Supporting Information

Copper-catalyzed tandem oxidative cyclization of cinnamamides with benzyl hydrocarbons through cross-dehydrogenative coupling

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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. Melting points were determined on a microscopic apparatus and were uncorrected.

Starting Materials

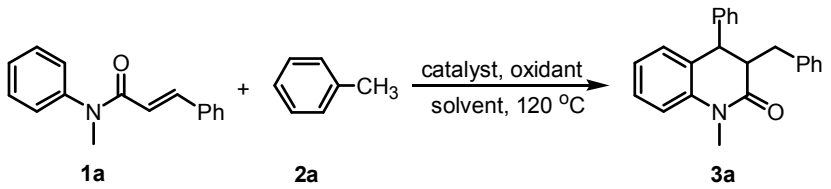
All of cinnamamides **1** were synthesized according to the literature, and the NMR spectroscopy were in full accordance with the data in the literature.[1]

Optimization of Reaction Conditions

General Procedure

A 10 mL oven-dried Schlenk-tube was charged with copper catalyst (See S-Table 1). The tube was evacuated and backfilled with nitrogen (three times). Cinnamamide (**1a**, 0.3 mmol, 1.0 equiv), toluene **2a** and oxidants (See S-Table 1) in 2 mL solvent were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 28 h at 120 ^{o}C. 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: 1/25 to 1/5) to yield the product **3a** as a white solid.

S-Table 1 Optimization of the reaction conditions[a]

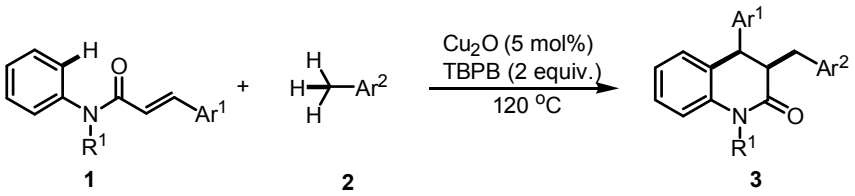


1a **2a** **3a**

Entry	Catalyst (mol%)	Oxidant (equiv.)	Solvent	Yield [b] (%)
1	Cu_2O (2)	TBPB (2.0)	CH_3CN	19
2	Cu_2O (2)	TBPB (2.0)	EtOAc	30
3	Cu_2O (2)	TBPB (2.0)	DMF	trace
4	Cu_2O (2)	TBPB (2.0)	DMSO	50
5	Cu_2O (2)	TBPB (2.0)	PhCl	46
6	Cu_2O (2)	TBPB (2.0)	DCE	15
7[c]	Cu_2O (2)	TBPB (2.0)	-	71
8[c]	Cu_2O (2)	TBHP (2.0)	-	30
9[c]	Cu_2O (2)	DTBP (2.0)	-	53
10[c]	Cu_2O (2)	DCP (2.0)	-	56
11[c]	CuCl (2)	TBPB (2.0)	-	68
12[c]	CuBr (2)	TBPB (2.0)	-	62
13[c]	$Cu(OAc)_2$ (2)	TBPB (2.0)	-	65
14[c]	$CuBr_2$ (2)	TBPB (2.0)	-	61
15[c]	CuO (2)	TBPB (2.0)	-	64
16[c]	$FeCl_2$ (2)	TBPB (2.0)	-	64
17[c]	$FeCl_3$ (2)	TBPB (2.0)	-	66
18[c]	**Cu_2O (5)**	**TBPB (2.0)**	**-**	**80** (78)[d]
19[c]	Cu_2O (10)	TBPB (2.0)	-	69
20[c]	-	TBPB (2.0)	-	49
21[c]	Cu_2O (5)	-	-	n.r.[e]

[a] Reaction conditions: 2 mol% of catalyst, **1a** (0.3 mmol, 1.0 equiv.), oxidant (2.0 equiv.), toluene (**2a**, 0.6 mmol, 2.0 equiv.), solvent (2.0 mL), 120 °C, 28 h. [b] Yield of isolated product. [c] **2a** (2 mL). [d] Yield on a 1 mmol scale is given in parentheses. [e] n.r. = no reaction.

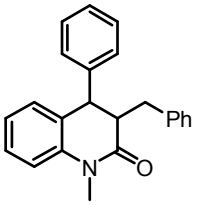
General Procedure for the Oxidative Coupling/Cyclization of Cinnamamides with Benzylic Hydrocarbons



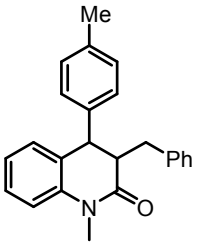
1 **2** **3**

A 10 mL oven-dried Schlenk-tube was charged with Cu_2O (2.1 mg, 5 mol %), cinnamamides (**1**, 0.3 mmol, 1.0 equiv). The tube was evacuated and backfilled with nitrogen (three times). TBPB (0.6 mmol, 2.0 equiv) in 2 mL of benzylic hydrocarbons were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 28 h at 120 ^{o}C. Upon completion of the reaction, the mixture was diluted with EtOAc. The solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/25 to 1/5) to give the corresponding products **3** in yields listed in Table 2.

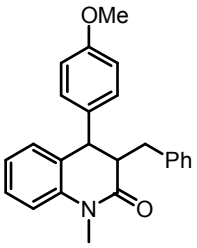
Characterization of Products 3



3a: A white solid, R_f 0.5 (EtOAc/petroleum ether = 1:4), mp = 139-140 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.33 (m, 3H), 7.29-7.26 (t, *J* = 7.2 Hz, 1H), 7.23-7.12 (m, 8H), 6.90-6.89 (d, *J* = 7.2 Hz, 2H), 3.91-3.90 (d, *J* = 2.8 Hz, 1H), 3.43 (s, 3H), 3.29-3.24 (m, 1H), 3.14-3.09 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.61-2.55 (dd, *J* = 13.2, 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 141.5, 139.7, 138.3, 129.8, 129.1, 128.6, 128.5, 128.1, 127.2, 126.7, 126.6, 125.9, 123.4, 114.7, 50.5, 44.2, 36.1, 29.6 ppm; IR (KBr): υ_{max} 1672, 1367 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{21}NNaO$ $[M+Na]^+$ 350.1515, found 350.1511.

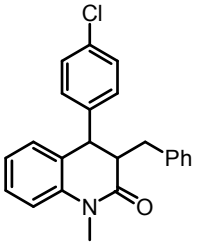


3b: A colorless oil, R_f 0.45 (EtOAc/petroleum ether = 1:5); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.24 (m, 4H), 7.15-7.08 (m, 5H), 7.00-6.98 (d, *J* = 8.0 Hz, 2H), 6.76-6.74 (d, *J* = 8.0 Hz, 2H), 3.83-3.82 (d, *J* = 3.2 Hz, 1H), 3.39 (s, 3H), 3.22-3.18 (m, 1H), 3.08-3.03 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.56-2.50 (dd, *J* = 13.2, 10.8 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 139.7, 138.5, 136.3, 129.8, 129.3, 129.1, 128.5, 128.0, 127.1, 126.6, 126.3, 123.5, 114.8, 50.5, 43.9, 36.1, 29.6, 20.9 ppm; IR (KBr): υ_{max} 1671, 1465, 1367 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}NNaO$ $[M+Na]^+$ 364.1672, found 364.1688.

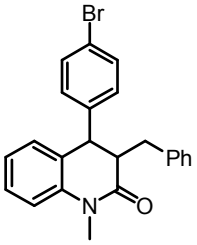


3c: A colorless oil, R_f 0.25 (EtOAc/petroleum ether = 1:5); ^1H NMR (400 MHz,

$CDCl_3$): δ = 7.36-7.22 (m, 4H), 7.15-7.08 (m, 5H), 6.79-6.77 (d, *J* = 8.8 Hz, 2H), 6.73-6.71 (d, *J* = 8.8 Hz, 2H), 3.82-3.81 (d, *J* = 3.2 Hz, 1H), 3.72 (s, 3H), 3.40 (s, 3H), 3.21-3.17 (m, 1H), 3.08-3.03 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.56-2.50 (dd, *J* = 13.6, 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 158.3, 139.7, 138.5, 133.6, 129.8, 129.1, 128.5, 128.2, 128.0, 126.6, 126.5, 123.5, 114.8, 114.0, 55.2, 50.6, 43.5, 36.0, 29.7 ppm; IR (KBr): υ_{max} 1670, 1507, 1368, 1253 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}NNaO_2$ $[M+Na]^+$ 380.1621, found 380.1638.

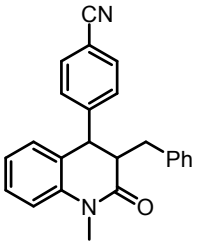


3d: A white solid, R_f 0.4 (EtOAc/petroleum ether = 1:5), mp = 156-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.23 (m, 4H), 7.16-7.05 (m, 7H), 6.78-6.76 (d, *J* = 8.4 Hz, 2H), 3.82 (d, *J* = 2.8 Hz, 1H), 3.40 (s, 3H), 3.19-3.14 (m, 1H), 3.09-3.05 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.55-2.49 (dd, *J* = 13.6, 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 140.0, 139.7, 138.2, 132.6, 129.8, 129.1, 128.7, 128.6, 128.4, 126.7, 125.4, 123.6, 114.9, 50.6, 43.7, 36.0, 29.7 ppm; IR (KBr): υ_{max} 1671, 1487, 1367 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{20}ClNNaO$ $[M+Na]^+$ 384.1126, found 384.1114.

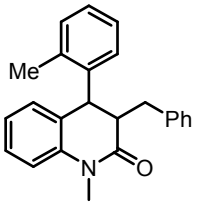


3e: A white solid, R_f 0.35 (EtOAc/petroleum ether = 1:10), mp = 151-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.23 (m, 6H), 7.14-7.05 (m, 5H), 6.72-6.70 (d, *J* = 8.4 Hz, 2H), 3.81-3.80 (d, *J* = 2.8 Hz, 1H), 3.39 (s, 3H), 3.19-3.14 (ddd, *J* = 10.8, 4.4, 3.2 Hz, 1H), 3.09-3.05 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.55-2.49 (dd, *J* = 13.6, 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 140.6, 139.7, 138.2, 131.7, 129.8, 129.1, 129.0, 128.6, 128.4, 126.7, 125.3, 123.6, 120.6, 114.9, 50.5, 43.8, 36.0, 29.7 ppm; IR (KBr): υ_{max} 1671, 1465, 1368, 730 cm^{-1}; HRMS (ESI) calcd for

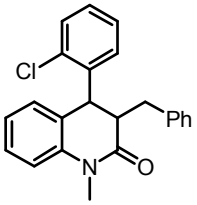
$C_{23}H_{20}BrNNaO$ $[M+Na]^+$ 428.0620, found 428.0621.



3f: A colorless thick oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.40 (m, 3H), 7.36-7.32 (m, 2H), 7.29-7.26 (m, 1H), 7.16-7.07 (m, 5H), 6.94-6.92 (d, *J* = 8.0 Hz, 2H), 3.89-3.88 (d, *J* = 2.0 Hz, 1H), 3.40 (s, 3H), 3.19-3.15 (ddd, *J* = 11.2, 4.4, 2.4 Hz, 1H), 3.12-3.08 (dd, *J* = 13.2, 4.4 Hz, 1H), 2.54-2.48 (dd, *J* = 13.2, 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 147.1, 139.7, 137.8, 132.4, 129.9, 129.0, 128.8, 128.7, 128.1, 126.9, 124.2, 123.8, 118.6, 115.1, 110.7, 50.6, 44.3, 36.1, 29.7 ppm; IR (KBr): υ_{max} 2230, 1671, 1467, 1369 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{20}N_2NaO$ $[M+Na]^+$ 375.1468, found 375.1466.

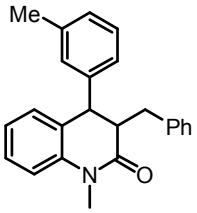


3g: A colorless thick oil, R_f 0.35 (EtOAc/petroleum ether = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.24 (m, 4H), 7.15-6.97 (m, 8H), 6.57-6.55 (d, *J* = 7.6 Hz, 1H), 4.09-4.08 (d, *J* = 3.2 Hz, 1H), 3.46 (s, 3H), 3.07-3.02 (dd, *J* = 13.2, 4.4 Hz, 1H), 2.98-2.93 (m, 1H), 2.64-2.58 (dd, *J* = 12.8, 10.4 Hz, 1H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 140.4, 139.2, 138.3, 135.5, 130.8, 129.8, 129.5, 128.4, 128.0, 126.9, 126.7, 126.6, 126.3, 123.6, 114.7, 49.6, 40.8, 36.3, 29.7, 18.6 ppm; IR (KBr): υ_{max} 1671, 1464, 1367 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}NNaO$ $[M+Na]^+$ 364.1672, found 364.1675.

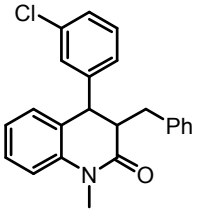


3h: A white solid, R_f 0.3 (EtOAc/petroleum ether = 1:10), mp = 150-152 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.37 (m, 1H), 7.31-7.23 (m, 4H), 7.16-6.98 (m, 7H),

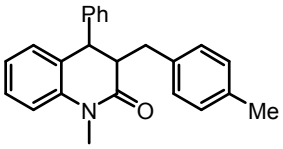
6.55-6.53 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.35-4.34 (d, *J* = 2.4 Hz, 1H), 3.43 (s, 3H), 3.20-3.17 (m, 1H), 3.09-3.04 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.60-2.54 (dd, *J* = 13.2, 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 140.5, 138.6, 137.8, 133.4, 130.0, 129.9, 129.5, 128.6, 128.5, 128.2, 128.1, 127.0, 126.6, 125.1, 123.8, 114.8, 48.9, 41.7, 36.7, 29.6 ppm; IR (KBr): υ_{max} 1671, 1467, 1367, 753 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{20}ClNNaO$ $[M+Na]^+$ 384.1126, found 384.1120.



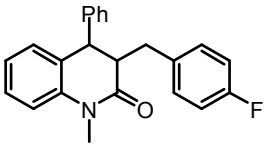
3i: A white solid, R_f 0.35 (EtOAc/petroleum ether = 1:10), mp = 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.24 (m, 4H), 7.15-7.05 (m, 6H), 6.96-6.94 (d, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 6.64-6.62 (d, *J* = 7.6 Hz, 1H), 3.83-3.82 (d, *J* = 3.2 Hz, 1H), 3.40 (s, 3H), 3.23-3.19 (m, 1H), 3.09-3.04 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.57-2.50 (dd, *J* = 13.2, 10.8 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 141.4, 139.8, 138.5, 138.2, 129.9, 129.1, 128.5, 128.0, 127.5, 126.6, 126.2, 124.2, 123.5, 114.8, 50.5, 44.3, 36.1, 29.6, 21.4 ppm; IR (KBr): υ_{max} 1672, 1466, 1366 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}NNaO$ $[M+Na]^+$ 364.1672, found 364.1672.



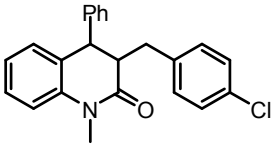
3j: A white solid, R_f 0.35 (EtOAc/petroleum ether = 1:10), mp = 144-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.25 (m, 4H), 7.15-7.05 (m, 7H), 6.78-6.76 (d, *J* = 8.4 Hz, 2H), 3.82 (d, *J* = 2.4 Hz, 1H), 3.39 (s, 3H), 3.19-3.14 (m, 1H), 3.09-3.05 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.55-2.49 (dd, *J* = 13.2, 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 140.0, 139.7, 138.2, 132.5, 129.8, 129.1, 128.7, 128.6, 128.4, 126.7, 125.4, 123.6, 114.9, 50.6, 43.7, 36.0, 29.6 ppm; IR (KBr): υ_{max} 1672, 1465, 1368, 732 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{20}ClNNaO$ $[M+Na]^+$ 384.1126, found 384.1127.



3l: A colorless thick oil, R_f 0.4 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.34 (m, 1H), 7.19-7.08 (m, 8H), 7.04-7.02 (d, *J* = 8.0 Hz, 2H), 6.86-6.84 (d, *J* = 7.2 Hz, 2H), 3.87-3.86 (d, *J* = 2.4 Hz, 1H), 3.39 (s, 3H), 3.22-3.17 (m, 1H), 3.05-3.00 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.52-2.46 (dd, *J* = 14.6, 11.2 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 141.6, 139.8, 136.1, 135.2, 129.9, 129.2, 129.0, 128.6, 128.1, 127.2, 126.7, 126.0, 123.4, 114.7, 50.7, 44.2, 35.7, 29.6, 21.0 ppm; IR (KBr): υ_{max} 1672, 1466, 1367 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}NNaO$ $[M+Na]^+$ 364.1672, found 364.1667.

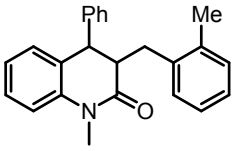


3m: A white solid, R_f 0.4 (EtOAc/petroleum ether = 1:5), mp = 131-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.34 (m, 1H), 7.21-7.16 (m, 3H), 7.11-7.06 (m, 5H), 7.01-6.97 (t, *J* = 8.4 Hz, 2H), 6.88-6.86 (d, *J* = 7.2 Hz, 2H), 3.85-3.84 (d, *J* = 3.6 Hz, 1H), 3.40 (s, 3H), 3.19-3.15 (m, 1H), 3.04-3.00 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.60-2.54 (dd, *J* = 13.6, 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 161.7 (d, $J_{C, F}$ = 243.3 Hz), 141.3, 139.7, 134.1 (d, $J_{C, F}$ = 3.4 Hz), 130.6 (d, $J_{C, F}$ = 7.9 Hz), 129.8, 128.7, 128.2, 127.3, 126.9, 126.2, 123.5, 115.3 (d, $J_{C, F}$ = 21.1 Hz), 114.8, 50.5, 44.6, 35.3, 29.7 ppm; IR (KBr): υ_{max} 1671, 1505, 1367, 1224 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{20}FNNaO$ $[M+Na]^+$ 368.1421, found 368.1433.

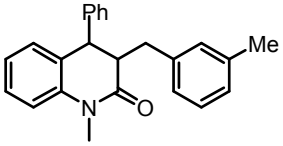


3n: A white solid, R_f 0.5 (EtOAc/petroleum ether = 1:5), mp = 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.33 (m, 1H), 7.28-7.25 (m, 2H), 7.21-7.16 (m, 3H), 7.11-7.04 (m, 5H), 6.88-6.87 (d, *J* = 6.8 Hz, 2H), 3.84-3.83 (d, *J* = 4.0 Hz, 1H), 3.40 (s, 3H), 3.20-3.15 (m, 1H), 3.04-3.00 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.60-2.54 (dd, *J* =

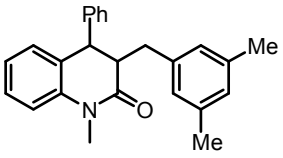
13.6, 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 141.2, 139.7, 137.0, 132.4, 130.5, 129.7, 128.7, 128.6, 128.2, 127.4, 126.9, 126.2, 123.5, 114.8, 50.2, 44.6, 35.4, 29.7 ppm; IR (KBr): υ_{max} 1671, 1488, 1368, 750 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{20}ClNNaO$ $[M+Na]^+$ 384.1126, found 384.1144.



3o: A colorless oil, R_f 0.45 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.35 (m, 1H), 7.17-7.09 (m, 9H), 7.04-7.02 (m, 1H), 6.84-6.82 (d, *J* = 7.2 Hz, 2H), 3.90-3.89 (d, *J* = 1.2 Hz, 1H), 3.41 (s, 3H), 3.24-3.20 (ddd, *J* = 11.2, 4.8, 2.0 Hz, 1H), 3.08-3.03 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.61-2.55 (dd, *J* = 14.0, 11.2 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 141.8, 139.8, 136.6, 136.4, 130.7, 130.2, 129.8, 128.6, 128.2, 127.0, 126.8, 126.7, 125.9, 123.5, 114.8, 49.4, 44.5, 33.7, 29.6, 19.3 ppm; IR (KBr): υ_{max} 1670, 1608, 1465, 1368 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}NNaO$ $[M+Na]^+$ 364.1672, found 364.1662.



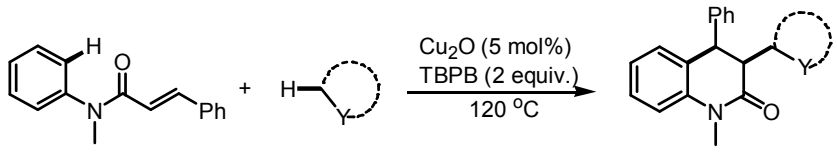
3q: A colorless oil, R_f 0.45 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.33 (m, 1H), 7.24-7.04 (m, 8H), 6.96 (s, 1H), 6.95-6.93 (d, *J* = 8.0 Hz, 1H), 6.87-6.85 (d, *J* = 7.2 Hz, 2H), 3.88-3.87 (d, *J* = 2.8 Hz, 1H), 3.39 (s, 3H), 3.23-3.19 (ddd, *J* = 10.8, 4.4, 2.8 Hz, 1H), 3.06-3.01 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.53-2.47 (dd, *J* = 13.2, 10.8 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 141.6, 139.8, 138.3, 138.2, 129.9, 128.6, 128.4, 128.1, 127.3, 127.2, 126.7, 126.1, 123.5, 114.8, 50.5, 44.3, 36.1, 29.6, 21.4 ppm; IR (KBr): υ_{max} 1671, 1610, 1466, 1366 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}NNaO$ $[M+Na]^+$ 364.1672, found 364.1661.



