Supporting information

Synthesis of 2-trifluoromethylquinolines through rhodium-catalysed redox-neutral [3+3] annulation between anilines and CF_3-ynones using traceless directing group

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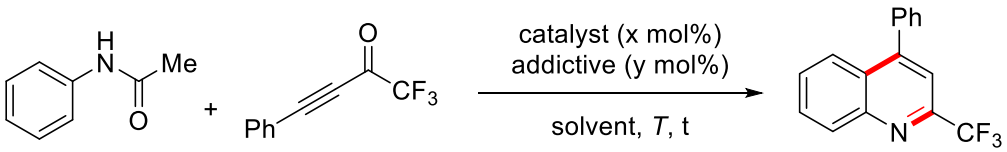
1. General information

All reactions were performed using flame-dried glassware under an atmosphere of dry Nitrogen, and all commercial materials and solvents were used directly without further purification, unless otherwise noted. Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluents. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light. Melting points were determined in open glass capillaries and were uncorrected. ^{1}H NMR spectra were recorded on a Bruker Avance III instrument (500 MHz). ^{13}C NMR spectra were recorded on a Bruker Avance III instrument (126 MHz) and were fully decoupled by broad band proton decoupling. ^{19}F NMR spectra were recorded on a Bruker Avance III instrument (471 MHz). NMR spectra were recorded in $CDCl_3$. All NMR spectra were referenced to the solvent peaks (^{1}H NMR: residual $CDCl_3$ = 7.26 ppm, ^{13}C NMR: $CDCl_3$ = 77.16 ppm). Chemical shifts (δ) are reported in ppm, and coupling constants (J) are reported in hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on an Agilent 1290 mass spectrometer using ESI-TOF (electrospray ionization time-of-flight). Crystal structure and data were recorded on an Agilent Gemini E diffractometer. Fluorescence spectra were recorded with a F-7000 fluorescence spectrometer (Hitachi, Japan). Acetanilides,[1] *N*-phenylpivalamide,[2] *t*-Butyl phenylcarbamate,[3] and trifluoromethyl ynones[4] were synthesized according to the previously reported procedure.

2. Optimization of reaction conditions

Table S1. Optimization of reaction conditions[a]



1a **2a** **3aa**

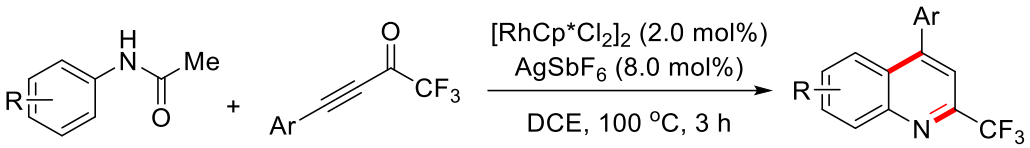
Entry	Catalyst (x)	Additive (y)	Solvent	*T* (°C)	t (h)	**3aa** (%)[b]
1	$[IrCp^*Cl_2]_2$ (2.0)	$AgSbF_6$ (8.0)	DCE	100	3	trace
2	$[Cp^*Co(CO)I_2]$ (4.0)	$AgSbF_6$ (8.0)	DCE	100	3	52
3	$[RuCl_2p$-cymene$]_2$ (2.0)	$AgSbF_6$ (8.0)	DCE	100	3	17
4	$Pd(OAc)_2$ (4.0)	---	DCE	100	3	0
5	$[RhCp^*Cl_2]_2$ (2.0)	$AgSbF_6$ (8.0)	DCE	100	3	94
6	$[RhCp^*Cl_2]_2$ (1.0)	$AgSbF_6$ (4.0)	DCE	100	3	45

7	$[RhCp^*Cl_2]_2$ (3.0)	$AgSbF_6$ (12)	DCE	100	3	96
8	$[RhCp^*Cl_2]_2$ (2.0)	AgOAc (8.0)	DCE	100	3	27
9	$[RhCp^*Cl_2]_2$ (2.0)	AgOTf (8.0)	DCE	100	3	86
10	$[RhCp^*Cl_2]_2$ (2.0)	$AgNTf_2$ (8.0)	DCE	100	3	86
11	$[RhCp^*Cl_2]_2$ (2.0)	$AgSbF_6$ (8.0)	DMF	100	3	0
12	$[RhCp^*Cl_2]_2$ (2.0)	$AgSbF_6$ (8.0)	MeCN	100	3	0
13	$[RhCp^*Cl_2]_2$ (2.0)	$AgSbF_6$ (8.0)	PhMe	100	3	0
14	$[RhCp^*Cl_2]_2$ (3.0)	$AgSbF_6$ (12)	*t*-AmOH	100	3	12
15	$[RhCp^*Cl_2]_2$ (2.0)	$AgSbF_6$ (8.0)	DCE	60	3	86
16	$[RhCp^*Cl_2]_2$ (2.0)	$AgSbF_6$ (8.0)	DCE	80	3	86
17	$[RhCp^*Cl_2]_2$ (2.0)	$AgSbF_6$ (8.0)	DCE	120	3	89
18	$[RhCp^*Cl_2]_2$ (2.0)	$AgSbF_6$ (8.0)	DCE	100	1	93
19	$[RhCp^*Cl_2]_2$ (2.0)	$AgSbF_6$ (8.0)	DCE	100	5	94
20	$[RhCp^*Cl_2]_2$ (2.0)	$AgSbF_6$ (8.0)	DCE	100	12	96
21	$Cp^*Rh(MeCN)_3(SbF_6)_2$ (4.0)	---	DCE	100	3	93

[a] Reaction conditions: **1a** (0.30 mmol), **2a** (0.33 mmol), catalyst (1.0-3.0 mol%), additives (4.0-12 mol%) and solvent (1.0 mL) at 60-120 °C under N_2 atmosphere for 1-12 h. [b]Isolated yields.

3. General catalytic procedure

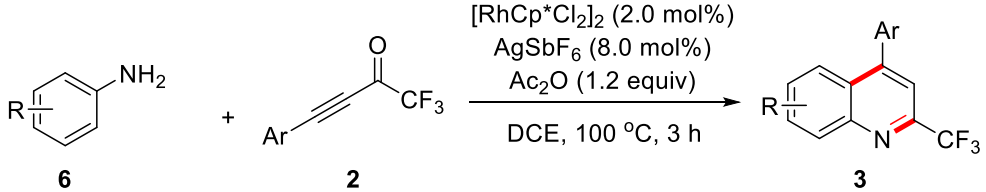
General procedure A: rhodium-catalysed [3+3] annulation between acetanilines 1 and CF_3-ynones 2



1 **2** **3**

The mixture of acetanilides (**1**, 0.30 mmol, 1.0 equiv), CF_3-ynones (**2**, 0.33 mmol, 1.1 equiv), $[RhCp^*Cl_2]_2$ (3.7 mg, 0.006 mmol) and $AgSbF_6$ (8.2 mg, 0.024 mmol) in DCE (1.0 mL) was stirred at 100 °C under N_2 for 3 h. After reaction completion, the solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (v/v) afforded the corresponding 2-trifluoromethylquinoline products **3**.

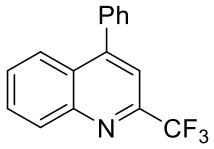
General procedure B: rhodium-catalysed one-pot [3+3] annulation between anilides 4 and CF_3-ynones 2



6 **2** **3**

The mixture of anilides (**4**, 0.30 mmol, 1.0 equiv), Ac_2O (36.8 mg, 0.36 mmol, 1.2 equiv), CF_3-ynones (**2**, 0.33 mmol, 1.1 equiv), $[RhCp^*Cl_2]_2$ (3.7 mg, 0.006 mmol) and $AgSbF_6$ (8.2 mg, 0.024 mmol) in DCE (1.0 mL) was stirred at 100 ℃ under N_2 for 3 h. After reaction completion, the solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (v/v) afforded the corresponding 2-trifluoromethylquinoline products **3**.

4. Characterization of compounds 3, 5 and 10



4-Phenyl-2-(trifluoromethyl)quinoline (**3aa**).

The compound (77.3 mg, 94%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as yellow solid; the compound (77.2 mg, 94%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow solid.

M. p. 59-62 ℃.

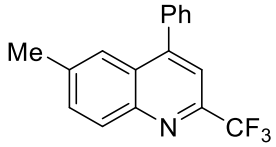
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.77 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.68 (s, 1H), 7.59-7.45 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 147.8, 147.5 (q, $^2J_{C\text{-}F}$ = 34 Hz), 137.1, 130.5, 130.4, 129.5, 129.0, 128.8, 128.6, 127.4, 125.8, 121.8 (q, $^1J_{C\text{-}F}$ = 276 Hz), 117.0 (q, $^3J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.3.

HRMS (ESI) m/z calcd for $C_{16}H_{11}F_3N^+$ $[M+H]^+$: 274.0838, Found 274.0840.

The spectral data were in accordance with those reported in the literature.[5]



6-Methyl-4-phenyl-2-(trifluoromethyl)quinoline (**3ba**).

The compound (72.9 mg, 84%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil; the compound (71.7 mg, 83%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil.

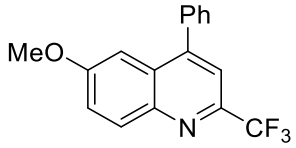
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, J = 8.7 Hz, 1H), 7.75 (s, 1H), 7.65 (s, 1H), 7.62 (dd, J = 8.7, 2.1 Hz, 1H), 7.59-7.49 (m, 5H), 2.49 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 146.7 (q, $^{2}J_{C\text{-}F}$ = 34 Hz), 146.5, 139.0, 137.4, 132.9, 130.2, 129.5, 129.0, 128.8, 127.5, 124.6, 122.0 (q, $^{1}J_{C\text{-}F}$ = 276 Hz), 117.1 (q, $^{3}J_{C\text{-}F}$ = 2 Hz), 22.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.2.

HRMS (ESI) m/z calcd for $C_{17}H_{13}F_3N^+$ $[M+H]^+$:288.0995, Found 288.0998.

The spectral data were in accordance with those reported in the literature.[5]



6-Methoxy-4-phenyl-2-(trifluoromethyl)quinoline (**3ca**).

The compound (88.4 mg, 97%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow solid; the compound (77.0 mg, 84%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow solid.

M. p. 69-71 °C.

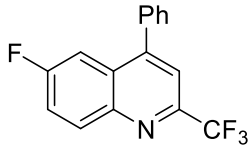
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 9.2 Hz, 1H), 7.65 (s, 1H), 7.61-7.53 (m, 5H), 7.47 (dd, J = 9.3, 2.8 Hz, 1H), 7.24 (d, J = 2.8 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 149.1, 145.2 ($^{2}J_{C\text{-}F}$ = 35 Hz), 143.9, 137.5, 131.9, 129.3, 129.0, 129.0, 128.8, 123.4, 122.0 ($^{1}J_{C\text{-}F}$ = 276 Hz), 117.4 ($^{3}J_{C\text{-}F}$ = 2 Hz), 103.4, 55.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.0.

HRMS (ESI) m/z calcd for $C_{17}H_{13}F_3NO^+$ $[M+H]^+$: 304.0944, Found 304.0948.

The spectral data were in accordance with those reported in the literature.[5]



6-Fluoro-4-phenyl-2-(trifluoromethyl)quinoline (**3da**).

The compound (79.4 mg, 90%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a pale yellow solid; the compound (77.5 mg, 88%) was

prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a pale yellow solid.

M. p. 94-95 °C.

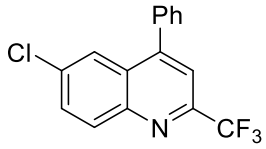
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (dd, J = 8.6, 5.7 Hz, 1H), 7.70 (s, 1H), 7.64-7.54 (m, 5H), 7.51 (dd, J = 7.6, 1.7 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5 (d, $^{1}J_{C\text{-}F}$ = 249 Hz), 150.6, 150.5, 147.2 (q, $^{2}J_{C\text{-}F}$ = 35 Hz) , 145.0, 136.8, 133.3 (d, $^{3}J_{C\text{-}F}$= 10 Hz), 129.4, 129.1, 128.7 (d, $^{3}J_{C\text{-}F}$ = 10 Hz),121.7 (q, $^{1}J_{C\text{-}F}$ = 275 Hz), 121.2 (d, $^{2}J_{C\text{-}F}$ = 27 Hz), 117.7 (q, $^{3}J_{C\text{-}F}$ = 2) , 109.5 (d, $^{2}J_{C\text{-}F}$ = 24 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.4, −108.9

HRMS (ESI) m/z calcd for $C_{16}H_{10}F_4N^+$ $[M+H]^+$: 292.0744, Found 292.0746.

The spectral data were in accordance with those reported in the literature.[5]



6-Chloro-4-phenyl-2-(trifluoromethyl)quinoline (**3ea**).

The compound (66.0 mg, 71%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a pale yellow solid.

M. p. 88-90 °C.

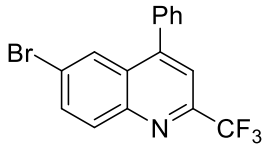
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 2.2 Hz, 1H), 7.74-7.69 (dd, 9.0, 2.3 Hz, 2H), 7.60-7.48 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 147.8 (q, $^{2}J_{C\text{-}F}$ = 35 Hz), 146.2, 136.5, 135.0, 132.1, 131.6, 129.5, 129.4, 129.1, 128.1, 124.8, 121.6 (q. $^{1}J_{C\text{-}F}$ = 275 Hz), 117.9 (q, $^{3}J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.5.

HRMS (ESI) m/z calcd for $C_{16}H_{10}ClF_3N^+$ $[M+H]^+$: 308.0448, Found 308.0451.

The spectral data were in accordance with those reported in the literature.[6]



6-Bromo-4-phenyl-2-(trifluoromethyl)quinoline (**3fa**).

The compound (91.5 mg, 86%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow solid.

M. p. 83-83 °C.

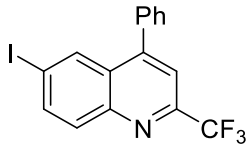
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 9.1 Hz, 2H), 7.87 (dd, J = 8.9, 2.2 Hz, 1H), 7.70 (s, 1H), 7.61-7.55 (m, 3H), 7.53-7.47 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 148.0 (q, $^2J_{C\text{-}F}$ = 35 Hz), 146.5, 136.5, 134.3, 132.2, 129.5, 129.5, 129.1, 128.6, 128.2, 123.4, 121.6 (q, $^1J_{C\text{-}F}$ = 274 Hz), 117.9 (q, $^3J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.5.

HRMS (ESI) m/z calcd for $C_{16}H_{10}BrF_3N^+$ $[M+H]^+$: 351.9943, Found 351.9944.

The spectral data were in accordance with those reported in the literature.[5]



6-Iodo-4-phenyl-2-(trifluoromethyl)quinoline (**3ga**).

The compound (104.3 mg, 87%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow solid.

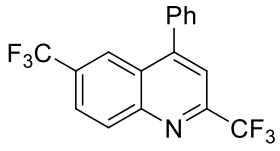
M. p. 100-102 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, J = 1.8 Hz, 1H), 8.04 (dd, J = 8.9, 1.9 Hz, 1H), 7.98 (d, J = 8.9 Hz, 1H), 7.68 (s, 1H), 7.61-7.55 (m, 3H), 7.54-7.48 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 148.0 (q, $^2J_{C\text{-}F}$ = 35 Hz), 146.8, 139.5, 136.5, 134.8, 132.0, 129.5, 129.4, 129.1, 129.0, 121.6 (q, $^1J_{C\text{-}F}$ = 275 Hz), 117.8 (q, $^3J_{C\text{-}F}$ = 2 Hz), 95.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.5.

HRMS (ESI) m/z calcd for $C_{16}H_{10}F_3IN^+$ $[M+H]^+$: 399.9805, Found 399.9807.



4-Phenyl-2,6-bis(trifluoromethyl)quinoline (**3ha**).

The compound (82.7 mg, 80%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a white solid. The compound (70.0 mg, 68%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a white solid.

M. p. 99-101 °C.

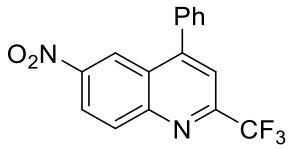
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, J = 8.9 Hz, 1H), 8.33 (s, 1H), 8.00 (dd, J = 8.9, 1.9 Hz, 1H), 7.80 (s, 1H), 7.65-7.59 (m, 3H), 7.58-7.49 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4, 149.7 (q, $^2J_{C\text{-}F}$ = 34Hz), 148.9, 136.3, 132.0, 130.5 (q, $^2J_{C\text{-}F}$ = 33 Hz), 129.8, 129.6, 129.3, 126.7, 126.4, 124.1 (q, $^3J_{C\text{-}F}$ = 5 Hz), 123.9 (q, $^1J_{C\text{-}F}$ = 274 Hz), 123.7 (q, $^1J_{C\text{-}F}$ = 276 Hz), 118.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ −62.7, −67.8.

HRMS (ESI) m/z calcd for $C_{17}H_{10}F_6N^+$ $[M+H]^+$: 342.0712, Found 342.0713.

The spectral data were in accordance with those reported in the literature.[7]



6-Nitro-4-phenyl-2-(trifluoromethyl)quinoline (**3ia**).

The compound (90.7 mg, 94%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→30:1, v/v) as a light yellow solid.

M. p. 173-175 °C.

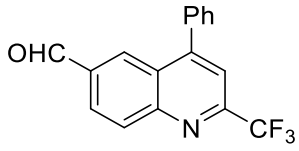
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (d, J = 2.5 Hz, 1H), 8.56 (dd, J = 9.3, 2.5 Hz, 1H), 8.43 (d, J = 9.3 Hz, 1H), 7.84 (s, 1H), 7.66-7.61 (m, 3H), 7.58-7.53 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 150.8 (q, $^2J_{C\text{-}F}$ = 35 Hz), 149.8, 147.1, 135.7, 132.6, 130.1, 129.6, 129.5, 126.7, 124.1, 123.0, 121.2 (q, $^1J_{C\text{-}F}$ = 275 Hz), 118.7 (q, $^3J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.9.

HRMS (ESI) m/z calcd for $C_{16}H_{10}F_3N_2O_2^+$ $[M+H]^+$: 319.06689, Found 319.0691 .

The spectral data were in accordance with those reported in the literature.[5]



4-Phenyl-2-(trifluoromethyl)quinoline-6-carbaldehyde (**3ja**).

The compound (75.0 mg, 82%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow solid.

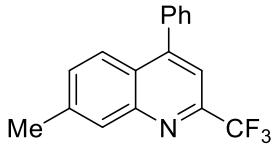
M. p. 127-128 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.49 (d, J = 1.6 Hz, 1H), 8.37 (d, J = 8.8 Hz, 1H), 8.27 (dd, J = 8.8, 1.7 Hz, 1H), 7.78 (s, 1H), 7.67-7.58 (m, 3H), 7.58-7.52 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.3, 152.8, 150.5, 150.0 (q, $^{2}J_{C\text{-}F}$ = 35 Hz), 136.3, 135.8, 131.9 131.9, 129.8, 129.6, 129.3, 127.6, 127.2, 121.3 (q, $^{1}J_{C\text{-}F}$ = 275 Hz), 118.1 (q, $^{3}J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.8.

HRMS (ESI) m/z calcd for $C_{17}H_{11}F_3NO^+$ $[M+H]^+$: 302.0787, Found 302.0788.



7-Methyl-4-phenyl-2-(trifluoromethyl)quinoline (**3ka**).

The compound (76.9 mg, 89%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil; the compound (79.5 mg, 92%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil.

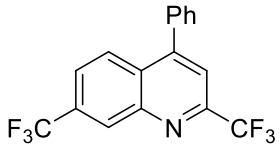
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.87 (d, J = 8.6 Hz, 1H), 7.62 (s, 1H), 7.57-7.52 (m, 3H), 7.52-7.49 (m, 2H), 7.43 (dd, J = 8.7, 1.7 Hz, 1H), 2.58 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 148.2, 147.6 (q, $^{2}J_{C\text{-}F}$ = 35 Hz), 141.2, 137.4, 131.0, 129.6, 129.5, 129.0, 128.9, 125.6, 125.6, 121.9 (q, $^{1}J_{C\text{-}F}$ = 276 Hz), 116.3 (q, $^{3}J_{C\text{-}F}$ = 2 Hz), 21.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.4.

HRMS (ESI) m/z calcd for $C_{17}H_{13}F_3N^+$ $[M+H]^+$: 288.0995, Found 288.0998.

The spectral data were in accordance with those reported in the literature.[8]



4-Phenyl-2,7-bis(trifluoromethyl)quinoline (**3la**).

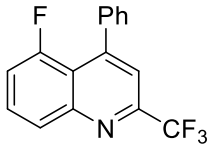
The compound (85.7mg, 83%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.15 (d, J = 8.9 Hz, 1H), 7.79 (dd, J = 8.5, 1.8 Hz, 2H), 7.63-7.58 (m, 3H), 7.55-7.47 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.4, 149.1 (q, $^2J_{C\text{-}F}$= 35 Hz), 147.0, 136.5, 132.6 (q, $^2J_{C\text{-}F}$ = 33 Hz), 129.6, 129.6, 129.2, 129.0, 128.5 (q, $^3J_{C\text{-}F}$ = 5 Hz), 127.6, 124.3 (q, $^3J_{C\text{-}F}$ = 3 Hz), 123.6 (q, $^1J_{C\text{-}F}$ = 273 Hz), 121.6 (q, $^1J_{C\text{-}F}$ = 275 Hz), 118.9 (q, $^3J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −63.1, −67.8.

HRMS (ESI) m/z calcd for $C_{17}H_{10}F_6N^+$ $[M+H]^+$: 342.0712, Found 342.0715.



5-Fluoro-4-phenyl-2-(trifluoromethyl)quinoline (**3ma**).

The compound **3ma** (55.2 mg, 63%) and **3m'a** (16.7 mg, 19%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow solid and a white solid, respectively.

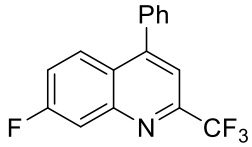
M. p. 87-88 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.6 Hz, 1H), 7.78 (ddd, J = 8.0, 8.0, 5.2 Hz, 1H), 7.63 (s, 1H), 7.52-7.47 (m, 3H), 7.46-7.41 (m, 2H), 7.29 (ddd, J = 11.7, 7.8, 0.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1 (d, $^1J_{C\text{-}F}$ = 258 Hz), 149.0 (q, $^3J_{C\text{-}F}$ = 2 Hz), 148.0 (q, $^2J_{C\text{-}F}$ = 35 Hz), 139.4 (d, $^4J_{C\text{-}F}$ = 4 Hz), 130.4 (d, $^3J_{C\text{-}F}$ = 10 Hz), 128.6, 128.4 (d, $^4J_{C\text{-}F}$ = 4 Hz), 128.0, 126.9 (d, $^4J_{C\text{-}F}$ = 4.0 Hz), 121.5 (q, $^1J_{C\text{-}F}$ = 275 Hz), 119.2, 118.2 (d, $^3J_{C\text{-}F}$ = 10 Hz), 118.1 (d, $^2J_{C\text{-}F}$ = 24 Hz), 113.7 (d, $^2J_{C\text{-}F}$ = 22 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.7, −104.9.

HRMS (ESI) m/z calcd for $C_{16}H_{10}F_4N^+$ $[M+H]^+$: 292.0744, Found 292.0747.



7-Fluoro-4-phenyl-2-(trifluoromethyl)quinoline (**3m'a**).

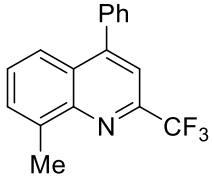
M. p. 100-102 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, J = 9.3, 6.0 Hz, 1H), 7.91 (dd, J = 9.7, 2.6 Hz, 1H), 7.65 (s, 1H), 7.60-7.54 (m, 3H), 7.53-7.48 (m, 2H), 7.41 (ddd, J = 9.4, 8.0, 2.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6 (d, $^1J_{C\text{-}F}$ = 252 Hz), 153.3, 149.2 (d, $^3J_{C\text{-}F}$ = 12 Hz), 148.8 (q, $^2J_{C\text{-}F}$ = 35 Hz), 137.0, 129.6, 129.4, 129.1, 128.5 (d, $^3J_{C\text{-}F}$ = 10 Hz), 124.7, 121.6 (q, $^1J_{C\text{-}F}$ = 274 Hz), 119.3 (d, $^2J_{C\text{-}F}$ = 25 Hz), 116.6 (q, $^3J_{C\text{-}F}$ = 2 Hz), 114.1 (d, $^2J_{C\text{-}F}$ = 21 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.7, −107.7.

HRMS (ESI) m/z calcd for $C_{16}H_{10}F_4N^+$ $[M+H]^+$: 292.0744 , Found 292.0748.



8-Methyl-4-phenyl-2-(trifluoromethyl)quinoline (**3na**).

The compound (72.4 mg, 84%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a pale yellow oil. The compound (68.8 mg, 79%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a pale yellow oil.

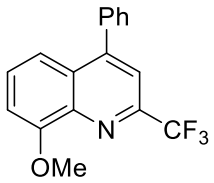
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.5 Hz, 1H), 7.73 (s, 1H), 7.67 (d, J = 6.9 Hz, 1H), 7.61-7.48 (m, 6H), 2.94 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 147.0, 146.3 (q, $^2J_{C\text{-}F}$ = 35 Hz), 138.9, 137.8, 130.6, 129.7, 128.9, 128.8, 128.3, 127.6, 123.9, 122.1 (q, $^1J_{C\text{-}F}$ =275 Hz), 116.9 (q, $^3J_{C\text{-}F}$ = 2 Hz), 18.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.3.

HRMS (ESI) m/z calcd for $C_{17}H_{13}F_3N^+$ $[M+H]^+$: 288.0995, Found 288.0999.

The spectral data were in accordance with those reported in the literature.[6]



8-Methoxy-4-phenyl-2-(trifluoromethyl)quinoline (**3oa**).

The compound (73.3 mg, 80%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→30:1, v/v) as a white solid; the compound (74.6 mg, 81%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→30:1, v/v) as a white solid.

M. p. 70-72 °C.

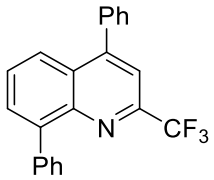
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.57-7.47 (m, 7H), 7.16 (dd, J = 4.9, 3.9 Hz, 1H), 4.12 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 150.8, 146.3 (q, $^{2}J_{C\text{-}F}$ = 35 Hz), 139.9, 137.6, 129.6, 129.0, 128.9, 128.8, 121.8 (q, $^{1}J_{C\text{-}F}$ = 276 Hz), 117.9, 117.6, 108.8, 56.5. (One carbon is invisible)

^{19}F NMR (471 MHz, $CDCl_3$) δ −66.9.

HRMS (ESI) m/z calcd for $C_{17}H_{13}F_3NO^+$ $[M+H]^+$: 304.0944, Found 304.0946.

The spectral data were in accordance with those reported in the literature.[5]



4,8-Diphenyl-2-(trifluoromethyl)quinoline (**3pa**).

The compound (96.2 mg, 91%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow solid.

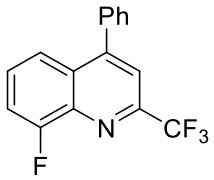
M. p. 112-113 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.5, 1.4 Hz, 1H), 7.92 (dd, J = 7.1, 1.4 Hz, 1H), 7.88 (dd, J = 8.2, 1.3 Hz, 2H), 7.76 (s, 1H), 7.70 (dd, J = 8.5, 7.2 Hz, 1H), 7.63-7.55 (m, 7H), 7.52-7.47 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.1, 147.0 (q, $^{2}J_{C\text{-}F}$ = 35 Hz), 145.4, 141.8, 138.8, 137.7, 131.4, 131.2, 129.6, 129.0, 128.9, 128.4, 128.0, 127.9, 127.7, 125.5, 121.9 (q, $^{1}J_{C\text{-}F}$ = 275 Hz), 117.1 (q, $^{3}J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.3.

HRMS (ESI) m/z calcd for $C_{22}H_{15}F_3N^+$ $[M+H]^+$: 350.1151, Found 350.1153.



8-Fluoro-4-phenyl-2-(trifluoromethyl)quinoline (**3qa**).

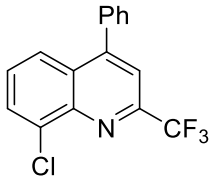
The compound (74.5 mg, 85%) was prepared from the general procedure 3 (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil; The compound (70.0 mg, 80%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.6 Hz, 1H), 7.73 (s, 1H), 7.59-7.46 (m, 7H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3 (d, $^{1}J_{C\text{-}F}$ = 255 Hz), 151.1 (d, $^{4}J_{C\text{-}F}$ = 3 Hz), 147.7 (q, $^{2}J_{C\text{-}F}$ = 36 Hz), 138.4 (d, $^{3}J_{C\text{-}F}$ = 12 Hz), 136.8, 129.5, 129.4, 129.1, 129.0 (d, $^{2}J_{C\text{-}F}$ = 17 Hz), 128.5 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 121.8 (d, $^{4}J_{C\text{-}F}$ = 5 Hz), 121.5 (q, $^{1}J_{C\text{-}F}$ = 274 Hz), 118.1 (q, $^{3}J_{C\text{-}F}$ = 2 Hz), 114.6 (d, $^{2}J_{C\text{-}F}$ = 19 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.4, −122.0.

HRMS (ESI) m/z calcd for $C_{16}H_{10}F_4N^+$ $[M+H]^+$: 292.0744 , Found 292.0749.



8-Chloro-4-phenyl-2-(trifluoromethyl)quinoline (**3ra**).

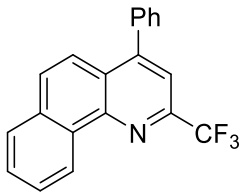
The compound (83.5 mg, 90%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a red oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, J = 7.9, 1.2 Hz, 2H), 7.74 (d, J = 1.7 Hz, 1H), 7.63-7.46 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7, 147.8 (q, $^{2}J_{C\text{-}F}$ = 35 Hz), 144.2, 136.8, 134.9, 130.7, 129.5, 129.3, 128.9, 128.9, 128.3, 125.0, 121.5 (q, $^{1}J_{C\text{-}F}$ = 275 Hz), 118.0 (q, $^{3}J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.3.

HRMS (ESI) m/z calcd for $C_{16}H_{10}ClF_3N^+$ $[M+H]^+$: 308.0488, Found 308.0450.



4-Phenyl-2-(trifluoromethyl)benzo[*h*]quinoline (**3sa**).

The compound (67.5 mg, 69%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a white solid.

M. p. 87-89 °C.

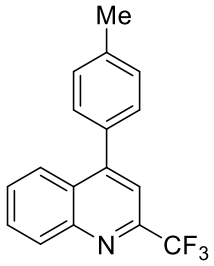
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (dd, J = 8.0, 1.4 Hz, 1H), 7.91 (dd, J = 7.8, 1.4 Hz, 1H), 7.8 -7.74 (m, 5H), 7.61-7.53 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 146.6, 145.9 (q, $^2J_{C\text{-}F}$ = 35 Hz), 137.6, 133.5, 131.4, 129.8, 129.6, 129.1, 128.9, 128.8, 127.7, 127.7, 125.7, 125.4, 122.4, 121.9 (q, $^1J_{C\text{-}F}$ = 274 Hz), 118.2 (q, $^3J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.0.

HRMS (ESI) m/z calcd for $C_{20}H_{13}F_3N^+$ $[M+H]^+$: 324.0955, Found 324.0998.

The spectral data were in accordance with those reported in the literature.[5]



4-(*p*-Tolyl)-2-(trifluoromethyl)quinoline (**3ab**).

The compound (84.5 mg, 98%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil.

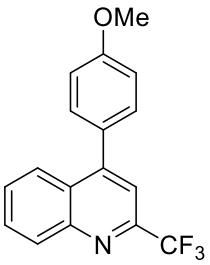
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 8.5 Hz, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.83-7.79 (ddd, J = 8.8, 6.7, 1.4 Hz, 1H), 7.68 (s, 1H), 7.63-7.58 (ddd, J = 8.5, 6.8, 1.2 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 7.9 Hz, 2H), 2.48 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.1, 147.9, 147.6 (q, $^2J_{C\text{-}F}$ = 35 Hz), 139.2, 134.3, 130.6, 130.6, 129.6, 129.5, 128.6, 127.6, 126.1, 121.8 (q, $^1J_{C\text{-}F}$ = 276 Hz), 117.0 (q, $^3J_{C\text{-}F}$ = 2 Hz), 21.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.4.

HRMS (ESI) m/z calcd for $C_{17}H_{13}F_3N^+$ $[M+H]^+$: 288.0995, Found 288.0999.

The spectral data were in accordance with those reported in the literature.[8]



4-(4-Methoxyphenyl)-2-(trifluoromethyl)quinoline (**3ac**).

The compound (79.9 mg, 87%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil; the compound (78.4 mg, 86%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil.

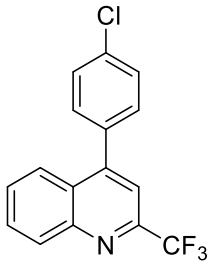
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.81 (ddd, J = 8.3, 6.7, 1.4 Hz, 1H), 7.66 (s, 1H), 7.61 (ddd, J = 7.8, 7.8, 1.1 Hz, 1H), 7.47 (ddd, J = 8.2, 6.9, 1.3 Hz, 2H), 7.13-7.06 (m, 2H), 3.91 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 150.8, 148.0, 147.7 (q, $^2J_{C\text{-}F}$ = 35 Hz), 131.0, 130.6, 130.6, 129.5, 128.6, 127.7, 126.1, 121.8 (q, $^1J_{C\text{-}F}$ = 273 Hz), 117.0 (q, $^3J_{C\text{-}F}$ = 2 Hz), 114.4, 55.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.5.

HRMS (ESI) m/z calcd for $C_{17}H_{13}F_3NO^+$ $[M+H]^+$:304.0944, Found 304.0947.

The spectral data were in accordance with those reported in the literature.[5]



4-(4-Chlorophenyl)-2-(trifluoromethyl)quinoline (**3ad**).

The compound (81.5 mg, 88%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a white solid.

M. p. 93-94 °C.

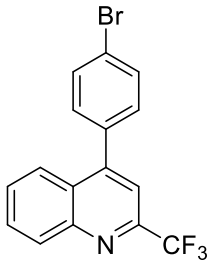
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.82 (ddd, J = 8.3, 6.0, 1.4 Hz, 1H), 7.67-7.60 (m, 2H), 7.56-7.51 (m, 2H), 7.50-7.44 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 147.8, 147.6 (q, $^2J_{C\text{-}F}$ = 34 Hz), 135.5, 135.4, 130.8, 130.7, 130.6, 129.1, 128.9, 127.2, 125.5, 121.6 (q, $^1J_{C\text{-}F}$ = 275 Hz), 116.9 (q, $^3J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.4.

HRMS (ESI) m/z calcd for $C_{16}H_{10}ClF_3N^+$ $[M+H]^+$: 308.0448, Found 308.0452.

The spectral data were in accordance with those reported in the literature.[5]



4-(4-Bromophenyl)-2-(trifluoromethyl)quinoline (**3ae**).

The compound (85.5 mg, 80%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a pale yellow solid.

M. p. 94-97 °C.

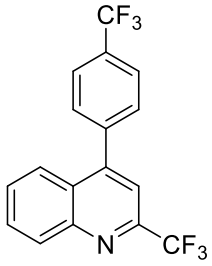
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 8.5 Hz, 1H), 8.02-7.90 (dd, J = 31.6, 8.2 Hz, 1H), 7.84 (dd, J = 7.6, 5.3 Hz, 1H), 7.77-7.59 (m, 4H), 7.40 (d, J = 8.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 147.8, 147.6 (q, $^{1}J_{C\text{-}F}$ = 35 Hz), 136.0, 132.1, 131.1, 130.7, 130.6, 128.9, 127.1, 125.5, 123.6, 121.6 (q, $^{1}J_{C\text{-}F}$ = 275 Hz), 116.9 (q, $^{3}J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.5.

HRMS (ESI) m/z calcd for $C_{16}H_{10}BrF_3N^+$ $[M+H]^+$: 351.9943 , Found 351.9948.

The spectral data were in accordance with those reported in the literature.[8]



2-(Trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)quinoline (**3af**).

The compound (85.0 mg, 83%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a white solid.

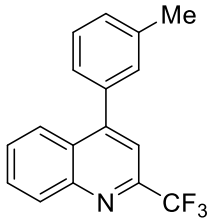
M. p. 119-121 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.88-7.81 (m, 3H), 7.73-7.63 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 147.9, 147.7 (q, $^{2}J_{C\text{-}F}$ = 35 Hz), 140.9, 131.4 (q, $^{2}J_{C\text{-}F}$ = 35 Hz), 131.0, 130.8, 130.1, 129.2, 127.1, 126.0 (q, $^{3}J_{C\text{-}F}$ = 2 Hz), 125.5, 124.0 (q, $^{1}J_{C\text{-}F}$ = 275 Hz), 121.6 (q, $^{1}J_{C\text{-}F}$ = 276 Hz), 117.1 (q, $^{3}J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.2, −67.5.

HRMS (ESI) m/z calcd for $C_{17}H_{10}F_6N^+$ $[M+H]^+$: 342.0712, Found 342.0716.



4-(*m*-Tolyl)-2-(trifluoromethyl)quinoline (**3ag**).

The compound (83.9 mg, 97%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil; The compound (74.3 mg, 86%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil.

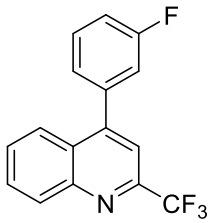
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 1H), 8.04 (dd, J = 8.5, 1.0 Hz, 1H), 7.82 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.69 (s, 1H), 7.61 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 7.44 (dd, J = 7.7, 7.7 Hz, 1H), 7.37-7.29 (m, 3H), 2.48 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.3, 147.9, 147.6 (q, $^2J_{C\text{-}F}$ = 36 Hz), 138.8, 137.2, 130.6, 130.6, 130.2, 129.9, 128.8, 128.6, 127.6, 126.7, 126.1, 121.8 (q, $^1J_{C\text{-}F}$ = 275 Hz), 117.1 (q, $^3J_{C\text{-}F}$ = 2 Hz), 21.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.4.

HRMS (ESI) m/z calcd for $C_{17}H_{13}F_3N^+$ $[M+H]^+$: 288.0995, Found 288.0999.

The spectral data were in accordance with those reported in the literature.[8]



4-(3-Fluorophenyl)-2-(trifluoromethyl)quinoline (**3ah**).

The compound (82.3 mg, 94%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a white solid.

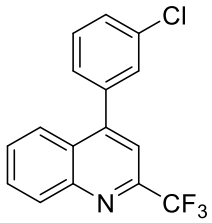
M. p. 92-93 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.6 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.84 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 7.69 (s, 1H), 7.66 (dd, J = 7.7, 7.7 Hz, 1H), 7.57-7.51 (m, 2H), 7.32-7.26 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3 (d, $^1J_{C\text{-}F}$ = 249 Hz), 149.9, 147.9, 147.6 (q, $^2J_{C\text{-}F}$ = 35 Hz), 133.2 (d, $^4J_{C\text{-}F}$ = 2 Hz), 131.4, 131.4, 130.7 (d, $^3J_{C\text{-}F}$ = 10 Hz), 130.7 (d, $^3J_{C\text{-}F}$ = 10 Hz), 128.9, 127.4, 125.7, 121.7 (q, $^1J_{C\text{-}F}$ = 275 Hz), 117.1 (q, $^3J_{C\text{-}F}$ = 2 Hz), 116.1 (d, $^2J_{C\text{-}F}$ = 22 Hz), 116.1 (d, $^2J_{C\text{-}F}$ = 22 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.4, −112.1.

HRMS (ESI) m/z calcd for $C_{16}H_{10}F_4N^+$ $[M+H]^+$: 292.0744, Found 292.0746.



4-(3-Chlorophenyl)-2-(trifluoromethyl)quinoline (**3ai**).

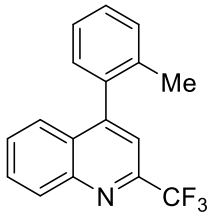
The compound (91.5 mg, 99%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil; The compound (65.5 mg, 70%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.83 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.68-7.61 (m, 2H), 7.54-7.47 (m, 3H), 7.40 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 147.9, 147.6 (q, $^2J_{C\text{-}F}$ = 35 Hz), 138.9, 135.0, 130.9, 130.7, 130.2, 129.6, 129.3, 129.1, 127.8, 127.2, 125.6, 121.6 (q, $^1J_{C\text{-}F}$ = 275 Hz), 117.1 (q, $^3J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.4.

HRMS (ESI) m/z calcd for $C_{16}H_{10}ClF_3N^+$ $[M+H]^+$: 308.0448, Found 308.0449.



4-(*o*-Tolyl)-2-(trifluoromethyl)quinoline (**3aj**).

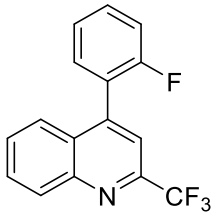
The compound (60.5 mg, 70%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, J = 8.5 Hz, 1H), 7.89-7.83 (m, 1H), 7.68 (s, 1H), 7.64-7.59 (m, 2H), 7.27 (dd, J = 7.5, 1.2 Hz, 1H), 2.09 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.2, 147.7 (q, $^2J_{C\text{-}F}$ = 35 Hz), 147.6, 136.7, 136.0, 130.8, 130.6, 130.5, 129.6, 129.1, 128.7, 128.1, 126.1, 126.1, 121.8 (q, $^1J_{C\text{-}F}$ = 275 Hz), 117.3 (q, $^3J_{C\text{-}F}$ = 2 Hz), 20.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.4.

HRMS (ESI) m/z calcd for $C_{17}H_{13}F_3N^+$ $[M+H]^+$: 288.0995 , Found 288.0997.



4-(2-Fluorophenyl)-2-(trifluoromethyl)quinoline (**3ak**).

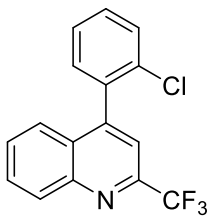
The compound (76.2 mg, 87%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a pale yellow oil; The compound (74.3 mg, 85%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, J = 8.5 Hz, 1H), 7.83 (ddd, J = 8.8, 7.8, 1.5 Hz, 1H), 7.78 (d, J = 8.6 Hz, 1H), 7.73 (s, 1H), 7.63 (ddd, J = 7.4, 7.4, 0.9 Hz, 1H), 7.57-7.50 (m, 1H), 7.42 (ddd, J = 7.5, 7.5, 1.8 Hz, 1H), 7.34 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 7.28 (ddd, J = 8.7, 8.7, 0.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6 (d, $^1J_{C\text{-}F}$ = 249 Hz), 147.6, 147.6 (q, $^2J_{C\text{-}F}$ = 35 Hz), 145.2, 131.6 (d, $^3J_{C\text{-}F}$ = 3 Hz), 131.3 (d, $^3J_{C\text{-}F}$ = 8 Hz), 130.8, 130.6, 128.9, 127.7, 125.9 (d, $^4J_{C\text{-}F}$ = 2 Hz), 124.7 (d, $^3J_{C\text{-}F}$ = 4 Hz), 124.7 (d, $^2J_{C\text{-}F}$ = 16 Hz), 121.6 (q, $^1J_{C\text{-}F}$ = 276 Hz), 118.0 (q, $^3J_{C\text{-}F}$ = 2 Hz), 116.3 (d, $^2J_{C\text{-}F}$ = 22 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.4, −113.5.

HRMS (ESI) m/z calcd for $C_{16}H_{10}F_4N^+$ $[M+H]^+$: 292.0744, Found 292.0747.



4-(2-Chlorophenyl)-2-(trifluoromethyl)quinoline (**3al**).

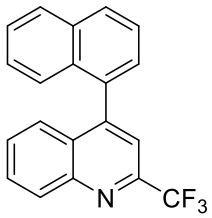
The compound (83.4 mg, 90%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, J = 8.5 Hz, 1H), 7.86-7.80 (m, 1H), 7.67 (s, 1H), 7.64-7.56 (m, 3H), 7.49 (ddd, J = 7.6, 7.6, 1.8 Hz, 1H), 7.44 (ddd, J = 7.6, 7.6, 1.8 Hz, 1H), 7.36 (dd, J = 7.5, 1.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 147.6, 147.6 (q, $^{2}J_{C\text{-}F}$ = 36 Hz), 135.9, 133.3, 131.3, 130.9, 130.6, 130.5, 130.2, 128.9, 127.7, 127.1, 126.0, 121.8 (q, $^{1}J_{C\text{-}F}$ = 275 Hz), 117.7 (q, $^{3}J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.4.

HRMS (ESI) m/z calcd for $C_{16}H_{10}ClF_3N^+$ $[M+H]^+$:308.0448, Found 308.0453.



4-(1-Naphthalenyl)-2-(trifluoromethyl)quinoline (**3am**).

The compound (92.4 mg, 95%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a pale yellow solid; the compound (93.8 mg, 96%) was prepared from the general procedure **B** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a pale yellow solid.

M. p. 96-98 °C.

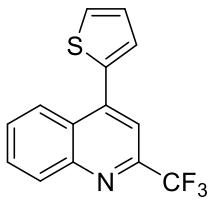
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, J = 8.5 Hz, 1H), 8.07-8.00 (m, 3H), 7.98-7.91 (m, 2H), 7.84 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.79 (s, 1H), 7.65-7.58 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 147.9, 147.7 (q, $^{2}J_{C\text{-}F}$ = 35 Hz), 134.6, 133.3, 133.3, 130.7, 130.6, 129.1, 128.8, 128.6, 128.4, 128.0, 127.7, 127.2, 127.0, 127.0, 126.1, 121.8 (q, $^{1}J_{C\text{-}F}$ = 276 Hz), 117.3 (q, $^{3}J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.3.

HRMS (ESI) m/z calcd for $C_{20}H_{13}F_3N^+$ $[M+H]^+$: 324.0995, Found 324.0998.

