

Electronic Supplementary Information
for
**Photoredox-catalyzed difluoroacetylation or fluoroacetylation
cascade cyclization of *N*-propargyl aromatic amines: access to 3-
difluoroacetylated or 3-fluoroacetylated quinolines**

Qinfei Deng, Yan Xu, Ping Liu,* Liping Tan and Peipei Sun*

*College of Chemistry and Materials Science, Jiangsu Provincial Key Laboratory of Material
Cycle Processes and Pollution Control, Jiangsu Collaborative Innovation Center of Biomedical
Functional Materials, Nanjing Normal University, Nanjing 210023, China*

E-mail: sunpeipei@njnu.edu.cn; pingliu@njnu.edu.cn

Table of Contents

1. General Information.....	S2
2. General procedure for the synthesis of 3-difluoroacetylated or 3-fluoroacetylated quinolines.....	S2-S6
3. The reduction of 3a	S6
4. The hydrolysis of 3a	S6-S7
5. References.....	S7
6. Copies of ¹ H and ¹³ C NMR spectra of the products.....	S8-S54

1. General Information

All reactions were run in a sealed tube with a Teflon lined cap under ambient Ar atmosphere. All commercially available reagent grade chemicals were used as received without further purification. The substrates **1** were prepared according to the literature procedures.¹ The NMR spectra were recorded on a Bruker Avance 400 spectrometers at 400 MHz (¹H), 100 MHz (¹³C) and 376 MHz (¹⁹F) in CDCl₃ or DMSO-*d*₆ using TMS as an internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, td = triplet of doublet, q = quartet, m = multiplet, ddd = doublet of doublet of doublet. High-resolution mass spectra (HRMS) were obtained with a Waters Q-TOF mass spectrometer. Column chromatography was performed on silica gel (300-400 mesh). Melting points are uncorrected.

2. General procedure for the synthesis of 3-difluoroacetylated or 3-fluoroacetylated quinolines

An oven-dried Schlenk tube (25 mL) was charged with *N*-(3-aryl-2-propynyl)aniline derivatives (**1**, 0.2 mmol), ethyl bromodifluoroacetate (101.5 mg, 64 μ L, 0.5 mmol) or ethyl bromofluoroacetate (92.5 mg, 59 μ L, 0.5 mmol), *fac*-Ir(ppy)₃ (2.6 mg, 2 mol%), K₂CO₃ (69.1 mg, 0.5 mmol) and CH₃CN (2 mL). The reaction mixture was stirred under Ar atmosphere upon irradiation of 5 W blue LEDs at room temperature for 12 h. Upon completion, the resulting solution was diluted with water (10 mL), extracted with CH₂Cl₂ (15 mL $\times$ 3). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography using hexane/ethyl acetate (8:1) as eluent to give the desired products (**3a–3y**, **5a**, **5e**, **5g**, **5r**).

Ethyl 2,2-difluoro-2-(4-phenylquinolin-3-yl)acetate (3a). Brown solid (56.3 mg, 86% yield); mp 69–71 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.31 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.83–7.80 (m, 1H), 7.55–7.48 (m, 4H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.28–7.26 (m, 2H), 3.99 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.1 (t, *J* = 33.6 Hz), 148.9, 147.9 (t, *J* = 4.7 Hz), 146.5 (t, *J* = 9.1 Hz), 133.4, 131.0, 130.1, 129.6, 129.0, 128.0, 127.5, 127.2, 126.9, 123.9 (t, *J* = 23.4 Hz), 113.2 (t, *J* = 251.6 Hz), 63.2, 13.6; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -95.8; HRMS (ESI) *m/z*: calcd for C₁₉H₁₆F₂NO₂ (M+H)⁺ 328.1144, found 328.1146.

Ethyl 2,2-difluoro-2-(6-methyl-4-phenylquinolin-3-yl)acetate (3b). Brown solid (55.9 mg, 82% yield); mp 78–80 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.23 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.63 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.56–7.49 (m, 3H), 7.29–7.25 (m, 2H), 7.16 (s, 1H), 3.99 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.1 (t, *J* = 33.7 Hz), 147.2 (t, *J* = 4.6 Hz), 147.1, 145.5 (t, *J* = 9.2 Hz), 137.6, 133.6, 133.3, 130.1, 129.3, 128.9, 128.0, 127.2, 125.5, 123.9 (t, *J* = 23.2 Hz), 113.2 (t, *J* = 251.5 Hz), 63.1, 21.8, 13.6; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -95.8; HRMS (ESI) *m/z*: calcd for C₂₀H₁₈F₂NO₂ (M+H)⁺ 342.1300, found 342.1300.

Ethyl 2,2-difluoro-2-(8-methyl-4-phenylquinolin-3-yl)acetate (3c). Yellow oil (54.6 mg, 80% yield); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.34 (s, 1H), 7.66 (d, *J* = 6.9 Hz, 1H), 7.54–7.48 (m, 3H), 7.39 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.28–7.25 (m, 3H), 4.00 (q, *J* = 7.2 Hz, 2H), 2.91 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.1 (t, *J* = 33.7 Hz), 148.0 (t, *J* = 4.5 Hz), 145.2 (t, *J* = 9.1 Hz), 137.4, 133.8, 131.1, 130.1, 128.8, 128.2, 127.9, 127.2, 127.1, 124.9, 123.7 (t, *J* = 23.4 Hz), 113.3 (t, *J* = 251.4 Hz), 63.1, 18.4, 13.7; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -96.0; HRMS (ESI) *m/z*: calcd for C₂₀H₁₈F₂NO₂ (M+H)⁺ 342.1300, found 342.1301.

Ethyl 2,2-difluoro-2-(7-methyl-4-phenylquinolin-3-yl)acetate (3d) and ethyl 2,2-difluoro-2-(5-methyl-4-phenylquinolin-3-yl)acetate (3d'). Yellow oil (55.3 mg, 81% yield); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.26–9.24 (m, 1H), 8.10–7.97 (m, 1H), 7.64–7.60 (m, 1H), 7.51–7.46 (m, 1H), 7.43–7.39 (m, 2H), 7.29–7.27 (m, 1H), 7.25–7.22 (m, 2H), 3.99–3.90 (m, 2H), 2.55–1.81 (m, 3H), 1.16–1.12 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.1 (t, *J* = 33.7 Hz), 162.9 (t, *J* = 33.6 Hz), 150.5, 149.2, 148.0 (t, *J* = 4.6 Hz), 147.6 (t, *J* = 4.6 Hz), 146.4 (t, *J* = 9.1 Hz), 145.4 (t, *J* = 10.6 Hz), 141.6, 136.9, 136.2, 133.6, 131.4, 130.7, 130.5, 130.1, 129.7, 129.1, 129.0, 128.9, 128.5, 128.0, 127.6, 126.5, 125.8, 125.3 (t, *J* = 22.9 Hz), 125.2, 123.1 (t, *J* = 23.5 Hz), 113.3 (t, *J* = 251.5 Hz), 113.2 (t, *J* = 250.9 Hz), 63.1, 63.0, 23.9, 21.6, 13.6, 13.5; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -95.0, -95.7; HRMS (ESI) *m/z*: calcd for C₂₀H₁₈F₂NO₂ (M+H)⁺ 342.1300, found 342.1300.

Ethyl 2,2-difluoro-2-(6-methoxy-4-phenylquinolin-3-yl)acetate (3e). Brown solid (59.3 mg, 83% yield); mp 69–71 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.17 (s, 1H), 8.18 (d, *J* = 8.9 Hz, 1H), 7.51 (dd, *J* = 20.1, 5.7 Hz, 4H), 7.28 (d, *J* = 4.6 Hz, 2H), 6.64 (d, *J* = 1.6 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.0 (t, *J* = 33.6 Hz), 158.5, 147.1 (t, *J* = 4.4 Hz), 144.4, 143.5 (t, *J* = 8.7 Hz), 133.5, 130.5, 130.0, 129.1, 128.6, 128.2, 124.0, 113.1 (t, *J* = 251.7 Hz), 104.5, 63.2, 55.4, 13.7; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -96.0; HRMS (ESI) *m/z*: calcd for C₂₀H₁₈F₂NO₃ (M+H)⁺ 358.1249, found 358.1249.

Ethyl 2,2-difluoro-2-(4-phenyl-6-(trifluoromethoxy)quinolin-3-yl)acetate (3f). Yellow solid (68.2 mg, 83% yield); mp 59–61 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.33 (s, 1H), 8.28 (d, *J* = 9.2 Hz, 1H), 7.68 (dd, *J* = 9.2, 1.7 Hz, 1H), 7.58–7.53 (m, 3H), 7.28–7.23 (m, 3H), 4.00 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 162.8 (t, *J* = 33.3 Hz), 147.9 (t, *J* = 4.7 Hz), 147.6 (q, *J* = 1.8 Hz), 147.1, 147.0 (t, *J* = 9.2 Hz), 132.5, 131.9, 129.9, 129.4, 128.4, 128.3, 127.8, 124.9, 121.3 (q, *J* = 258.4 Hz), 117.3, 112.9 (t, *J* = 252.1 Hz), 63.3, 13.6; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -57.9, -96.1; HRMS (ESI) *m/z*: calcd for C₂₀H₁₅F₅NO₃ (M+H)⁺ 412.0967, found 412.0963.

Ethyl 2,2-difluoro-2-(6-fluoro-4-phenylquinolin-3-yl)acetate (3g). Yellow solid (55.2 mg, 80% yield); mp 51–53 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.25 (s, 1H), 8.20 (dd, *J* = 9.2, 5.4 Hz, 1H), 7.56–7.48 (m, 4H), 7.25–7.23 (m, 2H), 7.01 (dd, *J* = 9.8, 2.8 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 162.9 (t, *J* = 33.5 Hz), 162.2, 159.7, 147.3 (dd, *J* = 10.3, 5.0 Hz), 146.1, 145.8 (td, *J* = 9.1, 2.8 Hz), 133.0, 132.2 (d, *J* = 9.2 Hz), 129.9, 129.2, 128.2, 124.6 (t, *J* = 23.4 Hz), 121.3 (d, *J* = 26.0 Hz), 113.0 (t, *J* = 252.0 Hz), 110.2 (d, *J* = 23.5 Hz), 63.2, 13.6; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -96.1, -110.5; HRMS (ESI) *m/z*: calcd for C₁₉H₁₅F₃NO₂ (M+H)⁺ 346.1049, found 346.1050.

Ethyl 2-(6-chloro-4-phenylquinolin-3-yl)-2,2-difluoroacetate (3h). Pale yellow solid (44.1 mg, 61% yield); mp 77–79 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.27 (s, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.69 (dd, *J* = 9.0, 1.7 Hz, 1H), 7.54–7.49 (m, 3H), 7.37 (d, *J* = 2.3 Hz, 1H), 7.25–7.23 (m, 2H), 3.97 (q, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 162.8 (t, *J* = 33.4 Hz), 147.3, 147.1 (t, *J* = 4.7 Hz), 146.7 (t, *J* = 9.1 Hz), 133.5, 132.7, 131.9, 131.2, 130.0, 129.3, 128.3, 128.0, 125.5, 124.8 (t, *J* = 23.5 Hz), 113.0 (t, *J* = 252.0 Hz), 63.3, 13.6; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -96.1; HRMS (ESI) *m/z*: calcd for C₁₉H₁₅ClF₂NO₂ (M+H)⁺ 362.0754, found 362.0754.

Ethyl 2,2-difluoro-2-(4-phenyl-6-(trifluoromethyl)quinolin-3-yl)acetate (3i). Pale yellow solid (27.7 mg, 35% yield); mp 98–100 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.41 (s, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 7.97 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.74 (s, 1H), 7.61–7.53 (m, 3H), 7.28 (d, *J* = 6.7 Hz, 2H), 3.99 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 162.8 (t, *J* = 33.3 Hz), 149.8, 148.9 (t, *J* = 4.7 Hz), 148.6 (t, *J* = 9.1 Hz), 132.2, 131.0, 130.0, 129.6, 129.3 (q, *J* = 32.7 Hz), 128.8, 126.6 (dd, *J* = 5.6, 2.6 Hz), 126.5, 125.3 (t, *J* = 23.6 Hz), 124.7 (q, *J* = 4.5 Hz), 123.6 (q, *J* = 272.6 Hz), 112.8 (t, *J* = 252.1 Hz), 63.4, 13.6; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -62.5, -96.1; HRMS (ESI) *m/z*: calcd for C₂₀H₁₅F₅NO₂ (M+H)⁺ 396.1018, found 396.1016.

Ethyl 2,2-difluoro-2-(4-(*p*-tolyl)quinolin-3-yl)acetate (3j). Yellow oil (51.2 mg, 75% yield); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.31 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.84–7.80 (m, 1H), 7.53–7.47 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 3.98 (q, *J* = 7.2 Hz, 2H), 2.49 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.0 (t, *J* = 33.6 Hz), 148.7 (t, *J* = 4.5 Hz), 148.4, 146.1 (t, *J* = 9.2 Hz), 139.0, 131.2, 130.1, 130.0, 129.2, 128.8, 127.6, 127.5, 127.0, 124.2 (t, *J* = 23.4 Hz), 113.1 (t, *J* = 251.4 Hz), 63.2, 21.5, 13.6; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -95.5; HRMS (ESI) *m/z*: calcd for C₂₀H₁₈F₂NO₂ (M+H)⁺ 342.1300, found 342.1300.

Ethyl 2,2-difluoro-2-(4-(*m*-tolyl)quinolin-3-yl)acetate (3k). Yellow solid (55.9 mg, 82% yield); mp 50–52 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.30 (s, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.78–7.73 (m, 1H), 7.46–7.45 (m, 2H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 5.7 Hz, 2H), 3.97 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.0 (t, *J* = 33.6 Hz), 148.9, 148.1 (t, *J* = 4.7 Hz), 146.5 (t, *J* = 9.1 Hz), 137.7, 133.3, 130.9, 130.6, 129.6 (d, *J* = 17.0 Hz), 127.9, 127.4, 127.2 (d, *J* = 3.6 Hz), 127.0, 123.9 (t, *J* = 23.3 Hz), 113.2 (t, *J* = 251.4 Hz), 63.1, 21.4, 13.6; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -95.34 (d, *J*_{F-F} = 277.5 Hz), -96.31 (d, *J*_{F-F} = 277.9 Hz); HRMS (ESI) *m/z*: calcd for C₂₀H₁₈F₂NO₂ (M+H)⁺ 342.1300, found 342.1300.

Ethyl 2,2-difluoro-2-(4-(*o*-tolyl)quinolin-3-yl)acetate (3l). Yellow oil (55.3 mg, 81% yield); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.30 (s, 1H), 8.20 (d, $J = 8.4$ Hz, 1H), 7.74 (ddd, $J = 8.4, 6.8, 1.4$ Hz, 1H), 7.45–7.37 (m, 2H), 7.32–7.25 (m, 3H), 7.06 (d, $J = 7.6$ Hz, 1H), 4.03–3.95 (m, 2H), 1.88 (s, 3H), 1.15 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 163.0 (t, $J = 33.6$ Hz), 148.9, 147.5 (t, $J = 4.7$ Hz), 146.9 (t, $J = 8.9$ Hz), 137.0, 133.1, 131.0, 130.0, 129.8, 129.2, 127.7, 126.4, 125.4, 123.9 (t, $J = 23.4$ Hz), 113.2 (t, $J = 252.2$ Hz), 63.2, 19.8, 13.6; ^{19}F NMR (376 MHz, CDCl_3): δ (ppm) -95.2 (d, $J_{\text{F-F}} = 275.2$ Hz), -100.1 (d, $J_{\text{F-F}} = 275.2$ Hz); HRMS (ESI) m/z : calcd for $\text{C}_{20}\text{H}_{18}\text{F}_2\text{NO}_2$ ($\text{M}+\text{H}$) $^+$ 342.1300, found 342.1301.

Ethyl 2,2-difluoro-2-(4-(4-methoxyphenyl)quinolin-3-yl)acetate (3m). Yellow solid (61.4 mg, 86% yield); mp 57–59 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.29 (s, 1H), 8.21 (d, $J = 8.4$ Hz, 1H), 7.79 (dt, $J = 8.4, 4.1$ Hz, 1H), 7.49 (d, $J = 3.7$ Hz, 2H), 7.19 (d, $J = 8.7$ Hz, 2H), 7.05–7.01 (m, 2H), 3.99 (q, $J = 7.2$ Hz, 2H), 3.91 (s, 3H), 1.17 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 163.1 (t, $J = 33.5$ Hz), 160.1, 149.0, 148.0 (t, $J = 4.8$ Hz), 146.5 (t, $J = 9.1$ Hz), 131.5, 130.9, 129.5, 127.6, 127.4, 126.9, 125.2, 124.4 (t, $J = 23.2$ Hz), 115.7, 113.2 (t, $J = 251.0$ Hz), 63.1, 55.3, 13.6; ^{19}F NMR (376 MHz, CDCl_3): δ (ppm) -95.5; HRMS (ESI) m/z : calcd for $\text{C}_{20}\text{H}_{18}\text{F}_2\text{NO}_3$ ($\text{M}+\text{H}$) $^+$ 358.1249, found 358.1249.

Ethyl 2-(4-(4-chlorophenyl)quinolin-3-yl)-2,2-difluoroacetate (3n). Yellow solid (46.2 mg, 64% yield); mp 69–71 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.27 (s, 1H), 8.21 (d, $J = 8.4$ Hz, 1H), 7.81–7.77 (m, 1H), 7.52–7.47 (m, 3H), 7.39 (dd, $J = 8.5, 0.8$ Hz, 1H), 7.21 (d, $J = 8.4$ Hz, 2H), 4.04 (q, $J = 7.2$ Hz, 2H), 1.19 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 163.1 (t, $J = 33.6$ Hz), 148.9, 146.6 (t, $J = 4.4$ Hz), 146.5 (t, $J = 9.0$ Hz), 135.2, 131.9, 131.4, 131.1, 129.7, 128.4, 127.7, 127.0, 126.5, 124.0 (t, $J = 23.4$ Hz), 113.1 (t, $J = 252.4$ Hz), 63.4, 13.7; ^{19}F NMR (376 MHz, CDCl_3): δ (ppm) -96.1; HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{15}\text{ClF}_2\text{NO}_2$ ($\text{M}+\text{H}$) $^+$ 362.0754, found 362.0754.

Ethyl 2-(4-(4-cyanophenyl)quinolin-3-yl)-2,2-difluoroacetate (3o). Brown solid (49.3 mg, 70% yield); mp 138–140 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.25 (s, 1H), 8.24 (d, $J = 8.4$ Hz, 1H), 7.87–7.82 (m, 3H), 7.54 (t, $J = 7.7$ Hz, 1H), 7.42 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 1H), 4.11 (q, $J = 7.1$ Hz, 2H), 1.23 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 163.0 (t, $J = 33.9$ Hz), 148.9, 146.6 (t, $J = 8.6$ Hz), 145.6 (t, $J = 4.0$ Hz), 138.8, 131.8, 131.4, 130.7, 129.9, 128.1, 126.3, 126.2, 123.5 (t, $J = 23.5$ Hz), 118.3, 113.0 (t, $J = 253.4$ Hz), 113.0, 63.6, 13.8; ^{19}F NMR (376 MHz, CDCl_3): δ (ppm) -96.5; HRMS (ESI) m/z : calcd for $\text{C}_{20}\text{H}_{15}\text{F}_2\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 353.1096, found 353.1097.

Ethyl 2-(4-(4-acetylphenyl)quinolin-3-yl)-2,2-difluoroacetate (3p). Brown solid (58.3 mg, 79% yield); mp 74–76 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.28 (s, 1H), 8.25 (d, $J = 8.4$ Hz, 1H), 8.11 (d, $J = 8.4$ Hz, 2H), 7.86–7.81 (m, 1H), 7.54–7.50 (m, 1H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 7.9$ Hz, 1H), 4.06 (q, $J = 7.2$ Hz, 2H), 2.72 (s, 3H), 1.19 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 197.5, 163.0 (t, $J = 33.9$ Hz), 148.7, 146.8 (t, $J = 4.1$ Hz), 146.5 (t, $J = 8.8$ Hz), 138.6, 137.2, 131.3, 130.3, 129.6, 127.9 (d, $J = 7.8$ Hz), 126.7, 126.5, 123.6 (t, $J = 23.5$ Hz), 115.6, 113.0 (t, $J = 252.6$ Hz), 63.5, 26.8, 13.7; ^{19}F NMR (376 MHz, CDCl_3): δ (ppm) -96.4; HRMS (ESI) m/z : calcd for $\text{C}_{21}\text{H}_{18}\text{F}_2\text{NO}_3$ ($\text{M}+\text{H}$) $^+$ 370.1249, found 370.1249.

Ethyl 4-(3-(2-ethoxy-1,1-difluoro-2-oxoethyl)quinolin-4-yl)benzoate (3q). Yellow oil (63.9 mg, 80% yield); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.28 (s, 1H), 8.25–8.18 (m, 3H), 7.82 (ddd, $J = 8.3, 6.9, 1.3$ Hz, 1H), 7.50 (ddd, $J = 8.2, 6.9, 1.1$ Hz, 1H), 7.35 (t, $J = 9.0$ Hz, 3H), 4.45 (q, $J = 7.1$ Hz, 2H), 4.06 (q, $J = 7.2$ Hz, 2H), 1.45 (t, $J = 7.1$ Hz, 3H), 1.19 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 166.0, 163.0 (t, $J = 33.8$ Hz), 148.8, 146.9 (t, $J = 4.3$ Hz), 146.5 (t, $J = 8.8$ Hz), 138.3, 131.2, 131.0, 130.0, 129.7, 129.2, 127.8, 126.7, 126.5, 123.7 (t, $J = 23.4$ Hz), 113.1 (t, $J = 252.6$ Hz), 63.4, 61.3, 14.4, 13.7; ^{19}F NMR (376 MHz, CDCl_3): δ (ppm) -96.3; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{20}\text{F}_2\text{NO}_4$ ($\text{M}+\text{H}$) $^+$ 400.1355, found 400.1355.

Ethyl 2-(4-([1,1'-biphenyl]-4-yl)quinolin-3-yl)-2,2-difluoroacetate (3r). Yellow solid (66.9 mg, 83% yield); mp 99–101 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.35 (s, 1H), 8.28 (d, $J = 8.2$ Hz, 1H), 7.84 (dd, $J = 7.8, 3.8$ Hz, 1H), 7.78–7.72 (m, 4H), 7.54 (dd, $J = 9.8, 5.7$ Hz, 4H), 7.44 (t, $J = 7.3$ Hz, 1H), 7.37 (d, $J = 7.9$ Hz, 2H), 4.00 (q, $J = 7.1$ Hz, 2H), 1.16 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 163.2 (t, $J = 33.4$ Hz), 148.8, 148.0 (t, $J = 4.3$ Hz), 146.4 (td, $J = 8.7, 2.0$ Hz), 141.8, 140.1, 132.2, 131.2, 130.7, 129.5, 129.0, 127.9, 127.6, 127.3, 127.2, 126.9, 126.7, 124.1 (t, $J = 25.0$ Hz), 113.2 (t, $J = 251.9$ Hz), 63.3, 13.7; ^{19}F NMR (376 MHz, CDCl_3): δ (ppm) -95.6; HRMS (ESI) m/z : calcd for $\text{C}_{25}\text{H}_{20}\text{F}_2\text{NO}_2$ ($\text{M}+\text{H}$) $^+$ 404.1457, found 404.1456.

Ethyl 2-(4-(4-(9H-fluoren-2-yl)phenyl)quinolin-3-yl)-2,2-difluoroacetate (3s). Yellow solid (71.4 mg, 86% yield); mp 88–90 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.36 (s, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.91 (dd, *J* = 14.1, 7.6 Hz, 2H), 7.82 (ddd, *J* = 8.4, 6.5, 1.7 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.56–7.50 (m, 2H), 7.48–7.44 (m, 2H), 7.40 (td, *J* = 7.4, 1.2 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 4.01 (s, 2H), 3.98–3.92 (m, 2H), 1.10 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.1 (t, *J* = 33.6 Hz), 149.0, 148.4 (t, *J* = 4.7 Hz), 146.6 (t, *J* = 9.0 Hz), 143.5, 142.9, 142.5, 140.9, 131.6, 131.0, 129.6, 128.9, 127.5, 127.4, 127.1, 127.0, 126.9, 125.2, 124.2 (t, *J* = 23.4 Hz), 120.3, 119.4, 113.3 (t, *J* = 251.4 Hz), 63.2, 37.0, 13.6; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -95.0 (d, *J*_{F-F} = 277.5 Hz), -96.0 (d, *J*_{F-F} = 277.5 Hz); HRMS (ESI) *m/z*: calcd for C₂₆H₂₀F₂NO₂ (M+H)⁺ 416.1457, found 416.1458.

Ethyl 2,2-difluoro-2-(4-(thiophen-2-yl)quinolin-3-yl)acetate (3t). Yellow solid (60.6 mg, 91% yield); mp 57–59 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.31 (s, 1H), 8.22 (d, *J* = 8.6 Hz, 1H), 7.80 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.69 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.63 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.54 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.21 (dd, *J* = 5.1, 3.5 Hz, 1H), 7.15 (d, *J* = 3.1 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 162.7 (t, *J* = 33.5 Hz), 148.6, 146.1 (t, *J* = 9.4 Hz), 141.4 (t, *J* = 4.7 Hz), 132.1, 131.5, 131.3, 129.4, 128.8, 128.1, 127.9, 127.1, 126.6, 125.8 (t, *J* = 23.4 Hz), 112.9 (t, *J* = 251.1 Hz), 63.4, 13.7; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -91.7, -92.5, -99.0, -99.7; HRMS (ESI) *m/z*: calcd for C₁₇H₁₄F₂NO₂S (M+H)⁺ 334.0708, found 334.0708.

Ethyl 2,2-difluoro-2-(6-methyl-4-(*p*-tolyl)quinolin-3-yl)acetate (3v). Yellow solid (56.8 mg, 80% yield); mp 48–50 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.23 (s, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.64 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.20 (s, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 3.99 (q, *J* = 7.2 Hz, 2H), 2.50 (s, 3H), 2.43 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.1 (t, *J* = 33.7 Hz), 147.7 (t, *J* = 4.7 Hz), 147.3, 145.4 (t, *J* = 9.2 Hz), 138.8, 137.6, 133.3, 130.4, 130.0, 129.1, 128.7, 127.4, 125.6, 124.1 (t, *J* = 23.3 Hz), 113.2 (t, *J* = 251.3 Hz), 63.1, 21.8, 21.5, 13.6; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -95.8; HRMS (ESI) *m/z*: calcd for C₂₁H₂₀F₂NO₂ (M+H)⁺ 356.1457, found 356.1457.

Ethyl 2-(4-(4-cyanophenyl)-6-methylquinolin-3-yl)-2,2-difluoroacetate (3w). Yellow solid (52.0 mg, 71% yield); mp 108–110 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.19 (s, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 7.85–7.82 (m, 2H), 7.68 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 6.99 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.1 (t, *J* = 34.0 Hz), 147.5, 145.7 (t, *J* = 8.6 Hz), 144.8 (t, *J* = 3.9 Hz), 139.0, 138.4, 133.7, 131.8, 130.7, 129.5, 126.3, 124.8, 123.5 (t, *J* = 23.4 Hz), 118.3, 113.1 (t, *J* = 253.4 Hz), 110.6, 63.5, 21.9, 13.8; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -96.4; HRMS (ESI) *m/z*: calcd for C₂₁H₁₇F₂N₂O₂ (M+H)⁺ 367.1253, found 367.1252.

Ethyl 2-(6-chloro-4-(4-methoxyphenyl)quinolin-3-yl)-2,2-difluoroacetate (3x). Yellow oil (43.8 mg, 56% yield); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.28 (s, 1H), 8.16 (d, *J* = 9.0 Hz, 1H), 7.73 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.44 (d, *J* = 2.3 Hz, 1H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.07–7.04 (m, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.93 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 162.9 (t, *J* = 33.4 Hz), 160.3, 147.4, 147.3 (t, *J* = 4.8 Hz), 146.7 (t, *J* = 9.2 Hz), 133.5, 131.9, 131.5, 131.2, 128.5, 125.6, 125.2 (t, *J* = 23.4 Hz), 124.5, 115.5, 113.0 (t, *J* = 252.7 Hz), 63.2, 55.4, 13.6; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -95.7; HRMS (ESI) *m/z*: calcd for C₂₀H₁₇ClF₂NO₃ (M+H)⁺ 392.0860, found 392.0860.

Ethyl 2-(4-([1,1'-biphenyl]-4-yl)-6-chloroquinolin-3-yl)-2,2-difluoroacetate (3y). Pale yellow solid (79.6 mg, 91% yield); mp 90–92 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.33 (s, 1H), 8.19 (d, *J* = 9.0 Hz, 1H), 7.79–7.72 (m, 5H), 7.54–7.50 (m, 3H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.0 (t, *J* = 33.3 Hz), 147.4, 147.0 (t, *J* = 4.6 Hz), 146.8 (t, *J* = 9.0 Hz), 142.1, 140.0, 133.7, 132.0, 131.6, 131.3, 130.6, 129.0, 128.1, 128.0, 127.2, 126.8, 125.6, 125.0 (t, *J* = 23.4 Hz), 113.1 (t, *J* = 252.4 Hz), 63.4, 13.7; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -95.8; HRMS (ESI) *m/z*: calcd for C₂₅H₁₉ClF₂NO₂ (M+H)⁺ 438.1067, found 438.1067.

Ethyl 2-fluoro-2-(4-phenylquinolin-3-yl)acetate (5a). Yellow oil (30.9 mg, 50% yield); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.08 (s, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.76 (ddd, *J* = 8.2, 6.3, 1.5 Hz, 1H), 7.58–7.47 (m, 5H), 7.45–7.42 (m, 1H), 7.38–7.35 (m, 1H), 5.79 (d, *J* = 46.8 Hz, 1H), 4.29–4.16 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 168.2 (d, *J* = 27.9 Hz), 148.8 (d, *J* = 4.9 Hz), 148.3 (d, *J* = 3.9 Hz), 134.1, 130.5, 130.4, 129.6, 129.4, 129.0, 128.5 (d, *J* = 7.4 Hz), 127.3, 127.1, 125.1 (d, *J* = 19.8 Hz), 85.8 (d, *J* = 184.2 Hz), 62.2, 14.0; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm)

-173.4; HRMS (ESI) *m/z*: calcd for C₁₉H₁₇FNO₂ (M+H)⁺ 310.1238, found 310.1238.

Ethyl 2-fluoro-2-(6-methoxy-4-phenylquinolin-3-yl)acetate (5e). Yellow solid (41.4 mg, 61% yield); mp 108–110 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.92 (s, 1H), 8.09 (d, *J* = 9.2 Hz, 1H), 7.60–7.54 (m, 3H), 7.45–7.36 (m, 2H), 7.37 (dt, *J* = 5.4, 2.1 Hz, 1H), 6.75 (d, *J* = 2.8 Hz, 1H), 5.75 (d, *J* = 46.8 Hz, 1H), 4.27–4.18 (m, 2H), 3.71 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 168.3 (d, *J* = 27.9 Hz), 158.3, 147.3 (d, *J* = 5.0 Hz), 146.3 (d, *J* = 4.0 Hz), 144.5 (d, *J* = 2.1 Hz), 134.4, 131.0, 130.3, 129.3, 128.9, 128.7 (d, *J* = 6.4 Hz), 125.3 (d, *J* = 19.7 Hz), 122.7, 105.0, 85.9 (d, *J* = 184.2 Hz), 62.1, 55.4, 14.0; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -173.3; HRMS (ESI) *m/z*: calcd for C₂₀H₁₉FNO₃ (M+H)⁺ 340.1344, found 340.1343.

Ethyl 2-fluoro-2-(6-fluoro-4-phenylquinolin-3-yl)acetate (5g). Yellow solid (36.0 mg, 55% yield); mp 78–80 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.04 (s, 1H), 8.19 (dd, *J* = 9.2, 5.5 Hz, 1H), 7.59–7.51 (m, 4H), 7.44–7.41 (m, 1H), 7.36–7.34 (m, 1H), 7.13 (dd, *J* = 9.9, 2.8 Hz, 1H), 5.78 (d, *J* = 46.7 Hz, 1H), 4.28–4.19 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 168.1 (d, *J* = 27.7 Hz), 162.1, 159.7, 148.1 (dd, *J* = 3.8, 2.9 Hz), 145.5, 133.6, 132.2 (d, *J* = 8.6 Hz), 130.3, 129.2 (d, *J* = 4.3 Hz), 128.8 (d, *J* = 7.5 Hz), 128.1 (d, *J* = 9.6 Hz), 125.7 (d, *J* = 19.8 Hz), 120.6 (d, *J* = 26.1 Hz), 110.5 (dd, *J* = 23.3, 0.7 Hz), 85.7 (d, *J* = 184.5 Hz), 62.3, 14.0; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -111.0, -111.1, -174.0, -174.1; HRMS (ESI) *m/z*: calcd for C₁₉H₁₆F₂NO₂ (M+H)⁺ 328.1144, found 328.1143.

Ethyl 2-(4-([1,1'-biphenyl]-4-yl)quinolin-3-yl)-2-fluoroacetate (5r). Pale yellow solid (53.9 mg, 70% yield); mp 79–81 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.13 (s, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 7.83–7.77 (m, 3H), 7.74–7.72 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.56–7.50 (m, 4H), 7.47–7.41 (m, 2H), 5.90 (d, *J* = 46.8 Hz, 1H), 4.30–4.22 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 168.3 (d, *J* = 27.8 Hz), 148.9 (d, *J* = 3.9 Hz), 148.5 (d, *J* = 5.0 Hz), 148.4, 141.8, 140.2, 133.0, 131.0, 130.5, 130.0, 129.7, 129.0, 127.9, 127.4, 127.3, 127.2, 127.1, 125.1 (d, *J* = 19.8 Hz), 85.9 (d, *J* = 184.4 Hz), 62.2, 14.1; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -173.0; HRMS (ESI) *m/z*: calcd for C₂₅H₂₁FNO₂ (M+H)⁺ 386.1551, found 386.1551.

3. The reduction of 3a

To a stirred solution of **3a** (65.4 mg, 0.2 mmol) in MeOH (2.0 mL) was added NaBH₄ (22.7 mg, 0.6 mmol) under argon at room temperature. When the reaction was completed (monitored by TLC), the reaction mixture was quenched with water (10 mL). The aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic layer was dried over anhydrous Na₂SO₄ and then concentrated in vacuo. The crude residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 8:1) to afford the product **6**.

