Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Iridium-catalyzed methylation of indoles and pyrroles using methanol as feedstock

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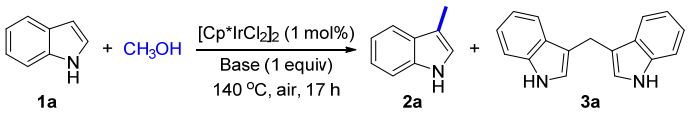
1. General information

All solvents and reagents were used as commercially supplied without further purification unless otherwise stated. Petrol refers to petroleum ether in the boiling range 60-90 °C. ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR spectra were recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz, 470 MHz, and 125 MHz in $CDCl_3$, respectively, and chemical shifts were reported in ppm relative to the center of the singlet at 7.26 ppm for $CDCl_3$ or downfield from internal tetramethylsilane. GC/MS were performed on an ISQ Trace 1300 (electrospray ionization: EI). GC analysis were performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: N_2, FID detector. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. Melting points (mp) were obtained using an X-6 micro-melting apparatus and were uncorrected. Preparative high performance liquid chromatography was performed on the column XDB-C18 (9.6 mm × 250 mm) with methanol/water as eluent.

2. Base screening

Table S1. Base screening. [a]



Entry	Base (equiv)	Conversion (%)[b]	Product (%)[b]	
			2a	**3a**
1	LiO*t*Bu (1)	100	90	2
2	NaO*t*Bu (1)	79	74	0
3	LiOH (1)	100	85	4
4	NaOH (1)	100	81	12
5	KOH (1)	100	86	1
6	Na_2CO_3 (1)	80	74	4
7	K_2CO_3 (1)	100	80	5
8	Cs_2CO_3 (1)	100	89	0

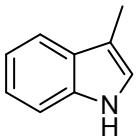
[a] Indole **1a** (0.3 mmol), $[Cp^*IrCl_2]_2$ (1 mol%), methanol (1 mL), base (1 euqiv), 140 °C for 17 h in air. [b] Determined by GC analysis.

3. General Procedure for the Methylation of Indoles and Pyrroles with Methanol Catalyzed by $[Cp^*IrCl_2]_2$

Under an open-air atmosphere, a resealable pressure tube (35 mL) was added starting indoles/pyrroles (**1**, 0.3 mmol), $[Cp^*IrCl_2]_2$ (0.003 mmol, 1 mol%), KOtBu (0.3 mmol, 1 equiv), and methanol (1 mL). The tube was sealed with a PFTE septa screw-cap and stirred at 140 °C in an oil bath for 17 h unless otherwise stated. After cooled to ambient temperature, the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography on silica gel with petrol/ethyl acetate to afford the corresponding products.

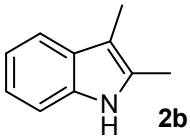
Note: The pressure tubes were purchased from Beijing Synthware Glass, Inc. (P.R. China). Tube O.D. × length was 26 mm×125 mm. During the reaction, the pressure tube was inserted into an oil bath at about 10 mm depth, with the solution in the pressure tube at the same level of the oil bath, to ensure the condensation of methanol. Under the present conditions, all experiments were performed safely.

Analytical data for the products.



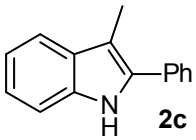
2a

3-Methyl-1*H*-indole (**2a**).[1] White crystal; 80% yield; mp 92-93 °C (lit.[1] mp 91-92 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.22 (dd, *J* = 11.0, 3.9 Hz, 1H), 6.99 (s, 1H), 2.42 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.41, 128.43, 122.02, 121.76, 119.27, 118.99, 111.83, 111.12, 9.82.



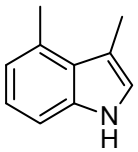
2b

2,3-Dimethyl-1*H*-indole (**2b**).[2] Brown solid; 82% yield; 103-105 °C (lit.[9] mp 107-109 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.55 (d, *J* = 6.9 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.17 (dq, *J* = 7.1, 6.1 Hz, 2H), 2.38 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.32, 130.82, 129.56, 121.02, 119.14, 118.08, 110.20, 107.20, 11.63, 8.60.