The spectral data were in accordance with those reported in the literature.[5]



4-(Thiophen-2-yl)-2-(trifluoromethyl)quinoline (**3an**).

The compound (42.0 mg, 50%) was prepared from the general procedure **A** for 6 h (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a yellow oil.

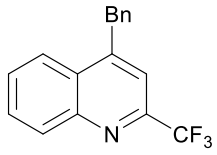
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H), 7.85 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.78 (s, 1H), 7.69 (ddd, J = 8.3, 6.7, 1.3 Hz, 1H), 7.59 (d, J = 5.1 Hz, 1H), 7.45 (dd, J = 3.6, 1.1 Hz, 1H), 7.29-7.26 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 147.6 (q, $^{2}J_{C\text{-}F}$ = 35 Hz), 143.4, 137.9, 130.8, 130.7, 129.5, 129.1, 128.3, 128.2, 127.1, 125.7, 121.6 (q, $^{1}J_{C\text{-}F}$ = 276 Hz), 117.3(q, $^{3}J_{C\text{-}F}$ = 2 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.5.

HRMS (ESI) m/z calcd for $C_{14}H_9F_3NS^+$ $[M+H]^+$: 280.0402 , Found 280.0403 .

The spectral data were in accordance with those reported in the literature.[5]



4-Benzyl-2-(trifluoromethyl)quinoline (**3ao**).

The compound (62.4 mg, 72%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a pale yellow solid.

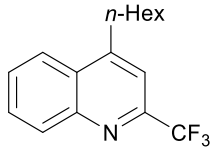
M. p. 86-88 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.80 (ddd, J = 8.4, 6.9, 1.2 Hz, 1H), 7.67-7.62 (ddd, J = 8.4, 7.5, 1.0 Hz, 1H), 7.50 (s, 1H), 7.36-7.31 (m, 2H), 7.31-7.26 (m, 1H), 7.21 (d, J = 7.4 Hz, 2H), 4.51 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 148.2 (q, $^{2}J_{C\text{-}F}$ = 34 Hz), 147.8, 138.2, 131.3, 130.8, 129.3, 129.2, 128.9, 128.6, 127.3, 124.3, 122.0 (q, $^{1}J_{C\text{-}F}$ = 274 Hz), 117.7 (q, $^{3}J_{C\text{-}F}$ = 2 Hz), 38.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.5.

HRMS (ESI) m/z calcd for $C_{17}H_{13}F_3NO^+$ $[M+H]^+$: 288.0995, Found 288.0996.



4-Hexyl-2-(trifluoromethyl)quinoline (**3ap**).

The compound (65.4 mg, 77%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→50:1, v/v) as a brown solid.

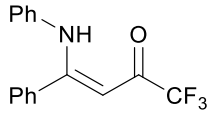
M. p. 52-54 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.76 (ddd, J = 8.6, 7.6, 1.4 Hz, 1H), 7.64 (ddd, J = 8.6, 8.2, 1.2 Hz, 1H), 7.55 (s, 1H), 3.15-3.04 (t, J = 7.9 Hz, 2H), 1.76 (m, 2H), 1.45 (m, 2H), 1.38-1.28 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7, 147.7 (q, $^2J_{C\text{-}F}$ = 34 Hz), 147.4, 131.0, 130.3, 128.3, 128.3, 123.6, 121.9 (q, $^1J_{C\text{-}F}$ = 276 Hz), 116.3 (q, $^3J_{C\text{-}F}$ = 2 Hz), 32.5, 31.7, 30.1, 29.4, 22.6, 14.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ −67.6.

HRMS (ESI) m/z calcd for $C_{16}H_{19}F_3NO^+$ $[M+H]^+$: 282.1464, Found 282.1466.



(*Z*)-1,1,1-trifluoro-4-phenyl-4-(phenylamino)but-3-en-2-one (**5**).

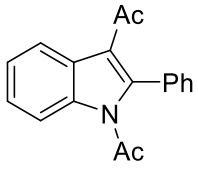
The compound (70.8 mg, 81%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→30:1, v/v) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 12.55 (br s, 1H), 7.42 (m, 1H), 7.37-7.30 (m, 4H), 7.18 (dd, J = 7.7, 7.7 Hz, 2H), 7.11 (dd, J = 7.4, 7.7 Hz, 1H), 6.84 (d, J = 7.7 Hz, 2H), 5.73 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.6 (q, $^2J_{C\text{-}F}$ = 34 Hz), 166.6, 138.0, 134.0, 130.8, 129.1, 128.8, 128.4, 126.1, 124.1, 117.6 (q, $^1J_{C\text{-}F}$ = 288 Hz), 92.8 (q, $^3J_{C\text{-}F}$ = 1.0 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ −76.6.

HRMS (ESI) m/z calcd for $C_{16}H_{13}F_3NO^+$ $[M+H]^+$: 292.0944, Found 292.0946.



1,1'-(2-Phenyl-1*H*-indole-1,3-diyl)bis(1-ethanone) (**10**).

The compound (14.0 mg, 16%) was prepared from the general procedure **A** (petroleum ether : ethyl acetate = 100:1→30:1, v/v) as a pale yellow solid.

M. p. 126-130 °C.

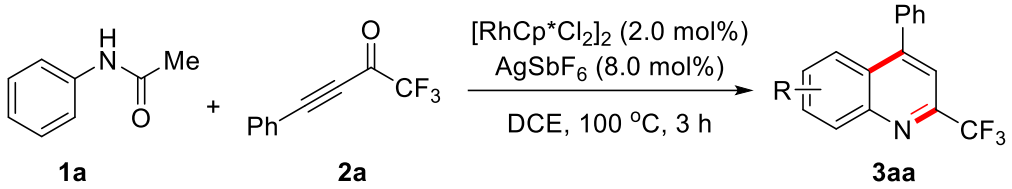
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37-8.22 (m, 2H), 7.61-7.54 (m, 3H), 7.64-7.50 (m, 2H), 7.44-7.36 (m, 2H), 1.94 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5, 171.7, 142.3, 136.2, 133.0, 130.8, 130.5, 129.2, 127.1, 126.1, 125.0, 122.2, 121.9, 115.6, 30.9, 27.9.

HRMS (ESI) m/z calcd for $C_{18}H_{16}NO_2^+$ $[M+H]^+$: 278.1176, Found 278.1179.

5. Experiments with scale-up reaction

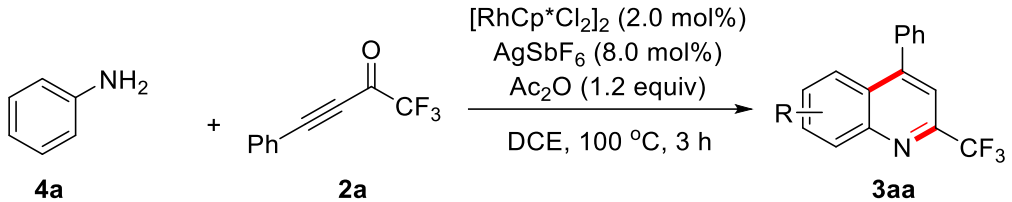
(A) Rhodium-catalysed [3+3] annulation between aniline 1a and CF_3-ynone 2a



1a **2a** **3aa**

The mixture of acetanilide (**1a**, 0.54 g, 4.0 mmol, 1.0 equiv), CF_3-ynone **2a** (0.87 g, 4.4 mmol, 1.1 equiv), $[RhCp^*Cl_2]_2$ (49.4 mg, 0.08 mmol) and $AgSbF_6$ (55.0 mg, 0.16 mmol) in DCE (13.0 mL) was stirred at 100 ℃ under N_2 for 3 h. After reaction completion, the solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 100:1→50:1, v/v) afforded the corresponding 2-trifluoromethylquinoline product **3aa** (1.002 g, 91%) as a yellow solid.

(B) Rhodium-catalysed one-pot [3+3] annulation between anilide 4a and trifluoromethyl ynone 2a

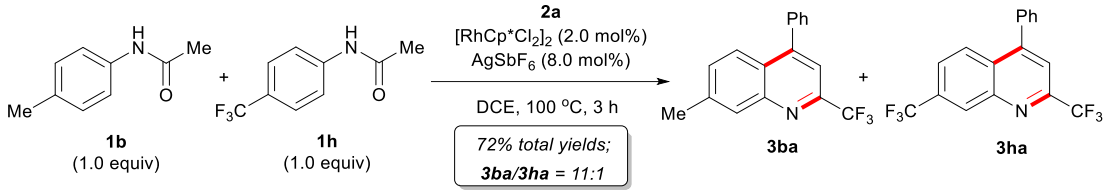


4a **2a** **3aa**

The mixture of anilide (**4a**, 0.54 g, 4.0 mmol, 1.0 equiv), Ac_2O (0.49 g, 4.8 mmol, 1.2 equiv), CF_3-ynone **2a** (0.87 g, 4.4 mmol, 1.1 equiv), $[RhCp^*Cl_2]_2$ (49.4 mg, 0.08 mmol) and $AgSbF_6$ (55.0 mg, 0.16 mmol) in DCE (13.0 mL) was stirred at 100 ℃ under N_2 for 3 h. After reaction completion, the solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 100:1→50:1, v/v) afforded the corresponding 2-trifluoromethylquinoline product **3aa** (0.934 g, 85%) as a yellow solid.

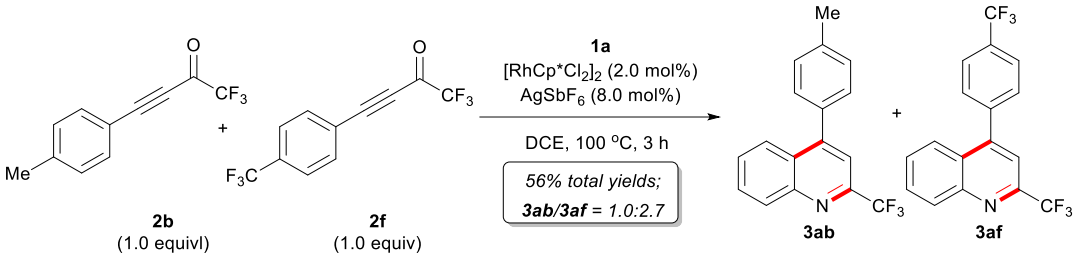
6. Intermolecular competition experiments

(A) Intermolecular competition experiment with anilides 1b and 1h



The mixture of *N*-(*p*-tolyl)acetamide (**1b**, 44.7 mg, 0.30 mmol, 1.0 equiv), *N*-{4-(trifluoromethyl)phenyl}acetamide (**1h**, 60.9 mg, 0.30 mmol, 1.0 equiv), 1,1,1-trifluoro-4-phenylbut-3-yn-2-one (**2a**, 59.4 mg, 0.30 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (3.7 mg, 0.006 mmol) and $AgSbF_6$ (8.2 mg, 0.024 mmol) in DCE (1.0 mL) was stirred at 100 ℃ under N_2 for 3 h. After reaction completion, the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel on silica gel (petroleum ether : ethyl acetate = 100:1→50:1, v/v) to afford **3ba** (56.8 mg, 66%) as a yellow oil and **3ha** (6.9 mg, 6%) as a white solid.

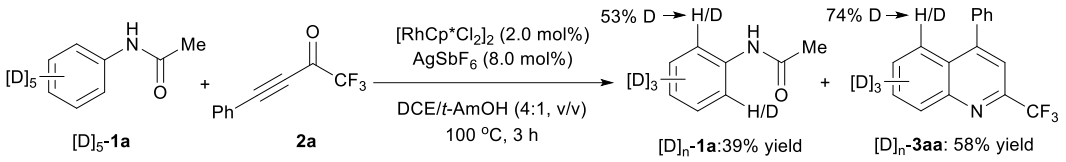
(B) Intermolecular competition experiment with CF_3-ynones 2b and 2f



The mixture of *N*-phenylacetamide (**1a**, 40.5 mg, 0.30 mmol, 1.0 equiv), 1,1,1-trifluoro-4-(*p*-tolyl)but-3-yn-2-one (**2b**, 63.7 mg, 0.30 mmol, 1.0 equiv), 1,1,1-trifluoro-4-{4-(trifluoromethyl)phenyl}but-3-yn-2-one (**2f**, 79.8 mg, 0.30 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (3.7 mg, 0.006 mmol) and $AgSbF_6$ (8.2 mg, 0.024 mmol) in DCE (1.0 mL) was stirred at 100 ℃ under N_2 for 3 h. After reaction completion, the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel on silica gel (petroleum ether : ethyl acetate = 100:1→50:1, v/v) to afford **3ab** (13.2 mg, 15%) as a yellow oil and **3af** (42.9 mg, 41%) as a white solid.

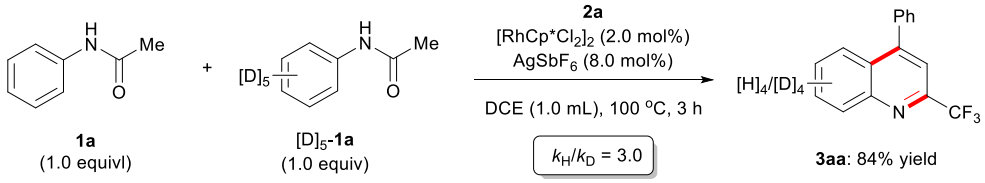
7. Deuterium-labeling experiments

(A) Rhodium-catalyzed [3+3] annulation of anilide $[D]_5$-1a with CF_3-ynone 2a in the presence of DCE/*t*-AmOH



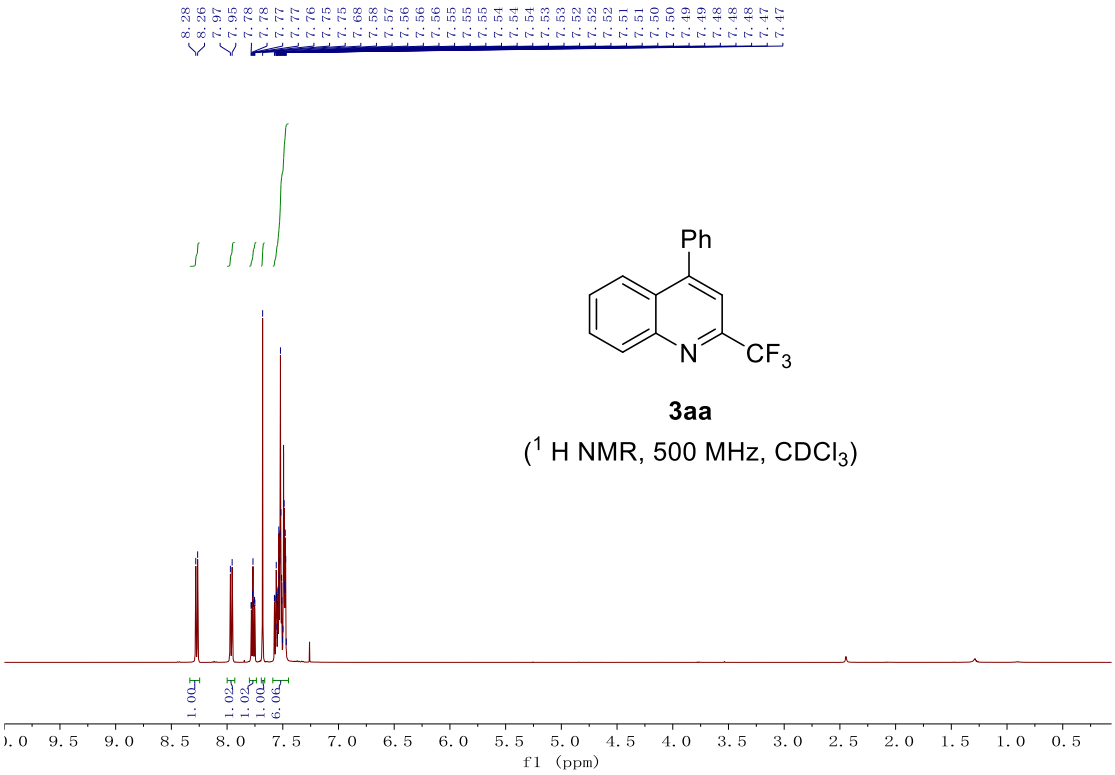
The mixture of anilide $[D]_5$-**1a** (42.0 mg, 0.30 mmol, 1.0 equiv), 1,1,1-trifluoro-4-phenylbut-3-yn-2-one (**2a**, 65.4 mg, 0.33 mmol, 1.1 equiv), $[RhCp^*Cl_2]_2$ (3.7 mg, 0.006 mmol) and $AgSbF_6$ (8.2 mg, 0.024 mmol) in DCE/*t*-AmOH (4:1, v/v, 1.0 mL) was stirred at 100 °C under N_2 for 3 h. After reaction completion, the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel on silica gel (petroleum ether : ethyl acetate = 100:1→50:1→10:1, v/v) to afford $[D]_n$-**3aa** (48.7 mg, 58%) as a yellow solid and $[D]_n$-**1a** (16.6 mg, 39%) as a white solid. The deuterium incorporation was estimated by ^{1}H-NMR spectroscopy.

(B) Kinetic isotope effect studies



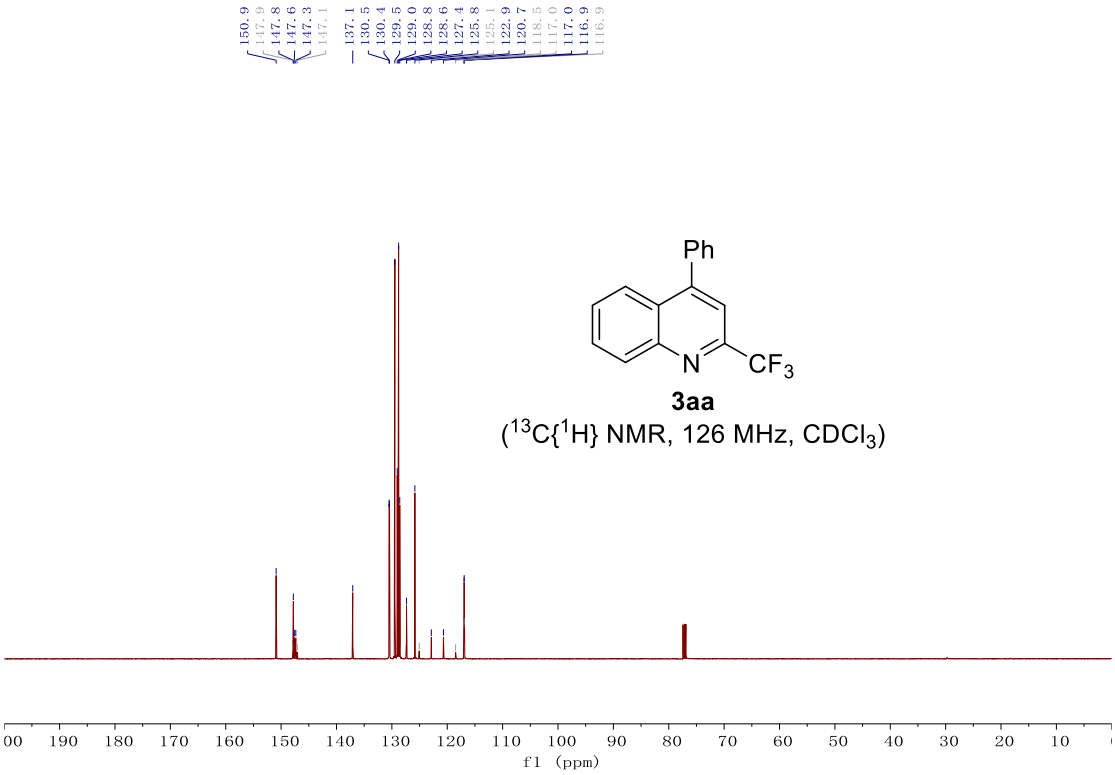
The mixture of anilide **1a** (40.5 mg, 0.30 mmol, 1.0 equiv), anilide $[D]_5$-**1a** (42.0 mg, 0.30 mmol, 1.0 equiv), 1,1,1-trifluoro-4-phenylbut-3-yn-2-one (**2a**, 59.4 mg, 0.30 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (3.7 mg, 0.006 mmol) and $AgSbF_6$ (8.2 mg, 0.024 mmol) in DCE (1.0 mL) was stirred at 100 °C under N_2 for 3 h. After reaction completion, the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 100:1→50:1, v/v) to afford $[D]_n$-**3aa** (69.1 mg, 84%) as a yellow solid. The deuterium incorporation was estimated by ^{1}H-NMR spectroscopy.

8. NMR spectra of compounds 3, 5 and 10.



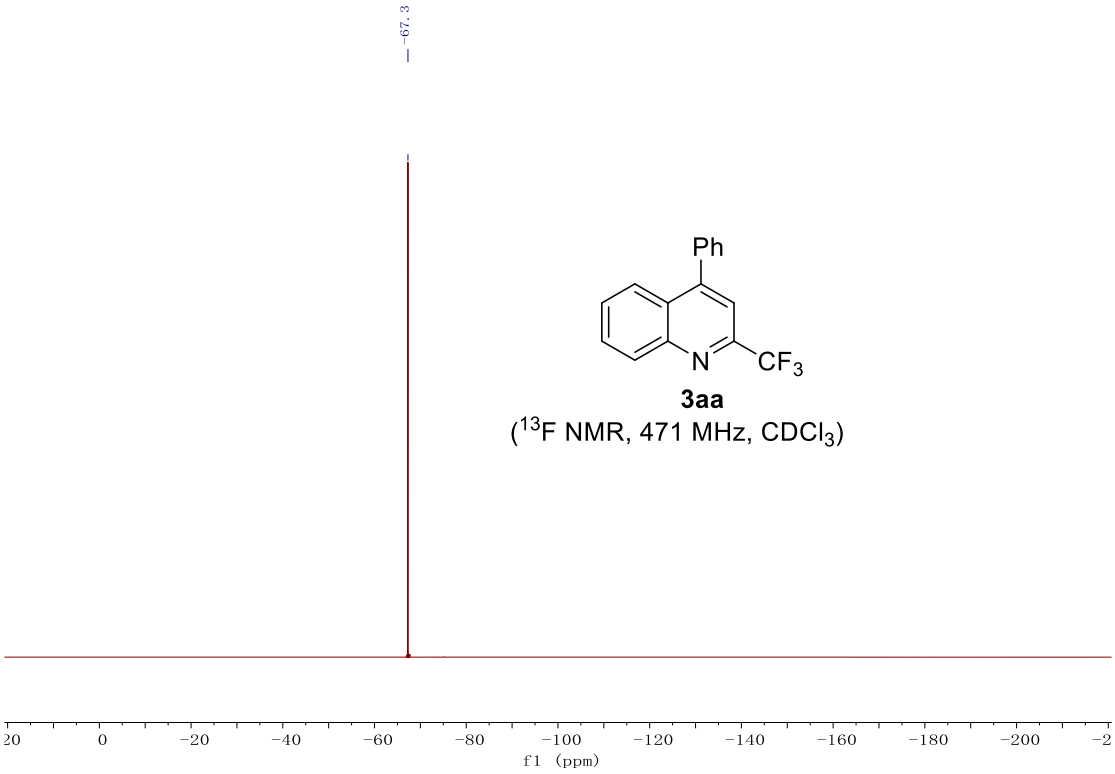
3aa

(^{1}H NMR, 500 MHz, $CDCl_3$)



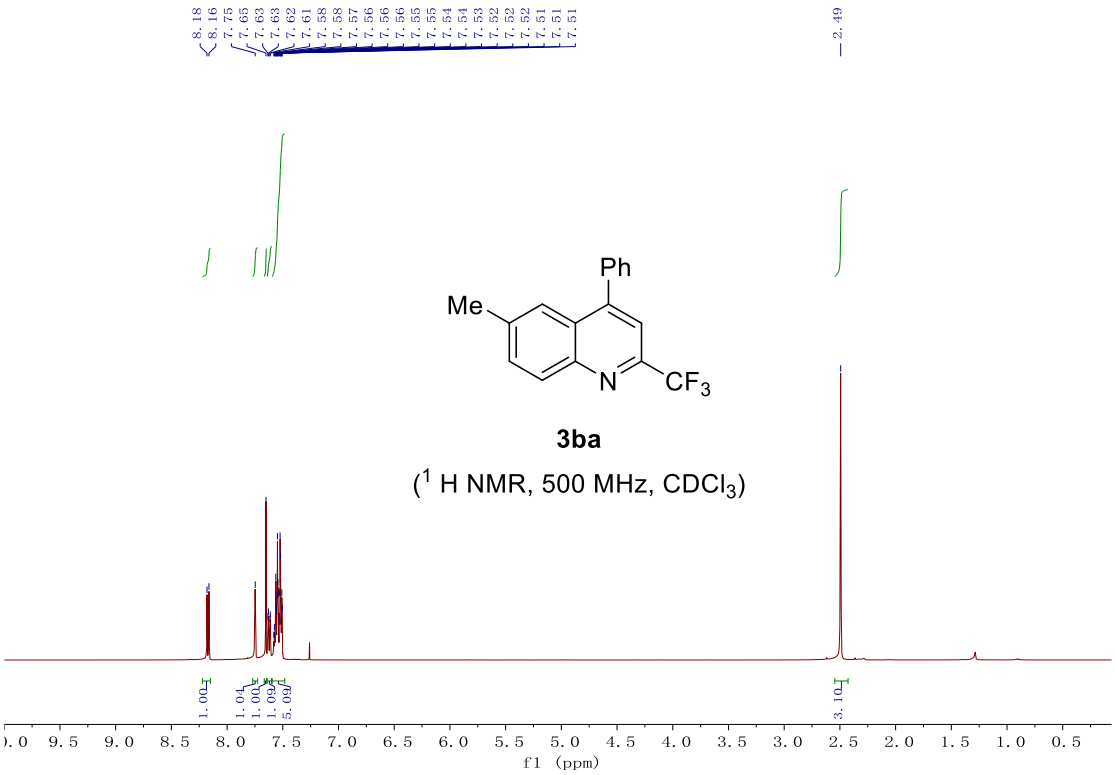
3aa

($^{13}C\{^1H\}$ NMR, 126 MHz, $CDCl_3$)



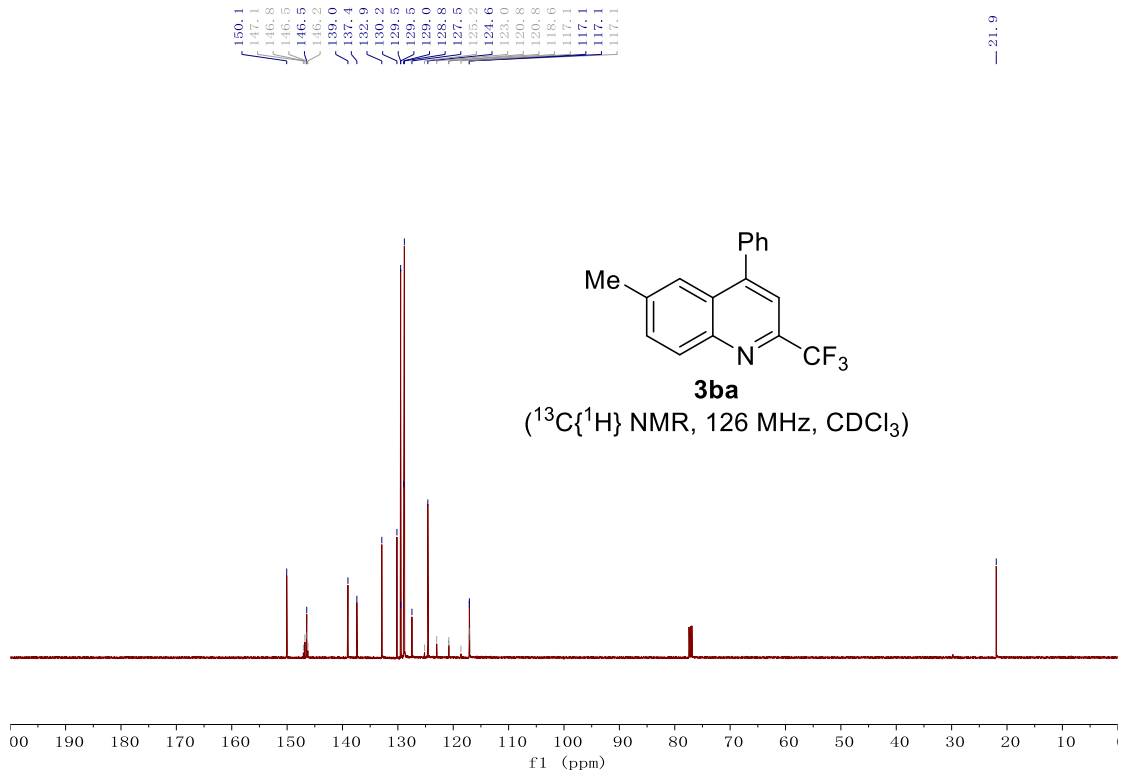
3aa

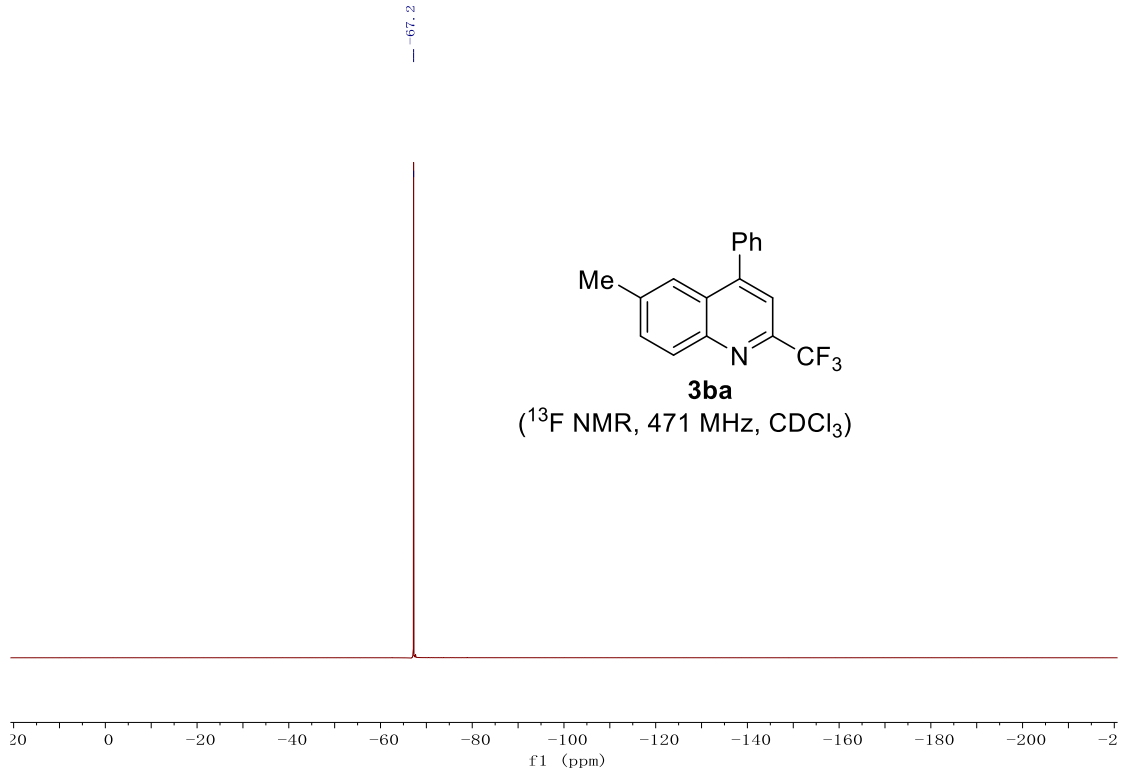
(^{13}F NMR, 471 MHz, $CDCl_3$)

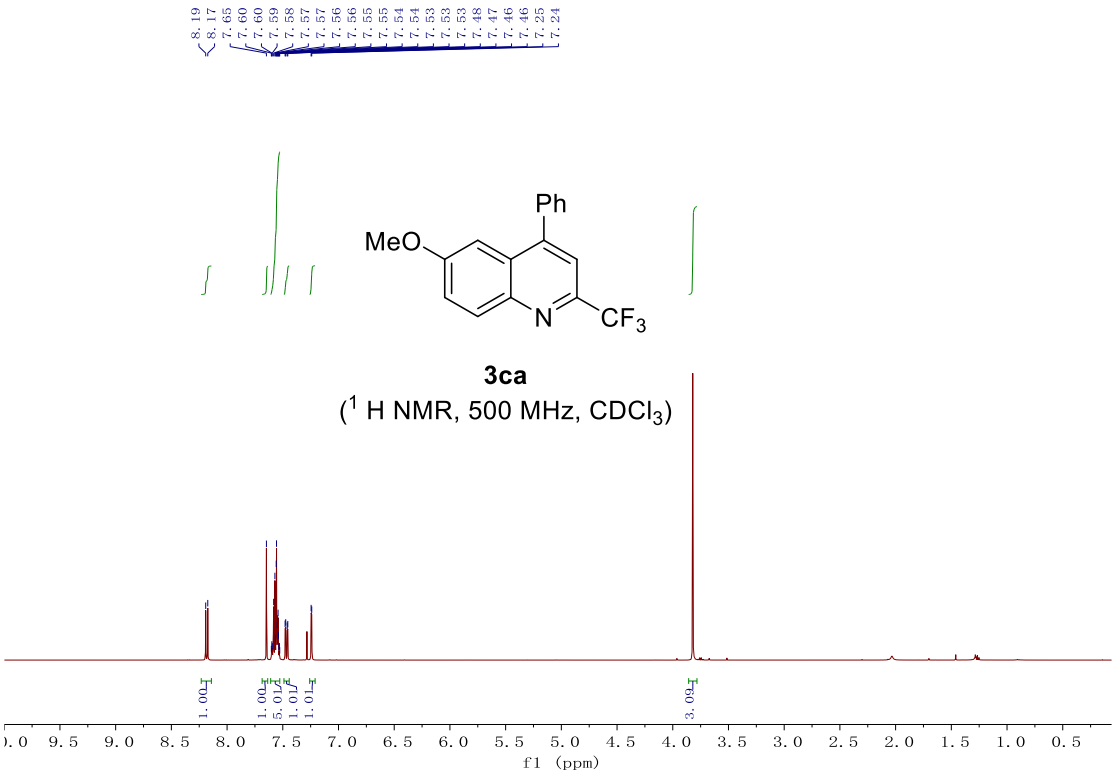


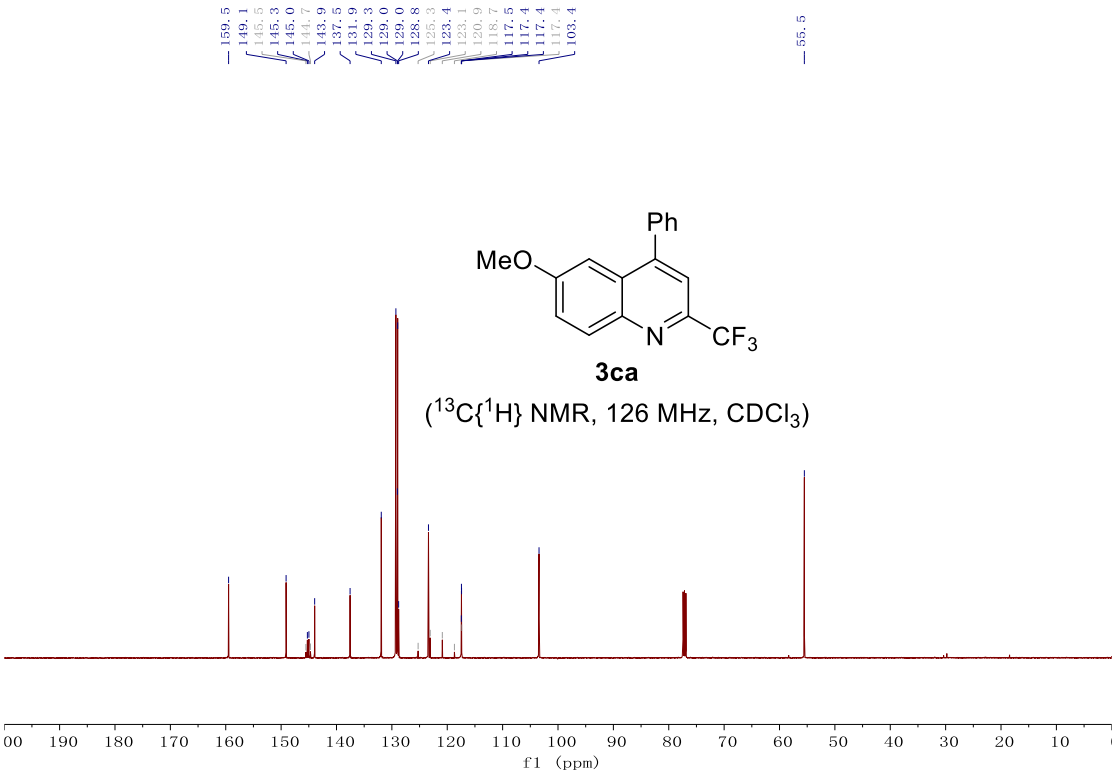
3ba

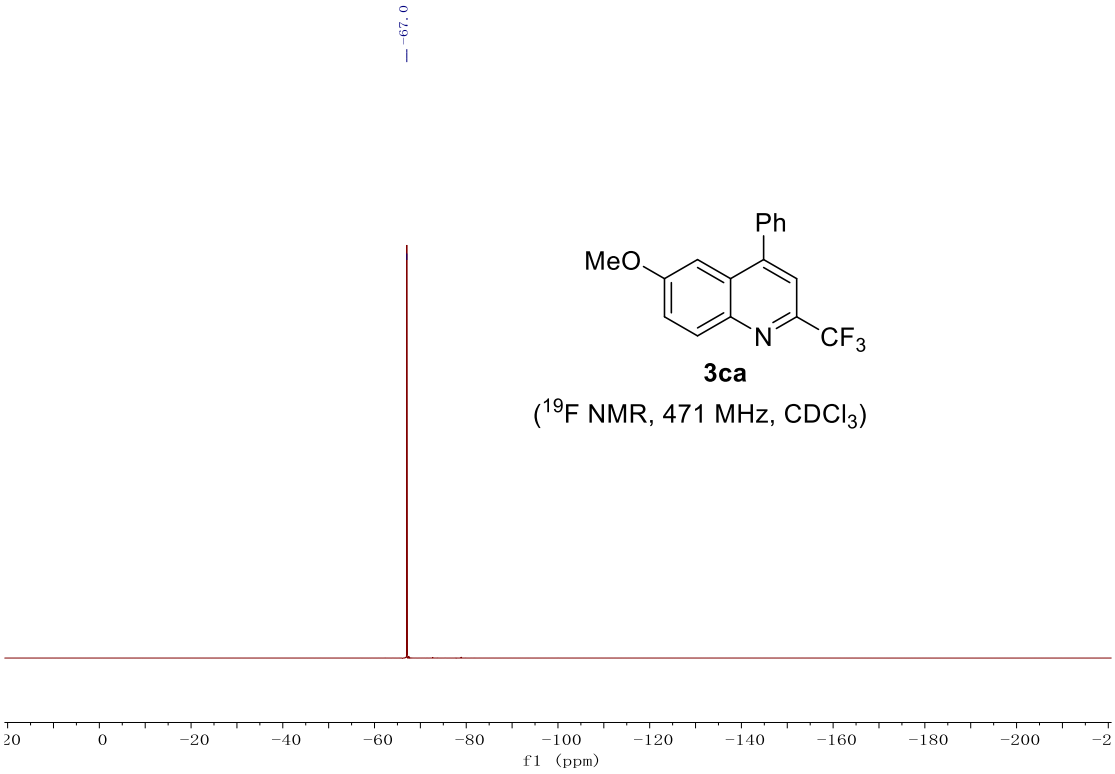
(^{1} H NMR, 500 MHz, $CDCl_3$)


150.1
147.1
146.8
146.5
146.5
146.2
139.0
137.4
132.9
130.2
129.5
129.5
129.0
128.8
127.5
125.2
124.6
123.0
120.8
120.8
118.6
117.1
117.1
117.1
117.1
21.9
Ph
Me
N
CF3
3ba
(13C{1H} NMR, 126 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-67.2
Ph
Me
N
CF3
3ba
(13F NMR, 471 MHz, CDCl3)
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)

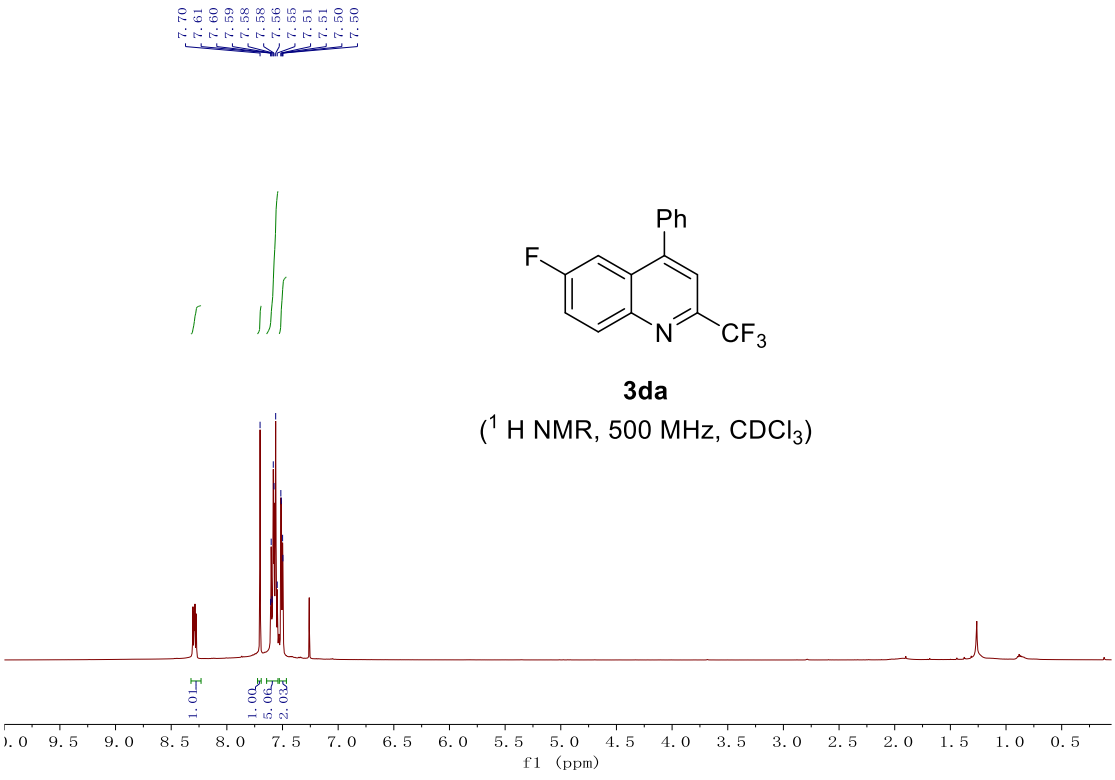

8.19
8.17
7.65
7.60
7.60
7.59
7.58
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.53
7.48
7.47
7.46
7.46
7.25
7.24
Ph
MeO
N
CF3
3ca
(1 H NMR, 500 MHz, CDCl3)
1.00
1.00
5.01
1.01
1.01
3.09
f1 (ppm)


159.5
149.1
145.5
145.3
145.0
144.7
143.9
137.5
131.9
129.3
129.0
129.0
128.8
125.3
123.4
123.1
120.9
118.7
117.5
117.4
117.4
117.4
103.4
55.5
Ph
MeO
N
CF3
3ca
(13C{1H} NMR, 126 MHz, CDCl3)
f1 (ppm)



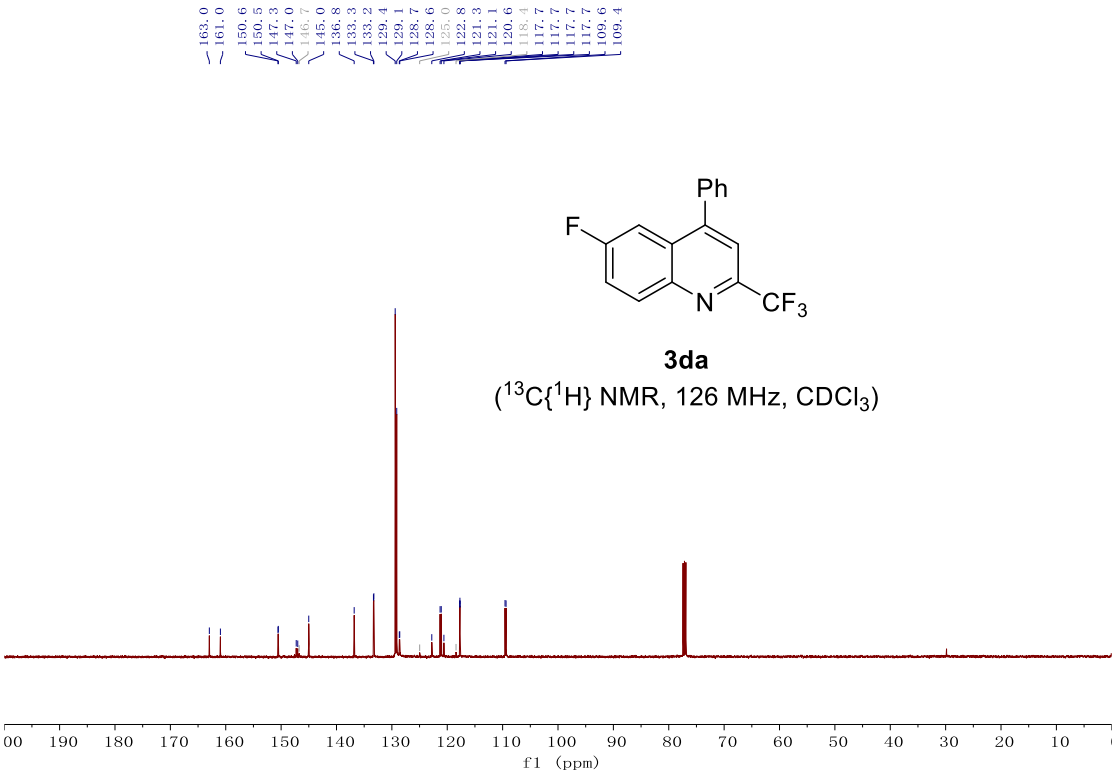
3ca

(^{19}F NMR, 471 MHz, $CDCl_3$)



