Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Document

Rapid access to 3-acyl indoles using ethyl acetate/triflic acid couple as acylium donor and $Cu(OAc)_2$ catalyzed aerial oxidation of indole benzoins

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1. General Experimental

Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F_{254} pre-coated plates. Visualization was accomplished with UV lamp or I_2 stain. Silica gel 230-400 mesh size was used for column chromatography using the combination of ethyl acetate and petroleum ether as an eluent. Wherever appropriate, solvents and reagents were purified prior to use following the guidelines of Perrin and Armarego[1] and Vogel[2]. Methyl benzoate, pyrrole, furan, thiophene and indole were purchased from Spectrochem India Ltd. and were used as received without further purification. Triflic acid and $Cu(OAc)_2$ were purchased from Sigma-Aldrich. *N*-alkyl/aryl indoles were synthesized using different alkyl/aryl halide(s) following known literature methods.[3] All other commercial reagents were used as received. Compound names were determined using ChemBioDraw Ultra (v.12) software. NMR spectra were recorded on a Bruker 400 Ultra Shield in $CDCl_3$. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 400 MHz. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00). ^{1}H NMR splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), doublet of doublets (dd), triplets (t), quartets (q), heptates (hpt) or multiplets (m). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 100 MHz. High Resolution Mass Spectra (HRMS) were obtained on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS spectrometer using electron spray ionization (ESI) technique. Melting points were determined on a Büchi Melting Point M-560 hot stage apparatus and are reported as uncorrected.

2. Experimental Procedure

General procedure of 3-acylation/benzoylation

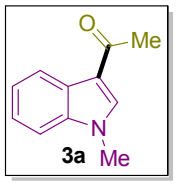
In a 25 ml double necked round bottomed flask fitted with a condenser and charged with a magnetic bar, 1.5 mmoles of heteroaryl substrate (**1**) was taken and was dissolved by adding 3.0 ml of ester solvent (**2a**/**2b**) in room temperature (27 °C) under argon atmosphere. At the same temperature, 0.6 mmoles of triflic acid (TfOH, 53 µl/91 mg) was added dropwise. The reaction was stirred at 80 °C for appropriate period of time (monitored by TLC). After completion of the reaction, the mixture was neutralized using saturated aq. $NaHCO_3$ solution and the crude product was extracted by adding 5ml x3 ethyl acetate. Then the solvent was evaporated at reduced pressure in a rotary evaporator and the crude mixture was subjected to column chromatography using 230-400 mesh sized silica using hexane-ethyl acetate (applying 10% to 40% of the later depending upon the product polarity) solvent system as eluent to obtain pure compounds (**3**/**4**).

General procedure of aerial oxidation of benzoins (5)

In a 25 ml double necked round bottomed flask fitted with a condenser and charged with a magnetic bar, 1.5 mmoles of indolyl benzoin (**5**)[4] was dissolved in 3 ml acetonitrile and $Cu(OAc)_2$

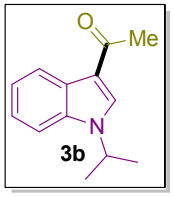
(0.3 mmol, 55 mg) was added at room temperature (27 °C). The reaction was stirred at 85 °C for appropriate period of time in open air (monitored by TLC). After completion of the reaction, 5 ml water was added and the crude product was extracted by adding 5ml x3 ethyl acetate. Then the solvent was evaporated at reduced pressure in a rotary evaporator and the crude mixture was subjected to column chromatography using 230-400 mesh sized silica using hexane-ethyl acetate (applying 10% to 40% of the later depending upon the product polarity) solvent system as eluent to obtain pure compounds (**4**).

3. Spectral Data of Compounds



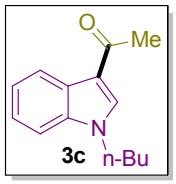
3a

1-(1-methyl-1*H*-indol-3-yl)ethanone (3a).[5] Following the general procedure outlined above, 197 mg 1-methyl-1*H*-indole (**1a**) was reacted with ethyl acetate (**2a**) to afford **3a** as brownish liquid in 71% yield (184 mg); R_f 0.27 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 3H), 3.82 (s, 3H), 7.29-7.32 (m, 3H), 7.67 (s, 1H), 8.37 (dd, *J* = 8.0, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2, 33.6, 109.7, 117.0, 122.6 (2), 123.4, 126.3, 135.9, 137.6, 193.1; HRMS (ESI) calcd for $C_{11}H_{12}NO$ $(M+H)^+$ 174.0919, found 174.0915.

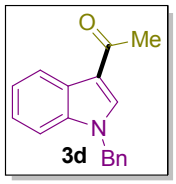


3b

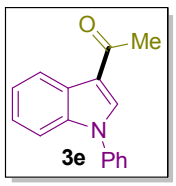
1-(1-isopropyl-1*H*-indol-3-yl)ethanone (3b).[6] Following the general procedure outlined above, 239 mg 1-isopropyl-1*H*-indole (**1b**) was reacted with ethyl acetate (**2a**) to afford **3b** as brownish white low melting solid in 77% yield (232 mg); R_f 0.28 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (d, *J* = 8.0 Hz, 6H), 2.42 (s, 3H), 4.56 (hpt, *J* = 8.0 Hz, 1H), 7.14-7.18 (m, 2H), 7.23-7.26 (m, 1H), 7.74 (s, 1H), 8.25-8.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 27.7, 47.8, 109.9, 117.2, 122.6, 122.8, 123.1, 126.5, 130.8, 136.5, 192.7; HRMS (ESI) calcd for $C_{13}H_{16}NO$ $(M+H)^+$ 202.1232, found 202.1241.



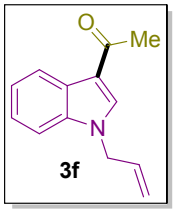
1-(1-butyl-1*H*-indol-3-yl)ethanone (3c).[7] Following the general procedure outlined above, 260 mg 1-butyl-1*H*-indole (**1c**) was reacted with ethyl acetate (**2a**) to afford **3c** as brownish liquid in 68% yield (220 mg); R_f 0.31 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, *J* = 8.0 Hz, 3H), 1.36 (t, *J* = 8.0 Hz, 2H), 1.86 (q, *J* = 8.0 Hz, 2H), 2.53 (s, 3H), 4.15 (t, *J* = 8.0 Hz, 2H), 7.27-7.38 (m, 3H), 7.74 (s, 1H), 8.37-8.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 20.2, 27.8, 32.0, 47.0, 110.0, 117.0, 122.6, 122.7, 123.3, 126.5, 134.9, 136.9, 193.2; HRMS (ESI) calcd for $C_{14}H_{18}NO$ $(M+H)^+$ 216.1388, found 216.1382.



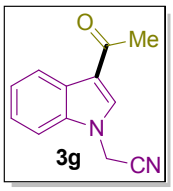
1-(1-benzyl-1*H*-indol-3-yl)ethanone (3d).[5] Following the general procedure outlined above, 311 mg 1-benzyl-1*H*-indole (**1d**) was reacted with ethyl acetate (**2a**) to afford **3d** as light brown low melting solid in 60% yield (224 mg); R_f 0.24 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 5.29 (s, 2H), 7.13 (d, *J* = 4.0 Hz, 2H), 7.23-7.31 (m, 6H), 7.72 (s, 1H), 8.40 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7, 50.7, 110.2, 117.5, 122.7 (2), 127.0, 128.3, 129.1, 135.2, 135.9, 137.1, 193.2; HRMS (ESI) calcd for $C_{17}H_{16}NO$ $(M+H)^+$ 250.1232, found 250.1233.



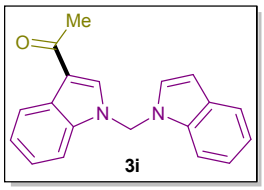
1-(1-phenyl-1*H*-indol-3-yl)ethanone (3e).[5] Following the general procedure outlined above, 290 mg 1-phenyl-1*H*-indole (**1e**) was reacted with ethyl acetate (**2a**) to afford **3e** as white low melting solid in 47% yield (166 mg); R_f 0.34 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 3H), 7.20-7.29 (m, 2H), 7.38-7.52 (m, 6H), 7.86 (s, 1H), 8.39 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.8, 110.9, 118.8, 122.9, 123.3, 124.1, 125.1, 126.7, 128.2, 130.0, 134.8, 137.2, 138.5, 193.5; HRMS (ESI) calcd for $C_{16}H_{14}NO$ $(M+H)^+$ 236.1075, found 236.1066.



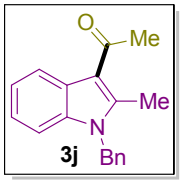
1-(1-allyl-1*H*-indol-3-yl)ethanone (3f).[5] Following the general procedure outlined above, 236 mg 1-allyl-1*H*-indole (**1f**) was reacted with ethyl acetate (**2a**) to afford **3f** as transparent brownish thick liquid in 52% yield (155 mg); R_f 0.30 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H), 4.76 (d, *J* = 4.0 Hz, 2H), 5.16 (d, *J* = 16.0 Hz, 1H), 5.29 (d, *J* = 12.0 Hz, 1H), 5.96-6.05 (m, 1H), 7.27-7.34 (m, 3H), 7.73 (s, 1H), 8.36-8.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.8, 49.5, 110.1, 117.4, 118.8, 122.8 (2), 123.5, 126.5, 132.2, 134.8, 137.0, 193.2; HRMS (ESI) calcd for $C_{13}H_{14}NO$ $(M+H)^+$ 200.1075, found 200.1073.



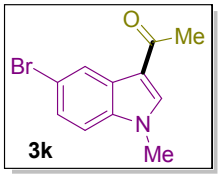
2-(3-acetyl-1*H*-indol-1-yl)acetonitrile (3g).[8] Following the general procedure outlined above, 234 mg 2-(1*H*-indol-1-yl)acetonitrile (**1g**) was reacted with ethyl acetate (**2a**) to afford **3g** as white crystalline solid in 67% yield (199 mg); Melting point: 178-180 °C; R_f 0.24 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.47 (s, 3H), 5.63 (s, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.41 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 27.5, 34.5, 110.6, 116.0, 117.2, 121.9, 123.0, 123.8, 125.8, 136.2, 137.0, 192.7; HRMS (ESI) calcd for $C_{12}H_{11}N_2O$ $(M+H)^+$ 199.0871, found 199.0861.



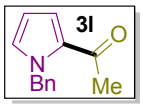
1-(1-((1*H*-indol-1-yl)methyl)-1*H*-indol-3-yl)ethanone (3i). Following the general procedure outlined above, 369 mg di(1*H*-indol-1-yl)methane (**1i**) was reacted with ethyl acetate (**2a**) to afford **3i** as white solid in 58% yield (251 mg); Melting point: 186-188 °C; R_f 0.30 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 6.28 (s, 2H), 6.58 (d, *J* = 2.0 Hz, 1H), 7.16-7.20 (m, 2H), 7.24-7.38 (m, 5H), 7.63-7.64 (m, 2H), 8.35-8.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 56.7, 104.3, 109.1, 109.6, 118.4, 120.9, 121.7, 123.0 (2), 123.2, 124.2, 126.5, 127.2, 129.2, 133.3, 135.8, 136.4, 193.5; HRMS (ESI) calcd for $C_{19}H_{17}N_2O$ $(M+H)^+$ 289.1341, found 289.1335.



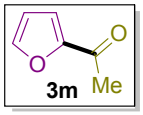
1-(1-benzyl-2-methyl-1*H*-indol-3-yl)ethanone (3j).[9] Following the general procedure outlined above, 332 mg 1-benzyl-2-methyl-1*H*-indole (**1j**) was reacted with ethyl acetate (**2a**) to afford **3j** as yellowish white solid in 70% yield (277 mg); Melting point: 105-107 °C; R_f 0.35 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 6H), 5.11 (s, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 7.02-7.14 (m, 6H), 7.89 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6, 31.7, 46.2, 109.9, 114.6, 120.8, 122.1, 122.2, 125.9, 126.4, 127.7, 128.9, 136.1, 136.4, 144.8, 194.6; HRMS (ESI) calcd for $C_{18}H_{18}NO$ $(M+H)^+$ 264.1388, found 264.1378.



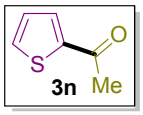
1-(5-bromo-1-methyl-1*H*-indol-3-yl)ethanone (3k).[10] Following the general procedure outlined above, 315 mg 5-bromo-1-methyl-1*H*-indole (**1k**) was reacted with ethyl acetate (**2a**) to afford **3k** as white crystalline solid in 72% yield (272 mg); Melting point: 145-147 °C; R_f 0.30 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.77 (s, 3H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.59 (s, 1H), 8.47 (d, *J* = 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5, 33.7, 111.1, 116.3, 116.4, 125.1, 126.3, 127.7, 136.2, 136.5, 192.6; HRMS (ESI) calcd for $C_{11}H_{11}BrNO$ $(M+H)^+$ 252.0024, found 252.0016.



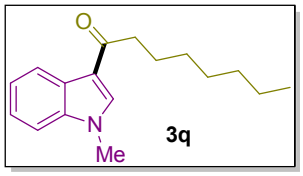
1-(1-benzyl-1*H*-pyrrol-2-yl)ethanone (3l).[11] Following a modified general procedure outlined above (0.6 equivalent TfOH), 236 mg 1-benzyl-1*H*-pyrrole (**1l**) was reacted with ethyl acetate (**2a**) to afford **3l** as light brownish liquid in 44% yield (132 mg); R_f 0.33 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 4.95 (s, 2H), 6.53 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.20-7.26 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.1, 53.9, 109.7, 122.8, 126.2, 127.3, 128.2, 129.0, 136.6, 193.5; HRMS (ESI) calcd for $C_{13}H_{14}NO$ $(M+H)^+$ 200.1075, found 200.1070.



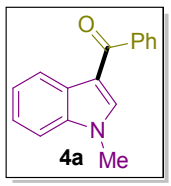
1-(furan-2-yl)ethanone (3m).[12] Following a modified general procedure outlined above (0.6 equivalent TfOH), 102 mg furan (**1m**) was reacted with ethyl acetate (**2a**) to afford **3m** as brownish liquid in 39% yield (64 mg); R_f 0.31 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 6.47 (d, *J* = 4.0 Hz, 1H), 7.11 (d, *J* = 4.0 Hz, 1H), 7.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8, 112.1, 116.8, 146.1, 152.8, 186.2; HRMS (ESI) calcd for $C_6H_7O_2$ $(M+H)^+$ 111.0446, found 111.0442.



1-(thiophen-2-yl)ethanone (3n).[13] Following a modified general procedure outlined above (0.6 equivalent TfOH), 126 mg thiophene (**1n**) was reacted with ethyl acetate (**2a**) to afford **3n** as colorless liquid in 41% yield (78 mg); R_f 0.33 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H), 7.09 (t, *J* = 4.0 Hz, 1H), 7.61 (d, *J* = 4.0 Hz, 1H), 7.67 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.7, 128.0, 132.3, 133.6, 144.5, 190.1; HRMS (ESI) calcd for C_6H_7OS $(M+H)^+$ 127.0218, found 127.0211.



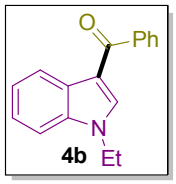
1-(1-methyl-1*H*-indol-3-yl)octan-1-one (3q). Following the general procedure outlined above, 197 mg 1-methyl-1*H*-indole (**1a**) was reacted with methyl octanoate (**2b**) to afford **3q** as colorless thick liquid in 50% yield (193 mg); R_f 0.38 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76-0.78 (m, 3H), 1.17-1.27 (m, 8H), 1.61-1.66 (m, 2H), 2.65 (t, *J* = 8.0 Hz, 2H), 3.59 (s, 3H), 7.12-7.16 (m, 3H), 7.49 (s, 1H), 8.28-8.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 25.3, 29.2, 29.5, 31.8, 33.3, 39.8, 109.6, 116.4, 122.3, 122.5, 123.1, 126.3, 135.3, 137.4, 196.0; HRMS (ESI) calcd for $C_{17}H_{24}NO$ $(M+H)^+$ 258.1858, found 258.1849.



(1-methyl-1*H*-indol-3-yl)(phenyl)methanone (4a).[14] Following the general procedure outlined above, 197 mg 1-methyl-1*H*-indole (**1a**) was reacted with methyl benzoate (**2c**) to afford **4a** as light brown low melting solid in 21% yield (74 mg); R_f 0.24 (EtOAc : petroleum ether, 1 : 3); ^{1}H

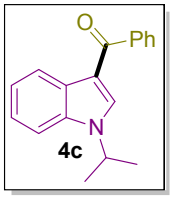
NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 7.35-7.37 (m, 3H), 747-7.57 (m, 4H), 7.82 (d, *J* = 8.0 Hz, 2H), 8.43 (t, *J* = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.6, 109.7, 115.7, 122.8, 123.7, 127.3, 128.4, 128.8, 131.2, 137.6, 138.1, 140.0, 191.0; HRMS (ESI) calcd for $C_{16}H_{14}NO$ $(M+H)^+$ 236.1075, found 236.1071.

The $Cu(OAc)_2$ catalysed aerial oxidation of 2-(1-methyl-1*H*-indol-3-yl)-1,2-diphenylethanone (**5a**, 488 mg) gave the above product in 67% yield (236 mg).



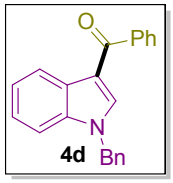
(1-ethyl-1*H*-indol-3-yl)(phenyl)methanone (4b).[15] Following the general procedure outlined above, 218 mg 1-ethyl-1*H*-indole (**1o**) was reacted with methyl benzoate (**2c**) to afford **4b** as brownish white low melting solid in 25% yield (93 mg); R_f 0.27 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (t, *J* = 8.0 Hz, 3H), 4.09 (q, *J* = 8.0 Hz, 2H), 7.24-7.31 (m, 3H), 7.37-7.45 (m, 3H), 7.49 (s, 1H), 7.74 (d, *J* = 4.0 Hz, 2H), 8.36-8.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 41.8, 109.8, 115.7, 122.7, 122.8, 123.6, 127.5, 128.3, 128.7, 131.1, 136.4, 136.7, 141.0, 190.9; HRMS (ESI) calcd for $C_{17}H_{16}NO$ $(M+H)^+$ 250.1232, found 250.1240.

The $Cu(OAc)_2$ catalysed aerial oxidation of 2-(1-ethyl-1*H*-indol-3-yl)-1,2-diphenylethanone (**5b**, 509 mg) gave the above product in 61% yield (228 mg).



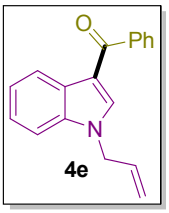
(1-isopropyl-1*H*-indol-3-yl)(phenyl)methanone (4c). Following the general procedure outlined above, 239 mg 1-isopropyl-1*H*-indole (**1b**) was reacted with methyl benzoate (**2c**) to afford **4c** as white low melting solid in 29% yield (115 mg); R_f 0.29 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56 (d, *J* = 8.0 Hz, 6H), 4.71 (hpt, *J* = 8.0 Hz, 1H), 7.34-7.36 (m, 2H), 7.44-7.58 (m, 4H), 7.70 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 8.47-8.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6, 48.0, 110.1, 115.8, 122.7, 122.8, 123.4, 127.4, 128.3, 128.7, 131.1, 133.2, 136.6, 141.0, 190.9; HRMS (ESI) calcd for $C_{18}H_{18}NO$ $(M+H)^+$ 264.1388, found 264.1390.

The $Cu(OAc)_2$ catalysed aerial oxidation of 2-(1-isopropyl-1*H*-indol-3-yl)-1,2-diphenylethanone (**5c**, 530 mg) gave the above product in 60% yield (238 mg).



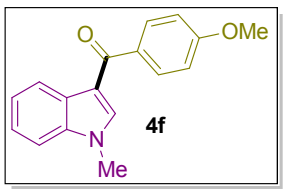
(1-benzyl-1*H*-indol-3-yl)(phenyl)methanone (4d).[16] Following the general procedure outlined above, 311 mg 1-benzyl-1*H*-indole (**1d**) was reacted with methyl benzoate (**2c**) to afford **4d** as white low melting solid in 16% yield (75 mg); R_f 0.27 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.28-7.36 (m, 6H), 7.46-7.57 (m, 3H), 7.63 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 8.47 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.9, 110.4, 116.2, 122.9, 123.9, 126.9, 127.5, 128.3, 128.4, 128.9, 129.1, 131.3, 135.9, 137.2, 137.3, 140.9, 191.0; HRMS (ESI) calcd for $C_{22}H_{18}NO$ $(M+H)^+$ 312.1388, found 312.1378.

The $Cu(OAc)_2$ catalysed aerial oxidation of 2-(1-benzyl-1*H*-indol-3-yl)-1,2-diphenylethanone (**5d**, 602 mg) gave the above product in 55% yield (257 mg).



(1-allyl-1*H*-indol-3-yl)(phenyl)methanone (4e).[17] Following the general procedure outlined above, 236 mg 1-allyl-1*H*-indole (**1g**) was reacted with methyl benzoate (**2c**) to afford **4e** as light brown low melting solid in 31% yield (122 mg); R_f 0.28 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75 (d, *J* = 4.0 Hz, 2H), 5.15 (d, *J* = 16.0 Hz, 1H), 5.27 (d, *J* = 8.0 Hz, 1H), 5.99 (oct, *J* = 4.0 Hz, 1H), 7.34-7.36 (m, 3H), 7.47-7.57 (m, 4H), 7.83 (d, *J* = 8.0 Hz, 2H), 8.47-8.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.4, 110.2, 115.9, 118.6, 122.8 (2), 123.7, 127.4, 128.4, 128.7, 131.2, 132.1, 137.0 (2), 140.9, 191.0; HRMS (ESI) calcd for $C_{18}H_{16}NO$ $(M+H)^+$ 262.1232, found 262.1241.