3r: A white solid, R_f 0.5 (EtOAc/petroleum ether = 1:5), mp = 104-105 ^{o}C; ^{1}H NMR

(400 MHz, $CDCl_3$): δ = 7.36-7.33 (m, 1H), 7.20-7.09 (m, 6H), 6.88-6.86 (m, 3H), 6.75 (s, 2H), 3.89-3.88 (d, *J* = 2.8 Hz, 1H), 3.39 (s, 3H), 3.23-3.18 (ddd, *J* = 10.8, 4.4, 2.8 Hz, 1H), 3.02-2.97 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.49-2.43 (dd, *J* = 13.6, 11.2 Hz, 1H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 141.7, 139.8, 138.2, 138.0, 129.9, 128.6, 128.2, 128.0, 127.2, 126.9, 126.7, 126.1, 123.4, 114.7, 50.4, 44.3, 36.0, 29.6, 21.3 ppm; IR (KBr): υ_{max} 1670, 1602, 1467, 1368 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{25}NNaO$ $[M+Na]^+$ 378.1828, found 378.1821.

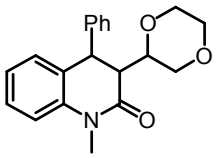
General Procedure for the Oxidative Coupling/Cyclization of Cinnamamides with Ethers, Acohols and Alkanes



1a **4** **5**

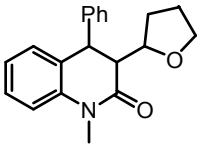
A 10 mL oven-dried Schlenk-tube was charged with Cu_2O (2.1 mg, 5 mol %), cinnamamide (**1a**, 0.3 mmol, 1.0 equiv). The tube was evacuated and backfilled with nitrogen (three times). TBPB (0.6 mmol, 2.0 equiv) in 2 mL of ethers or alkanes **4** were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 28 h at 120 °C. Upon completion of the reaction, the mixture was diluted with EtOAc. The solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/25 to 1/5) to give the corresponding products **5** in yields listed in Table 3.

Characterization of Products 5

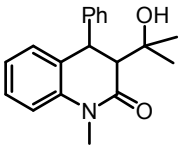


5a: A colorless oil, R_f 0.25 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.33 (t, *J* = 7.6 Hz, 1H), 7.26-7.20 (m, 3H), 7.17-7.16 (m, 1H), 7.12-7.07 (m, 2H), 7.00-6.98 (d, *J* = 7.2 Hz, 2H), 4.52 (s, 1H), 3.84-3.81 (m, 2H), 3.71-3.52 (m, 5H), 3.36 (s, 3H), 3.00-2.97 (dd, *J* = 10.0, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 141.5, 139.6, 130.0, 128.7, 128.2, 127.2, 126.8, 126.0, 123.7, 115.0, 72.1, 70.3, 67.2, 66.3, 52.1, 42.2, 29.7 ppm; IR (KBr): υ_{max} 1671, 1614, 1467, 1369 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{21}NNaO_3$ $[M+Na]^+$ 346.1414, found 346.1415.

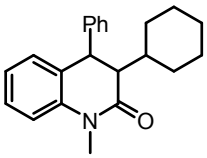
5a': A colorless oil, R_f 0.20 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.31 (m, 1H), 7.27-7.19 (m, 3H), 7.12-7.05 (m, 3H), 7.02-7.00 (d, *J* = 7.2 Hz, 2H), 4.13-4.12 (d, *J* = 3.2 Hz, 1H), 3.83-3.80 (d, *J* = 10.4 Hz, 1H), 3.76-3.74 (d, *J* = 8.4 Hz, 1H), 3.68-3.54 (m, 5H), 3.40 (s, 3H), 3.09-3.07 (dd, *J* = 6.4, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 141.1, 139.8, 129.1, 128.9, 128.3, 127.3, 127.1, 126.4, 123.5, 115.0, 74.8, 69.1, 67.0, 66.4, 51.0, 43.8, 29.8 ppm.



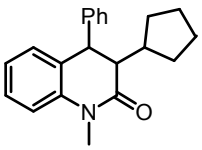
5b: A colorless oil, R_f 0.2 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.33 (m, 1H), 7.29-7.18 (m, 4H), 7.11-7.05 (m, 2H), 7.03-7.02 (d, *J* = 7.2 Hz, 2H), 4.07 (s, 1H), 3.96-3.88 (m, 2H), 3.75-3.70 (m, 1H), 3.43 (s, 3H), 3.04-3.01 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.09-1.96 (m, 2H), 1.88-1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 141.6, 140.0, 129.3, 128.8, 128.2, 127.0, 126.9, 126.1, 123.2, 114.9, 78.4, 68.4, 54.4, 45.1, 30.4, 29.6, 25.2 ppm; IR (KBr): υ_{max} 1675, 1605, 1466, 1363 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{21}NNaO_2$ $[M+Na]^+$ 330.1465, found 330.1470.



5c: A pale yellow oil, R_f 0.20 (EtOAc/petroleum ether = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.30 (m, 1H), 7.26-7.22 (m, 2H), 7.19-7.16 (m, 2H), 7.08-7.05 (m, 2H), 7.00-6.98 (d, *J* = 7.2 Hz, 2H), 4.37 (s, 1H), 3.43 (s, 3H), 3.12 (s, 1H), 3.00 (s, 1H), 1.31 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.8, 143.4, 139.6, 129.3, 128.9, 128.2, 126.9, 126.8, 126.5, 123.9, 114.7, 72.6, 60.0, 43.5, 29.6, 27.9, 27.6 ppm; IR (KBr): υ_{max} 3416, 1648, 1601, 1467, 1369 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{21}NNaO_2$ $[M+Na]^+$ 318.1465, found 318.1453.



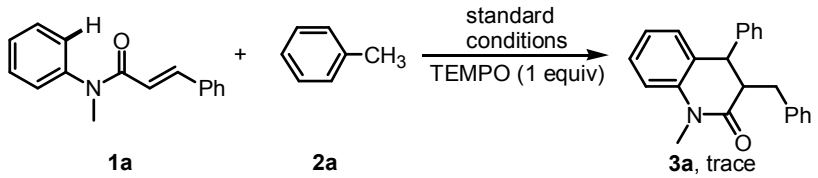
5d: A colorless oil, R_f 0.6 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.31 (m, 1H), 7.23-7.15 (m, 4H), 7.08-7.04 (m, 2H), 6.97-6.95 (d, *J* = 7.6 Hz, 2H), 4.22 (s, 1H), 3.36 (s, 3H), 2.69-2.66 (dd, *J* = 8.8, 1.6 Hz, 1H), 1.94-1.92 (m, 1H), 1.71-1.56 (m, 4H), 1.39-1.37 (m, 1H), 1.26-1.12 (m, 1H), 1.10-1.05 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 142.3, 140.1, 129.6, 128.7, 128.0, 127.0, 126.7, 126.6, 123.2, 114.8, 55.6, 44.4, 37.7, 31.4, 31.1, 29.4, 26.1, 25.9 ppm; IR (KBr): υ_{max} 1663, 1467, 1368 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{25}NNaO$ $[M+Na]^+$ 342.1828, found 342.1819.



5e: A colorless oil, R_f 0.5 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.32 (m, 1H), 7.24-7.20 (m, 3H), 7.17-7.13 (t, *J* = 7.2 Hz, 1H), 7.08-7.05 (m, 2H), 6.99-6.97 (d, *J* = 7.6 Hz, 2H), 4.13 (s, 1H), 3.36 (s, 3H), 2.72-2.69 (dd, *J* = 10.4, 1.6 Hz, 1H), 1.92-1.90 (m, 1H), 1.79-1.65 (m, 3H), 1.56-1.44 (m, 4H), 1.37-1.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8, 142.0, 140.0, 129.7, 128.7, 128.0, 127.0, 126.7, 126.4, 123.2, 114.7, 55.0, 46.5, 40.2, 31.3, 30.8, 29.4, 25.1, 24.5 ppm; IR (KBr): υ_{max} 1674, 1468, 1363 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{23}NNaO$

$[M+Na]^+$ 328.1672, found 328.1662.

Investigation of the Reaction Mechanism



1a **2a** **3a**, trace

When the TEMPO was added to the reaction of **1a** with **2a** under the standard conditions, only trace amount of the desired product **3a** was detected. The result indicates that the radical intermediate should be involved in the catalytic cycle of the reaction.

Isotope Labeling Experiment

a) Intermolecular Kinetic Isotope Effect (KIE) Experiment:

Toluene-D_8 (99.5%, cat. No. DLM-5-5) was purchased from Cambridge Isotope Laboratories. The isotope reagent was used without further purification. A 10 mL oven-dried Schlenk-tube was charged with Cu_2O (2.1 mg, 5 mol %), **1a** (0.3 mmol). The tube was evacuated and backfilled with nitrogen (three times). TBPB (0.6 mmol, 2 equiv) in 2 mL of toluene/D_8-toluene (1:1) were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 28 h at 120 °C. 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 to give the corresponding product. The product was analyzed by ^{1}H NMR (Figure 1).

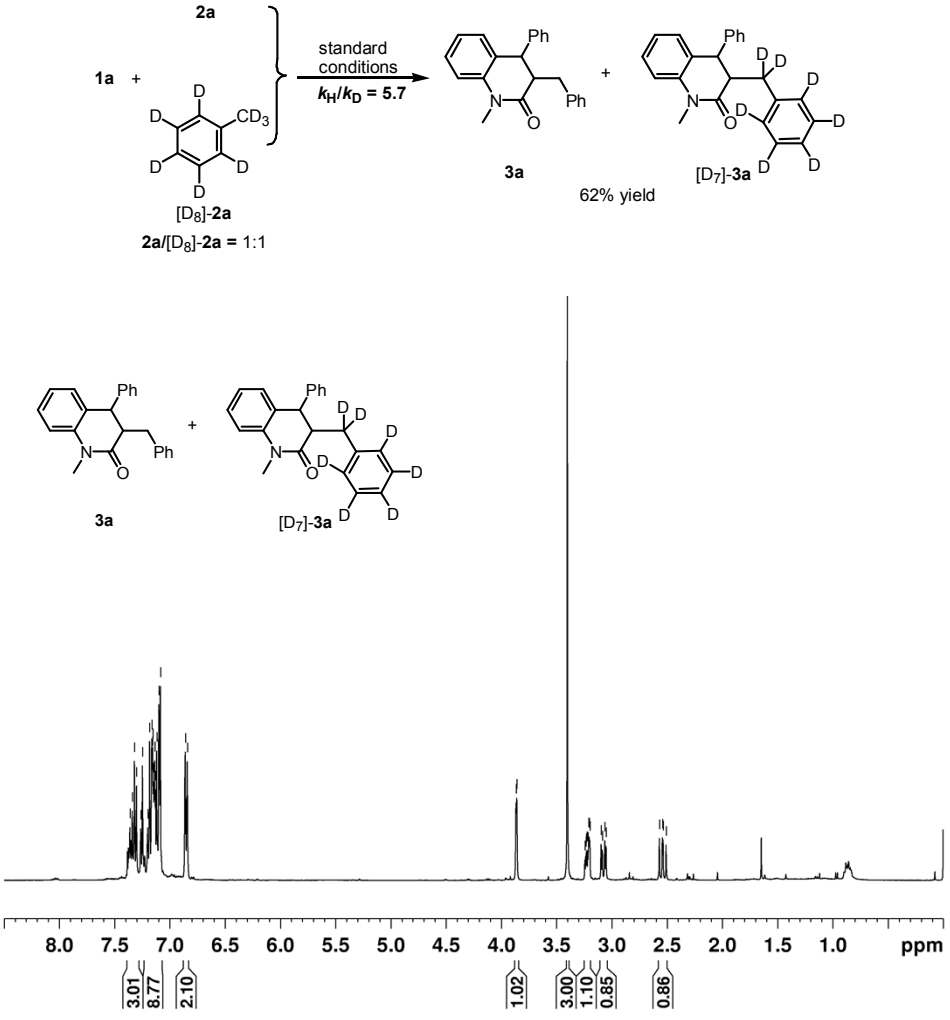
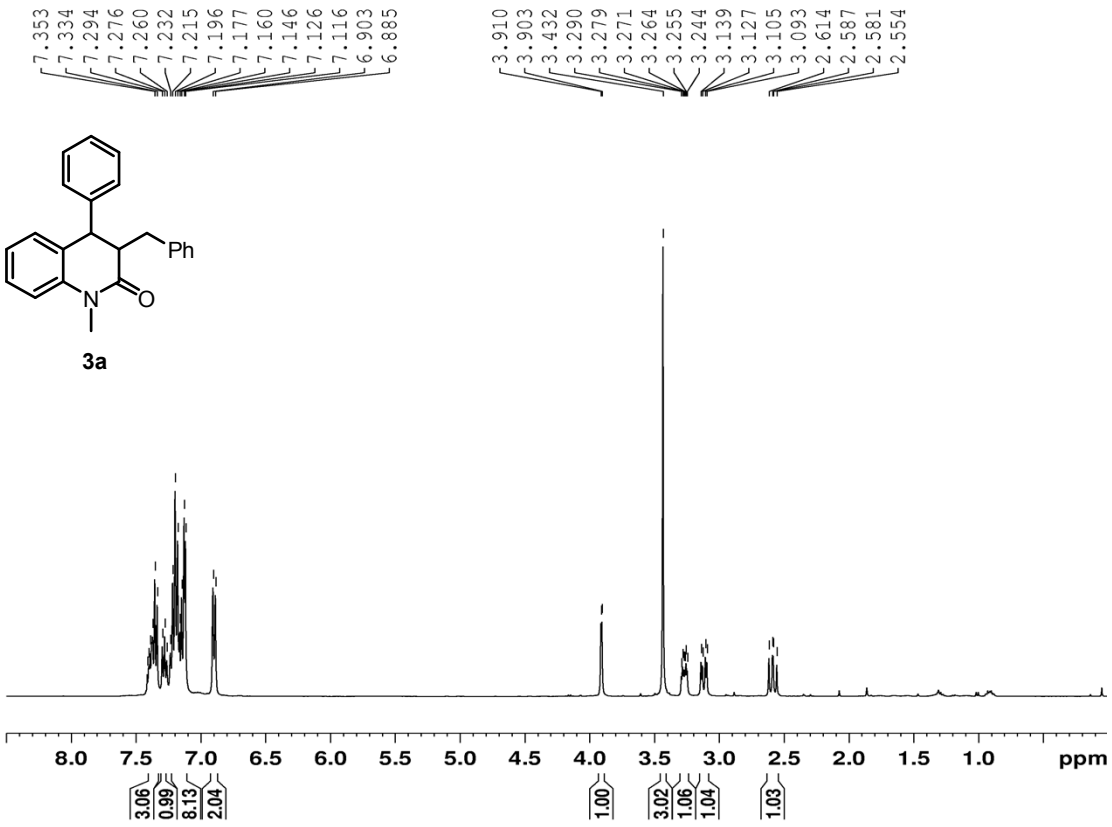


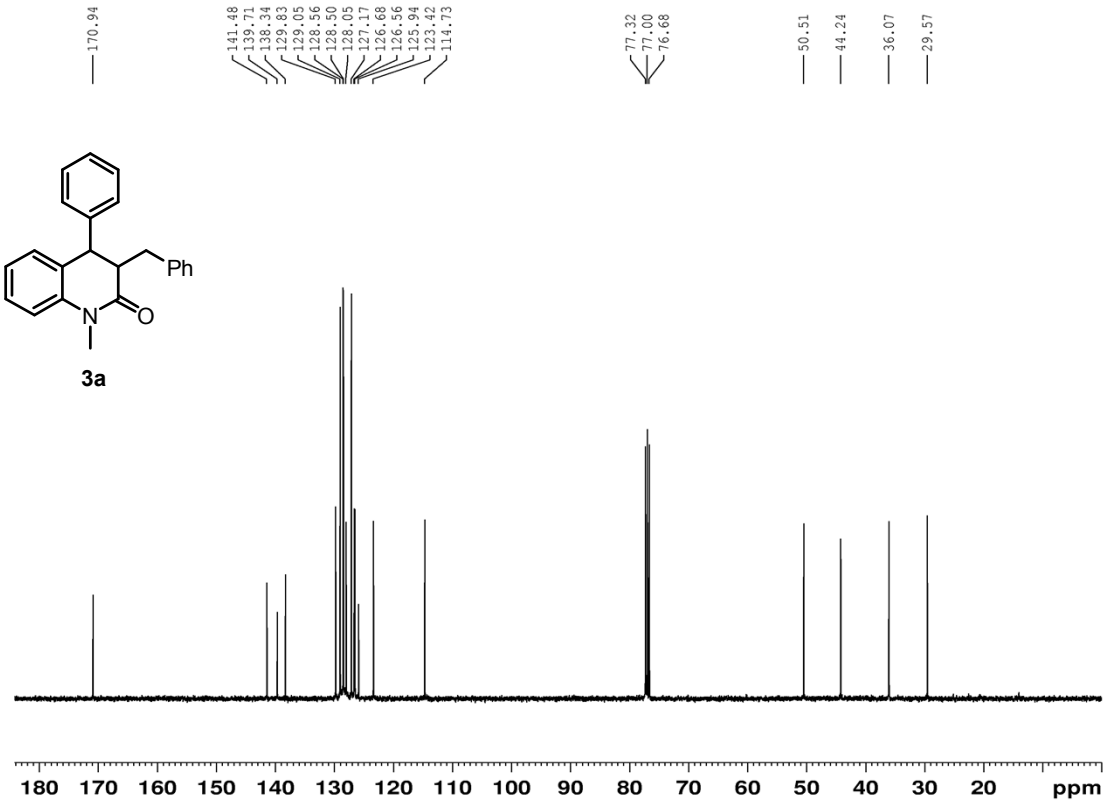
Figure 1. ^{1}H NMR spectra of the mixture of the product **3a** and [D_7]-**3a**.

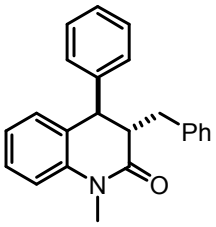
References

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.

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



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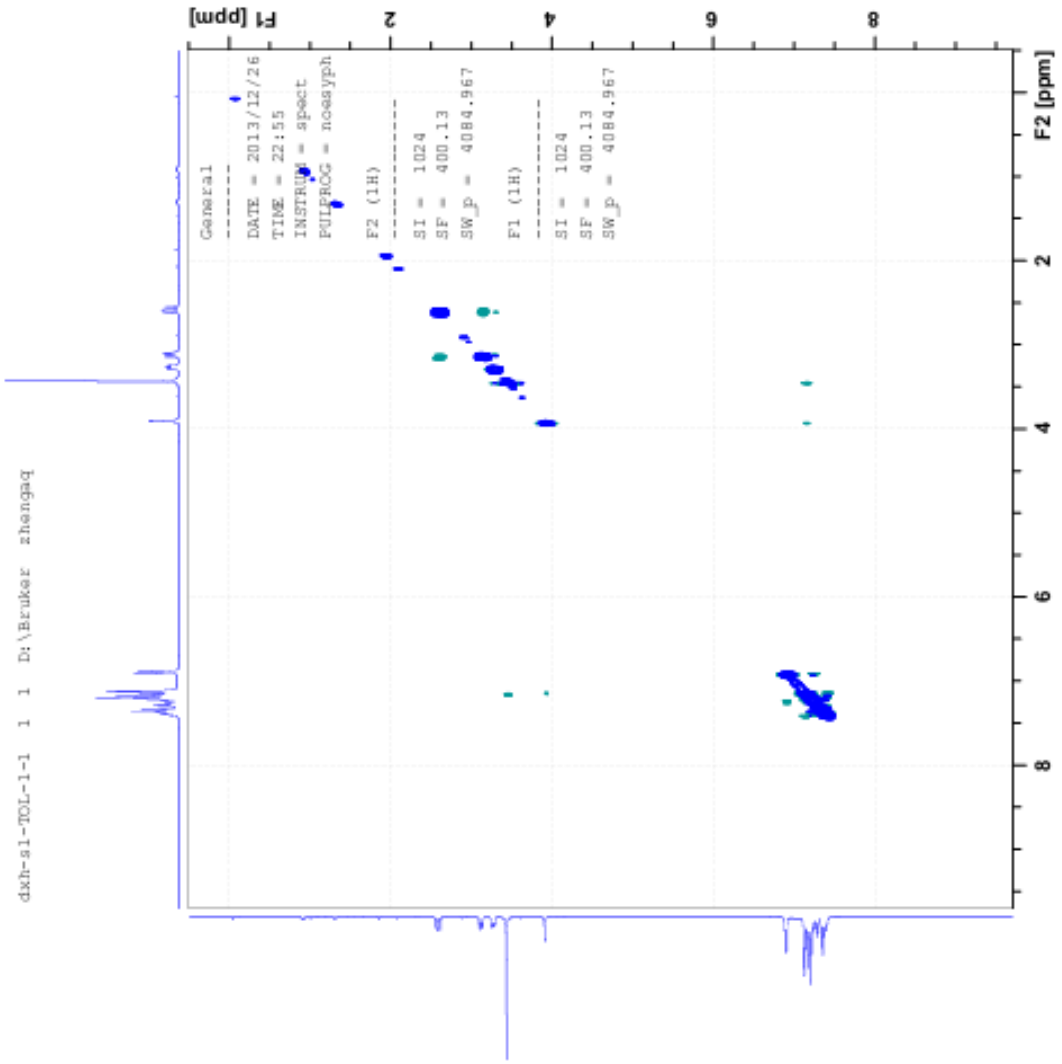
O

