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# Supporting Information

# For

## One-pot regioselective synthesis of 2,4-disubstituted quinolines via copper(II)-catalyzed cascade annulation

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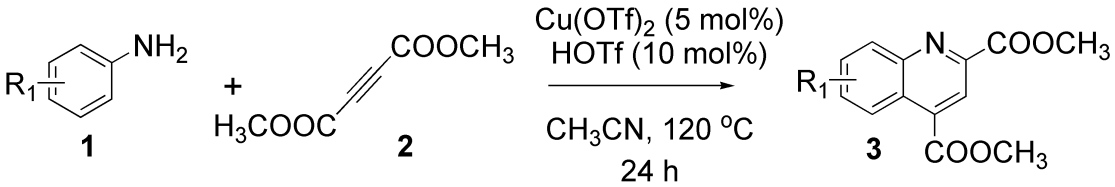
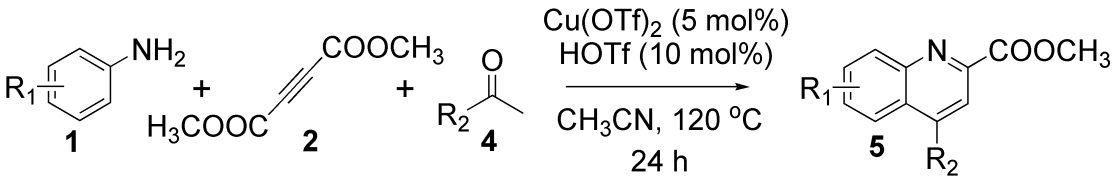
## General Methods and Materials

$Cu(OTf)_2$, HOTf and $Tf_2O$ were purchased from Energy Chemical and used without further purification. Other chemicals were purchased from commercial suppliers, further dried and purified if necessary. The water used was re-distillated and ion-free. $^1H$ and $^{13}C$ NMR spectra were achieved on a Bruker AVANCE 400 MHz spectrometer ($^1H$ 400 MHz; $^{13}C$ 100 MHz) in $CDCl_3$. Abbreviations for data quoted are s-singlet; brs-broad singlet; d-doublet; t-triplet; dd-doublet of doublets; m-multiplet. High-resolution mass spectra were measured on a Waters Micromass GCT facility. Thin-layer chromatographies were done on pre-coated silica gel 60F254 plates (Merck). Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography.

## General catalytic procedure for the synthesis of quinolines

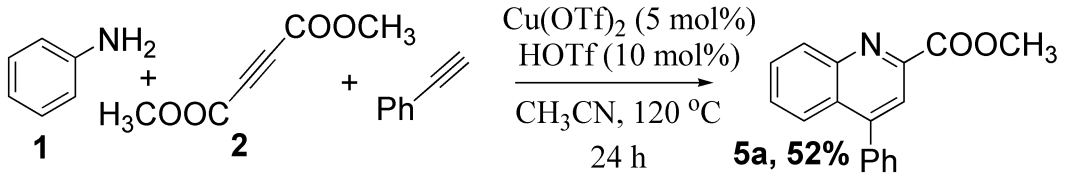



A seal tube (30 mL) was charged with aniline (1.0 mmol, 1.0 equiv.), alkyne ester (2.2 mmol, 2.2 equiv.), then the $Cu(OTf)_2$ (0.05 mmol), $CH_3CN$ (2 mL) and HOTf (0.1 mmol) were added. The mixture was stirred at 120 $^oC$ for 24 hours, the mixture was quenched by *sat. aq.* $NaHCO_3$, and diluted with 20 mL of dichloromethane and washed with 10 mL of $H_2O$. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over $Na_2SO_4$. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 7:1) to afford the corresponding quinoline products. All other compounds are synthesized in a similar manner, with the yields listed in the main text calculated from the isolated, pure products.



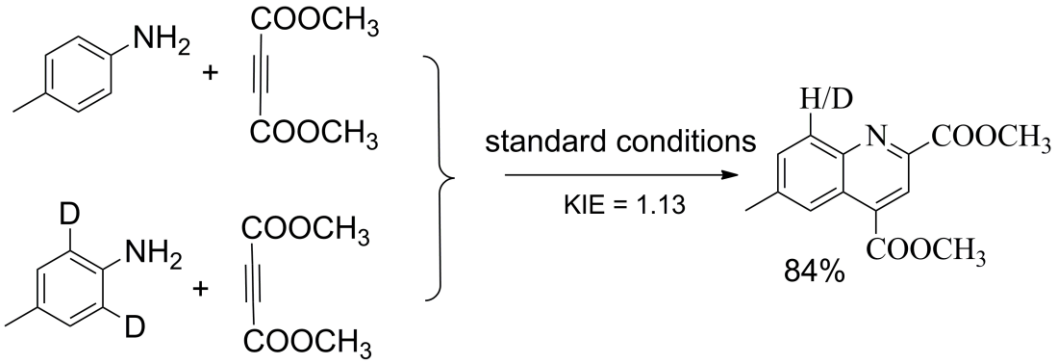

A seal tube (30 mL) was charged with aniline (1.0 mmol, 1.0 equiv.), alkyne ester (1.0 mmol, 1.0 equiv.) and ketone (1.2 mmol, 1.2 equiv.), then the $Cu(OTf)_2$ (0.05 mmol), $CH_3CN$ (2 mL) and HOTf (0.1 mmol) were added. The mixture was stirred at 120 $^oC$ for 24 hours. After the reaction finished, the mixture was quenched by *sat. aq.* $NaHCO_3$, and diluted with 20 mL of dichloromethane and washed with 10 mL of $H_2O$. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over $Na_2SO_4$. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 2:1) to afford the corresponding quinoline products. All other compounds are synthesized in a similar manner, with the yields listed in the main text calculated from the isolated, pure

products.

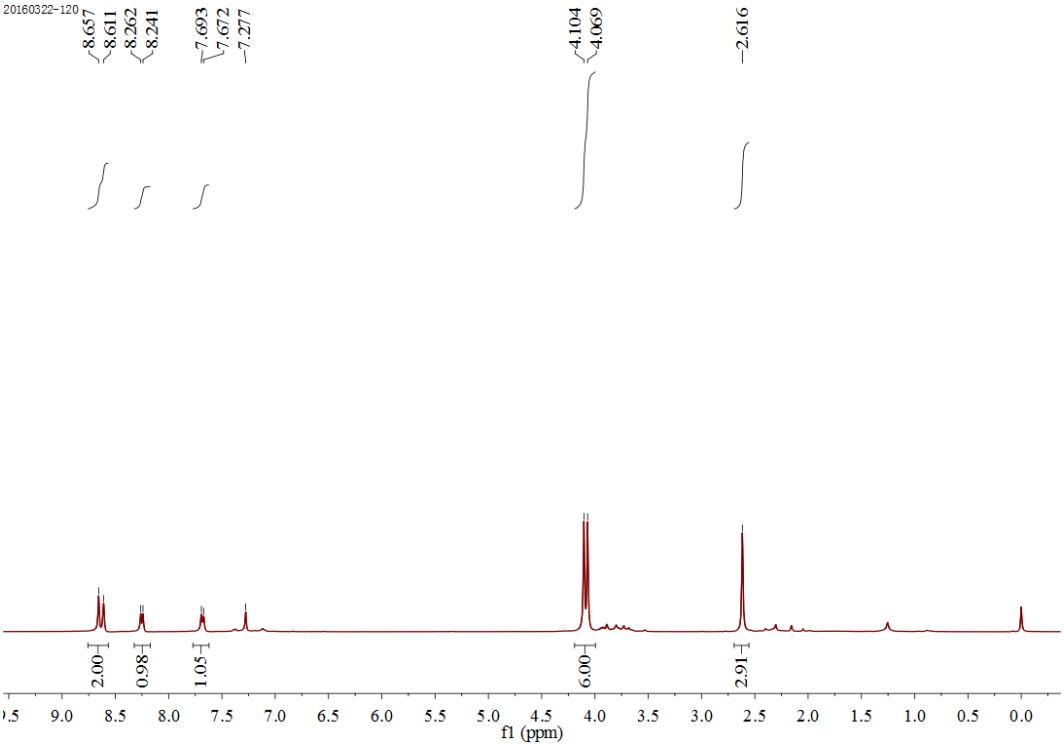


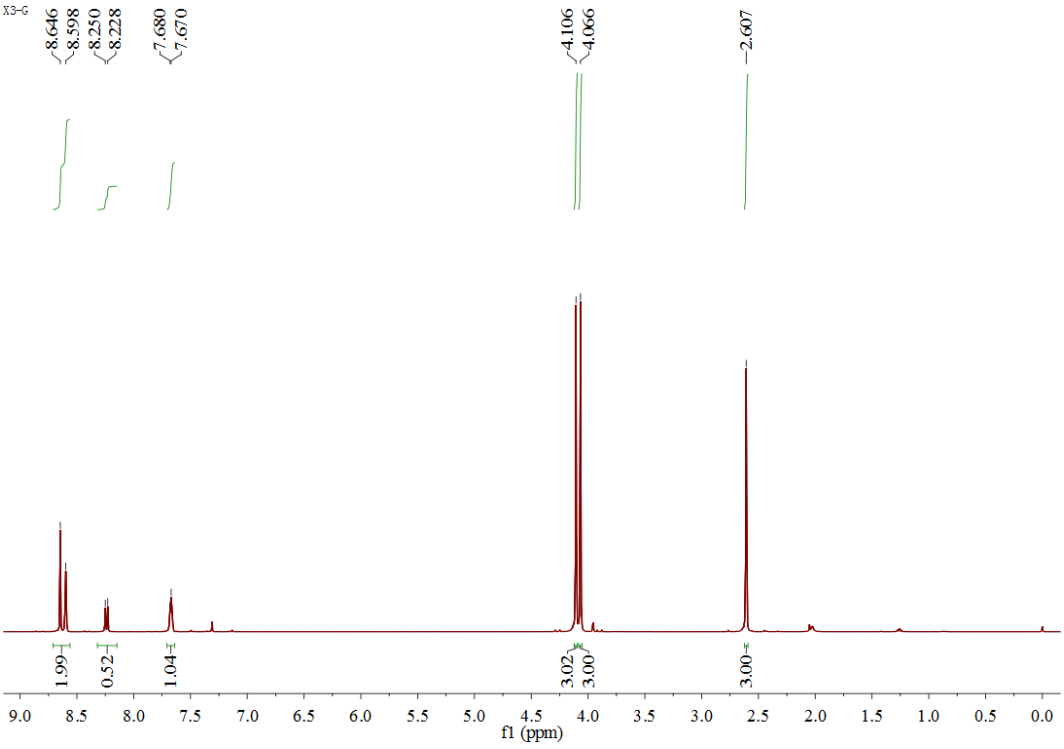

A seal tube (30 mL) was charged with aniline (1.0 mmol, 1.0 equiv.), alkyne ester (1.0 mmol, 1.0 equiv.) and phenylacetylene (1.2 mmol, 1.2 equiv.), then the $Cu(OTf)_2$ (0.05 mmol), $CH_3CN$ (2 mL) and HOTf (0.1 mmol) were added. The mixture was stirred at 120 $^oC$ for 24 hours. After the reaction finished, the mixture was quenched by *sat. aq.* $NaHCO_3$, and diluted with 20 mL of dichloromethane and washed with 10 mL of $H_2O$. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over $Na_2SO_4$. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 10:1) to afford the product **5a** in 52% yield.

## Kinetic isotope experiment




To two separate pressure tubes were charged with *p*-toluidine (0.5 mmol, 1.0 equiv) or *p*-Toluidine-$d_2$ (0.5 mmol, 1.0 equiv), alkyne ester (1.1 mmol, 2.2 equiv.), then the $Cu(OTf)_2$ (0.05 mmol), $CH_3CN$ (2 mL) and HOTf (0.05 mmol) were added. The mixture was stirred at 120 $^oC$ for 10 hours. Next, the two reaction mixtures were combined, then diluted with 30 mL of dichloromethane and washed with 10 mL of $H_2O$. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over $Na_2SO_4$. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 7:1) to afford quinoline (217.6 mg, 84% yield).


20160322-120
8.657
8.611
8.262
8.241
7.693
7.672
7.277
4.104
4.069
2.616
2.00
0.98
1.05
6.00
2.91
f1 (ppm)


X3-G
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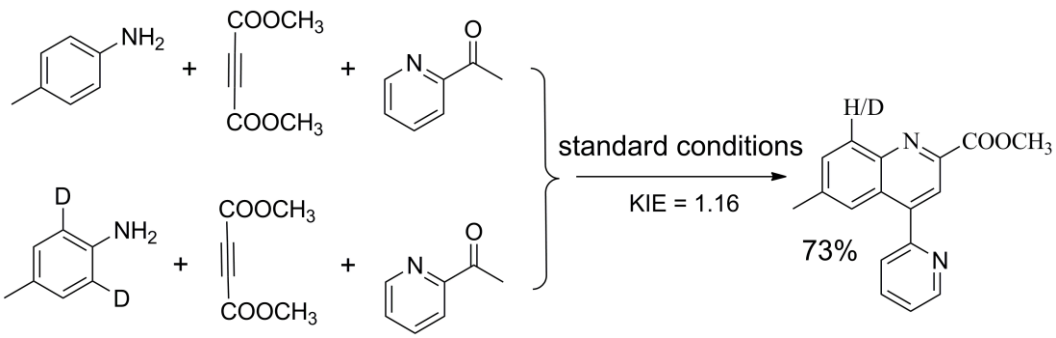
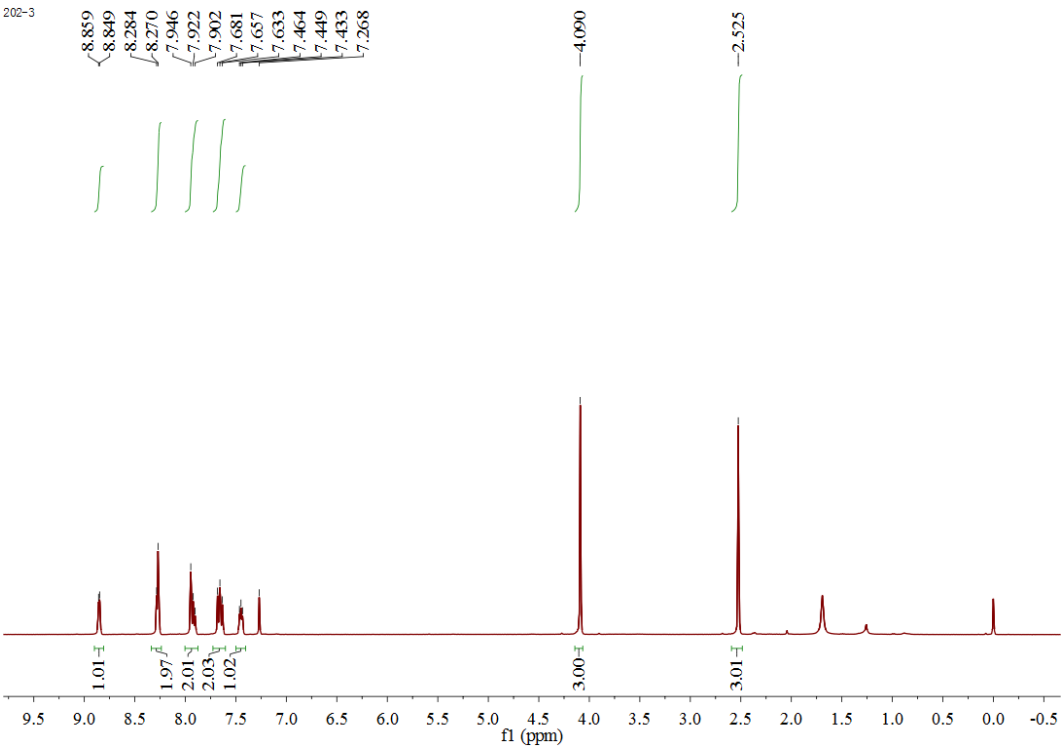
8.598
8.250
8.228
7.680
7.670
4.106
4.066
2.607
1.99
0.52
1.04
3.02
3.00
3.00
f1 (ppm)




To two separate pressure tubes were charged with *p*-toluidine (0.5 mmol, 1.0 equiv) or *p*-Toluidine-$d_2$ (0.5 mmol, 1.0 equiv), alkyne (0.5 mmol, 1.0 equiv), and ketone (1.2 mmol), then the $Cu(OTf)_2$ (0.05 mmol), $CH_3CN$ (2 mL) and HOTf (0.05 mmol) were added. The mixture was stirred at 120 $^oC$ for 10 hours. Next, the two reaction mixtures were combined, then diluted with 30 mL of dichloromethane and washed with 10 mL of $H_2O$. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over $Na_2SO_4$. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 3:1) to afford quinoline (202.9 mg, 73% yield).


202-3
8.859
8.849
8.284
8.270
7.946
7.922
7.902
7.681
7.657
7.633
7.464
7.449
7.433
7.268
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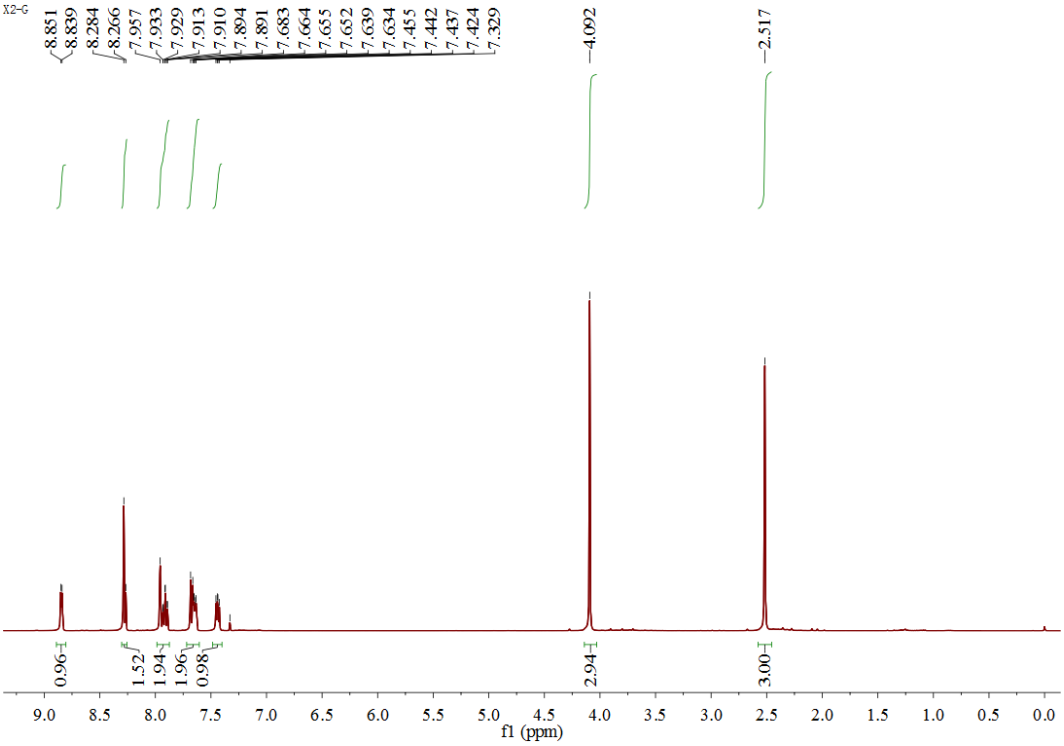
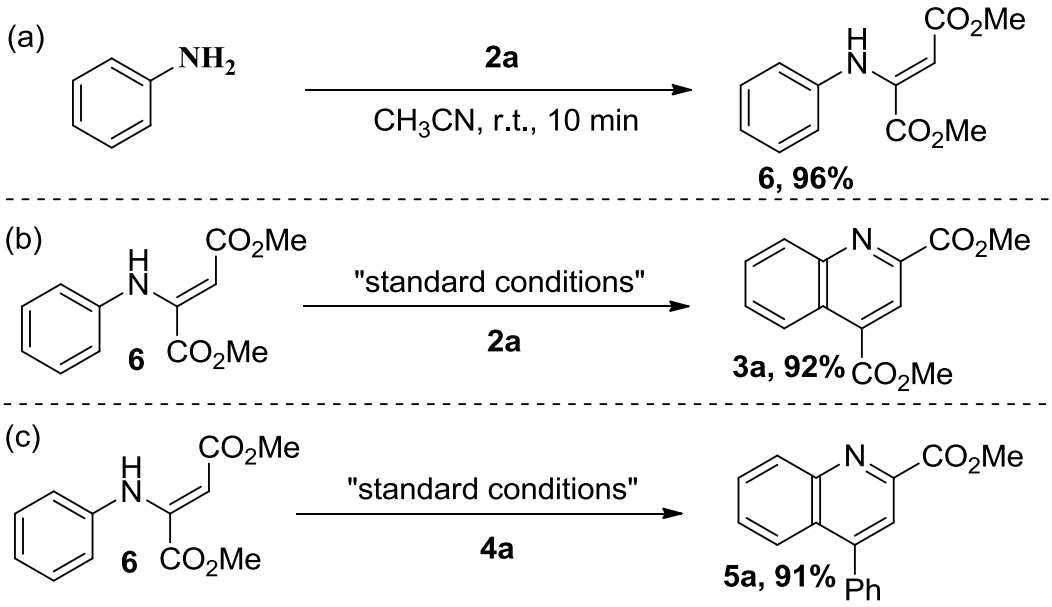
1.97
2.01
2.03
1.02
3.00
3.01
f1 (ppm)


X2-G
8.851
8.839
8.284
8.266
7.957
7.933
7.929
7.913
7.910
7.894
7.891
7.683
7.664
7.655
7.652
7.639
7.634
7.455
7.442
7.437
7.424
7.329
4.092
2.517
0.96
1.52
1.94
1.96
0.98
2.94
3.00
f1 (ppm)

## The experimental investigation for the Reaction Mechanism




**For the synthesis of the enamine 6 from the procedure (a):**

A sealed tube (30 mL) was charged with aniline (**1a**, 1.0 mmol), and dimethyl acetylenedicarboxylate (**2a**, 1.0 mmol) in $CH_3CN$ (2 mL). The mixture was stirred at room temperature for 10 minutes, then evaporated in vacuo. The obtained residue was purified by flash column chromatography using a mixture of PE and EA as the eluent to afford the enamine **6** in 96% yield: **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ ppm: 9.66 (s, 1H), 7.26 - 7.30 (m, 2H), 7.07 - 7.11 (t, 1H), 6.90 (d, $J$ = 8.0 Hz, 2H), 3.74 (s, 3H), 3.69 (s, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ ppm: 169.9, 164.9, 148.0, 140.3, 129.2, 124.2, 120.7, 93.6, 52.7, 51.2; **HRMS (ESI-TOF)** m/z calcd for $C_{12}H_{14}NO_4$ $[M + H]^+$ 236.0917, found 236.0920.

**For the synthesis of 3a from the procedure (b):**

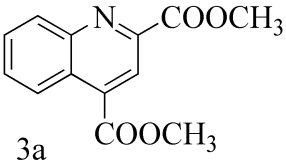
A sealed tube (30 mL) was charged with the enamine (**6**, 1.0 mmol), alkyne ester (**2a**, 1.1 mmol, 1.1 equiv.), then the $Cu(OTf)_2$ (0.05 mmol), $CH_3CN$ (2 mL) and HOTf (0.1 mmol) were added. The mixture was stirred at 120 $^oC$ for 24 hours, the mixture was quenched by *sat. aq.* $NaHCO_3$, and diluted with 20 mL dichloromethane and washed with 10 mL $H_2O$. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over $Na_2SO_4$.

After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 7:1) to afford the quinoline product **3a** in 92% yield.

**For the synthesis of 5a from the procedure (c):**

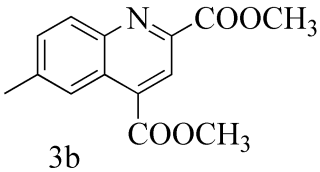
A sealed tube (30 mL) was charged with the enamine (**6**, 1.0 mmol), and ketone (**4a**, 1.1 mmol), then the $Cu(OTf)_2$ (0.05 mmol), HOTf (0.1 mmol) and $CH_3CN$ (2 mL) were added. The mixture was stirred at 100 $^oC$ for 24 hours. After the reaction finished, the mixture was quenched by *sat. aq.* $NaHCO_3$, and diluted with 20 mL of dichloromethane and washed with 10 mL of $H_2O$. The aqueous layer was extracted twice with dichloromethane (10 mL) and the combined organic phase was dried over $Na_2SO_4$. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 2:1) to afford the quinoline product **5a** in 91% yield.

## Characterization data for products



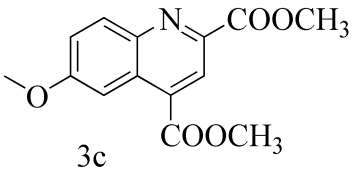
3a

**Quinoline-2,4-dicarboxylic acid dimethyl ester (3a):** Obtained as a yellow solid (223.0 mg, 91% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.86 (d, $J$ = 8.4 Hz, 1H), 8.70 (s, 1H), 8.38 (d, $J$ = 8.4 Hz, 1H), 7.84 - 7.88 (t, 1H), 7.76 - 7.80 (t, 1H), 4.12 (s, 3H), 4.08 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 166.6, 165.3, 148.6, 147.5, 136.0, 131.3, 130.6, 130.3, 126.3, 125.5, 122.3, 53.4, 52.9; **HRMS (ESI-TOF)** m/z Calcd. for $C_{13}H_{11}NO_4$ $[M + H]^+$ 246.0761. Found: m/z 246.0782.



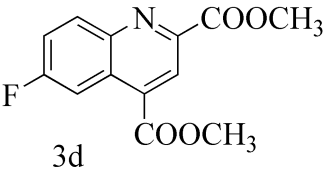
3b

**6-Methyl-quinoline-2,4-dicarboxylic acid dimethyl ester (3b):** Obtained as a gray solid (248.6 mg, 96% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.63 (d, $J$ = 18.4 Hz, 2H), 8.25 (d, $J$ = 8.4 Hz, 1H), 7.68 (d, $J$ = 8.4 Hz, 1H), 4.10 (s, 3H), 4.07 (s, 3H), 2.62 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 166.2, 165.4, 147.3, 146.5, 141.1, 135.1, 132.9, 130.9, 126.4, 124.3, 122.4, 53.4, 52.9, 22.3; **HRMS (ESI-TOF)** m/z Calcd. for $C_{14}H_{13}NO_4$ $[M + H]^+$ 260.0917. Found: m/z 260.0942.



3c

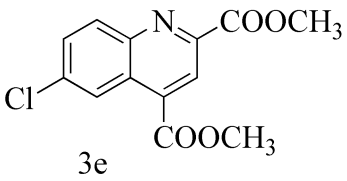
**6-Methoxy-quinoline-2,4-dicarboxylic acid dimethyl ester (3c):** Obtained as a light yellow solid (258.5 mg, 94% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.74 (s, 1H), 8.32 (d, $J$ = 2.8 Hz, 1H), 8.25 (d, $J$ = 9.6 Hz, 1H), 7.49 (dd, $J$ = 9.2 Hz, 1H), 4.10 (s, 3H), 4.06 (s, 3H), 4.10 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 166.2, 165.5, 161.1, 145.2, 144.6, 133.2, 132.8, 128.5, 123.9, 103.0, 55.8, 53.2, 52.7; **HRMS (ESI-TOF)** m/z Calcd. for $C_{14}H_{13}NO_5$ $[M + H]^+$ 276.0867. Found: m/z 276.0894.



3d

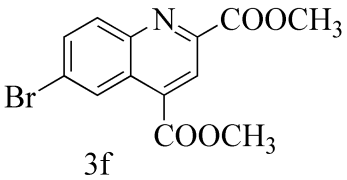
**6-Fluoro-quinoline-2,4-dicarboxylic acid dimethyl ester (3d):** Obtained as a light yellow solid (189.4 mg, 72% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.63 (d, $J$ =

18.4 Hz, 2H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 4.10 (s, 3H), 4.07 (s, 3H), 2.62 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 165.6, 165.1, 164.3, 161.8, 146.9, 145.9, 135.1, 133.9 (d, *J* = 10 Hz), 127.6 (d, *J* = 11 Hz), 123.3, 121.2 (d, *J* = 26 Hz), 109.7 (d, *J* = 25 Hz), 53.4, 53.0; **HRMS (ESI-TOF)** m/z Calcd. for $C_{13}H_{10}FNO_4$ $[M + H]^+$ 264.0667. Found: m/z 264.0772.



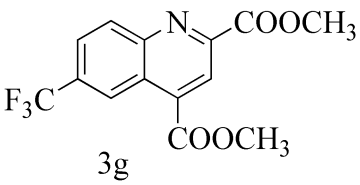
3e

**6-Chloro-quinoline-2,4-dicarboxylic acid dimethyl ester (3e):** Obtained as a light yellow solid (231.5 mg, 83% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 8.76 (s, 1H), 8.62 (dd, *J* = 10.4 Hz, 1H), 8.38 (dd, *J* = 9.6, 9.2 Hz, 1H), 7.63 (m, 1H), 4.12 (s, 3H), 4.08 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 165.5, 165.0, 147.7, 147.0, 137.0, 134.9, 132.6, 131.7, 126.9, 124.7, 123.3, 53.4, 53.0; **HRMS (ESI-TOF)** m/z Calcd. for $C_{13}H_{10}ClNO_4$ $[M + H]^+$ 280.0371. Found: m/z 280.0381.



3f

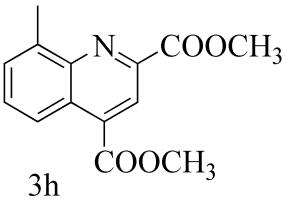
**6-Bromo-quinoline-2,4-dicarboxylic acid dimethyl ester (3f):** Obtained as a light yellow solid (274.5 mg, 85% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 9.12 (d, *J* = 2.4 Hz, 2H), 8.73 (s, 1H), 8.22 (d, *J* = 9.2 Hz, 1H), 7.93 (dd, *J* = 9.2, 8.8 Hz, 1H), 4.12 (s, 3H), 4.08 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 165.5, 165.0, 147.8, 147.2, 134.8, 134.3, 132.6, 128.0, 127.2, 125.6, 123.2, 53.5, 53.1; **HRMS (ESI-TOF)** m/z Calcd. for $C_{13}H_{10}BrNO_4$ $[M + H]^+$ 323.9866. Found: m/z 323.9880.



3g

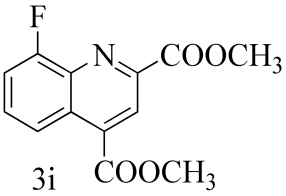
**6-Trifluoromethyl-quinoline-2,4-dicarboxylic acid dimethyl ester (3g):** Obtained as a Brownish-black solid (200.3 mg, 64% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 9.27 (s, 1H), 8.78 (s, 1H), 8.48 (d, *J* = 9.2 Hz, 1H), 8.01 (dd, *J* = 1.6, 8.8 Hz, 1H), 4.14 (s, 3H), 4.11 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 165.2, 164.8, 149.6, 149.4, 136.7, 132.3, 131.5 (q, *J* = 10 Hz), 126.3 (q, *J* = 11 Hz), 125.4 (q,

*J* = 8.8 Hz), 125.0, 123.8 (q, *J* = 9.2, 8.8 Hz), 123.4, 53.4, 53.0; **HRMS (ESI-TOF)** m/z Calcd. for $C_{14}H_{10}F_3NO_4$ $[M + H]^+$ 314.0635. Found: m/z 314.0669.



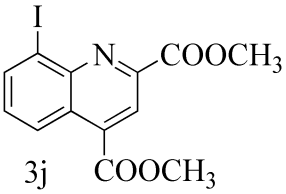
3h

**8-Methyl-quinoline-2,4-dicarboxylic acid dimethyl ester (3h):** Obtained as a light yellow solid (230.5 mg, 89% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 8.63 - 8.65 (m, 2H), 7.65 - 7.68 (m, 2H), 4.09 (s, 3H), 4.06 (s, 3H), 2.92 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 166.4, 135.6, 147.8, 146.2, 139.3, 136.2, 130.6, 130.1, 126.3, 123.3, 121.9, 53.1, 52.8, 18.3; **HRMS (ESI-TOF)** m/z Calcd. for $C_{14}H_{13}NO_4$ $[M + H]^+$ 260.0917. Found: m/z 260.0918.



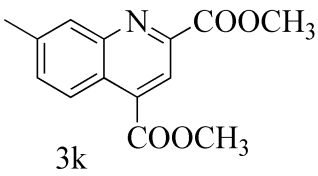
3i

**8-Fluoro-quinoline-2,4-dicarboxylic acid dimethyl ester (3i):** Obtained as a light yellow solid (178.8 mg, 68% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 8.75 (s, 1H), 8.66 (d, J = 8.8 Hz, 1H), 7.70 - 7.75 (q, 1H), 7.52 - 7.57 (t, 1H), 4.11 (s, 3H), 4.08 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 165.6, 165.0, 159.7, 157.1, 147.7, 139.2 (d, J = 19.7 Hz), 136.0, 130.3 (d, J = 8.1 Hz), 127.5, 123.2, 121.4 (d, J = 5.1 Hz), 114.6 (d, J = 18.5 Hz), 53.4, 53.0; **HRMS (ESI-TOF)** m/z Calcd. for $C_{13}H_{10}FNO_4$ $[M + H]^+$ 264.0667. Found: m/z 264.0668.



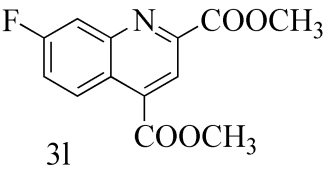
3j

**8-Iodo-quinoline-2,4-dicarboxylic acid dimethyl ester (3j):** Obtained as a yellow solid (259.7 mg, 70% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 8.85 (d, *J* = 8.4 Hz, 1H), 8.71 (s, 1H), 8.49 (d, *J* = 7.2 Hz, 1H), 7.43 - 7.47 (t, 1H), 4.11 (s, 3H), 4.07 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 165.5, 164.9, 148.3, 147.3, 141.4, 136.9, 131.1, 127.1, 126.3, 123.1, 105.4, 53.4, 53.1; **HRMS (ESI-TOF)** m/z Calcd. for $C_{13}H_{10}INO_4$ $[M + H]^+$ 371.9727. Found: m/z 371.9729.



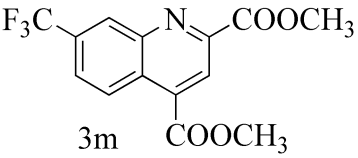
3k

**7-Methyl-quinoline-2,4-dicarboxylic acid dimethyl ester (3k):** Obtained as a light yellow solid (238.3 mg, 92% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.74 (d, $J$ = 8.8 Hz, 1H), 8.63 (s, 1H), 8.15 (s, 1H), 7.60 (d, $J$ = 8.8 Hz, 1H), 4.10 (s, 3H), 4.06 (s, 3H), 2.60(s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 166.1, 165.5, 148.9, 147.4, 141.1, 135.7, 132.7, 130.1, 125.1, 124.4, 121.5, 53.3, 52.8, 21.6; **HRMS (ESI-TOF)** m/z Calcd. for $C_{14}H_{13}NO_4$ $[M + H]^+$ 260.0917. Found: m/z 260.0918.



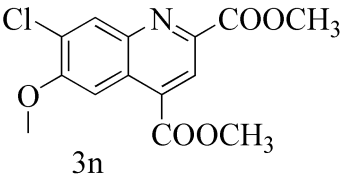
3l

**7-Fluoro-quinoline-2,4-dicarboxylic acid dimethyl ester (3l):** Obtained as a white solid (181.5 mg, 69% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.86 (d, $J$ = 9.2 Hz, 1H), 8.69 (s, 1H), 8.37 (d, J = 2.0 Hz, 1H), 7.60 (dd, $J$ = 9.2, 2.0 Hz, 1H), 4.12 (s, 3H), 4.08 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 165.5, 165.0, 149.0, 148.6, 136.8, 136.0, 131.2, 129.9, 127.0, 124.7, 122.5, 53.5, 53.0; **HRMS (ESI-TOF)** m/z Calcd. for $C_{13}H_{10}FNO_4$ $[M + H]^+$ 264.0667. Found: m/z 264.0668.



3m

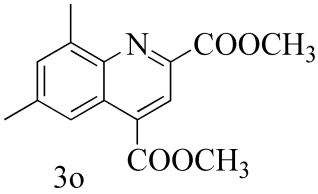
**7-Trifluoromethyl-quinoline-2,4-dicarboxylic acid dimethyl ester (3m):** Obtained as a light yellow solid (274.5 mg, 85% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.86 (d, $J$ = 9.2 Hz, 1H), 8.69 (s, 1H), 8.37 (d, J = 2.0 Hz, 1H), 7.60 (dd, $J$ = 9.2, 2.0 Hz, 1H), 4.12 (s, 3H), 4.08 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 165.3, 164.7, 149.0, 147.6, 136.0, 132.3 (q, J = 67 Hz), 128.8 (q, J = 9 Hz), 127.7, 127.2, 125.6 (q, J = 3 Hz), 124.0, 122.1, 53.5, 53.1; **HRMS (ESI-TOF)** m/z Calcd. for $C_{14}H_{10}F_3NO_4$ $[M + H]^+$ 314.0635. Found: m/z 314.0636.



3n

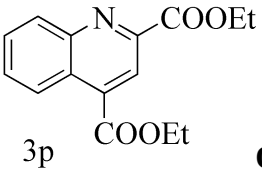
**7-Chloro-6-methoxy-quinoline-2,4-dicarboxylic acid**

**dimethyl ester (3n):** Obtained as a light yellow solid (287.4 mg, 93% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.73 (s, 1H), 8.45 (s, 1H), 7.39 (s, 1H), 4.10 (s, 3H), 4.10 (s, 3H), 4.06 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 165.9, 165.2, 156.5, 145.7, 144.7, 133.1, 131.8, 129.5, 127.0, 123.2, 103.9, 56.6, 53.3, 52.8; **HRMS (ESI-TOF)** m/z Calcd. for $C_{14}H_{12}ClNO_5$ $[M + H]^+$ 310.0477. Found: m/z 310.0447.



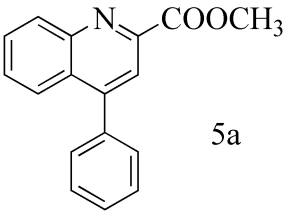
3o

**6,8-Dimethyl-quinoline-2,4-dicarboxylic acid dimethyl ester (3o):** Obtained as a light yellow solid (259.4 mg, 95% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.60 (s, 1H), 8.40 (s, 1H), 7.53 (s, 1H), 4.07 (s, 3H), 4.05 (s, 3H), 2.87 (s, 3H), 2.56 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 166.5, 165.7, 146.5, 145.2, 140.7, 138.8, 135.2, 133.0, 126.4, 122.1, 121.9, 53.0, 52.7, 22.3, 18.2; **HRMS (ESI-TOF)** m/z Calcd. for $C_{15}H_{15}NO_4$ $[M + H]^+$ 274.1074. Found: m/z 274.1074.



3p

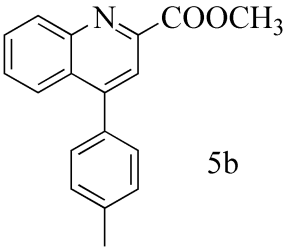
**Quinoline-2,4-dicarboxylic acid diethyl ester (3p):** Obtained as a light red solid (237.5 mg, 87% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.82 (d, $J$ = 8.4 Hz, 1H), 8.65 (s, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.82 - 7.86 (t, 1H), 7.73 - 7.78 (t, 1H), 4.52 - 4.62 (m, 4H), 1.48 - 1.53 (m, 6H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 165.7, 164.9, 148.6, 147.9, 136.5, 131.3, 130.4, 130.1, 126.2, 125.5, 122.1, 62.5, 62.1, 14.4, 14.3; **HRMS (ESI-TOF)** m/z Calcd. for $C_{15}H_{15}NO_4$ $[M + H]^+$ 274.1074. Found: m/z 274.1074.



5a

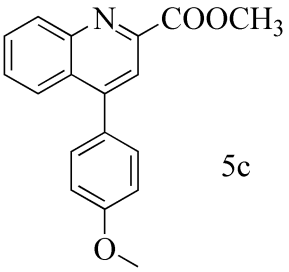
**4-Phenyl-quinoline-2-carboxylic acid methyl ester (5a):** Obtained as a light yellow solid (192.0 mg, 73% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)**

$\delta$ ppm: 8.38 (d, $J$ = 8.8 Hz, 1H), 8.16 (s, 1H), 7.98 (d, $J$ = 8.8 Hz, 1H), 7.77 - 7.81 (t, 1H), 7.53 - 7.62 (m, 6H), 4.10 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: 166.0, 149.9, 148.2, 147.5, 137.5, 131.1, 130.1, 129.6, 128.8, 128.7, 128.7, 127.9, 125.8, 121.3, 53.2; **HRMS (ESI-TOF)** m/z calcd for $C_{17}H_{14}NO_2$ $[M + H]^+$ 264.1079, found 264.0985.



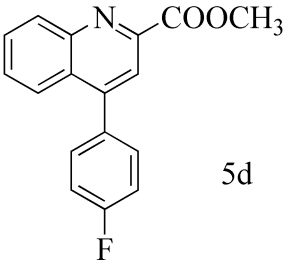

5b

**4-p-Tolyl-quinoline-2-carboxylic acid methyl ester (5b):** Obtained as a light yellow solid (216.1 mg, 78% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: 8.37 (d, $J$ = 8.8 Hz, 1H), 8.14 (s, 1H), 8.01 (d, $J$ = 8.4 Hz, 1H), 7.76 - 7.80 (t, 1H), 7.57 - 7.61 (t, 1H), 7.43 (d, $J$ = 7.6 Hz, 2H), 7.35 (d, $J$ = 7.6 Hz, 2H), 4.09 (s, 3H), 2.47 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: 166.1, 150.0, 148.2, 147.5, 138.8, 134.6, 131.1, 130.0, 129.5, 129.4, 128.5, 128.0, 125.8, 121.2, 53.2, 21.3; **HRMS (ESI-TOF)** m/z calcd for $C_{18}H_{16}NO_2$ $[M + H]^+$ 278.1176, found 278.1177.



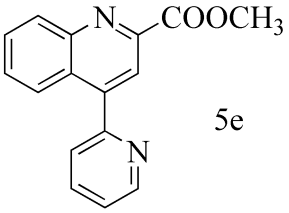

5c

**4-(4-Methoxy-phenyl)-quinoline-2-carboxylic acid methyl ester (5c):** Obtained as a yellow solid (222.5 mg, 76% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.36 (d, J = 8.4 Hz, 1H), 8.14 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.97 - 7.81 (t, 1H), 7.58 - 7.62 (t, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 4.10 (s, 3H), 3.91 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 166.1, 160.1, 149.6, 148.2, 147.4, 131.1, 130.9, 130.0, 128.5, 127.9, 125.8, 121.2, 114.2, 55.4, 53.1; **HRMS (ESI-TOF)** m/z Calcd. for $C_{18}H_{15}NO_3$ $[M + H]^+$ 294.1125. Found: m/z 294.1127.



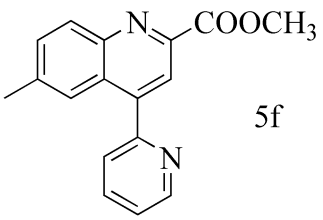
5d

**4-(4-Fluoro-phenyl)-quinoline-2-carboxylic acid methyl ester (5d):** Obtained as a light yellow solid (196.7 mg, 70% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: 8.38 (d, $J$ = 8.4 Hz, 1H), 8.13 (s, 1H), 7.93 (d, $J$ = 8.4 Hz, 1H), 7.78 - 7.82 (t, 1H), 7.60 - 7.63 (t, 1H), 7.50 - 7.53 (m, 2H), 7.23 - 7.28 (m, 2H), 4.10 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: 166.0, 163.1 (d, $J$ = 247.4), 148.5 (d, $J$ = 68), 147.4, 133.4 (d, $J$ = 3.6), 131.4, 131.3, 131.2, 130.2, 128.8, 127.8, 125.5, 121.3, 115.8 (d, $J$ = 21.6), 53.2; **HRMS (ESI-TOF)** m/z calcd for $C_{17}H_{13}FNO_2$ $[M + H]^+$ 282.0925, found 282.0953.



5e

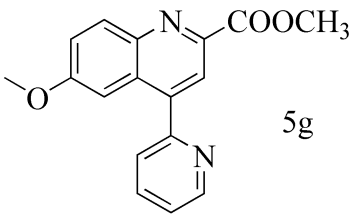
**4-Pyridin-2-yl-quinoline-2-carboxylic acid methyl ester (5e):** Obtained as a gray solid (235.0 mg, 89% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.86 (d, J = 4.8 Hz, 1H), 8.39 (d, J = 8.4 Hz, 1H), 8.33 (s, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.91 - 7.95 (td, 1H), 7.80 - 7.84 (m, 1H), 7.64 - 7.71 (m, 2H), 7.44 - 7.47 (m, 1H), 4.11 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 165.8, 156.1, 149.8, 148.4, 147.5, 137.0, 131.0, 130.2, 129.1, 127.1, 125.6, 124.9, 123.4, 121.3, 53.2; **HRMS (ESI-TOF)** m/z Calcd. for $C_{16}H_{12}N_2O_2$ $[M + H]^+$ 265.0972. Found: m/z 265.0969.



5f

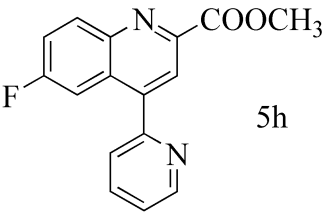
**6-Methyl-4-pyridin-2-yl-quinoline-2-carboxylic acid**

**methyl ester (5f):** Obtained as a light yellow solid (269.7 mg, 97% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.85 (d, J = 4.0 Hz, 1H), 8.28 (d, J = 9.6 Hz, 1H), 8.27 (s, 1H), 7.90 - 7.95 (m, 2H), 7.63 - 7.68 (m, 2H), 7.43 - 7.46 (m, 1H), 4.09 (s, 3H), 2.53 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 165.9, 156.4, 149.8, 146.6, 146.5, 139.6, 137.0, 132.6, 132.4, 130.8, 127.2, 124.9, 124.3, 123.3, 121.5, 53.1, 22.1; **HRMS (ESI-TOF)** m/z Calcd. for $C_{17}H_{14}N_2O_2$ $[M + H]^+$ 279.1128. Found: m/z 279.1125.




5g

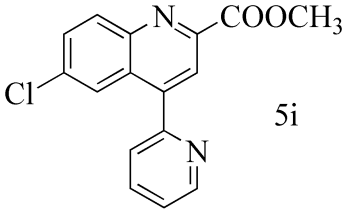
**6-Methoxy-4-pyridin-2-yl-quinoline-2-carboxylic acid methyl ester (5g):** Obtained as a light yellow solid (273.4 mg, 93% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.85 (d, J = 4.0 Hz, 1H), 8.26 - 8.28 (m, 2H), 7.91 - 7.94 (t, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.57 (s, 1H), 7.43 - 7.47 (m, 2H), 4.08 (s, 3H), 3.86 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 165.9, 159.9, 156.6, 149.7, 145.4, 144.9, 144.6, 137.1, 132.5, 128.5, 124.7, 123.3, 123.0, 121.9, 103.3, 55.4, 53.0; **HRMS (ESI-TOF)** m/z Calcd. for $C_{17}H_{14}N_2O_3$ $[M + H]^+$ 295.1083. Found: m/z 295.1075.




5h

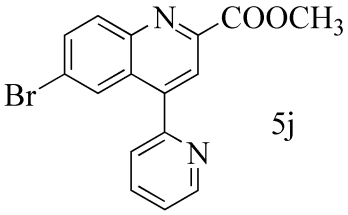
**6-Fluoro-4-pyridin-2-yl-quinoline-2-carboxylic acid methyl ester (5h):** Obtained as a light yellow solid (203.0 mg, 72% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.86 (d, J = 4.8 Hz, 1H), 8.37 - 8.41 (m, 1H), 8.34 (s, 1H), 7.92 - 7.97 (m, 2H), 7.70 (d, J = 7.6 Hz, 1H), 7.57 - 7.61 (m, 1H), 7.45 - 7.48 (m, 2H), 4.10 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 165.6, 160.9, 155.8, 149.9, 146.9 (d, J = 2.9 Hz), 146.7 (d, J = 6.0 Hz), 145.6, 137.2, 133.7 (d, J = 9.4 Hz), 128.2 (d, J = 10.5 Hz), 124.7, 123.6, 121.9, 120.7 (d, J = 26.1 Hz), 109.4 (d, J = 23.8 Hz),

53.2; **HRMS (ESI-TOF)** m/z Calcd. for $C_{16}H_{11}FN_2O_2$ $[M + H]^+$ 283.0883. Found: m/z 283.0876.



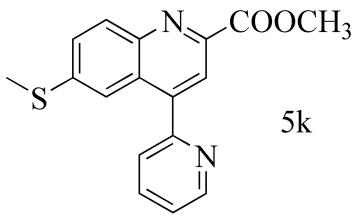

5i

**6-Chloro-4-pyridin-2-yl-quinoline-2-carboxylic acid methyl ester (5i):** Obtained as a light gray solid (223.5 mg, 75% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 8.87 (d, *J* = 4.0 Hz, 1H), 8.28 - 8.33 (m, 3H), 7.92 - 7.96 (t, 1H), 7.75 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H),7.46 - 7.49 (m, 1H), 4.10 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ165.5, 155.6, 149.9, 147.6, 146.8, 146.5, 137.2, 135.4, 132.5, 131.3, 127.7, 124.79, 124.76, 123.6, 122.1, 53.3; **HRMS (ESI-TOF)** m/z Calcd. for $C_{16}H_{11}ClN_2O_2$ $[M + H]^+$ 299.0582. Found: m/z 299.0579.




5j

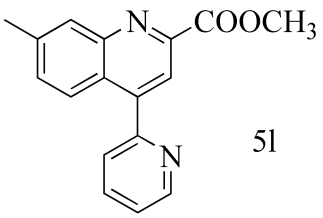
**6-Bromo-4-pyridin-2-yl-quinoline-2-carboxylic acid methyl ester (5j):** Obtained as a gray solid (266.7 mg, 78% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 8.86 (d, *J* = 4.0 Hz, 1H), 8.45 (s, 1H), 8.32 (s, 1H), 8.24 (d, *J* = 9.2 Hz, 1H), 7.92 - 7.96 (t, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.46 - 7.49 (t, 1H), 4.11 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 165.5, 155.6, 150.0, 147.8, 147.0, 146.5, 137.3, 133.9, 132.6, 128.2, 128.1, 124.8, 123.9, 123.7, 122.1, 53.3; **HRMS (ESI-TOF)** m/z Calcd. for $C_{16}H_{11}BrN_2O_2$ $[M + H]^+$ 343.0077. Found: m/z 343.0076.




5k

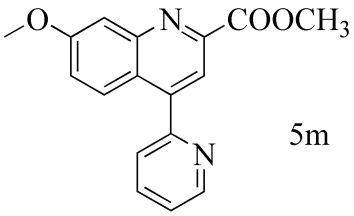
**6-Methylsulfanyl-4-pyridin-2-yl-quinoline-2-carboxylic**

**acid methyl ester (5k):** Obtained as a yellow solid (285.2 mg, 92% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.85 (d, *J* = 4.8 Hz, 1H), 8.29 (s, 1H), 8.24 (d, *J* = 9.2 Hz, 1H), 8.00 (s, 1H), 7.91 - 7.94 (t, 1H), 7.65 - 7.71 (m, 2H), 7.43 - 7.46 (m, 1H), 4.09 (s, 3H), 2.51 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 165.7, 156.1, 149.7, 146.5, 146.2, 145.4, 141.3, 137.0, 130.9, 129.2, 127.4, 124.8, 123.4, 122.0, 119.6, 53.1, 15.1; **HRMS (ESI-TOF)** m/z Calcd. for $C_{17}H_{14}N_2O_2S$ $[M + H]^+$ 311.0849. Found: m/z 311.0848.




5l

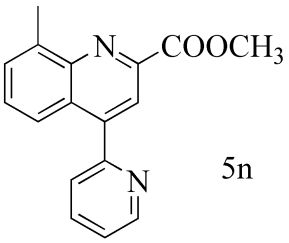
**7-Methyl-4-pyridin-2-yl-quinoline-2-carboxylic acid methyl ester (5l):** Obtained as a dark red solid (261.3 mg, 94% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.81 (d, J = 2.8 Hz, 1H), 8.25 (s, 1H), 8.15 (s, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.85 - 7.88 (t, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.39 - 7.41 (t, 1H), 4.08 (s, 3H), 2.56 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 165.8, 156.2, 149.8, 148.6, 147.3, 147.1, 140.5, 136.9, 131.4, 129.9, 125.19, 125.14, 124.8, 123.3, 120.6, 53.0, 21.6; **HRMS (ESI-TOF)** m/z Calcd. for $C_{17}H_{14}N_2O_2$ $[M + H]^+$ 279.1128. Found: m/z 279.1126.




5m

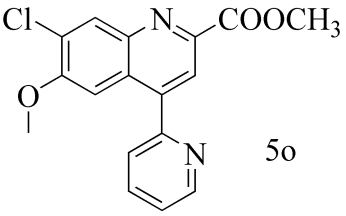
**7-Methoxy-4-pyridin-2-yl-quinoline-2-carboxylic acid methyl ester (5m):** Obtained as a yellow solid (267.5 mg, 91% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.84 (d, J = 4.4 Hz, 1H), 8.20 (s, 1H), 8.13 (d, J = 9.2 Hz, 1H), 7.89 - 7.93 (t, 1H), 7.69 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.42 - 7.45 (t, 1H), 7.30 (d, J = 9.2 Hz, 1H), 4.10 (s, 3H), 3.98 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 166.0, 161.1, 156.4, 150.5, 149.8, 147.7, 147.2, 137.0, 126.7, 124.9, 123.4, 122.6, 122.5, 119.6, 108.5, 55.7, 53.2; **HRMS (ESI-TOF)** m/z Calcd. for $C_{17}H_{14}N_2O_3$ [M +

H] $^{+}$ 295.1077. Found: m/z 295.1076.



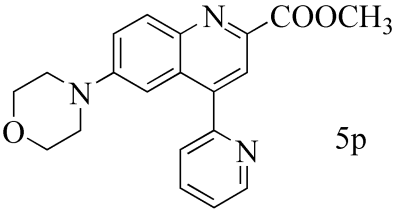
5n

**8-Methyl-4-pyridin-2-yl-quinoline-2-carboxylic acid methyl ester (5n):** Obtained as a light yellow solid (250.1 mg, 90% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 8.84 (d, J = 4.4 Hz, 1H), 8.28 (s, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.88 - 7.92 (t, 1H), 7.66 (d, J = 7.2 Hz, 2H), 7.51 - 7.55 (t, 1H), 7.42 - 7.45 (t, 1H), 4.07 (s, 3H), 2.95 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 166.1, 156.3, 149.8, 147.6, 147.5, 146.3, 139.1, 136.8, 130.3, 128.8, 127.2, 125.0, 123.4, 123.2, 121.2, 52.9, 18.3; **HRMS (ESI-TOF)** m/z Calcd. for $C_{17}H_{14}N_2O_2$ [M + H] $^{+}$ 279.1128. Found: m/z 279.1128.



5o

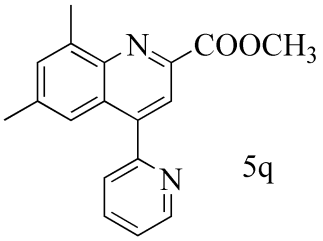
**7-Chloro-6-methoxy-4-pyridin-2-yl-quinoline-2-carboxylic acid methyl ester (5o):** Obtained as a yellow solid (275.5 mg, 84% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 8.85 (d, J = 4.4 Hz, 1H), 8.42 (s, 1H), 8.28 (s, 1H), 7.93 - 7.97 (t, 1H), 7.71 - 7.74 (m, 2H), 7.45 - 7.48 (m, 1H), 4.09 (s, 3H), 3.95 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 165.7, 164.6, 162.1, 150.0, 149.9, 148.7, 136.1, 128.1, 128.0, 123.4, 121.7, 120.9, 120.7, 114.7, 114.5, 53.4, 53.0; **HRMS (ESI-TOF)** m/z Calcd. for $C_{17}H_{13}ClN_2O_3$ [M + H] $^{+}$ 329.0687. Found: m/z 329.0664.



5p

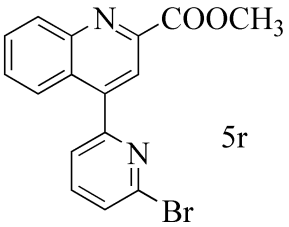
**6-Morpholin-4-yl-4-pyridin-2-yl-quinoline-2-carboxylic acid methyl ester (5p):** Obtained as a yellow solid (293.2 mg, 84% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 8.84 (d, J = 4.4 Hz, 1H), 8.23 - 8.25 (t, 2H), 7.90 - 7.94 (t, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.54 - 7.56 (m, 1H), 7.41 - 7.47

(m, 2H), 4.07 (s, 3H), 3.85 - 3.87 (t, 2H), 3.27 - 3.29 (t, 2H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 166.0, 156.8, 150.9, 149.6, 144.8, 144.1, 143.9, 137.0, 131.9, 128.6, 124.6, 123.2, 122.1, 121.9, 105.5, 66.5, 52.9, 48.3; **HRMS (ESI-TOF)** m/z Calcd. for $C_{20}H_{19}N_3O_3$ $[M + H]^+$ 350.1499. Found: m/z 350.1496.



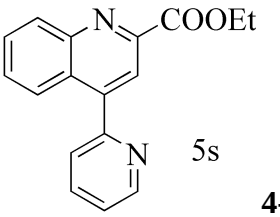

5q

**6,8-Dimethyl-4-pyridin-2-yl-quinoline-2-carboxylic acid methyl ester (5q):** Obtained as a light yellow solid (265.7 mg, 91% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.84 (d, J = 4.8 Hz, 1H), 8.23 (s, 1H), 7.88 - 7.92 (t, 1H), 7.73 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.50 (s, 1H), 7.41 - 7.44 (t, 1H), 4.16 (s, 3H), 2.91 (s, 3H), 2.47 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 166.2, 156.9, 149.8, 146.7, 146.3, 145.4, 139.1, 138.6, 136.8, 132.7, 127.3, 124.9, 123.1, 122.1, 121.3, 52.9, 22.1, 18.2; **HRMS (ESI-TOF)** m/z Calcd. for $C_{18}H_{16}N_2O_2$ $[M + H]^+$ 293.1285. Found: m/z 293.1288.



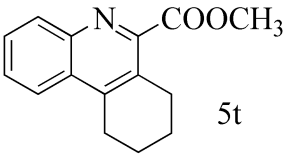

5r

**4-(6-Bromo-pyridin-2-yl)-quinoline-2-carboxylic acid methyl ester (5r):** Obtained as a light yellow solid (301.0 mg, 88% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.39 (d, J = 8.4 Hz, 1H), 8.31 (s, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.76 - 7.85 (m, 2H), 7.64 - 7.71 (m, 3H), 4.11 (s, 3H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 165.6, 156.8, 148.3, 147.4, 145.5, 142.1, 139.2, 131.1, 130.3, 129.4, 127.9, 126.7, 125.2, 123.7, 121.4, 53.2; **HRMS (ESI-TOF)** m/z Calcd. for $C_{16}H_{11}BrN_2O_2$ $[M + H]^+$ 343.0077. Found: m/z 343.0077.



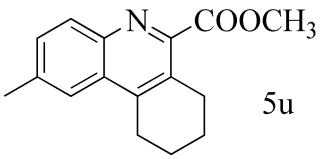
5s

**4-Pyridin-2-yl-quinoline-2-carboxylic acid ethyl ester (5s):** Obtained as a light yellow solid (241.9 mg, 87% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 8.85 (d, J = 4.4 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H), 8.30 (s, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.90 - 7.94 (t, 1H), 7.79 - 7.83 (t, 1H), 7.63 - 7.70 (m, 2H), 7.43 - 7.46 (m, 1H), 4.55 - 4.61 (q, 2H), 1.48 - 1.52 (t, 2H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 165.3, 156.2, 149.9, 148.4, 147.9, 147.4, 136.9, 131.2, 130.0, 129.0, 127.1, 125.6, 124.9, 123.3, 121.3, 62.2, 14.4; **HRMS (ESI-TOF)** m/z Calcd. for $C_{17}H_{14}N_2O_2$ $[M + H]^+$ 279.1128. Found: m/z 279.1114.



5t

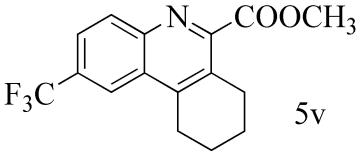
**7,8,9,10-Tetrahydro-phenanthridine-6-carboxylic acid methyl ester (5t):** Obtained as a red solid (209.7 mg, 87% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 8.15 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.66 - 7.70 (t, 1H), 7.58 - 7.62 (t, 1H), 4.10 (s, 3H), 3.18 - 3.19 (t, 2H), 3.04 - 3.07 (t, 2H), 1.95 - 1.98 (m, 2H), 1.85 - 1.90 (m, 2H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 167.4, 150.4, 144.8, 143.5, 130.4, 128.7, 128.2, 128.1, 127.7, 127.4, 52.7, 26.5, 25.6, 22.1, 21.8; **HRMS (ESI-TOF)** m/z Calcd. for $C_{15}H_{15}NO_2$ $[M + H]^+$ 242.1176. Found: m/z 242.1175.



5u

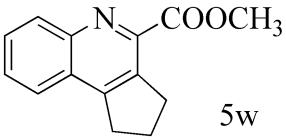
**2-Methyl-7,8,9,10-tetrahydro-phenanthridine-6-carboxylic acid methyl ester (5u):** Obtained as a light yellow solid (232.1 mg, 91% yield); **$^{1}$H NMR (400 MHz, $CDCl_3$)** *δ* ppm: δ 8.03 (d, J = 8.4 Hz, 1H), 7.70 (s, 1H), 7.50 (d, J = 8.4 Hz, 1H), 4.02 (s, 3H), 3.12 - 3.15 (t, 2H), 3.03 - 3.06 (t, 2H), 2.55 (s, 3H), 1.92 - 1.98 (m, 2H), 1.83 - 1.88 (m, 2H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** *δ* ppm: δ 167.5149.3,

143.4, 142.8, 137.9, 131.0, 130.2, 128.5, 128.2, 121.5, 52.7, 26.6, 25.8, 22.3, 22.1, 21.9; **HRMS (ESI-TOF)** m/z Calcd. for $C_{16}H_{17}NO_2$ $[M + H]^+$ 256.1332. Found: m/z 256.1332.




5v

**2-Trifluoromethyl-7,8,9,10-tetrahydro-phenanthridine-6-carboxylic acid methyl ester (5v):** Obtained as a yellow solid (234.8 mg, 76% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 8.26 - 8.28 (m, 2H), 7.84 - 7.87 (dd, J = 8.8, 1.6 Hz, 1H), 4.05 (s, 3H), 3.21 - 3.24 (t, 2H), 3.04 - 3.07 (t, 2H), 1.98 - 2.04 (m, 2H), 1.87 - 1.93 (m, 2H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 166.9, 152.6, 145.9, 144.7, 131.5, 129.2 (q), 127.2 (q), 125.4, 124.3 (q), 122.7, 120.6 (q), 52.8, 26.3, 25.6, 21.9, 21.5; **HRMS (ESI-TOF)** m/z Calcd. for $C_{16}H_{14}F_3NO_2$ $[M + H]^+$ 310.1049. Found: m/z 310.1050.

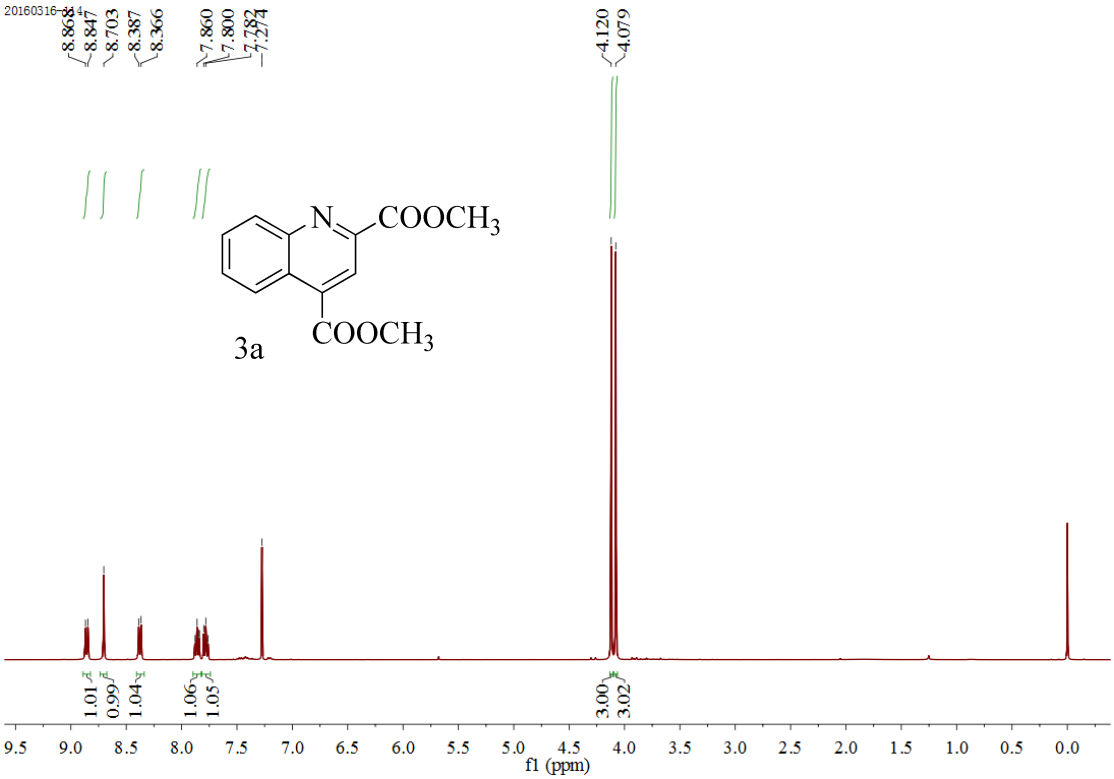


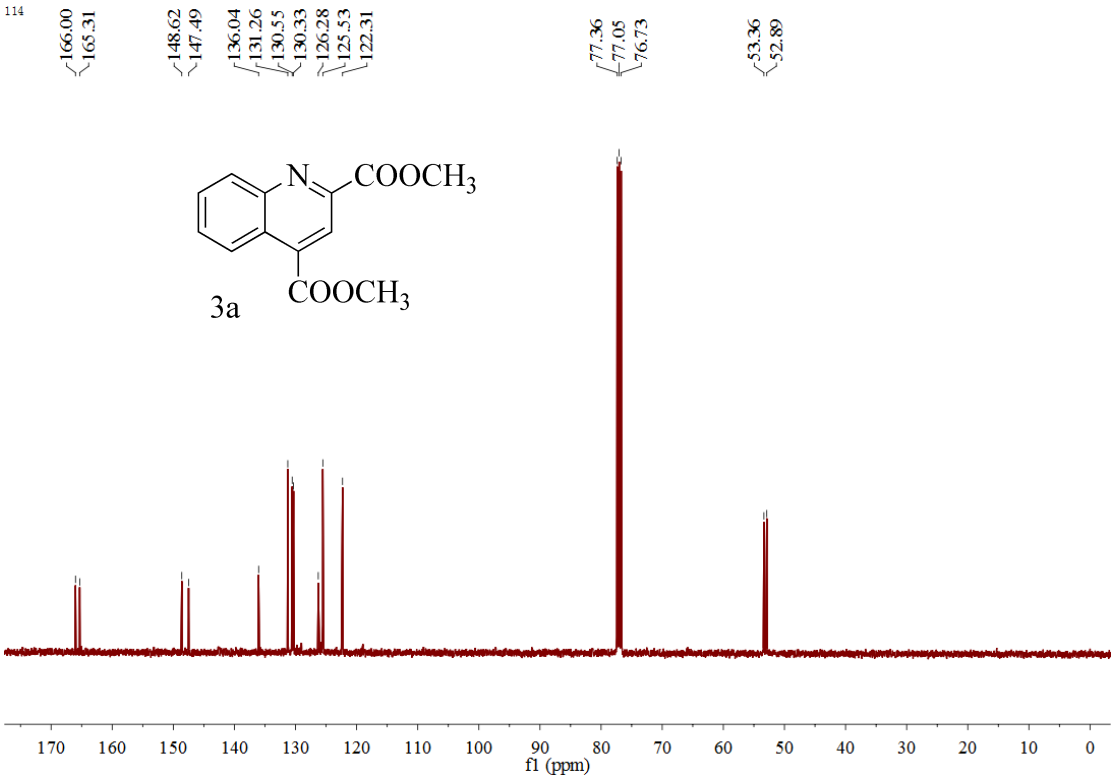

5w

**2,3-Dihydro-1H-cyclopenta[c]quinoline-4-carboxylic acid methyl ester (5w):** Obtained as a light yellow solid (186.1 mg, 82% yield); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ ppm: δ 7.43 - 7.53 (m, 2H), 7.23 (d, J = 7.2 Hz, 2H), 7.13 (t, 1H), 3.91 (s, 3H), 3.08 - 3.11 (t, 2H), 2.48 - 2.52 (t, 2H), 1.99 - 2.07 (m, 2H); **$^{13}$C NMR (100 MHz, $CDCl_3$)** $\delta$ ppm: δ 165.7, 163.4, 152.0, 138.8, 138.5, 129.6, 129.0, 127.0, 120.2, 117.3, 52.5, 33.1, 31.1, 22.2; **HRMS (ESI-TOF)** m/z Calcd. for $C_{14}H_{13}NO_2$ $[M + H]^+$ 228.1019. Found: m/z 228.0978.

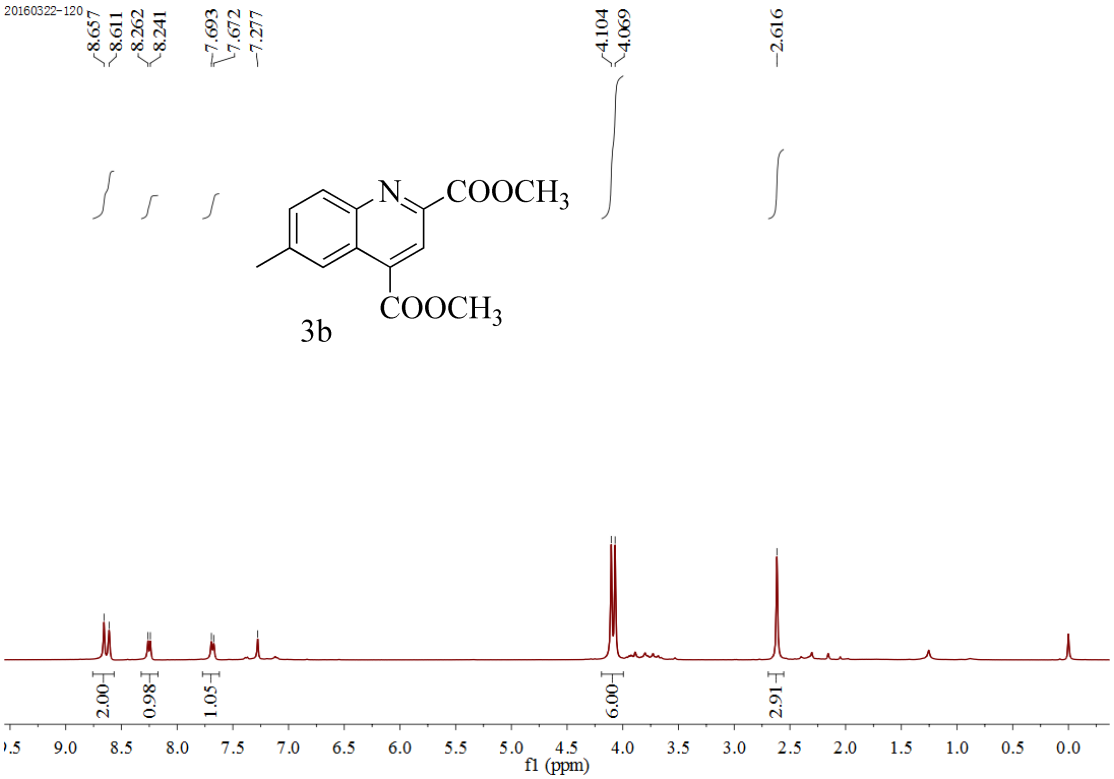
# Copies of $^{1}H$ and $^{13}C$ NMR spectra of products

## Product 3a



**Product 3b**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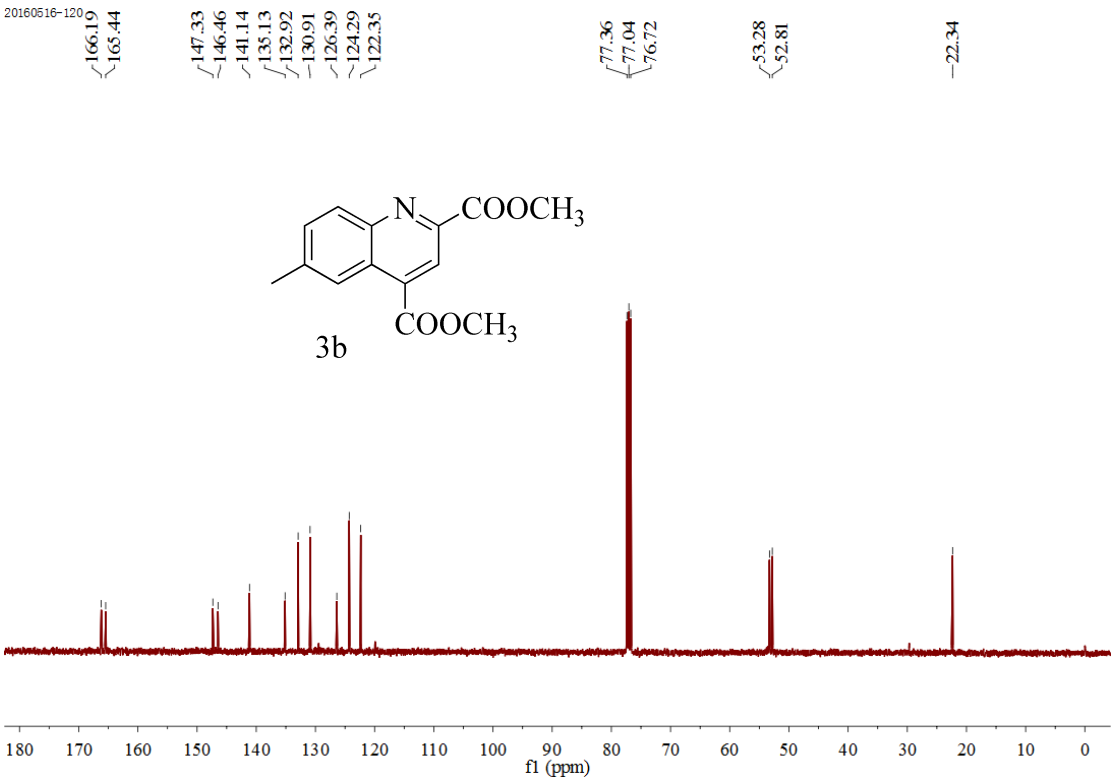
8.262
8.241
7.693
7.672
7.277
4.104
4.069
2.616
N
COOCH3
COOCH3
3b
2.00
0.98
1.05
6.00
2.91
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


20160516-120
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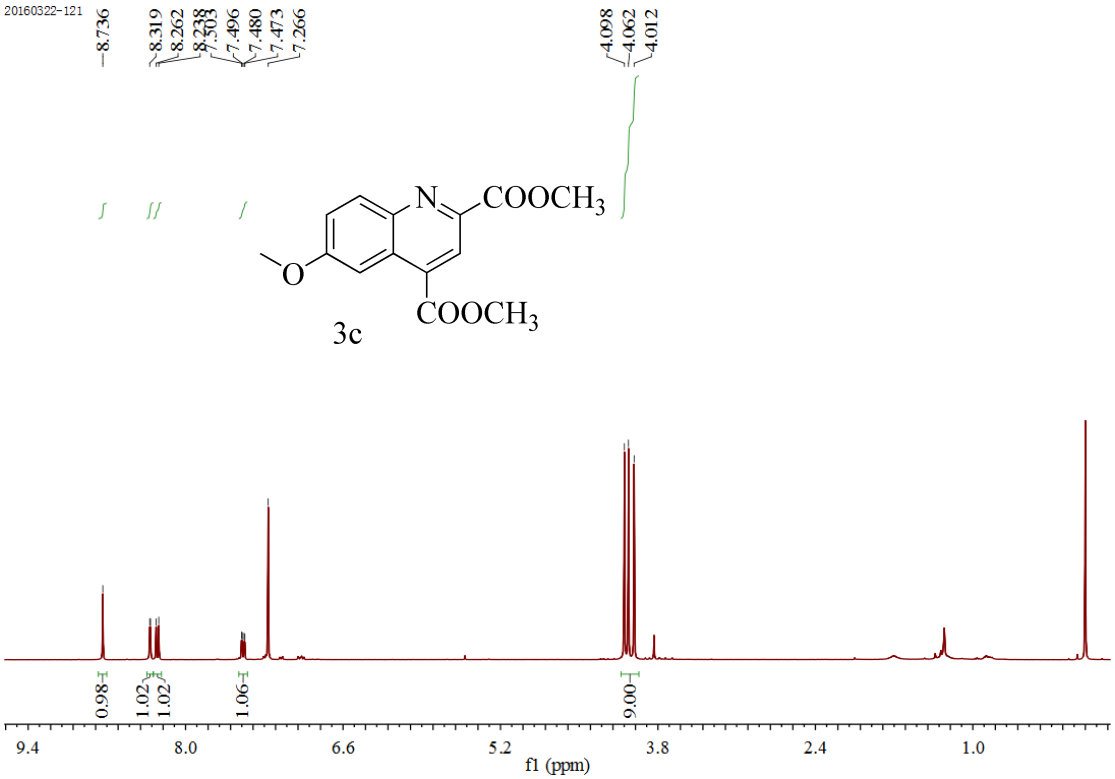
165.44
147.33
146.46
141.14
135.13
132.92
130.91
126.39
124.29
122.35
77.36
77.04
76.72
53.28
52.81
22.34
N
COOCH3
COOCH3
3b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

## Product 3c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8.238
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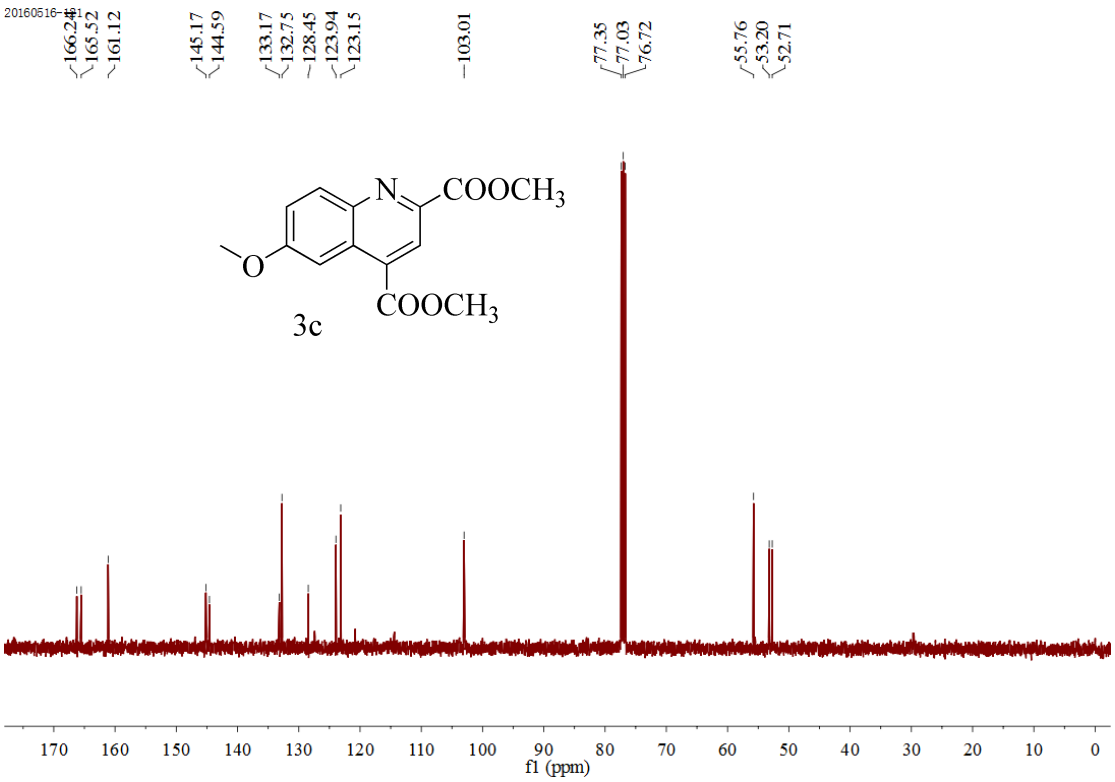
7.496
7.480
7.473
7.266
4.098
4.062
4.012
N
COOCH3
O
COOCH3
3c
0.98
1.02
1.02
1.06
9.00
9.4
8.0
6.6
5.2
3.8
2.4
1.0
f1 (ppm)


20160516-121
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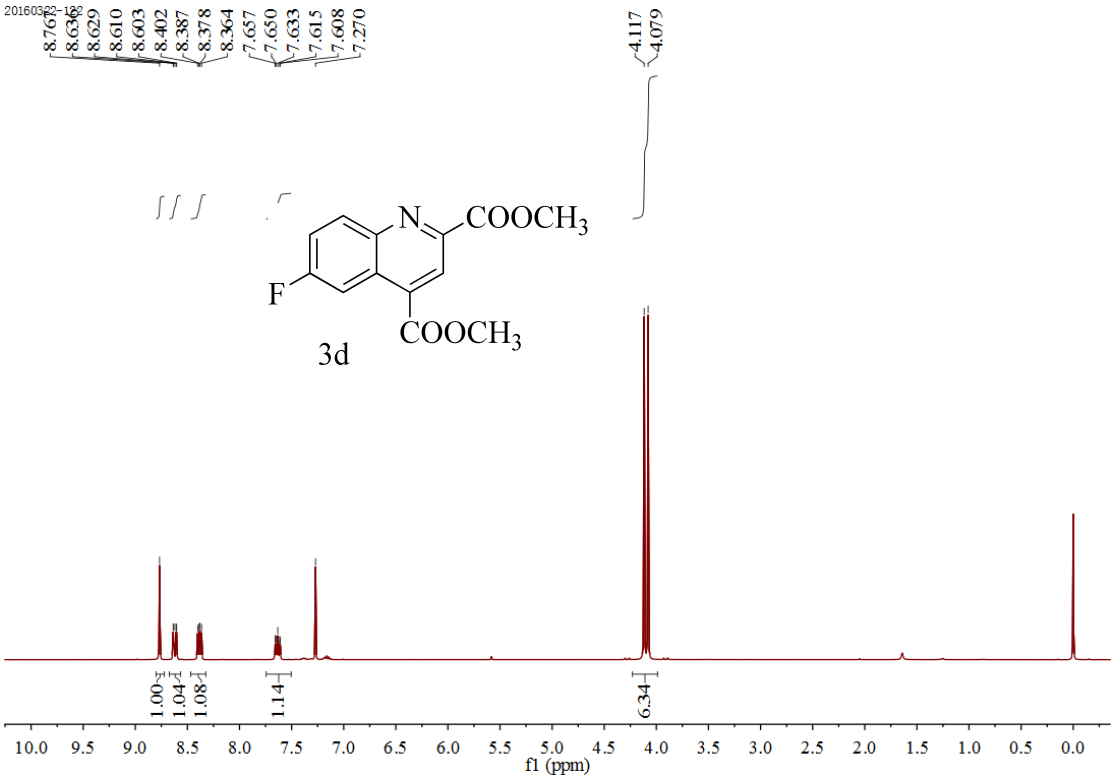
161.12
145.17
144.59
133.17
132.75
128.45
123.94
123.15
103.01
77.35
77.03
76.72
55.76
53.20
52.71
N
COOCH3
O
COOCH3
3c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**Product 3d**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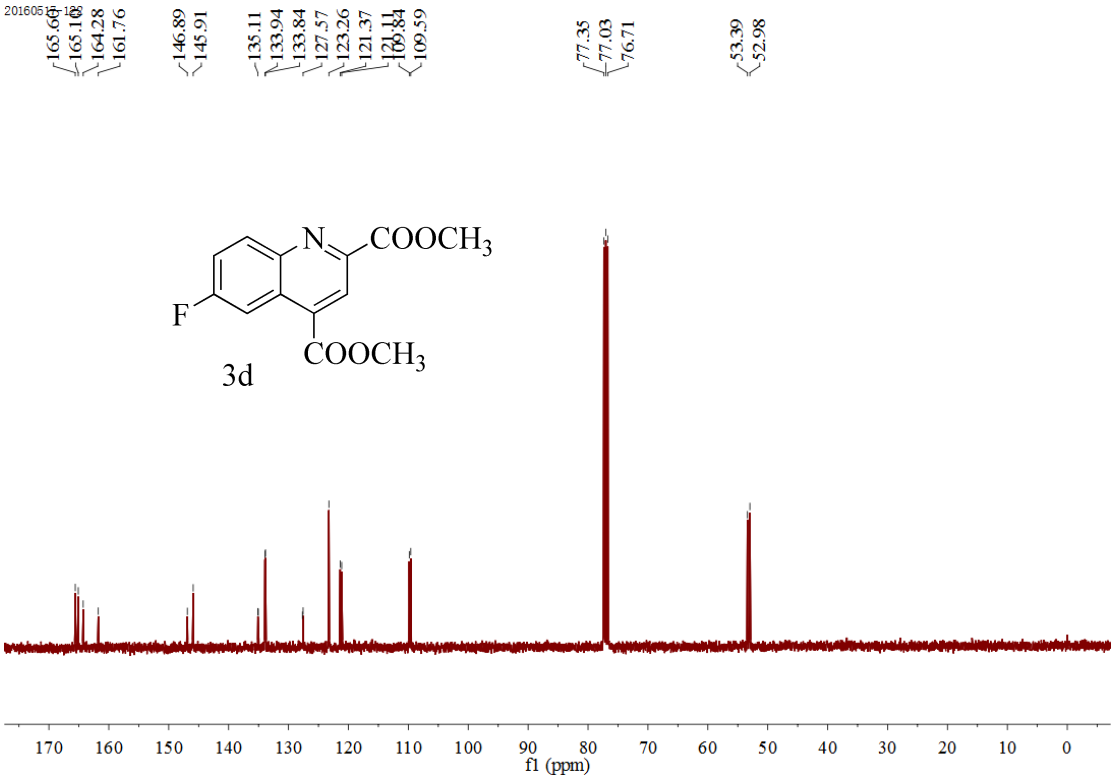
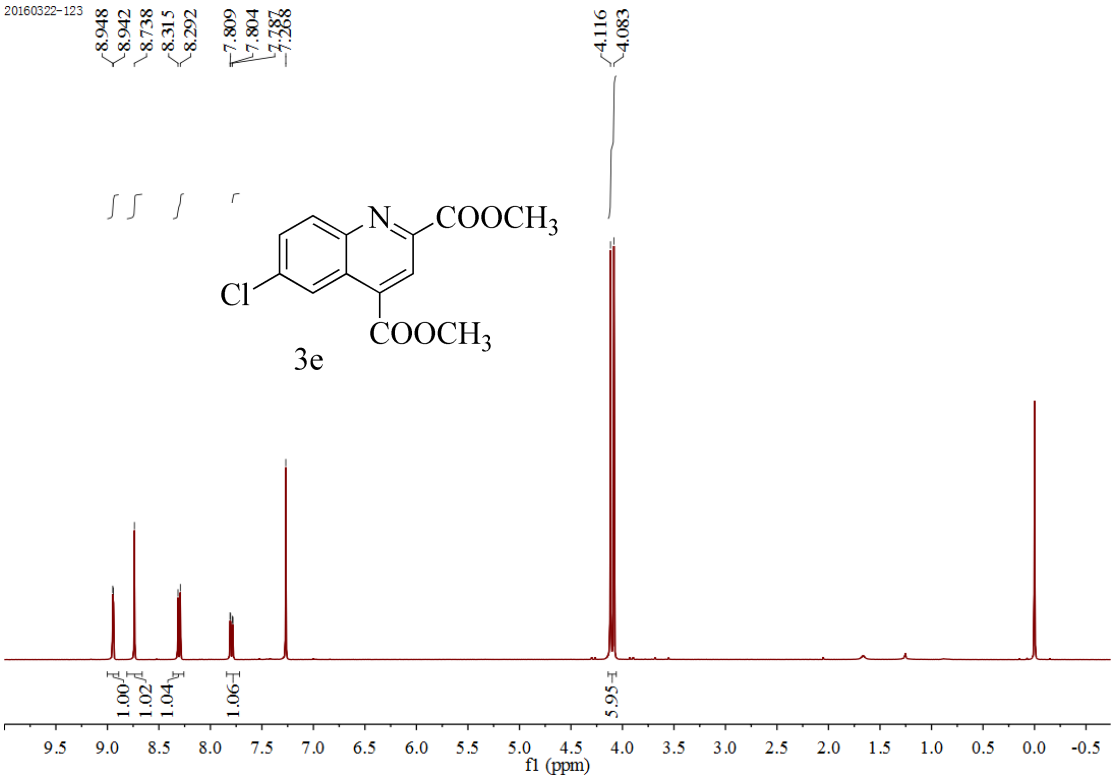
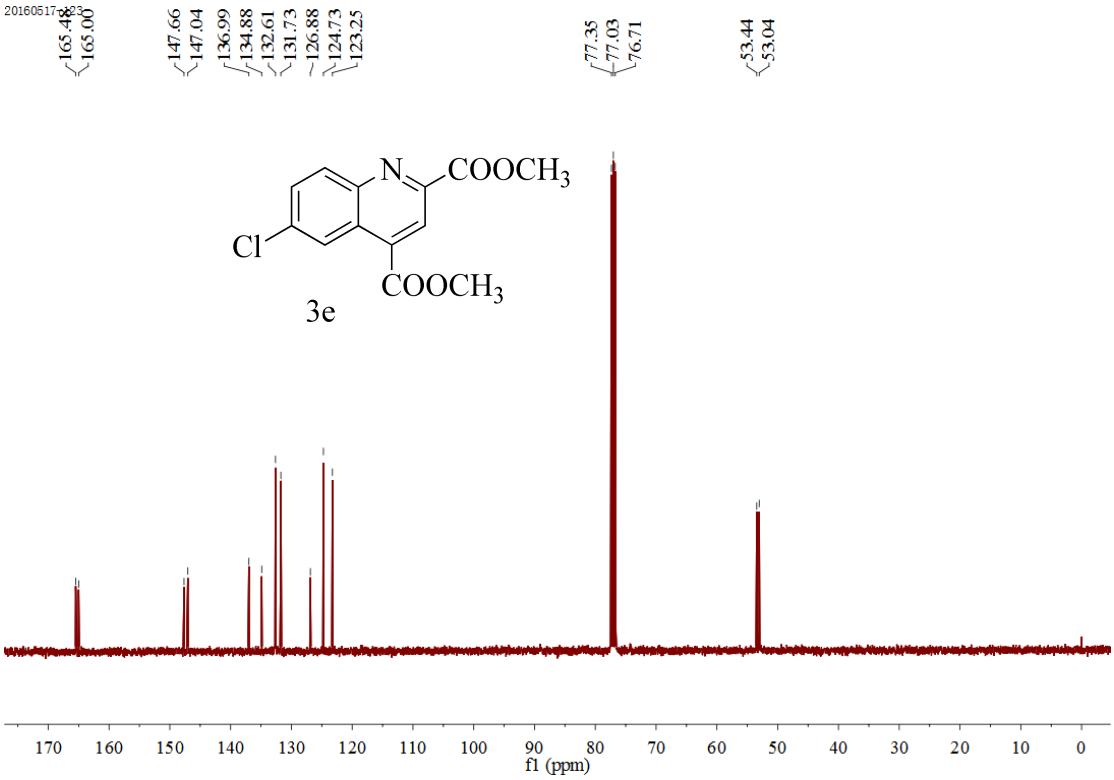
8.610
8.603
8.402
8.387
8.378
8.364
7.657
7.650
7.633
7.615
7.608
7.270
4.117
4.079
N
COOCH3
F
COOCH3
3d
1.00
1.04
1.08
1.14
6.34
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

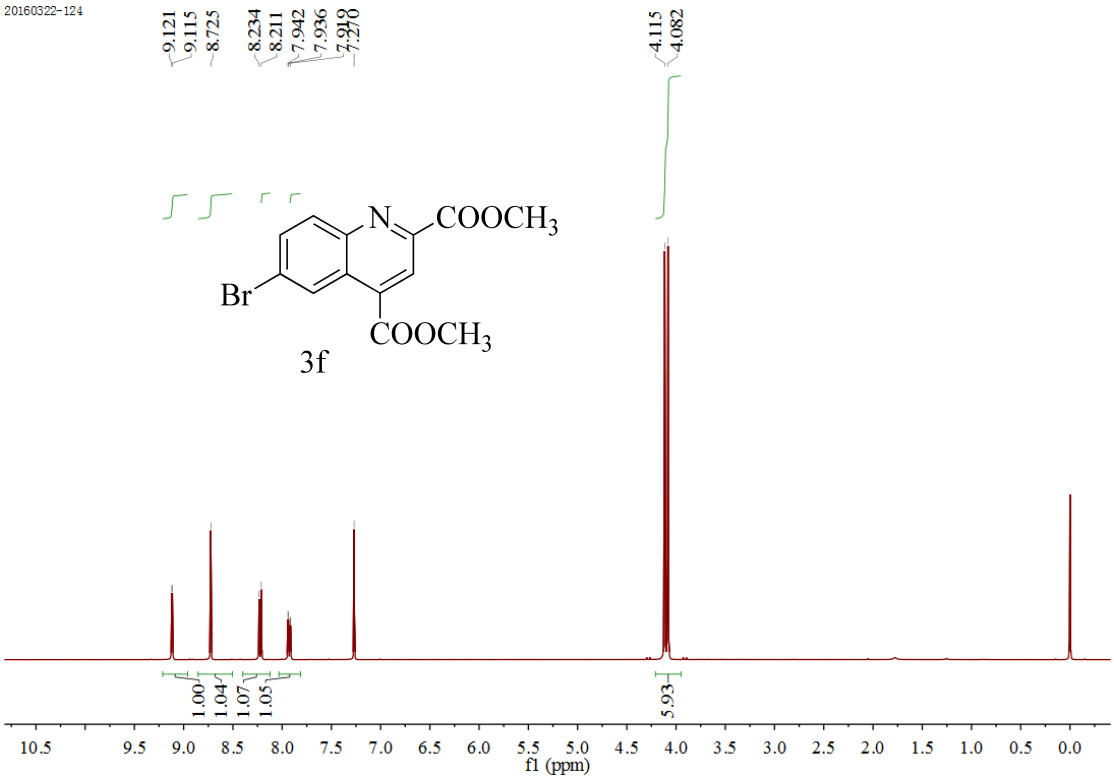

165.66
165.10
164.28
161.76
146.89
145.91
135.11
133.94
133.84
127.57
123.26
121.37
121.11
110.84
109.59
77.35
77.03
76.71
53.39
52.98
N
COOCH3
F
COOCH3
3d
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

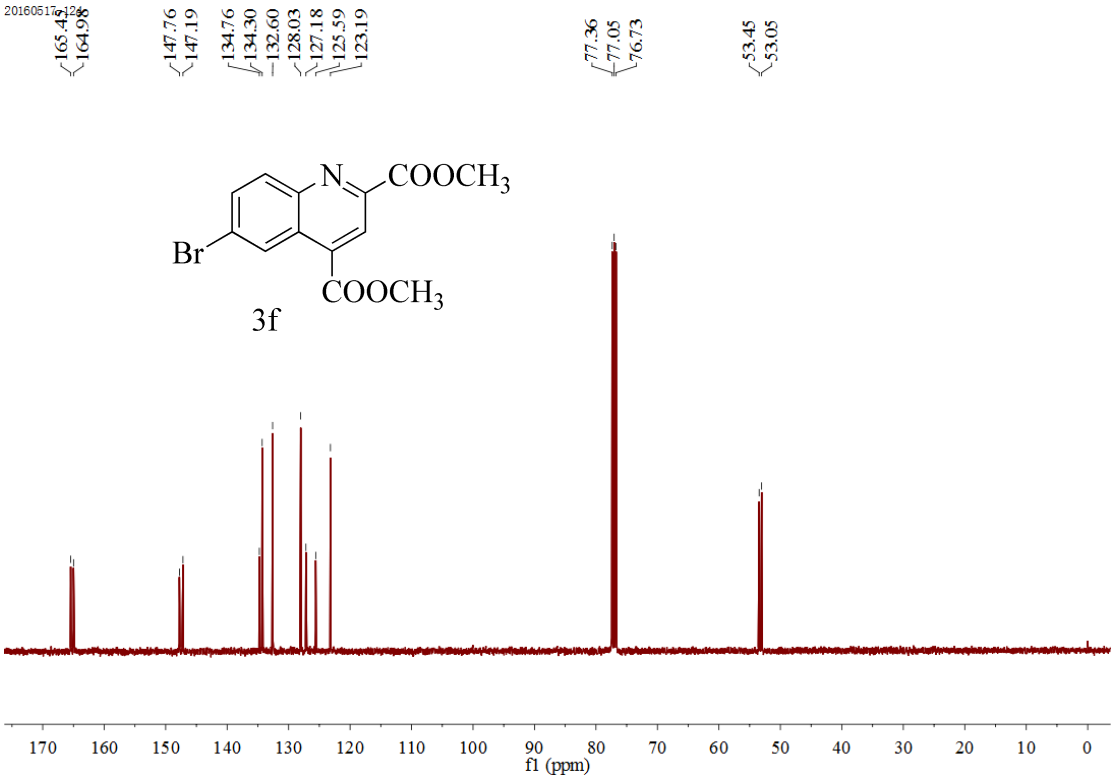
**Product 3e**


20160322-123
8.948
8.942
8.738
8.315
8.292
7.809
7.804
7.787
7.268
4.116
4.083
N
COOCH3
Cl
COOCH3
3e
1.00
1.02
1.04
1.06
5.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

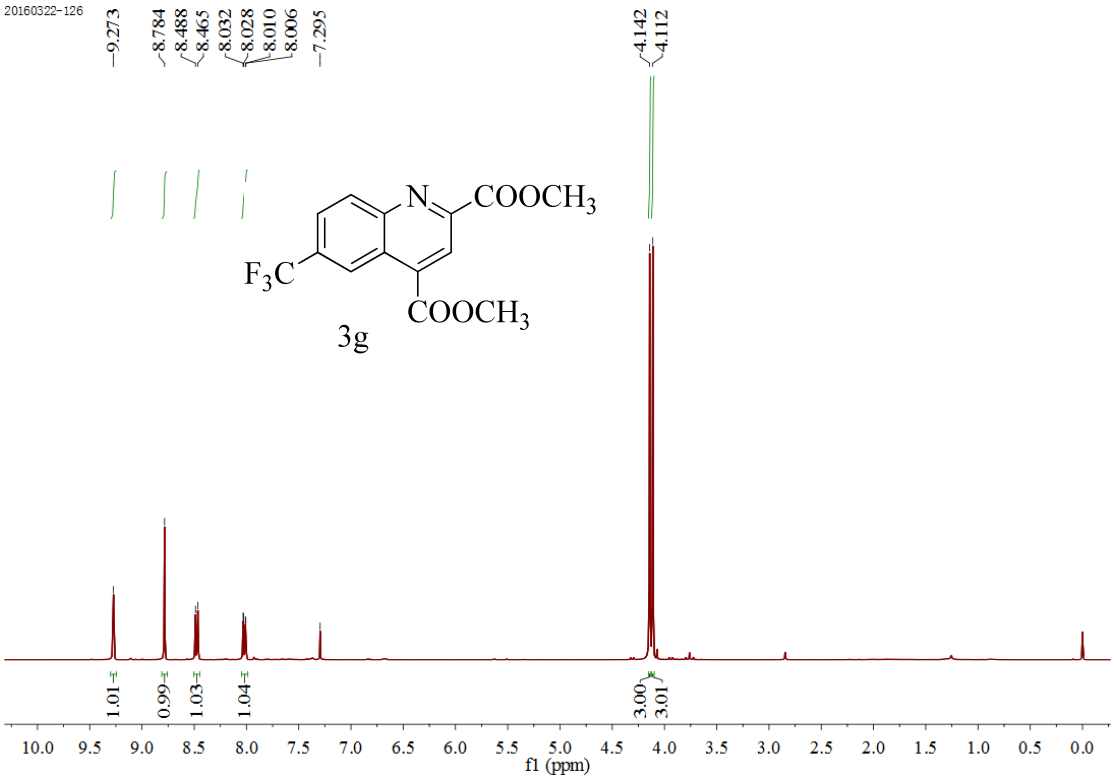

20160517-123
165.48
165.00
147.66
147.04
136.99
134.88
132.61
131.73
126.88
124.73
123.25
77.35
77.03
76.71
53.44
53.04
N
COOCH3
Cl
COOCH3
3e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

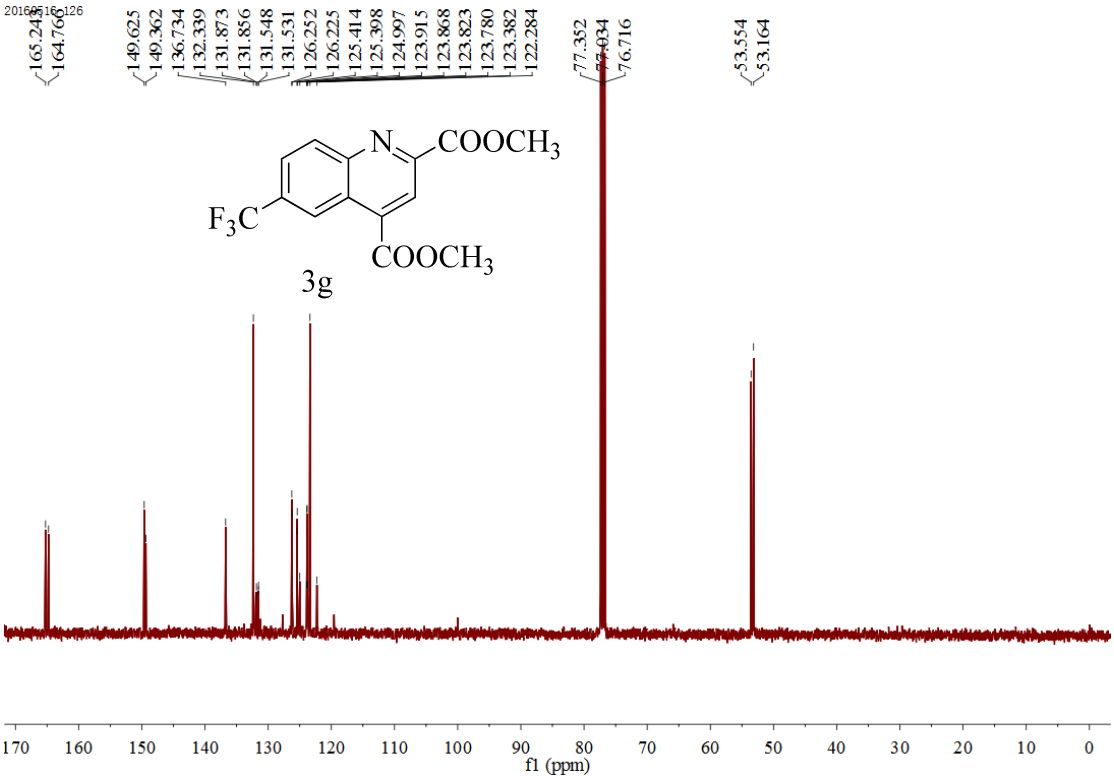
**Product 3f**


20160322-124
9.121
9.115
8.725
8.234
8.211
7.942
7.936
7.919
7.270
4.115
4.082
N
COOCH3
Br
COOCH3
3f
1.00
1.04
1.07
1.05
5.93
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

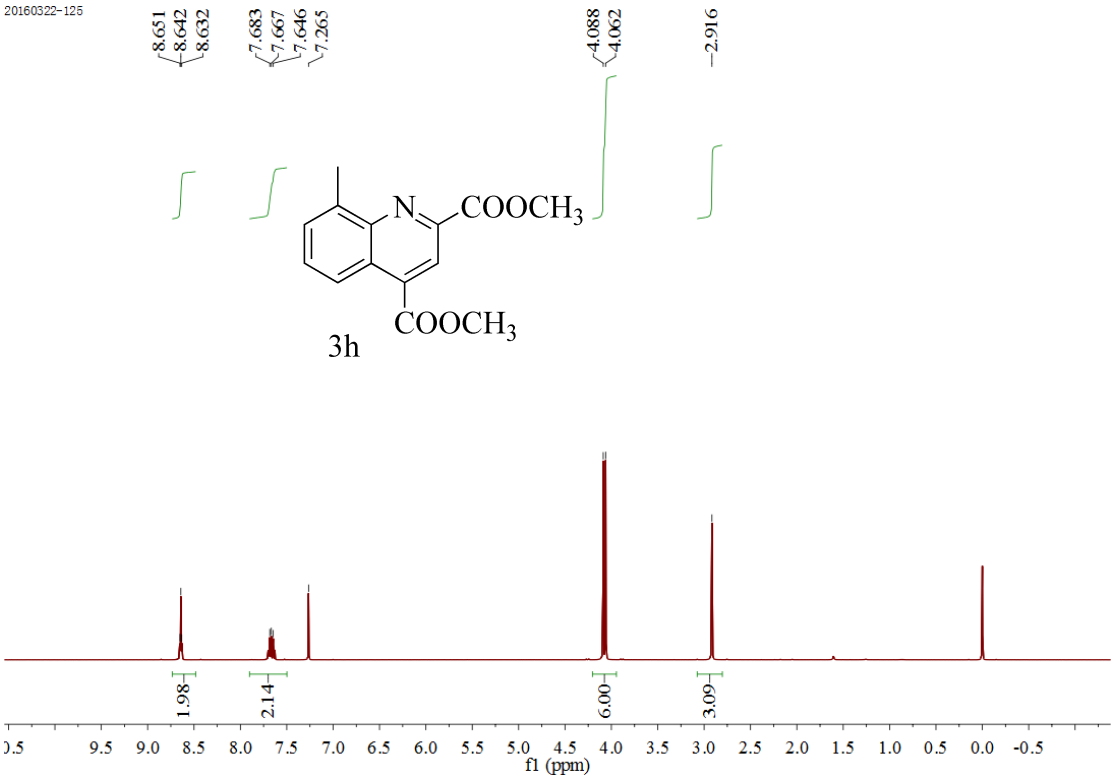

20160517-124
165.47
164.98
147.76
147.19
134.76
134.30
132.60
128.03
127.18
125.59
123.19
77.36
77.05
76.73
53.45
53.05
N
COOCH3
Br
COOCH3
3f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

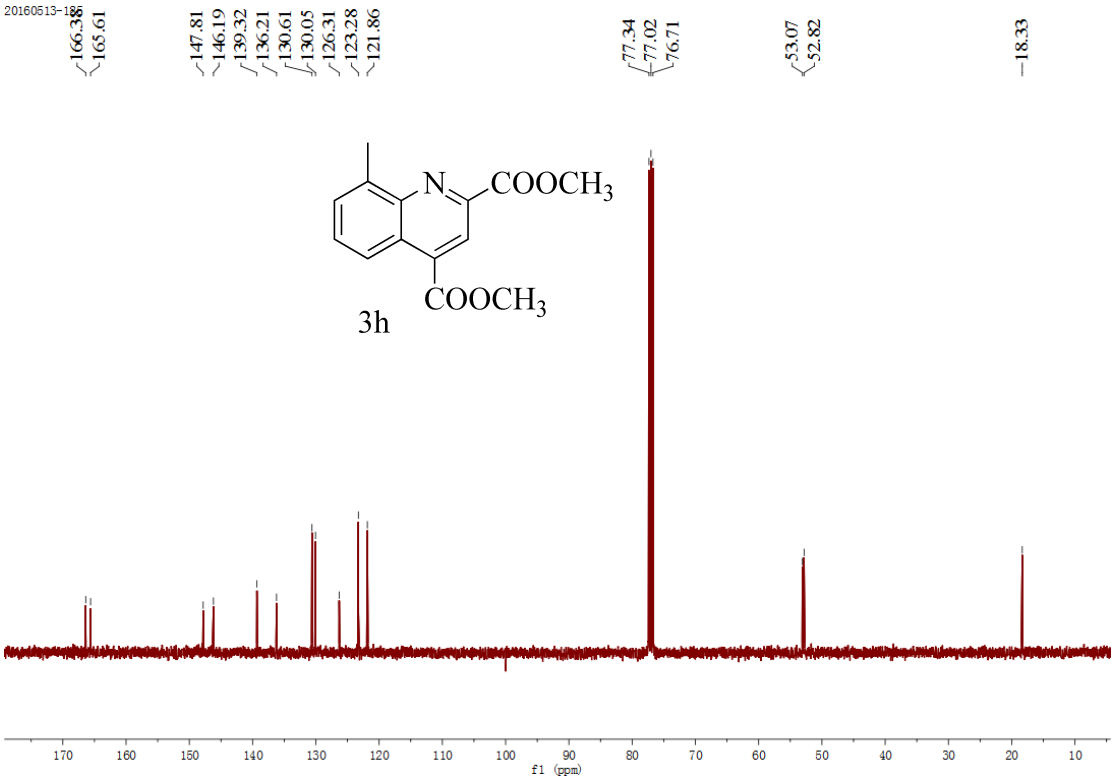
## Product 3g


20160322-126
9.273
8.784
8.488
8.465
8.032
8.028
8.010
8.006
7.295
4.142
4.112
N
COOCH3
F3C
COOCH3
3g
1.01
0.99
1.03
1.04
3.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

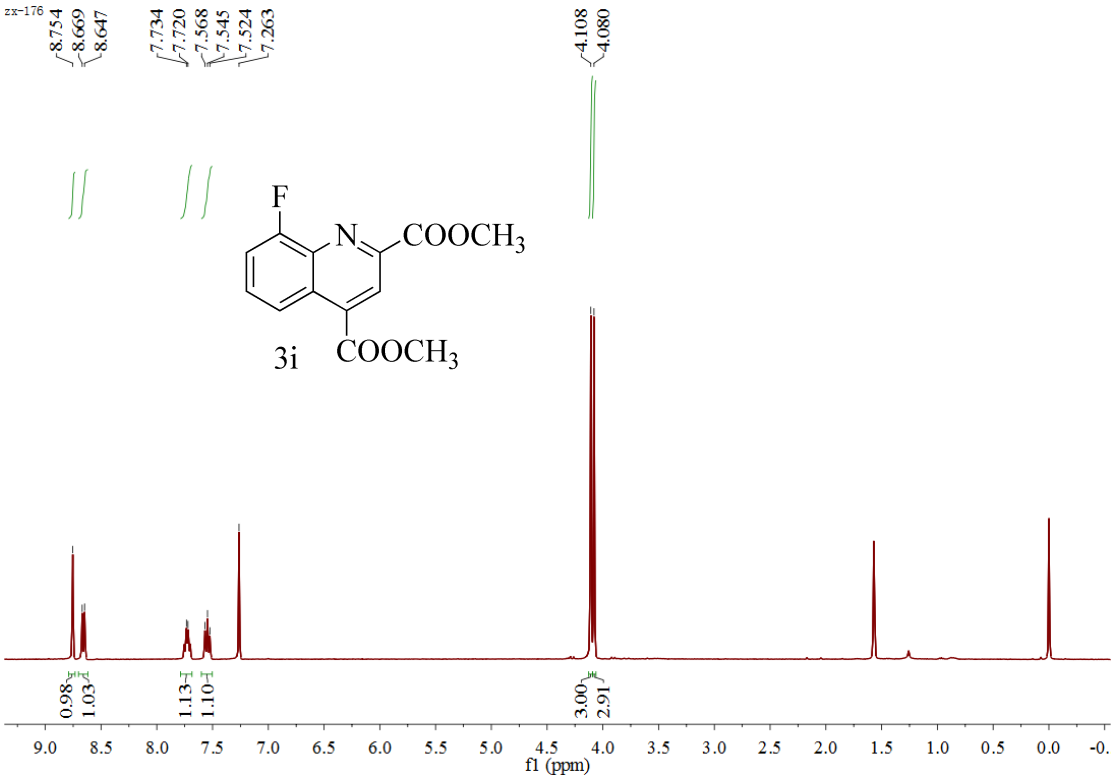

20160516-126
165.243
164.760
149.625
149.362
136.734
132.339
131.873
131.856
131.548
131.531
126.252
126.225
125.414
125.398
124.997
123.915
123.868
123.823
123.780
123.382
122.284
77.352
77.034
76.716
53.554
53.164
N
COOCH3
F3C
COOCH3
3g
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

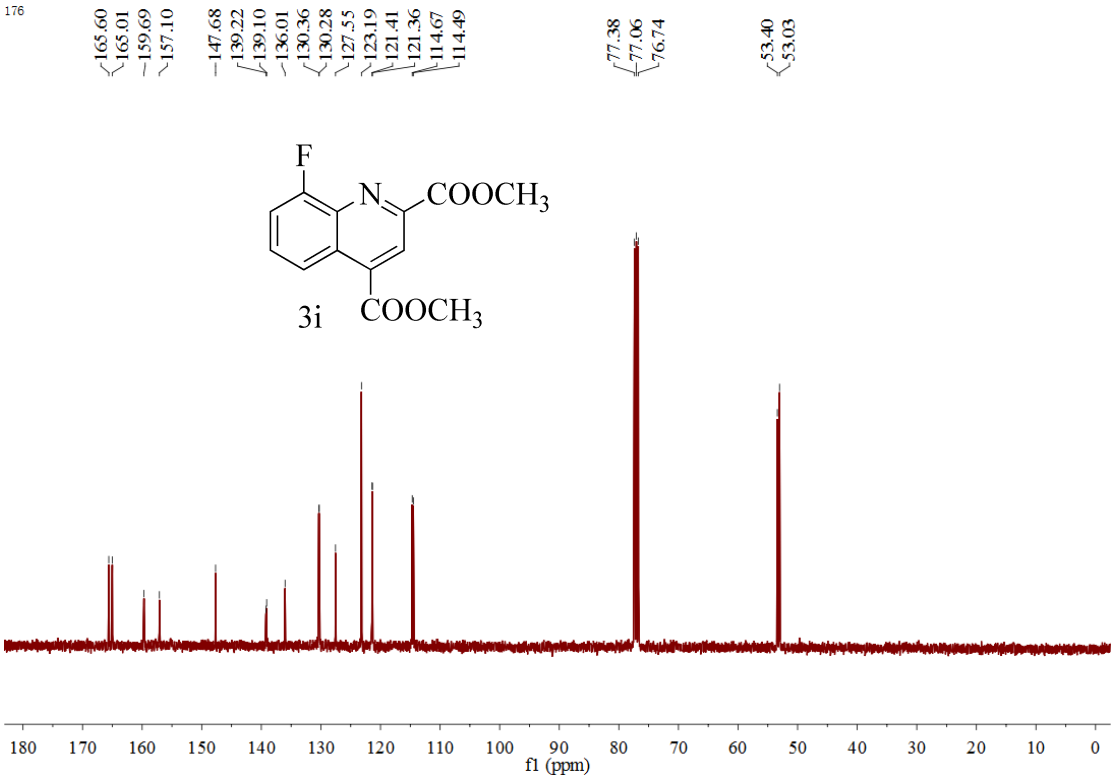
## Product 3h


20160322-125
8.651
8.642
8.632
7.683
7.667
7.646
7.265
4.088
4.062
2.916
N
COOCH3
COOCH3
3h
1.98
2.14
6.00
3.09
f1 (ppm)

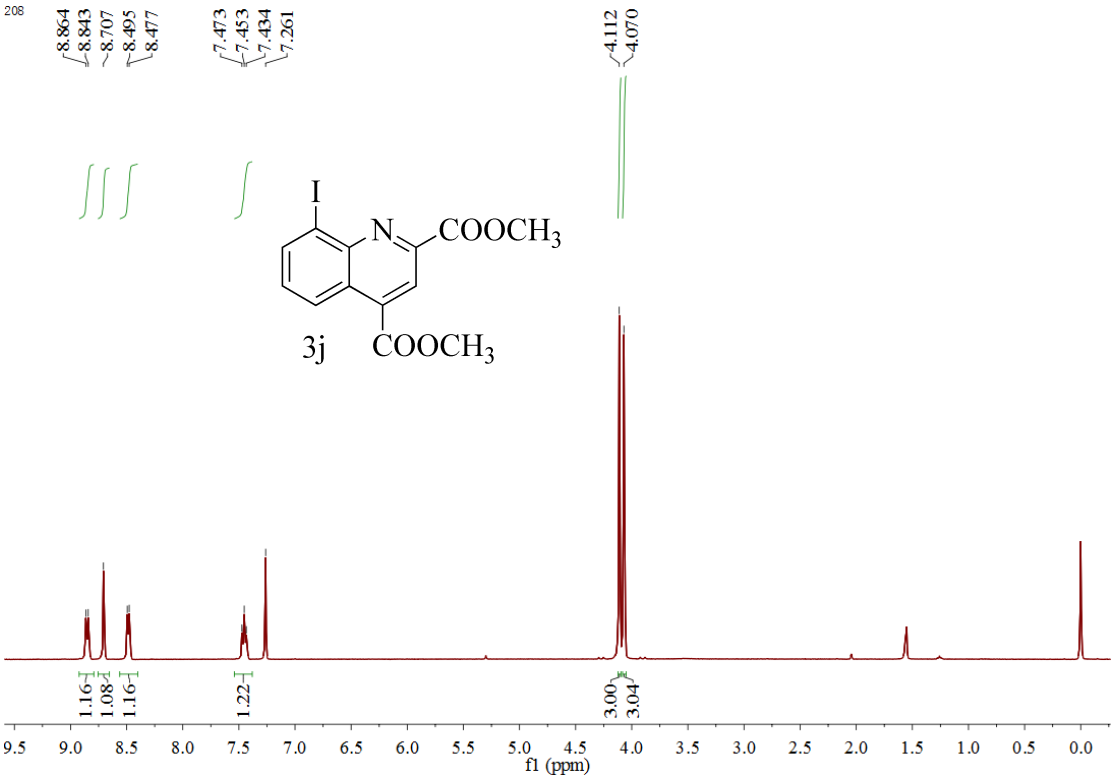

20160513-186
166.38
165.61
147.81
146.19
139.32
136.21
130.61
130.05
126.31
123.28
121.86
77.34
77.02
76.71
53.07
52.82
18.33
N
COOCH3
COOCH3
3h
f1 (ppm)

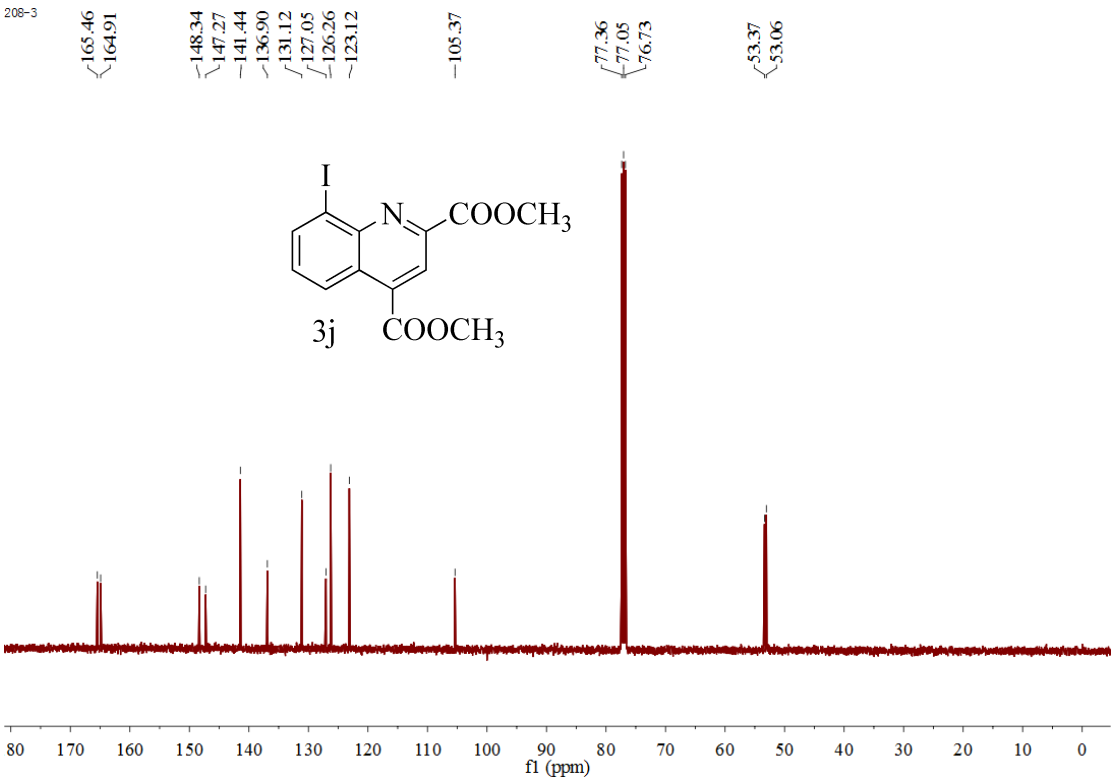
**Product 3i**


zx-176
8.754
8.669
8.647
7.734
7.720
7.568
7.545
7.524
7.263
4.108
4.080
F
N
COOCH3
COOCH3
3i
0.98
1.03
1.13
1.10
3.00
2.91
f1 (ppm)

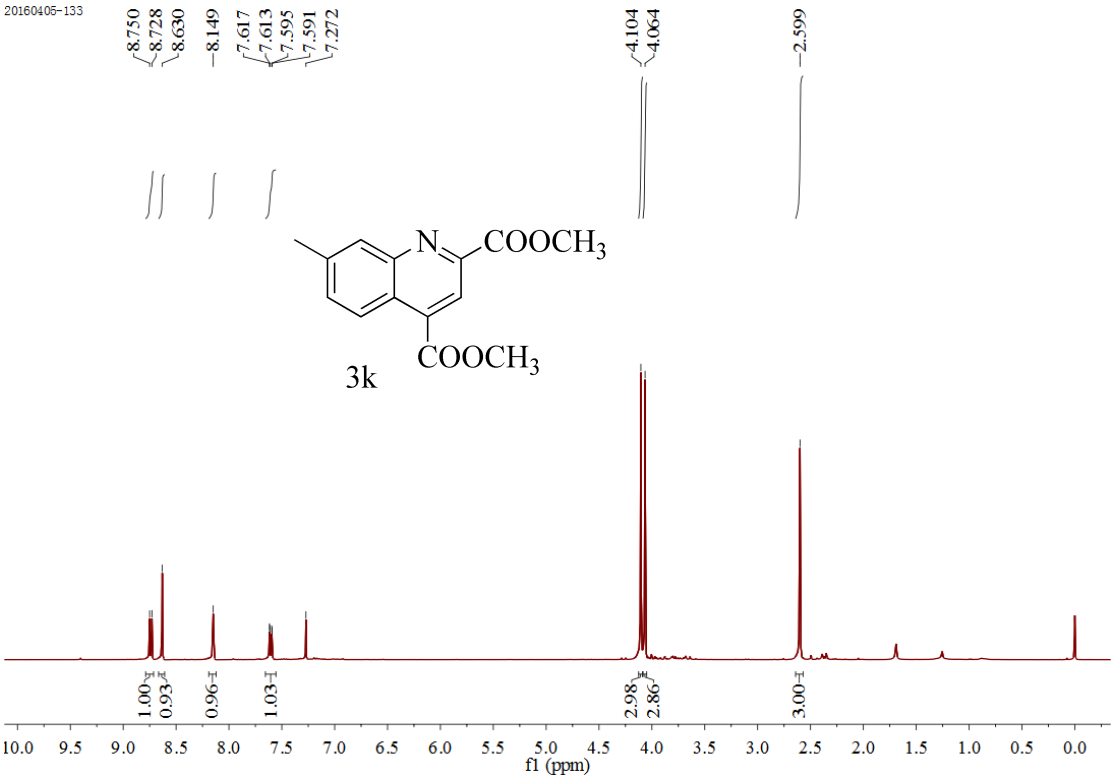

176
165.60
165.01
159.69
157.10
147.68
139.22
139.10
136.01
130.36
130.28
127.55
123.19
121.41
121.36
114.67
114.49
77.38
77.06
76.74
53.40
53.03
F
N
COOCH3
COOCH3
3i
f1 (ppm)

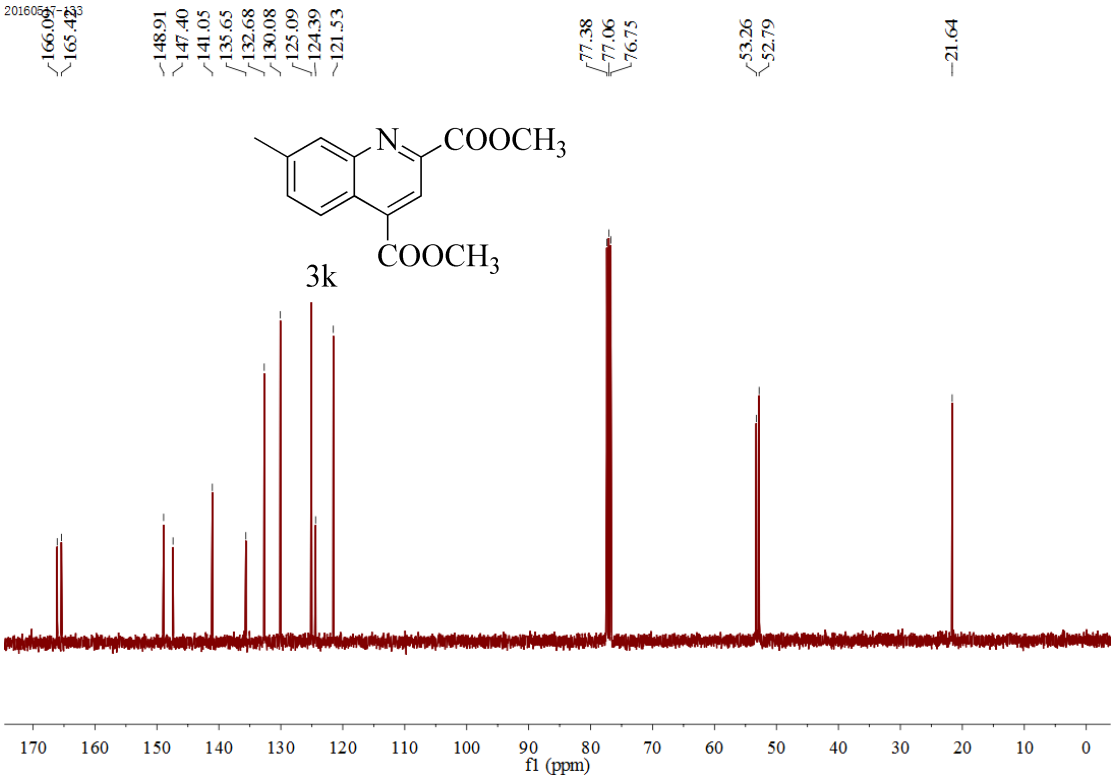
**Product 3j**


208
8.864
8.843
8.707
8.495
8.477
7.473
7.453
7.434
7.261
4.112
4.070
I
N
COOCH3
3j
COOOCH3
1.16
1.08
1.16
1.22
3.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

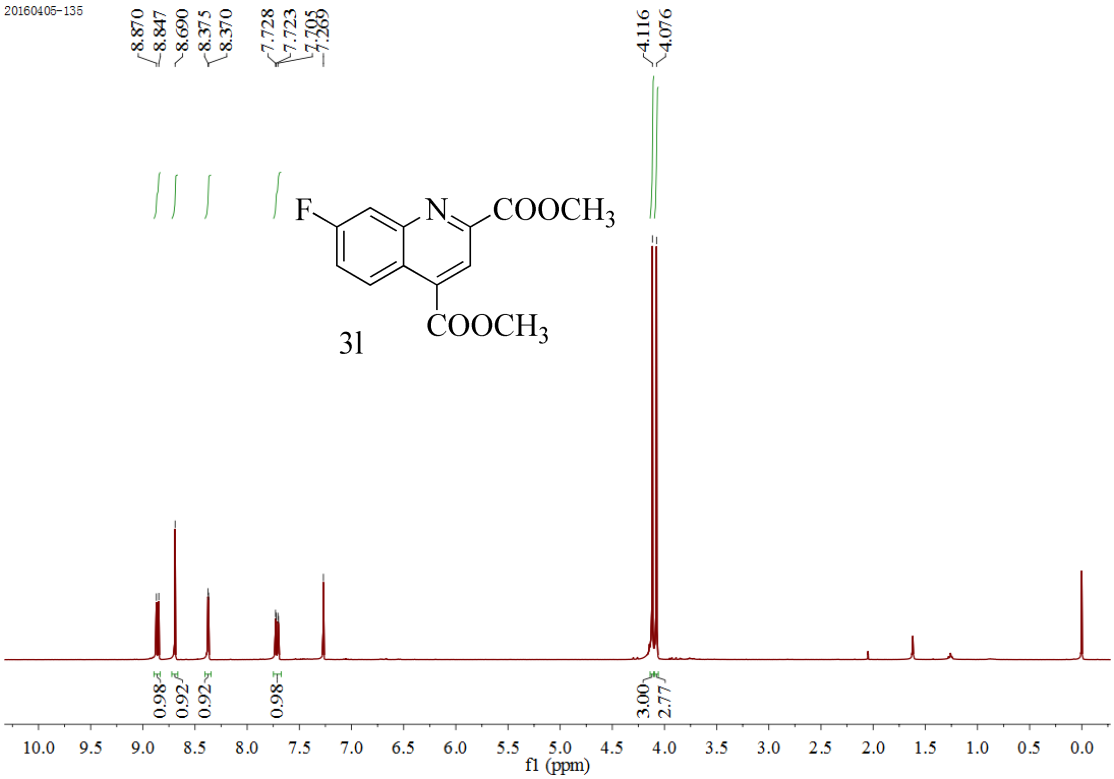

208-3
165.46
164.91
148.34
147.27
141.44
136.90
131.12
127.05
126.26
123.12
105.37
77.36
77.05
76.73
53.37
53.06
I
N
COOCH3
3j
COOOCH3
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

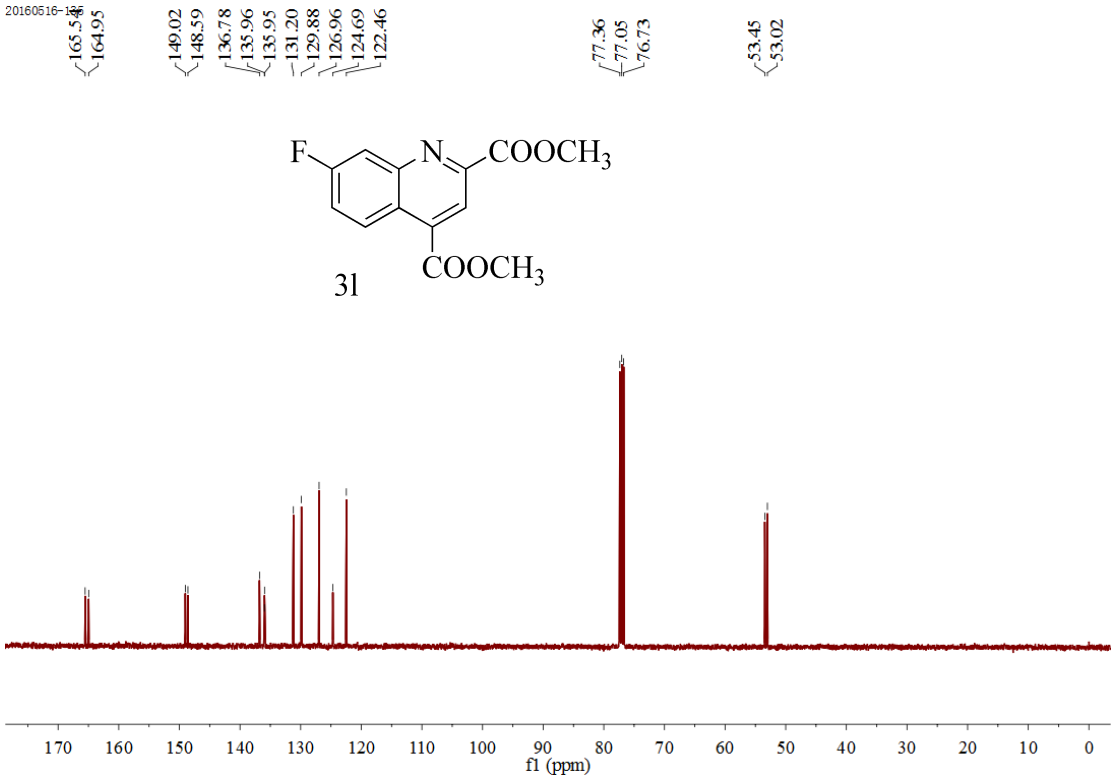
**Product 3k**


20160405-133
8.750
8.728
8.630
8.149
7.617
7.613
7.595
7.591
7.272
4.104
4.064
2.599
N
COOCH3
COOCH3
3k
1.00
0.93
0.96
1.03
2.98
2.86
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

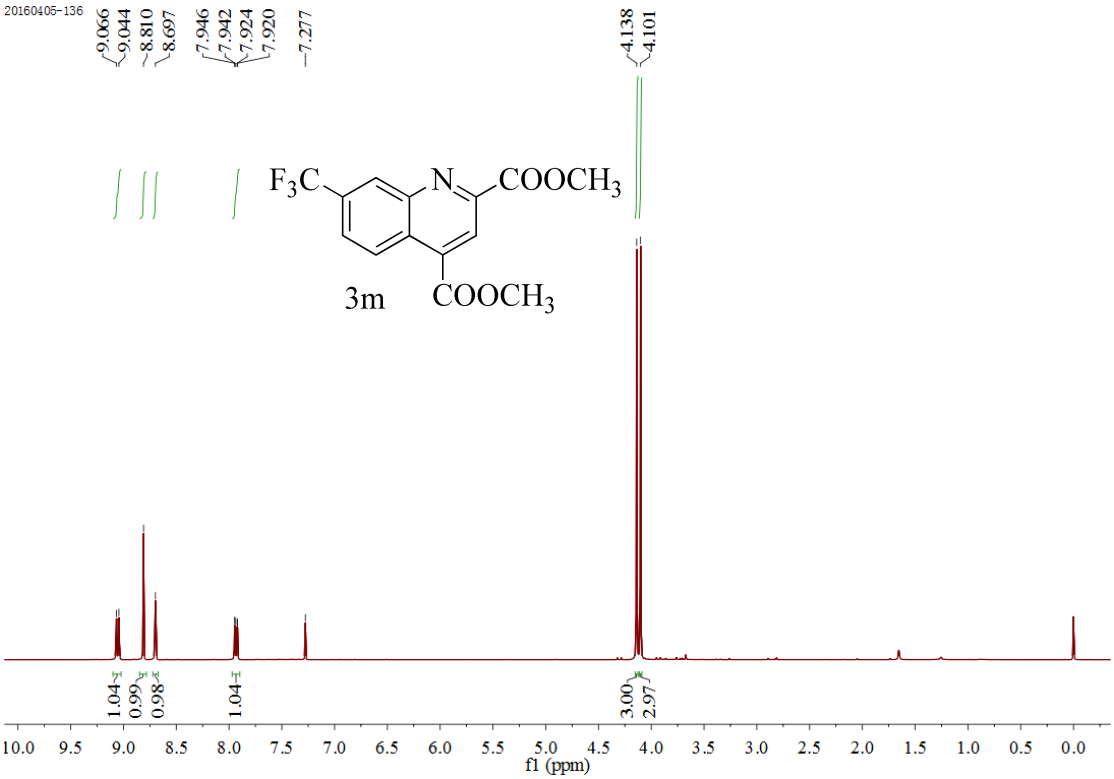

166.09
165.42
148.91
147.40
141.05
135.65
132.68
130.08
125.09
124.39
121.53
77.38
77.06
76.75
53.26
52.79
21.64
N
COOCH3
COOCH3
3k
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

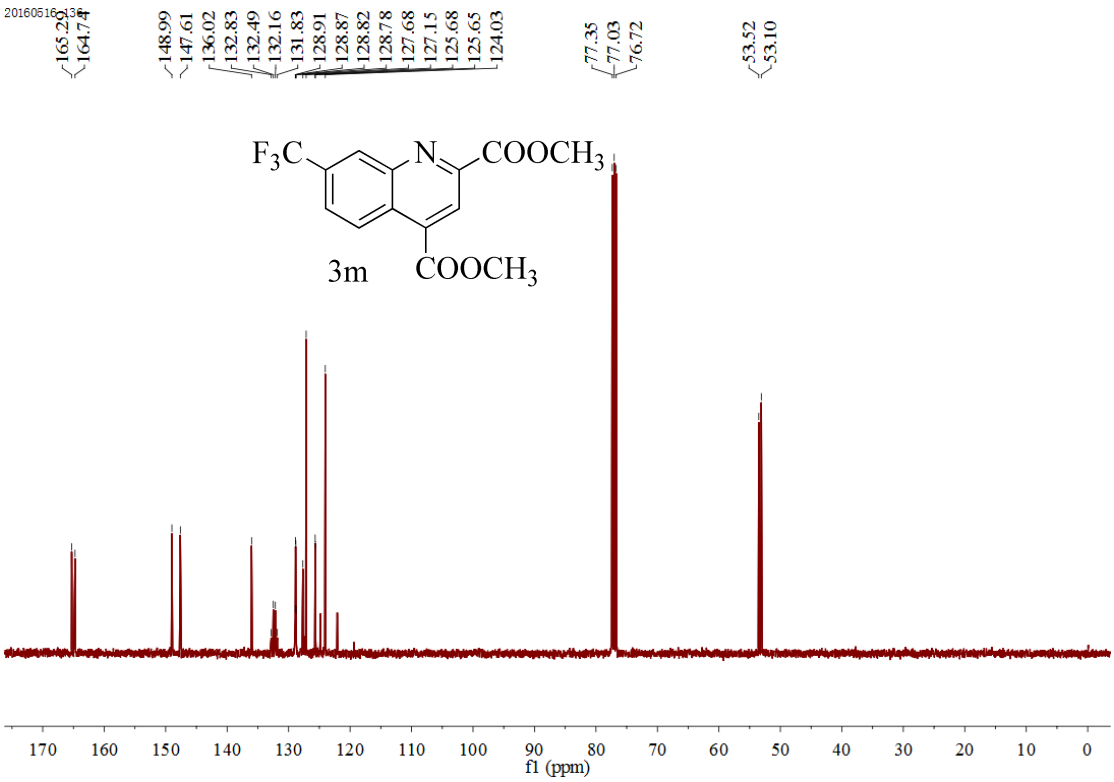
**Product 3l**


20160405-135
8.870
8.847
8.690
8.375
8.370
7.728
7.723
7.705
7.269
4.116
4.076
F
N
COOCH3
COOCH3
3l
0.98
0.92
0.92
0.98
3.00
2.77
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

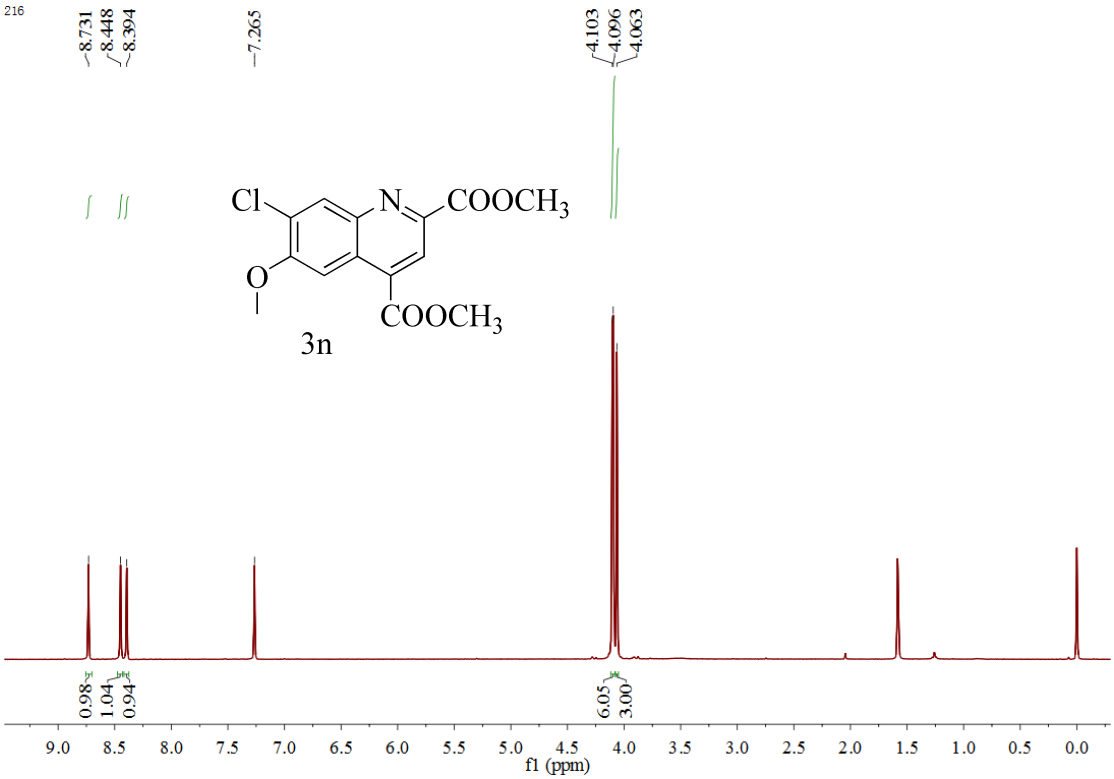

20160516-135
165.54
164.95
149.02
148.59
136.78
135.96
135.95
131.20
129.88
126.96
124.69
122.46
77.36
77.05
76.73
53.45
53.02
F
N
COOCH3
COOCH3
3l
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

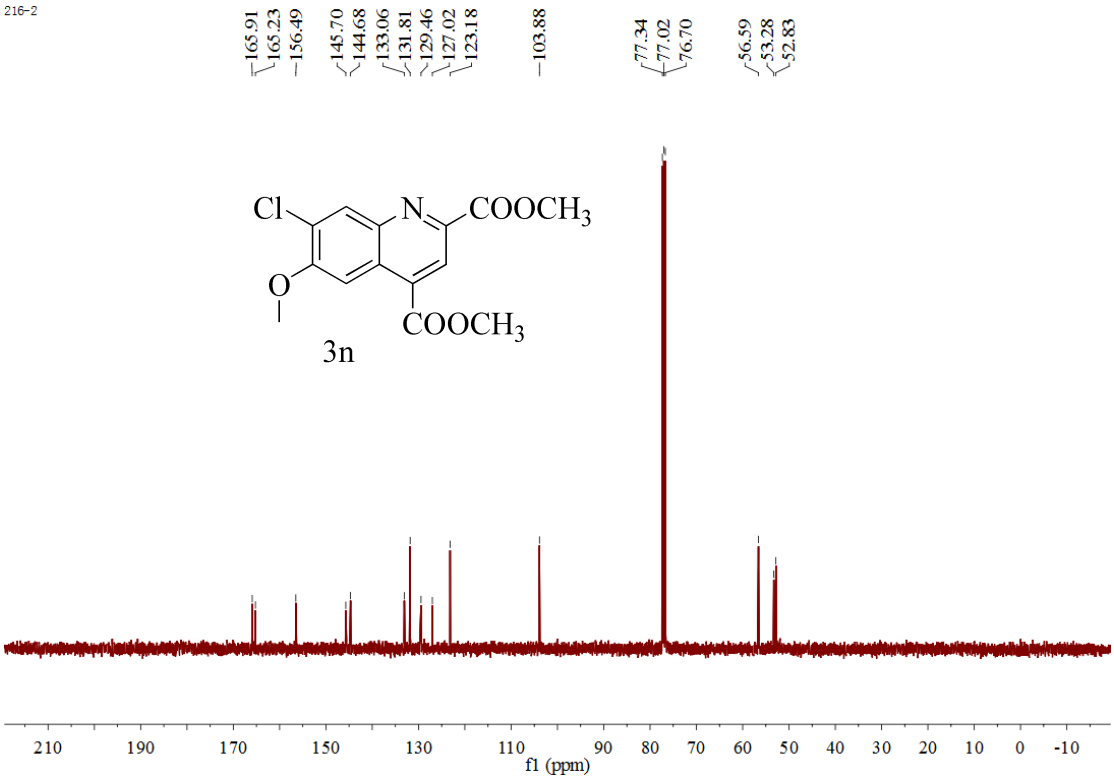
## Product 3m


20160405-136
9.066
9.044
8.810
8.697
7.946
7.942
7.924
7.920
7.277
4.138
4.101
F3C
N
COOCH3
3m
COOCH3
1.04
0.99
0.98
1.04
3.00
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

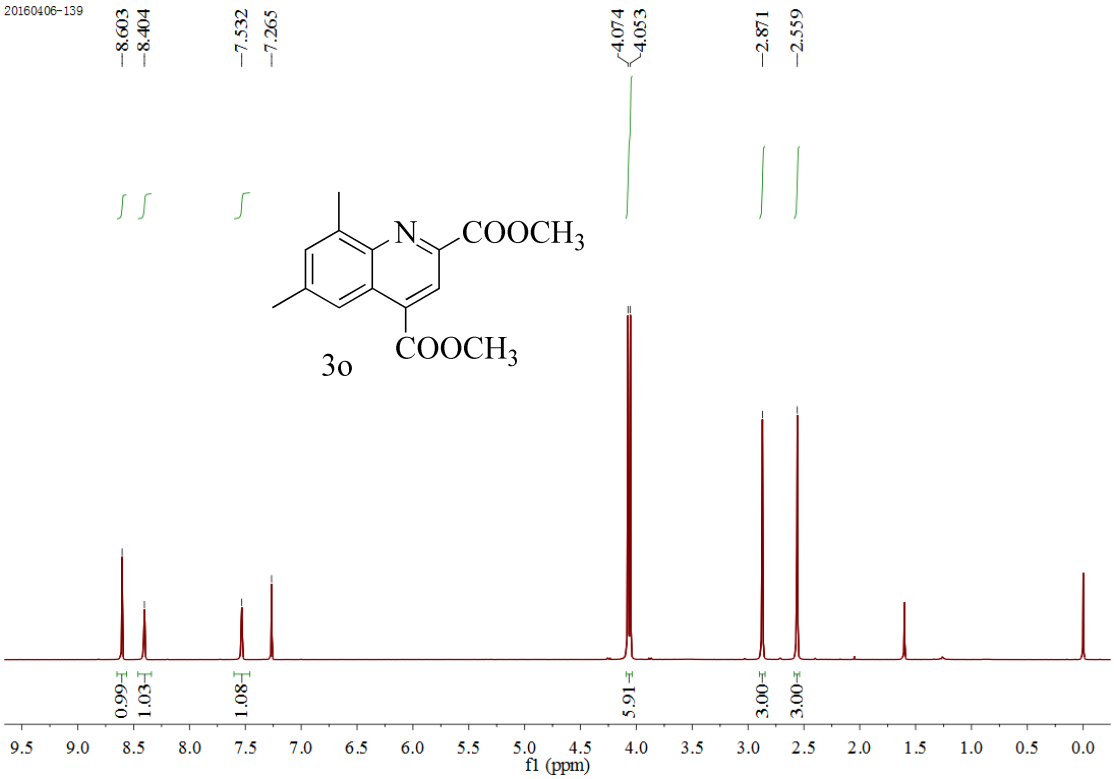

20160516-136
165.29
164.74
148.99
147.61
136.02
132.83
132.49
132.16
131.83
128.91
128.87
128.82
128.78
127.68
127.15
125.68
125.65
124.03
77.35
77.03
76.72
53.52
53.10
F3C
N
COOCH3
3m
COOCH3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

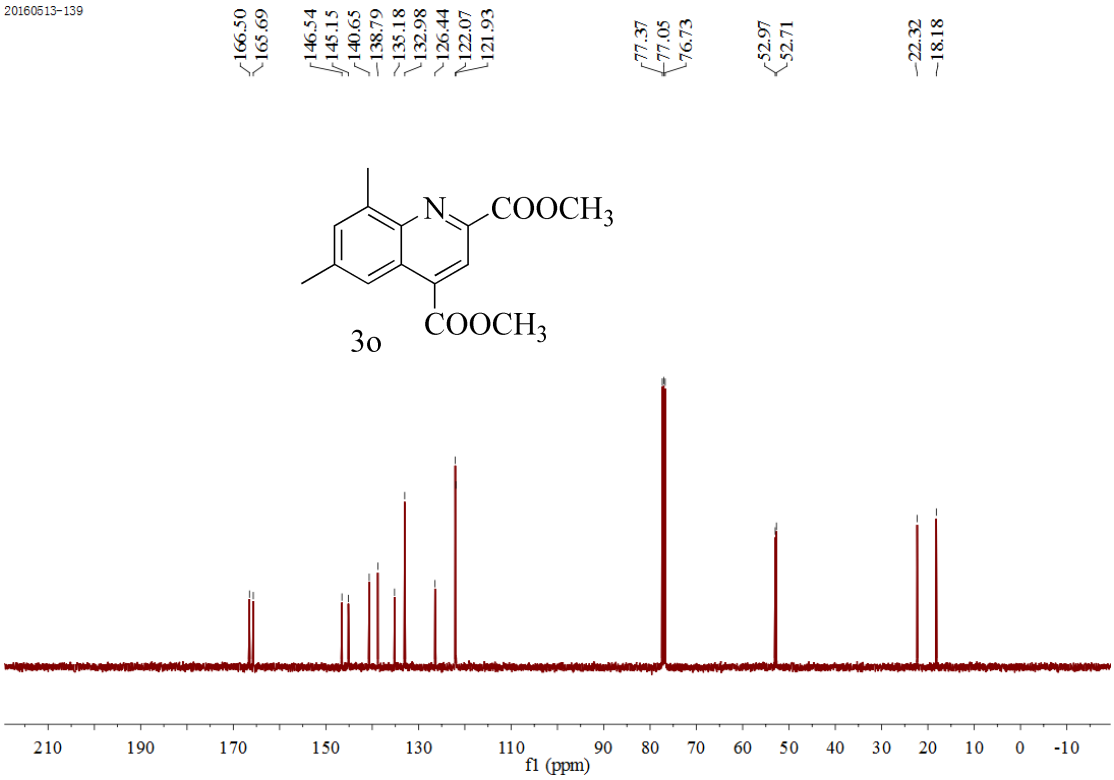
## Product 3n


216
8.731
8.448
8.394
7.265
4.103
4.096
4.063
Cl
N
COOCH3
O
COOCH3
3n
0.98
1.04
0.94
6.05
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

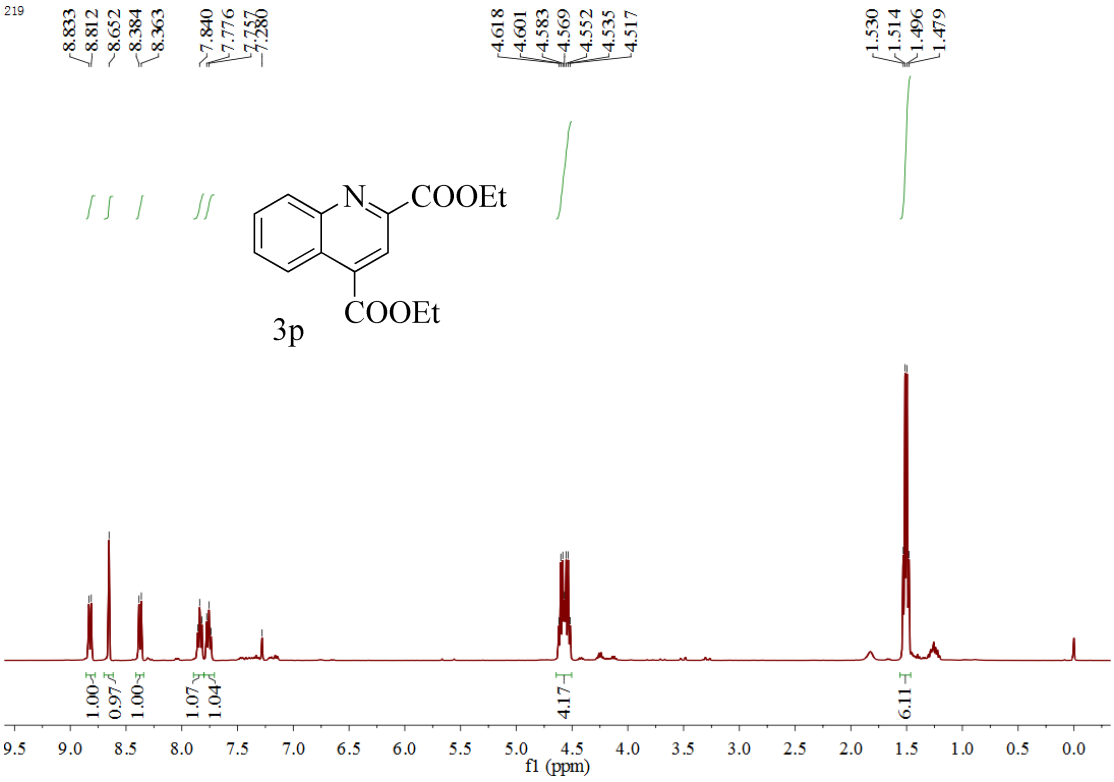

216-2
165.91
165.23
156.49
145.70
144.68
133.06
131.81
129.46
127.02
123.18
103.88
77.34
77.02
76.70
56.59
53.28
52.83
Cl
N
COOCH3
O
COOCH3
3n
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

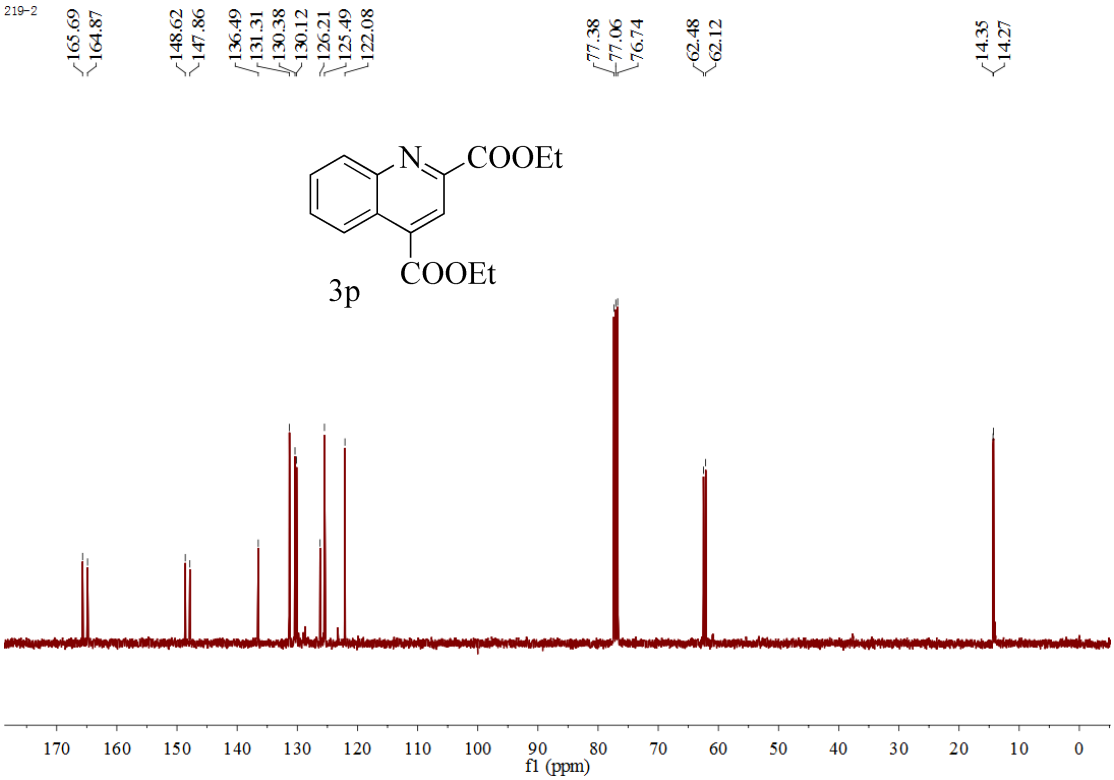
## Product 3o


20160406-139
8.603
8.404
7.532
7.265
4.074
4.053
2.871
2.559
N
COOCH3
COOCH3
3o
0.99
1.03
1.08
5.91
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

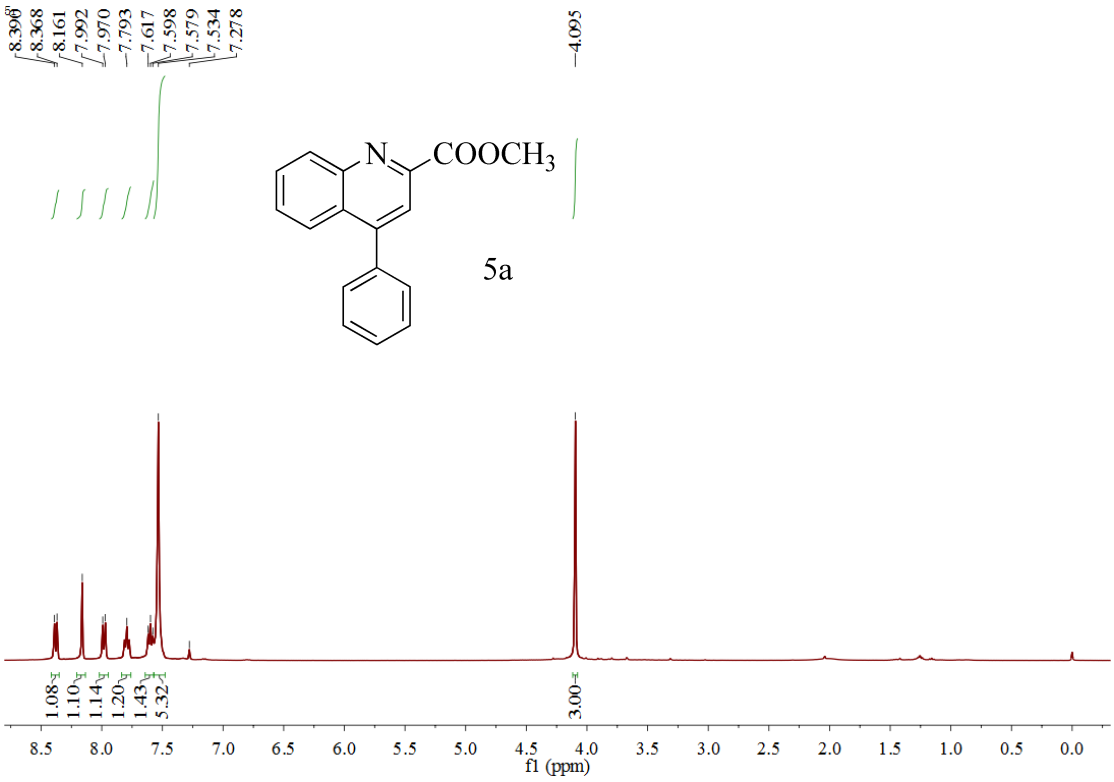

20160513-139
166.50
165.69
146.54
145.15
140.65
138.79
135.18
132.98
126.44
122.07
121.93
77.37
77.05
76.73
52.97
52.71
22.32
18.18
N
COOCH3
COOCH3
3o
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

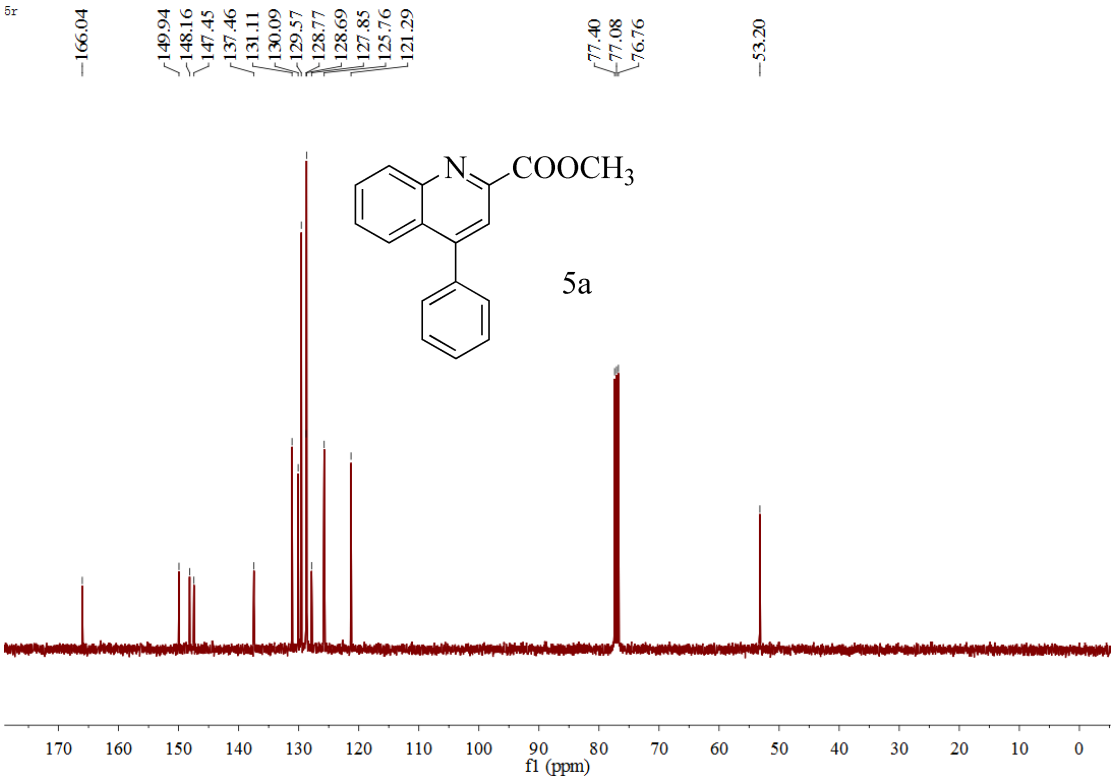
**Product 3p**


219
8.833
8.812
8.652
8.384
8.363
7.840
7.776
7.757
7.280
4.618
4.601
4.583
4.569
4.552
4.535
4.517
1.530
1.514
1.496
1.479
N
COOEt
COOEt
3p
1.00
0.97
1.00
1.07
1.04
4.17
6.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

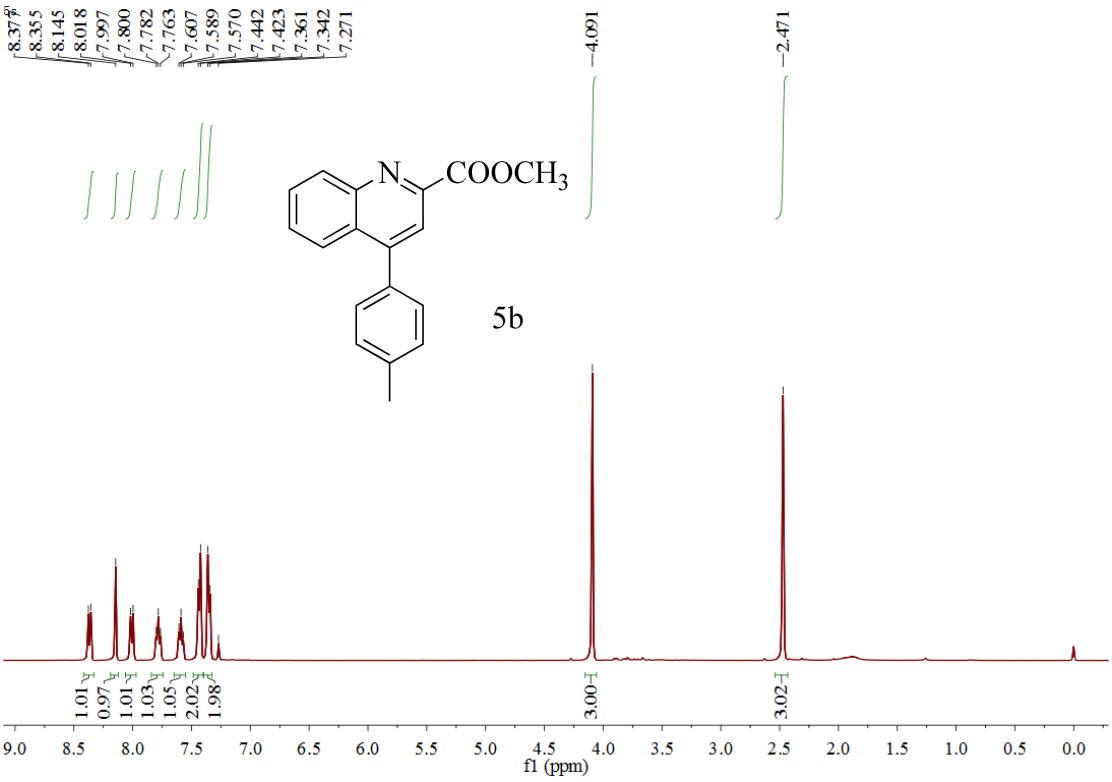

219-2
165.69
164.87
148.62
147.86
136.49
131.31
130.38
130.12
126.21
125.49
122.08
77.38
77.06
76.74
62.48
62.12
14.35
14.27
N
COOEt
COOEt
3p
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

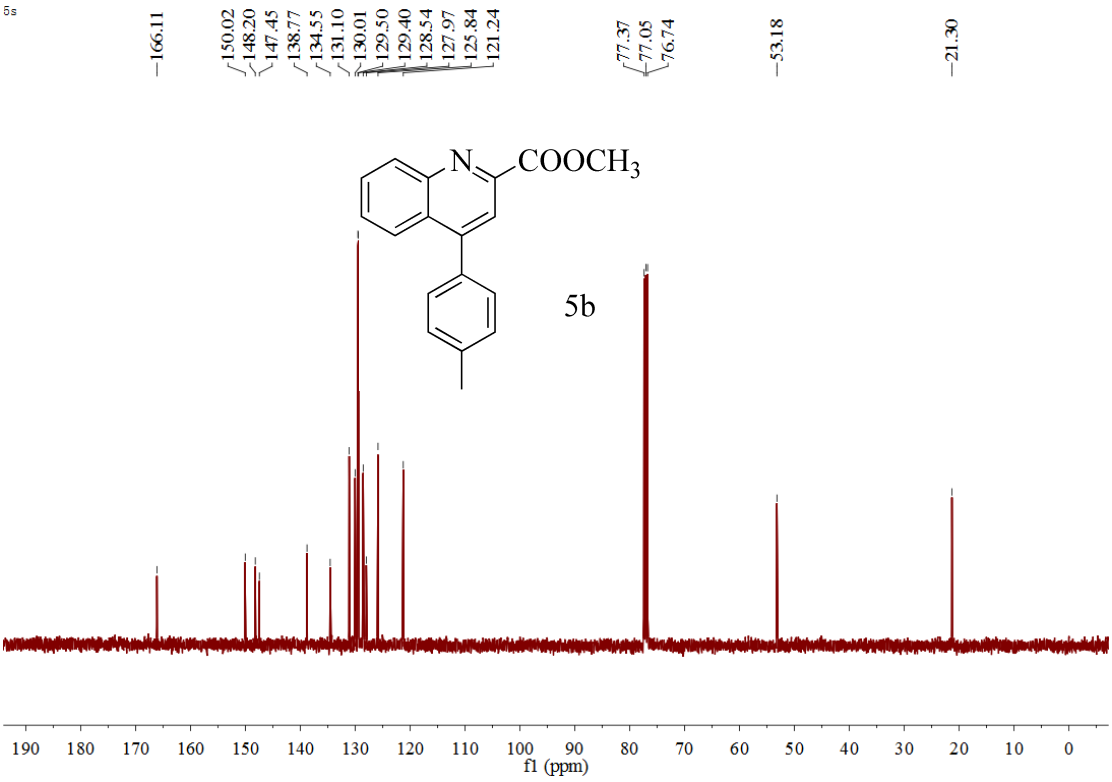
## Product 5a


8.398
8.368
8.161
7.992
7.970
7.793
7.617
7.598
7.579
7.534
7.278
4.095
N
COOCH3
5a
1.08
1.10
1.14
1.20
1.43
5.32
3.00
f1 (ppm)

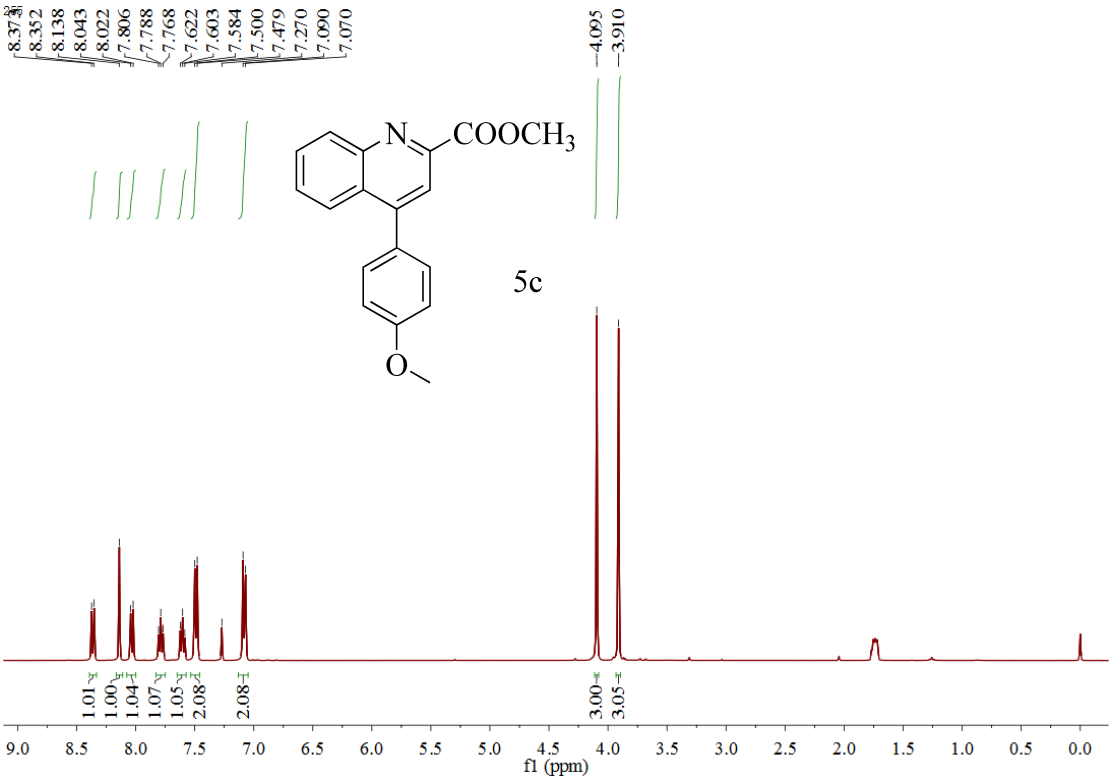

166.04
149.94
148.16
147.45
137.46
131.11
130.09
129.57
128.77
128.69
127.85
125.76
121.29
77.40
77.08
76.76
53.20
N
COOCH3
5a
f1 (ppm)

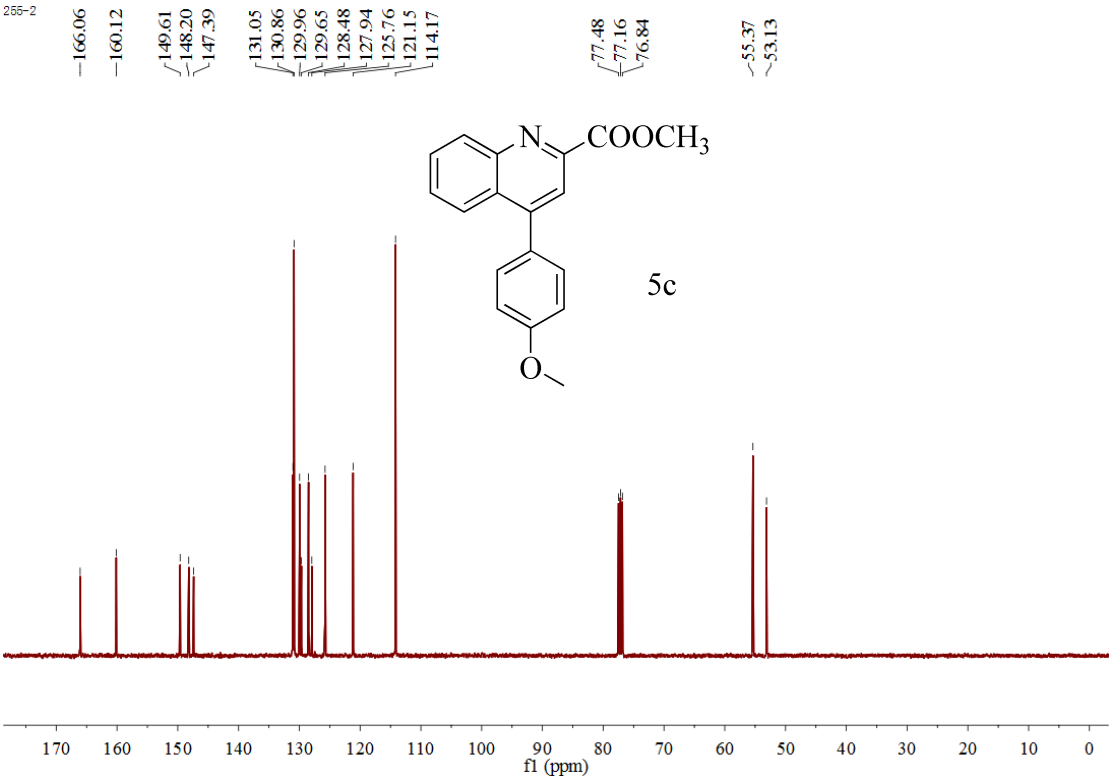
**Product 5b**


8.377
8.355
8.145
8.018
7.997
7.800
7.782
7.763
7.607
7.589
7.570
7.442
7.423
7.361
7.342
7.271
4.091
2.471
N
COOCH3
5b
1.01
0.97
1.01
1.03
1.05
2.02
1.98
3.00
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

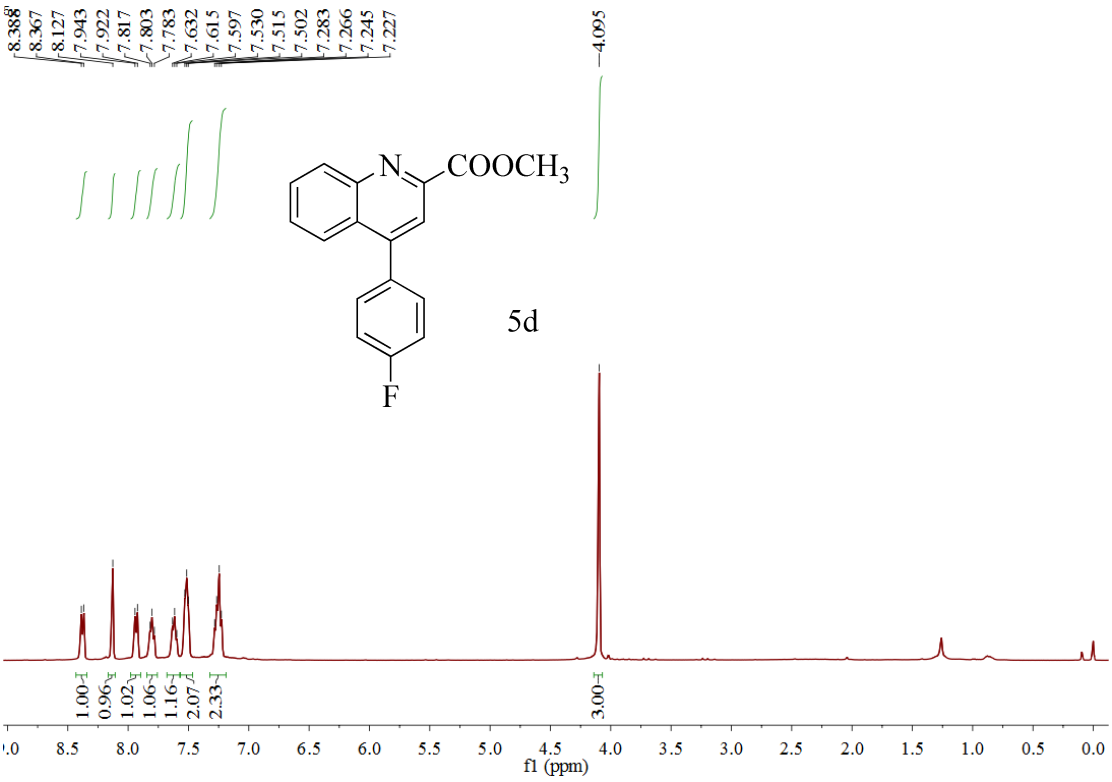

5s
166.11
150.02
148.20
147.45
138.77
134.55
131.10
130.01
129.50
129.40
128.54
127.97
125.84
121.24
77.37
77.05
76.74
53.18
21.30
N
COOCH3
5b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

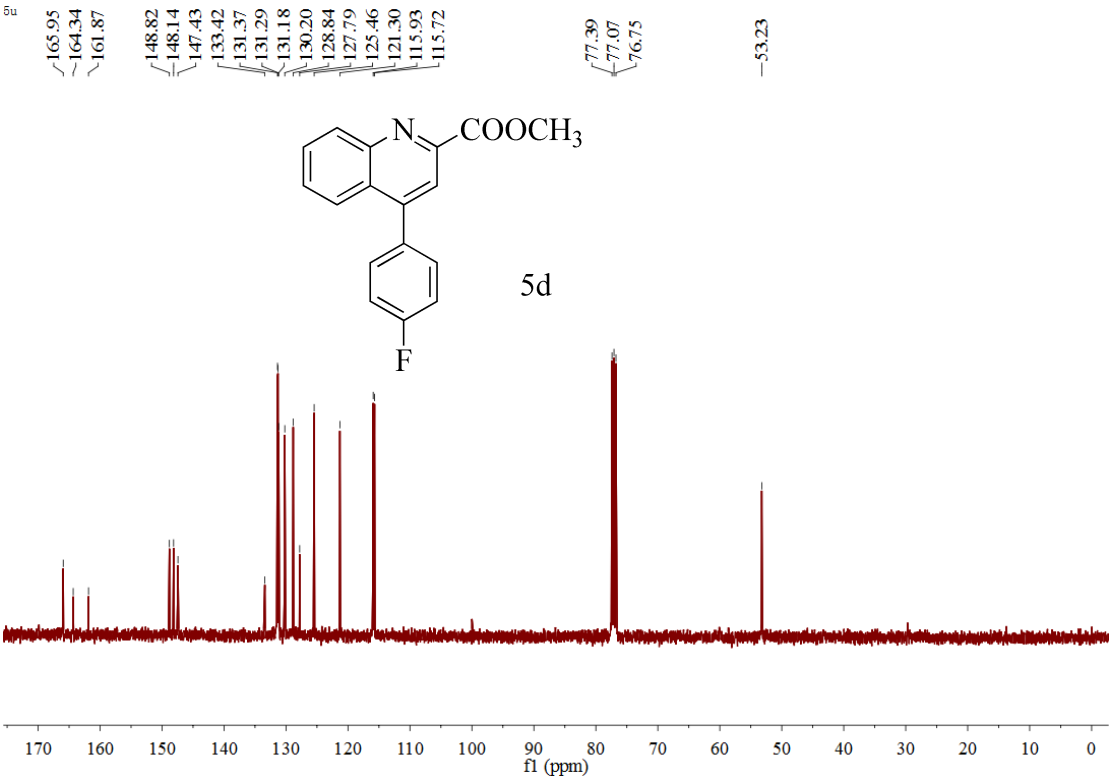
**Product 5c**


8.373
8.352
8.138
8.043
8.022
7.806
7.788
7.768
7.622
7.603
7.584
7.500
7.479
7.270
7.090
7.070
4.095
3.910
N
COOCH3
O
5c
1.01
1.00
1.04
1.07
1.05
2.08
2.08
3.00
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

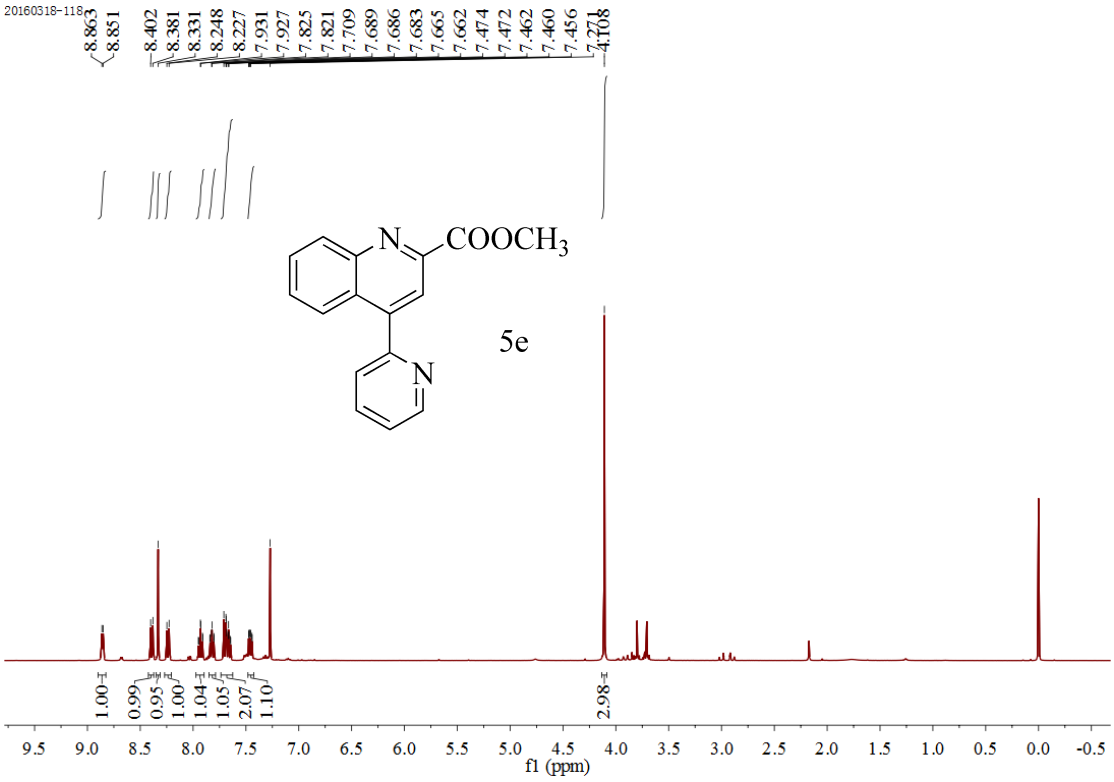

255-2
166.06
160.12
149.61
148.20
147.39
131.05
130.86
129.96
129.65
128.48
127.94
125.76
121.15
114.17
77.48
77.16
76.84
55.37
53.13
N
COOCH3
O
5c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

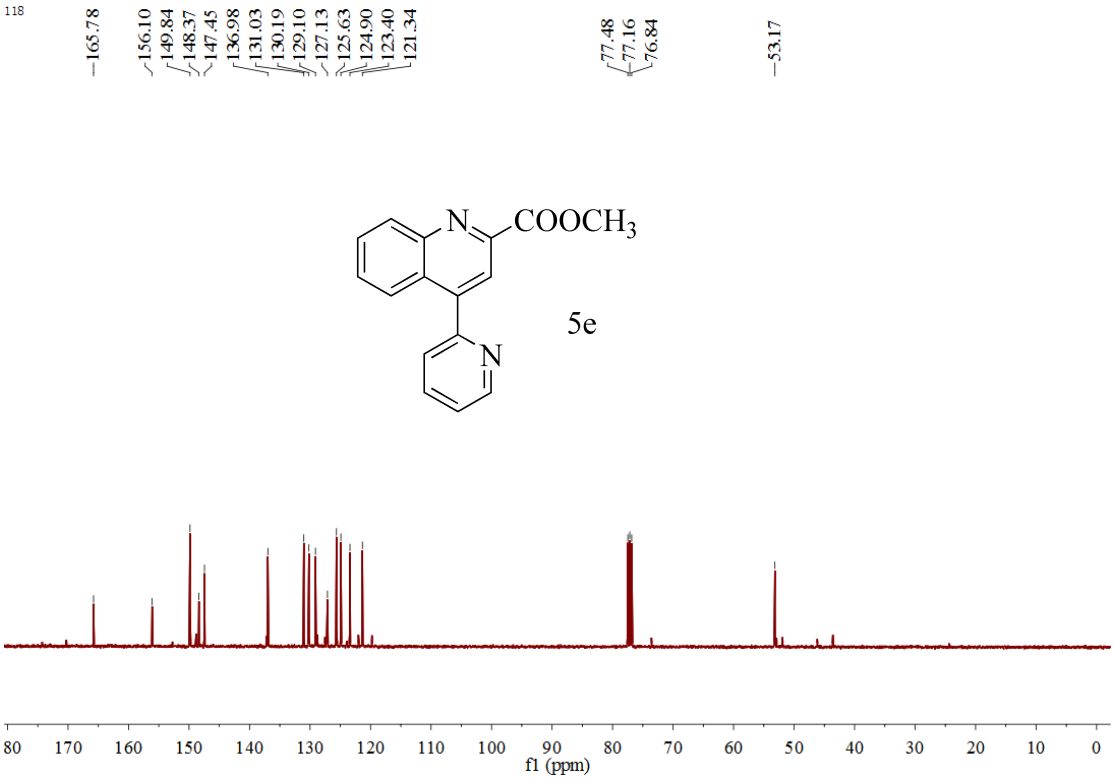
**Product 5d**


8.388
8.367
8.127
7.943
7.922
7.817
7.803
7.783
7.632
7.615
7.597
7.530
7.515
7.502
7.283
7.266
7.245
7.227
4.095
N
COOCH3
F
5d
1.00
0.96
1.02
1.06
1.16
2.07
2.33
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

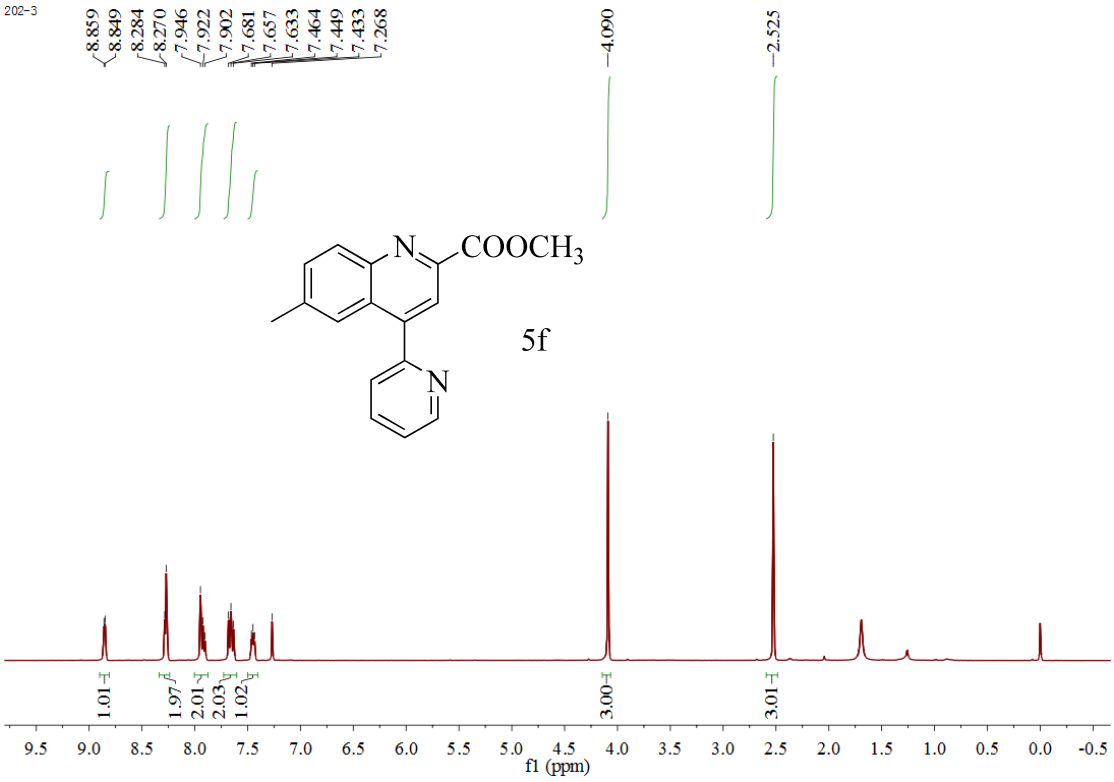

165.95
164.34
161.87
148.82
148.14
147.43
133.42
131.37
131.29
131.18
130.20
128.84
127.79
125.46
121.30
115.93
115.72
77.39
77.07
76.75
53.23
N
COOCH3
F
5d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

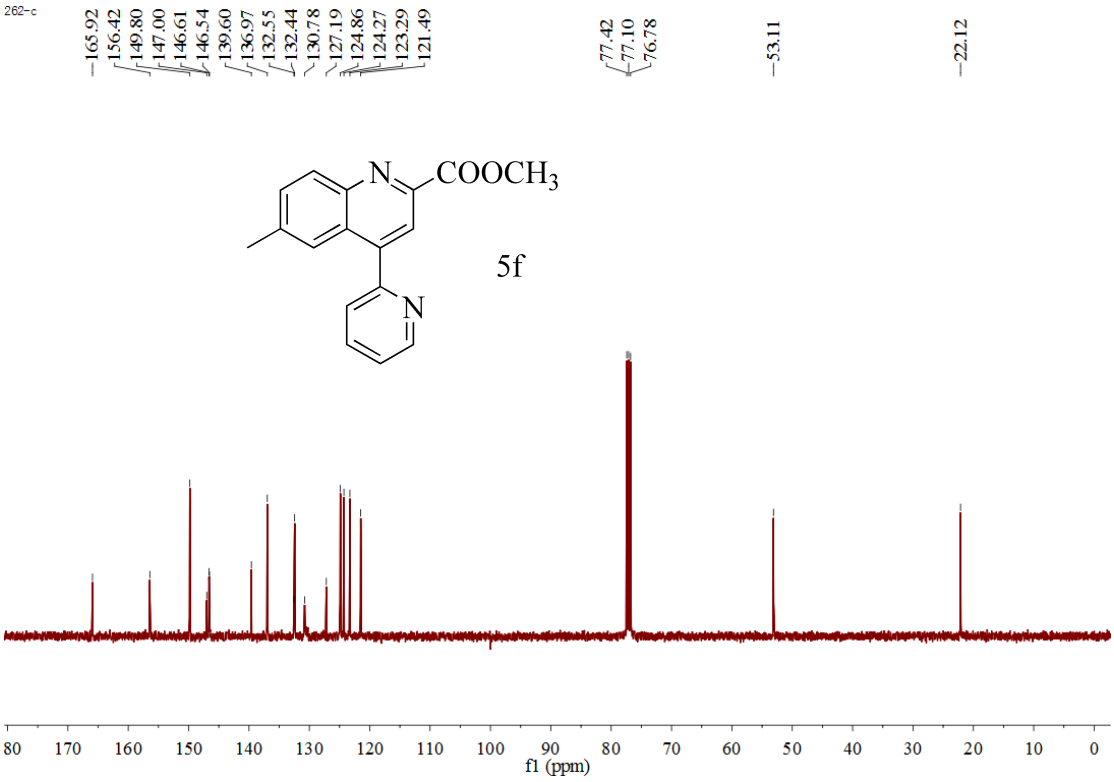
## Product 5e


20160318-118
8.863
8.851
8.402
8.381
8.331
8.248
8.227
7.931
7.927
7.825
7.821
7.709
7.689
7.686
7.683
7.665
7.662
7.474
7.472
7.462
7.460
7.456
7.771
4.108
N
COOCH3
N
5e
1.00
0.99
0.95
1.00
1.04
1.05
2.07
1.10
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

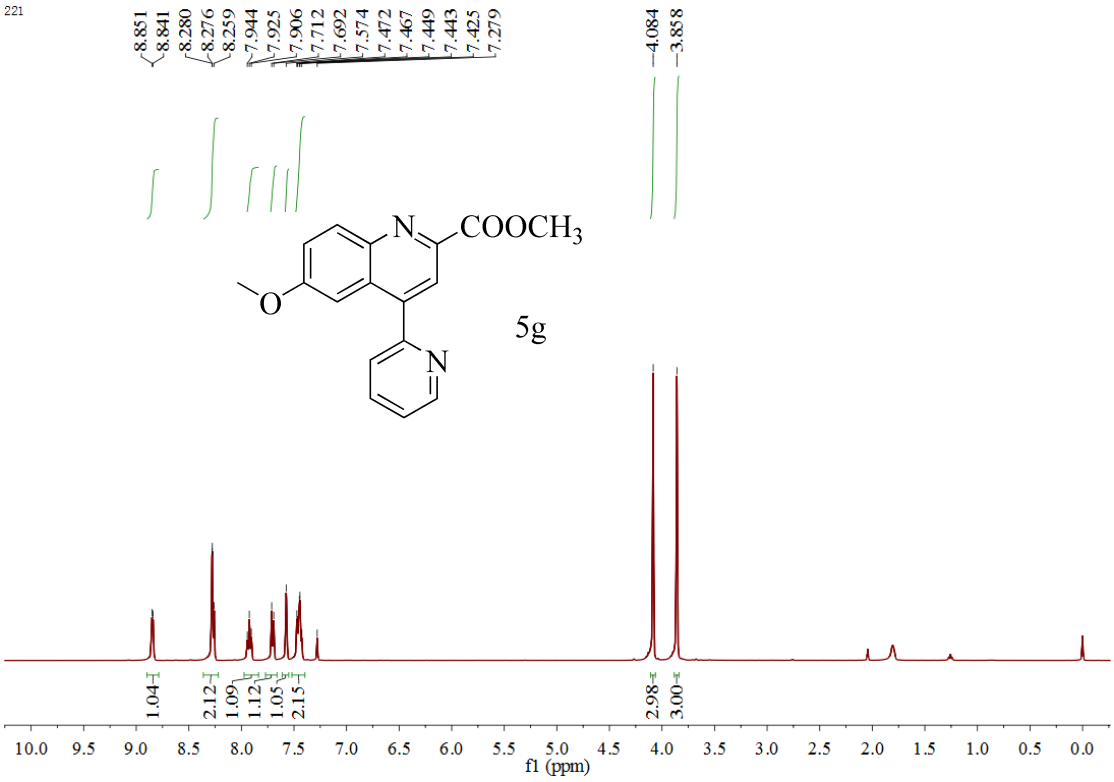

118
165.78
156.10
149.84
148.37
147.45
136.98
131.03
130.19
129.10
127.13
125.63
124.90
123.40
121.34
77.48
77.16
76.84
53.17
N
COOCH3
N
5e
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

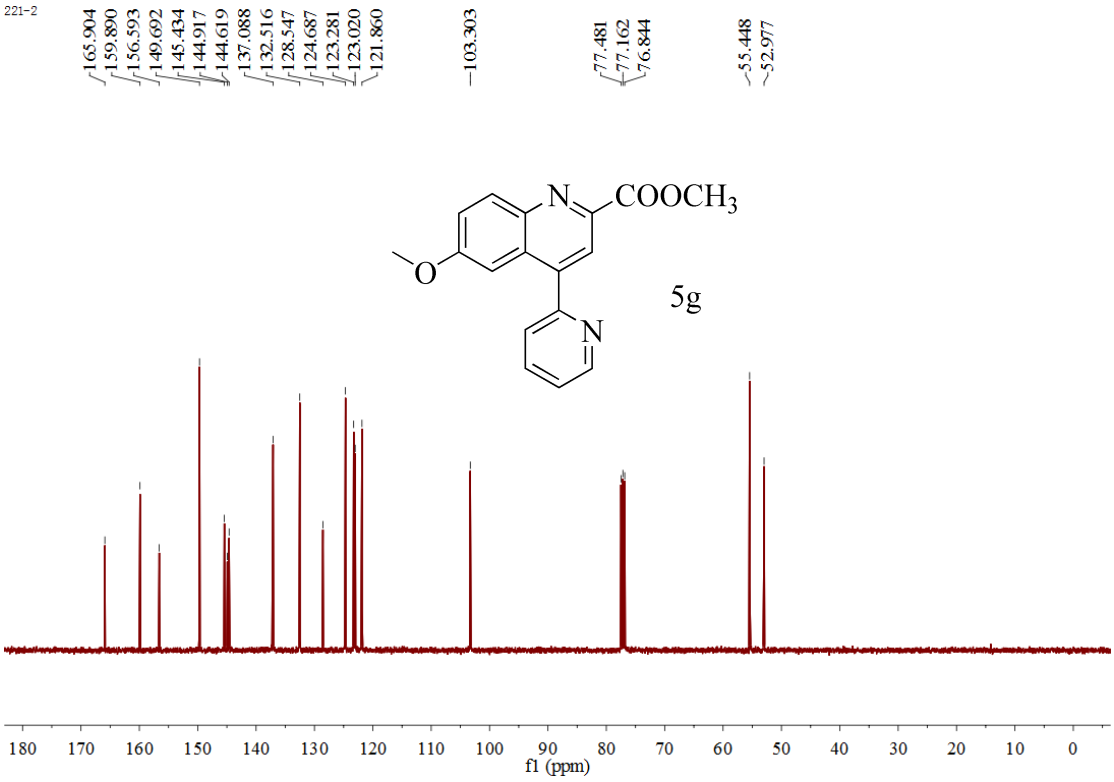
## Product 5f


202-3
8.859
8.849
8.284
8.270
7.946
7.922
7.902
7.681
7.657
7.633
7.464
7.449
7.433
7.268
4.090
2.525
N
COOCH3
5f
N
1.01
1.97
2.01
2.03
1.02
3.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

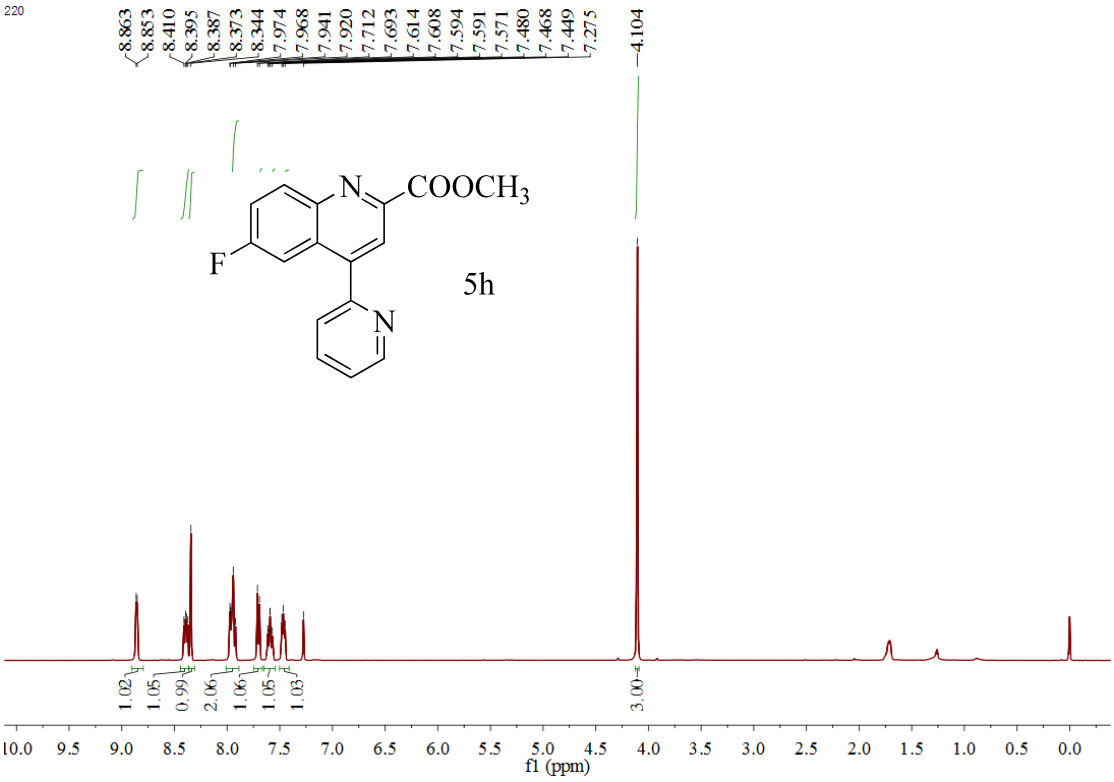

262-c
165.92
156.42
149.80
147.00
146.61
146.54
139.60
136.97
132.55
132.44
130.78
127.19
124.86
124.27
123.29
121.49
77.42
77.10
76.78
53.11
22.12
N
COOCH3
5f
N
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

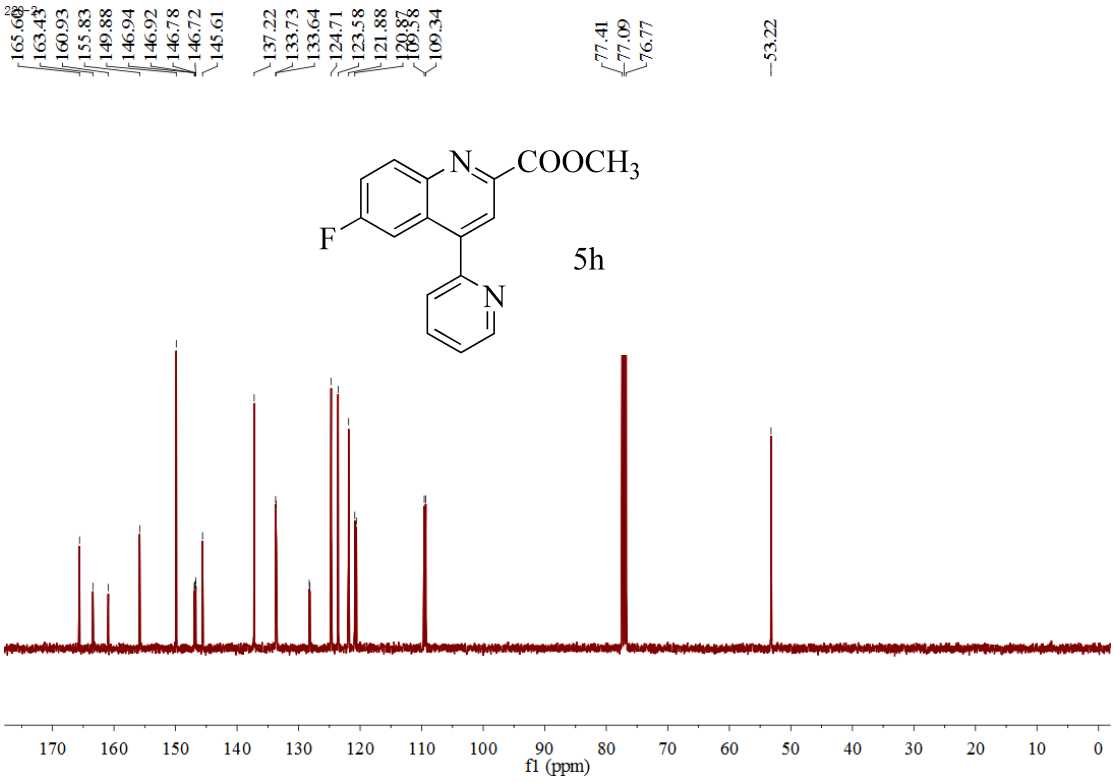
## Product 5g


221
8.851
8.841
8.280
8.276
8.259
7.944
7.925
7.906
7.712
7.692
7.574
7.472
7.467
7.449
7.443
7.425
7.279
4.084
3.858
N
COOCH3
O
N
5g
1.04
2.12
1.09
1.12
1.05
2.15
2.98
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

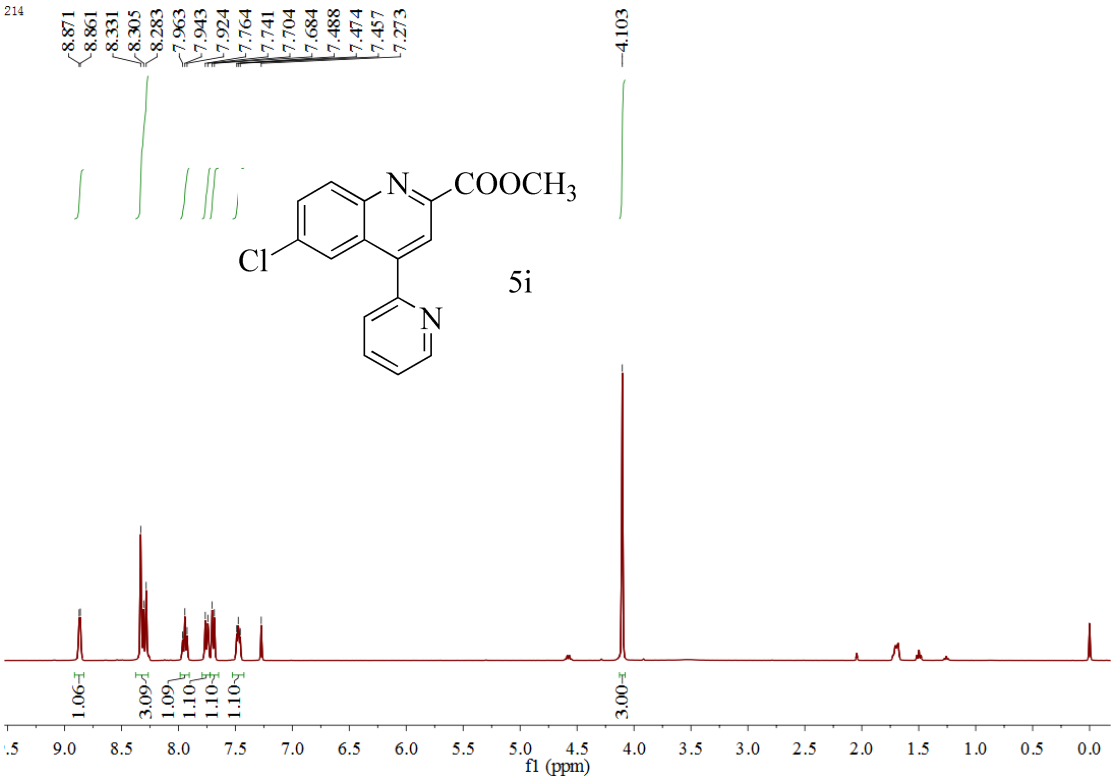

221-2
165.904
159.890
156.593
149.692
145.434
144.917
144.619
137.088
132.516
128.547
124.687
123.281
123.020
121.860
103.303
77.481
77.162
76.844
55.448
52.977
N
COOCH3
O
N
5g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

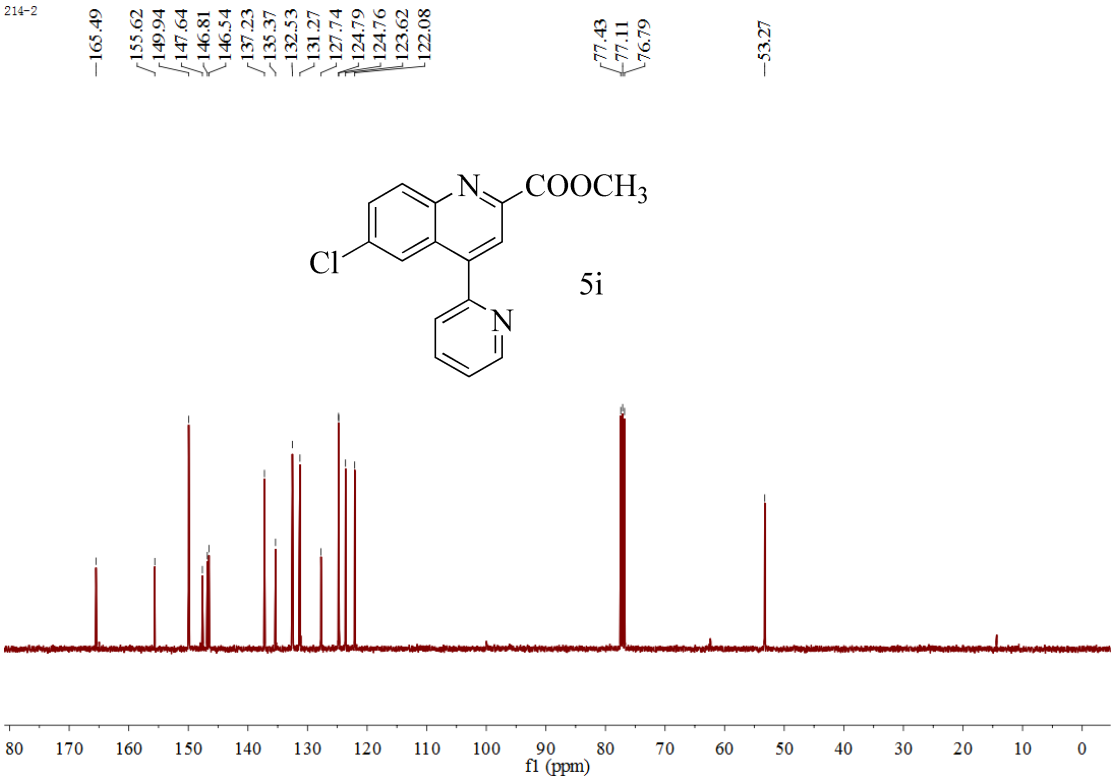
## Product 5h


8.863
8.853
8.410
8.395
8.387
8.373
8.344
7.974
7.968
7.941
7.920
7.712
7.693
7.614
7.608
7.594
7.591
7.571
7.480
7.468
7.449
7.275
4.104
N
COOCH3
F
N
5h
1.02
1.05
0.99
2.06
1.06
1.05
1.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

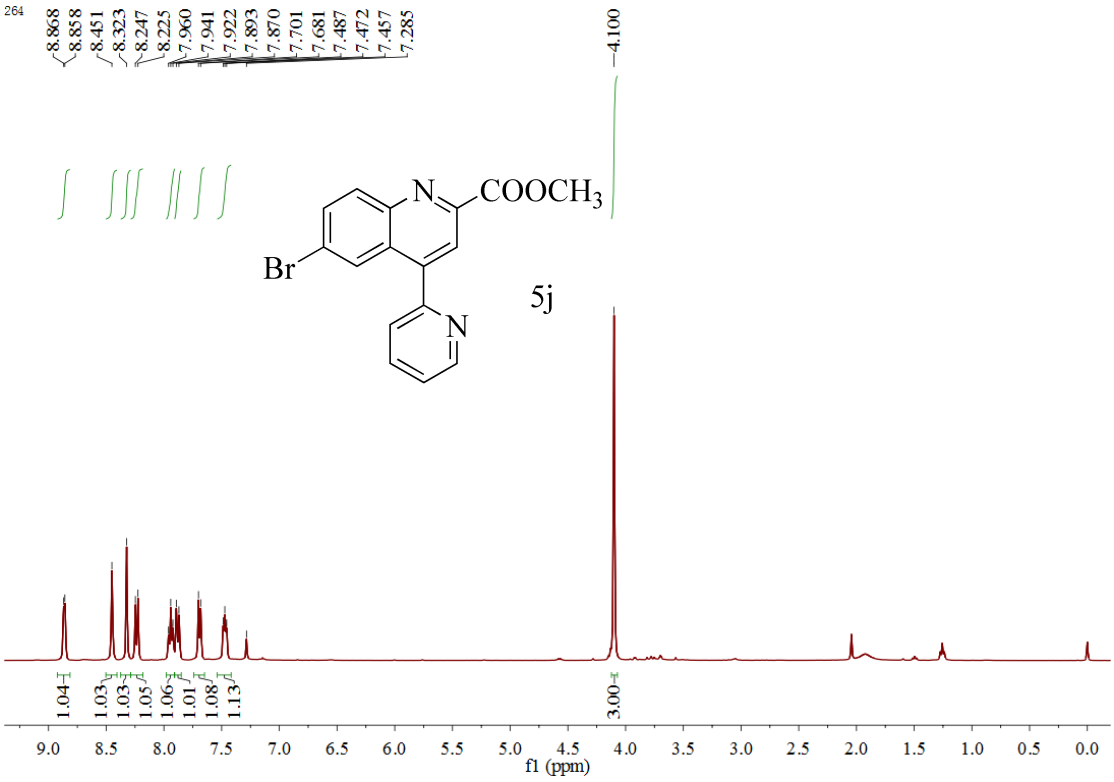

165.60
163.43
160.93
155.83
149.88
146.94
146.92
146.78
146.72
145.61
137.22
133.73
133.64
124.71
123.58
121.88
120.87
109.58
109.34
77.41
77.09
76.77
53.22
N
COOCH3
F
N
5h
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

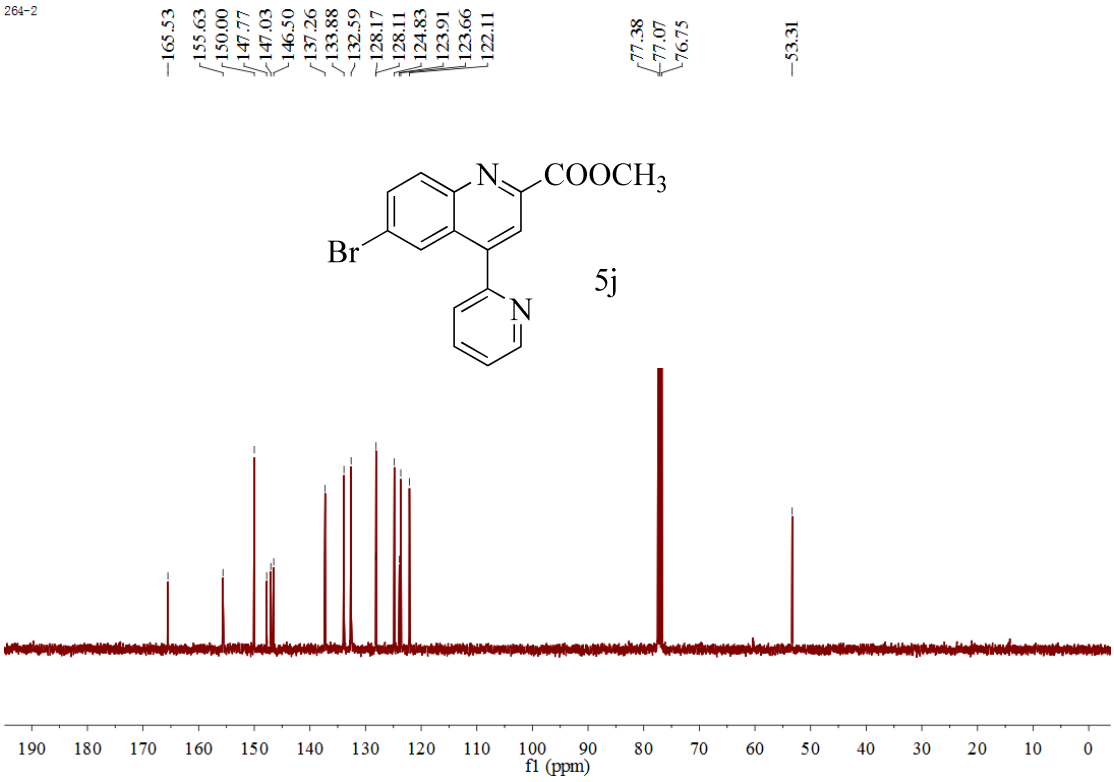
## Product 5i


214
8.871
8.861
8.331
8.305
8.283
7.963
7.943
7.924
7.764
7.741
7.704
7.684
7.488
7.474
7.457
7.273
4.103
N
COOCH3
Cl
N
5i
1.06
3.09
1.09
1.10
1.10
3.00
f1 (ppm)

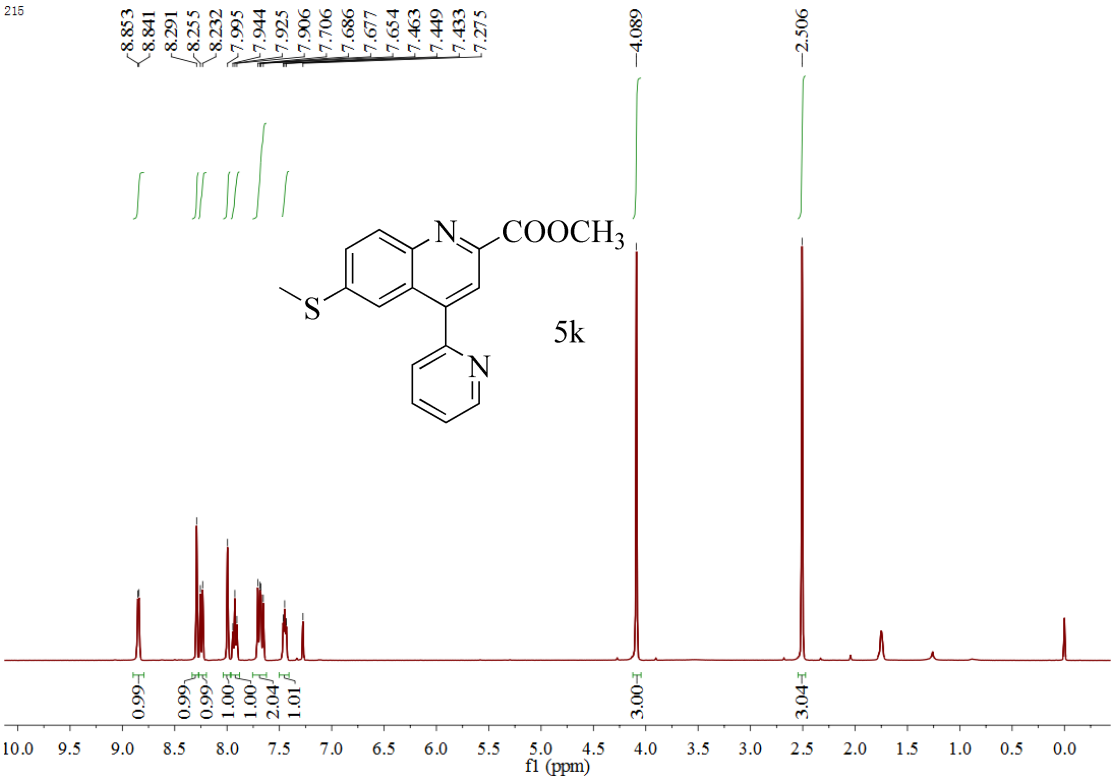

214-2
165.49
155.62
149.94
147.64
146.81
146.54
137.23
135.37
132.53
131.27
127.74
124.79
124.76
123.62
122.08
77.43
77.11
76.79
53.27
N
COOCH3
Cl
N
5i
f1 (ppm)

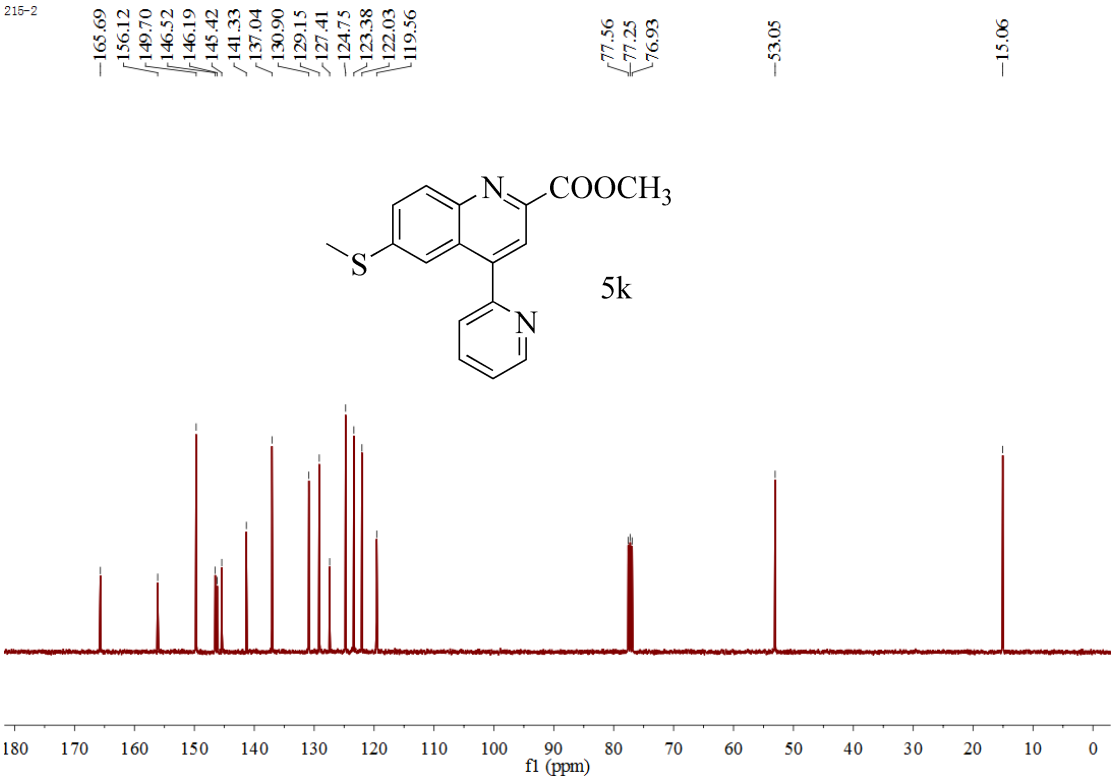
**Product 5j**


264
8.868
8.858
8.451
8.323
8.247
8.225
7.960
7.941
7.922
7.893
7.870
7.701
7.681
7.487
7.472
7.457
7.285
4.100
N
COOCH3
Br
N
5j
1.04
1.03
1.03
1.05
1.06
1.01
1.08
1.13
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

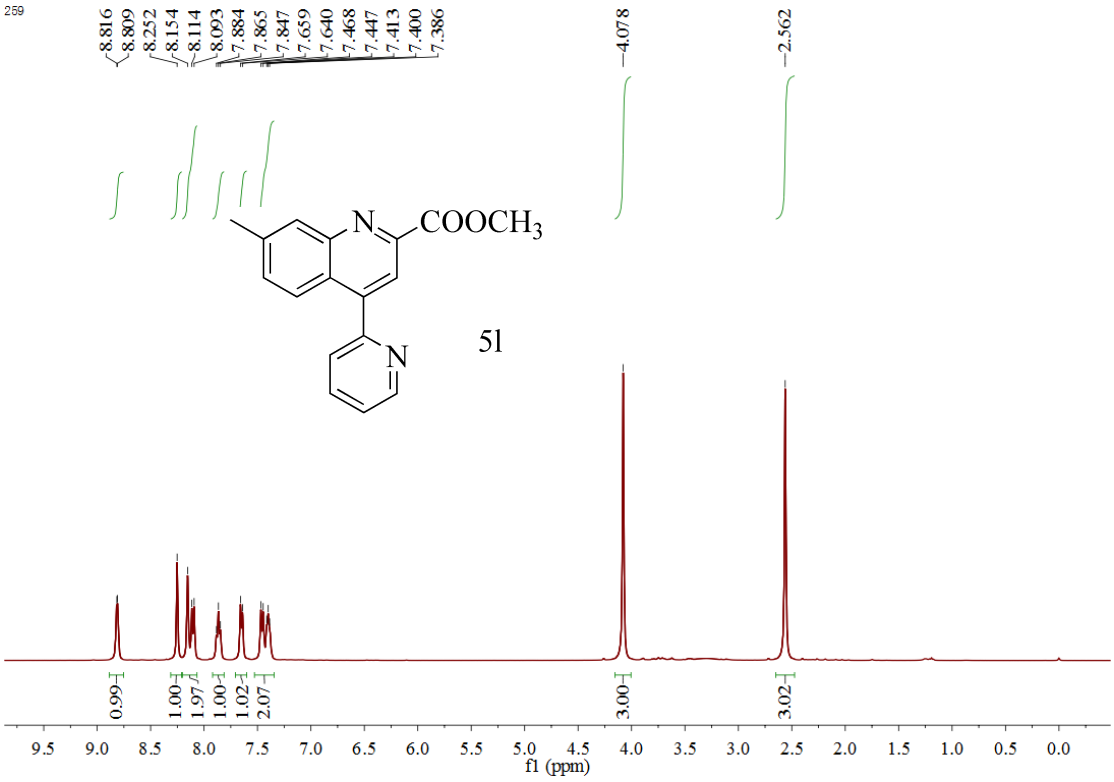

264-2
165.53
155.63
150.00
147.77
147.03
146.50
137.26
133.88
132.59
128.17
128.11
124.83
123.91
123.66
122.11
77.38
77.07
76.75
53.31
N
COOCH3
Br
N
5j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

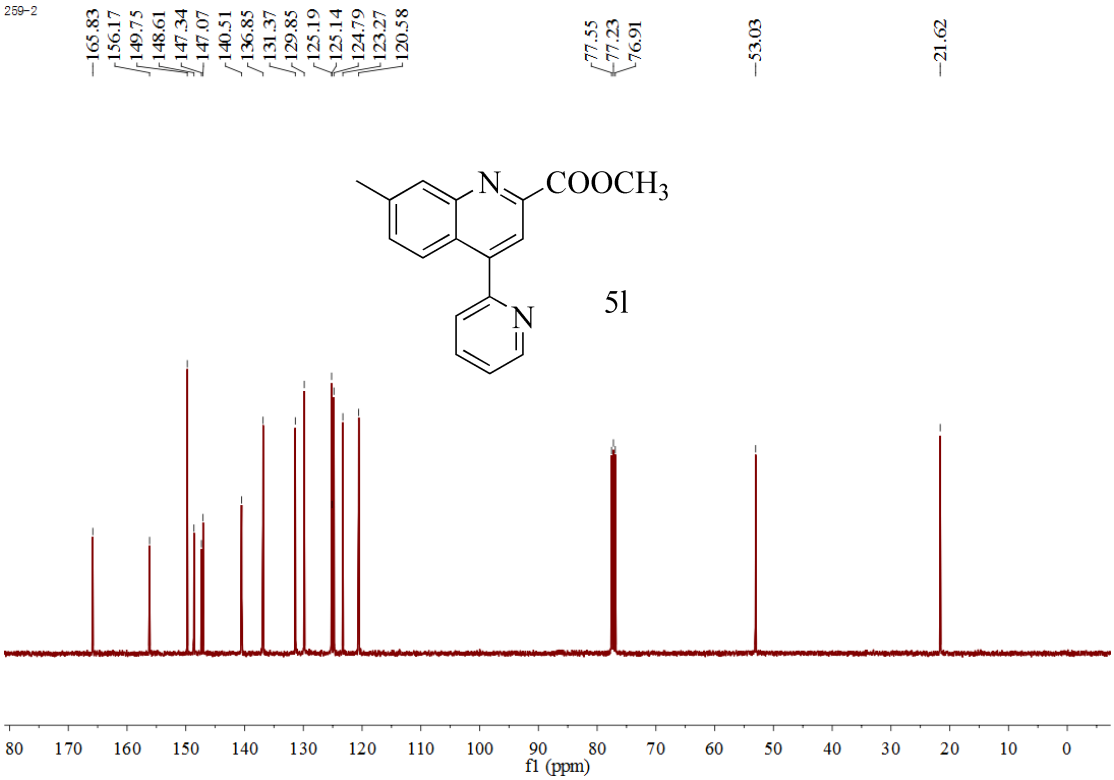
## Product 5k


215
8.853
8.841
8.291
8.255
8.232
7.995
7.944
7.925
7.906
7.706
7.686
7.677
7.654
7.463
7.449
7.433
7.275
4.089
2.506
N
COOCH3
S
N
5k
0.99
0.99
0.99
1.00
1.00
2.04
1.01
3.00
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

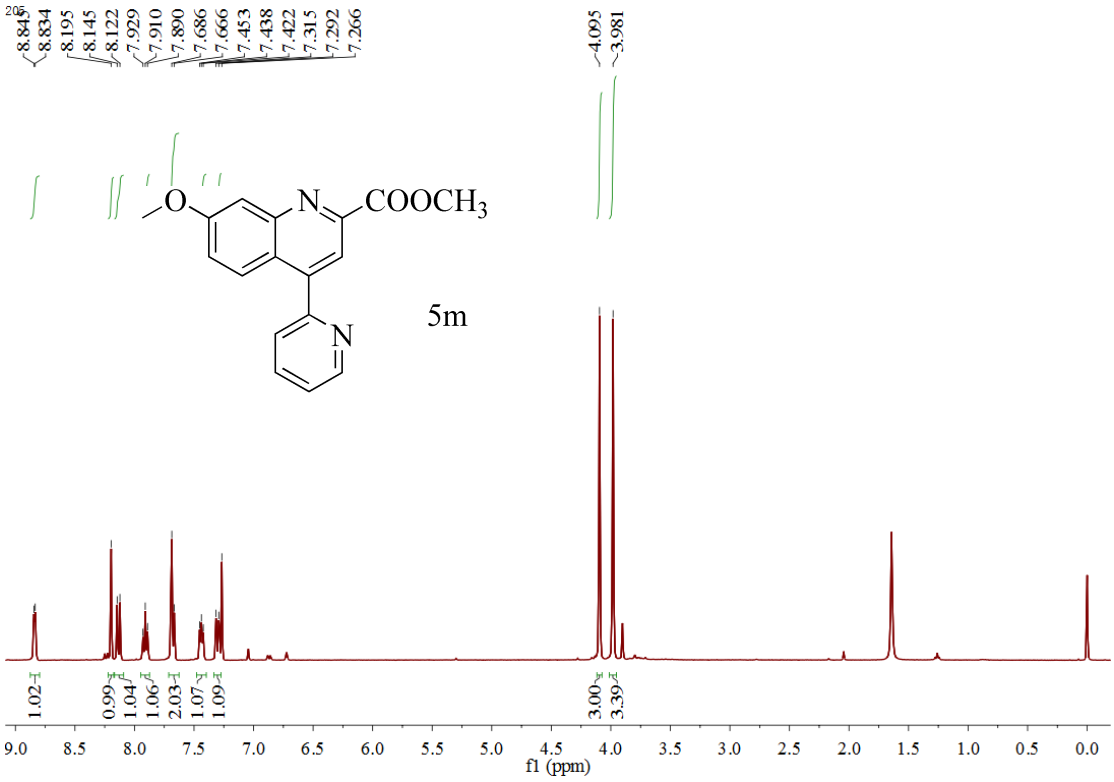

215-2
165.69
156.12
149.70
146.52
146.19
145.42
141.33
137.04
130.90
129.15
127.41
124.75
123.38
122.03
119.56
77.56
77.25
76.93
53.05
15.06
N
COOCH3
S
N
5k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

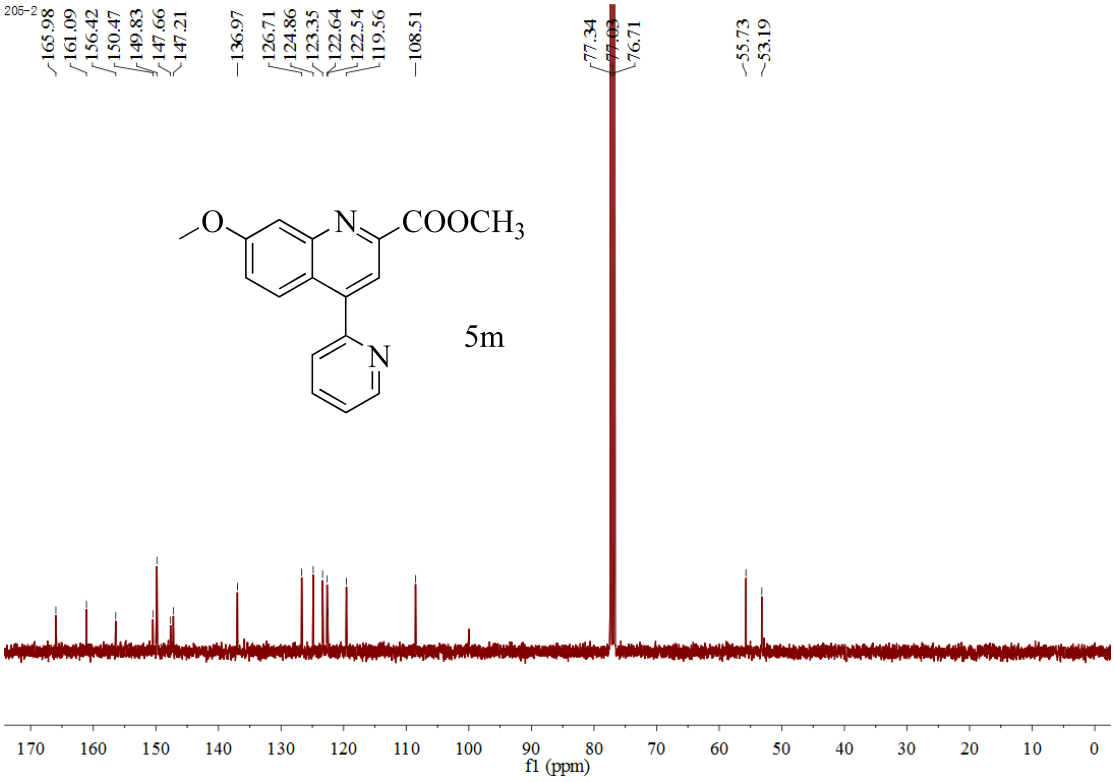
## Product 5l


259
8.816
8.809
8.252
8.154
8.114
8.093
7.884
7.865
7.847
7.659
7.640
7.468
7.447
7.413
7.400
7.386
4.078
2.562
N
COOCH3
N
5l
0.99
1.00
1.97
1.00
1.02
2.07
3.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

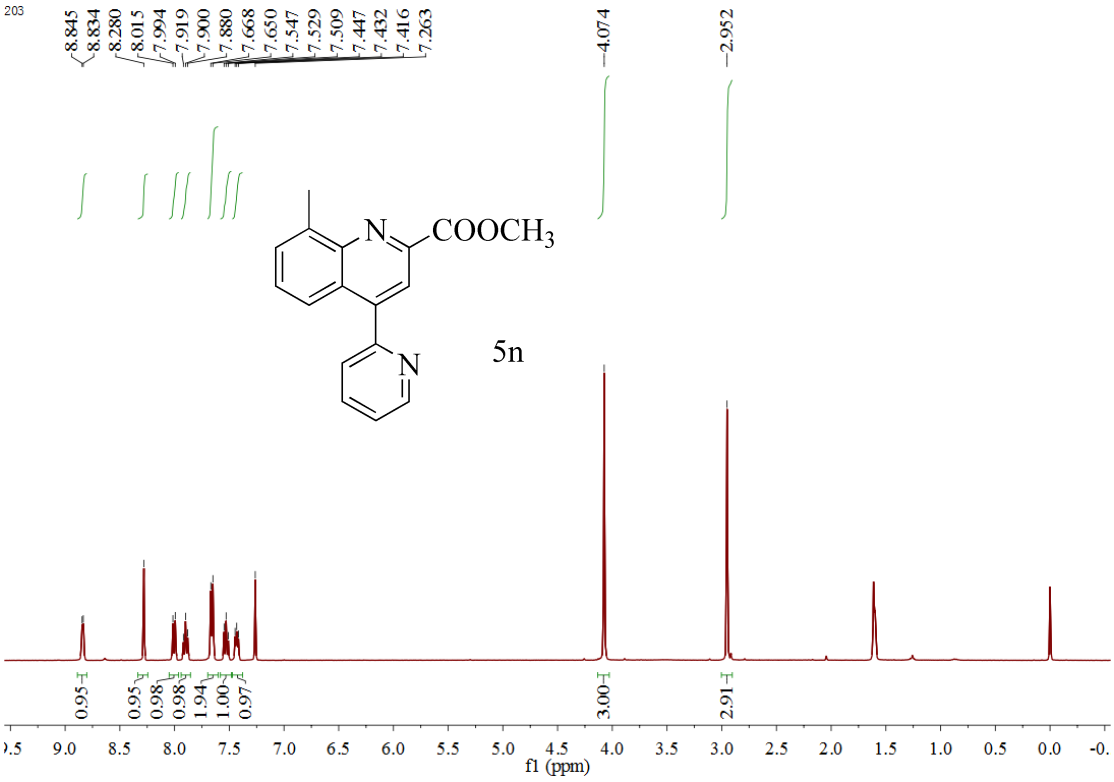

259-2
165.83
156.17
149.75
148.61
147.34
147.07
140.51
136.85
131.37
129.85
125.19
125.14
124.79
123.27
120.58
77.55
77.23
76.91
53.03
21.62
N
COOCH3
N
5l
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

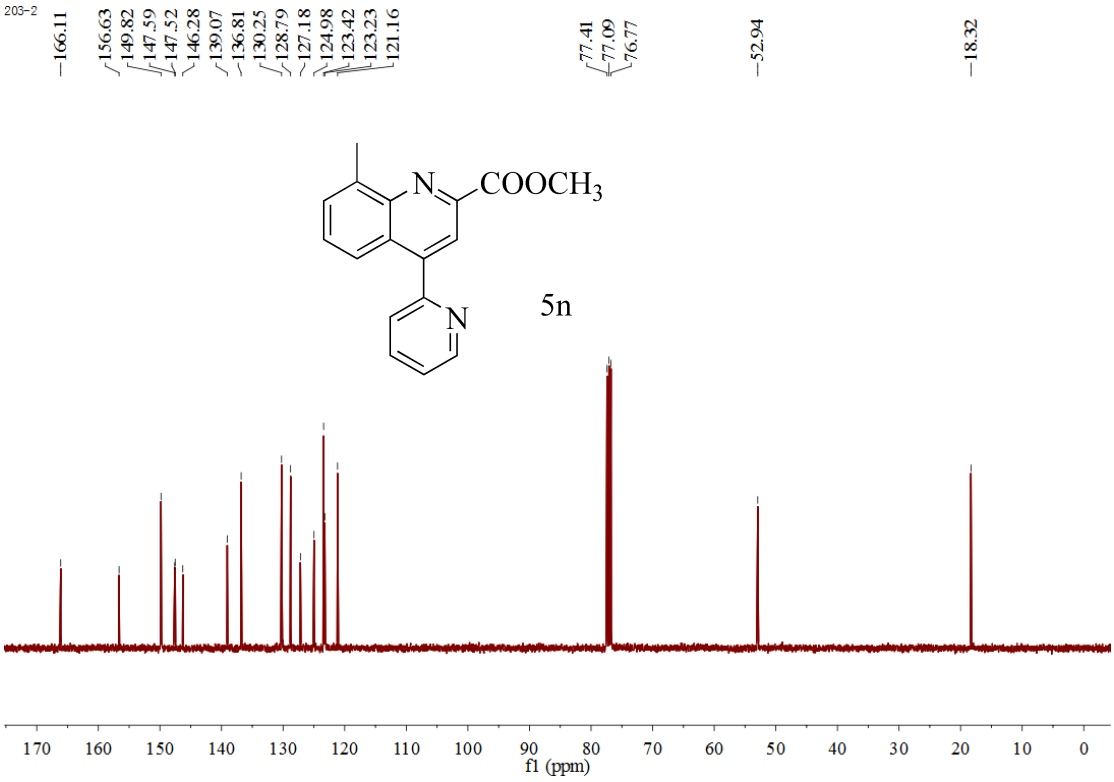
**Product 5m**


8.845
8.834
8.195
8.145
8.122
7.929
7.910
7.890
7.686
7.666
7.453
7.438
7.422
7.315
7.292
7.266
4.095
3.981
O
N
COOCH3
N
5m
1.02
0.99
1.04
1.06
2.03
1.07
1.09
3.00
3.39
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

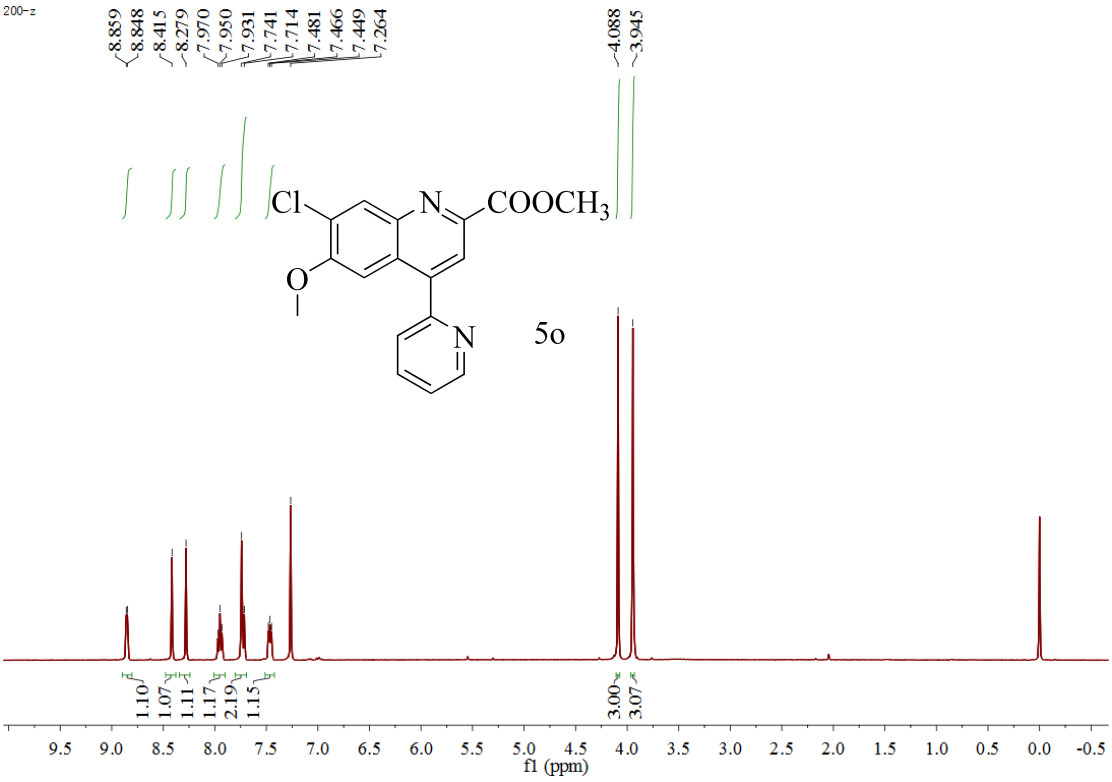

165.98
161.09
156.42
150.47
149.83
147.66
147.21
136.97
126.71
124.86
123.35
122.64
122.54
119.56
108.51
77.34
77.03
76.71
55.73
53.19
O
N
COOCH3
N
5m
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

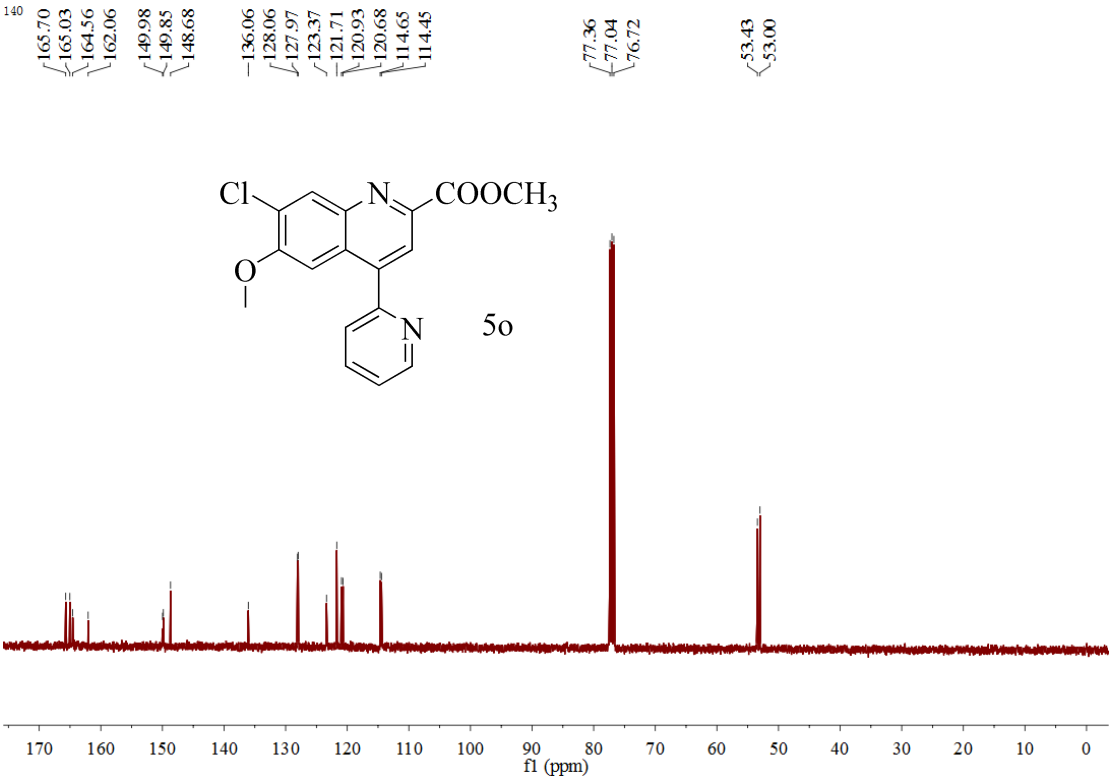
## Product 5n


203
8.845
8.834
8.280
8.015
7.994
7.919
7.900
7.880
7.668
7.650
7.547
7.529
7.509
7.447
7.432
7.416
7.263
4.074
2.952
N
COOCH3
N
5n
0.95
0.95
0.98
0.98
1.94
1.00
0.97
3.00
2.91
f1 (ppm)

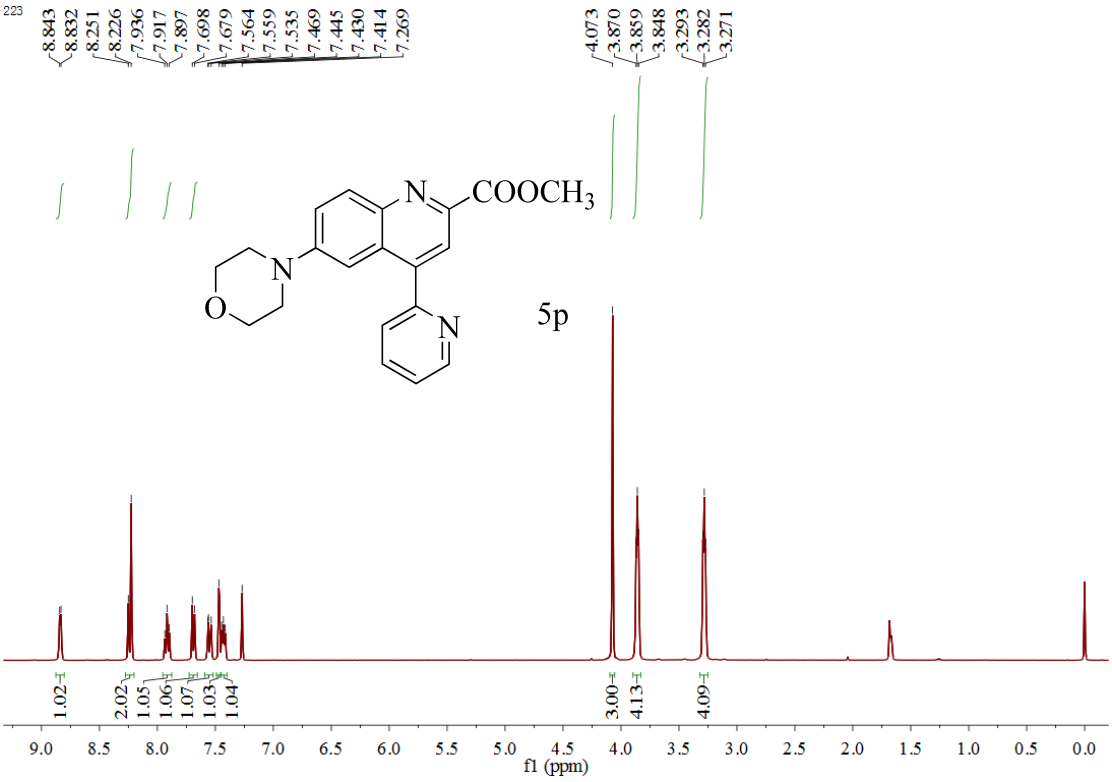

203-2
166.11
156.63
149.82
147.59
147.52
146.28
139.07
136.81
130.25
128.79
127.18
124.98
123.42
123.23
121.16
77.41
77.09
76.77
52.94
18.32
N
COOCH3
N
5n
f1 (ppm)

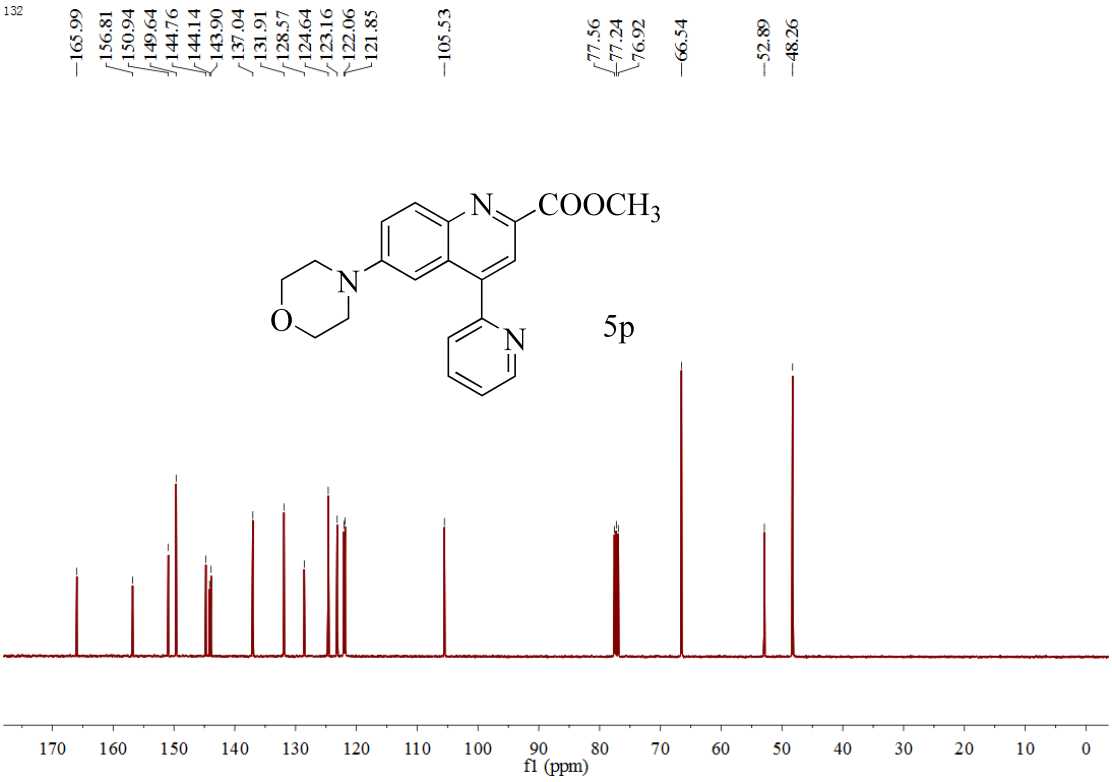
**Product 5o**


200-z
8.859
8.848
8.415
8.279
7.970
7.950
7.931
7.741
7.714
7.481
7.466
7.449
7.264
4.088
3.945
Cl
N
COOCH3
O
N
5o
1.10
1.07
1.11
1.17
2.19
1.15
3.00
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

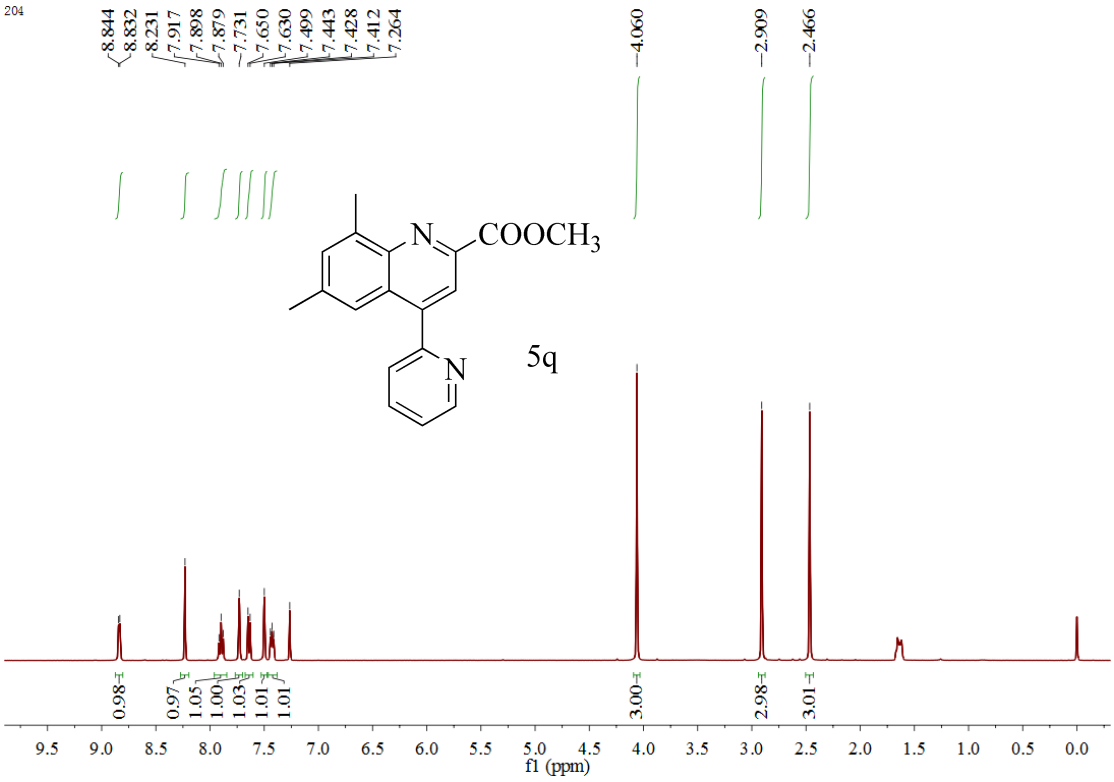

140
165.70
165.03
164.56
162.06
149.98
149.85
148.68
136.06
128.06
127.97
123.37
121.71
120.93
120.68
114.65
114.45
77.36
77.04
76.72
53.43
53.00
Cl
N
COOCH3
O
N
5o
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

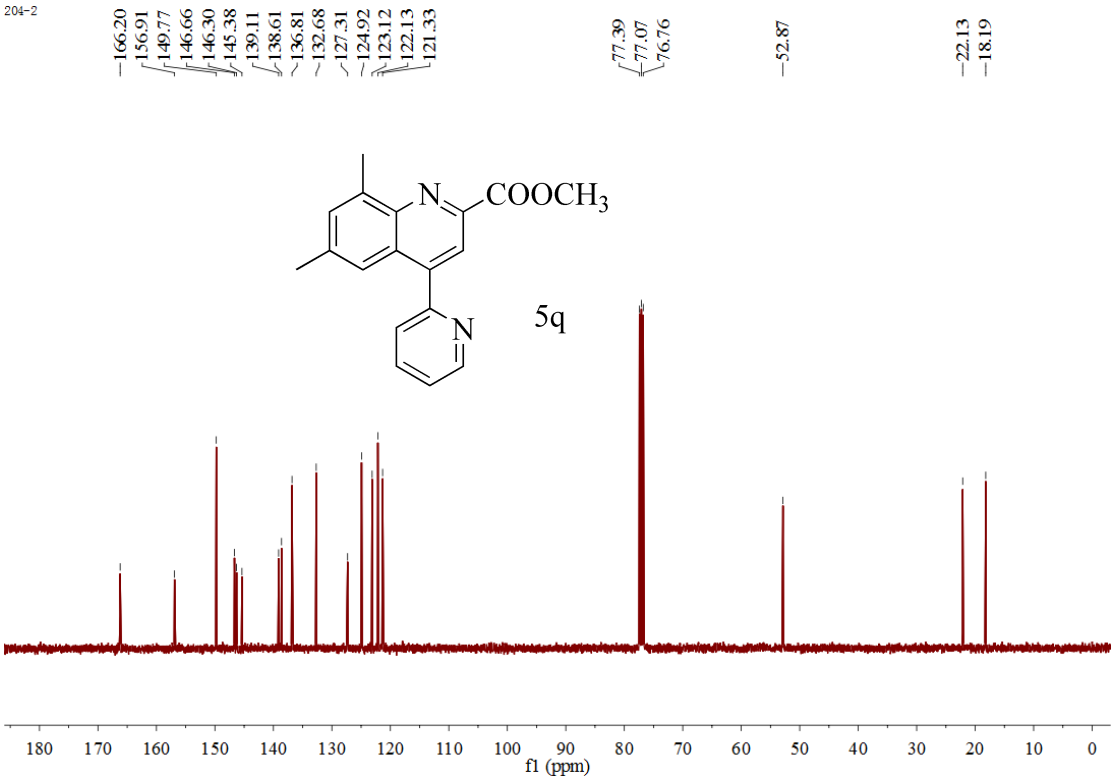
**Product 5p**


223
8.843
8.832
8.251
8.226
7.936
7.917
7.897
7.698
7.679
7.564
7.559
7.535
7.469
7.445
7.430
7.414
7.269
4.073
3.870
3.859
3.848
3.293
3.282
3.271
COOCH3
N
O
5p
1.02
2.02
1.05
1.06
1.07
1.03
1.04
3.00
4.13
4.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

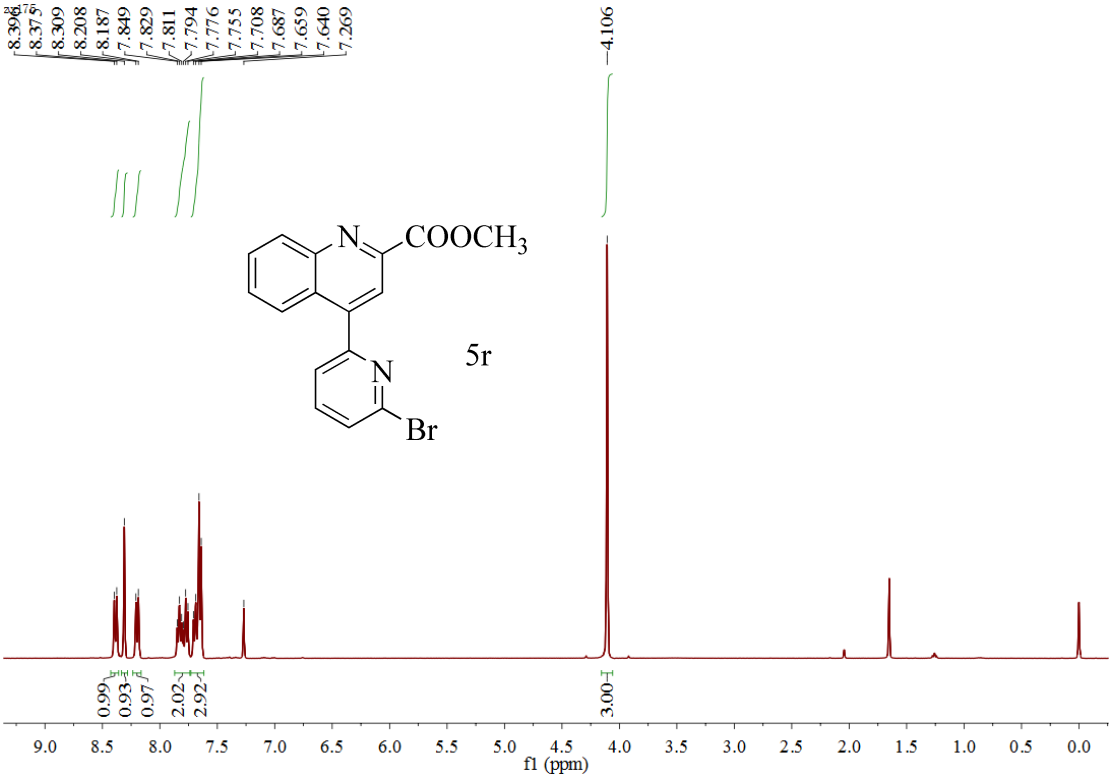

132
165.99
156.81
150.94
149.64
144.76
144.14
143.90
137.04
131.91
128.57
124.64
123.16
122.06
121.85
105.53
77.56
77.24
76.92
66.54
52.89
48.26
COOCH3
N
O
5p
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

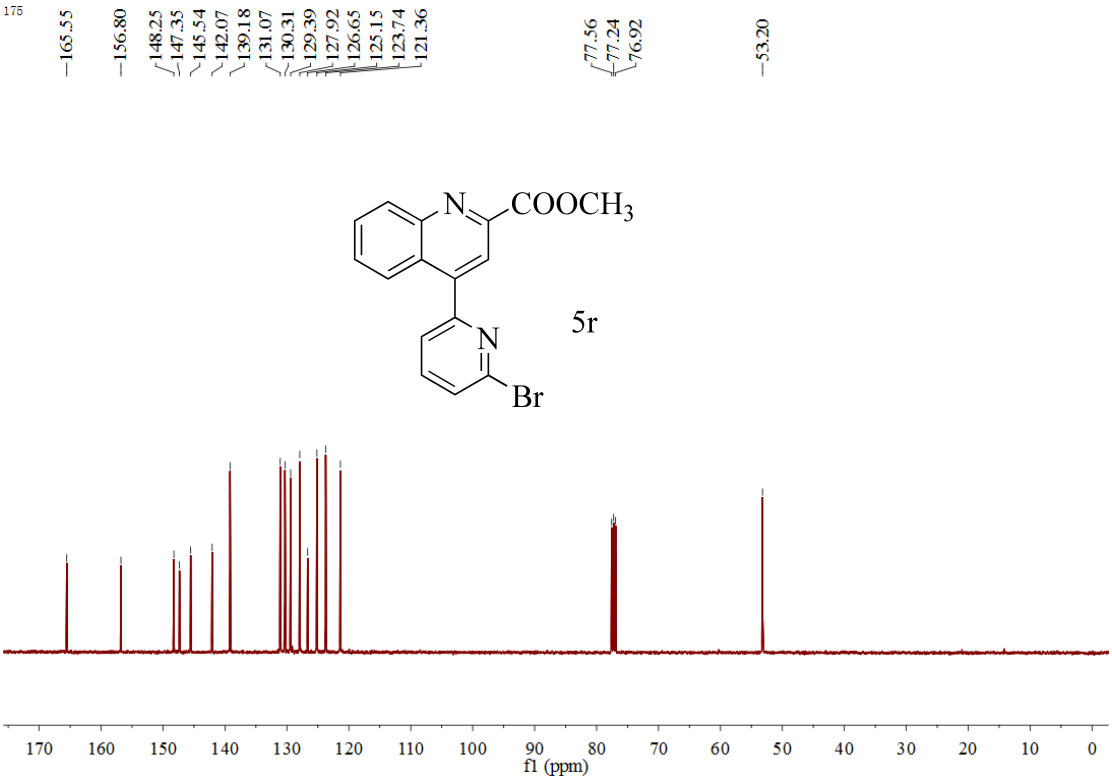
## Product 5q


204
8.844
8.832
8.231
7.917
7.898
7.879
7.731
7.650
7.630
7.499
7.443
7.428
7.412
7.264
4.060
2.909
2.466
N
COOCH3
N
5q
0.98
0.97
1.05
1.00
1.03
1.01
1.01
3.00
2.98
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

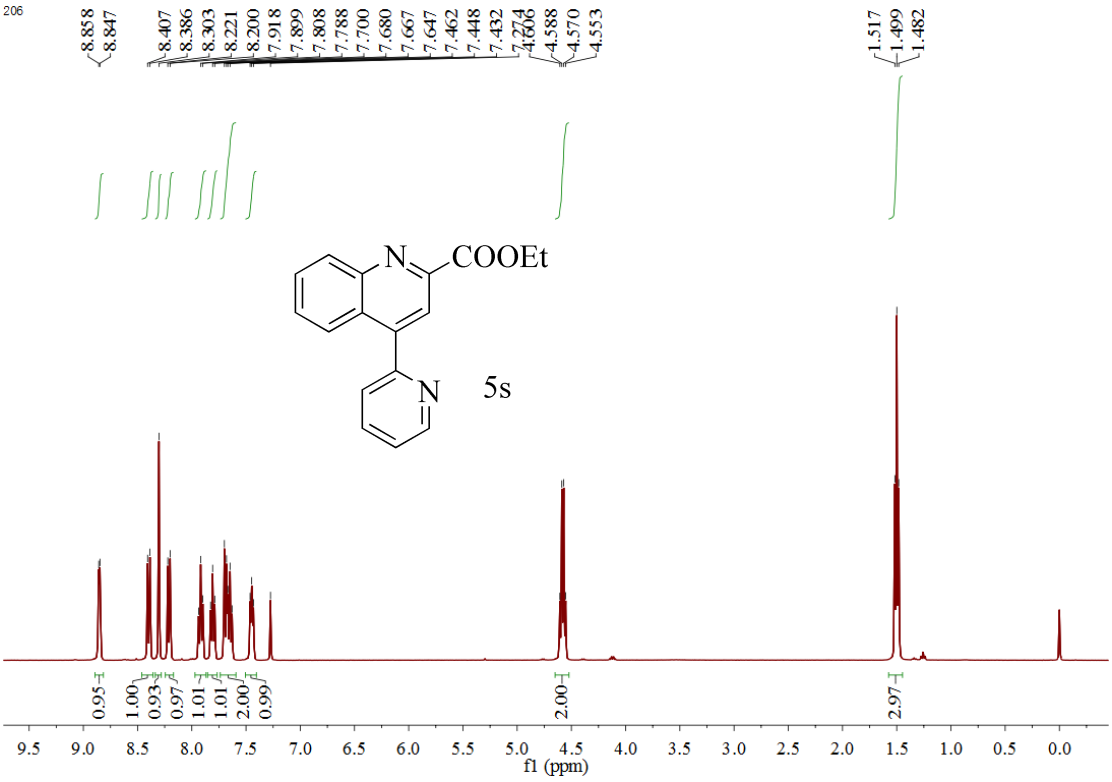

204-2
166.20
156.91
149.77
146.66
146.30
145.38
139.11
138.61
136.81
132.68
127.31
124.92
123.12
122.13
121.33
77.39
77.07
76.76
52.87
22.13
18.19
N
COOCH3
N
5q
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

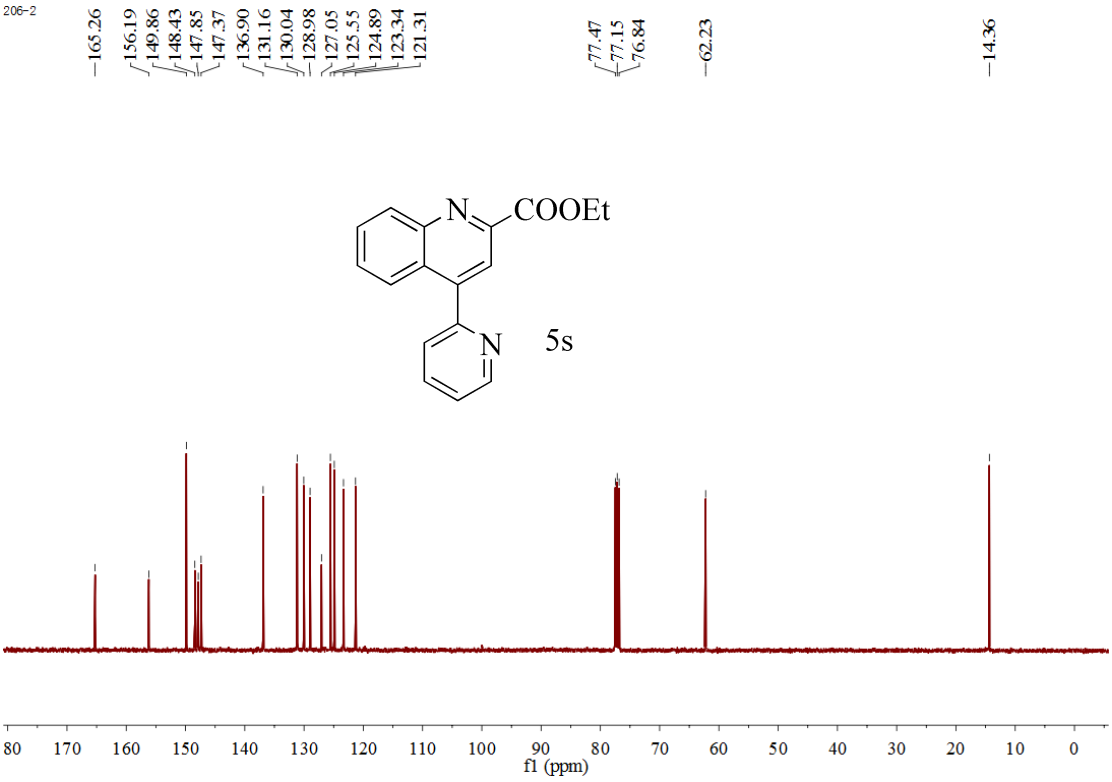
## Product 5r


8.396
8.375
8.309
8.208
8.187
7.849
7.829
7.811
7.794
7.776
7.755
7.708
7.687
7.659
7.640
7.269
4.106
N
COOCH3
N
Br
5r
0.99
0.93
0.97
2.02
2.92
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

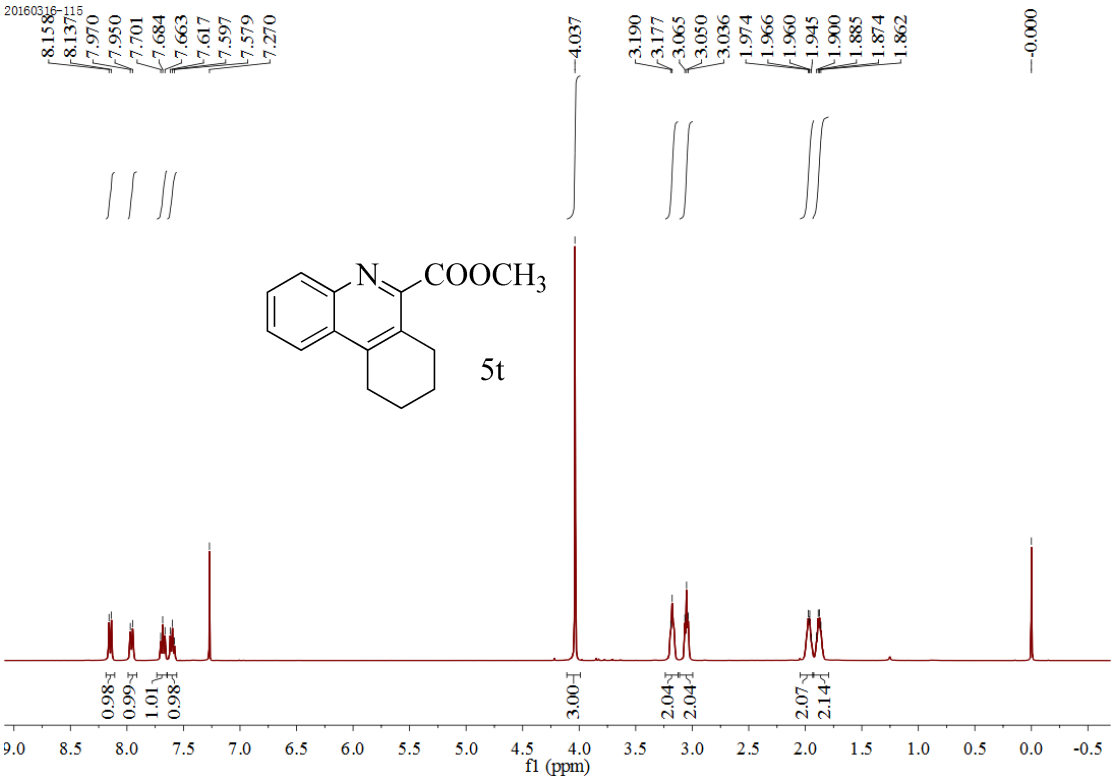

165.55
156.80
148.25
147.35
145.54
142.07
139.18
131.07
130.31
129.39
127.92
126.65
125.15
123.74
121.36
77.56
77.24
76.92
53.20
N
COOCH3
N
Br
5r
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

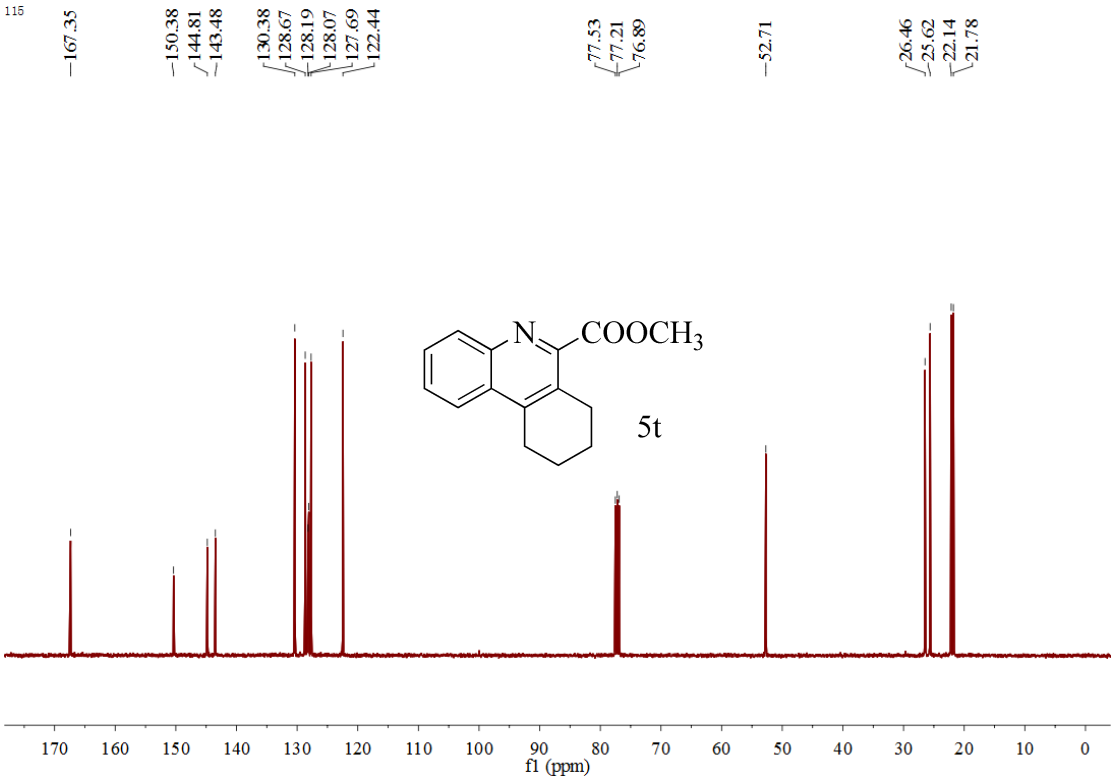
## Product 5s


206
8.858
8.847
8.407
8.386
8.303
8.221
8.200
7.918
7.899
7.808
7.788
7.700
7.680
7.667
7.647
7.462
7.448
7.432
7.274
4.606
4.588
4.570
4.553
1.517
1.499
1.482
N
COOEt
N
5s
0.95
1.00
0.93
0.97
1.01
1.01
2.00
0.99
2.00
2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

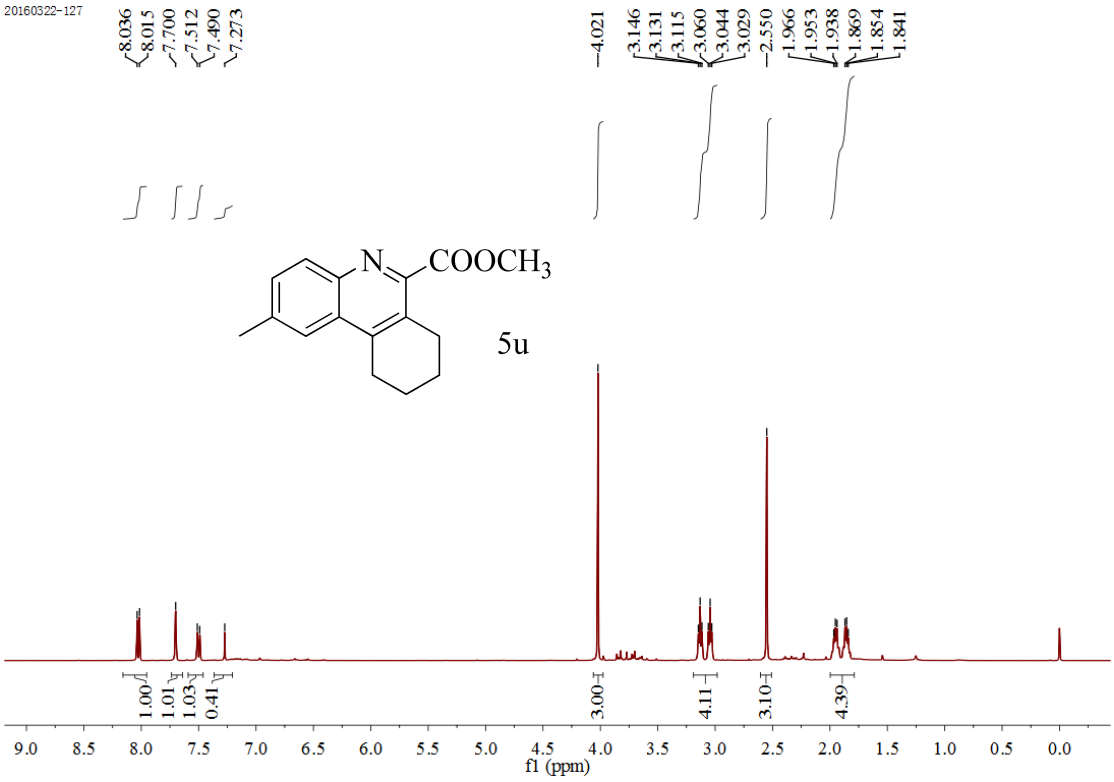

206-2
165.26
156.19
149.86
148.43
147.85
147.37
136.90
131.16
130.04
128.98
127.05
125.55
124.89
123.34
121.31
77.47
77.15
76.84
62.23
14.36
N
COOEt
N
5s
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

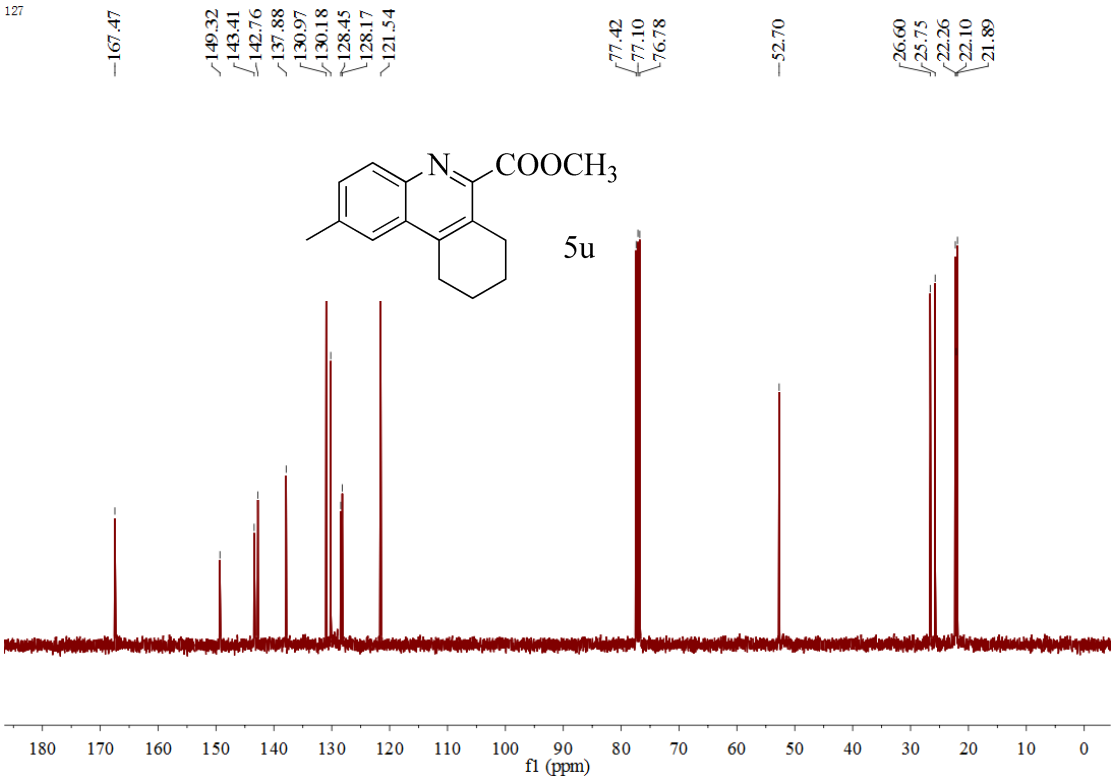
**Product 5t**


20160316-115
8.158
8.137
7.970
7.950
7.701
7.684
7.663
7.617
7.597
7.579
7.270
4.037
3.190
3.177
3.065
3.050
3.036
1.974
1.966
1.960
1.945
1.900
1.885
1.874
1.862
-0.000
N
COOCH3
5t
0.98
0.99
1.01
0.98
3.00
2.04
2.04
2.07
2.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

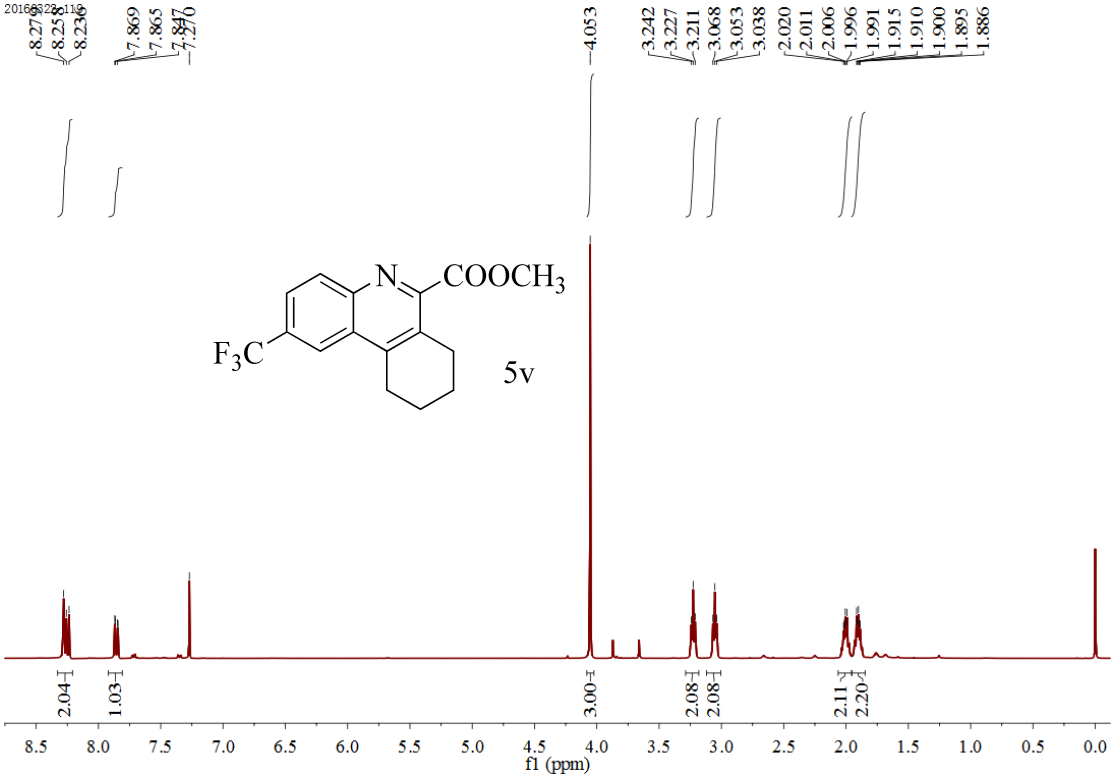

115
167.35
150.38
144.81
143.48
130.38
128.67
128.19
128.07
127.69
122.44
77.53
77.21
76.89
52.71
26.46
25.62
22.14
21.78
N
COOCH3
5t
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

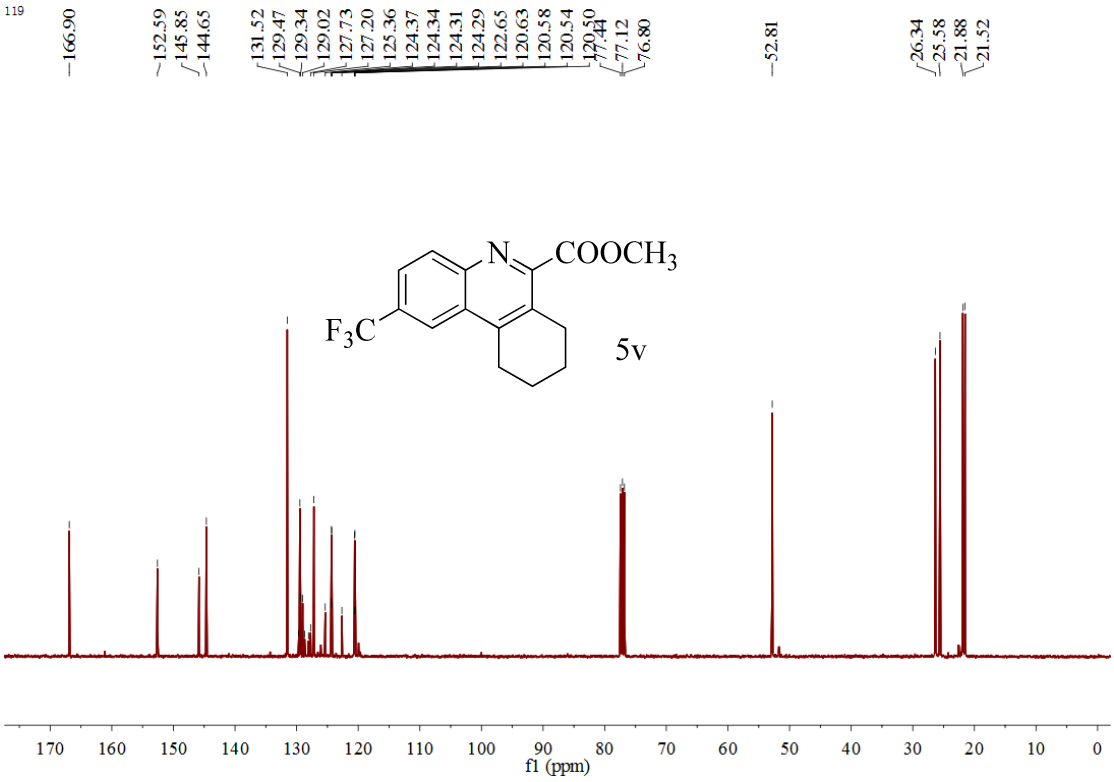
## Product 5u


20160322-127
8.036
8.015
7.700
7.512
7.490
7.273
4.021
3.146
3.131
3.115
3.060
3.044
3.029
2.550
1.966
1.953
1.938
1.869
1.854
1.841
N
COOCH3
5u
1.00
1.01
1.03
0.41
3.00
4.11
3.10
4.39
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

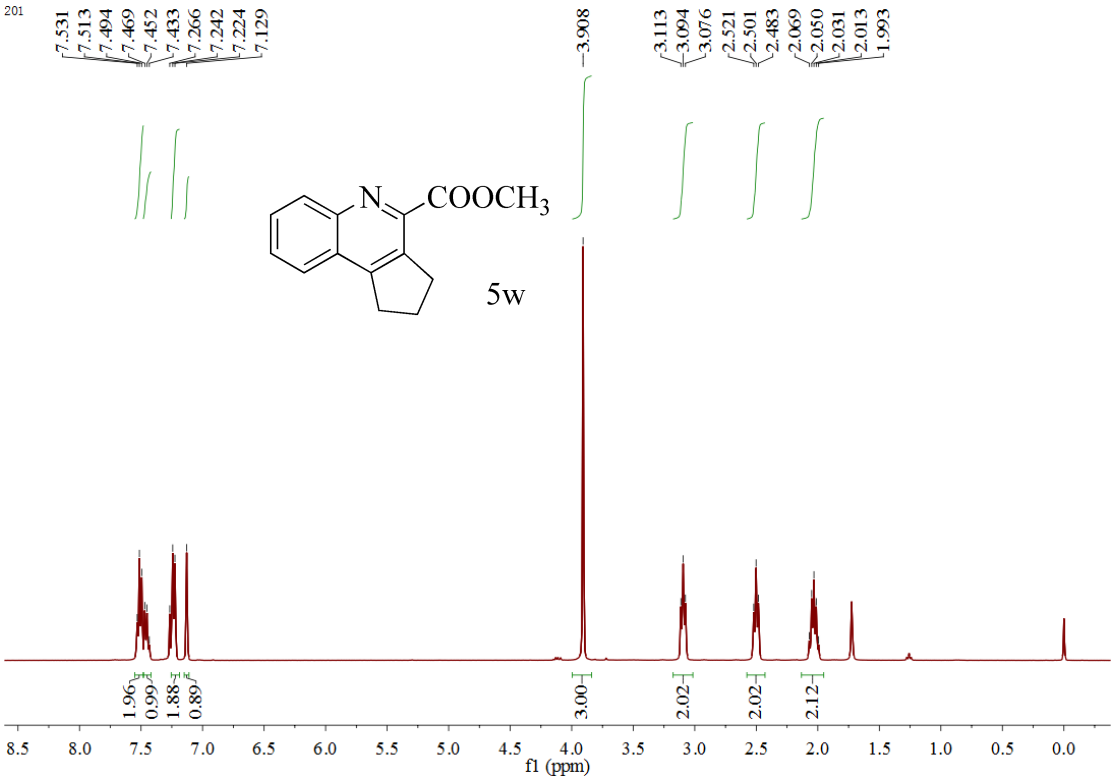

127
167.47
149.32
143.41
142.76
137.88
130.97
130.18
128.45
128.17
121.54
77.42
77.10
76.78
52.70
26.60
25.75
22.26
22.10
21.89
N
COOCH3
5u
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

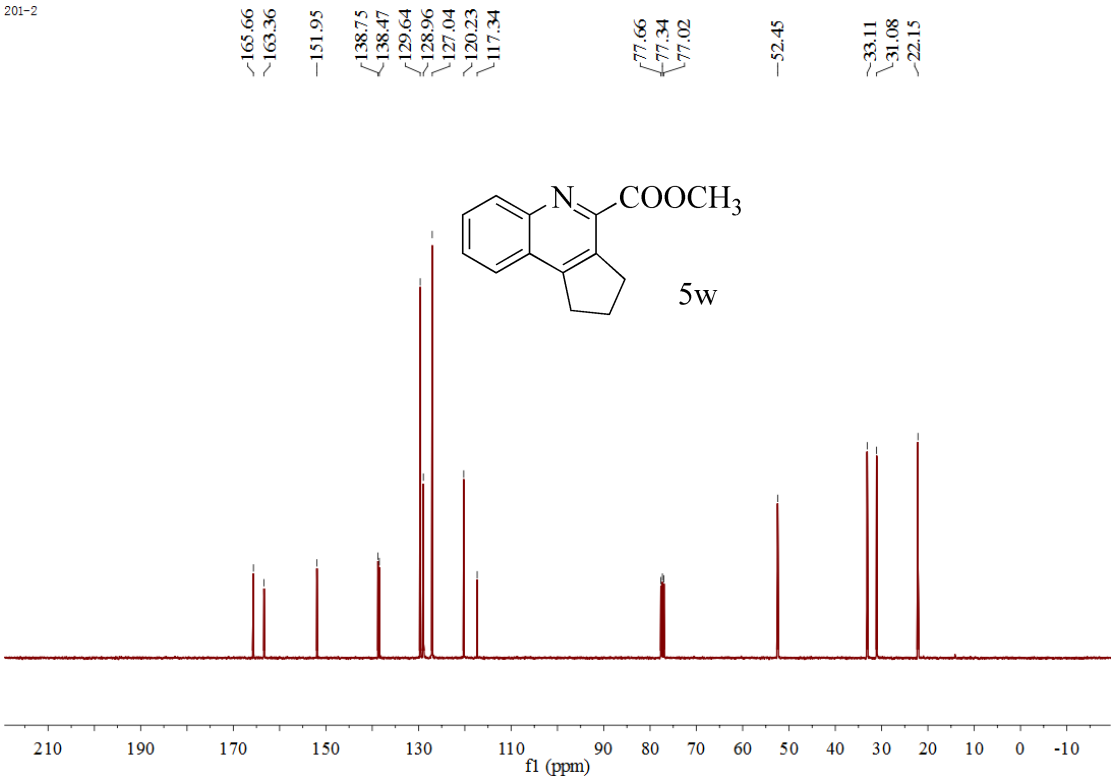
## Product 5v


8.277
8.255
8.236
7.869
7.865
4.053
3.242
3.227
3.211
3.068
3.053
3.038
2.020
2.011
2.006
1.996
1.991
1.915
1.910
1.900
1.895
1.886
N
COOCH3
F3C
5v
2.04
1.03
3.00
2.08
2.08
2.11
2.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


119
166.90
152.59
145.85
144.65
131.52
129.47
129.34
129.02
127.73
127.20
125.36
124.37
124.34
124.31
124.29
122.65
120.63
120.58
120.54
120.50
77.41
77.12
76.80
52.81
26.34
25.58
21.88
21.52
N
COOCH3
F3C
5v
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

## Product 5w


201
7.531
7.513
7.494
7.469
7.452
7.433
7.266
7.242
7.224
7.129
3.908
3.113
3.094
3.076
2.521
2.501
2.483
2.069
2.050
2.031
2.013
1.993
N
COOCH3
5w
1.96
0.99
1.88
0.89
3.00
2.02
2.02
2.12
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


201-2
165.66
163.36
151.95
138.75
138.47
129.64
128.96
127.04
120.23
117.34
77.66
77.34
77.02
52.45
33.11
31.08
22.15
N
COOCH3
5w
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)