Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Silver-catalyzed tandem radical acylarylation of cinnamamides in aqueous media

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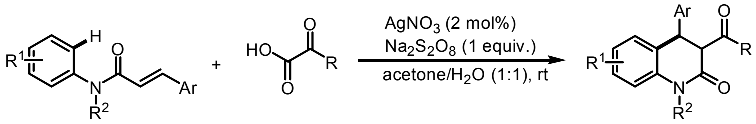
General Information

All Reactions were carried out under an atmosphere of nitrogen with the strict exclusion of air. Column chromatography was carried out on silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance III-400 in solvents as indicated. Chemical shift are reported in ppm from $CDCl_3$ using TMS as internal standard. IR spectra were recorded on a Bruker Tensor 27 spectrometer and only major peaks are reported in cm^{-1}. HRMS were obtained on a Q-TOF micro spectrometer.

Starting Materials

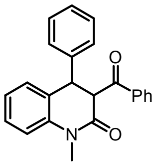
All of cinnamamides **1** were synthesized according to the literature, and the NMR spectroscopy were in full accordance with the data in the literature.[1] Phenylglyoxylic acid **2a** was purchased from Sigma-Aldrich. Other α-oxocarboxylic acids **2** were prepared from the corresponding methyl ketones according to the reported procedure.[2]

General Procedure for the Decarboxylative Cyclization of Cinnamamides with α-Oxocarboxylic Acids

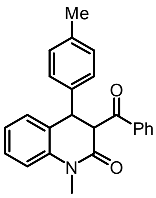


A 10 mL oven-dried Schlenk-tube was charged with $AgNO_3$ (0.7 mg, 2 mol%), cinnamamides (**1**, 0.2 mmol, 1.0 equiv.) and $Na_2S_2O_8$ (51 mg, 0.2 mmol, 1.0 equiv.). The tube was evacuated and backfilled with nitrogen (three times). α-Oxocarboxylic acids (**2**, 0.24 mmol, 1.2 equiv.) in acetone/H_2O (1:1) 2 mL were added by syringe. Upon completion of the reaction, the mixture was diluted with EtOAc, filtered through a pad of Celite, and the filtrate was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/30 to 1/15) to give the corresponding products **3** or **4** in yields listed in Table 2 and Table 3.

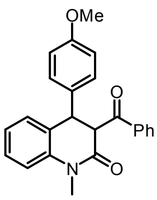
Characterization of Products 3



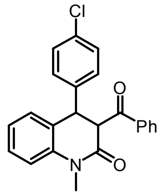
3a: R_f 0.2 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99-7.97 (d, *J* = 7.2 Hz, 2H), 7.63-7.60 (t, *J* = 6.8 Hz, 1H), 7.52-7.48 (t, *J* = 7.2 Hz, 2H), 7.41-7.24 (m, 6H), 7.18-7.17 (d, *J* = 7.6 Hz, 1H), 7.09-7.05 (t, *J* = 7.2 Hz, 1H), 6.95-6.93 (d, *J* = 7.2 Hz, 1H), 5.03-5.01 (d, *J* = 7.6 Hz, 1H), 4.80-4.78 (d, *J* = 8.0 Hz, 1H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 166.7, 140.0, 139.4, 136.6, 133.3, 129.0, 128.7, 128.6, 128.1, 128.0, 127.4, 127.3, 123.5, 114.9, 55.7, 44.8, 29.9 ppm; IR (KBr): υ_{max} 1694, 1659, 1493, 1371 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$ 342.1489, found 342.1496.



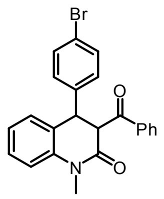
3b: R_f 0.2 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.90 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.56-7.53 (t, *J* = 7.2 Hz, 1H), 7.45-7.41 (t, *J* = 7.2 Hz, 2H), 7.33-7.29 (td, *J* = 8.4, 1.2 Hz, 1H), 7.10-7.05 (m, 5H), 7.01-6.97 (t, *J* = 7.2 Hz, 1H), 6.88-6.86 (d, *J* = 7.6 Hz, 1H), 4.93-4.81 (d, *J* = 7.6 Hz, 1H), 4.68-4.66 (d, *J* = 8.0 Hz, 1H), 3.45 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.7, 166.8, 139.4, 137.0, 136.9, 136.6, 133.3, 129.7, 128.7, 128.6, 128.0, 127.8, 127.6, 123.4, 114.9, 55.8, 44.4, 29.9, 21.0 ppm; IR (KBr): υ_{max} 1696, 1663, 1492, 1371 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{22}NO_2$ $[M+H]^+$ 356.1645, found 356.1650.



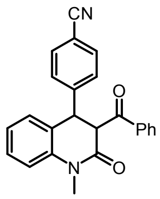
3c: R_f 0.15 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91-7.89 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.56-7.52 (t, *J* = 7.6 Hz, 1H), 7.45-7.41 (t, *J* = 7.2 Hz, 2H), 7.33-7.29 (td, J = 8.0, 0.8 Hz, 1H), 7.10-7.08 (m, 3H), 7.02-6.98 (m, 1H), 6.88-6.86 (d, J = 7.6 Hz, 1H), 6.82-6.80 (d, J = 8.8 Hz, 2H), 4.91-4.89 (d, J = 8.4 Hz, 1H), 4.69-4.67 (d, J = 8.4 Hz, 1H), 3.76 (s, 3H), 3.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.8, 166.9, 158.7, 139.4, 136.7, 133.3, 131.9, 129.1, 128.7, 128.6, 128.0, 127.8, 123.4, 114.9, 114.4, 55.9, 55.2, 44.1, 29.9 ppm; IR (KBr): υ_{max} 1693, 1657, 1509, 1370 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{21}NNaO_3$ [M+Na]$^+$ 394.1414, found 394.1417.



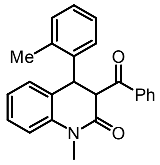
3d: R_f 0.2 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90-7.88 (m, 2H), 7.58-7.54 (t, J = 7.2 Hz, 1H), 7.46-7.42 (t, J = 7.2 Hz, 2H), 7.35-7.31 (td, J = 8.0, 0.8 Hz, 1H), 7.28-7.24 (m, 2H), 7.14-7.09 (m, 3H), 7.03-6.99 (td, J = 8.0, 0.8 Hz, 1H), 6.83-6.81 (d, J = 7.2 Hz, 1H), 4.90-4.88 (d, J = 8.8 Hz, 1H), 4.73-4.71 (d, J = 8.4 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.4, 166.5, 139.4, 138.4, 136.6, 133.5, 133.3, 129.6, 129.2, 128.7, 128.4, 128.3, 127.1, 123.6, 115.0, 55.4, 44.1, 30.0 ppm; IR (KBr): υ_{max} 1695, 1665, 1464, 1371 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}ClNO_2$ [M+H]$^+$ 376.1099, found 376.1101.



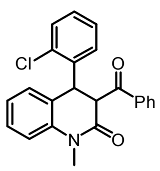
3e: R_f 0.2 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90-7.88 (dd, J = 8.4, 1.2 Hz, 2H), 7.55-7.53 (m, 1H), 7.46-7.40 (m, 4H), 7.39-7.31 (td, J = 8.0, 0.8 Hz, 1H), 7.11-6.99 (m, 4H), 6.83-6.81 (d, J = 7.6 Hz, 1H), 4.90-4.88 (d, J = 8.8 Hz, 1H), 4.72-4.70 (d, J = 8.8 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.3, 166.5, 139.4, 139.0, 136.6, 133.5, 132.1, 129.9, 128.7, 128.4, 128.3, 127.0, 123.6, 121.4, 115.0, 55.3, 44.1, 30.0 ppm; IR (KBr): υ_{max} 1694, 1665, 1465, 1371 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}BrNO_2$ [M+H]$^+$ 420.0594, found 420.0603.



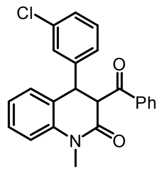
3f: R_f 0.1 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.88 (d, *J* = 7.6 Hz, 2H), 7.60-7.55 (m, 3H), 7.46-7.42 (t, *J* = 7.6 Hz, 2H), 7.37-7.31 (m, 3H), 7.13-7.11 (d, *J* = 8.0 Hz, 1H), 7.05-7.01 (t, *J* = 7.6 Hz, 1H), 6.79-6.77 (d, *J* = 7.6 Hz, 1H), 4.91-4.89 (d, *J* = 8.8 Hz, 1H), 4.82-4.80 (d, *J* = 8.8 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9, 166.0, 145.5, 139.4, 136.4, 133.6, 132.8, 129.1, 128.7, 128.3, 126.2, 123.7, 118.4, 115.2, 111.5, 55.1, 44.6, 30.0 ppm; IR (KBr): υ_{max} 2229, 1685, 1660, 1467, 1369 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{18}N_2NaO_2$ $[M+Na]^+$ 389.1260, found 389.1265.



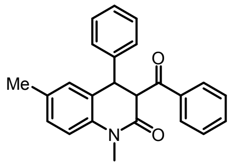
3g: R_f 0.2 (EtOAc/petroleum ether = 1:4), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88-7.86 (d, *J* = 8.4 Hz, 2H), 7.53-7.50 (t, *J* = 7.6 Hz, 1H), 7.42-7.38 (t, *J* = 7.6 Hz, 2H), 7.33-7.28 (d, *J* = 7.6 Hz, 1H), 7.20-7.18 (d, *J* = 7.6 Hz, 1H), 7.13-6.94 (m, 5H), 6.65-6.63 (d, *J* = 7.2 Hz, 1H), 5.10-5.07 (d, *J* = 11.2 Hz, 1H), 4.99-4.97 (d, *J* = 11.6 Hz, 1H), 3.46 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.2, 167.6, 139.6, 137.6, 137.5, 137.2, 133.1, 130.8, 128.6, 128.5, 127.9, 127.8, 127.2, 126.7, 126.6, 123.6, 114.7, 53.8, 39.6, 30.0, 19.7 ppm; IR (KBr): υ_{max} 1691, 1662, 1463, 1364 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{21}NNaO_2$ $[M+Na]^+$ 378.1464, found 378.1470.



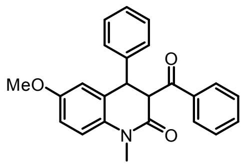
3h: R_f 0.2 (EtOAc/petroleum ether = 1:4), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01-7.99 (m, 2H), 7.58-7.54 (m, 1H), 7.46-7.40 (m, 3H), 7.35-7.32 (m, 1H), 7.20-7.16 (td, *J* = 7.6, 2.0 Hz, 1H), 7.14-7.11 (m, 2H), 7.10-7.02 (m, 1H), 6.91-6.86 (m, 2H), 5.19-5.17 (d, *J* = 6.8 Hz, 1H), 5.04-5.02 (d, *J* = 6.8 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.5, 166.3, 140.0, 137.5, 136.8, 134.2, 133.7, 130.6, 129.7, 129.3, 129.0, 128.8, 128.7, 128.6, 127.8, 126.7, 124.1, 115.3, 54.8, 41.8, 30.4 ppm; IR (KBr): υ_{max} 1689, 1669, 1458, 1359 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}ClNO_2$ $[M+H]^+$ 376.1099, found 376.1098.



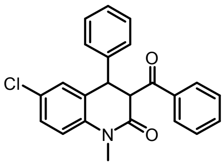
3i: R_f 0.2 (EtOAc/petroleum ether = 1:4), ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90-7.88 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.57-7.54 (t, *J* = 7.2 Hz, 1H), 7.46-7.42 (t, *J* = 7.2 Hz, 2H), 7.35-7.31 (td, *J* = 8.0, 0.8 Hz, 1H), 7.27-7.25 (m, 2H), 7.13-7.09 (m, 3H), 7.03-6.99 (td, *J* = 8.0, 0.8 Hz, 1H), 6.83-6.82 (d, *J* = 7.2 Hz, 1H), 4.90-4.88 (d, *J* = 8.8 Hz, 1H), 4.73-4.71 (d, *J* = 8.8 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.4, 166.5, 139.4, 138.4, 136.6, 133.5, 133.2, 129.6, 129.2, 128.7, 128.4, 128.3, 127.1, 123.6, 115.0, 55.4, 44.1, 30.0 ppm; IR (KBr): υ_{max} 1695, 1665, 1463, 1371 cm^{-1}.



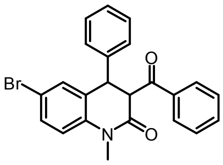
3k: R_f 0.3 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.90 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.55-7.52 (m, 1H), 7.44-7.41 (m, 2H), 7.30-7.17 (m, 3H), 7.15-7.13 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.09-7.07 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.99-6.97 (d, *J* = 8.4 Hz, 1H), 6.69 (s, 1H), 4.91-4.89 (d, *J* = 7.2 Hz, 1H), 4.65-4.63 (d, *J* = 7.2 Hz, 1H), 3.42 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 166.3, 140.3, 137.1, 136.4, 133.3, 133.1, 129.3, 129.0, 128.7, 128.6, 127.9, 127.3, 126.9, 114.8, 56.2, 44.9, 29.9, 20.6 ppm; IR (KBr): υ_{max} 1688, 1663, 1472, 1372 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{21}NNaO_2$ $[M+Na]^+$ 378.1464, found 378.1475.



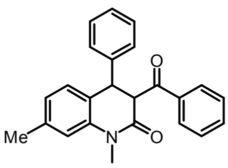
3l: R_f 0.1 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.93-7.90 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.56-7.52 (t, *J* = 7.6 Hz, 1H), 7.45-7.41 (t, *J* = 8.0 Hz, 2H), 7.30-7.16 (m, 5H), 7.03-7.00 (d, *J* = 8.8 Hz, 1H), 6.85-6.82 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.45-6.44 (d, J = 2.8 Hz, 1H), 4.91-4.89 (d, J = 7.6 Hz, 1H), 4.67-4.65 (d, J = 7.6 Hz, 1H), 3.69 (s, 3H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 166.1, 155.7, 139.9, 136.6, 133.3, 133.1, 129.0, 128.8, 128.7, 128.6, 128.0, 127.4, 115.9, 114.9, 112.4, 55.9, 55.4, 45.0, 30.1 ppm; IR (KBr): υ_{max} 1688, 1653, 1499, 1376 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{21}NNaO_3$ $[M+Na]^+$ 394.1414, found 394.1416.



3m: R_f 0.2 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.90 (dd, J = 8.8, 1.6 Hz, 2H), 7.58-7.54 (td, J = 7.6, 1.2 Hz, 1H), 7.46-7.42 (t, J = 8.0 Hz, 2H), 7.31-7.24 (m, 4H), 7.17-7.14 (dd, J = 8.8, 1.6 Hz, 2H), 7.03-7.01 (d, J = 8.8 Hz, 1H), 6.87 (d, J = 2.0 Hz, 1H), 4.93-4.91 (d, J = 7.6 Hz, 1H), 4.67-4.65 (d, J = 7.2 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.2, 166.2, 139.3, 138.2, 136.3, 133.5, 129.2, 129.1, 128.8, 128.7, 128.6, 128.1, 127.9, 127.7, 116.2, 55.6, 44.7, 30.1 ppm; IR (KBr): υ_{max} 1689, 1664, 1452, 1368 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}ClNO_2$ $[M+H]^+$ 376.1099, found 376.1103.

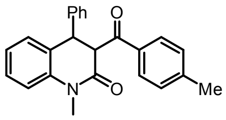


3n: R_f 0.2 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.90 (d, J = 7.6 Hz, 2H), 7.58-7.55 (t, J = 7.6 Hz, 1H), 7.47-7.41 (m, 3H), 7.32-7.24 (m, 3H), 7.16-7.14 (d, J = 7.2 Hz, 2H), 7.02 (d, J = 1.6 Hz, 1H), 6.98-6.96 (d, J = 8.8 Hz, 1H), 4.92-4.90 (d, J = 7.2 Hz, 1H), 4.66-4.65 (d, J = 7.6 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.1, 166.2, 139.4, 138.7, 136.2, 133.6, 131.5, 131.0, 129.4, 129.2, 128.8, 128.7, 127.8, 127.7, 116.6, 116.4, 55.7, 44.7, 30.0 ppm; IR (KBr): υ_{max} 1689, 1664, 1466, 1368 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{18}BrNNaO_2$ $[M+Na]^+$ 442.0413, found 442.0428.

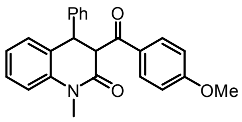


3o: R_f 0.25 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91-7.90 (d, *J* = 7.2 Hz, 2H), 7.56-7.52 (t, *J* = 7.2 Hz, 1H), 7.45-7.41 (t, *J* = 7.6 Hz, 2H), 7.33-7.29 (td, *J* = 8.4, 1.2 Hz, 1H), 7.17-7.14 (t, *J* = 7.6 Hz, 1H), 7.10-7.08 (d, *J* = 8.0 Hz, 1H), 7.03-6.98 (m, 3H), 6.95-6.93 (d, *J* = 8.0 Hz, 1H), 6.88-6.86 (d, *J* = 7.6 Hz, 1H), 4.94-4.92 (d, *J* = 7.6 Hz, 1H), 4.67-4.65 (d, *J* = 8.0 Hz, 1H), 3.45 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.7, 166.8, 139.9, 139.4, 138.6, 136.6, 133.3, 128.9, 128.8, 128.7, 128.6, 128.2, 128.1, 127.4, 124.8, 123.4, 114.9, 55.7, 44.8, 29.9, 21.5 ppm; IR (KBr): υ_{max} 1693, 1663, 1465, 1369 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{21}NNaO_2$ $[M+Na]^+$ 378.1464, found 378.1476.

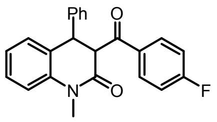
Characterization of Products 4



4a: R_f 0.25 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83-7.81 (d, *J* = 8.4 Hz, 2H), 7.31-7.17 (m, 8H), 7.11-7.09 (d, *J* = 8.0 Hz, 1H), 7.02-6.98 (t, *J* = 7.6 Hz, 1H), 6.89-6.87 (t, *J* = 7.2 Hz, 1H), 4.93-4.91 (d, *J* = 7.6 Hz, 1H), 4.71-4.69 (d, *J* = 7.2 Hz, 1H), 3.45 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.1, 166.7, 144.3, 140.2, 139.5, 134.0, 129.3, 129.0, 128.9, 128.7, 128.1, 128.0, 127.3, 123.4, 114.9, 55.7, 44.9, 29.9, 21.6 ppm; IR (KBr): υ_{max} 1668, 1600, 1456, 1365 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{21}NNaO_2$ $[M+Na]^+$ 378.1464, found 378.1475.

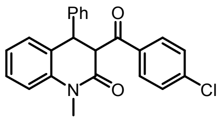


4b: R_f 0.1 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.89 (d, *J* = 8.8 Hz, 2H), 7.28-7.14 (m, 6H), 7.08-7.06 (d, *J* = 8.4 Hz, 1H), 7.00-6.96 (t, *J* = 7.6 Hz, 1H), 6.89-6.87 (dd, *J* = 8.8, 2.4 Hz, 3H), 4.88-4.86 (d, *J* = 7.2 Hz, 1H), 4.68-4.66 (d, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.7, 166.7, 163.7, 140.3, 139.5, 131.2, 129.4, 129.0, 128.7, 128.0, 127.9, 127.4, 127.3, 123.4, 114.8, 113.8, 55.53, 55.46, 44.9, 29.9 ppm; IR (KBr): υ_{max} 1665, 1599, 1458, 1371 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{21}NNaO_3$ $[M+Na]^+$ 394.1414, found 394.1421.

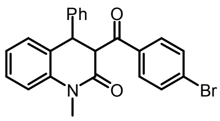


4c: R_f 0.25 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96-7.92 (dd, *J* = 8.4, 4.2 Hz, 2H), 7.34-7.07 (m, 9H), 7.03-6.99 (t, *J* = 8.0 Hz, 1H), 6.88-6.86 (d, *J* = 7.6 Hz, 1H), 4.90-4.88 (d, *J* = 8.4 Hz, 1H), 4.73-4.71 (d, *J* = 8.4 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.0, 166.5, 165.8 (d, $J_{C\text{-}F}$ = 253.9 Hz), 139.8, 139.3, 133.2, 131.4 (d, $J_{C\text{-}F}$ = 9.4 Hz), 129.0, 128.6, 128.1, 127.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 123.6, 115.7 (d, $J_{C\text{-}F}$ = 21.8 Hz), 114.9, 55.6, 44.7, 29.7 ppm; IR (KBr): υ_{max} 1697, 1664, 1468, 1373 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{18}FNNaO_2$ $[M+Na]^+$

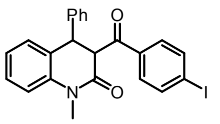
382.1214, found 382.1215.