3a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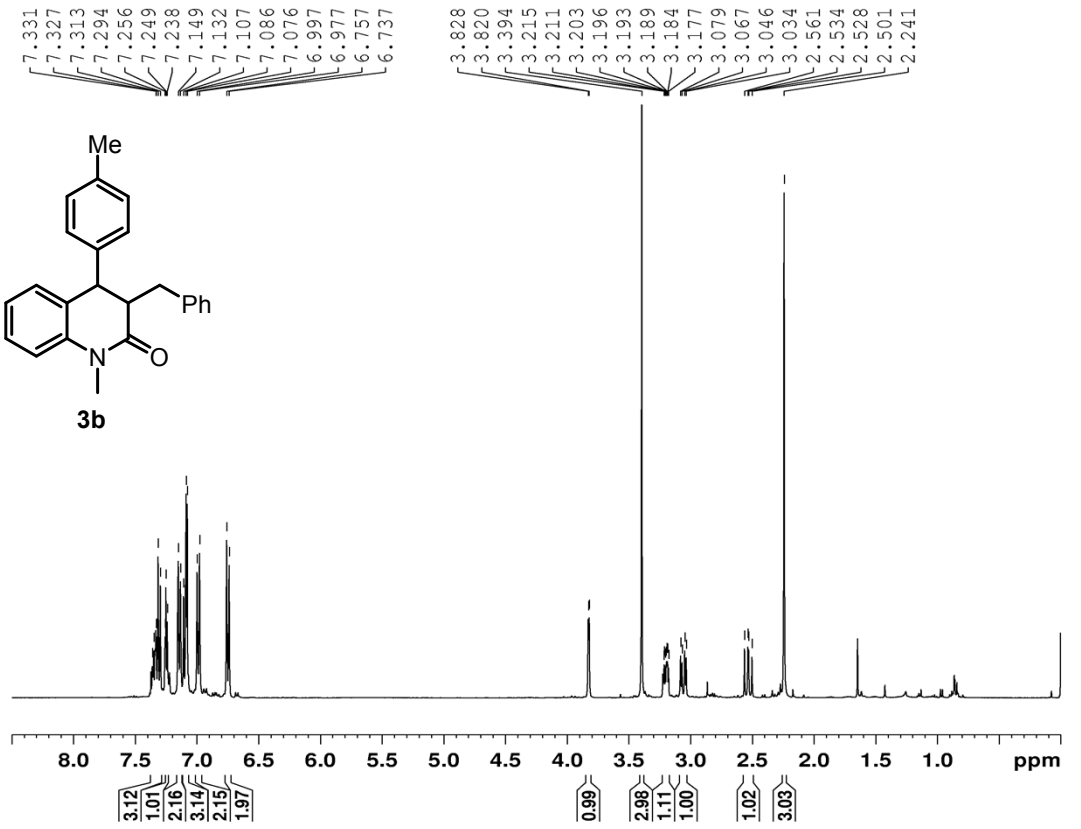
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3.189
3.184
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Ph
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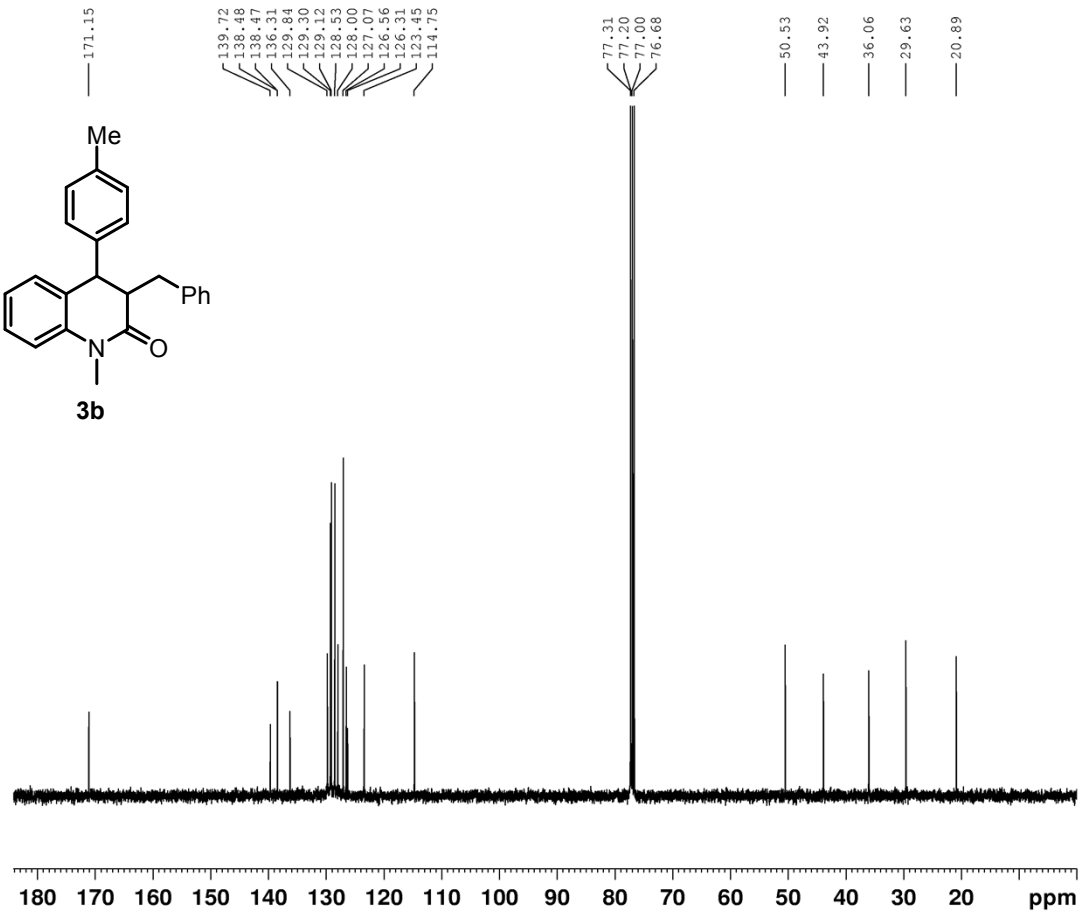
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Ph
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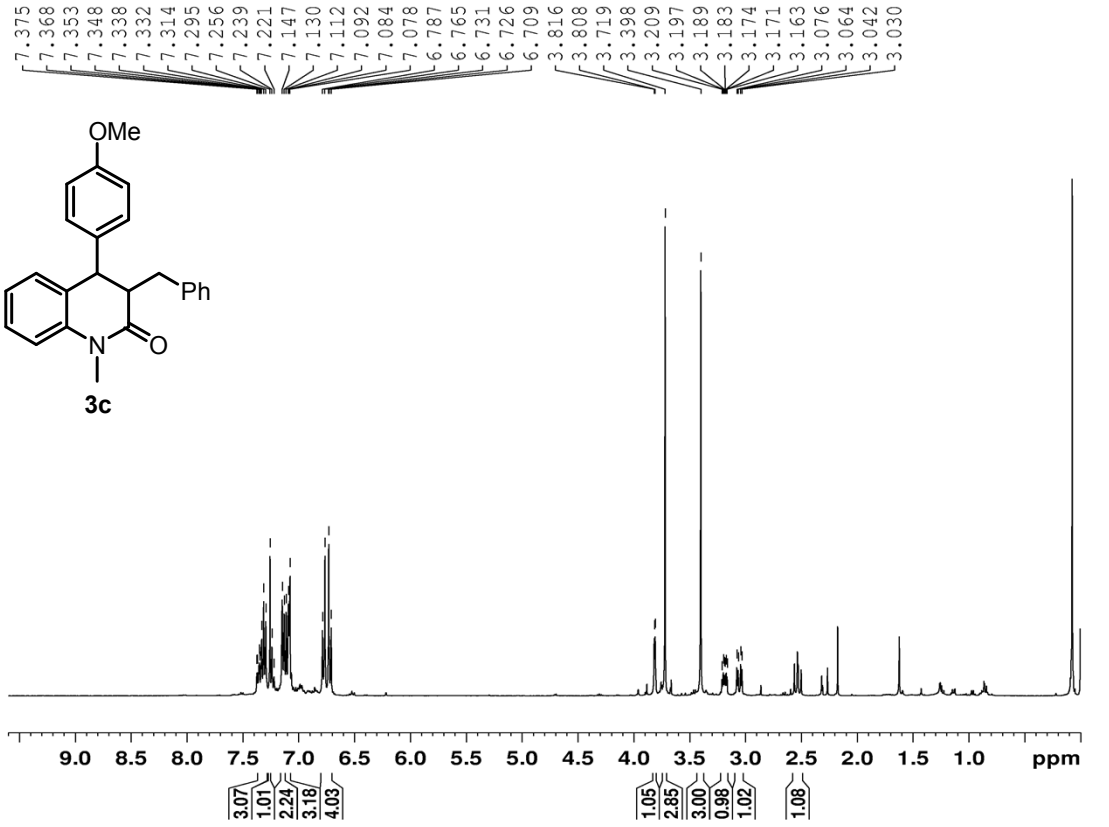
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3.197
3.189
3.183
3.174
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3.163
3.076
3.064
3.042
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OMe
Ph
N
O
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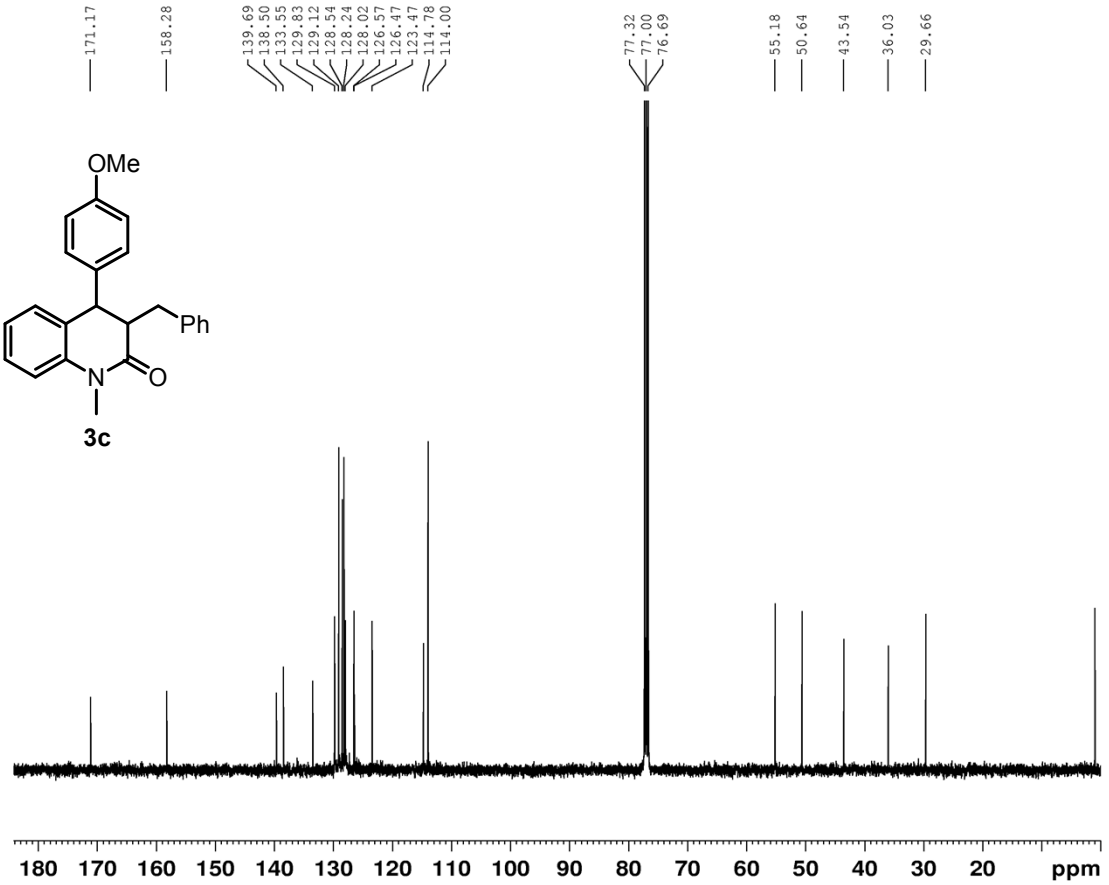
1.08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55.18
50.64
43.54
36.03
29.66
OMe
Ph
N
O
3c
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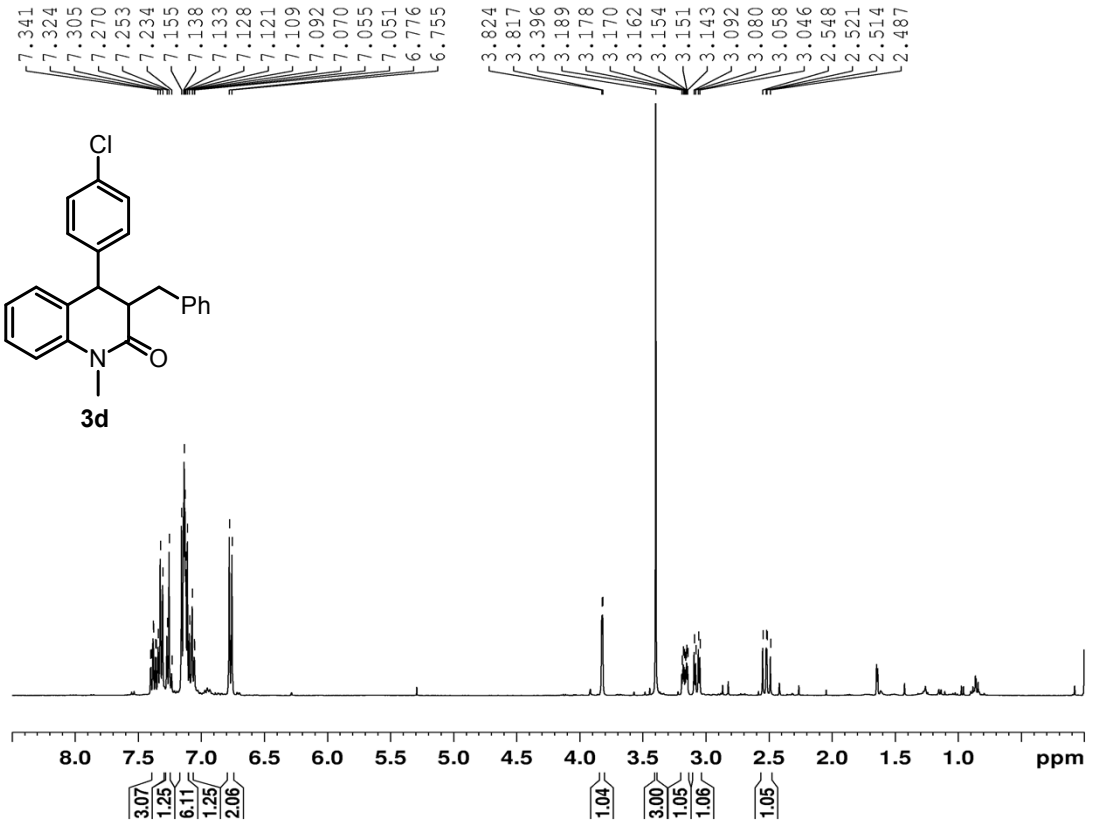
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7.070
7.055
7.051
6.776
6.755
3.824
3.817
3.396
3.189
3.178
3.170
3.162
3.154
3.151
3.143
3.092
3.080
3.058
3.046
2.548
2.521
2.514
2.487
Cl
Ph
N
O
3d
8.0
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7.0
6.5
6.0
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5.0
4.5
4.0
3.5
3.0
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2.0
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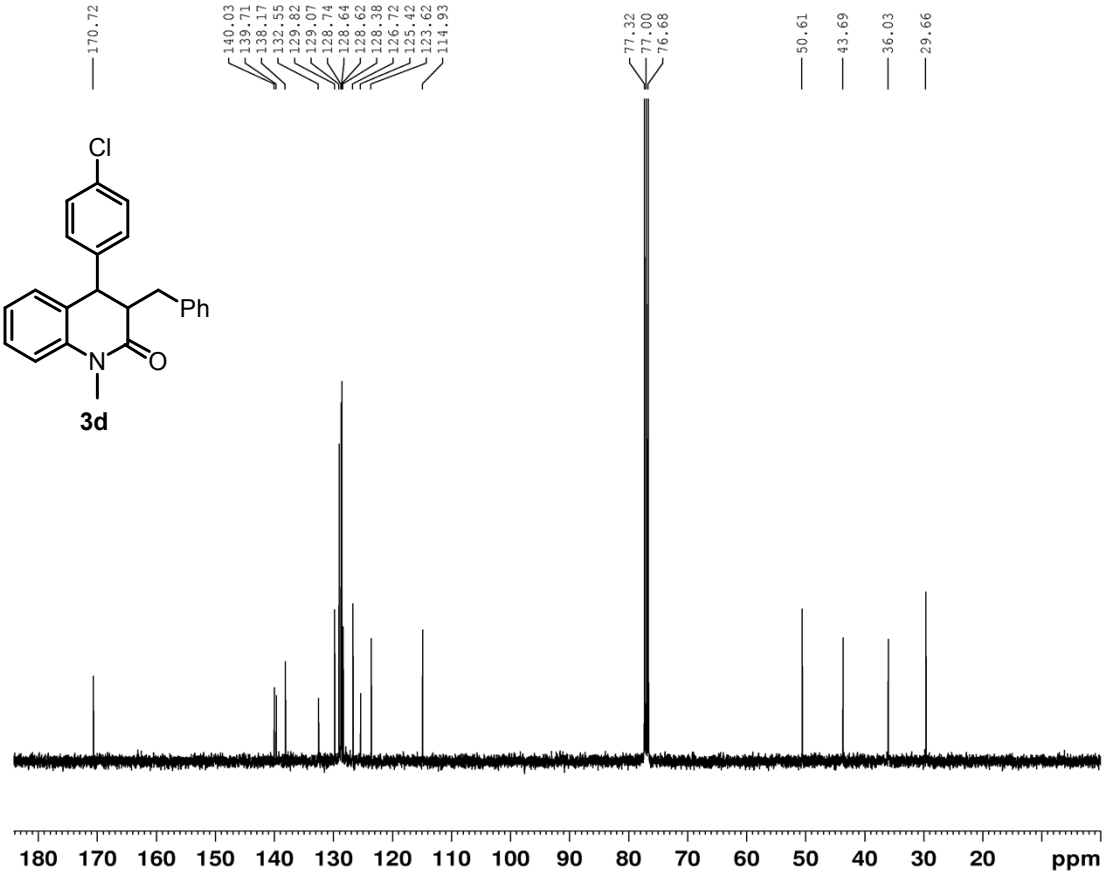
1.06
1.05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123.62
114.93
77.32
77.00
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50.61
43.69
36.03
29.66
Cl
Ph
N
O
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160
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120
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40
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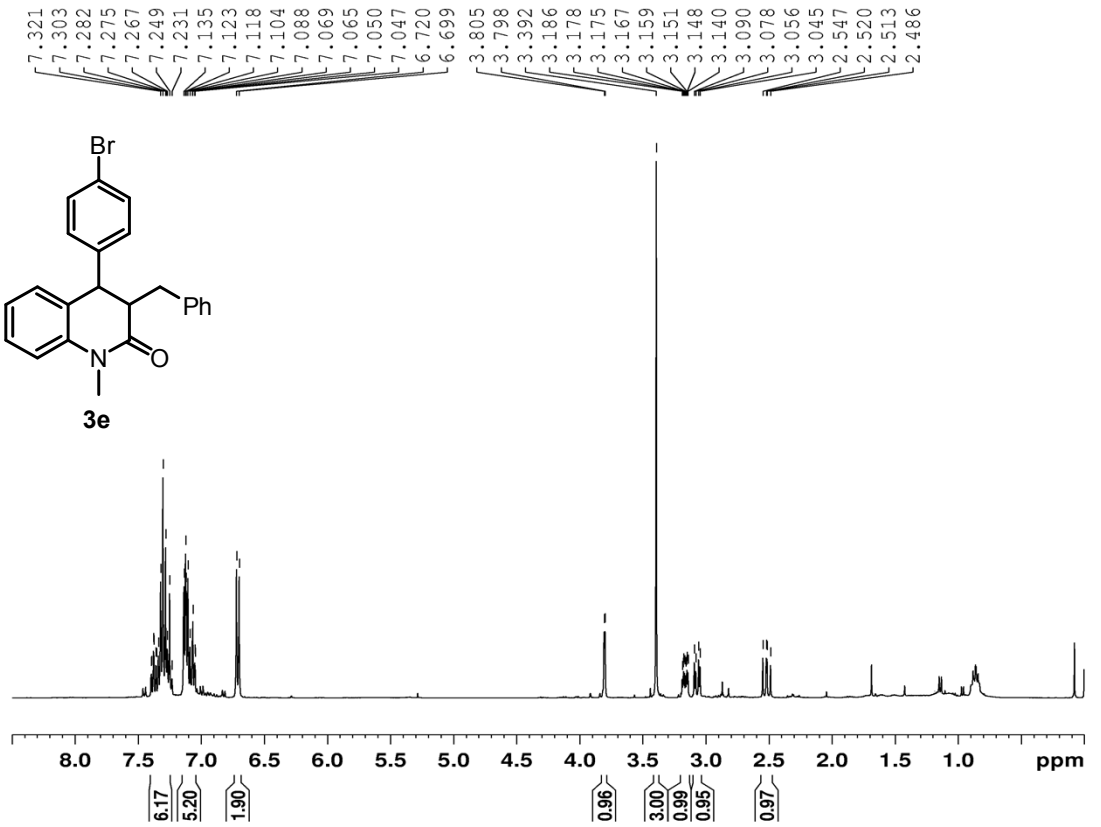
20
ppm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7.047
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3.175
3.167
3.159
3.151
3.148
3.140
3.090
3.078
3.056
3.045
2.547
2.520
2.513
2.486
Br
Ph
N
O
3e
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7.5
7.0
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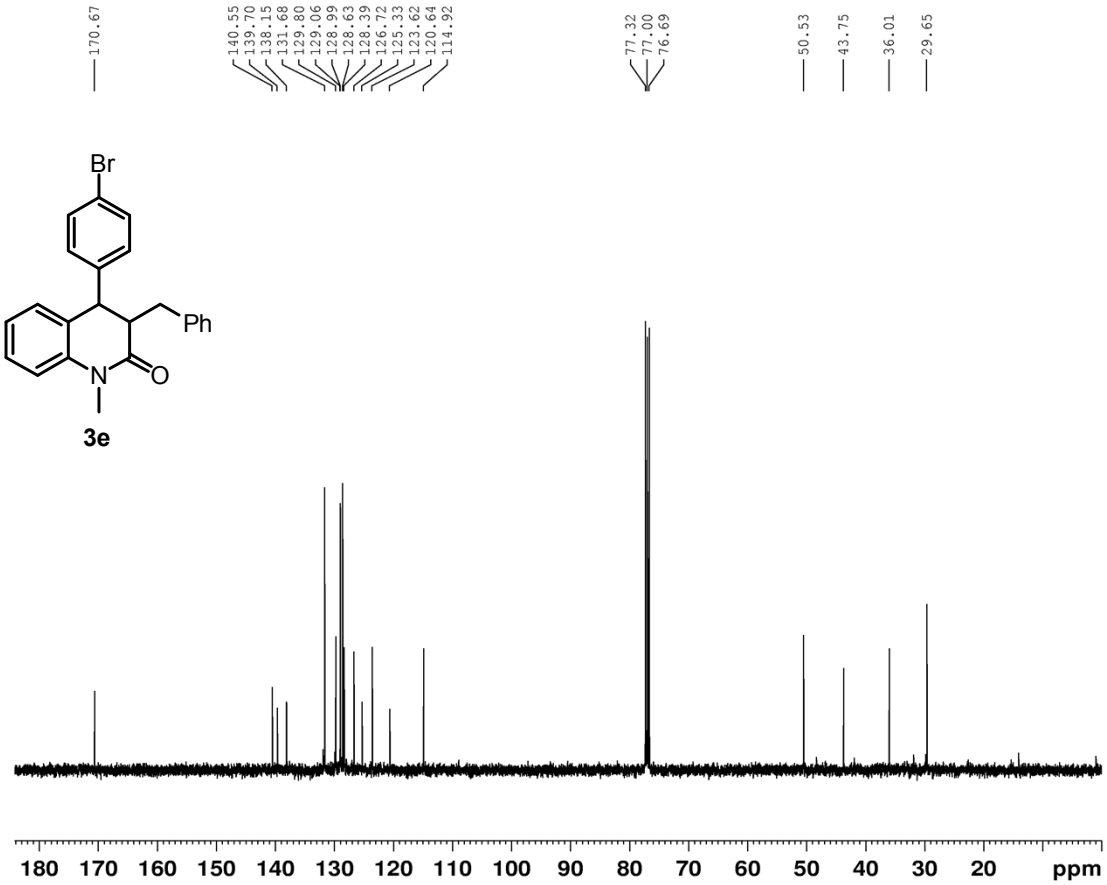