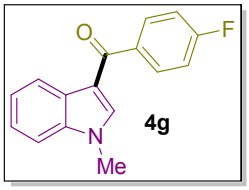
The $Cu(OAc)_2$ catalysed aerial oxidation of 2-(1-allyl-1*H*-indol-3-yl)-1,2-diphenylethanone (**5e**, 527 mg) gave the above product in 52% yield (205 mg).



(4-methoxyphenyl)(1-methyl-1*H*-indol-3-yl)methanone (4f).[18] Following the general procedure outlined above, 197 mg 1-methyl-1*H*-indole (**1a**) was reacted with methyl 4-methoxybenzoate

(**2d**) to afford **4f** as bright white crystalline solid in 28% yield (111 mg); M.P. 131-133 °C; R_f 0.30 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.87 (s, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 7.31-7.33 (m, 3H), 7.51 (s, 1H), 7.82 (d, *J* = 8.0, 8.0 Hz, 2H), 8.37-8.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.5, 55.5, 109.7, 113.6, 115.7, 122.5, 122.7, 123.5, 127.4, 130.9, 133.5, 137.2, 137.5, 162.3, 189.8; HRMS (ESI) calcd for $C_{17}H_{16}NO_2$ $(M+H)^+$ 266.1181, found 266.1175.

The $Cu(OAc)_2$ catalysed aerial oxidation of 1,2-bis(4-methoxyphenyl)-2-(1-methyl-1*H*-indol-3-yl)ethanone (**5f**, 578 mg) gave the above product in 72% yield (287 mg).



(4-fluorophenyl)(1-methyl-1*H*-indol-3-yl)methanone (4g).[19] Following the general procedure outlined above, 197 mg 1-methyl-1*H*-indole (**1a**) was reacted with methyl 4-fluorobenzoate (**2e**) to afford **4g** as grey crystalline solid in 27% yield (103 mg); M.P. 135-137 °C; R_f 0.35 (EtOAc : petroleum ether, 1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 4.0 Hz, 3H), 7.45 (s, 1H), 7.80 (dd, *J* = 8.0, 8.0 Hz, 2H), 8.40-8.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.5, 109.8, 115.2, 115.3, 115.4, 122.5, 122.7, 123.7, 127.1, 130.9, 131.0, 137.0(2), 137.5, 137.6, 163.3, 165.8, 189.2; HRMS (ESI) calcd for $C_{16}H_{13}FNO$ $(M+H)^+$ 254.0981, found 254.0977.

The $Cu(OAc)_2$ catalysed aerial oxidation of 1,2-bis(4-fluorophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethanone (**5g**, 542 mg) gave the above product in 68% yield (258 mg).

4. References

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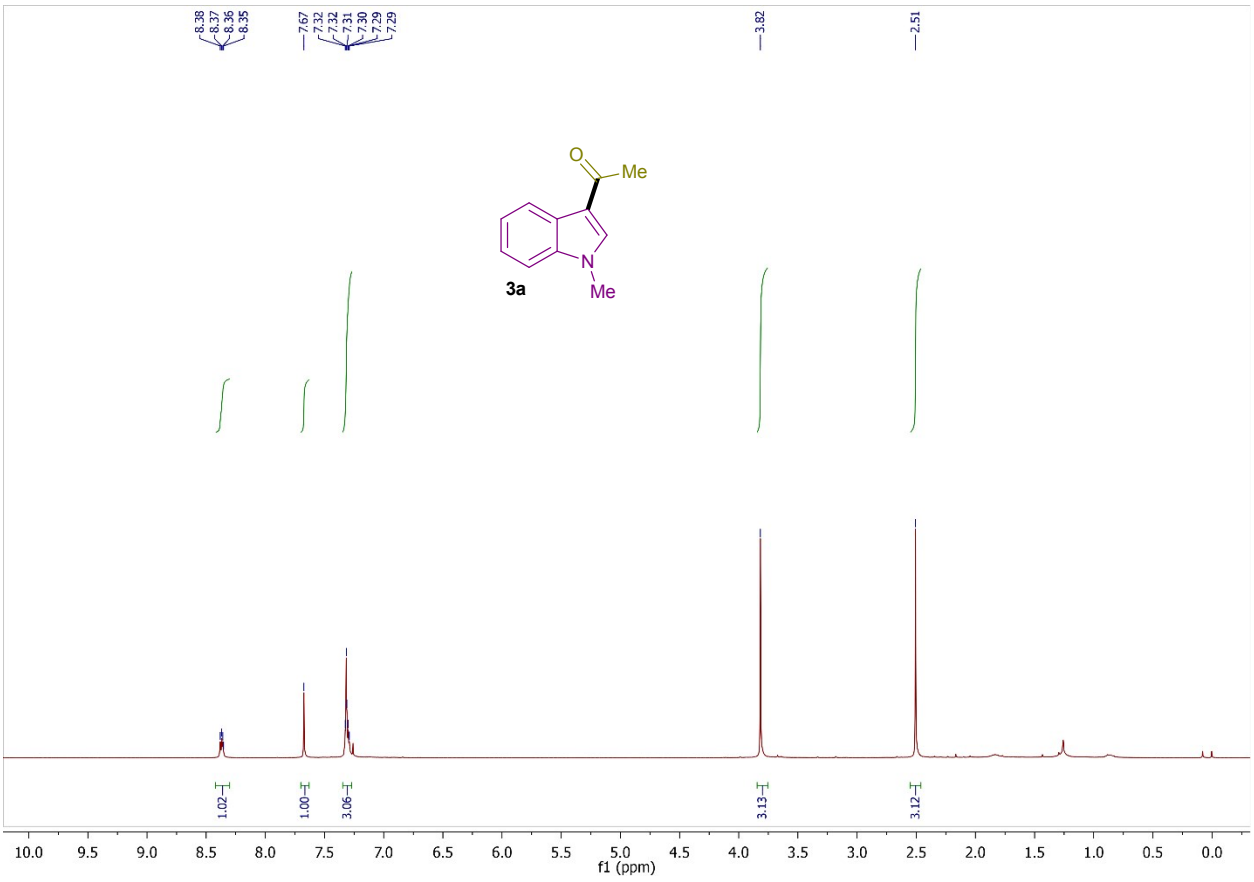
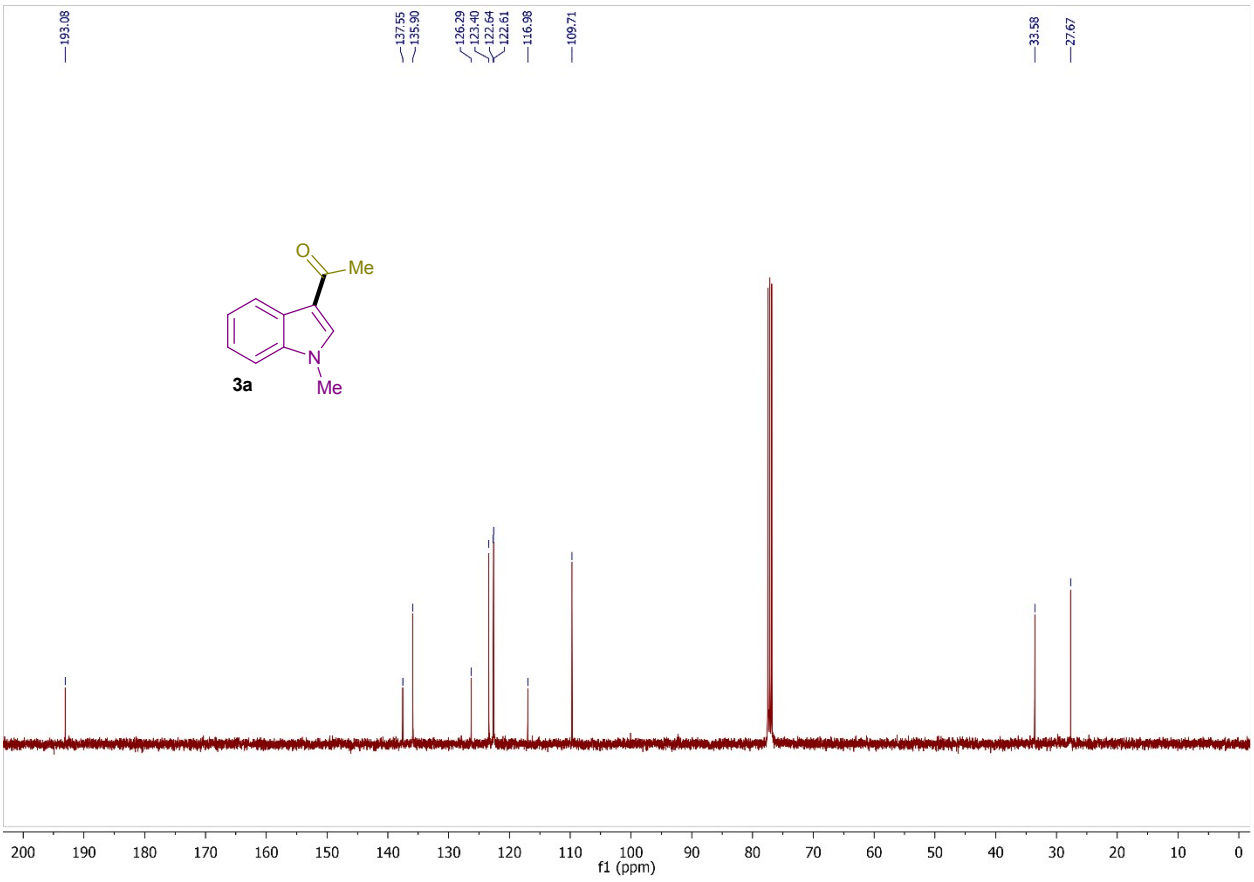
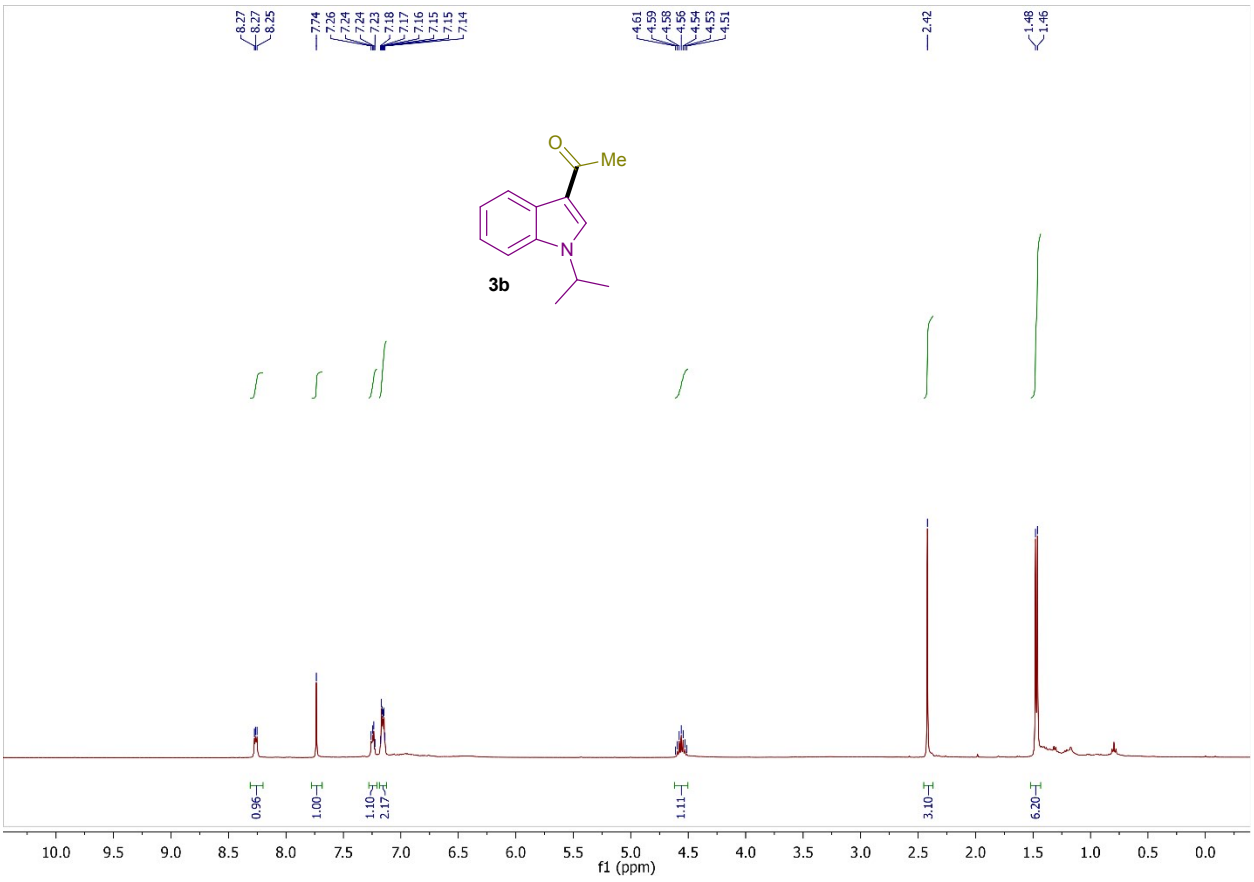
5. Selected NMR Spectra



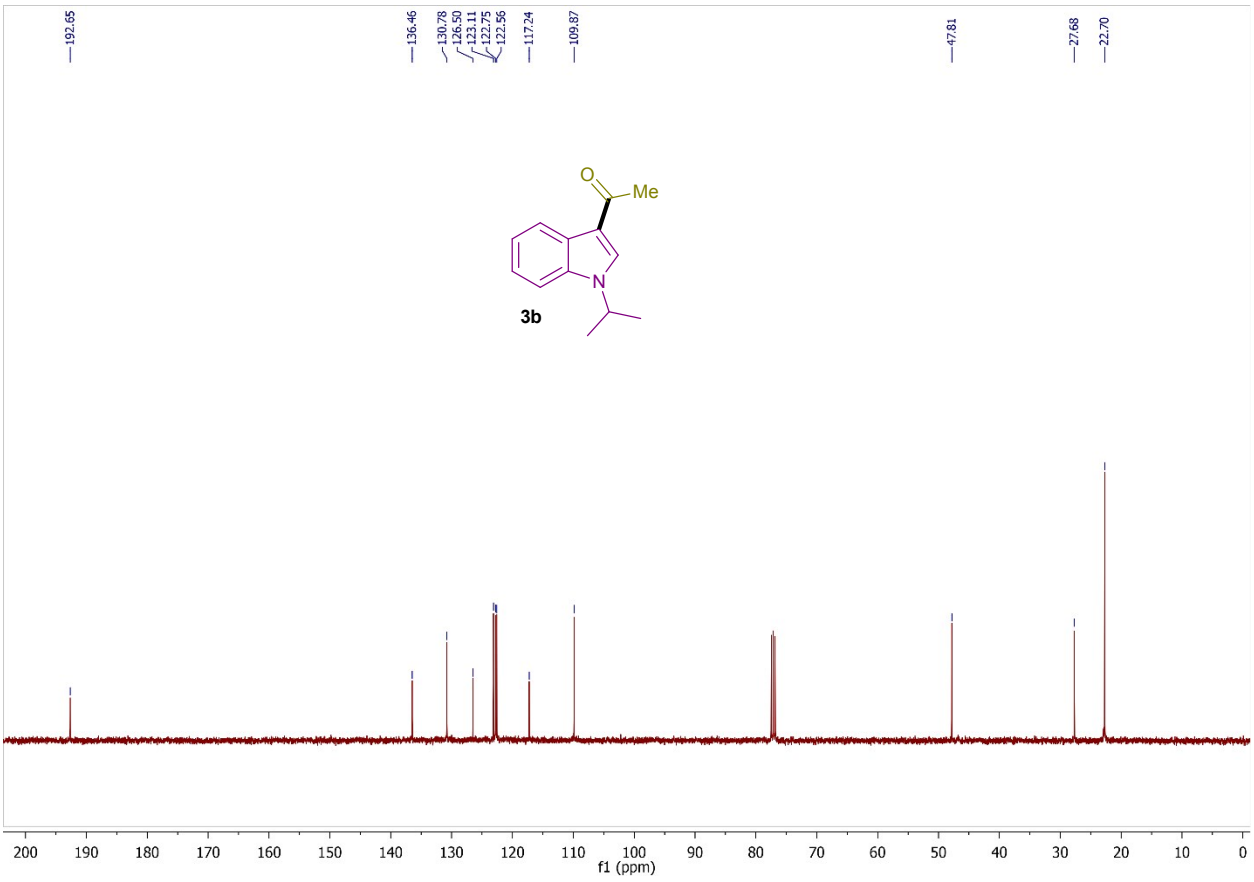
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **3a**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**



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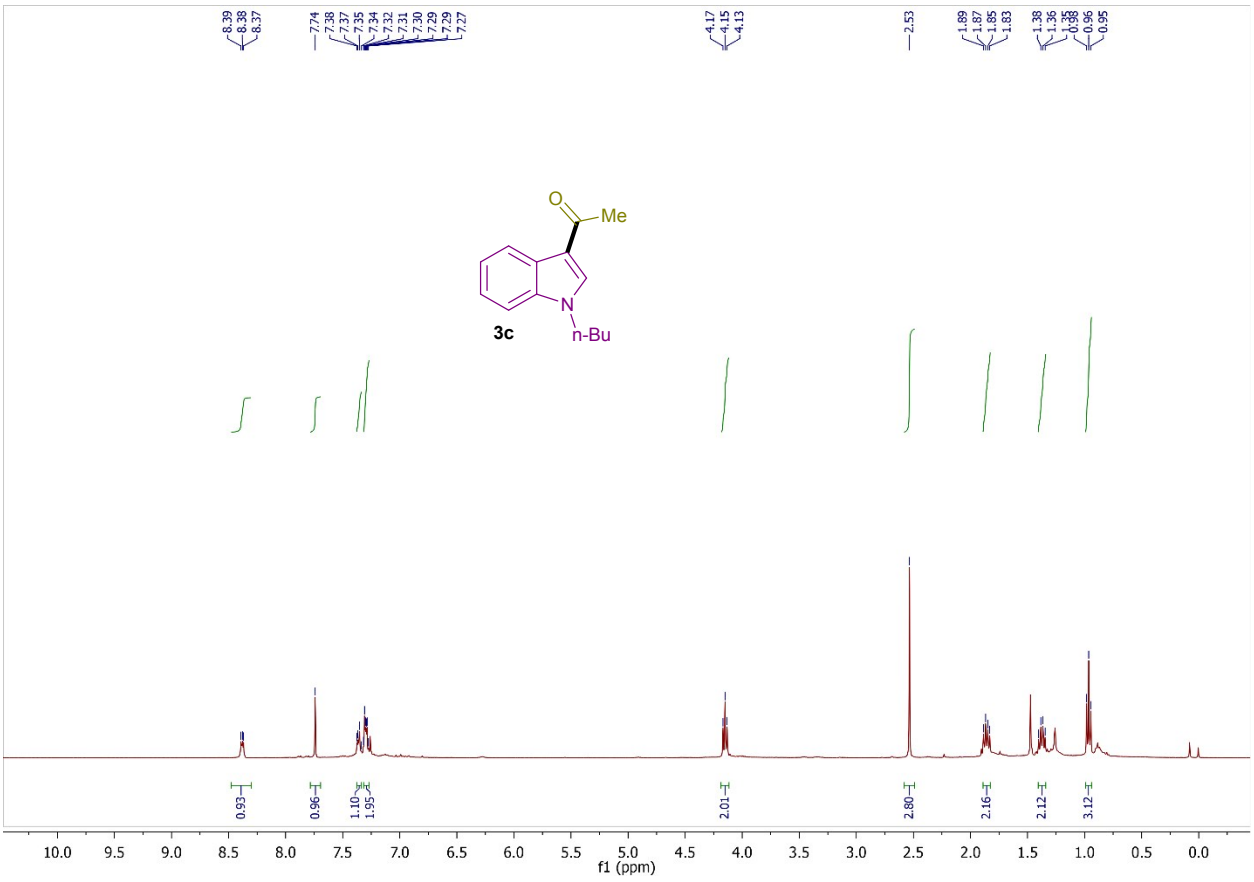
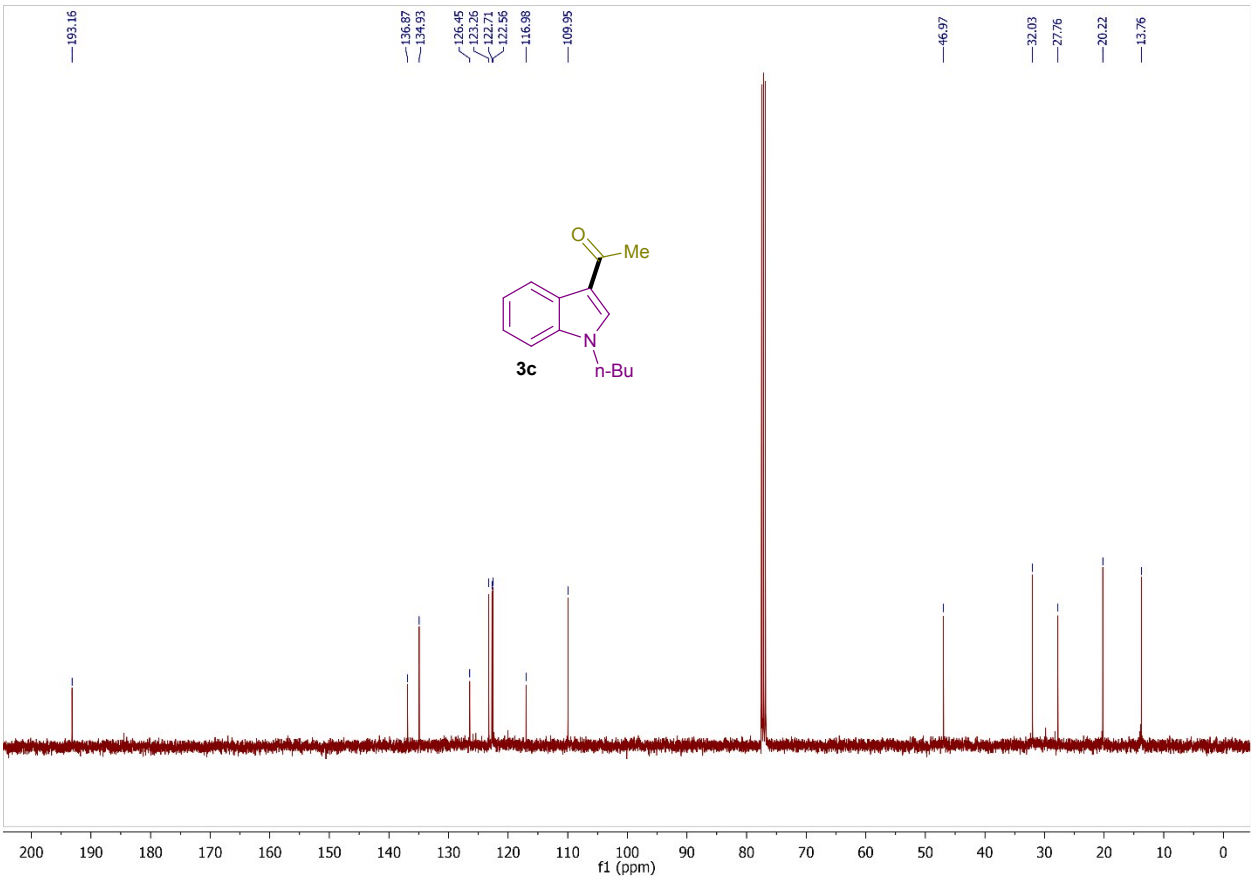