2,2-Difluoro-2-(4-phenylquinolin-3-yl)ethan-1-ol (6). Pale yellow solid (51.9 mg, 91% yield); mp 150–151 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 9.13 (s, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.84–7.80 (m, 1H), 7.55–7.51 (m, 4H), 7.36 (dd, *J* = 6.3, 2.7 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 1H), 5.72 (s, 1H), 3.79–3.72 (m, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) 148.4 (t, *J* = 8.5 Hz), 148.3, 147.2 (t, *J* = 3.4 Hz), 135.5, 131.1, 129.6, 129.5, 128.7, 128.3, 127.9, 127.6, 127.0, 125.4 (t, *J* = 23.4 Hz), 122.2 (t, *J* = 246.0 Hz), 64.7 (t, *J* = 31.3 Hz); ¹⁹F NMR (376 MHz, DMSO-*d*₆): δ (ppm) -97.3; HRMS (ESI) *m/z*: calcd for C₁₇H₁₄F₂NO (M+H)⁺ 286.1038, found 286.1038.

4. The hydrolysis of 3a

To a solution of **3a** (65.4 mg, 0.2 mmol) in EtOH (4.0 mL) was added NaOH aq. (160.0 mg, 4.0 mmol in 4 mL of H₂O) at room temperature and stirred at room temperature for 3 h. Then the reaction mixture was diluted with water (20 mL), washed with CH₂Cl₂ (15 mL × 3). The aqueous solution was acidified to pH 1 with HCl aq. (2 M). The suspension was extracted with CH₂Cl₂ (15 mL × 3). The combined organic layers were dried with anhydrous Na₂SO₄, and then concentrated in vacuo. The residue was recrystallized from the solvents of CH₂Cl₂ and hexane (1:1) to afford the desired product **7**.

2,2-Difluoro-2-(4-phenylquinolin-3-yl)acetic acid (7). Brown solid (53.8 mg, 90% yield); mp 125–127 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 9.20 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.88–7.84 (m, 1H), 7.59–7.49 (m, 4H), 7.31–7.25 (m, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) 164.5 (t, *J* = 32.5 Hz), 148.6, 147.7 (t, *J* = 3.9 Hz), 146.7 (t, *J* = 8.8 Hz), 133.9, 131.6, 129.9, 129.5, 129.1, 128.5,

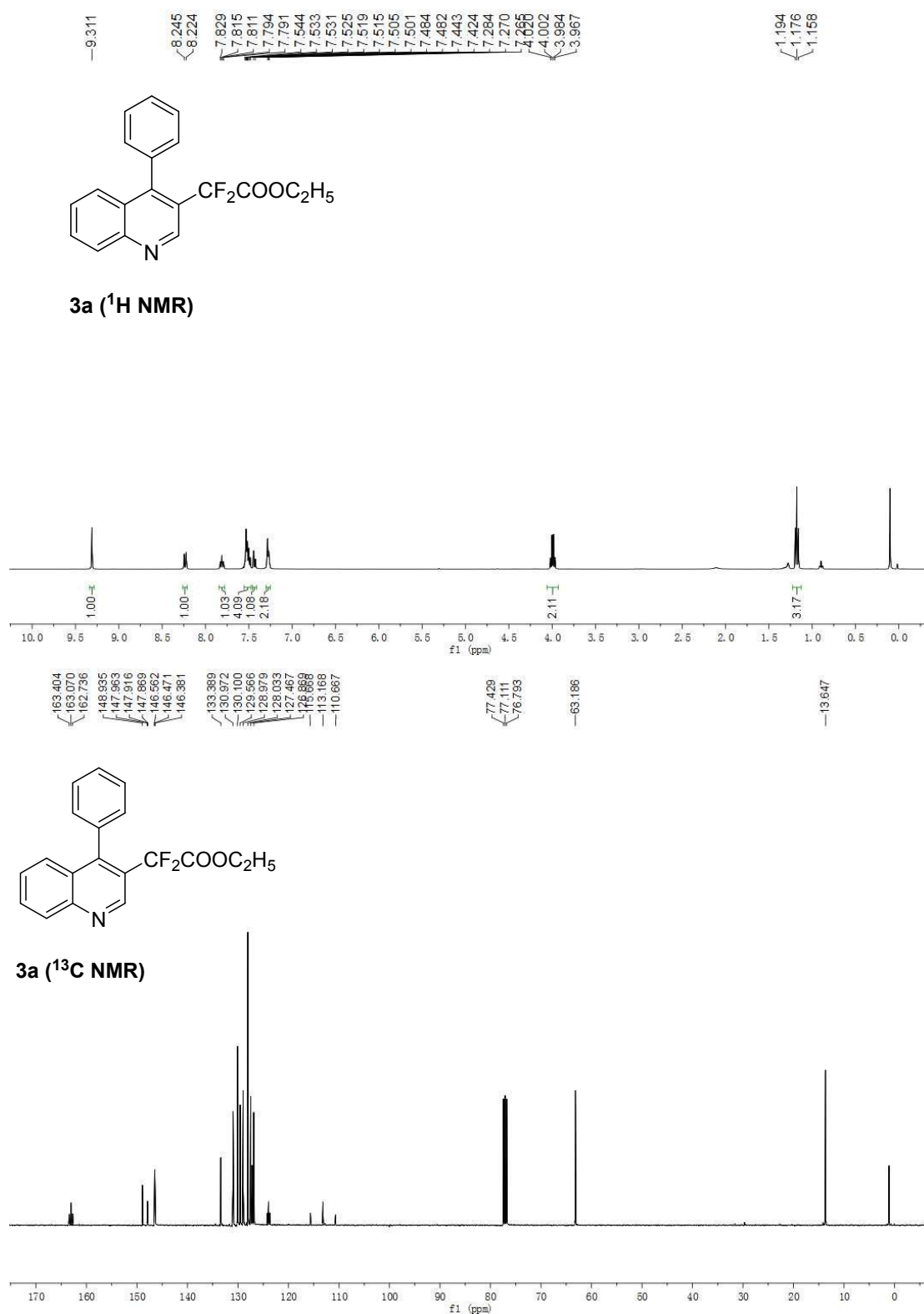
128.3, 127.1, 126.9, 124.4 (t, $J = 23.1$ Hz), 113.9 (t, $J = 251.2$ Hz); ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$): δ (ppm) -96.2; HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{12}\text{F}_2\text{NO}_2$ ($\text{M}+\text{H}$) $^+$ 300.0831, found 300.0831.

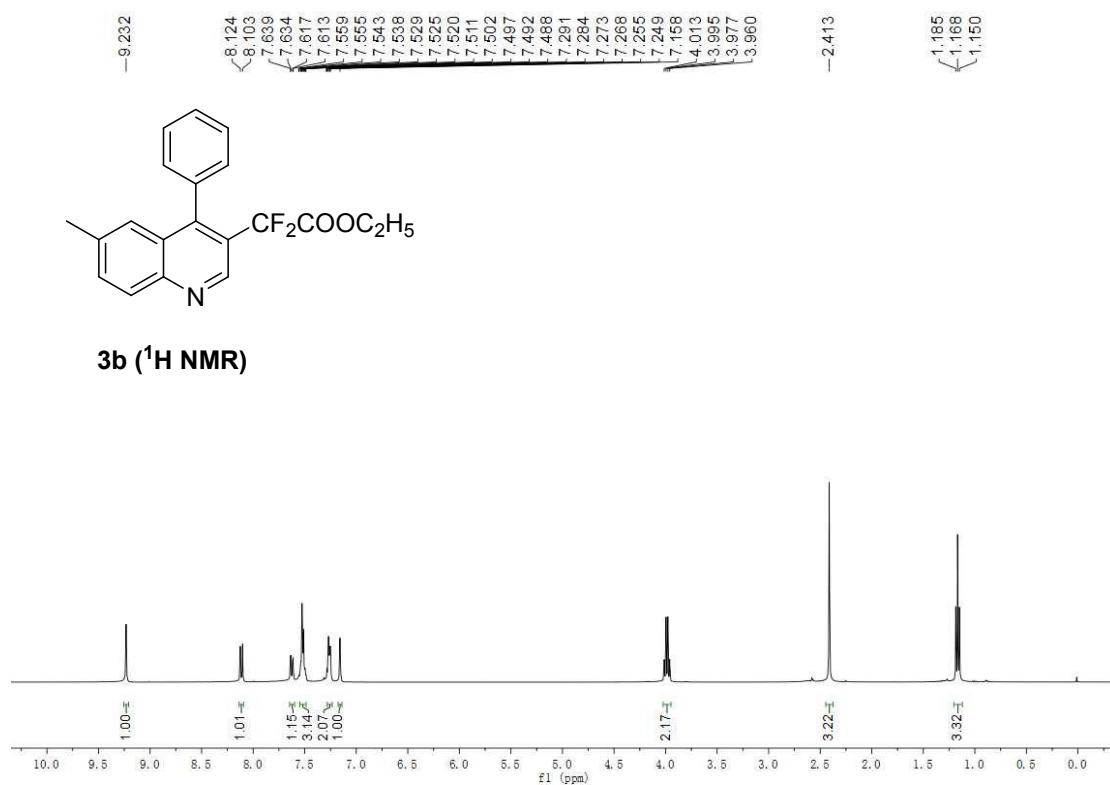
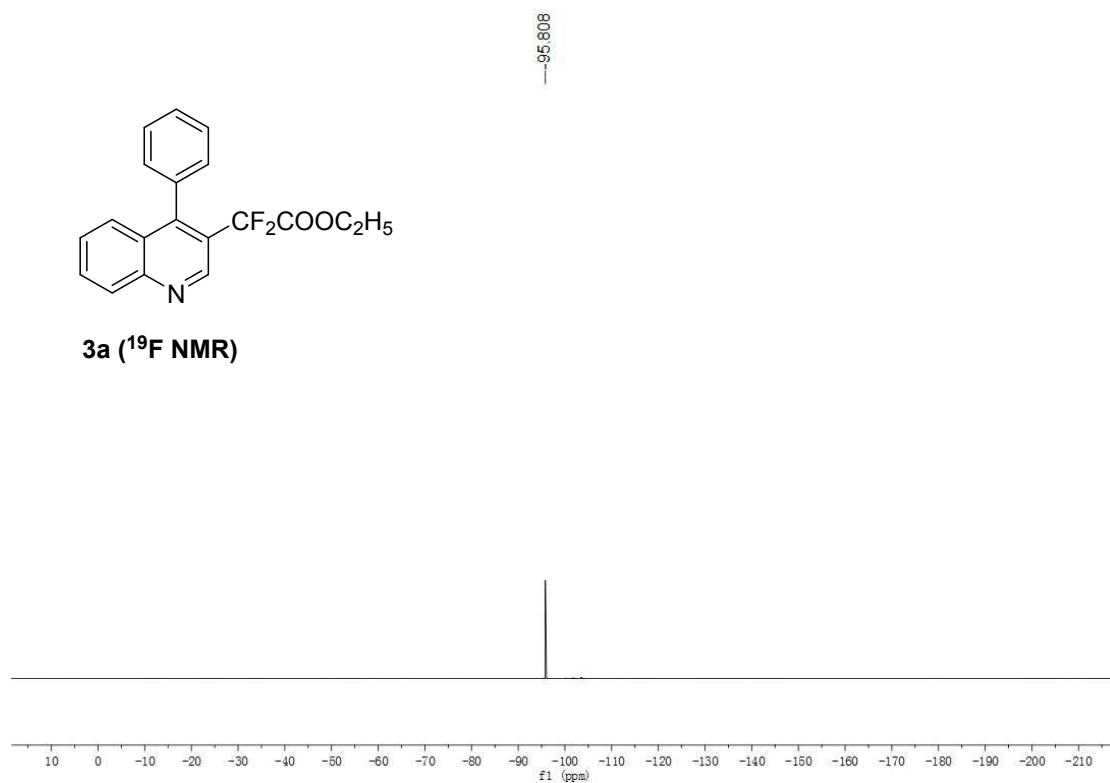
Ethyl 2,2-difluoro-4,4-diphenylbut-3-enoate (8).² Colorless oil (99.7 mg, 66% yield); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.48–7.44 (m, 3H), 7.42–7.35 (m, 5H), 7.34–7.31 (m, 2H), 6.42 (t, $J = 11.8$ Hz, 1H), 3.99 (q, $J = 7.2$ Hz, 2H), 1.24 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 163.5 (t, $J = 33.9$ Hz), 151.1 (t, $J = 9.5$ Hz), 140.5, 137.2, 130.0, 129.3, 128.7, 128.5, 128.1, 128.0, 119.6 (t, $J = 28.5$ Hz), 112.8 (t, $J = 244.8$ Hz), 62.8, 13.7; ^{19}F NMR (376 MHz, CDCl_3): δ (ppm) -90.8.

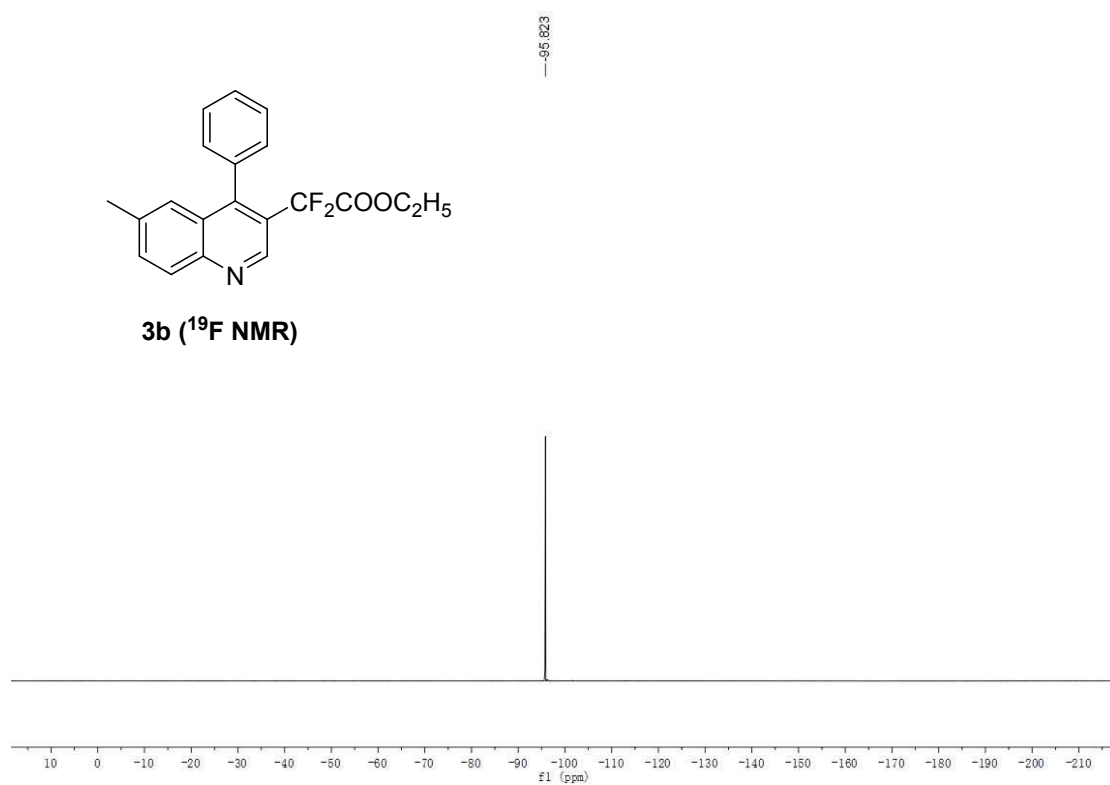
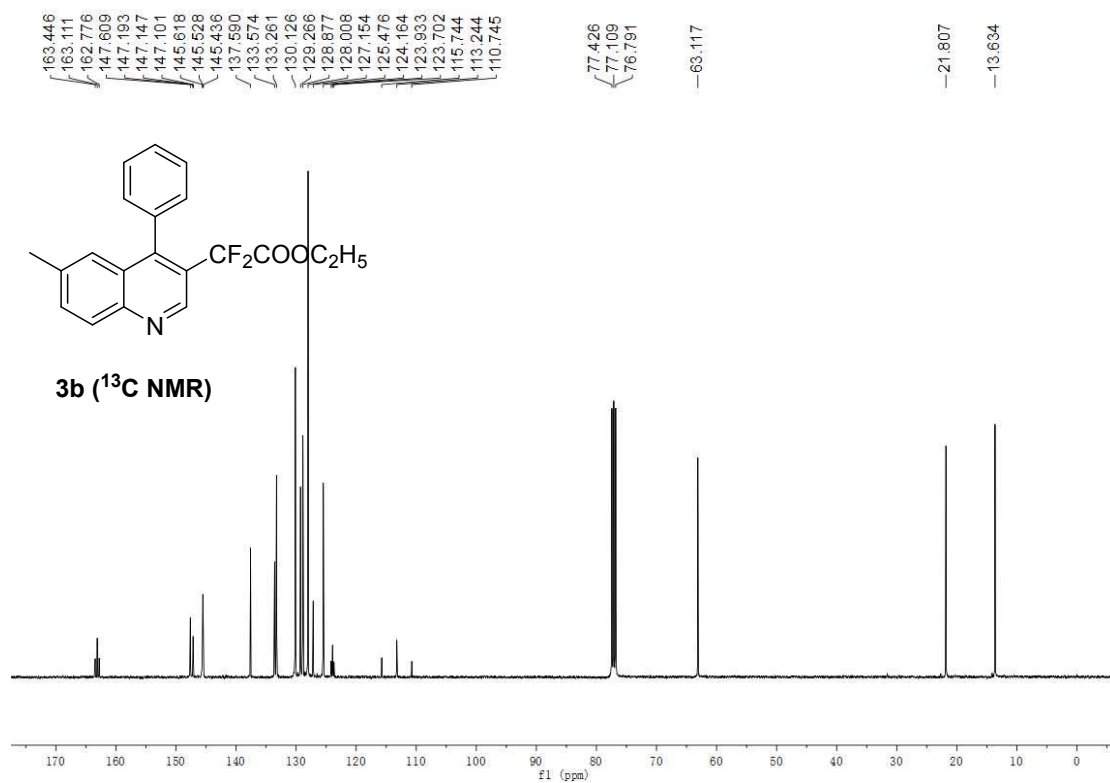
5. References

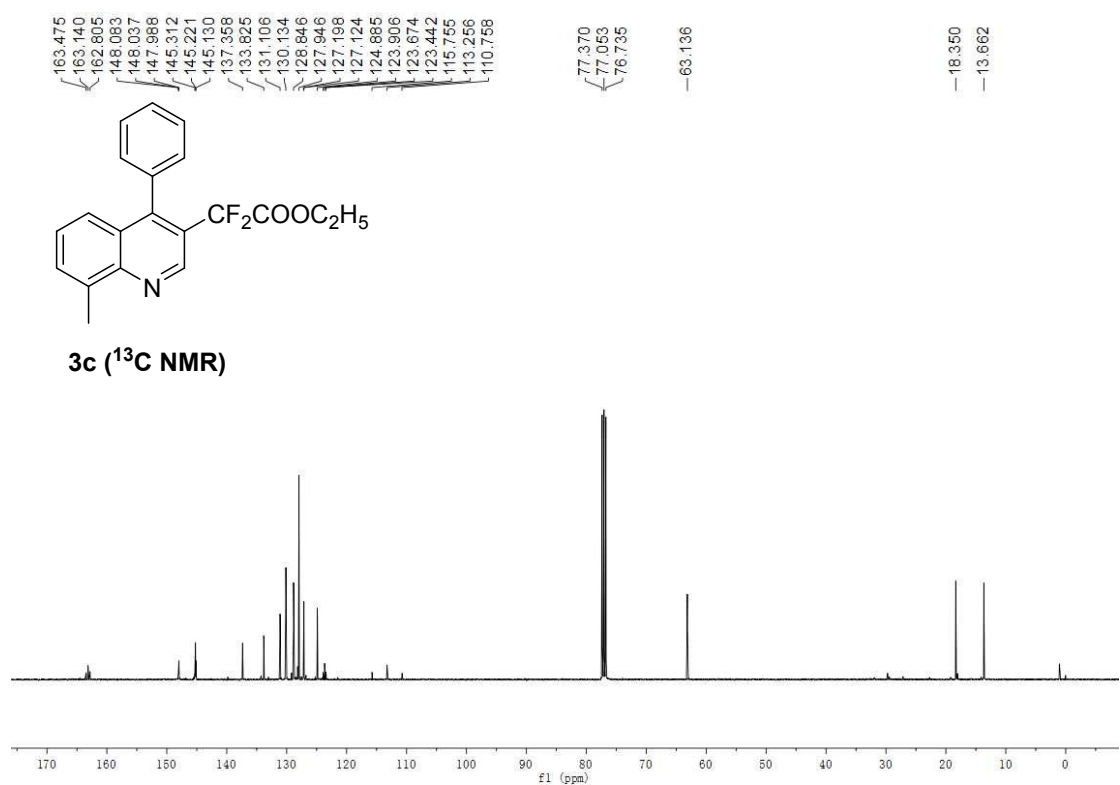
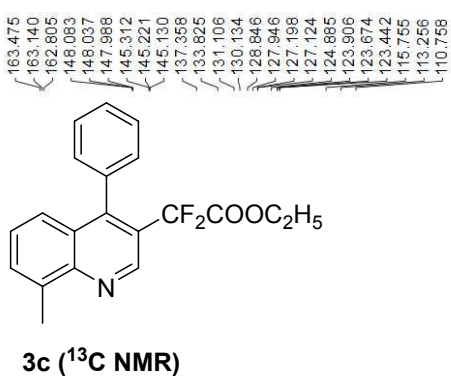
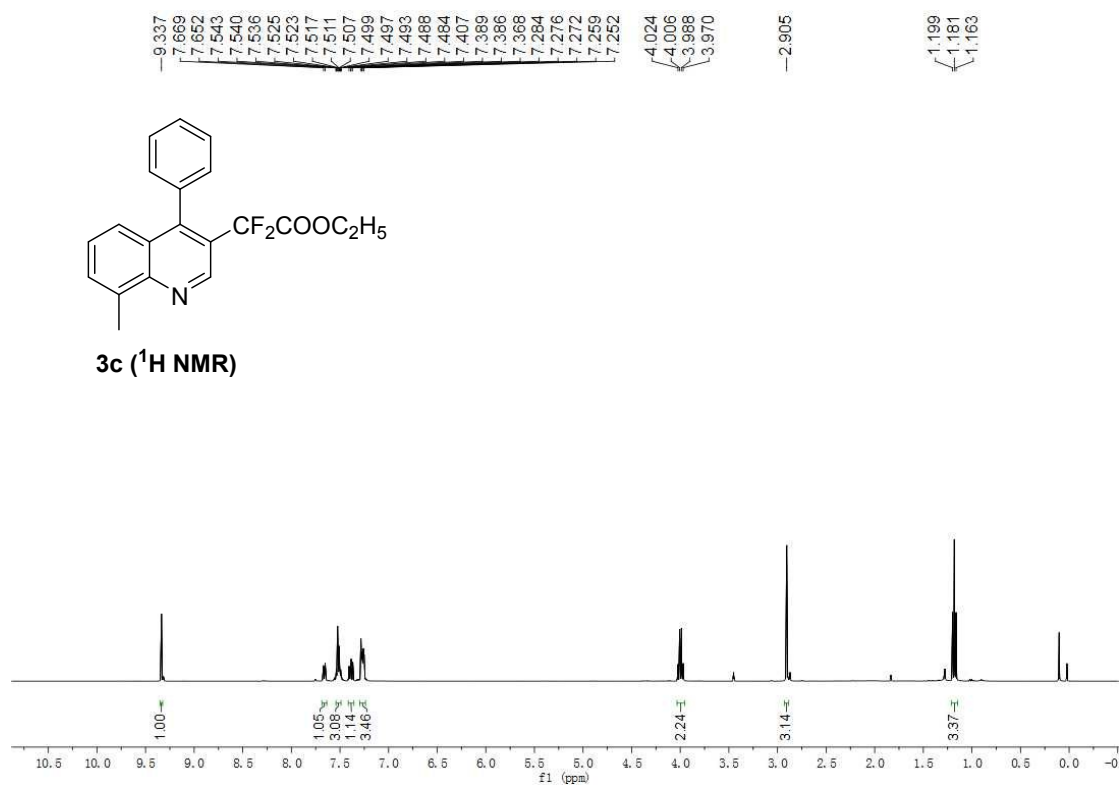
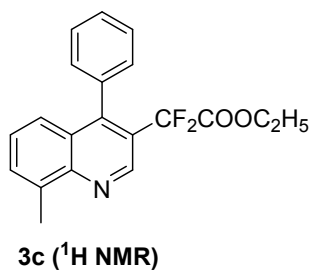
1. L.-L. Zhang, S. Chen, Y.-Z. Gao, P.-B. Zhang, Y.-L. Wu, G. Tang and Y.-F. Zhao, *Org. Lett.*, 2016, **18**, 1286.
2. Y.-T. He, Q. Wang, L.-H. Li, X.-Y. Liu, P.-F. Xu and Y.-M. Liang, *Org. Lett.*, 2015, **17**, 5188.

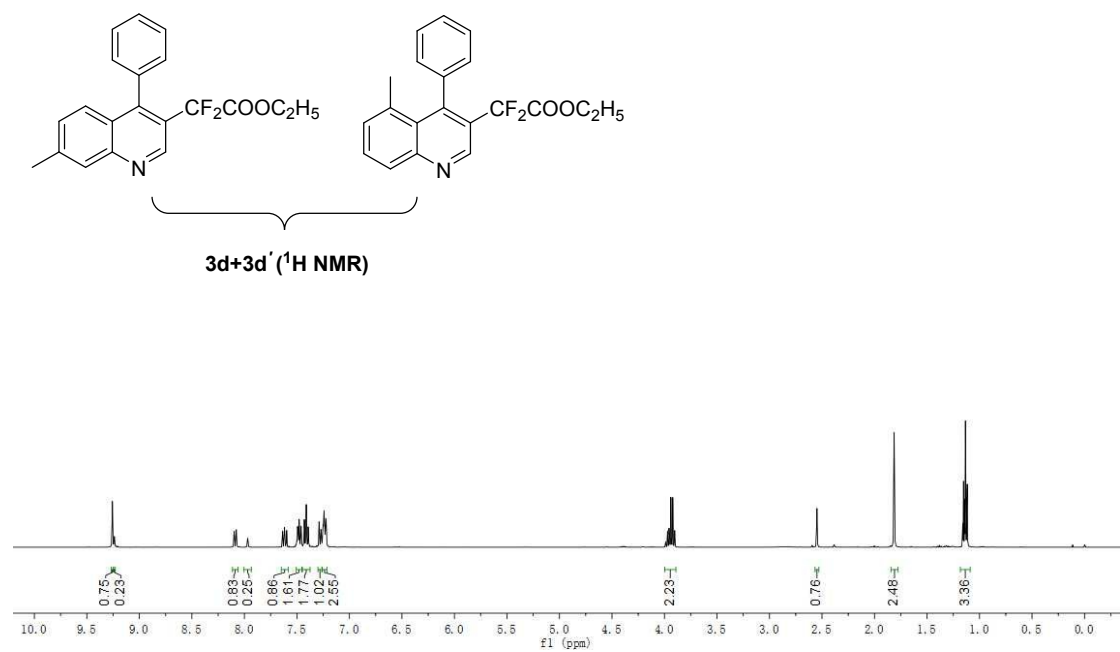
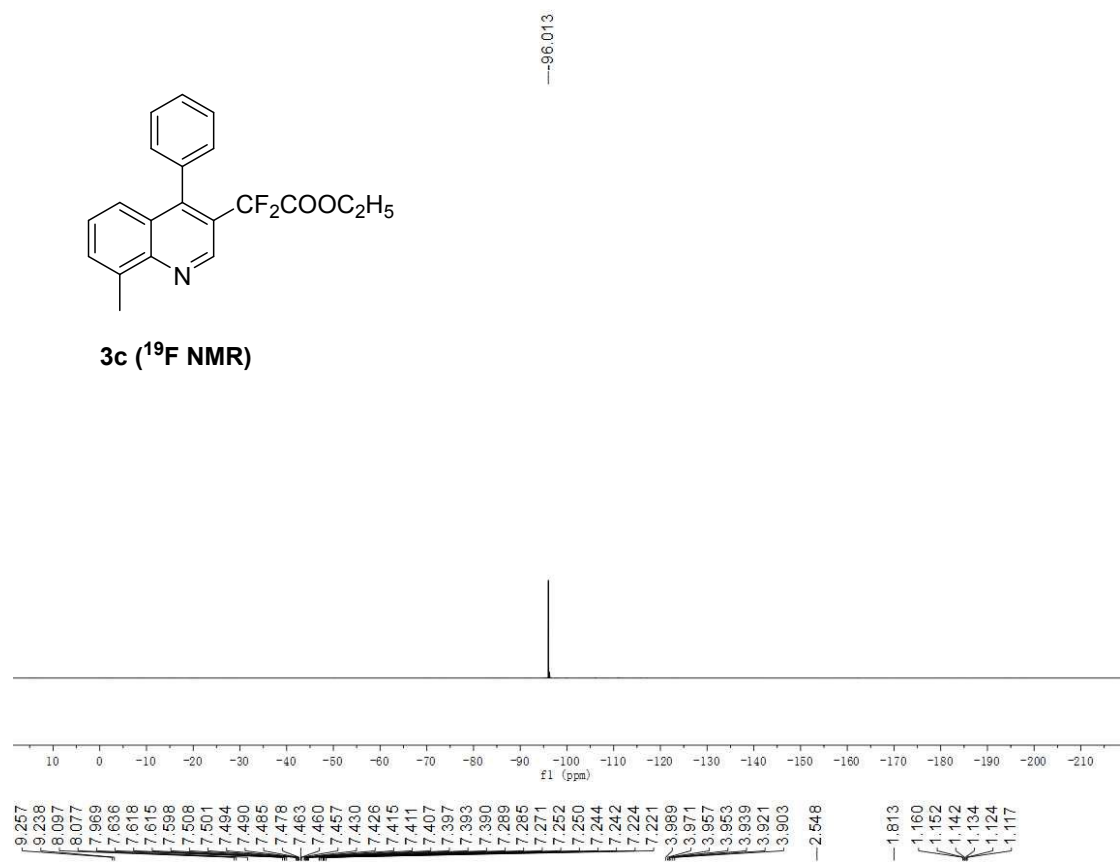
6. Copies of ^1H and ^{13}C NMR spectra of the products

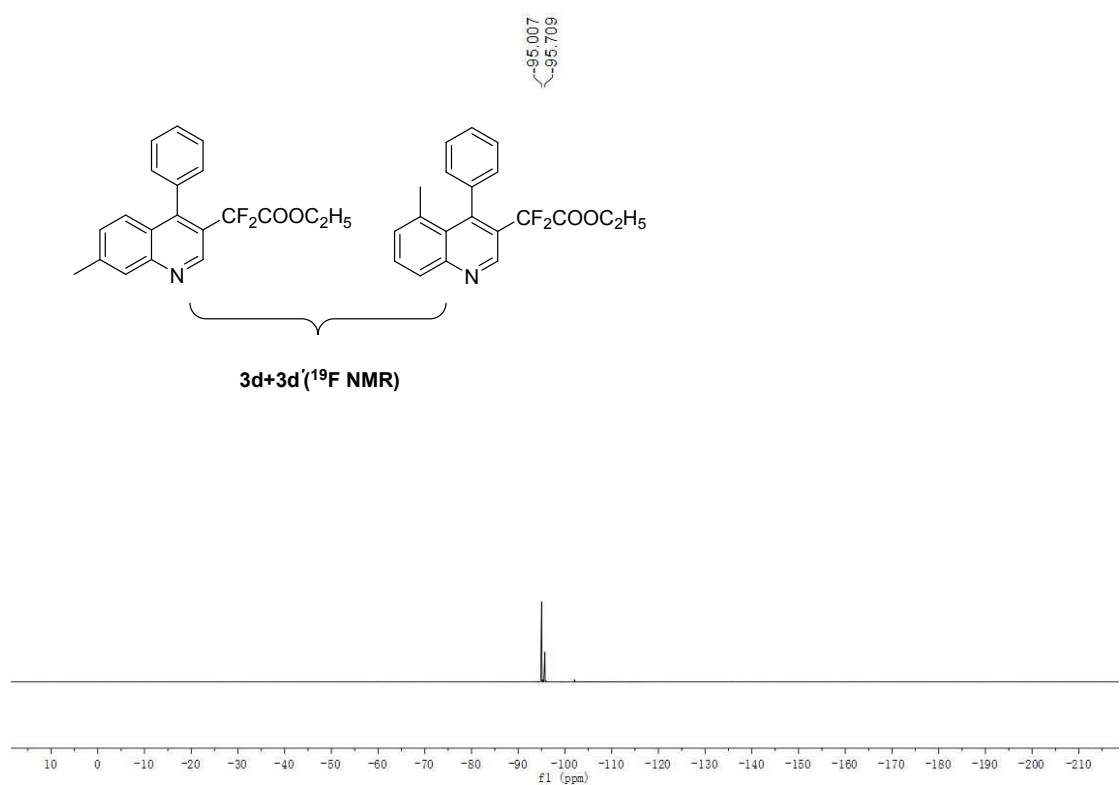
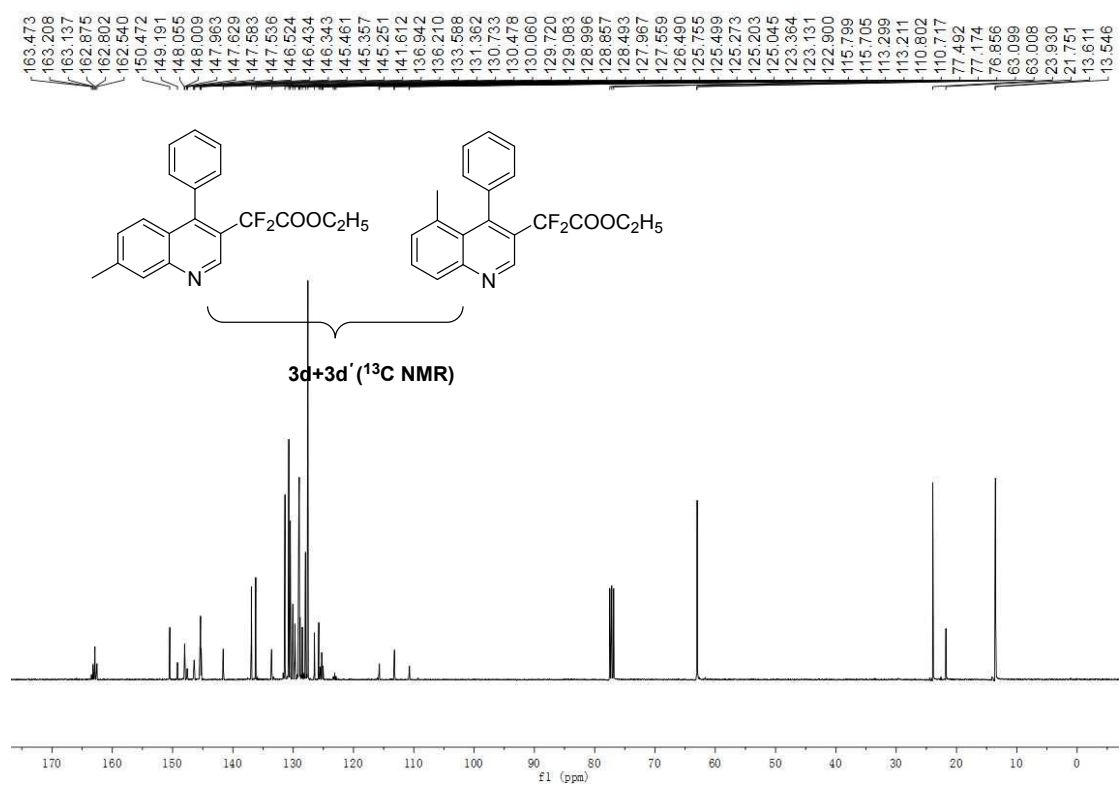


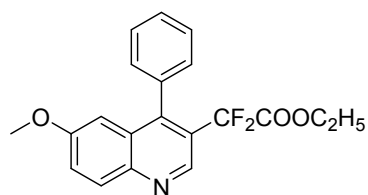




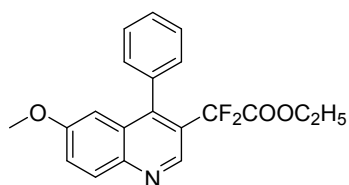
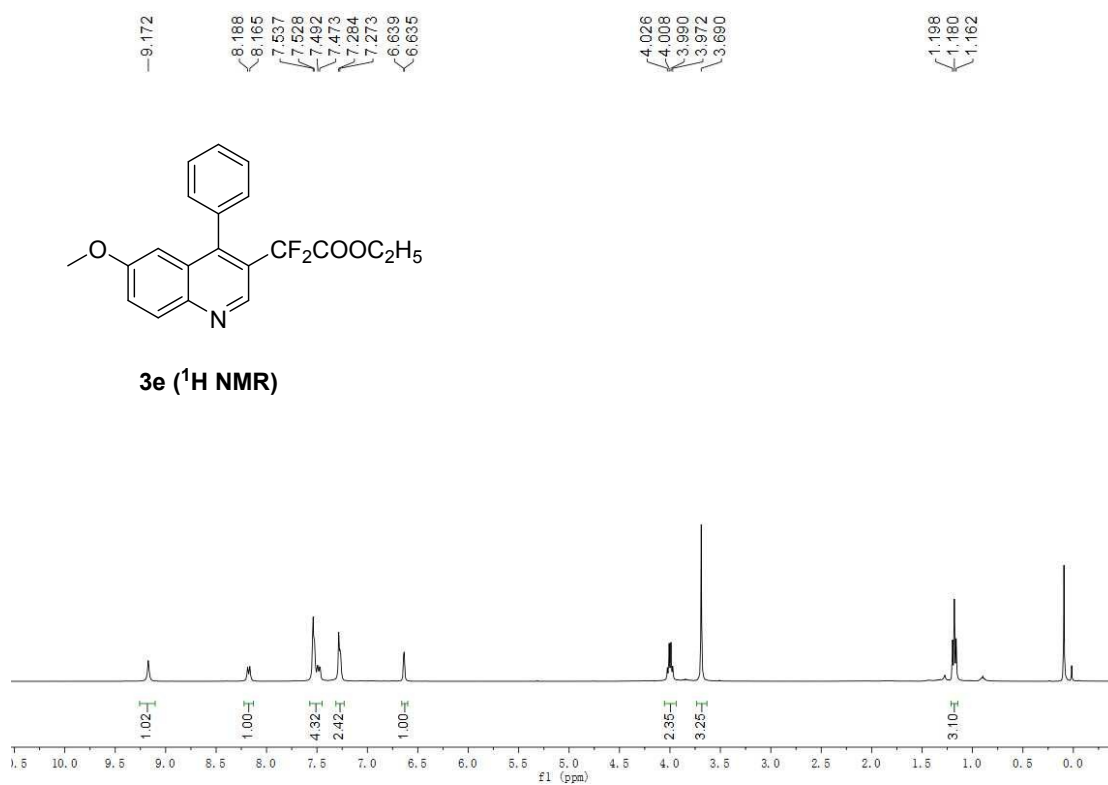




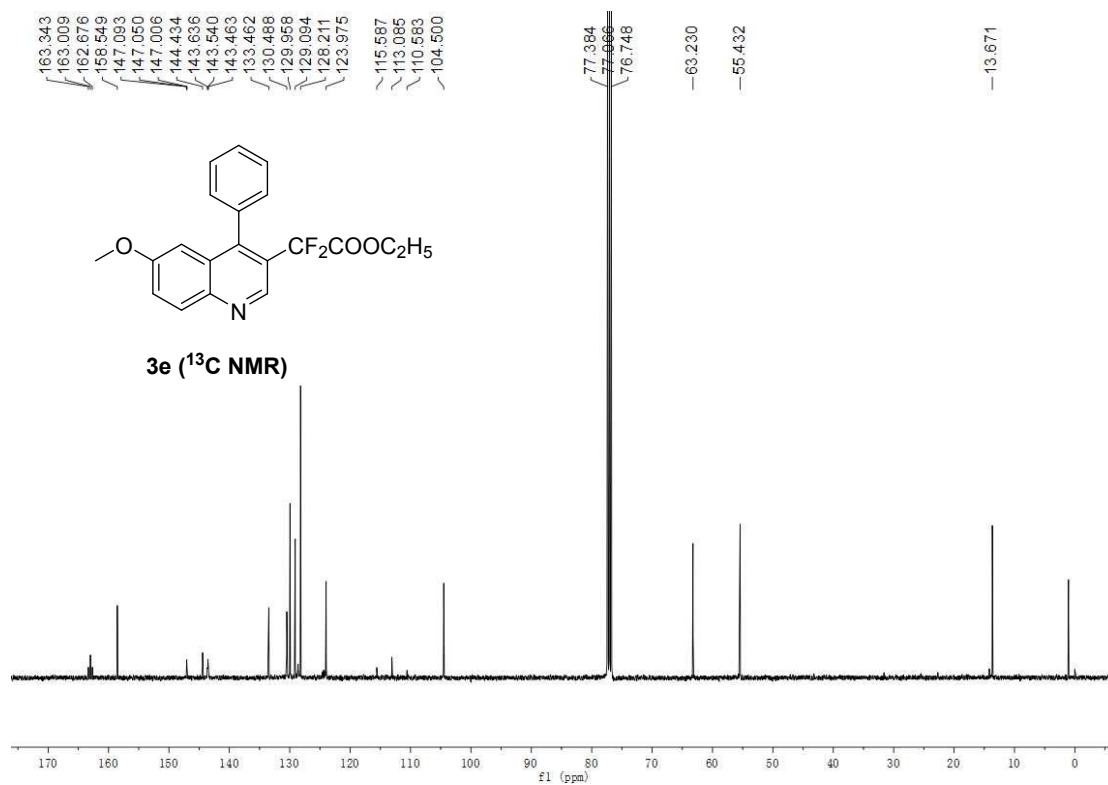


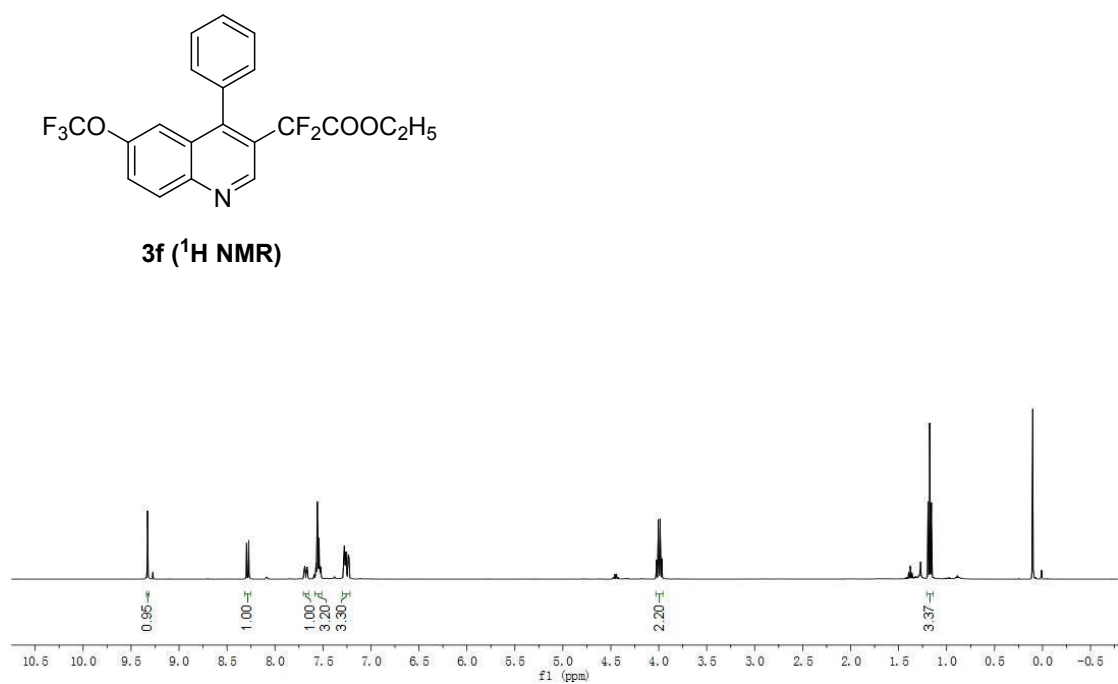
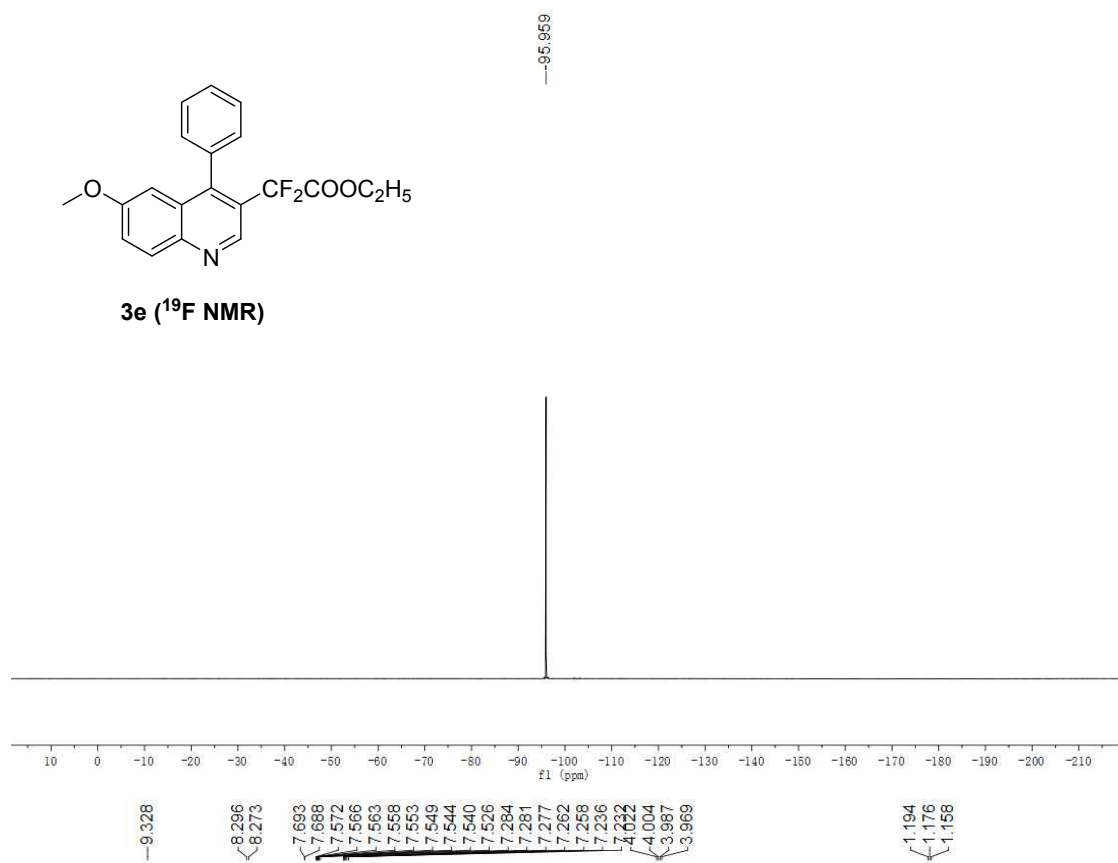


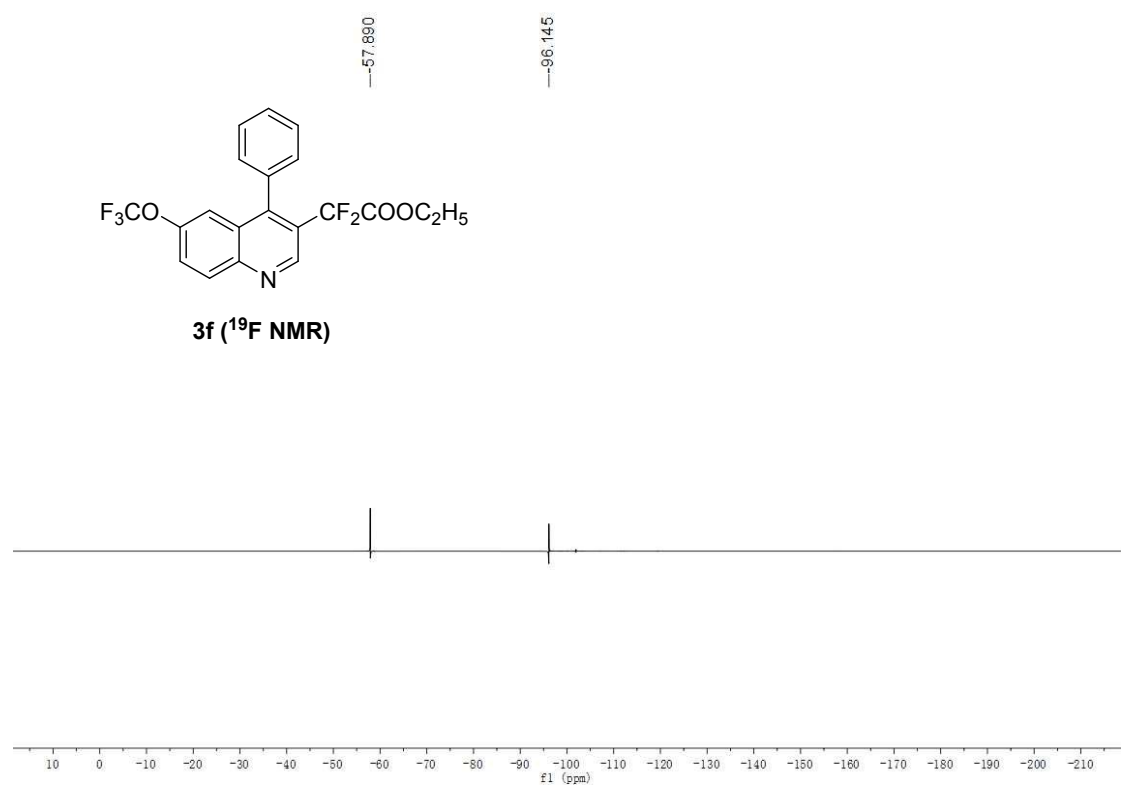
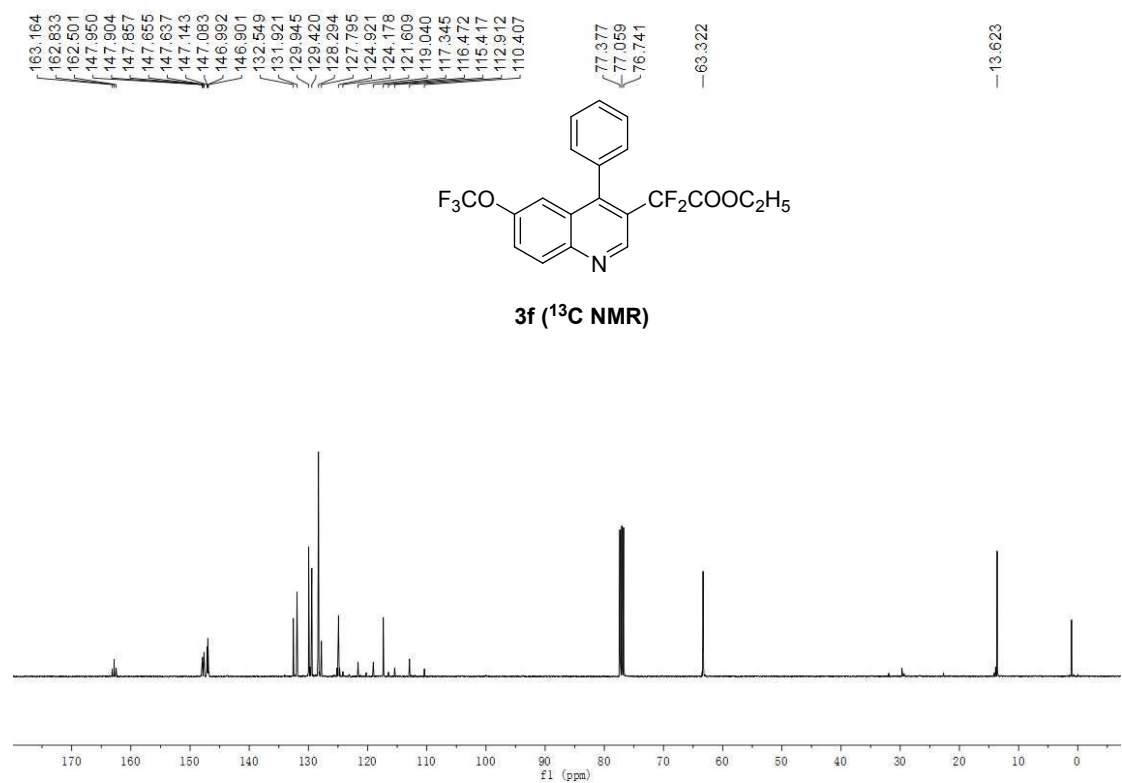
3e (¹H NMR)

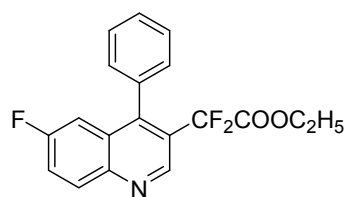


3e (¹³C NMR)

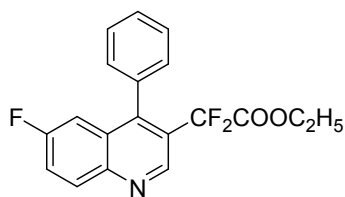
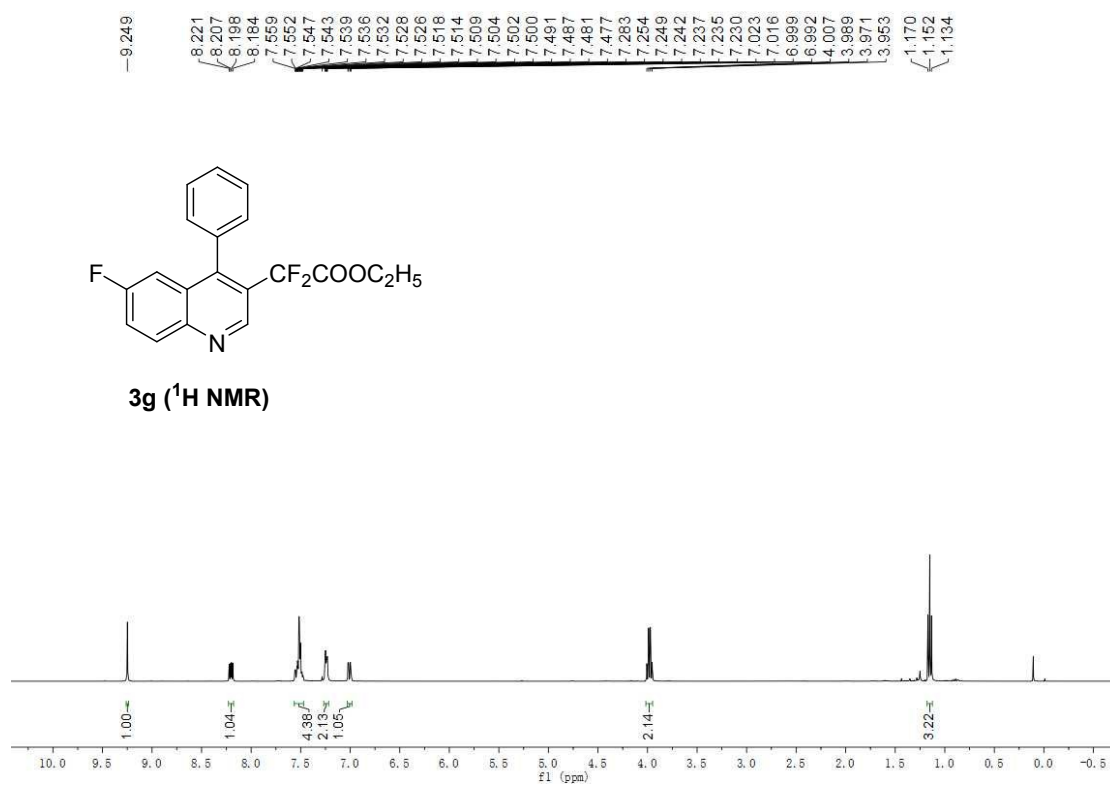




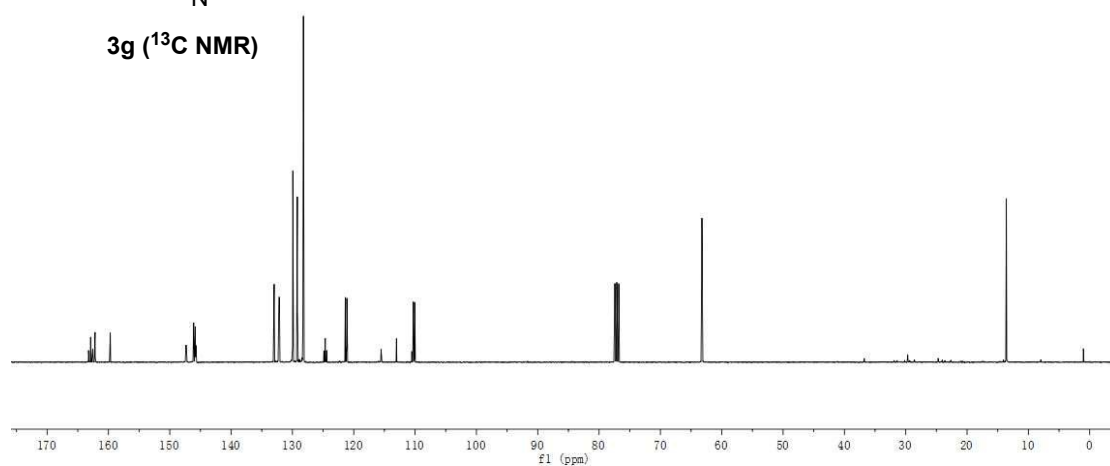


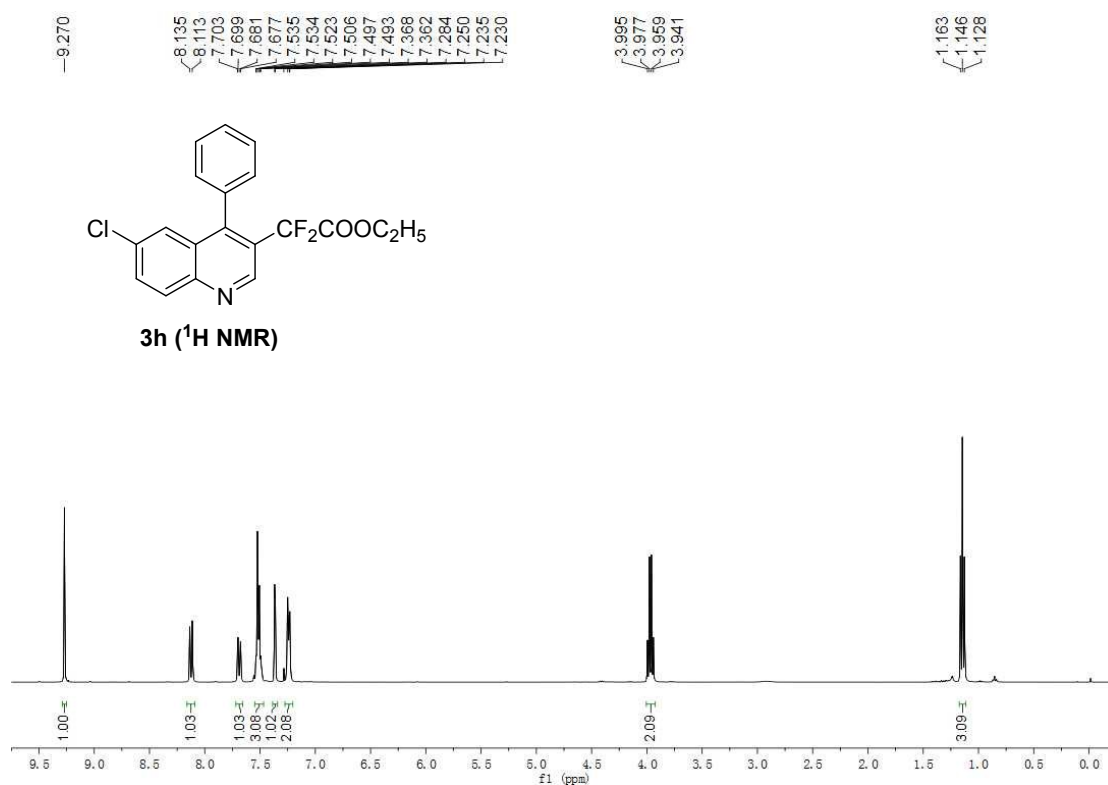
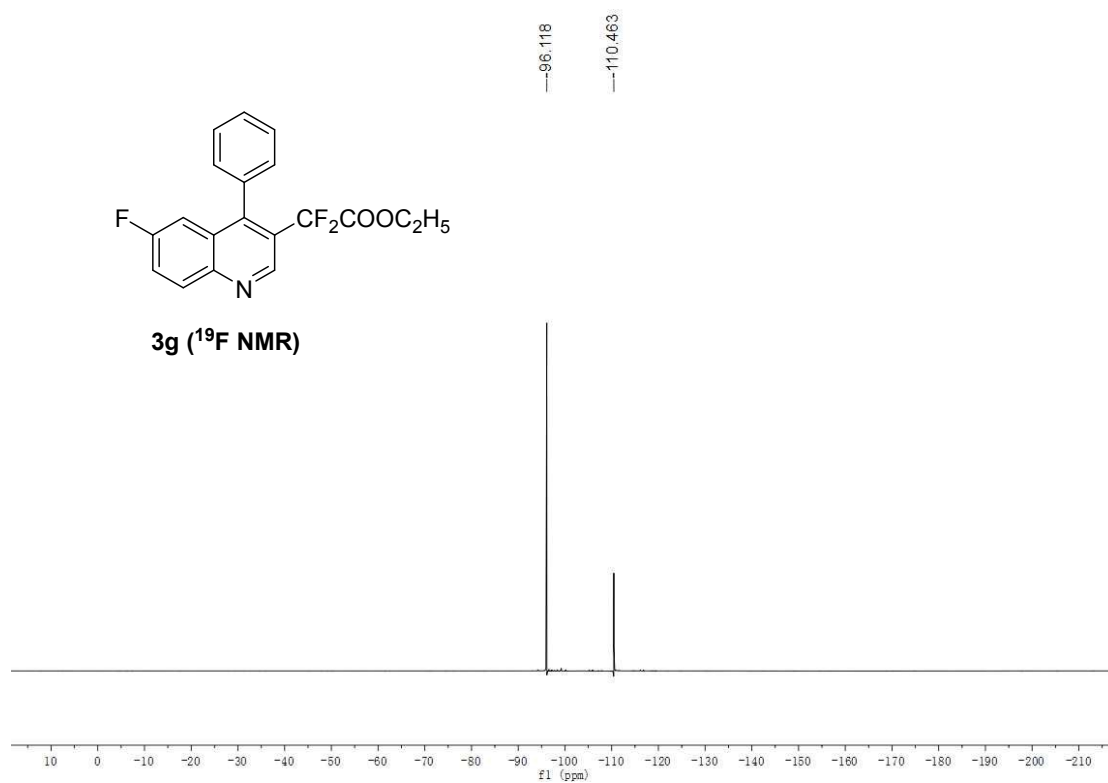


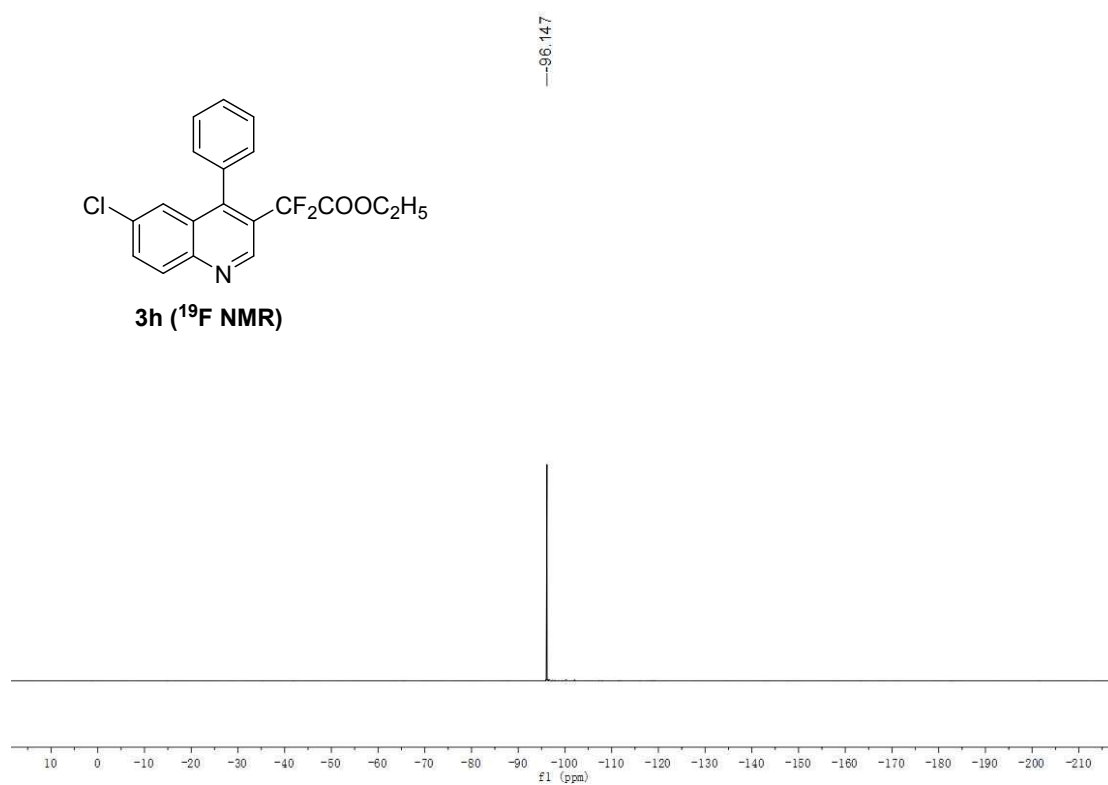
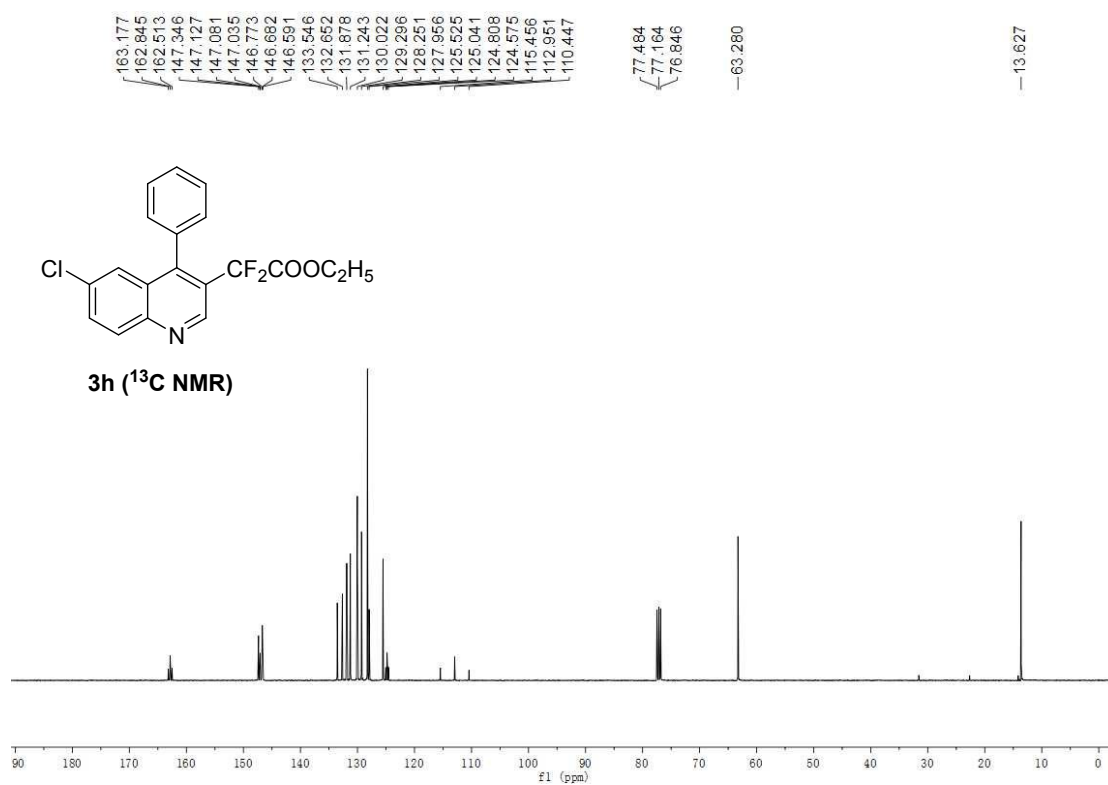
3g (^1H NMR)

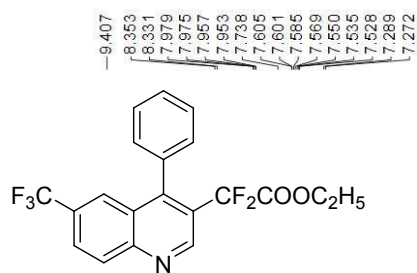


3g (^{13}C NMR)

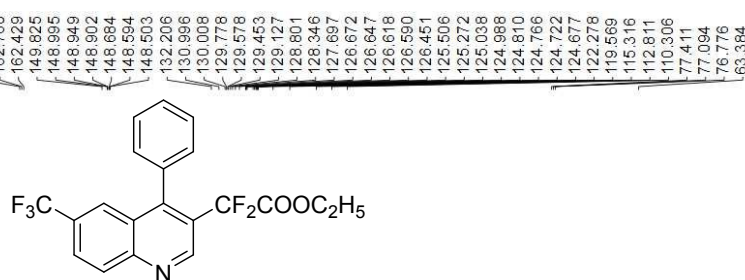
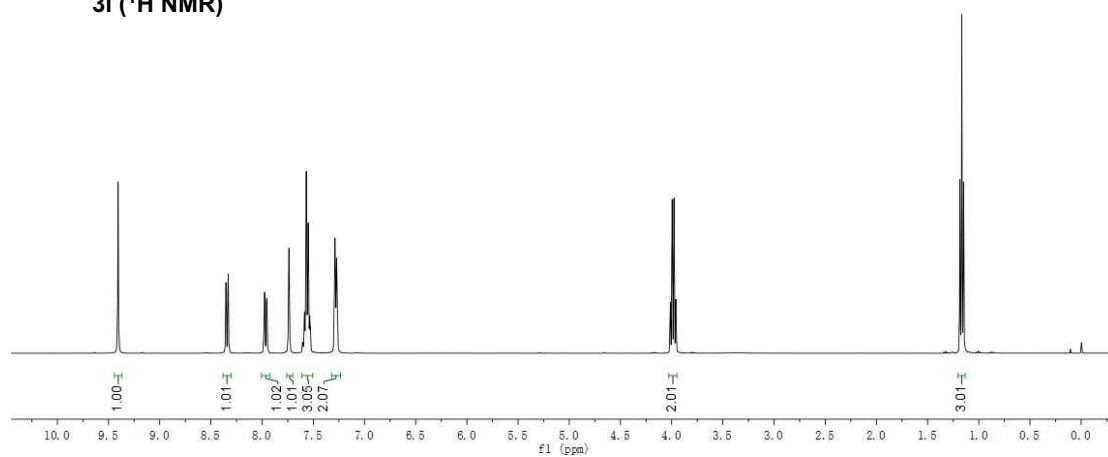




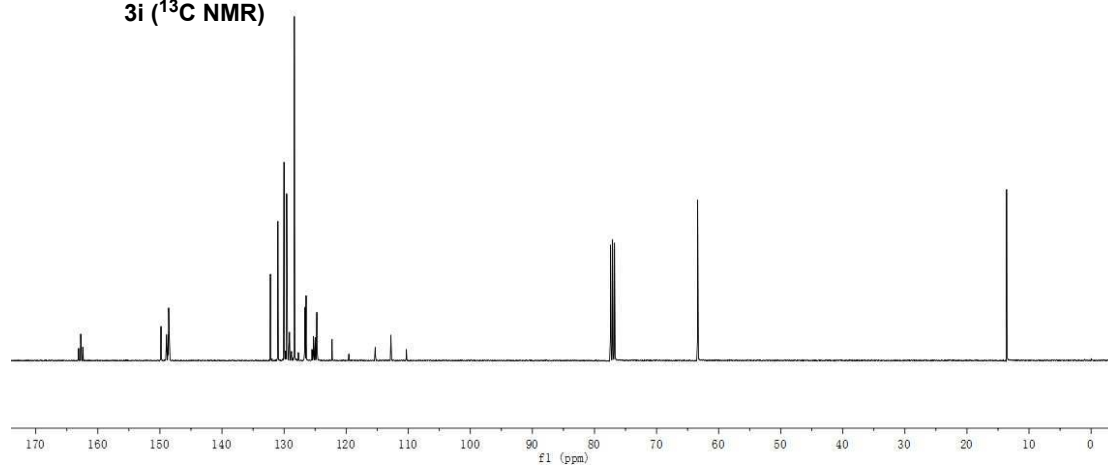


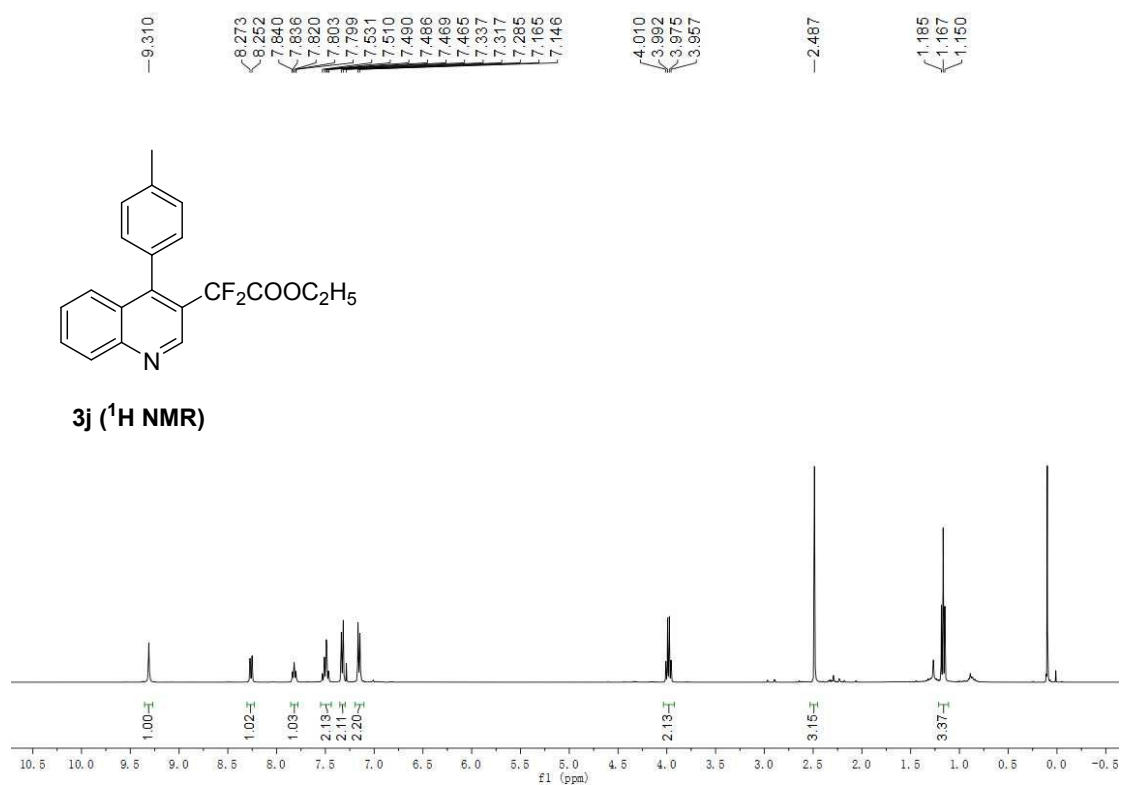
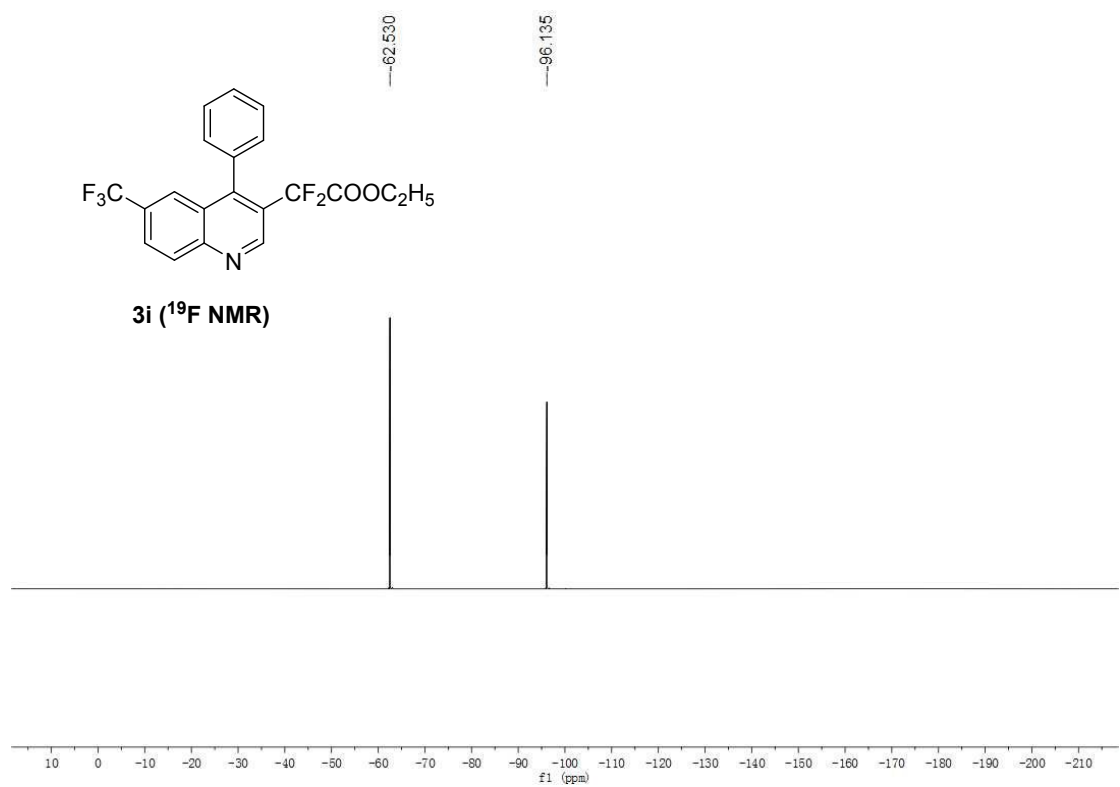


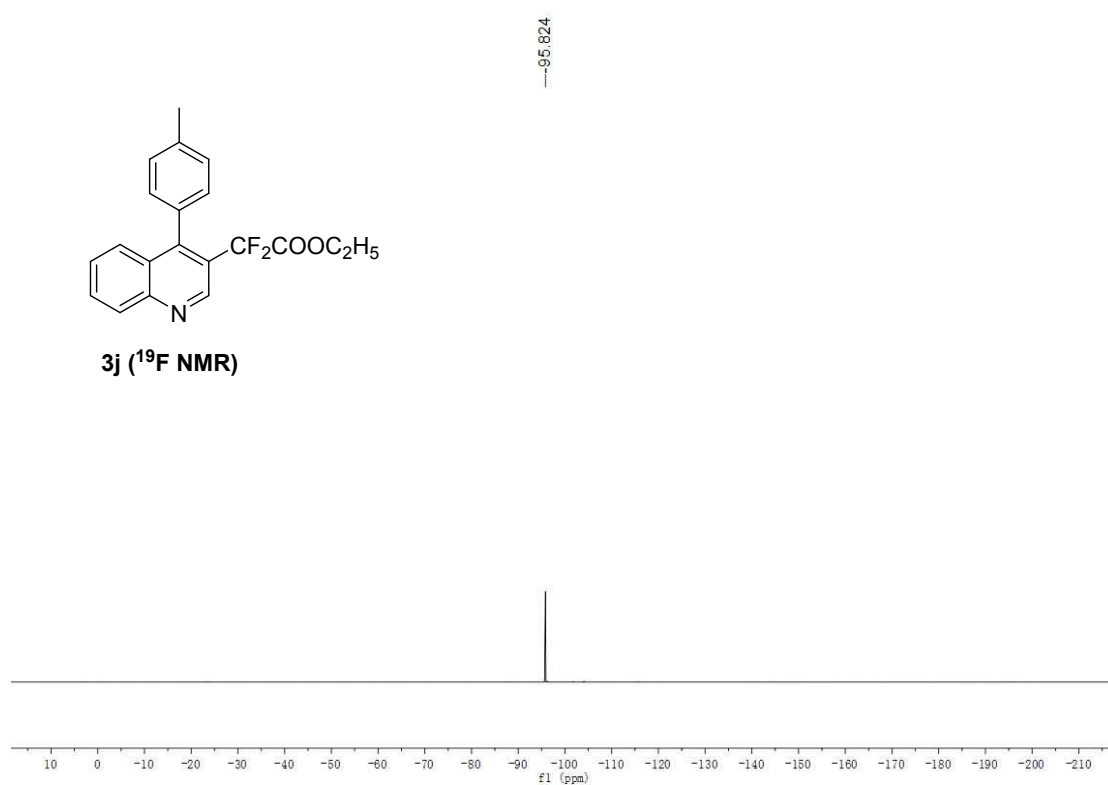
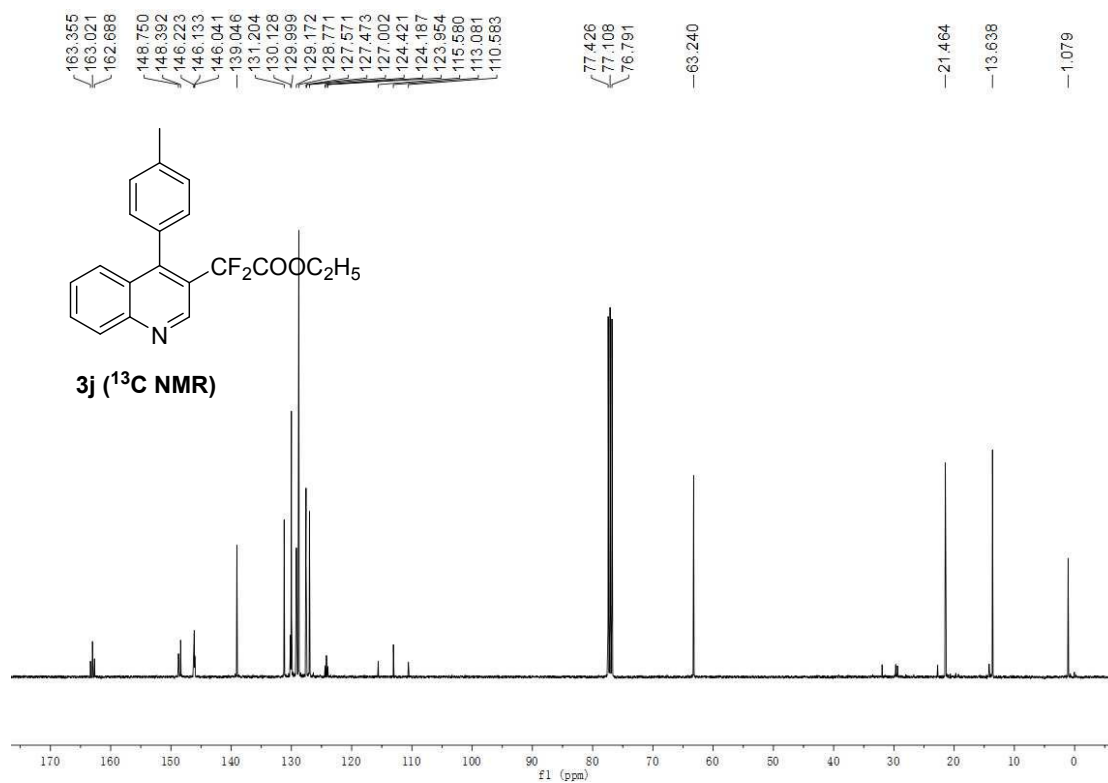
3i (¹H NMR)

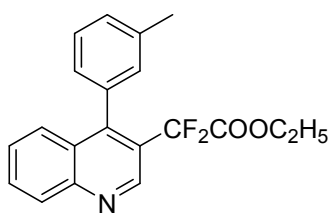


3i (¹³C NMR)

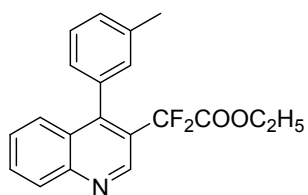
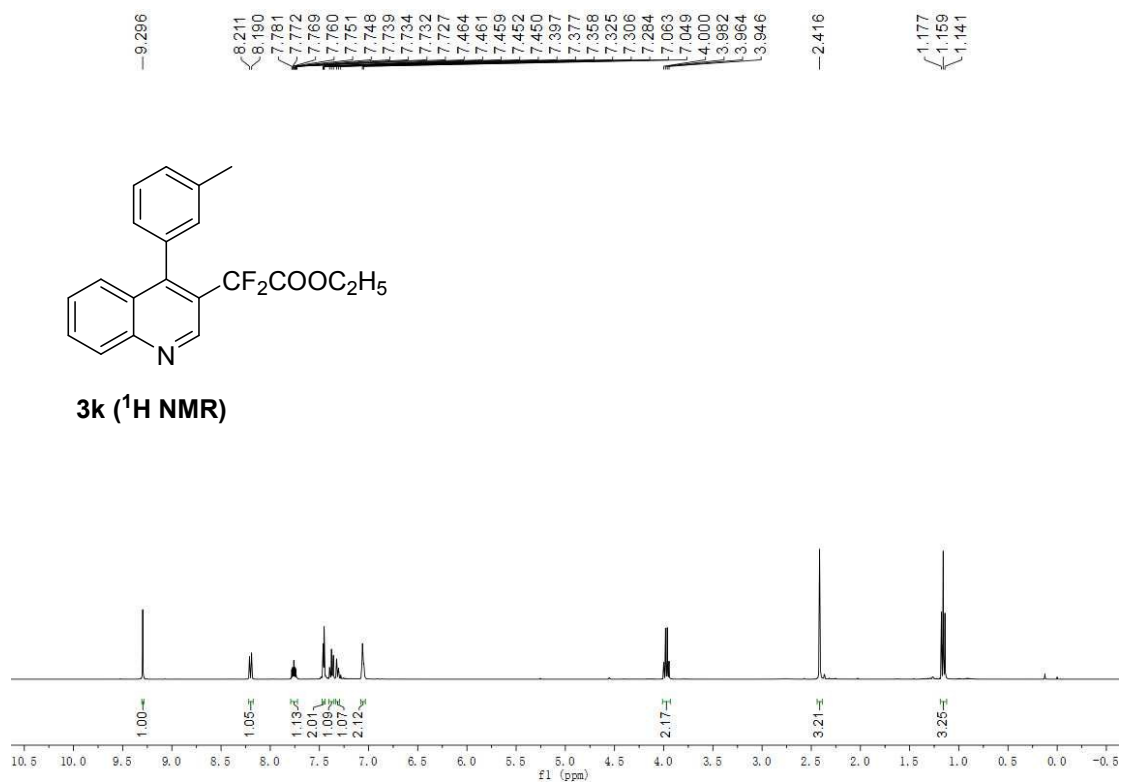




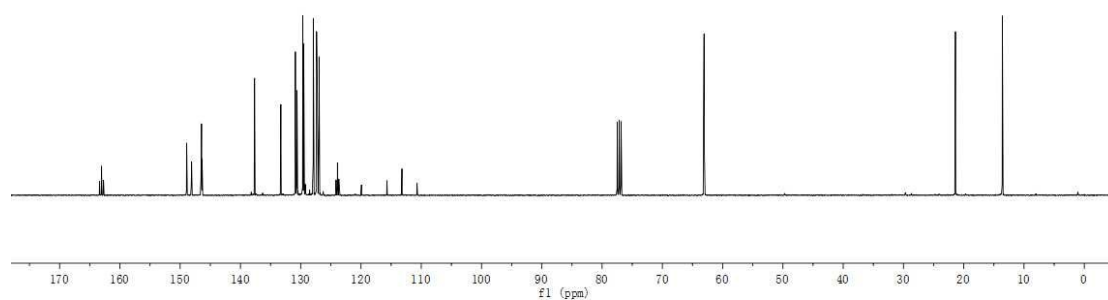


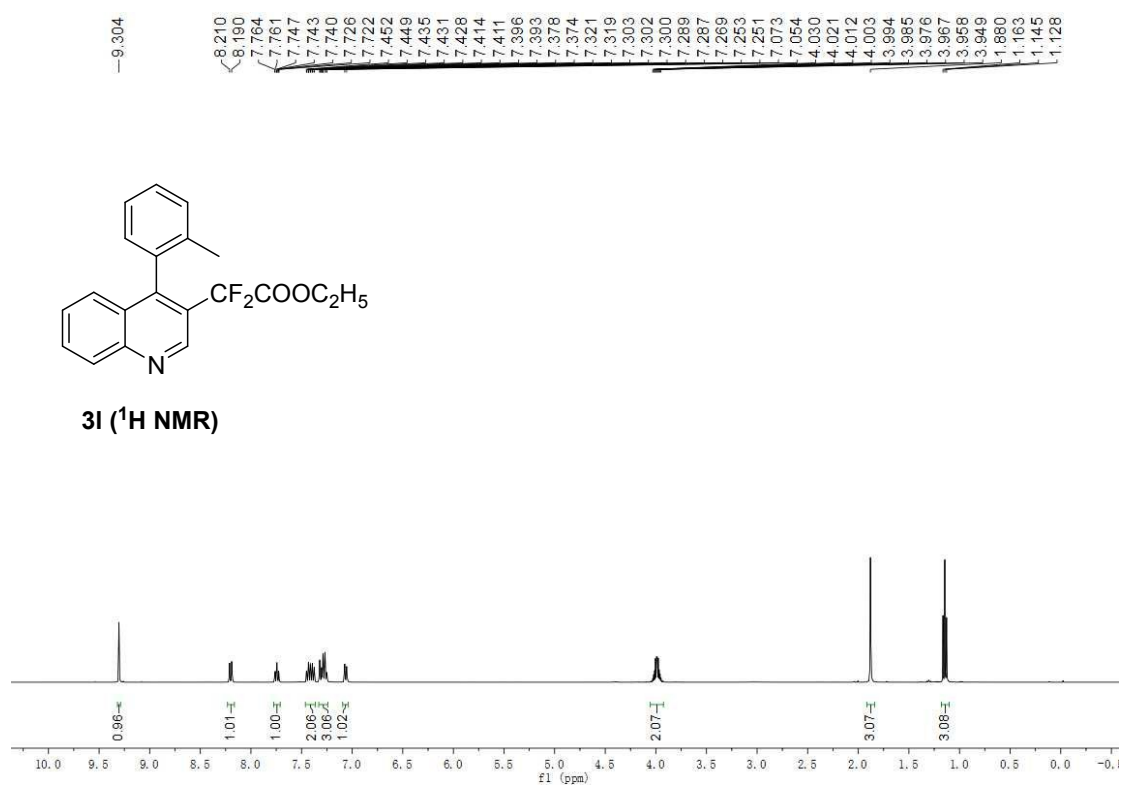
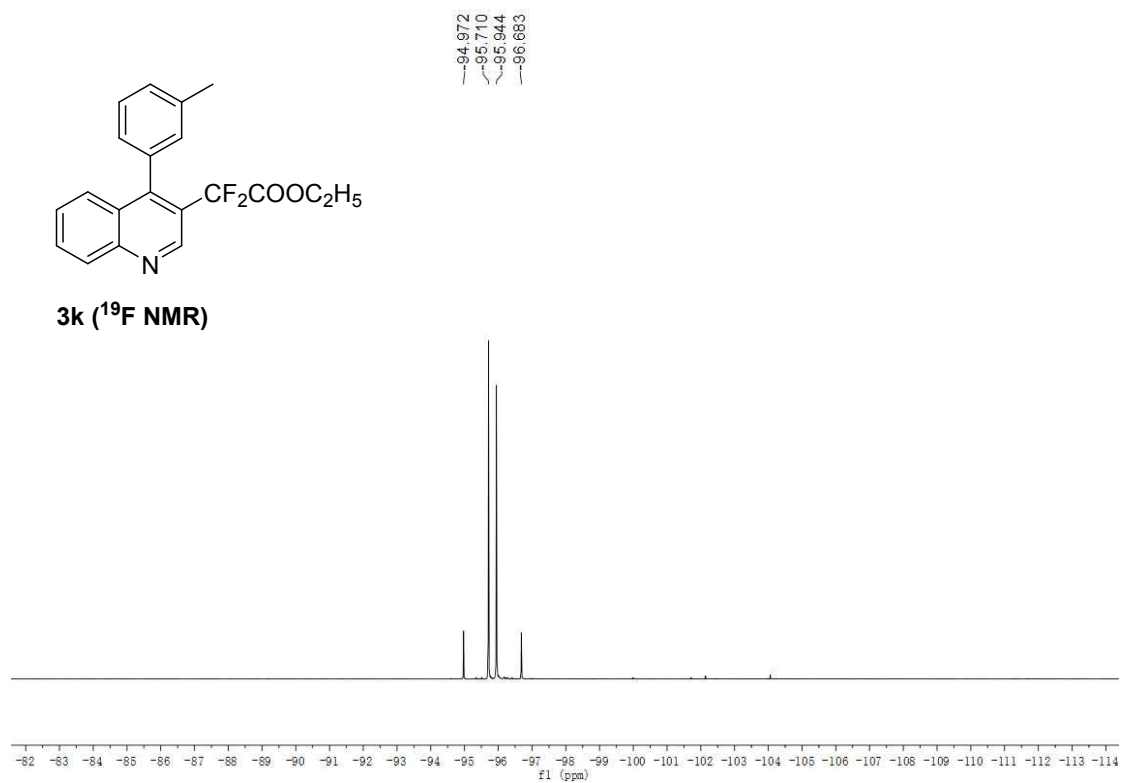


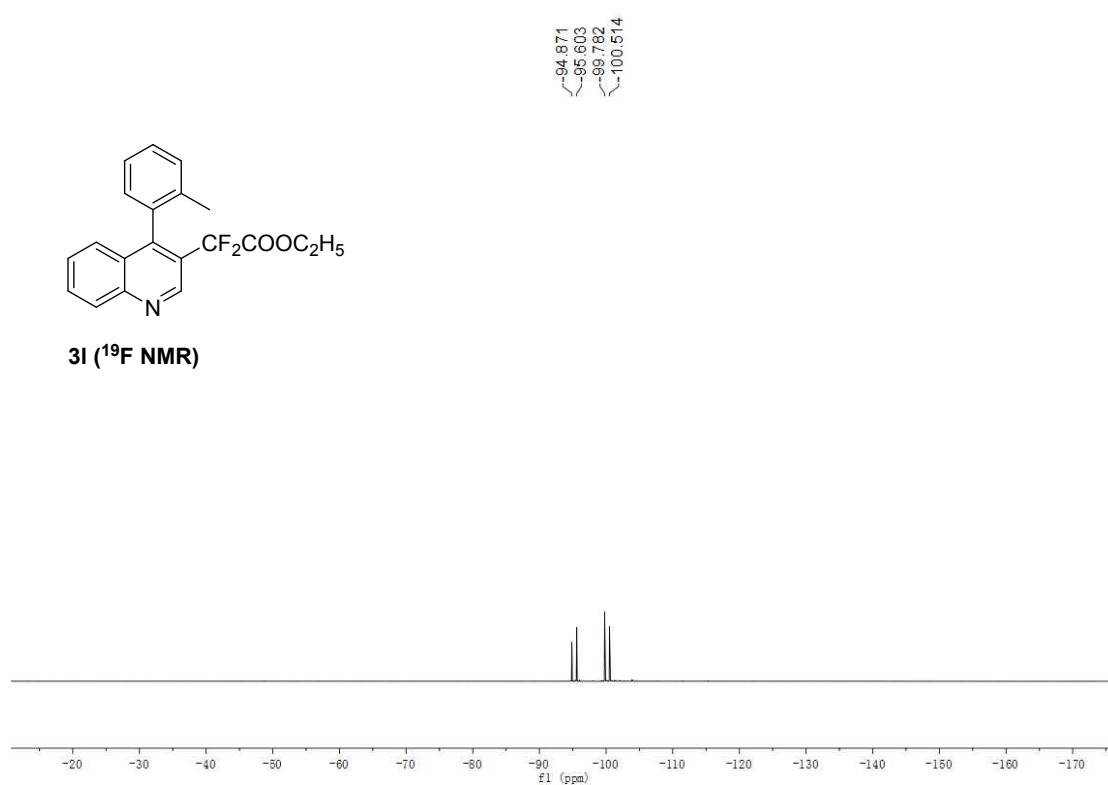
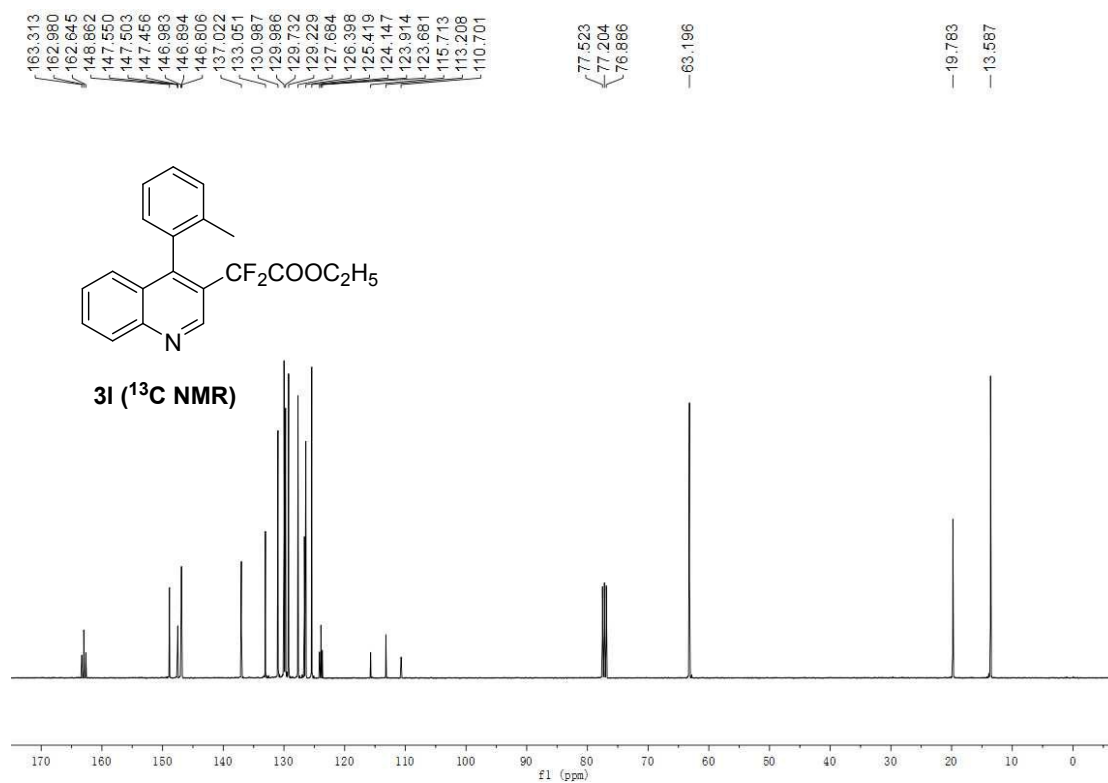
3k (¹H NMR)

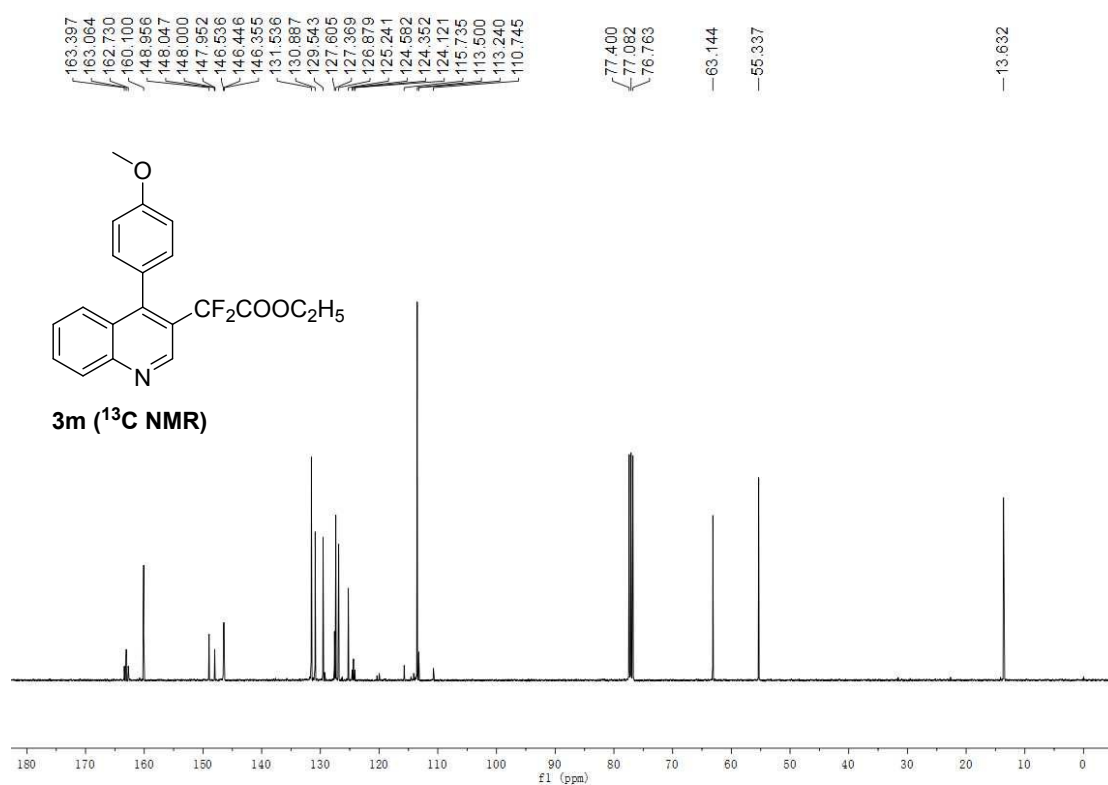
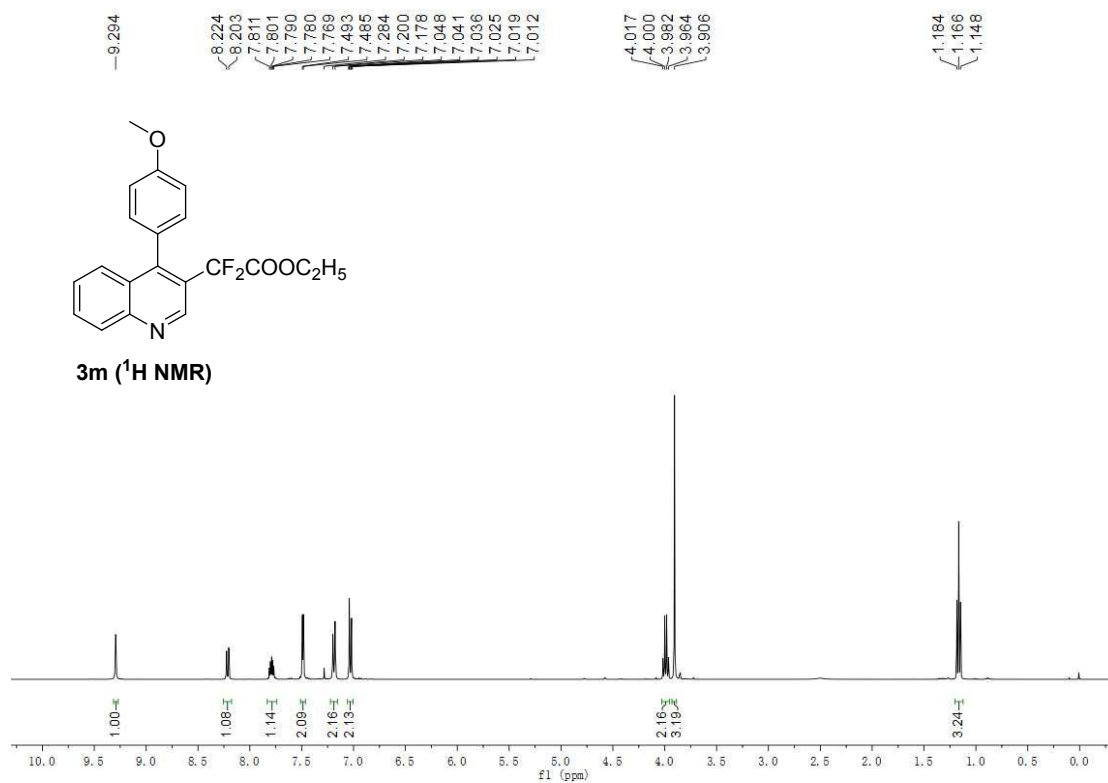


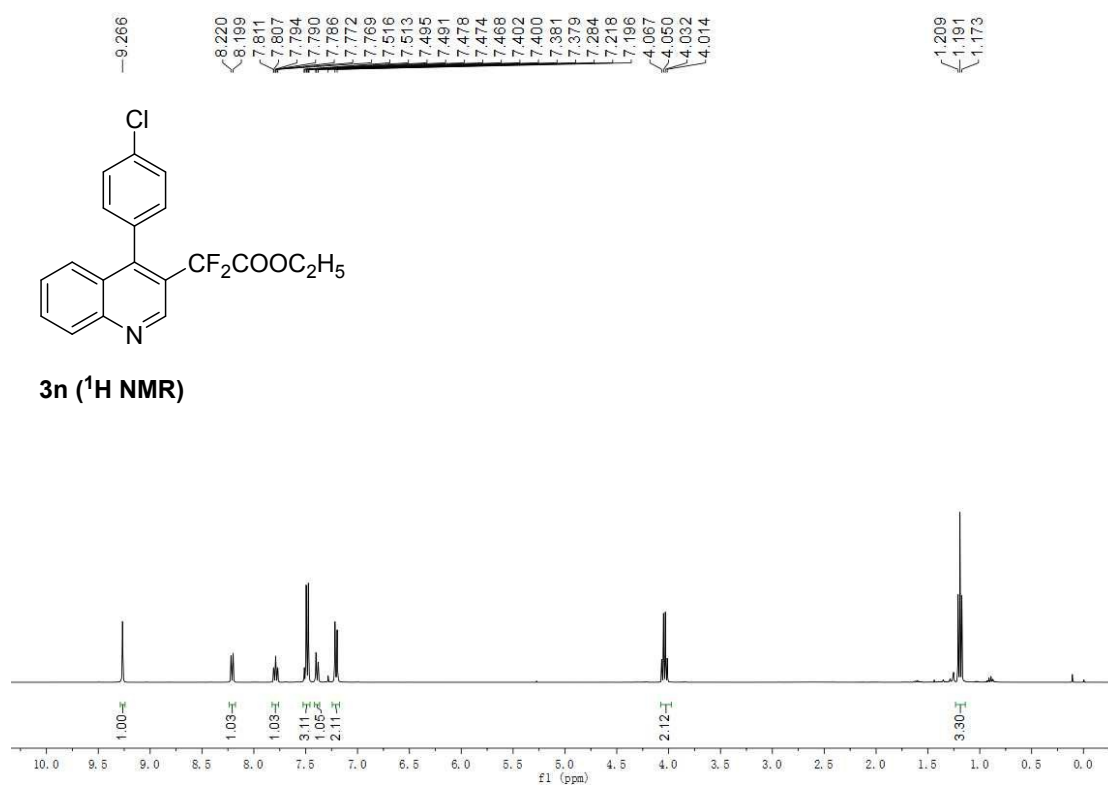
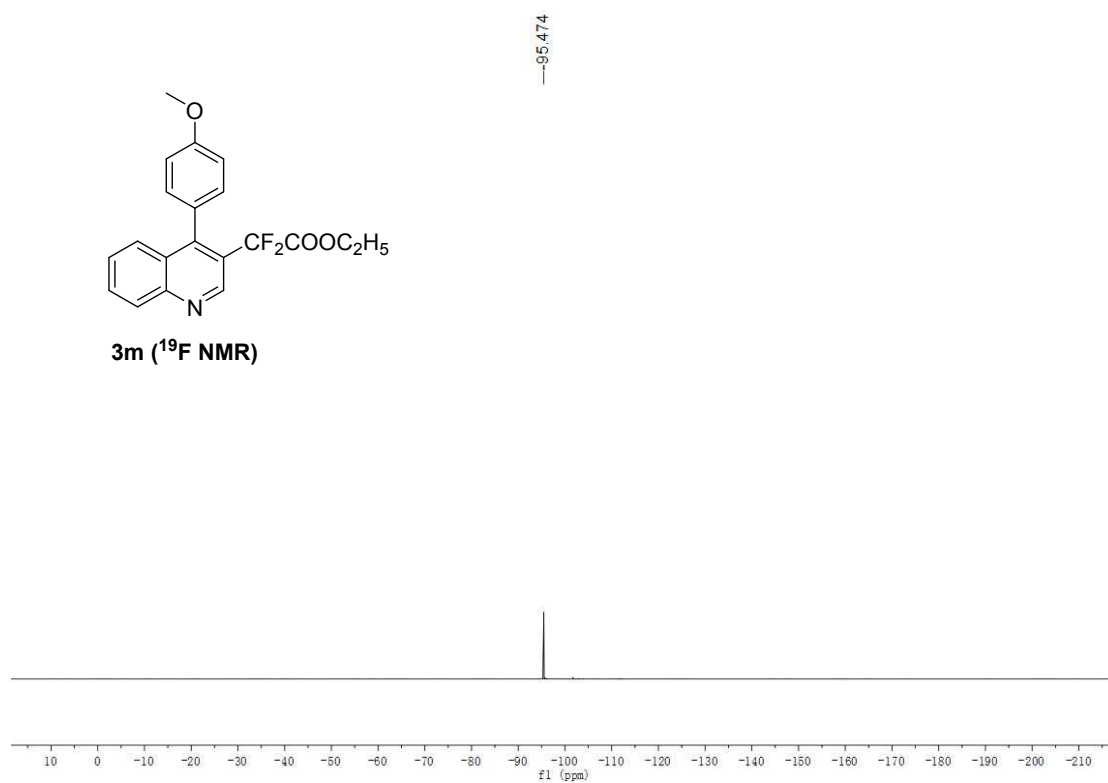
3k (¹³C NMR)

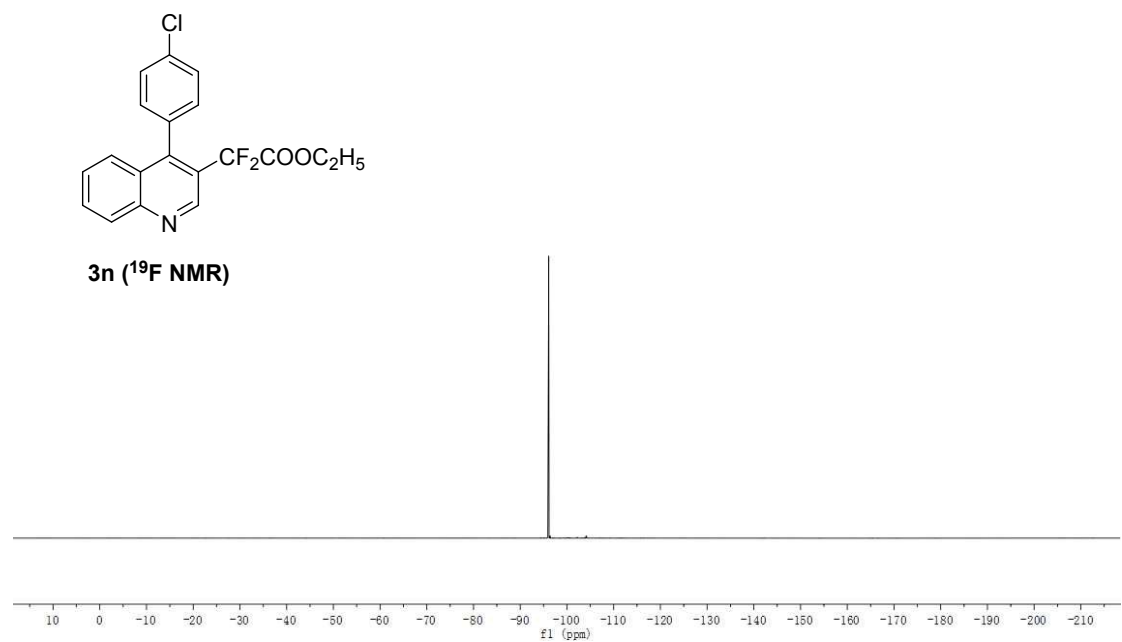
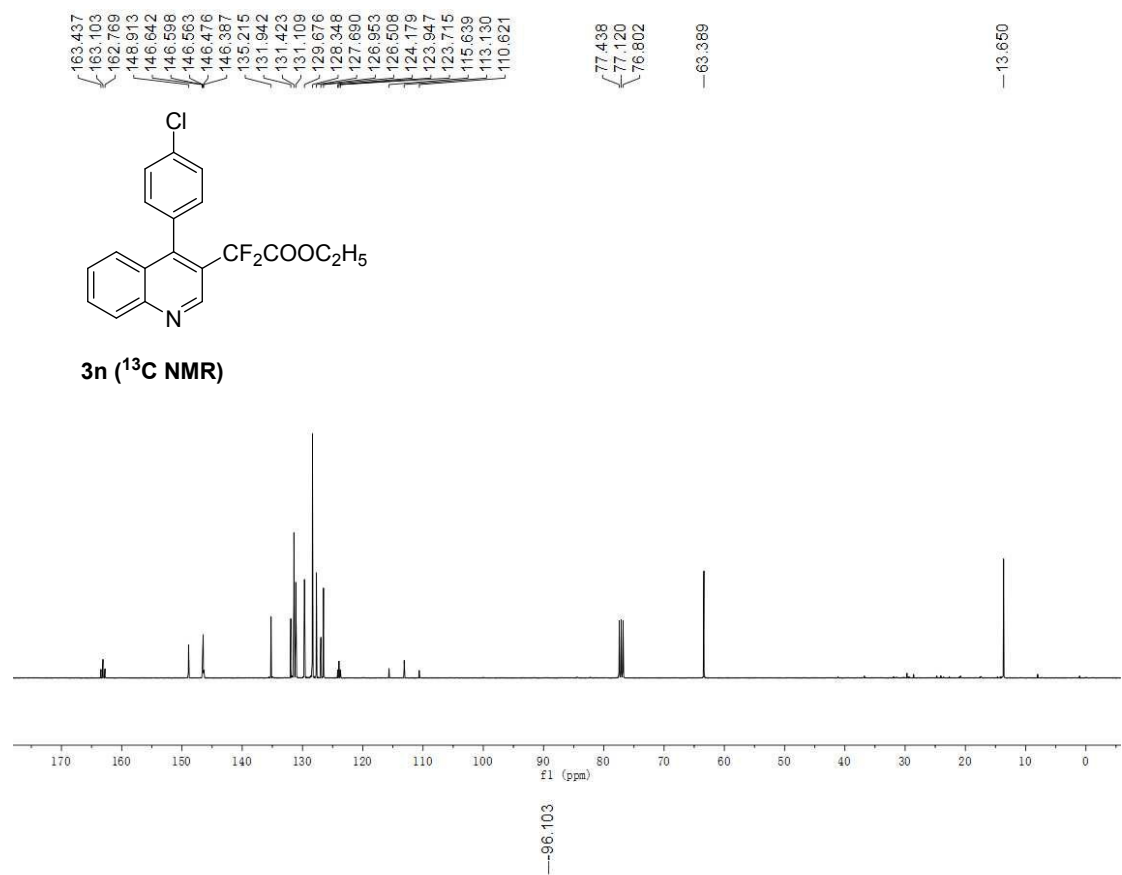


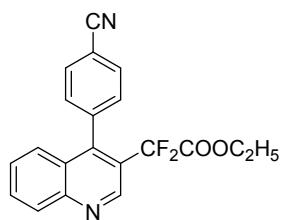




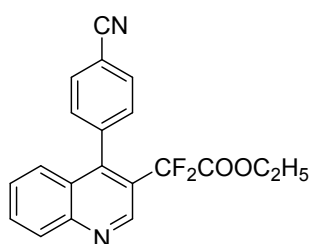
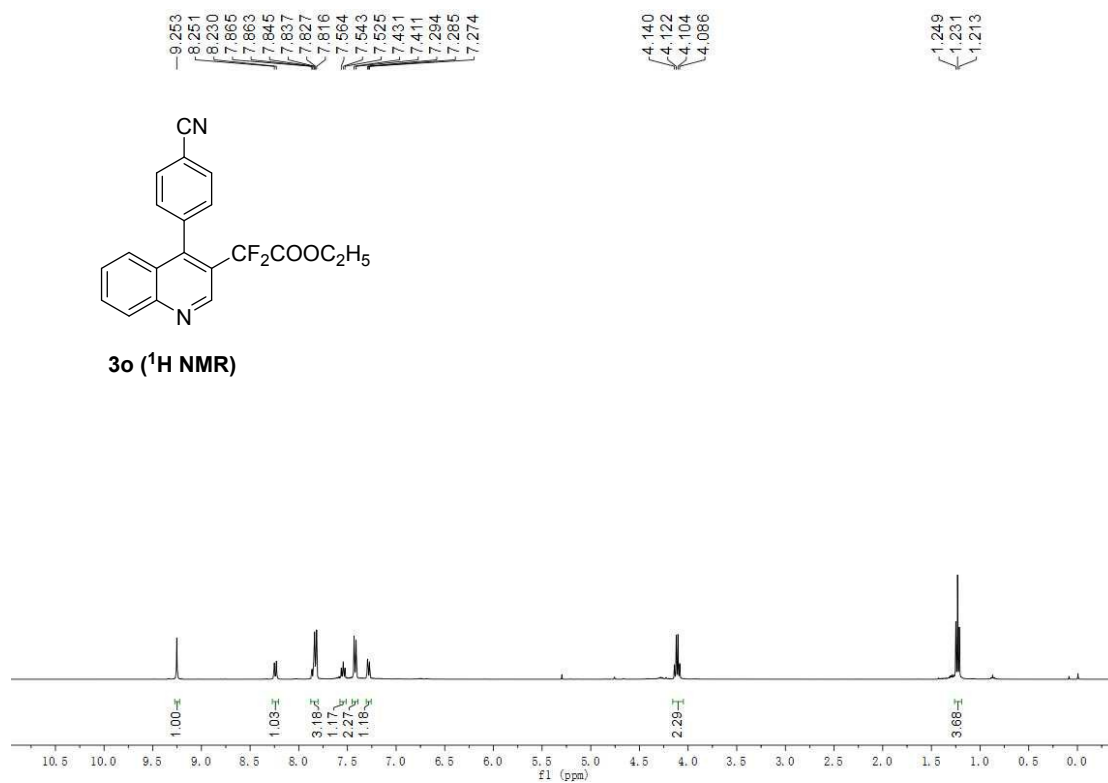




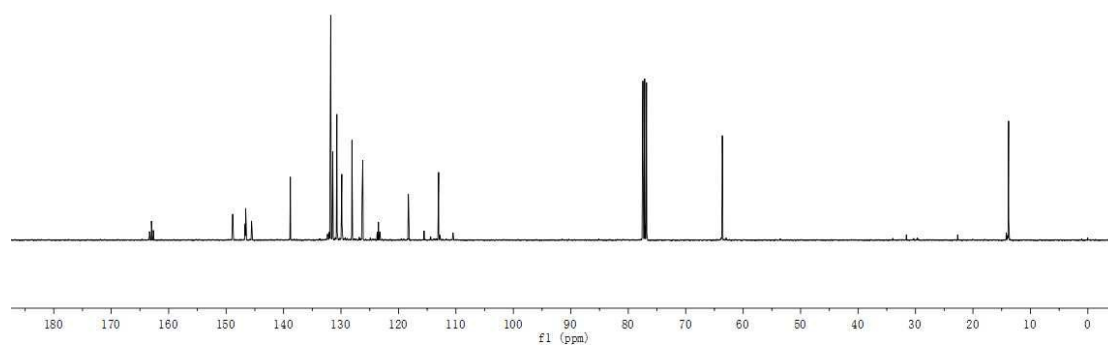


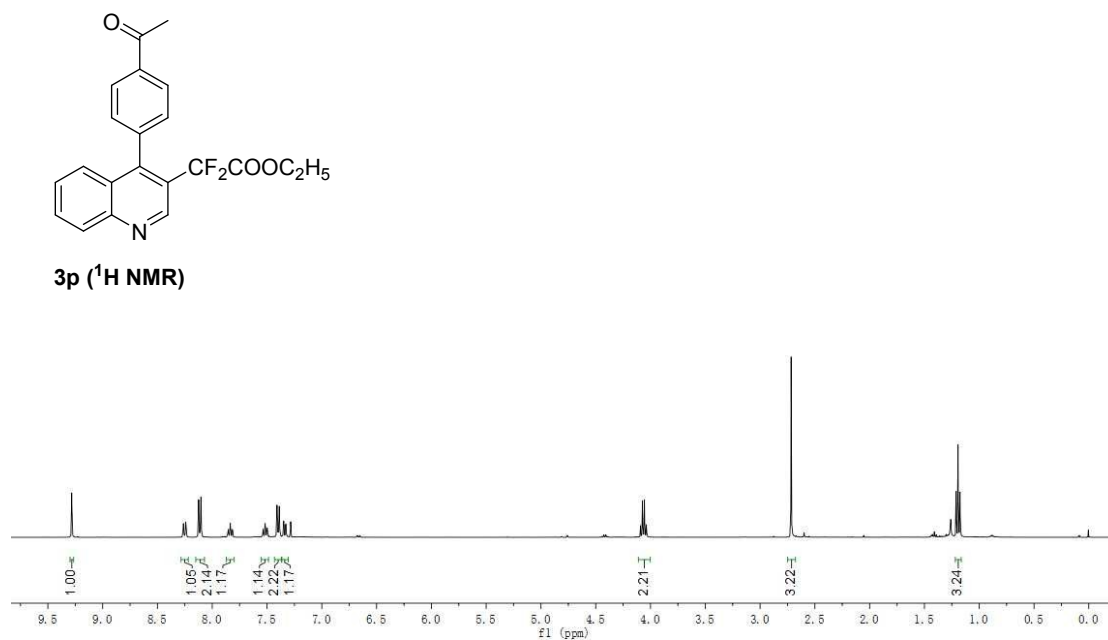
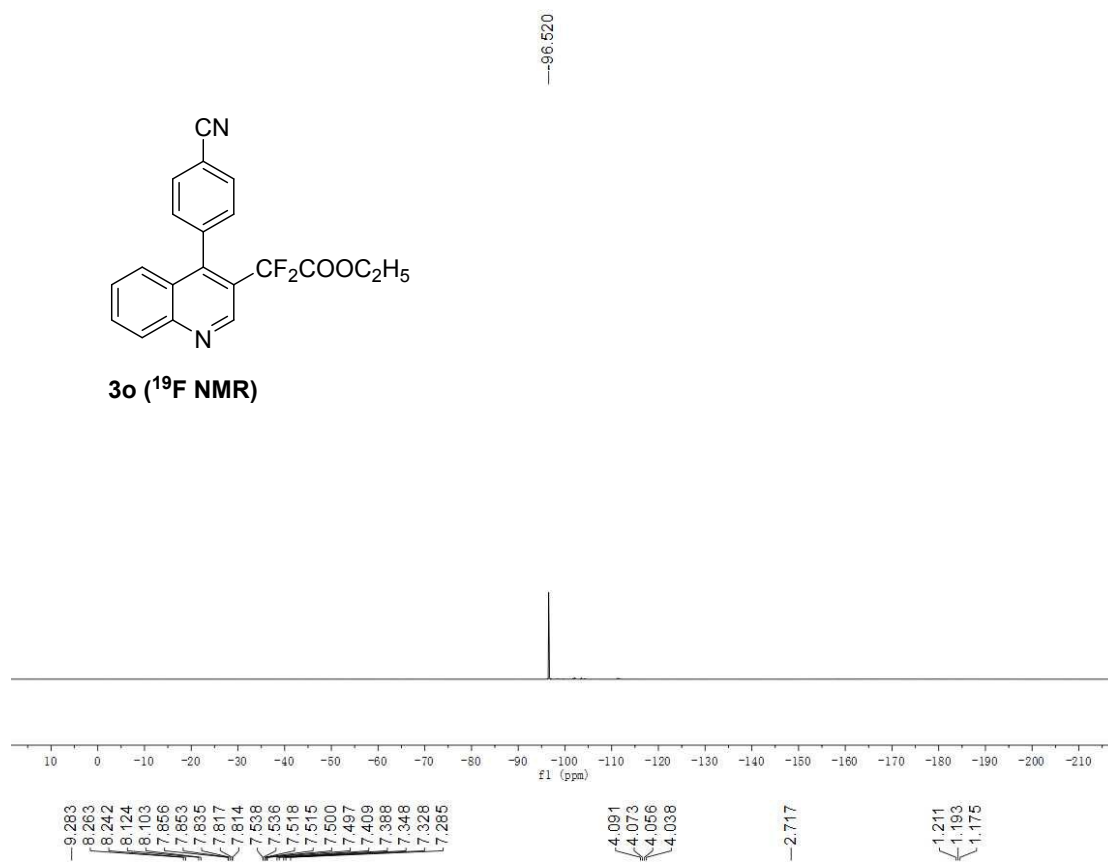


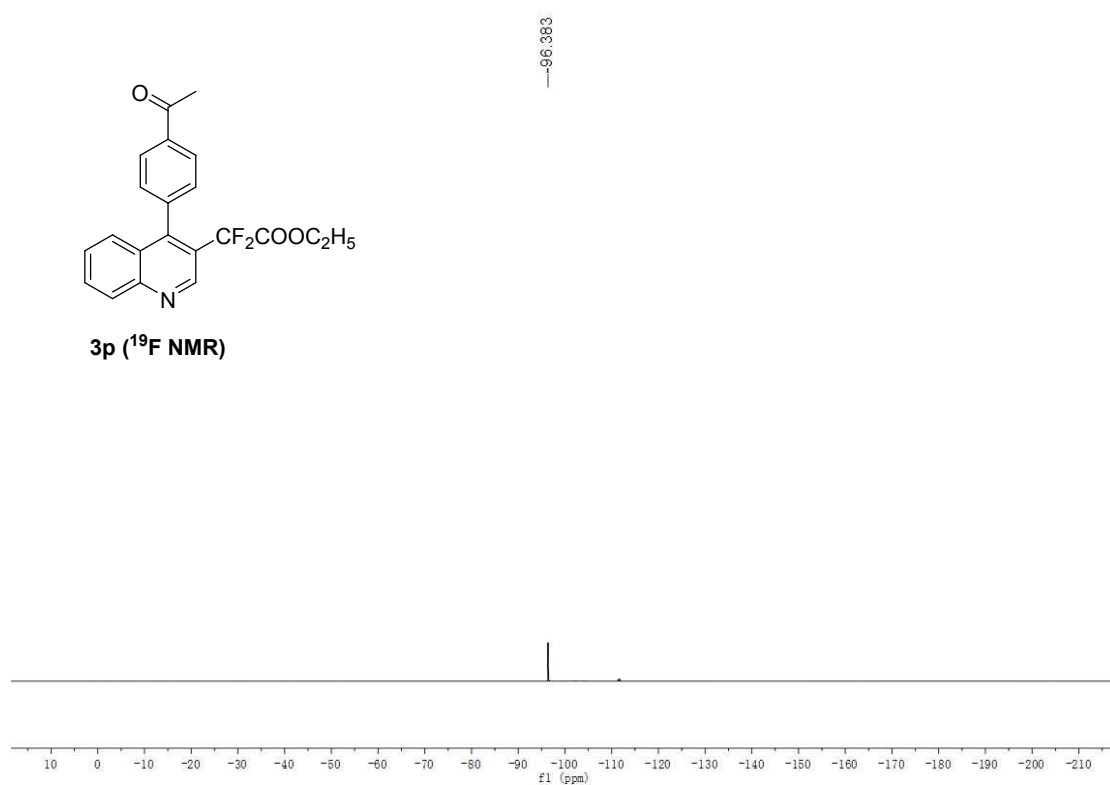
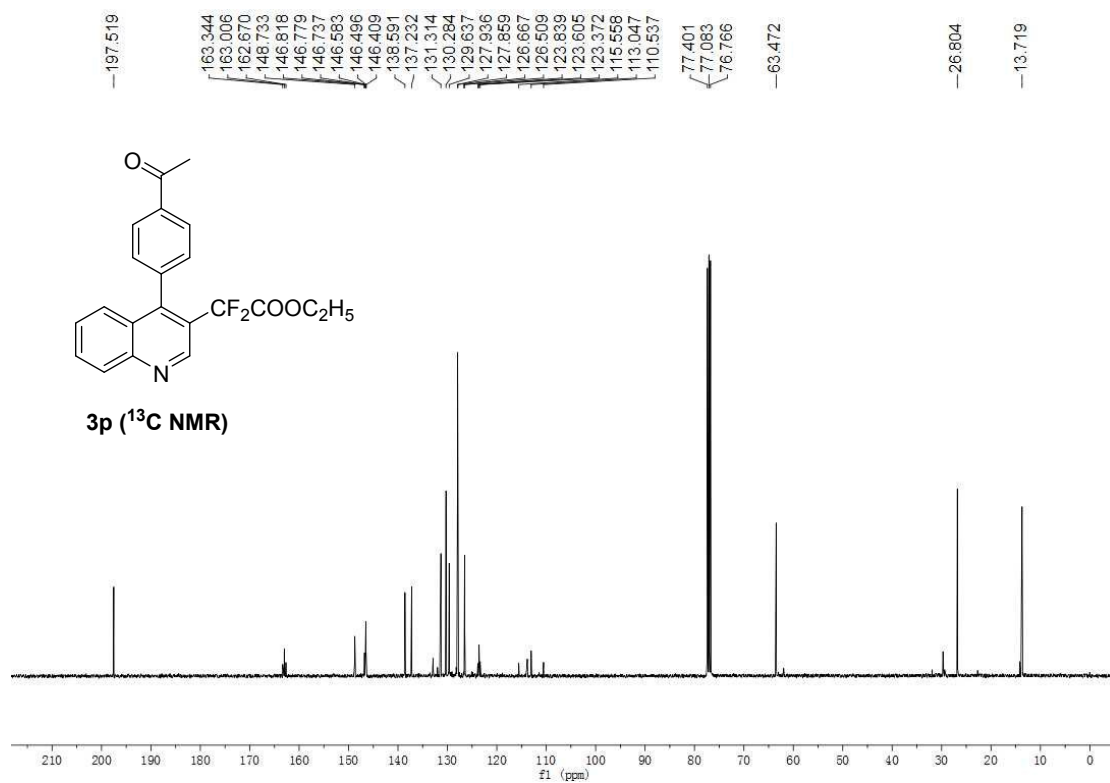
3o (¹H NMR)

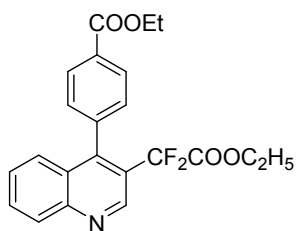


3o (¹³C NMR)

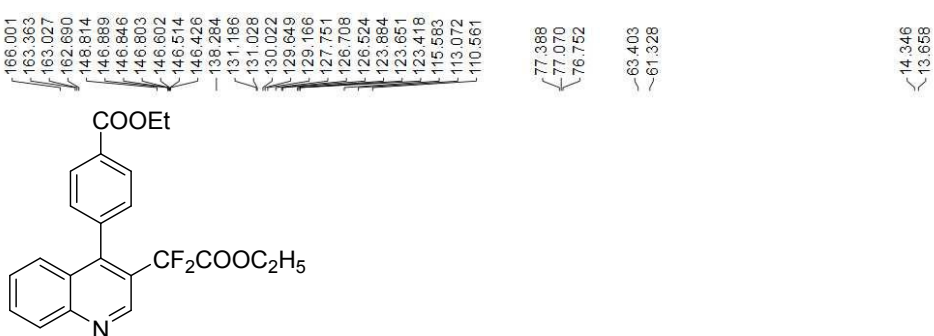
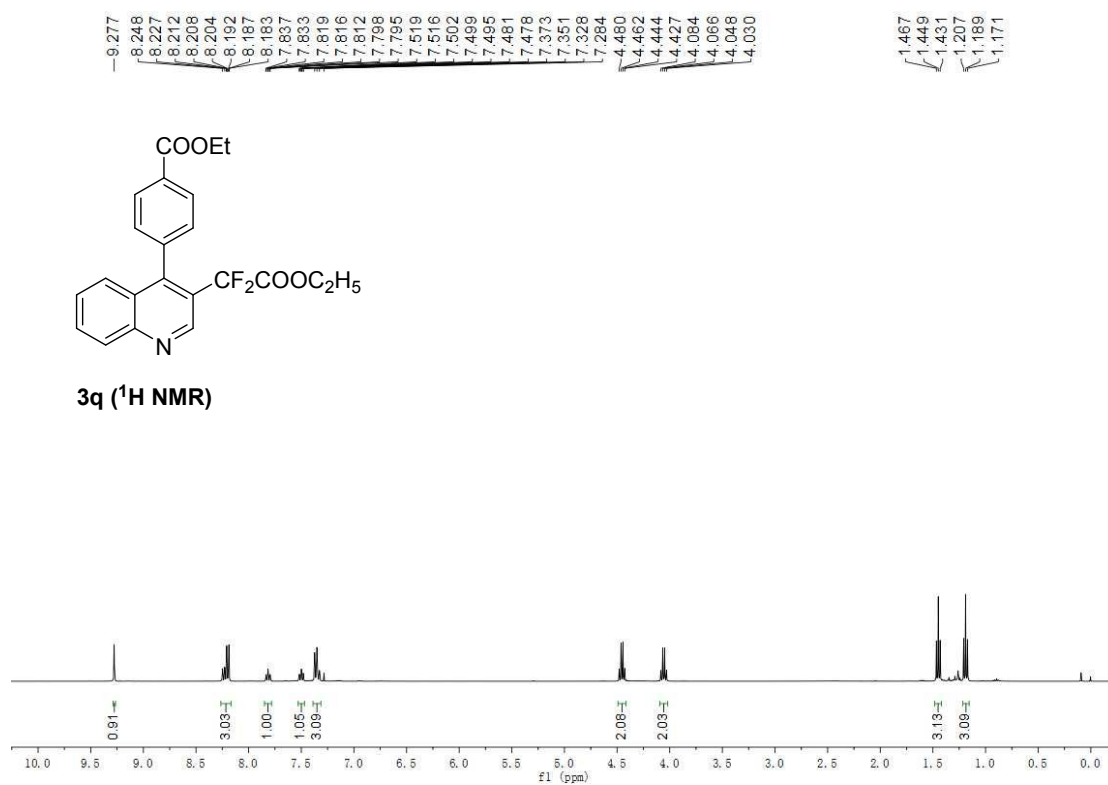




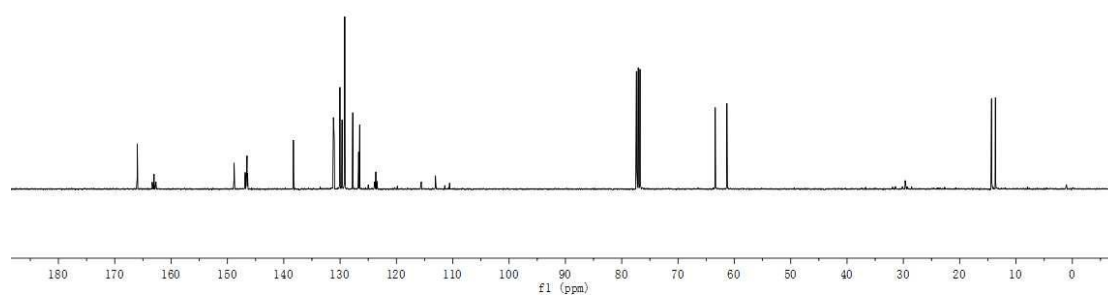


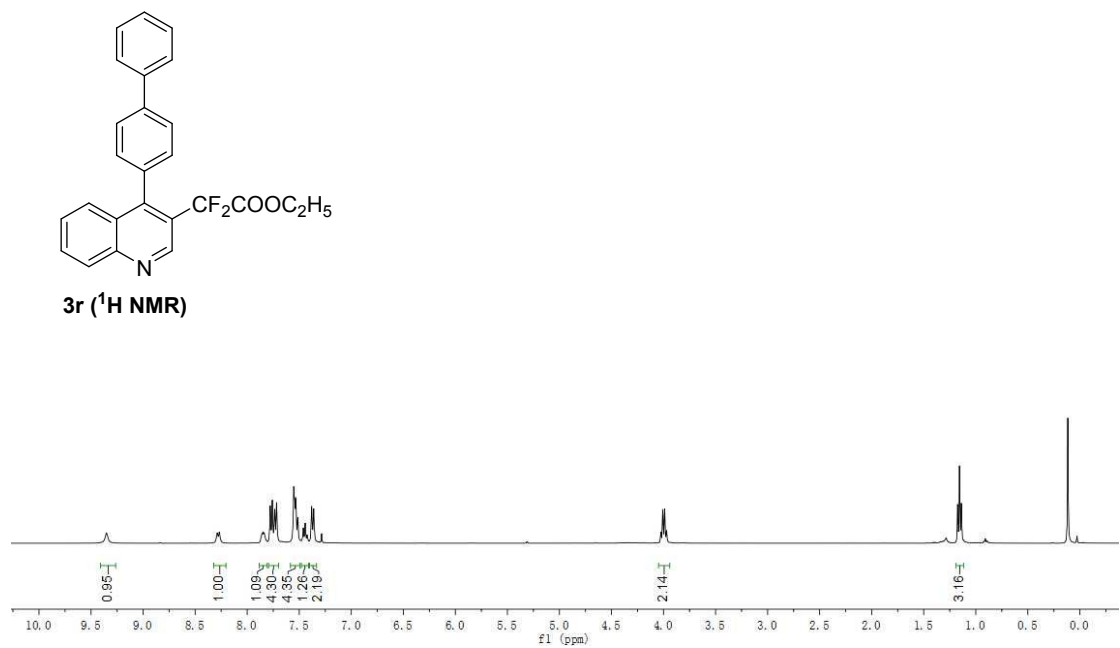
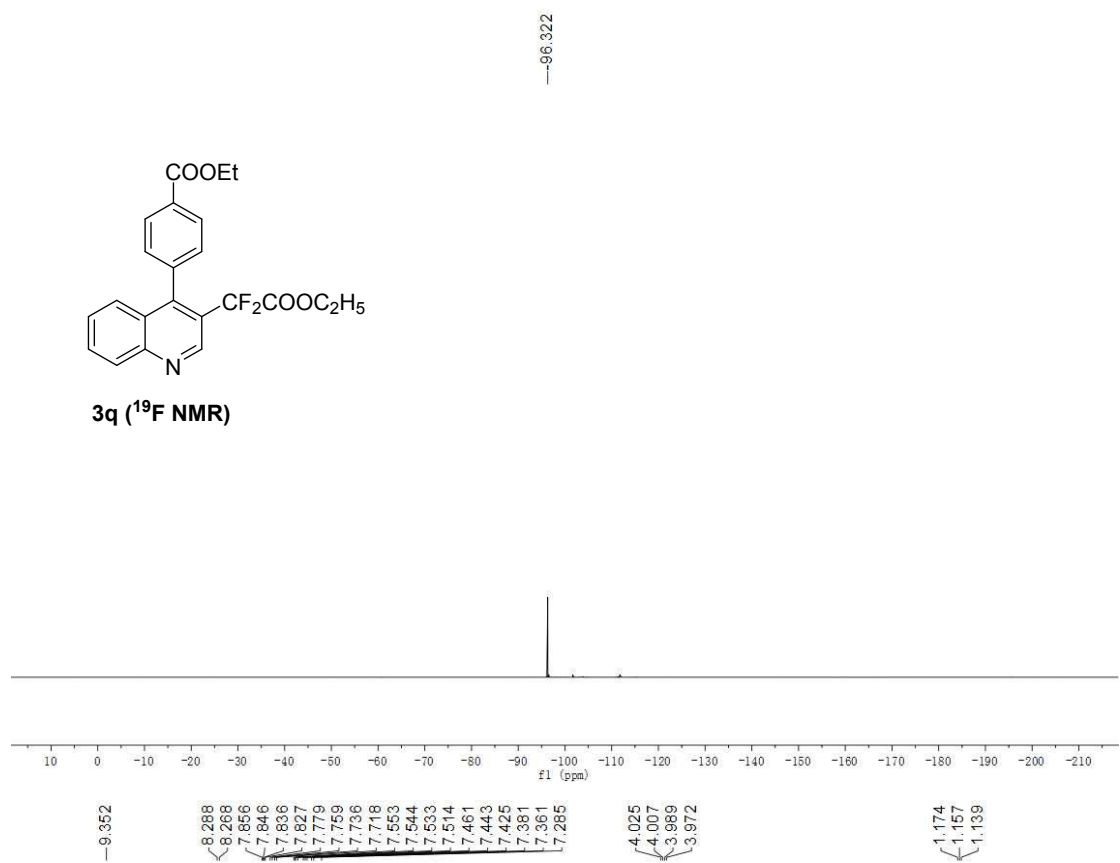


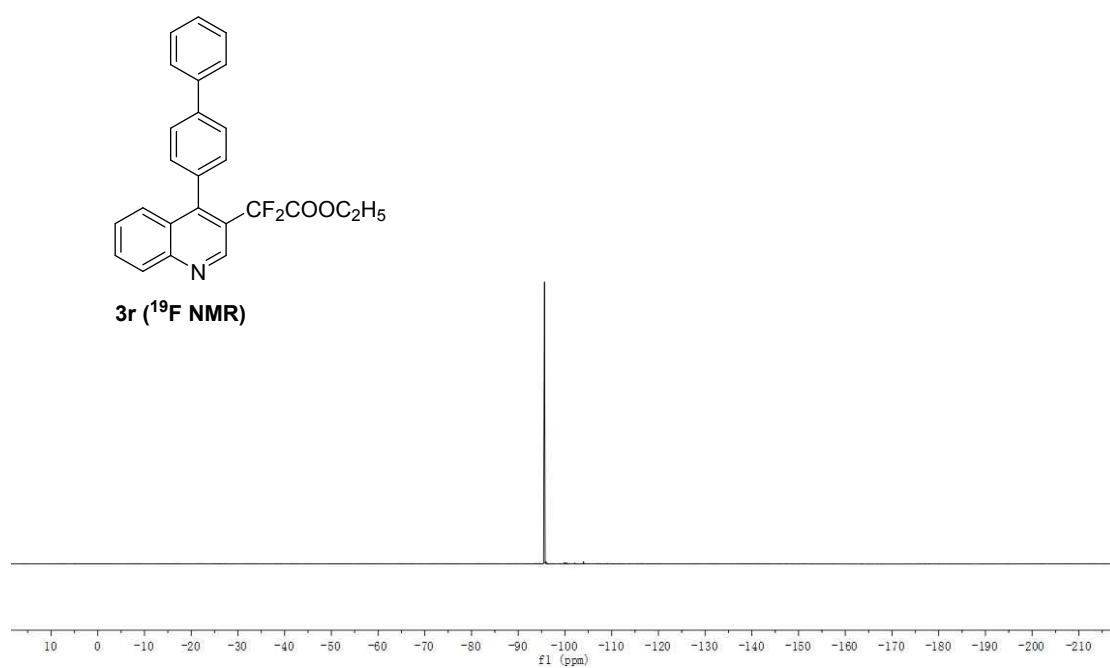
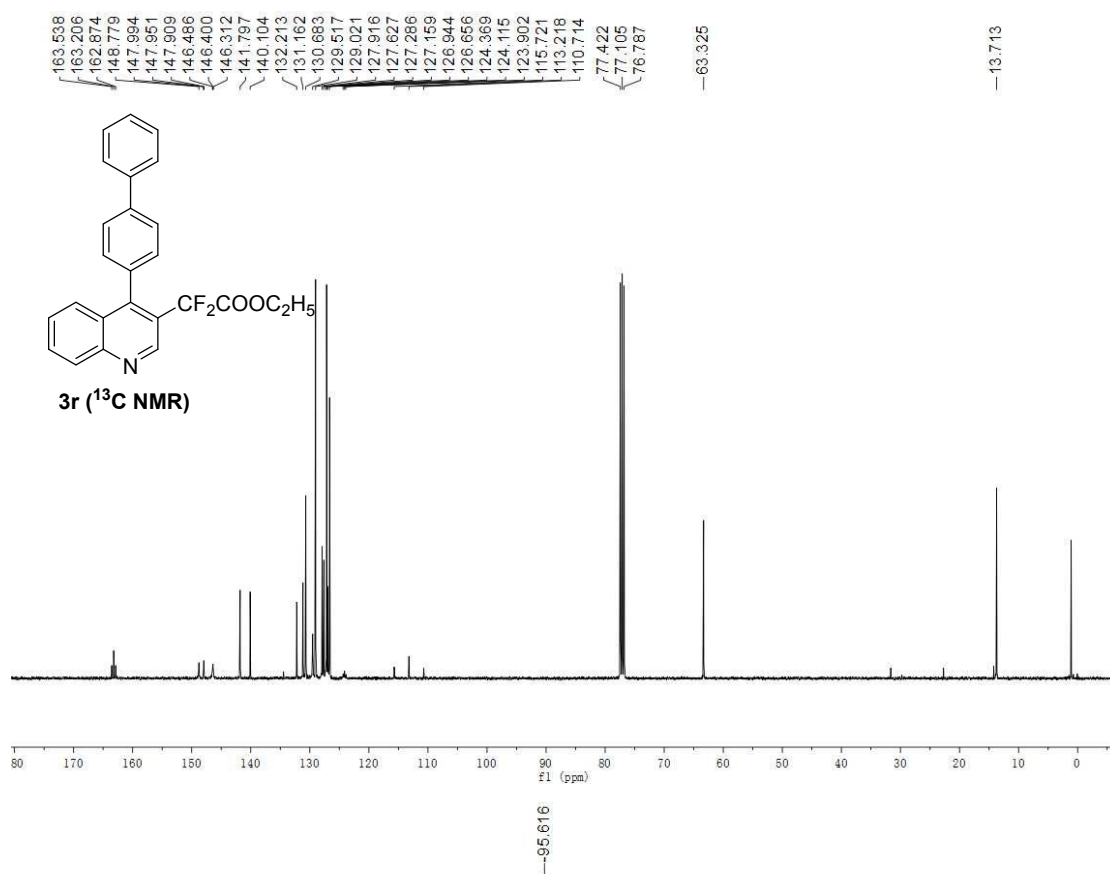
3q (¹H NMR)

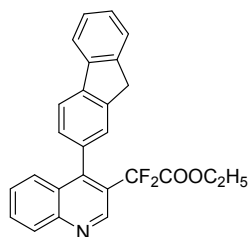


3q (¹³C NMR)

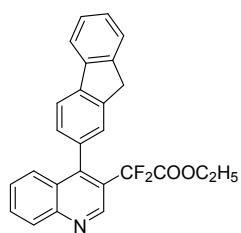
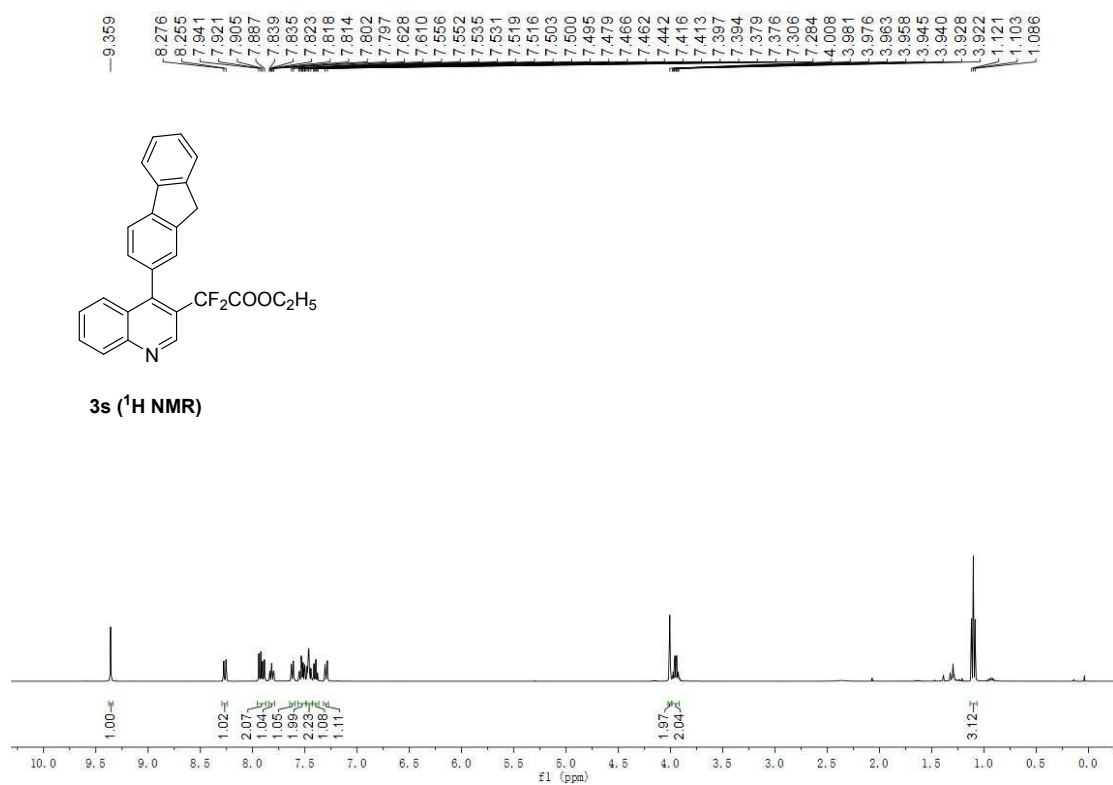




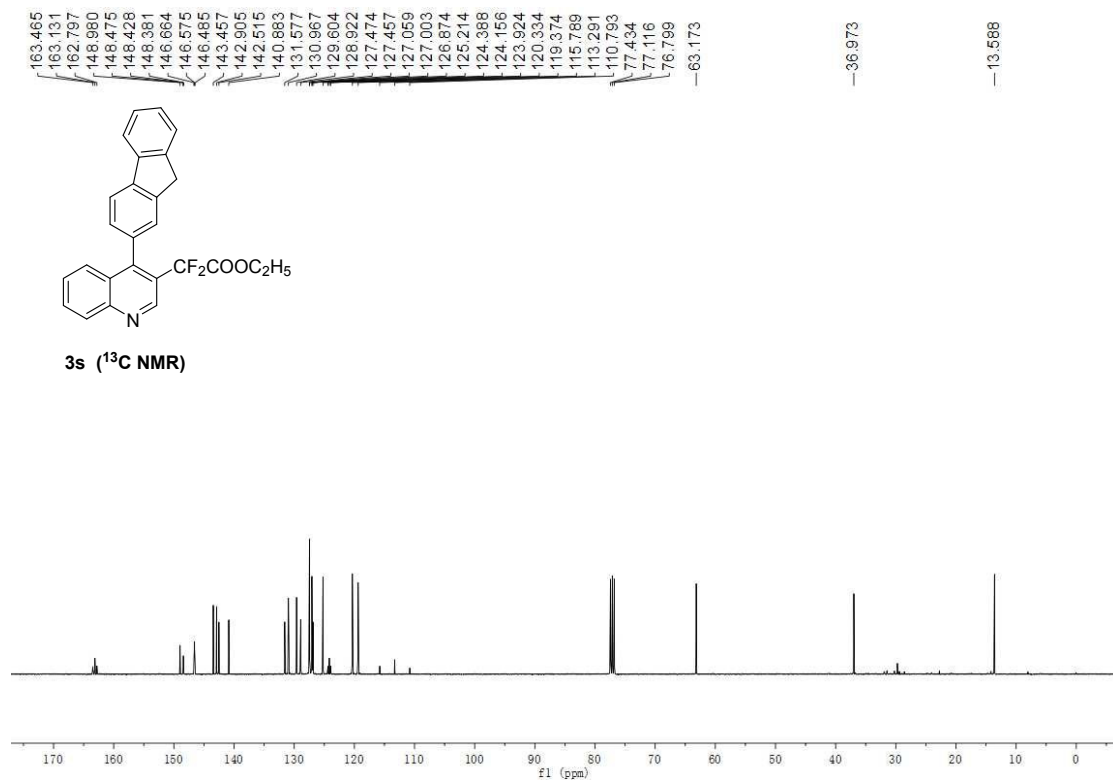


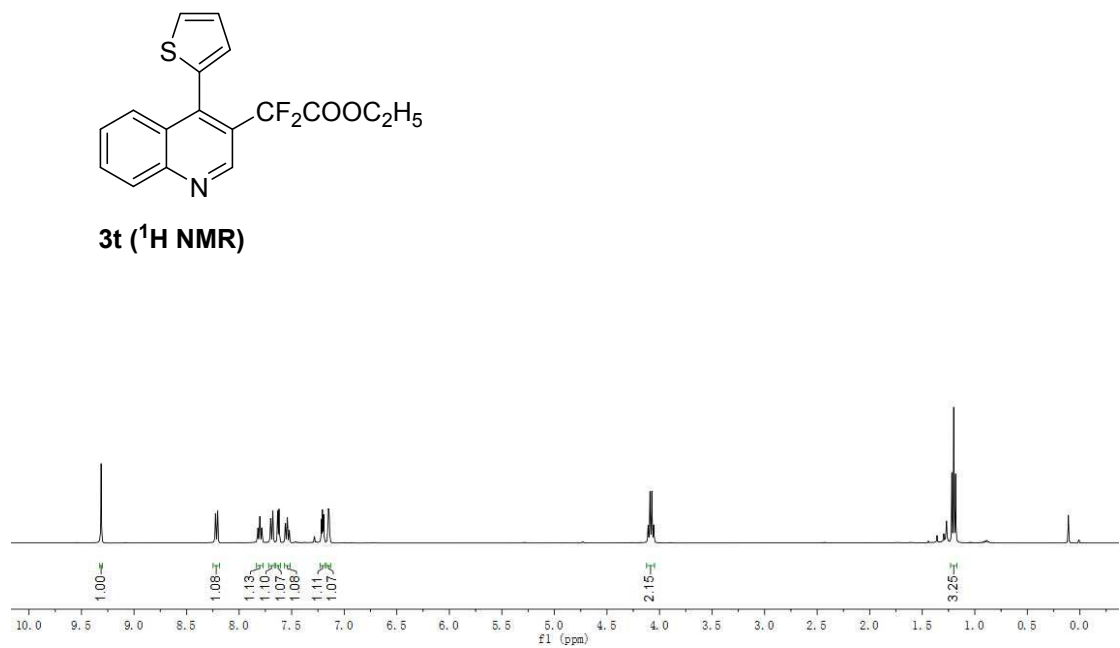
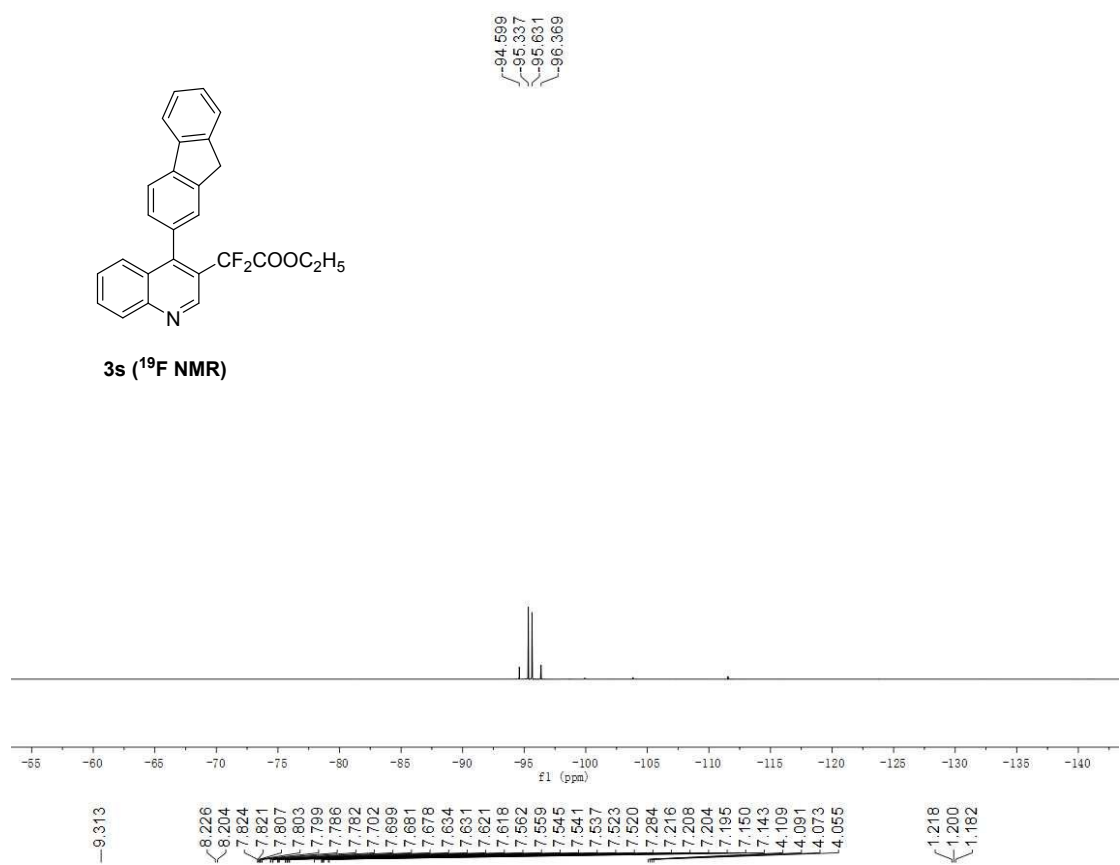


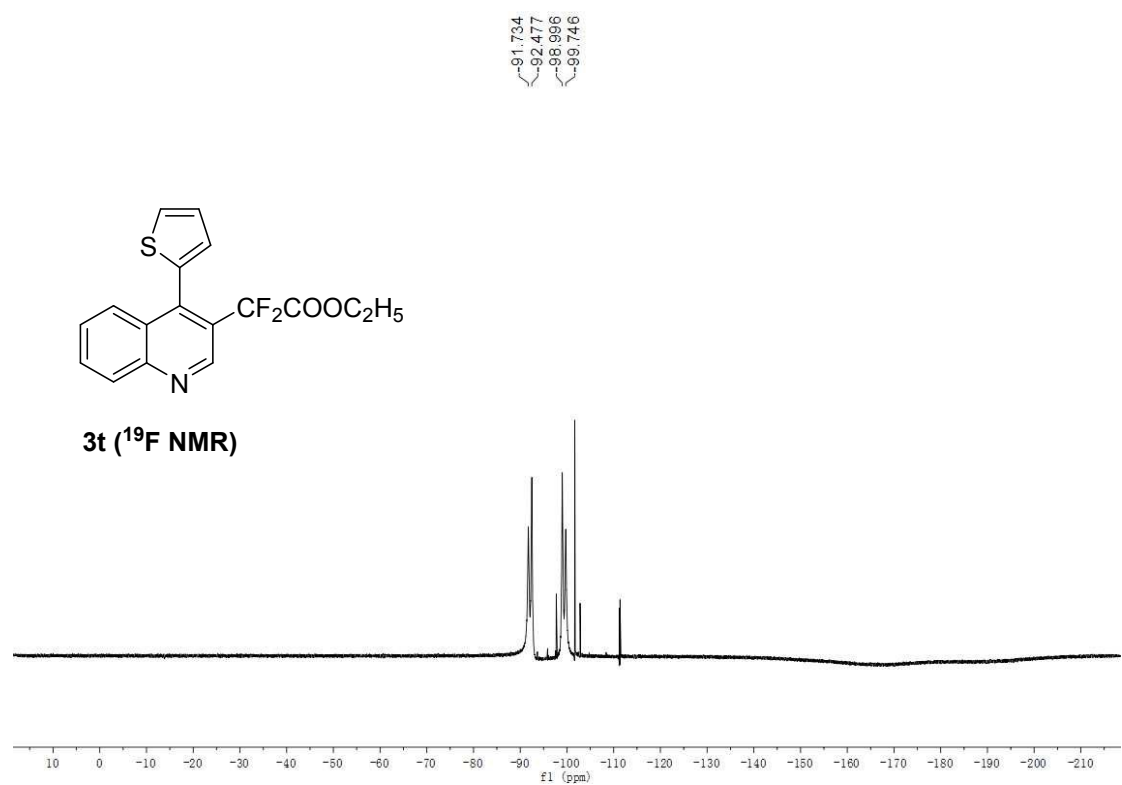
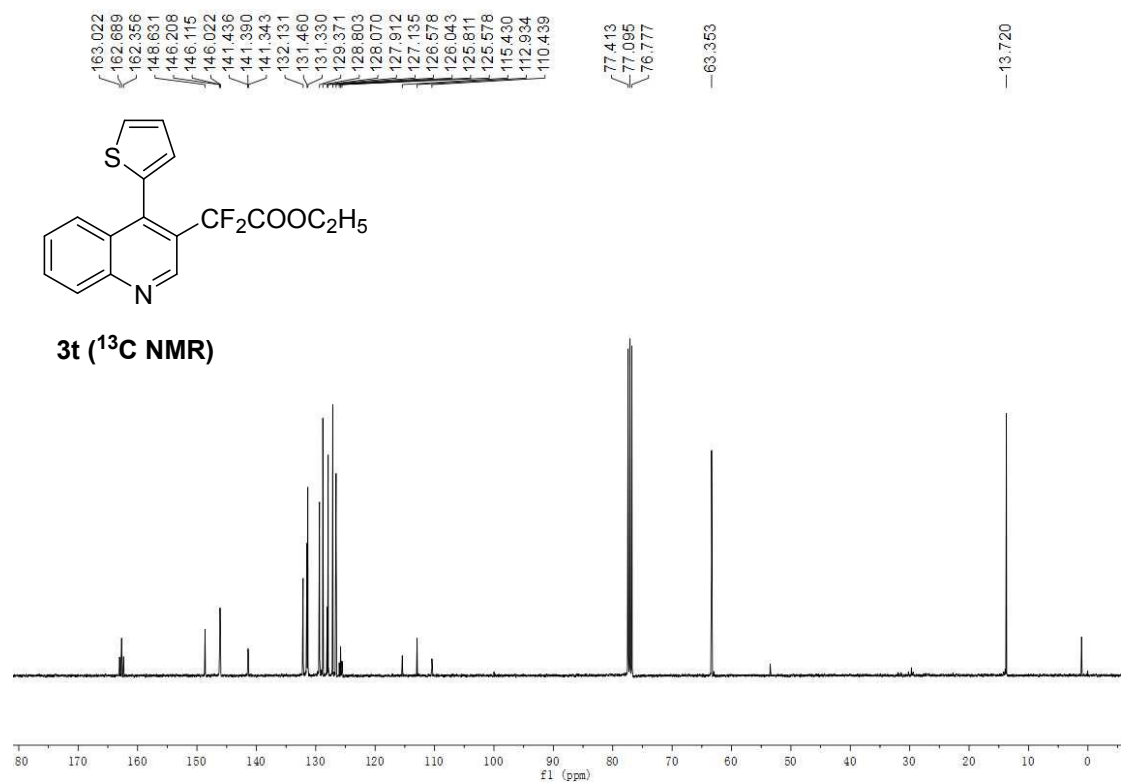
3s (¹H NMR)

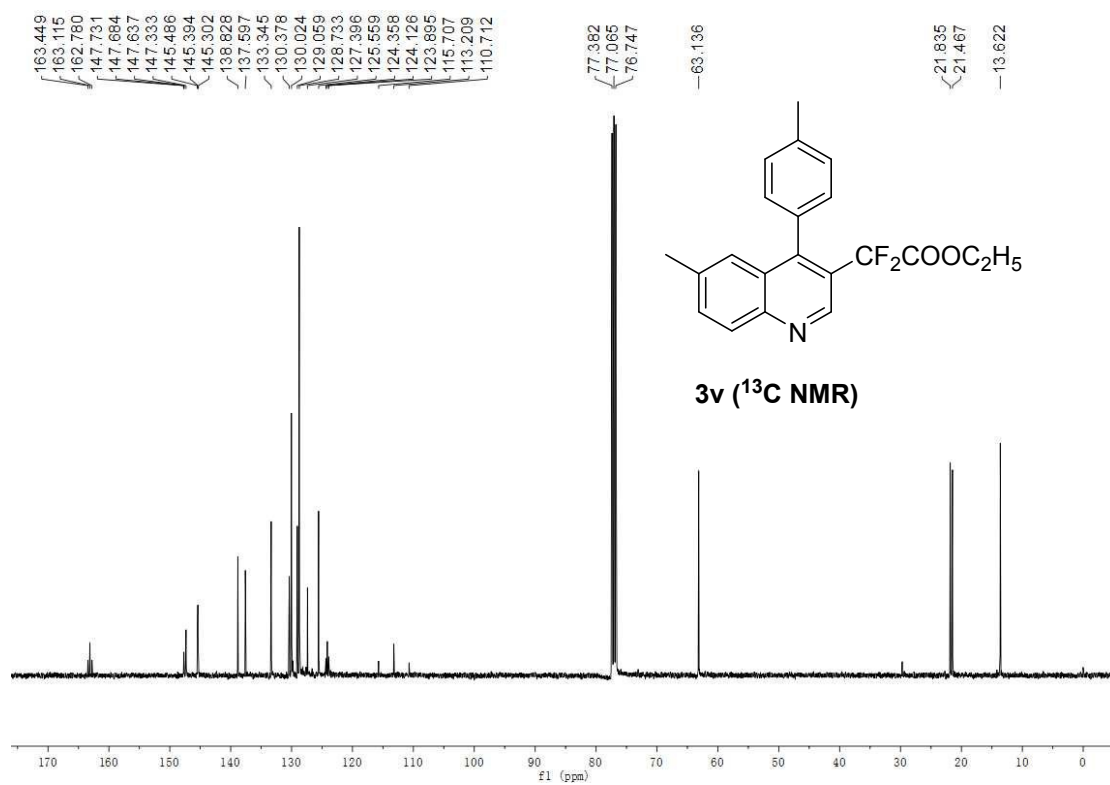
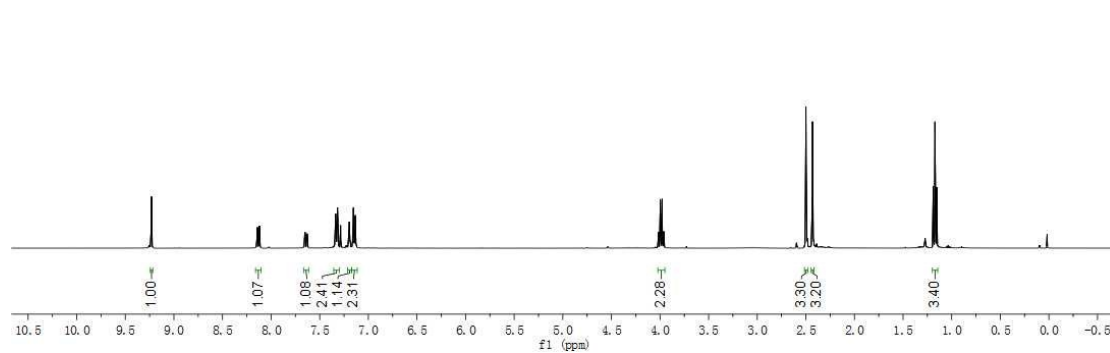
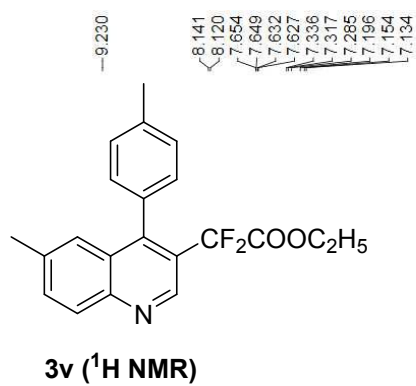


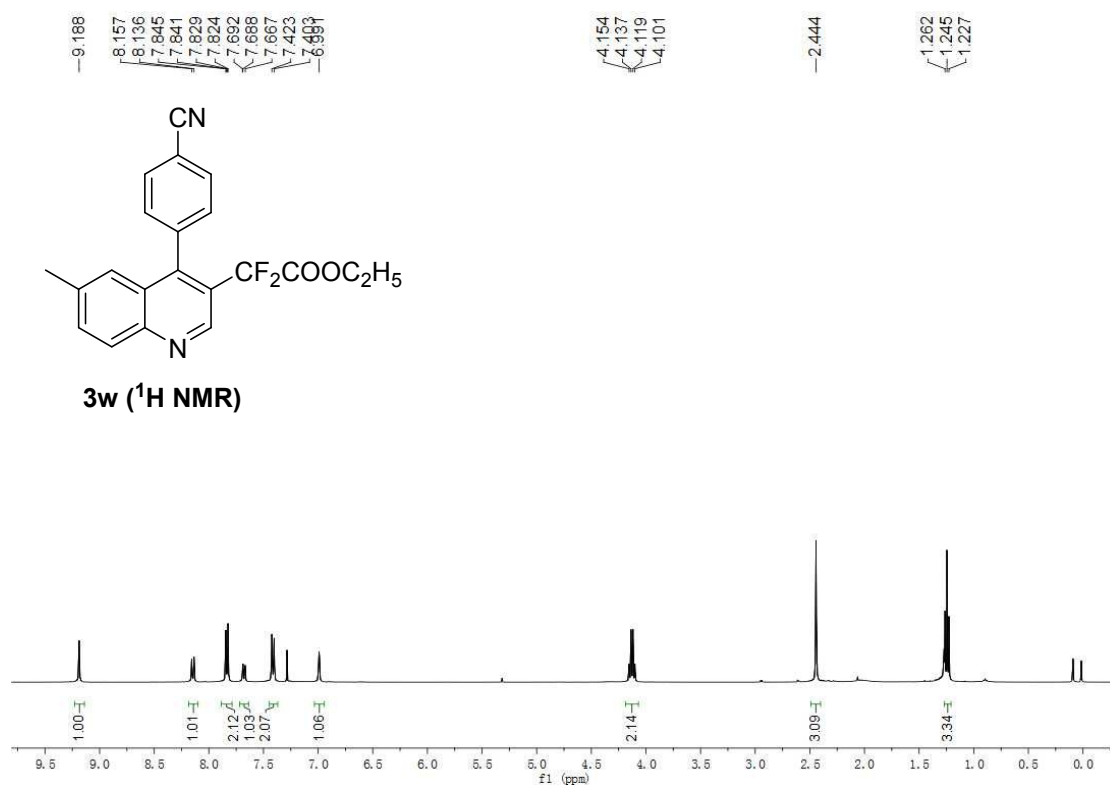
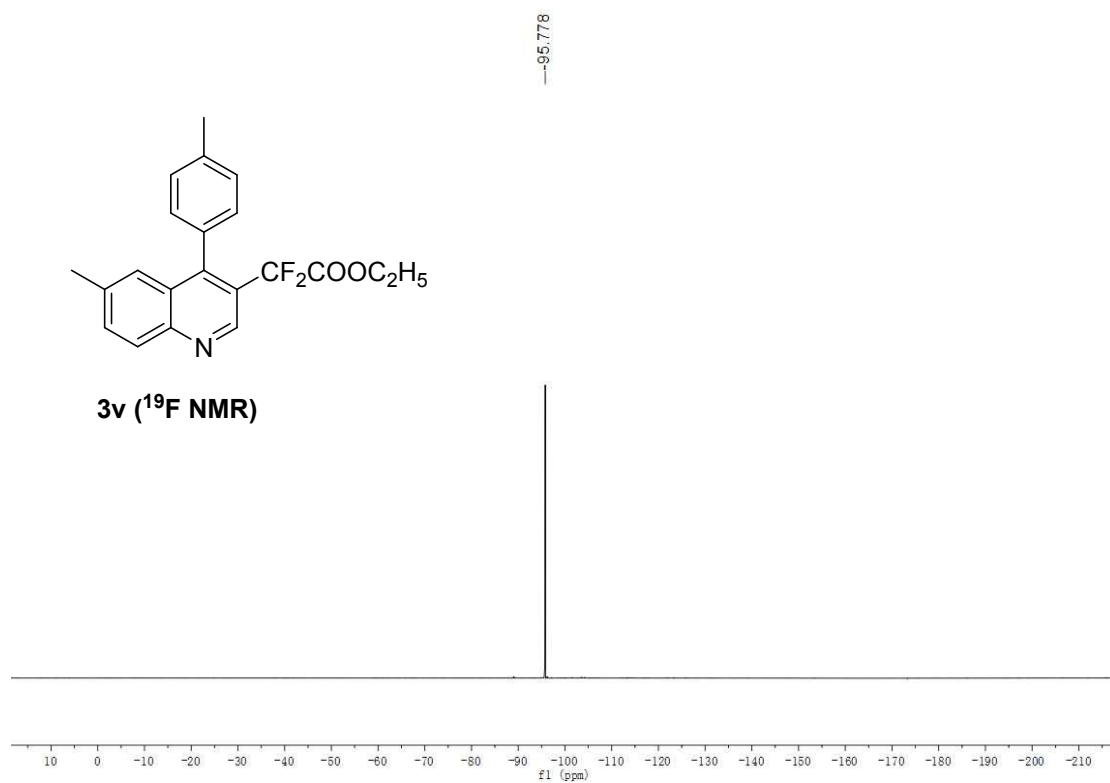
3s (¹³C NMR)

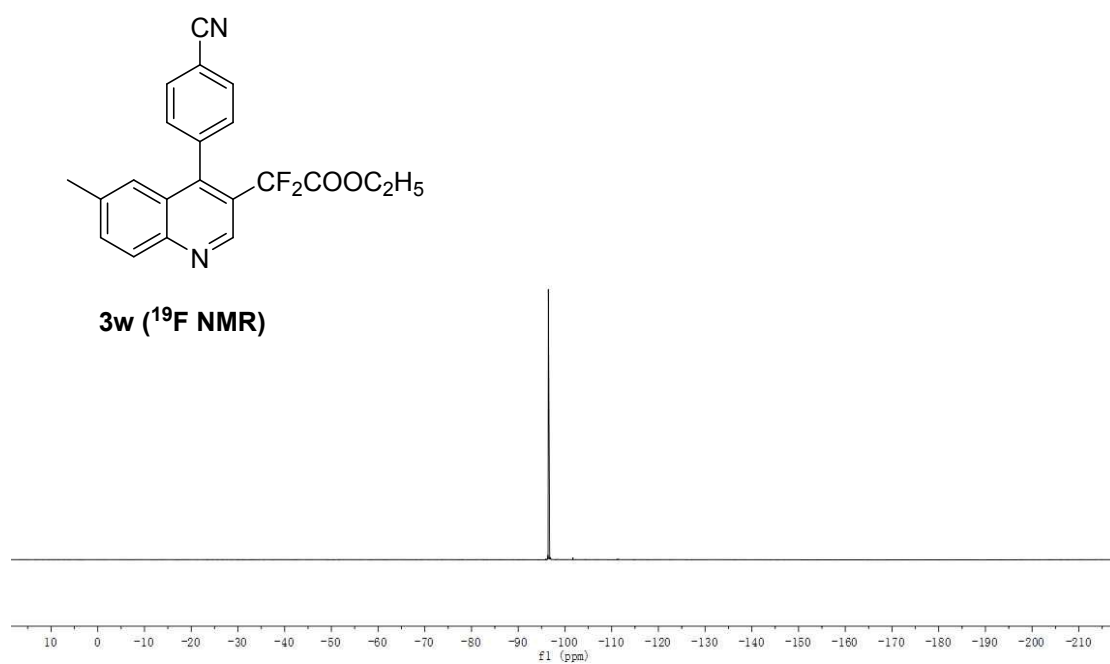
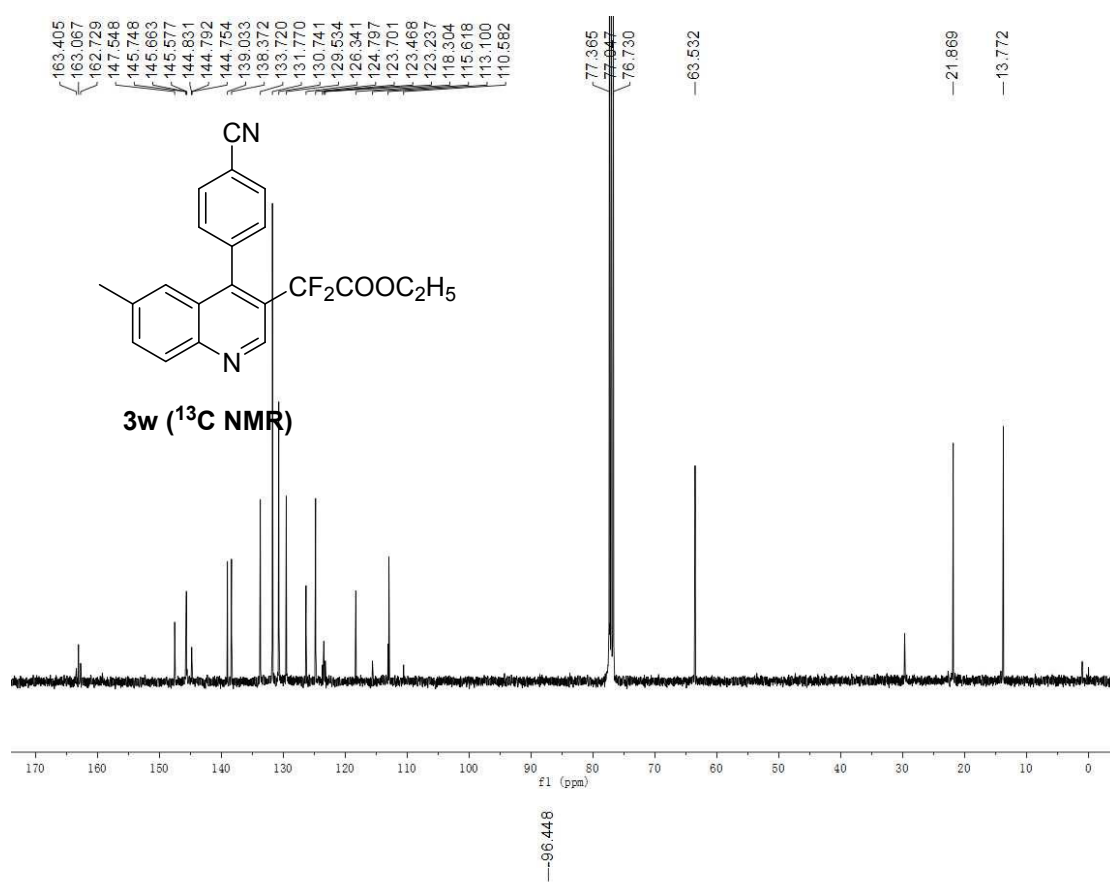


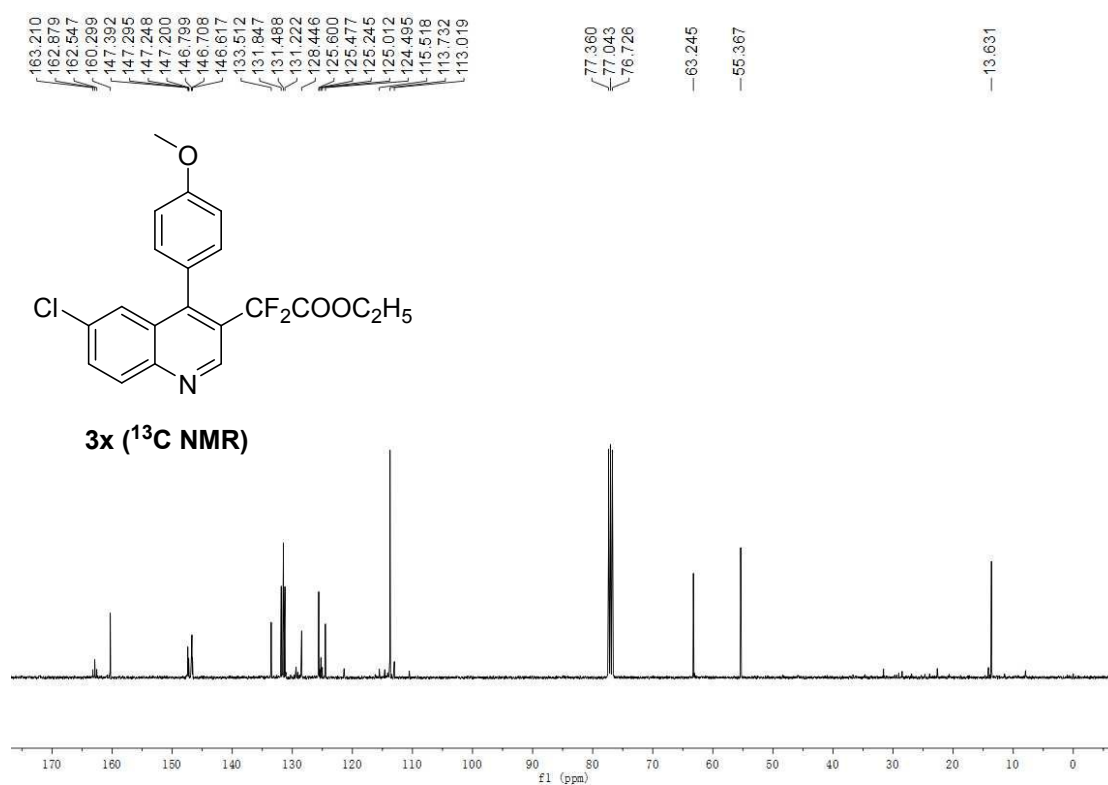
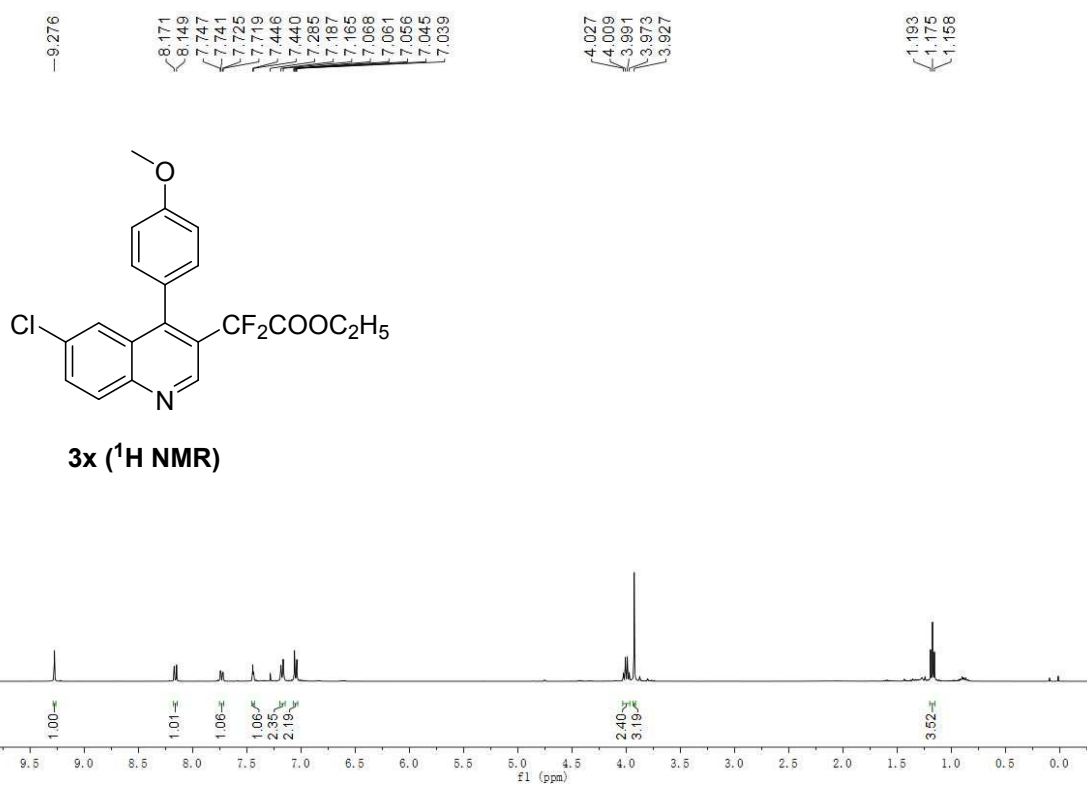


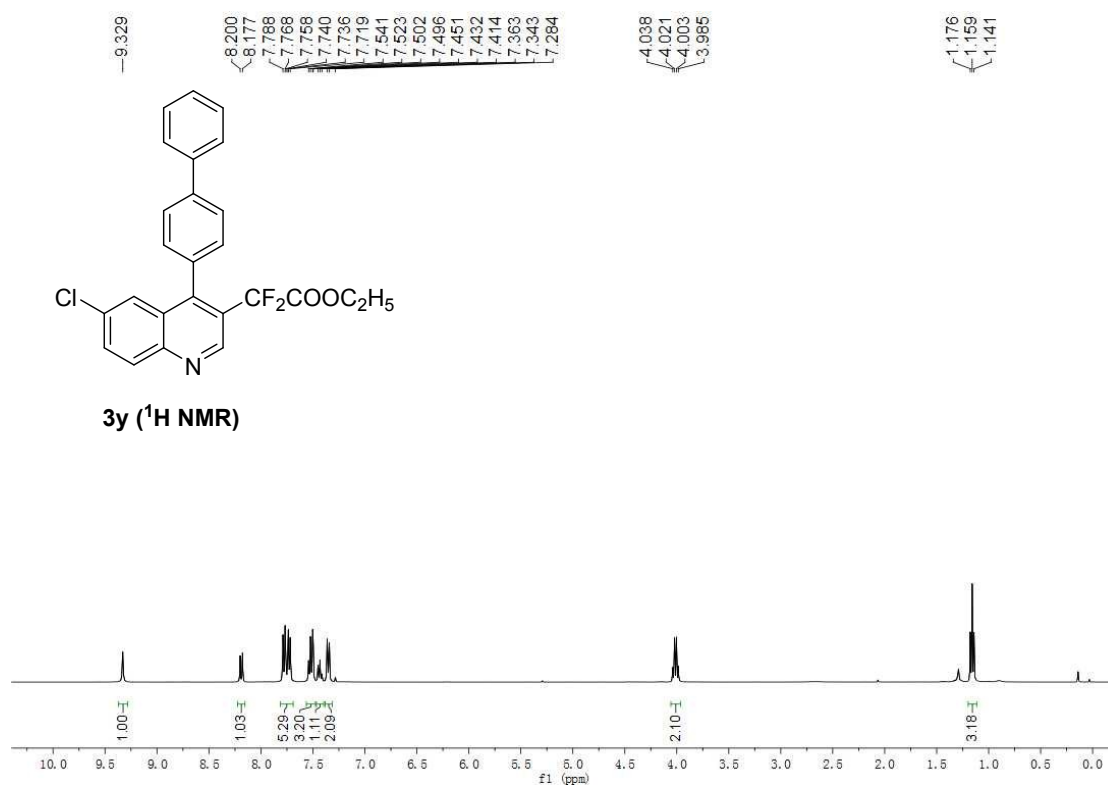
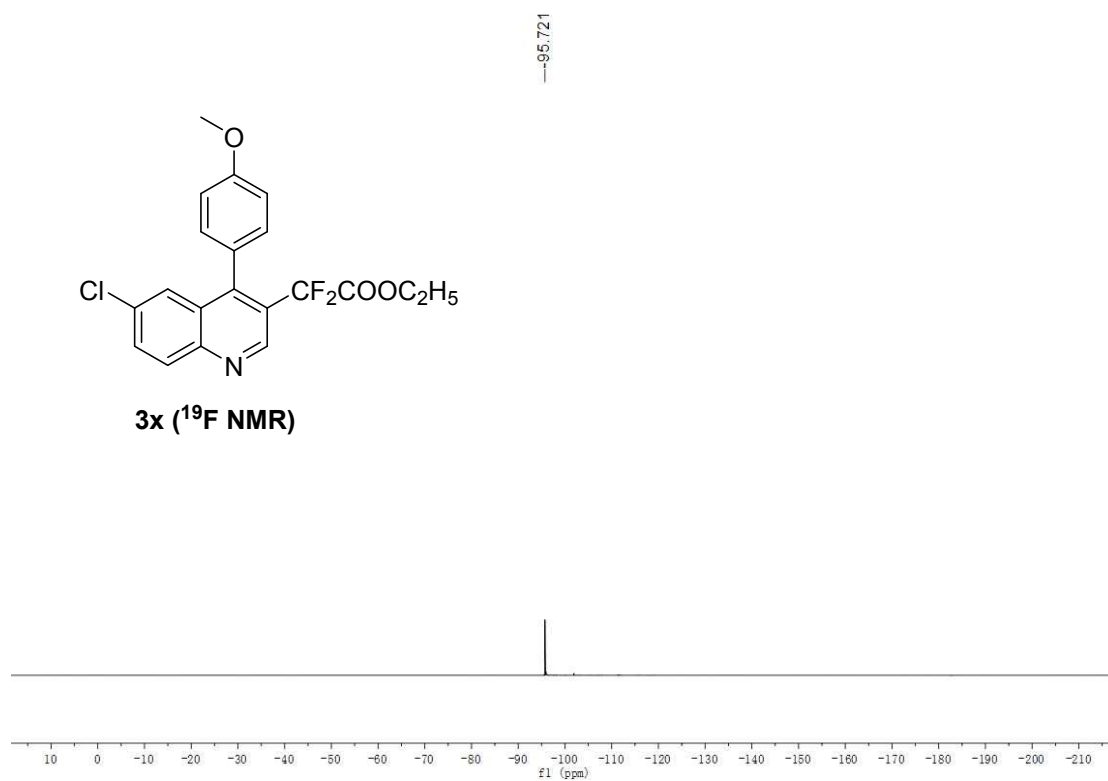


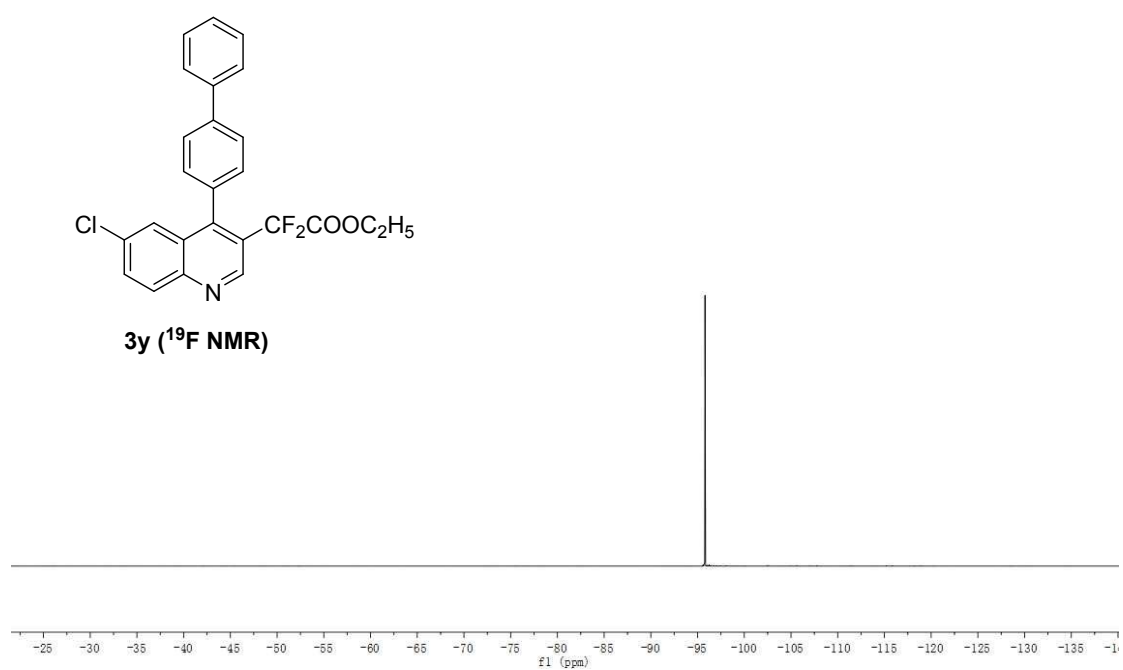
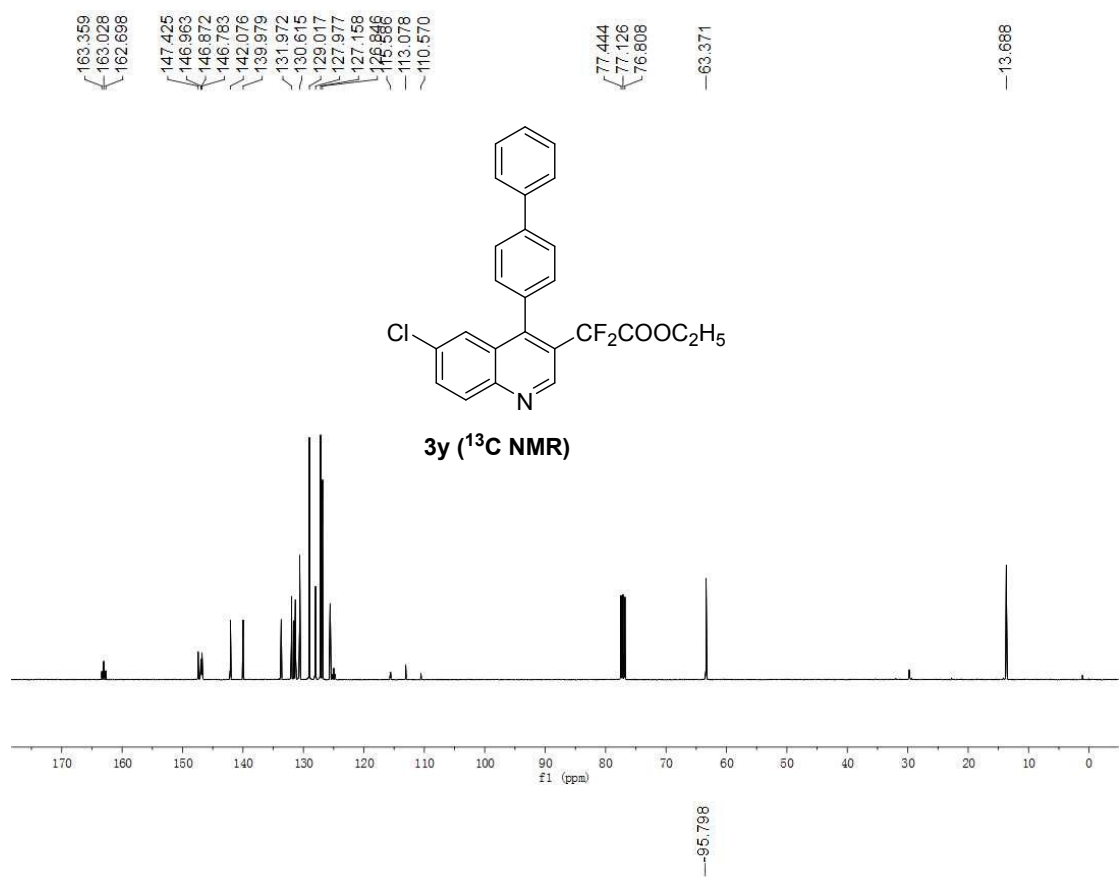


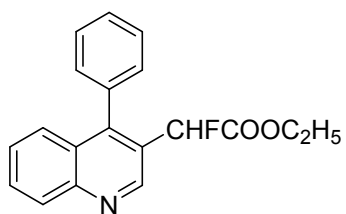




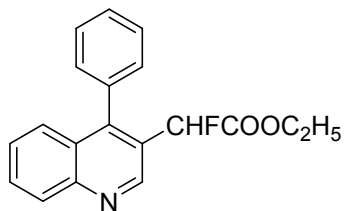
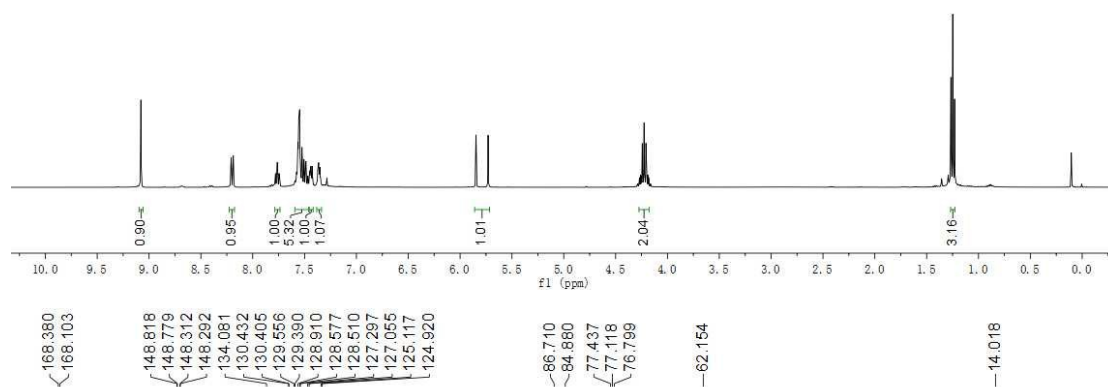




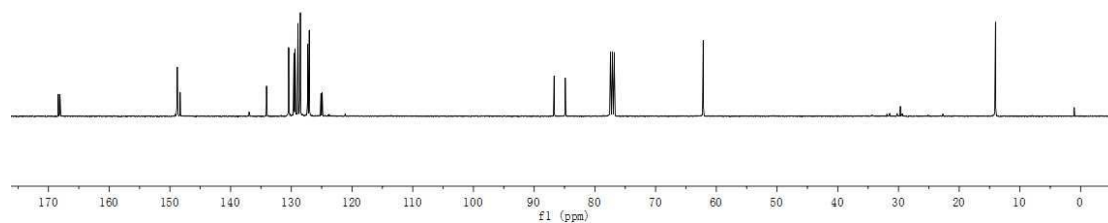


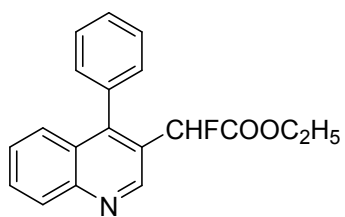


5a (¹H NMR)

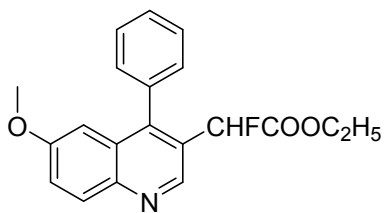
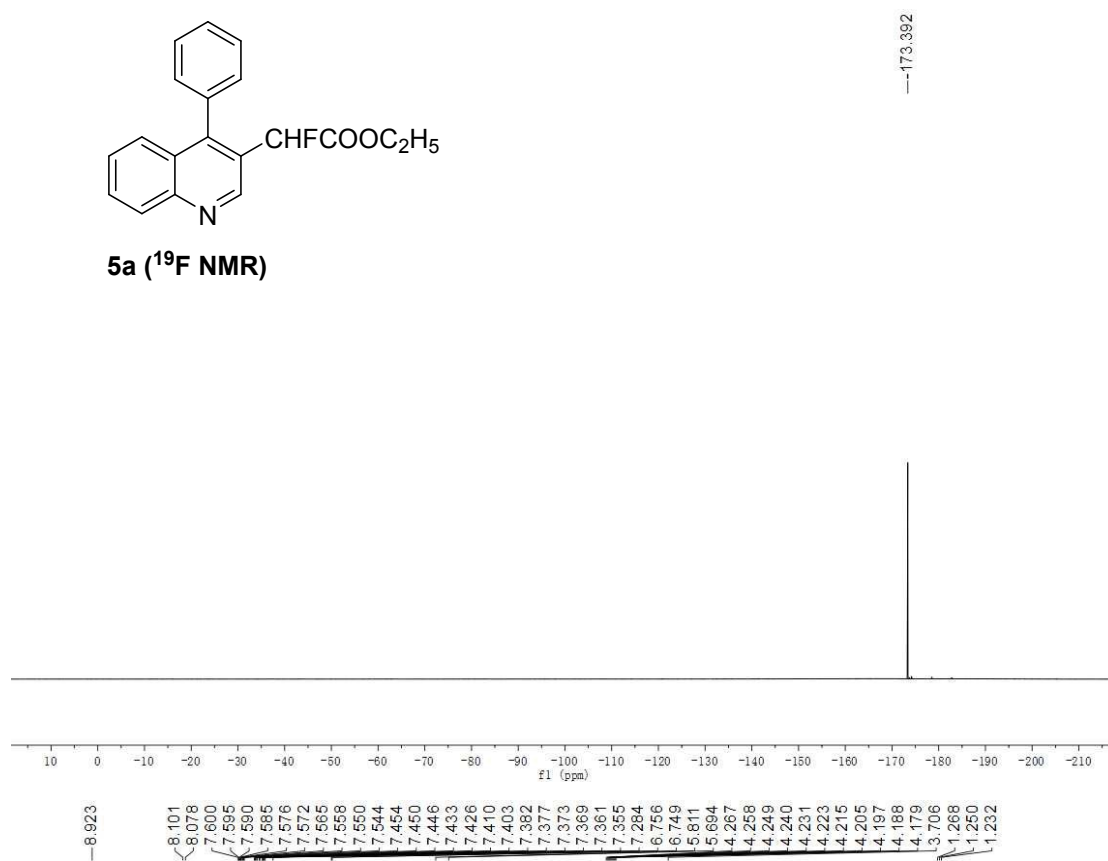


5a (¹³C NMR)

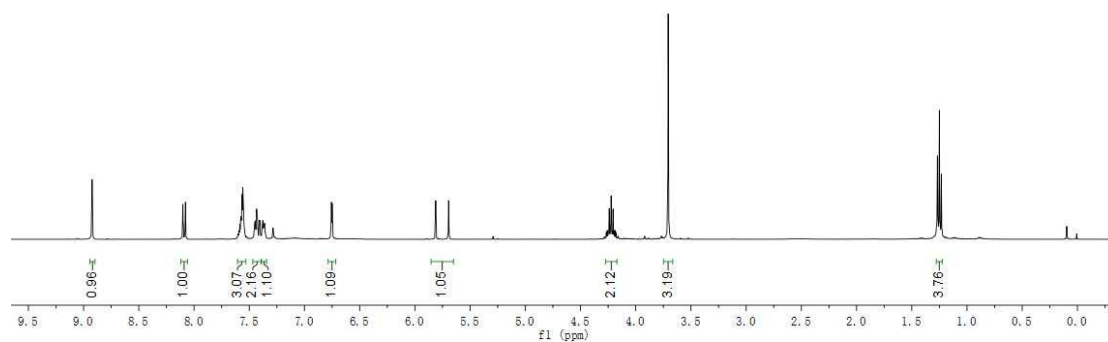


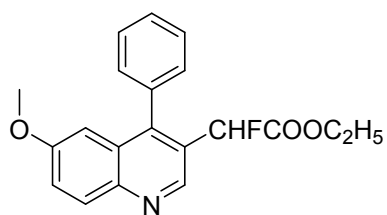


5a (^{19}F NMR)

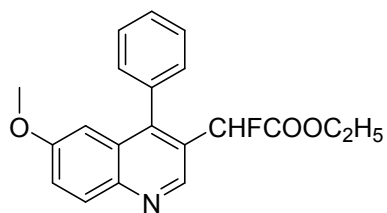
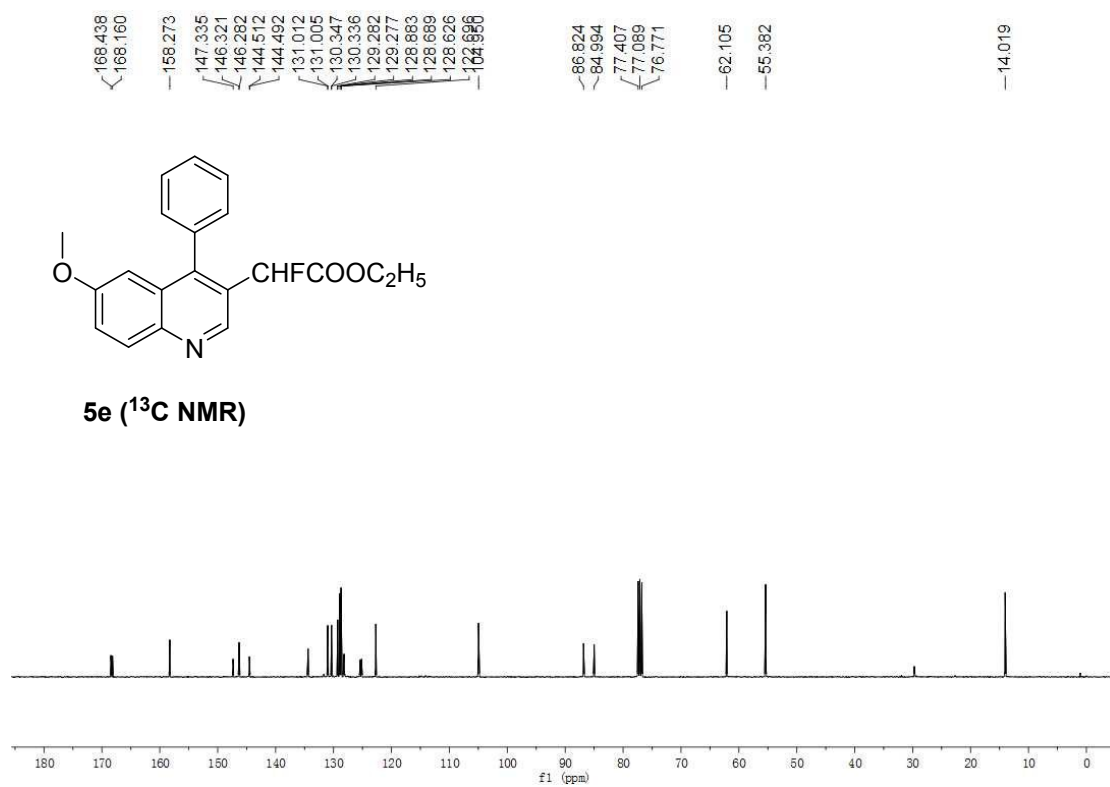


5e (^1H NMR)

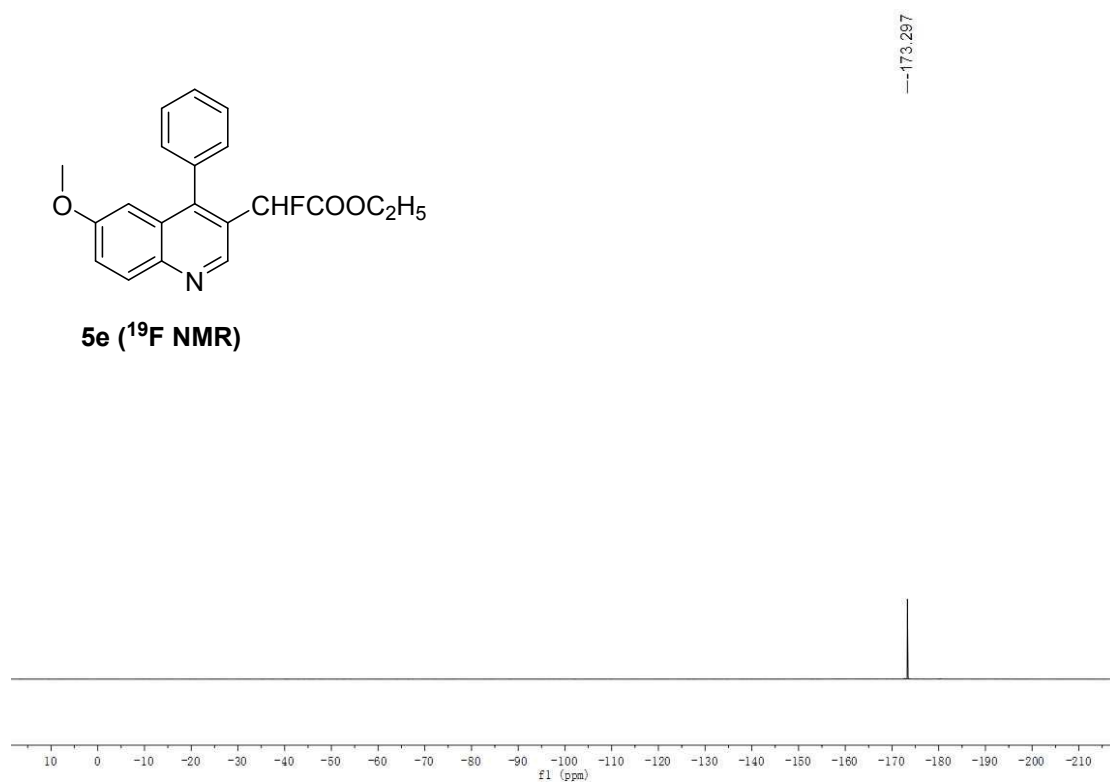


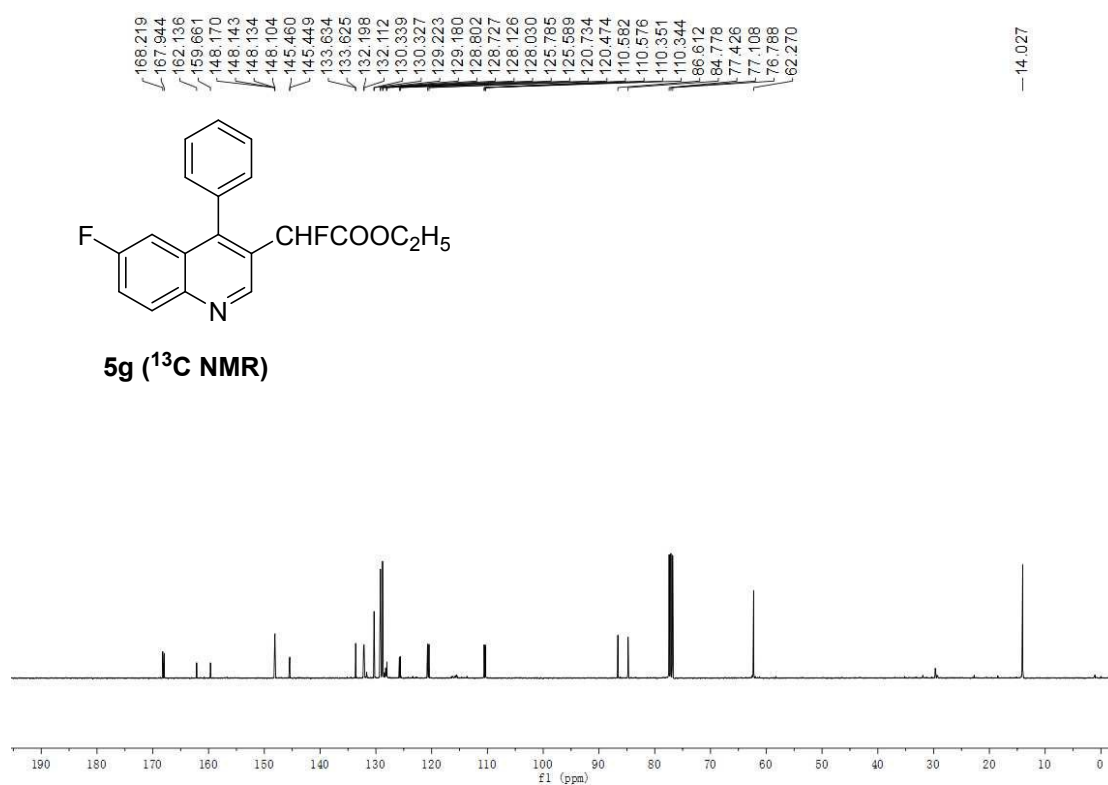
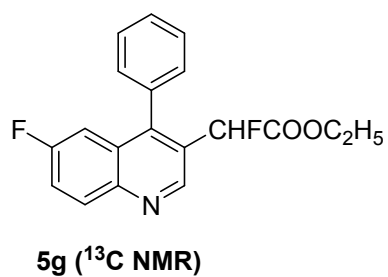
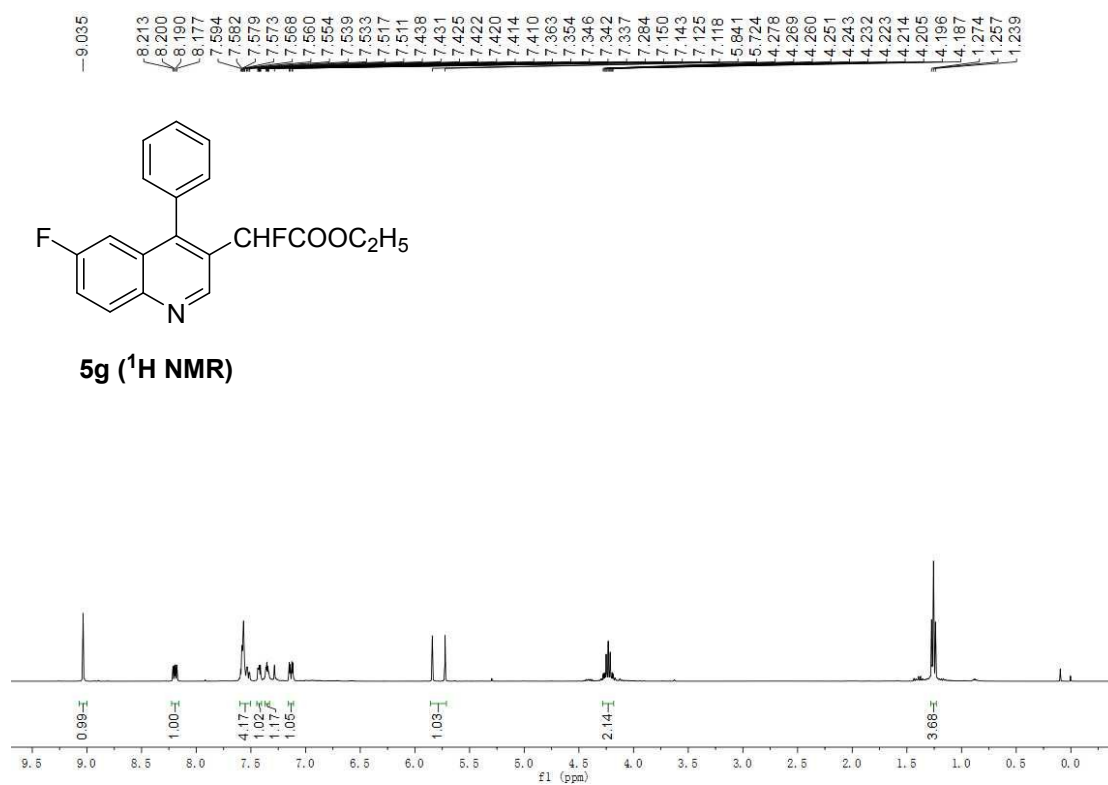
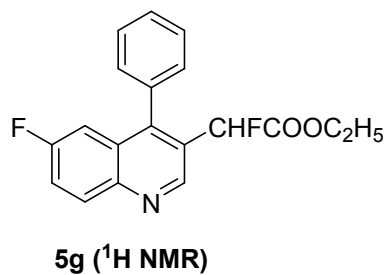


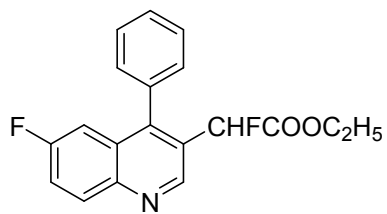
5e (^{13}C NMR)



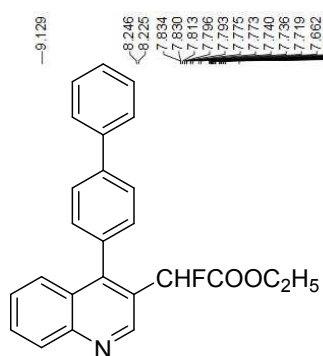
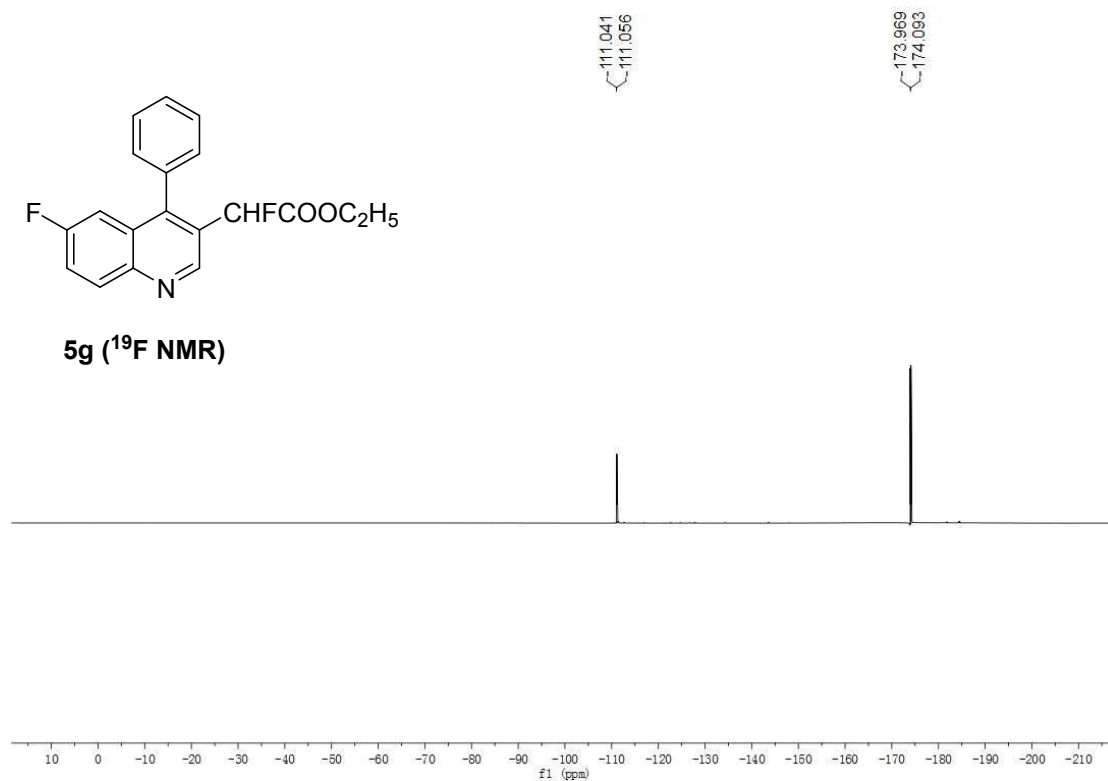
5e (^{19}F NMR)



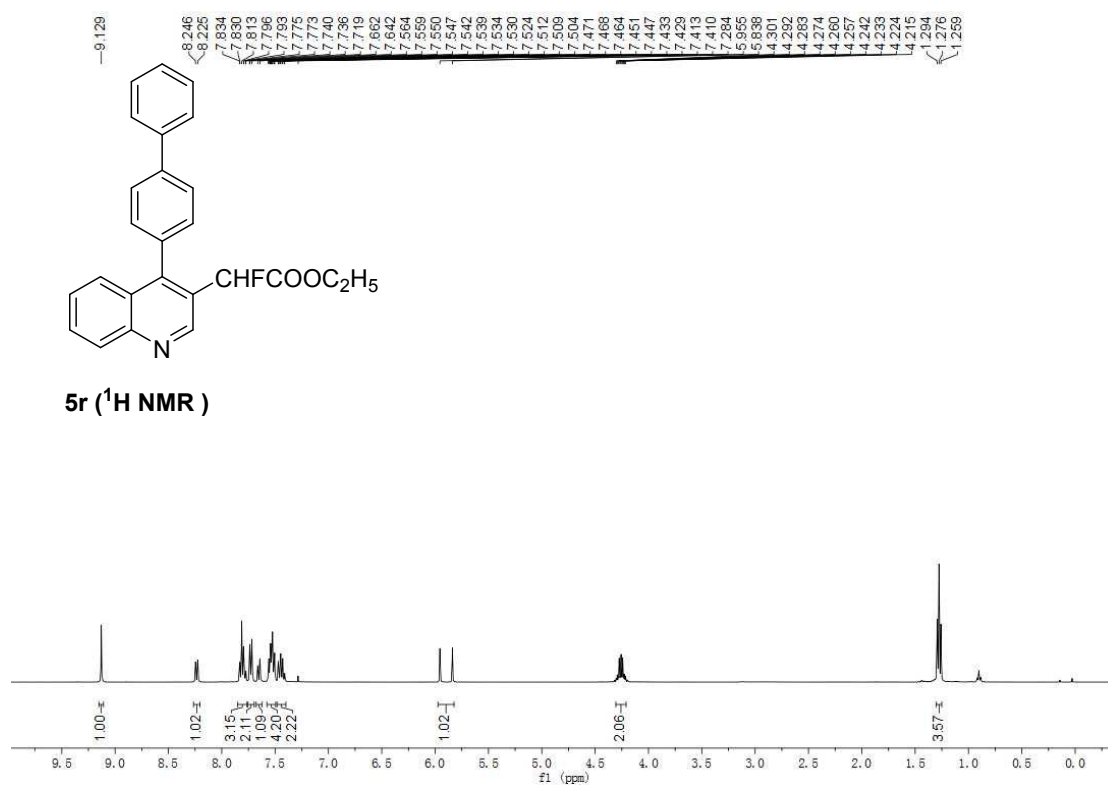


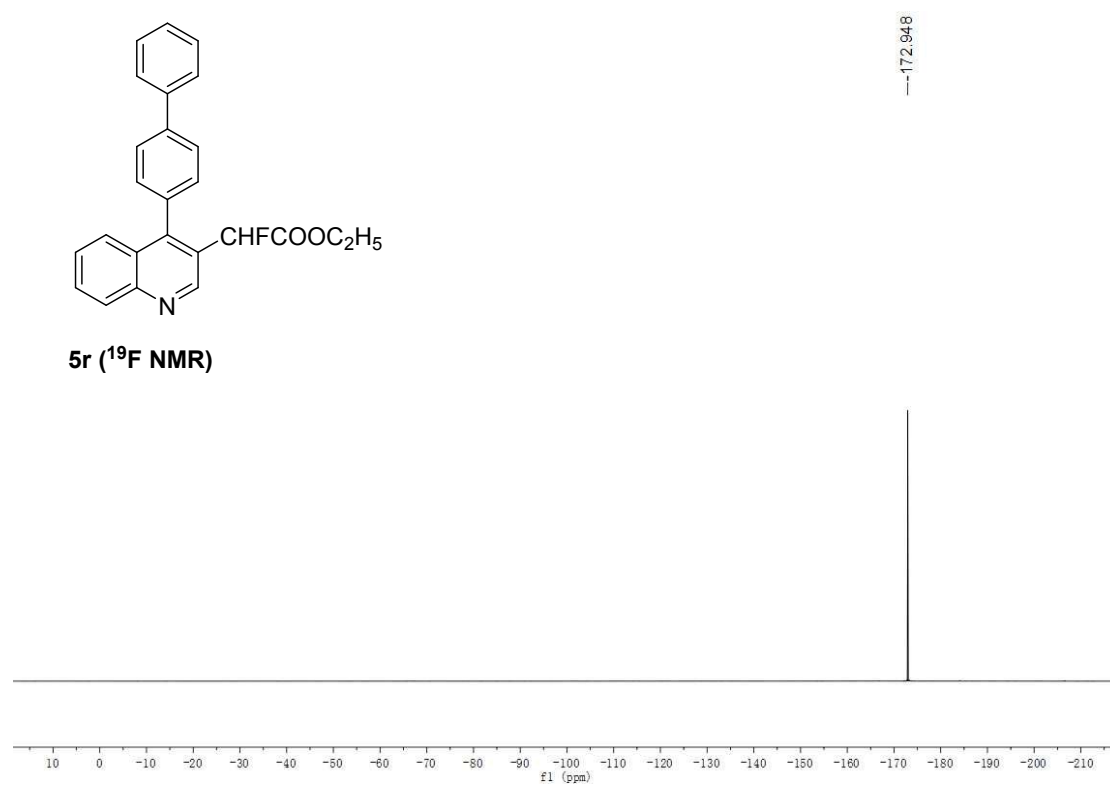
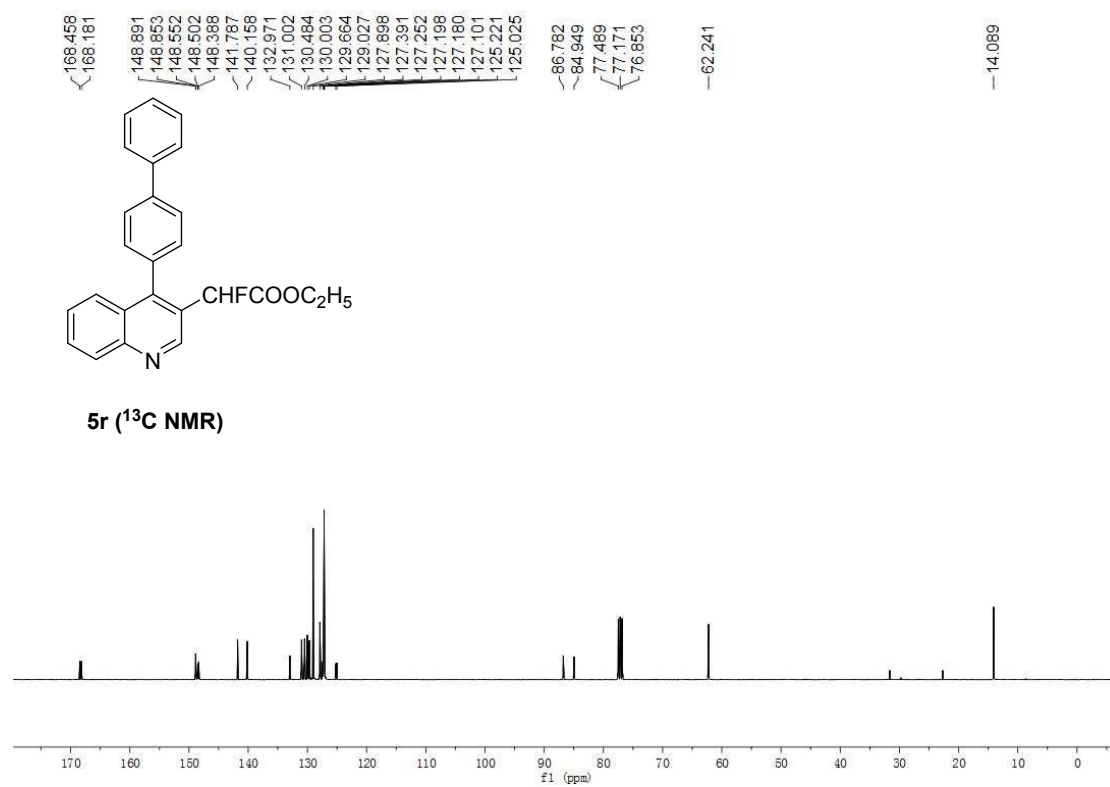


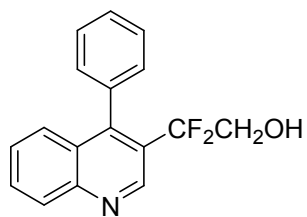
5g (^{19}F NMR)



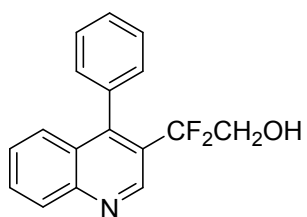
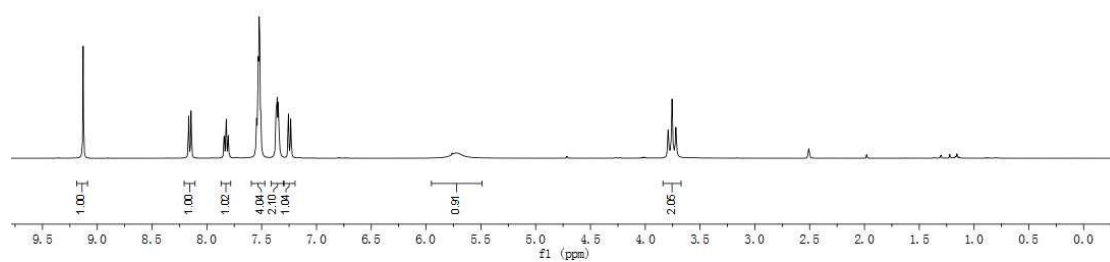
5r (^1H NMR)



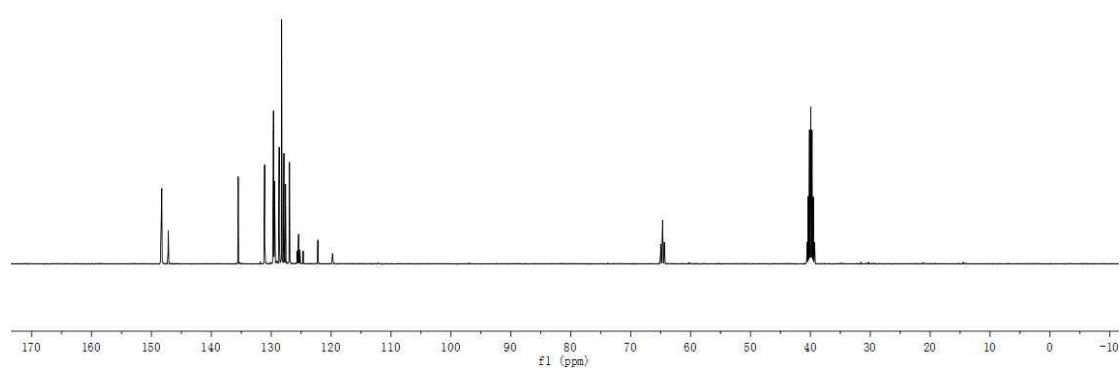


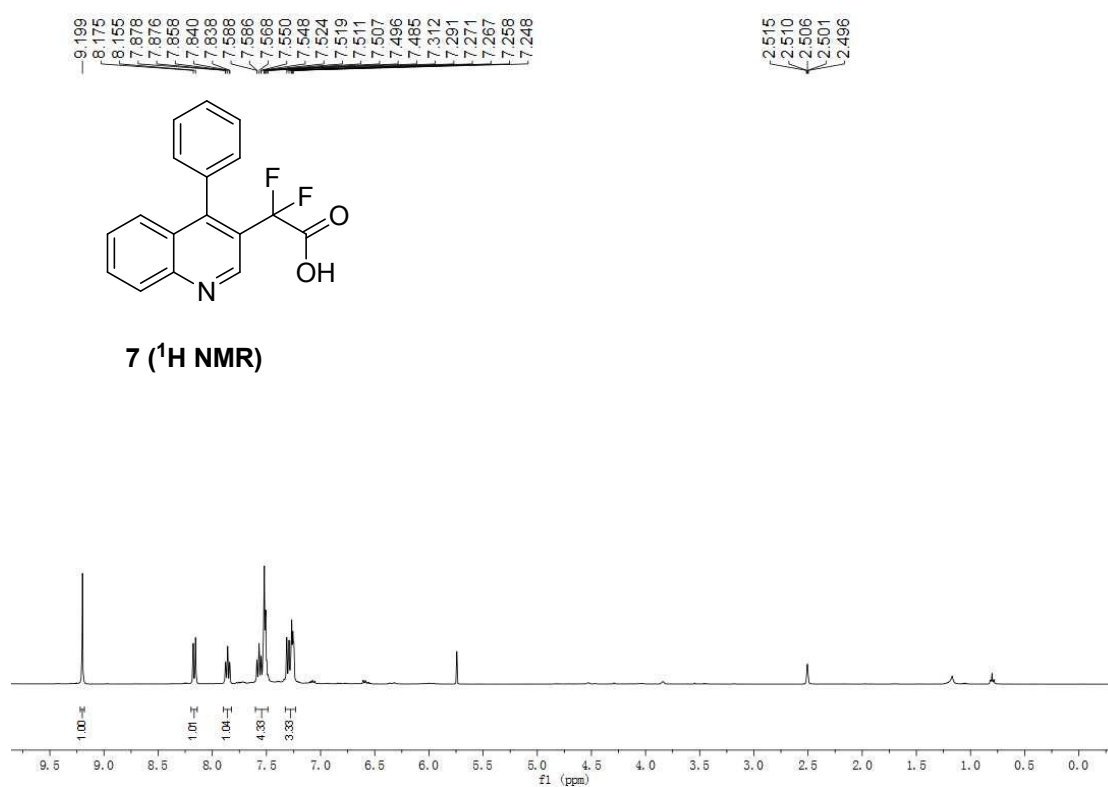
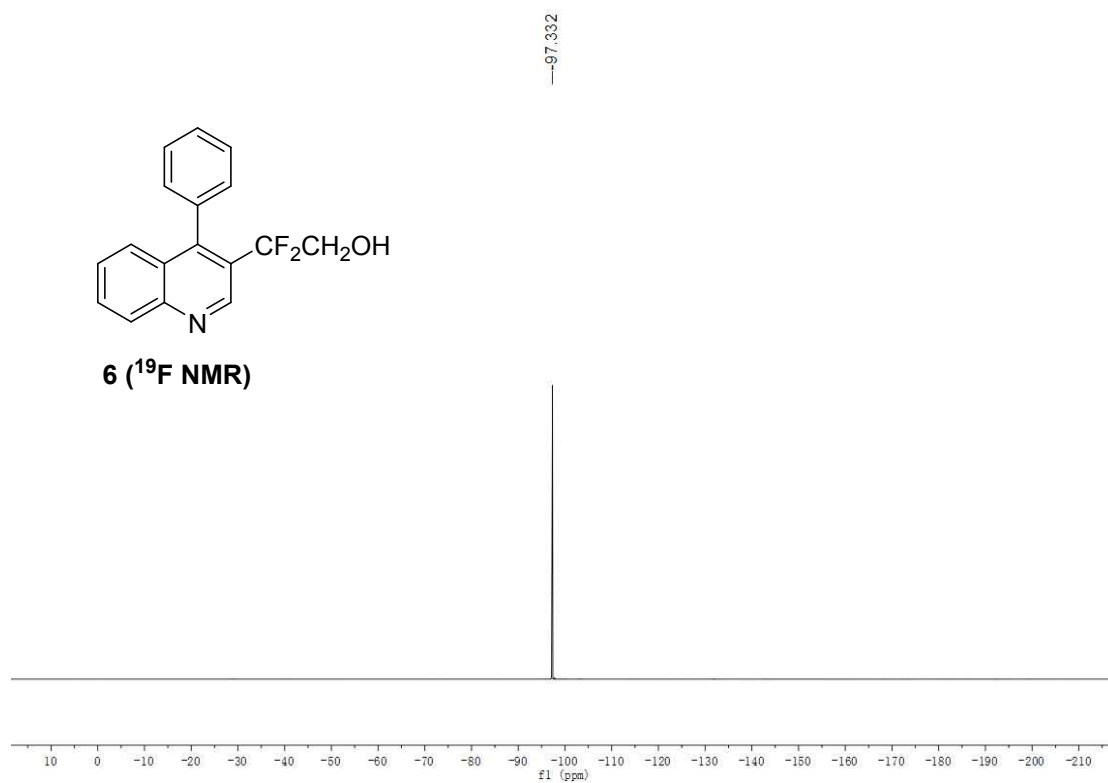


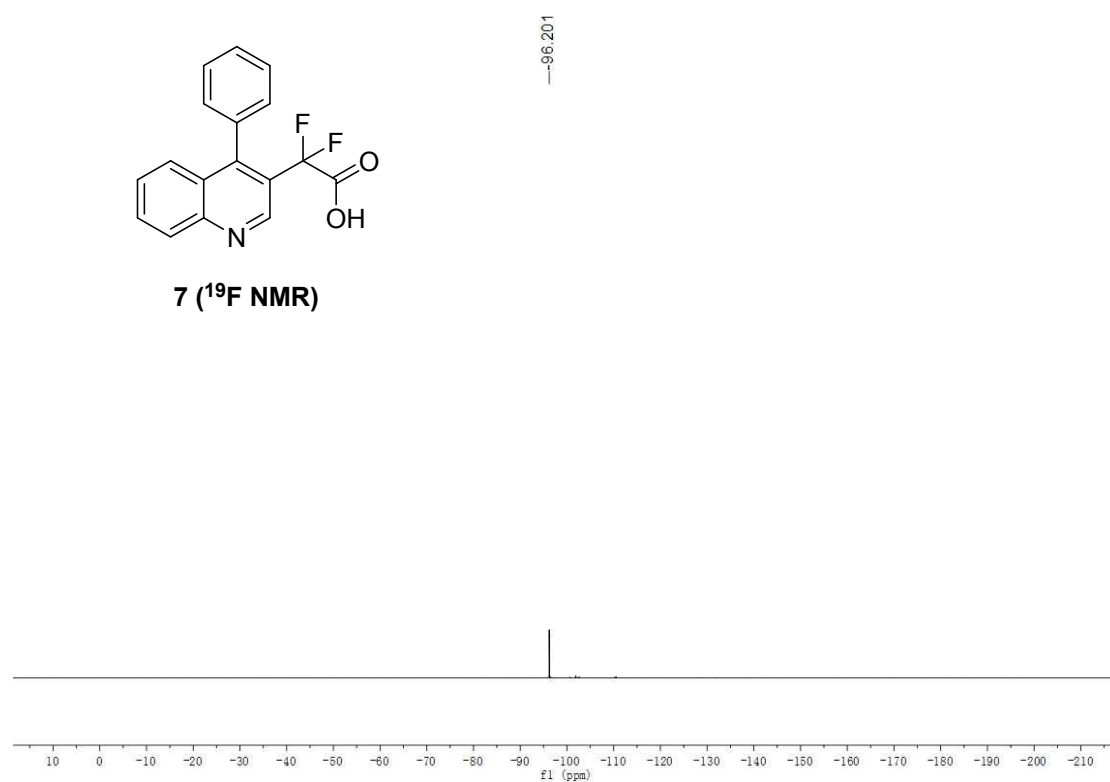
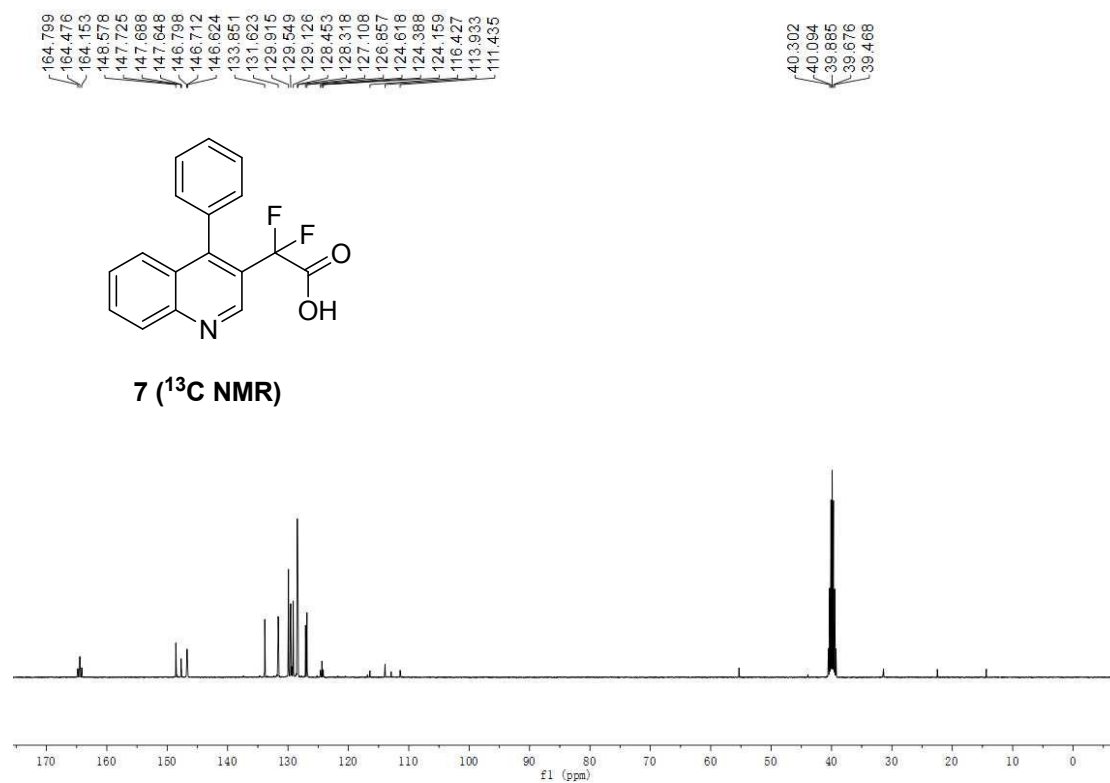
6 (¹H NMR)

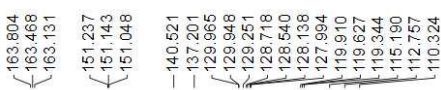


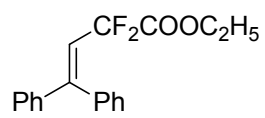
6 (¹³C NMR)











8 (^{19}F NMR)

