Supporting Information

Copper-catalyzed rapid C-H nitration of 8-aminoquinolines by using sodium nitrite as the nitro source under mild conditions

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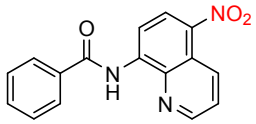
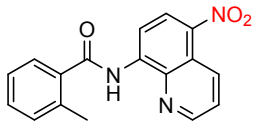
1. Characterization of the Products

N-(5-nitroquinolin-8-yl)benzamide (2a)



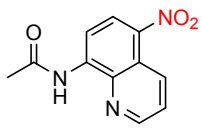
Obtained as a yellow solid in 86% yield; mp 215-216 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.10 (s, 1H), 9.32 (dd, *J* = 8.8, 1.6 Hz, 1H), 9.03 (d, *J* = 8.8, 3.7 Hz, 1H), 8.97 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.62 (d, *J* = 8.8, 4.1 Hz, 1H), 8.10 (dt, *J* = 3.5, 2.4 Hz, 2H), 7.77 (dd, *J* = 8.8, 4.2 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.62 – 7.58 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.75, 149.11, 146.56, 140.88, 137.78, 134.14, 133.47, 132.68, 129.06, 127.96, 127.49, 124.77, 121.86, 113.76; HRMS (ESI$^+$): Calcd for $C_{16}H_{11}N_3O_3$: $[M+H]^+$ 294.0873, Found 294.0882.

2-methyl-*N*-(5-nitroquinolin-8-yl)benzamide (2b)



Obtained as a yellow solid in 84% yield; mp 192-193 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.51 (s, 1H), 9.22 (dd, *J* = 8.8, 1.5 Hz, 1H), 8.94 (d, *J* = 8.8 Hz, 1H), 8.81 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.54 (d, *J* = 8.8 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.37 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.29 (dd, *J* = 9.5, 7.9 Hz, 2H), 2.54 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.32, 149.05, 140.96, 138.75, 137.63, 137.24, 135.45, 133.35, 131.73, 131.08, 127.85, 127.31, 126.21, 124.69, 121.82, 113.66, 20.32; HRMS (ESI$^+$): Calcd for $C_{17}H_{13}N_3O_3$: $[M+H]^+$ 308.1017, Found 308.1019.

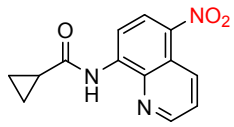
N-(5-nitroquinolin-8-yl)acetamide (2c)



Obtained as a yellow solid in 63% yield; mp 168-169 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.12 (s, 1H), 9.26 (dd, *J* = 8.8, 1.5 Hz, 1H), 8.89 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.83 – 8.80 (d,*J* = 8.8 Hz, 1H), 8.52 (d, *J* = 8.8 Hz, 1H), 7.72 (dd, *J* = 8.8, 4.2 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.26, 148.90, 140.67, 138.52, 137.16,

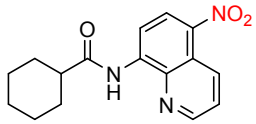
133.29, 127.80, 124.63, 121.71, 113.52, 22.70; HRMS (ESI$^+$): Calcd for $C_{11}H_9N_3O_3$: $[M+H]^+$ 232.0717, Found 232.0707.

***N*-(5-nitroquinolin-8-yl)cyclopropanecarboxamide (2d)**



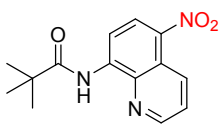
Obtained as a yellow solid in 68% yield; mp 143-144 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 9.29 (dd, J = 8.8, 1.5 Hz, 1H), 8.91 (dd, J = 4.2, 1.5 Hz, 1H), 8.81 (d, J = 8.8 Hz, 1H), 8.54 (d, J = 8.8 Hz, 1H), 7.73 (dd, J = 8.8, 4.2 Hz, 1H), 1.89 – 1.82 (m, 1H), 1.23 – 1.19 (m, 2H), 1.03 – 0.98 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.95, 148.81, 140.84, 138.28, 137.10, 133.41, 128.00, 124.62, 121.84, 113.55, 16.56, 9.05; HRMS (ESI$^+$): Calcd for $C_{13}H_{11}N_3O_3$: $[M+H]^+$ 258.0873, Found 258.0870.

***N*-(5-nitroquinolin-8-yl)cyclohexanecarboxamide (2e)**



Obtained as a yellow solid in 71% yield; mp 121-122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 9.27 (dd, J = 8.8, 1.3 Hz, 1H), 8.91 (dd, J = 4.1, 1.3 Hz, 1H), 8.85 (d, J = 8.8 Hz, 1H), 8.54 (d, J = 8.8 Hz, 1H), 7.72 (dd, J = 8.8, 4.2 Hz, 1H), 2.52 (tt, J = 11.7, 3.5 Hz, 1H), 2.10 (dd, J = 13.5, 1.7 Hz, 2H), 1.94 – 1.86 (m, 2H), 1.76 (dd, J = 9.2, 3.2 Hz, 1H), 1.70 – 1.58 (m, 3H), 1.46 – 1.36 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.35, 148.89, 140.96, 138.34, 137.43, 133.32, 127.94, 124.60, 121.77, 113.55, 46.91, 29.59, 25.68, 25.63; HRMS (ESI$^+$): Calcd for $C_{16}H_{17}N_3O_3$: $[M+H]^+$ 300.1343, Found 300.1342.

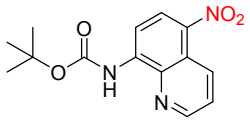
***N*-(5-nitroquinolin-8-yl)pivalamide (2f)**



Obtained as a yellow solid in 74% yield; mp 172-173 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.60 (s, 1H), 9.28 (dd, J = 8.8, 1.6 Hz, 1H), 8.92 (dd, J = 4.2, 1.6 Hz, 1H), 8.85 (d,

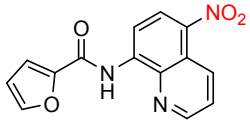
J = 8.8 Hz, 1H), 8.55 (d, *J* = 8.8 Hz, 1H), 7.72 (dd, *J* = 8.8, 4.2 Hz, 1H), 1.44 (s, 9H).^{13}C NMR (126 MHz, $CDCl_3$) δ 177.80, 149.01, 141.03, 138.36, 137.73, 133.34, 127.96, 124.59, 121.78, 113.39, 40.68, 27.57; HRMS (ESI$^+$): Calcd for $C_{14}H_{15}N_3O_3$: $[M+H]^+$ 274.1186, Found 274.1187.

tert-butyl (5-nitroquinolin-8-yl)carbamate (2g)



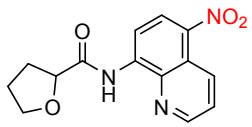
Obtained as a yellow solid in 67% yield; mp 143-144 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.40 (s, 1H), 9.26 (dd, *J* = 8.8, 1.4 Hz, 1H), 8.87 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.53 (d, *J* = 8.9 Hz, 1H), 8.46 (d, *J* = 8.9 Hz, 1H), 7.69 (dd, *J* = 8.8, 4.1 Hz, 1H), 1.61 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.08, 148.68, 141.94, 137.42, 136.95, 133.18, 128.00, 124.62, 121.88, 111.43, 81.87, 28.27; HRMS (ESI$^+$): Calcd for $C_{14}H_{15}N_3O_3$: $[M+H]^+$ 386.0135, Found 386.0135.

***N*-(5-nitroquinolin-8-yl)furan-2-carboxamide (2h)**



Obtained as a yellow solid in 61% yield; mp 232-233 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.11 (s, 1H), 9.30 (dd, *J* = 8.8, 1.4 Hz, 1H), 8.99 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.95 (d, *J* = 8.8 Hz, 1H), 8.59 (d, *J* = 8.8 Hz, 1H), 7.76 (dd, *J* = 8.8, 4.2 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.38 (d, *J* = 3.5 Hz, 1H), 6.64 (dd, *J* = 3.4, 1.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.49, 149.18, 147.61, 145.22, 140.54, 138.81, 137.68, 133.33, 127.79, 124.75, 121.85, 116.54, 113.79, 112.88; HRMS (ESI$^+$): Calcd for $C_{14}H_9N_3O_4$: $[M+H]^+$ 284.0666, Found 284.0665.

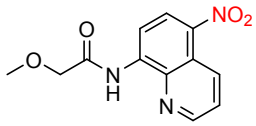
***N*-(5-nitroquinolin-8-yl)tetrahydrofuran-2-carboxamide (2i)**



Obtained as a yellow solid in 65% yield; mp 161-162 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.25 (s, 1H), 9.26 (dd, *J* = 8.8, 1.3 Hz, 1H), 9.00 – 8.94 (m, 1H), 8.88 (d, *J* = 8.8

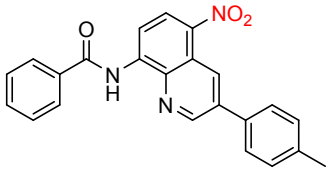
Hz, 1H), 8.55 (d, J = 8.8 Hz, 1H), 7.72 (dd, J = 8.8, 4.1 Hz, 1H), 4.63 (dd, J = 8.4, 5.8 Hz, 1H), 4.23 (dd, J = 14.2, 7.1 Hz, 1H), 4.09 (dd, J = 15.1, 7.1 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.26 (dt, J = 13.1, 6.1 Hz, 1H), 2.07 – 1.96 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.96, 149.40, 140.19, 139.01, 137.99, 133.08, 127.59, 124.61, 121.83, 113.74, 79.14, 69.95, 30.45, 25.61; HRMS (ESI$^+$): Calcd for $C_{14}H_{13}N_3O_4$: $[M+H]^+$ 288.0979, Found 288.0979.

2-methoxy-*N*-(5-nitroquinolin-8-yl)acetamide (2j)



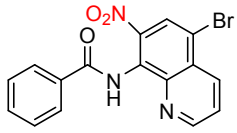
Obtained as a yellow solid in 69% yield; mp 154-155 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.06 (s, 1H), 9.24 (dd, J = 8.8, 1.5 Hz, 1H), 8.95 (dd, J = 4.1, 1.5 Hz, 1H), 8.86 (d, J = 8.8 Hz, 1H), 8.53 (d, J = 8.8 Hz, 1H), 7.72 (dd, J = 8.8, 4.2 Hz, 1H), 4.19 (s, 2H), 3.62 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.00, 149.36, 139.99, 139.03, 137.81, 133.06, 127.52, 124.62, 121.75, 113.89, 72.60, 59.63; HRMS (ESI$^+$): Calcd for $C_{12}H_{11}N_3O_4$: $[M+H]^+$ 262.0822, Found 262.0823.

***N*-(5-nitro-3-(p-tolyl)quinolin-8-yl)benzamide (2k)**



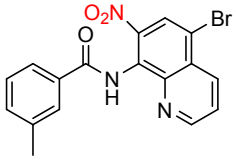
Obtained as a yellow solid in 84% yield; mp 182-183 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.06 (s, 1H), 9.44 (d, J = 2.1 Hz, 1H), 9.19 (d, J = 2.1 Hz, 1H), 8.97 (d, J = 8.8 Hz, 1H), 8.62 (d, J = 8.8 Hz, 1H), 8.10 (d, J = 7.1 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 7.2 Hz, 1H), 7.59 (t, J = 7.3 Hz, 2H), 7.38 (d, J = 7.8 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.70, 148.53, 140.81, 139.29, 138.78, 137.58, 136.58, 134.17, 133.81, 132.64, 130.20, 129.97, 129.04, 128.35, 127.51, 127.47, 121.88, 113.38, 21.27; HRMS (ESI$^+$): Calcd for $C_{23}H_{17}N_3O_4$: $[M+H]^+$ 384.1343, Found 384.1346.

***N*-(5-bromo-7-nitroquinolin-8-yl)benzamide (4a)**



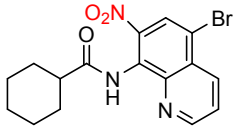
Obtained as a yellow solid in 75% yield; mp 196-197 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 8.96 (dd, *J* = 4.2, 1.3 Hz, 1H), 8.59 (d, *J* = 8.5 Hz, 1H), 8.33 (s, 1H), 8.11 – 8.05 (m, 2H), 7.74 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.20, 150.72, 140.96, 140.17, 138.89, 136.20, 133.68, 132.99, 129.05, 128.78, 128.72, 128.06, 125.40, 125.02, 124.97, 115.66, 21.40; HRMS (ESI$^+$): Calcd for $C_{16}H_{10}BrN_3O_3$: $[M+H]^+$ 371.9973, Found 371.9973.

***N*-(5-bromo-7-nitroquinolin-8-yl)-3-methylbenzamide (4b)**



Obtained as a yellow solid in 72% yield; mp 196-197 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.95 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.57 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.30 (s, 1H), 7.87 (dd, *J* = 7.8, 4.6 Hz, 2H), 7.73 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.44 – 7.40 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.20, 150.72, 140.96, 140.17, 138.89, 136.20, 133.68, 132.99, 129.05, 128.78, 128.72, 128.06, 125.40, 125.02, 124.97, 115.66, 21.40; HRMS (ESI$^+$): Calcd for $C_{17}H_{12}BrN_3O_3$: $[M+H]^+$ 386.0135, Found 386.0132.

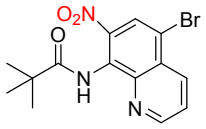
***N*-(5-bromo-7-nitroquinolin-8-yl)cyclohexanecarboxamide (4c)**



Obtained as a yellow solid in 63% yield; mp 178-179 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.96 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.56 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.25 (s, 1H), 7.72 (dd, *J* = 8.5, 4.2 Hz, 1H), 2.54 (tt, *J* = 11.5, 3.5 Hz, 1H), 2.07 (dt, *J* = 14.4, 7.1 Hz, 2H), 1.90 – 1.83 (m, 2H), 1.76 – 1.69 (m, 1H), 1.63 (ddd, *J* = 24.7, 12.4, 3.2 Hz, 3H), 1.40 (ddt, *J* = 18.2, 8.5, 4.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.79, 150.67, 140.98, 140.35, 136.15, 129.01, 127.69, 125.37, 124.88, 115.46, 45.86, 29.15,

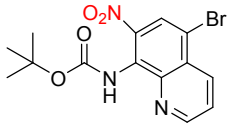
25.68, 25.52; HRMS (ESI$^+$): Calcd for $C_{16}H_{16}BrN_3O_3$: $[M+H]^+$ 378.0448, Found 378.0450.

***N*-(5-bromo-7-nitroquinolin-8-yl)pivalamide (4d)**



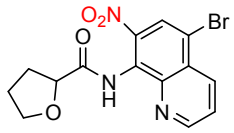
Obtained as a yellow solid in 71% yield; mp 189-190 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.97 (d, *J* = 4.1 Hz, 1H), 8.61 – 8.51 (m, 1H), 8.29 – 8.21 (m, 1H), 7.72 (dd, *J* = 8.5, 4.2 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.25, 150.75, 141.14, 141.12, 140.28, 128.97, 128.95, 127.97, 125.32, 125.30, 124.89, 115.38, 40.03, 27.17; HRMS (ESI$^+$): Calcd for $C_{14}H_{14}BrN_3O_3$: $[M+H]^+$ 352.0292, Found 352.0292.

tert-butyl (5-bromo-7-nitroquinolin-8-yl)carbamate (4e)



Obtained as a yellow solid in 74% yield; mp 186-187 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.89 (s, 1H), 8.53 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.25 (s, 1H), 7.70 (dd, *J* = 8.5, 4.2 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.73, 150.55, 140.74, 139.13, 136.03, 129.37, 129.01, 125.52, 124.92, 114.48, 82.78, 28.13; HRMS (ESI$^+$): Calcd for $C_{14}H_{14}BrN_3O_4$: $[M+H]^+$ 368.0002, Found 368.0005.

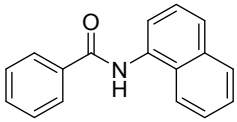
***N*-(5-bromo-7-nitroquinolin-8-yl)tetrahydrofuran-2-carboxamide (4f)**



Obtained as a yellow solid in 63% yield; mp 175-176 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.59 (s, 1H), 9.02 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.58 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.29 (s, 1H), 7.73 (dd, *J* = 8.5, 4.2 Hz, 1H), 4.61 (dd, *J* = 8.4, 5.5 Hz, 1H), 4.24 (dt, *J* = 13.3, 6.6 Hz, 1H), 4.07 (dd, *J* = 15.1, 7.1 Hz, 1H), 2.39 – 2.32 (m, 1H), 2.28 (td, *J* = 12.7, 6.7 Hz, 1H), 2.03 (dd, *J* = 9.5, 4.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.57,

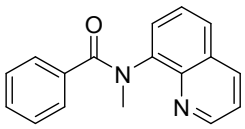
151.13, 141.40, 140.79, 136.00, 129.22, 127.06, 125.31, 124.93, 116.31, 114.07, 78.93, 70.11, 25.55, 22.70; HRMS (ESI^+): Calcd for $C_{14}H_{12}BrN_3O_4$: $[M+H]^+$ 366.0084, Found 366.0080.

_N_-(naphthalen-1-yl)benzamide (6)[2]



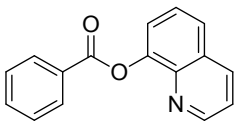
Obtained as a white solid in 92% yield; mp 160-161 °C. ^1H NMR (500 MHz, DMSO) δ 10.43 (s, 1H), 8.12 (d, *J* = 7.3 Hz, 2H), 8.04 – 7.94 (m, 2H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.62 (t, *J* = 7.9 Hz, 2H), 7.59 – 7.52 (m, 5H); ^{13}C NMR (126 MHz, DMSO) δ 166.66, 134.98, 134.36, 134.25, 132.08, 129.71, 128.89, 128.52, 128.26, 126.72, 126.49, 126.40, 125.98, 124.34, 123.79.

_N_-methyl-_N_-(quinolin-8-yl)benzamide (7)[3]



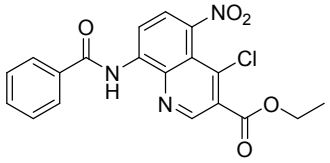
Obtained as a white solid in 83% yield; mp 137-138 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 2H), 3.60 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.11, 150.52, 143.84, 142.39, 136.73, 136.31, 129.27, 129.24, 129.19, 127.91, 127.63, 127.35, 126.24, 121.70, 38.48.

quinolin-8-yl benzoate (8)[4]



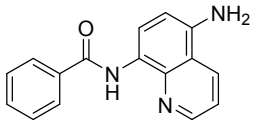
Obtained as a white solid in 96% yield; mp 125-126 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.37 – 8.32 (m, 2H), 8.16 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.50 (m, 4H), 7.38 (dd, *J* = 8.3, 4.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.43, 149.49, 146.68, 140.29, 135.02, 132.51, 129.53, 128.56, 128.53, 127.53, 125.22, 124.95, 120.67, 120.62.

ethyl 8-benzamido-4-chloro-5-nitroquinoline-3-carboxylate (2l)



Obtained as a yellow solid in 78% yield; mp 238-239 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.81 (s, 1H), 9.30 (s, 1H), 8.90 (d, J = 8.5 Hz, 1H), 8.37 (d, J = 8.5 Hz, 1H), 8.07 – 8.04 (m, 2H), 7.73 – 7.69 (m, 1H), 7.65 (t, J = 7.6 Hz, 2H), 4.47 (q, J = 7.1 Hz, 2H), 2.51 (dt, J = 3.6, 1.8 Hz, 3H); ^{13}C NMR (151 MHz, DMSO) δ 165.54, 163.74, 149.48, 141.52, 139.71, 138.54, 134.02, 133.26, 129.59, 128.55, 127.83, 127.60, 118.13, 116.97, 63.08, 14.39; HRMS (ESI$^+$): Calcd for $C_{19}H_{14}ClN_3O_5$: $[M+H]^+$ 399.0625, Found 399.0613.

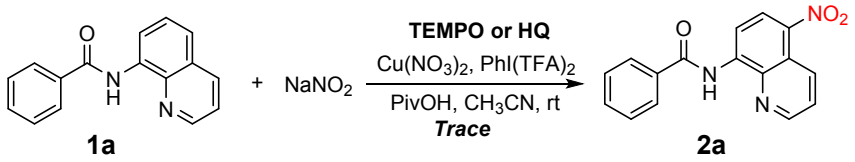
***N*-(5-aminoquinolin-8-yl)benzamide (5)**



Obtained as a pale yellow solid in 88% yield; mp 202-203 °C.^{1}H NMR (600 MHz, DMSO-d_6) δ 10.30 (s, 1H), 8.89 (dd, J = 4.1, 1.5 Hz, 1H), 8.63 (d, J = 8.5 Hz, 1H), 8.43 (d, J = 8.3 Hz, 1H), 8.01 (t, J = 8.2 Hz, 2H), 7.65 – 7.57 (m, 3H), 7.53 (dd, J = 8.5, 4.2 Hz, 1H), 6.77 (d, J = 8.3 Hz, 1H), 5.91 (s, 2H); ^{13}C NMR (151 MHz, DMSO) δ 164.12, 149.30, 141.78, 140.01, 135.52, 132.35, 132.03, 129.35, 127.28, 123.84, 120.12, 120.05, 118.08, 107.34; HRMS (ESI$^+$): Calcd for $C_{16}H_{13}N_3O$: $[M+H]^+$ 286.0952, Found 286.0954.