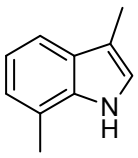
2c

3-Methyl-2-phenyl-1*H*-indole (**2c**).[2] White solid (decompose rapidly in $CDCl_3$); 91% yield; mp 91-92 °C (lit.[10] mp 92-93 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.62 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.52 (dd, *J* = 10.7, 4.9 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.30 – 7.25 (m, 1H), 7.24 – 7.20 (m, 1H), 2.53 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.99, 134.19, 133.49, 130.17, 128.93, 127.89, 127.42, 122.42, 119.64, 119.11, 110.85, 108.79, 9.81.



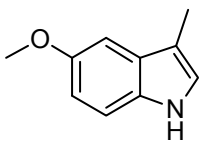
2d

3,4-Dimethyl-1*H*-indole (**2d**).[5] White solid; 84% yield; mp 113-115 °C (lit.[11] mp 114-116 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 0.8 Hz, 1H), 6.87 (d, *J* = 7.1 Hz, 1H), 2.78 (s, 3H), 2.56 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.96, 131.43, 126.73, 122.15, 121.95, 120.69, 112.72, 109.12, 20.15, 13.19.



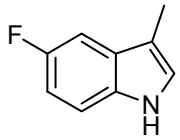
2e

3,7-Dimethyl-1*H*-indole (**2e**). White solid; 85% yield; mp 57-59 °C (lit.[12] mp 55-56 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.05 – 6.97 (m, 2H), 2.51 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.96, 127.94, 122.51, 121.37, 120.18, 119.46, 116.67, 112.37, 16.67, 9.91. GCMS (EI) m/z: 145 (M^+); Anal. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.88; H, 7.41; N, 9.33.



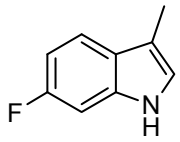
2f

5-Methoxy-3-methyl-1*H*-indole (**2f**).[3] White solid; 83% yield; mp 64-65 °C (lit.[13] mp 64-66 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.25 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.97 (s, 1H), 6.87 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.90 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.01, 131.53, 128.75, 122.53, 112.18, 111.74, 111.58, 100.81, 56.05, 9.81.



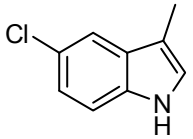
2g

5-Fluoro-3-methyl-1*H*-indole (**2g**).[1] Brown solid; 74% yield; mp 79-80 °C (lit.[1] mp 82-83 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.27 – 7.25 (m, 1H), 7.23 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.03 (s, 1H), 6.95 (td, *J* = 9.0, 2.5 Hz, 1H), 2.31 (d, *J* = 0.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.76, 156.77, 132.84, 128.83, 128.76, 123.49, 112.02, 111.59, 111.52, 110.38, 110.17, 103.91, 103.73, 9.70. ^{19}F NMR (470 MHz, $CDCl_3$) δ -125.24.



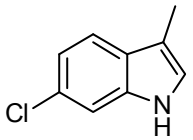
2h

6-Fluoro-3-methyl-1*H*-indole (**2h**).[1] White solid; 82% yield; mp 100-101 °C (lit.[1] mp 100-101 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.49 (dd, *J* = 8.6, 5.4 Hz, 1H), 7.04 (dd, *J* = 9.7, 2.2 Hz, 1H), 6.96 (s, 1H), 6.91 (td, *J* = 9.6, 2.2 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.10, 159.22, 136.29, 136.19, 125.05, 121.86, 119.65, 119.57, 111.96, 108.03, 107.83, 97.42, 97.21, 9.72. ^{19}F NMR (470 MHz, $CDCl_3$) δ -121.75.



2i

5-Chloro-3-methyl-1*H*-indole (**2i**).[1] White solid; 88% yield; mp 111-113 °C (lit.[1] mp 112-113 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.57 (d, *J* = 1.8 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.16 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.01 (s, 1H), 2.32 (d, *J* = 0.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.69, 129.55, 125.00, 123.09, 122.23, 118.52, 112.01, 111.68, 9.63.

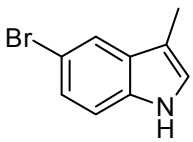


2j

6-Chloro-3-methyl-1*H*-indole (**2j**).[1] White solid; 83% yield; mp 115-116 °C (lit.[1] mp 118-119 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 1.5 Hz, 1H), 7.09 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.95 (dd, *J* = 2.0, 0.9 Hz, 1H), 2.31 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.67, 127.93, 127.05, 122.32, 119.94, 119.82, 112.03, 110.96, 9.67.

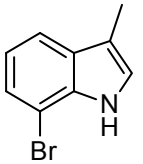
2k

4-Bromo-3-methyl-1*H*-indole (**2k**).[4] Brown solid; 84% yield; mp 79-80 °C (lit.[4] mp 80-82 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.28 – 7.24 (m, 2H), 7.03 – 6.95 (m, 2H), 2.57 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.71, 126.33, 123.65, 123.51, 122.86, 114.93, 113.15, 110.52, 12.65.



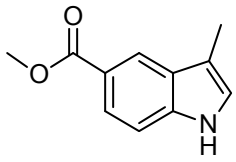
2l

5-Bromo-3-methyl-1*H*-indole (**2l**).[5] Brown solid; 82% yield; mp 73-75 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.73 (d, *J* = 1.6 Hz, 1H), 7.29 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 1H), 6.99 (s, 1H), 2.32 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.96, 130.22, 124.76, 122.95, 121.64, 112.50, 111.60, 9.64.



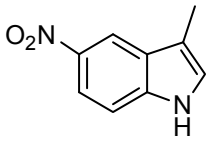
2m

7-Bromo-3-methyl-1*H*-indole (**2m**).[6] Yellow liquid; 85% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.08 – 6.97 (m, 2H), 2.35 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.07, 129.64, 124.31, 122.33, 120.42, 118.23, 113.13, 104.75, 9.97.



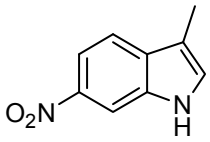
2n

Methyl 3-methyl-1*H*-indole-5-carboxylate (**2n**).[7] Yellow solid; 80% yield; mp 145-147 °C (lit.[7] mp 142-144 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.17 (s, 1H), 7.92 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.04 (s, 1H), 3.96 (d, *J* = 3.9 Hz, 3H), 2.38 (d, *J* = 0.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.45, 138.97, 128.08, 123.41, 122.89, 122.08, 121.31, 113.41, 110.69, 51.93, 9.67.



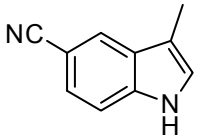
2o

3-Methyl-5-nitro-1*H*-indole (**2o**). Yellow solid; 82% yield; mp 130-131 °C (lit.[14] mp 128 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.9 Hz, 1H), 8.52 (s, 1H), 8.11 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 7.14 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.53, 139.34, 127.91, 124.72, 117.69, 116.45, 114.53, 110.96, 9.58. GCMS (EI) m/z: 176 (M^+); Anal. Calcd for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.66; H, 4.75; N, 15.76.



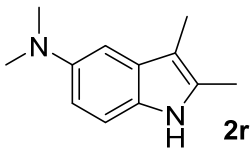
2p

3-Methyl-6-nitro-1*H*-indole (**2p**). Yellow solid; 77% yield; mp 149-150 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.35 (d, *J* = 1.9 Hz, 1H), 8.04 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.30 (d, *J* = 1.1 Hz, 1H), 2.38 (d, *J* = 0.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.36, 134.71, 133.06, 127.82, 118.86, 114.83, 112.99, 108.07, 9.58. GCMS (EI) m/z: 176 (M^+); Anal. Calcd for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.69; H, 4.83; N, 15.67.



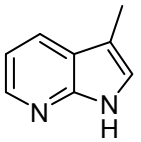
2q

3-Methyl-1*H*-indole-5-carbonitrile (**2q**). Gray solid; 87% yield; mp 110-111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.94 (s, 1H), 7.45 – 7.37 (m, 2H), 7.11 (s, 1H), 2.35 (d, *J* = 0.8 Hz, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ 138.02, 128.29, 124.88, 124.73, 123.86, 121.10, 112.79, 111.93, 102.16, 9.52. GCMS (EI) m/z: 156 (M^+); Anal. Calcd for $C_{10}H_8N_2$: C, 76.90; H, 5.16; N, 17.94. Found: C, 77.07; H, 4.94; N,18.05.



