46 (dd, *J* = 11.2, 4.0 Hz, 1H), 3.00 – 2.95 (m, 2H), 2.60 (s, 3H), 2.43 (s, 3H), 1.82 – 1.75 (m, 2H), 1.07 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ = 161.8, 146.0, 141.1, 129.4, 127.9, 127.4, 127.1, 125.4, 123.5; *m/z* (EI) (%): 198.9 (42), 170.9 (16), 169.9 (100), 127.9 (23); HRMS-ESI calcd. for C<sub>14</sub>H<sub>18</sub>N: 200.1434, found: 200.1437 ([M + H]<sup>+</sup>); IR (KBr): ν = 2955, 2874, 1580, 1496, 1451, 1374, 1094, 1016, 863, 754 cm<sup>-1</sup>.

**3pb**: <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.96 (ddd, *J* = 11.3, 8.4, 0.8 Hz, 1H), 7.60 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.47 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 2.83 – 2.79 (m, 2H), 2.74 (s, 3H), 2.63 (s, 3H), 1.62 – 1.54 (m, 2H), 1.07 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ = 158.4, 146.0, 140.5, 132.5, 129.2, 128.1, 127.4, 125.5, 123.7, 32.0, 24.4, 23.2, 14.7, 14.3; *m/z* (EI) (%): 198.9 (42), 170.9 (16), 169.9 (100), 127.9 (23); HRMS-ESI calcd. for C<sub>14</sub>H<sub>18</sub>N:

200.1434, found: 200.1437 ( $[M + H]^+$ ); IR (KBr):  $\nu = 2955, 2874, 1580, 1496, 1451, 1374, 1094, 1016, 863, 754 \text{ cm}^{-1}$ .

**2-Butyl-3-ethyl-4-methylquinoline (3qa) + 3-Butyl-2-ethyl-4-methylquinoline (3qb)**

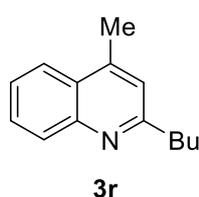


According to the general procedure A 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), 3-octyne **2k** (82.7 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and purification by column chromatography (pentane/EtOAc = 100:1 → 50:1) afforded product **3qa/3qb** as an inseparable 1:1.9 mixture of regioisomers as a yellow liquid (33.4 mg, 0.15 mmol, 59%).

**3qa:** <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 8.01 - 7.91$  (m, 2H), 7.59 (t,  $J = 7.5$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 1H), 3.09 (q,  $J = 7.6$  Hz, 2H), 2.81 – 2.77 (m, 2H), 2.75 (s, 3H), 1.63 (m, 1H), 1.60 – 1.49 (m, 3H), 1.31 (t,  $J = 7.6$  Hz, 3H), 1.01 (t,  $J = 7.2$  Hz, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>):  $\delta = 158.6, 145.1, 131.9, 129.3, 126.3, 125.6, 123.7, 32.6, 29.3, 24.2, 23.5, 21.3, 15.2, 14.1$ ;  $m/z$  (EI) (%): 228.0 (74), 226.9 (100), 211.9 (17), 197.7 (27), 184.9 (33), 184.9 (91), 169.9 (25), 167.9 (16); HRMS-ESI calcd. for C<sub>16</sub>H<sub>22</sub>N: 228.1747, found: 228.1751 ( $[M + H]^+$ ); IR (KBr):  $\nu = 2958, 2929, 2870, 1580, 1500, 1457, 1404, 1375, 1289, 1256, 1178, 1116, 1056, 945, 862, 809, 757, 692 \text{ cm}^{-1}$ .

**3qb:** <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 8.01 - 7.91$  (m, 2H), 7.59 (t,  $J = 7.5$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 1H), 3.07 – 3.03 (m, 2H), 2.85 (q,  $J = 7.6$  Hz, 2H), 2.75 (s, 3H), 1.63 (m, 1H), 1.60 – 1.49 (m, 3H), 1.23 (t,  $J = 7.6$  Hz, 3H), 1.01 (t,  $J = 7.2$  Hz, 3H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>):  $\delta = 158.4, 146.3, 133.3, 129.3, 128.1, 126.7, 125.6, 123.7, 33.2, 28.0, 24.1, 23.6, 22.6, 14.6, 14.1$ ;  $m/z$  (EI) (%): 228.0 (74), 226.9 (100), 211.9 (17), 197.7 (27), 184.9 (33), 184.9 (91), 169.9 (25), 167.9 (16); HRMS-ESI calcd. for C<sub>16</sub>H<sub>22</sub>N: 228.1747, found: 228.1751 ( $[M + H]^+$ ); IR (KBr):  $\nu = 2958, 2929, 2870, 1580, 1500, 1457, 1404, 1375, 1289, 1256, 1178, 1116, 1056, 945, 862, 809, 757, 692 \text{ cm}^{-1}$ .

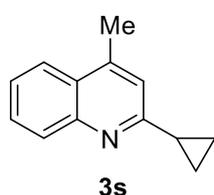
## 2-Butyl-4-methylquinoline (**3r**)<sup>18</sup>



According to the general procedure B 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), 1-hexyne **2l** (61.6 mg, 0.75 mmol, 3.0 equiv) and  $\text{BF}_3 \cdot \text{OEt}_2$  (42.6 mg, 0.30 mmol, 1.2 equiv.) were stirred in DCE at 40 °C for 20 min. Work-up and purification by column chromatography (pentane/EtOAc = 100:1) afforded product **3r** as a brownish oil (31.0 mg, 0.16 mmol, 62%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.02 (dd,  $J$  = 8.4, 0.6 Hz, 1H), 7.93 (dd,  $J$  = 8.3, 1.1 Hz, 1H), 7.65 (ddd,  $J$  = 8.4, 6.9, 1.4 Hz, 1H), 7.48 (ddd,  $J$  = 8.2, 6.9, 1.2 Hz, 1H), 7.12 (s, 1H), 2.93 – 2.88 (m, 2H), 2.65 (d,  $J$  = 0.8 Hz, 3H), 1.82 – 1.72 (m, 2H), 1.47 – 1.38 (m, 2H), 0.94 (t,  $J$  = 7.4 Hz, 3H).  $^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 162.9, 147.9, 144.2, 129.5, 129.1, 126.9, 125.5, 123.7, 122.2, 39.2, 32.4, 22.9, 18.8, 14.2;  $m/z$  (EI) (%): 199.9 (20), 198.9 (37), 156.9 (100), 155.8 (53), 129.0 (22), 127.9 (34), 126.9 (19), 116.0 (15), 114.9 (44), 89.0 (21), ; HRMS-ESI calcd. for  $\text{C}_{14}\text{H}_{18}\text{N}$ : 200.1433, found: 200.1434 ( $[\text{M} + \text{H}]^+$ ); IR (KBr):  $\nu$  = 2955, 2928, 1603, 1561, 1507, 1448, 1411, 1289, 1177, 951, 862, 755  $\text{cm}^{-1}$ .

The analytic data matched with that reported previously.<sup>18</sup>

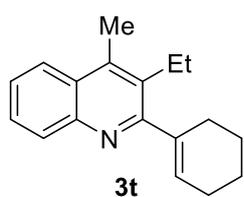
## 2-Cyclopropyl-4-methylquinoline (**3s**)<sup>19</sup>



According to the general procedure B 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), ethynylcyclopropane **2m** (49.6 mg, 0.75 mmol, 3.0 equiv) and  $\text{BF}_3 \cdot \text{OEt}_2$  (42.6 mg, 0.30 mmol, 1.2 equiv.) were stirred in DCE at 40 °C for 20 min. Work-up and purification by column chromatography (pentane → pentane/EtOAc 100:1) afforded product **3s** as a yellow oil (42.5 mg, 0.23 mmol, 93%).  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.98 – 7.94 (m, 1H), 7.91 (dd,  $J$  = 8.3, 0.8 Hz, 1H), 7.63 (ddd,  $J$  = 8.3, 6.9, 1.3 Hz, 1H), 7.45 (ddd,  $J$  = 8.2, 6.9, 1.2 Hz, 1H), 7.00 (d,  $J$  = 0.5 Hz, 1H), 2.65 (d,  $J$  = 0.8 Hz, 3H), 2.20 (tt,  $J$  = 8.3, 4.9 Hz, 1H), 1.15 – 1.12 (m, 2H), 1.08 – 1.05 (m, 2H).  $^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.2, 148.0, 143.9, 129.3, 129.1, 127.0, 125.1, 123.7, 120.0, 18.8, 18.1, 10.1;  $m/z$  (EI) (%): 184.0 (28), 183.0 (90), 182.0 (100), 168.0 (31), 167.0 (38), 115.0 (19); HRMS-ESI calcd. for  $\text{C}_{13}\text{H}_{14}\text{N}$ : 184.1121, found: 184.1116 ( $[\text{M} + \text{H}]^+$ ); IR (KBr):  $\nu$  = 3065, 3004, 2925, 2121, 1604, 1559, 1508, 1448, 1405, 1294, 1197, 1168, 1086, 1023, 955, 897, 855, 815, 755  $\text{cm}^{-1}$ .

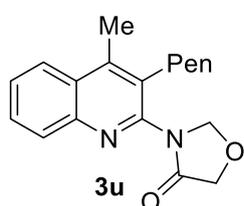
The analytic data matched with that reported previously.<sup>19</sup>

### 2-(Cyclohex-1-en-1-yl)-3-ethyl-4-methylquinoline (3t)



According to the general procedure A 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), 1-(but-1-yn-1-yl)cyclohex-1-ene **2n** (100.7 mg, 0.75 mmol, 3.0 equiv.), HNTf<sub>2</sub> (7.0 mg, 0.025 mmol, 10 mol%) and *p*-toluenesulfonic acid (64.6 mg, 0.375 mmol, 1.5 equiv.) were stirred in DCE at 60 °C for 3 h. Work-up and purification by column chromatography (pentane/EtOAc = 100:1) afforded product **3t** as a orange oil (52.9 mg, 0.21 mmol, 84%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.08 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.96 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.60 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.48 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 5.78 (tt, *J* = 3.6, 1.7 Hz, 1H), 2.85 (q, *J* = 7.5 Hz, 2H), 2.66 (s, 3H), 2.37 (m, 2H), 2.27 – 2.21 (m, 2H), 1.88 – 1.82 (m, 2H), 1.81 – 1.73 (m, 2H), 1.17 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 163.2, 145.9, 141.4, 139.6, 133.2, 129.9, 128.1, 127.5, 126.4, 125.8, 123.5, 29.7, 25.2, 23.2, 22.9, 22.1, 15.4, 14.3; *m/z* (EI) (%): 252.9 (23), 251.8 (100), 250.8 (69), 249.8 (39), 221.8 (33), 207.8 (26), 194.9 (15), 193.8 (21); HRMS-ESI calcd. for C<sub>18</sub>H<sub>22</sub>N: 252.1747, found: 252.1750 ([M + H]<sup>+</sup>); IR (KBr): ν = 3062, 2926, 1574, 1492, 1446, 1320, 1261, 1226, 1134, 1056, 1025, 960, 919, 843, 797, 754 cm<sup>-1</sup>.

### 3-(4-Methyl-3-pentylquinolin-2-yl)oxazolidin-4-one (3u)



According to the general procedure A 1-(2-azidophenyl)ethanol **1a** (40.8 mg, 0.25 mmol, 1.0 equiv.), 3-(hept-1-yn-1-yl)oxazolidin-2-one **2o** (100.7 mg, 0.75 mmol, 3.0 equiv.) and BF<sub>3</sub>·OEt<sub>2</sub> (42.6 mg, 0.30 mmol, 1.2 equiv.) were stirred in DCE at 40 °C for 1 h. Work-up and purification by column chromatography (pentane/EtOAc = 20:1 → 5:1) afforded product **3u** as a white solid (68.5 mg, 0.23 mmol, 92%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.00 (dd, *J* = 8.5, 0.8 Hz, 1H), 7.92 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.64 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 4.59 (t, *J* = 7.8 Hz, 2H), 4.33 (t, *J* = 7.8 Hz, 2H), 2.95 (m, 2H), 2.71 (s, 3H), 1.57 – 1.47 (m, 2H), 1.35 (m, 4H), 0.89 (m, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 157.3, 150.0, 145.3, 144.8, 131.4, 129.2, 128.9, 128.2, 126.6, 123.9, 63.1, 47.0, 32.1, 30.2, 28.5, 22.6, 15.1, 14.2; *m/z* (EI) (%): 299.0 (14), 297.9 (28), 283.0 (40), 254.9 (55), 239.0 (40), 225.0 (18), 213.0 (16), 212.0 (100), 211.0 (89), 198.0 (56), 197.0 (63), 196.0 (24), 195.0 (35), 184.0 (15), 182.9 (89), 182.0 (20), 181.0 (18), 168.0 (17), 166.9 (31), 157.0 (15), 156.0 (23), 154.0 (14), 140.0 (14), 129.1 (18), 128.1 (22), 127.0 (18), 116.1 (14), 115.0 (20); HRMS-ESI calcd. for C<sub>18</sub>H<sub>22</sub>O<sub>2</sub>N<sub>2</sub>Na: 321.1574, found: 321.1578 ([M + Na]<sup>+</sup>); IR (KBr): ν = 3458, 2941, 2867, 1721, 1439, 1346, 1253, 1098, 966, 904, 755, 690 cm<sup>-1</sup>.

## Assignment of the Relative Configuration of Substituents in the Product

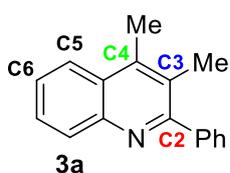
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The high reactivity of both, the initially formed vinyl cation and the nitrenium ion intermediate within the Schmidt reaction might induce unforeseen alternative rearrangement processes. Therefore, a thorough assignment of the configuration/positions of the substituents in the quinolone product, and hence the regioisomeric outcome of the reaction is highly important. As this is not always straightforward in aromatic and heteroaromatic systems our methods shall be outlined and exemplified in the following.

Our first example is the analysis of the quinolone **3a**, the product formed during the optimization studies. As this compound is literature known,<sup>13</sup> and was therefore characterized unambiguously via comparison with reported NMR data, it represents an excellent opportunity to confirm the accuracy of our assignment method.

The analysis begins with the assignment of the three carbon atoms in the heteroaromatic ring of the quinolone, C2, C3 and C4. This is easily done by a combination of APT/DEPT analysis – identify the signals for quaternary aromatic carbon atoms – and HMBC analysis – identify the three carbon atoms with the most cross peaks to aliphatic H-atoms among the quaternary aromatic carbon atoms. The chemical shift for the three carbon signals is very characteristic with C2 ~ 160 ppm, C4 ~ 140-145 ppm and C3 ~ 125-130 ppm (see figures 1 to 6). Analysis of all HMBC cross peaks of each of the three carbons then reveals the relative position of the substituents:

**3a:**



**C2:** cross peaks with Me-H@C3, Ph-H, and weakly with Me-H@C4

→ bears Ph and must be in between the nitrogen of the quinoline (chemical shift) and Me@C3

**C3:** cross peaks with Me-H@C4, Ph-H, Me-H@C3

→ bears Me@C3 and must be in between Me@C4 and Ph

**C4:** cross peaks with H@C5, H@C6, Me-H@C4, Me-H@C3

→ bears Me@C4 and must be in between aromatic ring of the quinoline and Me@C3

For a depiction of these results and the original HMBC spectrum see Figure 1.

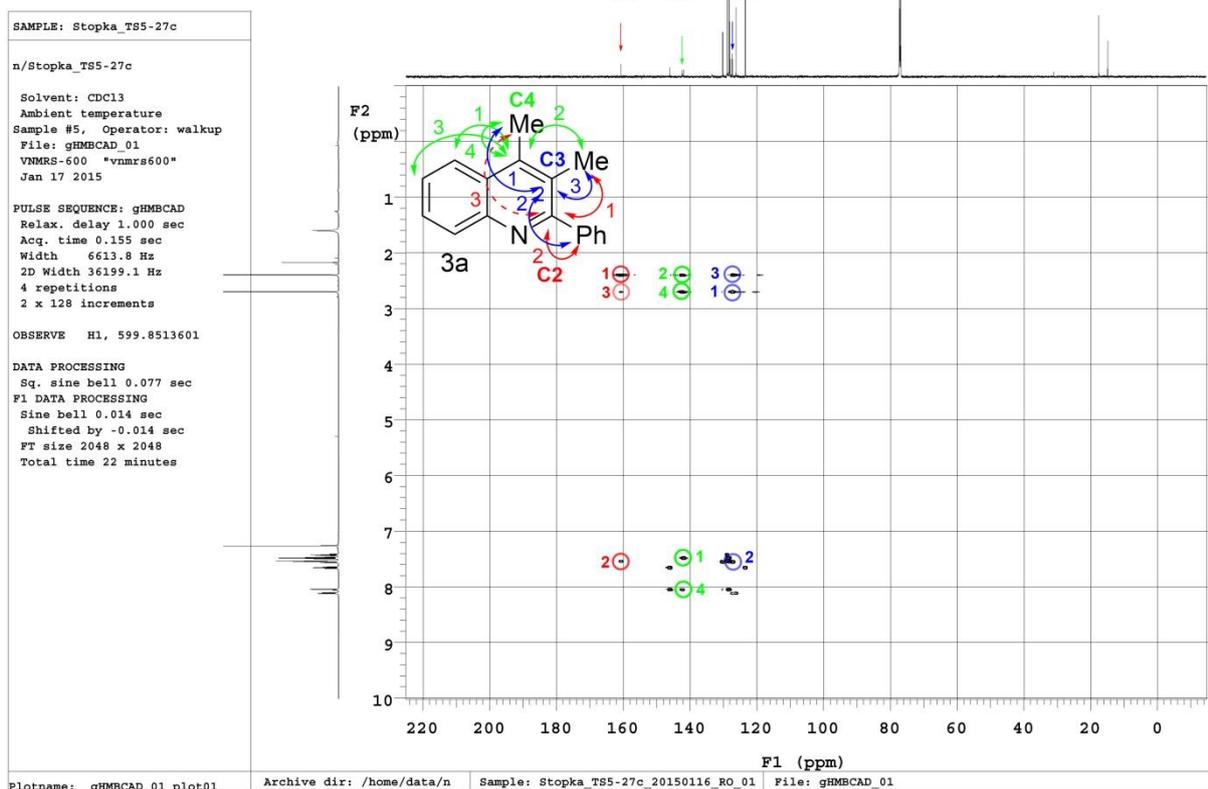
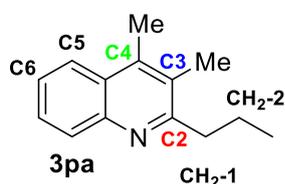


Figure 1. HMBC spectrum of quinoline **3a** (600 MHz, CDCl<sub>3</sub>).

Further examples represent assignments of quinoline products formed by the reaction of azides with unsymmetrical aliphatic alkynes and were taken from Table 4 in the manuscript, to showcase the efficiency of the assignment also for more intricate cases.

The first example is the regioisomeric mixture of quinolines **3pa** and **3pb**, which were fully separated by semi-preparative HPLC-chromatography.

### 3pa:



**C2**: cross peaks with CH<sub>2</sub>-1@C2, CH<sub>2</sub>-2@C2, Me-H@C3 and weakly with Me-H@C4

→ bears Pr@C2 and must be in between the nitrogen of the quinoline (chemical shift) and Me@C3

**C3**: cross peaks with Me-H@C4, CH<sub>2</sub>-1@C2, Me-H@C3

→ bears Me@C3 and must be in between Me@C4 and Pr@C2

**C4**: cross peaks with H@C5, Me-H@C4, Me-H@C3

→ bears Me@C4 and must be in between aromatic ring of the quinoline and Me@C3

For a depiction of these results and the original HMBC spectrum see Figure 2.

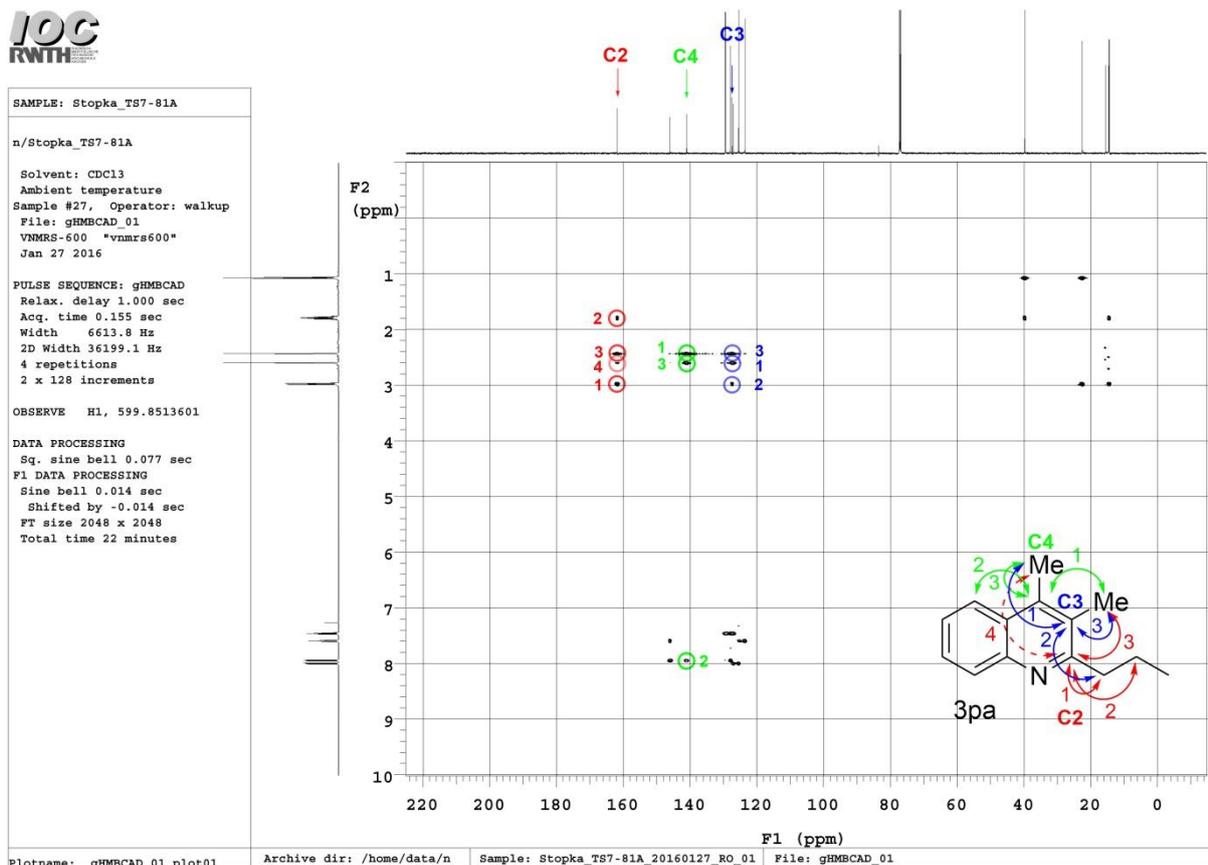
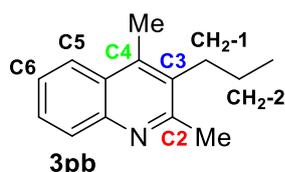


Figure 2. HMBC spectrum of quinoline **3pa** (600 MHz, CDCl<sub>3</sub>).

**3pb**:



**C2**: cross peaks with Me-H@C2, CH<sub>2</sub>-1@C3, and weakly with Me-H@C4

→ bears Me@C2 and must be in between the nitrogen of the quinoline (chemical shift) and Pr@C3

**C3**: cross peaks with Me-H@C4, CH<sub>2</sub>-1@C3, CH<sub>2</sub>-2@C3, Me-H@C2

→ bears Pr@C3 and must be in between Me@C2 and Me@C4

**C4**: cross peaks with H@C5, CH<sub>2</sub>-1@C3, Me-H@C4

→ bears Me@C4 and must be in between aromatic ring of the quinoline and Pr@C3

For a depiction of these results and the original HMBC spectrum see Figure 3.

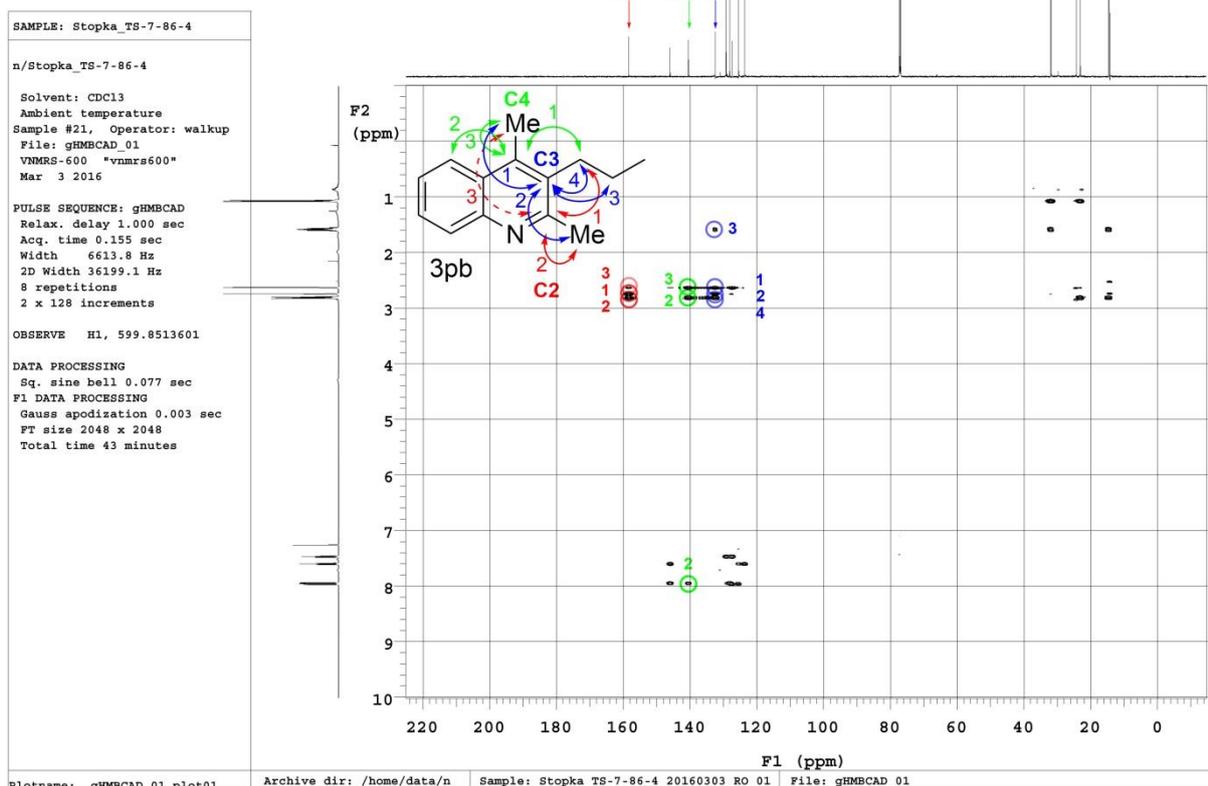
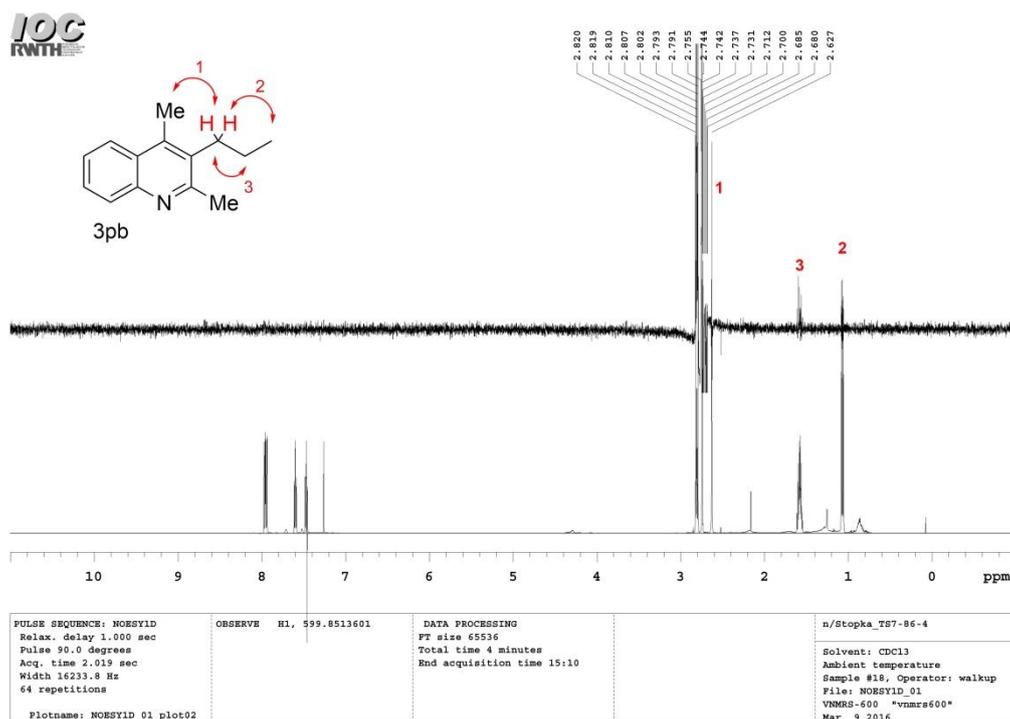


Figure 3. HMBC spectrum of quinoline **3pb** (600 MHz, CDCl<sub>3</sub>).

For a further confirmation of the assignment of the relative configuration of the substituents in **3pb** 1D selective NOESY NMR-experiments were performed. The results clearly support the assignment (see Figure 4).



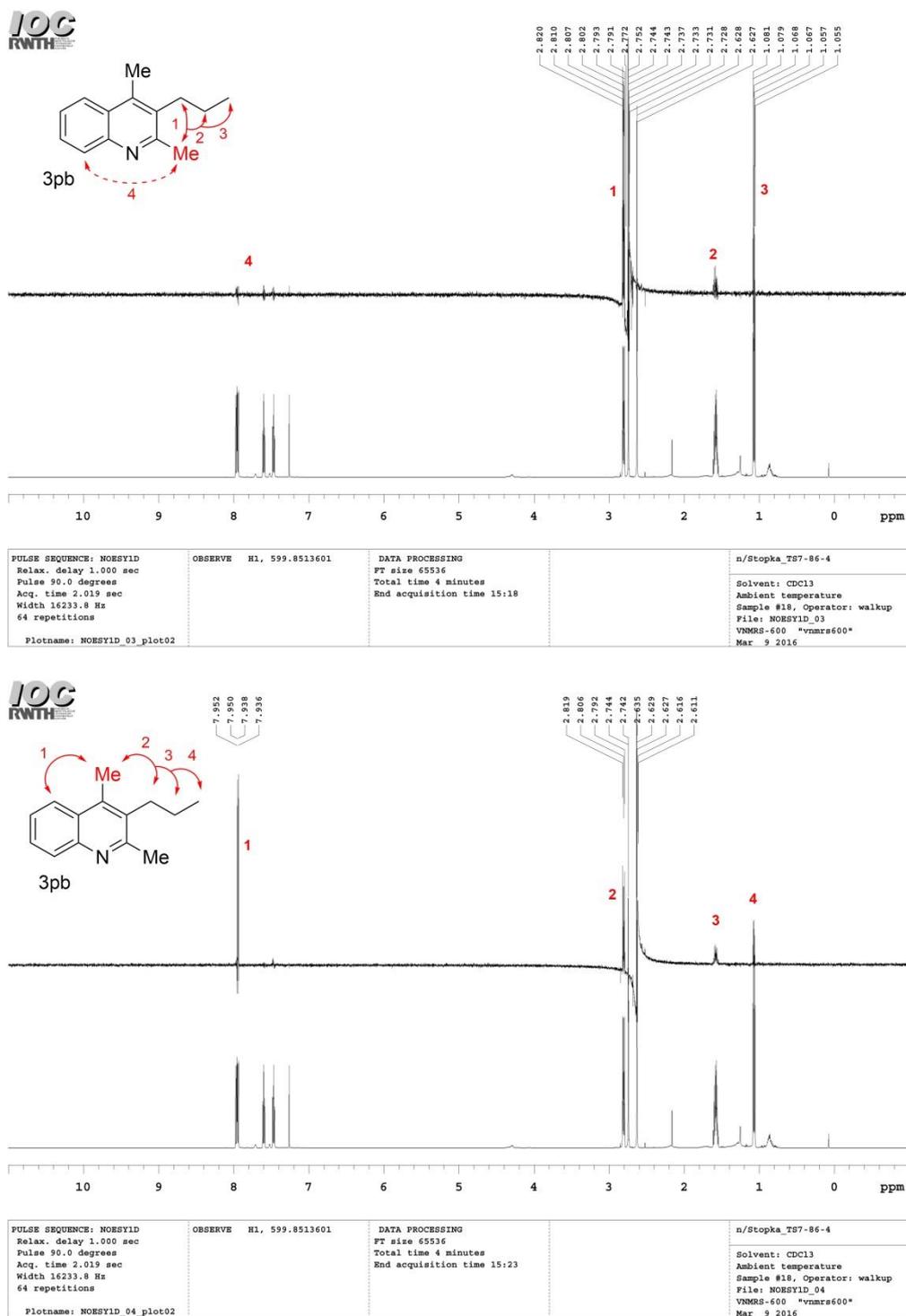
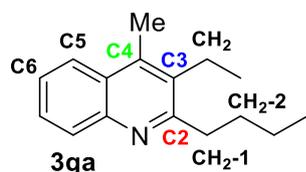


Figure 4. NOESY spectrum of quinoline **3pb** (600 MHz, CDCl<sub>3</sub>).

The last example illustrates the broad applicability of the assignment method as it can be used to even characterize both products in inseparable mixtures. The signals in the spectrum were assigned unambiguously to the respective compounds by comparison with <sup>1</sup>H and <sup>13</sup>C-NMR

data of the respective compounds, which were separated by semi-preparative SFC-chromatography. The amount of substance obtained by this separation method was unfortunately too small for an efficient 2D-NMR analysis (see appendix for spectra).

### 3qa:



**C2:** cross peak with CH<sub>2</sub>-1@C2

→ bears Bu@C2 and must be next to the nitrogen of the quinoline (chemical shift)

**C3:** cross peaks with Me-H@C4, CH<sub>2</sub>@C3

→ bears Et@C3 and must be next to Me@C4

**C4:** cross peaks with H@C5, H@C6, CH<sub>2</sub>@C3, CH<sub>3</sub>@C3

→ bears Me@C4 and must be in between aromatic ring of the quinoline and Et@C3

For a depiction of these results and the original HMBC spectrum see Figure 5.

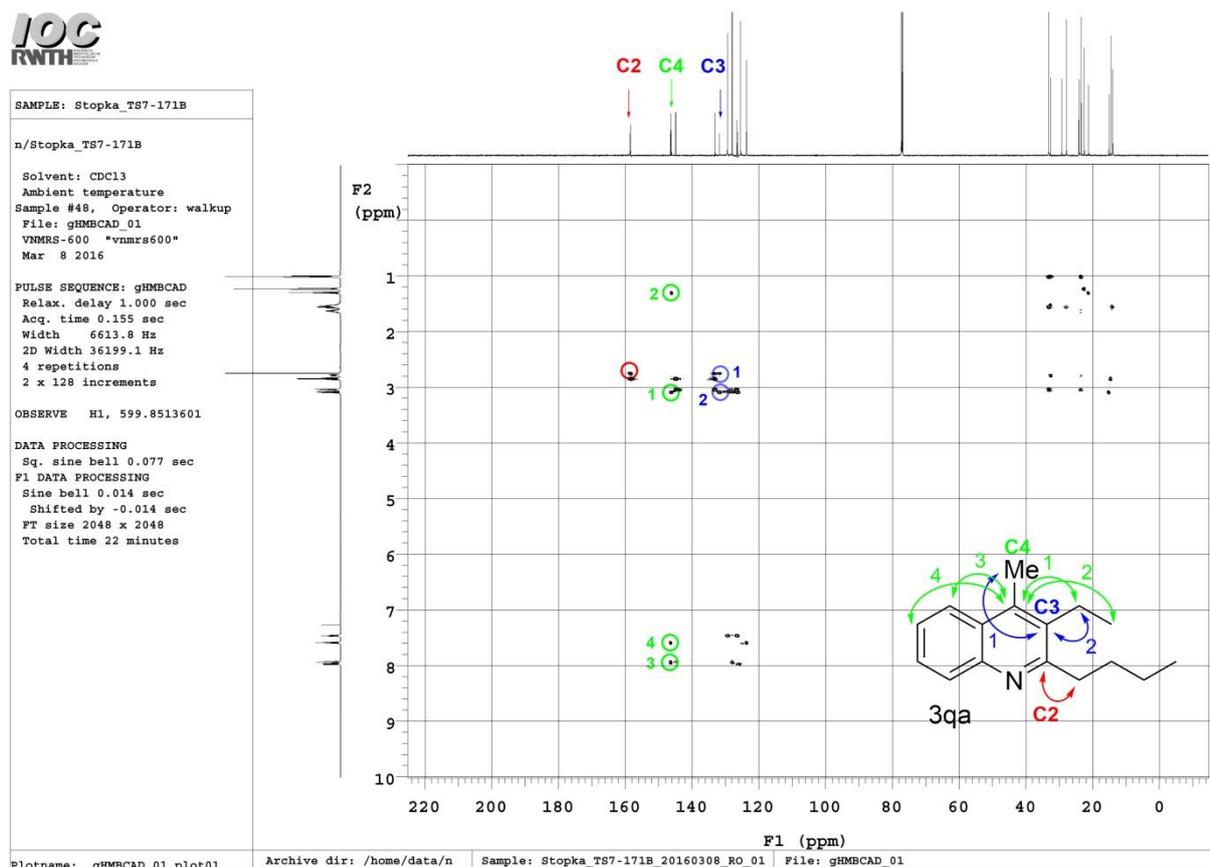
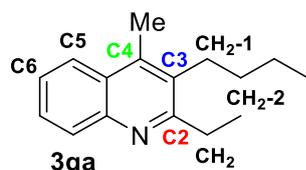


Figure 5. HMBC spectrum of quinoline **3qa** (600 MHz, CDCl<sub>3</sub>).

### 3qb:



**C2:** cross peak with CH<sub>2</sub>@C2

→ bears Et@C2 and must be next to the nitrogen of the quinoline (chemical shift)

**C3:** cross peaks with Me-H@C4, CH<sub>2</sub>-1@C3, CH<sub>2</sub>@C2

→ bears Bu@C3 and must be in between Me@C4 and Et@C2

**C4:** cross peaks with CH<sub>2</sub>-1@C3, CH<sub>2</sub>@C2, and weakly with H@C5

→ bears Me@C4 and must be in between aromatic ring of the quinoline and Bu@C3

For a depiction of these results and the original HMBC spectrum see Figure 6.

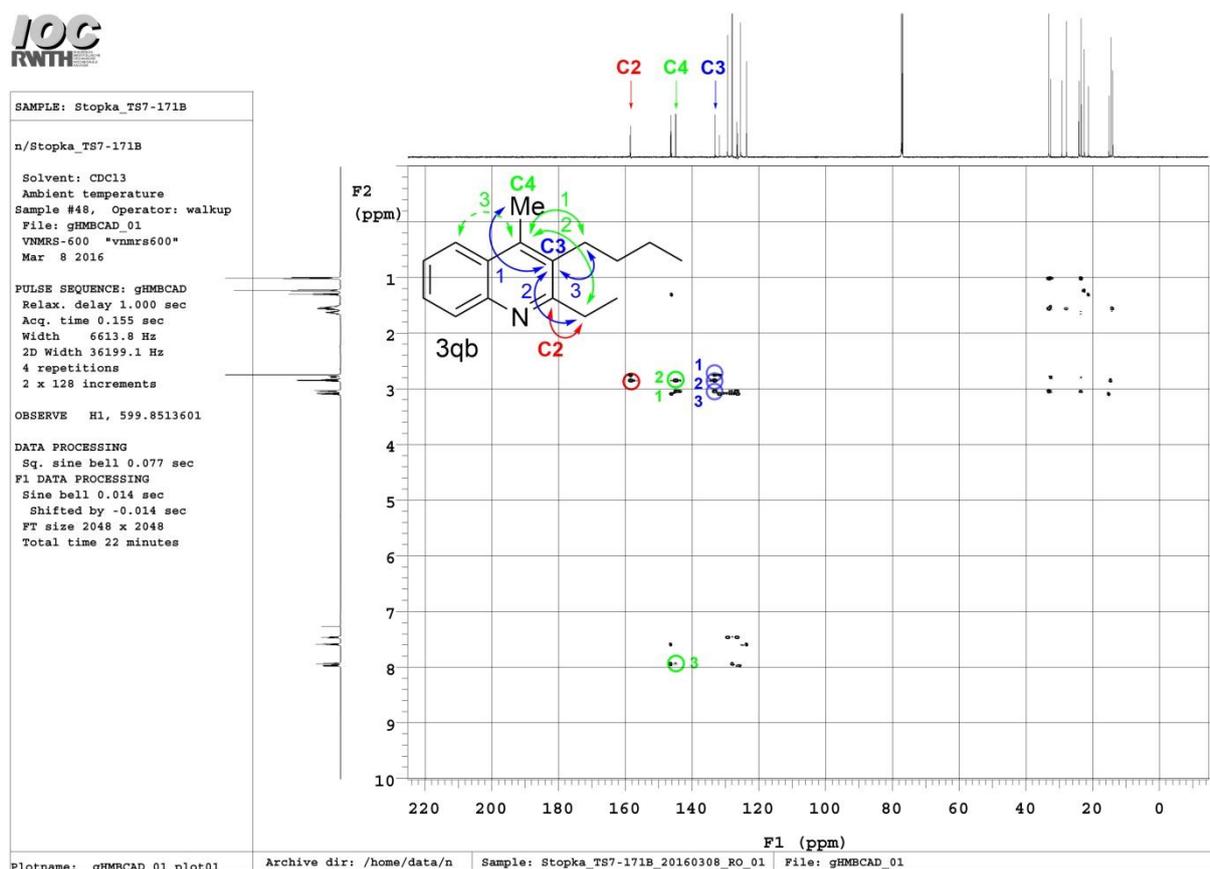


Figure 6. HMBC spectrum of quinoline **3pb** (600 MHz, CDCl<sub>3</sub>).

## References

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# $^1\text{H}$ -NMR Spectra, $^{13}\text{C}$ -NMR Spectra

