Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Brønsted acidic ionic liquid-promoted direct C3-acylation of *N*-unsubstituted indoles with acid anhydrides under microwave irradiation

Phuong Hoang Tran, Anh-Thanh Duy Nguyen, Hai Truong Nguyen, Thach Ngoc Le

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Section S1. Chemicals and instruments

Indole (assay ≥ 99%), 5-methylindole (assay ≥ 99%), 5-methoxyindole (assay ≥ 99%), 5-fluoroindole (assay ≥ 98%), 5-chloroindole (assay ≥ 98%), 5-bromoindole (assay ≥ 99%), 4-bromoindole (assay ≥ 96%), acetic anhydride (ACS reagent, assay ≥ 98.0%), propionic anhydride (assay ≥ 99%), butyric anhydride (assay ≥ 98%), isobutyric anhydride (assay ≥ 97%), *tert*-butyric anhydride (assay ≥ 97%), benzoic anhydride (assay ≥ 95%), *N*-methylimidazole (ReagentPlus®, assay ≥ 99%) and 1,4-butane sultone (assay ≥ 97%) were purchased from Sigma-Aldrich and immediately used without further purification. Silica gel 230–400 mesh (for column chromatography) was obtained from Merck. Ethyl acetate (purity ≥ 99.5%), *n*-hexane, and chloroform (purity ≥ 99%) were obtained from Xilong Chemical Co., Ltd (China). Chloroform-*d*, 99.8 Atom %D was obtained from Armar (Switzerland). All starting materials were used without further purification. Microwave irradiation was performed on a CEM Discover for organic synthesis with safe pressure regulation using a 10 mL pressurized glass tube with a Teflon-coated septum and vertically-focused IR temperature sensor controlling the reaction temperature. Ultrasound irradiation was performed on Elmasonic S 30 (H) Ultrasonic cleaning unit (37 kHz). GC–MS spectra were performed on an Agilent GC System 7890 equipped with a mass selective detector Agilent 5973N and a capillary DB–5MS column (30 m x 250 μm x 0.25 μm). FT-IR spectra were analyzed from KBr pellets by a Bruker Vertex 70. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 500. HRMS (ESI) data were performed on Bruker micrOTOF-QII MS at 80 eV.

Section S2. Synthesis of [(4-SO_3H)BMIM]HSO_4 under solvent-free sonication

The synthesis of the [(4-SO_3H)BMIM]HSO_4 was similar to those used in the previous literature, and the comprehensive synthesis was as follows:

The first step: 1-Methylimidazole (1.5 mmol, 0.123 g) and 1,4-butane sultone (1.5 mmol, 0.204 g) were added into a 10 mL pressurized glass tube with Teflon-coated septum. The reaction mixture was irradiated by ultrasound for 5 min at 80 ^{o}C (37 kHz)**.** After completion of the reaction, the zwitterion [4-(SO_3-

)BMIM]$^+$ was washed with diethyl ether (6 x 5 mL), and dried under vacuum at 80 ^{o}C for 30 min to give the pure product.

The second step: A mixture of [4-(SO_3^-)BMIM]$^+$ (1.5 mmol, 0.327 g) and sulfuric acid 98% (1.5 mmol, 0.147 g) was added into a 10 mL pressurized glass tube with Teflon-coated septum, which was irradiated by ultrasound for 60 min at 60 ^{o}C (37 kHz). The mixture reaction was washed with diethyl ether (10 x 3 mL). Then, the mixture [(4-SO_3H)BMIM]HSO_4 was dried under vacuum at 40 ^{o}C. The product was then characterized by ^{1}H and ^{13}C NMR, and HR-MS (ESI).

Table S1. Optimization of reaction condition for the first step.

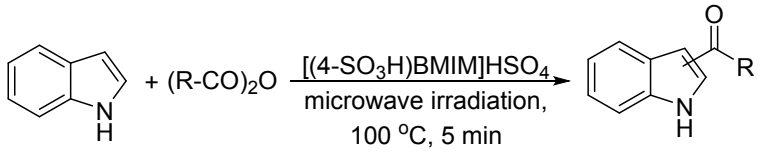
Entry	Time (min)	Temperature (^{o}C)	Isolated yield (%)
1	5	50	65
2	5	60	76
3	5	70	88
4	5	80	99
5	1	80	42
6	3	80	57

Table S2. Optimization of reaction conditions for the second step.

Entry	Time (min)	Temperature (^{o}C)	Isolated yield (%)
1	30	RT (30)	0
2	30	40	21
3	30	50	34
4	30	60	53
5	30	70	40
6	40	60	75
7	60	60	95
8	90	60	97

Section S3. Effect of different catalyst and heating method in propionylation of indole.

Table S3. Effect of different catalysts and heating method for the Friedel–Crafts C3-propionylation of indole.[a]

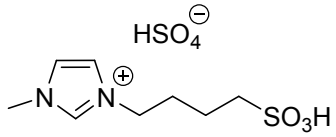


Entry	Catalyst	Heating method	Yield (%)	Selectivity (1:2:3)
1	$[BMIM]PF_6$	Microwave irradition	0	-
2	[BMIM]OTf	Microwave irradition	14	1:0:99
3	[EMIM]Cl	Microwave irradition	0	-
4	$[BMIM]H_2PO_4$	Microwave irradition	27	2:0:98
4	H_2SO_4	Microwave irradition	0	-
5	H_2SO_4	Microwave irradition	0	-
6	$[(4\text{-}SO_3H)BMIM]HSO_4$	Microwave irradition	92	1:0:99
7	$[(4\text{-}SO_3H)BMIM]HSO_4$	Magnetic stirring[d]	10	50:0:50
8	$[(4\text{-}SO_3H)BMIM]HSO_4$	Ultrasound irradiation[e]	0	-

[a] Reaction condition: Indole (1.0 mmol), propionic anhydrides (1.0 mmol), and catalyst (25 mol%) at 100 °C for 8 min.
[b] Isolated yield. [c] Determined by GC-MS.
[d] For 60 min. [e] At 80 °C for 60 min

Section S4. Spectral data

1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate (BAIL)



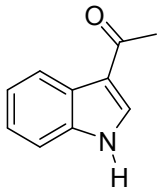
FT-IR (KBr, 4000 – 400 cm^{-1}) 3410, 1639, 1457, 1171, 1042, 752.

^{1}H NMR (500 MHz, D_2O) δ 8.59 (s, 1H), 7.35 (t, J = 1.7 Hz, 1H), 7.29 (t, J = 1.7 Hz, 1H), 4.10 (t, J = 7.0 Hz, 2H), 3.75 (s, 3H), 2.83 (t, J = 8.0, 2H), 1.82 (m, 2H), 1.60 (m, 2H).

^{13}C NMR (125 MHz, D_2O) δ 135.9, 123.6, 122.1, 50.0, 48.9, 35.7, 28.1, 20.9.

HRMS (ESI) *m/z* calcd for $[M^+]$ $C_8H_{15}N_2O_3S^+$ 219.0798; found 219.0783.

3-Acetylindole[1]

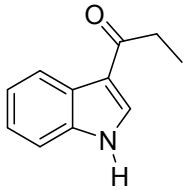


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (br s, 1H), 8.40–8.39 (m, 1H), 7.87 (s, 1H), 7.43–7.41 (m, 1H), 7.30–7.29 (m, 2H), 2.56 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 136.4, 131.4, 125.4, 123.7, 122.7, 122.4, 118.7, 111.3, 27.6.

GC–MS (EI, 70 eV) *m/z* 159 (50, $[M^+]$).

3-Propionylindole[1]

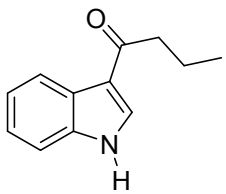


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (br s, 1H), 8.41–8.40 (m, 1H), 7.88 (s, 1H), 7.43– 7.41 (m, 1H), 7.30–7.28 (m, 2H), 2.93 (q, J = 7.4 Hz, 2H), 1.28 (t, J = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 136.3, 130.9, 125.6, 123.7, 122.6, 122.5, 117.9, 111.4, 33.1, 9.0.

GC–MS (EI, 70 eV) *m/z* 173 (25, $[M^+]$).

3-Butyrylindole[2]

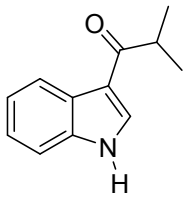


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (br s, 1H), 8.43–8.41 (m, 1H), 7.88 (d, J = 2.6 Hz, 1H), 7.43–7.41 (m, 1H), 7.30–7.28 (m, 2H), 2.86 (t, J = 7.4, 2H), 1.83 (hext, J = 7.4 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7, 136.4, 131.1, 125.5, 123.7, 122.6, 122.5 118.3, 111.4, 41.9, 18.6, 14.1.

GC–MS (EI, 70 eV) *m/z* 187 (25, [M^+]).

3-Isobutyrylindole[1]

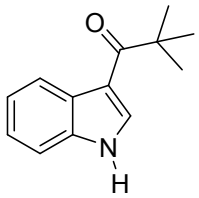


^{1}H NMR (300 MHz, DMSO-d_6) δ 11.90 (br s, 1H), 8.34 (s, 1H), 8.24–8.19 (m, 1H), 7.48–7.45 (m, 1H), 7.23–7.14 (m, 2H), 3.45 (hept, J = 6.8 Hz, 1H), 1.11 (d, J = 6.8 Hz, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 199.4, 136.7, 133.4, 125.7, 122.7, 121.6, 121.5, 114.9, 112.0, 35.8, 19.8.

GC–MS (EI, 70 eV) *m/z* 187 (25, [M^+]).

3-Pivaloylindole[1]

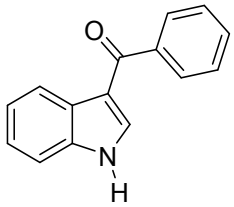


^{1}H NMR (300 MHz, DMSO-d_6) δ 11.84 (br s, 1H), 8.34 (s, 1H), 8.29–8.26 (m, 1H), 7.46–7.43 (m, 1H), 7.21–7.11 (m, 2H), 1.34 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 201.1, 135.6, 132.4, 127.2, 122.5, 122.0, 121.4, 112.2, 111.7, 43.4, 28.6.

GC–MS (EI, 70 eV) *m/z* 201 (15, [M^+]).

3-Benzoylindole[1,2]

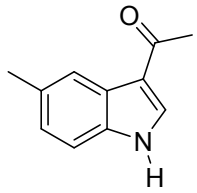


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (br s, 1H), 8.43 (dd, J = 6.2, 2.9 Hz, 1H), 7.84 (dd, J = 8.2, 1.3 Hz, 2H), 7.69 (d, J = 2.7 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.50–7.44 (m, 3H), 7.35–7.33 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.8, 140.7, 136.3, 133.5, 131.3, 128.8, 128.3, 126.40, 124.0, 122.8, 122.6, 111.3.

GC–MS (EI, 70 eV) *m/z* 221 (50, [M^+]).

3-Acetyl-5-methylindole[3]

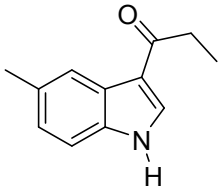


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (br s, 1H), 8.20 (s, 1H), 7.82 (d, J = 2.3 Hz, 1H), 7.30 (d, J = 8.3 Hz, 1H), 7.11 (m, 1H), 2.54 (s, 3H), 2.48 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 134.6, 132.3, 131.5, 125.7, 125.3, 122.1, 118.3, 110.9, 27.6, 21.6.

GC–MS (EI, 70 eV) *m/z* 173 (50, [M^+]).

3-Propionyl-5-methylindole



Pale yellow solid mp. 208-209 °C

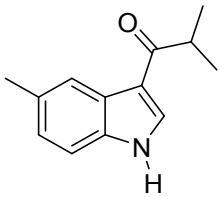
^{1}H NMR (300 MHz, DMSO-d_6) δ 11.75 (s, 1H), 8.23 (s, 1H), 8.041 (m, 1H), 7.34 (d, J = 8.3 Hz, 1H), 7.02 (m, 1H), 2.84 (q, J = 7.4 Hz, 2H), 2.38 (s, 3H), 1.10 (t, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 195.7, 134.9, 133.4, 130.2, 125.7, 124.1, 121.1, 115.6, 111.6, 31.7, 21.3, 9.2.

GC–MS (EI, 70 eV) *m/z* 187 ([M^+]).

HRMS (ESI) *m/z* calcd for ([M+Na]$^+$) $C_{12}H_{13}NONa^+$ 210.0889, found 210.0917

3-Isobutyryl-5-methylindole



Pale yellow solid mp. 210-211 °C

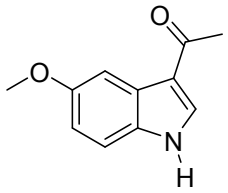
^{1}H NMR (300 MHz, DMSO-d_6) δ 11.76 (s, 1H), 8.26 (m, 1H), 8.00 (s, 1H), 7.31 (d, J = 8.3 Hz, 1H), 7.00 (m, 1H), 3.41 (hept, J = 6.8 Hz, 1H), 2.36 (s, 3H), 1.09 (d, J = 6.8 Hz, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 199.2, 135.0, 133.5, 130.3, 126.0, 124.1, 121.2, 114.6, 111.5, 35.7, 21.3, 19.8.

GC–MS (EI, 70 eV) *m/z* 201 ([M^+]).

HRMS (ESI) *m/z* calcd for ([M+Na]$^+$) $C_{12}H_{14}NONa^+$ 224.1046, found 224.1063

3-Acetyl-5-methoxyindole[3]

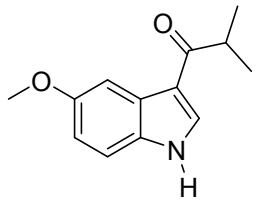


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (br s, 1H), 7.90 (d, J = 2.5 Hz, 1H), 7.81 (d, J = 3.1 Hz, 1H), 7.29 (d, J = 8.8 Hz, 1H), 6.93 (dd, J = 8.8, 2.5 Hz, 1H), 3.90 (s, 3H), 2.53 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 156.4, 131.6, 126.2, 117.4, 114.4, 112.0, 106.7, 103.7, 55.8, 27.4.

GC–MS (EI, 70 eV) *m/z* 189 (50, $[M^+]$).

3-Isobutyryl-5-methoxyindole



White solid, mp. 158-159 ^{o}C

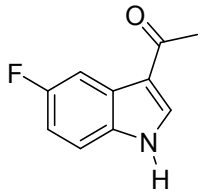
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.97 (m, 1H), 7.85 (m, 1H), 7.29 (d, J = 8.8 Hz, 1H), 6.92 (m, 1H), 3.87 (s, 3H), 3.32 (hept, J = 6.8 Hz, 1H), 1.26 (d, J = 6.8 Hz, 7H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 201.1, 156.4, 131.2, 131.0, 126.7, 116.5, 114.4, 112.1, 103.6, 55.7, 37.1, 19.8.

GC–MS (EI, 70 eV) *m/z* 217 (25, $[M^+]$).

HRMS (ESI) *m/z* calcd for ($[M+Na]^+$) $C_{13}H_{15}NO_2Na^+$ 240.0995, found 240.1035

3-Acetyl-5-fluoroindole[4]

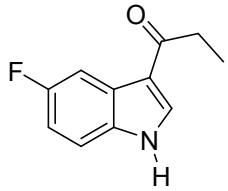


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (br s, 1H), 8.20 (dd, J = 2.5 Hz, 1H), 7.97 (d, J = 3.0 Hz, 1H), 7.32 (dd, J = 4.5 Hz, 4.0 Hz, 1H), 7.02 (dt, J = 2.5 Hz, 1H), 1.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 159.7 (d, J = 235.5 Hz), 131.7, 131.1, 112.1 (d, J = 26.5 Hz), 111.6 (d, J = 9.8 Hz), 111.5, 108.7, 108.5, 28.8.

GC–MS (EI, 70 eV) *m/z* 177 (50, [M^+]).

3-Propionyl-5-fluoroindole[4]

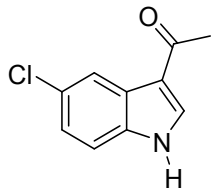


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.08 (dd, J = 9.7, 2.5 Hz, 1H), 7.90 (d, J = 2.5 Hz, 1H), 7.33 (dd, J = 8.8, 4.3 Hz, 1H), 7.03 (td, J = 8.9, 2.5 Hz, 1H), 2.90 (q, J = 7.4 Hz, 2H), 1.26 (t, J = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.6, 159.6 (d, J = 239.4 Hz), 132.3 (d, J = 20.8 Hz), 126.3 (d, J = 11.1 Hz), 118.1, 112.2 (d, J = 25.0 Hz), 107.9 (d, J = 25.0 Hz), 32.9, 8.8.

GC–MS (EI, 70 eV) *m/z* 191 (25, [M^+]).

3-Acetyl-5-chloroindole[5,6]

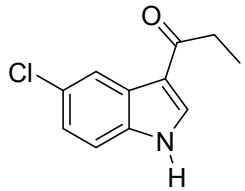


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (br s, 1H), 8.40 (d, J = 1.9 Hz, 1H), 7.86 (s, 1H), 7.33 (d, J = 8.6 Hz, 1H), 7.24 (d, J = 2.0 Hz, 1H), 2.54 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1, 134.6, 132.1, 128.7, 126.5, 124.3, 122.1, 118.4, 112.3, 27.6.

GC–MS (EI, 70 eV) *m/z* 193 (25, $[M^+]$).

3-Propionyl-5-chloroindole[7]

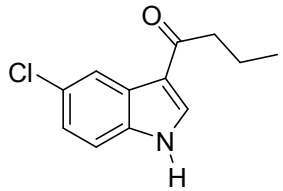


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (br s, 1H), 8.41 (d, J = 1.9 Hz, 1H), 7.88 (d, J = 2.4 Hz, 1H), 7.33 (d, J = 8.6 Hz, 1H), 7.24 (m, 1H), 2.90 (q, J = 7.4 Hz, 2H), 1.26 (t, J = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.5, 138.7, 137.3, 134.6, 131.3, 124.1, 122.2, 117.7, 112.2, 33.0, 29.7, 8.8.

GC–MS (EI, 70 eV) *m/z* 207 (25, $[M^+]$).

3-Butyryl-5-chloroindole



Pale yellow solid, mp. 214-215 °C

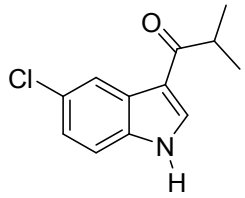
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.42 (m, 1H), 7.87 (m, 1H), 7.33 (m, 1H), 7.24 (*m*, 1H), 2.83 (t, J = 7.4 Hz, 2H), 1.80 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.1, 134.6, 131.6, 130.2, 126.6, 124.1, 122.2, 118.1, 112.2, 41.7, 18.4, 14.0.

GC–MS (EI, 70 eV) *m/z* 221 (25, $[M^+]$).

HRMS (ESI) *m/z* calcd for ($[M+Na]^+$) $C_{12}H_{12}ClNONa^+$ 244.0499, found 244.0472

3-Isobutyryl-5-chloroindole



Pale yellow solid, mp. 198-199 °C

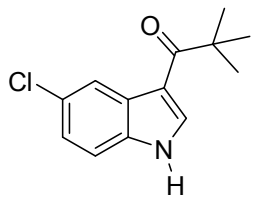
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.44 (m, 1H), 7.89 (d, J = 2.7 Hz, 1H), 7.33 (d, J = 8.6 Hz, 1H), 7.24 (m, 1H), 3.31 (hept, J = 6.8 Hz, 1H), 1.26 (d, J = 6.8 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 200.4, 134.7, 131.3, 128.6, 127.0, 124.1, 122.3, 116.7, 112.2, 37.3, 19.6.

GC–MS (EI, 70 eV) *m/z* 221 (25, $[M^+]$).

HRMS (ESI) *m/z* calcd for ($[M+Na]^+$) $C_{12}H_{11}ClNONa^+$ 244.0499, found 244.0537

3-Pivaloyl-5-chloroindole[8]

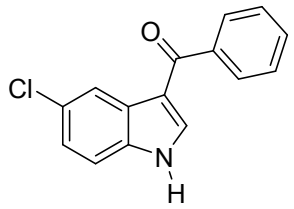


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (br s, 1H), 8.53 (d, J = 2.0 Hz, 1H), 7.95 (d, J = 3.0 Hz, 1H), 7.31 (d, J = 8.6 Hz, 1H), 7.23 (dd, J = 8.6, 2.0 Hz, 1H), 1.41 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 133.6, 130.7, 128.6, 128.5, 124.1, 122.9, 114.2, 111.9, 44.2, 28.8.

GC–MS (EI, 70 eV) *m/z* 235 (15, [M^+]).

3-Benzoyl-5-chloroindole[9]

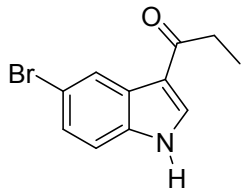


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (br s, 1H), 8.44 (d, J = 1.8 Hz, 1H), 7.83–7.82 (m, 2H), 7.70 (d, J = 2.7 Hz, 1H), 7.56 (m, 1H), 7.50 (m, 2H), 7.37 (d, J = 8.7 Hz, 1H), 7.29 (dd, J = 8.6, 2.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$ and DMSO-d_6) δ 195.6, 145.3, 140.7, 140.6, 140.2, 136.0, 133.3, 133.1, 132.4, 128.3, 126.3, 120.4, 118.0.

GC–MS (EI, 70 eV) *m/z* 255 (60, [M^+]).

3-Propionyl-5-bromoindole[10]

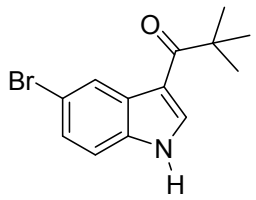


^{1}H NMR (300 MHz, DMSO-d_6) δ 12.06 (s, 1H), 8.35 (s, 1H), 8.31 (d, J = 2.0 Hz, 1H), 7.41 (d, J = 8.6 Hz, 1H), 7.31 (m, 1H), 2.85 (q, J = 7.4 Hz, 2H), 1.08 (t, J = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 196.4, 135.8, 135.2, 127.6, 125.7, 123.9, 115.9, 114.8, 114.6, 32.3, 9.4.

GC–MS (EI, 70 eV) *m/z* 253 (25, [M^+]).

3-Pivaloyl-5-bromoindole



White solid, mp. 234-235 °C

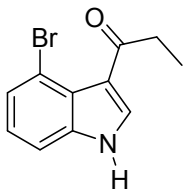
^{1}H NMR (300 MHz, DMSO-d_6) δ 12.04 (s, 1H), 8.42 (m, 1H), 8.40 (s, 1H), 7.41 (dd, J = 8.6, 0.5 Hz, 1H), 7.30 (m, 1H), 1.31 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 201.1, 134.3, 133.5, 128.9, 125.0, 124.1, 114.2, 113.7, 111.6, 43.3, 28.3.

GC–MS (EI, 70 eV) *m/z* 279 (15, [M^+]).

HRMS (ESI) *m/z* calcd for ([M+Na]$^+$) $C_{13}H_{14}BrNONa^+$ 302.0151, found 302.0186

3-Propionyl-4-bromoindole



Reddish brown solid, mp. 112-113 °C

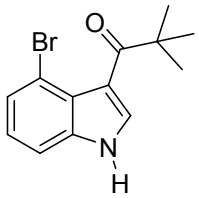
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.40 (m, 1H), 7.33 (m, 1H), 7.24 (dd, J = 2.3, 0.9 Hz, 1H), 7.19 (m, 1H), 3.04 (q, J = 7.4 Hz, 2H), 1.30 (t, J = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 194.1, 137.4, 135.1, 128.5, 126.8, 123.7, 116.8, 111.5, 108.9, 31.6, 8.6.

GC–MS (EI, 70 eV) *m/z* 251 (70, [M^+]).

HRMS (ESI) *m/z* calcd for ([M+Na]$^+$) $C_{11}H_9BrNONa^+$ 273.9838, found 273.9814

3-Pivaloyl-4-bromoindole



Pale yellow solid, mp. 154 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (s, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.32 (m, 1H), 7.25 (dd, J = 2.3, 0.9 Hz, 1H), 7.17 (m, 1H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 136.1, 132.5, 128.7, 126.6, 123.6, 116.8, 111.2, 108.8, 43.5, 28.4.

GC–MS (EI, 70 eV) *m/z* 279 (40, $[M^+]$).

HRMS (ESI) *m/z* calcd for ($[M+Na]^+$) $C_{13}H_{14}BrNONa^+$ 302.0151, found 302.0189

Section S5. Reference

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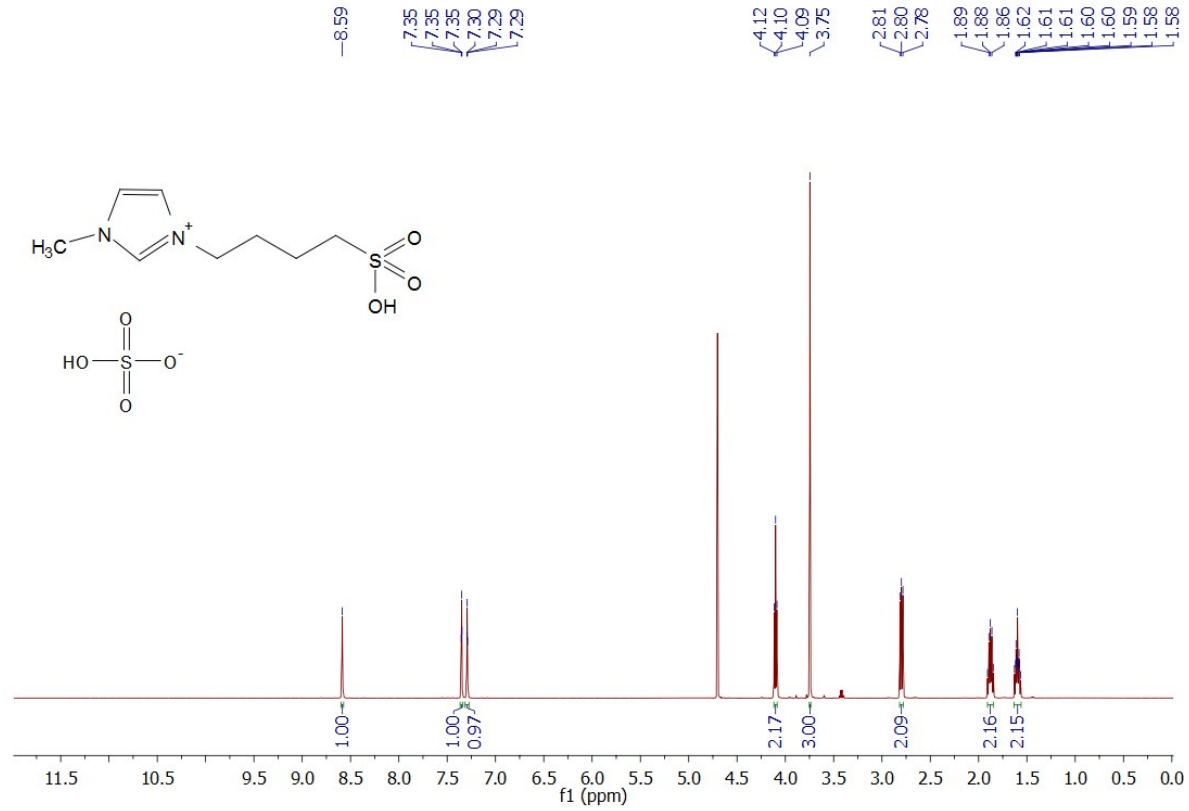
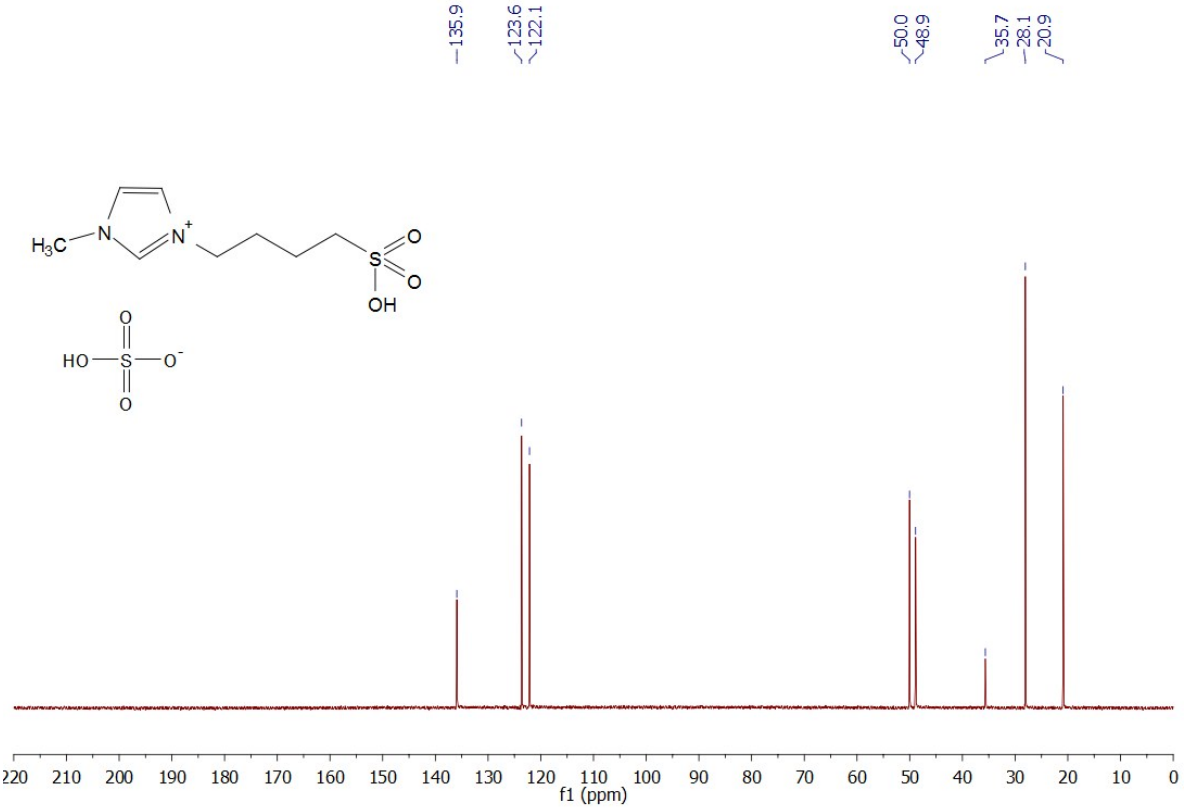
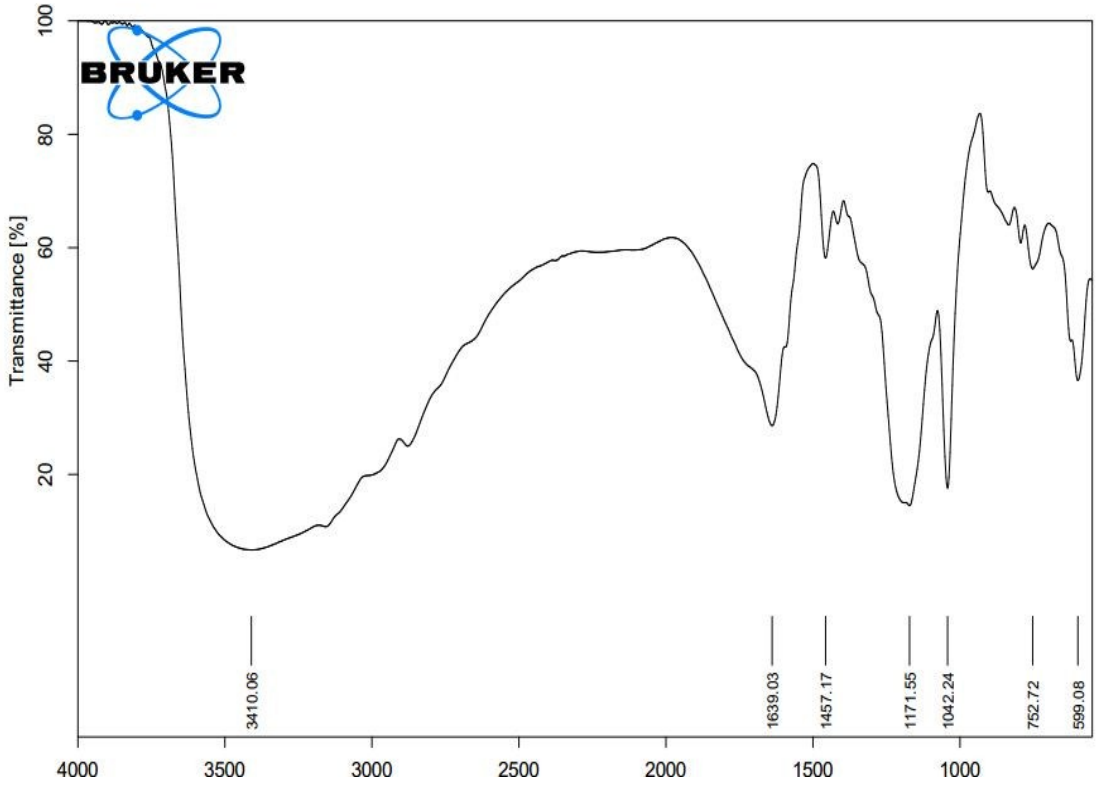
Section S6. ^{1}H, ^{13}C NMR and HRMS spectra

^{1}H NMR, ^{13}C NMR, IR, and HR-ESI-MS of 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate (BAIL)






BRUKER
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1171.55
1042.24
752.72
599.08
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3500
3000
2500
2000
1500
1000

Display Report

Analysis Info

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Comment	10 ML CR3 QUA C18, RUA GIAI BANG 1 ML MEOH		

Acquisition Parameter

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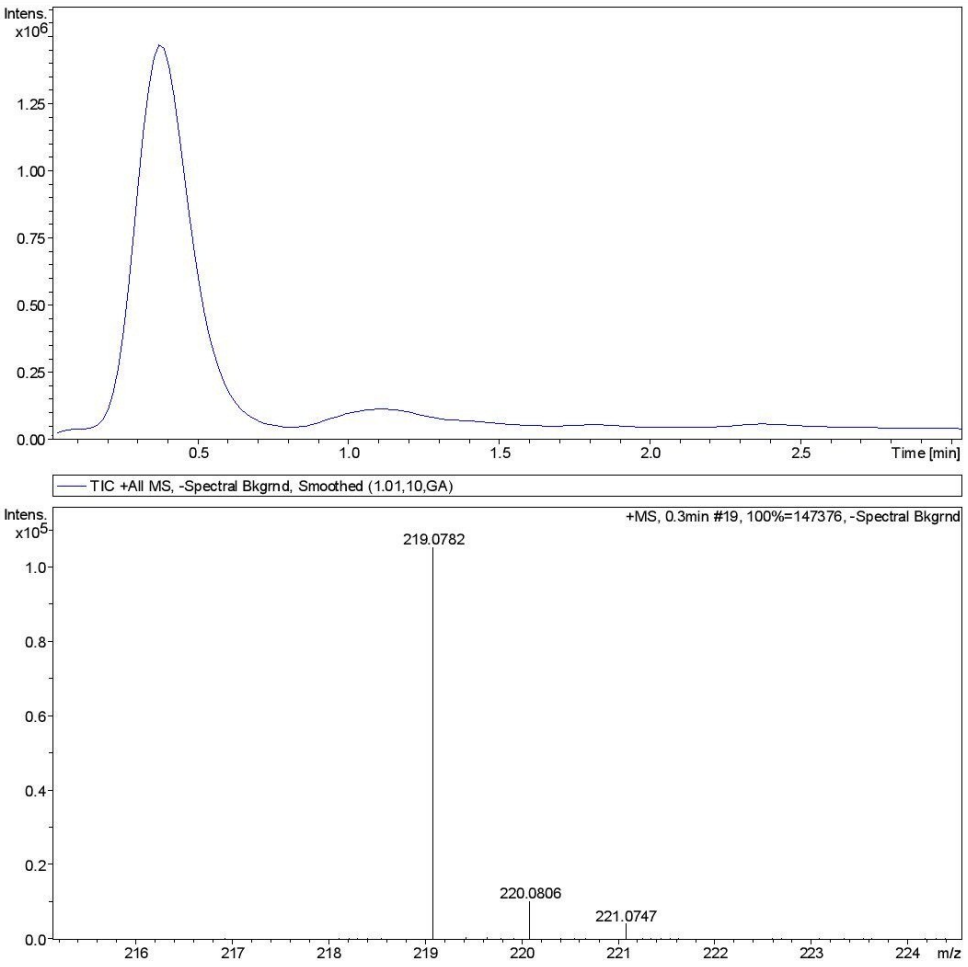
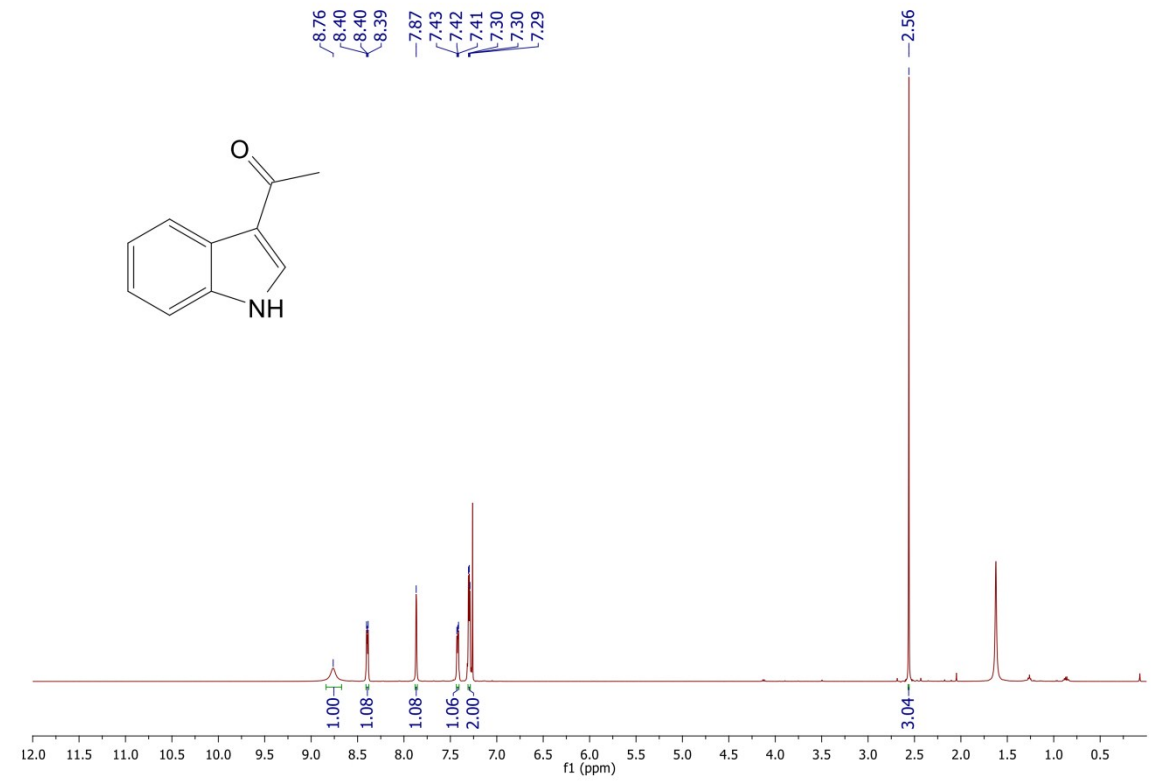
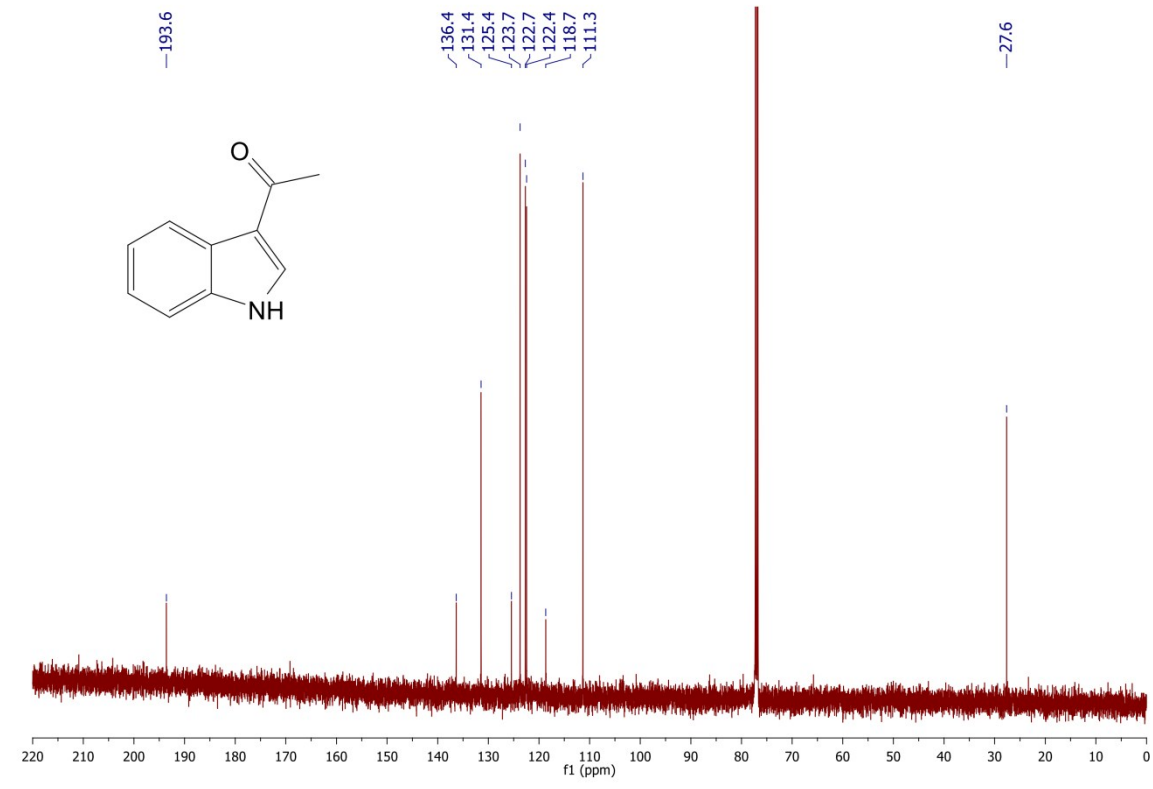
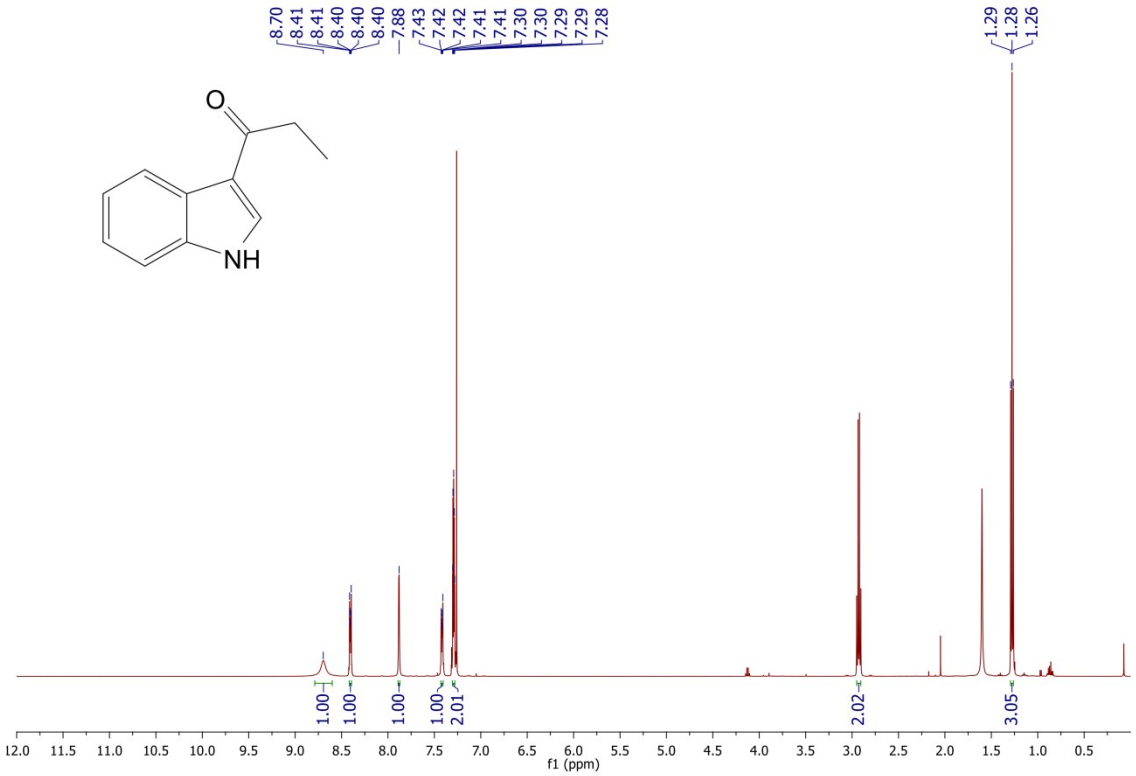


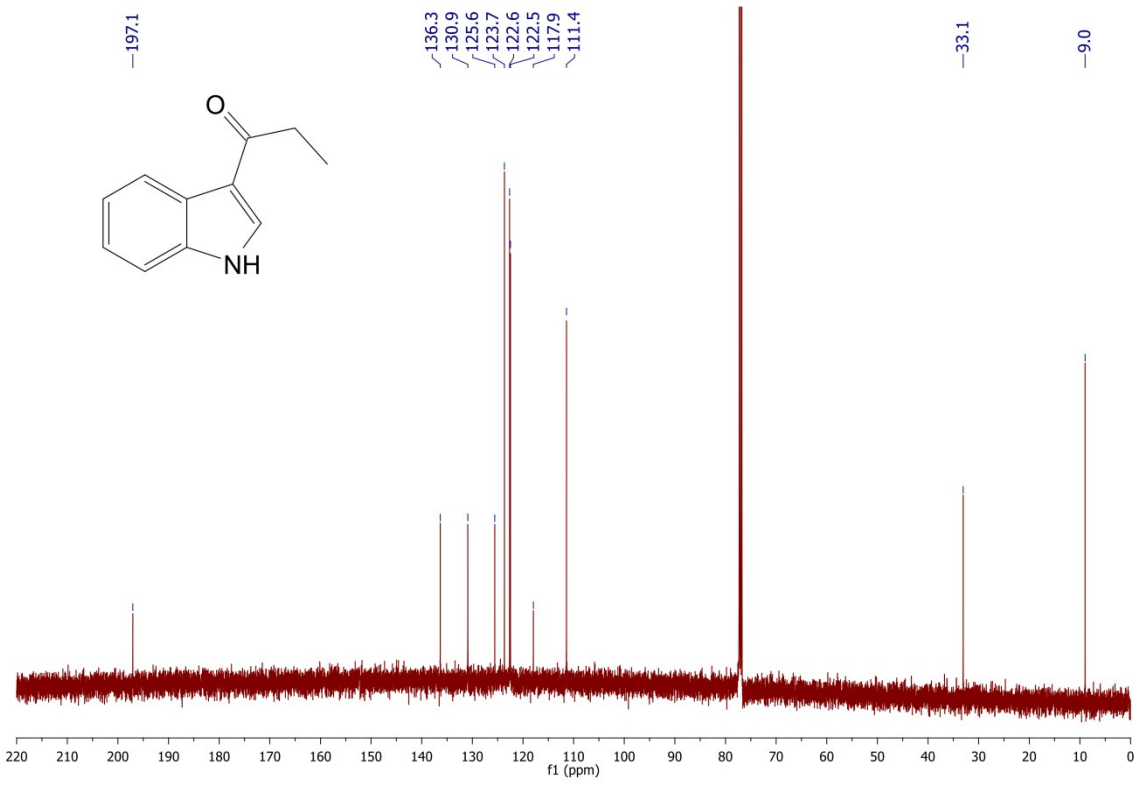
^{1}H NMR, ^{13}C NMR of 3-Acetylindole



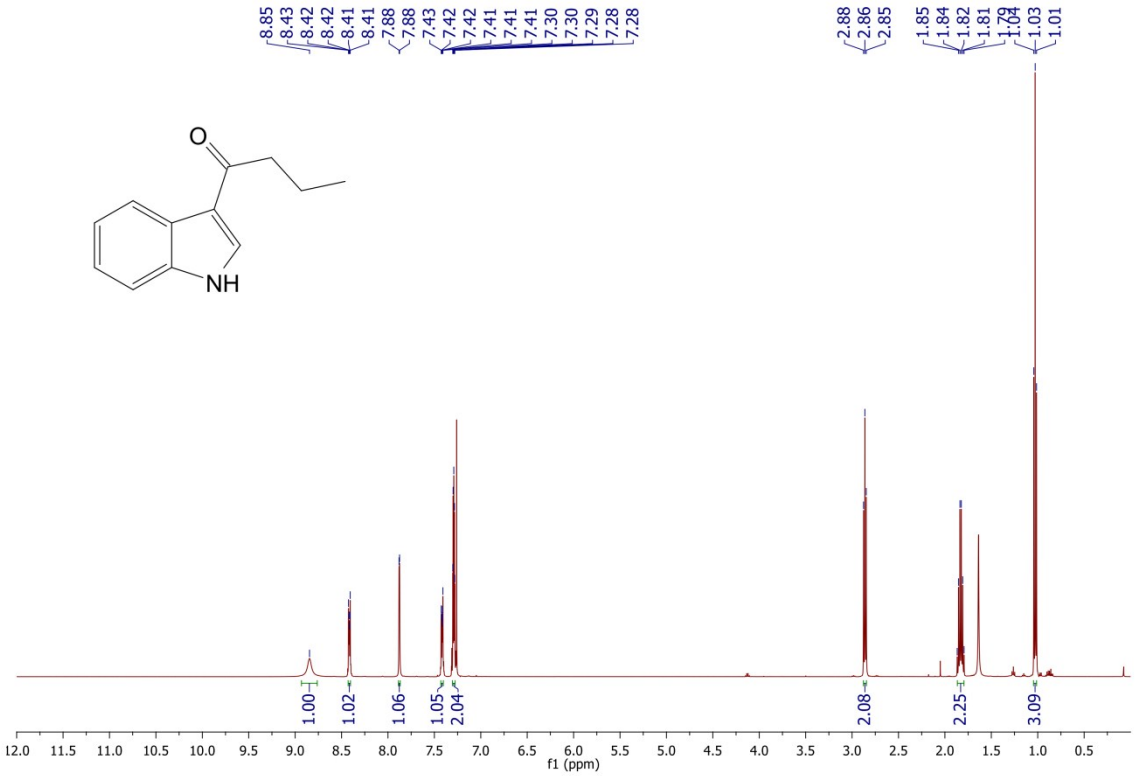


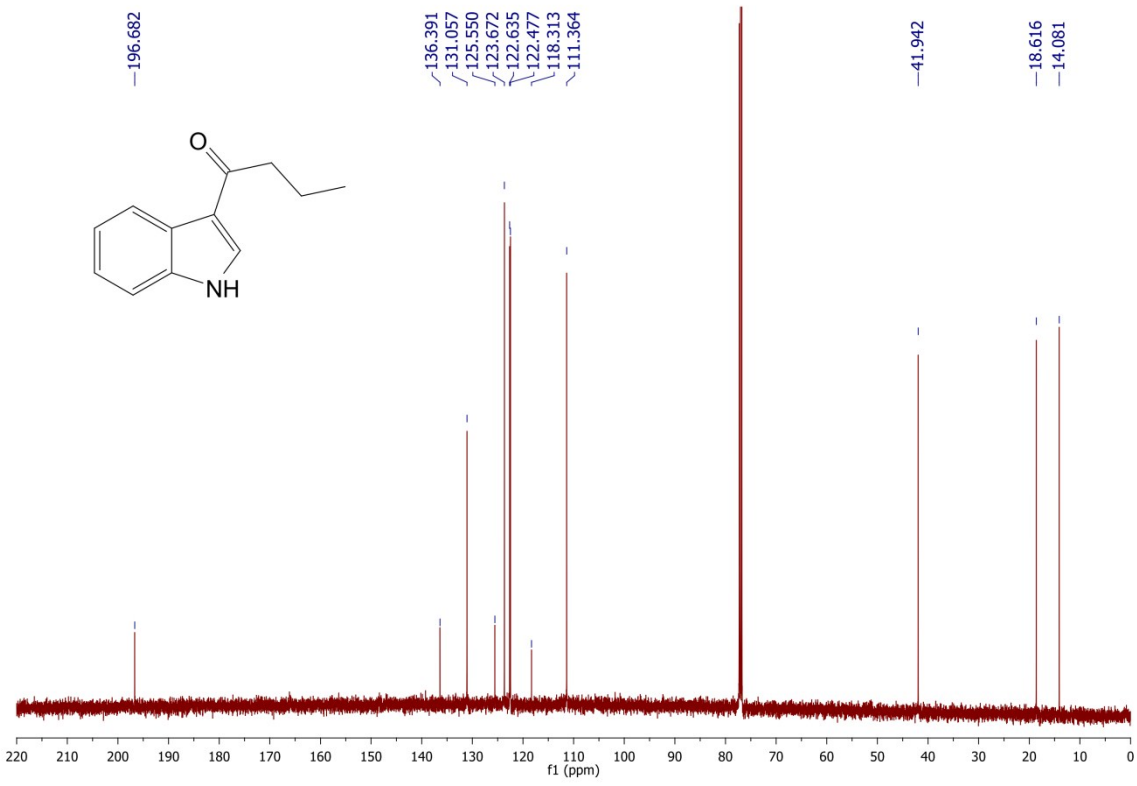
^{1}H NMR, ^{13}C NMR of 3-Propionylindole



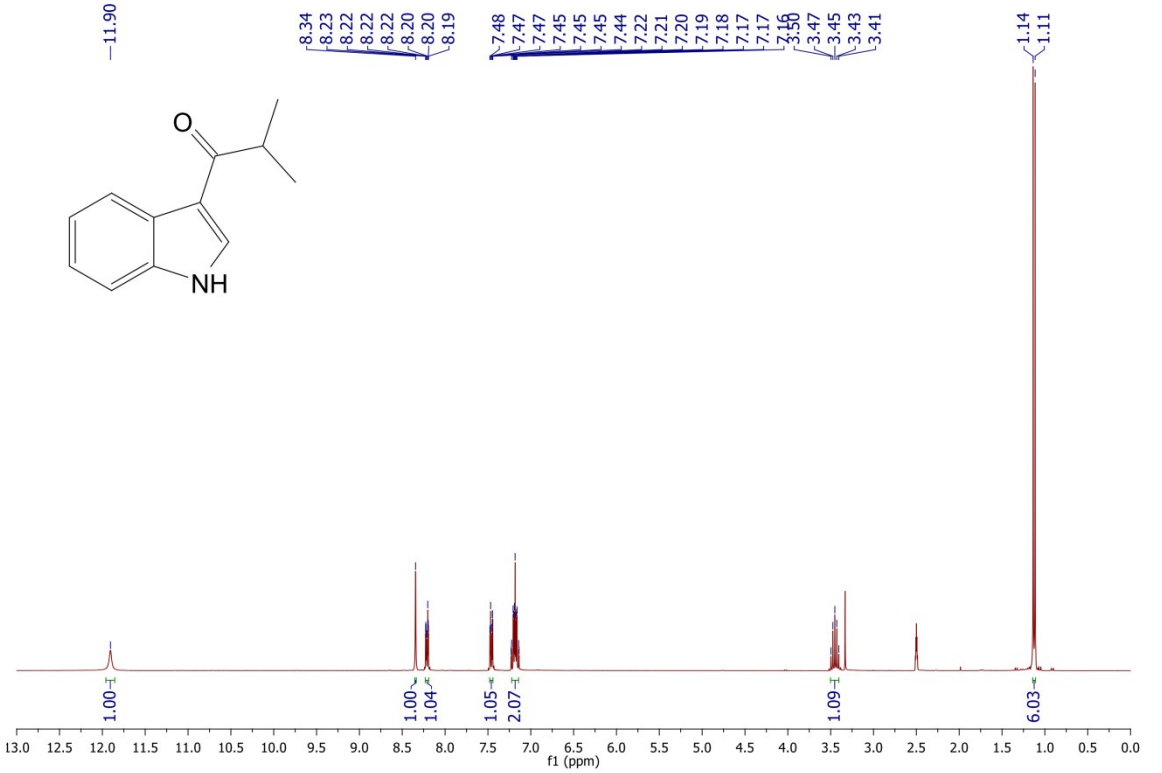


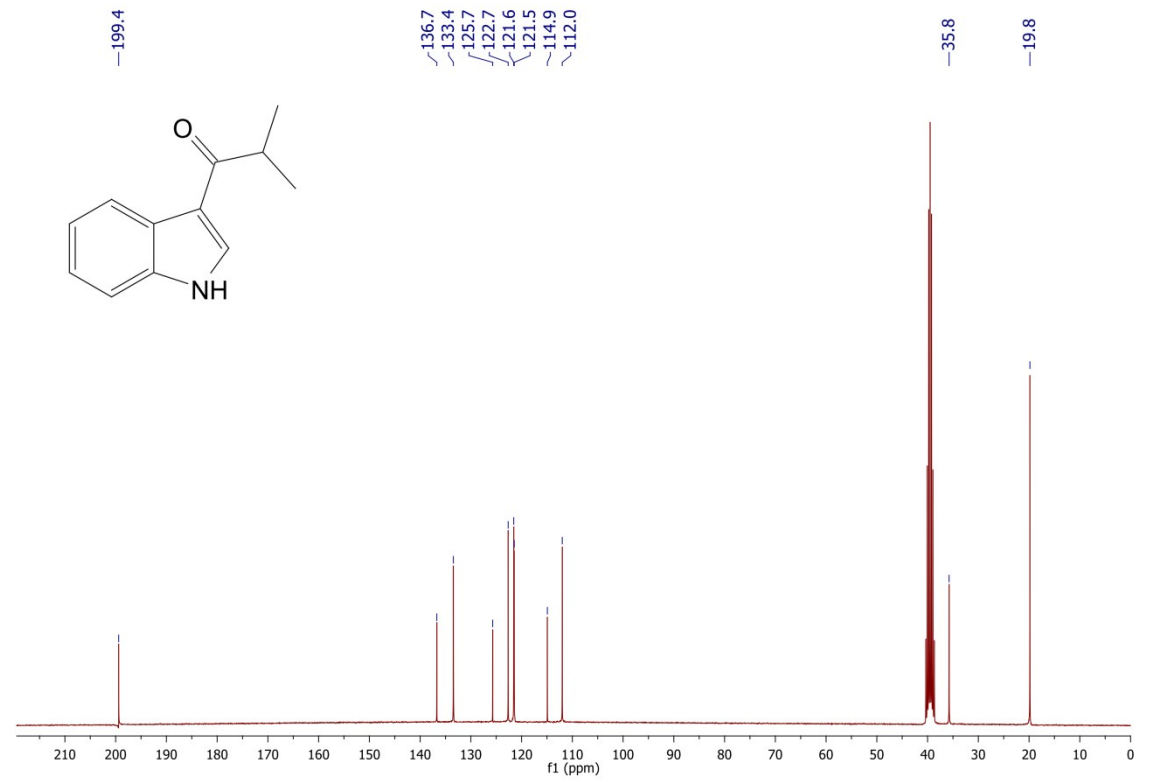
^{1}H NMR, ^{13}C NMR of 3-Butyrylindole



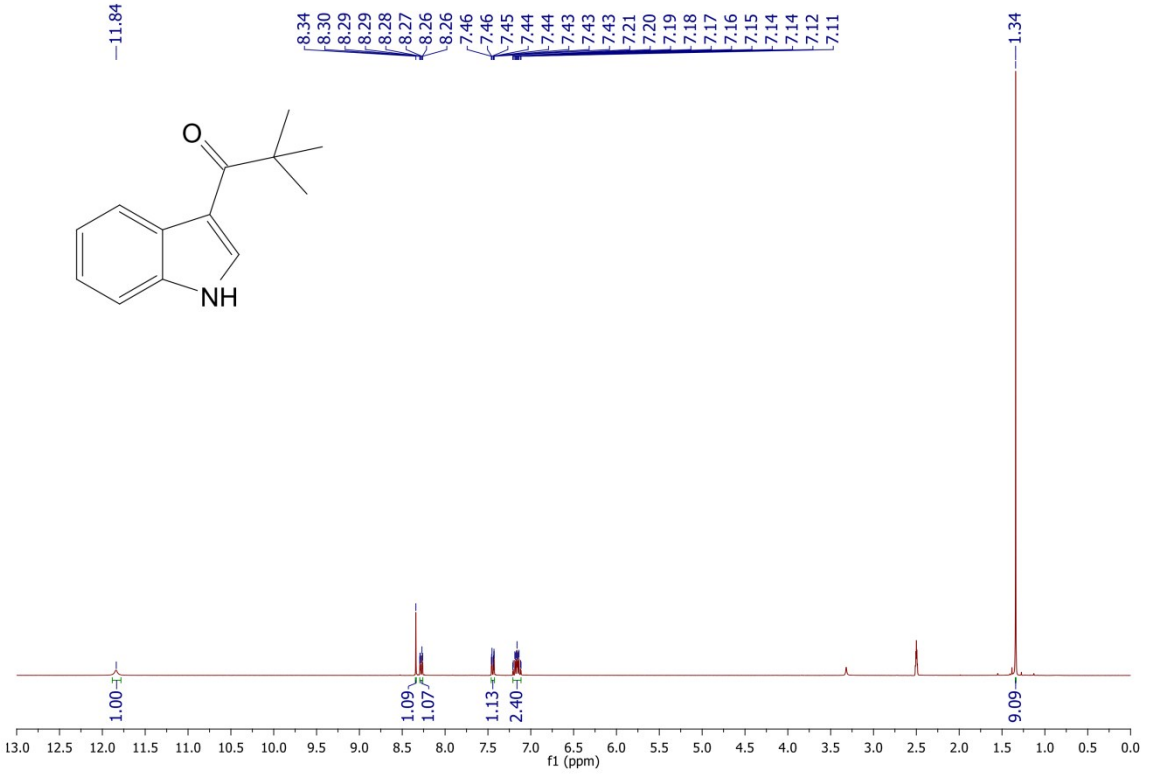


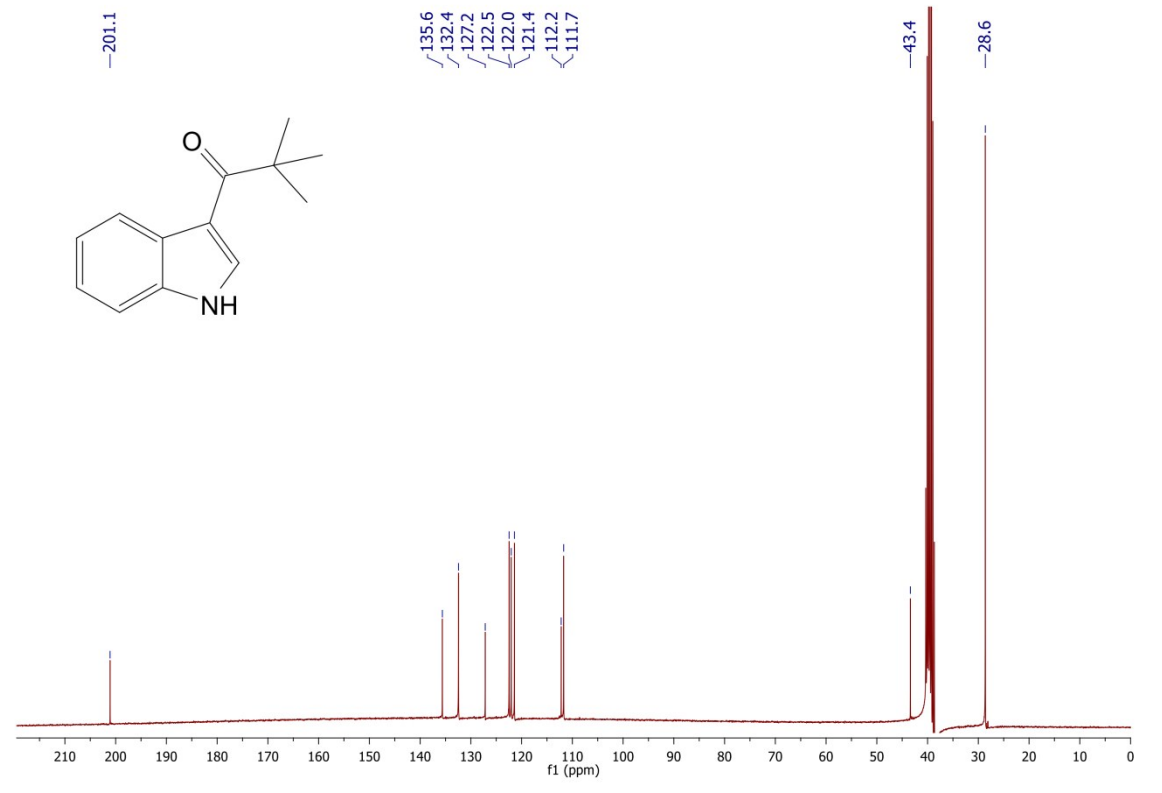
^{1}H NMR, ^{13}C NMR of 3-Isobutyrylindole



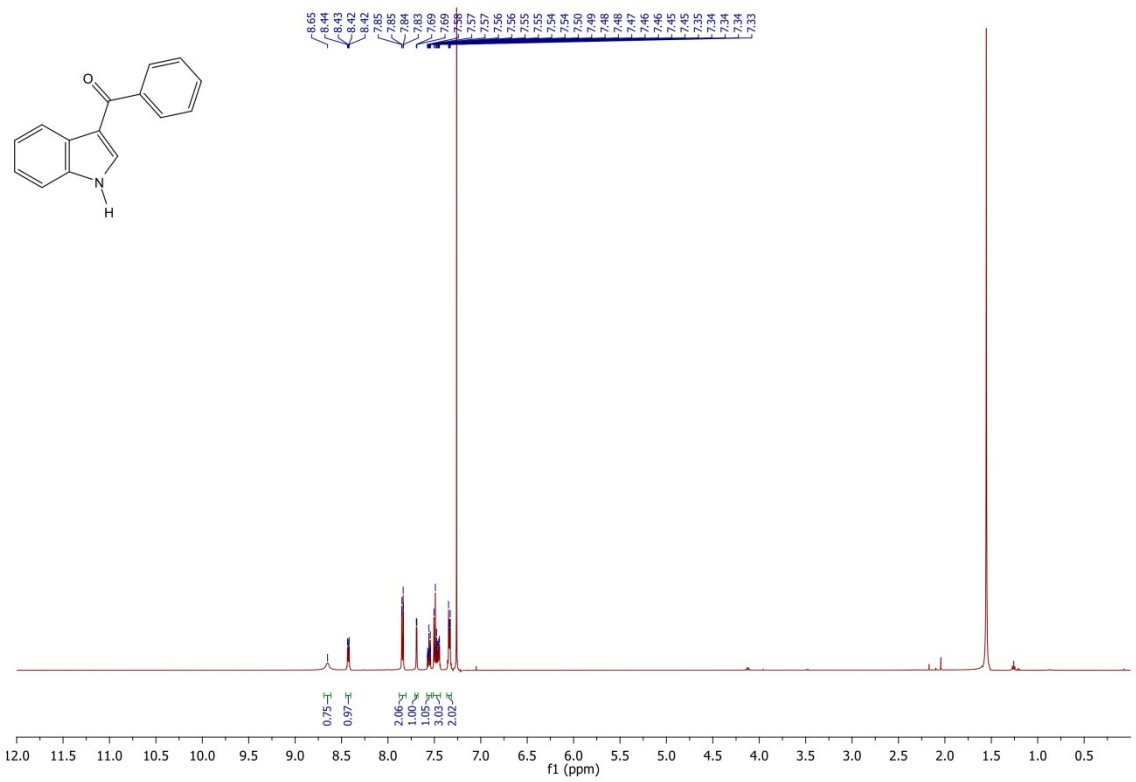


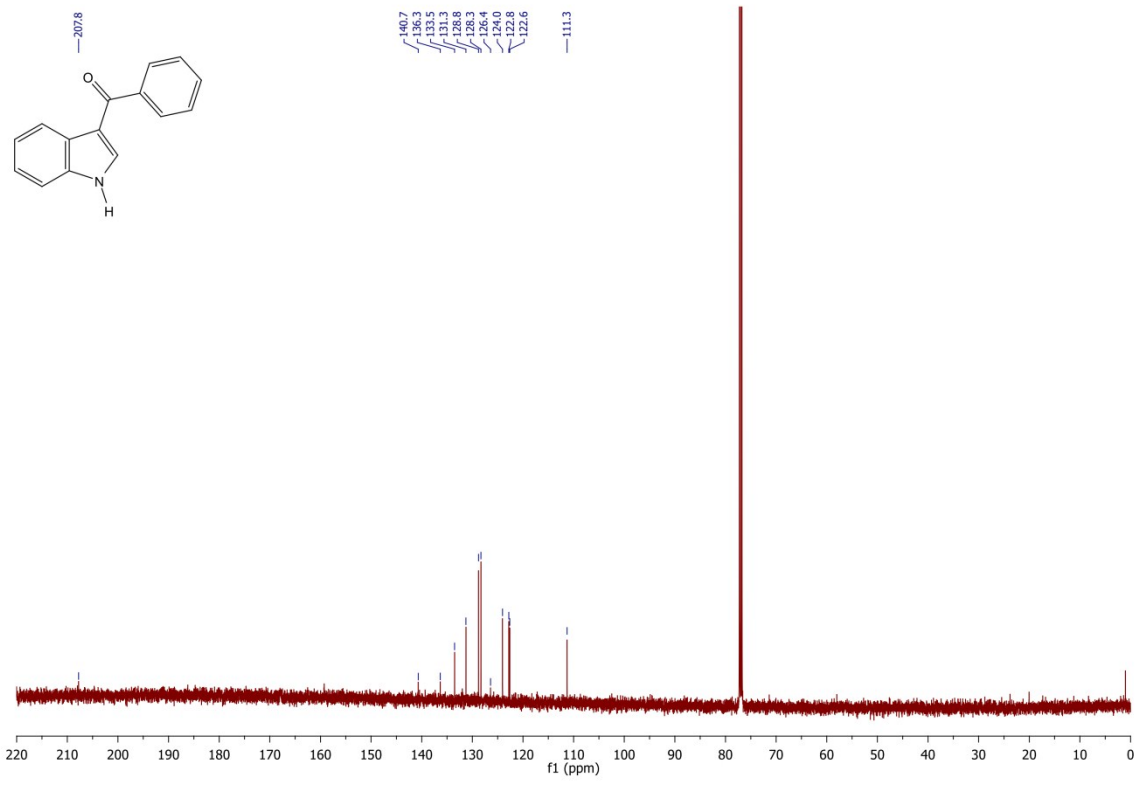
^{1}H NMR, ^{13}C NMR of 3-Pivaloylindole



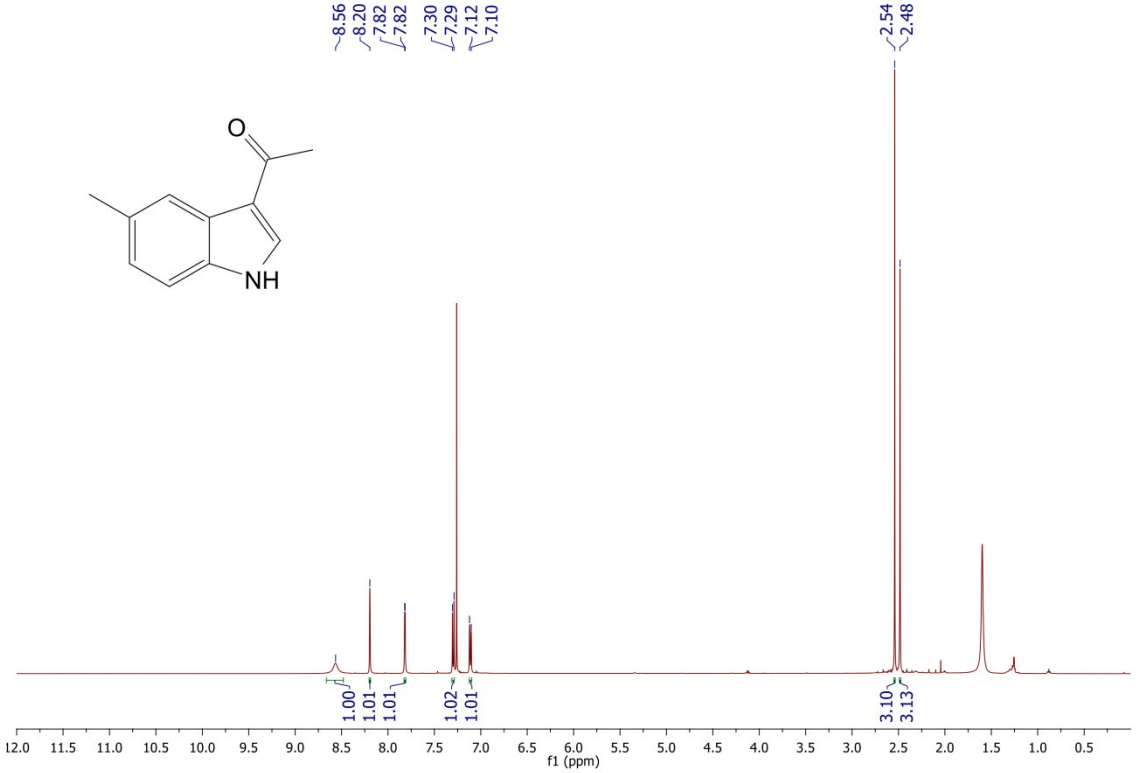


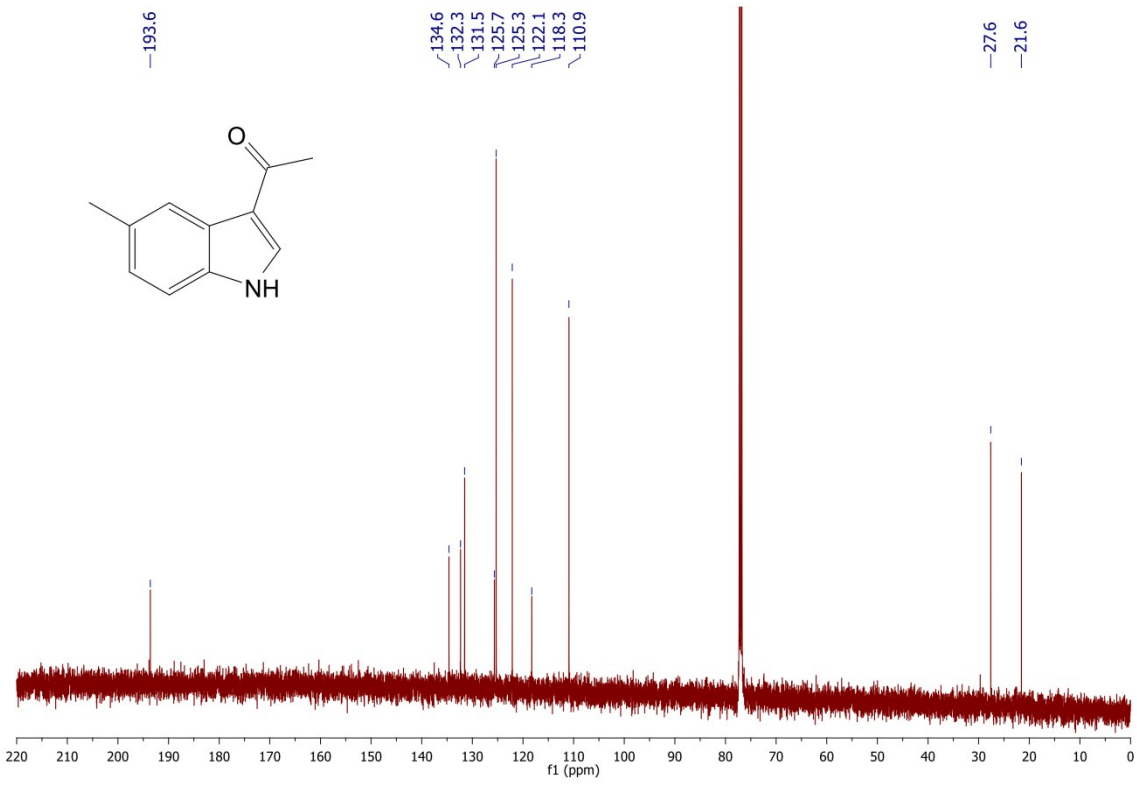
^{1}H NMR, ^{13}C NMR of 3-Benzoylindole



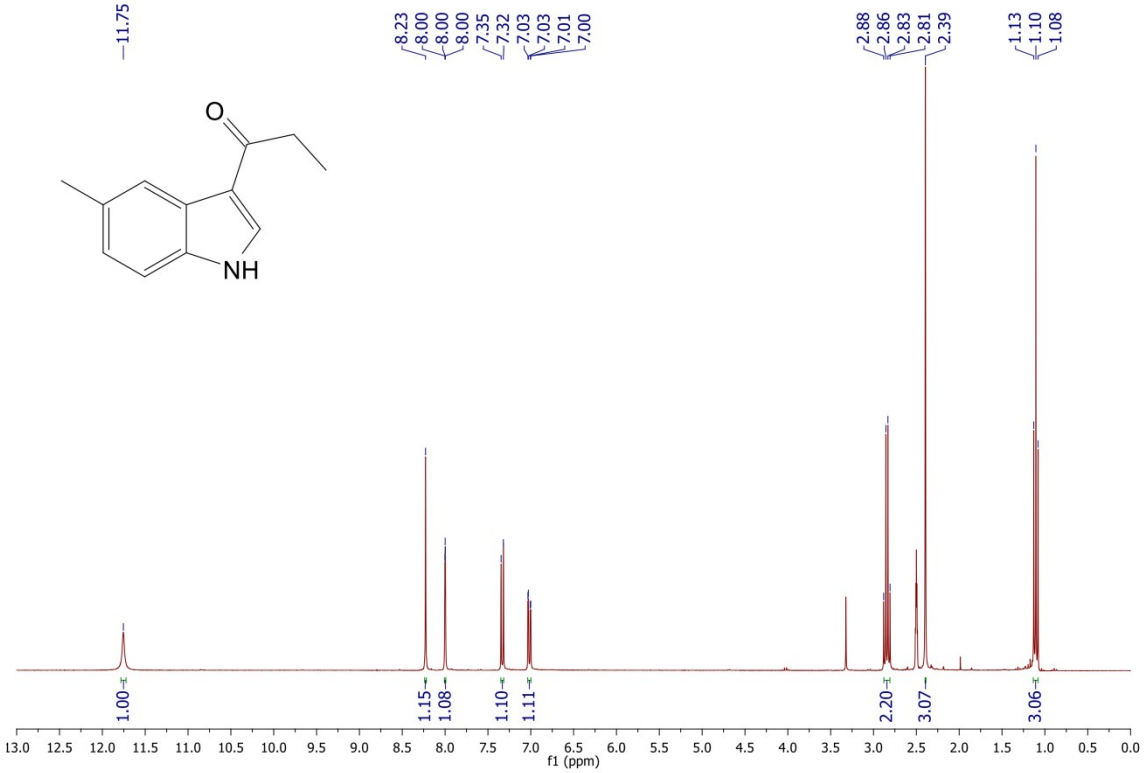


^{1}H NMR, ^{13}C NMR of 3-Acetyl-5-methylindole





^{1}H NMR, ^{13}C NMR and HR-MS of 3-Propionyl-5-methylindole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8.00
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7.32
7.03
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7.01
7.00
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2.86
2.83
2.81
2.39
1.13
1.10
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NH
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1.08
1.10
1.11
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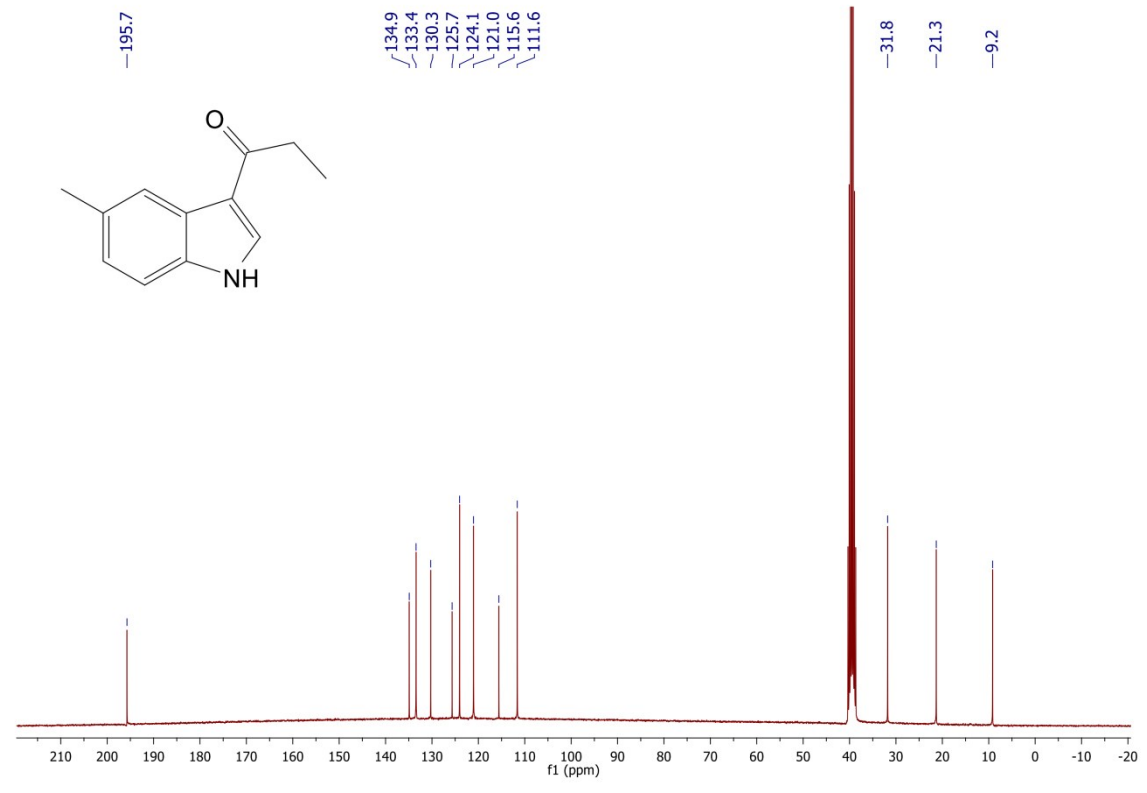
3.06
f1 (ppm)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115.6
111.6
31.8
21.3
9.2
O
NH
f1 (ppm)

Display Report

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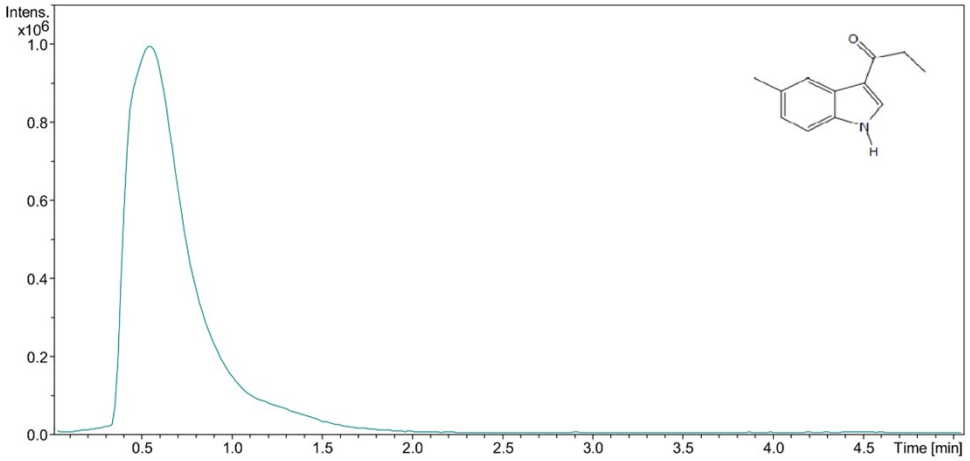

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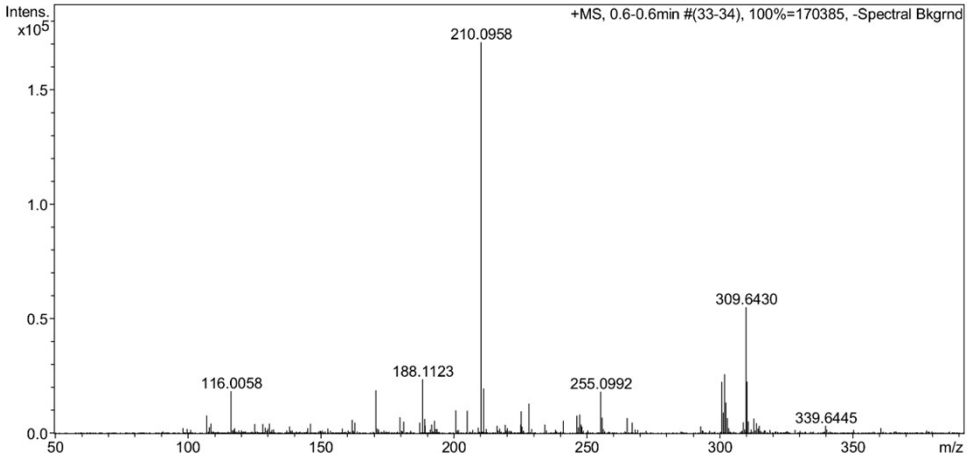
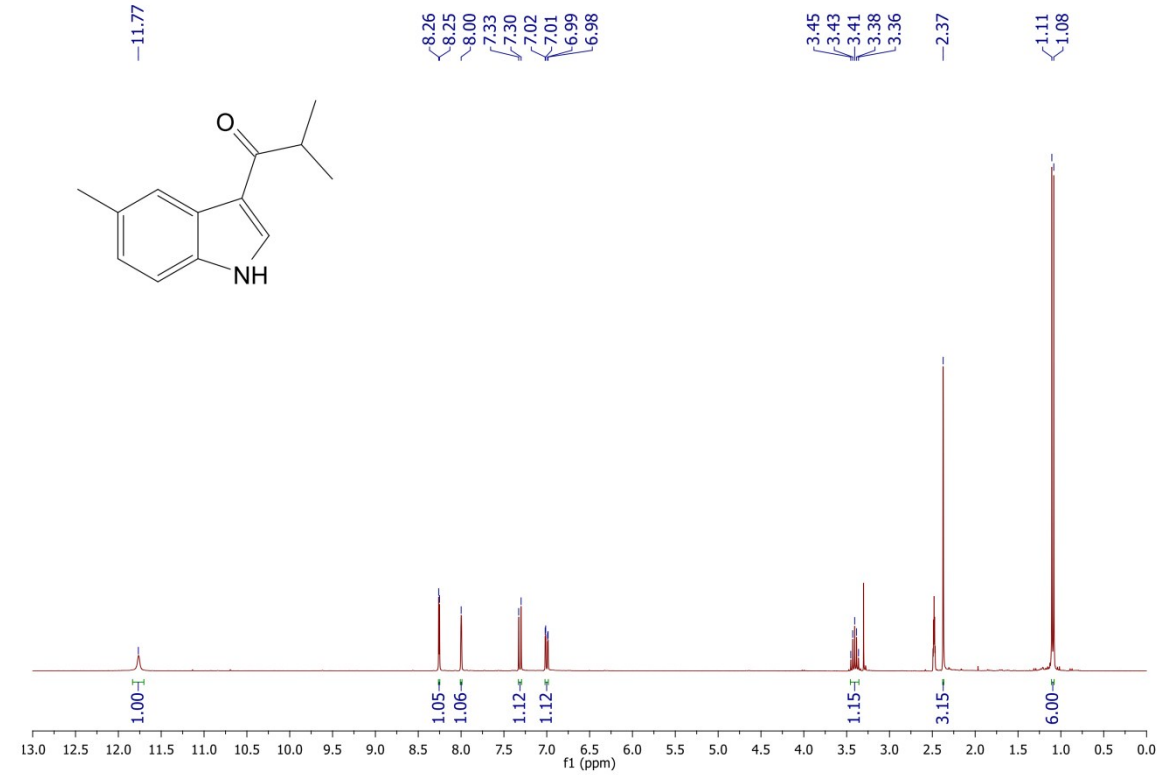
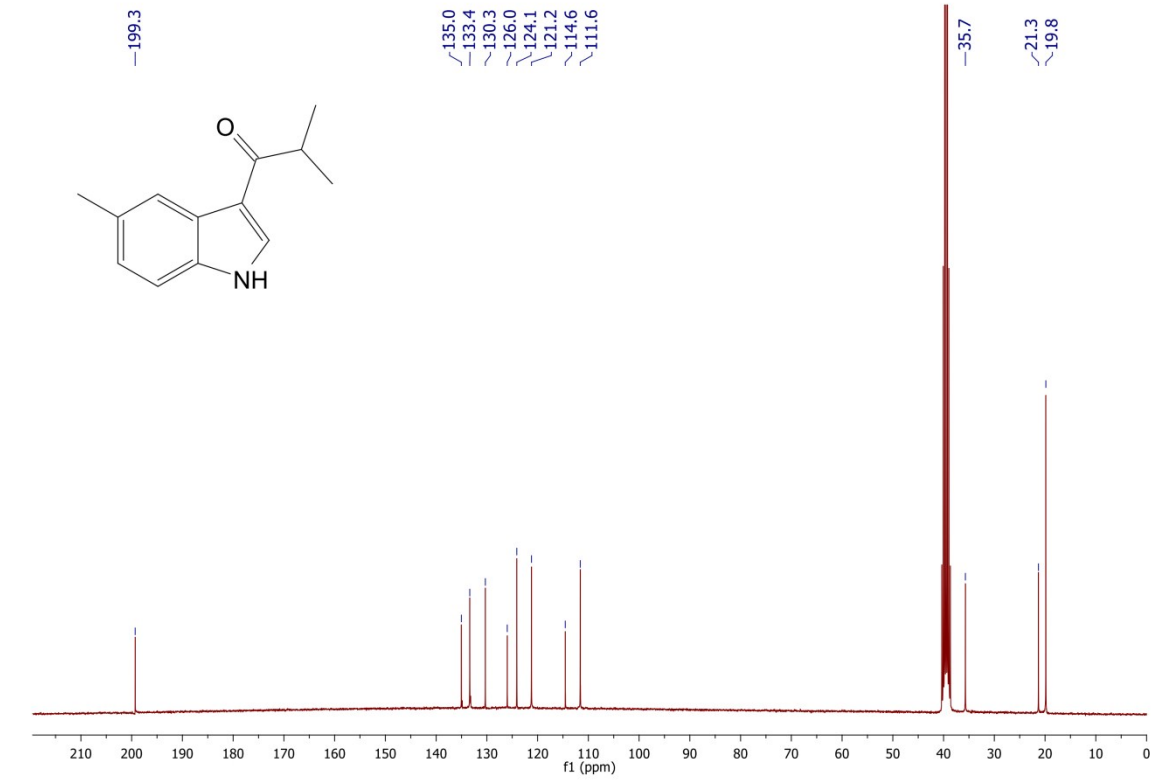


^{1}H NMR, ^{13}C NMR and HR-MS of 3-Isobutyryl-5-methylindole





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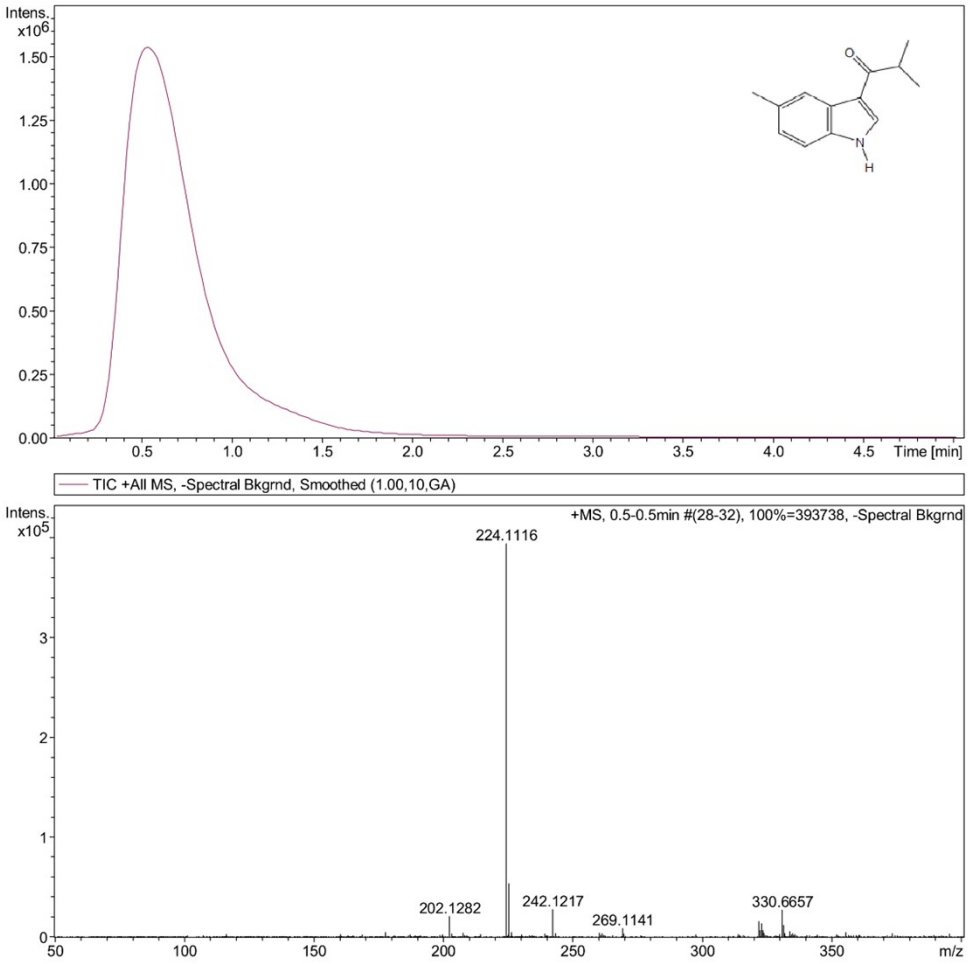

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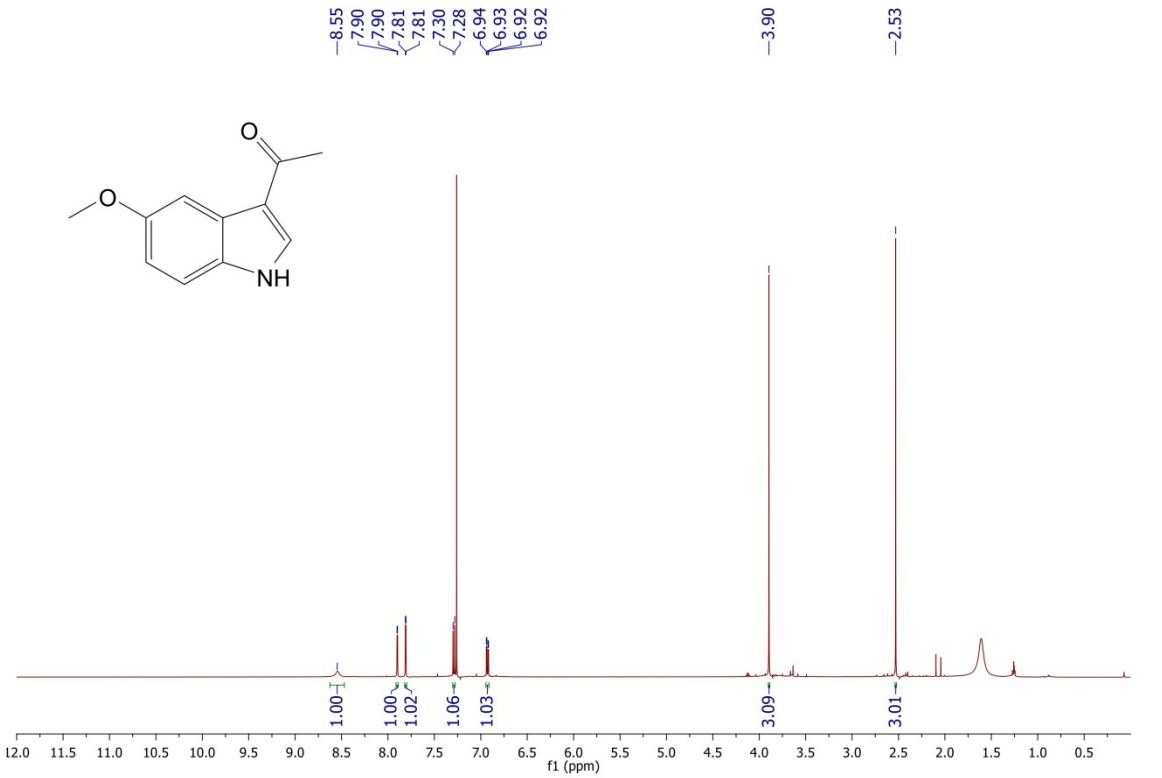
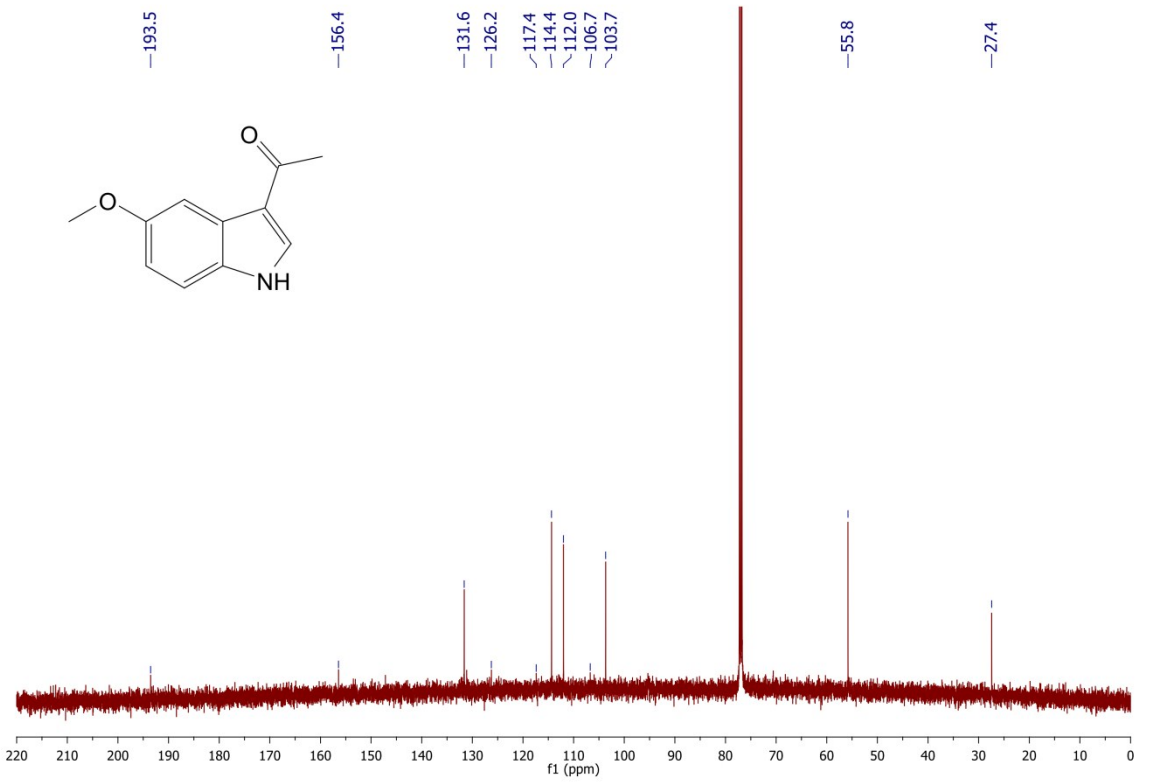
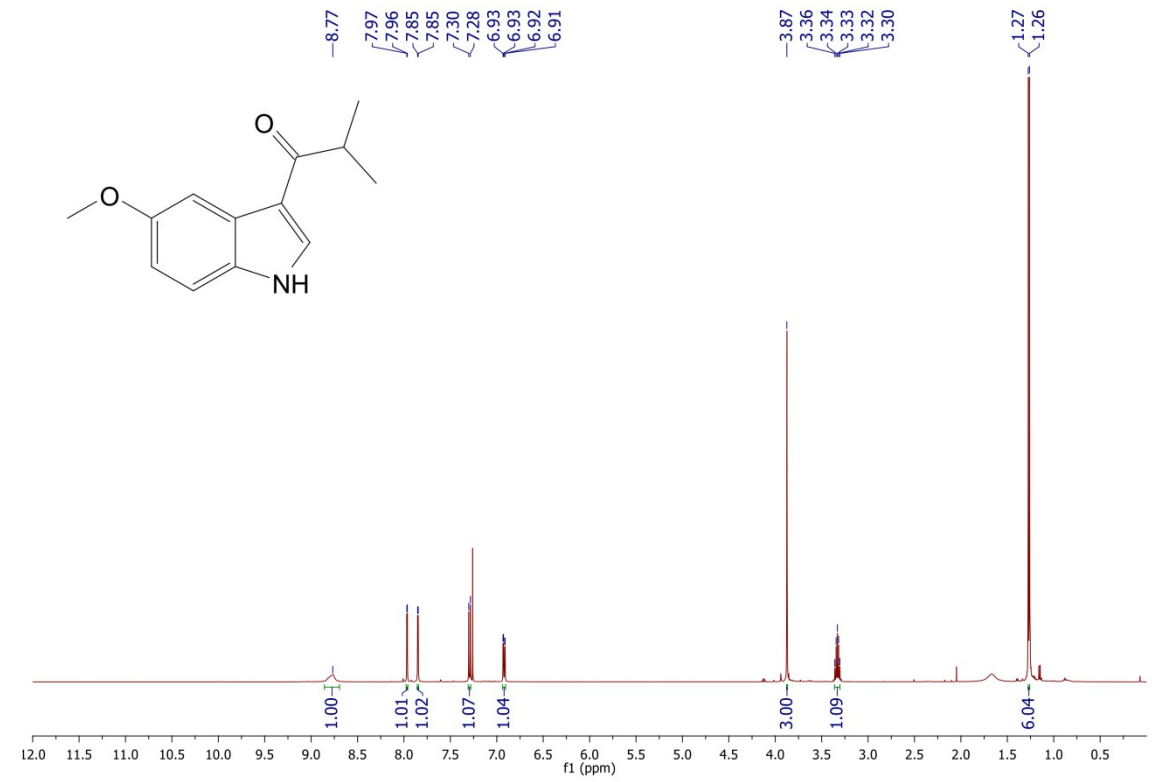
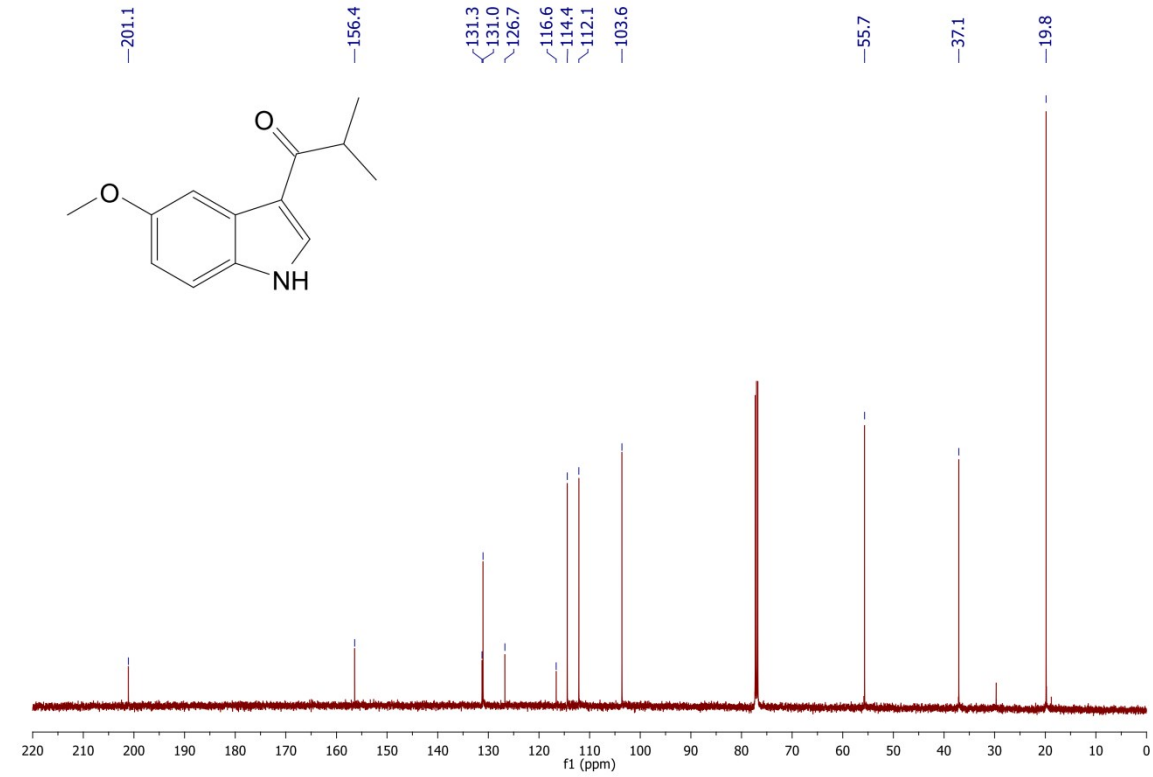
^{1}H NMR, ^{13}C NMR of 3-Acetyl-5methoxyindole





^{1}H NMR, ^{13}C NMR and HR-MS of 3-Isobutyryl-5-methoxyindole





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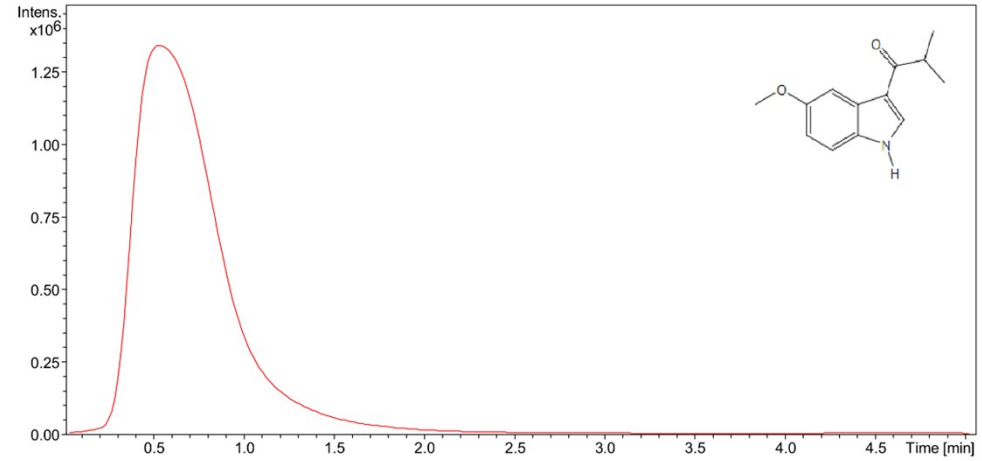
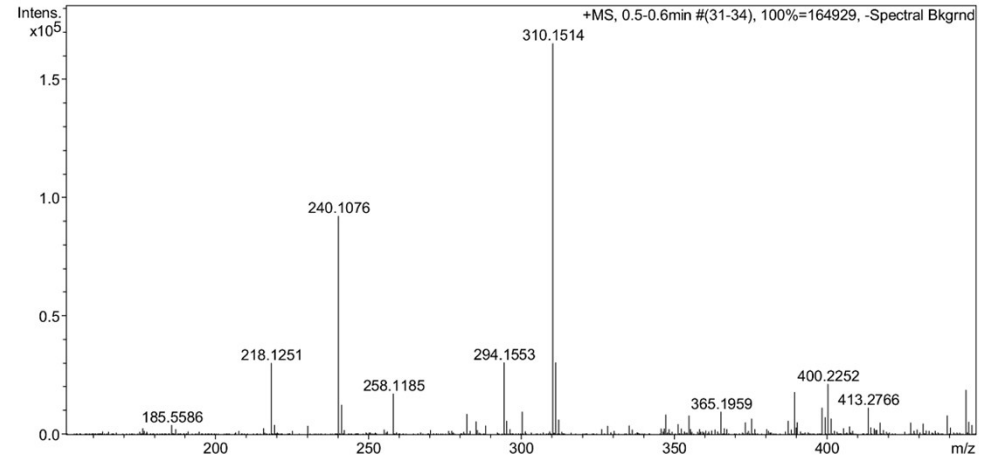
Sample Name	OME-IBU	Instrument	micrOTOF-Q 10187
Comment			

Acquisition Parameter

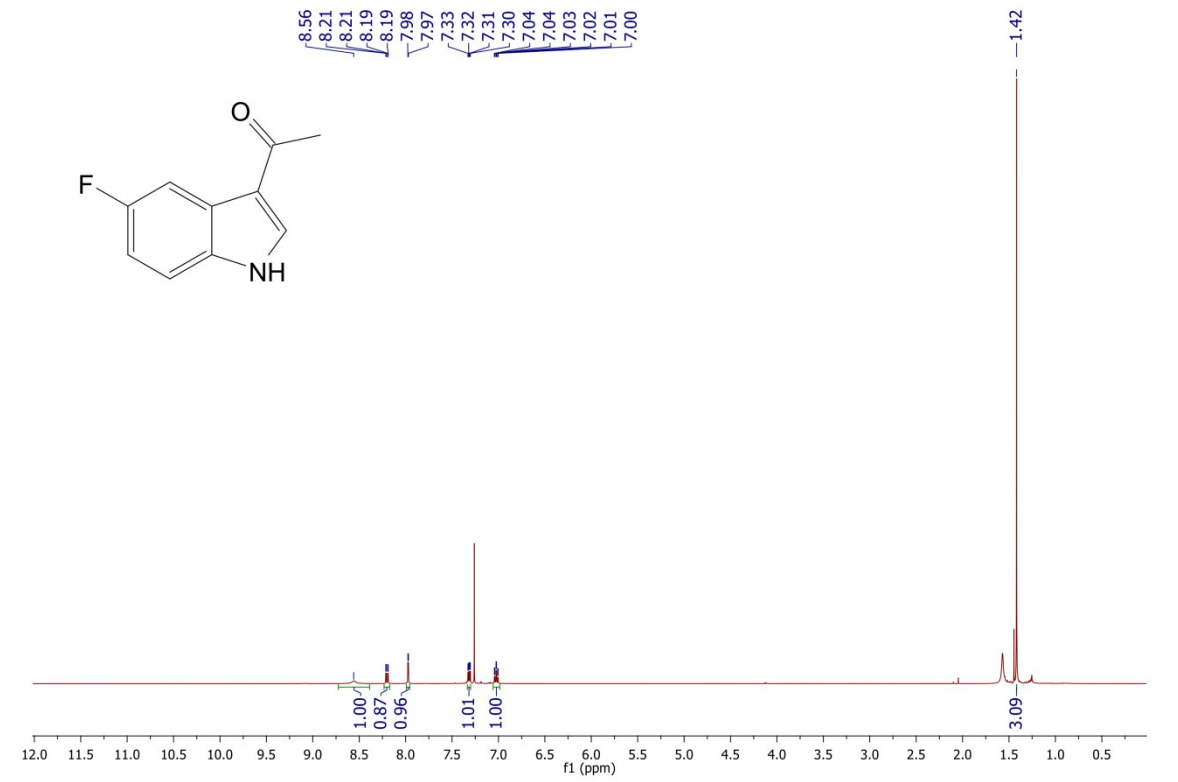
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	600 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Source

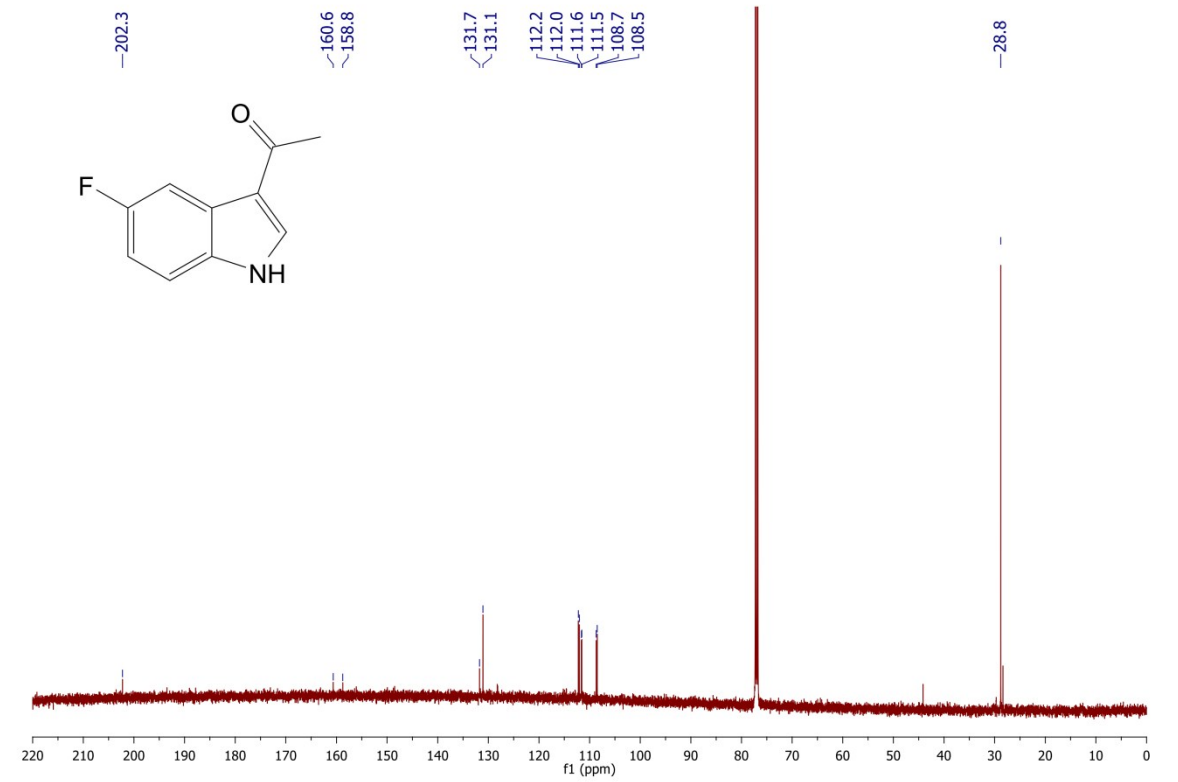


TIC +All MS, -Spectral Bkgrnd, Smoothed (1.00,10,GA)

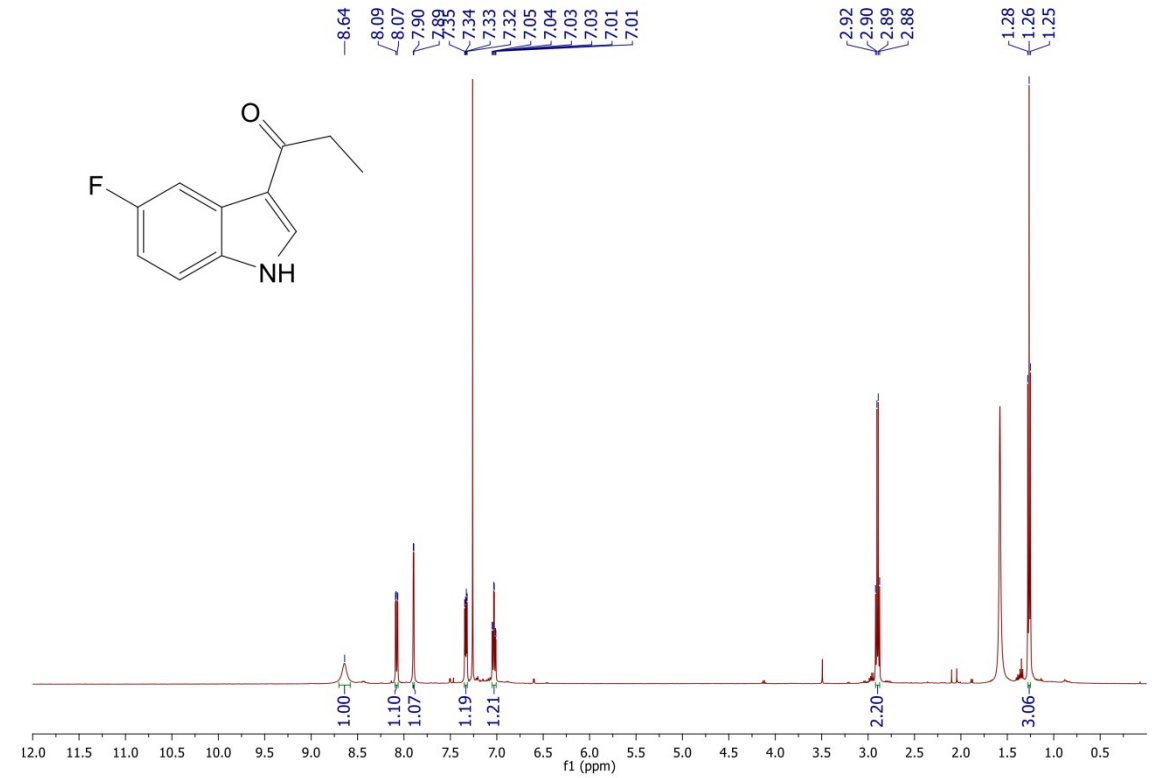


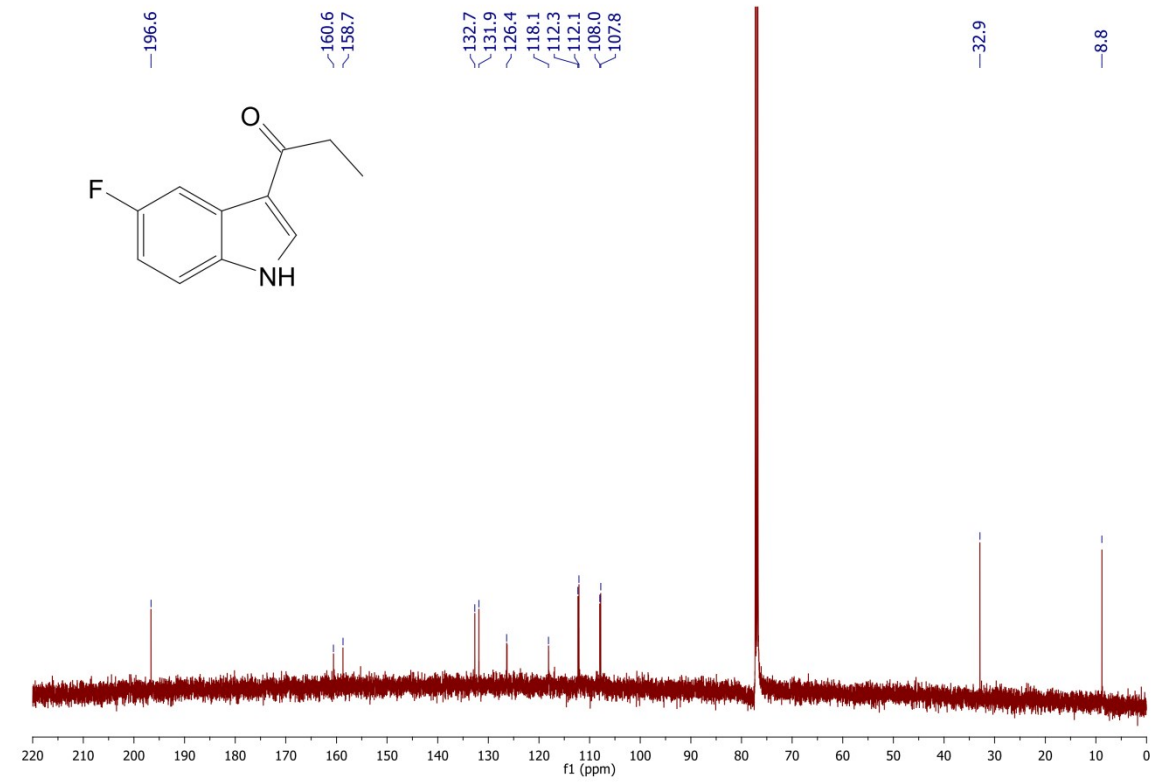
^{1}H NMR, ^{13}C NMR of 3-Acetyl-5-fluoroindole



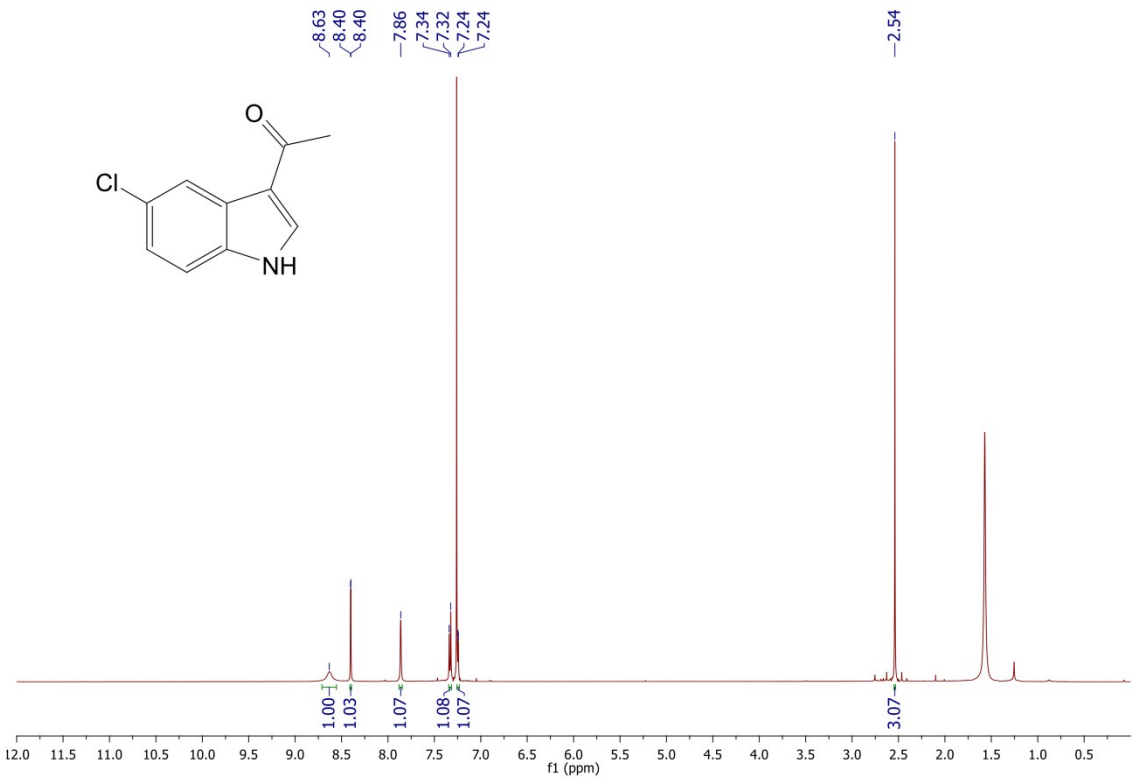


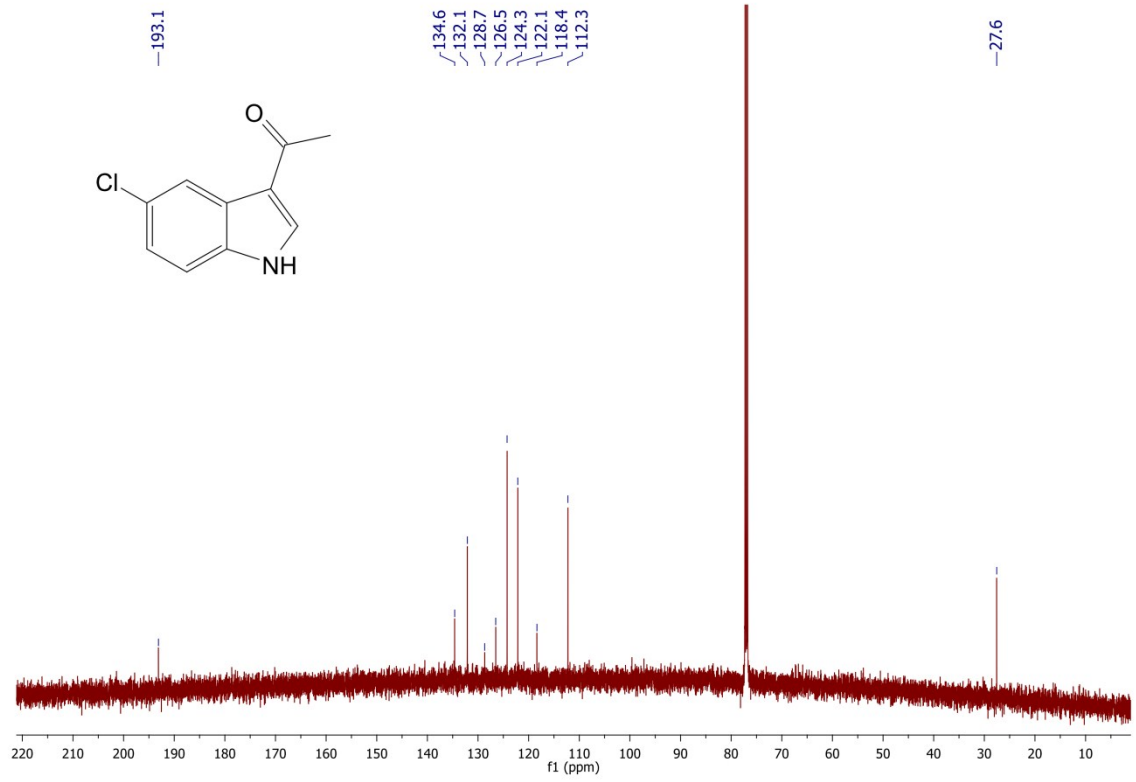
^{1}H NMR, ^{13}C NMR of 3-Propionyl-5-fluoroindole



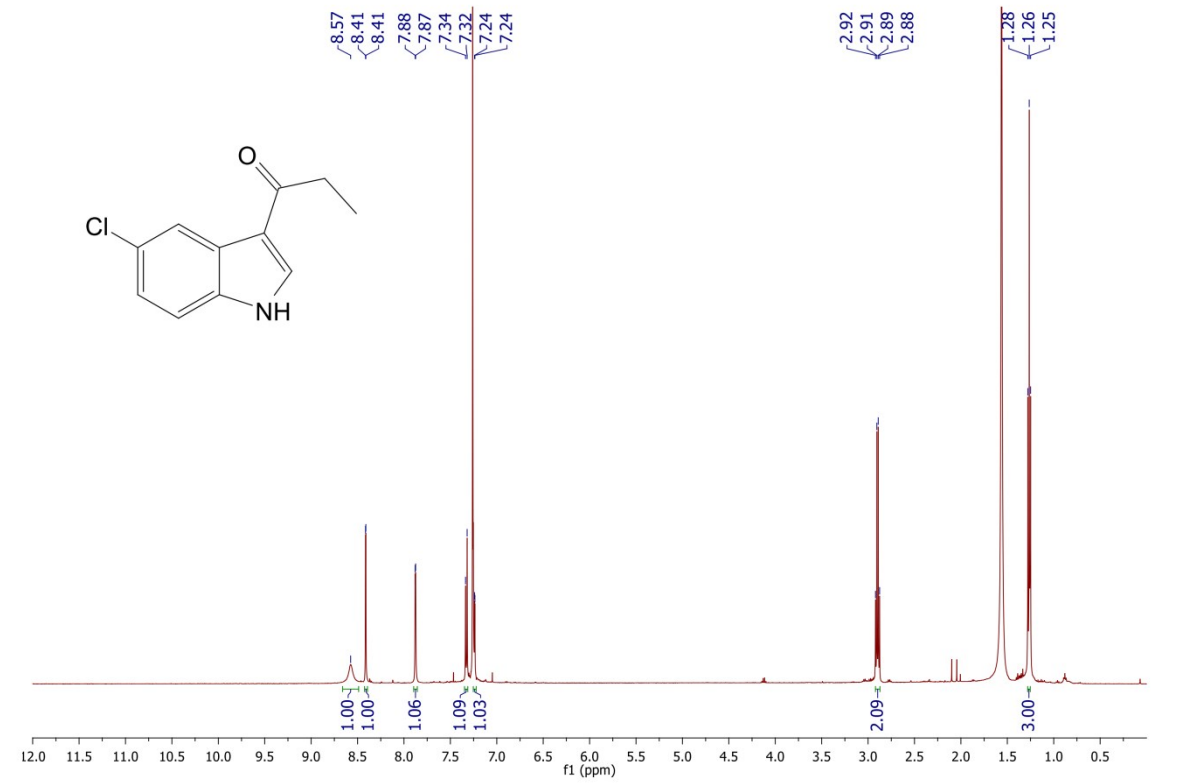


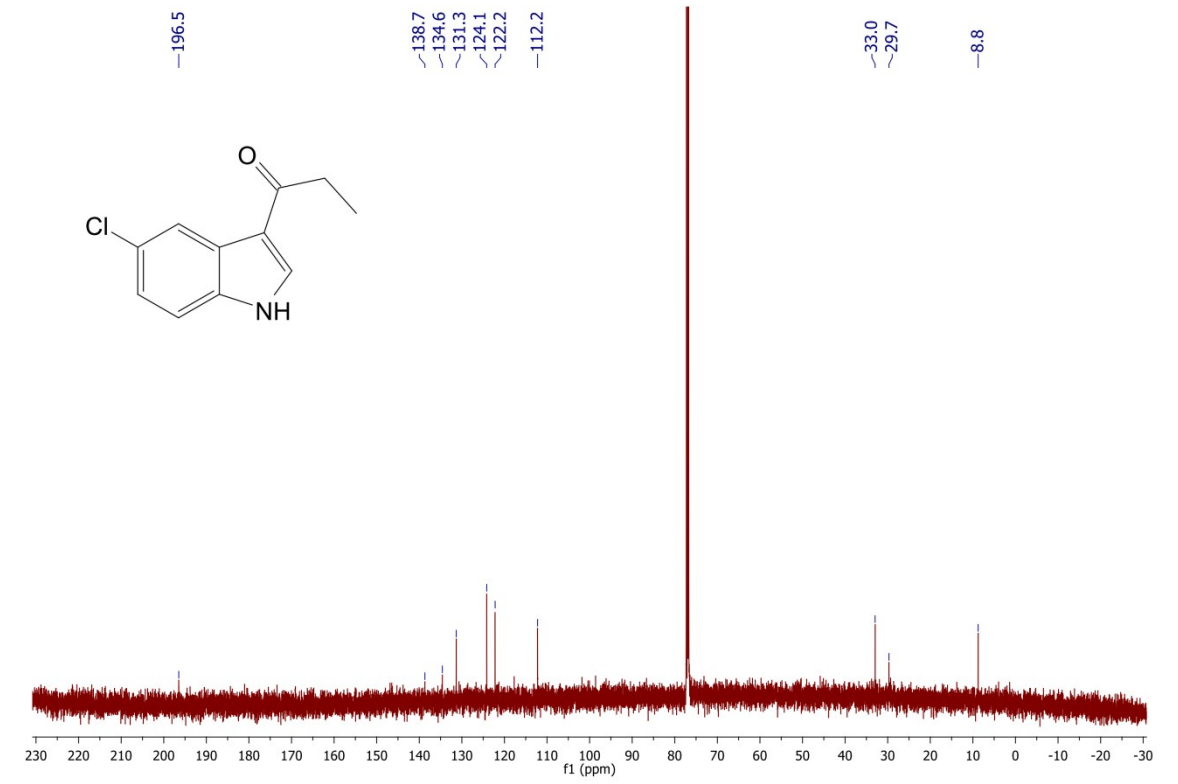
^{1}H NMR, ^{13}C NMR of 3-Acetyl-5-chloroindole



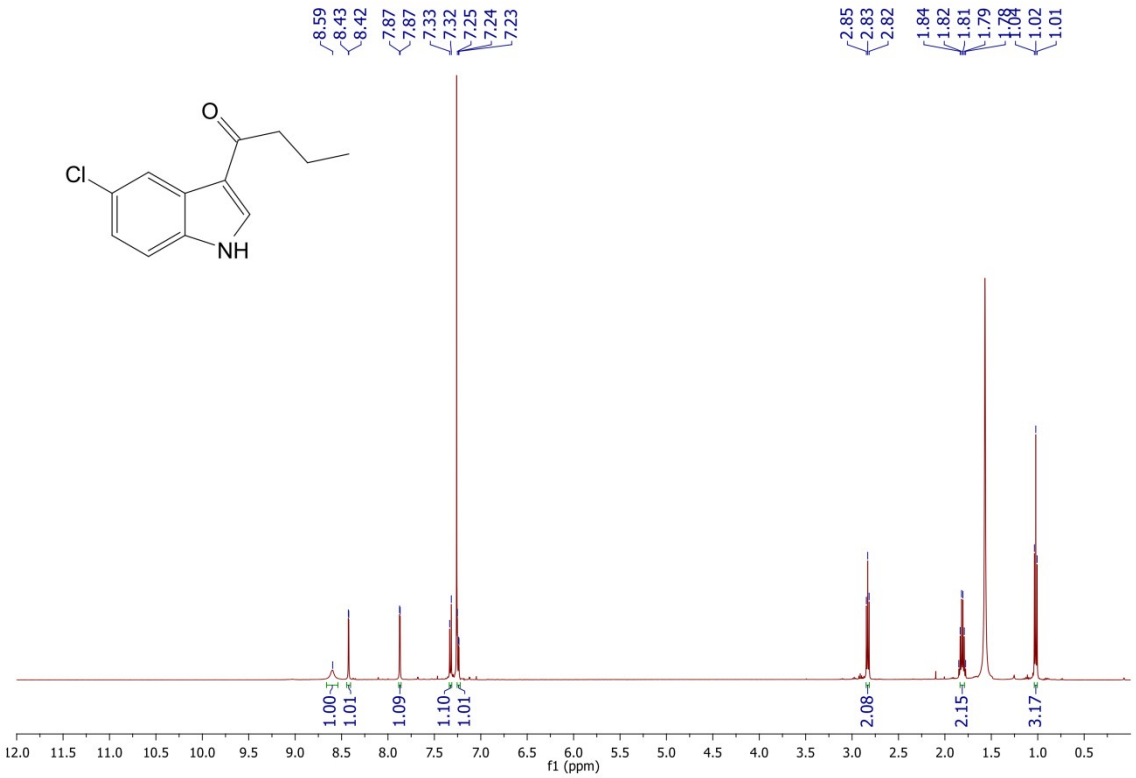


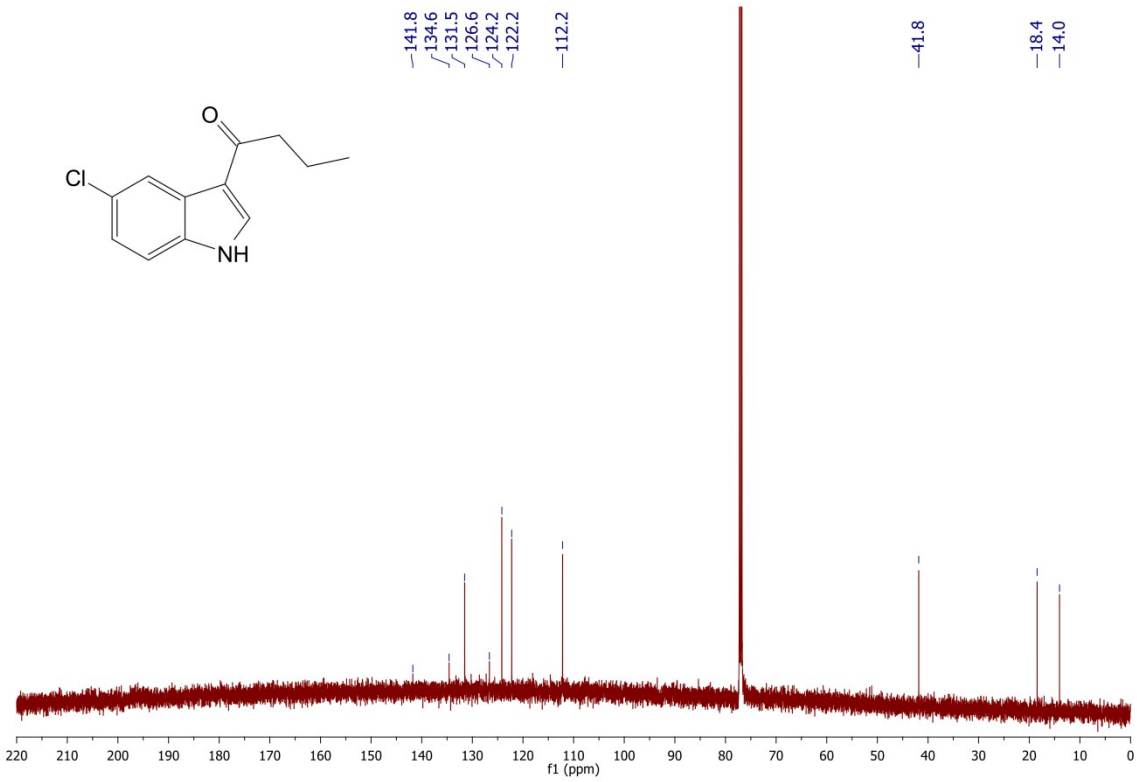
^{1}H NMR, ^{13}C NMR of 3-Propionyl-5-chloroindole





^{1}H NMR, ^{13}C NMR of 3-Butyryl-5-chloroindole





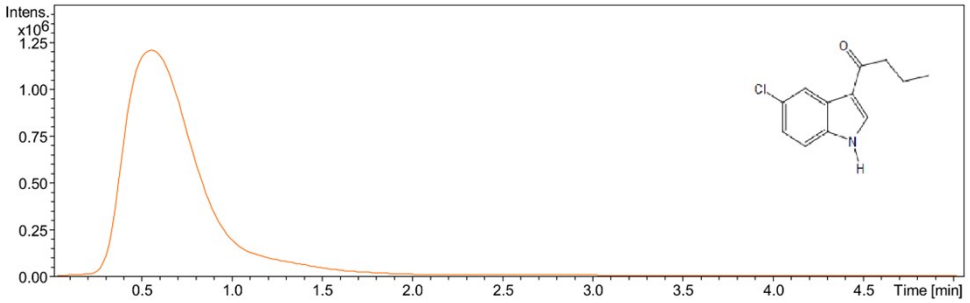
Display Report

Analysis Info

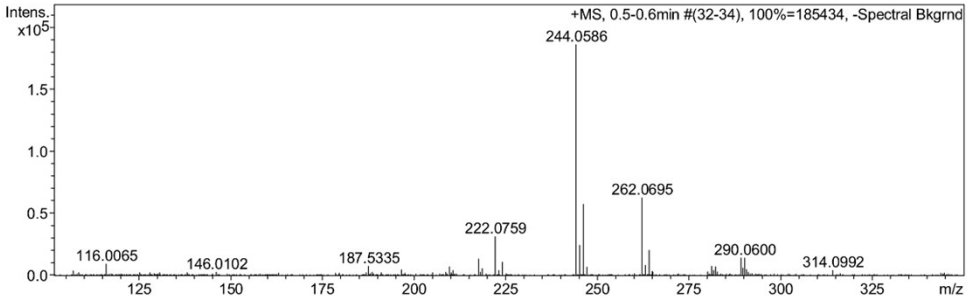
Analysis Name	D:\Data\dmm 2015\CL-BU_1-a,1_01_15137.d	Acquisition Date	3/28/2015 4:43:16 PM
Method	dmm.m	Operator	Mai
Sample Name	CL-BU	Instrument	micrOTOF-Q 10187
Comment			

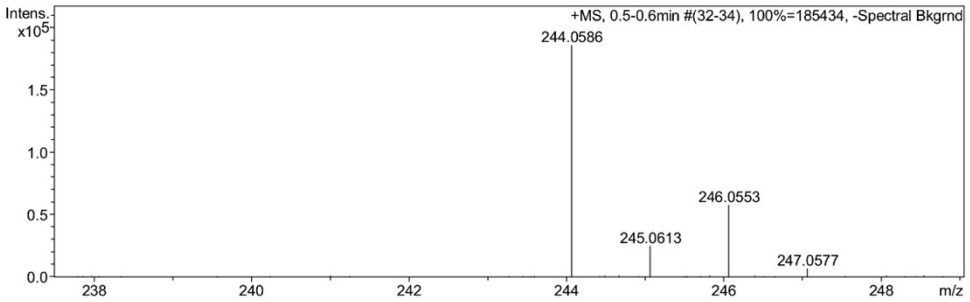
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	600 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Source



TIC +All MS, -Spectral Bkgrnd, Smoothed (1.00,10,GA)





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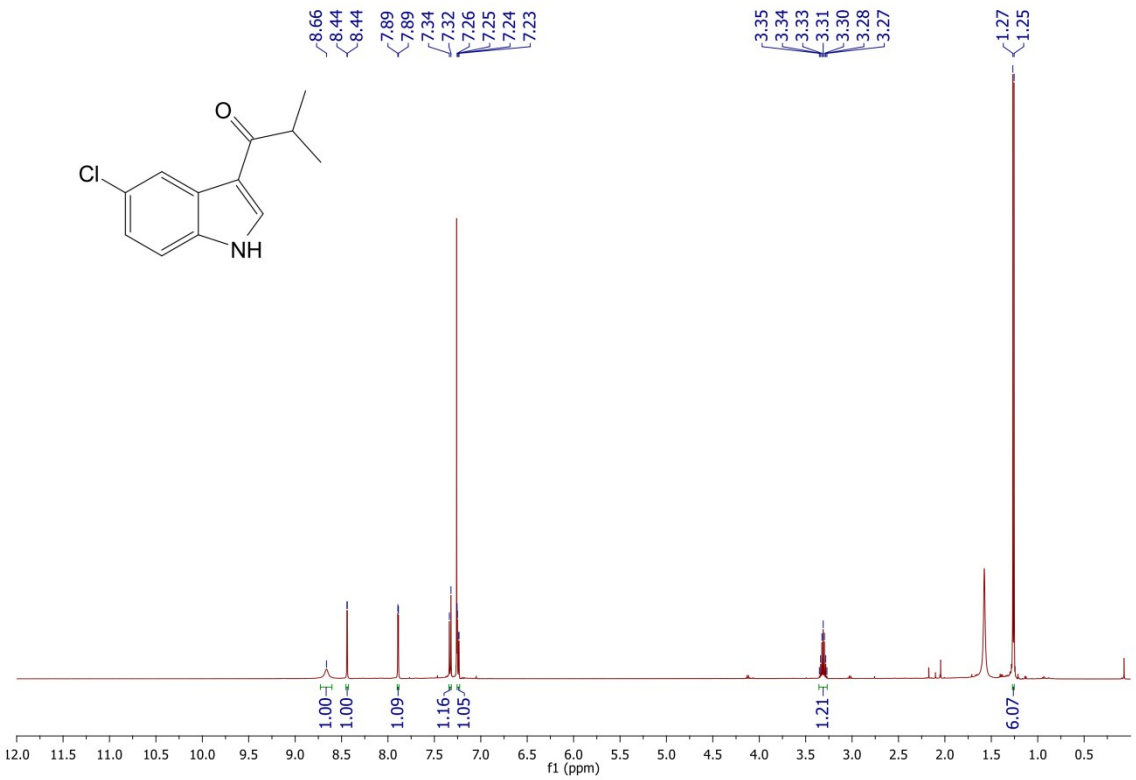
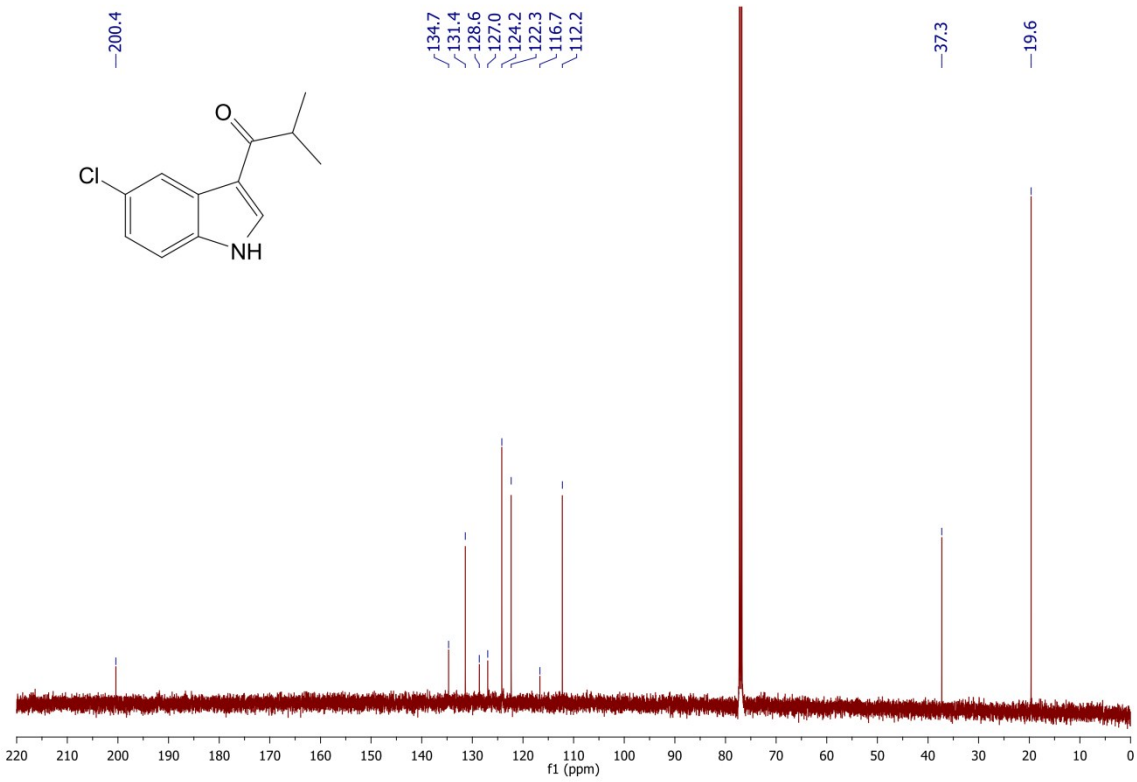
^{1}H NMR, ^{13}C NMR and HR-MS of 3-Isobutyryl-5-chloroindole





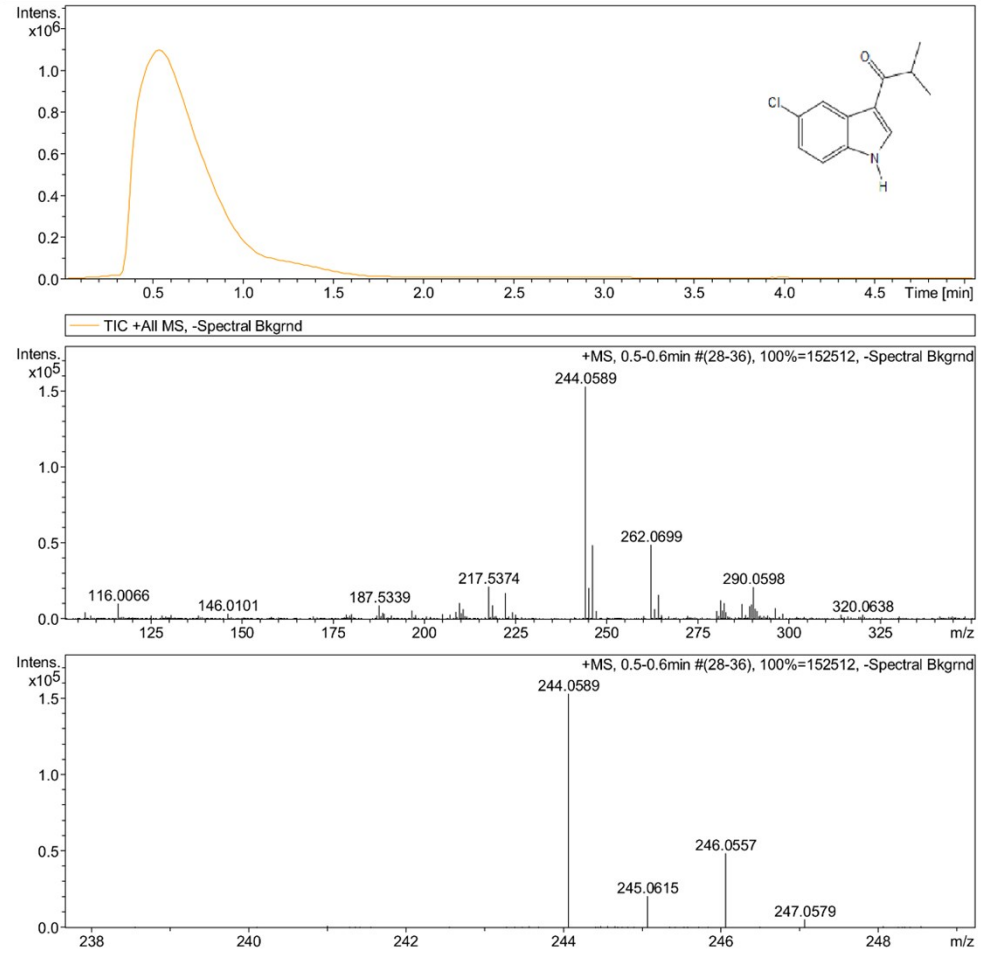
Display Report

Analysis Info

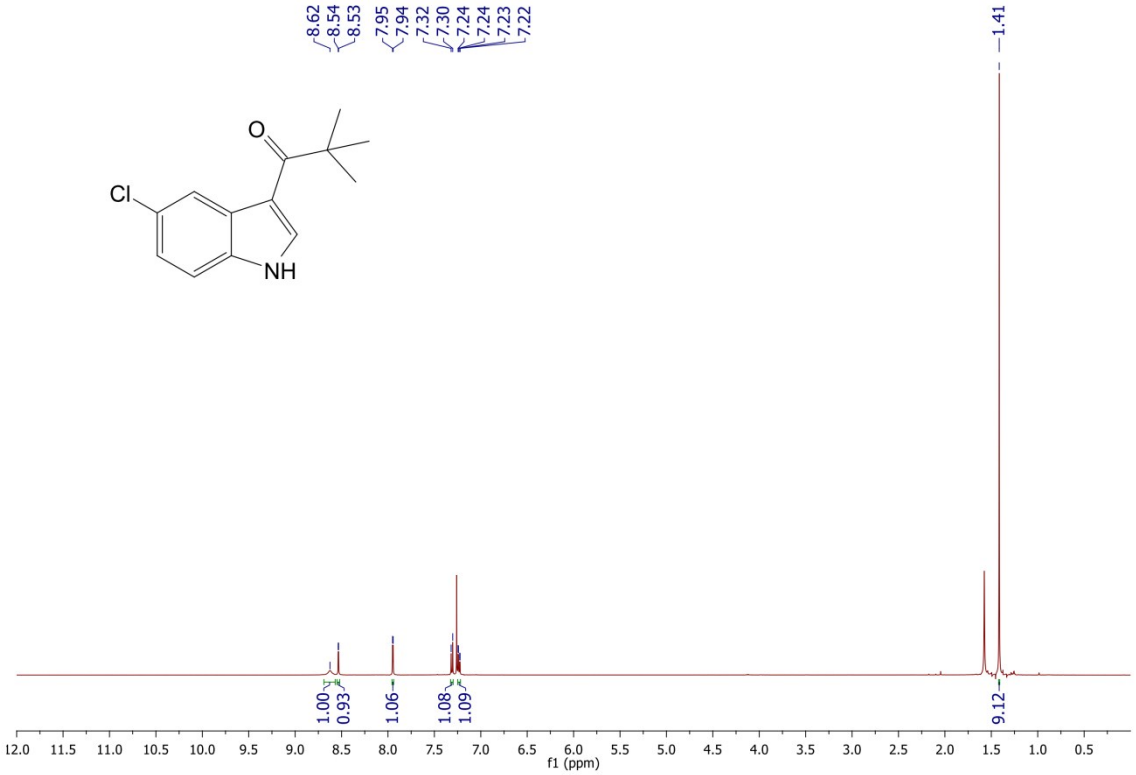
Analysis Name	D:\Data\dmm 2015\CL-IBU_1-a,1_01_15141.d	Acquisition Date	3/28/2015 5:19:10 PM
Method	dmm.m	Operator	Mai
Sample Name	CL-IBU	Instrument	micrOTOF-Q 10187
Comment			

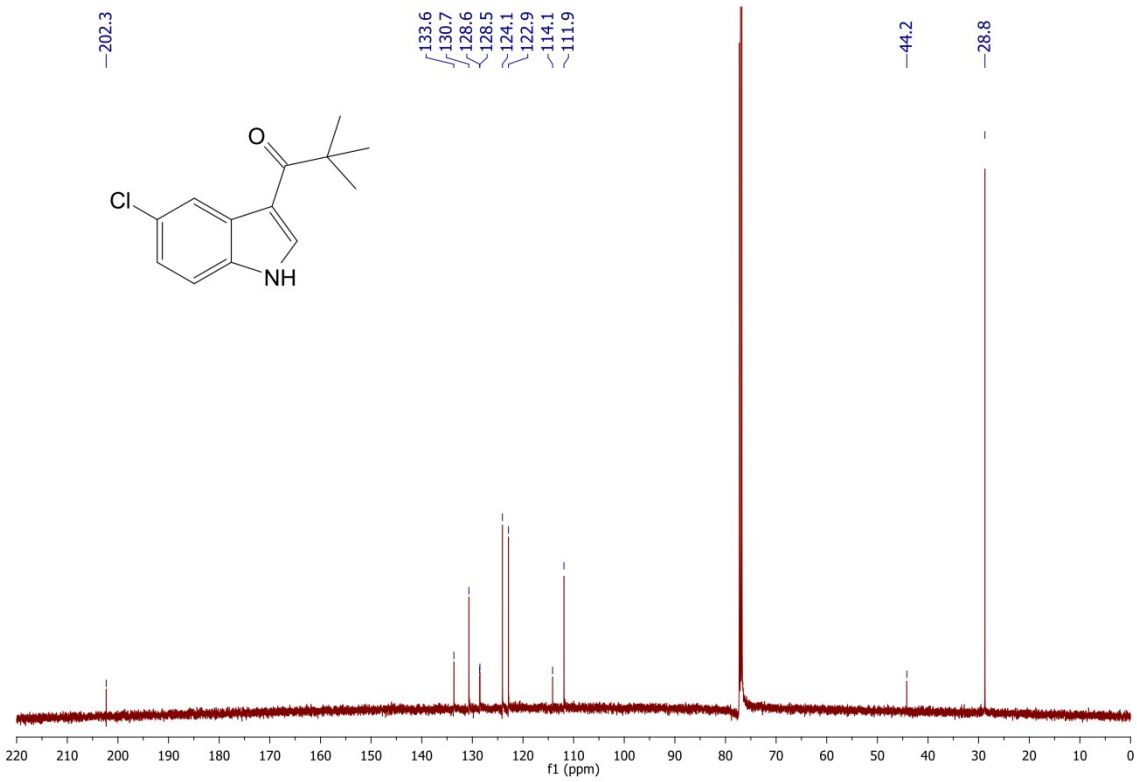
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	600 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Source

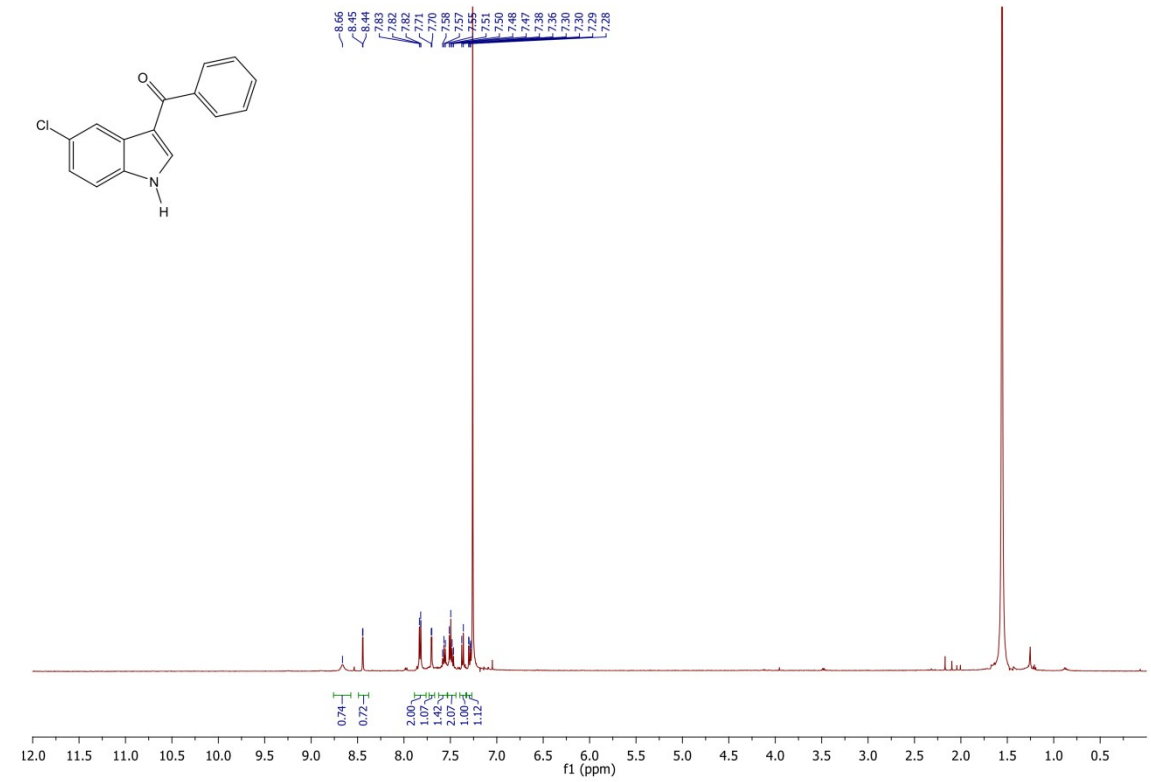


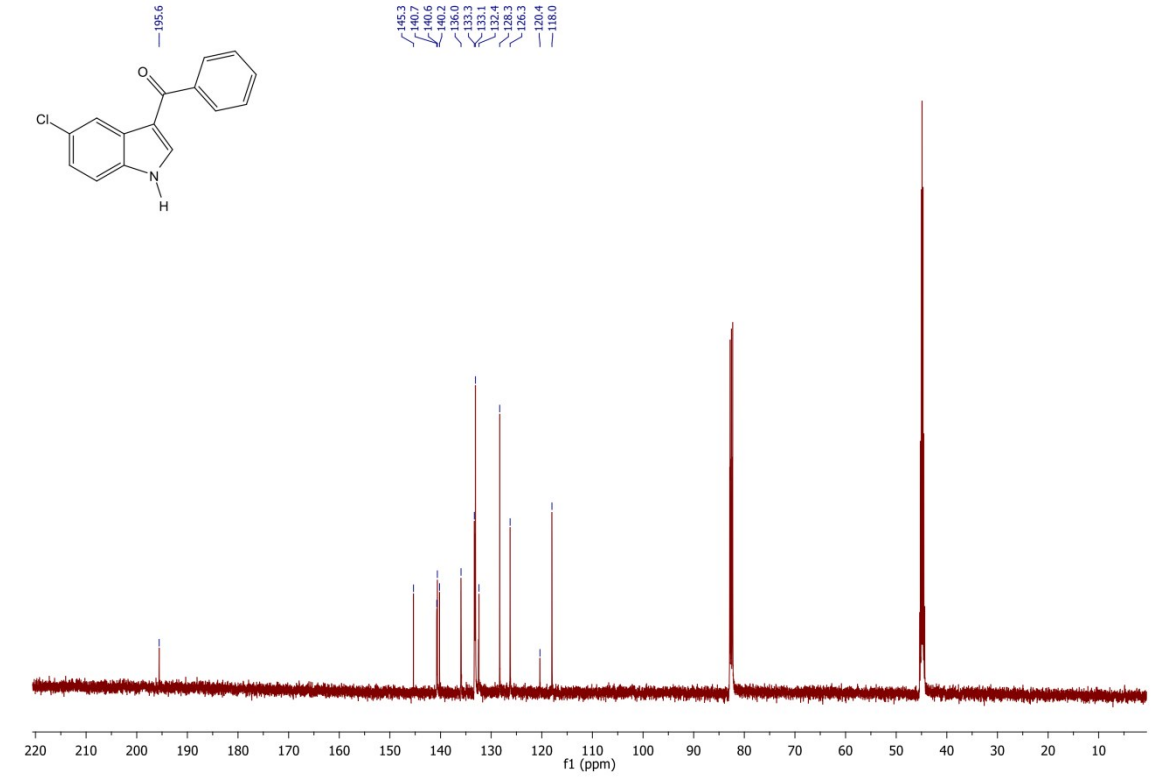
^{1}H NMR, ^{13}C NMR of 3-Pivaloyl-5-chloroindole



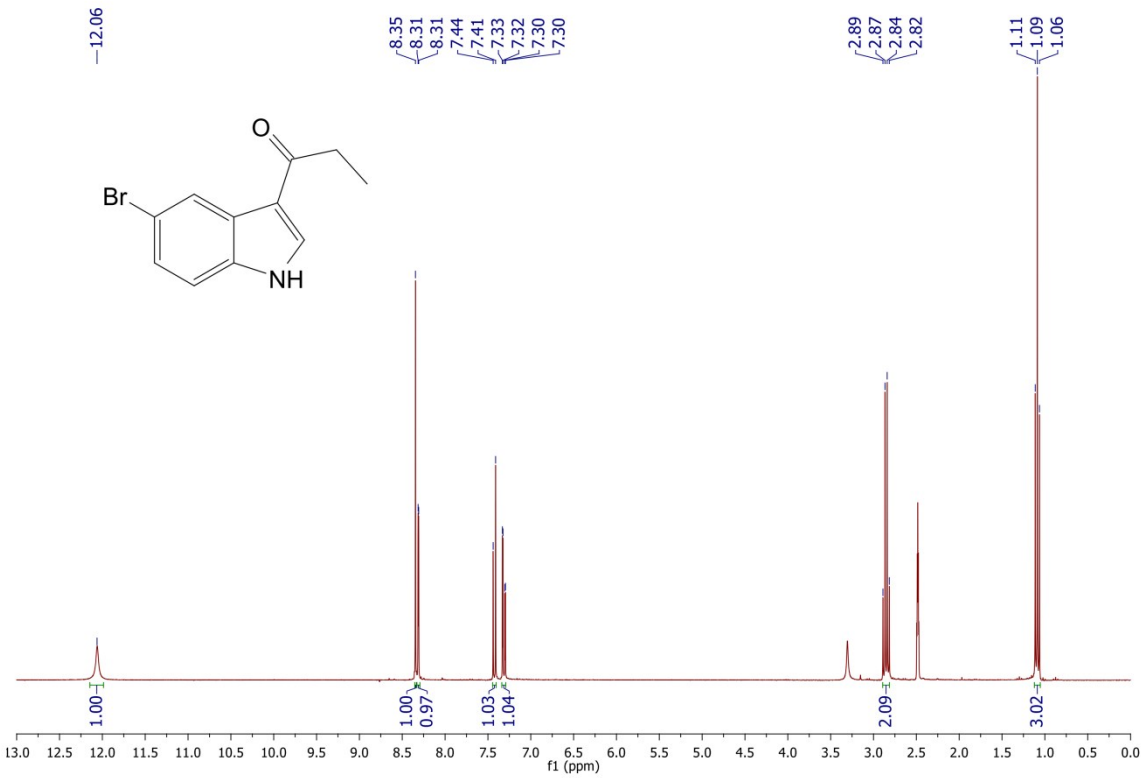


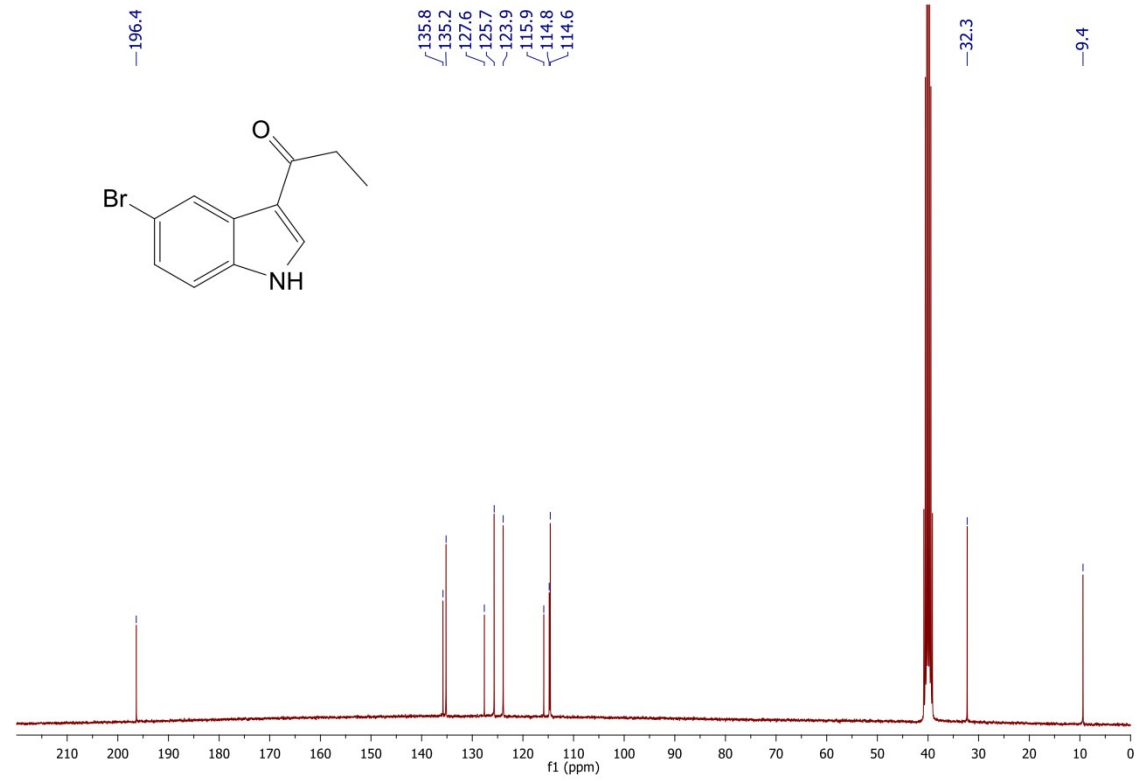
^{1}H NMR, ^{13}C NMR of 3-Benzoyl-5-chloroindole



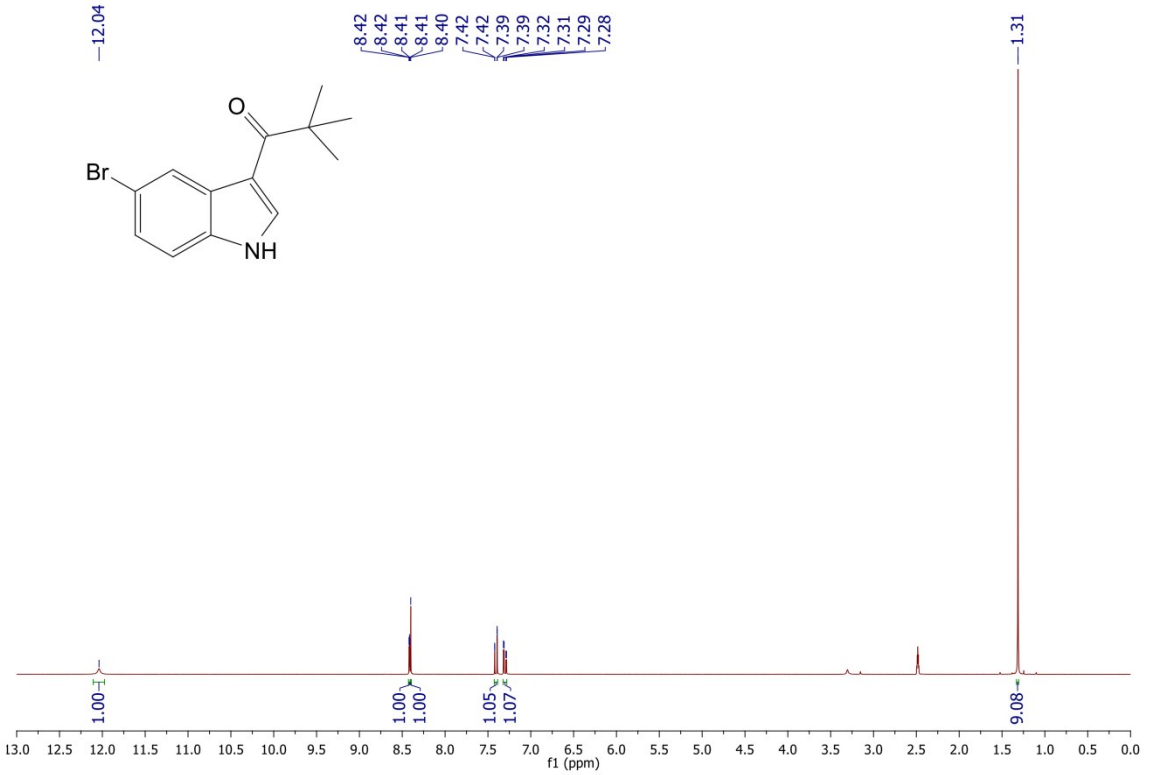


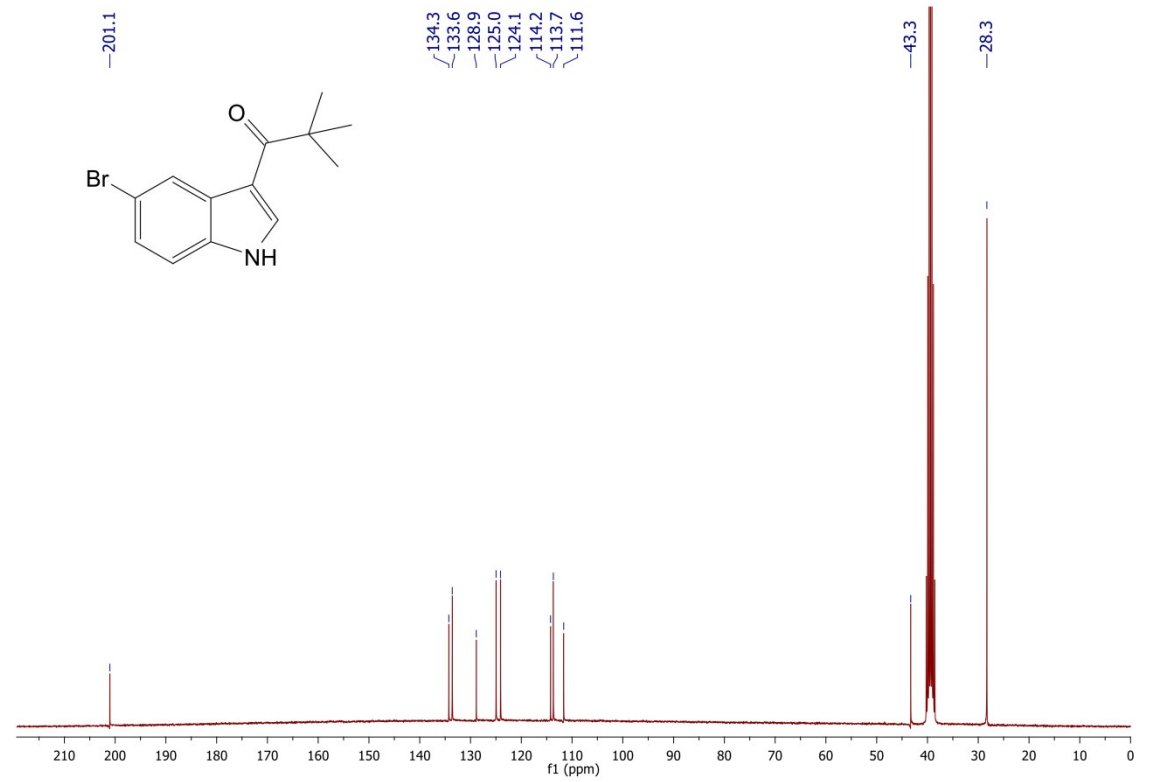
^{1}H NMR, ^{13}C NMR of 3-Propionyl-5-bromoindole





^{1}H NMR, ^{13}C NMR and HR-MS of 3-Pivaloyl-5-bromoindole





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Analysis Info

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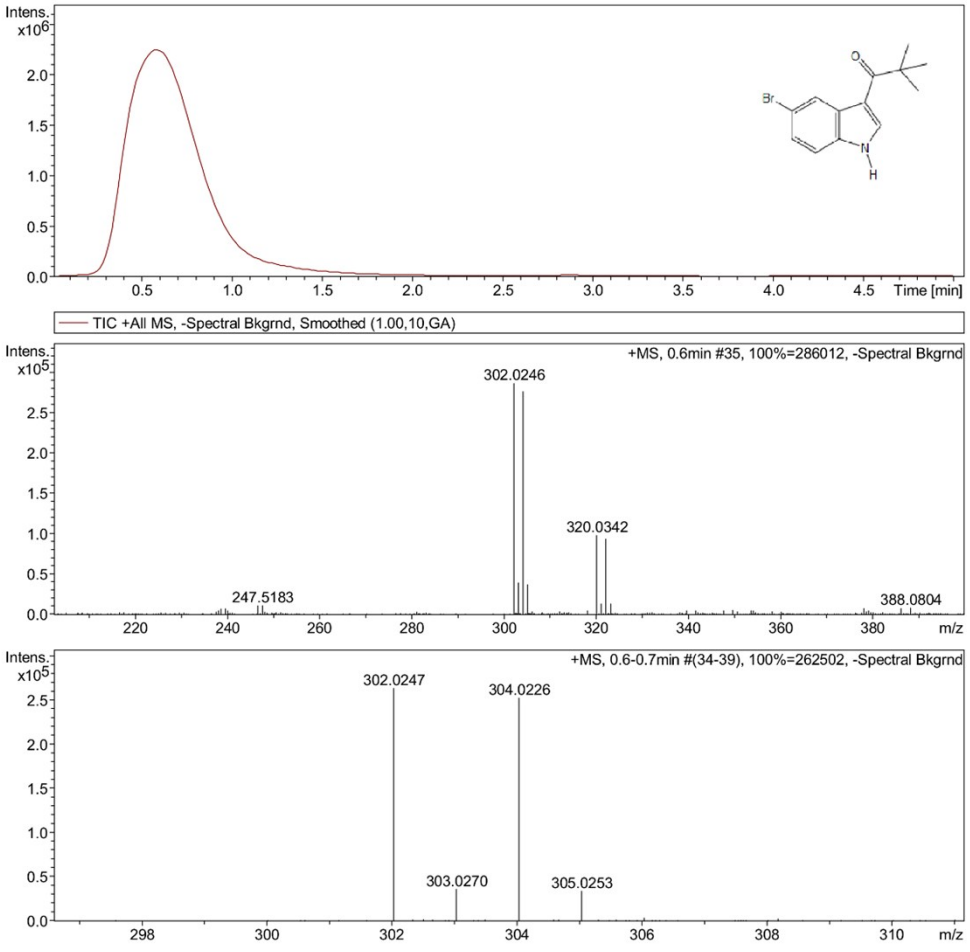
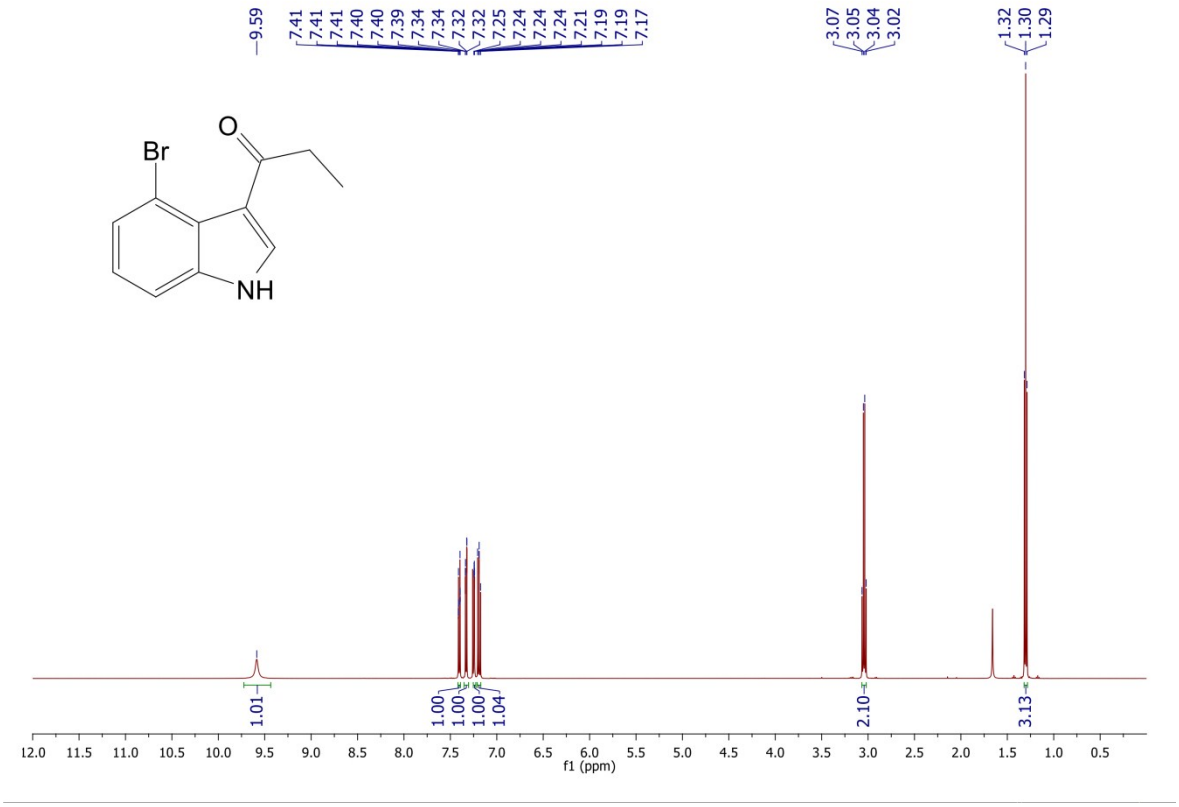
Method	dmm.m	Operator	Mai
Sample Name	5BR-TME	Instrument	micrOTOF-Q 10187
Comment			

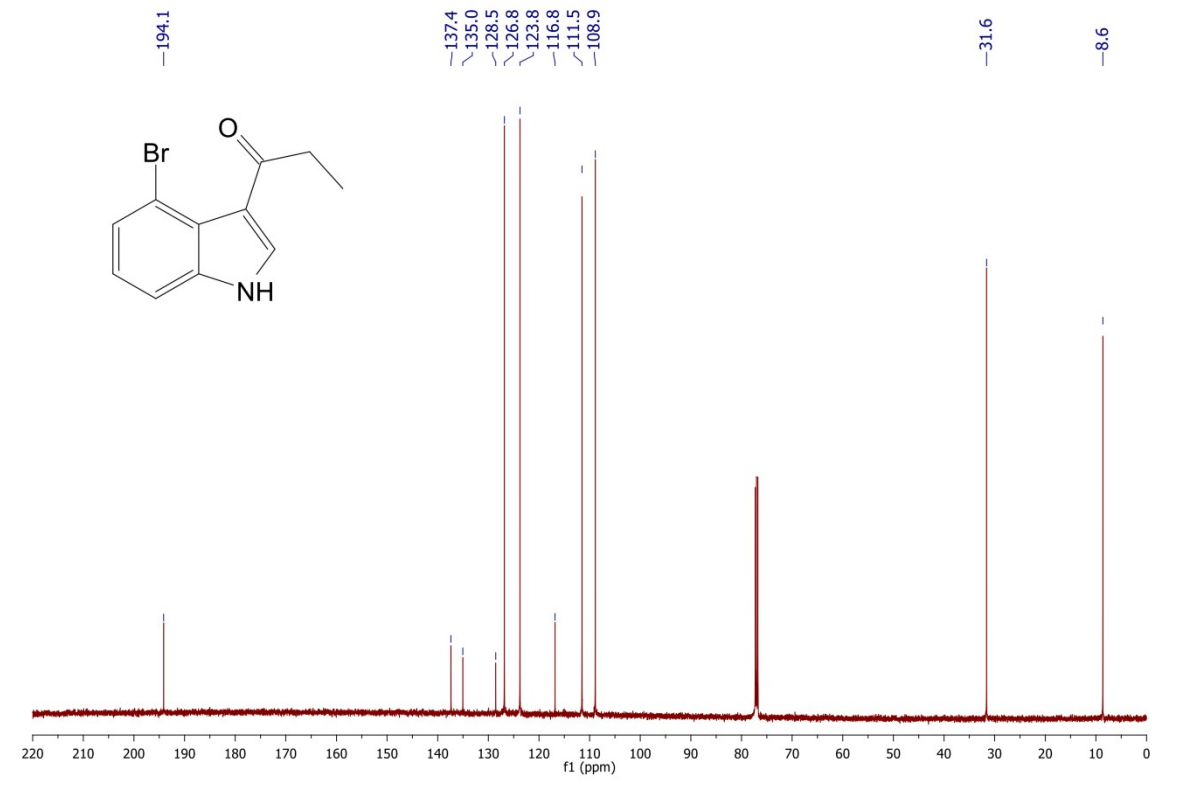
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	600 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Source



^{1}H NMR, ^{13}C NMR and HR-MS of 3-Propionyl-4-bromoindole





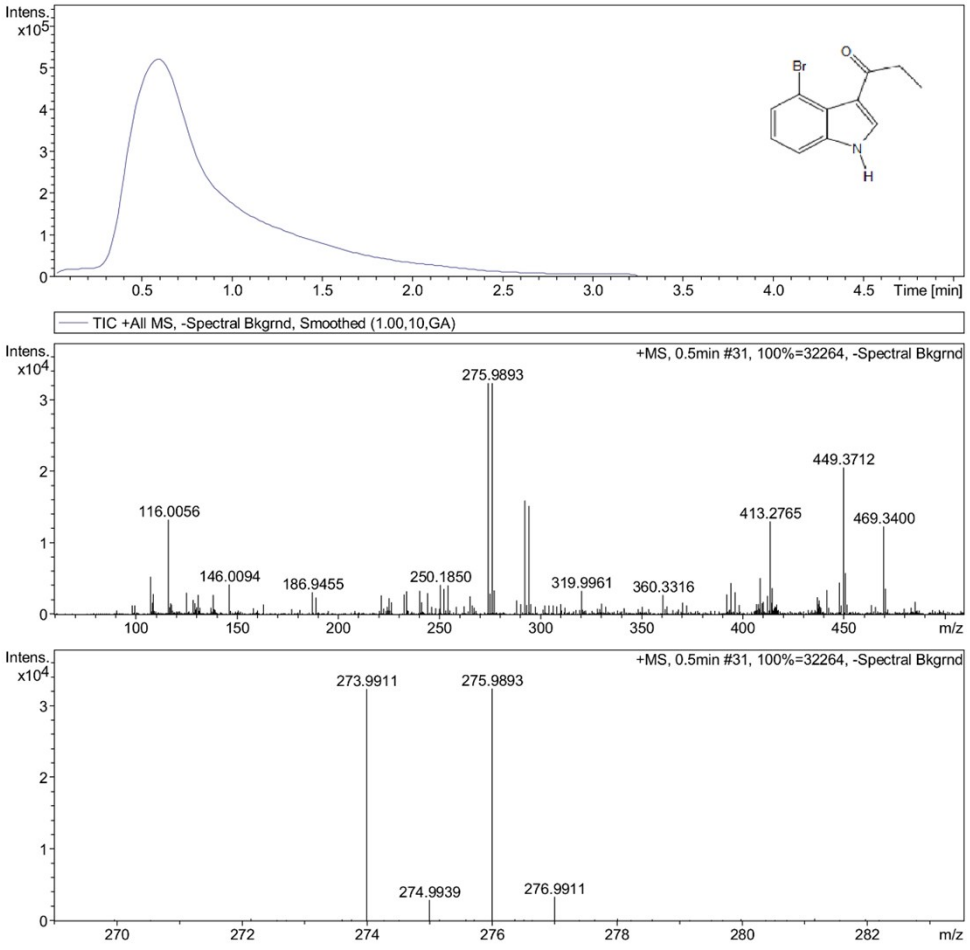
Display Report

Analysis Info

Analysis Name	D:\Data\dmm 2015\4BR-PR_1-a,1_01_15139.d	Acquisition Date	3/28/2015 5:06:33 PM
Method	dmm.m	Operator	Mai
Sample Name	4BR-PR	Instrument	micrOTOF-Q 10187
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	600 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Source



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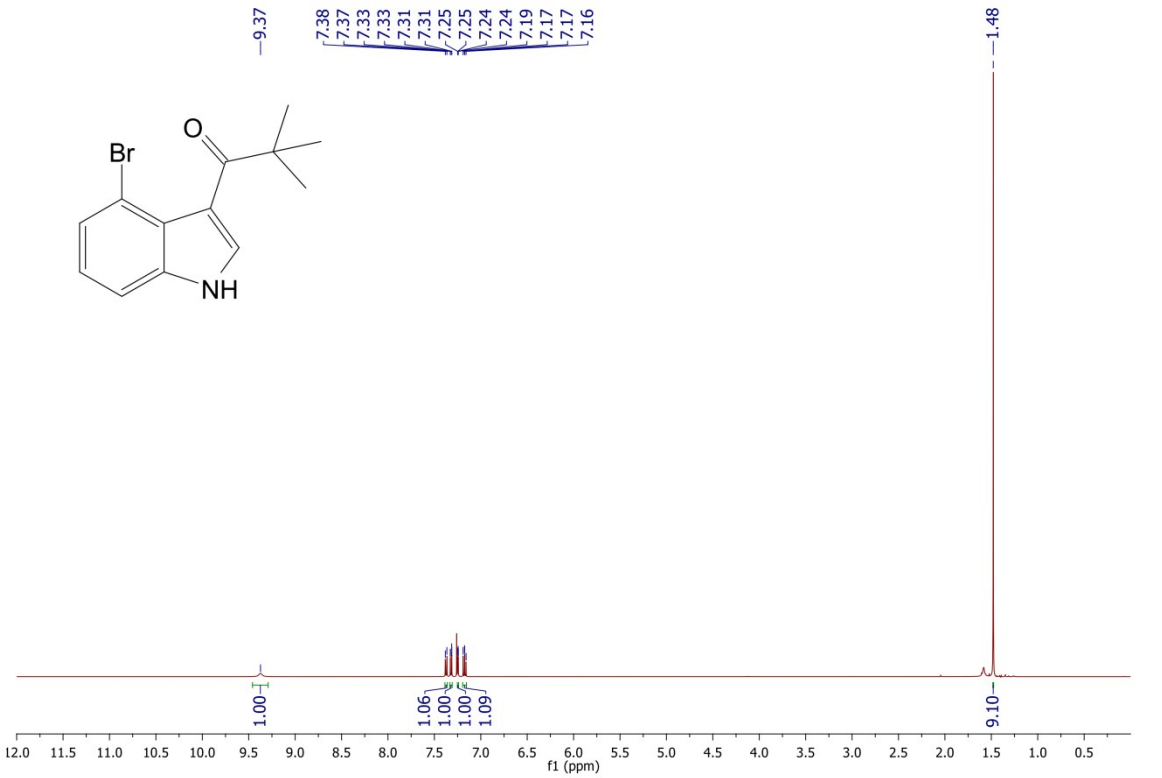
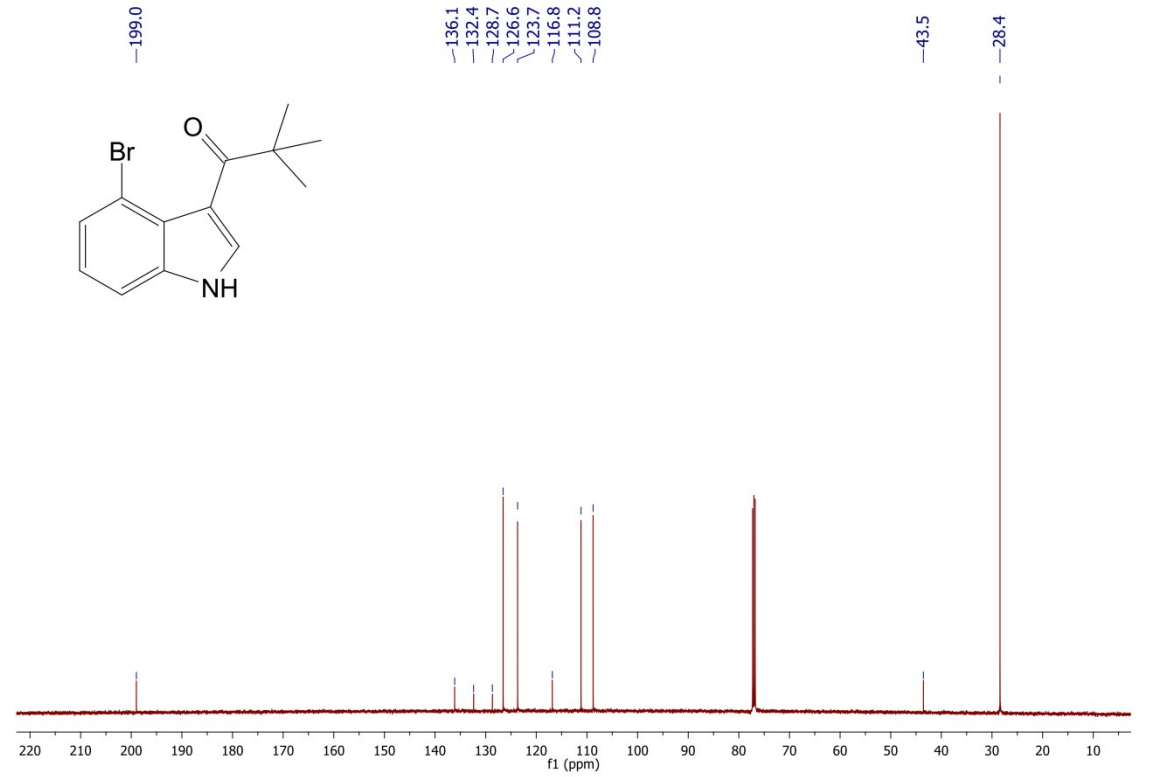
^{1}H NMR, ^{13}C NMR and HR-MS of 3-Pivaloyl-4-bromoindole





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Analysis Info

Analysis Name	D:\Data\dmm 2015\4BR-TME_1-a,1_01_15138.d	Acquisition Date	3/28/2015 4:58:59 PM
Method	dmm.m	Operator	Mai
Sample Name	4BR-TME	Instrument	micrOTOF-Q 10187
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	600 m/z	Set Collision Cell RF	180.0 Vpp	Set Divert Valve	Source