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120.64
114.92
77.32
77.00
76.69
50.53
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29.65
Br
Ph
N
O
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80
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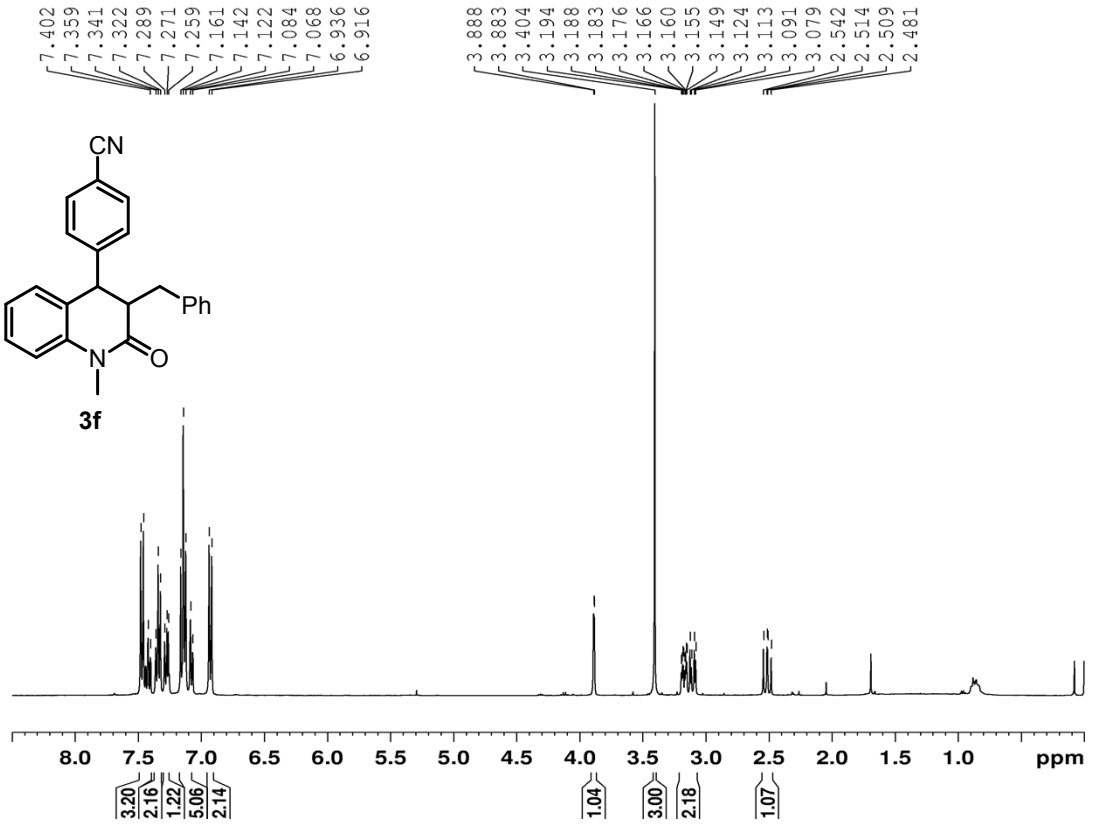
ppm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3.188
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3.160
3.155
3.149
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3.113
3.091
3.079
2.542
2.514
2.509
2.481
CN
Ph
N
O
3f
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6.0
5.5
5.0
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4.0
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3.0
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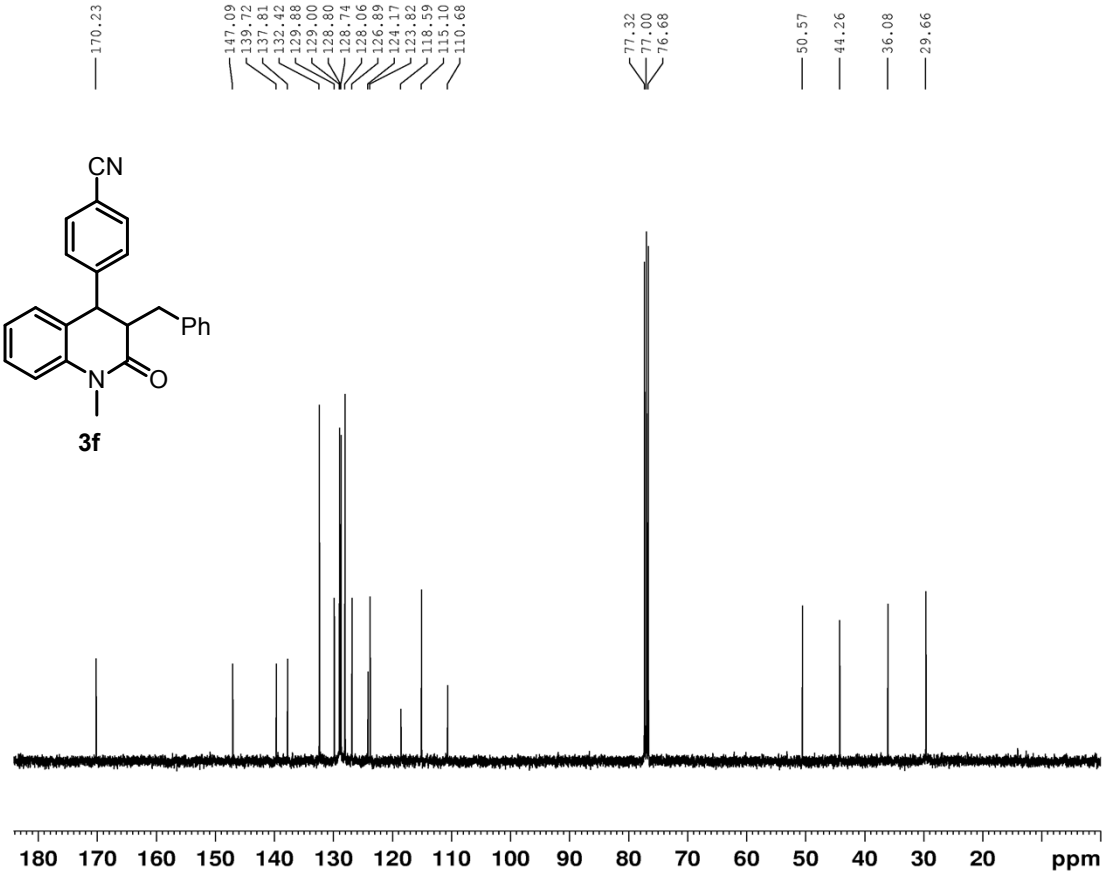
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124.17
123.82
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115.10
110.68
77.32
77.00
76.68
50.57
44.26
36.08
29.66
CN
Ph
N
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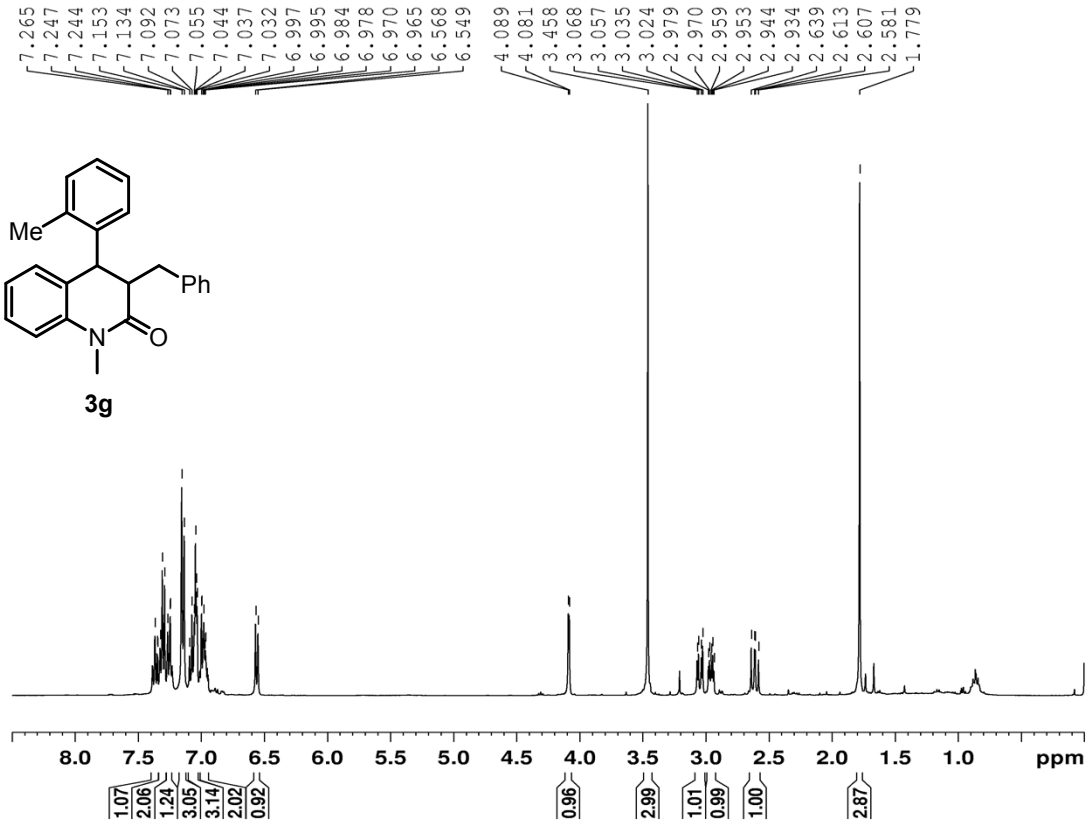
ppm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6.984
6.978
6.970
6.965
6.568
6.549
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4.081
3.458
3.068
3.057
3.035
3.024
2.979
2.970
2.959
2.953
2.944
2.934
2.639
2.613
2.607
2.581
1.779
Me
Ph
N
O
3g
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7.5
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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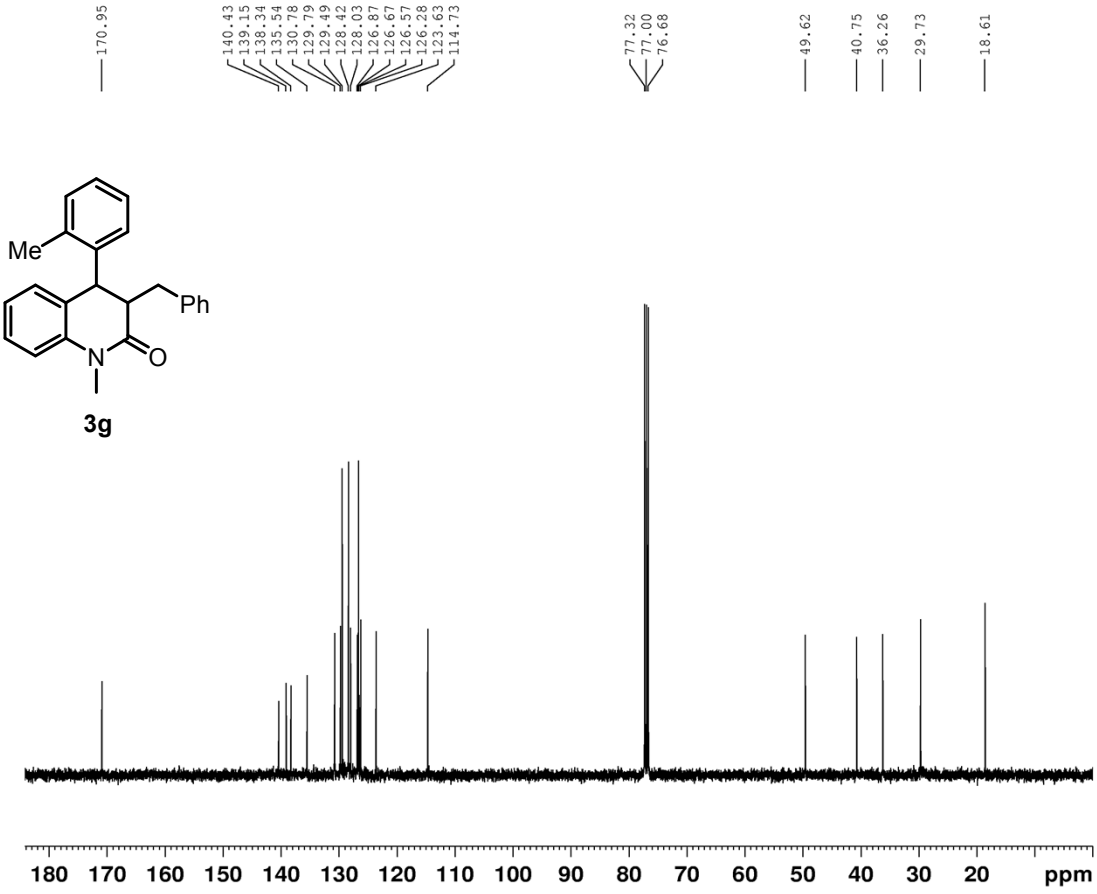
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123.63
114.73
77.32
77.00
76.68
49.62
40.75
36.26
29.73
18.61
Me
Ph
N
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80
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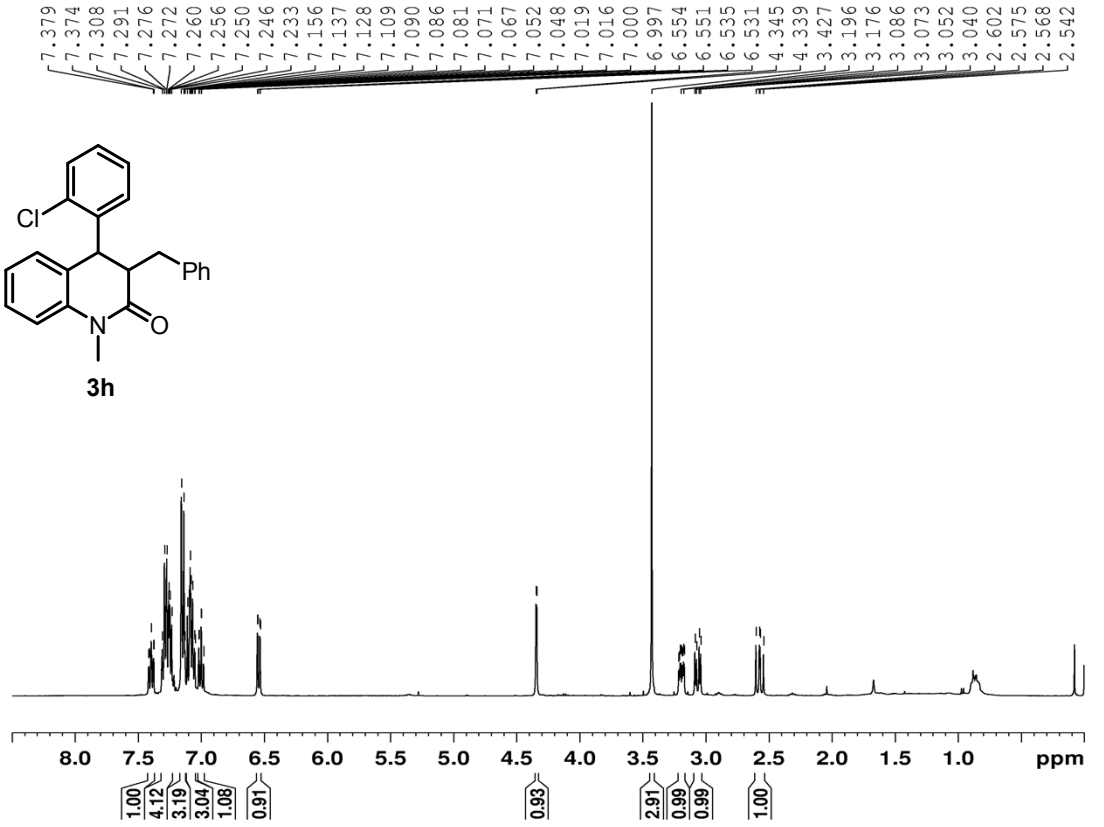
ppm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7.090
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7.081
7.071
7.067
7.052
7.048
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7.016
7.000
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6.531
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3.073
3.052
3.040
2.602
2.575
2.568
2.542
Cl
Ph
N
O
3h
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5.5
