## Synthesis and fluorescence properties of boroisoquinolines, a new family of fluorophores

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Table of Contents
Synthesis and fluorescence properties of boroisoquinolines, a new family of fluorophores 1

1. Experimental 2
2. Optical spetroscopy data for boroisoquinolines 25
3. X-Ray diffraction data for boroisoquinolines $\mathbf{1 8 f}$ and 19c 26
4. ${ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}$ NMR spectra 27
5. References 58

## 1. Experimental

## General

All melting points were determined on a Jasco SRS OptiMelt apparatus and are uncorrected. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded in $\mathrm{CDCl}_{3}$ solution at room temperature, on a Varian Unity Inova 500 spectrometer ( 500 and 125 MHz for ${ }^{1} \mathrm{H}$ and APT NMR spectra, respectively), and on a Varian Unity Inova 300 spectrometer ( 282 MHz for ${ }^{19} \mathrm{~F}$ NMR spectra), with the deuterium signal of the solvent as the lock and TMS as the internal standard. Chemical shifts $(\delta)$ and coupling constants $(J)$ are given in ppm and Hz , respectively. High resolution mass spectra were recorded on a Waters Q-TOF Premier mass spectrometer in positive ESI ionization mode. The microwave reactions were conducted in an Anton Paar Monowave 300 microwave reactor. The reactions were followed by analytical thin layer chromatography on silica gel $60 \mathrm{~F}_{254}$ and HPLC-MS chromatography with a Shimadzu LCMS-2020 device using a Reprospher 100 C 18 ( $5 \mu \mathrm{~m} ; 100 \mathrm{x} 3 \mathrm{~mm}$ ) column and positivenegative double ion source (DUIS $\pm$ ) with a quadrupole MS analysator in a range of 50-1000 $\mathrm{m} / \mathrm{z}$. All reagents were purchased from commercial sources. Analytical samples of new compounds were obtained by trituration or recrystallization from the solvents or solvent mixtures given below in parentheses. Single crystal X-ray measurements were carried on a Rigaku R-Axis Rapid imaging plate area detector with graphite monochromated $\mathrm{Cu}-\mathrm{K} \alpha$ radiation.

## Photophysical measurements

The fluorescence and absorbance measurements were carried out on a Jasco FP8300 spectrofluorometer, in a standard cell quartz cuvette with 1 cm light path length. The widths of the excitation slit and the emission slit were both set to 2.5 nm with the scanning speed at $1000 \mathrm{~nm} / \mathrm{min}$. Pure solvents were used as blank correction. We used acetonitrile as solvent if not mentioned else, the concentration was $5 \mu \mathrm{M}$ or $0.5 \mu \mathrm{M}$.
The quantum yields were determined by recording the fluorescence spectra of a series of different concentrations. The gradient of the integrated fluorescence intensities plotted against absorbance at the excitation wavelength was used for the calculation of the quantum yields:
$\Phi_{x}=\Phi_{S t} \cdot\left(\frac{\operatorname{Grad}_{x}}{\operatorname{Grad}_{S t}}\right) \cdot\left(\frac{\eta_{x}^{2}}{\eta_{S t}^{2}}\right)$

The $\mathbf{1 8 d}, \mathbf{h}, \mathbf{l}, \mathbf{k}, \mathbf{m}$ and $\mathbf{2 1 1}$ compounds were excited at 380 nm , Coumarin-153 was used as reference $\left(\Phi_{\mathrm{F}}{ }^{\mathrm{EtOH}}=0.55\right)$. The 18b and 22b compounds were excited at 339 nm , quinine sulfate was used as reference $\left.\left(\Phi_{\mathrm{F}(0.5} \mathrm{m}_{2} \mathrm{SO}_{4}\right)=0.54\right)$ During the computations we used refraction coefficients from literature. ${ }^{1}$

The solvent screen measurement was carried out with $5 \mu \mathrm{M}$ solutions of the $\mathbf{1 8 1}$ boroisoquinoline in acetonitrile, 1,4-dioxane, water, toluene, dichloromethane, tetrahydrofuran, ethanol, hexane and ethyl acetate.

The photostability measurement was carried out with $5 \mu \mathrm{M}$ solutions of compound $\mathbf{1 8 1}$ in acetonitrile. We used $8 \mathrm{~W}, 366 \mathrm{~nm}$ emitting UV lamp, and measured the emission spectrum in every hour for 4 hours. During the photophysical measurments the solutions were excited at 380 nm .

## General procedure for the preparation of $\mathbf{N}$-phenethylacetamides

In a three-necked round bottom flask 5.0 g 2-(3,4-dimethoxyphenyl)ethyl-amine or 4.2 g 2-(3-dimethoxyphenyl)ethan-1-amine or 5.6 g 2-(3-bromophenyl)ethan-1-amine or 3.9 g 2-(3-fluorophenyl)ethan-1-amine ( 28 mmol ) and 5.1 mL triethyl-amine ( $3.8 \mathrm{~g}, 36.4 \mathrm{mmol}, 1.3$ equiv) was dissolved in 50 mL dichloromethane. To this solution was added dropwise 2.4 mL acetyl chloride ( $2.6 \mathrm{~g}, 34.0 \mathrm{mmol}, 1.2$ equiv) and the mixture was stirred at room temperature for 30 minutes. The reaction mixture was quenched with 50 mL water. The layers were separated, and the organic layer was washed with 40 mL 1 M HCl and then $40 \mathrm{~mL} 5 \%$ $\mathrm{Na}_{2} \mathrm{CO}_{3}$ solution, dried over $\mathrm{MgSO}_{4}$, filtered and evaporated under reduced pressure.
N-[2-(3,4-Dimethoxyphenyl)ethyl]acetamide ${ }^{2}$
Yield: 6.1 g ( $98 \%$ ), light yellow crystals, m.p. $98-99^{\circ} \mathrm{C}$ (EtOAc-hexane) (lit. $100-101{ }^{\circ} \mathrm{C}$ ), ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 6.81(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.73(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}$ ), $5.56(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 3.87\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.86\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.49\left(\mathrm{q}, J=6.7 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.76$ (t, $J=7.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}$ ), $1.94\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm}$.
N-[2-(3-Methoxyphenyl)ethyl]acetamide ${ }^{3}$
Yield: $4.6 \mathrm{~g}(86 \%)$; yellow oil; ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.21(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 6.79-6.74 (m, 2H, ArH), 6.72 (s, 1H, ArH), 5.65 (s, 1H, NH), 3.78 (s, 3H, OCH $)$, 3.49 (q, J $\left.=6.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.77\left(\mathrm{t}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 1.92\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm}$.
$N$-[2-(3-Bromophenyl)ethyl]acetamide ${ }^{4}$
Yield: $5.6 \mathrm{~g}(83 \%)$, brown oil; ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.34(\mathrm{~d}, J=11.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH})$, $7.19-7.14(\mathrm{~m}, 1 \mathrm{H}, \mathrm{ArH}), 7.11(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 5.65(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 3.47(\mathrm{q}, J=13.2$. $\left.6.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}_{2}\right), 2.78\left(\mathrm{t}, J=7.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}_{2}\right), 1.93\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm}$.

## $N-[2-(3-F l u o r o p h e n y l) e t h y l] a c e t a m i d e{ }^{3}$

Yield: $4,2 \mathrm{~g}(83 \%)$, yellow oil; ${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.25(\mathrm{dd}, J=13.9 .7 .9 \mathrm{~Hz}, 1 \mathrm{H}$, ArH), 6.96 (d, $J=7.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), $6.90(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 5.63(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 3.49$ (dd, $\left.J=13.1 .6 .8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.80\left(\mathrm{t}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 1.93\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm}$.

## General procedure for the preparation of 1-methyl-3,4-dihydroisoquinolines (16a,b)

Method A
In a three-necked round bottom flask $5.5 \mathrm{~g} N$-[2-(3,4-dimethoxyphenyl)ethyl]acetamide or 4.8 g of $N$-[2-(3-methoxyphenyl)ethyl]acetamide ( 24.7 mmol ) was dissolved in 50 mL toluene and 2.3 mL phosphorus oxychloride ( $24.7 \mathrm{mmol}, 1$ equiv.) was added dropwise. The solution was stirred at reflux temperature for 1 h . The reaction mixture was cooled to room temperature, and the solvent was removed in vacuo. The brown crystallic hydrochloride salt was triturated with diethyl ether, and filtered. The remaining solid was suspended in 50 mL of dichloromethane, and 200 mL concd. $\mathrm{NaHCO}_{3}$ solution was added. The layers were separated, and the aqueous phase was washed with $2 \times 30 \mathrm{~mL}$ dichloromethane. The combined organic phases were dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, filtered and the solvent was removed in vacuo. 6-Methoxy-1-methyl-3,4-dihydroisoquinoline (16a) ${ }^{5}$
Yield: $3.2 \mathrm{~g}(73 \%)$; brown oil; ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.41$ ( $\mathrm{d}, J=8,5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), $6.77\left(\mathrm{dd}, J_{1}=8.4 \mathrm{~Hz}, J_{2}=2.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right), 6.69(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 3.82\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.62(\mathrm{t}, J$ $\left.=6.9 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.67\left(\mathrm{t}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.33\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm}$.
6,7-Dimethoxy-1-methyl-3,4-dihydroisoquinoline (16b) ${ }^{6}$
Yield: $4.8 \mathrm{~g}(95 \%)$; pale brown crystals; m.p. $101-102{ }^{\circ} \mathrm{C}\left(\mathrm{Et}_{2} \mathrm{O}\right)\left(\right.$ lit. $\left.102-103^{\circ} \mathrm{C}\right) ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.00(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.69(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 3.92\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.91(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{OCH}_{3}\right), 3.63\left(\mathrm{t}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.64\left(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.36\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm}$.

## Method B

In a three-necked round bottom flask 4.6 g N-[2-(3-bromophenyl)ethyl]acetamide or 3.4 g N -[2-(3-fluorophenyl)ethyl]acetamide ( 18.9 mmol ) was dissolved in 100 mL dichloromethane and 1.8 mL oxalyl chloride ( $2.6 \mathrm{~g}, 20.7 \mathrm{mmol}, 1.1$ equiv) was added dropwise under nitrogen atmosphere. The solution was stirred at room temperature for 30 minutes. Then the reaction mixture was cooled below $-10{ }^{\circ} \mathrm{C}$, and $3.7 \mathrm{~g} \mathrm{FeCl}_{3}(22.7 \mathrm{mmol}, 1.2$ equiv) was added. The mixture was stirred at room temperature overnight. Aqueous $2 \mathrm{M} \mathrm{HCl}(10 \mathrm{~mL}, 20.0 \mathrm{mmol})$ was added to quench the reaction. The mixture was stirred at room temperature for 1 h , then the layers were separated. The organic layer was washed with brine, and dried over $\mathrm{MgSO}_{4}$ ),
filtered, and the solvent was removed in vacuo. The oxalyl adduct was dissolved in 180 mL methanol, 9.5 mL concentrated sulphuric acid was added, and stirred at reflux overnight. The next morning the reaction mixture was allowed to cool room temperature, and the solvent was removed in vacuo. The crude material was dissolved in ethyl acetate, and washed with water. The aqueous layer was basified with $10 \%$ sodium hydroxide solution, and extracted with ethyl acetate. The combined organic phases were dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and the solvent was removed in vacuo.

## 6-Bromo-1-methyl-3,4-dihydroisoquinoline (16c) ${ }^{7}$

Yield: 3.5 g ( $82 \%$ ), brown oil; ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.45-7.37(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}$ ), 7.32 (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}$ ), $3.64\left(\mathrm{~s}, J=7.5 .1 .3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.72-2.60\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.35$ (s, $3 \mathrm{H}, \mathrm{CH}_{3}$ ) ppm; ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 163.4$ ( $\mathrm{C}=$ ), 139.5 ( $\mathrm{C}=$ ), 130.4 ( $=\mathrm{CH}$ ), $130.0(=\mathrm{CH}), 128.3(\mathrm{C}=)$, $126.8(=\mathrm{CH})$, $124.6(\mathrm{C}=), 46.7\left(\mathrm{CH}_{2}\right), 25.8\left(\mathrm{CH}_{2}\right), 23.2\left(\mathrm{CH}_{3}\right) \mathrm{ppm}$.

