

Supplementary information

Ionic liquid as an efficient medium for the synthesis of quinoline derivatives via α -chymotrypsin-catalyzed Friedlander condensation

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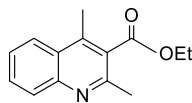
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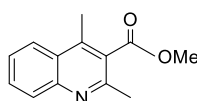
Spectroscopic data of products

Ethyl-2,4-dimethylquinoline-3-carboxylate (3a)



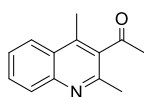
Yellow oil, yield 81 %; ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 4.49 (q, J = 7.0 Hz, 2H), 2.71 (s, 3H), 2.65 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.18, 154.32, 147.07, 141.45, 130.05, 129.24, 127.99, 126.31, 125.77, 123.98, 61.66, 23.77, 15.68, 14.24.

Methyl 2,4-dimethyl quinoline-3-carboxylate (3b)



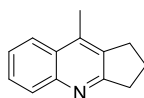
Yellow oil, yield 83 %; ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.71 (t, J = 7.0 Hz, 1H), 7.53 (s, 1H), 4.00 (s, 3H), 2.70 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.68, 154.36, 147.12, 141.69, 130.14, 129.26, 127.71, 126.35, 125.71, 124.02, 52.51, 23.83, 15.82.

1-(2,4-Dimethylquinolin-3-yl)ethanone (3c)



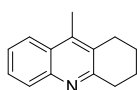
Yellow oil, yield 91 %; ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 2.64 (s, 3H), 2.58 (d, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 206.66, 152.61, 146.89, 138.68, 135.73, 129.87, 129.23, 126.43, 125.98, 123.68, 32.68, 23.54, 15.27.

9-Methyl-2,3-dihydro-1H-cyclopenta[b]quinolone (3d)



White solid, yield 45 %, m.p. 56-60°C; ^1H NMR (500 MHz, CDCl_3) δ 8.01 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 3.16 (t, J = 7.5 Hz, 2H), 3.04 (t, J = 7.2 Hz, 2H), 2.57 (s, 3H), 2.23 – 2.13 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.94, 147.38, 138.13, 134.02, 129.11, 128.00, 127.05, 125.25, 123.34, 35.10, 29.64, 22.98, 14.89.

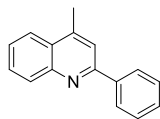
9-Methyl-1,2,3,4-tetrahydroacridine (3e)



White solid, yield 40 %, m.p. 73-77 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.01 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 3.15 (s, 2H), 2.91 (s, 2H), 2.57 (s, 3H), 1.94 (s, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.50, 145.67, 141.58, 130.93, 128.78, 128.24,

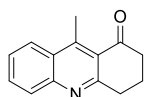
126.94, 125.34, 123.32, 34.36, 27.09, 23.19, 22.73, 13.58.

4-Methyl-2-phenylquinoline (3f)



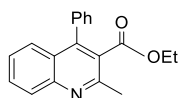
Yellow oil, yield 49%; ^1H NMR (500 MHz, CDCl_3) δ 8.24 (d, $J = 7.6$ Hz, 1H), 8.15 (d, $J = 7.4$ Hz, 2H), 8.01 (d, $J = 8.3$ Hz, 1H), 7.74 (d, $J = 11.7$ Hz, 2H), 7.59 – 7.44 (m, 4H), 2.79 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.02, 147.79, 145.27, 139.49, 130.03, 129.54, 129.36, 128.83, 127.66, 127.27, 126.18, 123.65, 119.89, 19.10.

9-Methyl -3,4-dihydroacridin-1(2H)-one (3g)



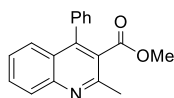
White solid, yield 74%, m.p. 62-65 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.21 (d, $J = 8.5$ Hz, 1H), 8.02 (d, $J = 8.3$ Hz, 1H), 7.78 (t, $J = 7.5$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 3.28 (t, $J = 5.9$ Hz, 2H), 3.05 (s, 3H), 2.81 (t, $J = 6.4$ Hz, 2H), 2.26 – 2.18 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 199.96, 161.54, 149.46, 147.24, 130.99, 128.54, 127.13, 125.83, 124.92, 124.81, 40.54, 34.17, 20.79, 15.51.

Ethyl-2-methyl-4-phenylquinoline-3-carboxylate (3h)



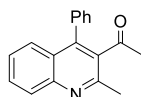
White solid, yield 90%, m.p. 98-100 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.10 (d, $J = 8.4$ Hz, 1H), 7.73 (t, $J = 7.5$ Hz, 1H), 7.59 (d, $J = 8.3$ Hz, 1H), 7.48 (s, 3H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.37 (s, 2H), 4.07 (q, $J = 7.0$ Hz, 2H), 2.80 (s, 3H), 0.95 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.45, 154.73, 147.67, 146.32, 135.75, 130.29, 129.39, 128.84, 128.47, 128.24, 127.44, 126.52, 126.44, 125.17, 61.35, 23.81, 13.65.

Methyl-2-methyl-4-phenylquinoline-3-carboxylate (3i)



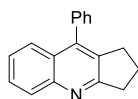
White solid, yield 90%, m.p. 99-100 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, $J = 8.4$ Hz, 1H), 7.73 (t, $J = 7.6$ Hz, 1H), 7.60 (d, $J = 8.3$ Hz, 1H), 7.49 (d, $J = 5.3$ Hz, 3H), 7.44 (t, $J = 7.7$ Hz, 1H), 7.36 (d, $J = 6.4$ Hz, 2H), 3.58 (s, 3H), 2.79 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.01, 154.55, 147.75, 146.43, 135.68, 130.35, 129.25, 128.87, 128.52, 128.29, 127.29, 126.55, 126.48, 125.09, 52.18, 23.83.

1-(2-Methyl-4-phenylquinolin-3-yl)ethanone (3j):



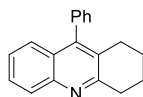
White solid, yield 94%, m.p. 114-116 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, $J = 8.3$ Hz, 1H), 7.73 (t, $J = 7.5$ Hz, 1H), 7.63 (d, $J = 8.3$ Hz, 1H), 7.52 (s, 3H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.37 (s, 2H), 2.71 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 205.72, 153.56, 147.52, 143.97, 135.21, 134.84, 130.14, 130.05, 128.93, 128.87, 128.73, 126.55, 126.18, 125.05, 31.96, 23.90.

9-Phenyl-2,3-dihydro-1H-cyclopenta[b]quinolone (3k)



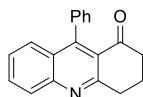
White solid, yield 48 %, 138-141 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.0 Hz, 2H), 7.48 (d, J = 7.1 Hz, 1H), 7.38 (t, J = 10.0 Hz, 3H), 3.26 (t, J = 7.4 Hz, 2H), 2.91 (t, J = 7.1 Hz, 2H), 2.21 – 2.14 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.42, 147.93, 142.74, 136.76, 133.67, 129.30, 128.81, 128.52, 128.25, 128.00, 126.23, 125.66, 125.51, 35.22, 30.35, 23.54.

9-Phenyl-1, 2, 3, 4-tetrahydroacridine (3l)



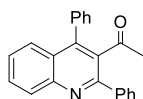
White solid, yield 42 %, 139-142 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.03 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 2.9 Hz, 1H), 7.52 (t, J = 7.1 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.32 (s, 2H), 7.23 (d, J = 7.0 Hz, 2H), 3.21 (t, J = 6.3 Hz, 2H), 2.61 (t, J = 6.2 Hz, 2H), 2.00 – 1.92 (m, 2H), 1.80 (d, J = 4.8 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.09, 146.55, 146.29, 137.16, 129.13, 128.62, 128.40, 128.38, 128.37, 127.75, 126.69, 125.81, 125.40, 34.27, 28.07, 23.04, 22.93.

9-Phenyl-3,4-dihydroacridin-1(2H)-one (3m)



White solid, yield 94 %, 154-156 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.08 (d, J = 8.4 Hz, 1H), 7.77 (t, J = 7.5 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.41 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 6.6 Hz, 2H), 3.39 (t, J = 5.9 Hz, 2H), 2.71 (t, J = 6.3 Hz, 2H), 2.30 – 2.22 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 197.35, 161.76, 150.88, 148.15, 137.17, 131.24, 128.02, 127.72, 127.61, 127.06, 126.99, 125.95, 123.37, 40.15, 34.13, 20.90.

