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# Microwave-Assisted Synthesis of Polysubstituted 4-Quinolones from Deprotonated α-Aminonitriles

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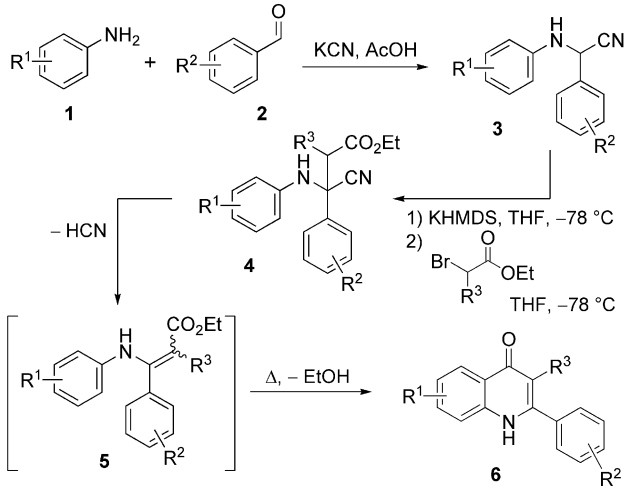
The α-alkylation of deprotonated *N*-aryl-α-aminonitriles with α-bromoesters furnishes intermediates that can be cyclized to 4-quinolones upon microwave irradiation. Alternatively, base-induced dehydrocyanation of the alkylation products furnishes enaminoesters, which can, for example, be converted into quinoline-3-carboxylates.

## Introduction

Their antibacterial properties make 4-quinolones an interesting compound class for medicinal chemistry.[1] For instance, the blockbuster antibiotics ciprofloxacin[2] and levofloxacin[3] are based on a 4-quinolone scaffold. Moreover, cytotoxic activities have been found for simple members of the 2-aryl-substituted series. These could be attributed to the interaction with the colchicine binding site on tubulin, which results in the blocking of mitosis in a broad spectrum of human cancer cell lines both in vitro and in vivo.[4] Numerous methods have been developed for the preparation of 4-quinolones, including the *N*-acylation of 2-aminoacetophenone and subsequent intramolecular condensation according to Camps, the reaction of anthranilates with ketals, or processes involving Cu- or Pd-catalyzed C–N bond formation.[1a,4b,5] A classical and widely employed approach is the Conrad–Limpach synthesis from anilines and β-keto esters,[6] which is closely related to the Combes synthesis of quinolines from anilines and β-diketones.[7] Herein, we describe a modular approach relying on the same ring closure, which does not require the preformation of the C2–C4 fragment and which uses only readily available classes of starting materials.

## Results and Discussion

Under certain conditions, Strecker products derived from aromatic, heteroaromatic, or α,β-unsaturated aldehydes and primary amines or ammonia can be deprotonated quantitatively without inducing the retro-Strecker reaction.[8] The resulting keteneiminate salts can serve as stabilized α-aminocarbanion equivalents in the preparation of pyrrolidines, pyrroles, indoles, diamines, amino alcohols, or imidazoles.[8,9] Their alkylation with α-haloesters yields intermediates that slowly release HCN with formation of enamino esters.[10] In the case of aniline-derived aminonitriles, these compounds are susceptible to the Conrad–Limpach cyclization, which would permit the three-step synthesis of polysubstituted 2-aryl-4-quinolones from an aniline, an aromatic aldehyde, and an α-haloester (Scheme 1).




Scheme 1. Modular synthesis of 4-quinolones by alkylation of deprotonated aminonitriles.

The concentrations of base and aminonitrile **3** were of great importance for the suppression of the formation of byproducts. The best results were seen with concentrations of 40–120 mM aminonitrile and 85–250 mM KHMDS in dry THF at –78 °C by using a short deprotonation period while either increasing the concentrations of the reactants or extension of the deprotonation time led to a significant decrease in the reaction yield. Under these conditions, several α,*N*-diaryl-α-aminonitriles and α-bromoesters were tested

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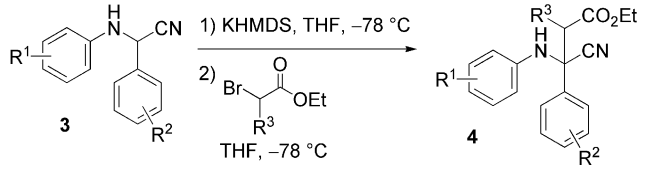
in *C*-alkylation reactions, and the results are shown in Table 1. In all cases, moderate to good alkylation yields were observed. As experienced with similar reactions by using different electrophiles, electron-donating substituents in the aminonitrile and steric hindrance in the α-bromoester led to diminished yields. The introduction of a substituent $R^3 \neq H$ resulted in the formation of inconsequential diastereomeric mixtures; in the case of 2 phenyl-substituted aminonitrile **4j**, separation of both diastereomers could be achieved by flash chromatography.

Table 1. Alkylation of compounds 3 with α-haloesters.



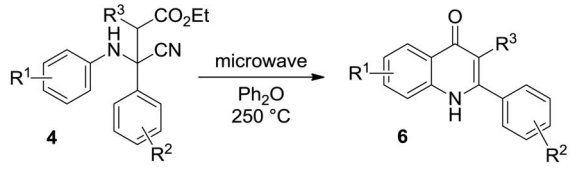

| Entry | Aminonitrile | $R^1$ | $R^2$ | $R^3$ | *t* [h] | Product, % Yield |
|---|---|---|---|---|---|---|
| 1 | **3a** | H | H | H | 1.5 | **4a**, 87 |
| 2 | **3b** | 4-$CH_3$ | H | H | 4 | **4b**, 70 |
| 3 | **3c** | 4-$OCH_3$ | H | H | 2 | **4c**, 67[a] |
| 4 | **3d** | 3-$OCH_3$ | H | H | 4 | **4d**, 55 |
| 5 | **3e** | 3-Cl | H | H | 0.5 | **4e**, 83[b] |
| 6 | **3f** | H | 4-$OCH_3$ | H | 1 | **4f**, 33 |
| 7 | **3g** | H | 2-Cl | H | 1 | **4g**, 61 |
| 8 | **3a** | H | H | $CH_3$ | 2 | **4h**, 54[b,c] |
| 9 | **3a** | H | H | $C_2H_5$ | 1 | **4i**, 63[c] |
| 10 | **3a** | H | H | $C_6H_5$ | 4 | **4j**, 59[c] |

[a] Contained trace amounts of starting material **3c**. [b] Contained trace amounts of impurities due to decomposition during flash chromatography. [c] Mixture of diastereomers.

The thermal dehydrocyanation of alkylation products **4** furnishes enamino esters, qualified for the Conrad–Limpach reaction although higher yields of the latter products can be obtained under basic conditions (vide infra). However, heating of compounds **4** to 180–250 °C in inert solvents such as diphenyl ether or decalin directly gives quinolones **6** in high yields.[11] A drastic increase in the reaction rates was observed when switching from classical heating (oil bath) to microwave irradiation, where complete conversion could be achieved in 10–30 min instead of up to 12 h. The results of a study involving all prepared intermediates **4** are summarized in Table 2.

While complete regioselectivity in favor of the 7-substituted product was observed for *meta*-methoxy-substituted compound **4d**, the corresponding chlorine derivative **4e** gave a 7:1 mixture of the 7- and 5-substituted quinolone. Due to their low solubility in common organic solvents, 4-quinolone **6e** and its 5-Cl isomer could not be separated by chromatography. In contrast to the workup protocol by Kuo et al.,[4a] purification of the products by flash chromatography or recrystallization was not necessary, as the product precipitated from diphenyl ether during the reaction. Precipitation was completed by addition of *n*-hexane, and washing with the same solvent gave products of high purity. For the preparation of enamino esters **5**, microwave heating of intermediates **4** to 100 °C in the presence of DBU turned out to be the method of choice. Well-known β-anilinocinnamate **5a**[5a,12] was thus obtained from **4a** in

Table 2. Cyclization of compounds **4** into 4-quinolones.

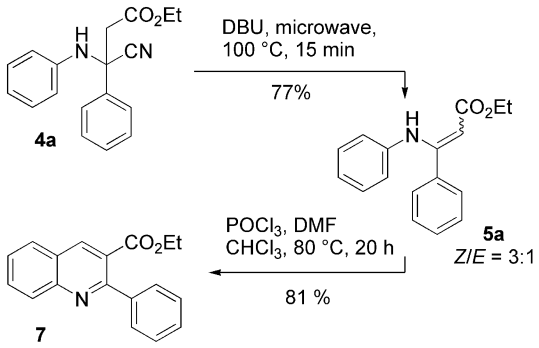



| Aminonitrile | *t* [min] | Product | % Yield |
|---|---|---|---|
| **4a** | 15 | **6a** | 72 |
| **4b** | 30 | **6b** | 71 |
| **4c** | 10 | **6c** | 73 |
| **4d** | 20 | **6d** | 81 |
| **4e** | 20 | **6e** | 71[a] |
| **4f** | 15 | **6f** | 91 |
| **4g** | 30 | **6g** | 81 |
| **4h** | 15 | **6h** | 86 |
| **4i** | 15 | **6i** | 75 |
| **4j** | 15 | **6j** | 81 |

[a] In addition, 14% of 5-isomer **6k** was obtained.

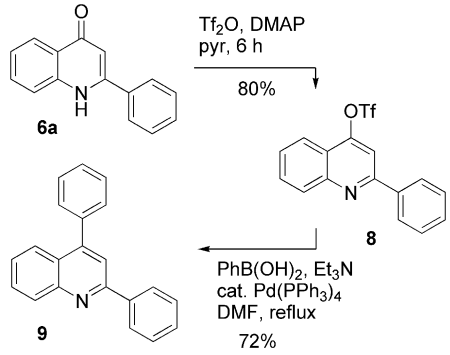
  

77% yield within 15 min as a 3:1 mixture of *Z*/*E* isomers. Formylation of the material according to a procedure by Anzini et al. gave ethyl 2-phenylquinoline-3-carboxylate (**7**) in 81% yield (Scheme 2).[13]




Scheme 2. Synthesis of quinoline-3-carboxylates from intermediates **4**.

Another route to quinolines converts quinolones **4** into the corresponding triflates, which can in turn be subjected to standard Pd-catalyzed coupling reactions. As an example, 2,4-diphenylquinoline (**9**) was prepared from 2-phenyl-4-quinonole (**6a**) by DMAP-catalyzed triflylation with $Tf_2O$ in pyridine and subsequent Suzuki coupling with phenylboronic acid (Scheme 3).[14]




Scheme 3. Conversion of 4-quinolone **6a** into quinoline **9**.

## Conclusions

In summary, a modular synthesis of 2-aryl-4-quinolones from aromatic aldehydes, anilines, and α-bromoesters was developed. Its key step is the alkylation of a deprotonated Strecker product, which is followed by a thermal double elimination. The procedure allows variation at the 2- and 3-positions as well as of the benzoid part of the products. While attempts to introduce substituents to the 1-position by using *N*-substituted anilines as precursors have so far met with little success, as the final cyclization did not occur in these cases, the elaboration of the intermediate enamino esters or final products into quinolines is feasible.

## Experimental Section

**General Experimental Methods:** All reactions were carried out in dried glassware and under an argon atmosphere. THF was dried by distillation from Na/benzophenone. Solvents used for flash chromatography were distilled before use. Aminonitriles **3** were prepared according to known procedures.[15–20] Other solvents and reagents were purchased from commercial suppliers and were used without further purification. TLC experiments were performed on glass plates coated with silica gel (60 $F_{254}$, Merck). Spots were visualized with UV-light at 254 nm and developed with phosphomolybdic acid, which was prepared by dissolving phosphomolybdic acid (25 g), $Ce(SO_4)_2{\cdot}4H_2O$ (10 g), and $H_2SO_4$ (60 mL) in water (940 mL).[21] Flash chromatography was carried out on silica gel (32–63 μm, Acros). $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker AV-400 or DRX 500 spectrometer and signals were referred to the residual solvent signal ($CDCl_3$: $\delta_H$ = 7.26 ppm, $\delta_C$ = 77.16 ppm; $CD_3OD$: $\delta_H$ = 3.31 ppm, $\delta_C$ = 49.00 pm; [$D_6$]DMSO: $\delta_H$ = 2.50 ppm, $\delta_C$ = 39.52 ppm).[22] Low- and high-resolution mass spectra in the ESI mode were measured by using an Agilent 6224 TOF with LC–MS system. Low- and high-resolution mass spectra in the FAB mode were recorded with a VG70S spectrometer (Xe-FAB ionization) by using *m*-nitrobenzyl alcohol as the matrix. IR spectra were measured with a Thermo-Nicolet Avatar 370 FTIR spectrometer or with a Bruker Tensor diamond-ATR FTIR spectrometer. Melting points were determined with a Kleinfeld Labortechnik Apotec apparatus. Microwave reactions were carried out in a CEM Discover monomode apparatus at the indicated maximum temperature and power setting.

**Ethyl 3-Cyano-3-phenylamino-3-phenylpropanoate (4a):** α-(Phenylamino)phenylacetonitrile[15,20] (500 mg, 2.40 mmol) was dissolved in THF (20 mL) and cooled to –78 °C. A solution of KHMDS (527 mg, 2.64 mmol) in THF (10 mL) was added dropwise within 5 min to the stirred solution. Immediately after complete addition of the base, ethyl bromoacetate (441 mg, 2.64 mmol, 295 μL) in THF (5 mL) was added. The mixture was allowed to stir for 1.5 h at –78 °C. Subsequently, the mixture was quenched with saturated aqueous $NaHCO_3$ solution (10 mL) and extracted with ethyl acetate (20 mL). The organic layer was washed with brine and concentrated in vacuo. Purification was carried out by flash chromatography (cyclohexane → cyclohexane/ethyl acetate, 19:1) to yield the title compound as a colorless oil (613 mg, 2.08 mmol, 87%). $R_f$ = 0.75 (cyclohexane/ethyl acetate, 5:1). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.67–7.65 (m, 2 H, H2′,6′), 7.44–7.36 (m, 3 H, H3′′,4′′,5′′), 7.13–7.09 (m, 2 H, H3′,5′), 6.84–6.80 (m, 1 H, H4′), 6.57–6.54 (m, 2 H, H2′,6′), 5.80 (s, 1 H, NH), 4.27 (dq, $^3J_q$ = 7.2 Hz, $^2J_d$ = 10.8 Hz, 2 H, -$OCH_2CH_3$), 3.04 (d, $^2J$ = 15.4 Hz, 1 H, H2a), 2.49 (d, $^2J$ = 15.4 Hz, 1 H, H2b), 1.28 (t, $^3J$ = 7.2 Hz, 3 H, $OCH_2CH_3$) ppm. $^{13}C$ NMR, HSQC, HMBC (100 MHz, $CDCl_3$): $\delta$ = 168.9 (C1), 143.5 (C1′), 138.3 (C1′′), 129.5 (C3′′,5′′,4′′), 129.0 (C3′,5′), 125.5 (C2′′,6′′), 120.6 (C4′), 118.6 (-CN), 116.9 (C2′,6′), 61.9 (-$OCH_2CH_3$), 59.2 (C3), 48.1 (C2), 14.2 (-$OCH_2CH_3$) ppm. MS (FAB): *m*/*z* (%) = 295.1 (85) [M + H]$^+$, 294.1 (100) [M]$^+$, 268.1 (75) [M – CN]$^+$, 221.1 (7) [M – $C_3H_5O_2$]$^+$, 207.1 (60) [M – $C_4H_7O_2$]$^+$, 180.1 (35) [M – CN – $C_4H_7O_2$]$^+$. HRMS (FAB): calcd. for [M]$^+$ 294.1368; found 294.1363. IR (film): $\tilde{\nu}$ = 3054, 2986, 2305, 1725, 1498, 1421, 1265, 1191, 895 cm$^{-1}$.

**Ethyl 3-Cyano-3-(4-methylphenylamino)-3-phenylpropanoate (4b):** α-(4-Methylphenylamino)phenylacetonitrile[16] (102 mg, 0.459 mmol) was dissolved in THF (10 mL) and cooled to –78 °C. KHMDS (110 mg, 0.551 mmol) was dissolved in THF (5 mL) and added to the stirred solution within 2 min. Ethyl bromoacetate (48.3 mg, 0.505 mmol, 564 μL) in THF (3 mL) was added immediately after

deprotonation to the reaction mixture and stirred for 0.5 h at –78 °C. Aqueous workup was performed according to the procedure for the preparation of **4a**. Purification of the crude product by flash chromatography (cyclohexane → cyclohexane/ethyl acetate, 19:1) yielded the title compound as slightly yellowish oil (98 mg, 0.32 mmol, 70%). $R_f$ = 0.71 (cyclohexane/ethyl acetate, 5:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.65 (d, $^3J$ = 7.0 Hz, 2 H, H2′′,6′′), 7.43–7.37 (m, 3 H, H3′′,4′′,5′′), 6.92–6.90 (AA′-part of AA′BB′-spin system, 2 H, H3′,5′), 6.49–6.46 (BB′-part of AA′BB′-spin system, 2 H, H2′,6′), 5.67 (s, 1 H, -NH), 4.25 (dq, $^2J$ = 10.8 Hz, $^3J$ = 7.2 Hz, 2 H, -$OCH_2CH_3$), 3.00 (d, $^2J$ = 15.4 Hz, 1 H, H2a), 2.95 (d, $^2J$ = 15.4 Hz, 1 H, H2b) 2.19 (s, 3 H, -$CH_3$), 1.29 (t, $^3J$ = 7.1 Hz, 3 H, -$OCH_2CH_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 169.1 (C1), 141.4 (C1′), 138.4 (C1′′), 129.6 (C3′′,4′′,5′′), 129.5 (C2′,6′), 129.3 (C4′′), 125.5 (C2′′,6′′), 122.4 (C4′), 118.9 (-CN), 116.9 (C2′,6′), 62.0 (-$OCH_2CH_3$), 59.4 (C3), 47.2 (C2), 20.6 (-$CH_3$), 14.3 (-$OCH_2CH_3$) ppm. MS (FAB): *m*/*z* (%) = 309 (55) $[M + H]^+$, 308 (100) $[M]^+$, 282 (64) $[M – CN]^+$, 235 (8) $[M – C_3H_5O_2]^+$, 221 (63) $[M – C_4H_7O_2]^+$, 194 (41) $[M – CN – C_4H_7O_2]^+$. HRMS (FAB): calcd. for $[M]^+$ 308.1525; found 308.1525. IR (film): $\tilde{\nu}$ = 3358, 2983, 1727, 1655, 1518, 1265, 1217, 1190, 737, 700 cm$^{-1}$.

**Ethyl 3-Cyano-3-(4-methoxyphenylamino)-3-phenylpropanoate (4c):** To a stirred solution of α-(4-methoxyphenylamino)phenylacetonitrile (**3c**;[16,17] 500 mg, 2.10 mmol) in THF (20 mL) was dropwise added a solution of KHMDS (461 mg, 2.31 mmol) in THF (10 mL) within 5 min at –78 °C. Ethyl bromoacetate (386 mg, 2.31 mmol, 258 μL) in THF (3 mL) was added, and the reaction mixture was stirred for 2 h at –78 °C. Aqueous workup was performed according to the procedure for the preparation of **4a**, and purification by flash chromatography (cyclohexane → cyclohexane/ethyl acetate, 8:2) yielded the title compound as an orange oil (462 mg, 1.43 mmol, 67%). $R_f$ = 0.73 (cyclohexane/ethyl acetate, 5:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.66 (d, $^3J$ = 7.2 Hz, 2 H, H6′′,2′′), 7.44–7.38 (m, 3 H, H3′′,4′′,5′′), 6.69–6.67 (AA′ part of AA′BB′ spin system, 2 H, H3′,5′), 6.53–6.51 (BB′ part of AA′BB′ spin system, 2 H, H2′,6′), 5.57 (s, 1 H, -NH), 4.25 (dq, $^3J_q$ = 7.2 Hz, $^2J_d$ = 10.8 Hz, 2 H, -$OCH_2CH_3$), 3.69 (s, 3 H, -$OCH_3$), 2.98 (s, 2 H, H2), 1.30 (t, $^3J$ = 7.2 Hz, 3 H, -$OCH_2CH_3$) ppm. The $^1$H NMR spectrum showed trace amounts of unreacted starting material **3c**. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 169.4 (C1), 154.1 (C4′), 138.2 (C1′), 137.0 (C1′′), 129.4 (C3′′,5′′), 128.9 (C4′′), 118.9 (C3′,5′), 119.2 (-CN), 114.4 (C2′,6′), 62.1 (-$OCH_2CH_3$), 59.9 (C3), 55.5 (-$OCH_3$), 47.8 (C2), 14.0 (-$OCH_2CH_3$) ppm. MS (FAB): *m*/*z* (%) = 325.3 (35) $[M + H]^+$, 324.3 (100) $[M]^+$, 198.3 (40) $[M – CN]^+$, 237.2 $[M – C_4H_7O_2]$, 210.2 $[M – C_4H_7O_2–CN]$. HRMS (FAB): calcd. for $[M]^+$ 324.1474; found 324.1489 ppm. IR (film): $\tilde{\nu}$ = 3054, 2986, 2305, 1727, 1513, 1265, 1216, 1035, 738, 703 cm$^{-1}$.

**Ethyl 3-Cyano-3-(3-methoxyphenylamino)-3-phenylpropanoate (4d):** α-(3-Methoxyphenylamino)phenylacetonitrile (**3d**;[17,18] 105 mg, 0.441 mmol) was dissolved in THF (10 mL) and cooled to –78 °C. KHMDS (96 mg, 0.49 mmol) in THF (5 mL) was added within 2 min to the stirred solution. Subsequently, ethyl bromoacetate (80.2 mg, 0.485 mmol, 53.7 μL) in THF (3 mL) was added to the mixture, which was stirred for 3.5 h at –78 °C. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (5 mL) and extracted with ethyl acetate (10 mL). The organic layer was washed with brine and concentrated in vacuo. Purification of the crude product by flash chromatography (cyclohexane → cyclohexane/ethyl acetate, 19:1) yielded the title compound as a colorless oil (76 mg, 0.24 mmol, 55%). $R_f$ = 0.48 (cyclohexane/ethyl acetate, 2:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.67–7.65 (m, 2 H, H2′′,6′′), 7.44–7.36 (m, 3 H, H3′′,4′′,5′′), 7.01 (t, $^3J$ = 8.2 Hz, 1 H, H5′), 6.37 (dd, $^3J$ = 8.2 Hz, $^4J$ = 2.2 Hz, $^4J$ = 0.7 Hz, 1 H, H4′), 6.16 (dd, $^3J$ = 8.2 Hz, $^4J$ = 2.3 Hz, $^4J$ = 0.7 Hz, 1 H, H6′), 6.09 (t, $^3J$ = 2.3 Hz, 1 H, H2′), 5.84 (s, 1 H, -NH), 4.26 (dq, $^2J$ = 10.8 Hz, $^3J$ = 7.2 Hz, 2 H, -$OCH_2CH_3$), 3.62 (s, 3 H, -$OCH_3$), 3.01 (d, $^2J$ = 15.4 Hz, 1 H, H2a), 2.95 (d, $^3J$ = 15.4 Hz, 1 H, H2b), 1.30 (t, $^3J$ = 7.2 Hz, 3 H, -$OCH_2CH_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 169.2 (C1), 160.6 (C3′), 145.1 (C1′), 138.4 (C1′′), 129.9 (C5′), 129.6 (C3′′,5′′), 129.1 (C4′′), 125.4 (C2′′,6′′), 118.9 (-CN), 109.5 (C6′), 106.3 (C4′), 102.5 (C2′), 62.0 (-$OCH_2CH_3$), 59.2 (C3), 55.0 (-$OCH_3$), 48.2 (C2), 14.3 (-$OCH_2CH_3$) ppm. MS (ESI): *m*/*z* (%) = 325.2 (60) $[M + H]^+$. HRMS (ESI): calcd. for $[M + H]^+$ 325.1474; found 325.1475. IR (film): $\tilde{\nu}$ = 3365, 2983, 2359, 1728, 1603, 1520, 1492, 1164, 1037, 765 cm$^{-1}$.

**Ethyl 3-Cyano-3-(3-chlorphenylamino)-3-phenylpropanoate (4e):** α-(3-Chlorophenylamino)phenylacetonitrile (**3e**;[16,18] 100 mg, 0.41 mmol) was dissolved in THF (10 mL) and cooled to –78°. To the stirred solution was added KHMDS (90 mg, 0.45 mmol) in THF (5 mL) within 2 min. Ethyl bromoacetate (75.3 mg, 0.450 mmol, 50.4 μL) in THF (3 mL) was added, and the mixture was allowed to stir for 0.5 h at –78 °C. Workup was performed according to the procedure for the preparation of **4a**. Flash chromatographic purification (cyclohexane → cyclohexane/ethyl acetate, 99:1) yielded compound **4e** as a slightly yellow oil (111 mg, 0.340 mmol, 83%). $R_f$ = 0.45 (cyclohexane/ethyl acetate, 2:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.64–7.61 (m, 2 H, H2′′,6′′), 7.45–7.39 (m, 3 H, H3′′,4′′,5′′), 7.00 (t, $^3J$ = 8.2 Hz, 1 H, H5′), 6.78 (dd, $^3J$ = 7.9 Hz, $^4J$ = 2.1 Hz, $^4J$ = 0.8 Hz, 1 H, H4′), 6.59 (t, $^4J$ = 2.1 Hz, 1 H, H2′), 6.37 (dd, $^3J$ = 8.2 Hz, $^4J$ = 2.1 Hz, $^3J$ = 0.8 Hz, 1 H, H6′), 5.96 (s, 1 H, -NH), 4.26 (dq, $^2J_d$ = 8.6 Hz, $^3J_q$ = 8.6 Hz, 2 H, -$OCH_2CH_3$), 3.02 (d, $^2J$ = 15.4 Hz, 1 H, H2a), 2.93 (d, $^2J$ = 15.4 Hz, 1 H, H2b), 1.30 (t, $^3J$ = 7.2 Hz, 3 H, -$OCH_2CH_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 169.7 (C1), 145.3 (C3′), 137.9 (C1′′), 134.8 (C1′), 129.9 (C5′), 129.6 (C3′′,5′′), 129.3 (C4′′), 127.1 (C4′), 125.5 (C2′′,6′′), 120.5 (C4′), 118.4 (-CN), 117.0 (C2′), 114.5 (C6′), 62.5 (-$OCH_2CH_3$), 58.9 (C3), 48.0 (C2), 14.1 (-$OCH_2CH_3$) ppm. MS (ESI): *m*/*z* (%) = 351.1 (30) $[M + Na]^+$, 329.1 (100) $[M + H]^+$. HRMS (ESI): calcd. for $[M + H]^+$ 329.1061; found 329.1051. IR (film): $\tilde{\nu}$ = 3358, 3054, 2986, 2359, 1724, 1598, 1265, 1218, 739, 704 cm$^{-1}$.

**Ethyl 3-Cyano-3-phenylamino-3-(4-methoxyphenyl)propanoate (4f):** A solution of KHMDS (94.4 mg, 0.473 mmol) in THF (5 mL) was added within 3 min to a stirred solution of α-(phenylamino)-4-methoxyphenylacetonitrile (**3f**;[16,19] 102 mg, 0.430 mmol) in THF (10 mL) at –78 °C. Ethyl bromoacetate (77.9 mg, 0.473 mmol, 53.5 μL) in THF (3 mL) was added immediately after addition of the KHMDS solution, and the mixture was allowed to stir for 1 h at –78 °C. Workup was performed according to the procedure for the preparation of **4a**. The crude product was purified by flash chromatography (cyclohexane → cyclohexane/ethyl acetate, 4:1) to yield the title compound as a colorless oil (46 mg, 0.14 mmol, 33%). $R_f$ = 0.42 (cyclohexane/ethyl acetate, 2:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.56–7.54 (AA′ part of the AA′BB′ spin system, 2 H, H2′′,6′′), 7.11 (dd, $^3J$ = 8.3 Hz, $^3J$ = 7.7 Hz, 2 H, H3′,5′), 6.93–6.91 (BB′ part of the AA′BB′ spin system, 2 H, H3′′,5′′), 6.82 (t, $^3J$ = 7.4 Hz, 1 H, H4′), 6.57 (d, $^3J$ = 7.7 Hz, 2 H, H2′,6′), 5.75 (s, 1 H, -NH), 4.25 (dq, $^2J_d$ = 10.2 Hz, $^3J_q$ = 7.2 Hz, 2 H, -$OCH_2CH_3$), 3.82 (s, 3 H, -$OCH_3$), 2.99 (d, $^2J$ = 15.4 Hz, 1 H, H2a), 2.94 (d, $^2J$ = 15.4 Hz, 1 H, H2b), 1.30 (t, $^3J$ = 7.2 Hz, 3 H, -$OCH_2CH_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 169.2 (C1), 160.3 (C4′′), 143.6 (C1′), 130.2 (C1′′), 129.0 (C3′,5′), 126.9 (C3′′,5′′), 120.9 (C4′), 118.9 (-CN), 116.8 (C2′,6′), 114.6 (C2′′,6′′), 62.1 (-$OCH_2CH_3$), 60.2 (C3), 55.6 (-$OCH_3$), 48.4 (C2), 14.3 (-$OCH_2CH_3$) ppm. MS (ESI): *m*/*z* (%) = 325.2 (100) $[M + H]^+$.

HRMS (ESI): calcd. for $[M + H]^+$ 325.1547; found 325.1550. IR (film): $\tilde{\nu}$ = 2980, 2359, 1731, 1605, 1510, 1254, 1175, 1030, 752 $cm^{-1}$.

**Ethyl 3-Cyano-3-phenylamino-3-(2-chlorophenyl)propanoate (4g):** To a solution of α-(phenylamino)-2-chlorophenylacetonitrile (**3g**;[16,18] 100 mg, 0.412 mmol) in THF (10 mL) was added KHMDS (89.8 mg, 0.453 mmol) in THF (5 mL) dropwise within 2 min at –78 °C. Ethyl bromoacetate (75.3 mg, 0.453 mmol, 50.4 μL) in THF (3 mL) was added to the mixture, which was then stirred for 1 h at –78 °C. Workup was performed according to the procedure for the preparation of **4a**. Purification was achieved by flash chromatography (cyclohexane → cyclohexane/ethyl acetate, 19:1) to yield the title compound as a colorless oil (84 mg, 0.25 mmol, 61%). $R_f$ = 0.41 (cyclohexane/ethyl acetate, 2:1). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.72 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.3 Hz, 1 H, H3′′), 7.46 (dd, $^3J$ = 7.8 Hz, $^3J$ = 0.9 Hz, 1 H, H6′′), 7.33 (dt, $^3J$ = 7.8 Hz, $^4J$ = 1.5 Hz, 1 H, H4′′), 7.28 (dd, $^3J$ = 7.8 Hz, $^4J$ = 0.9 Hz, 1 H, H5′′), 7.13 (t, $^3J$ = 7.5 Hz, 2 H, H3′,5′), 6.82 (t, $^3J$ = 7.5 Hz, 1 H, H4′), 6.56 (d, $^3J$ = 7.5 Hz, 2 H, H2′,6′), 5.74 (s, 1 H, -NH), 4.21 (m, 2 H, -$OCH_2CH_3$), 3.42 (d, $^2J$ = 14.9 Hz, 1 H, H2a), 3.12 (d, $^2J$ = 14.9 Hz, 1 H, H2b), 1.25 (t, $^3J$ = 7.1 Hz, 3 H, -$OCH_2CH_3$) ppm. The $^1H$ NMR spectrum showed trace amounts of impurities due to the decomposition of **4g** during flash chromatography. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 168.0 (C1), 142.3 (C1′), 132.1 (C6′′), 131.2 (C2′′), 130.7 (C1′′), 129.6 (C4′′), 128.7 (C3′′), 128.1 (C3′,5′), 126.7 (C5′′), 119.5 (C4′), 116.5 (-CN), 115.5 (C2′,6′), 61.1 (-$OCH_2CH_3$), 56.7 (C3), 42.6 (C2), 13.1 (-$OCH_2CH_3$) ppm. MS (ESI): *m*/*z* (%) = 351.1 (10) $[M + Na]^+$, 329.1 (100) $[M + H]^+$. HRMS (ESI): calcd. for $[M + H]^+$ 329.1051; found 329.1058. IR (film): $\tilde{\nu}$ = 3380, 2982, 2360, 1727, 1603, 1498, 1213, 753, 737 $cm^{-1}$.

**Ethyl 3-Cyano-2-methyl-3-phenylamino-3-phenylpropanoate (4h):** α-(Phenylamino)phenylacetonitrile (**3a**;[15,20] 99.7 mg, 0.479 mmol) was dissolved in THF (10 mL) and a solution of KHMDS (105 mg, 0.527 mmol) in THF (5 mL) was added at –78 °C within 2 min. Ethyl bromopropionate (95.9 mg, 0.527 mmol, 69.1 μL) in THF (3 mL) was added, and the reaction mixture was stirred for 2 h at –78 °C. Workup was performed according to the procedure for the preparation of **4a**. Purification of the crude product by flash chromatography (cyclohexane → cyclohexane/ethyl acetate, 19:1) gave the title compound as a colorless oil (80 mg, 0.26 mmol, 54%). Ratio of diastereomers A/B = 10:7, determined by $^1H$ NMR spectroscopy. $R_f$ = 0.62 (cyclohexane/ethyl acetate, 5:1). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.59–7.56 (m, 4 H, $H3''^A$,$5''^A$, overlap of signals with $H3''^B$,$5''^B$), 7.42–7.34 (m, 6 H, $H2''^A$,$4''^A$,$6''^A$, overlap of signals with $H2''^B$,$4''^B$,$6''^B$), 7.12–7.06 (m, 4 H, $H3'^A$,$5'^A$, overlap of signals with $H3'^B$,$5'^B$), 6.80 (t, $^3J$ = 7.4 Hz, 1 H, $H4'^B$), 6.77 (t, $^3J$ = 7.4 Hz, 1 H, $H4'^A$), 6.54 (d, $^3J$ = 7.9 Hz, 4 H, $H2'^A$,$6'^A$, overlap of signals with $H2'^B$,$6'^B$), 5.63 (s, 2 H, -$NH^A$, overlap of the signal with -$NH^B$), 4.31–4.24 (m, 2 H, -$OCH_2CH_3{}^B$), 4.21–4.12 (m, 2 H, -$OCH_2CH_3{}^A$), 3.06 (q, $^3J$ = 7.2 Hz, 2 H, $H3^B$), 3.00 (q, $^3J$ = 7.2 Hz, 2 H, $H3^A$), 1.31–1.29 (m, 6 H, -$OCH_2CH_3{}^A$, overlap of signals with -$CH_3{}^B$), 1.22–1.18 (m, 6 H, -$CH_3{}^A$, ppm, overlap of signals with -$OCH_2CH_3{}^B$). The $^1H$ NMR spectrum shows trace amounts of impurities due to decomposition during flash chromatography. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 172.0 ($C1^B$), 170.9 ($C1^A$), 141.8 ($C1'^{A,B}$), 135.4 ($C1''^{A,B}$), 129.3 ($C2''^B$,$6''^B$), 129.3 ($C4''^B$), 129.2 ($C4''^A$), 129.1 ($C2''^A$,$6''^A$), 129.0 ($C3'^{A,B}$,$5'^{A,B}$), 126.8 ($C3''^B$,$5''^B$), 126.3 ($C3''^A$,$5''^A$), 120.2 ($C4'^B$), 120.0 ($C4'^A$), 118.0 (-$CN^{A,B}$), 116.5 ($C2'^B$,$6'^B$), 116.0 ($C2'^A$,$6'^A$), 63.6 ($C3^{A,B}$), 62.0 (-$OCH_2CH_3{}^B$), 61.9 (-$OCH_2CH_3{}^A$), 51.2 ($C2^A$), 50.7 ($C2^B$), 14.2 (-$CH_3{}^B$), 14.1 (-$CH_3{}^A$), 13.5 (-$OCH_2CH_3{}^A$), 12.0 (-$OCH_2CH_3{}^B$) ppm. MS (ESI): *m*/*z* (%) = 331.2 (25) $[M + Na]^+$, 309.2 (65) $[M + H]^+$. HRMS (ESI): calcd. for $[M]^+$ 308.1525; found 308.1526. IR (film): $\tilde{\nu}$ = 3386, 2983, 2359, 1720, 1603, 1499, 1190, 752 $cm^{-1}$.

**Ethyl 3-Cyano-2-ethyl-3-phenylamino-3-phenylpropanoate (4i):** A solution of KHMDS (105 mg, 0.528 mmol) in THF (5 mL) was added within 3 min to a stirred solution of α-(phenylamino)phenylacetonitrile (**3a**;[15,20] 99.4 mg, 0.480 mmol) in THF (10 mL) at –78 °C. Ethyl bromobutyrate (0.528 mmol, 77.4 μL) in THF (3 mL) was added, and the mixture was stirred for 1 h at –78 °C. Workup was performed according to the procedure for the preparation of **4a**. Purification of the crude product by flash chromatography (cyclohexane → cyclohexane/ethyl acetate, 49:1) gave the title compound as a colorless oil (95 mg, 0.30 mmol, 63%). Ratio of diastereomers: A/B = 10:3, determined by $^1H$ NMR spectroscopy. $R_f$ = 0.67 (cyclohexane/ethyl acetate, 5:1). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.58 (d, $^3J$ = 6.5 Hz, 2 H, $H2''^B$,$6''^B$), 7.52 (d, $^3J$ = 6.8 Hz, 2 H, $H2''^A$,$6''^A$), 7.40–7.33 (m, 6 H, $H3''^A$,$4''^A$,$5''^A$, overlap of signals with $H3''^B$,$4''^B$,$5''^B$), 7.09 (t, $^3J$ = 7.7 Hz, 4 H, $H3'^A$,$5'^A$, overlap of signals with $H3'^B$,$5'^B$), 6.80 (t, $^3J$ = 7.6 Hz, 1 H, $H4'^B$), 6.75 (t, $^3J$ = 7.3 Hz, 1 H, $H4'^A$), 6.55 (d, $^3J$ = 8.1 Hz, 2 H, $H2'^A$,$6'^A$), 6.54–6.53 (m, 4 H, $H2'^B$,$6'^B$, overlap of signals with $H2'^A$,$6'^A$), 5.62 (s, 1 H, -$NH^B$), 5.37 (s, 1 H, -$NH^A$), 4.27 (dq, $^2J$ = 10.7 Hz, $^3J$ = 6.9 Hz, 2 H, -$OCH_2CH_3{}^B$), 4.08 (dq, $^2J$ = 10.3 Hz, $^3J$ = 7.2 Hz, 2 H, -$OCH_2CH_3{}^A$), 2.83 (dd, $^2J$ = 12.0 Hz, $^3J$ = 3.0 Hz, 2 H, $H2^A$, overlap of signals with $H2^B$), 2.10 (dq, $^3J$ = 7.1 Hz, 2 H, -$CH_2CH_3{}^A$), 1.93–1.76 (m, 2 H, -$CH_2CH_3{}^B$), 1.32 (t, $^3J$ = 7.1 Hz, 3 H, -$OCH_2CH_3{}^B$), 1.10 (t, $^3J$ = 7.1 Hz, 3 H, -$OCH_2CH_3{}^A$), 0.93 (t, $^3J$ = 7.3 Hz, 3 H, -$CH_2CH_3{}^A$), 0.83 (t, $^3J$ = 7.4 Hz, 3 H, -$CH_2CH_3{}^B$) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 172.9 ($C1^B$), 171.8 ($C1^A$), 143.2 ($C1'^{A,B}$), 137.1 ($C1''^A$), 135.6 ($C1''^B$), 129.1 ($C3'^B$,$4'^B$,$5'^B$), 129.0 ($C3''^A$,$4''^A$,$5''^A$), 128.9 ($C3'^A$,$5'^A$), 128.8 ($C3'^B$,$5'^B$), 126.5 ($C2''^B$,$6''^B$), 125.8 ($C2''^A$,$6''^A$), 119.9 ($C4'^B$), 119.3 ($C4'^A$), 118.9 (-$CN^B$), 118.2 (-$CN^A$), 116.3 ($C2'^B$,$6'^B$), 115.4 ($C2'^A$,$6'^A$), 62.7 ($C3^{A,B}$), 61.9 (-$OCH_2CH_3{}^B$), 61.5 (-$OCH_2CH_3{}^A$), 59.2 ($C2^A$), 58.1 ($C2^B$), 22.0 (-$CH_2CH_3{}^{A,B}$), 14.2 (-$OCH_2CH_3{}^B$), 14.1 (-$OCH_2CH_3{}^A$), 11.9 (-$CH_2CH_3{}^A$), 11.6 (-$CH_2CH_3{}^B$) ppm. MS (ESI): *m*/*z* (%) = 345.2 (30) $[M + Na]^+$, 323.2 (100) $[M + H]^+$. HRMS (ESI): calcd. for $[M + H]^+$ 323.1754; found 323.1764. IR (ATR): $\tilde{\nu}$ = 3341, 1652, 1634, 1597, 1522, 1434, 1254, 748, 688, 642 $cm^{-1}$.

**Ethyl 3-Cyano-2,3-diphenyl-3-phenylaminopropanoate (4j):** α-(Phenylamino)phenylacetonitrile (**3a**;[15,20] 100 mg, 0.480 mmol) was dissolved in THF (10 mL) and a solution of KHMDS (106 mg, 0.528 mmol) in THF (5 mL) was added within 2 min while stirring at –78 °C. Ethyl α-bromophenylacetate (128 mg, 0.528 mmol, 92.4 μL) in THF (3 mL) was added, and the mixture was stirred for 4 h at –78 °C. Workup was performed according to the procedure for the preparation of **4a**. Purification of the crude product by flash chromatography (cyclohexane → cyclohexane/ethyl acetate, 19:1) yielded the title compound as a light yellow oil (57 mg, 0.15 mmol, 32%). Both diastereomers could be separated. The $^1H$ NMR spectrum of the less mobile diastereomer showed impurities that could not be removed by flash chromatography. The more mobile diastereomer was obtained as a colorless oil (50 mg, 0.13 mmol, 27%), showing no impurities in its $^1H$ NMR spectrum. $R_f$ (diastereomer 1) = 0.42 (cyclohexane/ethyl acetate, 2:1). $^1H$ NMR (400 MHz, $CDCl_3$, diastereomer 1): $\delta$ = 7.53–7.51 (m, 2 H, H2′′′,6′′′), 7.41–7.38 (m, 2 H, H2′′,6′′), 7.37–7.30 (m, 6 H, H3′′,4′′,5′′,3′′′,4′′′,5′′′), 7.06–7.01 (m, 2 H, H3′,5′), 6.80–6.75 (m, 1 H, H4′), 6.46 (d, $^3J$ = 8.6, $^4J$ = 0.9 Hz, 2 H, H2′,6′), 5.24 (s, 1 H, -NH), 4.22–3.99 (m, 3 H, -$OCH_2CH_3$, H2), 1.12 (t, $^3J$ = 7.3 Hz, 3 H, -$OCH_2CH_3$) ppm. $R_f$ (diastereomer 2) = 0.51 (cyclohexane/ethyl acetate, 2:1). $^1H$ NMR (400 MHz, $CDCl_3$, diastereomer 2,

COSY): $\delta$ = 7.36 (dd, $^3J$ = 7.9 Hz, $^3J$ = 1.8 Hz, 2 H, H2′′′,6′′′), 7.31–7.27 (m, 2 H, H2′′,6′′), 7.25–7.22 (m, 3 H, H3′′,4′′,5′′), 7.20–7.17 (m, 3 H, H3′′′,4′′′,5′′′), 7.07–7.05 (m, 2 H, H3′,5′), 6.77 (t, $^3J$ = 7.3 Hz, 1 H, H4′), 6.54 (d, $^3J$ = 7.7 Hz, 2 H, H2′,6′), 5.46 (s, 1 H, -NH), 4.19 (q, $^3J$ = 7.1 Hz, 2 H, -$OCH_2CH_3$), 4.05 (s, 1 H, H2), 1.17 (t, $^3J$ = 7.1 Hz, 3 H, -$OCH_2CH_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$, diastereomer 2, HMBC, HSQC): $\delta$ = 170.9 (C1), 149.7 (C1′), 136.7 (C1′′), 131.9 (C1′′′), 129.8 (C4′′), 128.7 (C3′′′,5′′′), 128.2 (C2′′′,6′′′), 126.7 (C3′,5′), 126.3 (C2′′,6′′), 120.2 (C4′), 118.8 (-CN), 116.7 (C2′,6′), 64.2 (C3), 62.8 (-$OCH_2CH_3$), 40.5 (C2), 13.3 (-$OCH_2CH_3$) ppm. The resonances of C3′′, 4′′, and 5′′ could not be assigned. MS (ESI): *m*/*z* (%) = 371.2 (50) [M + H]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 370.1681; found 370.1679. IR (film): $\tilde{\nu}$ = 3352, 2360, 1739, 1606, 1502, 1448, 1205, 685 cm$^{-1}$.

**Ethyl 3-(Phenylamino)cinnamate (5a):** The reaction was carried out under microwave irradiation with a maximum power of 300 W by using air cooling. To aminonitrile **4a** (104 mg, 0.353 mmol) was added DBU (59.2 mg, 0.389 mmol, 58.6 μL, 1.1 equiv.), and the mixture was heated for 15 min to 100 °C. Purification was carried out by filtration through silica (cyclohexane) to yield the title compound as a colorless oil (71.4 mg, 0.267 mmol, 77%). The ratio of *E*/*Z* isomers was 1:3, as determined by $^1$H NMR spectroscopy. The NMR signals were assigned by comparison with literature data.[23] $R_f$ = 0.21 (cyclohexane/ethyl acetate, 5:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 12.56 (s, 1 H, -$NH^E$), 10.28 (s, 1 H, -$NH^Z$), 7.93 (d, $^3J$ = 7.5 Hz, 2 H, H2′$^E$,6′$^E$), 7.58 (t, $^3J$ = 7.4 Hz, 1 H, H4′$^E$), 7.47 (t, $^3J$ = 7.6 Hz, 2 H, H3′$^E$,5′$^E$), 7.34–7.29 (m, 3 H, H3′′$^Z$,4′′$^Z$,5′′$^Z$, overlap of signals with H3′′$^E$,4′′$^E$,5′′$^E$), 7.29–7.25 (m, 2 H, H2′′$^Z$,6′′$^Z$, overlap of signals with 2′′$^E$,6′′$^E$), 7.08–7.03 (m, 2 H, H3′$^Z$,5′$^Z$), 6.91–6.86 (m, 1 H, H4′$^Z$), 6.65–6.62 (m, 2 H, H2′$^Z$,6′$^Z$), 4.97 (s, 1 H, H2$^Z$), 4.19 (q, $^3J$ = 7.1 Hz, 2 H, -$OCH_2CH_3^{E,Z}$), 3.97 (s, 1 H, H2$^E$), 1.30 (t, $^3J$ = 7.1 Hz, 3 H, -$OCH_2CH_3^Z$), 1.24 (t, $^3J$ = 7.1 Hz, 3 H, -$OCH_2CH_3^E$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 170.3 (C1$^Z$), 167.8 (C1$^E$), 159.3 (C3$^Z$), 140.7 (C1′$^E$), 140.5 (C1′$^Z$), 136.2 (C1′′$^Z$), 133.9 (C4$^E$), 129.6 (C3′$^E$,5′$^E$), 129.0 (C2′$^E$,6$^E$), 128.9 (C3′$^Z$,5′$^Z$), 128.7 (C2′′$^E$,6′′$^E$), 128.7 (C4′′$^Z$), 128.6 (C3′′$^Z$,5′′$^Z$), 128.4 (C2′′$^Z$,6′′$^Z$), 123.6 (C3′′$^E$,5′′$^E$), 123.1 (C4′$^Z$), 121.4 (C4′′$^E$), 122.3 (C2′$^Z$,6′$^Z$), 91.3 (C2$^Z$), 61.6 (-$OCH_2CH_3^E$), 59.5 (-$OCH_2CH_3^Z$), 46.1 (C2$^E$), 14.6 (-$OCH_2CH_3^Z$), 14.2 (-$OCH_2CH_3^E$) ppm. The resonances of C1′′$^E$ and C3$^E$ could not be detected. MS (ESI): *m*/*z* (%) = 268.1 (25) [M + H]$^+$, 222.1 (100) [M – $C_2H_5O$]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 268.1332; found 268.1330. IR (film): $\tilde{\nu}$ = 2978, 1658, 1615, 1596, 1574, 1503, 1484, 1286, 1174, 1039, 769 cm$^{-1}$. The analytical data correspond to those reported in the literature.[23]

**Synthesis of 2-Phenyl-1*H*-quinolin-4-ones:** The following reactions were carried out in sealed reaction vessels under microwave irradiation with a maximum power of 300 W by using air cooling.

**2-Phenyl-1*H*-quinolin-4-one (6a):** Aminonitrile **4a** was dissolved in diphenyl ether (2 mL) and heated for 15 min to 250 °C. The product was precipitated with *n*-hexane and separated by centrifugation and decantation. To remove the remaining diphenyl ether, the product was washed four times with *n*-hexane (1 mL), yielding the title compound as a colorless solid (25 mg, 0.11 mmol, 72%). M.p. 251–253 °C (ref.[24] 251–253 °C). $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 11.72 (s, 1 H, -NH), 8.10 (dd, $^3J$ = 8.1 Hz, $^4J$ = 1.1 Hz, 1 H, H5), 7.84 (dd, $^3J$ = 6.7 Hz, $^4J$ = 3.0 Hz, 2 H, H2′,6′), 7.77 (d, $^3J$ = 7.9 Hz, 1 H, H7), 7.67 (dd, $^3J$ = 8.4 Hz, $^3J$ = 6.9 Hz, $^4J$ = 1.6 Hz, 1 H, H6), 7.61–7.57 (m, 3 H, H3′,4′,5′), 7.36–7.32 (m, 1 H, H8), 6.35 (s, 1 H, H3) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO, HSQC, HMBC): $\delta$ = 166.3 (C4), 150.0 (C2), 140.9 (C8a), 134.2 (C1′), 131.7 (C6), 130.4 (C4′), 129.0 (5′, C3′), 127.3 (6′, C2′), 124.9 (C4a), 124.6 (C5), 123.2 (C8), 118.7 (C7), 107.3 (C3) ppm. MS (FAB): *m*/*z* (%) = 222.1 (100) [M]$^+$. HRMS (FAB): calcd. for [M]$^+$ 222.0919; found 222.0919. IR (ATR): $\tilde{\nu}$ = 1633, 1545, 1498, 1472, 1254, 753, 688 cm$^{-1}$. The analytical data correspond to those reported in the literature.[25,26]

**6-Methyl-2-phenyl-1*H*-quinolin-4-one (6b):** Aminonitrile **4b** (91 mg, 0.30 mmol) was dissolved in diphenyl ether (1.5 mL) and heated for 15 min to 250 °C. The product was precipitated with *n*-hexane (1 mL), centrifuged, and decanted. The crude product was washed four times with *n*-hexane (1 mL) to remove the diphenyl ether completely, yielding the title compound as a colorless solid (50 mg, 0.21 mmol, 71%). M.p. 289–293 °C (ref.[24] 282–293 °C). $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 11.6 (s, 1 H, -NH), 7.89 (m, 1 H, H5), 7.83 (dd, $^3J$ = 6.5 Hz, $^3J$ = 3.7 Hz, 2 H, H2′,6′), 7.67 (d, $^3J$ = 8.5 Hz, 1 H, H8), 7.60–7.57 (m, 3 H, H3′,4′,5′), 7.50 (dd, $^3J$ = 8.5 Hz, $^4J$ = 1.9 Hz, 1 H, H7), 6.31 (s, 1 H, H3), 2.97 (s, 3 H, -$CH_3$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 171.4 (C4), 154.7 (C2), 141.0 (C4a), 135.6 (C1′), 133.0 (C7), 132.5 (C8a), 130.2 (C4′), 128.9 (C3′,5′), 127.2 (C2′,6′), 123.9 (C5), 119.1 (C7), 107.3 (C3), 20.7 (-$CH_3$) ppm. MS (FAB): *m*/*z* (%) = 237.2 (20) [M + H]$^+$, 236.2 (100) [M]$^+$. HRMS (FAB): calcd. for [M]$^+$ 236.107539; found 236.107128. IR (ATR): $\tilde{\nu}$ = 3067, 2957, 1635, 1543, 1498, 823, 770, 691 cm$^{-1}$. The analytical data correspond to those reported in the literature.[25,27]

**6-Methoxy-2-phenyl-1*H*-quinolin-4-one (6c):** Cyclization of aminonitrile **4c** (50 mg, 0.15 mmol) in diphenyl ether (2 mL) was effected by heating the mixture at 250 °C for 10 min. Subsequently, the product was precipitated with *n*-hexane (1 mL), centrifuged, decanted, and washed four times with *n*-hexane (1 mL) to furnish quinolone **6c** as a slightly brownish solid (28 mg, 0.11 mmol, 73%). M.p. 309–311 °C (ref.[25] 302–304 °C). $^1$H NMR (400 MHz, [D$_6$]-DMSO): $\delta$ = 11.70 (s, 1 H, -NH), 7.85–7.79 (m, 2 H, H2′,6′), 7.73 (d, $^3J$ = 8.9 Hz, 1 H, H8), 7.58 (m, 3 H, H3′,4′,5′), 7.51 (d, $^4J$ = 2.5 Hz, 1 H, H5), 7.33 (dd, $^3J$ = 8.9 Hz, $^4J$ = 2.5 Hz, 1 H, H7), 6.32 (s, 1 H, H3), 3.85 (s, 3 H, -$OCH_3$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 176.6 (C4), 156.9 (C8a), 155.2 (C6), 134.6 (C1′), 133.4 (C4a), 130.3 (C2), 129.4 (C2′,6′), 127.3 (C3′,5′), 126.5 (C4′), 123.9 (C8), 122.2 (C7), 104.7 (C5), 100.6 (C3), 55.2 (-$OCH_3$) ppm. MS (ESI): *m*/*z* (%) = 252.1 (100) [M + H]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 252.1019; found 252.1022. IR (ATR): $\tilde{\nu}$ = 1631, 1594, 1579, 1497, 869, 838, 671 cm$^{-1}$. The analytical data correspond to those reported in the literature.[25]

**7-Methoxy-2-phenyl-1*H*-quinolin-4-one (6d):** A solution of **4d** (76 mg, 0.23 mmol) in diphenyl ether (1.5 mL) was heated to 250 °C for 20 min, yielding a light brown solid, which was triturated with *n*-hexane (1 mL), decanted, and centrifuged. The crude product was washed four times with *n*-hexane (1 mL), yielding the title compound as a colorless solid (22 mg, 0.088 mmol, 81%). M.p. 286 °C (ref.[25] 284–286 °C). $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 11.53 (s, 1 H, -NH), 7.99 (d, $^3J$ = 8.9 Hz, 1 H, H5), 7.83–7.81 (m, 2 H, H2′,6′), 7.60–7.57 (m, 3 H, H3′,4′,5′), 7.21 (d, $^4J$ = 2.4 Hz, 1 H, H8), 6.94 (dd, $^3J$ = 8.9 Hz, $^4J$ = 2.4 Hz, 1 H, H6), 6.27 (s, 1 H, H3), 3.87 (s, 3 H, -$OCH_3$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 176.8 (C4), 162.5 (C7), 149.9 (C2), 142.3 (C8a), 134.5 (C1′), 130.2 (C4′), 128.8 (3,5′), 127.4 (C2′,6′), 126.8 (C5), 119.8 (C4a), 113.4 (C6), 107.4 (C3), 100.4 (C8), 55.33 (-$OCH_3$) ppm. MS (ESI): *m*/*z* (%) = 252.1 (100) [M + H]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 252.1019; found 252.1022. IR (ATR): $\tilde{\nu}$ = 2965, 1610, 1577, 1537, 1460, 1250, 854, 838, 699 cm$^{-1}$. The analytical data correspond to those reported in the literature.[25,26]

**7-Chloro-2-phenyl-1*H*-quinolin-4-one (6e):** α-Aminonitrile **4e** (45 mg, 0.14 mmol) was dissolved in diphenyl ether (1.5 mL) and

heated for 20 min to 250 °C. Precipitation with *n*-hexane as described for the synthesis of **6a** gave the title compound as a colorless solid (30 mg, 0.12 mmol, 86%) consisting of the regioisomers **6e** and 5-chloro-1*H*-quinolin-4-one (**6k**) in a ratio of 5:1 determined by intensity of proton signals in the $^1$H NMR spectrum (A/B = 5:1). Due to their low solubility in common organic solvents, the isomers could not be separated by chromatography or crystallization. M.p. (isomeric mixture): 352–355 °C [ref.[25] m.p. (7-isomer) 361–362 °C). $^1$H NMR (400 MHz, [D$_6$]DMSO, HMBC, HSQC): $\delta$ = 11.73 (s, 1 H, -NH$^A$), 8.09 (d, $^3J$ = 8.6 Hz, 1 H, H5$^A$), 7.85 (m, 4 H, H2′$^A$,6′$^A$, overlap of signals with H2′$^B$,6′$^B$), 7.80 (d, $^4J$ = 1.9 Hz, 1 H, H8$^A$), 7.70 (dd, $^3J$ = 8.4 Hz, $^4J$ = 1.0 Hz, 1 H, H8$^B$), 7.61–757 (m, 7 H, H3′$^A$,4′$^A$,5′$^A$, overlap of signals with H3′$^B$,4′$^B$,5′$^B$,H7$^B$), 7.36 (dd, $^3J$ = 8.6 Hz, $^4J$ = 2.0 Hz, 1 H, H6$^A$), 7.27 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.0 Hz, 1 H, H6$^B$), 6.39 (s, 1 H, H3$^A$), 6.32 (s, 1 H, H3$^B$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 176.6 (C4$^A$), 151.0 (C2$^A$), 141.9 (C8a$^A$), 136.7 (C7$^A$), 134.5 (C1′$^A$), 131.9 (C7$^B$), 130.5 (4′$^A$), 128.9 (C3′$^A$,5′$^A$), 127.9 (C3′$^B$,5′$^B$), 127.8 (C2′$^A$,6′$^A$), 126.6 (C2′$^B$,6′$^B$), 127.3 (C5$^A$), 126.3 (C4a$^A$), 126.1 (C6$^B$), 123.6 (C6$^A$), 118.8 (C8$^B$), 118.4 (C8$^A$), 109.7 (C3$^B$), 108.1 (C3$^A$) ppm. The resonances of C1′$^B$, C4′$^B$, C4$^B$, C4a$^B$ and C8a$^B$ could not be detected due to the low solubility of **6e** in DMSO. MS (ESI): *m*/*z* (%) = 256.1 (100) [M + H]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 256.0524; found 256.0529. IR (ATR): $\tilde{\nu}$ = 1632, 1581, 1547, 1495, 1076, 819, 762, 687 cm$^{-1}$. The analytical data correspond to those reported in the literature.[25]

**2-(4-Methoxyphenyl)-1*H*-quinolin-4-one (6f):** Aminonitrile **4f** (37 mg, 0.11 mmol) was dissolved in diphenyl ether (1.5 mL) and heated for 15 min to 250 °C. The product was precipitated with *n*-hexane (1 mL) and separated by centrifugation and decantation from diphenyl ether. The remainder was washed four times with *n*-hexane (1 mL) to yield quinolone **6f** as a colorless solid (26 mg, 0.10 mmol, 91%). M.p. 294–295 °C (ref.[24] 294–296 °C). $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 11.59 (s, 1 H, -NH), 8.08 (d, $^3J$ = 8.0 Hz, 1 H, H5), 7.81 (AA′ part of the AA′BB′ spin system, 2 H, H3′,H5′) 7.76 (d, $^3J$ = 8.2 Hz, 1 H, H8), 7.65 (t, $^3J$ = 6.9 Hz, 1 H, H6), 7.31 (t, $^3J$ = 7.4 Hz, 1 H, H7), 7.13 (BB′ part of the AA′BB′ spin system, 2 H, H2′,H6′), 6.32 (s, 1 H, H3), 3.85 (s, 3 H, -OCH$_3$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 161.0 (C4′), 149.8 (C2), 140.9 (C8a), 131.4 (C6), 128.6 (C3′,5′), 126.5 (C1′), 124.9 (C4a), 124.6 (C5), 123.0 (C7), 119.2 (C8), 114.3 (C2′,6′), 106.4 (C3), 55.4 (-OCH$_3$) ppm. The resonance of C4 could not be detected. MS (ESI): *m*/*z* (%) = 252.1 (100) [M + H]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 251.0946; found 251.0949. IR (ATR): $\tilde{\nu}$ = 1631, 1550, 1248, 1030, 818, 676 cm$^{-1}$. The analytical data correspond to those reported in the literature.[28]

**2-(2-Chlorophenyl)-1*H*-quinolin-4-one (6g):** A solution of aminonitrile **4g** (51 mg, 0.16 mmol) in diphenyl ether (2 mL) was heated for 20 min to 250 °C. The addition of *n*-hexane (1 mL) yielded a brownish solid, which was centrifuged, decanted, and washed five times with *n*-hexane (1 mL). For further purification, the crude product was passed over a short pad of silica ($CH_2Cl_2$). Elution with methanol gave the title compound as a brownish oil (33 mg, 0.13 mmol, 81%). $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ = 8.25 (d, $^3J$ = 8.3 Hz, 1 H, H5), 7.72–7.68 (m, 1 H, H7), 7.63 (d, $^3J$ = 8.3 Hz, 1 H, H6), 7.62–7.40 (m, 5 H, H8, 3′, 4′, 5′, 6′), 6.30 (s, 1 H, H3) ppm. $^{13}$C NMR (100 MHz, CD$_3$OD): $\delta$ = 180.4 (C4), 151.5 (C2′), 141.7 (C8a), 133.9 (C7), 133.8 (C3′), 133.6 (C2), 132.8 (5′), 132.0 (4′), 131.3 (C1′), 128.6 (C6′), 126.1 (C5), 125.8 (C4a), 125.6 (C8), 119.5 (C6), 111.1 (C3) ppm. MS (ESI): *m*/*z* (%) = 256.1 (100) [M + H]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 256.0524; found 256.0527. IR (film): $\tilde{\nu}$ = 3062, 2796, 1634, 1569, 1544, 1411, 1355, 1139, 712, 671 cm$^{-1}$. The analytical data correspond to those reported in the literature.[26]

**3-Methyl-2-phenyl-1*H*-quinolin-4-one (6h):** Aminonitrile **4h** (22 mg, 0.073 mmol) was dissolved in diphenyl ether (1.5 mL) and treated as described for the synthesis of **6a**, yielding the title product as a colorless solid (15 mg, 0.063 mmol, 86%). M.p. 287–290 °C (ref.[29] 287–290 °C). $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ = 8.30 (dd, $^3J$ = 8.3 Hz, $^4J$ = 0.9 Hz, 1 H, H5), 7.66 (dd, $^3J$ = 8.3 Hz, $^3J$ = 6.8 Hz, $^4J$ = 1.5 Hz, 1 H, H6), 7.60 (m, 1 H, H8), 7.58–7.52 (m, 5 H, H2′,3′,4′,5′,6′), 7.39 (dd, $^3J$ = 8.3 Hz, $^3J$ = 6.8 Hz, $^4J$ = 1.2 Hz, 1 H, H7), 2.04 (s, 3 H, -CH$_3$) ppm. $^{13}$C NMR (100 MHz, CD$_3$OD): $\delta$ = 161.8 (C4), 153.4 (C2), 141.2 (C8a), 136.5 (C1′), 133.1 (C6), 130.9 (C4′), 130.1 (C2′,6′), 130.0 (C3′,5′), 126.3 (C5), 124.9 (C7), 124.6 (C4a), 119.4 (C8), 117.2 (C3), 12.7 (-CH$_3$) ppm. MS (ESI): *m*/*z* (%) = 250.1 (5) [M + Na]$^+$, 236.1 (100) [M + H]$^+$. HRMS (ESI): calcd. for [M]$^+$ 235.0997; found 235.1001. IR (ATR): $\tilde{\nu}$ = 1627, 1573, 1547, 1427, 1008, 760, 696 cm$^{-1}$. The analytical data correspond to those reported in the literature.[29]

**3-Ethyl-2-phenyl-1*H*-quinolin-4-one (6i):** Aminonitrile **4i** (78 mg, 0.24 mmol) was dissolved in diphenyl ether (2 mL), and the mixture was heated to 250 °C for 15 min. The product was precipitated with *n*-hexane (1 mL), centrifuged, decanted, and washed four times with *n*-hexane (1 mL) to remove the remaining diphenyl ether. The title compound was obtained as a light brown solid (46 mg, 0.19 mmol, 75%). M.p. 230–232 °C. $^1$H NMR (400 MHz, [D$_6$]DMSO): $\delta$ = 11.58 (s, 1 H, -NH), 8.17–8.15 (m, 1 H, H7), 7.66–7.61 (m, 5 H, H2′,3′,4′,5′,6′), 7.60–7.58 (m, 2 H, H5,6), 7.28 (dt, $^3J$ = 8.1 Hz, $^4J$ = 6.0 Hz, $^5J$ = 2.0 Hz, 1 H, H8), 2.32 (q, $^3J$ = 15.4 Hz, 2 H, -CH$_2$CH$_3$), 0.95 (t, $^3J$ = 7.36 Hz, 3 H, -CH$_2$CH$_3$) ppm. $^{13}$C NMR (100 MHz, [D$_6$]DMSO): $\delta$ = 176.5 (C4), 147.9 (C2), 139.6 (C8a), 135.1 (C1′), 129.2 (C4′), 129.1 (C6), 128.5 (C3′), 124.88 (C7), 122.5 (C8), 120.5 (C3), 118.3 (C5), 117.9 (C4a), 19.09 (-CH$_2$CH$_3$), 13.95 (-CH$_2$CH$_3$) ppm. MS (FAB): *m*/*z* (%) = 251.2 (20) [M + H]$^+$, 250.2 (100) [M]$^+$, 234.2 (7) [M – CH$_3$]$^+$. HRMS (FAB): calcd. for [M]$^+$ 249.1154; found 249.1154. IR (ATR): $\tilde{\nu}$ = 2957, 1625, 1542, 1492, 758, 697, 688 cm$^{-1}$. The analytical data correspond to those reported in the literature.[30]

**2,3-Diphenyl-1*H*-quinolin-4-one (6j):** Aminonitrile **4j** (16 mg, 0.043 mmol) was dissolved in diphenyl ether (1.5 mL) and heated to 250 °C. Workup was performed as described for the synthesis of **6a**, furnishing quinolone **6j** as a colorless solid (10 mg, 0.035 mmol, 81%). M.p. 342–345 °C (ref.[31] 342–345 °C). $^1$H NMR (400 MHz, CD$_3$OD, COSY): $\delta$ = 8.33 (d, $^3J$ = 8.2 Hz, 1 H, H5), 7.75–7.67 (m, 2 H, H6,7), 7.44 (dt, $^3J$ = 7.1 Hz, 1 H, H8), 7.37–7.08 (m, 5 H, H2′′,3′′,4′′,5′′,6′′), 7.22–7.13 (m, 5 H, H2′,3′,4′,5′,6′) ppm. $^{13}$C NMR (100 MHz, CD$_3$OD, HSQC, HMBC): $\delta$ = 176.9 (C4), 152.4 (C2), 150.6 (C3), 141.7 (C8a), 136.9 (C1′′), 134.2 (C4a), 133.5 (C1′), 133.0 (C7), 130.7 (C5′,3′), 130.3 (C4′′), 129.3 (C5′′,3′′), 127.8 (C2′′,6′′), 128.8 (C2′,6′), 127.7 (C4′), 126.7 (C5), 125.2 (C8), 119.3 (C6) ppm. MS (ESI): *m*/*z* (%) = 320.1 (2) [M + Na]$^+$, 298.1 (100) [M + H]$^+$. HRMS (ESI): calcd. for [M]$^+$ 297.1154; found 297.1155. IR (ATR): $\tilde{\nu}$ = 1621, 1577, 1508, 1485, 756, 698 cm$^{-1}$. The analytical data correspond to those reported in the literature.[31]

**Ethyl 2-Phenylquinoline-3-carboxylate (7):**[32] DMF (22 mg, 0.30 mmol, 23 μL) was cooled to 0 °C, then $POCl_3$ (46 mg, 0.30 mmol, 27 μL) was added. The yellow mixture was stirred for 30 min at room temperature. Subsequently, a solution of **5a** (67 mg, 0.25 mmol) in chloroform (800 μL) was added, and the mixture was stirred for 20 h at 80 °C. The reaction was quenched by addition saturated aqueous $NaHCO_3$ solution (1 mL) and extracted with ethyl acetate. The organic layer was washed with a saturated aque-

ous $NaHCO_3$ solution and concentrated in vacuo. Purification was carried out by flash chromatography (cyclohexane/ethyl acetate, 9:1), yielding the title compound as a slightly yellowish oil (56 mg, 20 mmol, 81%). $R_f$ = 0.16 (cyclohexane/ethyl acetate, 1:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.68 (s, 1 H, H4), 8.27–8.25 (m, 1 H, H5), 7.94 (d, $^3J$ = 8.1 Hz, 1 H, H8), 7.84 (t, $^3J$ = 7.7 Hz, 1 H, H7), 7.65–7.61 (m, 3 H, H6, H2′,6′), 7.49–7.45 (m, 3 H, H3′,4′,5′), 4.20 (q, $^3J$ = 7.1 Hz, 2 H, -$OCH_2CH_3$), 1.08 (t, $^3J$ = 7.1 Hz, 3 H, -$OCH_2CH_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 167.4 (CO), 157.5 (C2), 147.2 (C8a), 139.6 (C4), 132.1 (C7), 129.2 (C3), 129.0 (C6), 128.9 (C2′,6′), 128.9 (C5), 128.4 (C8), 128.4 (C3′,5′), 127.7 (C4′), 126.0 (C4a), 61.6 (-$OCH_2CH_3$), 13.7 (-$OCH_2CH_3$) ppm. MS (ESI): *m/z* (%) = 278.1 (100) $[M + H]^+$. HRMS (ESI): calcd. for $[M + H]^+$ 278.1176; found 278.1184. IR (film): $\tilde{\nu}$ = 3059, 2981, 1722, 1619, 1555, 1445, 1200, 1019, 803, 771 $cm^{-1}$. The analytical data correspond to those reported in the literature.[33]

**2-Phenyl-4-trifluoromethylsulfonyloxyquinoline (8):** Quinolone **6a** (70 mg, 0.32 mmol) and DMAP (23 mg, 0.19 mmol, 0.50 equiv.) were coevaporated with pyridine (0.2 mL) to remove trace amounts of water, and the residue was dissolved in pyridine (5 mL). The mixture was cooled to 0 °C, then trifluoromethanesulfonic acid anhydride (108 mg, 0.380 mmol, 64.2 µL, 1.2 equiv.) was added. The mixture was allowed to stir for 6 h at room temperature. Pyridine was removed in vacuo, and the remainder was purified by filtration through a short pad of silica (dichloromethane) to furnish the title compound as a yellowish oil (89 mg, 0.25 mmol, 79%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.25 (d, $^3J$ = 8.5 Hz, 1 H, H5), 8.15 (d, $^3J$ = 8.2 Hz, 2 H, H2′,6′), 8.07 (d, $^3J$ = 8.3 Hz, 1 H, H8), 7.86–7.83 (m, 2 H, H3, H7), 7.68 (t, $^3J$ = 7.6 Hz, 1 H, H6), 7.58–7.50 (m, 3 H, H3′,4′,5′) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 158.4 (C4), 153.7 (C2), 150.5 (8a), 138.4 (C1), 131.4 (C5), 130.5 (C7), 130.2 (C4′), 129.3 (C3′,5′), 128.6 (C6), 127.7 (C2′,6′), 120.7 (C8), 120.3 (C4a), 118.7 (q, $^1J_{C,F}$ = 320 Hz, $CF_3$), 109.9 (C3) ppm. MS (ESI): *m/z* (%) = 354.0 (100) $[M + H]^+$. HRMS (ESI): calcd. for $[M]^+$ 353.0333; found 353.0337. IR (film): $\tilde{\nu}$ = 2957, 1644, 1606, 1428, 1293, 1221, 1140, 1029 $cm^{-1}$.

**2,4-Diphenylquinoline (9):**[34] Triflate **8** (88 mg, 0.25 mmol), phenylboronic acid (46 mg, 0.38 mmol, 1.5 equiv.), and triethylamine (50 mg, 0.50 mmol, 67 µL, 2 equiv.) were dissolved in DMF (5 mL), then argon was bubbled into the solution. Tetrakis(triphenylphosphane)palladium(0) (9 mg, 3 mol-%) was added, and the reaction mixture was heated at reflux for 4 h. For workup, brine (5 mL) was added, and the mixture was extracted with dichloromethane (5 mL). The organic layer was separated and washed with brine. Dichloromethane was removed in vacuo, and the crude product was purified by flash chromatography (dichloromethane), yielding the title compound as a colorless oil (50 mg, 0.18 mmol, 72%). $R_f$ = 0.67 (dichloromethane). $^1$H NMR (400 MHz, $CDCl_3$, COSY): $\delta$ = 8.28 (d, $^3J$ = 8.4 Hz, 1 H, H8), 8.21–8.18 (m, 2 H, H2′,6′), 7.92–7.89 (m, 1 H, H5), 7.82 (s, 1 H, H3), 7.73 (dd, $^3J$ = 8.4 Hz, $^3J$ = 7.0 Hz, $^4J$ = 1.3 Hz, 1 H, H7), 7.57–7.44 (m, 9 H, H6,3′,4′,5′,2″, 3″,4″,5″,6″) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$, HSQC, HMBC): $\delta$ = 156.9 (C2), 149.2 (C4), 148.8 (C8), 139.5 (C1′), 138.4 (C1″), 136.5 (C8a), 130.0 (C7), 129.6 (C2″,6″), 129.5 (C4′), 129.4 (C6), 128.9 (C3′,5′), 128.6 (C3″,5″), 128.4 (C4″), 127.6 (C2′,6′), 126.7 (C5), 125.8 (C5b), 125.7 (C4a), 119.4 (C3) ppm. MS (ESI): *m/z* (%) = 282.1 (100) $[M + H]^+$. HRMS (ESI): calcd. for $[M]^+$ 281.1204; found 281.1206. IR (film): $\tilde{\nu}$ = 3059, 2923, 1633, 1574, 1508, 1406, 731, 669 $cm^{-1}$. The analytical data correspond to those reported in the literature.[35]

**Supporting Information** (see footnote on the first page of this article): Copies of the NMR spectra of all compounds.

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