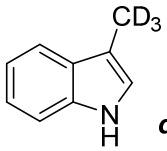
2r

N,*N*,2,3-Tetramethyl-1*H*-indol-5-amine (**2r**). Yellowish solid; 34% yield; mp 109-111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.19 (s, 1H), 8.55 (d, *J* = 9.2 Hz, 1H), 7.14 (s, 1H), 6.99 (dd, *J* = 9.2, 2.8 Hz, 1H), 2.96 (s, 6H), 2.65 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.15, 168.92, 146.10, 131.48, 123.14, 122.29, 119.86, 114.57, 41.04, 28.71, 25.44. GCMS (EI) m/z: 188 (M^+); Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.79; H, 8.40; N, 15.19.



2s

3-Methyl-1*H*-pyrrolo[2,3-*b*]pyridine (**2s**).[1] White solid; 62% yield; mp 131-132 °C (lit.[1] mp 130-131 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.27 (s, 1H), 8.31 (d, *J* = 4.3 Hz, 1H), 7.90 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.11 (s, 1H), 7.07 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.14, 142.60, 127.26, 122.38, 121.05, 115.22, 110.11, 9.87.



***d*$_3$-skatole**

***d*$_3$-skatole**.[8] White solid; 84% yield; mp 92-93 °C (lit.[8] mp 92-94 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.18 – 7.12 (m, 1H), 6.97 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.41, 128.45, 121.98, 121.70, 119.23, 118.96, 111.72, 111.06, 8.99(m, *J* = 18.8 Hz, 1C).

References

[1] Jensen, T.; Pedersen, H.; Bang-Andersen, B.; Madsen, R.; Jorgensen, M., *Angew. Chem., Int. Ed.* 2008, **47**, 888-890.

[2] Liu, K. G.; Robichaud, A. J.; Lo, J. R.; Mattes, J. F.; Cai, Y., *Org. Lett.* 2006, **8**, 5769-5771.

[3] Okuro, K.; Gurnham, J.; Alper, H., *J. Org. Chem.* 2011, **76**, 4715-4720.

[4] Barluenga, J.; Fañanás, F. J.; Sanz, R.; Fernández, Y., *Chem.-Eur. J.* 2002, **8**, 2034 -2046.

[5] Cheng, H. G.; Lu, L. Q.; Wang, T.; Yang, Q. Q.; Liu, X. P.; Li, Y.; Deng, Q. H.; Chen, J. R.; Xiao, W. J., *Angew. Chem., Int. Ed.* 2013, **52**, 3250-3254.

[6] Ghosh, R.; Sarkar, A., *J. Org. Chem.* 2010, **75**, 8283-8286.

[7] Kotha, S.; Shah, V. R., *Eur. J. Org. Chem.* 2008, 1054-1064.

[8] Fischer, J.; Elsinghorst, P. W.; Wüst, M., *Journal of Labelled Compounds and Radiopharmaceuticals* 2011, **54**, 591-596.

[9] Yi, F. P.; Sun, H. Y.; Pan, X. H.; Xu, Y.; Li, J. Z., *Chinese Chemical Letters* 2009, **20**, 275-278.

[10] Xu, D.-Q.; Wu, J.; Luo, S.-P.; Zhang, J.-X.; Wu, J.-Y.; Du, X.-H.; Xu, Z.-Y., *Green Chemistry* 2009, **11**, 1239-1246.

[11] Plieninger, H., *Chemische Berichte* 1954, **87**, 228-231.

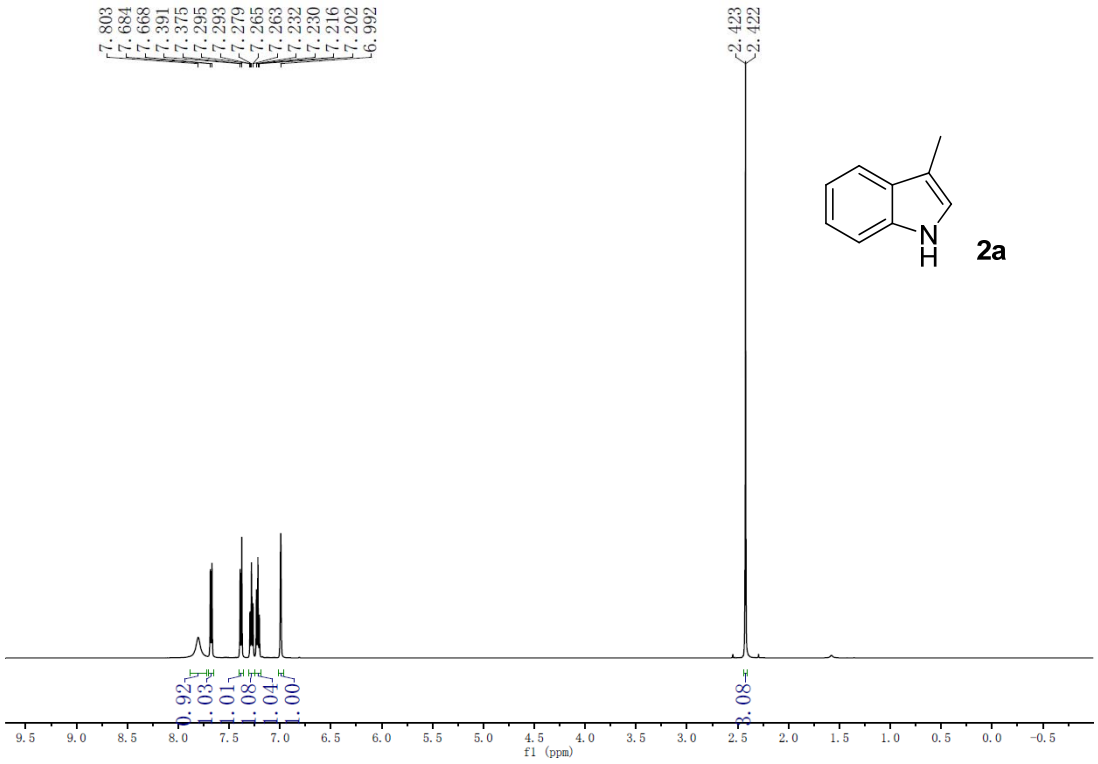
[12] Bosco, M.; Dalpozzo, R.; Bartoli, G.; Palmieri, G.; Petrini, M., *Journal of the Chemical Society, Perkin Transactions* 2 1991, 657-663.

[13] Kobayashi, K.; Shirai, Y.; Fukamachi, S.; Konishi, H., *Heterocycles* 2010, 81, 433-439.

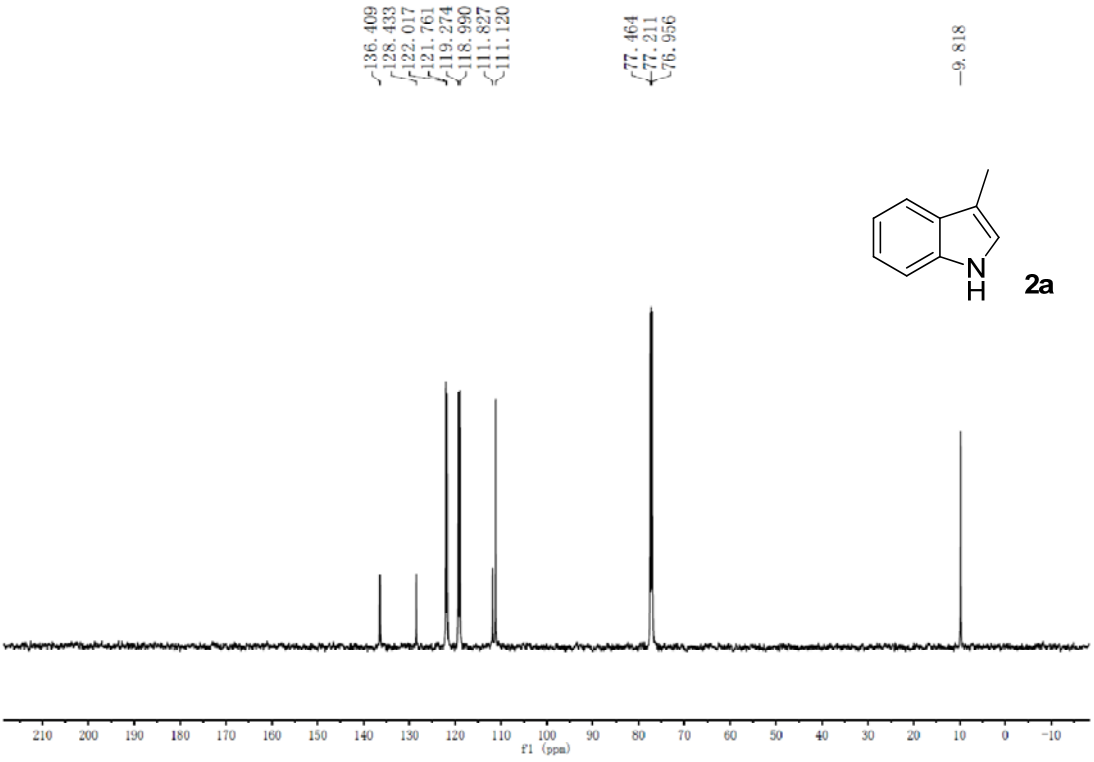
[14] Fadda, A. A.; *Indian Journal of Chemistry, Section B: Organic Chemistry Including Medicinal Chemistry* 1990, **29B**, 1017-1019.

Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra

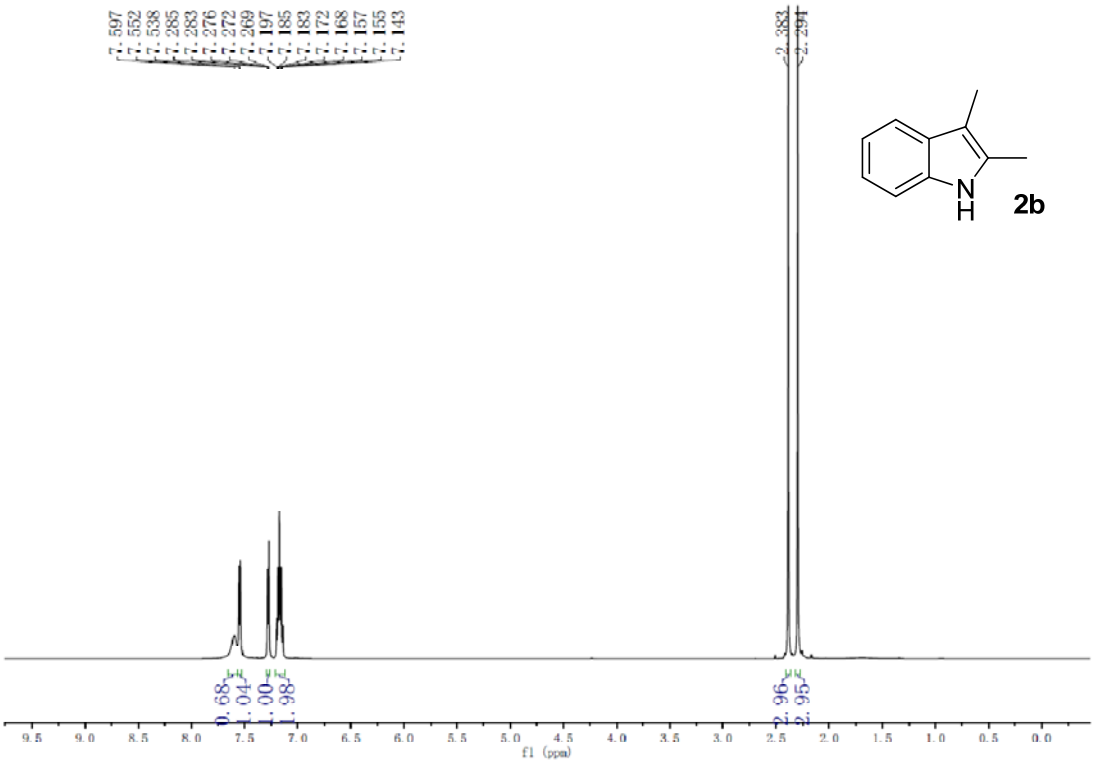
3-Methyl-1*H*-indole (**2a**, ^{1}H NMR, $CDCl_3$, 500 MHz)