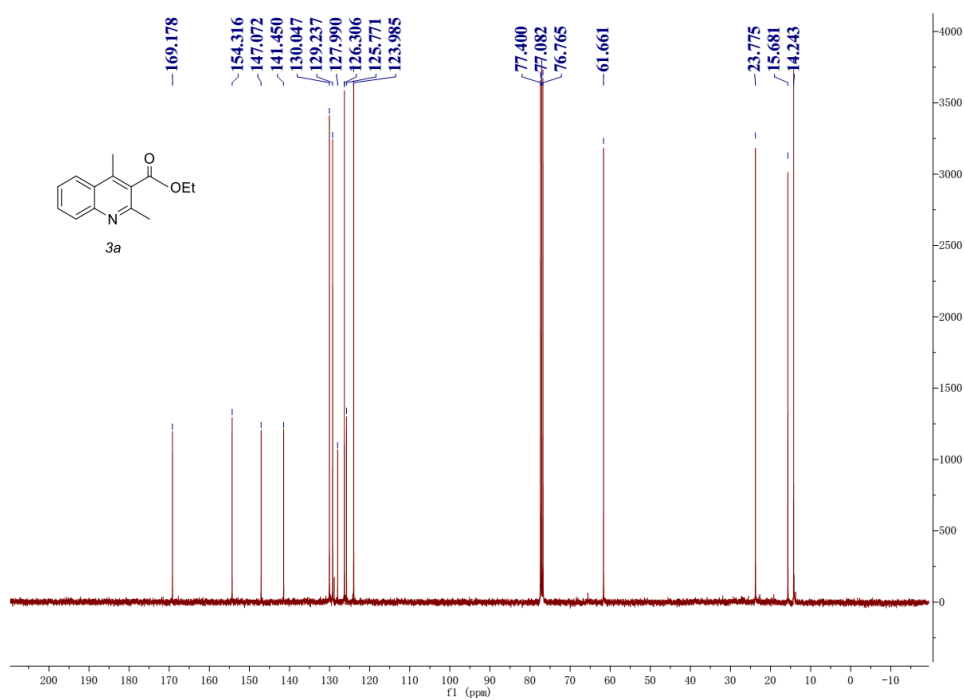
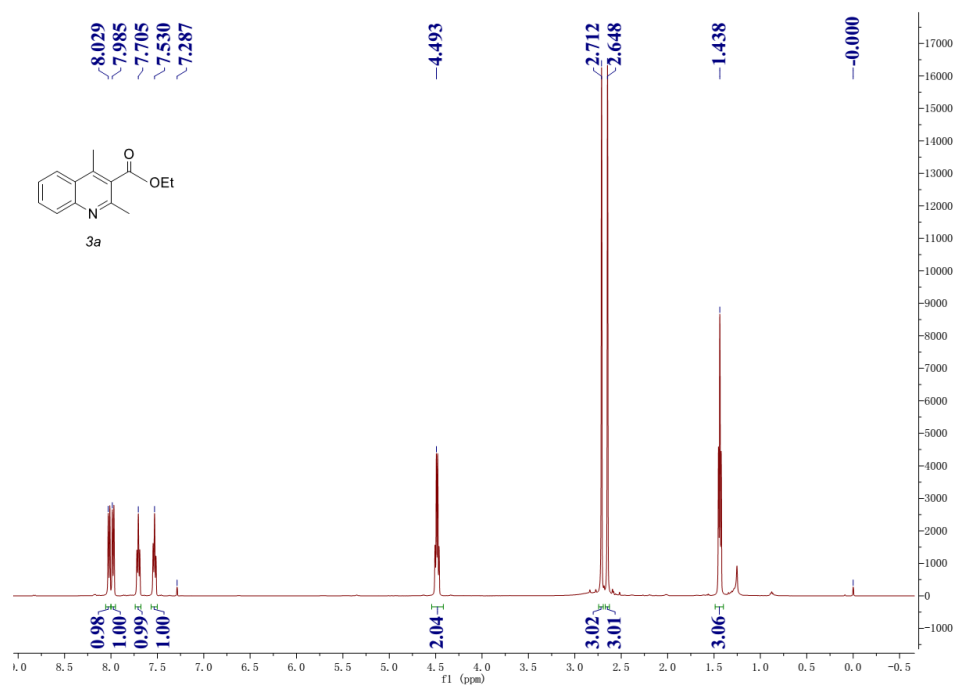
1-(2,4-Diphenyl quinolin-3-yl)ethanone (3n)



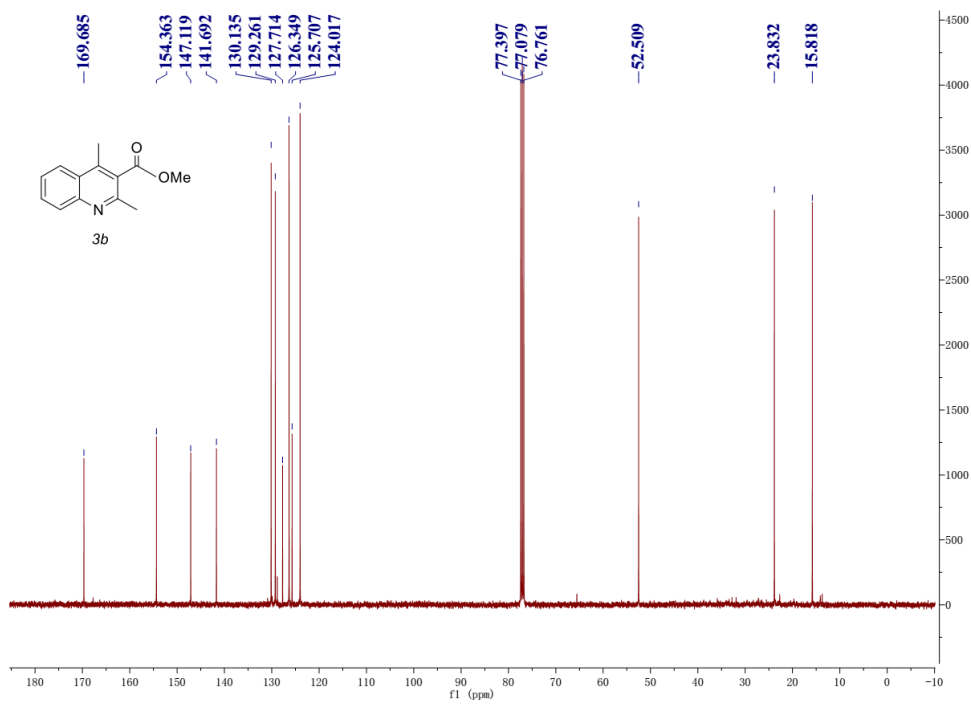
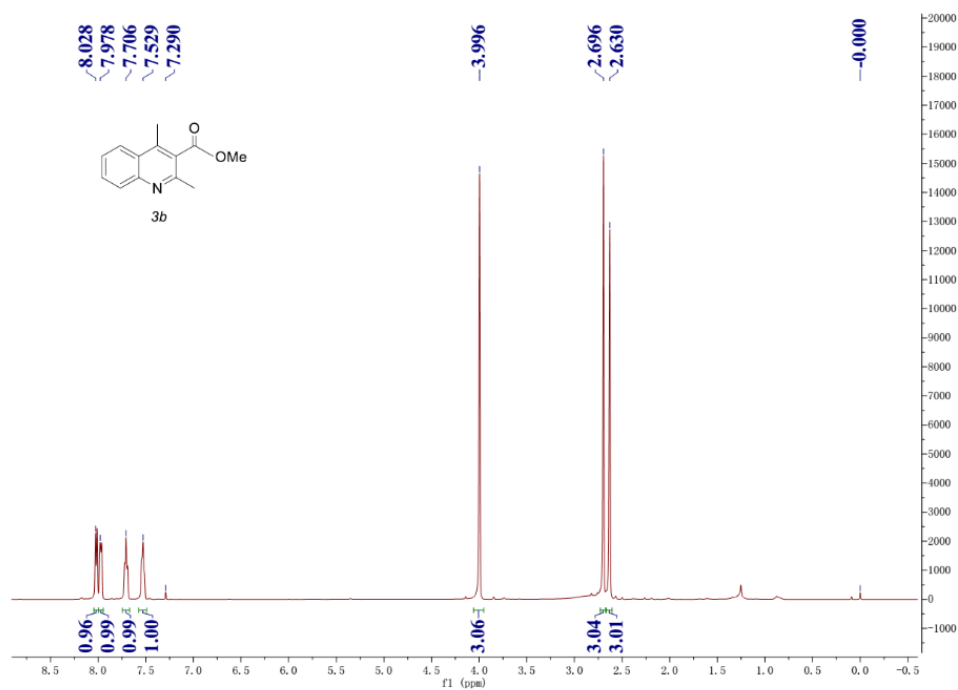
White solid, yield 80 %, 136-138 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.15 (d, J = 8.4 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 7.60 (d, J = 7.6 Hz, 3H), 7.46 (t, J = 7.5 Hz, 2H), 7.33 – 7.15 (m, 7H), 2.64 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 197.24, 154.17, 147.26, 145.20, 136.70, 134.33, 133.07, 132.01, 129.68, 129.54, 128.77, 128.36, 127.99, 127.83, 127.56, 126.08, 125.78, 124.82, 23.52.

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

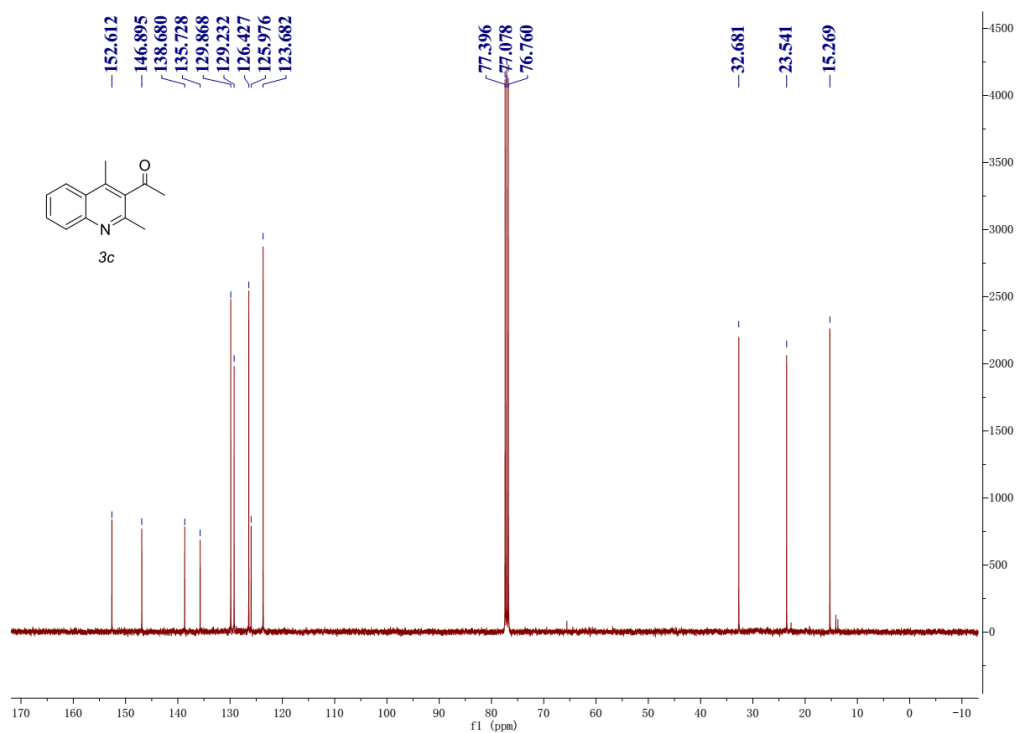
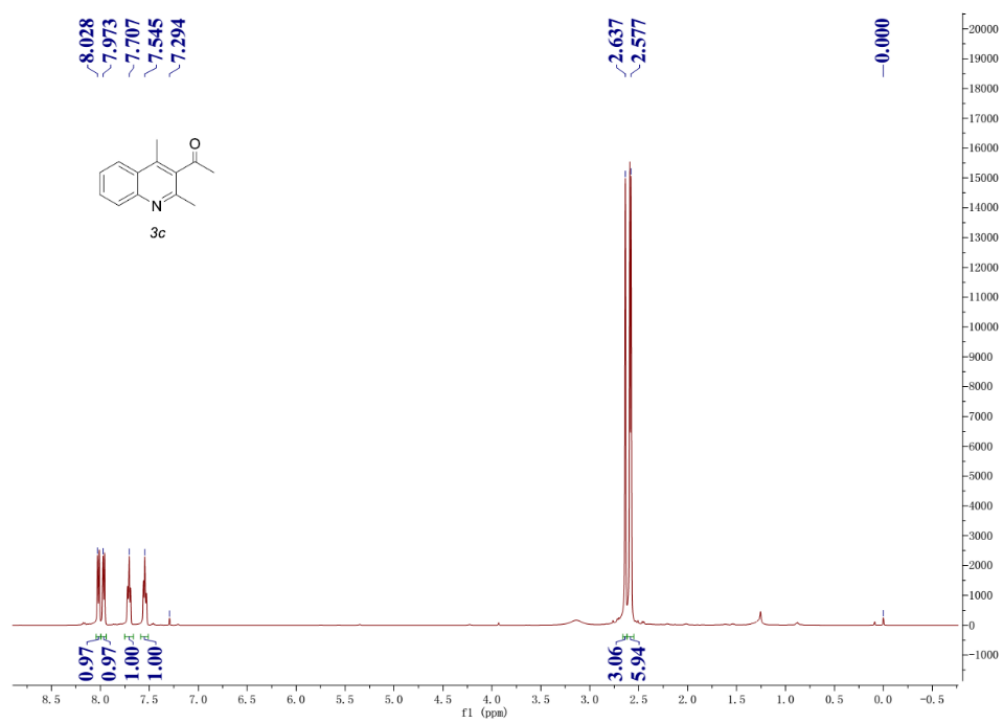
Ethyl-2,4-dimethylquinoline-3-carboxylate (3a)



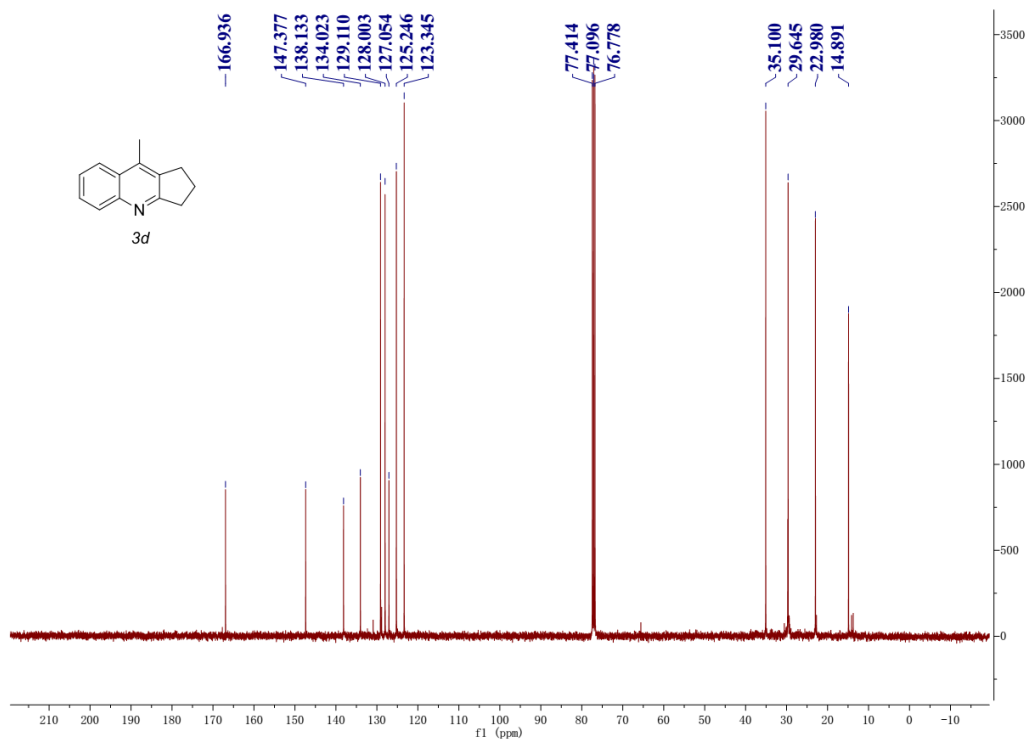
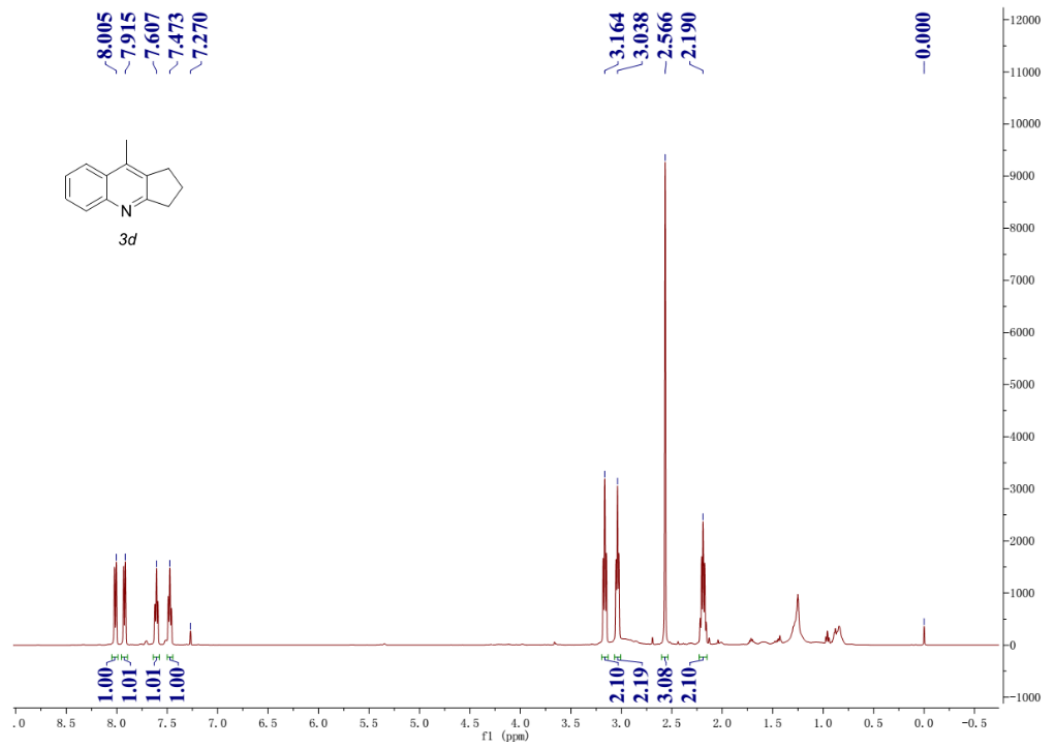
Methyl 2,4-dimethyl quinoline-3-carboxylate (3b)



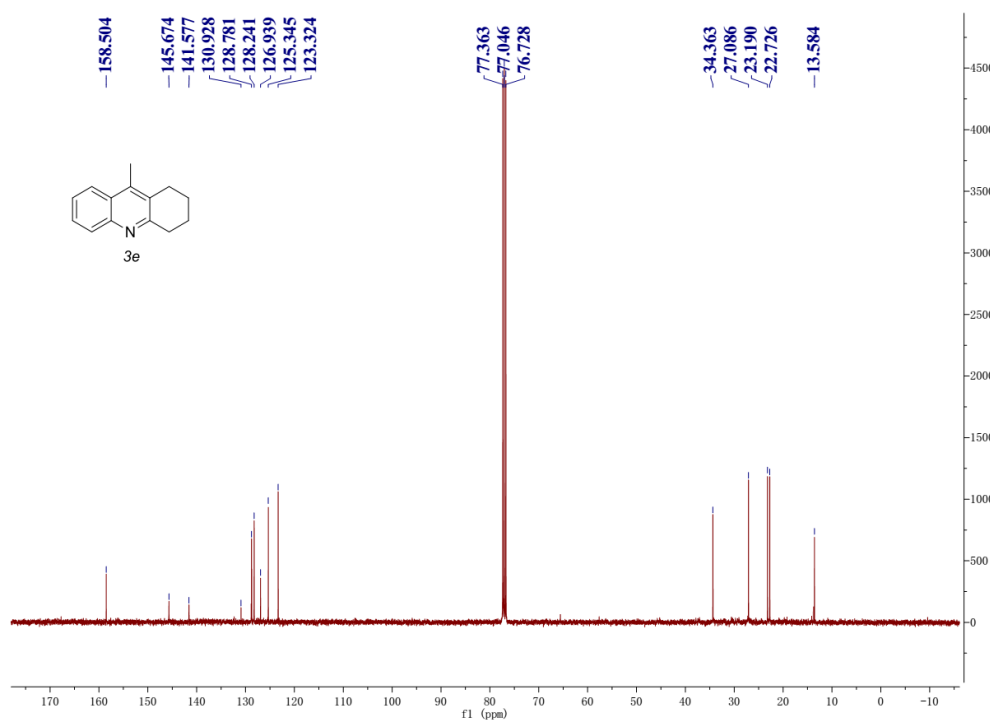
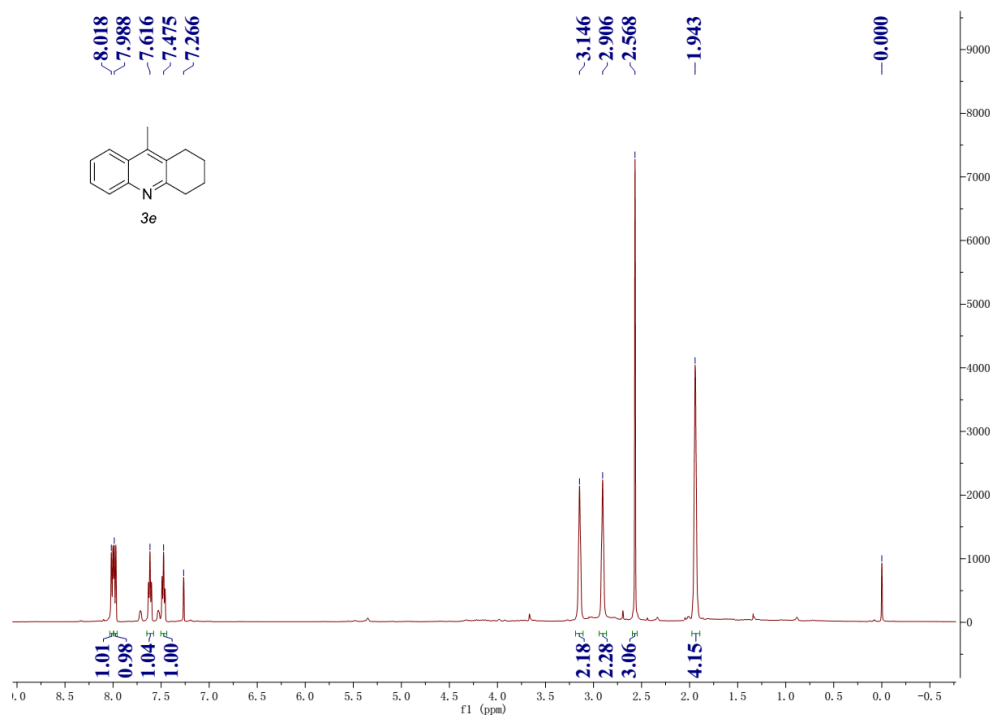
1-(2,4-Dimethylquinolin-3-yl)ethanone (3c)



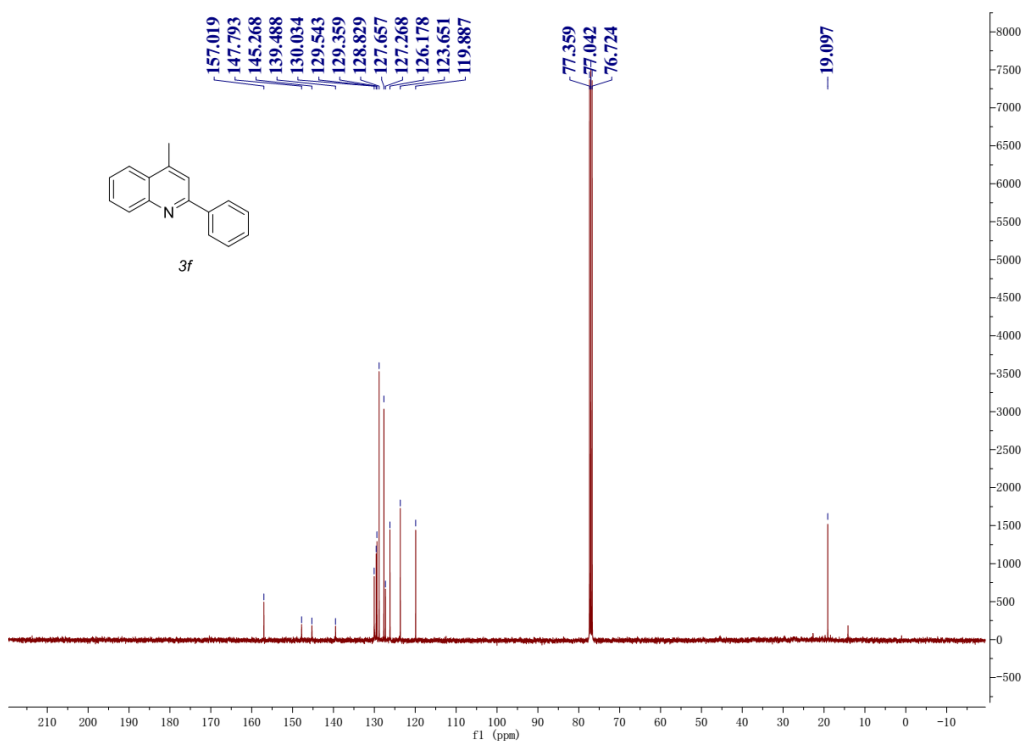
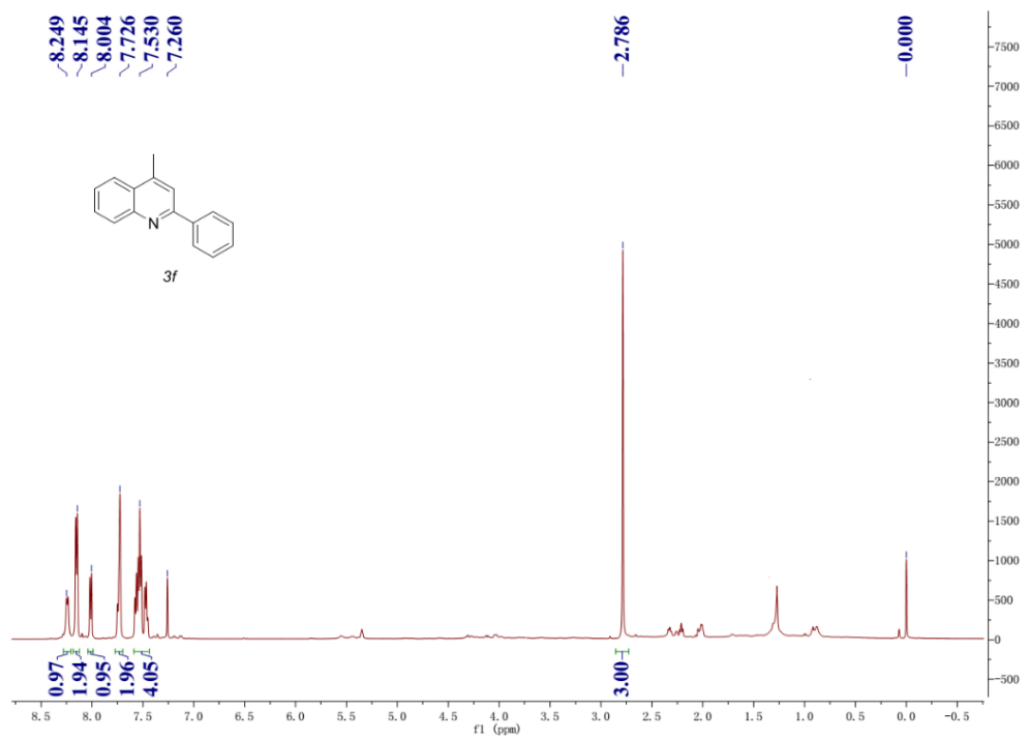
9-Methyl-2,3-dihydro-1H-cyclopenta[b]quinolone (3d)



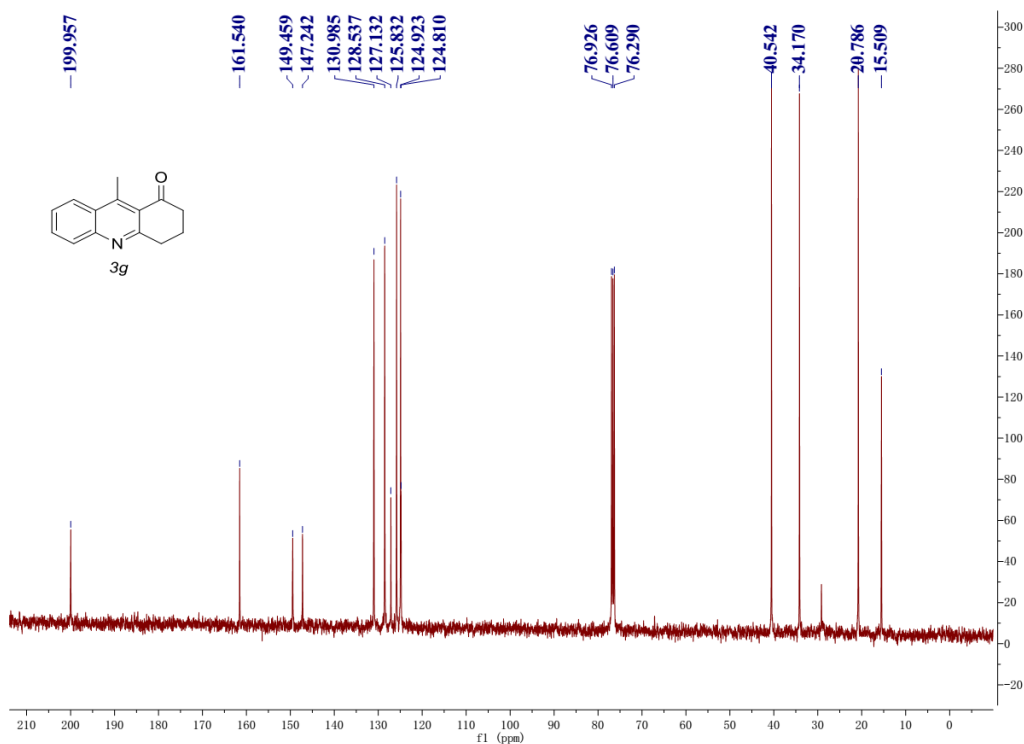
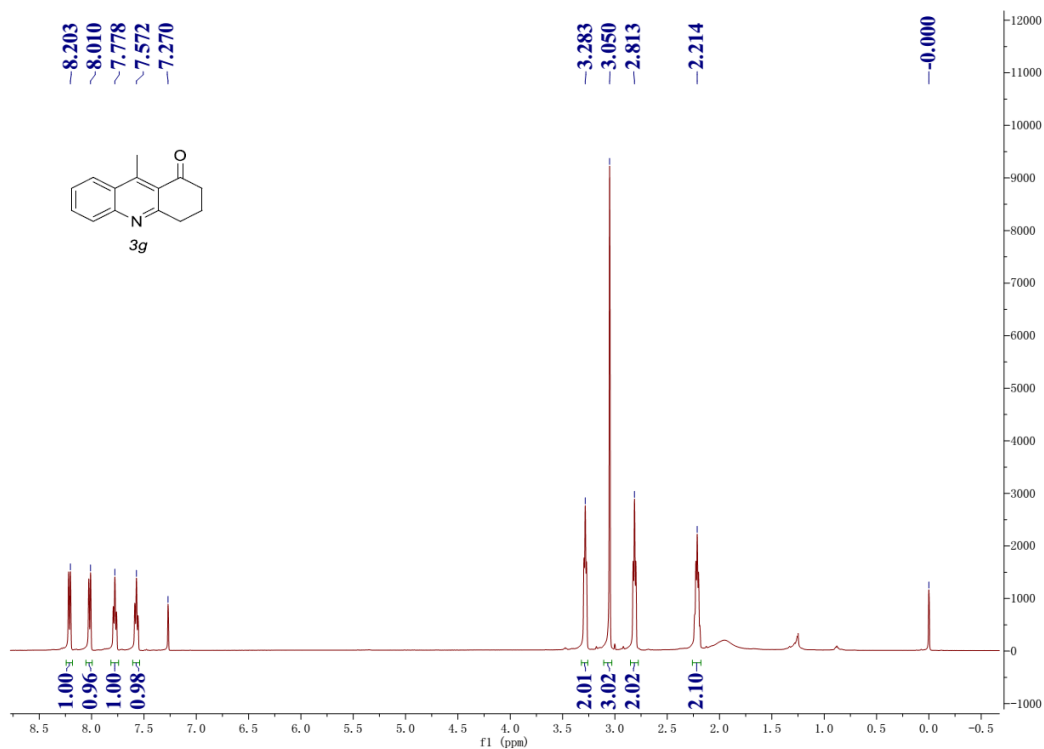
9-Methyl-1,2,3,4-tetrahydroacridine (3e)



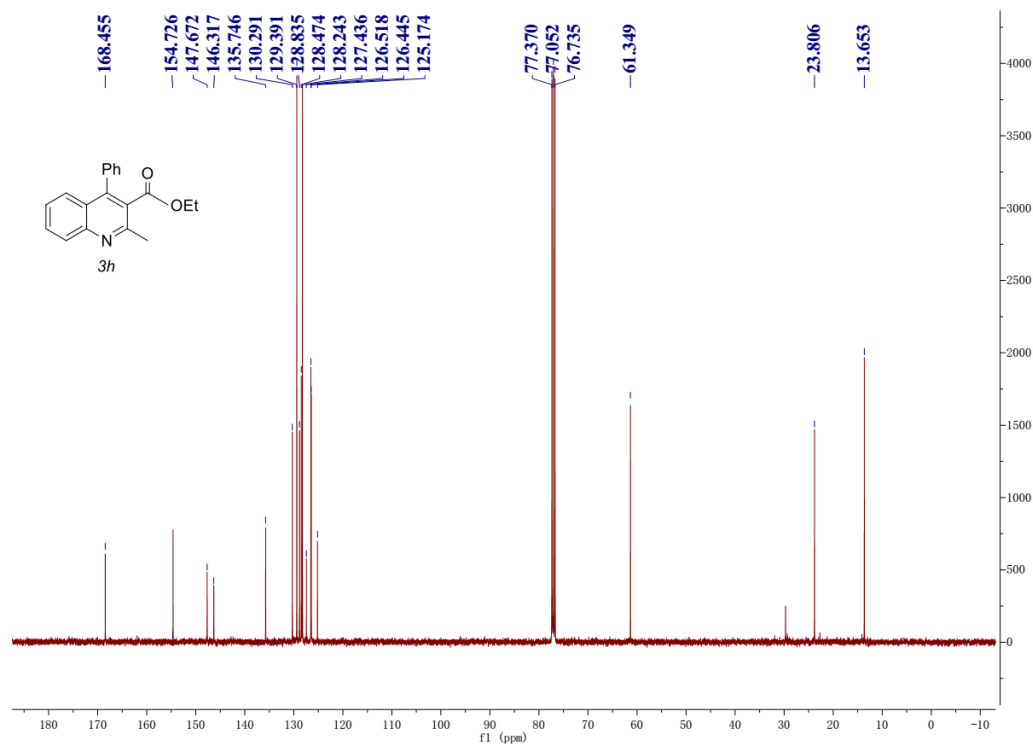
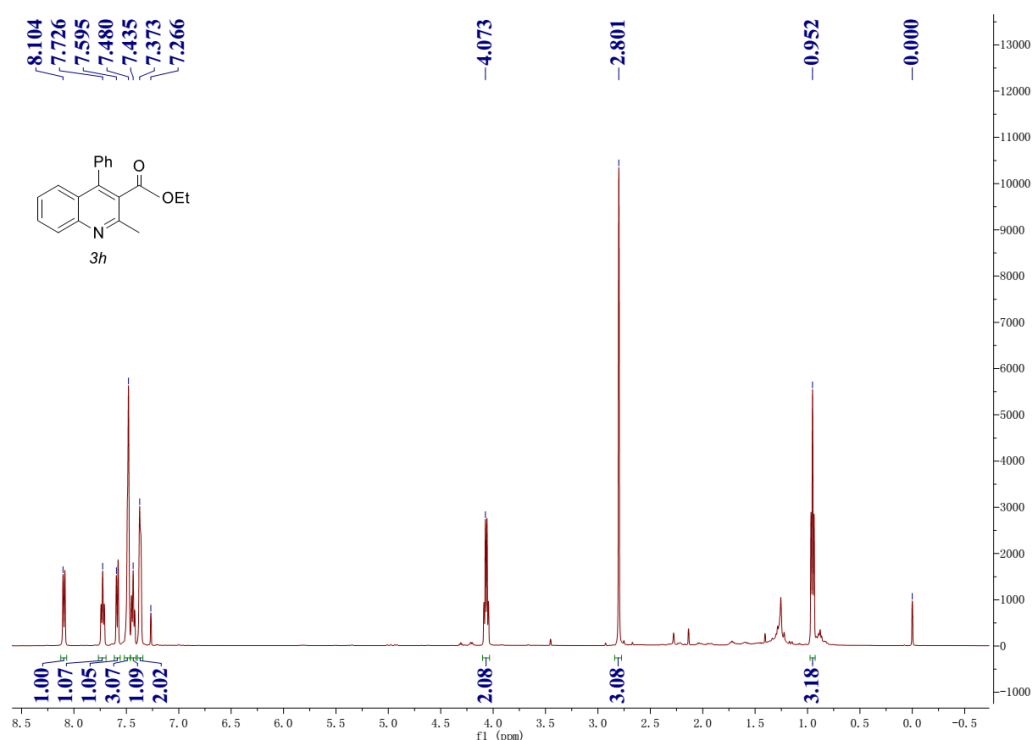
4-Methyl-2-phenylquinoline (3f)



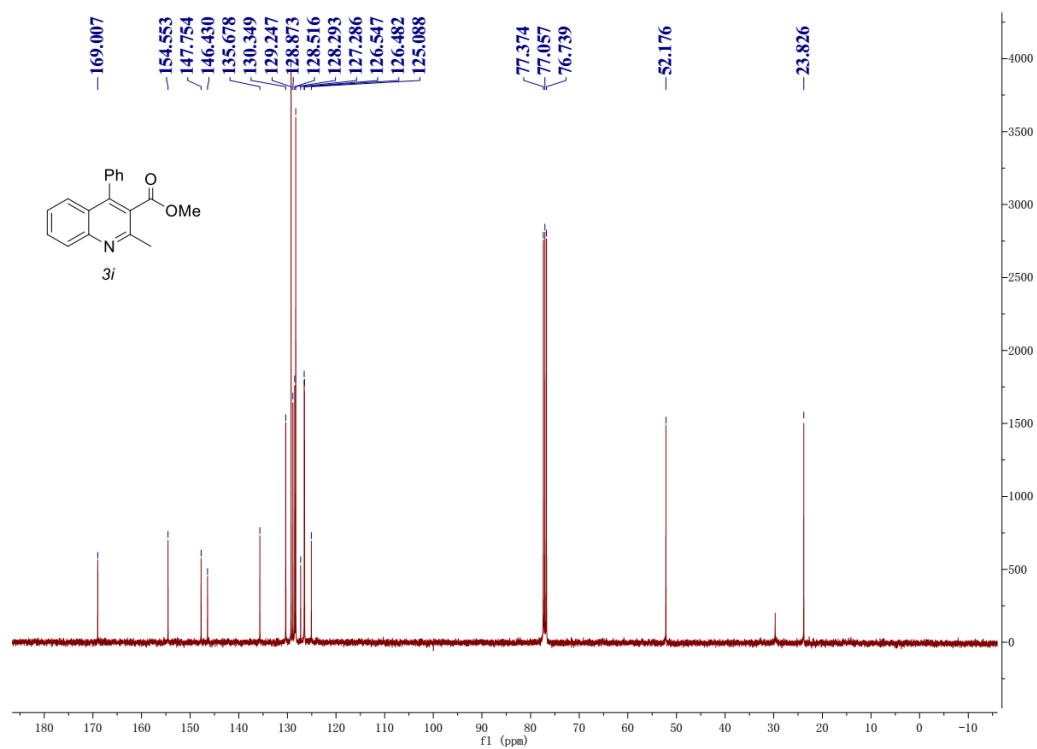
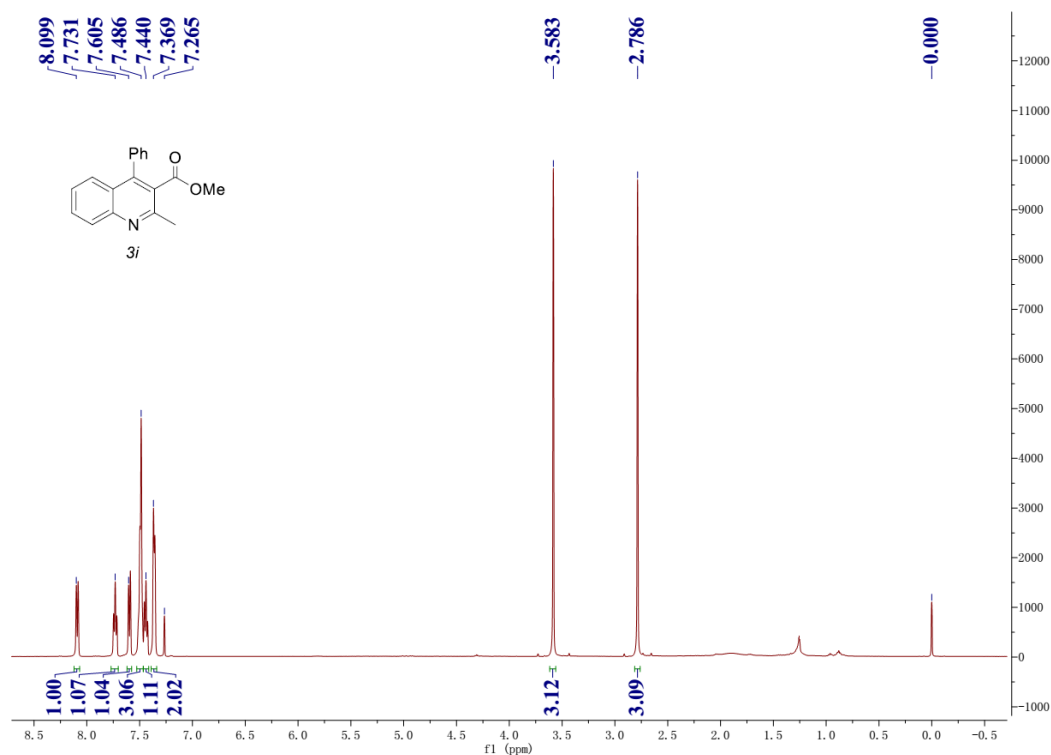
9-Methyl -3,4-dihydroacridin-1(2H)-one (3g)



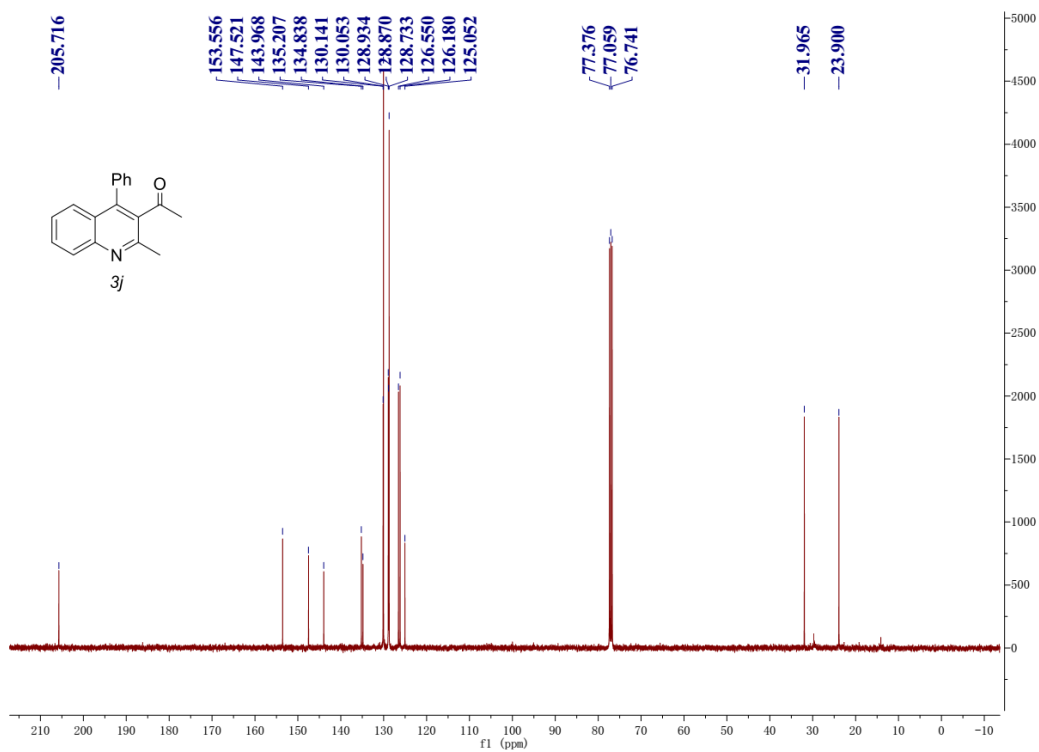
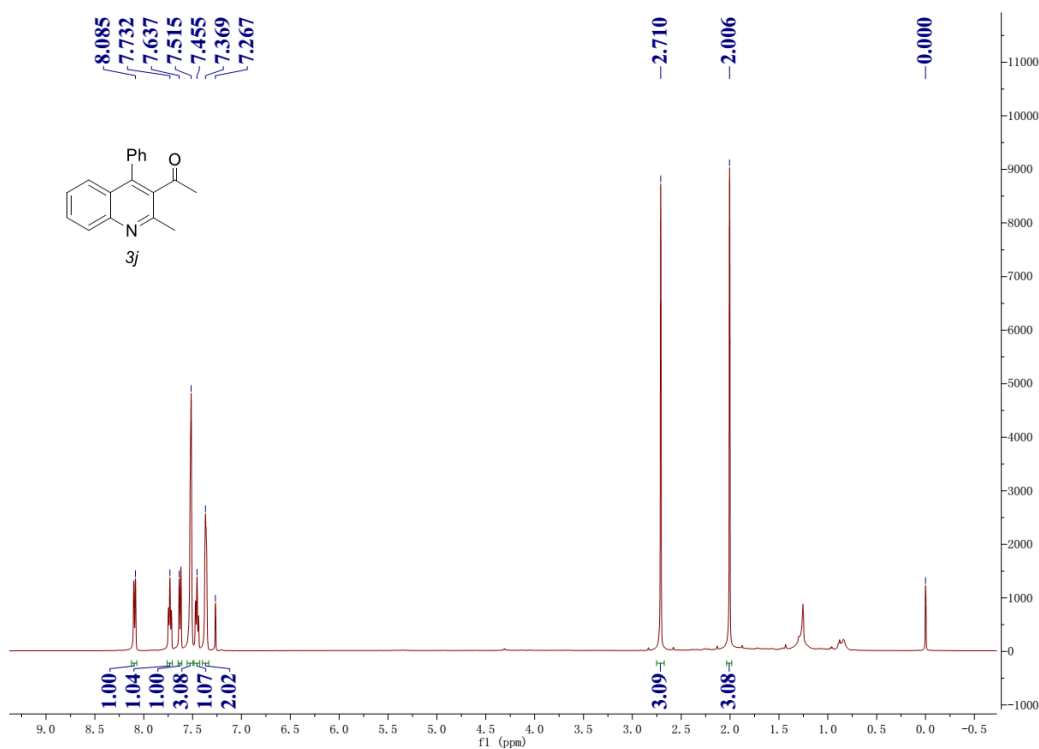
Ethyl-2-methyl-4-phenylquinoline-3-carboxylate (3h)



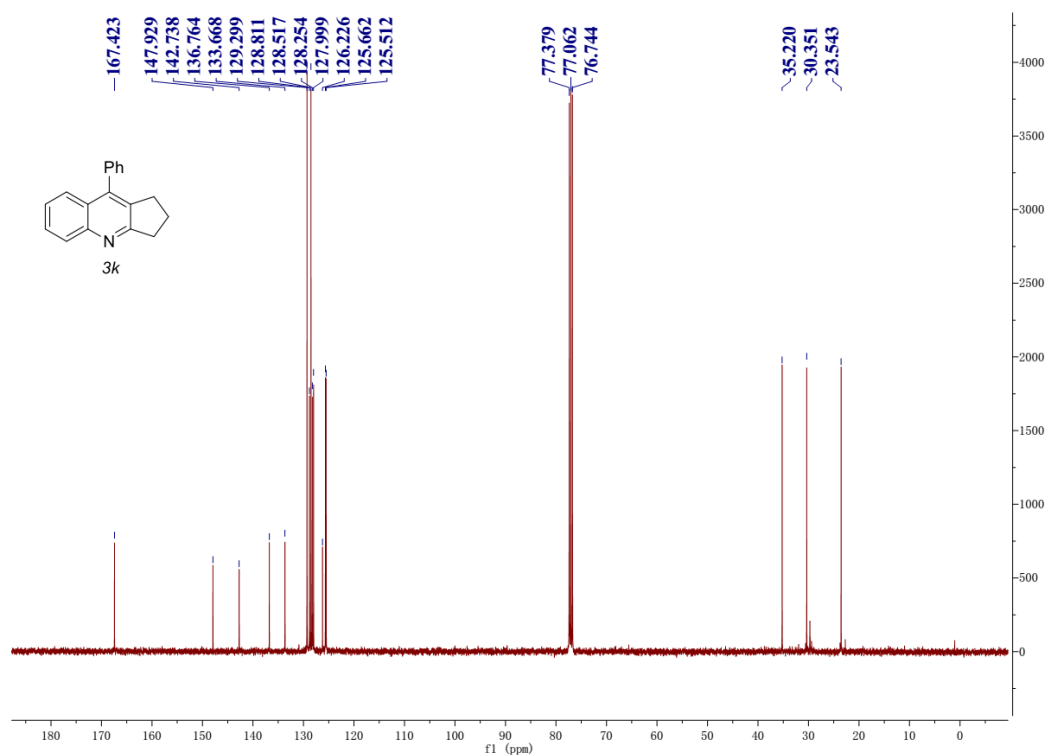
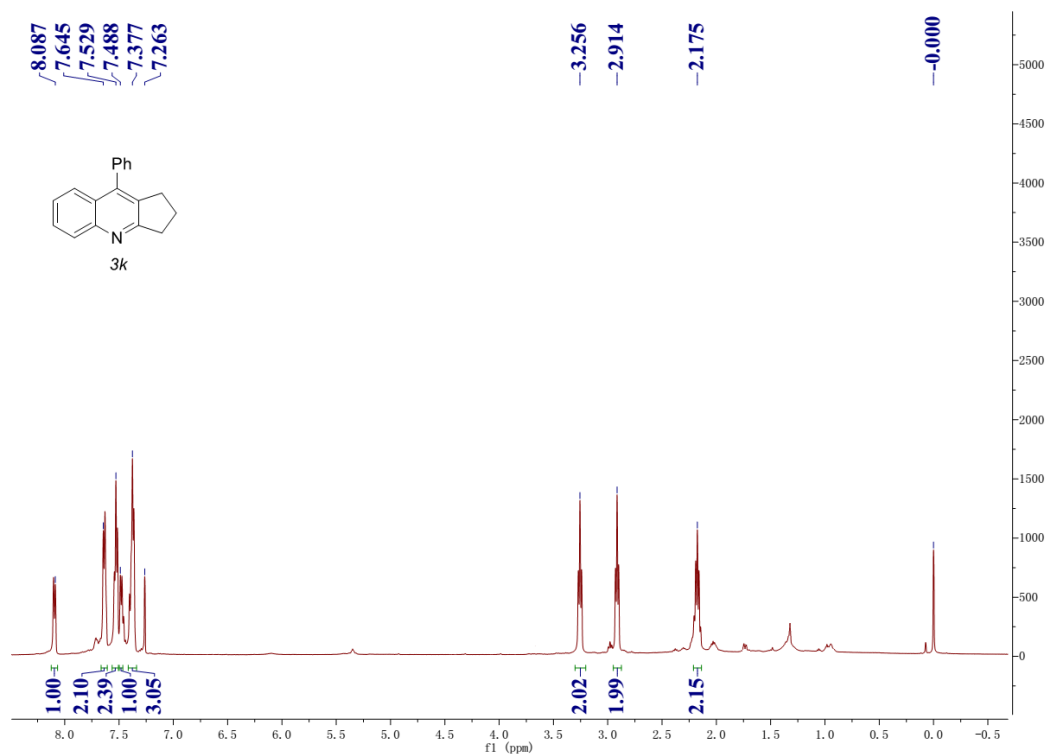
Methyl-2-methyl-4-phenylquinoline-3-carboxylate (3i)



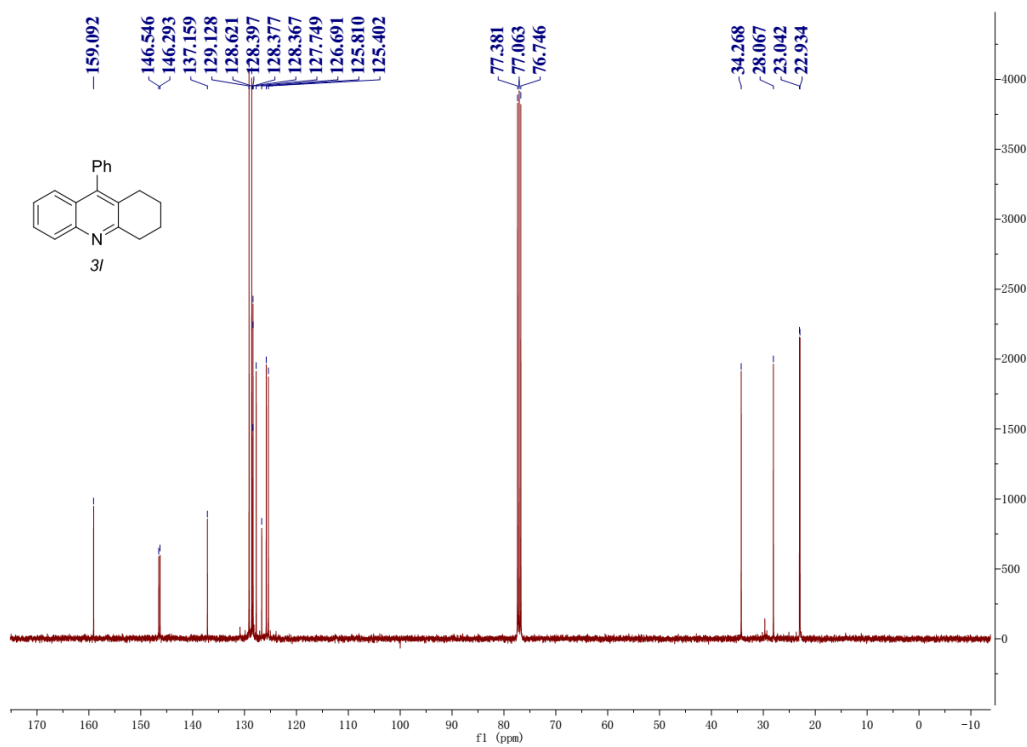
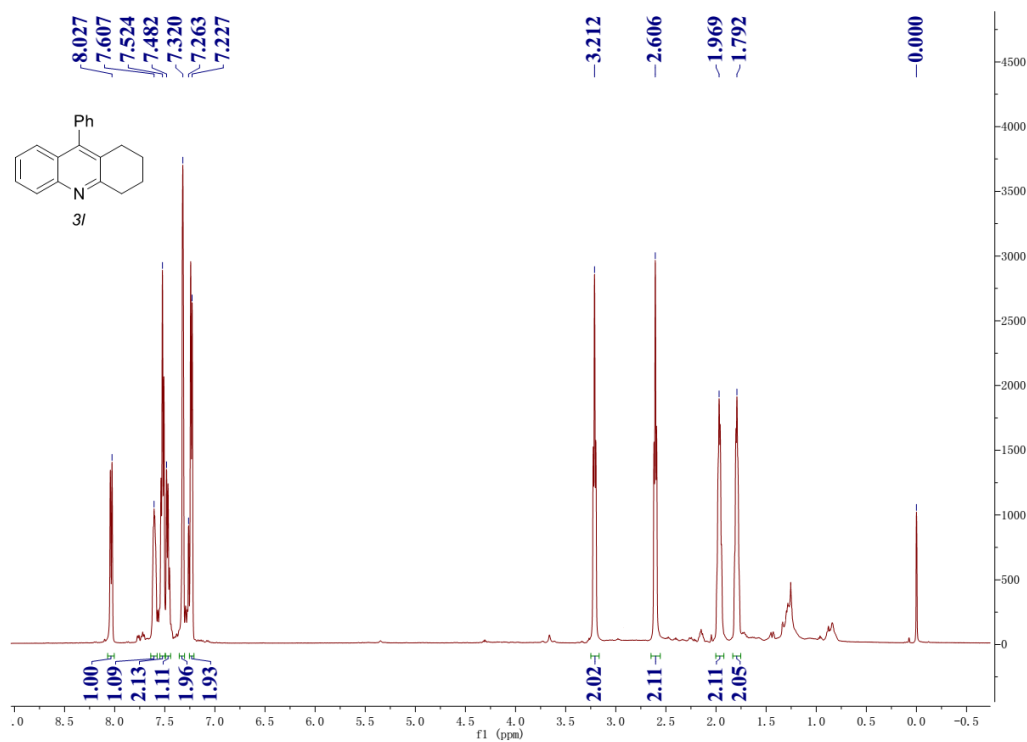
1-(2-Methyl-4-phenylquinolin-3-yl)ethanone (3j)



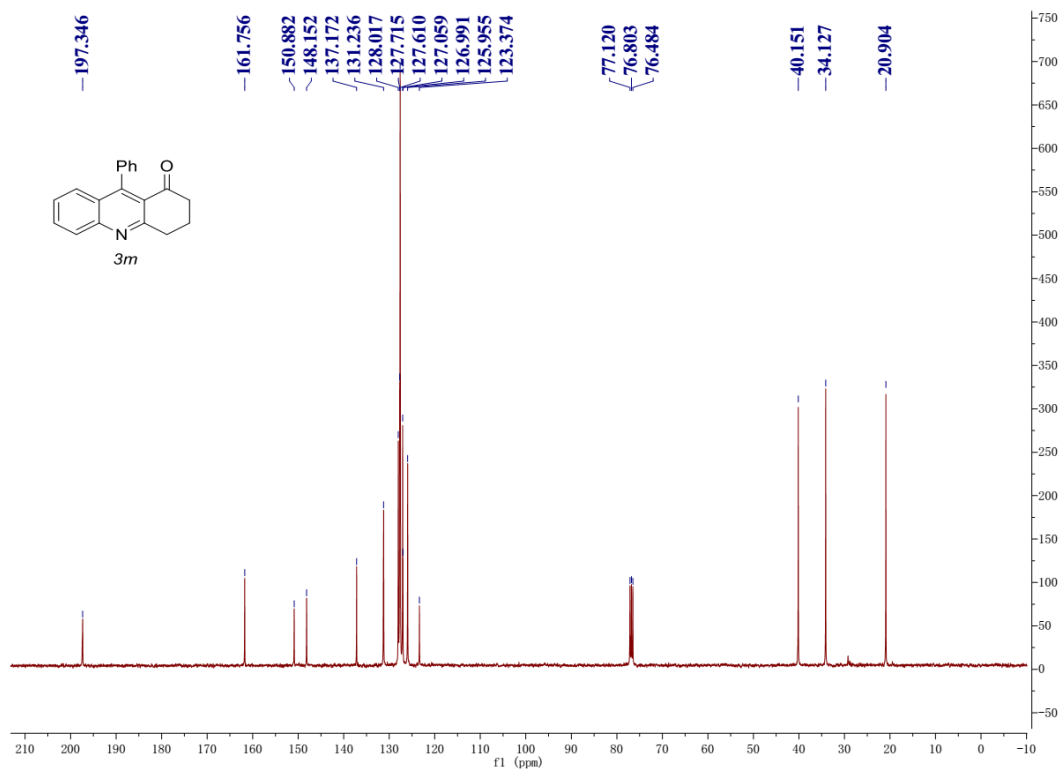
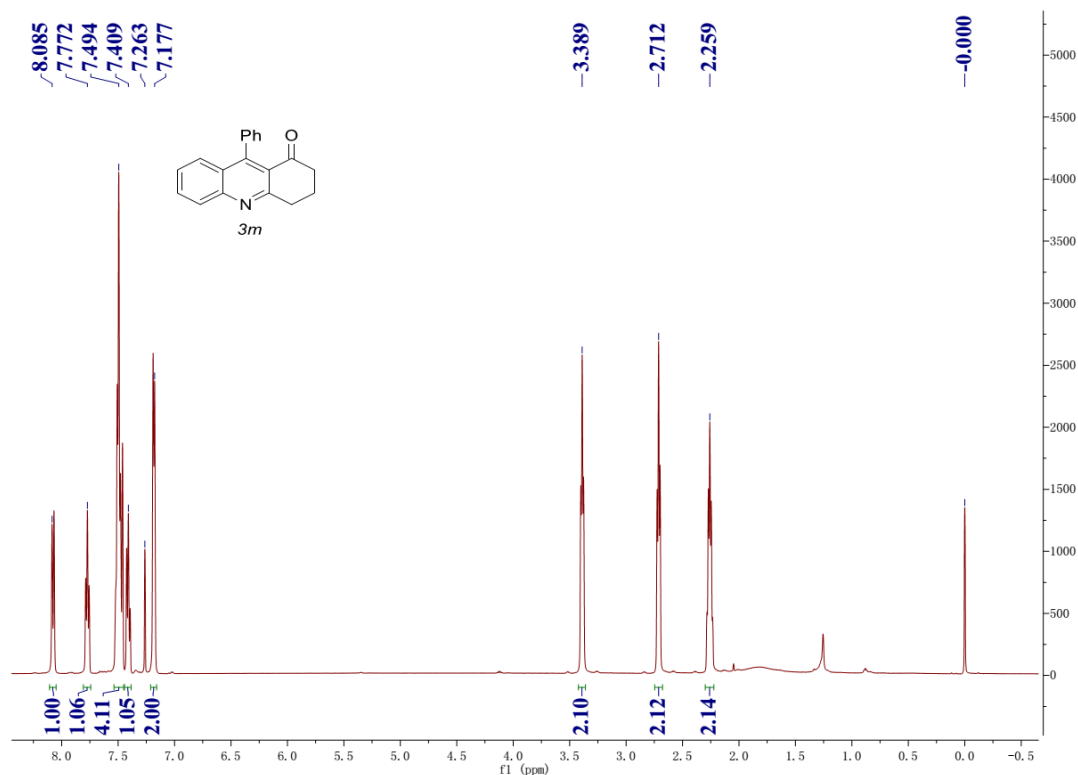
9-Phenyl-2,3-dihydro-1H-cyclopenta[b]quinolone (3k)



9-Phenyl-1, 2, 3, 4-tetrahydroacridine (3I)



9-Phenyl-3,4-dihydroacridin-1(2H)-one (3m)



1-(2,4-Diphenyl quinolin-3-yl)ethanone (3n)