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4.5
4.0
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3.0
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2.0
1.5
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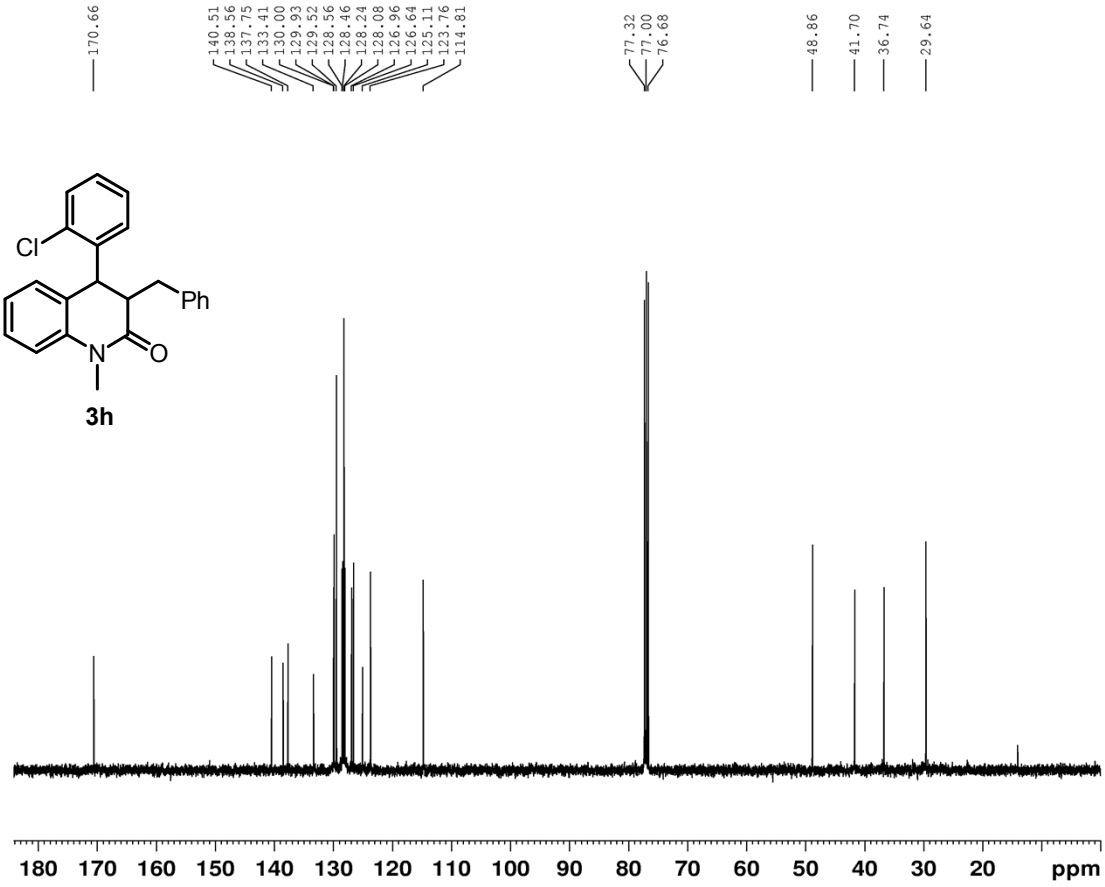
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126.64
125.11
123.76
114.81
77.32
77.00
76.68
48.86
41.70
36.74
29.64
Cl
Ph
N
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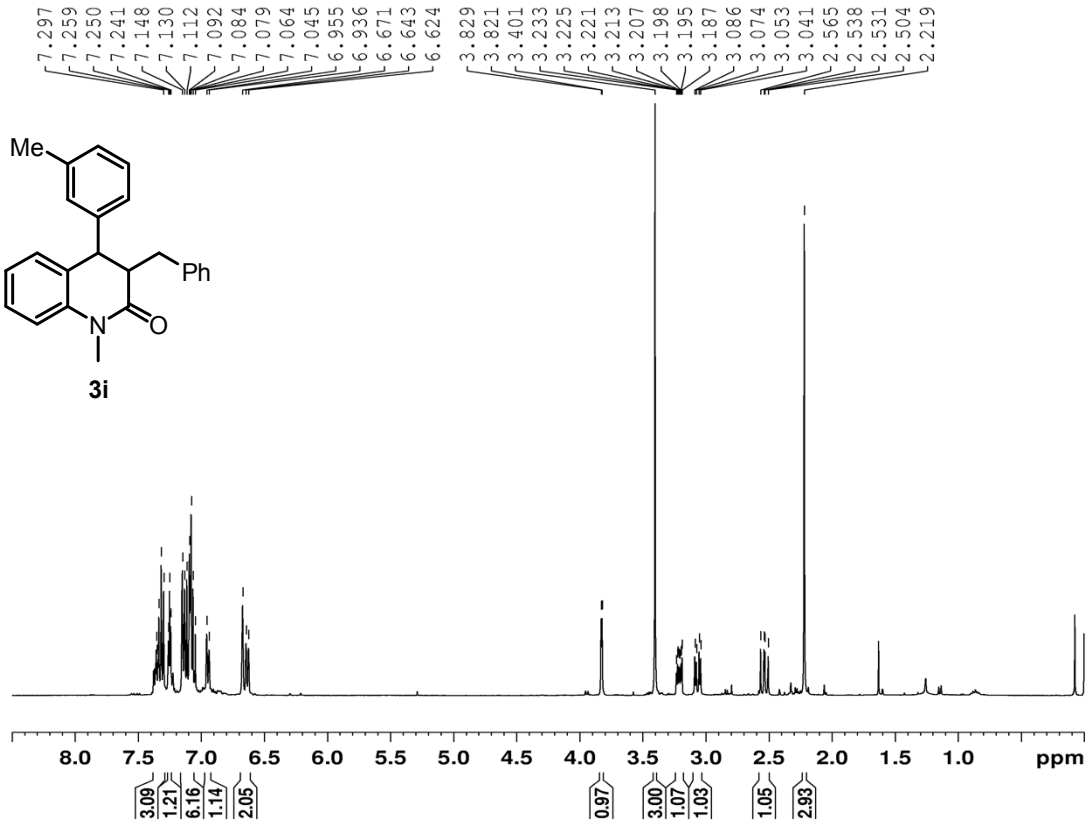
ppm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3.187
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2.219
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Ph
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O
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6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
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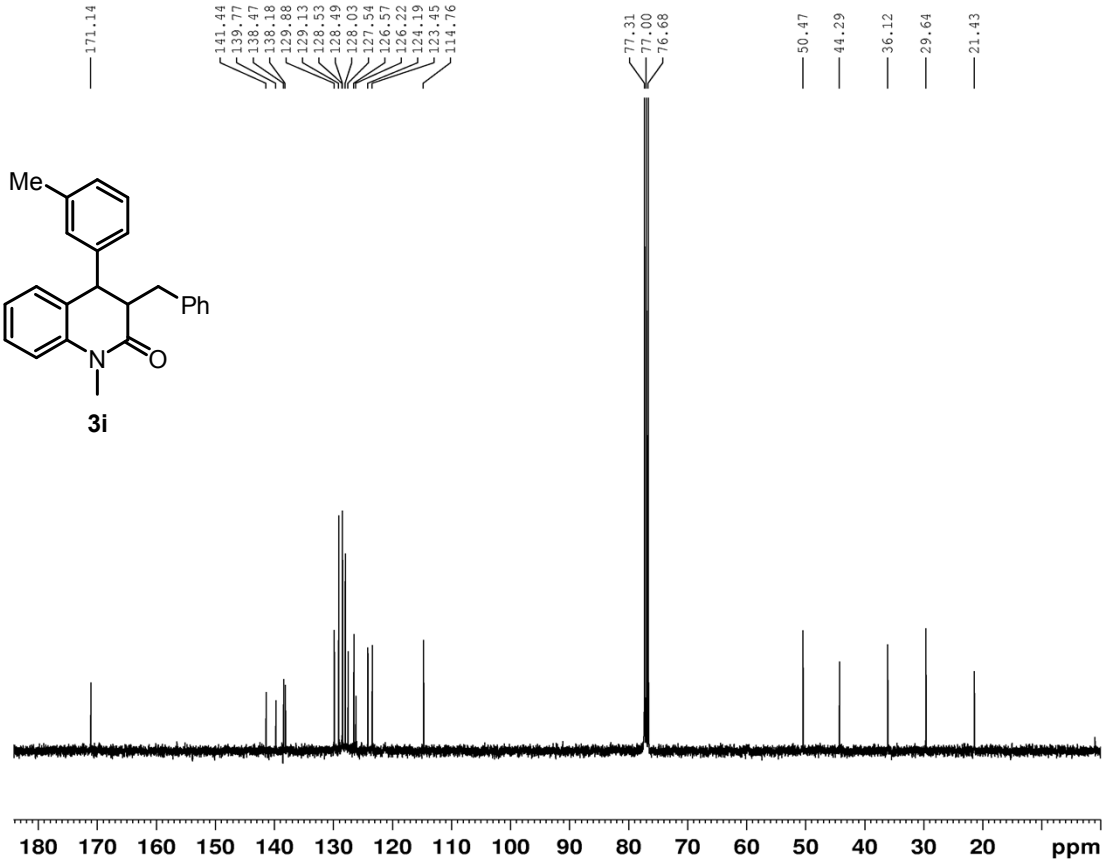
1.05
2.93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126.57
126.22
124.19
123.45
114.76
77.31
77.00
76.68
50.47
44.29
36.12
29.64
21.43
Me
Ph
N
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150
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80
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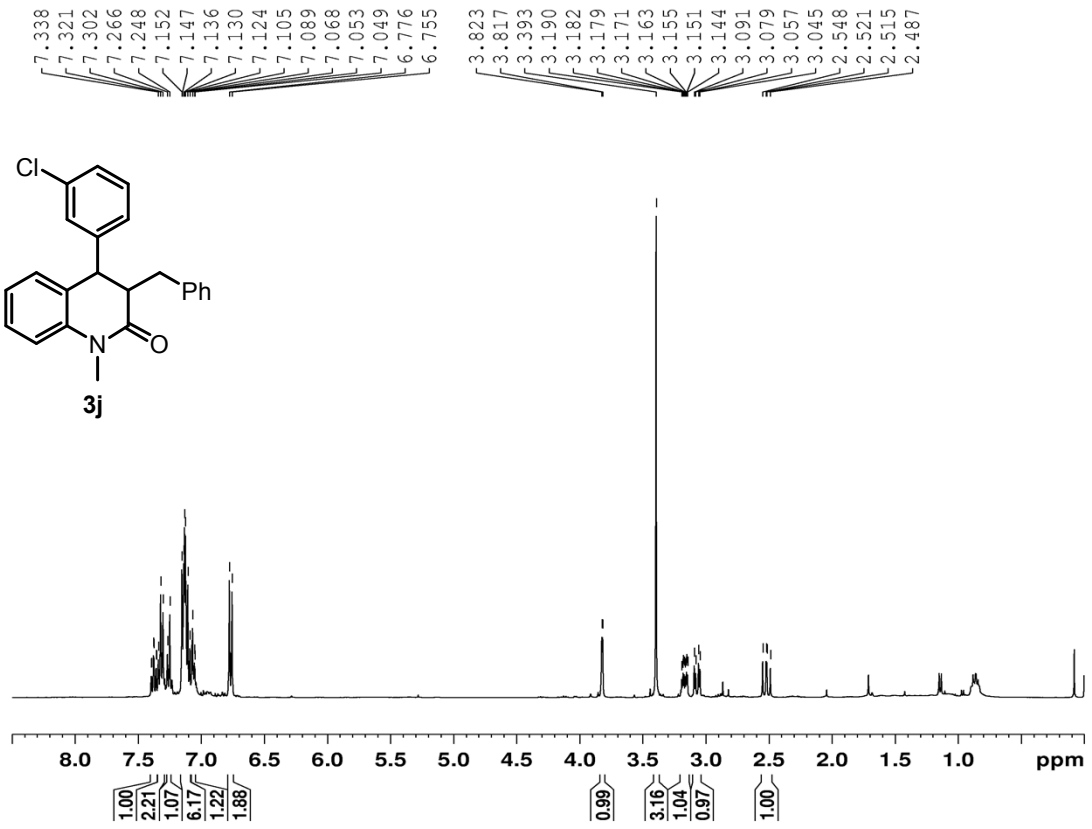
20
ppm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7.049
6.776
6.755
3.823
3.817
3.393
3.190
3.182
3.179
3.171
3.163
3.155
3.151
3.144
3.091
3.079
3.057
3.045
2.548
2.521
2.515
2.487
Cl
Ph
N
O
3j
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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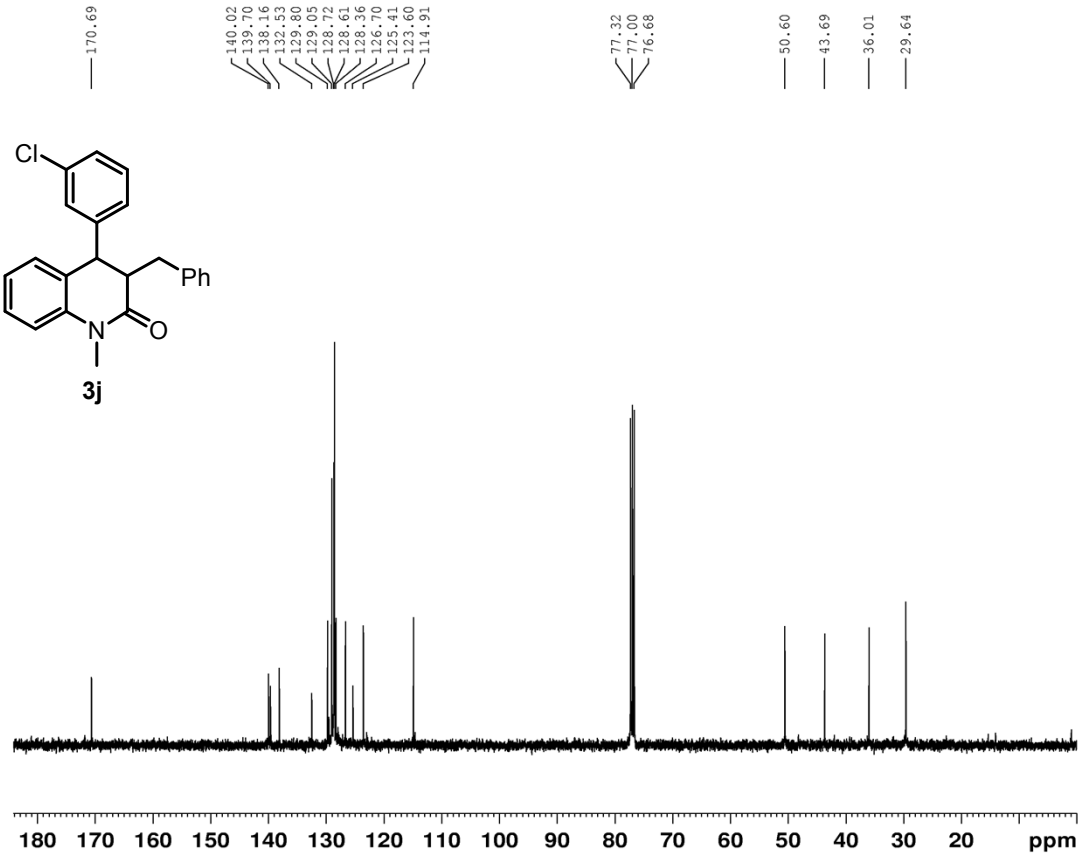
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77.32
77.00
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36.01
29.64
Cl
Ph
N
O
3j
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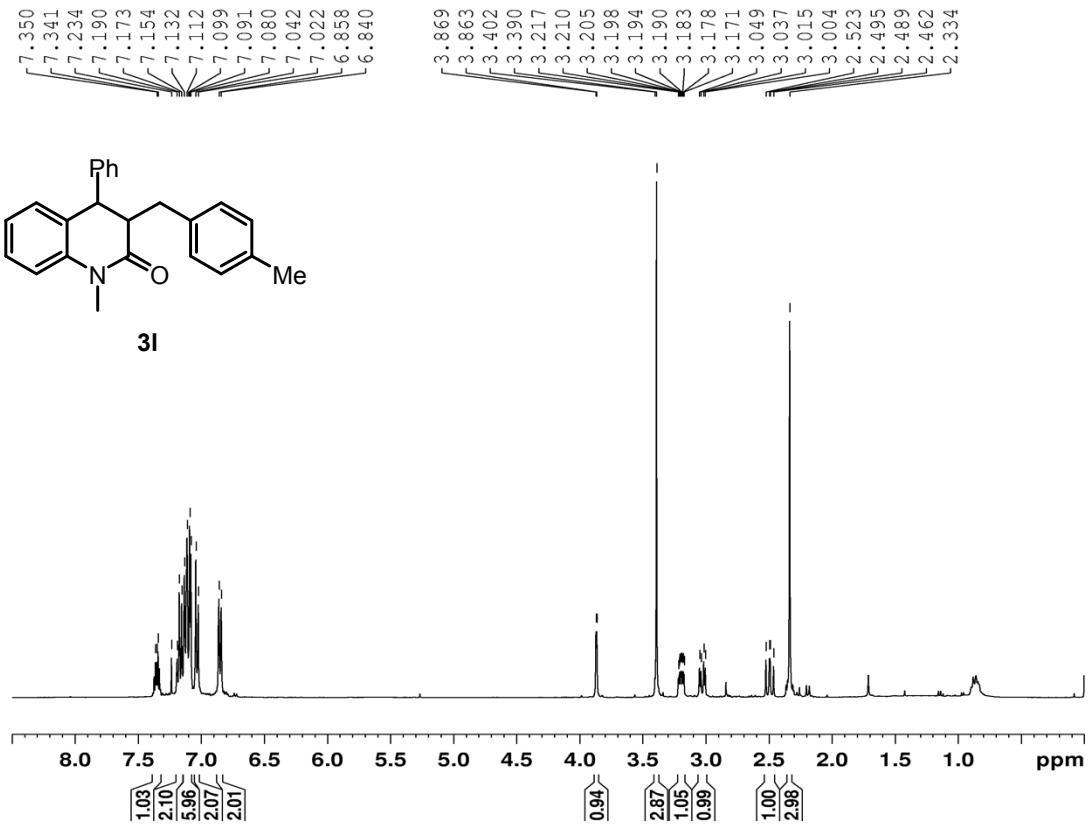
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O
Me
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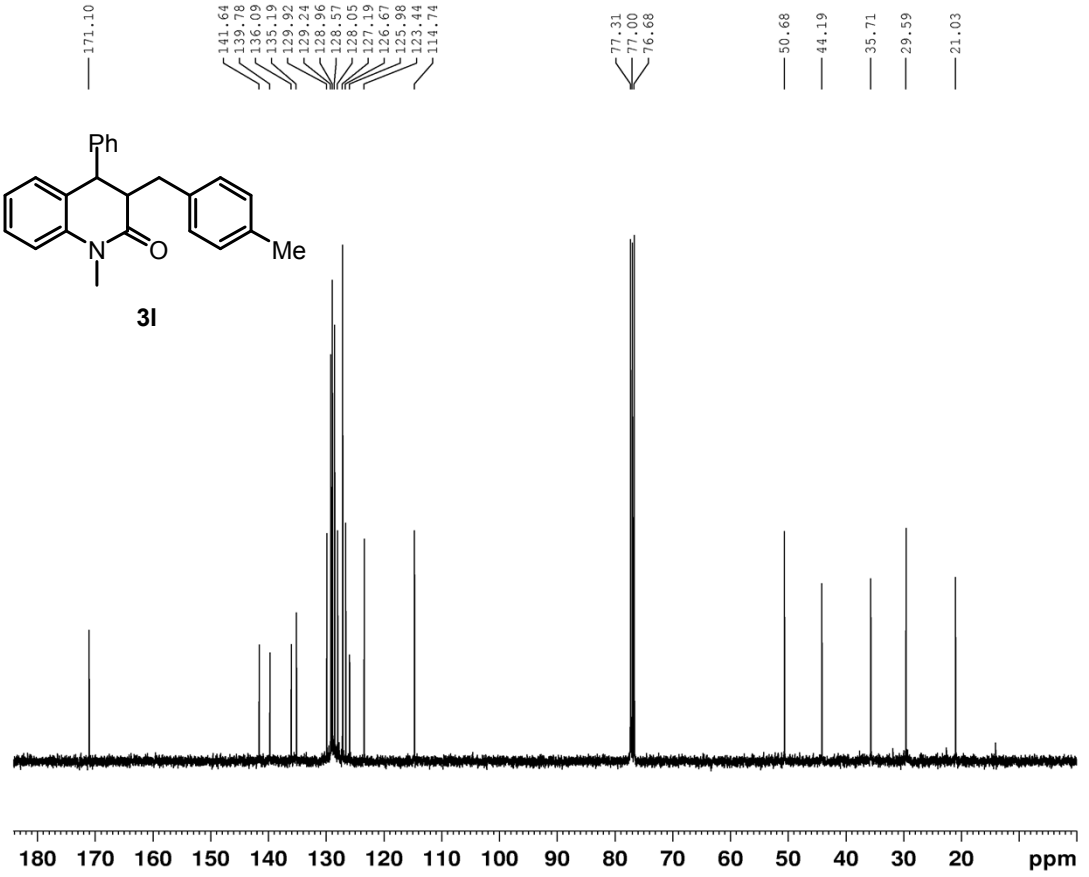
3l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125.98
123.44
114.74
77.31
77.00
76.68
50.68
44.19
35.71
29.59
21.03
Ph
N
O
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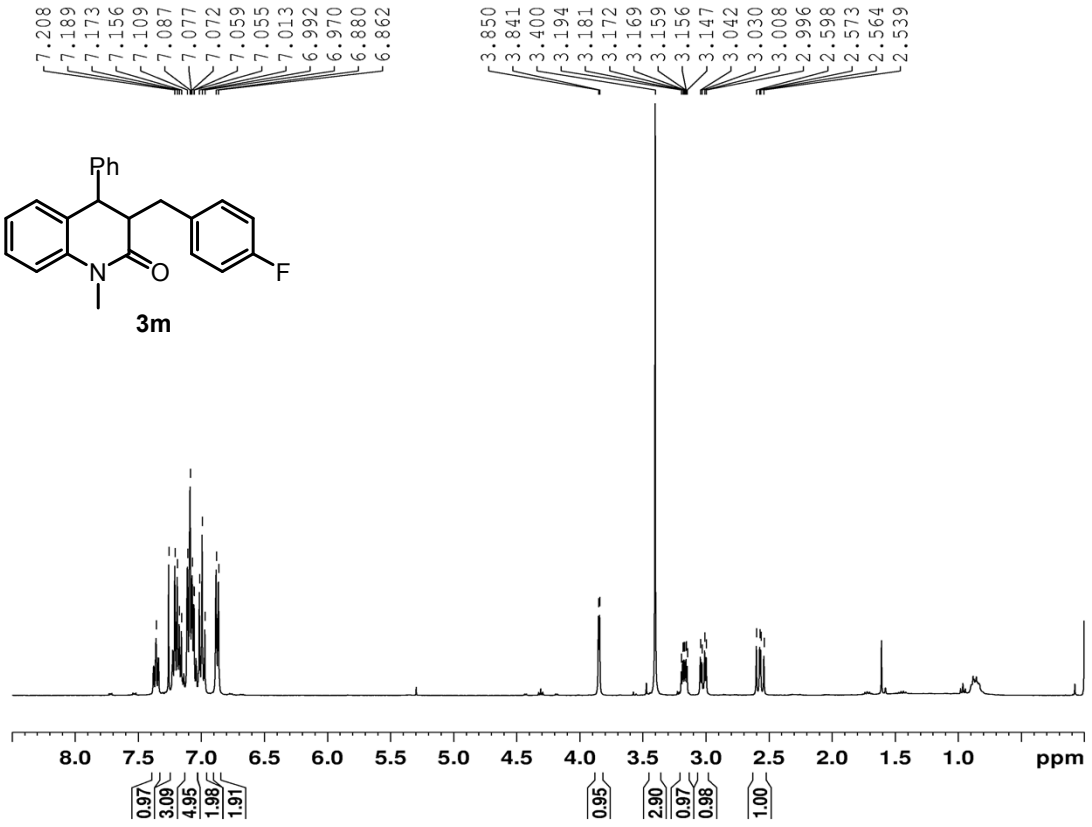
ppm

3l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2.539
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3m
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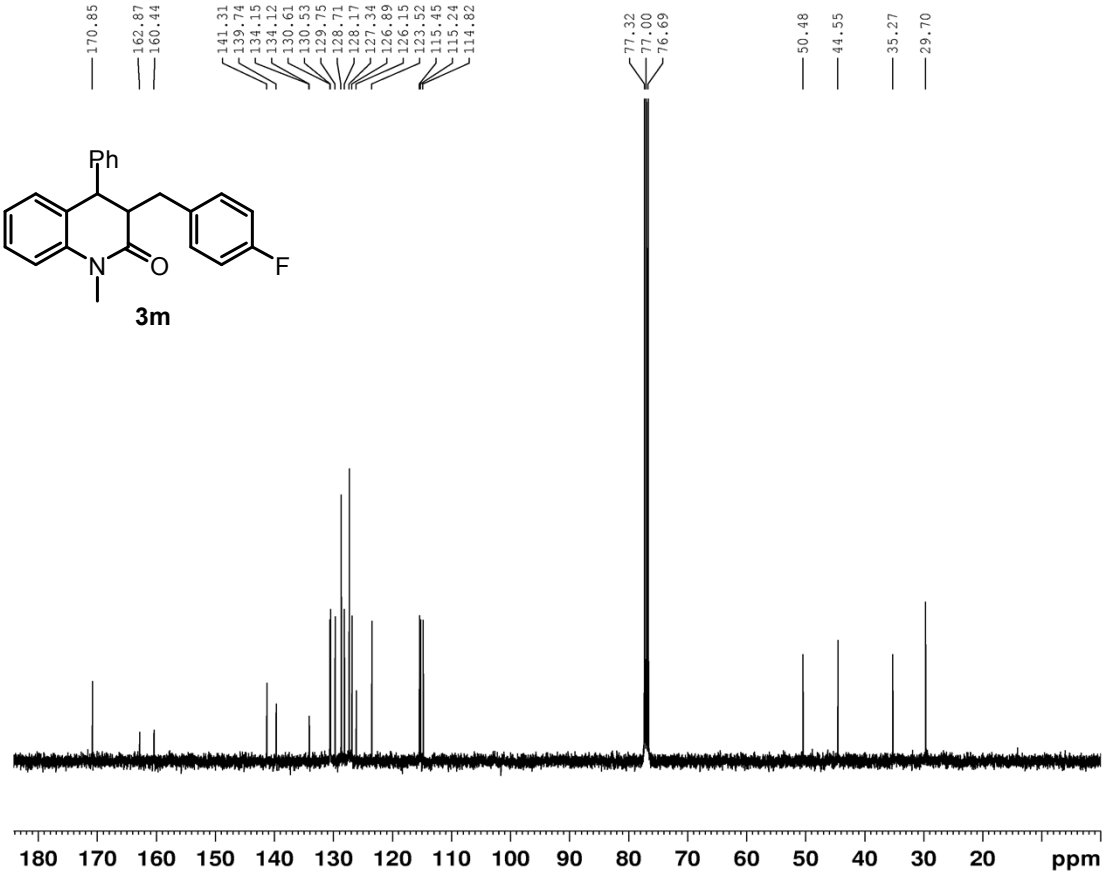
1.00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115.45
115.24
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77.00
76.69
50.48
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Ph
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O
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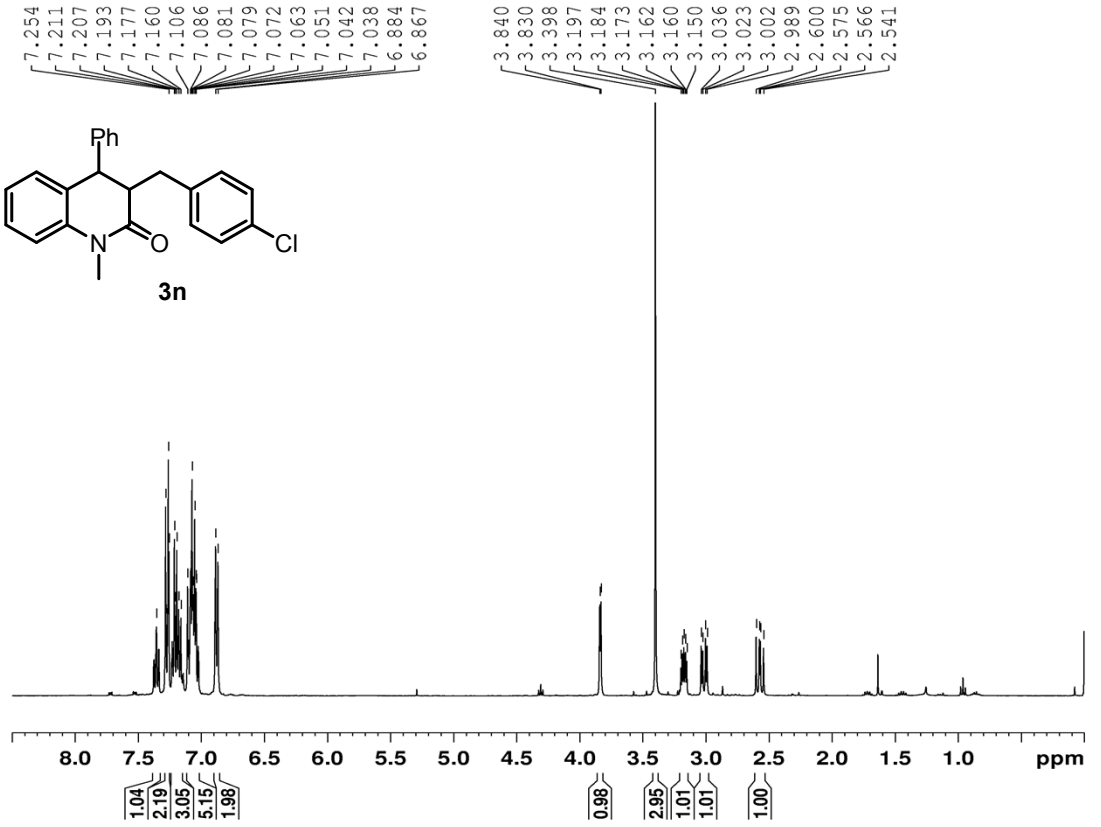
ppm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3.150
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Cl
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4.0
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3.0
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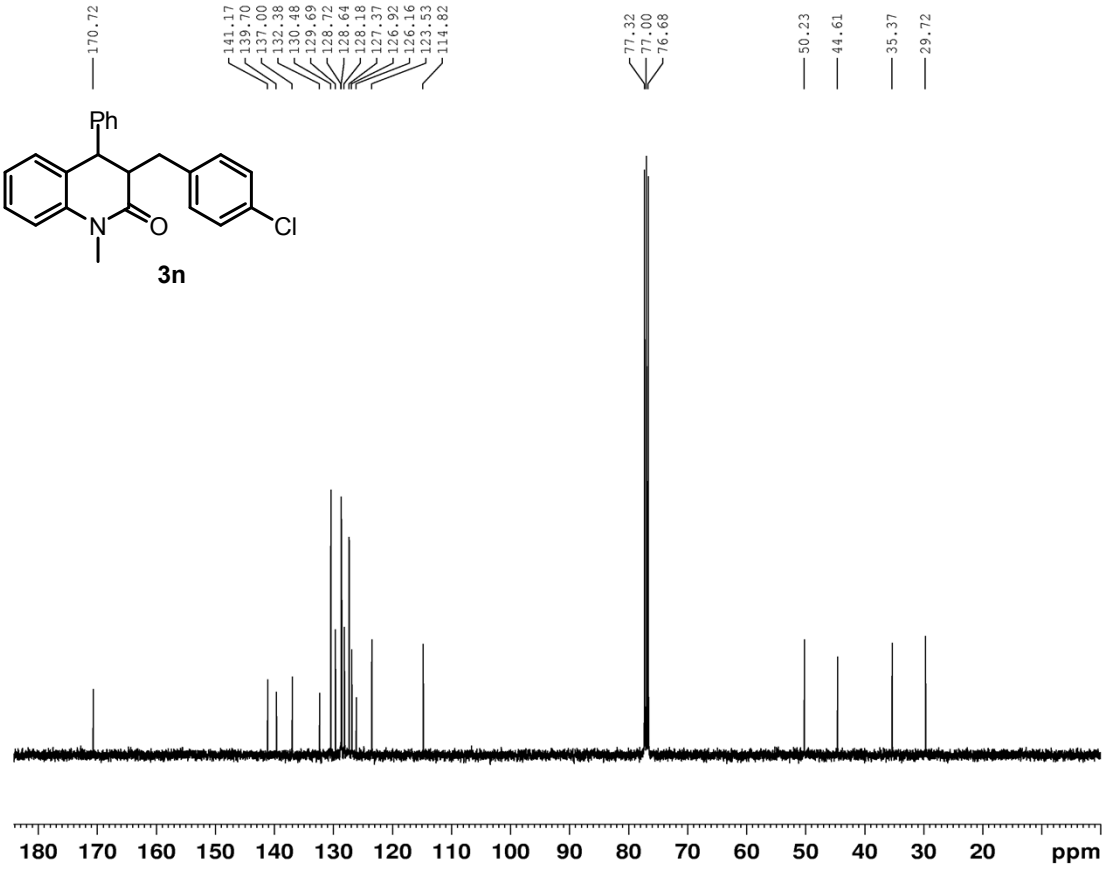
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123.53
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50.23
44.61
35.37
29.72
Ph
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O
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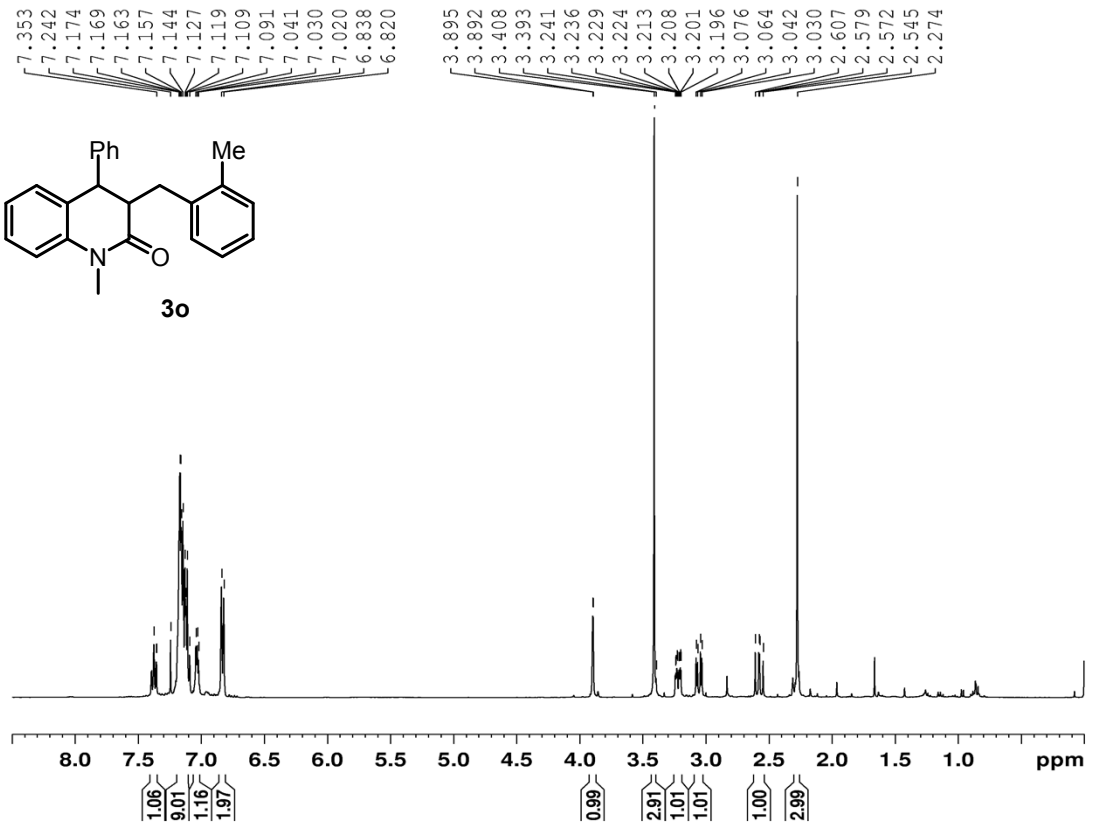
ppm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1.0
ppm
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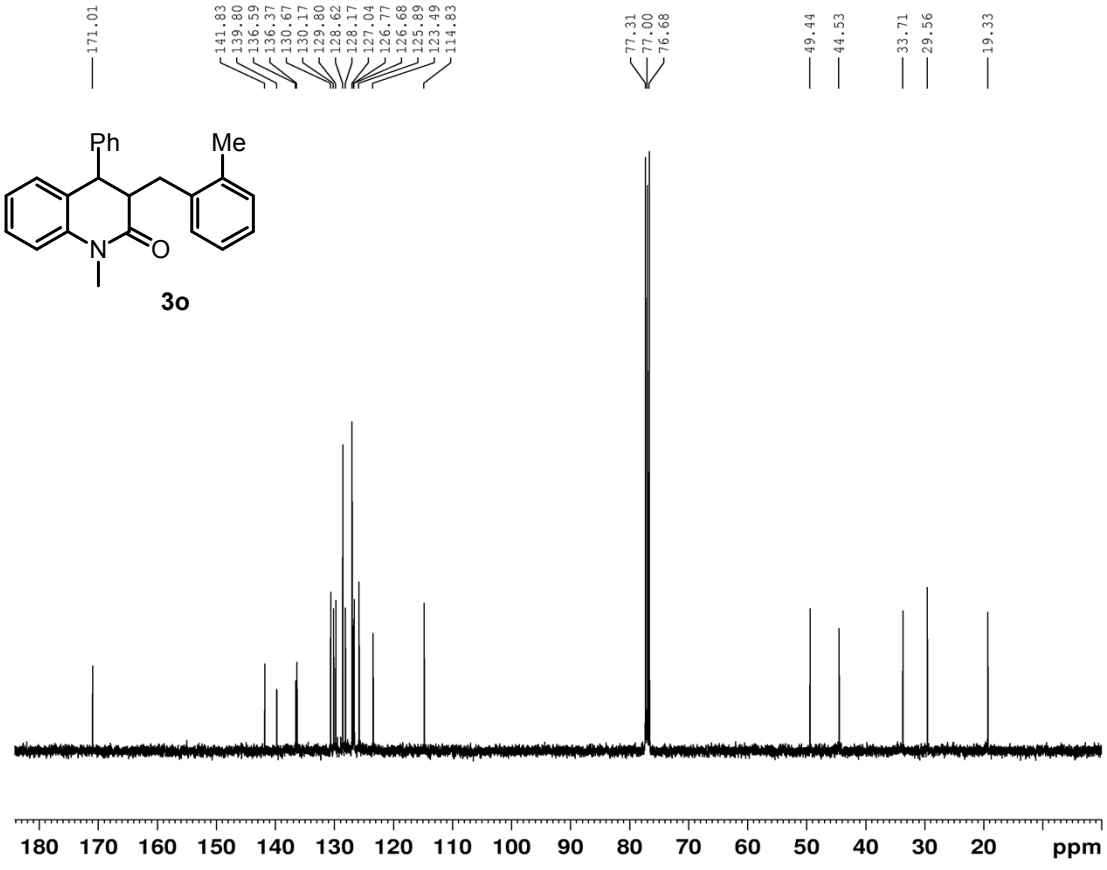
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123.49
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77.00
76.68
49.44
44.53
33.71
29.56
19.33
Ph
Me
N
O
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150
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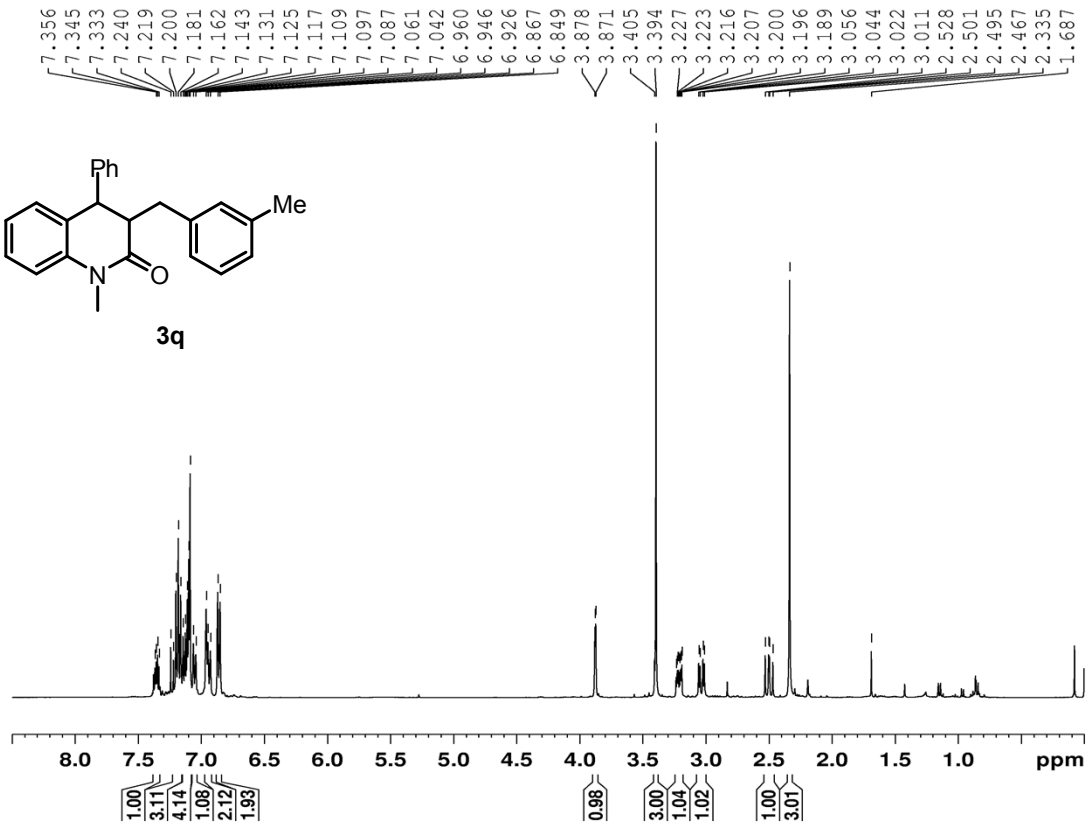
ppm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7.117
7.109
7.097
7.087
7.061
7.042
6.960
6.946
6.926
6.867
6.849
3.878
3.871
3.405
3.394
3.227
3.223
3.216
3.207
3.200
3.196
3.189
3.056
3.044
3.022
3.011
2.528
2.501
2.495
2.467
2.335
1.687
Ph
Me
N
O
3q
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7.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.0
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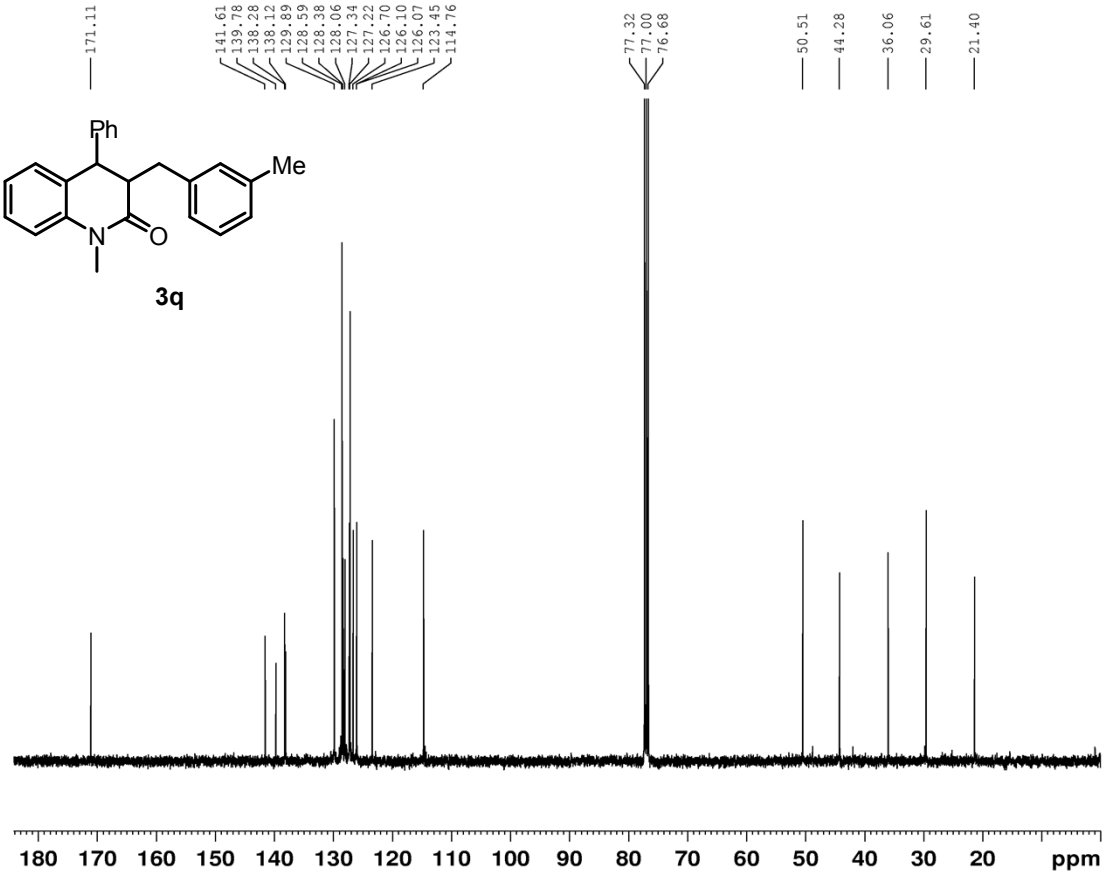
3.01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126.70
126.10
126.07
123.45
114.76
77.32
77.00
76.68
50.51
44.28
36.06
29.61
21.40
Ph
Me
N
O
3q
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150
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130
120
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80
70
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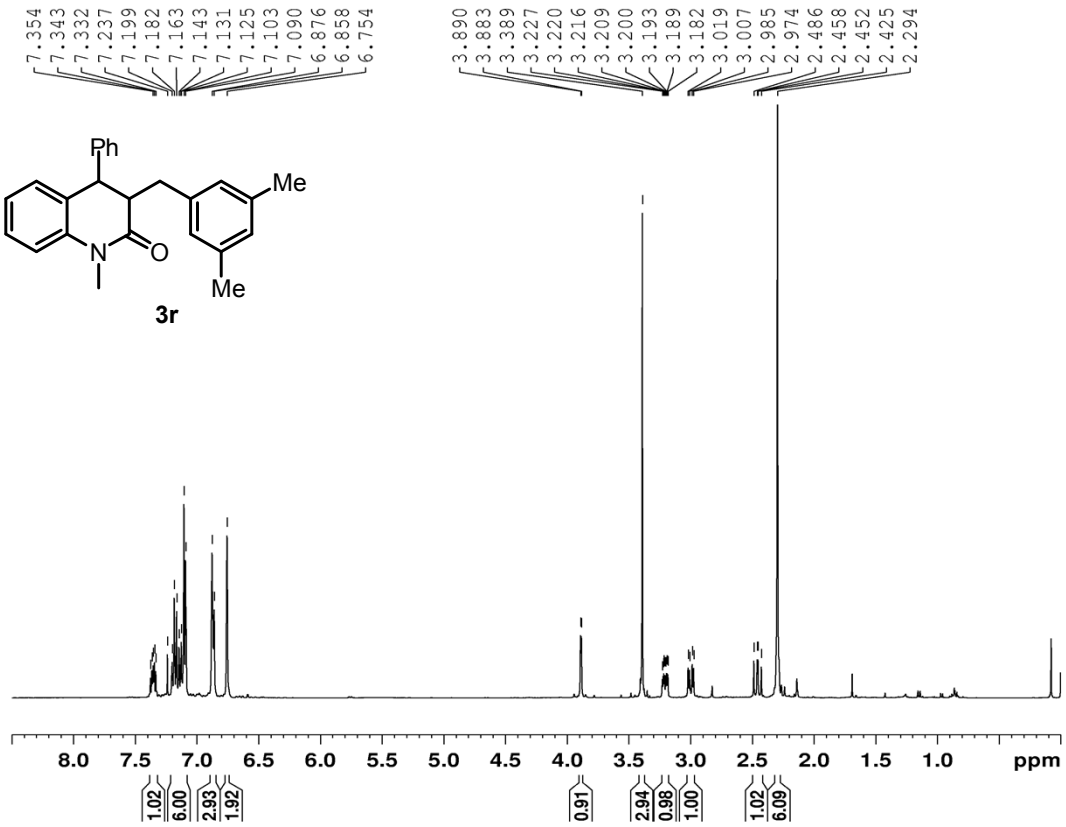
50
40
30
20
ppm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6.754
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3.227
3.220
3.216
3.209
3.200
3.193
3.189
3.182
3.019
3.007
2.985
2.974
2.486
2.458
2.452
2.425
2.294
Ph
Me
N
O
Me
3r
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6.0
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4.0
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3.0
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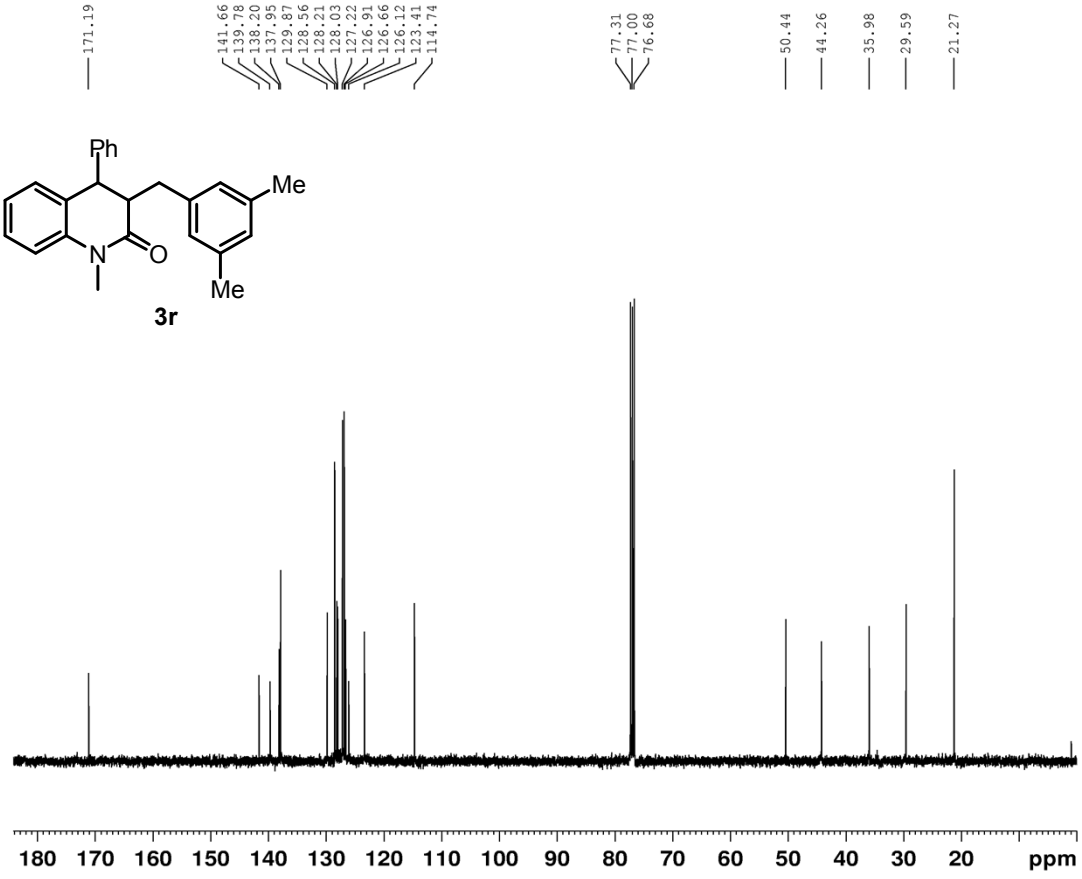
6.09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123.41
114.74
77.31
77.00
76.68
50.44
44.26
35.98
29.59
21.27
Ph
Me
N
O
Me
3r
180
170
160
150
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100
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80
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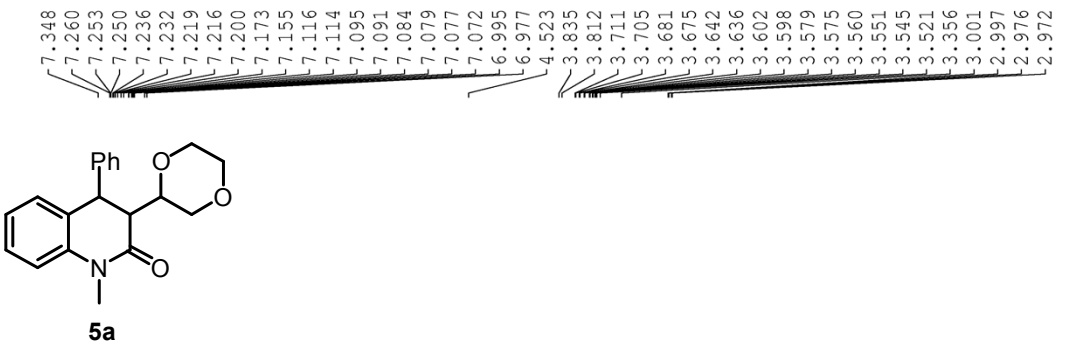
60
50
40
30
20
ppm