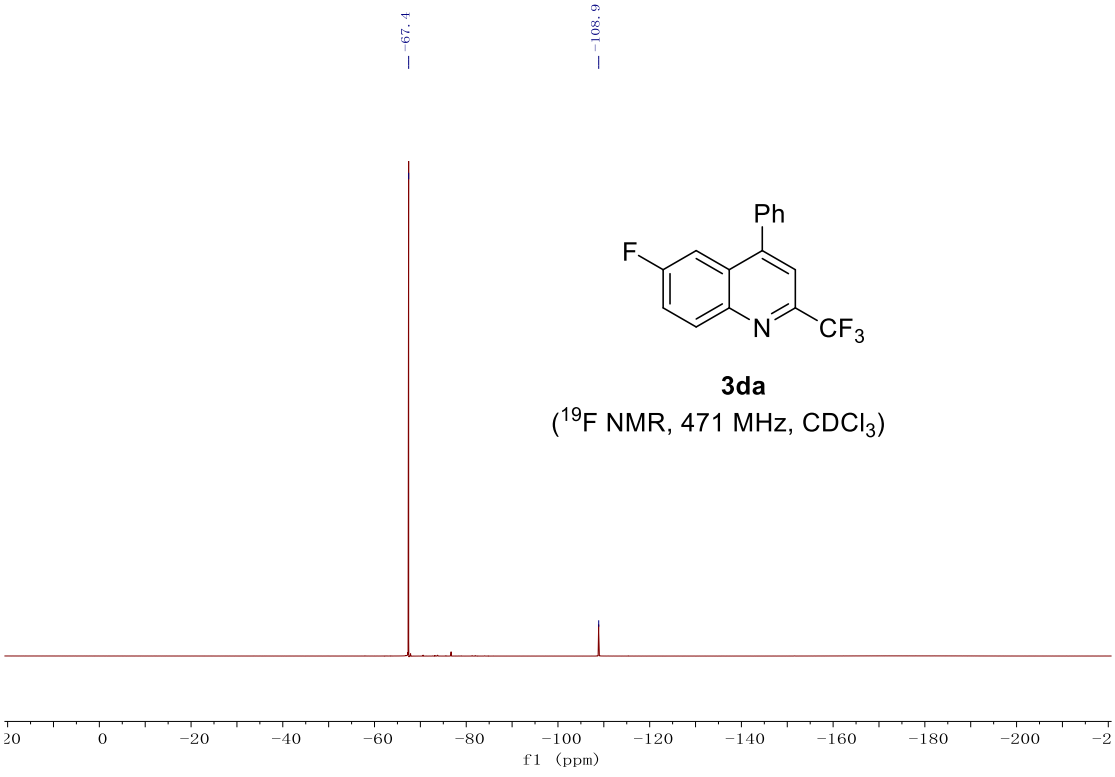
3da

(^{1}H NMR, 500 MHz, $CDCl_3$)



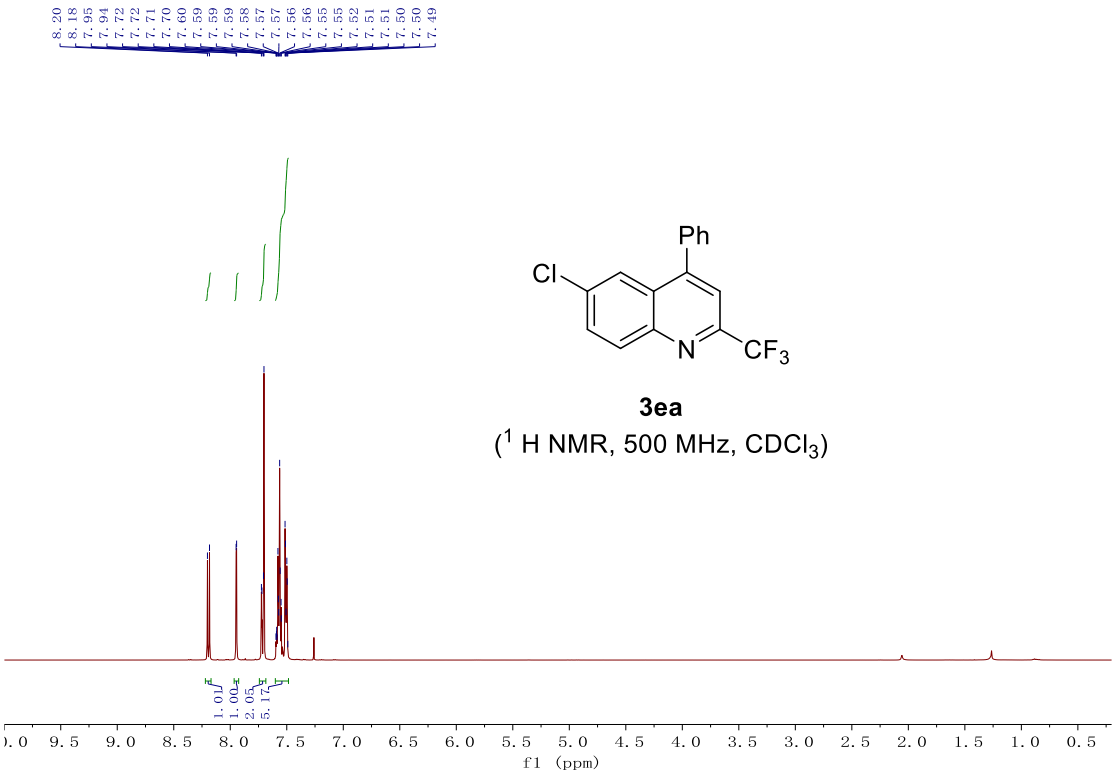
3da

($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)



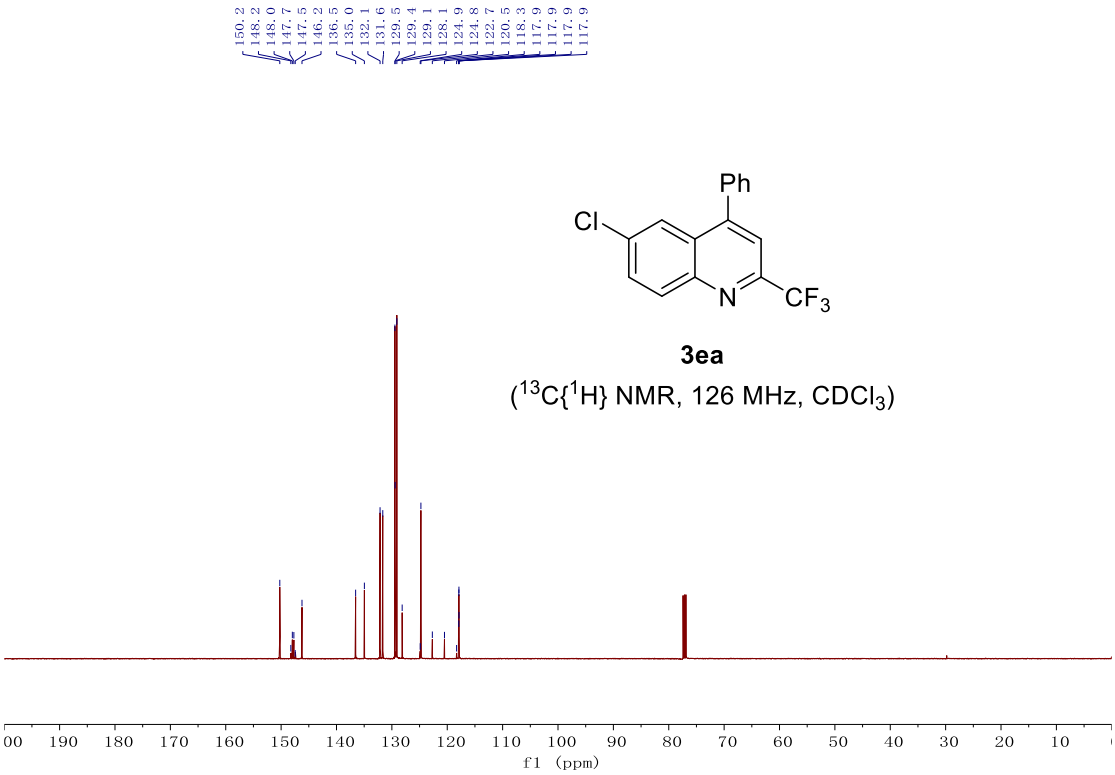
3da

(^{19}F NMR, 471 MHz, $CDCl_3$)



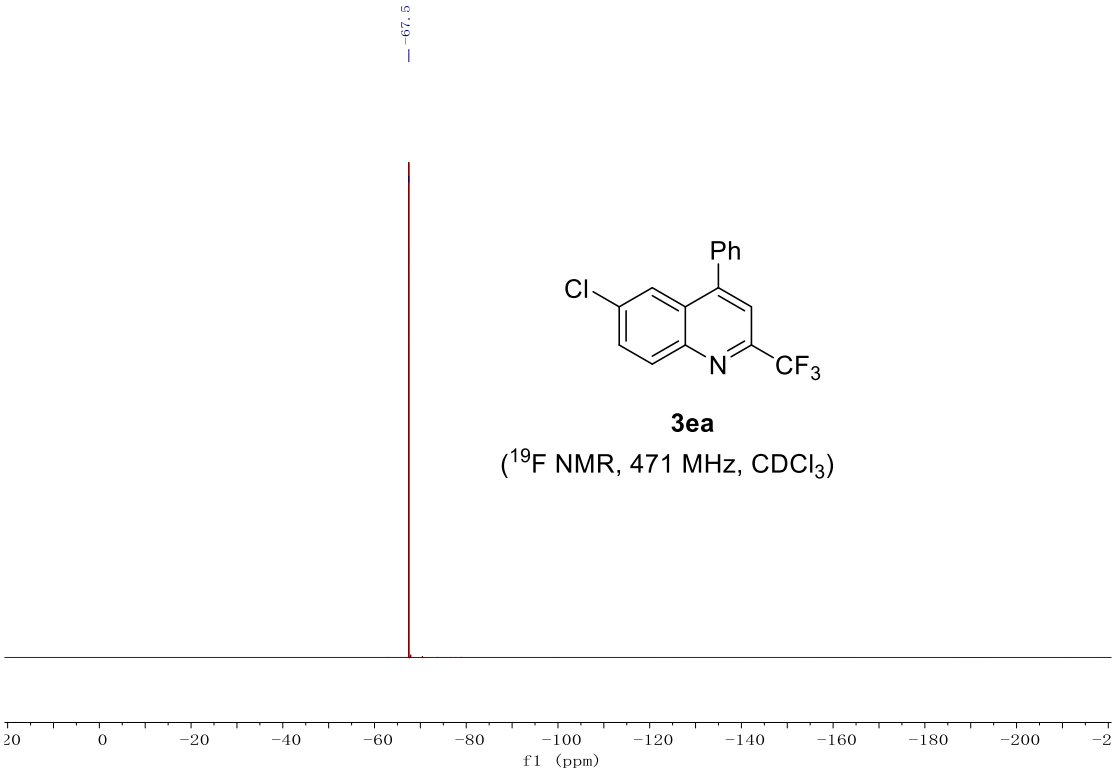
3ea

(^{1}H NMR, 500 MHz, $CDCl_3$)



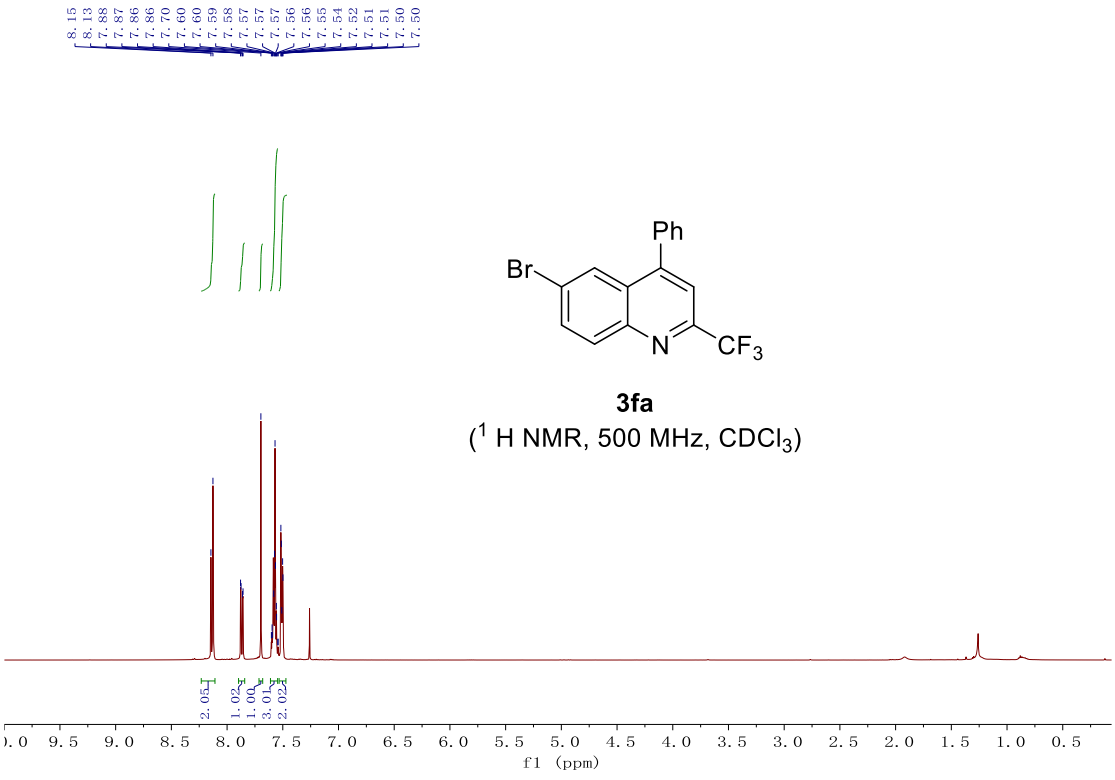
3ea

($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)



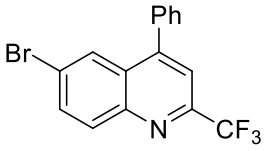
3ea

(^{19}F NMR, 471 MHz, $CDCl_3$)



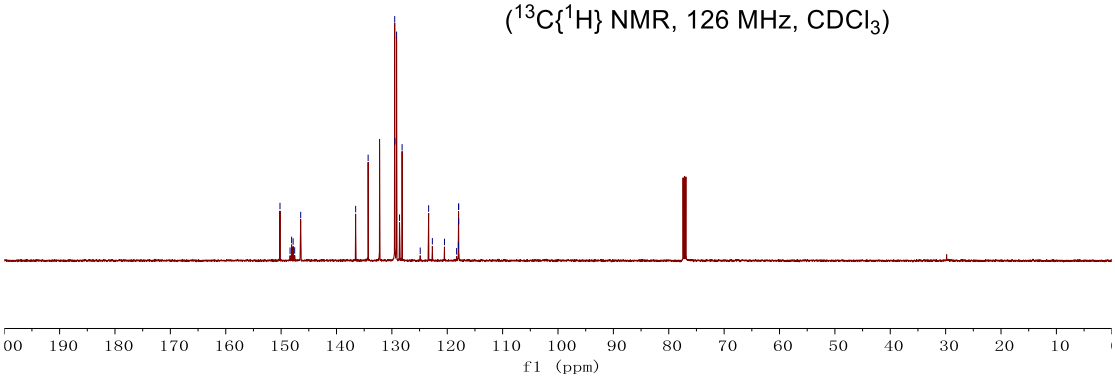
3fa

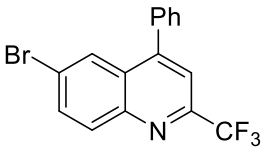
(^{1}H NMR, 500 MHz, $CDCl_3$)



3fa

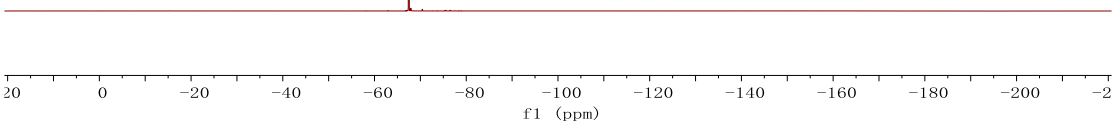
($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)

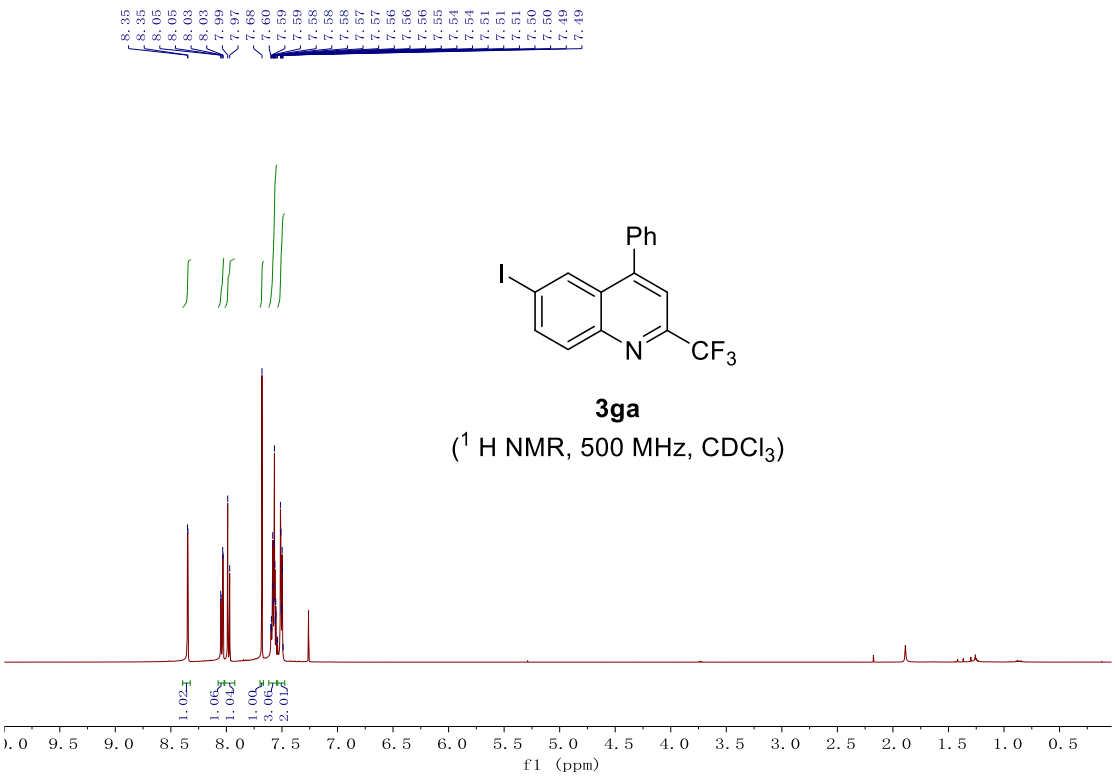




3fa

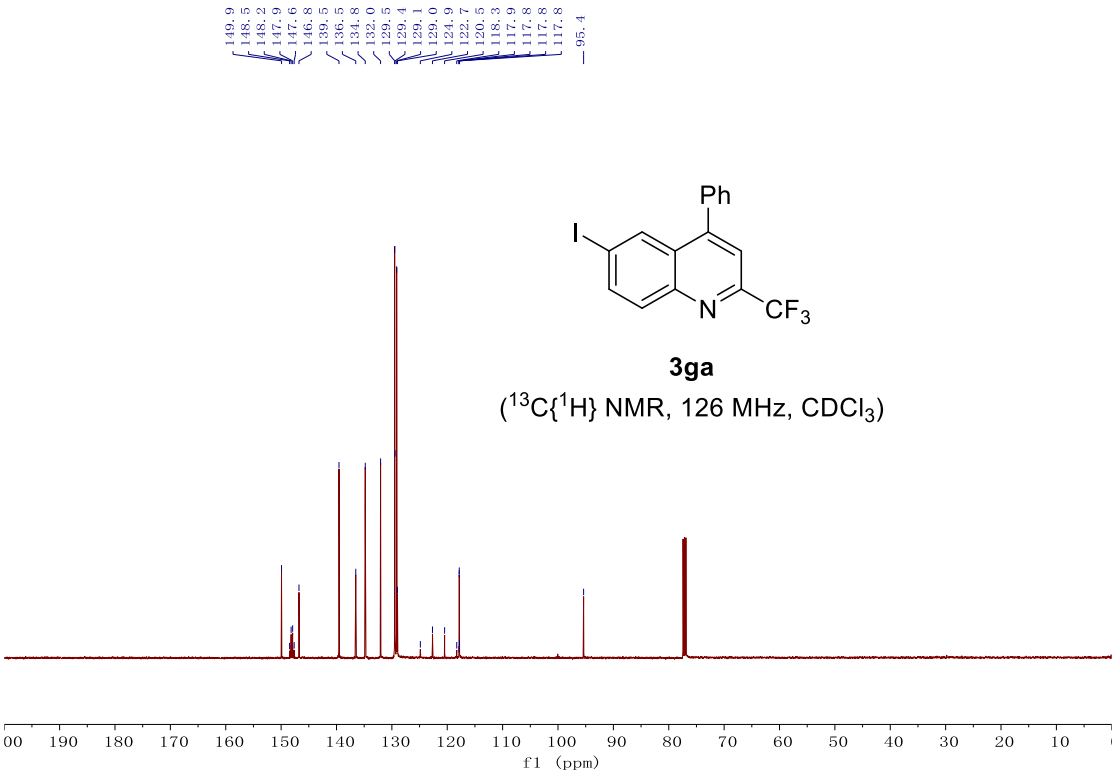
(^{19}F NMR, 471 MHz, $CDCl_3$)





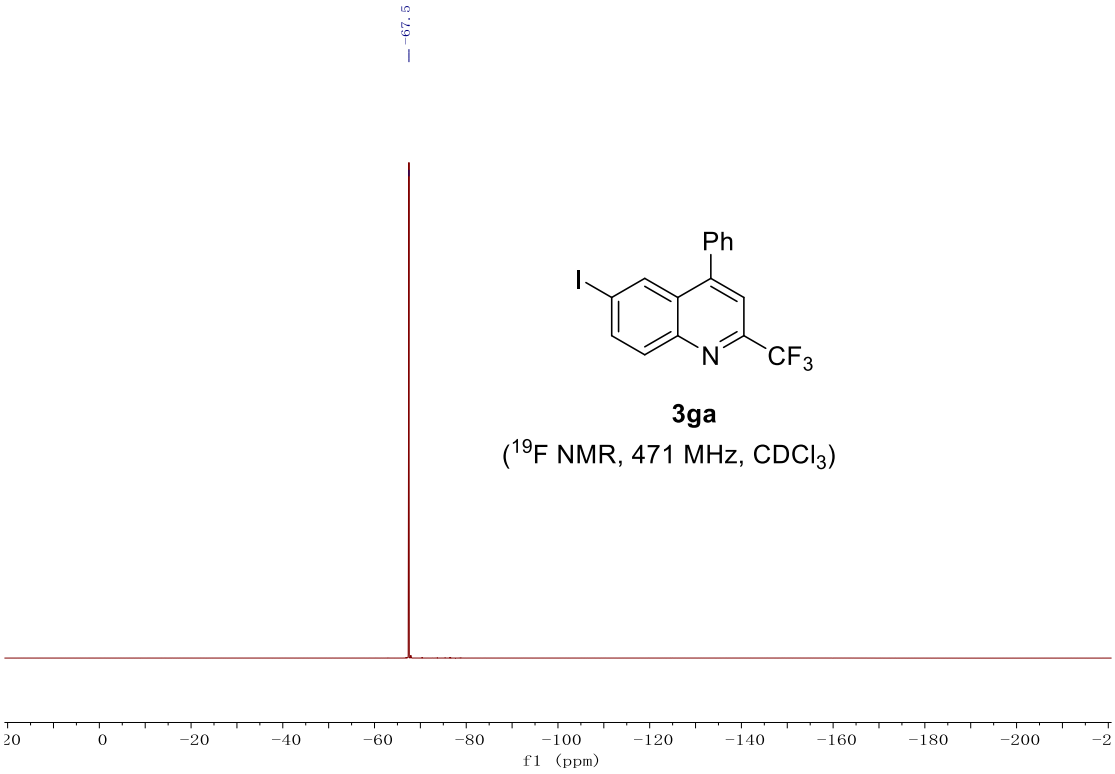
3ga

(^{1}H NMR, 500 MHz, $CDCl_3$)



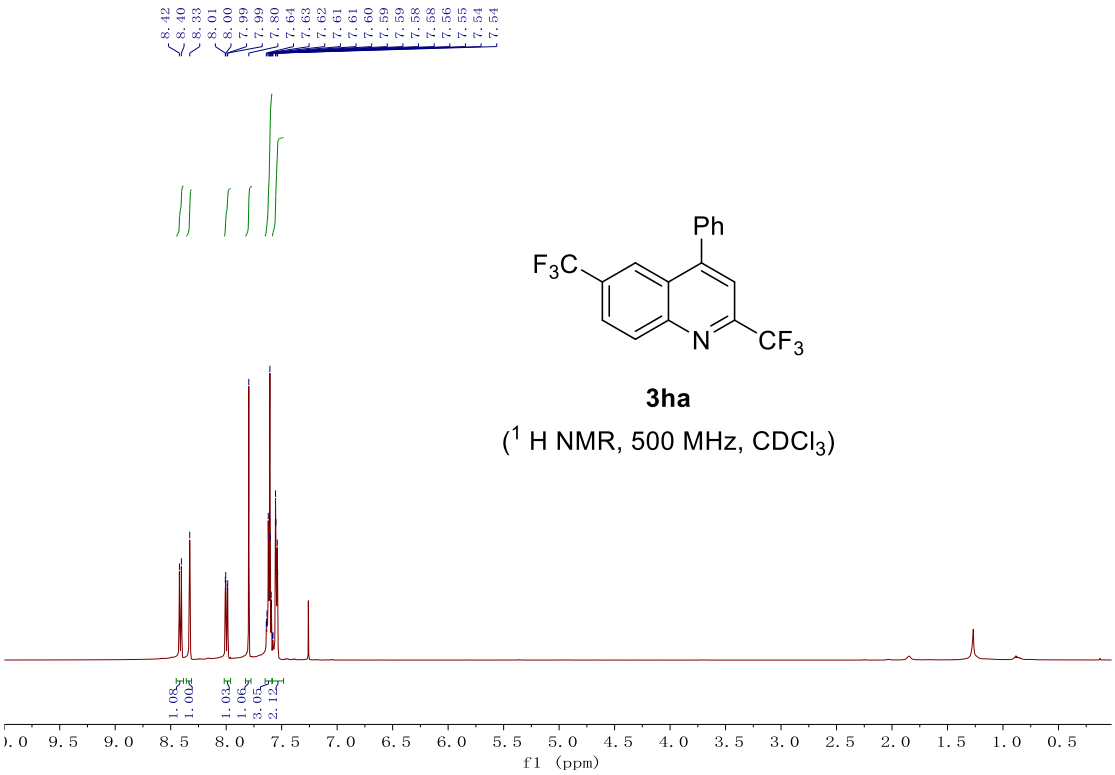
3ga

($^{13}C\{^1H\}$ NMR, 126 MHz, $CDCl_3$)



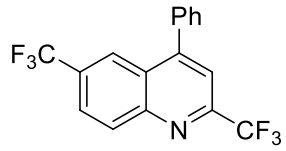
3ga

(^{19}F NMR, 471 MHz, $CDCl_3$)



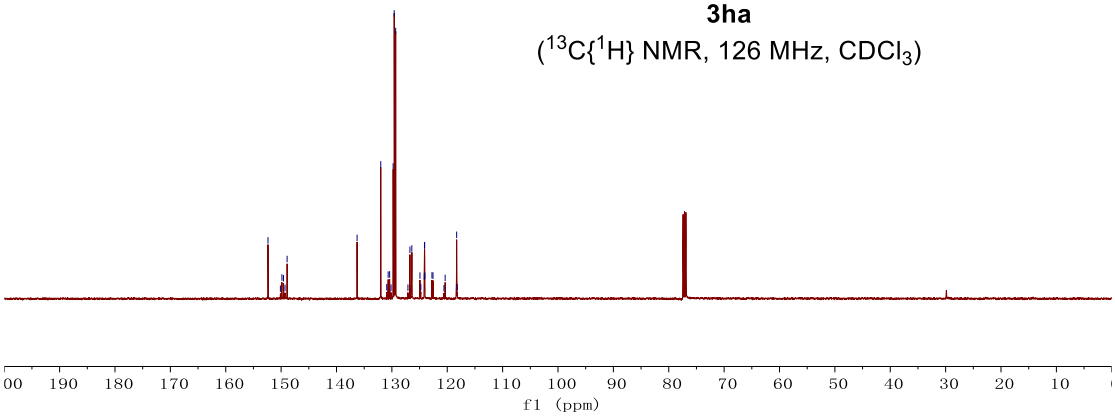
3ha

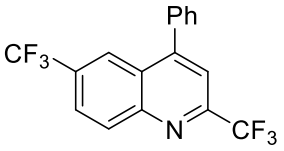
(^{1} H NMR, 500 MHz, $CDCl_3$)



3ha

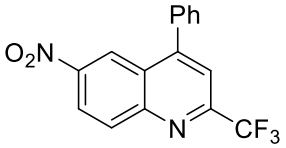
($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)





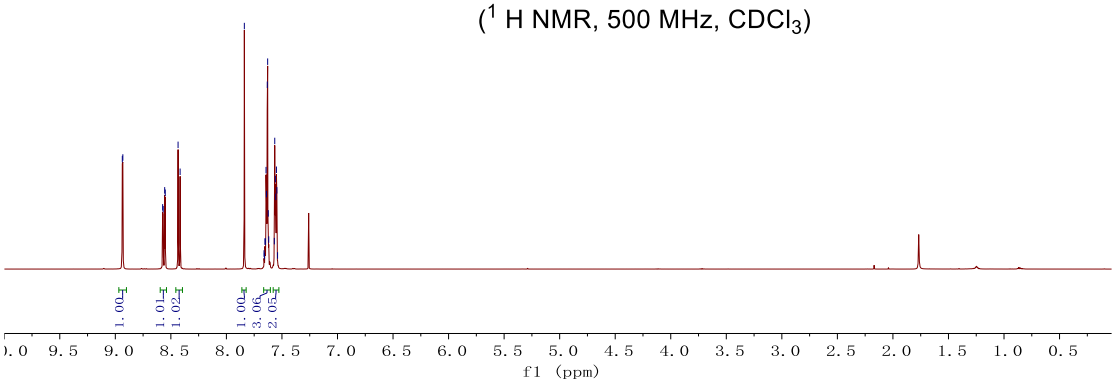
3ha

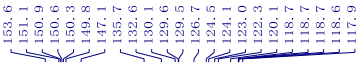
(^{19}F NMR, 471 MHz, $CDCl_3$)

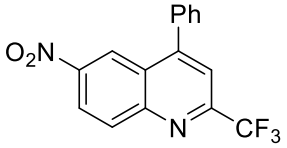


3ia

(^{1}H NMR, 500 MHz, $CDCl_3$)

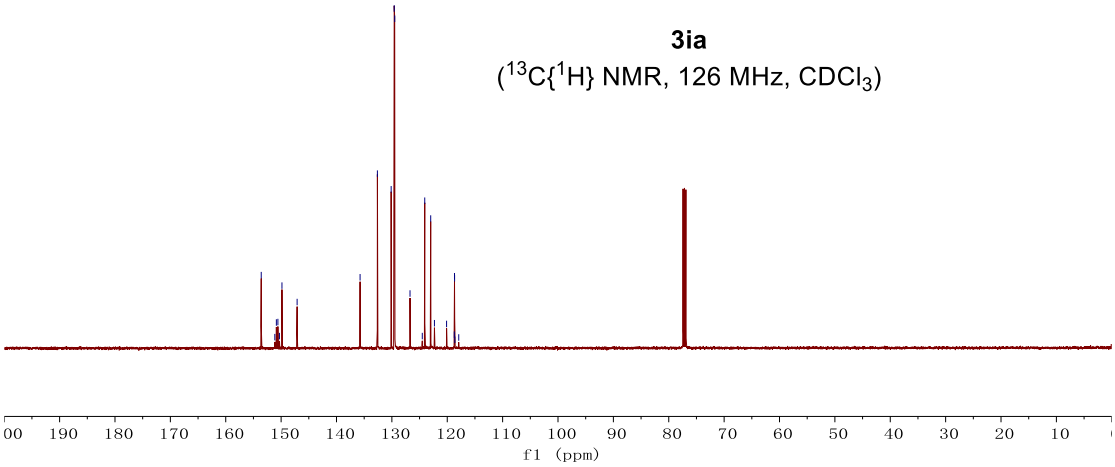


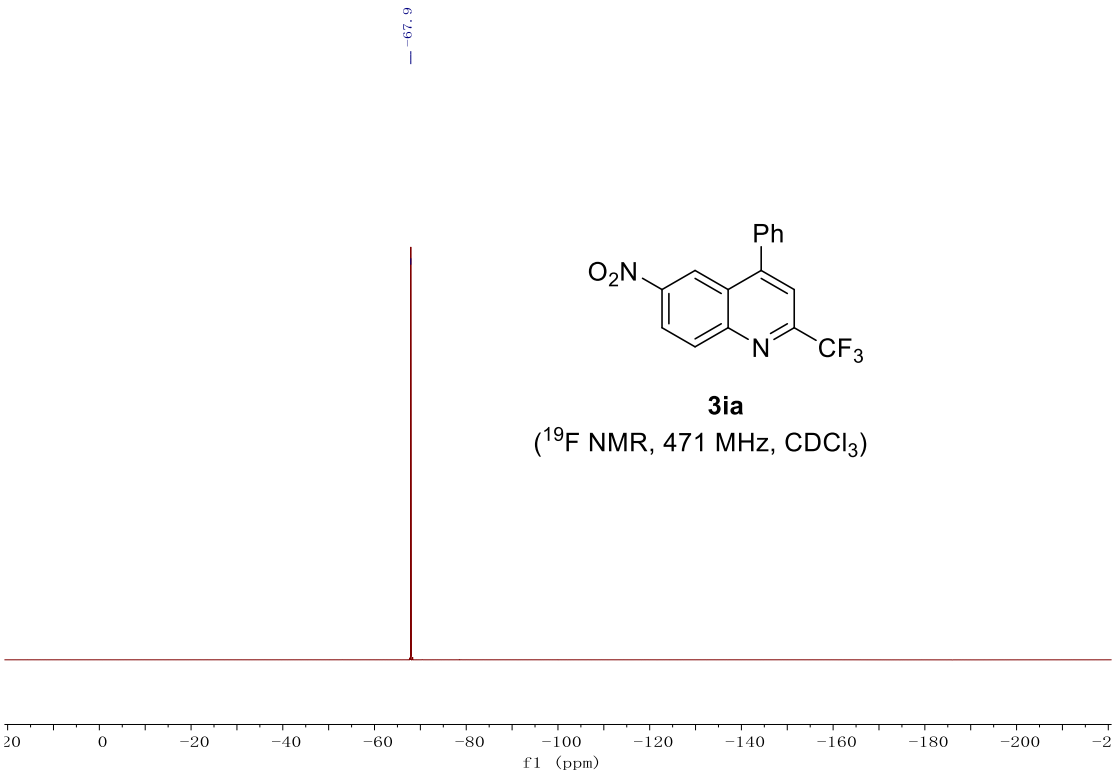




3ia

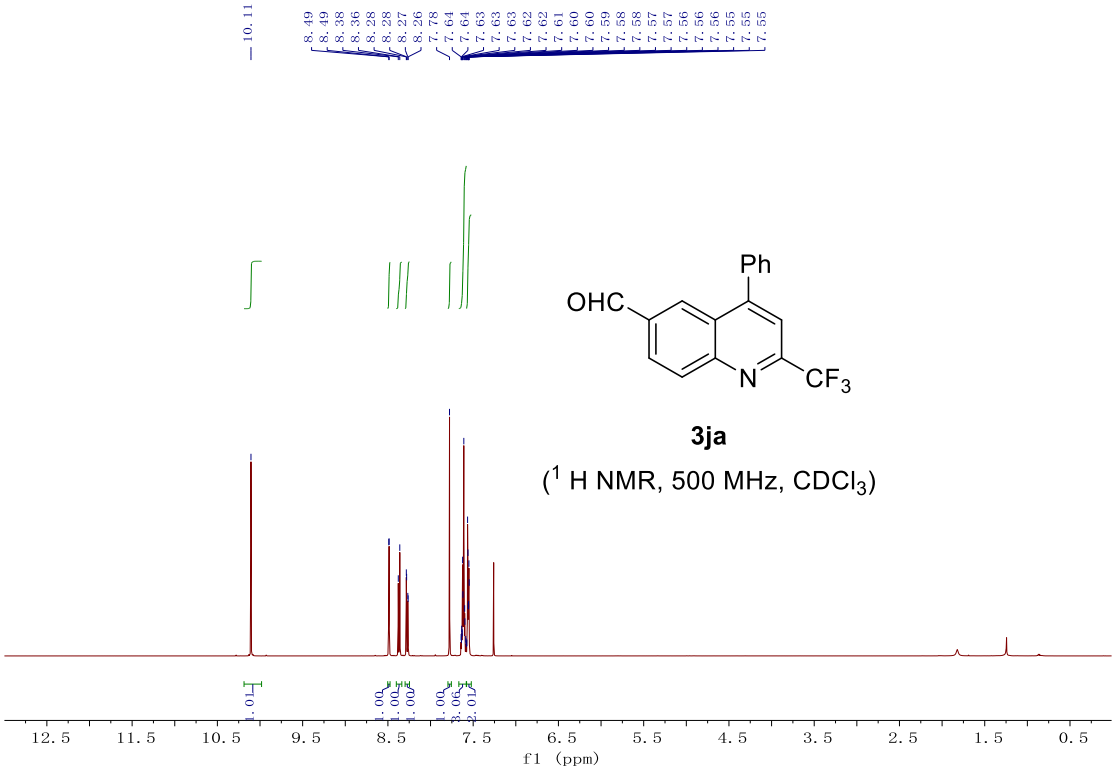
($^{13}C\{^1H\}$ NMR, 126 MHz, $CDCl_3$)





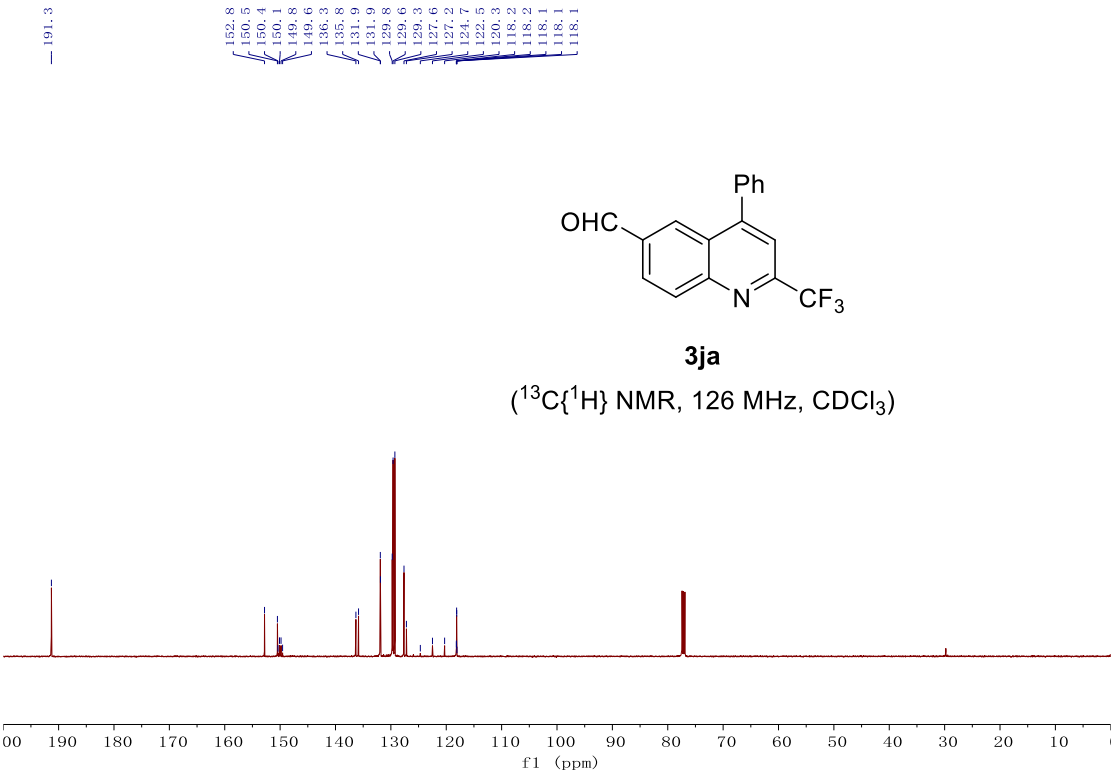
3ia

(^{19}F NMR, 471 MHz, $CDCl_3$)



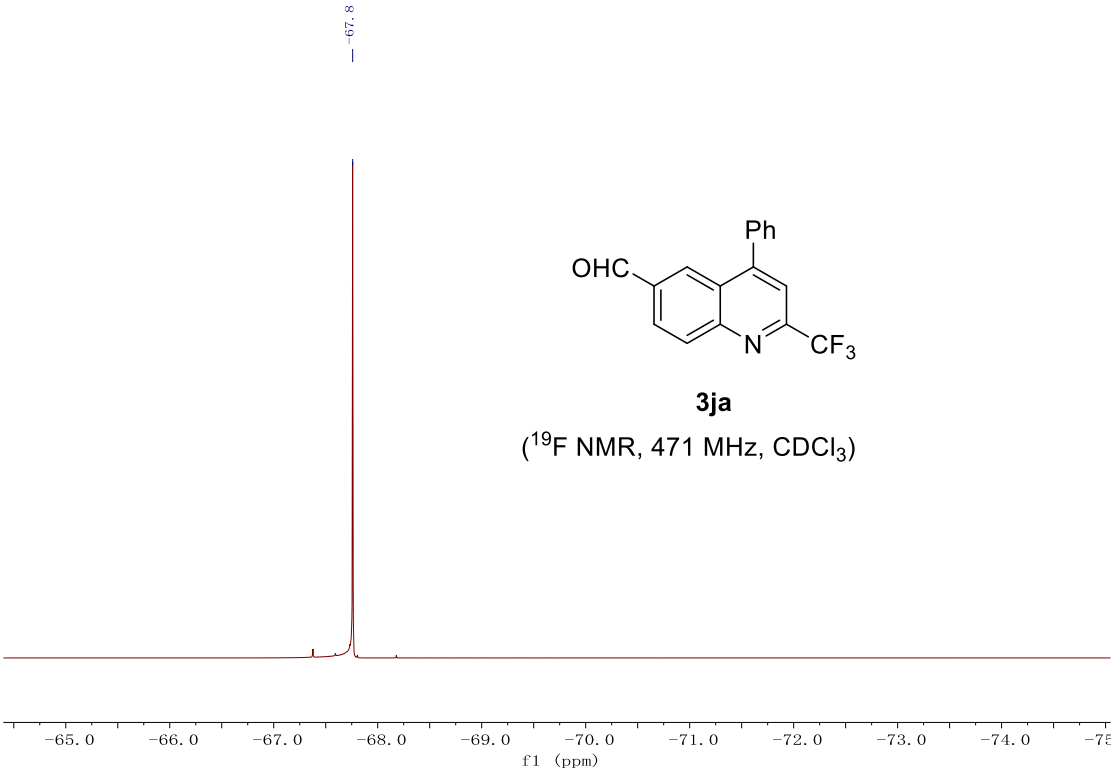
3ja

(^{1} H NMR, 500 MHz, $CDCl_3$)



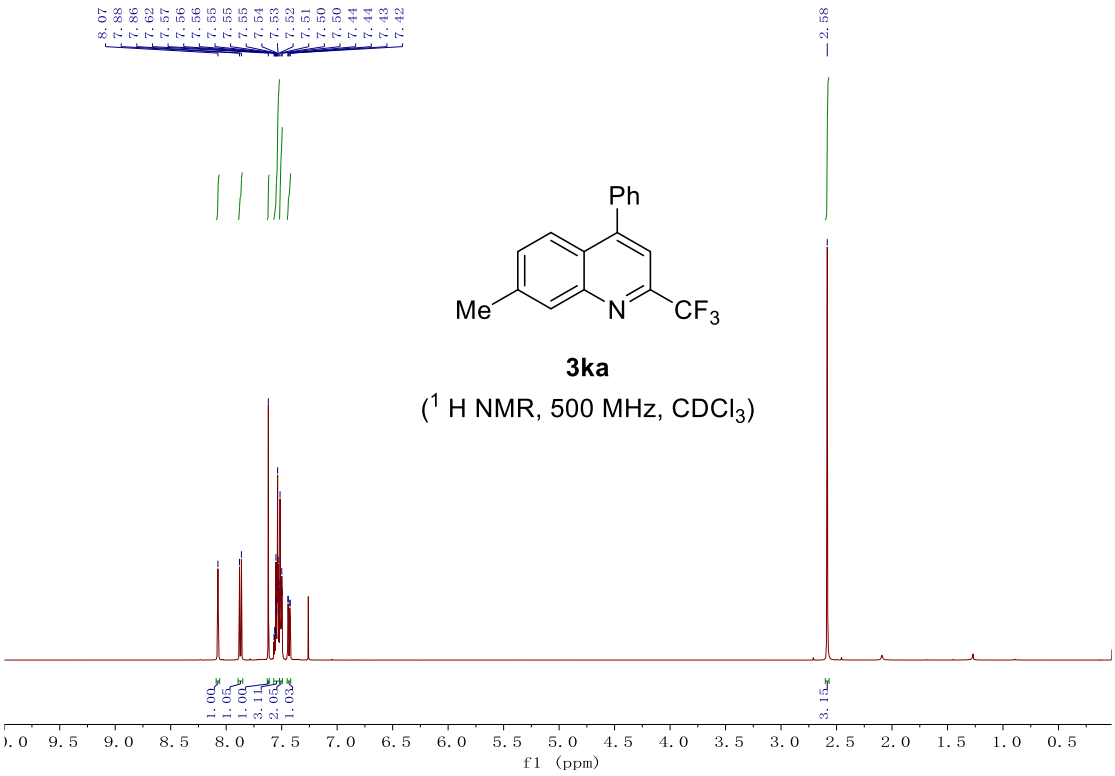
3ja

($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)