4d: R_f 0.3 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82-7.80 (d, J = 8.4 Hz, 2H), 7.37-7.35 (d, J = 8.8 Hz, 2H), 7.31-7.20 (m, 4H), 7.15-7.13 (d, J = 7.2 Hz, 2H), 7.08-7.06 (d, J = 8.4 Hz, 1H), 7.00-6.96 (t, J = 7.2 Hz, 1H), 6.84-6.82 (d, J = 7.6 Hz, 1H), 4.86-4.84 (d, J = 8.8 Hz, 1H), 4.71-4.68 (d, J = 8.8 Hz, 1H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.5, 166.5, 139.8, 139.7, 139.3, 135.1, 130.1, 129.0, 128.9, 128.6, 128.1, 127.5, 123.6, 114.9, 55.6, 44.6, 30.0 ppm; IR (KBr): υ_{max} 1701, 1658, 1463, 1374 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}ClNO_2$ $[M+H]^+$ 376.1099, found 376.1103.

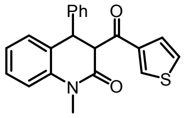


4e: R_f 0.3 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.77-7.75 (d, J = 8.8 Hz, 2H), 7.57-7.55 (d, J = 8.4 Hz, 2H), 7.32-7.23 (m, 4H), 7.17-7.15 (d, J = 7.2 Hz, 2H), 7.10-7.08 (d, J = 8.0 Hz, 1H), 7.03-6.99 (t, J = 7.6 Hz, 1H), 6.87-6.85 (d, J = 7.2 Hz, 1H), 4.88-4.85 (d, J = 8.8 Hz, 1H), 4.73-4.71 (d, J = 8.8 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.7, 166.5, 139.7, 139.3, 135.6, 131.9, 130.2, 129.0, 128.6, 128.1, 127.5, 123.6, 114.9, 55.7, 44.6, 30.0 ppm; IR (KBr): υ_{max} 1689, 1663, 1459, 1376 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}BrNO_2$ $[M+H]^+$ 420.0594, found 420.0596.

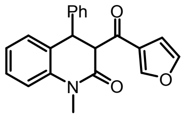


4f: R_f 0.3 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79-7.77 (d, J = 8.4 Hz, 2H), 7.61-7.59 (d, J = 8.8 Hz, 2H), 7.31-7.22 (m, 4H), 7.17-7.15 (d, J = 7.2 Hz, 2H), 7.10-7.08 (d, J = 8.0 Hz, 1H), 7.02-6.98 (t, J = 7.6 Hz, 1H), 6.86-6.84 (d, J = 7.6 Hz, 1H), 4.86-4.84 (d, J = 8.4 Hz, 1H), 4.72-4.70 (d, J = 8.8 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.0, 166.5, 139.7, 139.3, 137.9, 136.1, 130.0, 129.0, 128.7, 128.6, 128.1, 127.5, 123.6, 114.9, 101.5, 55.6, 44.6, 30.0 ppm; IR

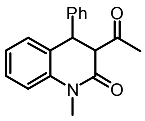
(KBr): υ_{max} 1689, 1661, 1461, 1377 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{19}INO_2$ [M+H]$^+$ 468.0455, found 468.0455.



4g: R_f 0.1 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86-7.84 (d, *J* = 3.2 Hz, 1H), 7.64-7.62 (d, *J* = 4.4 Hz, 1H), 7.34-7.17 (m, 6H), 7.12-7.09 (m, 2H), 7.04-7.00 (t, *J* = 7.6 Hz, 1H), 6.94-6.92 (d, *J* = 7.6 Hz, 1H), 4.76-4.72 (m, 2H), 3.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.6, 166.0, 143.7, 139.9, 139.4, 134.7, 133.4, 129.0, 128.7, 128.3, 128.1, 127.4, 127.3, 123.6, 114.9, 57.5, 44.9, 30.0 ppm; IR (KBr): υ_{max} 1652, 1665, 1495, 1366 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{17}NNaO_2S$ [M+Na]$^+$ 370.0872, found 370.0886.

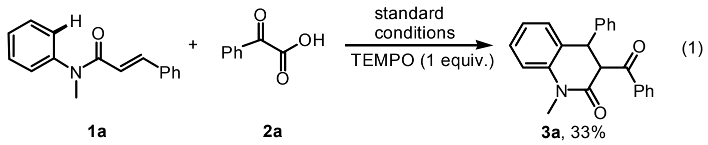


4h: R_f 0.1 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (s, 1H), 7.33-7.19 (m, 7H), 7.10-7.08 (d, *J* = 8.0 Hz, 1H), 7.01-6.97 (t, *J* = 7.6 Hz, 1H), 6.84-6.82 (d, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 2.0 Hz, 1H), 4.77 (s, 2H), 3.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.9, 166.5, 152.5, 146.7, 139.5, 128.9, 128.5, 128.3, 128.1, 127.5, 127.4, 123.4, 118.4, 114.8, 112.6, 56.0, 44.3, 29.9 ppm; IR (KBr): υ_{max} 1665, 1598, 1497, 1369 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{18}NO_3$ [M+H]$^+$ 332.1281, found 332.1287.

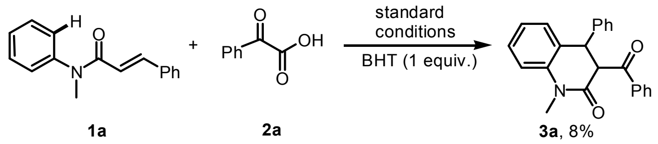


4i: R_f 0.2 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.25 (m, 4H), 7.12-6.94 (m, 5H), 4.66-4.64 (d, *J* = 7.6 Hz, 1H), 3.97-3.95 (d, *J* = 7.6 Hz, 1H), 3.43 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 139.8, 139.1, 129.0, 128.8, 128.1, 127.9, 127.4, 123.7, 114.9, 61.6, 43.6, 29.88, 29.86 ppm; IR (KBr): υ_{max} 1718, 1656, 1455, 1369 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{17}NNaO_2$ [M+Na]$^+$ 302.1151, found 302.1150.

Investigation of the Reaction Mechanism



When the TEMPO was added to the reaction of **1a** with **2a** under the standard condition, the yield of **3a** was decreased dramatically. This result indicates that the radical intermediate might be involved in the catalytic cycle of the reaction.



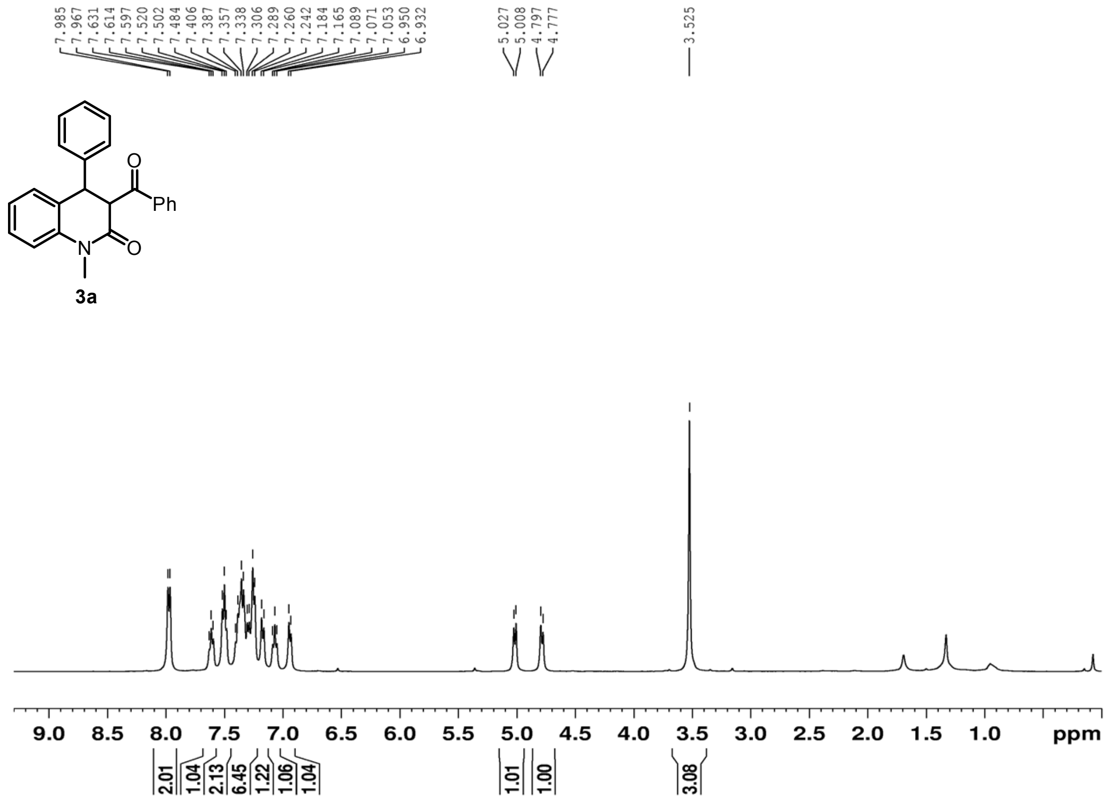
When the BHT was added to the reaction of **1a** with **2a** under the standard condition, the yield of **3a** was decreased dramatically. This result also indicates that the radical intermediate might be involved in the catalytic cycle of the reaction.

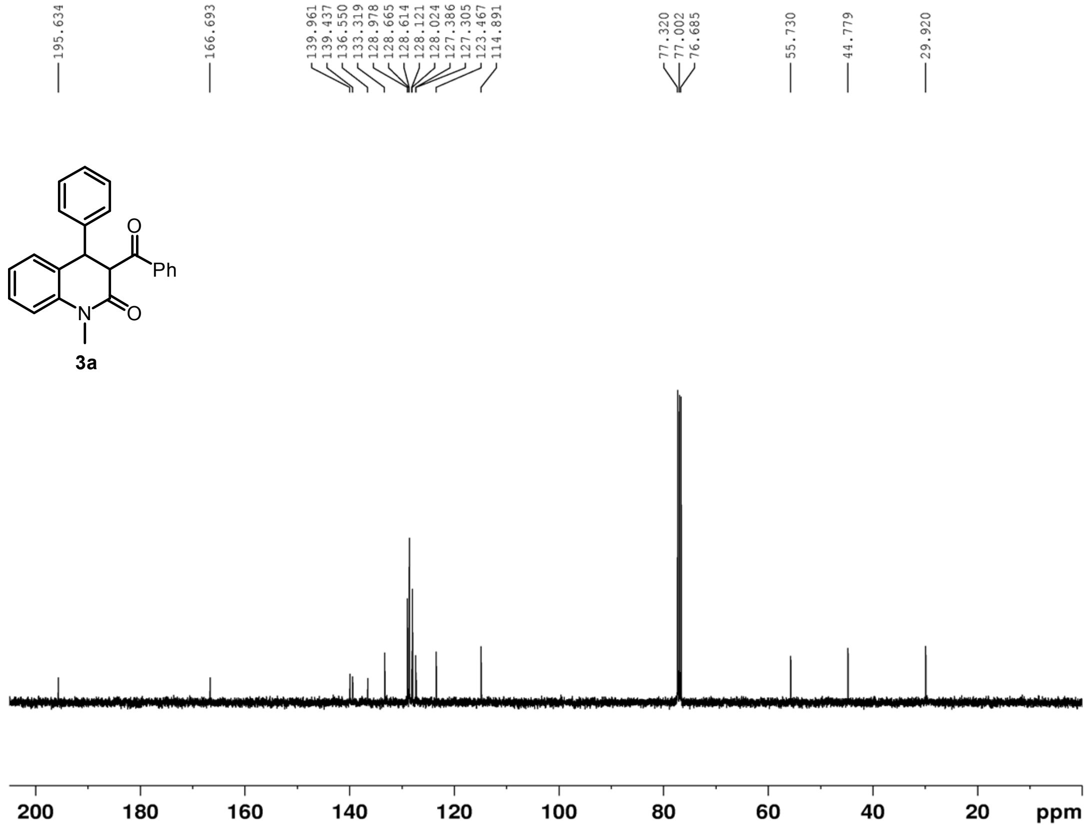
References

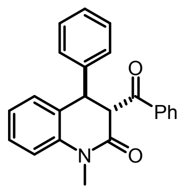
1 (a) S. Ueda, T. Okada and H. Nagasawa, *Chem. Commun.*, 2010, **46**, 2462; (b) L. Liu, H. Lu, H. Wang, C. Yang, X. Zhang, D. Zhang-Negrerie, Y. Du and K. Zhao, *Org. Lett.*, 2013, **15**, 2906; (c) M. C. Elliott and S. V. Wordingham, *Synlett*, 2004, 898.

2 Wadhwa, K.; Yang, C.; West, P. R.; Deming, K. C.; Chemburkar, S. R.; Reddy, R. E. *Synth. Commun.* **2008**, *38*, 4434.

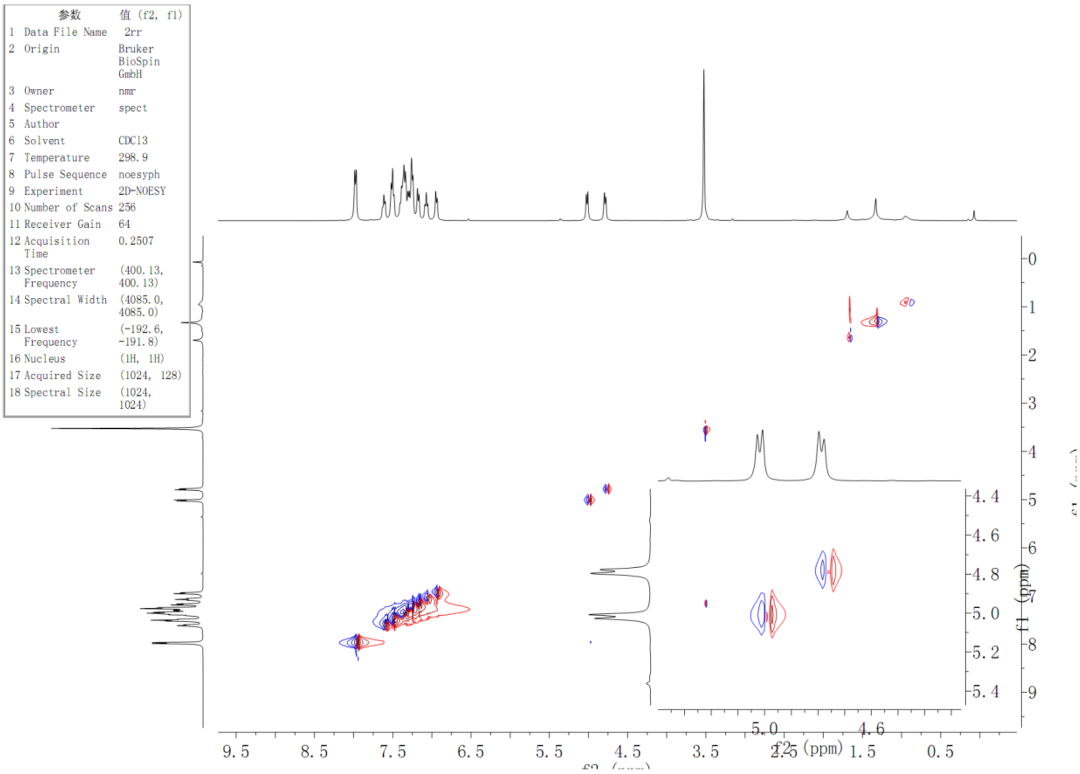
^{1}H NMR and ^{13}C NMR Spectra of the Products 3







