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Supporting Information

Silver-catalyzed oxidative coupling/cyclization of acrylamides with 1,3-dicarbonyl compounds

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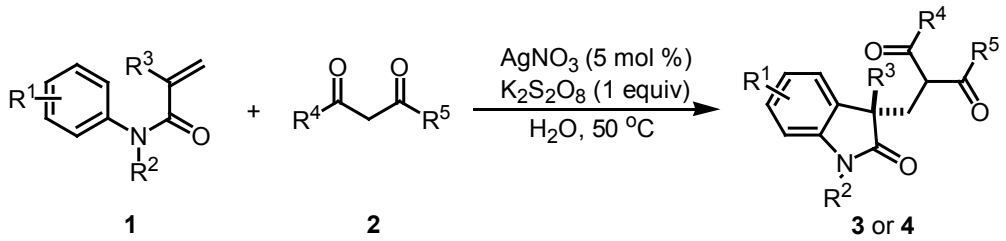
General Information

All reactions were carried out under an atmosphere of nitrogen with 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

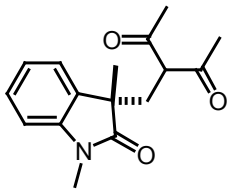
All of acrylamides **1** were synthesized according to the literature, and the NMR spectroscopy were in full accordance with the data in the literature.[1]

General Procedure for the Oxidative Coupling of Acrylamides with 1,3-Dicarbonyl compounds

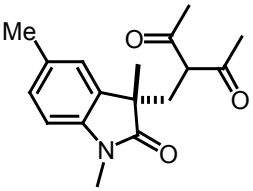


A 10 mL oven-dried Schlenk-tube was charged with $AgNO_3$ (1.7 mg, 5 mol %), acrylamide (**1**, 0.2 mmol, 1.0 equiv) and $K_2S_2O_8$ (54 mg, 0.2 mmol, 1.0 equiv). The tube was evacuated and backfilled with nitrogen (three times). 1,3-Dicarbonyl compounds (**2**, 0.4 mmol, 2.0 equiv) and H_2O 1 mL were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 28 h at 50 ^oC. The resulting mixture was then extracted with EtOAc. The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/15 to 1/5) to give the corresponding products **3** or **4** in yields listed in Table 2 and Table 3.

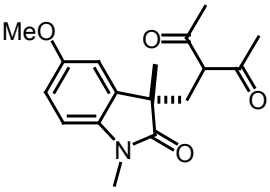
Characterization of Products 3



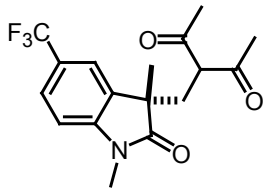
3a: A pale yellow solid, R_f 0.3 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.25 (m, 1H), 7.08-7.00 (m, 2H), 6.85-6.83 (d, *J* = 8.0 Hz, 1H), 3.28-3.25 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.21 (s, 3H), 2.57-2.51 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.40-2.35 (dd, *J* = 14.0, 4.4 Hz, 1H), 2.10 (s, 3H), 1.68 (s, 3H), 1.36 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 202.9, 179.4, 143.1, 132.1, 128.4, 123.9, 122.7, 108.1, 64.9, 47.2, 35.5, 29.4, 27.9, 26.2, 23.7 ppm; IR (KBr): υ_{max} 1704, 1613, 1471, 1355, 1255 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{19}NNaO_3$ $[M+Na]^+$ 296.1257, found 296.1270.



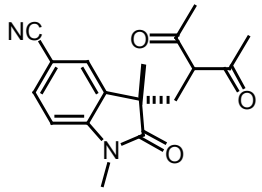
3b: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07-7.05 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.87 (s, 1H), 6.73-6.71 (d, *J* = 8.0 Hz, 1H), 3.29-3.26 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.18 (s, 3H), 2.51-2.46 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.39-2.34 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.30 (s, 3H), 2.09 (s, 3H), 1.70 (s, 3H), 1.33 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.3, 203.0, 179.4, 140.7, 132.3, 132.2, 128.5, 124.6, 107.9, 64.9, 47.1, 35.6, 29.4, 28.0, 26.2, 23.6, 21.0 ppm; IR (KBr): υ_{max} 1705, 1621, 1499, 1357 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{21}NNaO_3$ $[M+Na]^+$ 310.1414, found 310.1420.



3c: A pale yellow oil, R_f 0.2 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.78-6.77 (d, *J* = 2.4 Hz, 1H), 6.74-6.72 (d, *J* = 8.4 Hz, 1H), 6.67-6.66 (d, *J* = 2.4 Hz, 1H), 3.75 (s, 3H), 3.30-3.27 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.16 (s, 3H), 2.50-2.44 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.38-2.33 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.09 (s, 3H), 1.72 (s, 3H), 1.33 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.2, 202.8, 179.0, 156.1, 136.5, 133.4, 112.9, 111.0, 108.5, 64.9, 55.8, 47.5, 35.4, 29.4, 27.9, 26.2, 23.7 ppm; IR (KBr): υ_{max} 1703, 1601, 1499, 1359, 1290, 1033 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{21}NNaO_4$ $[M+Na]^+$ 326.1363, found 326.1372.

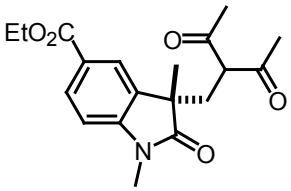


3d: A pale yellow solid, R_f 0.2 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58-7.56 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.32 (d, *J* = 1.6 Hz, 1H), 6.93-6.91 (d, *J* = 8.0 Hz, 1H), 3.38-3.35 (dd, *J* = 6.8, 5.2 Hz, 1H), 3.22 (s, 3H), 2.52-2.46 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.42-2.37 (dd, *J* = 14.8, 5.2 Hz, 1H), 2.11 (s, 3H), 1.81 (s, 3H), 1.38 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.0, 202.4, 179.3, 146.1, 133.1, 126.1 (q, *J* = 40.0 Hz), 124.9 (q, *J* = 32.5 Hz), 124.2 (q, *J* = 269.9 Hz), 120.6 (q, *J* = 36.0 Hz), 108.0, 64.9, 46.9, 35.1, 29.1, 27.9, 26.4, 23.5 ppm; IR (KBr): υ_{max} 1722, 1624, 1505, 1460, 1328, 1118 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{18}F_3NNaO_3$ $[M+Na]^+$ 364.1131, found 364.1141.

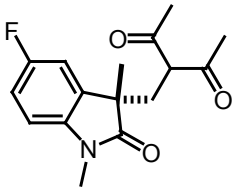


3e: A white solid, R_f 0.2 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64-7.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.37 (d, *J* = 1.2 Hz, 1H), 6.94-6.92 (d, *J* = 8.0 Hz, 1H), 3.41-3.37 (t, *J* = 6.4 Hz, 1H), 3.22 (s, 3H), 2.48-2.43 (dd, *J* = 14.4, 6.4 Hz, 1H), 2.40-2.35 (dd, *J* = 14.4, 5.6 Hz, 1H), 2.12 (s, 3H), 1.90 (s, 3H), 1.38 (s, 3H).

The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.0, 202.2, 179.1, 146.9, 133.8, 133.7, 126.6, 118.8, 108.7, 105.9, 65.0, 46.6, 34.9, 29.2, 27.9, 26.4, 23.5 ppm; IR (KBr): υ_{max} 2223, 1723, 1615, 1497, 1346 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{18}N_2NaO_3$ $[M+Na]^+$ 321.1210, found 321.1214.

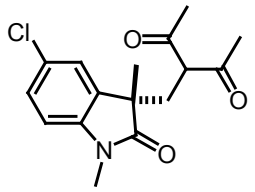


3f: A white solid, R_f 0.2 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02-7.99 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.75-7.74 (d, *J* = 1.2 Hz, 1H), 6.87-6.85 (d, *J* = 8.0 Hz, 1H), 4.35-4.30 (q, *J* = 7.2 Hz, 2H), 3.40-3.37 (t, *J* = 6.4 Hz, 1H), 3.19 (s, 3H), 2.41-2.39 (m, 2H), 2.07 (s, 3H), 1.82 (s, 3H), 1.37-1.34 (m, 6H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 202.4, 179.6, 166.1, 147.0, 132.4, 131.0, 124.9, 124.3, 107.7, 65.0, 60.9, 46.5, 35.1, 29.0, 27.9, 26.3, 23.4, 14.3 ppm; IR (KBr): υ_{max} 1708, 1616, 1499, 1353, 1284, 1259 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{23}NNaO_5$ $[M+Na]^+$ 368.1468, found 368.1476.

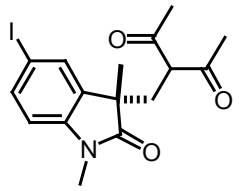


3g: A pale yellow oil, R_f 0.2 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00-6.95 (td, *J* = 8.8, 2.4 Hz, 1H), 6.85-6.83 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.78-6.75 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.34-3.31 (t, *J* = 5.6 Hz, 1H), 3.18 (s, 3H), 2.49-2.43 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.39-2.34 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.11 (s, 3H), 1.81 (s, 3H), 1.34 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 202.6, 179.0, 159.3 (d, *J* = 240.0 Hz), 139.0, 134.0 (d, *J* = 8.0 Hz), 114.6 (d, *J* = 23.0 Hz), 111.8 (d, *J* = 25.0 Hz), 108.7 (d, *J* = 8.0 Hz), 64.9, 47.5, 35.1, 29.3, 27.9, 26.3, 23.6 ppm; IR (KBr): υ_{max} 1709, 1621, 1495, 1356, 1275 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{18}FNNaO_3$ $[M+Na]^+$

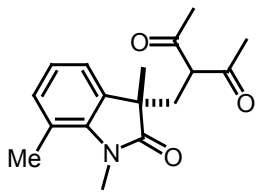
314.1163, found 314.1168.



3h: A white solid, R_f 0.2 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.24 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.07-7.06 (d, *J* = 2.0 Hz, 1H), 6.78-6.76 (d, *J* = 8.4 Hz, 1H), 3.37-3.34 (t, *J* = 6.0 Hz, 1H), 3.17 (s, 3H), 2.47-2.41 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.39-2.34 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.10 (s, 3H), 1.84 (s, 3H), 1.34 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 202.6, 178.9, 141.6, 134.1, 128.3, 128.1, 124.0, 109.2, 65.0, 47.2, 35.1, 29.2, 27.9, 26.3, 23.5 ppm; IR (KBr): υ_{max} 1712, 1610, 1490, 1361 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{18}ClNNaO_3$ $[M+Na]^+$ 330.0867, found 330.0879.

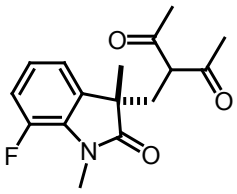


3i: A white solid, R_f 0.2 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60-7.58 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.37-7.36 (d, *J* = 1.6 Hz, 1H), 6.64-6.62 (d, *J* = 8.4 Hz, 1H), 3.37-3.34 (t, *J* = 6.4 Hz, 1H), 3.16 (s, 3H), 2.45-2.40 (dd, *J* = 14.4, 6.4 Hz, 1H), 2.39-2.34 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.10 (s, 3H), 1.84 (s, 3H), 1.33 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 202.6, 178.6, 142.8, 137.2, 134.9, 132.3, 110.3, 85.1, 65.0, 46.9, 35.2, 29.2, 27.9, 26.2, 23.5 ppm; IR (KBr): υ_{max} 1711, 1603, 1486, 1416, 1360 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{18}INNaO_3$ $[M+Na]^+$ 422.0224, found 422.0233.

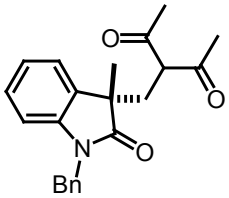


3j: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 7.01-6.99 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.95-6.89 (m, 2H), 3.49 (s, 3H), 3.32-3.29 (dd, *J* = 7.2, 4.8 Hz, 1H), 2.58 (s, 3H), 2.51-2.45 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.40-2.35 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.11 (s, 3H), 1.74 (s, 3H), 1.34 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.4, 203.0, 180.2, 140.9, 132.9, 132.1, 122.7, 121.6, 119.9, 65.1, 46.5, 35.9, 29.5, 29.4, 28.0, 24.0, 19.0 ppm; IR (KBr): υ_{max} 1702, 1601, 1461, 1363, 1245 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{21}NNaO_3$ $[M+Na]^+$ 310.1414, found 310.1419.

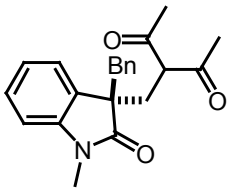


3k: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.03-6.95 (m, 2H), 6.88-6.86 (m, 1H), 3.43-3.42 (d, *J* = 2.8 Hz, 3H), 3.35-3.33 (dd, *J* = 6.8, 4.8 Hz, 1H), 2.53-2.47 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.40-2.35 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.13 (s, 3H), 1.80 (s, 3H), 1.36 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 202.7, 179.1, 147.6 (d, *J* = 243 Hz), 135.3, 129.8, 123.3 (d, *J* = 6 Hz), 119.5 (d, *J* = 3 Hz), 116.3 (d, *J* = 19 Hz), 64.9, 47.5, 35.4, 29.5, 28.7, 28.1, 24.0 ppm; IR (KBr): υ_{max} 1709, 1631, 1481, 1359, 1237 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{18}FNNaO_3$ $[M+Na]^+$ 314.1163, found 314.1169.

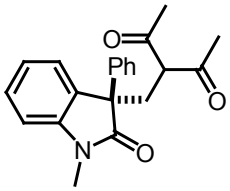


3l: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.28 (m, 5H), 7.20-7.15 (td, *J* = 7.6, 1.2 Hz, 1H), 7.08-7.06 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.03-7.01 (m, 1H), 6.80-6.78 (d, *J* = 7.6 Hz, 1H), 4.97-4.93 (d, *J* = 15.6 Hz, 1H), 4.88-4.84 (d, *J* = 15.2 Hz, 1H), 3.35-3.32 (dd, *J* = 8.0, 3.2 Hz, 1H), 2.64-2.58 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.42-2.37 (dd, *J* = 14.0, 3.2 Hz, 1H), 2.08 (s, 3H), 1.57 (s, 3H), 1.42 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals

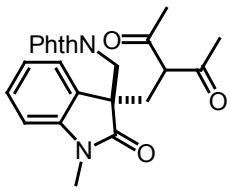
due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.8, 202.7, 179.7, 142.2, 136.0, 132.2, 128.8, 128.2, 127.8, 127.6, 127.0, 124.2, 122.7, 109.1, 64.5, 47.2, 43.8, 35.7, 29.5, 28.0, 23.8 ppm; IR (KBr): υ_{max} 1705, 1611, 1453, 1358, 1174 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{23}NNaO_3$ $[M+Na]^+$ 372.1570, found 372.1577.



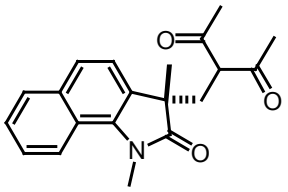
3n: A pale yellow oil, R_f 0.2 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.15 (m, 1H), 7.03-6.99 (m, 5H), 6.77-6.75 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.58-6.56 (d, *J* = 7.6 Hz, 1H), 3.26-3.23 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.15-3.12 (d, *J* = 12.8 Hz, 1H), 3.02-2.97 (d, *J* = 12.8 Hz, 1H), 2.94 (s, 3H), 2.76-2.71 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.56-2.51 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.13 (s, 3H), 1.64 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.0, 202.9, 178.0, 143.8, 135.0, 129.7, 129.1, 128.5, 127.5, 126.6, 125.0, 122.2, 107.8, 65.0, 53.7, 44.1, 34.2, 29.6, 27.9, 25.8 ppm; IR (KBr): υ_{max} 1705, 1611, 1494, 1470, 1357, 1255 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{23}NNaO_3$ $[M+Na]^+$ 372.1570, found 372.1574.



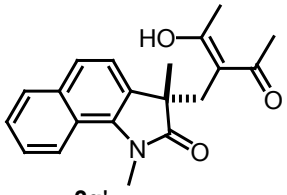
3o: A white solid, R_f 0.2 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.25 (m, 6H), 7.14-7.06 (m, 2H), 6.92-6.90 (d, *J* = 8.0 Hz, 1H), 3.38-3.35 (dd, *J* = 6.8, 4.4 Hz, 1H), 3.26 (s, 3H), 3.02-2.96 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.95-2.90 (dd, *J* = 14.0, 4.4 Hz, 1H), 2.11 (s, 3H), 1.73 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.2, 202.7, 177.6, 143.6, 139.2, 130.7, 128.8, 128.7, 127.6, 126.7, 125.9, 122.9, 108.5, 65.0, 55.4, 35.2, 29.6, 28.1, 26.5 ppm; IR (KBr): υ_{max} 1701, 1611, 1469, 1353, 1258 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{21}NNaO_3$ $[M+Na]^+$ 358.1414, found 358.1422.



3p: A pale yellow oil, R_f 0.2 (EtOAc/petroleum ether = 1:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79-7.77 (m, 2H), 7.69-7.67 (m, 2H), 7.28-7.23 (m, 1H), 7.06-7.04 (d, *J* = 7.6 Hz, 1H), 6.98-6.95 (t, *J* = 7.6, 1H), 6.81-6.79 (d, *J* = 7.6 Hz, 1H), 4.09-4.01 (m, 2H), 3.23-3.20 (m, 4H), 2.87-2.81 (dd, *J* = 14.4, 8.4 Hz, 1H), 2.57-2.53 (dd, *J* = 14.4, 3.6 Hz, 1H), 2.13 (s, 3H), 1.66 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.8, 202.6, 176.7, 167.8, 143.9, 134.0, 131.5, 129.2, 127.3, 125.3, 123.4, 122.5, 108.2, 64.8, 51.7, 43.1, 32.9, 29.5, 27.9, 26.4 ppm; IR (KBr): υ_{max} 1776, 1720, 1611, 1424, 1395 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{22}N_2NaO_5$ $[M+Na]^+$ 441.1421, found 441.1420.

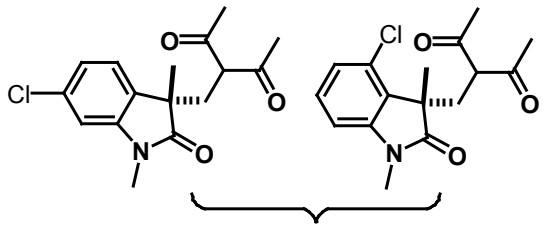


3q



3q'

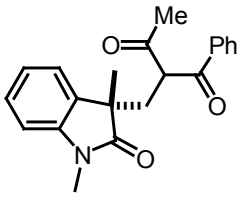
3q/3q' (1.25:1): A white solid, R_f 0.3 (EtOAc/petroleum ether = 1:5); **3q**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75-7.73 (d, *J* = 8.4 Hz, 1H), 7.56-7.42 (m, 3H), 7.37-7.35 (d, *J* = 7.2 Hz, 1H), 7.00-6.98 (d, *J* = 7.6 Hz, 1H), 3.54-3.48 (m, 4H), 2.71-2.66 (dd, *J* = 14.0, 5.2 Hz, 1H), 2.64-2.59 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.07 (s, 3H), 2.13 (s, 3H), 1.69 (s, 3H), 1.39 (s, 3H); **3q'**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79-7.77 (d, *J* = 8.0 Hz, 1H), 7.56-7.42 (m, 3H), 7.37-7.35 (d, *J* = 7.2 Hz, 1H), 6.93-6.92 (d, *J* = 7.6 Hz, 1H), 3.48 (s, 3H), 2.90-2.86 (d, *J* = 17.2 Hz, 1H), 2.58-2.54 (d, *J* = 17.2 Hz, 1H), 1.88 (s, 3H), 1.73 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.4, 202.8, 192.0, 172.2, 136.8, 136.6, 136.4, 136.1, 133.2, 132.9, 127.0, 126.7, 126.6, 123.5, 123.3, 122.7, 122.3, 120.5, 119.4, 108.8, 108.7, 105.3, 66.3, 49.0, 46.6, 44.0, 41.8, 29.8, 29.6, 29.3, 29.2, 27.8, 22.6, 22.3 ppm; IR (KBr): υ_{max} 3500, 1699, 1658, 1585, 1465, 1380, 1314 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{21}NNaO_3$ $[M+Na]^+$ 346.1414, found 346.1422.



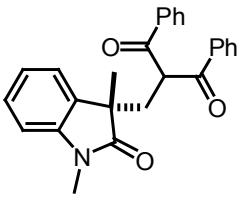
3r+ 3r', 85%, (1:1.8)

3r: R_f 0.2 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.22 (d, *J* = 8.0, 1H), 7.02-7.00 (d, *J* = 6.0 Hz, 1H), 6.85 (s, 1H), 3.30-3.27 (t, *J* = 6.0 Hz, 1H), 3.19 (s, 3H), 2.52-2.47 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.39-2.34 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.11 (s, 3H), 1.79 (s, 3H), 1.34 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 202.7, 179.4, 144.3, 134.2, 130.5, 124.7, 122.5, 109.0, 65.0, 46.9, 35.1, 29.7, 28.0, 26.3, 23.8 ppm. **3r':** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.24 (d, *J* = 8.4, 1H), 7.00-6.98 (d, *J* = 8.4 Hz, 1H), 6.77-6.75 (d, *J* = 7.6 Hz, 1H), 3.30-3.27 (t, *J* = 6.4 Hz, 1H), 3.18 (s, 3H), 2.81-2.75 (dd, *J* = 14.4, 6.4 Hz, 1H), 2.52-2.47 (dd, *J* = 14.4, 6.4 Hz, 1H), 2.06 (s, 3H), 1.89 (s, 3H), 1.52 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.5, 202.5, 178.7, 145.1, 130.9, 129.8, 128.4, 123.8, 106.8, 65.6, 48.4, 32.9, 28.8, 27.8, 26.4, 21.2 ppm; IR (KBr): υ_{max} 1715, 1609, 1460, 1360 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{18}ClNNaO_3$ $[M+Na]^+$ 330.0867, found 330.0869.

Characterization of Products 4

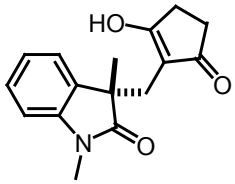


4a: A pale yellow oil, R_f 0.2 (EtOAc/petroleum ether = 1:5); The mixture of isomers cannot be separated by column chromatography on silica gel. The NMR spectroscopy of mixture (d.r.= 1.3:1), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85-7.83 (d, *J* = 7.6 Hz, 1H), 7.56-7.41 (m, 3H), 7.30-7.16 (m, 2H), 7.07-6.89 (m, 2H), 6.75-6.73 (d, *J* = 8.0 Hz, 0.42H), 6.49-6.47 (d, *J* = 8.0 Hz, 0.55H), 4.48-4.44 (t, *J* = 6.0 Hz, 0.43H), 4.26-4.22 (dd, *J* = 7.6, 5.2 Hz, 0.57H), 3.10 (s, 1.7H), 2.97 (s, 1.3H), 2.67-2.48 (m, 2H), 2.06 (s, 1.7H), 1.84 (s, 1.3H), 1.36 (s, 1.7H), 1.32 (s, 1.3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.5, 202.1, 195.5, 195.3, 179.5, 179.3, 142.9, 142.8, 136.0, 135.8, 133.6, 133.3, 132.7, 131.8, 128.7, 128.3, 128.2, 123.7, 123.2, 122.7, 122.5, 108.1, 107.8, 58.7, 58.2, 47.2, 46.8, 36.4, 36.3, 28.5, 27.9, 26.0, 25.8, 24.3, 23.6 ppm; IR (KBr): υ_{max} 1711, 1612, 1471, 1352, 1256 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{21}NNaO_3$ $[M+Na]^+$ 358.1414, found 358.1425.

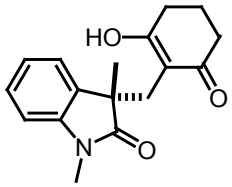


4b: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97-7.95 (d, *J* = 7.2 Hz, 2H), 7.72-7.70 (d, *J* = 7.2 Hz, 2H), 7.55-7.51 (t, *J* = 7.2 Hz, 1H), 7.48-7.41 (m, 3H), 7.34-7.30 (t, *J* = 7.6 Hz, 2H), 7.19-7.12 (m, 2H), 7.02-6.98 (t, *J* = 7.6 Hz, 1H), 6.63-6.61 (d, *J* = 7.6 Hz, 1H), 5.59-5.56 (t, *J* = 5.6 Hz, 1H), 3.12 (s, 3H), 2.88-2.83 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.55-2.50 (dd, *J* = 14.4, 6.0 Hz, 1H), 1.36 (s, 3H). The ^{1}H NMR spectrum also displayed a minor set of signals due to enol isomers; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.0, 194.8, 179.9, 142.6, 136.0, 135.7, 133.4, 133.2, 132.9, 128.7, 128.5, 128.4, 128.1, 123.6, 122.7, 107.9, 52.1, 47.1, 36.6, 26.0, 23.5 ppm; IR (KBr): υ_{max} 1703, 1613, 1449, 1379, 1266 cm^{-1}; HRMS (ESI)

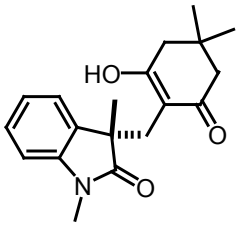
calcd for $C_{26}H_{23}NNaO_3$ $[M+Na]^+$ 420.1570, found 420.1577.



4c: A white solid, R_f 0.3 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.20 (s, 1H), 7.44-7.42 (d, *J* = 7.2 Hz, 1H), 7.31-7.23 (t, *J* = 7.6 Hz, 1H), 7.18-7.14 (t, *J* = 7.6 Hz, 1H), 6.91-6.89 (d, *J* = 7.6 Hz, 1H), 3.28 (s, 3H), 3.02-2.98 (d, *J* = 16.0 Hz, 1H), 2.56-2.44 (m, 4H), 2.24-2.20 (d, *J* = 15.6 Hz, 1H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 184.9, 141.6, 135.4, 128.1, 124.1, 123.4, 112.1, 108.7, 48.4, 33.2, 27.7, 27.2, 26.7, 22.2 ppm; IR (KBr): υ_{max} 3446, 1704, 1613, 1384, 1124 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{17}NNaO_3$ $[M+Na]^+$ 294.1101, found 294.1107.

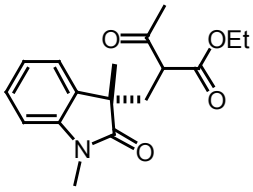


4d: A white solid, R_f 0.3 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.06 (s, 1H), 7.51-7.49 (d, *J* = 7.2 Hz, 1H), 7.27-7.23 (m, 1H), 7.15-7.11 (m, 1H), 6.85-6.84 (d, *J* = 7.6 Hz, 1H), 3.24 (s, 3H), 3.12-3.08 (d, *J* = 14.8 Hz, 1H), 2.63-2.59 (d, *J* = 14.8 Hz, 1H), 2.51-2.40 (m, 2H), 2.25-2.24 (m, 2H), 1.90-1.76 (m, 2H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.6, 185.5, 174.3, 142.0, 135.4, 127.7, 124.2, 123.7, 111.4, 108.2, 48.9, 36.4, 29.7, 27.6, 26.6, 23.3, 20.5 ppm; IR (KBr): υ_{max} 3056, 1710, 1611, 1493, 1380, 1274, 1107 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{19}NNaO_3$ $[M+Na]^+$ 308.1257, found 308.1268.

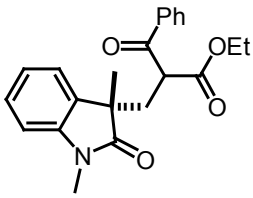


4e: A white solid, R_f 0.3 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.56 (s, 1H), 7.49-7.47 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.26-7.22 (td, *J* = 7.6, 1.2 Hz,

1H), 7.14-7.10 (td, J = 7.6, 0.8 Hz, 1H), 6.84-6.82 (d, J = 8.0 Hz, 1H), 3.23 (s, 3H), 3.06-3.02 (d, J = 14.8 Hz, 1H), 2.77-2.74 (d, J = 14.8 Hz, 1H), 2.35-2.31 (d, J = 17.6 Hz, 1H), 2.26-2.22 (d, J = 17.2 Hz, 1H), 2.14-2.10 (d, J = 16.0 Hz, 1H), 2.04-2.00 (d, J = 16.0 Hz, 1H), 1.26 (s, 3H), 0.99 (s, 3H) 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.9, 185.3, 172.1, 142.0, 134.8, 127.8, 124.4, 123.6, 110.1, 108.2, 50.2, 49.1, 43.3, 31.2, 28.7, 27.7, 27.3, 26.6, 23.7 ppm; IR (KBr): υ_{max} 3476, 1694, 1613, 1470, 1381, 1256 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{23}NNaO_3$ $[M+Na]^+$ 336.1570, found 336.1575.

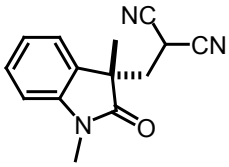


4f: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); The mixture of isomers cannot be separated by column chromatography on silica gel. The NMR spectroscopy of mixture (d.r.= 1:1), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.23 (m, 1H), 7.14-7.12 (d, J = 7.6 Hz, 0.6H), 7.09-7.07 (d, J = 6.8 Hz, 0.4H), 7.04-7.00 (m, 1H), 6.84-6.82 (d, J = 7.6 Hz, 1H), 4.13-4.08 (q, J = 7.2 Hz, 1H), 3.82-3.62 (m, 1H), 3.24-3.04 (m, 4H), 2.48-2.44 (m, 2H), 2.11 (s, 1.5H), 1.83 (s, 1.5H), 1.35 (s, 3H), 1.23-1.19 (t, J = 7.2 Hz, 1.5H), 1.05-1.01 (t, J = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.9, 201.7, 179.5, 179.4, 169.0, 143.3, 143.1, 132.6, 132.0, 128.2, 123.6, 122.6, 122.4, 108.1, 108.0, 61.6, 61.3, 56.5, 55.4, 47.2, 46.7, 35.4, 34.9, 29.2, 28.1, 26.1, 24.5, 23.5, 13.9, 13.7 ppm; IR (KBr): υ_{max} 1712, 1613, 1493, 1378, 1351, 1250 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{21}NNaO_4$ $[M+Na]^+$ 326.1363, found 326.1370.



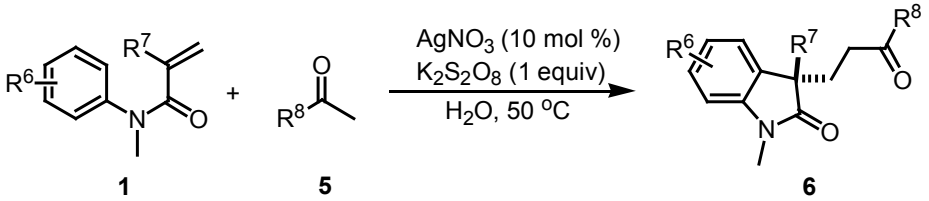
4g: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); The mixture of isomers cannot be separated by column chromatography on silica gel. The NMR spectroscopy of mixture (d.r.= 1.2:1), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88-7.86 (dd, J = 8.4, 1.2 Hz, 1H), 7.59-7.57 (dd, J = 8.4, 1.2 Hz, 1H), 7.56-7.40 (m, 2H), 7.31-7.7.20 (m, 2H),

7.08-6.91 (m, 2H), 6.79-6.77 (d, J = 7.6 Hz, 0.45H), 6.46-6.44 (d, J = 7.6 Hz, 0.55H), 4.21-4.17 (m, 1H), 4.10-4.01 (m, 1H), 3.75-3.61 (m, 1H), 3.08 (s, 3H), 2.67-2.60 (m, 2H), 1.38 (s, 1.5H), 1.35 (s, 1.5H), 1.12-1.08 (t, J = 7.2 Hz, 1.5H), 0.96-0.93 (t, J = 7.2 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.7, 194.4, 179.6, 179.4, 169.1, 168.9, 143.1, 142.8, 135.9, 135.7, 133.4, 133.0, 132.4, 132.1, 128.8, 128.5, 128.3, 128.2, 128.1, 123.8, 123.5, 122.6, 122.5, 108.0, 107.8, 61.6, 61.3, 50.2, 49.4, 47.1, 47.0, 36.6, 36.1, 26.0, 24.5, 24.1, 13.8, 13.6; IR (KBr): υ_{max} 1710, 1613, 1450, 1383 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{23}NNaO_4$ $[M+Na]^+$ 388.1519, found 388.1537.



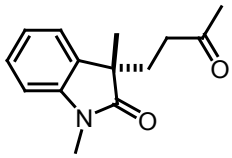
4h: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.35 (td, J = 7.6, 1.2 Hz, 1H), 7.24-7.22 (dd, J = 7.6, 0.8 Hz, 1H), 7.17-7.13 (td, J = 7.6, 0.8 Hz, 1H), 6.94-6.92 (d, J = 8.0 Hz, 1H), 3.81-3.78 (dd, J = 9.2, 5.6 Hz, 1H), 3.24 (s, 3H), 2.78-2.72 (dd, J = 14.4, 9.2 Hz, 1H), 2.38-2.33 (dd, J = 14.4, 5.6 Hz, 1H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.8, 143.1, 130.0, 129.5, 123.3, 122.9, 112.0, 109.1, 46.1, 37.6, 30.9, 26.5, 18.4 ppm; IR (KBr): υ_{max} 2256, 1714, 1613, 1471, 1382 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{13}N_3NaO$ $[M+Na]^+$ 262.0951, found 262.0961.

General Procedure for the Oxidative Coupling of Acrylamides with Ketones

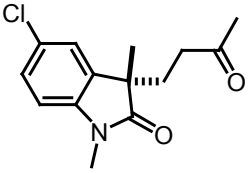


A 10 mL oven-dried Schlenk-tube was charged with $AgNO_3$ (3.4 mg, 10 mol %), acrylamide (**1**, 0.2 mmol, 1.0 equiv) and $K_2S_2O_8$ (54 mg, 0.2 mmol, 1.0 equiv). The tube was evacuated and backfilled with nitrogen (three times). Aetone/H_2O (1:1) 1 mL were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 28 h at 50 ^{o}C. The resulting mixture was then extracted with EtOAc. The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/20 to 1/5) to give the corresponding products **6** in yields listed in Table 4.

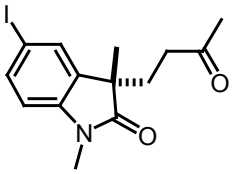
Characterization of Products 6



6a: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.26 (m, 1H), 7.16-7.14 (d, *J* = 7.2 Hz, 1H), 7.08-7.04 (t, *J* = 7.2 Hz, 1H), 6.86-6.84 (d, *J* = 7.6 Hz, 1H), 3.22 (s, 3H), 2.24-2.05 (m, 3H), 2.02 (s, 3H), 1.96-1.89 (m, 1H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.7, 180.0, 143.1, 133.2, 128.0, 122.7, 122.6, 108.0, 47.3, 38.5, 31.7, 29.8, 26.1, 23.6 ppm; IR (KBr): υ_{max} 1712, 1613, 1470, 1453, 1384, 1129 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{17}NNaO_2$ $[M+Na]^+$ 254.1151, found 254.1161.

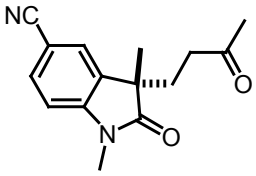


6b: A pale yellow solid, R_f 0.3 (EtOAc/petroleum ether = 1:3), mp = 96-98 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.23 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.13-7.12 (d, *J* = 2.0 Hz, 1H), 6.78-6.76 (d, *J* = 8.4 Hz, 1H), 3.20 (s, 3H), 2.24-1.93 (m, 7H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.2, 179.5, 141.7, 135.1, 128.1, 127.9, 123.2, 109.0, 47.5, 38.4, 31.6, 29.8, 26.3, 23.5 ppm; IR (KBr): υ_{max} 1716, 1610, 1490, 1364, 1345, 1270 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{16}ClNNaO_2$ $[M+Na]^+$ 288.0762, found 288.0766.

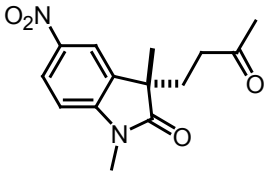


6c: A pale yellow solid, R_f 0.3 (EtOAc/petroleum ether = 1:3), mp = 100-102 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58-7.56 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.41 (d, *J* = 1.6 Hz, 1H), 6.64-6.62 (d, *J* = 8.4 Hz, 1H), 3.17 (s, 3H), 2.20-2.10 (m, 2H), 2.08-1.94 (m, 5H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.2, 179.2, 142.8, 136.8, 135.7, 131.4, 110.1, 85.3, 47.3, 38.3, 31.5, 29.8, 26.2, 23.5 ppm; IR (KBr): υ_{max} 1715, 1603,

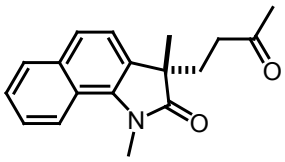
1487, 1362, 1242 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{16}INNaO_2$ $[M+Na]^+$ 380.0118, found 380.0129.



6d: A pale yellow solid, R_f 0.2 (EtOAc/petroleum ether = 1:3), mp = 122-123 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.63-7.61 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.41 (d, *J* = 1.6 Hz, 1H), 6.94-6.91 (d, *J* = 8.4 Hz, 1H), 3.25 (s, 3H), 2.26-1.98 (m, 7H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.8, 179.7, 146.9, 134.5, 133.5, 126.0, 119.0, 108.5, 105.9, 47.1, 38.2, 31.5, 29.8, 26.4, 23.3 ppm; IR (KBr): υ_{max} 2222, 1720, 1614, 1455, 1384, 1062 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{16}N_2NaO_2$ $[M+Na]^+$ 279.1104, found 279.1115.

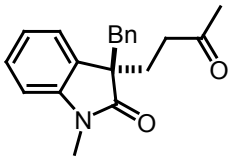


6e: A pale yellow oil, R_f 0.1 (EtOAc/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.27-8.25 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.05-8.04 (d, *J* = 2.4 Hz, 1H), 6.95-6.93 (d, *J* = 8.4 Hz, 1H), 3.28 (s, 3H), 2.28-2.05 (m, 4H), 2.04 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.7, 180.0, 148.7, 143.5, 134.3, 125.4, 118.5, 107.7, 47.2, 38.1, 31.4, 29.8, 26.6, 23.2 ppm; IR (KBr): υ_{max} 1723, 1613, 1495, 1335, 1108, 1052 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{16}N_2NaO_4$ $[M+Na]^+$ 299.1002, found 299.1013.

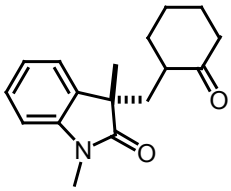


6f: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.74-7.72 (d, *J* = 8.0 Hz, 1H), 7.55-7.52 (m, 2H), 7.47-7.41 (m, 2H), 6.98-6.96 (d, *J* = 7.6 Hz, 1H), 3.54 (s, 3H), 2.61-2.54 (m, 1H), 2.36-2.19 (m, 2H), 2.08-2.00 (m, 4H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.9, 172.8,

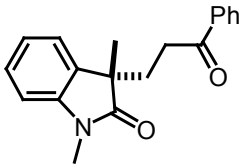
137.3, 136.6, 133.3, 127.2, 126.4, 126.2, 122.6, 119.5, 108.5, 46.7, 39.7, 37.0, 31.0, 29.8, 29.6 ppm; IR (KBr): υ_{max} 1715, 1660, 1585, 1465, 1383, 1315 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{19}NNaO_2$ $[M+Na]^+$ 304.1308, found 304.1317.



6g: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:3); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.21-7.17 (td, *J* = 7.6, 0.8 Hz, 1H), 7.13-7.12 (d, *J* = 6.8 Hz, 1H), 7.06-6.99 (m, 4H), 6.80-6.77 (m, 2H), 6.60-6.58 (d, *J* = 7.6 Hz, 1H), 3.16-3.13 (d, *J* = 12.8 Hz, 1H), 3.03-2.99 (d, *J* = 13.2 Hz, 1H), 2.96 (s, 3H), 2.34-2.20 (m, 3H), 1.97-1.87 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.6, 178.6, 143.7, 135.5, 130.3, 129.7, 128.1, 127.4, 126.4, 123.6, 122.3, 107.7, 53.8, 44.3, 38.6, 30.3, 29.9, 25.8 ppm; IR (KBr): υ_{max} 1710, 1612, 1494, 1377, 1259, 1164 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{21}NNaO_2$ $[M+Na]^+$ 330.1464, found 330.1479.

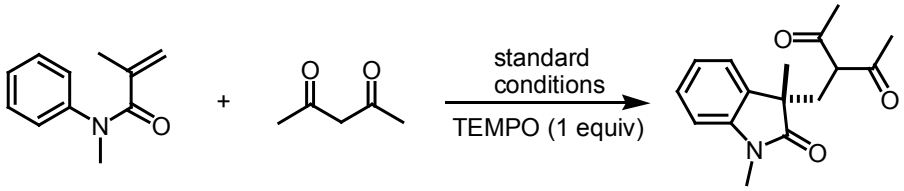


6h: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); The mixture of isomers cannot be separated by column chromatography on silica gel. The NMR spectroscopy of mixture (d.r.= 1.5:1), ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.22 (m, 1H), 7.18-7.13 (m, 1H), 7.04-7.02 (m, 1H), 6.84-6.82 (d, *J* = 8.0 Hz, 1H), 3.21 (s, 1.7H), 3.19 (s, 1.3H), 2.73-2.63 (m, 1H), 2.42-2.39 (m, 1H), 2.26-2.22 (m, 1H), 2.06-1.98 (m, 1H), 1.91-1.82 (m, 3H), 1.76-1.46 (m, 4H), 1.34 (s, 1.7H), 1.31 (s, 1.3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.4, 211.5, 180.7, 180.3, 143.0, 142.9, 134.5, 133.2, 127.8, 123.1, 122.5, 122.4, 108.0, 107.9, 47.3, 47.1, 46.9, 41.7, 41.5, 37.0, 36.0, 35.6, 35.0, 28.1, 27.9, 26.2, 26.1, 25.1, 25.0, 24.5, 24.3 ppm; IR (KBr): υ_{max} 1712, 1613, 1493, 1378, 1253, 1127 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{21}NNaO_2$ $[M+Na]^+$ 294.1465, found 294.1475.



6i: A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79-7.77 (m, 2H), 7.52-7.48 (m, 1H), 7.39-7.37 (m, 2H), 7.30-7.20 (m, 2H), 7.10-7.09 (m, 1H), 7.08-7.06 (m, 1H), 6.87-6.85 (d, *J* = 7.6 Hz, 1H), 3.25 (s, 3H), 2.80-2.76 (m, 1H), 2.52-2.45 (m, 1H), 2.34-2.30 (m, 1H), 2.27-2.23 (m, 1H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.3, 180.2, 143.2, 136.6, 133.4, 133.0, 128.5, 128.0, 122.8, 122.7, 108.1, 47.6, 33.6, 32.4, 26.2, 23.8 ppm; IR (KBr): υ_{max} 1710, 1639, 1493, 1377, 1260, 1126 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{19}NNaO_2$ $[M+Na]^+$ 316.1308, found 316.1315.

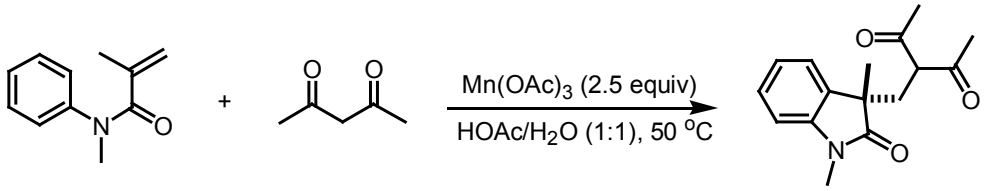
Investigation of the Reaction Mechanism



1a **2a** **3a**, 26%

When the TEMPO was added to the reaction of **1a** with **2a** under the standard conditions, the desired product **3a** was only isolated in 26% yield. The result indicates that the radical intermediate should be involved in the catalytic cycle of the reaction.

Investigation of the Reaction Mechanism



1a **2a** **3a**, 29%

A 10 mL oven-dried Schlenk-tube was charged with $Mn(OAc)_3 \cdot 2H_2O$ (134 mg, 0.5 mmol, 2.5 equiv) and acrylamide (**1a**, 0.2 mmol, 1.0 equiv). The tube was evacuated backfilled with nitrogen (three times). 2,4-pentadione (**2a**, 0.4 mmol, 2.0 equiv) and $HOAc/H_2O$ (1:1) 1 mL were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 24 h at 50 ^{o}C. The resulting mixture was then extracted with EtOAc. The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/15 to 1/5) to give the corresponding products **3a** in 29% yield.

Isotope Labeling Experiment

a) Intramolecular Kinetic Isotope Effect (KIE) Experiment:

[D_1]-**1a** was synthesized according the literature procedure.[1] A 10 mL oven-dried Schlenk-tube was charged with $AgNO_3$ (1.7 mg, 5 mol %), [D_1]-**1a** (0.2 mmol, 1.0 equiv) and $K_2S_2O_8$ (54 mg, 0.2 mmol, 1.0 equiv). The tube was evacuated and backfilled with nitrogen (three times). 2,4-pentadione (**2a**, 0.4 mmol, 2.0 equiv) and H_2O 1 mL were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred at 50 ^oC for 28 h. Upon completion of the reaction, the mixture was extracted with EtOAc, dried over Na_2SO_4 and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel to give the corresponding product. The product was analysed by ^1H NMR (Figure 1).

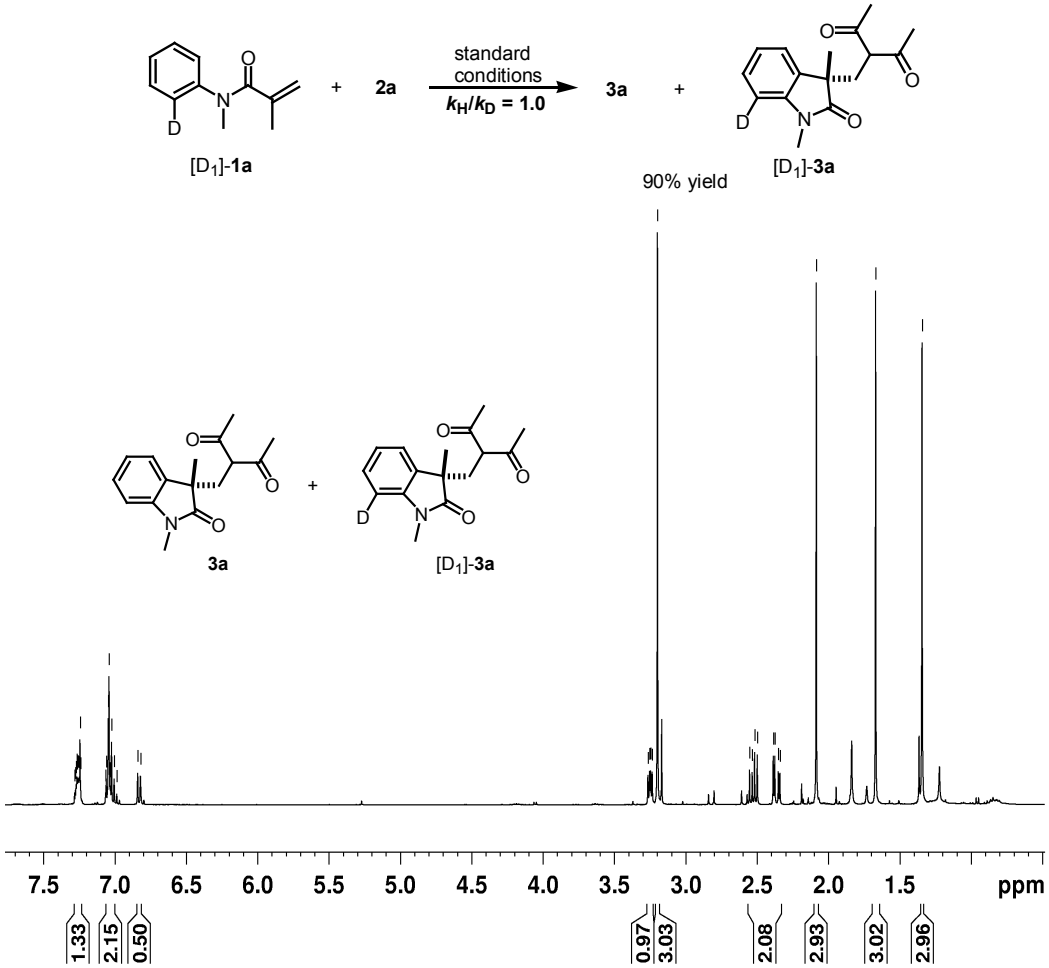


Figure 1. ^1H NMR spectra of the mixture of the product **3a** and [D_1]-**3a**.

b) Intermolecular Kinetic Isotope Effect (KIE) Experiment:

Aniline (ring-D_5, 98%, cat. No. DLM-862-0) was purchased from Cambridge Isotope Laboratories. The isotope reagent was used without further purification. [D_5]-**1a** was synthesized according the literature procedure using D_5-aniline as starting material.[1] A 10 mL oven-dried Schlenk-tube was charged with $AgNO_3$ (1.7 mg, 5 mol %), [D_5]-**1a** (0.1 mmol), **1a** (0.1 mmol) and $K_2S_2O_8$ (54 mg, 0.2 mmol, 1.0 equiv). The tube was evacuated and backfilled with nitrogen (three times). 2,4-pentadione (**2a**, 0.4 mmol, 2.0 equiv) and H_2O 1 mL were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred at 50 ^oC for 28 h. Upon completion of the reaction, the mixture was extracted with EtOAc, dried over Na_2SO_4 and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel to give the corresponding product. The product was analysed by ^1H NMR (Figure 2).

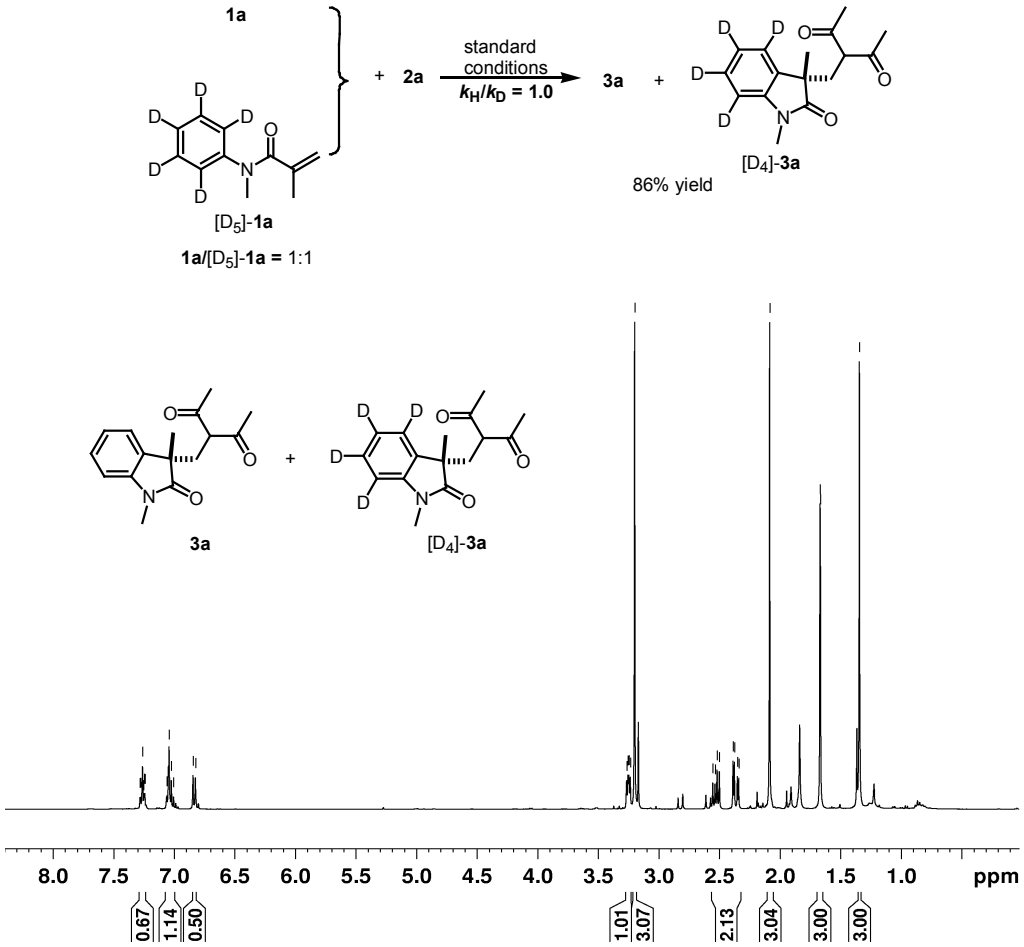


Figure 2. ^1H NMR spectra of the mixture of the product **3a** and [D_4]-**3a**.

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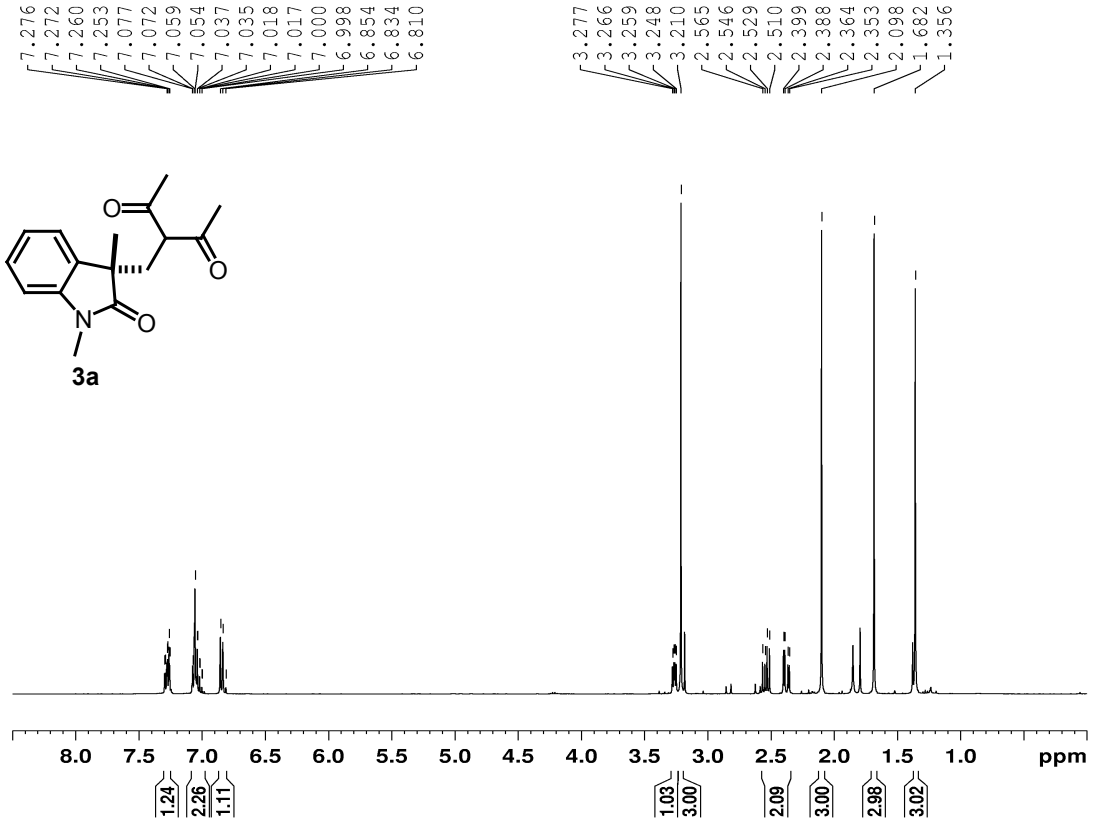
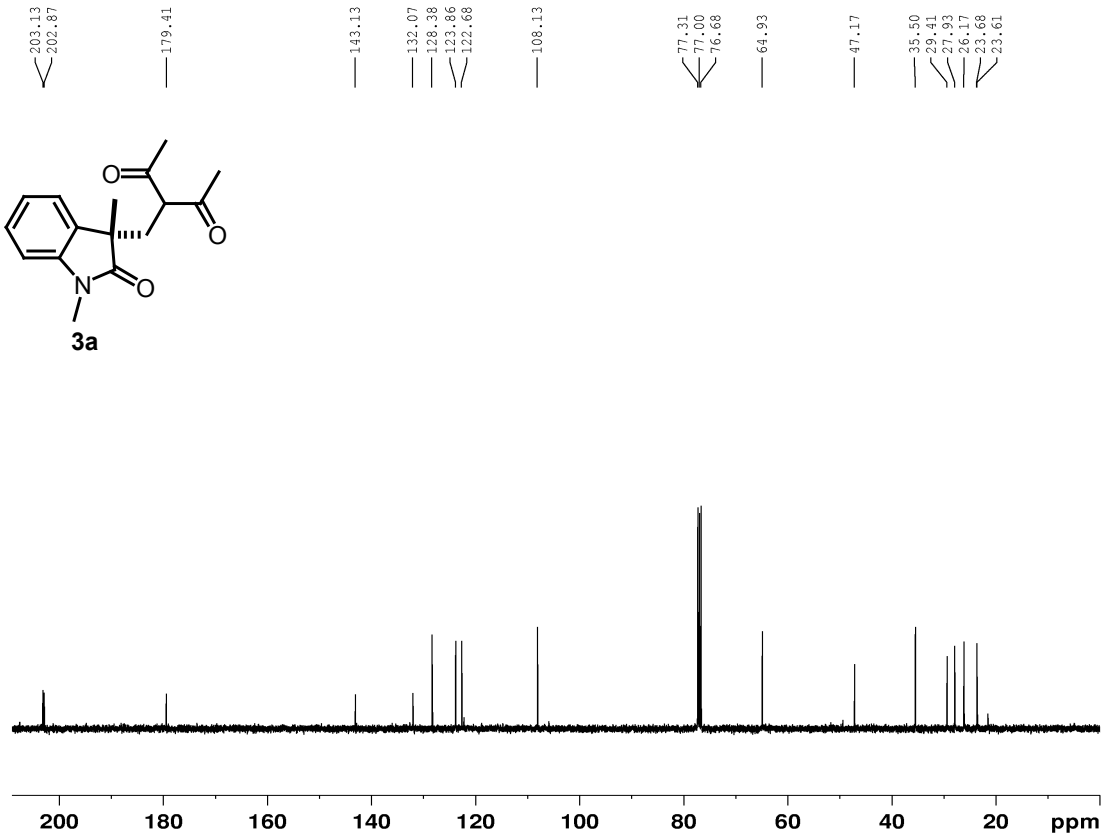
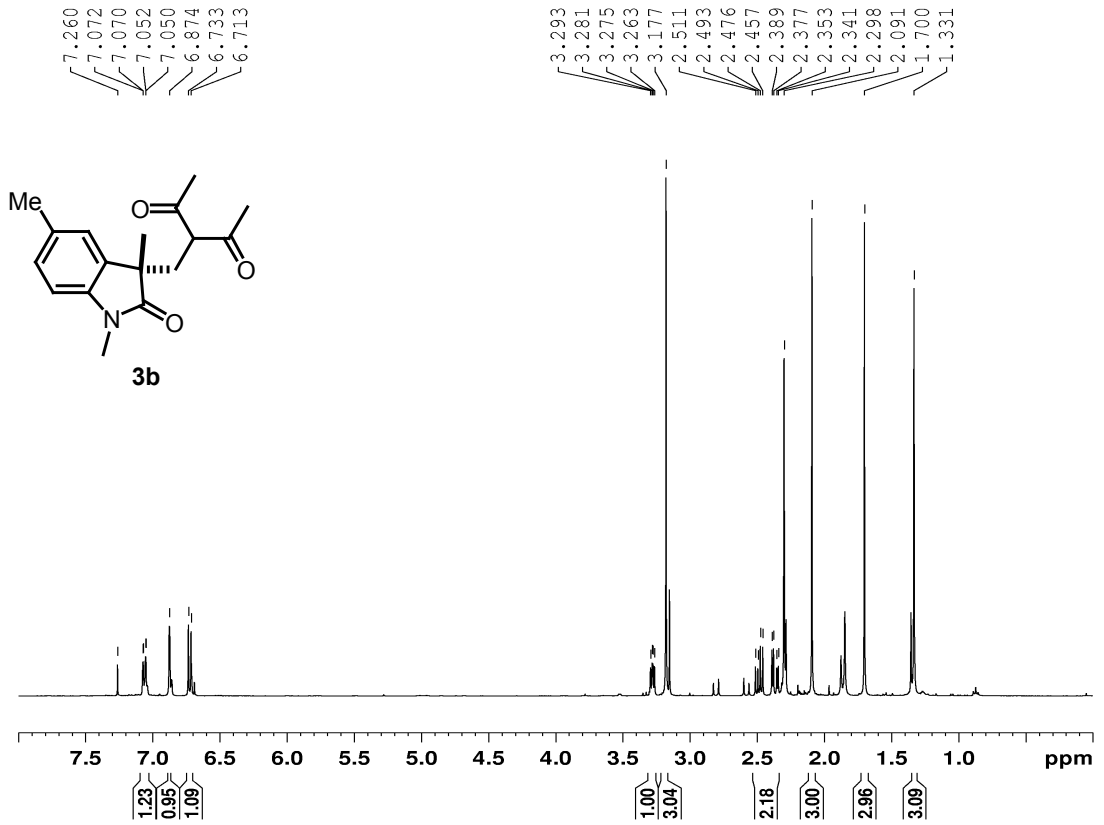
References

(1) (a) T. Wu, X. Mu and G. Liu, *Angew. Chem.*, *Int. Ed.*, 2011, **50**, 12578; (b) X. Mu, T. Wu, H.-Y. Wang, Y.-L. Guo and G. Liu, *J. Am. Chem. Soc.*, 2012, **134**, 878; (c) D. C. Fabry, M. Stodulski, S. Hoerner and T. Gulder, *Chem. Eur. J.*, 2012, **18**, 10834.

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



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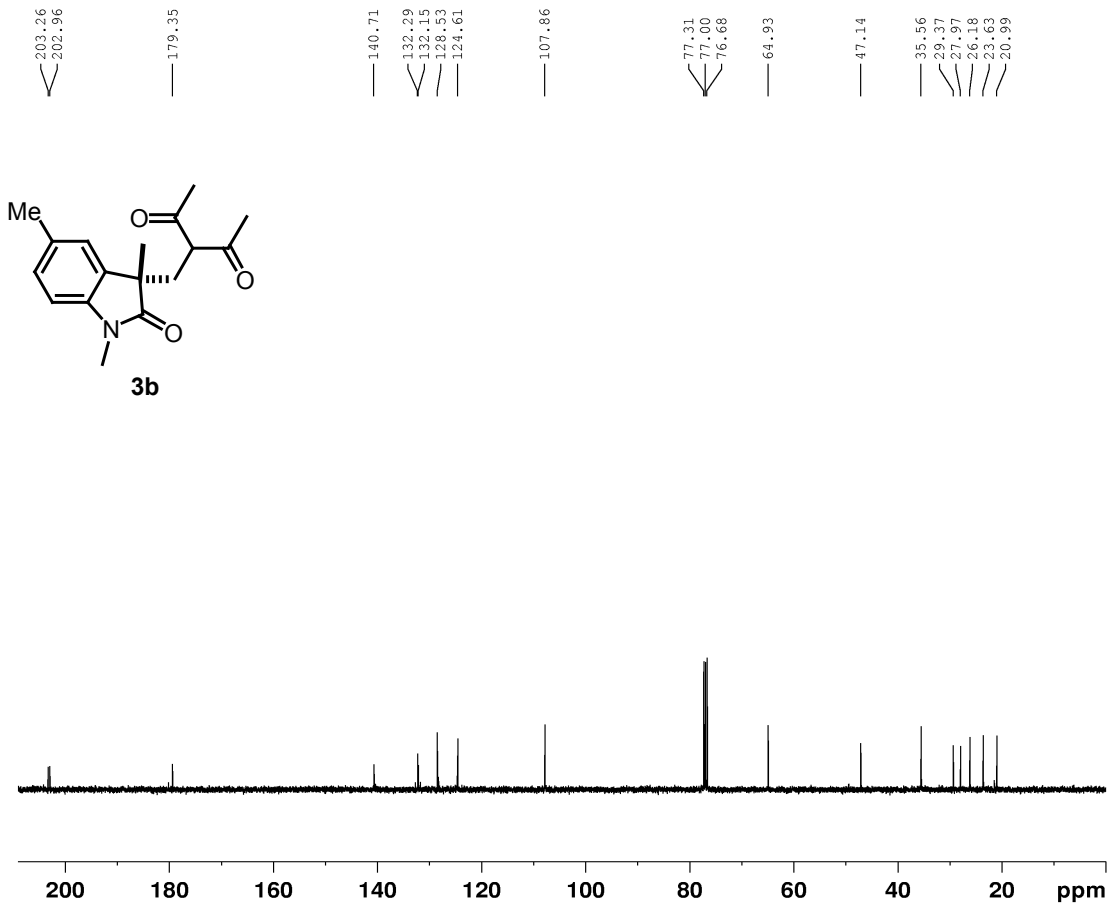
3.09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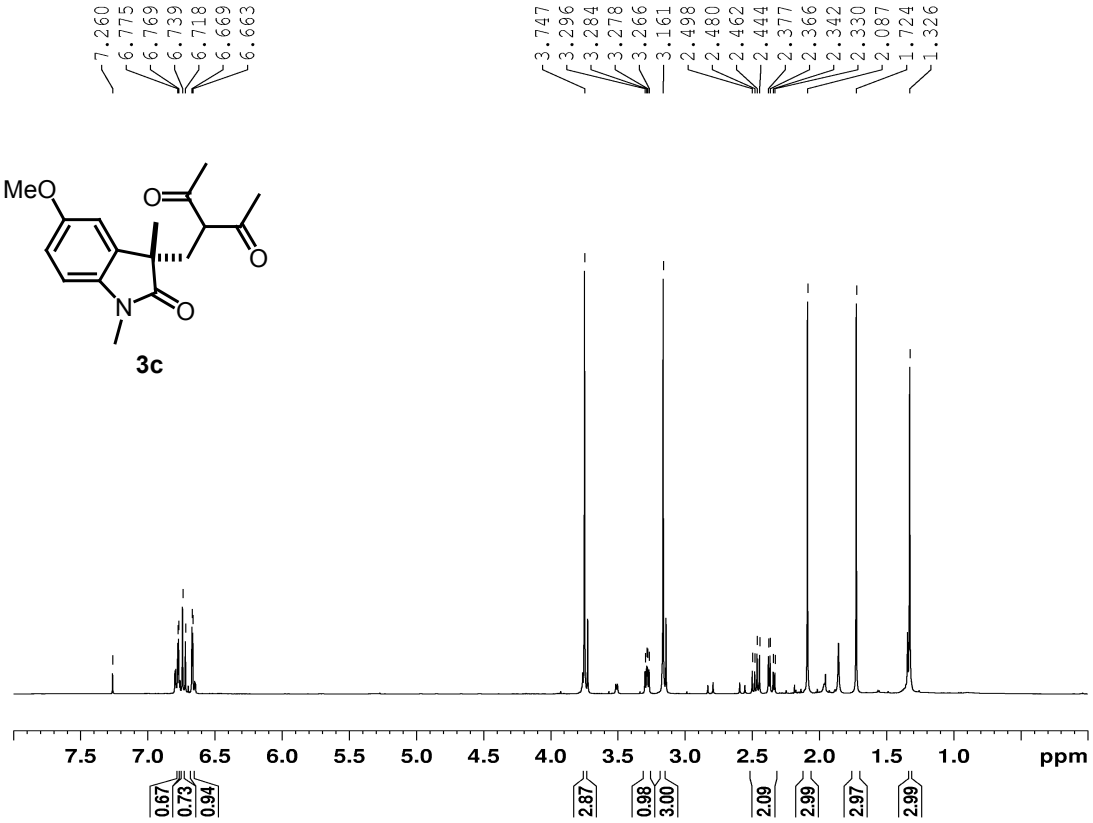
124.61
107.86
77.31
77.00
76.68
64.93
47.14
35.56
29.37
27.97
26.18
23.63
20.99
Me
O
O
N
O
3b
200
180
160
140
120
100
80
60
40
20
ppm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6.669
6.663
3.747
3.296
3.284
3.278
3.266
3.161
2.498
2.480
2.462
2.444
2.377
2.366
2.342
2.330
2.087
1.724
1.326
MeO
O
O
N
O
3c
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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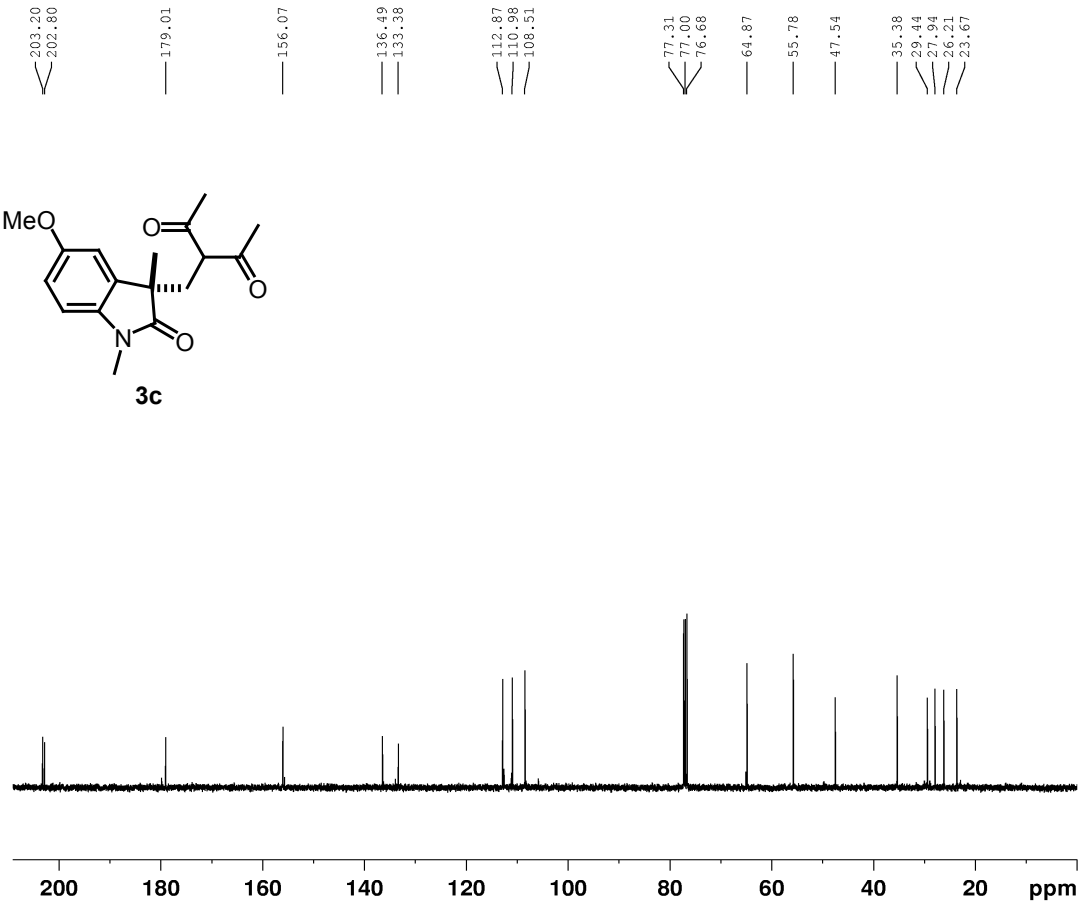
0.73
0.94
2.87
0.98
3.00
2.09
2.99
2.97
2.99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112.87
110.98
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77.31
77.00
76.68
64.87
55.78
47.54
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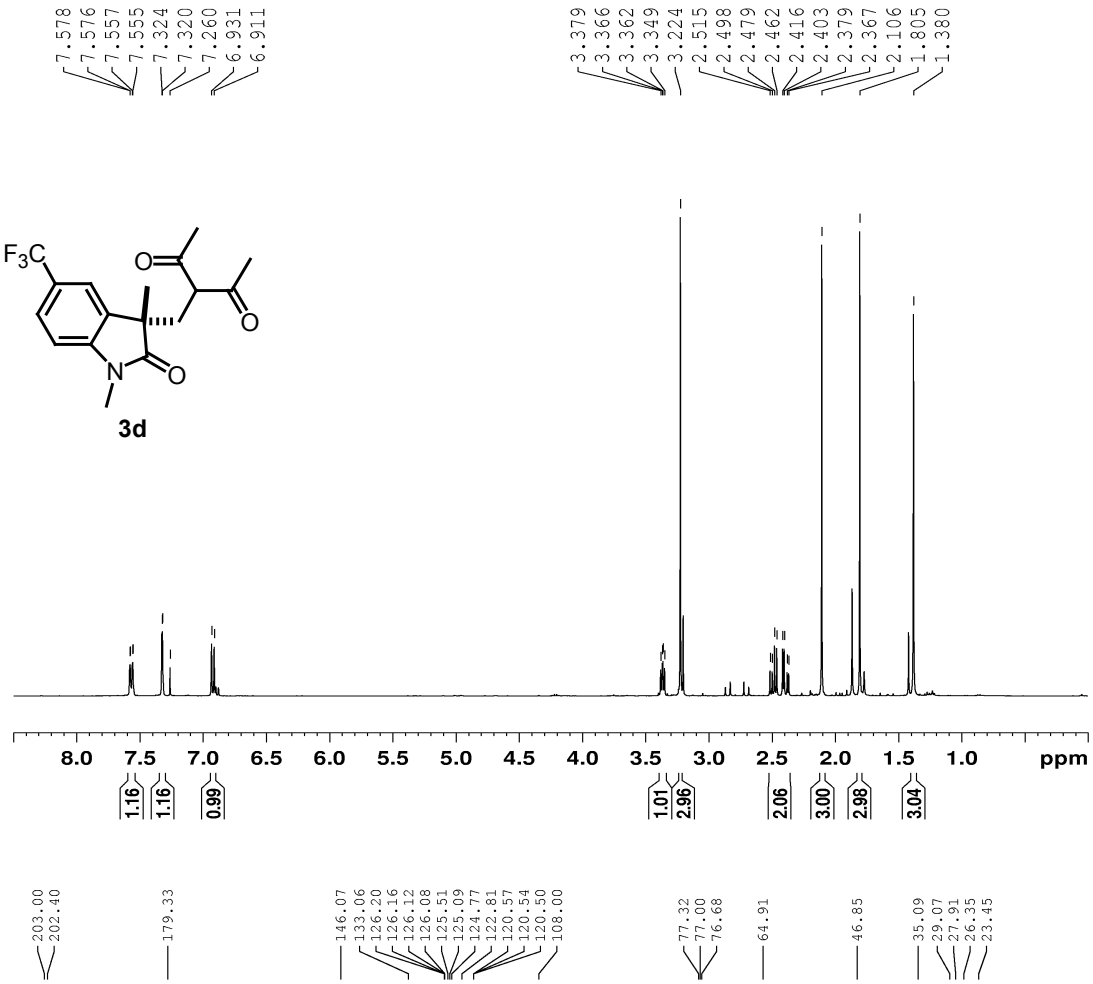
27.94
26.21
23.67
MeO
O
O
N
O
3c
200 180 160 140 120 100 80 60 40 20 ppm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7.557
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7.260
6.931
6.911
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3.366
3.362
3.349
3.224
2.515
2.498
2.479
2.462
2.416
2.403
2.379
2.367
2.106
1.805
1.380
F3C
O
O
N
O
3d
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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1.16
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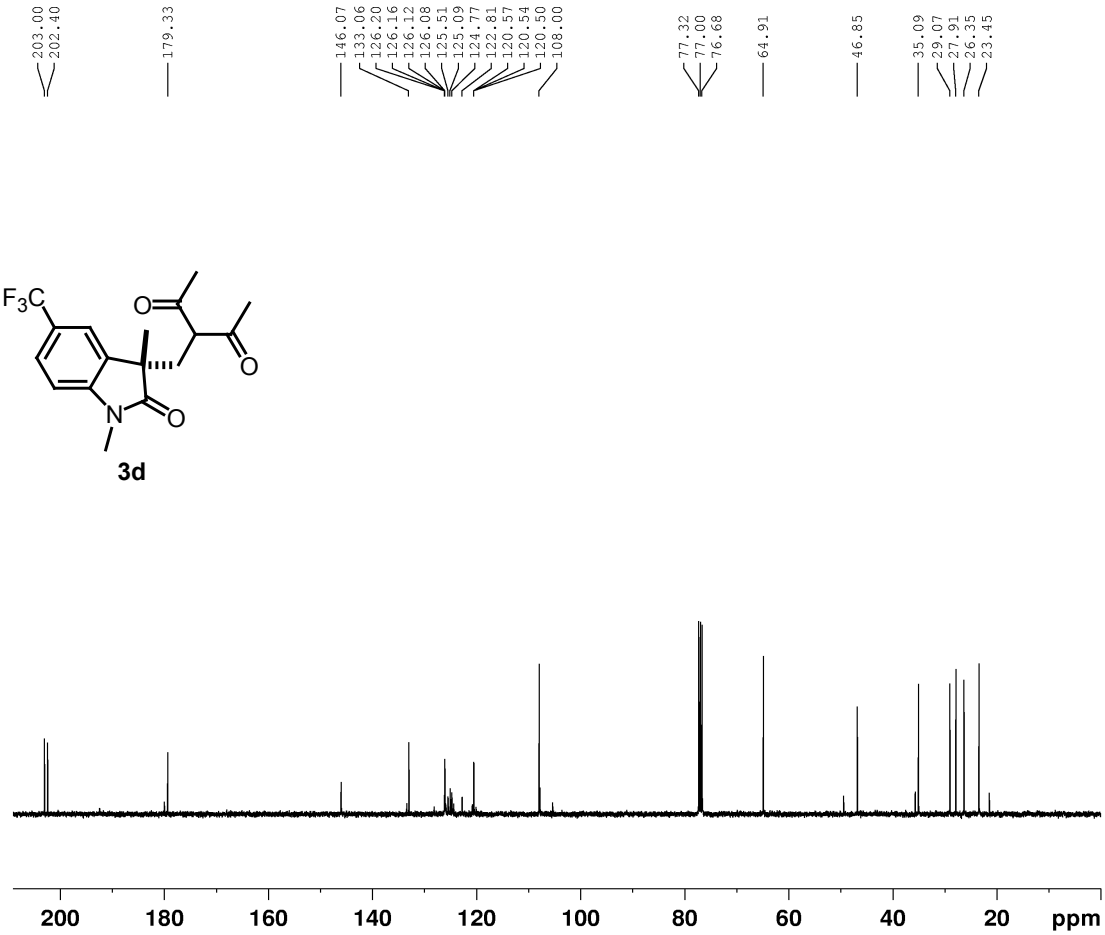
3.00
2.98
3.04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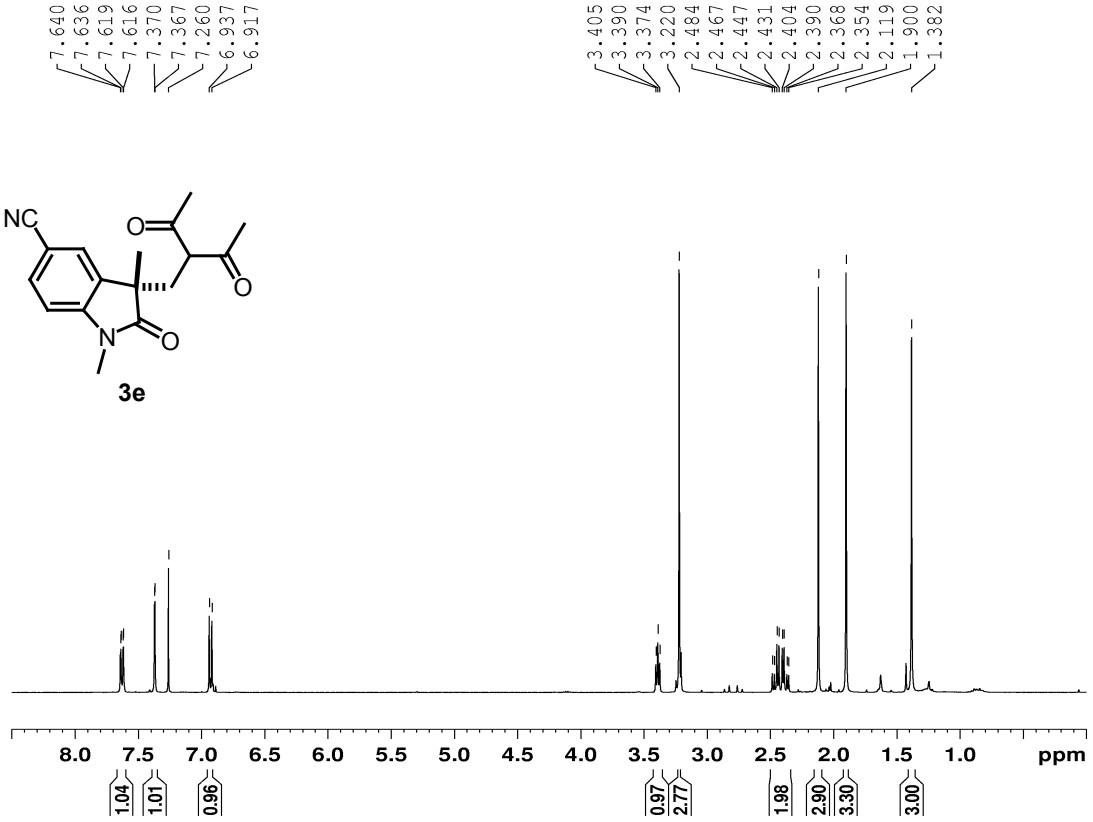
126.20
126.16
126.12
126.08
125.51
125.09
124.77
122.81
120.57
120.54
120.50
108.00
77.32
77.00
76.68
64.91
46.85
35.09
29.07
27.91
26.35
23.45
F3C
O
O
N
O
3d
200 180 160 140 120 100 80 60 40 20 ppm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7.367
7.260
6.937
6.917
3.405
3.390
3.374
3.220
2.484
2.467
2.447
2.431
2.404
2.390
2.368
2.354
2.119
1.900
1.382
NC
O
O
N
O
3e
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
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ppm
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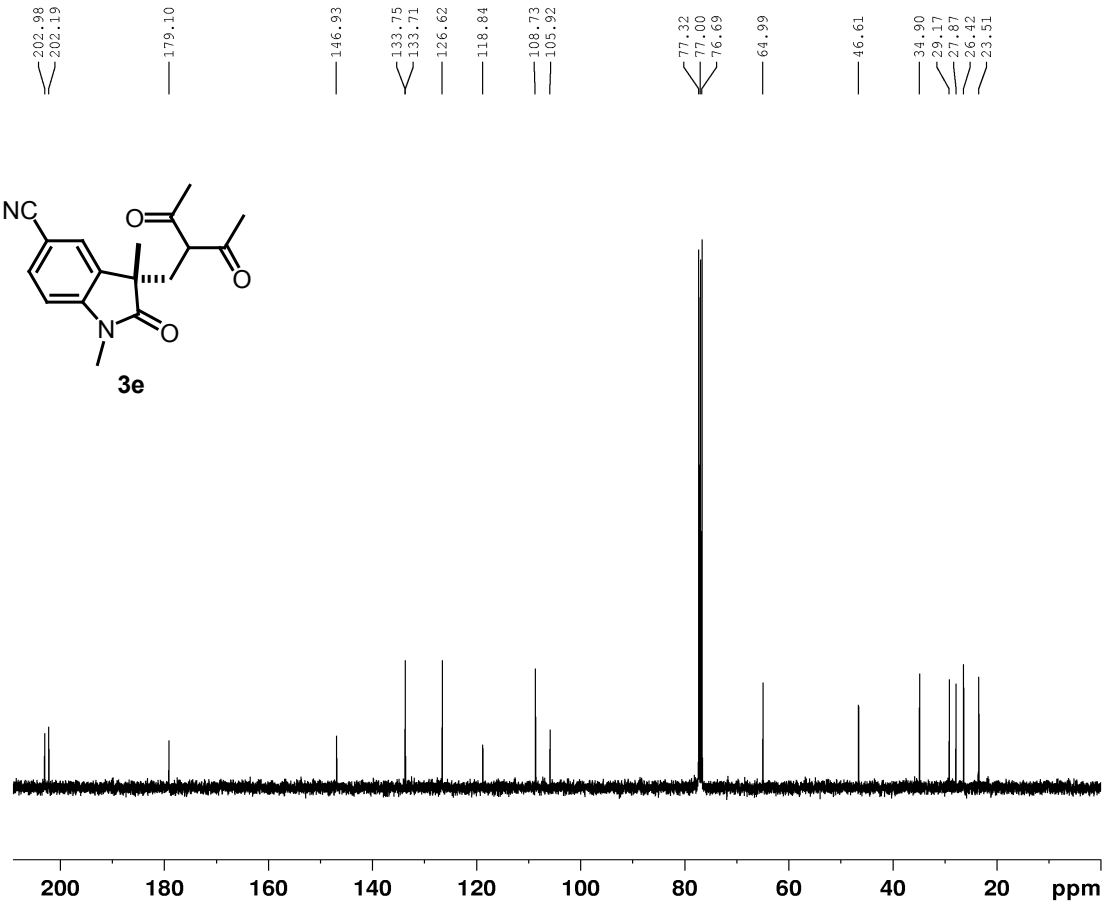
1.98
2.90
3.30
3.00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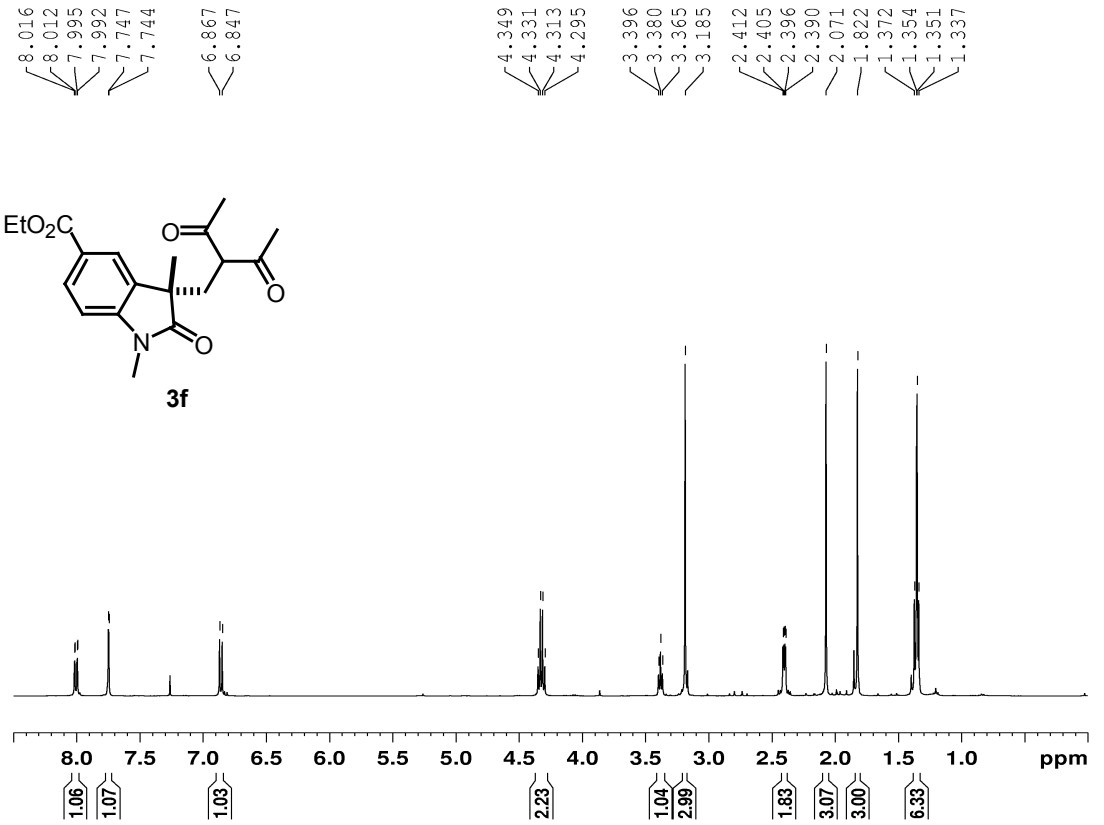
133.75
133.71
126.62
118.84
108.73
105.92
77.32
77.00
76.69
64.99
46.61
34.90
29.17
27.87
26.42
23.51
NC
O
O
N
O
3e
200
180
160
140
120
100
80
60
40
20
ppm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7.744
6.867
6.847
4.349
4.331
4.313
4.295
3.396
3.380
3.365
3.185
2.412
2.405
2.396
2.390
2.071
1.822
1.372
1.354
1.351
1.337
EtO2C
O
O
N
O
3f
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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1.07
1.03
2.23
1.04
2.99
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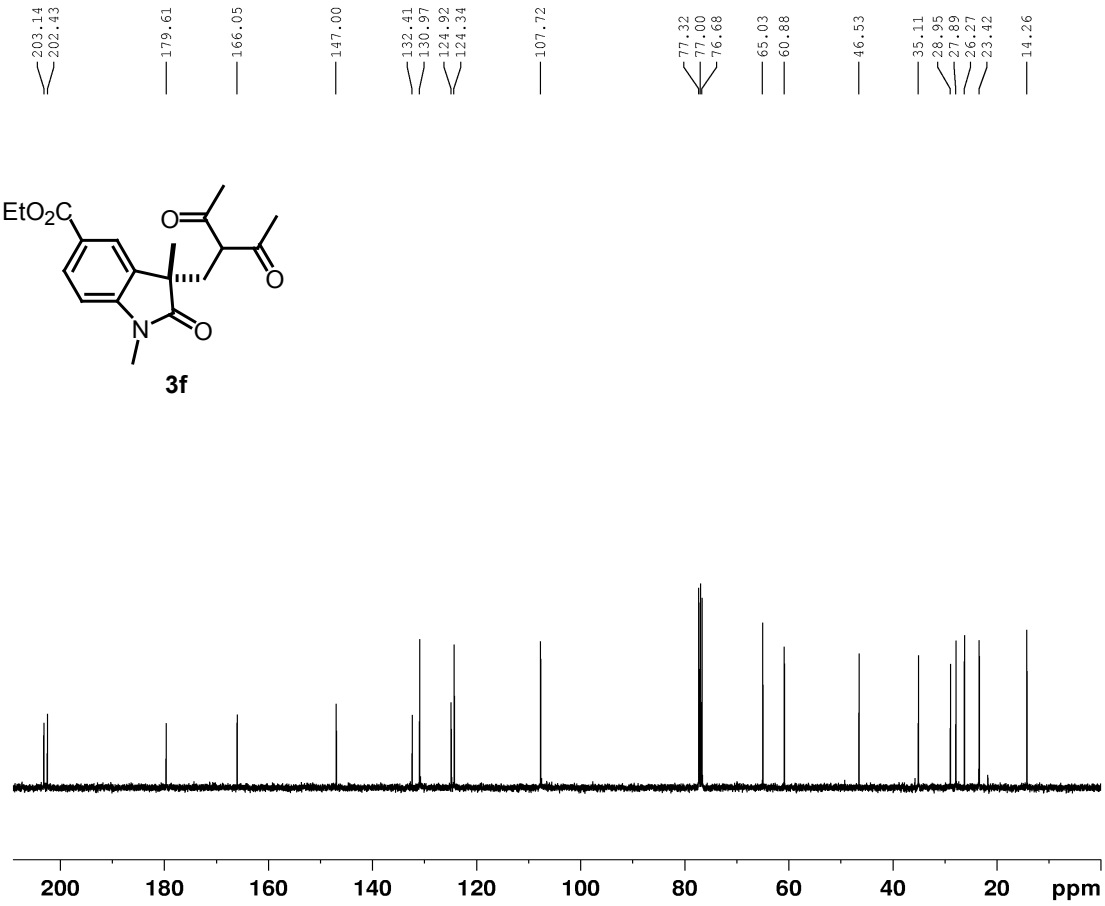
3.07
3.00
6.33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202.43
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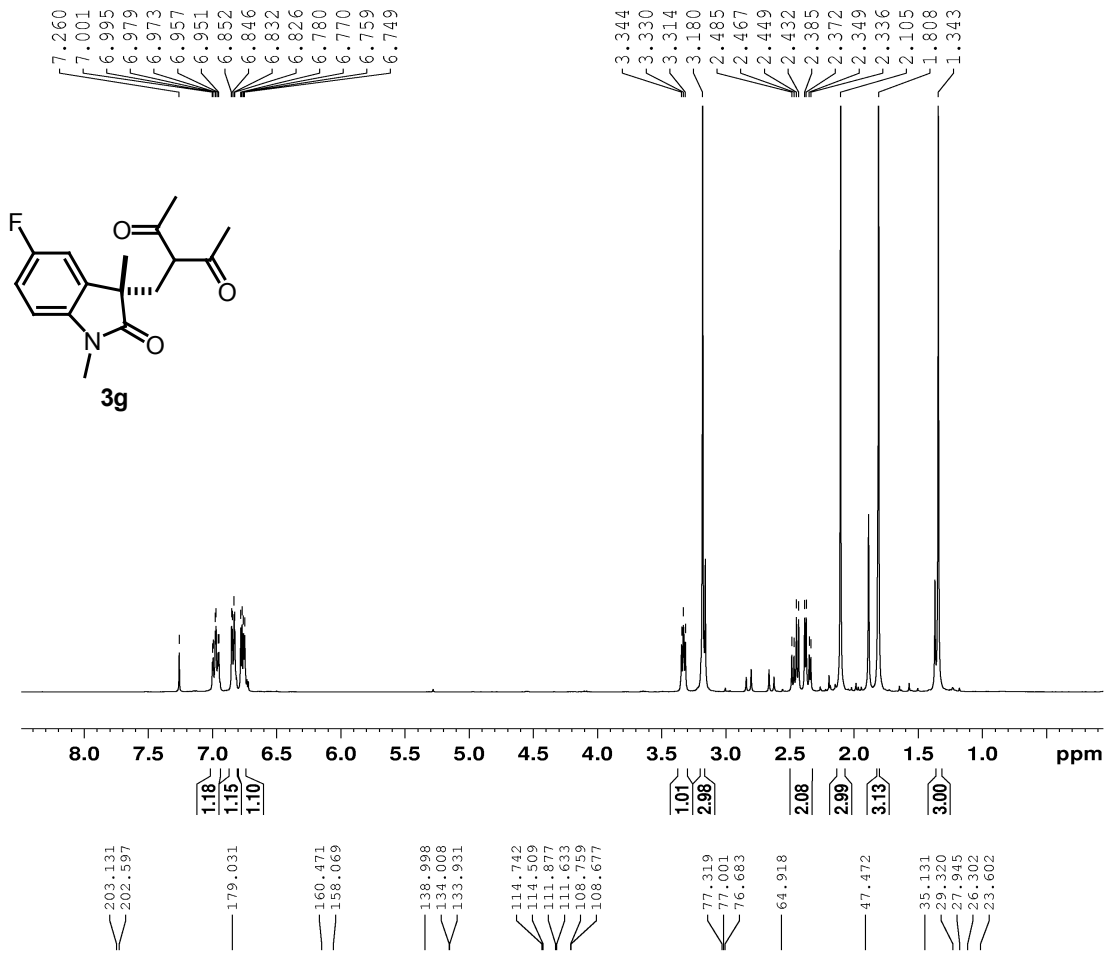
166.05
147.00
132.41
130.97
124.92
124.34
107.72
77.32
77.00
76.68
65.03
60.88
46.53
35.11
28.95
27.89
26.27
23.42
14.26
EtO2C
O
O
N
O
3f
200 180 160 140 120 100 80 60 40 20 ppm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6.979
6.973
6.957
6.951
6.852
6.846
6.832
6.826
6.780
6.770
6.759
6.749
3.344
3.330
3.314
3.180
2.485
2.467
2.449
2.432
2.385
2.372
2.349
2.336
2.105
1.808
1.343
F
O
O
N
O
3g
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
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ppm
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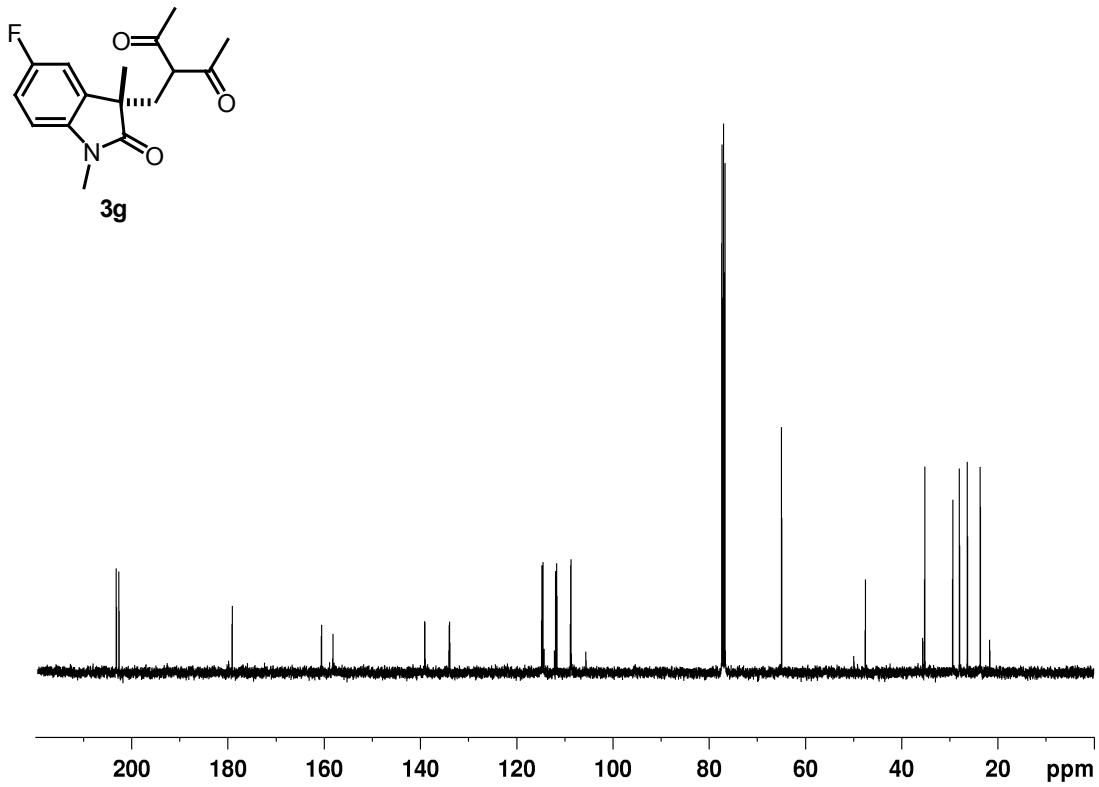
1.01
2.98
2.08
2.99
3.13
3.00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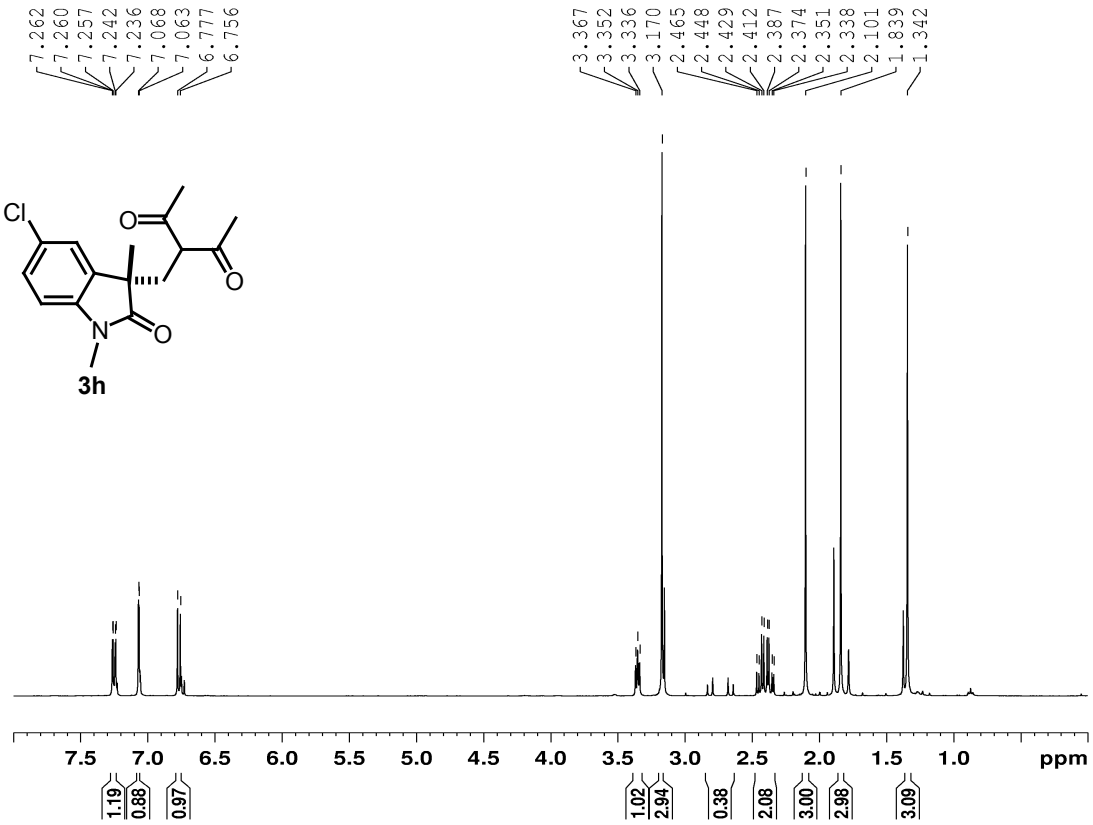
179.031
160.471
158.069
138.998
134.008
133.931
114.742
114.509
111.877
111.633
108.759
108.677
77.319
77.001
76.683
64.918
47.472
35.131
29.320
27.945
26.302
23.602
F
O
O
N
O
3g
200
180
160
140
120
100
80
60
40
20
ppm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7.236
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7.063
6.777
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3.367
3.352
3.336
3.170
2.465
2.448
2.429
2.412
2.387
2.374
2.351
2.338
2.101
1.839
1.342
Cl
O
O
N
O
3h
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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0.88
0.97
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0.38
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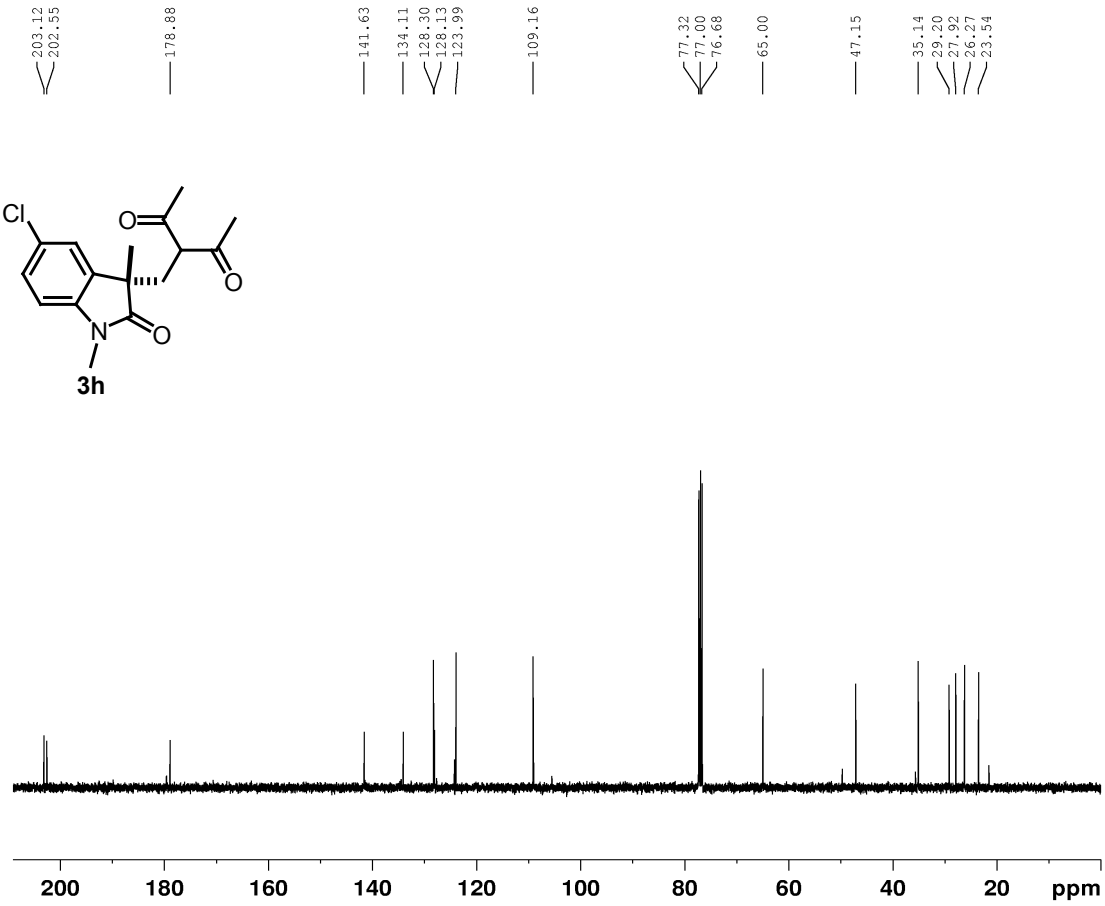
2.98
3.09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202.55
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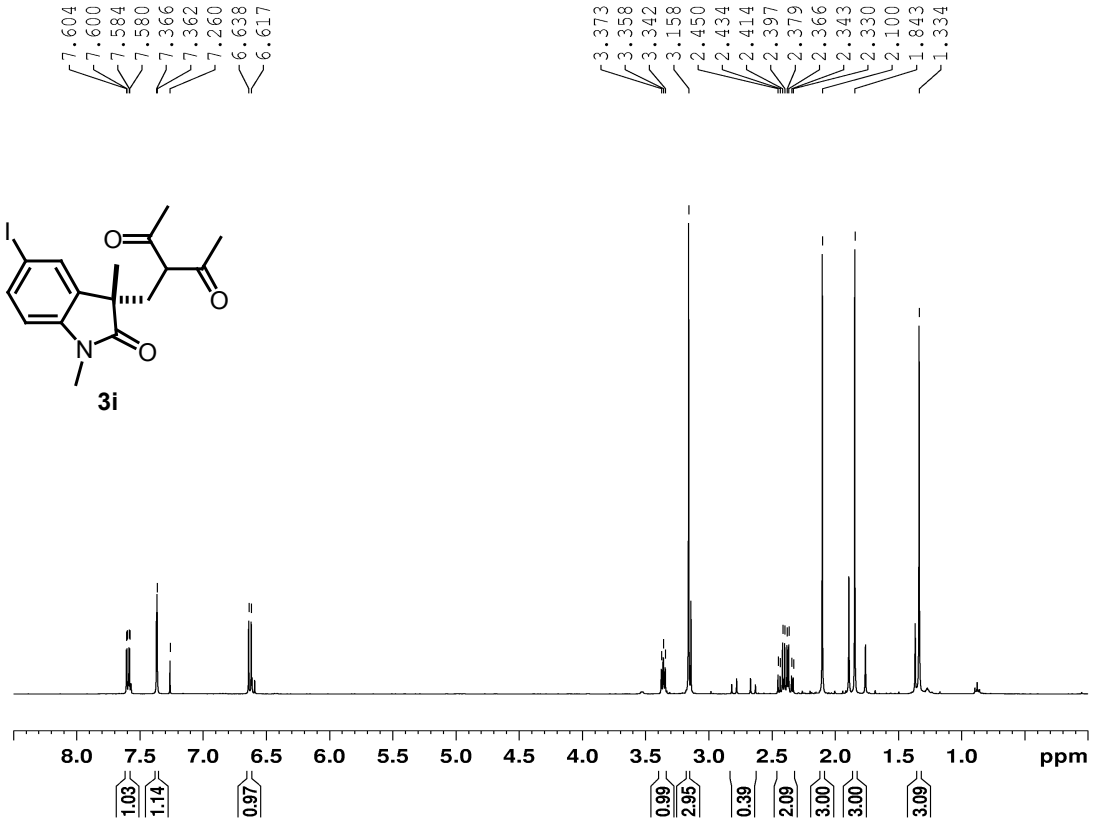
141.63
134.11
128.30
128.13
123.99
109.16
77.32
77.00
76.68
65.00
47.15
35.14
29.20
27.92
26.27
23.54
Cl
O
O
N
O
3h
200
180
160
140
120
100
80
60
40
20
ppm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7.584
7.580
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7.362
7.260
6.638
6.617
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3.358
3.342
3.158
2.450
2.434
2.414
2.397
2.379
2.366
2.343
2.330
2.100
1.843
1.334
I
O
O
N
O
3i
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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1.14
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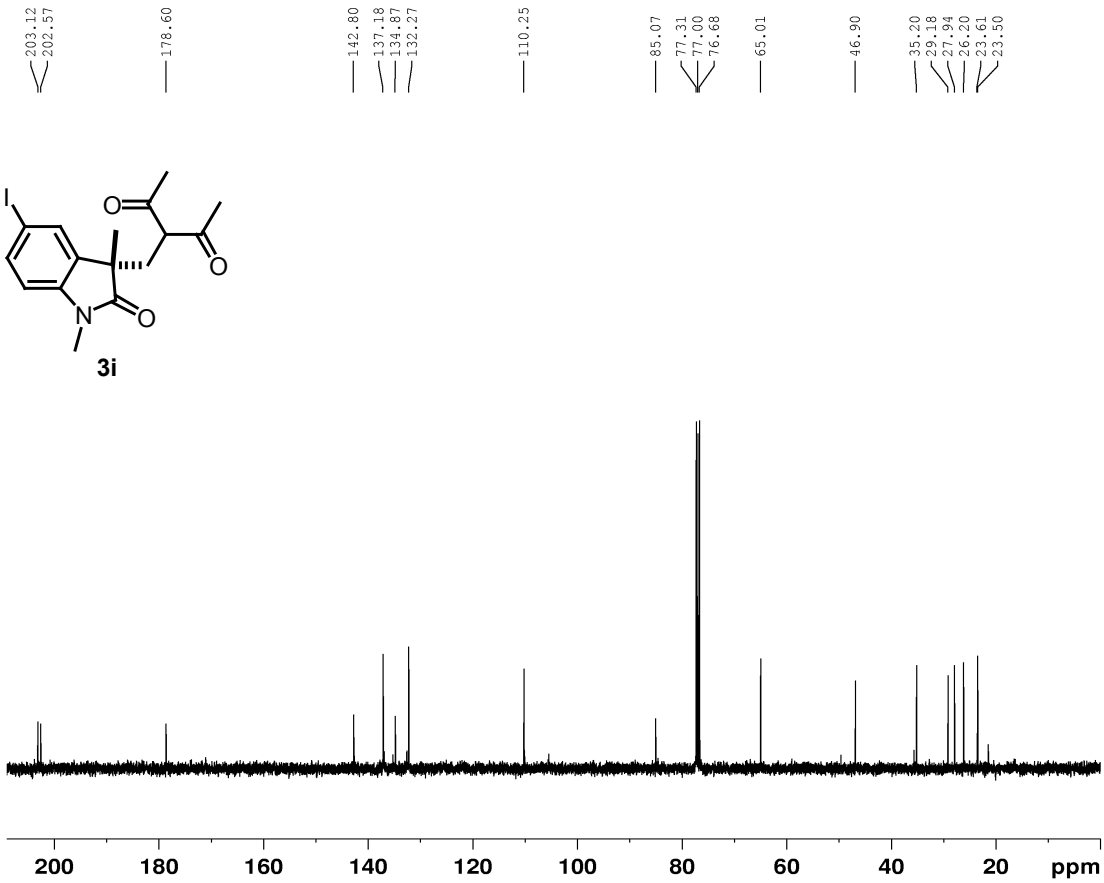
0.39
2.09
3.00
3.00
3.09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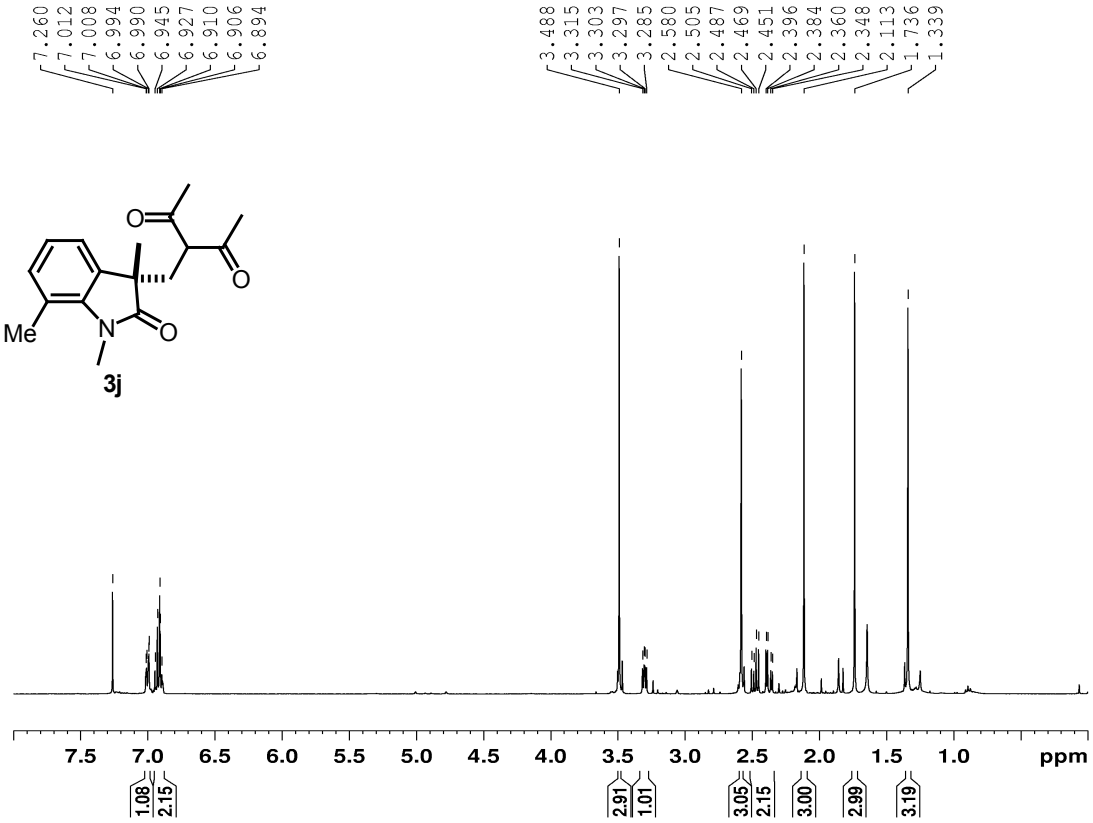
132.27
110.25
85.07
77.31
77.00
76.68
65.01
46.90
35.20
29.18
27.94
26.20
23.61
23.50
I
O
O
N
O
3i
200 180 160 140 120 100 80 60 40 20 ppm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6.910
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6.894
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3.315
3.303
3.297
3.285
2.580
2.505
2.487
2.469
2.451
2.396
2.384
2.360
2.348
2.113
1.736
1.339
Me
N
O
3j
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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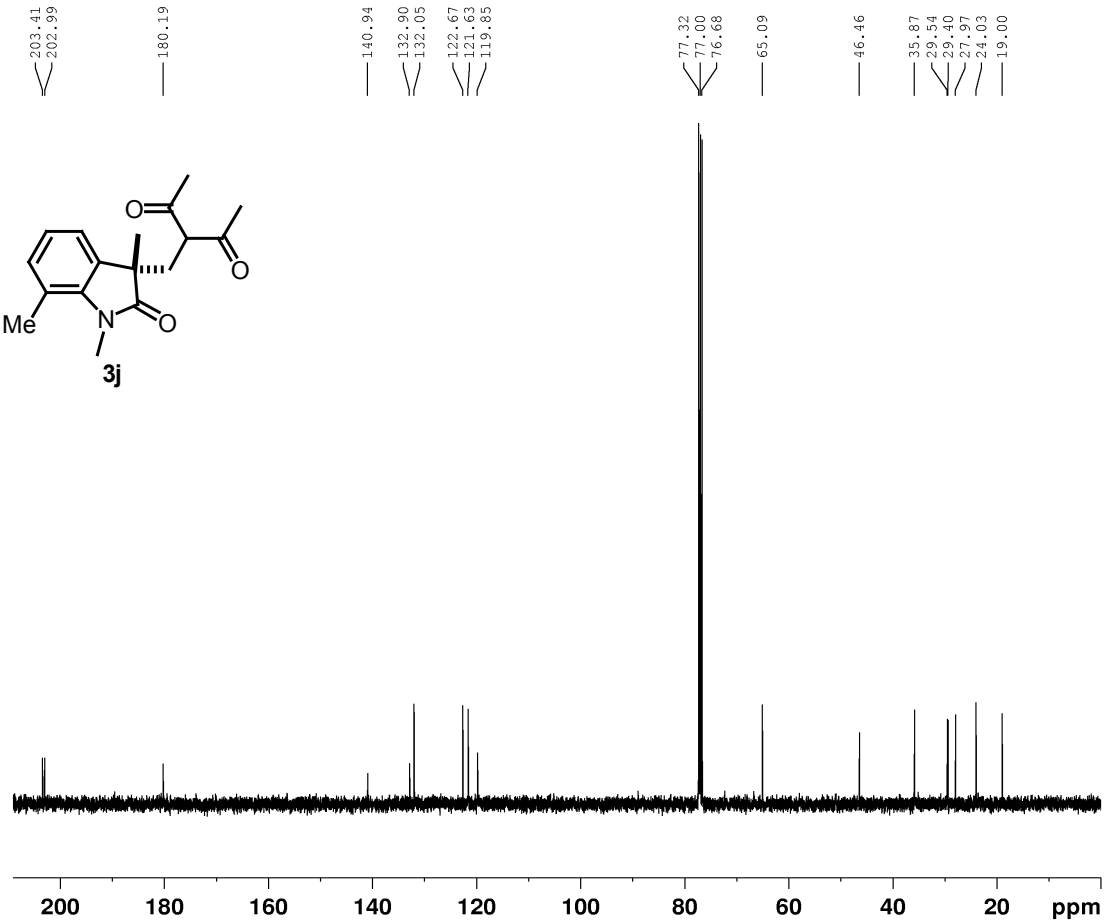
3.19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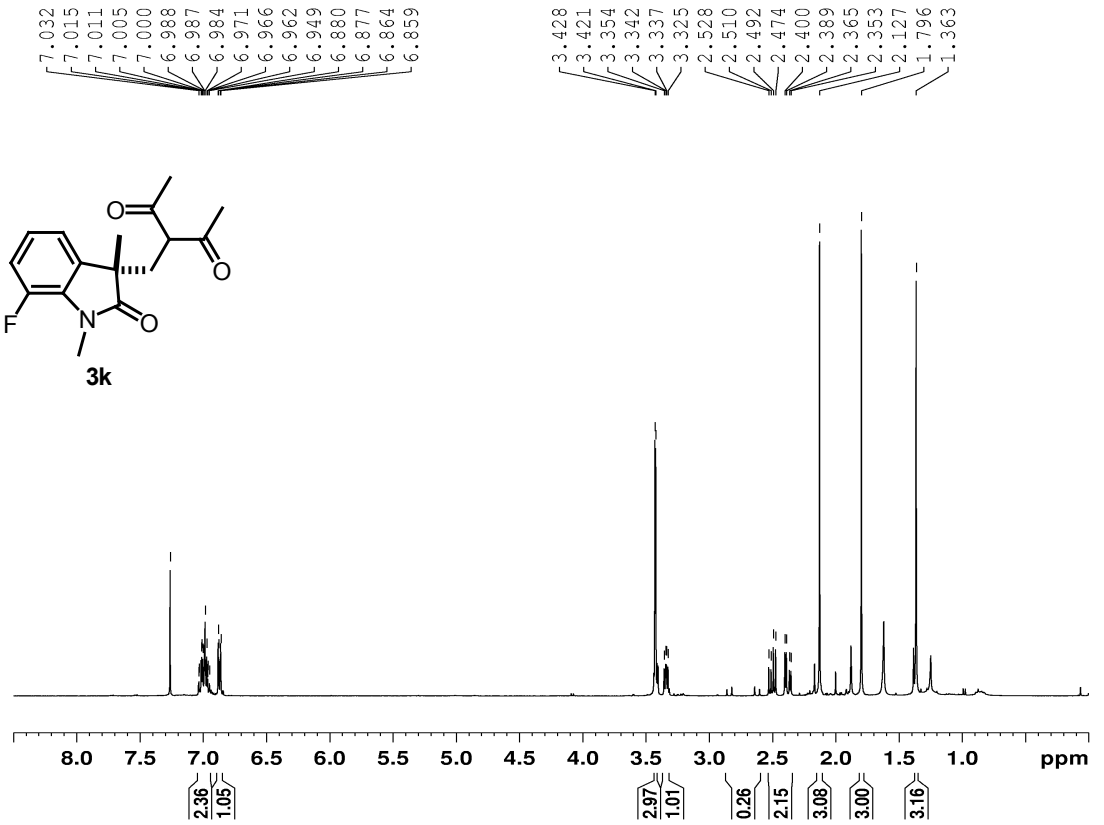
77.32
77.00
76.68
65.09
46.46
35.87
29.54
29.40
27.97
24.03
19.00
Me
N
O
3j
200 180 160 140 120 100 80 60 40 20 ppm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6.966
6.962
6.949
6.880
6.877
6.864
6.859
3.428
3.421
3.354
3.342
3.337
3.325
2.528
2.510
2.492
2.474
2.400
2.389
2.365
2.353
2.127
1.796
1.363
O
O
F
N
O
3k
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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ppm
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0.26
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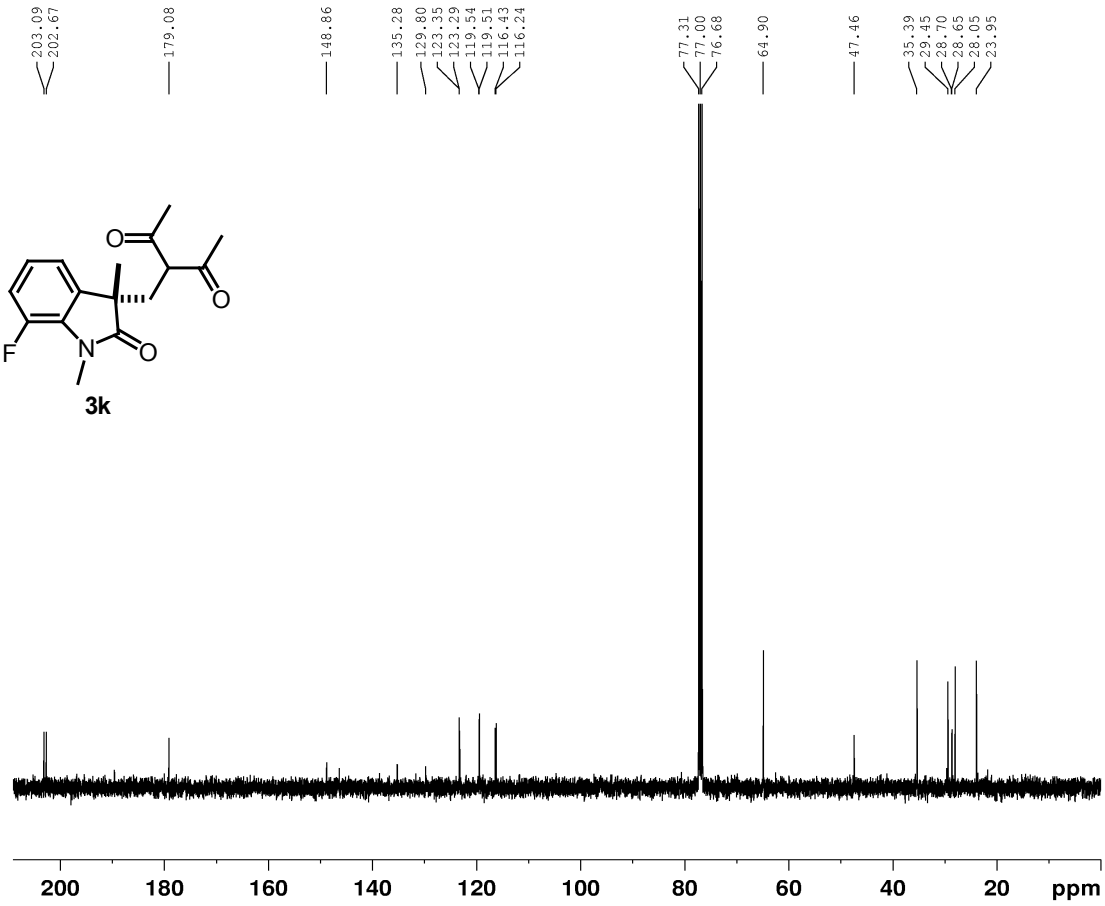
3.16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119.51
116.43
116.24
77.31
77.00
76.68
64.90
47.46
35.39
29.45
28.70
28.65
28.05
23.95
O
O
F
N
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3k
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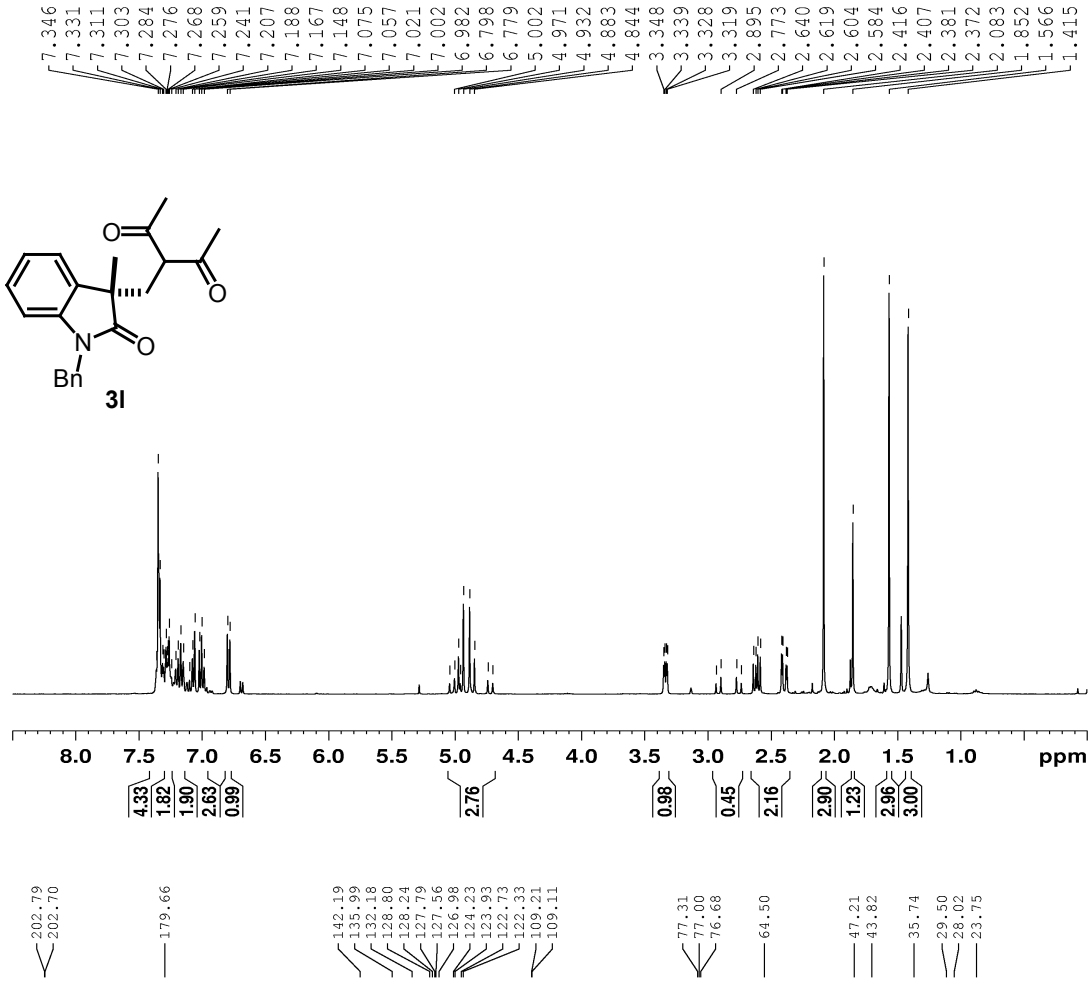
140
120
100
80
60
40
20
ppm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7.188
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7.148
7.075
7.057
7.021
7.002
6.982
6.798
6.779
5.002
4.971
4.932
4.883
4.844
3.348
3.339
3.328
3.319
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2.619
2.604
2.584
2.416
2.407
2.381
2.372
2.083
1.852
1.566
1.415
O
O
N
O
Bn
3l
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
4.33
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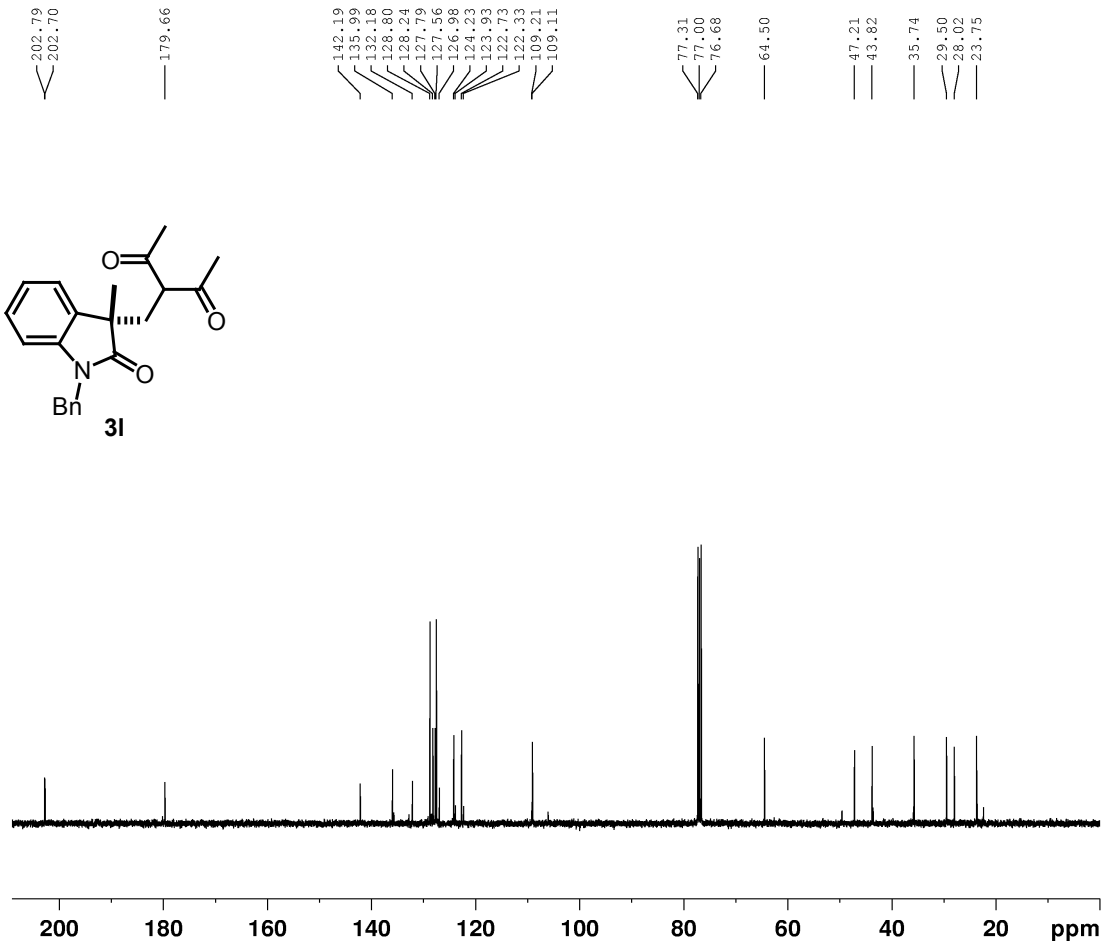
1.23
2.96
3.00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128.24
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127.56
126.98
124.23
123.93
122.73
122.33
109.21
109.11
77.31
77.00
76.68
64.50
47.21
43.82
35.74
29.50
28.02
23.75
O
O
N
O
Bn
3l
200
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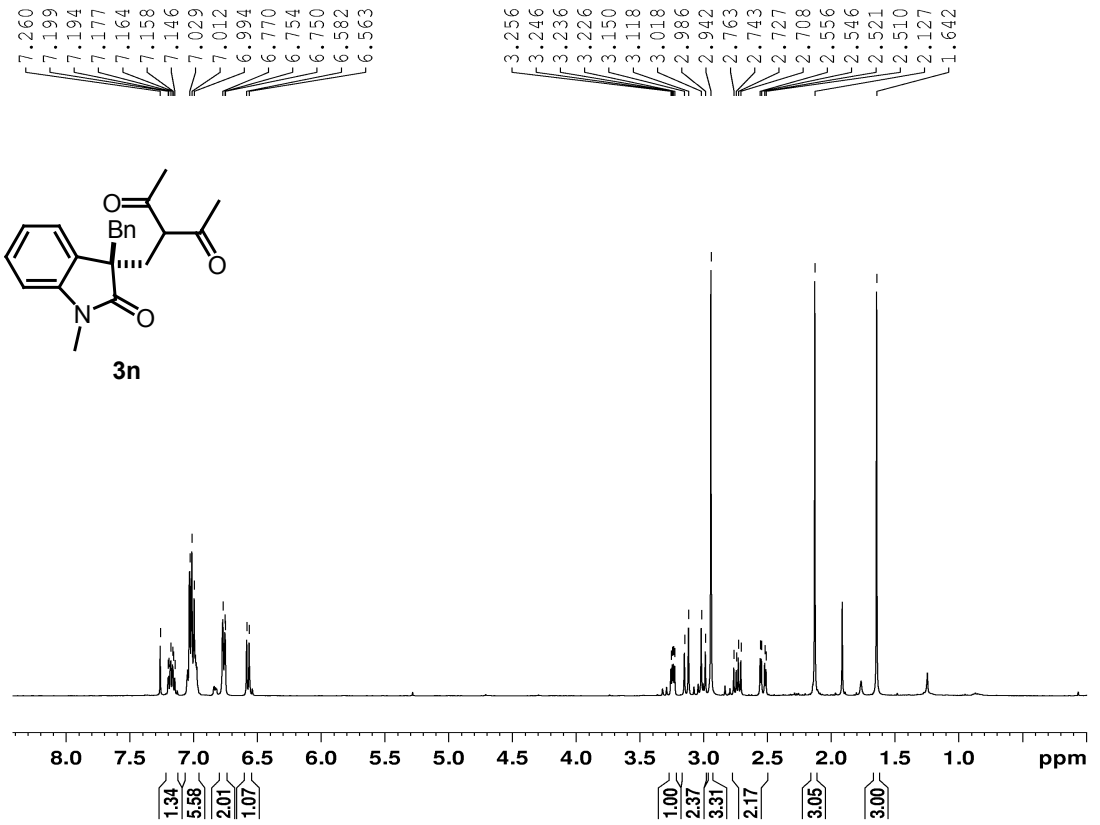
160
140
120
100
80
60
40
20
ppm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6.770
6.754
6.750
6.582
6.563
3.256
3.246
3.236
3.226
3.150
3.118
3.018
2.986
2.942
2.763
2.743
2.727
2.708
2.556
2.546
2.521
2.510
2.127
1.642
O
Bn
O
N
O
3n
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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ppm
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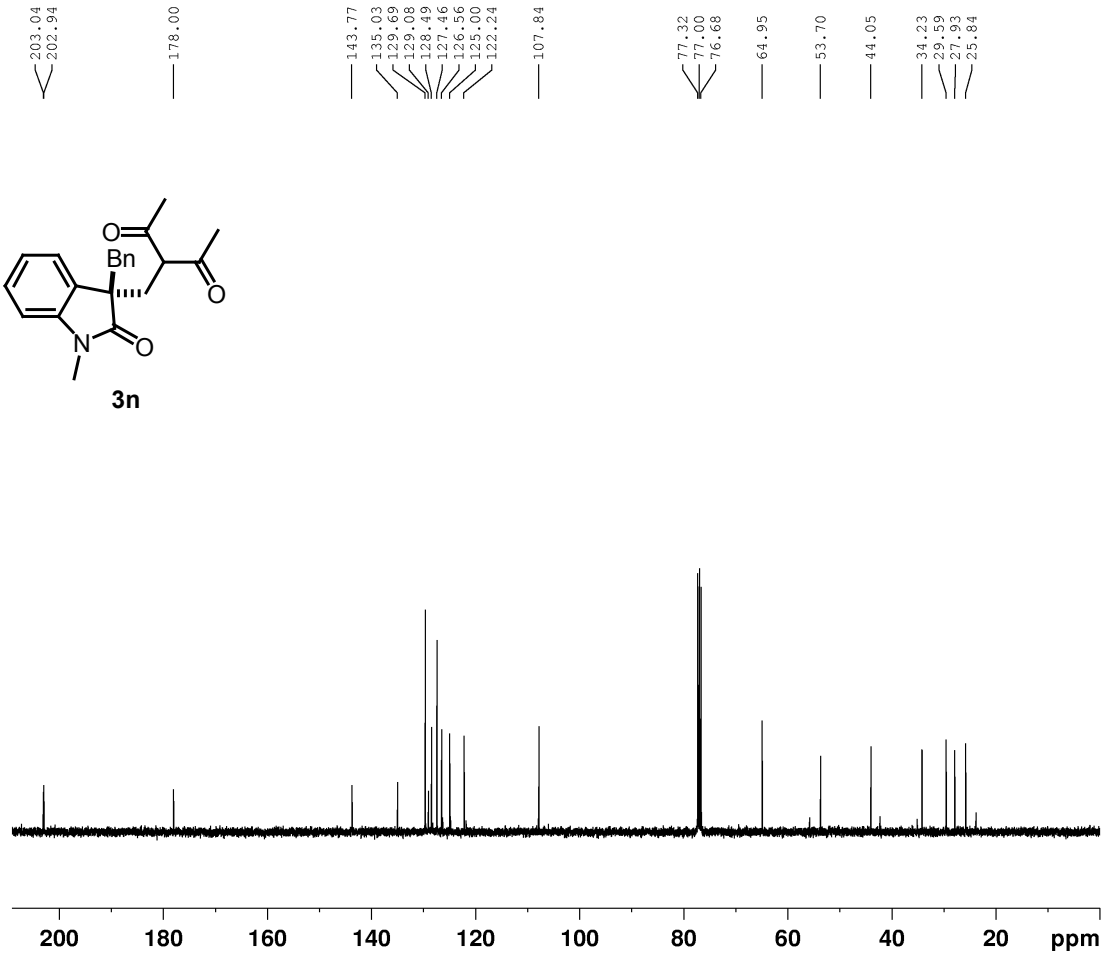
2.17
3.05
3.00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128.49
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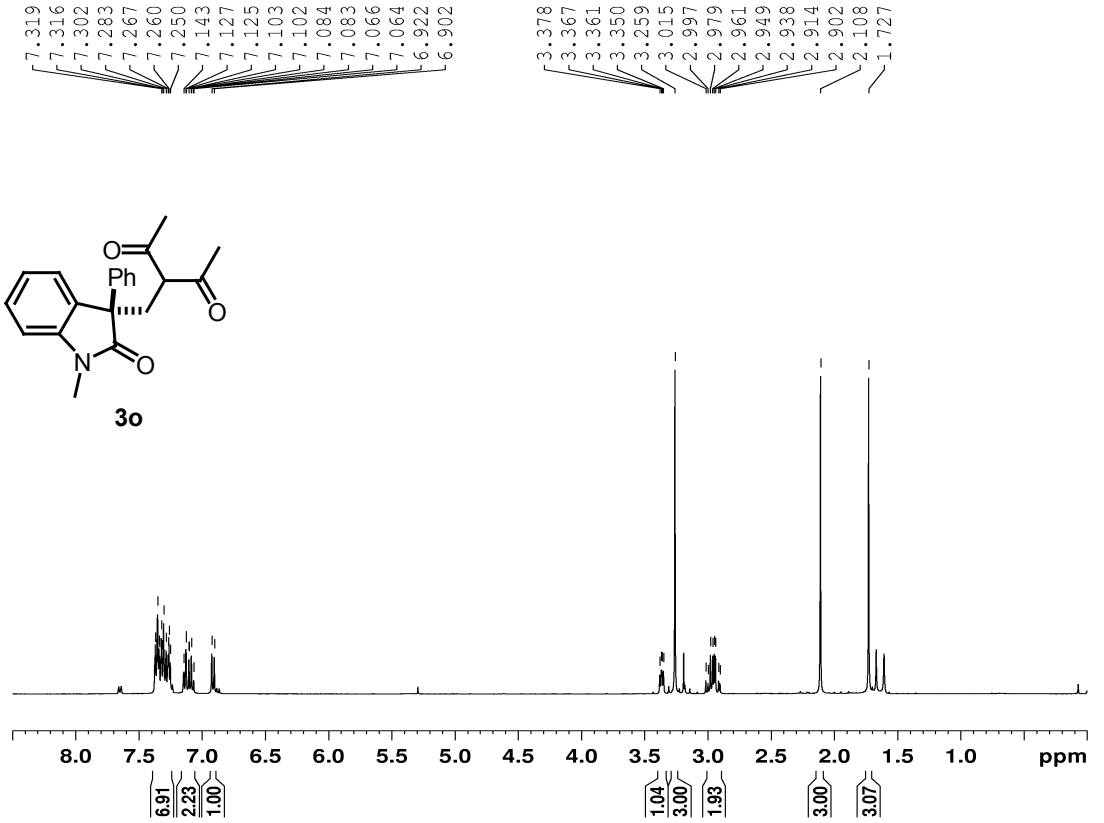
126.56
125.00
122.24
107.84
77.32
77.00
76.68
64.95
53.70
44.05
34.23
29.59
27.93
25.84
O
Bn
O
N
O
3n
200
180
160
140
120
100
80
60
40
20
ppm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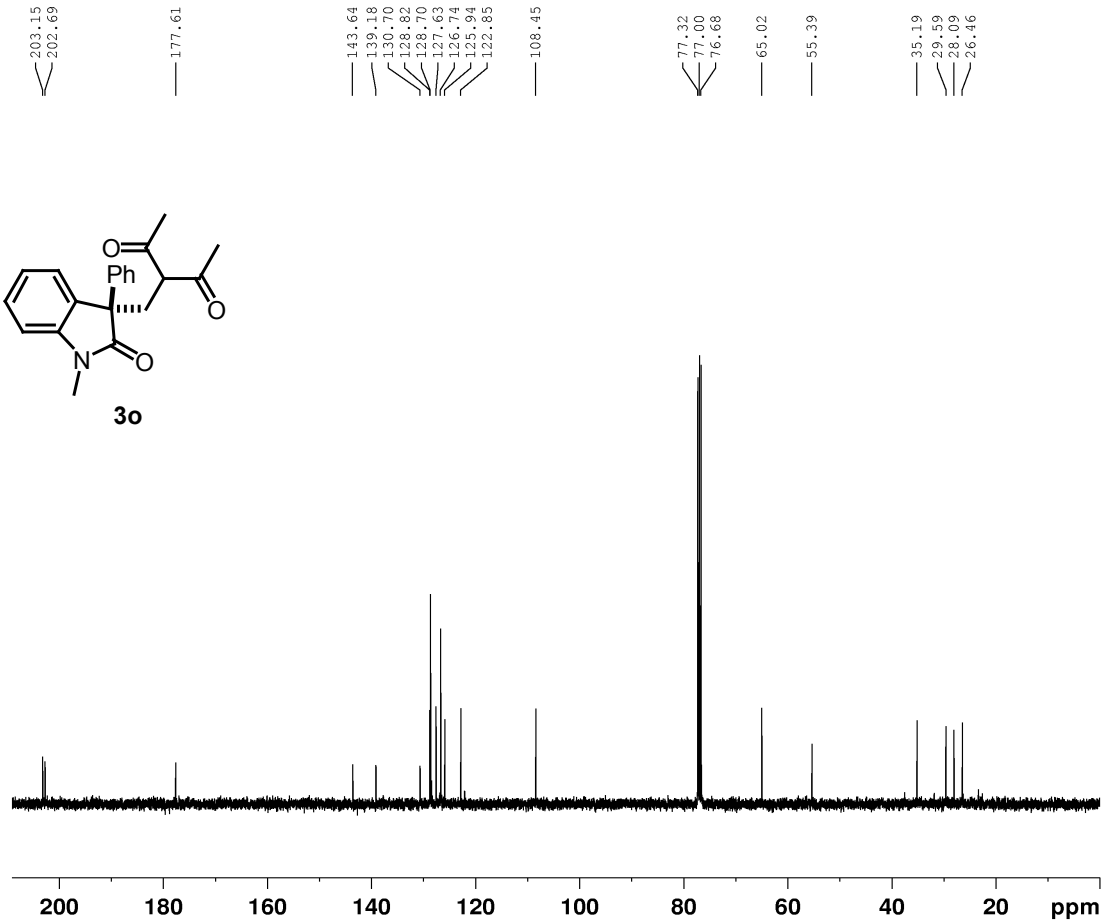
7.316
7.302
7.283
7.267
7.260
7.250
7.143
7.127
7.125
7.103
7.102
7.084
7.083
7.066
7.064
6.922
6.902
3.378
3.367
3.361
3.350
3.259
3.015
2.997
2.979
2.961
2.949
2.938
2.914
2.902
2.108
1.727
Ph
N
O
3o
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
6.91
2.23
1.00
1.04
3.00
1.93
3.00
3.07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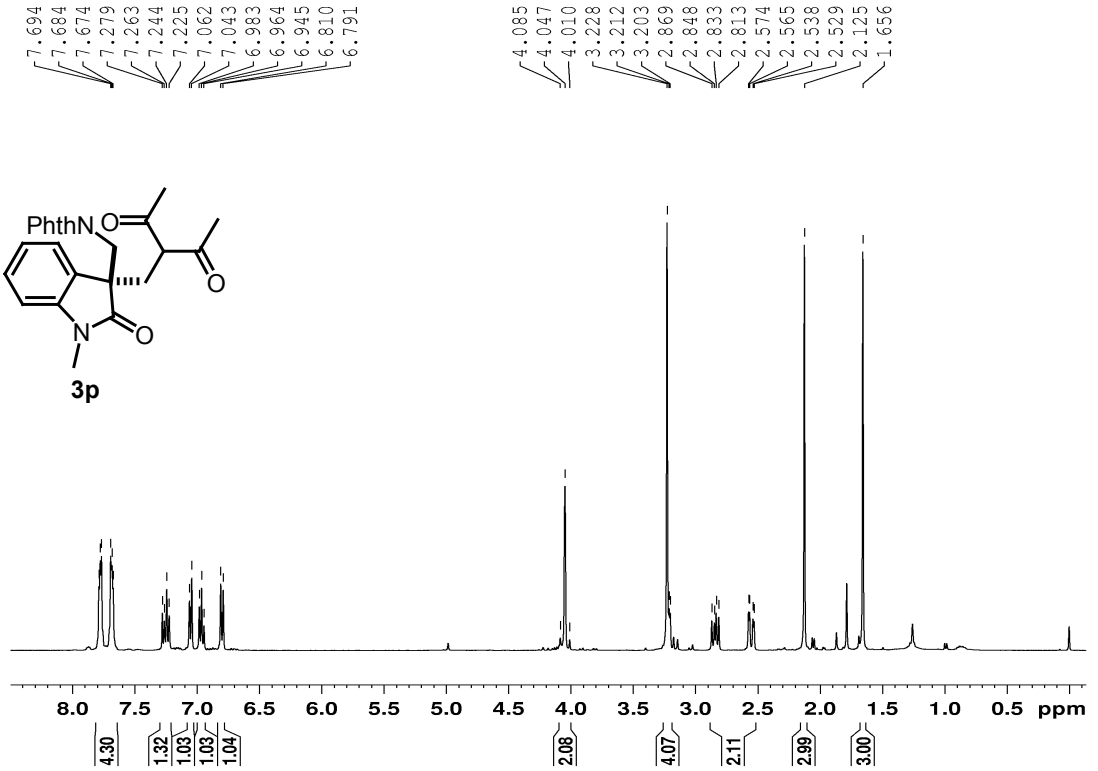
202.69
177.61
143.64
139.18
130.70
128.82
128.70
127.63
126.74
125.94
122.85
108.45
77.32
77.00
76.68
65.02
55.39
35.19
29.59
28.09
26.46
Ph
N
O
3o
200 180 160 140 120 100 80 60 40 20 ppm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7.684
7.674
7.279
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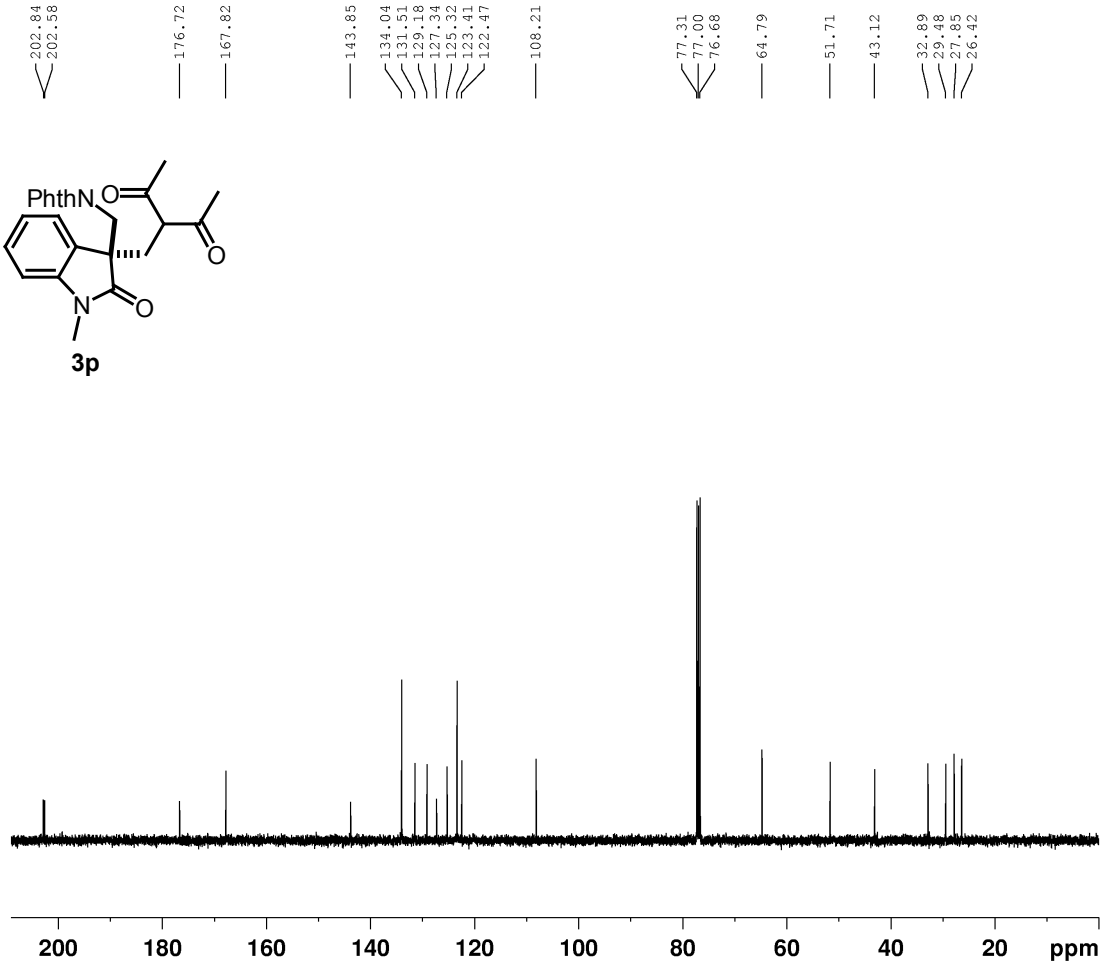
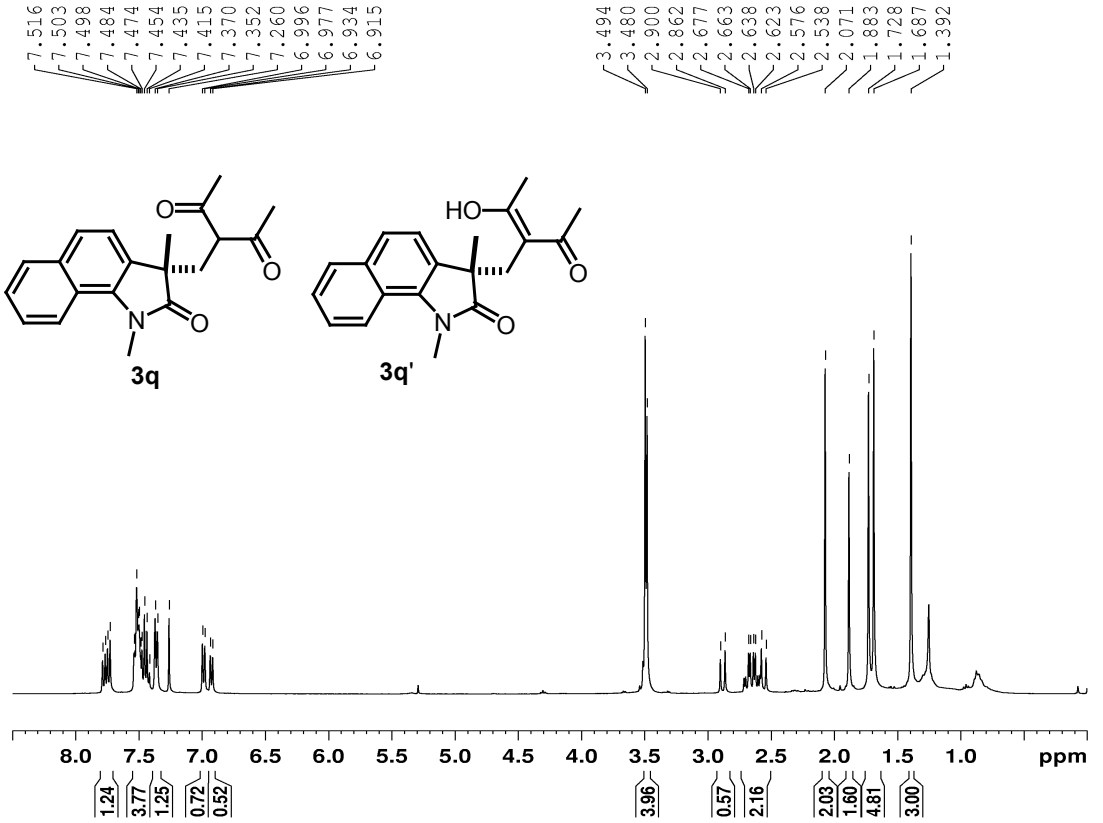
7.244
7.225
7.062
7.043
6.983
6.964
6.945
6.810
6.791
4.085
4.047
4.010
3.228
3.212
3.203
2.869
2.848
2.833
2.813
2.574
2.565
2.538
2.529
2.125
1.656
PhthN
O
O
N
O
3p
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.30
1.32
1.03
1.03
1.04
2.08
4.07
2.11
2.99
3.00


202.84
202.58
176.72
167.82
143.85
134.04
131.51
129.18
127.34
125.32
123.41
122.47
108.21
77.31
77.00
76.68
64.79
51.71
43.12
32.89
29.48
27.85
26.42
PhthN
O
O
N
O
3p
200 180 160 140 120 100 80 60 40 20 ppm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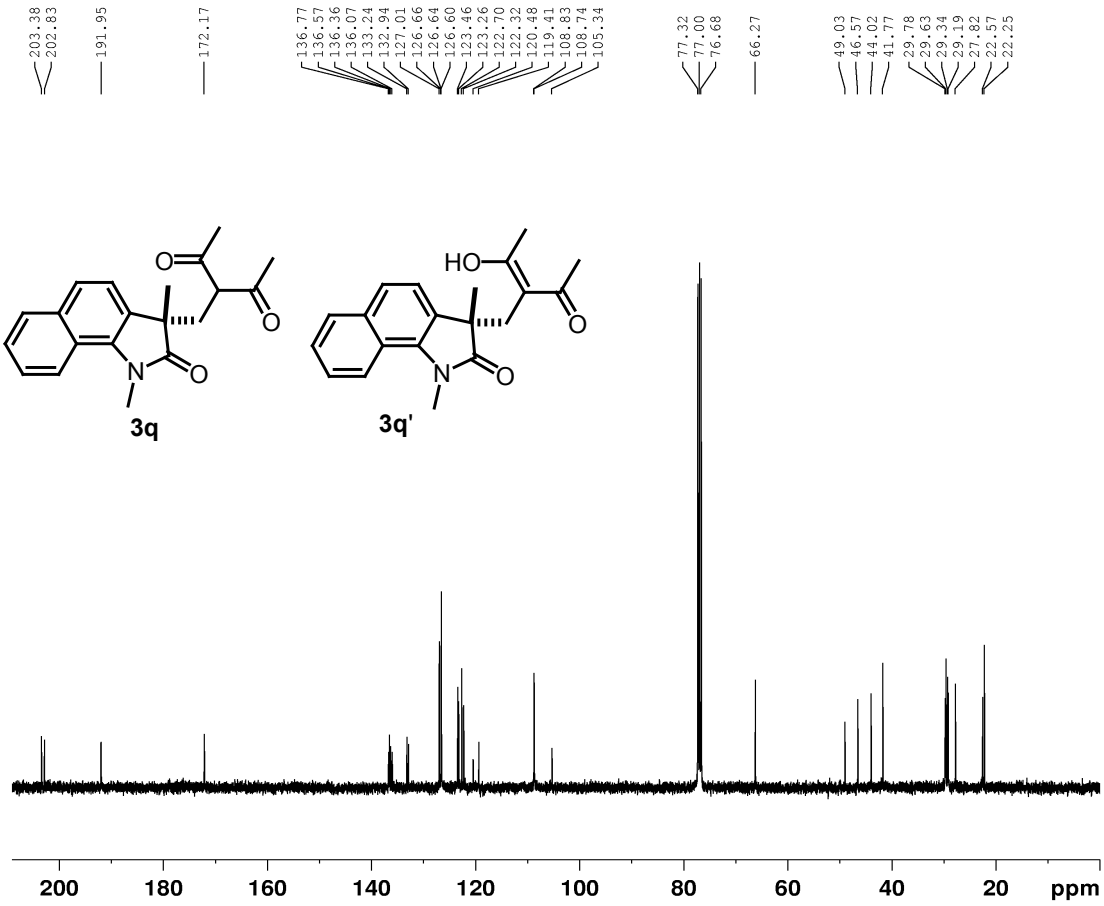
7.503
7.498
7.484
7.474
7.454
7.435
7.415
7.370
7.352
7.260
6.996
6.977
6.934
6.915
3.494
3.480
2.900
2.862
2.677
2.663
2.638
2.623
2.576
2.538
2.071
1.883
1.728
1.687
1.392
3q
3q'
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.24
3.77
1.25
0.72
0.52
3.96
0.57
2.16
2.03
1.60
4.81
3.00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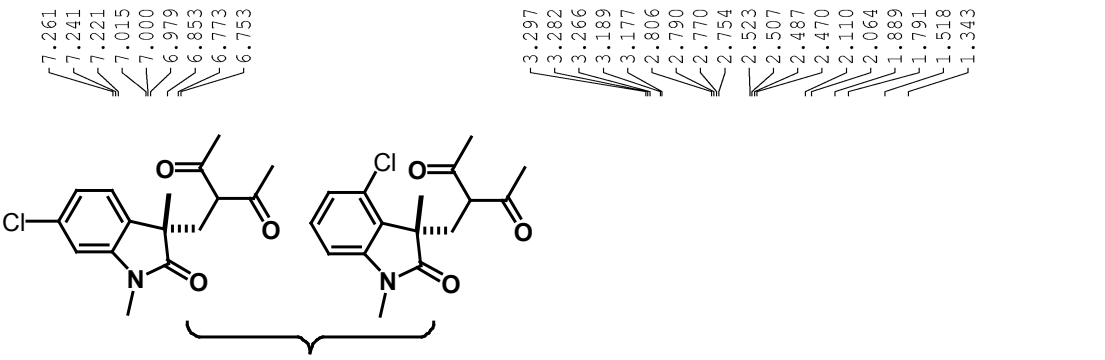
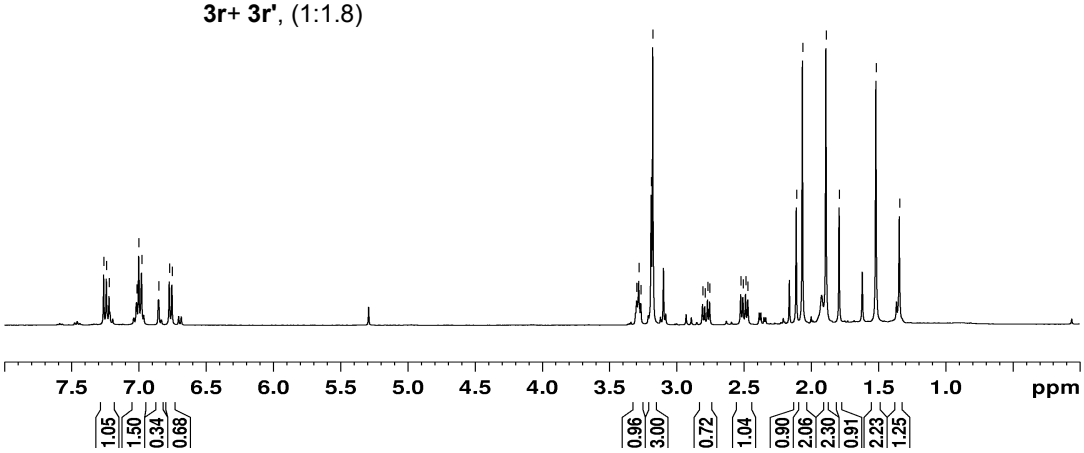
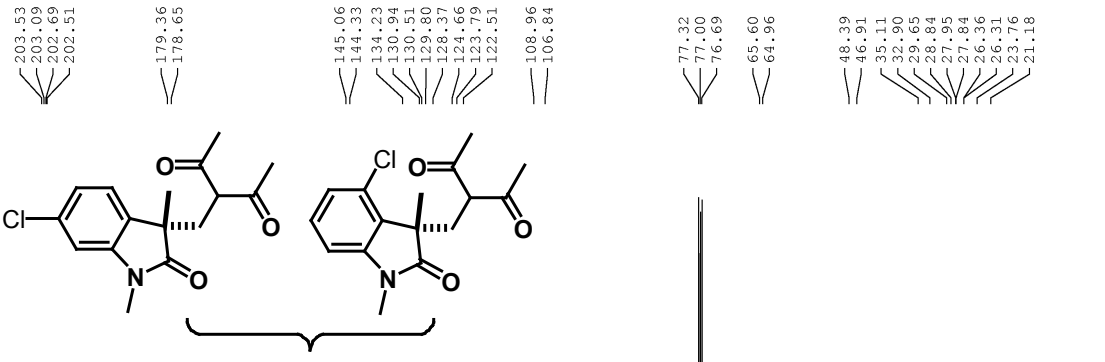
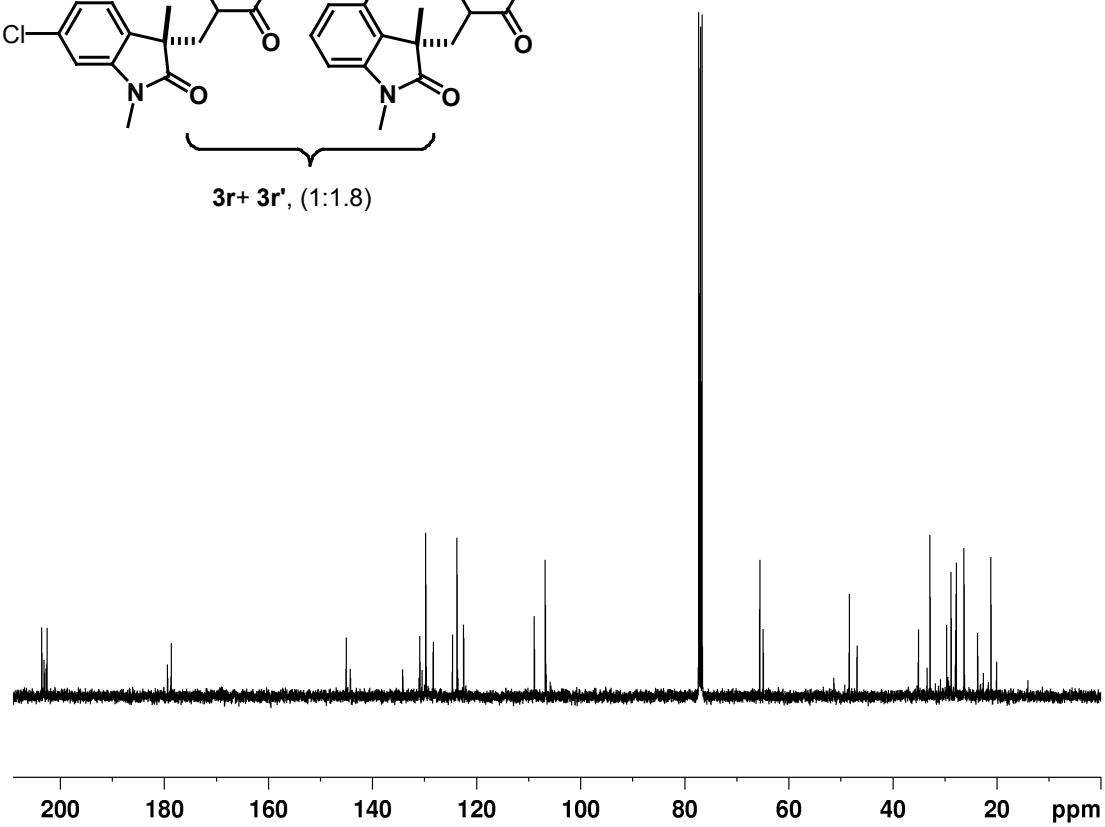
202.83
191.95
172.17
136.77
136.57
136.36
136.07
133.24
132.94
127.01
126.66
126.64
126.60
123.46
123.26
122.70
122.32
120.48
119.41
108.83
108.74
105.34
77.32
77.00
76.68
66.27
49.03
46.57
44.02
41.77
29.78
29.63
29.34
29.19
27.82
22.57
22.25
3q
3q'
200 180 160 140 120 100 80 60 40 20 ppm

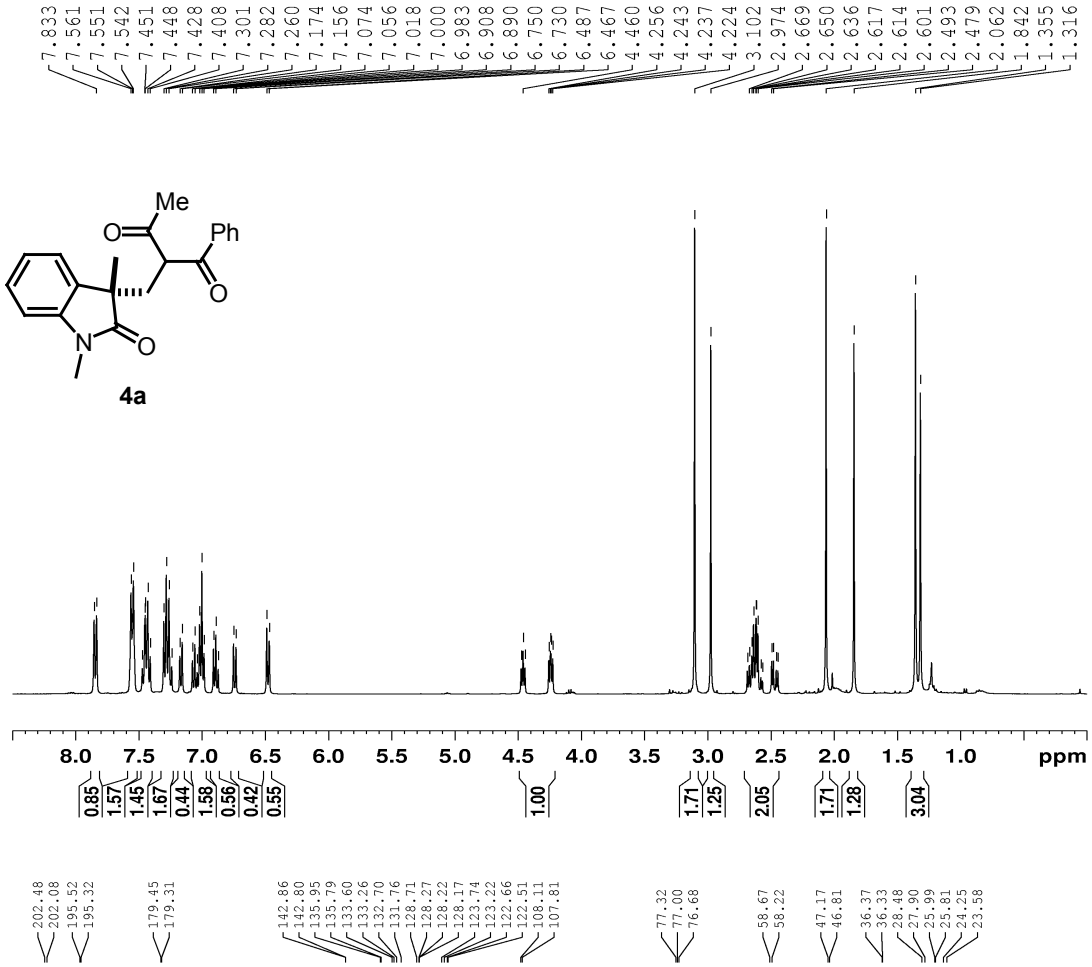

7.261
7.241
7.221
7.015
7.000
6.979
6.853
6.773
6.753
3.297
3.282
3.266
3.189
3.177
2.806
2.790
2.770
2.754
2.523
2.507
2.487
2.470
2.110
2.064
1.889
1.791
1.518
1.343
Cl
O
N
3r+ 3r', (1:1.8)

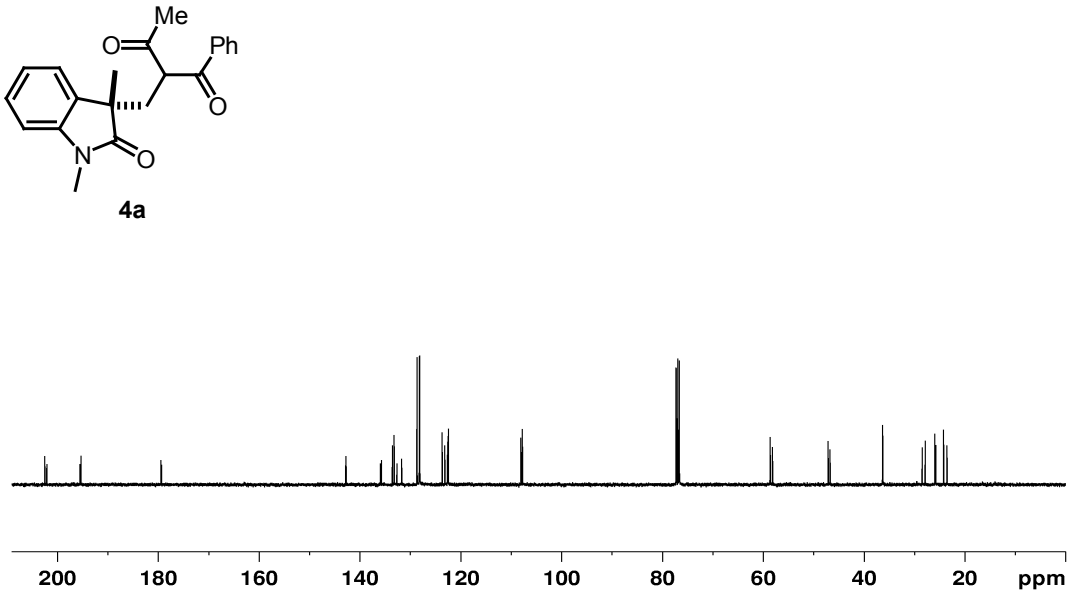

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.05
1.50
0.34
0.68
0.96
3.00
0.72
1.04
0.90
2.06
2.30
0.91
2.23
1.25

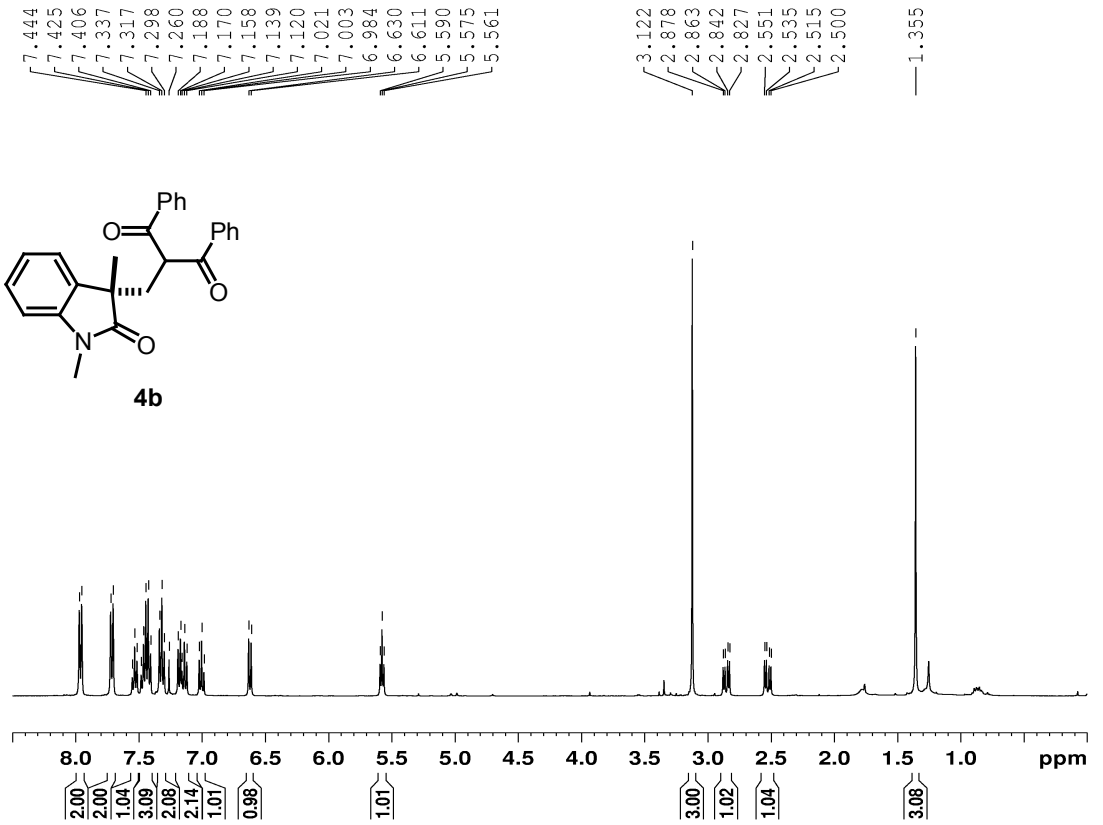

203.53
203.09
202.69
202.51
179.36
178.65
145.06
144.33
134.23
130.94
130.51
129.80
128.37
124.66
123.79
122.51
108.96
106.84
77.32
77.00
76.69
65.60
64.96
48.39
46.91
35.11
32.90
29.65
28.84
27.95
27.84
26.36
26.31
23.76
21.18
Cl
O
N
3r+ 3r', (1:1.8)


200
180
160
140
120
100
80
60
40
20
ppm

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



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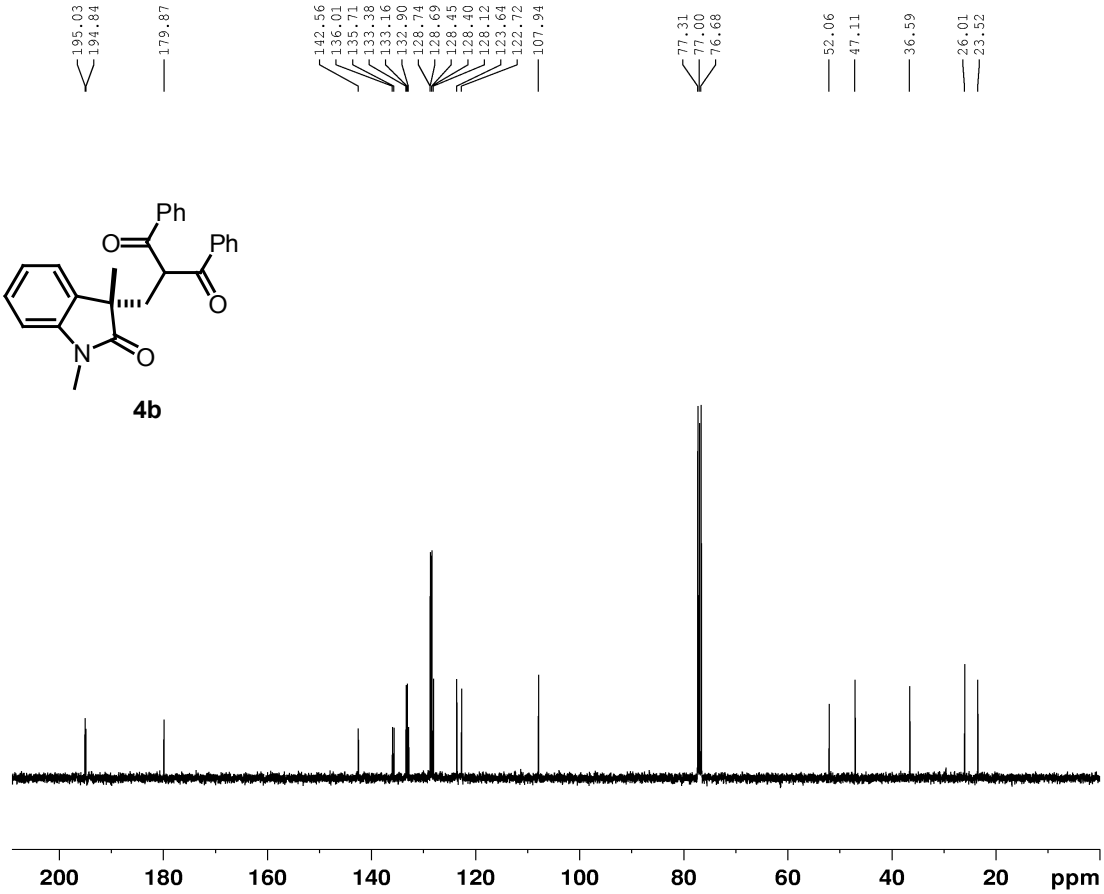
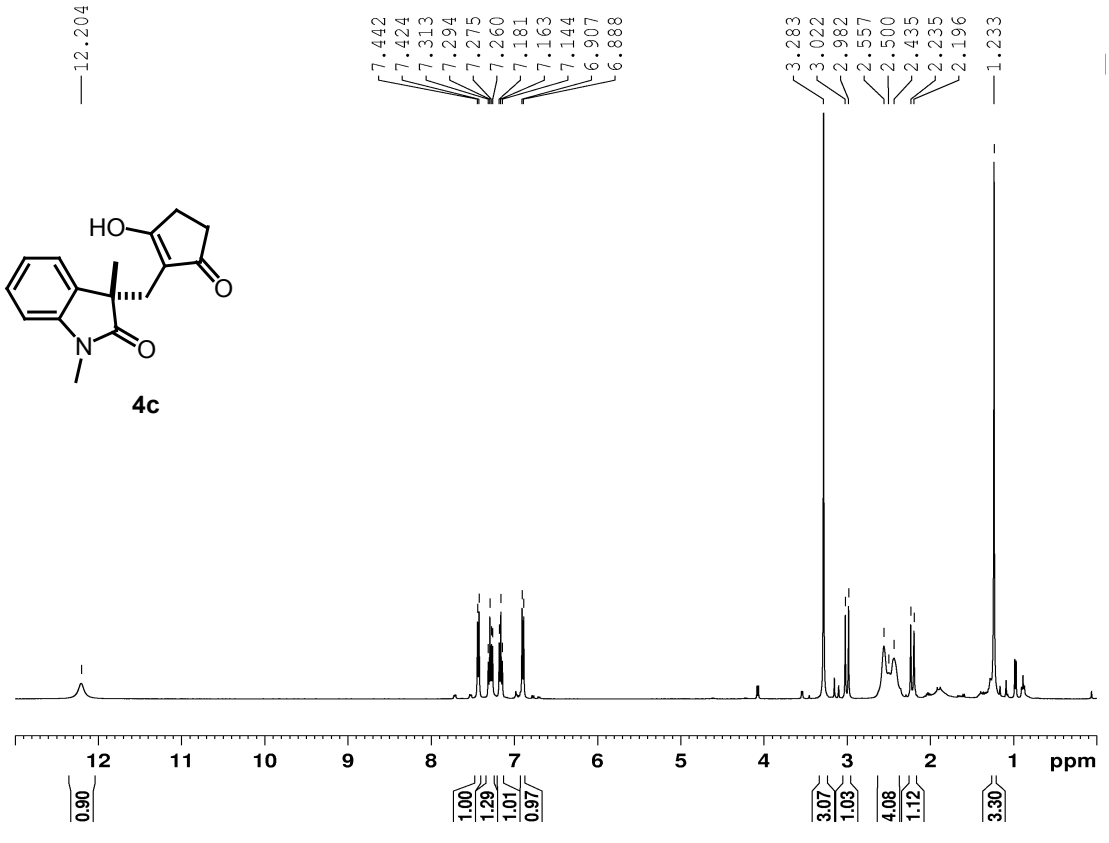
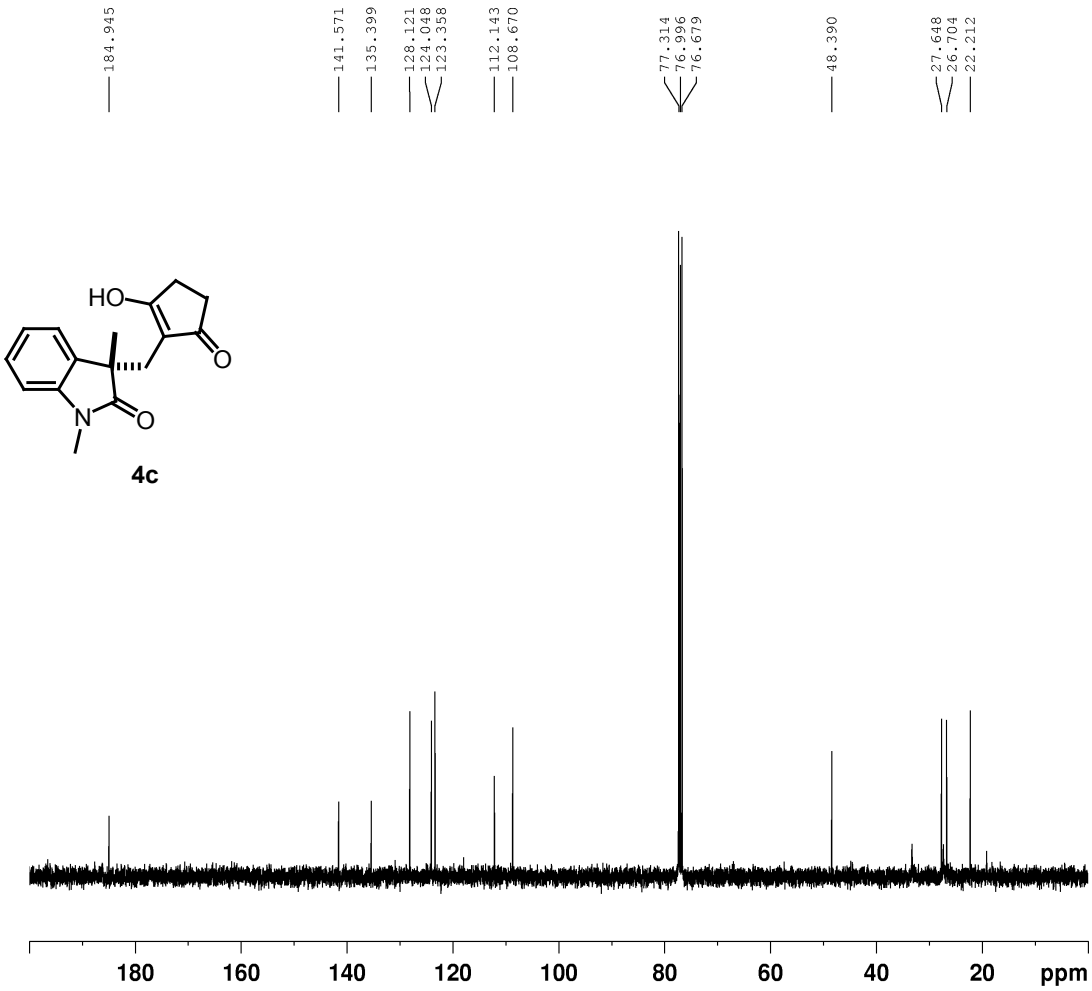
7.425
7.406
7.337
7.317
7.298
7.260
7.188
7.170
7.158
7.139
7.120
7.021
7.003
6.984
6.630
6.611
5.590
5.575
5.561
3.122
2.878
2.863
2.842
2.827
2.551
2.535
2.515
2.500
1.355
Ph
O
Ph
O
N
O
4b
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
2.00
1.04
3.09
2.08
2.14
1.01
0.98
1.01
3.00
1.02
1.04
3.08


195.03
194.84
179.87
142.56
136.01
135.71
133.38
133.16
132.90
128.74
128.69
128.45
128.40
128.12
123.64
122.72
107.94
77.31
77.00
76.68
52.06
47.11
36.59
26.01
23.52
Ph
O
Ph
O
N
O
4b
200
180
160
140
120
100
80
60
40
20
ppm


12.204
7.442
7.424
7.313
7.294
7.275
7.260
7.181
7.163
7.144
6.907
6.888
3.283
3.022
2.982
2.557
2.500
2.435
2.235
2.196
1.233
HO
O
N
O
4c
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.90
1.00
1.29
1.01
0.97
3.07
1.03
4.08
1.12
3.30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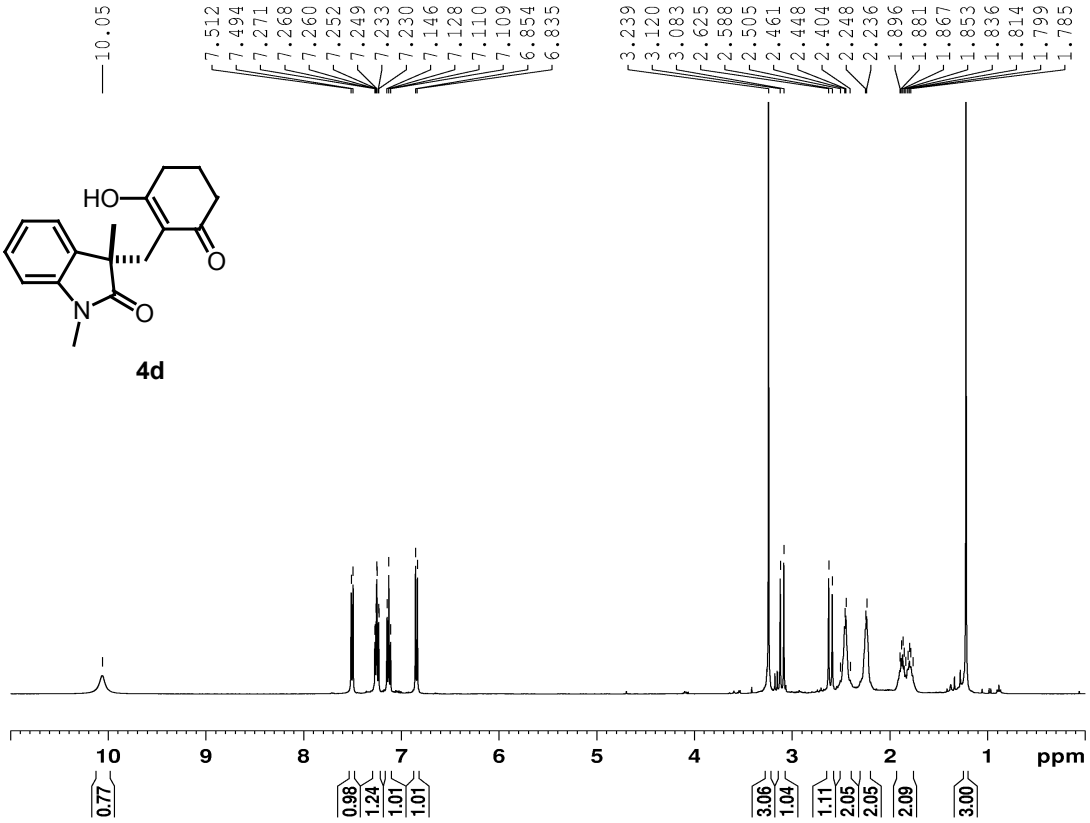
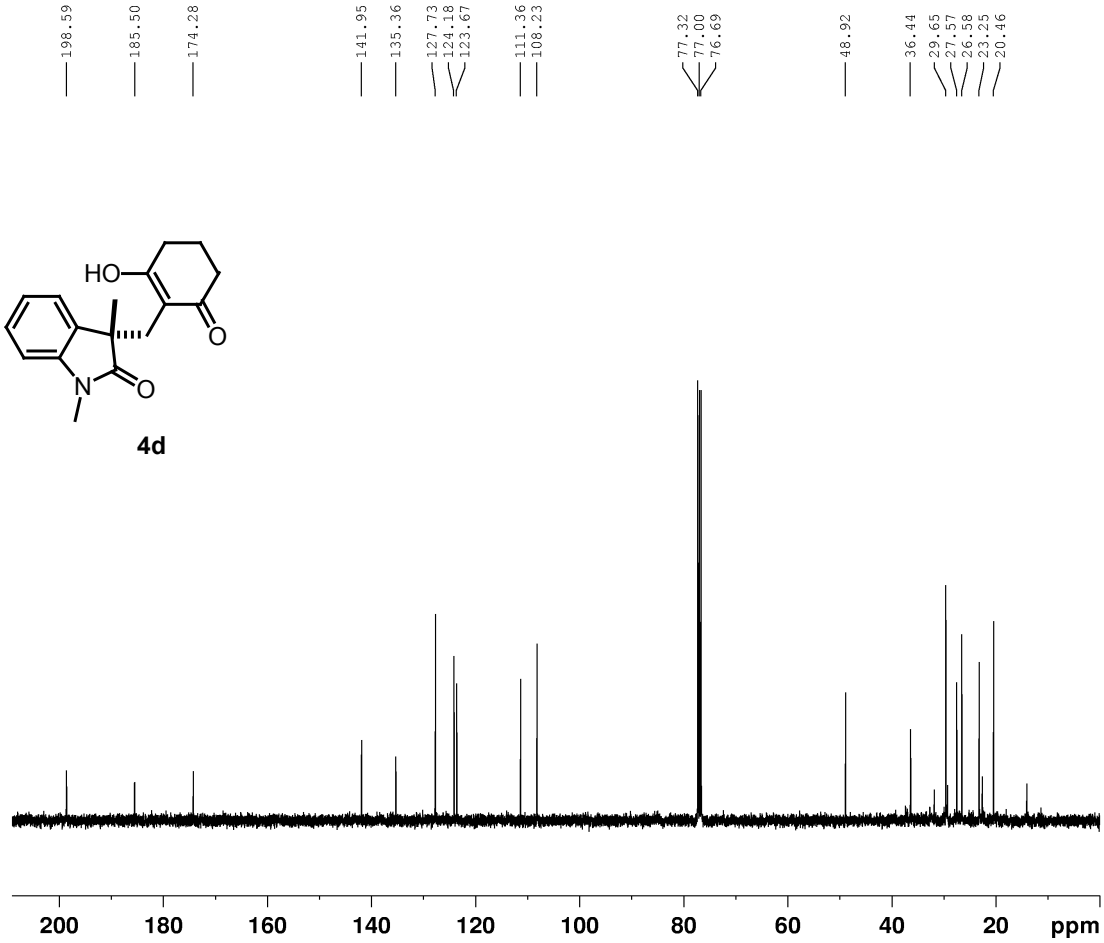
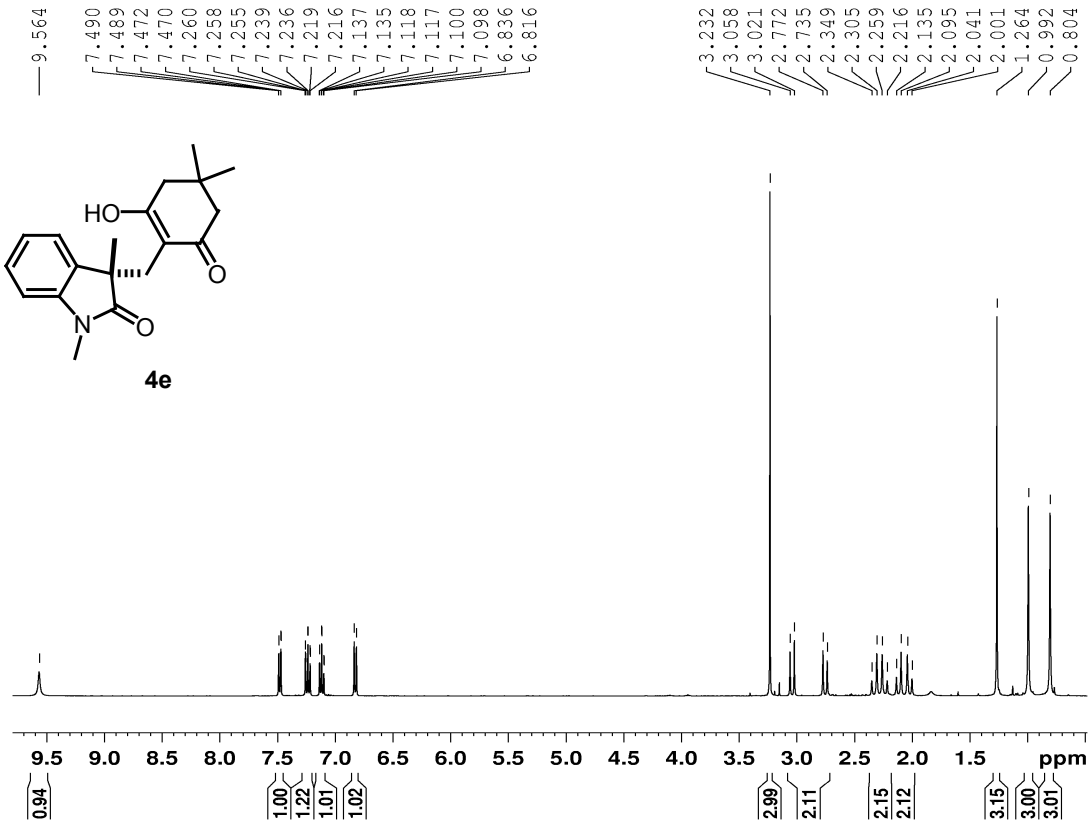
141.571
135.399
128.121
124.048
123.358
112.143
108.670
77.314
76.996
76.679
48.390
27.648
26.704
22.212
HO
O
N
O
4c
180
160
140
120
100
80
60
40
20
ppm


10.05
7.512
7.494
7.271
7.268
7.260
7.252
7.249
7.233
7.230
7.146
7.128
7.110
7.109
6.854
6.835
3.239
3.120
3.083
2.625
2.588
2.505
2.461
2.448
2.404
2.248
2.236
1.896
1.881
1.867
1.853
1.836
1.814
1.799
1.785
HO
O
N
O
4d
10
9
8
7
6
5
4
3
2
1
ppm
0.77
0.98
1.24
1.01
1.01
3.06
1.04
1.11
2.05
2.05
2.09
3.00


198.59
185.50
174.28
141.95
135.36
127.73
124.18
123.67
111.36
108.23
77.32
77.00
76.69
48.92
36.44
29.65
27.57
26.58
23.25
20.46
HO
O
N
O
4d
200
180
160
140
120
100
80
60
40
20
ppm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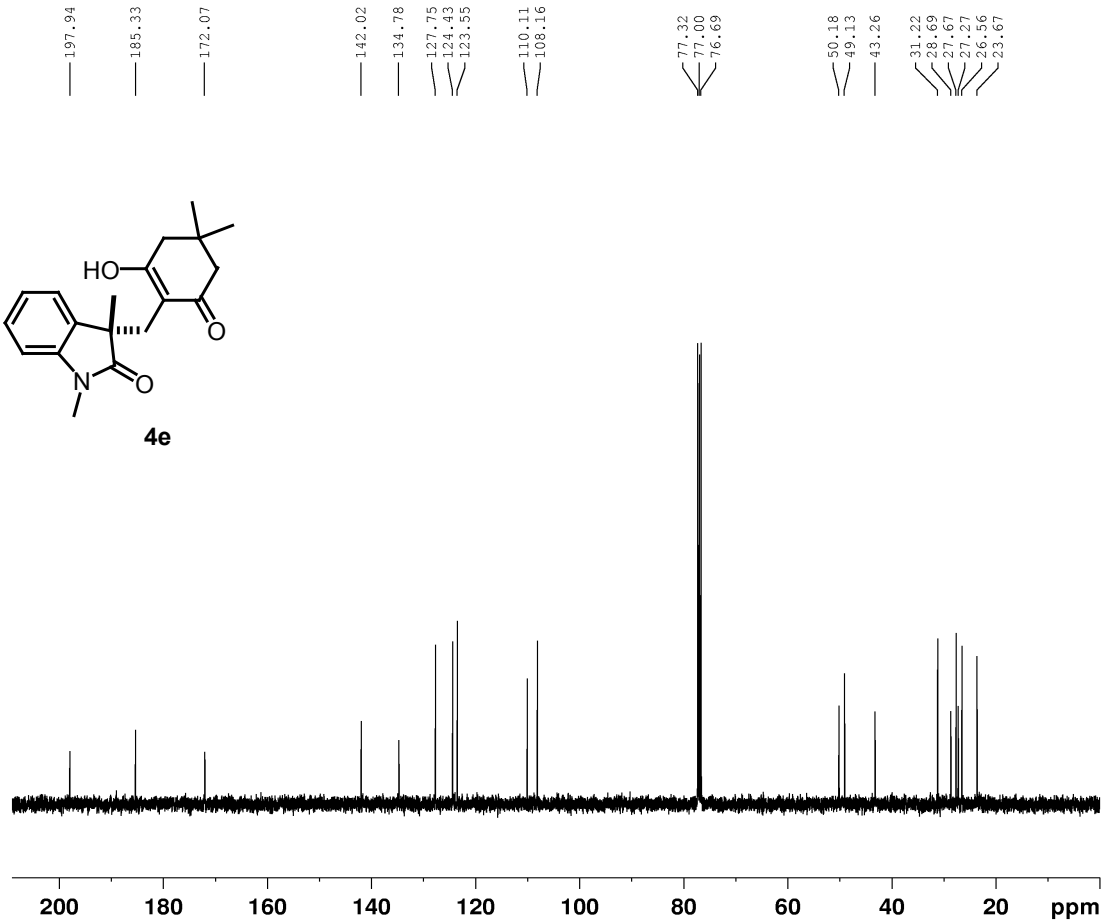
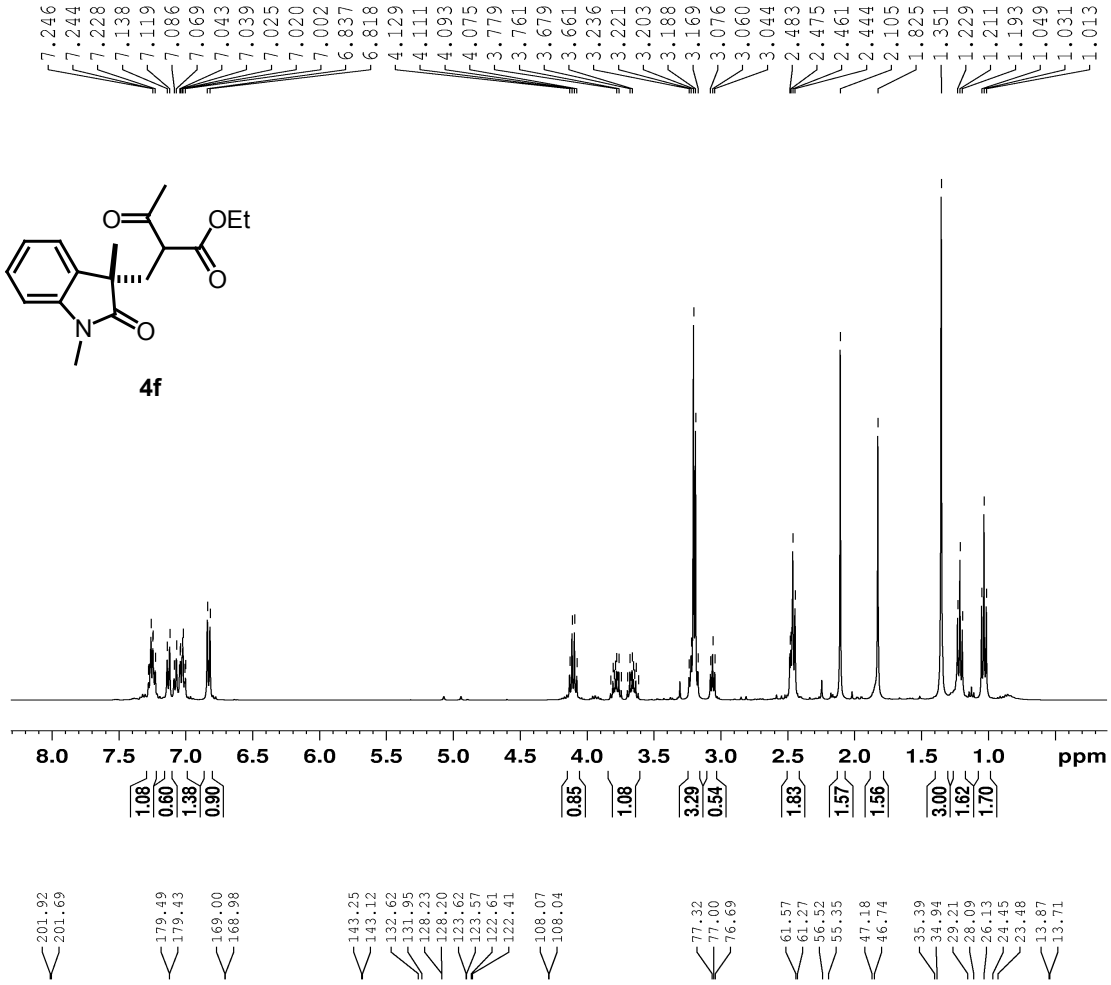
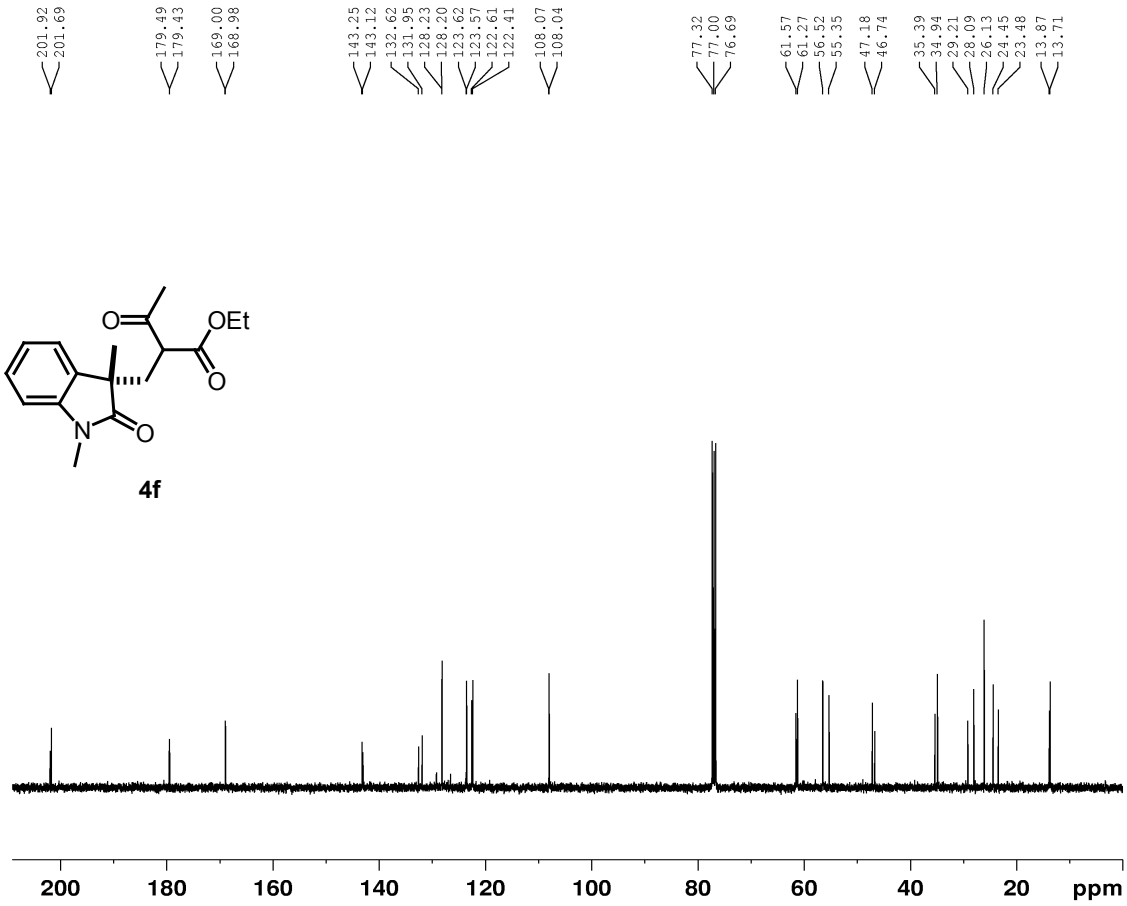
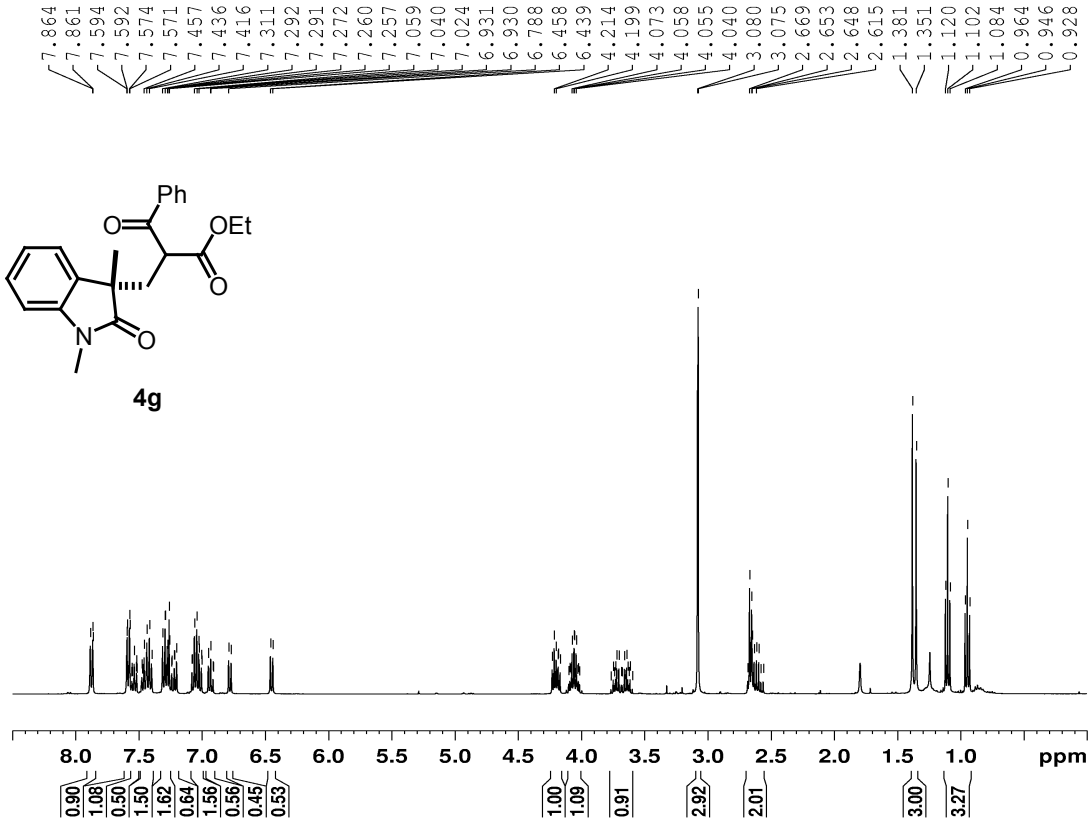
7.489
7.472
7.470
7.260
7.258
7.255
7.239
7.236
7.219
7.216
7.137
7.135
7.118
7.117
7.100
7.098
6.836
6.816
3.232
3.058
3.021
2.772
2.735
2.349
2.305
2.259
2.216
2.135
2.095
2.041
2.001
1.264
0.992
0.804
HO
O
N
O
4e
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
0.94
1.00
1.22
1.01
1.02
2.99
2.11
2.15
2.12
3.15
3.00
3.01


197.94
185.33
172.07
142.02
134.78
127.75
124.43
123.55
110.11
108.16
77.32
77.00
76.69
50.18
49.13
43.26
31.22
28.69
27.67
27.27
26.56
23.67
HO
O
N
O
4e
200 180 160 140 120 100 80 60 40 20 ppm


7.246 7.244 7.228 7.138 7.119 7.086 7.069 7.043 7.039 7.025 7.020 7.002 6.837 6.818 4.129 4.111 4.093 4.075 3.779 3.761 3.679 3.661 3.236 3.221 3.203 3.188 3.169 3.076 3.060 3.044 2.483 2.475 2.461 2.444 2.105 1.825 1.351 1.229 1.211 1.193 1.049 1.031 1.013
O
OEt
O
N
O
4f
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
1.08 0.60 1.38 0.90 0.85 1.08 3.29 0.54 1.83 1.57 1.56 3.00 1.62 1.70


201.92 201.69 179.49 179.43 169.00 168.98 143.25 143.12 132.62 131.95 128.23 128.20 123.62 123.57 122.61 122.41 108.07 108.04 77.32 77.00 76.69 61.57 61.27 56.52 55.35 47.18 46.74 35.39 34.94 29.21 28.09 26.13 24.45 23.48 13.87 13.71
O
OEt
O
N
O
4f
200 180 160 140 120 100 80 60 40 20 ppm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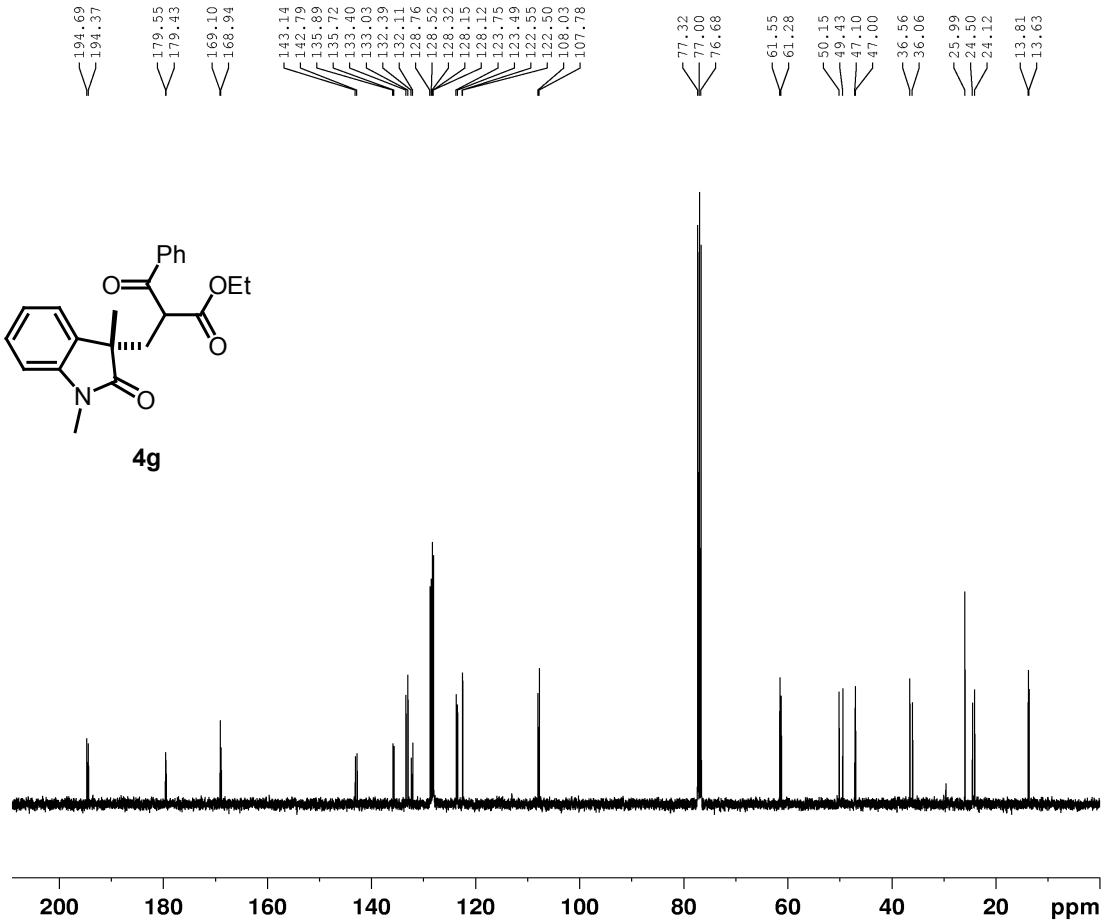
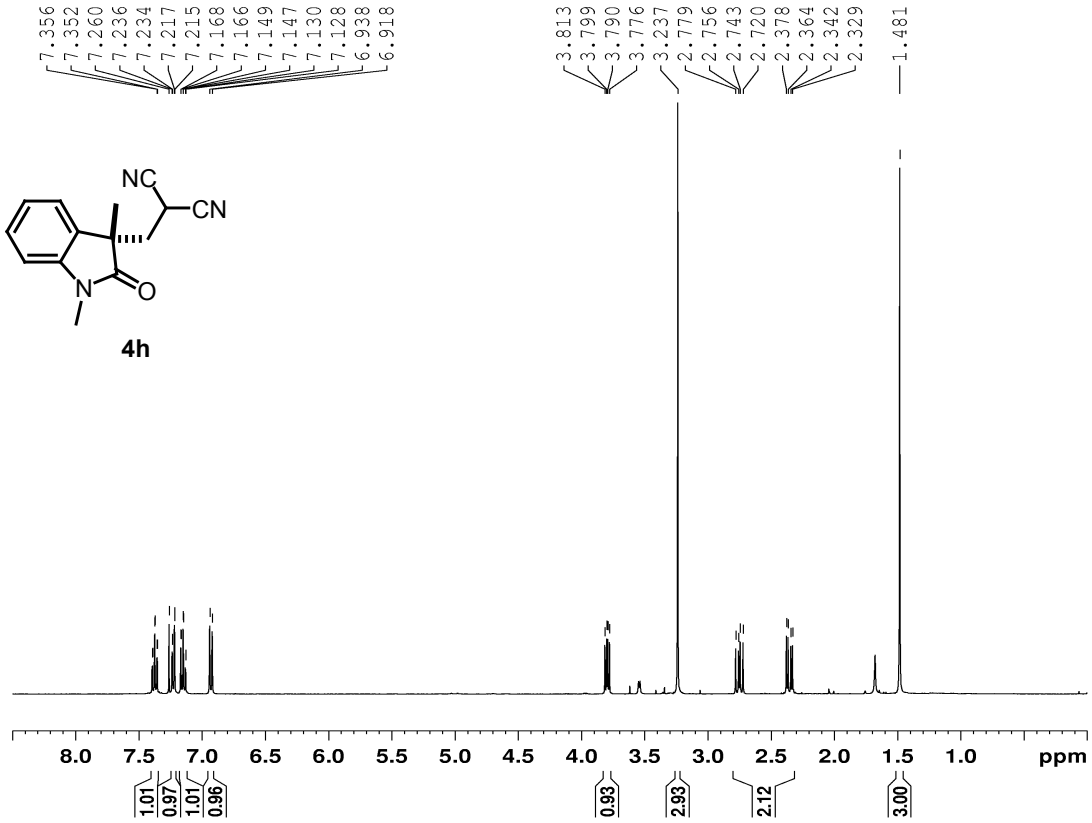
7.592
7.574
7.571
7.457
7.436
7.416
7.311
7.292
7.291
7.272
7.260
7.257
7.059
7.040
7.024
6.931
6.930
6.788
6.458
6.439
4.214
4.199
4.073
4.058
4.055
4.040
3.080
3.075
2.669
2.653
2.648
2.615
1.381
1.351
1.120
1.102
1.084
0.964
0.946
0.928
Ph
O
OEt
O
N
O
4g
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.90
1.08
0.50
1.50
1.62
0.64
1.56
0.56
0.45
0.53
1.00
1.09
0.91
2.92
2.01
3.00
3.27


194.69
194.37
179.55
179.43
169.10
168.94
143.14
142.79
135.89
135.72
133.40
133.03
132.39
132.11
128.76
128.52
128.32
128.15
128.12
123.75
123.49
122.55
122.50
108.03
107.78
77.32
77.00
76.68
61.55
61.28
50.15
49.43
47.10
47.00
36.56
36.06
25.99
24.50
24.12
13.81
13.63
Ph
O
OEt
O
N
O
4g
200
180
160
140
120
100
80
60
40
20
ppm


7.356
7.352
7.260
7.236
7.234
7.217
7.215
7.168
7.166
7.149
7.147
7.130
7.128
6.938
6.918
3.813
3.799
3.790
3.776
3.237
2.779
2.756
2.743
2.720
2.378
2.364
2.342
2.329
1.481
NC
CN
N
O
4h
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
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1.0
ppm
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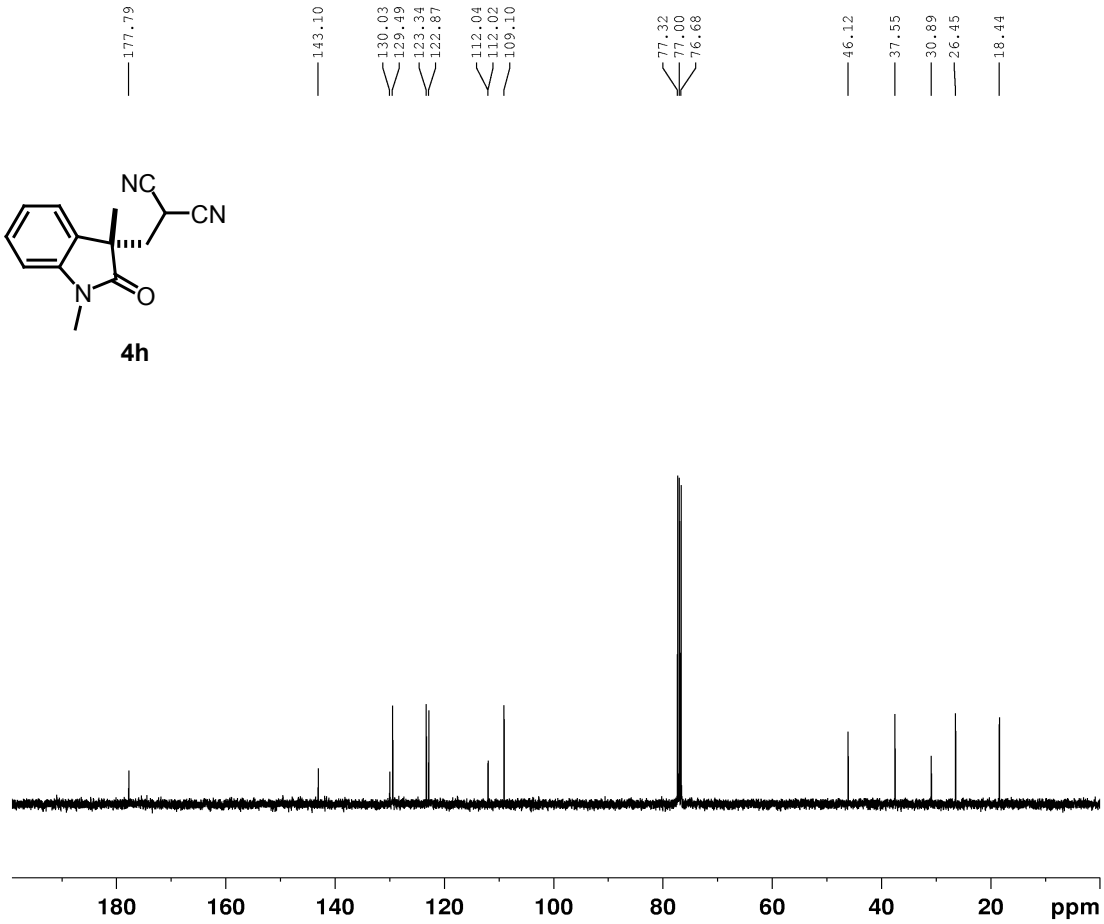
0.97
1.01
0.96
0.93
2.93
2.12
3.00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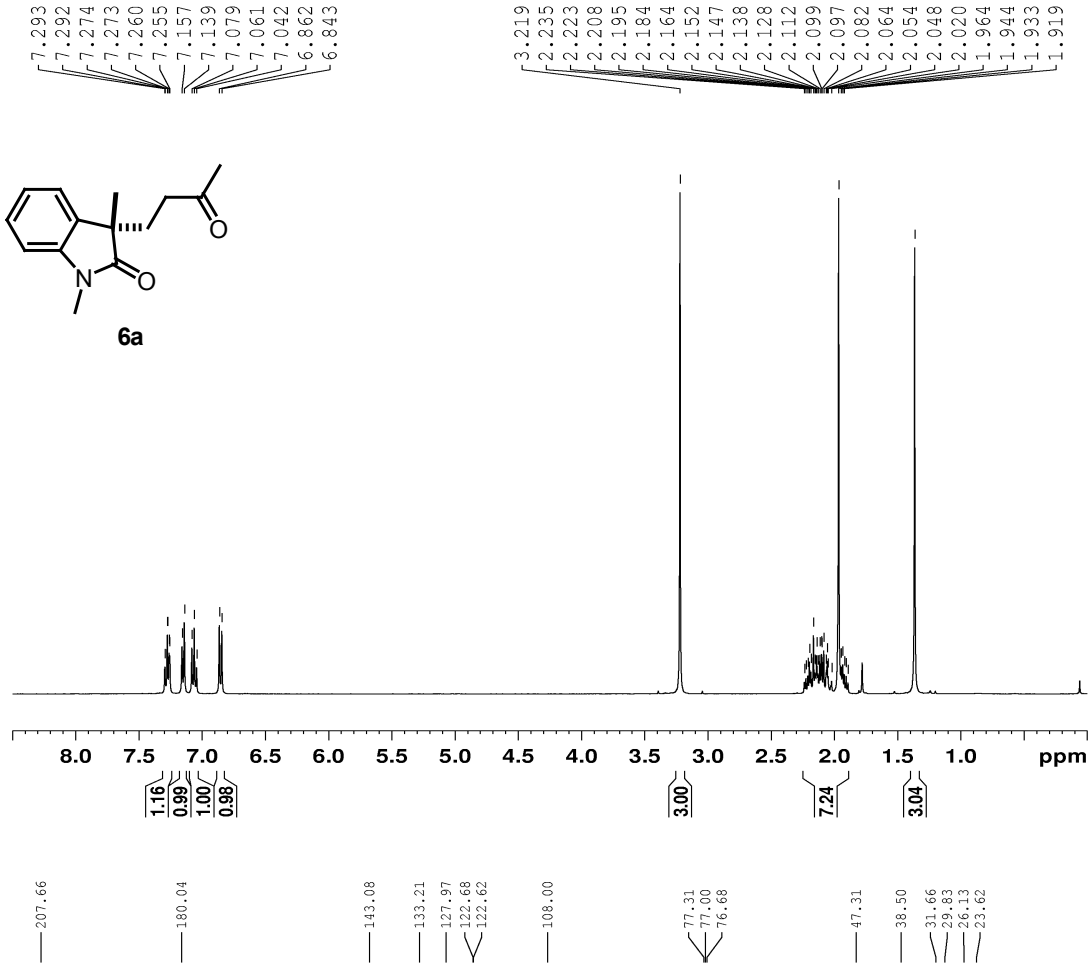
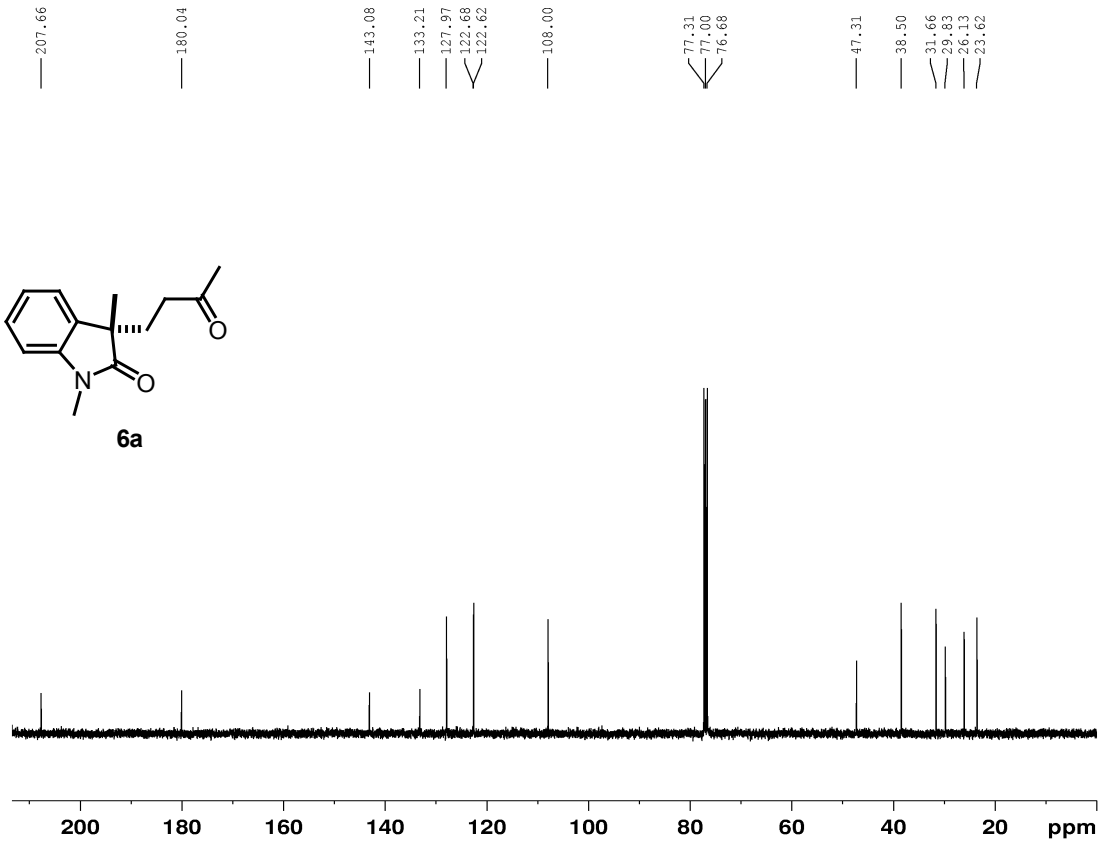
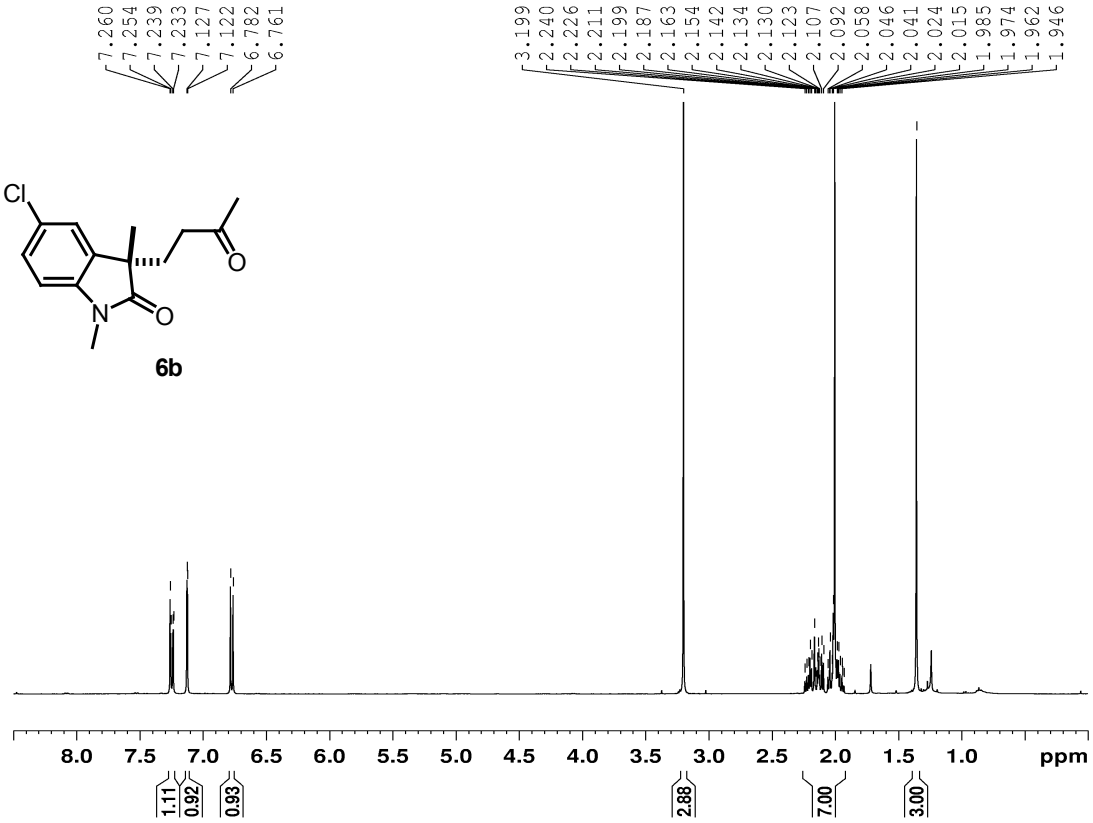
143.10
130.03
129.49
123.34
122.87
112.04
112.02
109.10
77.32
77.00
76.68
46.12
37.55
30.89
26.45
18.44
NC
CN
N
O
4h
180
160
140
120
100
80
60
40
20
ppm

^{1}H NMR and ^{13}C NMR Spectra of the Products 6



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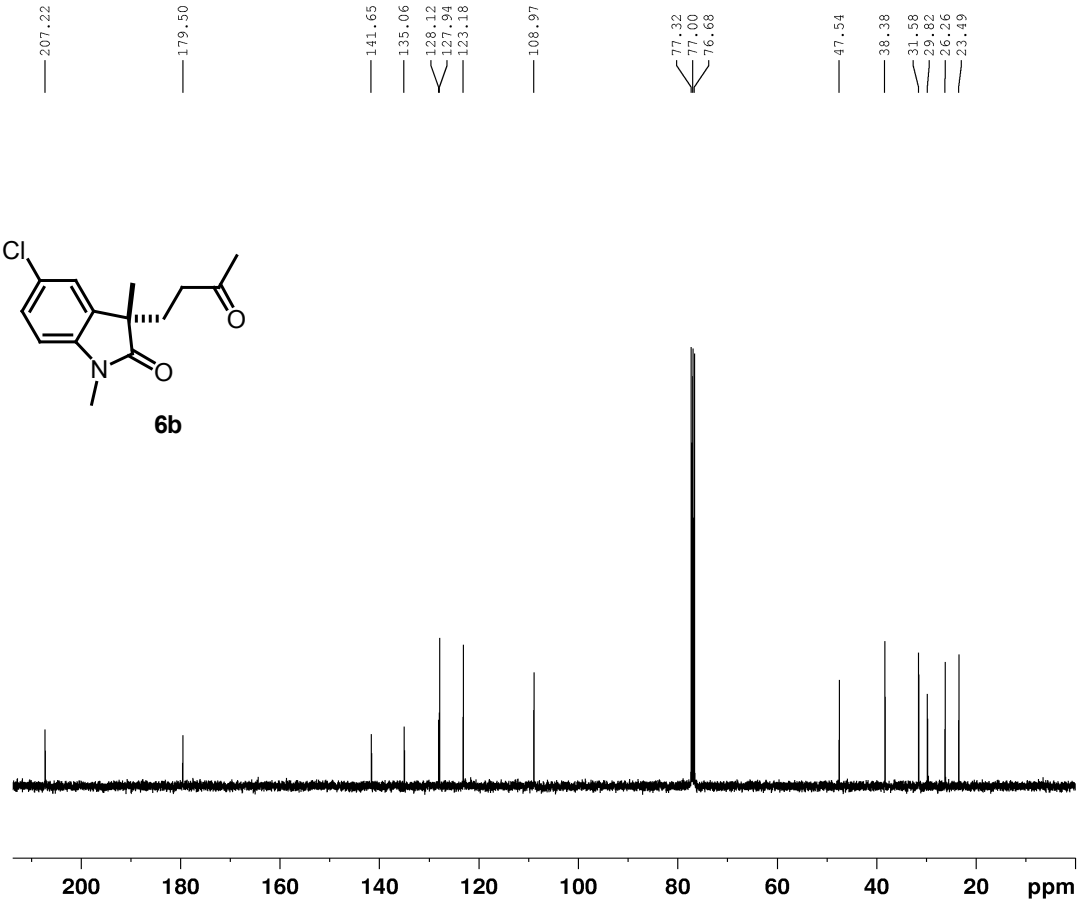
7.239
7.233
7.127
7.122
6.782
6.761
3.199
2.240
2.226
2.211
2.199
2.187
2.163
2.154
2.142
2.134
2.130
2.123
2.107
2.092
2.058
2.046
2.041
2.024
2.015
1.985
1.974
1.962
1.946
Cl
O
N
O
6b
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.11
0.92
0.93
2.88
7.00
3.00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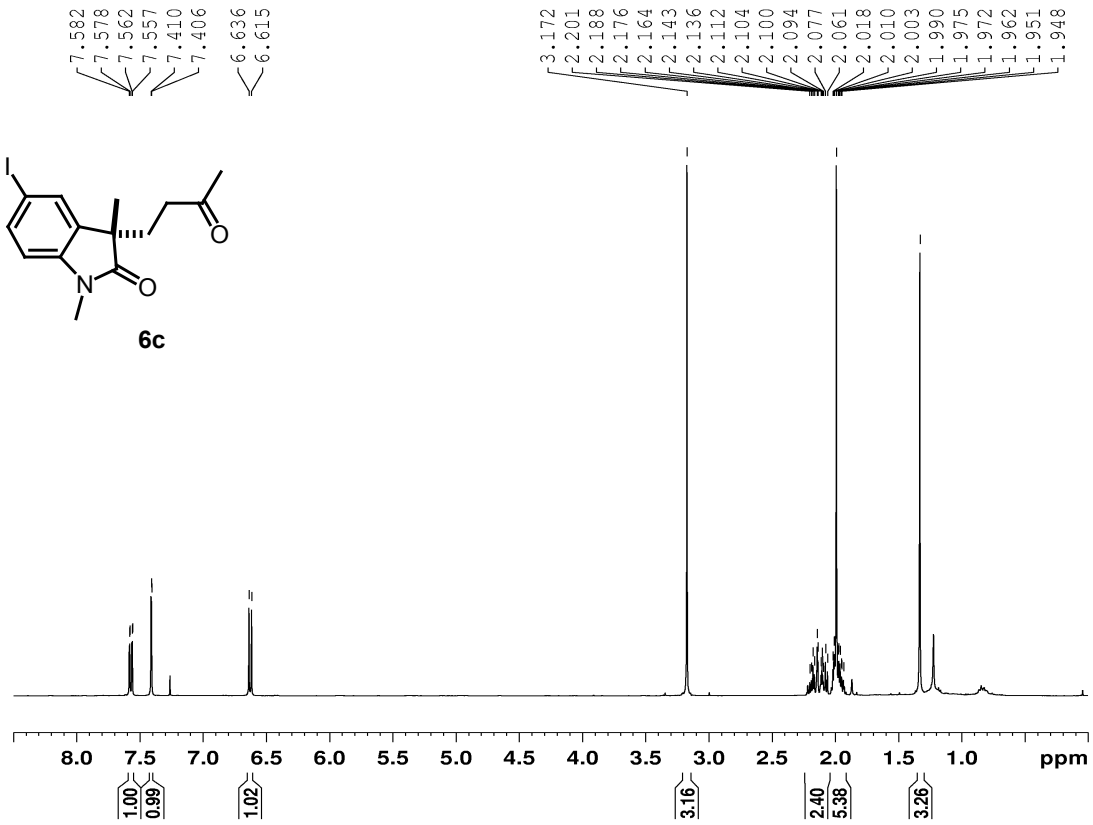
179.50
141.65
135.06
128.12
127.94
123.18
108.97
77.32
77.00
76.68
47.54
38.38
31.58
29.82
26.26
23.49
Cl
O
N
O
6b
200 180 160 140 120 100 80 60 40 20 ppm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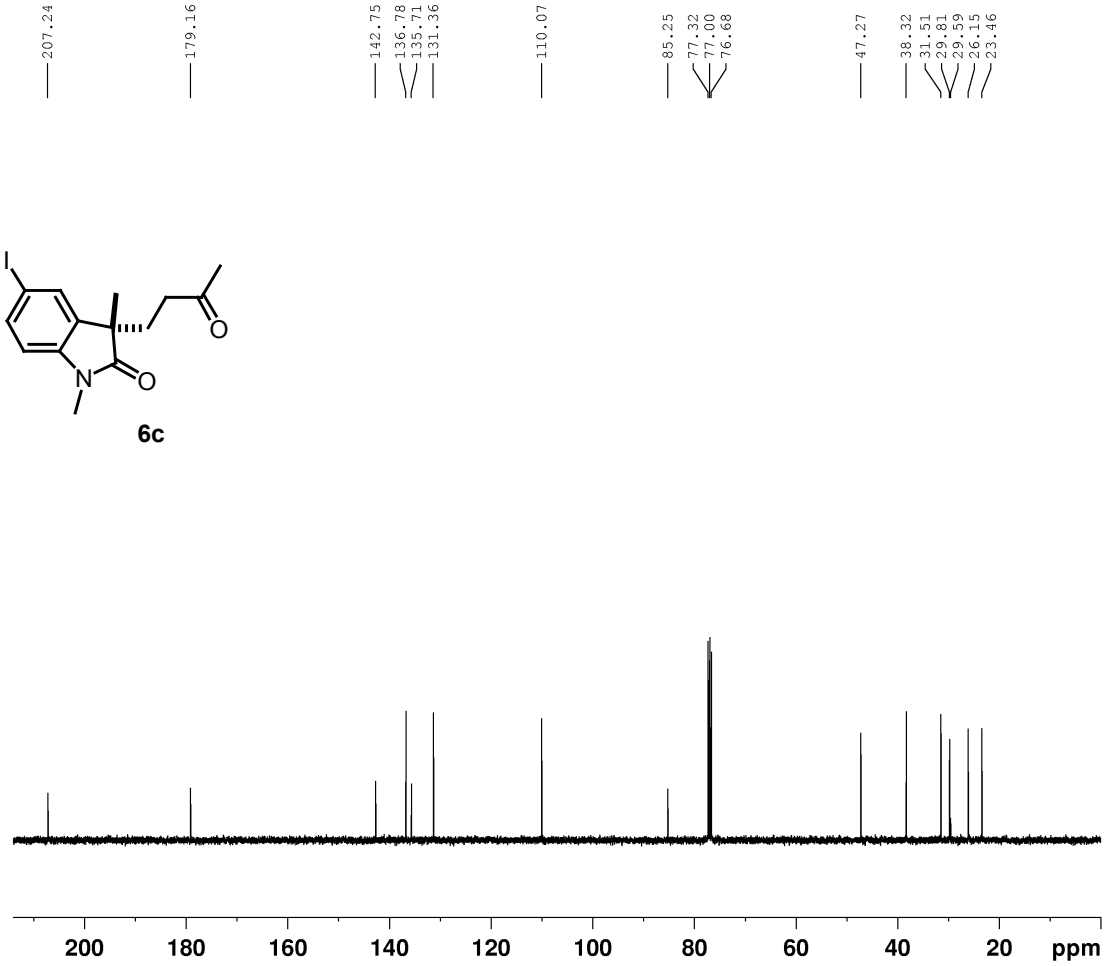
7.578
7.562
7.557
7.410
7.406
6.636
6.615
3.172
2.201
2.188
2.176
2.164
2.143
2.136
2.112
2.104
2.100
2.094
2.077
2.061
2.018
2.010
2.003
1.990
1.975
1.972
1.962
1.951
1.948
I
O
N
O
6c
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.99
1.02
3.16
2.40
5.38
3.26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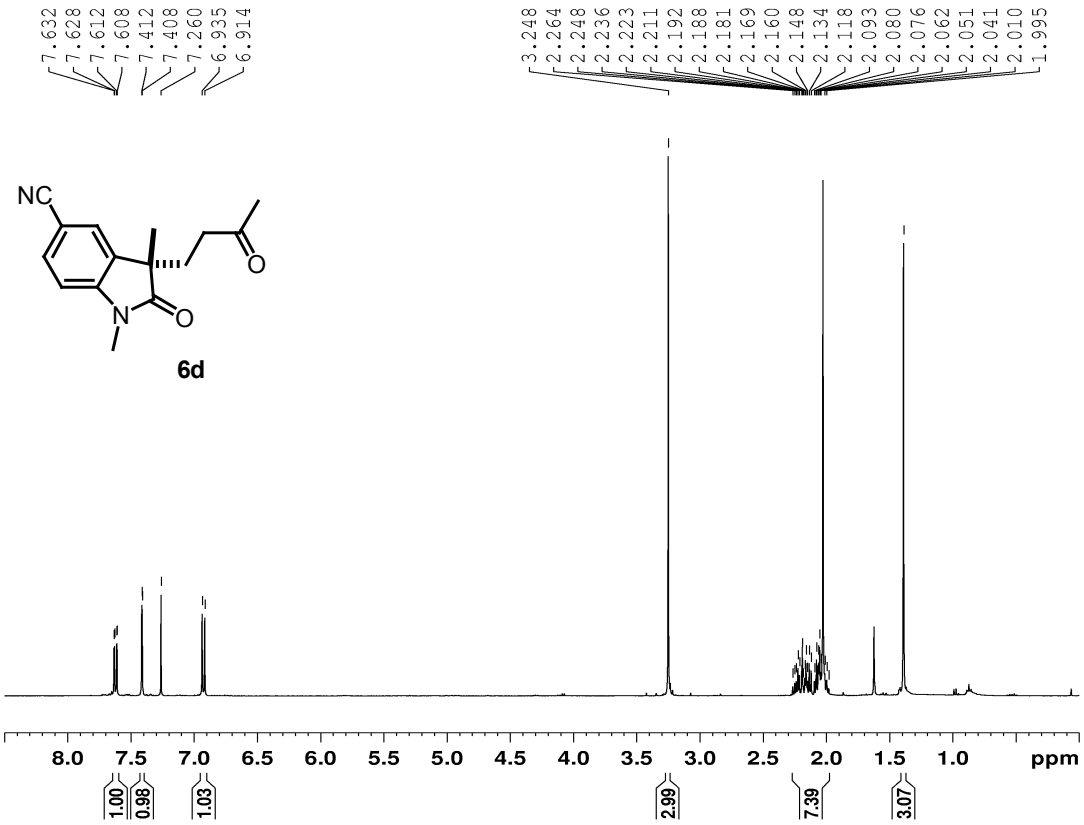
142.75
136.78
135.71
131.36
110.07
85.25
77.32
77.00
76.68
47.27
38.32
31.51
29.81
29.59
26.15
23.46
I
O
N
O
6c
200
180
160
140
120
100
80
60
40
20
ppm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7.628
7.612
7.608
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7.408
7.260
6.935
6.914
3.248
2.264
2.248
2.236
2.223
2.211
2.192
2.188
2.181
2.169
2.160
2.148
2.134
2.118
2.093
2.080
2.076
2.062
2.051
2.041
2.010
1.995
NC
O
N
O
6d
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
ppm
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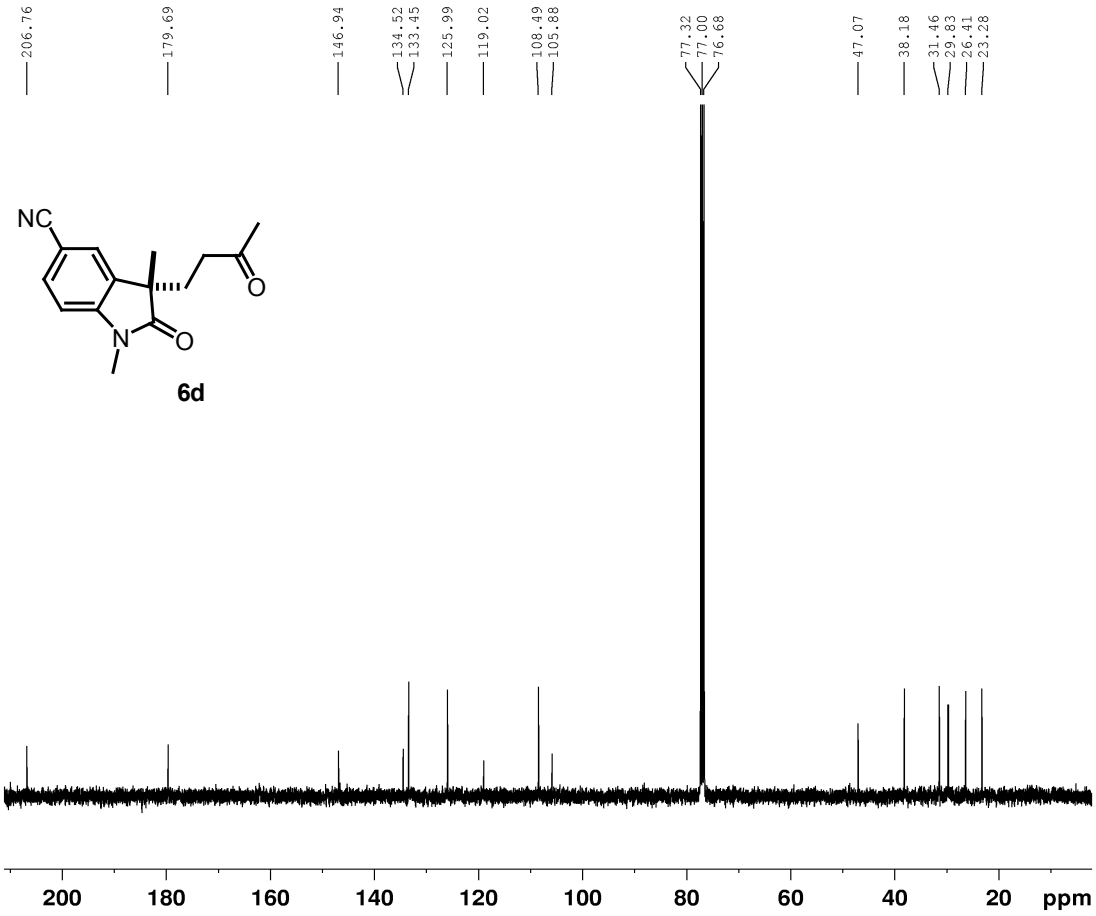
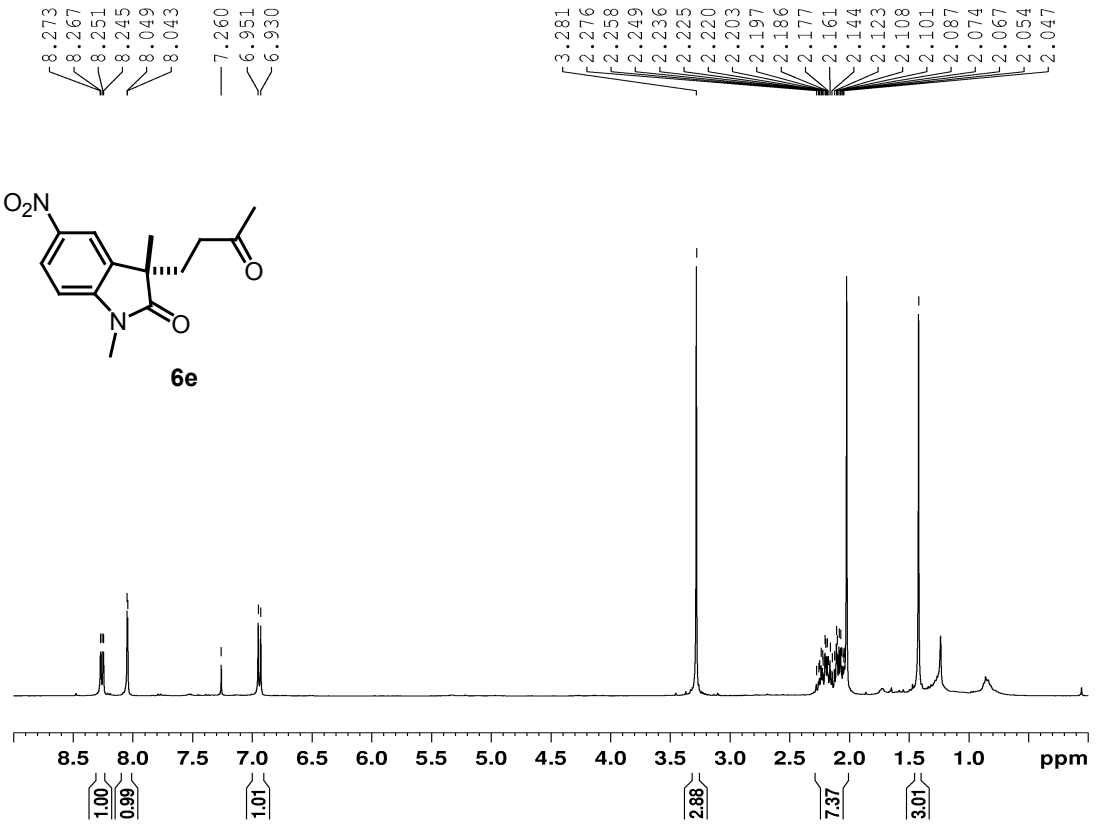
0.98
1.03
2.99
7.39
3.07


206.76
179.69
146.94
134.52
133.45
125.99
119.02
108.49
105.88
77.32
77.00
76.68
47.07
38.18
31.46
29.83
26.41
23.28
NC
O
N
O
6d
200
180
160
140
120
100
80
60
40
20
ppm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8.267
8.251
8.245
8.049
8.043
7.260
6.951
6.930
3.281
2.276
2.258
2.249
2.236
2.225
2.220
2.203
2.197
2.186
2.177
2.161
2.144
2.123
2.108
2.101
2.087
2.074
2.067
2.054
2.047
O2N
O
N
O
6e
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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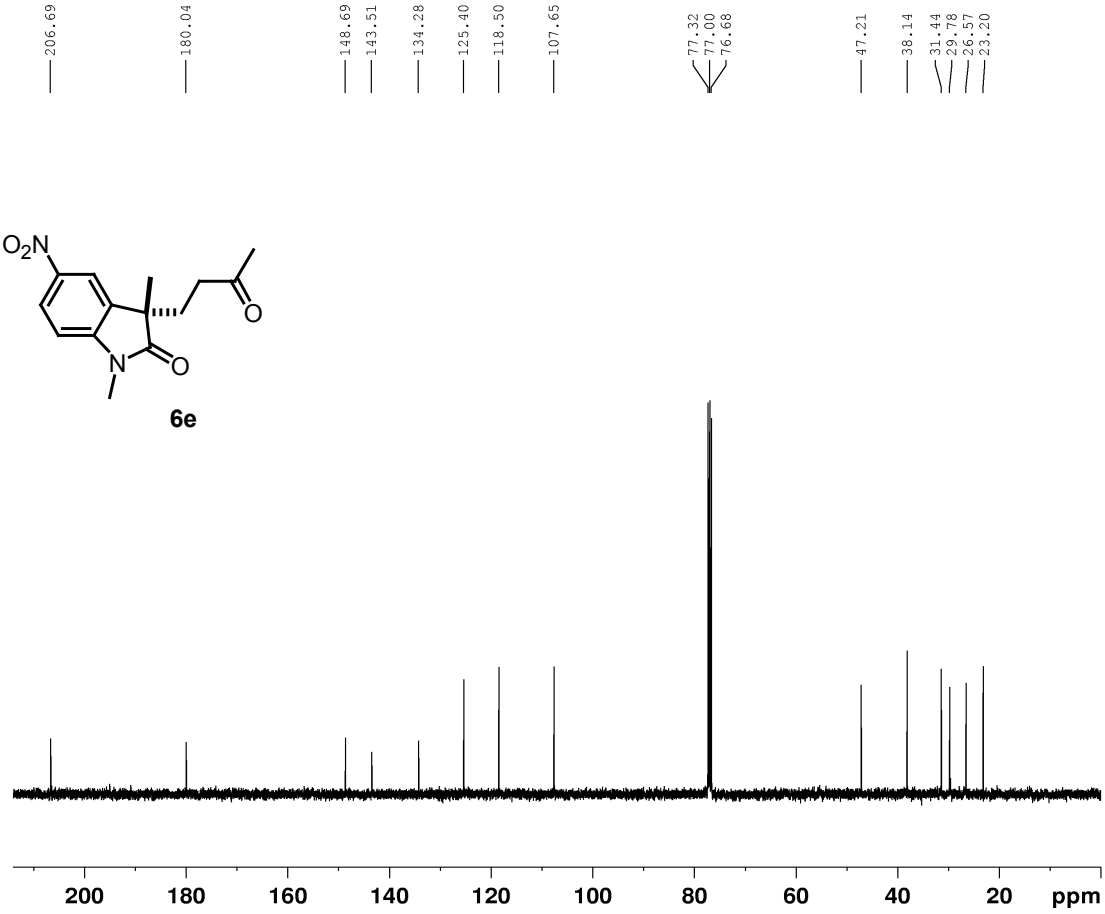
0.99
1.01
2.88
7.37
3.01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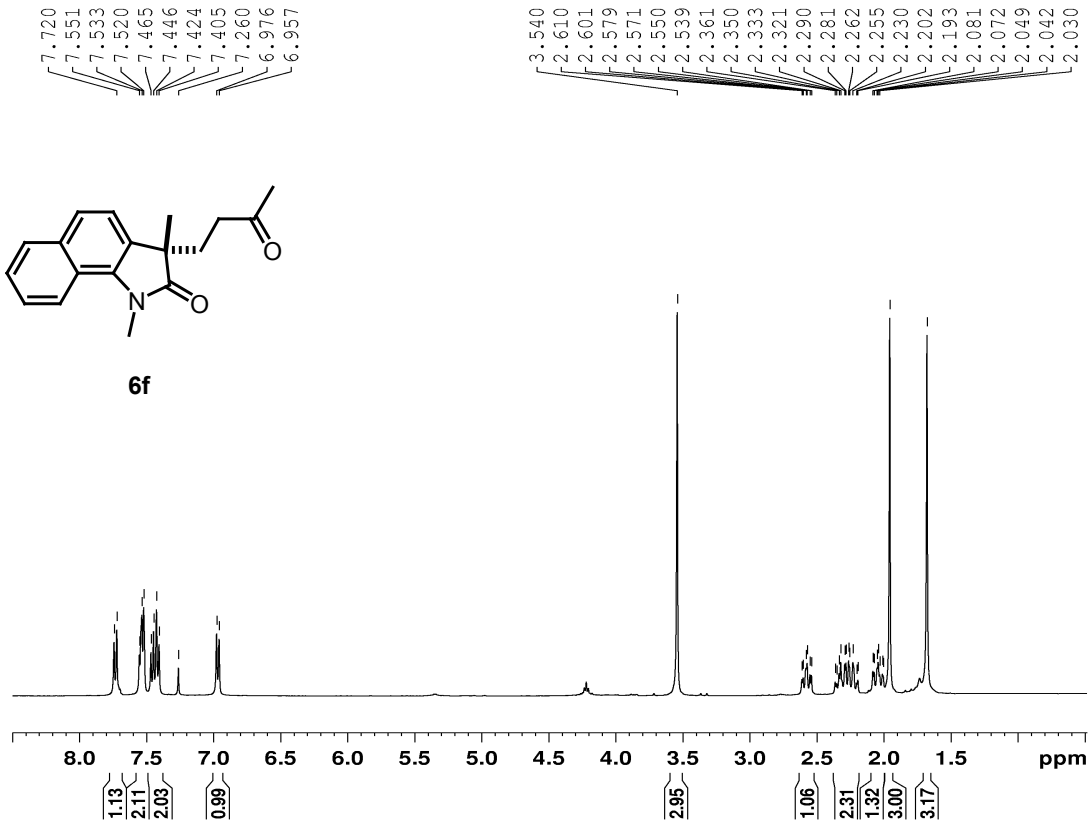
180.04
148.69
143.51
134.28
125.40
118.50
107.65
77.32
77.00
76.68
47.21
38.14
31.44
29.78
26.57
23.20
O2N
O
N
O
6e
200 180 160 140 120 100 80 60 40 20 ppm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7.533
7.520
7.465
7.446
7.424
7.405
7.260
6.976
6.957
3.540
2.610
2.601
2.579
2.571
2.550
2.539
2.361
2.350
2.333
2.321
2.290
2.281
2.262
2.255
2.230
2.202
2.193
2.081
2.072
2.049
2.042
2.030
N
O
O
6f
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
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2.11
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0.99
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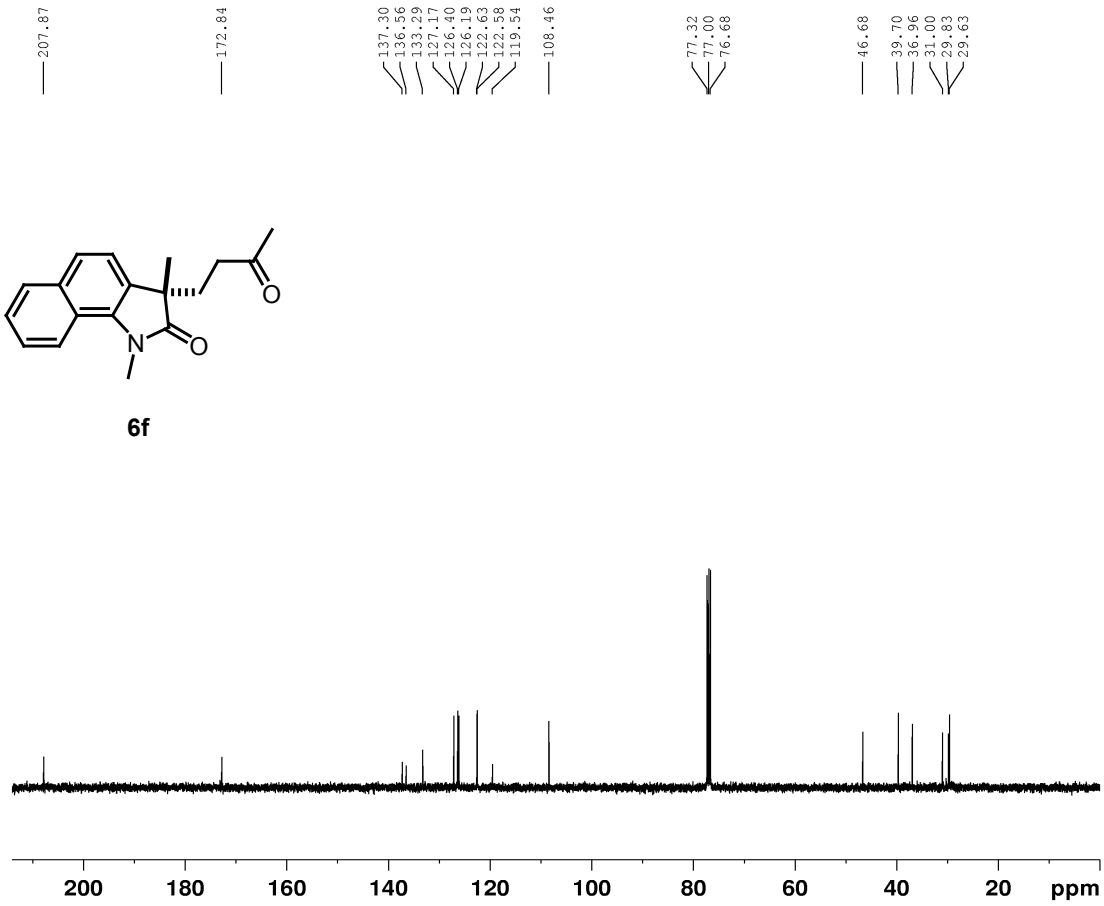
1.06
2.31
1.32
3.00
3.17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136.56
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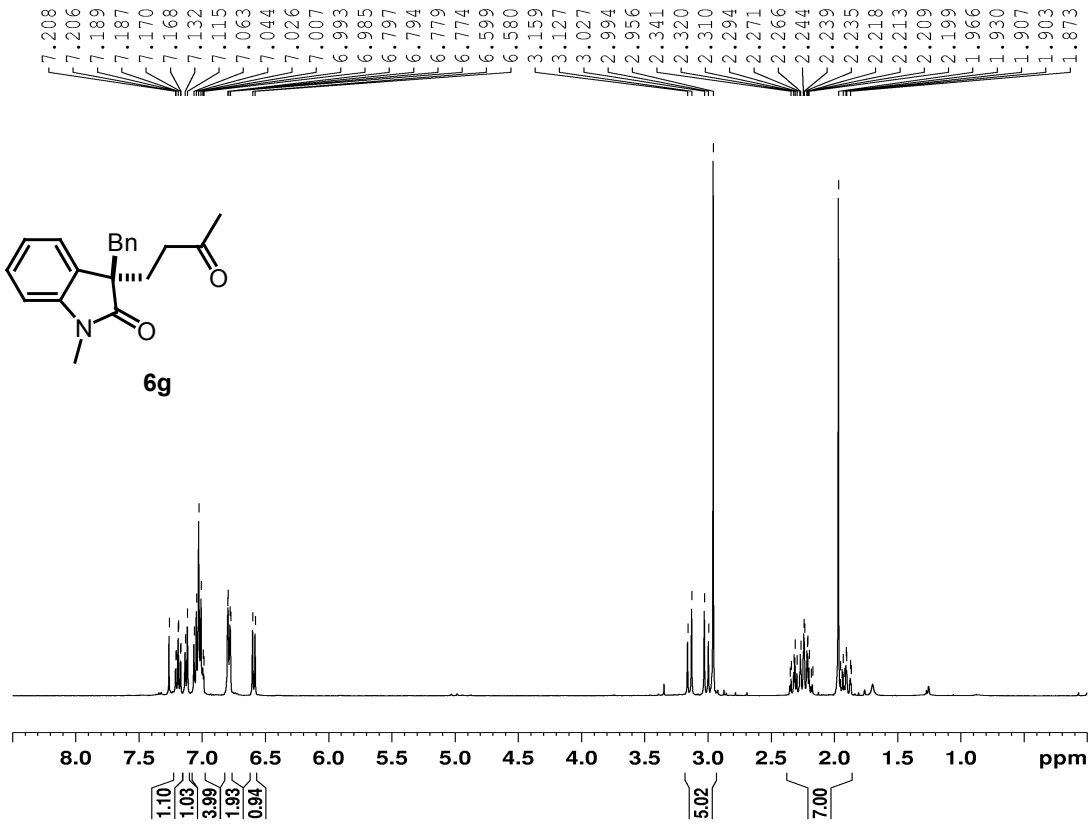
126.40
126.19
122.63
122.58
119.54
108.46
77.32
77.00
76.68
46.68
39.70
36.96
31.00
29.83
29.63
N
O
O
6f
200
180
160
140
120
100
80
60
40
20
ppm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7.170
7.168
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7.115
7.063
7.044
7.026
7.007
6.993
6.985
6.797
6.794
6.779
6.774
6.599
6.580
3.159
3.127
3.027
2.994
2.956
2.341
2.320
2.310
2.294
2.271
2.266
2.244
2.239
2.235
2.218
2.213
2.209
2.199
1.966
1.930
1.907
1.903
1.873
Bn
O
N
O
6g
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.5
1.0
ppm
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3.99
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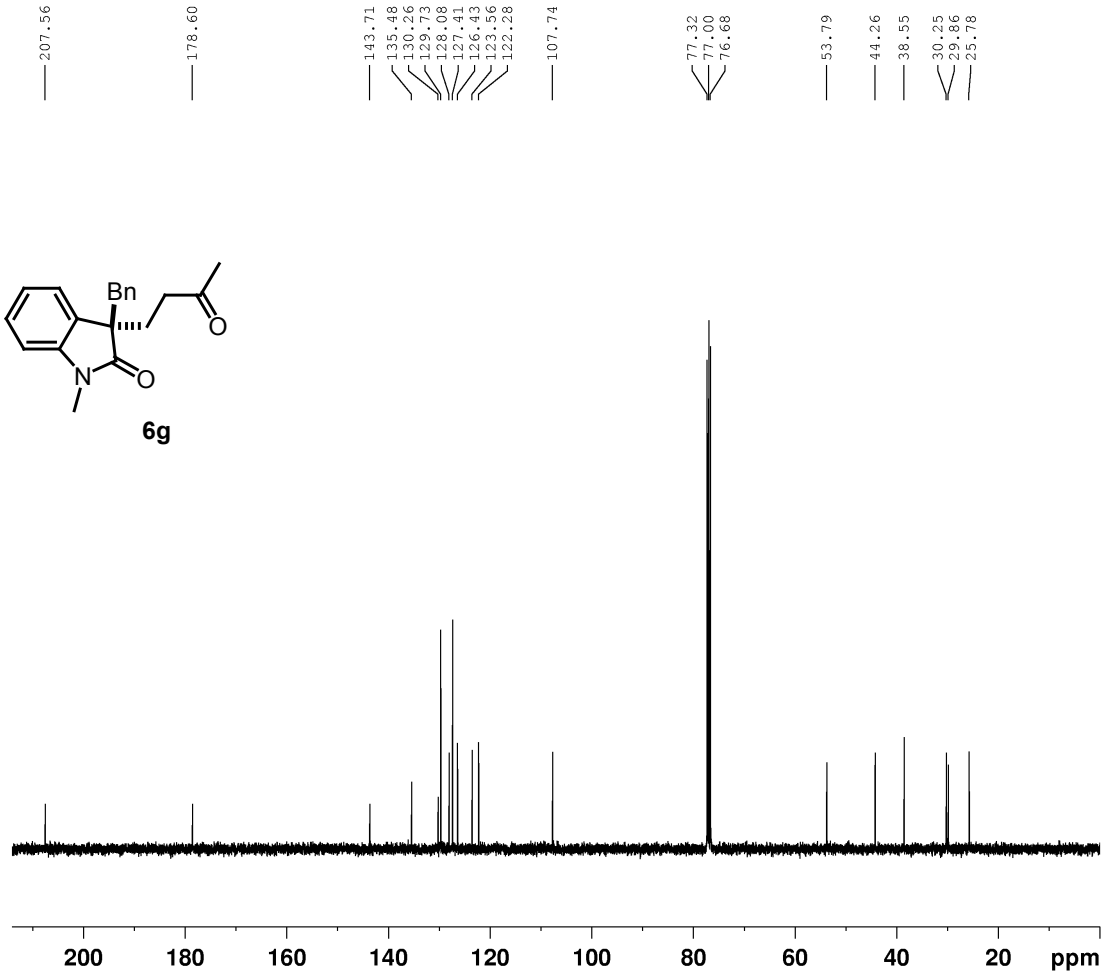
5.02
7.00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127.41
126.43
123.56
122.28
107.74
77.32
77.00
76.68
53.79
44.26
38.55
30.25
29.86
25.78
Bn
O
N
O
6g
200
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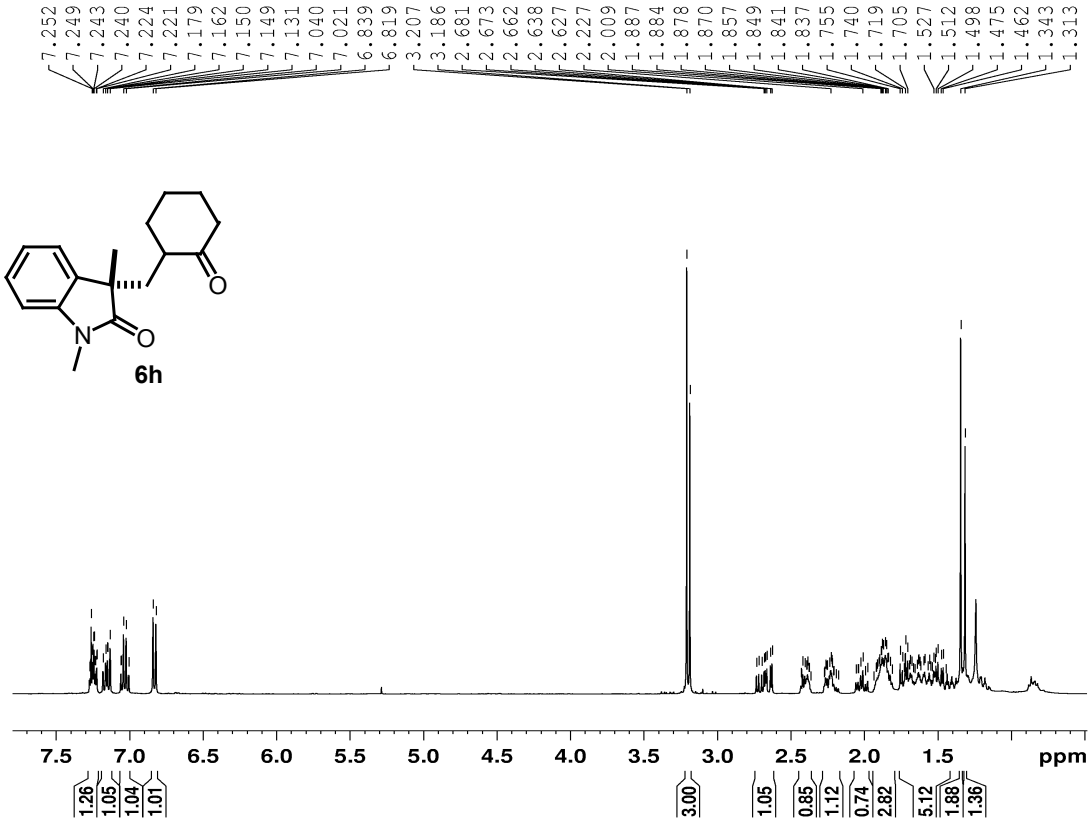
160
140
120
100
80
60
40
20
ppm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7.240
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7.221
7.179
7.162
7.150
7.149
7.131
7.040
7.021
6.839
6.819
3.207
3.186
2.681
2.673
2.662
2.638
2.627
2.227
2.009
1.887
1.884
1.878
1.870
1.857
1.849
1.841
1.837
1.755
1.740
1.719
1.705
1.527
1.512
1.498
1.475
1.462
1.343
1.313
N
O
O
O
6h
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
ppm
1.26
1.05
1.04
1.01
3.00
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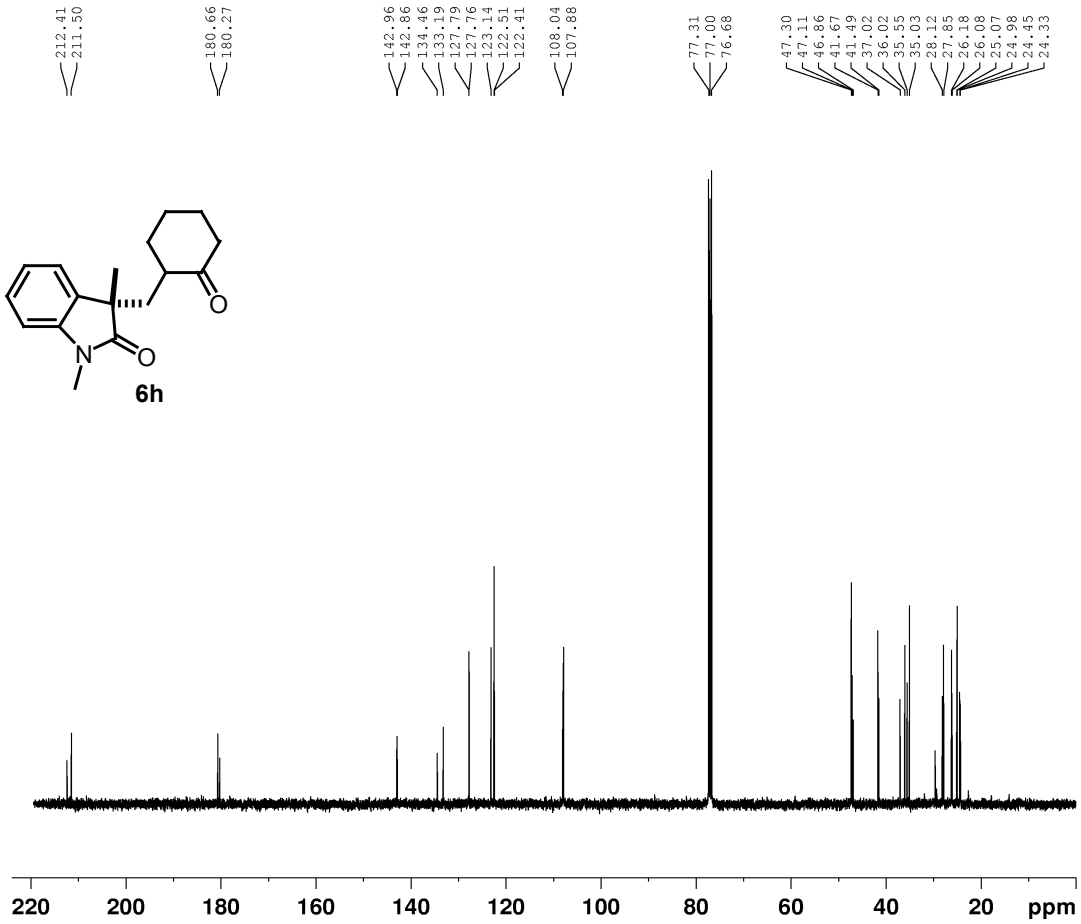
0.74
2.82
5.12
1.88
1.36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142.86
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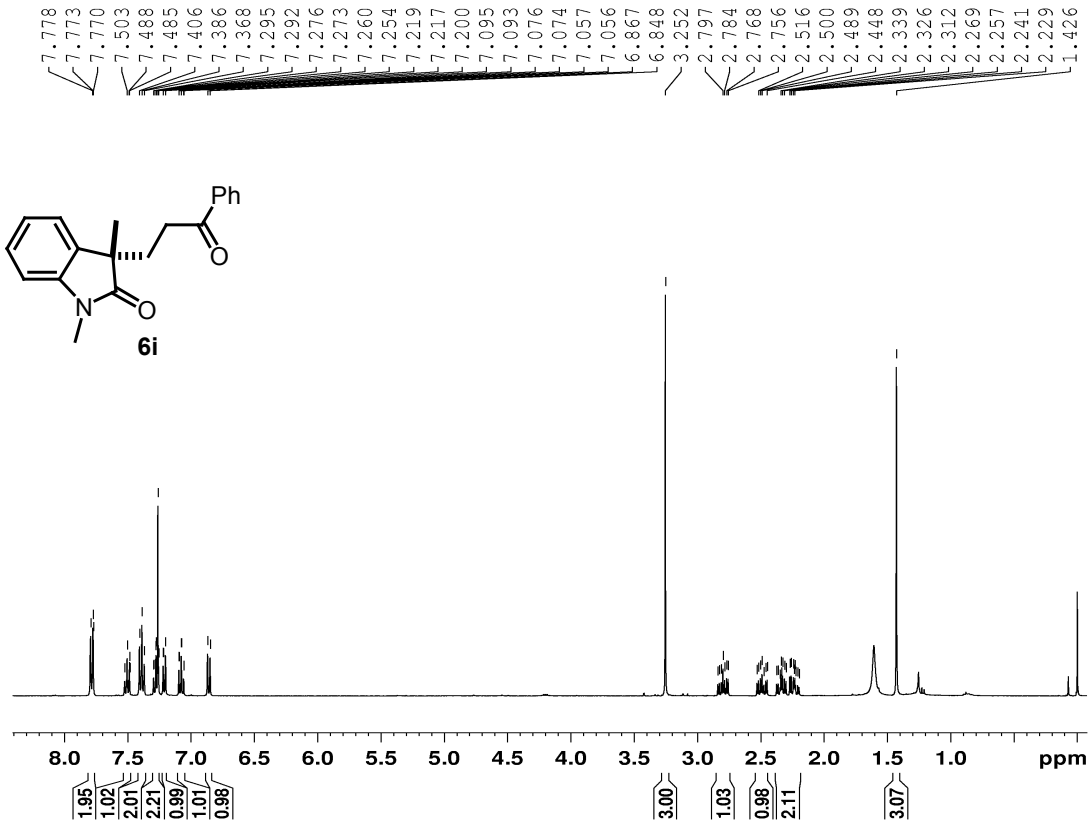
133.19
127.79
127.76
123.14
122.51
122.41
108.04
107.88
77.31
77.00
76.68
47.30
47.11
46.86
41.67
41.49
37.02
36.02
35.55
35.03
28.12
27.85
26.18
26.08
25.07
24.98
24.45
24.33
N
O
O
O
6h
220
200
180
160
140
120
100
80
60
40
20
ppm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7.292
7.276
7.273
7.260
7.254
7.219
7.217
7.200
7.095
7.093
7.076
7.074
7.057
7.056
6.867
6.848
3.252
2.797
2.784
2.768
2.756
2.516
2.500
2.489
2.448
2.339
2.326
2.312
2.269
2.257
2.241
2.229
1.426
Ph
O
N
O
6i
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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2.21
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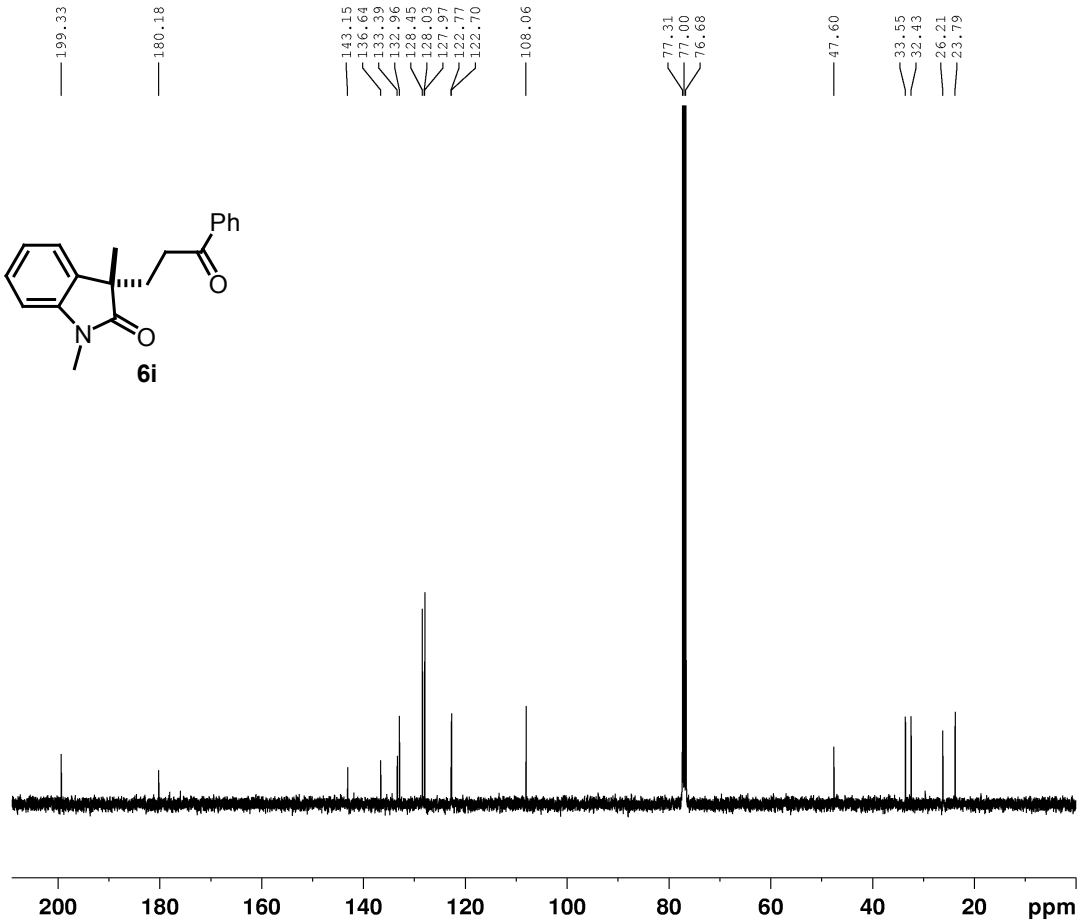
1.01
0.98
3.00
1.03
0.98
2.11
3.07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133.39
132.96
128.45
128.03
127.97
122.77
122.70
108.06
77.31
77.00
76.68
47.60
33.55
32.43
26.21
23.79
Ph
O
N
O
6i
200
180
160
140
120
100
80
60
40
20
ppm