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Supporting Information

Nickel-Catalyzed C3-Alkylation of Indoles with Alcohols through Borrowing Hydrogen Strategy

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1. X-ray analysis of Ni1

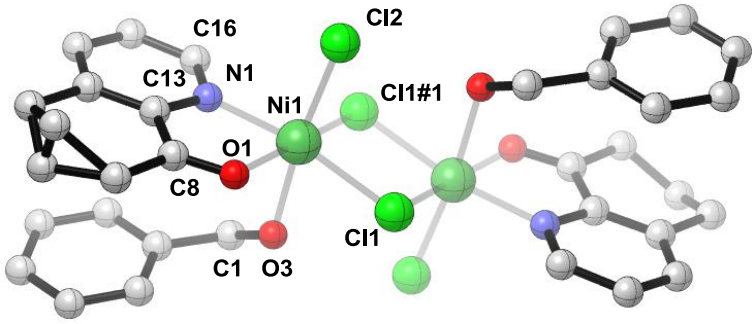


Figure S1. Solid structure of **Ni1**. Hydrogen atoms were emitted for clarity.

Table S1. Crystal data and structure refinement for **Ni1**.

Identification code	a	
Empirical formula	C32 H34 Cl4 N2 Ni2 O4	
Formula weight	769.83	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 13.0105(6) Å	α= 90 °.
	b = 11.6307(5) Å	β= 90 °.
	c = 21.7397(9) Å	γ = 90 °.
Volume	3289.7(2) $Å^3$	
Z	4	
Density (calculated)	1.554 Mg/m^3	
Absorption coefficient	1.509 mm^{-1}	
F(000)	1584	
Crystal size	0.12 x 0.1 x 0.1 mm^3	
Theta range for data collection	2.442 to 27.502°.	
Index ranges	-16<=h<=13, -15<=k<=14, -28<=l<=28	
Reflections collected	26736	
Independent reflections	3772 [R(int) = 0.0589]	
Completeness to theta = 25.242 °	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6588	
Refinement method	Full-matrix least-squares on F^2	

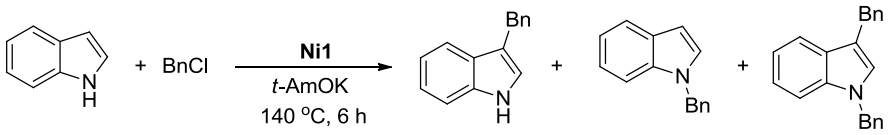
Data / restraints / parameters	3772 / 10 / 212
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0318, wR2 = 0.0676
R indices (all data)	R1 = 0.0501, wR2 = 0.0762
Extinction coefficient	n/a
Largest diff. peak and hole	0.286 and -0.329 e.$Å^{-3}$

Table S2. Bond lengths [Å] and angles [°] for **Ni1**.

selected bond lengths [Å]			
Ni(1)-Cl(1)	2.3738(6)	O(1)-C(8)	1.227(3)
Ni(1)-Cl(2)	2.3722(7)	O(3)-C(1)	1.441(3)
Ni(1)-Cl(1)#1	2.4019(6)	N(1)-C(13)	1.352(3)
Ni(1)-O(1)	2.0879(17)	N(1)-C(16)	1.323(3)
Ni(1)-O(3)	2.1585(18)	C(8)-C(13)	1.472(3)
Ni(1)-N (1)	2.0505(19)		
selected angles [°]			
Cl(1)-Ni(1)-Cl(1)#1	91.13(2)	N(1)-Ni(1)-Cl(2)	94.50(6)
Cl(2)-Ni(1)-Cl(1)#1	92.31(2)	N(1)-Ni(1)-O(1)	79.40(7)
Cl(2)-Ni(1)-Cl(1)	92.14(2)	N(1)-Ni(1)-O(3)	91.68(7)
O(1)-Ni(1)-Cl(1)	172.99(5)	Ni(1)-Cl(1)-Ni(1)#1	88.87(2)
O(1)-Ni(1)-Cl(1)#1	92.54(5)	C(8)-O(1)-Ni(1)	113.48(16)
O(1)-Ni(1)-Cl(2)	93.68(6)	Ni(1)-O(3)-H(3)	109.5(13)
O(1)-Ni(1)-O(3)	88.52(7)	C(1)-O(3)-Ni(1)	122.93(15)
O(3)-Ni(1)-Cl(1)	86.10(5)	C(13)-N(1)-Ni(1)	112.96(15)
O(3)-Ni(1)-Cl(1)#1	81.71(5)	C(16)-N(1)-Ni(1)	128.75(17)
O(3)-Ni(1)-Cl(2)	173.72(5)	C(16)-N(1)-C(13)	118.3(2)
N(1)-Ni(1)-Cl(1)#1	169.75(6)	N(1)-C(13)-C(8)	114.34(19)
N(1)-Ni(1)-Cl(1)	96.25(6)	O(1)-C(8)-C(13)	119.7(2)

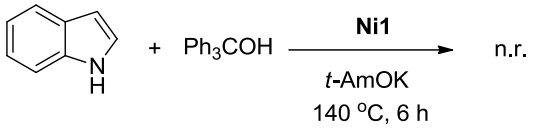
2. Mechanistic experiments

2.1 The reaction of indole (1a) with benzyl chloride



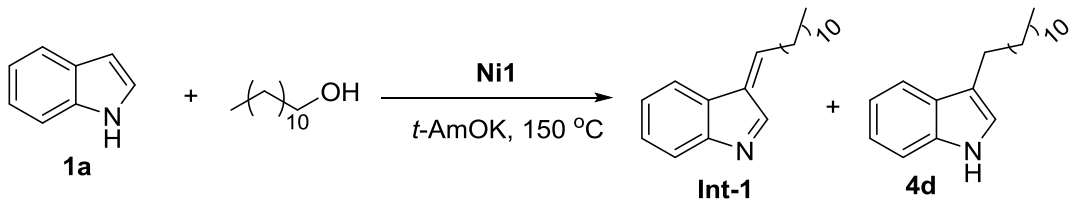
To a Young tube was added **1a** (117 mg, 1 mmol), **Ni1** (0.05 mmol), benzyl chloride (252 mg, 2 mmol) and *t*-AmOK (189 mg, 1.5 mmol). The mixture was stirred at 140 °C for 6 hours. The crude mixture was purified by flash column chromatography on silica gel using PE as the eluent to give the mixture of 3-benzyl-1*H*-indole (10%), 1-benzyl-1*H*-indole(51%) and 1, 3-dibenzyl-1*H*-indole (26%) according to ^{1}H NMR spectra.

2.2 The reaction of indole (1a) with triphenylmethanol



To a Young tube was added **1a** (117 mg, 1 mmol), **Ni1** (0.05 mmol), triphenylmethanol (520 mg, 2 mmol) and *t*-AmOK (189 mg, 1.5 mmol). The mixture was stirred at 140 °C for 6 hours. GC and TLC analysis showed that no reaction occurred.

2.3 Kinetic experiments



A series of experiments were carried out in order to obtain kinetic data. For example, to a Young tube was added **1a** (35 mg, 0.3 mmol), **Ni1** (0.015 mmol), 1-dodecanol (112 mg, 0.6 mmol) and *t*-AmOK (57 mg, 0.45 mmol). The mixture was stirred at 150 °C for 0.5 hours. GC yield of **1a**, **4d** and **Int-1** were obtained with fluorene as the internal standard as shown in the table below.

Table S3. Kinetic data for 1-dodecanol and **Int-1**.

Entry	Time/h	**1a**	1-dodecanol	**Int-1**
1	0	0.3	0	0
2	0.5	2.723	0.039	0.050
3	1.0	1.993	0.044	0.061
4	1.5	1.127	0.071	0.094
5	2.0	0.467	0.096	0.118
6	3.0	0.247	0.144	0.157
7	4.0	0.043	0.152	0.131
8	6.0	0.003	0.192	0.102
9	8.0	0.003	0.215	0.081
10	10.0	0.003	0.255	0.051
11	13.0	0.003	0.261	0.034

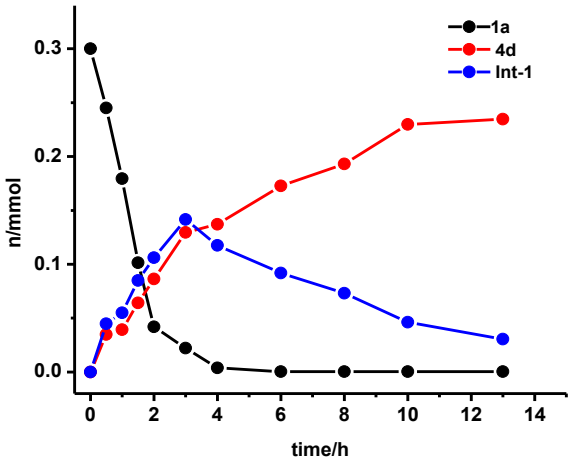
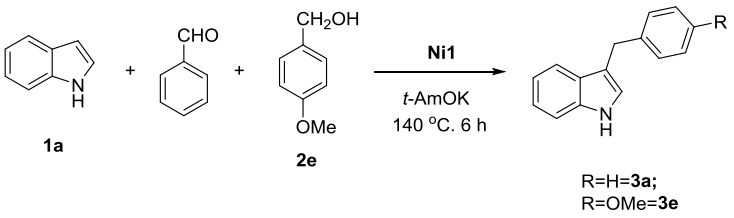


Figure S2. Kinetic diagram.

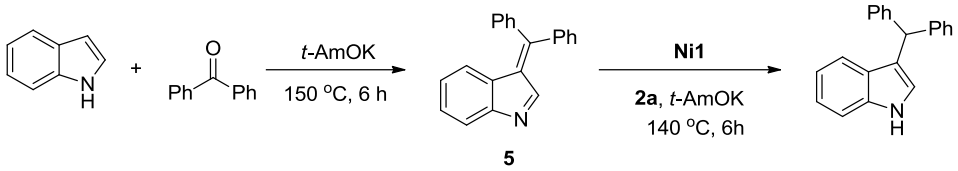
2.4 The competitive reaction of indole (1a) with benzaldehyde and (4-methoxyphenyl)methanol (2e)



To a Young tube was added **1a** (117 mg, 1 mmol), **Ni1** (0.05 mmol), benzaldehyde (106 mg, 1 mmol), **2e** (272 mg, 2 mmol) and *t*-AmOK (189 mg, 1.5 mmol). The mixture was stirred at 140 °C for 6 hours. 48% GC yield of **3a** and 35% GC yield of **3e** were

obtained with fluorene as the internal standard.

2.5 The reduction of intermediate 5 by benzyl alcohol

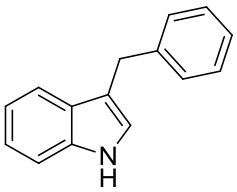


5

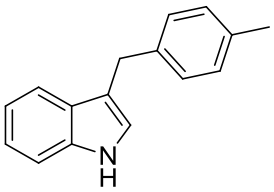
To a Young tube was added **1a** (117 mg, 1 mmol), benzophenone (364 mg, 2 mmol) and *t*-AmOK (189 mg, 1.5 mmol). The mixture was stirred at 140 ^{o}C for 6 hours. The crude mixture was purified by flash column chromatography on silica gel using PE and EA as the eluent to give 222 mg of **5** (79% yield).

To a Young tube was added **5** (141 mg, 0.5 mmol), **2a** (108 mg, 1 mmol) and *t*-AmOK (95 mg, 1.5 mmol). The mixture was stirred at 140 ^{o}C for 6 hours. The crude mixture was purified by flash column chromatography on silica gel using PE and EA as the eluent to give 249 mg of **3m** (88% yield).

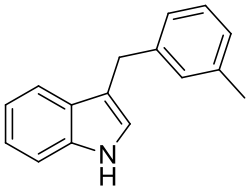
3. NMR of all products



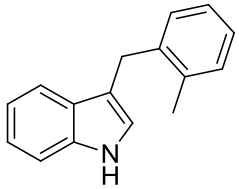
3-benzyl-1*H*-indole (3a)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (br. s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.35-7.27 (m, 4H), 7.25-7.18 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.91 (s, 1H), 4.15 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ141.3, 136.6, 128.8, 128.5, 127.6, 126.0, 122.5, 122.2, 119.5, 119.3, 116.0, 111.2, 31.7.



3-(4-methylbenzyl)-1*H*-indole (3b)[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (br. s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.24-7.18 (m, 3H), 7.11-7.08 (m, 3H), 6.91 (s, 1H), 4.11 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ138.3, 136.6, 135.4, 129.1, 128.7, 127.6, 122.4, 122.1, 119.4, 116.2, 111.2, 31.3, 21.1.

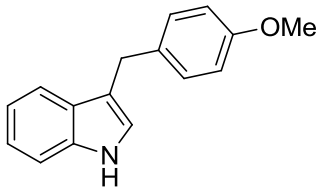


3-(3-methylbenzyl)-1*H*-indole (3c)[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (br. s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.25-7.19 (m, 2H), 7.17-7.10 (m, 3H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.91 (s, 1H), 4.12 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ141.3, 138.0, 136.5, 129.6, 128.2, 127.6, 126.8, 125.9, 122.4, 122.1, 119.4, 119.3, 116.1, 111.2, 31.6, 21.6.

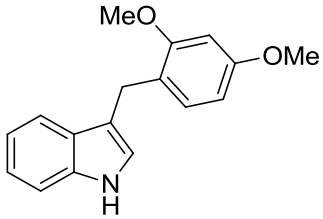


3-(2-methylbenzyl)-1*H*-indole (3d)[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (br. s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.23-7.09 (m, 6H), 6.73 (s, 1H),

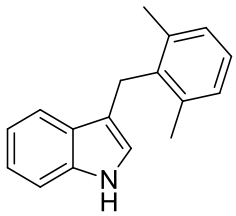
4.08 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 136.6, 130.2, 129.5, 127.7, 126.3, 126.1, 122.5, 122.2, 119.5, 119.2, 115.4, 111.2, 29.4, 19.6.



3-(4-methoxybenzyl)-1*H*-indole (3e)[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (br. s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.23-7.17 (m, 3H), 7.11-7.06 (m, 1H), 6.90 (s, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.07 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9, 136.6, 133.4, 129.7, 127.6, 122.3, 122.1, 119.4, 119.3, 116.4, 113.9, 111.2, 55.4, 30.8.

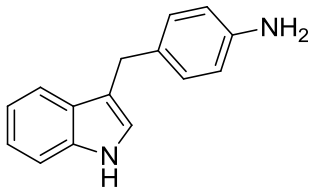


3-(2,4-dimethoxybenzyl)-1*H*-indole (3f)[2] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (br. s, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.22-7.17 (m, 1H), 7.16-7.10 (m, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.91 (s, 1H), 6.51 (d, *J* = 2.1 Hz,1H), 6.38 (dd, *J* = 8.3, 2.1 Hz,1H), 4.07 (s, 2H), 3.87 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 158.2, 136.5, 130.2, 127.8, 122.4, 122.2, 121.9, 119.4, 119.3, 115.8, 111.1, 104.0, 98.6, 55.5, 55.5, 24.6.

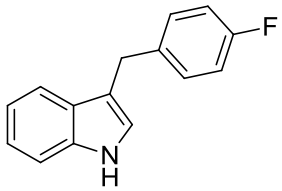


3-(2,6-dimethylbenzyl)-1H-indole (3g) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (br. s, 1H), 7.71 (d, *J*=7.8 Hz, 1H), 7.36 (d, *J*=8.0 Hz, 1H), 7.25-7.17 (m, 2H), 7.15-7.08 (m, 3H), 6.40-6.38 (m, 1H), 4.10 (s, 2H), 2.32 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ137.5, 137.5, 137.1, 136.7, 128.1, 127.7, 126.1, 122.2, 121.6, 119.4, 118.9, 114.8, 111.2, 25.6, 20.0. HRMS (ESI+): calc. for $C_{17}H_{18}N$ $[M+H]^+$: 236.1439, found

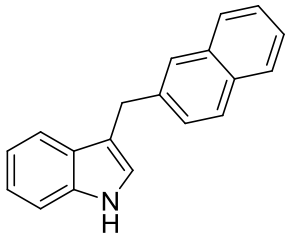
236.1434.



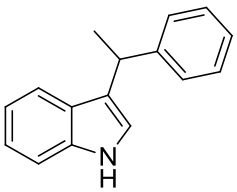
4-((1*H*-indol-3-yl)methyl)aniline (3h)[3] ^{1}H NMR (500 MHz, DMSO-d_6) δ10.77 (br. s, 1H), 7.41 (d, *J*=7.9 Hz, 1H)), 7.33 (d, *J*=8.1 Hz, 1H)), 7.10-7.02 (m, 2H), 6.96-6.89 (m, 3H), 6.48 (d, *J*=8.4 Hz, 2H), 4.84 (br. s, 2H), 3.86 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ146.3, 136.4, 128.8, 128.8, 127.1, 122.7, 120.8, 118.7, 118.1, 115.0, 113.9, 111.3, 30.3.



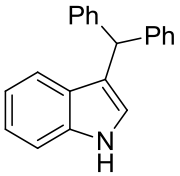
3-(4-fluorobenzyl)-1*H*-indole (3i)[1] ^{1}H NMR (600 MHz, $CDCl_3$, contains 20% of **2a**) δ 7.87 (br. s, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.22-7.14 (m, 3H), 7.09-7.03(m, 1H), 6.96-6.89 (m, 2H), 6.85 (s, 1H), 4.05 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.7 (d, J=243.3 Hz), 136.9 (d, J=2.4 Hz), 136.6, 130.1 (d, J=7.7 Hz), 128.6 (d, J=45.6 Hz), 127.4, 122.2, 119.5, 119.2, 115.8, 115.1 (d, J=21.2 Hz), 111.2, 30.1.



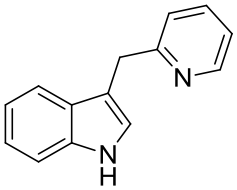
3-(naphthalen-2-ylmethyl)-1*H*-indole (3j)[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (br. s, 1H), 7.85-7.70 (m, 4H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.51-7.40 (m, 3H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.93 (s 1H), 4.30 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 136.6, 133.8, 132.2, 128.0, 127.7, 127.7, 127.6, 126.8, 126.0, 125.3, 122.6, 122.2, 119.6, 119.3, 115.9, 111.2, 32.0.



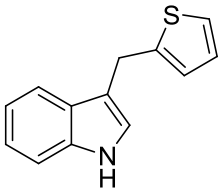
3-(1-phenylethyl)-1*H*-indole (3k)[1] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (br. s, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.37-7.27 (m, 5H), 7.24-7.15 (m, 2H), 7.05-7.00 (m, 2H), 4.40 (q, *J* = 7.1 Hz, 1H), 1.74 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.9, 136.8, 128.4, 127.6, 127.0, 126.0, 122.1, 121.6, 121.2, 119.8, 119.3, 111.1, 37.1, 22.5.



3-benzhydryl-1*H*-indole (3l)[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (br. s, 1H), 7.43-7.13 (m, 13H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.58 (s, 1H), 5.70 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 136.8, 129.2, 128.4, 127.1, 126.4, 124.2, 122.2, 120.1, 120.1, 119.5, 111.2, 49.0.

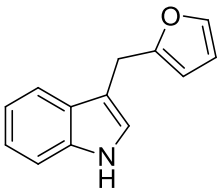


3-(pyridin-2-ylmethyl)-1*H*-indole (3m)[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.8, 1H), 8.41 (br. s, 1H), 7.58-7.49 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.21-7.14 (m, 2H), 7.13-7.01 (m, 3H), 4.33 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 149.2, 136.6, 136.6, 127.5, 122.9, 122.9, 122.1, 121.2, 119.5, 119.2, 113.8, 111.3, 34.6.

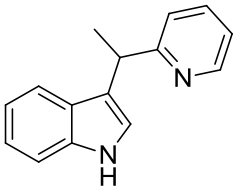


3-(thiophen-2-ylmethyl)-1*H*-indole (3n)[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (br. s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.24-7.19 (m, 1H), 7.16-7.09 (m, 2H), 7.04 (s, 1H), 6.96-6.88 (m, 2H), 4.33 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ

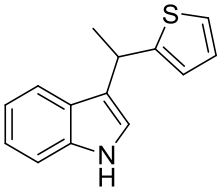
144.8, 136.5, 127.2, 126.8, 124.8, 123.5, 122.4, 122.3, 119.6, 119.2, 115.4, 111.3, 26.1.



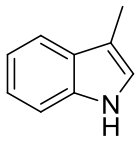
3-(furan-2-ylmethyl)-1*H*-indole (3o)[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (br. s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.38-7.32 (m, 2H), 7.24-7.19 (m, 1H), 7.16-7.10 (m, 1H), 7.05 (s, 1H), 6.31 (dd, *J* = 3.1, 1.0 Hz, 1H), 6.05 (dd, *J* = 3.1, 1.9 Hz, 1H), 4.15 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.0, 141.2, 136.4, 127.4, 122.4, 122.2, 119.6, 119.2, 112.7, 111.2, 110.4, 105.8, 24.6.



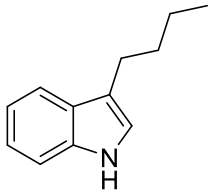
3-(1-(pyridin-2-yl)ethyl)-1*H*-indole (3p) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.8 Hz, 1H), 8.50 (br. s, 1H), 7.56-7.49 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.19-7.13 (m, 2H), 7.11-7.05 (m, 2H), 7.05-6.98 (m, 1H), 4.57 (q, *J* = 7.2 Hz, 1H), 1.78 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 149.0, 136.8, 136.7, 127.0, 122.0, 121.9, 121.5, 121.3, 119.9, 119.6, 119.3, 111.2, 39.6, 21.0. HRMS (ESI+): calc. for $C_{15}H_{15}N_2[M+H]^+$:223.1235, found 223.1230.



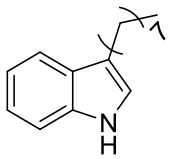
3-(1-(thiophen-2-yl)ethyl)-1H-indole (3q)[6] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.22-7.17 (m, 1H), 7.13 (dd, J = 5.0, 1.1 Hz, 1H), 7.10-7.06 (m, 1H), 7.04 (d, *J* = 1.9 Hz, 1H), 6.93-6.87 (m, 2H), 4.68 (q, *J* = 7.1 Hz, 1H), 1.82 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 136.6, 126.6, 126.6, 123.5, 123.1, 122.2, 121.5, 121.1, 119.6, 119.5, 111.3, 32.5, 23.5.



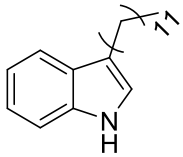
3-methyl-1*H*-indole (4a)[7] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (br. s, 1H), 7.64 (d, *J* =7.9 Hz, 1H), 7.37 (d, *J* =8.1 Hz, 1H), 7.27-7.22 (m, 1H), 7.18 (t, *J* =7.4 Hz, 1H), 6.98 (s, 1H), 2.39 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) 136.4, 128.4, 122.0, 121.7, 119.2, 118.9, 111.8, 111.1, 9.8.



3- butyl-1*H*-indole (4b)[8] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (br. s, 1H), 7.69 (d, *J* =7.8 Hz, 1H), 7.39 (d, *J* =8.1 Hz, 1H), 7.29-7.16 (m, 2H), 7.00 (s, 1H), 2.83 (t, *J* =7.6 Hz, 2H), 1.85-1.72 (m, 2H), 1.56-1.44 (m, 2H), 1.03 (t, *J* =7.4 Hz, 3H) . ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 127.9, 121.9, 121.1, 119.2, 117.3, 111.2, 32.5, 25.0, 22.8, 14.1.

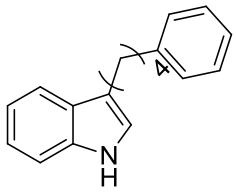


3-octyl-1*H*-indole (4c)[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (br. s, 1H), 7.64 (d, *J* =7.8 Hz, 1H), 7.36 (d, *J* =8.1 Hz, 1H), 7.24-7.11 (m, 2H), 6.97 (s, 1H), 2.78 (t, *J* =7.6 Hz, 2H), 1.78-1.70 (m, 2H), 1.48-1.24 (m, 10H), 0.92 (t, *J* =6.9 Hz, 3H) . ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 127.8, 121.9, 121.1, 119.2, 117.4, 111.1, 32.1, 30.3, 29.8, 29.7, 29.5, 25.3, 22.8, 14.3.

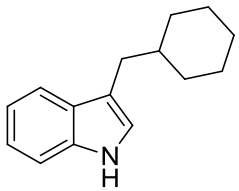


3-dodecyl-1*H*-indole (4d) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (br. s, 1H), 7.63 (d, *J* =7.9 Hz, 1H), 7.36 (d, *J* =8.1 Hz, 1H), 7.22-7.17 (m, 1H), 7.16-7.09 (m, 1H), 6.97 (s, 1H), 2.76 (t, *J* =7.5 Hz, 2H), 1.77-1.66 (m, 2H), 1.46-1.19 (m, 18H), 0.90 (t, *J* =7.0 Hz, 3H) . ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 127.8, 121.9, 121.1, 119.2, 117.4,

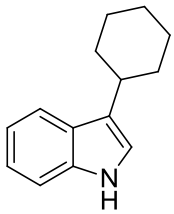
111.1, 32.1, 30.3, 29.9, 29.8, 29.8, 29.7, 29.5, 25.3, 22.8, 14.3. HRMS (ESI+): calc. for $C_{20}H_{32}N$ $[M+H]^+$:286.2535, found 286.2529.



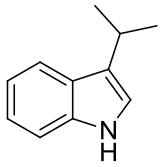
3-Phenylbutyl-1H-indole (4e) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (br. s, 1H), 7.64 (d, *J* =7.9 Hz, 1H), 7.37 (d, *J* =8.1 Hz, 1H), 7.31 (t, *J* =7.5 Hz, 2H), 7.25-7.19 (m, 4H), 7.15 (t, *J* =7.5 Hz, 1H), 6.95 (s, 1H), 2.83 (t, *J* =7.1 Hz, 2H), 2.70 (t, *J* =7.1 Hz, 2H), 1.85-1.72 (m, 4H) . ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.9, 136.5, 128.6, 128.4, 127.7, 125.7, 122.0, 121.2, 119.2, 119.1, 117.0, 111.2, 36.0, 31.5, 29.9, 25.1. HRMS (ESI+): calc. for $C_{18}H_{20}N[M+H]^+$:250.1596, found 250.1590.



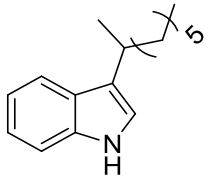
3-(cyclohexylmethyl)-1*H*-indole (4f)[1] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (br. s, 1H), 7.63 (d, *J* =7.8 Hz, 1H), 7.36 (d, *J* =8.1 Hz, 1H), 7.22-7.10 (m, 2H), 6.96 (d, *J* =1.9 Hz, 1H), 2.65 (d, *J* =7.0 Hz, 2H), 1.82-1.59 (m, 6H), 1.26-1.11 (m, 3H), 1.05-0.96 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.4, 128.2, 122.0, 121.8, 119.4, 119.1, 115.6, 111.1, 38.9, 33.7, 33.2, 26.8, 26.5.



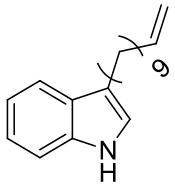
3-cyclohexyl-1*H*-indole (4g)[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (br. s, 1H), 7.70 (d, *J* =7.9 Hz, 1H), 7.36 (d, *J* =8.1 Hz, 1H), 7.21 (t, *J* =7.5 Hz, 1H), 7.13 (t, *J* =7.5 Hz, 1H), 6.95 (s, 1H), 2.91-2.82 (m, 1H), 2.19-2.06 (m, 2H), 1.94-1.76 (m, 3H), 1.57-1.42 (m, 4H), 1.38-1.27 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 126.9, 123.4, 121.9, 119.5, 119.1, 111.2, 35.6, 34.2, 27.1, 26.7.



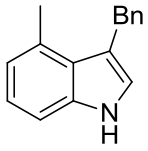
3-isopropyl-1*H*-indole (4h)[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (br. s, 1H), 7.69 (d, *J* =7.9 Hz, 1H), 7.36 (d, *J* =8.1 Hz, 1H), 7.24-7.10 (m, 2H), 6.96 (s, 1H), 3.29-3.20 (m, 1H), 1.39 (d, *J* =7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ136.8, 126.9, 124.2, 122.0, 119.5, 119.4, 119.1, 111.2, 25.6, 23.5.



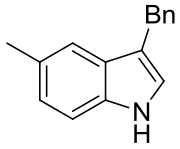
3-(1-methylheptyl)-1*H*-indole (4i)[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (br. s, 1H), 7.68 (d, *J* =7.9 Hz, 1H), 7.36 (d, *J* =8.1 Hz, 1H), 7.23-7.11 (m, 2H), 6.95 (d, *J* =2.2 Hz, 1H), 3.10-2.99 (m, 1H), 1.90-1.74 (m, 1H), 1.68-1.59 (m, 1H), 1.37 (d, *J* =6.9 Hz, 3H)，1.33-1.26 (m, 8H), 0.91-0.87 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.6, 127.1, 123.0, 121.8, 120.0, 119.6, 119.0, 111.2, 37.8, 32.0, 31.0, 29.7, 27.9, 22.8, 21.6, 14.2.



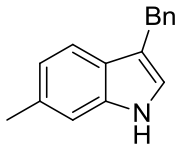
3-(undec-10-en-1-yl)-1*H*-indole (4j) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (br. s, 1H), 7.63 (d, *J*=7.8 Hz, 1H), 7.35 (d, *J*=8.1 Hz, 1H), 7.19 (t, *J*=7.4 Hz, 1H), 7.12 (t, *J*=7.4 Hz, 1H), 6.97 (s, 1H), 5.88-5.76 (m, 1H), 5.05-4.90 (m, 2H), 2.76 (t, *J*=7.6 Hz, 2H), 2.09-2.00 (m, 2H), 1.76-1.67 (m, 2H), 1.42-1.14 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ139.4, 136.5, 127.8, 121.9, 121.1, 119.2, 119.1, 117.4, 114.2, 111.1, 34.0, 30.3, 29.8, 29.8, 29.7, 29.7, 29.3, 29.1, 25.3. HRMS (ESI+): calc. for $C_{19}H_{28}N$ $[M+H]^+$: 270.2222, found 270.2216.



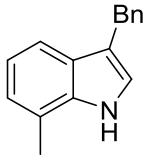
3-benzyl-4-methyl-1*H*-indole (5a)[1] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (br. s, 1H), 7.27-7.11(m, 7H), 6.96 (d, *J* =8.2 Hz, 1H), 6.76 (s, 1H), 4.03 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) 141.5, 134.9, 128.8, 128.7, 128.4, 127.8, 127.7, 125.9, 123.8, 122.6, 118.8, 115.4, 110.9, 31.6, 21.6.



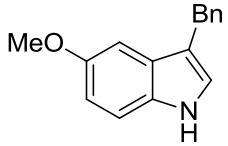
3-benzyl-5-methyl-1*H*-indole (5b)[1] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (br. s, 1H), 7.35 (s, 1H), 7.34-7.39 (m, 4H), 7.28-7.20 (m, 2H), 7.05 (d, *J* =8.2 Hz, 1H), 6.87 (s, 1H), 4.12 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.5, 134.9, 128.8, 128.4, 127.8, 126.0, 123.8, 122.6, 118.8, 115.4, 110.9, 31.6, 21.6.



3- benzyl-6-methyl-1*H*-indole (5c)[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (br. s, 1H), 7.41 (d, *J* =8.1 Hz, 1H), 7.33-7.26 (m, 4H), 7.23-7.18 (m, 1H), 7.15 (s, 1H), 6.93 (d, *J* =8.1 Hz, 1H), 6.87-6.81 (m, 1H), 4.12 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 137.0, 132.0, 128.8, 128.4, 125.9, 125.5, 121.8, 121.2, 118.9, 115.7, 111.2, 31.8, 21.8.

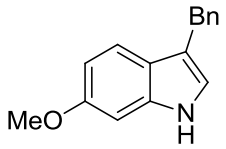


3-benzyl-7-methyl-1*H*-indole (5d)[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (br. s, 1H), 7.41 (d, *J* =6.8 Hz 1H), 7.35-7.27 (m, 4H), 7.23-7.18 (m, 1H), 7.07-6.99 (m, 2H), 6.93 (s, 1H), 4.14 (s, 2H), 2.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ141.4, 136.2, 128.8, 128.4, 127.1, 126.0, 122.7, 122.2, 120.3, 119.7, 117.0, 116.5, 31.8, 16.7.

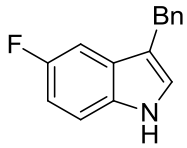


3-benzyl-5-methoxy-1*H*-indole (5e)[1] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (br. s, 1H), 7.37-7.23 (m, 6H), 7.01 (d, *J* =2.4 Hz, 1H), 6.93-6.89 (m, 2H), 4.12 (s, 2H), 3.83 (s,

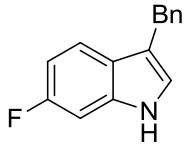
3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.0, 141.3, 131.7, 128.8, 128.5, 128.0, 126.0, 123.3, 115.6, 112.2, 111.9, 101.2, 56.0, 31.7.



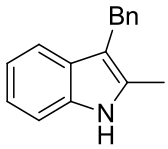
3-benzyl-6-methoxy-1*H*-indole (5f)[5] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (br. s, 1H), 7.39 (d, *J* =8.6 Hz, 1H), 7.33-7.27 (m, 4H), 7.24-7.19 (m, 1H), 6.84 (d, *J* =2.2 Hz, 1H), 6.82-6.76 (m, 2H), 4.10 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.6, 141.4, 137.4, 128.8, 128.4, 126.0, 122.1, 121.2, 119.9, 115.9, 109.4, 94.8, 55.8, 31.8.



3-benzyl-5-fluoro-1*H*-indole (5g)[1] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (br. s, 1H), 7.33-7.21(m, 6H), 7.16 (d, *J* =9.1 Hz, 1H), 6.98 (d, *J* =2.1 Hz, 1H), 6.95 (td, *J* =9.0, 2.2 Hz, 1H), 4.09 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8 (d, J = 234.8 Hz), 140.9, 133.1, 128.7, 128.5, 127.9 (d, J = 9.6 Hz), 126.2, 124.2, 116.1 (d, J = 4.8 Hz), 111.8 (d, J = 9.7 Hz), 110.5 (d, J = 26.4 Hz), 104.2 (d, J = 23.3 Hz), 31.7.

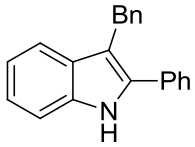


3-benzyl-6-fluoro-1*H*-indole (5h)[10] ^{1}H NMR (500 MHz, $CDCl_3$, contains 5% of **2a**) δ 7.97 (br. s, 1H), 7.43-7.37 (m, 1H), 7.30-7.26 (m, 3H), 7.23-7.18 (m, 1H), 7.03 (dd, *J* =9.6, 2.2 Hz, 1H), 6.88-6.81 (m, 1H), 4.09 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1 (d, J=237.4 Hz), 159.3, 141.0, 136.5 (d, J=12.4 Hz), 128.8, 128.5, 126.1, 124.2, 122.7 (d, J=3.5 Hz), 120.0 (d, J = 10.3 Hz), 116.1, 108.3, 108.2 (d, J = 24.5 Hz), 97.6 (d, J = 26.1 Hz), 31.7.



3-benzyl-2-methyl-1*H*-indole (5i)[1] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (br. s, 1H),

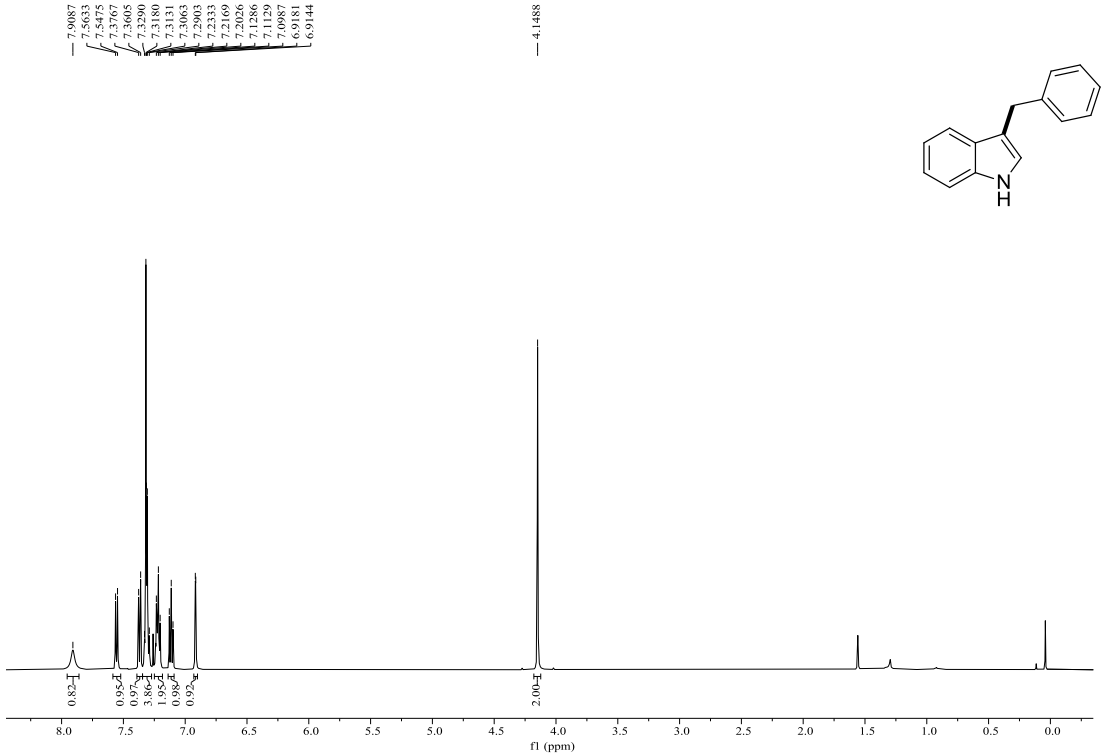
7.44 (d, *J* =7.8 Hz, 1H), 7.33-7.24 (m, 5H), 7.22-7.17 (m, 1H), 7.15 (t, *J* =7.5 Hz, 1H), 7.08 (t, *J* =7.4 Hz, 1H), 4.11 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.8, 135.4, 131.8, 129.0, 128.4, 128.4, 125.8, 121.1, 119.4, 118.5, 110.7, 110.3, 30.2, 11.9.

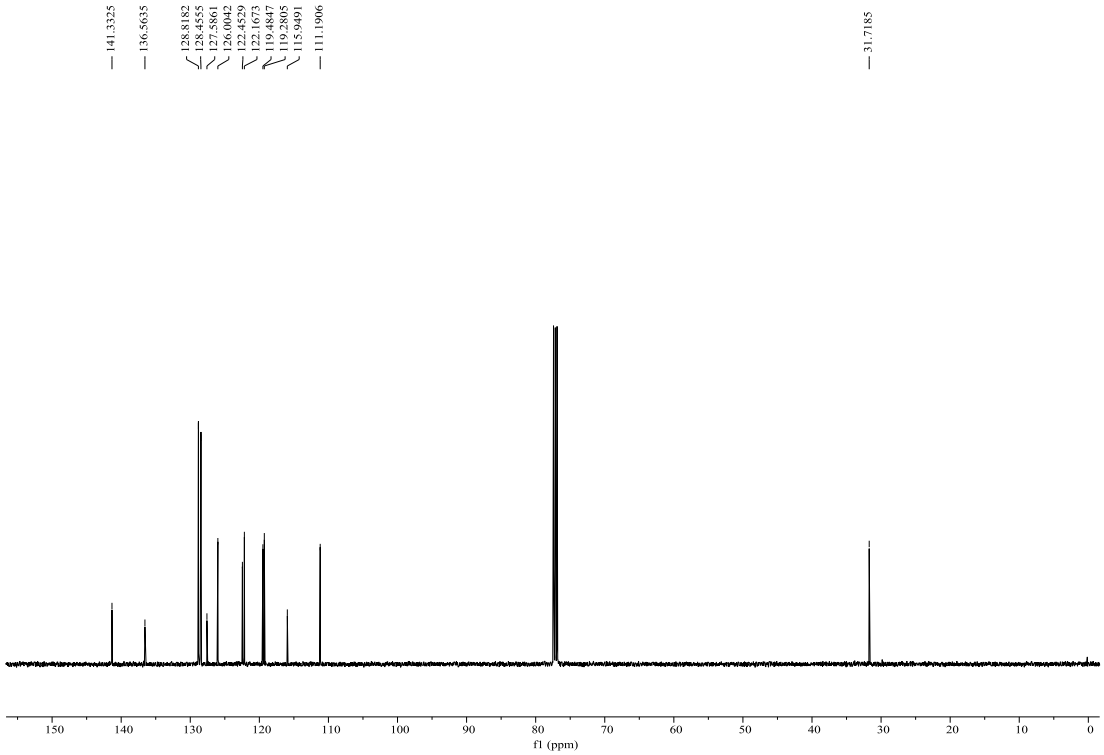


3-benzyl-2-phenyl-1*H*-indole (5j)[4] ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (br. s, 1H), 7.54 (d, J=7.3 Hz, 2H), 7.47-7.24 (m, 5H), 7.30-7.17 (m, 6H), 7.09 (t, J=7.5 Hz, 1H), 4.30 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ141.6, 136.1, 135.6, 133.0, 129.6, 129.0, 128.5, 128.4, 128.0, 127.9, 125.9, 122.5, 119.9, 119.8, 111.2, 110.9, 30.56.

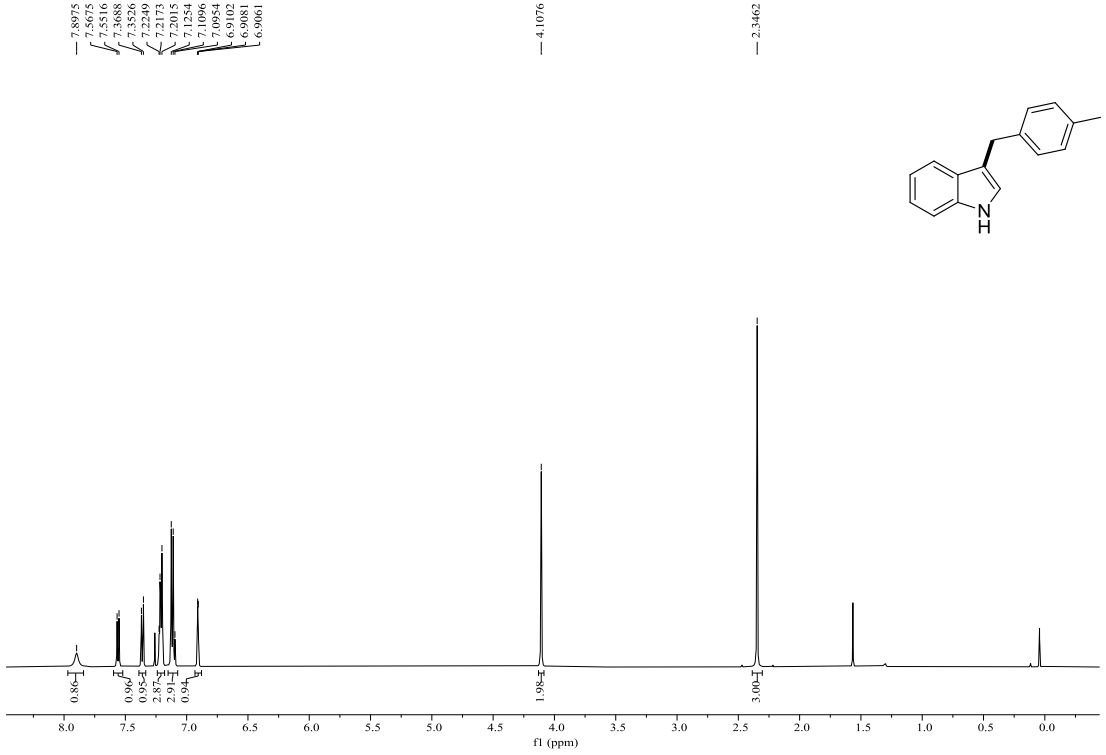
4. Copies of ^{1}H NMR and ^{13}C NMR spectra

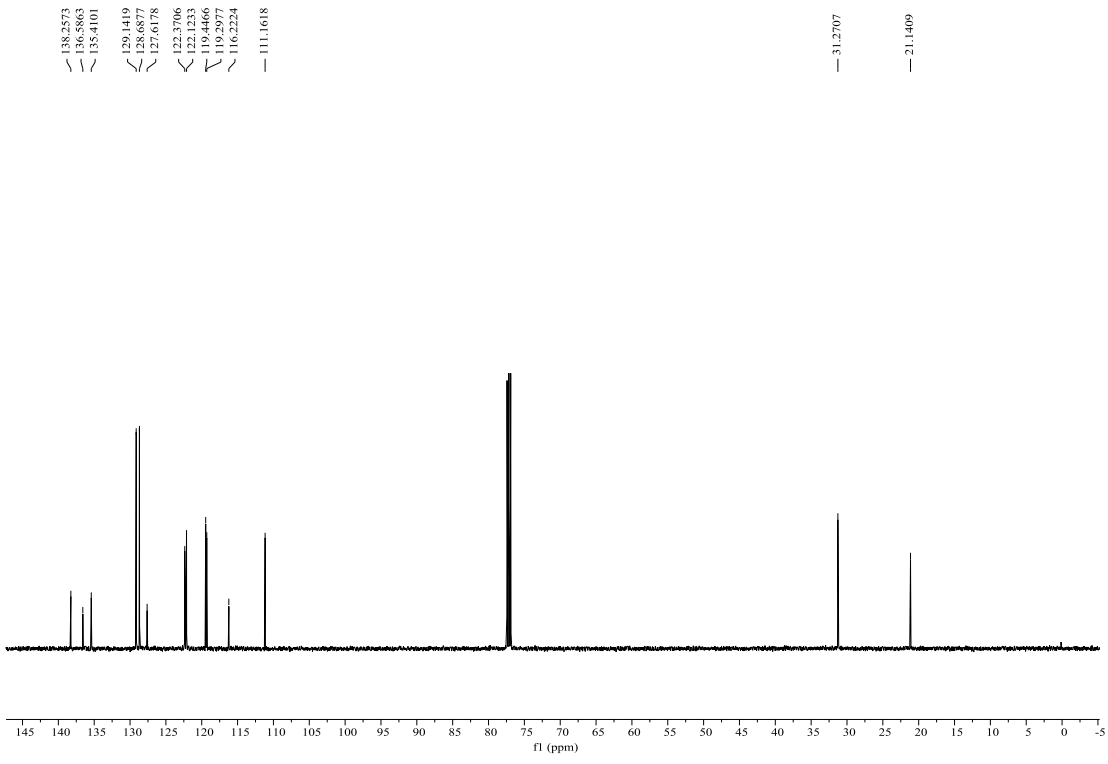
3-benzyl-1*H*-indole (3a)



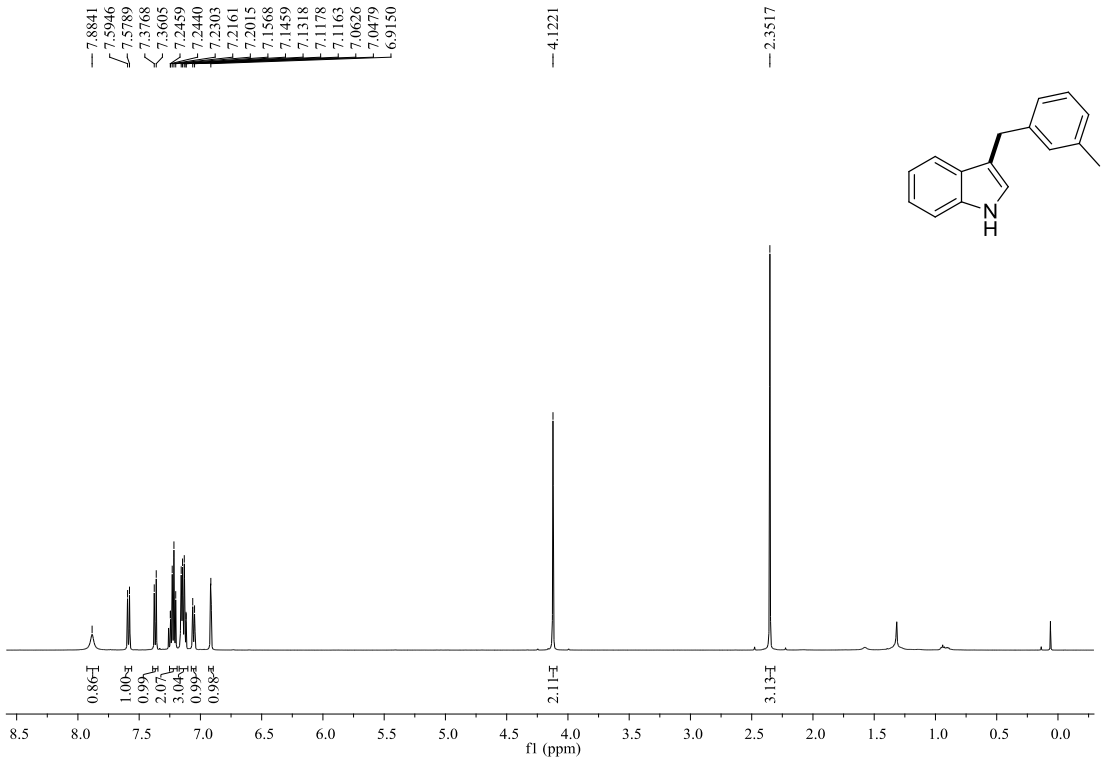


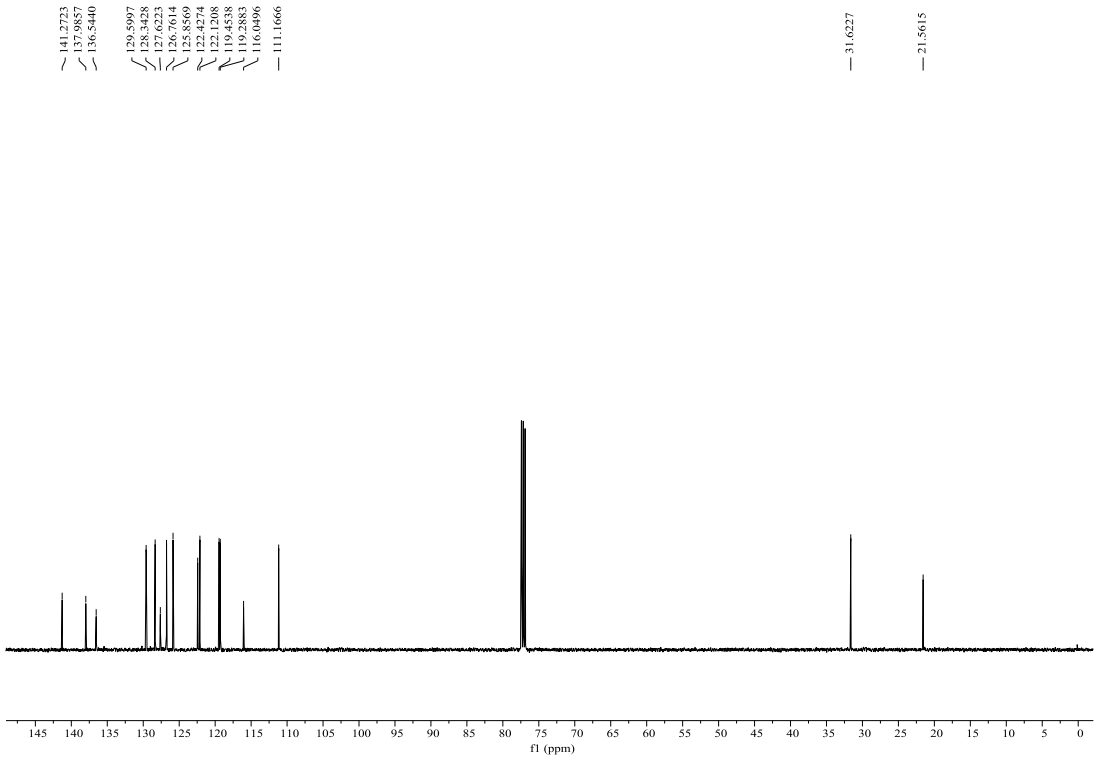
3-(4-methylbenzyl)-1*H*-indole (3b)



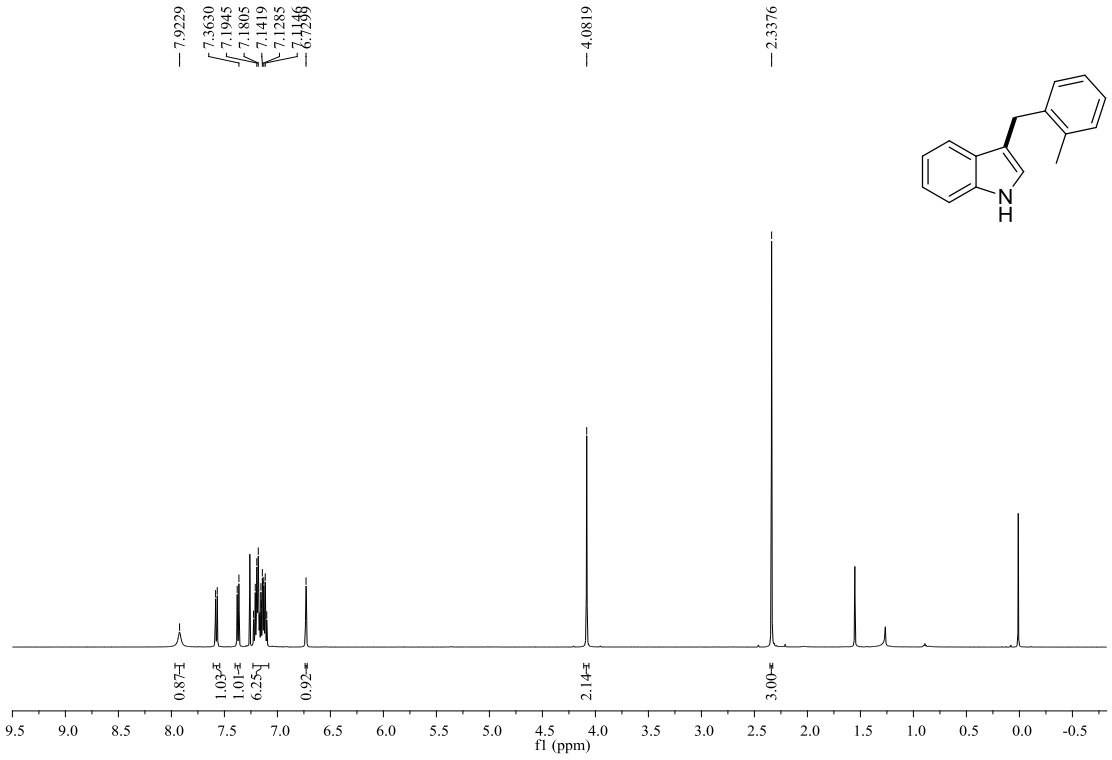


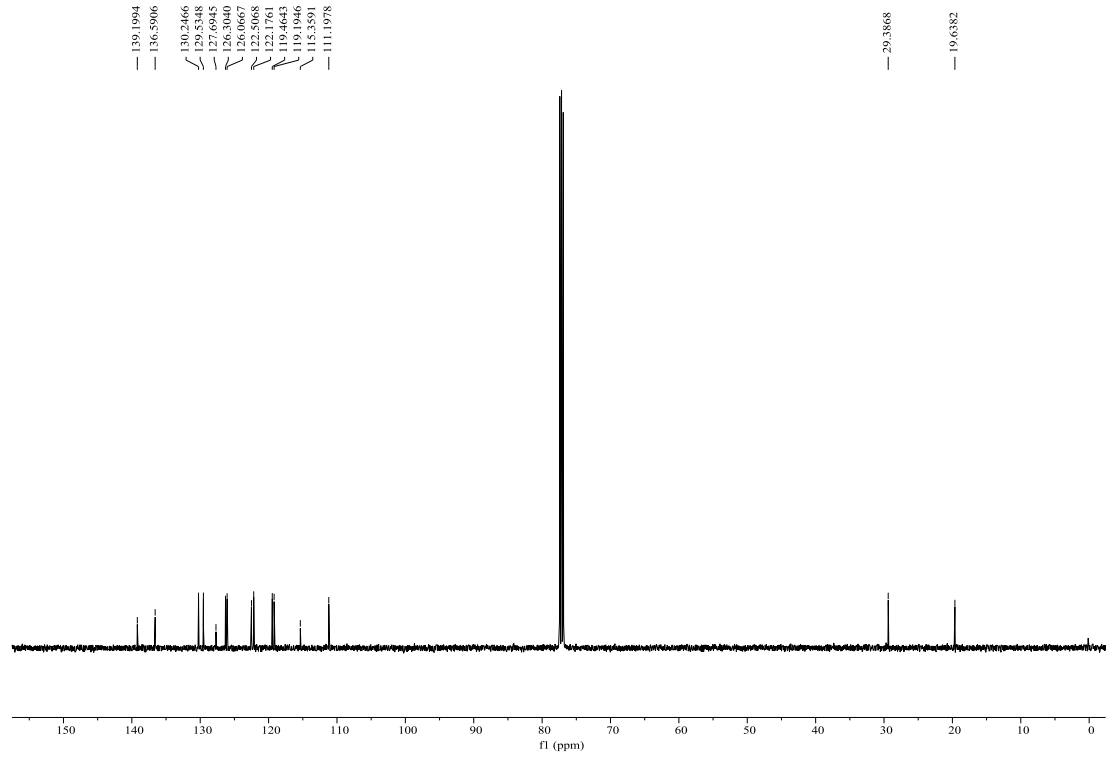
3-(3-methylbenzyl)-1*H*-indole (3c)



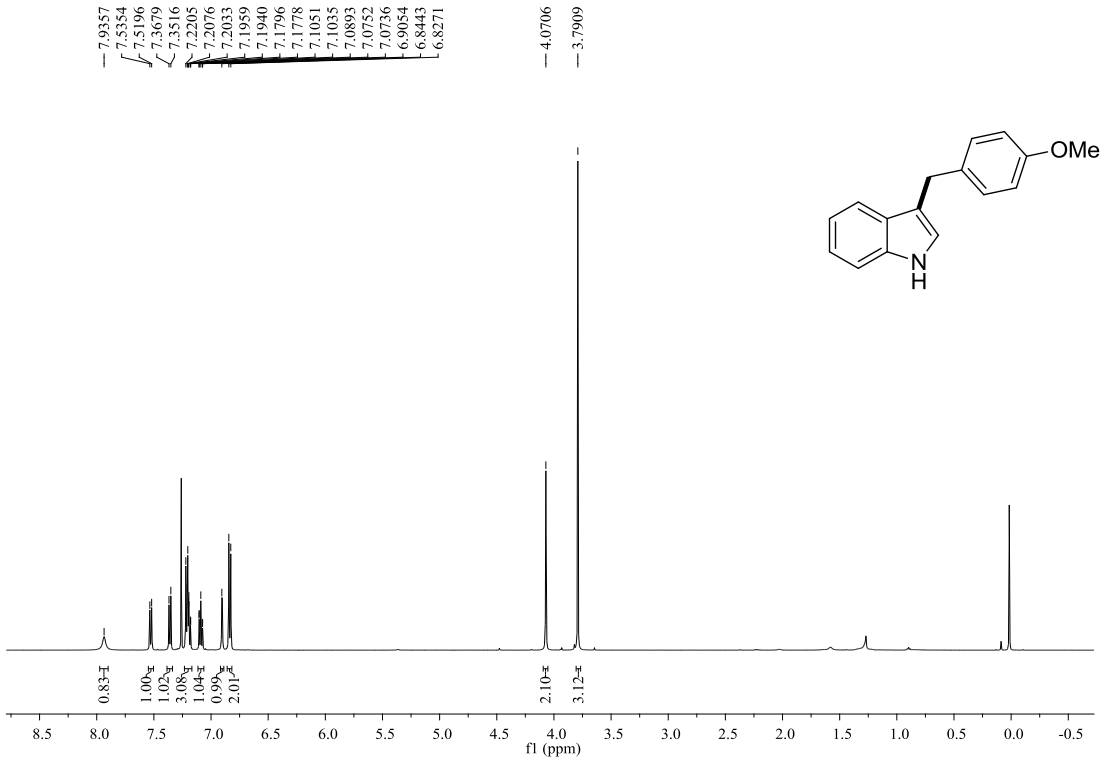


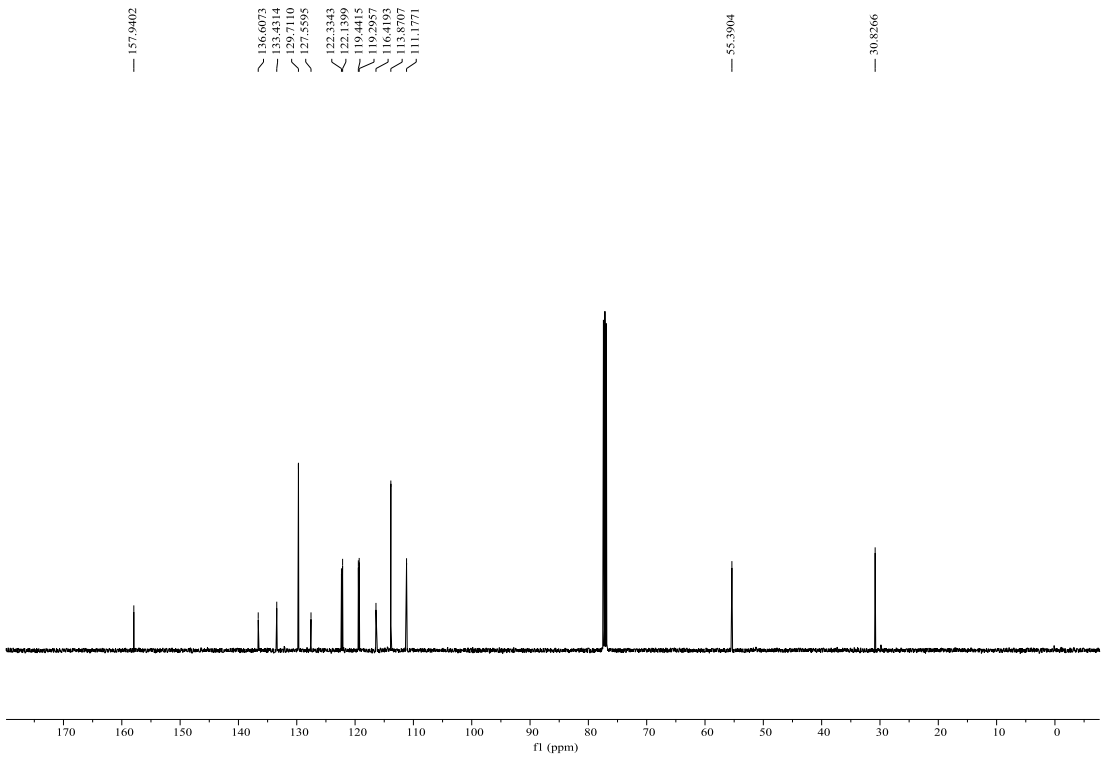
3-(2-methylbenzyl)-1*H*-indole (3d)



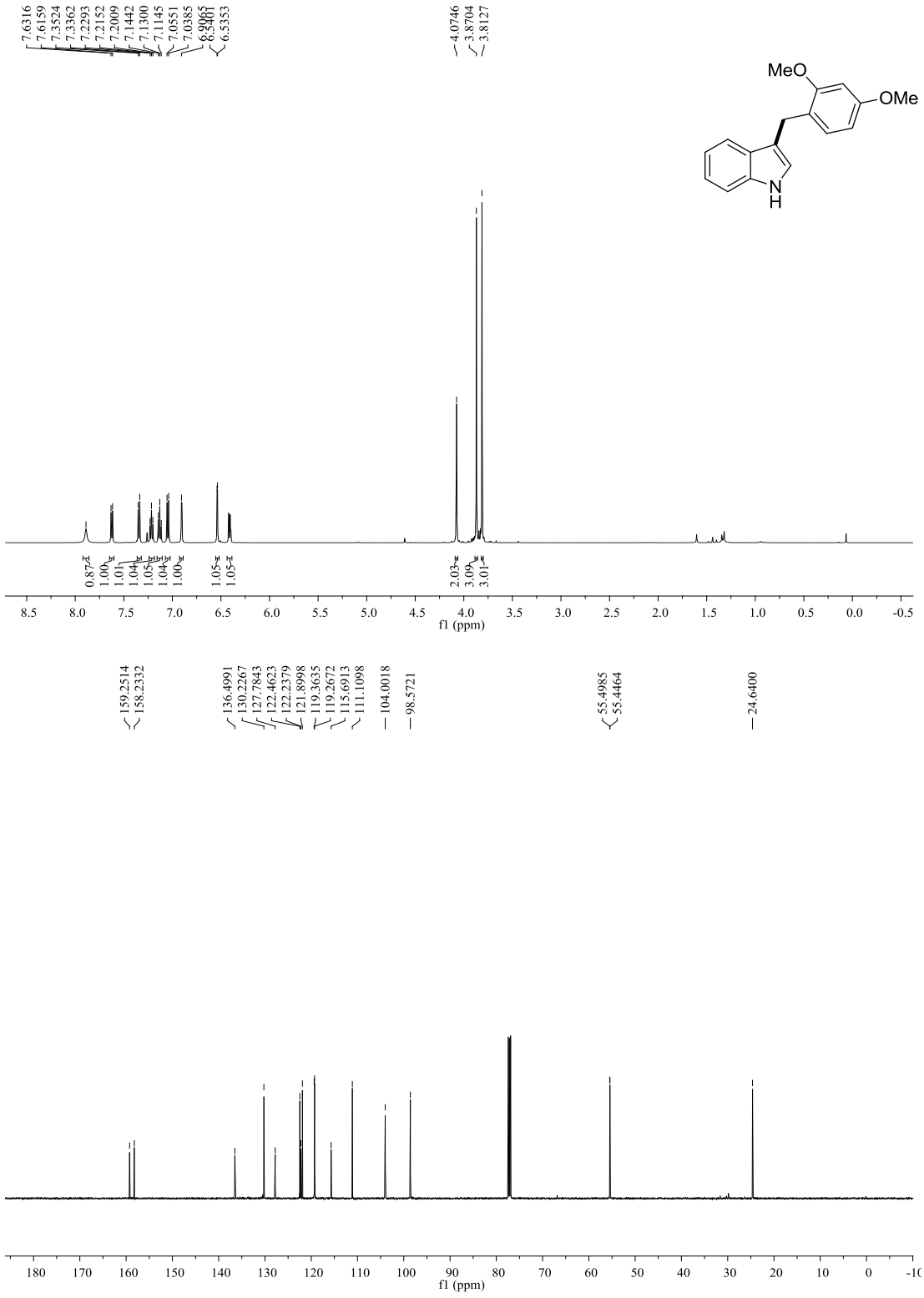


3-(4-methoxybenzyl)-1*H*-indole (3e)

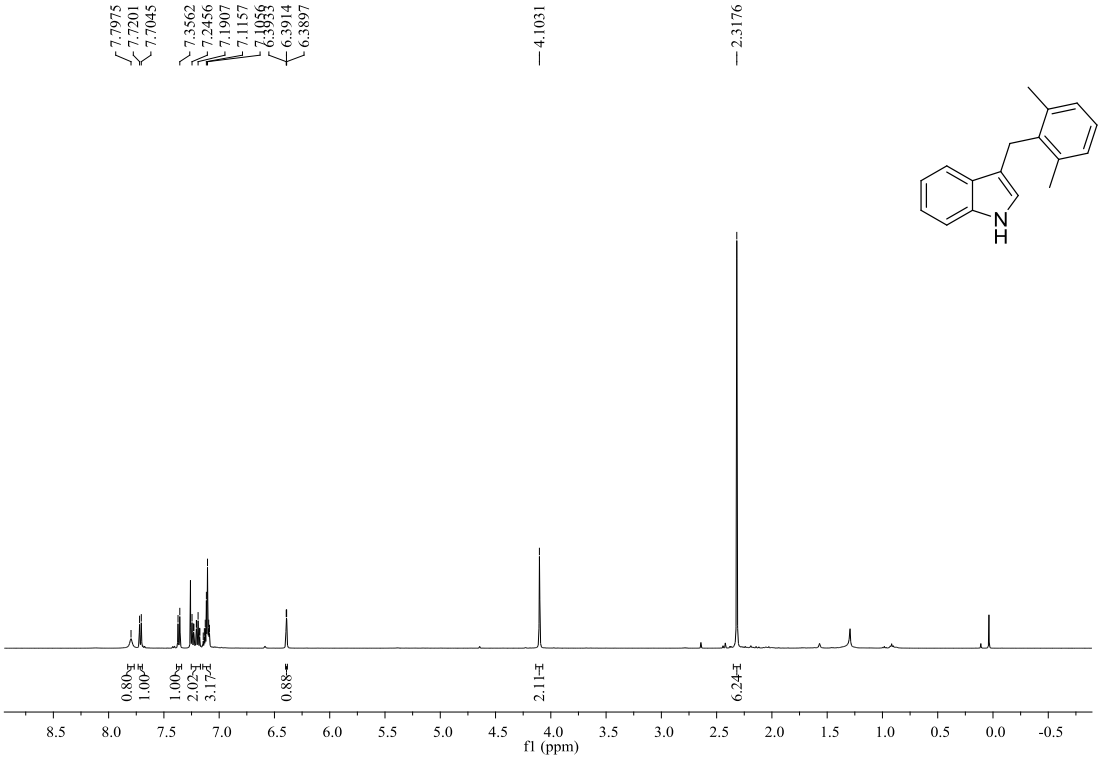


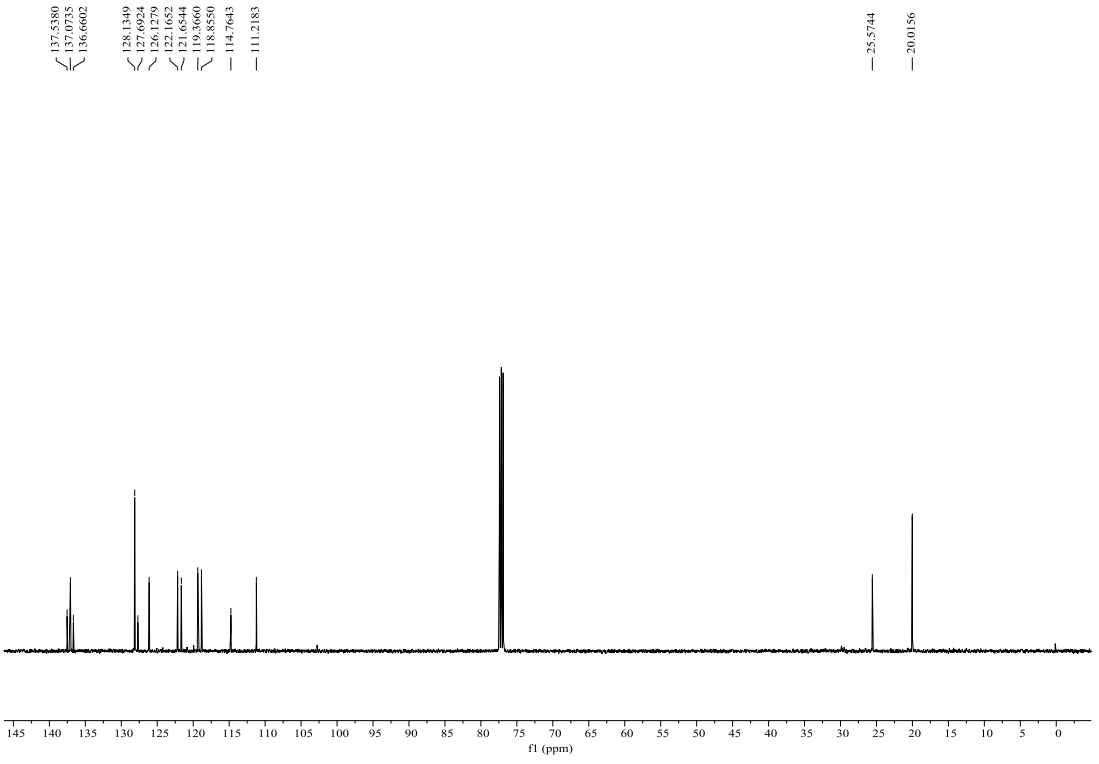


3-(2,4-dimethoxybenzyl)-1*H*-indole (3f)

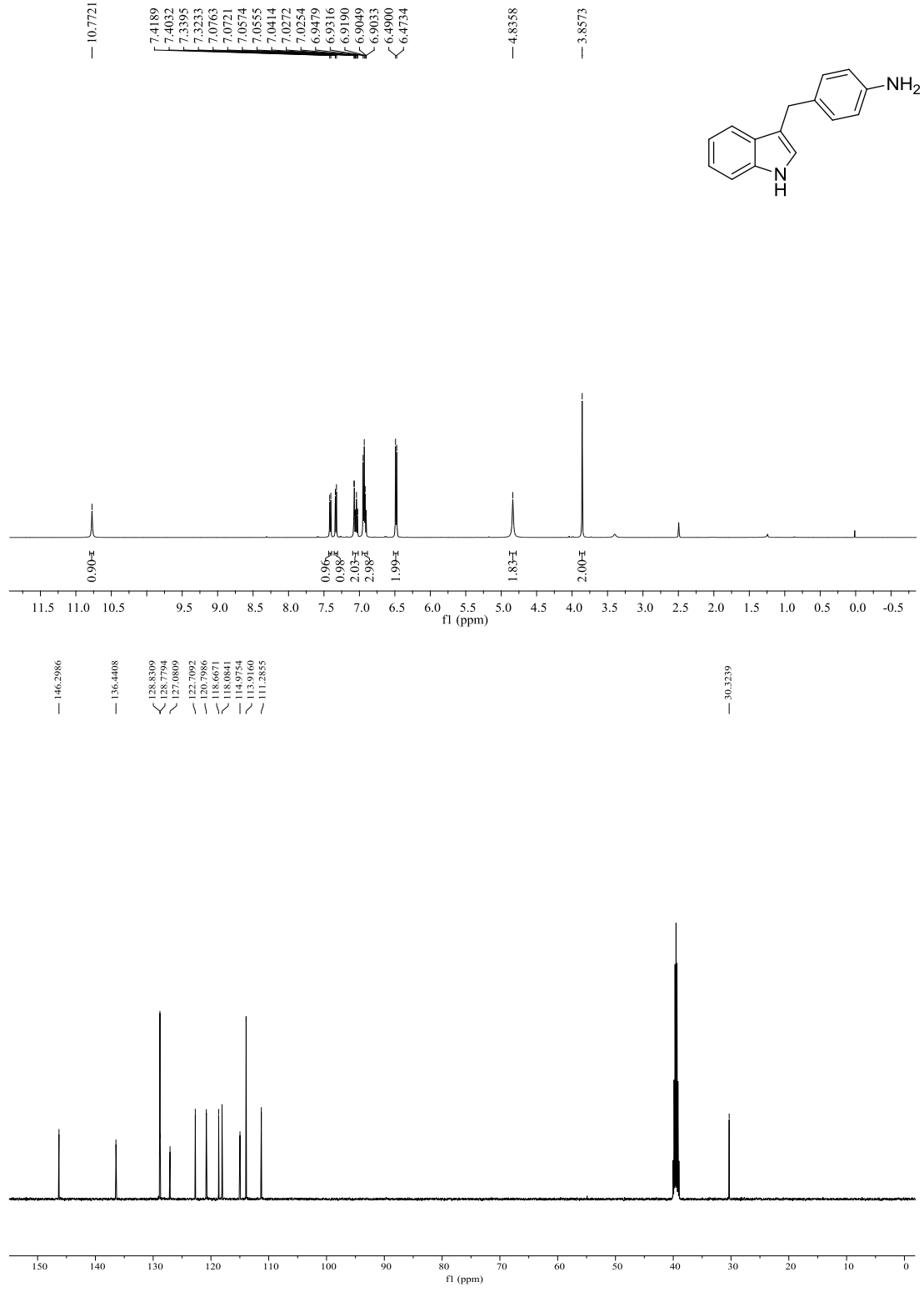


3-(2,6-dimethylbenzyl)-1*H*-indole (3g)

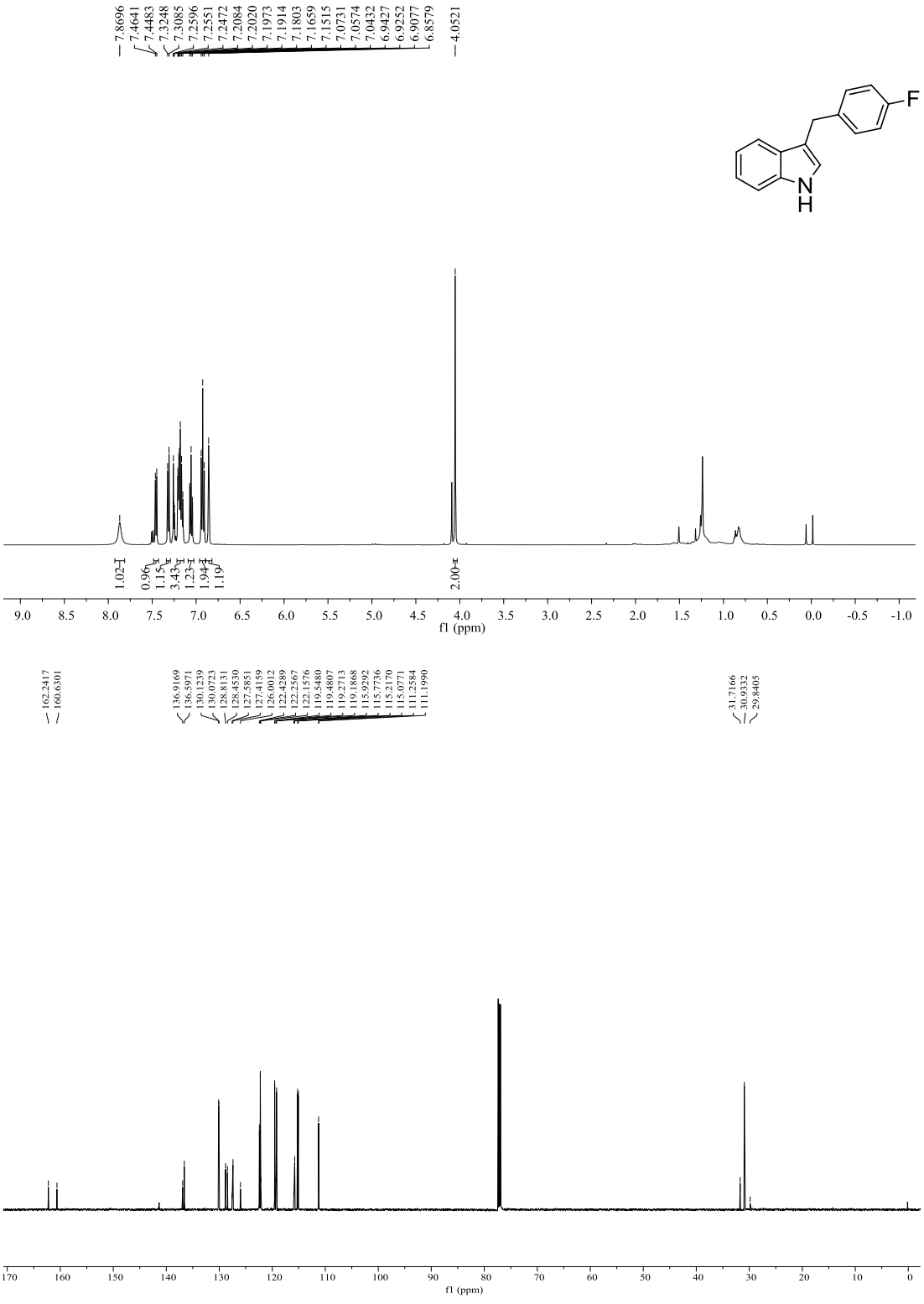




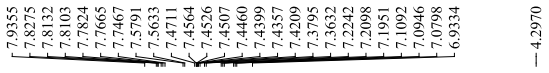
4-((1*H*-indol-3-yl)methyl)aniline (3h)

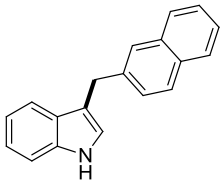


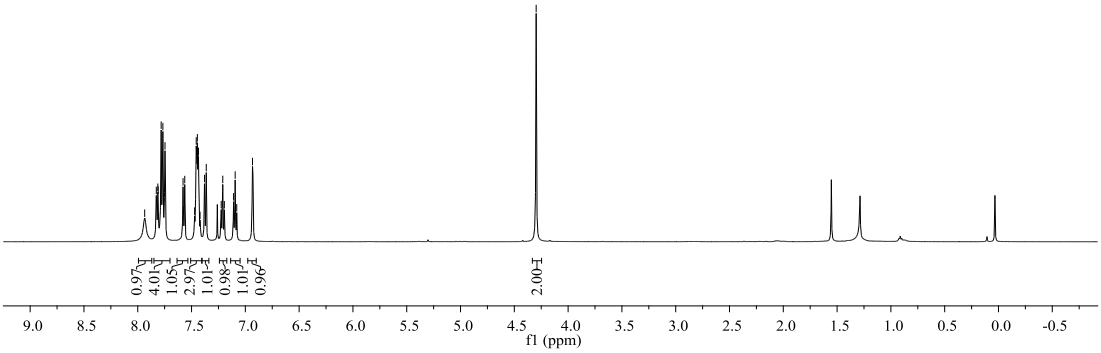
3-(4-fluorobenzyl)-1*H*-indole (3i)

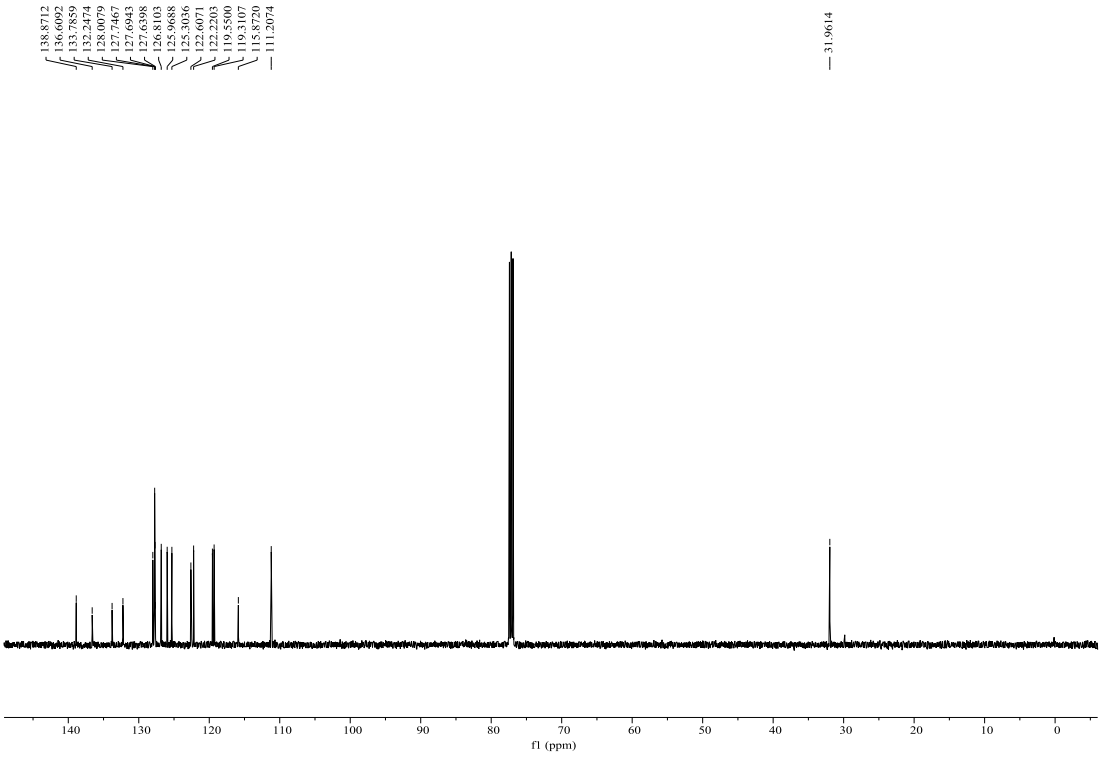


3-(naphthalen-2-ylmethyl)-1*H*-indole (3j)

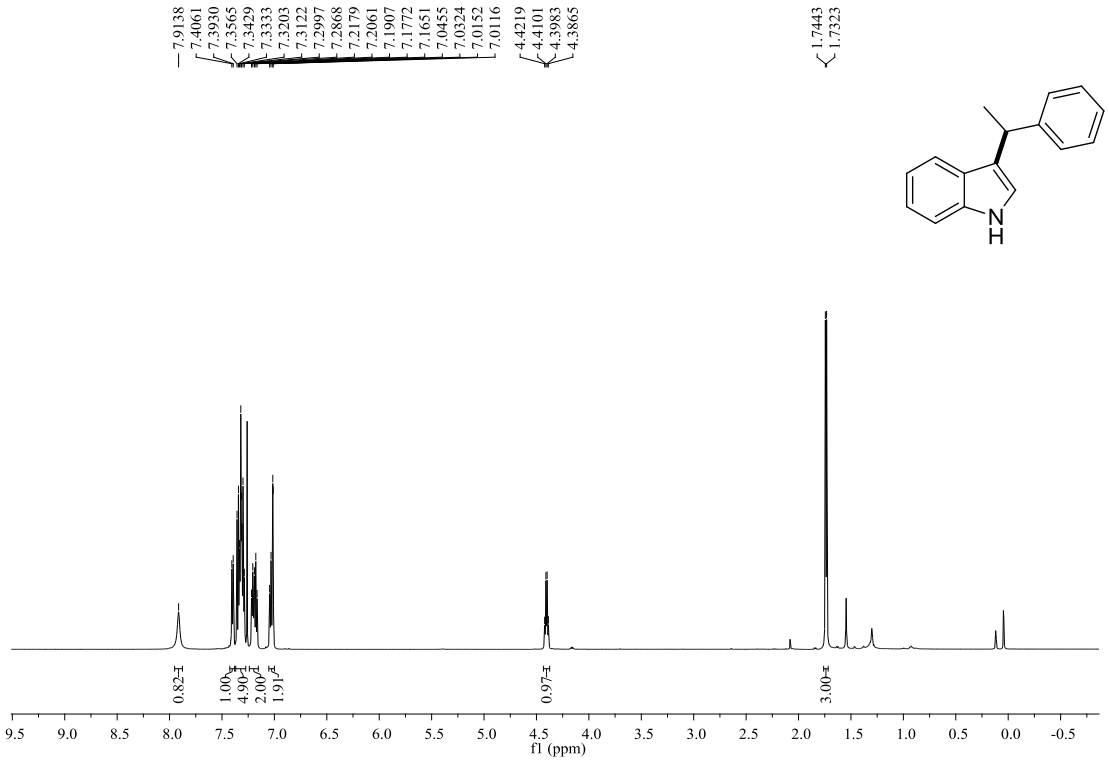


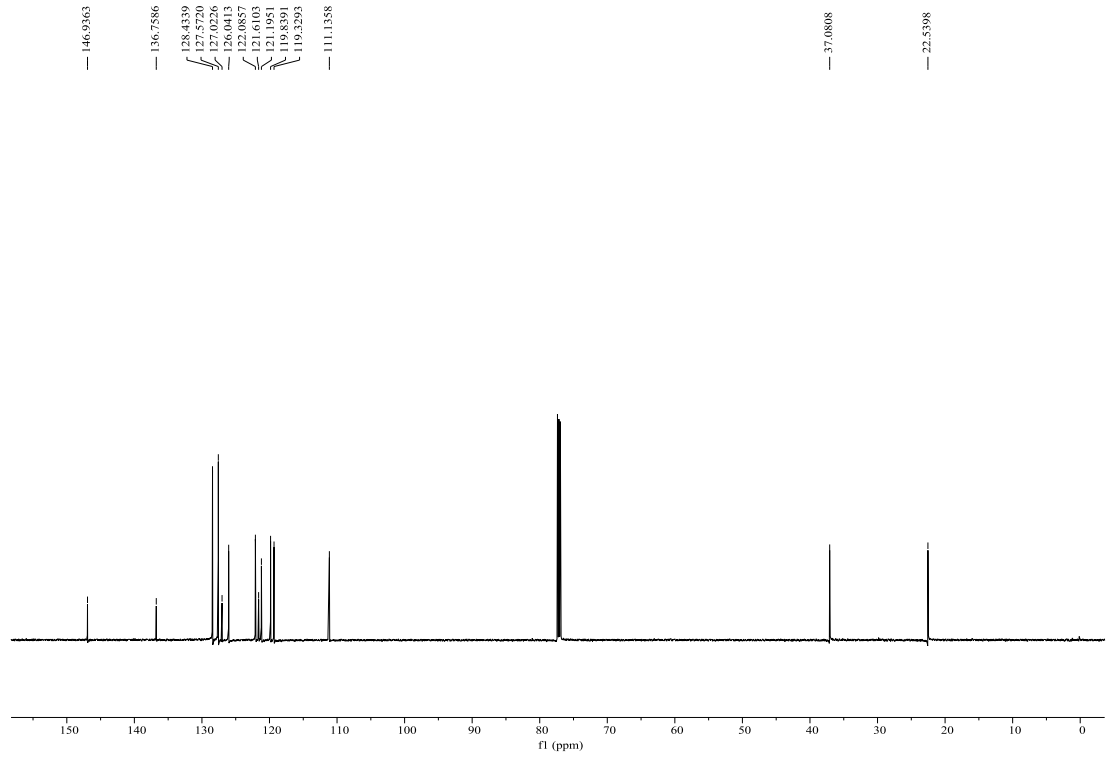




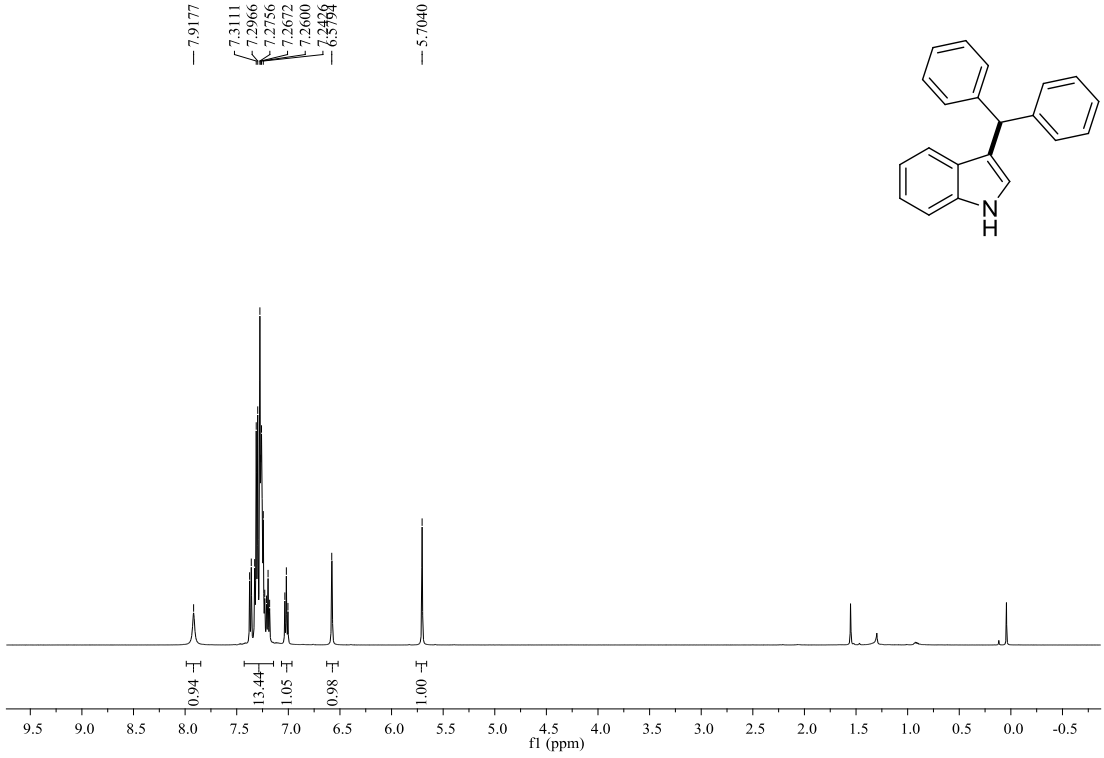


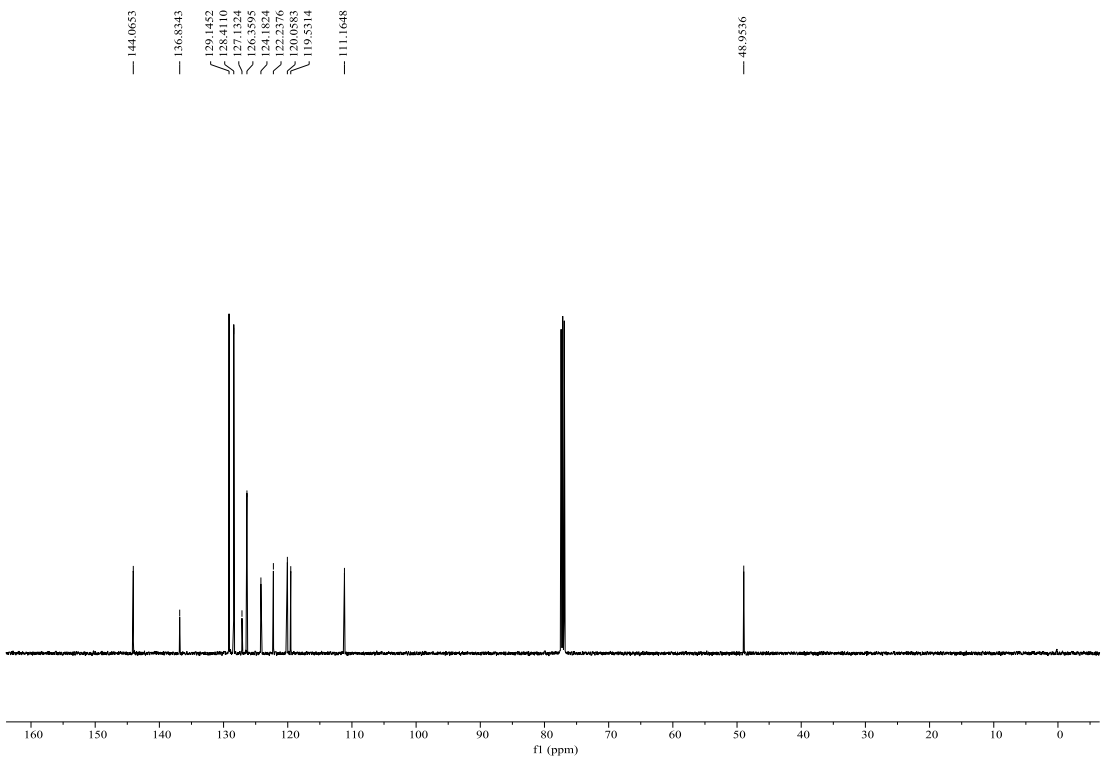
3-(1-phenylethyl)-1*H*-indole (3k)



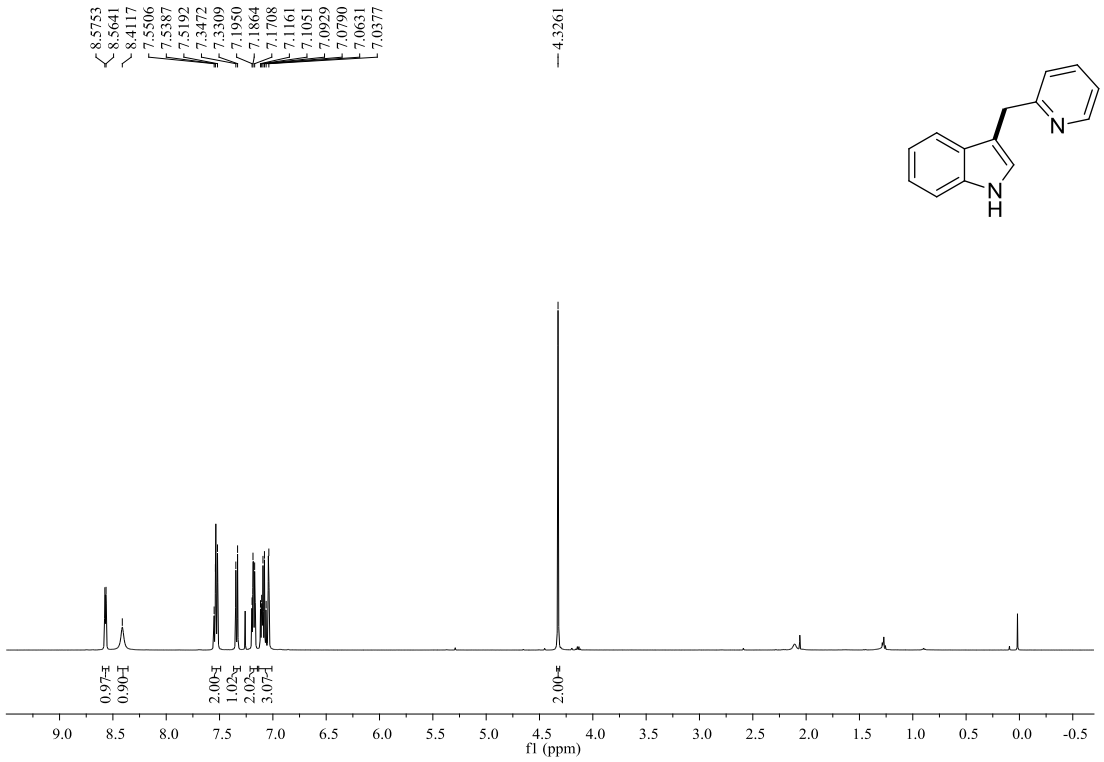


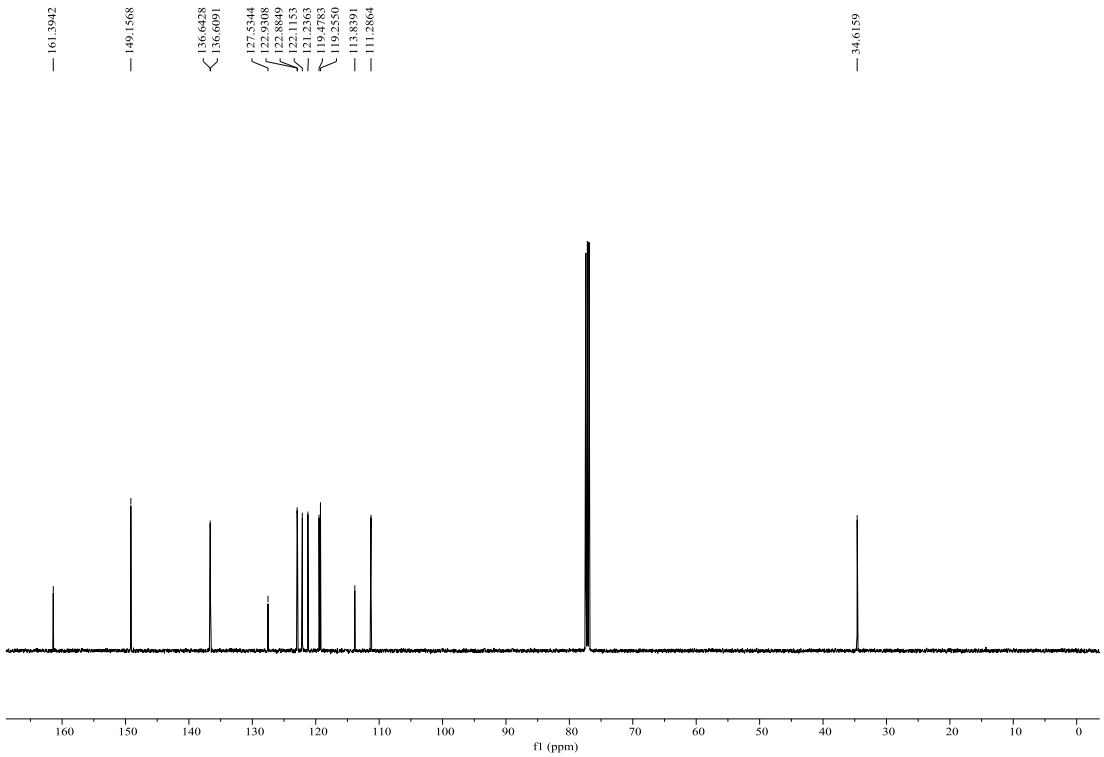
3-benzhydryl-1*H*-indole (3l)



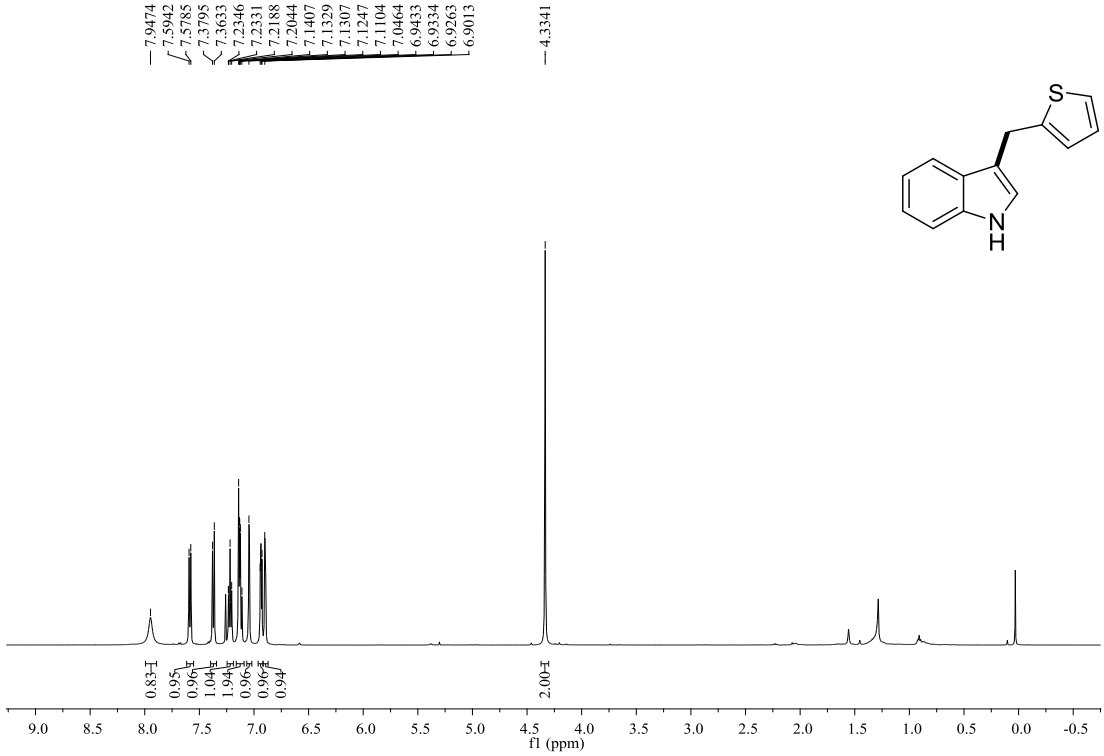


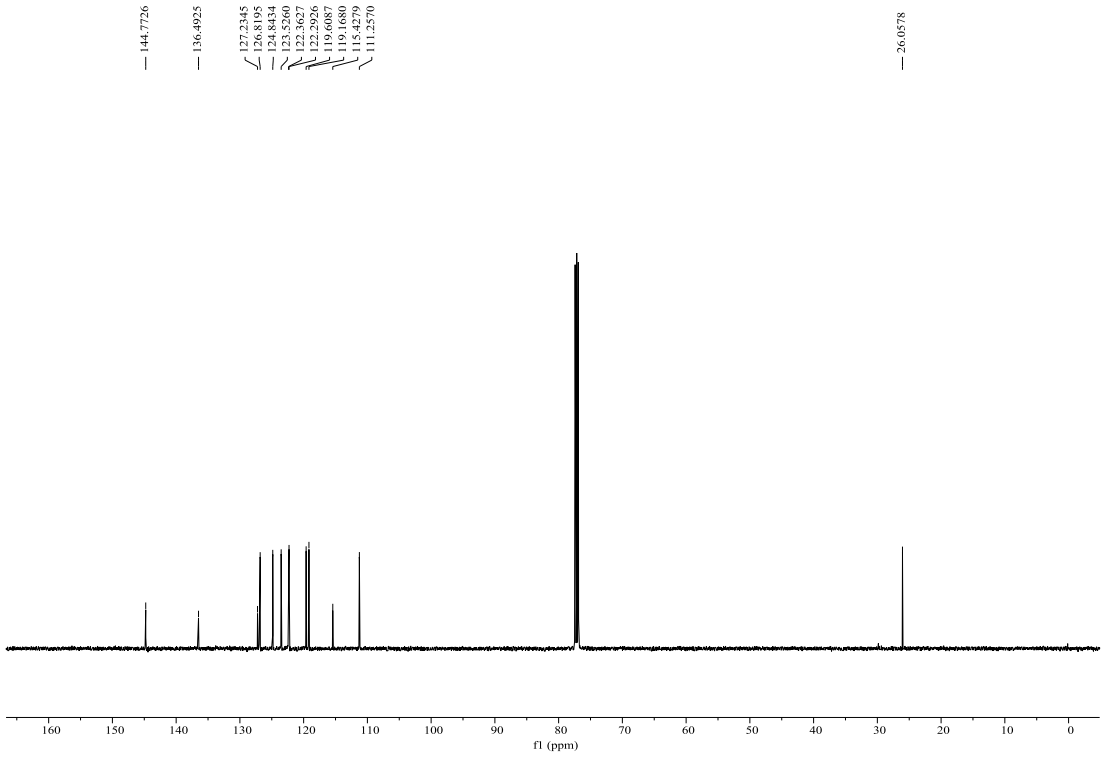
3-(pyridin-2-ylmethyl)-1*H*-indole (3m)



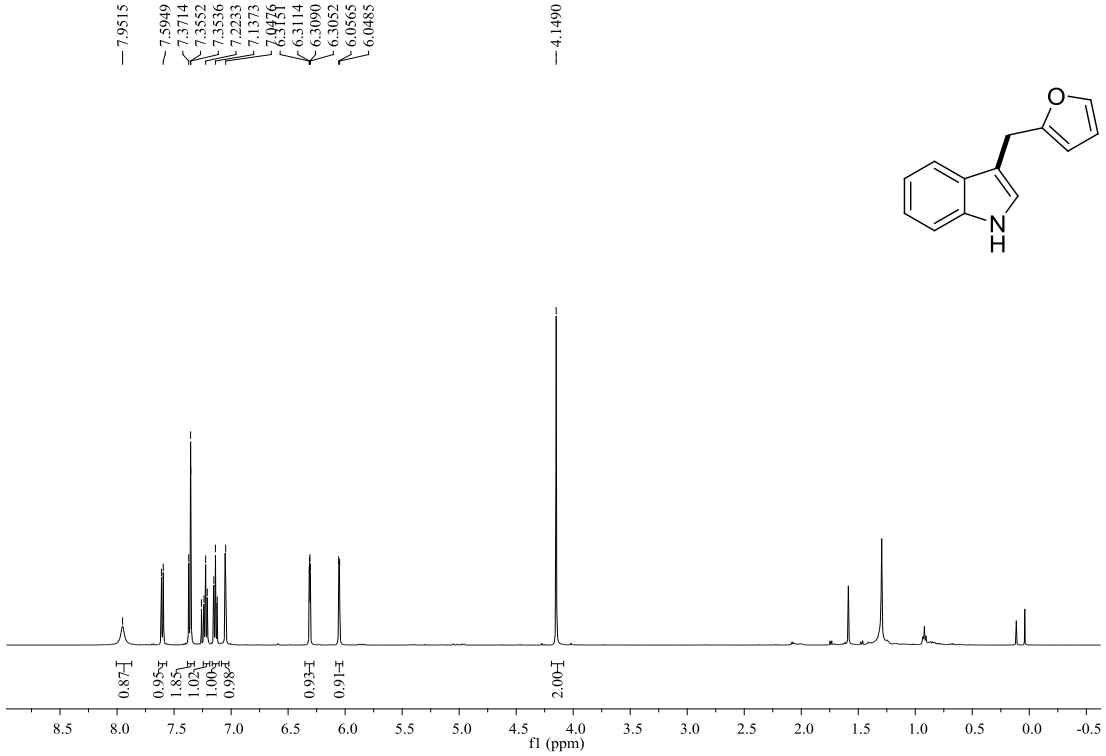


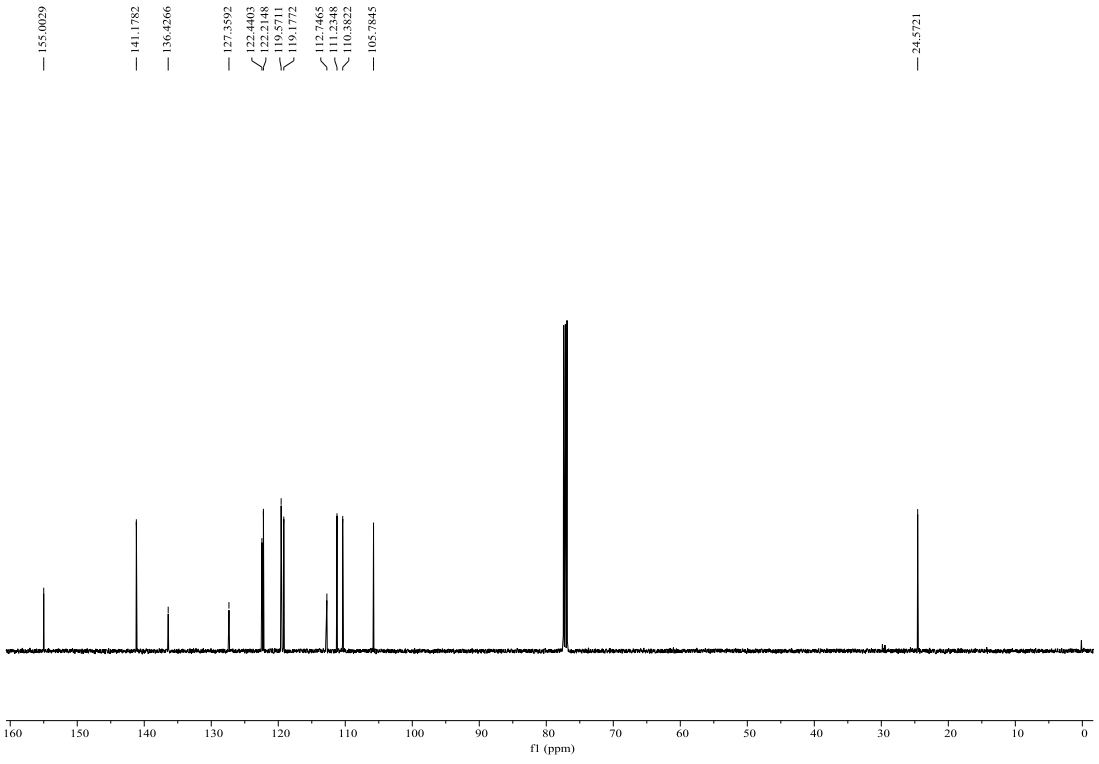
3-(thiophen-2-ylmethyl)-1*H*-indole (3n)



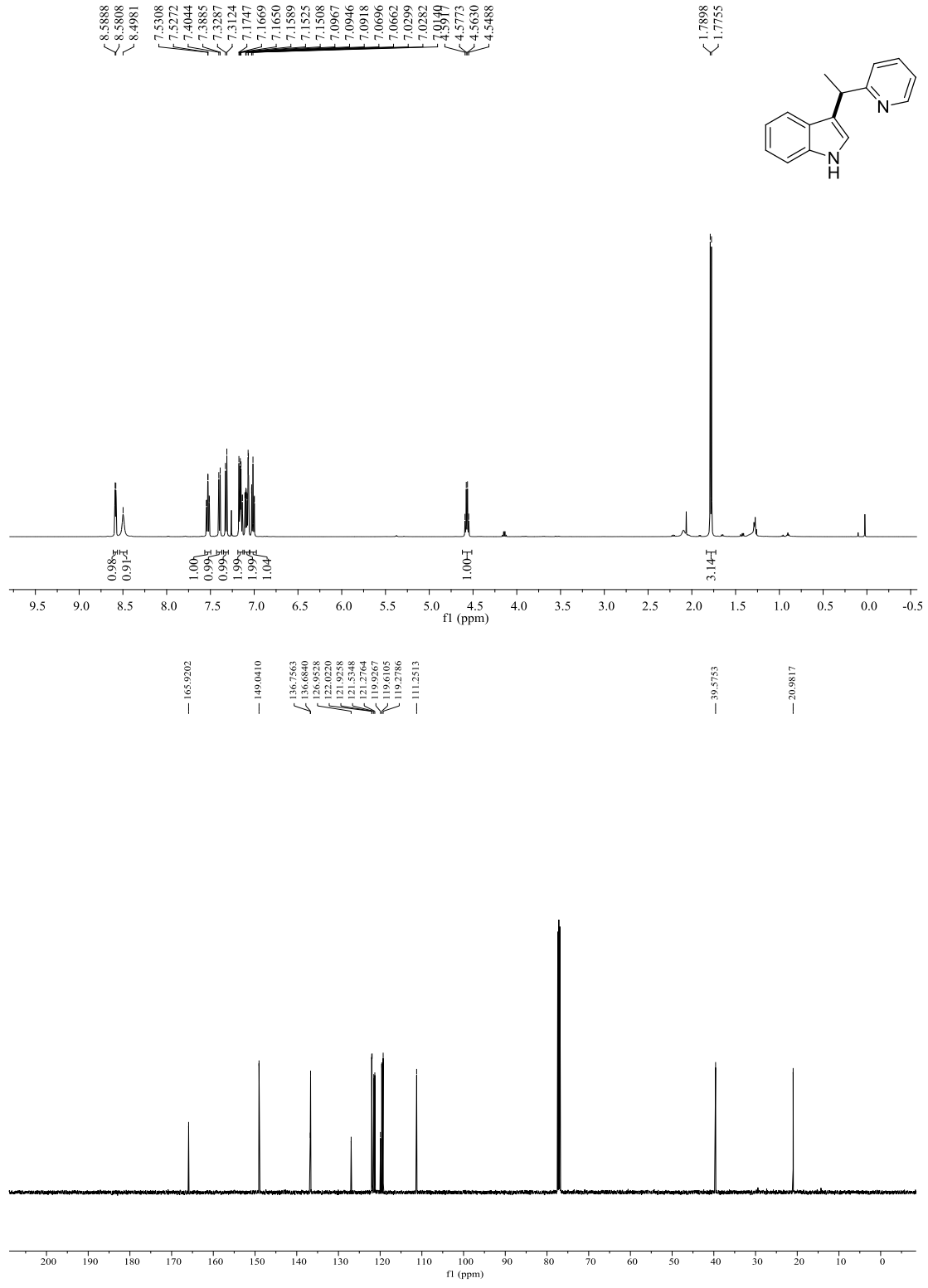


3-(furan-2-ylmethyl)-1*H*-indole (3o)

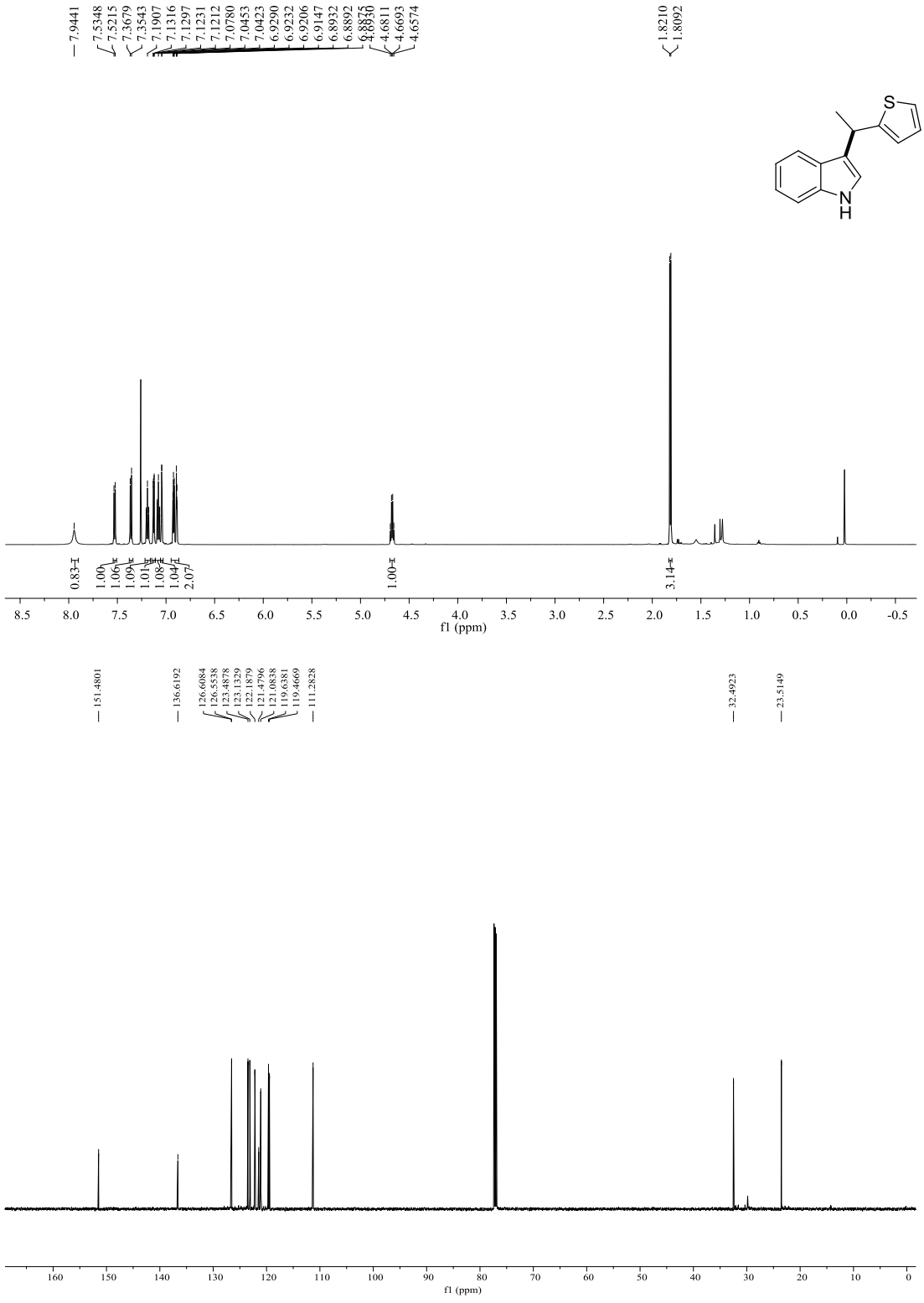




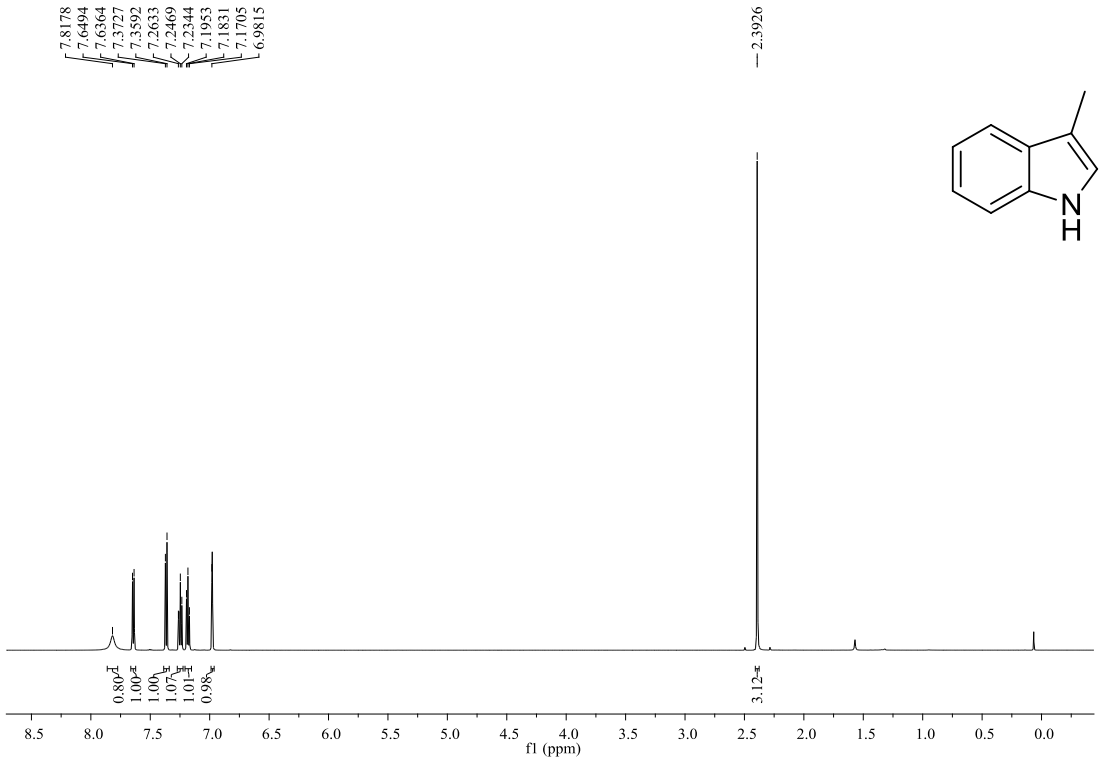
3-(1-(pyridin-2-yl)ethyl)-1*H*-indole (3p)

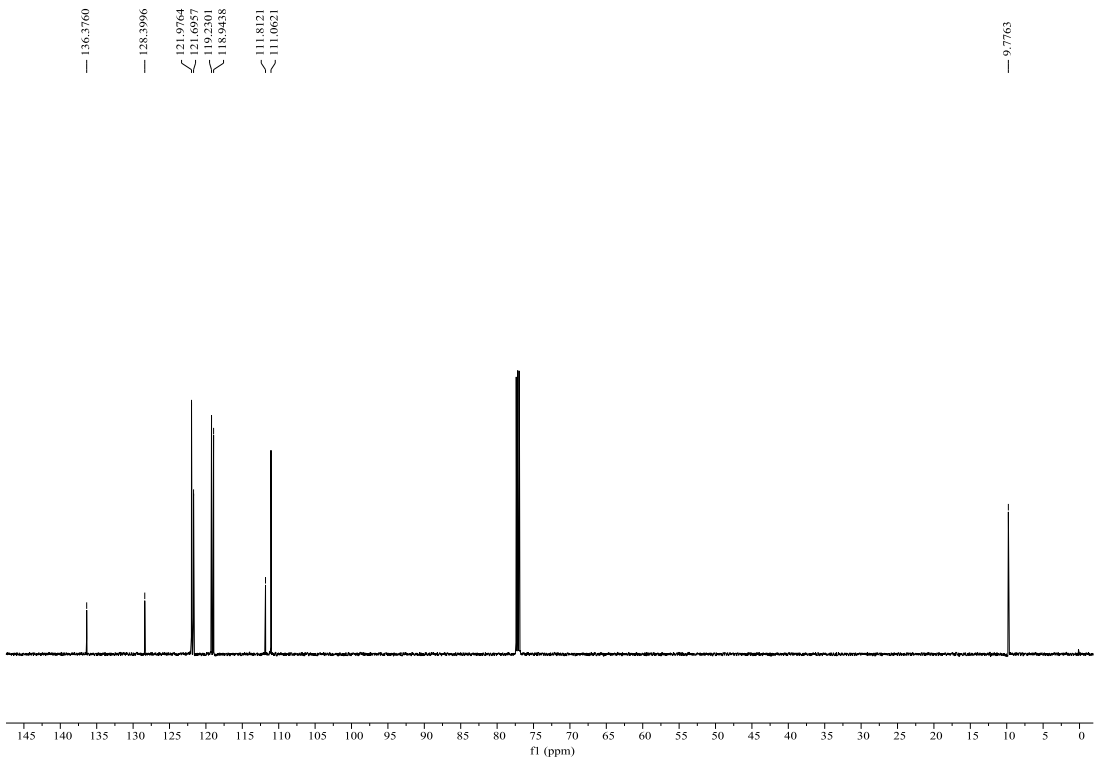


3-(1-(thiophen-2-yl)ethyl)-1*H*-indole (3q)

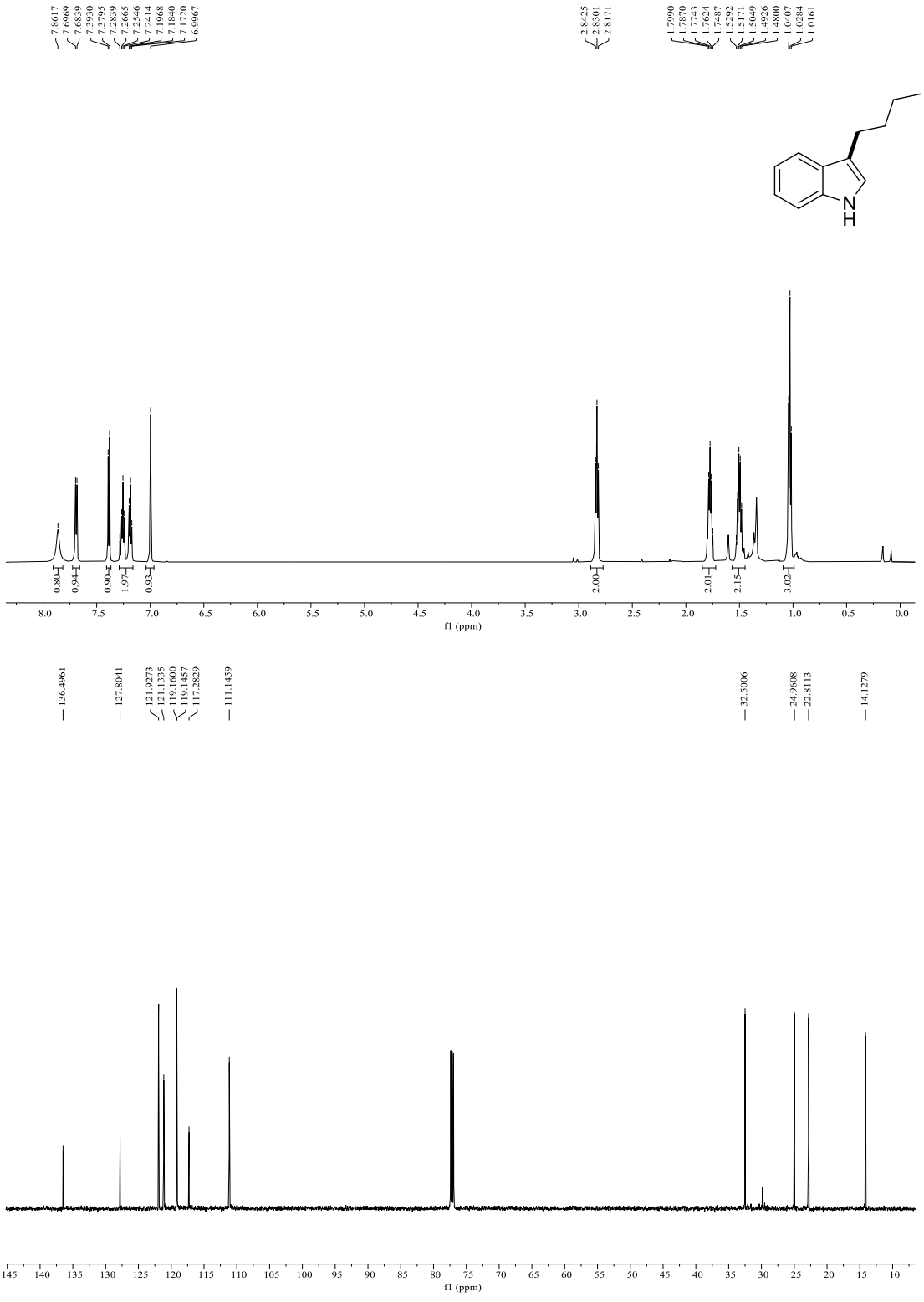


3-methyl-1*H*-indole (4a)

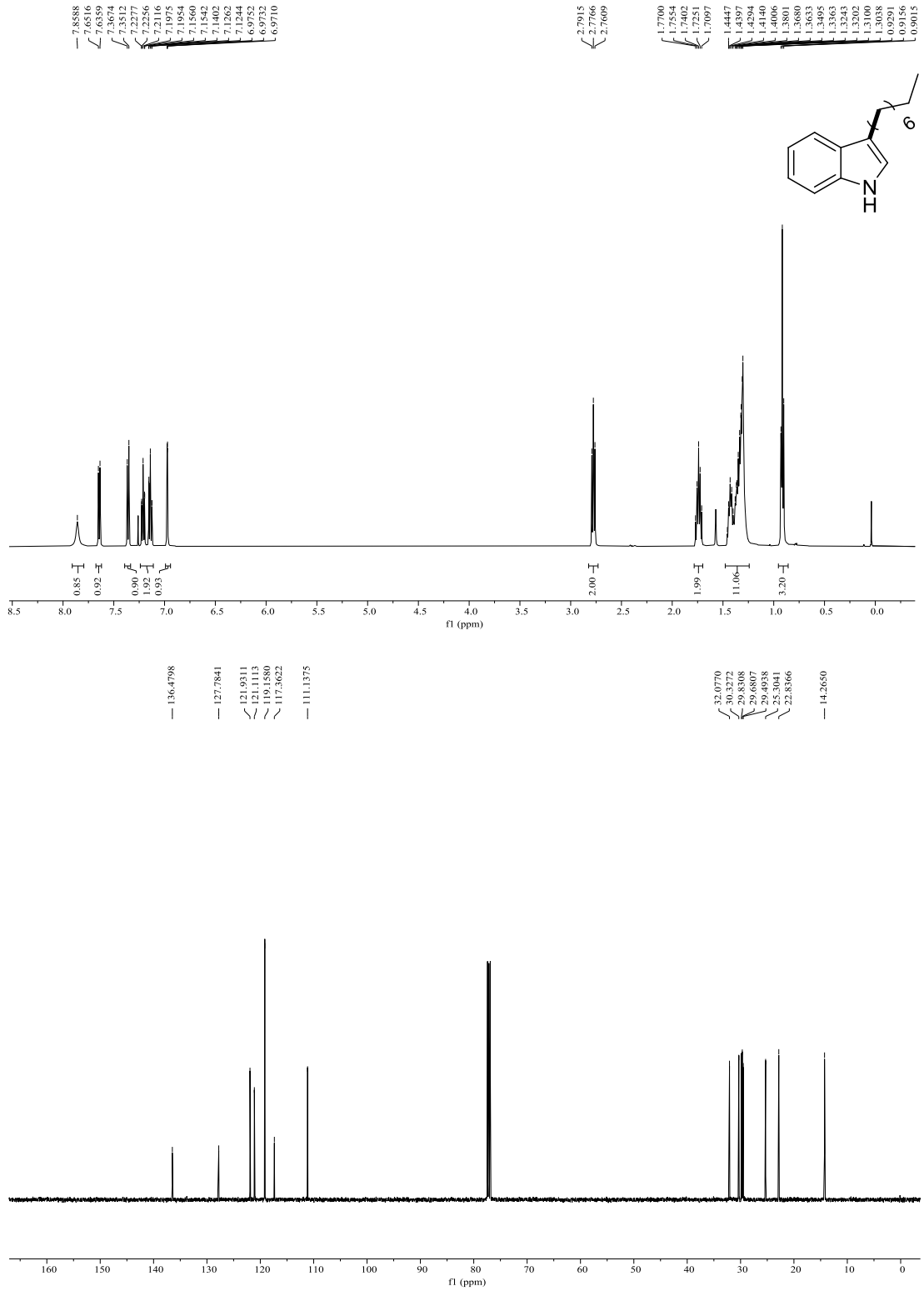




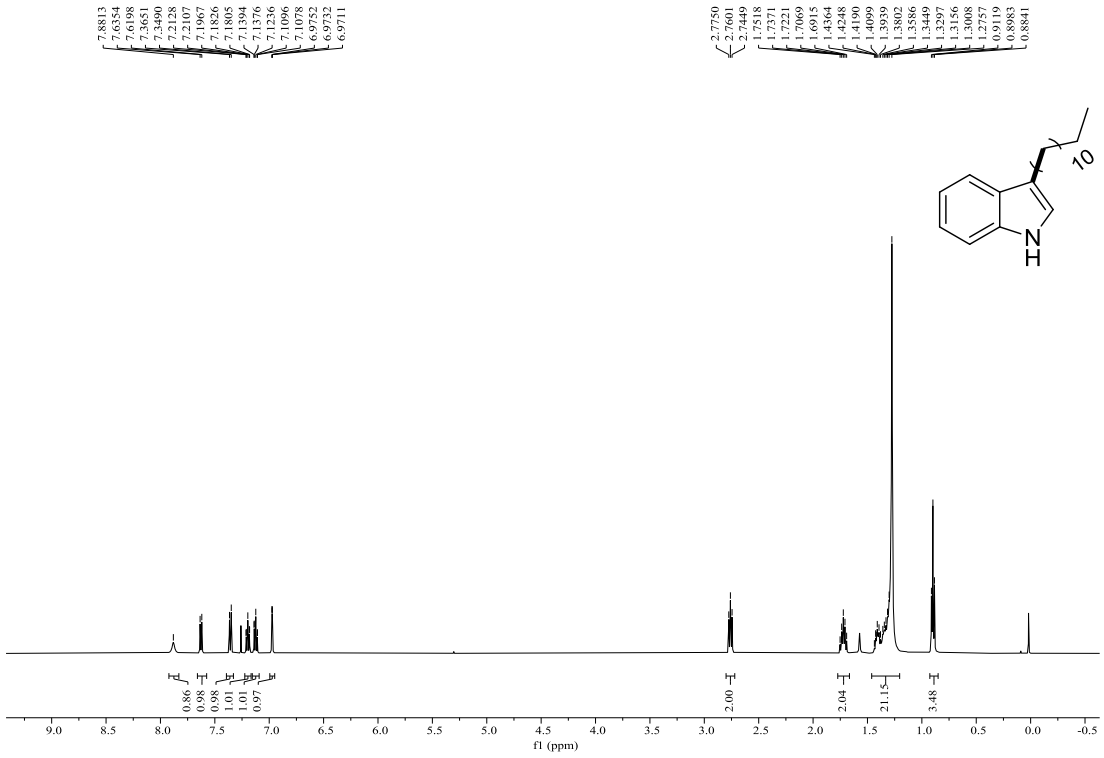
3- butyl-1*H*-indole (4b)

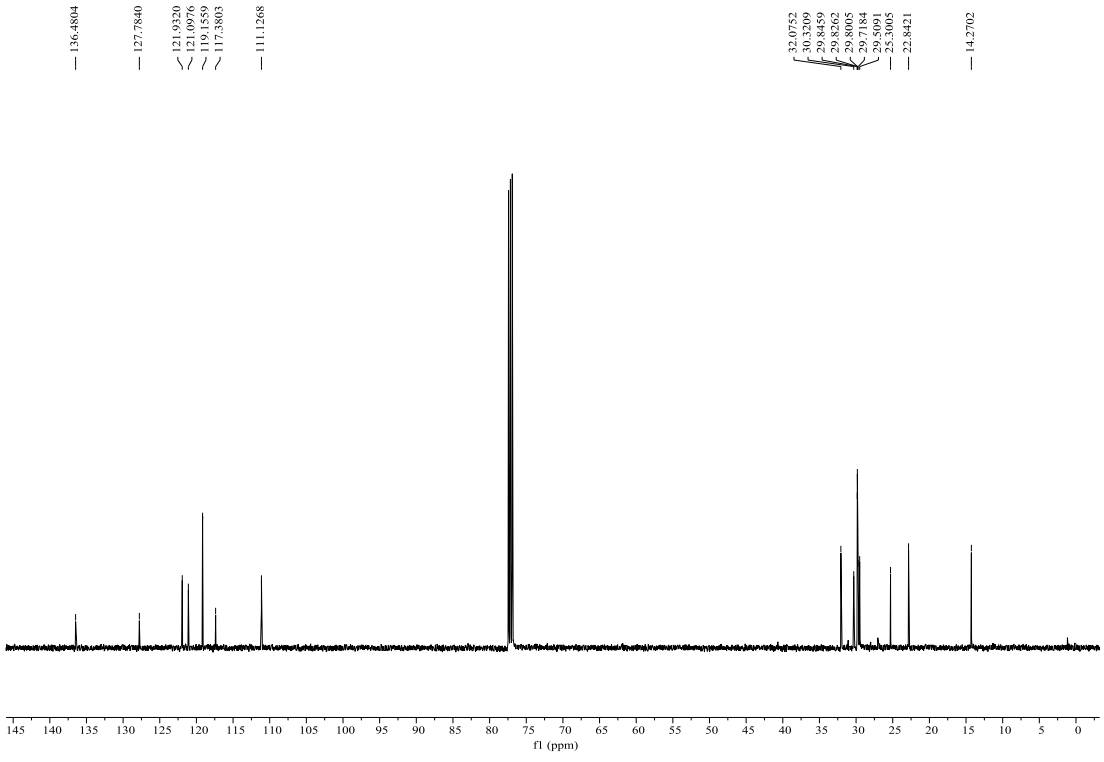


3-octyl-1*H*-indole (4c)

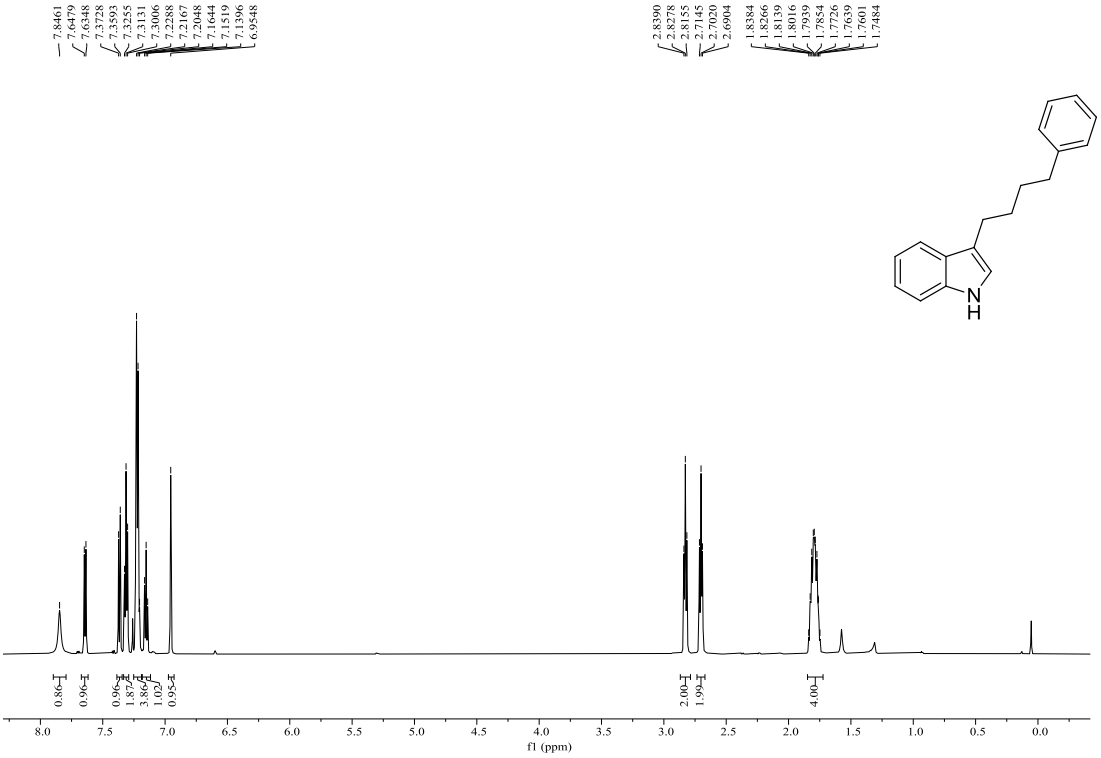


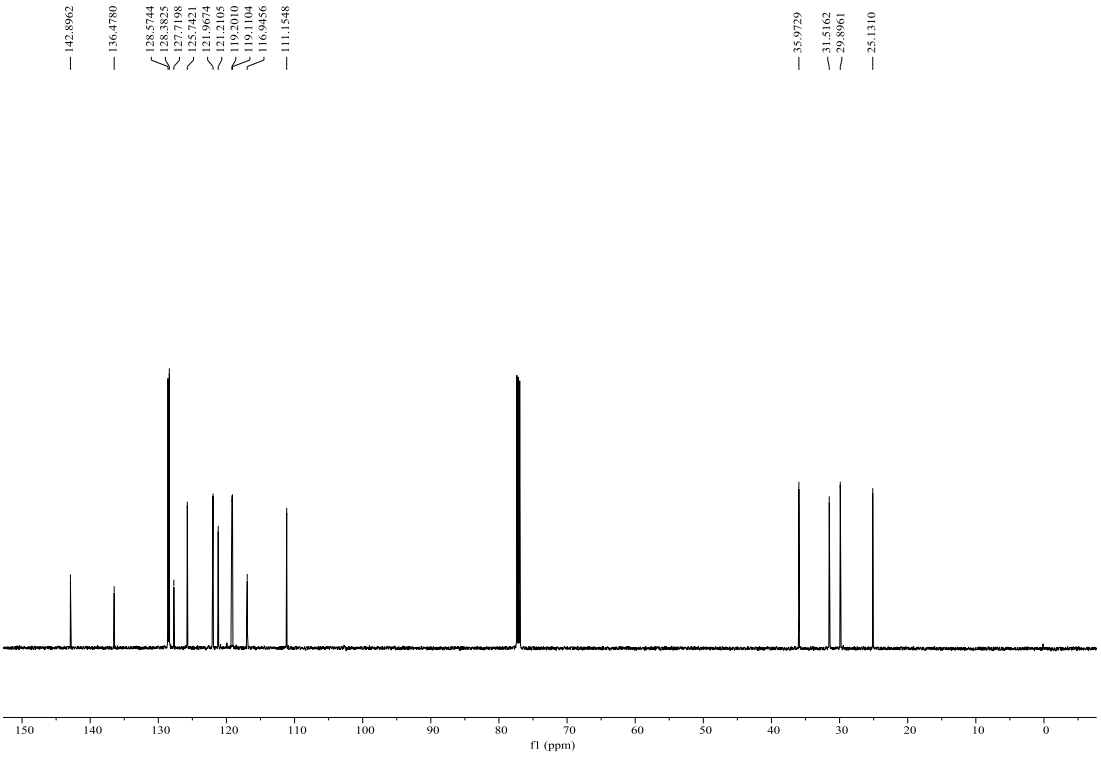
3-dodecyl-1*H*-indole (4d)



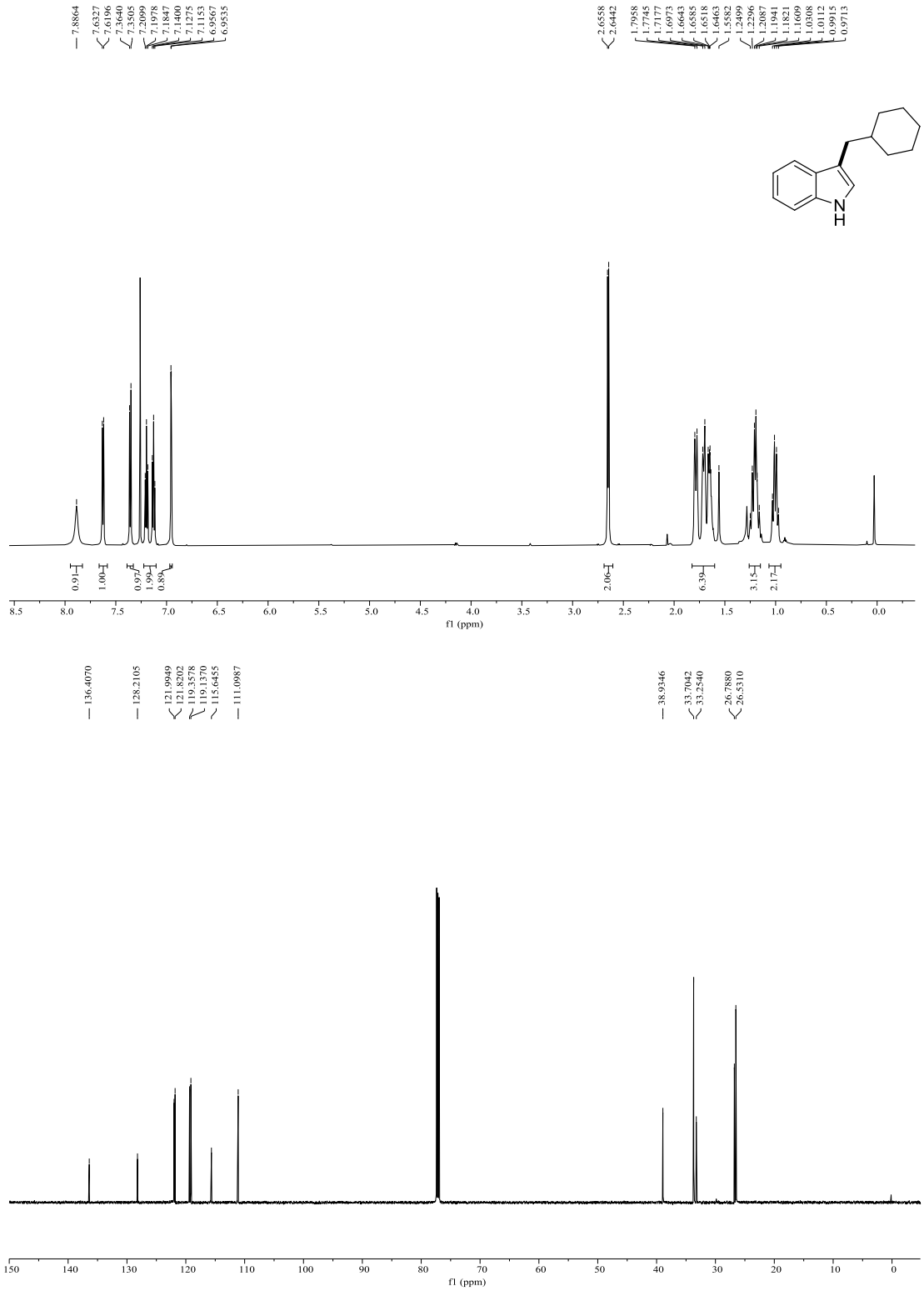


3- phenylbutyl-1*H*-indole (4e)

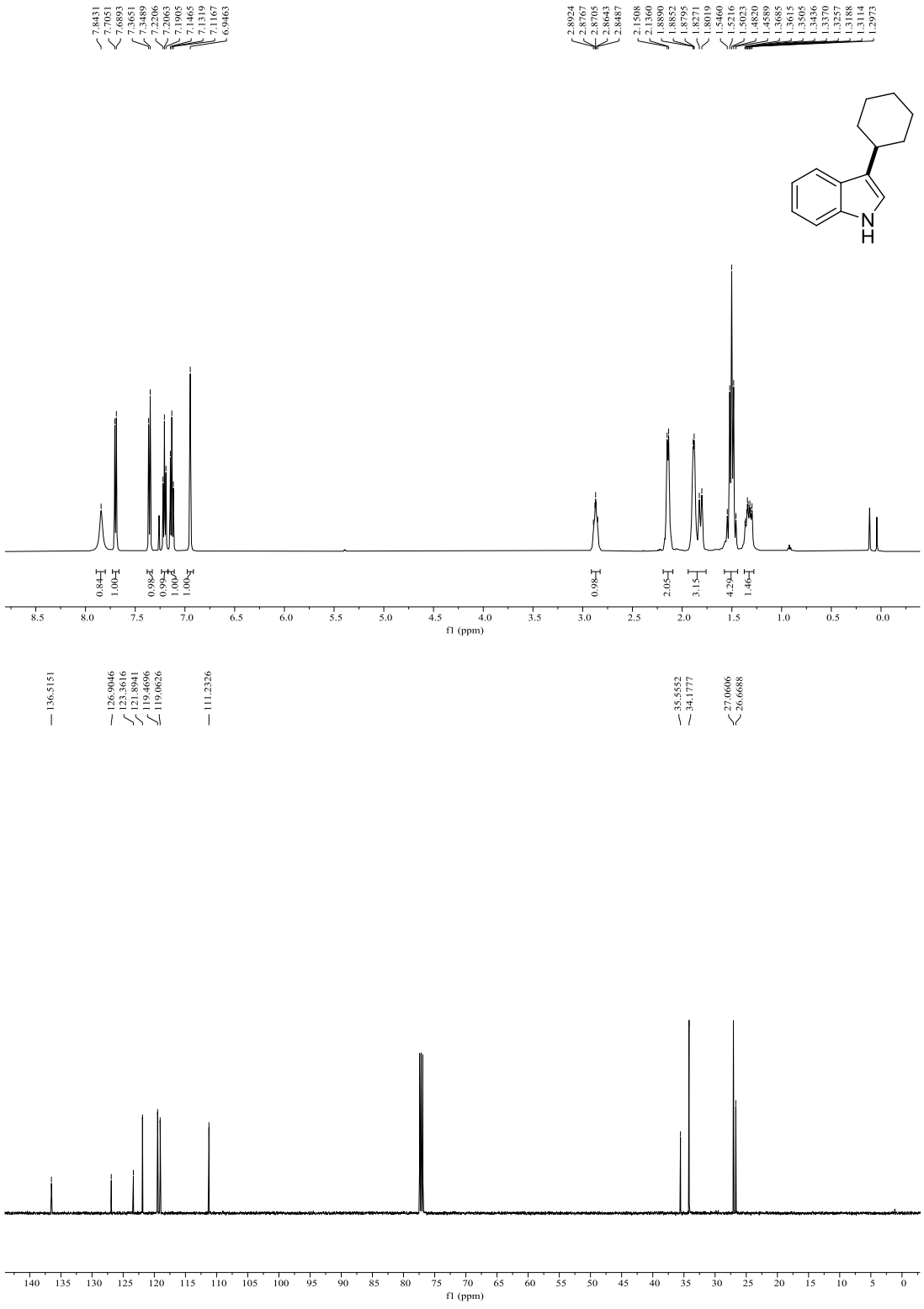




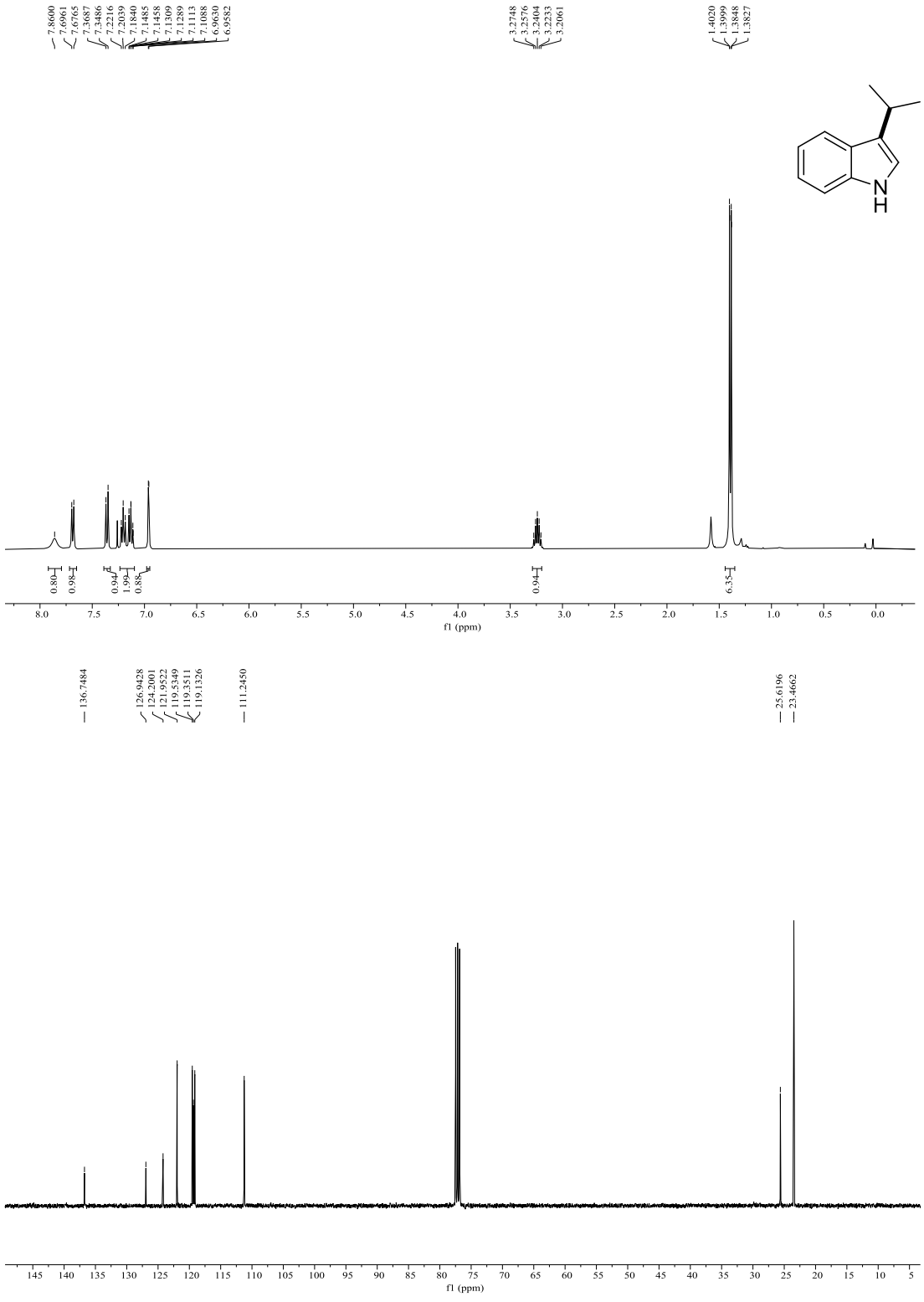
3-(cyclohexylmethyl)-1*H*-indole (4f)



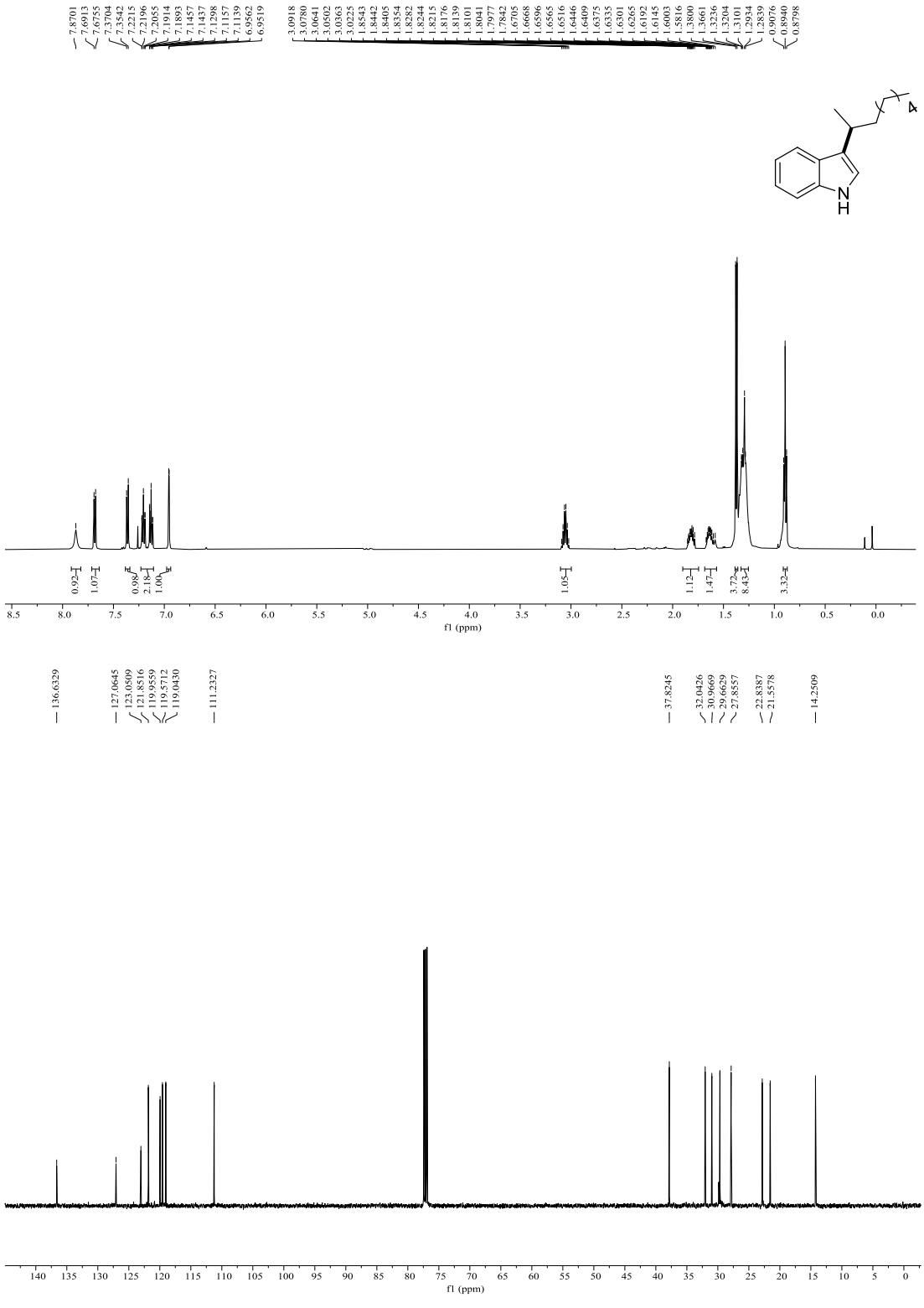
3-cyclohexyl-1*H*-indole (4g)



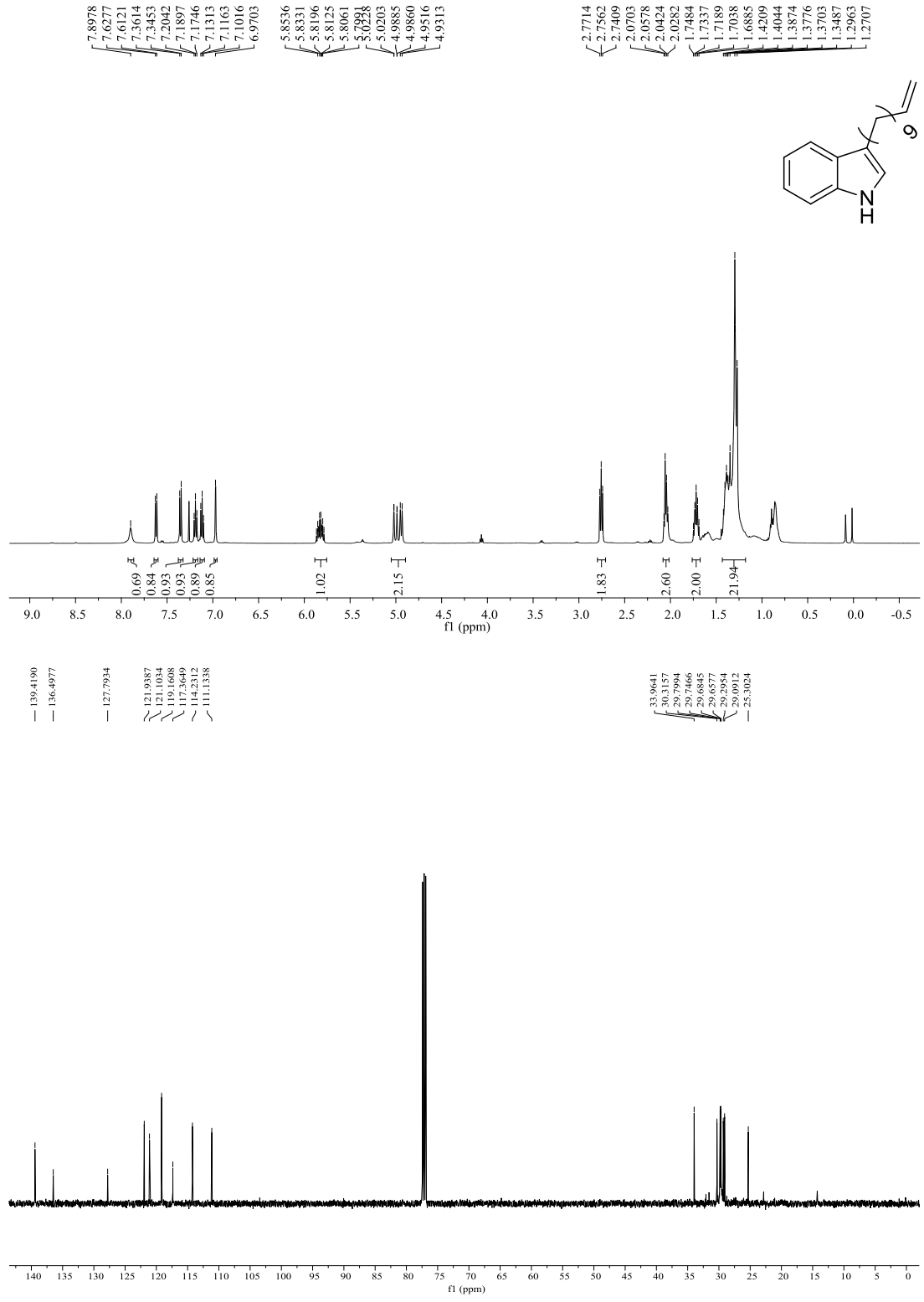
3-isopropyl-1*H*-indole (4h)



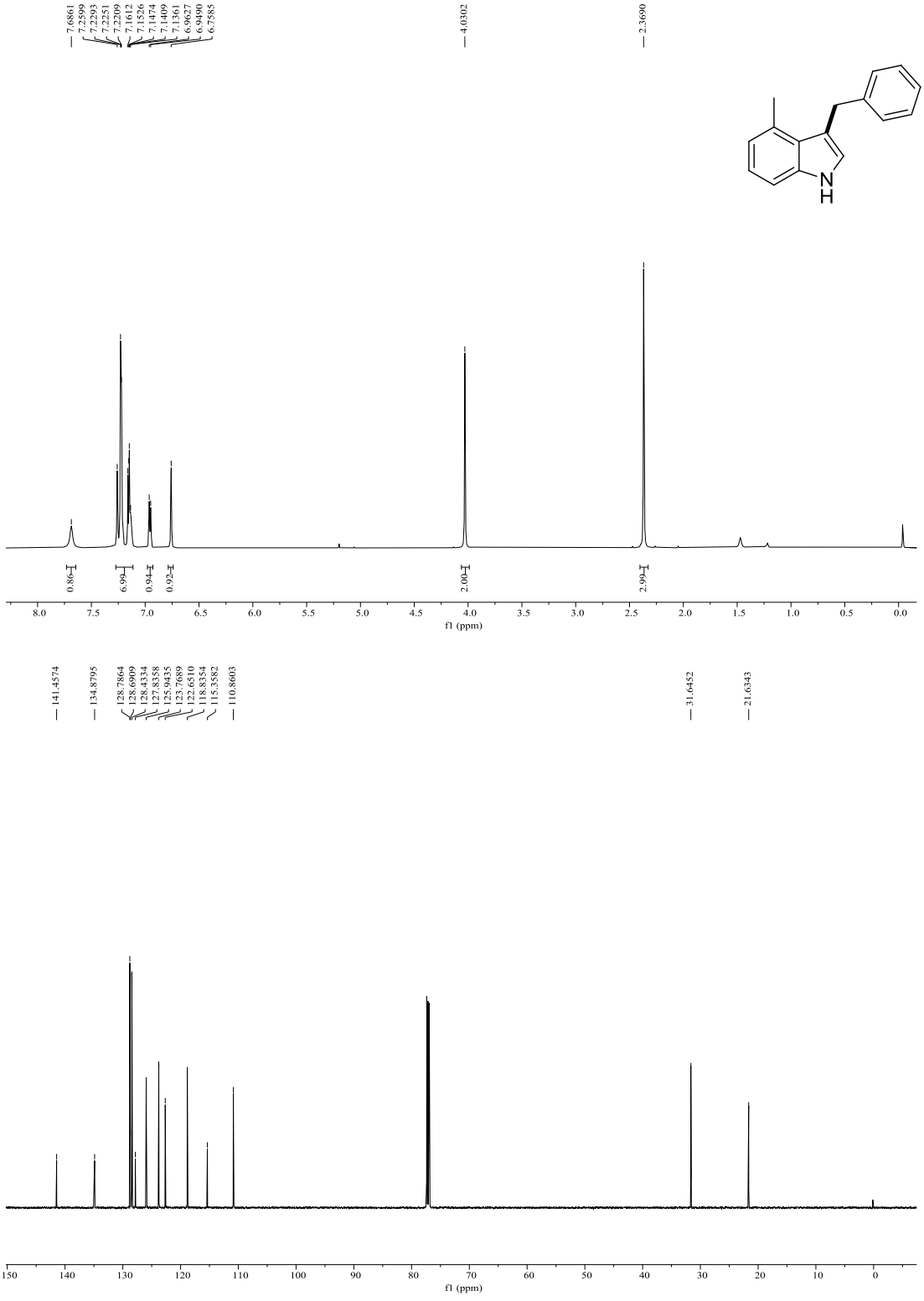
3-(1-methylheptyl)-1*H*-indole (4i)



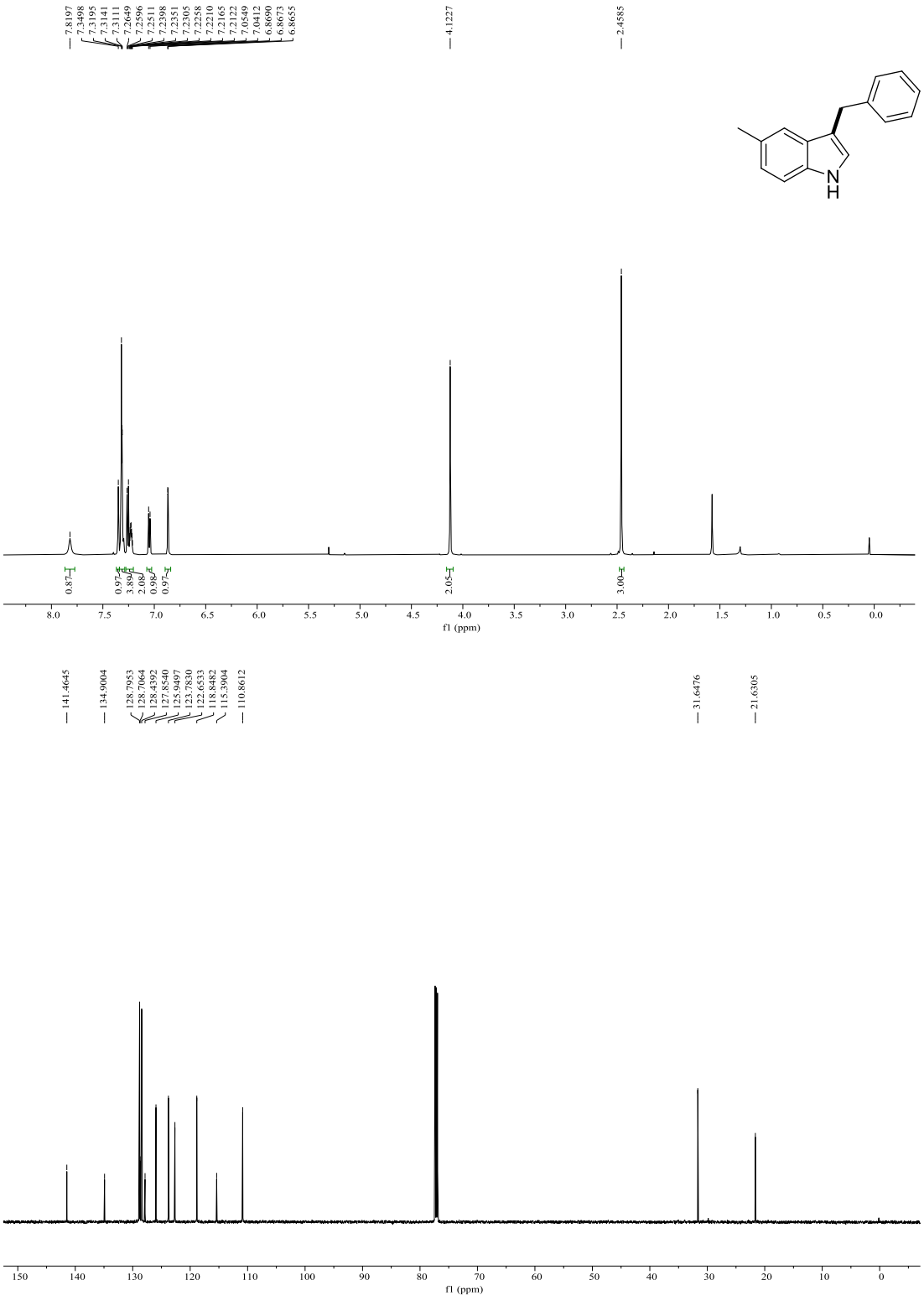
3-(undec-10-en-1-yl)-1*H*-indole (4j)



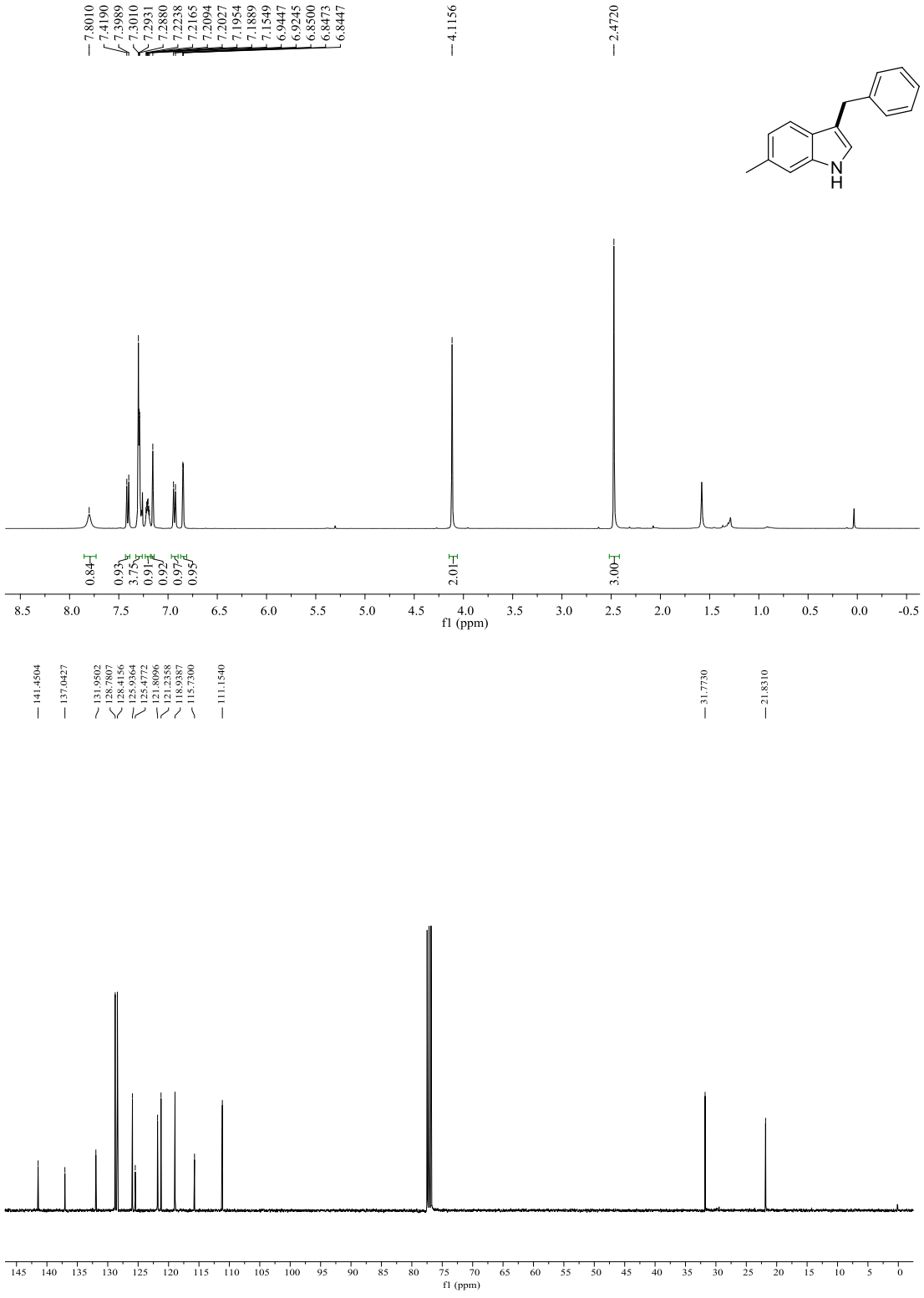
3-benzyl-4-methyl-1*H*-indole (5a)



3-benzyl-5-methyl-1*H*-indole (5b)



3- benzyl-6-methyl-1*H*-indole (5c)



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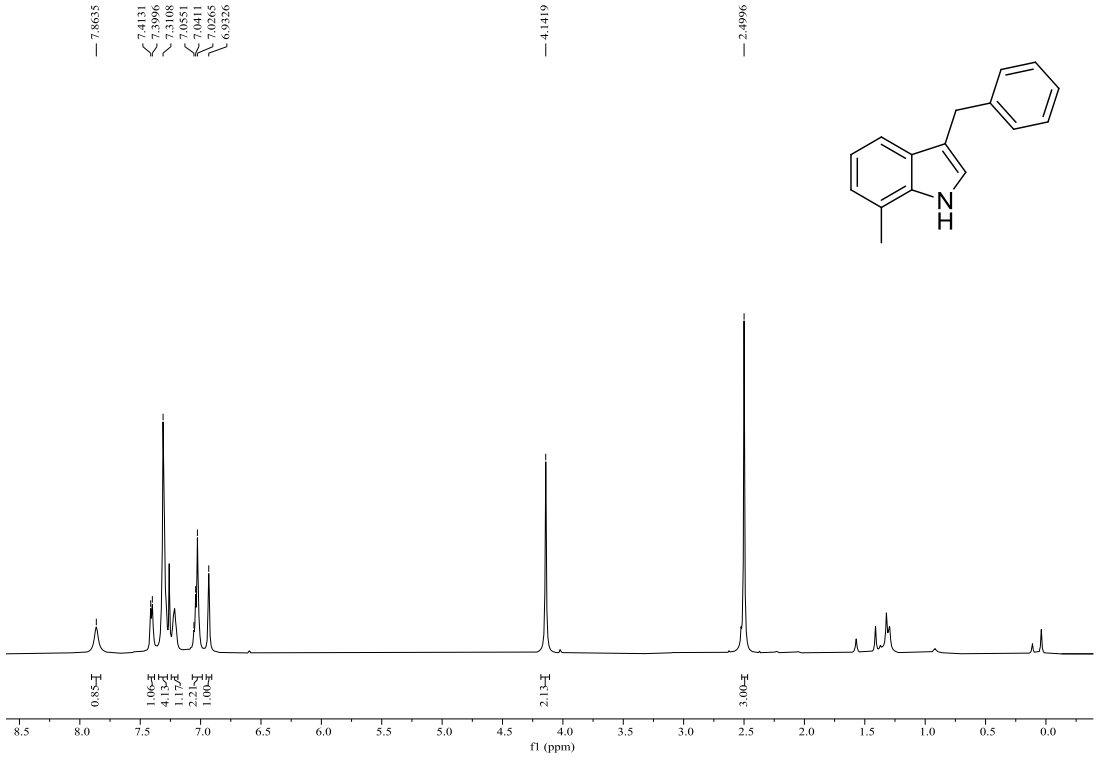

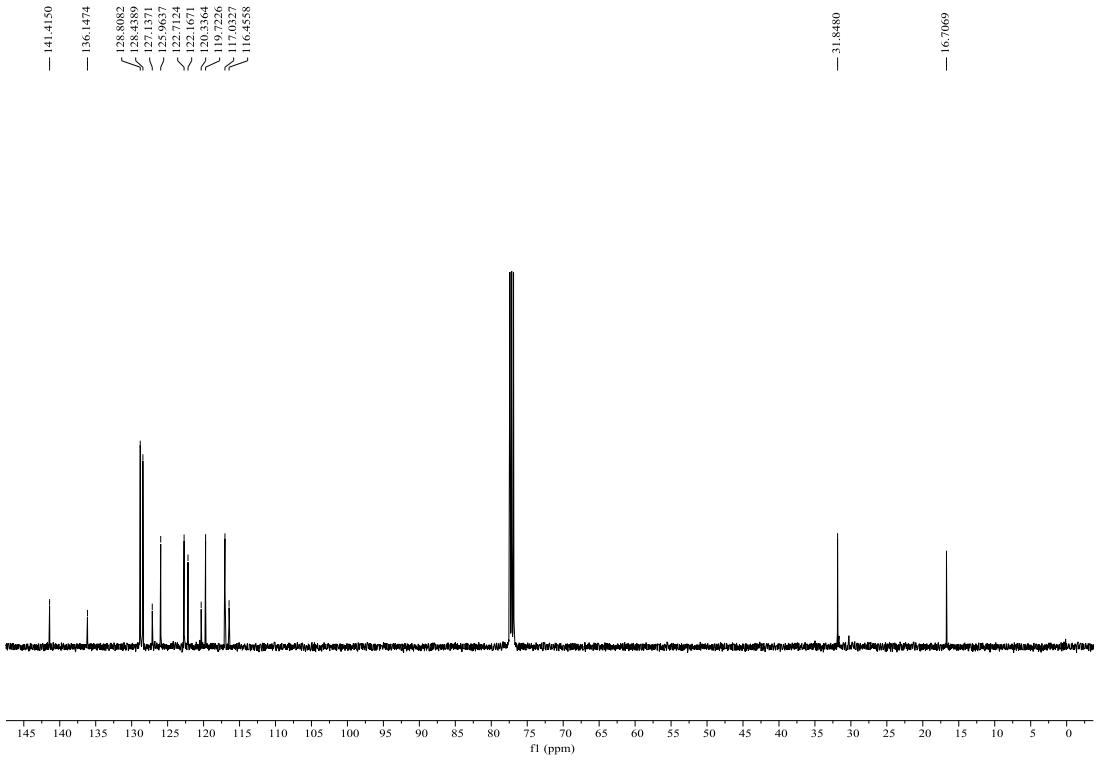

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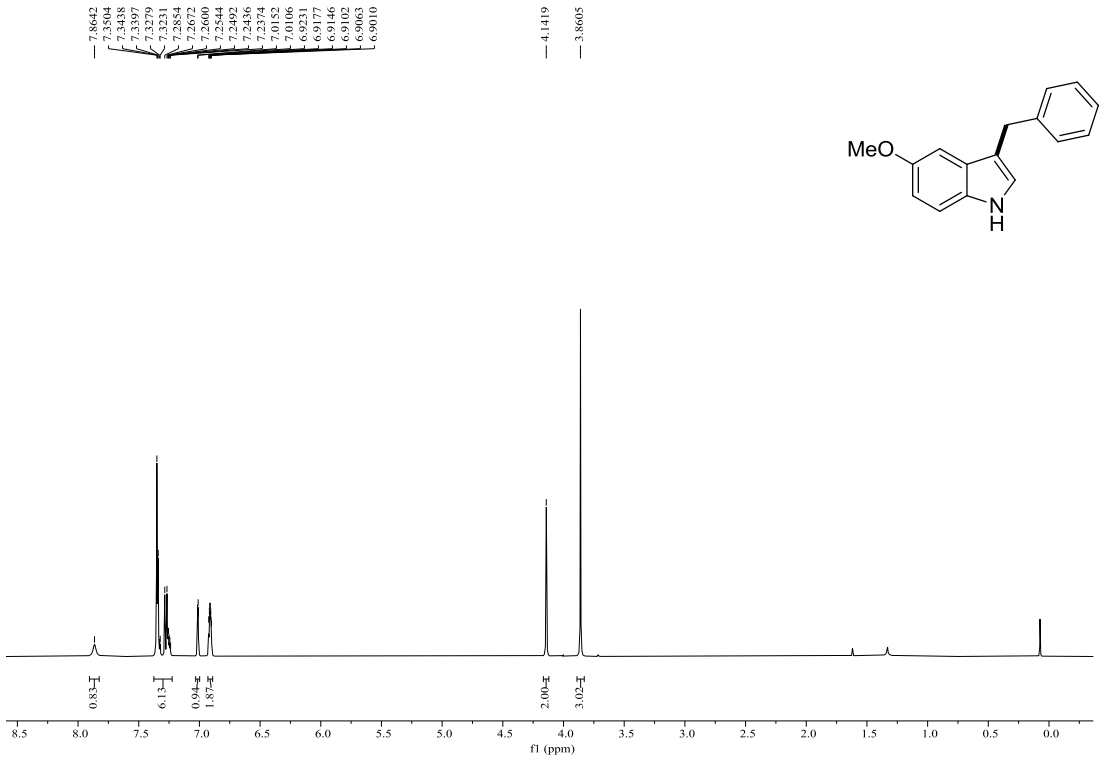
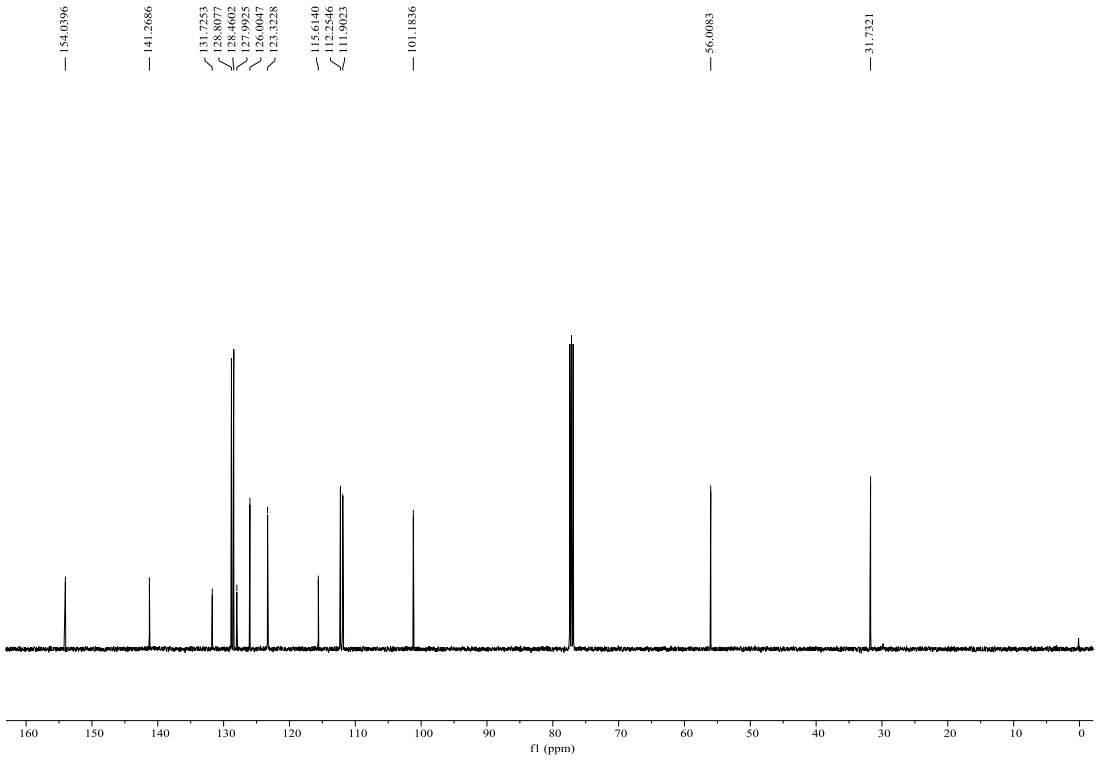
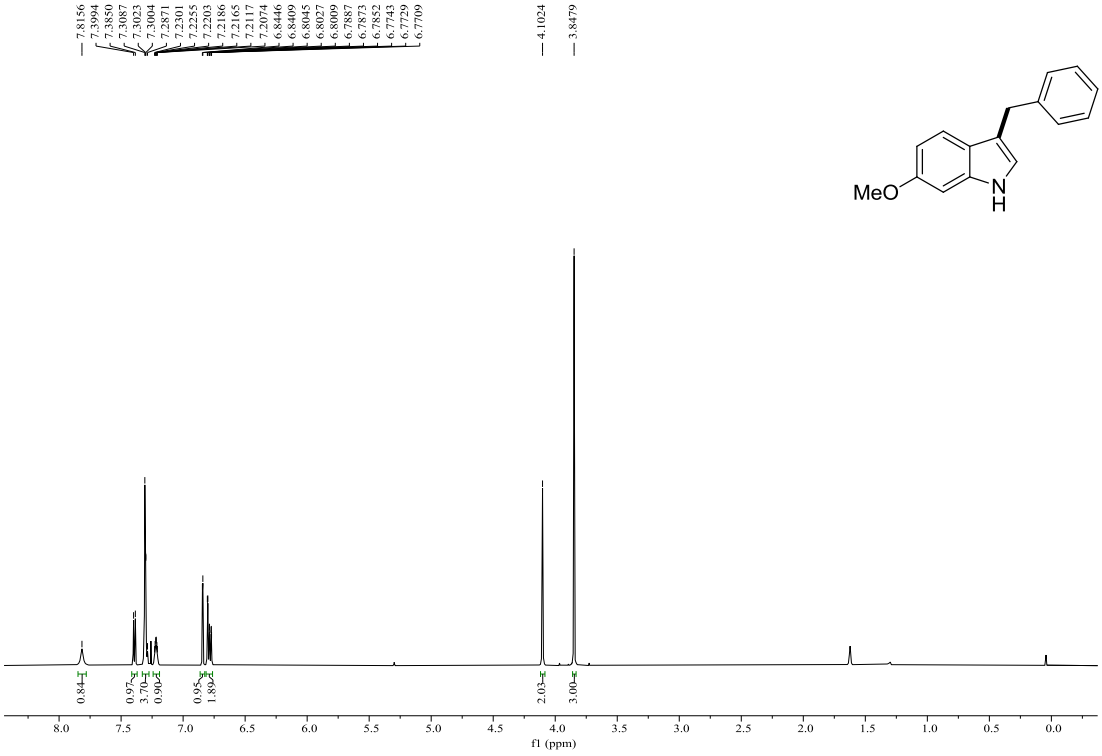
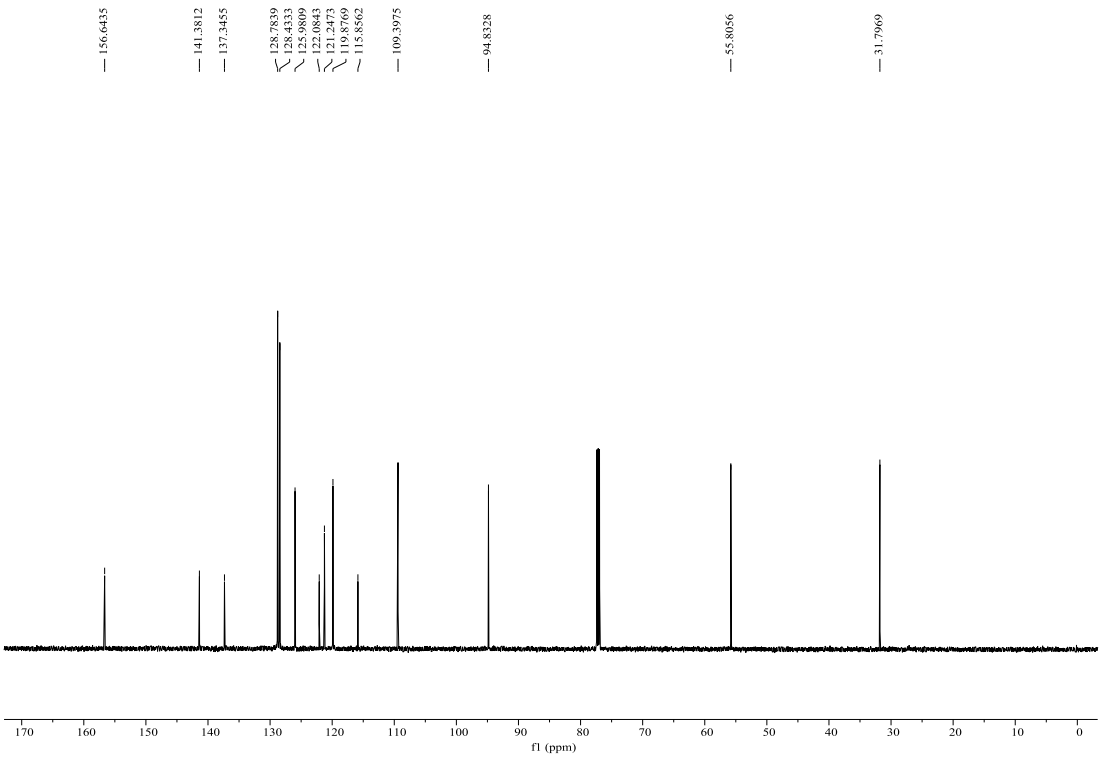




3-benzyl-6-methoxy-1*H*-indole (5f)





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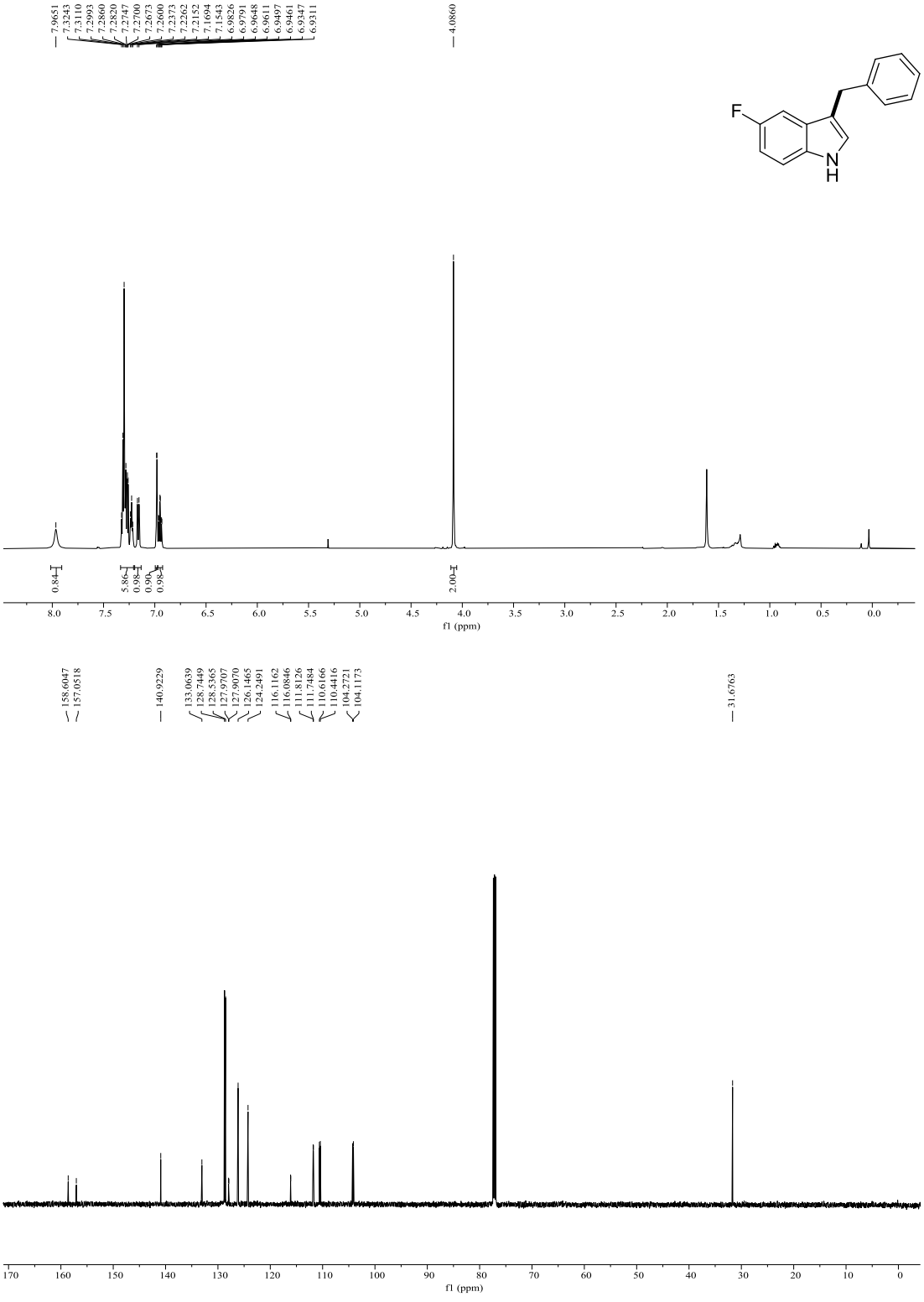
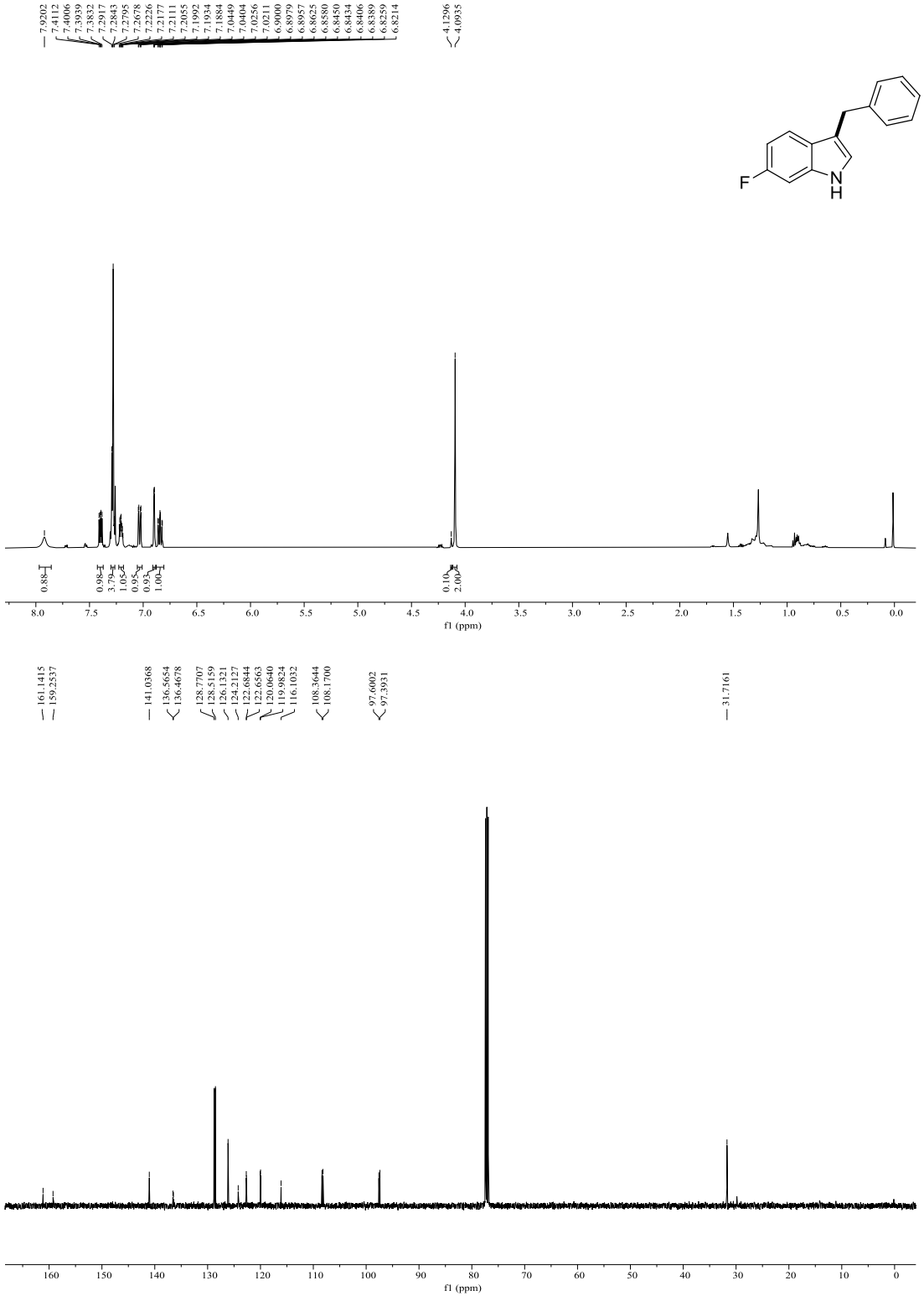
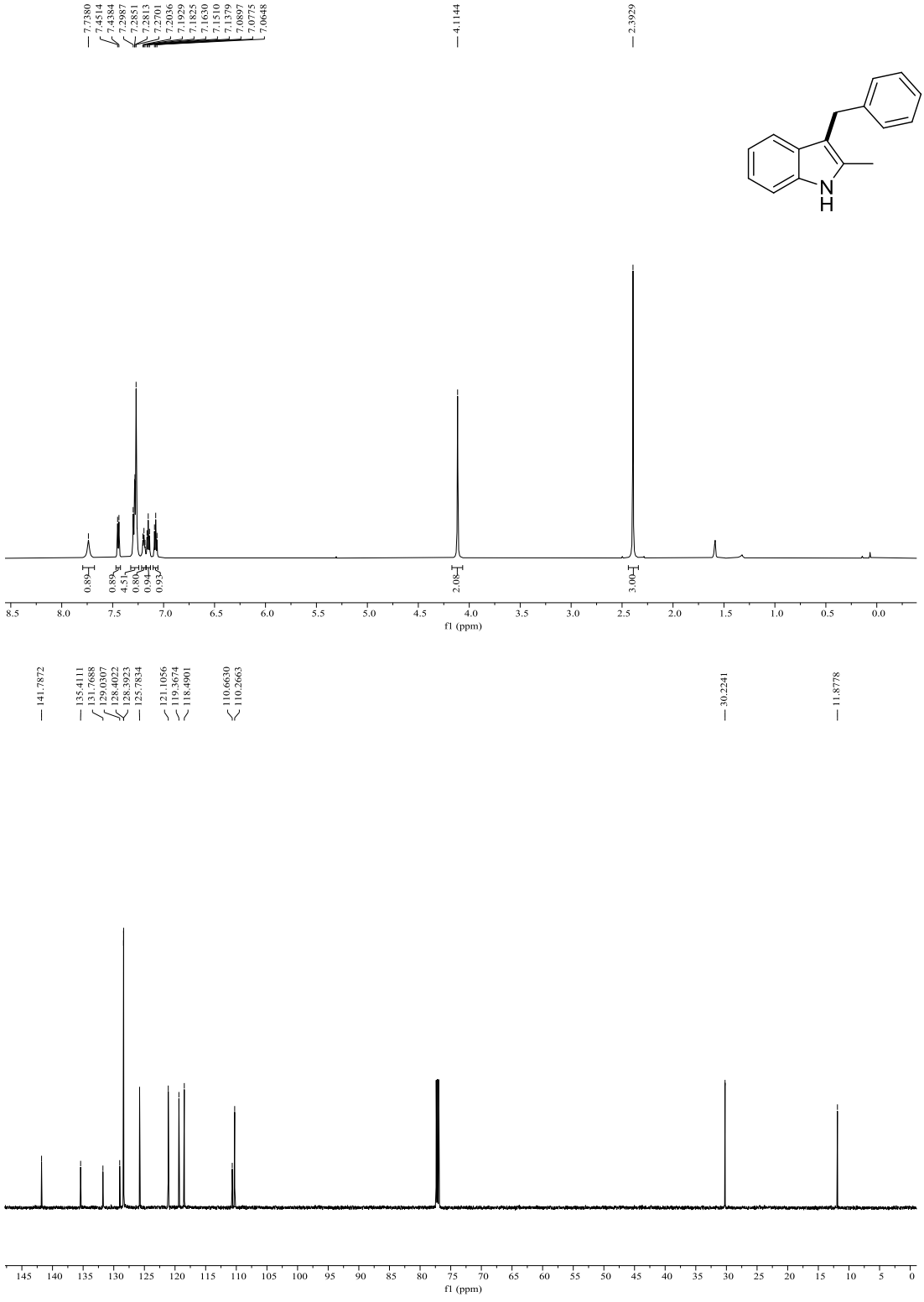


3-benzyl-6-fluoro-1*H*-indole (5h)



3-benzyl-2-methyl-1*H*-indole (5i)



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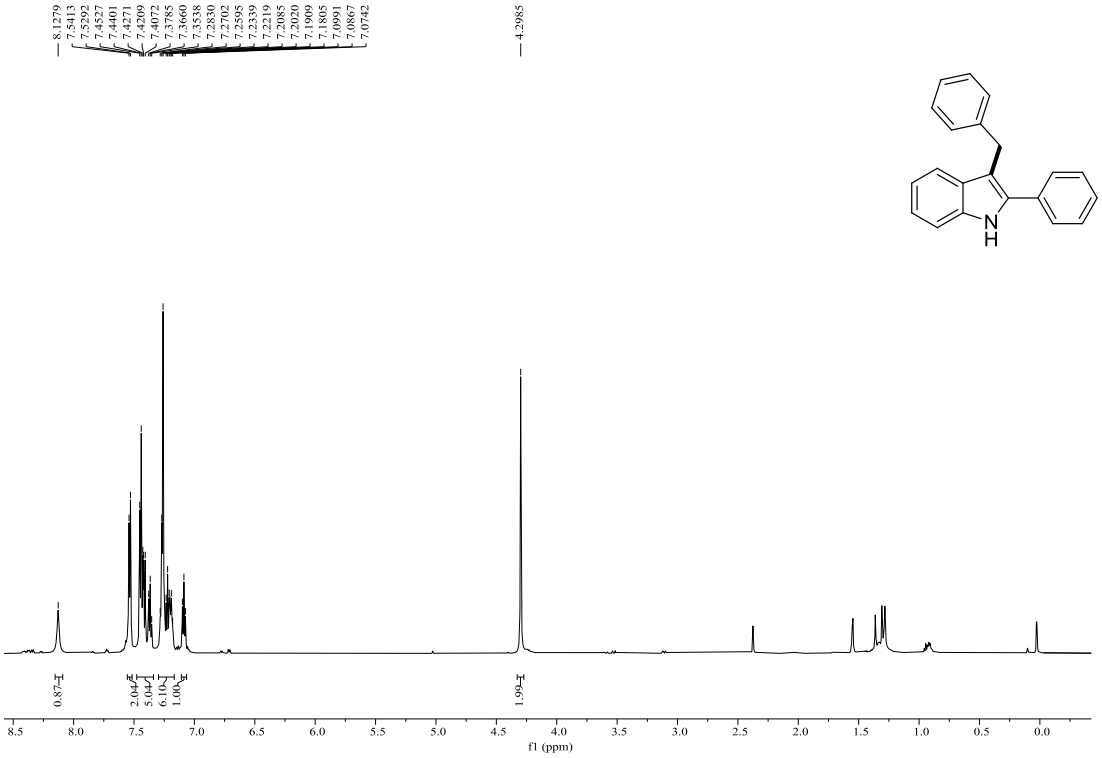

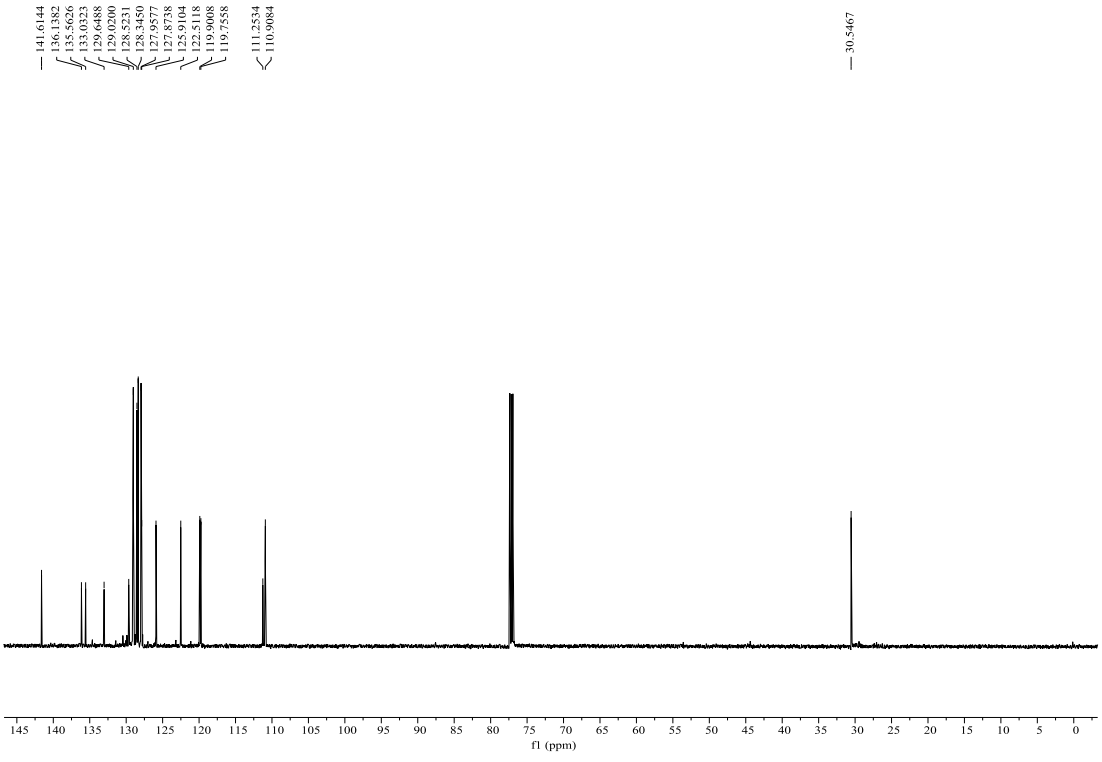

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