trans-3a



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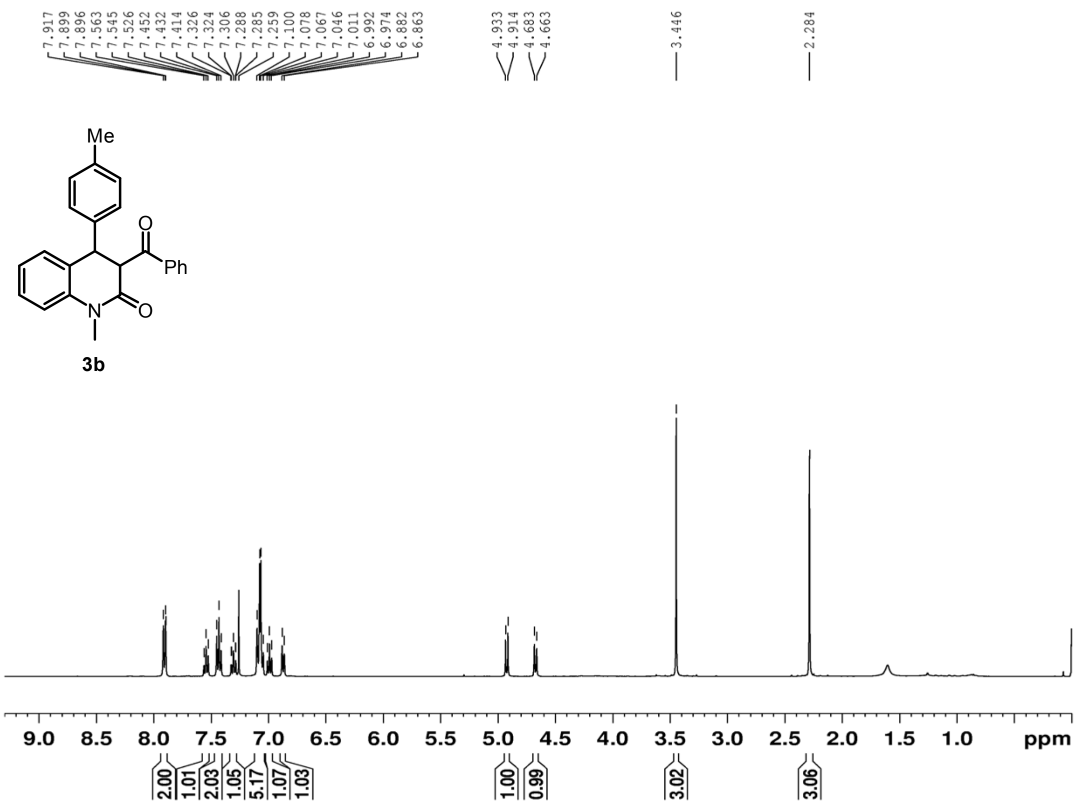
2 Origin Bruker BioSpin GmbH
3 Owner nmr
4 Spectrometer spect
5 Author
6 Solvent CDCl3
7 Temperature 298.9
8 Pulse Sequence noesyph
9 Experiment 2D-NOESY
10 Number of Scans 256
11 Receiver Gain 64
12 Acquisition Time 0.2507
13 Spectrometer Frequency (400.13, 400.13)
14 Spectral Width (4085.0, 4085.0)
15 Lowest Frequency (-192.6, -191.8)
16 Nucleus (1H, 1H)
17 Acquired Size (1024, 128)
18 Spectral Size (1024, 1024)
f2 (ppm)
f1 (ppm)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3.446
2.284
Me
O
Ph
N
O
3b
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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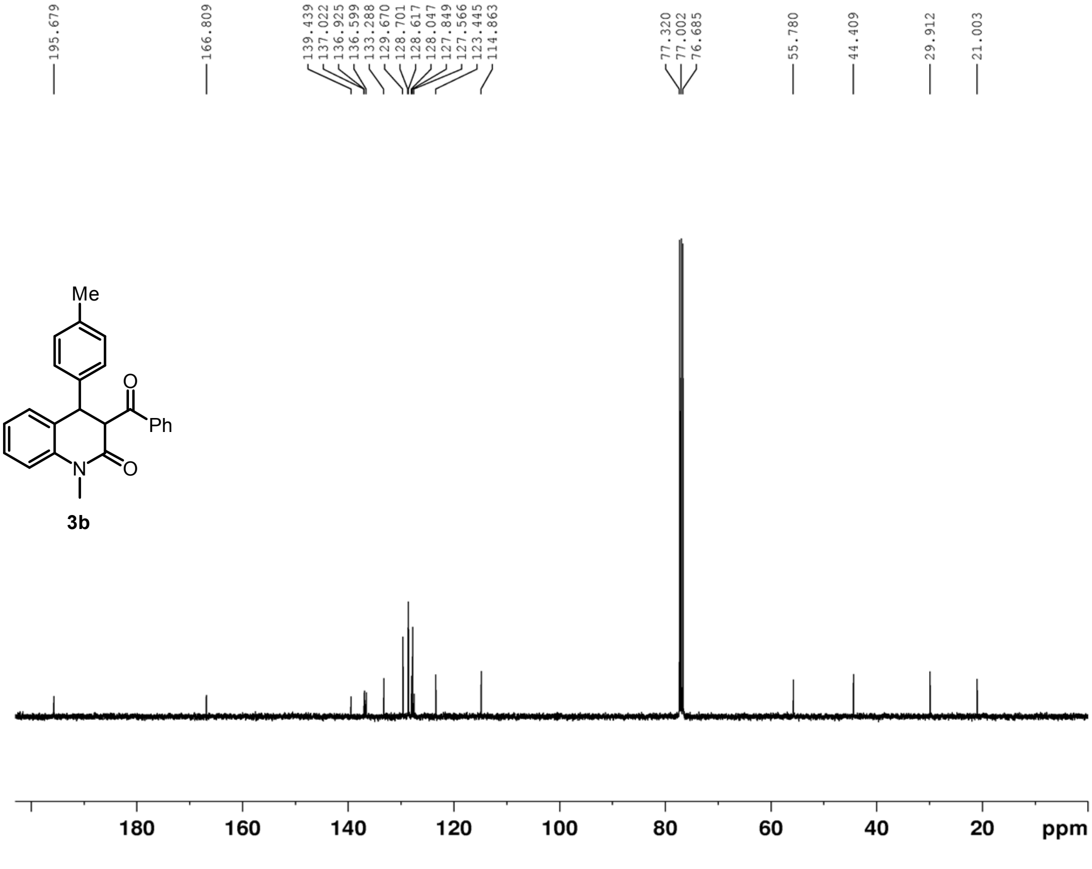
3.02
3.06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55.780
44.409
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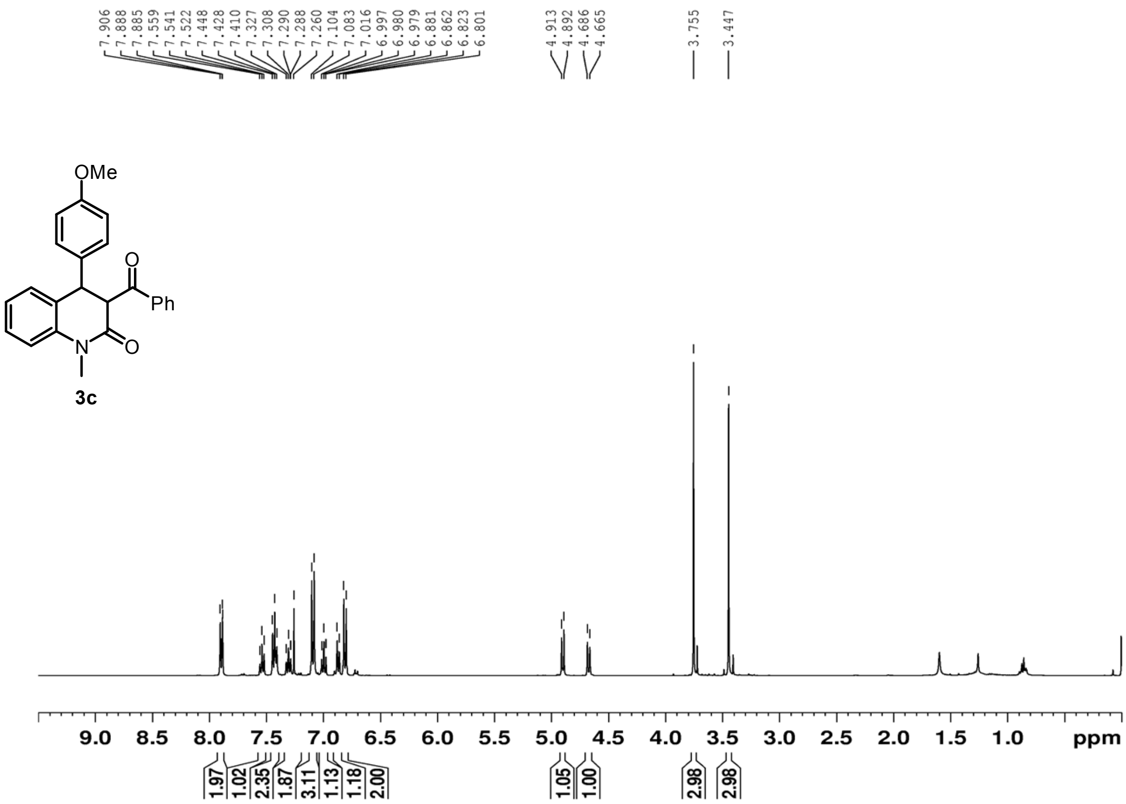
21.003
Me
O
Ph
N
O
3b
180 160 140 120 100 80 60 40 20 ppm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4.913 4.892 4.686 4.665
3.755
3.447
OMe
O
Ph
N
O
3c
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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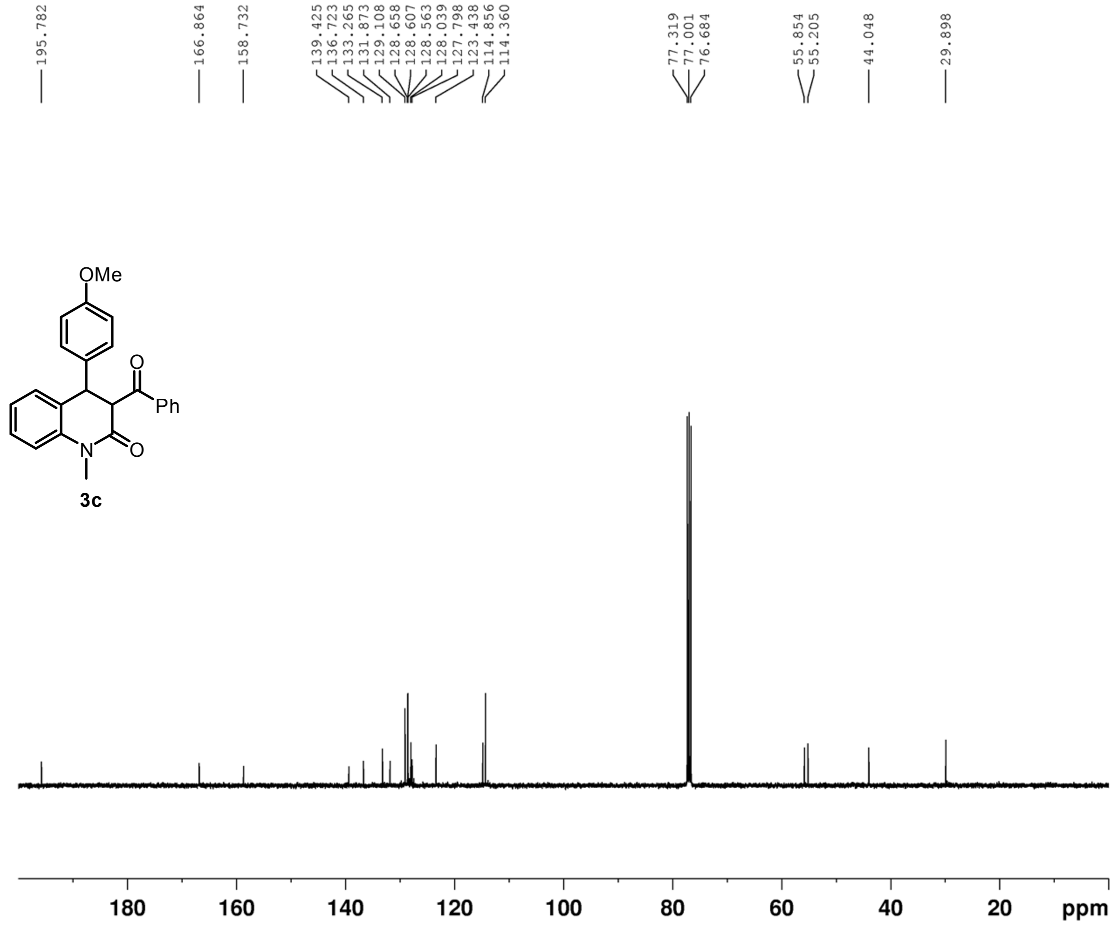
2.98 2.98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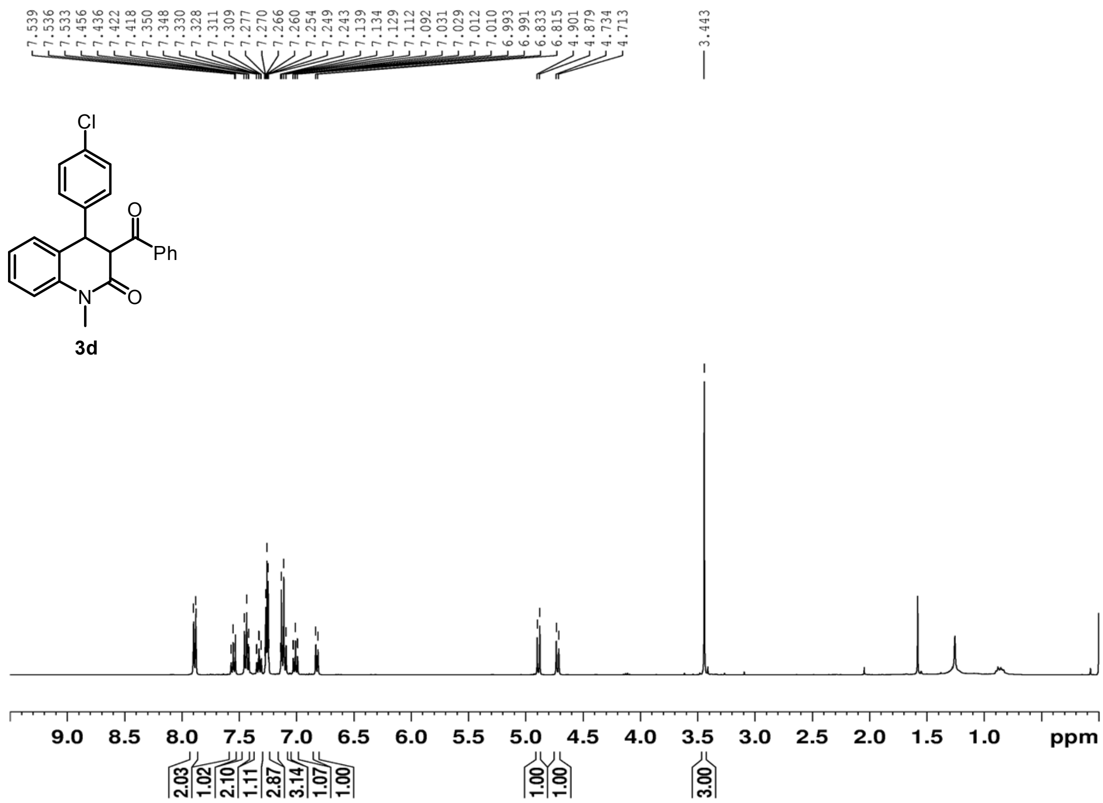
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7.260
7.254
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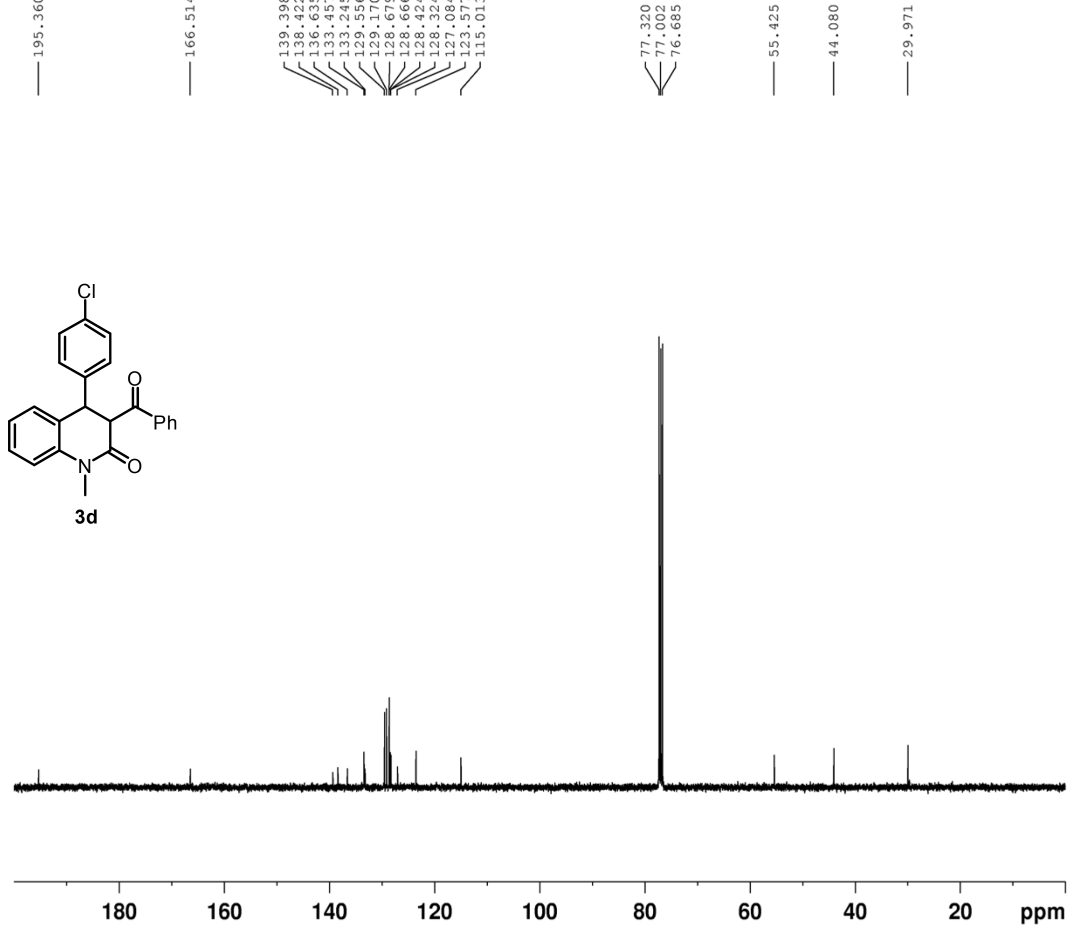
3.00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115.013
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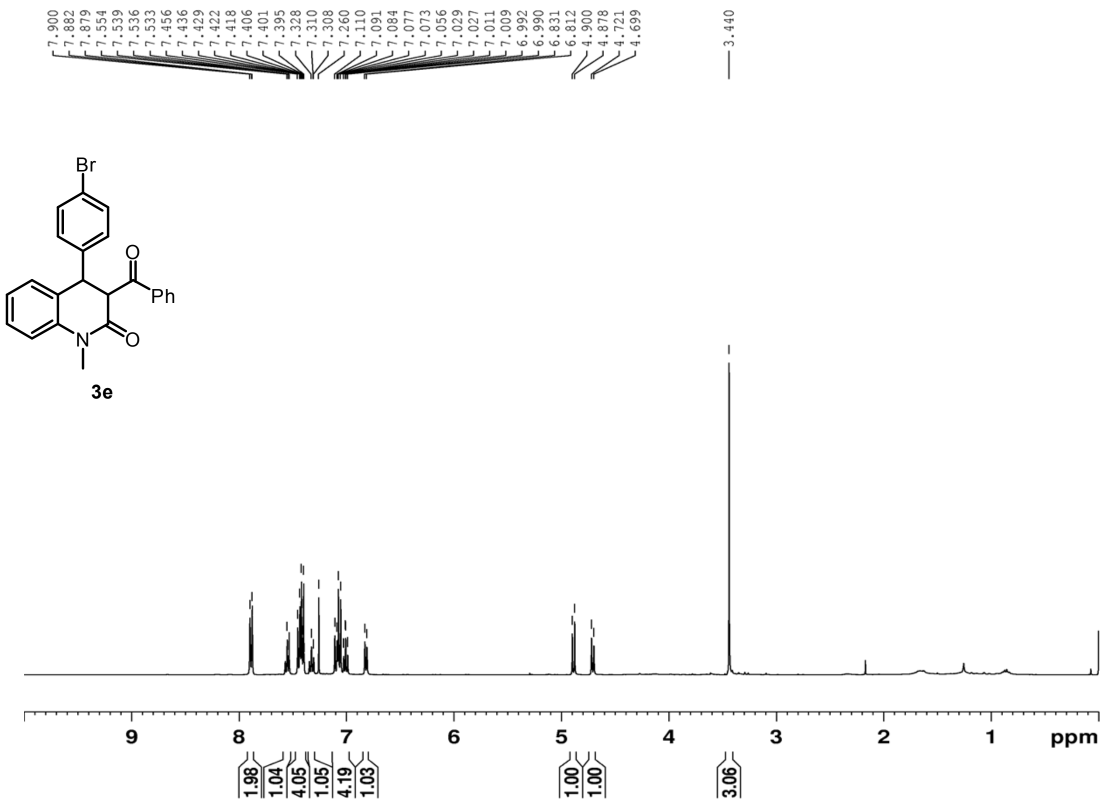
180 160 140 120 100 80 60 40 20 ppm



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7.328
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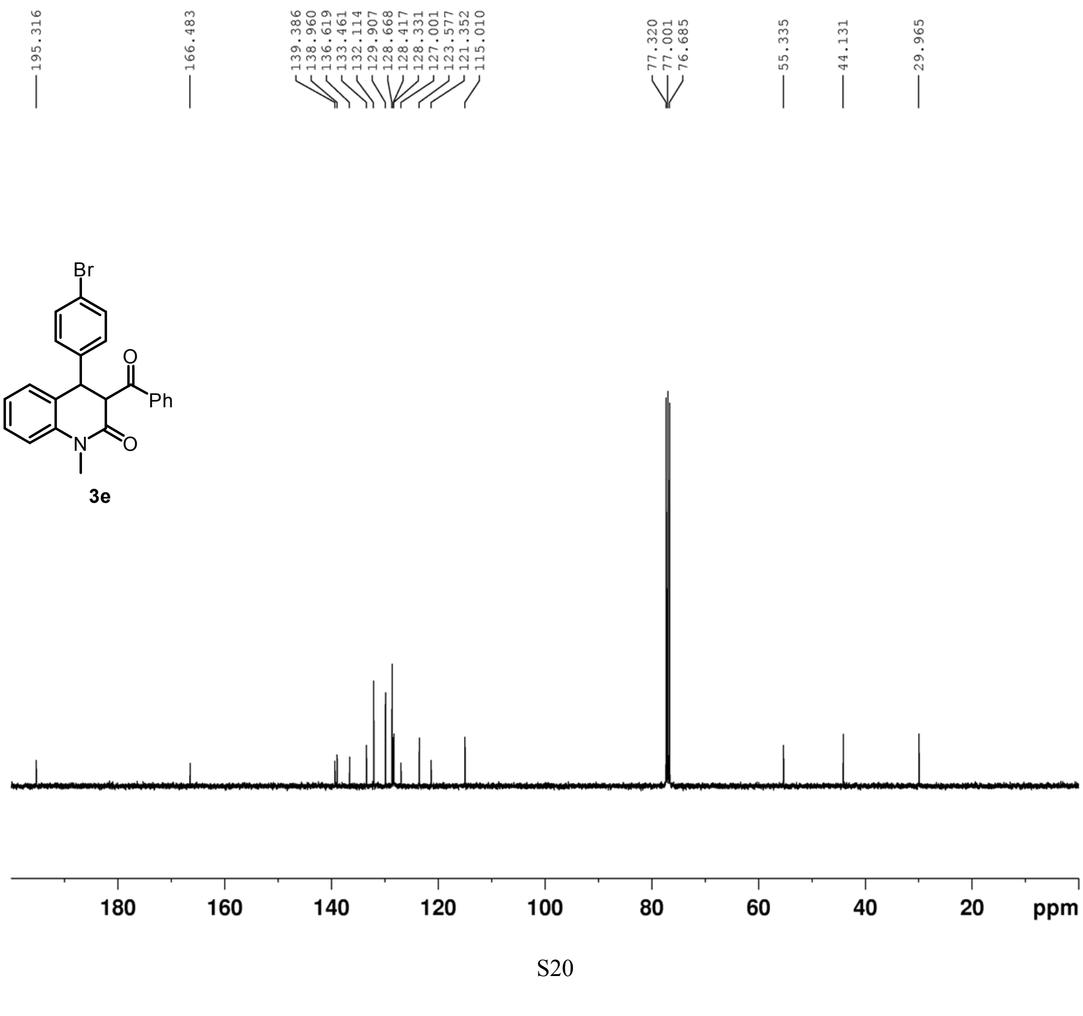
3e