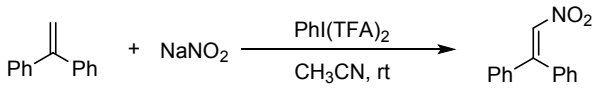
2. Control experiments for mechanism study

Radical inhibition experiment



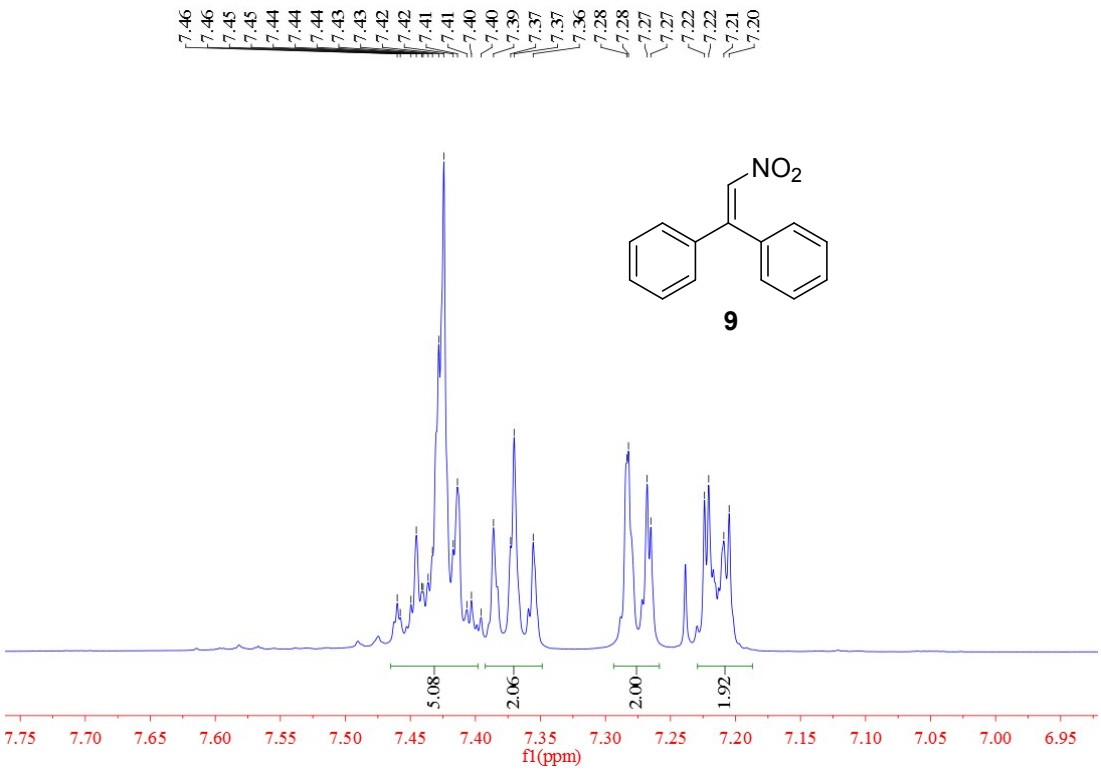
A mixture of amide **1a** (50 mg, 0.2 mmol), $NaNO_2$ (15.0 mg, 0.22 mmol, 1.1 equiv), $PhI(TFA)_2$ (172.0 mg, 0.4 mmol, 2.0 equiv), $Cu(NO_3)_2$ (3.8 mg, 0.02 mmol, 0.1 equiv), PivOH (4.0 mg, 0.04 mmol, 0.20 equiv), TEMPO/ HQ (62.5 mg/44.0 mg, 2.0 equiv) and CH_3CN (2.0 mL) were stirred at room temperature for 5 min. After completion (monitored by TLC). We found no desired product was obtained in the presence of the radical inhibitor TEMPO or HQ, which showed that a radical pathway should be involved.

Radical capture experiment



9

A mixture of 1,1-diphenylethylene (36 mg, 0.2 mmol), $NaNO_2$ (15.0 mg, 0.22 mmol, 1.1 equiv), $PhI(TFA)_2$ (172.0 mg, 0.4 mmol, 2.0 equiv), and CH_3CN (2.0 mL) were stirred at room temperature for 2 min. After completion (monitored by TLC). The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (PE/EA = 80:1) to give the radical coupling product **9** (70%) as a yellow solid.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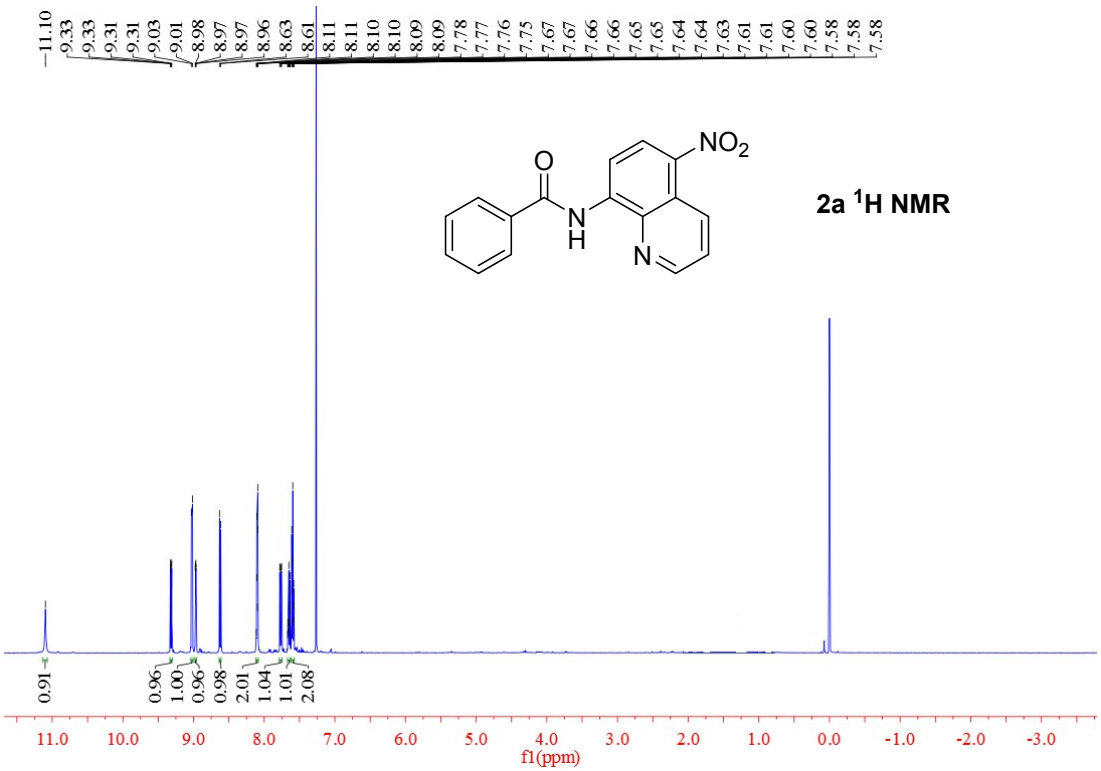
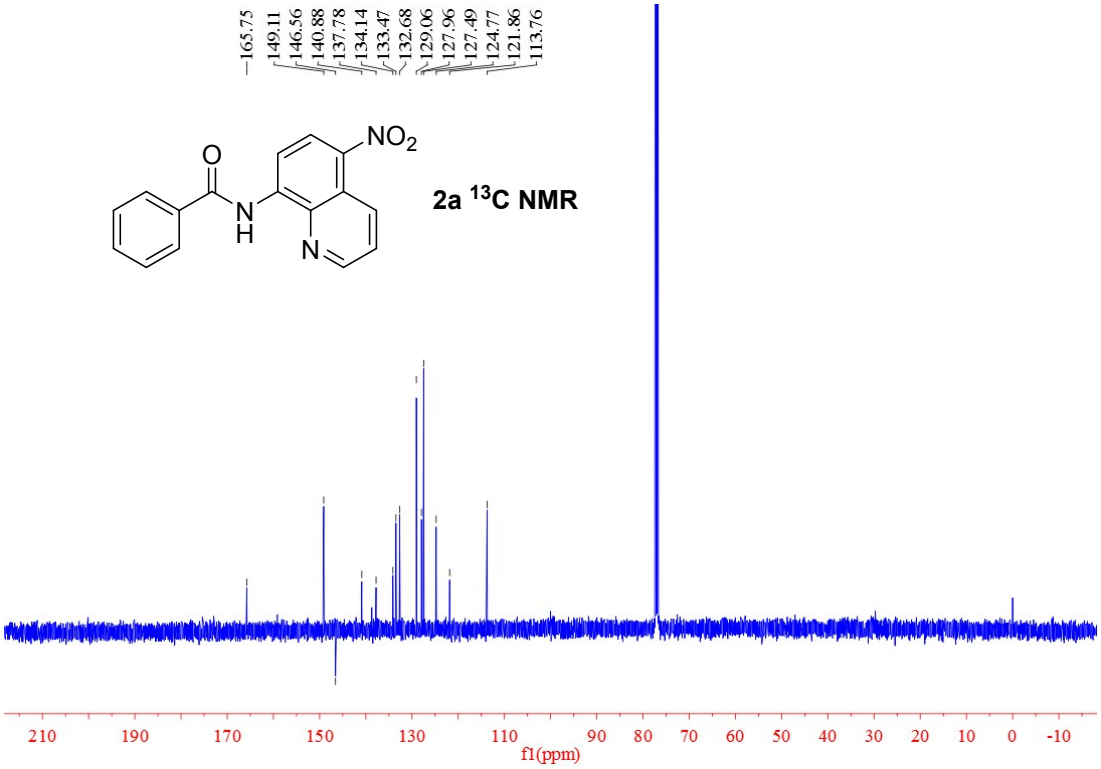
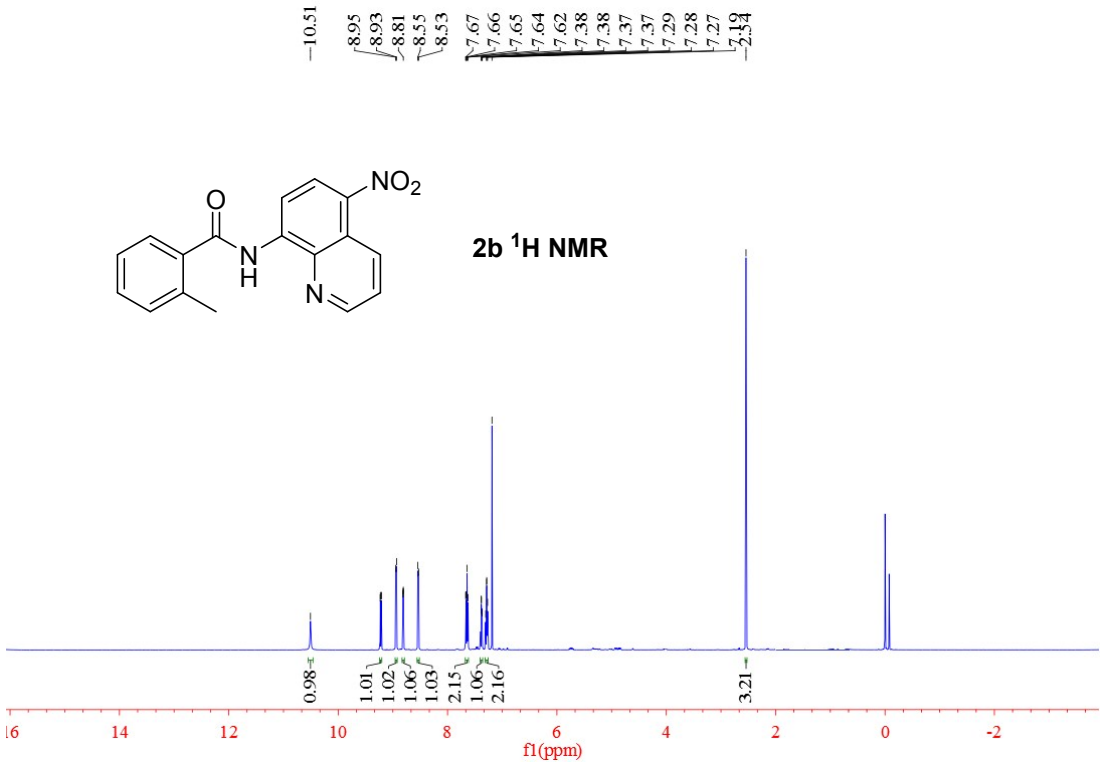
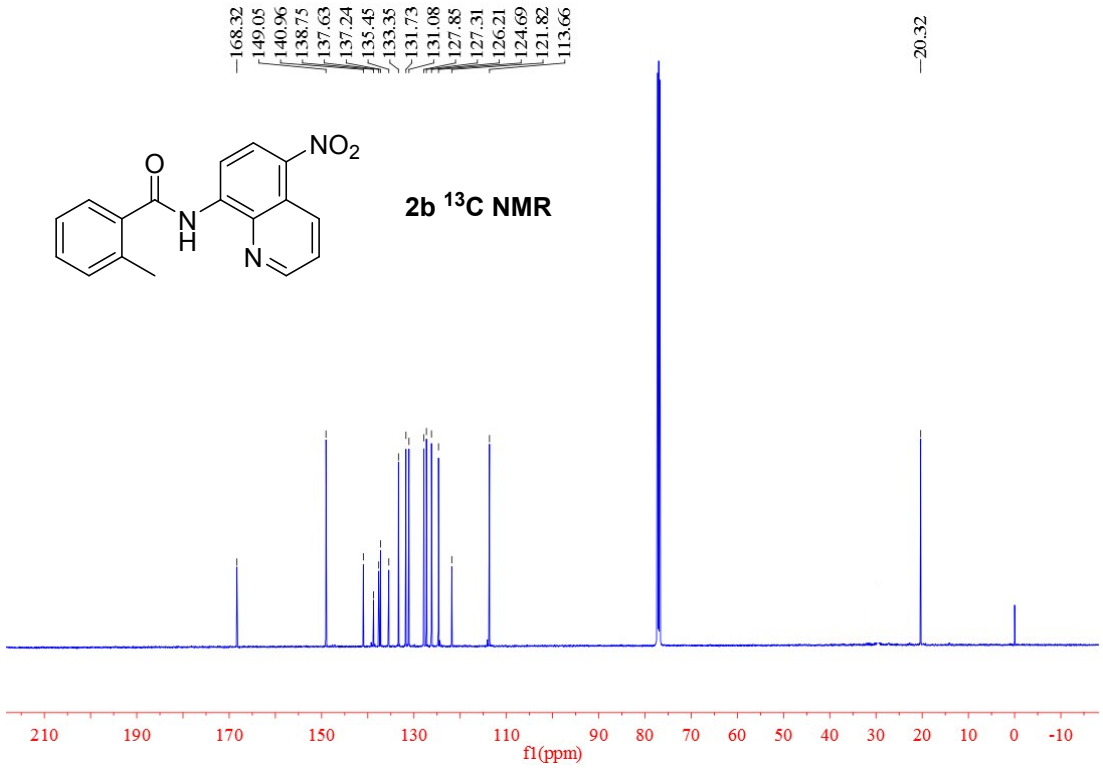
7.46
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.37
7.37
7.36
7.28
7.28
7.27
7.27
7.22
7.22
7.21
7.20
NO2
9
5.08
2.06
2.00
1.92
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
f1(ppm)

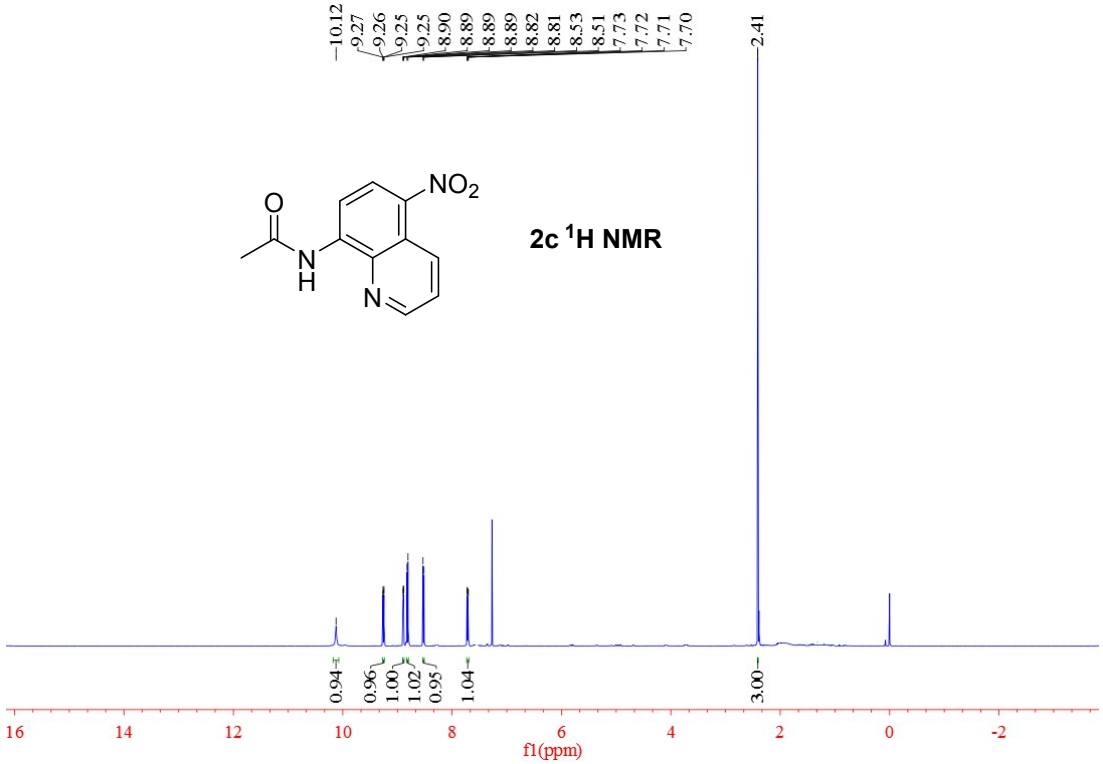
3. Copies of ^{1}H NMR and ^{13}C NMR Spectra

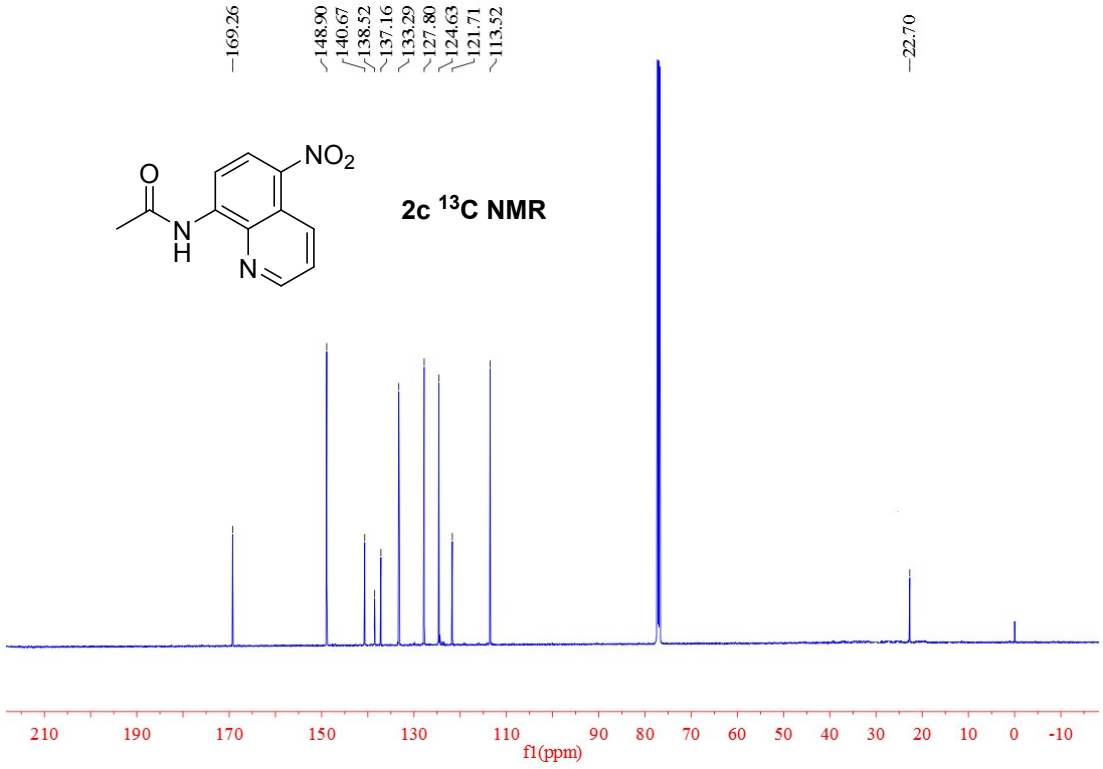





10.51
8.95
8.93
8.81
8.55
8.53
7.67
7.66
7.65
7.64
7.62
7.38
7.38
7.37
7.37
7.29
7.28
7.27
7.19
2.34
NO2
O
N
H
N
2b 1H NMR
0.98
1.01
1.02
1.06
1.03
2.15
1.06
2.16
3.21
16
14
12
10
8
6
4
2
0
-2
f1(ppm)


168.32
149.05
140.96
138.75
137.63
137.24
135.45
133.35
131.73
131.08
127.85
127.31
126.21
124.69
121.82
113.66
20.32
NO2
O
N
H
N
2b 13C NMR
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1(ppm)


