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SUPPORTING INFORMATION

Combining enzyme and photoredox catalysis for aminoalkylation of indoles via a relay catalysis strategy in one pot

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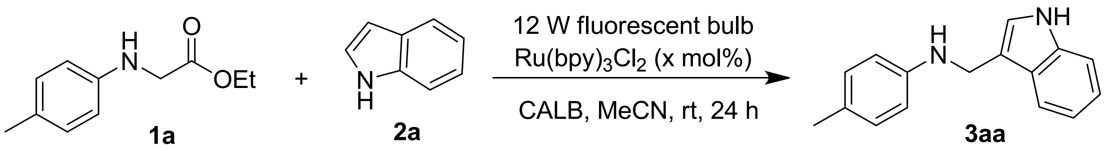
1. Analytical methods

Reactions were monitored by thin-layer chromatography (TLC) with Haiyang GF254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd. Qingdao, China) using UV light and vanillic aldehyde as visualizing agents. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AM 600 (600 MHz) (Bruker BioSpin AG Ltd., Beijing, China). Chemical shifts were reported in ppm from TMS with the solvent resonance as the internal standard. Data were reported as follows: chemical shifts (δ) in ppm, coupling constants (J) in Hz, and solvent ($CDCl_3$). High-resolution mass spectra were obtained by using ESI ioniza-tion sources (Varian 7.0T FTICR-MS).

2. Extra information for optimization of the reaction conditions

Supplementary Table S1 Effect of photocatalyst loading on the model reaction [a]

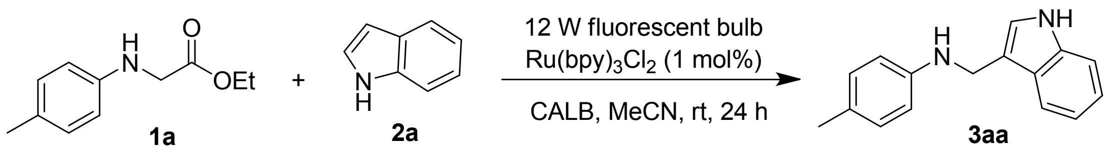


Entry	$Ru(bpy)_3Cl_2$ (x mol%)	Yield (%)[b]
1	1	66
2	2	70
3	3	71
4	4	73
5	5	75
6	7	79
7	10	76

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), MeCN (1 mL, containing 1.59% water), $Ru(bpy)_3Cl_2$ (1-10 mol%) and CALB (114 U) under irradiation of 12 W fluorescent bulb at rt for 24 h.

[b] Determined by HPLC.

Supplementary Table S2 Effect of molar ratio of substrates on the model reaction [a]

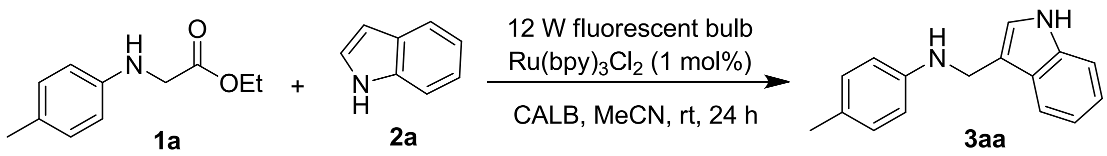


Entry	Molar ratio (1a : 2a)	Yield (%)[b]
1	1 : 1	48
2	1 : 1.5	66
3	1 : 2	80
4	1 : 2.5	74
5	1 : 3	72
6	1.5 : 1	88
7	2 : 1	75
8	2.5 : 1	72
9	3 : 1	73

[a] Reaction conditions: **1a** (0.2-0.6 mmol), **2a** (0.2-0.6 mmol), MeCN (1 mL, containing 1.59% water), $Ru(bpy)_3Cl_2$ (1 mol%) and CALB (114 U) under irradiation of 12 W fluorescent bulb at rt for 24 h.

[b] Determined by HPLC.

Supplementary Table S3 Effect of enzyme loading on the model reaction [a]



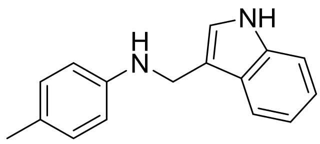
Entry	Enzyme loading (U)	Yield (%)[b]
1	38	29
2	76	59
3	114	88
4	152	90
5	190	95
6	228	79

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), MeCN (1 mL, containing 1.59% water), $Ru(bpy)_3Cl_2$ (1 mol%) and CALB (38-228 U) under irradiation of 12 W fluorescent bulb at rt for 24 h.

[b] Determined by HPLC.

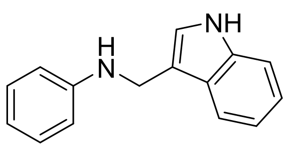
3. Characterization data of the products

N-((1H-indol-3-yl)methyl)-4-methylaniline (3aa)



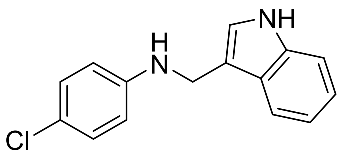
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (br, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.17 – 7.10 (m, 2H), 7.01 (d, J = 8.2 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 4.72 (br, 1H), 4.45 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 136.5, 129.8, 126.9, 126.6, 122.7, 122.4, 119.8, 119.0, 114.4, 113.2, 111.3, 40.5, 20.4. HRMS (ESI) m/z 235.1240 (M - H^+), Cal. $C_{16}H_{15}N_2$, 235.1240.

N-((1H-indol-3-yl)methyl)aniline (3ba)



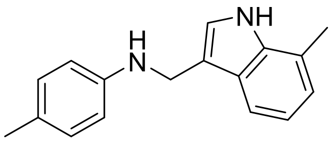
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (br, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.30 - 7.27 (m, 3H), 7.24 - 7.22 (m, 2H), 6.81 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 8.1 Hz, 2H), 4.83 (br, 1H), 4.55 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 136.6, 129.3, 126.9, 122.9, 122.5, 119.8, 119.1, 117.5, 114.2, 113.0, 111.4, 40.2. HRMS (ESI) m/z 221.1080 (M - H^+), Cal. $C_{15}H_{13}N_2$, 221.1084.

N-((1H-indol-3-yl)methyl)-4-chloroaniline (3ca)



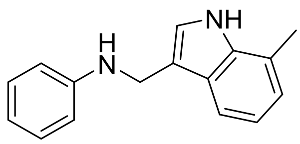
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 7.0 Hz, 1H), 7.31 (s, 1H), 7.24 – 7.20 (m, 3H), 7.18 – 7.16 (m, 1H), 6.68 (d, J = 7.8 Hz, 2H), 4.82 (br, 1H), 4.52 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.1, 136.7, 129.1, 126.9, 123.0, 122.6, 122.0, 119.9, 119.0, 116.4, 114.0, 111.6, 40.3. HRMS (ESI) m/z 255.0698 (M - H^+), Cal. $C_{15}H_{12}ClN_2$, 255.0694.

4-methyl-*N*-((7-methyl-1*H*-indol-3-yl)methyl)aniline (3ab)



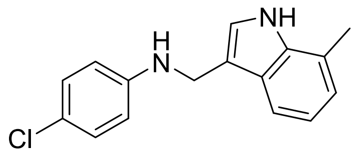
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (br, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.21 (s, 1H), 7.10 (d, J = 7.7 Hz, 1H), 7.08 – 7.04 (m, 3H), 6.67 (d, J = 8.3 Hz, 2H), 4.49 (s, 2H), 2.53 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 136.1, 129.8, 129.7, 126.6, 126.3, 122.9, 122.3, 120.0, 116.7, 115.3, 113.1, 40.6, 20.4, 16.5. HRMS (ESI) m/z 249.1399 (M - H^+), Cal. $C_{17}H_{17}N_2$, 249.1397.

***N*-((7-methyl-1*H*-indol-3-yl)methyl)aniline (3bb)**



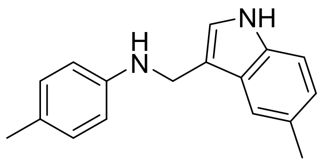
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (br, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.21 (s, 1H), 7.12 (d, J = 7.4 Hz, 1H), 7.09 – 7.07 (m, 1H), 6.78 (t, J = 7.3 Hz, 1H), 6.75 (d, J = 8.3 Hz, 2H), 4.52 (s, 2H), 2.54 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 136.1, 129.3, 126.3, 122.9, 122.4, 120.5, 120.0, 117.4, 116.7, 114.6, 112.9, 40.2, 16.5. HRMS (ESI) m/z 235.1241 (M - H^+), Cal. $C_{16}H_{15}N_2$, 235.1240.

4-chloro-*N*-((7-methyl-1*H*-indol-3-yl)methyl)aniline (3cb)



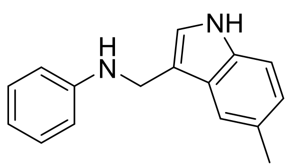
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (br, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.20 (s, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.09 – 7.07 (m, 1H), 6.64 (d, *J* = 4.8 Hz, 2H), 4.48 (s, 2H), 2.54 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.1, 136.1, 129.0, 126.2, 123.0, 122.4, 122.4, 121.9, 120.1, 116.6, 116.3, 114.0, 40.3, 16.5. HRMS (ESI) m/z 269.0853 (M - H^+), Cal. $C_{16}H_{14}ClN_2$, 269.0851.

4-methyl-*N*-((5-methyl-1H-indol-3-yl)methyl)aniline (3ac)



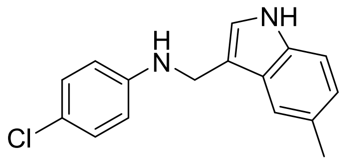
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (br, 1H), 7.50 (s, 1H), 7.29 (d, *J* = 4.0 Hz, 1H), 7.16 (s, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.68 (d, *J* = 8.2 Hz, 2H), 4.46 (s, 2H), 2.49 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 134.8, 129.7, 129.0, 127.0, 126.6, 124.0, 122.8, 118.6, 113.3, 113.1, 110.9, 40.5, 21.4, 20.4. HRMS (ESI) m/z 249.1395 (M - H^+), Cal. $C_{17}H_{17}N_2$, 249.1397.

***N*-((5-methyl-1H-indol-3-yl)methyl)aniline (3bc)**



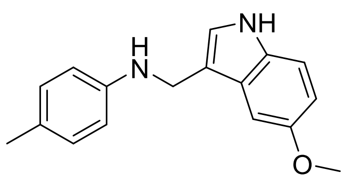
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (br, 1H), 7.50 (s, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.25 – 7.24 (m, 2H), 7.16 (s, 1H), 7.10 (d, J = 8.1 Hz, 1H), 6.75 (d, J = 8.1 Hz, 2H), 6.66 (d, J = 8.1 Hz, 1H), 4.48 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 134.8, 129.3, 129.1, 127.0, 124.0, 122.9, 118.6, 117.4, 113.1, 112.9, 110.9, 40.1, 21.4. HRMS (ESI) m/z 237.1395 (M + H^+), Cal. $C_{16}H_{17}N_2$, 237.1386.

4-chloro-*N*-((5-methyl-1H-indol-3-yl)methyl)aniline (3cc)



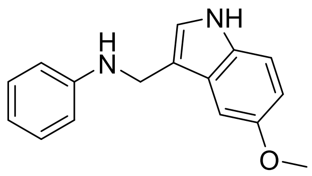
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (br, 1H), 7.47 (s, 1H), 7.31 (d, J = 8.3 Hz, 1H), 7.18 – 7.16 (m, 3H), 7.09 (d, J = 7.9 Hz, 1H), 6.64 (d, J = 8.6 Hz, 2H), 4.44 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.1, 134.8, 129.2, 129.0, 126.9, 124.1, 122.8, 118.5, 116.2, 114.1, 113.9, 111.0, 40.2, 21.4. HRMS (ESI) m/z 269.0844 (M - H^+), Cal. $C_{16}H_{14}ClN_2$, 269.0851.

***N*-((5-methoxy-1H-indol-3-yl)methyl)-4-methylaniline (3ad)**



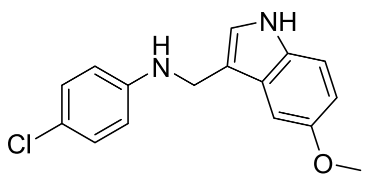
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (br, 1H), 7.28 (d, J = 2.8 Hz, 1H), 7.17 (s, 1H), 7.12 (s, 1H), 7.06 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 8.8 Hz, 1H), 6.69 (d, J = 8.3 Hz, 2H), 4.45 (s, 2H), 3.87 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.3, 146.5, 131.6, 129.7, 127.2, 126.6, 123.4, 113.2, 112.8, 112.0, 100.8, 55.9, 40.5, 20.4. HRMS (ESI) m/z 265.1343 (M - H^+), Cal. $C_{17}H_{17}N_2O$, 265.1346.

***N*-((5-methoxy-1H-indol-3-yl)methyl)aniline (3bd)**



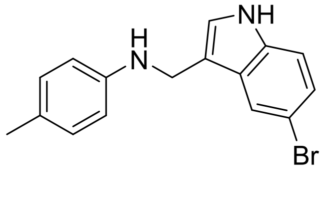
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (br, 1H), 7.29 (s, 1H), 7.24 (m, 2H), 7.17 (s, *J* = 2.1 Hz, 1H), 7.13 (s, *J* = 2.2 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 1H), 4.47 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.3, 148.7, 129.3, 127.2, 123.5, 117.4, 115.1, 113.0, 112.8, 112.0, 100.8, 56.0, 40.2. HRMS (ESI) m/z 253.1337 (M - H^+), Cal. $C_{16}H_{17}N_2O$, 253.1336.

4-chloro-*N*-((5-methoxy-1H-indol-3-yl)methyl)aniline (3cd)



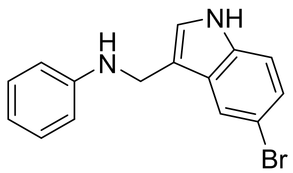
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (br, 1H), 7.17 – 7.16 (m, 3H), 7.09 (d, *J* = 1.8 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.65 (d, *J* = 8.8 Hz, 2H), 4.43 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.4, 147.1, 129.1, 127.1, 123.5, 123.1, 116.2, 114.1, 112.8, 112.1, 100.7, 56.0, 40.3. HRMS (ESI) m/z 285.0798 (M - H^+), Cal. $C_{16}H_{14}ClN_2O$, 285.0800.

***N*-((5-bromo-1H-indol-3-yl)methyl)-4-methylaniline (3ae)**



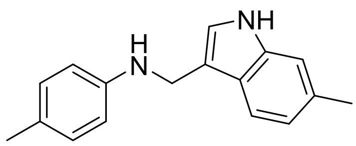
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (br, 1H), 7.83 (s, 1H), 7.32 (d, J = 8.6 Hz, 1H), 7.28 (d, J = 8.1 Hz, 1H), 7.19 (s, 1H), 7.05 (d, J = 8.1 Hz, 2H), 6.66 (d, J = 8.2 Hz, 2H), 4.44 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, CDCl3) δ 146.1, 135.1, 129.8, 128.6, 127.0, 125.2, 123.8, 121.7, 114.1, 113.2, 113.0, 112.7, 40.3, 20.4. HRMS (ESI) m/z 315.0498 (M + H^+), Cal. $C_{16}H_{16}BrN_2$, 315.0492.

***N*-((5-bromo-1H-indol-3-yl)methyl)aniline (3be)**



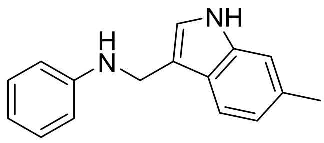
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (br, 1H), 7.84 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.29 - 7.25 (m, 3H), 7.20 (s, 1H), 6.79 (t, J = 7.3 Hz, 1H), 6.74 (d, J = 7.8 Hz, 2H), 4.46 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.3, 135.1, 129.3, 128.5, 125.3, 123.9, 121.7, 117.7, 113.8, 113.1, 112.7, 40.0. HRMS (ESI) m/z 301.0341 (M + H^+), Cal. $C_{15}H_{14}BrN_2$, 301.0335.

4-methyl-*N*-((6-methyl-1H-indol-3-yl)methyl)aniline (3af)



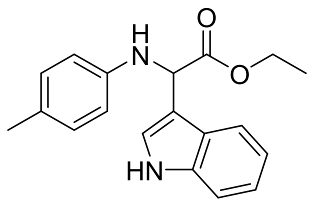
Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (br, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.20 (s, 1H), 7.12 (s, 1H), 7.06 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.0 Hz, 1H), 6.67 (d, J = 8.3 Hz, 2H), 4.47 (s, 2H), 2.51 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 136.9, 132.2, 129.7, 126.6, 122.0, 121.5, 118.7, 114.1, 113.1, 111.2, 40.5, 21.7, 20.4. HRMS (ESI) m/z 251.1549 (M + H^+), Cal. $C_{17}H_{19}N_2$, 251.1543.

_N_-((6-methyl-1H-indol-3-yl)methyl)aniline (3bf)



Brown liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (br, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.20 (s, 1H), 7.12 (s, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 4.49 (s, 2H), 2.51 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 136.9, 132.3, 129.3, 122.0, 121.6, 118.7, 117.4, 115.2, 112.9, 111.2, 111.0, 40.2, 21.7. HRMS (ESI) m/z 237.1389 (M + H^+), Cal. $C_{16}H_{17}N_2$, 237.1386.

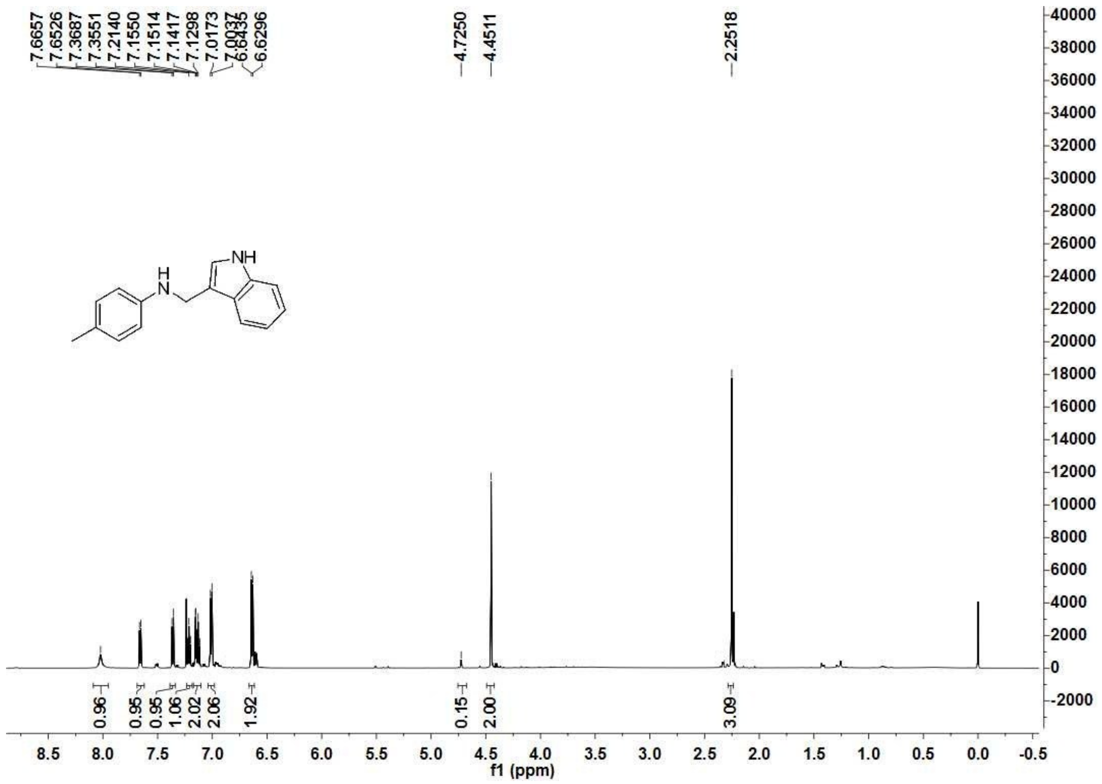
ethyl 2-(1*H*-indol-3-yl)-2-(p-tolylamino)acetate (4)[1]

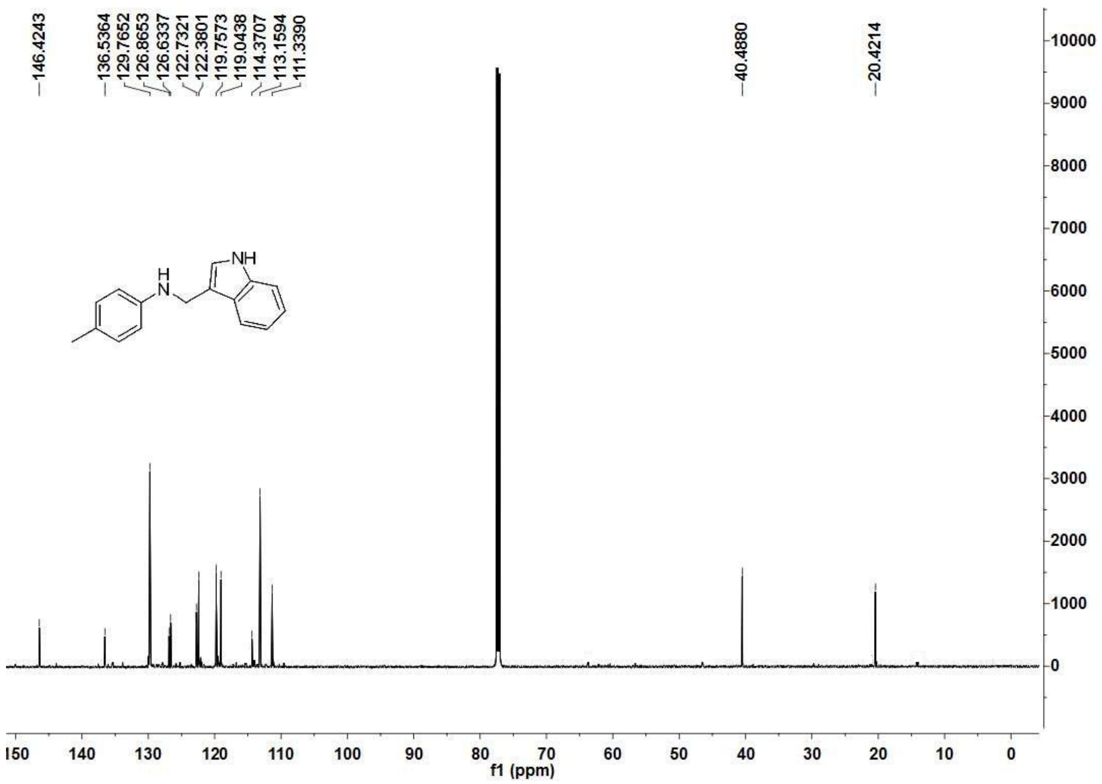


Yellow liquid; ^{1}H NMR (600 MHz, CDCl3) δ 8.15 (s, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.23 – 7.12 (m, 3H), 6.95 (d, J = 8.1 Hz, 2H), 6.56 (d, J = 8.2 Hz, 2H), 5.36 (s, 1H), 4.18 (ddd, J = 75.3, 10.8, 7.1 Hz, 2H), 2.21 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, CDCl3) δ 172.7, 144.3, 136.5, 129.8, 127.4, 125.9, 123.1, 122.5, 120.0, 119.6, 113.7, 112.8, 111.4, 61.5, 54.7, 20.4, 14.2.

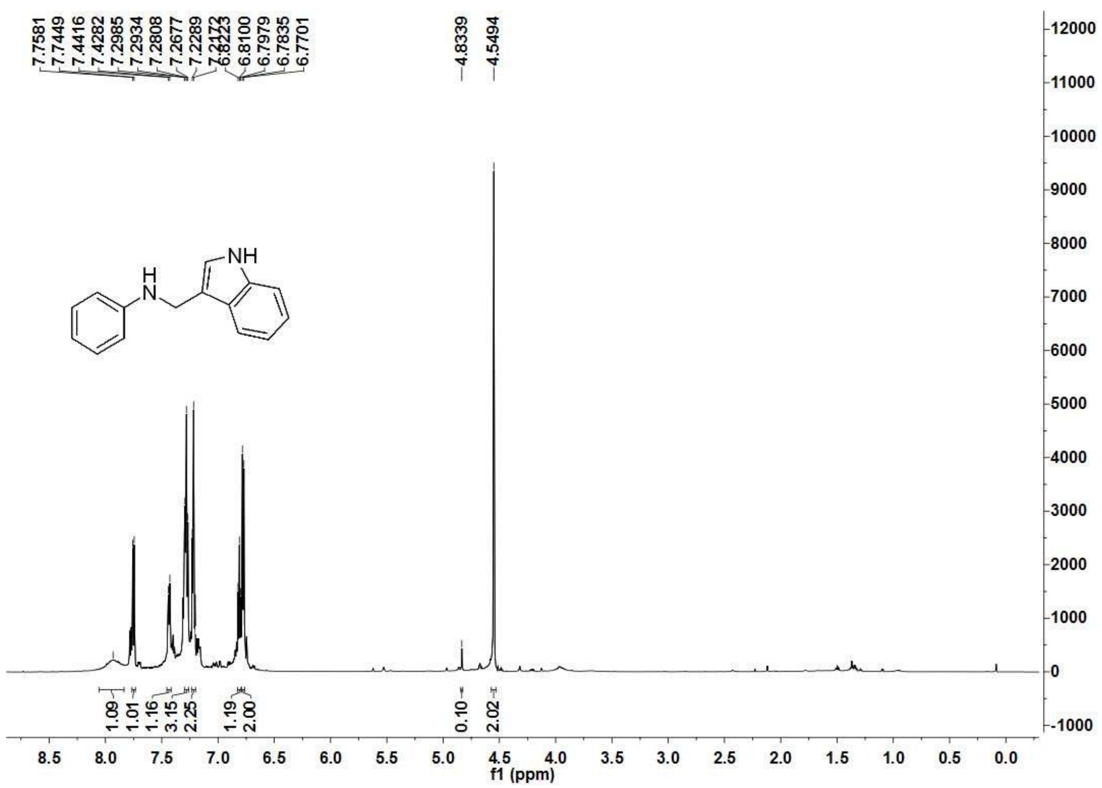
4. ^{1}H NMR and ^{13}C NMR spectra of the products

3aa





3ba



7.7581
7.7449
7.4416
7.4282
7.2985
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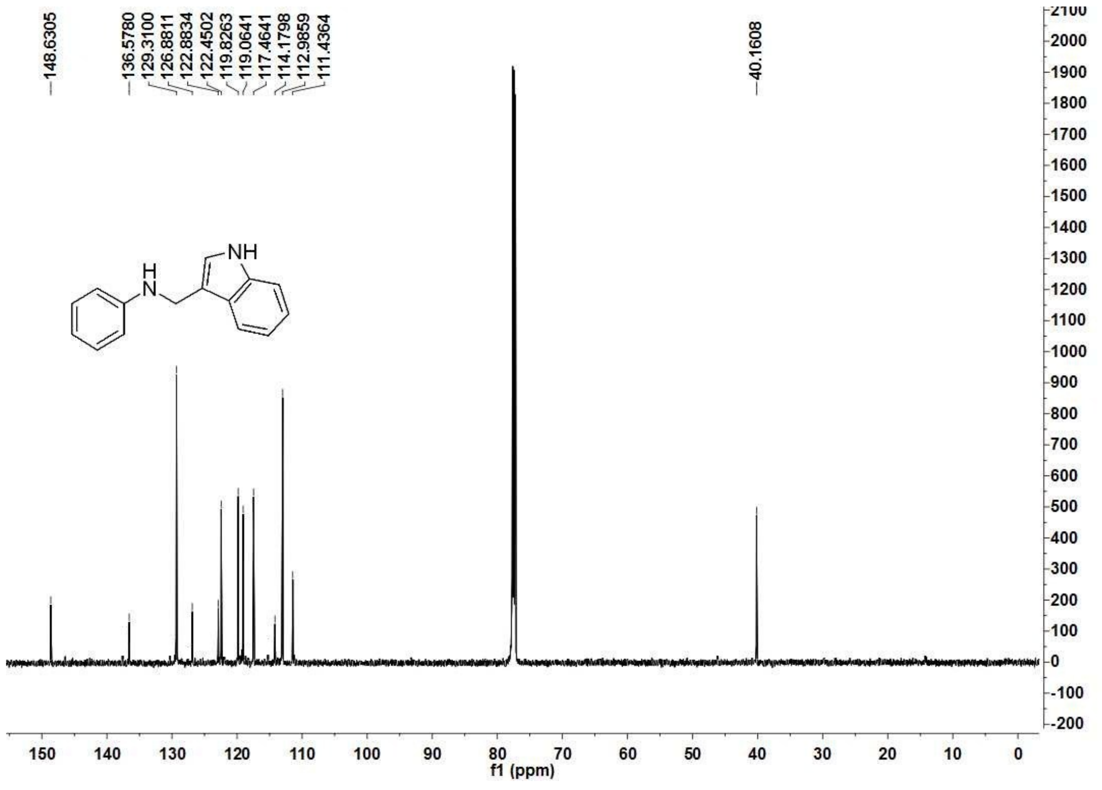
7.2677
7.2289
7.2172
6.8223
6.8100
6.7979
6.7835
6.7701
4.8339
4.5494
1.09
1.01
1.16
3.15
2.25
1.19
2.00
0.10
2.02
f1 (ppm)



148.6305
136.5780
129.3100
126.8811
122.8834
122.4502
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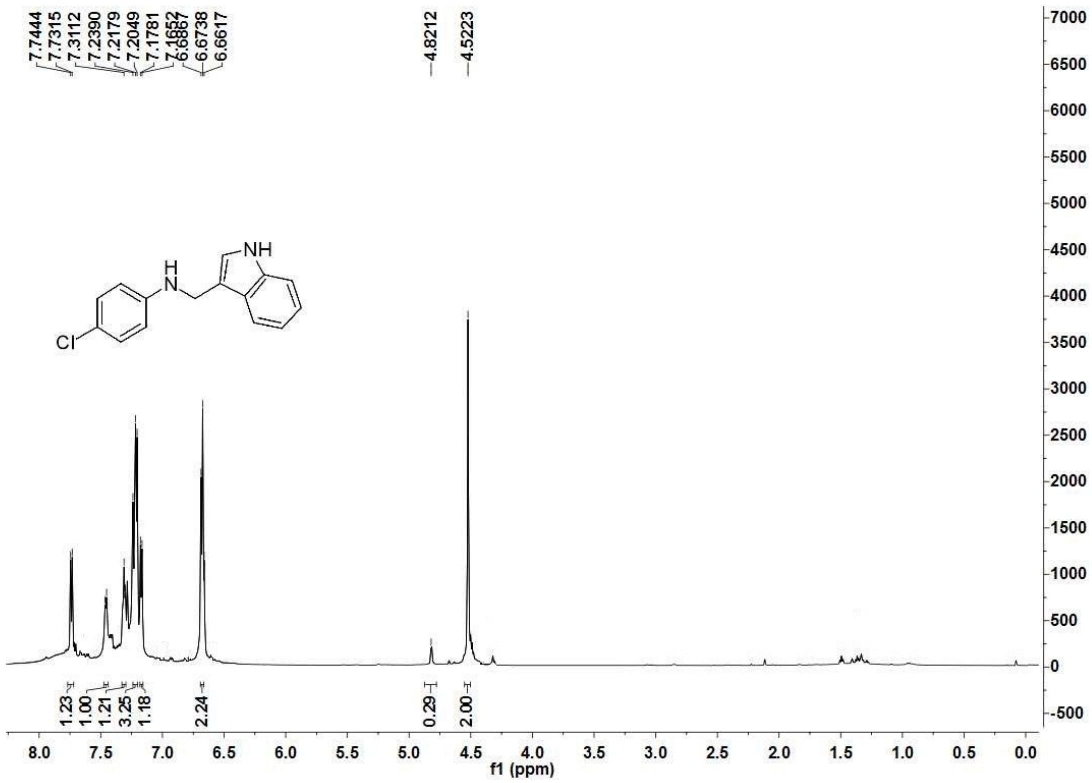
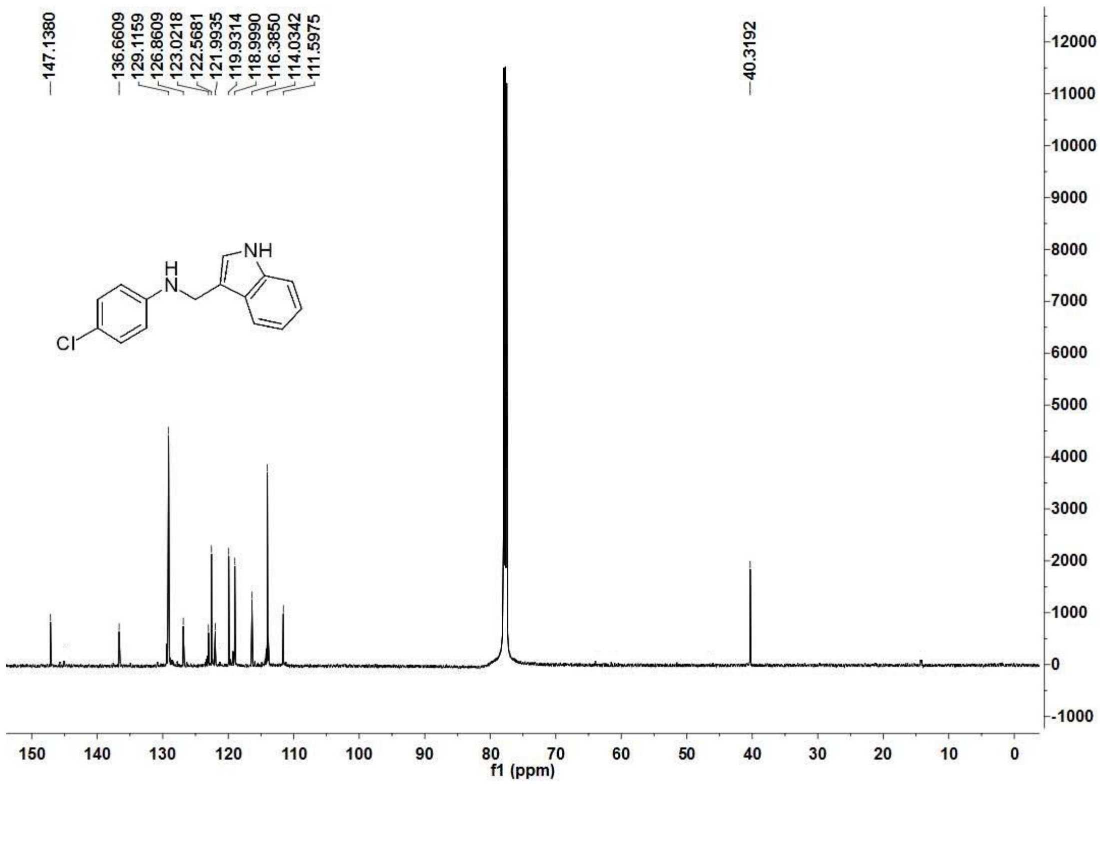
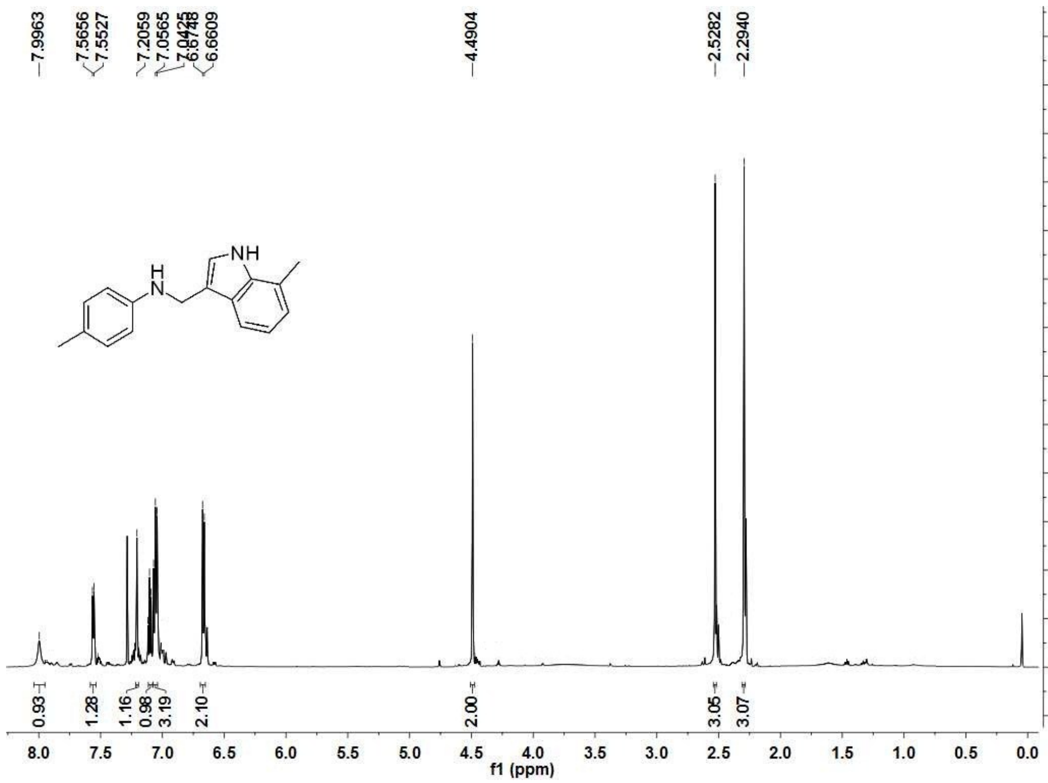
119.0641
117.4641
114.1798
112.9859
111.4364
40.1608
f1 (ppm)

3ca

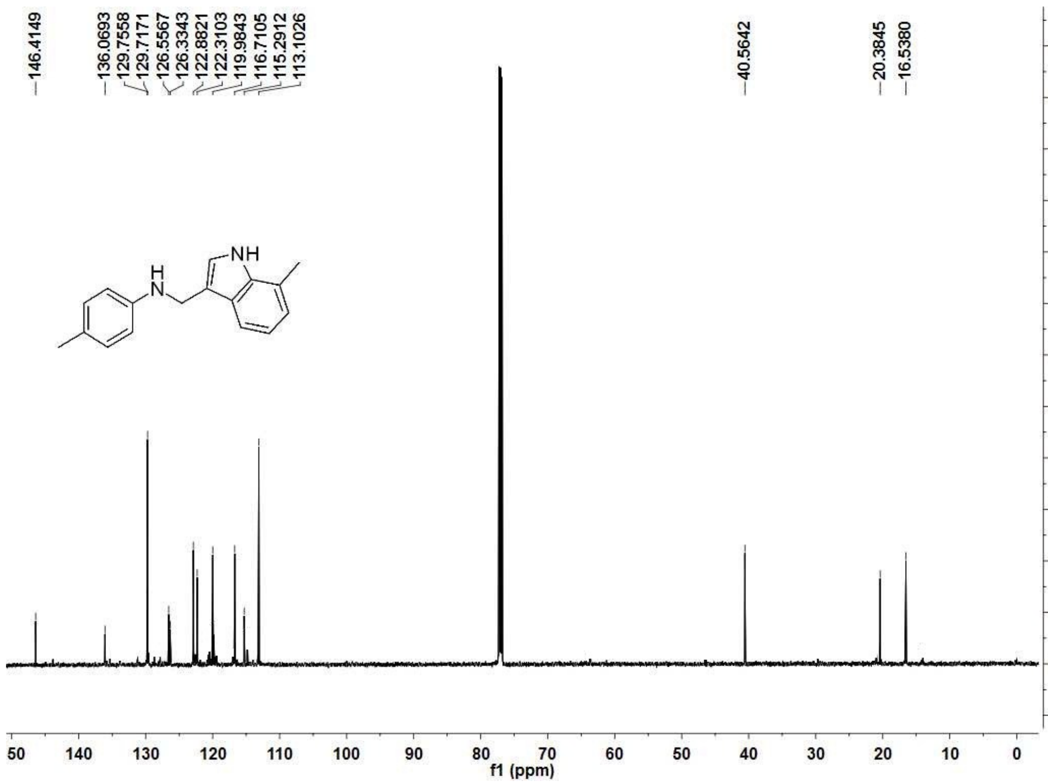

7.7444
7.7315
7.3112
7.2390
7.2179
7.2049
7.1781
7.1652
6.6867
6.6738
6.6617
4.8212
4.5223
NH
H
N
Cl
1.23
1.00
1.21
3.25
1.18
2.24
0.29
2.00
f1 (ppm)


147.1380
136.6609
129.1159
126.8609
123.0218
122.5681
121.9935
119.9314
118.9990
116.3850
114.0342
111.5975
40.3192
NH
H
N
Cl
f1 (ppm)

3ab



7.9963
7.5656
7.5527
7.2059
7.0565
7.0425
6.6748
6.6609
4.4904
2.5282
2.2940
0.93
1.28
1.16
0.98
3.19
2.10
2.00
3.05
3.07
NH
H
N
f1 (ppm)



146.4149
136.0693
129.7558
129.7171
126.5567
126.3343
122.8821
122.3103
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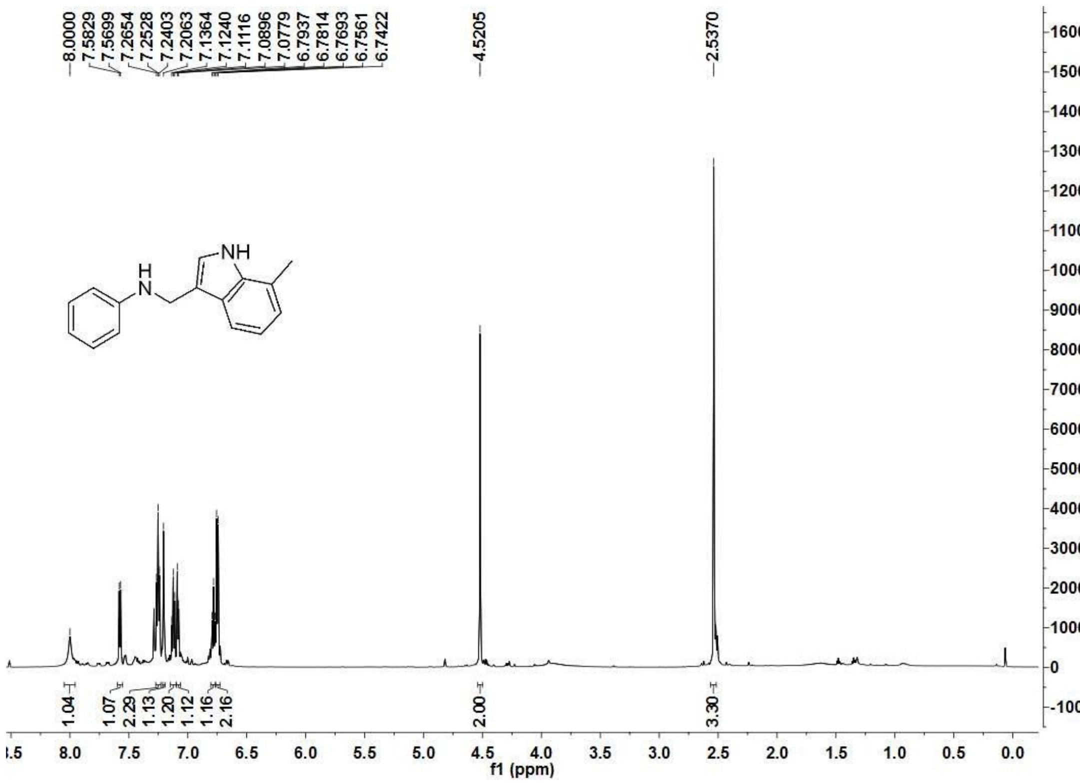
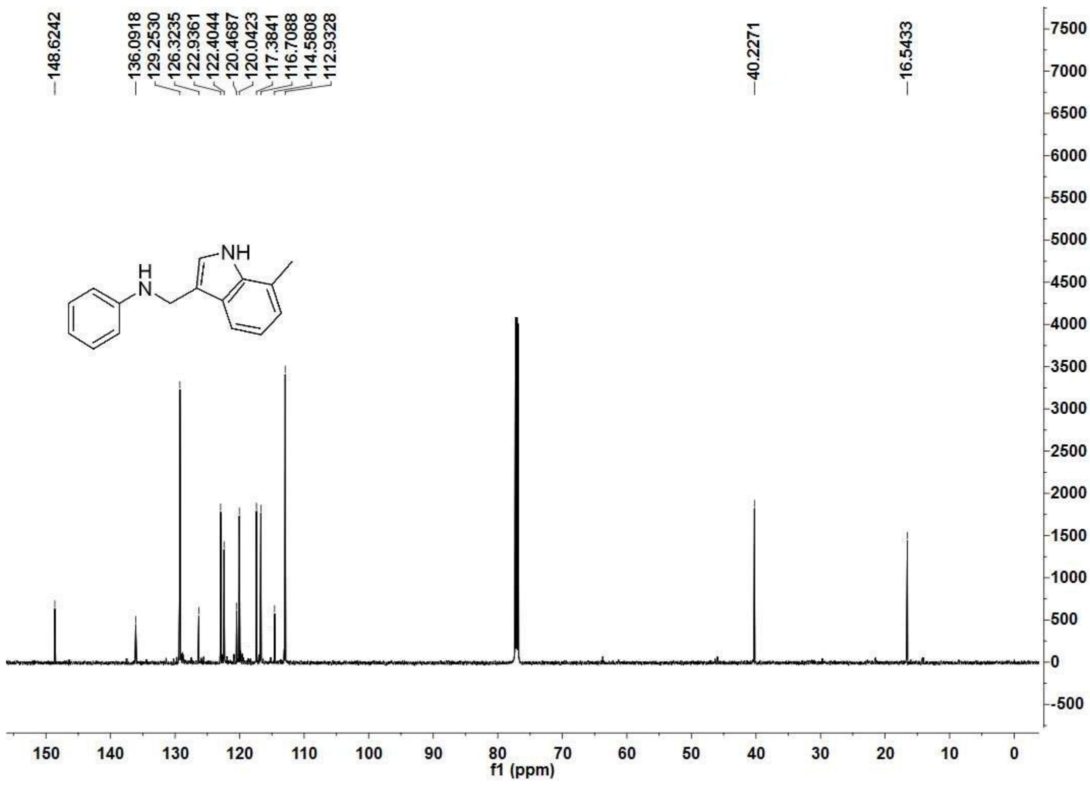
115.2912
113.1026
40.5642
20.3845
16.5380
NH
H
N
f1 (ppm)

3bb



8.0000
7.5829
7.5699
7.2654
7.2528
7.2403
7.2063
7.1364
7.1240
7.1116
7.0896
7.0779
6.7937
6.7814
6.7693
6.7561
6.7422
4.5205
2.5370
1.04
1.07
2.29
1.13
1.20
1.12
1.16
2.16
2.00
3.30
f1 (ppm)



148.6242
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126.3235
122.9361
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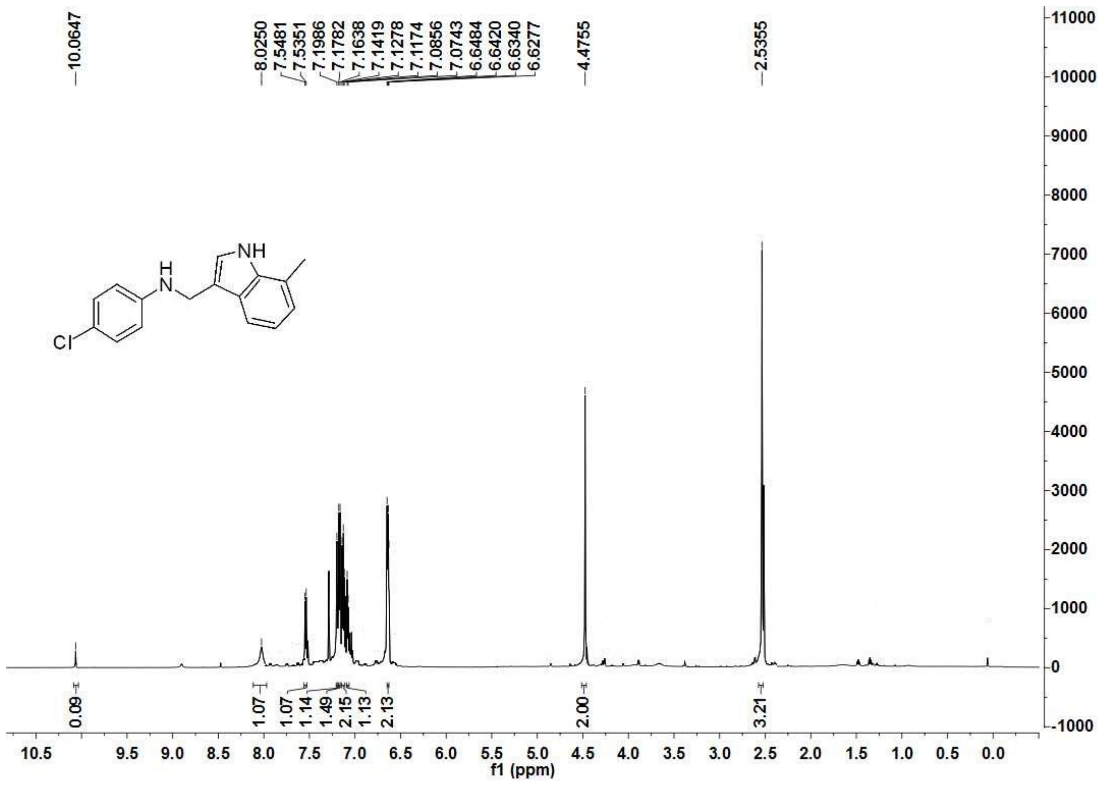
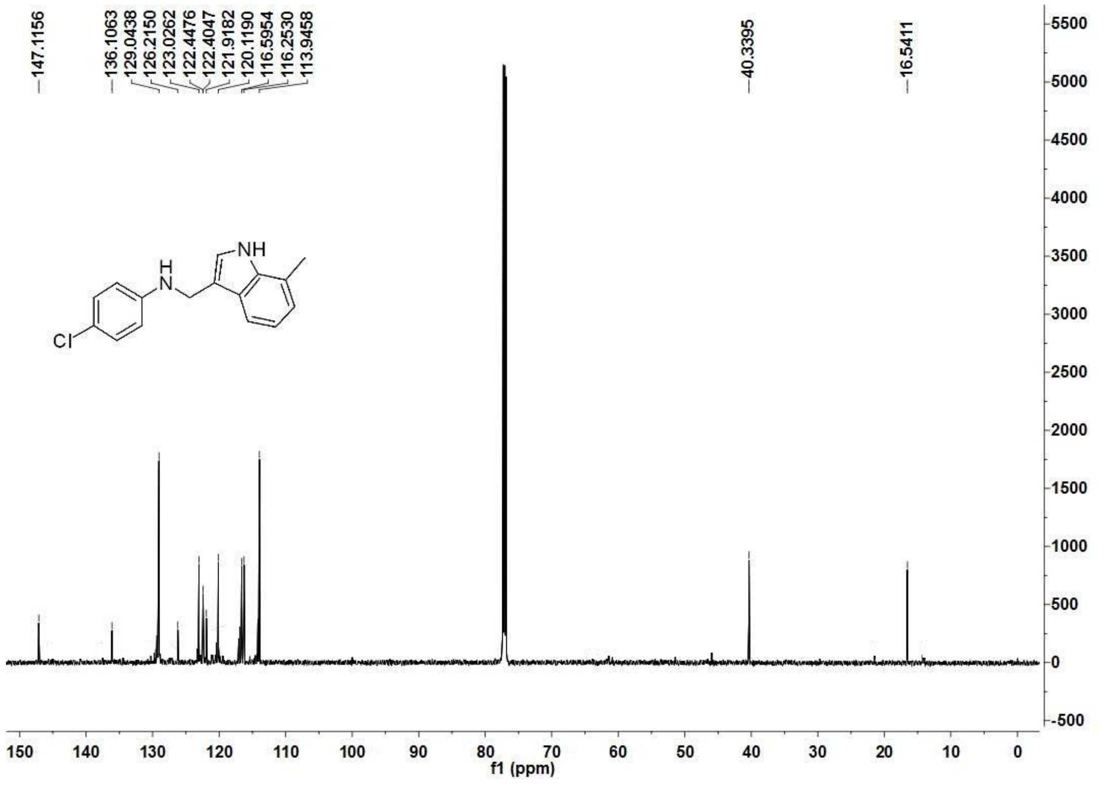
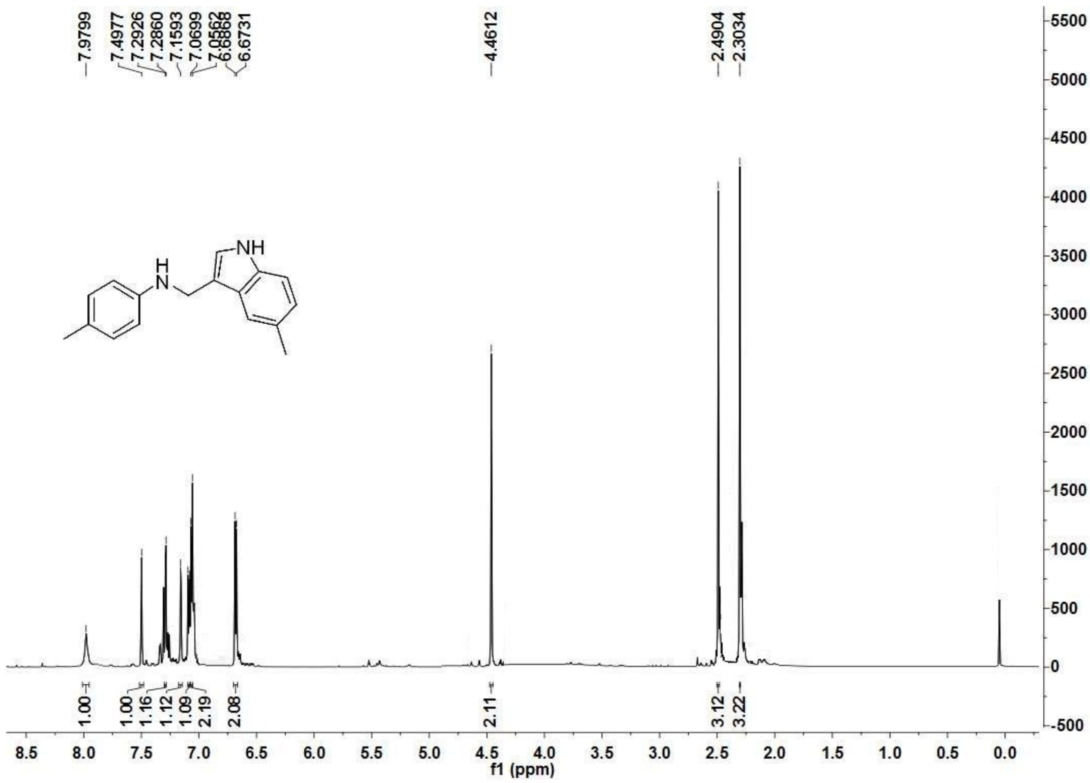
117.3841
116.7088
114.5808
112.9328
40.2271
16.5433
f1 (ppm)

3cb

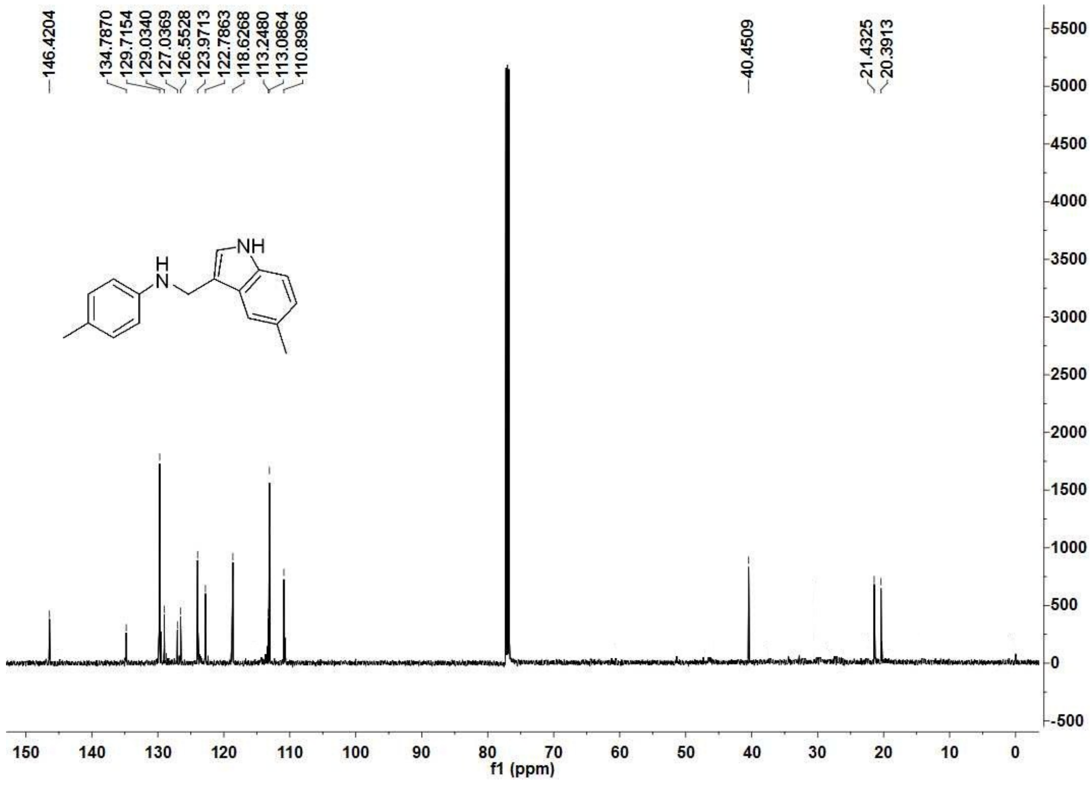




3ac

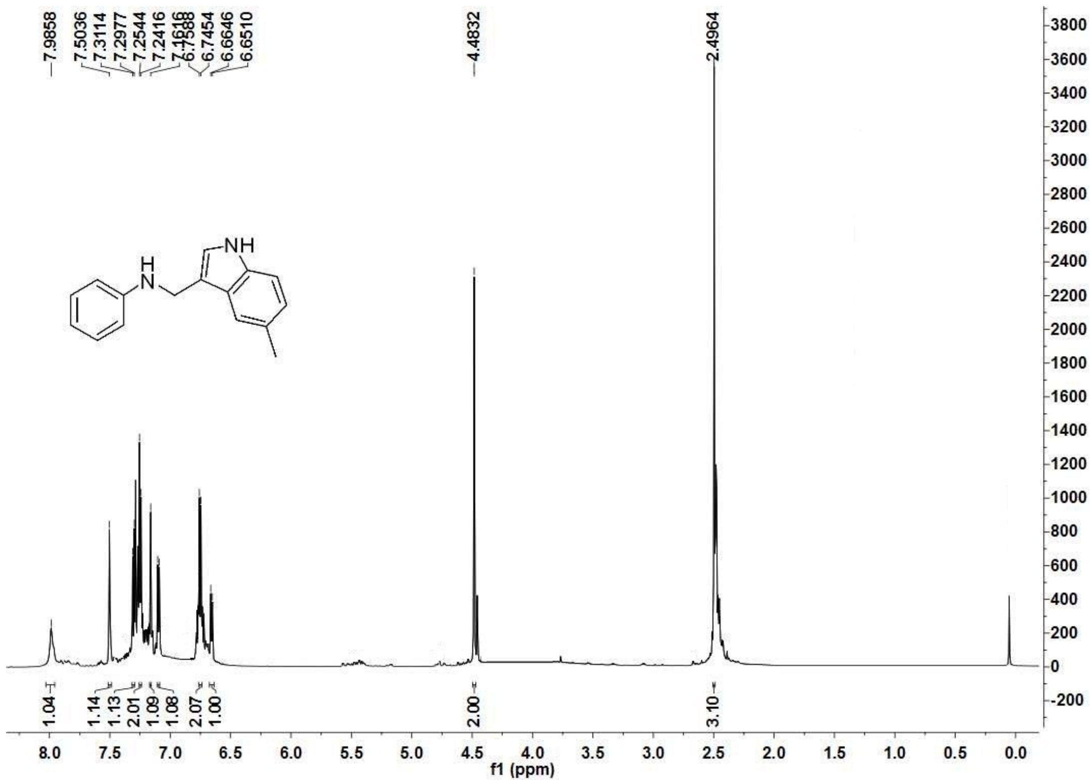


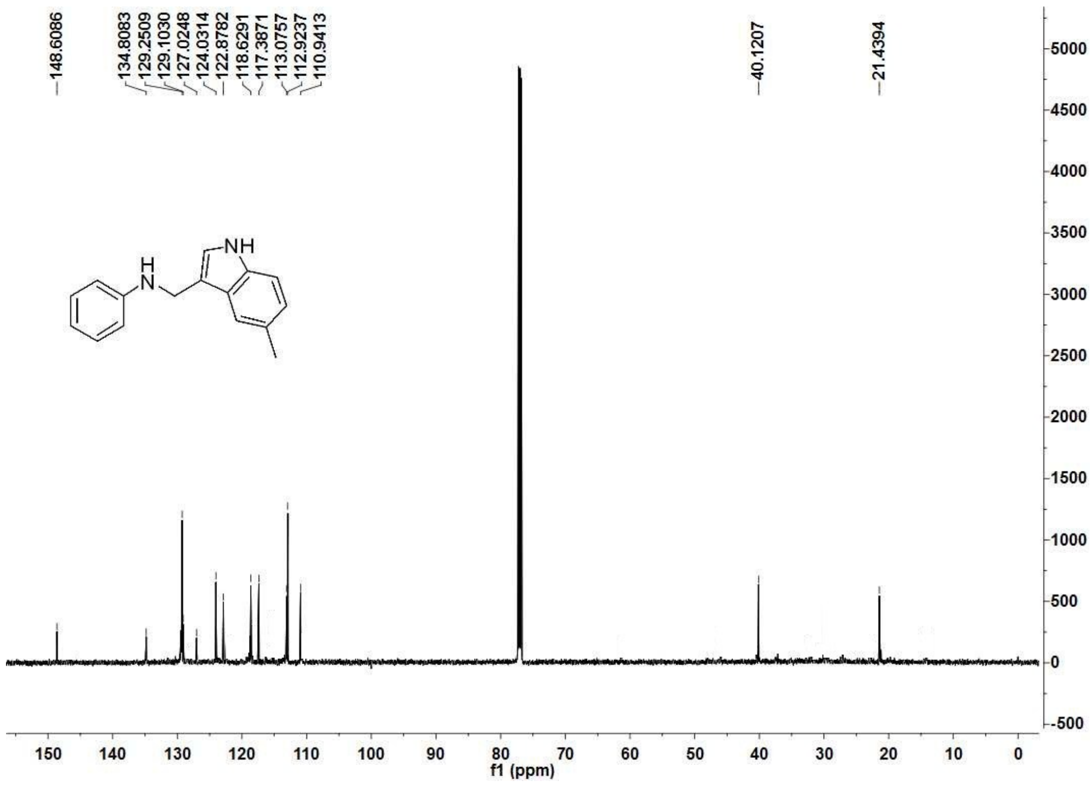
7.9799
7.4977
7.2926
7.2860
7.1593
7.0699
7.0562
6.6868
6.6731
4.4612
2.4904
2.3034
1.00
1.00
1.16
1.12
1.09
2.19
2.08
2.11
3.12
3.22
f1 (ppm)



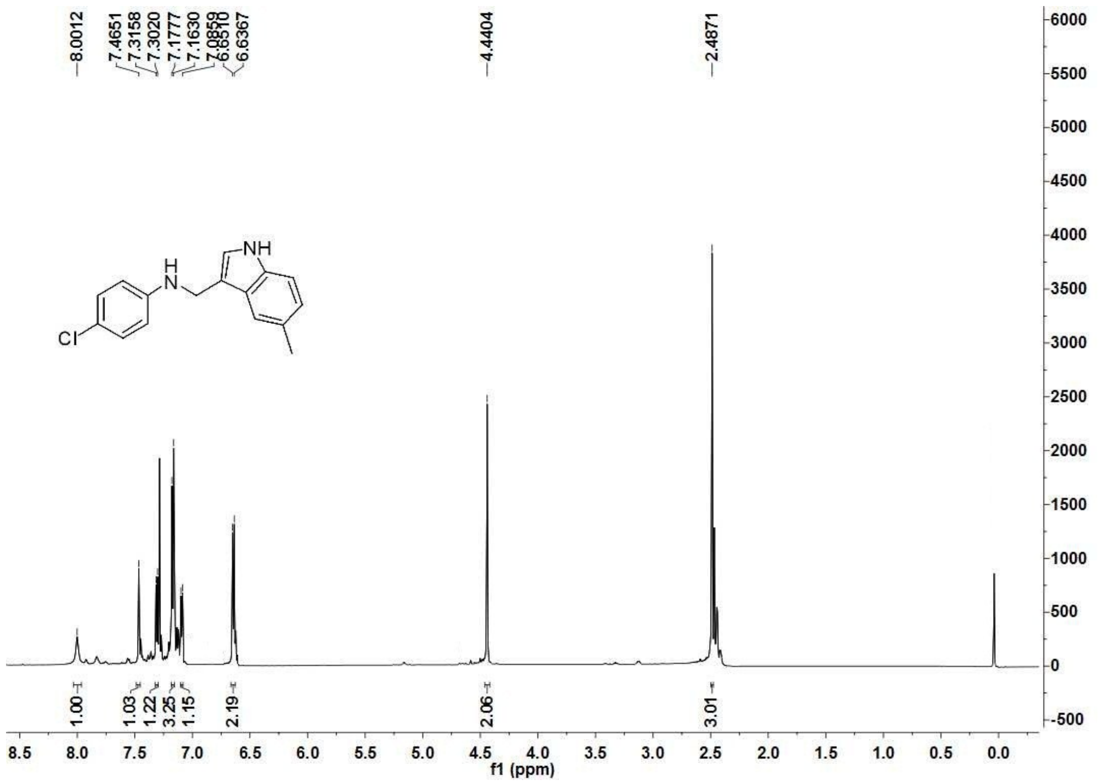
146.4204
134.7870
129.7154
129.0340
127.0369
126.5528
123.9713
122.7863
118.6268
113.2480
113.0864
110.8986
40.4509
21.4325
20.3913
f1 (ppm)

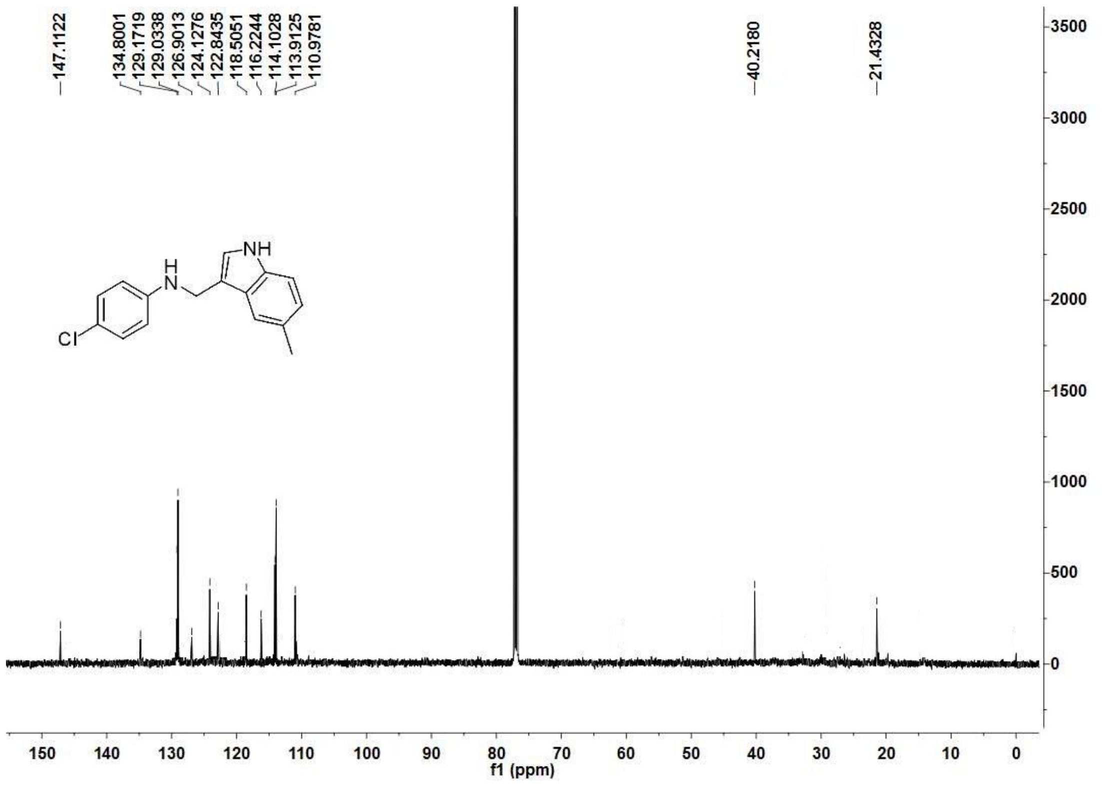
3bc


7.9858
7.5036
7.3114
7.2977
7.2544
7.2416
7.1616
7.1588
6.7454
6.6646
6.6510
4.4832
2.4964
NH
H
N
1.04
1.14
1.13
2.01
1.09
1.08
2.07
1.00
2.00
3.10
f1 (ppm)

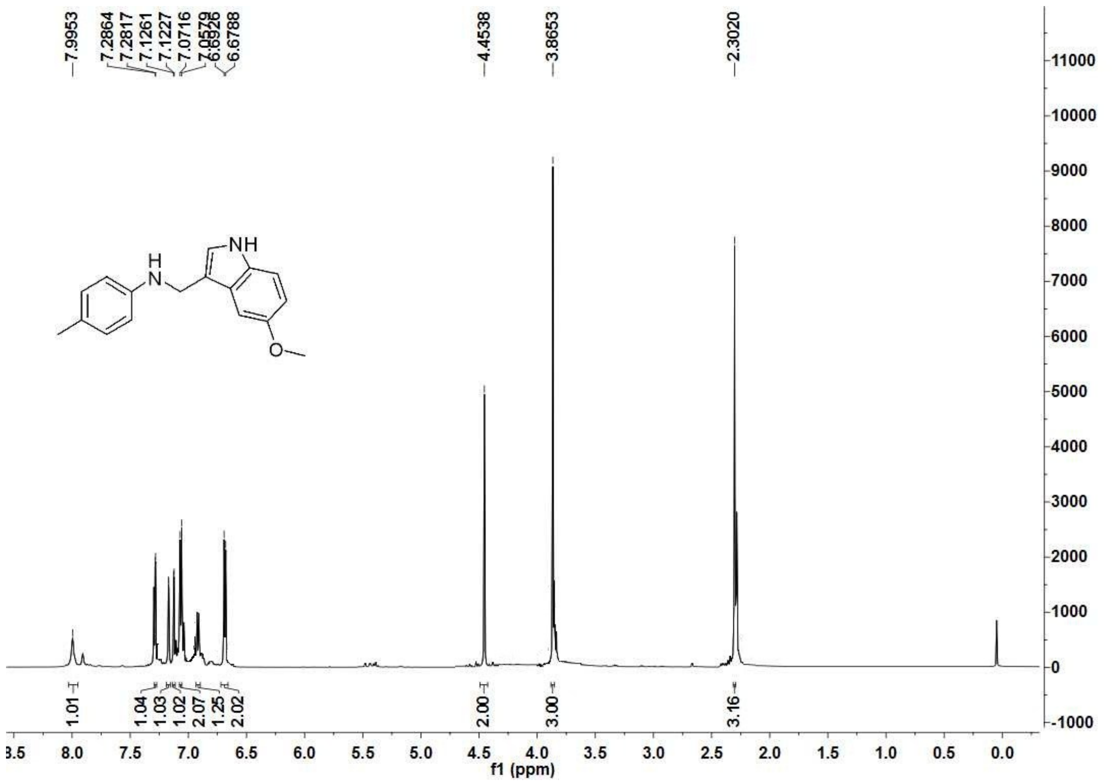

148.6086
134.8083
129.2509
129.1030
127.0248
124.0314
122.8782
118.6291
117.3871
113.0757
112.9237
110.9413
40.1207
21.4394
NH
H
N
f1 (ppm)

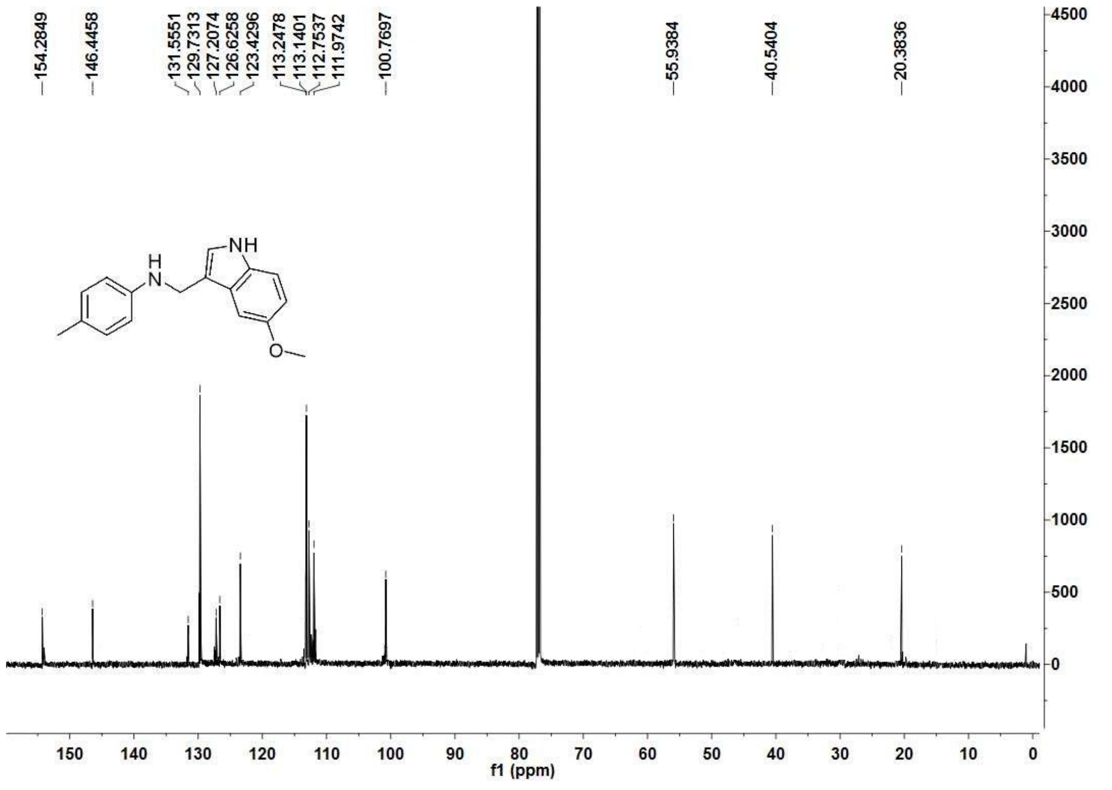
3cc


8.0012
7.4651
7.3158
7.3020
7.1777
7.1630
7.0859
6.6510
6.6367
4.4404
2.4871
NH
H
N
Cl
1.00
1.03
1.22
3.25
1.15
2.19
2.06
3.01
f1 (ppm)

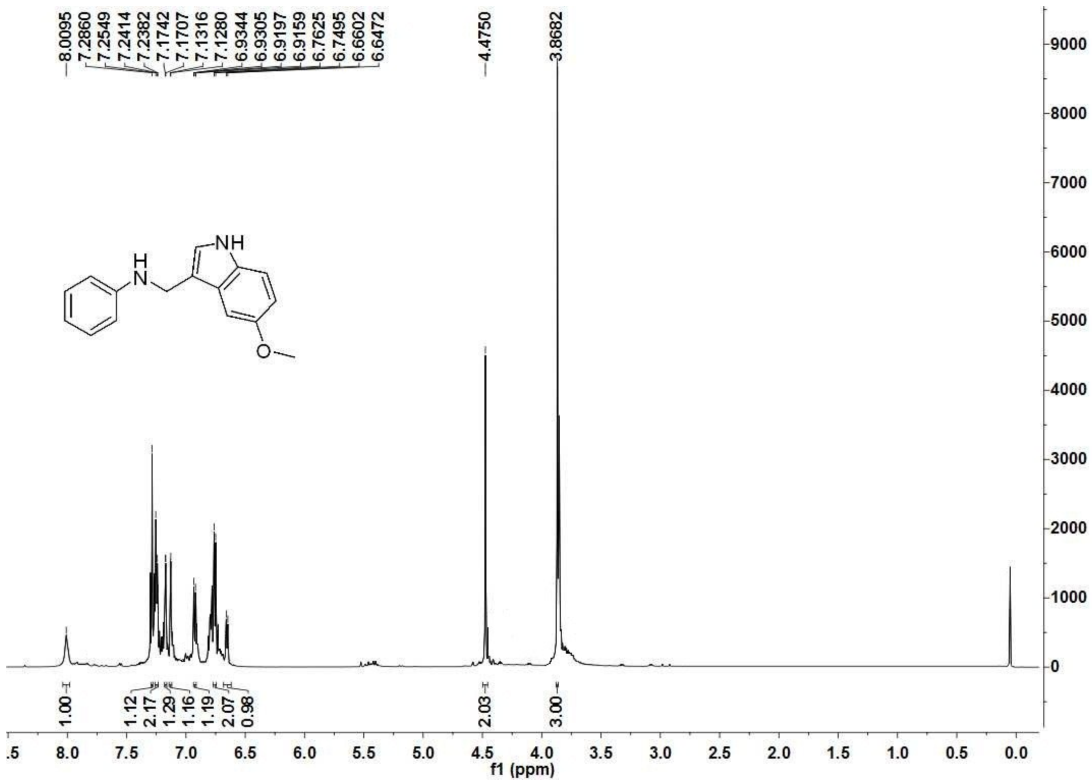

147.1122
134.8001
129.1719
129.0338
126.9013
124.1276
122.8435
118.5051
116.2244
114.1028
113.9125
110.9781
40.2180
21.4328
NH
H
N
Cl
f1 (ppm)

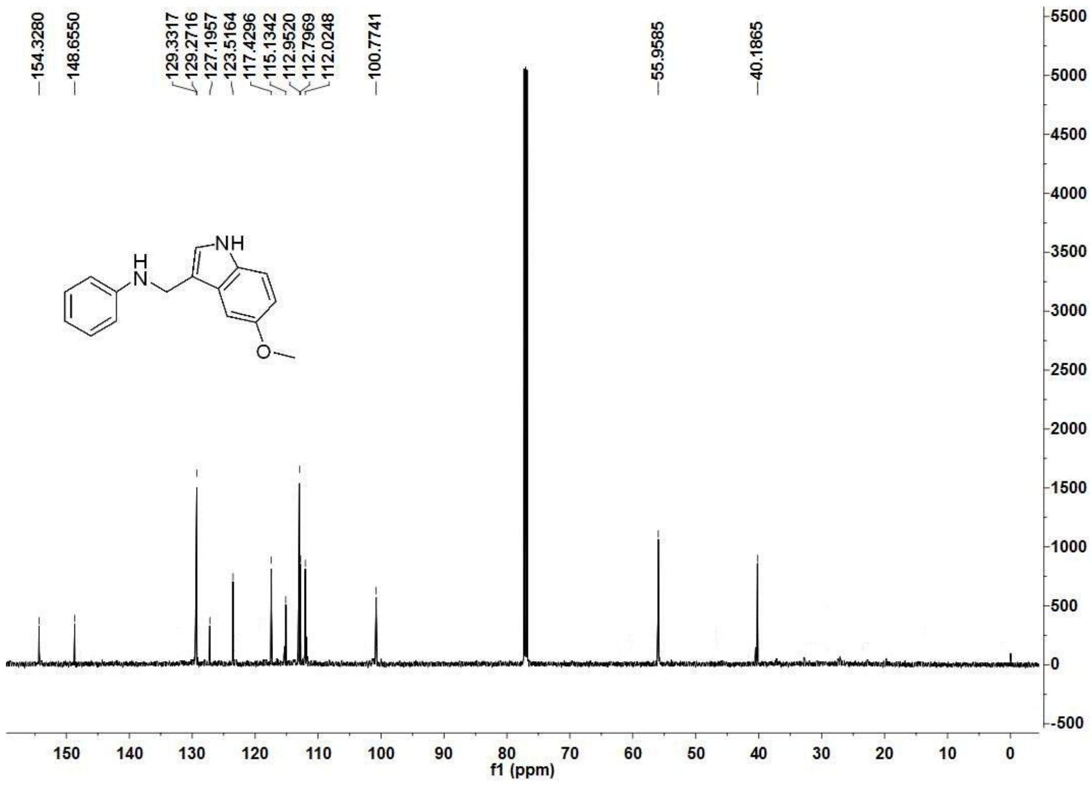
3ad


7.9953
7.2864
7.2817
7.1261
7.1227
7.0716
7.0579
6.6926
6.6788
4.4538
3.8653
2.3020
NH
H
N
O
1.01
1.04
1.03
1.02
2.07
1.25
2.02
2.00
3.00
3.16
f1 (ppm)

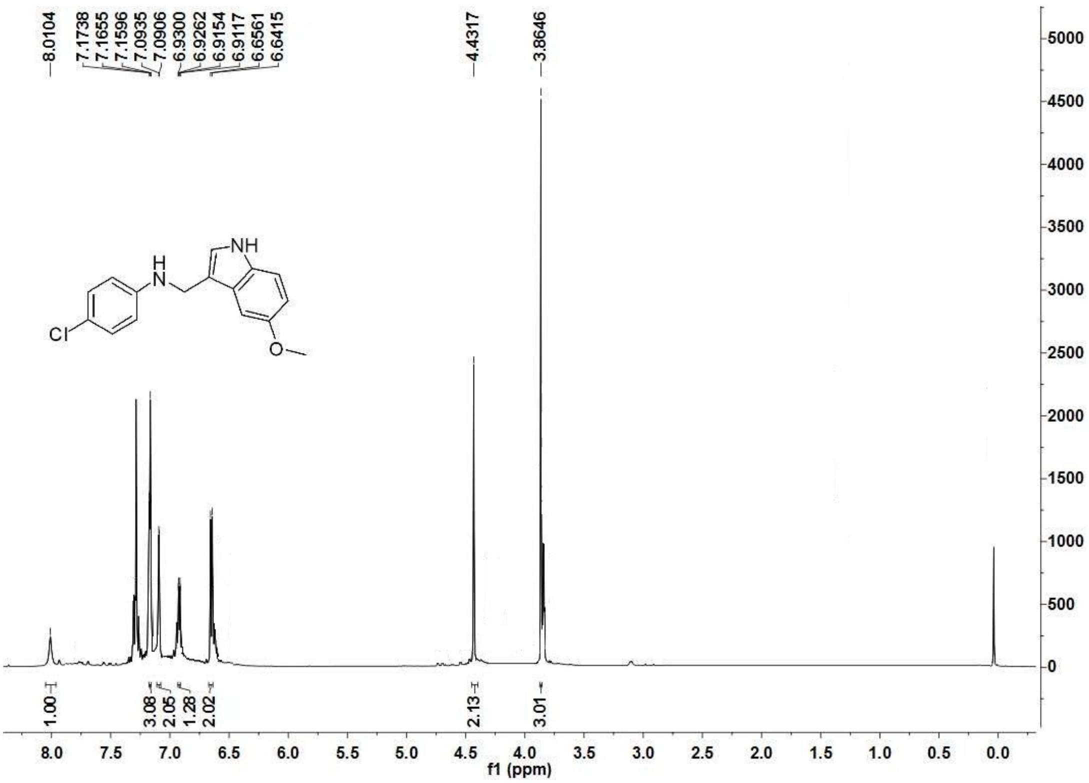

154.2849
146.4458
131.5551
129.7313
127.2074
126.6258
123.4296
113.2478
113.1401
112.7537
111.9742
100.7697
55.9384
40.5404
20.3836
NH
H
N
O
f1 (ppm)

3bd

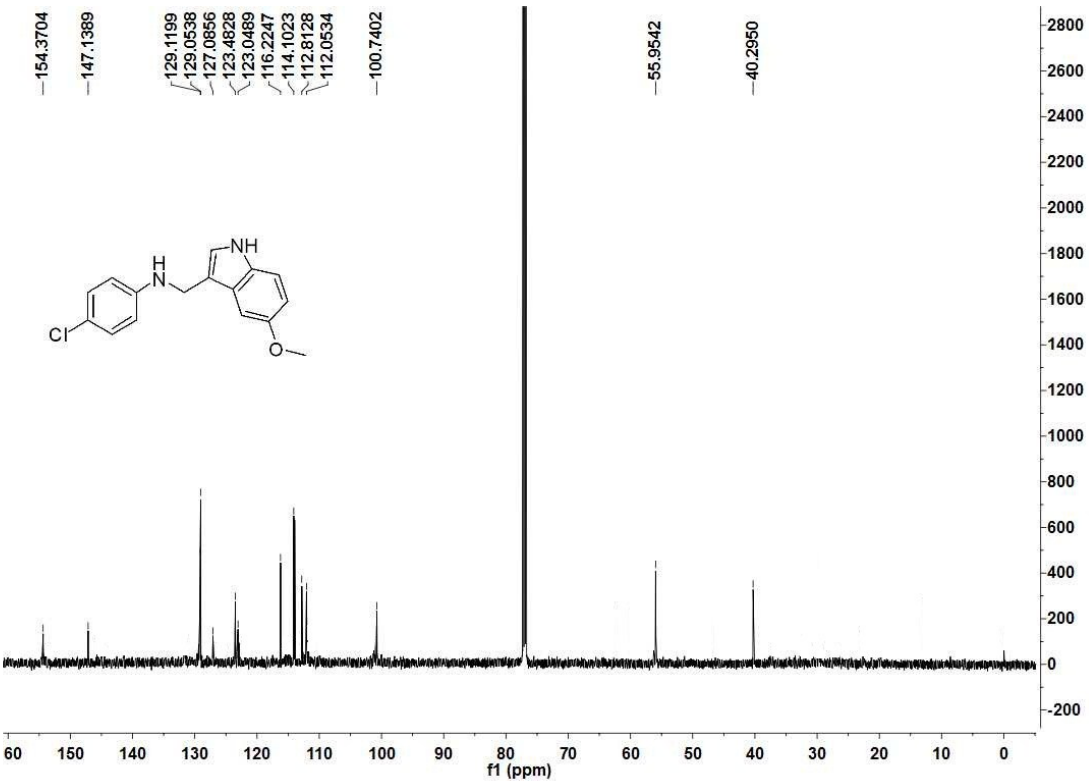

8.0095
7.2860
7.2549
7.2414
7.2382
7.1742
7.1707
7.1316
7.1280
6.9344
6.9305
6.9197
6.9159
6.7625
6.7495
6.6602
6.6472
4.4750
3.8682
NH
H
N
O
1.00
1.12
2.17
1.29
1.16
1.19
2.07
0.98
2.03
3.00
f1 (ppm)


154.3280
148.6550
129.3317
129.2716
127.1957
123.5164
117.4296
115.1342
112.9520
112.7969
112.0248
100.7741
55.9585
40.1865
NH
H
N
O
f1 (ppm)

3cd



8.0104
7.1738
7.1655
7.1596
7.0935
7.0906
6.9300
6.9262
6.9154
6.9117
6.6561
6.6415
4.4317
3.8646
1.00
3.08
2.05
1.28
2.02
2.13
3.01
f1 (ppm)



154.3704
147.1389
129.1199
129.0538
127.0856
123.4828
123.0489
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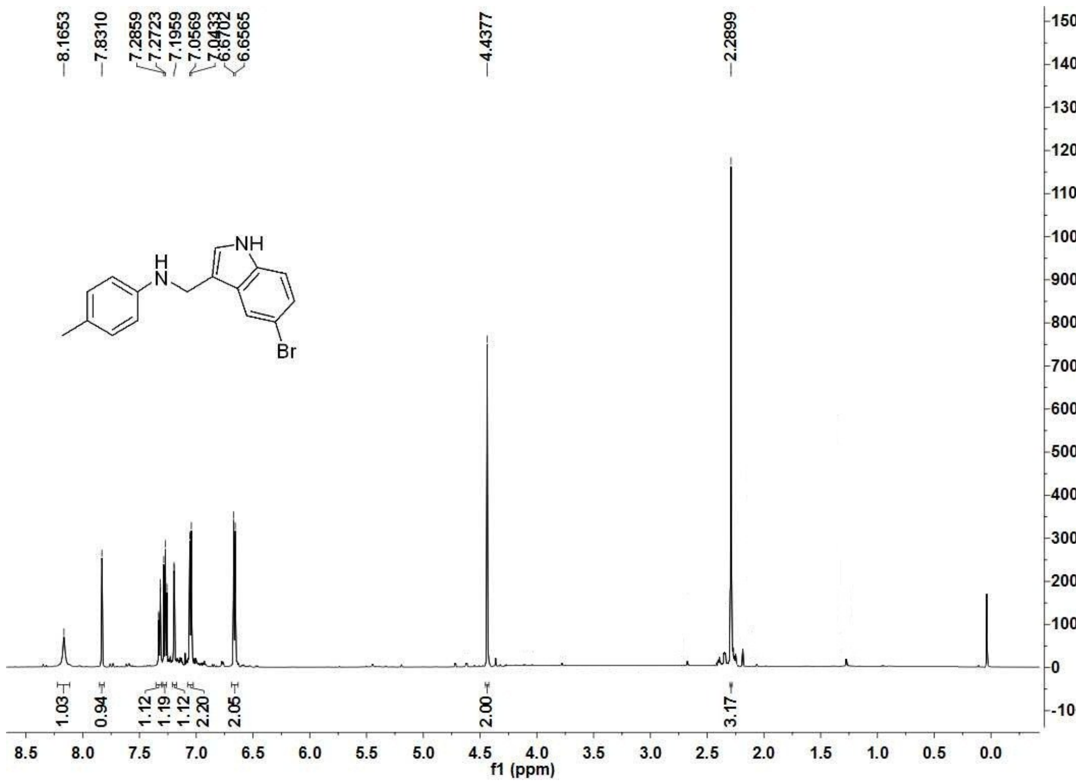
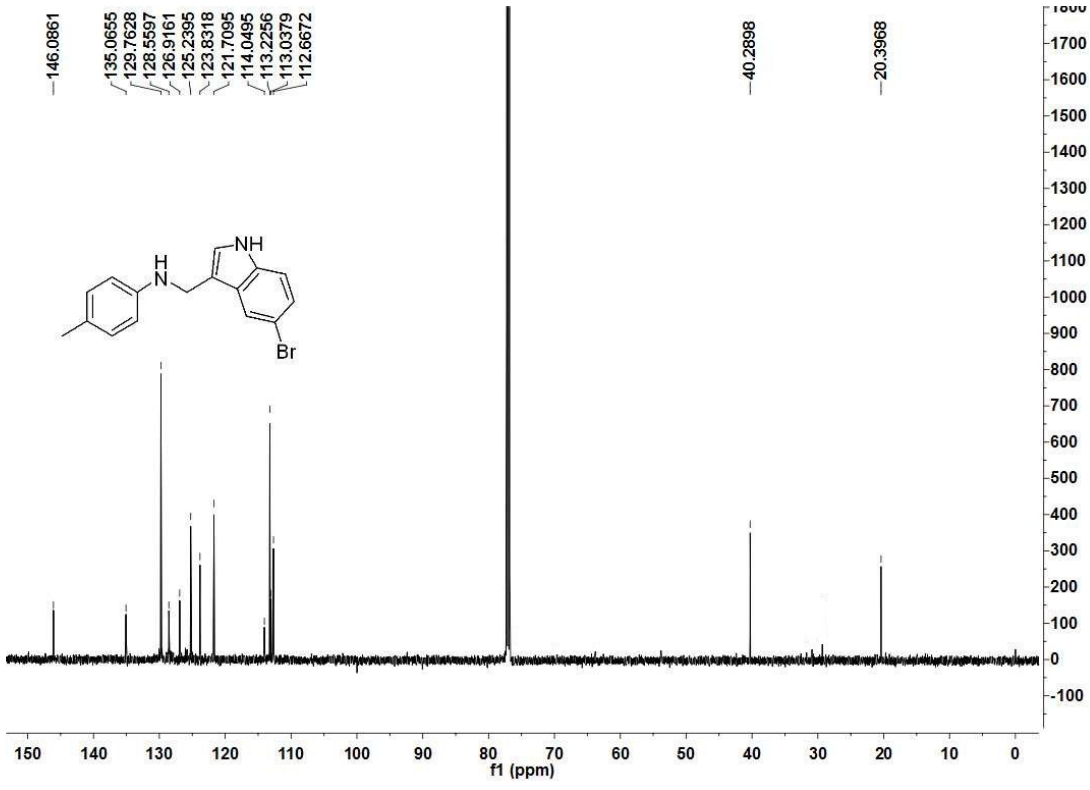
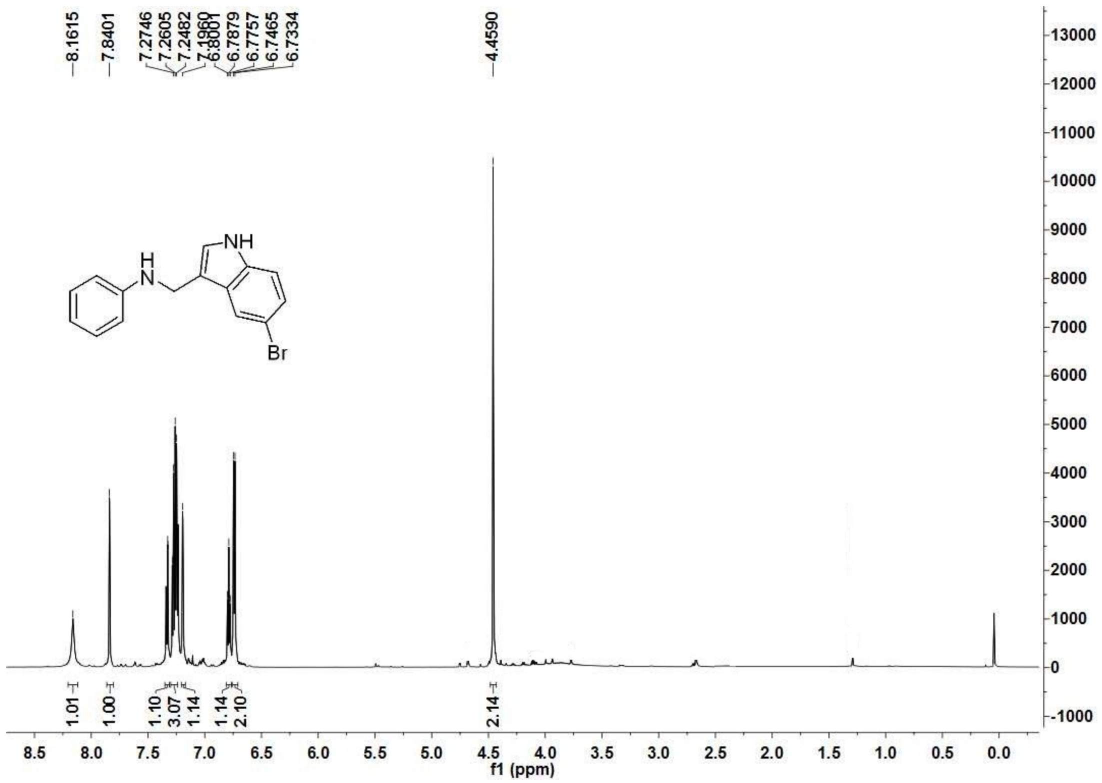
112.0534
100.7402
55.9542
40.2950
f1 (ppm)

3ae





3be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7.2482
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6.8001
6.7879
6.7757
6.7465
6.7334
4.4590
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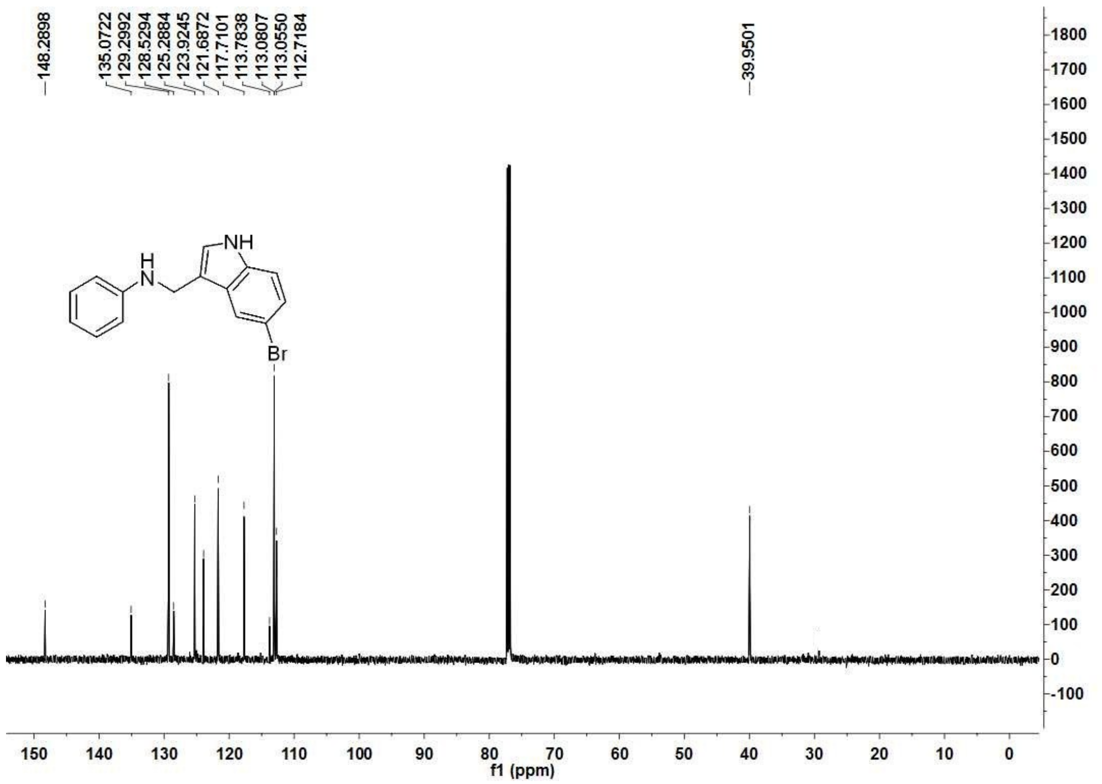
H
N
Br
1.01
1.00
1.10
3.07
1.14
1.14
2.10
2.14
f1 (ppm)


148.2898
135.0722
129.2992
128.5294
125.2884
123.9245
121.6872
117.7101
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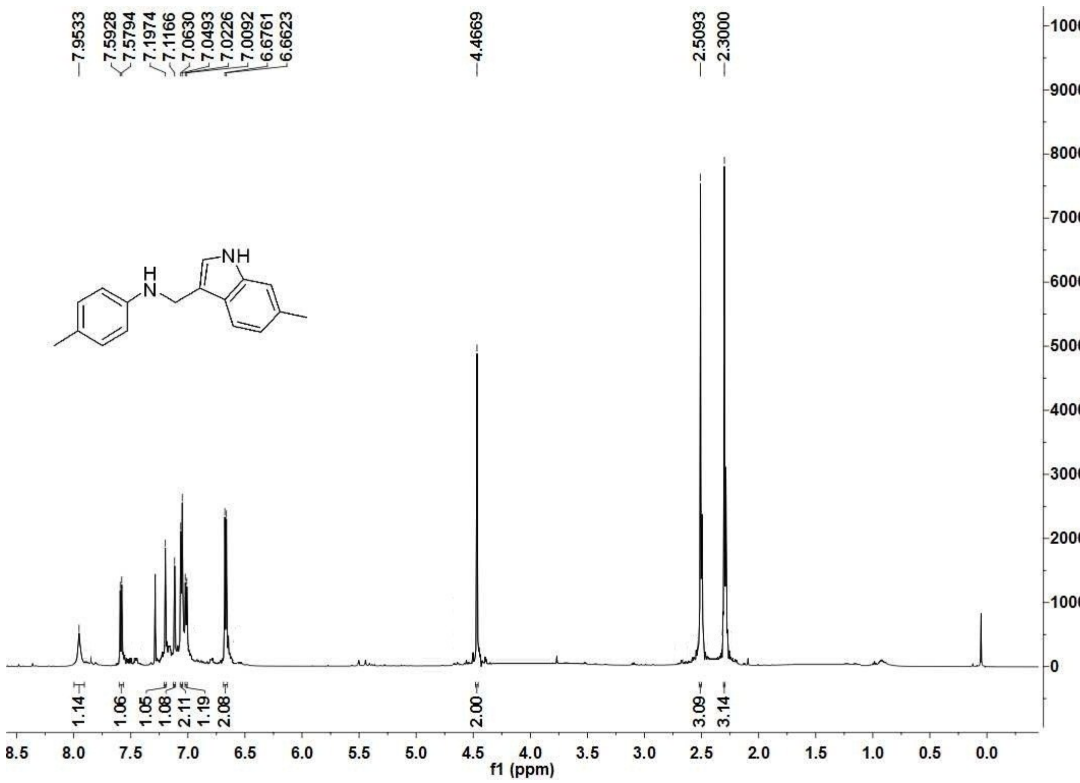
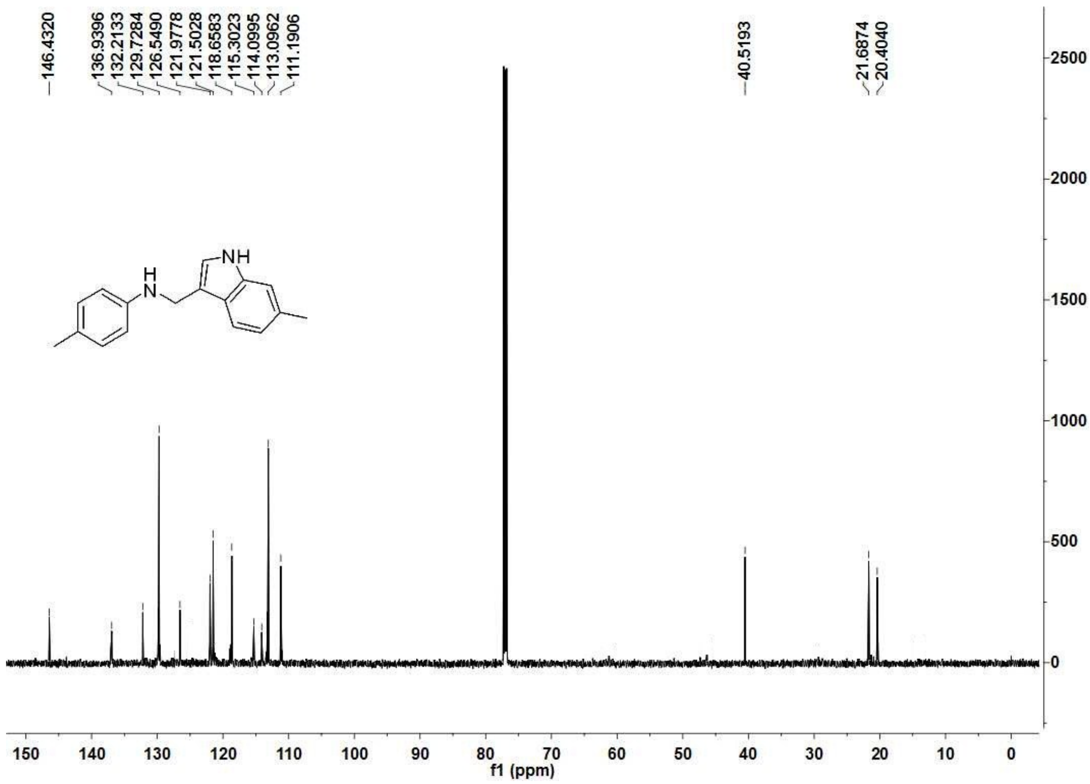
113.0807
113.0550
112.7184
39.9501
NH
H
N
Br
f1 (ppm)

3af



7.9533
7.5928
7.5794
7.1974
7.1166
7.0630
7.0493
7.0226
7.0092
6.6761
6.6623
4.4669
2.5093
2.3000
1.14
1.06
1.05
1.08
2.11
1.19
2.08
2.00
3.09
3.14
f1 (ppm)



146.4320
136.9396
132.2133
129.7284
126.5490
121.9778
121.5028
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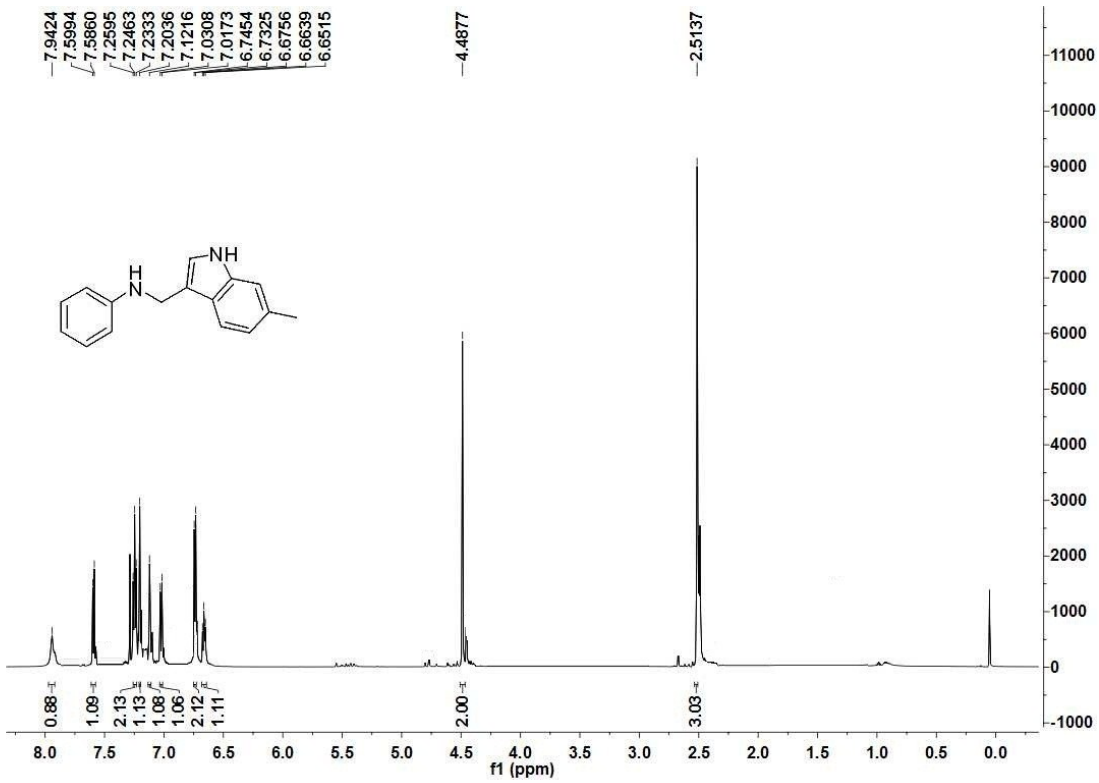
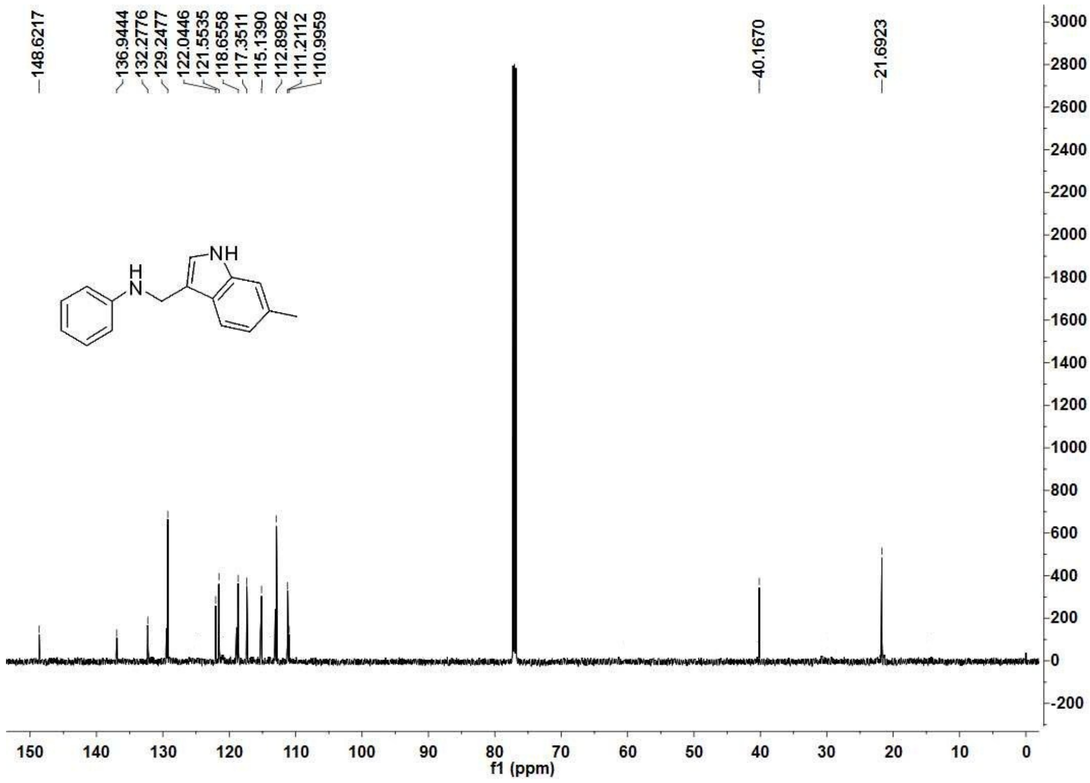
114.0995
113.0962
111.1906
40.5193
21.6874
20.4040
f1 (ppm)

3bf



7.9424
7.5994
7.5860
7.2595
7.2463
7.2333
7.2036
7.1216
7.0308
7.0173
6.7454
6.7325
6.6756
6.6639
6.6515
4.4877
2.5137
NH
H
N
0.88
1.09
2.13
1.13
1.08
1.06
2.12
1.11
2.00
3.03
f1 (ppm)



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122.0446
121.5535
118.6558
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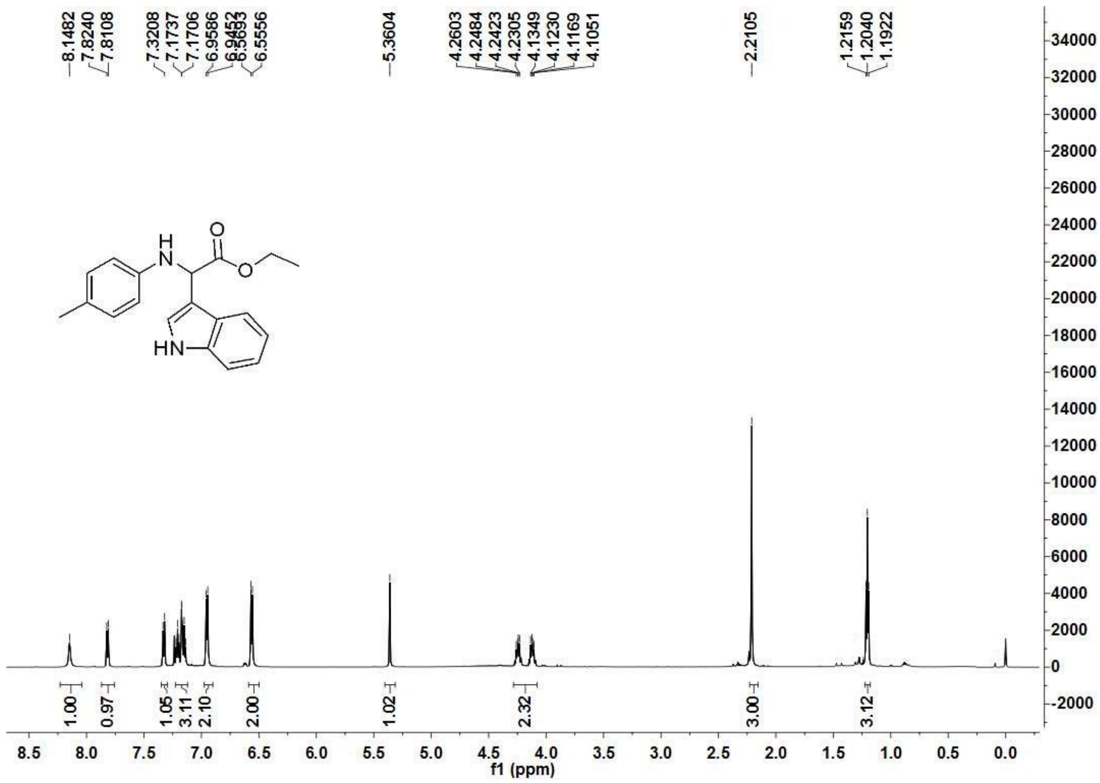
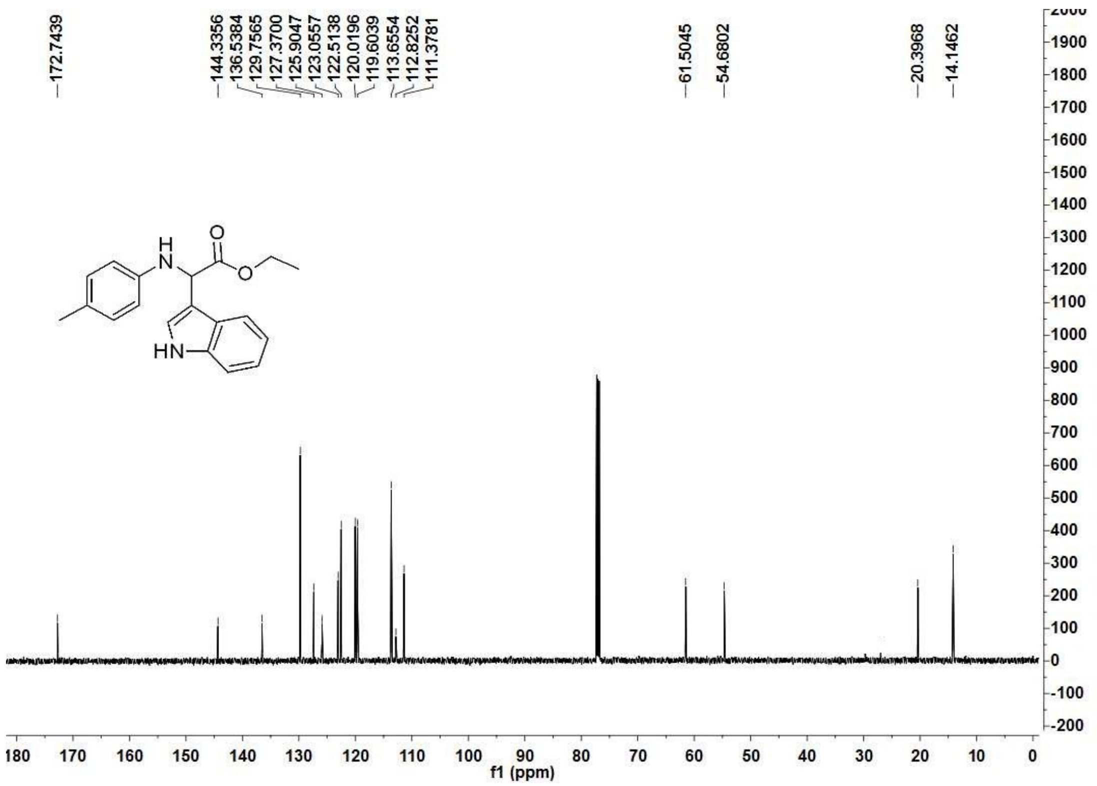
112.8982
111.2112
110.9959
40.1670
21.6923
NH
H
N
f1 (ppm)

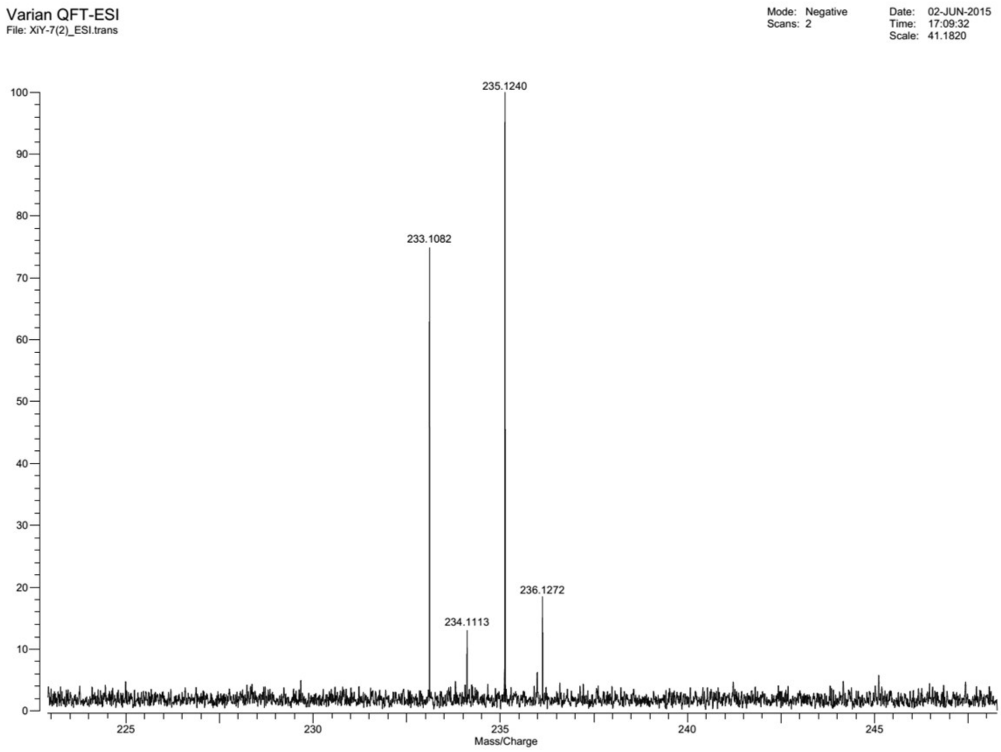
4



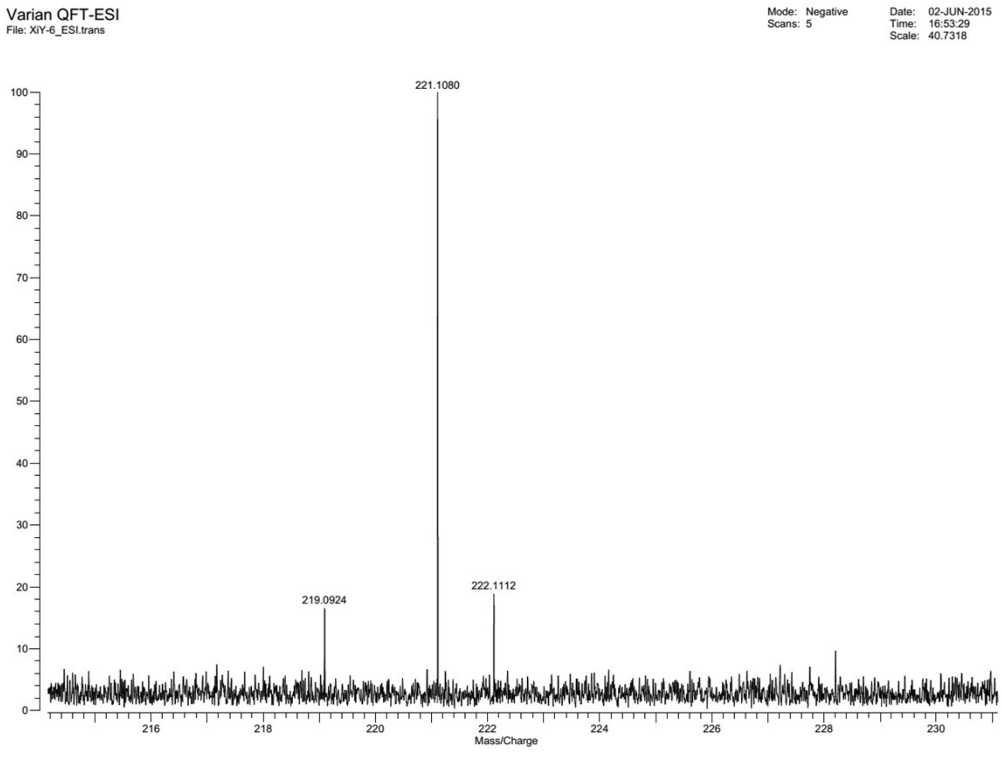


5. HRMS spectra of new compounds

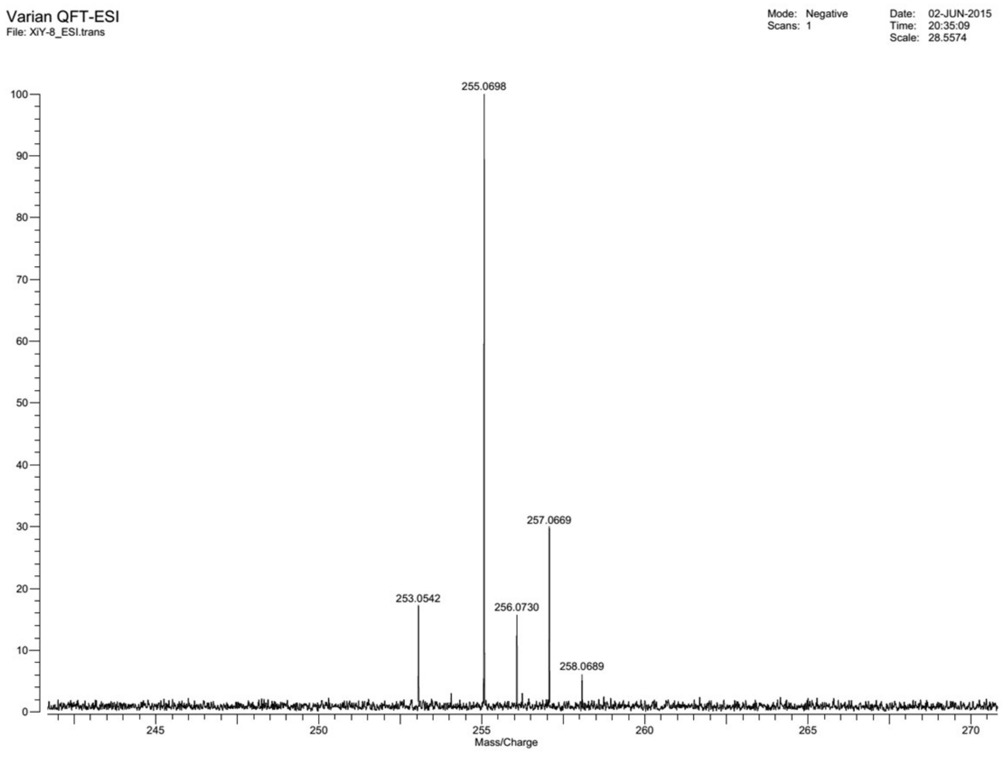
3aa



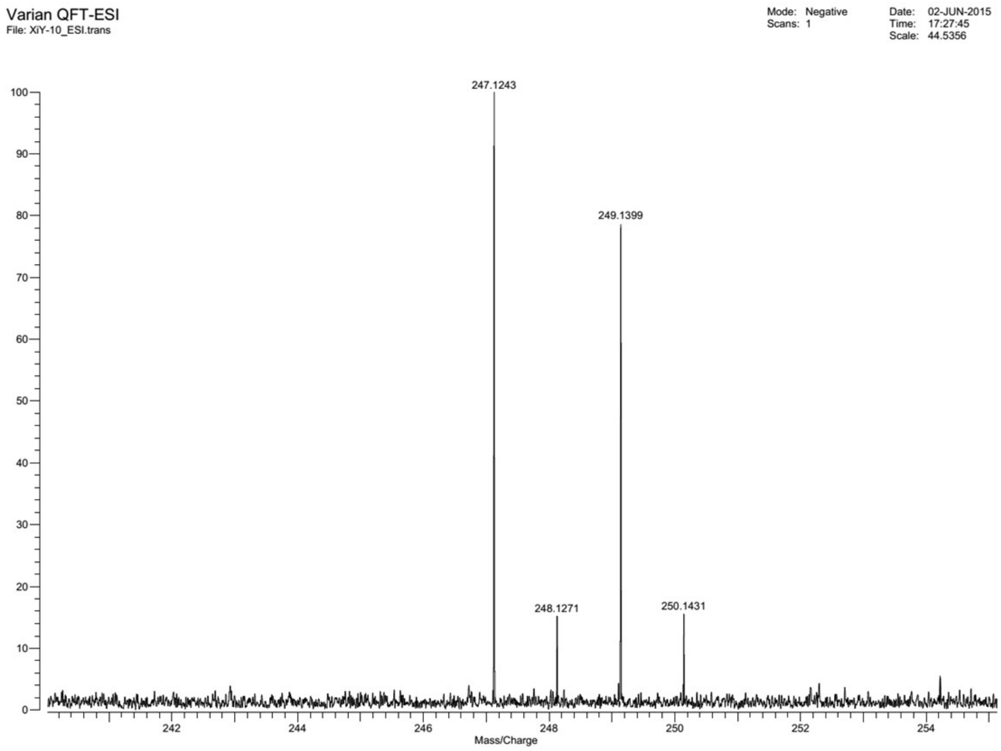
3ba


Varian QFT-ESI
File: XiY-6_ESI.trans
Mode: Negative
Scans: 5
Date: 02-JUN-2015
Time: 16:53:29
Scale: 40.7318
221.1080
219.0924
222.1112
Mass/Charge

3ca


Varian QFT-ESI
File: XiY-8_ESI.trans
Mode: Negative
Scans: 1
Date: 02-JUN-2015
Time: 20:35:09
Scale: 28.5574
255.0698
257.0669
253.0542
256.0730
258.0689
Mass/Charge

3ab


Varian QFT-ESI
File: XiY-10_ESI.trans
Mode: Negative
Scans: 1
Date: 02-JUN-2015
Time: 17:27:45
Scale: 44.5356
247.1243
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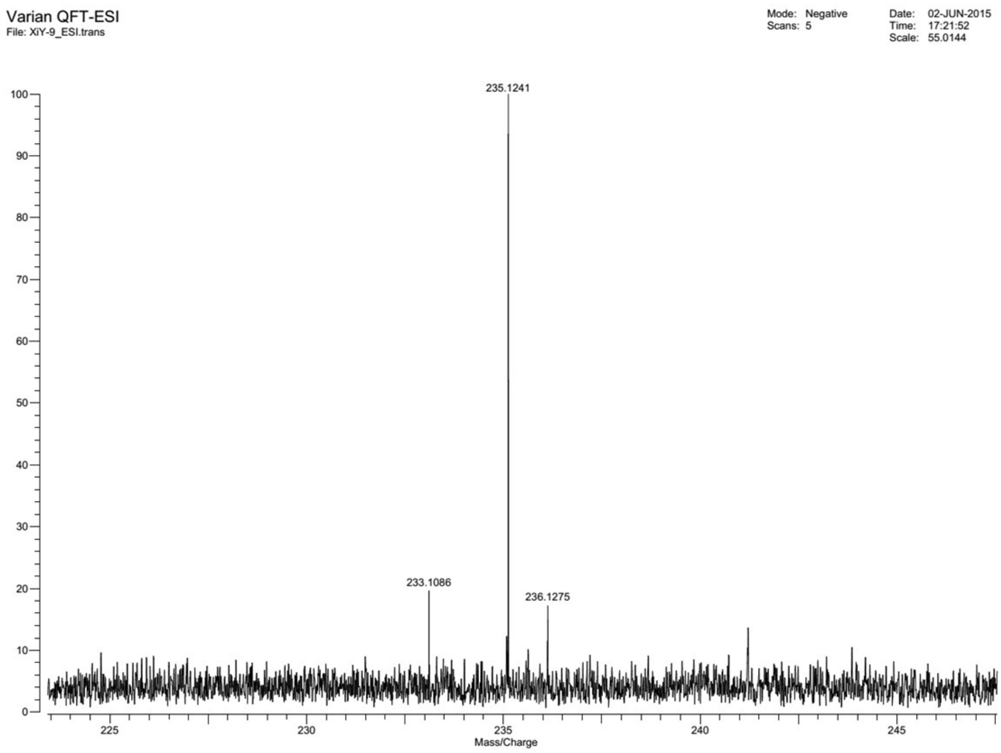
248.1271
250.1431
Mass/Charge

3bb


Varian QFT-ESI
File: XiY-9_ESI.trans
Mode: Negative
Scans: 5
Date: 02-JUN-2015
Time: 17:21:52
Scale: 55.0144
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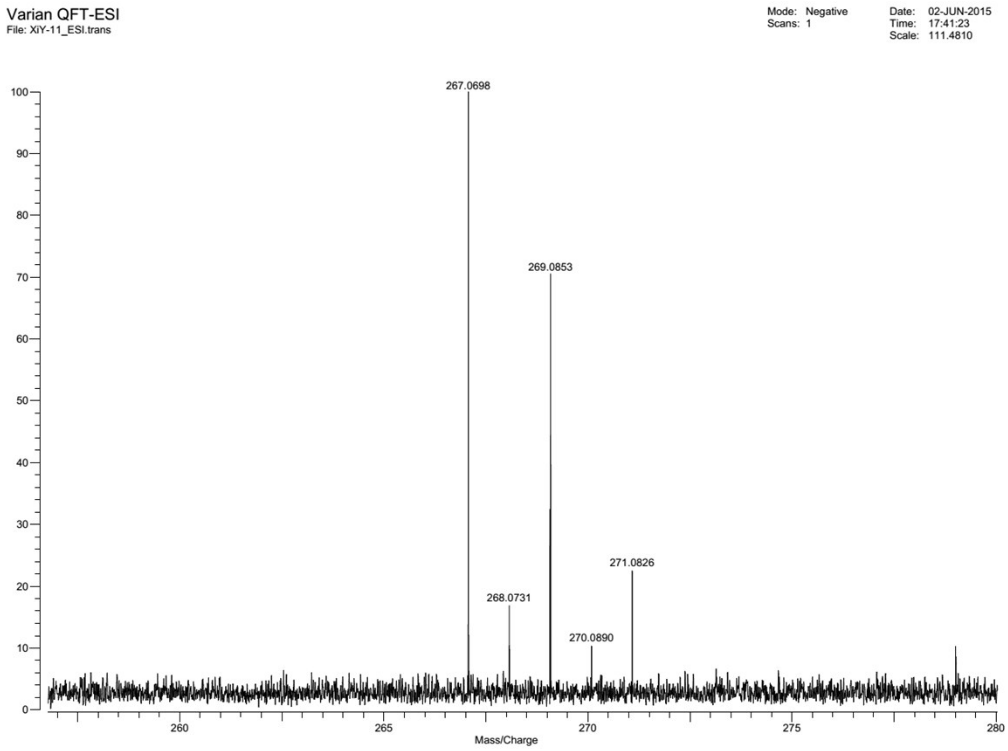
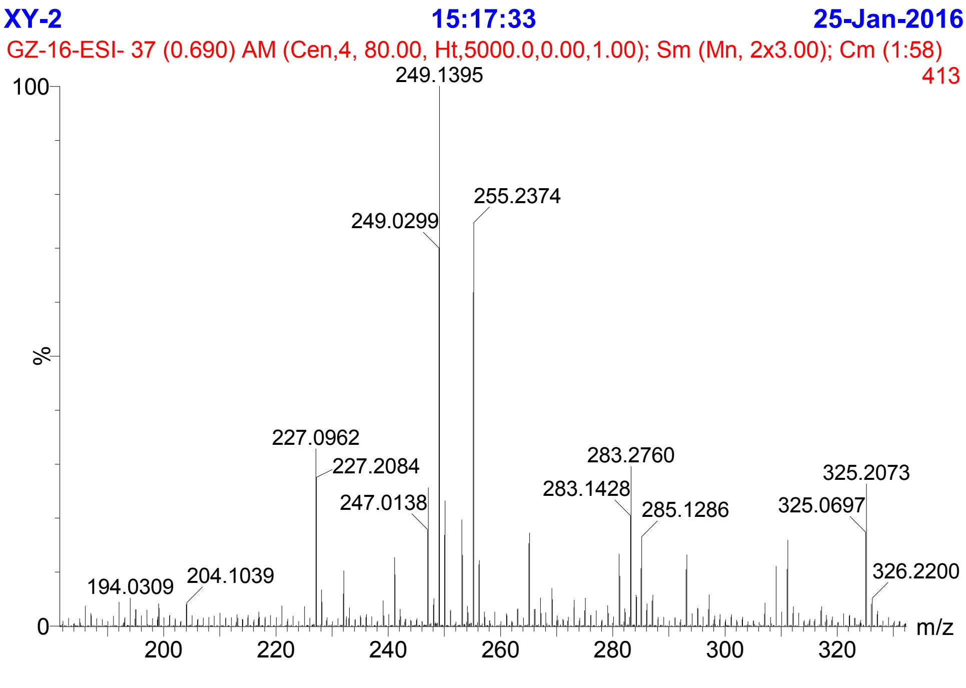
233.1086
236.1275
Mass/Charge

3cb



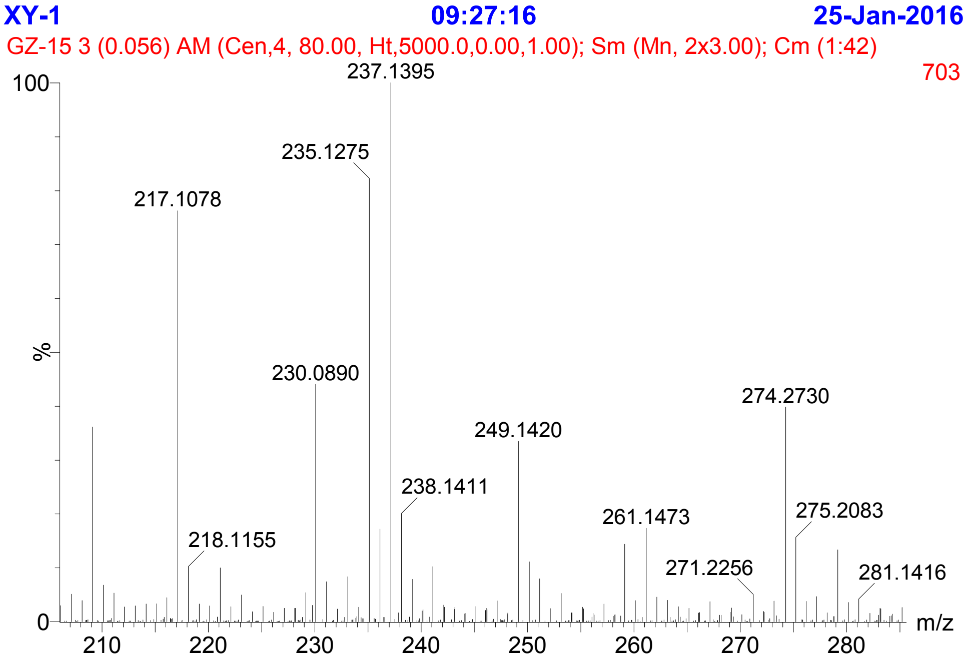
Varian QFT-ESI
File: XiY-11_ESI.trans
Mode: Negative
Scans: 1
Date: 02-JUN-2015
Time: 17:41:23
Scale: 111.4810
267.0698
269.0853
271.0826
268.0731
270.0890
Mass/Charge

3ac

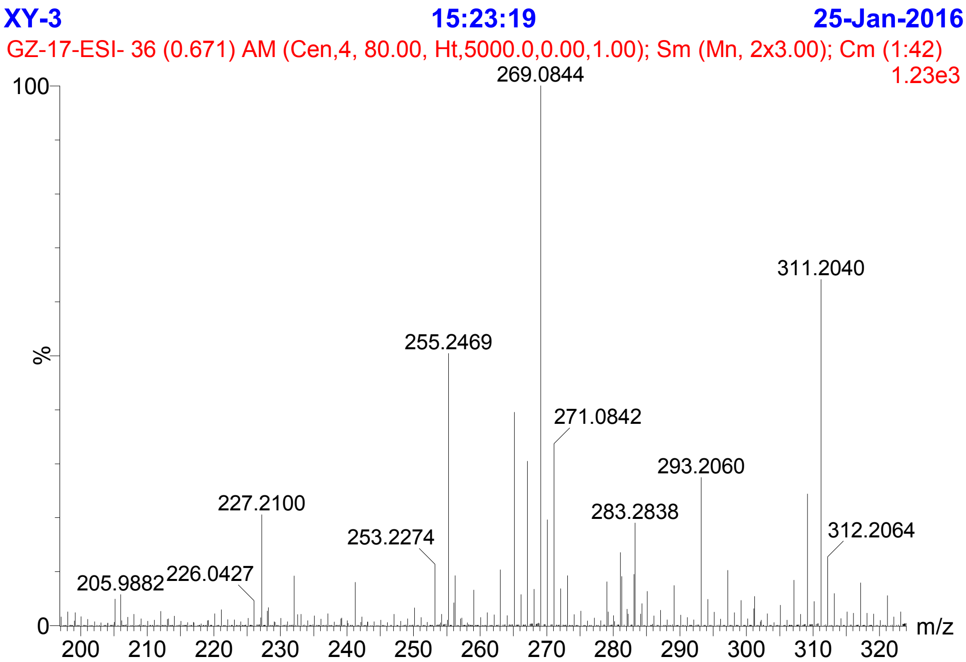


XY-2
15:17:33
25-Jan-2016
GZ-16-ESI- 37 (0.690) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:58)
413
249.1395
255.2374
249.0299
227.0962
227.2084
247.0138
283.2760
283.1428
285.1286
325.2073
325.0697
326.2200
194.0309
204.1039
%
m/z

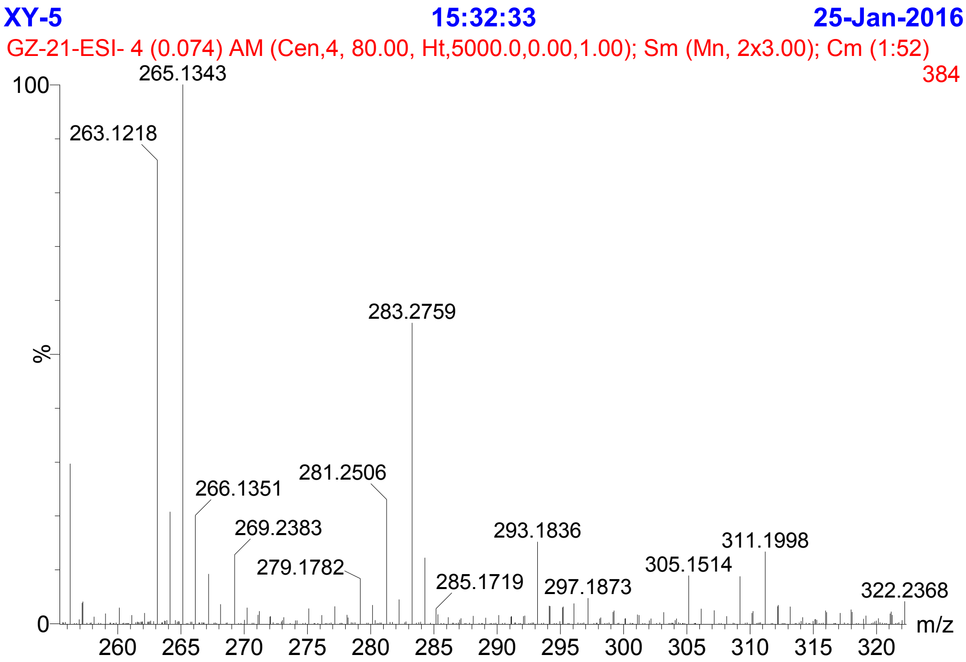
3bc


XY-1
09:27:16
25-Jan-2016
GZ-15 3 (0.056) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:42)
703
100
%
0
237.1395
235.1275
217.1078
230.0890
274.2730
249.1420
238.1411
261.1473
275.2083
218.1155
271.2256
281.1416
210
220
230
240
250
260
270
280
m/z

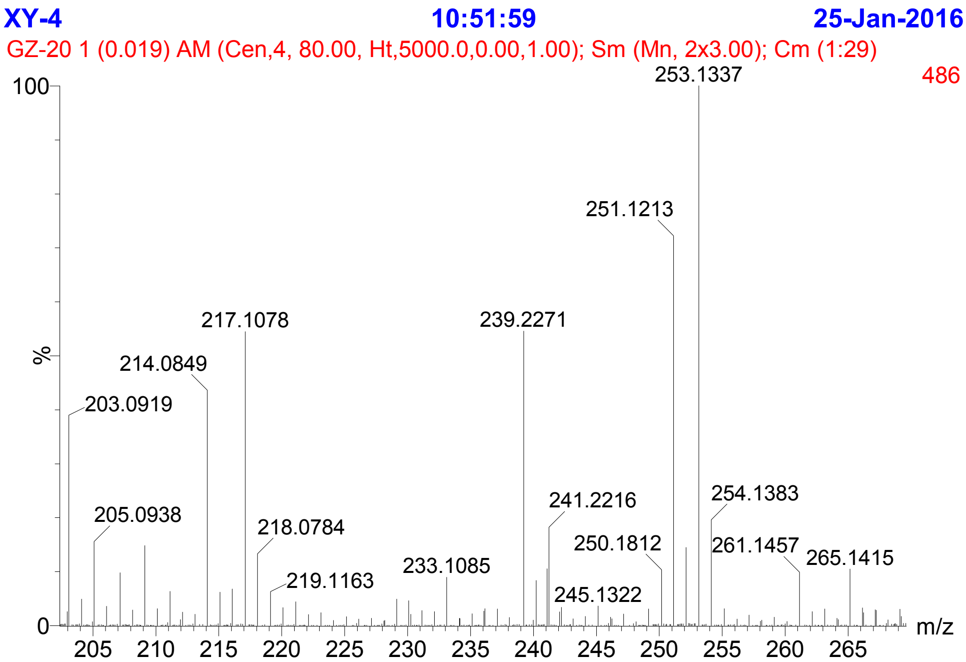
3cc


XY-3
15:23:19
25-Jan-2016
GZ-17-ESI- 36 (0.671) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:42)
1.23e3
100
%
0
269.0844
311.2040
255.2469
271.0842
293.2060
227.2100
283.2838
253.2274
312.2064
205.9882
226.0427
200
210
220
230
240
250
260
270
280
290
300
310
320
m/z

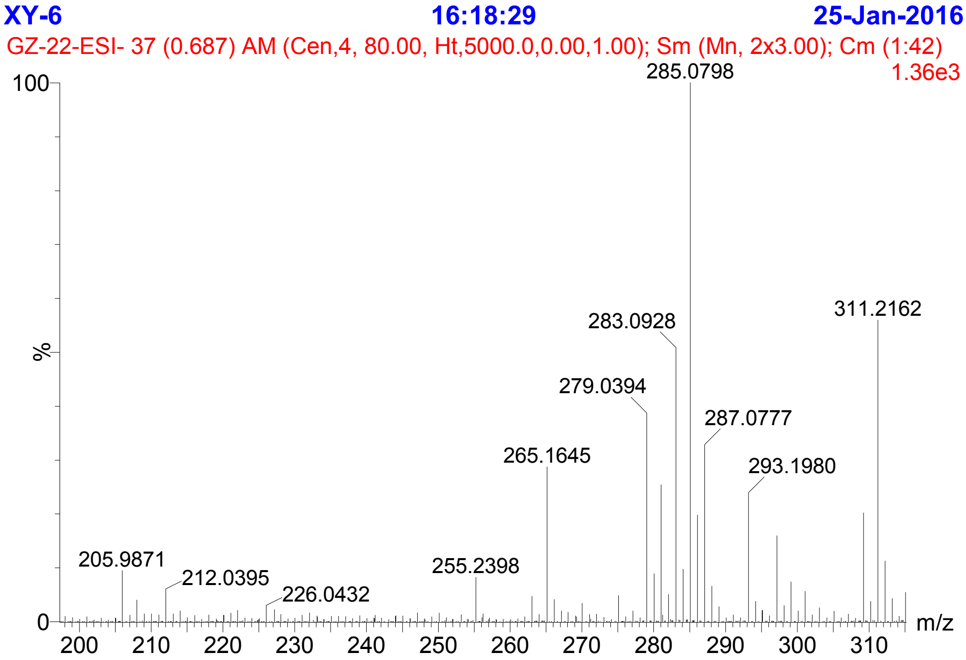
3ad


XY-5
15:32:33
25-Jan-2016
GZ-21-ESI- 4 (0.074) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:52)
384
100
%
0
265.1343
263.1218
283.2759
266.1351
281.2506
269.2383
279.1782
293.1836
285.1719
297.1873
305.1514
311.1998
322.2368
260
265
270
275
280
285
290
295
300
305
310
315
320
m/z

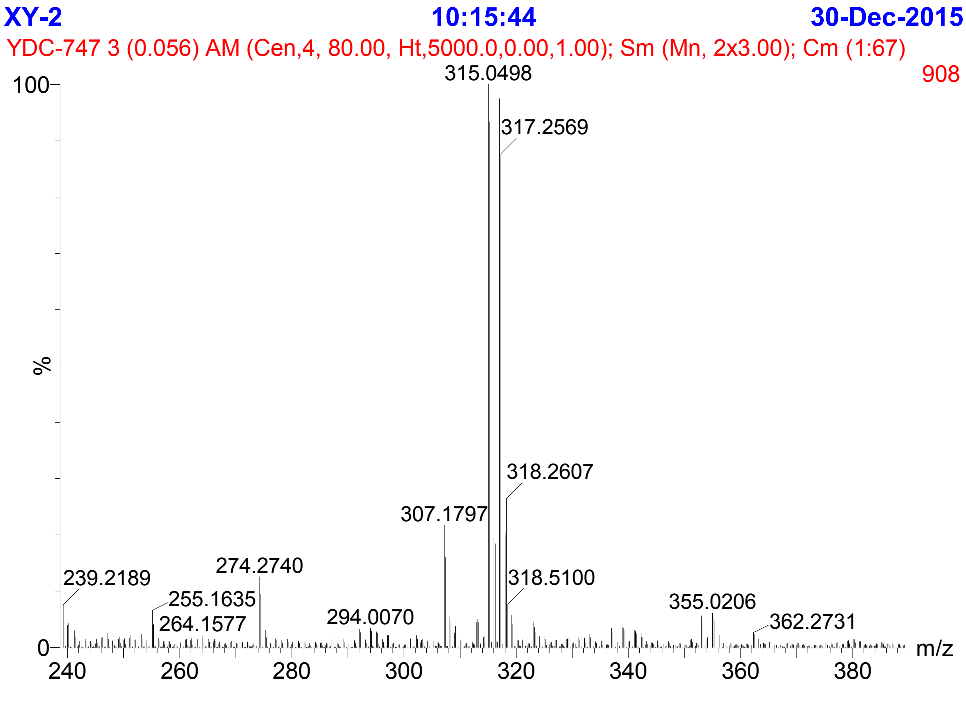
3bd


XY-4
10:51:59
25-Jan-2016
GZ-20 1 (0.019) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:29)
486
100
%
0
253.1337
251.1213
217.1078
239.2271
214.0849
203.0919
205.0938
218.0784
219.1163
233.1085
241.2216
250.1812
245.1322
254.1383
261.1457
265.1415
205
210
215
220
225
230
235
240
245
250
255
260
265
m/z

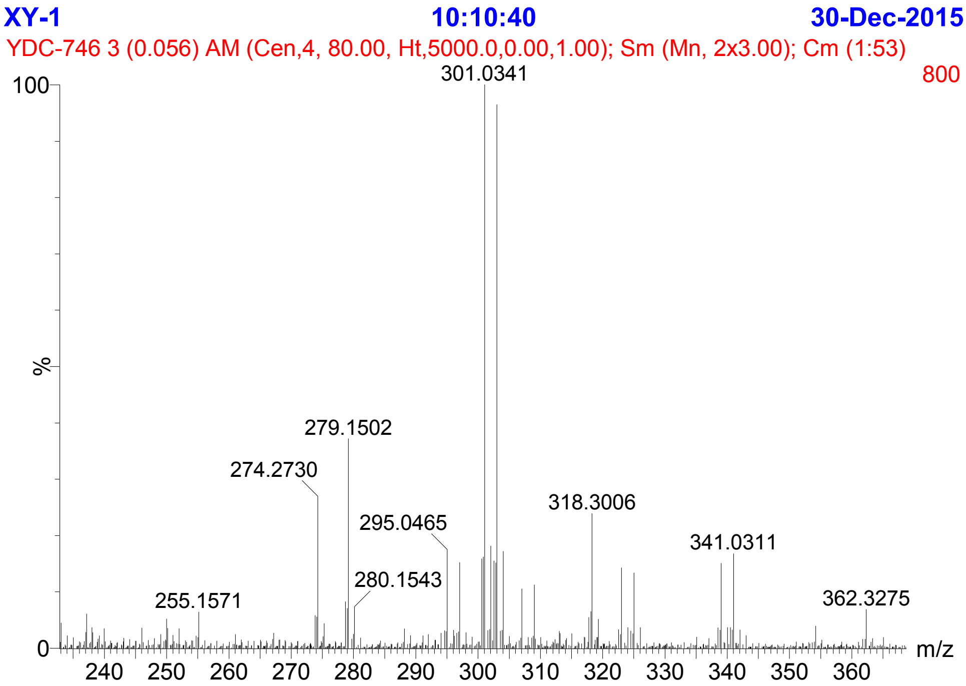
3cd


XY-6
16:18:29
25-Jan-2016
GZ-22-ESI- 37 (0.687) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:42)
1.36e3
100
%
0
285.0798
283.0928
311.2162
279.0394
287.0777
265.1645
293.1980
205.9871
212.0395
226.0432
255.2398
200
210
220
230
240
250
260
270
280
290
300
310
m/z

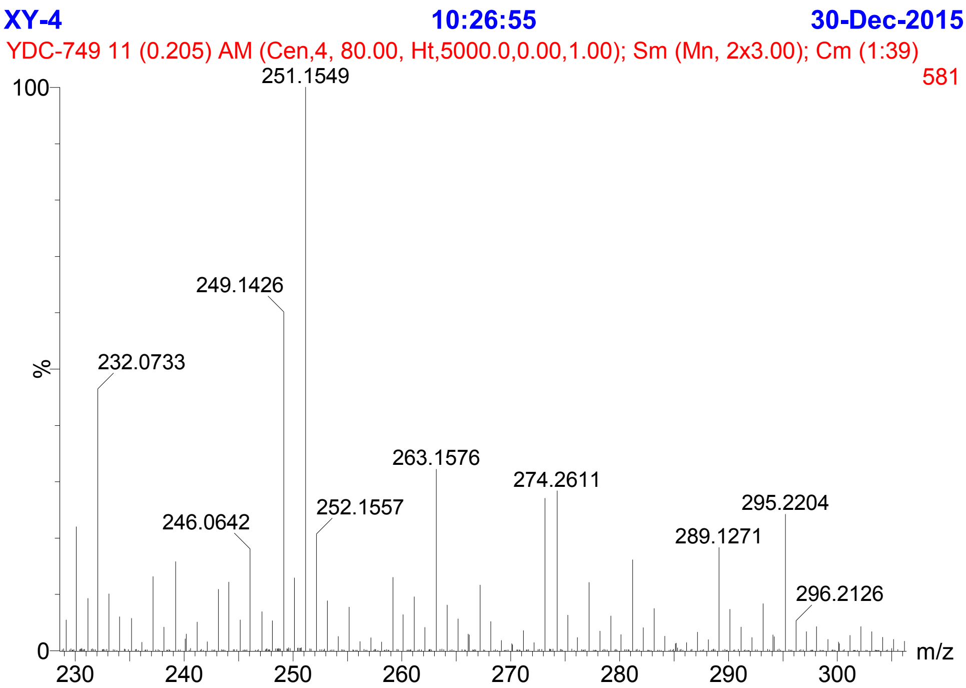
3ae


XY-2
10:15:44
30-Dec-2015
YDC-747 3 (0.056) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:67)
908
100
%
0
315.0498
317.2569
318.2607
307.1797
274.2740
239.2189
255.1635
264.1577
294.0070
318.5100
355.0206
362.2731
240
260
280
300
320
340
360
380
m/z

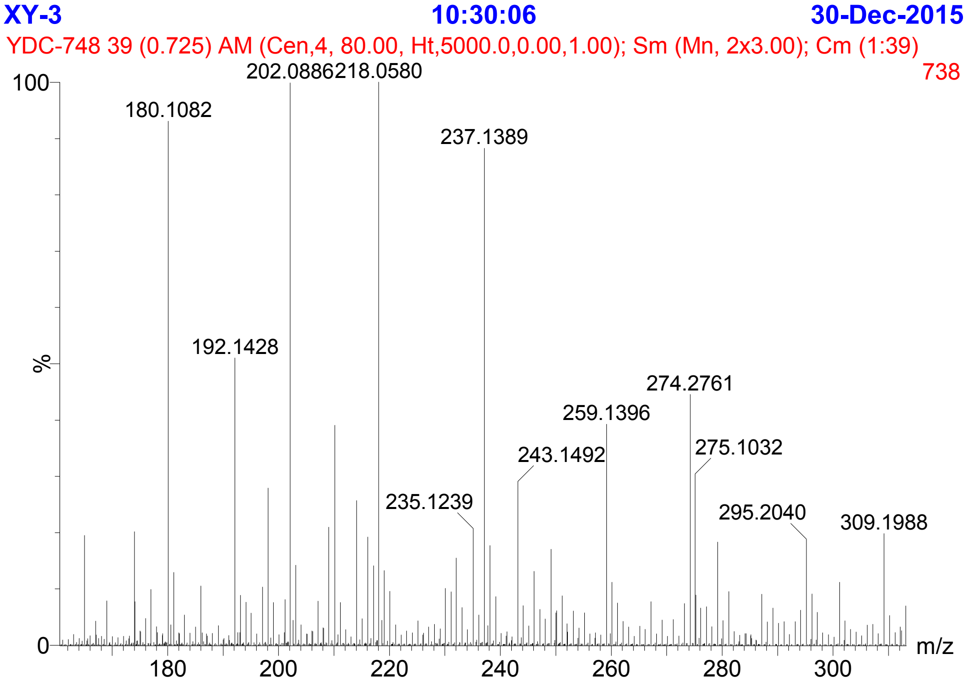
3be


XY-1
10:10:40
30-Dec-2015
YDC-746 3 (0.056) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:53)
800
100
%
0
301.0341
279.1502
274.2730
295.0465
318.3006
341.0311
280.1543
255.1571
362.3275
240
250
260
270
280
290
300
310
320
330
340
350
360
m/z

3af


XY-4
10:26:55
30-Dec-2015
YDC-749 11 (0.205) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:39)
581
100
%
0
251.1549
249.1426
232.0733
263.1576
274.2611
295.2204
252.1557
246.0642
289.1271
296.2126
230
240
250
260
270
280
290
300
m/z

3bf


XY-3
10:30:06
30-Dec-2015
YDC-748 39 (0.725) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:39)
738
100
%
0
202.0886
218.0580
180.1082
237.1389
192.1428
274.2761
259.1396
275.1032
243.1492
235.1239
295.2040
309.1988
180
200
220
240
260
280
300
m/z

6. References

1 S.-Q. Zhu and M. Rueping, *Chem. Commun.*, 2012, **48**, 11960.