Supporting Information

Synthesis of 4-Quinolones via Cyclocondensation of Substituted ortho-Amidoacetophenones: A Refit of the Camps Cyclization by Applying Trimethylsilyl Trifluoromethanesulfonate/Triethylamine

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1. Preparation of ortho-amidoacetophenones

Typical procedure for the preparation of ortho-amidoacetophenones by reaction of aminoacetophenone derivatives with acyl chlorides (method A): To a solution of benzoyl chloride (312 mg, 2.22 mmol) in anhydrous CH₂Cl₂ (11 mL) was added pyridine (0.23 mL, 2.8 mmol) followed by 2'-aminoacetophenone (300 mg, 2.22 mmol). The resulting mixture was stirred at r.t. for 16 h. After complete consumption of the starting materials (as indicated by TLC) sat. aq. NH₄Cl solution was added and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (3 x 30 mL) and the combined organic layers were dried with Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude material was purified by flash column chromatography (silica gel, hexane:EtOAc = 95:5 to 80:20, linear gradient) to afford 525 mg (99%) of N-(2-acetylphenyl)benzamide (3a) as colorless crystals; mp 93-94 °C.

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\end{array}
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\[\delta = 2.72 \text{ (s, 3 H, Me)}, 7.16 \text{ (m, 1 H, Ar)}, 7.46-7.67 \text{ (m, 4 H, Ar)}, 7.96, 8.08, 8.99 \text{ (3 m, 1 H, 2 H, 1 H, Ar)}, 12.71 \text{ (br s, 1 H, NH) ppm.}
\]

The analytical data is in agreement with those reported in the literature.[12c]

Typical procedure for the preparation of ortho-amidoacetophenones by reaction of aminoacetophenone derivatives with carboxylic acids (method B): To a solution of picolinic acid (246 mg, 2.00 mmol) in CH₂Cl₂ (7 mL) were added 2'-aminoacetophenone (270 mg, 2.00 mmol), NEt₃ (0.55 mL, 4.0 mmol) and PyBrop (932 mg, 2.0 mmol). The resulting mixture was stirred at r.t. for 24 h. Then sat. aq. NH₄Cl solution was added and the phases were separated. The aqueous layer was extracted with CH₂Cl₂ (3 x 15 mL) and the combined organic layers were dried with Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude material was purified by flash column chromatography (silica gel, hexane:EtOAc = 95:5 to 80:20, linear gradient) to afford 434 mg (90%) of N-(2-acetylphenyl)picolinamide (3b) as yellow solid; mp 111-112 °C.
**N-(2-Acetylphenyl)thiophene-2-carboxamide (3c):** Following the typical procedure (method b) reaction of thiophene 2-carboxylic acid (500 mg, 3.90 mmol), 2'-aminoacetophenone (527 mg, 3.90 mmol), PyBrop (1.82 g, 3.90 mmol) and NEt₃ (0.83 mL, 6.0 mmol) in CH₂Cl₂ (13 ml) provided 500 mg (68%) of 3c as yellow oil after flash column chromatography (silica gel, hexane:EtOAc = 9:1); mp 127-130 °C.

\[
\begin{align*}
\text{1H NMR (250 MHz, CDCl}_3\text{): } & \delta = 2.72 (s, 3 \text{ H, Me}), 7.11-7.20, 7.55-7.65 (2 \text{ m, 2 H each, Ar}), 7.84, 7.95, 8.88 (3 \text{ m c, 1 H each, Ar}), 12.73 (\text{br s, 1 H, NH}) \text{ ppm. The analytical data is in agreement with those reported in the literature.}\text{[12c]} 
\end{align*}
\]

**N-(2-Acetylphenyl)hexanamide (3d):** Following the typical procedure (method a) reaction of hexanoyl chloride (2.39 g, 17.8 mmol), 2'-aminoacetophenone (2.00 g, 14.8 mmol) and pyridine (1.50 mL, 18.5 mmol) in CH₂Cl₂ (36 mL) provided 3.42 g (99%) of 7 as yellow oil after flash column chromatography (silica gel, hexane:EtOAc = 100:0 to 90:10 linear gradient).

\[
\begin{align*}
\text{1H NMR (250 MHz, CDCl}_3\text{): } & \delta = 0.87-0.95 (\text{m, 3 H, 6-H}), 1.30-1.42 (\text{m, 4 H, 5-H, 4-H}), 1.68-1.83 (\text{m, 2 H, 3-H}), 2.44 (t, J = 7.4 \text{ Hz, 2 H, 2-H}), 2.67 (s, 3 \text{ H, Me}), 7.10, 7.55, 7.78, 7.90 (4 \text{ m c, 1 H each, Ar}) \text{ ppm. The signal for the NH proton was not detected. The analytical data is in agreement with those reported in the literature.}\text{[12c]} 
\end{align*}
\]
Typical procedure for the preparation of ortho-amidoacetophenones by reaction of 2'-aminoacetophenone derivatives with in-situ generated acyl chlorides (method A): To a solution of isovaleric acid (300 mg, 2.94 mmol) in CH₂Cl₂ (15 mL) was added (COCl)₂ (410 mg, 3.23 mmol) followed by a few drops of DMF. The resulting mixture was stirred at r.t. for 3 h before 2'-aminoacetophenone (397 mg, 2.94 mmol) and NEt₃ (0.45 mL, 3.2 mmol) were added at 0 °C. The resulting mixture was stirred for 16 h in which period it was allowed to warm to r.t. The reaction was quenched by the addition of water (20 mL) and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (3 x 20 mL) and the combined organic layers were dried with Na₂SO₄, filtered and evaporated. The crude product was purified by flash column chromatography (silica gel, hexane:EtOAc = 4:1) to provide 640 mg (99%) of N-(2-acetylphenyl)-3-methylbutanamide (3e) as colorless oil.

IR (ATR): $\nu = 3260$ (NH), 3110-2880 (=C-H, C-H), 1690, 1650 (C=O), 1605-1445 (C=C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.92$ (d, $J = 6.4$ Hz, 6 H, i-Pr), 2.11-2.21 (m, 3 H, i-Pr, 2-H), 2.54 (s, 3 H, COCH₃), 6.96-7.00, 7.40-7.44 (2 m, 1 H each, Ar), 7.77, 8.68 (2 m, 1 H each, Ar) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 22.2, 25.9$ (q, d, i-Pr), 28.3 (C-2), 47.7 (q, 3 H, COCH₃), 120.3, 121.3, 121.9, 134.8 (4 d, Ar), 131.4, 140.8 (2 s, Ar), 171.8, 202.5 (2 s, C-1, COCH₃) ppm. HRMS: $m/z$ [M+Na]⁺ calcd for C₁₃H₁₇NNaO₂: 242.1152; found: 242.1164.

(R)-N-(2-Acetylphenyl)-2-phenylbutanamide (3f): Following the typical procedure (method a) (R)-2-phenylbutyric acid (158 mg, 0.96 mmol) was converted into the respective acyl chloride with (COCl)₂ (135 mg, 1.06 mmol) and catalytical amounts of DMF in CH₂Cl₂ (20 mL). The crude acyl chloride was reacted with 2'-aminoacetophenone (104 mg, 0.77 mmol) in the presence of NEt₃ (0.12 mL, 0.9 mmol) to provide 231 mg of 3f (86%) as slight yellow oil after flash column chromatography (silica gel, hexane:EtOAc = 95:5).

$\alpha_d^{22} = +78.5$ ($c = 1.0$, CHCl₃). IR (ATR): $\nu = 3245$ (NH), 3090-2875 (=C-H, C-H), 1695-1575 (C=O, C=C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.95$ (t, $J = 7.5$ Hz, 3 H, 4-H), 1.91,
2.26 (2 m, 1 H each, 3-H), 2.59 (s, 3 H, COCH₃), 3.46 (t, J = 7.6 Hz, 1 H, 2-H), 7.04 (m, 1 H, 2-H), 7.20-7.52 (m, 6 H, Ar), 7.81, 8.76 (2 m, 1 H each, Ar), 11.84 (br s, 1 H, NH) ppm. 

¹³C NMR (101 MHz, CDCl₃): δ = 12.2 (q, C-4), 26.1 (t, C-3), 28.4 (q, COCH₃), 57.2 (d, C-2), 120.6 (s, Ar), 121.6, 122.2, 127.2, 127.9, 128.7, 131.5, 135.0 (7 d, Ar), 139.6, 141.1 (2 s, Ar), 173.0, 202.7 (2 s, CONHR, COCH₃) ppm. HRMS: m/z [M+Na]+ calcd for C₁₇H₁₇NNaO₂: 304.1308; found: 304.1311.

N-(2-Acetyl-5-fluorophenyl)hexanamide (3g) (method C): To a suspension of CuI (13 mg, 0.07 mmol), N,N'-dimethylethane diamine (25 mg, 0.28 mmol), K₂CO₃ (386 mg, 2.76 mmol) and molecular sieves (5 Å) in toluene (3 mL) was added 1-(2-bromo-4-fluorophenyl)ethanone (300 mg, 1.38 mmol) and hexaneamide (191 mg, 1.66 mmol). The resulting mixture was heated to 110 °C under an atmosphere of argon for 16 h. Since the reaction was not complete after 22 h additional hexaneamide (70 mg, 0.61 mmol) and CuI (23 mg, 0.12 mmol) were added and the mixture was stirred at 110 °C for additional 16 h. After cooling to r.t. the reaction mixture was diluted with EtOAc (20 mL) and water was added (15 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried with Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude material was purified by flash column chromatography (silica gel, hexane:EtOAc 9:1) to provide 116 mg (33%) of 3g as a colorless oil.

IR (ATR): v = 3190 (NH), 2960-2860 (=C-H), 1690-1645 (C=O), 1600-1520 (C=C) cm⁻¹. 

¹H NMR (400 MHz, CDCl₃): δ = 0.90 (t, J = 7.1 Hz, 3 H, 6-H), 1.31-1.39 (m, 4 H, 5-H/4-H), 1.69-1.79 (m, 2 H, 3-H), 2.43 (t, J = 7.7 Hz, 2 H, 2-H), 2.63 (s, 3 H, COCH₃), 6.77, 7.90, 8.60 (3 m, 1 H each, Ar), 11.93 (br s, 1 H, NH) ppm. 

¹³C NMR (101 MHz, CDCl₃): δ = 13.9 (q, C-6), 22.3, 25.0, 31.3, 38.7 (4 t, C-5/C-4/C-3/C-2), 28.6 (q, COCH₃), 107.6 (d, J_CF = 28.8 Hz, C-4' or C-6'), 109.4 (d, J_CF = 23.0 Hz, C-4' or C-6'), 118.1 (s, C-2'), 134.0 (d, J_CF = 10.5 Hz, C-1'), 143.7 (d, J_CF = 13.4 Hz, C-3'), 166.3 (d, J_CF = 254.0 Hz, C-5'), 173.0, 201.4 (2 s, CONHR, COCH₃) ppm. 

¹⁹F NMR (376 MHz, CDCl₃): δ = -99.45 (m, 5'-F) ppm. HRMS: m/z [M+Na]+ calcd for C₁₄H₁₈FNaNO₂: 274.1214; found: 274.1225.
Methyl 3-acetyl-4-hexanamidobenzoate (3h): Following the typical procedure (method a) reaction of hexanoyl chloride (69 mg, 0.51 mmol), methyl 3-acetyl-4-aminobenzoate (90 mg, 0.47 mmol) and NEt3 (0.07 mL, 0.5 mmol) in CH2Cl2 (5 mL) to provided 100 mg (79%) of 3h as colorless oil after flash column chromatography (silica gel, hexane:EtOAc = 4:1).

IR (ATR): ν = 3225 (NH), 3000-2855 (=C-H, C-H), 1715, 1650 (C=O), 1530-1450 (C=C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 0.87 (t, J = 7.0 Hz, 3 H, 6-H), 1.24-1.38 (m, 4 H, 5-H/4-H), 1.64-1.79 (m, 2 H, 3-H), 2.42 (t, J = 7.5 Hz, 2 H, 2-H), 2.69 (s, 3 H, COCH₃), 3.89 (s, CO₂CH₃), 8.12 (dd, J = 2.0, 8.9 Hz, 1 H, Ar), 8.54 (d, J = 2.0 Hz, 1 H, Ar), 8.81 (d, J = 8.9 Hz, 1 H, Ar), 11.89 (br s, 1 H, NH) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 13.8 (q, C-6), 22.3, 24.9, 31.2, 38.6 (4 t, C-5/C-4/C-3/C-2), 28.6 (q, COCH₃), 52.2 (q, CO₂CH₃), 120.1, 120.8, (2 s Ar), 123.4, 133.4, 135.8 (3 d, Ar), 144.7 (s, Ar), 165.7 (s, CO₂CH₃), 172.9 (s, CONHR), 202.5 (s, COCH₃) ppm. HRMS: m/z [M+Na]⁺ calcd for C₁₆H₂₁NNaO₄: 314.1363; found: 314.1376.

N-(4-Methoxy-2-propionylphenyl)benzamide (3i) (method C): To a suspension of CuI (31 mg, 0.17 mmol), N,N'-dimethylethane-1,2-diamine (58 mg, 0.66 mmol), K₂CO₃ (921 mg, 6.58 mmol) and molecular sieves (5 Å) in toluene (7 mL) was added 1-(2-bromo-5-methoxyphenyl)propan-1-one (800 mg, 3.29 mmol) and phenylbenzamide (479 mg, 3.95 mmol). The resulting mixture was heated to 110 °C under an atmosphere of argon for 16 h. After cooling to r.t. the reaction mixture was diluted with EtOAc (20 mL) and water was added (15 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried with Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude material was purified by flash column chromatography (silica gel, hexane:EtOAc = 4:1) to provide 537 mg (58%) of 3i as a colorless oil.
IR (ATR): ν = 3225 (NH), 3110-2840 (=C-H, C-H), 1660-1530 (C=O, C=C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 1.25 (t, J = 7.2 Hz, 3 H, CH₂CH₃), 3.09 (q, J = 7.2 Hz, 2 H, CH₂CH₃), 3.86 (s, 3 H, OCH₃), 7.18 (dd, J = 3.0, 9.2 Hz, 1 H, Ar), 7.47 (d, J = 3.0 Hz, 1 H, Ar), 7.49-7.61 (m, 3 H, Ph), 8.01-8.07 (m, 2 H, Ph), 8.91 (d, J = 9.2 Hz, 1 H, Ar), 12.39 (br s, 1 H, NH) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 8.54, 33.3 (q, t, CH₂CH₃), 55.7 (q, OCH₃), 116.0 (s, Ar), 119.9, 122.5, 123.0, 127.4, 128.8, 131.7 (6 d, Ar, Ph), 134.7, 135.0 (2 s, Ph, Ar), 154.4 (s, Ar), 165.7, 205.4 (2 s, CONHR, COCH₂) ppm. HRMS: m/z [M+Na]⁺ calcd for C₁₆H₁₅NNaO₃: 306.1101; found: 306.1108. Anal. calcd for C₁₆H₁₅NO₃ (283.2): C, 72.07; H, 6.05; N, 4.94. Found: C, 72.00; H, 6.13; N, 5.06.

(R)-N-(2-Acetylphenyl)-2-(tert-butyldimethylsiloxy)-2-phenylacetamide (3j): To a solution of (R)-mandelic acid (500 mg, 3.29 mmol) in THF (30 mL) was added TBSCl (1.04 g, 6.90 mmol) followed by imidazole (538 mg, 7.90 mmol). The resulting mixture was stirred at r.t. for 16 h. The white precipitate formed in the reaction was filtered off and the obtained solution was evaporated under reduced pressure. The residual material was dissolved in Et₂O (50 mL) and water (50 mL) was added. The organic layer was separated and the aqueous layer was extracted with Et₂O (3 x 30 mL). The combined organic layers were washed with brine, dried with Na₂SO₄, filtered and the solvent was removed under reduced pressure to provide the silyl ester/ether as colorless oil and was used in the next step without further purification. The silyl ester/ether was dissolved in CH₂Cl₂ (16 mL) and (COCl)₂ (459 mg, 3.62 mmol) followed by a few drops of DMF were added. The resulting mixture was stirred at r.t. for 4 h before 2'-aminoacetophenone (445 mg, 3.29 mmol) and NEt₃ (0.46 mL, 3.3 mmol) were added at 0 °C. The resulting solution was stirred for 16 h in which period it was allowed to slowly reach r.t. The reaction was quenched by addition of water (20 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 30 mL). The combined organic layers were dried with Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane:EtOAc = 9:1) to provide 1.04 g (82%) of 3j as colorless oil.
S-8

$[\alpha]_D^{22} = -120.6 \ (c \ 1.0, \ CHCl_3)$ IR (ATR): $\nu = 3225 \ (NH), \ 3070-2850 \ (=C-H, \ C-H), \ 1695$-$1580 \ (C=O, \ C=C) \ cm^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.09, \ 0.14, \ 0.97 \ (3 \ s, \ 3 \ H, \ 3 \ H, \ 9 \ H, \ OTBS), \ 2.65 \ (s, \ 3 \ H, \ COCH_3), \ 5.22 \ (s, \ 1 \ H, \ CHPh), \ 7.03-7.16 \ (m, \ 1 \ H, \ Ar), \ 7.21-7.38 \ (m, \ 3 \ H, \ Ar), \ 7.44-7.52 \ (m, \ 1 \ H, \ Ar), \ 7.54-7.65 \ (m, \ 2 \ H, \ Ar), \ 7.87, \ 8.74 \ (2 \ m, \ 1 \ H \ each, \ Ar), \ 12.44 \ (br \ s, \ 1 \ H, \ NH) \ ppm. ^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = -5.0, \ -4.9, \ 18.4, \ 25.8 \ (2 \ q, \ s, \ q, \ OTBS), \ 28.6 \ (q, \ COCH_3), \ 76.9 \ (d, \ CHPh), \ 120.9 \ (s, \ Ar), \ 122.6, \ 122.9, \ 126.2, \ 128.0, \ 128.3, \ 131.4, \ 134.6 \ (7 \ d, \ Ar), \ 140.0, \ 140.1 \ (2 \ s, \ Ar), \ 172.2, \ 201.4 \ (2 \ s, \ CONHR, \ COCH_3) \ ppm. HRMS: $m/z \ [M+Na]^+ \ calcd \ for \ C_{22}H_{29}NNaO_3Si: \ 406.1809; \ found: \ 406.1816.$

**N-(2-Acetylphenyl)-6-oxoheptanamide**$^{[ii]}$ (3k): Following the typical procedure (method a) 6-oxoheptanoic acid (300 mg, 2.10 mmol) was converted into the respective acyl chloride with (COCl)$_2$ (289 mg, 2.28 mmol) and catalytical amounts of DMF in CH$_2$Cl$_2$ (7 mL). The crude acyl chloride was reacted with 2'-aminoacetophenone (227 mg, 1.68 mmol) in the presence of NEt$_3$ (0.26 mL, 1.9 mmol) to provide 206 mg of 3k (47%) as slight yellow oil after flash column chromatography (silica gel, hexane:EtOAc = 80:20).

![Image](image1.png)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.44-189 \ (m, \ 4 \ H, \ 3-H/4-H), \ 2.46 \ (t, \ J = 7.5 \ Hz, \ 2 \ H, \ 2-H), \ 2.50 \ (t, \ J = 7.4 \ Hz, \ 2 \ H, \ 5-H), \ 2.15, \ 2.67 \ (2 \ s, \ 3 \ H \ each, \ COCH_3), \ 7.06-7.18, \ 7.49-7.64, \ 7.89-7.91, \ 8.68-8.86 \ (4 \ m, \ 1 \ H \ each, \ Ar), \ 11.74 \ (br \ s, \ 1 \ H, \ NH) \ ppm.

**(E)-N-(2-Acetylphenyl)but-2-enamide** (3l): Following the typical procedure (method b) the reaction of vinyl carboxylic acid* (336 mg, 3.90 mmol), 2'-aminoacetophenone (405 mg, 3.00 mol), PyBrop (1.82 g, 3.90 mmol) and NEt$_3$ (0.83 mL, 6.0 mmol) in CH$_2$Cl$_2$ (10 mL) provided 603 mg (99%) of 3l as colorless crystals after flash column chromatography (silica gel, hexane:EtOAc = 8:2); mp 80-83 °C.

![Image](image2.png)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.91 \ (dd, \ J = 1.7, \ 6.9 \ Hz, \ 3 \ H, \ 4-H), \ 2.65 \ (s, \ 3 \ H, \ COCH_3), \ 6.02 \ (qd, \ J = 1.7, \ 15.2 \ Hz, \ 1 \ H, \ 2-H), \ 6.96 \ (qd, \ J = 6.9 \ Hz, \ 15.2 \ Hz, \ 1 \ H, \ 3-H), \ 7.06-7.12,
7.51-7.56, 7.86-7.89 (3 m, 1 H each, Ar), 8.81 (m, 1 H, Ar), 11.80 (br s, 1 H, NH) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta =$ 17.9, 28.5 (2 q, C-4, CO$_2$H), 120.8, 121.8 (d, s, Ar), 122.4, 141.2 (2 d, C-2/C-3), 126.8, 131.6, 135.1 (3 d, Ar), 141.3 (s, Ar), 164.9, 202.8 (C-1, COCH$_3$) ppm. HRMS: $m/z$ [M+Na]$^+$ calcd for C$_{12}$H$_{13}$NNaO$_2$: 226.0844; found: 226.0820. *during the reaction isomerization of the double bond to the more stable trisubstituted olefin was observed. 3I was isolated as a 2:3 mixture of internal:terminal olefin. Spectroscopic data is provided only for the major isomer.
2. Cyclization to 4-quinolones

2-(Pyridin-2-yl)quinolin-4(1H)-one (4b): Following the typical procedure a solution of 3b (200 mg, 0.83 mmol), TMOSTf (1.11 g, 5.00 mmol) and NEt₃ (0.35 mL, 2.5 mmol) in 1,2-DCE (9 mL) was heated to 95 °C for 24 h to provide 157 mg (85%) of 4b as a colorless solid after flash column chromatography (silica gel, 2% MeOH in CH₂Cl₂); mp 229-231 °C.

\[ \text{1H NMR (400 MHz, CDCl}_3+\text{CD}_3\text{OD): } \delta = 6.98 (s, 1 H, 3-H), 7.38-7.42 (m, 1 H, Ar), 7.47 (ddd, } J = 1.0, 4.8, 7.5 \text{ Hz, 1 H, Ar}), 7.59-7.78 (m, 2 H, Ar), 7.92 (dt, } J = 1.7, 7.8 \text{ Hz, 1 H, Ar}, 8.05, 8.31 (2 m, 1 H each, Ar), 8.72-8.75 (m, 1 H, Ar) \text{ ppm. 13C NMR (101 MHz, CDCl}_3+\text{CD}_3\text{OD): } \delta = 105.6 (d, C-3), 118.2, 121.0, 124.1, 125.3, 132.6, 137.6, 139.2 (7 d, Ar), 143.4, 148.3 (2 s, Ar), 148.9 (d, Ar), 151.6 (s, Ar), 184.7 (s, C-4) \text{ ppm. HRMS: } m/z [M+H]^+ \text{ calcld for C}_{14}H_{11}N_2O: 223.0871; \text{ found: 223.0869. The analytical data is in agreement with those reported in the literature.}^{[12c]} \]

2-(Thiophene-2-yl)quinolin-4(1H)-one (4c): Following the typical procedure a solution of 3c (200 mg, 0.82 mmol), TMSOTf (1.09 g, 4.89 mmol) and NEt₃ (0.35 mL, 2.45 mmol) in 1,2-DCE (9 mL) was heated to 95 °C for 24 h to provide 72 mg (39%) of 4c as yellowish solid after flash column chromatography (silica gel, 3% MeOH in CH₂Cl₂); mp > 230 °C.

\[ \text{1H NMR (400 MHz, CDCl}_3+\text{CD}_3\text{OD): } \delta = 4.51 (s, 1 H, NH), 6.65 (s, 1 H, 3-H), 7.22, 7.39 (2 m, 1 H each, Ar), 7.34-7.55 (m, 4 H, Ar), 8.02 (m, 1 H, Ar) \text{ ppm. 13C NMR (176 MHz, CDCl}_3+\text{CD}_3\text{OD): } \delta = 106.4 (d, C-3), 118.4, 124.0, 124.6, 124.8, 127.7, 128.3, 129.2, 132.2 (7 d, s, Ar), 136.3, 140.7, 145.6 (3 s, Ar), 179.0 (s, C-4) \text{ ppm. HRMS: } m/z [M+H]^+ \text{ calcld for C}_{13}H_{9}NOS: found; 228.0465. The analytical data is in agreement with those reported in the literature.}^{[12c]} \]
2-Pentylquinolin-4(1H)-one (4d): Following the typical procedure, a solution of 3d (200 mg, 0.86 mmol), TMSOTf (571 mg, 2.57 mmol) and NEt$_3$ (0.36 mL, 2.6 mmol) in 1,2-DCE (9 mL) was heated to 95 °C. After 24 h additional TMSOTf (571 mg, 2.57 mmol) was added and the reaction was heated to 95 °C for 48 h to provide 169 mg (92%) of 4d as a yellow solid after flash column chromatography (silica gel, 5% MeOH in CH$_2$Cl$_2$); mp 138-141 °C.

IR (ATR): $\nu = 3075$ (NH), 2950-2870 (=C-H, C-H), 1620-1590 (C=O, C=C) cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 0.77$ (t, $J = 7.0$ Hz, 3 H, 5'-H), 1.12-129 (m, 4 H, 4'-H/3'-H), 1.62-1.78 (m, 2 H, 2'-H), 2.71 (t, $J = 7.6$ Hz, 2 H, 1'-H), 6.26 (s, 1 H, 3-H), 7.33, 7.59 (2 t, $J = 7.5$ Hz, 1 H each, Ar), 7.86, 8.37 (2 d, $J = 8.3$ Hz, 1 H each, Ar) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 13.8, 22.3, 28.8, 31.3, 34.3$ (q, 4 t, C-5'/ C-4'/ C-3'/ C-2'/ C-1'), 108.0 (d, C-3), 118.8, 132.5, 124.9, 125.0, 131.7 (4 d, s, Ar), 140.7, 149.5, 155.7 (2 s, Ar), 178.9 (s, C-4) ppm. HRMS: $m/z$ [M+H]$^+$ calcd for C$_{14}$H$_{17}$NO: 216.1388; found: 216.1381. Anal. calcd for C$_{14}$H$_{17}$NO (215.3): C, 78.10; H, 7.96; N, 6.51. Found: C, 77.81; H, 8.36; N, 6.38. The analytical data is in agreement with those reported in the literature.$^{[12c]}$

2-Isobutylquinolin-4(1H)-one (4e): Following the typical procedure, a solution of 3e (174 mg, 0.79 mmol), TMSOTf (1.07 g, 4.74 mmol) and NEt$_3$ (0.33 mL, 2.4 mmol) in 1,2-DCE (16 mL) was heated to 95 °C for 3 d to provide 50 mg (31% - 60 mg of starting material were re-isolated; 48% brsm) of 4e as a yellowish solid after flash column chromatography (silica gel, 5% MeOH in CH$_2$Cl$_2$); mp 158-160 °C.

IR (ATR): $\nu = 3270$ (NH), 3165-2800 (=C-H, C-H), 1630-1550 (C=O, C=C) cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$+ CD$_3$OD): $\delta = 0.90$ (d, $J = 6.6$ Hz, 6 H, i-Pr), 2.07-2.19 (m, 1 H, i-Pr), 2.58 (d, $J = 7.4$ Hz, 2 H, 1'-H), 6.25 (s, 1 H, 3-H), 7.34, 7.34, 7.87, 8.37 (4 m, 1 H each, Ar) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$+ CD$_3$OD): $\delta = 22.2, 28.7$ (q, d, i-Pr), 43.3 (t, C-1'), 108.7 (d, C-3), 118.8, 123.6, 124.8, 125.0, 131.7 (4 d, s, Ar), 140.7, 154.7 (2 s, Ar), 178.6 (s, C-4) ppm. HRMS: $m/z$ [M+Na]$^+$ calcd for C$_{13}$H$_{15}$NNaO: 224.1046; found: 224.1056.
**7-Fluoro-2-pentylquinolin-4(1H)-one (4g):** Following the typical procedure a solution of 3g (84 mg, 0.33 mmol), TMSOTf (447 mg, 2.01 mmol) and NEt₃ (0.14 mL, 1.0 mmol) in 1,2-DCE (5 mL) was heated to 90 ºC for 3 d to provide 49 mg (63% - 27 mg starting material were re-isolated: 93% brsm) of 4g as a slight yellow solid after flash column chromatography (silica gel, 3% MeOH in CH₂Cl₂); mp 165-166 ºC.

![](image1)

IR (ATR): ν = 3270 (NH), 3155-2705 (=C-H), 1645-1550 (C=O, C=C) cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ = 0.80 (t, J = 7.0 Hz, 3 H, 5'-H), 1.14-1.39 (m, 4 H, 4'-H/3'-H), 1.69-1.75 (m, 2 H, 2'-H), 2.69 (t, J = 7.6 Hz, 2 H, 1'-H), 6.21 (s, 1 H, 3-H), 7.07, 7.50, 8.35 (3 m c, 1 H each, Ar), 12.84 (br s, 1 H, NH) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 13.8, 22.3, 28.7, 31.3, 34.3 (q, 4 t, C-5'/C-4'/C-3'/C-2'/C-1'), 104.0 (d, ²J_CF = 25.3 Hz, Ar), 108.0 (d, C-3), 112.8 (d, ²J_CF = 23.3, Ar), 121.7 (s, Ar), 128.0 (d, ³J_CF = 11.1 Hz, Ar), 142.1 (d, ³J_CF = 13.1 Hz, Ar), 156.3 (s, Ar), 164.8 (d, ¹J_CF = 252.5 Hz, Ar), 178.3 (s, C-4) ppm. HRMS: m/z [M+Na]+ calcd for C₁₄H₁₆FNO: 256.1108; found: 256.1101.

**Methyl 4-oxo-2-pentyl-1,4-dihydroquinoline-6-carboxylate (4h):** Following the typical procedure, a solution of 3h (100 mg, 0.37 mmol), TMSOTf (488 mg, 2.20 mmol) and NEt₃ (0.16 mL, 1.1 mmol) in 1,2-DCE (7 mL) was heated to 95 ºC for 3 d to provide 51 mg (51%) of 4h as a yellow solid after flash column chromatography (silica gel, 3% MeOH in CH₂Cl₂); mp 206-207 ºC.

![](image2)

IR (ATR): ν = 3260 (NH), 3140-2855 (=C-H), 1720-1495 (C=O, C=C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃+ CD₃OD): δ = 0.81 (t, J = 7.0 Hz, 3 H, 5'-H), 1.15-1.42 (m, 4 H, 4'-H/3'-H), 1.66-1.84 (m, 2 H, 2'-H), 2.72 (t, J = 7.7 Hz, 2 H, 1'-H), 3.90 (3 H, CO₂CH₃), 6.27 (s, 1 H, 3-H), 7.78 (d, J = 8.7 Hz, 1 H, Ar), 8.22 (dd, J = 1.9, 8.7 Hz, 1 H, Ar), 9.04 (d, J = 1.9 Hz, 1 H, Ar), 12.2 (br s, 1 H, NH) ppm. ¹³C NMR (101 MHz, CDCl₃+ CD₃OD): δ = 13.6, 22.1, 28.2, 31.0, 33.8 (q, 4 t, C-5'/C-4'/C-3'/C-2'/C-1'), 52.0 (q, CO₂CH₃), 108.9 (d, C-3), 117.8, 128.1, 131.8 (3 d, Ar), 123.7, 124.8 (2 s, Ar), 166.6 (s, CO₂Me), 179.1 (s, C-4) ppm. The signals for
two carbon atoms could not be detected. HRMS: \( m/z \ [M+H]^+ \) calcd for \( C_{15}H_{20}NO_3 \): 274.1438; found: 274.1475.

6-Methoxy-3-methyl-2-phenylquinolin-4(1H)-one (4i): Following the typical procedure, a solution of 3i (100 mg, 0.35 mmol), TMSOTf (471 mg, 2.12 mmol) and NEt\(_3\) (0.15 mL, 1.1 mmol) in 1,2-DCE (7 mL) was heated to 95 °C for 5 d to provide 41 mg (44% - 62% brsm) of 4i as a colorless solid after flash column chromatography (silica gel, 3% MeOH in CH\(_2\)Cl\(_2\)); mp > 230 °C.

![Chemical structure of 6-Methoxy-3-methyl-2-phenylquinolin-4(1H)-one (4i)](image)

IR (ATR): \( \nu = 3250 \) (NH), 3110-2900 (=C-H, C-H), 1620-1540 (C=O, C=C) cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)+ CD\(_3\)OD): \( \delta = 2.07 \) (s, 3 H, CH\(_3\)), 3.93 (s, 3 H, OCH\(_3\)), 7.28 (dd, \( J = 2.9, 9.1 \) Hz, 1 H, Ar), 7.45-7.58 (m, 6 H, Ar), 7.71 (d, \( J = 2.9 \) Hz, 1H, Ar) ppm. \(^13\)C NMR (101 MHz, CDCl\(_3\)+ CD\(_3\)OD): \( \delta = 11.9 \) (q, CH\(_3\)), 55.1 (q, OCH\(_3\)), 103.4 (s, C-3), 114.9, 119.6, 132.2, 124.4, 128.5, 128.7, 129.5, 134.4, 135.2, 148.9, 156.5 (6 d, 5 s, Ar), 178.0 (s, C-4) ppm. HRMS: \( m/z \ [M+Na]^+ \) for \( C_{17}H_{15}NO_2 \): 288.0995; found: 288.1007. Anal. calcd for \( C_{17}H_{15}NO_2 \) (265.3): C, 79.96; H, 5.70; N, 5.28. Found: C, 81.00; H, 6.39; N, 5.98.

(R)-2-[(tert-Butyldimethylsiloxy)(phenyl)methyl]quinolin-4(1H)-one (4j): Following the typical procedure, a solution of 3j (570 mg, 1.48 mmol), TMSOTf (1.98 g, 8.92 mmol) and NEt\(_3\) (0.65, 4.5 mmol) was heated to 95 °C for 32 h to provide 438 mg (81%) of 4j as colorless solid after flash column chromatography (silica gel, 3% MeOH in CH\(_2\)Cl\(_2\)); mp 76-77 °C.

\([\alpha]_D^{22} = + 9.9 \) (c 2.5, MeOH). IR (ATR): \( \nu = 3250 \) (NH), 3070-2850 (=C-H, C-H), 1635-1550 (C=O, C=C) cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)+ CD\(_3\)OD): \( \delta = -0.08, -0.01, 0.83 \) (3 s, 3 H, 3 H, 9 H, OTBS), 5.64 (s, 1 H, CH/Ph), 6.31 (s, 1 H, 3-H), 7.13-7.26 (m, 4 H, Ar), 7.35-7.37 (m, 2 H, Ar), 7.41-7.55 (m, 2 H, Ar), 8.16-8.19 (m, 1 H, Ar) ppm. \(^13\)C NMR (101 MHz, CDCl\(_3\)+ CD\(_3\)OD): \( \delta = -5.4, -5.2, 18.0, 25.4 \) (2 q, s, q, OTBS), 73.8 (d, CH/Ph), 106.2 (d, C-3), 117.8,
123.9, 124.9, 125.3, 126.0, 128.2, 128.4, 132.0, 139.2, 140.6, 154.5 (7 d, 4 s, Ar), 179.1 (s, C-4) ppm. HRMS: m/z [M+H2O+Na]+ calcd for C22H27NNaO2Si: 406.1809; found: 406.1816. Anal. calcd for C22H27NO2Si (365.5): C, 72.29; H, 7.44; N, 3.83. Found: C, 72.32; H, 7.36; N, 3.94.

2-(5-Oxohexyl)quinolin-4(1H)-one (4k): Following the typical procedure, a solution of 3k (99 mg, 0.46 mmol), TMSOTf (611 mg, 2.75 mmol) and NEt3 (0.19, 1.4 mmol) was heated to 95 °C for 24 h to provide 29 mg (26%) of 4k as colorless oil after flash column chromatography (silica gel, 5% MeOH in CH2Cl2 to 15% MeOH in CH2Cl2, gradient elution).

IR (ATR): ν = 3250 (NH), 3060-2800 (=C-H, C-H), 1710-1595 (C=O, C=C) cm⁻¹. ¹H NMR (500 MHz, CDCl3): δ = 1.60-1.74 (m, 4 H, 2'-H/3'-H), 2.05 (s, 3 H, 6'-H), 2.38 (t, J = 7.1 Hz, 2 H, 4'-H), 2.70-2.74 (m, 2 H, 1'-H), 6.22 (s, 1 H, 3-H), 7.30-7.35, 7.55-7.60, 7.75-7.86, 8.33-8.36 (4 m, 1 H each, Ar), 12.34 (br s, 1 H, NH) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 22.8, 28.1, 29.9, 33.7, 43.0 (q, 4 t, C-6'/ C-4'/ C-3'/ C-2'/ C-1'), 108.2 (d, C-3), 118.5, 123.6, 124.9, 125.2, 131.8, 140.6, 154.5 (4 d, 3 s, Ar), 178.8 (s, C-4), 208.9 (s, C-5') ppm. HRMS: m/z [M+H]+ calcd for C15H18NO2: 244.1332; found: 244.1380.

(E)-2-(Prop-1-enyl)quinolin-4(1H)-one (4l): Following the typical procedure, a solution of 3l (200 mg, 0.99 mmol), TMSOTf (1.33 g, 6.00 mmol) and NEt3 (0.42 mL, 3.0 mmol) in 1,2-DCE (8 mL) was heated to 95 °C for 16 h to provide 60 mg (33%) of 4l as colorless solid after flash column chromatography (silica gel, 5% MeOH in CH2Cl2); mp >230 °C.

IR (ATR): ν = 3060-2900 (-C-H, =C-H), 1630-1500 (C=O, C=C) cm⁻¹. ¹H NMR (500 MHz, CDCl₃+ CD3OD): δ = 1.93 (dd, J = 1.5, 6.7 Hz, 3 H, 3'-H), 6.26 (dd, J = 1.5, 15.8 Hz, 1 H, 1'H), 6.70 (qd, J = 6.7, 15.8 Hz, 1 H, 2'-H), 6.35 (s, 1 H, 3-H), 7.29-7.32 (m, 1 H, Ar), 7.56-7.57 (m, 2 H, Ar), 8.23 (m, 1 H, Ar) ppm. ¹³C NMR (101 MHz, CDCl₃+ CD3OD): δ = 18.4
(q, C-3’), 105.3 (d, C-3), 117.8, 123.6, 124.4, 124.6, 131.8 (4 d, s, Ar), 127.7 (d, C-1’), 135.3 (d, C-2), 139.8, 148.5 (2 s, Ar), 179.0 (s, C-4) ppm. HRMS: m/z [M+H]+ calcd for C₁₂H₁₁NO: 186.0919; found: 186.0909. Anal. calcd for C₁₂H₁₃NO (185.2): C, 77.81; H, 5.99; N, 7.56. Found: C, 76.27; H, 6.16; N, 7.43.

2-Pentyl-4-phenylquinoline (12): A screw-top vial was charged with quinolylnonaflate 11 (17 mg, 0.03 mmol), phenyl boronic acid (5.0 mg, 0.04 mmol), Pd(PPh₃)₄ (3.9 mg, 0.003 mmol) and K₂CO₃ (5.6 mg, 0.04 mmol) and DMF (0.3 mL). The mixture was heated to 90 °C under argon atmosphere for 4 h. Then the solution was cooled to r.t. and the mixture was directly purified by flash column chromatography (silica gel, hexane/EtOAc = 9:1) to provide 8 mg (85%) of 12 as yellow oil.

IR (ATR): ν = 3060-2860 (=C-H), 1595-1555 (C=C) cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ = 0.90 (t, J = 7.1 Hz, 3 H, 5’-H), 1.35-1.45 (m, 4 H, 4’-H/3’-H), 1.81-1.88 (m, 2 H, 2’-H), 2.92-3.07 (m, 2 H, 1’-H), 7.24 (d, J = 3.6 Hz, 2 H, Ar), 7.41-7.55 (m, 5-H, Ar, 3-H), 7.66-7.71, 7.85-7.88, 8.10-8.12 (3 m, 1 H each, Ar) ppm. ¹³C NMR (176 MHz, CDCl₃): δ = 14.0, 22.5, 29.8, 31.8, 39.0 (q, 4 t, C-5’, C-4’, C-3’, C-2’, C-1’), 121.6, 125.3, 125.7, 125.9, 128.4, 128.6, 128.8, 129.5 (8 d, Ar), 138.2, 162.5 (2 s, Ar) ppm. The signals of two carbon atoms were not detected. HRMS: m/z [M+H]+ calcd for C₂₀H₂₂N: 276.1747; found: 276.1752.

(R)-(4-Methoxyquinolin-2-yl)(phenyl)methanol (14): To a solution of 13 (43 mg, 0.11 mmol) in THF (1 mL) was added TBAF (1 M in THF, 0.13 mL, 0.13 mmol) and the resulting mixture was stirred at r.t. for 2 h. Then water and EtOAc were added and the organic layer was separated. The aqueous layer was extracted with EtOAc (2 x 20 mL) and the combined organic layers were dried with Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane/EtOAc = 1:1) to provide 26 mg (92%) of 14 as colorless oil.
[α]D22°= -0.1 (c = 1.2, CHCl3). IR (ATR): ν = 3340 (OH), 3060-2850 (=C-H), 1620-1510 (C-C cm⁻¹). ¹H NMR (500 MHz, CDCl3): δ = 3.91 (s, 3 H, OCH3), 5.79 (s, 1 H, CHPh), 6.47 (s, 1 H, 3-H), 7.26-7.52 (m, 6 H, Ar), 7.71-7.74, 8.05-8.07, 8.13-8.15 (3 m, 1 H each Ar) ppm. ¹³C NMR (101 MHz, CDCl3): δ = 55.7 (q, OCH3), 75.3 (d, CHPh), 97.6 (d, C-3), 120.9, 121.9, 125.7, 127.4, 127.9, 128.3, 128.6, 130.1 (7 d, s, Ar), 143.0, 146.8, 161.8, 162.8 (4 s, Ar) ppm. HRMS: m/z [M+H]+ calcd for C17H16NO2: 266.1176; found: 266.1189.

3. Determination of the optical purity of 4j

To determine its optical purity quinolone 4j was esterificated with (S)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl chloride (15) and ent-15. The resulting products were obtained in diastereomeric pure form, proving that no racemization in the cyclization process occurred (Scheme S-1). HPLC analysis of 4j on a chiral stationary phase was not possible, due to the high polarity of that quinolone.

(R)-2-[(R)-(tert-Butyldimethylsiloxy)(phenyl)methyl]quinolin-4-yl 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (16): To a solution of 4j (40 mg, 0.11 mmol) in CH₂Cl₂ (0.6 mL) and pyridine (0.6 mL) was added (S)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl chloride (15 - 35 mg, 0.14 mmol) and the resulting solution was stirred under argon atmosphere at r.t. for 16 h. After complete consumption of the starting material (as indicated by TLC), sat. aq. NaHCO₃ solution (15 mL) and CH₂Cl₂ (15 mL) were added. The phases were separated and the organic layer was washed with 1 M HCl (20 mL) and water (20 mL). The organic layer was dried with Na₂SO₄, filtered and the solvent was removed under reduced pressure to afford 63 mg (99%) of pure 16a as yellow oil.
IR (ATR): $\nu = 3065-2860$ (C-H, C-H), 1770 (C=O), 1625-1500 (C=C) cm$^{-1}$. $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta = 0.07, 0.08, 1.05$ (3 s, 3 H, 3 H, 9 H, OTBS), 3.44 (s, 3 H, OMe), 6.42 (s, 1 H, CHPh), 7.00-7.24 (m, 6 H, Ar), 7.25-7.27 (m, 1 H, Ar), 7.73-7.83 (m, 5 H, Ar), 8.12 (s, 1 H, Ar), 8.21-8.23 (m, 1 H, Ar) ppm. $^{13}$C NMR (101 MHz, C$_6$D$_6$): $\delta = -4.83, -4.77, 18.5, 26.0$ (2 q, s, q, OTBS), 55.5 (q, OMe), 78.8 (d, CHPh), 109.8 (d, C-3), 120.9, 121.2 (Ar), 123.8 (q, $^1$J$_{CF} = 288.5$ Hz, CF$_3$), 126.3, 126.8, 128.6, 128.8, 129.7, 130.0, 130.2, 132.0, 143.3, 149.6, 154.0, 164.1, 165.7 (8 d, 6 s, Ar)* ppm. The signal for one carbon atom could not be detected. $^{19}$F NMR (376 MHz, C$_6$D$_6$): $\delta = -71.2$ (CF$_3$) ppm. HRMS: $m/z$ [M+H]$^+$ calcd for C$_{32}$H$_{35}$F$_3$NO$_4$Si: 582.2282; found: 582.2304.

(S)-2-[(R)-(tert-Butyldimethylsiloxy)(phenyl)methyl]quinolin-4-yl 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (16b): To a solution of 4j (30 mg, 0.08 mmol) in CH$_2$Cl$_2$ (0.6 mL) and pyridine (0.6 mL) was added (R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl chloride (ent-15 ~ 28 mg, 0.11 mmol) and the resulting solution was stirred under argon atmosphere at r.t. for 16 h. After complete consumption of the starting material (as indicated by TLC), sat. aq. NaHCO$_3$ solution (15 mL) and CH$_2$Cl$_2$ (15 mL) were added. The phases were separated and the organic layer was washed with 1 M HCl (20 mL) and water (20 mL). The organic layer was dried with Na$_2$SO$_4$, filtered and the solvent was removed under reduced pressure to leave 40 mg (84%) of pure 16b as yellow oil.
128.8, 129.0, 129.9, 130.1, 130.4, 132.4, 143.6, 149.8, 154.2, 164.4, 166.0 (10 d, 6 s, Ar)* ppm. The signal for one carbon atom could not be detected, the CF$_3$ could not be detected. $^{19}$F NMR (376 MHz, C$_6$D$_6$): $\delta = -71.2$ (CF$_3$) ppm. HRMS: $m/z$ [M+H]$^+$ calcd for C$_{32}$H$_{35}$F$_3$NO$_4$Si: 582.2282; found: 582.2297.

4. NMR Spectra of Representative Example
$^1$H NMR (400 MHz, CDCl$_3$+CD$_3$OD)
$^{13}$C NMR (101 MHz, CDCl$_3$+CD$_2$OD)

[Diagram of a molecule with chemical shifts and other NMR data]
$^1$H NMR (400 MHz, CDCl$_3$+CD$_3$OD)

![Chemical Structure Image]
$^{13}$C NMR (101 MHz, CDCl$_3$+CD$_3$OD)
$^1$H NMR (500 MHz, CDCl$_3$)

![NMR spectrum image]
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$+CD$_3$OD)

![NMR Spectrum Image]

S-27
$^1$H NMR (400 MHz, CDCl$_3$+CD$_3$OD)
5. References