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**



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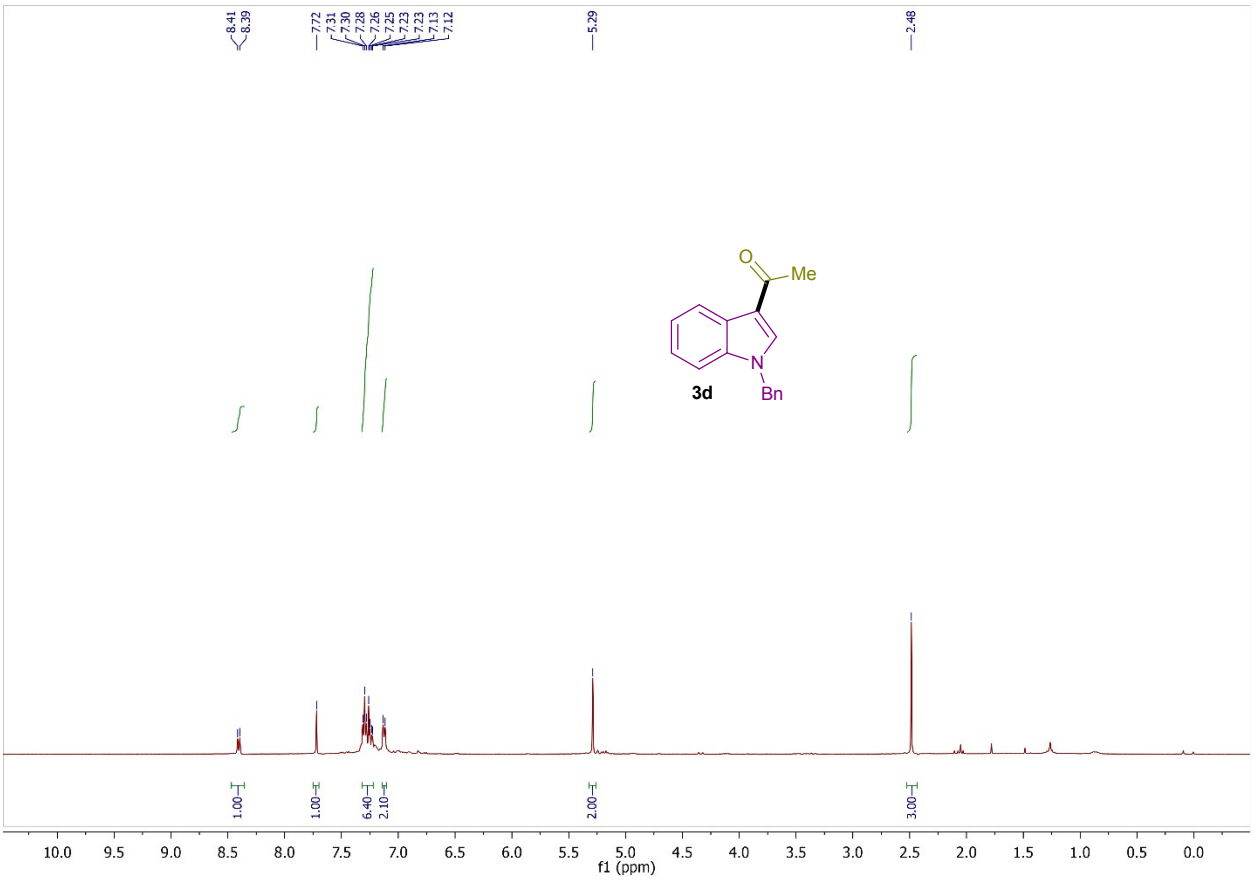
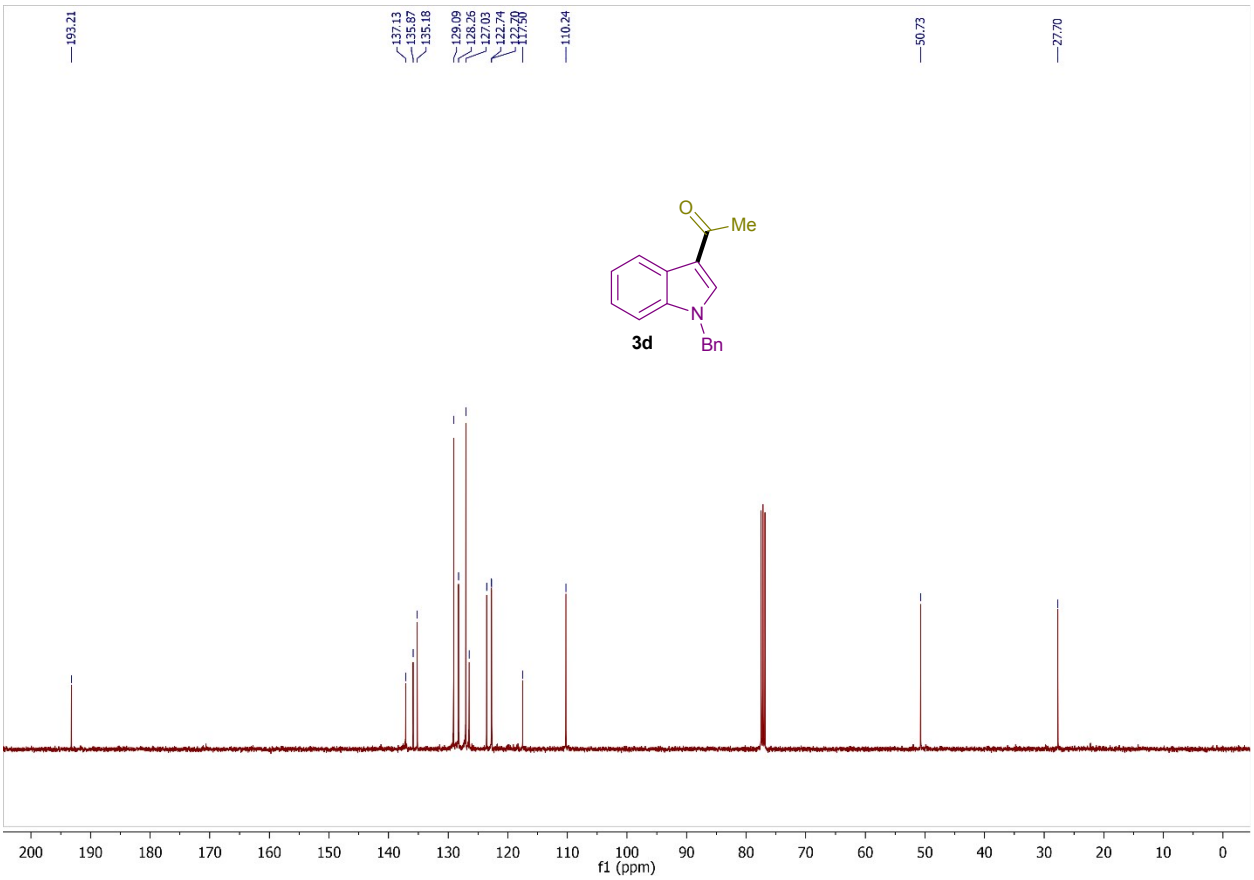


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**



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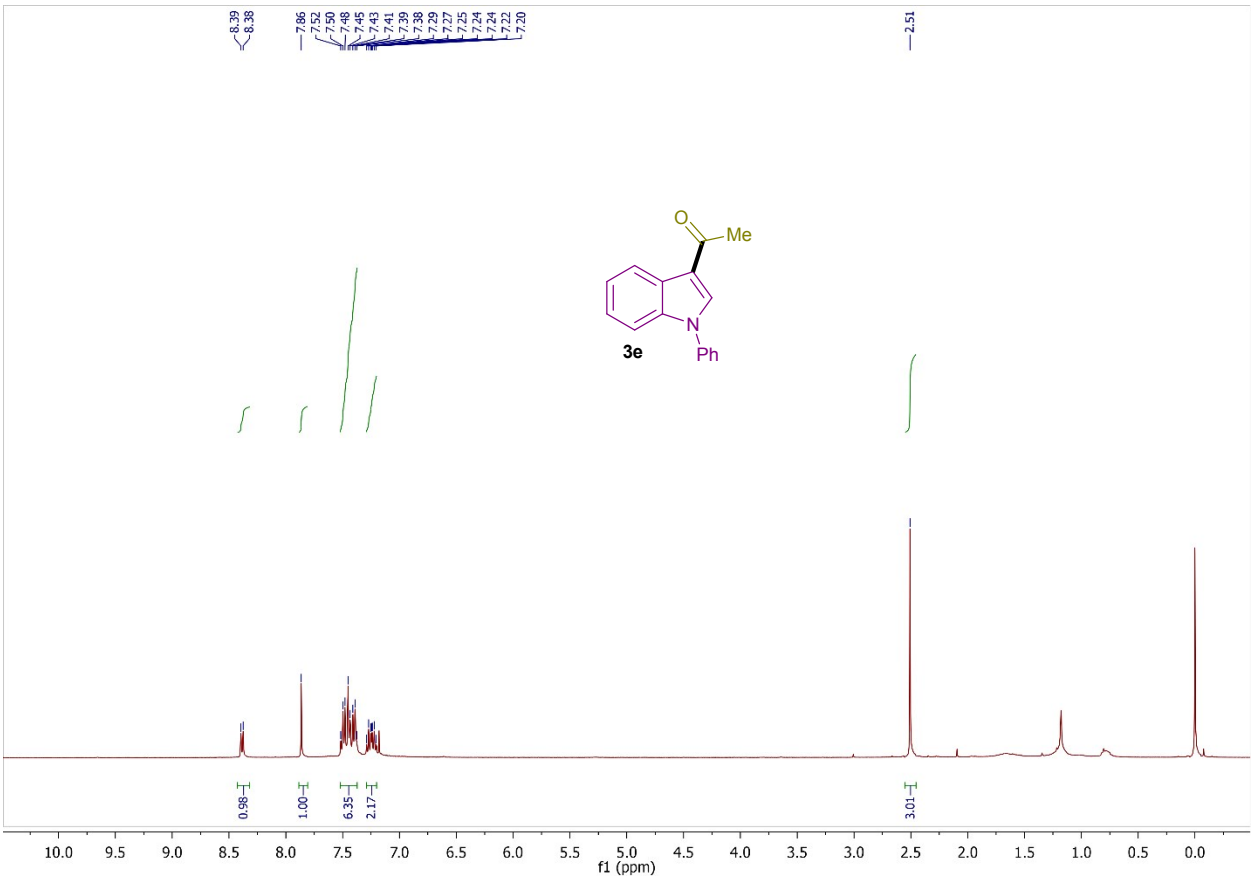

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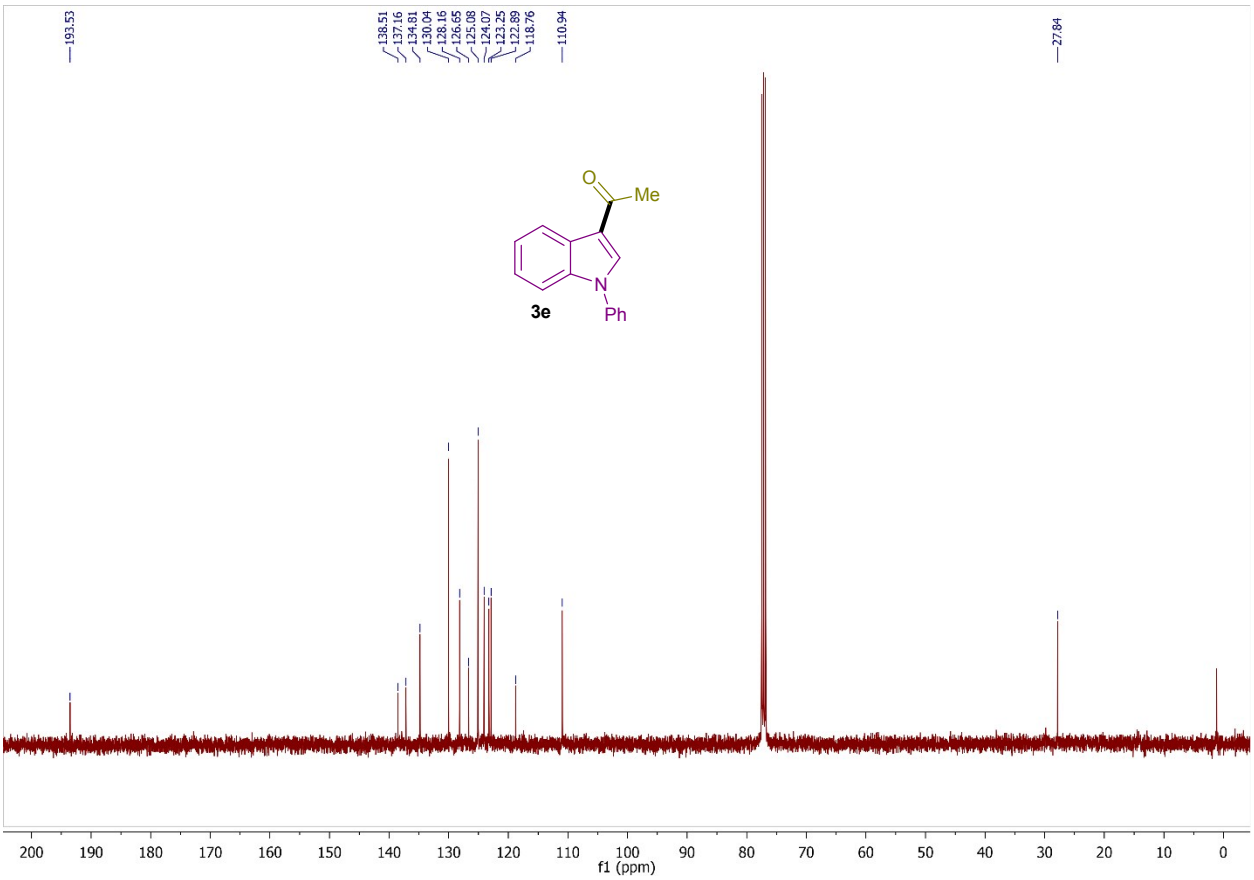

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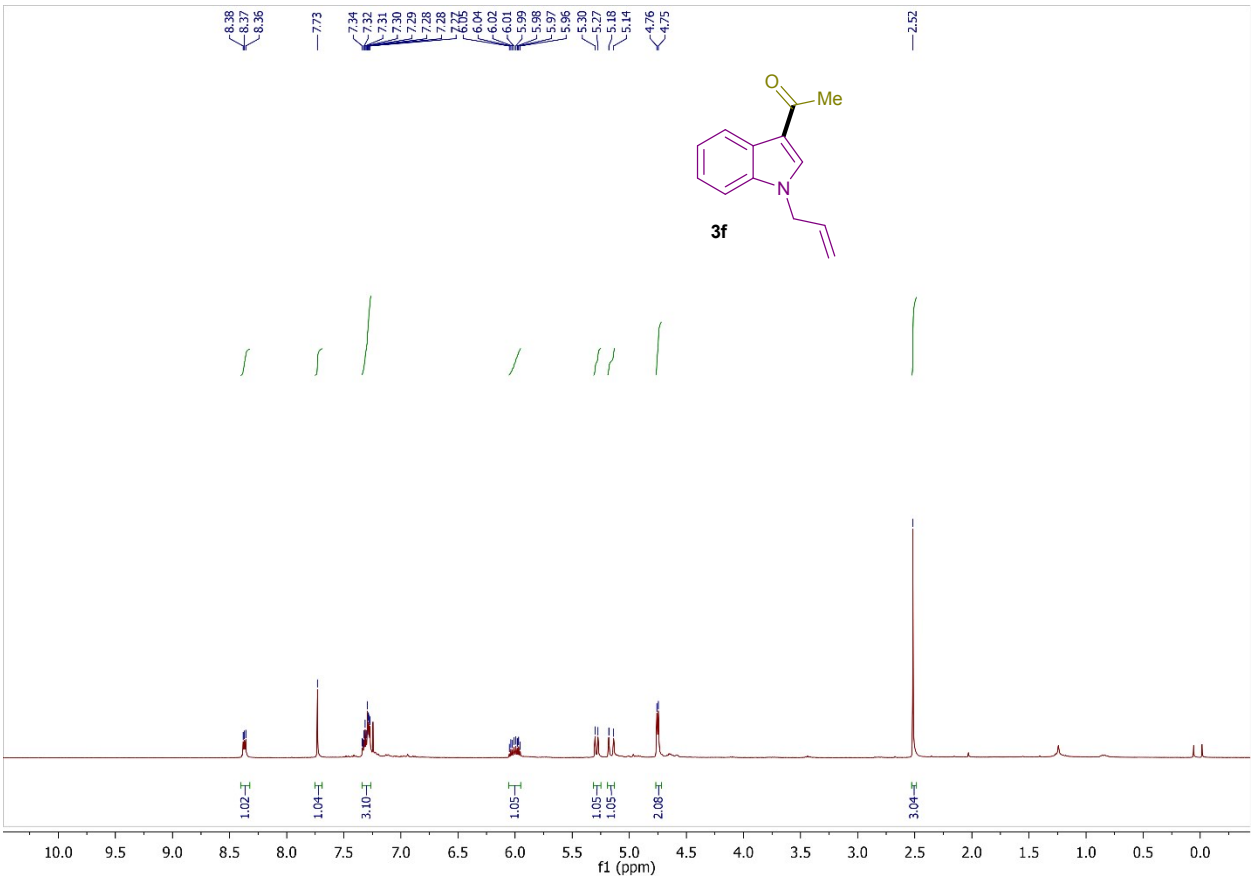
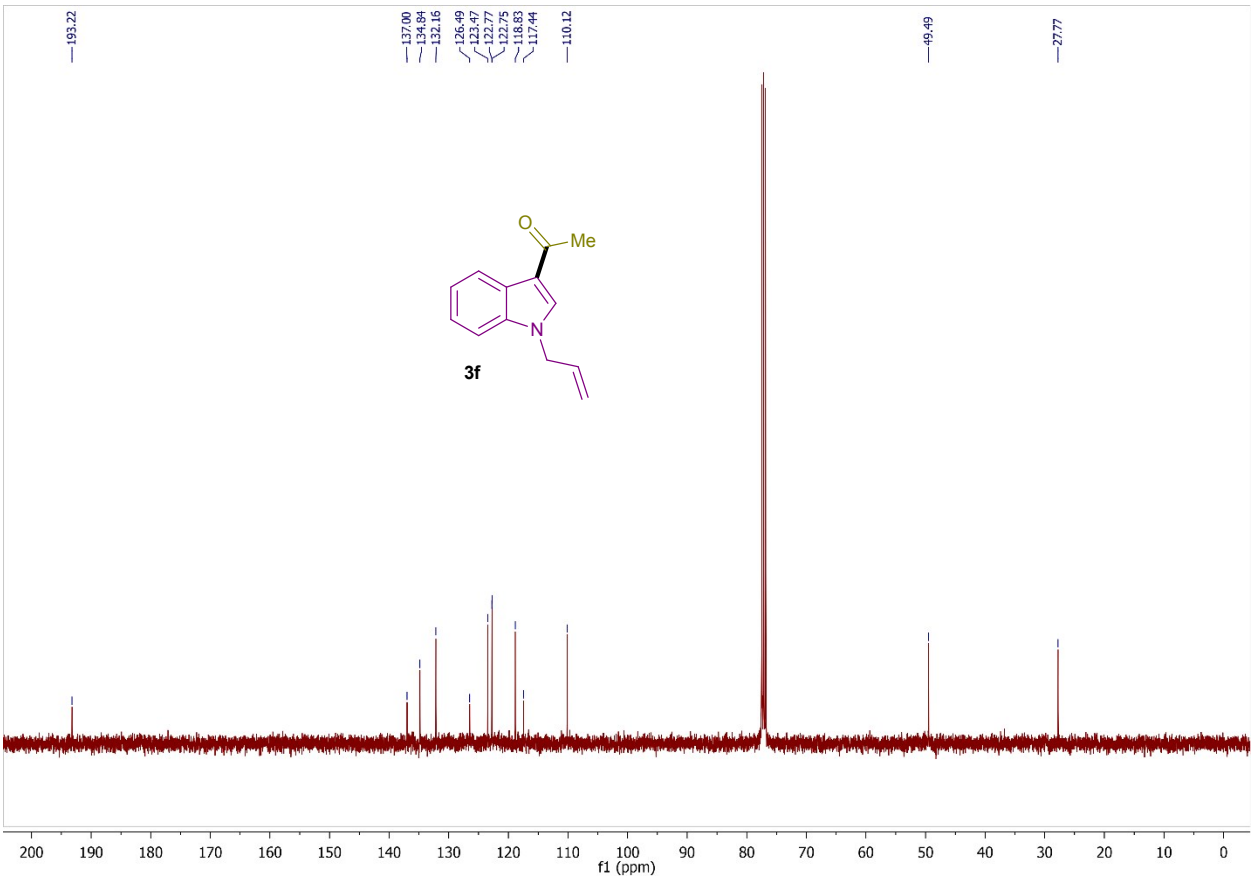


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**



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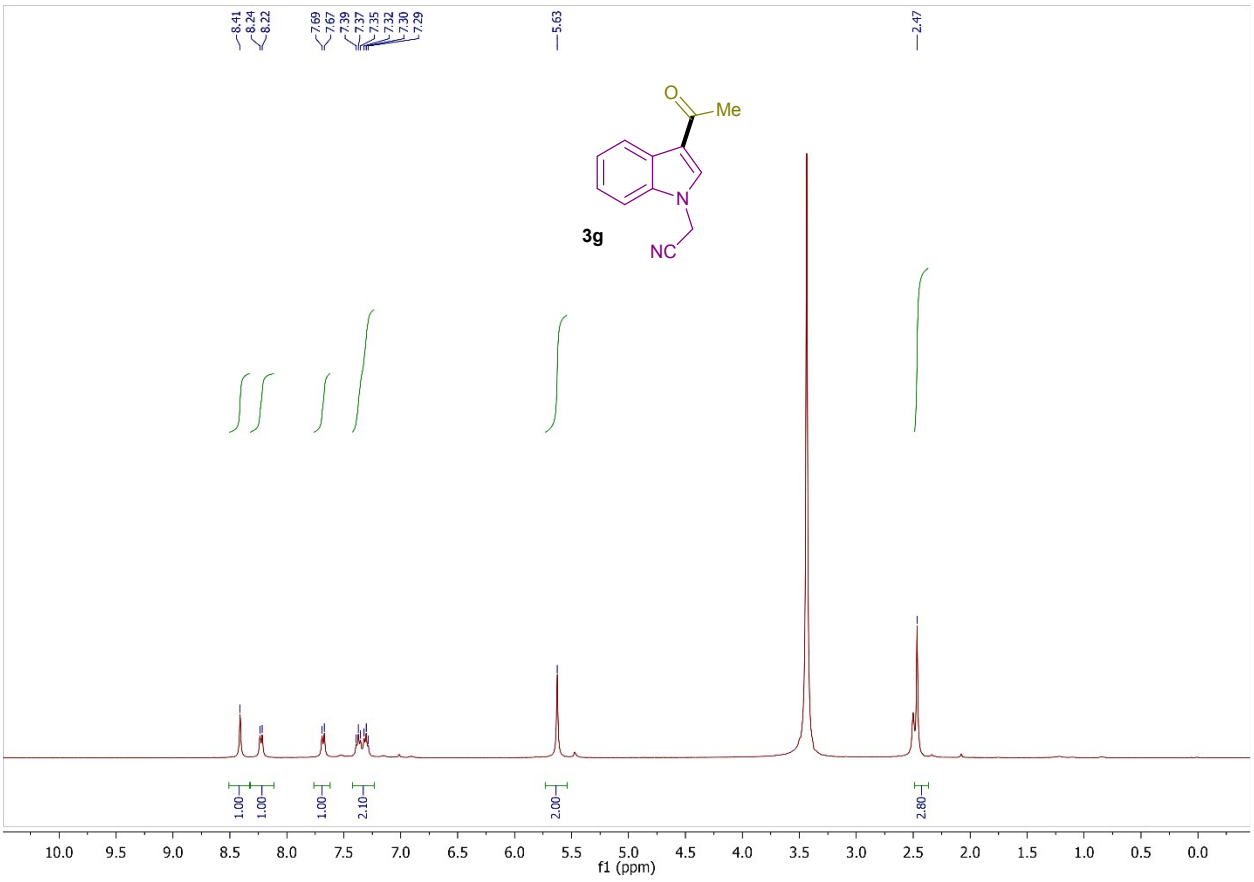
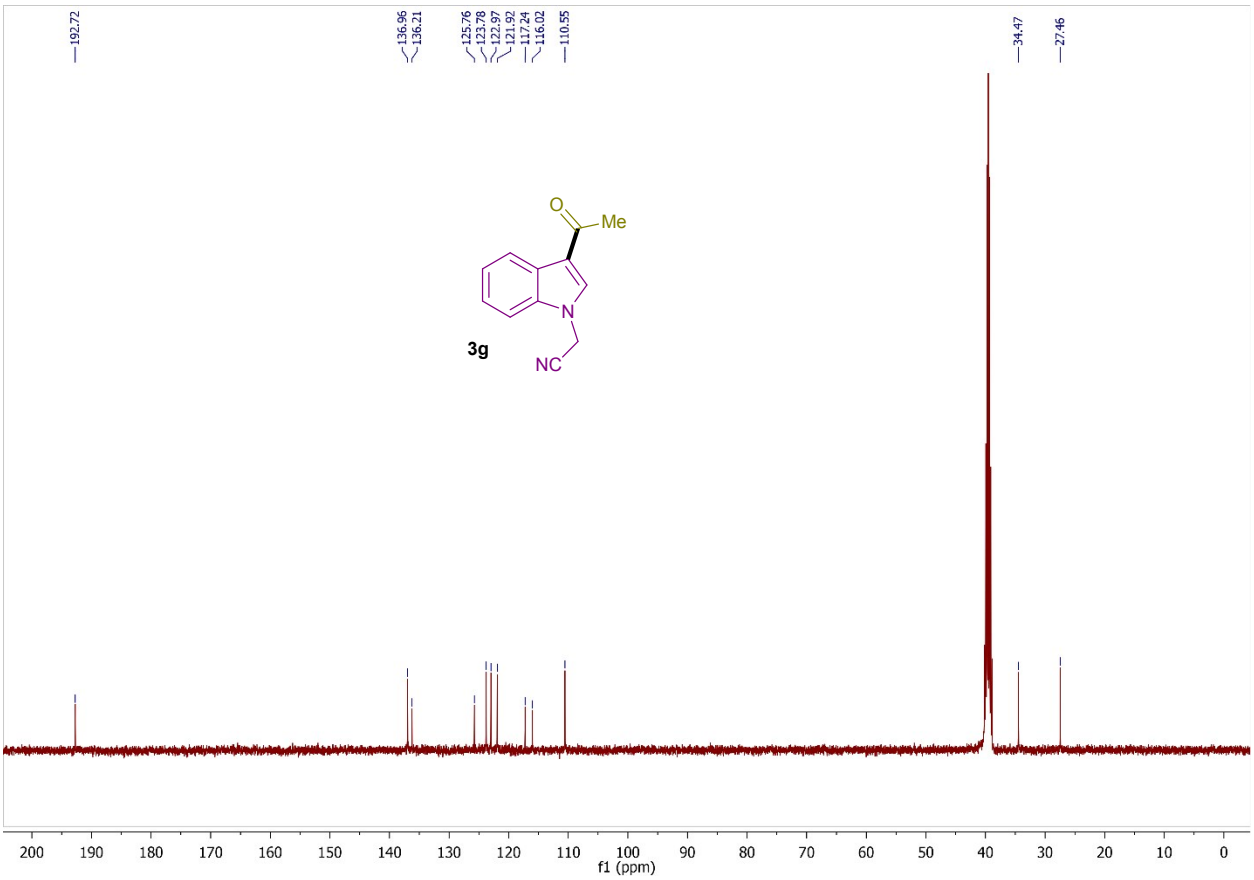
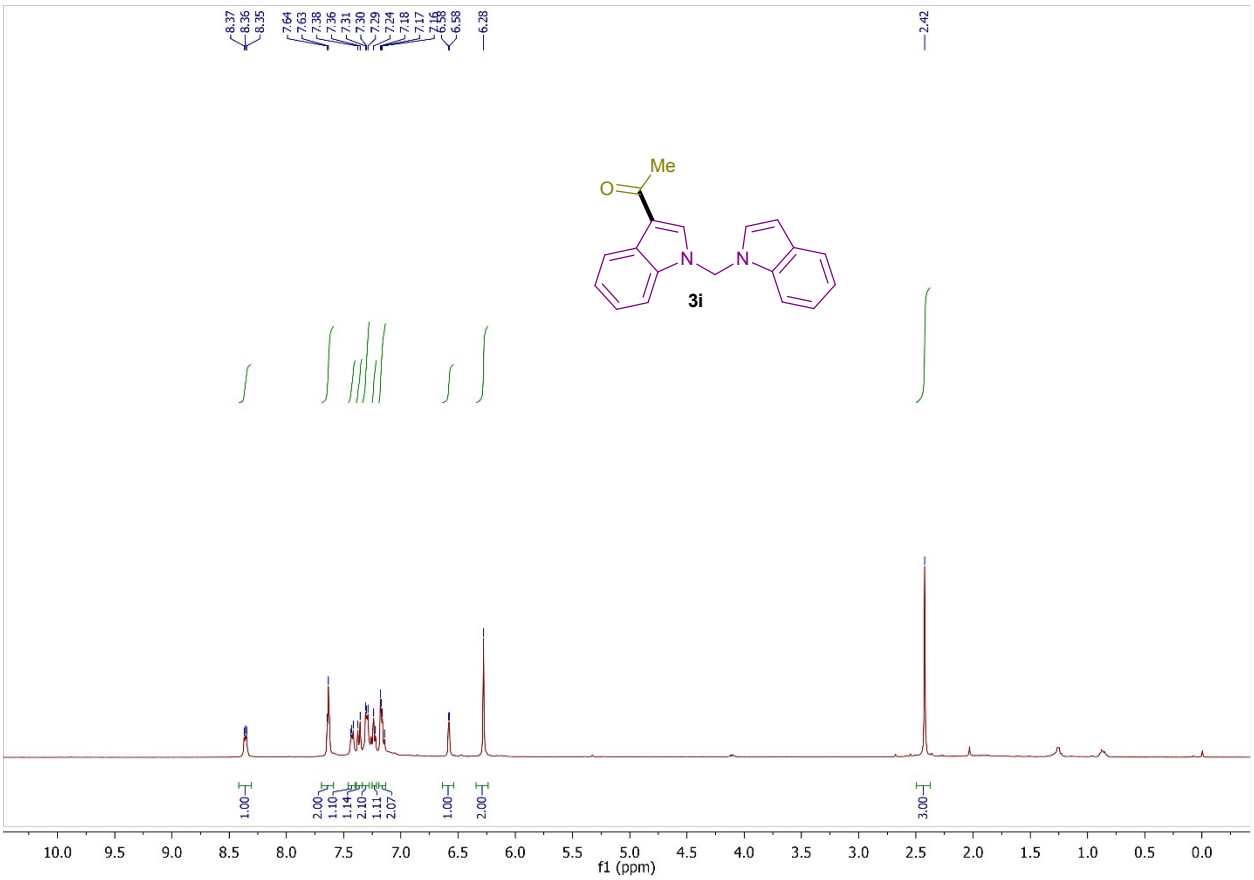


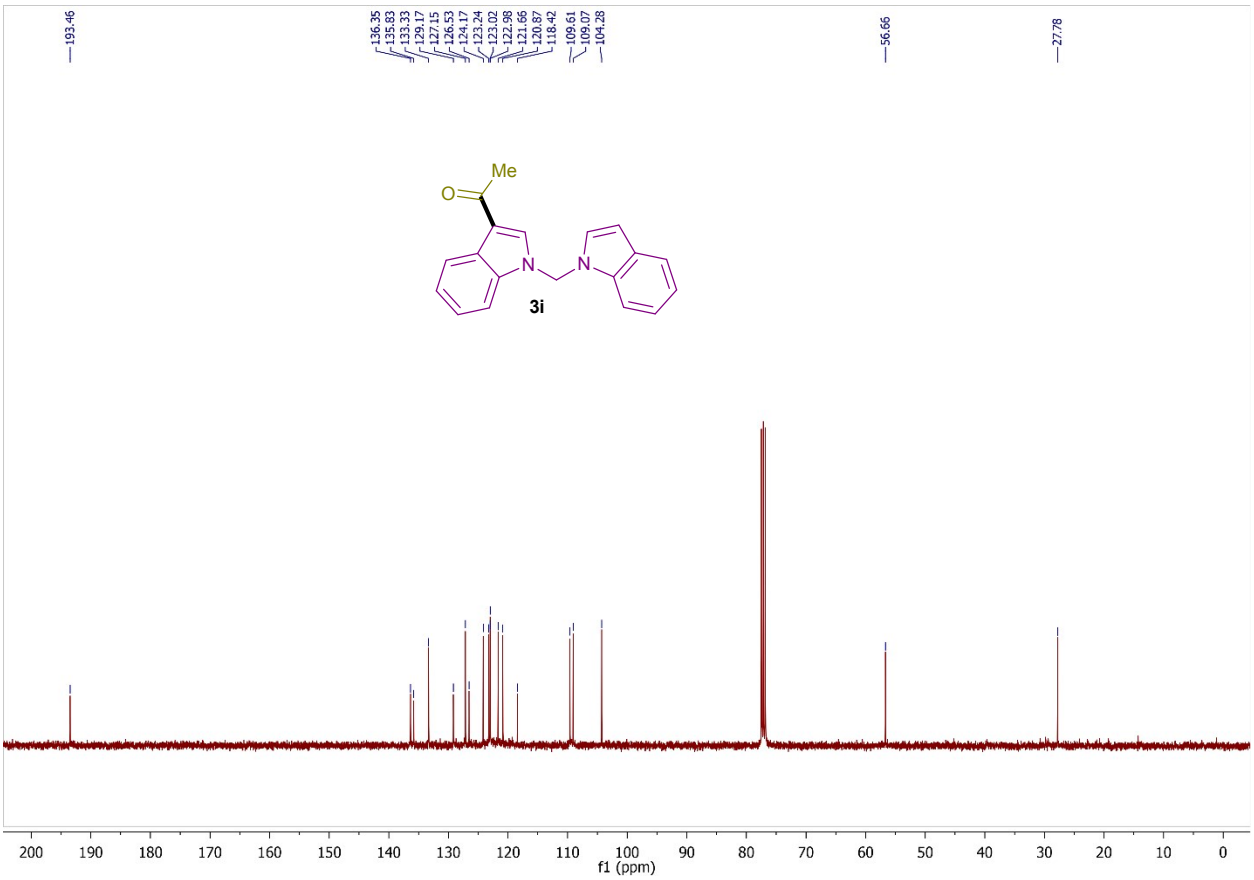
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3g**



$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) of compound **3g**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**



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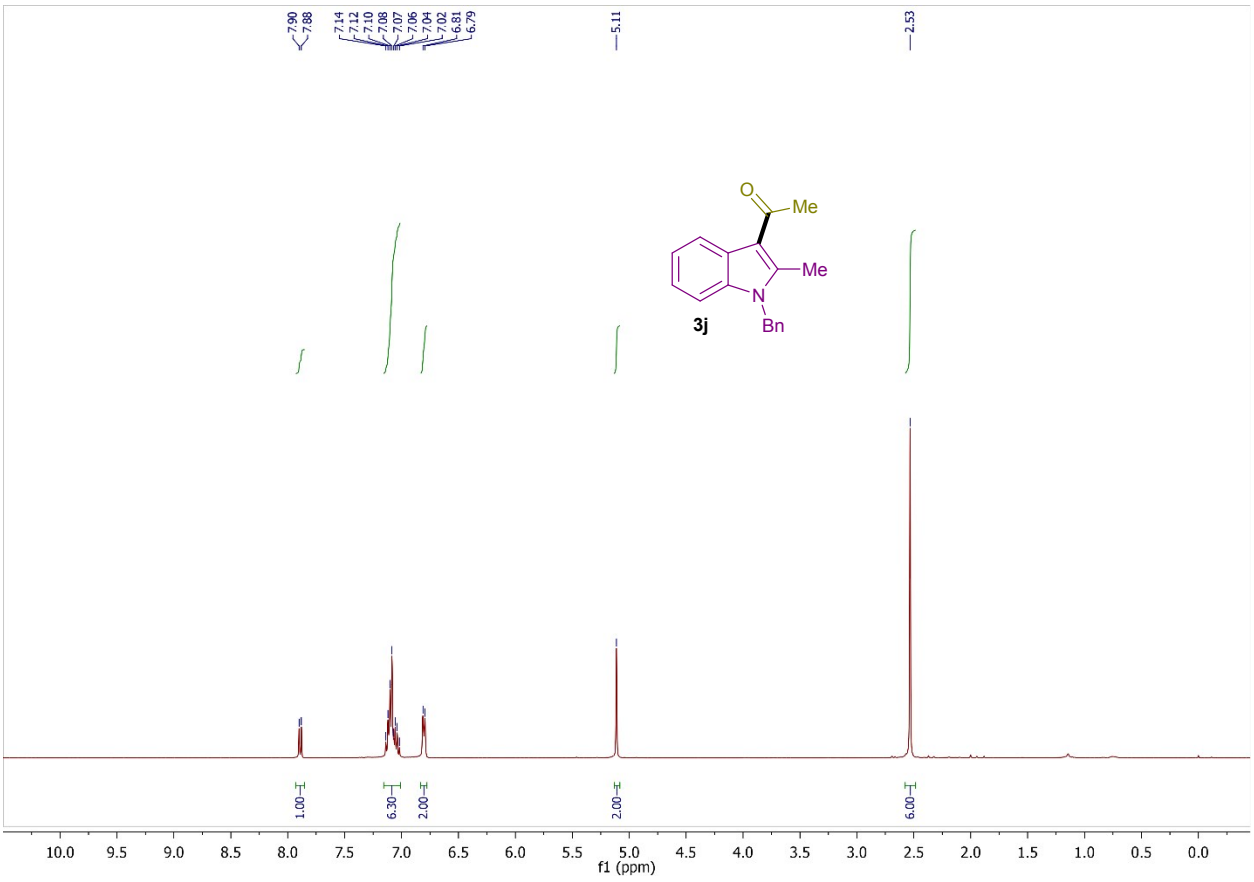

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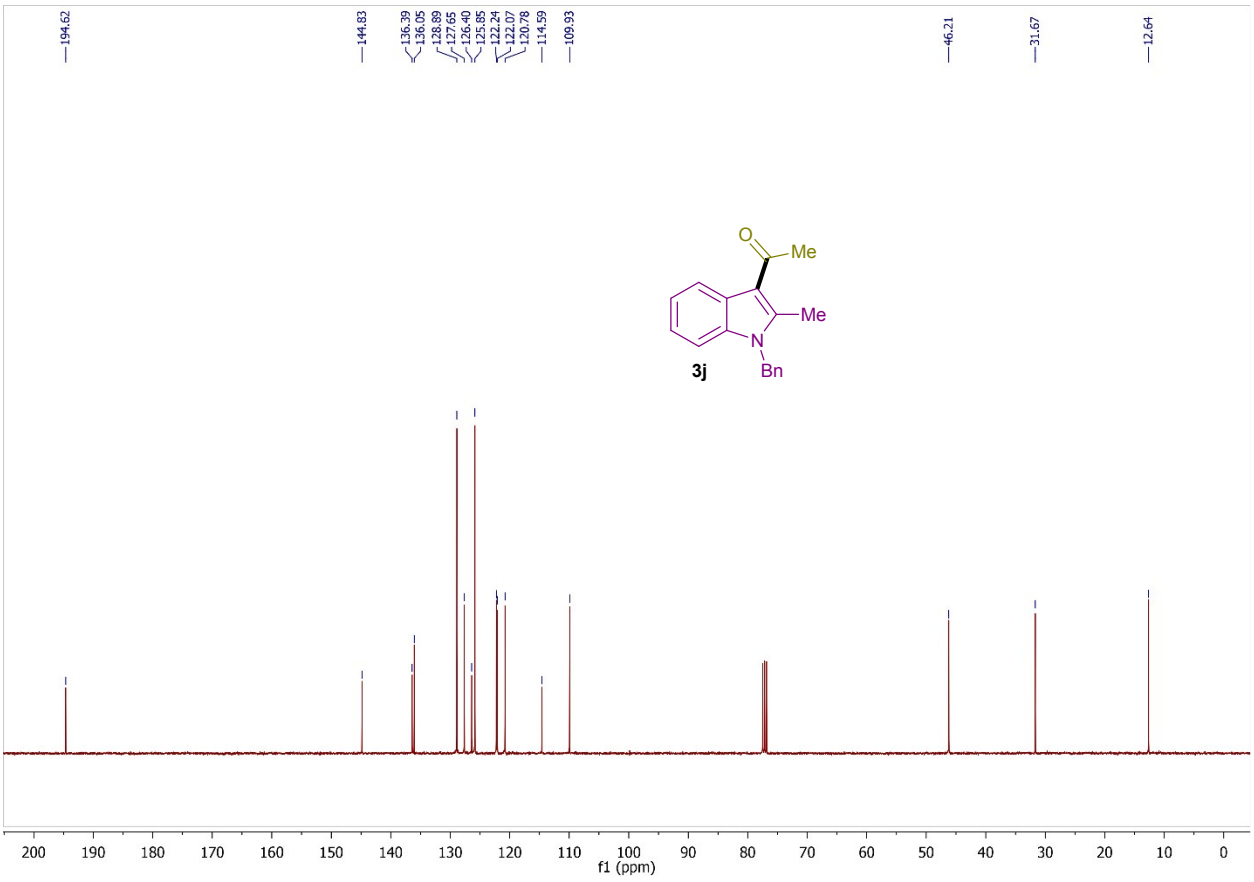

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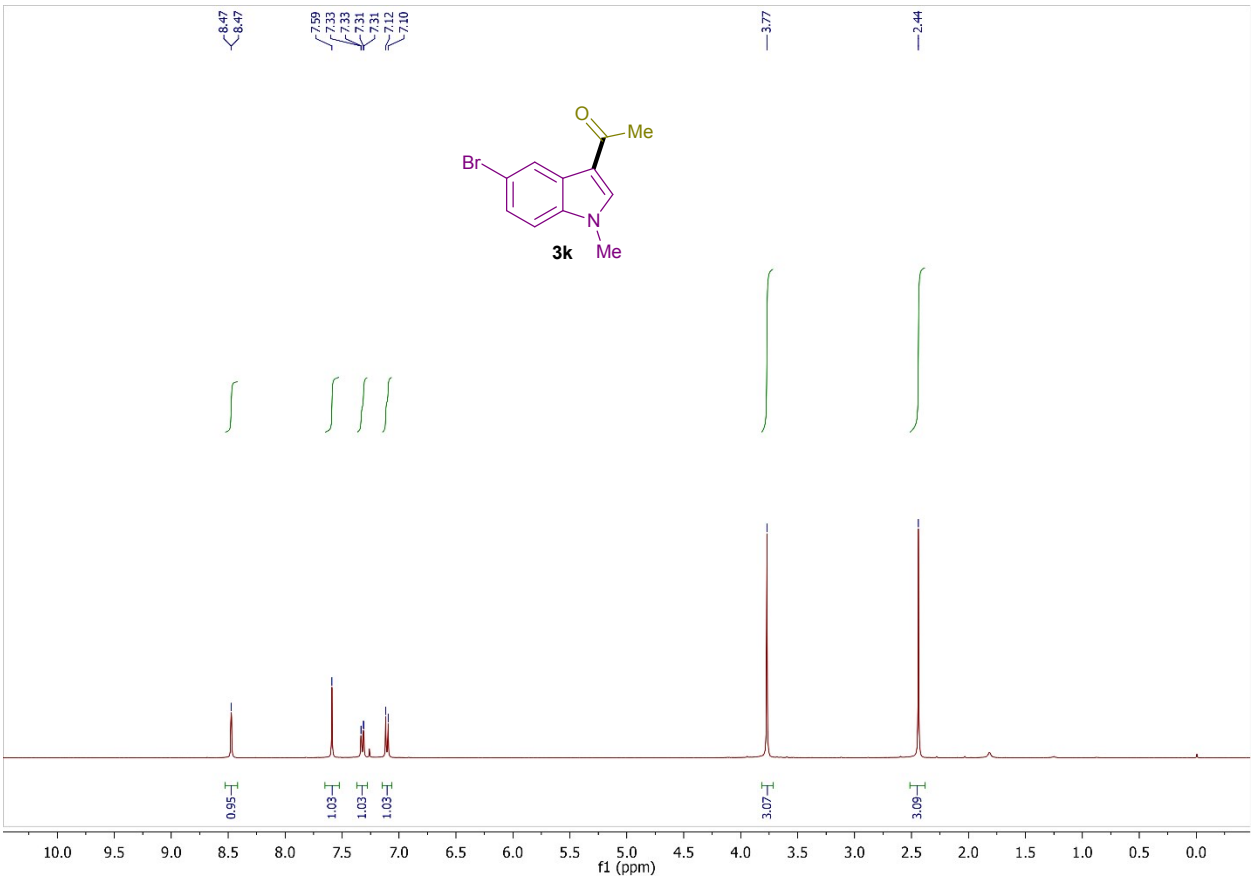

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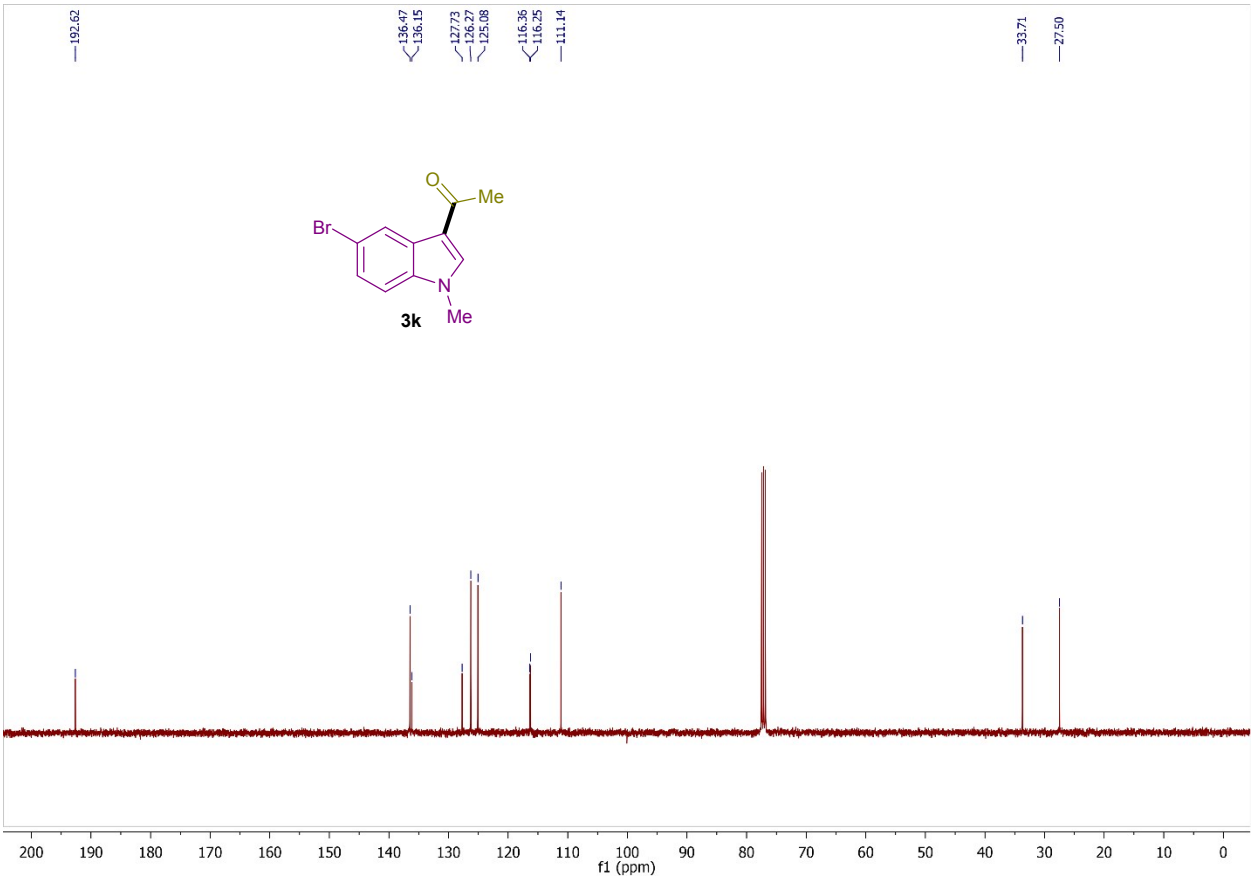

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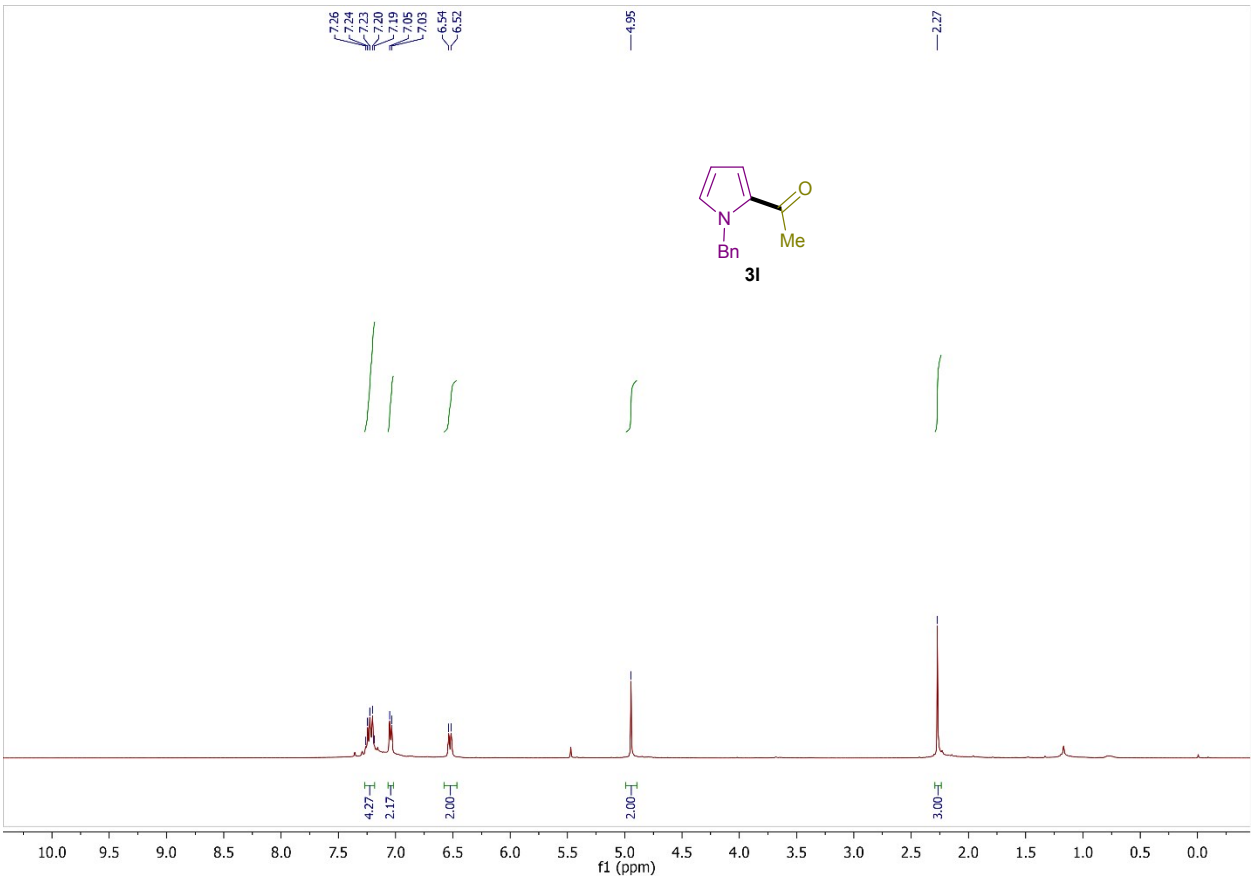
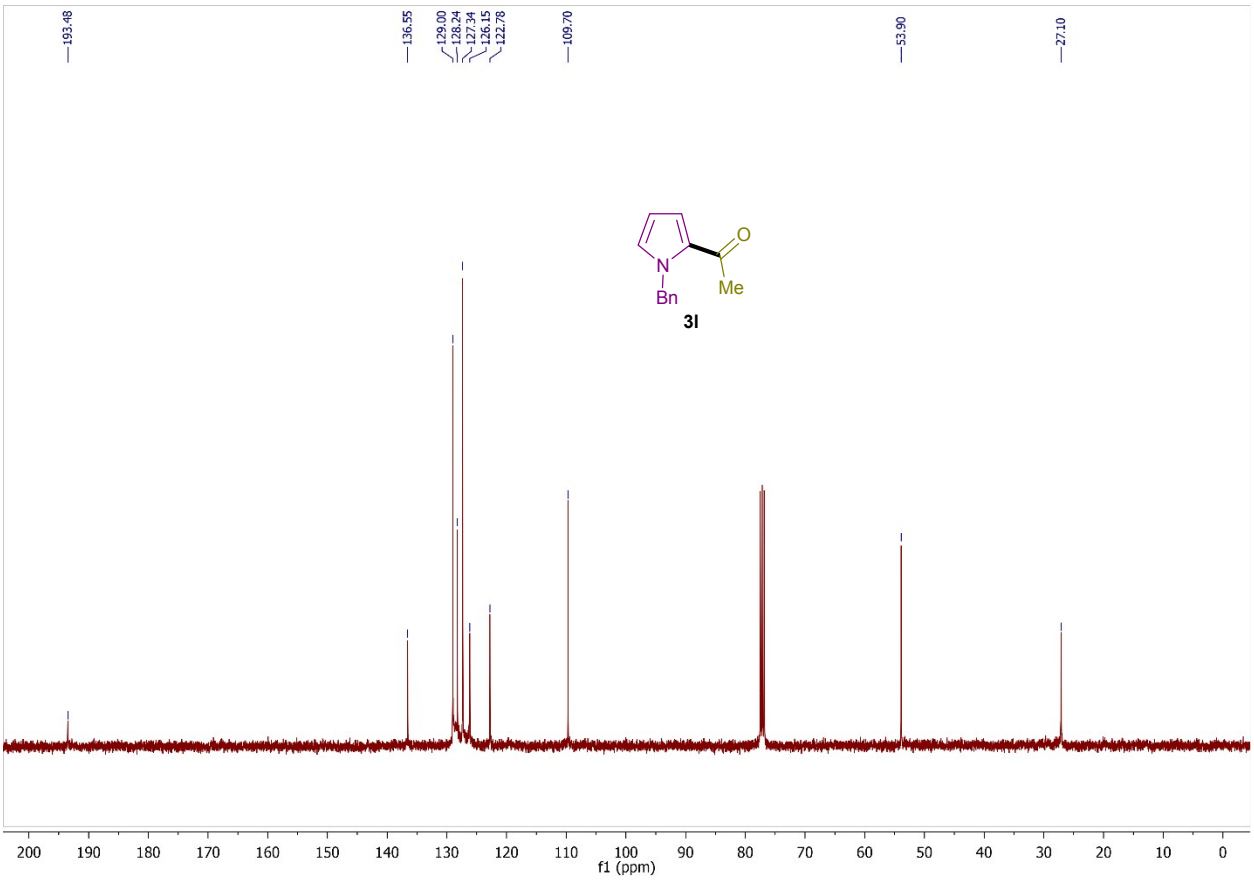


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l**



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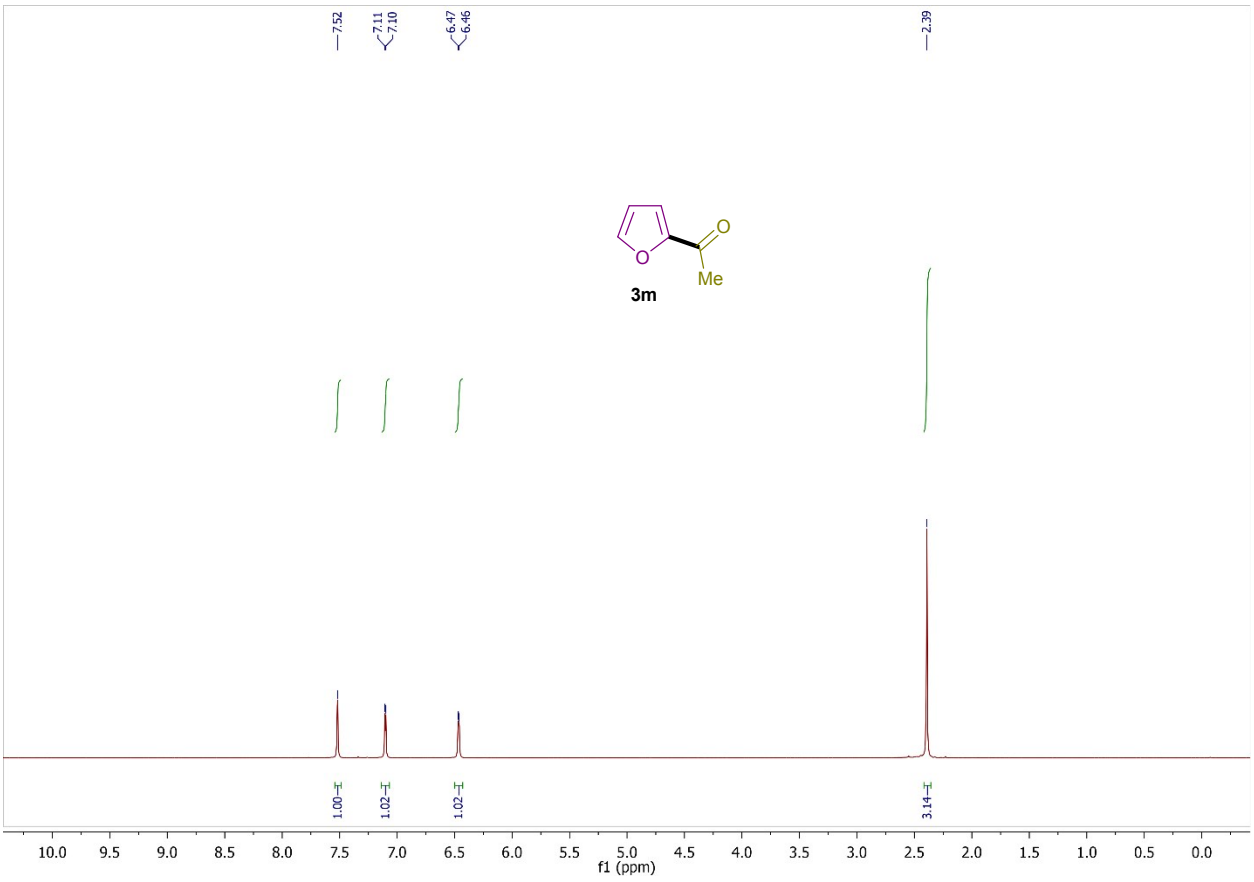
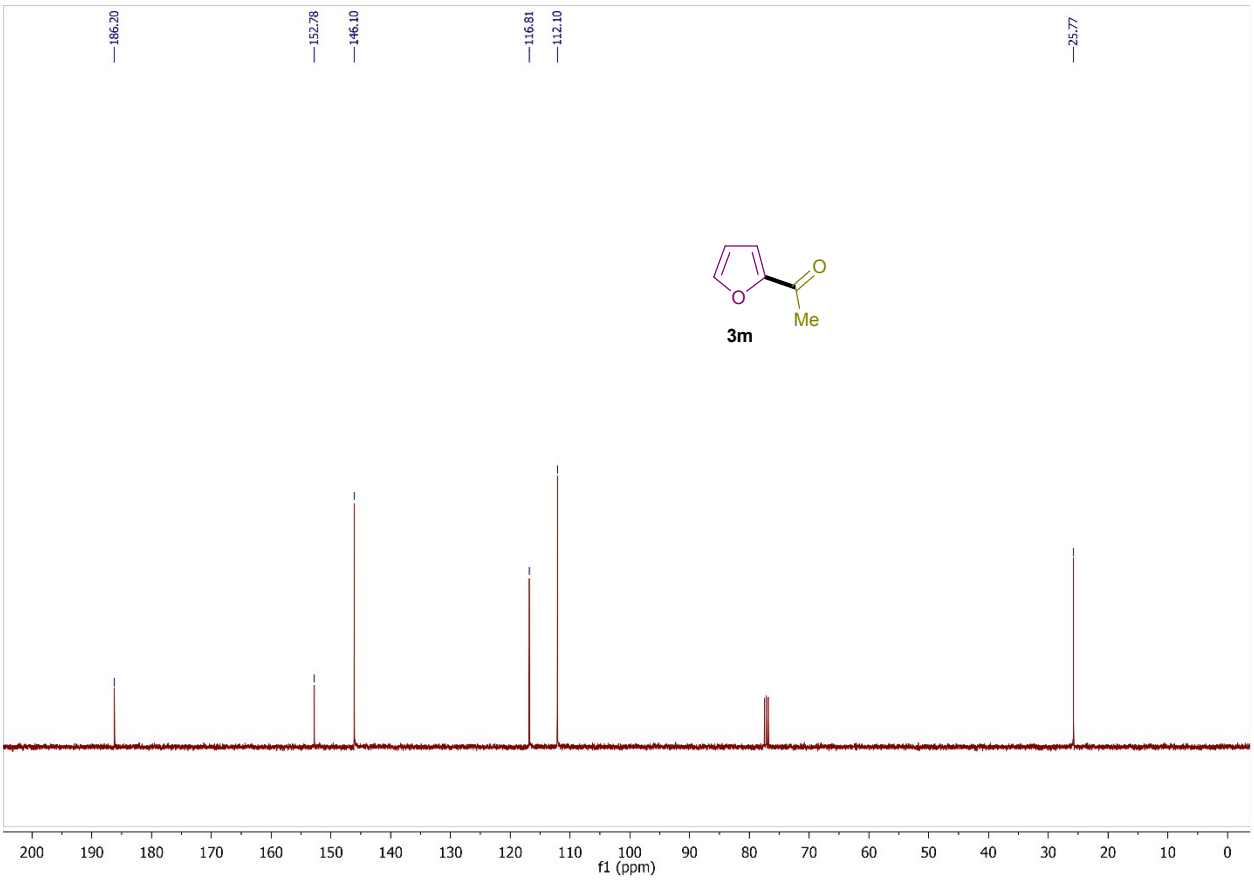


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m**



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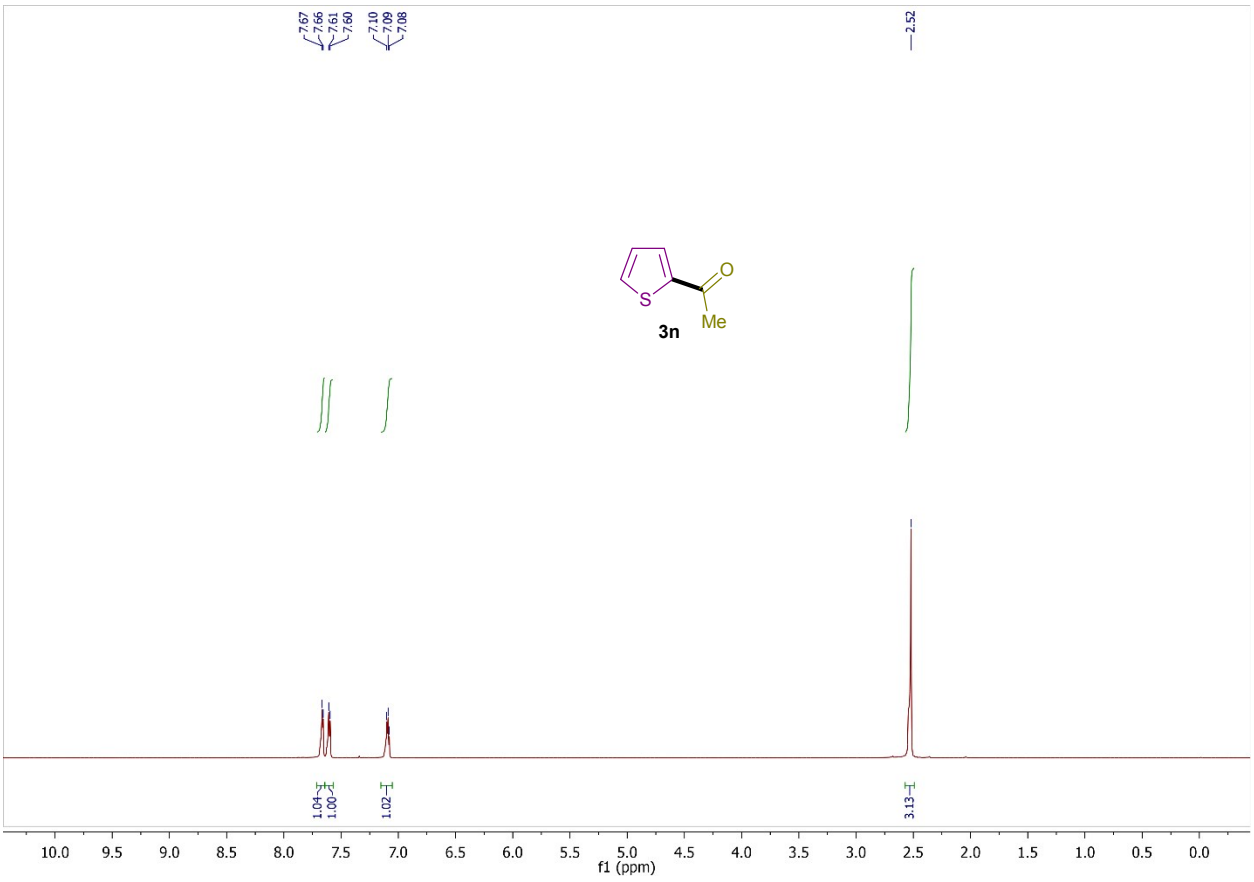
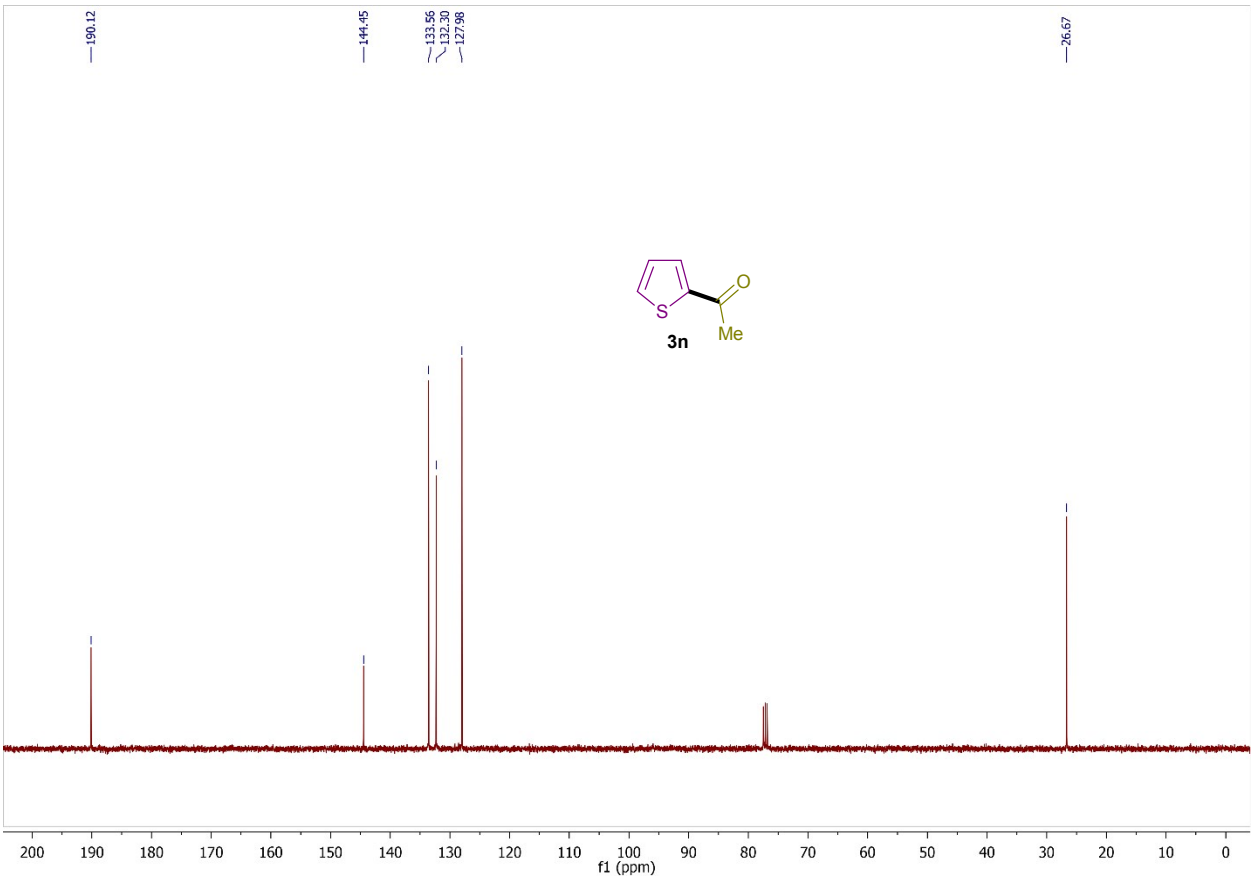
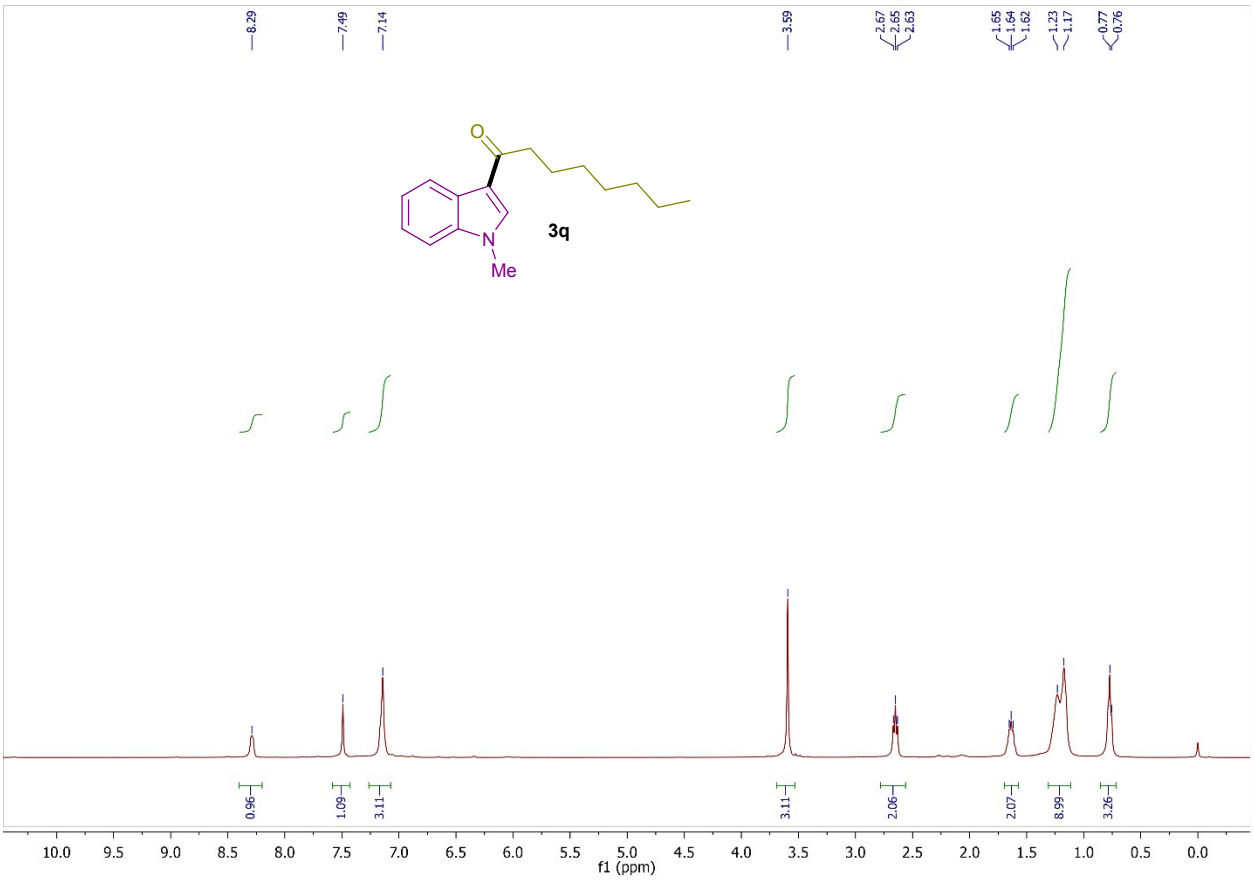


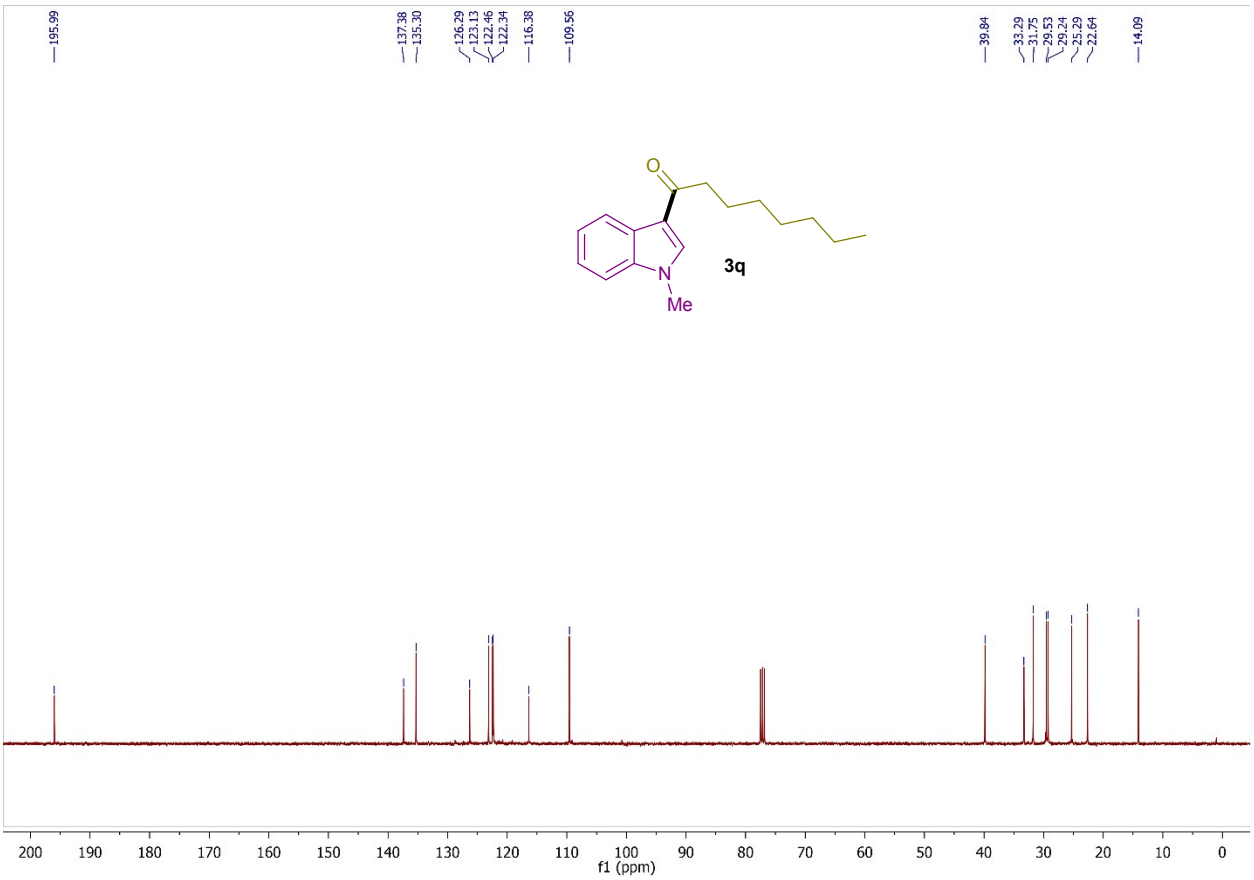
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3n**



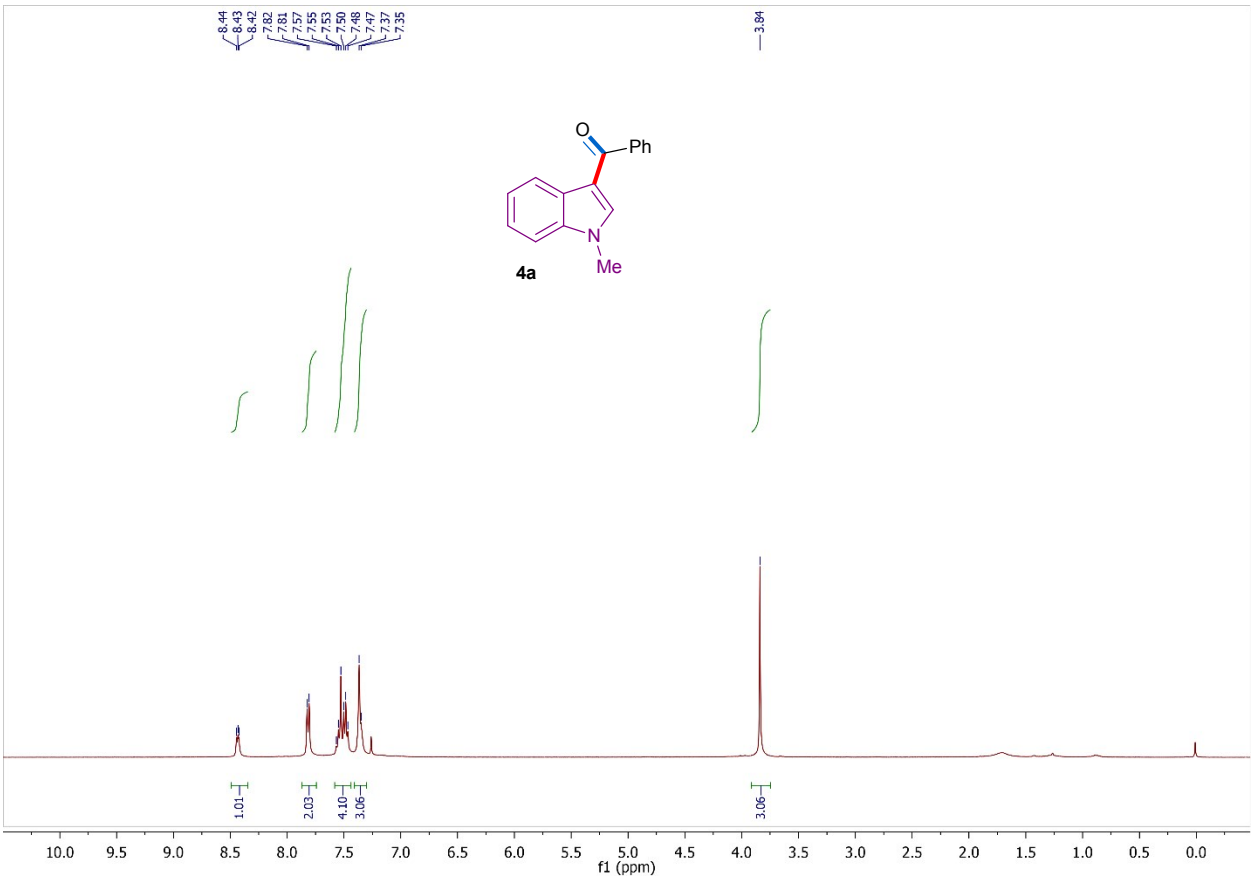
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **3n**



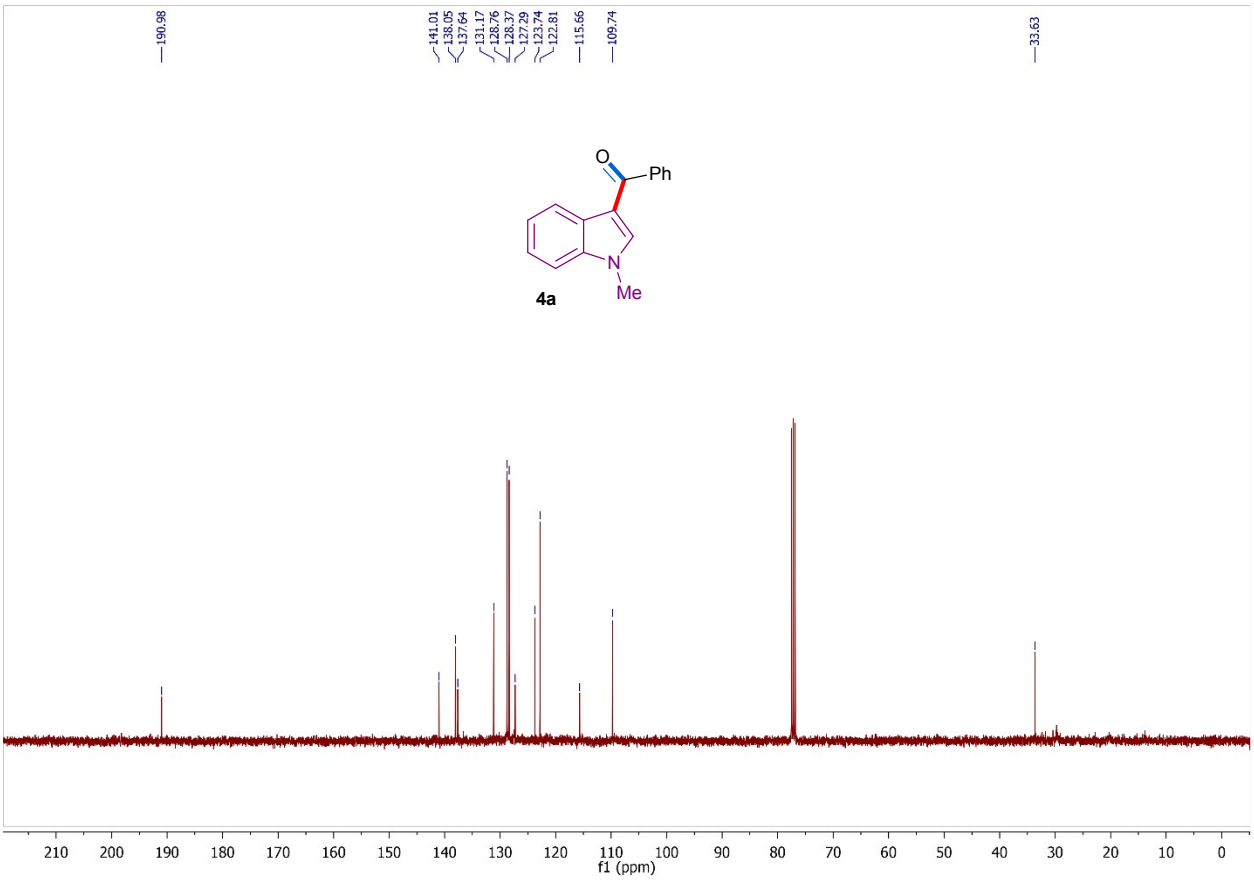
^{1}H NMR (100 MHz, $CDCl_3$) of compound **3q**



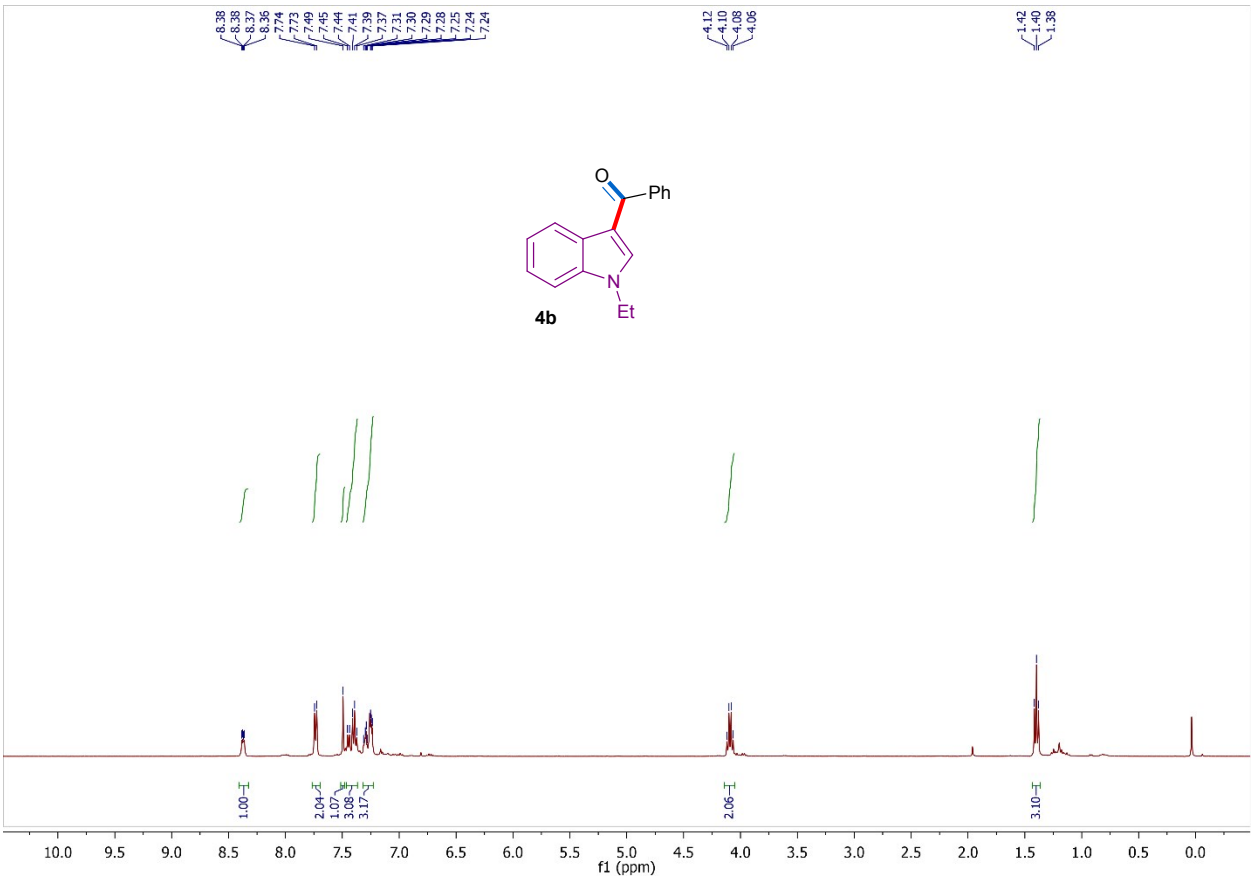
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **3q**



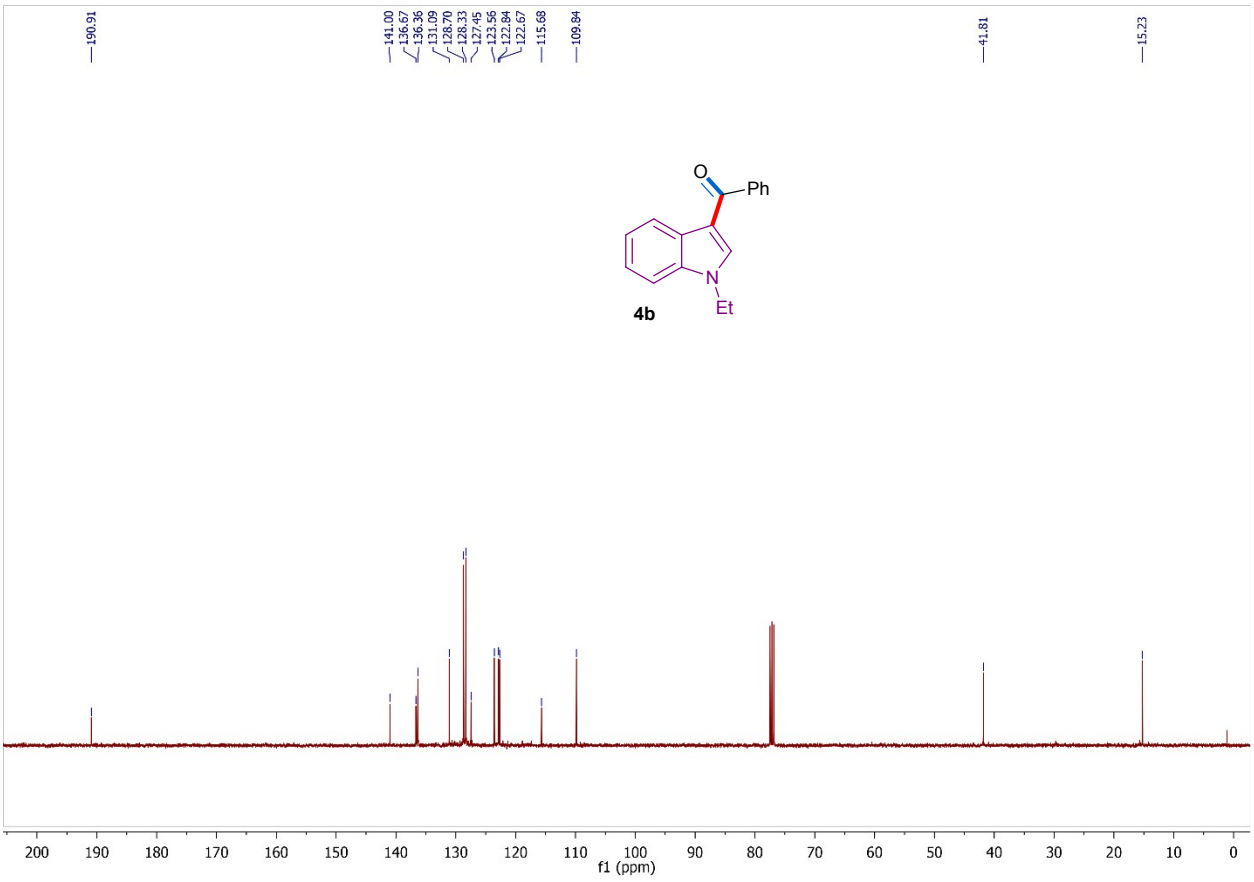
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4a**



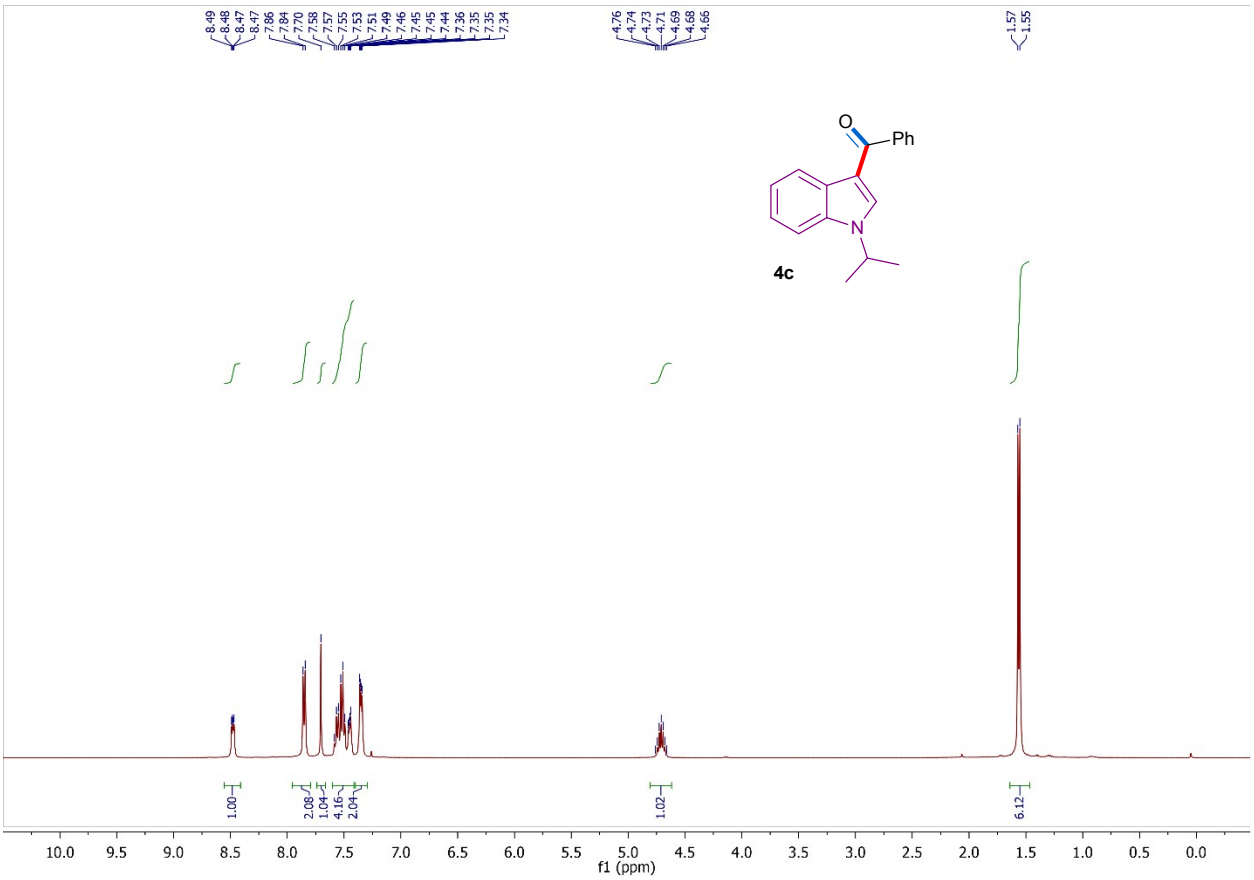
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4a**



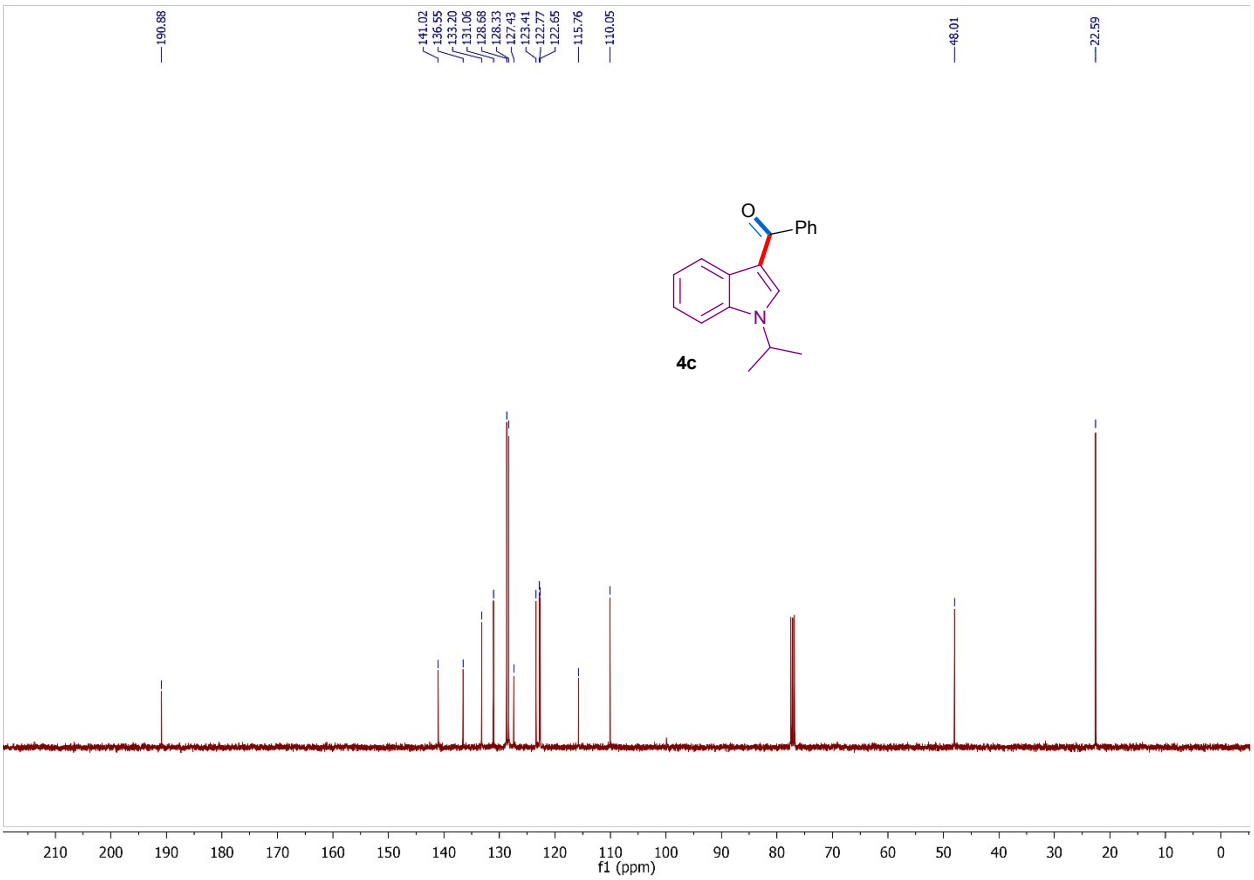
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b**



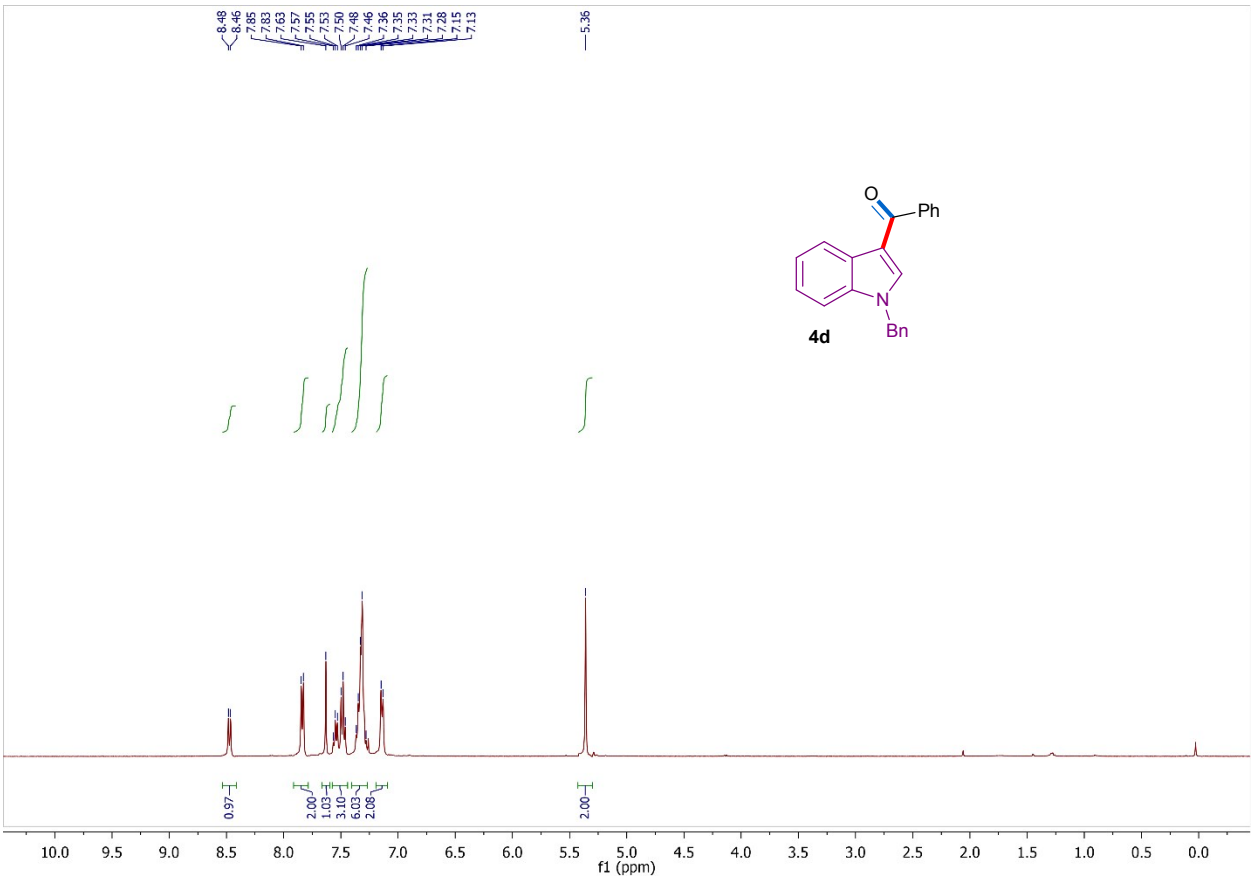
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4b**



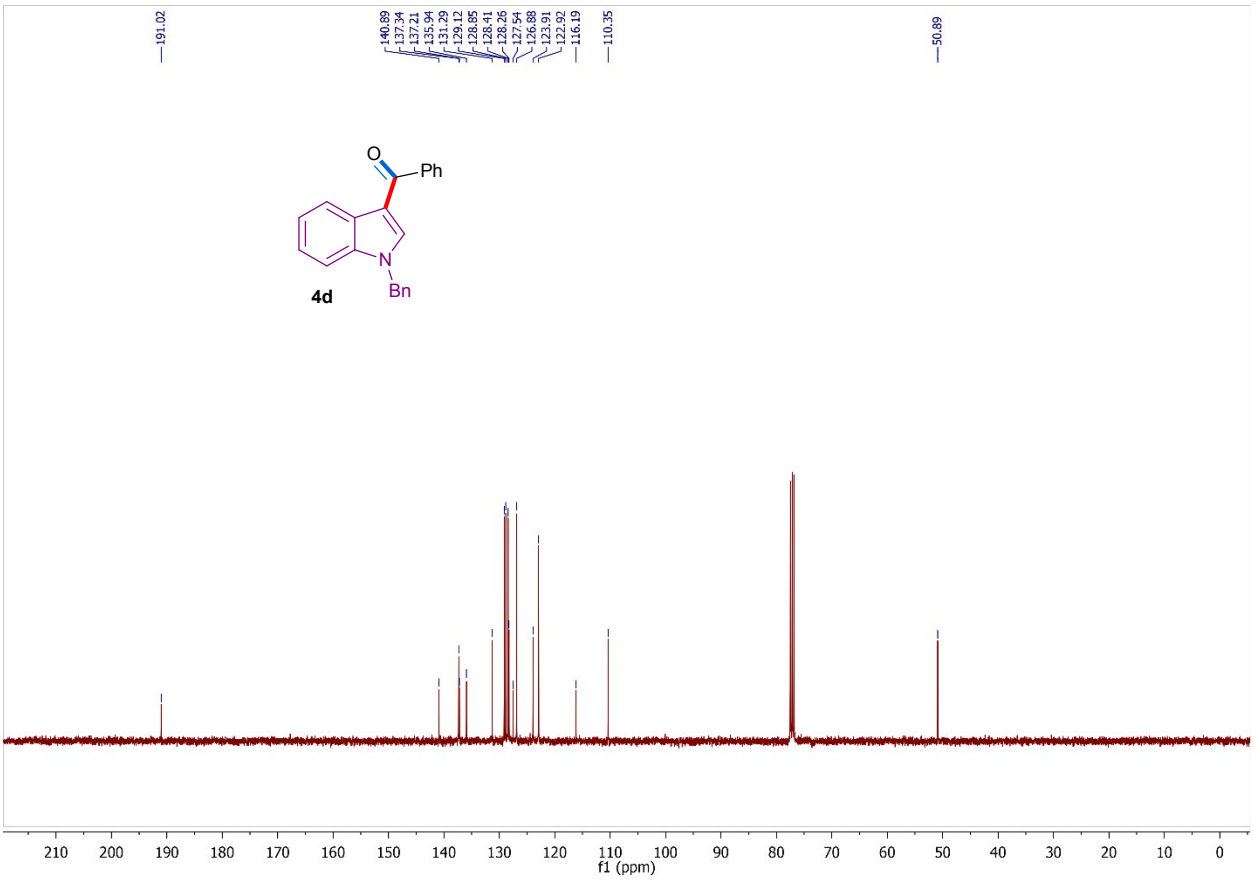
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4c**



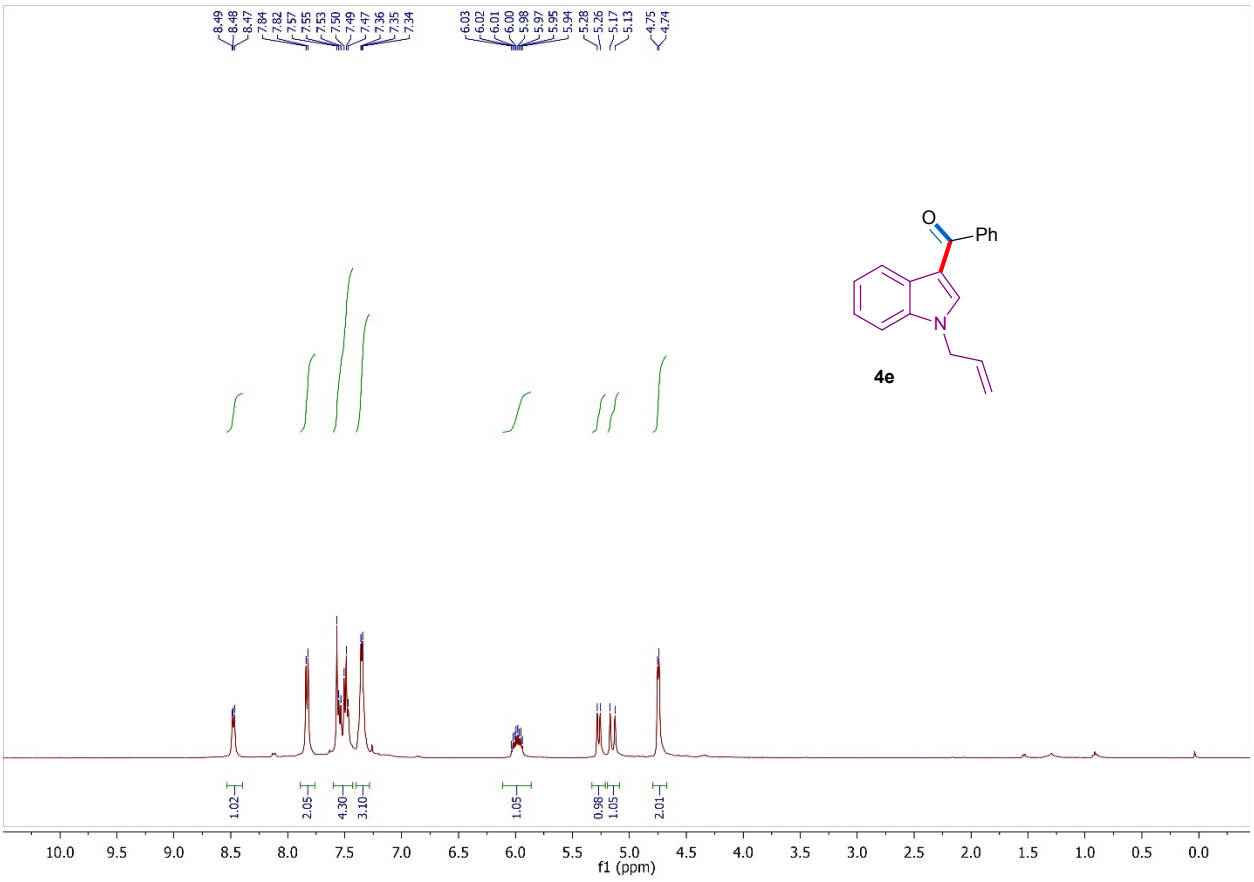
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4c**



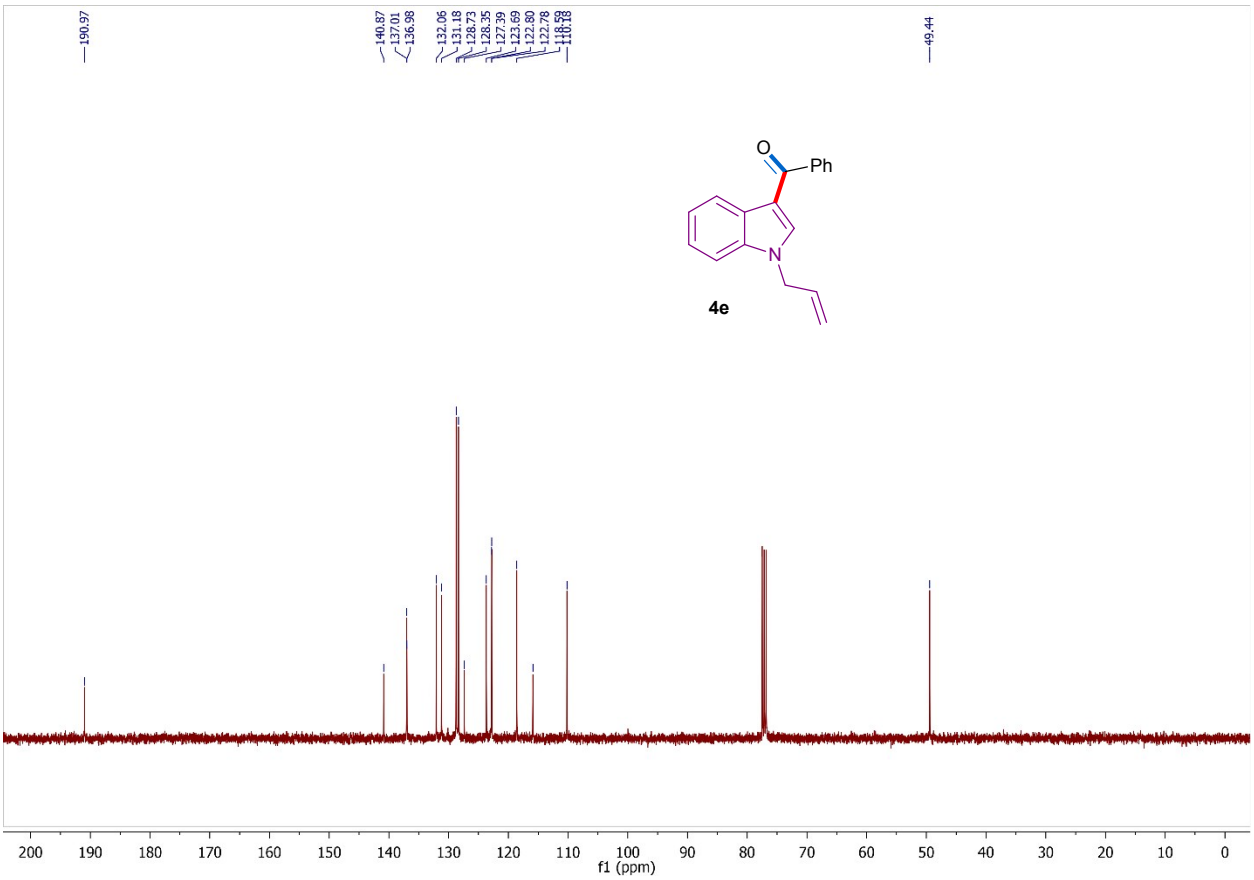
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4d**



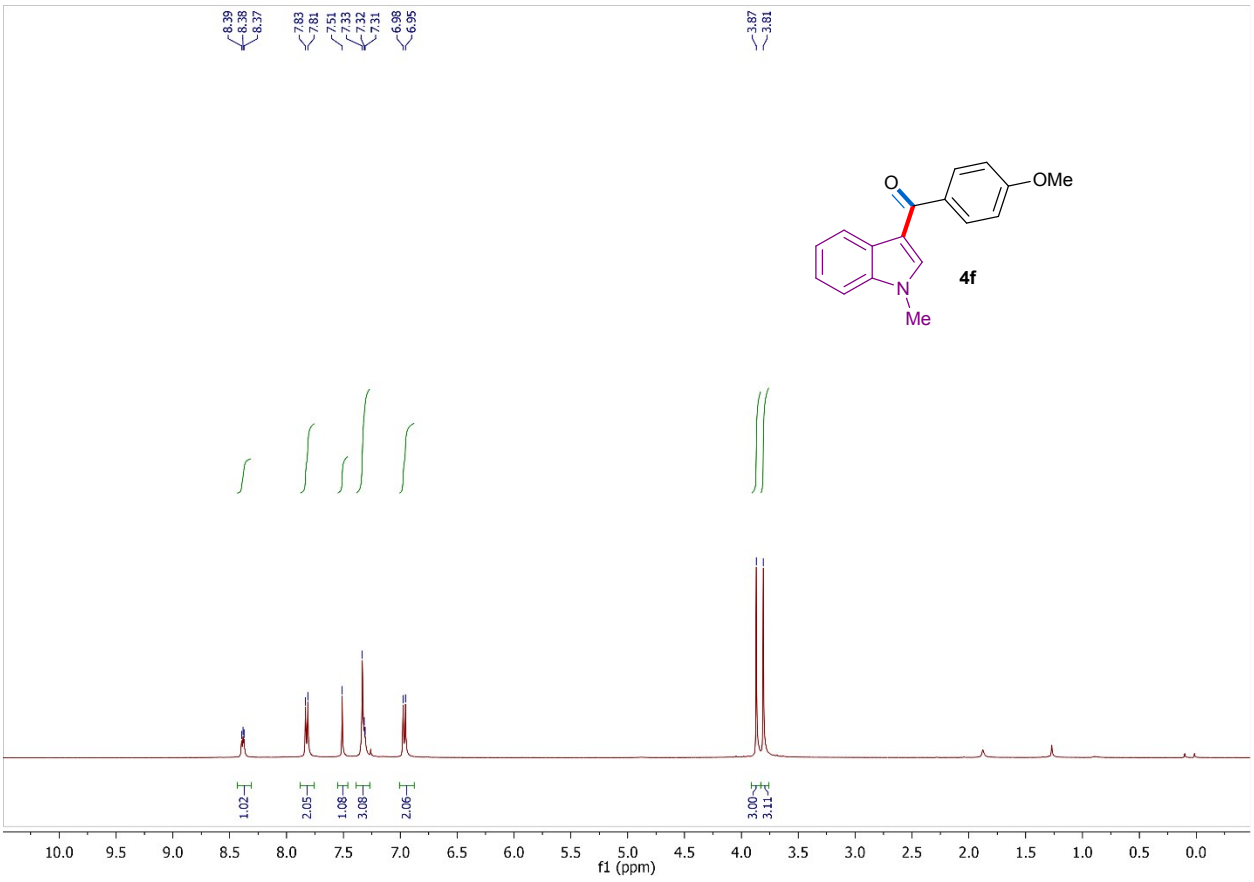
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4d**



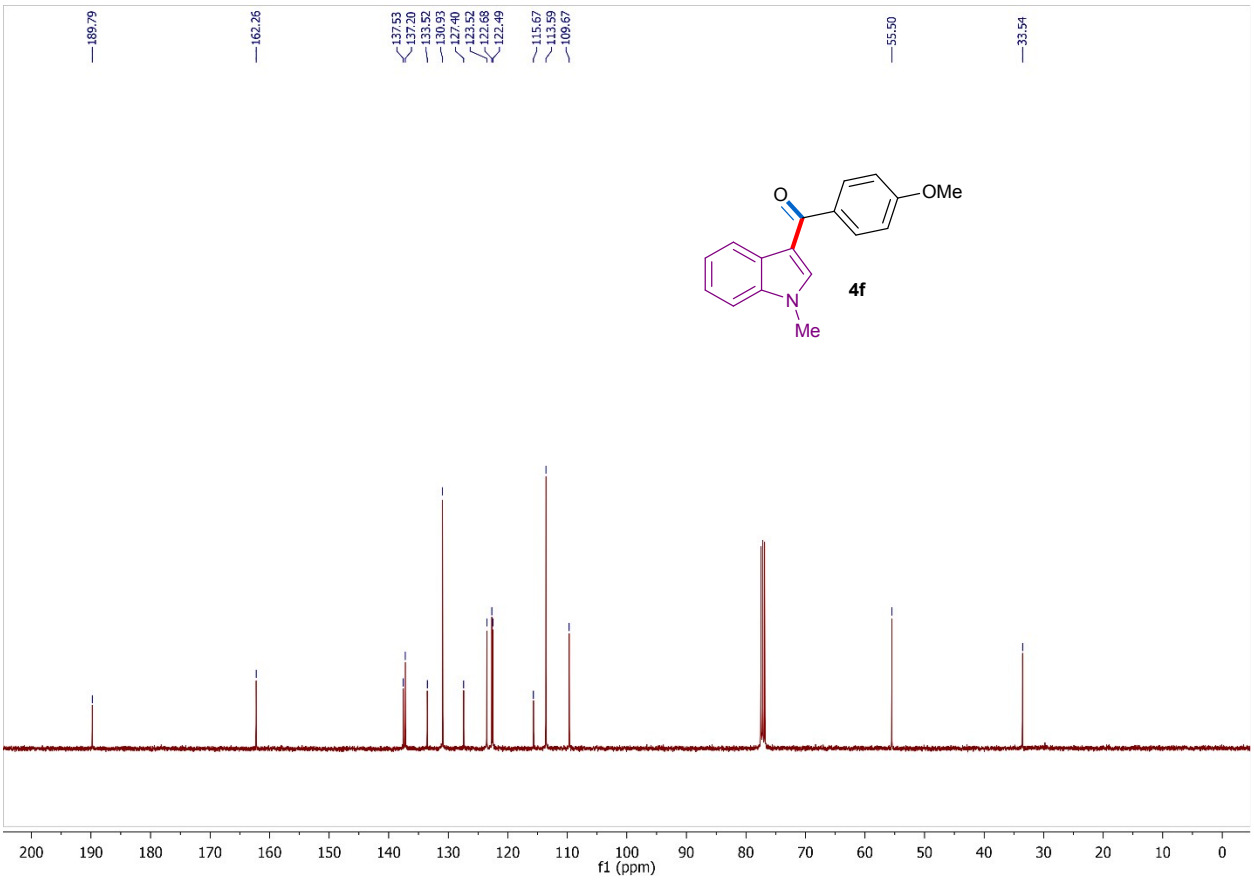
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4e**



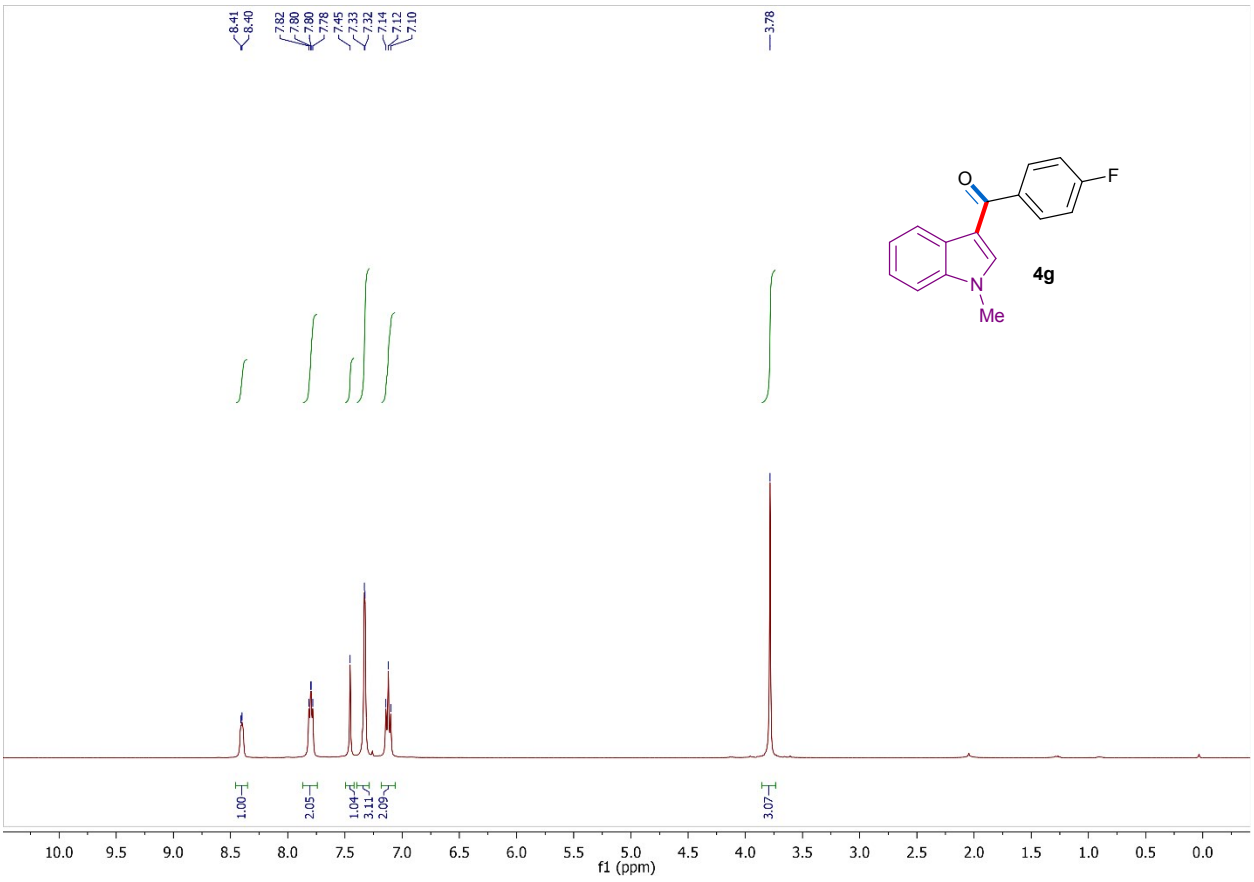
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4e**



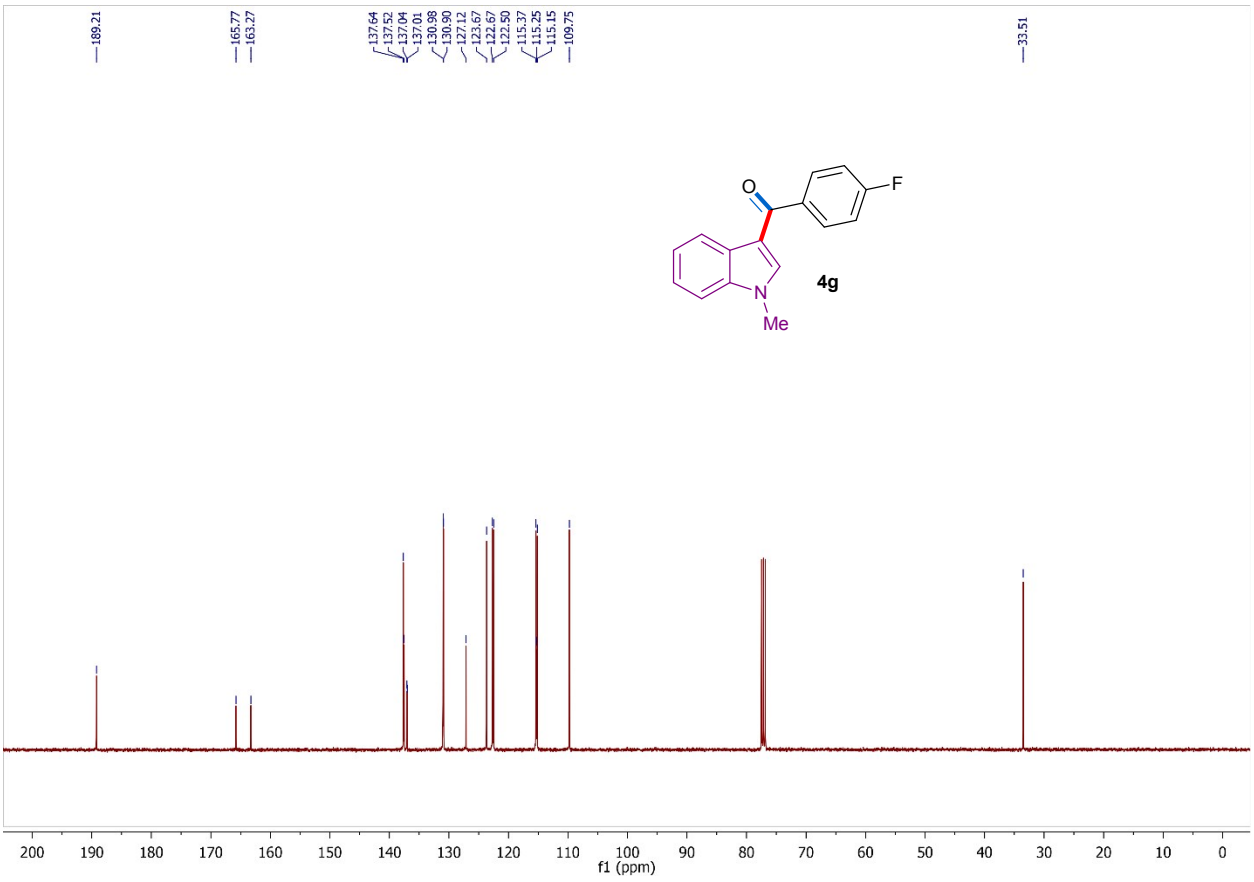
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4f**



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4f**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **4g**



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4g**