10.12
9.27
9.26
9.25
9.25
8.90
8.89
8.89
8.89
8.82
8.81
8.53
8.51
7.73
7.72
7.71
7.70
2.41
NO2
O
N
H
N
2c 1H NMR
0.94
0.96
1.00
1.02
0.95
1.04
3.00
16
14
12
10
8
6
4
2
0
-2
f1(ppm)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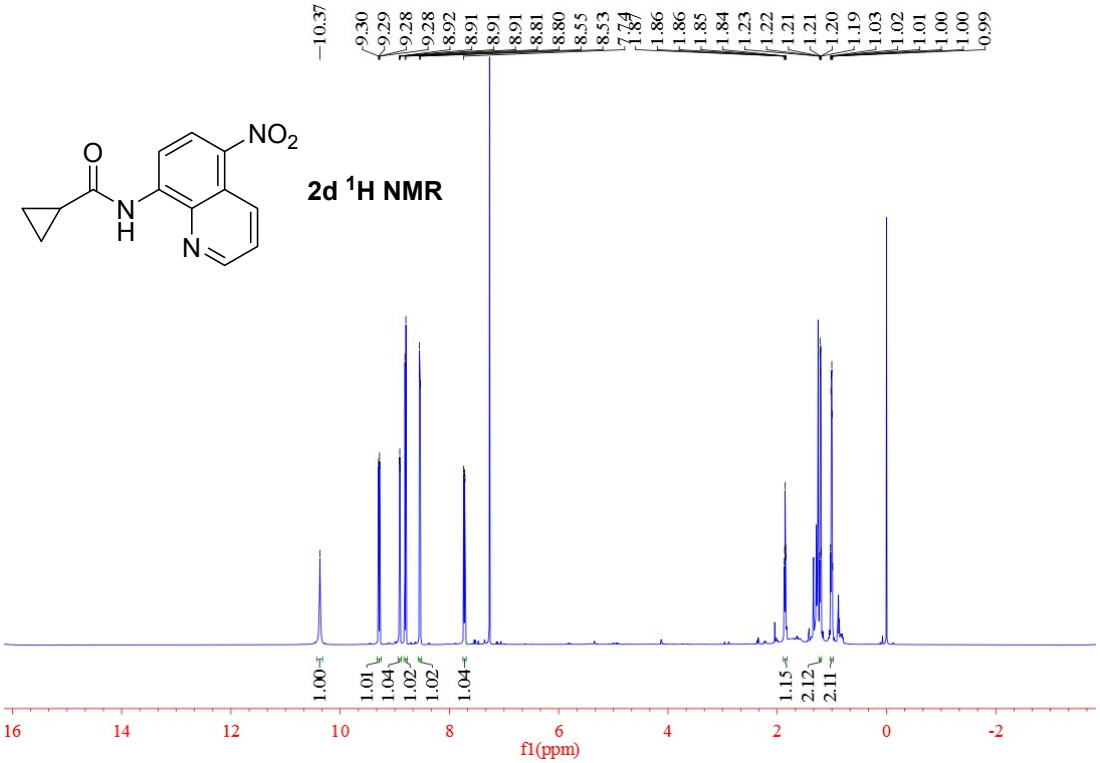
138.52
137.16
133.29
127.80
124.63
121.71
113.52
22.70
NO2
O
N
H
N
2c 13C NMR
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1(ppm)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9.30
9.29
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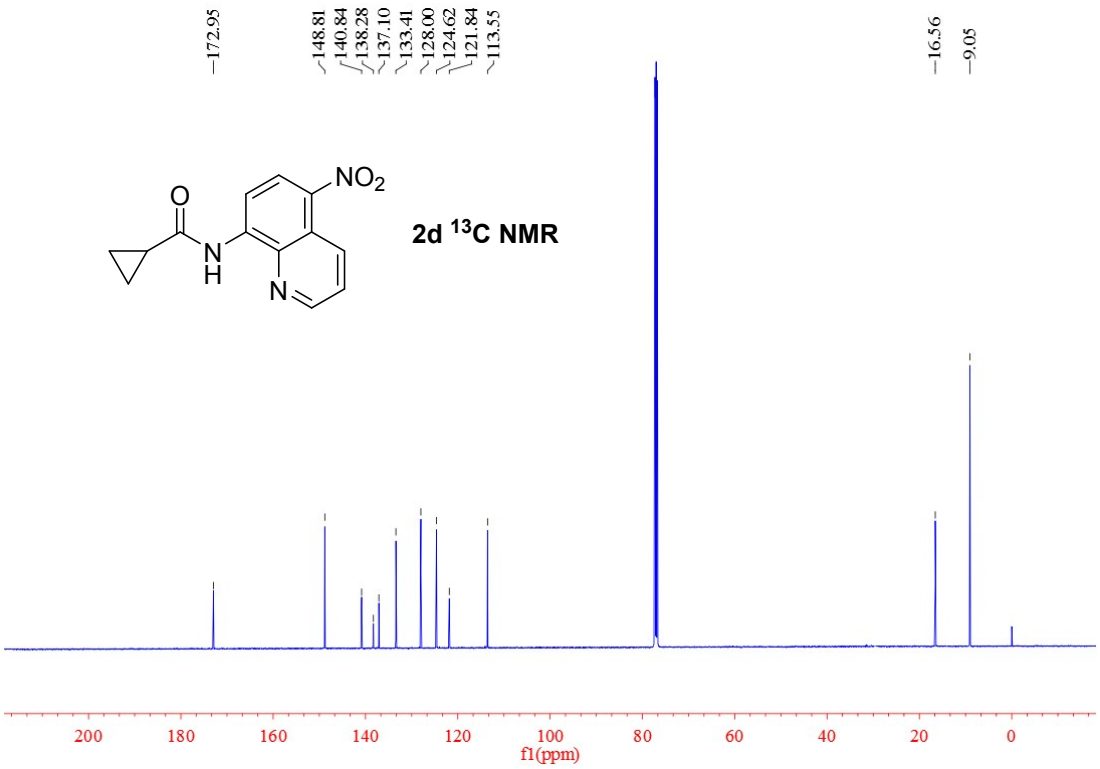
9.28
8.92
8.91
8.91
8.91
8.81
8.80
8.55
8.53
7.74
7.87
1.86
1.86
1.85
1.84
1.23
1.22
1.21
1.21
1.20
1.19
1.03
1.02
1.01
1.00
1.00
0.99
NO2
O
N
H
N
2d 1H NMR
1.00
1.01
1.04
1.02
1.02
1.04
1.15
2.12
2.11
16
14
12
10
8
6
4
2
0
-2
f1(ppm)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133.41
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124.62
121.84
113.55
16.56
9.05
NO2
O
N
H
N
2d 13C NMR
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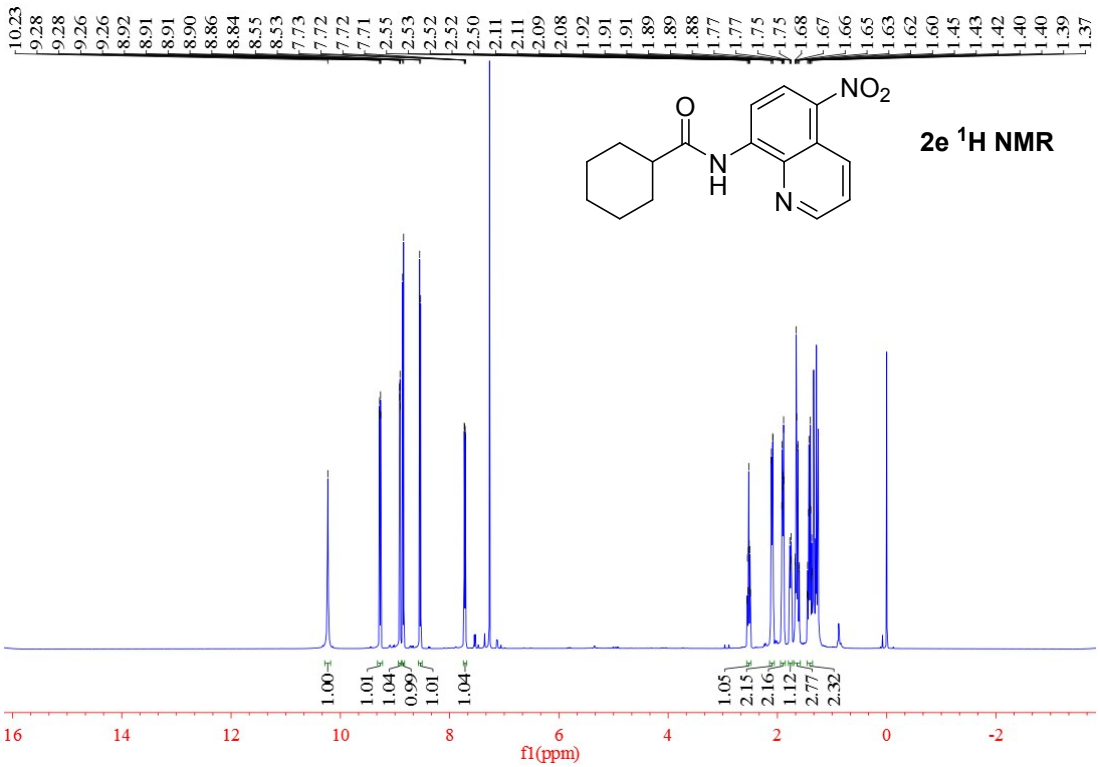
180
160
140
120
100
80
60
40
20
0
f1(ppm)


10.23
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9.26
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8.91
8.91
8.90
8.86
8.84
8.55
8.53
7.73
7.72
7.72
7.71
2.55
2.53
2.52
2.52
2.50
2.11
2.09
2.08
1.92
1.91
1.91
1.89
1.89
1.88
1.77
1.77
1.75
1.75
1.68
1.67
1.66
1.65
1.63
1.62
1.60
1.45
1.43
1.42
1.40
1.40
1.39
1.37
O
N
H
N
NO2
2e 1H NMR
1.00
1.01
1.04
0.99
1.01
1.04
1.05
2.15
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2.77
2.32
16
14
12
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8
6
4
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0
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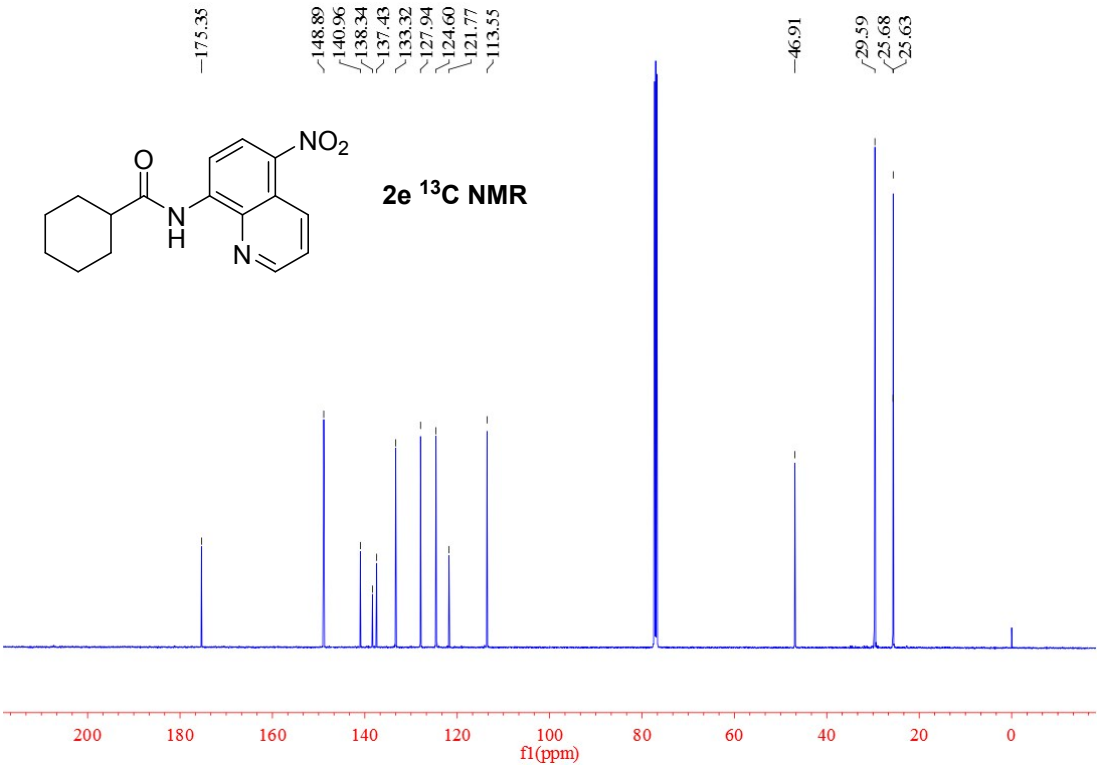
f1(ppm)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121.77
113.55
46.91
29.59
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25.63
O
N
H
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NO2
2e 13C NMR
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180
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140
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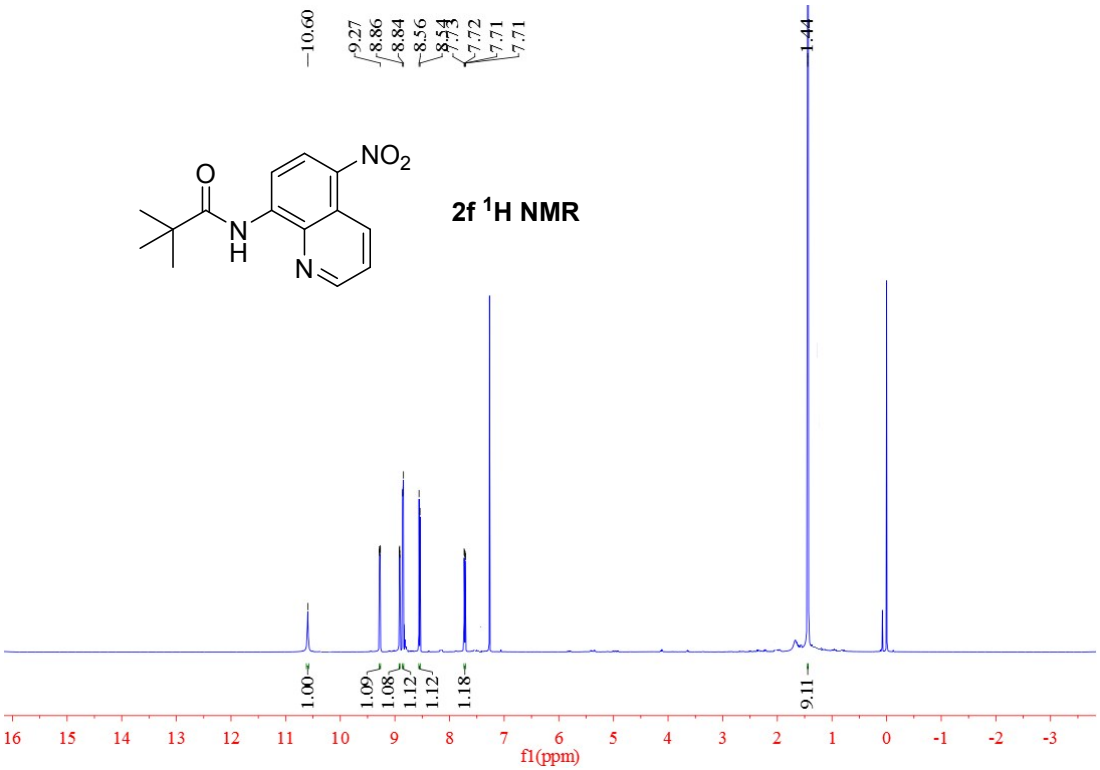
100
80
60
40
20
0
f1(ppm)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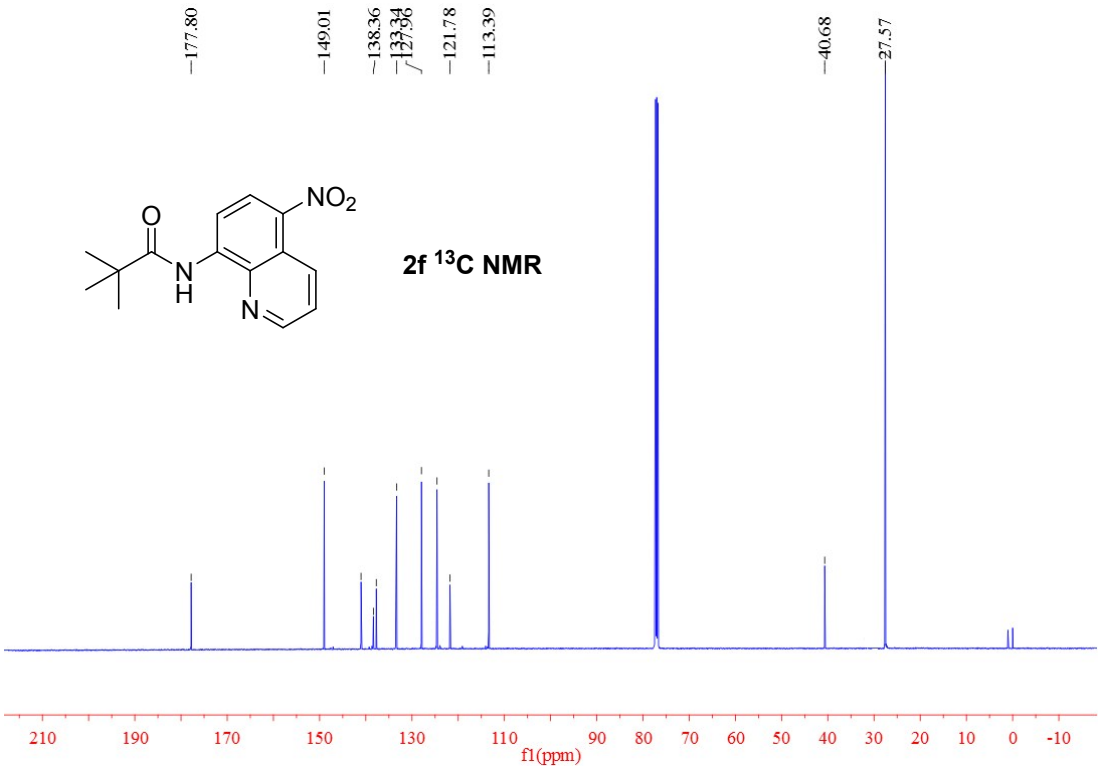
8.54
8.53
7.72
7.71
7.71
1.44
NO2
O
N
H
N
2f 1H NMR
1.00
1.09
1.08
1.12
1.12
1.18
9.11
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1(ppm)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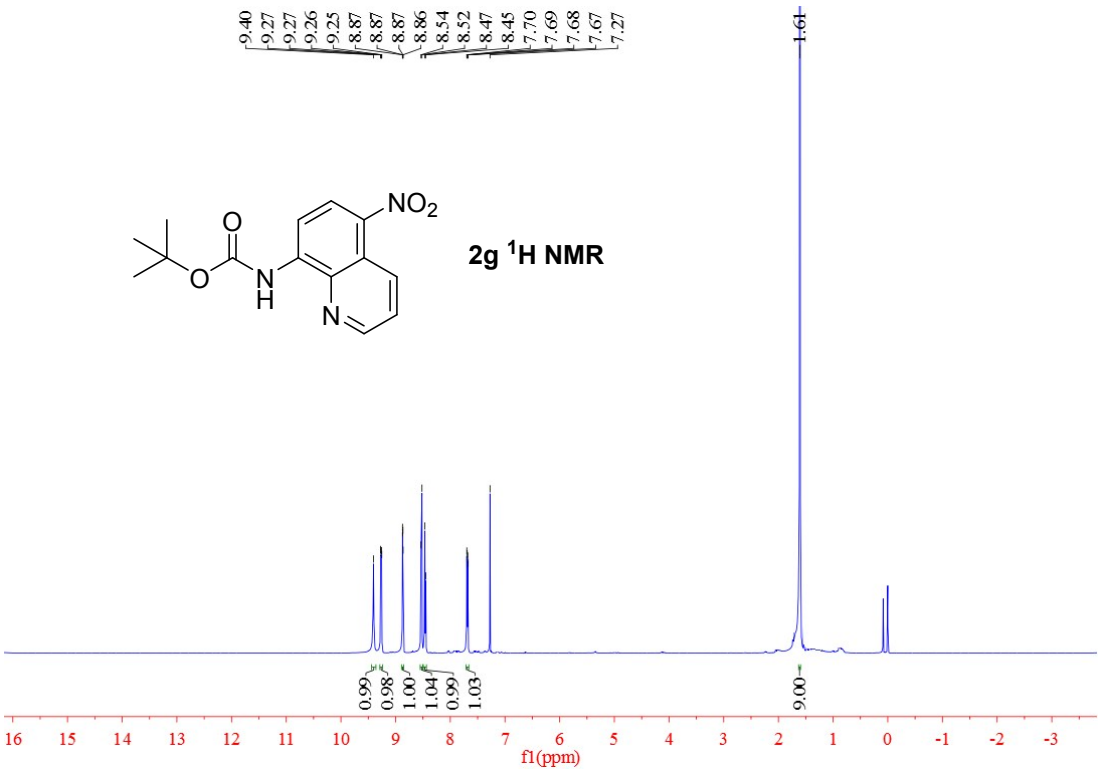
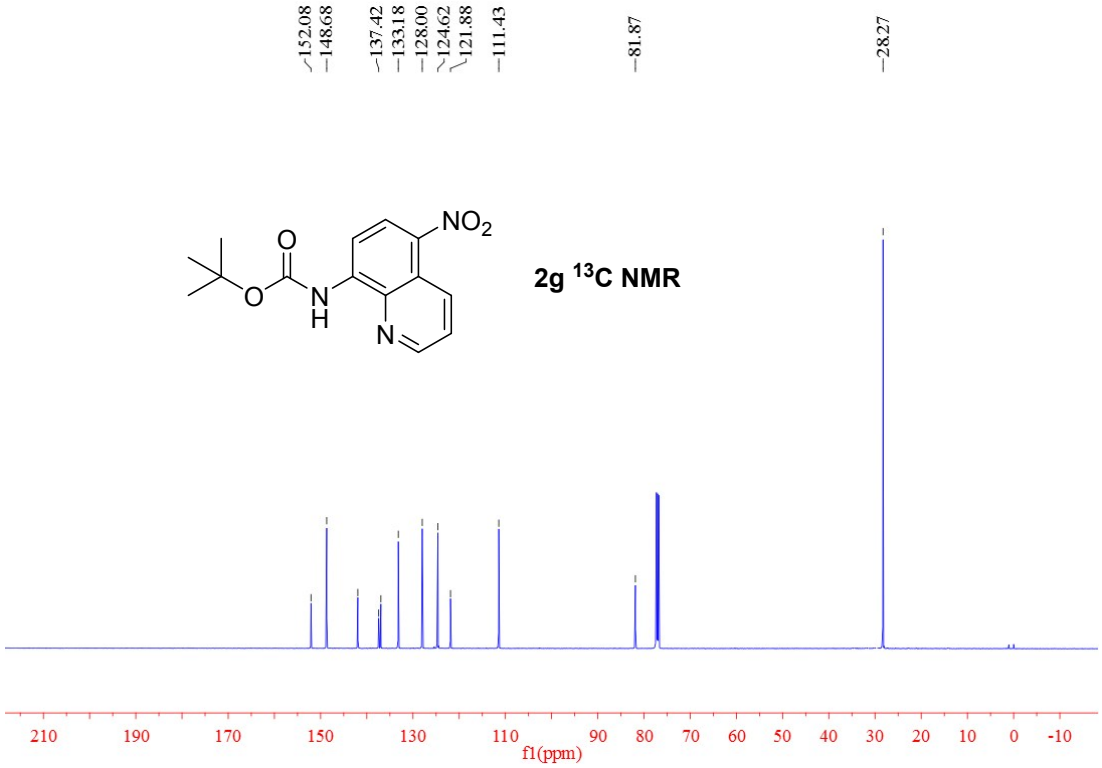
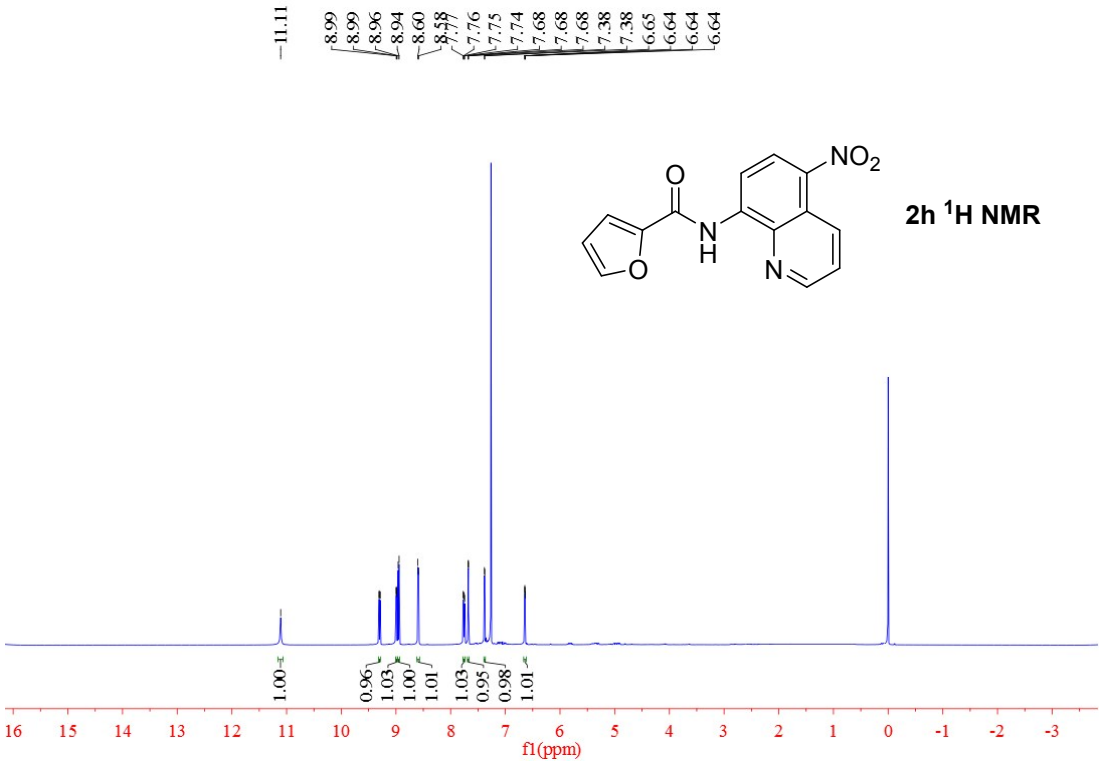
133.34
127.96
121.78
113.39
40.68
27.57
NO2
O
N
H
N
2f 13C NMR
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1(ppm)