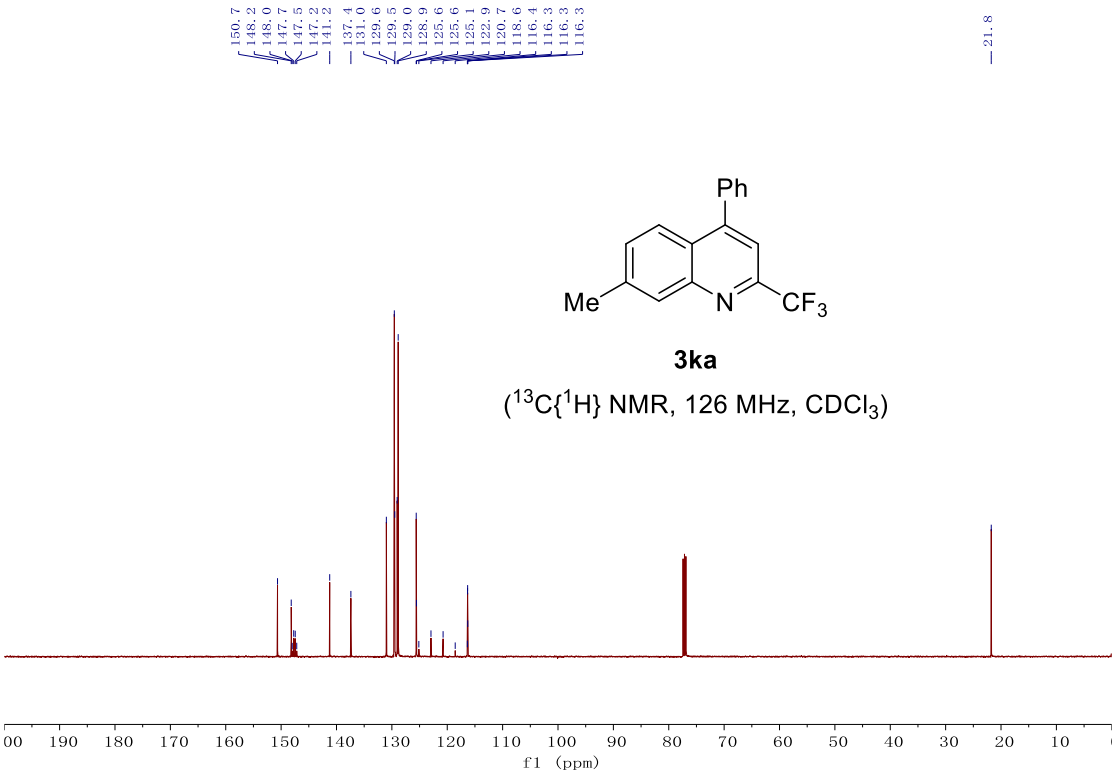
3ja

(^{19}F NMR, 471 MHz, $CDCl_3$)



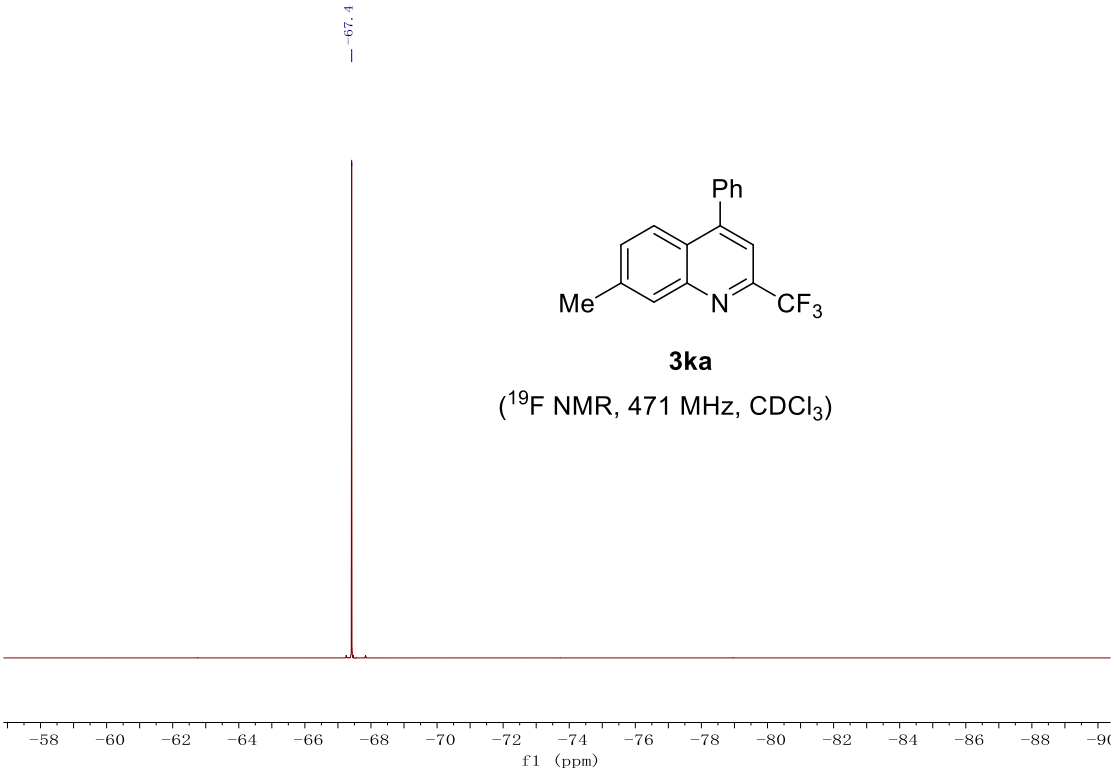
3ka

(^{1}H NMR, 500 MHz, $CDCl_3$)



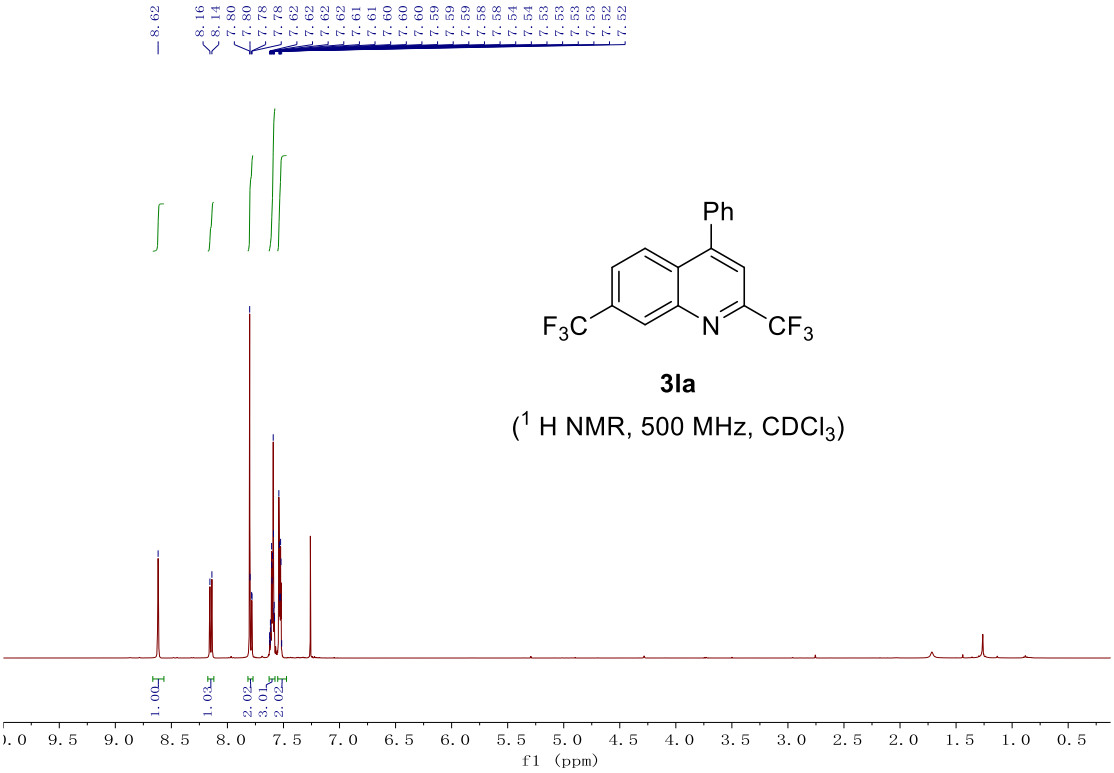
3ka

($^{13}C\{^1H\}$ NMR, 126 MHz, $CDCl_3$)



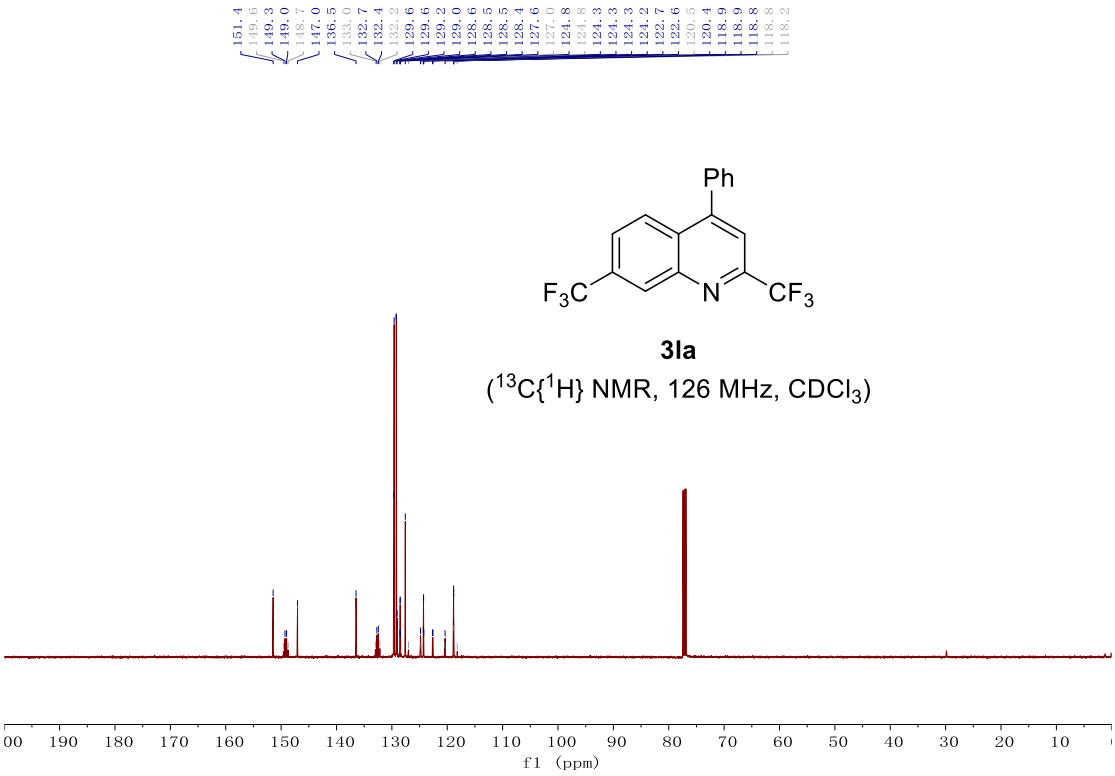
3ka

(^{19}F NMR, 471 MHz, $CDCl_3$)



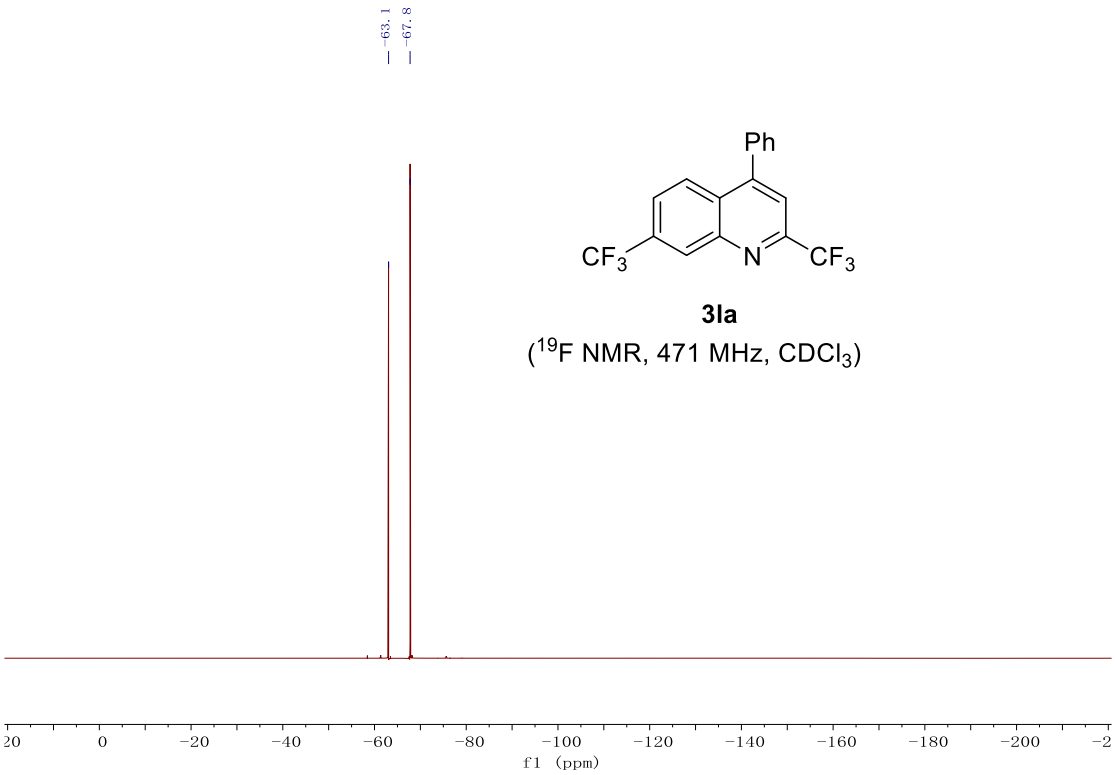
3la

(^{1} H NMR, 500 MHz, $CDCl_3$)



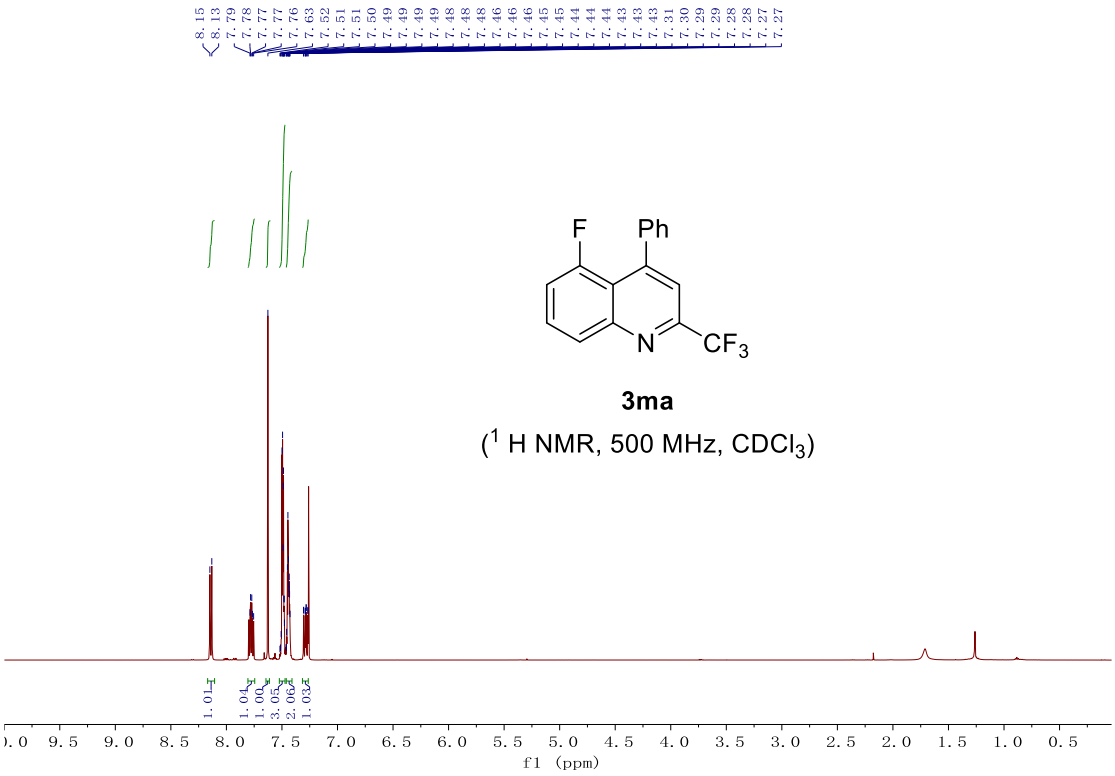
3la

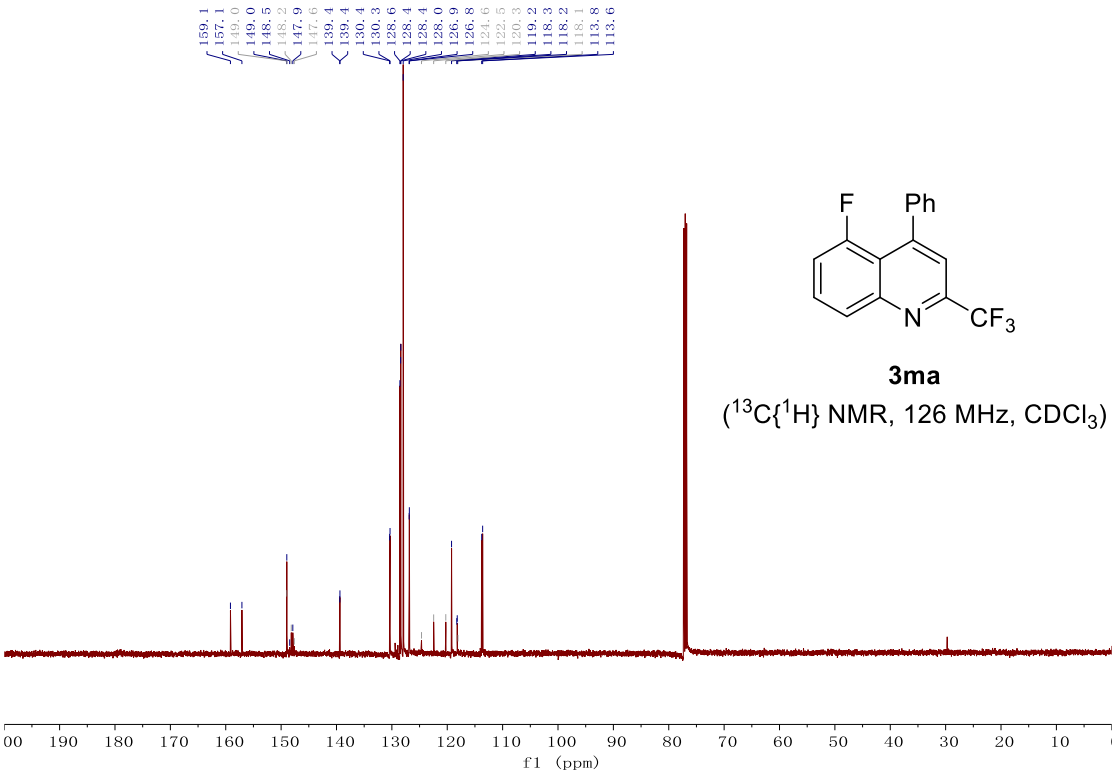
($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)

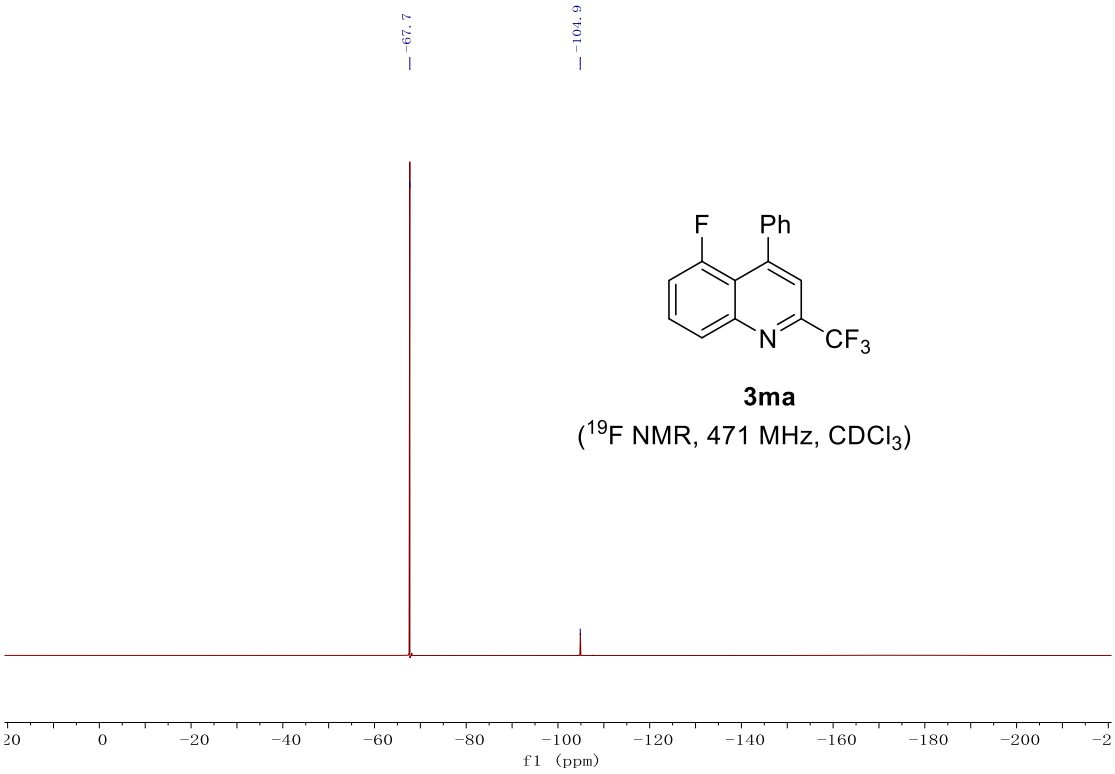


3la

(^{19}F NMR, 471 MHz, $CDCl_3$)

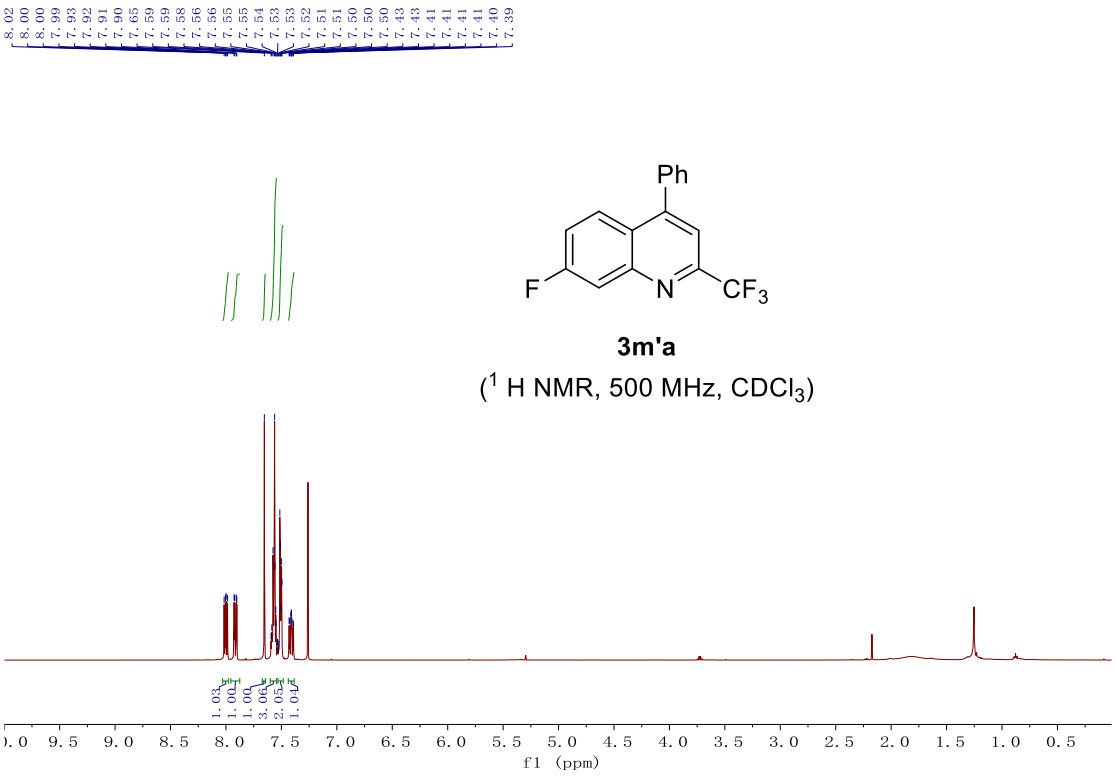

F
Ph
N
CF3
3ma
(1 H NMR, 500 MHz, CDCl3)
f1 (ppm)


F
Ph
N
CF3
3ma
(13C{1H} NMR, 126 MHz, CDCl3)
f1 (ppm)



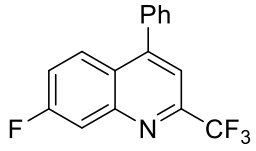
3ma

(^{19}F NMR, 471 MHz, $CDCl_3$)



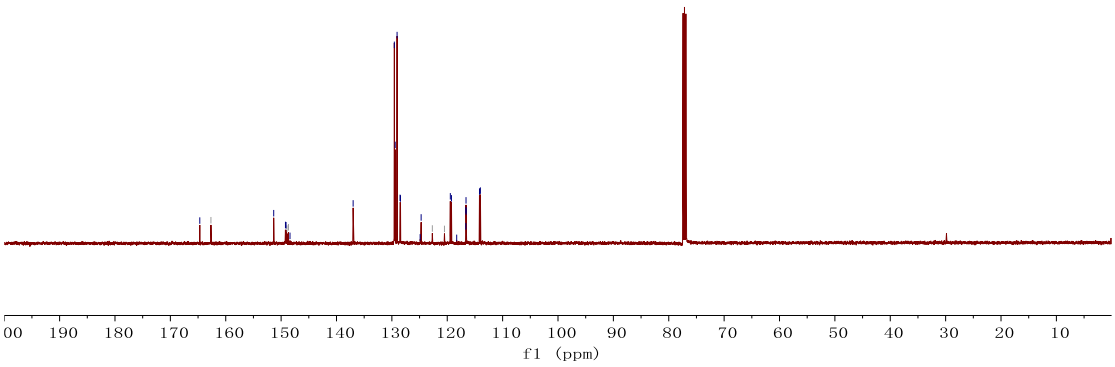
3m'a

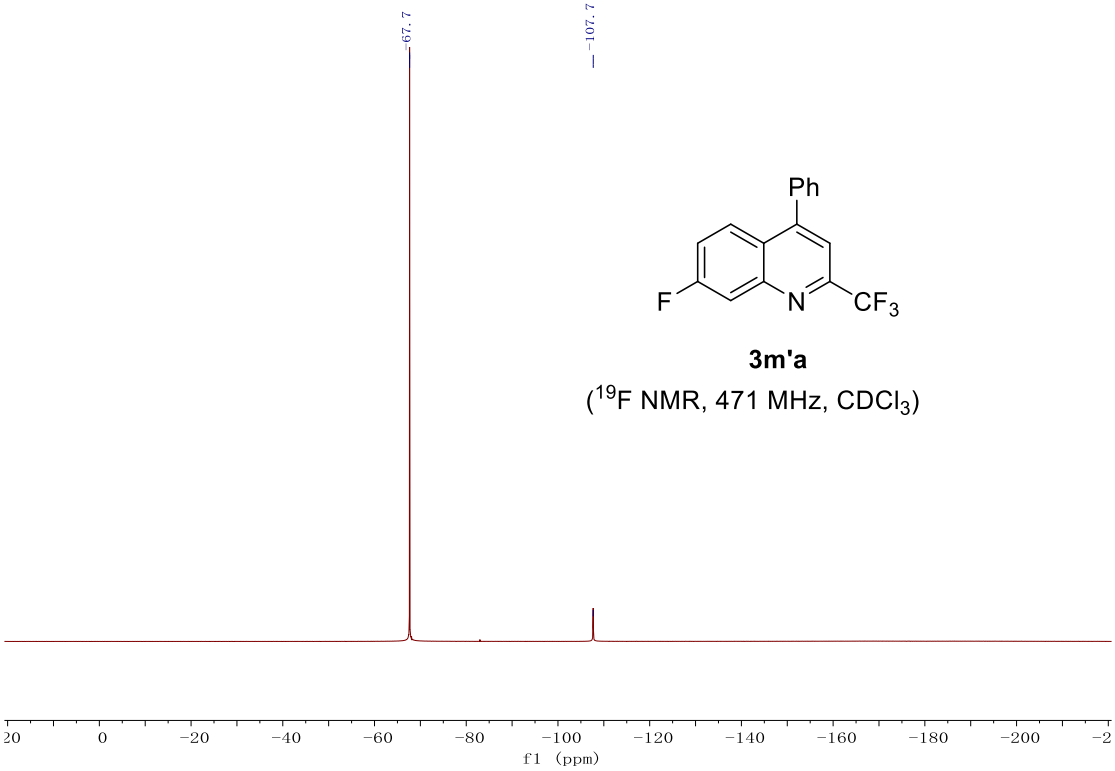
(^{1} H NMR, 500 MHz, $CDCl_3$)



3m'a

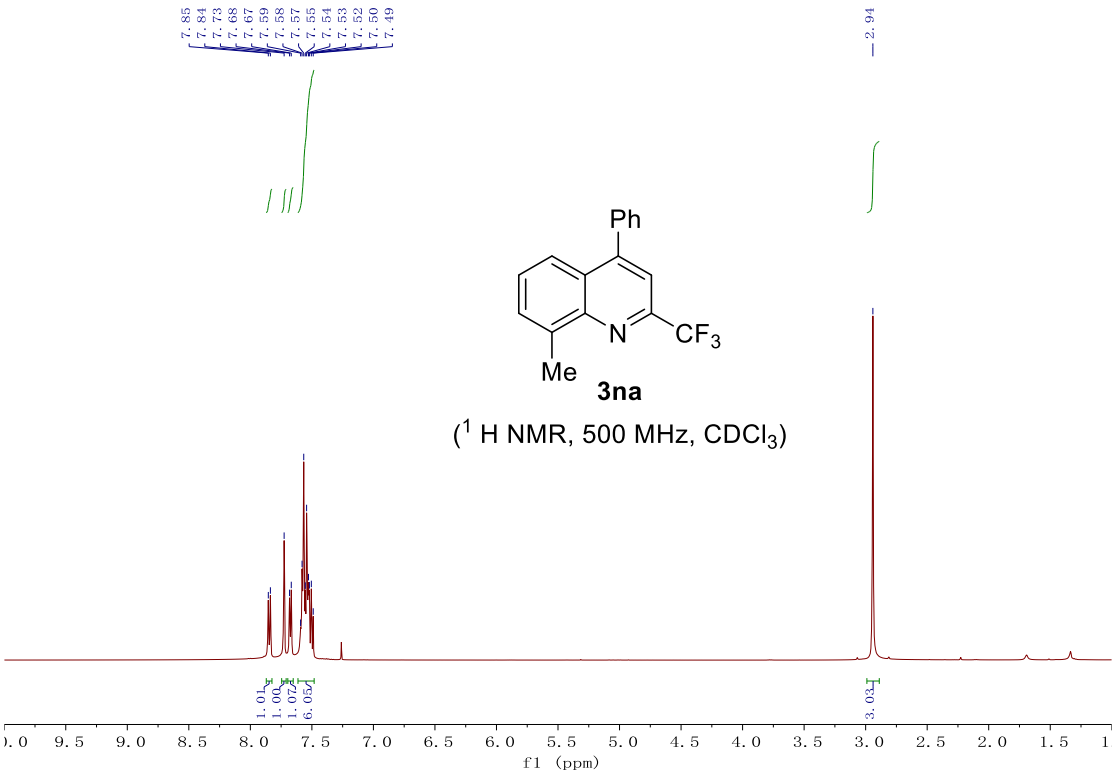
($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)





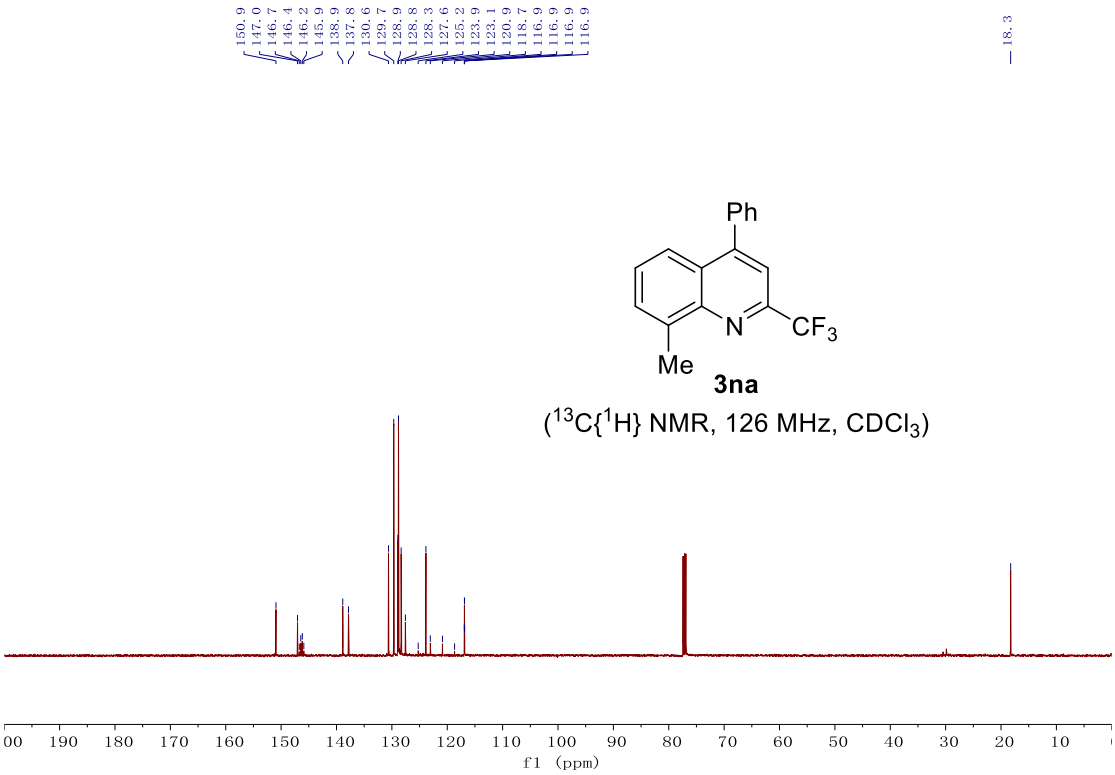
3m'a

(^{19}F NMR, 471 MHz, $CDCl_3$)



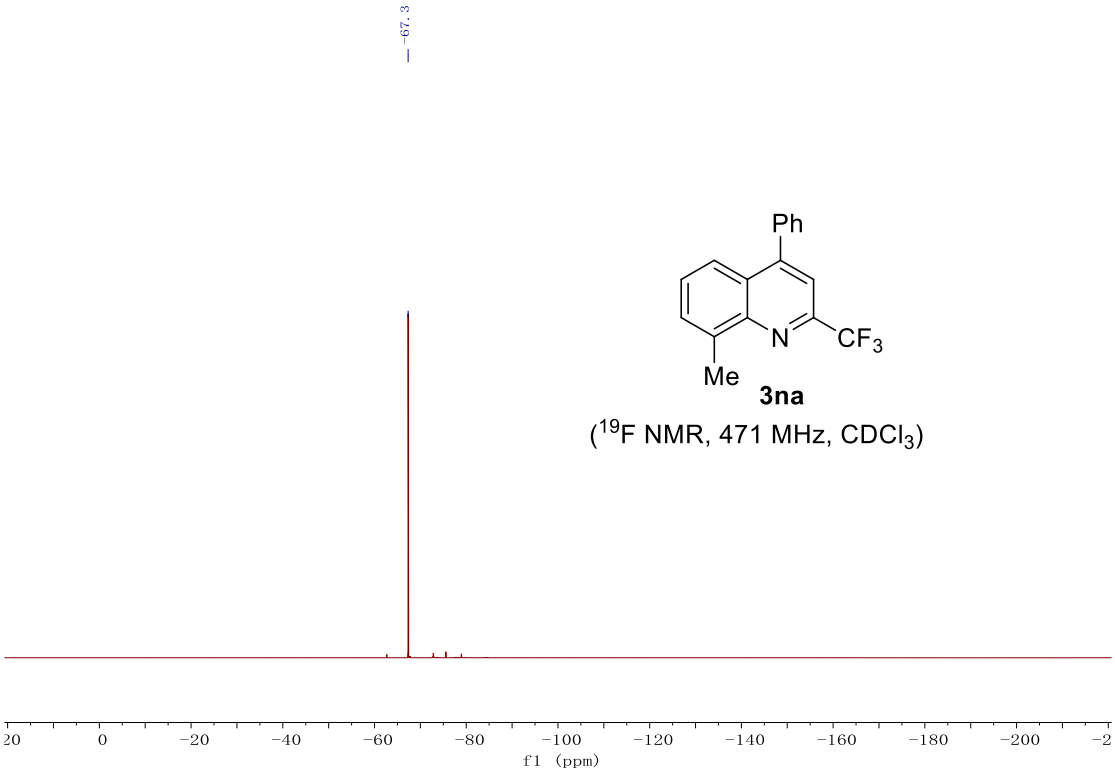
3na

(^{1}H NMR, 500 MHz, $CDCl_3$)



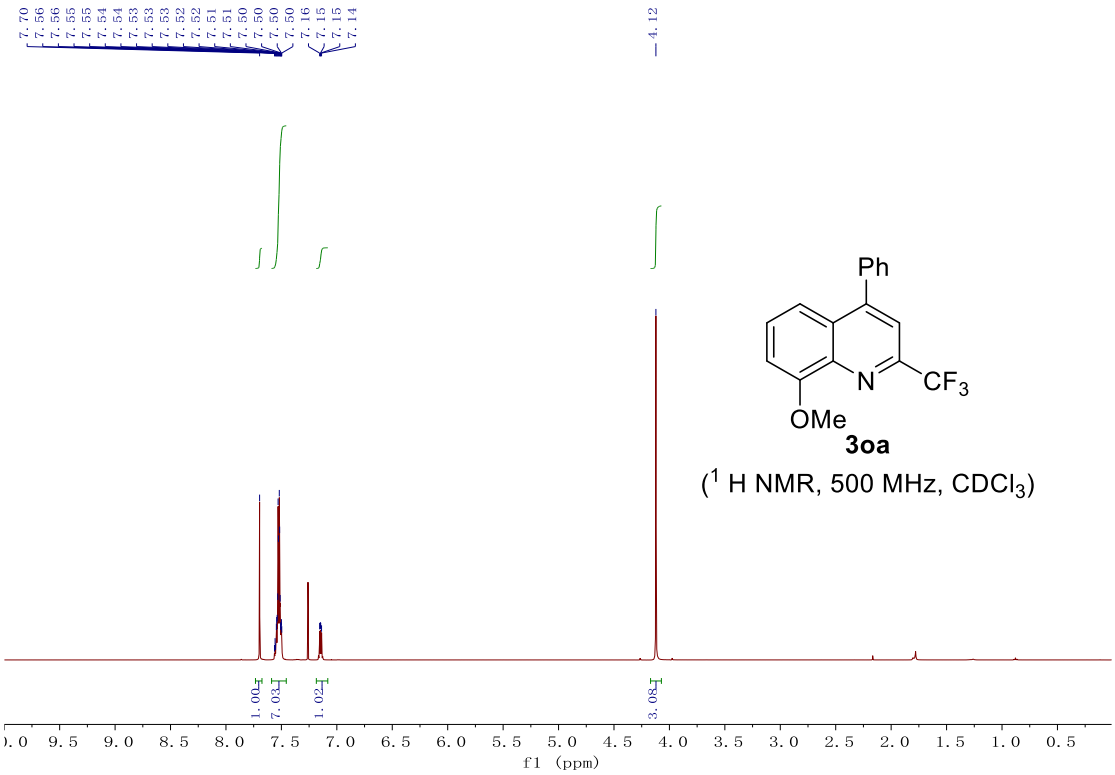
3na

($^{13}C\{^1H\}$ NMR, 126 MHz, $CDCl_3$)



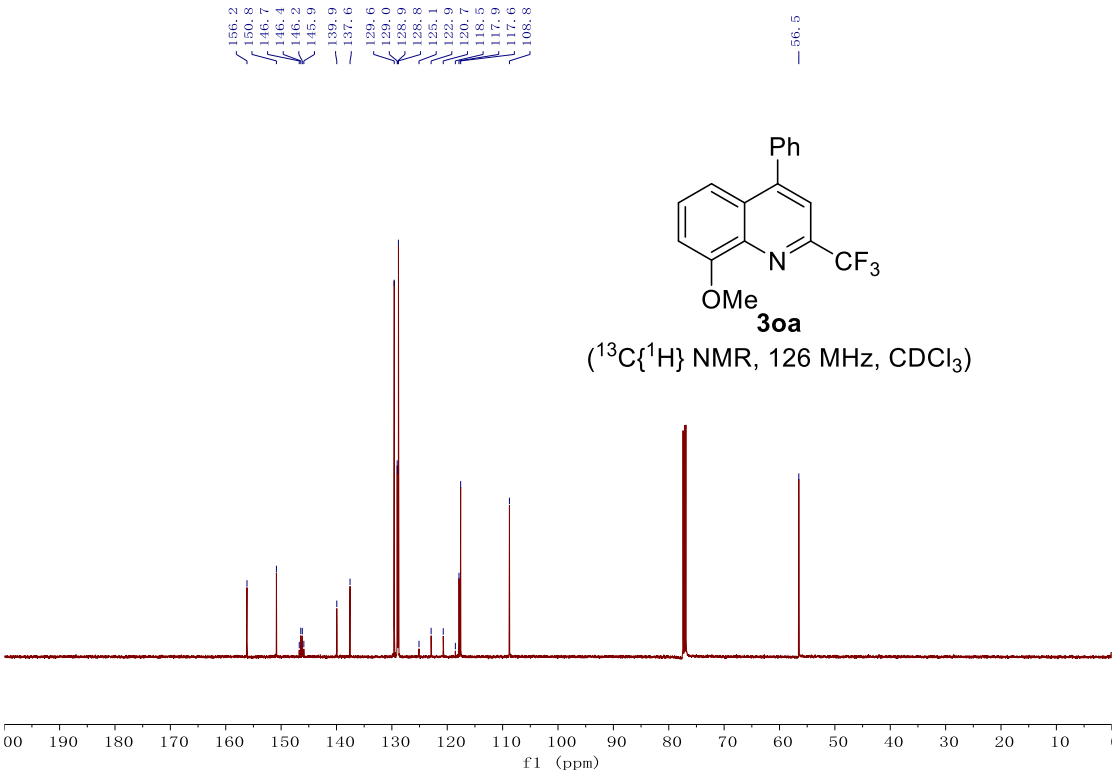
3na

(^{19}F NMR, 471 MHz, $CDCl_3$)



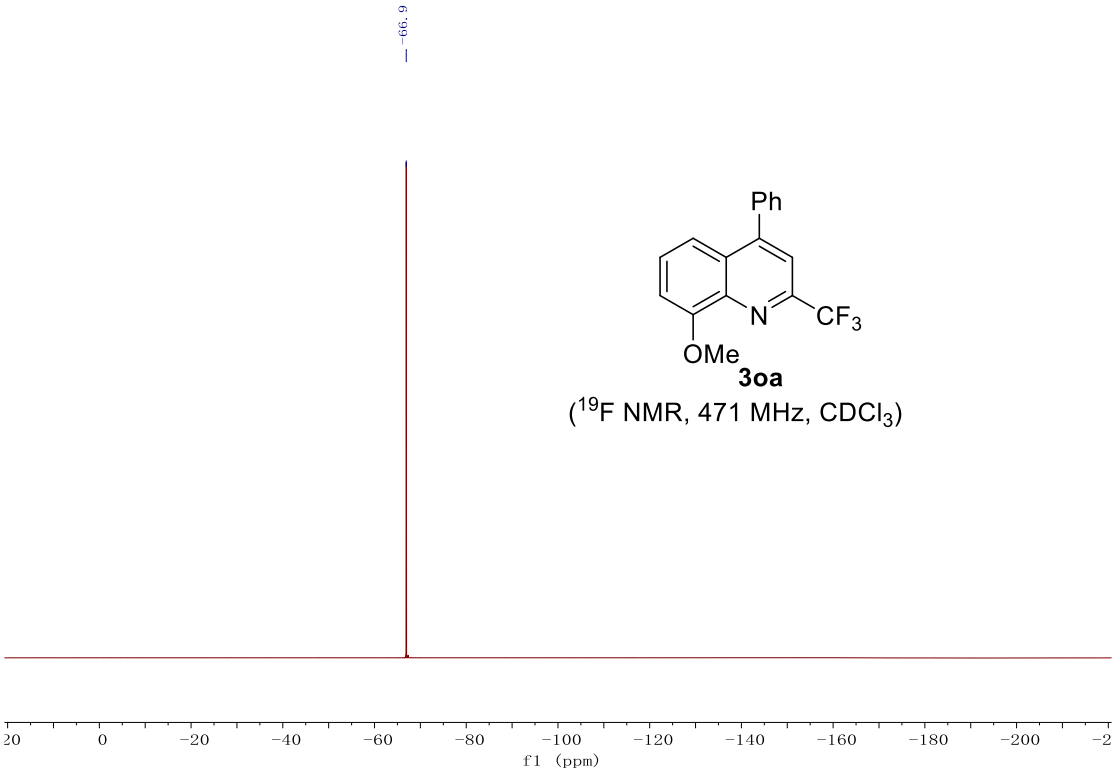
3oa

(^{1}H NMR, 500 MHz, $CDCl_3$)



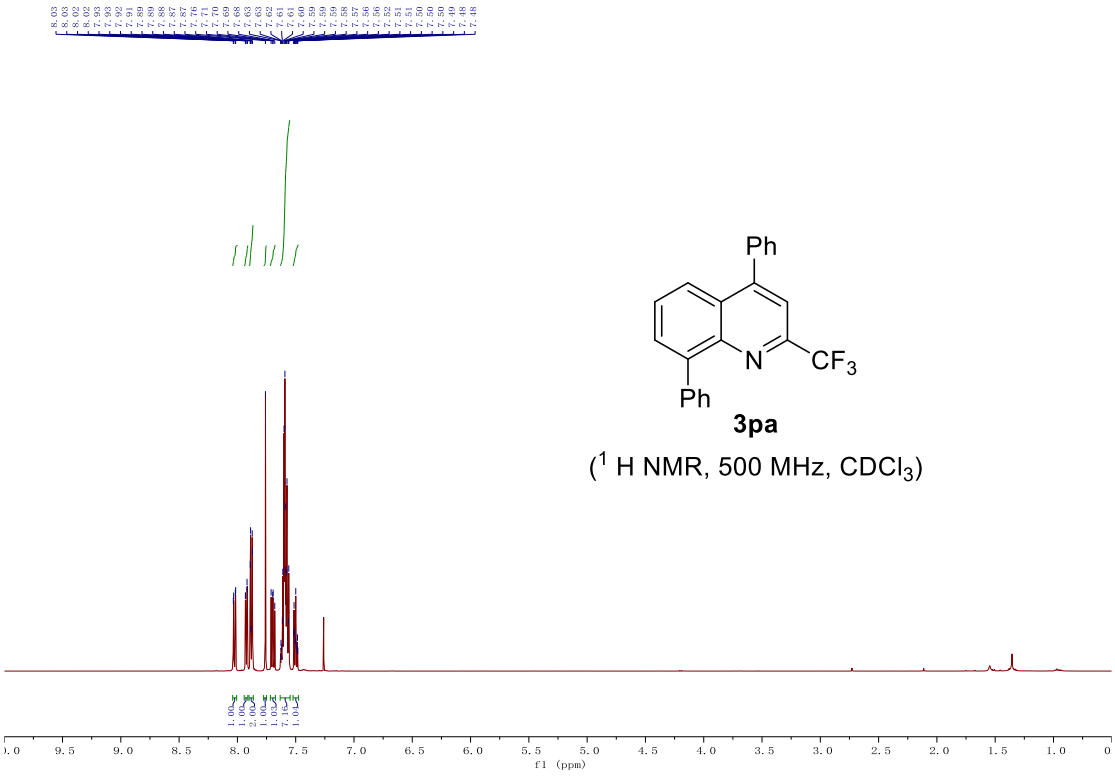
3oa

($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)



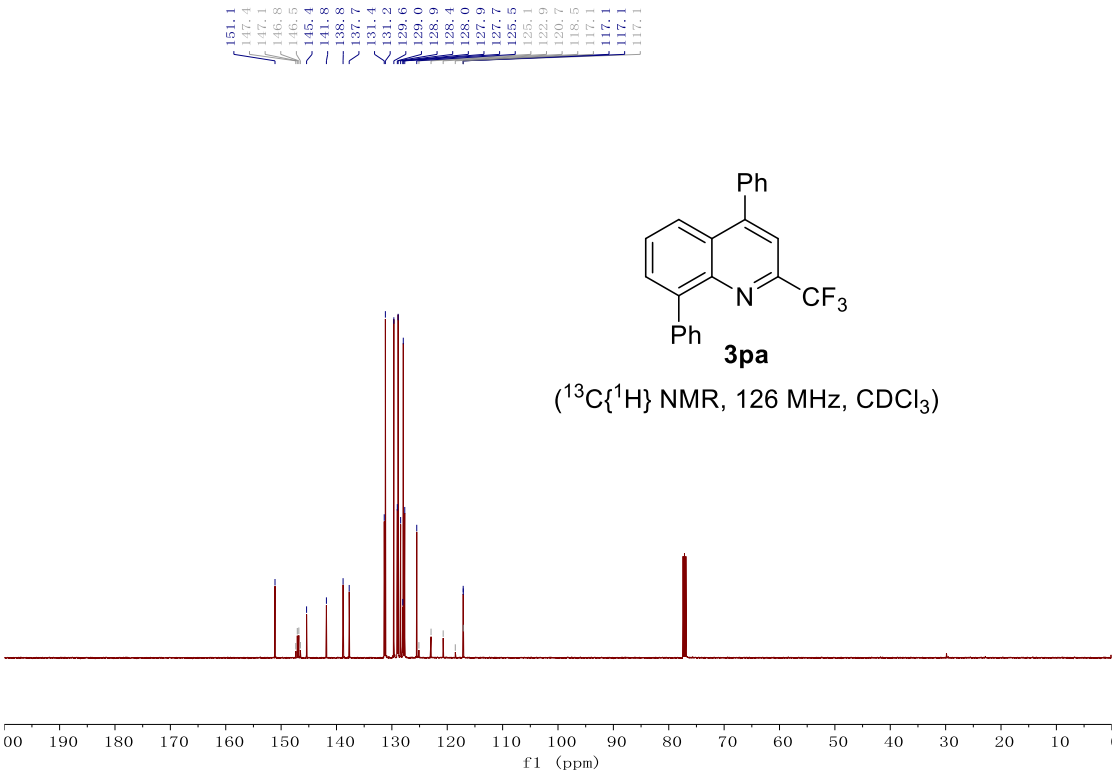
3oa

(^{19}F NMR, 471 MHz, $CDCl_3$)



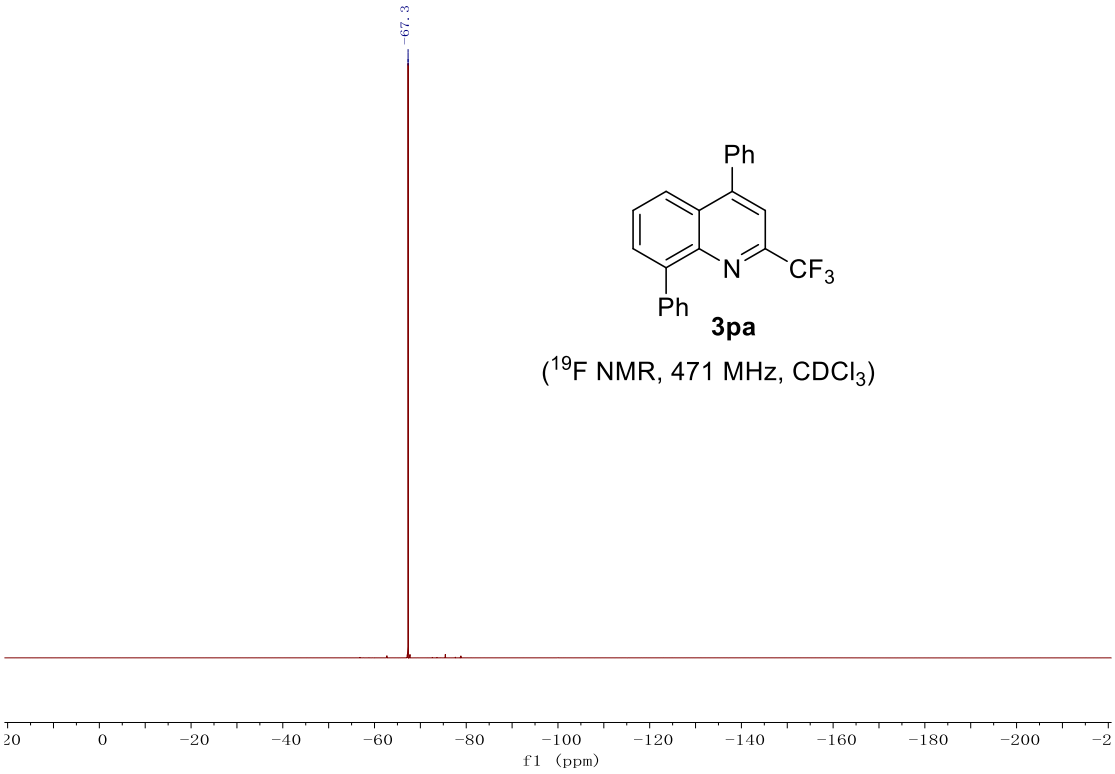
3pa

(^{1}H NMR, 500 MHz, $CDCl_3$)



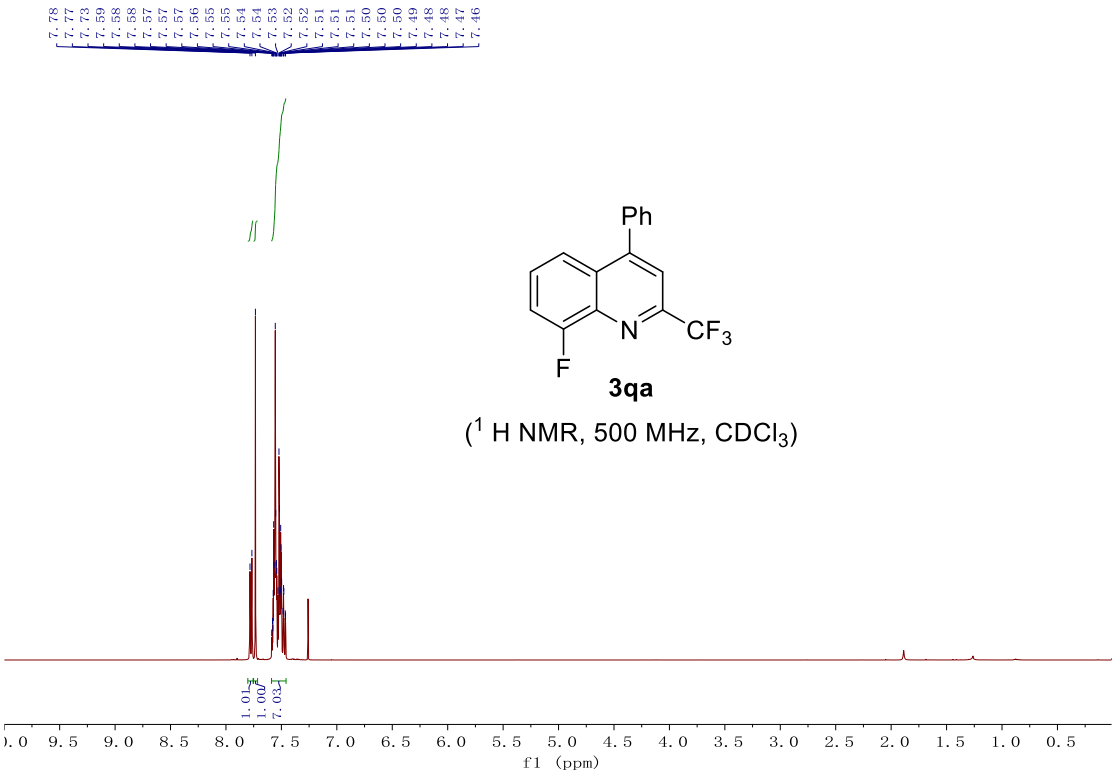
3pa

($^{13}C\{^1H\}$ NMR, 126 MHz, $CDCl_3$)



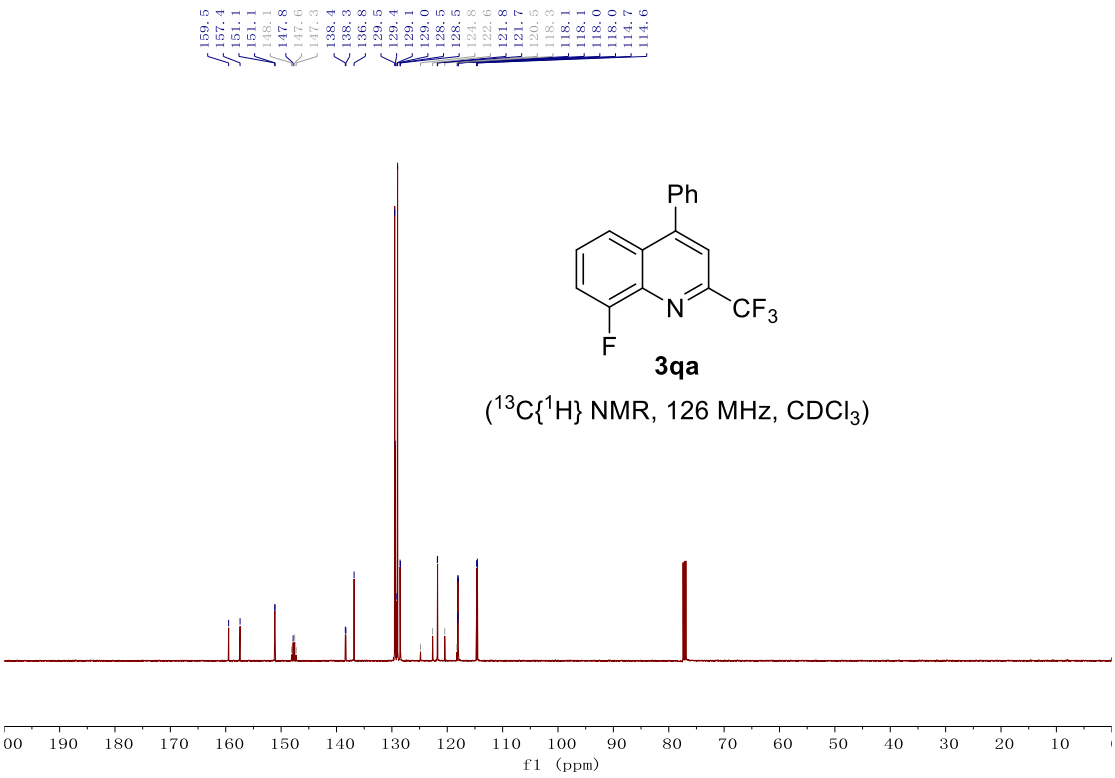
3pa

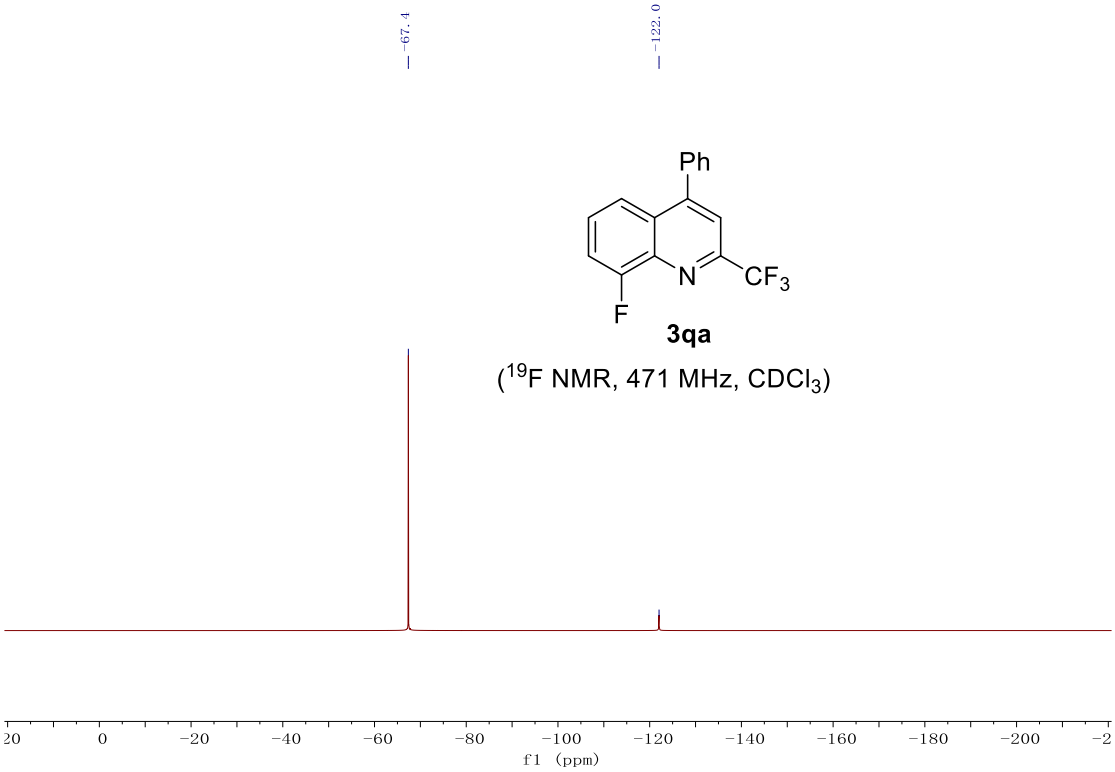
(^{19}F NMR, 471 MHz, $CDCl_3$)

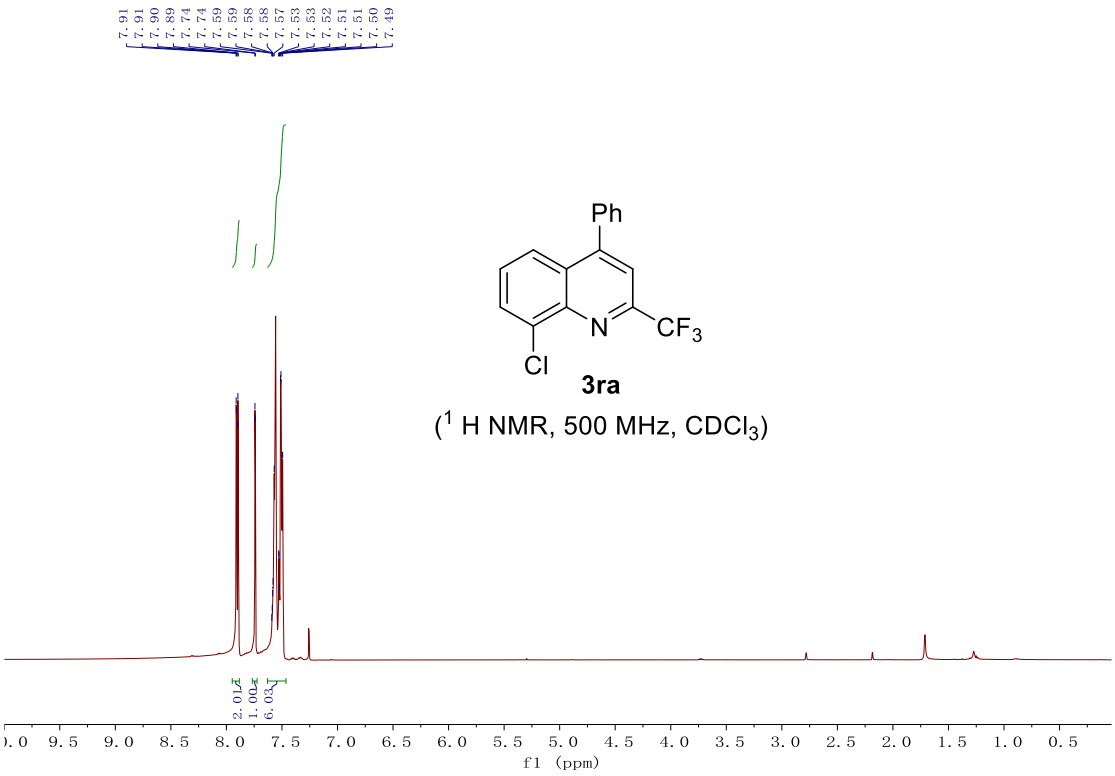


3qa

(^{1} H NMR, 500 MHz, $CDCl_3$)

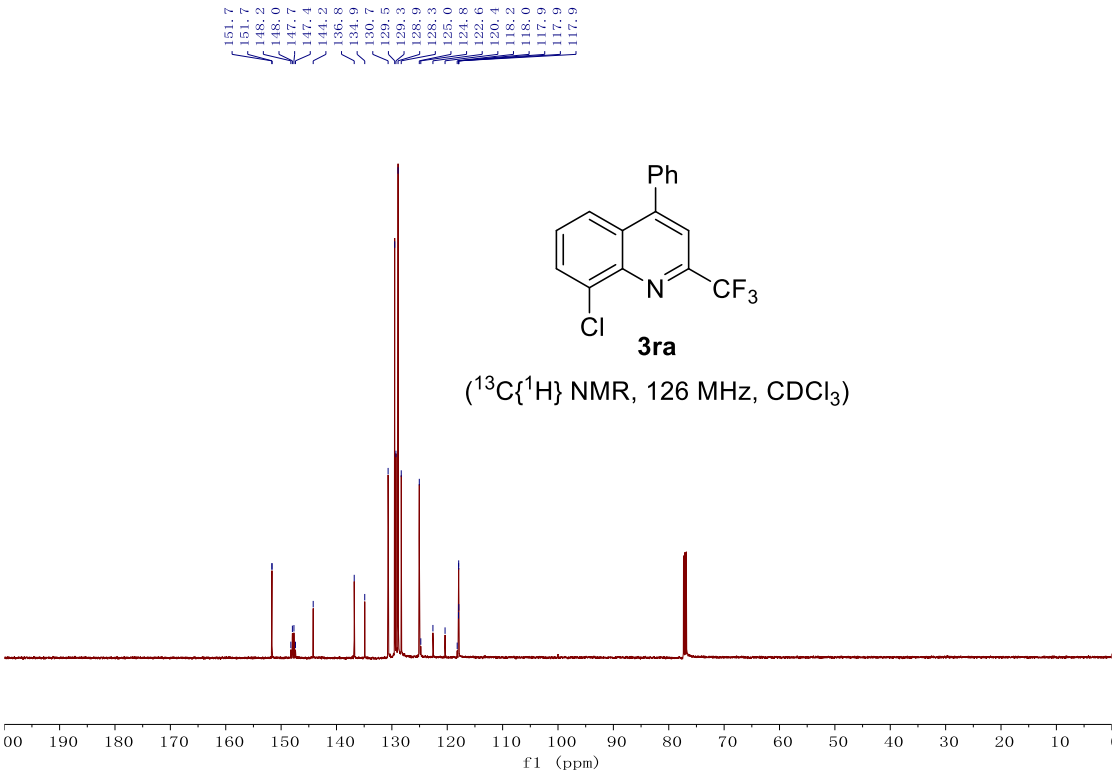

159.5
157.4
151.1
151.1
148.1
147.8
147.6
147.3
138.4
138.3
136.8
129.5
129.4
129.1
129.0
128.5
128.5
124.8
122.6
121.8
121.7
120.5
118.3
118.1
118.1
118.0
118.0
114.7
114.6
Ph
N
CF3
F
3qa
(13C{1H} NMR, 126 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-67.4
-122.0
Ph
N
CF3
F
3qa
(19F NMR, 471 MHz, CDCl3)
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
f1 (ppm)



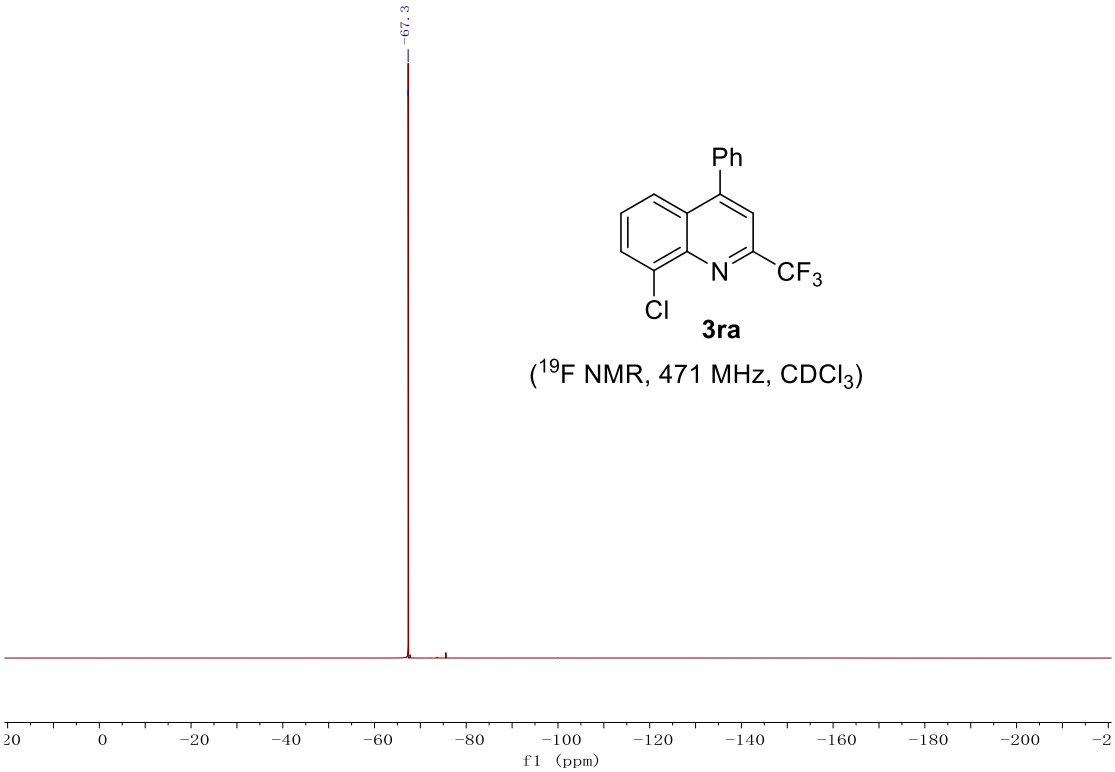
3ra

(^{1}H NMR, 500 MHz, $CDCl_3$)



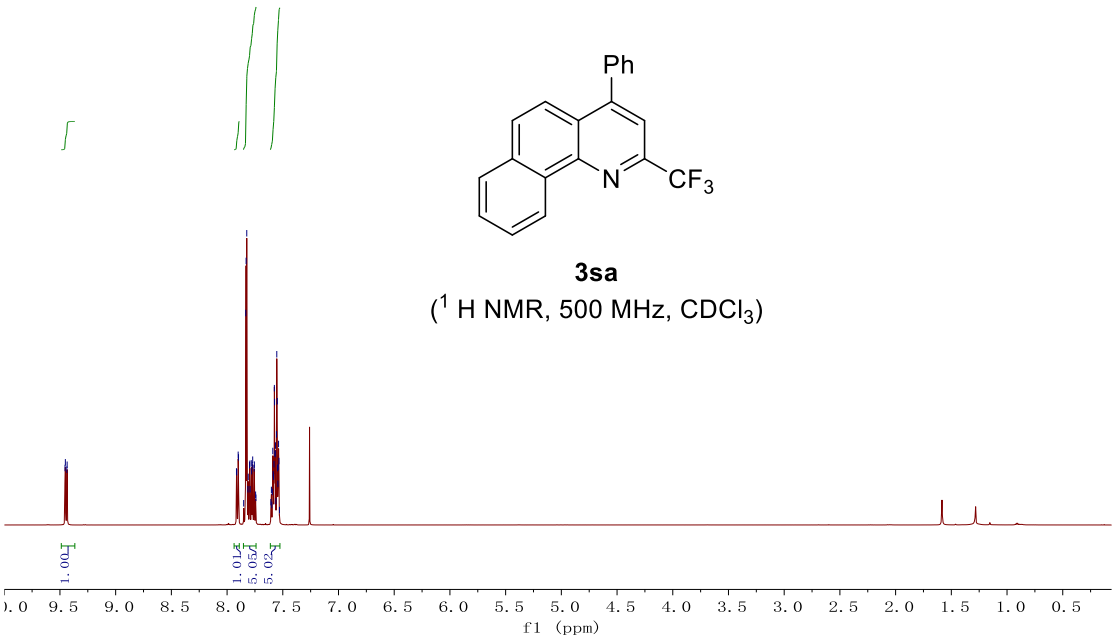
3ra

(^{13}C{^{1}H} NMR, 126 MHz, $CDCl_3$)



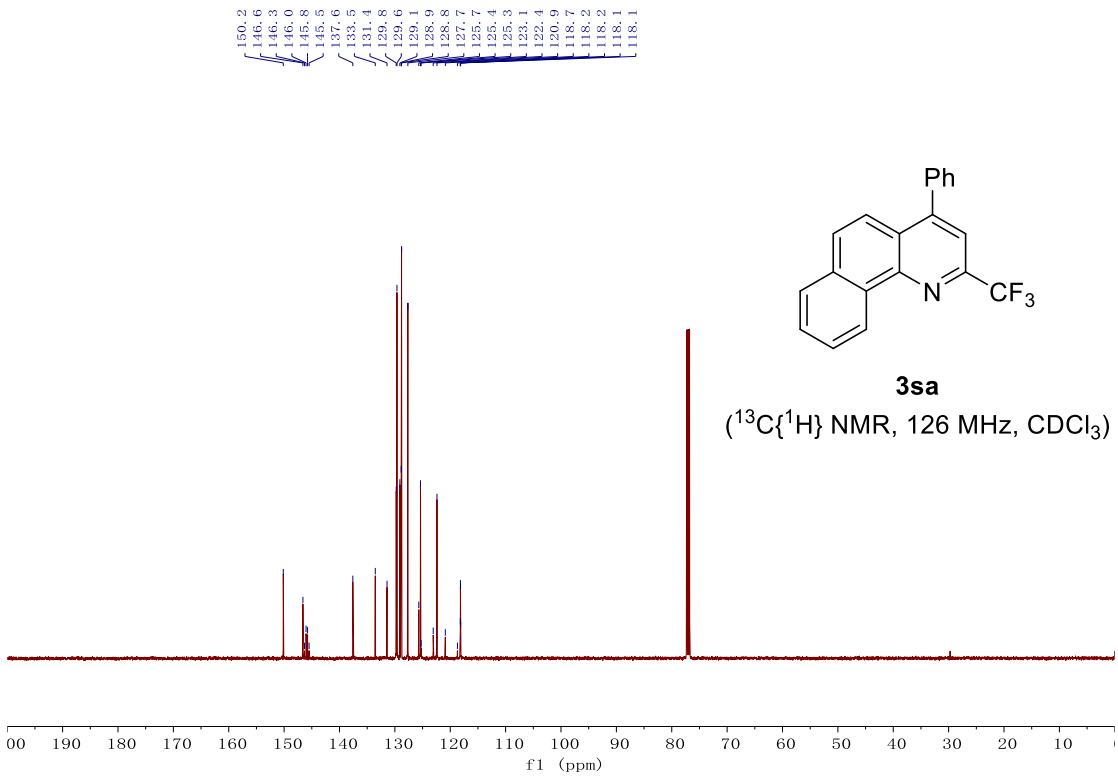
3ra

(^{19}F NMR, 471 MHz, $CDCl_3$)



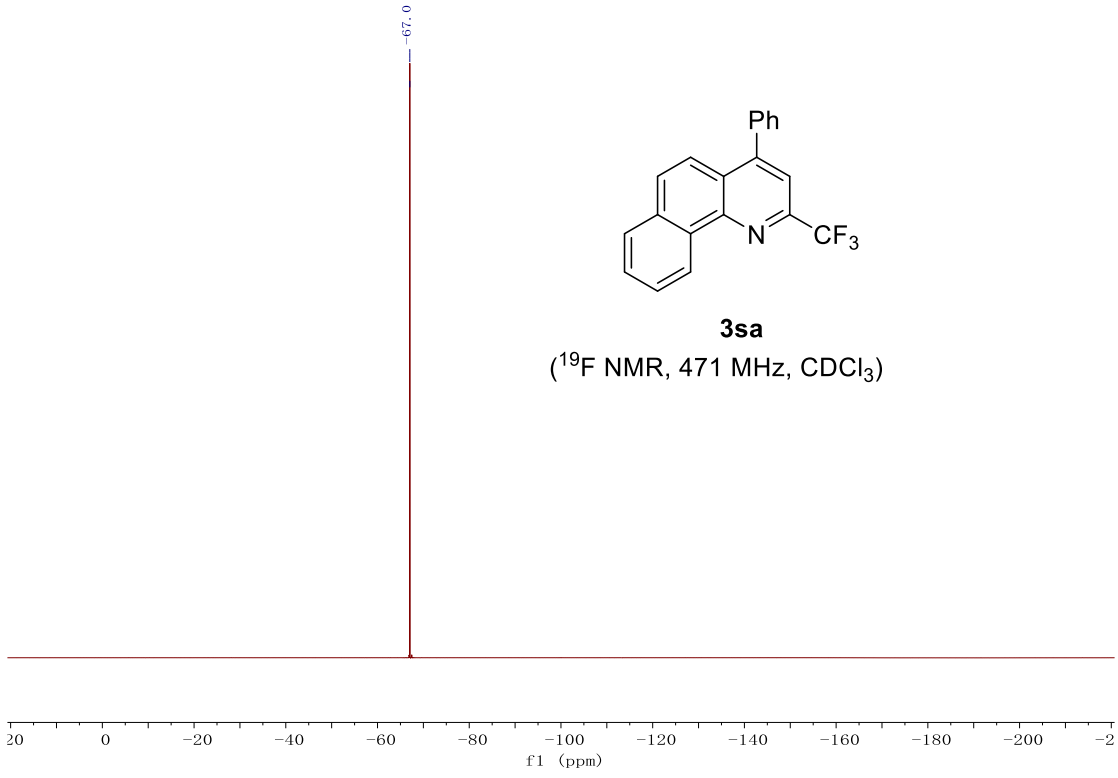
3sa

(^{1} H NMR, 500 MHz, $CDCl_3$)



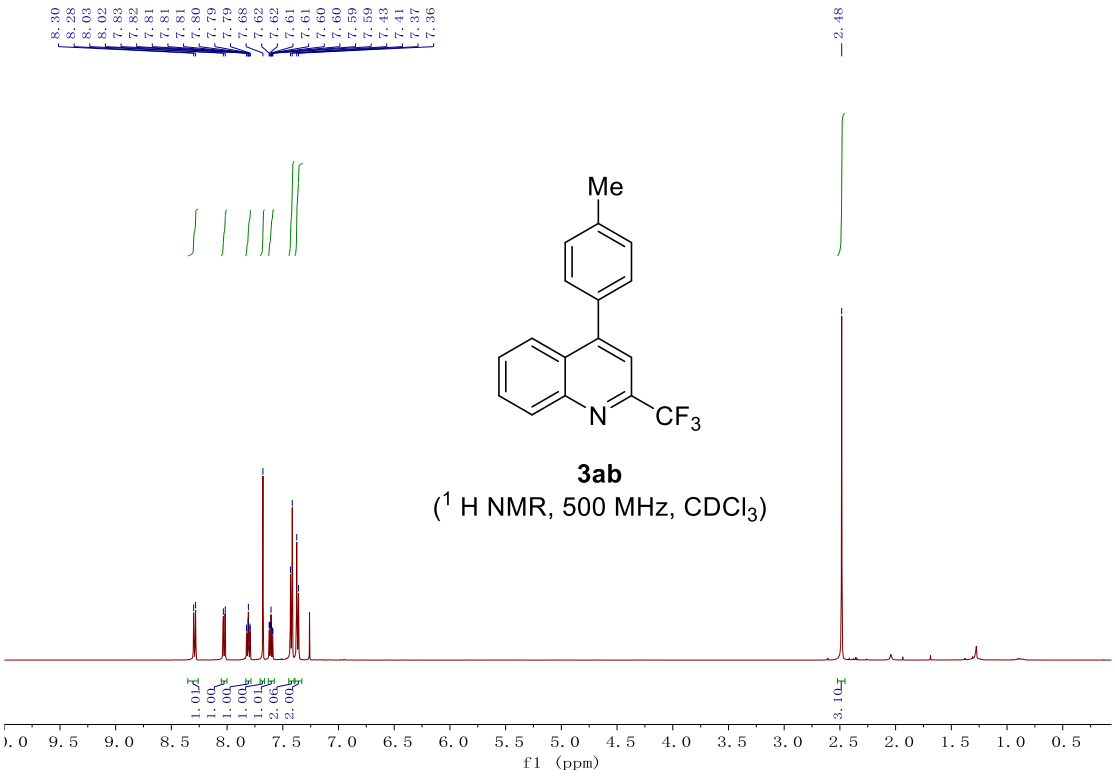
3sa

($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)



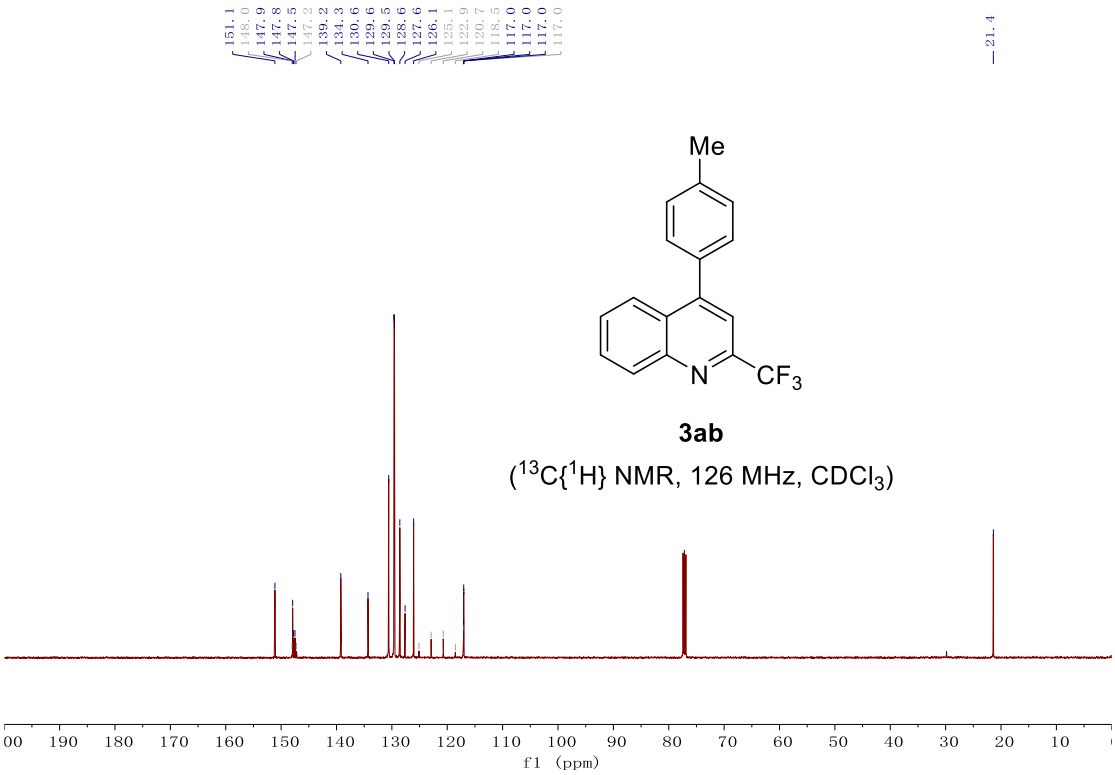
3sa

(^{19}F NMR, 471 MHz, $CDCl_3$)



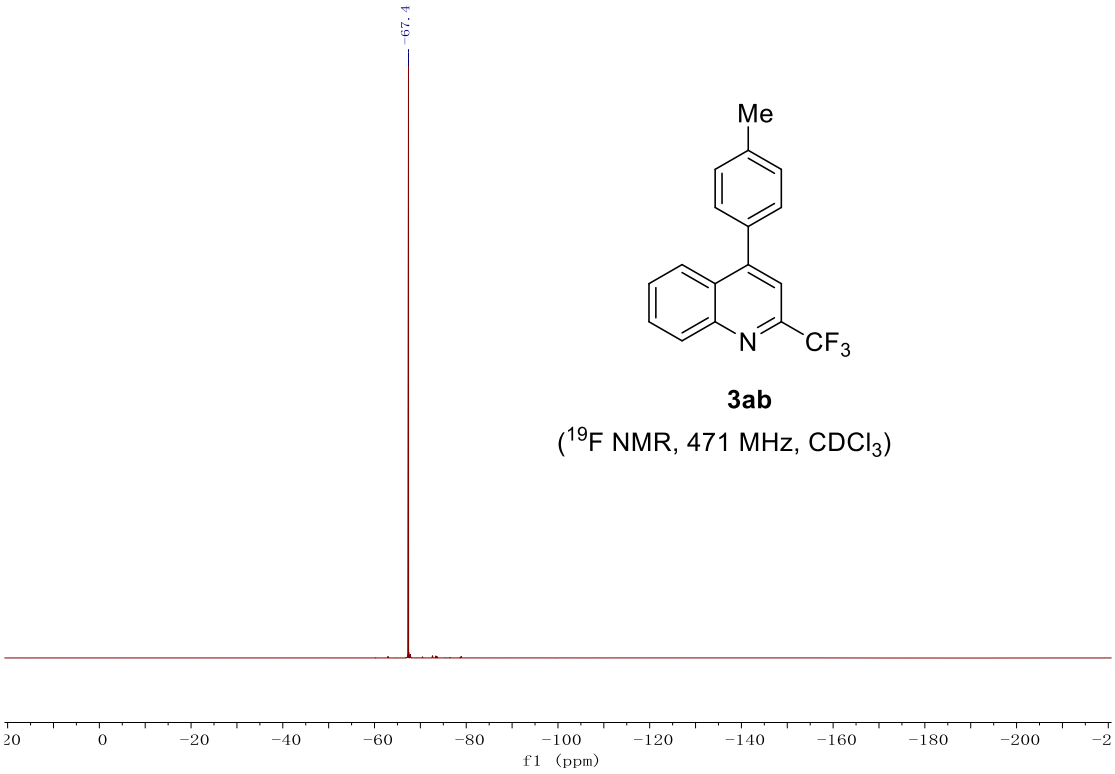
3ab

(^{1}H NMR, 500 MHz, $CDCl_3$)



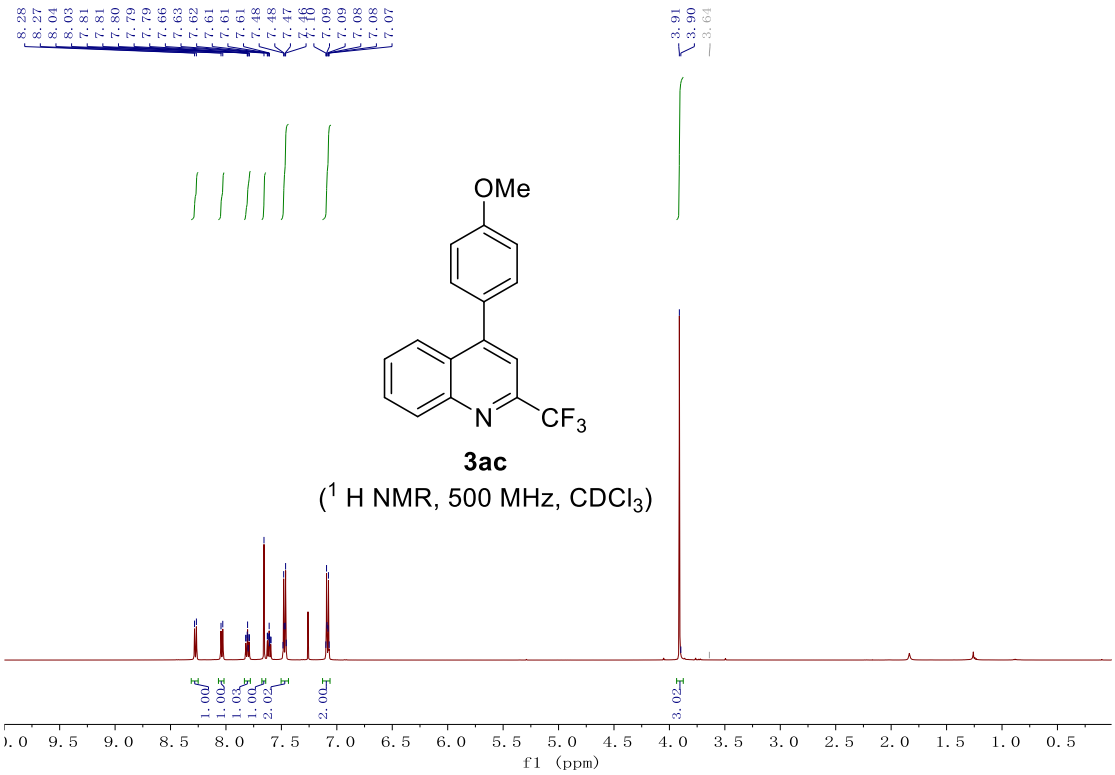
3ab

($^{13}C\{^1H\}$ NMR, 126 MHz, $CDCl_3$)



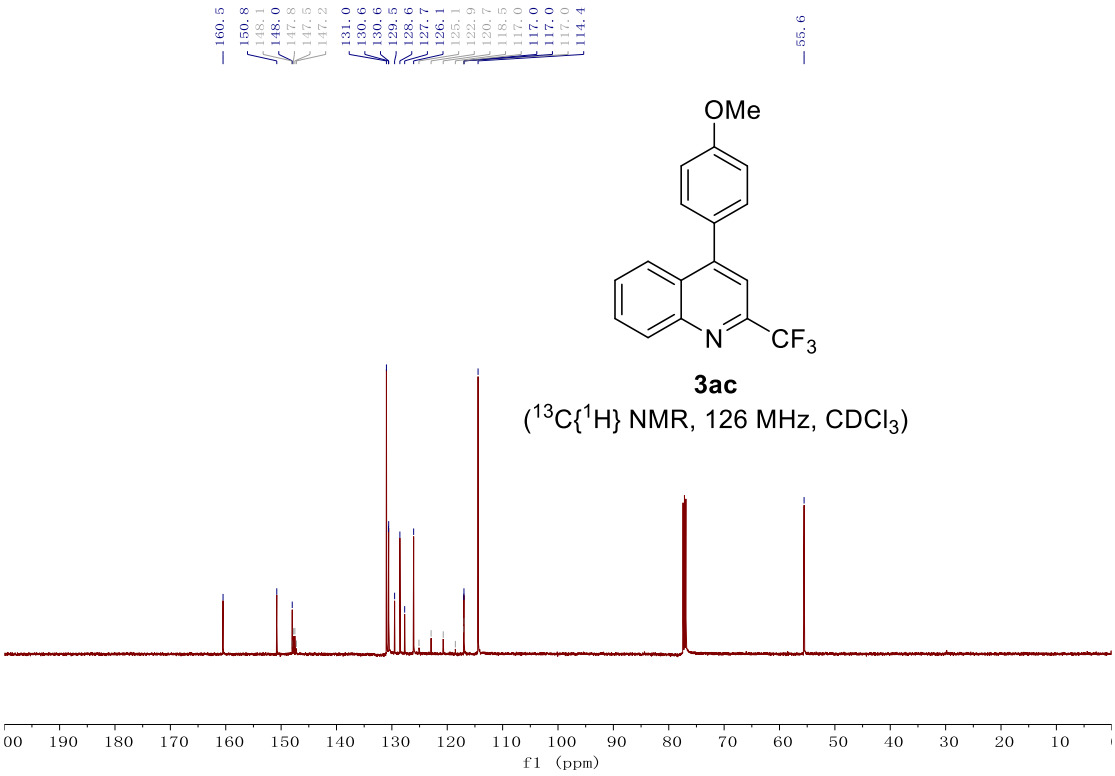
3ab

(^{19}F NMR, 471 MHz, $CDCl_3$)



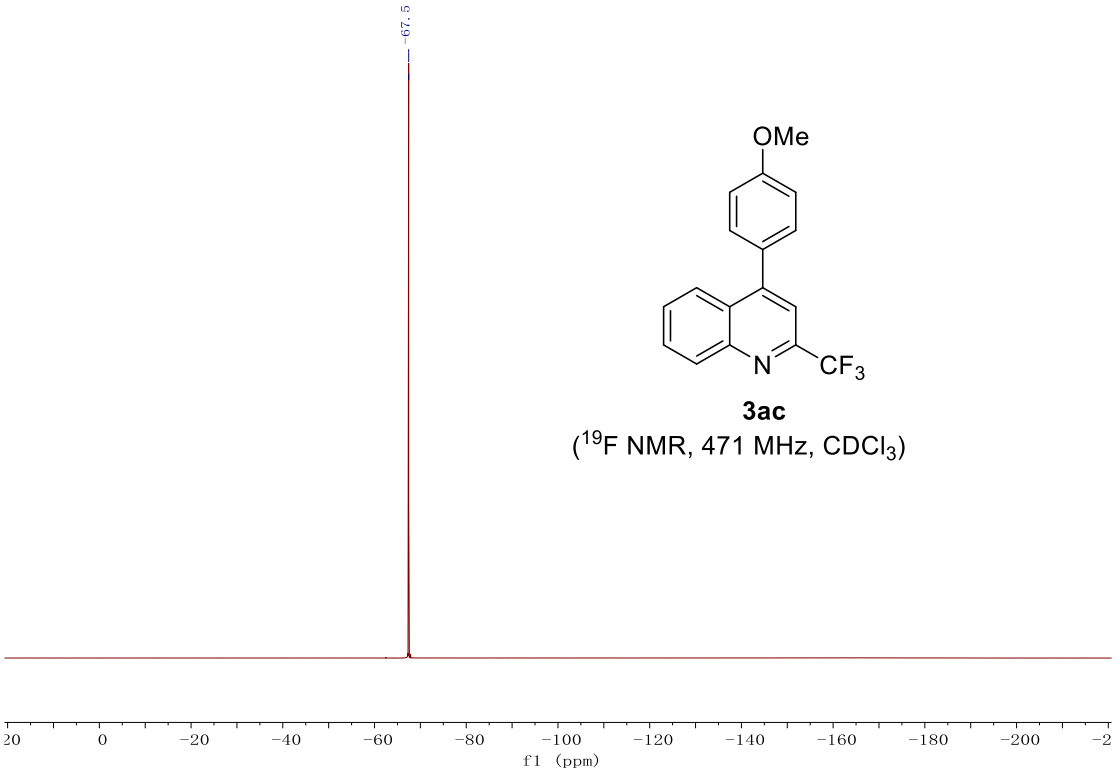
3ac

(^{1}H NMR, 500 MHz, $CDCl_3$)



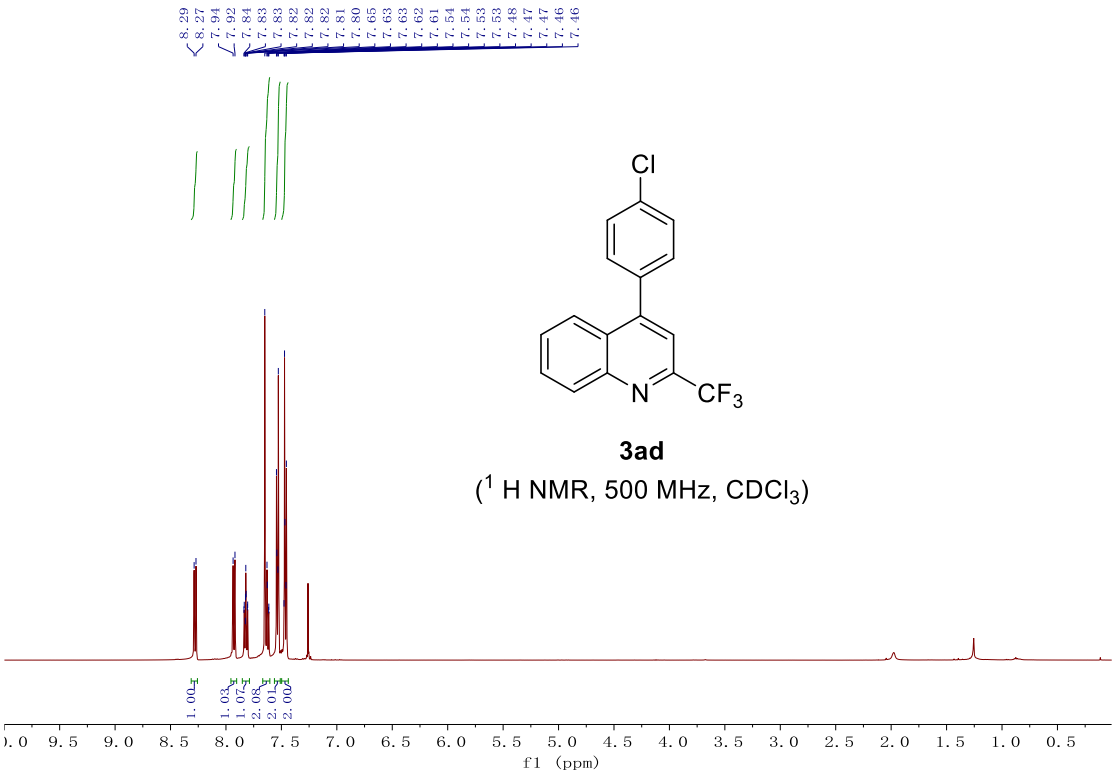
3ac

($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)



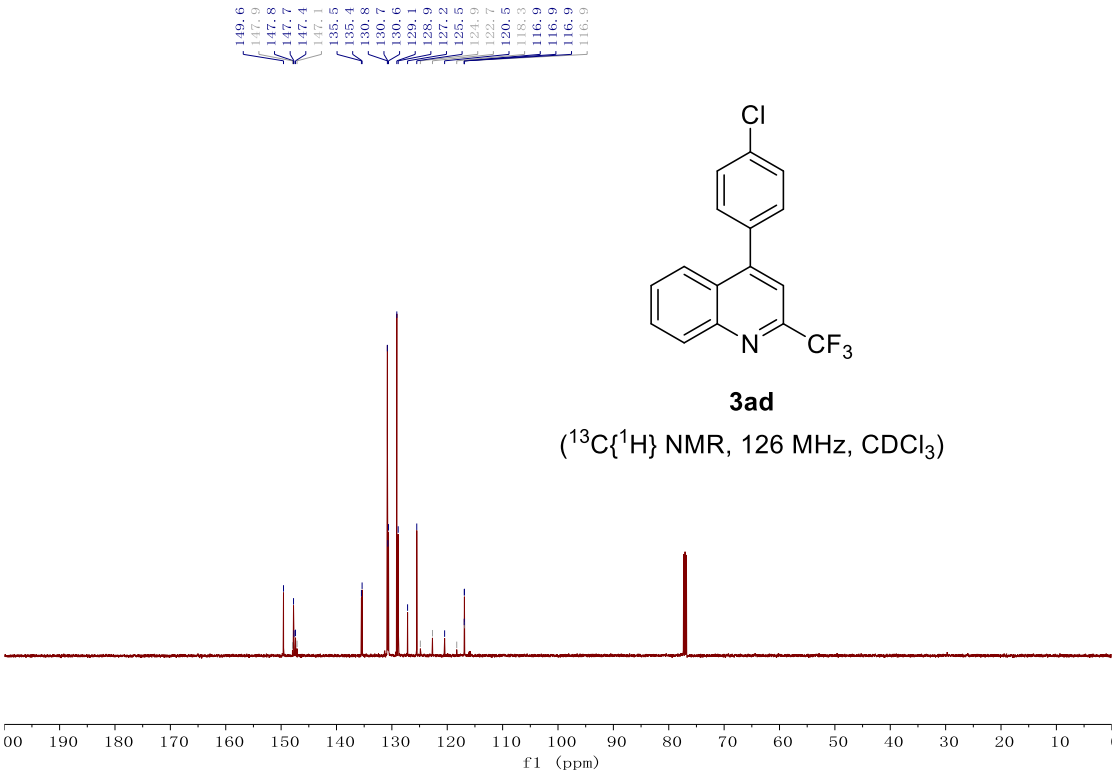
3ac

(^{19}F NMR, 471 MHz, $CDCl_3$)



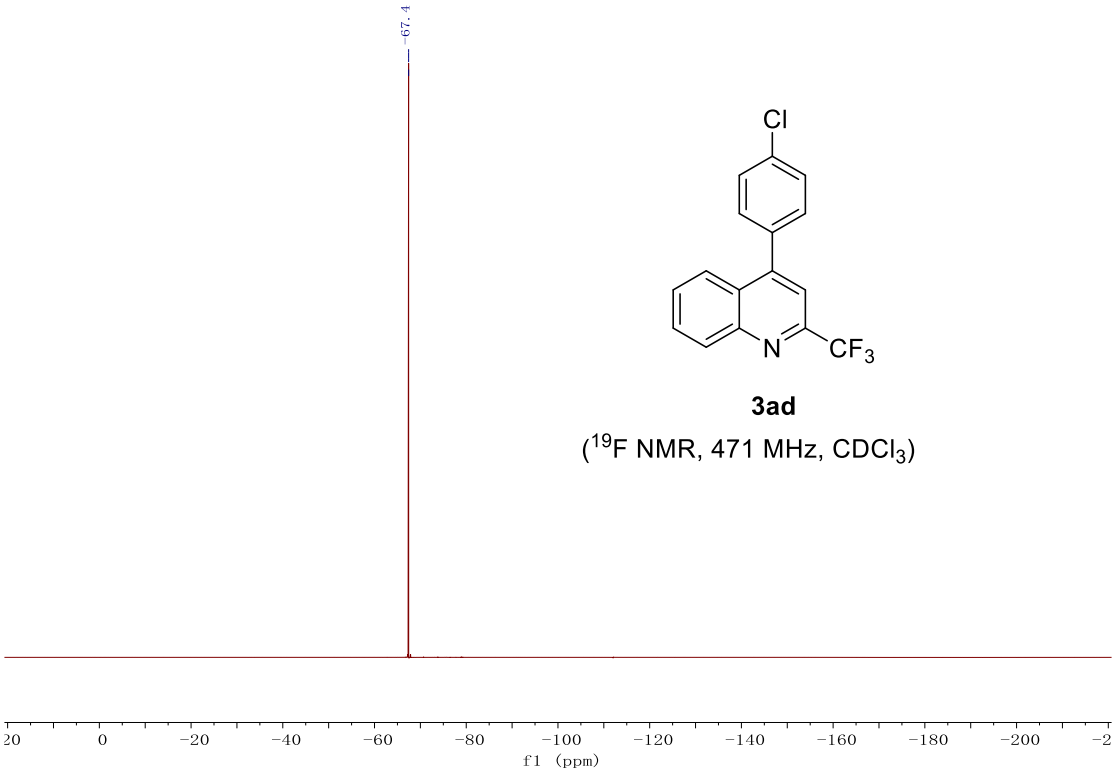
3ad

(^{1}H NMR, 500 MHz, $CDCl_3$)



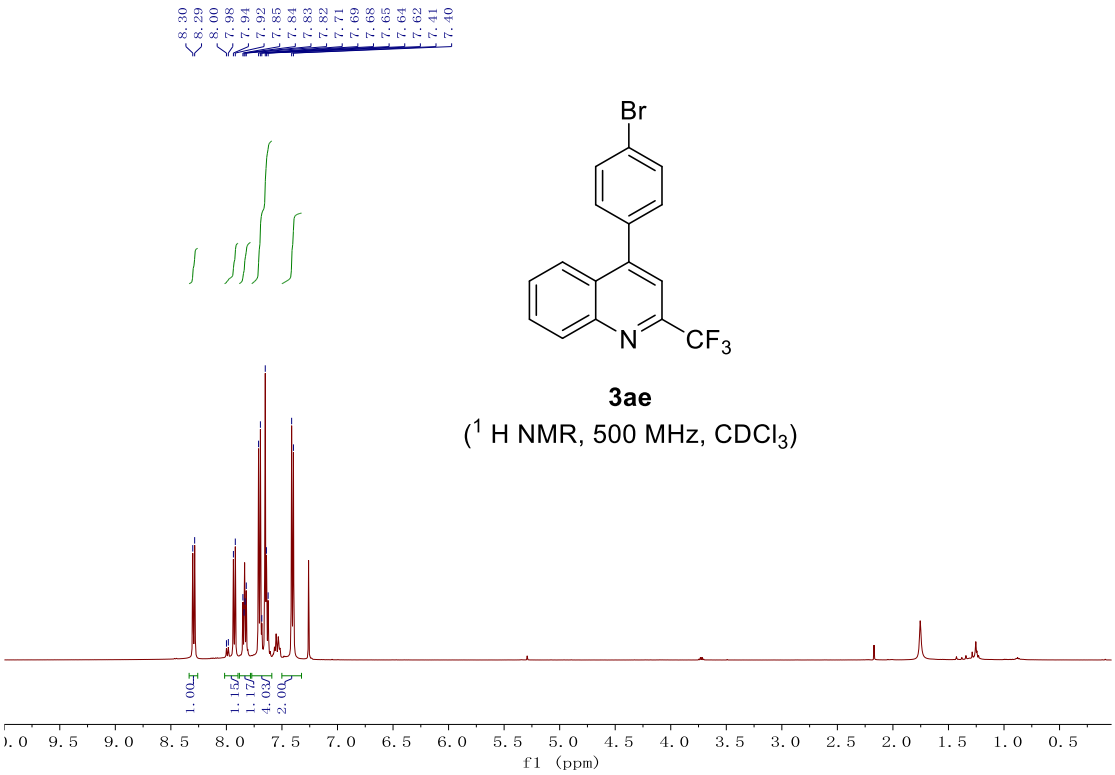
3ad

($^{13}C\{^1H\}$ NMR, 126 MHz, $CDCl_3$)



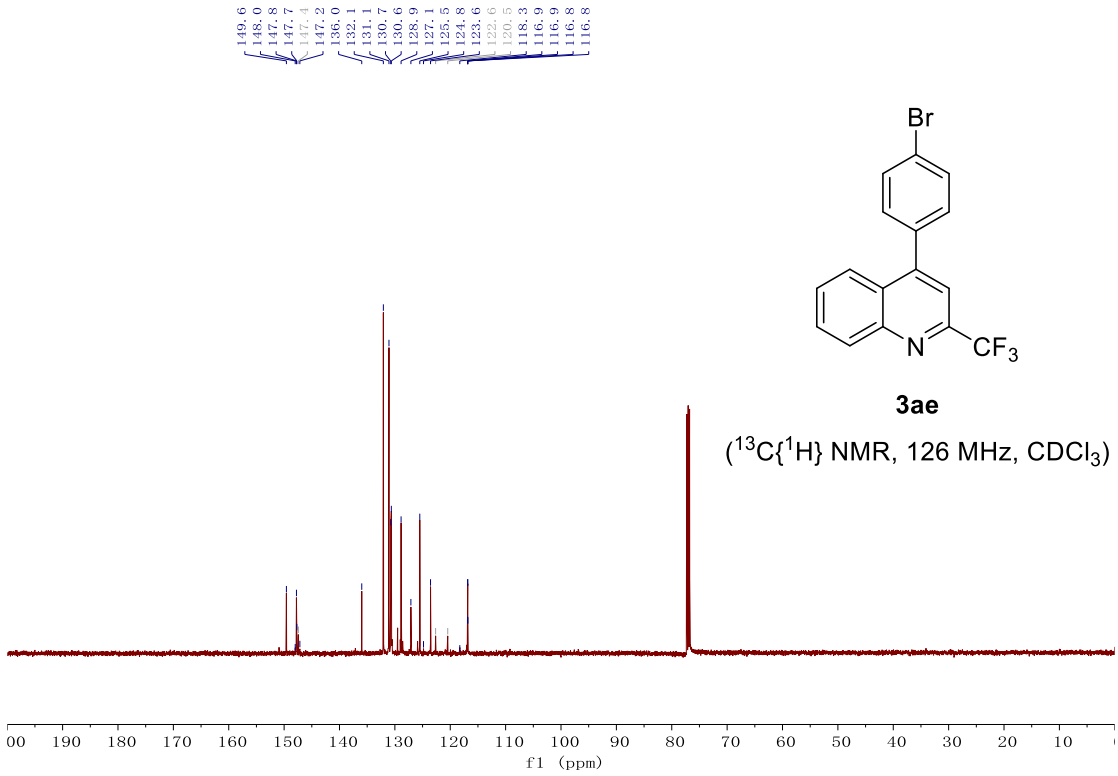
3ad

(^{19}F NMR, 471 MHz, $CDCl_3$)



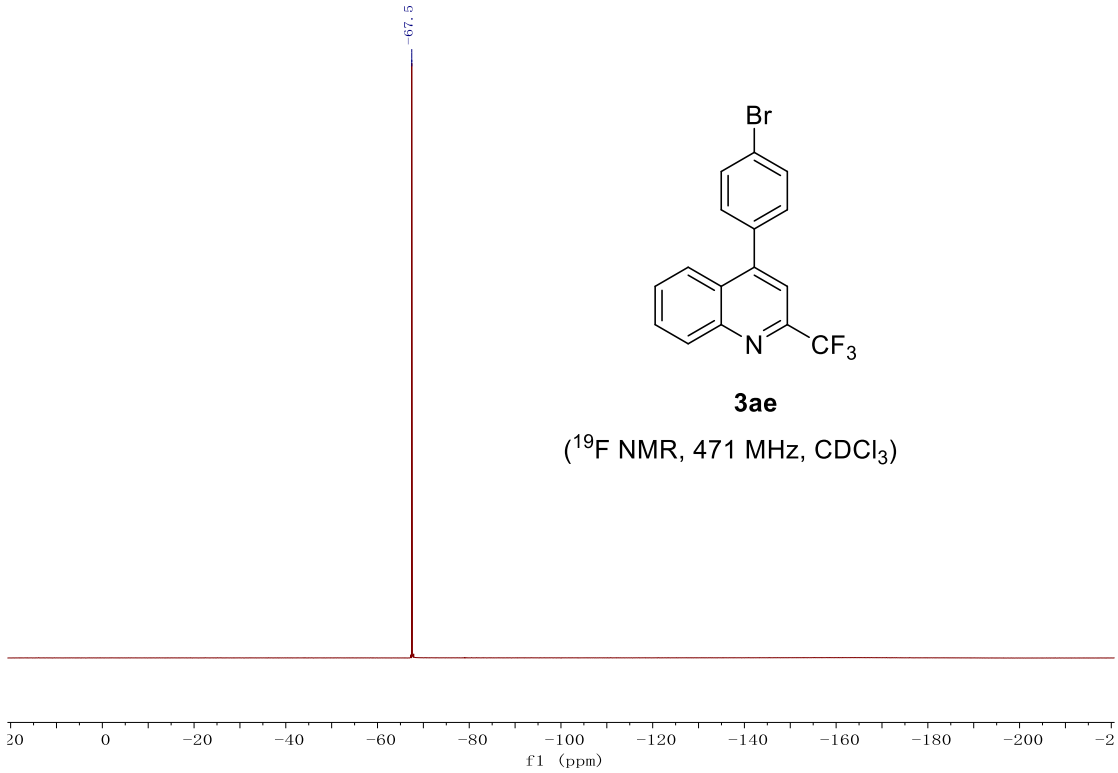
3ae

(^{1}H NMR, 500 MHz, $CDCl_3$)



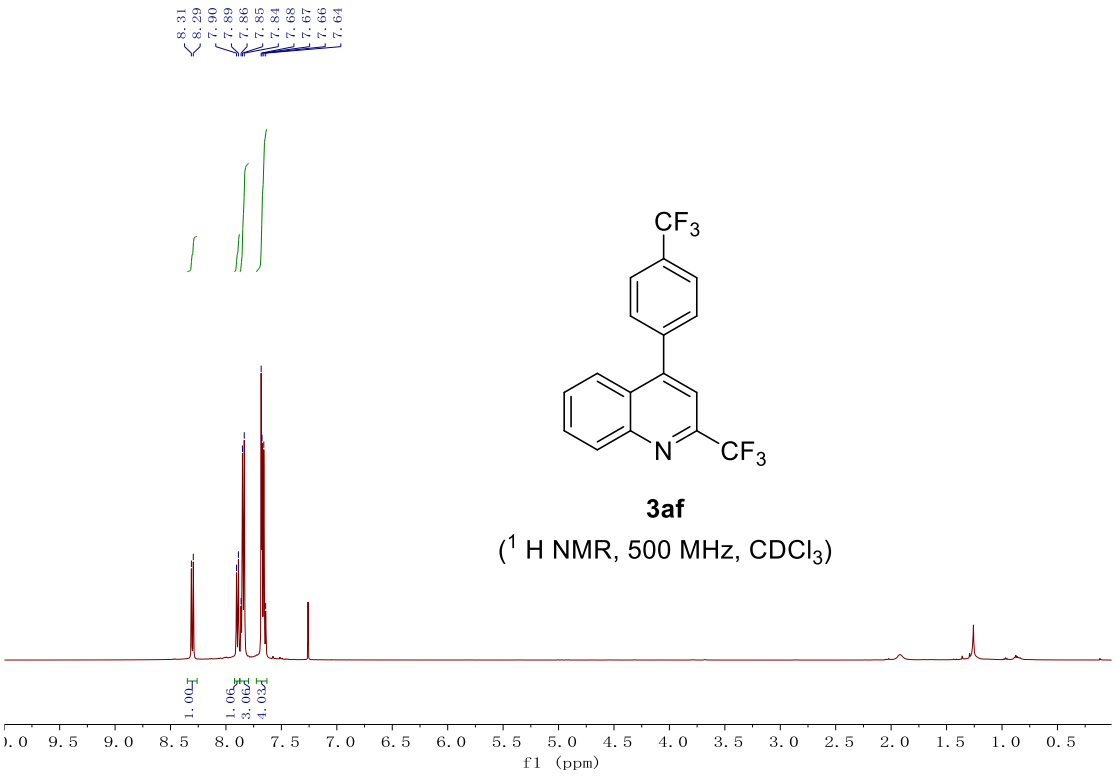
3ae

($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)



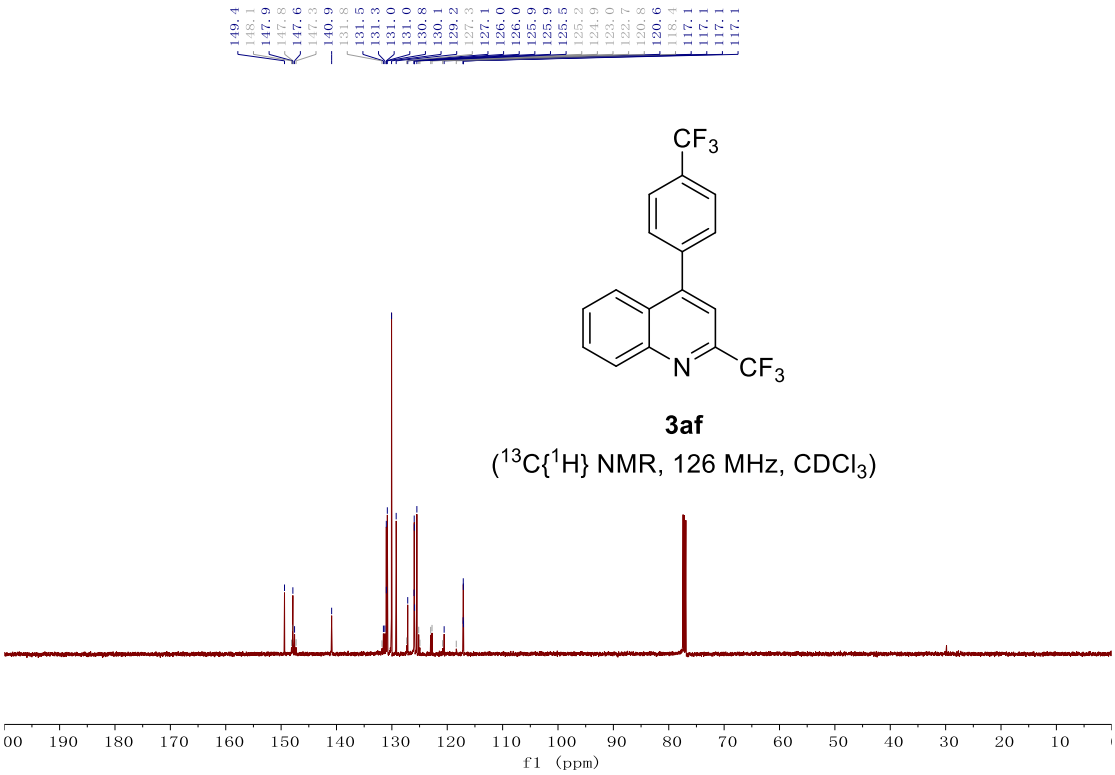
3ae

(^{19}F NMR, 471 MHz, $CDCl_3$)



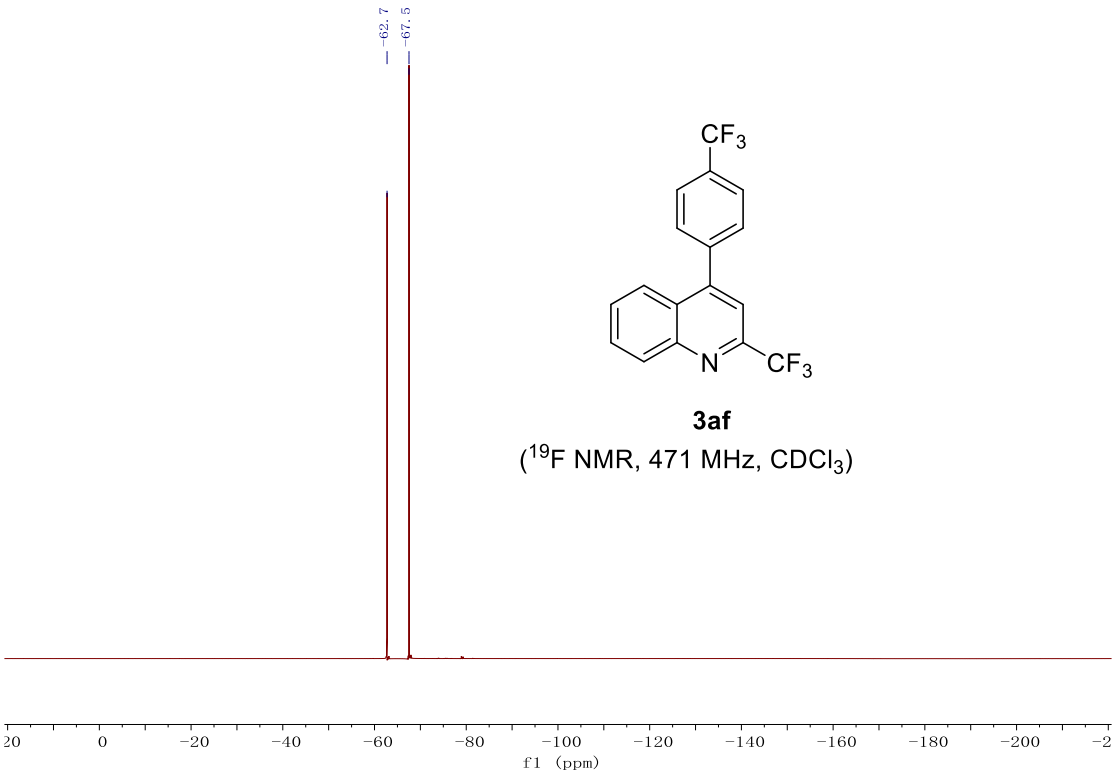
3af

(^{1}H NMR, 500 MHz, $CDCl_3$)



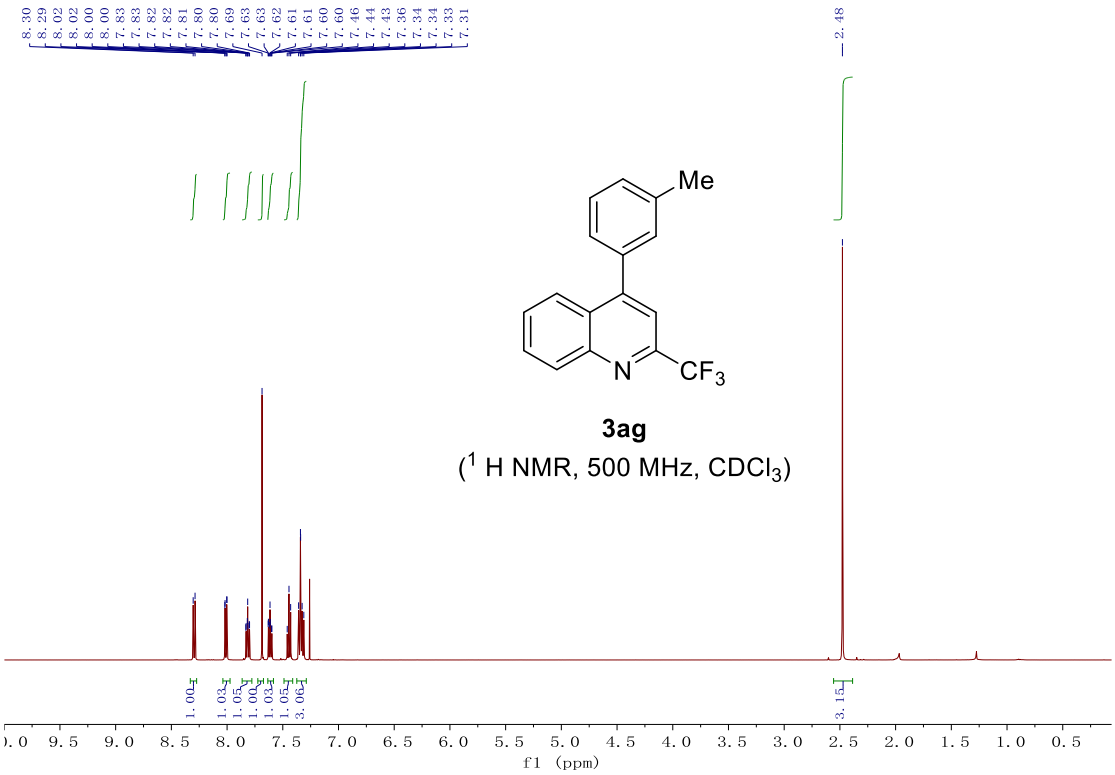
3af

($^{13}C\{^1H\}$ NMR, 126 MHz, $CDCl_3$)



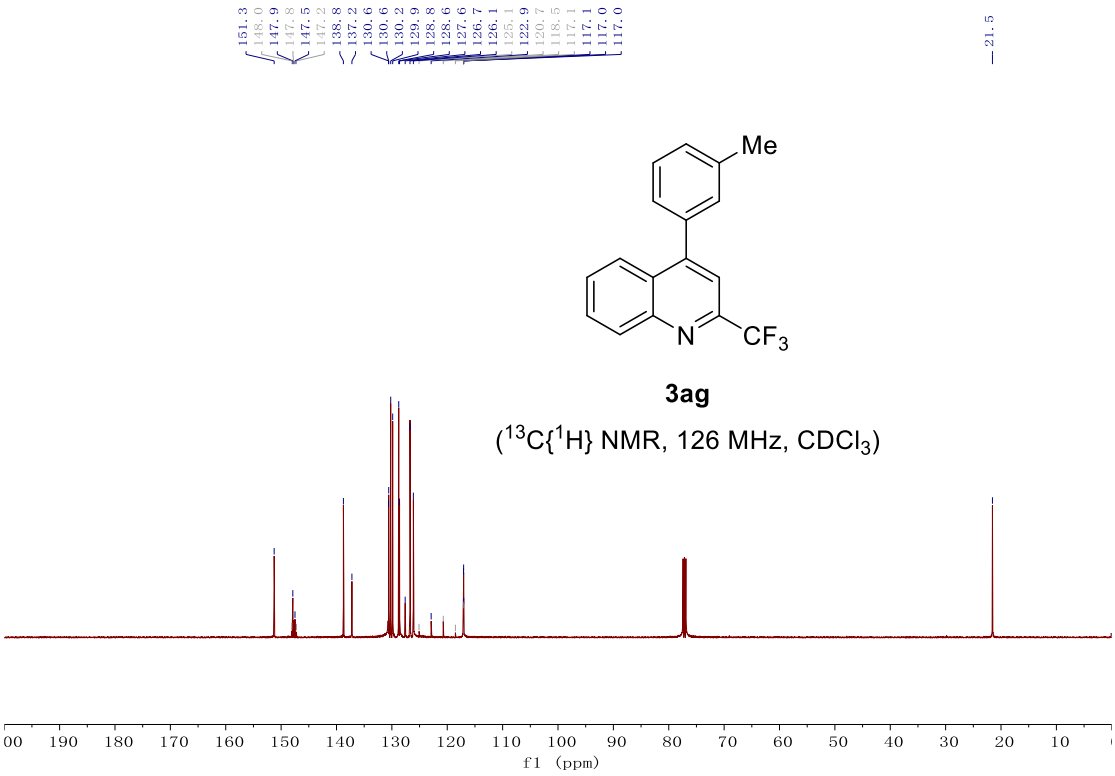
3af

(^{19}F NMR, 471 MHz, $CDCl_3$)



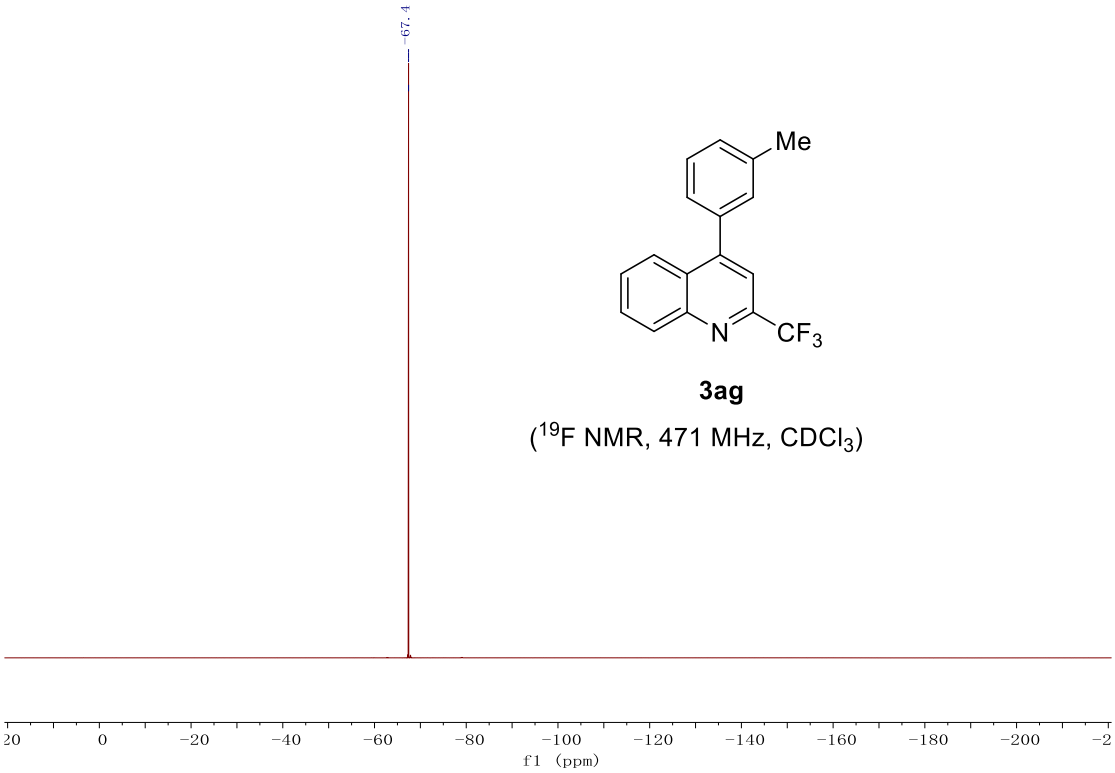
3ag

(^{1} H NMR, 500 MHz, $CDCl_3$)



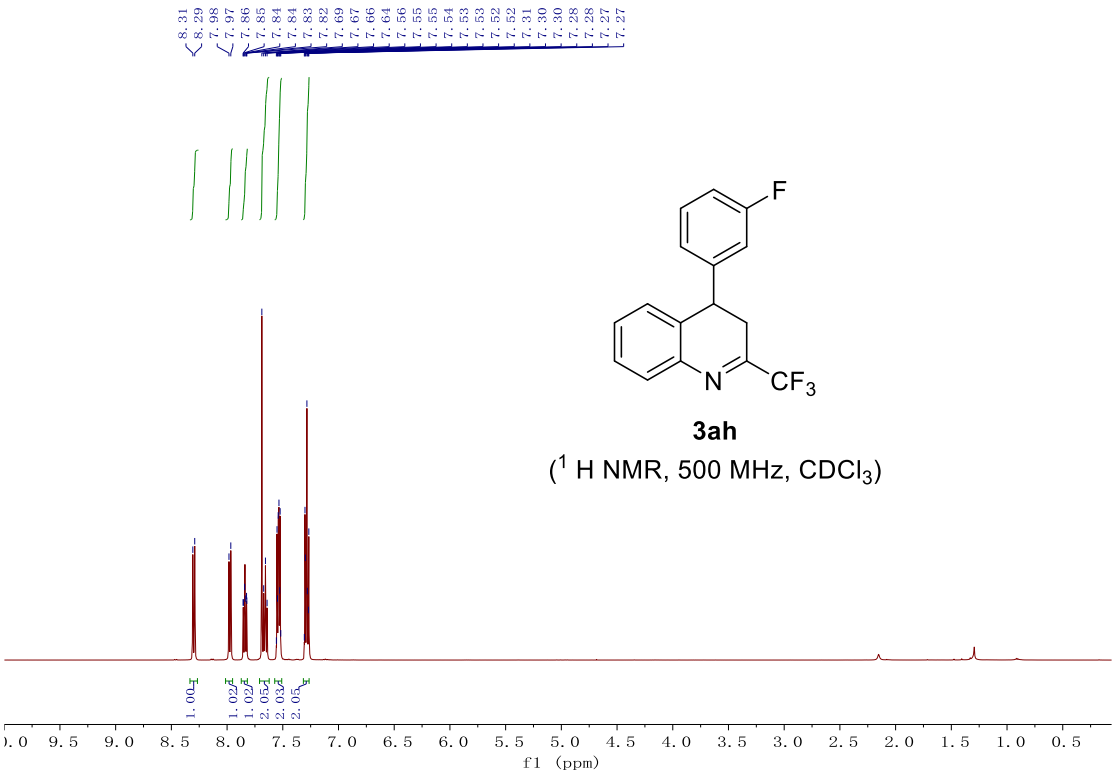
3ag

($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)



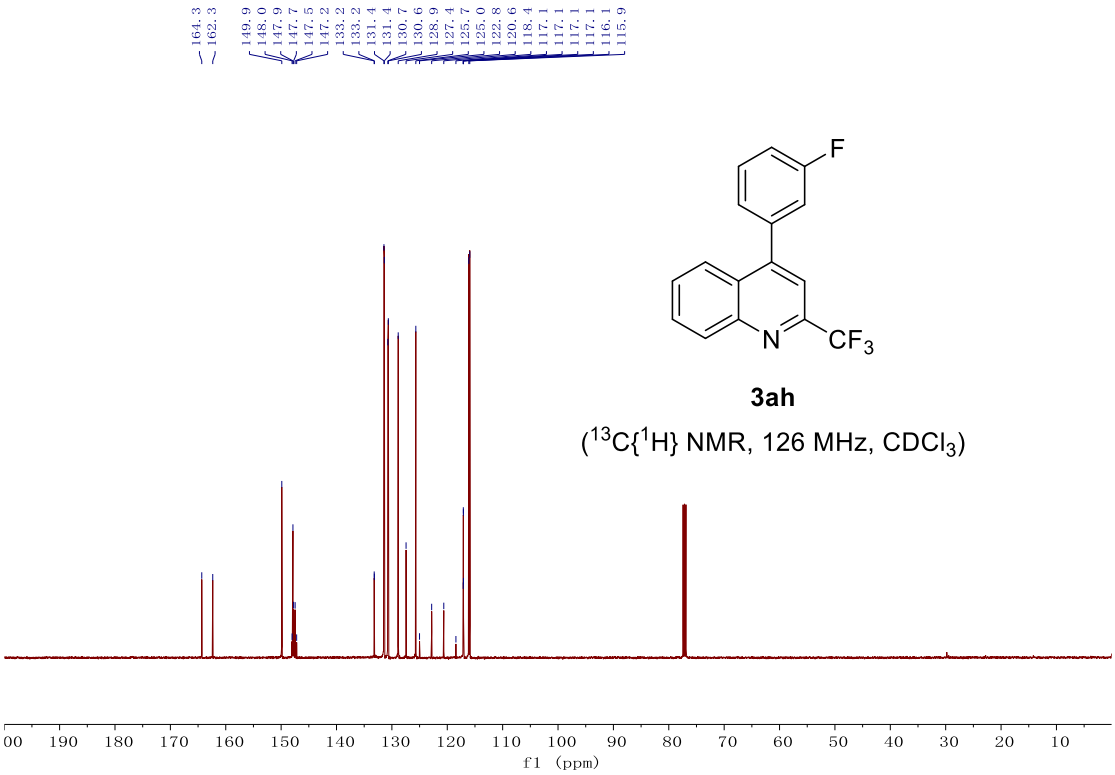
3ag

(^{19}F NMR, 471 MHz, $CDCl_3$)



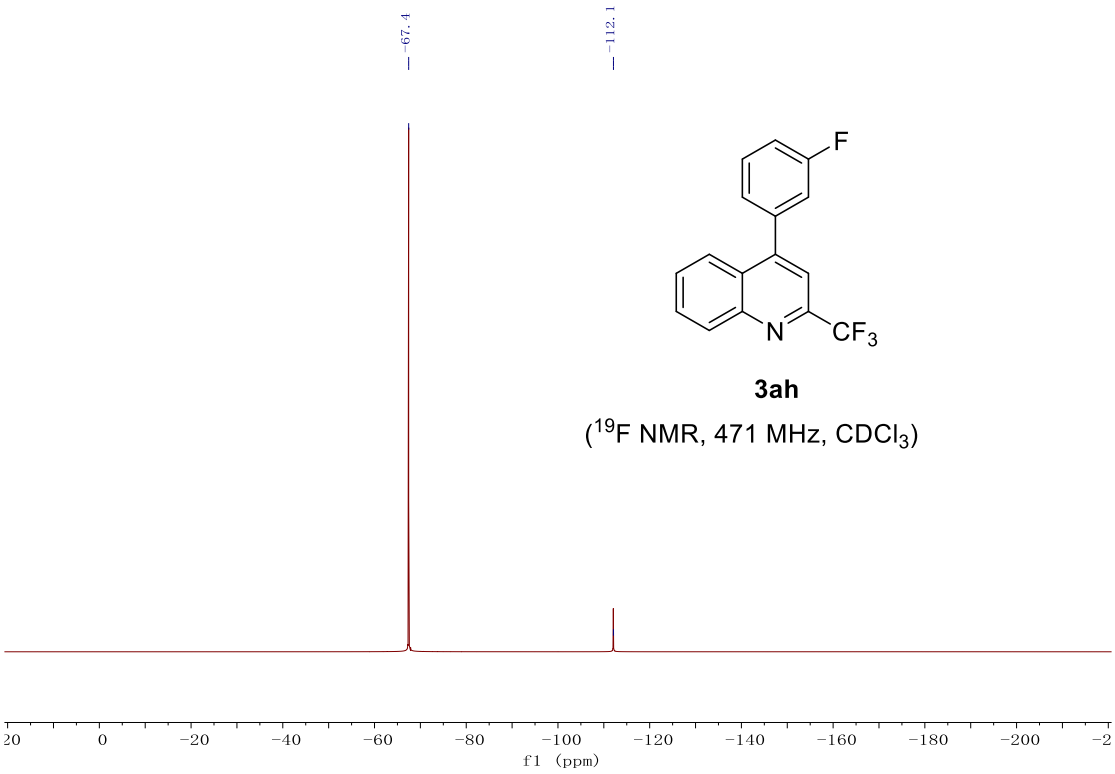
3ah

(^{1}H NMR, 500 MHz, $CDCl_3$)



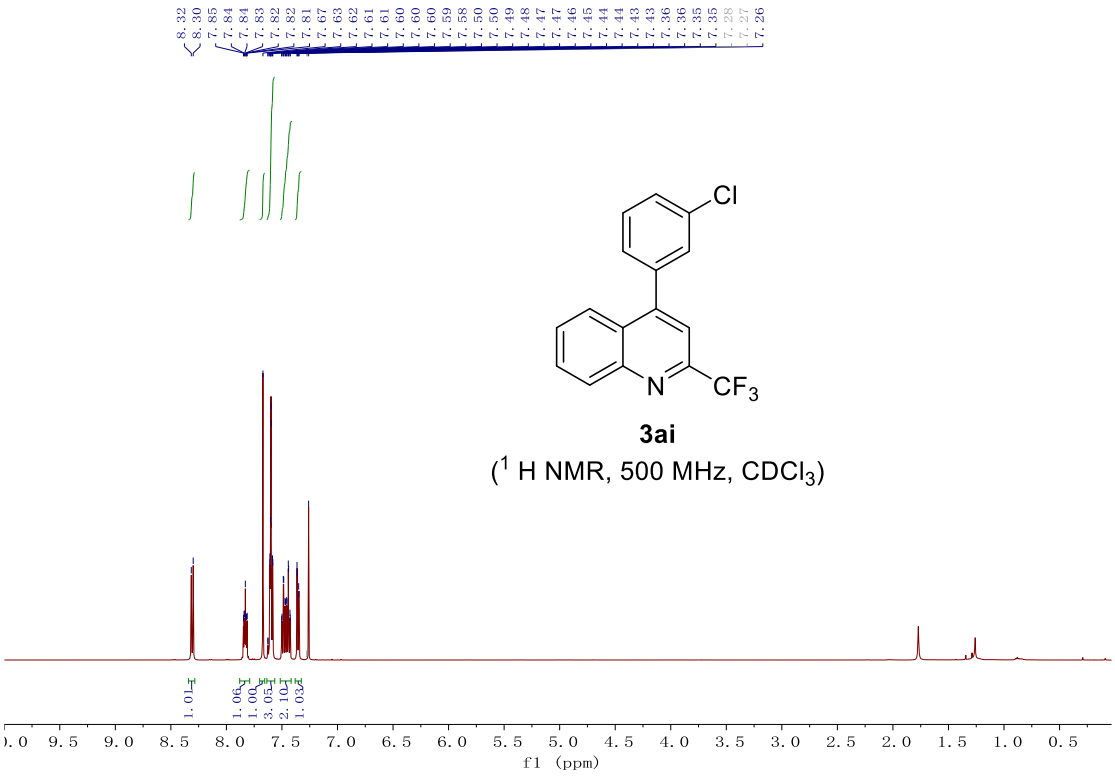
3ah

($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)



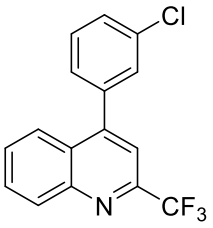
3ah

(^{19}F NMR, 471 MHz, $CDCl_3$)



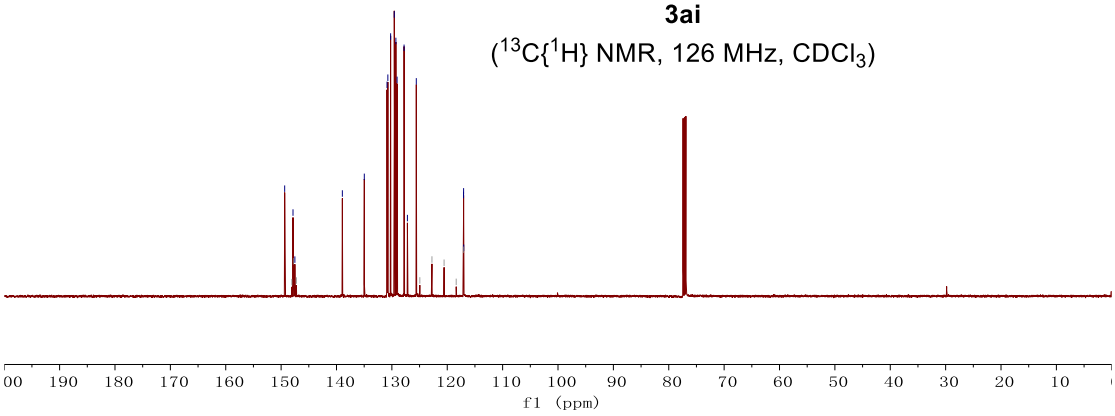
3ai

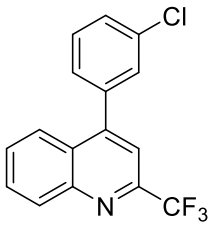
(^{1} H NMR, 500 MHz, $CDCl_3$)



3ai

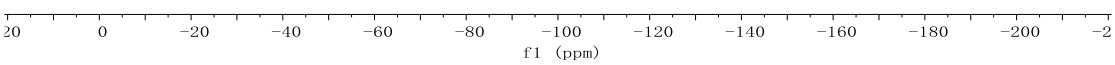
($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)

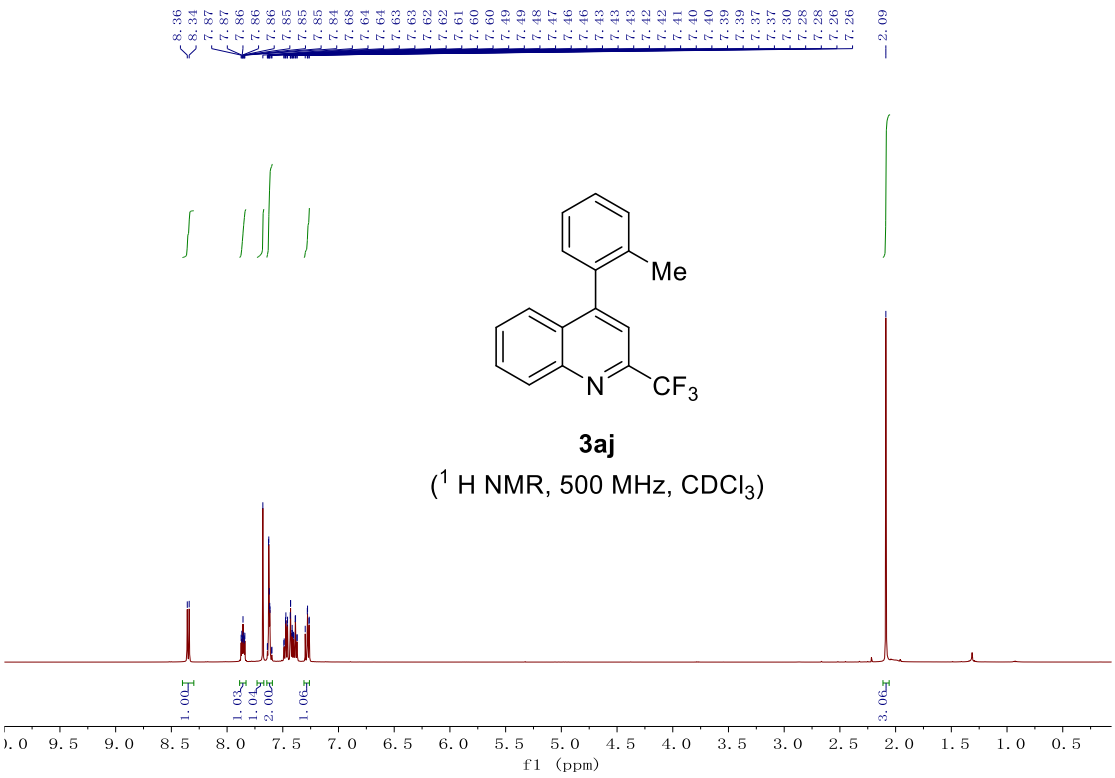


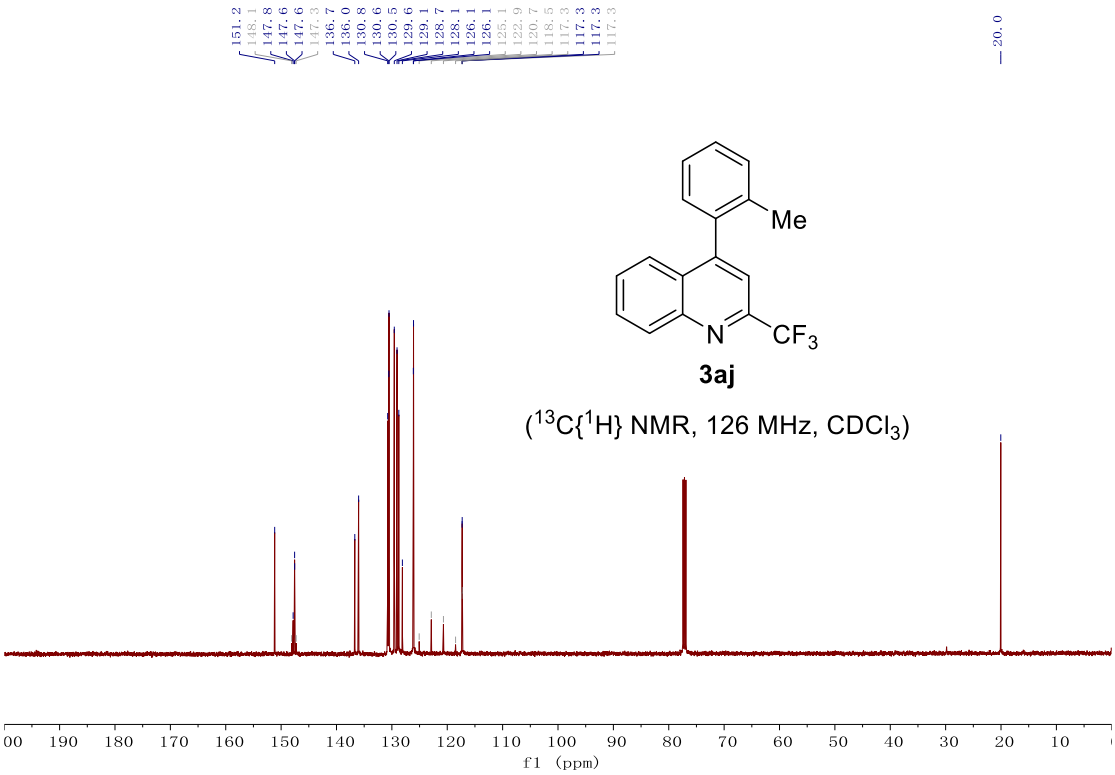


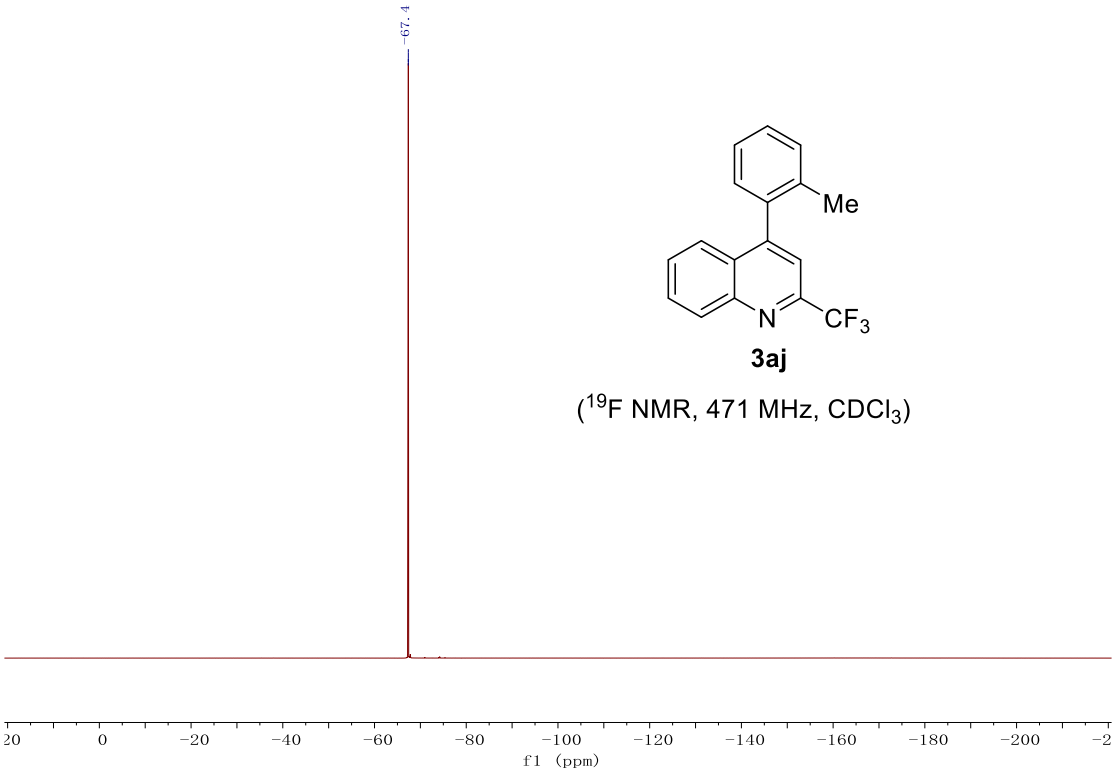
3ai

(^{19}F NMR, 471 MHz, $CDCl_3$)



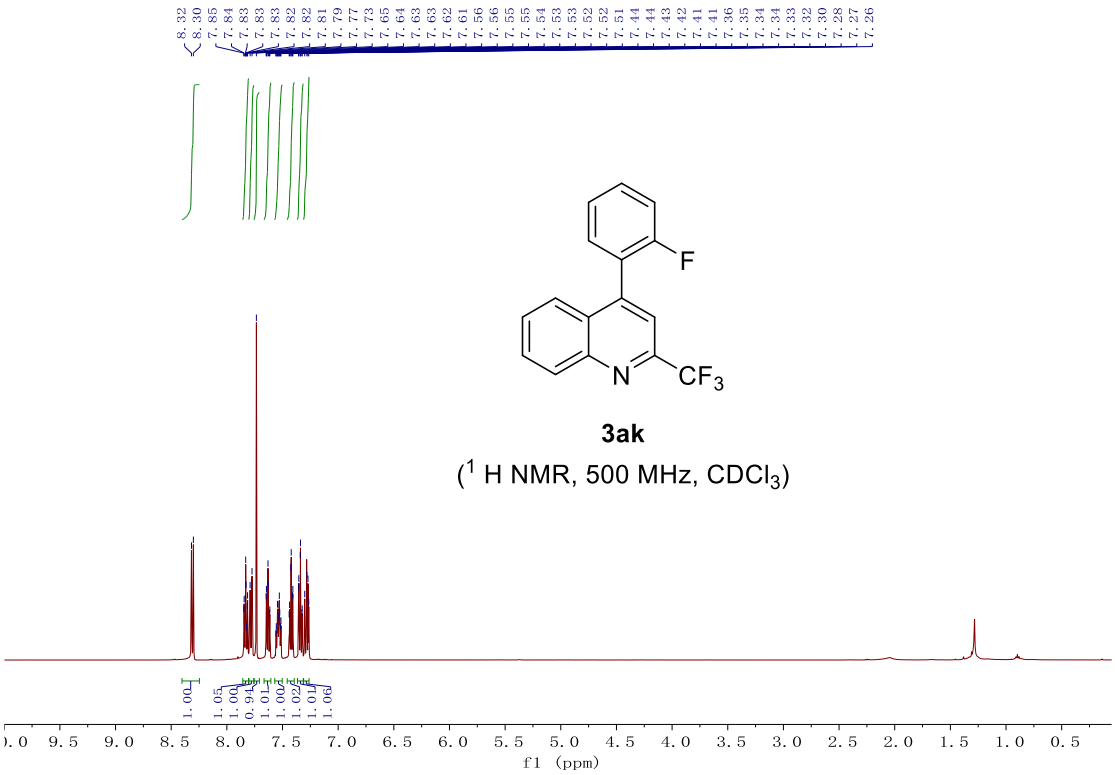

Me
N
CF3
3aj
(1 H NMR, 500 MHz, CDCl3)
f1 (ppm)


Me
N
CF3
3aj
(13C{1H} NMR, 126 MHz, CDCl3)
f1 (ppm)



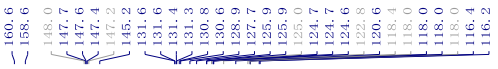
3aj

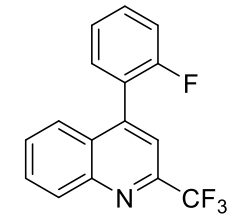
(^{19}F NMR, 471 MHz, $CDCl_3$)



3ak

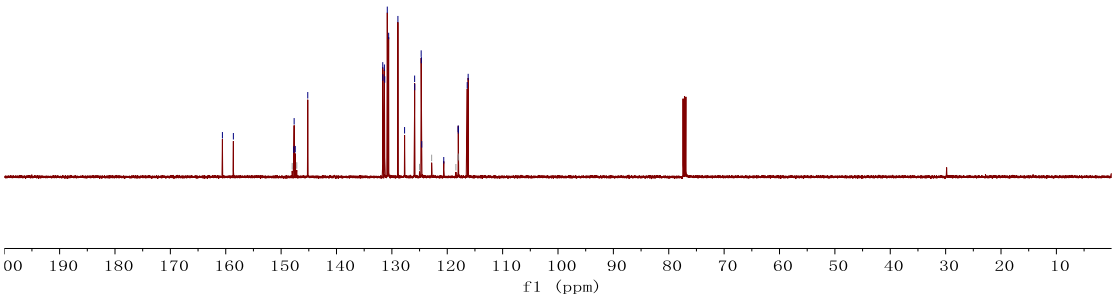
(^{1} H NMR, 500 MHz, $CDCl_3$)

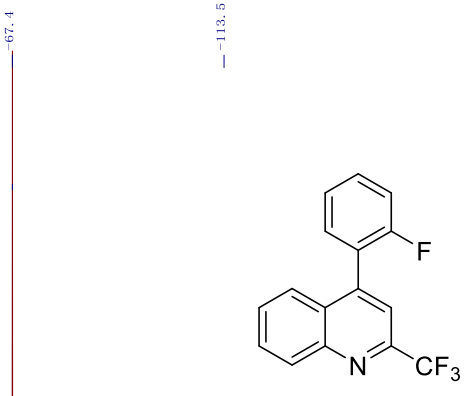




3ak

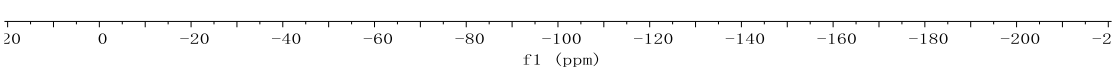
($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)

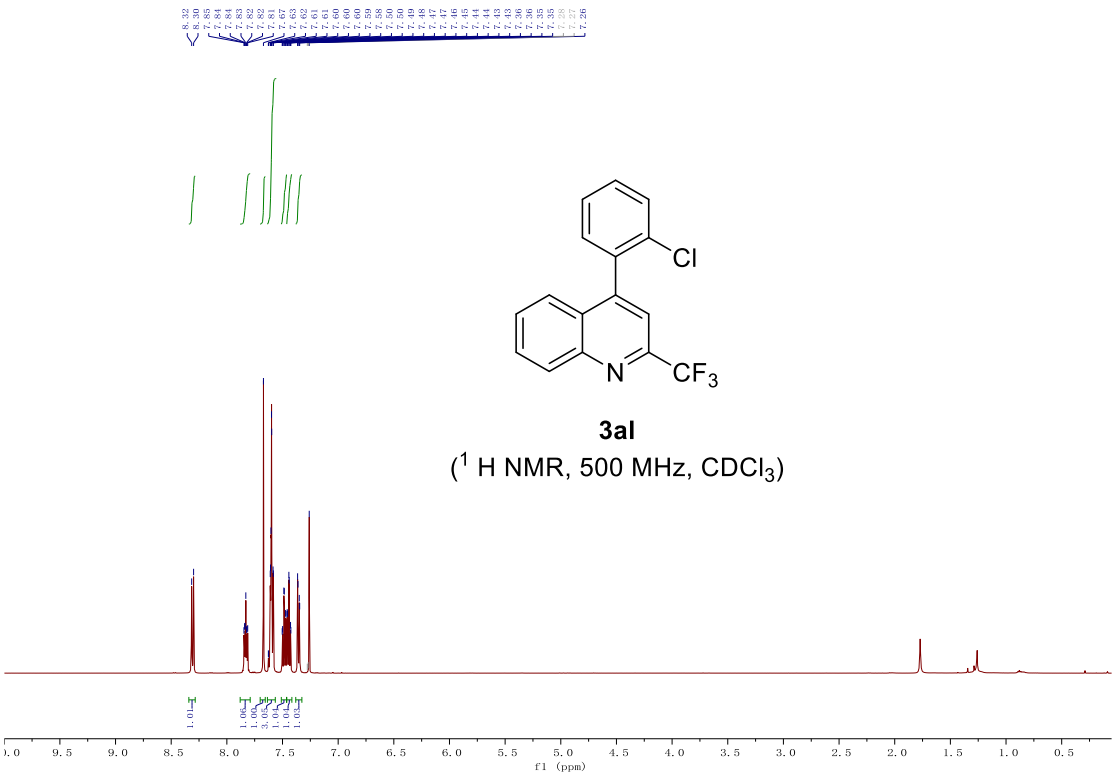




3ak

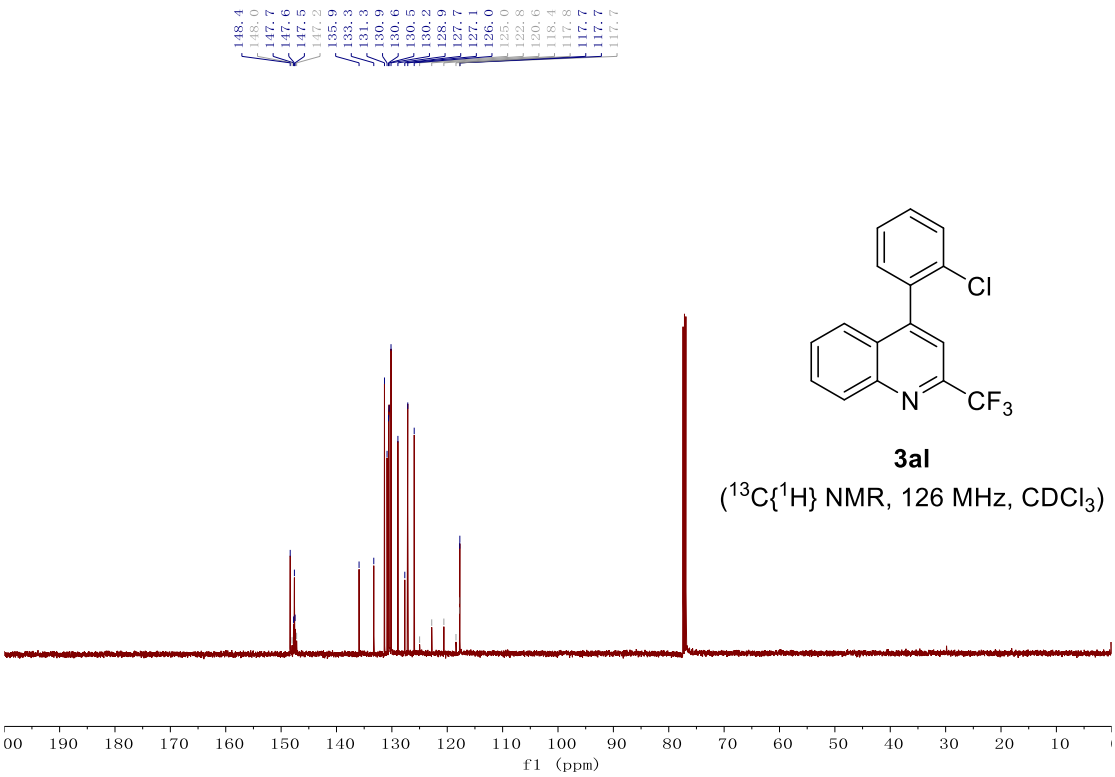
(^{19}F NMR, 471 MHz, $CDCl_3$)





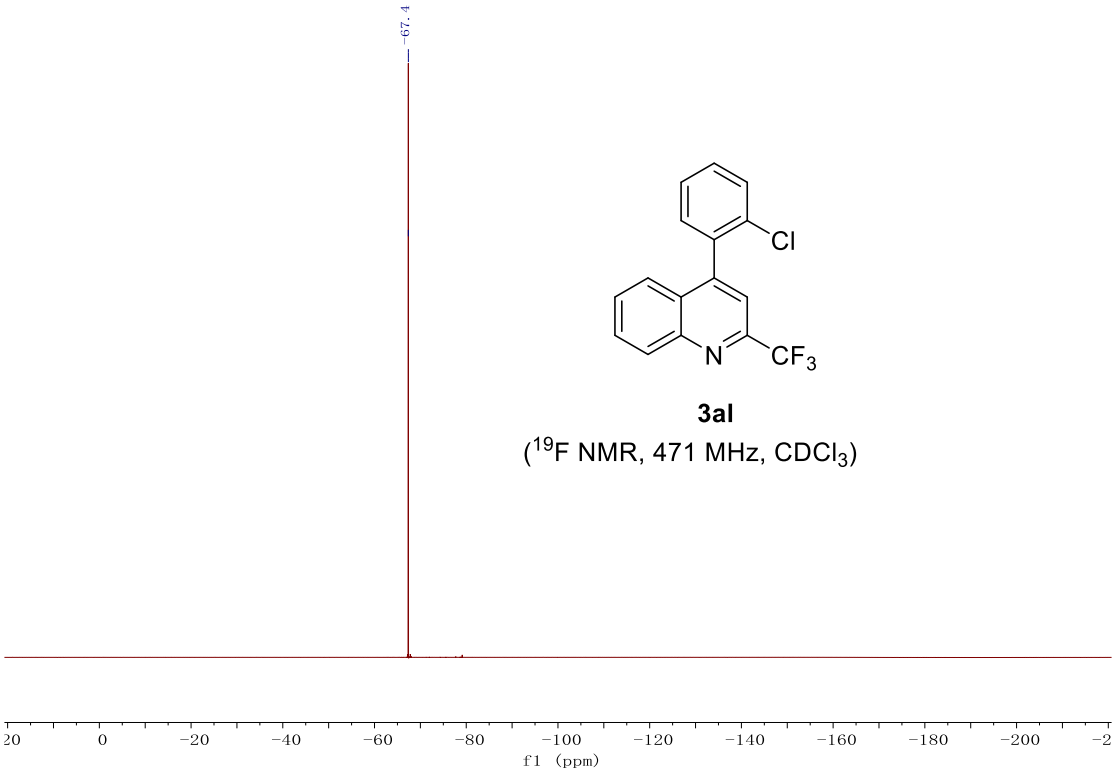
3al

(^{1}H NMR, 500 MHz, $CDCl_3$)



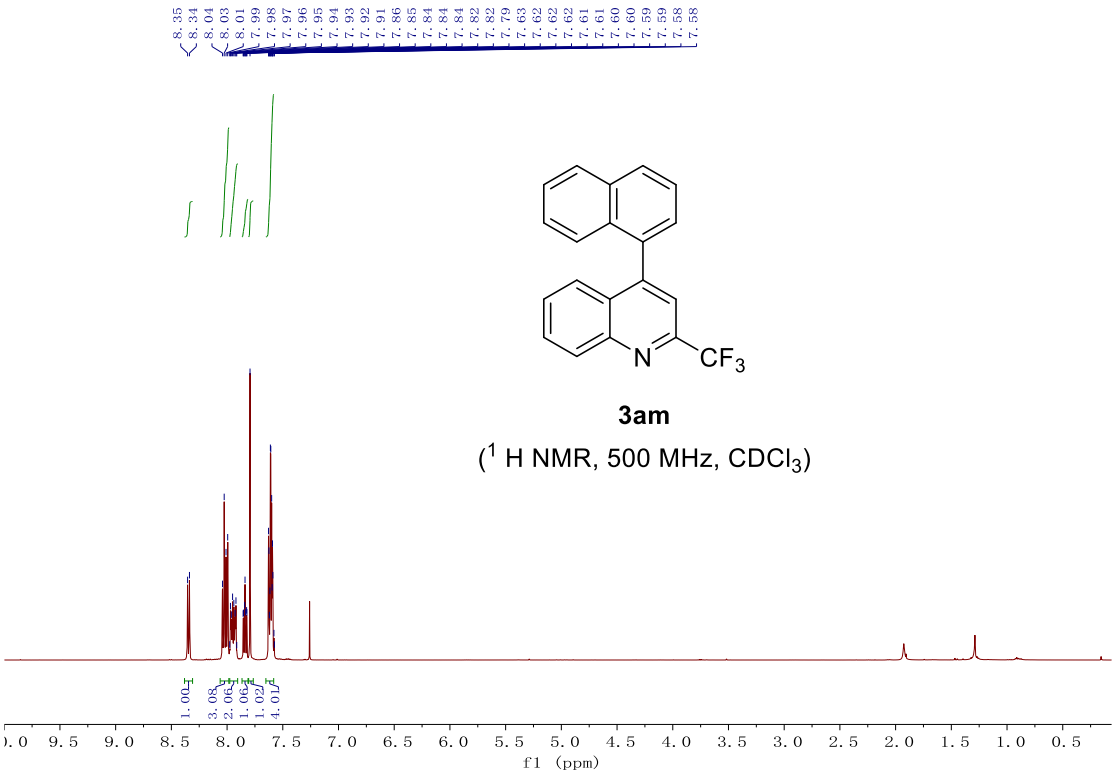
3al

($^{13}C\{^1H\}$ NMR, 126 MHz, $CDCl_3$)



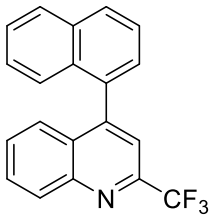
3al

(^{19}F NMR, 471 MHz, $CDCl_3$)



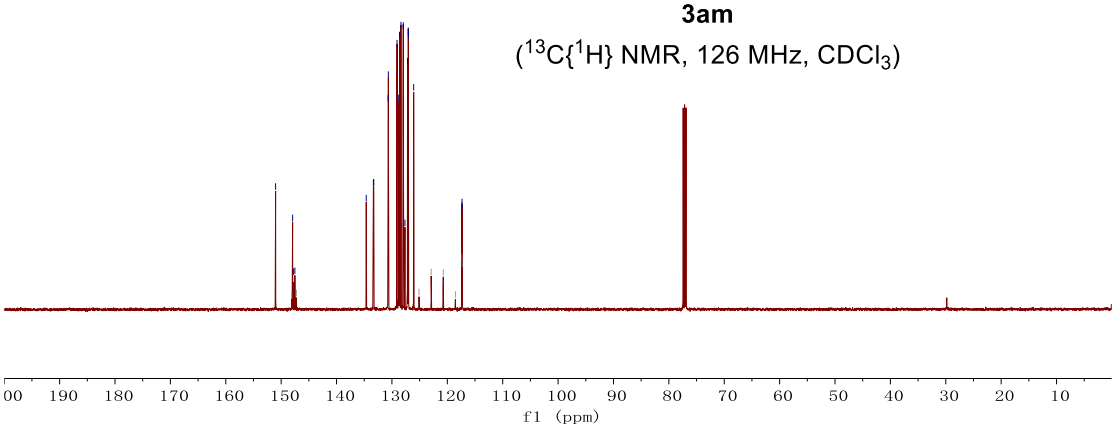
3am

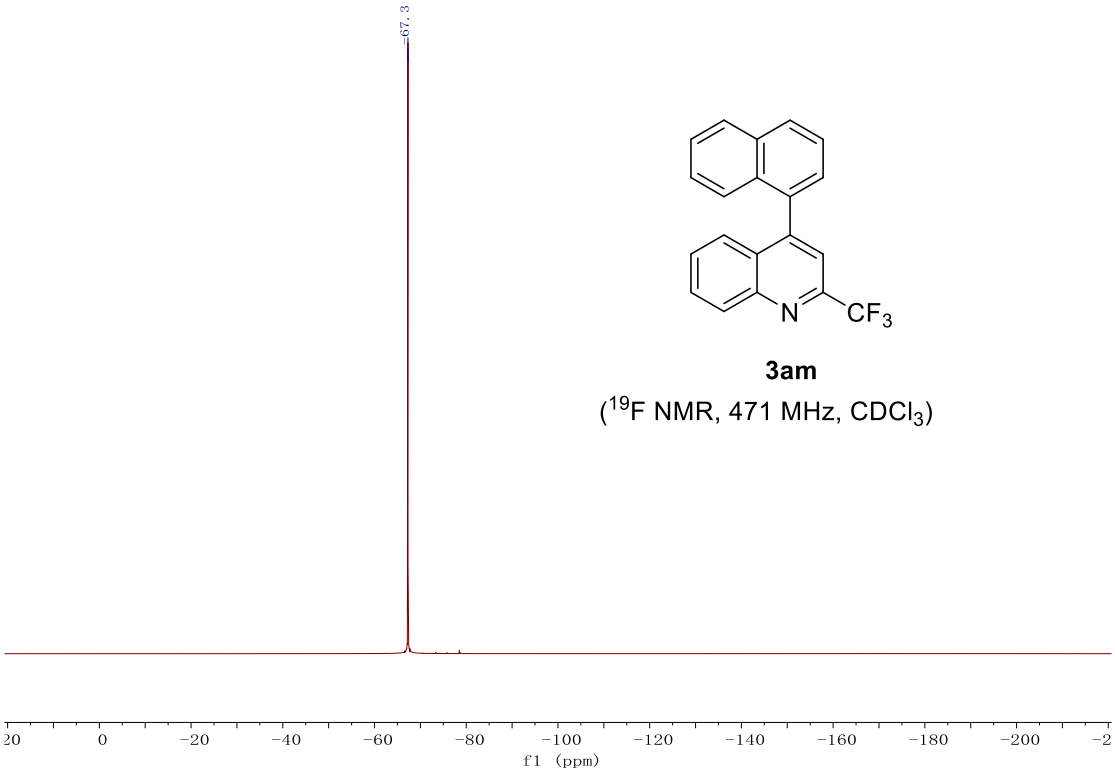
(^{1} H NMR, 500 MHz, $CDCl_3$)



3am

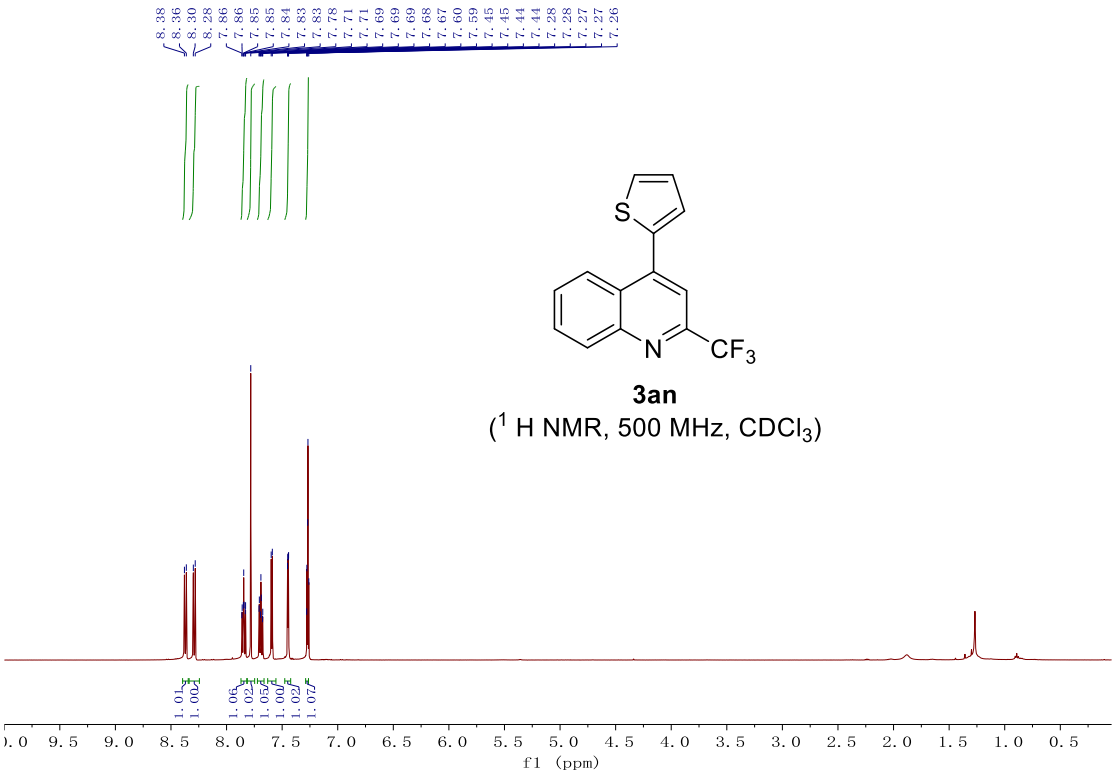
($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)





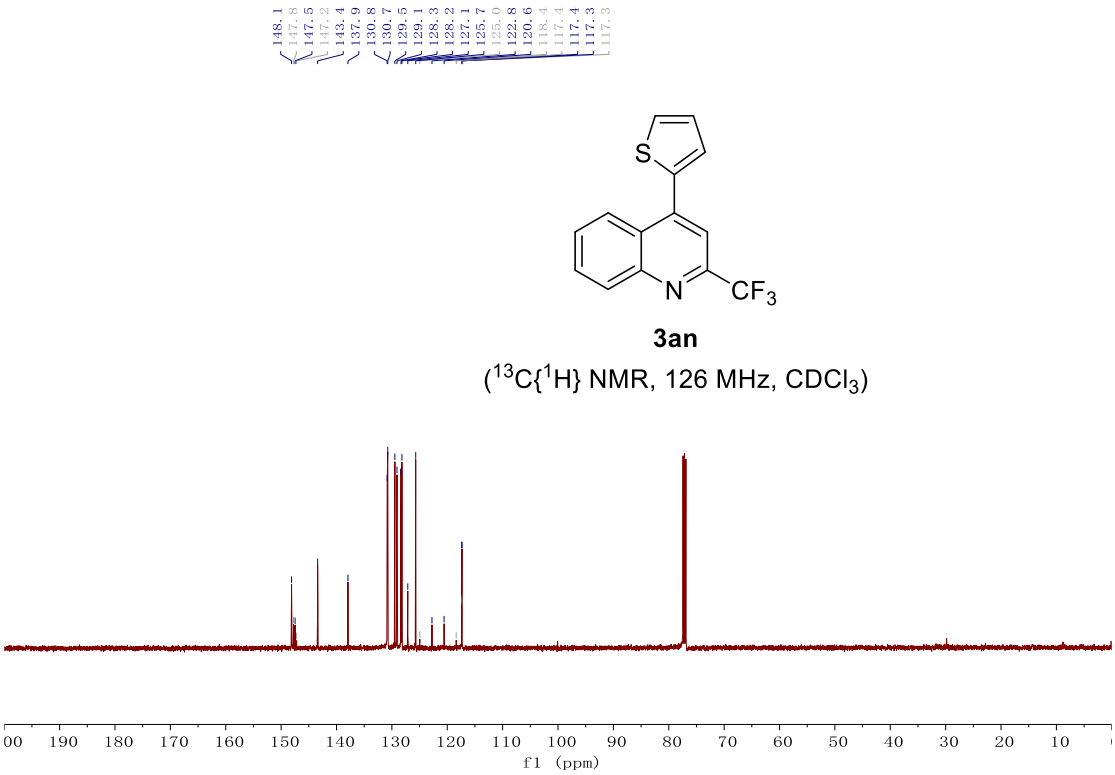
3am

(^{19}F NMR, 471 MHz, $CDCl_3$)



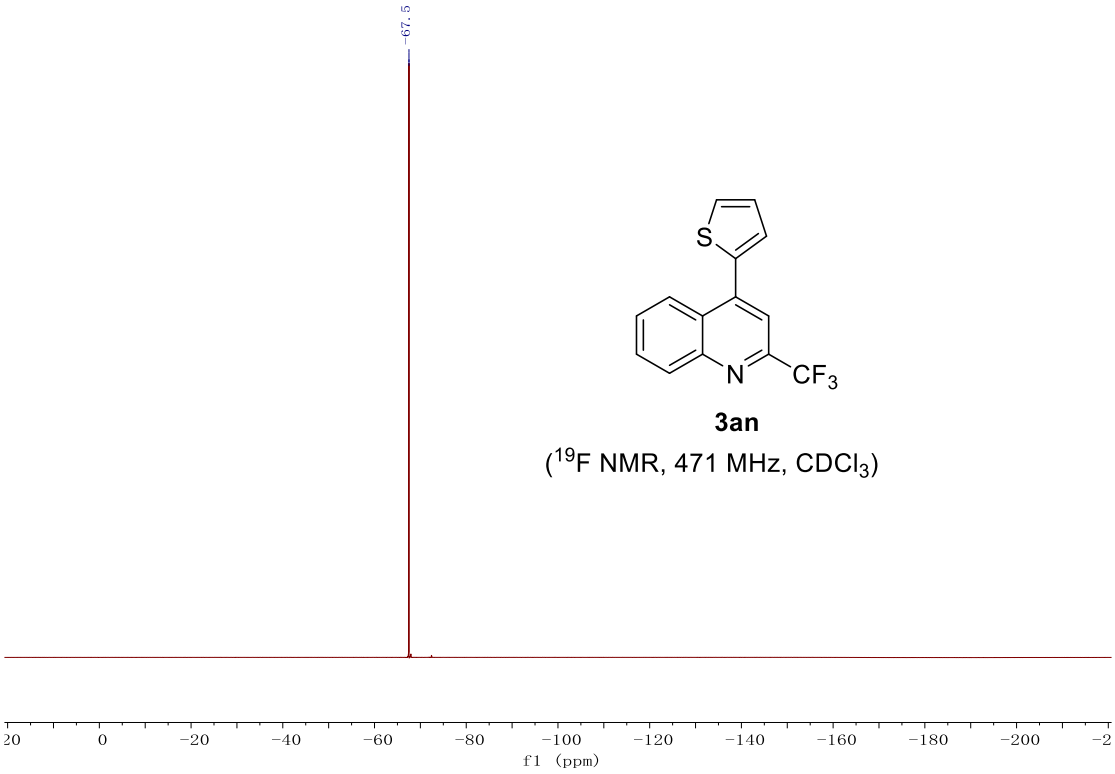
3an

(^{1}H NMR, 500 MHz, $CDCl_3$)



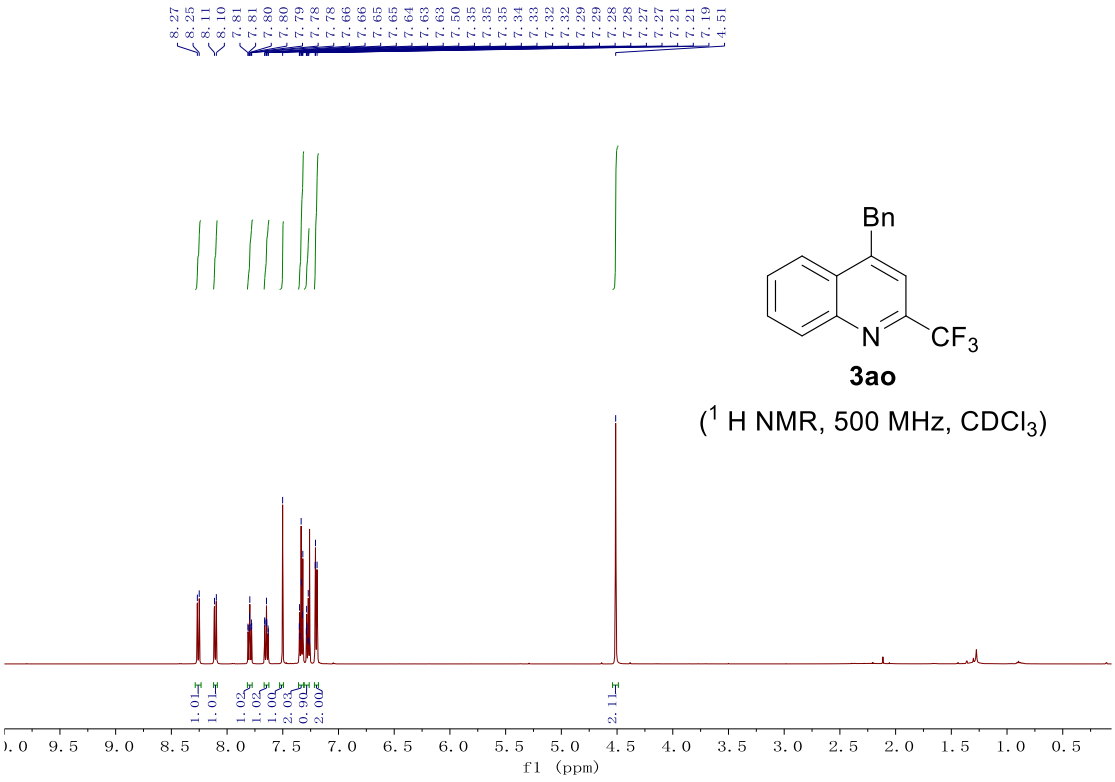
3an

($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)



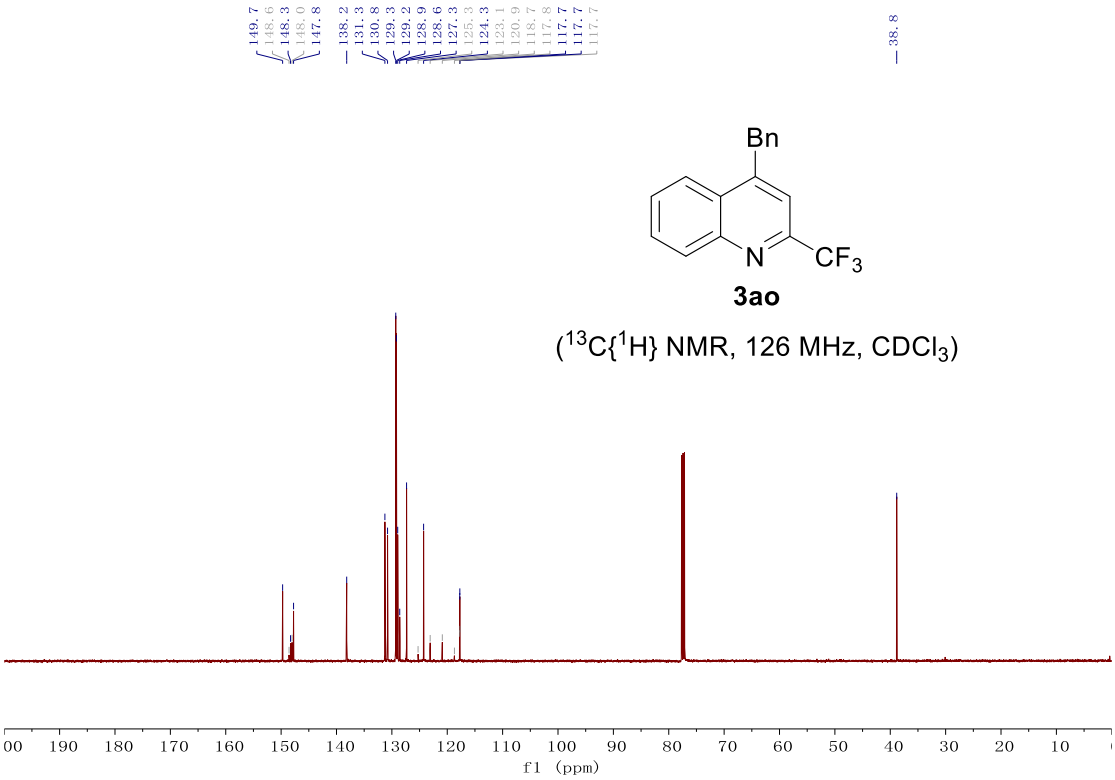
3an

(^{19}F NMR, 471 MHz, $CDCl_3$)



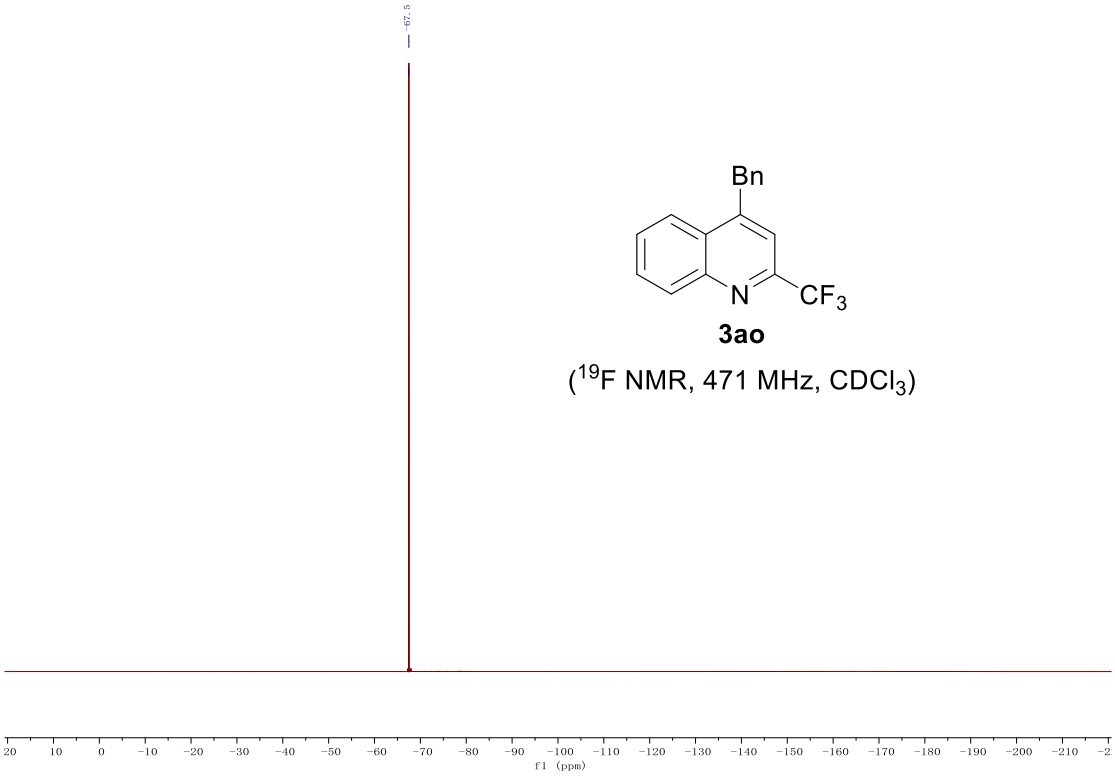
3ao

(^{1} H NMR, 500 MHz, $CDCl_3$)



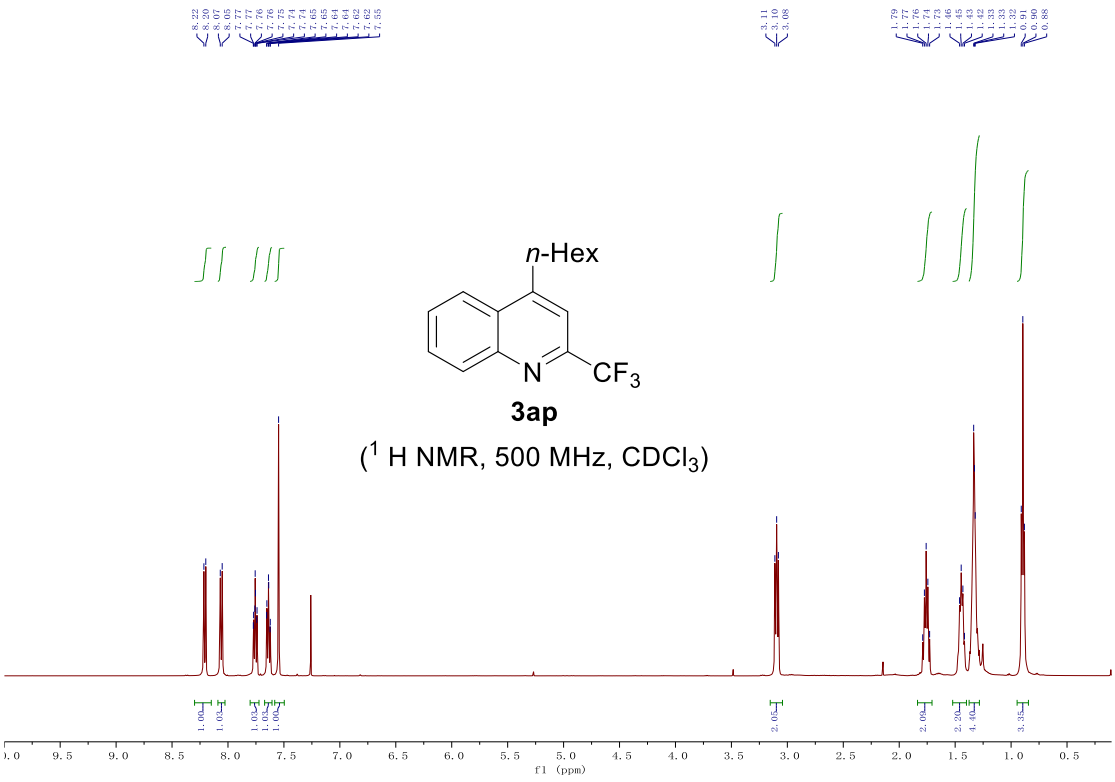
3ao

($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)



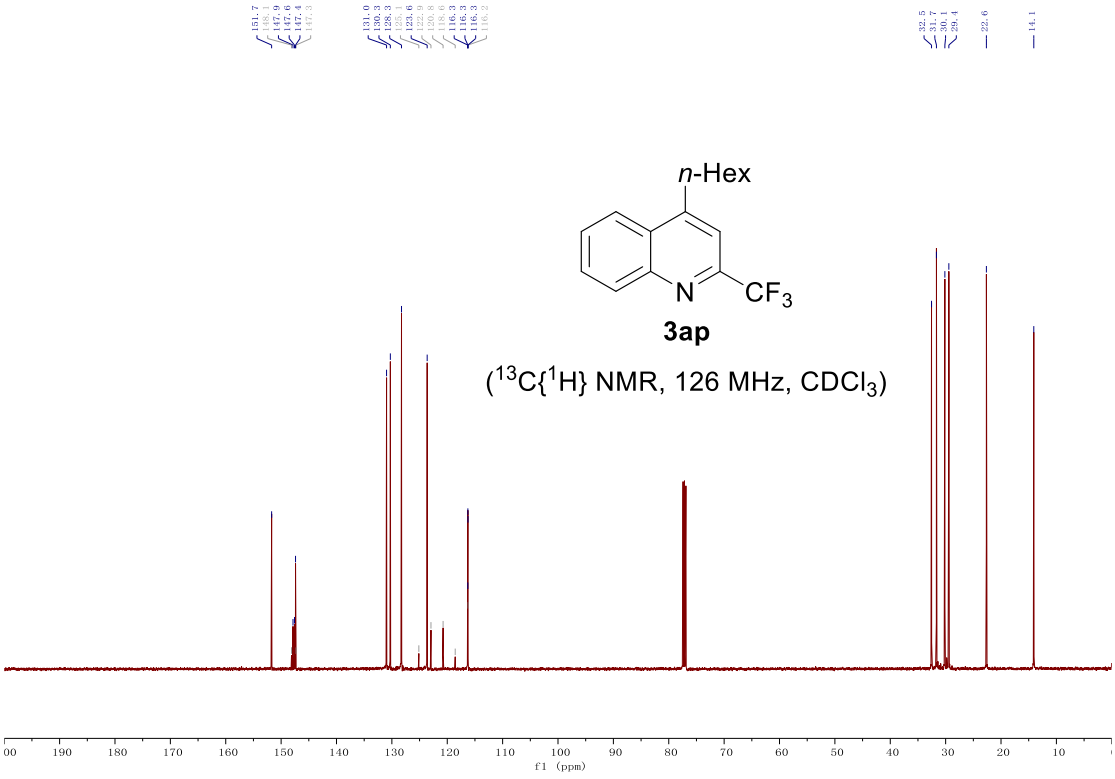
3ao

(^{19}F NMR, 471 MHz, $CDCl_3$)



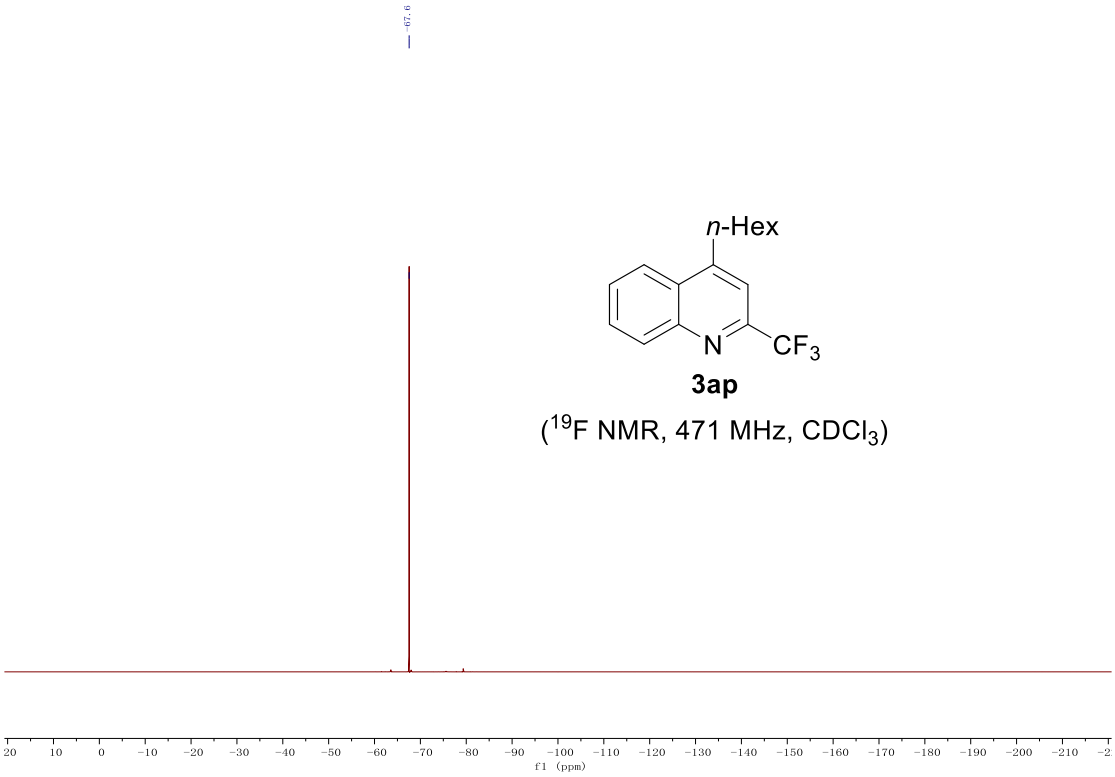
3ap

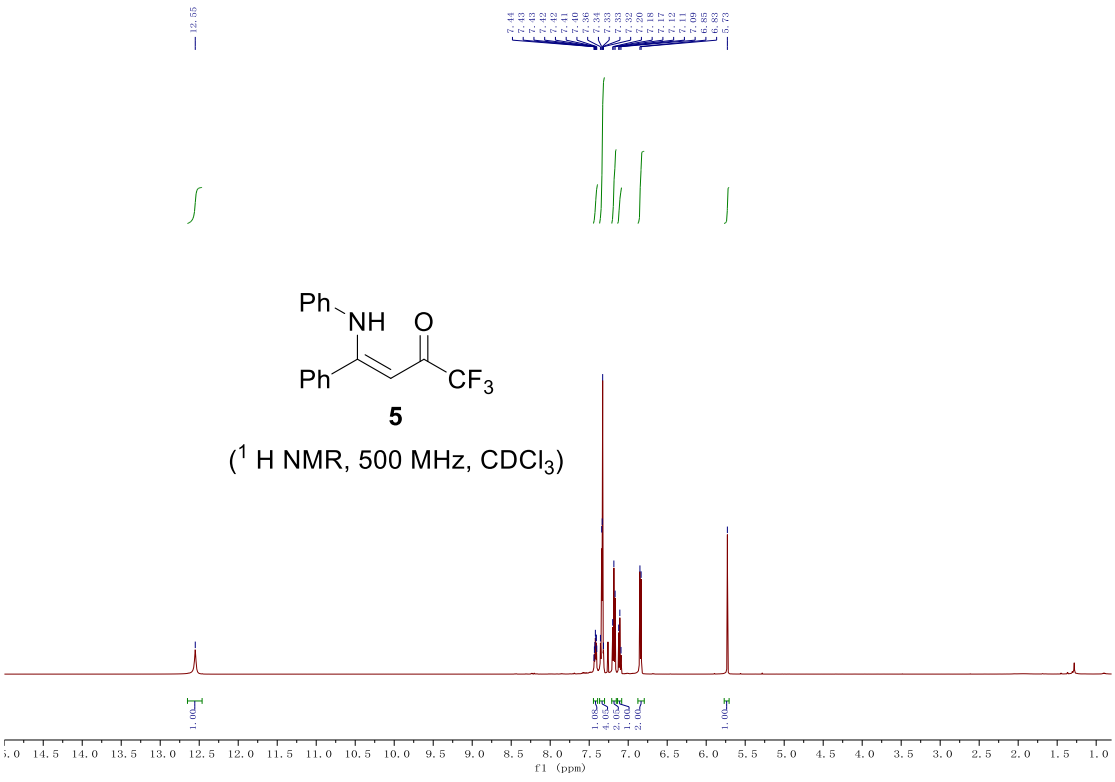
(^{1}H NMR, 500 MHz, $CDCl_3$)

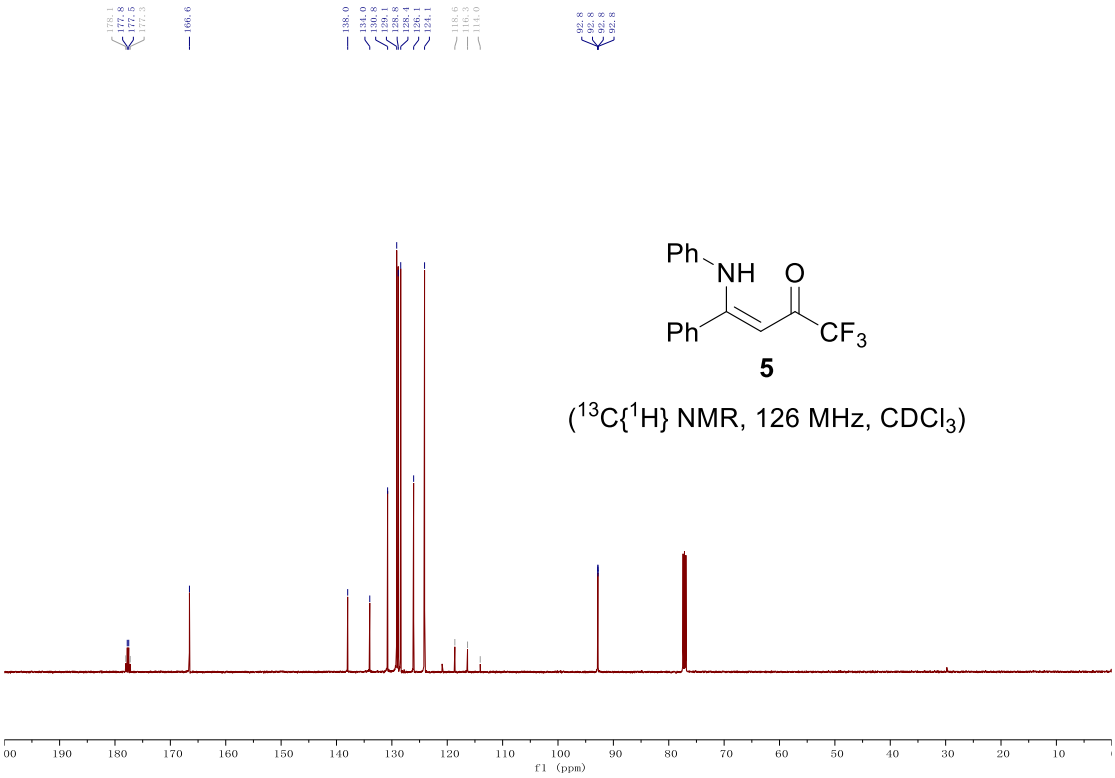


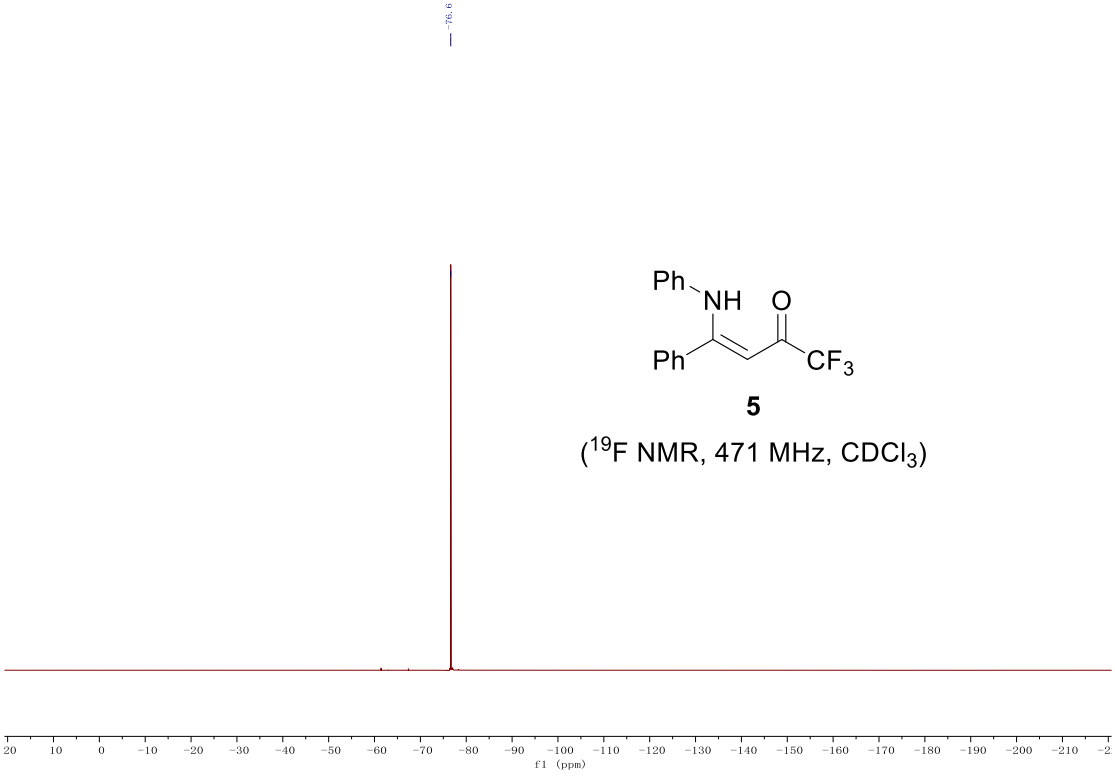
3ap

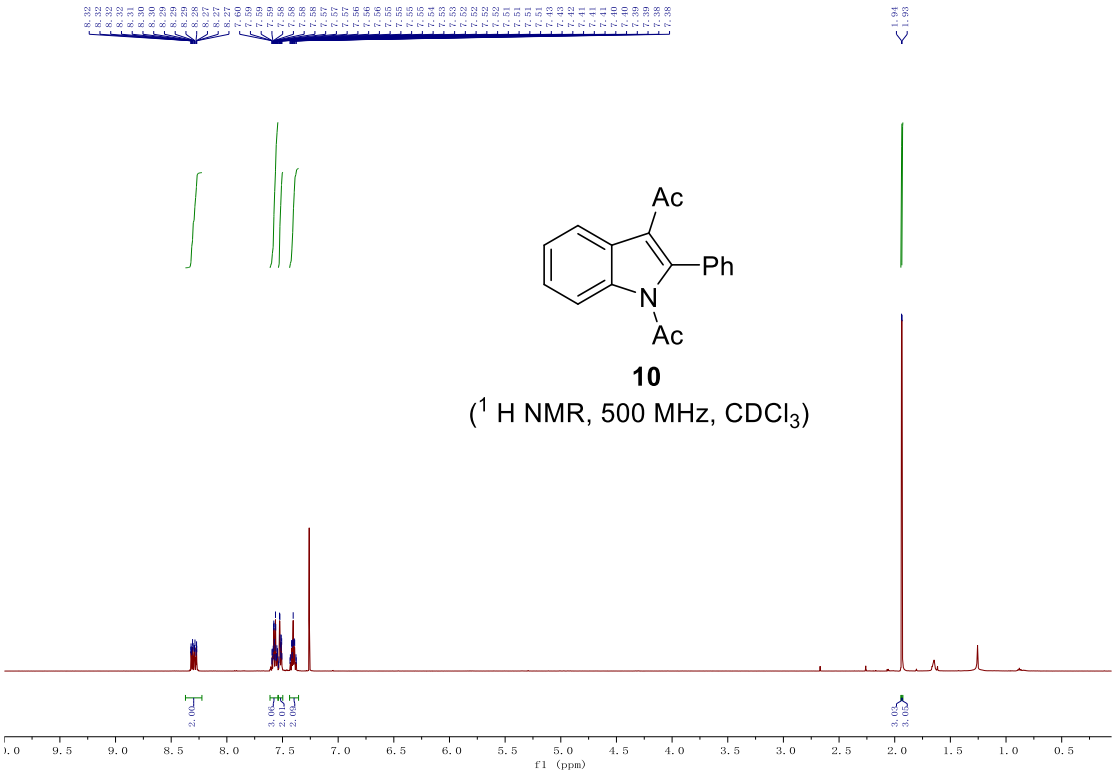
($^{13}C\{^1H\}$ NMR, 126 MHz, $CDCl_3$)


-67.6
n-Hex
N
CF3
3ap
(19F NMR, 471 MHz, CDCl3)
f1 (ppm)


12.55
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.36
7.34
7.33
7.33
7.32
7.20
7.18
7.17
7.12
7.11
7.09
6.85
6.83
5.73
Ph
NH
O
Ph
CF3
5
(1 H NMR, 500 MHz, CDCl3)
1.00
1.08
4.05
2.05
1.00
2.00
1.00
f1 (ppm)

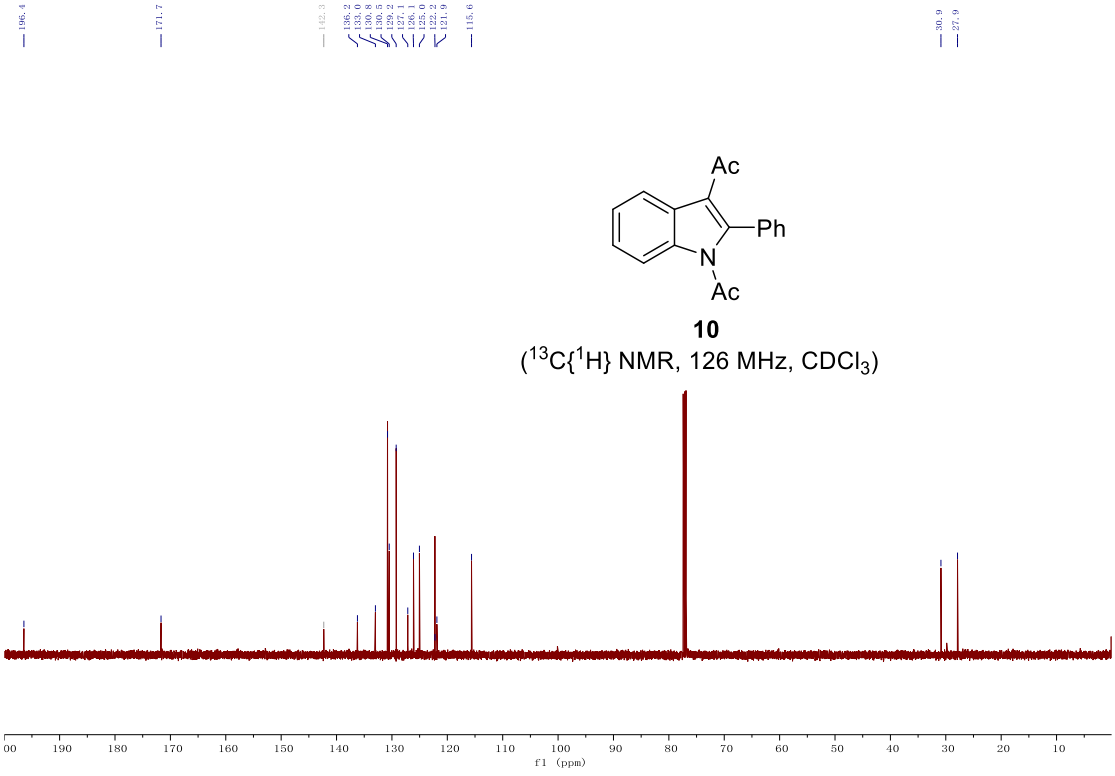

178.1
177.8
177.5
177.3
166.6
138.0
134.0
130.8
129.1
128.8
128.4
126.1
124.1
118.6
116.3
114.0
92.8
92.8
92.8
92.8
Ph
NH
O
Ph
CF3
5
(13C{1H} NMR, 126 MHz, CDCl3)
f1 (ppm)


-76.6
Ph
NH
O
Ph
CF3
5
(19F NMR, 471 MHz, CDCl3)
f1 (ppm)



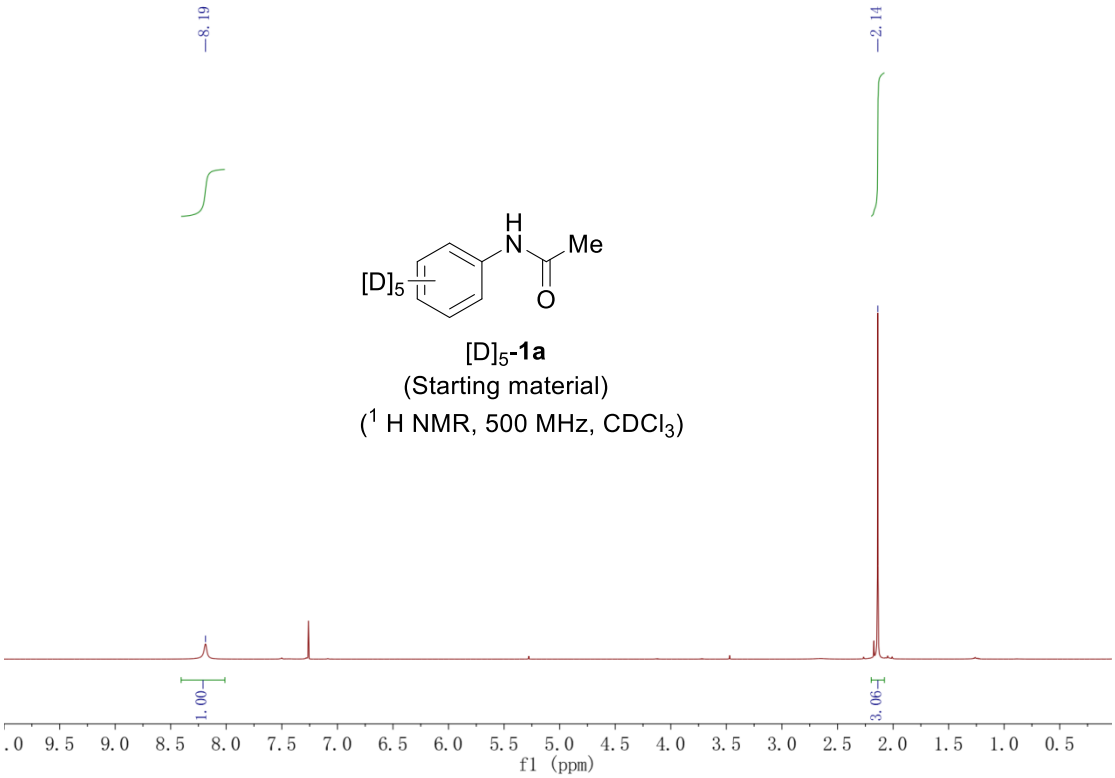
10

(^{1}H NMR, 500 MHz, $CDCl_3$)

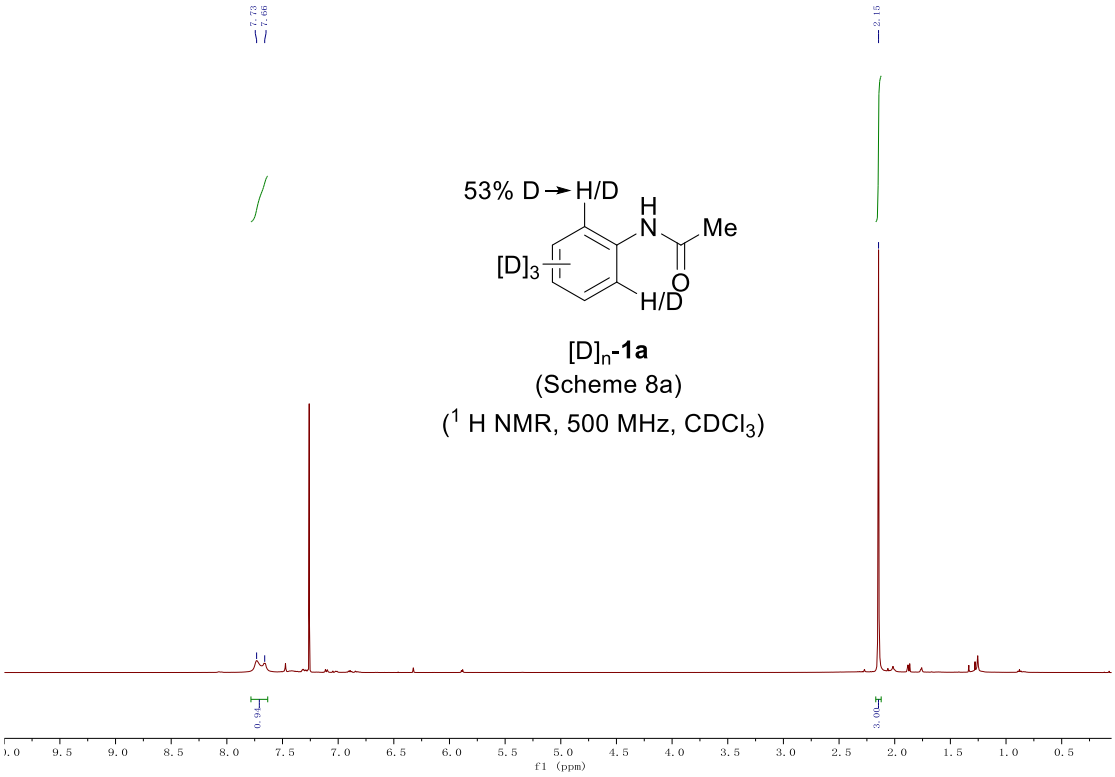


10

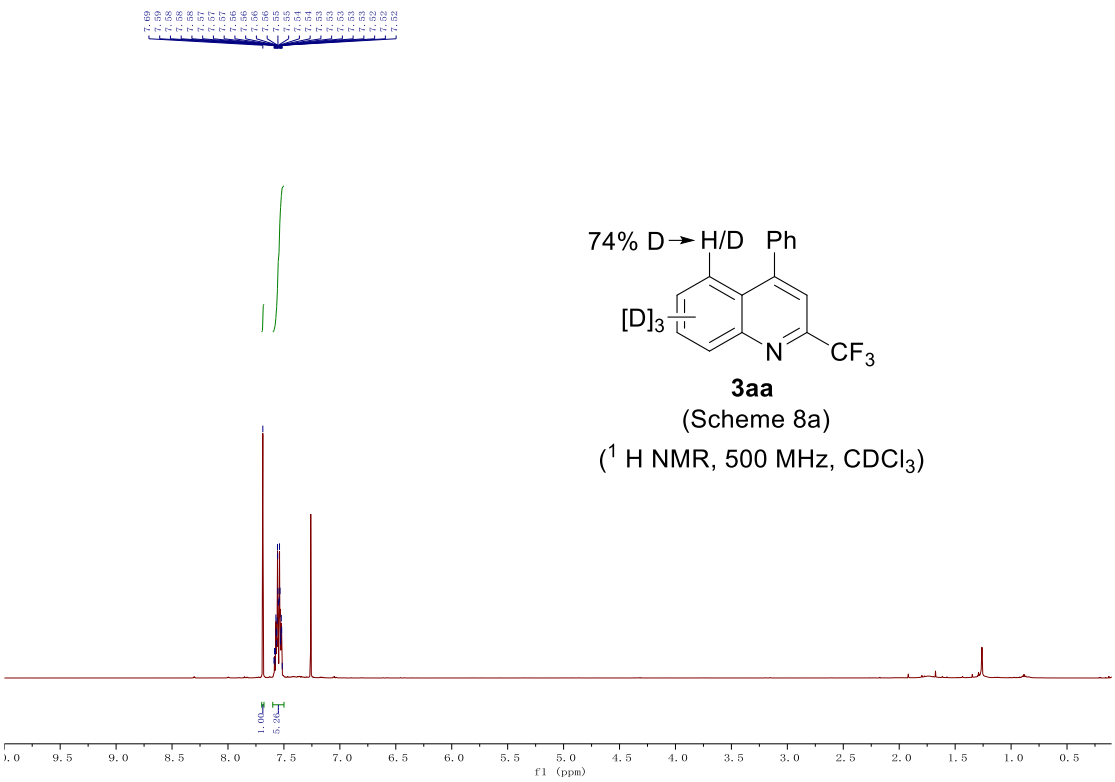
($^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$)

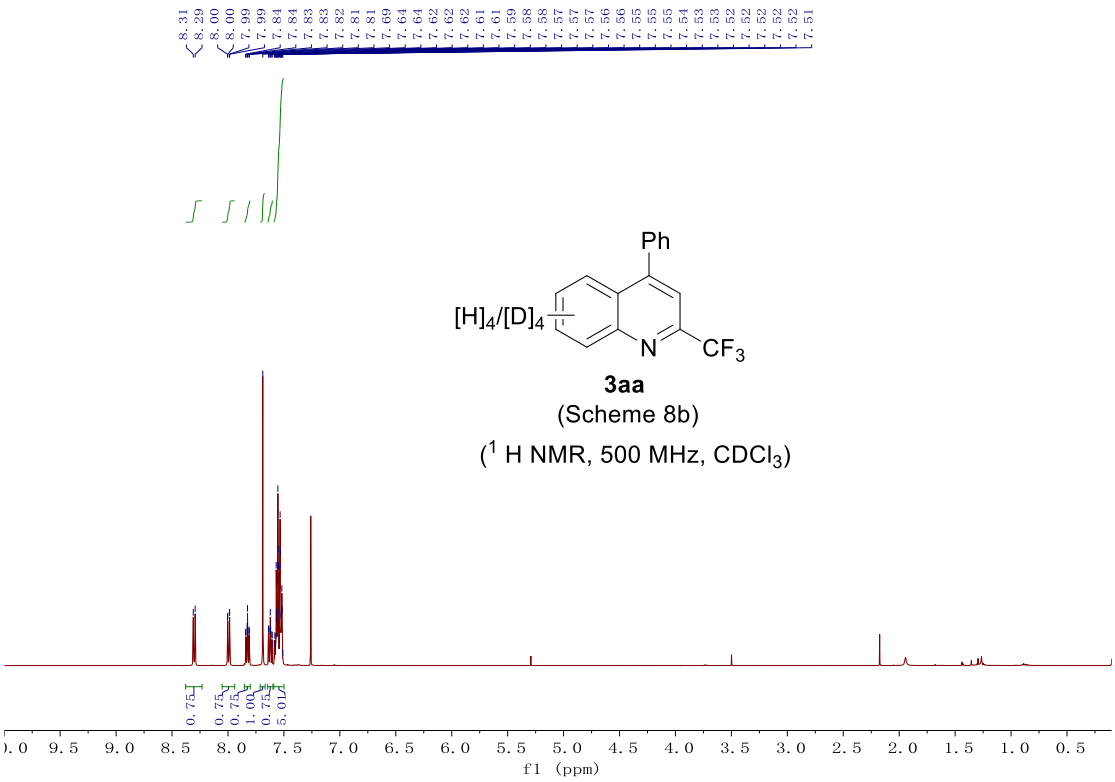


[D]$_5$-**1a**
(Starting material)
(^{1}H NMR, 500 MHz, $CDCl_3$)



[D]$_n$-**1a**
(Scheme 8a)
(^{1}H NMR, 500 MHz, $CDCl_3$)


74% D → H/D
Ph
[D]3
N
CF3
3aa
(Scheme 8a)
(1 H NMR, 500 MHz, CDCl3)
f1 (ppm)


Ph
[H]4/[D]4
N
CF3
3aa
(Scheme 8b)
(1 H NMR, 500 MHz, CDCl3)
f1 (ppm)

9. X-ray crystallographic analysis

Single crystals suitable for X-ray diffraction experiment were obtained by slow evaporation of *n*-hexane/acetone solution containing the corresponding compounds **3aa** and **10**.

Table S2. Crystal data and structure refinement for Exp_10398 (**3aa**)

Identification code	exp_10398
Empirical formula	$C_{16}H_{10}F_3N$
Formula weight	273.25
Temperature/K	293.00(10)
Crystal system	monoclinic
Space group	P 1 21/c 1
a/Å	8.8679(15)
b/Å	14.9200(17)
c/Å	10.3319(13)
α/°	90
β/°	103.788(16)
γ/°	90.00
Volume/Å^3	1327.6(3)
Z	4
ρ_{calc}g/cm^3	1.367
μ/mm^{-1}	0.110
F(000)	560
Crystal size/mm^3	0.36 × 0.35 × 0.08
Radiation	MoKα (λ = 0.71073)
Index ranges	-11 ≤ h ≤ -11, -19 ≤ k ≤ 19, -9 ≤ l ≤ 13
Reflections collected	5807
Independent reflections	3050 [R(int) = 0.0646]
Data/restraints/parameters	3050/39/208
Goodness-of-fit on F^2	0.965
Final R indexes [I>=2σ (I)]	R_1 = 0.0636, wR_2 = 0.1341
Final R indexes [all data]	R_1 = 0.1358, wR_2 = 0.1822
Largest diff. peak/hole / e Å^{-3}	0.236/-0.309

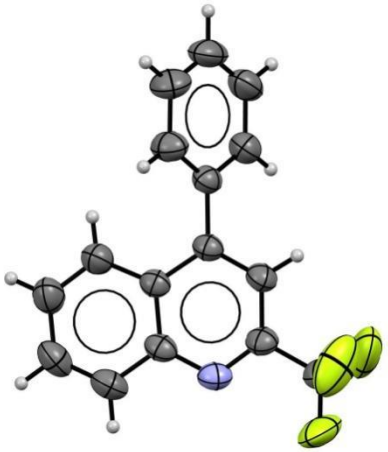


Figure S1. ORTEP plots for molecular structure of **3aa** with the probability at 50% Level

Table S3. Crystal data and structure refinement for Exp_10046 (**10**)

Identification code	exp_10046
Empirical formula	$C_{18}H_{15}NO_2$
Formula weight	277.31
Temperature/K	296.01(10)
Crystal system	monoclinic
Space group	P1 21/c 1
a/Å	8.3362(8)
b/Å	12.0976(8)
c/Å	14.4307(11)
α/°	90
β/°	92.893(8)
γ/°	90.00
Volume/Å^3	1453.5(2)
Z	4
ρ_{calc}g/cm^3	1.267
μ/mm^{-1}	0.083
F(000)	584
Crystal size/mm^3	0.30 × 0.26 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.65 to 29.08
Index ranges	-11 ≤ h ≤ 7, -16 ≤ k ≤ 10, -19 ≤ l ≤ 19
Reflections collected	6737
Independent reflections	3369 [R(int) = 0.0322]
Data/restraints/parameters	3369/0/193
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0679, wR_2 = 0.1256
Final R indexes [all data]	R_1 = 0.1297, wR_2 = 0.1542
Largest diff. peak/hole / e Å^{-3}	0.147/-0.169

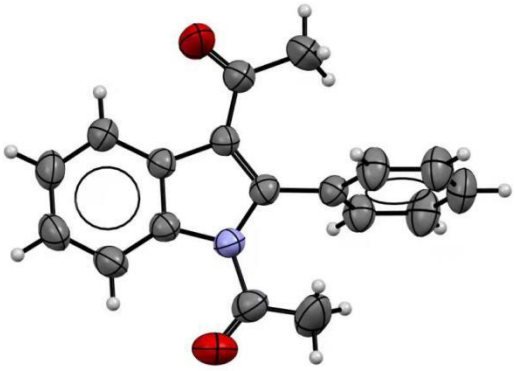


Figure S2. ORTEP plots for molecular structure of **5** with the probability at 50% Level

10. Photophysical data of compounds 3oa and 3pa

Table S4. Photophysical data of compounds **3oa** and **3pa**

Compounds	λ_{ex} (nm)[a] in DCM	λ_{em} (nm)[a] in DCM	(Φ_f)[b] in DCM
3oa	339	429	86
3pa	339	418	12

[a]Excitation maximum in DCM. [b]Exmission maximum in DCM. [c]The quantum yield determined in DCM relative to 55% of quinine sulfate.[9]

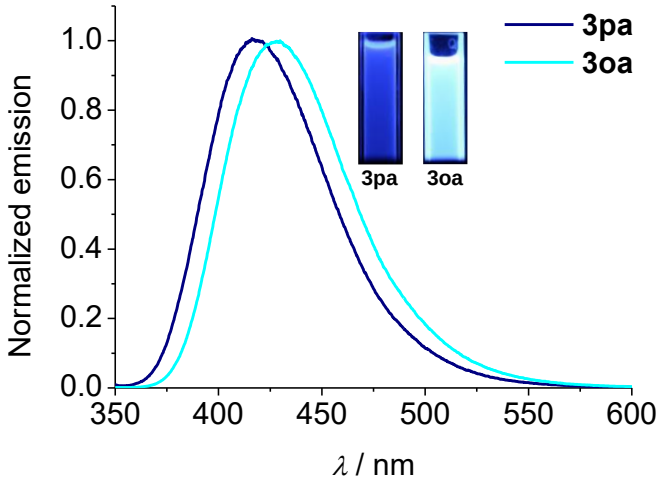


Figure S3. Normalized emission spectra of representative compounds **3oa** and **3pa** with a concentration of 10^{-5} M in CH_2Cl_2 on excitation at 339 nm. Inset: images of compounds **3oa** and **3pa** under a UV lamp (365 nm).

11. Reference

1 (a) P. Patel and G. Borah, Synthesis of oxindole from acetanilide via Ir(iii)-catalyzed C–H carbenoid functionalization, *Chem. Commun.*, 2017, **53**, 443-446; (b) D. C. Simkó, P. Elekes, V. Pázmándi and Z. Novák, Sulfonium salts as alkylating agents for palladium-catalyzed direct ortho alkylation of anilides and aromatic ureas, *Org. Lett.*, 2018, **20**, 676-679.

2 J. A. Leitch, C. L. McMullin, A. J. Paterson, M. F. Mahon, Y. Bhonoah and C. G. Frost, Ruthenium-catalyzed para-selective C−H alkylation of aniline derivatives, *Angew. Chem. Int. Ed.*, 2017, **56**, 15131-15135.

3 S. W. Youn and Y. H. Kim, Pd(II)/Ag(I)-promoted one-pot synthesis of cyclic ureas from (hetero)aromatic amines and isocyanates, *Org. Lett.*, 2016, **18**, 6140-6143.

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