^{1}H NMR and ^{13}C NMR Spectra of the Products 5



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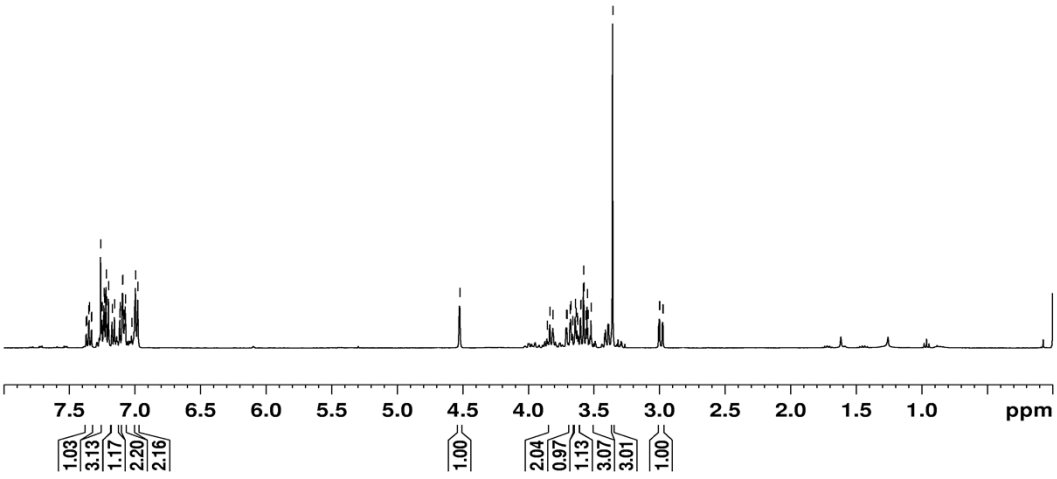

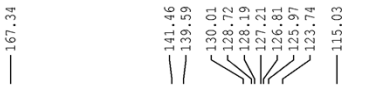

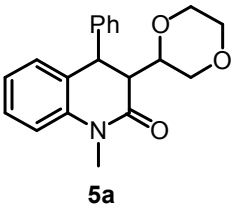

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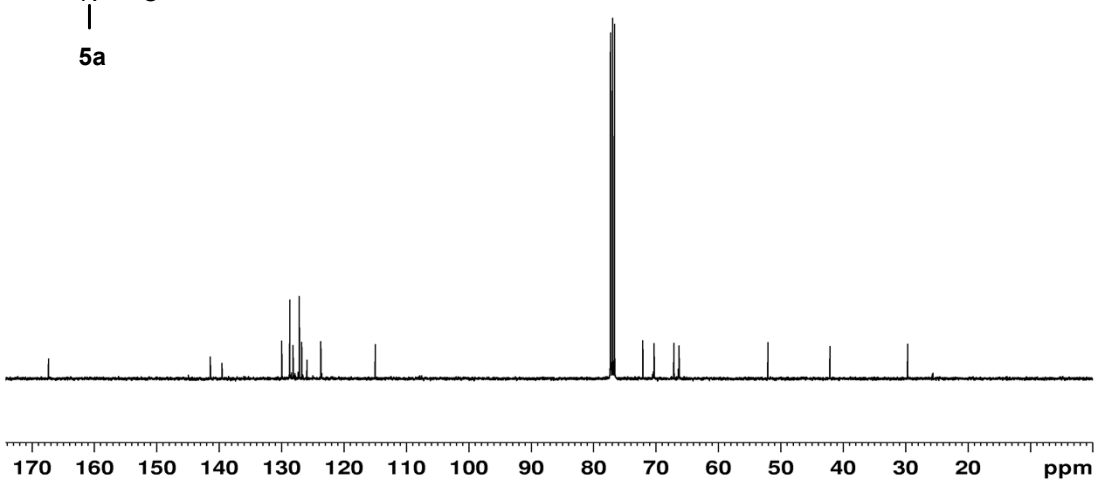