## 6-Fluoro-1-methyl-3,4-dihydroisoquinoline (16d) ${ }^{8}$

Yield: 2.3 g (76\%), tawny oil; ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.56$ (dd, $J=8.5 .5 .5 \mathrm{~Hz}, 1 \mathrm{H}$, ArH), 7.01 (td, $J=8.5 .2 .5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 6.93 (dd, $J=8.6 .2 .2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 3.73 (dd, $J=$ 12.8. $\left.5.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.83-2.76\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.49\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR (125 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 165.1(=\mathrm{CF}), 140.0(\mathrm{C}=), 135.8(\mathrm{C}=), 128.4(\mathrm{~d}, J=9.6 \mathrm{~Hz},=\mathrm{CH}), 124.6(\mathrm{C}=)$, $114.4(\mathrm{~d}, J=22.1 \mathrm{~Hz},=\mathrm{CH}), 113.7(\mathrm{~d}, J=22.1 \mathrm{~Hz},=\mathrm{CH}), 44.3\left(\mathrm{CH}_{2}\right), 25.5\left(\mathrm{CH}_{2}\right), 21.6\left(\mathrm{CH}_{3}\right)$ ppm; ${ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-130.01(\mathrm{~s}, 1 \mathrm{~F}, \mathrm{ArF}) \mathrm{ppm}$.

## Synthesis of 1-methyl-6-(pyrrolidin-1-yl)-3,4-dihydroisoquinoline (16e)

Method A: Buchwald-Hartwig coupling
Into a sealed tube 10 mL anhydrous toluene, 0.5 g 6-bromo-1-methyl-3,4-dihydroisoquinoline ( $\mathbf{1 6 c}$ ) $(2.3 \mathrm{mmol}), 0.025 \mathrm{~g} \mathrm{Pd}(\mathrm{OAc})_{2}(0.1 \mathrm{mmol}, 0.05$ equiv), 0.067 g JohnPhos ligand ( 0.2 $\mathrm{mmol}, 0.1$ equiv) was measured. The tube was flushed with argon, then 0.31 g potassium tertbutoxide ( $2.8 \mathrm{mmol}, 1.25$ equiv) was added. The tube was flushed again with argon and 0.55 mL pyrrolidine ( $0.5 \mathrm{~g}, 7.0 \mathrm{mmol}, 3$ equiv) was added. The tube was heated to $80^{\circ} \mathrm{C}$, then all of the reagents except potassium tert-butoxide were added again. After 30 minutes at $80^{\circ} \mathrm{C}$, the reaction mixture was filtered through celite. The crude product was purified by flash column chromatography on alumina using dichloromethane/methanol.
Yield: $0.34 \mathrm{~g}(40 \%)$, brown oil.
Method B
In a round bottom flask 0.1 g 6-fluoro-1-methyl-3,4-dihydroisoquinoline (16d) was dissolved in 2 mL pyrrolidine ( $1.7 \mathrm{~g}, 123 \mathrm{mmol}, 205$ equiv.). The reaction mixture was refluxed for 18 h ,
then concentrated in vacuo, and the residue was purified by flash column chromatography on alumina using dichloromethane/methanol.

Yield: 0.05 g (40\%), brown oil.

## Method C

In a sealed tube 0.1 g 6-fluoro-1-methyl-3,4-dihydroisoquinoline ( $\mathbf{1 6 d}$ ) ( 0.6 mmol ) and 2 mL pyrrolidine ( $1.7 \mathrm{~g}, 123 \mathrm{mmol}, 205$ equiv) were dissolved in 6 mL acetonitrile. The reaction mixture was heated at $80{ }^{\circ} \mathrm{C}$ for 9 days. The residue was purified by flash column chromatography on alumina using dichloromethane/methanol.

Yield: 0.05 g ( $42 \%$ ), brown oil.
Method D
In a sealed tube 4.4 g 6-fluoro-1-methyl-3,4-dihydroisoquinoline (16d) ( 27.0 mmol ) and 10 mL pyrrolidine ( $11.5 \mathrm{~g}, 162 \mathrm{mmol}, 6$ equiv) were dissolved in 10 mL dioxane. The reaction mixture was heated at $80^{\circ} \mathrm{C}$ for 3 days. The residue concentrated under reduced pressure, and purified with steam distillation. After all of the excess pyrrolidine was distilled, the leftover was dissolved in aqueous HCl , then extracted with dicholormethane ( $5 \times 50 \mathrm{~mL}$ ). For NMR purpose the crude product purified with reverse phase column chromatography using acetonitrile/water.

Yield: $4.0 \mathrm{~g}(70 \%)$, yellow crystals, m. p. $47-48{ }^{\circ} \mathrm{C}$ (water-MeCN); ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 7.45(\mathrm{~d}, J=8.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.41(\mathrm{dd}, J=8.9 .2 .3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.28(\mathrm{~s}, 1 \mathrm{H}$, ArH ), $3.66\left(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.38-3.28\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 2.84\left(\mathrm{t}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$, $2.59\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 1.97\left(\mathrm{dt}, J=17.0 .6 .7 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $170.0(\mathrm{C}=)$, $152.6(\mathrm{C}=)$, $139.7(\mathrm{C}=)$, $131.4(=\mathrm{CH})$, $113.3(\mathrm{C}=)$, $110.8(=\mathrm{CH}), 110.4(=\mathrm{CH})$, $47.9\left(\mathrm{CH}_{2}\right), 41.4\left(\mathrm{CH}_{2}\right), 26.6\left(\mathrm{CH}_{2}\right), 25.2\left(\mathrm{CH}_{2}\right), 19.2\left(\mathrm{CH}_{3}\right) \mathrm{ppm} .[\mathrm{M}+\mathrm{H}]^{+}$measured $=215.1560$, calcd. for $\mathrm{C}_{14} \mathrm{H}_{19} \mathrm{~N}_{2}$ : 215.1543.

General procedure for the preparation of 1-methylidene-3,4-dihydroisoquinolines (17)
Method A
In a three-necked round bottom flask 20 mL anhydrous tetrahydrofurane was cooled below $70{ }^{\circ} \mathrm{C}$, under nitrogen atmosphere. Then 6.25 mmol ( 2.5 equiv.) $n-\mathrm{BuLi}$ was added dropwise [except 17g,h when 3 mmol ( 1.2 equiv.) was used], then the corresponding 2.5 mmol isoquinoline in tetrahydrofuran solution ( $0.44 \mathrm{~g} \mathbf{1 6 a}, 0.51 \mathrm{~g} \mathbf{1 6 b}$ ) was added dropwise. The reaction mixture was then stirred for 30 minutes, and the appropriate ester ( $6.25 \mathrm{mmol}, 2.5$ equiv.) was added dropwise in 10 mL tetrahydrofuran [17a,b: ethyl acetate ( $0.55 \mathrm{~g}, 0.62 \mathrm{ml}$ ); $\mathbf{1 7 c}$,d: ethyl benzoate ( $0.94 \mathrm{~g}, 0.89 \mathrm{ml}$ ); 17i: ethyl 4-nitrobenzoate ( 1.2 g ); 17e,f: ethyl 2-
thiophenecarboxylate ( $0.98 \mathrm{~g}, 0.84 \mathrm{ml}$ ); 17g,h: ethyl pentafluorbenzoate $(1.5 \mathrm{~g}, 1.1 \mathrm{ml})]$. Then the reaction mixture was allowed to warm to room temperature, and stirred for 1 h . The solution was quenched with 30 mL water, and extracted with 80 mL ethyl acetate. The aqueous layer was washed with ethyl acetate $(2 \times 30 \mathrm{~mL})$ and dichloromethane $(2 \times 30 \mathrm{~mL})$. The combined organic phases were dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel using hexane/ethyl acetate.
(Z)-1-(6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one (17a) ${ }^{9}$

Yield: 0.25 g ( $46 \%$ ); tawny crystals; m. p. $87-88^{\circ} \mathrm{C}$ (hexane-EtOAc); ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 12.23(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.61(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.80\left(\mathrm{dd}, J_{1}=8.7 \mathrm{~Hz}, J_{2}=2.3\right.$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), $6.70(\mathrm{~d}, J=2.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 5.56(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.83\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.44(\mathrm{td}$, $\left.J_{1}=6.25 \mathrm{~Hz}, J_{2}=2.9 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.87\left(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.12\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm}$. (Z)-1-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one (17b) ${ }^{9}$ Yield: $0.32 \mathrm{~g}(50 \%)$; yellow crystals; m. p. $137-138{ }^{\circ} \mathrm{C}$ (hexane-EtOAc); ${ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 11.23(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.13(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.67(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 5.52(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=)$, $3.93\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.91\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.44\left(\mathrm{td}, J_{1}=6.5 \mathrm{~Hz}, J_{2}=3.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.83(\mathrm{t}$, $\left.J=6.5 .2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.14\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm}$.
(Z)-2-(6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (17c) ${ }^{10}$ Yield: $0.35 \mathrm{~g}(51 \%)$; brown oil; ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 11.81$ (s, 1H, NH), 7.93 (dd, $\left.J_{1}=6.4 \mathrm{~Hz}, J_{2}=3.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}\right), 7.76(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.48-7.39(\mathrm{~m}, 3 \mathrm{H}, \mathrm{ArH})$, $6.86(\mathrm{dd}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.75(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.26(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.86(\mathrm{~s}, 3 \mathrm{H}$, $\mathrm{OCH}_{3}$ ), $3.54\left(\mathrm{td}, J_{1}=6.5 \mathrm{~Hz}, J_{2}=3.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.94\left(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm}$. (Z)-2-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (17d) ${ }^{9}$ Yield: $0.41 \mathrm{~g}(53 \%)$; yellow crystalles; m. p. 137-139 ${ }^{\circ} \mathrm{C}$ (lit. $19135-136>{ }^{\circ} \mathrm{C}$ ); ${ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 11.81(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.92(\mathrm{~d}, J=3.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}), 7.45-7.42(\mathrm{~m}, 3 \mathrm{H}, \mathrm{ArH})$, $7.25(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.71(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.19(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.95\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.93(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{OCH}_{3}\right), 3.53\left(\mathrm{td}, J_{1}=6.5 \mathrm{~Hz}, J_{2}=3.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.89\left(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm}$. (Z)-2-(6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1-one (17e) ${ }^{9}$ Yield: $0.41 \mathrm{~g}(58 \%)$; brown oil; ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 11.47$ (s, 1H, NH), 7.75 (d, J $=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.64(\mathrm{~d}, J=3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.45(\mathrm{~d}, J=4.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.09\left(\mathrm{dd}, J_{1}\right.$ $\left.=4.7 \mathrm{~Hz}, J_{2}=4.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right), 6.87\left(\mathrm{dd}, J_{1}=8.7 \mathrm{~Hz}, J_{2}=2.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right), 6.75(\mathrm{~d}, J=2.0$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.16(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.87\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 3.53\left(\mathrm{td}, J_{1}=6.8 \mathrm{~Hz}, J_{2}=2.5 \mathrm{~Hz}, 2 \mathrm{H}\right.$, $\mathrm{CH}_{2}$ ), $2.93\left(\mathrm{t}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm}$.
(Z)-2-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1-one $(17 f)^{9}$

Yield: $0.37 \mathrm{~g}(48 \%)$; yellow crystals; m. p. $151-152{ }^{\circ} \mathrm{C}$ (hexane-EtOAc); ${ }^{1} \mathrm{H}$ NMR ( 500 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 11.45(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.62(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 7.44(\mathrm{~d}, J=3.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.23(\mathrm{~s}$, $1 \mathrm{H}, \mathrm{ArH}), 7.08(\mathrm{t}, J=4.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.70(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.09(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.96(\mathrm{~s}, 3 \mathrm{H}$, $\mathrm{OCH}_{3}$ ), $3.96\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.50\left(\mathrm{t}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.88\left(\mathrm{t}, J=6.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm}$. (Z)-2-(6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one (17g)
Instead of 2.5 equiv. we used 1.2 equiv. reagents.
Yield: 0.28 g ( $12 \%$ ); white crystals; m. p. $126-128{ }^{\circ} \mathrm{C}$ (water-MeCN); ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 11.55(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.62(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.80(\mathrm{t}, J=14.0 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH})$, $6.75(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 5.72(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.85\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.56\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.96(\mathrm{t}, J=6.1$ $\left.\mathrm{Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.0(\mathrm{C}=\mathrm{O}), 162.7(\mathrm{C}=), 159.9(\mathrm{C}=)$, $144.9(\mathrm{C}=), 143.8(\mathrm{~d}, \mathrm{~J}=241.6 \mathrm{~Hz},=\mathrm{CF})$, 140.1 (=CF), $138.9(\mathrm{C}=)$, 136.5 (=CF), 128.0 $(=\mathrm{CH}), 120.5(\mathrm{C}=), 113.4(=\mathrm{CH})$, $113.1(=\mathrm{CH})$, $91.8(=\mathrm{CH})$, $55.4\left(\mathrm{OCH}_{3}\right), 38.7\left(\mathrm{CH}_{2}\right), 28.2$ $\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-142.47(\mathrm{dd}, J=23.4,8.2 \mathrm{~Hz}, 2 \mathrm{~F}, \mathrm{ArF}),-155.13$ ( $\mathrm{t}, J=20.7 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{ArF}$ ), $-162.18(\mathrm{dt}, J=23.5,8.3 \mathrm{~Hz}, 2 \mathrm{~F}, \mathrm{ArF}) \mathrm{ppm} ;[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=$ 370.0858. calcd, $\mathrm{C}_{18} \mathrm{H}_{13} \mathrm{~F}_{5} \mathrm{NO}_{2}$ : 370.0861.
(Z)-2-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one (17h)
Instead of 2.5 equiv. we used 1.2 equiv. reagents.
Yield: $0.58 \mathrm{~g}(57 \%)$, yellow crystals; m. p. $178-180{ }^{\circ} \mathrm{C}(\mathrm{MeCN}) ;{ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 11.54(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.09(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.71(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 5.66(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.93(\mathrm{~s}$, $3 \mathrm{H}, \mathrm{OCH}_{3}$ ), $3.89\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.57-3.54\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.92\left(\mathrm{t}, J=14.0 .7 .3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$ ppm; ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.1(\mathrm{C}=\mathrm{O})$, $159.8(\mathrm{C}=)$, $152.5(\mathrm{C}=)$, $148.2(\mathrm{C}=)$, $144.85(\mathrm{C}=), 143.8(\mathrm{~d}, J=256.9 \mathrm{~Hz},=\mathrm{CF}), 141.1(\mathrm{~d}, J=255.0 \mathrm{~Hz},=\mathrm{CF}), 137.5(\mathrm{~d}, J=253.1$ $\mathrm{Hz},=\mathrm{CF}), 130.9(\mathrm{C}=)$, $120.3(\mathrm{C}=)$, $120.1(\mathrm{C}=)$, $117.7(\mathrm{C}=)$, $110.8(=\mathrm{CH}), 108.7(=\mathrm{CH}), 91.8$ $(=\mathrm{CH}), 56.2\left(\mathrm{OCH}_{3}\right), 56.1\left(\mathrm{OCH}_{3}\right), 38.8\left(\mathrm{CH}_{2}\right), 27.5\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR $(282 \mathrm{MHz}$, $\mathrm{CDCl}_{3}$ ) $\delta-142.49(\mathrm{dd}, J=23.5,8.0 \mathrm{~Hz}, 2 \mathrm{~F}, \mathrm{ArF}),-155.14(\mathrm{t}, J=20.7 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{ArF}),-161.89-$ $-162.35(\mathrm{~m}, 2 \mathrm{~F}, \mathrm{ArF}) \mathrm{ppm} . ;[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=400.0970$. calcd. for $\mathrm{C}_{19} \mathrm{H}_{15} \mathrm{~F}_{5} \mathrm{NO}_{3}: 400.0972$.
(Z)-2-(6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(4-nitrophenyl)ethan-1-one (17i)

Yield: $0.043 \mathrm{~g}(5 \%)$; orange crystals; m. p. $152-153{ }^{\circ} \mathrm{C}$ (hexane); ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 11.97(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 8.27(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}), 8.06(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH})$,
$7.77(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.89\left(\mathrm{dd}, J_{1}=8.7 \mathrm{~Hz}, J_{2}=2.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}\right), 6.79(\mathrm{~d}, J=2.1$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.24(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.89\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.60\left(\mathrm{td}, J_{1}=6.6 \mathrm{~Hz}, J_{2}=3.3 \mathrm{~Hz}, 2 \mathrm{H}\right.$, $\left.\mathrm{CH}_{2}\right), 2.98\left(\mathrm{t}, J=6.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm}$.

## Method B

In a three-necked round bottom flask 20 mL anhydrous tetrahydrofuran and 0.88 mL diisopropylamine ( $0.63 \mathrm{~g}, 6.25 \mathrm{mmol}, 2.5$ equiv.) was cooled below $-70^{\circ} \mathrm{C}$, under nitrogen atmosphere. Then 6.25 mmol ( 2.5 equiv.) $n$-BuLi was added dropwise [except $\mathbf{1 7 m}$ when 3 mmol ( 1.2 equiv.) was used], the reaction mixture was stirred for 1 h . Then the corresponding 2.5 mmol isoquinoline in tetrahydrofuran solution $(0.51 \mathrm{~g} \mathrm{16b}, 0.54 \mathrm{~g} \mathbf{1 6 e})$ was added dropwise. After it the reaction mixture was stirred for 1 h , then the appropriate ester ( 6.25 mmol, 2.5 equiv.) was added dropwise in 10 mL tetrahydrofuran [ $\mathbf{1 7 k}$ : ethyl acetate ( 0.55 g , 0.62 ml ); 171: ethyl benzoate ( $0.94 \mathrm{~g}, 0.89 \mathrm{ml}$ ); 17j : ethyl 4-nitrobenzoate ( 1.2 g ); $\mathbf{1 7 m}$ : ethyl pentafluorbenzoate $(1.5 \mathrm{~g}, 1.1 \mathrm{ml})]$. Then the reaction mixture was allowed to warm to room temperature, and stirred for 1 h . The solution was quenched with 30 mL water, and extracted with 80 mL ethyl acetate. The aqueous layer was washed with ethyl acetate ( $2 \times 30 \mathrm{~mL}$ ) and dichloromethane $(2 \times 30 \mathrm{~mL})$. The combined organic phases were dried $\left(\mathrm{MgSO}_{4}\right)$, filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel using hexane/ethyl acetate.
(Z)-2-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(4-nitrophenyl)ethan-1-one (17j)
Yield: $0.54 \mathrm{~g}(54 \%)$ [0.030 g (3\%)]; orange crystals; m. p. $187-188{ }^{\circ} \mathrm{C}(\mathrm{MeCN}) ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 11.96(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 8.26(\mathrm{~d}, J=5.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}), 8.04(\mathrm{~d}, J=6.1 \mathrm{~Hz}$, $2 \mathrm{H}, \mathrm{ArH}$ ), 7.23 (s, 1H, ArH), 6.73 (s, 1H, ArH), 6.15 (s, 1H, HC=), $3.96\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.95$ ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{OCH}_{3}$ ), $3.57\left(\mathrm{~s}, 2 \mathrm{H} \mathrm{CH}_{2}\right), 2.92\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm}$.
(Z)-1-(6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one ( $\mathbf{1 7 k} \mathbf{k})$

Yield: $0.27 \mathrm{~g}(41 \%)$ [0.17 g (26\%)]; yellow crystals; m. p. $108-110{ }^{\circ} \mathrm{C}\left(\mathrm{CDCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 11.25(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.54(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 6.43 (dd, $J=8.8,2.1$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 6.29 (s, 1H, ArH), 5.52 ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{HC}=$ ), 3.44 (td, $J=6.6,3.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}$ ), 3.35$3.31\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 2.84\left(\mathrm{t}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.11\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 2.04-2.00\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right)$ ppm; ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 193.4(\mathrm{C}=\mathrm{O})$, $157.8(\mathrm{C}=)$, $149.1(\mathrm{C}=), 137.9(\mathrm{C}=), 126.7$ $(=\mathrm{CH}), 115.2(\mathrm{C}=), 109.7(=\mathrm{CH}), 87.5(=\mathrm{CH}), 47.0\left(\mathrm{CH}_{2}\right), 38.2\left(\mathrm{CH}_{2}\right), 28.7\left(\mathrm{CH}_{3}\right), 28.6$ $\left(\mathrm{CH}_{2}\right), 24.9\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=257.1660$, calcd. for $\mathrm{C}_{16} \mathrm{H}_{21} \mathrm{~N}_{2} \mathrm{O}: 257.1650$
(Z)-1-phenyl-2-(6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)ethan-1-one (171) Yield: $0.56 \mathrm{~g}(72 \%)$ [0.21 g (27\%)]; yellow crystlas; m. p. $137-138{ }^{\circ} \mathrm{C}(\mathrm{MeCN}) ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 11.82(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.94(\mathrm{dd}, J=6.4,2.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}$ ), $7.68(\mathrm{~d}, J=8.8$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), $7.41(\mathrm{dd}, J=6.3,2.9 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{ArH}), 6.47(\mathrm{dd}, J=8.4,2.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.32$ (d, $J=1.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.22(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.53\left(\mathrm{t}, J=5.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.35(\mathrm{t}, J=6.5 \mathrm{~Hz}$, $\left.4 \mathrm{H}, \mathrm{CH}_{2}\right), 2.89\left(\mathrm{t}, J=6.6 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.04-2.00\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 187.2(\mathrm{C}=\mathrm{O}), 159.9(\mathrm{C}=)$, $159.5(\mathrm{C}=)$, $149.8(\mathrm{C}=), 141.7(\mathrm{C}=), 138.4(\mathrm{C}=), 129.9$ $(=\mathrm{CH}), 127.61(=\mathrm{CH})$, $128.0(=\mathrm{CH})$, $127.4(=\mathrm{CH})$, $126.8(=\mathrm{CH}), 110.27(=\mathrm{CH}), 110.24$ $(=\mathrm{CH}), 85.4(=\mathrm{CH}), 47.1\left(\mathrm{CH}_{2}\right), 47.5\left(\mathrm{CH}_{2}\right), 38.9\left(\mathrm{CH}_{2}\right), 29.0\left(\mathrm{CH}_{2}\right), 25.4\left(\mathrm{CH}_{2}\right) \mathrm{ppm}$; $[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=319.1800$, calcd. for $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}: 319.1805$.
(Z)-1-(perfluorophenyl)-2-(6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)ethan-1one ( $\mathbf{1 7 m}$ )

Instead of 2.5 equiv. we used 1.2 equiv. reagents.
Yield: $0.2 \mathrm{~g}(20 \%)$ [0.16 g (16\%)]; yellow crystals; m. p. 191-192 ${ }^{\circ} \mathrm{C}\left(\mathrm{CDCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR (500 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 11.49(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.52(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.43(\mathrm{dd}, J=8.8,2.4 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{ArH}), 6.32(\mathrm{~d}, J=2.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 5.65(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.55(\mathrm{td}, J=6.8,3.3 \mathrm{~Hz}, 2 \mathrm{H}$, $\left.\mathrm{CH}_{2}\right), 3.36\left(\mathrm{t}, J=6.6 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 2.92\left(\mathrm{t}, J=6.7 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.10-1.96\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right)$ ppm; ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 181.3(\mathrm{C}=\mathrm{O})$, $165.4(\mathrm{CF}), 160.9(\mathrm{C}=), 150.4(\mathrm{C}=), 145.0$ (CF), $138.6(\mathrm{C}=), 127.9(=\mathrm{CH}), 114.6(\mathrm{C}=)$, $110.4(=\mathrm{CH}), 110.2(=\mathrm{CH}), 105.1(\mathrm{CF}), 96.9$ $(\mathrm{C}=), 91.0(=\mathrm{CH}), 47.5\left(\mathrm{CH}_{2}\right), 39.0\left(\mathrm{CH}_{2}\right), 28.6\left(\mathrm{CH}_{2}\right), 25.4\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( 282 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta-142.49(\mathrm{dd}, J=23.7,8.3 \mathrm{~Hz}, 2 \mathrm{~F}, \mathrm{ArF}),-155.93(\mathrm{t}, J=20.8 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{ArF}),-162.48$ (dt, $J=23.9,8.5 \mathrm{~Hz}, 2 \mathrm{~F}, \mathrm{ArF}$ ) ppm; $[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=409.1337$, calcd. for $\mathrm{C}_{21} \mathrm{H}_{18} \mathrm{~F}_{5} \mathrm{~N}_{2} \mathrm{O}$ : 409.1334.

## General procedure for the preparation of boroisoquinolines

Into a round bottom flask 1 mmol appropriate 1-methylidene-3,4-dihydroisoquinoline (17) was measured $\{(Z)$-1-(6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one (17a) $(0.22 \mathrm{~g}), \quad(Z)$-1-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one (17b) $(0.25 \mathrm{~g}),(Z)$-2-(6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (17c) $(0.28 \mathrm{~g}),(Z)$-2-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (17d) $\quad(0.31 \quad \mathrm{~g}), \quad(Z)$-2-(6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1-one ( $\mathbf{1 7 e}$ ) ( 0.29 g ), (Z)-2-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1-one (17f) (0.32 g), (Z)-2-(6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one (17g) (0.32 g), (Z)-2-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one (17h) (0.40 g), (Z)-2-(6,7-
dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(4-nitrophenyl)ethan-1-one (17j) (0.35 g), (Z)-1-(6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one (17k) (0.26 g), (Z)-1-phenyl-2-(6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)ethan-1-one (171) ( 0.32 g ), ( $Z$ )-1-(perfluorophenyl)-2-(6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)ethan-1-one ( $\mathbf{1 7 m}$ ) $(0.41 \mathrm{~g})\}$, and dissolved in 5 mL dichloromethane. The solution was cooled to $0^{\circ} \mathrm{C}, 0.91 \mathrm{~mL}$ diisopropylethylamine ( $0.65 \mathrm{~g}, 5.0 \mathrm{mmol}, 5.0$ equiv) was added. 0.64 mL trifluorborane diethyl etherate ( $0.71 \mathrm{~g}, 5.0 \mathrm{mmol}, 5.0$ equiv) was added dropwise. The reaction mixture was stirred for 1 h at room temperature. The reaction mixture was concentrated and purified by flash column chromatography on silica gel using hexane/dichloromethane.
(Z)-1-(2-(difluoroboranyl)-6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one (18a)

Yield: $0.20 \mathrm{~g}(77 \%)$, white crystals, m. p. $164-165{ }^{\circ} \mathrm{C}(\mathrm{EtOAc}) ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.64(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.87(\mathrm{dd}, J=8.7,2.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.78(\mathrm{~d}, J=1.9 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{ArH}), 5.86(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.88\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.71\left(\mathrm{t}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.97-2.89(\mathrm{~m}$, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), $2.18\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 174.7(\mathrm{C}=\mathrm{O}), 163.8(\mathrm{C}=)$, $161.7(\mathrm{C}=), 140.2(\mathrm{C}=), 129.3(=\mathrm{CH}), 119.3(\mathrm{C}=), 113.3(=\mathrm{CH}), 92.4(=\mathrm{CH}), 55.6\left(\mathrm{OCH}_{3}\right)$, $40.2\left(\mathrm{CH}_{2}\right), 27.3\left(\mathrm{CH}_{2}\right), 23.1\left(\mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR $\left(282 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta-139.33(\mathrm{~d}, J=17.1$ $\mathrm{Hz}, 1 \mathrm{~F}, \mathrm{BF})$, $-139.45(\mathrm{~d}, J=17.0 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}) \mathrm{ppm} ;[\mathrm{M}+\mathrm{Na}]^{+}{ }_{\text {measured }}=288.0990$, calcd. for $\mathrm{C}_{13} \mathrm{H}_{14} \mathrm{BF}_{2} \mathrm{NO}_{2} \mathrm{Na}: 288.0983$.

(Z)-1-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2one (18b)

Yield: $0.23 \mathrm{~g}(78 \%)$, white crystals, m. p. $228-230{ }^{\circ} \mathrm{C}(\mathrm{EtOAc}) ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.11(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.75(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 5.82(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.95\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.93(\mathrm{~s}, 3 \mathrm{H}$, $\mathrm{OCH}_{3}$ ), $3.69\left(\mathrm{t}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.94-2.83\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.19\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$

NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 174.4(\mathrm{C}=\mathrm{O})$, $162.8(\mathrm{C}=)$, $161.1(\mathrm{C}=)$, $153.2(\mathrm{C}=)$, $147.8(\mathrm{C}=)$, $132.0(\mathrm{C}=), 118.3(\mathrm{C}=), 111.2(=\mathrm{CH}), 109.3(=\mathrm{CH}), 91.9(=\mathrm{CH}), 55.9\left(\mathrm{OCH}_{3}\right), 56.7\left(\mathrm{OCH}_{3}\right)$, $39.9\left(\mathrm{CH}_{2}\right), 26.1\left(\mathrm{CH}_{2}\right), 22.6\left(\mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR $\left(282 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta-139.21(\mathrm{~d}, J=16.5$ $\mathrm{Hz}, 1 \mathrm{~F}, \mathrm{BF}),-139.33(\mathrm{~d}, J=16.8 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}) \mathrm{ppm} ;[\mathrm{M}+\mathrm{Na}]^{+}{ }_{\text {measured }}=318.1094$, calcd. for $\mathrm{C}_{14} \mathrm{H}_{16} \mathrm{BF}_{2} \mathrm{NO}_{3} \mathrm{Na}$ : 318.1089.

(Z)-2-(2-(difluoroboranyl)-6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (18c)
Yield: $0.23 \mathrm{~g}(70 \%)$, yellow crystals, m. p. $183^{\circ} \mathrm{C}\left(\mathrm{CDCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 7.98 (d, $J=7.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}$ ), 7.79 (d, $J=8.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), $7.54-7.40$ (m, $J=24.5,7.2 \mathrm{~Hz}$, $3 \mathrm{H}, \mathrm{ArH}), 6.91(\mathrm{dd}, J=8.7,2.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.81(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.55(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.89(\mathrm{~s}$, $3 \mathrm{H}, \mathrm{OCH}_{3}$ ), $3.85-3.73\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.97\left(\mathrm{t}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( 125 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 169.3(\mathrm{C}=\mathrm{O})$, $163.8(\mathrm{C}=)$, $162.1(\mathrm{C}=)$, $140.2(\mathrm{C}=)$, $134.1(\mathrm{C}=)$, 131.8. $(=\mathrm{CH})$, $129.4(=\mathrm{CH})$, $128.6(=\mathrm{CH})$, $127.1(=\mathrm{CH})$, $119.8(\mathrm{C}=), 113.41\left(\mathrm{CH}_{2}\right), 113.39\left(\mathrm{CH}_{2}\right), 89.7$ $(=\mathrm{CH}), 55.7\left(\mathrm{OCH}_{3}\right), 40.4\left(\mathrm{CH}_{2}\right), 27.3\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR $\left(282 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta-139.70(\mathrm{~d}$, $J=16.6 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-139.82(\mathrm{~d}, J=16.6 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}) \mathrm{ppm} ;[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=328.1322$, calcd. for $\mathrm{C}_{18} \mathrm{H}_{17} \mathrm{BF}_{2} \mathrm{NO}_{2}: 328.1320$.

(Z)-2-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (18d)
Yield: $0.31 \mathrm{~g}(88 \%)$, yellow crystals, m. p. $219-221^{\circ} \mathrm{C}(\mathrm{EtOAc}) ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.00-7.91(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}), 7.51-7.39(\mathrm{~m}, 3 \mathrm{H}, \mathrm{ArH}), 7.25(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.77(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH})$, $6.49(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.98\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.97\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.75\left(\mathrm{t}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$, 2.93-2.89 (m, 2H, CH 2 ) ppm; ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.5(\mathrm{C}=\mathrm{O}), 162.0(\mathrm{C}=)$, $153.8(\mathrm{C}=)$, $148.4(\mathrm{C}=) 134.1(\mathrm{C}=)$, $132.4(\mathrm{C}=)$, $131.7(=\mathrm{CH})$, $128.5(=\mathrm{CH})$, $127.1(=\mathrm{CH})$, $119.3(\mathrm{C}=), 110.7(=\mathrm{CH}), 110.0(=\mathrm{CH}), 87.8(=\mathrm{CH}), 56.5\left(\mathrm{OCH}_{3}\right), 56.2\left(\mathrm{OCH}_{3}\right), 40.5\left(\mathrm{CH}_{2}\right)$, $26.6\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-139.46(\mathrm{~d}, J=16.0 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-139.57(\mathrm{~d}$, $J=16.1 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}) \mathrm{ppm} ;[\mathrm{M}+\mathrm{Na}]^{+}{ }_{\text {measured }}=380.1248$, calcd. for $\mathrm{C}_{19} \mathrm{H}_{18} \mathrm{BF}_{2} \mathrm{NO}_{2} \mathrm{Na}$ : 380.1246 .

(Z)-2-(2-(difluoroboranyl)-6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1-one (18e)

Yield: $0.17 \mathrm{~g}(50 \%)$, yellow crystals, m. p. $175-178^{\circ} \mathrm{C}\left(\mathrm{CDCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.79-7.77(\mathrm{~m}, 1 \mathrm{H}, \mathrm{ArH}), 7.75(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.53$ ( dd, J = $4.9,0.8 \mathrm{~Hz}, 1 \mathrm{H}$, ArH), 7.15-7.11 (m, 1H, ArH), 6.94-6.90 (m, 1H, ArH), 6.81 ( $\mathrm{d}, J=2.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 6.39 (s, $1 \mathrm{H}, \mathrm{HC}=$ ), $3.90\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.78\left(\mathrm{t}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.00-2.95\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$ ppm; ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 163.8(\mathrm{C}=\mathrm{O})$, $161.8(\mathrm{C}=), 140.1(\mathrm{C}=), 136.0(\mathrm{C}=), 130.7$ $(=\mathrm{CH}), 129.6(=\mathrm{CH})$, $129.3(=\mathrm{CH})$, $128.2(=\mathrm{CH})$, $114.1(\mathrm{C}=), 113.41(=\mathrm{CH}), 113.36(=\mathrm{CH})$, $111.0(\mathrm{C}=), 89.1(=\mathrm{CH}), 55.6\left(\mathrm{OCH}_{3}\right), 40.4\left(\mathrm{CH}_{2}\right), 27.4\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( 282 MHz , $\mathrm{CDCl}_{3}$ ) $\delta-140.33(\mathrm{~d}, J=16.6 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-140.45(\mathrm{~d}, J=16.6 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}) \mathrm{ppm}$; $[\mathrm{M}+\mathrm{Na}]^{+}{ }_{\text {measured }}=356.0700$, calcd. for $\mathrm{C}_{16} \mathrm{H}_{14} \mathrm{BF}_{2} \mathrm{NO}_{2} \mathrm{SNa}: 356.0704$.

(Z)-2-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1-one (18f)

Yield: 0.17 g ( $46 \%$ ), yellow crystals, m. p. $238-239{ }^{\circ} \mathrm{C}$ (EtOAc); ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , DMSO- $d_{6}$ ) $\delta 8.20(\mathrm{~d}, J=3.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.93(\mathrm{~d}, J=4.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.59(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH})$, $7.31-7.25(\mathrm{~m}, 1 \mathrm{H}, \mathrm{ArH}), 7.07(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.95(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.92\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.92(\mathrm{~s}$, $3 \mathrm{H}, \mathrm{OCH}_{3}$ ), $3.88\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.61\left(\mathrm{t}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.91\left(\mathrm{t}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$ ppm; ${ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 163.5(\mathrm{C}=\mathrm{O}), 162.1(\mathrm{C}=), 154.2(\mathrm{C}=), 148.4(\mathrm{C}=), 138.8$ $(\mathrm{C}=)$, $132.9(\mathrm{C}=), 132.8(=\mathrm{CH}), 131.0(=\mathrm{CH}), 129.2(=\mathrm{CH}), 118.8(\mathrm{C}=), 111.8(=\mathrm{CH}), 89.7$ $(=\mathrm{CH}), 56.8\left(\mathrm{OCH}_{3}\right), 56.4\left(\mathrm{OCH}_{3}\right), 40.7\left(\mathrm{CH}_{2}\right) 26.2\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( 282 MHz , DMSO$\left.d_{6}\right) \delta--137.09(\mathrm{~d}, ~ J=14.6 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-137.21(\mathrm{~d}, J=13.4 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}) \mathrm{ppm}$; $[\mathrm{M}+\mathrm{Na}]^{+}{ }_{\text {measured }}=386.0807, \mathrm{C}_{17} \mathrm{H}_{16} \mathrm{BF}_{2} \mathrm{NO}_{3} \mathrm{SNa}$ 386.081.

(Z)-2-(2-(difluoroboranyl)-6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one (18g)
Yield: $0,35 \mathrm{~g}(85 \%)$, white crystals, m. p. $144-145^{\circ} \mathrm{C}(\mathrm{MeCN}),{ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $7.69(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.89(\mathrm{dd}, J=8.8,2.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.81(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.32(\mathrm{~s}$, $1 \mathrm{H}, \mathrm{CH}), 3.89\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.80\left(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.05-2.97\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 171.0(\mathrm{C}=\mathrm{O})$, 168.5 (=CF), 161.9 ( $\mathrm{C}=$ ), 158.6 (=CF), 157.2 (=CF), $154.5(\mathrm{C}=)$, $148.6(\mathrm{C}=)$, $132.8(\mathrm{C}=)$, $120.7(=\mathrm{CH})$, $118.4(\mathrm{C}=)$, $110.8(=\mathrm{CH}), 109.9(=\mathrm{CH})$, $97.6(=\mathrm{CH}), 56.3\left(\mathrm{OCH}_{3}\right) 40.9\left(\mathrm{CH}_{2}\right), 26.3\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 138.64 - - 138.91 (m, 2F, ArF), -139.23 (d, $J=15.5 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}$ ), -139.34 (d, $J=15.5 \mathrm{~Hz}, 1 \mathrm{~F}$, BF), $-150.50--150.84(\mathrm{~m}, J=22.5,19.4 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{ArF}),-160.97--161.39$ (m, 2F, ArF) ppm; HRMS $\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+}{ }_{\text {measured }}=435.1100$, calcd. for $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{BF}_{7} \mathrm{~N}_{2} \mathrm{O}_{2}: 435.1109$.

(Z)-2-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one (18h)

Yield: $0.40 \mathrm{~g}(89 \%)$, yellow crystals, m. p. $217{ }^{\circ} \mathrm{C}(\mathrm{EtOAc}) ;{ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $7.10(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.81(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.23(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.98\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 3.92\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)$, $3.84-3.79\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.01-2.95\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$
$161.9(\mathrm{C}=\mathrm{O}), 158.6(\mathrm{C}=)$, $154.5(\mathrm{C}=), 148.6(\mathrm{C}=), 146.0(\mathrm{C}=), 143.8(=\mathrm{CF}), 137.8(\mathrm{~d}, \mathrm{~J}=$ $255.0 \mathrm{~Hz},=\mathrm{CF})$, 132.8 ( $\mathrm{C}=$ ), 130.3 (=CF), 118.4 ( $\mathrm{C}=$ ), 110.8 (=CH), $109.8(=\mathrm{CH}), 97.6$ $(=\mathrm{CH}), 56.34\left(\mathrm{OCH}_{3}\right), 56.28\left(\mathrm{OCH}_{3}\right), 40.9\left(\mathrm{CH}_{2}\right), 26.3\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( 282 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta-138.70-138.95(\mathrm{~m}, 2 \mathrm{~F}, \mathrm{ArF}),-139.02(\mathrm{~d}, J=15.1 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-139.13(\mathrm{~d}, J=$ $14.9 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-150.60(\mathrm{t}, J=20.2 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{ArF}),-160.97-161.35(\mathrm{~m}, 2 \mathrm{~F}, \mathrm{ArF}) . \mathrm{ppm}$; $[\mathrm{M}+\mathrm{H}]_{\text {measured }}^{+}=470.0769$, calcd. for $\mathrm{C}_{19} \mathrm{H}_{13} \mathrm{BF}_{7} \mathrm{NO}_{3}: 470.0774$.

(Z)-2-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(4-nitrophenyl)ethan-1-one (18j)
Yield: 0.19 g (49\%), yellow crystals, m. p. $275-276{ }^{\circ} \mathrm{C}(\mathrm{MeCN}) ;{ }^{1} \mathrm{H}$ NMR ( 500 MHz , DMSO- $d_{6}$ ) $\delta 8.34(\mathrm{~s}, 4 \mathrm{H}, \mathrm{ArH}), 4.66(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 7.17(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 7.08(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.92$ $\left(\mathrm{s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.88\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.67\left(\mathrm{t}, J=6.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.93\left(\mathrm{t}, J=6.2 \mathrm{~Hz}, \mathrm{CH}_{2}\right)$ ppm; ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.9(\mathrm{C}=\mathrm{O}), 164.8(\mathrm{C}=), 162.6(\mathrm{C}=), 154.6(\mathrm{C}=), 149.5$ $(\mathrm{C}=)$, $148.5(\mathrm{C}=)$, $139.9(\mathrm{C}=)$, $133.3(\mathrm{C}=)$, $128.7(=\mathrm{CH})$, $124.2(=\mathrm{CH})$, $112.2(=\mathrm{CH})$, 111.7 $(=\mathrm{CH}), 93.4(=\mathrm{CH}), 56.9\left(\mathrm{OCH}_{3}\right), 56.5\left(\mathrm{OCH}_{3}\right), 41.0\left(\mathrm{CH}_{2}\right), 26.0\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR (282 MHz, DMSO- $d_{6}$ ) $\delta-136.26--136.84(\mathrm{~m}, 2 \mathrm{~F}, \mathrm{BF}) \mathrm{ppm} ;[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=403.1271$, calcd. for $\mathrm{C}_{19} \mathrm{H}_{18} \mathrm{BF}_{2} \mathrm{~N}_{2} \mathrm{O}_{5}: 403.1271$.

(Z)-1-(2-(difluoroboranyl)-6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one ( $\mathbf{1 8 k}$ )

Yield: 0.24 g ( $78 \%$ ); yellow crystals; m. p. $196-198{ }^{\circ} \mathrm{C}\left(\mathrm{CDCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 7.52(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.45(\mathrm{dd}, J=8.8,2.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.33(\mathrm{~d}, J=1.9$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), $5.80(\mathrm{~s}, 1 \mathrm{H}),, 3.67\left(\mathrm{t}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.38\left(\mathrm{t}, J=6.6 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 2.91$ - $2.83\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.15\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 2.07-2.03\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 172.5(\mathrm{C}=\mathrm{O}), 161.5(\mathrm{C}=), 151.1(\mathrm{C}=), 139.9(\mathrm{C}=), 129.3(=\mathrm{CH}), 110.4(=\mathrm{CH}), 110.1$ $(=\mathrm{CH}), 92.1(=\mathrm{CH}), 47.6\left(\mathrm{CH}_{2}\right), 40.4\left(\mathrm{CH}_{2}\right), 27.8\left(\mathrm{CH}_{2}\right), 25.4\left(\mathrm{CH}_{2}\right), 23.0\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-140.27(\mathrm{~d}, J=17.1 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-140.40(\mathrm{~d}, J=17.4 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF})$ ppm; $[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=305.1640$, calcd. for $\mathrm{C}_{16} \mathrm{H}_{20} \mathrm{BF}_{2} \mathrm{~N}_{2} \mathrm{O}: 305.1631$.

(Z)-2-(2-(difluoroboranyl)-6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (181)
Yield: 0.36 g (97\%); orange crystals; m. p. 233-235 ${ }^{\circ} \mathrm{C}\left(\mathrm{CDCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 7.99-7.96(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}), 7.67(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.46-7.41(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH})$, $6.51-6.47(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}), 6.36(\mathrm{~d}, J=2.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{HC}=), 3.76\left(\mathrm{t}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.40$ ( $\mathrm{t}, J=6.6 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{CH}_{2}$ ), $2.94-2.88\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.10-2.00\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.5(\mathrm{C}=\mathrm{O})$, $167.4(\mathrm{C}=)$, $161.3(\mathrm{C}=), 150.7(\mathrm{C}=), 139.4(\mathrm{C}=), 130.7$ $(=\mathrm{CH}), 128.8(=\mathrm{CH}), 127.9(=\mathrm{CH}), 126.4(=\mathrm{CH}), 109.9(=\mathrm{CH}), 109.7(=\mathrm{CH}), 109.5(=\mathrm{C})$, $89.2(=\mathrm{CH}), 47.2\left(\mathrm{CH}_{2}\right), 40.0\left(\mathrm{CH}_{2}\right), 27.4\left(\mathrm{CH}_{2}\right), 24.9\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( 282 MHz , $\mathrm{CDCl}_{3}$ ) $\delta-140.65(\mathrm{~d}, J=16.8 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-140.77(\mathrm{~d}, J=17.2 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}) \mathrm{ppm}$; $[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=367.1780$, calcd. for $\mathrm{C}_{21} \mathrm{H}_{22} \mathrm{BF}_{2} \mathrm{~N}_{2} \mathrm{O}: 367.1788$.

(Z)-2-(2-(difluoroboranyl)-6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one (18m)
Yield: 0.37 g ( $81 \%$ ); yellow crystals; m. p. $214-216{ }^{\circ} \mathrm{C}\left(\mathrm{CDCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 7.52(\mathrm{~d}, J=8.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.47(\mathrm{dd}, J=8.9 .2 .4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.37(\mathrm{~d}, J=2.0$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{ArH}), 6.22(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.78\left(\mathrm{t}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.43-3.37\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right)$, $2.98-2.89\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.07\left(\mathrm{t}, J=6.6 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR $\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 181.0 ( $\mathrm{C}=\mathrm{O}$ ), 169.7 ( $\mathrm{C}=$ ), 161.4 ( $\mathrm{C}=$ ), 160.2 ( $\mathrm{C}=$ ), 156.4 ( $=\mathrm{CF}$ ), 151.7 ( $\mathrm{C}=$ ), $140.0(\mathrm{C}=)$, 136.8 (=CF), 135.3 (=CF), $129.7(=\mathrm{CH}), 110.6(=\mathrm{CH}), 110.3(=\mathrm{CH}), 97.7(=\mathrm{CH}), 47.7\left(\mathrm{CH}_{2}\right)$, $40.8\left(\mathrm{CH}_{2}\right), 27.5\left(\mathrm{CH}_{2}\right), 25.4\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-138.97(\mathrm{dd}, J=$ $23.8,6.5 \mathrm{~Hz}, 2 \mathrm{~F}, \mathrm{ArF}),-140.40(\mathrm{~d}, J=16.3 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-140.51$ ( $\mathrm{d}, J=16.4 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}$ ), 151.63 ( $\mathrm{t}, J=21.0 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{ArF}$ ), -161.59 ( $\mathrm{qd}, J=10.6,4.4 \mathrm{~Hz}, 2 \mathrm{~F}, \operatorname{ArF}$ ) ppm; $\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+}{ }_{\text {measured }}=474.1584$, calcd. for $\mathrm{C}_{21} \mathrm{H}_{20} \mathrm{BF}_{7} \mathrm{~N}_{3} \mathrm{O}: 474.1582$.


## General procedure of the dehydrogenation

Into a microwave reactor tube 0.1 g boroisoquinoline ( $Z$ )-1-(2-(difluoroboranyl)-6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one (18a) (0.38 mmol), (Z)-1-(2-
(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one ( 0.34 mmol ), (Z)-2-(2-(difluoroboranyl)-6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (18c) ( 0.31 mmol ), ( $Z$ )-2-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one ( 0.28 mmol ) ( $\mathbf{1 8 d}$ ), (Z)-2-(2-(difluoroboranyl)-6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1-one ( 0.30 mmol ) (18e), ( $Z$ )-2-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1-one (18f) ( 0.75 mmol ) was measured. 0.15 g Selcat Q6 $10 \% \mathrm{Pd} / \mathrm{C}$ catalyst and 2 mL dioxane was added. Then the reaction mixture was heated $200{ }^{\circ} \mathrm{C}$ for 1.5 h . The suspension was filtered through celite. The product was purified by flash column chromatography on silica gel using hexane/dichloromethane.
(Z)-1-(2-(difluoroboranyl)-6-methoxyisoquinolin-1(2H)-ylidene)propan-2-one (19a)

Yield: $0.072 \mathrm{~g}(73 \%)$, white crystals, m. p. $183-184^{\circ} \mathrm{C}$ (hexane-EtOAc) ${ }^{1}{ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz}$, DMSO- $d_{6}$ ) $\delta 8.47(\mathrm{~d}, J=9.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.03(\mathrm{~d}, J=6.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.66(\mathrm{~d}, J=6.8 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{ArH}$ ), 7.47 (d, $J=2.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{HC}=), 7.39$ (dd, $J=9.2,2.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{HC}=), 6.81$ (s, 1H, $\mathrm{HC}=$ ), $3.97\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 2.20\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz, DMSO- $d_{6}$ ) $\delta 169.2$ $(\mathrm{C}=\mathrm{O})$, $163.8(\mathrm{C}=), 151.4(\mathrm{C}=), 139.4(\mathrm{C}=), 132.0(=\mathrm{CH}), 128.9(=\mathrm{CH}), 121.2(=\mathrm{CH}), 118.4$ $(=\mathrm{CH}), 117.4(\mathrm{C}=), 107.1(=\mathrm{CH}), 92.2(=\mathrm{CH})$, $56.5\left(\mathrm{OCH}_{3}\right), 23.0\left(\mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR (282 $\left.\mathrm{MHz}, \mathrm{DMSO}-d_{6}\right) \delta-135.38(\mathrm{~d}, J=16.6 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-135.50(\mathrm{~d}, J=16.5 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}) \mathrm{ppm}$; $[\mathrm{M}+\mathrm{Na}]^{+}{ }_{\text {measured }}=286.0826$, calcd. for $\mathrm{C}_{13} \mathrm{H}_{12} \mathrm{BF}_{2} \mathrm{NO}_{2} \mathrm{Na}$ : 286.0827.

(Z)-1-(2-(difluoroboranyl)-6,7-dimethoxyisoquinolin-1(2H)-ylidene)propan-2-one (19b)

Yield: $0.070 \mathrm{~g}(70 \%)$, white crystals, m. p. $201-202{ }^{\circ} \mathrm{C}$ (EtOAc); ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , DMSO- $d_{6}$ ) $\delta 7.96(\mathrm{t}, \mathrm{J}=12.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.72(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 7.62(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{HC}=)$, 7.47 (s, 1H, HC=), $6.83(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.98\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.97\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 2.19(\mathrm{~s}, 3 \mathrm{H}$,
$\mathrm{CH}_{3}$ ) ppm; ${ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{DMSO}-d_{6}\right) \delta 167.9(\mathrm{C}=\mathrm{O})$, $155.6(\mathrm{C}=), 151.5(\mathrm{C}=), 149.6$ $(\mathrm{C}=)$, $134.0(\mathrm{C}=)$, $130.2(=\mathrm{CH})$, $118.02(\mathrm{C}=)$, $117.99(=\mathrm{CH})$, $106.9(=\mathrm{CH}), 105.4(=\mathrm{CH}), 92.4$ $(=\mathrm{CH}), 56.7\left(\mathrm{OCH}_{3}\right), 56.6\left(\mathrm{OCH}_{3}\right), 22.8\left(\mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( 282 MHz , DMSO- $d_{6}$ ) $\delta$ $135.87(\mathrm{~d}, J=16.1 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-135.99(\mathrm{~d}, J=16.3 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}) \mathrm{ppm} ;[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=$ 294.1113, calcd. for $\mathrm{C}_{14} \mathrm{H}_{15} \mathrm{BF}_{2} \mathrm{NO}_{2}$ : 294.1113 .

(Z)-2-(2-(difluoroboranyl)-6-methoxyisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (19c) Yield: $0.077 \mathrm{~g}(77 \%)$, yellow crystals, m. p. 228-234 ${ }^{\circ} \mathrm{C}$ (EtOAc); ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , DMSO- $d_{6}$ ) $\delta 8.90(\mathrm{~d}, J=9.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.22-8.17(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}), 8.16(\mathrm{~d}, J=6.7 \mathrm{~Hz}$, $1 \mathrm{H}, \mathrm{ArH}$ ), $7.76(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.60(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 7.54(\mathrm{dd}, J=13.4,4.3 \mathrm{~Hz}, 4 \mathrm{H}$, $2 \mathrm{xArH}, 2 \mathrm{xHC}=), 7.46(\mathrm{dd}, J=9.3 .2 .1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{HC}=), 3.99\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz , DMSO- $d_{6}$ ) $\delta 163.9(\mathrm{C}=\mathrm{O})$, $163.5(\mathrm{C}=)$, $151.5(\mathrm{C}=)$, $139.6(\mathrm{C}=)$, $134.3(\mathrm{C}=)$, 132.1 $(=\mathrm{CH})$, $131.8(=\mathrm{CH})$, $129.5(=\mathrm{CH})$, $129.2(=\mathrm{CH})$, $127.1(=\mathrm{CH})$, $121.4(=\mathrm{CH})$, $119.1(=\mathrm{CH})$, $118.5(\mathrm{C}=), 107.0(=\mathrm{CH}), 90.5(=\mathrm{CH}), 56.5\left(\mathrm{OCH}_{3}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( 282 MHz, DMSO- $d_{6}$ ) $\delta$ $136.77(\mathrm{~d}, J=15.3 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-136.88(\mathrm{~d}, J=14.5 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}) \mathrm{ppm} ;[\mathrm{M}+\mathrm{Na}]^{+}{ }_{\text {measured }}=$ 348.0990, $\mathrm{C}_{18} \mathrm{H}_{14} \mathrm{BF}_{2} \mathrm{NO}_{2} \mathrm{Na}: 348.0983$.

(Z)-2-(2-(difluoroboranyl)-6,7-dimethoxyisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (19d)

Yield: $0.87 \mathrm{~g}(87 \%)$, yellow crystals, m. p. $240-245{ }^{\circ} \mathrm{C}(\mathrm{EtOAc}) ;{ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz}$, DMSO- $d_{6}$ ) $\delta 8.18(\mathrm{dd}, J=6.4 .2 .7 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}), 8.10(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.00(\mathrm{~s}, 1 \mathrm{H}$, ArH), 7.74 (d, $J=6.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{HC}=$ ), $7.57-7.52$ (m, $5 \mathrm{H}, 3 \mathrm{xArH}, 2 \mathrm{xHC}=$ ), 4.08 ( $\mathrm{s}, 3 \mathrm{H}$, $\mathrm{OCH}_{3}$ ), $3.99\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{DMSO}-d_{6}$ ) $\delta 162.5(\mathrm{C}=\mathrm{O})$, 155.7 $(\mathrm{C}=)$, $151.8(\mathrm{C}=), 149.4(\mathrm{C}=)$, $138.4(\mathrm{C}=)$, $134.3(\mathrm{C}=)$, $131.6(=\mathrm{CH})$, $130.4(=\mathrm{CH})$, 129.1 $(=\mathrm{CH}), 127.1(=\mathrm{CH}), 119.2(\mathrm{C}=), 118.8(=\mathrm{CH}), 107.0(=\mathrm{CH}), 105.8(=\mathrm{CH}), 90.8(=\mathrm{CH}), 57.1$ $\left(\mathrm{OCH}_{3}\right), 56.7\left(\mathrm{OCH}_{3}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{DMSO}-d_{6}$ ) $\delta-137.46(\mathrm{~d}, J=14.9 \mathrm{~Hz}, 1 \mathrm{~F}$, $\mathrm{BF}),-137.57(\mathrm{~d}, J=14.8 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}) \mathrm{ppm} ;[\mathrm{M}+\mathrm{Na}]^{+}{ }_{\text {measured }}=378.1090$, calcd. for $\mathrm{C}_{19} \mathrm{H}_{16} \mathrm{BF}_{2} \mathrm{NO}_{3} \mathrm{Na}: 378.1089$.

(Z)-2-(2-(difluoroboranyl)-6-methoxyisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1one (19e)

After 1.5 h , further 0.15 g Selcat Q6 was added, and the reaction mixture was heated $200{ }^{\circ} \mathrm{C}$ for 1.5 h in MW reactor.

Yield: $0.052 \mathrm{~g}(52 \%)$, yellow crystals, m. p. $226-228^{\circ} \mathrm{C}$ (EtOAc); ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , DMSO- $d_{6}$ ) $\delta 8.78(\mathrm{t}, J=17.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.18(\mathrm{~d}, J=3.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.09(\mathrm{~d}, J=6.7$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 7.87 (d, $J=4.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), $7.70(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{HC}=), 7.50(\mathrm{~s}, 2 \mathrm{H}$, $\mathrm{ArH}, \mathrm{HC}=$ ), $7.44(\mathrm{~d}, J=9.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{HC}=), 7.30-7.23(\mathrm{~m}, 1 \mathrm{H}, \mathrm{HC}=), 3.97\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right)$ ppm; ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{DMSO}-d_{6}$ ) $\delta 163.9(\mathrm{C}=\mathrm{O})$, $159.2(\mathrm{C}=)$, $151.4(\mathrm{C}=)$, $139.5(\mathrm{C}=)$, $132.2(=\mathrm{CH}), 131.8(=\mathrm{CH}), 129.8(=\mathrm{CH})$, $129.4(=\mathrm{CH})$, $129.4(=\mathrm{CH}), 128.8(\mathrm{C}=), 121.3$ $(=\mathrm{CH}), 118.6(=\mathrm{CH}), 118.3(\mathrm{C}=), 107.1(=\mathrm{CH}), 89.3(=\mathrm{CH}), 56.5\left(\mathrm{OCH}_{3}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR
(282 MHz, DMSO- $d_{6}$ ) $\delta-137.21$ (d, $J=16.0 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}$ ), -137.33 (d, $J=14.9 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}$ ) ppm; $[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=332.0724$, calcd. for $\mathrm{C}_{16} \mathrm{H}_{13} \mathrm{BF}_{2} \mathrm{NO}_{2} \mathrm{~S}: 332.0728$.

(Z)-2-(2-(difluoroboranyl)-6,7-dimethoxyisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1-one (19f)
Yield: $0.048 \mathrm{~g}(48 \%)$, yellow crystals, m. p. $270-272{ }^{\circ} \mathrm{C}\left(\right.$ DMSO- $\left.d_{6}\right) ;{ }^{1} \mathrm{H}$ NMR ( 500 MHz , DMSO- $d_{6}$ ) $\delta 8.20(\mathrm{~d}, J=3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 8.05(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}), 7.92(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH})$, $7.85(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{HC}=), 7.68(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{HC}=), 7.52(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 7.42(\mathrm{~s}, 1 \mathrm{H}$, ArH ), 7.27 (t, $J=4.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{HC}=$ ), $4.06\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.98\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz , DMSO- $d_{6}$ ) $\delta 158.3(\mathrm{C}=\mathrm{O})$, $155.7(\mathrm{C}=)$, $151.8(\mathrm{C}=)$, $149.3(\mathrm{C}=)$, $139.5(\mathrm{C}=), 134.2$ $(\mathrm{C}=), 131.3(=\mathrm{CH}), 130.5(=\mathrm{CH}), 129.5(=\mathrm{CH}), 129.1(=\mathrm{CH}), 119.0(\mathrm{C}=), 118.4(=\mathrm{CH}), 107.0$ $(=\mathrm{CH}), 105.7(=\mathrm{CH}), 89.6(=\mathrm{CH}), 57.0\left(\mathrm{OCH}_{3}\right), 56.7\left(\mathrm{OCH}_{3}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR $(282 \mathrm{MHz}$, DMSO- $d_{6}$ ) $\delta-137.84(\mathrm{~d}, ~ J=14.7 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}),-137.96$ (d, $\left.J=14.7 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{BF}\right) \mathrm{ppm}$; $[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=362.0829$, calcd. for $\mathrm{C}_{17} \mathrm{H}_{15} \mathrm{BF}_{2} \mathrm{NO}_{3} \mathrm{~S}: 362.0834$.

(Z)-1-(2-(diphenylboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2one (20b)

In a sealed tube $0.25 \mathrm{~g}(Z)$-1-(6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one ( $\mathbf{1 7 a}$ ) ( 1.0 mmol ) was dissolved in 3 mL anhydrous toluene. The tube was flushed with argon, then heated $90^{\circ} \mathrm{C}$ for 1 h . The reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using hexane/dichloromethane.

Yield: $0.35 \mathrm{~g}(84 \%)$, yellow crystals, m. p. 207-208 ${ }^{\circ} \mathrm{C}$ (hexane); ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.48-7.45$ (m, 4H, ArH), 7.29 (t, $J=7.2 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{ArH}$ ), $7.25-7.21$ (m, 2H, ArH), 7.15 (s, $1 \mathrm{H}, \mathrm{ArH}$ ), $6.70(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 5.67(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.94\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.34-3.29(\mathrm{~m}, 2 \mathrm{H}$, $\mathrm{CH}_{2}$ ), $2.84-2.79\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.14\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 176.9$ $(\mathrm{C}=\mathrm{O})$, $159.9(\mathrm{C}=), 148.0(\mathrm{C}=), 133.0(=\mathrm{CH}), 131.8(\mathrm{C}=)$, $127.1(=\mathrm{CH}), 126.2(=\mathrm{CH}), 120.1$ $(\mathrm{C}=), 110.4(=\mathrm{CH}), 109.7(=\mathrm{CH}), 92.9(=\mathrm{CH}), 56.3\left(\mathrm{OCH}_{3}\right), 56.1\left(\mathrm{OCH}_{3}\right), 44.4\left(\mathrm{CH}_{2}\right), 26.9$ $\left(\mathrm{CH}_{2}\right)$, $23.7\left(\mathrm{CH}_{3}\right) \mathrm{ppm} ;[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=412.2078$, calcd. for $\mathrm{C}_{26} \mathrm{H}_{27} \mathrm{BNO}_{3}: 412.2079$.

(Z)-1-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one tris(perfluorophenyl)borane salt (22b)

In a sealed tube $0.25 \mathrm{~g}(\mathrm{Z})$-1-(6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one ( $\mathbf{1 7 a}$ ) ( 1.0 mmol ) was dissolved in 3 mL anhydrous toluene. The tube was flushed with argon, then heated $90^{\circ} \mathrm{C}$ for 1 h . The reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using hexane/dichloromethane.

Yield: $0.31 \mathrm{~g}(41 \%)$, yellow crystals, m. p. $100-101^{\circ} \mathrm{C}(\mathrm{MeCN}) ;{ }^{1} \mathrm{H}$ NMR ( 500 MHz , acetone$\left.d_{6}\right) \delta 10.71(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.53(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 7.08(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.18(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.96(\mathrm{~s}, 3 \mathrm{H}$, $\mathrm{OCH}_{3}$ ), $3.89\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.69\left(\mathrm{td}, J=7.4,3.7 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.07\left(\mathrm{t}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$, $2.02\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz , acetone- $d_{6}$ ) $\delta 177.9(\mathrm{C}=\mathrm{O})$, $163.7(\mathrm{C}=), 155.1$ ( $\mathrm{C}=$ ) , 152.8 (=CF), $148.8(\mathrm{C}=)$, $143.8(=\mathrm{CF})$, 138.0 ( $=\mathrm{CF}$ ), 133.2 ( $\mathrm{C}=$ ), $118.0(\mathrm{C}=)$, 111.5
$(=\mathrm{CH}), 110.8(=\mathrm{CH}), 94.2(=\mathrm{CH})$, $55.7\left(\mathrm{OCH}_{3}\right), 55.6\left(\mathrm{OCH}_{3}\right), 39.5\left(\mathrm{CH}_{2}\right), 25.9\left(\mathrm{CH}_{2}\right), 23.0$ $\left(\mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-134.79-135.11$ (m, 3F, ArF), $-136.07--136.41$ (m, 3F, ArF), -158.33 (t, $J=20.3 \mathrm{~Hz}, 3 \mathrm{~F}, \mathrm{ArF}),-164.27--164.56(\mathrm{~m}, 6 \mathrm{~F}, \mathrm{ArF})$. ppm; In the HRMS the isoquinolinium cation could be detected: $[\mathrm{M}+\mathrm{H}]^{+}$measured $=248.1291$, calcd. for $\mathrm{C}_{14} \mathrm{H}_{18} \mathrm{NO}_{3}$ : 248.1281 . The LRMS spectrum of the salt is presented in the Supplementary Material showing the full molecular mass in negative ionization.

(Z)-1-(2-(bis(perfluorophenyl)boranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one (21b)

In a sealed tube $0.76 \mathrm{~g}(Z)$-1-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2one tris(perfluorophenyl)borane salt (22b) ( 1.0 mmol ) was dissolved in 3 mL anhydrous toluene. The tube was flushed with argon, then heated $200{ }^{\circ} \mathrm{C}$ for 16 h . The reaction mixture was concentrated under reduced pressure. The residue was purified by preparative thin lyar chromatography on silica gel using dichloromethane.
Yield: $0.018 \mathrm{~g}(3 \%)$, yellow crystals, m. p. $171-173{ }^{\circ} \mathrm{C}(\mathrm{MeCN}) ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.15(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.71(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 5.80(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.95\left(\mathrm{~s}, 6 \mathrm{H}, 2 \mathrm{xOCH}_{3}\right), 3.37(\mathrm{t}, J=$ $7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}$ ), $2.88\left(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.12\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( 125 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 176.3(\mathrm{C}=\mathrm{O}), 161.1(\mathrm{C}=), 153.9(\mathrm{C}=), 149.4(=\mathrm{CF}), 148.2(\mathrm{C}=), 147.5(=\mathrm{CF})$, $143.7(=\mathrm{CF}), 132.2(\mathrm{C}=), 119.1(\mathrm{C}=), 110.4(=\mathrm{CH}), 109.9(=\mathrm{CH}), 93.2(=\mathrm{CH}), 56.3\left(\mathrm{OCH}_{3}\right)$, $56.2\left(\mathrm{OCH}_{3}\right), 43.5\left(\mathrm{CH}_{2}\right), 26.3\left(\mathrm{CH}_{2}\right), 23.1\left(\mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 135.51 (dd, $J=24.1,9.2 \mathrm{~Hz}, 4 \mathrm{~F}, \mathrm{ArF}$ ), $-157.38(\mathrm{t}, J=20.3 \mathrm{~Hz}, 2 \mathrm{~F}, \mathrm{ArF}),-164.08(\mathrm{td}, J=$ 23.9, $9.2 \mathrm{~Hz}, 4 \mathrm{~F}, \mathrm{ArF}) \mathrm{ppm} ;[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=592.1136$, calcd. for $\mathrm{C}_{26} \mathrm{H}_{17} \mathrm{BF}_{10} \mathrm{NO}_{3}: 592.1142$.

(Z)-2-(2-(bis(perfluorophenyl)boranyl)-6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (211)
In a sealed tube $0.32 \mathrm{~g}(\mathrm{Z})-1$-phenyl-2-(6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)ethan-1-one (171) ( 1.0 mmol ) was dissolved in 3 mL anhydrous toluene. The tube was flushed with argon, then heated $200{ }^{\circ} \mathrm{C}$ for 9 h . The reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using hexane/dichloromethane.

Yield: $0.013 \mathrm{~g}(2 \%)$, yellow crystals, m. p. $280-281^{\circ} \mathrm{C}(\mathrm{MeCN}) ;{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.88$ (d, J = $7.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{ArH}$ ), 7.73 (d, J = $8.9 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{ArH}$ ), 7.48 - 7.38 (m, 3H, ArH), 6.54 $-6.47(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}), 6.33(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 3.40\left(\mathrm{q}, \mathrm{J}=6.6 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 2.93(\mathrm{t}, \mathrm{J}=7.0 \mathrm{~Hz}$, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), $2.07\left(\mathrm{t}, \mathrm{J}=6.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 1.31-1.21\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 172.5(\mathrm{C}=\mathrm{O})$, $151.3(\mathrm{C}=), 147.5(=\mathrm{CF}), 144.5(=\mathrm{CF}), 143.9(=\mathrm{CF}) 140.5(\mathrm{C}=), 139.5$ $(\mathrm{C}=), 139.0(=\mathrm{CF}), 134.6(\mathrm{C}=), 132.2(\mathrm{C}=), 131.3(=\mathrm{CH}), 129.5(=\mathrm{CH}), 128.5(=\mathrm{CH}), 127.0$ $(=\mathrm{CH}), 110.4(=\mathrm{CH}), 110.1(=\mathrm{CH})$, $90.2(=\mathrm{CH})$, $47.8\left(\mathrm{CH}_{2}\right), 43.6\left(\mathrm{CH}_{2}\right)$, $29.7\left(\mathrm{CH}_{2}\right), 25.4$ $\left(\mathrm{CH}_{2}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-135.61(\mathrm{dd}, J=24.0,8.1 \mathrm{~Hz}, 4 \mathrm{~F}, \mathrm{ArF}),-158.02$ ( $\mathrm{t}, J=20.3 \mathrm{~Hz}, 2 \mathrm{~F}, \mathrm{ArF}$ ), $-164.27--164.58(\mathrm{~m}, 4 \mathrm{~F}, \mathrm{ArF}) . \mathrm{ppm} ;[\mathrm{M}+\mathrm{H}]^{+}{ }_{\text {measured }}=663.1657$, calcd. for $\mathrm{C}_{33} \mathrm{H}_{22} \mathrm{BF}_{10} \mathrm{~N}_{2} \mathrm{O}$ : 663.1665.


## Procedure for synthesis of acetyl cysteine adducts

$0.01 \mathrm{~g} \quad(Z)$-2-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one ( $\mathbf{1 8 h}$ ) ( 0.022 mmol ) was dissolved in 1 mL DMSO. 0.0015 g $\mathrm{K}_{2} \mathrm{CO}_{3}$ was added, and the reaction mixture was heated $36^{\circ} \mathrm{C}$ for 2 days. The product was purified by preparative HPLC using MeCN/water.
(Z)-N-acetyl-S-(4-(2-(2-(difluoroboranyl)-6,7-dimethoxyisoquinolin-1(2H)-ylidene)acetyl)-

## 2,3,5,6-tetrafluorophenyl)cysteine (24)

Yield: $0.013 \mathrm{~g}(81 \%)$; yellow crystals; m. p. 189-199 ${ }^{\circ} \mathrm{C}(\mathrm{MeCN}) ;{ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 7.365(\mathrm{~s}, 1 \mathrm{H}, \mathrm{COOH}), 7.355(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 7.13(\mathrm{~s}, 1 \mathrm{H}, \mathrm{ArH}), 6.80(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=)$, $6.30(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC}=), 4.70(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 3.97\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.93\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 3.83-3.77(\mathrm{~m}$, $\left.2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.52\left(\mathrm{~d}, J=4.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.00-2.91\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.02\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 171.7(\mathrm{C}=\mathrm{O}), 170.4(\mathrm{COOH}), 161.5(\mathrm{C}=\mathrm{O}), 158.5(\mathrm{C}=), 154.0$ ( $\mathrm{C}=$ ) , 148.1 ( $\mathrm{C}=$ ), $147.8(\mathrm{CF}), 154.9(\mathrm{CF}), 144.7(\mathrm{CF}), 142.8(\mathrm{CF}), 140.3(\mathrm{C}=), 132.3(\mathrm{C}=)$, $128.5(=\mathrm{CH}), 126.8(\mathrm{~d}, J=82.4 \mathrm{~Hz},=\mathrm{CH}), 117.9(\mathrm{C}=), 115.7(\mathrm{C}=), 109.8(\mathrm{~d}, J=105.4 \mathrm{~Hz}$, $=\mathrm{CH})$, $97.3(=\mathrm{CH})$, $55.8\left(\mathrm{OCH}_{3}\right), 51.8\left(\mathrm{OCH}_{3}\right), 40.4\left(\mathrm{CH}_{2}\right), 29.2\left(\mathrm{CH}_{2}\right), 25.8\left(\mathrm{CH}_{2}\right), 22.4$ $\left(\mathrm{CH}_{3}\right) \mathrm{ppm} ;{ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-132.45(\mathrm{dd}, J=23.7,12.0 \mathrm{~Hz}, 2 \mathrm{~F}, \mathrm{ArF}$ ), -138.22 --138.60 (m, 2F, BF), -138.61--138.80 (m), -139.27 (dd, $J=23.3,11.5 \mathrm{~Hz}, 2 \mathrm{~F}, \mathrm{ArF}) \mathrm{ppm}$; $\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+}{ }_{\text {measured }}=608.1451$, calcd. for $\mathrm{C}_{24} \mathrm{H}_{25} \mathrm{BF}_{6} \mathrm{~N}_{3} \mathrm{O}_{6} \mathrm{~S}: 608.1456$.


## 2. Optical spetroscopy data for boroisoquinolines

| Entry |  | $\mathrm{R}^{1^{*}}$ | $\mathrm{R}^{2}$ | $\mathrm{R}^{3}$ | BX | $\lambda_{\text {abs }}^{\max }$ <br> $[\mathrm{nm}]$ | $\lambda_{\text {exc }}{ }^{\max }$ <br> $[\mathrm{nm}]^{* *}$ | $\lambda_{\text {em }}{ }^{\max }$ <br> $[\mathrm{nm}]$ | $\Delta \lambda$ <br> $[\mathrm{nm}]$ | FWMH <br> $[\mathrm{nm}]$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathbf{1 8 a}$ | MeO | H | Me | $\mathrm{BF}_{2}$ | 328 |  | 390 | 62 | 53 |
| 2 | $\mathbf{1 8 b}$ | MeO | MeO | Me | $\mathrm{BF}^{2}$ | 321 | 339 | 431 | 110 | 45 |
| 3 | $\mathbf{1 8 k}$ | Py | H | Me | $\mathrm{BF}_{2}$ | 383 | 379 | 450 | 67 | 40 |
| 4 | $\mathbf{1 8 c}$ | MeO | H | Ph | $\mathrm{BF}_{2}$ | 357 |  | 411 | 54 | 60 |
| 5 | $\mathbf{1 8 d}$ | MeO | MeO | Ph | $\mathrm{BF}_{2}$ | 361 | 380 | 483 | 122 | 57 |
| 6 | $\mathbf{1 8 1}$ | Py | H | Ph | $\mathrm{BF}_{2}$ | 408 | 406 | 537 | 129 | 51 |
| 7 | $\mathbf{2 1 1}$ | Py | H | Ph | $\mathrm{B}_{\left.\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{2}}$ | 417 | 415 | 544 | 127 | 62 |


| 8 | $\mathbf{1 8 e}$ | MeO | H | 2- thienyl | $\mathrm{BF}_{2}$ | 374 |  | 437 | 63 | 55 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 9 | $\mathbf{1 8 f}$ | MeO | MeO | 2- thienyl | $\mathrm{BF}_{2}$ | 383 |  | 448 | 65 | 53 |
| 10 | $\mathbf{1 8 g}$ | MeO | H | $\mathrm{C}_{6} \mathrm{~F}_{5}$ | $\mathrm{BF}_{2}$ | 334 | 343 | 435 | 101 | 48 |
| 11 | $\mathbf{1 8 h}$ | MeO | MeO | $\mathrm{C}_{6} \mathrm{~F}_{5}$ | $\mathrm{BF}_{2}$ | 334 | 356 | 537 | 203 | 66 |
| 12 | $\mathbf{1 8 m}$ | Py | H | $\mathrm{C}_{6} \mathrm{~F}_{5}$ | $\mathrm{BF}_{2}$ | 411 | 410 | 565 | 154 | 53 |
| 13 | $\mathbf{2 0 b}$ | MeO | MeO | Me | $\mathrm{BPh}_{2}$ | 337 | 387 | 453 | 116 | 43 |
| 14 | $\mathbf{2 1 b}$ | MeO | MeO | Me | $\mathrm{B}^{\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{2}}$ | 346 | 372 | 440 | 94 | 48 |
| 15 | 22b | MeO | MeO | Me | $\mathrm{B}_{6} \mathrm{C}_{6} \mathrm{~F}_{5}$ | 357 | 368 | 465 | 108 | 57 |
| 16 | $\mathbf{1 9 a}$ | MeO | H | Me | $\mathrm{BF}_{2}$ | 355 |  | 410 | 55 | 36 |
| 17 | $\mathbf{1 9 b}$ | MeO | MeO | Me | $\mathrm{BF}_{2}$ | 371 |  | 415 | 45 | 47 |
| 18 | $\mathbf{1 9 c}$ | MeO | H | Ph | $\mathrm{BF}_{2}$ | 378 | 372 | 487 | 109 | 55 |
| 19 | $\mathbf{1 9 d}$ | MeO | MeO | Ph | $\mathrm{BF}_{2}$ | 396 |  | 458 | 62 | 54 |
| 20 | $\mathbf{1 9 e}$ | MeO | H | 2- thienyl | $\mathrm{BF}_{2}$ | 401 |  | 471 | 70 | 58 |
| 21 | $\mathbf{1 9 f}$ | MeO | MeO | 2- thienyl | $\mathrm{BF}_{2}$ | 410 |  | 480 | 70 | 62 |
| 22 | $\mathbf{1 8 j}$ | MeO | MeO | 4- $\mathrm{O}_{2} \mathrm{~N}^{2}-\mathrm{C}_{6} \mathrm{H}_{4}$ | $\mathrm{BF}_{2}$ | 370 | - | - | - | 60 |

* pyrrolidine-1-yl


## 3. X-Ray diffraction data for boroisoquinolines 18 f and 19 c

Indexing was performed from 4 oscillations that were exposed for 60 seconds. The crystal-to detector distance was 127.40 mm . The data were collected at a temperature of $20+1^{\circ} \mathrm{C}$ to a maximum $2 \theta$ value of $143.3^{\circ}$. A total of 180 oscillation images were collected. A sweep of data was done using $\omega$ scans from 20.0 to $200.0^{\circ}$ in $5.0^{\circ}$ step, at $\chi=0.0^{\circ}$ and $\varphi=0.0^{\circ}$. The exposure rate was 36.0 [sec./ ${ }^{\circ}$ ]. A second sweep was performed using $\omega$ scans from 20.0 to $200.0^{\circ}$ in $5.0^{\circ}$ step, at $\chi=54.0^{\circ}$ and $\varphi=0.0^{\circ}$. The exposure rate was 36.0 [sec. $/^{\circ}$ ]. Another sweep was performed using $\omega$ scans from 20.0 to $200.0^{\circ}$ in $5.0^{\circ}$ step, at $\chi=54.0^{\circ}$ and $\varphi=$ $90.0^{\circ}$. The exposure rate was $36.0\left[\mathrm{sec} . /^{\circ}\right]$. Another sweep was performed using $\omega$ scans from 20.0 to $200.0^{\circ}$ in $5.0^{\circ}$ step, at $\chi=54.0^{\circ}$ and $\varphi=180.0^{\circ}$. The exposure rate was $36.0\left[\mathrm{sec} . /^{\circ}\right]$. Another sweep was performed using $\omega$ scans from 20.0 to $200.0^{\circ}$ in $5.0^{\circ}$ step, at $\chi=54.0^{\circ}$ and $\varphi=270.0^{\circ}$. The exposure rate was 36.0 [sec./ ${ }^{\circ}$ ]. Readout was performed in the 0.100 mm pixel mode.


Crystal data and structural refinements for compounds 18 f and 19c.

|  | 18 f | 19c |
| :---: | :---: | :---: |
| CCDC | 1854625 | 1854624 |
| Empirical formula | $\mathrm{C}_{17} \mathrm{H}_{16} \mathrm{BF}_{2} \mathrm{NO}_{3} \mathrm{~S}$ | $\mathrm{C}_{18} \mathrm{H}_{14} \mathrm{BF}_{2} \mathrm{NO}_{2}$ |
| Formula weight | 363.19 | 325.12 |
| Temperature/K | 293 | 293 |
| Wavelength ( $\AA$ ) | 1.54187 | 1.54187 |
| Crystal Size (mm) | $0.56 \times 0.26 \times 0.21$ | $0.43 \times 0.17 \times 0.17$ |
| Crystal system | monoclinic | monoclinic |
| Space group | P21/c (\#14) | P21/n (\#14) |
| a/ $\AA$ | 12.1184(6) | 7.7350(3) |
| b/ $\AA$ | 8.1766(4) | 17.5815(7) |
| c/ $\AA$ | 16.5924(9) | 11.0299(4) |
| $\alpha /{ }^{\circ}$ | 90 | 90 |
| $\beta /{ }^{\circ}$ | 93.697(3) | 99.364(2) |
| $\gamma^{\prime}$ | 90 | 90 |
| V/ $\AA^{\mathbf{3}}$ | 1640.68(14) | 1480.01(10) |
| $\mathbf{Z} / \mathbf{D}_{\text {calcd }}\left(\mathrm{g} / \mathrm{cm}^{3}\right)$ | 4/1.470 | 4/1.459 |
| $\mu / \mathbf{c m}^{-1}$ | 21.050 | 9.326 |
| h, k, $\mathbf{l}_{\text {max }}$ | 14, 10, 20 | 9, 21, 13 |
| Final R indices [I >2 $\boldsymbol{\sigma}$ (I)] | $\mathrm{R}=0.1597, \mathrm{R}_{\mathrm{w}}=0.1982$ | $\mathrm{R}=0.0507, \mathrm{R}_{\mathrm{w}}=0.0665$ |
| S | 3.595 | 6.953 |
| Max./min. $\mathrm{e}^{-} / \AA^{-3}$ | 9.94/-20.10 | 4.22/-4.25 |

## 4. ${ }^{1} \mathrm{H} /{ }^{13} \mathrm{C}$ NMR spectra

6-Bromo-1-methyl-3,4-dihydroisoquinoline (16c)


6-Fluoro-1-methyl-3,4-dihydroisoquinoline (16d)



1-methyl-6-(pyrrolidin-1-yl)-3,4-dihydroisoquinoline (16e)

(Z)-2-(6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one (17g)


(Z)-2-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one (17h)


(Z)-1-(6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one (17k)


(Z)-1-phenyl-2-(6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)ethan-1-one (171)


(Z)-1-(perfluorophenyl)-2-(6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)ethan-1one ( $\mathbf{1 7 m}$ )


(Z)-1-(2-(difluoroboranyl)-6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one (18a)


(Z)-1-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2one (18b)


(Z)-2-(2-(difluoroboranyl)-6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (18c)


(Z)-2-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (18d)


(Z)-2-(2-(difluoroboranyl)-6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1-one (18e)

(Z)-2-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1-one (18f)

(Z)-2-(2-(difluoroboranyl)-6-methoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one (18g)


(Z)-2-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one (18h)


(Z)-2-(2-(difluoroboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(4-nitrophenyl)ethan-1-one (18j)


(Z)-1-(2-(difluoroboranyl)-6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one ( $\mathbf{1 8 k}$ )


(Z)-2-(2-(difluoroboranyl)-6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (181)

(Z)-2-(2-(difluoroboranyl)-6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-(perfluorophenyl)ethan-1-one (18m)


(Z)-1-(2-(difluoroboranyl)-6-methoxyisoquinolin-1(2H)-ylidene)propan-2-one (19a)

(Z)-1-(2-(difluoroboranyl)-6,7-dimethoxyisoquinolin-1(2H)-ylidene)propan-2-one (19b)


(Z)-2-(2-(difluoroboranyl)-6-methoxyisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (19c)


(Z)-2-(2-(difluoroboranyl)-6,7-dimethoxyisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (19d)


(Z)-2-(2-(difluoroboranyl)-6-methoxyisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1one (19e)


(Z)-2-(2-(difluoroboranyl)-6,7-dimethoxyisoquinolin-1(2H)-ylidene)-1-(thiophen-2-yl)ethan-1-one (19f)


(Z)-1-(2-(diphenylboranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2one (20b)

(Z)-1-(6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one tris(perfluorophenyl)borane salt (22b)





(Z)-1-(2-(bis(perfluorophenyl)boranyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-ylidene)propan-2-one (21b)


(Z)-2-(2-(bis(perfluorophenyl)boranyl)-6-(pyrrolidin-1-yl)-3,4-dihydroisoquinolin-1(2H)-ylidene)-1-phenylethan-1-one (211)


(Z)-N-acetyl-S-(4-(2-(2-(difluoroboranyl)-6,7-dimethoxyisoquinolin-1(2H)-ylidene)acetyl)-2,3,5,6-tetrafluorophenyl)cysteine (24)



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