2g ^{1}H NMR



2g ^{13}C NMR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8.99
8.96
8.94
8.60
8.58
7.77
7.76
7.75
7.74
7.68
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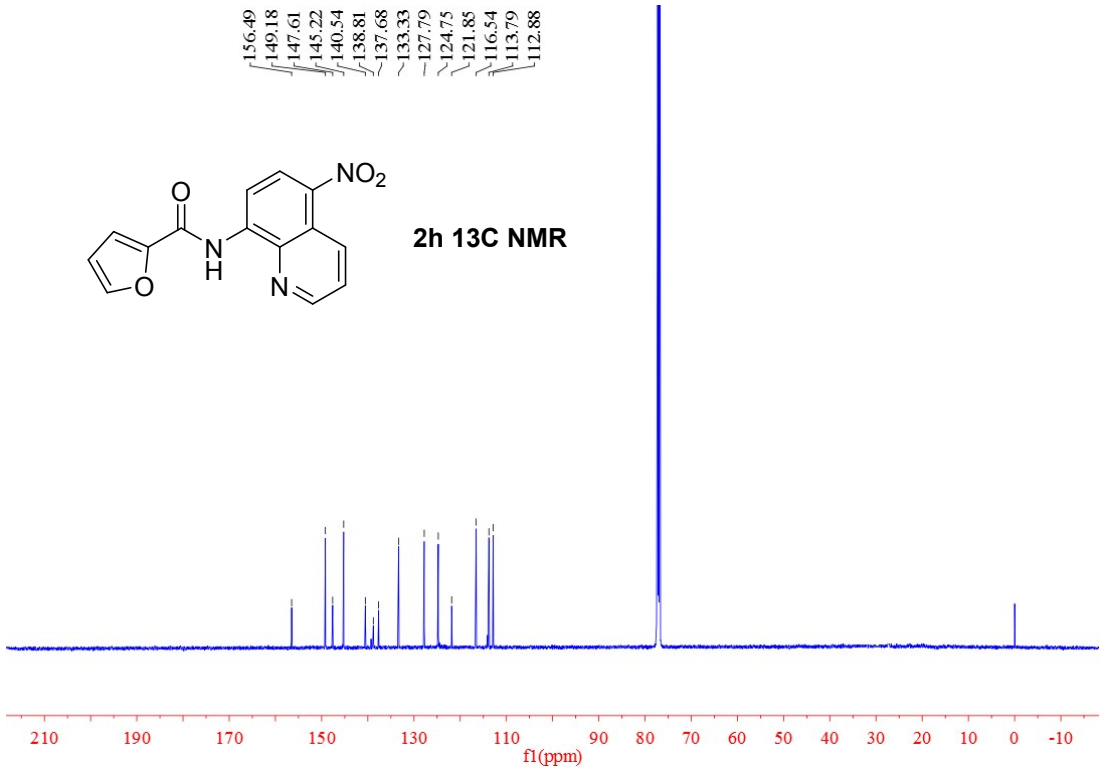
7.68
7.38
7.38
6.65
6.64
6.64
6.64
NO2
O
N
H
O
N
2h 1H NMR
1.00
0.96
1.03
1.00
1.01
1.03
0.95
0.98
1.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1(ppm)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145.22
140.54
138.81
137.68
133.33
127.79
124.75
121.85
116.54
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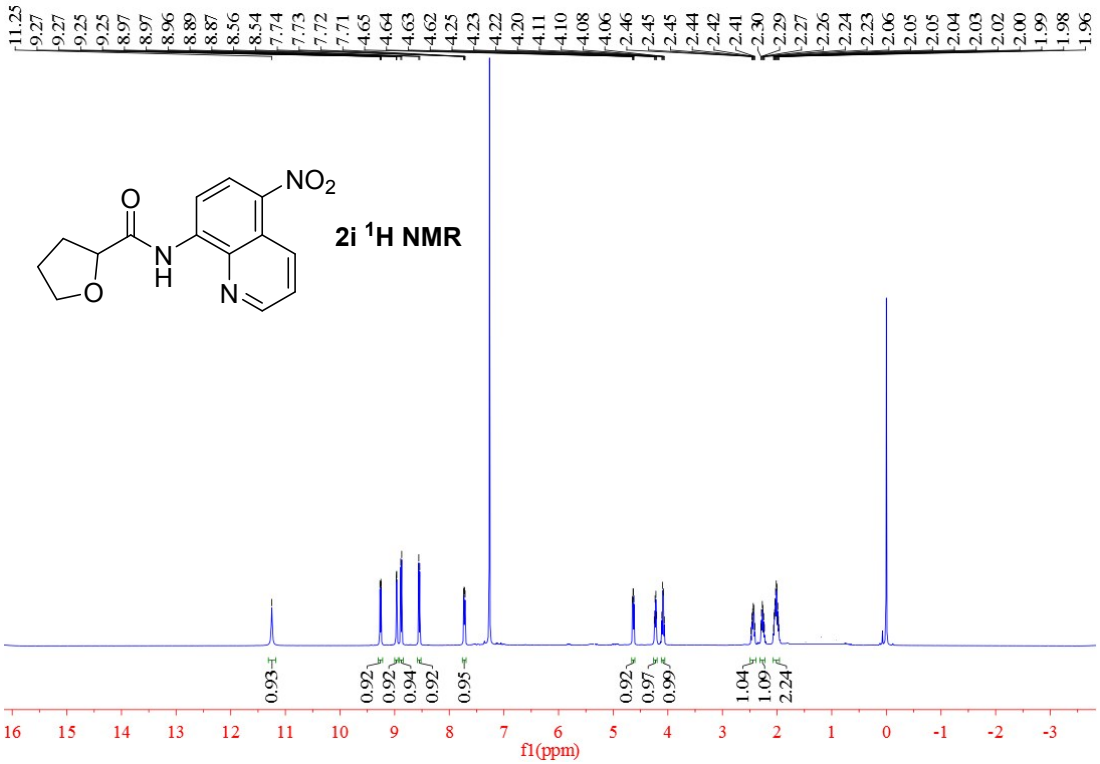
N
2h 13C NMR
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1(ppm)


11.25
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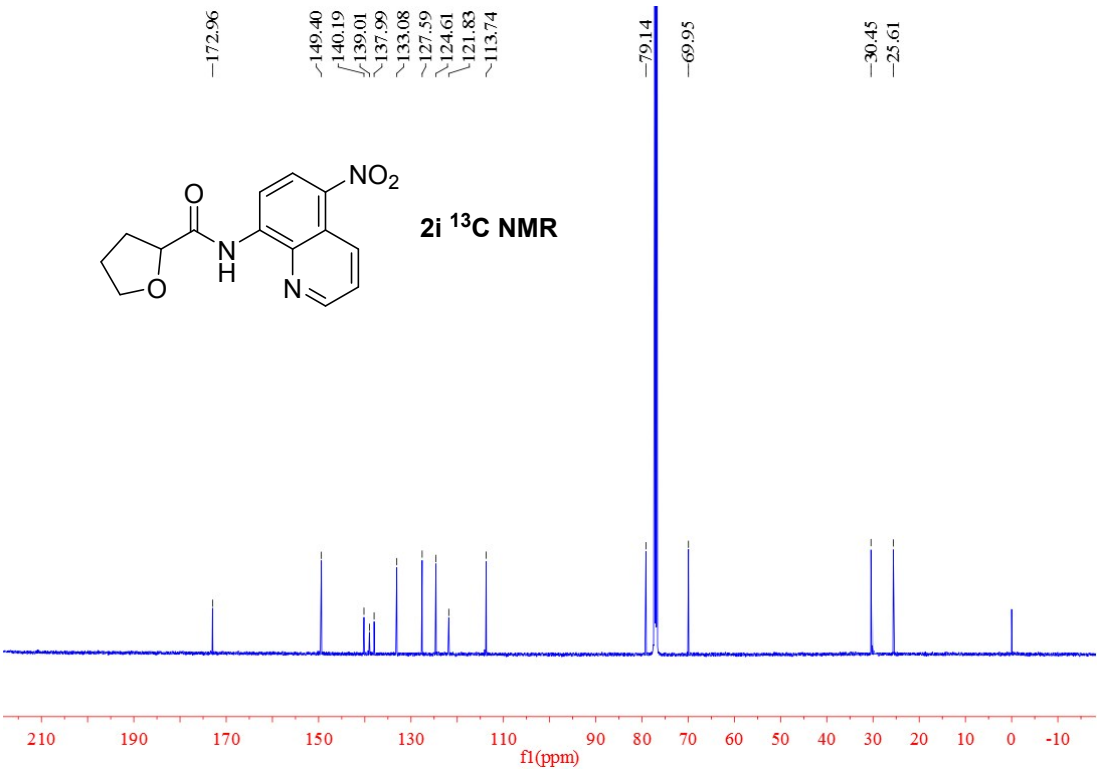
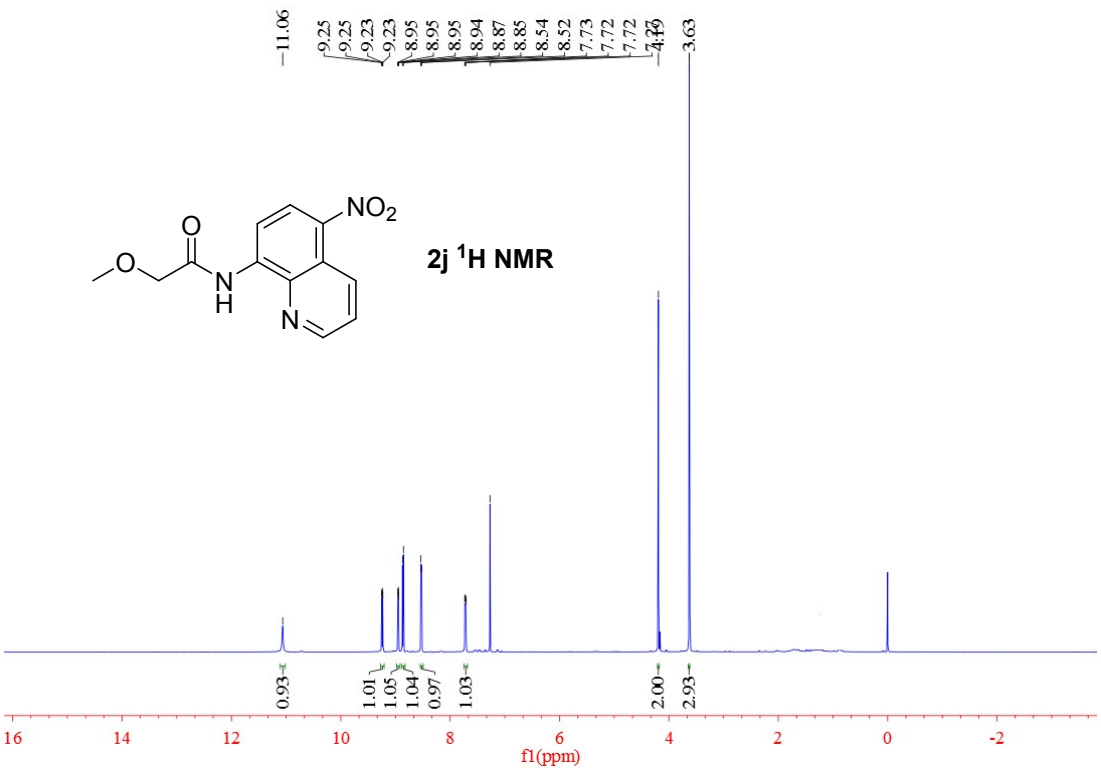
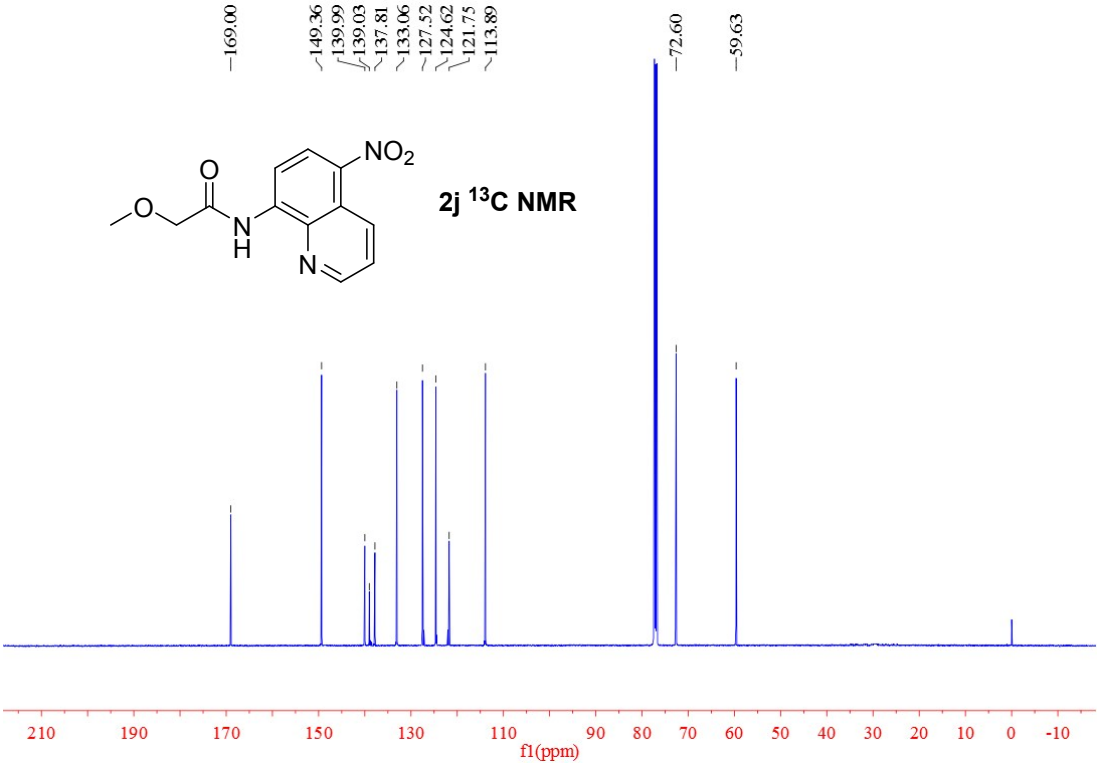
9.27
9.25
9.25
8.97
8.97
8.96
8.89
8.87
8.56
8.54
7.74
7.73
7.72
7.71
4.65
4.64
4.63
4.62
4.25
4.23
4.22
4.20
4.11
4.10
4.08
4.06
2.46
2.45
2.45
2.44
2.42
2.41
2.30
2.29
2.27
2.26
2.24
2.23
2.06
2.05
2.05
2.04
2.03
2.02
2.00
1.99
1.98
1.96
NO2
O
N
H
O
N
2i 1H NMR
0.93
0.92
0.92
0.94
0.92
0.95
0.92
0.97
0.99
1.04
1.09
2.24
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1(ppm)


172.96
149.40
140.19
139.01
137.99
133.08
127.59
124.61
121.83
113.74
79.14
69.95
30.45
25.61
NO2
O
N
H
O
N
2i 13C NMR
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1(ppm)


11.06
9.25
9.25
9.23
9.23
8.95
8.95
8.95
8.94
8.87
8.85
8.54
8.52
7.73
7.72
7.72
3.63
NO2
O
O
N
H
N
2j 1H NMR
0.93
1.01
1.05
1.04
0.97
1.03
2.00
2.93
16
14
12
10
8
6
4
2
0
-2
f1(ppm)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149.36
139.99
139.03
137.81
133.06
127.52
124.62
121.75
113.89
72.60
59.63
NO2
O
O
N
H
N
2j 13C NMR
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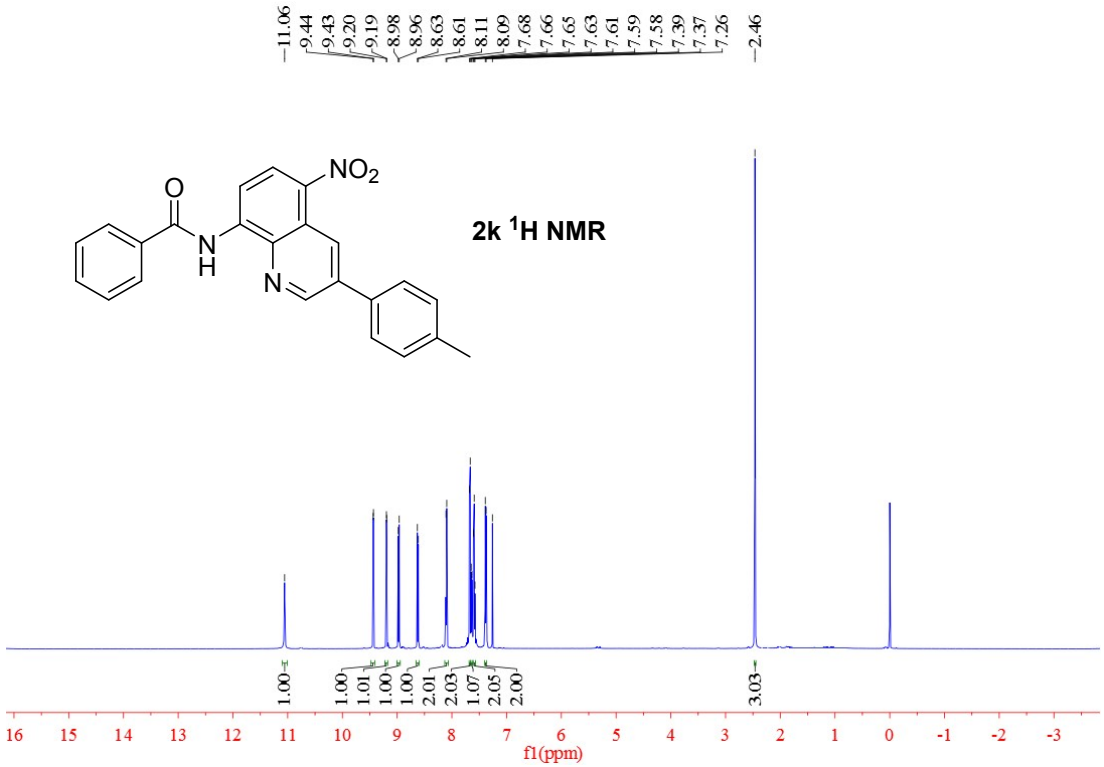
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1(ppm)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9.43
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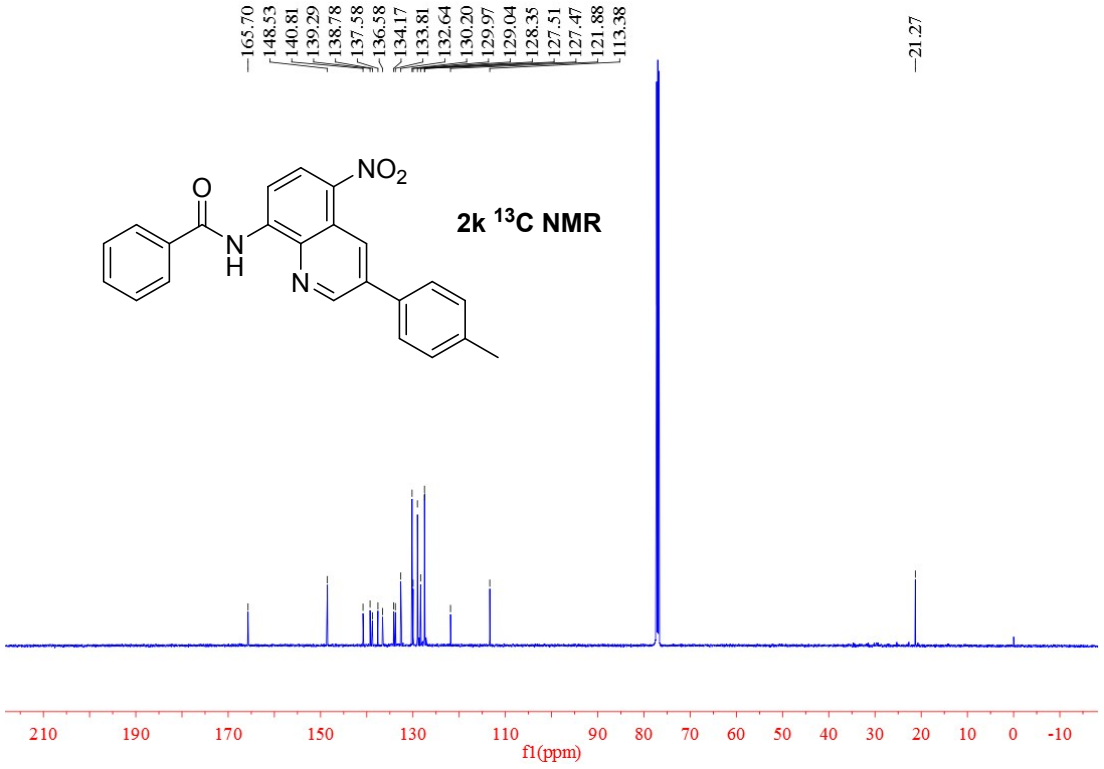
8.98
8.96
8.63
8.61
8.11
8.09
7.68
7.66
7.65
7.63
7.61
7.59
7.58
7.39
7.37
7.26
2.46
NO2
O
N
H
N
2k 1H NMR
1.00
1.00
1.01
1.00
1.00
2.01
2.03
1.07
2.05
2.00
3.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1(ppm)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148.53
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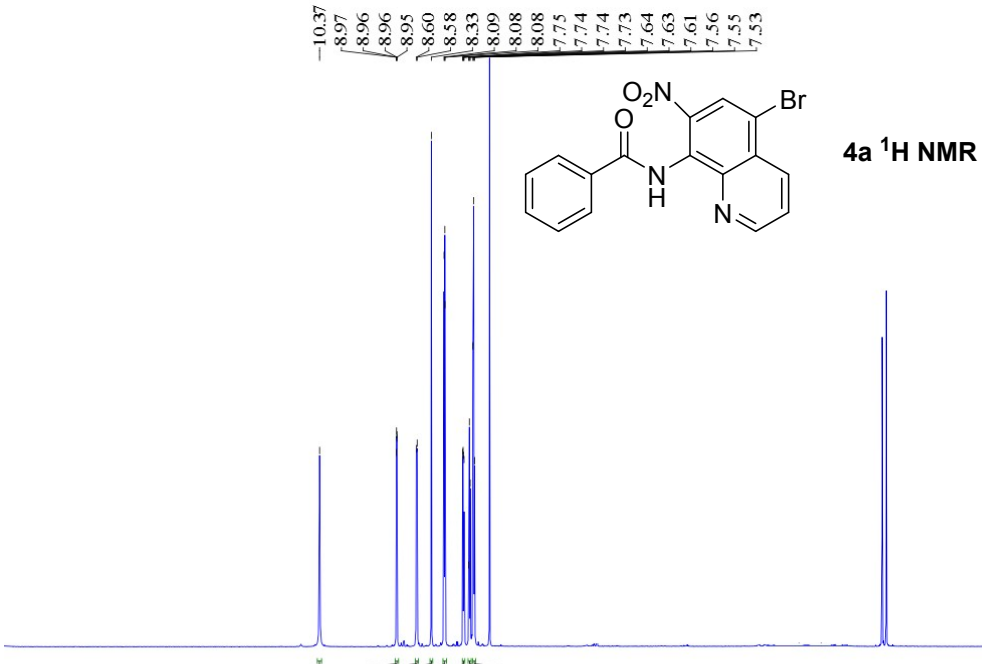
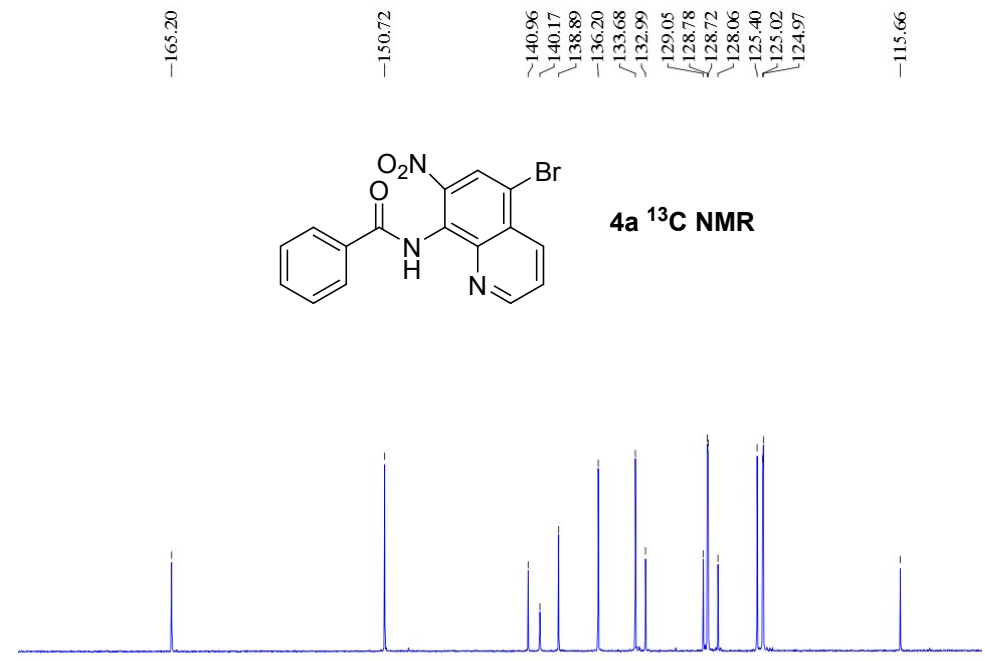
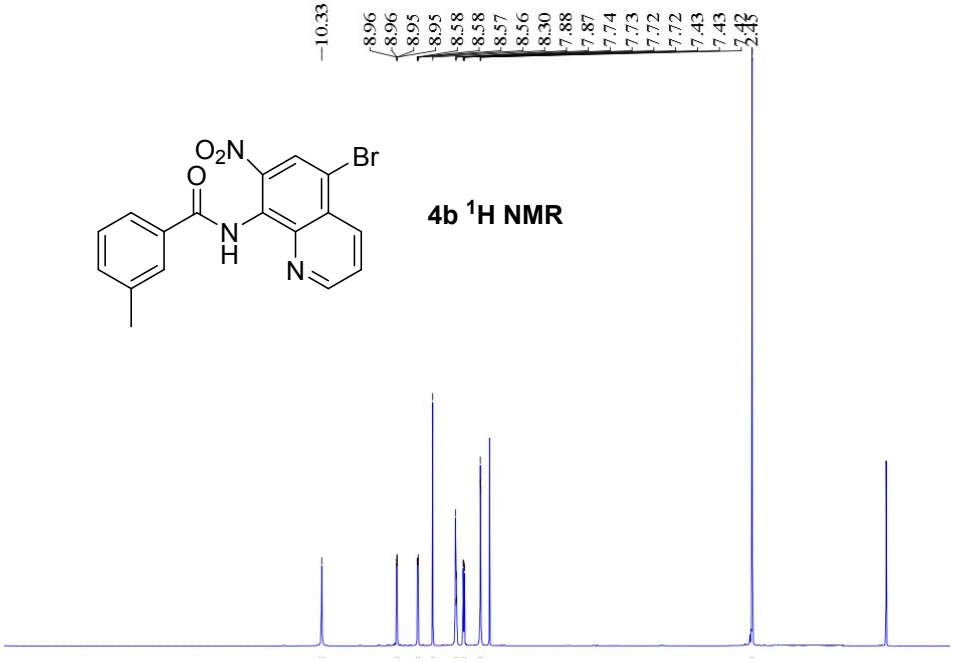
139.29
138.78
137.58
136.58
134.17
133.81
132.64
130.20
129.97
129.04
128.35
127.51
127.47
121.88
113.38
21.27
NO2
O
N
H
N
2k 13C NMR
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1(ppm)



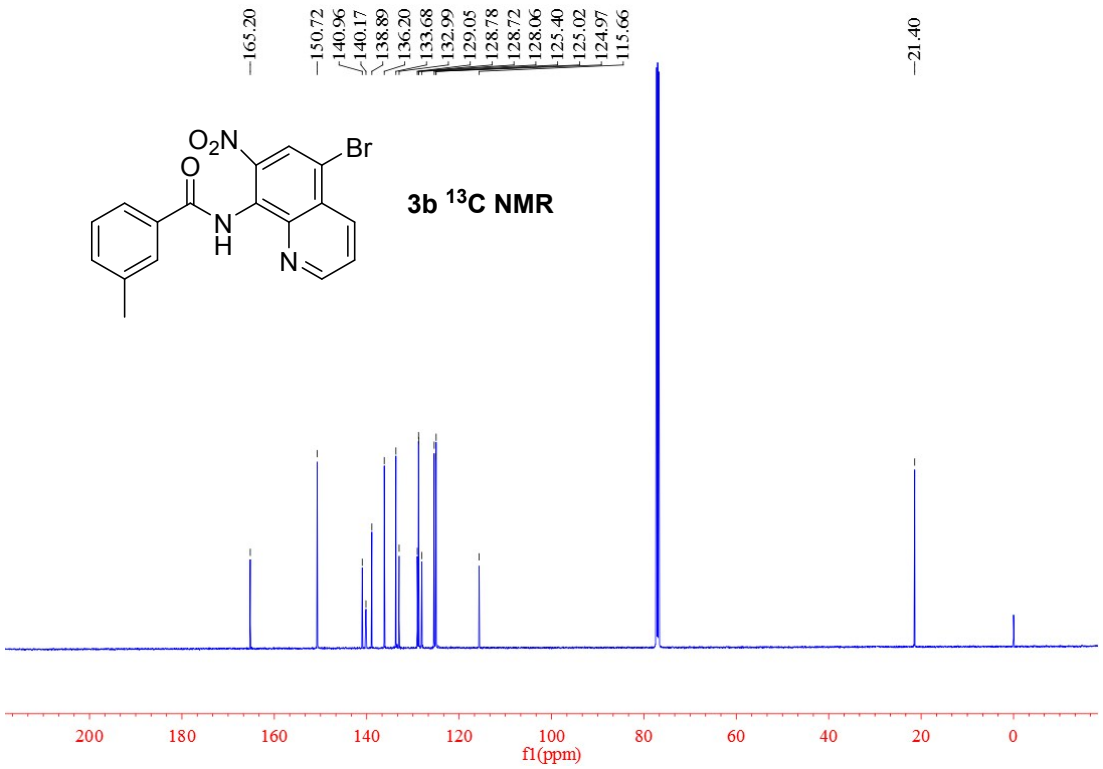
4a ^{1}H NMR



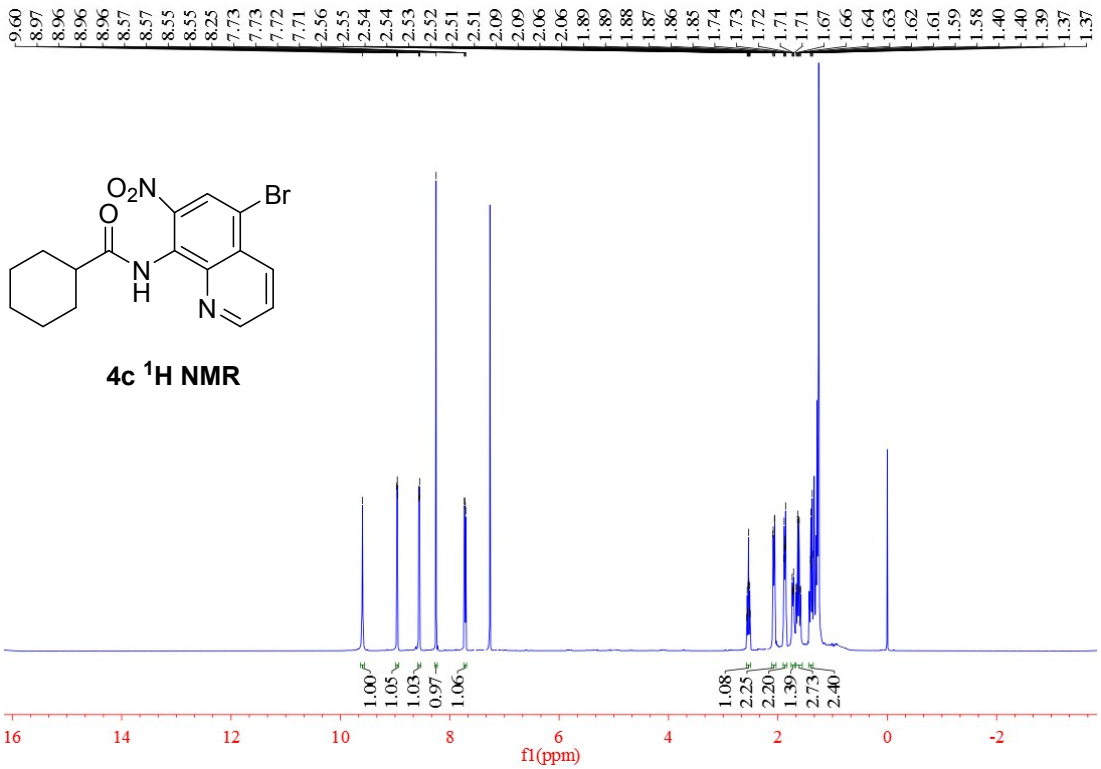
4a ^{13}C NMR



4b ^{1}H NMR



3b ^{13}C NMR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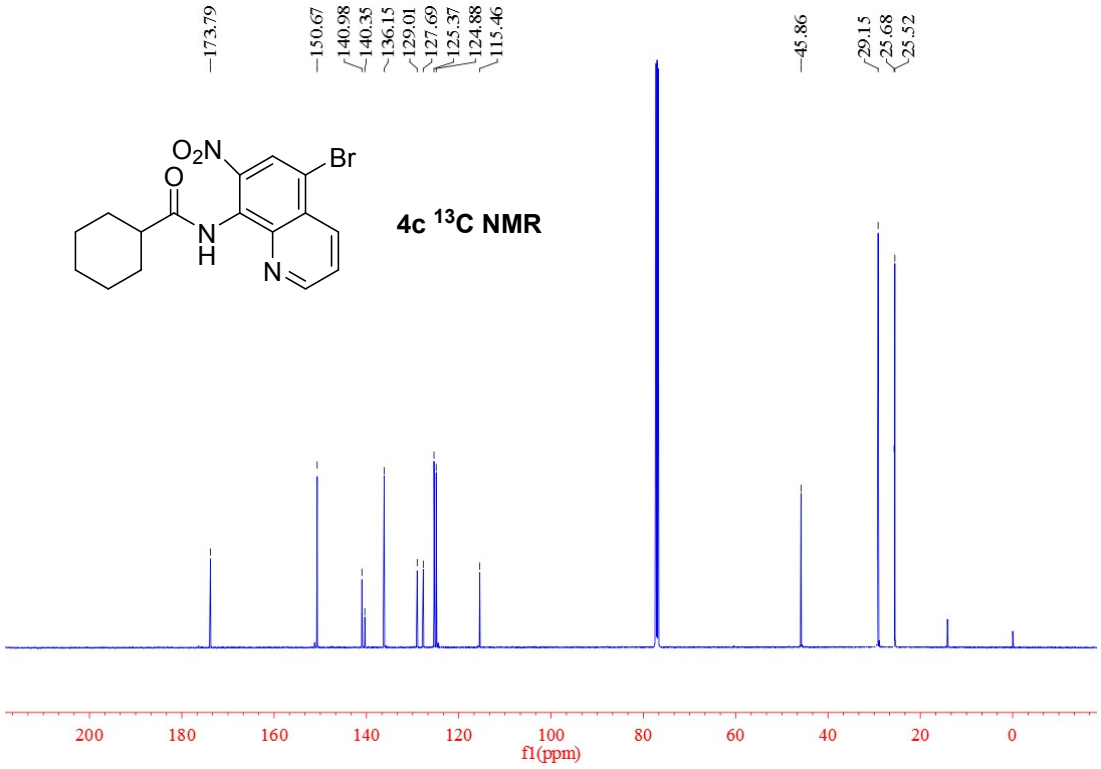
8.57
8.55
8.55
8.25
7.73
7.73
7.72
7.71
2.56
2.55
2.54
2.54
2.53
2.52
2.51
2.51
2.09
2.09
2.06
2.06
1.89
1.89
1.88
1.87
1.86
1.85
1.74
1.73
1.72
1.71
1.71
1.67
1.66
1.64
1.63
1.62
1.61
1.59
1.58
1.40
1.40
1.39
1.37
1.37
O2N
O
N
H
Br
N
4c 1H NMR
1.00
1.05
1.03
0.97
1.06
1.08
2.25
2.20
1.39
2.73
2.40
16
14
12
10
8
6
4
2
0
-2
f1(ppm)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150.67
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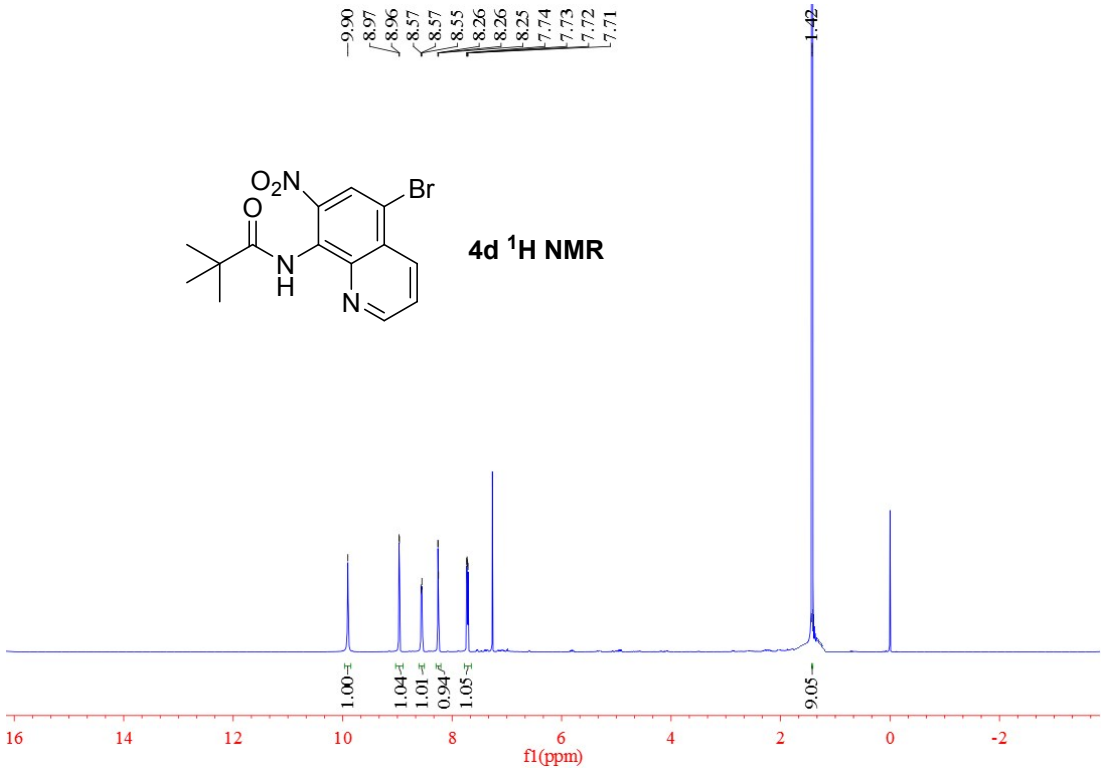
129.01
127.69
125.37
124.88
115.46
45.86
29.15
25.68
25.52
O2N
O
N
H
Br
N
4c 13C NMR
200
180
160
140
120
100
80
60
40
20
0
f1(ppm)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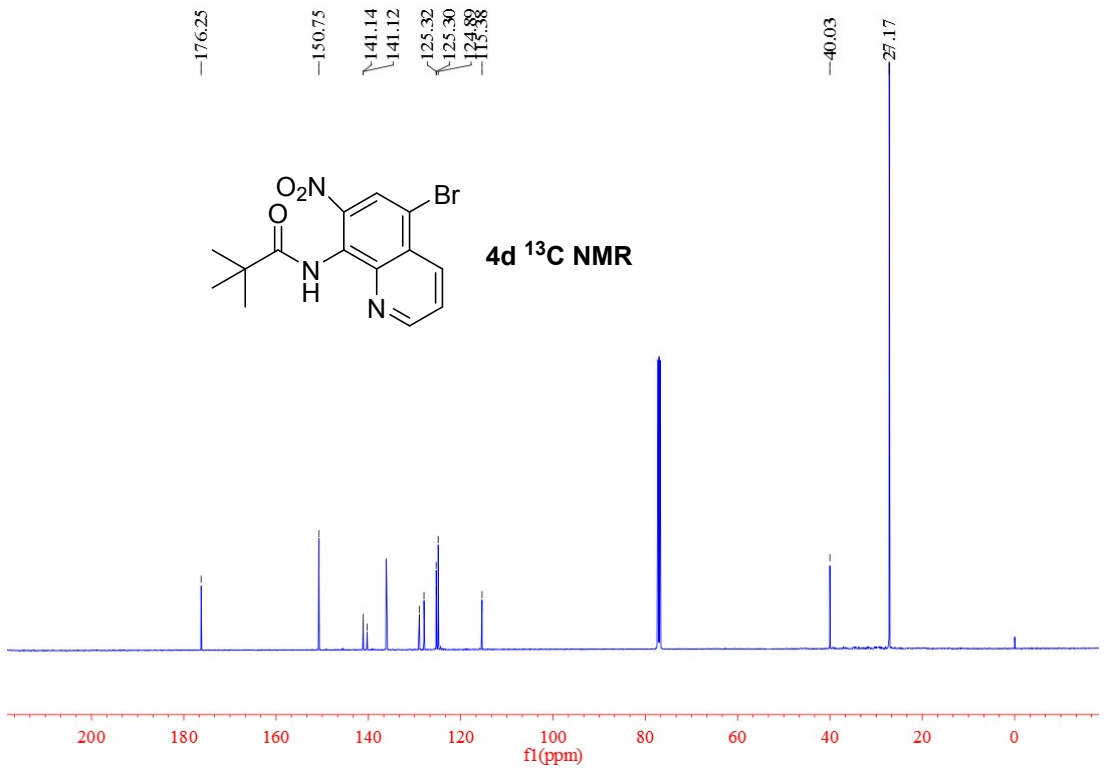
8.97
8.96
8.57
8.57
8.55
8.26
8.26
8.25
7.74
7.73
7.72
7.71
1.42
O2N
Br
O
N
H
N
4d 1H NMR
1.00
1.04
1.01
0.94
1.05
9.05
16
14
12
10
8
6
4
2
0
-2
f1(ppm)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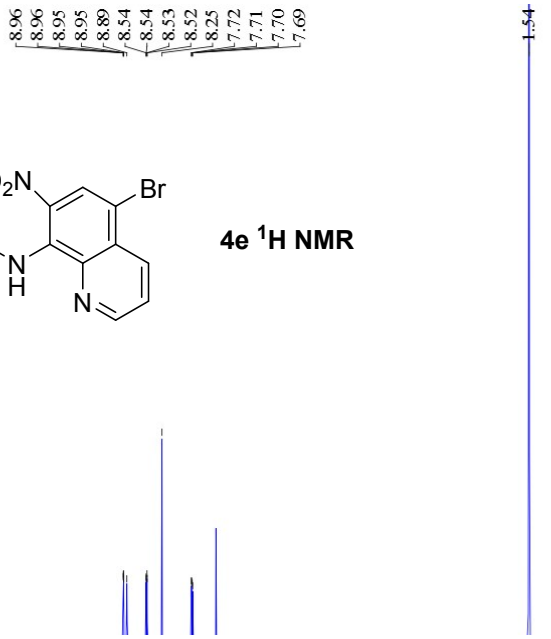
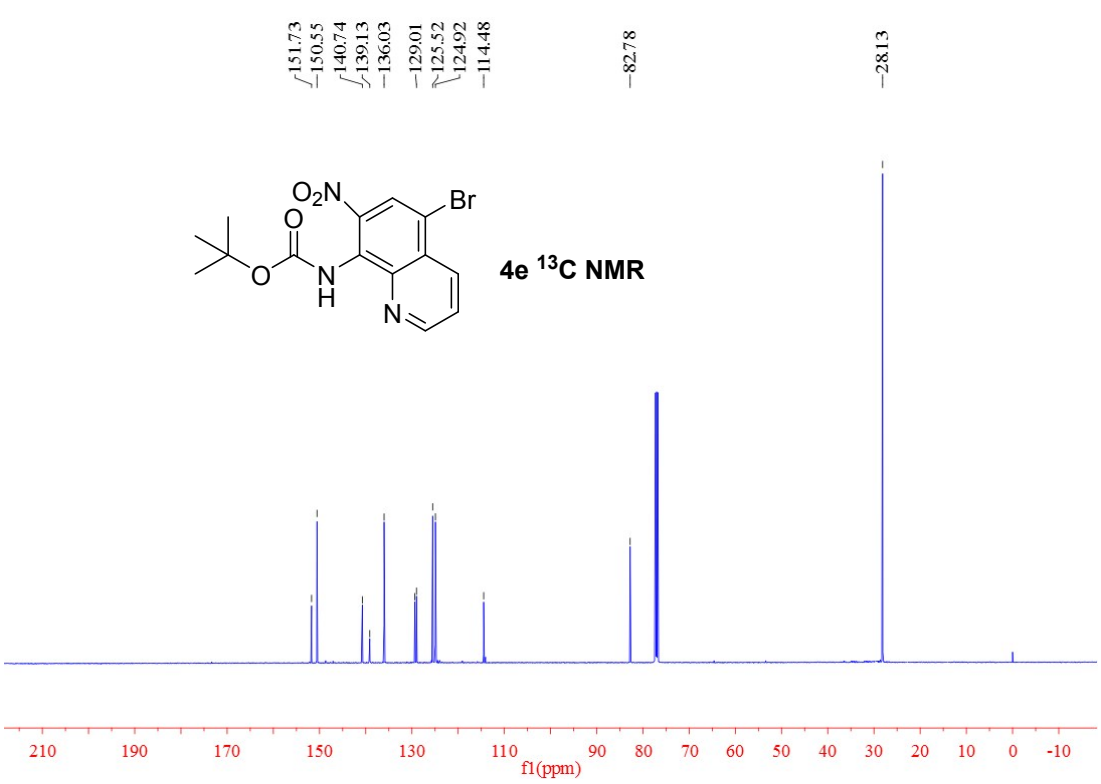
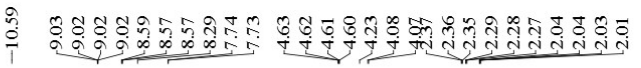
150.75
141.14
141.12
125.32
125.30
40.03
27.17
O2N
Br
O
N
H
N
4d 13C NMR
200
180
160
140
120
100
80
60
40
20
0
f1(ppm)

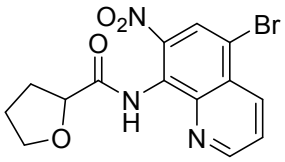


4e ^{1}H NMR

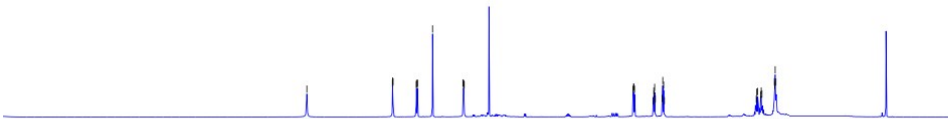


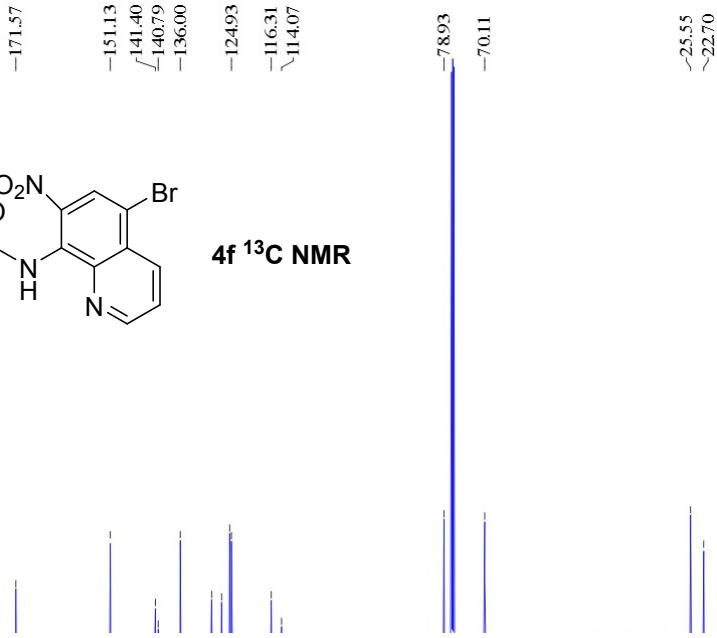
4e ^{13}C NMR



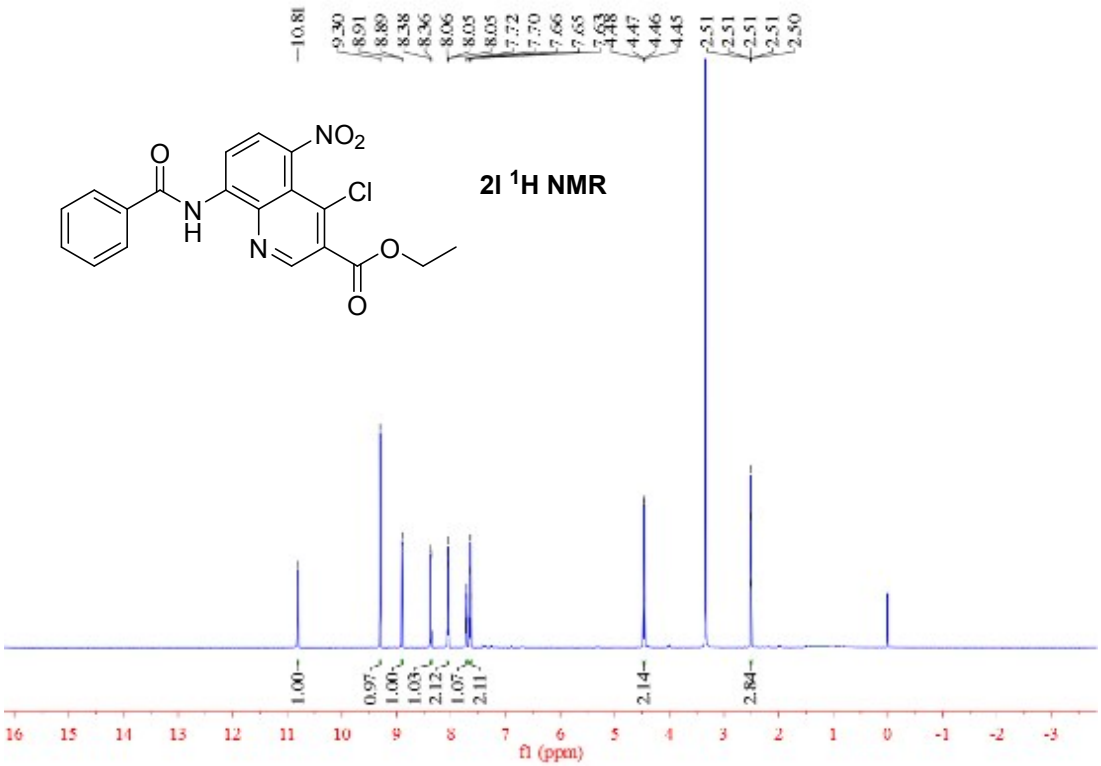


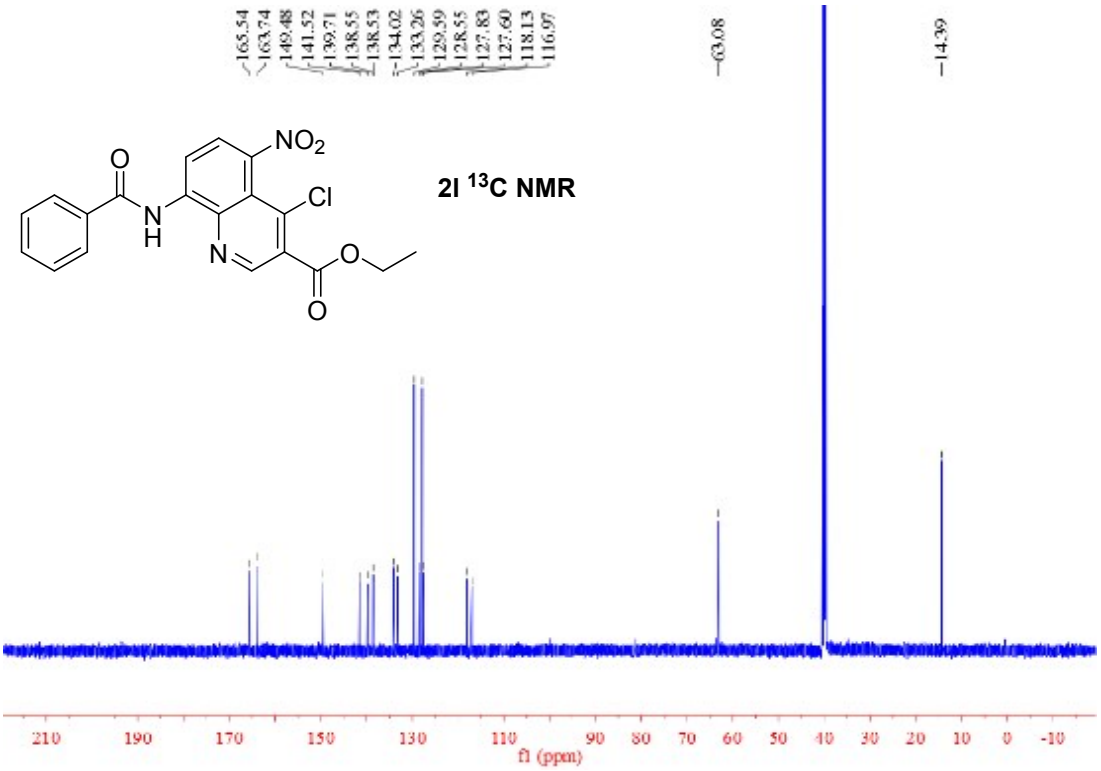
4f ^{1}H NMR

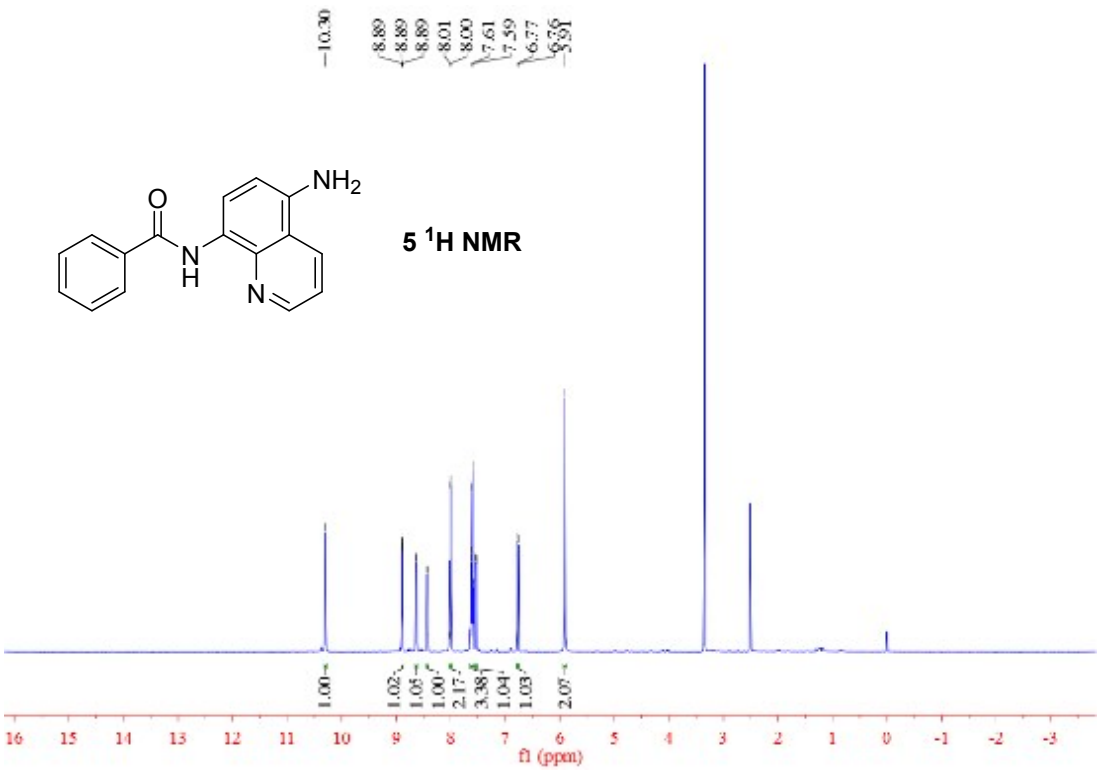




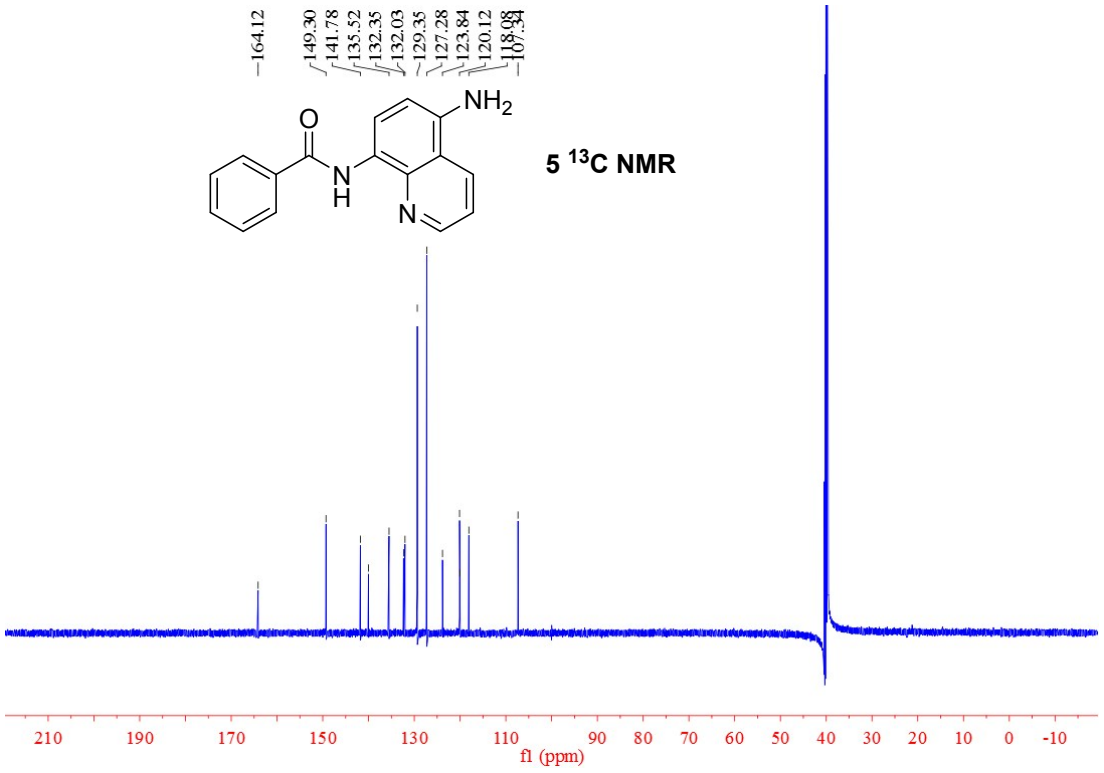
4f ^{13}C NMR


NO2
Cl
O
N
H
O
N
O
O
2l 1H NMR
f1 (ppm)


NO2
Cl
O
N
H
O
N
O
O
2l 13C NMR
f1 (ppm)

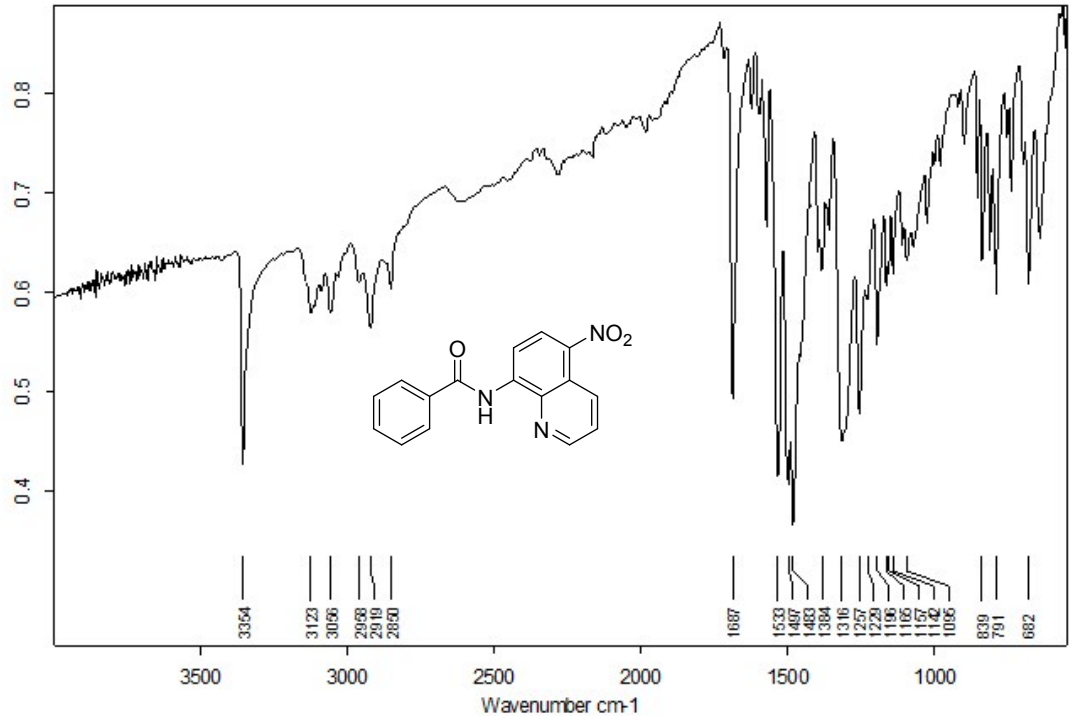


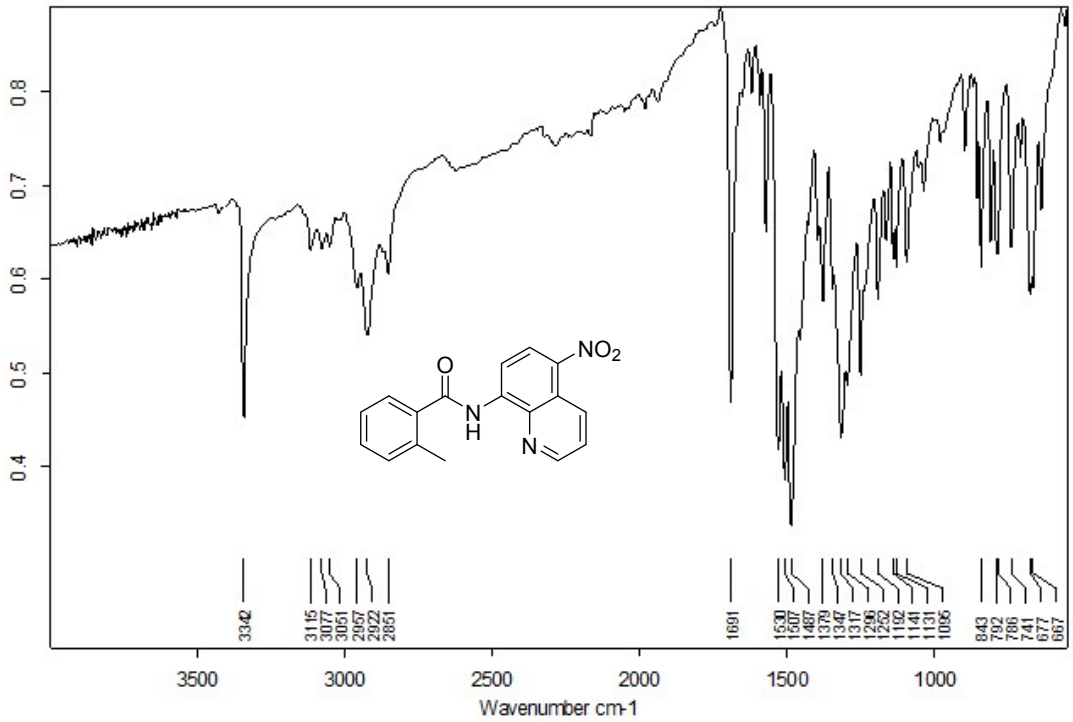
5 ^{1}H NMR

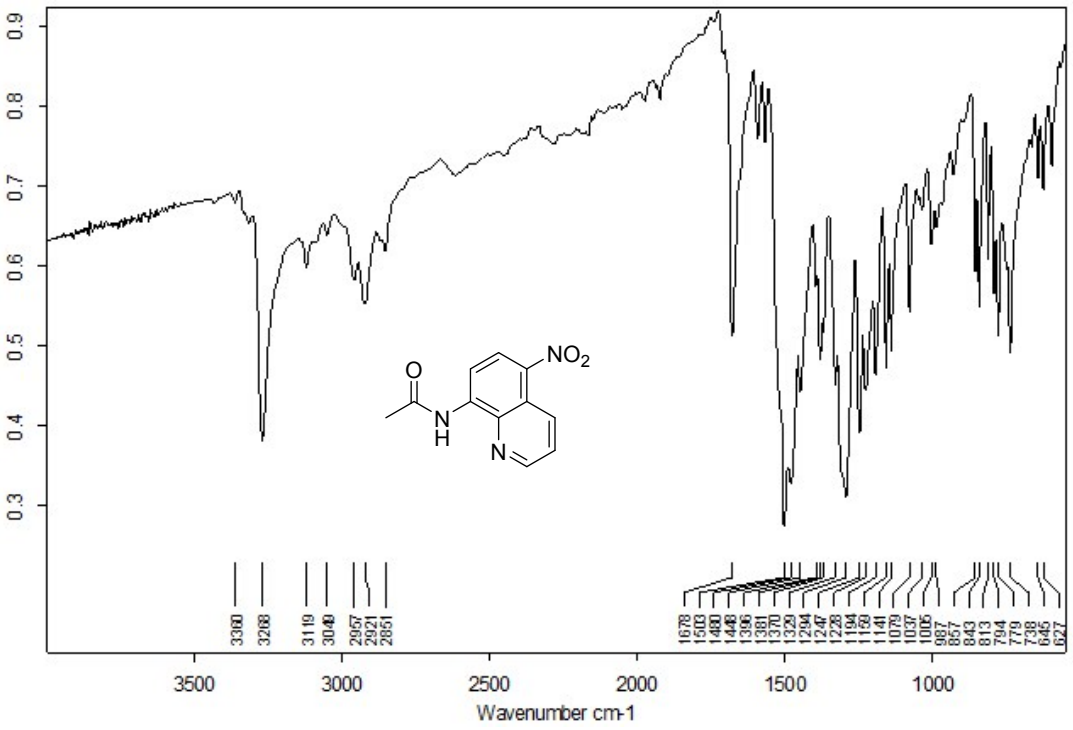


5 ^{13}C NMR

4. FT-IR spectra of the products






0.9
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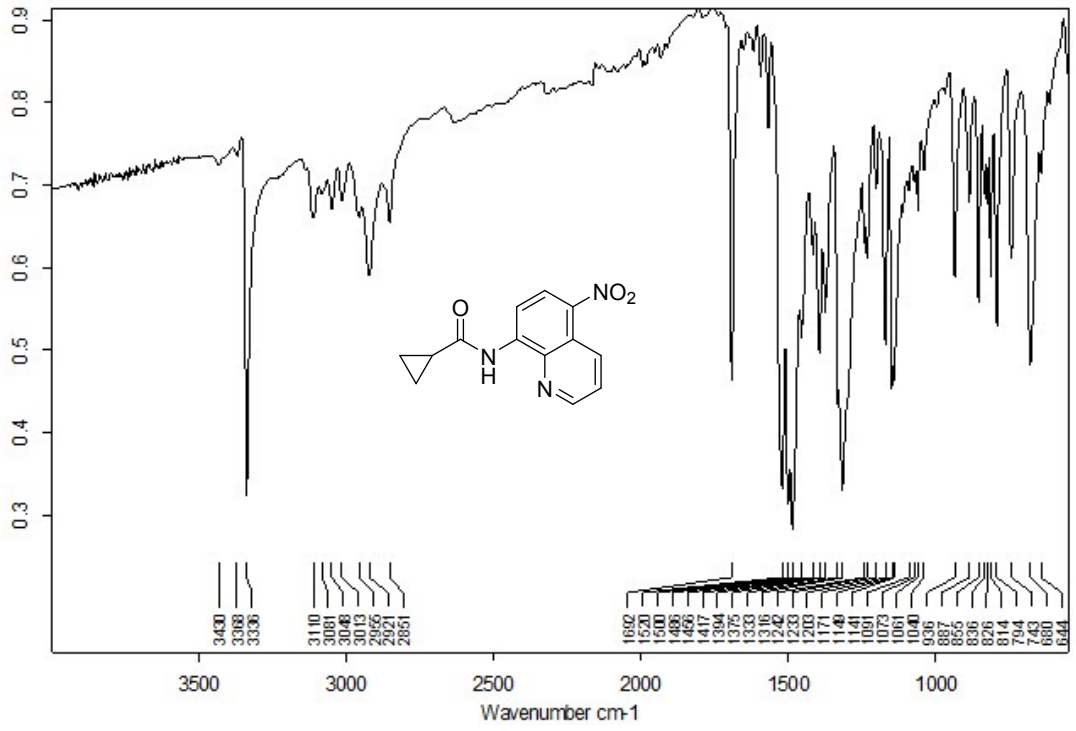
0.7
0.6
0.5
0.4
0.3
O
N
H
N
NO2
3360
3268
3119
3049
2957
2921
2851
1678
1503
1480
1448
1396
1381
1370
1329
1294
1247
1223
1194
1169
1141
1079
1037
1005
987
857
843
813
794
779
738
645
627
3500
3000
2500
2000
1500
1000
Wavenumber cm-1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0.6
0.5
0.4
0.3
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N
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NO2
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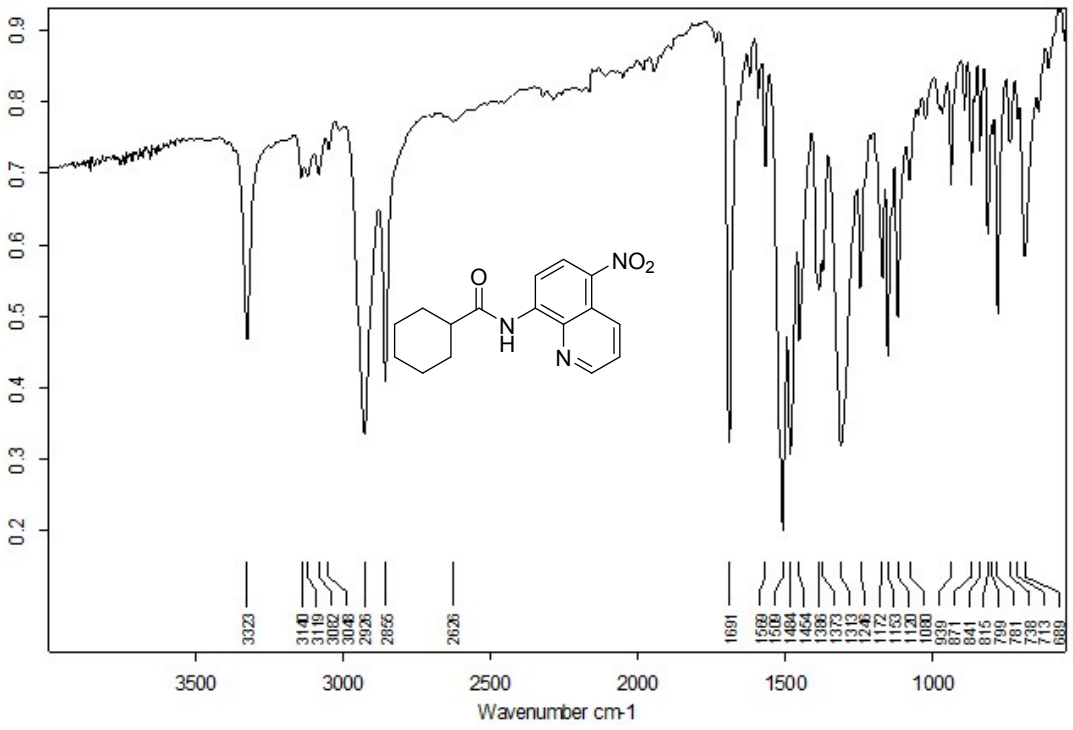
3336
3110
3081
3048
3013
2956
2921
2851
1692
1520
1500
1486
1456
1417
1394
1375
1333
1316
1242
1233
1203
1171
1149
1141
1091
1073
1061
1040
936
887
855
836
826
814
794
743
680
644
3500
3000
2500
2000
1500
1000
Wavenumber cm-1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0.4
0.3
0.2
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N
H
N
NO2
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3140
3119
3082
3046
2926
2855
2626
1691
1589
1509
1484
1454
1386
1373
1316
1246
1172
1153
1120
1080
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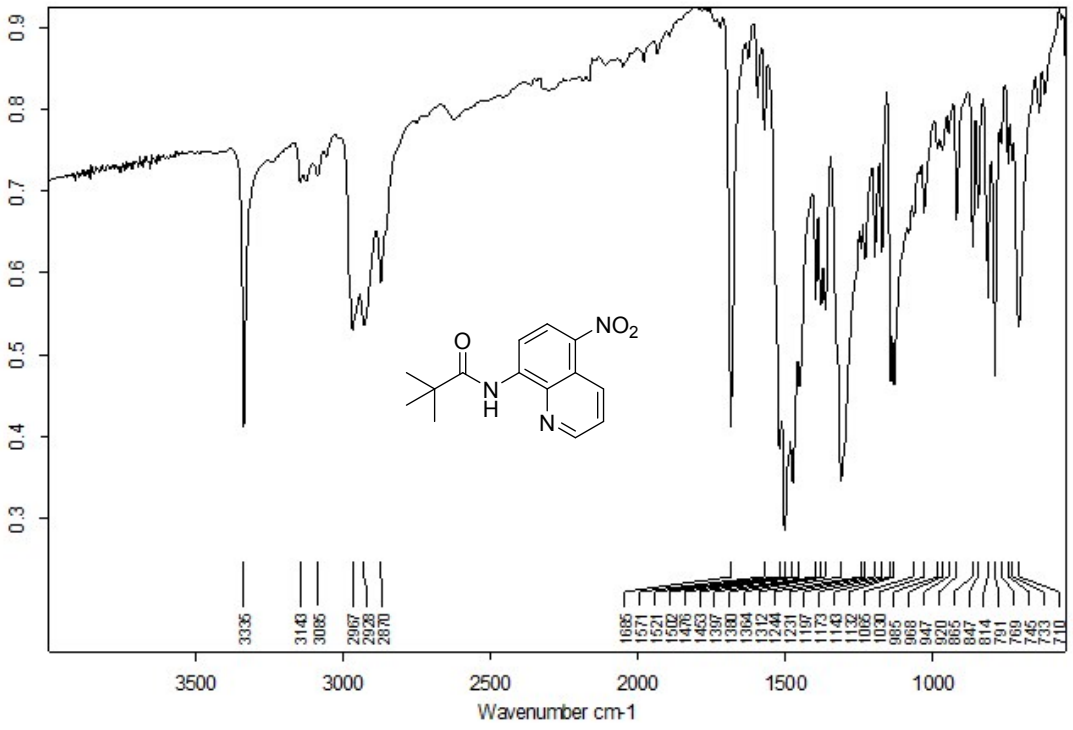
815
799
781
738
713
689
3500
3000
2500
2000
1500
1000
Wavenumber cm-1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0.7
0.6
0.5
0.4
0.3
O
N
H
N
NO2
3335
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3085
2967
2928
2870
1685
1571
1521
1502
1476
1463
1397
1380
1364
1312
1244
1231
1197
1173
1140
1132
1106
1030
985
968
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920
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814
791
769
745
733
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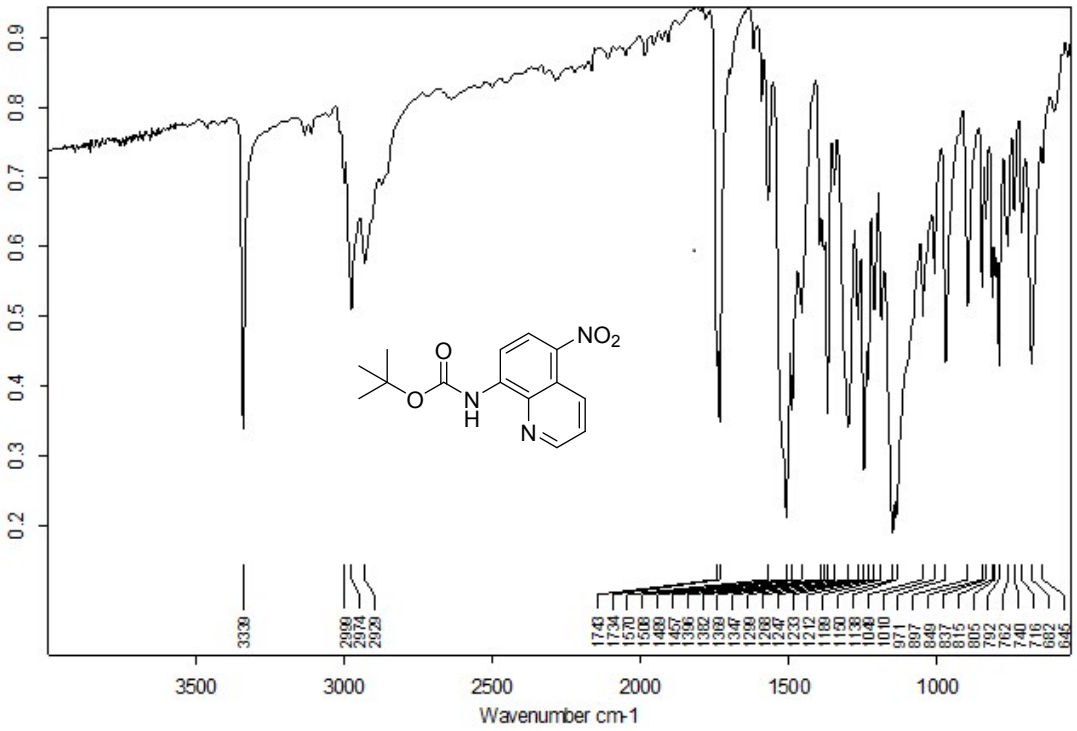
3000
2500
2000
1500
1000
Wavenumber cm-1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0.5
0.4
0.3
0.2
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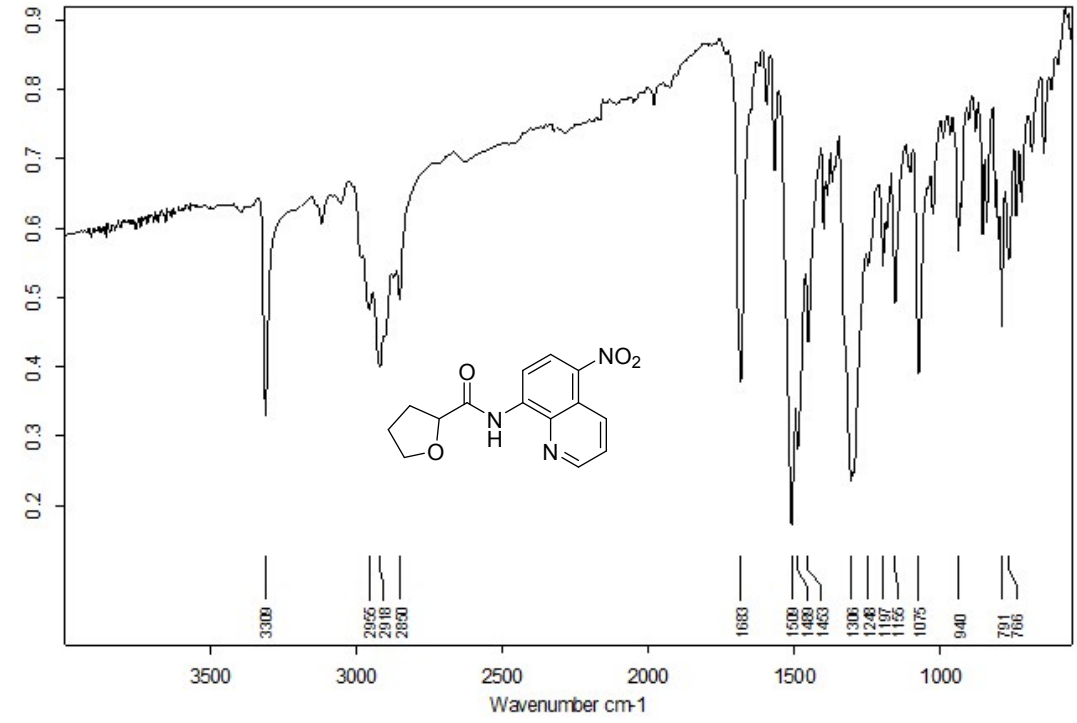
1734
1570
1508
1489
1467
1395
1362
1309
1347
1299
1268
1247
1233
1212
1189
1150
1138
1040
1010
971
897
849
837
815
805
792
762
740
716
682
645
3500
3000
2500
2000
1500
1000
Wavenumber cm-1
O
O
N
H
N
NO2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0.4
0.3
0.2
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1509
1489
1453
1306
1246
1197
1155
1075
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791
766
3500
3000
2500
2000
1500
1000
Wavenumber cm-1
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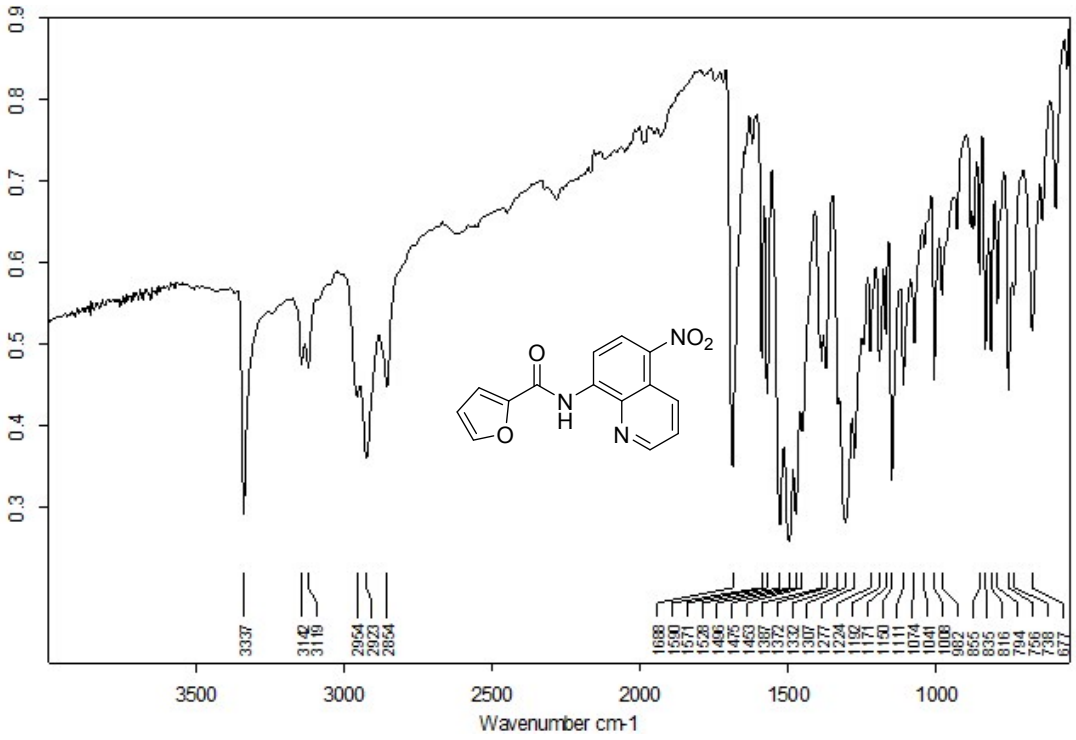
O
N
H
N
NO2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2954
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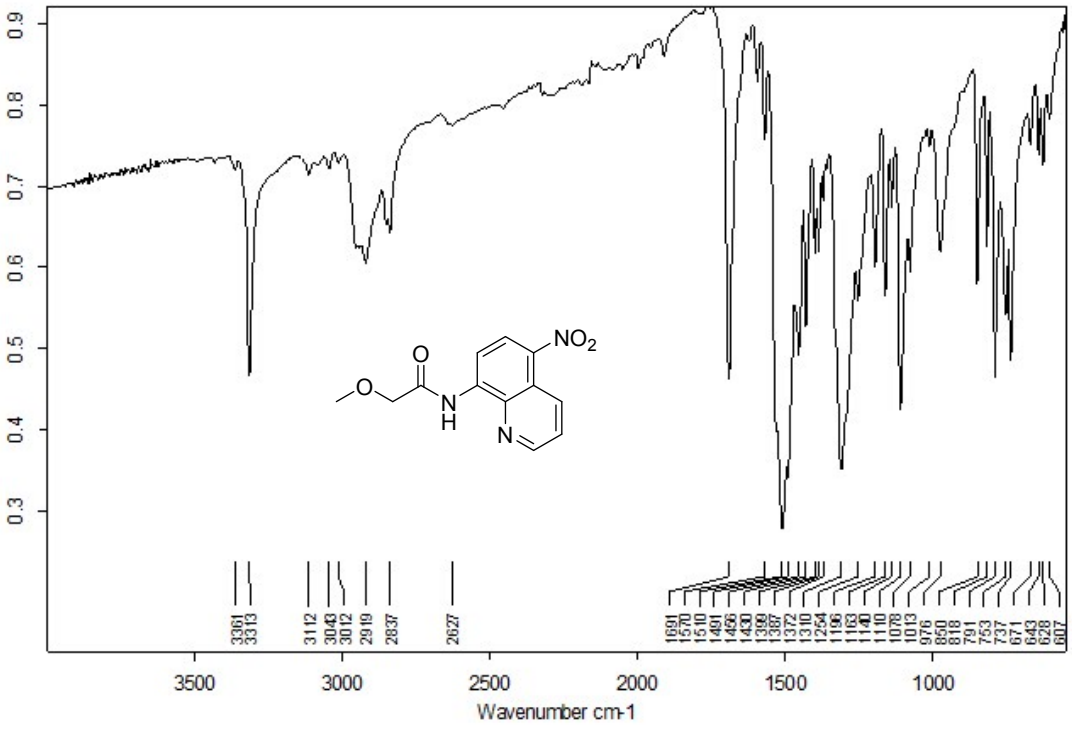
1688
1590
1571
1528
1496
1475
1453
1387
1372
1332
1307
1277
1224
1192
1171
1150
1111
1074
1041
1008
982
855
835
816
794
756
738
677
O
N
H
O
N
NO2
3500
3000
2500
2000
1500
1000
Wavenumber cm-1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0.6
0.5
0.4
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3361
3313
3112
3043
3012
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2837
2627
1691
1570
1510
1491
1456
1430
1399
1387
1372
1310
1254
1196
1163
1140
1110
1078
1013
976
850
818
791
753
737
671
643
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607
O
O
N
H
N
NO2
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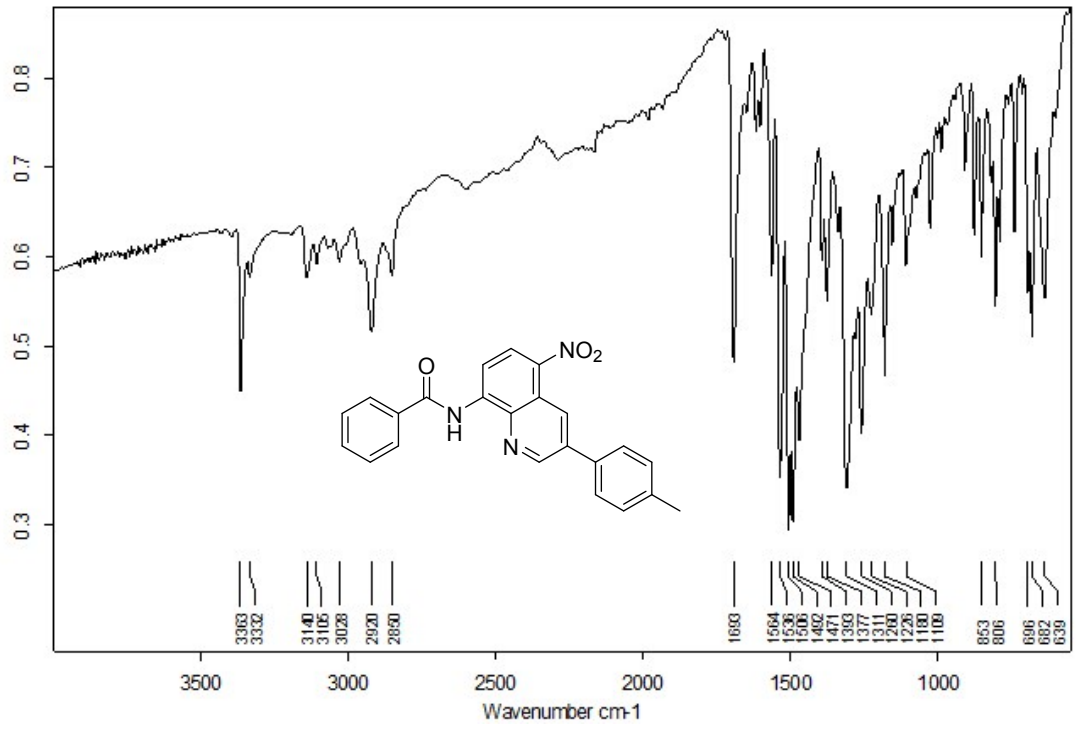
3000
2500
2000
1500
1000
Wavenumber cm-1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0.4
0.3
O
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H
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3105
3028
2920
2850
1693
1564
1536
1506
1492
1471
1393
1377
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853
806
696
682
639
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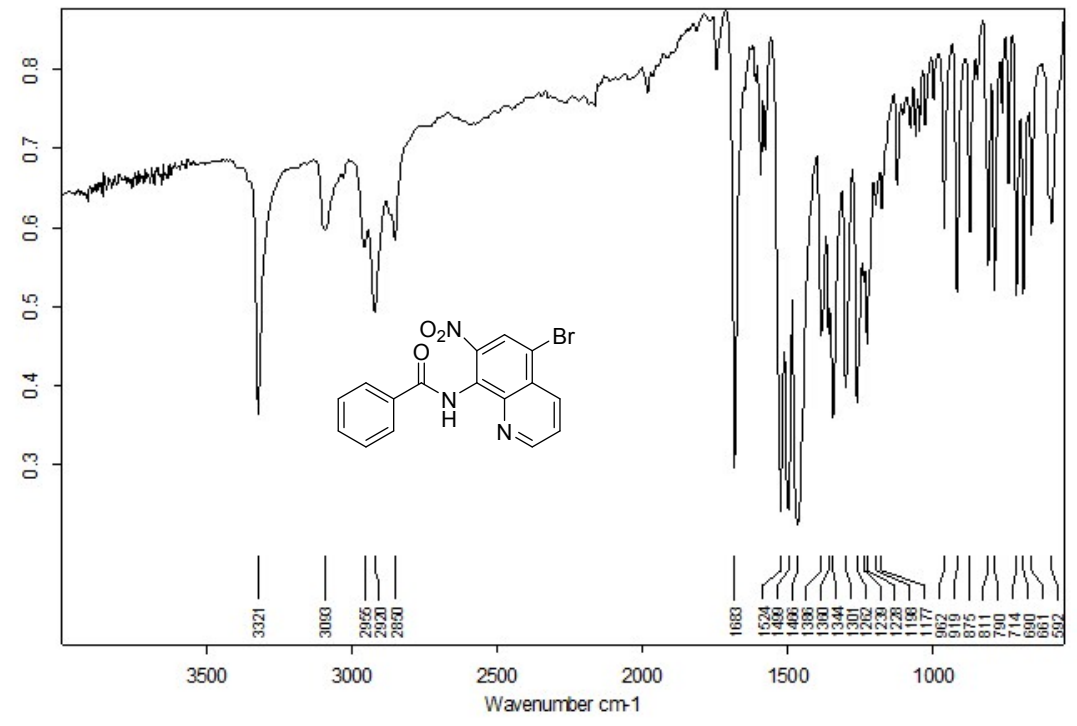
3000
2500
2000
1500
1000
Wavenumber cm-1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0.4
0.3
O2N
O
N
H
N
Br
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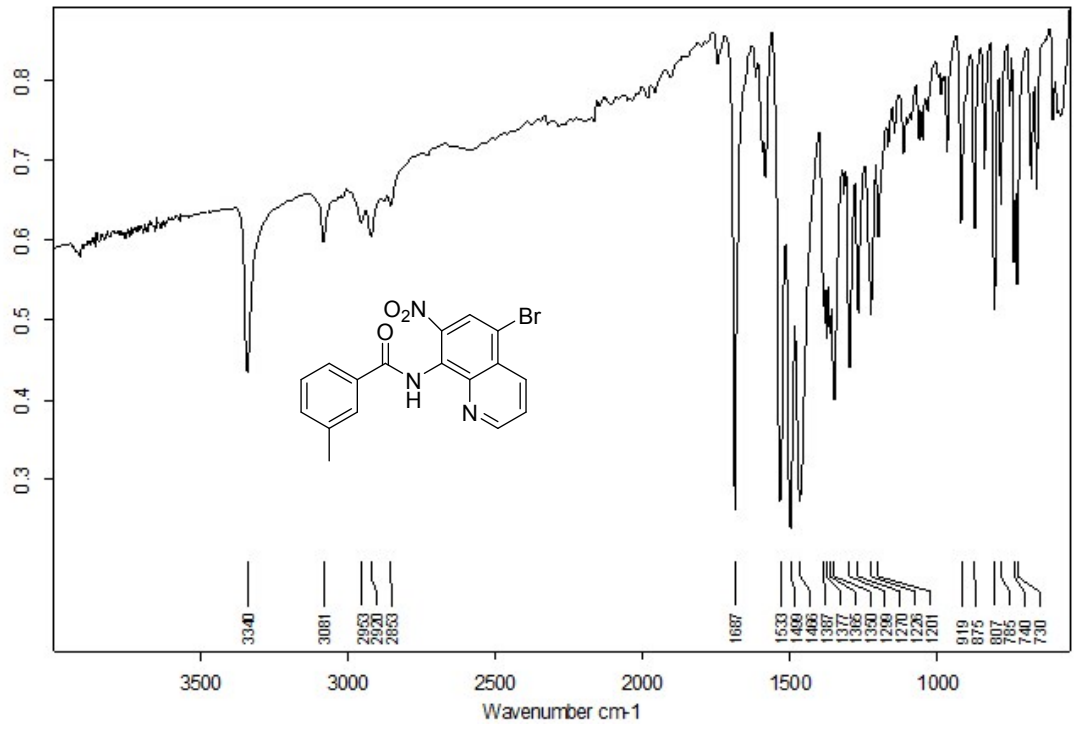
2955
2920
2850
1683
1524
1489
1466
1386
1360
1344
1301
1262
1239
1228
1198
1177
962
919
875
811
790
714
690
661
592
3500
3000
2500
2000
1500
1000
Wavenumber cm-1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Br
O
N
H
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2953
2920
2853
1687
1533
1499
1466
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1377
1365
1350
1299
1270
1226
1201
919
875
807
785
740
730
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0.4
0.5
0.6
0.7
0.8
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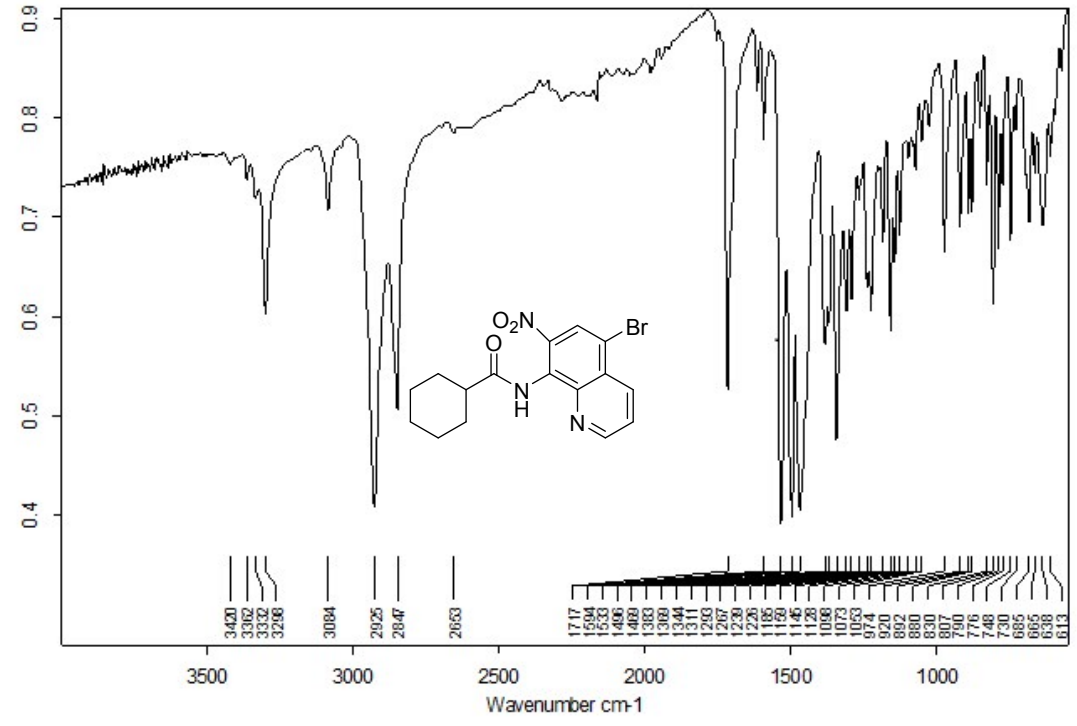
3000
2500
2000
1500
1000
Wavenumber cm-1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Br
O
N
H
N
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3280
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2653
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1533
1496
1469
1383
1369
1344
1311
1293
1267
1239
1226
1185
1160
1145
1128
1098
1073
1053
974
920
892
880
830
807
790
776
748
730
685
665
638
613
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0.6
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0.8
0.9
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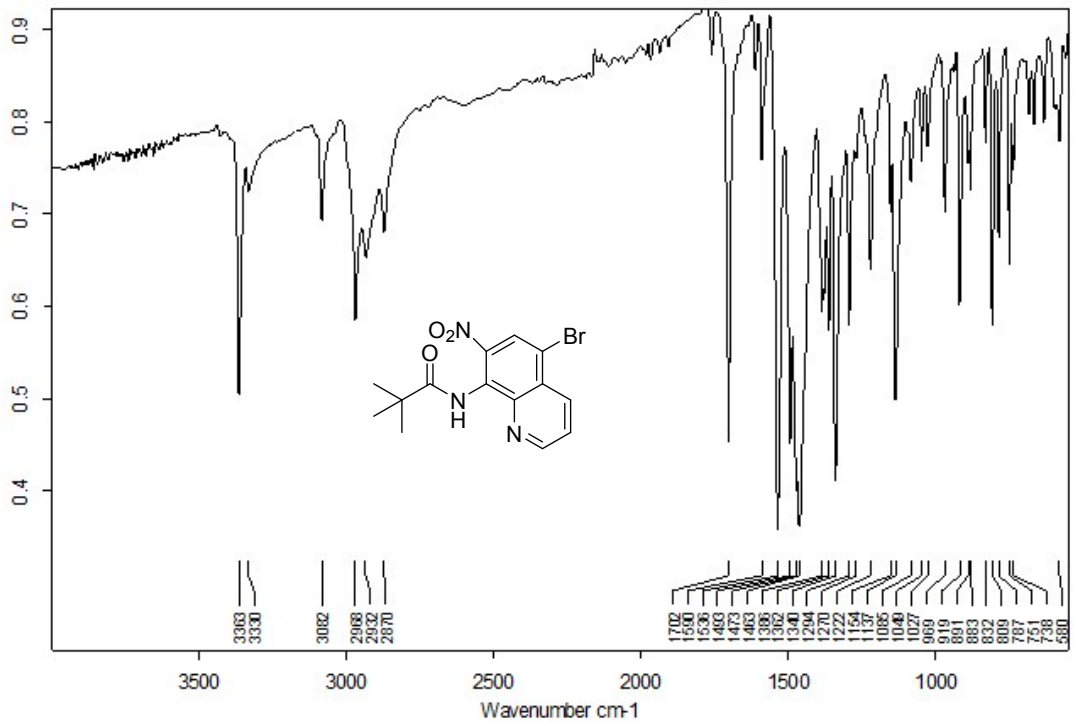
3000
2500
2000
1500
1000
Wavenumber cm-1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Br
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N
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1386
1362
1344
1294
1270
1222
1154
1137
1085
1049
1027
969
919
891
883
832
809
787
751
738
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0.5
0.4
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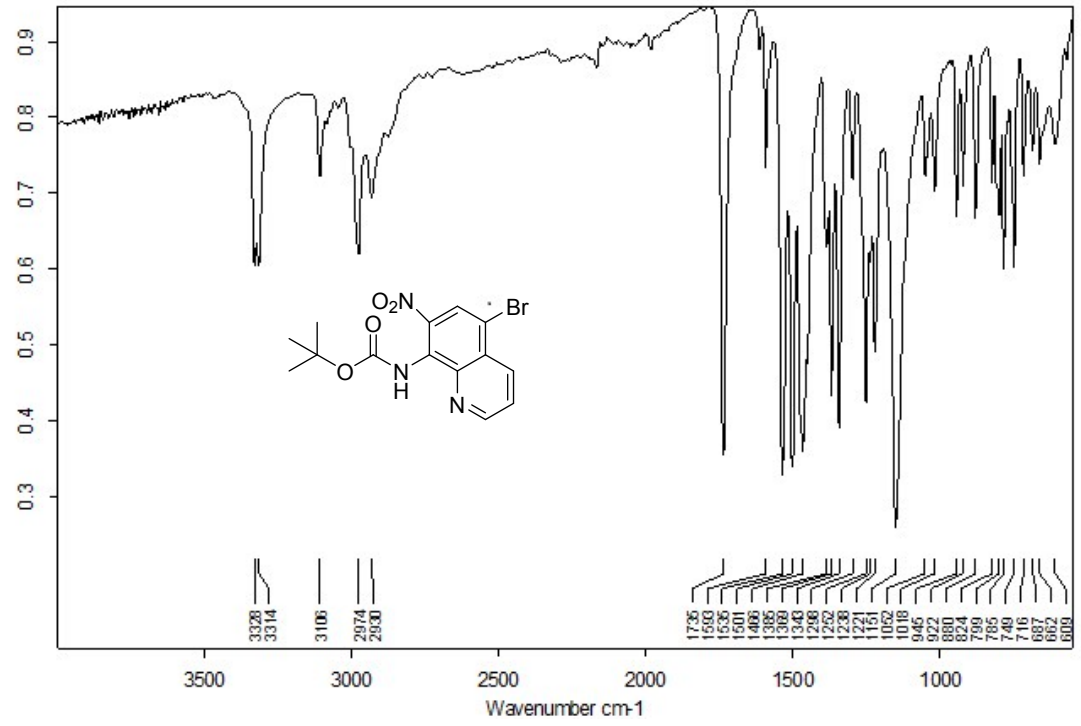
1000
Wavenumber cm-1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Br
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O
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H
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1385
1369
1348
1298
1252
1238
1221
1151
1052
1018
945
922
880
824
789
785
749
716
687
662
609
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0.6
0.5
0.4
0.3
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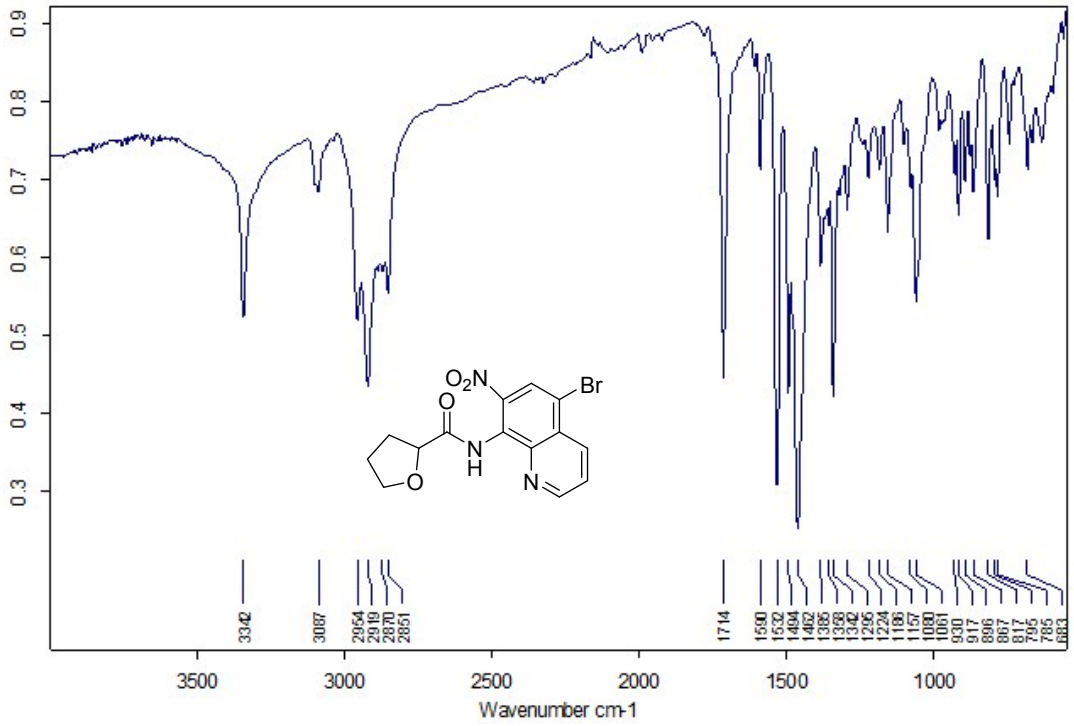
3000
2500
2000
1500
1000
Wavenumber cm-1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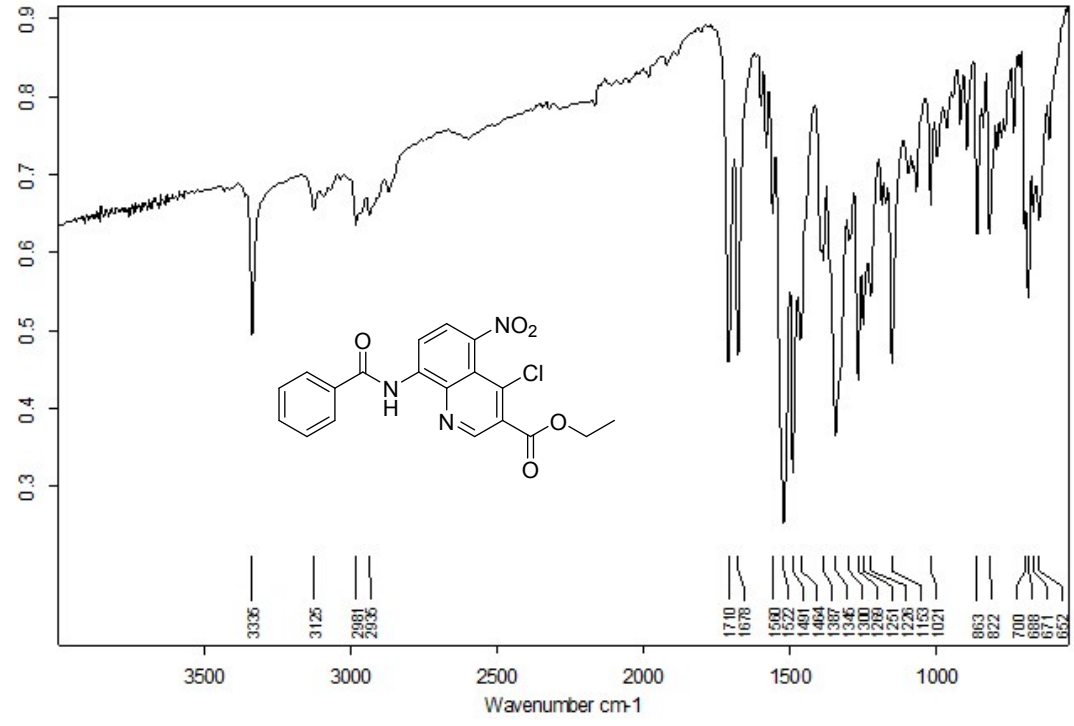
1494
1462
1385
1368
1342
1295
1224
1186
1157
1080
1061
930
917
896
867
817
795
785
683
3500
3000
2500
2000
1500
1000
Wavenumber cm-1
O2N
Br
O
N
H
O
N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0.4
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1710
1678
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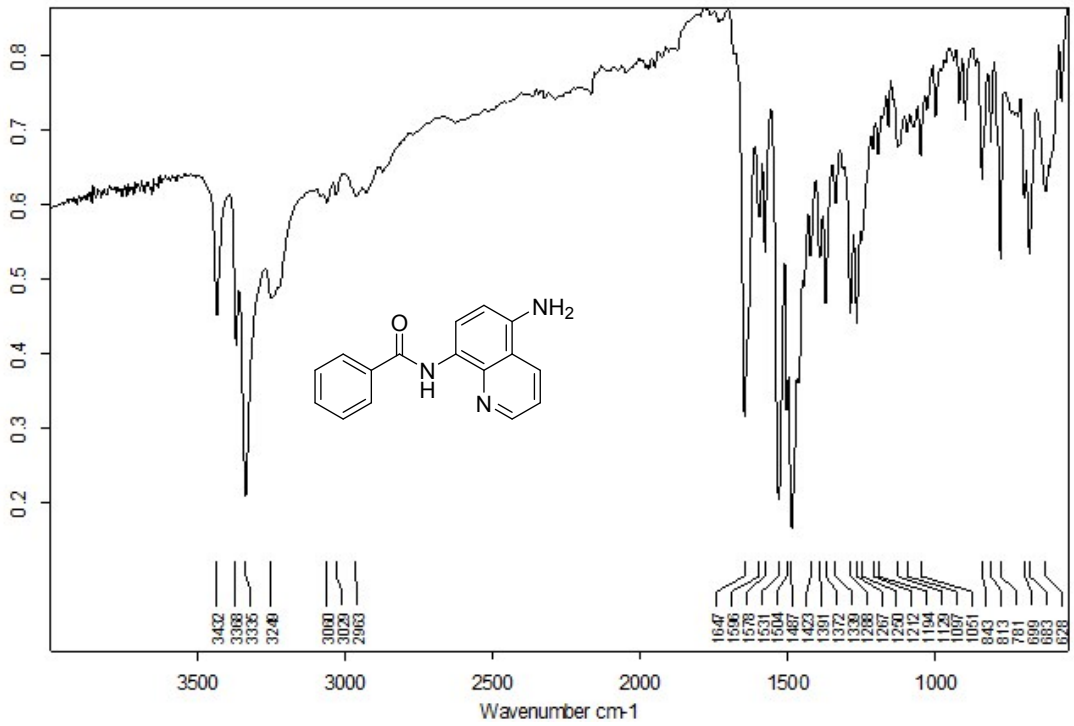
1522
1491
1464
1387
1345
1300
1289
1251
1226
1163
1021
863
822
700
688
671
652
3500
3000
2500
2000
1500
1000
Wavenumber cm-1
NO2
Cl
O
N
H
N
O
O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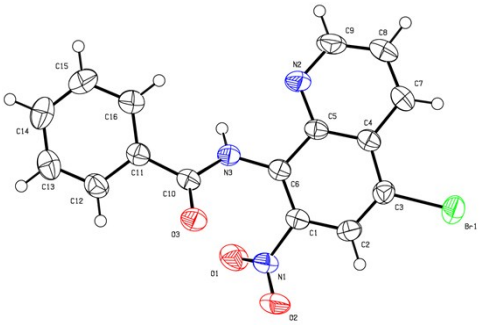
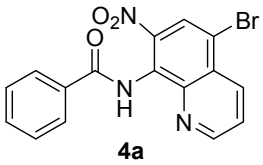
0.4
0.5
0.6
0.7
0.8
O
N
H
N
NH2
3432
3368
3335
3249
3060
3029
2963
1647
1596
1578
1531
1504
1487
1423
1391
1372
1339
1288
1267
1250
1212
1194
1129
1097
1051
843
813
781
699
683
628
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

5. X-ray Crystal Data for 4a





4a

Empirical formula	$C_{16}H_{10}BrN_3O_3$
Formula weight	372.18
Description	colorless, block
Crystal size (mm)	0.24 × 0.20 × 0.18
Temperature(K)	296(2)
Crystal system	Monoclinic
Space group	P2(1)/n
a (Å)	9.29(3)
b (Å)	9.545(3)
c (Å)	17.249(5)
α(°)	90.00
β(°)	98.859(4)
γ(°)	90.00
Volume ($Å^3$)	1468.9(7)
Z	4
D_{calc} (g cm^{-3})	1.683
F(000)	744
□ (mm^{-1})	2.818
θ Range (°)	2.41-27.40
Reflections collected / unique	8414 / 3258 [R(int) = 0.0229]
Unique reflections (Rint)	0.0229
Data, restraints, parameters	3258, 0, 208
Goodness of fit on F2	1.068
R1, wR2 [I ≥ 2□(I)][a)]	0.0338, 0.792
R1, wR2 (all data)[a)]	0.0463, 0.0836
A, B values in weighting scheme[b)]	0.0402, 0.4465
δρmax, δρmin (e·$Å^{-3}$)	0.326, -0.529

CCDC 1444178

6. References

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[2] Y. Kuninobu, T. Uesugi, A. Kawata, K. Takai, *Angew. Chem*. **2011**, *123*, 10590 - 10592; *Angew. Chem. Int. Ed*. **2011**, *50*, 10406 - 10408.

[3] A. M. Suess, M. Z. Ertem, C. J. Cramer, S. S. Stahl, *J. Am. Chem. Soc*. **2013**, *135*, 9797 - 9804.

[4] H. Zhang, L.-F. Han, K. A. Zachariasse, Y.-B. Jiang, *Org. Lett*. **2005**, *7*, 4217 - 4220.