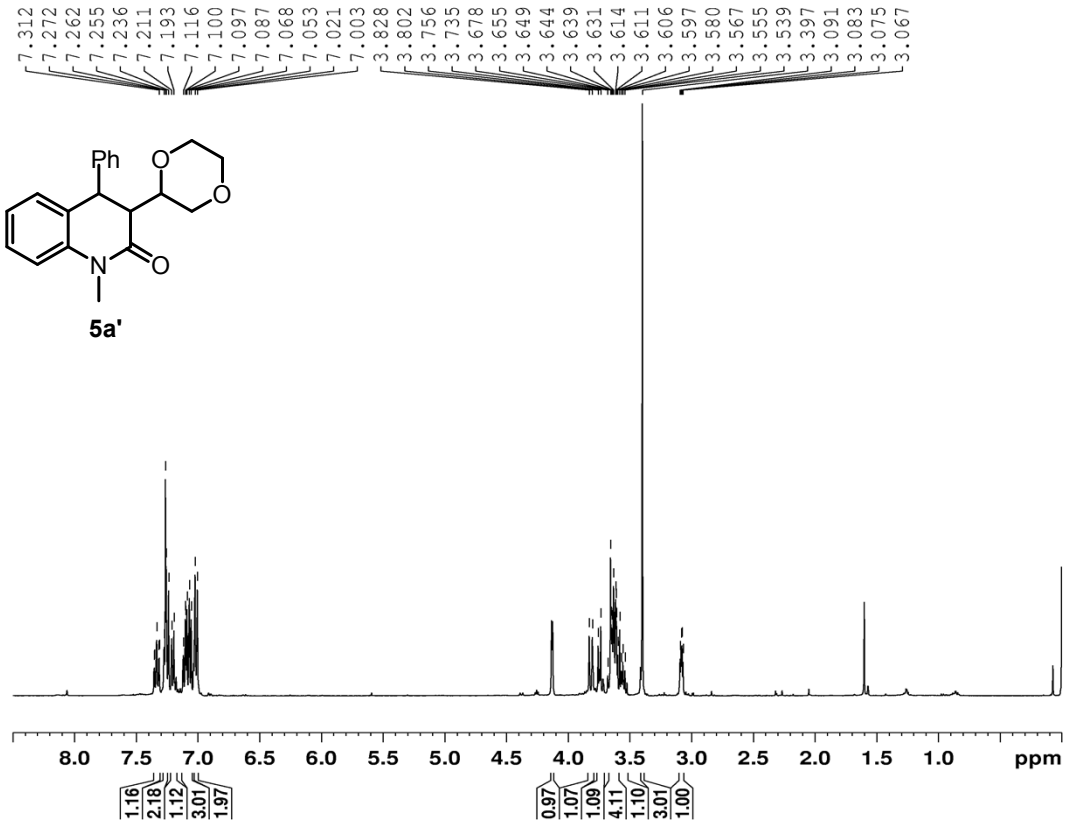
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7.087
7.068
7.053
7.021
7.003
3.828
3.802
3.756
3.735
3.678
3.655
3.649
3.644
3.639
3.631
3.614
3.611
3.606
3.597
3.580
3.567
3.555
3.539
3.397
3.091
3.083
3.075
3.067
Ph
O
O
N
O
5a'
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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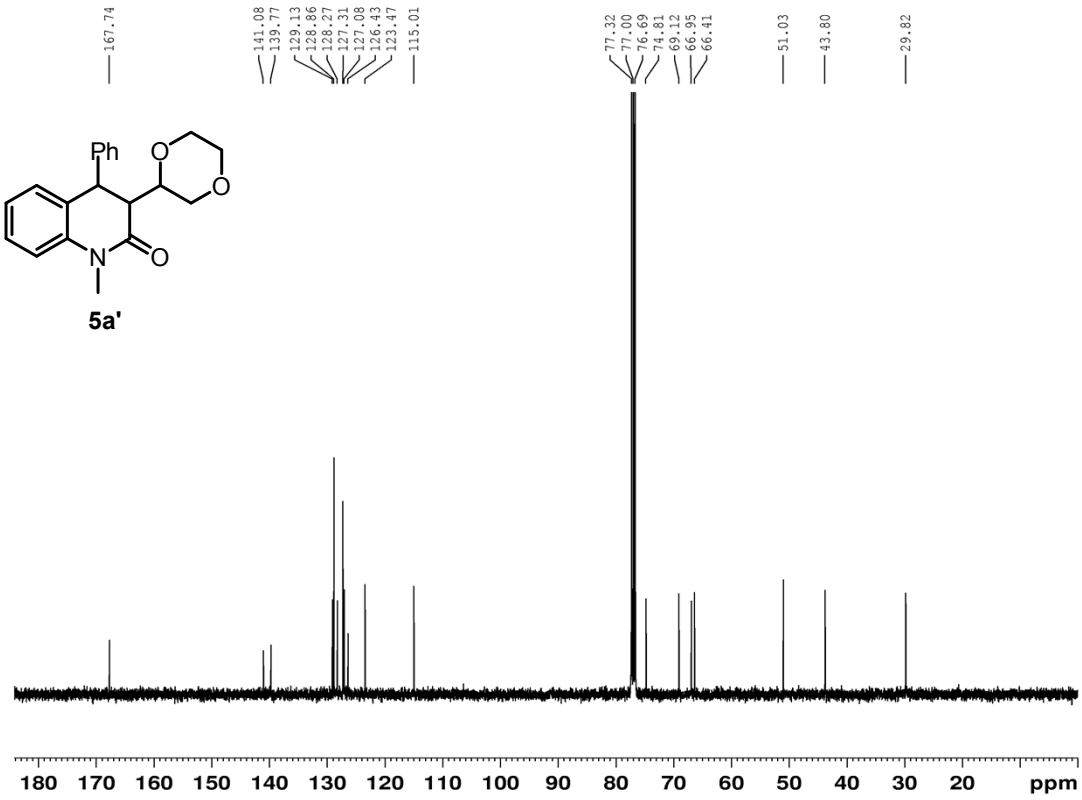
0.97
1.07
1.09
4.11
1.10
3.01
1.00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128.86
128.27
127.31
127.08
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123.47
115.01
77.32
77.00
76.69
74.81
69.12
66.95
66.41
51.03
43.80
29.82
Ph
O
O
N
O
5a'
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170
160
150
140
130
120
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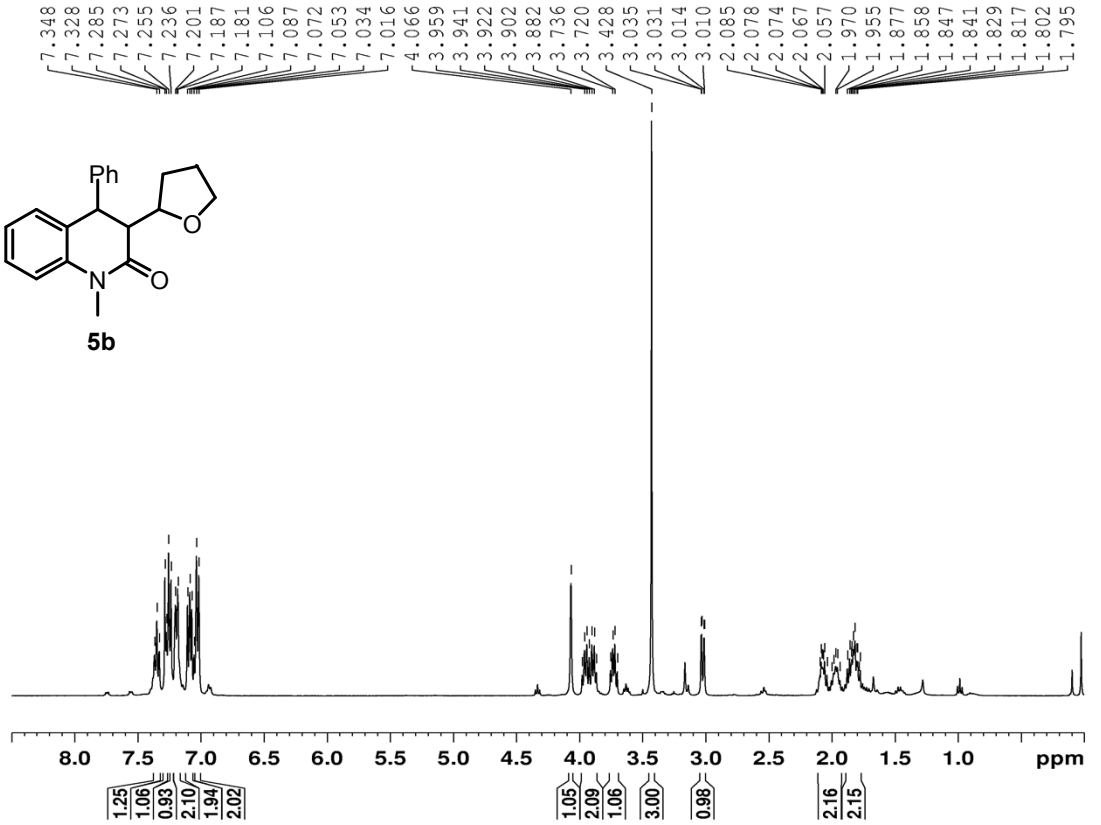
100
90
80
70
60
50
40
30
20
ppm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7.106
7.087
7.072
7.053
7.034
7.016
4.066
3.959
3.941
3.922
3.902
3.882
3.736
3.720
3.428
3.035
3.031
3.014
3.010
2.085
2.078
2.074
2.067
2.057
1.970
1.955
1.877
1.858
1.847
1.841
1.829
1.817
1.802
1.795
Ph
O
N
O
5b
8.0 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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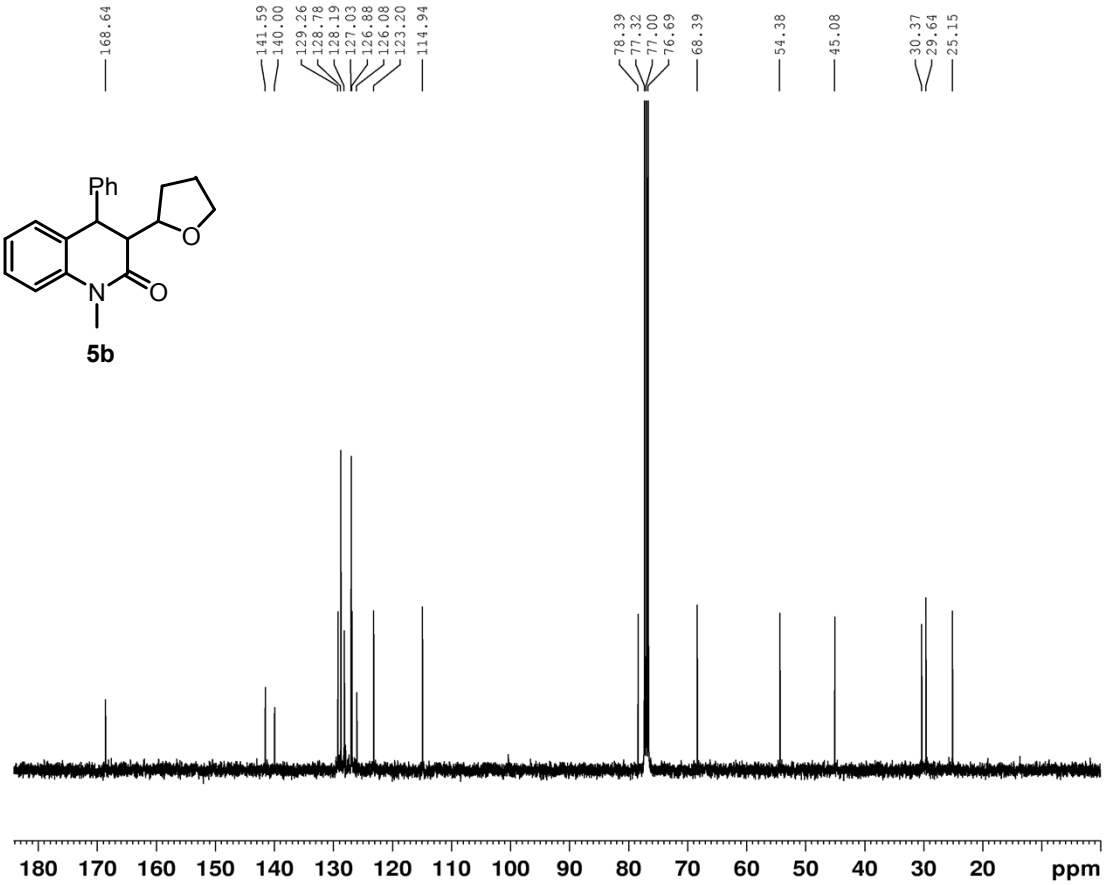
1.05 2.09 1.06 3.00 0.98 2.16 2.15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128.19
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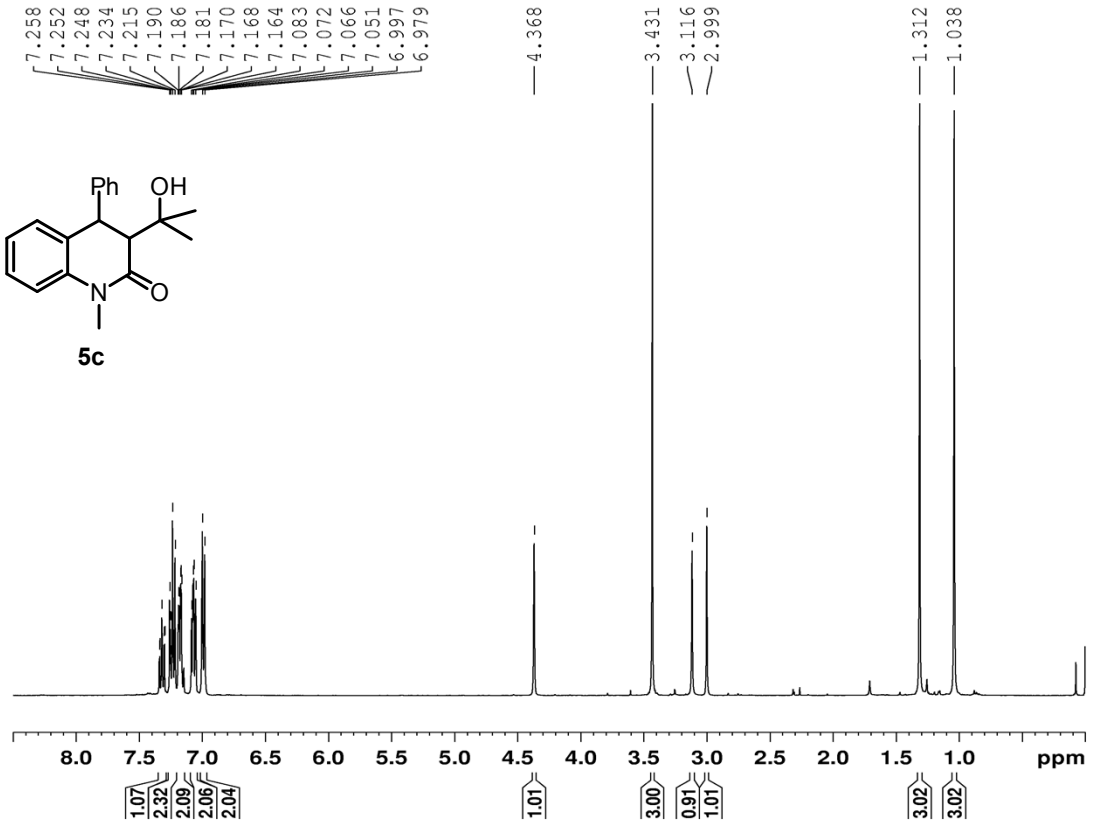
126.88
126.08
123.20
114.94
78.39
77.32
77.00
76.69
68.39
54.38
45.08
30.37
29.64
25.15
Ph
O
N
O
5b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.168
7.164
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7.072
7.066
7.051
6.997
6.979
4.368
3.431
3.116
2.999
1.312
1.038
Ph
OH
N
O
5c
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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
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ppm
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2.09
2.06
2.04
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3.00
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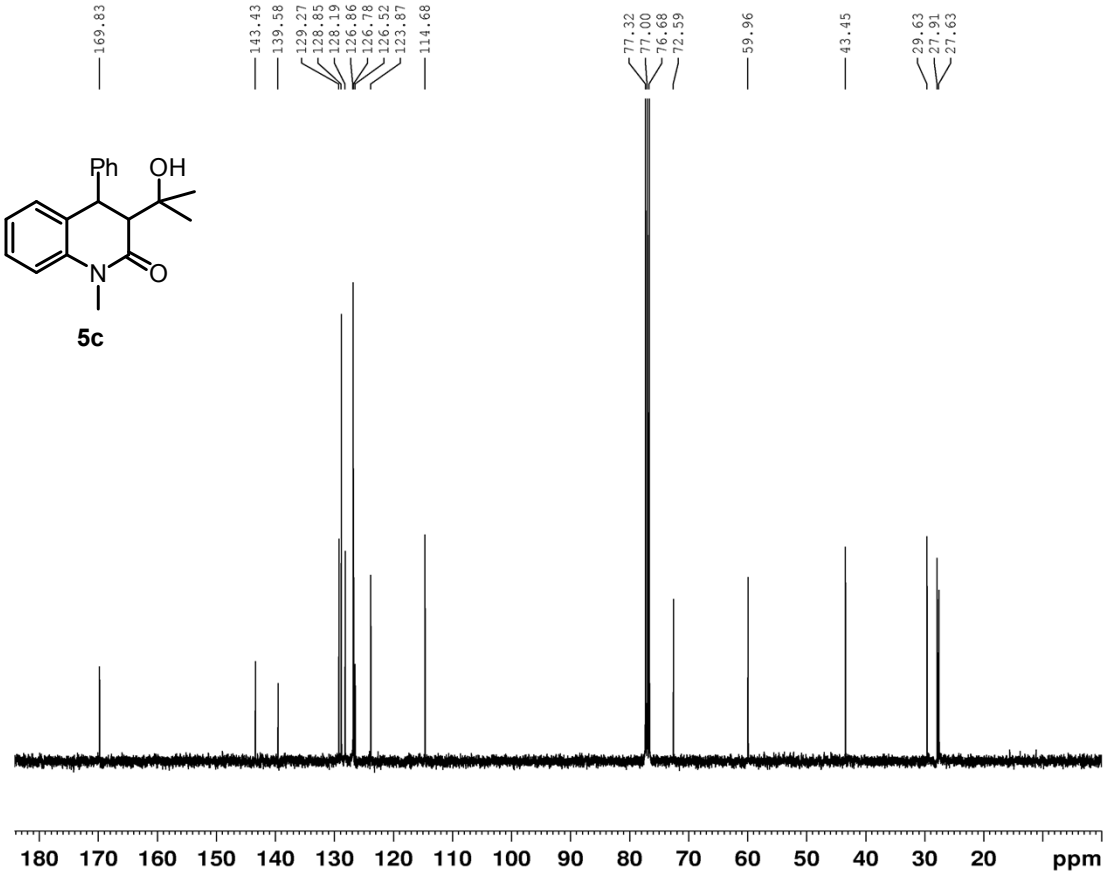
1.01
3.02
3.02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128.19
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126.78
126.52
123.87
114.68
77.32
77.00
76.68
72.59
59.96
43.45
29.63
27.91
27.63
Ph
OH
N
O
5c
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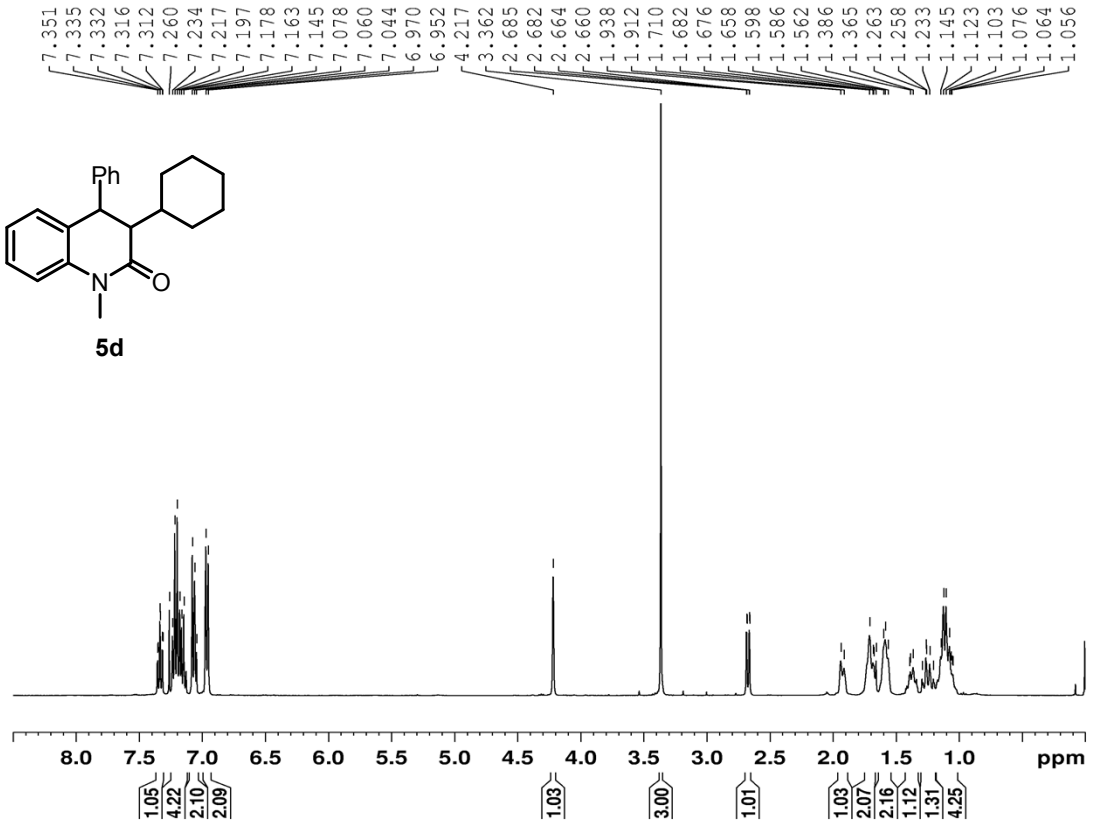
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.078
7.060
7.044
6.970
6.952
4.217
3.362
2.685
2.682
2.664
2.660
1.938
1.912
1.710
1.682
1.676
1.658
1.598
1.586
1.562
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1.365
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1.258
1.233
1.145
1.123
1.103
1.076
1.064
1.056
Ph
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5.5
5.0
4.5
4.0
3.5
3.0
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ppm
1.05
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1.03
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2.16
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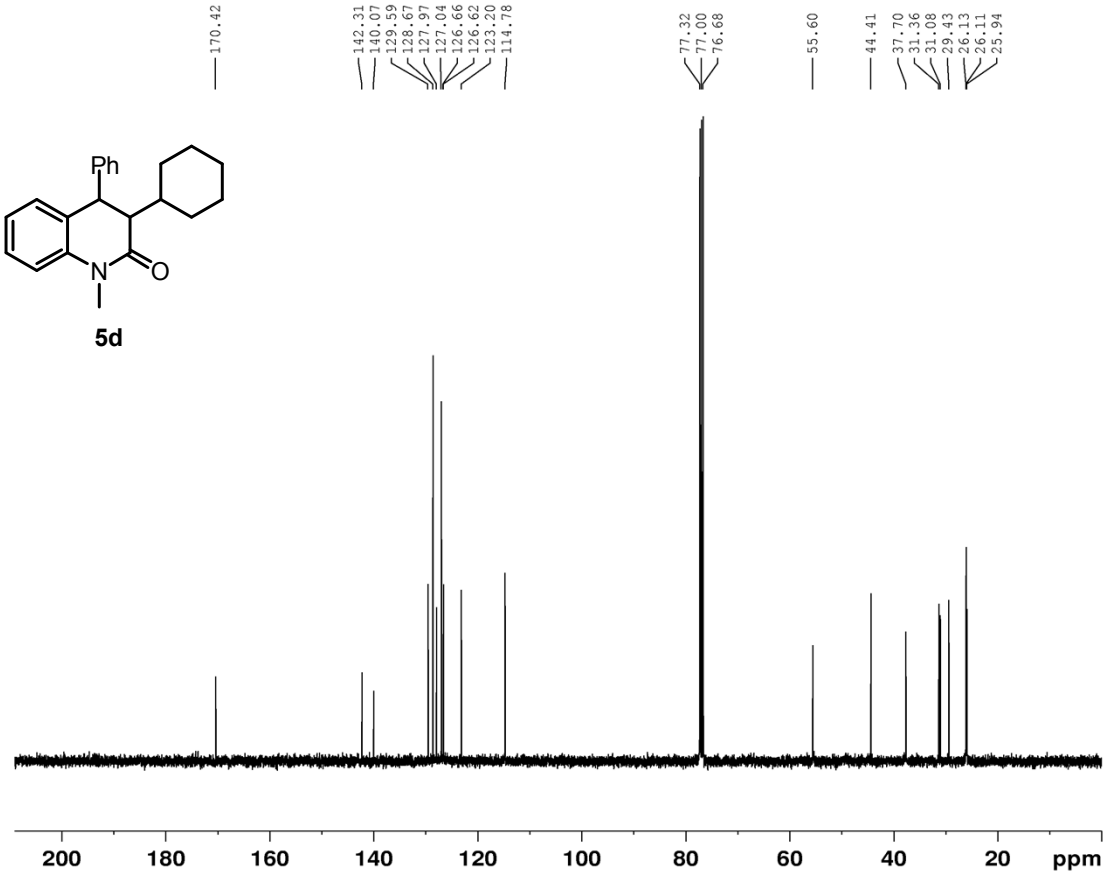
4.25

5d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77.00
76.68
55.60
44.41
37.70
31.36
31.08
29.43
26.13
26.11
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Ph
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O
200
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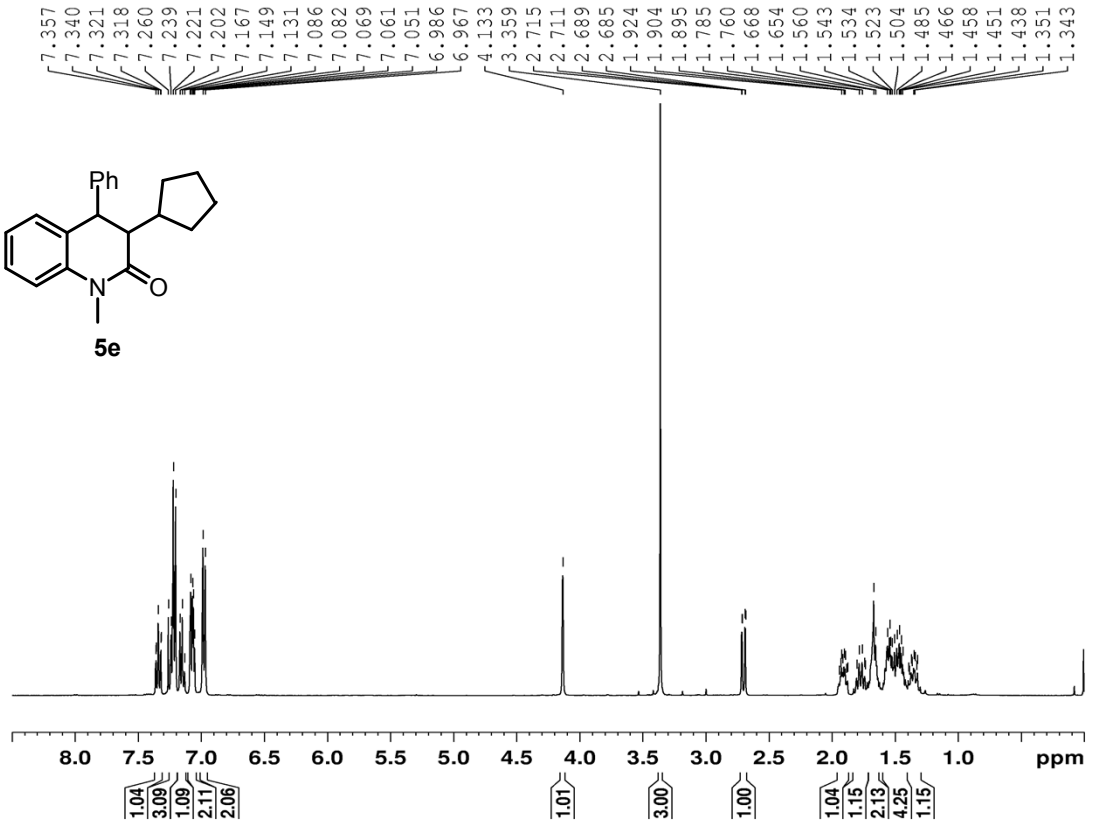
160
140
120
100
80
60
40
20
ppm

5d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7.069
7.061
7.051
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2.711
2.689
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1.904
1.895
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1.543
1.534
1.523
1.504
1.485
1.466
1.458
1.451
1.438
1.351
1.343
Ph
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O
5e
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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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3.09
1.09
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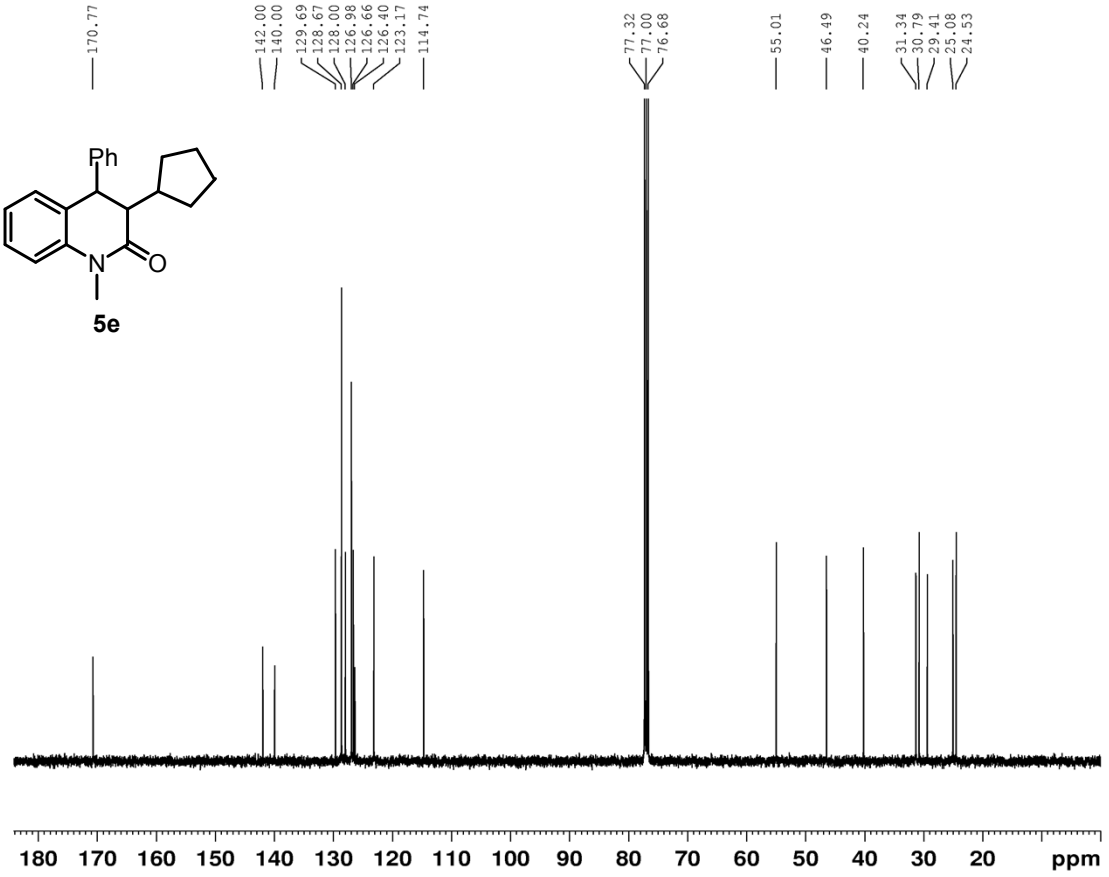
1.00
1.04
1.15
2.13
4.25
1.15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123.17
114.74
77.32
77.00
76.68
55.01
46.49
40.24
31.34
30.79
29.41
25.08
24.53
Ph
N
O
5e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm