Supporting Information

Addition of Indoles to Oxyallyl Cations for Facile Access to α-Indole Carbonyl Compounds

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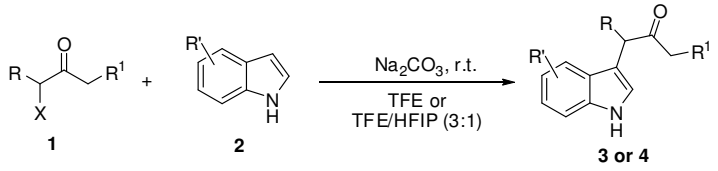
I. General Information.

Nuclear magnetic resonance spectra (^{1}H and ^{13}C) were recorded on a JEOL ECA400 (400 MHz), Bruker AV300 (300 MHz), AV400 (400 MHz), AV500 (500 MHz) or BBFO400 (400 MHz) spectrometers. ^{1}H NMR chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or DMSO (δ = 2.50, singlet), and the splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). High resolution mass spectral analysis (HRMS) was performed on Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp or chemical stains like $KMnO_4$ and 2,4-dinitrophenyl hydrazine solutions.

Commercially available materials purchased from Alfa Aesar or Aldrich were used as received, except *α*-haloketones that were further purified *via* distillation or column chromatography over silica gel prior to use. Some of the *α*-chloroketones (manuscript Table 2, **1c**,[1] **1d,**[2] **1e**,[3] **1h**[4]) and bromoketones (manuscript Table 2, **1g**, **1i**, **1j**, **1l**, **1o**, **1p**)[5] were prepared using literature method.

II-A. General procedure for addition of indoles to *α*-haloketones (for Scheme 1 and Table 2 in the manuscript).

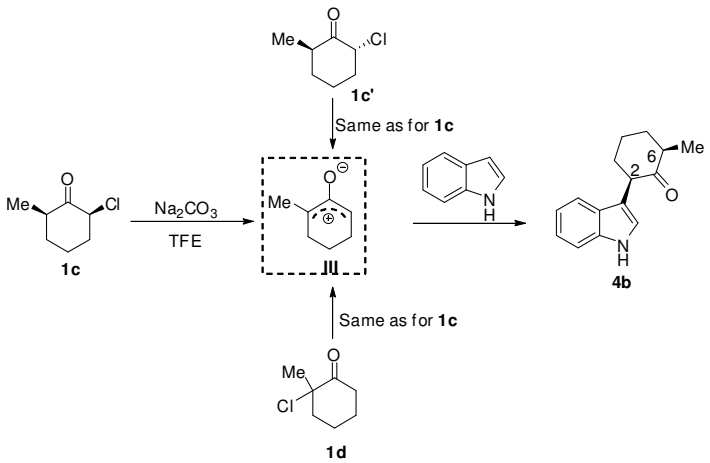


A 4 mL vial equipped with a magnetic stir bar was charged with freshly distilled *α*-haloketone **1** (0.5 mmol), indole **2** (0.5 mmol) and TFE (1.0 mL) or TFE/HFIP (3:1). Anhydrous Na_2CO_3 (0.6 mmol) was added to the reaction mixture and stirred at r.t. After completion of the reaction (monitored by TLC and crude ^{1}H NMR analysis), the reaction mixture was filtered through a celite pad using Et_2O or CH_2Cl_2 and the filtrate was concentrated under reduced pressure. The crude residue was purified by silica gel flash chromatography using EtOAc/hexanes as eluent to give pure product **3** or **4**. In some cases, analytically pure products could be obtained merely by simple filtration and evaporation under reduced pressure.

II-B. Studies of the reaction mechanism.

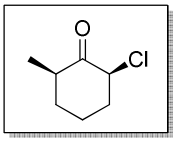
The three isomers of chloro methyl cyclohexanone (two diastereomers **1c** and **1c',** and one regiomer **1d**) were subjected to identical reaction conditions in presence of Na_2CO_3 in TFE. After completion of the reaction, they all produced the same product *cis*-**4b** in same d.r. These results suggest the formation of commom oxyallyl intermediate **III** and accordinly, the S_N1 pathway for the reactions (Scheme S1). The relative *cis*-configuration of **4b** was confirmed by NOE experiment. Irradiation of the multiplet peak at 3.94 ppm (corresponding to H-2) resulted in the observation of strong NOEs with the multiplet peak at 2.69 ppm (corresponding to H-6). Similar observations were obtained for the two regiomers of dichloroacetones (manuscript Table 2, **1m** and **1n**) also, as described in equation 1 in the manuscript, further supporting our postulated mechanism.

Entry	Chloroketone **1**	Time (d)	**4b**
1	*cis*-2-Chloro-6-methylcyclohexanone (**1c**)	3.0	73% yield, 10:1 d.r.
2	*trans*-2-Chloro-6-methylcyclohexanone (**1c'**)	3.0	76% yield, 10:1 d.r.
3	2-Chloro-2-methylcyclohexanone (**1d**)	1.5	88% yield, 10:1 d.r.

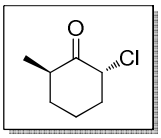


Scheme S1. Studies of the reaction mechanism.

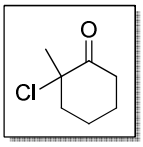
III. Characterizations of substrates and products:



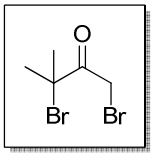
***cis*-2-Chloro-6-methylcyclohexanone (1c):**Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 – 4.39 (m, 1H), 2.67 – 2.54 (m, 1H), 2.49 (dt, J = 13.0, 6.5 Hz, 1H), 2.12 (dtd, J = 8.5, 5.7, 3.1 Hz, 1H), 2.01 – 1.90 (m, 2H), 1.89 – 1.75 (m, 1H), 1.42 (qd, J = 13.0, 3.8 Hz, 1H), 1.11 (d, J = 6.5 Hz, 3H).



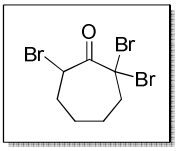
***trans*-2-Chloro-6-methylcyclohexanone (1c'):** Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (t, J = 2.9 Hz, 1H), 3.21 – 3.07 (m, 1H), 2.39 – 2.23 (m, 1H), 2.19 – 2.00 (m, 3H), 1.78 – 1.66 (m, 1H), 1.46 – 1.29 (m, 1H), 1.05 (d, J = 6.6 Hz, 3H).



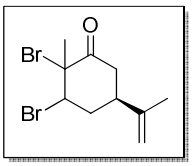
2-Chloro-2-methylcyclohexanone (1d): Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.12 – 2.96 (m, 1H), 2.40 – 2.25 (m, 2H), 2.15 – 1.97 (m, 2H), 1.86 (ddd, J = 14.7, 12.2, 3.8 Hz, 1H), 1.77 – 1.67 (m, 1H), 1.68 – 1.54 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 70.47, 42.96, 36.95, 27.05, 26.59, 21.39.



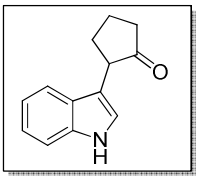
1,3-Dibromo-3-methylbutan-2-one (1j): Prepared using 2.2 equivalents of bromine as per the literature method in described in reference 5; Brown oil, 51% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.44 (s, 1H), 1.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7, 62.6, 29.9, 29.7; HRMS (ESI) calcd for $C_5H_9Br_2O$ $(M+1)^+$: 241.8942, Found: 241.8944.



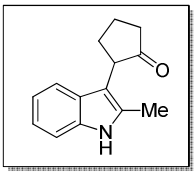
2,2,7-Tribromocycloheptanone (1p): Prepared using 3.5 equivalents of bromine as per the literature method described in reference 5; Brown solid, 48% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.01 (dd, J = 11.5, 2.9 Hz, 1H), 3.31 (dd, J = 16.1, 8.8 Hz, 1H), 2.77 (dd, J = 16.0, 10.2 Hz, 1H), 2.46 – 2.28 (m, 1H), 2.04 (qdd, J = 11.5, 4.1, 1.7 Hz, 1H), 1.99 – 1.83 (m, 2H), 1.77 – 1.59 (m, 1H), 1.51 – 1.32 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 67.3, 47.6, 46.9, 36.9, 28.09, 25.0; HRMS (ESI) calcd for $C_7H_{10}Br_3O$ $(M+1)^+$: 346.8282, Found: 346.8290.



(5*R*)-2,3-Dibromo-2-methyl-5-(prop-1-en-2-yl)cyclohexanone (1q):[6] Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (s, 1H), 4.85 – 4.81 (m, 2H), 3.27 (t, J = 14.0 Hz, 1H), 3.09 (t, J = 13.0 Hz, 1H), 2.85 (t, J = 13.0 Hz, 1H), 2.50 (d, J = 14.8 Hz, 1H), 2.23 (dd, J = 14.8, 2.1 Hz, 1H), 2.00 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.5, 145.6, 111.1, 63.0, 59.7, 40.4, 40.2, 35.7, 28.1, 20.4; HRMS (ESI) calcd for $C_{10}H_{15}Br_2O$ $(M+1)^+$: 308.9490, Found: 308.9495.

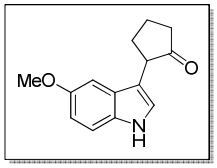


2-(1*H*-Indol-3-yl)cyclopentanone (3a): White solid, >95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (brs, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.20 (t, J = 8.0 Hz,1H), 7.10 (t, J = 8.0 Hz,1H), 7.05 (d, J = 2.3 Hz, 1H), 3.62 (t, J = 9.2 Hz, 1H), 2.65 – 2.45 (m, 2H), 2.44 – 2.30 (m, 1H), 2.26 – 2.08 (m, 2H), 2.08 – 1.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.9, 136.5, 126.8, 122.1, 121.7, 119.5, 119.3, 113.0, 111.3, 47.1, 38.1, 31.5, 21.1; HRMS (ESI) calcd for $C_{13}H_{14}NO$ $(M+1)^+$: 200.1075, Found: 200.1074.

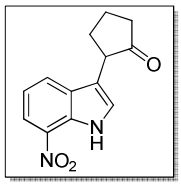


2-(2-Methyl-1*H*-indol-3-yl)cyclopentanone (3b): White solid, >95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (brs, 1H), 7.22 (d, J = 9.4 Hz, 2H), 7.08 (t, J = 8.0 Hz,1H), 7.00 (t, J = 8.0 Hz,1H), 3.50 (dd, J = 11.2, 8.6 Hz, 1H), 2.71 – 2.53 (m, 1H), 2.53 – 2.34 (m, 2H), 2.29 (s, 3H), 2.26 – 2.14

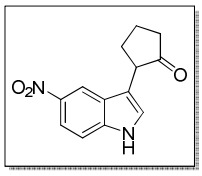
(m, 2H), 2.04 – 1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 219.9, 135.5, 132.6, 127.1, 121.0, 119.2, 118.1, 110.7, 108.5, 47.4, 38.6, 31.3, 21.4, 11.9; HRMS (ESI) calcd for $C_{14}H_{16}NO$ $(M+1)^+$: 214.1232, Found: 214.1231.



2-(5-Methoxy-1*H*-indol-3-yl)cyclopentanone (3c): White solid, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (brs, 1H), 7.24 (d, J = 7.2 Hz, 1H), 7.00 (t, J = 3.2 Hz, 2H), 6.85 (dd, J = 8.8, 2.4 Hz, 1H), 3.85 (s, 3H), 3.58 (t, J = 9.2 Hz, 1H), 2.56 (ddd, J = 14.9, 8.8, 2.4 Hz, 1H), 2.49 (ddd, J = 8.3, 7.7, 2.1 Hz, 1H), 2.44 – 2.25 (m, 1H), 2.29 – 2.08 (m, 2H), 2.09 – 1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.8, 154.0, 131.6, 127.3, 122.4, 112.8, 112.3, 111.9, 101.4, 55.9, 47.1, 38.1, 31.3, 21.1; HRMS (ESI) calcd for $C_{14}H_{16}NO_2$ $(M+1)^+$: 230.1181, Found: 230.1178.

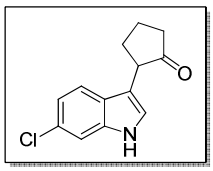


2-(7-Nitro-1*H*-indol-3-yl)cyclopentanone (3d): Yellow solid, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (brs, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.21 (t, J = 7.9 Hz, 1H), 3.65 (t, J = 8.4 Hz, 1H), 2.74 – 2.46 (m, 2H), 2.46 – 2.28 (m, 1H), 2.31 – 2.10 (m, 2H), 2.11 – 1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.6, 132.9, 130.8, 129.8, 127.8, 123.8, 119.5, 118.9, 114.7, 46.7, 37.9, 31.1, 21.1; HRMS (ESI) calcd for $C_{13}H_{13}N_2O_3$ $(M+1)^+$: 245.0926, Found: 245.0928.

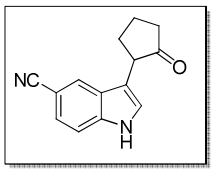


2-(5-Nitro-1*H*-indol-3-yl)cyclopentanone (3e): Yellow solid, 84% yield; ^{1}H NMR (400 MHz, DMSO) δ 11.70 (brs, 1H), 8.51 (d, J = 2.1 Hz, 1H), 7.99 (dd, J = 9.0 Hz, 2.2, 1H), 7.52 (d, J = 9.0 Hz, 1H), 7.44 (d, J = 1.8 Hz, 1H), 3.80 (dd, J = 10.6, 8.5 Hz, 1H), 2.47 – 2.21 (m, 3H), 2.22 – 2.05 (m, 2H), 1.98 (d, J = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 217.7, 140.7, 139.9, 126.79,

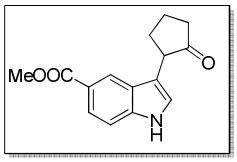
126.72, 117.1, 116.9, 115.5, 112.3, 46.5, 37.8, 30.7, 21.0; HRMS (ESI) calcd for $C_{13}H_{13}N_2O_3$ $(M+1)^+$: 245.0926, Found: 245.0930.



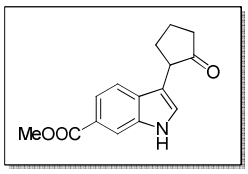
2-(6-Chloro-1*H*-indol-3-yl)cyclopentanone (3f): Light red solid, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (brs, 1H), 7.45 (d, *J* = 1.6 Hz, 1H), 7.07 (dt, *J* = 8.6, 5.2 Hz, 2H), 6.82 (d, *J* = 2.4 Hz, 1H), 3.50 (dd, *J* = 10.1, 9.1 Hz, 1H), 2.48 (ddd, *J* = 8.3, 7.4, 4.3 Hz, 2H), 2.42 – 2.22 (m, 1H), 2.22 – 1.79 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 219.5, 134.8, 127.7, 125.0, 123.5, 122.3, 118.6, 112.5, 112.3, 47.2, 38.1, 31.3, 21.0; HRMS (ESI) calcd for $C_{13}H_{13}ClNO$ $(M+1)^+$: 234.0686, Found: 234.0681.



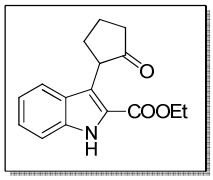
3-(2-Oxocyclopentyl)-1*H*-indole-5-carbonitrile (3g): White solid, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.43 (brs, 1H), 7.93 (s, 1H), 7.40 (q, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 2.3 Hz, 1H), 3.61 (t, *J* = 8.0 Hz, 1H), 2.73 – 2.47 (m, 2H), 2.47 – 2.29 (m, 1H), 2.29 – 2.17 (m, 1H), 2.17 – 1.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 218.3, 138.1, 126.6, 125.2, 125.0, 123.9, 120.7, 113.9, 112.2, 102.5, 46.9, 38.0, 31.2, 21.0; HRMS (ESI) calcd for $C_{14}H_{13}N_2O$ $(M+1)^+$: 225.1028, Found: 225.1025.



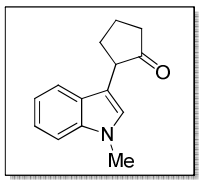
Methyl 3-(2-oxocyclopentyl)-1*H*-indole-5-carboxylate (3h): White solid, 90% yield; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.31 (s, 1H), 8.29 (brs, 1H), 7.90 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.13 (d, *J* = 2.1 Hz, 1H), 3.93 (s, 3H), 3.66 (dd, *J* = 11.0, 8.3 Hz, 1H), 2.73 – 2.59 (m, 1H), 2.61 – 2.46 (m, 1H), 2.39 (ddd, *J* = 18.9, 10.3, 8.8 Hz, 1H), 2.24 – 2.15 (m, 1H), 2.15 – 2.08 (m, 1H), 2.08 – 1.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 219.1, 168.3, 139.1, 126.4, 123.39, 123.35, 122.1, 121.3, 114.1, 111.1, 51.9, 47.1, 38.1, 31.6, 21.0; HRMS (ESI) calcd for $C_{15}H_{16}NO_3$ $(M+1)^+$: 258.1130, Found: 258.1128.



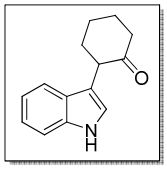
Methyl 3-(2-oxocyclopentyl)-1*H*-indole-6-carboxylate (3i): White solid, 89% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (brs, 1H), 8.05 (s, 1H), 7.76 (dd, J = 8.4, 1.3 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.12 (t, J = 5.0 Hz, 1H), 3.92 (s, 3H), 3.60 (t, J = 11.5 Hz, 1H), 2.67 – 2.45 (m, 2H), 2.38 (ddd, J = 18.9, 10.3, 8.8 Hz, 1H), 2.17 (dddd, J = 23.3, 18.0, 9.1, 4.5 Hz, 2H), 2.07 – 1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.8, 168.1, 135.7, 130.3, 125.3, 123.7, 120.5, 118.8, 113.8, 113.2, 51.9, 47.1, 38.1, 31.4, 21.1; HRMS (ESI) calcd for $C_{15}H_{16}NO_3$ $(M+1)^+$: 258.1130, Found: 258.1130.



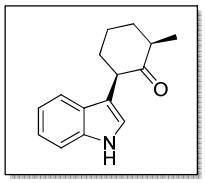
Ethyl 3-(2-oxocyclopentyl)-1*H*-indole-2-carboxylate (3j): Colorless oil, 91% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (brs, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.36 (d, J = 8.3 Hz, 1H), 7.29 (dd, J = 8.1, 7.2 Hz, 1H), 7.11 (dd, J = 7.9, 7.1 Hz, 1H), 4.43 – 4.25 (m, 2H), 4.26 – 4.16 (m, 1H), 2.62 – 2.52 (m, 2H), 2.50 – 2.38 (m, 1H), 2.37 – 2.18 (m, 2H), 2.01 (ddd, J = 18.4, 9.3, 6.0 Hz, 1H), 1.38 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.5, 161.3, 135.9, 127.1, 125.6, 123.6, 121.0, 120.4, 120.3, 112.2, 60.7, 47.4, 38.2, 31.5, 21.5, 14.4; HRMS (ESI) calcd for $C_{16}H_{18}NO_3$ $(M+1)^+$: 272.1287, Found: 272.1289.



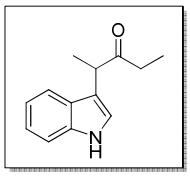
2-(1-Methyl-1*H*-indol-3-yl)cyclopentanone (3k): White solid, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 7.09 (t, J = 7.2, 1H), 6.94 (s, 1H), 3.75 (s, 3H), 3.61 (t, J = 9.2 Hz, 1H), 2.65 – 2.45 (m, 2H), 2.45 – 2.26 (m, 1H), 2.26 – 2.08 (m, 2H), 2.08 – 1.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 219.0, 137.3, 127.2, 126.5, 121.8, 119.4, 119.1, 111.5, 109.5, 47.2, 38.2, 32.8, 31.9, 21.2; HRMS (ESI) calcd for $C_{14}H_{16}NO$ $(M+1)^+$: 214.1232, Found: 214.1233.



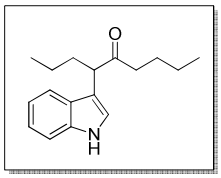
2-(1*H*-Indol-3-yl)cyclohexanone (4a): Yellow solid, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (brs, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 7.08 (t, J = 10.0 Hz, 2H), 3.92 (dd, J = 11.3, 5.5 Hz, 1H), 2.68 – 2.48 (m, 2H), 2.48 – 2.30 (m, 1H), 2.27 – 1.98 (m, 3H), 1.98 – 1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 136.1, 126.9, 122.0, 121.8, 119.4, 119.1, 113.9, 111.2, 48.7, 41.9, 35.0, 28.1, 25.3; HRMS (ESI) calcd for $C_{14}H_{16}NO$ $(M+1)^+$: 214.1232, Found: 214.1228.



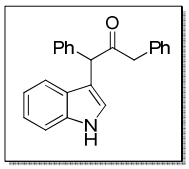
***cis*-2-(1*H*-Indol-3-yl)-6-methylcyclohexanone (4b):** White solid, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (brs, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 8.0 Hz, 1H), 7.04 (t, J = 8.4 Hz, 1H), 4.00 – 3.81 (m, 1H), 2.67 (dt, J = 12.9, 6.5 Hz, 1H), 2.42 (ddd, J = 11.7, 4.9, 2.5 Hz, 1H), 2.29 – 2.15 (m, 1H), 2.01 – 1.89 (m, 2H), 1.65 – 1.49 (m, 1H), 1.10 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.9, 136.1, 127.0, 122.2, 121.7, 119.2, 118.8, 113.6, 111.3, 48.8, 45.8, 37.5, 36.5, 26.0, 14.8; HRMS (ESI) calcd for $C_{15}H_{18}NO$ $(M+1)^+$: 228.1388, Found: 228.1386.



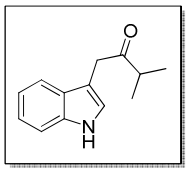
2-(1*H*-Indol-3-yl)pentan-3-one (4c): Yellow oil, >95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (brs, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 4.04 (q, J = 7.0 Hz, 1H), 2.65 – 2.28 (m, 2H), 1.50 (d, J = 7.0 Hz, 3H), 0.96 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.5, 136.3, 126.5, 122.3, 121.7, 119.8, 118.9, 115.9, 111.2, 43.8, 33.4, 16.8, 8.0; HRMS (ESI) calcd for $C_{13}H_{16}NO$ $(M+1)^+$: 202.1232, Found: 202.1231.



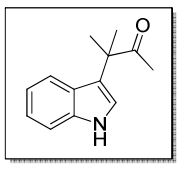
4-(1*H*-Indol-3-yl)nonan-5-one (4d): Yellow oil, 95% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (brs, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H), 7.03 (d, J = 2.4Hz, 1H), 3.93 (t, J = 7.4 Hz, 1H), 2.48 – 2.30 (m, 2H), 2.12 – 1.98 (m, 1H), 1.89 – 1.73 (m, 1H), 1.52 – 1.38 (m, 2H), 1.29 (dt, J = 14.6, 7.3 Hz, 2H), 1.24 – 1.09 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H), 0.78 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.8, 136.3, 126.8, 122.27, 122.23, 119.7, 119.0, 114.1, 111.3, 49.7, 40.9, 33.7, 26.0, 22.2, 21.0, 14.1, 13.8; HRMS (ESI) calcd for $C_{17}H_{24}NO$ $(M+1)^+$: 258.1858, Found: 258.1856.



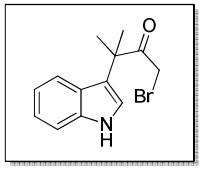
1-(1*H*-Indol-3-yl)-1,3-diphenylpropan-2-one (4e): Brown solid, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (brs, 1H), 7.42 – 7.21 (m, 10H), 7.22 – 7.11 (m, 3H), 7.04 (dd, J = 9.8, 5.2 Hz, 2H), 5.46 (s, 1H), 3.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 138.2, 136.2, 134.3, 129.6, 128.9, 128.7, 128.6, 127.1, 127.0, 126.7, 123.5, 122.3, 119.8, 118.8, 113.2, 111.2, 54.4, 49.2; HRMS (ESI) calcd for $C_{23}H_{20}NO$ $(M+1)^+$: 326.1545, Found: 326.1544.



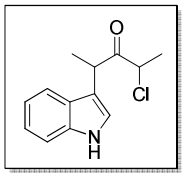
1-(1*H*-Indol-3-yl)-3-methylbutan-2-one (4f): White solid, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (brs, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.17 – 7.09 (m, 2H), 3.88 (s, 2H), 2.80 (dt, J = 13.8, 6.9 Hz, 1H), 1.11 (d, J = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.7, 136.1, 127.4, 123.0, 122.2, 119.7, 118.6, 111.1, 108.9, 39.5, 37.5, 18.5; HRMS (ESI) calcd for $C_{13}H_{16}NO$ $(M+1)^+$: 202.1232, Found: 202.1231.



3-(1*H*-Indol-3-yl)-3-methylbutan-2-one (4f', the regiomer of **4f):** White solid, 19% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (brs, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.20 (t, *J* = 8.2 Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 7.08 (t, *J* = 8.2 Hz, 1H), 1.95 (s, 3H), 1.57 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 136.9, 125.7, 122.2, 120.7, 120.6, 119.9, 119.8, 111.2, 48.0, 30.9, 24.7; HRMS (ESI) calcd for $C_{13}H_{16}NO$ $(M+1)^+$: 202.1232, Found: 202.1229.

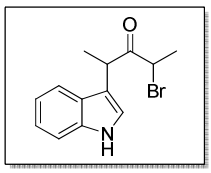


1-Bromo-3-(1*H*-indol-3-yl)-3-methylbutan-2-one (4g): Yellow solid, >95% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (brs, 1H), 7.40 (dd, *J* = 8.2, 3.1 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 2.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 3.94 (s, 2H), 1.66 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.1, 136.9, 125.4, 122.6, 121.0, 120.2, 119.5, 119.0, 111.5, 47.6, 32.6, 25.1; HRMS (ESI) calcd for $C_{13}H_{15}BrNO$ $(M+1)^+$: 280.0337, Found: 280.0338.



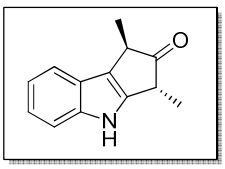
2-Chloro-4-(1*H*-indol-3-yl)pentan-3-one (4h) (The less polar major isomer)**:** yellow oil, 46% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (brs, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.24 (t, *J* = 8.4 Hz, 1H), 7.15 (t, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 4.60 (q, *J* = 6.9 Hz, 1H), 4.45 (q, *J* = 6.7 Hz, 1H), 1.54 (d, *J* = 6.9 Hz, 3H), 1.42 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 136.4, 126.1, 122.6, 122.5, 120.1, 118.7, 114.3, 111.4, 54.9, 40.1, 19.3, 17.0; HRMS (ESI) calcd for $C_{13}H_{15}ClNO$ $(M+1)^+$: 236.0842, Found: 236.0850.

2-Chloro-4-(1*H*-indol-3-yl)pentan-3-one (4h', more polar minor diastereomer of **4h):** yellow oil, 47% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (brs, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.22 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 7.15 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 4.54 (q, *J* = 7.0 Hz, 1H), 4.44 (q, *J* = 7.0 Hz, 1H), 1.56 (d, *J* = 7.0 Hz, 3H), 1.56 – 1.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 136.3, 126.2, 122.5, 122.3, 120.1, 118.7, 114.4, 111.4, 57.2, 40.3, 21.3, 17.9; HRMS (ESI) calcd for $C_{13}H_{15}ClNO$ $(M+1)^+$: 236.0842, Found: 236.0848.

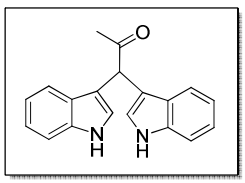


2-Bromo-4-(1*H*-indol-3-yl)pentan-3-one (4i) (the less polar major isomer)**: y**ellow solid, 46% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (brs, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.26 (t, J = 8.0 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 7.08 (d, J = 2.4 Hz, 1H), 4.66 (q, J = 6.9 Hz, 1H), 4.57 (q, J = 6.7 Hz, 1H), 1.59 (dd, J = 9.0, 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.5, 136.3, 126.1, 122.6, 122.3, 120.1, 118.7, 114.7, 111.4, 44.9, 40.2, 19.7, 17.0; HRMS (ESI) calcd for $C_{13}H_{15}BrNO$ $(M+1)^+$: 280.0337, Found: 280.0345.

2-Bromo-4-(1*H*-indol-3-yl)pentan-3-one (4i') (the more polar minor diastereomer of **4i):** yellow solid, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (brs, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.17 – 7.12 (m, 2H), 4.59 (q, J = 6.9 Hz, 1H), 4.45 (q, J = 7.1 Hz, 1H), 1.72 – 1.47 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 136.2, 126.3, 122.5, 122.2, 119.9, 118.7, 114.6, 111.35, 46.2, 40.8, 21.3, 18.6; HRMS (ESI) calcd for $C_{13}H_{15}BrNO$ $(M+1)^+$: 280.0337, Found: 280.0341.

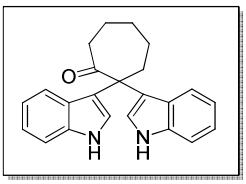


***trans*-1,3-Dimethyl-3,4-dihydrocyclopenta[*b*]indol-2(1*H*)-one (4j):** Yellow solid, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.6 Hz, 1H), 7.33 – 7.27 (m, 1H), 6.89 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 4.61 (s, 1H), 4.53 (d, J = 2.8 Hz, 1H), 2.62 (qd, J = 7.2, 3.6 Hz, 1H), 1.97 (d, J = 2.9 Hz, 3H), 1.34 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 168.6 156.2, 132.8, 127.1, 124.9, 122.7, 120.2, 112.2, 72.8, 51.6, 13.4, 8.58; HRMS (ESI) calcd for $C_{13}H_{14}NO$ $(M+1)^+$: 200.1075, Found: 200.1080.

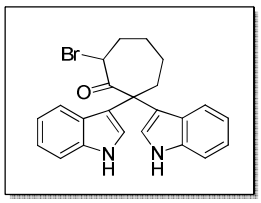


1,1-Di(1*H*-indol-3-yl)propan-2-one (4k): Yellow solid, 72% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (brs, 2H), 7.50 (d, J = 7.9 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.15 (t, J = 7.1 Hz, 2H), 7.08 (t, J =

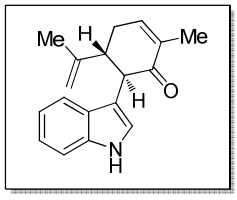
7.1 Hz, 2H), 6.80 (d, *J* = 2.2 Hz, 2H), 5.53 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 136.4, 126.7, 123.6, 122.2, 119.7, 119.0, 113.2, 111.4, 48.1, 28.9; HRMS (ESI) calcd for $C_{19}H_{17}N_2O$ $(M+1)^+$: 289.1341, Found: 289.1346.



2,2-Di(1*H*-indol-3-yl)cycloheptanone (4l): White solid, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (brs, 1H), 7.42 (d, *J* = 2.5 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.79 (dd, *J* = 11.2, 4.0 Hz, 1H), 2.79 – 2.69 (m, 1H), 2.69 – 2.59 (m, 1H), 1.87 – 1.78 (m, 1H), 1.78 – 1.69 (m, 1H), 1.61 (dd, *J* = 10.2, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 136.6, 126.5, 123.3, 121.6, 121.2, 119.1, 117.8, 110.8, 56.1, 40.0, 36.3, 30.4, 26.8, 24.6; HRMS (ESI) calcd for $C_{23}H_{22}N_2O$ $(M+1)^+$: 342.1732, Found: 342.1733.

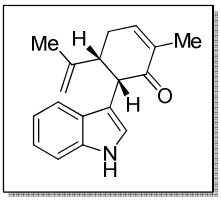


7-Bromo-2,2-di(1*H*-indol-3-yl)cycloheptanone (4m): White solid, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (brs, 1H), 8.07 (brs, 1H), 7.40 (t, *J* = 2.6 Hz, 1H), 7.36 (t, *J* = 2.5 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 3.8 Hz, 1H), 7.25 (d, *J* = 3.8 Hz, 1H), 7.04 (ddd, *J* = 16.9, 9.8, 4.0 Hz, 3H), 6.80 (ddd, *J* = 17.6, 11.6, 4.0 Hz, 2H), 5.16 (dd, *J* = 12.3, 3.0 Hz, 1H), 2.96 (dd, *J* = 14.6, 8.9 Hz, 1H), 2.56 (dd, *J* = 14.6, 9.9 Hz, 1H), 2.44 – 2.31 (m, 1H), 2.12 (ddd, *J* = 25.9, 12.3, 4.9 Hz, 1H), 1.92 (d, *J* = 14.3 Hz, 1H), 1.82 (dd, *J* = 14.7, 6.3 Hz, 1H), 1.76 – 1.61 (m, 1H), 1.53 – 1.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 136.8, 136.3, 126.3, 126.1, 123.9, 122.3, 122.2, 121.38, 121.34, 120.6, 119.8, 118.9, 117.1, 116.7, 111.05, 111.01, 55.1, 52.4, 37.9, 36.0, 29.5, 23.8; HRMS (ESI) calcd for $C_{23}H_{22}BrN_2O$ $(M+1)^+$: 342.1732, Found: 342.1733.



(5*R*,6*R*)-6-(1*H*-Indol-3-yl)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enone (5):[7] White solid, 57% yield; $[\alpha]_D^{20}$ = +58° (c = 0.011 g/mL, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (brs, 1H), 7.42 (d,

J = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.15 (dt, *J* = 8.0, 2.4 Hz, 1H), 7.07 (dt, *J* = 7.5, 2.4 Hz, 1H), 6.88 (s, 1H), 6.75 (d, *J* = 2.0 Hz, 1H), 4.67 (s, 1 H), 4.63 (s, 1 H), 3.91 (d, *J* = 10.8 Hz, 1H), 3.31 – 3.18 (m, 1H), 2.68 – 2.40 (m, 2H), 1.87 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 145.9, 143.5, 136.2, 135.4, 127.1, 122.5, 121.8, 119.3, 119.2, 112.9, 112.8, 111.2, 49.0, 48.3, 30.9, 19.3, 16.2; HRMS (ESI) calcd for $C_{18}H_{20}NO$ $(M+1)^+$: 266.1545, Found: 266.1547.



(5*R*,6*S*)-6-(1*H*-Indol-3-yl)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enone (5'): White solid, 11% yield; $[\alpha]_D^{20}$ = -31° (c = 0.008 g/mL, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (brs, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.16 (t, *J* = 10.0 Hz, 1H), 7.10 (t, *J* = 10.0 Hz, 1H), 7.06 (dd, *J* = 18.6, 1.6 Hz, 1H), 6.86 (dd, *J* = 3.1, 1.5 Hz, 1H), 4.70 (d, *J* = 0.8 Hz, 1H), 4.58 (s, 1H), 4.29 (d, *J* = 4.4 Hz, 1H), 3.08-3.05 (m, 1H), 2.75-2.68 (m, 1H), 2.44-2.38 (m, 1H),1.86 (d, *J* = 1.5 Hz, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 145.2, 144.6, 135.7, 135.2, 128.1, 122.1, 121.5, 119.6, 119.4, 112.0, 110.8, 109.7, 47.5, 45.5, 27.8, 22.0, 16.4; HRMS (ESI) calcd for $C_{18}H_{20}NO$ $(M+1)^+$: 266.1545, Found: 266.1548.

IV. References

(1) (a) Laskovics, F. M.; Schulman, E. M., *J. Am. Chem. Soc.* **1977,** *99,* 6672. (b) Laskovics, F. M.; Schulman, E. M., *Tetrahedron Lett.* **1977,** *18,* 759.

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(3) Brummond, K. M.; Gesenberg, K. D., *Tetrahedron Lett.* **1999,** *40,* 2231.

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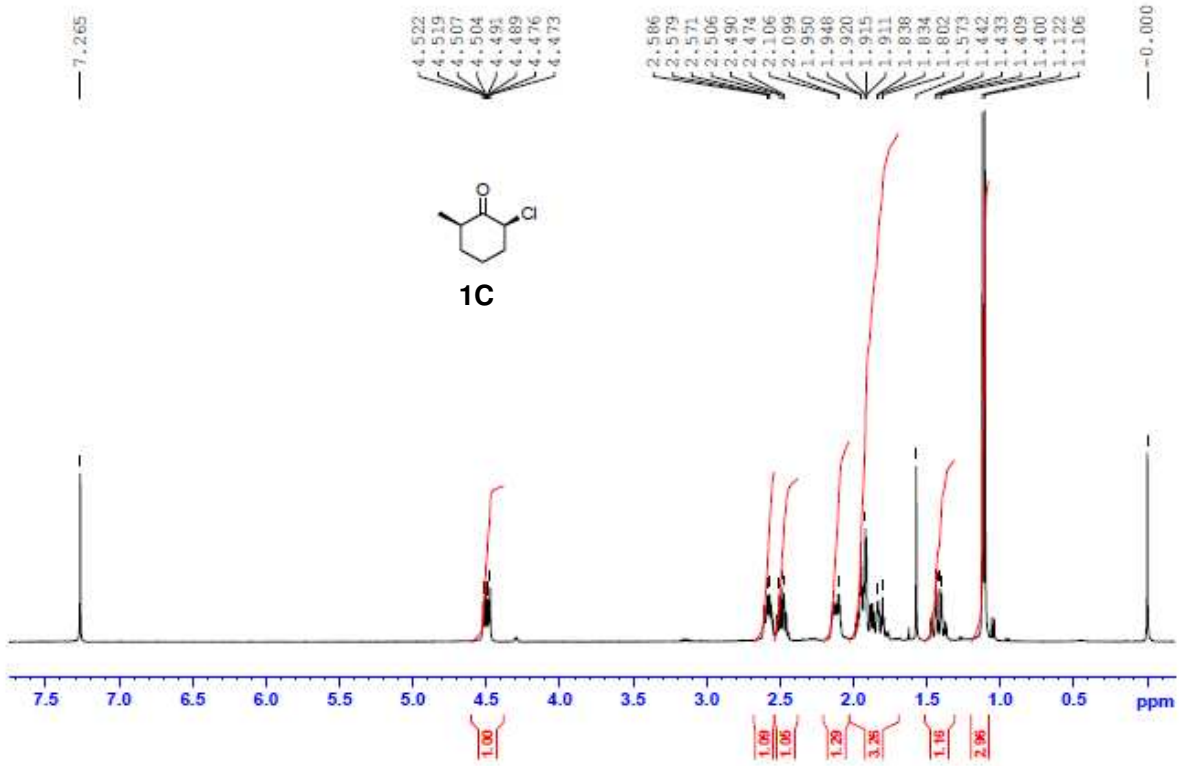
(7) Baran, P. S.; Richter, J. M., *J. Am. Chem. Soc.* **2004,** *126,* 7450.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4.507
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4.491
4.489
4.476
4.473
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2.506
2.490
2.474
2.106
2.099
1.950
1.948
1.920
1.915
1.911
1.838
1.834
1.802
1.573
1.442
1.433
1.409
1.400
1.122
1.106
0.000
Cl
1C
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
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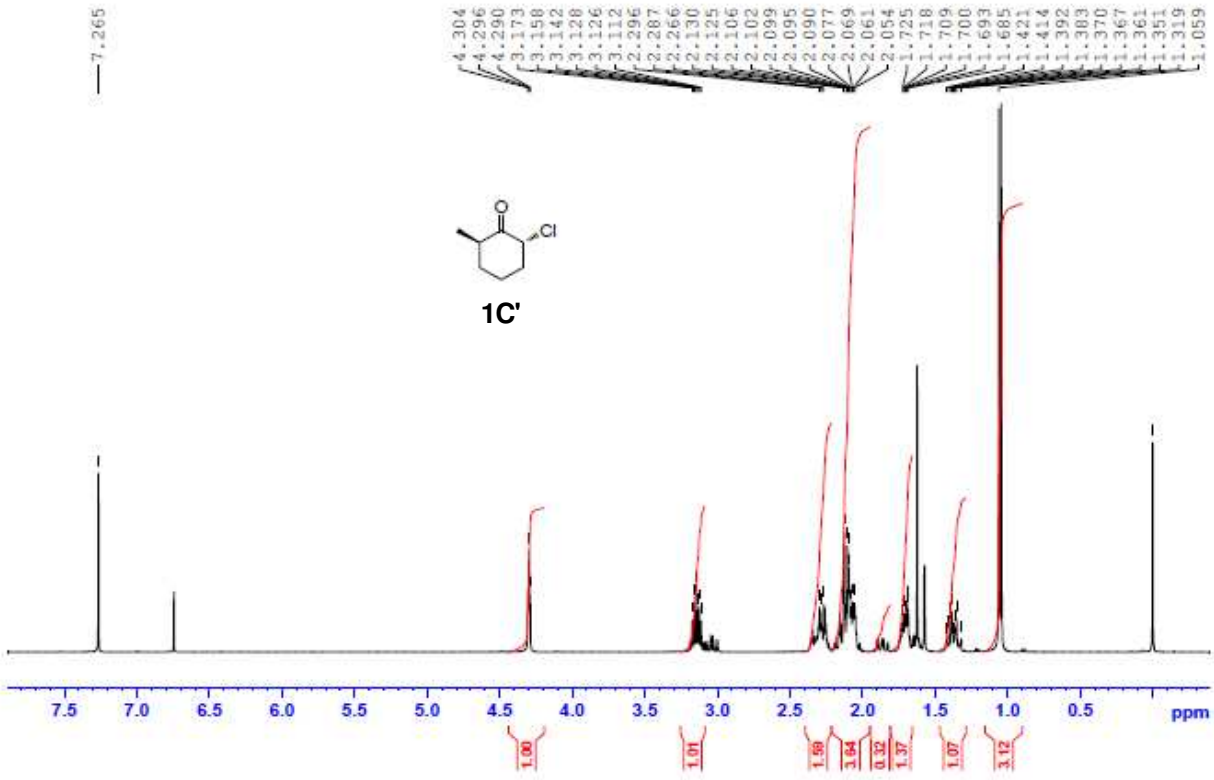
1.06
1.29
3.26
1.16
2.06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4.296
4.290
3.173
3.158
3.142
3.128
3.126
3.112
2.296
2.287
2.266
2.130
2.125
2.106
2.102
2.099
2.095
2.090
2.077
2.069
2.061
2.054
1.725
1.718
1.709
1.700
1.693
1.685
1.421
1.414
1.392
1.383
1.370
1.367
1.361
1.351
1.319
1.059
Cl
1C'
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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0.5
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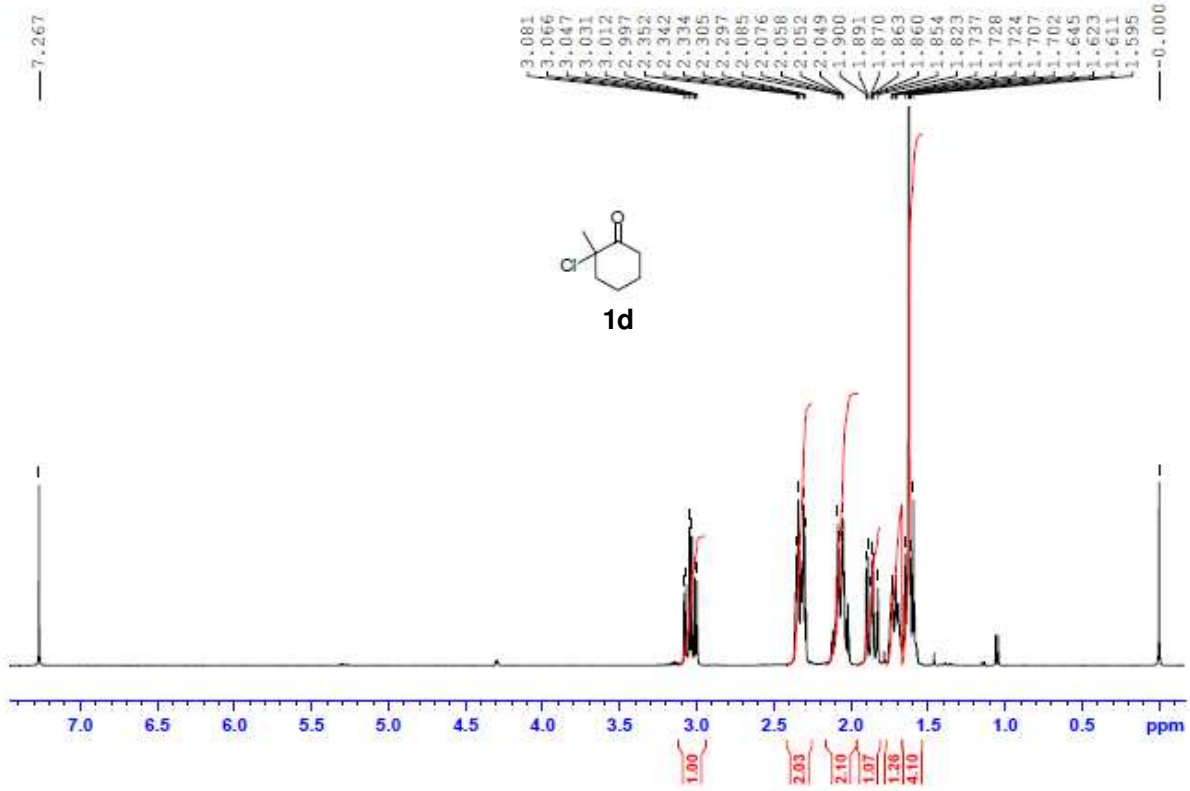
3.12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3.066
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3.012
2.997
2.352
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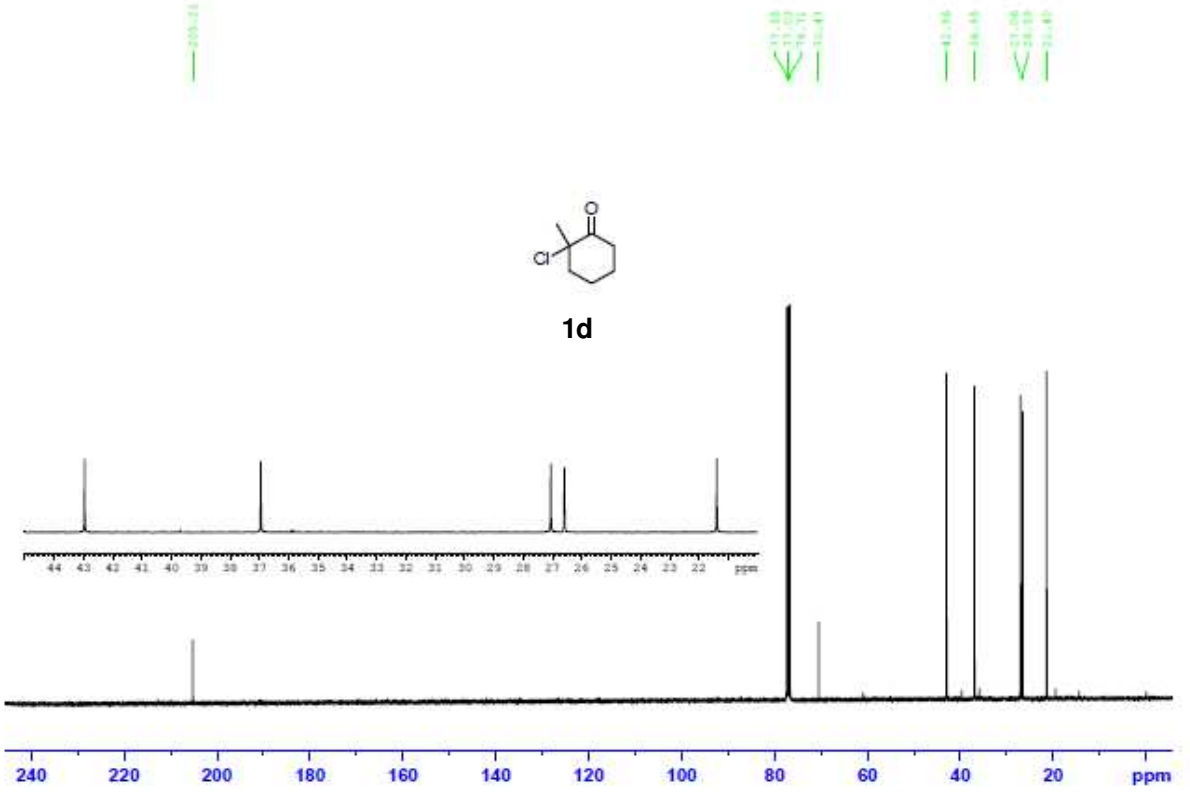
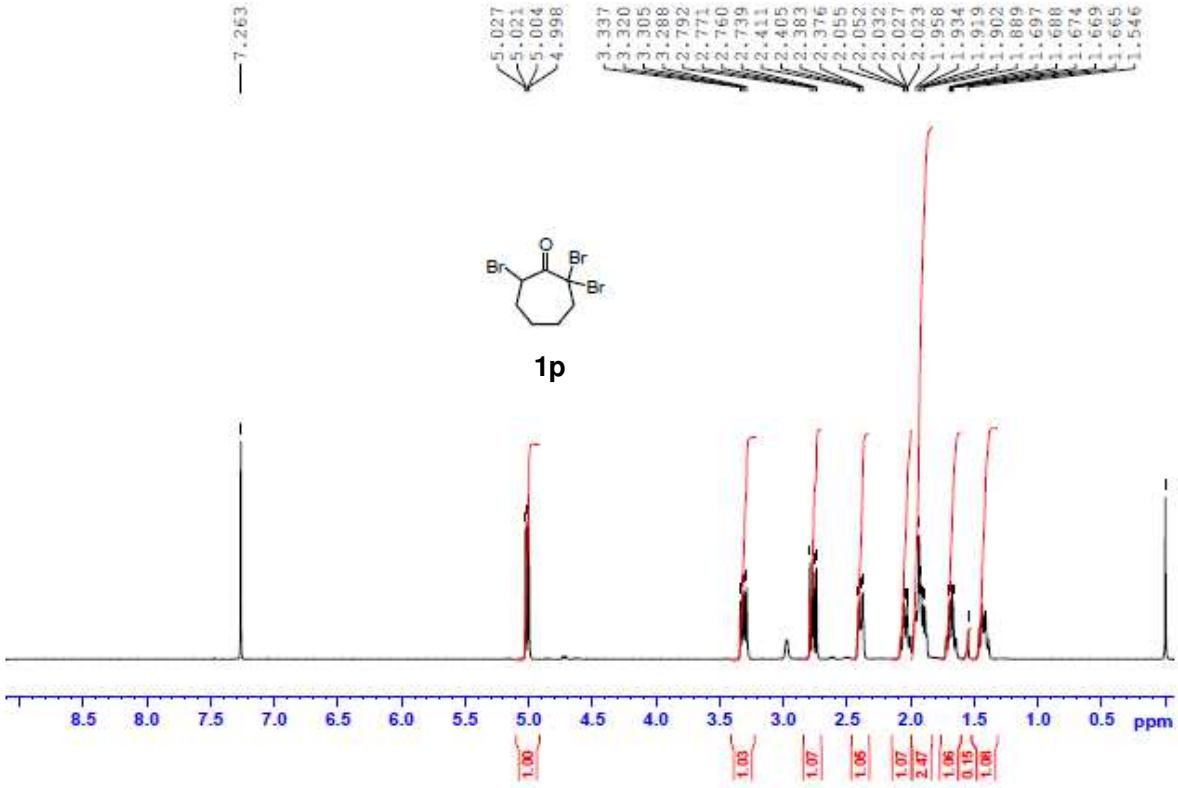
2.334
2.305
2.297
2.085
2.076
2.058
2.052
2.049
1.900
1.891
1.870
1.863
1.860
1.854
1.823
1.737
1.728
1.724
1.707
1.702
1.645
1.623
1.611
1.595
0.000
1d
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.03
2.10
1.07
1.26
4.10


1d
240
220
200
180
160
140
120
100
80
60
40
20
ppm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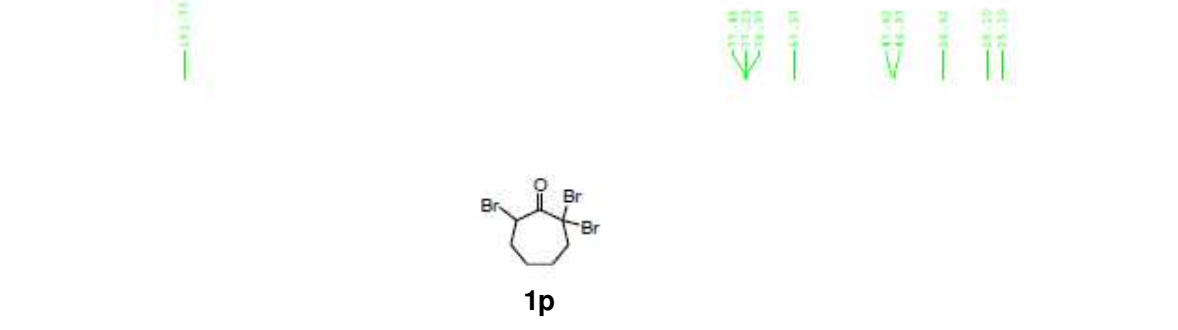
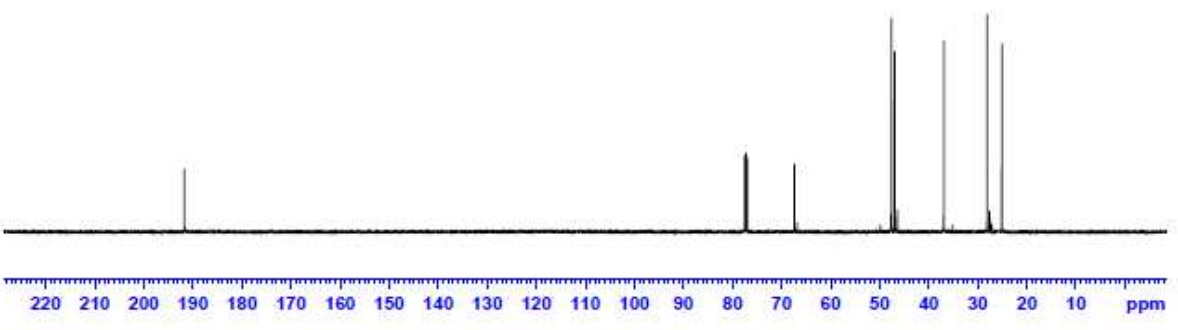
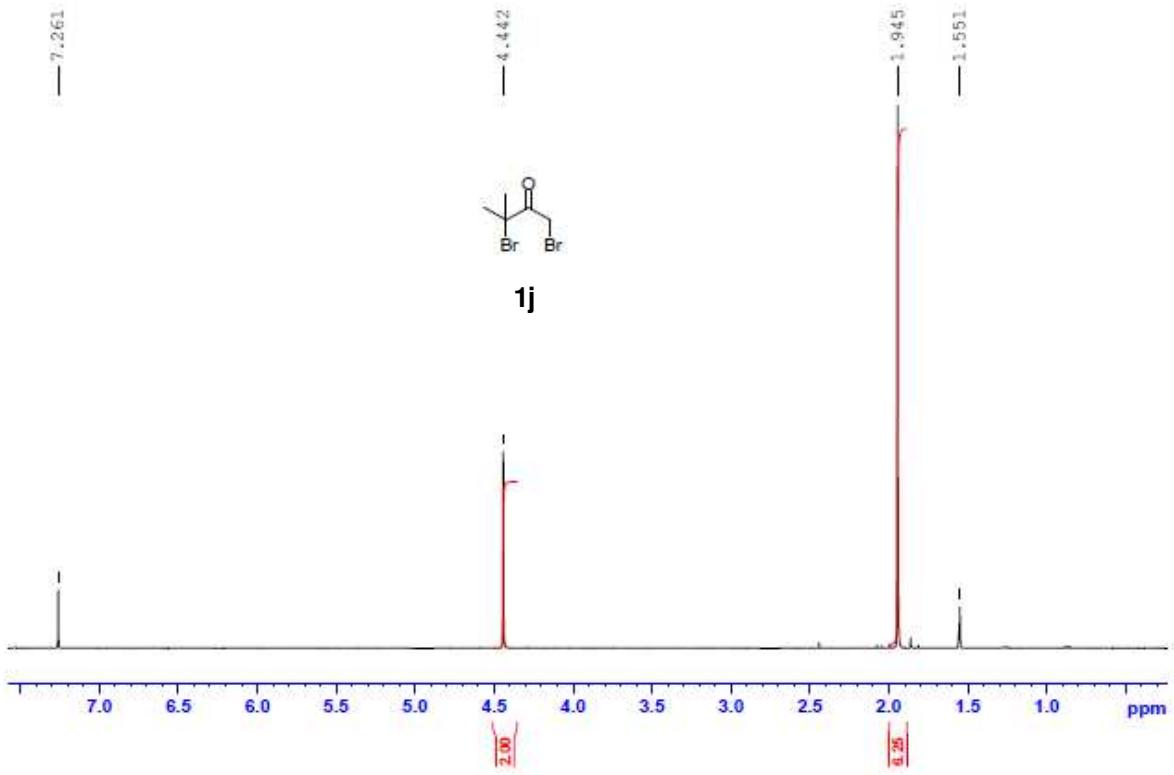
2.760
2.739
2.411
2.405
2.383
2.376
2.055
2.052
2.032
2.027
2.023
1.958
1.934
1.919
1.902
1.889
1.697
1.688
1.674
1.669
1.665
1.546
O
Br
Br
Br
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.03
1.07
1.05
1.07
2.47
1.06
0.15
1.06

1p


O
Br
Br
Br

1p


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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Br
Br
1j
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6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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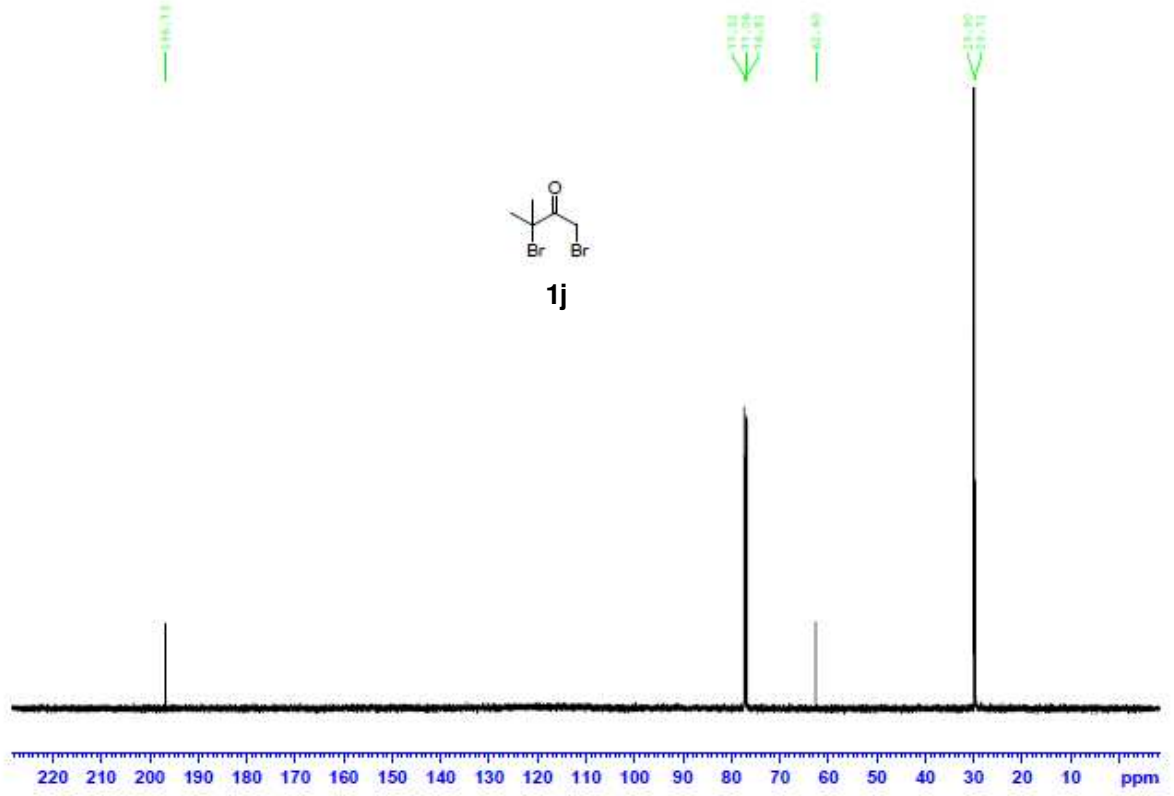
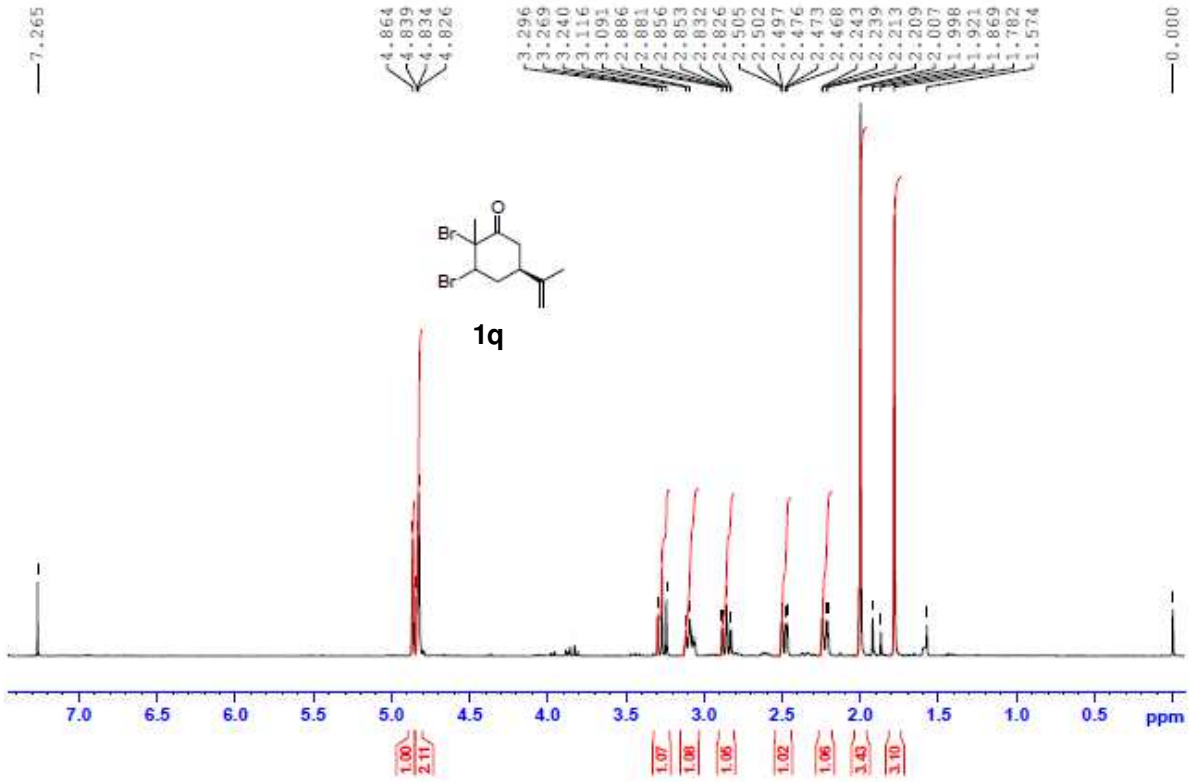
1.5
1.0
ppm
2.00
6.25


Br
Br
1j
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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4.834
4.826
3.296
3.269
3.240
3.116
3.091
2.886
2.881
2.856
2.853
2.832
2.826
2.505
2.502
2.497
2.476
2.473
2.468
2.243
2.239
2.213
2.209
2.007
1.998
1.921
1.869
1.782
1.574
0.000
Br
Br
O
1q
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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ppm
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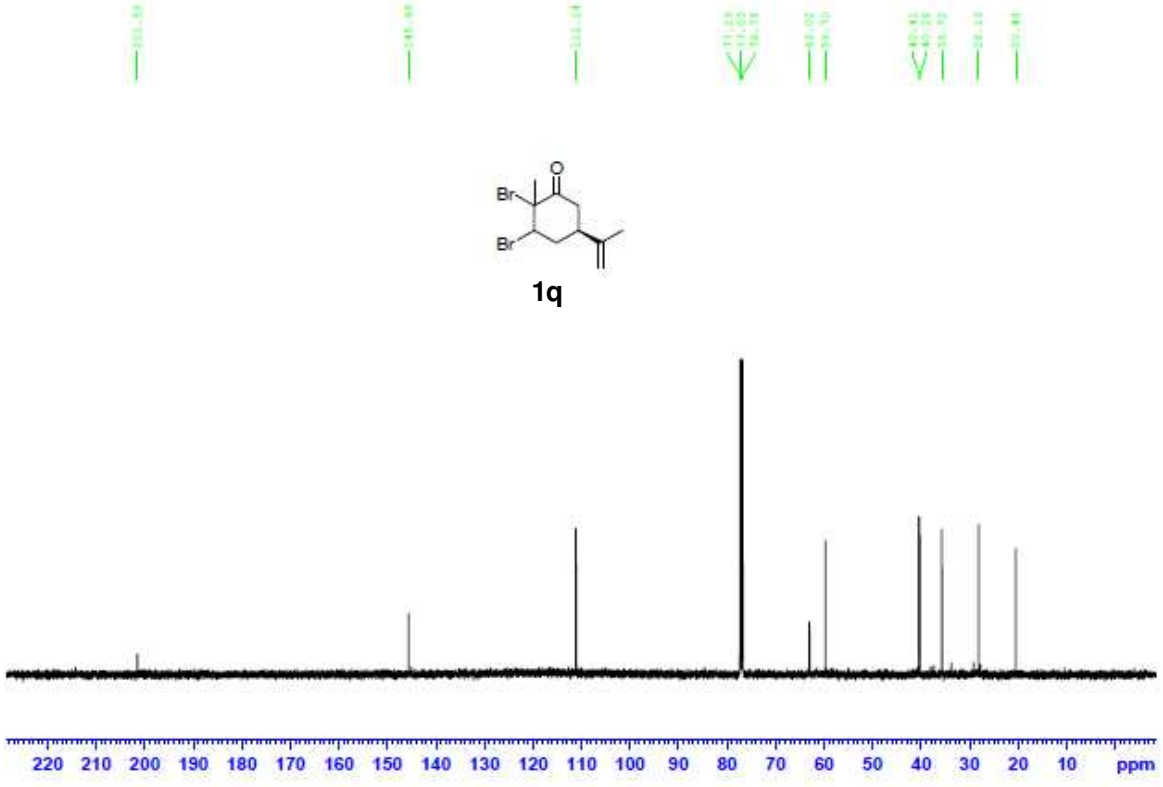
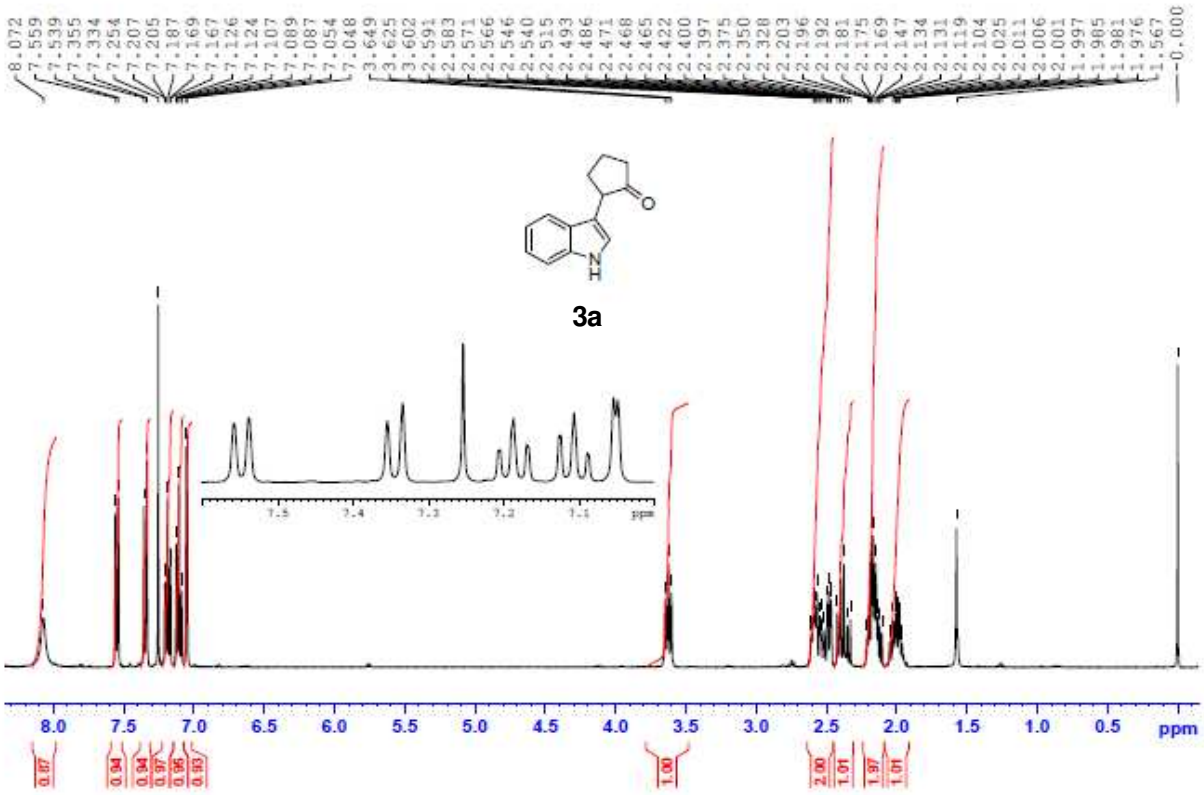
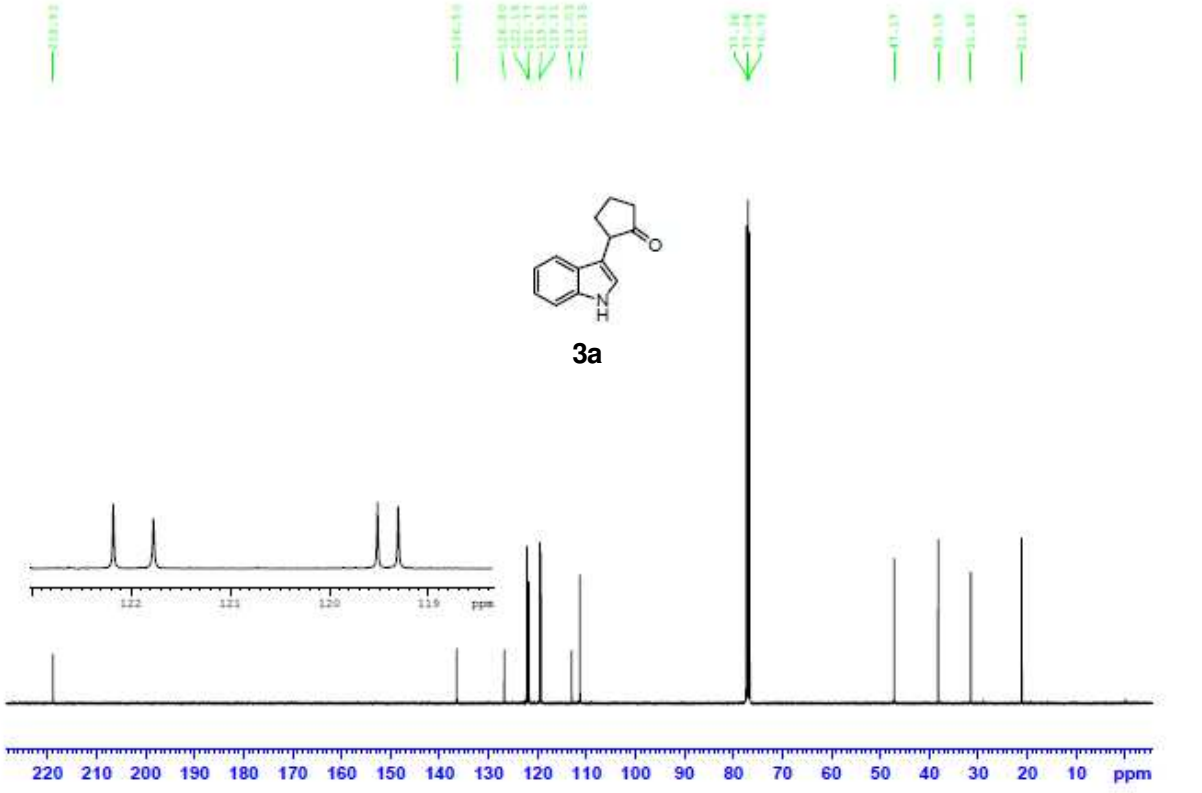
1.05
1.02
1.06
3.43
3.10

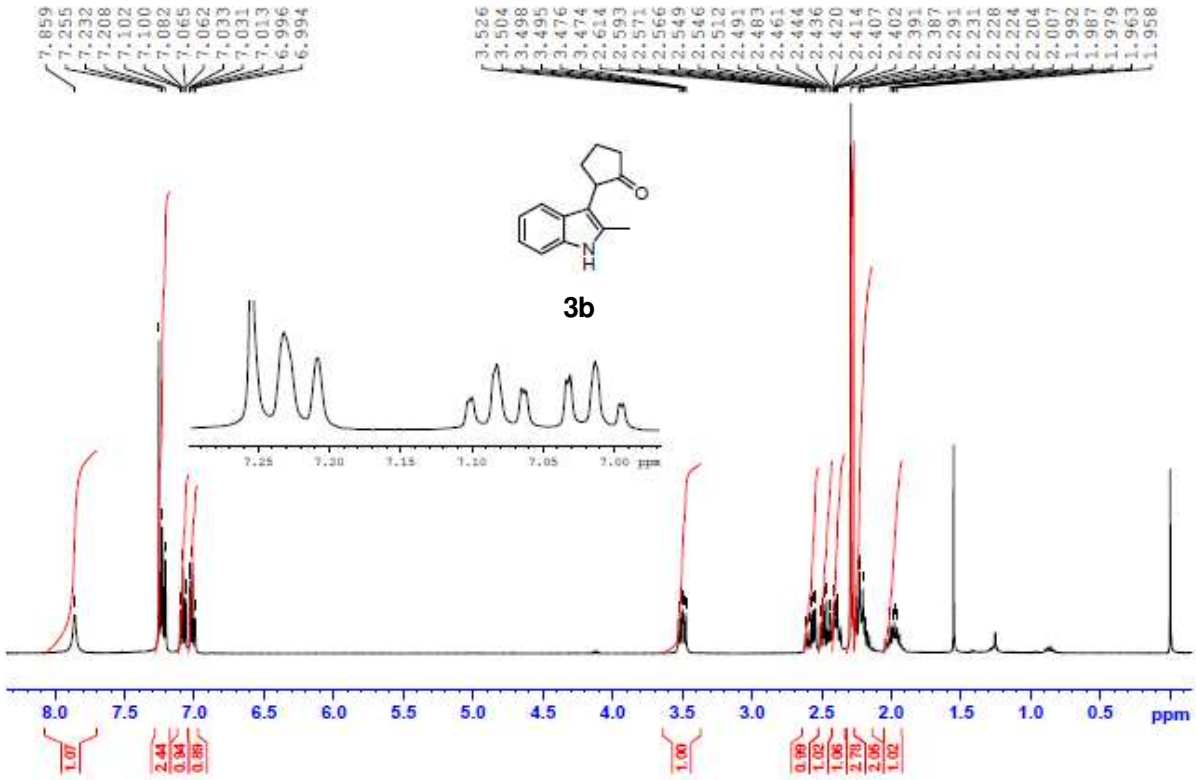

Br
Br
O
1q
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



3a



3a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6.994
3.526
3.504
3.498
3.495
3.476
3.474
2.614
2.593
2.571
2.566
2.549
2.546
2.512
2.491
2.483
2.461
2.444
2.436
2.420
2.414
2.407
2.402
2.391
2.387
2.291
2.231
2.228
2.224
2.204
2.007
1.992
1.987
1.979
1.963
1.958
O
N
H
3b
7.25
7.20
7.15
7.10
7.05
7.00 ppm
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
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0.99
1.02
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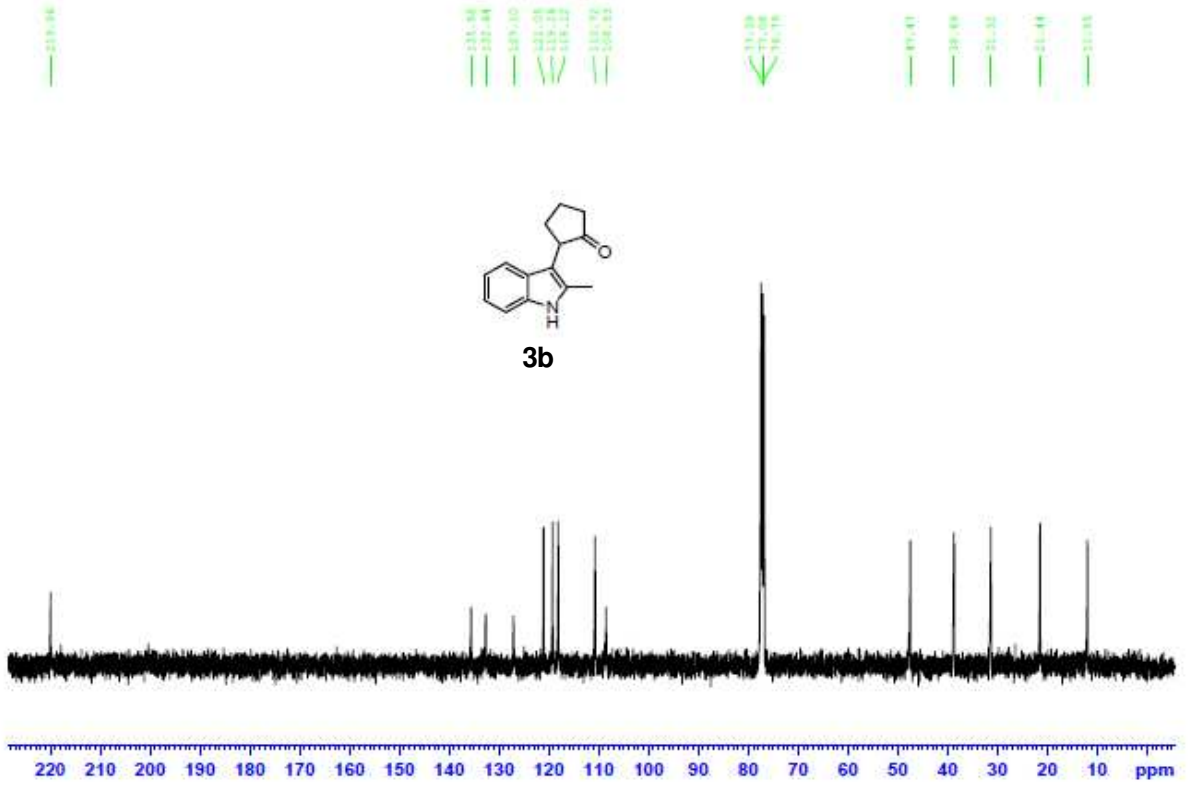
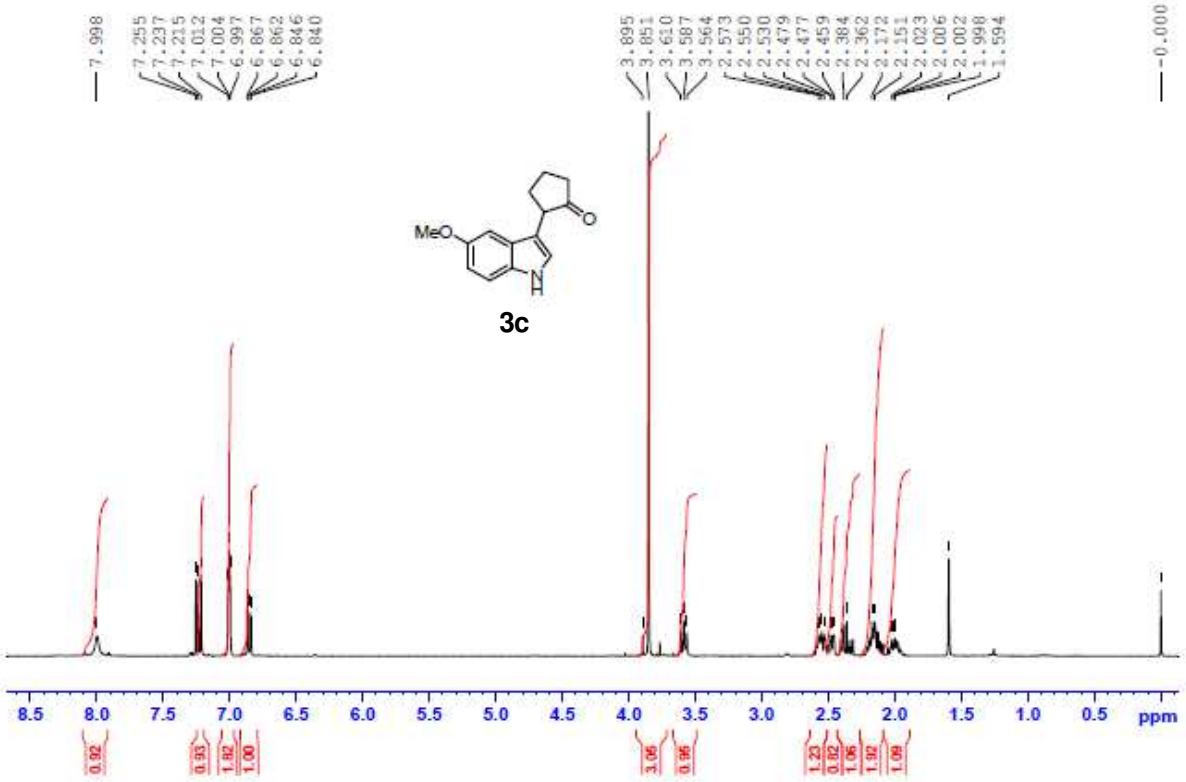
2.78
2.06
1.02


O
N
H
3b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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6.840
3.895
3.851
3.610
3.587
3.564
2.573
2.550
2.530
2.479
2.477
2.459
2.384
2.362
2.172
2.151
2.023
2.006
2.002
1.998
1.594
-0.000
MeO
O
N
H
3c
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
0.5
ppm
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1.23
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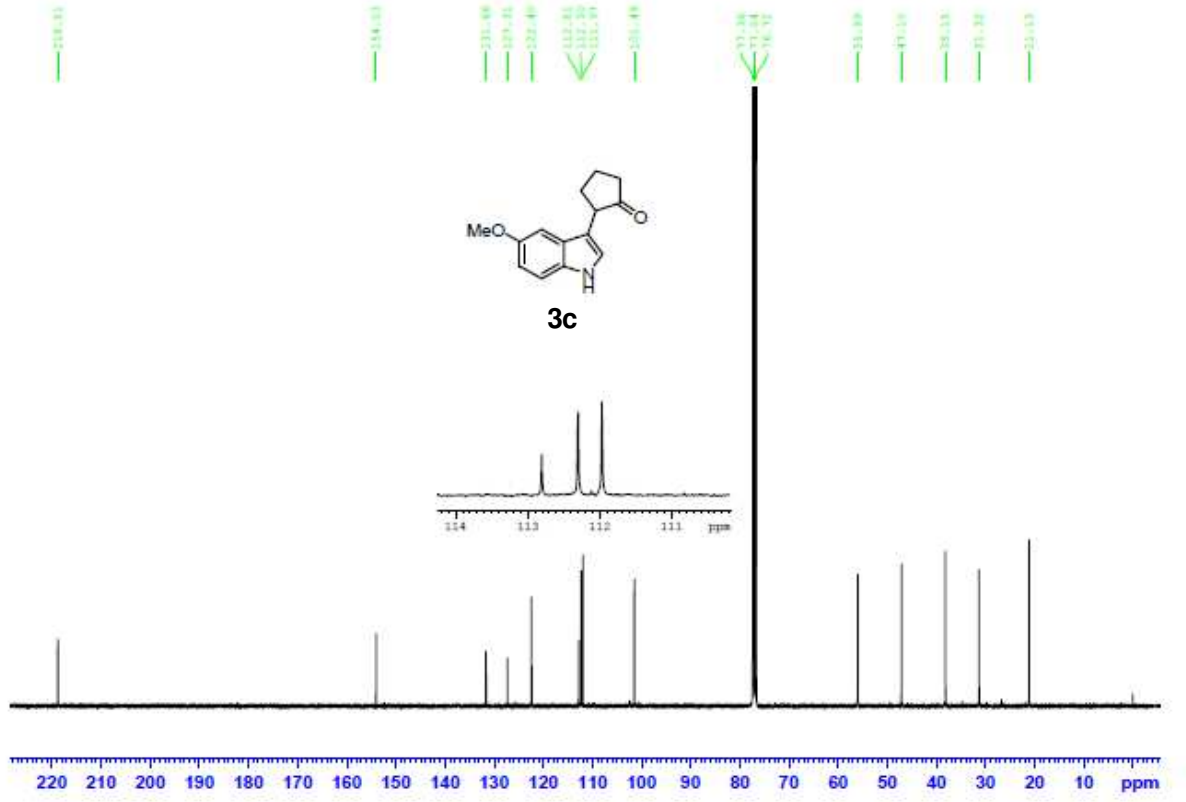
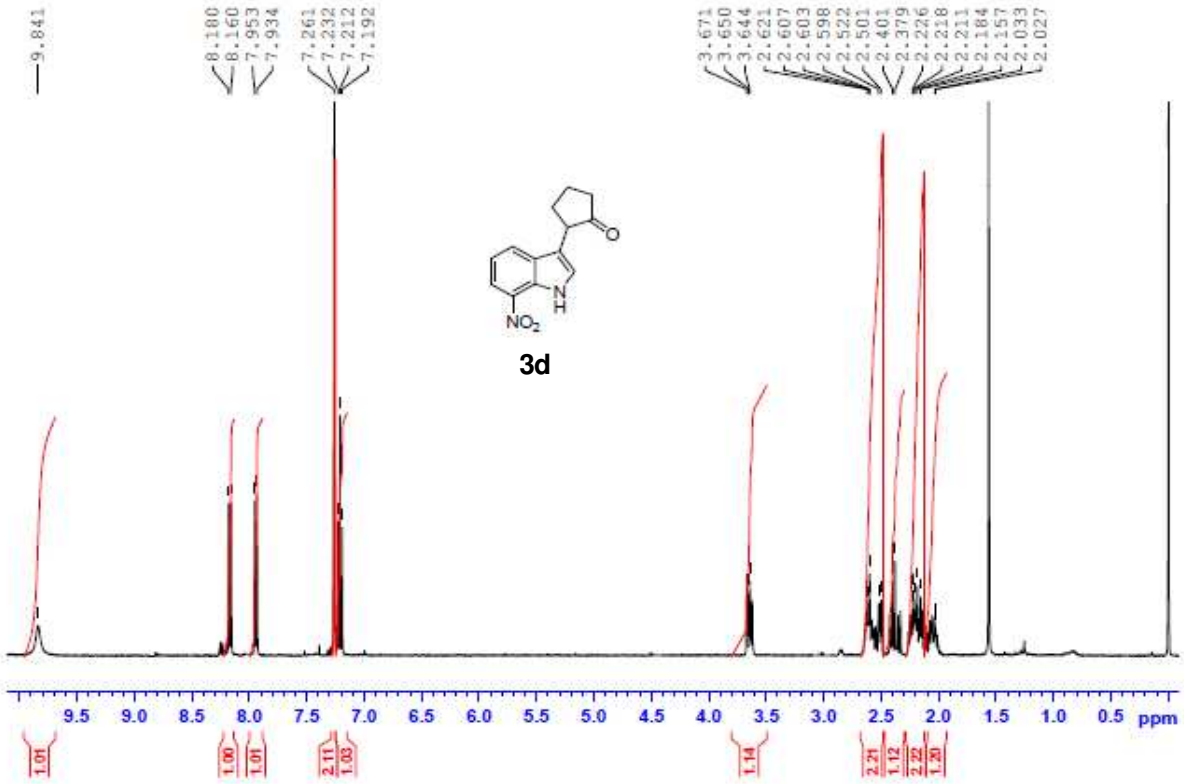
1.06
1.92
1.08


MeO
O
N
H
3c
114
113
112
111
ppm
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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3.644
2.621
2.607
2.603
2.598
2.522
2.501
2.401
2.379
2.226
2.218
2.211
2.184
2.157
2.033
2.027
O
N
H
NO2
3d
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 1.0 0.5 ppm
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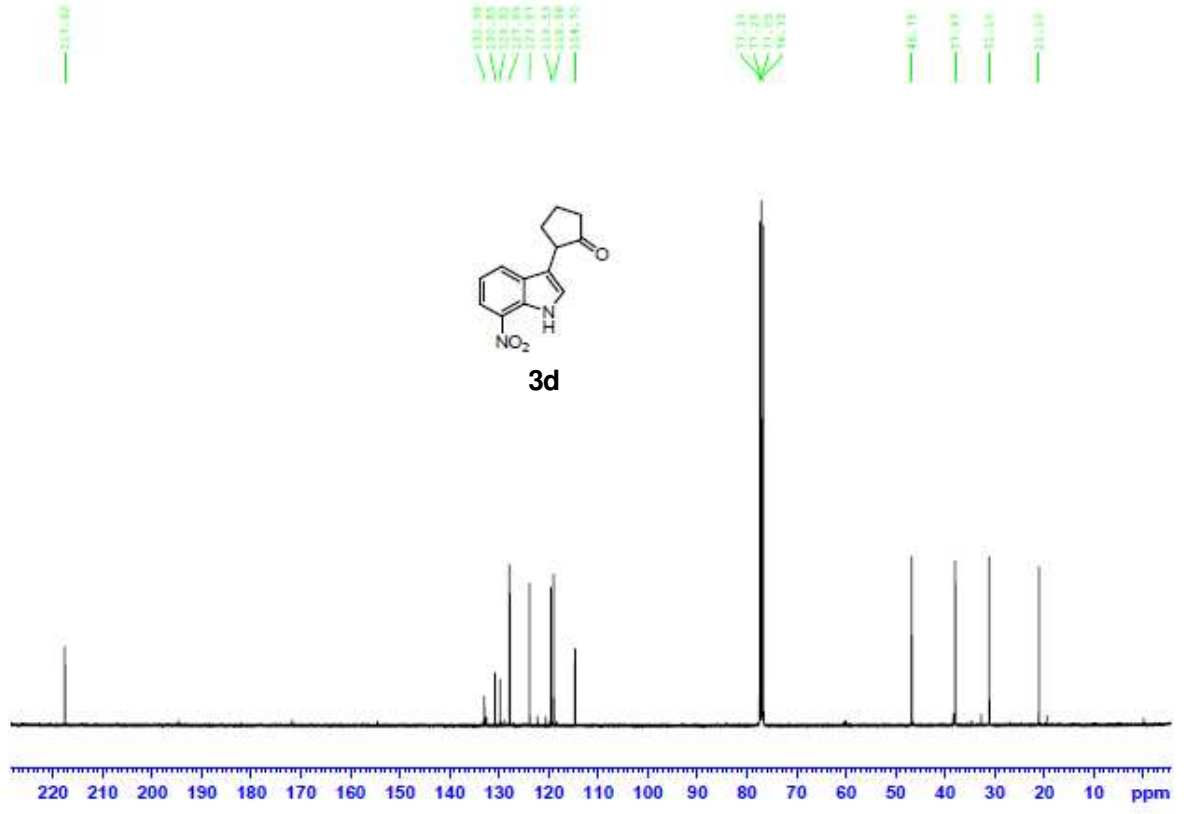
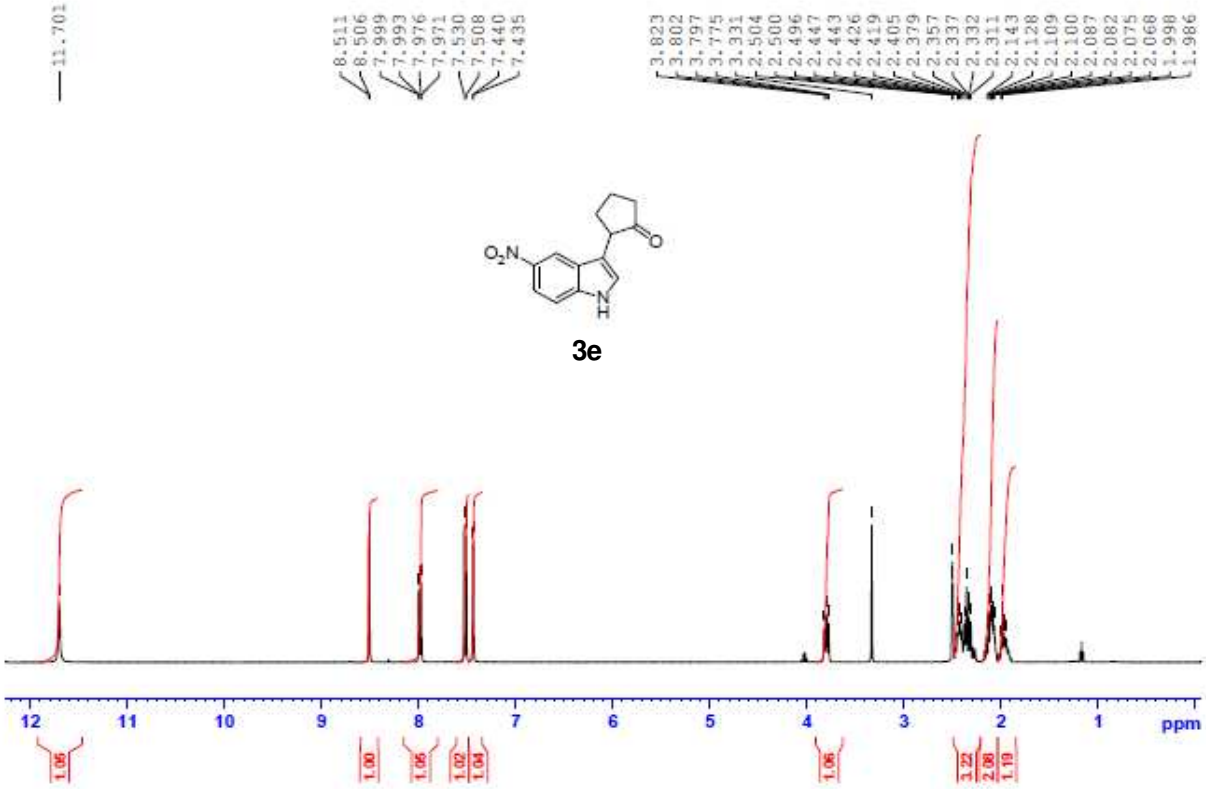
1.00
1.01
2.11
1.03
1.14
2.21
1.12
2.22
1.20


O
N
H
NO2
3d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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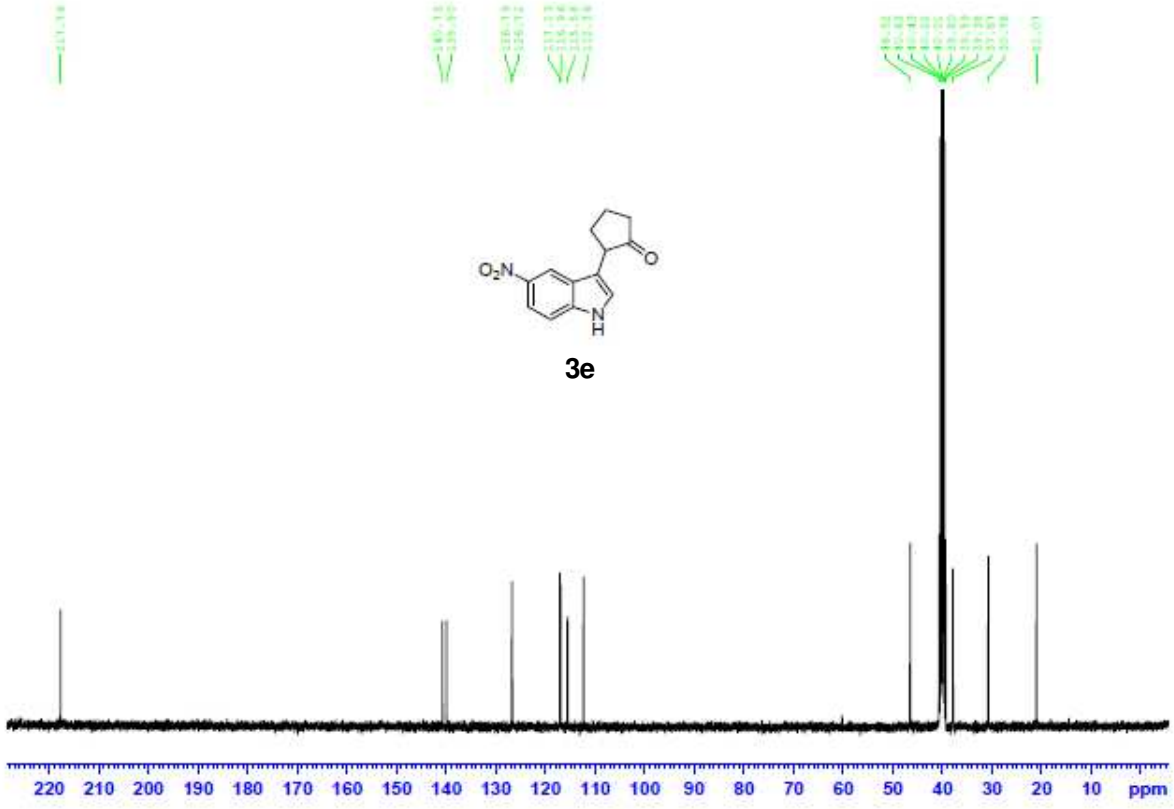
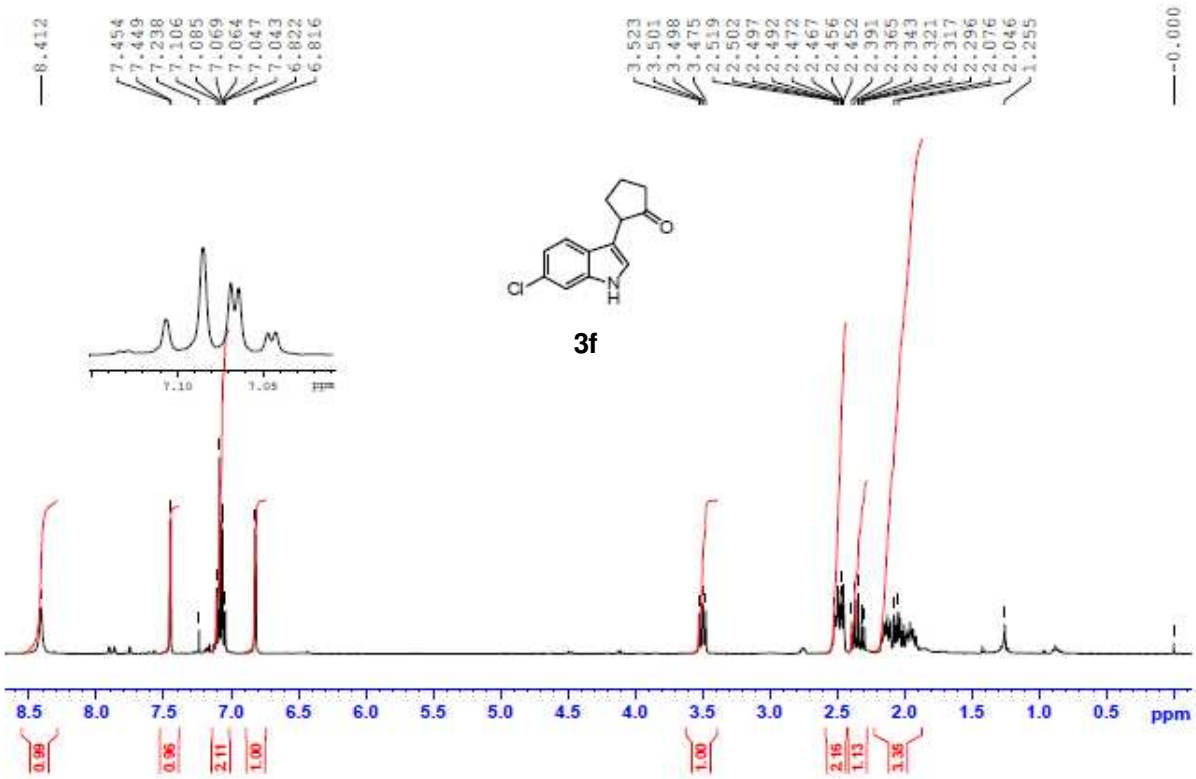
7.971
7.530
7.508
7.440
7.435
3.823
3.802
3.797
3.775
3.331
2.504
2.500
2.496
2.447
2.443
2.426
2.419
2.405
2.379
2.357
2.337
2.332
2.311
2.143
2.128
2.109
2.100
2.087
2.082
2.075
2.068
1.998
1.986
O2N
O
N
H
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.05
1.00
1.06
1.02
1.04
1.06
3.22
2.06
1.19

3e


O2N
O
N
H
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

3e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7.069
7.064
7.047
7.043
6.822
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3.498
3.475
2.519
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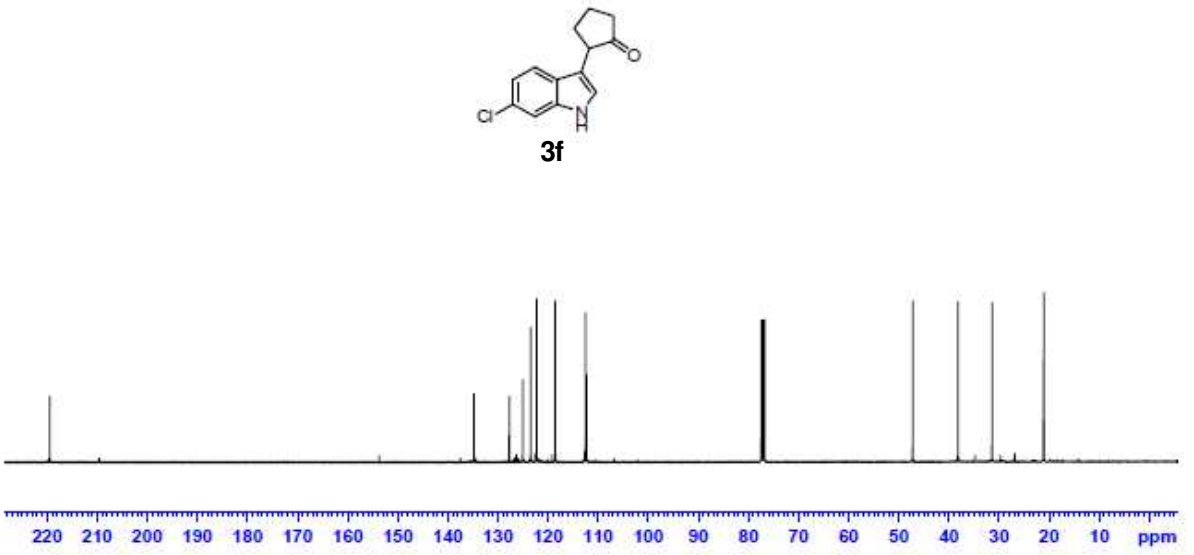
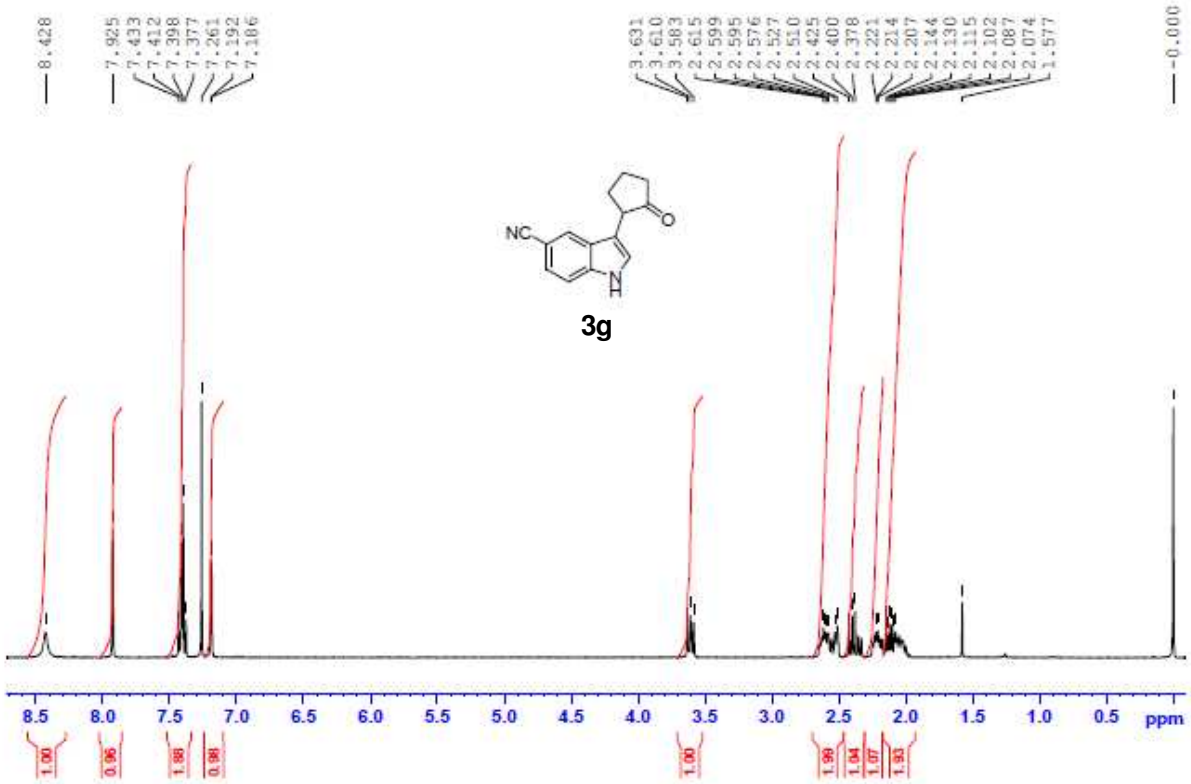
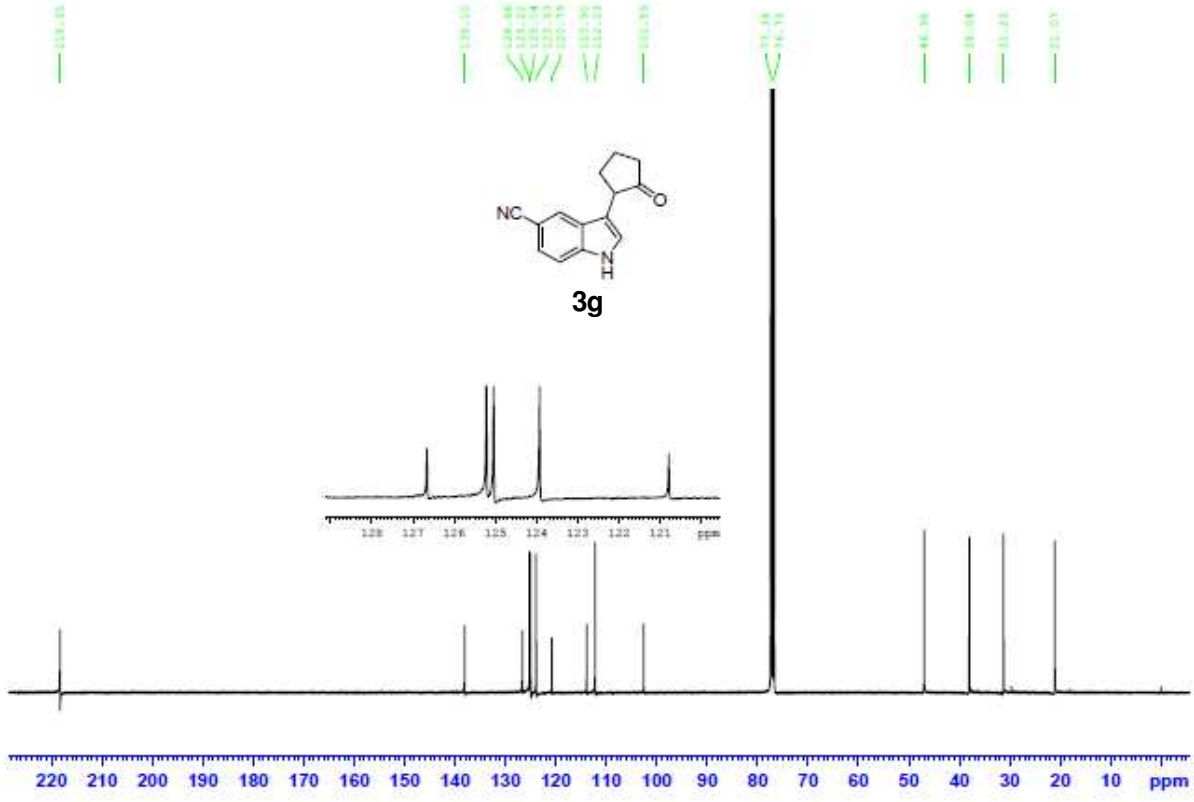
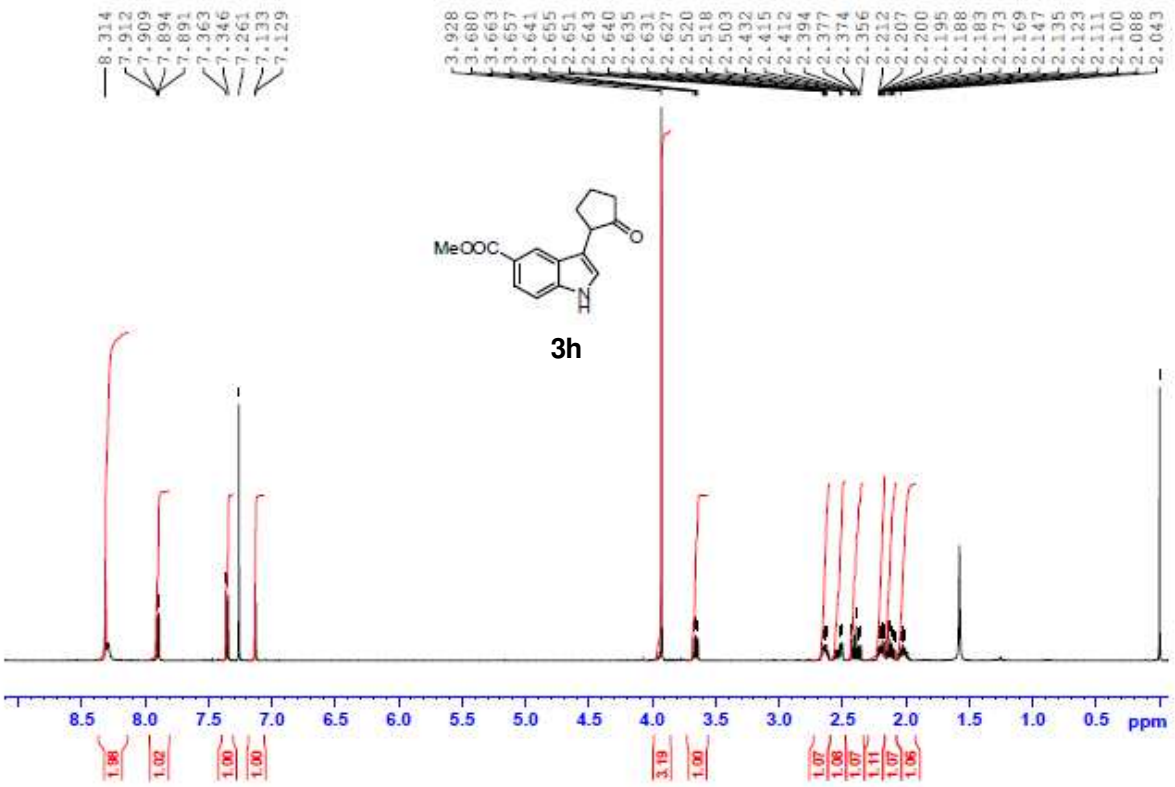
2.467
2.456
2.452
2.391
2.365
2.343
2.321
2.317
2.296
2.076
2.046
1.255
0.000
Cl
O
N
H
3f
7.10
7.05
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.99
0.96
2.11
1.00
1.00
2.16
1.13
3.36

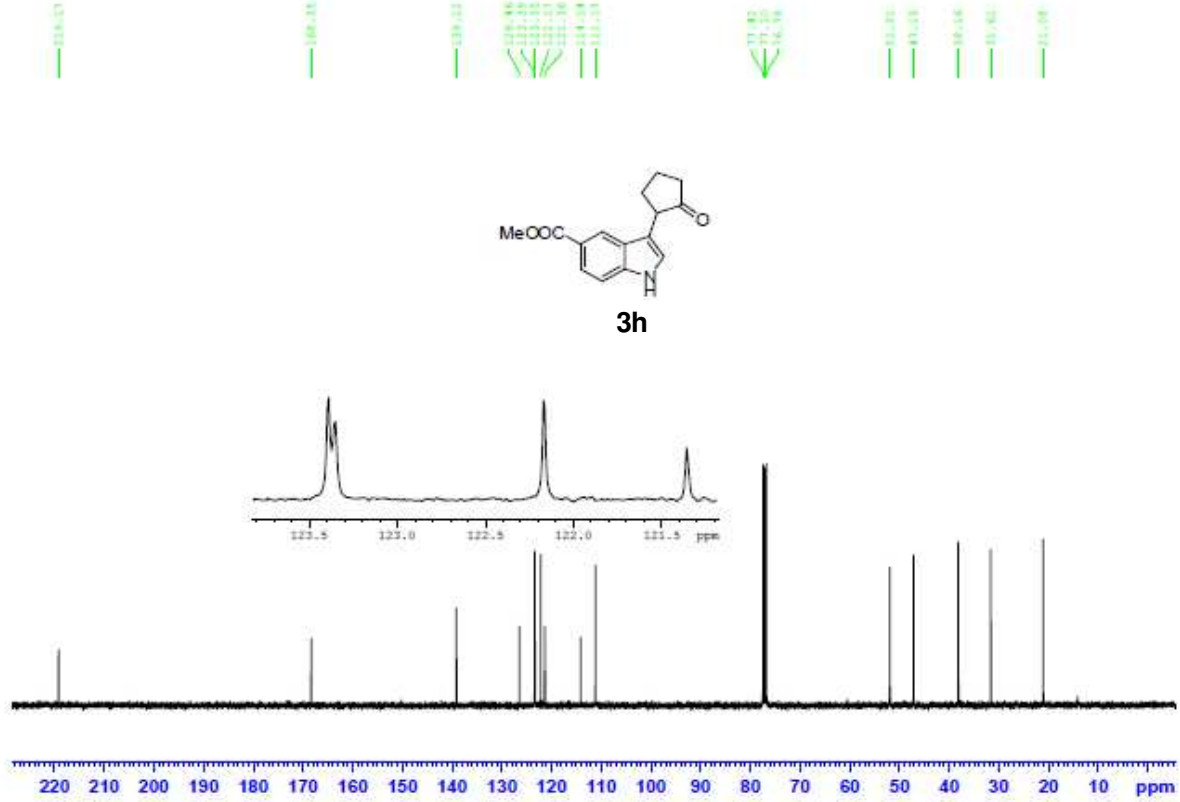

Cl
O
N
H
3f
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.428
7.925
7.433
7.412
7.398
7.377
7.261
7.192
7.186
3.631
3.610
3.583
2.615
2.599
2.595
2.576
2.527
2.510
2.425
2.400
2.378
2.221
2.214
2.207
2.144
2.130
2.115
2.102
2.087
2.074
1.577
0.000
NC
O
N
H
3g
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
0.5
ppm
1.00
0.96
1.98
0.98
1.00
1.99
1.04
1.07
1.93

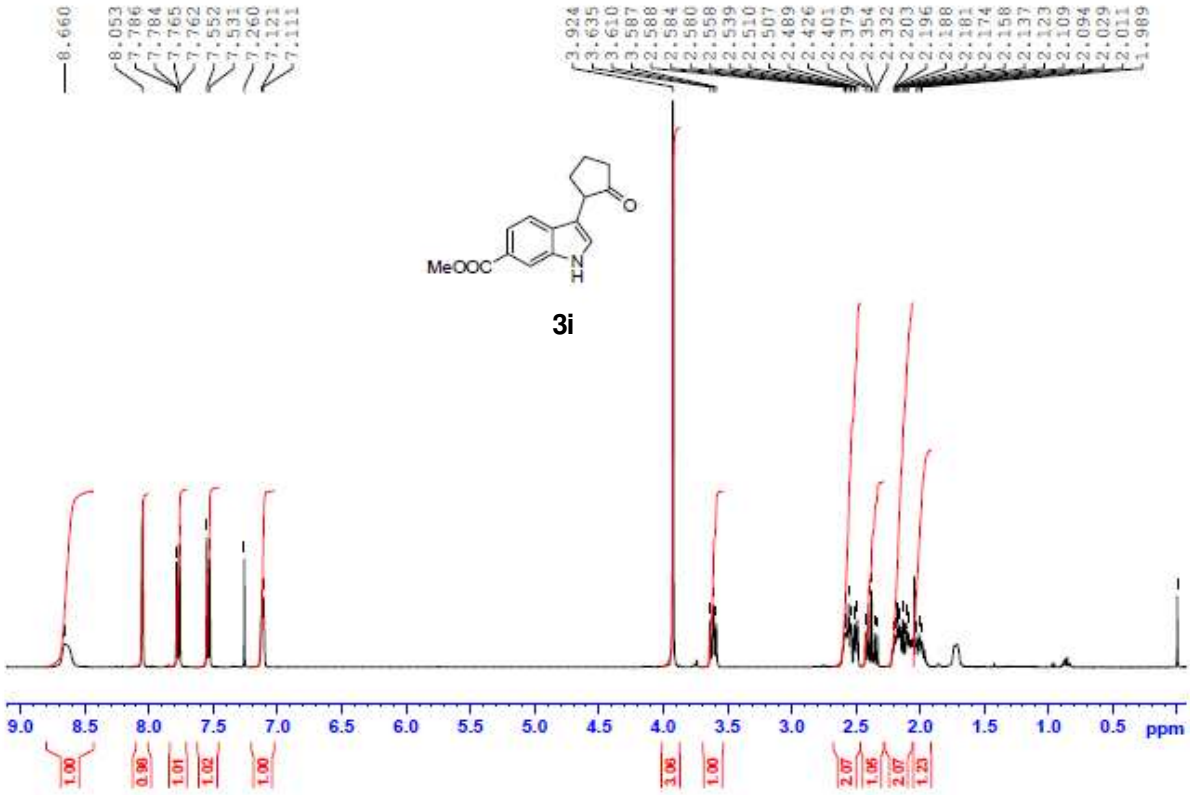

NC
O
N
H
3g
128
127
126
125
124
123
122
121
ppm
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.314
7.912
7.909
7.894
7.891
7.363
7.346
7.261
7.133
7.129
3.928
3.680
3.663
3.657
3.641
2.655
2.651
2.643
2.640
2.635
2.631
2.627
2.520
2.518
2.503
2.432
2.415
2.412
2.394
2.377
2.374
2.356
2.212
2.207
2.200
2.195
2.188
2.183
2.173
2.169
2.147
2.135
2.123
2.111
2.100
2.088
2.043
MeOOC
O
H
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
0.5
ppm
1.98
1.02
1.00
1.00
3.19
1.00
1.07
1.06
1.07
1.11
1.07
1.06

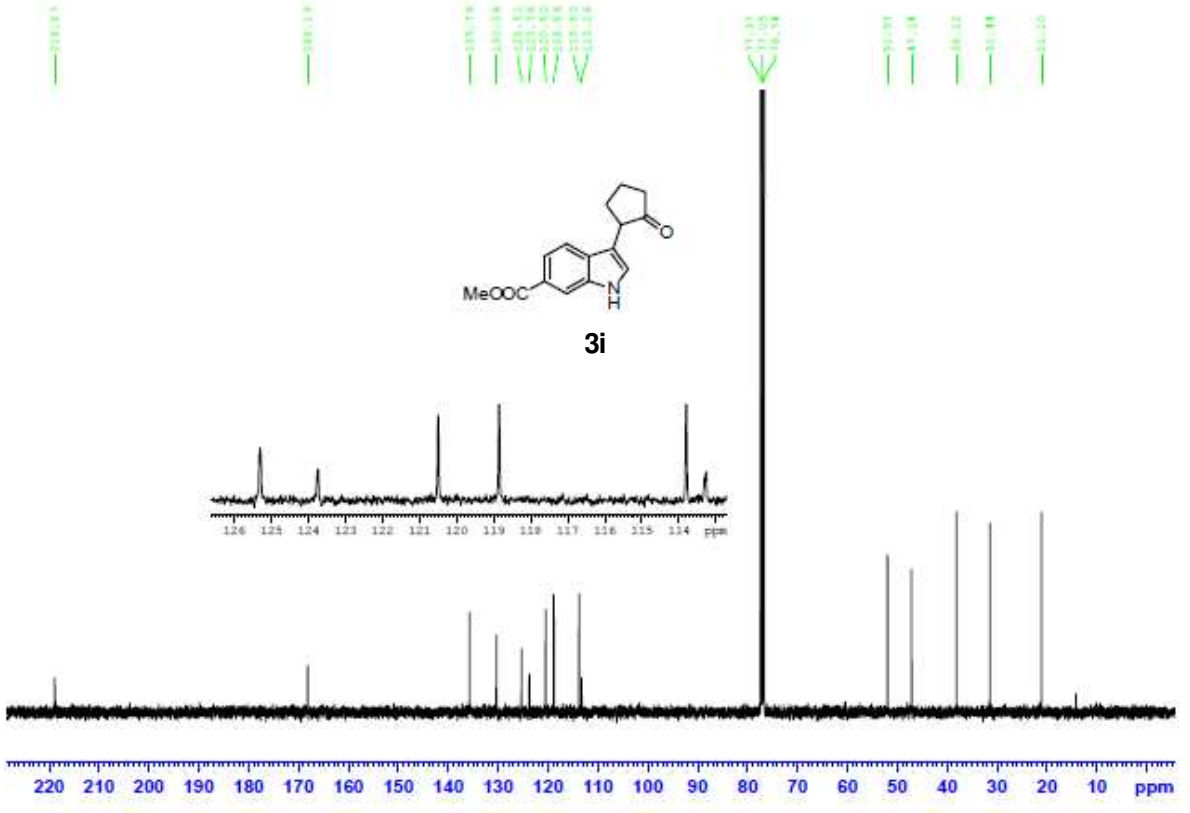
3h


MeOOC
O
H
123.5
123.0
122.5
122.0
121.5
ppm
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

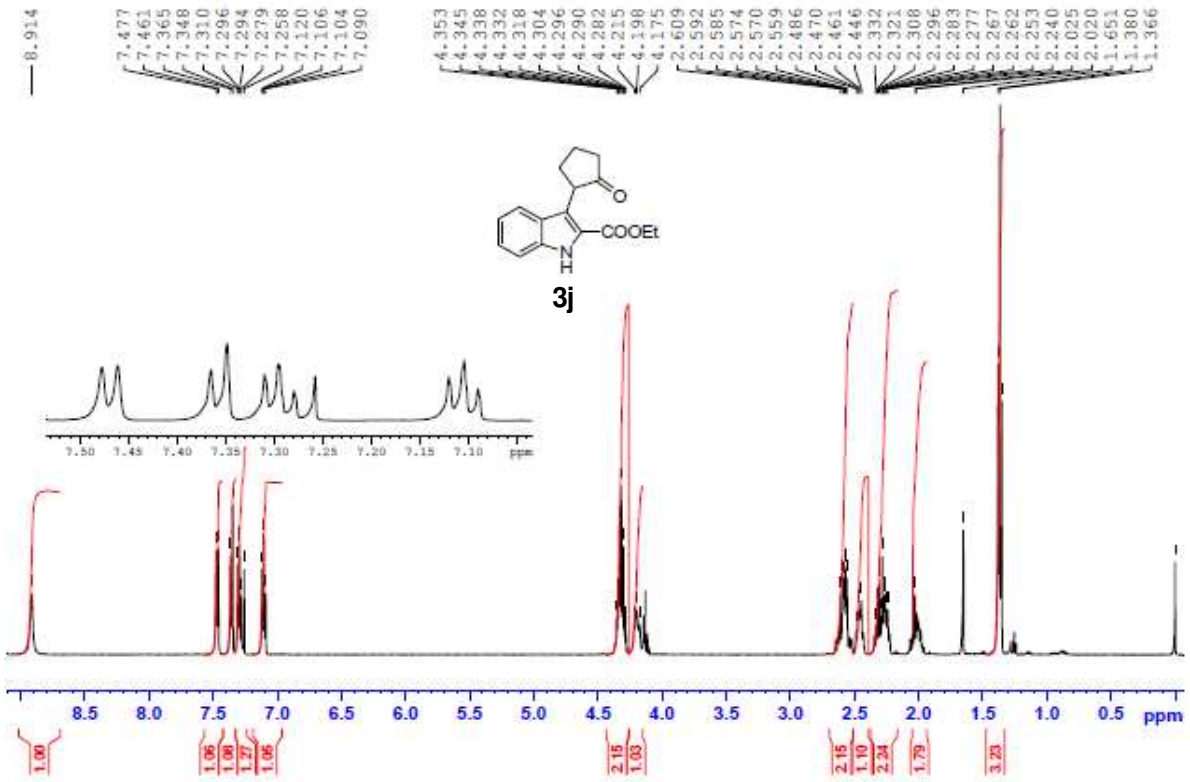
3h

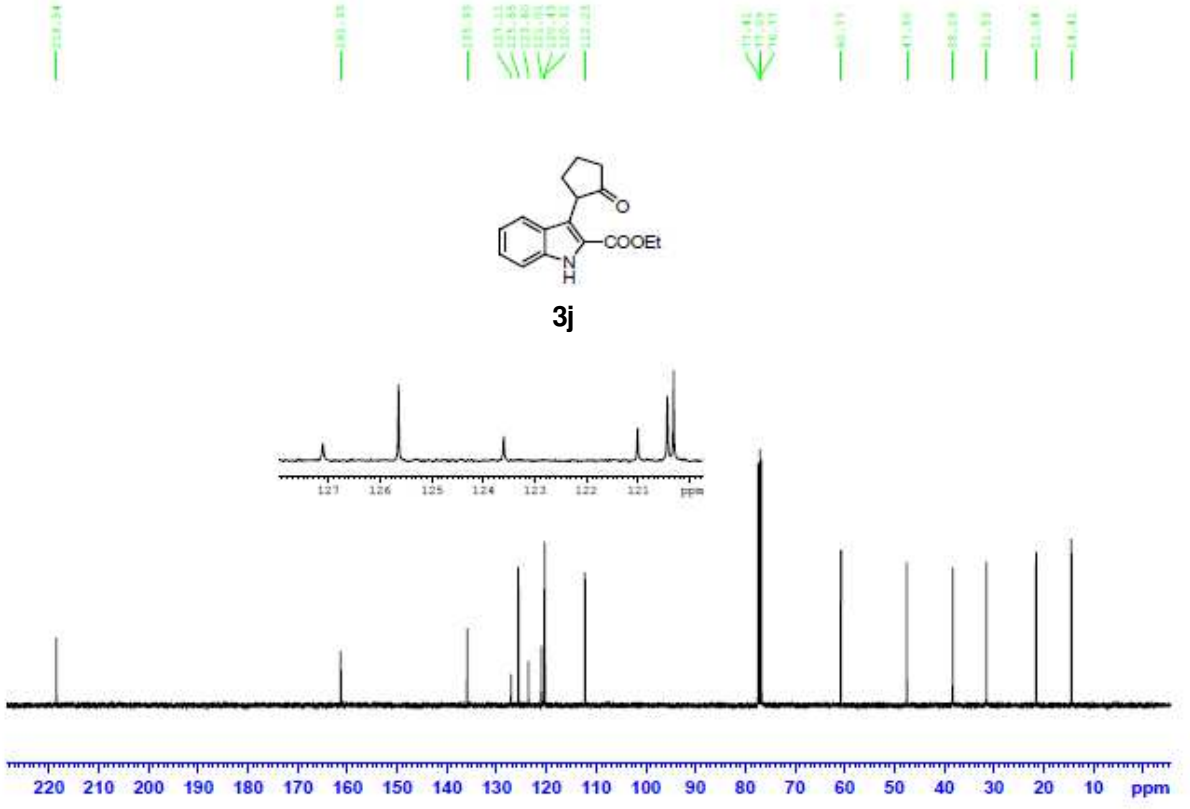

8.660
8.053
7.786
7.784
7.765
7.762
7.552
7.531
7.260
7.121
7.111
3.924
3.635
3.610
3.587
2.588
2.584
2.580
2.558
2.539
2.510
2.507
2.489
2.426
2.401
2.379
2.354
2.332
2.203
2.196
2.188
2.181
2.174
2.158
2.137
2.123
2.109
2.094
2.029
2.011
1.989
MeOOC
O
N
H
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 0.96 1.01 1.02 1.00 3.06 1.00 2.07 1.06 2.07 1.23

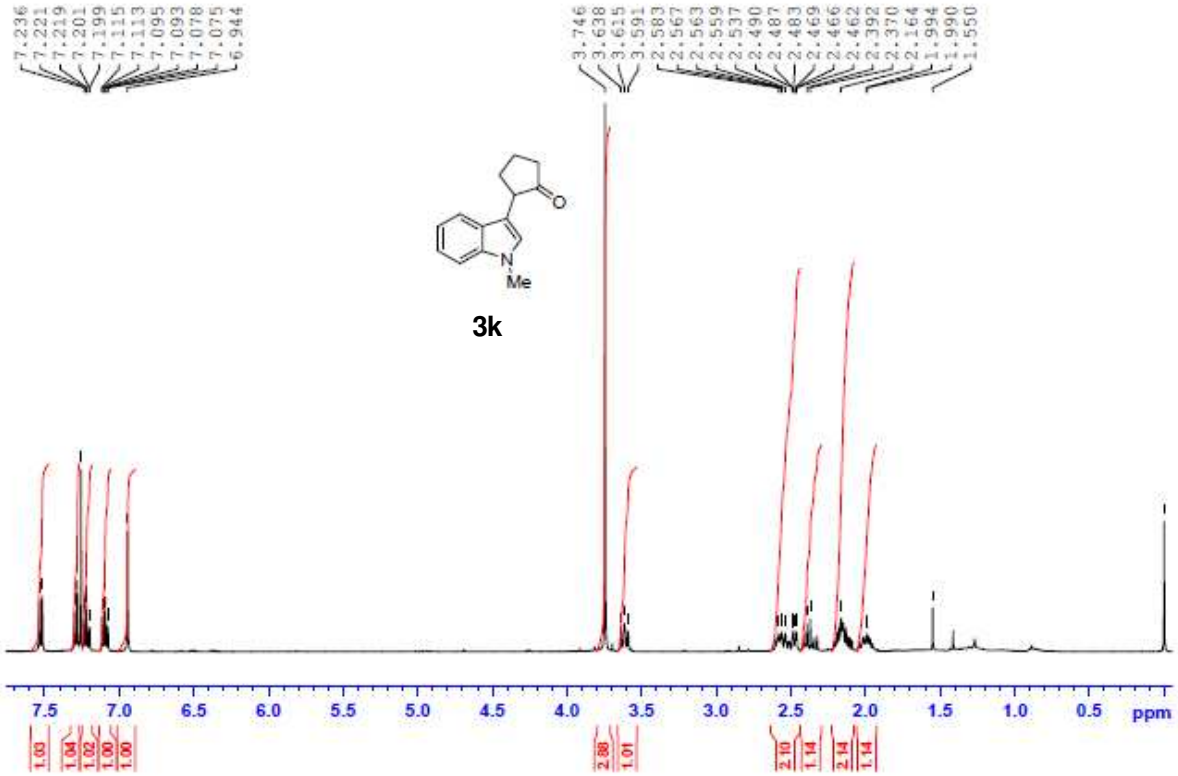
3i


MeOOC
O
N
H
126 125 124 123 122 121 120 119 118 117 116 115 114 ppm
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

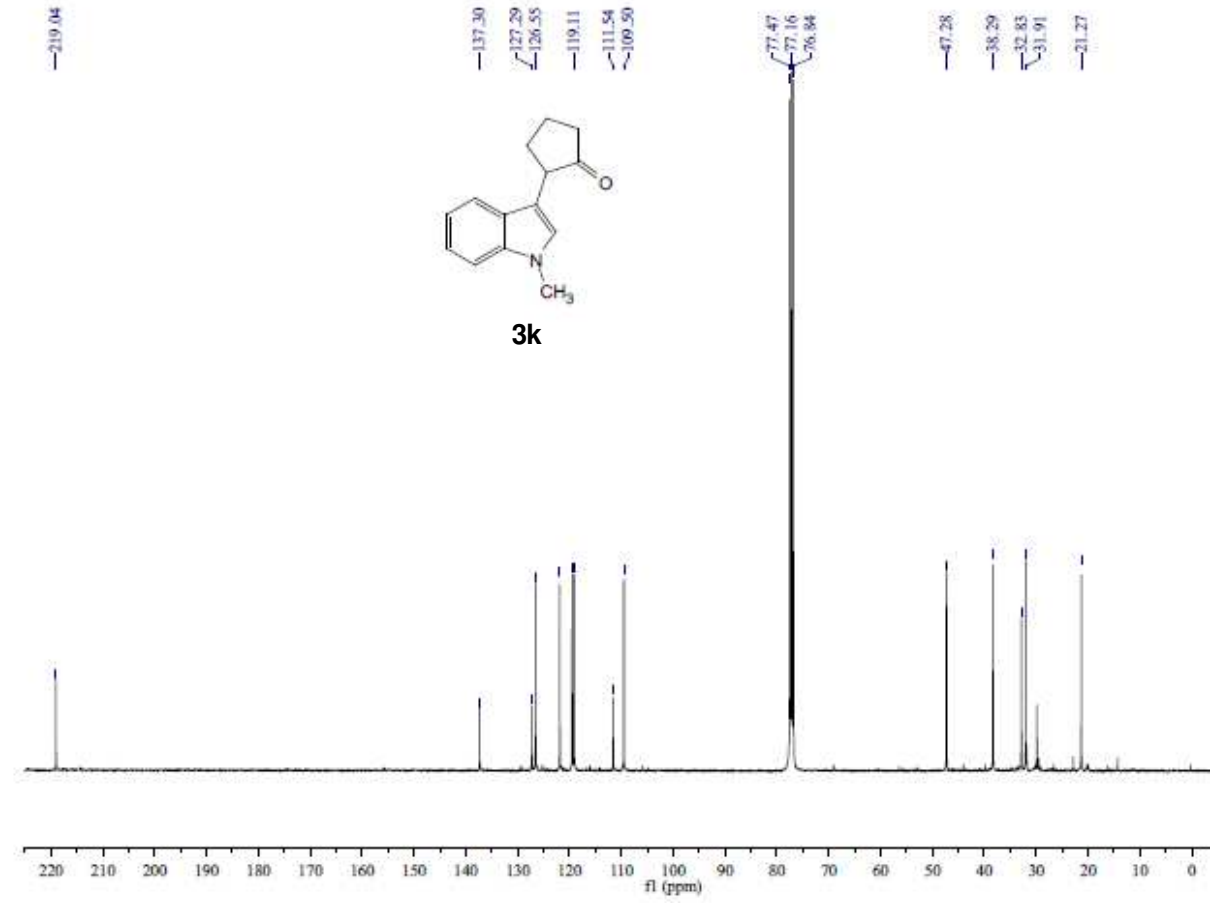
3i


8.914
7.477
7.461
7.365
7.348
7.310
7.296
7.294
7.279
7.258
7.120
7.106
7.104
7.090
4.353
4.345
4.338
4.332
4.318
4.304
4.296
4.290
4.282
4.215
4.198
4.175
2.609
2.592
2.585
2.574
2.570
2.559
2.486
2.470
2.461
2.446
2.332
2.321
2.308
2.296
2.283
2.277
2.267
2.262
2.253
2.240
2.025
2.020
1.651
1.380
1.366
O
COOEt
N
H
3j
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 0.5 ppm
1.00
1.06
1.06
1.27
1.05
2.15
1.03
2.15
1.10
2.24
1.79
3.23

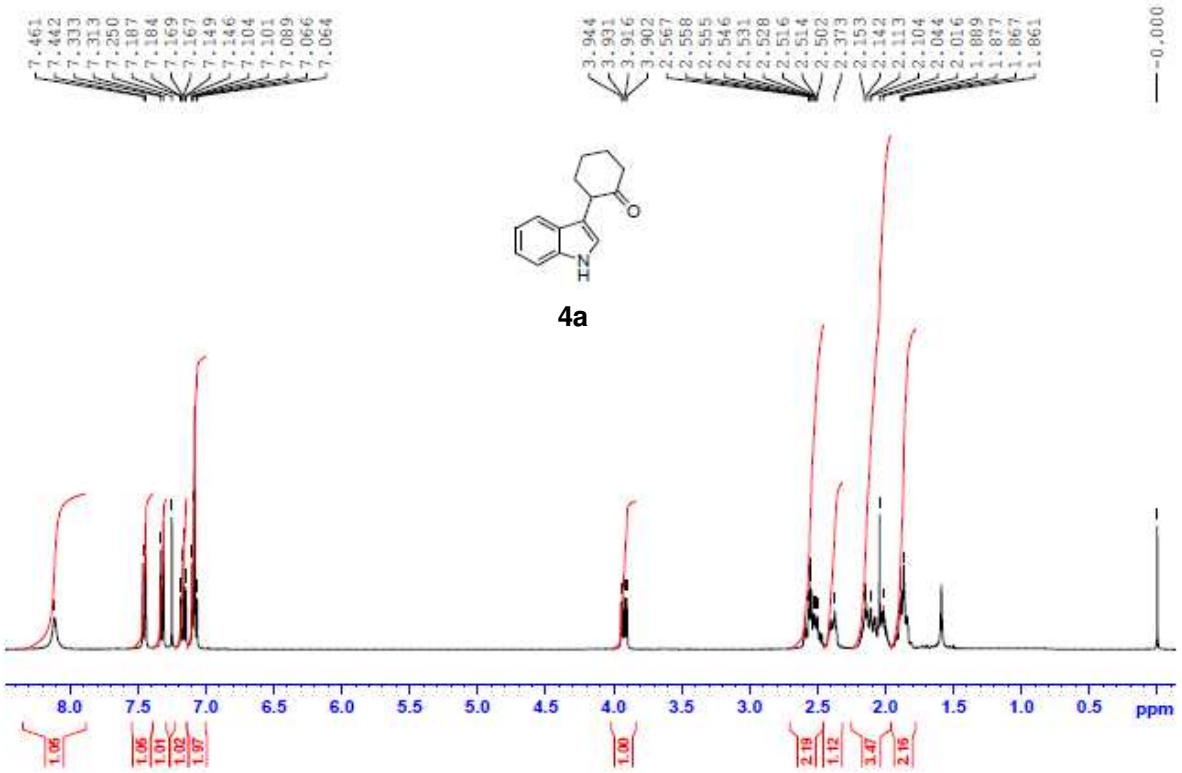

O
COOEt
N
H
3j
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.236
7.221
7.219
7.201
7.199
7.115
7.113
7.095
7.093
7.078
7.075
6.944
3.746
3.638
3.615
3.591
2.583
2.567
2.563
2.559
2.537
2.490
2.487
2.483
2.469
2.466
2.462
2.392
2.370
2.164
1.994
1.990
1.550
O
N
Me
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
1.03
1.04
1.02
1.00
1.00
2.88
1.01
2.10
1.14
2.14
1.14

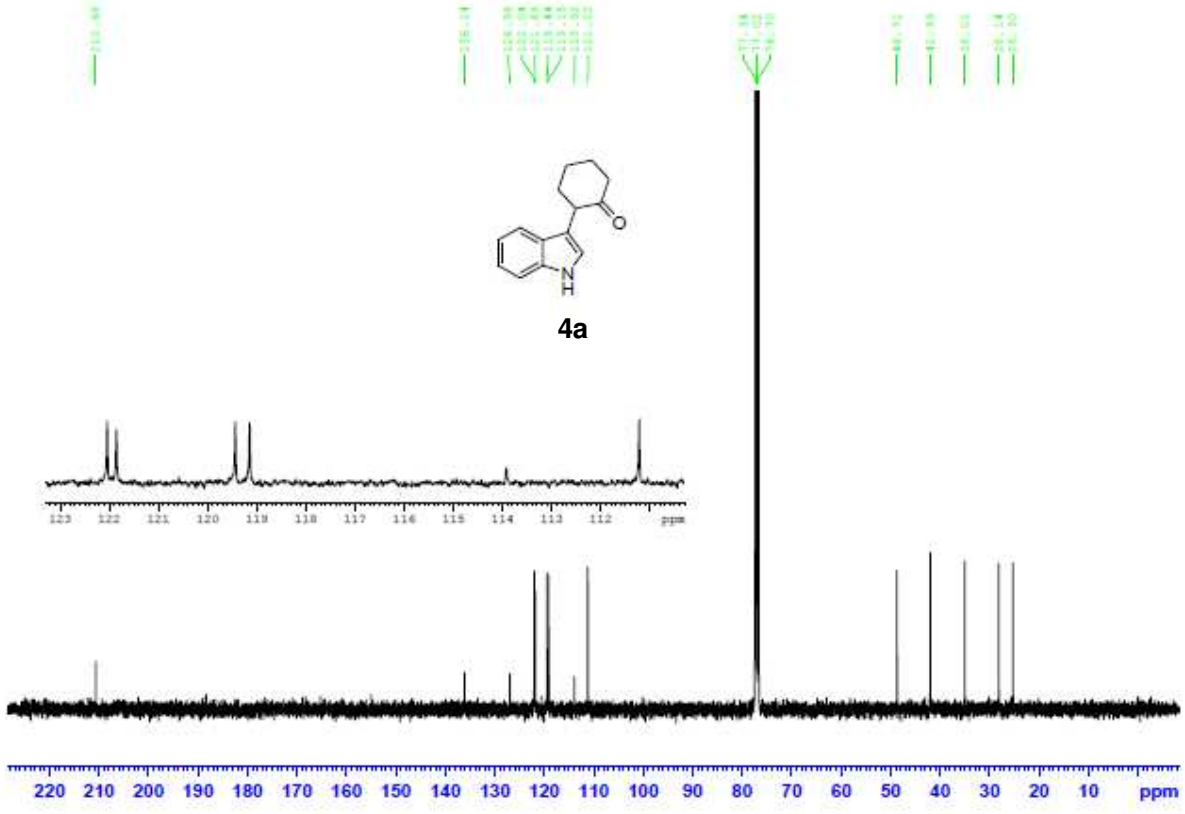
3k


219.04
137.30
127.29
126.55
119.11
111.54
109.50
77.47
77.16
76.84
47.28
38.29
32.83
31.91
21.27
O
N
CH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

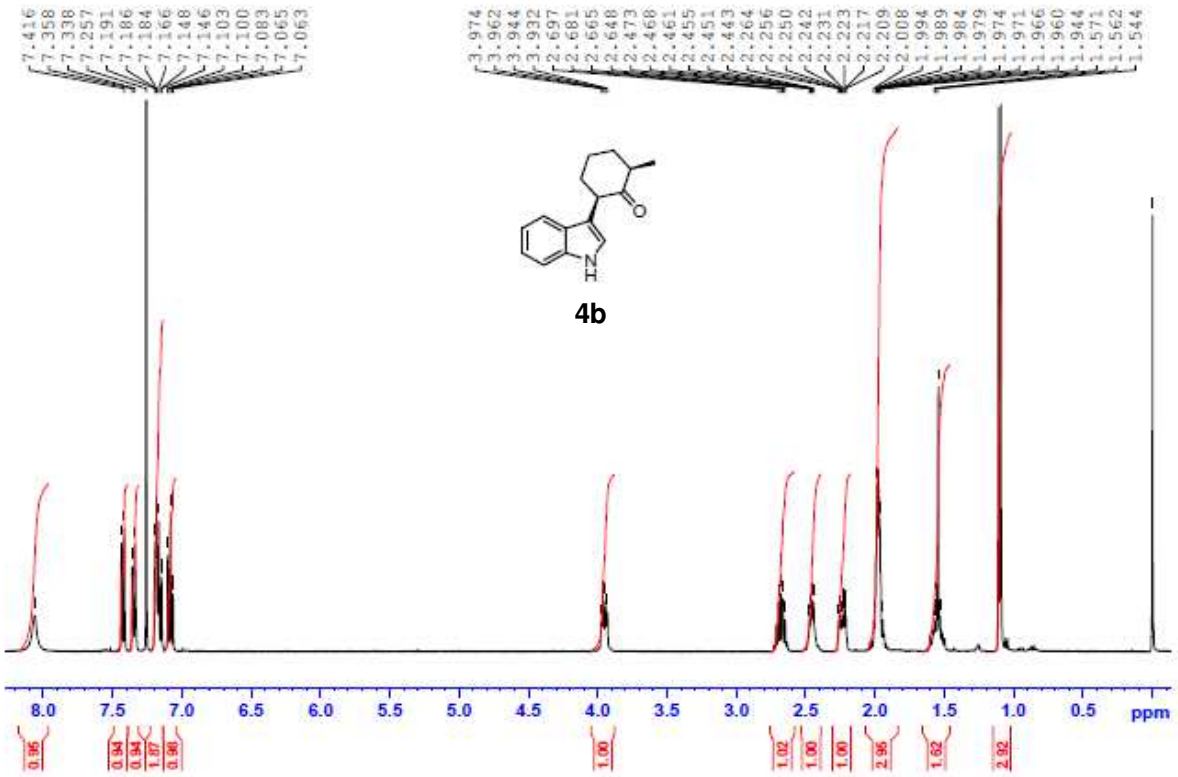
3k


7.461
7.442
7.333
7.313
7.250
7.187
7.184
7.169
7.167
7.149
7.146
7.104
7.101
7.089
7.066
7.064
3.944
3.931
3.916
3.902
2.567
2.558
2.555
2.546
2.531
2.528
2.516
2.514
2.502
2.373
2.153
2.142
2.113
2.104
2.044
2.016
1.889
1.877
1.867
1.861
0.000
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
1.06
1.06
1.01
1.02
1.97
1.00
2.19
1.12
3.47
2.16

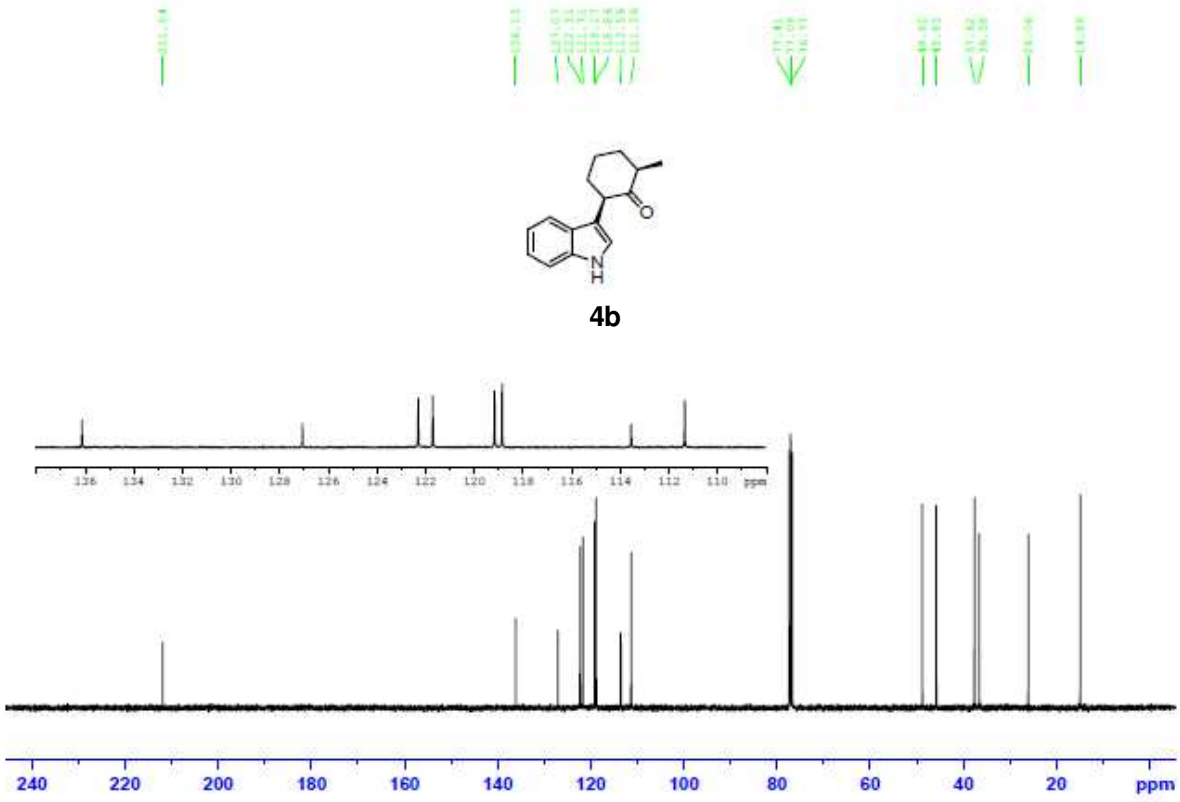
4a


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

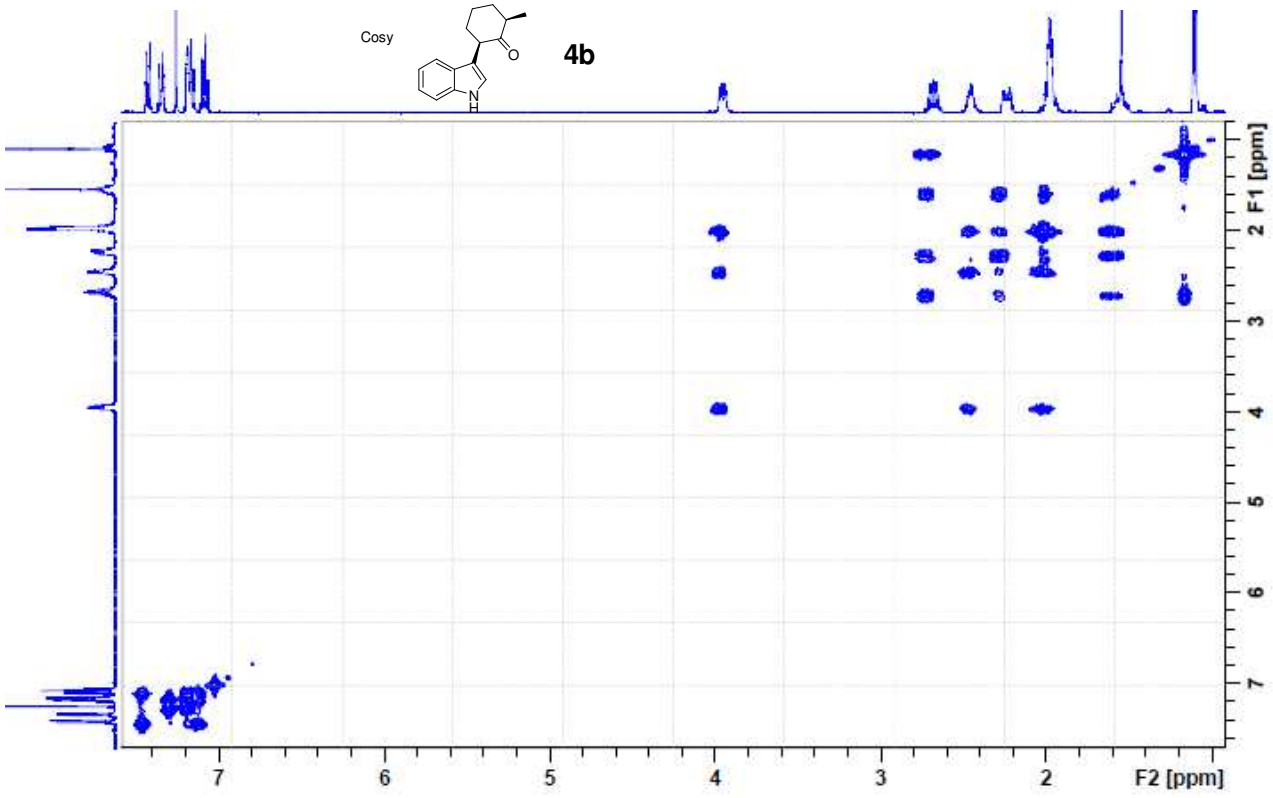
4a

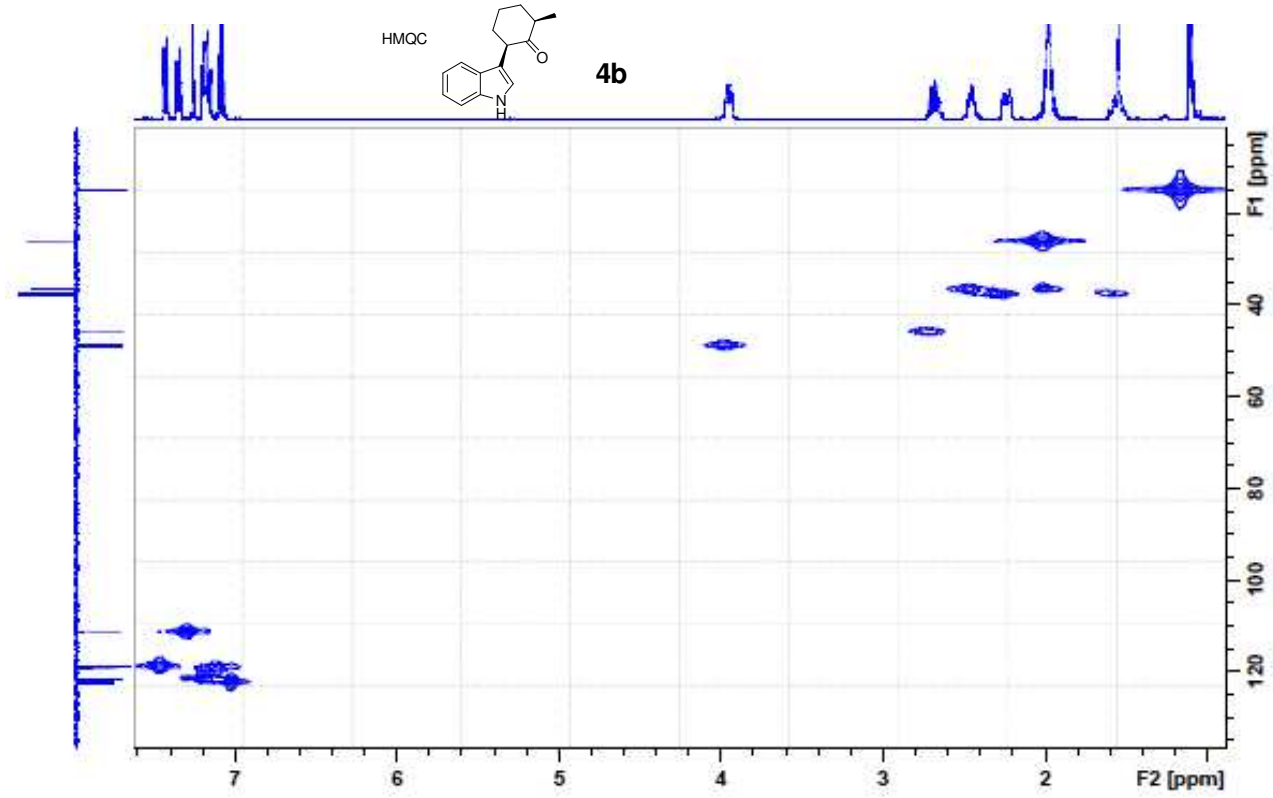

7.416
7.358
7.338
7.257
7.191
7.186
7.184
7.166
7.148
7.146
7.103
7.100
7.083
7.065
7.063
3.974
3.962
3.944
3.932
2.697
2.681
2.665
2.648
2.473
2.468
2.461
2.455
2.451
2.443
2.264
2.256
2.250
2.242
2.231
2.223
2.217
2.209
2.008
1.994
1.989
1.984
1.979
1.974
1.971
1.966
1.960
1.944
1.571
1.562
1.544
8.0
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
0.95
0.94
0.94
1.07
0.96
1.00
1.02
1.00
1.00
2.96
1.62
2.92

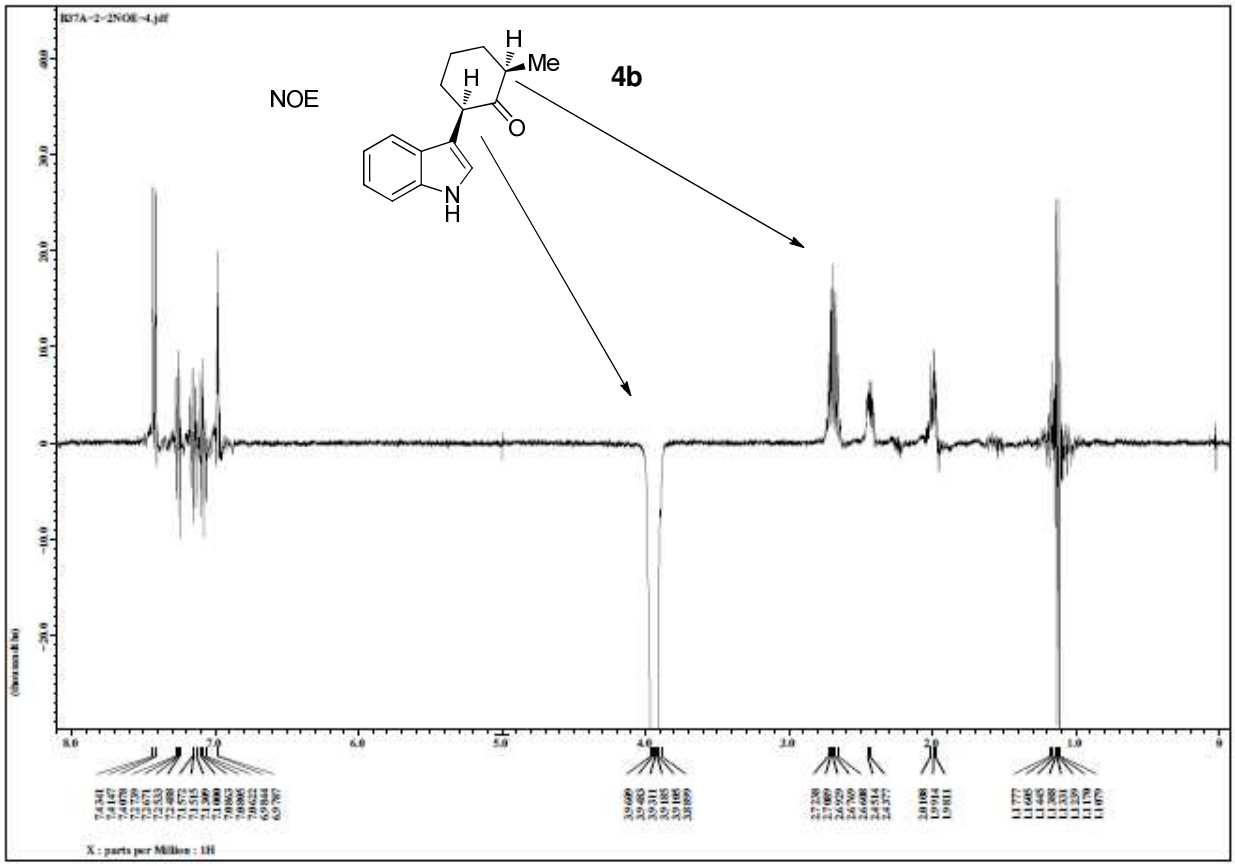
4b

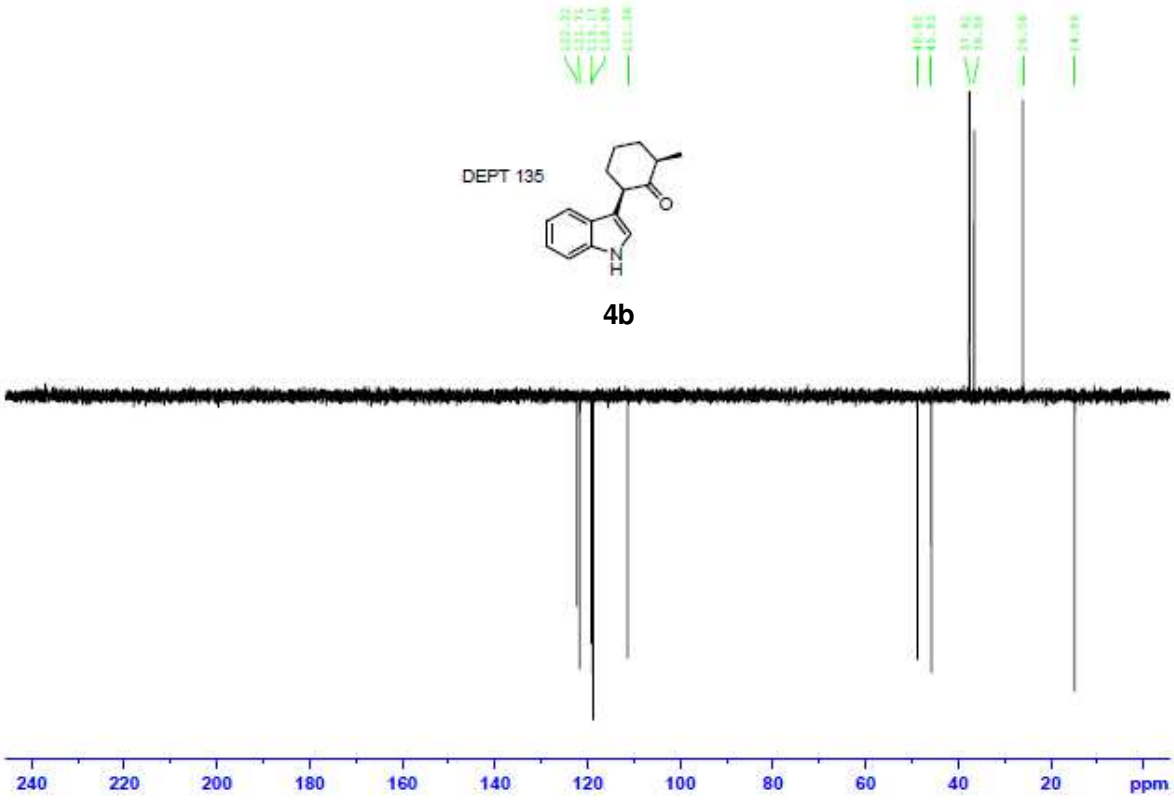

136
134
132
130
128
126
124
122
120
118
116
114
112
110
ppm
240
220
200
180
160
140
120
100
80
60
40
20
ppm

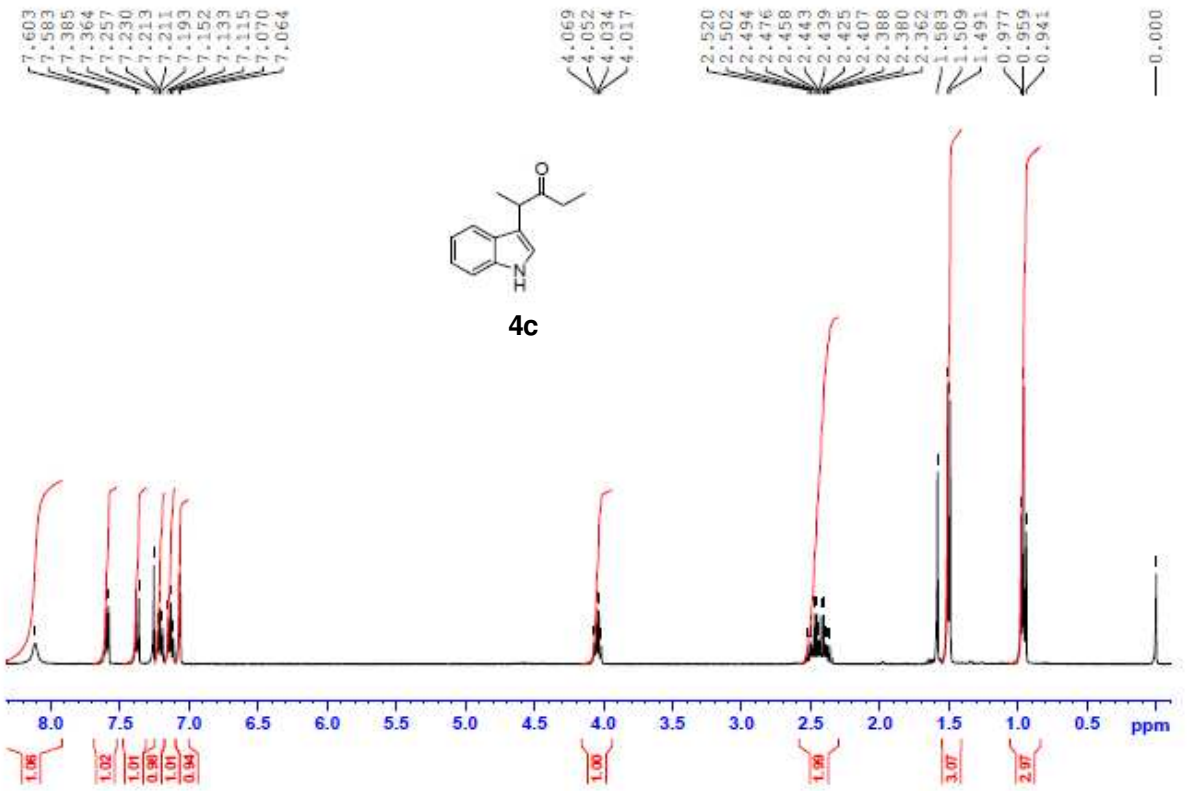
4b


Cosy
4b
F1 [ppm]
F2 [ppm]

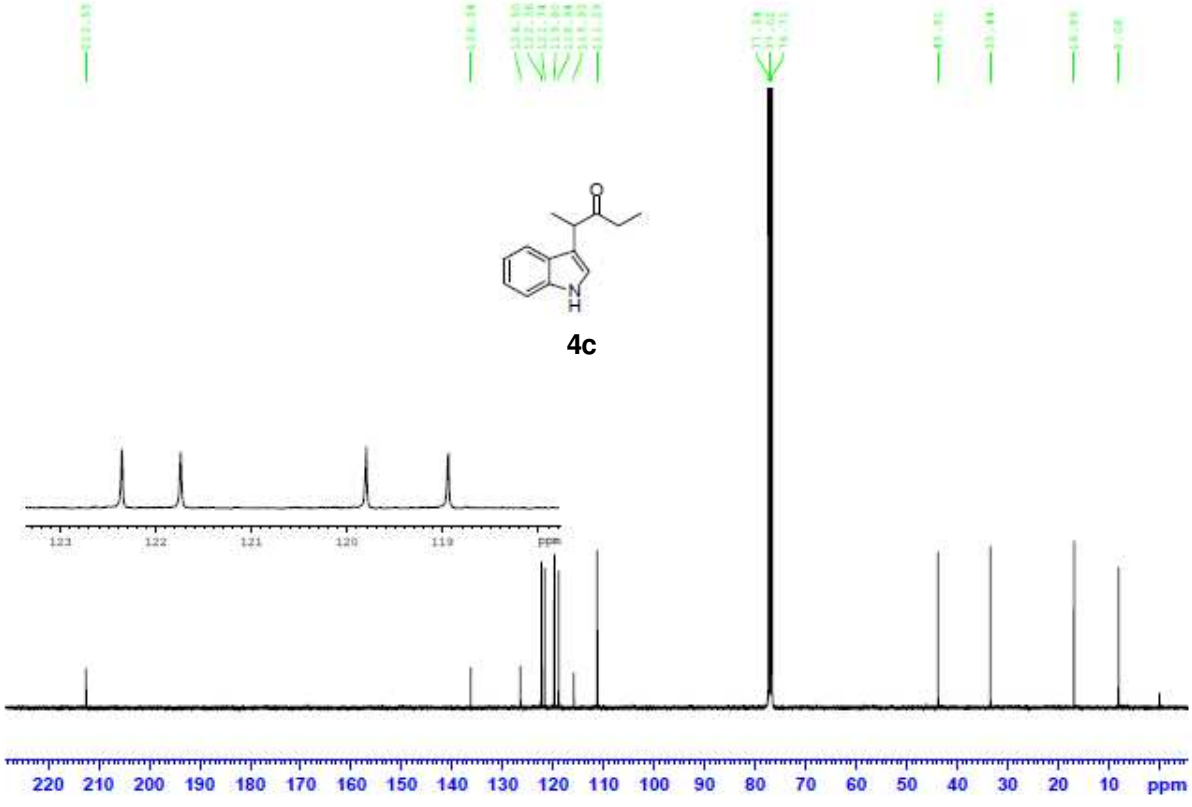

HMQC
4b
F1 [ppm]
F2 [ppm]


NOE
H
Me
H
O
N
H
4b
X : parts per Million : 1H

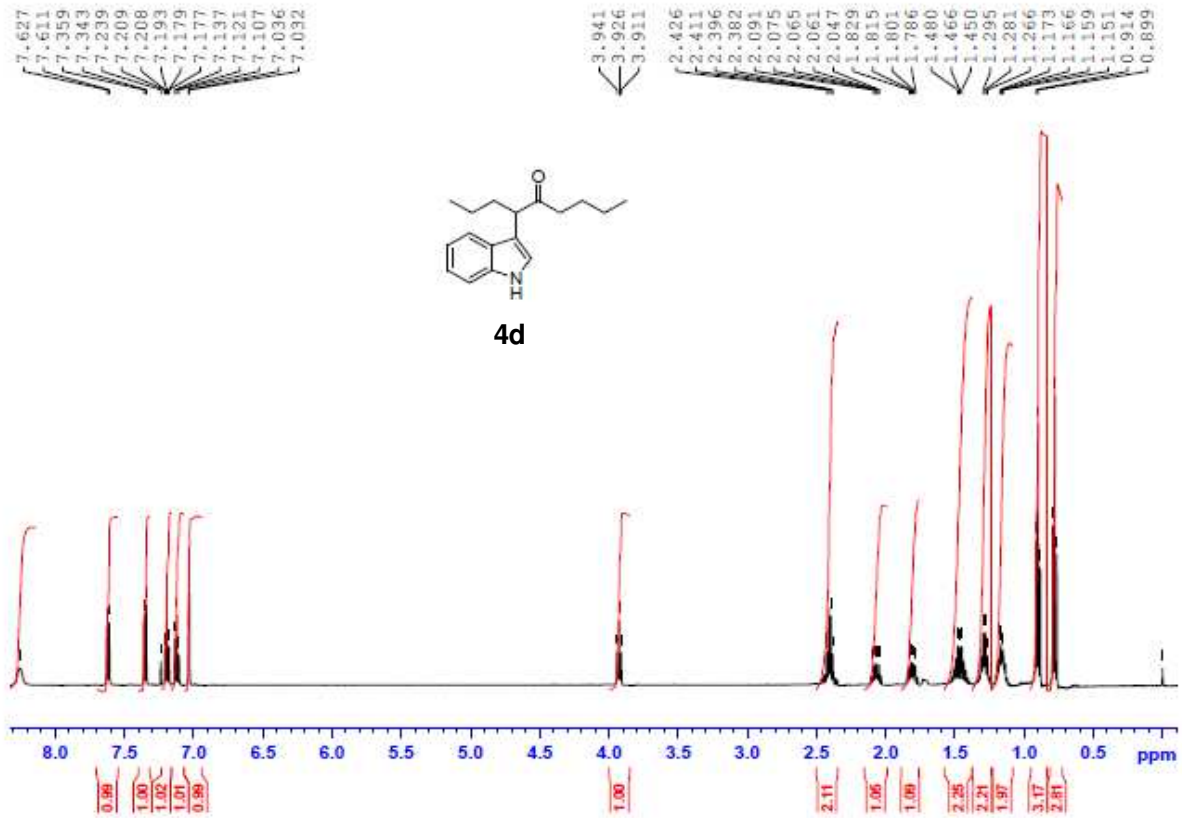

DEPT 135
O
N
H
4b
240
220
200
180
160
140
120
100
80
60
40
20
ppm


7.603
7.583
7.385
7.364
7.257
7.230
7.213
7.211
7.193
7.152
7.133
7.115
7.070
7.064
4.069
4.052
4.034
4.017
2.520
2.502
2.494
2.476
2.458
2.443
2.439
2.425
2.407
2.388
2.380
2.362
1.583
1.509
1.491
0.977
0.959
0.941
0.000
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
1.06
1.02
1.01
0.98
1.01
0.94
1.00
1.99
3.07
2.97

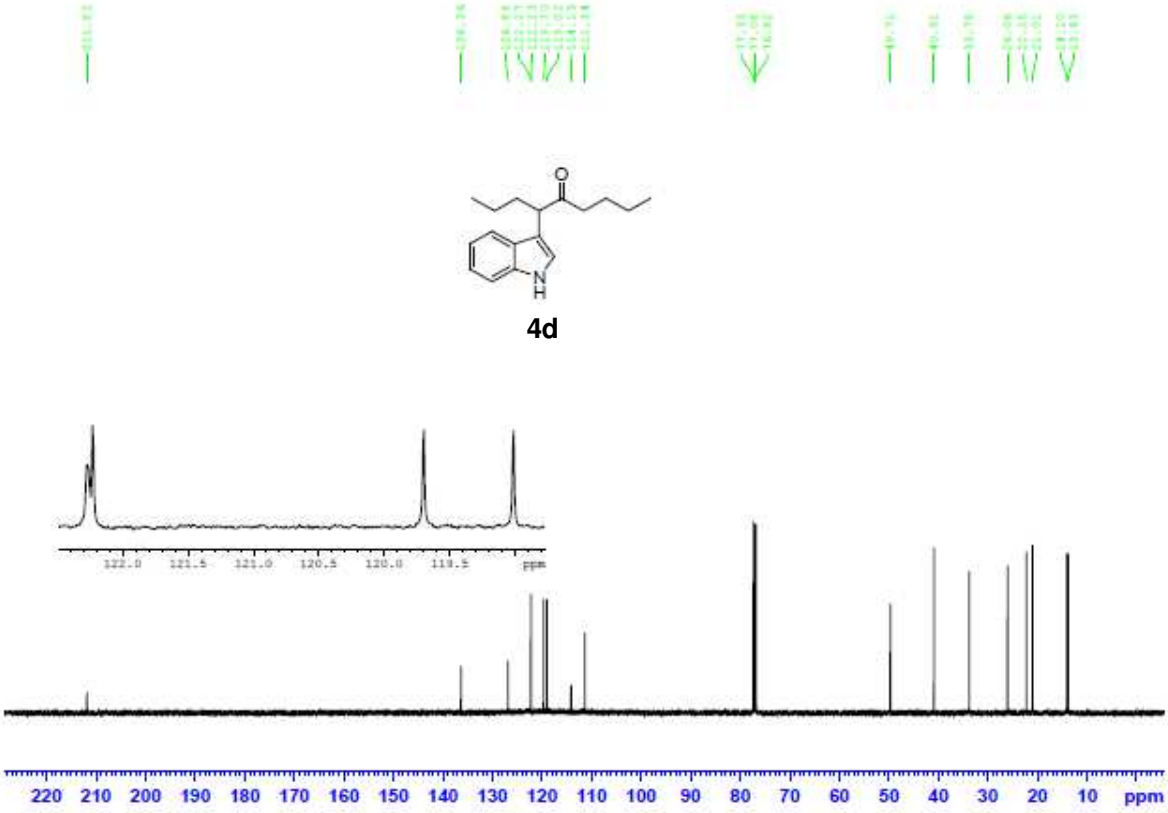
4c


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

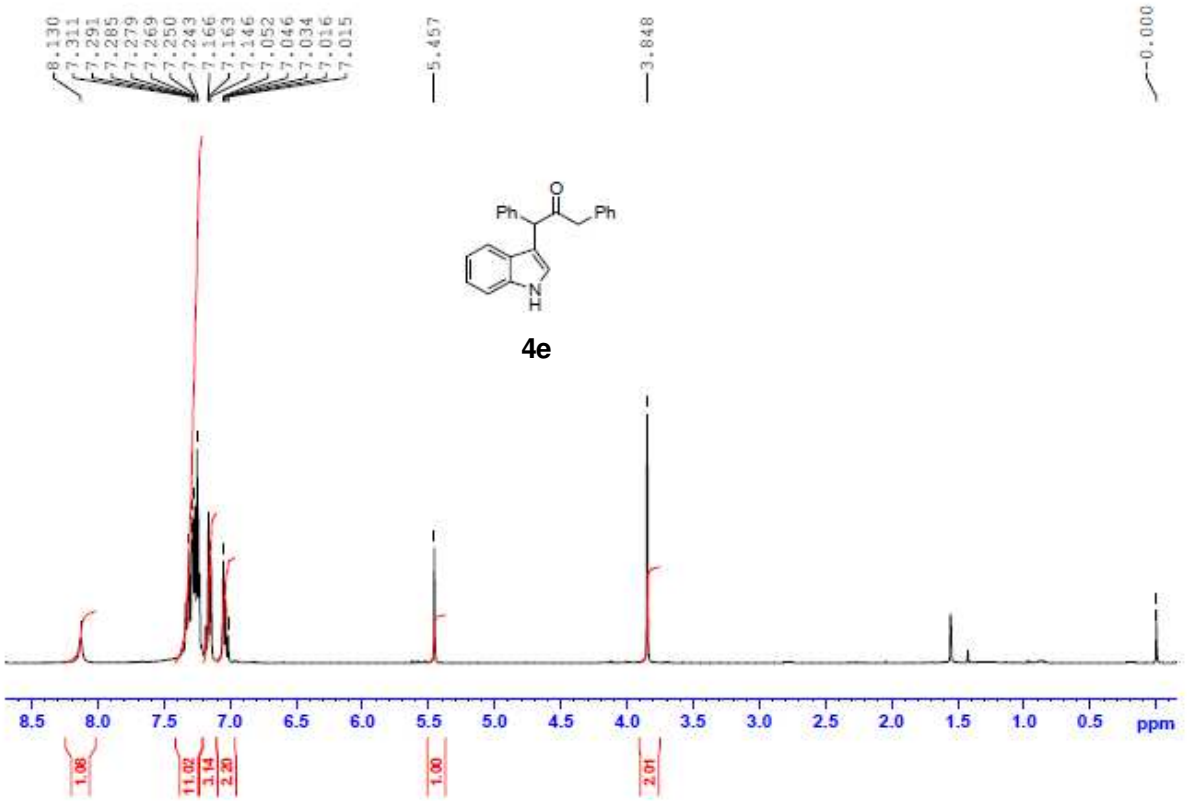
4c


7.627
7.611
7.359
7.343
7.239
7.209
7.208
7.193
7.179
7.177
7.137
7.121
7.107
7.036
7.032
3.941
3.926
3.911
2.426
2.411
2.396
2.382
2.091
2.075
2.065
2.061
2.047
1.829
1.815
1.801
1.786
1.480
1.466
1.450
1.295
1.281
1.266
1.173
1.166
1.159
1.151
0.914
0.899
O
N
H
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
0.99
1.00
1.02
1.01
0.99
1.00
2.11
1.06
1.09
2.25
2.24
1.97
3.17
2.81

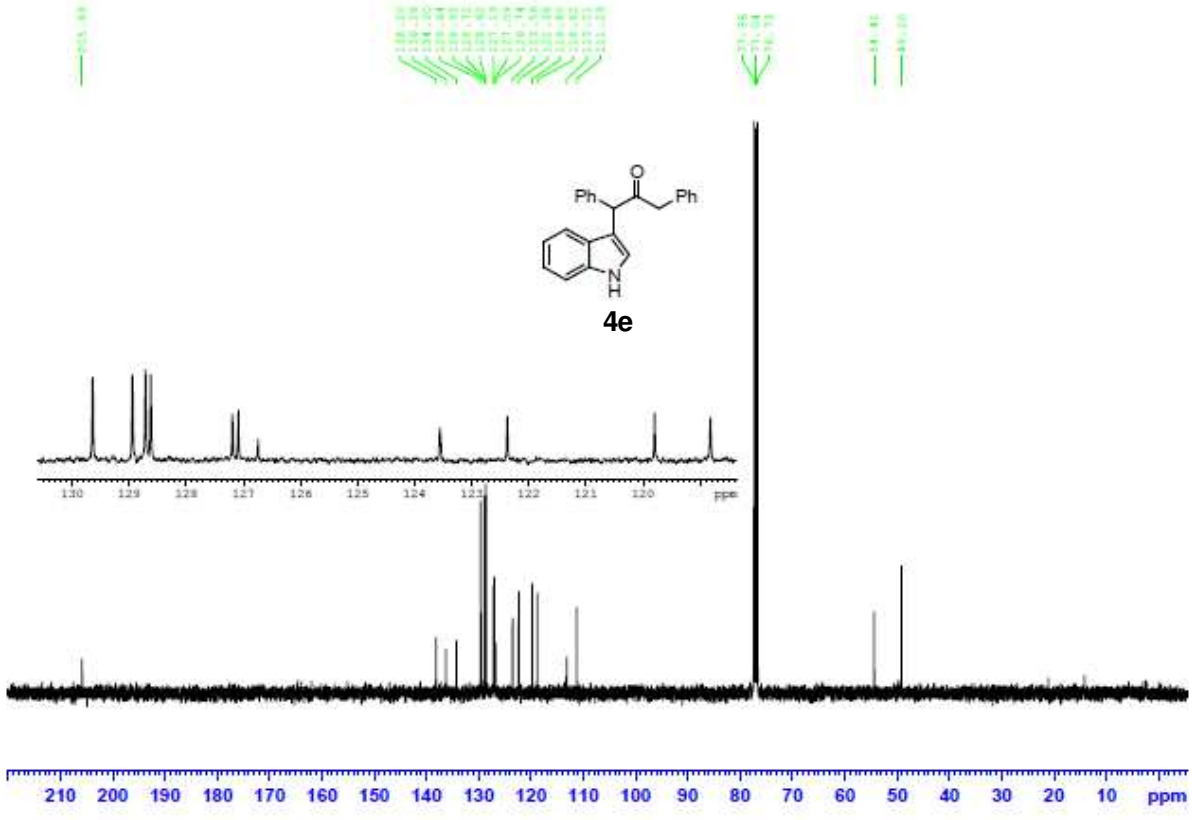
4d


O
N
H
122.0
121.5
121.0
120.5
120.0
119.5
ppm
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

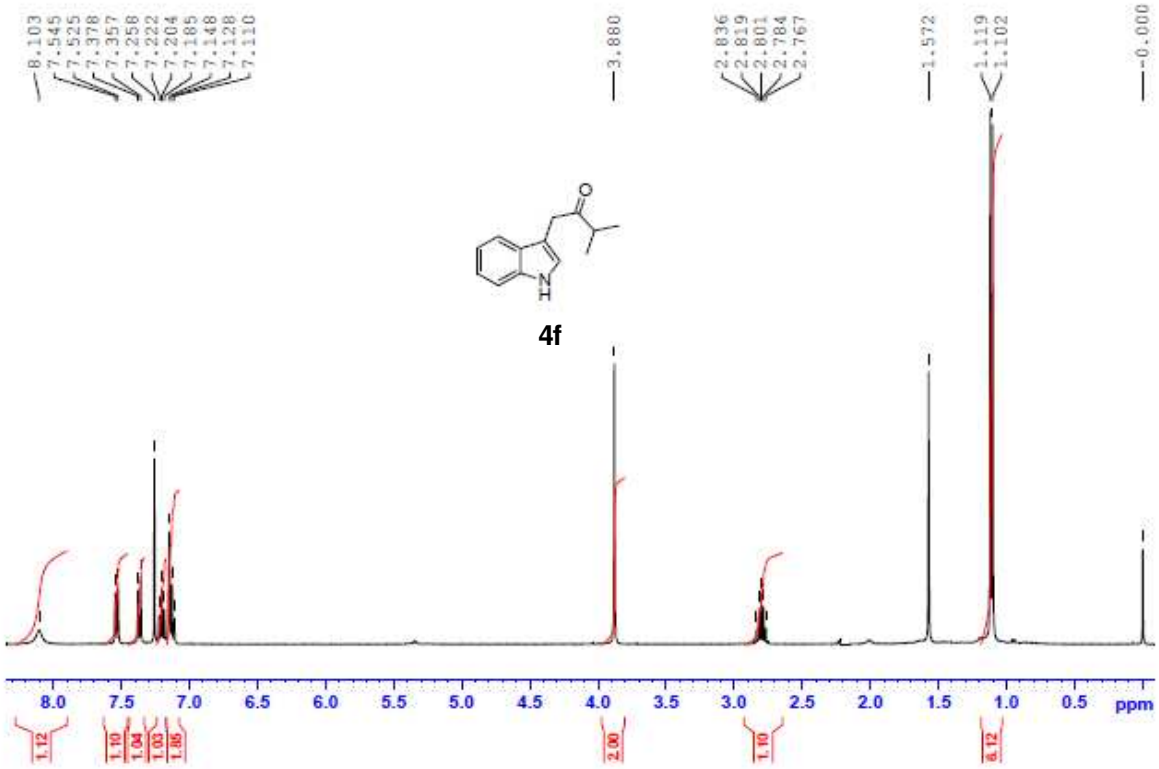
4d

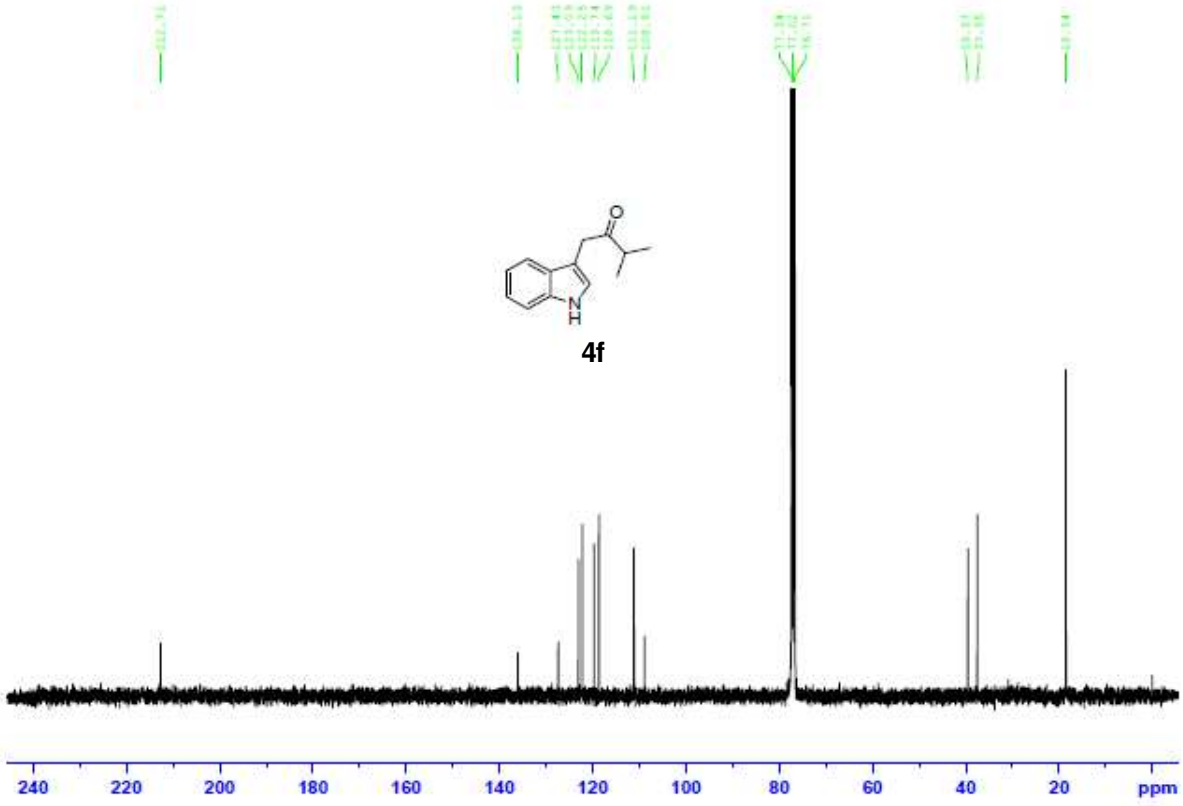

8.130
7.311
7.291
7.285
7.279
7.269
7.250
7.243
7.166
7.163
7.146
7.052
7.046
7.034
7.016
7.015
5.457
3.848
0.000
Ph
Ph
O
N
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.08
11.02
3.14
2.20
1.00
2.01

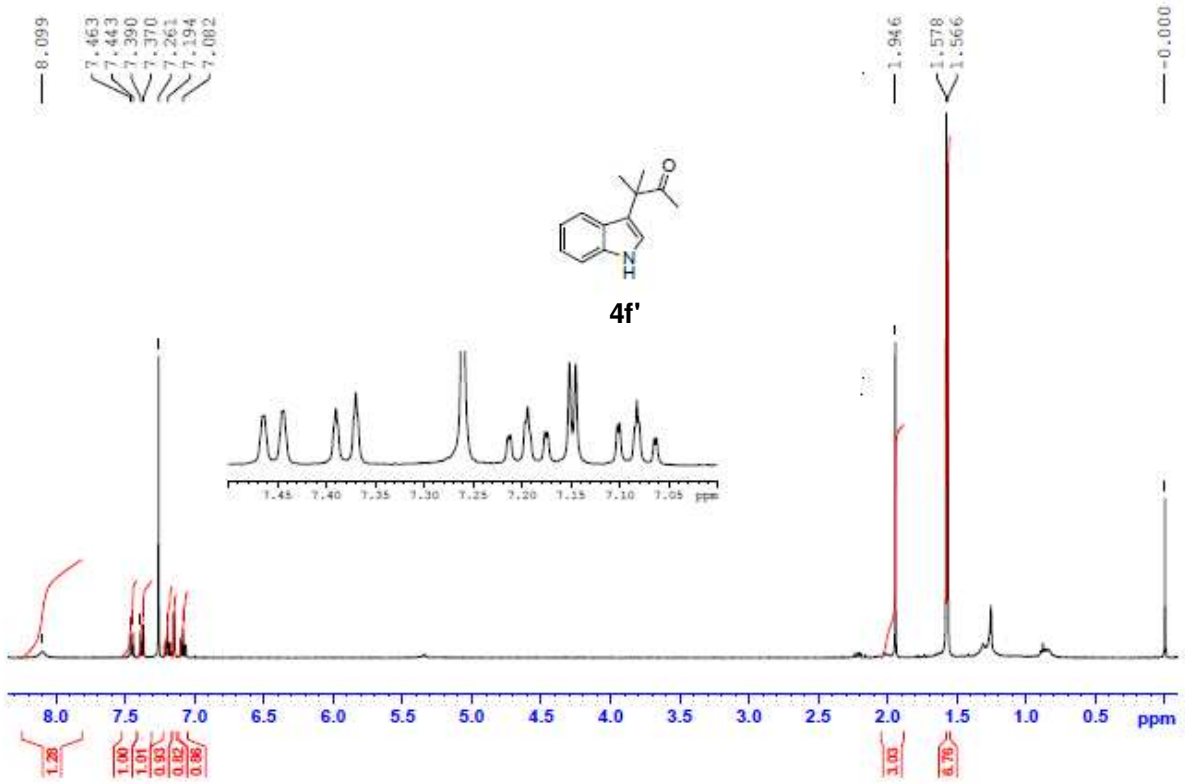
4e

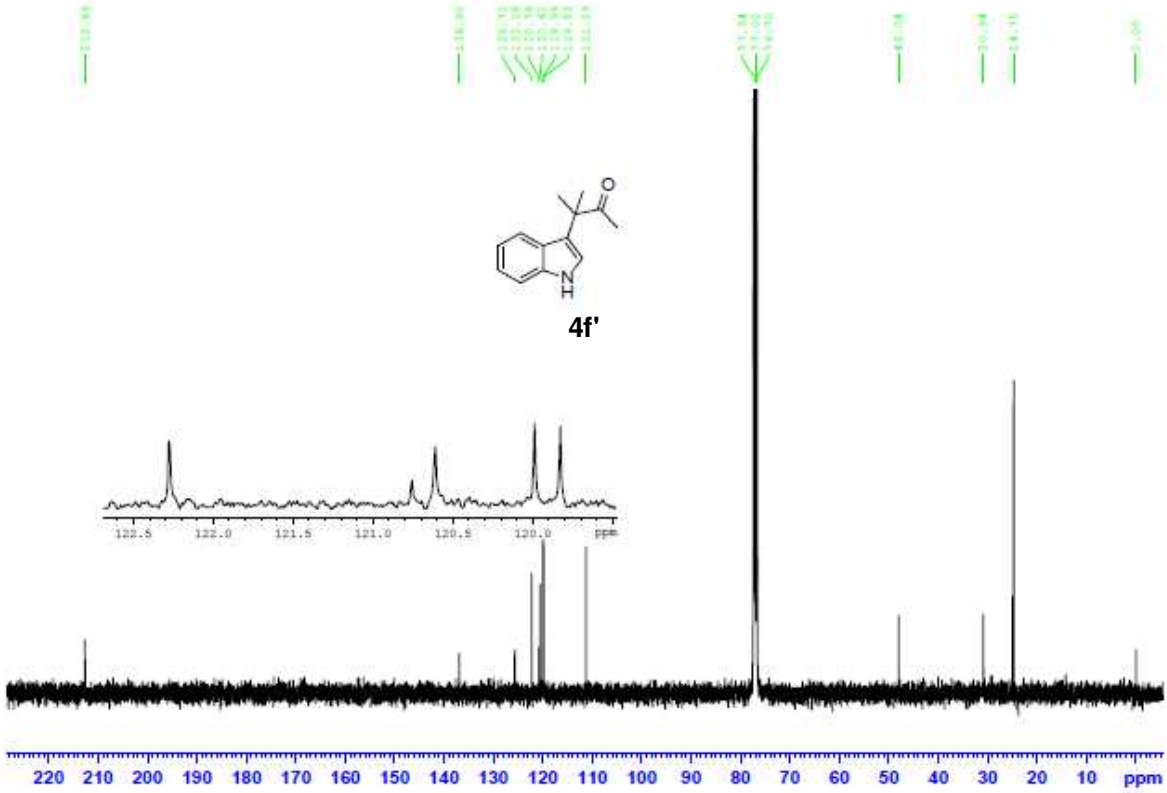

Ph
Ph
O
N
H
130
129
128
127
126
125
124
123
122
121
120
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

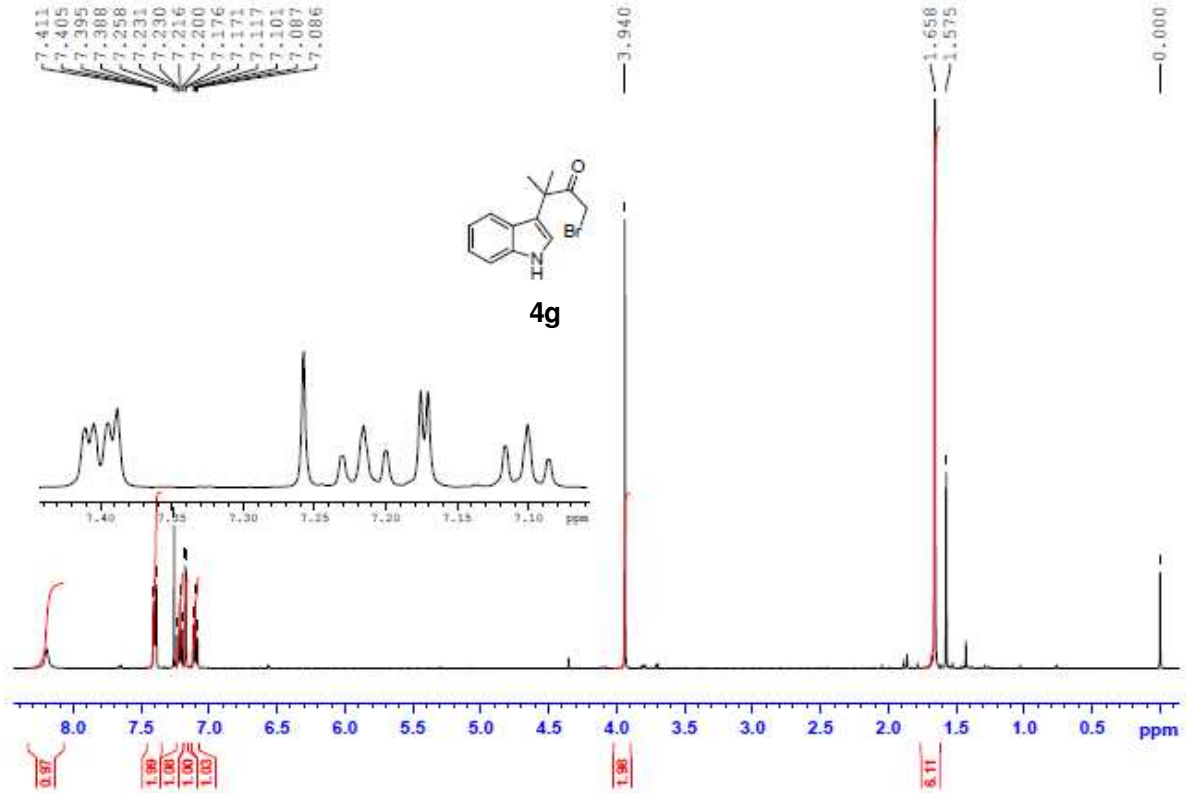
4e

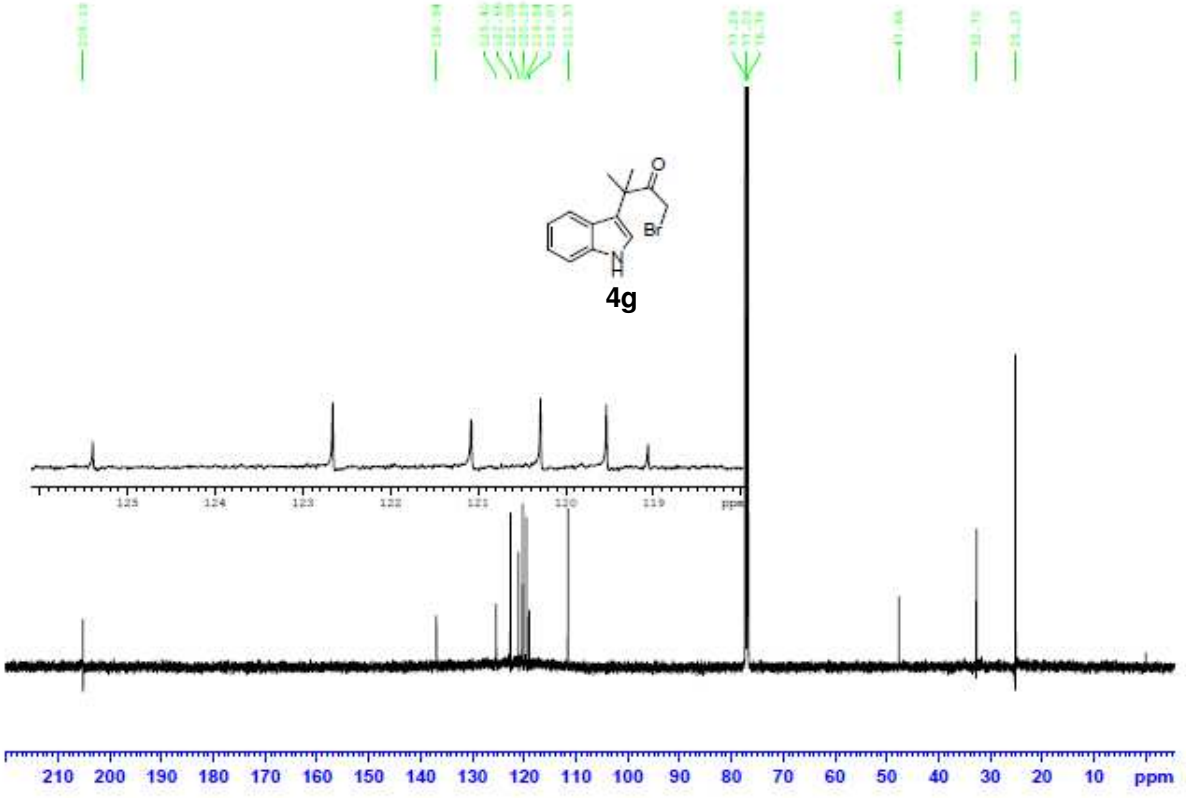

8.103
7.545
7.525
7.378
7.357
7.258
7.222
7.204
7.185
7.148
7.128
7.110
3.880
2.836
2.819
2.801
2.784
2.767
1.572
1.119
1.102
0.000
4f
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.12
1.10
1.04
1.03
1.00
2.00
1.10
6.12

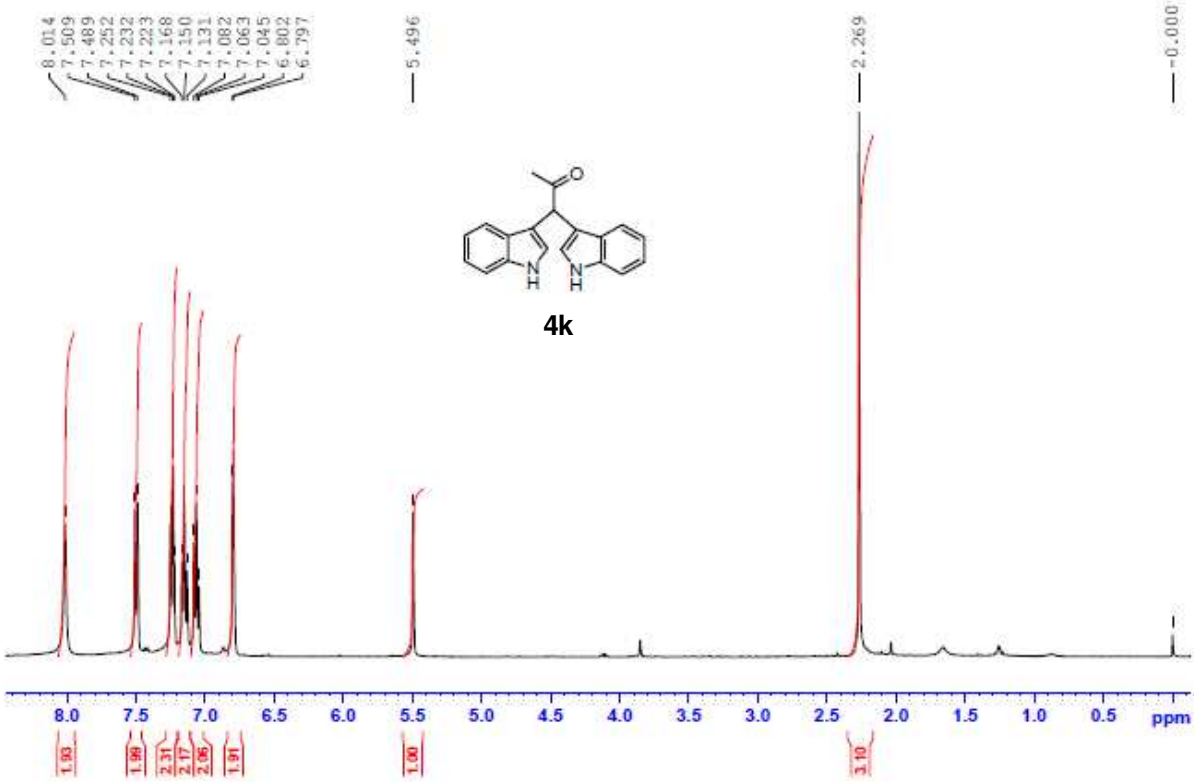

4f
240
220
200
180
160
140
120
100
80
60
40
20
ppm

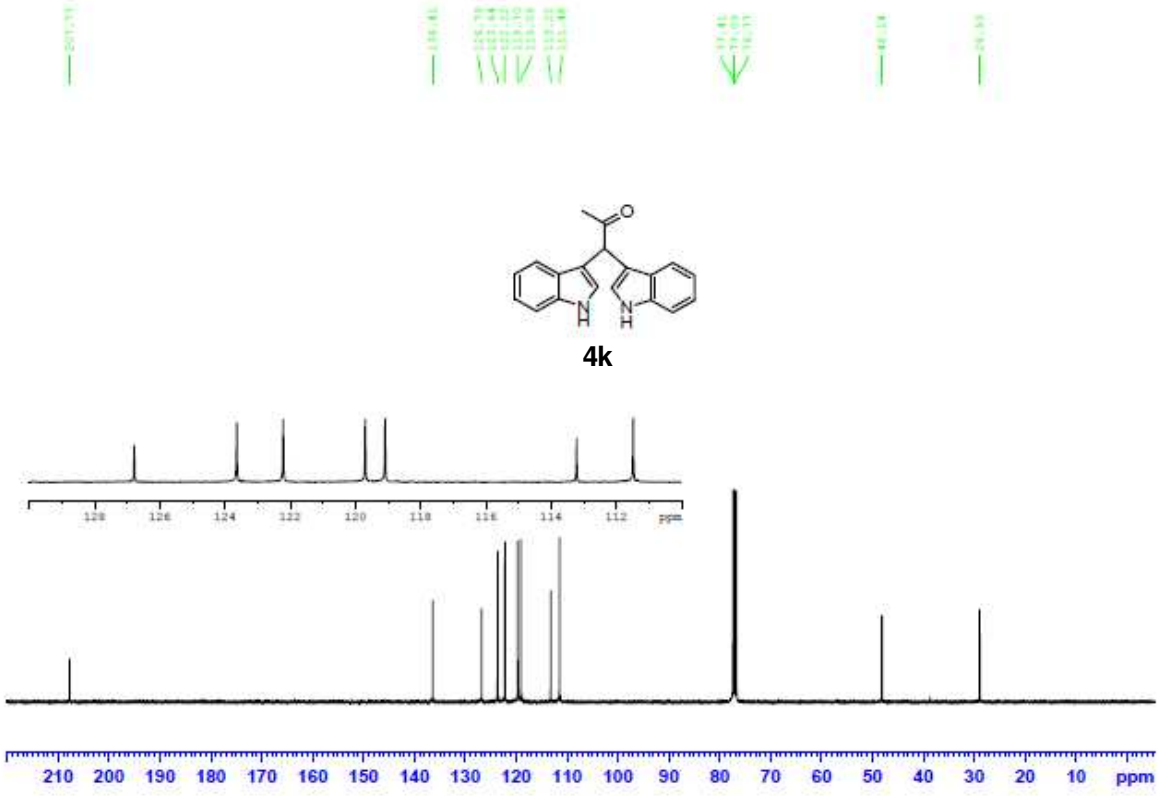

8.099
7.463
7.443
7.390
7.370
7.261
7.194
7.082
1.946
1.578
1.566
0.000
4f'
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

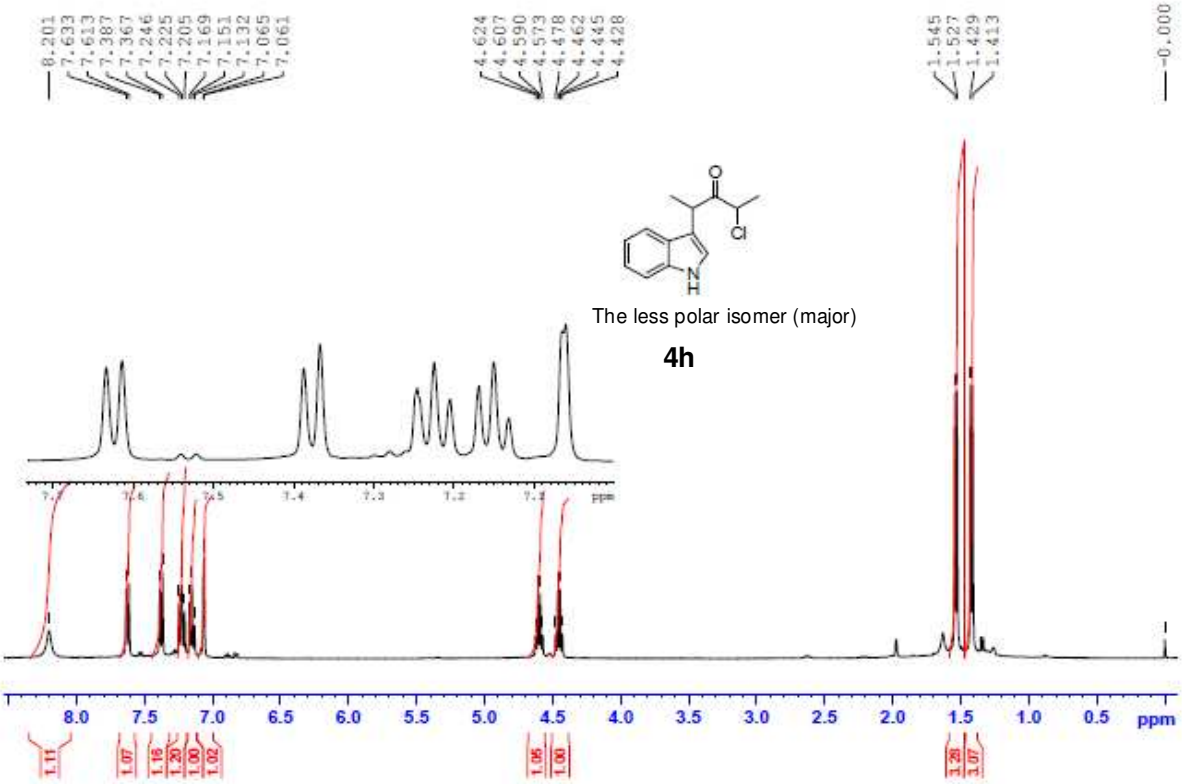

4f'
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.411
7.405
7.395
7.388
7.258
7.231
7.230
7.216
7.200
7.176
7.171
7.117
7.101
7.087
7.086
3.940
1.658
1.575
0.000
Br
N
H
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
0.5
ppm
0.97
1.98
1.00
1.00
1.03
1.96
6.11


Br
N
H
4g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

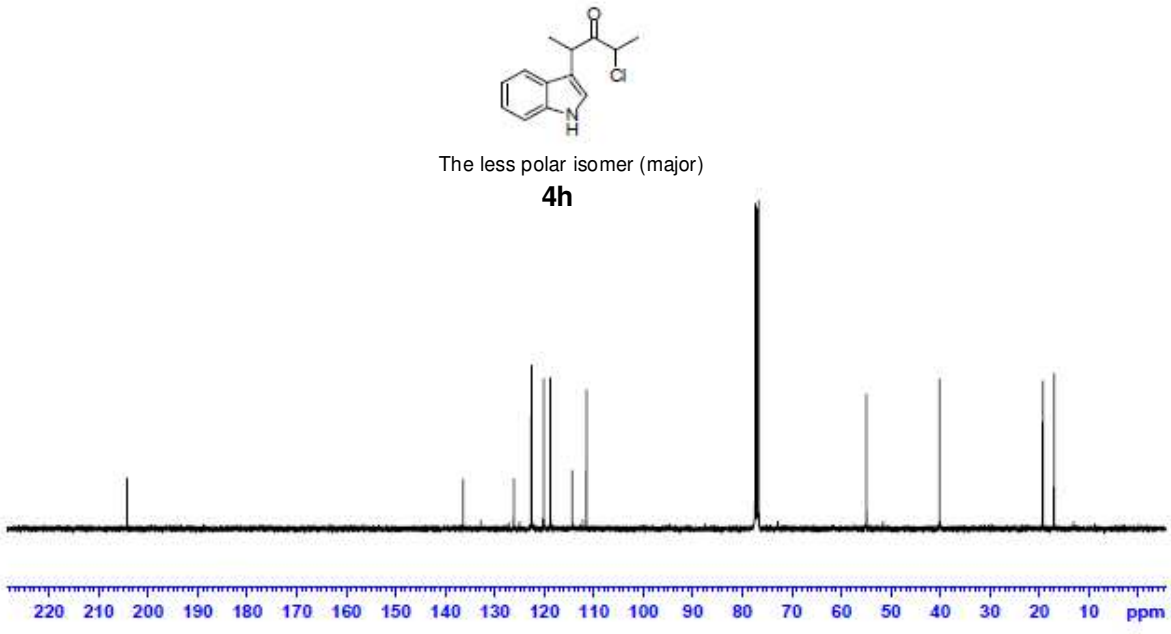

8.014
7.509
7.489
7.252
7.232
7.223
7.168
7.150
7.131
7.082
7.063
7.045
6.802
6.797
5.496
2.269
0.000
4k
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.93
1.98
2.31
2.17
2.06
1.91
1.00
3.10


4k
128
126
124
122
120
118
116
114
112
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



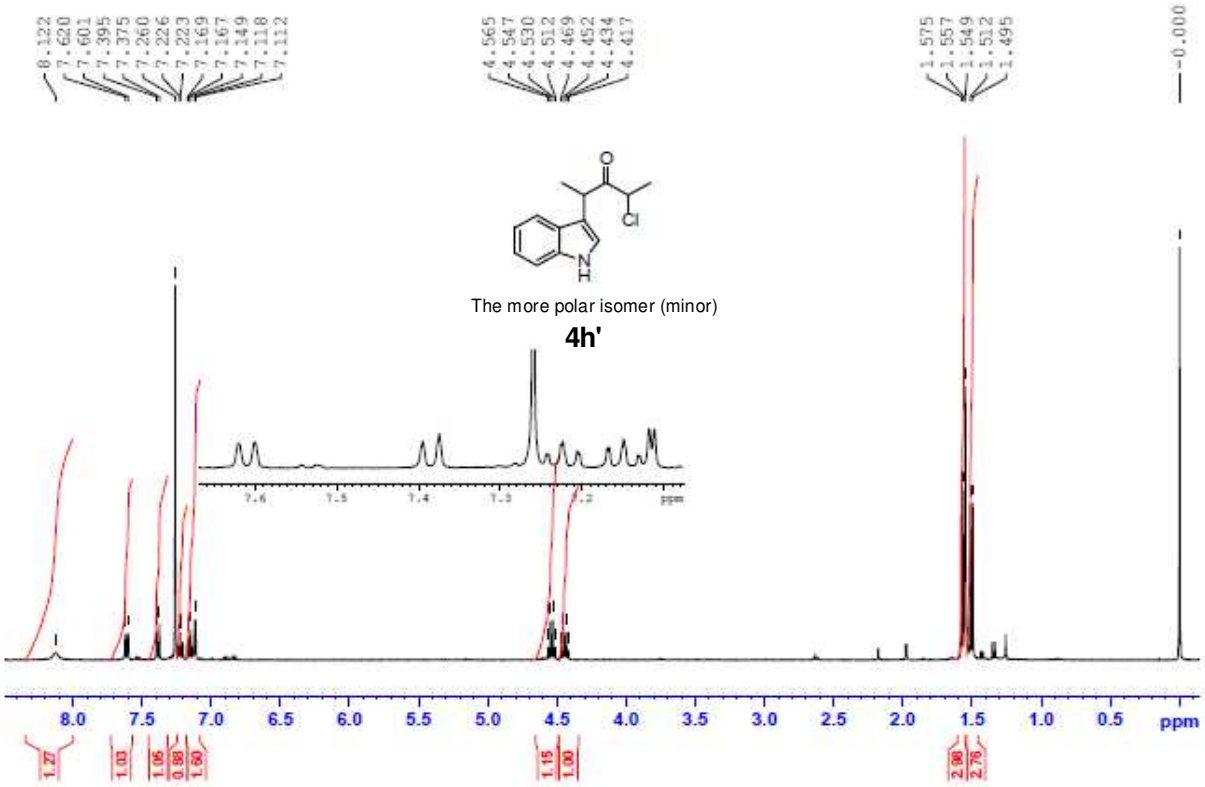
The less polar isomer (major)

4h



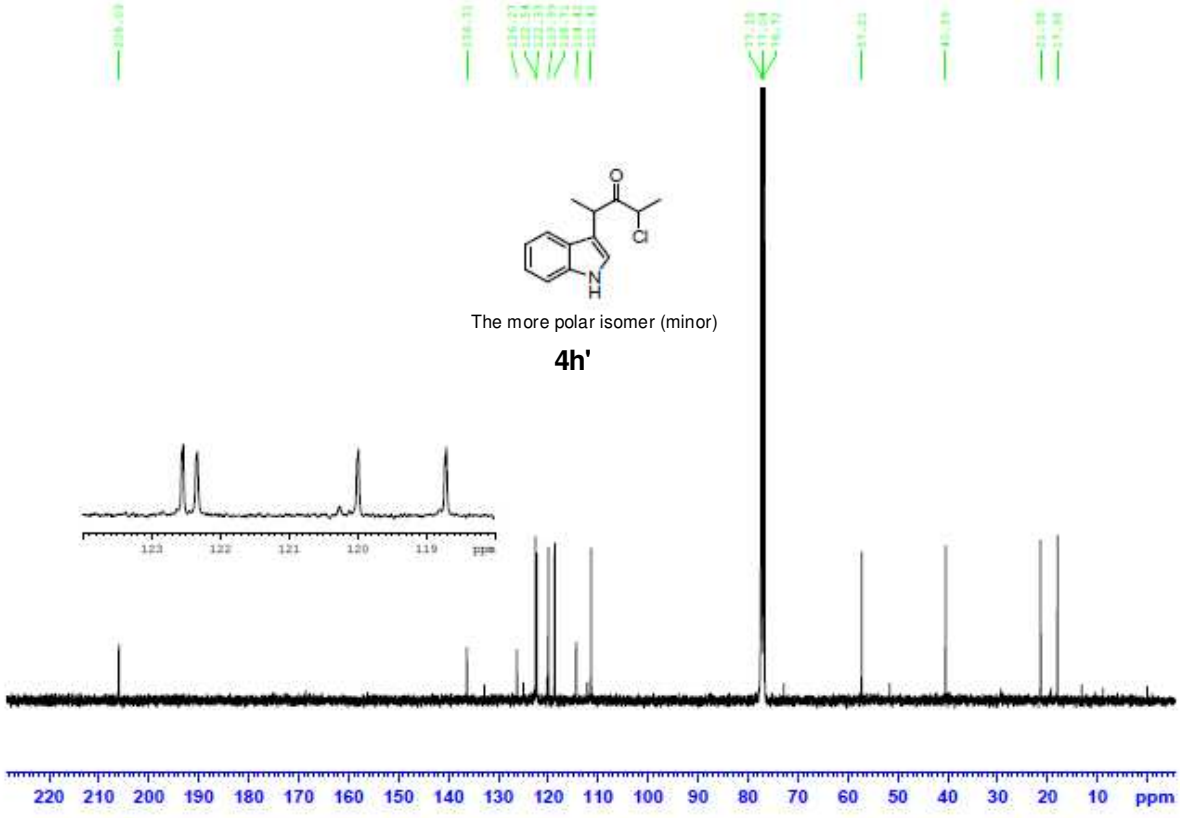
The less polar isomer (major)

4h



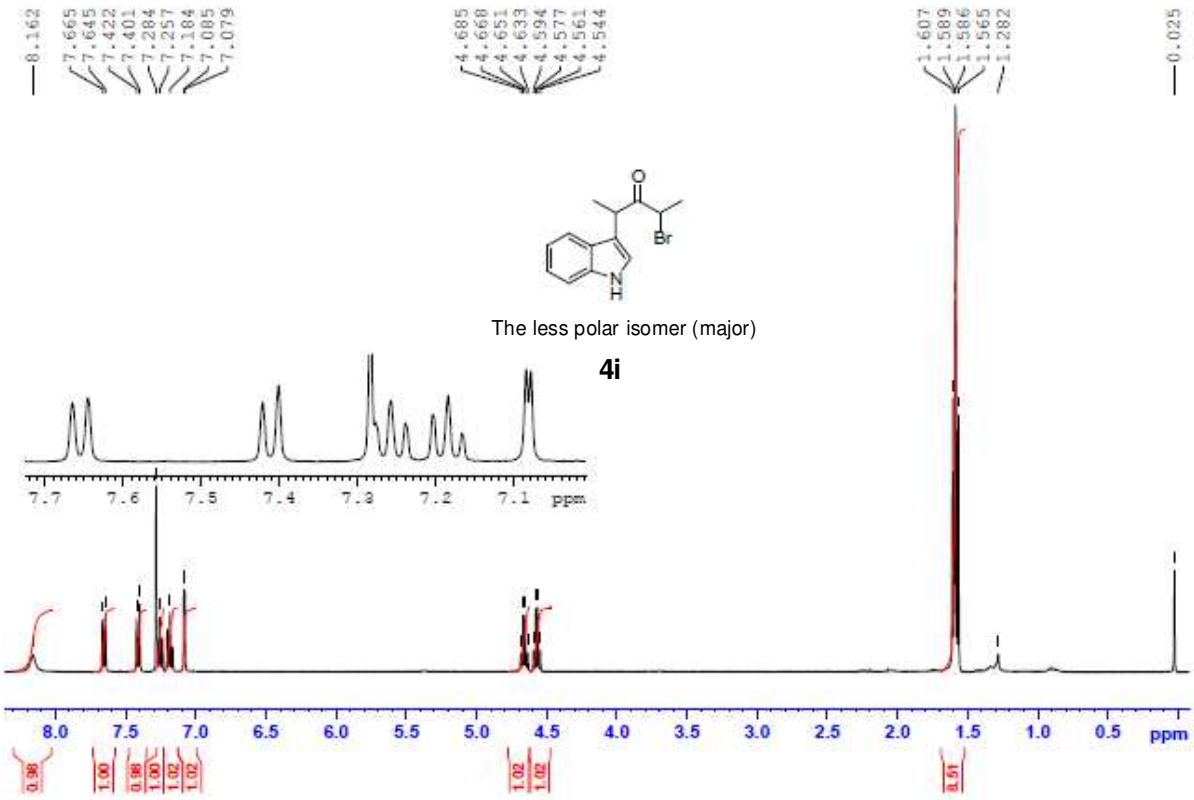
The more polar isomer (minor)

4h'



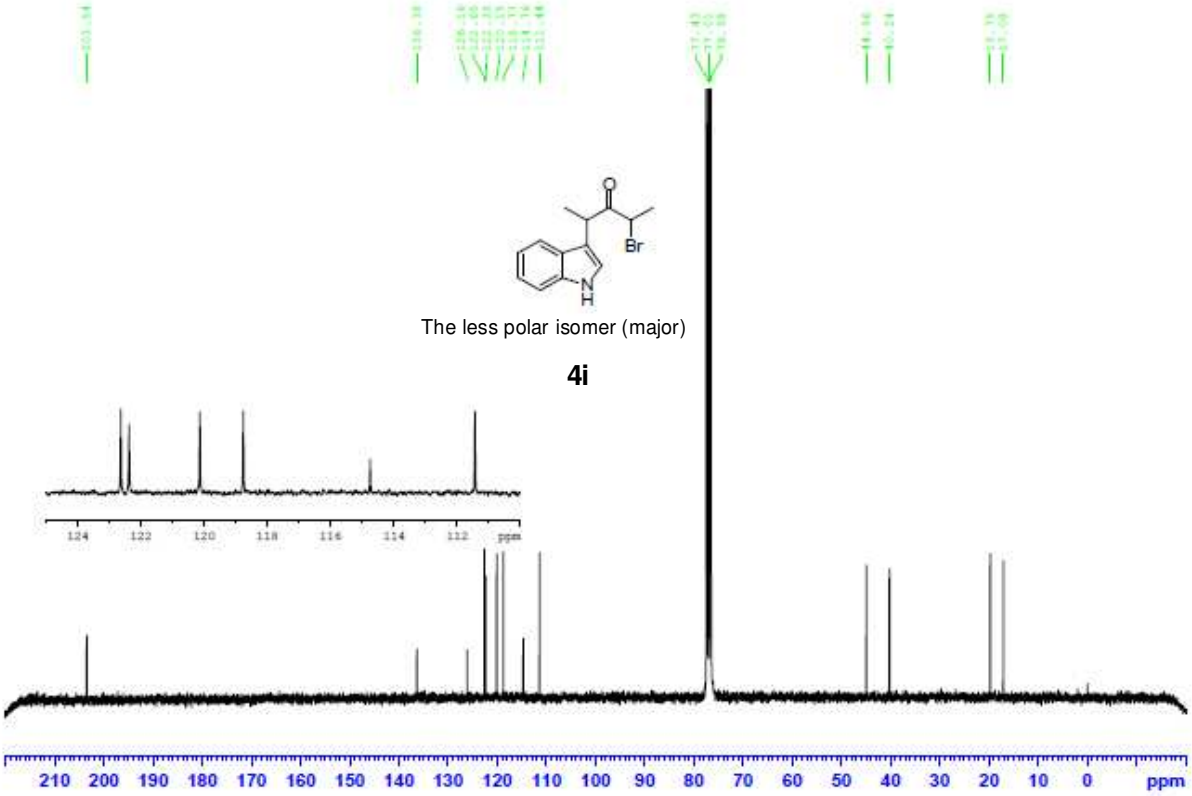
The more polar isomer (minor)

4h'



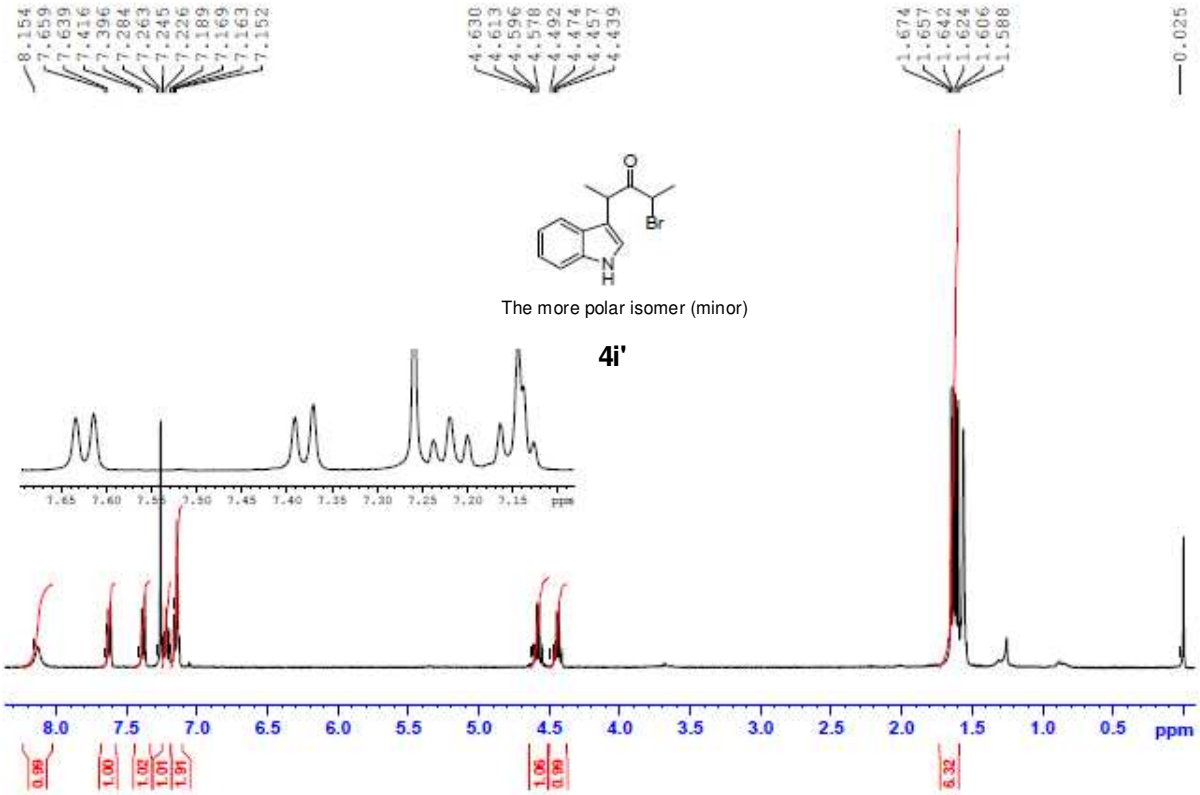
The less polar isomer (major)

4i



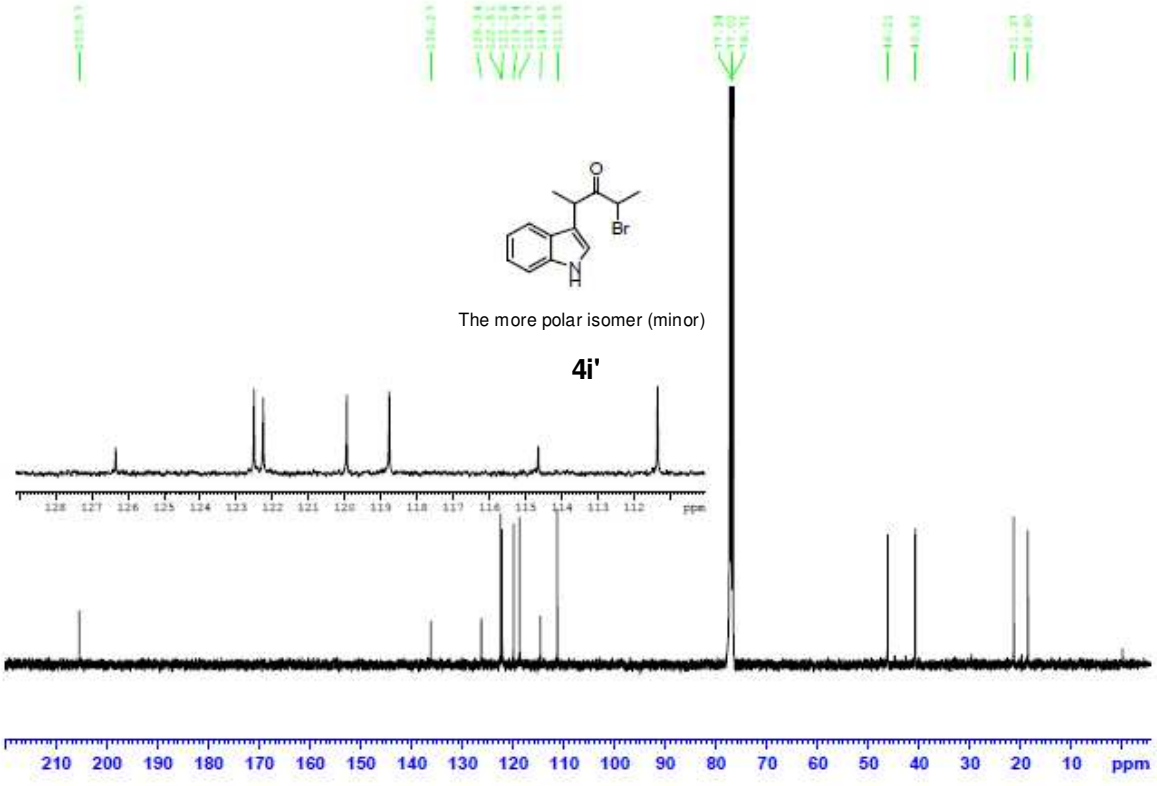
The less polar isomer (major)

4i



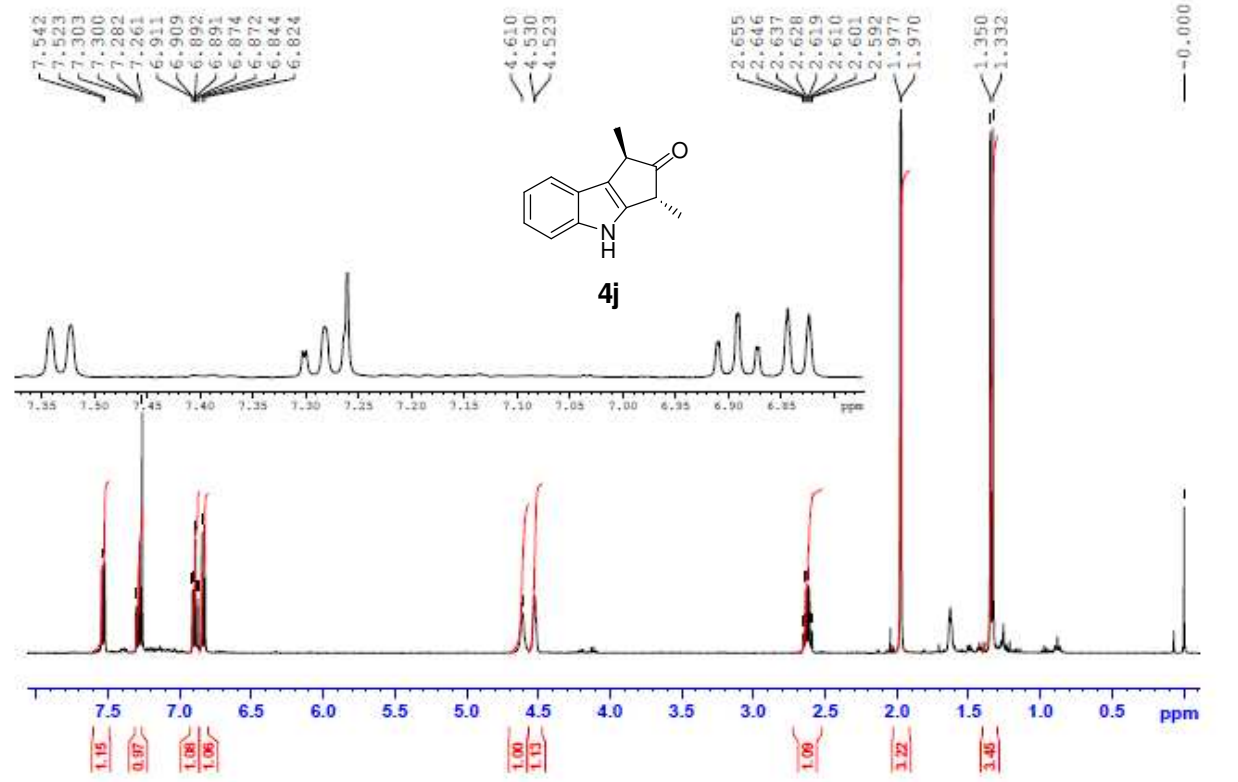
The more polar isomer (minor)

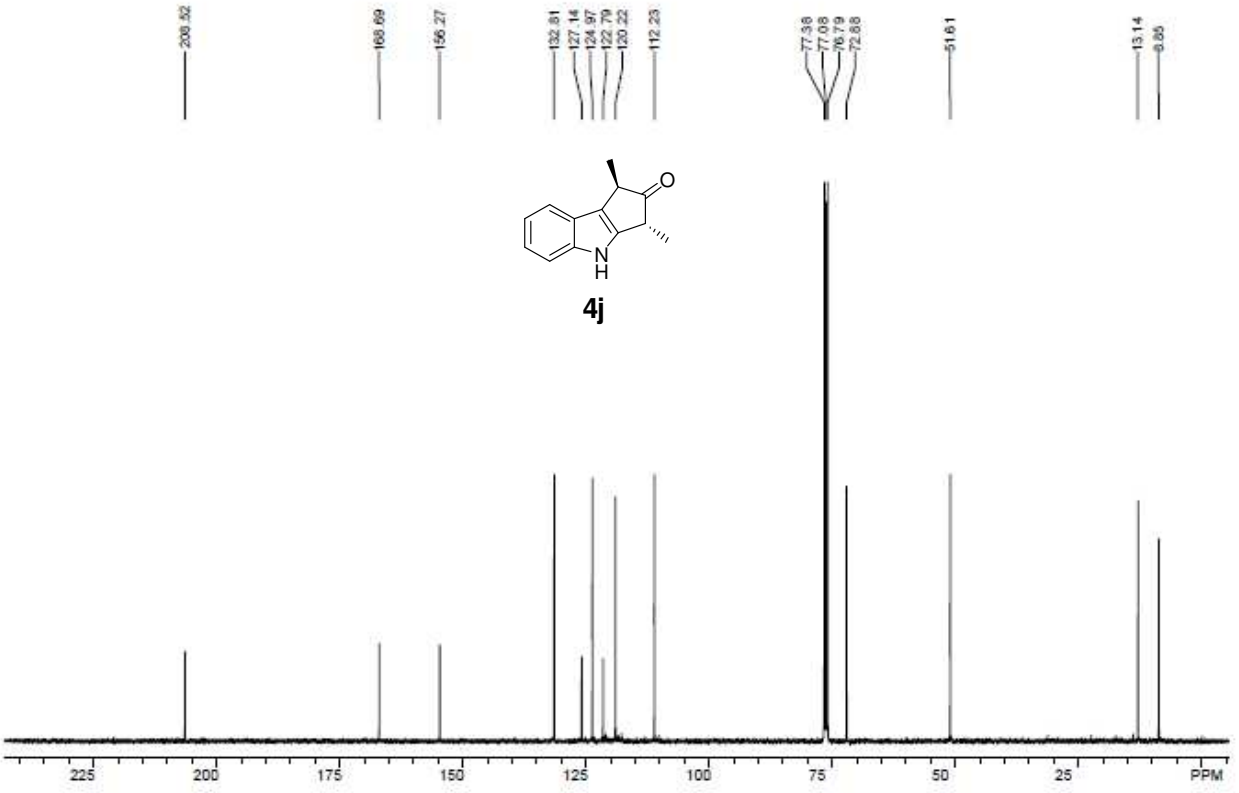
4i'

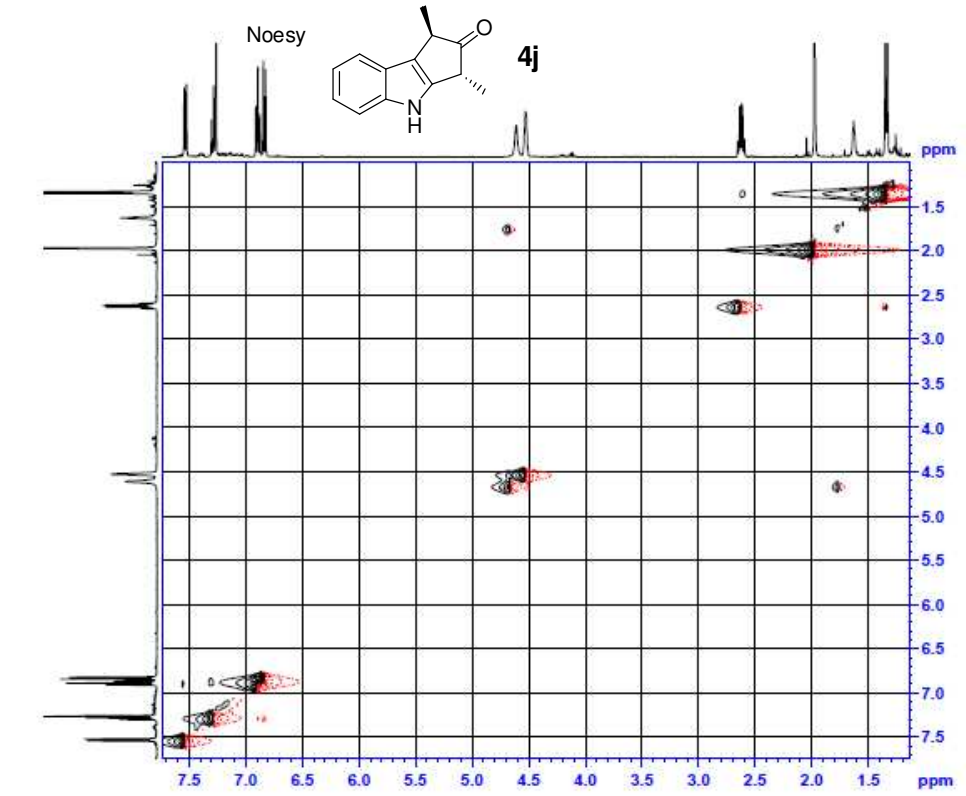


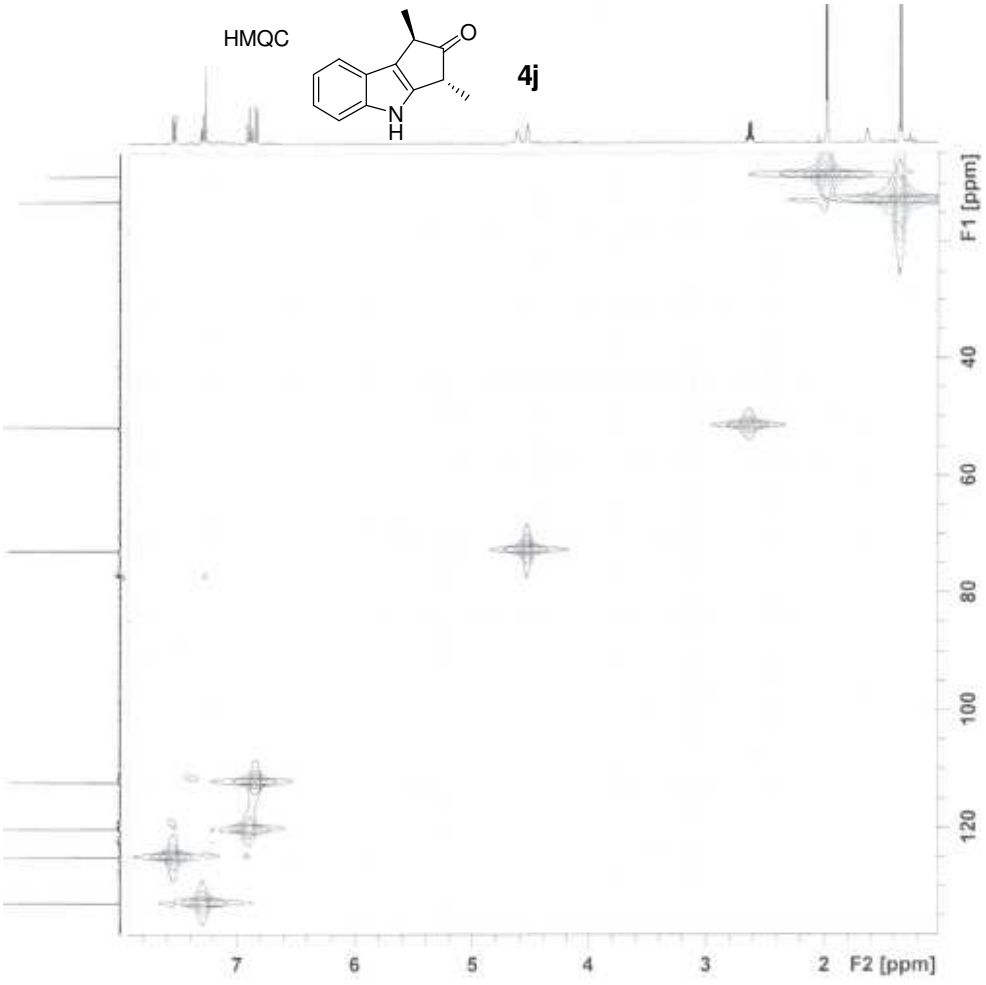
The more polar isomer (minor)

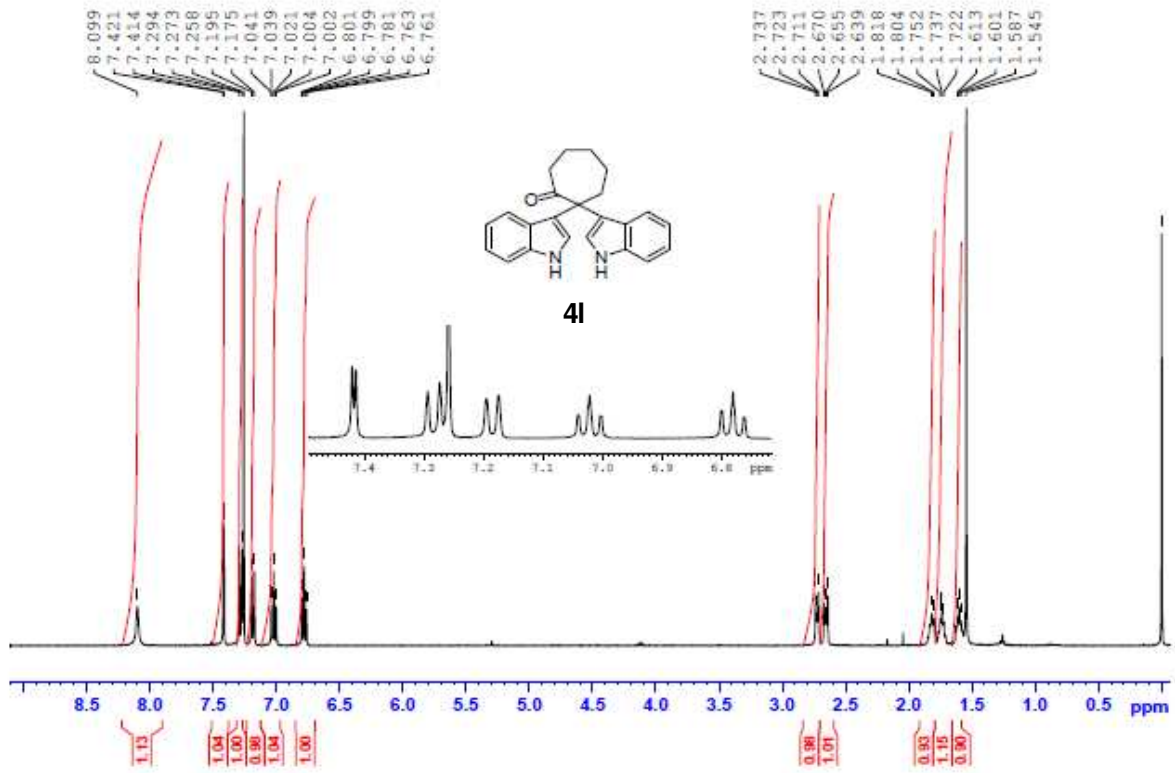
4i'

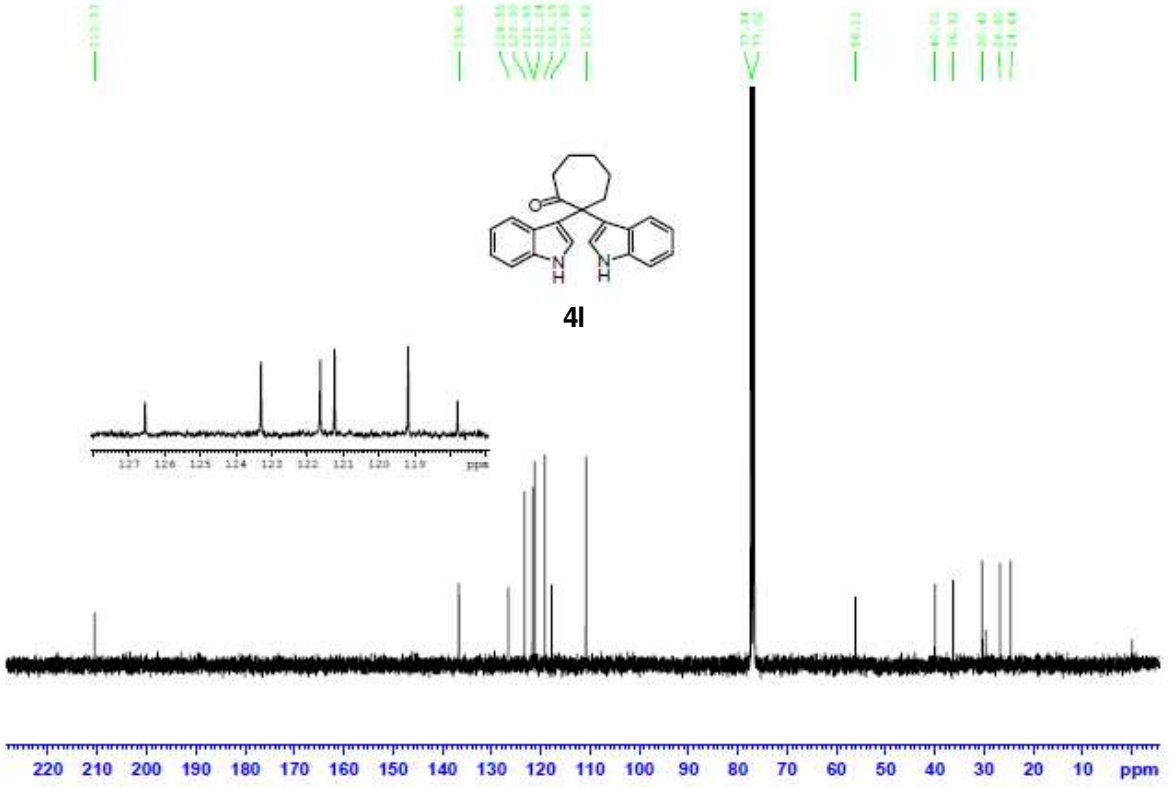

7.542
7.523
7.303
7.300
7.282
7.261
6.911
6.909
6.892
6.891
6.874
6.872
6.844
6.824
4.610
4.530
4.523
2.655
2.646
2.637
2.628
2.619
2.610
2.601
2.592
1.977
1.970
1.350
1.332
-0.000
O
N
H
4j
ppm
1.15
0.97
1.08
1.06
1.00
1.13
1.00
3.22
3.45

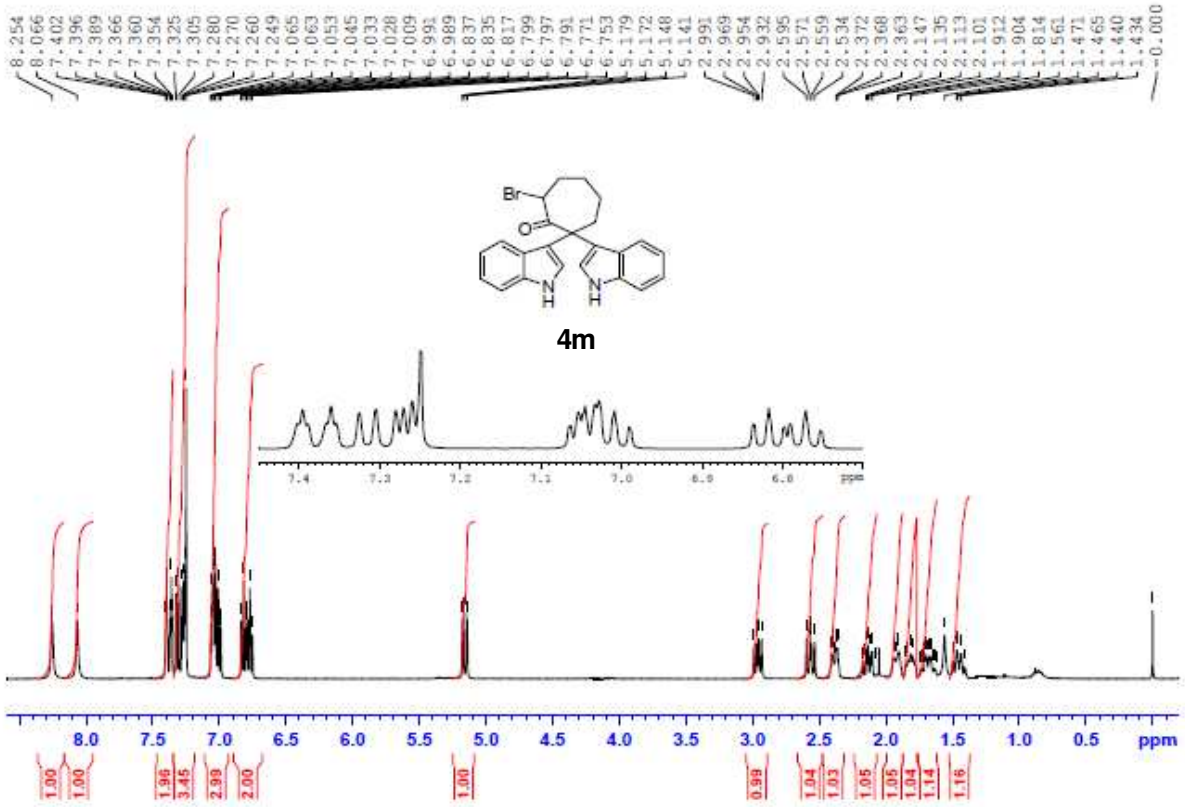

206.52
168.69
156.27
132.81
127.14
124.97
122.79
120.22
112.23
77.38
77.08
76.79
72.88
51.61
13.14
8.86
O
N
H
4j
PPM


Noesy
4j
O
N
H
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
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


HMQC
4j
O
N
H
F1 [ppm]
40
60
80
100
120
7 6 5 4 3 2 F2 [ppm]


8.099
7.421
7.414
7.294
7.273
7.258
7.195
7.175
7.041
7.039
7.021
7.004
7.002
6.801
6.799
6.781
6.763
6.761
2.737
2.723
2.711
2.670
2.655
2.639
1.818
1.804
1.752
1.737
1.722
1.613
1.601
1.587
1.545
4l
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 0.5 ppm
1.13
1.04
1.00
0.98
1.04
1.00
0.98
1.01
0.93
1.15
0.90


4l
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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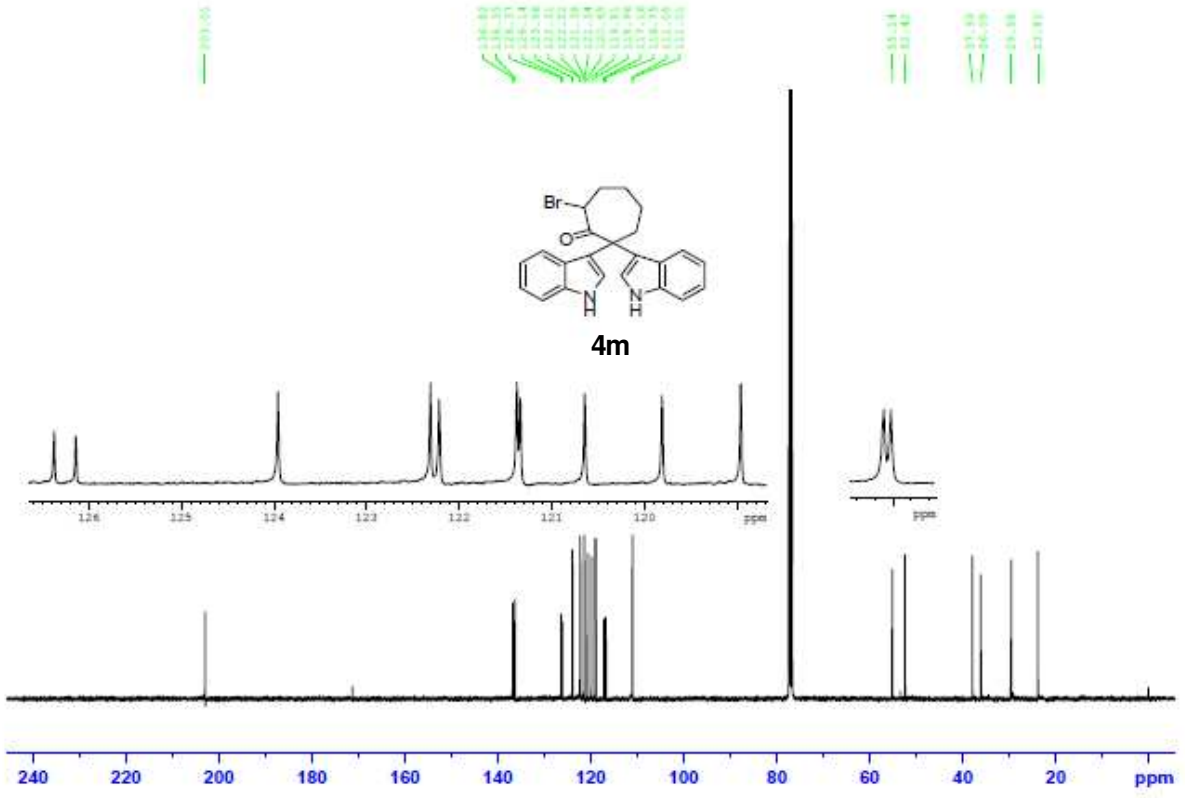
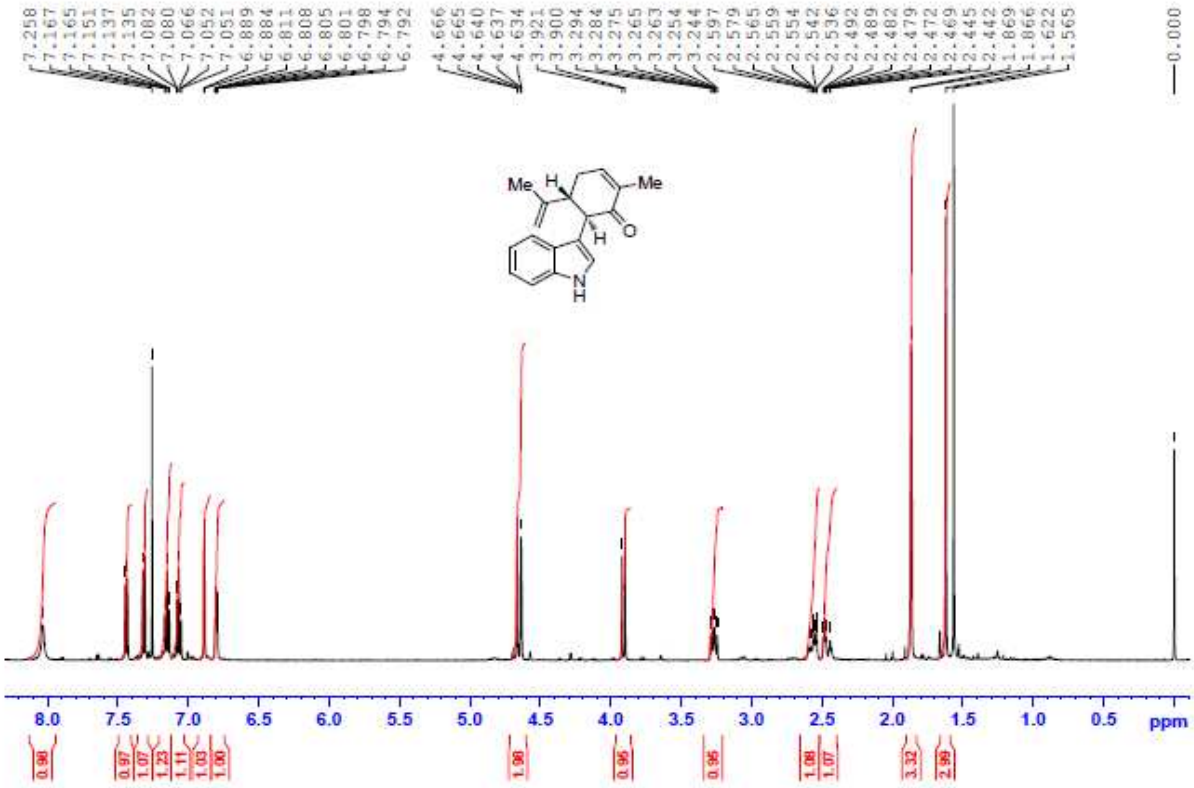
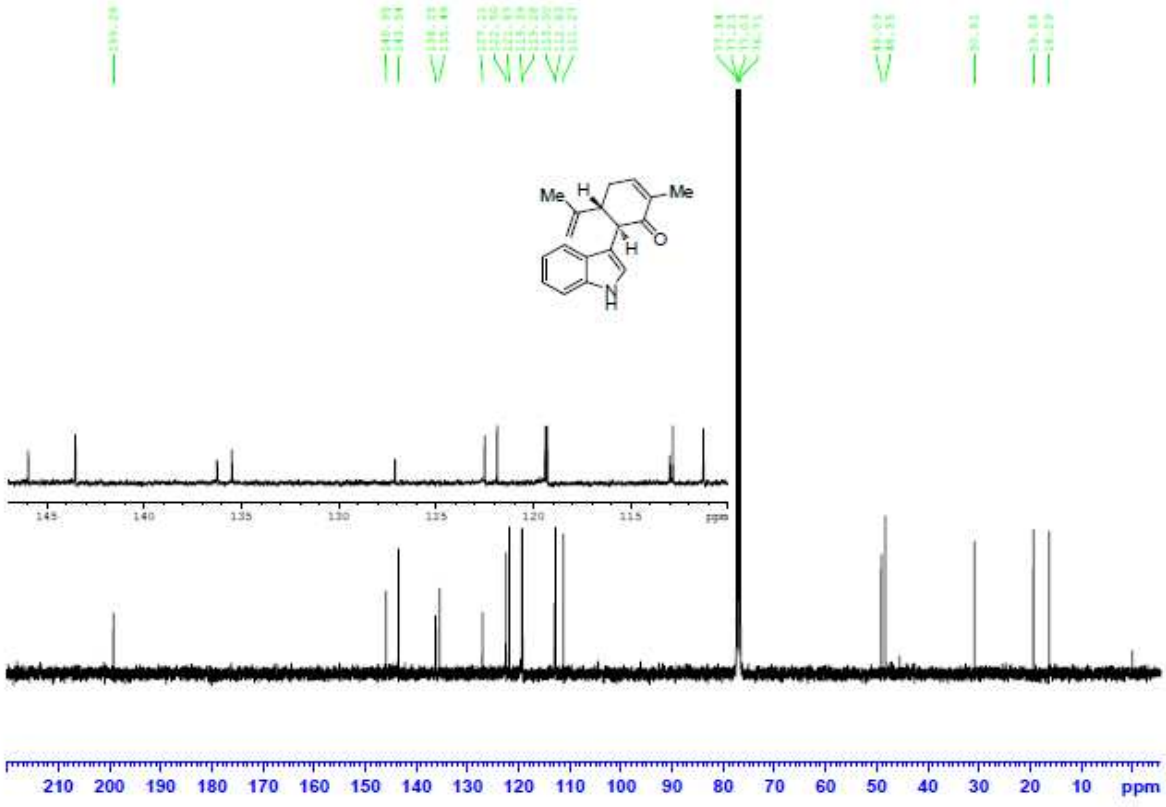
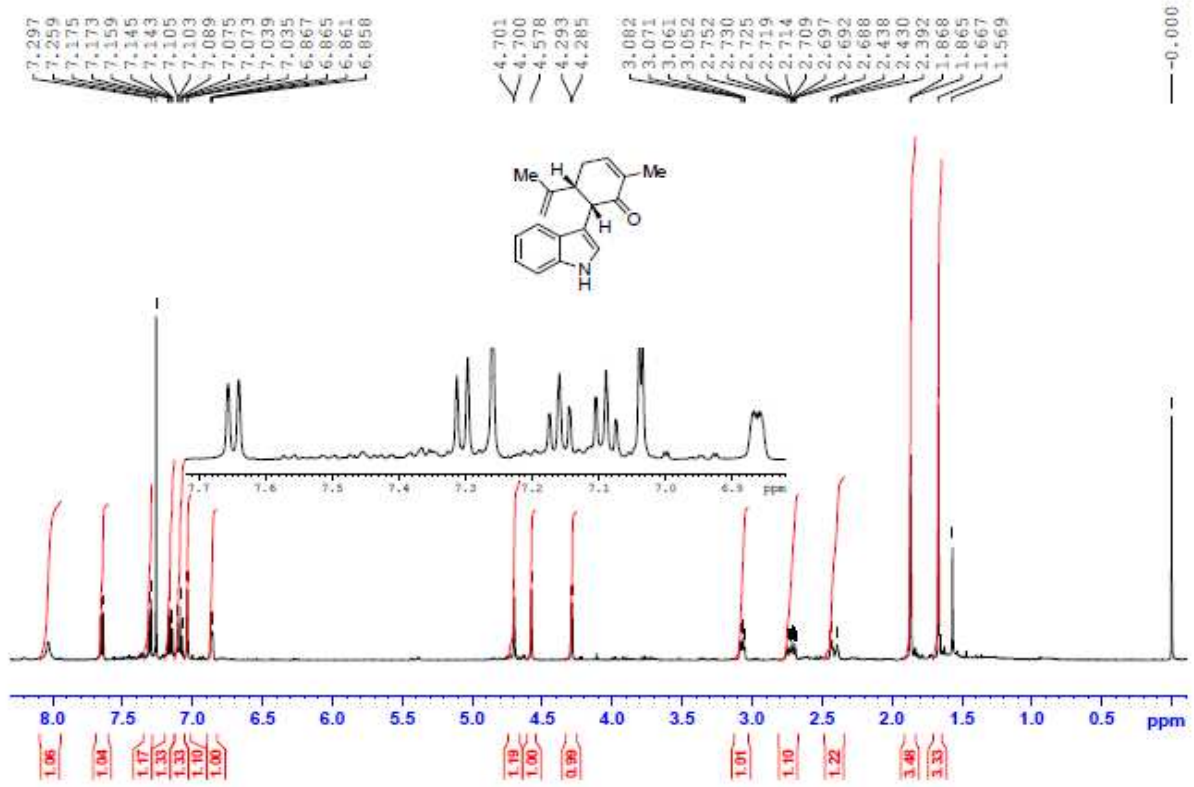
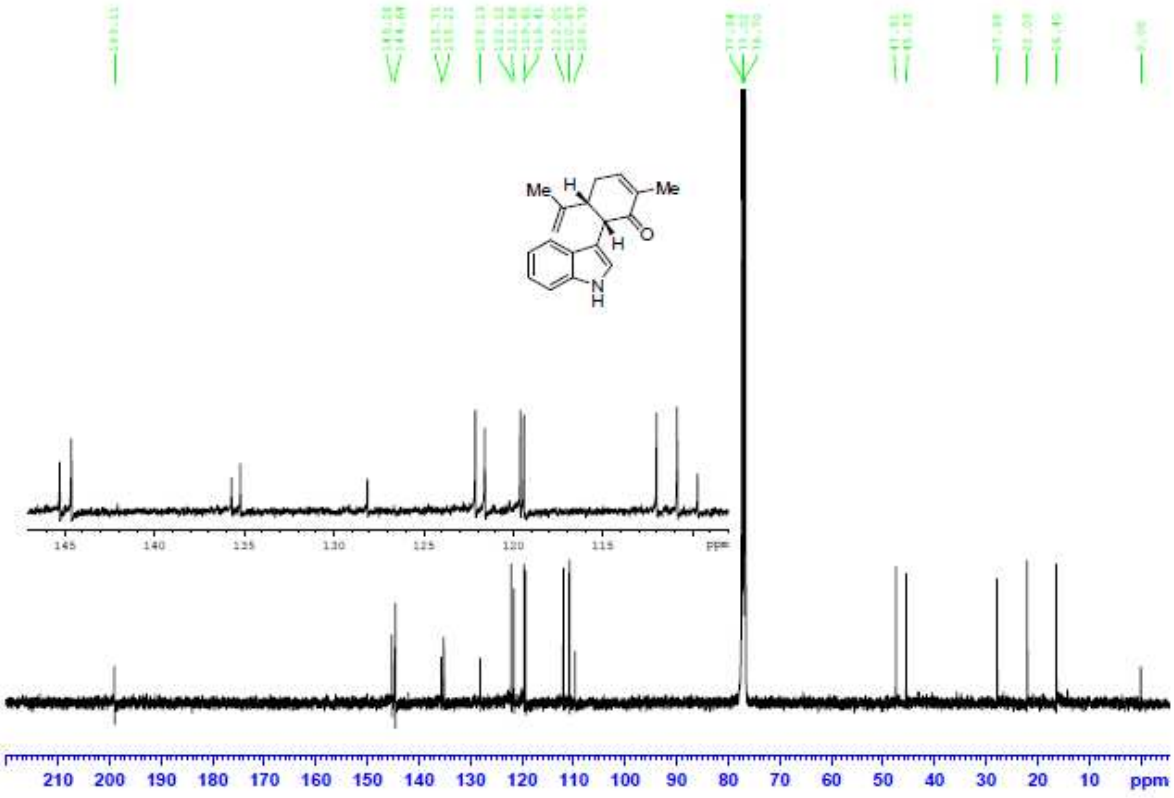
8.066
7.402
7.396
7.389
7.366
7.360
7.354
7.325
7.305
7.280
7.270
7.260
7.249
7.065
7.063
7.053
7.045
7.033
7.028
7.009
6.991
6.989
6.837
6.835
6.817
6.799
6.797
6.791
6.771
6.753
5.179
5.172
5.148
5.141
2.991
2.969
2.954
2.932
2.595
2.571
2.559
2.534
2.372
2.368
2.363
2.147
2.135
2.113
2.101
1.912
1.904
1.814
1.561
1.471
1.465
1.440
1.434
0.000
Br
O
N
H
4m
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
1.00
1.00
1.96
3.45
2.99
2.00
1.00
0.99
1.04
1.03
1.05
1.05
1.04
1.14
1.16


Br
O
N
H
4m
240
220
200
180
160
140
120
100
80
60
40
20
ppm


7.258
7.167
7.165
7.151
7.137
7.135
7.082
7.080
7.066
7.052
7.051
6.889
6.884
6.811
6.808
6.805
6.801
6.798
6.794
6.792
4.666
4.665
4.640
4.637
4.634
3.921
3.900
3.294
3.284
3.275
3.265
3.263
3.254
3.244
2.597
2.579
2.565
2.559
2.554
2.542
2.536
2.492
2.489
2.482
2.479
2.472
2.469
2.445
2.442
1.869
1.866
1.622
1.565
0.000
Me
H
Me
O
H
N
H
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
0.98
0.97
1.07
1.23
1.11
1.03
1.00
1.96
0.96
0.96
1.08
1.07
3.32
2.99


Me
H
Me
O
H
N
H
145
140
135
130
125
120
115
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.297
7.259
7.175
7.173
7.159
7.145
7.143
7.105
7.103
7.089
7.075
7.073
7.039
7.035
6.867
6.865
6.861
6.858
4.701
4.700
4.578
4.293
4.285
3.082
3.071
3.061
3.052
2.752
2.730
2.725
2.719
2.714
2.709
2.697
2.692
2.688
2.438
2.430
2.392
1.868
1.865
1.667
1.569
0.000
Me
H
Me
O
H
N
H
ppm
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
1.06
1.04
1.17
1.33
1.13
1.10
1.00
1.19
1.00
0.99
1.01
1.10
1.22
3.48
3.33


Me
H
Me
O
H
N
H
145
140
135
130
125
120
115
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm