Supporting Information

Brønsted Acid-Catalyzed Metal- and Solvent-Free Quinoline Synthesis from *N*-alkyl Anilines and Alkynes or Alkenes

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[†] *These authors contributed equally to this work.*

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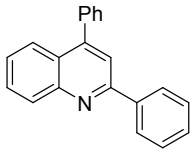
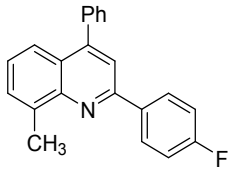
1. Analytical Data for Products

2,4-Diphenylquinoline (3a)[1]



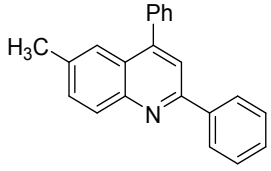
The title compound was obtained as pale yellow oil (46.7 mg, 83% yield from alkyne; 43.9 mg, 78% yield from olefin); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.3 Hz, 1H), 7.82 (s, 1H), 7.75–7.71 (m, 1H), 7.57–7.46 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 149.1, 148.8, 139.6, 138.4, 130.1, 129.5, 129.5, 129.3, 128.8, 128.6, 128.4, 127.5, 126.3, 125.7, 125.6, 119.3.

2-(4-Fluorophenyl)-8-methyl-4-phenylquinoline (3b)



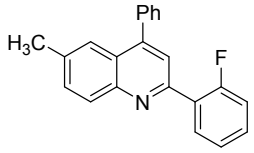
The title compound was obtained as pale yellow solid (52.6 mg, 84% yield from alkyne; 48.9 mg, 78% yield from olefin), m.p. 107.0–108.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28–8.25 (m, 2H), 7.77 (s, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 6.9 Hz, 1H), 7.53–7.48 (m, 4H), 7.34 (dd, J = 8.4, 6.9 Hz, 1H), 7.23–7.16 (m, 2H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8 (d, $^1J_{C\text{-}F}$ = 249.0 Hz), 153.8, 149.4, 147.6, 138.8, 137.8, 136.0 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 129.7, 129.6, 129.2 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 128.5, 128.3, 126.0, 125.6, 123.6, 118.2, 115.6 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 18.4; HRMS (ESI, *m/z*) calcd for $C_{22}H_{17}FN^+$: 314.1340 $[M+H]^+$; found: 314.1345; IR (neat): 3056, 2971, 2915, 2848, 1578, 1561, 1459, 1348, 1176, 831, 791, 682 cm^{-1}

6-Methyl-2,4-diphenylquinoline (3c)[2]



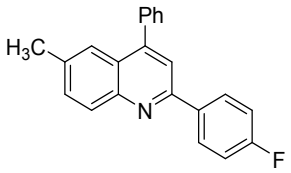
The title compound was obtained as pale yellow solid (47.8 mg, 81% yield from alkyne; 44.3 mg, 75% yield from olefin), m. p. 128.1–129.0 °C (lit. 129.0–130.0 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17–8.12 (m, 3H), 7.75 (s, 1H), 7.63 (s, 1H), 7.53–7.39 (m, 9H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 148.4, 147.3, 139.7, 138.6, 136.2, 131.7, 129.8, 129.5, 129.1, 128.7, 128.5, 128.2, 127.4, 125.7, 124.3, 119.4, 21.8.

2-(2-Fluorophenyl)-6-methyl-4-phenylquinoline (3d)



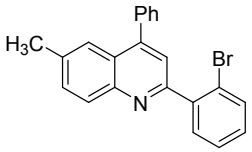
The title compound was obtained as pale yellow solid (52.0 mg, 83% yield from alkyne; 49.5 mg, 79% yield from olefin), m.p. 113.0–113.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.02 (m, 2H), 7.71 (d, J = 4.0 Hz, 1H), 7.61 (s, 1H), 7.52–7.45 (m, 6H), 7.25 (t, J = 7.6 Hz, 1H), 7.18 (s, 1H), 7.11 (dd, J = 8.0, 4.0 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.8 (d, $^1J_{C\text{-}F}$ = 248.0), 155.9, 147.3 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 139.6, 136.4, 134.5 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 131.8, 131.2 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 129.9, 129.2, 128.8, 127.4, 125.6, 124.1, 119.3, 115.6 ($^2J_{C\text{-}F}$ = 21.5 Hz), 21.8; HRMS (ESI, *m/z*) calcd for $C_{22}H_{17}FN^+$: 314.1340 $[M+H]^+$; found: 314.1338; IR (neat): 3042, 2951, 2927, 2859, 1589, 1541, 1495, 1349, 1169, 828, 786, 699 cm^{-1}

2-(4-Fluorophenyl)-6-methyl-4-phenylquinoline (3e)[3]



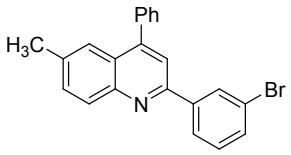
The title compound was obtained as pale yellow solid (55.2 mg, 88% yield from alkyne; 50.8 mg, 81% yield from olefin), m.p. 109.8–111.0 °C (lit. 111.0 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17–8.12 (m, 3H), 7.73 (s, 1H), 7.58–7.44 (m, 7H), 7.23 (t, J = 8.6 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.6 (d, $^1J_{C\text{-}F}$ = 248.7 Hz), 154.7, 148.4, 147.2, 138.4, 136.2, 135.8, 135.7, 131.7, 129.7, 129.4, 129.2 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 128.5, 128.2, 125.5, 124.3, 118.8, 115.6 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 112.9, 21.7.

2-(2-Bromophenyl)-6-methyl-4-phenylquinoline (3f)



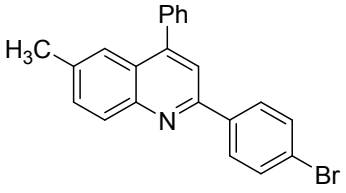
The title compound was obtained as pale yellow solid (60.6 mg, 81% yield from alkyne; 53.9 mg, 72% yield from olefin), m.p. 153.0–153.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.4 Hz, 1H), 7.72 (s, 1H), 7.66 (dd, J = 7.4, 4.2 Hz, 2H), 7.61 (s, 1H), 7.57–7.38 (m, 7H), 7.23 (d, J = 8.4 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 147.1, 147.0, 141.5, 138.1, 136.7, 133.1, 131.6, 131.5, 129.8, 129.7, 128.5, 128.2, 127.6, 125.5, 124.3, 122.9, 121.9, 21.8; HRMS (ESI, m/z) calcd for $C_{22}H_{17}BrN^+$: 374.0539 $[M+H]^+$; found: 374.0536; IR (neat): 3059, 2923, 2862, 1571, 1492, 1416, 910, 874, 823, 790, 762, 702, 616, 592 cm^{-1}

2-(3-Bromophenyl)-6-methyl-4-phenylquinoline (3g)[4]



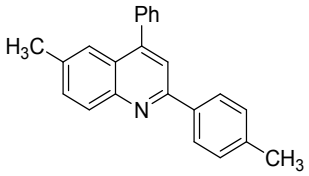
The title compound was obtained as pale yellow solid (59.9 mg, 80% yield from alkyne; 53.9 mg, 72% yield from olefin), m.p. 146.0–146.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (t, J = 2.0 Hz, 1H), 8.09 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 7.9 Hz, 1H), 7.67 (s, 1H), 7.62 (s, 1H), 7.53–7.48 (m, 7H), 7.30 (t, J = 7.9 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 148.5, 147.2, 141.6, 138.3, 136.5, 131.9, 131.8, 130.4, 130.1, 129.8, 129.4, 128.5, 128.3, 125.8, 125.7, 124.3, 123.0, 118.8, 21.7.

2-(4-Bromophenyl)-6-methyl-4-phenylquinoline (3h)[5]



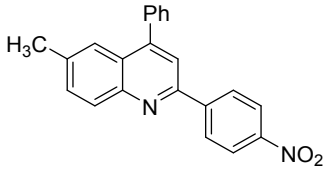
The title compound was obtained as pale yellow solid (59.9 mg, 80% yield from alkyne; 54.6 mg, 73% yield from olefin), m.p. 143.0–143.9 °C (lit. 142.1–144.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17–8.13 (m, 2H), 7.78 (s, 1H), 7.71 (d, J = 8.3 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 6.0 Hz, 1H), 7.53–7.50 (m, 5H), 7.37–7.33 (m 1H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 149.6, 147.6, 138.7, 138.6, 137.9, 131.9, 129.5, 129.0, 128.5, 128.3, 126.2, 125.7, 123.8, 123.6, 118.2, 18.4.

6-Methyl-4-phenyl-2-(*p*-tolyl)quinoline (3i)[5]



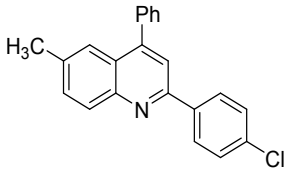
The title compound was obtained as pale yellow solid (51.4 mg, 83% yield from alkyne; 48.3 mg, 78% yield from olefin), m.p. 121.0–121.8 °C (lit. 119.6–121.2 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 8.6 Hz, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.71 (s, 1H), 7.60 (s, 1H), 7.50–7.43 (m, 6H), 7.25 (d, J = 8.2 Hz, 2H), 2.38 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 148.3, 147.3, 139.1, 138.6, 136.8, 135.9, 131.6, 129.6, 129.4, 129.4, 128.5, 128.1, 127.3, 125.5, 124.3, 119.2, 21.7, 21.2.

6-Methyl-2-(4-nitrophenyl)-4-phenylquinoline (3j)[1]



The title compound was obtained as pale yellow solid (61.3 mg, 90% yield from alkyne; 58.5 mg, 86% yield from olefin), m.p. 149.0–149.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36–8.31 (m, 4H), 8.13 (d, J = 8.6 Hz, 1H), 7.79 (s, 1H), 7.67 (s, 1H), 7.61–7.53 (m, 6H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 149.0, 148.1, 147.4, 145.5, 138.1, 137.4, 132.2, 130.0, 129.4, 128.7, 128.6, 128.1, 126.1, 124.4, 123.9, 119.1, 21.9; HRMS (ESI, m/z) calcd for $C_{22}H_{17}N_2O_2^+$: 341.1285 $[M+H]^+$; found: 341.1279; IR (neat) 3290, 2956, 2922, 2852, 1718, 1457, 1081, 723, 541 cm^{-1}

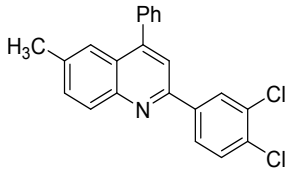
2-(4-Chlorophenyl)-6-methyl-4-phenylquinoline (3k)[2]



The title compound was obtained as white solid (54.1 mg, 82% yield from alkyne; 49.5 mg, 75% yield from olefin), m.p. 131.0–132.0 °C (lit. 129.0–131.0 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ

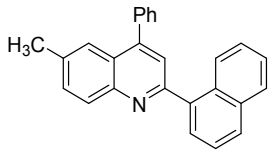
8.15–8.10 (m, 3H), 7.73 (s, 1H), 7.64 (s, 1H), 7.56–7.53 (m, 5H), 7.47 (d, J = 8.7 Hz, 2H), 7.26 (d, J = 8.7 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 148.7, 147.4, 138.5, 138.2, 136.5, 135.4, 132.0, 129.8, 129.5, 129.0, 128.7, 128.6, 128.4, 125.8, 124.4, 119.0, 21.9.

2-(2, 4-Dichlorophenyl)-6-methyl-4-phenylquinoline (3l)[5]



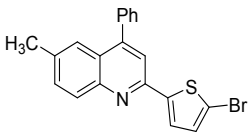
The title compound was obtained as white solid (67.0 mg, 92% yield from alkyne; 63.4 mg, 87% yield from olefin), m.p. 143.0–143.6 ^{o}C (lit. 141.8–143.1 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 8.5 Hz, 1H), 7.71–7.68 (m, 2H), 7.62 (s, 1H), 7.58–7.48 (m, 7H), 7.37 (dd, J = 8.5, 2.1 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.8, 147.5, 147.2, 138.1, 138.1, 137.0, 135.0, 133.1, 132.6, 131.8, 129.8, 129.7, 129.5, 128.5, 128.3, 127.4, 125.6, 124.4, 122.7, 21.8.

6-Methyl-2-(naphthalen-1-yl)-4-phenylquinoline (3m)[6]



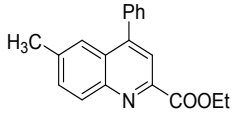
The title compound was obtained as brown solid (58.0 mg, 84% yield from alkyne; 49.1 mg, 71% yield from olefin), m.p. 159.1–160.3 ^{o}C (lit. 161.0–163.0 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23–8.18 (m, 2H), 7.91 (dd, J = 7.4, 6.1 Hz, 2H), 7.74 (d, J = 7.4 Hz, 2H), 6.62–6.46 (m, 10H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 147.9, 147.2, 138.7, 138.3, 136.6, 134.0, 131.8, 131.3, 129.8, 129.6, 129.0, 128.6, 128.3,128.3, 127.7, 126.5, 125.9, 125.8, 125.5, 125.3, 124.4, 123.4, 120.5, 21.8; HRMS (ESI, m/z) calcd for $C_{26}H_{20}N^+$ $[M+H]^+$ 346.1590; found: 346.1594; IR (neat) 3290, 2956, 2922, 2852, 1718, 1457, 1081, 723, 541 cm^{-1}

2-(5-Bromothiophen-2-yl)-6-methyl-4-phenylquinoline (3n)



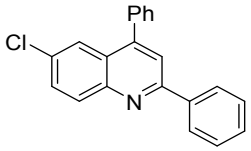
The title compound was obtained as brown solid (59.3 mg, 78% yield from alkyne; 47.9 mg, 63% yield from olefin), m.p. 181.1–182.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.6 Hz, 1H), 7.56–7.50 (m, 8H), 7.42 (d, J = 4.0 Hz, 1H), 7.06 (d, J = 4.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 148.9, 146.6, 138.0, 136.5, 132.2, 131.0, 129.4, 128.9, 128.6, 128.5, 125.8, 125.7, 124.5, 117.1, 116.0, 21.8; HRMS (ESI, m/z) calcd for $C_{20}H_{15}NBrS^+$: 380.0103 $[M+H]^+$; found: 380.0109; IR (neat) 3046, 2959, 2825, 1608, 1563, 1442, 1021, 850, 790, 732, 574 cm^{-1}

Ethyl 2-(6-methyl-4-phenylquinolin-2-yl)acetate (3o)[7]



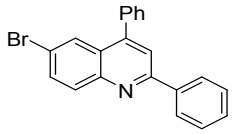
The title compound was obtained as brown solid (50.7 mg, 87% yield from alkyne; 51.9 mg, 89% yield from olefin), m.p. 115.4–116.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.7 Hz, 1H), 8.10 (s, 1H), 7.70 (s, 1H), 7.61 (dd, J = 8.7, 1.8 Hz, 1H), 7.56–7.51 (m, 5H), 4.56 (q, J = 7.1 Hz, 2H), 2.49 (s, 3H), 1.49 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 148.9, 146.8, 146.7, 138.9, 137.7, 132.3, 130.8, 129.5, 128.6, 128.5, 127.7, 124.3, 121.3, 62.1, 21.9, 14.3.

6-Chloro-2,4-diphenylquinolinem (3p)[6]



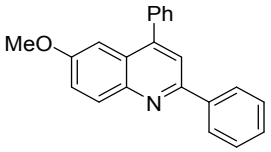
The title compound was obtained as light brown solid (53.7 mg, 85% yield from alkyne; 49.9 mg, 79% yield from olefin), m.p. 99–101 °C (lit. 98–99 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18–8.14 (m 3H), 7.85 (d, J = 2.3 Hz, 1H), 7.81 (s, 1H), 7.64 (dd, J = 9.0, 2.3 Hz, 1H), 7.55–7.44 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.0, 148.4, 147.2, 139.1, 137.7, 132.1, 131.7, 130.4, 129.5, 129.4, 128.8, 128.8, 128.7, 127.5, 126.4, 124.4, 120.0.

6-Bromo-2,4-diphenylquinoline (3q)[8]



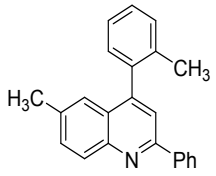
The title compound was obtained as pale yellow solid (58.4 mg, 81% yield from alkyne; 54.8 mg, 76% yield from olefin), m.p. 152.1–153.9 °C (lit. 151.9–153.3 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, J = 8.6 Hz, 1H), 8.08 (d, J = 8.9 Hz, 1H), 8.02 (d, J = 2.1 Hz, 1H), 7.81(s, 1H), 7.77 (dd, J = 9.1, 2.1 Hz, 1H), 7.56–7.44 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.1, 148.3, 147.4, 139.1, 137.7, 132.9, 131.8, 129.4, 128.8, 128.8, 128.7, 127.7, 127.5, 126.9, 120.4, 119.9.

6-Methoxy-2,4-diphenylquinoline (3r)[2]



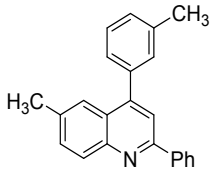
The title compound was obtained as yellow solid (52.3 mg, 84% yield from alkyne; 49.8 mg, 80% yield from olefin), m.p. 121–122 °C (lit. 119–120 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16–8.13 (m, 3H), 7.76 (s, 1H), 7.56–7.48 (m, 7H), 7.43–7.37 (m, 2H), 7.18 (d, J = 2.7 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 154.6, 147.7, 144.9, 139.7, 138.7, 131.6, 129.3, 128.7, 128.6, 128.3, 127.3, 126.6, 121.8, 119.6, 103.7.

6-Methyl-2-phenyl-4-(o-tolyl)quinoline (3s)[9]



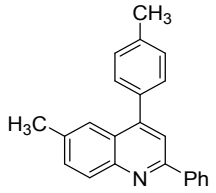
The title compound was obtained as brown solid (49.5 mg, 80% yield from alkyne; 48.3 mg, 78% yield from olefin), m.p. 122.1–123.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18–8.12 (m, 3H), 7.71 (s, 1H), 7.53–7.22 (m, 9H), 2.39 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 148.3, 147.1, 139.6, 138.0, 136.2, 136.0, 131.7, 130.1, 129.7, 129.6, 129.1, 128.7, 128.2, 127.4, 126.1, 125.7, 124.4, 119.3, 21.6, 20.0.

6-Methyl-2-phenyl-4-(m-tolyl)quinoline (3t)



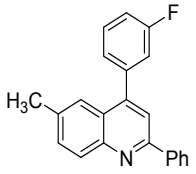
The title compound was obtained as brown solid (49.5 mg, 80% yield from alkyne; 48.9 mg, 79% yield from olefin), m.p. 127.0–127.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17–8.12 (m, 3H), 7.74 (s, 1H), 7.64 (s, 1H), 7.53–7.46 (m, 3H), 7.42–7.27 (m, 5H), 2.43 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 148.3, 147.0, 139.6, 138.0, 136.2, 136.0, 131.7, 130.1, 129.7, 129.5, 129.1, 128.7, 128.2, 127.4, 126.1, 125.7, 124.4, 119.3, 21.6, 20.0; HRMS (ESI, m/z) calcd for $C_{23}H_{20}N$: 310.1590 $[M+H]^+$; found: 310.1583; IR (neat): 3052, 3025, 2918, 2857, 1593, 1578, 1485, 1547, 1359, 919, 825, 773, 696 cm^{-1}

6-Methyl-2-phenyl-4-(p-tolyl)quinoline (3u)[9]



The title compound was obtained as brown solid (50.1 mg, 81% yield from alkyne; 49.5 mg, 80% yield from olefin); m.p. 123.8–124.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16–8.11 (m, 3H), 7.73 (s, 1H), 7.66 (s, 1H), 7.52–7.40 (m, 6H), 7.31 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 148.2, 147.2, 139.0, 138.5, 136.8, 135.9, 131.6, 129.6, 129.4, 128.4, 128.1, 127.2, 125.5, 124.2, 119.1, 21.6, 21.2.

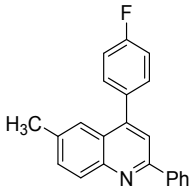
4-(3-Fluorophenyl)-6-methyl-2-phenylquinoline (3v)



The title compound was obtained as pale yellow solid (50.8 mg, 81% yield from alkyne; 47.6 mg, 76% from olefin), m.p. 116.6–117.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17–8.12 (m, 3H), 7.75 (s, 1H), 8.63 (s, 1H), 7.55–7.46 (m, 7H), 7.42 (ddd, J = 7.3, 3.7, 1.3 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.7 (d, $^1J_{C\text{-}F}$ = 247.2 Hz), 156.0, 147.4, 140.7 (d, $^3J_{C\text{-}F}$ = 7.6

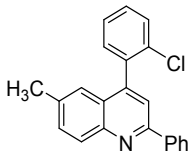
Hz), 139.5, 136.6, 131.9, 130.2 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 129.9, 129.9, 129.2, 128.8, 127.4, 125.4, 125.3 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 124.0, 119.2, 116.6 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 115.2 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 113.5, 21.8; HRMS (ESI, m/z) calcd for $C_{22}H_{17}FN^{+}$: 314.1340 $[M+H]^{+}$; found: 314.1332; IR (neat): 3051, 2957, 2921, 2855, 1585, 1547, 1485, 1359, 1182, 823, 784, 694 cm^{-1}.

4-(4-Fluorophenyl)-6-methyl-2-phenylquinoline (3w)[10]



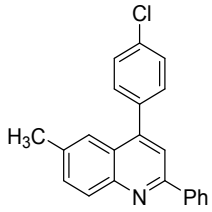
The title compound was obtained as pale yellow solid (50.4 mg, 80% yield from alkyne; 44.5 mg, 71% from olefin); m.p. 159.3–160.7 °C (lit. 160.0–161.0 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17–8.12 (m, 3H), 7.72 (s, 1H), 7.58–7.43 (m, 7H), 7.25–7.20 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7 (d, $^{1}J_{C\text{-}F}$ = 248.0), 154.8, 148.6, 147.3, 138.5, 136.3, 135.9 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 131.8, 129.7, 129.5, 129.2 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 128.6, 128.3, 125.6, 124.4, 119.0, 115.7 (d, $^{2}J_{C\text{-}F}$ = 21.5 Hz), 113.0, 21.8.

4-(2-Chlorophenyl)-6-methyl-2-phenylquinoline (3x)



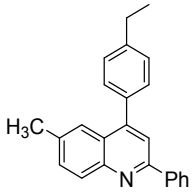
The title compound was obtained as brownish solid (50.8 mg, 77% yield from alkyne; 46.8 mg, 71% from olefin), m.p. 129.8–130.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19–8.13 (m, 3H), 7.75 (s, 1H), 7.59–7.36 (m, 8H), 8.23 (d, J = 4.6 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 147.1, 145.7, 139.6, 137.2, 136.4, 133.3, 131.9, 131.4, 129.8, 129.7, 129.2, 128.8, 127.5, 126.7, 125.7, 124.2, 119.8, 113.4, 21.8; HRMS (ESI, m/z) calcd for $C_{22}H_{17}ClN^{+}$: 330.1044 $[M+H]^{+}$; found: 330.1038; IR (neat): 3054, 2917, 2855, 1601, 1585, 1546, 1444, 1358, 825, 785, 762, 688 cm^{-1}.

4-(4-Chlorophenyl)-6-methyl-2-phenylquinoline (3y)



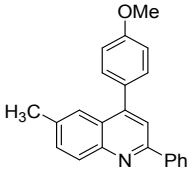
The title compound was obtained as yellowish solid (54.8 mg, 83% yield from alkyne; 50.1 mg, 76% from olefin), m.p. 131.8–132.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16–8.11 (m, 3H), 7.71 (s, 1H), 7.56–7.43 (m, 9H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 147.4, 147.1, 139.5, 137.0, 136.5, 134.4, 131.9, 130.8, 129.9, 129.2, 128.8, 128.8, 127.4, 125.4, 124.0, 119.2, 21.8; HRMS (ESI, m/z) calcd for $C_{22}H_{17}ClN^{+}$: 330.1044 $[M+H]^{+}$; found: 330.1037; IR (neat): 3057, 2967, 2913, 1593, 1547, 1488, 1445, 1359, 1086, 1013, 848, 784, 767, 689 cm^{-1}.

4-(4-Ethylphenyl)-6-methyl-2-phenylquinoline (3z)



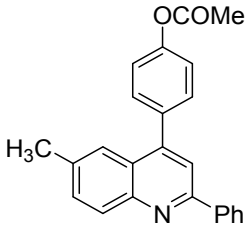
The title compound was obtained as brown oil (53.7 mg, 83% yield from alkyne); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16–8.12 (m, 3H), 7.74 (s, 1H), 7.68 (s, 1H), 7.53–7.33 (m, 8H), 2.74 (q, J = 7.6 Hz, 2H), 2.43 (s, 3H), 1.31 (t, J = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 148.4, 147.4, 144.4, 139.8, 136.0, 135.8, 131.6, 129.8, 129.5, 129.0, 128.7, 128.0, 127.4, 125.7, 124.4, 119.3, 28.6, 21.7, 15.4; HRMS (ESI, m/z) calcd for $C_{24}H_{22}N^{+}$: 324.1747 $[M+H]^{+}$; found: 324.1739; IR (neat): 3055, 2963, 2922, 2871, 1587, 1546, 1492, 1445, 1360, 851, 824, 783, 768, 690 cm^{-1}.

4-(4-Methoxyphenyl)-6-methyl-2-phenylquinoline (3α)[10]



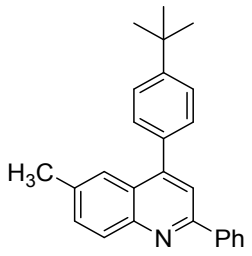
The title compound was obtained as pale yellow solid (56.0 mg, 86% yield from alkyne; 52.1 mg, 80% from olefin); m.p. 116.7–117.8 °C (lit. 117.0–118.0 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17–8.11 (m, 3H), 7.73 (s, 1H), 7.67 (s, 1H), 7.54–7.41 (m, 6H), 7.07–7.03 (m, 2H), 3.86 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 155.9, 148.1, 147.4, 139.8, 136.0, 131.6, 130.8, 130.7, 129.8, 129.0, 128.7, 127.4, 125.8, 124.4, 119.3, 114.0, 55.3, 21.8.

4-(6-Methyl-2-phenylquinolin-4-yl)phenyl acetate (3β)[9]



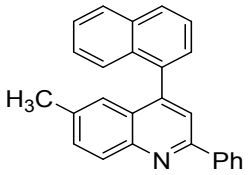
The title compound was obtained as light brown solid (48.1 mg, 68% from Alkyne; 43.1 mg, 61% from olefin); m.p. 126.5–127.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16–8.13 (m, 3H), 7.75 (s, 1H), 7.64 (s, 1H), 7.57–7.43 (m, 6H), 7.27 (d, J = 8.5 Hz, 2H), 2.47 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 156.0, 150.7, 147.5, 147.3, 139.6, 136.4, 136.1, 131.8, 130.6, 129.8, 129.2, 128.8, 127.4, 125.6, 124.2, 121.8, 119.5, 21.8, 21.2.

6-Methyl-2-phenyl-4-(p-tert.butyl)phenyl)quinoline (3γ)[11]



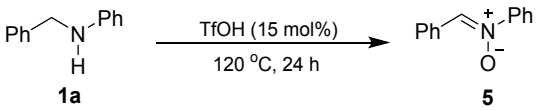
The title compound was obtained as brown oil (45.7 mg, 65% yield from olefin); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16–8.11 (m, 3H), 7.75 (s, 1H), 7.70 (s, 1H), 7.54–7.40 (m, 8H), 2.43 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 151.3, 148.3, 147.4, 139.8, 136.0, 135.6, 131.6, 129.8, 129.2, 129.0, 128.7, 127.4, 125.7, 125.5, 124.5, 119.4, 34.7, 31.3, 21.8.

6-Methyl-4-(naphthalen-1-yl)-2-phenylquinoline (3δ)



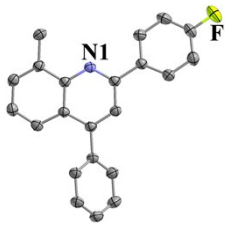
The title compound was obtained as light brown solid (53.2 mg, 77% from olefin), m.p. 157.3–158.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19–8.16 (m, 3H), 7.93 (dd, J = 13.0, 8.5 Hz, 2H), 7.58–7.38 (m, 8H), 7.28 (dd, J = 8.5, 6.8 Hz, 1H), 7.18 (s, 1H), 2.26 (s, 3H).); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 147.1, 139.5, 136.2, 136.1, 133.4, 131.9, 131.9, 129.7, 129.1, 128.7, 128.5, 128.2, 127.4, 127.3, 126.9, 126.4, 126.1, 126.0, 125.2, 124.7, 120.4, 21.5; HRMS (ESI, m/z) calcd for $C_{26}H_{20}N^+$: 346.1590 $[M+H]^+$; found: 346.1587; IR (neat) 3292, 2955, 2928, 2843, 1713, 1697, 1463, 1092, 986, 729, 549 cm^{-1}

(*Z*)-*N*,1-Diphenylmethanimine oxide (5)[12]



The title compound was obtained as white solid (232.7 mg, 59 %), m.p. 112.5–113.0 °C (lit. 110.0–112.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41–8.39 (m, 2H), 7.93 (s, 1H), 7.78 (dd, J = 7.9, 2.3 Hz, 2H), 7.51–7.46 (m, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.1, 134.6, 130.9, 130.6, 129.9, 129.1, 129.0, 128.6, 121.7.

2. X-Ray Data of 2-(4-fluorophenyl)-8-methyl-4-phenylquinoline (3b)



CCDC No. 1448399 (**3b**) contains the supplementary crystallographic data for this paper. The crystal data can be obtained free of charge from the Cambridge crystallographic Data Centre through www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement for 3b.

Identification code	**3b**
Empirical formula	C22 H16 F N
Formula weight	313.36
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 19.293(4) A alpha = 90 deg.
	b = 7.2555(14) A beta = 90 deg.
	c= 23.177(5) A gamma = 90 deg.
Volume	3244.3(11) A^3
Z, Calculated density	8, 1.283 Mg/m^3
Absorption coefficient	0.082 mm^-1
F(000)	1312
Crystal size	.29 x 0.26 x 0.24 mm
Theta range for data collection	2.05 to 27.44 deg.
Limiting indices	-24<=h<=24, -9<=k<=6, -30<=l<=27
Reflections collected / unique	19405 / 3701 [R(int) = 0.0650]
Completeness to theta = 27.44	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3701 / 0 / 218
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)	R1 = 0.0506, wR2 = 0.1157
R indices (all data)	R1 = 0.1207, wR2 = 0.1482
Largest diff. peak and hole	0.137 and -0.176 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 0. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
N(1)	1518(1)	8163(2)	1370(1)	49(1)
C(2)	2753(1)	8153(3)	1315(1)	48(1)
C(17)	873(1)	7289(3)	2235(1)	45(1)
C(8)	907(1)	7854(3)	1648(1)	45(1)
C(1)	2105(1)	7908(3)	1650(1)	47(1)
C(9)	2112(1)	7424(3)	2242(1)	51(1)
C(10)	1512(1)	7156(3)	2542(1)	47(1)
C(21)	287(1)	8048(3)	1318(1)	51(1)
C(11)	1543(1)	6714(3)	3170(1)	50(1)
C(18)	219(1)	6809(3)	2467(1)	54(1)
C(7)	3401(1)	8174(3)	1564(1)	62(1)
C(20)	-328(1)	7610(3)	1570(1)	58(1)
F	4515(1)	8917(2)	349(1)	103(1)
C(19)	-365(1)	6960(3)	2137(1)	60(1)
C(6)	3994(1)	8422(3)	1242(1)	72(1)
C(16)	1132(1)	7632(3)	3565(1)	58(1)
C(12)	2003(1)	5405(3)	3378(1)	62(1)
C(22)	329(1)	8669(3)	698(1)	68(1)
C(5)	3933(1)	8656(3)	668(1)	69(1)
C(4)	3311(1)	8633(4)	400(1)	88(1)
C(15)	1168(1)	7232(3)	4148(1)	68(1)
C(3)	2722(1)	8380(4)	723(1)	77(1)
C(13)	2037(1)	4995(4)	3961(1)	73(1)
C(14)	1615(1)	5897(4)	4341(1)	74(1)

Table 3. Bond lengths [A] and angles [deg] for 0

N(1)-C(1)	1.317(2)
N(1)-C(8)	1.362(2)
C(2)-C(7)	1.375(3)
C(2)-C(3)	1.383(3)
C(2)-C(1)	1.483(3)
C(17)-C(18)	1.415(3)
C(17)-C(8)	1.424(2)
C(17)-C(10)	1.427(3)
C(8)-C(21)	1.427(3)
C(1)-C(9)	1.416(2)
C(9)-C(10)	1.365(2)
C(10)-C(11)	1.491(2)
C(21)-C(20)	1.361(3)
C(21)-C(22)	1.507(3)
C(11)-C(16)	1.383(3)
C(11)-C(12)	1.386(3)
C(18)-C(19)	1.367(3)
C(7)-C(6)	1.377(3)
C(20)-C(19)	1.399(3)
F-C(5)	1.358(2)
C(6)-C(5)	1.348(3)
C(16)-C(15)	1.383(3)
C(12)-C(13)	1.384(3)
C(5)-C(4)	1.360(3)
C(4)-C(3)	1.374(3)
C(15)-C(14)	1.371(3)
C(13)-C(14)	1.366(3)
C(1)-N(1)-C(8)	119.23(16)

C(7)-C(2)-C(3)	117.04(19)
C(7)-C(2)-C(1)	123.30(18)
C(3)-C(2)-C(1)	119.67(18)
C(18)-C(17)-C(8)	118.35(18)
C(18)-C(17)-C(10)	124.36(18)
C(8)-C(17)-C(10)	117.20(17)
N(1)-C(8)-C(17)	122.60(17)
N(1)-C(8)-C(21)	117.18(17)
C(17)-C(8)-C(21)	120.18(18)
N(1)-C(1)-C(9)	121.34(18)
N(1)-C(1)-C(2)	116.81(17)
C(9)-C(1)-C(2)	121.85(18)
C(10)-C(9)-C(1)	121.45(18)
C(9)-C(10)-C(17)	117.91(17)
C(9)-C(10)-C(11)	119.69(17)
C(17)-C(10)-C(11)	122.39(17)
C(20)-C(21)-C(8)	118.53(18)
C(20)-C(21)-C(22)	121.76(19)
C(8)-C(21)-C(22)	119.68(18)
C(16)-C(11)-C(12)	117.80(18)
C(16)-C(11)-C(10)	121.32(18)
C(12)-C(11)-C(10)	120.85(17)
C(19)-C(18)-C(17)	120.26(19)
C(2)-C(7)-C(6)	121.9(2)
C(21)-C(20)-C(19)	121.8(2)
C(18)-C(19)-C(20)	120.7(2)
C(5)-C(6)-C(7)	118.6(2)
C(11)-C(16)-C(15)	121.1(2)

C(13)-C(12)-C(11)	121.2(2)
C(6)-C(5)-C(4)	122.0(2)
C(6)-C(5)-F	118.9(2)
C(4)-C(5)-F	119.1(2)
C(5)-C(4)-C(3)	119.1(2)
C(14)-C(15)-C(16)	119.9(2)
C(4)-C(3)-C(2)	121.3(2)
C(14)-C(13)-C(12)	119.8(2)
C(13)-C(14)-C(15)	120.2(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 0. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	50(1)	53(1)	44(1)	-2(1)	-1(1)	1(1)
C(2)	50(1)	48(1)	47(1)	-4(1)	1(1)	-1(1)
C(17)	48(1)	45(1)	42(1)	-5(1)	1(1)	1(1)
C(8)	49(1)	45(1)	43(1)	-5(1)	-2(1)	2(1)
C(1)	51(1)	47(1)	41(1)	-7(1)	0(1)	-1(1)
C(9)	49(1)	59(1)	44(1)	-5(1)	-4(1)	2(1)
C(10)	53(1)	47(1)	40(1)	-5(1)	0(1)	2(1)
C(21)	52(1)	52(1)	49(1)	-6(1)	-4(1)	4(1)
C(11)	51(1)	56(1)	42(1)	-1(1)	-1(1)	1(1)
C(18)	57(1)	56(1)	49(1)	-3(1)	5(1)	1(1)
C(7)	56(1)	77(2)	54(1)	1(1)	2(1)	4(1)
C(20)	53(1)	64(2)	58(1)	-7(1)	-10(1)	6(1)
F	81(1)	117(1)	112(1)	2(1)	46(1)	-6(1)
C(19)	48(1)	66(2)	68(1)	-7(1)	4(1)	-2(1)

C(6)	53(1)	83(2)	80(2)	-4(1)	7(1)	3(1)
C(16)	56(1)	70(2)	46(1)	-3(1)	0(1)	4(1)
C(12)	61(1)	72(2)	53(1)	1(1)	-3(1)	9(1)
C(22)	67(2)	87(2)	51(1)	3(1)	-14(1)	4(1)
C(5)	58(2)	71(2)	77(2)	-2(1)	25(1)	-2(1)
C(4)	85(2)	126(2)	54(1)	11(1)	17(1)	-9(2)
C(15)	65(2)	93(2)	46(1)	-7(1)	6(1)	-1(1)
C(3)	62(2)	119(2)	51(1)	8(1)	0(1)	-8(1)
C(13)	71(2)	88(2)	60(1)	15(1)	-14(1)	5(1)
C(14)	72(2)	107(2)	43(1)	8(1)	-7(1)	-10(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 0.

	x	y	z	U(eq)
H(9)	2535	7286	2429	61
H(18)	187	6388	2845	65
H(7)	3439	8016	1961	75
H(20)	-736	7746	1360	70
H(19)	-792	6628	2292	73
H(6)	4427	8429	1418	86
H(16)	826	8534	3437	69
H(12)	2293	4792	3122	75
H(22A)	602	7808	481	103
H(22B)	540	9866	681	103
H(22C)	-130	8730	538	103
H(4)	3282	8785	2	106
H(15)	890	7866	4409	81
H(3)	2293	8362	541	93

H(13)	2347	4108	4093	87
H(14)	1631	5605	4731	89

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4. Copies of ^{1}H and ^{13}C Spectra

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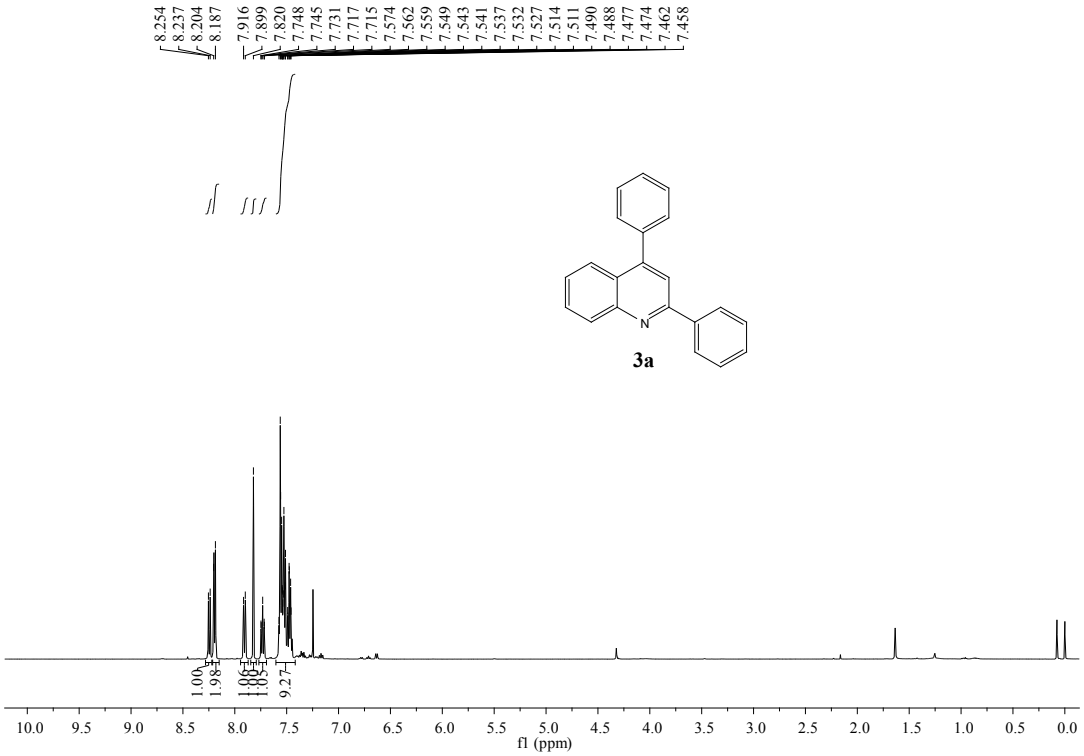
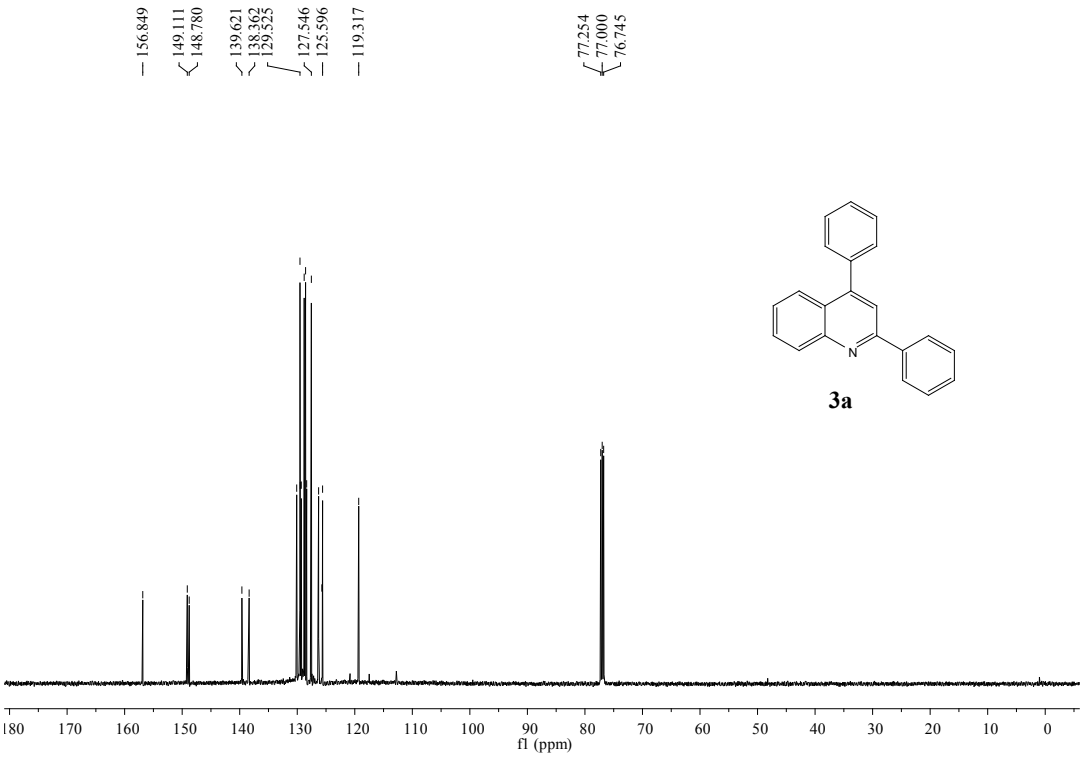


^{13}C NMR (125 MHz, $CDCl_3$)



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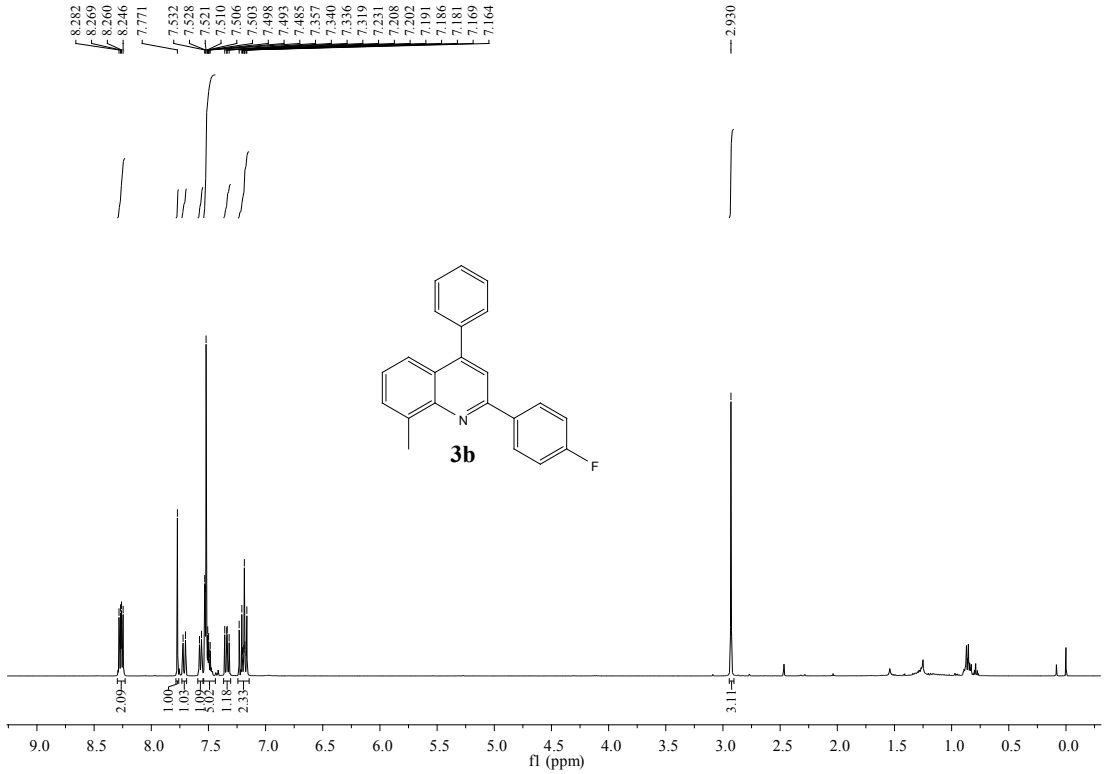

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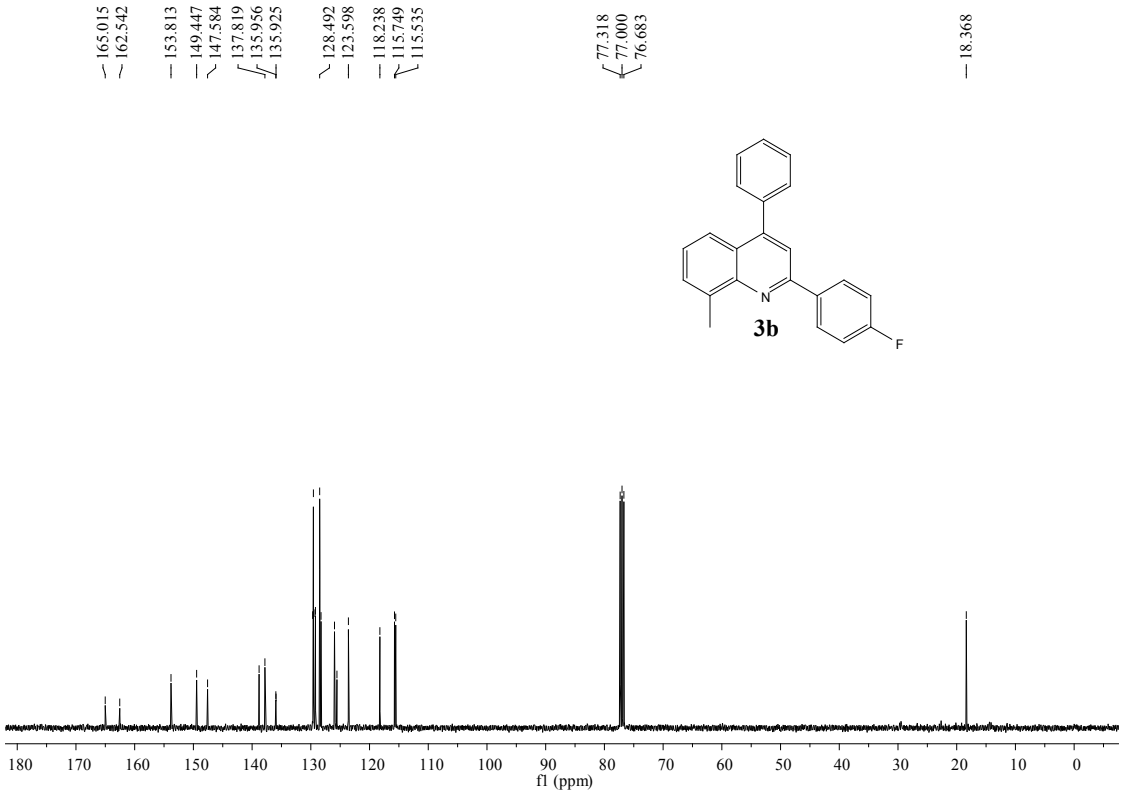

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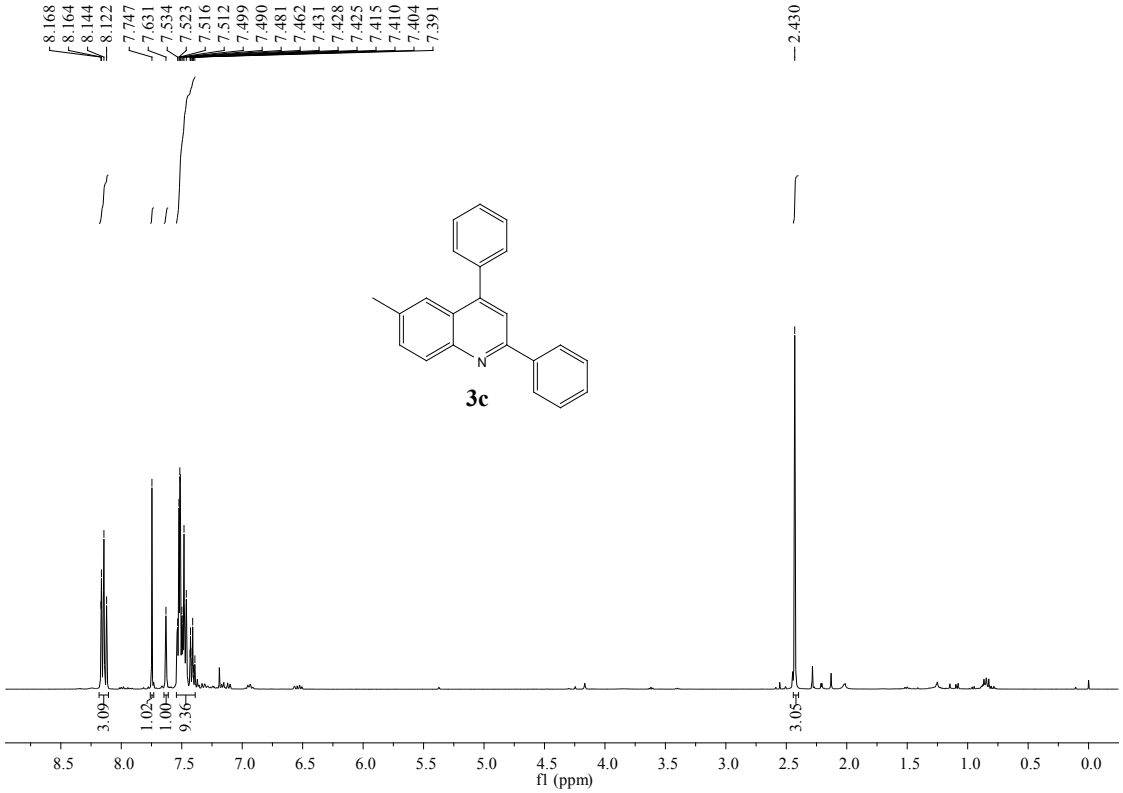

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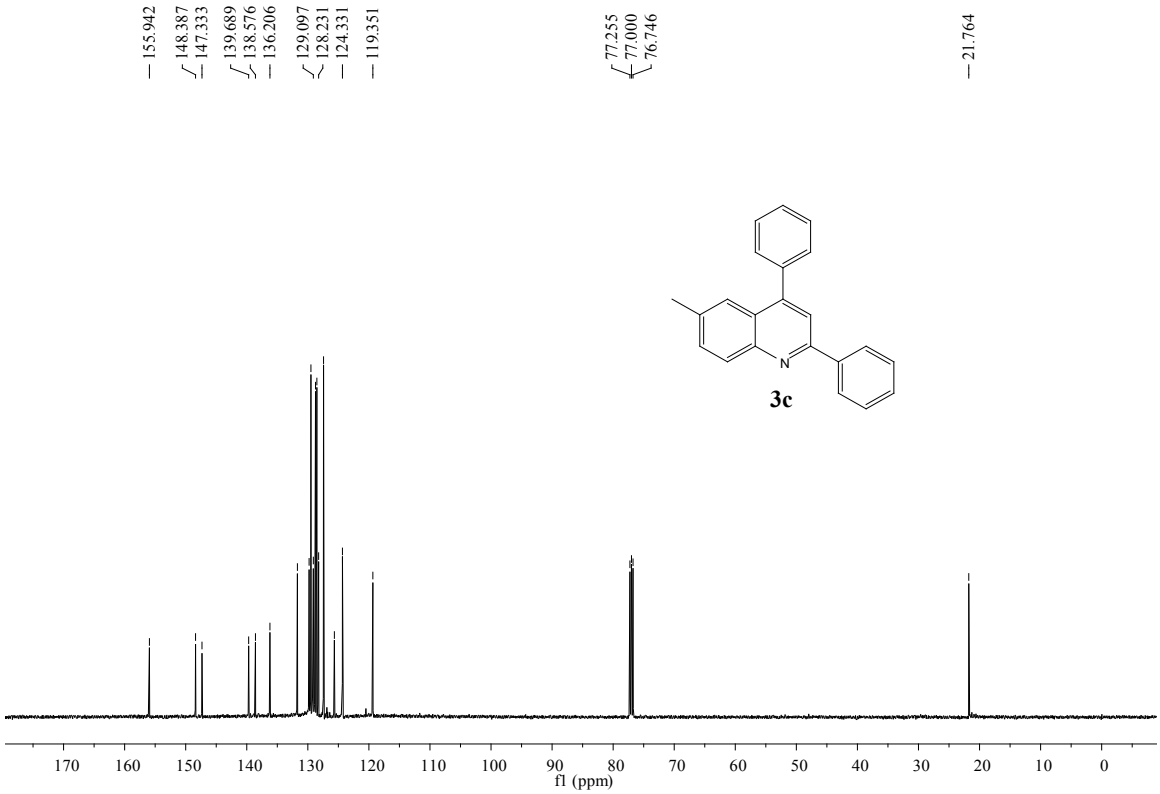

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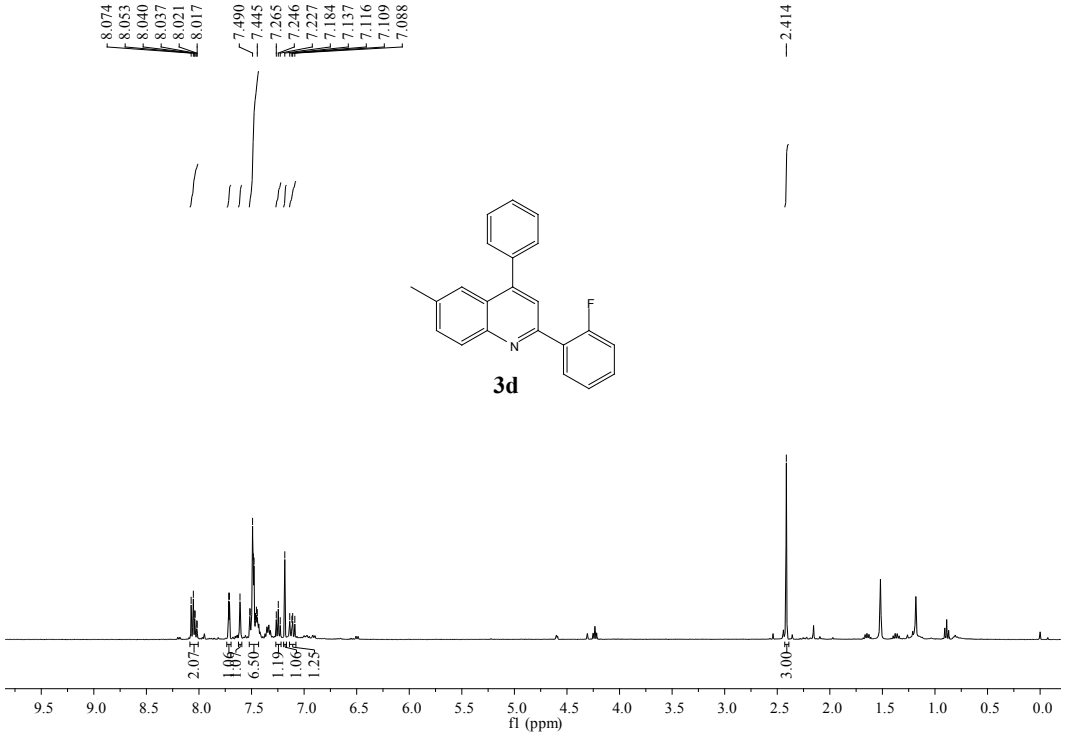

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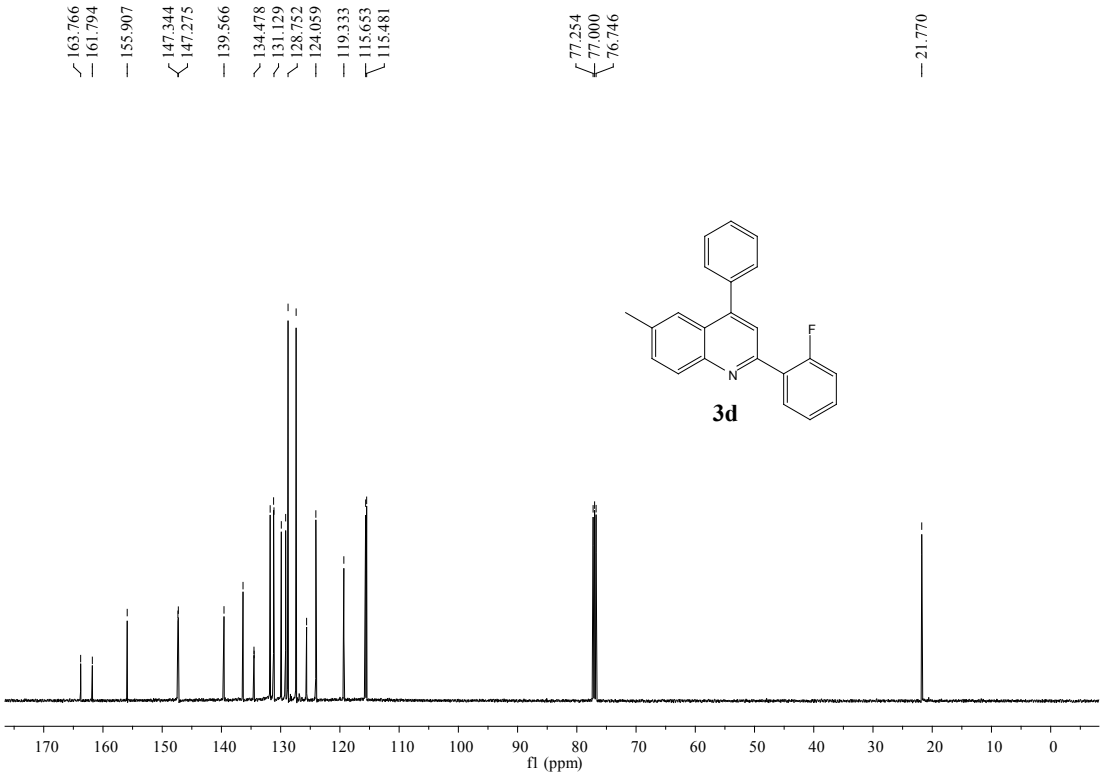

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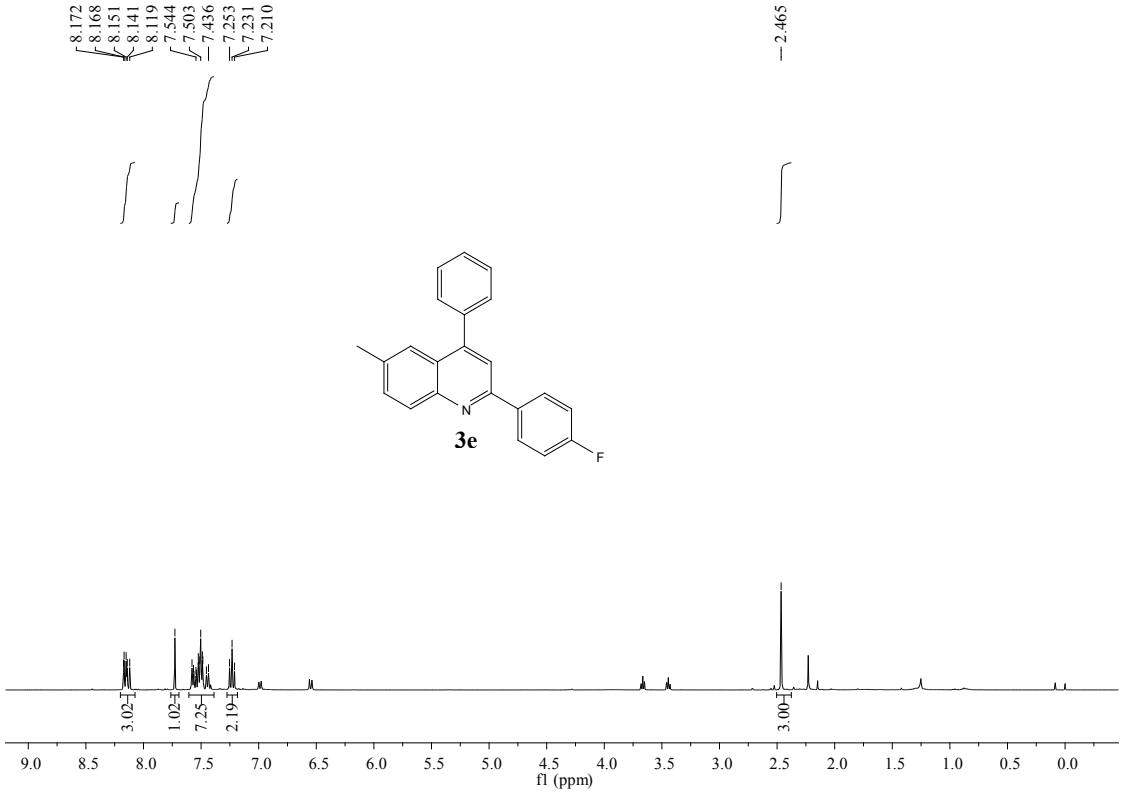

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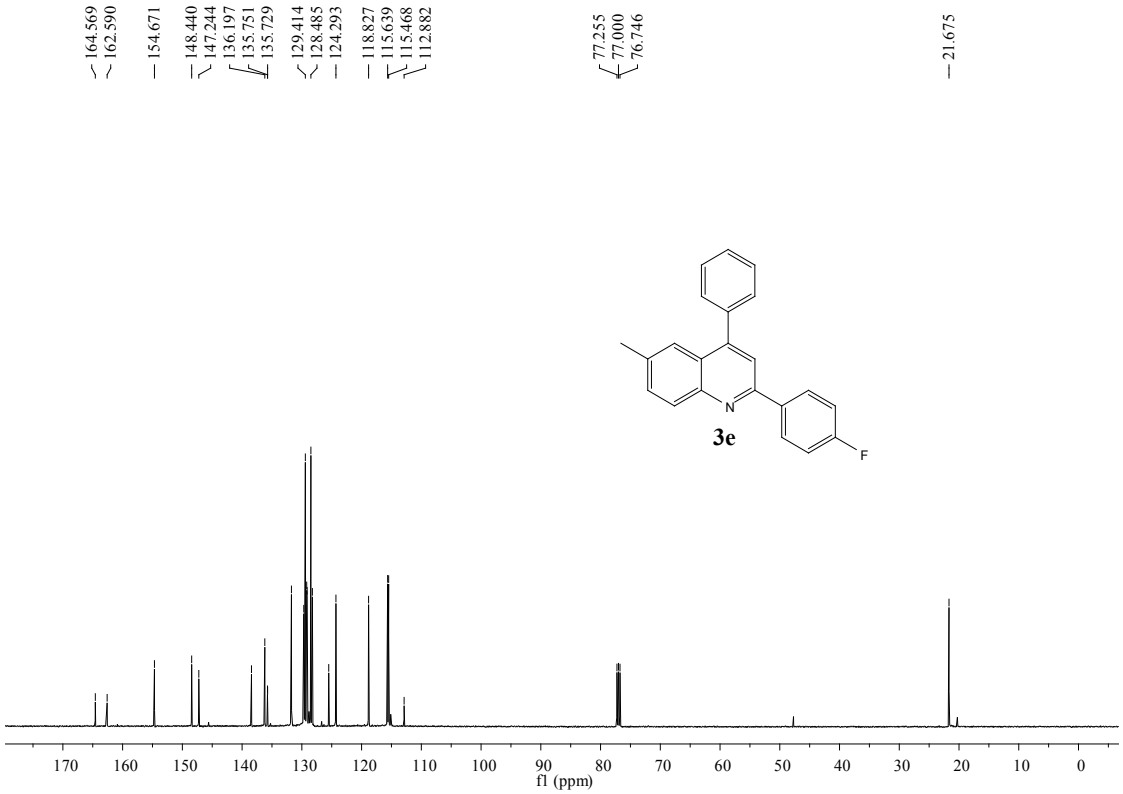

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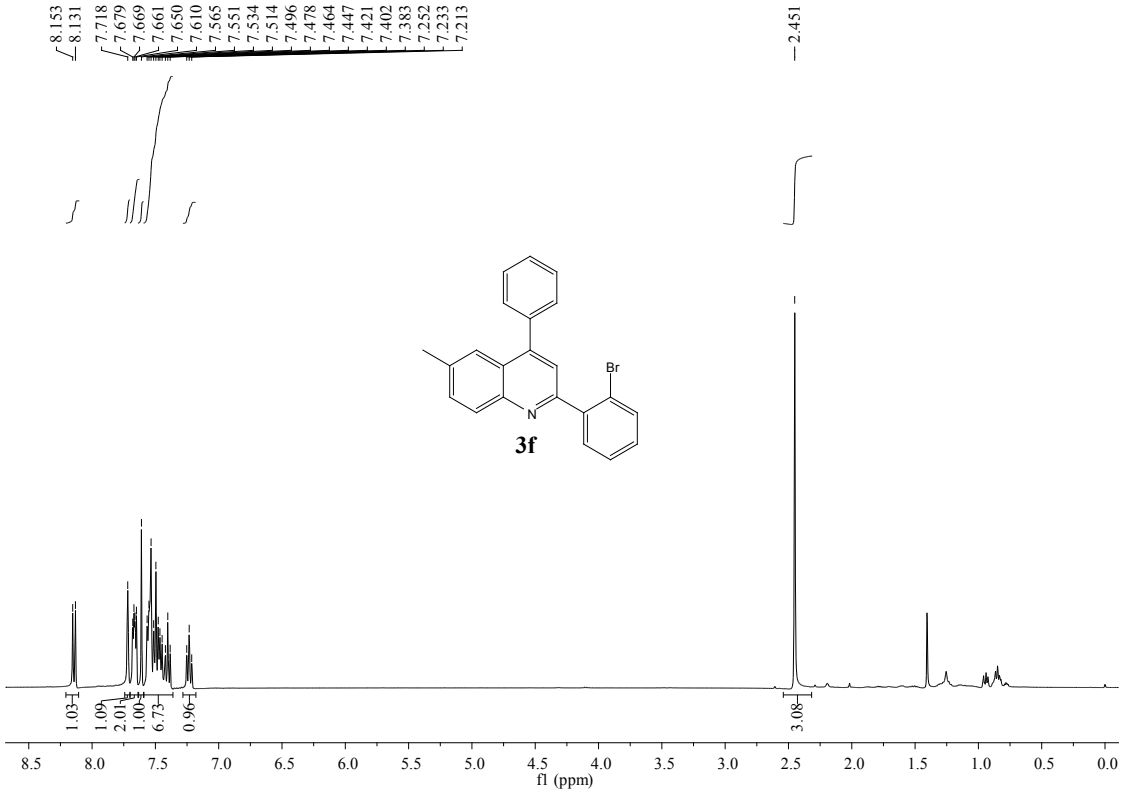

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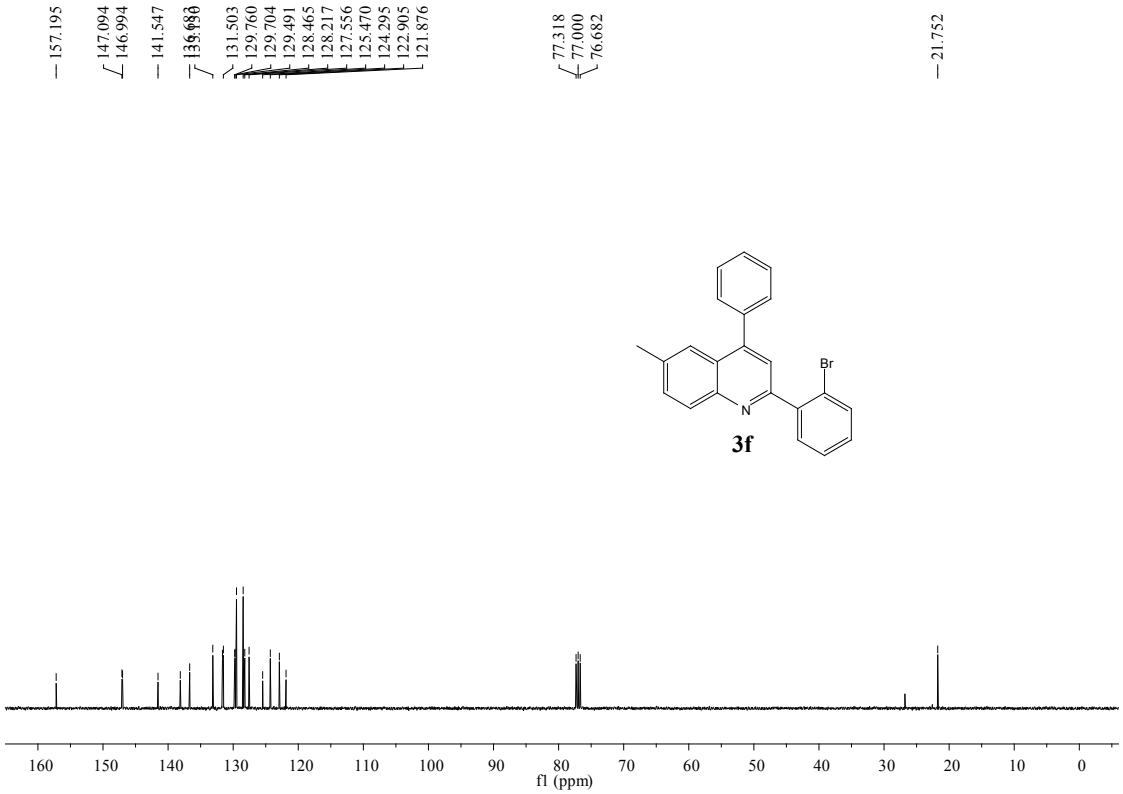

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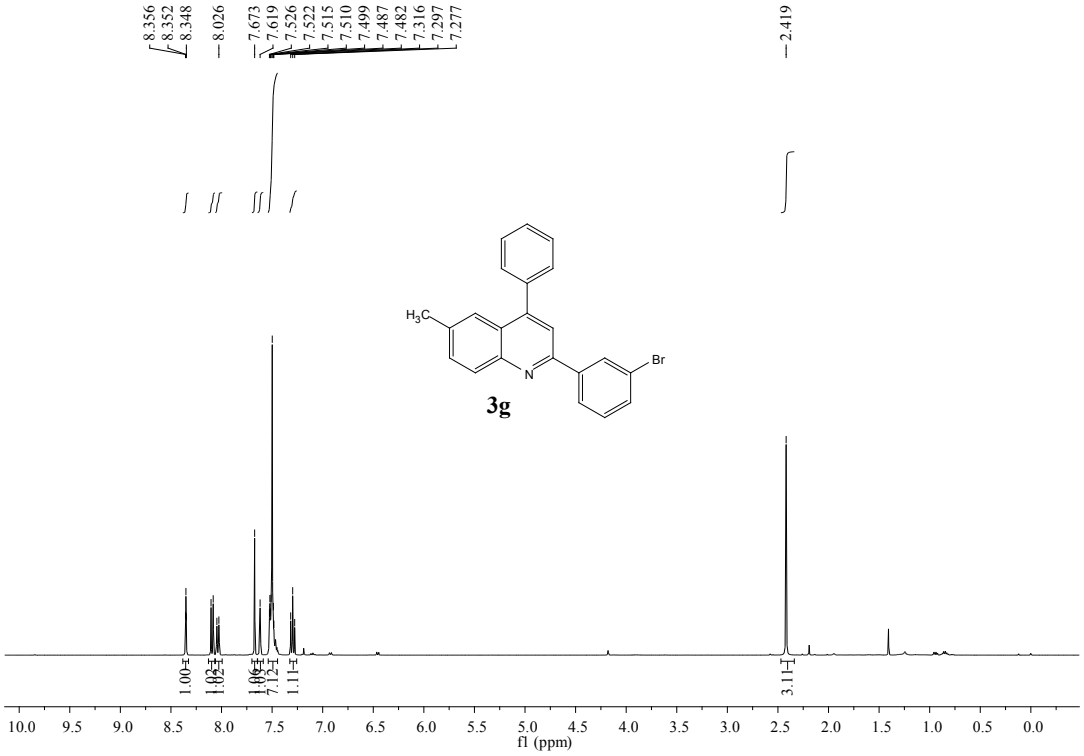

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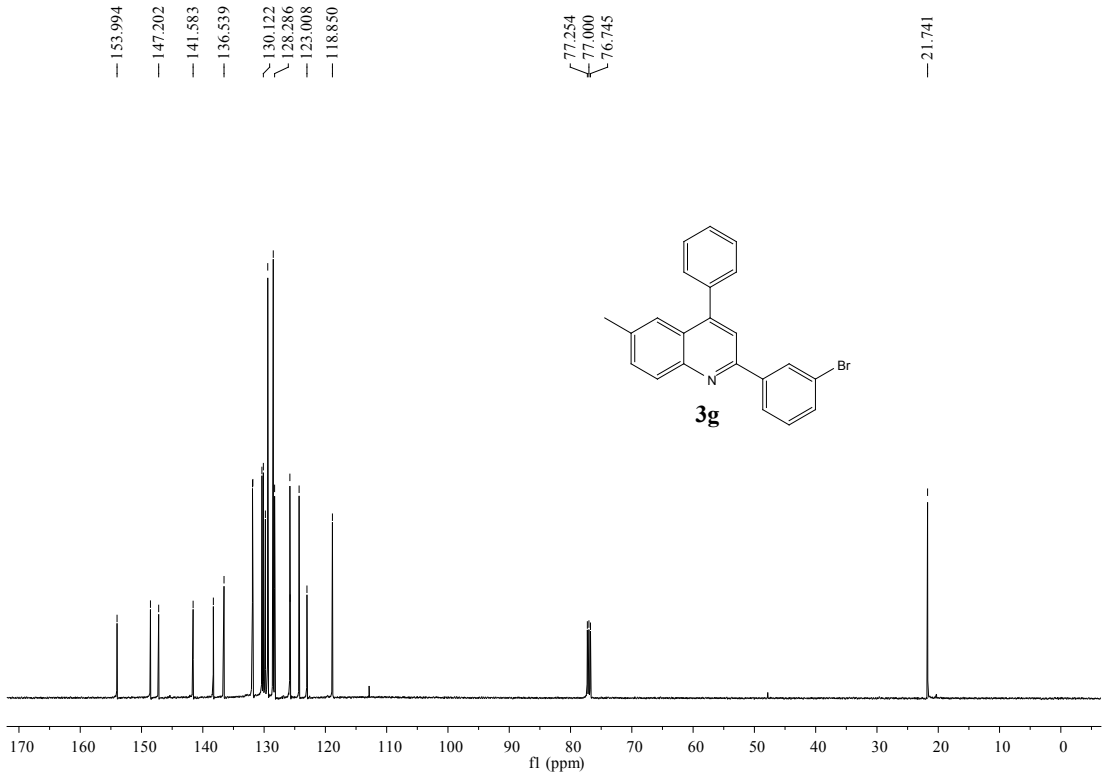

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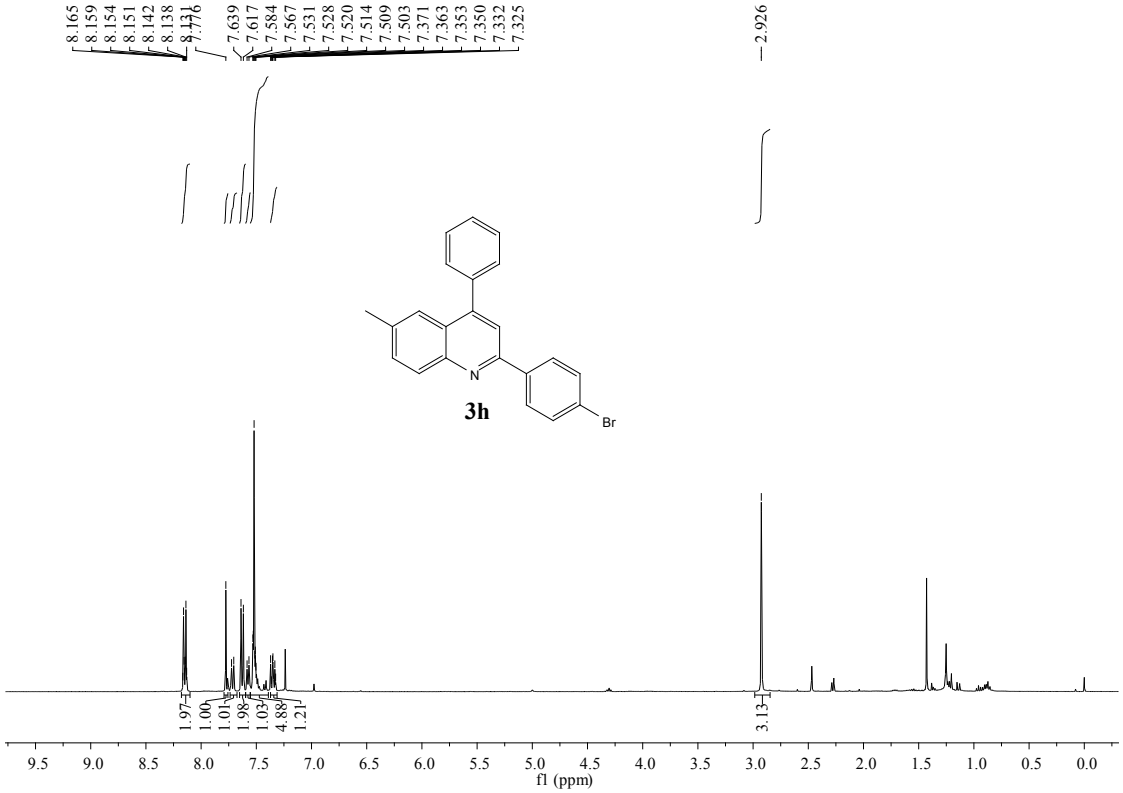

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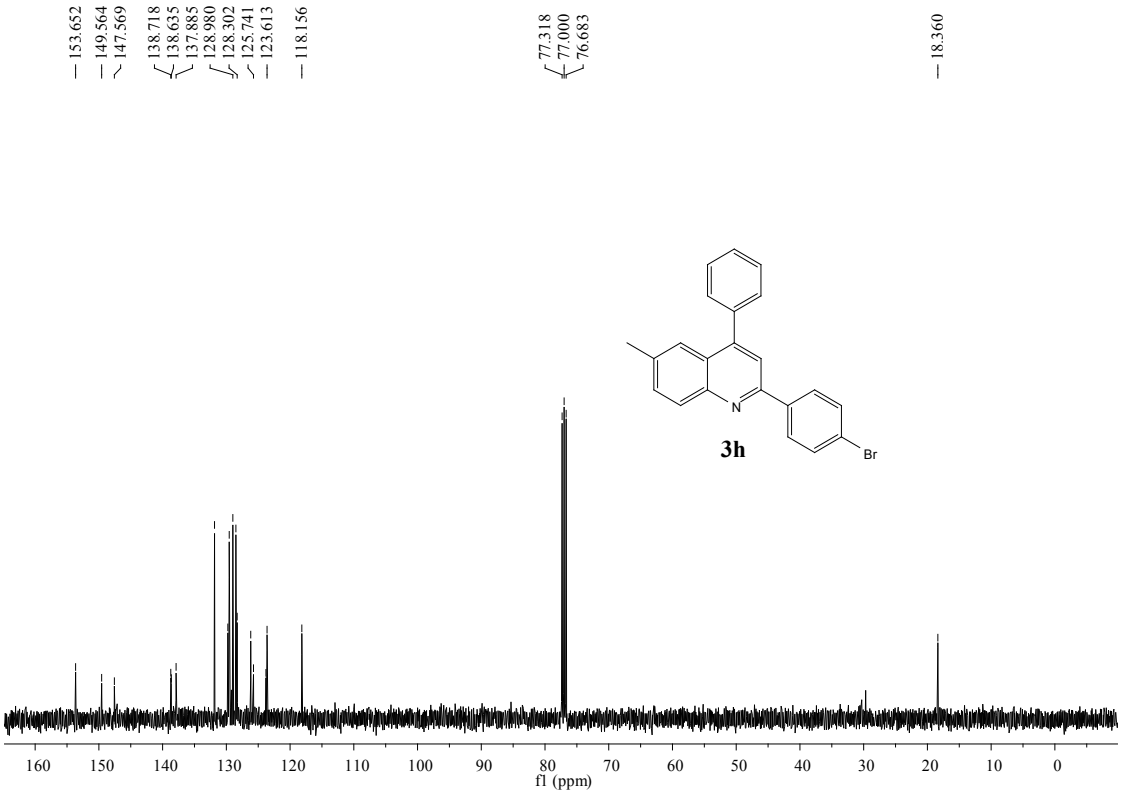

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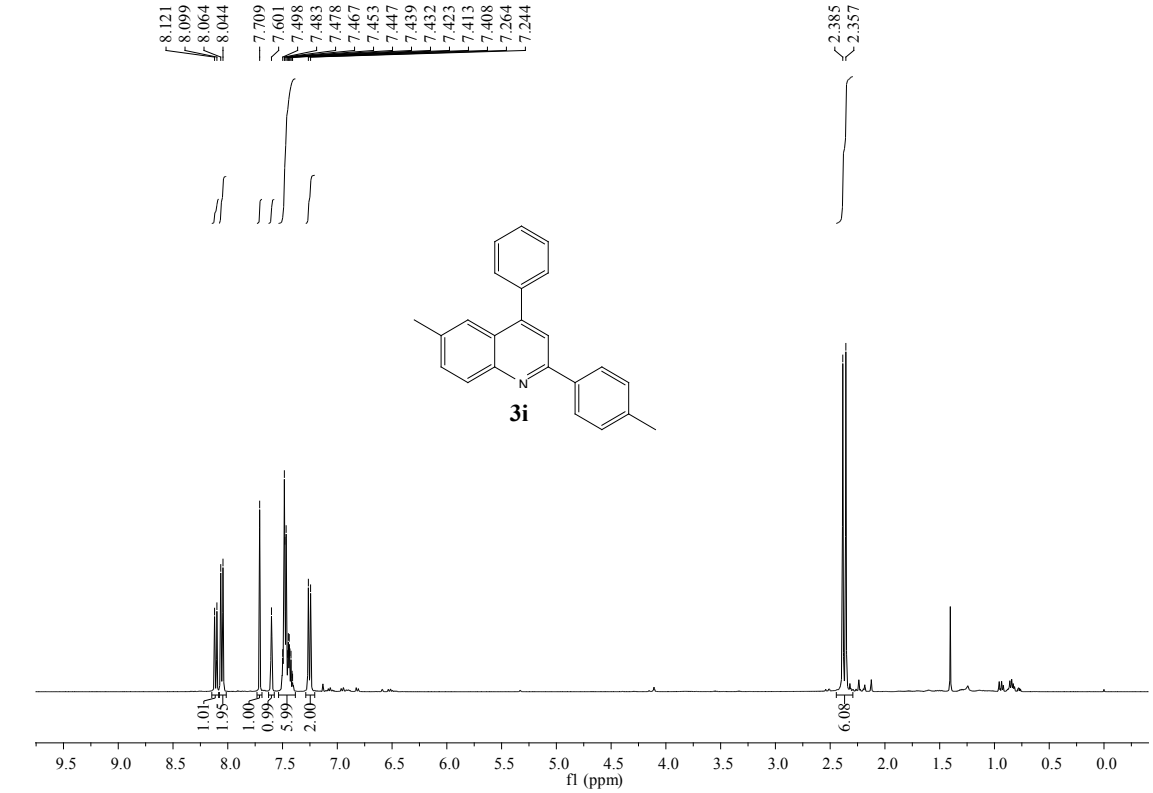

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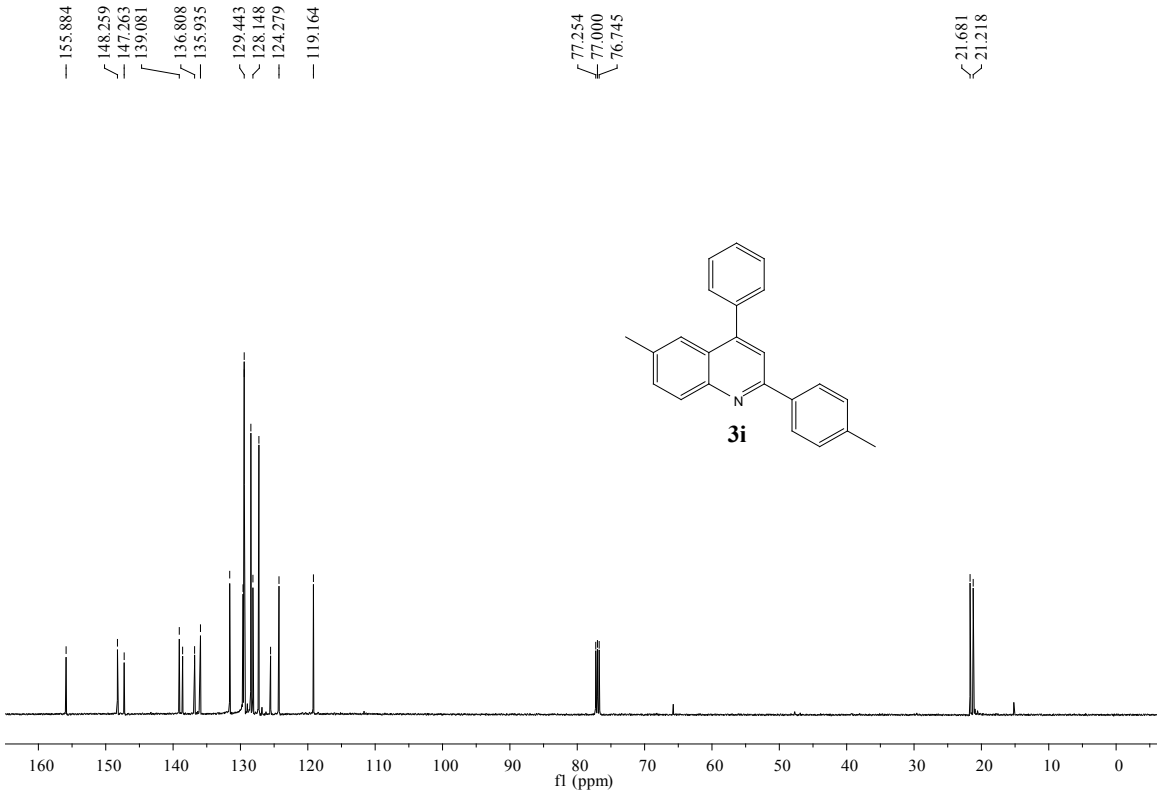

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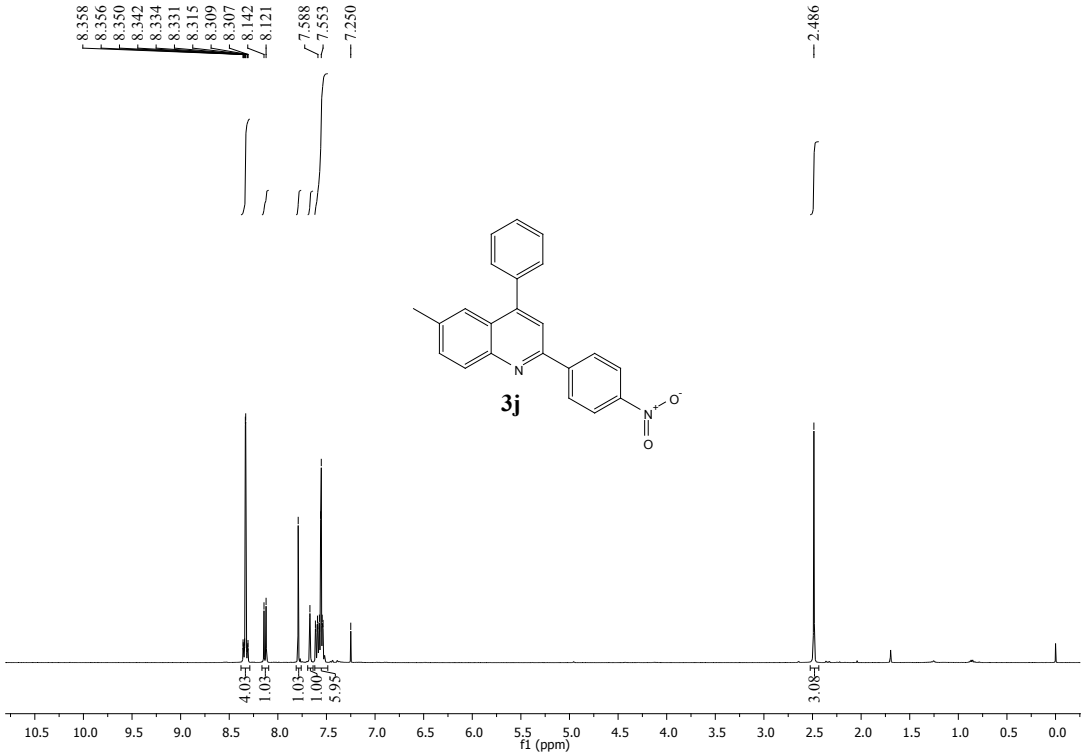

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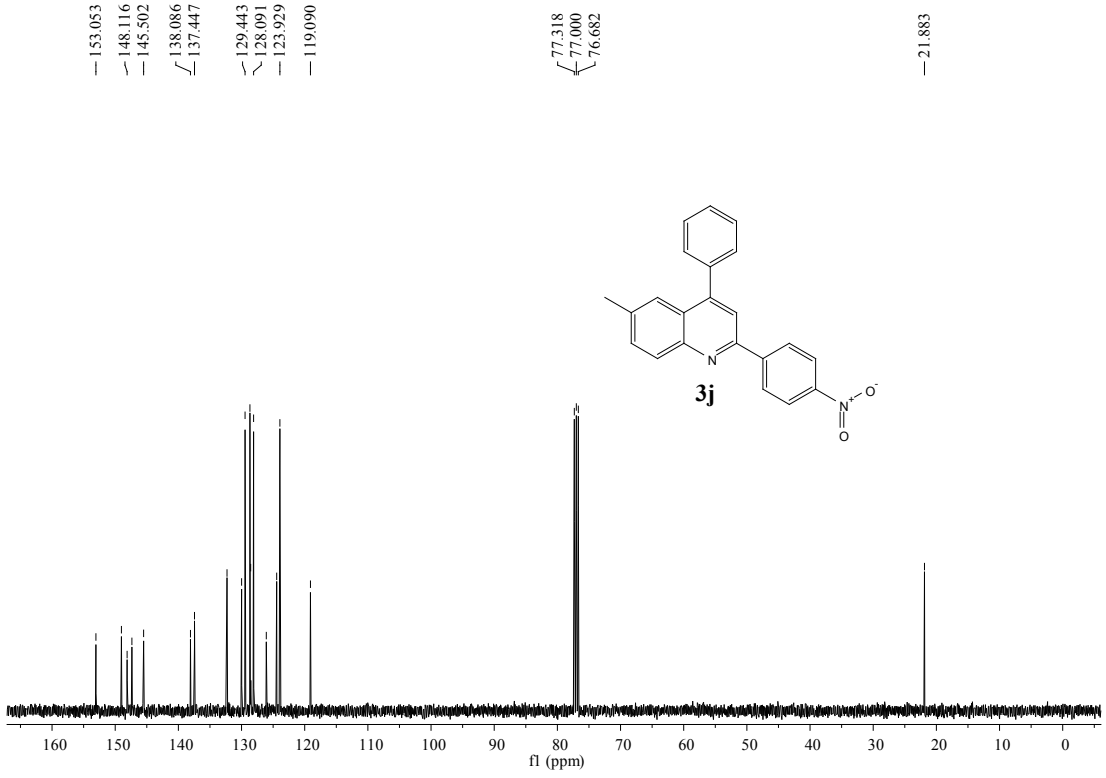

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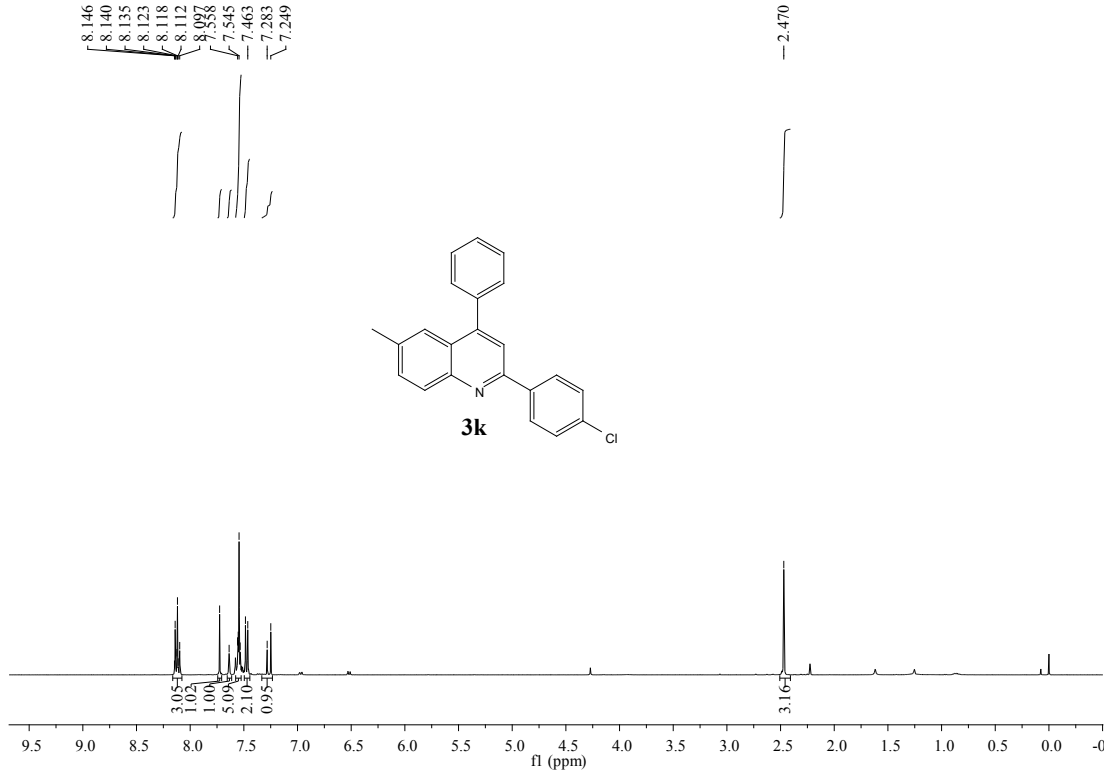

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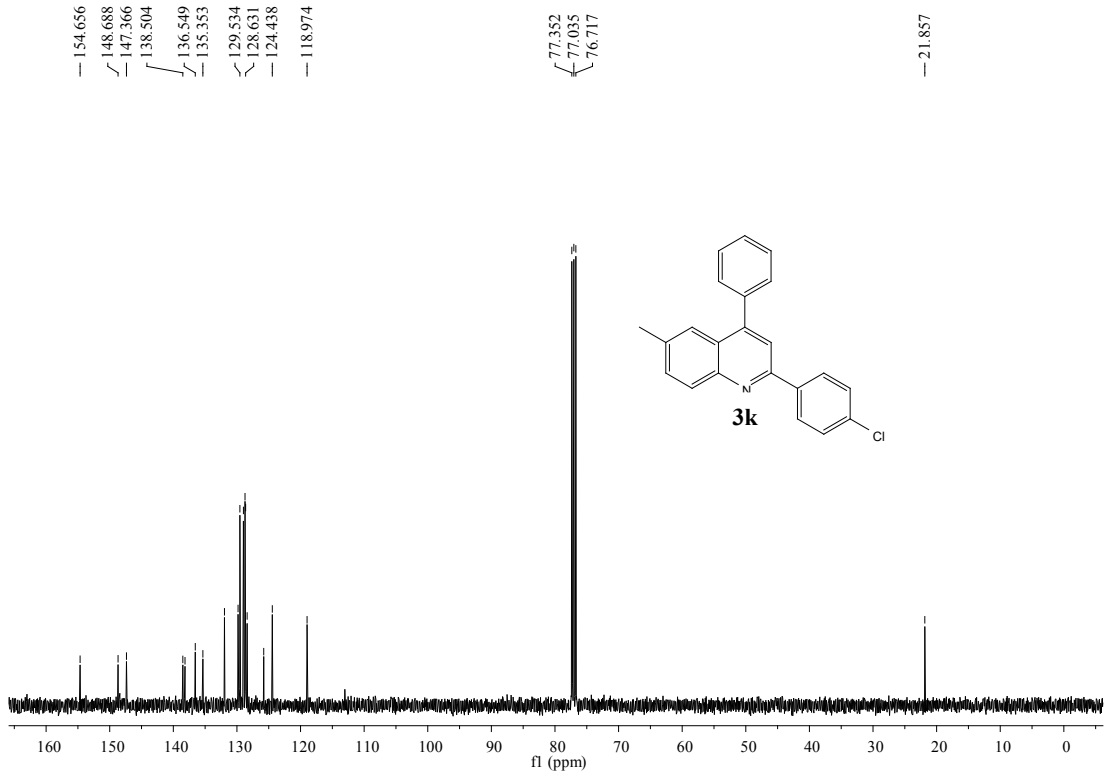

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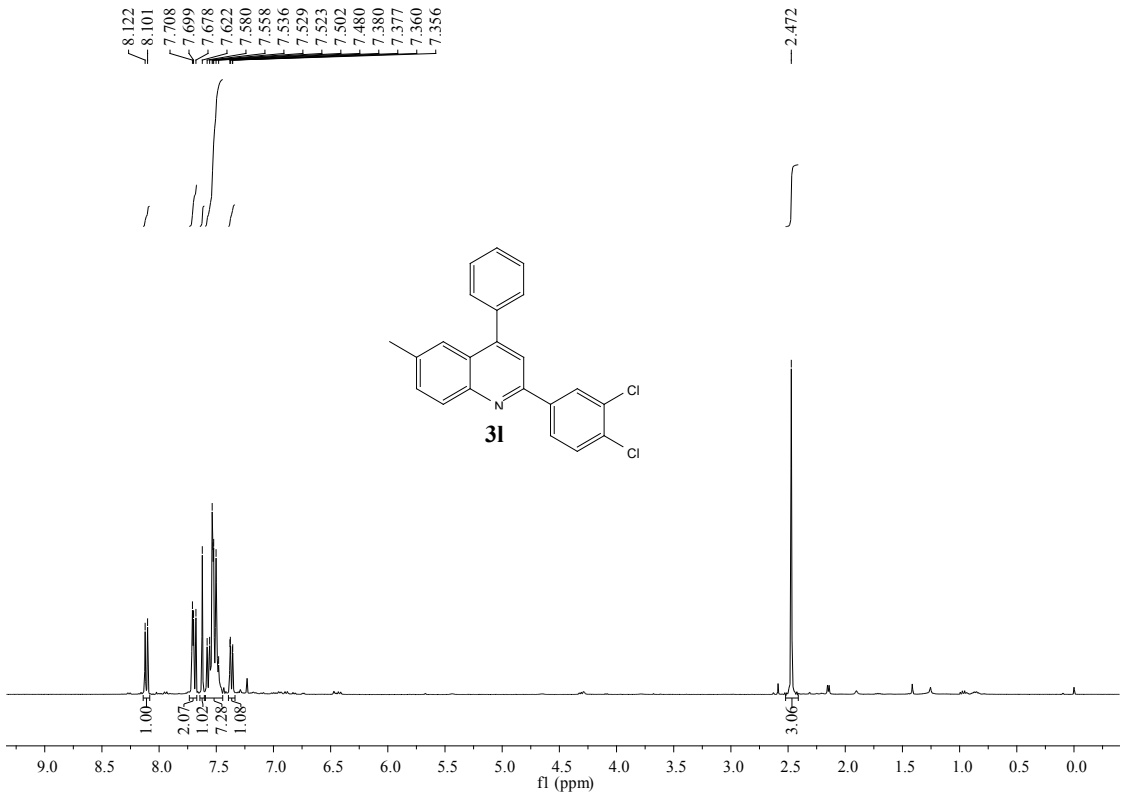

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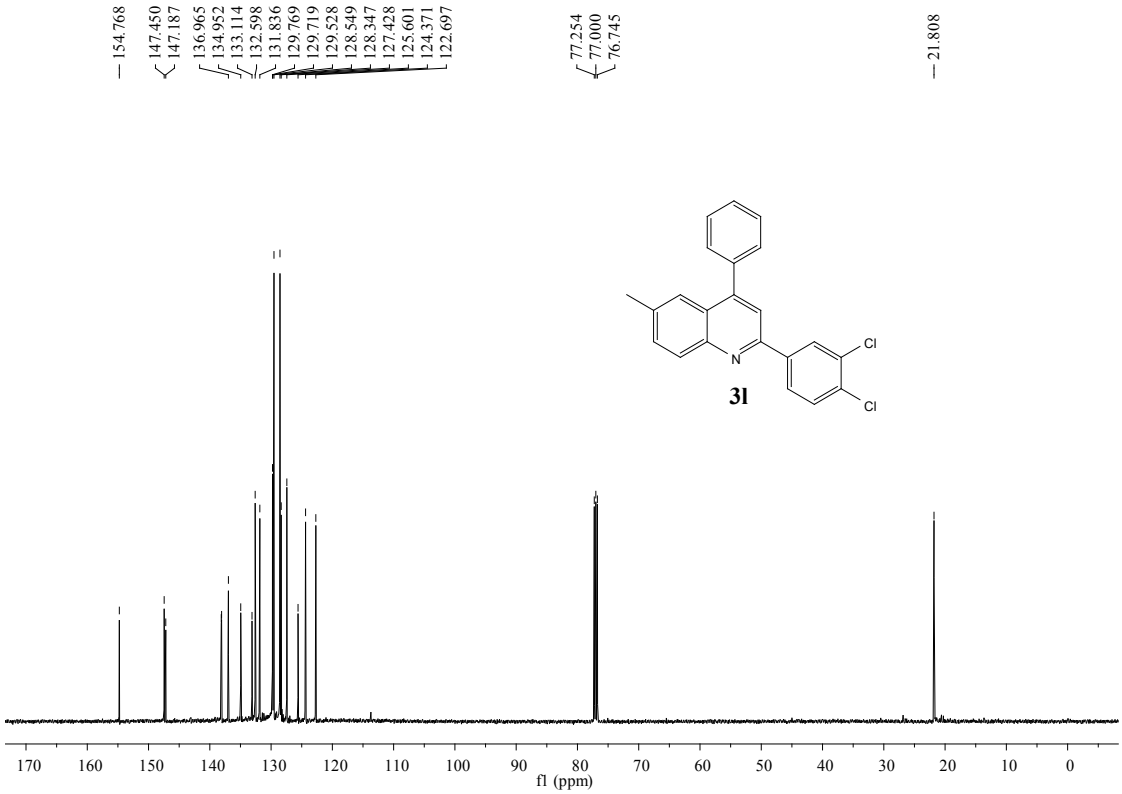

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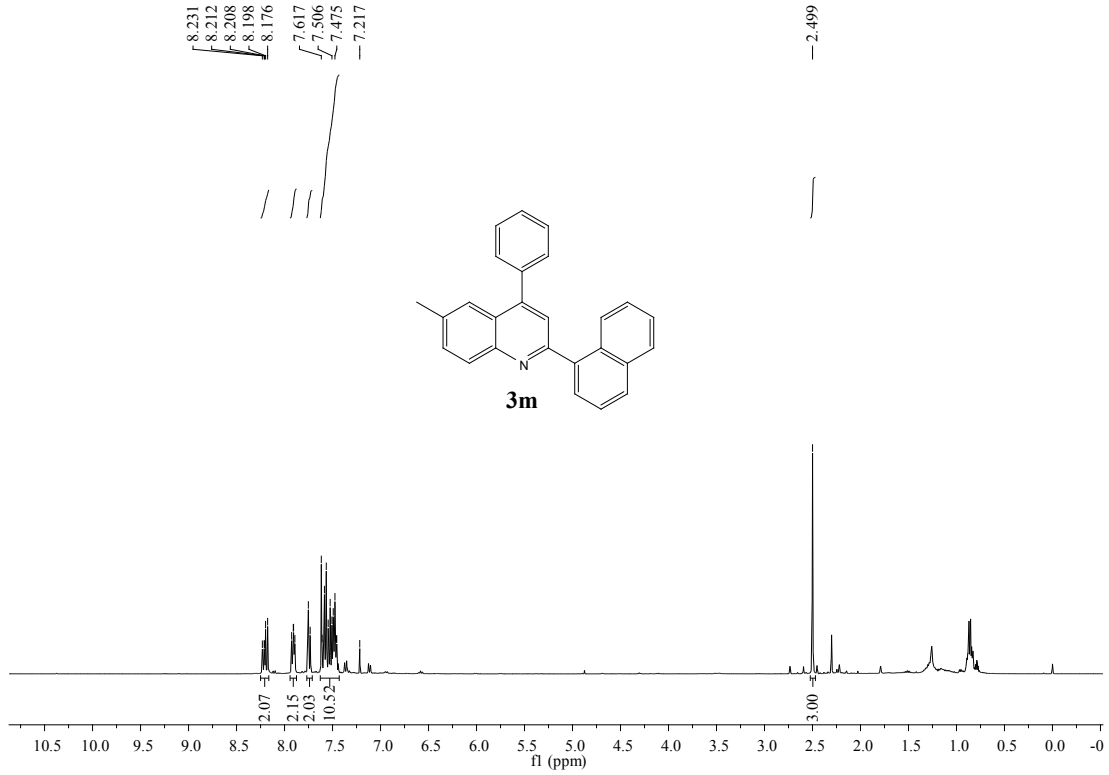

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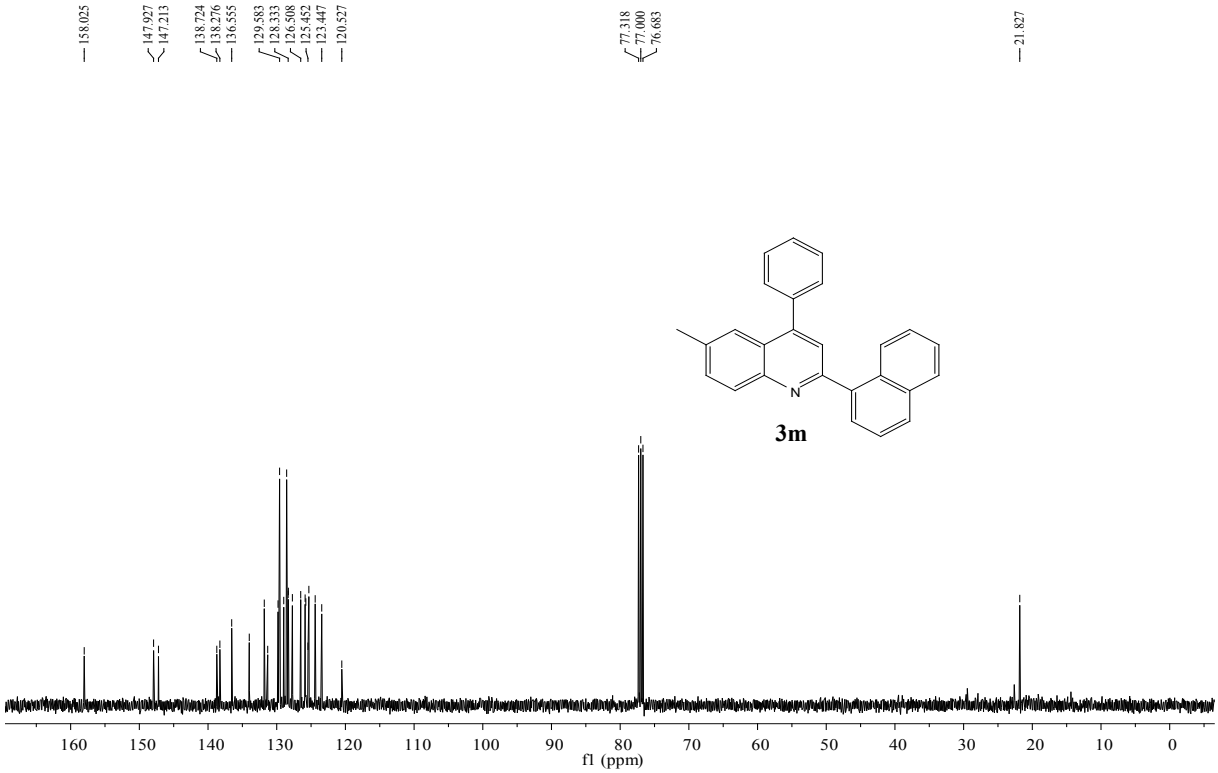

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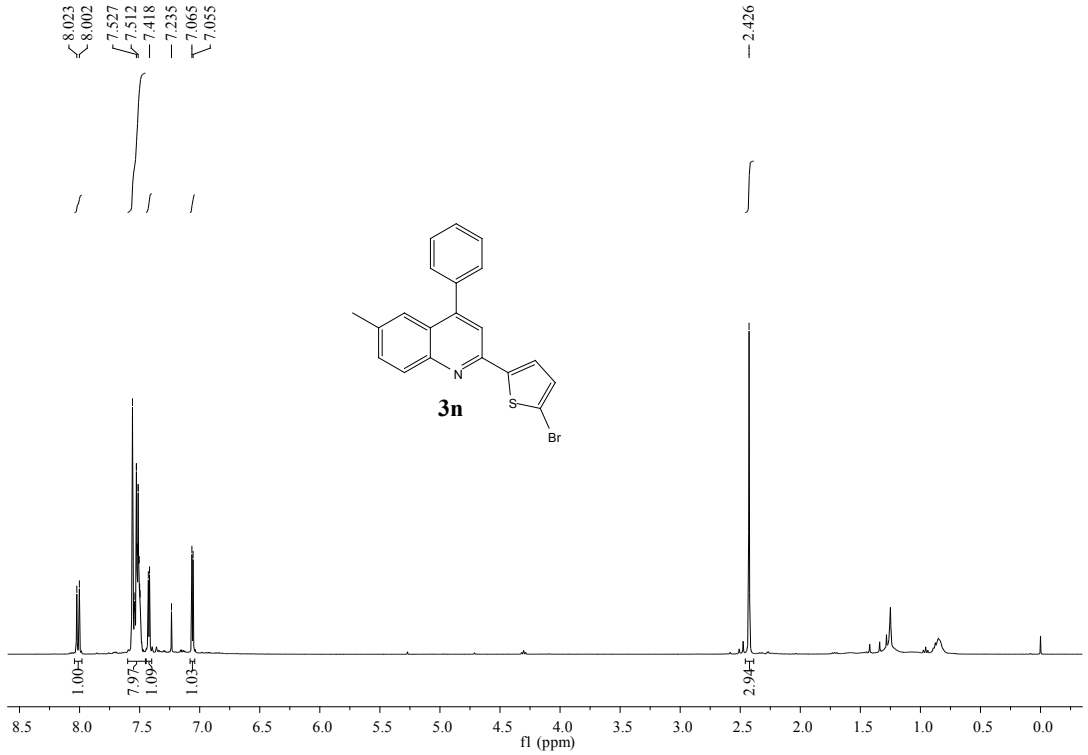

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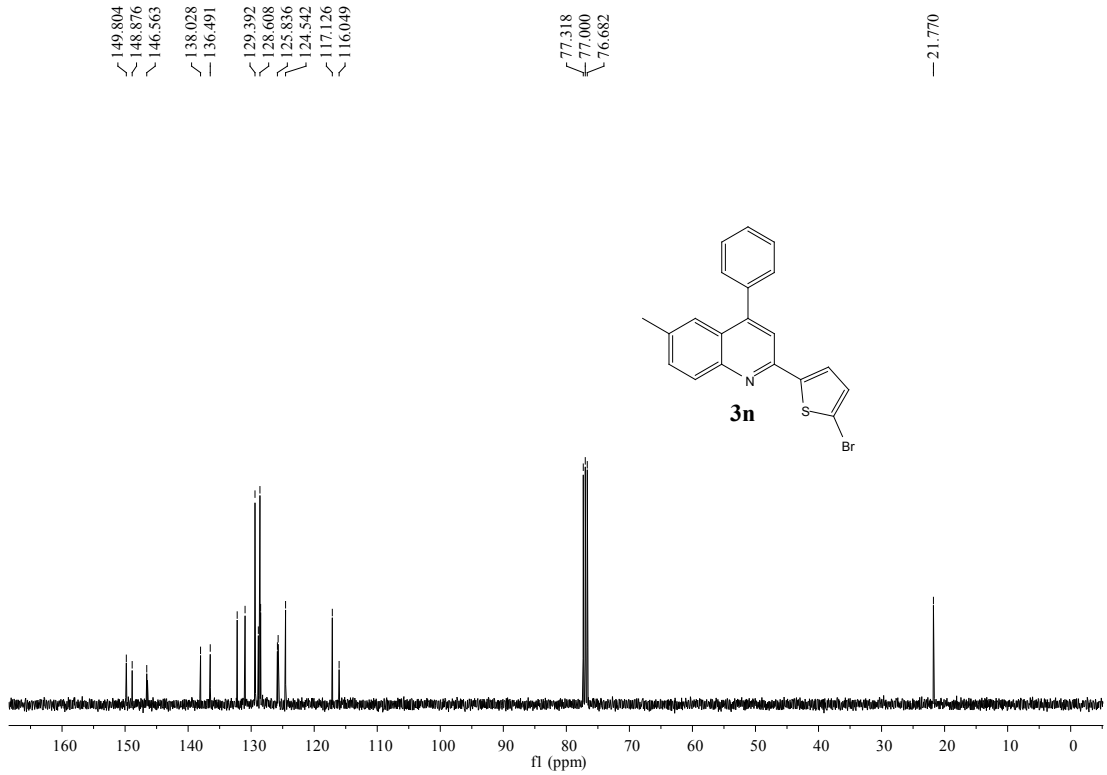

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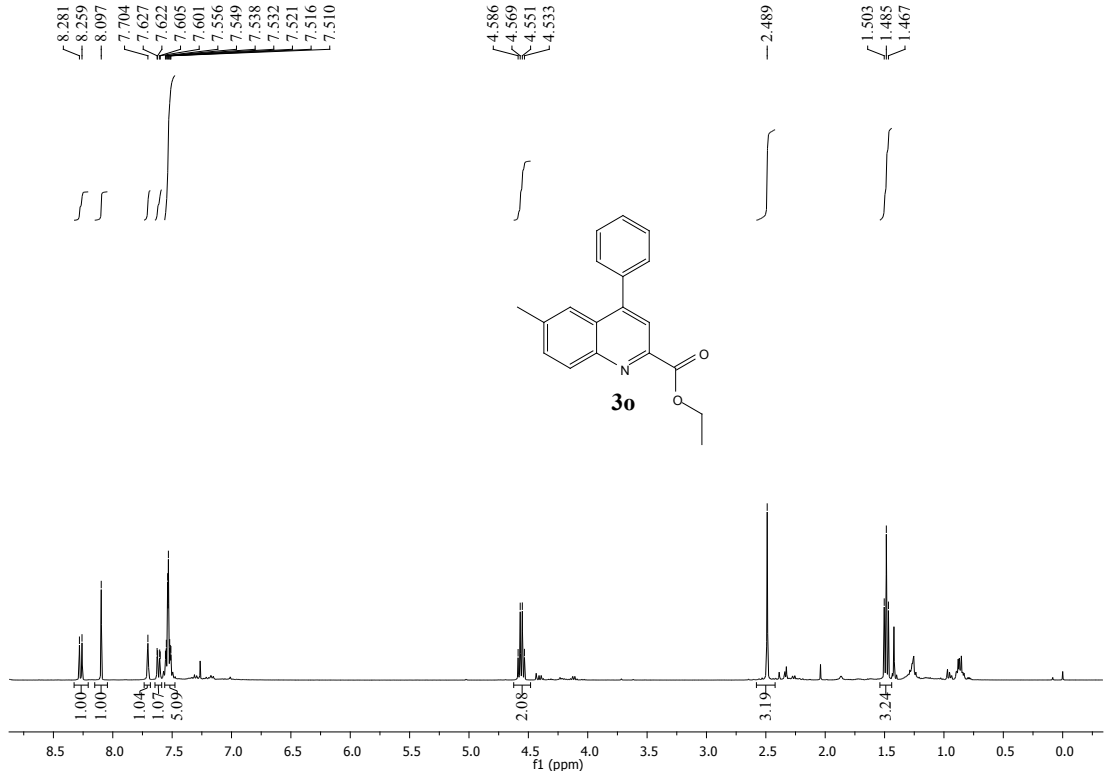

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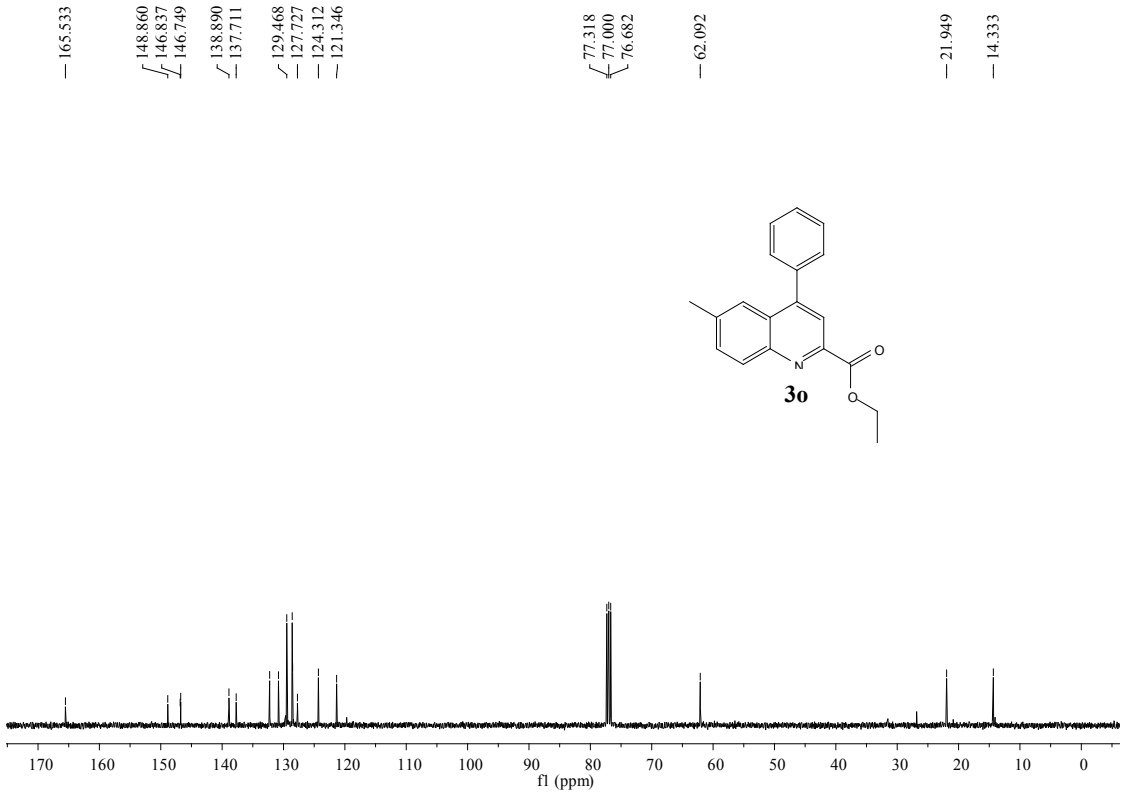

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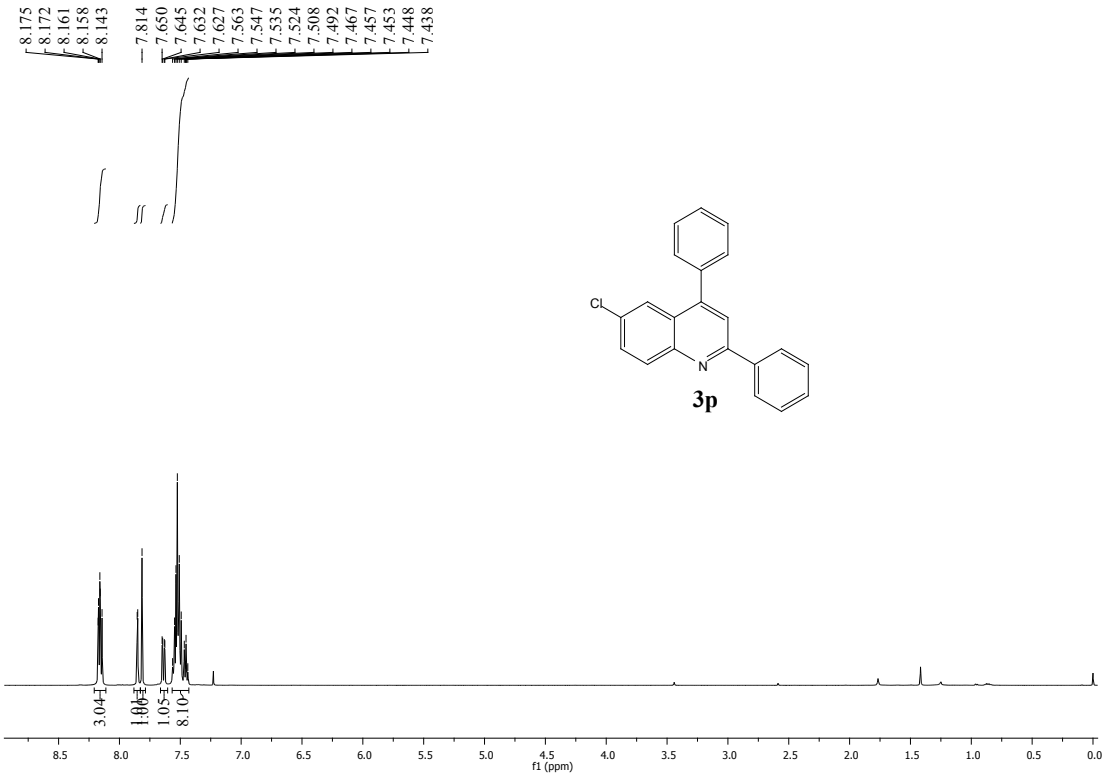
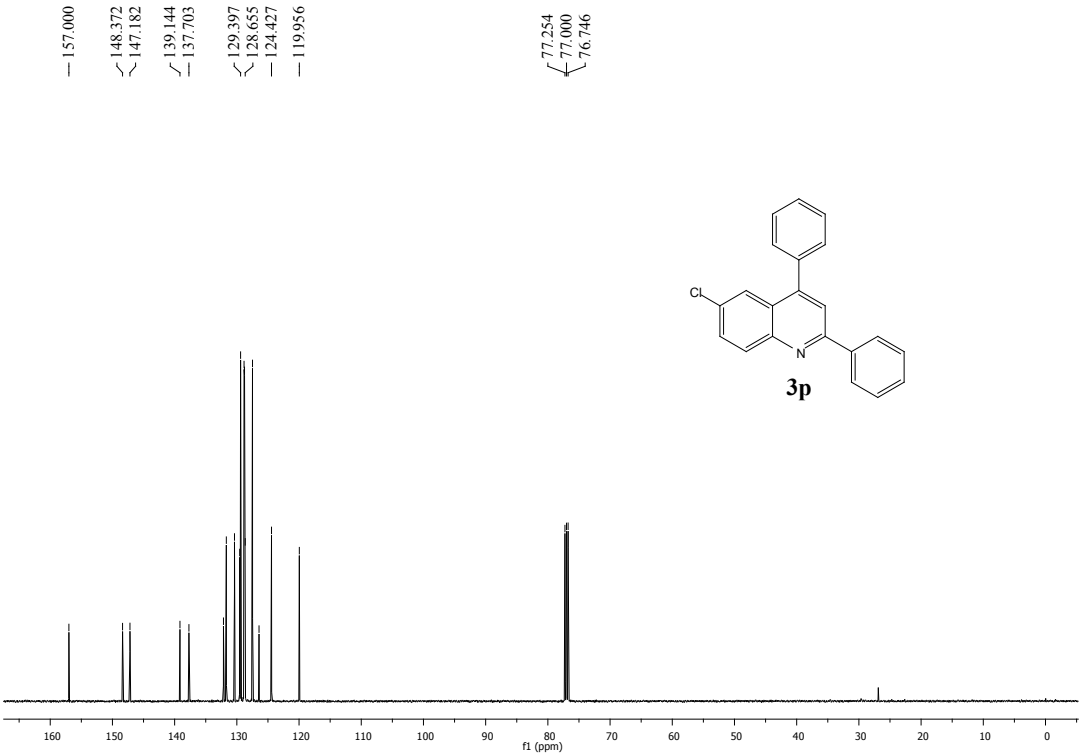


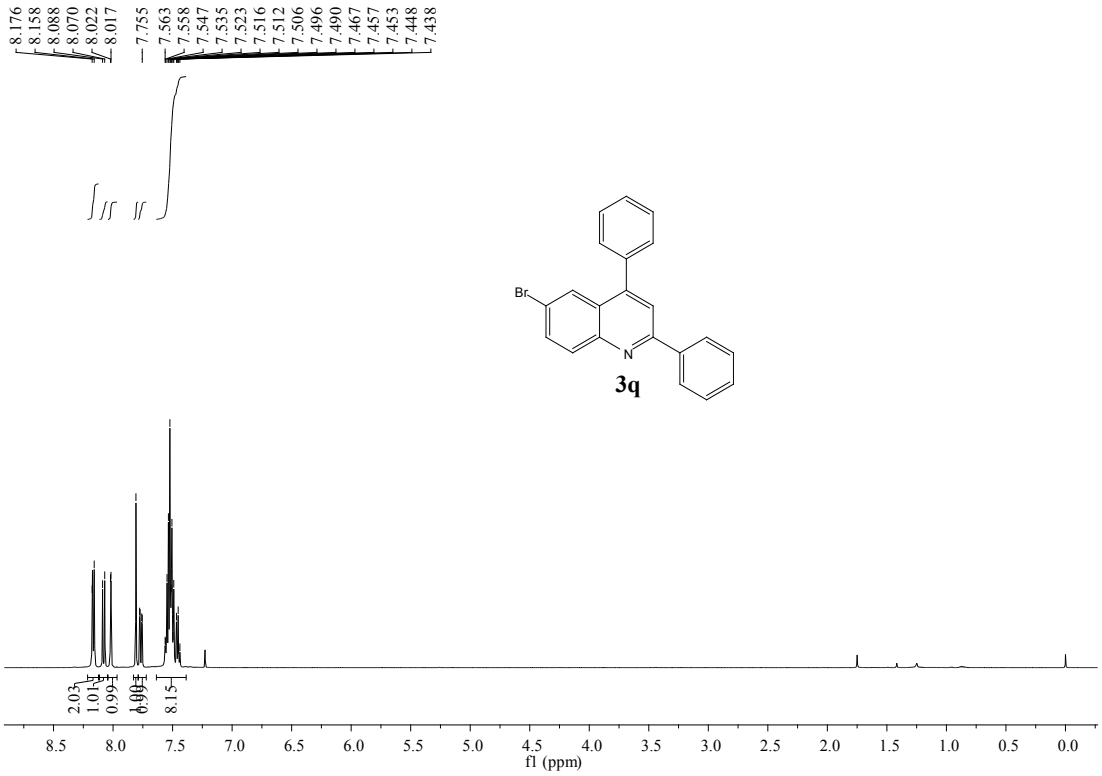
3p

^{13}C NMR (125 MHz, $CDCl_3$)



3p

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



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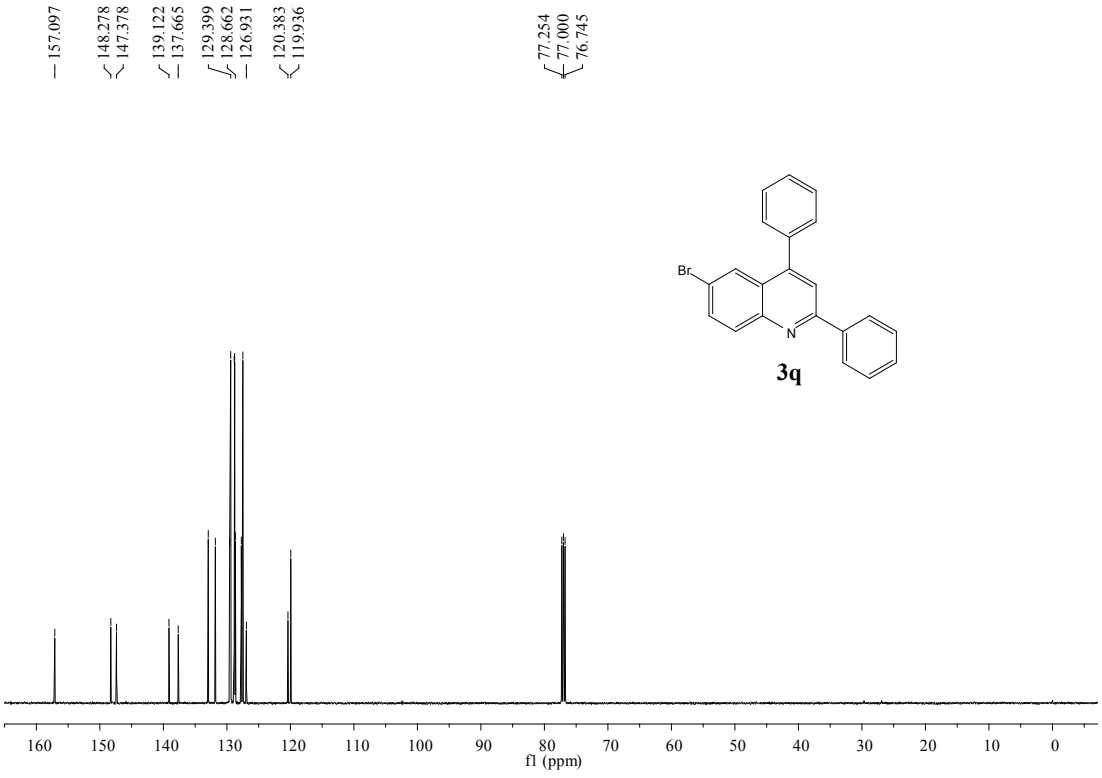

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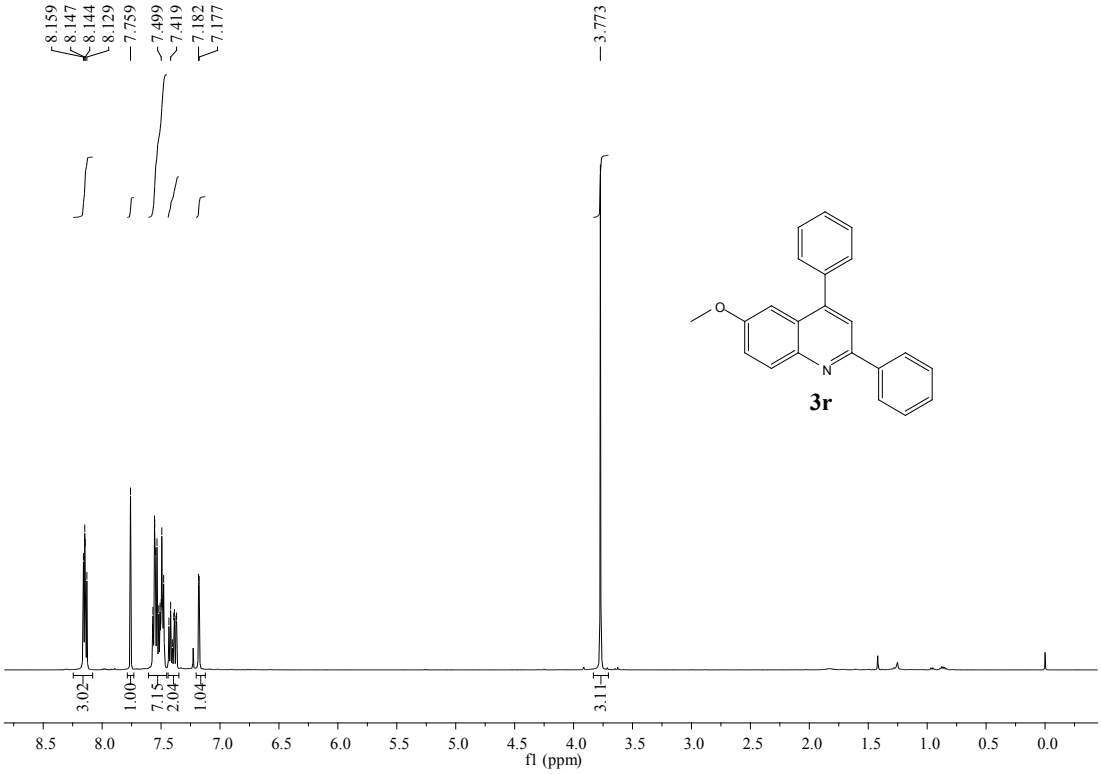

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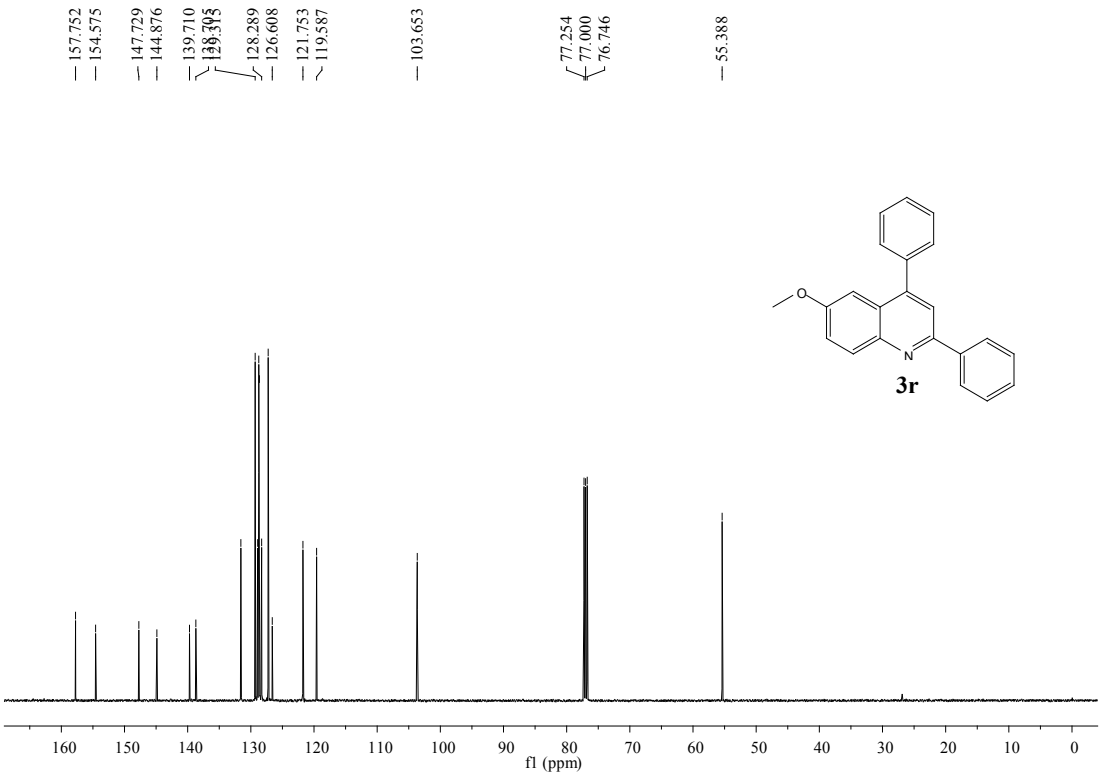

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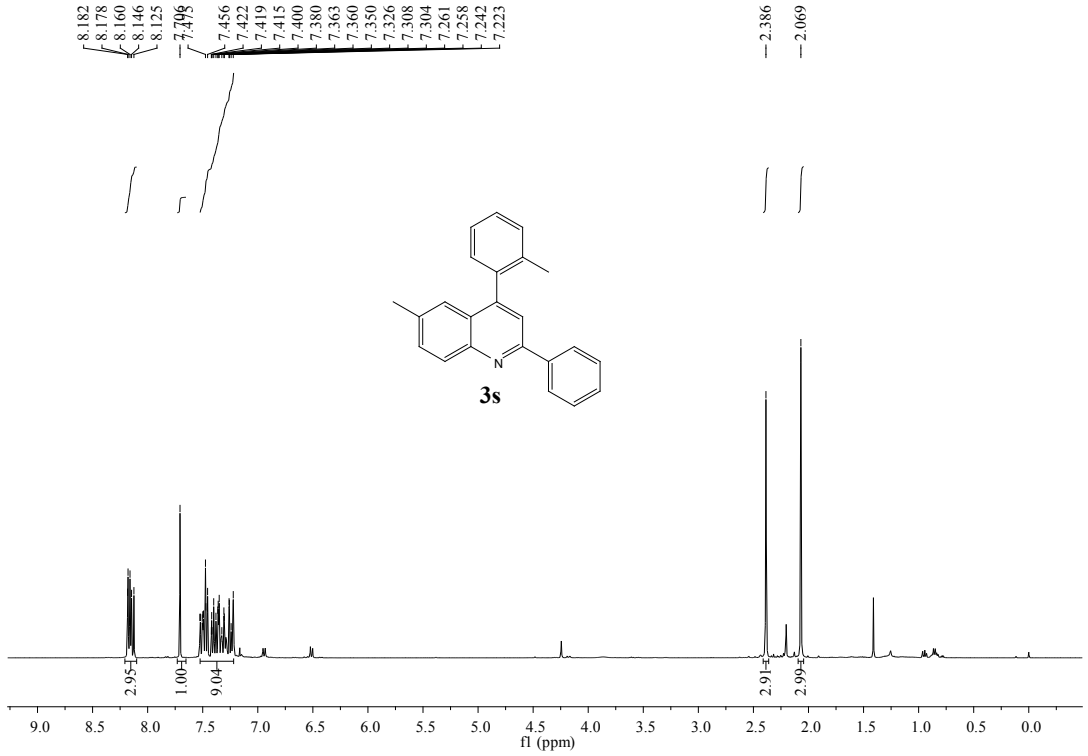

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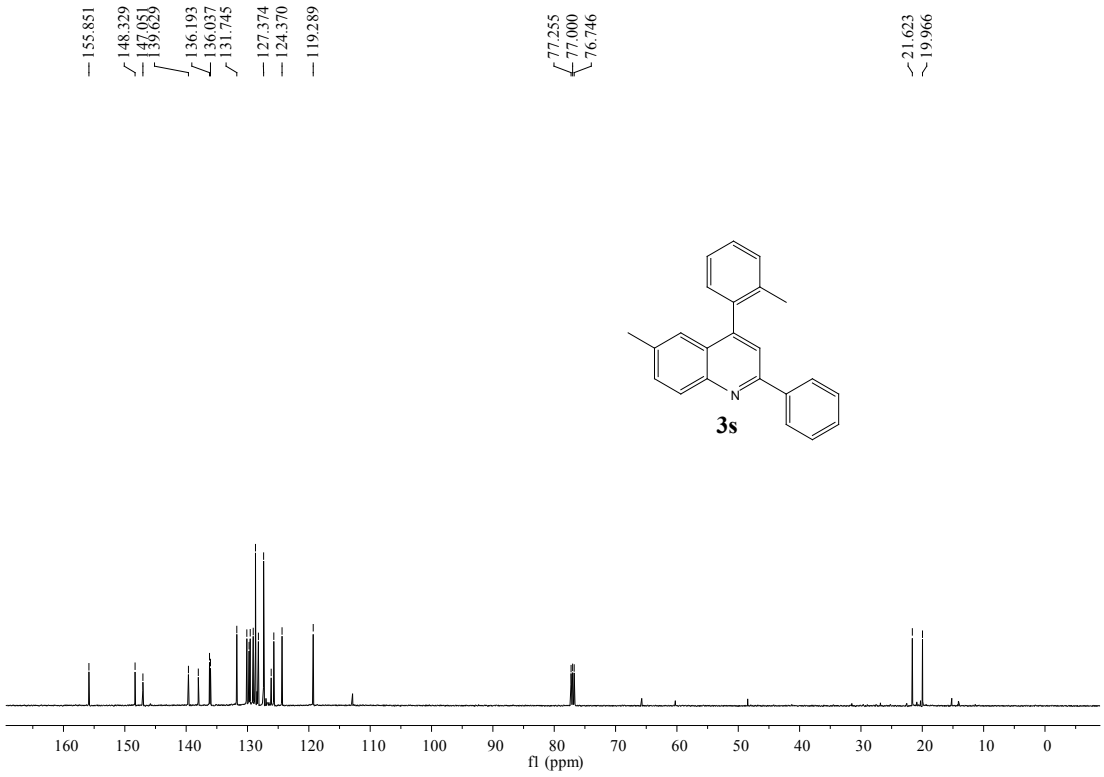
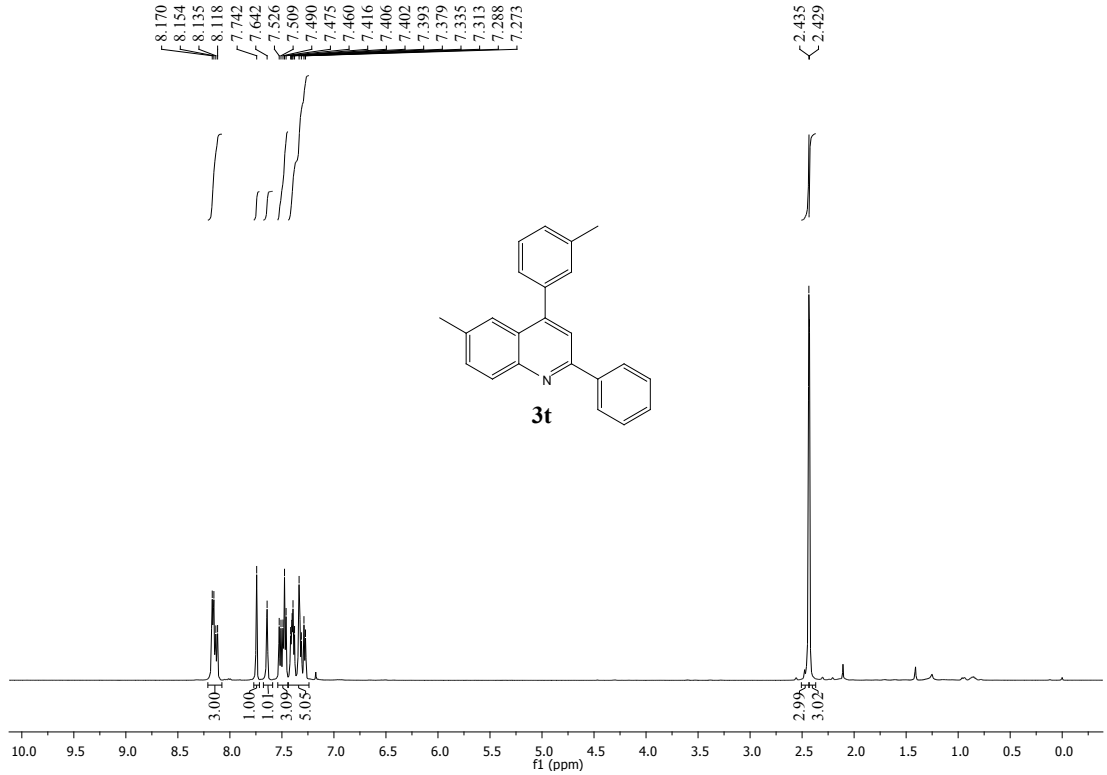
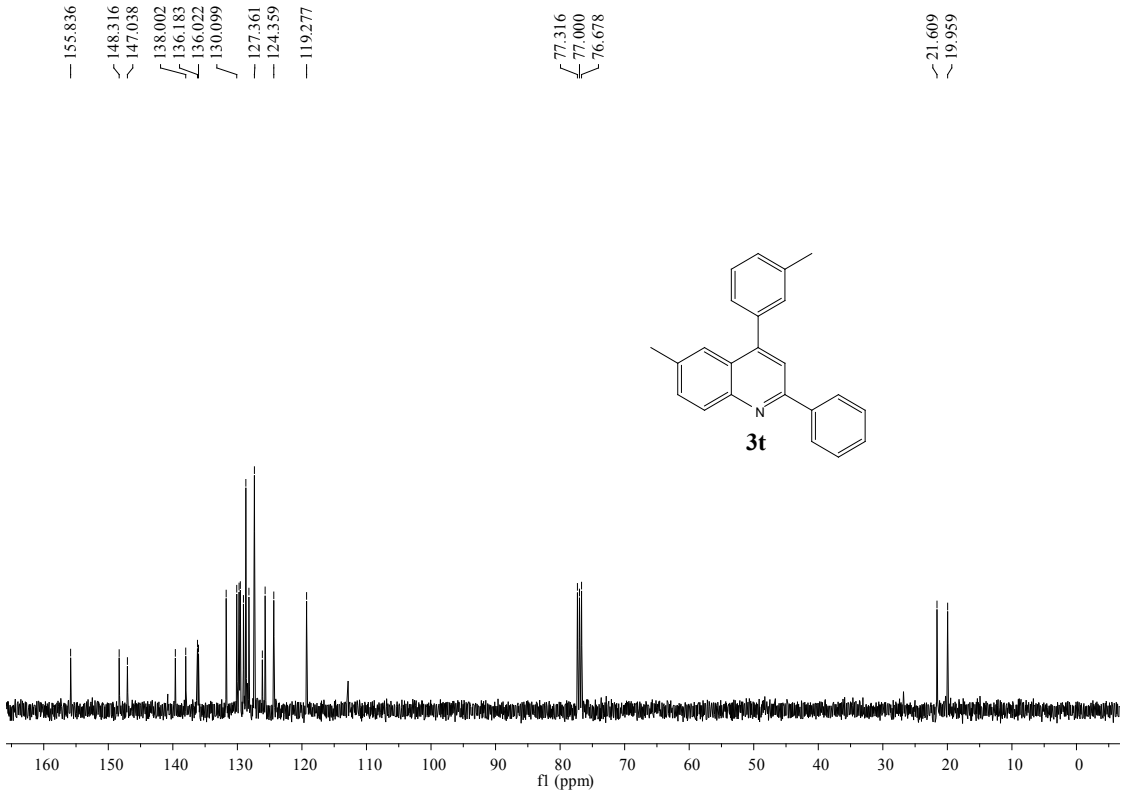


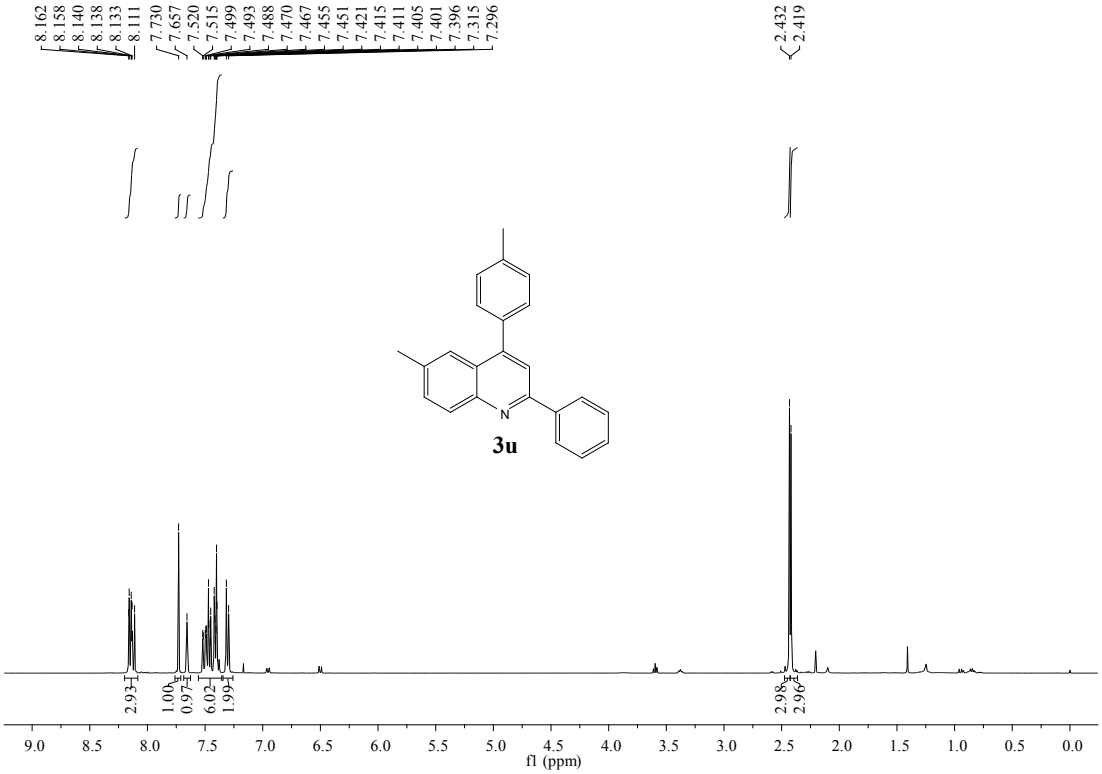
^{1}H NMR (400 MHz, $CDCl_3$)



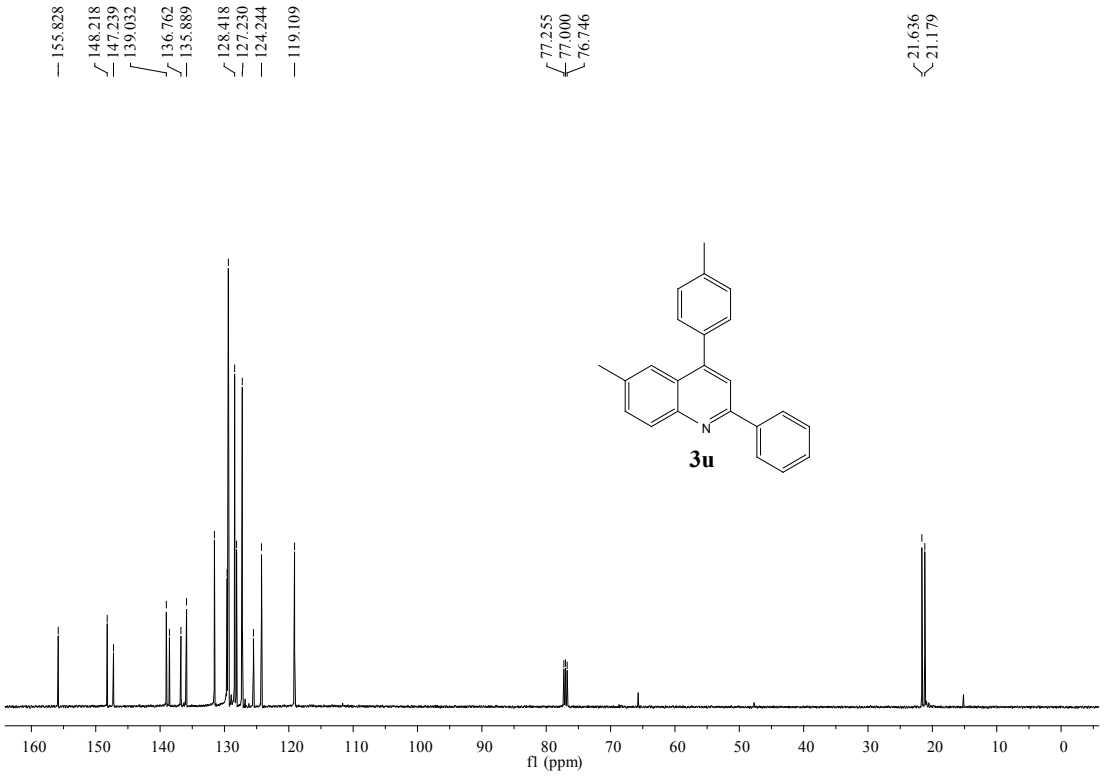
^{13}C NMR (100 MHz, $CDCl_3$)



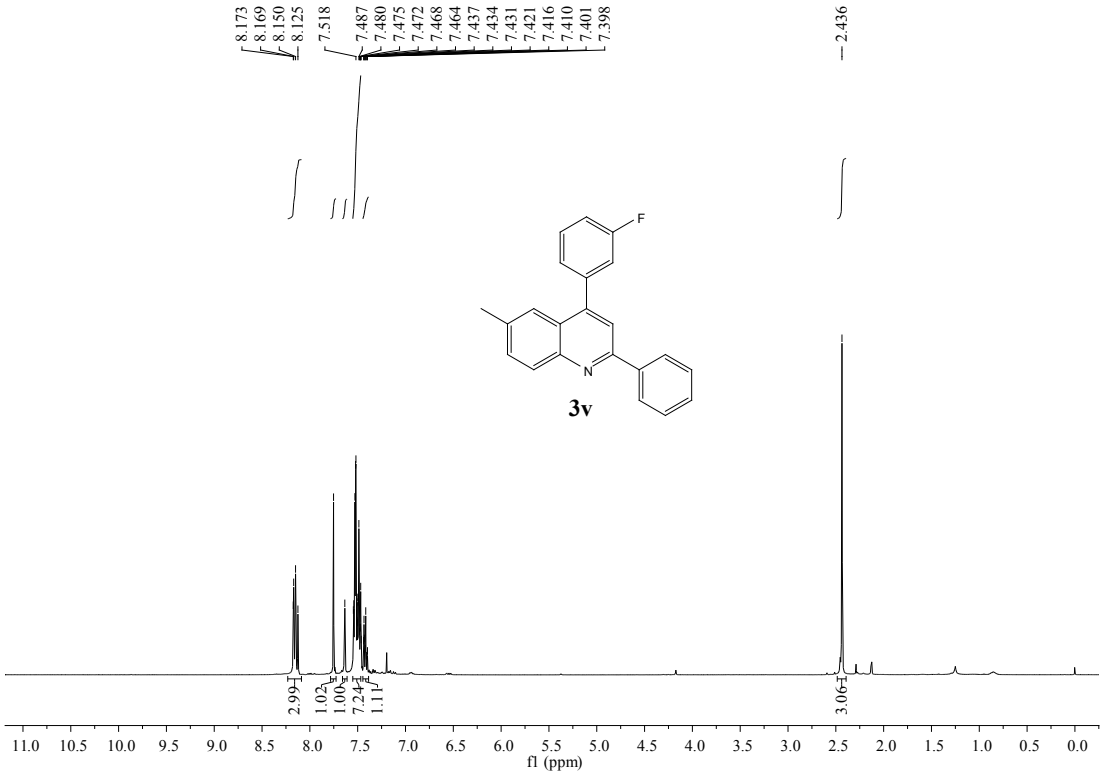
^{1}H NMR (400 MHz, $CDCl_3$)



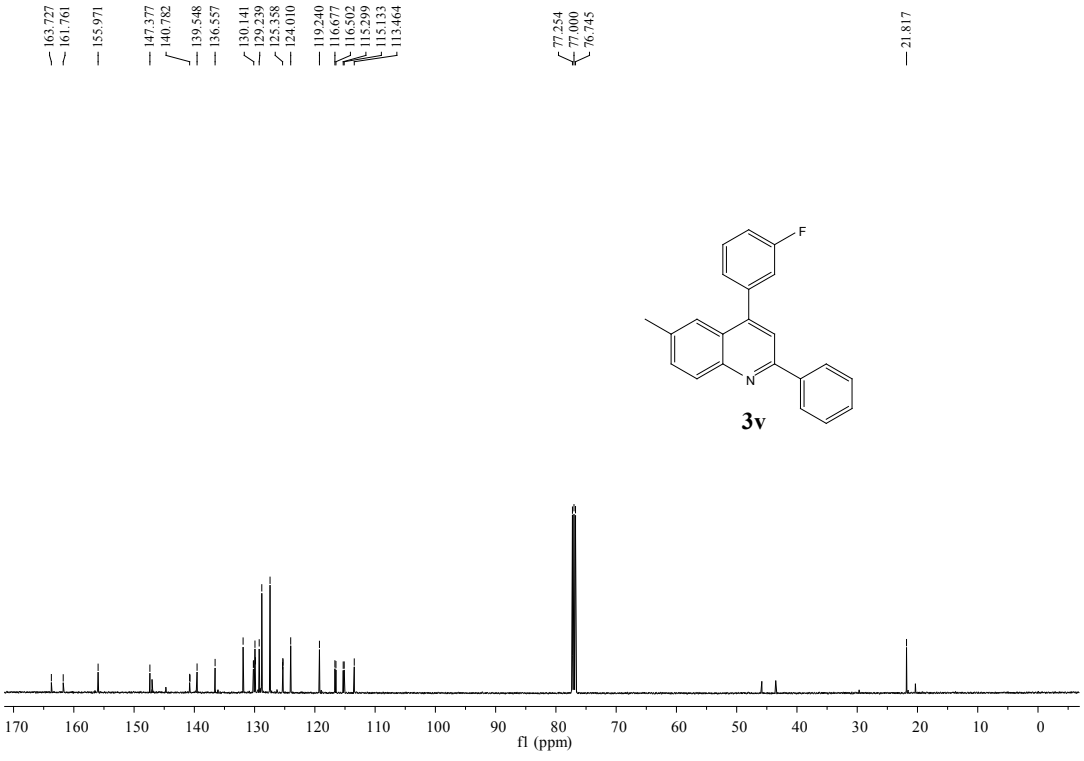
^{13}C NMR (125 MHz, $CDCl_3$)



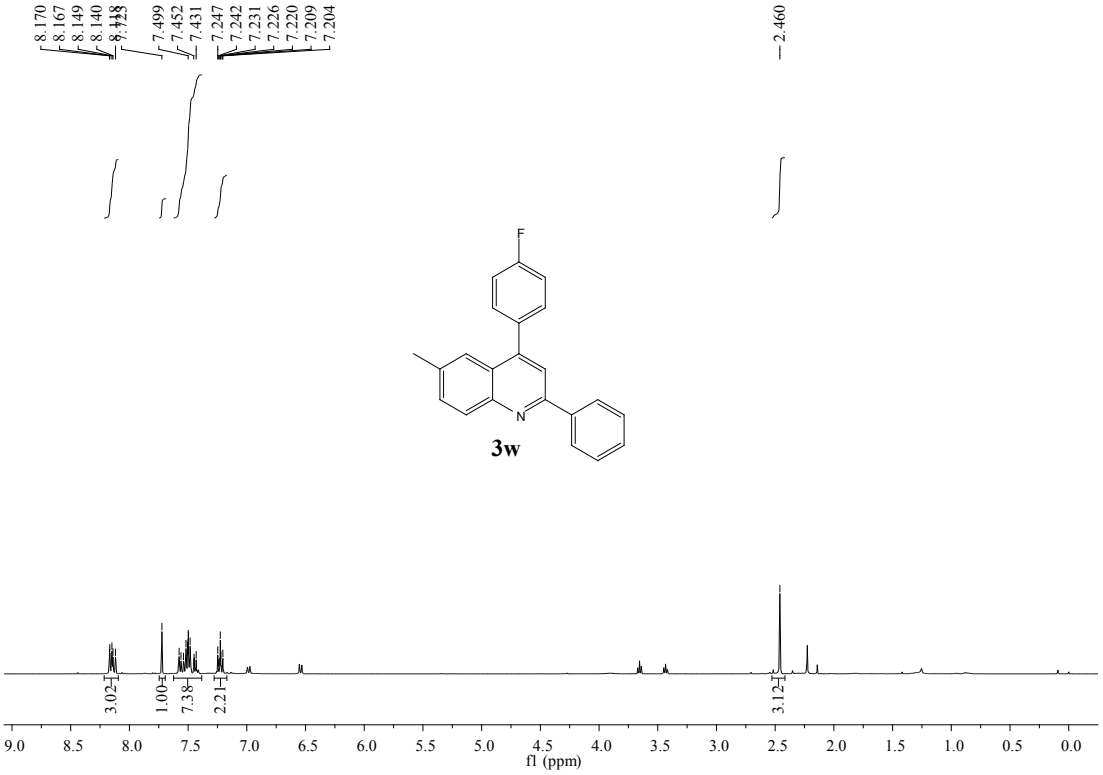
^{1}H NMR (400 MHz, $CDCl_3$)



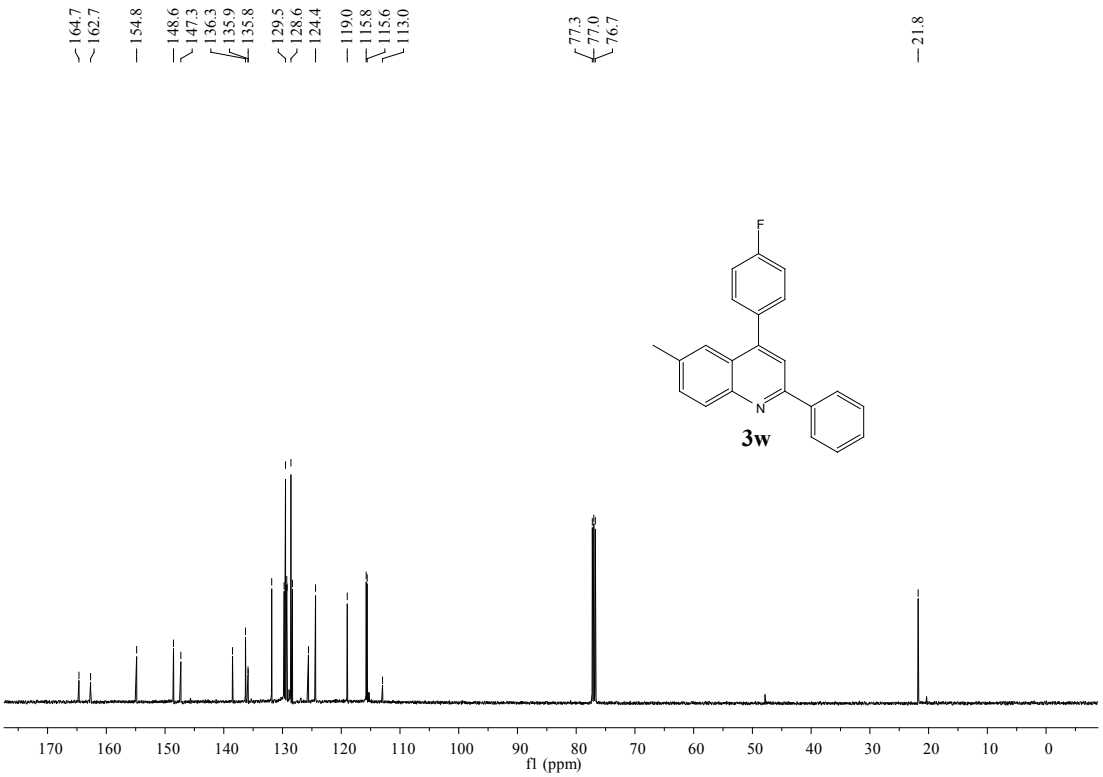
^{13}C NMR (125 MHz, $CDCl_3$)



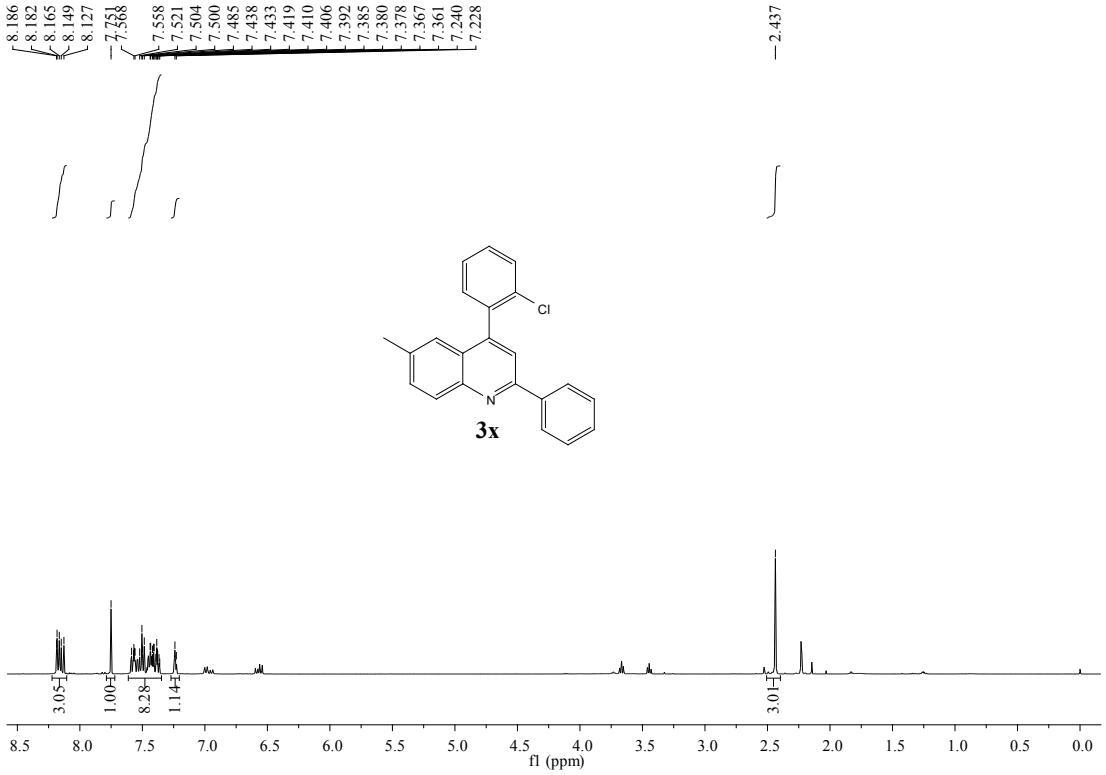
^{1}H NMR (400 MHz, $CDCl_3$)



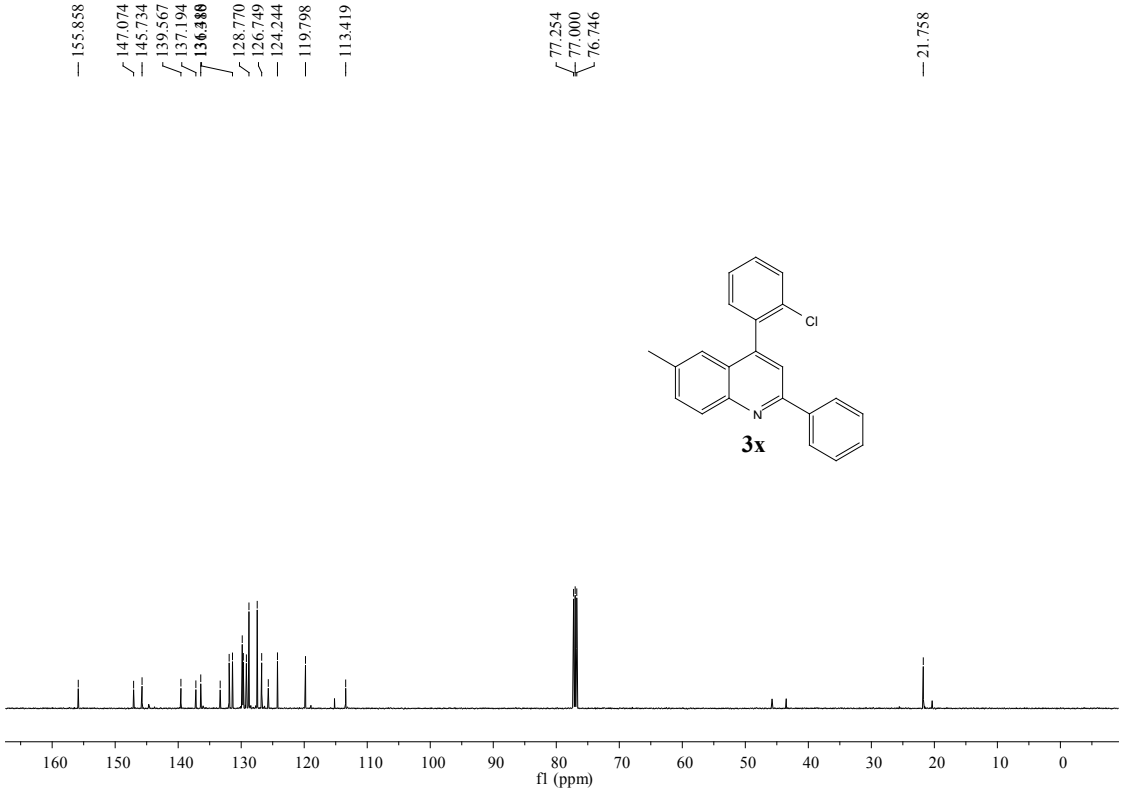
^{13}C NMR (125 MHz, $CDCl_3$)



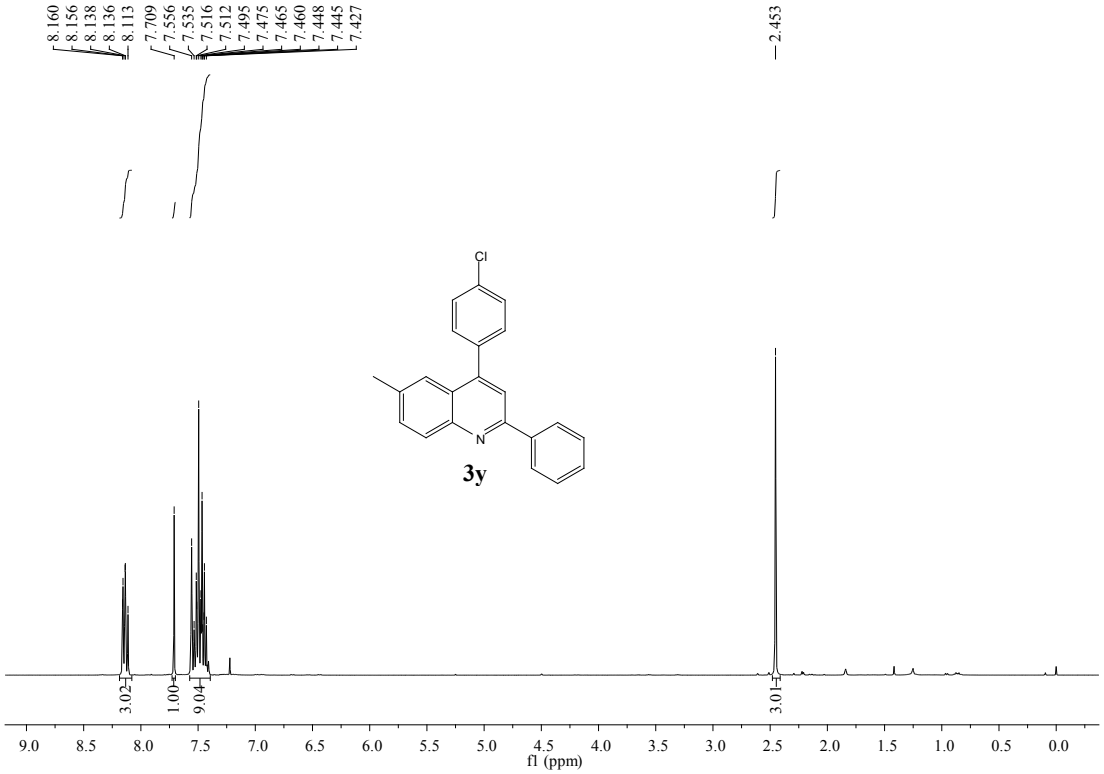
^{1}H NMR (400 MHz, $CDCl_3$)



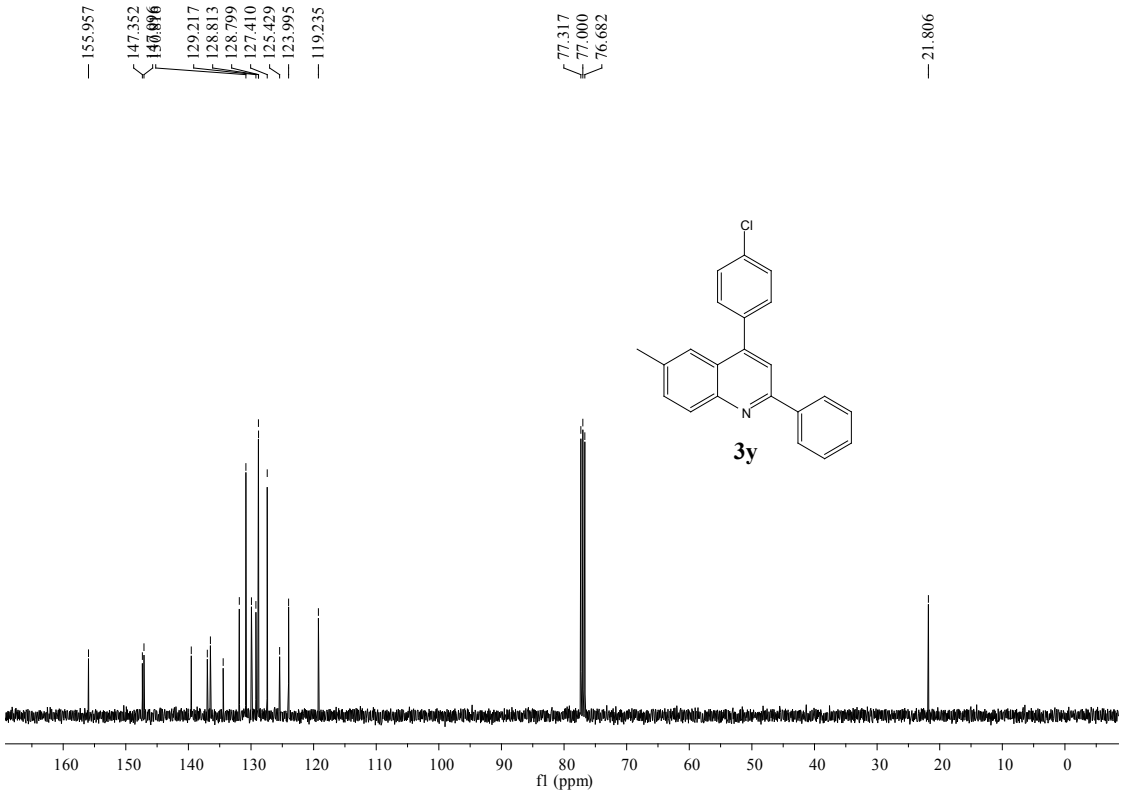
^{13}C NMR (125 MHz, $CDCl_3$)



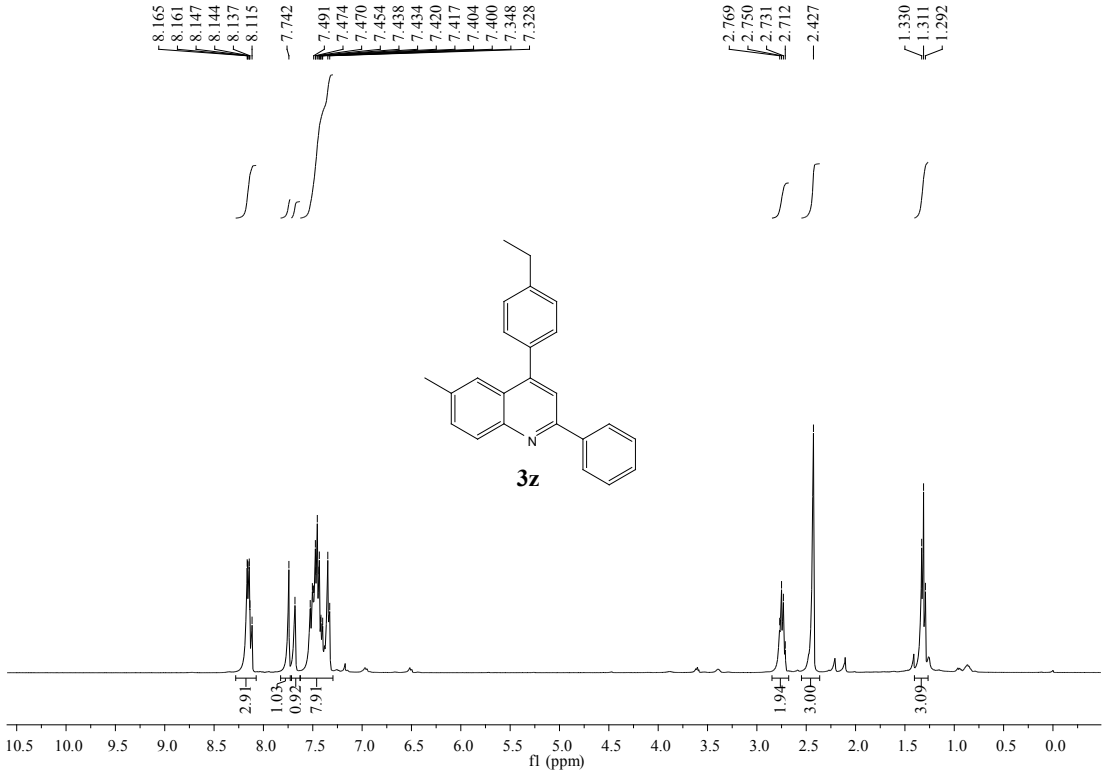
^{1}H NMR (400 MHz, $CDCl_3$)



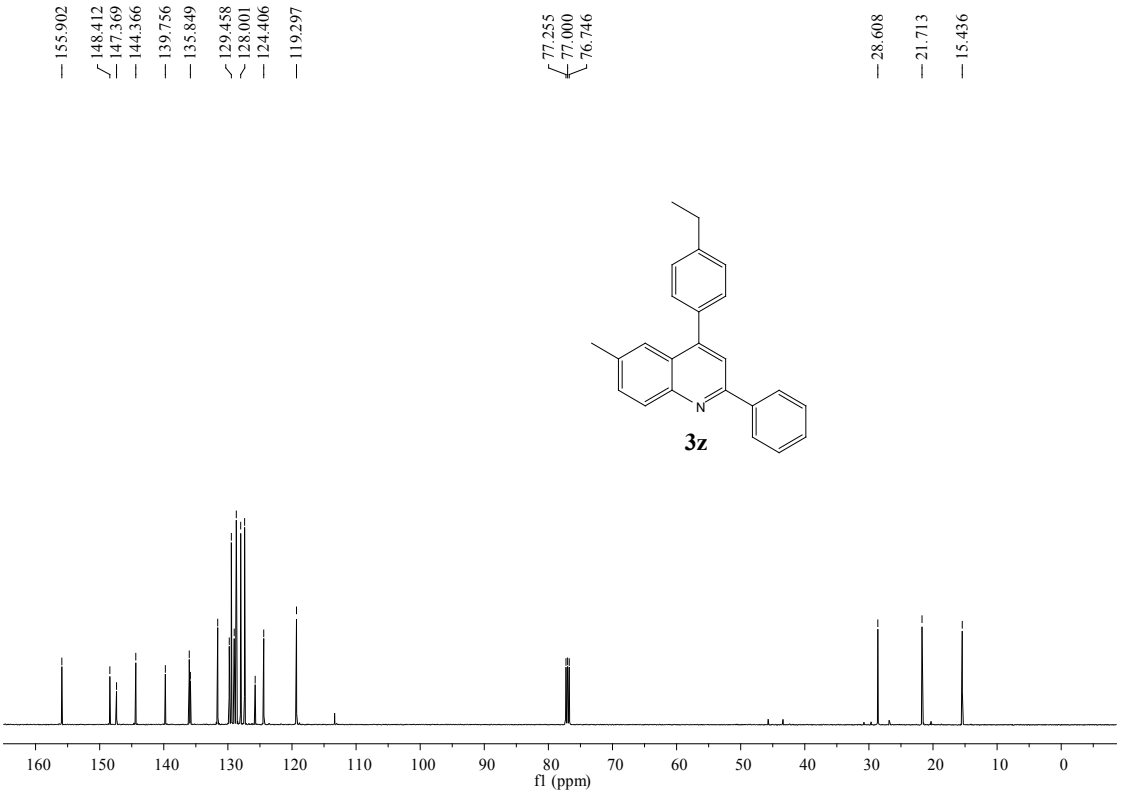
^{13}C NMR (100 MHz, $CDCl_3$)



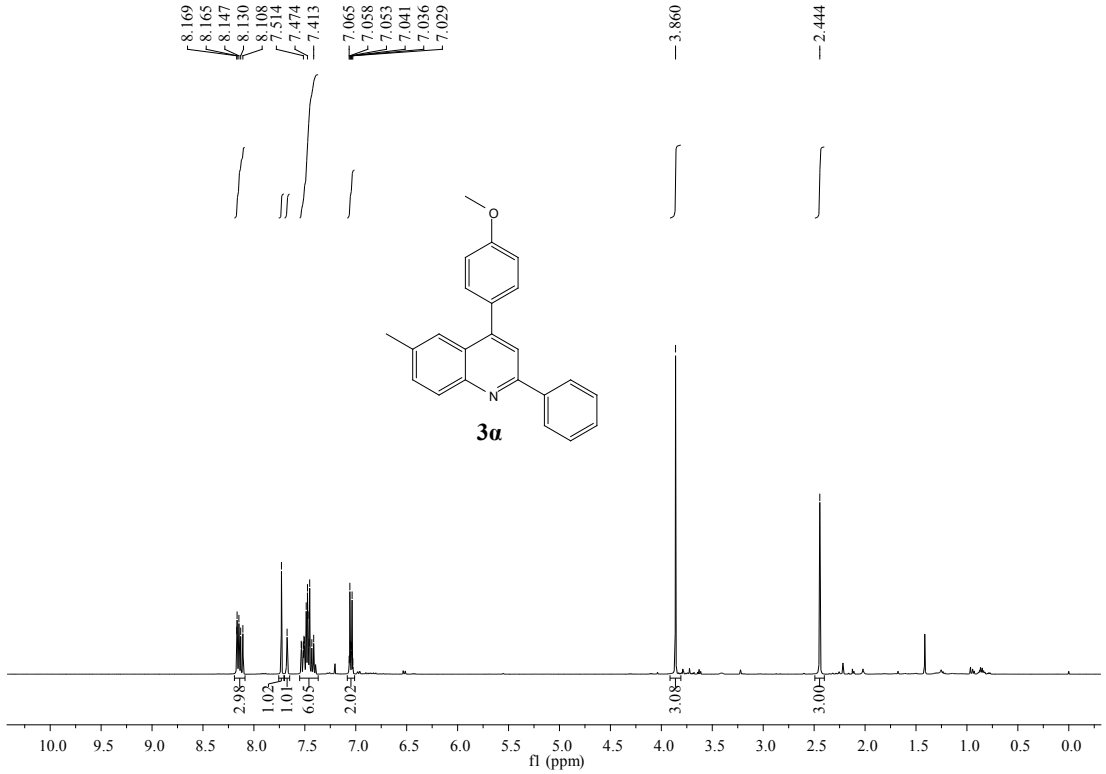
^{1}H NMR (400 MHz, $CDCl_3$)



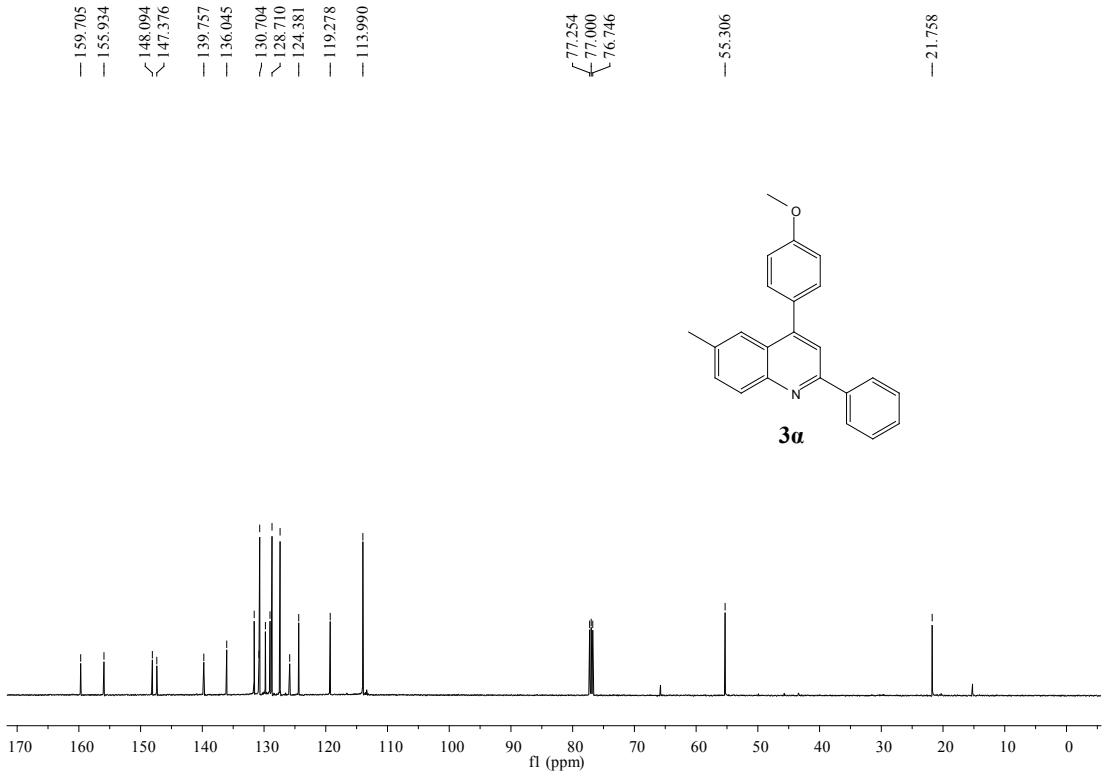
^{13}C NMR (125 MHz, $CDCl_3$)



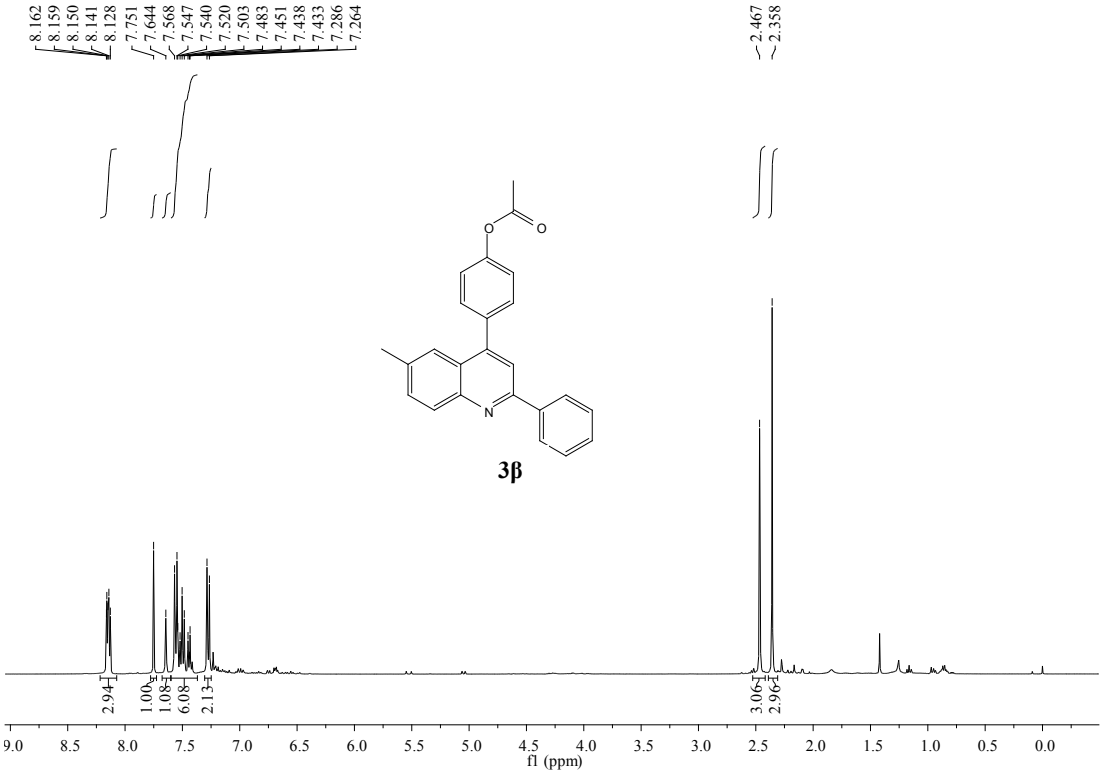
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

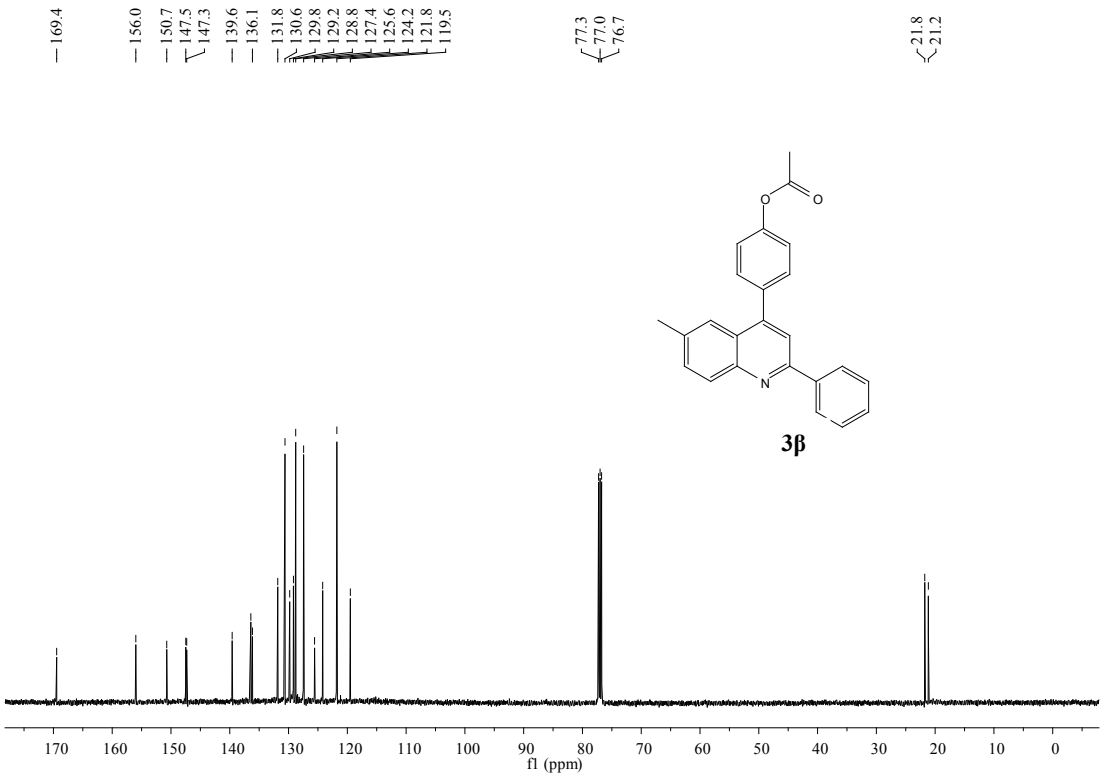


^{1}H NMR (400 MHz, $CDCl_3$)



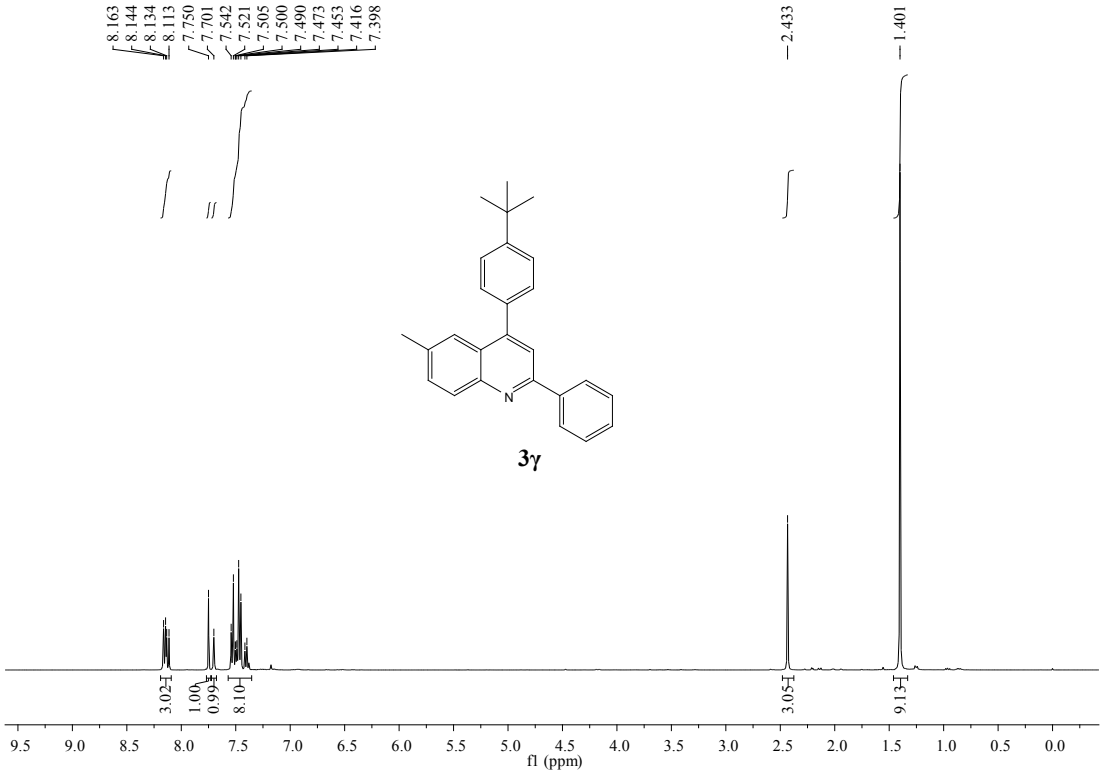
3β

^{13}C NMR (125 MHz, $CDCl_3$)

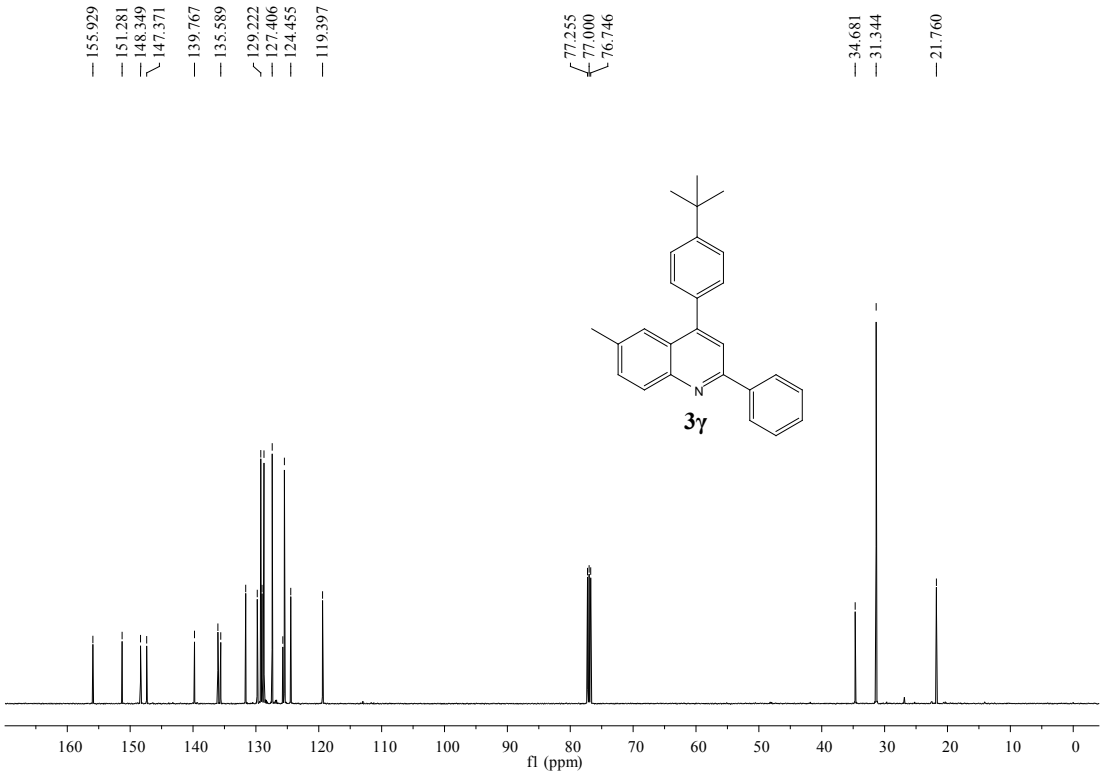


3β

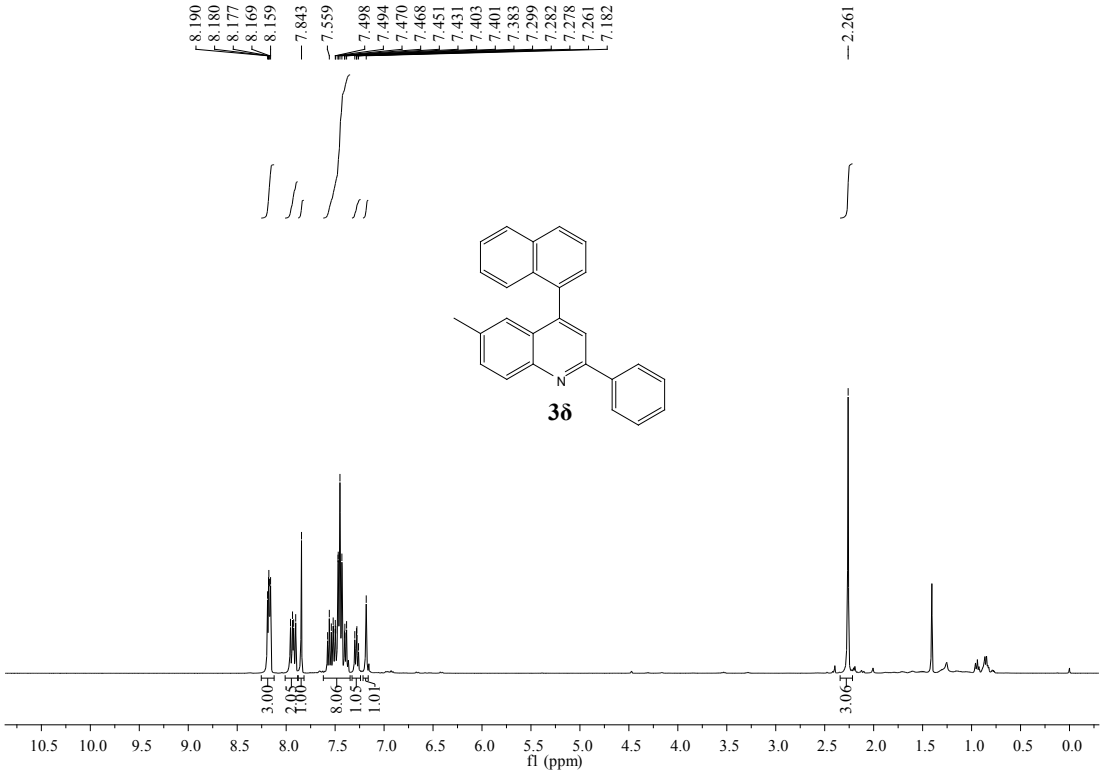
^{1}H NMR (400 MHz, $CDCl_3$)



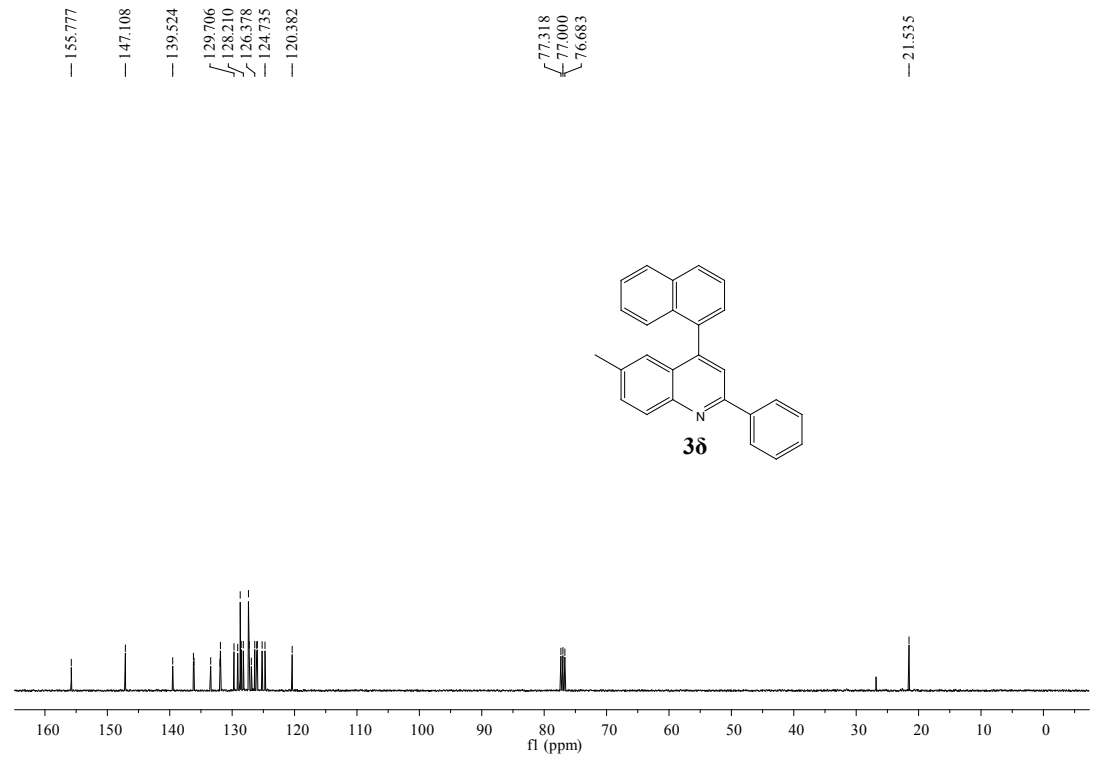
^{13}C NMR (125 MHz, $CDCl_3$)



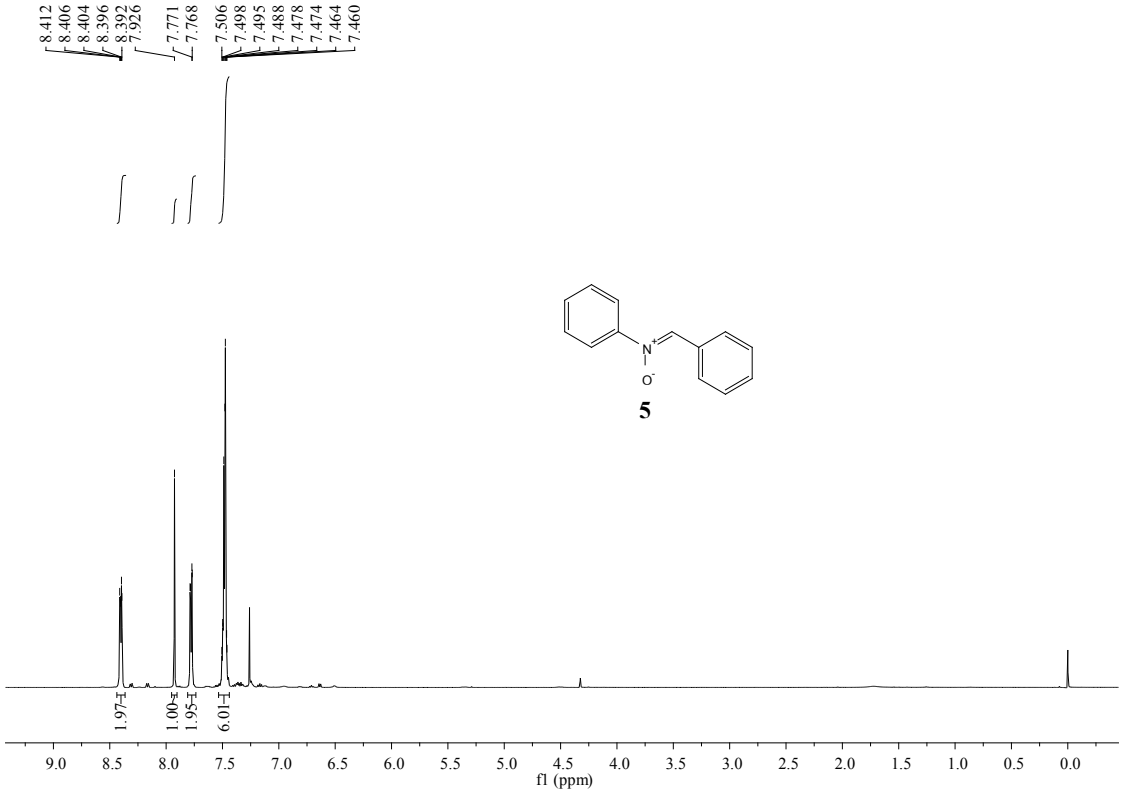
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

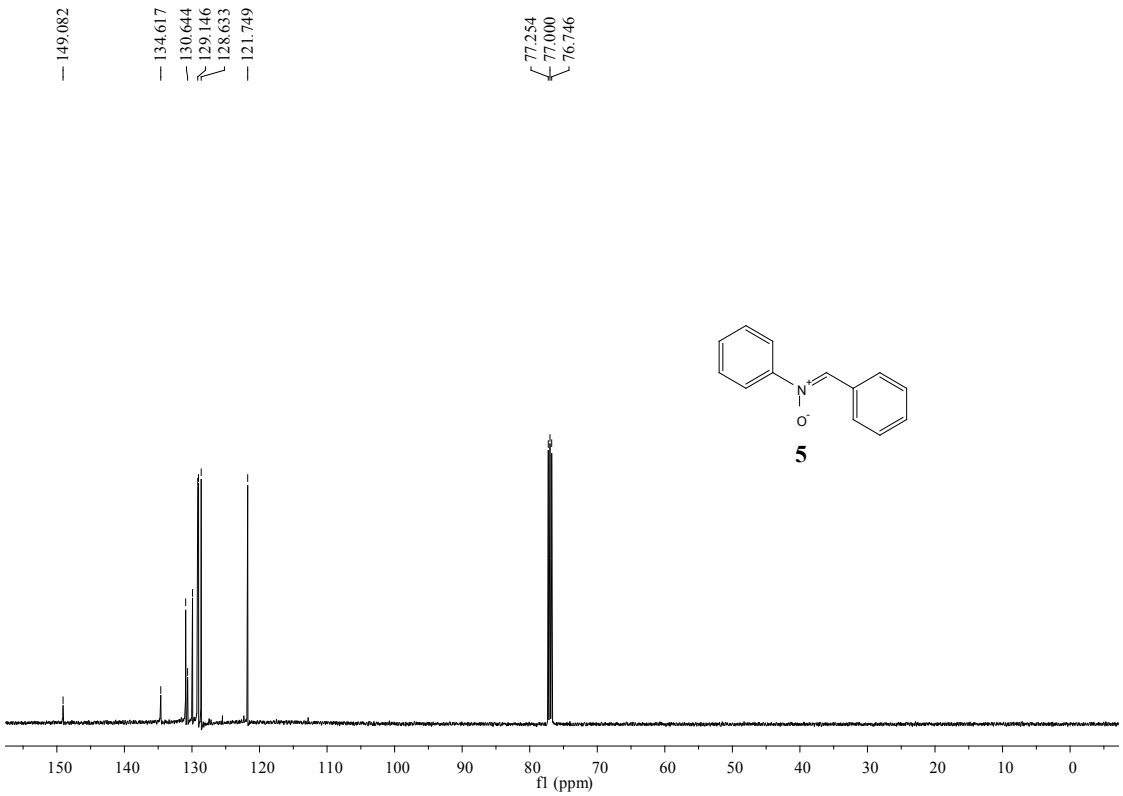


^{1}H NMR (400 MHz, $CDCl_3$)



5

^{13}C NMR (125 MHz, $CDCl_3$)



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