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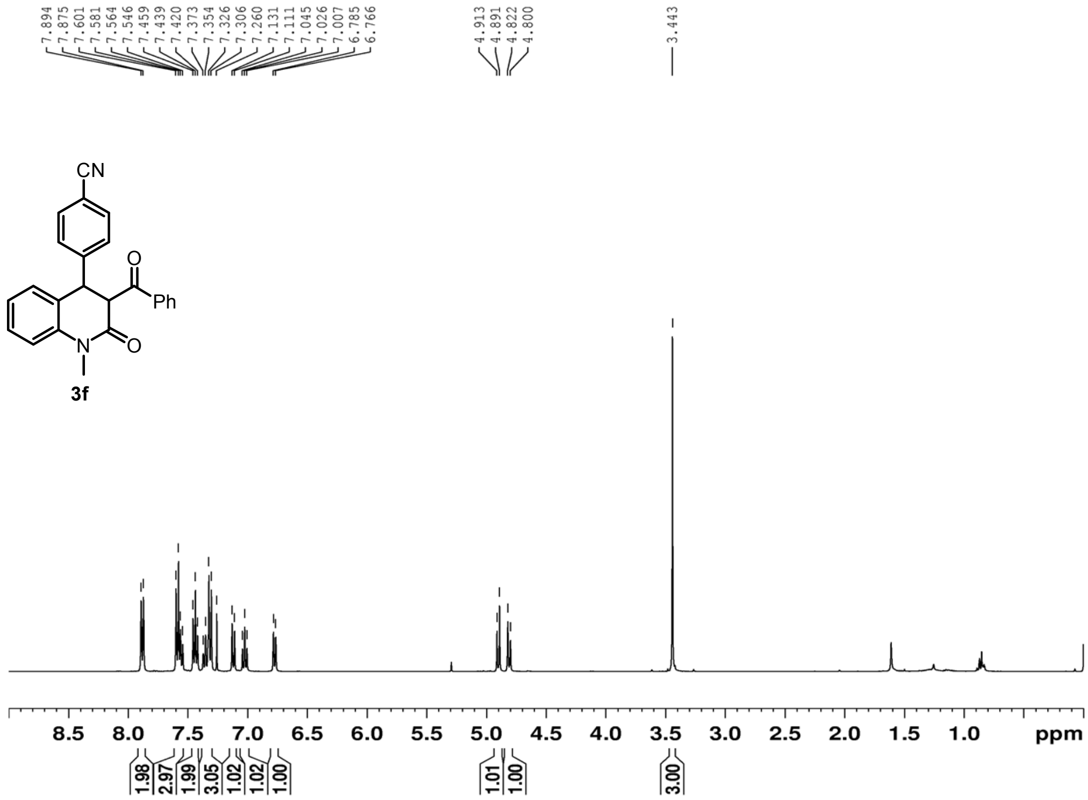
3e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Ph
N
O
3f
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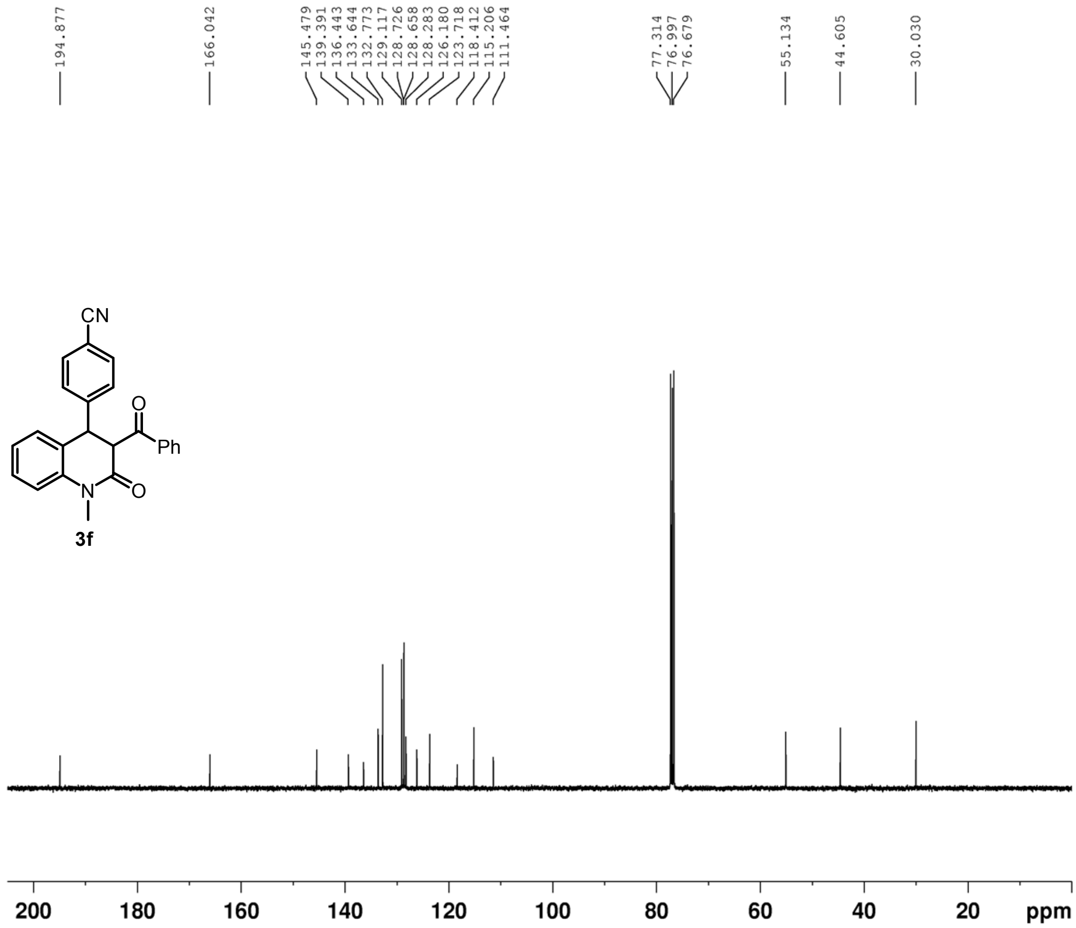
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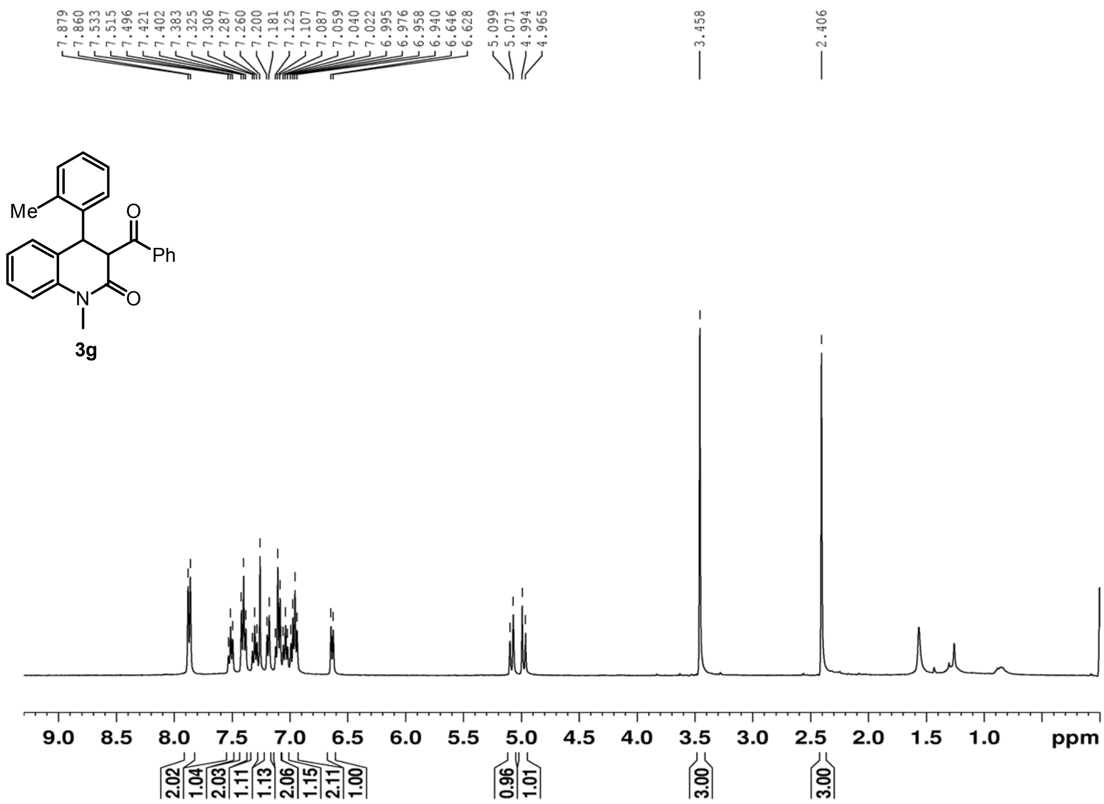
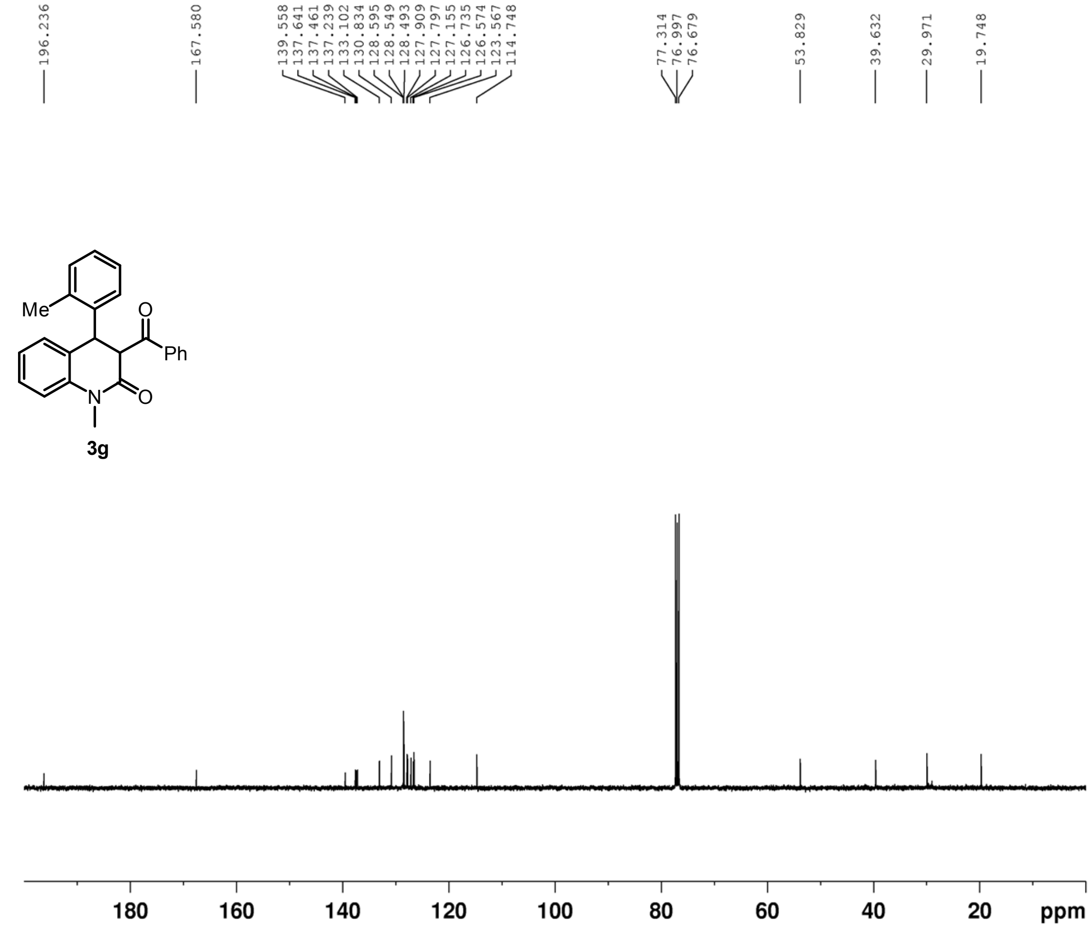
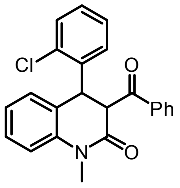
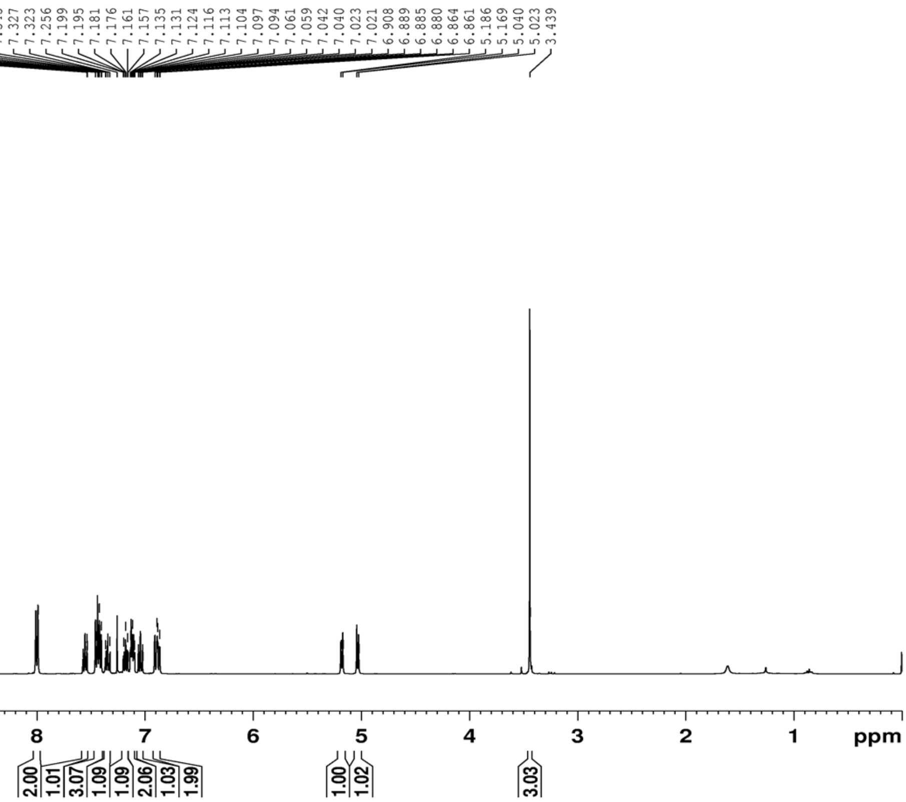
30.030
CN
O
Ph
N
O
3f
200 180 160 140 120 100 80 60 40 20 ppm


7.879
7.860
7.533
7.515
7.496
7.421
7.402
7.383
7.325
7.306
7.287
7.260
7.200
7.181
7.125
7.107
7.087
7.059
7.040
7.022
6.995
6.976
6.958
6.940
6.646
6.628
5.099
5.071
4.994
4.965
3.458
2.406
Me
O
Ph
N
O
3g
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.02
1.04
2.03
1.11
1.13
2.06
1.15
2.11
1.00
0.96
1.01
3.00
3.00

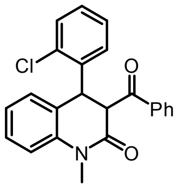

196.236
167.580
139.558
137.641
137.461
137.239
133.102
130.834
128.595
128.549
128.493
127.909
127.797
127.155
126.735
126.574
123.567
114.748
77.314
76.997
76.679
53.829
39.632
29.971
19.748
Me
O
Ph
N
O
3g
180
160
140
120
100
80
60
40
20
ppm



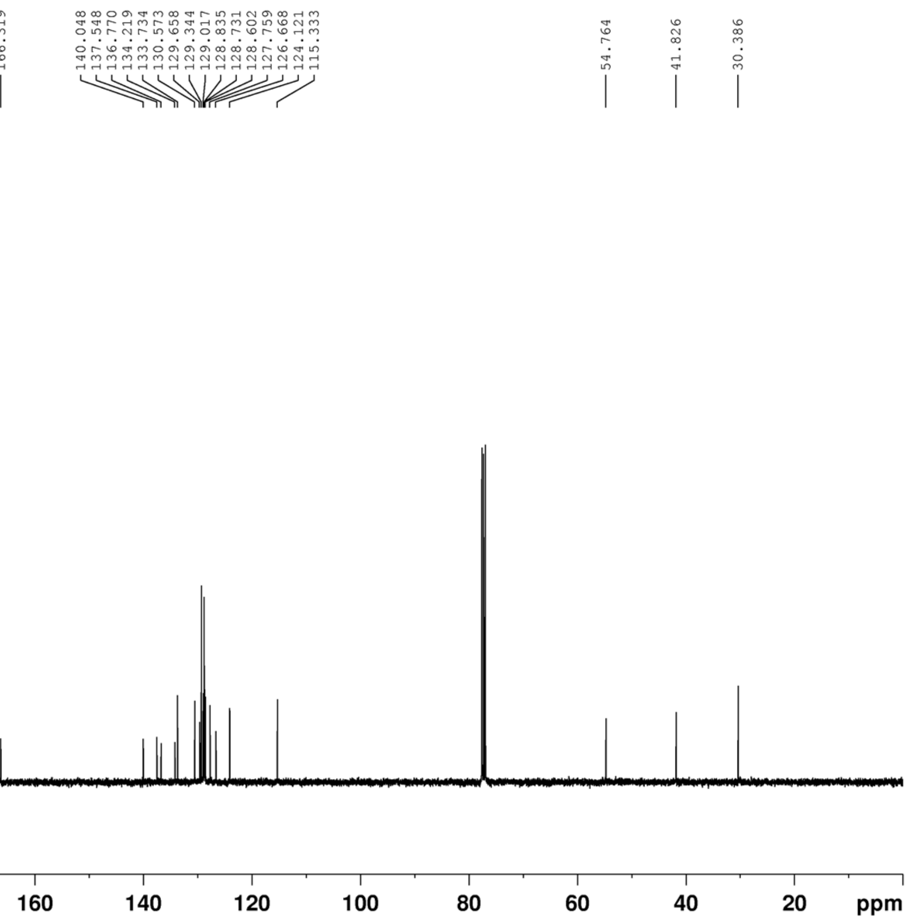
3h



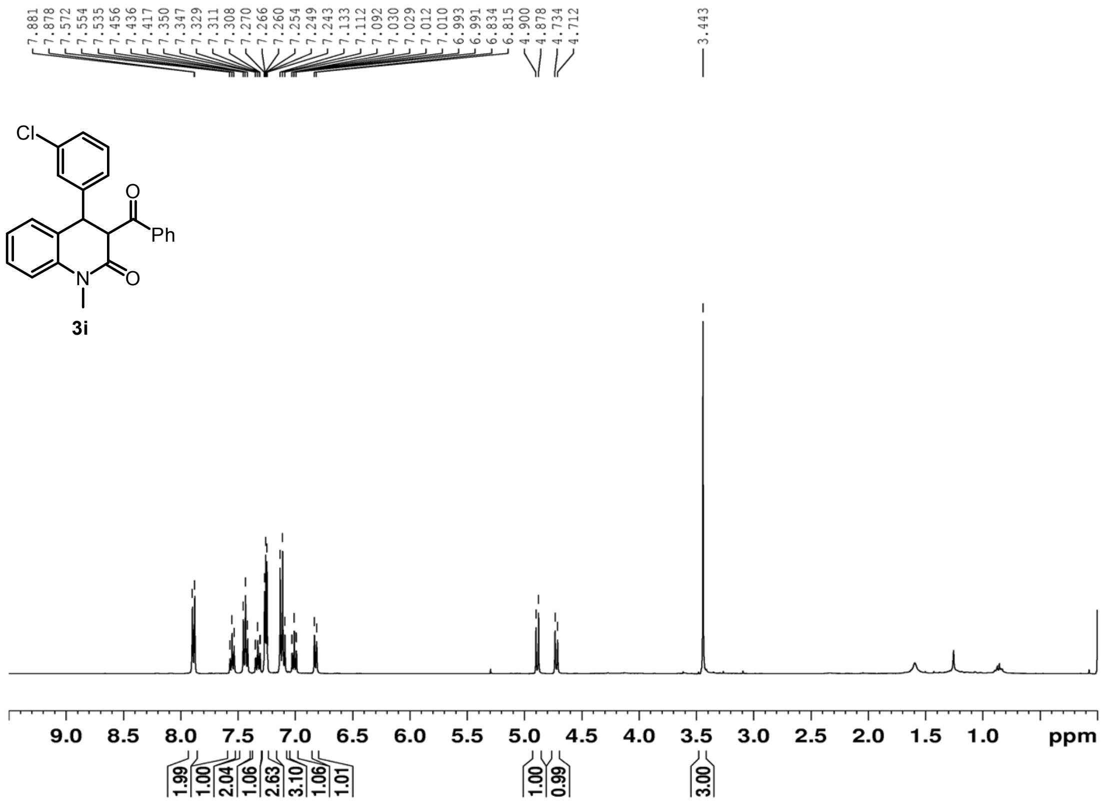
7.535
7.532
7.457
7.437
7.424
7.420
7.404
7.401
7.365
7.362
7.345
7.327
7.323
7.256
7.199
7.195
7.181
7.176
7.161
7.157
7.135
7.131
7.124
7.116
7.113
7.104
7.097
7.094
7.061
7.059
7.042
7.040
7.023
7.021
6.908
6.889
6.885
6.880
6.864
6.861
5.186
5.169
5.040
5.023
3.439
9
8
7
6
5
4
3
2
1
ppm
2.00
1.01
3.07
1.09
1.09
2.06
1.03
1.99
1.00
1.02
3.03

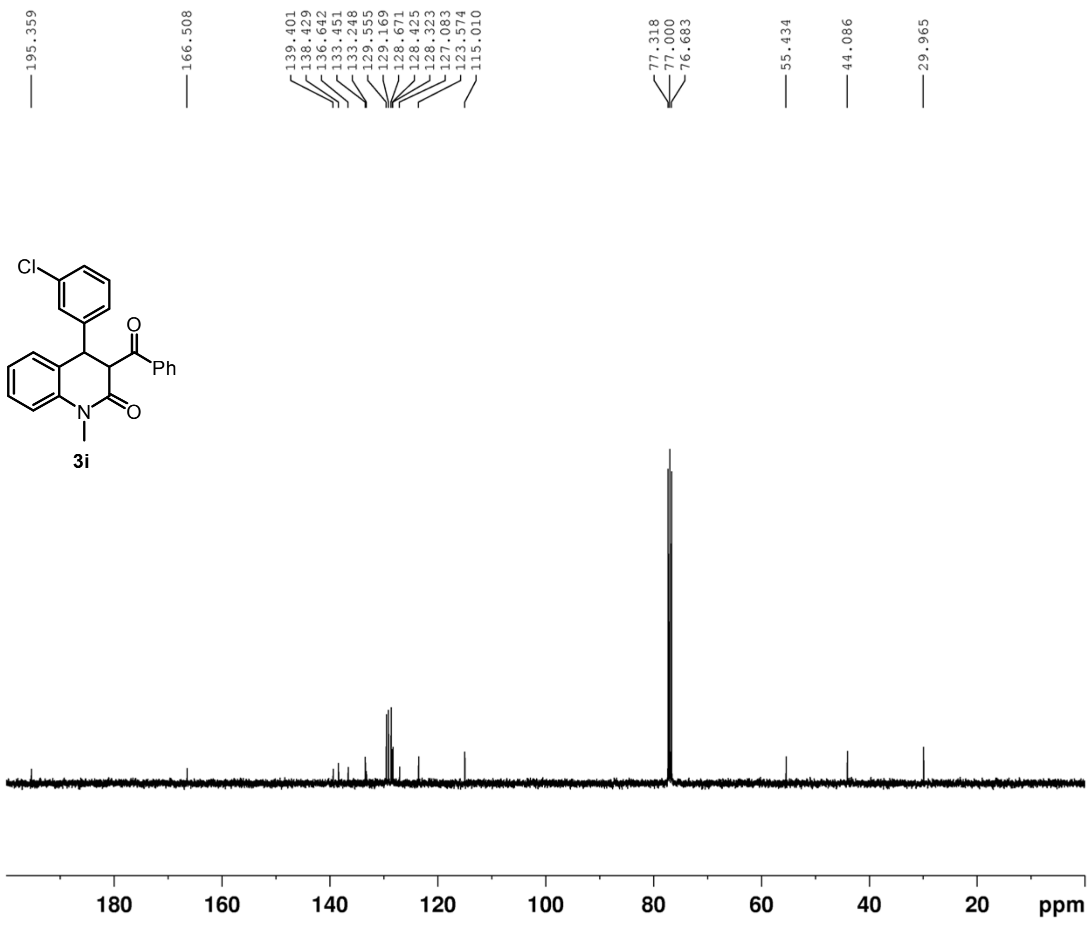


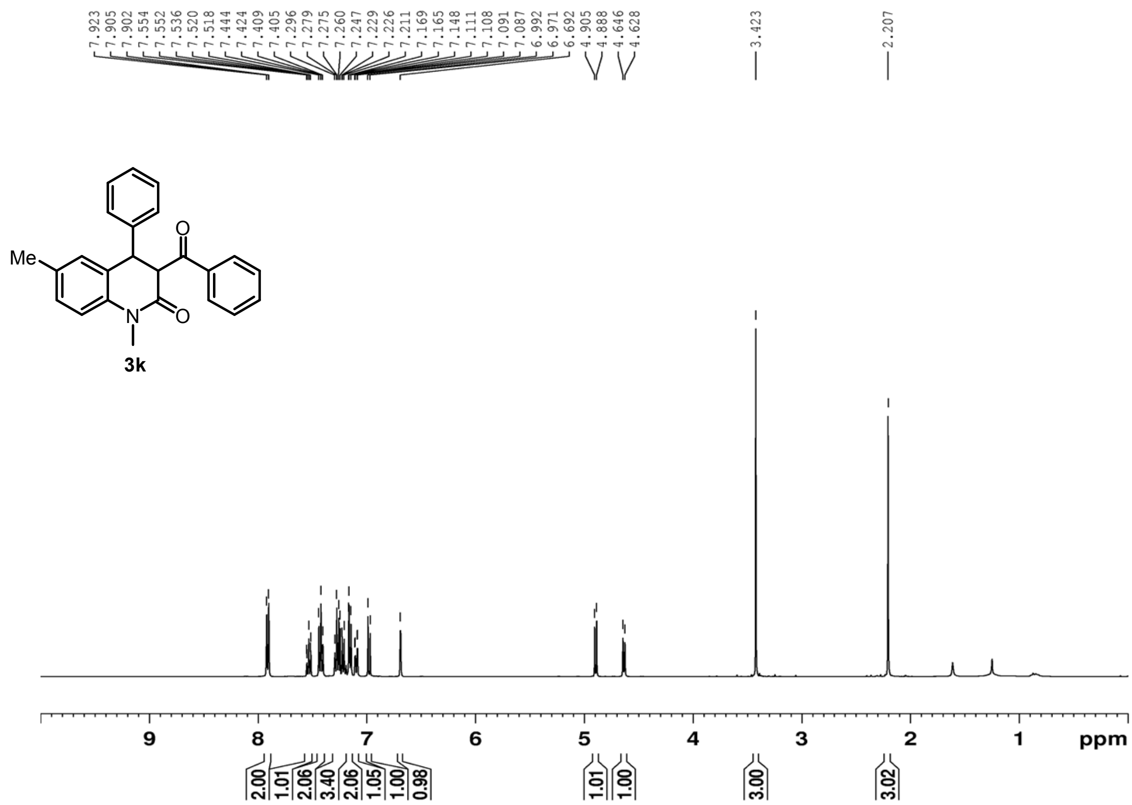
3h

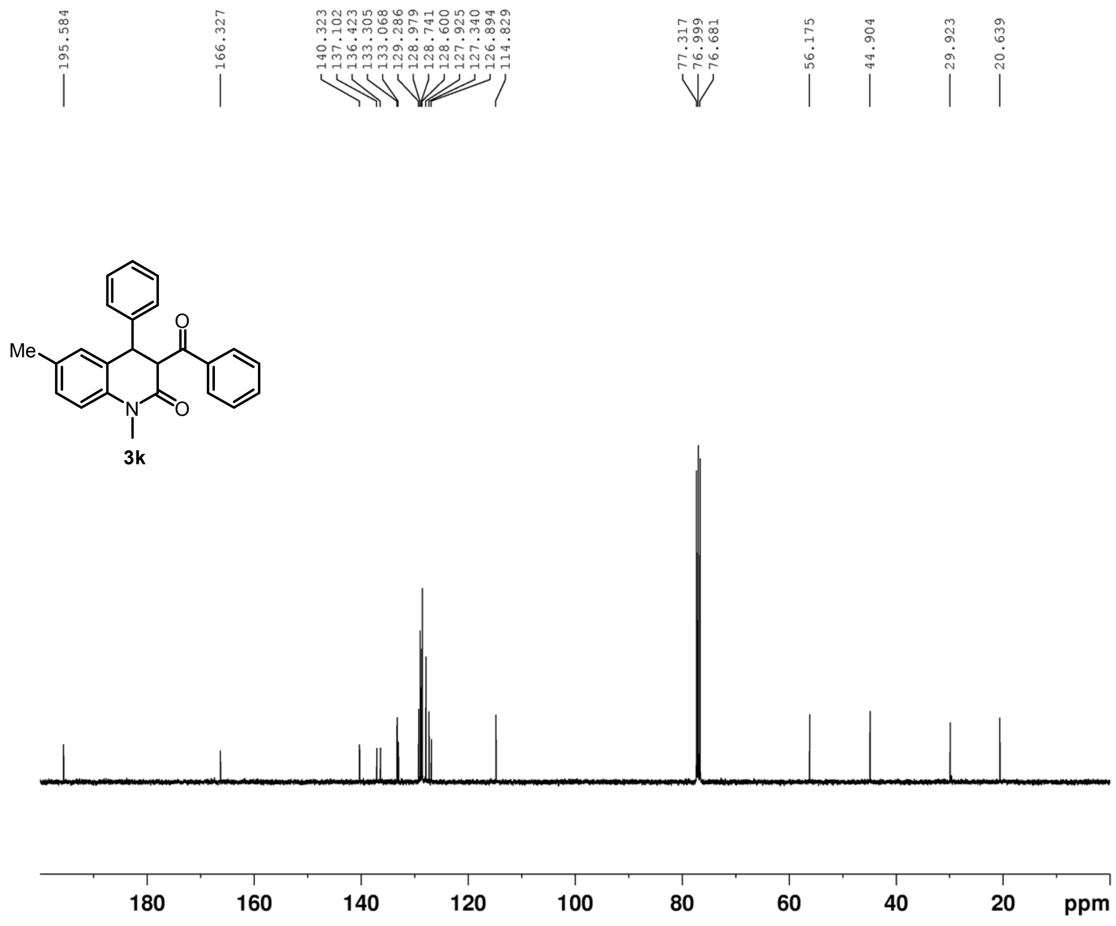


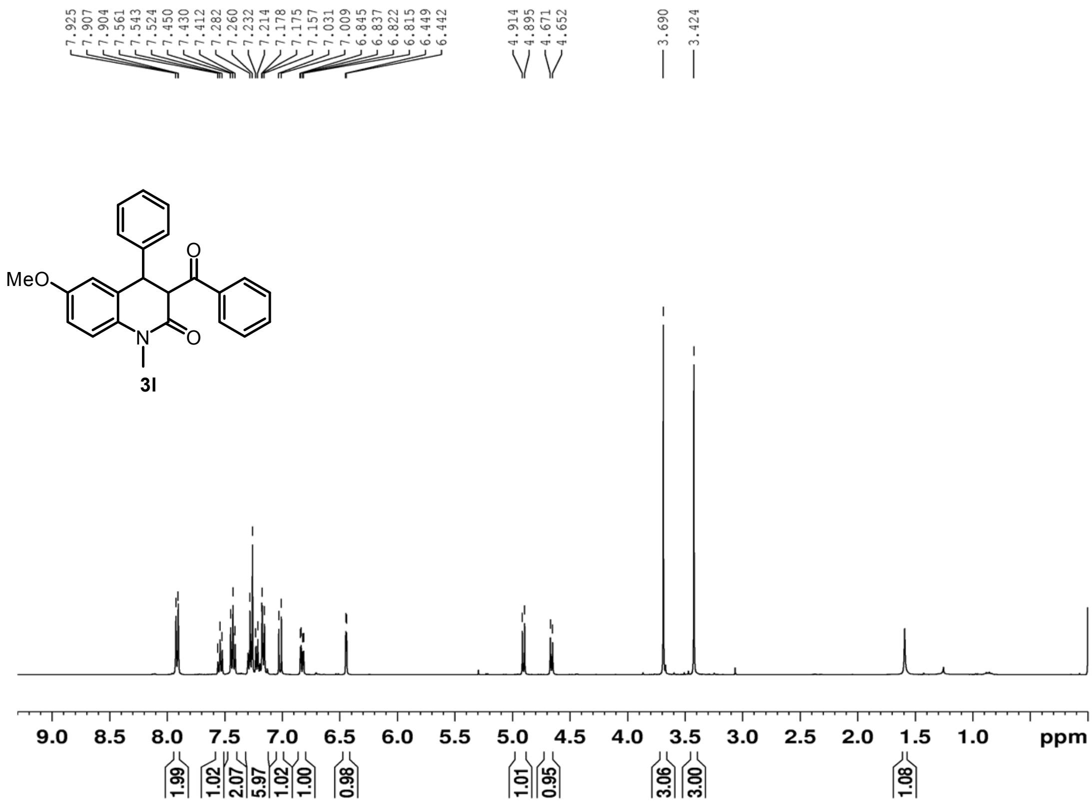
195.468
166.319
140.048
137.548
136.770
134.219
133.734
130.573
129.658
129.344
129.017
128.835
128.731
128.602
127.759
126.668
124.121
115.333
54.764
41.826
30.386
180
160
140
120
100
80
60
40
20
ppm

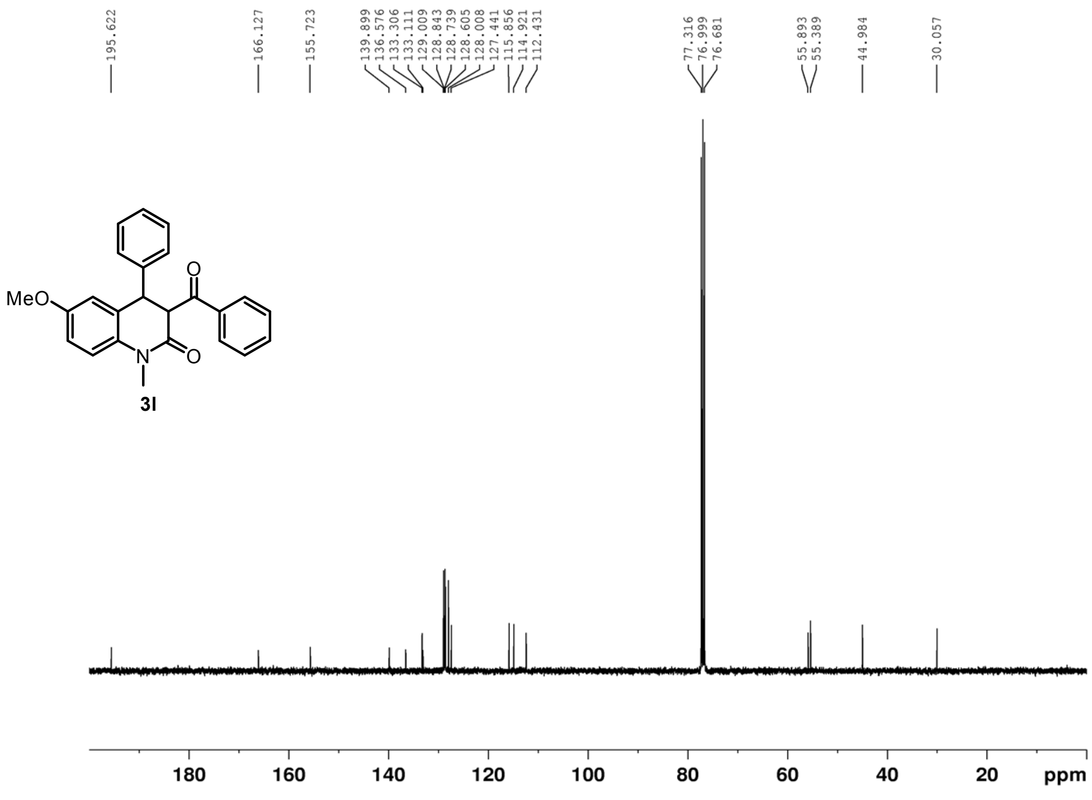


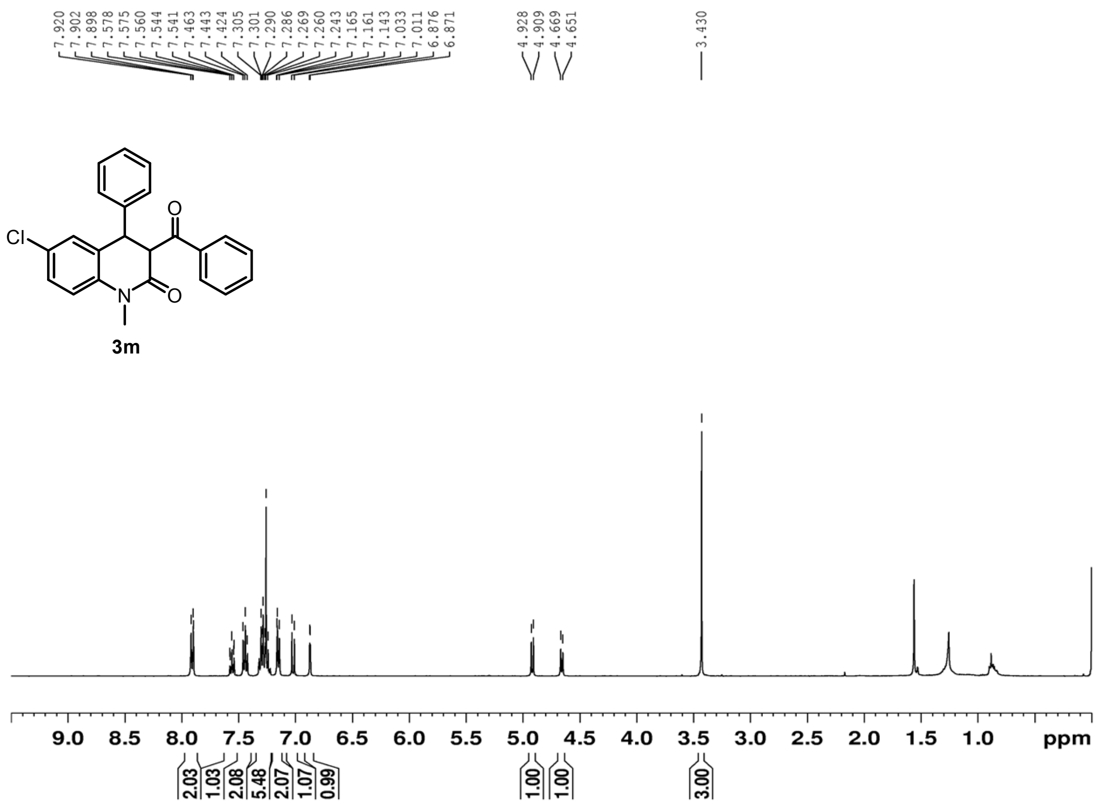


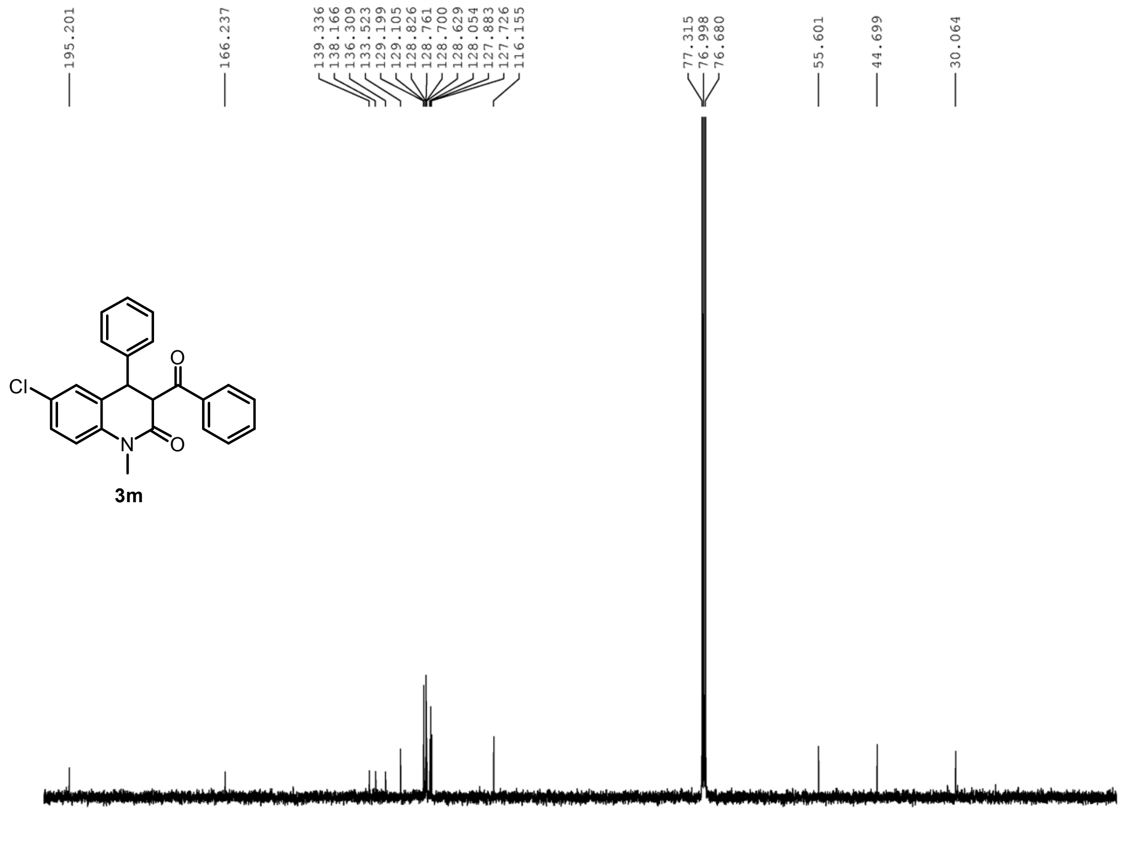

Me
N
O
O
3k
ppm

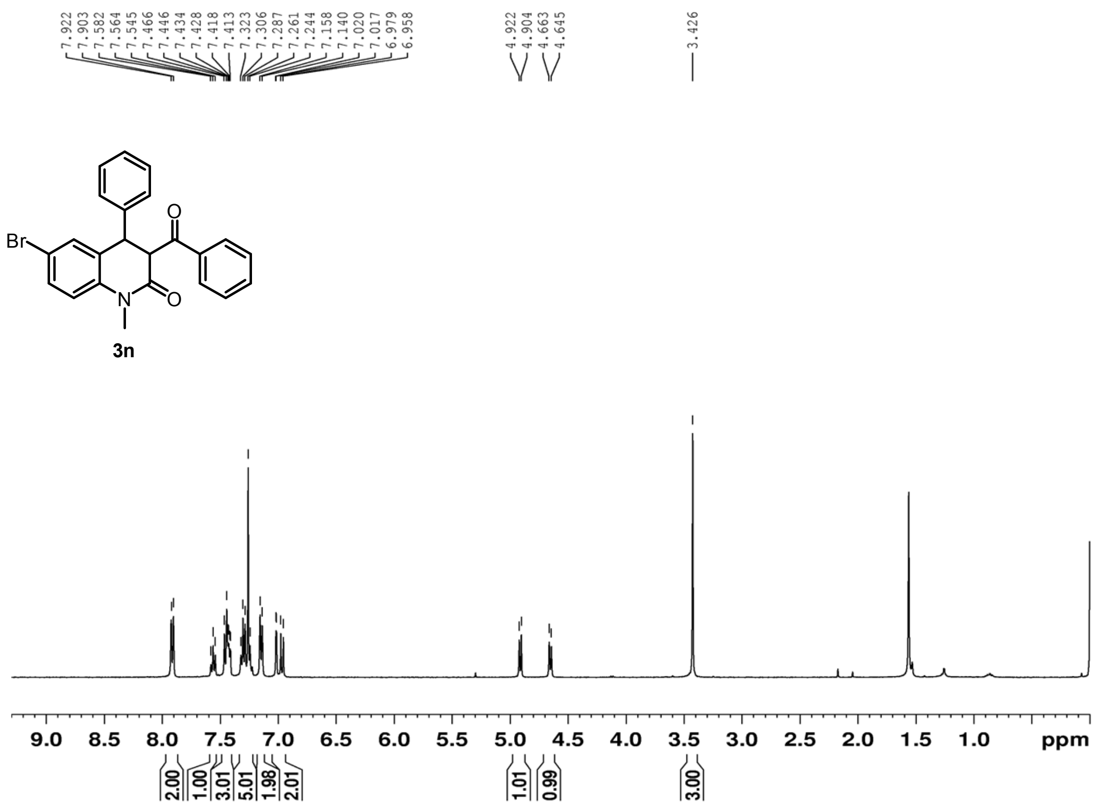

Me
N
O
O
3k
ppm

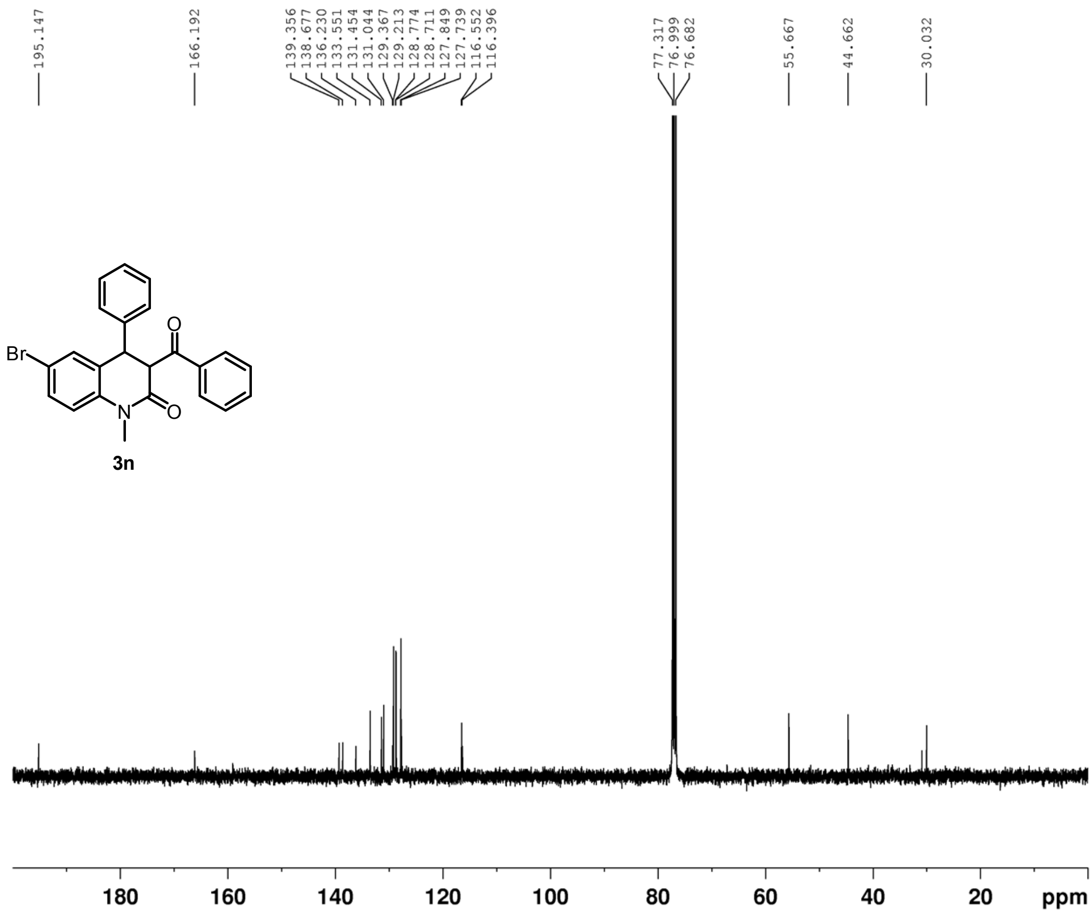

7.925 7.907 7.904 7.561 7.543 7.524 7.450 7.430 7.412 7.282 7.260 7.232 7.214 7.178 7.175 7.157 7.031 7.009 6.845 6.837 6.822 6.815 6.449 6.442
4.914 4.895 4.671 4.652
3.690
3.424
MeO
N
O
O
3l
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.99 1.02 2.07 5.97 1.02 1.00 0.98 1.01 0.95 3.06 3.00 1.08

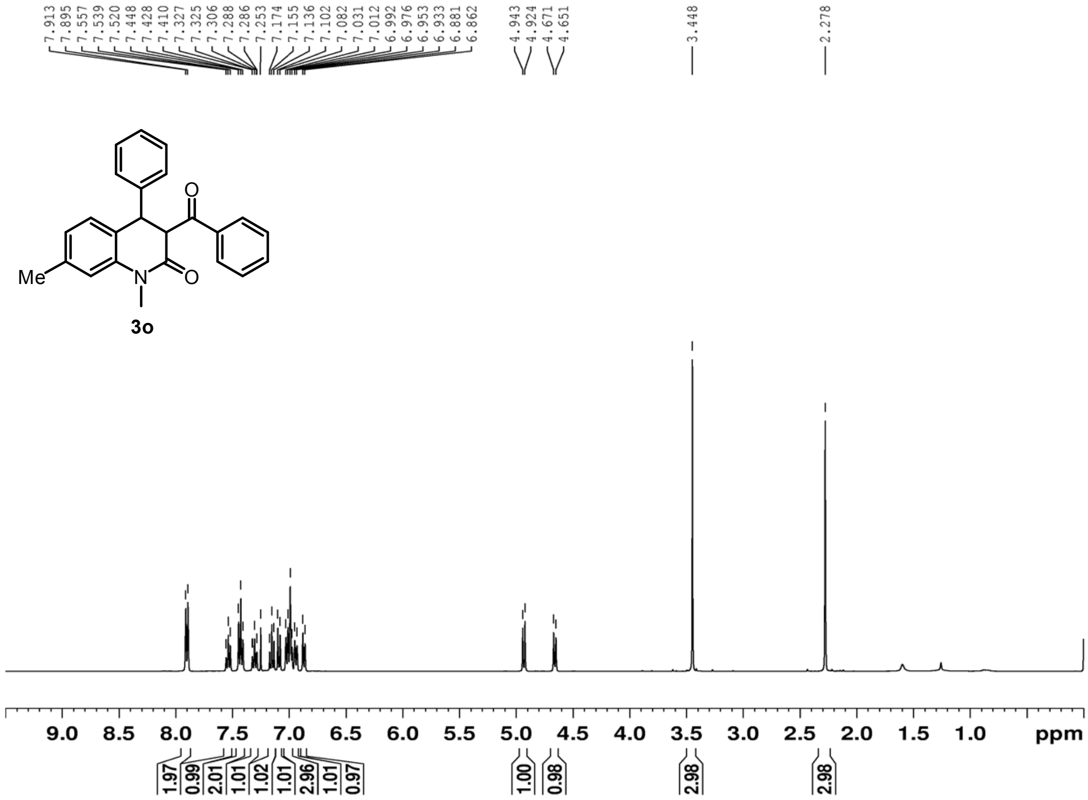

195.622
166.127
155.723
139.899 136.576 133.306 133.111 129.009 128.843 128.739 128.605 128.008 127.441 115.856 114.921 112.431
77.316 76.999 76.681
55.893 55.389
44.984
30.057
MeO
N
O
O
3l
180 160 140 120 100 80 60 40 20 ppm

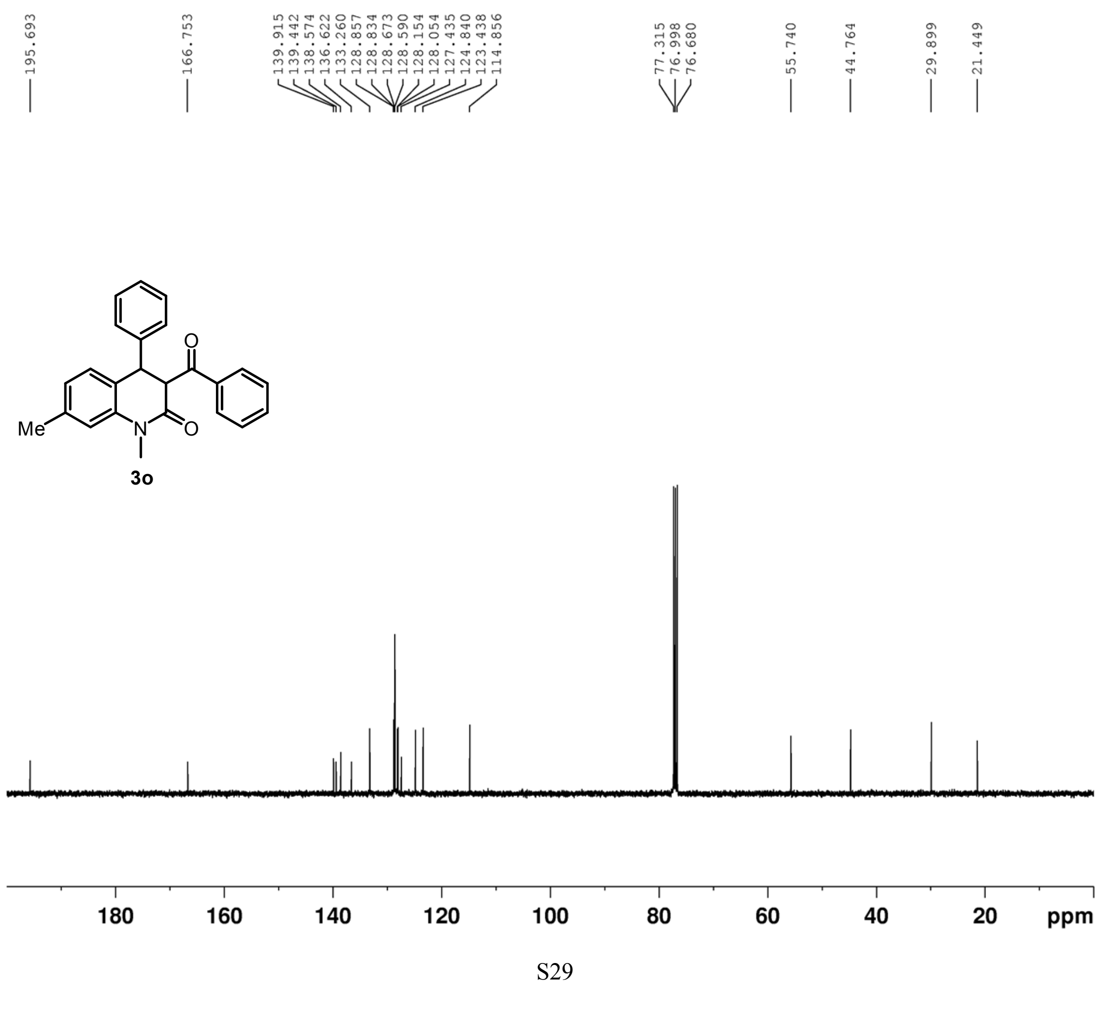

7.920 7.902 7.898 7.578 7.575 7.560 7.544 7.541 7.463 7.443 7.424 7.305 7.301 7.290 7.286 7.269 7.260 7.243 7.165 7.161 7.143 7.033 7.011 6.876 6.871
4.928 4.909 4.669 4.651
3.430
Cl
O
N
O
3m
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.03 1.03 2.08 5.48 2.07 1.07 0.99
1.00 1.00
3.00


195.201
166.237
139.336 138.166 136.309 133.523 129.199 129.105 128.826 128.761 128.700 128.629 128.054 127.883 127.726 116.155
77.315 76.998 76.680
55.601
44.699
30.064
Cl
O
N
O
3m
180 160 140 120 100 80 60 40 20 ppm

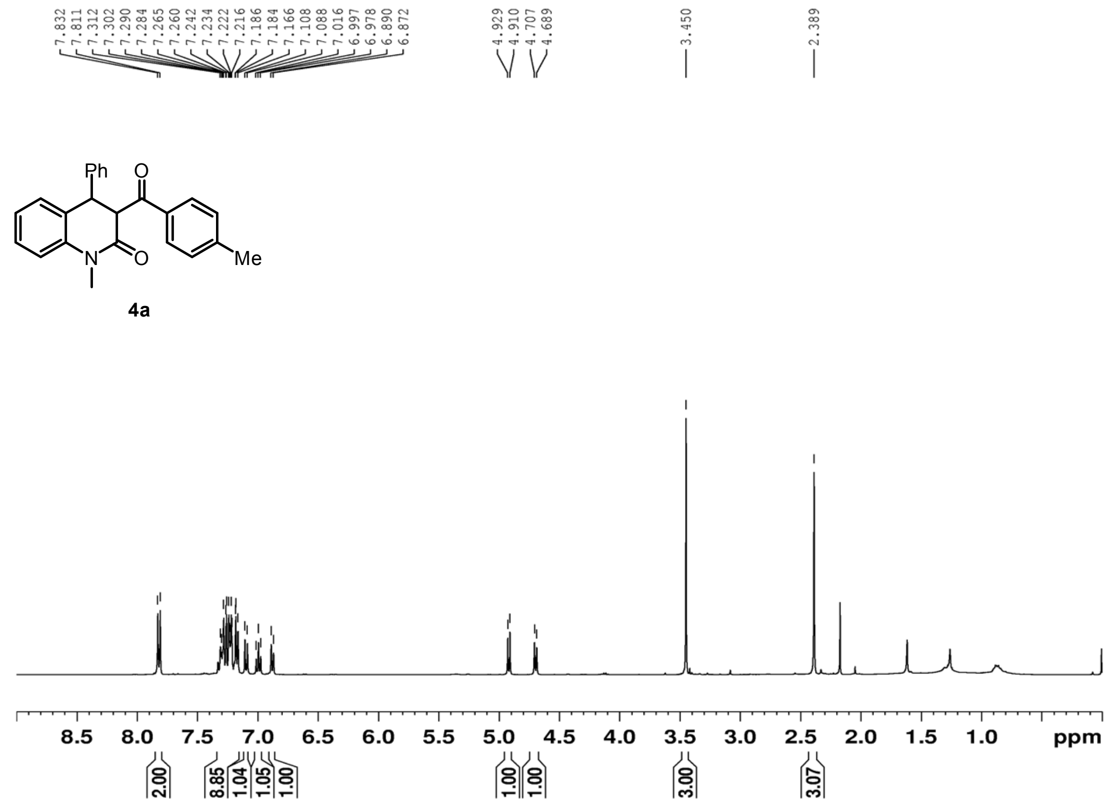

7.922
7.903
7.582
7.564
7.545
7.466
7.446
7.434
7.428
7.418
7.413
7.323
7.306
7.287
7.261
7.244
7.158
7.140
7.020
7.017
6.979
6.958
4.922
4.904
4.663
4.645
3.426
Br
O
N
O
3n
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00 1.00 3.01 5.01 1.98 2.01
1.01 0.99
3.00

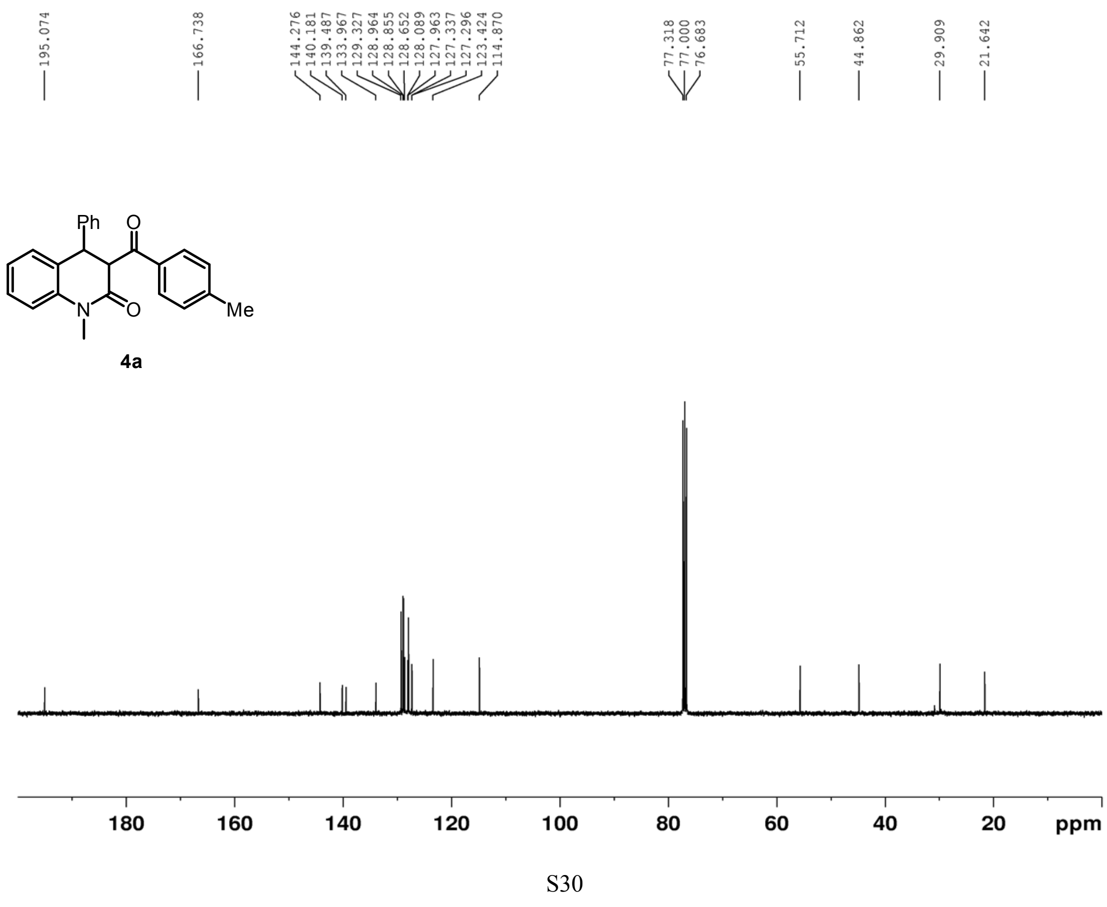

195.147
166.192
139.356
138.677
136.230
133.551
131.454
131.044
129.367
129.213
128.774
128.711
127.849
127.739
116.552
116.396
77.317
76.999
76.682
55.667
44.662
30.032
Br
O
N
O
3n
180 160 140 120 100 80 60 40 20 ppm

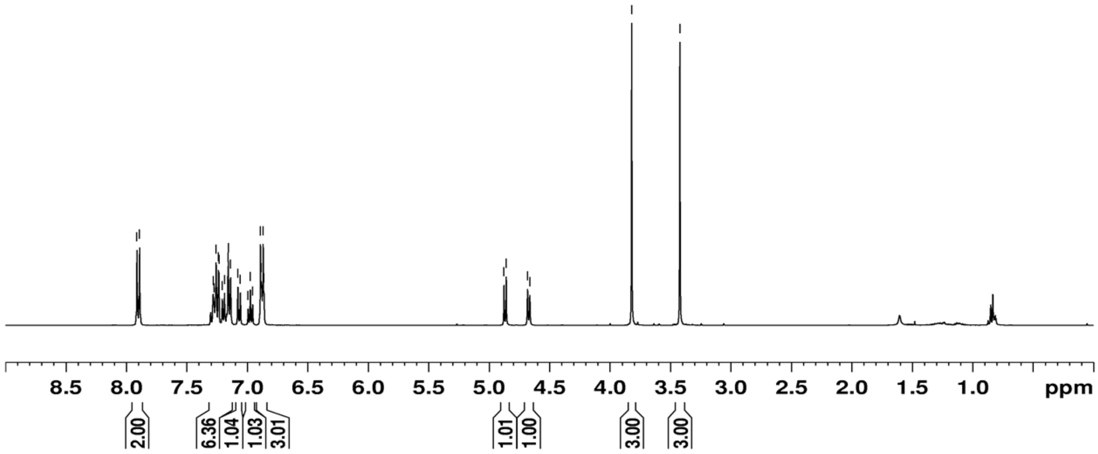

7.913
7.895
7.557
7.539
7.520
7.448
7.428
7.410
7.327
7.325
7.306
7.288
7.286
7.253
7.174
7.155
7.136
7.102
7.082
7.031
7.012
6.992
6.976
6.953
6.933
6.881
6.862
4.943
4.924
4.671
4.651
3.448
2.278
O
Me
N
O
3o
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.97
0.99
2.01
1.01
1.02
1.01
2.96
1.01
0.97
1.00
0.98
2.98
2.98


195.693
166.753
139.915
139.442
138.574
136.622
133.260
128.857
128.834
128.673
128.590
128.154
128.054
127.435
124.840
123.438
114.856
77.315
76.998
76.680
55.740
44.764
29.899
21.449
O
Me
N
O
3o
180 160 140 120 100 80 60 40 20 ppm

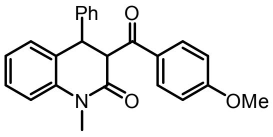
^{1}H NMR and ^{13}C NMR Spectra of the Products 4





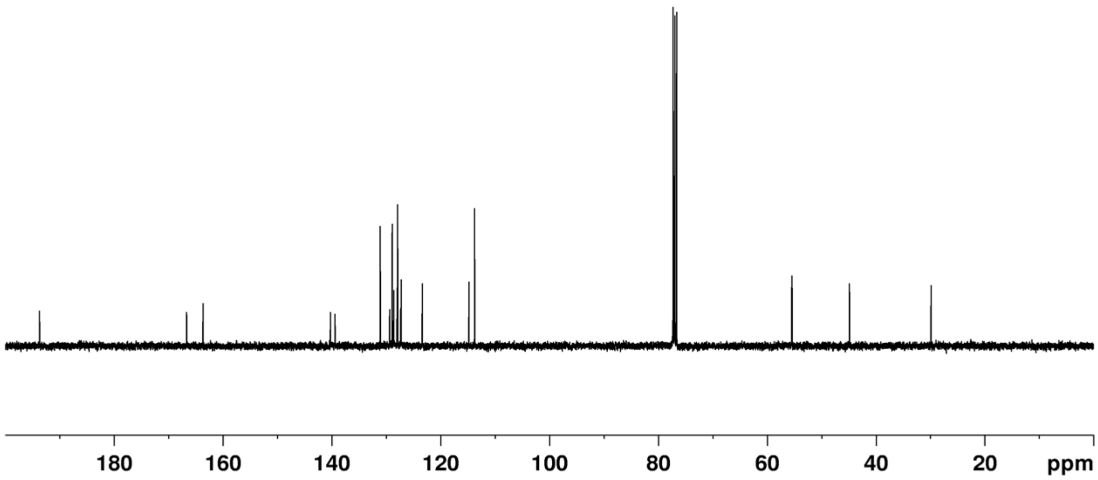


7.915
7.893
7.283
7.277
7.260
7.241
7.235
7.208
7.191
7.161
7.158
7.140
7.080
7.059
6.996
6.977
6.958
6.893
6.887
6.871
6.865
4.878
4.860
4.683
4.664
3.821
3.423
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00
6.36
1.04
1.03
3.01
1.01
1.00
3.00
3.00

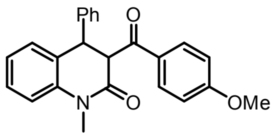


Ph
O
N
O
OMe

4b

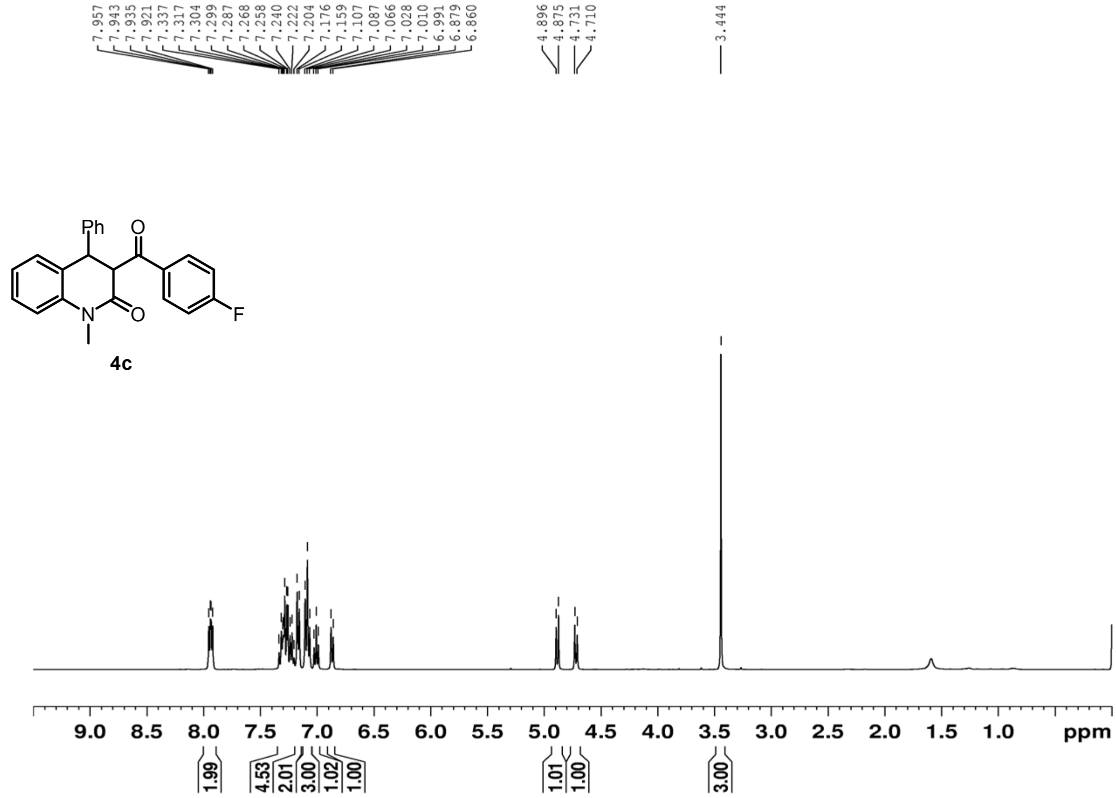


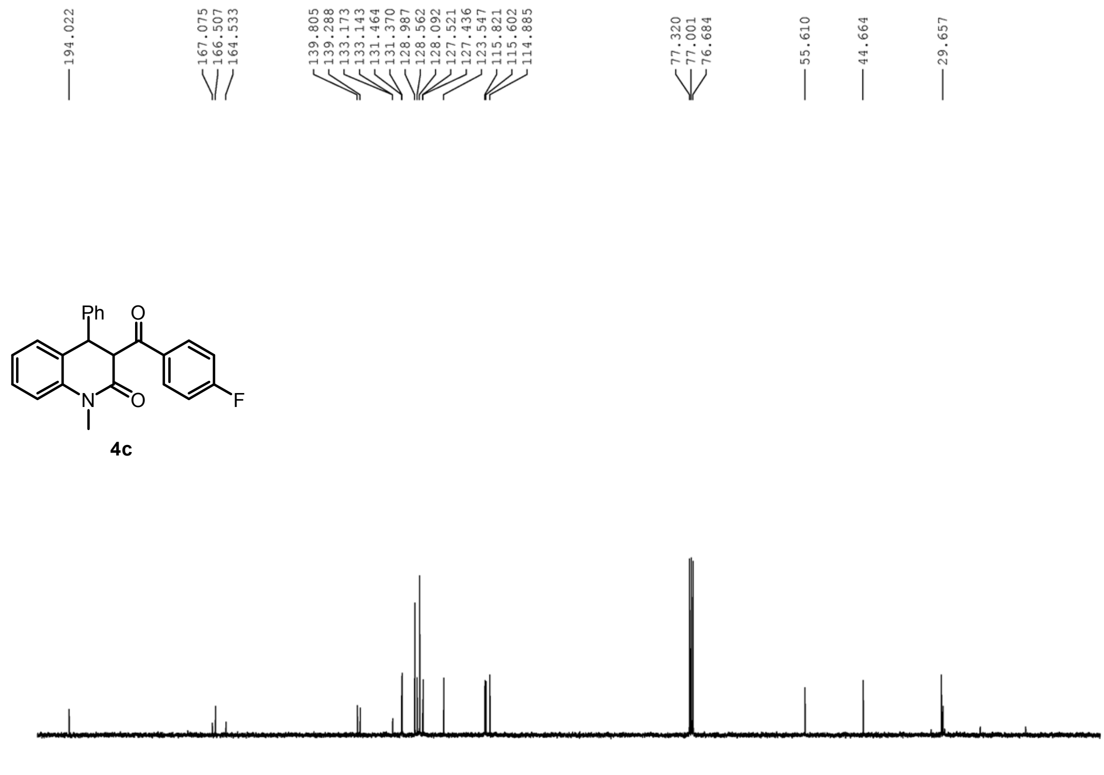
193.747
166.724
163.722
140.301
139.450
131.164
129.425
128.953
128.654
128.044
127.944
127.398
127.311
123.430
114.848
113.807
77.320
77.002
76.685
55.533
55.461
44.910
29.930
180 160 140 120 100 80 60 40 20 ppm

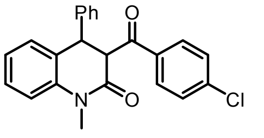


Ph
O
N
O
OMe

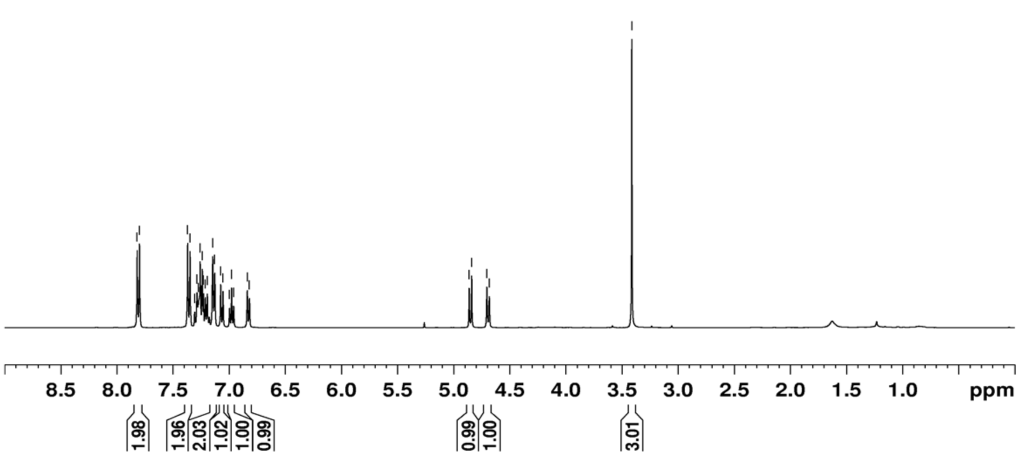
4b

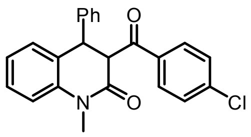

7.957 7.943 7.935 7.921 7.337 7.317 7.304 7.299 7.287 7.268 7.258 7.240 7.222 7.204 7.176 7.159 7.107 7.087 7.066 7.028 7.010 6.991 6.879 6.860
4.896 4.875 4.731 4.710
3.444
Ph
O
N
O
F
4c
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.99 4.53 2.01 3.00 1.02 1.00 1.01 1.00 3.00


194.022
167.075 166.507 164.533
139.805 139.288 133.173 133.143 131.464 131.370 128.987 128.562 128.092 127.521 127.436 123.547 115.821 115.602 114.885
77.320 77.001 76.684
55.610
44.664
29.657
Ph
O
N
O
F
4c
180 160 140 120 100 80 60 40 20 ppm

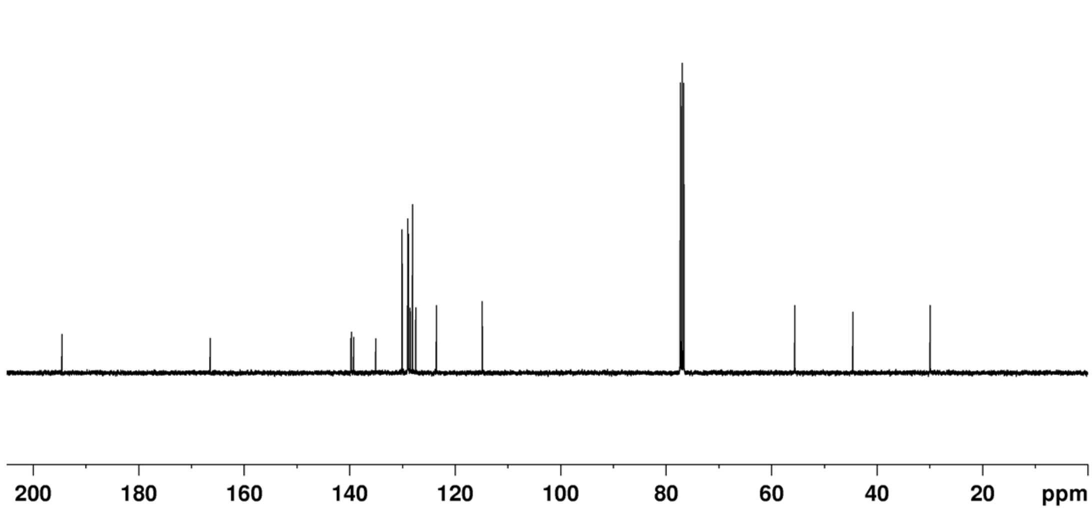

Ph
O
N
O
Cl

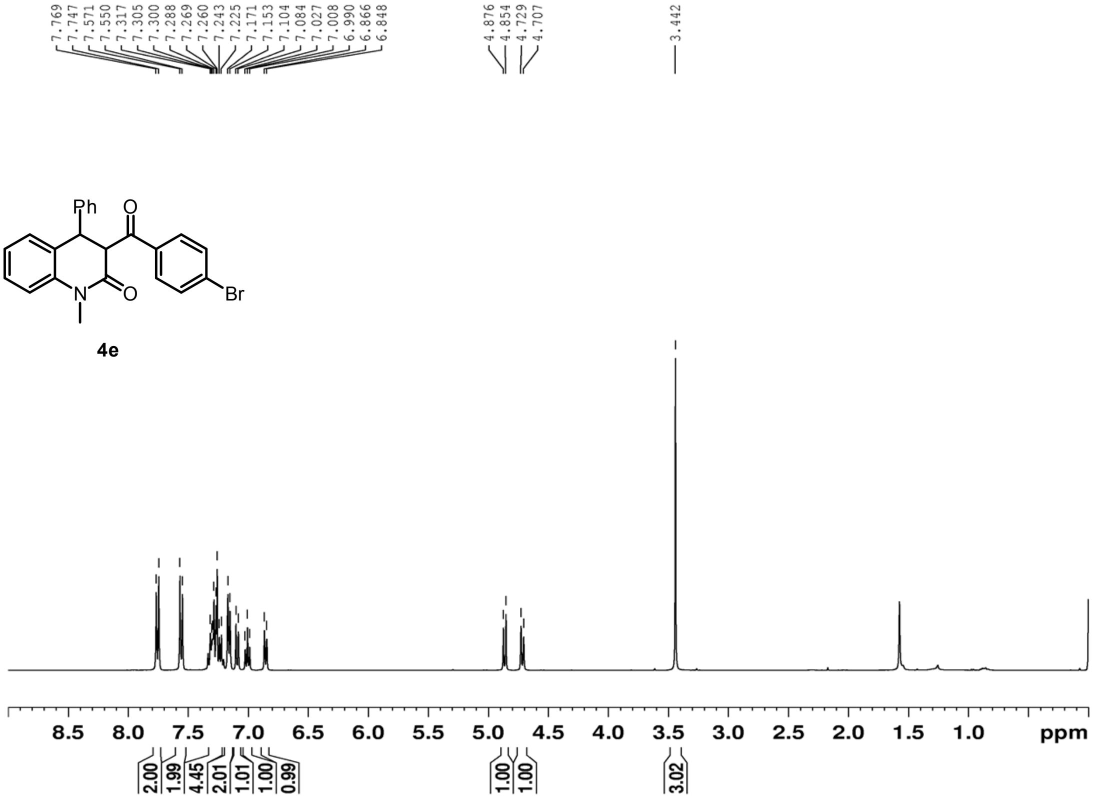
4d


7.821
7.800
7.372
7.350
7.308
7.288
7.277
7.260
7.241
7.230
7.214
7.196
7.148
7.130
7.077
7.056
6.998
6.980
6.961
6.840
6.821
4.862
4.840
4.705
4.683
3.413
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.98
1.96
2.03
1.02
1.00
0.99
0.99
1.00
3.01

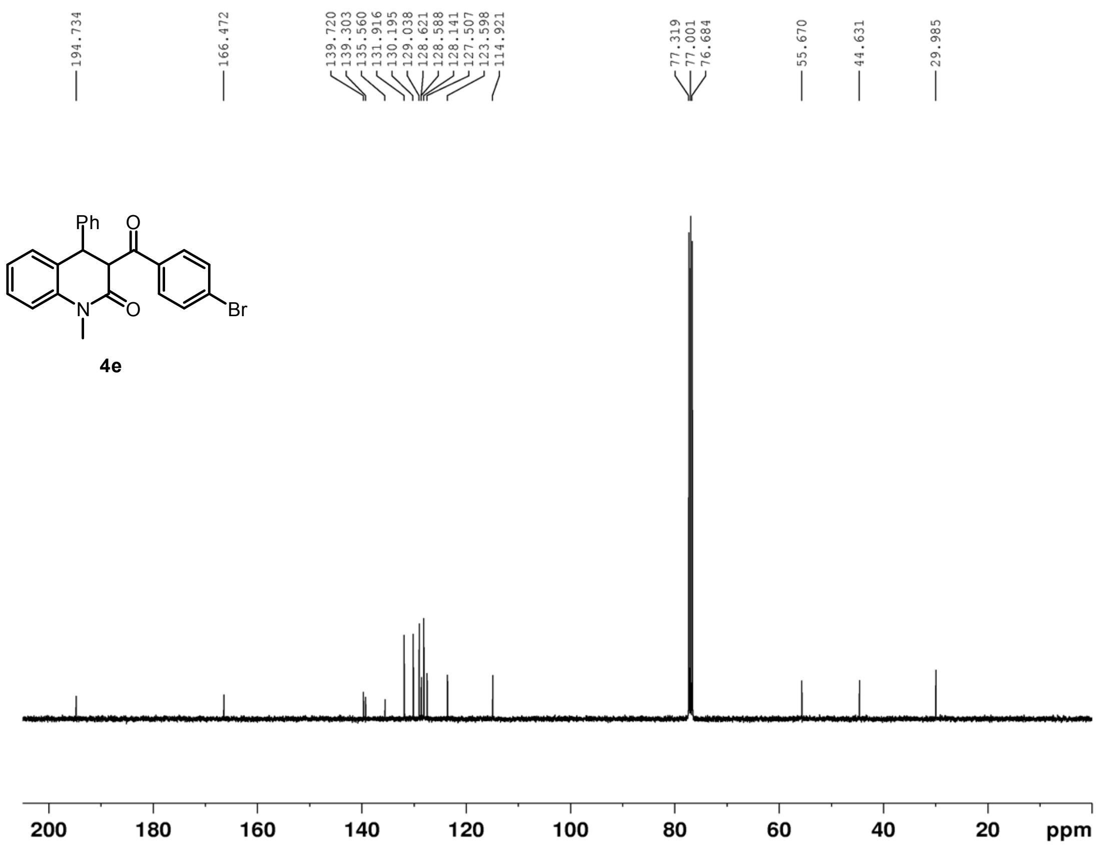

Ph
O
N
O
Cl

4d

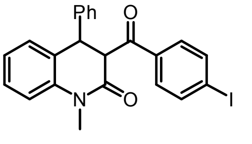

194.506
166.473
139.809
139.698
139.268
135.102
130.089
129.009
128.898
128.554
128.117
127.506
127.475
123.571
114.899
77.318
77.000
76.682
55.622
44.608
29.962
200 180 160 140 120 100 80 60 40 20 ppm


7.769
7.747
7.571
7.550
7.317
7.305
7.300
7.288
7.269
7.260
7.243
7.225
7.171
7.153
7.104
7.084
7.027
7.008
6.990
6.866
6.848
4.876
4.854
4.729
4.707
3.442
Ph
O
N
O
Br
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00 1.99 4.45 2.01 1.01 1.00 0.99 1.00 1.00 3.02

4e

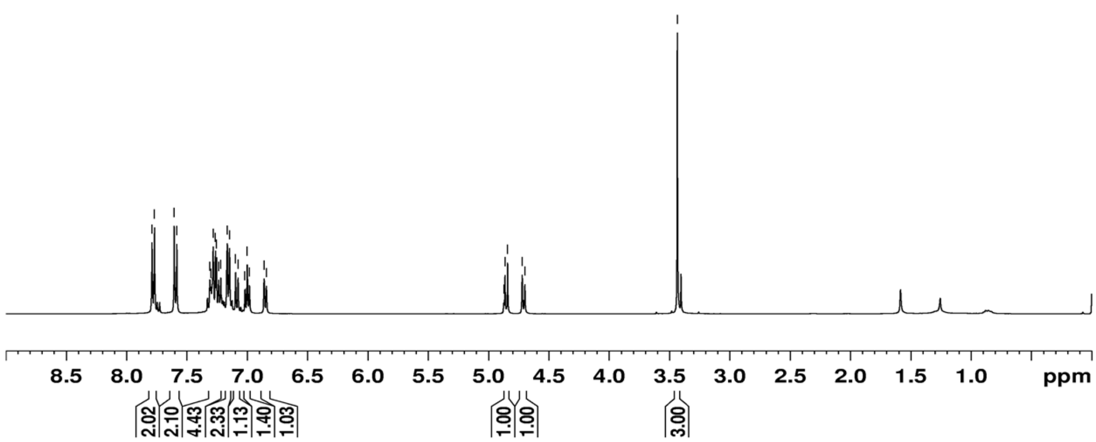

194.734
166.472
139.720
139.303
135.560
131.916
130.195
129.038
128.621
128.588
128.141
127.507
123.598
114.921
77.319
77.001
76.684
55.670
44.631
29.985
Ph
O
N
O
Br
200 180 160 140 120 100 80 60 40 20 ppm

4e

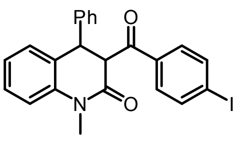


Ph
O
N
O
I

4f

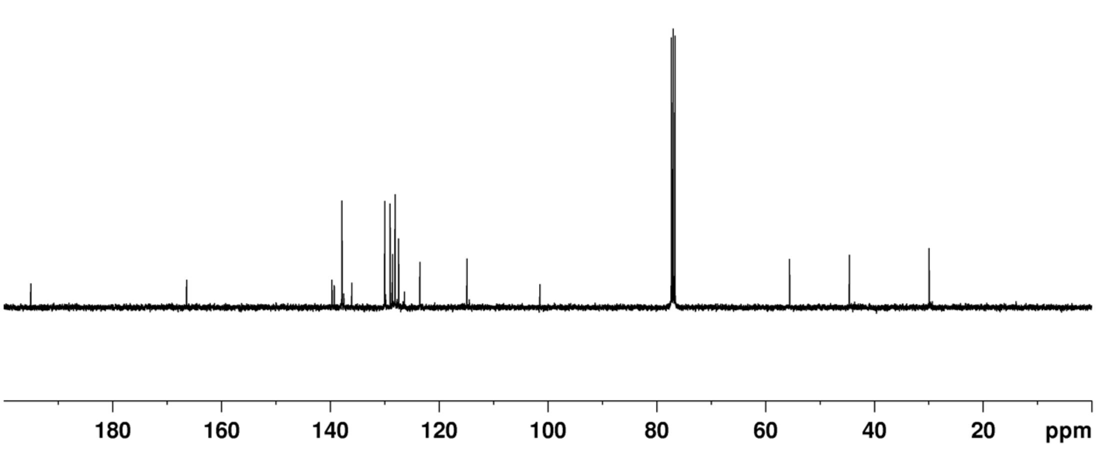


7.791 7.770 7.607 7.585 7.311 7.301 7.284 7.265 7.255 7.239 7.221 7.167 7.149 7.098 7.078 7.021 7.002 6.983 6.862 6.843
4.874 4.864 4.843 4.722 4.700
3.436
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.02 2.10 4.43 2.33 1.13 1.40 1.03
1.00 1.00
3.00

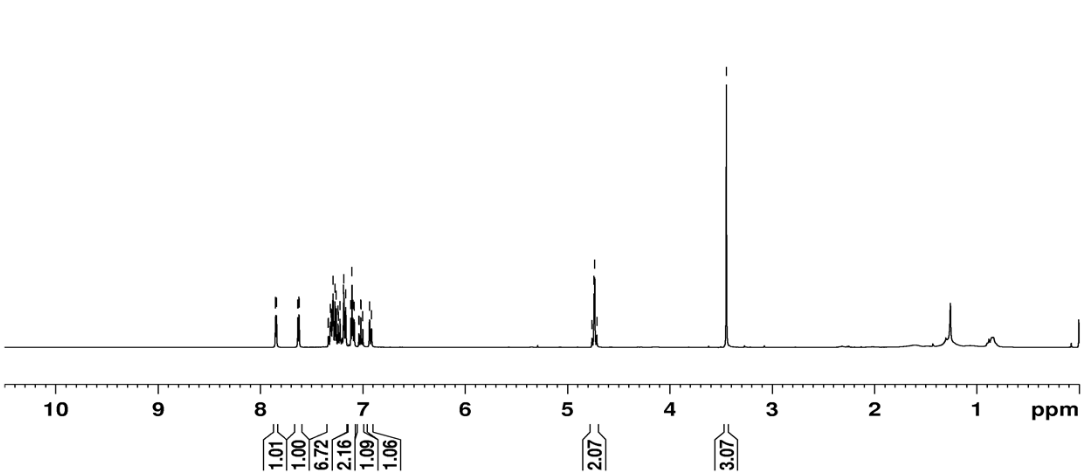


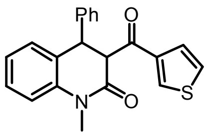
Ph
O
N
O
I

4f

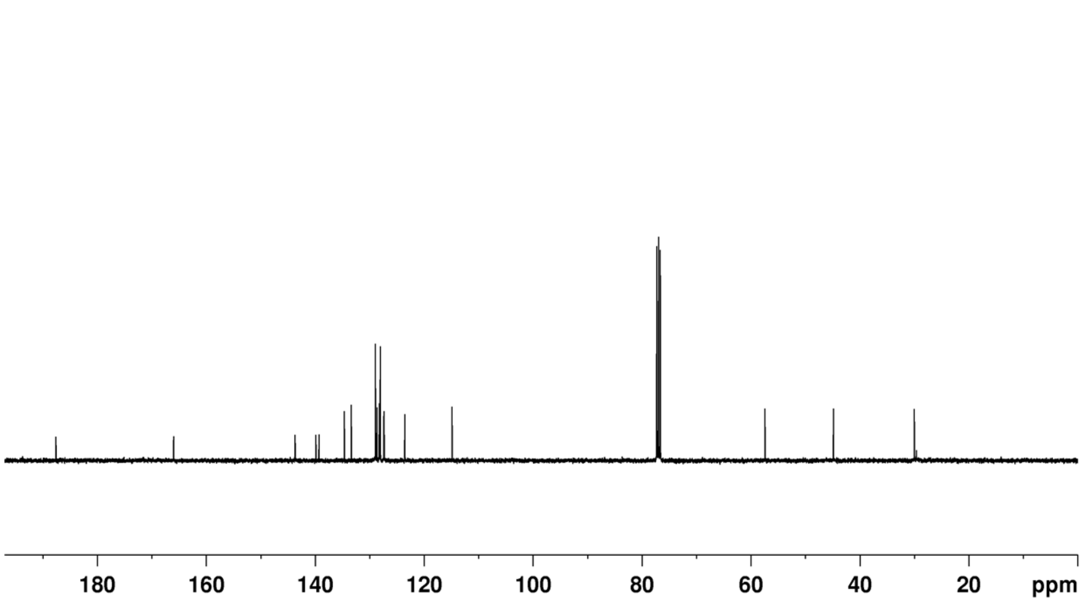


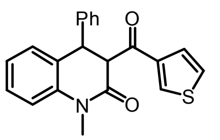
195.026
166.450
139.726 139.302 137.903 136.079 130.024 129.025 128.579 128.121 127.492 123.574
114.905
101.500
77.316 76.999 76.680
55.607
44.605
29.964
180 160 140 120 100 80 60 40 20 ppm


7.856
7.853
7.846
7.844
7.637
7.635
7.625
7.623
7.339
7.336
7.316
7.310
7.306
7.300
7.296
7.292
7.273
7.260
7.242
7.239
7.224
7.191
7.187
7.170
7.119
7.107
7.097
7.086
7.040
7.038
7.021
7.019
7.003
7.001
6.936
6.918
4.761
4.742
4.734
4.715
3.449
10 9 8 7 6 5 4 3 2 1 ppm
1.01
1.00
6.72
2.16
1.09
1.06
2.07
3.07

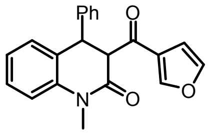

Ph
O
O
N
S

4g

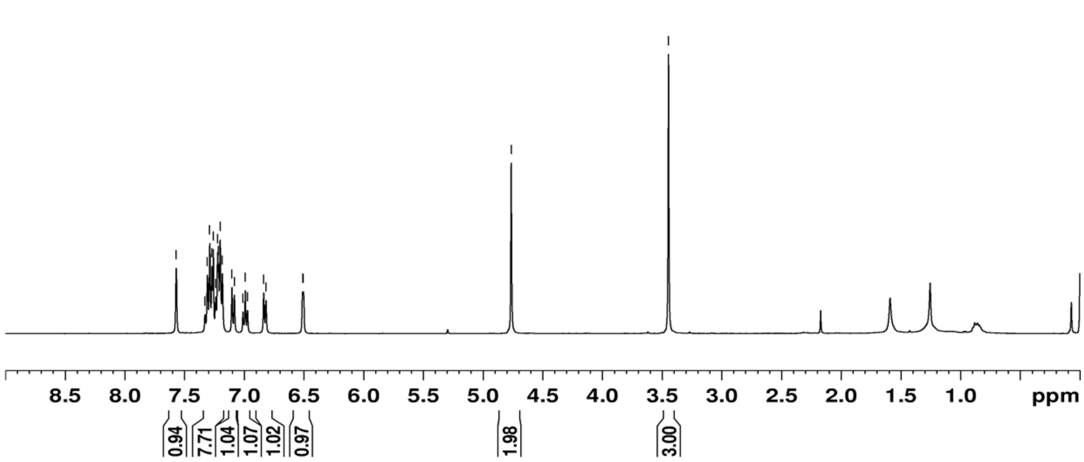

187.572
165.962
143.656
139.914
139.333
134.680
133.413
128.987
128.687
128.272
128.103
128.069
127.421
127.341
123.567
114.907
77.319
77.001
76.683
57.459
44.889
30.032
180 160 140 120 100 80 60 40 20 ppm

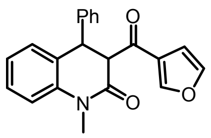

Ph
O
O
N
S

4g

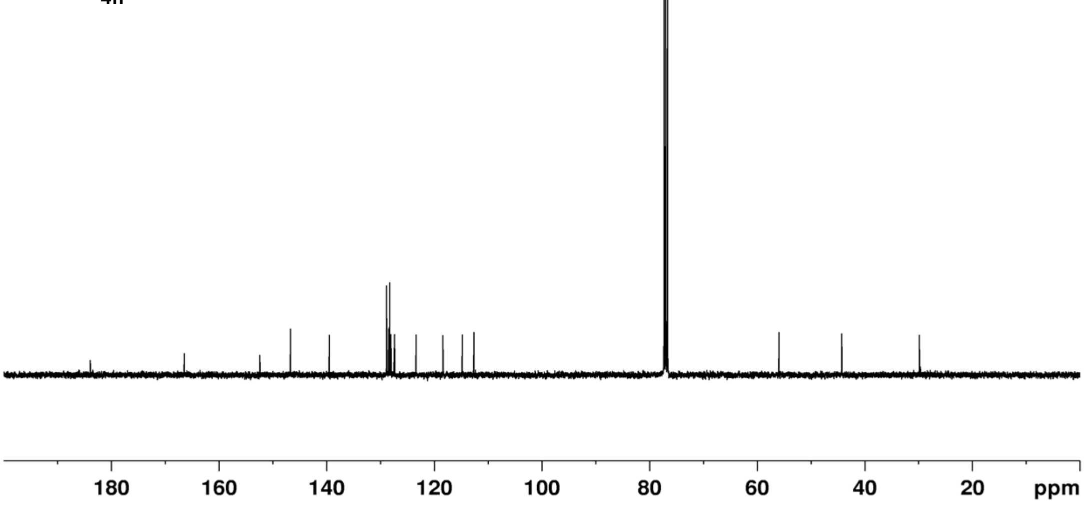

Ph
O
N
O
O

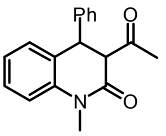
4h


7.571 7.330 7.310 7.291 7.272 7.261 7.241 7.225 7.217 7.204 7.185 7.104 7.084 7.012 6.993 6.974 6.838 6.819 6.511 6.506
4.765
3.447
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.94 7.71 1.04 1.07 1.02 0.97
1.98
3.00

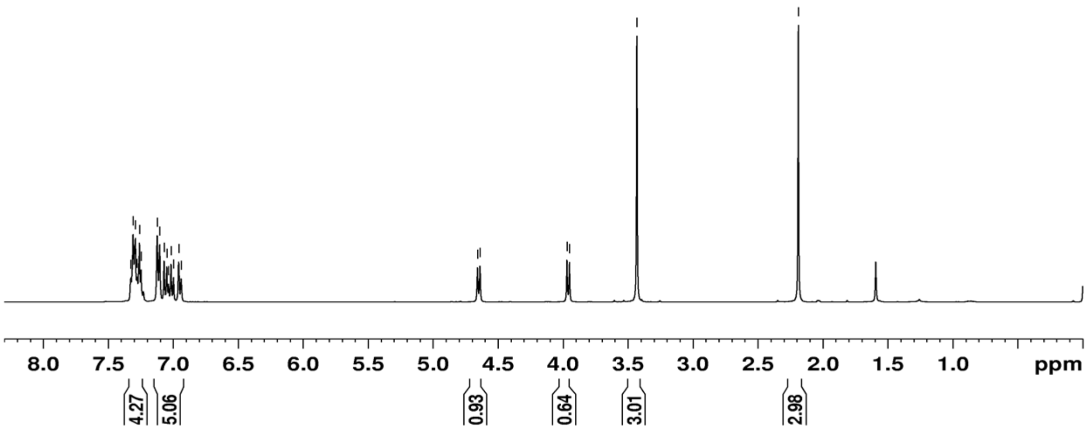

Ph
O
N
O
O

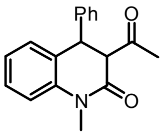
4h


183.944
166.495
152.456
146.748
139.544 128.920 128.534 128.330 128.102 127.498 127.416 123.425 118.438 114.844 112.649
77.314 76.996 76.679
55.973
44.308
29.902
180 160 140 120 100 80 60 40 20 ppm

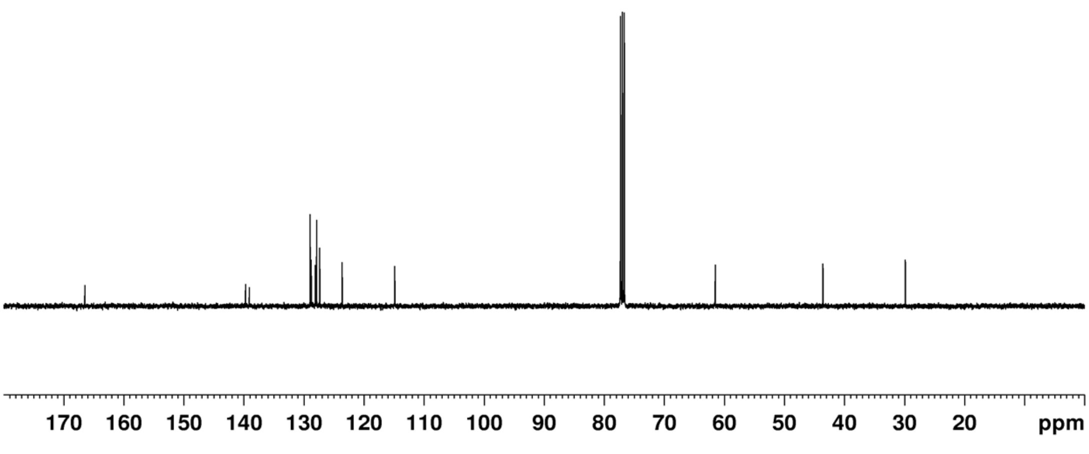

Ph
O
N
O

4i


7.326
7.309
7.291
7.279
7.260
7.247
7.122
7.104
7.070
7.049
7.035
7.016
6.998
6.957
6.939
4.658
4.639
3.969
3.950
3.431
2.189
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.27
5.06
0.93
0.64
3.01
2.98


Ph
O
N
O

4i


166.508
139.756
139.123
129.002
128.818
128.143
127.931
127.406
123.673
114.924
77.315
76.998
76.680
61.537
43.605
29.881
29.862
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm