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Iodine-Catalyzed Synthesis of *N, N′*-Chelate Organoboron Aminoquinolate

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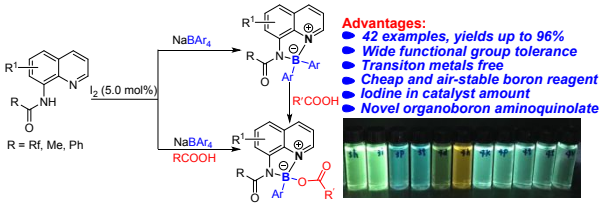
Supporting Information Placeholder



ABSTRACT: We disclose a novel method for the synthesis of fluorescent *N,N′*-chelate organoboron compounds in high efficiency by treatment of aminoquinolates with $NaBAr_4$/R'COOH in the presence of an iodine catalyst. These compounds display high air and thermal stability. A possible catalytic mechanism based on the results of control experiments has been proposed. Fluorescence quantum yield of **3b** is up to 0.79 in dichloromethane.

INTRODUCTION

N,N′-chelate organoboron fluorescents have wide applications in areas such as luminescent materials,[1] fluorescent dyes,[2] photosensitizers,[3] molecular switches,[4] photodynamic therapy,[5] molecular probes,[6] and cell imaging.[7] For example (Figure 1), boron dipyrromethene derivatives have been successfully applied in photodynamic therapy and as fluorescence probe (**A1**),[8] while 2,2′-(pyridine2,6-diyl)diphenolate derivatives (**A2**), with great thermally activated delayed fluorescence, in organic light-emitting devices (OLEDs).[9] Moreover, BPh_2(aq) polymer (**A3**), which is a class of fluorescent main-chain type organoboron aminoquinolate polymers with efficient energy transfer and well π-extended linker units, plays a role in light harvesting antenna.[10] Very recently, the aminoquinolate diarylboron complexes were synthesized and utilized as photocatalysts (**A4**).[11]

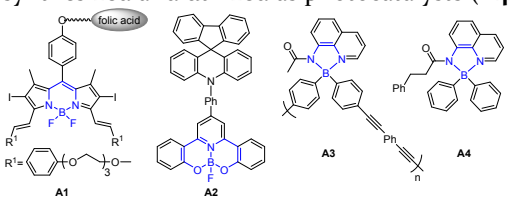
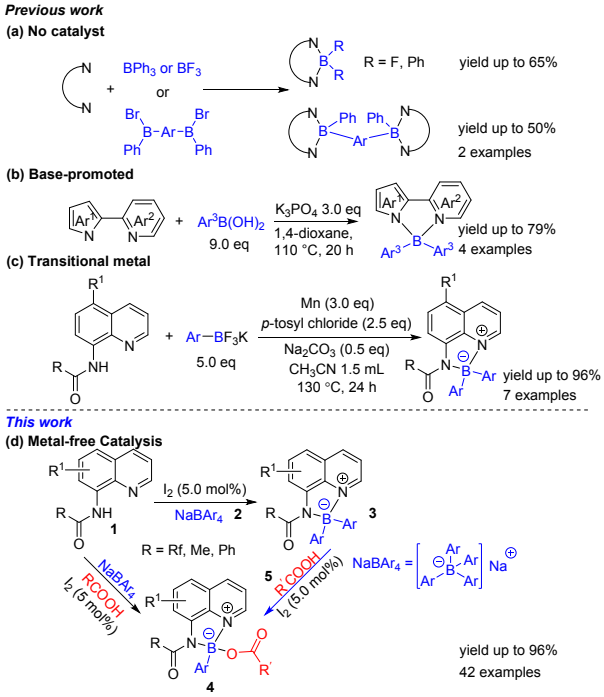


Figure 1. *N,N′*-chelate organoboron fluorescents

Scheme 1. Synthesis of *N,N′*-chelate organoboron fluorescents



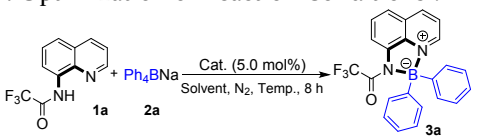
To fulfil the ever increasing demand of *N,N′*-chelate organoboron in material chemistry, efficient production is required. There are two kinds of synthetic methods (Scheme 1). In Scheme 1a, BF_3,[12] BPh_3[13] or complex $ArB_2Ph_2Br_2$[14] reacts with *N, N′*-bidendate ligand without the need of a catalyst to yield the desired four-coordinate organoboron with moderate efficiency (30–60%). In Scheme 1b, the base-promoted one-pot synthesis of four-coordinate organoboron is also an efficient route,[15] but nine equivalents of aryl boronic acids were required. Therefore, the development of a highly efficient method for the synthesis of such kind of molecular framework is still meaningful. Very recently, Xu's group studied the use of transition metal (Mn powder, 3.0 equiv.) in the synthesis of aminoquinolate diarylboron complexes successfully (Scheme 1c).[11] Herein, in continuation of our study on aminoquinoline synthesis,[16] we disclose a new protocol to afford *N,N′*-chelate organoboron with fluorescence properties by treatment of aminoquinolates with $NaBAr_4$/R'COOH in the presence of an iodine catalyst (Scheme 1d).

RESULTS AND DISCUSSION

Initially, 2,2,2-trifluoro-N-(quinolin-8-yl)acetamide (**1a**) and sodium tetraphenylborate (**2a**) were selected as substrates for the optimization of reaction conditions (Table 1). When the reaction was carried out in the presence of catalytic amount of $CuBr_2$ (0.05 equiv.), (κ^2-(N,N)-8-trifluoroacetyl aminoquinolate) diphenylborane **3a** was generated in 38% yield as the only product (entry 1, the structure of **3a** has been confirmed by X-ray analysis, see Supporting information, SI).[17] Over $Cu(OAc)_2{\bullet}H_2O$, the yield is in trace amount, whereas over CuCl and CuBr the yield is around 43% (entries 2–4). Adding $AgNO_3$, $K_2S_2O_8$, $PhI(OAc)_2$ or I_2 together with $CuBr_2$ would increase the **3a** yield to 53%~90% (entries 5–9). It was found that the use of I_2 alone can give a **3a** yield of up to 90% (entry 10). The results of solvent screening reveal that toluene is the most suitable for the reaction (entries 12–15). Lowering of reaction temperature from 150 °C to 120 °C would decrease the yield of **3a** (entries 14–15). There is no reaction when O_2 is present (entries 16).

With the standard reaction conditions in hand, we investigated the substrate scope with respect to quinoline derivatives (Scheme 2). The reaction displayed good tolerance towards a wide range of functional groups such as Cl (**3b**, 76%), Br (**3c**, 82%), thienyl (**3g**, 96%), methyl (**3h**, 78%), and methoxy (**3i**, 80%) that are attached to the quinoline ring. Notably, substrates with electron withdrawing groups gave higher yields (**3d**–**3f**, 86–92%) than did substrates with electron-donating groups (**3h**–**3i**, 78–80%). Replacing the CF_3 group of **1a** by a methyl group would result in lower yield (**3j**, 47%). Comparing with previous report[10], the yield of **3j** was less than 43% by treating air-sensitive triarylborane (BPh_3) with N-(quinolin-8-yl)acetamide. Replacing CF_3 group with C_2F_5, C_3F_7 or C_6F_5 resulted in medium yields (**3k**–**3m**, 63–81%). Various sodium tetraarylborate derivatives **2** were screened to extend the substrate scope, and **3n**–**3t** were generated in moderate to good yields (67%–82%). The substrate with an electron-donating group at the para-position of aryl group in sodium tetraarylborate still gave 82% yield of **3q**. Furthermore, the substrate with a large electron-withdrawing group C_6F_5 still gave 67% yield of **3t**. The above results indicate that the electronic property of BAr_2 had little effect on **3n**–**3t** yields.

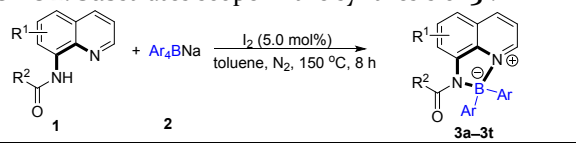
Table 1. Optimization of Reaction Conditions[a].

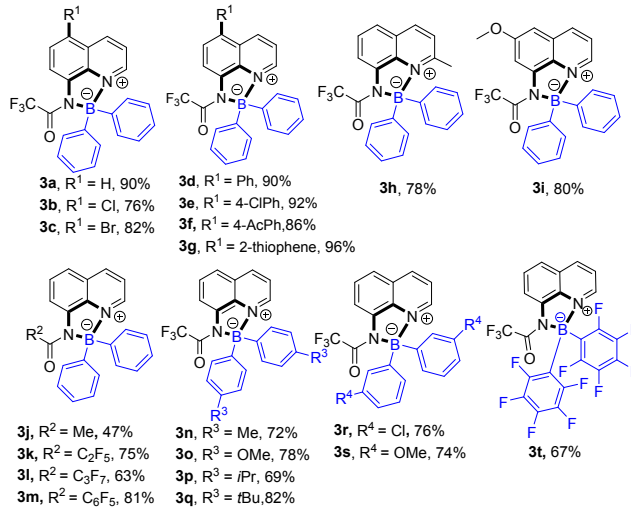


Entry	[Cat]	Sol.(1 mL)	Temp.(°C)	Yield(%)(3a)[b]
1	$CuBr_2$	toluene	150	38
2	$Cu(OAc)_2{\cdot}H_2O$	toluene	150	trace
3	CuBr	toluene	150	42
4	CuCl	toluene	150	43
5[c]	***$CuBr_2$***	***toluene***	***150***	***70***
6[d]	$CuBr_2$	toluene	150	53
7[e]	$CuBr_2$	toluene	150	74
8[f]	$CuBr_2$	toluene	150	82
9[g]	I_2	toluene	150	90
10	***I_2***	***toluene***	***150***	***90***
11	I_2	NMP	150	65
12	I_2	DMF	150	60
13	I_2	DMSO	150	NR
14	I_2	toluene	100	37
15	I_2	toluene	140	79
16[h]	I_2	toluene	150	NR

[a]1a (0.1 mmol), 2a (0.2 mmol), Cat. (0.005 mmol), solvent (1.0 mL), N_2; [b]isolated yield; [c]2 equiv. of $AgNO_3$ was added; [d]2 equiv. of $K_2S_2O_8$ was added; [e]2 equiv. of $PhI(OAc)_2$ was added; [f]2 equiv. of KIO_3 was added; [g]1 equiv. of I_2; [h]O_2.

Scheme 2. Substrates scope in the synthesis of **3**[a].

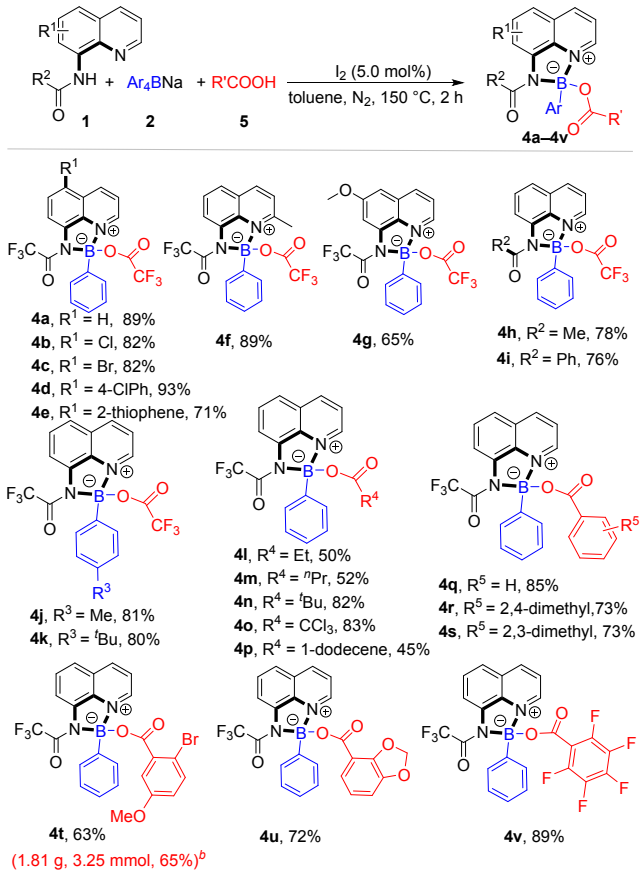




[a]**1** (0.1 mmol), **2** (0.2 mmol), I_2 (0.005 mmol), toluene (1.0 mL), N_2, 150 °C, 8 h, isolated yield of **3**.

Surprisingly, in the synthesis of **3a**, **1a** in the presence of a tiny amount of CF_3COOH resulted in the formation of novel boron compound **4a**. We investigated the scope of quinoline derivatives [(8-A^{f}Q)BAr(X)] (**4**) by a slightly modified synthetic protocol using 1 equivalent of **2** and 2 equivalents of acyl acid **5** (Scheme 3). The reaction showed good tolerance towards a wide range of functional groups attached to quinoline such as Cl (**4b**, 82%), Br (**4c**, 82%), thienyl (**4e**, 71%), methyl (**4f**, 89%), and methoxy (**4g**, 65%). Notably, substrates attached with an electron-donating group showed higher yields (**4d**, 93%) than did those with an electron-withdrawing group (**4b**, 82%; **4c**, 82%). Replacing trifluoromethyl with methyl or phenyl could result in the desired products (**4h**, 78%; **4i**, 76%). Various sodium tetraarylborate derivatives **2** were also screened (**4j**, 81%; **4k**, 80%). The fact that the substrate with electron-donating propionic acid only gave 50% yield of **4l**, while that with electron-withdrawing pentafluorobenzoic acid gave 89% yield of **4v** signifies considerable electronic effect on the yields of [(8-A^{f}Q)BAr(X)] (**4j**–**4v**). The structure of **4t** has been confirmed by X-ray analysis, see **SI**.[18]

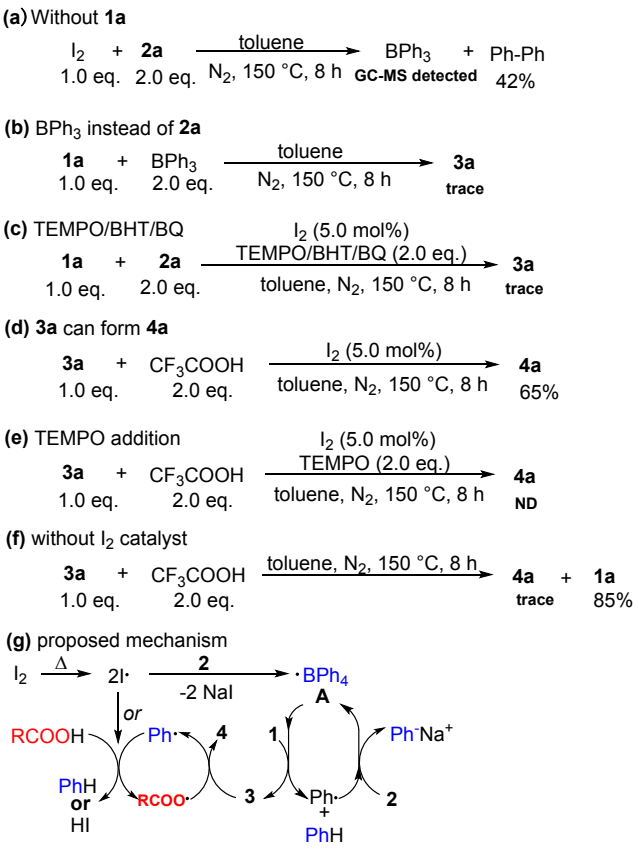
Scheme 3. Substrates scope in the synthesis of **4**[a].



[a]**1** (0.1 mmol), **2** (0.1 mmol), **5** (0.2 mmol), I_2 (5.0 mol%), toluene (1.0 mL), N_2, 150 °C, 2 h, isolated yield of **4**. [b] 5 mmol-scale, 12 h (1.81 g, 3.25 mmol, 65%).

To understand the synthesis mechanism of **3** and **4**, we performed a series of control experiments (Scheme 4). I_2 reacted with **2a** to give BPh_3 (GC-MS analysis, air-sensitive) and biphenyl (42%) (Scheme 4a), confirming I_2 first reacted with **2a** to generate those active species. BPh_3 reacted with **1a** to give a trace amount of desired **3a** (Scheme 4b), suggesting BPh_3 might not be a possible intermediate. In addition, when radical scavenger TEMPO/BHT/BQ was employed in the reaction system, the reaction was almost completely quenched (Scheme 4c), indicating that the present protocol involves a radical pathway. These results may suggest the intermediacy of phenyl radical Ph• in the transformation, in which diphenyl could be found (Scheme 4a). In addition, benzene was detected by GC-MS (see **SI**). We also chose compound **3a** as starting material to react with trifluoroacetic acid (CF_3COOH) for the direct production of **4a** (yield 65%) (Scheme 4d). The reaction could be quenched by TEMPO (Scheme 4e), and in the absence of I_2 did not proceed (Scheme 4f).

Scheme 4. Control experiments and mechanism.



On the basis of the above results and literature precedents,[10] a plausible mechanism is proposed (Scheme 4g). As a first step, iodine radical is generated by high temperature homolytic cleavage. Addition of **2** with iodine radical affords intermediate radical A (•BPh_4)[19], which reacts with **1** to form **3** together with a phenyl radical. Combination of the phenyl radical with **2** regenerates •BPh_4[19] and Ph^-Na^+. With the involvement of phenyl radical or iodine radical, the reaction of **3** with CF_3COOH forms **4**. In the whole process, a catalytic amount of iodine is good enough.

With two series of B–N complexes (**3a**–**3t**, 20 examples, **4a**–**4v**, 22 examples) in hand, we proceeded to characterize their physical and chemical properties. (i) Air-stability:

The organoboron aminoquinolates **3** and **4** exhibited good air-stability, both of them were found stable in open air for four years at room temperature. (ii) Solubility: They can be well dissolved in solvents such as toluene, dimethyl sulfoxide, N,N-dimethylformamide, tetrahydrofuran, dichloromethane, chloroform, acetone, and acetonitrile. (iii) Fluorescent ability: They show a wide-range green, blue or yellow fluorescence emission (Figure 2).

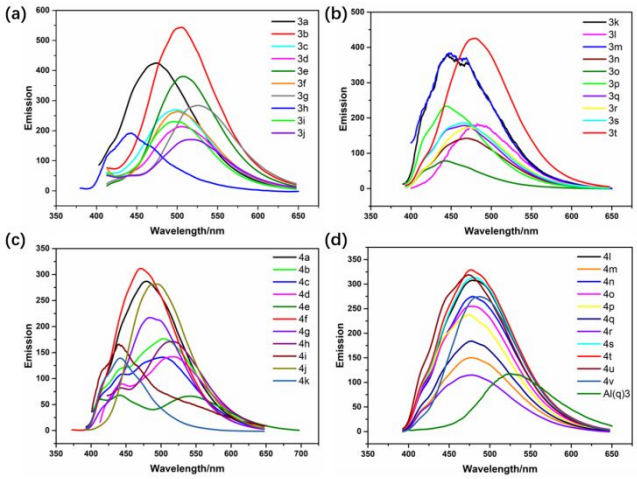


Figure 2. Fluorescence spectra of (a–b) **3** and (c–d) **4** [used solutions in DCM], $Al(q)_3$ as reference.[10]

Table 2. UV absorption and fluorescence properties[a]

Compd	λ_{max} (nm)	λ_{em} (nm)	Φ (%)	Compd	λ_{max} (nm)	λ_{em} (nm)	Φ (%)
3a	374	474	49	**3k**	372	445	40
3b	390	506	79	**3l**	369	482	17
3c	388	499	38	**3m**	372	450	55
3d	387	505	24	**3n**	372	469	24
3e	392	507	55	**3o**	371	442	13
3f	385	500	33	**3p**	378	444	32
3g	397	527	31	**3q**	372	466	30
3h	366	441	19	**3r**	372	471	24
3i	399	495	37	**3s**	374	465	21
3j	399	518	18	**3t**	377	479	75
4a	365	479	38	**4l**	369	478	46
4b	380	502	26	**4m**	359	476	20
4c	384	502	20	**4n**	369	479	45
4d	390	515	25	**4o**	369	477	43
4e	397	440	13	**4p**	366	473	34
4f	357	471	36	**4q**	362	477	37
4g	368	483	32	**4r**	368	477	21
4h	398	513	28	**4s**	369	481	41
4i	391	439	31	**4t**	369	477	44
4j	370	493	50	**4u**	369	473	40
4k	370	441	16	**4v**	372	487	67
Alq_3	390	513	17 *ref.10*				

[a]The UV absorption was controlled between 0.025 and 0.050 for fluorescence quantum yield. The data of fluorescence emission was excited at maximum absorption wavelength.

The UV absorption wavelengths of 42 compounds ranged from 366 nm to 399 nm. The fluorescence emission of them are from 441 nm to 518 nm. The fluorescence quantum yield of **3a** is 0.49. However, with an group (including chlorine, bromine, phenyl, chlorophenyl, phenylacetyl, thienyl, **3b**–**3g**) was attached on the C5 position of quinoline ring, the fluorescence quantum yield of the compounds (**3c**, **3d**, **3f**, **3g**, 0.38, 0.24, 0.33, 0.31) decreased but **3b** and **3e** displayed better (0.79, 0.55). Compound **3t** with more fluorine atoms also exhibited excellent quantum yield (0.75). As a whole, the fluorescence quantum yield of **4a**–**4v** was similar to that of **3a**–**3t** (Figure 2 and Table 2). We used different carboxylic acid to synthesize **4l**–**4v**, and found good quantum yield (**4v**, 0.67). The products utilized as photocatalysts and Lewis acid catalysts are still under investigation in our lab.

CONCLUSIONS

In summary, we have developed a highly efficient method for the synthesis of two kinds of B–N quenched organoboron aminoquinolate [(8-A^fQ)BAr_2] and [(8-A^fQ)BAr(X)] by treatment of aminoquinolates with NaBAr4/R'COOH using iodine as catalyst. This protocol has wide substrate scope. The produced compounds display high air and thermal stability as well as fluorescent ability. Fluorescence quantum yield of **3b** is up to 0.79 in dichloromethane.

EXPERIMENTAL SECTION

All reactions were carried out under N_2 atmosphere using standard Schlenk techniques unless stated otherwise. The glassware was dried in an oven (110 °C) and heated under reduced pressure before use. The thin layer chromatography (TLC) analysis and column chromatography were performed using silica gel (200–300) with distilled solvents. NMR spectra were recorded on a Bruker Advance 400 spectrometer operating at 400 MHz (^{1}H NMR) and 101 MHz (^{13}C NMR) in $CDCl_3$. All ^{1}H and ^{13}C NMR chemical shifts were reported in ppm relative to internal references of $CDCl_3$ at 7.26 ppm and carbon resonance in chloroform-*d*, at 77.00 ppm, respectively. The following abbreviations are used to describe peak patterns where appropriate: singlet (s), doublet (d), triplet (t), multiplet (m), broad resonances (br). Unless noted otherwise, the materials obtained from commercial suppliers were used without further purification. All solvents were distilled. The UV absorption data was tested by SHIMADZU UV 2600 at room temperature. The data of the fluorescence emission was tested by HITACHI FV4600 at room temperature.

Typical Experimental Procedure for the Preparation of Starting Materials N-trifluoroacetyl aminoquinolines Derivatives (1)

N-trifluoroacetyl aminoquinolines derivatives were prepared according to the literatures.[20] Trifluoroacetic anhydride or trifluoroacetyl chloride (11.0 mmol) was added dropwise into a solution of 8-aminoquinoline (1.44 g, 10.0 mmol) and Et_3N (1.7 mL, 12.0 mmol) in CH_2Cl_2 (15.0 mL) at 0 °C. The mixture was stirred overnight at room temperature. Then the mixture was diluted with CH_2Cl_2 (10.0 mL), and washed successively with water, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography

on silica gel and eluted with EtOAc/Hexane (1:10, v/v) to afford the corresponding 8-aminoquinolinyl amides **1**.

General Procedure for N-(5-halogen-)-2,2,2-trifluoro-8-quinolinylacetamide Generation

N-(5-halogen-)-2,2,2-trifluoro-8-quinolinylacetamide was prepared according to the literatures.[16d] To a 10.0 mL screw capped vial equipped with a magnetic stirring bar was added N-(quinolin-8-yl)pivalamide (**1**) (0.2 mmol), N-halogensuccinimide (NXS, X = Cl, Br, 0.22 mmol) and DMF (1.0 mL) under N_2 atmosphere. To halogenate quinolone, the reaction mixture was placed in an oil bath preheated to 50 °C and vigorously stirred for 1 h. Subsequently the reaction mixture was cooled down to room temperature, filtered through a plug of celite and then washed with saturated brine and extracted by ethyl acetate (3 × 5.0 mL). The solvents were removed under reduced pressure and the crude reaction mixture was purified by chromatography on silica gel using PE/EtOAc(20:1 v/v) as eluent to obtain the desired products.

To a solution of halogenated quinoline (0.2 mmol, 67.2 mg) in EtOH (1.0 mL) was added NaOH (2.0 mmol, 80.0 mg). The mixture was heated at 100 °C for 12 h. Then, the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate=5/1, v/v) to afford 5-(halogen)quinoline-8-amine.

Then trifluoroacetic anhydride (1.1 mmol) was added dropwise to a solution of 5-(halogen)quinoline-8-amine (1.0 mmol) and Et_3N (170 μL, 1.2 mmol) in CH_2Cl_2 (15.0 mL) at 0 °C. The mixture was stirred overnight at room temperature. Afterward the mixture was diluted with CH_2Cl_2 (10.0 mL), and washed successively with water, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel and eluted with EtOAc/Hexane (1:10, v/v) to afford the corresponding 8-aminoquinolinyl amides.

General Procedure for N-(5-Substrates-quinolin-8-yl)-2,2,2-Trifluoroacetamide formation

2,2,2-Trifluoro-N-(5-Substrates-)8-quinolinylacetamide was prepared according to the literatures.[16d] To a 10.0 mL screw capped vial equipped with a magnetic stirring bar was added brominated quinoline (3.0 mmol). Then the reaction mixture was added with boronic acid derivatives (6.0 mmol), sodium carbonate (6.0 mmol), $Pd(PPh_3)_4$ (0.15 mmol), and DMSO (5.0 mL) under N_2 atmosphere. The as-resulted mixture was placed in an oil bath preheated to 140 °C and vigorously stirred for 12 h. Subsequently it was cooled down to room temperature, filtered through a plug of celite and then washed with saturated brine and extracted by ethyl acetate (3 × 5.0 mL). The solvents were removed under reduced pressure and the crude reaction mixture was purified by chromatography on silica gel using PE/EtOAc (20:1, v/v) as eluent to obtain the desired product.

To a solution of N-(5-(Substrates)quinoline-8-yl)pivalamide (0.2 mmol, 67.2 mg) in EtOH (1.0 mL), was added NaOH (2.0 mmol, 80.0 mg). The mixture was heated at 100 °C for 12 h. Then, the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate=5:1, v/v) to afford 5-(Substrates)quinoline-8-amine, which reacted with fluoroanhydride to get the related products. At last, using previous method, there is the formation of the target amine.

General Procedure for Sodium Tetraarylborates production

Sodium tetraarylborates were prepared according to the literature with some modifications.[21] The synthesis of sodium tetra-p-tolylborate was chosen as representative reaction. A mixture of sodium tetrafluoroborate (1.47 g, 13.4 mmol) and magnesium turnings (2.16 g, 88.7 mmol) were placed in an oven-dried sealed tube. The tube was filled with N_2 by the standard Schlenk technique. To this mixture, 30.0 mL of THF and iodine (10.0 mg) were added and the mixture was stirred for 1 min. Finally, p-bromotoluene (10.0 mL, 80.2 mmol) was added and the suspension was stirred for 12 h at room temperature. After 12 h, the solution became gray and white precipitates were formed. Then the reaction mixture was added to aqueous $Na2CO_3$, stirred for 30 min, and then extracted with ethyl acetate/diethyl ether (1:1; 3 × 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure with a rotary evaporator. The crude residue was purified by precipitation using chloroform/hexane (1:4) to afford an off-white powder of sodium tetra-p-anisylborate (4.54 g, 11.4 mmol, 85%).

General Procedure for the Synthesis of Products 3–4. To a 10.0 mL screw capped vial equipped with a magnetic stirring bar was added aminoquinolines derivatives (**1**) (0.1 mmol), sodium tetraphenylborate derivatives (**2**) (0.1–0.2 mmol), I_2 (0.005 mmol), (or adding 2 equivalents of acid for the synthesis of **4**) and toluene (1.0 mL) under N_2 atmosphere. The reaction mixture was placed in an oil bath preheated to 150 °C, and vigorously stirred for 8 h. Afterward it was cooled to ambient temperature, filtered through a plug of celite and then washed with ethyl acetate (3 × 5.0 mL). The solvents were removed under reduced pressure and the crude reaction mixture was purified by chromatography on silica gel (PE/EtOAc, 10:1 v/v as an eluent) to obtain the desired products **3**.

Procedure for the synthesis of (κ²-(N,N′)-8-trifluoroacetyaminoquinolate)-5-methoxyl-2-bromophenylacetateborane (4t) in scale of 1 gram. To a 50.0 mL screw capped vial equipped with a magnetic stirring bar was added 2,2,2-trifluoro-N-(quinolin-8-yl)acetamide (**1a**) (5 mmol, 1.2 g), sodium tetraphenylborate (**2a**) (5 mmol, 1.71 g), 2-bromo-5-methoxybenzoic acid (10 mmol, 2.31 g), I_2 (0.25 mmol, 63.3 mg) and toluene (10.0 mL) under N_2 atmosphere. The reaction mixture was placed in an oil bath preheated to 150 °C, and vigorously stirred for 12 h. Afterward it was cooled to ambient temperature, filtered through a plug of celite and then washed with ethyl acetate (3 × 5.0 mL). The solvents were removed under reduced pressure and the crude reaction mixture was purified by chromatography on silica gel (PE/EtOAc, 10:1 v/v as an eluent) to obtain the desired products (**4t**, 1.81 g, 65%).

Procedure for UV-vis absorption and fluorescence quantum yield of 3a–4v. We first used 1.0 μmol/L **3a**–**4v** in DMF to test UV absorption, but the extent of absorption was too low. Finally, we found 40.0 μmol/L **3a**–**4v** in DMF suitable for graphic purpose. The data was tested by SHIMADZU UV 2600 at room temperature (SI, Figure S29). We chose compound **4t** as sample to screen serval solvents, such as 1,4-dioxane, DCM, DMF, DMSO, CH_3CN, THF, Toluene in 5 μmol/L. We found that DCM is the best solvent for the fluorescence emission. The data of the fluorescence emission was tested by HITACHI FV4600 at room temperature (SI, Figure S30). We controlled **3a**–**4v** to test the UV absorption between 0.025 and 0.050 in DCM for fluorescence quantum yield by SHIMADZU UV 2600 at room temperature. Next, we tested the data of fluorescence emission when excited at their maximum absorption wavelength by HITACHI FV 4600 (SI, Table S3, S4).
Calculation formula of quantum yield[22] was adopted as the following: $\Phi_F = \Phi_{F,cal} \frac{s}{S_{cal}} \cdot \frac{A_{cal}}{A} \cdot \frac{n^2}{n_{cal}^2}$

*N-(quinolin-8-yl)-2,2,2-trifluoroacetamide (**1a**).*[16b] The amide was obtained as white solid, 2.2 g, 90% yield. mp:82.4–83.1 °C. EtOAc/petroleum ether = 1:20, R_f = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 8.81 (d, *J* = 4.1 Hz, 1H), 8.65 (d, *J* = 7.6 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.56–7.45 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.6, 148.9, 138.4, 136.4, 132.0, 127.9, 127.0, 123.8, 122.2, 117.5, 115.8 (q, *J* = 288.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.72 (s, 3F). MS (EI): m/z=240.0.

*N-(2-methylquinolin-8-yl)-2,2,2-trifluoroacetamide (**1b**).*[16b] The amide was obtained as white solid, 2.5 g, 98% yield. mp:83.4–84.3 °C. EtOAc/petroleum ether = 1:20, R_f = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.64 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 2.75 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.2, 154.8, 154.5, 137.7, 136.4, 131.3, 126.0, 123.5, 123.0, 117.4, 115.9 (q, *J* = 288.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.79(s, 3F). MS (EI): m/z=254.1.

*N-(6-methoxyquinolin-8-yl)-2,2,2-trifluoroacetamide (**1c**).*[16b] The amide was obtained as faint yellow solid, 2.1 g, 81% yield. mp:127.3–128.6 °C. EtOAc/petroleum ether = 1:20, R_f = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 8.96–8.52 (m, 1H), 8.37 (s, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.43 (dd, *J* = 8.1, 4.2 Hz, 1H), 6.87 (s, 1H), 3.92 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.0, 154.9, 154.6, 146.3, 135.0, 134.8, 132.8, 128.9, 122.6, 115.7 (q, *J* = 288.4 Hz), 110.5, 101.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.76(s, 3F). MS (EI): m/z=269.1.

*N-(quinolin-8-yl)-2,2,3,3,3-pentafluoropropenamide (**1d**).*[16b] The amide was obtained as yellow oil, 2.6 g, 91% yield. EtOAc/petroleum ether = 1:20, R_f = 0.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.88 (s, 1H), 8.84 (d, *J* = 3.9 Hz, 1H), 8.78–8.61 (m, 1H), 8.32–8.09 (m, 1H), 7.69–7.61 (m, 1H), 7.60–7.47 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.6, 155.4, 155.1, 149.0, 138.3, 136.4, 132.0, 127.8, 126.9, 123.8, 122.2, 119.8, 119.4, 119.1, 117.5, 116.9, 116.6, 116.3, 113.7, 109.7, 109.3, 107.5, 107.1, 106.7, 104.4, 104.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −82.53 (s, 3F), −122.43 (s, 2F), −122.14 (d, *J* = 216.8 Hz, 2F). MS (EI): m/z=290.1.

*N-(quinolin-8-yl)-2,2,3,3,4,4,4-heptafluorobutanamide (**1e**).*[16b] The amide was obtained as yellow oil, 2.7 g, 79% yield. EtOAc/petroleum ether = 1:20, R_f = 0.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.84 (s, 1H), 8.81 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.67 (d, *J* = 7.6 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.68–7.56 (m, 1H), 7.56–7.44 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.5, 155.2, 154.9, 149.0, 138.4, 136.4, 132.1, 129.9, 127.9, 127.1, 123.9, 122.2, 119.3, 119.0, 118.7, 117.6, 116.5, 116.1, 115.8, 113.6, 113.3, 111.5, 111.2, 110.9, 109.0, 108.8, 108.6, 108.5, 108.2, 108.2, 107.9, 106.2, 105.9, 105.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.45 (t, *J* = 8.8 Hz, 2F), −120.16 (q, *J* = 8.8 Hz, 3F), −126.66 (s, 2F). MS (EI): m/z=340.0.

*N-(quinolin-8-yl)-2,3,4,5,6-pentafluorobenzamide (**1f**).*[23] The amide was obtained as white solid, 2.7 g, 80% yield. mp:134.5–135.2 °C. EtOAc/petroleum ether = 1:20, R_f = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.90–8.80 (m, 2H), 8.24 (d, *J* = 8.1 Hz, 1H), 7.65 (m, 2H), 7.52 (dd, *J* = 8.2, 4.3 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.3, 148.5, 145.6, 143.1, 141.2, 138.9, 138.1, 136.4, 133.5, 127.8, 127.2, 122.9, 121.9, 117.2, 111.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −140.03 (d, *J* = 15.9 Hz, 2F), −150.38 (t, *J* = 20.7 Hz, 1F), −156.59–163.62 (m, 2F). MS (EI): m/z=338.1.

*N-(5-chloroquinolin-8-yl)-2,2,2-trifluoroacetamide (**1g**).* The amide was obtained as white solid, 227.4 mg, 83% yield. mp:131.5–132.5 °C. EtOAc/petroleum ether = 1:20, R_f = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.85 (d, *J* = 3.7 Hz, 1H), 8.54(t, *J* = 9.8 2H), 7.60–7.42 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.3 (q, *J* = 37.8 Hz), 149.4, 138.7, 133.4, 131.1, 126.8, 126.8, 125.8, 122.8, 117.3, 115.7 (q, *J* = 288.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.74 (s, 3F). MS (EI): m/z=274.0, HRMS m/z (EI) calcd for [$C_{11}H_6ClF_3N_2O$]: 274.0121 found 274.0125.

*N-(5-bromoquinolin-8-yl)-2,2,2-trifluoroacetamide (**1h**).*[24] The amide was obtained as white solid, 222.5 mg, 70% yield. mp:122.5–123.4 °C. EtOAc/petroleum ether = 1:20, R_f = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 1H), 8.85 (d, *J* = 2.5 Hz, 1H), 8.53 (t, *J* = 7.9 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.60 (dd, *J* = 8.4, 4.1 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.7 (q, *J* = 37.7 Hz), 149.4, 138.9, 136.1, 131.8, 130.5, 127.2, 123.2, 115.4 (q, *J* = 288.4 Hz), 117.1, 116.9, 116.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.72 (s, 3F). MS (EI): m/z=317.9.

*N-(5-phenylquinolin-8-yl)-2,2,2-trifluoroacetamide (**1i**).*[16b] The amide was obtained as white solid, 2.9 g, 92% yield. mp:107.8–109.3 °C. EtOAc/petroleum ether = 1:20, R_f = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.85 (s, 1H), 8.87 (d, *J* = 3.8 Hz, 1H), 8.76 (d, *J* = 7.9 Hz, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 7.60–7.40 (m, 7H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.8 (q, *J* = 37.3 Hz), 148.7, 138.6, 138.5, 136.7, 135.0, 131.3, 130.0, 128.6, 127.8, 127.5, 126.3, 122.1, 115.8 (q, *J* = 274.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.65 (s, 3F). MS (EI): m/z=316.1.

*N-(5-chlorophenylquinolin-8-yl)-2,2,2-trifluoroacetamide (**1j**).* The amide was obtained as white solid, 3.0 g, 85% yield. mp:150.5–151.4 °C. EtOAc/petroleum ether = 1:20, R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.83 (s, 1H), 8.88 (d, *J* = 2.2 Hz, 1H), 8.75 (d, *J* = 7.9 Hz, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 7.50 (t, *J* = 8.5 Hz, 4H), 7.38 (d, *J* = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.8, 138.5, 137.0, 135.3, 135.3, 134.6, 131.7,

131.2, 128.9, 127.6, 126.2, 122.3, 117.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.68 (s, 3F). MS (EI): m/z=350.1, HRMS m/z (EI) calcd for [$C_{17}H_{10}ClF_3N_2O$]: 350.0434 found 350.0437.

*N-(5-(thiophen-2-yl)-quinolin-8-yl)-2,2,2-trifluoroacetam-ide (**1k**).* The amide was obtained as white solid, 3.0 g, 93% yield. mp:121.3–122.4 °C. EtOAc/petroleum ether = 1:20, R_f = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (s, 1H), 8.87 (d, *J* = 3.4 Hz, 1H), 8.72 (d, *J* = 7.9 Hz, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 3.4 Hz, 2H), 7.39 (s, 1H), 7.26 (d, *J* = 4.3 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.8 (q, *J* = 38.4 Hz), 148.7, 139.1, 138.5, 134.9, 131.4, 129.1, 127.4, 126.5, 126.1, 124.1, 122.2, 115.8 (q, *J* = 279.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.67 (s, 3F). MS (EI): m/z=322.0, HRMS m/z (EI) calcd for [$C_{15}H_9F_3N_2OS$]: 322.0388 found 322.0386.

*N-(5-(4-acetylphenyl)quinolin-8-yl)-2,2,2-trifluoroaceta-mide (**1l**).* The amide was obtained as white solid, 3.2 g, 90% yield. mp:219.5–221.1 °C. EtOAc/petroleum ether = 1:20, R_f = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.85 (s, 1H), 8.89 (d, *J* = 3.0 Hz, 1H), 8.77 (d, *J* = 7.9 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.62–7.46 (m, 4H), 2.69 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.6, 148.9, 143.4, 138.4, 136.4, 135.4, 134.5, 132.0, 130.2, 128.7, 127.7, 126.0, 122.4, 115.7 (q, *J* = 275.8 Hz), 101.4, 26.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.68 (s, 3F). MS (EI): m/z=358.2, HRMS m/z (EI) calcd for [$C_{19}H_{13}F_3N_2O_2$]: 358.0929 found 358.0921.

*5-(thiophen-3-yl)quinolin-8-amine (**1m**).*[25] EtOAc/petroleum ether = 1:10, R_f = 0.40, 38.9 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.0 Hz, 1H), 8.33 (d, *J* = 8.6 Hz, 1H), 7.49–7.41 (m, 1H), 7.40–7.32 (m, 2H), 7.32–7.27 (m, 1H), 7.23 (d, *J* = 4.8 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 5.07 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.2, 143.5, 140.5, 138.3, 134.1, 129.6, 128.0, 127.2, 125.3, 123.4, 122.6, 121.4, 109.4.

*5-phenylquinolin-8-amine (**1n**).*[16d] EtOAc/petroleum ether = 1:10, R_f = 0.42, 36.5 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.0 Hz, 1H), 8.23 (d, *J* = 8.6 Hz, 1H), 7.53–7.28 (m, 7H), 6.99 (d, *J* = 7.7 Hz, 1H), 5.06 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.2, 143.4, 140.0, 138.3, 134.2, 130.2, 128.9, 128.4, 128.1, 127.0, 126.8, 121.3, 109.5.

*1-(4-(8-aminoquinolin-5-yl)phenyl)ethenone (**1o**).* EtOAc/petroleum ether = 1: 10, R_f = 0.40, 40.3 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90–8.64 (m, 1H), 8.19 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.36–7.31 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 5.16 (s, 2H), 2.66 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.8, 147.4, 145.1, 144.2, 138.2, 135.4, 133.7, 130.2, 128.5, 128.4, 127.2, 126.5, 121.6, 109.2, 26.6, HRMS m/z (EI) calcd for [$C_{17}H_{14}N_2O$]: 262.1106 found 262.1101.

*5-chloroquinolin-8-amine (**1p**).*[26] EtOAc/petroleum ether = 1:10, R_f = 0.45, 33.8 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 3.6 Hz, 1H), 8.47 (d, *J* = 8.5 Hz, 1H), 7.49 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.26 (s, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.01 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.8, 143.3, 138.8, 132.9, 127.2, 126.5, 122.0, 118.1, 109.5.

*5-(4-chlorophenyl)quinolin-8-amine (**1q**).*[25] EtOAc/petroleum ether = 1:10, R_f = 0.42, 23.9 mg, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 3.9 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.44–7.35 (m, 3H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 5.17 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.2, 143.7, 138.4, 138.2, 133.7, 132.7, 131.3, 128.5, 128.1, 127.2, 126.7, 121.4, 109.3.

*5-bromoquinolin-8-amine (**1r**).*[27] EtOAc/petroleum = 1:10, R_f = 0.45, 43.3 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 3.2 Hz, 1H), 8.38 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.43 (dd, *J* = 8.5, 4.1 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 5.05 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 147.7, 144.0, 139.1, 135.4, 130.8, 127.8, 122.4, 110.1, 107.3.

*sodium tetra-p-tolylborate (**2aa**).*[28] The borate was obtained as white solid, 4.5 g, 85% yield. ^{1}H NMR (400 MHz, D_2O) δ 7.30 (s, 8H), 7.03 (d, *J* = 6.0 Hz, 8H), 2.26 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, D_2O) δ 135.6, 134.6, 132.3, 127.3, 19.9. MS (EI): m/z=398.2.

*sodium tetrakis(4-methoxyphenyl)borate (**2b**).*[29] The borate was obtained as white solid, 5.5 g, 88% yield. ^{1}H NMR (400 MHz, D_2O) δ 7.07 (s, 12H), 6.61–6.59 (m, 4H), 3.64–3.60 (m, 12H). ^{13}C{^{1}H} NMR (101 MHz, Acetone) δ 206.2, 156.2, 137.5, 111.7, 111.7, 111.7, 111.7, 54.9. MS (EI): m/z=462.2.

*sodium tetrakis(3-methoxyphenyl)borate (**2c**).*[29] The borate was obtained as faint yellow solid, 5.4 g, 87% yield. ^{1}H NMR (400 MHz, D_2O) δ 7.07 (s, 12H), 6.61–6.59 (m, 4H), 3.64–3.60 (m, 12H). ^{13}C{^{1}H} NMR (101 MHz, D2O) δ 165.9, 157.4, 128.7, 127.7, 120.5, 108.7, 54.9. MS (EI): m/z=462.2.

*sodium tetrakis(3-chlorophenyl)borate (**2d**).*[28] The borate was obtained as white solid, 4.0 g, 66% yield. ^{1}H NMR (400 MHz, D_2O) δ 7.29 (d, *J* = 22.2 Hz, 8H), 7.00 (s, 8H). ^{13}C{^{1}H} NMR (101 MHz, D_2O) δ 134.4, 133.6, 132.4, 128.4, 123.1. MS (EI): m/z=455.0.

*sodium tetrakis(4-(tert-butyl)phenyl)borate (**2e**).* The borate was obtained as white solid, 6.0 g, 79% yield. ^{1}H NMR (400 MHz, DMSO) δ 7.16 (s, 8H), 6.95 (d, *J* = 7.7 Hz, 8H), 1.23 (s, 36H). ^{13}C{^{1}H} NMR (101 MHz, Acetone) δ 205.4, 161.8, 161.3, 160.8, 160.3, 142.6, 135.8, 121.8, 33.5, 31.3, 29.6, 29.4, 29.2, 29.0, 28.8, 28.6, 28.4. MS (EI): m/z=566.4, HRMS m/z (ESI) calcd for [$C_{40}H_{52}B$]$^-$: 543.4168 found 543.4161.

*sodium tetrakis(4-isopropylphenyl)borate (**2f**).*[30] The borate was obtained as white solid, 3.1 g, 46% yield. ^{1}H NMR (400 MHz, DMSO) δ 7.14 (s, 8H), 6.80 (d, *J* = 7.5 Hz, 8H), 2.72 (dt, *J* = 13.6, 6.8 Hz, 4H), 1.17 (d, *J* = 6.8 Hz, 24H). ^{13}C{^{1}H} NMR (101 MHz, Acetone) δ 206.2, 141.4, 137.0, 123.9, 123.9, 34.5, 24.8. MS (EI): m/z=510.3.

*(κ^2-(N,N′)-8-trifluoacetylaminoquinolate)diphenylboran (**3a**).* The borane was obtained as faint yellow solid, 36.1 mg, 90% yield. mp:223.2–224.3 °C. EtOAc/petroleum ether = 1:10, R_f = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 5.8 Hz, 1H), 8.53–8.34 (m, 2H), 7.86 (t, *J* = 7.4 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.56 (s, 1H), 7.48 (d, *J* = 5.2 Hz, 4H), 7.25 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.1, 140.8, 140.2, 139.5, 136.7, 133.2, 132.2, 127.5, 127.3, 127.2, 122.9, 121.3, 119.9, 114.2 (q, *J* = 287.45 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.19 (s, 3F). HRMS m/z (EI) calcd for [$C_{23}H_{16}BF_3N_2O$]: 404.1308, found 404.1309.

*(κ^2-(N,N′)-5-chloro-8-trifluoroacetylaminoquinolate)diphenylboran (**3b**).* The borane was obtained as yellow solid, 33.3 mg, 76% yield. mp:228.5–229.8 °C. EtOAc/petroleum ether = 1:10, R_f = 0.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 8.4 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 4.8 Hz,

1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.69 (dd, *J* = 8.5, 5.2 Hz, 1H), 7.57–7.46 (m, 4H), 7.35–7.27 (m, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.2 (q, *J* = 38.7 Hz), 145.1, 141.1, 139.9, 137.3, 137.2, 133.1, 131.4, 127.6, 127.4, 125.6, 123.7, 123.6, 121.2, 115.5 (q, *J* = 287.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.18 (s, 3F). HRMS m/z (EI) calcd for $[C_{23}H_{15}BClF_3N_2O]$: 438.0918 found 438.0913.

*(κ²-(N,N′)-5-bromo-8-trifluoroacetylaminoquinolate)diphenylboran (**3c**)*. The borane was obtained as yellow solid, 39.5 mg, 82% yield. mp:237.7–238.8 °C. EtOAc/petroleum ether = 1:10, R_f = 0.46. ^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 8.3 Hz, 1H), 8.68 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 4.8 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.68 (dd, *J* = 8.5, 5.3 Hz, 1H), 7.56–7.44 (m, 4H), 7.34–7.27 (m, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.2 (q, *J* = 38.6 Hz), 145.2, 141.0, 140.5, 139.4, 137.3, 134.9, 134.7, 133.1, 130.5, 127.8, 127.6, 127.3, 126.9, 123.8, 123.3, 121.6, 119.8, 118.0, 115.5 (q, *J* = 287.4 Hz), 112.7, 111.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.20 (s, 3F). HRMS m/z (EI) calcd for $[C_{23}H_{15}BBrF_3N_2O]$: 482.0413 found 482.0389.

*(κ²-(N,N′)-5-phenyl-8-trifluoroacetylaminoquinolate)diphenylborane (**3d**)*. The borane was obtained as yellow solid, 43.2 mg, 90% yield. mp:195.5–196.7 °C. EtOAc/petroleum ether = 1:10, R_f = 0.48. ^1H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 7.9 Hz, 1H), 8.59 (d, *J* = 8.5 Hz, 1H), 8.51 (d, *J* = 5.1 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.66–7.46 (m, 10H), 7.32 (t, *J* = 7.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.2, 140.0, 138.6, 137.0, 137.0, 133.8, 133.3, 132.1, 129.7, 129.0, 128.4, 127.6, 127.2, 125.9, 122.8, 121.1, 115.7 (q, *J* = 287.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.11 (s, 3F). HRMS m/z (EI) calcd for $[C_{29}H_{20}BF_3N_2O]$: 480.1621 found 480.1627.

*(κ²-(N,N′)-5-(p-chlorophenyl)-8-trifluoroacetylaminoquinolate)diphenylborane (**3e**)*. The borane was obtained as light yellow solid, 47.3 mg, 92% yield. mp:227.1–228.7 °C. EtOAc/petroleum ether = 1:10, R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ 9.08 (d, *J* = 7.9 Hz, 1H), 8.59–8.34 (m, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.53 (dd, *J* = 8.3, 5.4 Hz, 1H), 7.48 (dd, *J* = 6.9, 3.9 Hz, 6H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.29–7.17 (m, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.4, 145.4, 140.4, 140.3, 138.2, 136.9, 135.4, 134.6, 133.2, 132.3, 132.1, 130.9, 129.3, 127.6, 127.2, 125.8, 123.0, 120.9, 115.6 (q, *J* = 287.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.06 (s, 3F). HRMS m/z (EI) calcd for $[C_{29}H_{19}BClF_3N_2O]$: 514.1231 found 514.1244.

*(κ²-(N,N′)-5-(p-phenylacetyl)-8-trifluoroacetylaminoquinolate)diphenylborane (**3f**)*. The borane was obtained as light yellow solid, 44.9 mg, 86% yield. mp:215.5–216.8 °C. EtOAc/petroleum ether = 1:10, R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ 9.12 (d, *J* = 8.0 Hz, 1H), 8.52 (t, *J* = 6.2 Hz, 2H), 8.13 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.59 (dd, *J* = 8.3, 4.4 Hz, 3H), 7.53–7.46 (m, 4H), 7.29 (m, 6H), 2.68 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.4, 160.4 (q, *J* = 38.5 Hz), 115.6 (d, *J* = 285.5 Hz), 141.8, 140.5, 138.1, 137.0, 136.8, 133.3, 132.4, 132.3, 129.9, 129.0, 127.6, 127.3, 125.7, 123.2, 121.0, 115.6 (q, *J* = 285.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.19 (s, 3F). HRMS m/z (EI) calcd for $[C_{31}H_{22}BF_3N_2O_2]$: 522.1726 found 522.1710.

*(κ²-(N,N′)-5-(2-thienyl)-8-trifluoroacetylaminoquinolate)diphenylborane (**3g**)*. The borane was obtained as light yellow solid, 46.7 mg, 96% yield. mp:193.2–194.2 °C. EtOAc/petroleum ether = 1:10, R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 7.7 Hz, 1H), 8.68 (d, *J* = 8.4 Hz, 1H), 8.49 (d, *J* = 4.8 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.69–7.47 (m, 6H), 7.45 (s, 1H), 7.35–7.20 (m, 7H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.1 (q, *J* = 37.8 Hz), 145.4, 140.3, 139.8, 138.4, 137.5, 136.9, 133.2, 131.7, 128.5, 127.5, 127.2, 126.9, 126.0, 124.2, 122.9, 121.0, 115.6 (q, *J* = 287.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.13 (s, 3F). HRMS m/z (EI) calcd for $[C_{27}H_{18}BF_3N_2OS]$: 486.1185 found 486.1189.

*(κ²-(N,N′)-2-methyl-8-trifluoroacetylaminoquinolate)diphenylborane (**3h**)*. The borane was obtained as faint yellow solid, 32.6 mg, 78% yield. mp:186.1–187.8 °C. EtOAc/petroleum ether = 1:10, R_f = 0.50. ^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.85 (t, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.64–7.57 (m, 4H), 7.40–7.28 (m, 7H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.6, 140.6, 139.4, 137.3, 133.6, 130.7, 127.5, 127.0, 126.1, 125.8, 120.7, 120.1, 115.6 (q, *J* = 287.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.11 (s, 3F). HRMS m/z (EI) calcd for $[C_{24}H_{18}BF_3N_2O]$: 418.1464 found 418.1453.

*(κ²-(N,N′)-6-methoxyl-8-trifluoroacetylaminoquinolate)diphenylborane (**3i**)*. The borane was obtained as yellow solid, 34.7 mg, 80% yield. mp:262.0–263.3 °C. EtOAc/petroleum ether = 1:10, R_f = 0.50. ^1H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.59 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 5.1 Hz, 1H), 7.60 (dd, *J* = 8.5, 5.2 Hz, 1H), 7.45 (d, *J* = 5.6 Hz, 4H), 7.26 (d, *J* = 5.9 Hz, 7H), 4.18 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.6 (q, *J* = 38.7 Hz), 158.3, 138.0, 137.8, 133.1, 132.8, 127.6, 127.4, 127.3, 124.1, 115.5 (q, *J* = 287.3 Hz), 109.0, 98.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.24 (s, 3F). HRMS m/z (EI) calcd for $[C_{24}H_{18}BF_3N_2O_2]$: 434.1413 found 434.1418.

*(κ²-(N,N′)-8-acetylaminoquinolate)diphenylborane (**3j**)*. The borane was obtained as faint yellow solid,16.5 mg, 47% yield. mp:216.8–218.7 °C. EtOAc/petroleum ether = 1:10, R_f = 0.49. ^1H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 7.7 Hz, 1H), 8.40 (dd, *J* = 19.0, 6.6 Hz, 2H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 9.4 Hz, 6H), 7.29 (p, *J* = 6.4 Hz, 6H), 1.95 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.3, 142.0, 139.5, 139.0, 137.6, 133.5, 132.6, 127.8, 127.5, 127.1, 122.4, 118.7, 117.0. HRMS m/z (EI) calcd for $[C_{23}H_{19}BN_2O]$: 350.1590 found 350.1597.

*(κ²-(N,N′)-8-pentafluoropropylaminoquinolate)diphenylborane (**3k**)*. The borane was obtained as faint yellow solid, 34.1 mg, 75% yield. mp:172.4–173.8 °C. EtOAc/petroleum ether = 1:10, R_f = 0.45. ^1H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 7.5 Hz, 1H), 8.50 (dd, *J* = 18.1, 6.6 Hz, 2H), 7.92 (t, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.64–7.60 (m, 1H), 7.55 (d, *J* = 6.3 Hz, 4H), 7.33 (d, *J* = 6.6 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.1, 161.9, 140.8, 140.2, 139.4, 136.6, 133.1, 132.1, 127.6, 127.3, 127.1, 122.9, 121.5, 120.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −81.60 (s, 3F), −113.82 (s, 2F). HRMS m/z (EI) calcd for $[C_{24}H_{16}BF_5N_2O]$: 454.1276 found 454.1276.

*(κ²-(N,N′)-8-heptafluorobutanoylaminoquinolate)diphenylborane (**3l**)*. The borane was obtained as faint yellow solid, 31.8 mg, 63% yield. mp:245.1–246.7 °C. EtOAc/petroleum ether = 1:10, R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 7.8 Hz, 1H), 8.55–8.38 (m, 2H), 7.90 (t, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.60 (dd, *J* = 8.0, 5.5 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 4H), 7.39–7.19 (m, 6H). $^{13}C\{^1H\}$

NMR (101 MHz, $CDCl_3$) δ 162.3, 162.0, 161.8, 145.7, 140.9, 140.2, 139.4, 136.6, 133.0, 132.1, 127.6, 127.3, 127.1, 122.9, 121.6, 120.1, 119.3, 119.0, 118.7, 116.5, 116.1, 115.8, 111.3, 108.9, 108.6, 108.3, 105.9, 105.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.13 (t, *J* = 8.8 Hz, 3F), −110.79 (d, *J* = 7.8 Hz, 2F), −124.53 (s, 2F). HRMS m/z (EI) calcd for $[C_{25}H_{16}BF_7N_2O]$: 504.1244 found 504.1233.

*(κ²-(N,N′)-8-pentafluorobenzoylaminoquinolate)diphenylborane (**3m**)*. The borane was obtained as faint yellow solid, 40.7 mg, 81% yield. mp:234.1–235.8 °C. EtOAc/petroleum ether = 1:10, R_f = 0.41. ^1H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 7.7 Hz, 1H), 8.41 (dd, *J* = 16.9, 6.6 Hz, 2H), 7.88 (t, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.57 (dd, *J* = 7.9, 5.4 Hz, 1H), 7.29–7.15 (m, 10H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.0, 145.0, 144.0, 143.9, 142.6, 141.5, 141.0, 140.1, 139.5, 138.2, 137.4, 135.7, 133.4, 132.4, 127.5, 127.4, 122.8, 120.0, 119.3, 114.2, 99.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −137.84 (dd, *J* = 21.8, 6.3 Hz, 2F), −155.35 (t, *J* = 20.7 Hz, 1F), −162.46–−162.58 (m, 2F). HRMS m/z (EI) calcd for $[C_{28}H_{16}BF_5N_2O]$: 502.1276 found 502.1256.

*(κ²-(N,N′)-8-trifluoroacetylaminoquinolate)di(p-methylphenyl)borane (**3n**)*. The borane was obtained as faint yellow solid, 31.1 mg, 72% yield. mp:234.5–235.7 °C. EtOAc/petroleum ether = 1:10, R_f = 0.48. ^1H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 7.4 Hz, 1H), 8.48 (d, *J* = 5.2 Hz, 1H), 8.41 (d, *J* = 8.3 Hz, 1H), 7.88 (t, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.58–7.54 (m, 1H), 7.42 (d, *J* = 7.5 Hz, 4H), 7.13 (d, *J* = 7.5 Hz, 4H), 2.34 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.3 (q, *J* = 37.5 Hz), 142.4, 140.7, 140.1, 139.3, 136.6, 133.2, 132.0, 128.3, 127.3, 122.8, 121.1, 119.9, 112.8 (q, *J* = 287.4 Hz), 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.89 (s, 3F). HRMS m/z (EI) calcd for $[C_{25}H_{20}BF_3N_2O]$: 432.1621 found 432.1612.

*(κ²-(N,N′)-8-trifluoroacetylaminoquinolate)di(p-methoxylphenyl)borane (**3o**)*. The borane was obtained as faint yellow solid, 36.2 mg, 78% yield. mp:171.8–173.0 °C. EtOAc/petroleum ether = 1:10, R_f = 0.48. ^1H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 7.2 Hz, 1H), 8.44 (t, *J* = 7.5 Hz, 2H), 7.87 (t, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.58 (dd, *J* = 7.9, 5.4 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 4H), 6.83 (d, *J* = 8.2 Hz, 4H), 3.77 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.2 (q, *J* = 39.0 Hz), 158.8, 140.6, 140.1, 139.3, 137.3, 136.6, 136.5, 134.4, 132.0, 127.3, 122.8, 121.1, 119.9, 115.7 (q, *J* = 287.5 Hz), 113.0, 54.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.19 (s, 3F). HRMS m/z (EI) calcd for $[C_{25}H_{20}BF_3N_2O_3]$: 464.1519 found 464.1507.

*(κ²-(N,N′)-8-trifluoroacetylaminoquinolate)di(p-isopropylphenyl)borane (**3p**)*. The borane was obtained as faint yellow solid, 33.7 mg, 69% yield. mp:211.6–212.9 °C. EtOAc/petroleum ether = 1:10, R_f = 0.48. ^1H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 7.4 Hz, 1H), 8.48 (d, *J* = 5.1 Hz, 1H), 8.38 (d, *J* = 8.3 Hz, 1H), 7.85 (t, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.55 (dd, *J* = 7.5, 6.0 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 4H), 7.13 (d, *J* = 7.4 Hz, 4H), 2.87 (dt, *J* = 13.7, 6.8 Hz, 2H), 1.24 (t, *J* = 10.7 Hz, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.4 (q, *J* = 35.9 Hz), 147.4, 142.8, 140.8, 140.3, 139.2, 136.7, 133.2, 132.0, 127.5, 127.3, 125.5, 122.8, 121.1, 119.8, 115.7 (q, *J* = 287.4 Hz), 33.7, 23.9, 23.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.02 (s, 3F). HRMS m/z (EI) calcd for $[C_{29}H_{28}BF_3N_2O]$: 488.2247 found 488.2243.

*(κ²-(N,N′)-8-trifluoroacetylaminoquinolate)di(p-tert-butylphenyl)borane (**3q**)*. The borane was obtained as faint yellow solid, 42.3 mg, 82% yield. mp:229.6–230.9 °C. EtOAc/petroleum ether = 1:10, R_f = 0.46. ^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 7.5 Hz, 1H), 8.61–8.49 (m, 1H), 8.44 (d, *J* = 8.3 Hz, 1H), 7.90 (t, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.60 (dd, *J* = 8.3, 5.2 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 4H), 7.32 (d, *J* = 7.4 Hz, 5H), 1.33 (s, 18H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.7, 140.3, 140.2, 139.1, 136.7, 133.0, 132.0, 127.3, 124.3, 122.8, 121.2, 119.8, 115.7 (q, *J* = 287.4 Hz), 34.3, 31.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.02 (s, 3F). HRMS m/z (EI) calcd for $[C_{31}H_{32}BF_3N_2O]$: 516.2560 found 516.2562.

*(κ²-(N,N′)-8-trifluoroacetylaminoquinolate)di(m-chlorophenyl)borane (**3r**)*. The borane was obtained as faint yellow solid, 35.9 mg, 76% yield. mp:176.3–177.8 °C. EtOAc/petroleum ether = 1:10, R_f = 0.45. ^1H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 6.3 Hz, 1H), 8.51 (d, *J* = 8.3 Hz, 1H), 8.43 (d, *J* = 5.2 Hz, 1H), 7.90 (t, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.65 (dd, *J* = 7.2, 5.2 Hz, 1H), 7.41–7.31 (m, 4H), 7.24–7.17 (m, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.1, 147.5, 140.2, 136.5, 133.8, 132.7, 132.3, 131.2, 129.2, 127.5, 127.4, 123.1, 121.5, 120.4, 115.5 (q, *J* = 287.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.06 (s, 3F). HRMS m/z (EI) calcd for $[C_{23}H_{14}BCl_2F_3N_2O]$: 472.0528 found 472.0531.

*(κ²-(N,N′)-8-trifluoroacetylaminoquinolate)di(m-methoxylphenyl)borane (**3s**)*. The borane was obtained as faint yellow solid, 34.4 mg, 74% yield. mp:157.3–158.5 °C. EtOAc/petroleum ether = 1:10, R_f = 0.47. ^1H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 7.2 Hz, 1H), 8.43 (dd, *J* = 18.2, 6.7 Hz, 2H), 7.86 (t, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.57–7.53 (m, 1H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 10.2 Hz, 4H), 6.80 (d, *J* = 8.1 Hz, 2H), 3.74 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.8, 147.4, 140.6, 140.3, 139.5, 136.6, 132.0, 128.59, 127.3, 125.6, 122.9, 121.2, 120.0, 119.4, 115.6 (q, *J* = 287.5 Hz), 111.7, 55.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −69.01 (s, 3F). HRMS m/z (EI) calcd for $[C_{25}H_{20}BF_3N_2O_3]$: 464.1519 found 464.1510.

*(κ²-(N,N′)-8-trifluoroacetylaminoquinolate)di(perfluorphenyl)borane (**3t**)*. The borane was obtained as faint yellow solid. 39.1 mg, 67% yield. mp:212.3–213.7 °C. EtOAc/petroleum ether = 1:10, R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.84 (d, *J* = 5.2 Hz, 1H), 8.66 (d, *J* = 8.2 Hz, 1H), 7.90 (t, *J* = 8.0 Hz, 1H), 7.85–7.78 (m, 1H), 7.75 (d, *J* = 8.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.2, 159.1, 158.7, 150.0, 147.6, 142.4, 142.4, 142.3, 142.2, 142.2, 142.1, 141.6, 140.9, 139.9, 139.8, 139.7, 139.6, 139.3, 138.7, 138.5, 138.4, 137.1, 136.2, 136.0, 135.9, 135.8, 132.5, 127.6, 123.3, 121.8, 120.4, 119.9, 117.1, 114.2, 111.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −71.47 (s, 3F), −133.79 (s, 4F), −153.85 (t, *J* = 19.7 Hz, 2F), −162.33 (t, *J* = 17.9 Hz, 4F). HRMS m/z (EI) calcd for $[C_{23}H_6BF_{13}N_2O]$: 584.0366 found 584.0360.

*(κ²-(N,N′)-8-trifluoroacetylaminoquinolate) trifluoroacetatephenylborane (**4a**)*. The borane was obtained as faint yellow solid, 39.1 mg, 89% yield. mp:111.2–112.3 °C. EtOAc/petroleum ether = 1:10, R_f = 0.46. ^1H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 7.7 Hz, 1H), 8.66 (d, *J* = 8.3 Hz, 1H), 8.40 (d, *J* = 5.2 Hz, 1H), 7.92 (t, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.73 (dd, *J* = 8.3, 5.3 Hz, 1H), 7.47–7.44 (m, 2H),

7.31–7.28 (m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.3 (q, *J* = 39.1 Hz), 157.7 (q, *J* = 41.4 Hz), 142.0, 140.6, 139.4, 136.5, 132.3, 130.6, 128.6, 128.0, 127.0, 123.1, 121.0, 120.5, 115.5 (q, *J* = 287.2 Hz), 114.8 (q, *J* = 286.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.89 (s, 3F), −76.33 (s, 3F). HRMS m/z (EI) calcd for $[C_{19}H_{11}BF_6N_2O_3]$: 440.0767, found 440.0771.

*(κ²-(N,N′)-8-trifluoroacetyl-5-chloro-aminoquinolate) trifluoroacetatephenylborane (**4b**)*. The borane was obtained as faint yellow solid, 37.9 mg, 82% yield. mp:234.2–235.4 °C. EtOAc/petroleum ether = 1:10, R_f = 0.45. ^1H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 18.3, 8.4 Hz, 2H), 8.45 (d, *J* = 5.0 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.90–7.79 (m, 1H), 7.42 (d, *J* = 6.4 Hz, 2H), 7.30 (d, *J* = 6.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.3 (q, *J* = 39.3 Hz), 157.8 (q, *J* = 42.1 Hz), 141.4, 139.7, 138.6, 137.1, 131.7, 130.7, 128.8, 128.1, 125.4, 124.4, 123.7, 121.1, 115.4 (q, *J* = 287.1 Hz), 114.7 (q, *J* = 286.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −71.01 (s, 3F), −76.33 (s, 3F). HRMS m/z (EI) calcd for $[C_{19}H_{10}BClF_6N_2O_3]$: 474.0377, found 474.0372.

*(κ²-(N,N′)-8-trifluoroacetyl-5-bromo-aminoquinolate) trifluoroacetatephenylborane (**4c**)*. The borane was obtained as faint yellow solid, 42.5 mg, 82% yield. mp:242.7–244.5 °C. EtOAc/petroleum ether = 1:10, R_f = 0.46. ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.4 Hz, 1H), 8.85 (d, *J* = 8.1 Hz, 1H), 8.43 (d, *J* = 4.7 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.91–7.75 (m, 1H), 7.42 (d, *J* = 5.7 Hz, 2H), 7.31 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4 (q, *J* = 39.5 Hz), 157.8 (q, *J* = 41.8 Hz), 142.0, 141.4, 139.2, 137.2, 135.3, 130.7, 128.8, 128.1, 126.8, 124.0, 121.6, 115.4 (q, *J* = 286.6 Hz), 114.7 (q, *J* = 286.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −71.01 (s, 3F), −76.34 (s, 3F). HRMS m/z (EI) calcd for $[C_{19}H_{10}BBrF_6N_2O_3]$: 517.9872, found 517.9867.

*(κ²-(N,N′)-8-trifluoroacetyl-5-(p-chlorophenyl)-aminoquinolate)trifluoroacetatephenylborane (**4d**)*. The borane was obtained as faint yellow solid, 51.1 mg, 93% yield. mp:149.6–153.2 °C. EtOAc/petroleum ether = 1:10, R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, *J* = 7.9 Hz, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 8.43 (d, *J* = 4.9 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.78–7.68 (m, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 4H), 7.33 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.3 (q, *J* = 39.2 Hz), 157.8 (q, *J* = 41.7 Hz), 140.7, 140.7, 139.0, 136.7, 135.0, 132.9, 132.4, 131.0, 130.7, 129.4, 128.7, 128.0, 125.6, 123.2, 120.8, 115.4 (q, *J* = 287.2 Hz), 114.8 (q, *J* = 286.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.98 (s, 3F), −76.36 (s, 3F). HRMS m/z (EI) calcd for $[C_{25}H_{14}BClF_6N_2O_3]$: 550.0690, found 550.0685.

*(κ²-(N,N′)-8-trifluoroacetyl-5-thiophene-aminoquinolate) trifluoroacetatephenylborane (**4e**)*. The borane was obtained as faint yellow solid, 37.1 mg, 71% yield. mp:199.3–200.5 °C. EtOAc/petroleum ether = 1:10, R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 8.0 Hz, 1H), 8.88 (d, *J* = 8.5 Hz, 1H), 8.41 (d, *J* = 5.1 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.73 (dd, *J* = 8.1, 5.4 Hz, 1H), 7.64–7.55 (m, 1H), 7.49 (s, 3H), 7.32 (t, *J* = 4.8 Hz, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.3 (q, *J* = 39.2 Hz), 157.8 (q, *J* = 41.5 Hz), 141.1, 140.7, 138.6, 137.2, 136.8, 132.0, 130.8, 129.2, 128.7, 128.6, 128.1, 127.3, 125.9, 124.7, 123.1, 121.0, 115.6 (q, *J* = 287.2 Hz), 114.9 (q, *J* = 286.6 Hz), 100.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.87 (s, 3F), −76.31 (s, 3F). HRMS m/z (EI) calcd for $[C_{23}H_{13}BF_6N_2O_3S]$: 522.0644, found 522.0661.

*(κ²-(N,N′)-8-trifluoroacetyl-2-methyl-aminoquinolate)trifluoroacetatephenylborane (**4f**)*. The borane was obtained as faint yellow solid, 40.4 mg, 89% yield. mp:230.8–239.5 °C. EtOAc/petroleum ether = 1:10, R_f = 0.48. ^1H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 7.7 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.47–7.41 (m, 3H), 7.28 (s, 3H), 2.54 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.7 (q, *J* = 40.0 Hz), 158.3 (q, *J* = 42.9 Hz), 154.8, 141.6, 139.0, 136.9, 131.5, 131.1, 128.4, 127.7, 125.6, 125.3, 120.9, 120.4, 115.5 (q, *J* = 287.2 Hz), 114.9 (q, *J* = 286.9 Hz), 20.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.98 (s, 3F), −76.25 (s, 3F). HRMS m/z (EI) calcd for $[C_{20}H_{13}BF_6N_2O_3]$: 454.0923, found 454.0918.

*(κ²-(N,N′)-8-trifluoroacetyl-6-methoxyl-aminoquinolate) trifluoroacetatephenylborane (**4g**)*. The borane was obtained as faint yellow solid, 30.6 mg, 65% yield. mp:145.3–146.7 °C. EtOAc/petroleum ether = 1:10, R_f = 0.48. ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.46 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 5.1 Hz, 1H), 7.79–7.54 (m, 1H), 7.52–7.38 (m, 2H), 7.29 (d, *J* = 5.1 Hz, 3H), 7.00 (s, 1H), 4.02 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.0, 159.4 (q, *J* = 39.3 Hz), 157.6 (q, *J* = 41.6 Hz), 140.2, 139.7, 137.1, 133.4, 130.7, 128.6, 128.0, 127.9, 123.4, 115.4 (q, *J* = 287.2 Hz), 114.8 (q, *J* = 286.7 Hz), 98.4, 56.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −71.04 (s, 3F), −76.37 (s, 3F). HRMS m/z (EI) calcd for $[C_{20}H_{13}BF_6N_2O_4]$: 470.0873, found 470.0877.

*(κ²-(N,N′)-8-acetyl-aminoquinolate)trifluoroacetatephenylborane (**4h**)*. The borane was obtained as faint yellow solid, 30.1 mg, 78% yield. mp:152.3–153.7 °C. EtOAc/petroleum ether = 1:10, R_f = 0.50. ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 7.7 Hz, 1H), 8.56 (d, *J* = 8.2 Hz, 1H), 8.41 (d, *J* = 5.0 Hz, 1H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.64 (dd, *J* = 8.3, 5.3 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.55–7.49 (m, 2H), 7.39–7.28 (m, 3H), 2.06 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.2, 157.5 (q, *J* = 40.8 Hz), 141.6, 140.4, 136.9, 135.5, 133.9, 132.6, 132.5, 131.1, 128.5, 128.2, 127.9, 127.6, 127.1, 122.4, 118.7, 118.0, 114.9 (q, *J* = 287.0 Hz), 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.15 (s, 3F). HRMS m/z (EI) calcd for $[C_{19}H_{14}BF_3N_2O_3]$: 386.1050, found 386.1033.

*(κ²-(N,N′)-8-phenyl-aminoquinolate)trifluoroacetatephenylborane (**4i**)*. The borane was obtained as faint yellow solid, 34.0 mg, 76% yield. mp:68.8–70.3 °C. EtOAc/petroleum ether = 1:10, R_f = 0.49. ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 7.6 Hz, 1H), 8.54 (d, *J* = 8.2 Hz, 1H), 8.31 (d, *J* = 4.9 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 6.8 Hz, 2H), 7.15 (dd, *J* = 7.5, 4.4 Hz, 1H), 7.07–6.87 (m, 7H), 6.79 (d, *J* = 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.1, 157.7, 141.8, 141.4, 140.8, 138.0, 137.5, 132.4, 130.9, 129.2, 127.7, 127.3, 127.3, 127.1, 126.8, 122.5, 120.0, 118.4, 114.9 (q, *J* = 287.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.04 (s, 3F). HRMS m/z (EI) calcd for $[C_{24}H_{16}BF_3N_2O_3]$: 448.1206, found 448.1208.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate) trifluoroacetate-p-methyl-phenyl-borane (**4j**)*. The borane was obtained as faint yellow solid, 36.8 mg, 81% yield. mp:207.6–208.4 °C. EtOAc/petroleum ether = 1:10, R_f = 0.48. ^1H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 7.6 Hz, 1H), 8.66 (d, *J* = 8.2 Hz, 1H), 8.40 (d, *J* = 5.0 Hz, 1H), 7.93 (t, *J* = 8.0 Hz, 1H), 7.83–7.61 (m, 2H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 2H), 2.32 (s,

3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.7 (q, *J* = 41.3 Hz), 141.8, 140.5, 139.5, 138.3, 136.5, 132.5, 130.7, 128.7, 127.0, 123.0, 121.1, 120.3, 115.5 (q, *J* = 286.6 Hz), 114.8 (q, *J* = 286.3 Hz), 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.92 (s, 3F), −76.37 (s, 3F). HRMS m/z (EI) calcd for $[C_{20}H_{13}BF_6N_2O_3]$: 454.0923, found 454.0918.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate) trifluoroacetate-p-tert-butyl-phenyl-borane (**4k**)*. The borane was obtained as faint yellow solid, 40.1 mg, 80% yield. mp:227.6–228.4 °C. EtOAc/petroleum ether = 1:10, R_f = 0.45. ^1H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 7.7 Hz, 1H), 8.64 (d, *J* = 8.2 Hz, 1H), 8.43 (d, *J* = 5.1 Hz, 1H), 7.90 (t, *J* = 8.1 Hz, 1H), 7.80–7.68 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 1.30 (s, 11H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4 (q, *J* = 39.1 Hz), 157.7 (q, *J* = 41.4 Hz), 151.4, 141.7, 140.6, 139.5, 136.5, 132.4, 130.5, 127.0, 124.8, 123.0, 121.0, 120.3, 115.5 (q, *J* = 287.3 Hz), 114.8 (q, *J* = 286.6 Hz), 34.5, 31.2. 19F NMR (376 MHz, $CDCl_3$) δ −70.93 (s, 3F), −76.38 (s, 3F). HRMS m/z (EI) calcd for $[C_{23}H_{19}BF_6N_2O_3]$: 496.1393, found 496.1396.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate) propionicateborane (**4l**)*. The borane was obtained as faint yellow solid, 20.1 mg, 50% yield. mp:153.1–155.4 °C. EtOAc/petroleum ether = 1:10, R_f = 0.49. ^1H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 7.8 Hz, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 8.35 (d, *J* = 5.2 Hz, 1H), 7.85 (t, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.65–7.58 (m, 1H), 7.43 (d, *J* = 2.6 Hz, 2H), 7.25 (d, *J* = 1.4 Hz, 3H), 2.47–2.41 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 175.9, 159.2 (q, *J* = 39.0 Hz), 140.8, 140.0, 136.7, 135.6, 133.6, 132.7, 132.0, 131.0, 130.5, 128.0, 127.0, 127.7, 127.0, 122.7, 120.6, 120.0, 115.7 (q, *J* = 287.5 Hz), 29.3, 9.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.78 (s, 3F). HRMS m/z (EI) calcd for $[C_{20}H_{16}BF_3N_2O_3]$: 400.1206, found 400.1213.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate)-n-butylacetateborane (**4m**)*. The borane was obtained as faint yellow solid, 21.5 mg, 52% yield. mp:166.4–167.7 °C. EtOAc/petroleum ether = 1:10, R_f = 0.48. ^1H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 7.8 Hz, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 8.34 (d, *J* = 5.1 Hz, 1H), 7.85 (t, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.63 (dd, *J* = 8.2, 5.4 Hz, 1H), 7.42 (d, *J* = 2.5 Hz, 2H), 7.25 (d, *J* = 1.2 Hz, 3H), 2.39 (dd, *J* = 17.5, 7.9 Hz, 2H), 1.63–1.60 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 175.0, 159.2 (q, *J* = 38.9 Hz), 141.5, 140.8, 140.0, 139.9, 136.7, 133.6, 132.0, 130.5, 127.9, 127.7, 127.0, 122.6, 120.6, 120.0, 115.7 (q, *J* = 287.6 Hz), 38.1, 18.2, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.72 (s, 3F). HRMS m/z (EI) calcd for $[C_{21}H_{18}BF_3N_2O_3]$: 414.1363, found 414.1352.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate)trimethylacetateborane (**4n**)*. The borane was obtained as faint yellow solid, 35.1 mg, 82% yield. mp:236.5–237.7 °C. EtOAc/petroleum ether = 1:10, R_f = 0.45. ^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 7.2 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.28 (s, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.69 (dd, *J* = 22.3, 5.2 Hz, 2H), 7.46 (s, 2H), 7.27 (s, 3H), 1.25 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 179.7, 140.9, 140.0, 139.4, 136.9, 132.1, 130.6, 129.0, 128.0, 127.8, 127.0, 122.7, 120.8, 120.0, 116.4 (q, *J* = 278.9 Hz), 39.7, 27.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.59 (s, 3F). HRMS m/z (EI) calcd for $[C_{22}H_{20}BF_3N_2O_3]$: 428.1519, found 428.1514.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate) trichloroacetateborane (**4o**)*. The borane was obtained as faint yellow solid, 40.5 mg, 83% yield. mp:222.6–223.5 °C. EtOAc/petroleum ether = 1:10, R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 7.7 Hz, 1H), 8.66 (d, *J* = 8.3 Hz, 1H), 8.39 (d, *J* = 5.0 Hz, 1H), 7.93 (t, *J* = 8.0 Hz, 1H), 7.83–7.66 (m, 2H), 7.51 (d, *J* = 4.7 Hz, 2H), 7.31 (d, *J* = 4.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.6, 161.2, 160.8, 141.9, 141.6, 140.2, 139.6, 136.7, 132.4, 130.8, 130.6, 128.6, 128.0, 127.0, 123.0, 121.2, 120.3, 66.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.67 (s, 3F). HRMS m/z (EI) calcd for $[C_{19}H_{11}BCl_3F_3N_2O_3]$: 487.9880, found 487.9875.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate) undecylacetateborane (**4p**)*. The borane was obtained as faint yellow solid, 22.9 mg, 45% yield. mp:94.2–96.1 °C. EtOAc/petroleum ether = 1:10, R_f = 0.42. ^1H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 7.7 Hz, 1H), 8.57 (d, *J* = 8.3 Hz, 1H), 8.37 (d, *J* = 5.1 Hz, 1H), 7.89 (t, *J* = 8.1 Hz, 1H), 7.73–7.64 (m, 2H), 7.44–7.42 (m, 2H), 7.27 (d, *J* = 5.8 Hz, 3H), 5.82 (m, 1H), 5.02□4.92 (m, 2H), 2.44–2.35 (m, 2H), 2.04 (dd, *J* = 13.2, 6.3 Hz, 2H), 1.39–1.28 (m, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 175.2, 140.8, 140.0, 139.9, 139.2, 136.8, 132.1, 130.5, 127.9, 127.7, 127.0, 122.6, 120.7, 119.9, 114.1, 36.1, 33.8, 29.3, 29.3, 29.2, 29.1, 29.0, 28.9, 24.8, 24.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.74 (s, 3F). HRMS m/z (EI) calcd for $[C_{28}H_{30}BF_3N_2O_3]$: 510.2085, found 510.2091.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate) benzoateborane (**4q**)*. The borane was obtained as faint yellow solid, 38.1 mg, 85% yield. mp:239.3–241.8 °C. EtOAc/petroleum ether = 1:10, R_f = 0.46. ^1H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 7.6 Hz, 1H), 8.59 (d, *J* = 8.2 Hz, 1H), 8.41 (d, *J* = 4.8 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 2H), 7.91 (t, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.70–7.62 (m, 1H), 7.56 (t, *J* = 6.9 Hz, 3H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.31 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.3, 159.3 (q, *J* = 39.1 Hz), 141.0, 140.2, 140.0, 136.8, 133.0, 132.7, 132.1, 130.6, 130.1, 129.9, 128.3, 128.1, 127.9, 127.0, 122.8, 120.7, 120.2, 115.8 (q, *J* = 289.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.67 (s, 3F). HRMS m/z (EI) calcd for $[C_{24}H_{16}BF_3N_2O_3]$: 448.1206, found 448.1201.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate)-2,4-dimethylphenylacetateborane (**4r**)*. The borane was obtained as faint yellow solid, 34.7 mg, 73% yield. mp:215.2–216.3 °C. EtOAc/petroleum ether = 1:10, R_f = 0.45. ^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 7.7 Hz, 1H), 8.51 (d, *J* = 8.3 Hz, 1H), 8.39 (d, *J* = 5.1 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.85 (t, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.61–7.57 (m, 1H), 7.52 (d, *J* = 4.6 Hz, 2H), 7.27 (d, *J* = 4.6 Hz, 3H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 2.43 (s, 3H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.9, 159.3 (q, *J* = 39.0 Hz), 142.2, 140.8, 140.6, 140.0, 139.9, 136.7, 132.4, 132.0, 131.6, 130.5, 128.5, 127.9, 127.8, 127.1, 126.5, 122.6, 120.7, 120.1, 115.8 (q, *J* = 287.6 Hz), 21.9, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.68 (s, 3F). HRMS m/z (EI) calcd for $[C_{26}H_{20}BF_3N_2O_3]$: 476.1519, found 476.1514.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate)-2,3-dimethylphenylacetateborane (**4s**)*. The borane was obtained as faint yellow solid, 34.7 mg, 73% yield. mp:193.6–195.4 °C. EtOAc/petroleum ether = 1:10, R_f = 0.45. ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 7.7 Hz, 1H), 8.53 (d, *J* = 8.2 Hz, 1H),

8.40 (d, *J* = 5.1 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.87 (t, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.62 (dd, *J* = 8.2, 5.5 Hz, 1H), 7.51 (d, *J* = 3.8 Hz, 2H), 7.28 (d, *J* = 6.8 Hz, 4H), 7.19 (t, *J* = 7.6 Hz, 1H), 2.32 (s, 3H), 2.27 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.0, 159.3 (q, *J* = 38.8 Hz), 140.9, 139.9, 138.0, 137.8, 136.8, 132.9, 132.6, 132.1, 130.5, 128.5, 128.0, 127.8, 127.1, 125.1, 122.7, 120.8, 120.0, 115.8 (q, *J* = 287.6 Hz), 20.5, 16.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.67 (s, 3F). HRMS m/z (EI) calcd for $[C_{26}H_{20}BF_3N_2O_3]$: 476.1519, found 476.1514.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate)-5-methoxyl-2-bromophenylacetateborane (**4t**)*. The borane was obtained as faint yellow solid, 35.0 mg, 63% yield. mp:183.5–184.7 °C. EtOAc/petroleum ether = 1:10, R_f = 0.45. ^1H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 7.7 Hz, 1H), 8.60 (dd, *J* = 20.9, 8.3 Hz, 2H), 7.94 (t, *J* = 8.1 Hz, 1H), 7.85–7.66 (m, 2H), 7.66–7.44 (m, 4H), 7.32 (dd, *J* = 2.9, 2.1 Hz, 3H), 6.92 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.86 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.7, 159.2 (q, *J* = 38.8 Hz), 141.1, 140.4, 139.8, 136.7, 135.1, 134.6, 132.0, 130.6, 128.0, 127.8, 127.0, 122.7, 120.8, 120.2, 118.5, 116.3, 115.7 (q, *J* = 287.7 Hz), 111.3, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.56 (s, 3F). HRMS m/z (EI) calcd for $[C_{25}H_{17}BF_3N_2O_4Br]$: 556.0417, found 556.0423.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate) piperinicacetateborane (**4u**)*. The borane was obtained as faint yellow solid, 35.4 mg, 72% yield. mp:163.4–165.1 °C. EtOAc/petroleum ether = 1:10, R_f = 0.42. ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 7.7 Hz, 1H), 8.57 (d, *J* = 8.3 Hz, 1H), 8.40 (d, *J* = 5.0 Hz, 1H), 7.90 (t, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.66–7.63 (m, 1H), 7.56–7.53 (m, 3H), 7.30 (d, *J* = 4.3 Hz, 3H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.03 (s, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.6, 151.4, 147.6, 140.9, 140.2, 140.1, 136.8, 132.1, 130.6, 128.0, 127.9, 127.0, 126.3, 125.7, 122.7, 120.7, 120.1, 115.7 (q, *J* = 287.7 Hz), 109.9, 107.9, 101.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.66 (s, 3F). HRMS m/z (EI) calcd for $[C_{25}H_{16}BF_3N_2O_5]$: 492.1104, found 492.1115.

*(κ²-(N,N′)-8-trifluoroacetyaminoquinolate) pentafluorobenzoateborane (**4v**)*. The borane was obtained as faint yellow solid, 47.8 mg, 89% yield. mp:189.1–190.2 °C. EtOAc/petroleum ether = 1:10, R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, *J* = 7.6 Hz, 1H), 8.65 (d, *J* = 8.2 Hz, 1H), 8.46 (d, *J* = 4.7 Hz, 1H), 7.94 (t, *J* = 8.0 Hz, 1H), 7.85–7.68 (m, 2H), 7.49 (s, 2H), 7.29 (d, *J* = 9.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4, 159.1, 146.8, 144.3, 141.4, 140.1, 139.7, 136.6, 132.4, 130.4, 128.3, 127.9, 127.1, 122.9, 121.0, 120.2, 115.6 (q, *J* = 287.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −70.99 (s, 3F), −139.10 (d, *J* = 18.8 Hz, 2F), −149.60 (t, *J* = 20.9 Hz, 1F), −160.69 (dt, *J* = 20.4, 6.2 Hz, 2F). HRMS m/z (EI) calcd for $[C_{24}H_{11}BF_8N_2O_3]$: 538.0735, found 538.0729.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxxxxxxxxx.

Detailed experimental procedures, compound characterization data, and NMR spectra (PDF).

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Notes

The authors declare no competing financial interest.

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