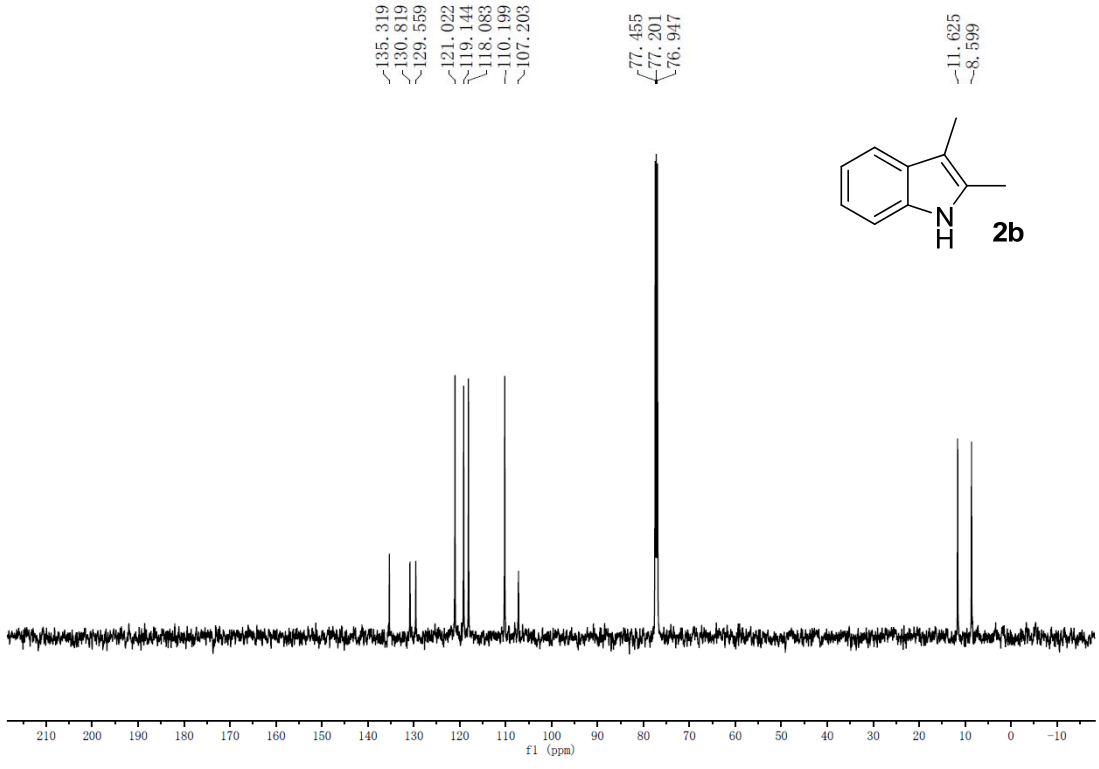
3-Methyl-1*H*-indole (**2a**, ^{13}C NMR, $CDCl_3$, 125 MHz)



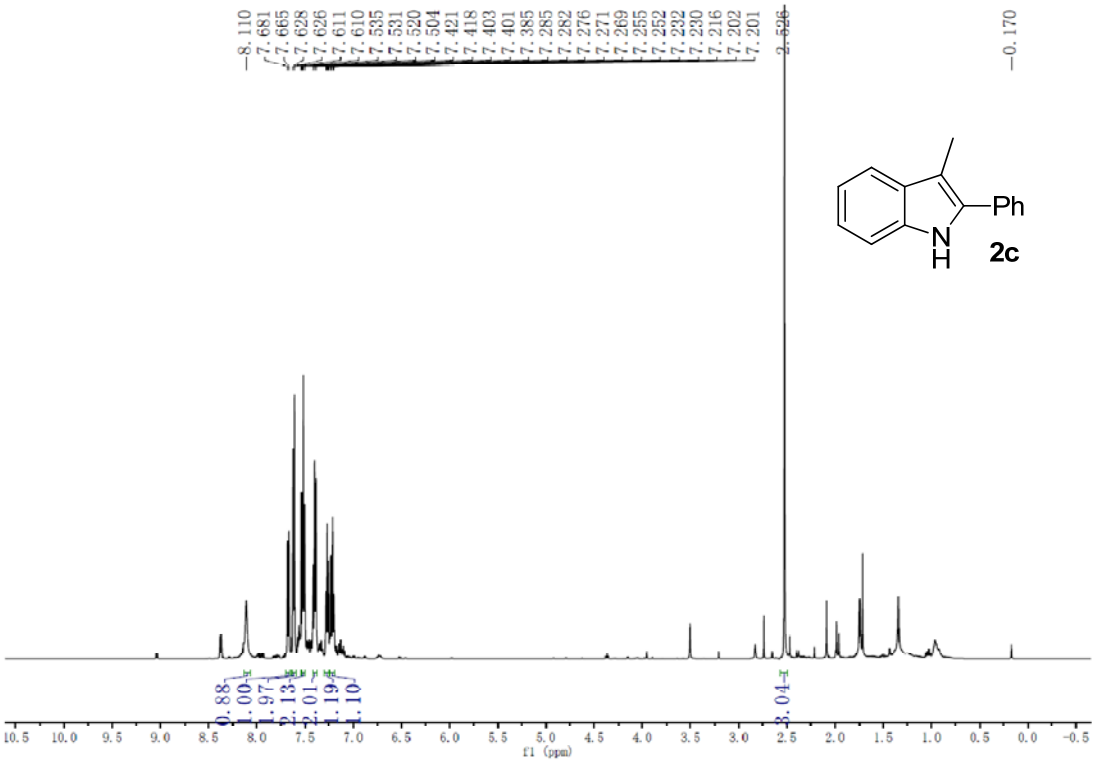
2,3-Dimethyl-1*H*-indole (**2b**, ^{1}H NMR, $CDCl_3$, 500 MHz)



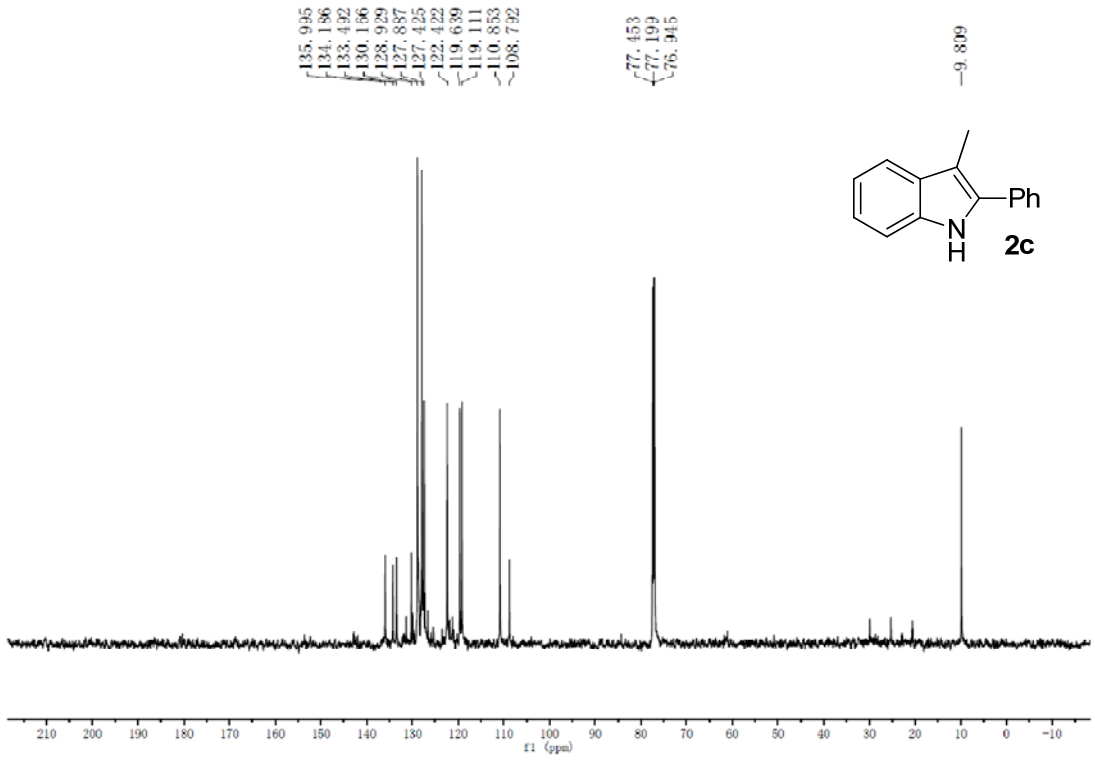
2,3-Dimethyl-1*H*-indole (**2b**, ^{13}C NMR, $CDCl_3$, 125 MHz)



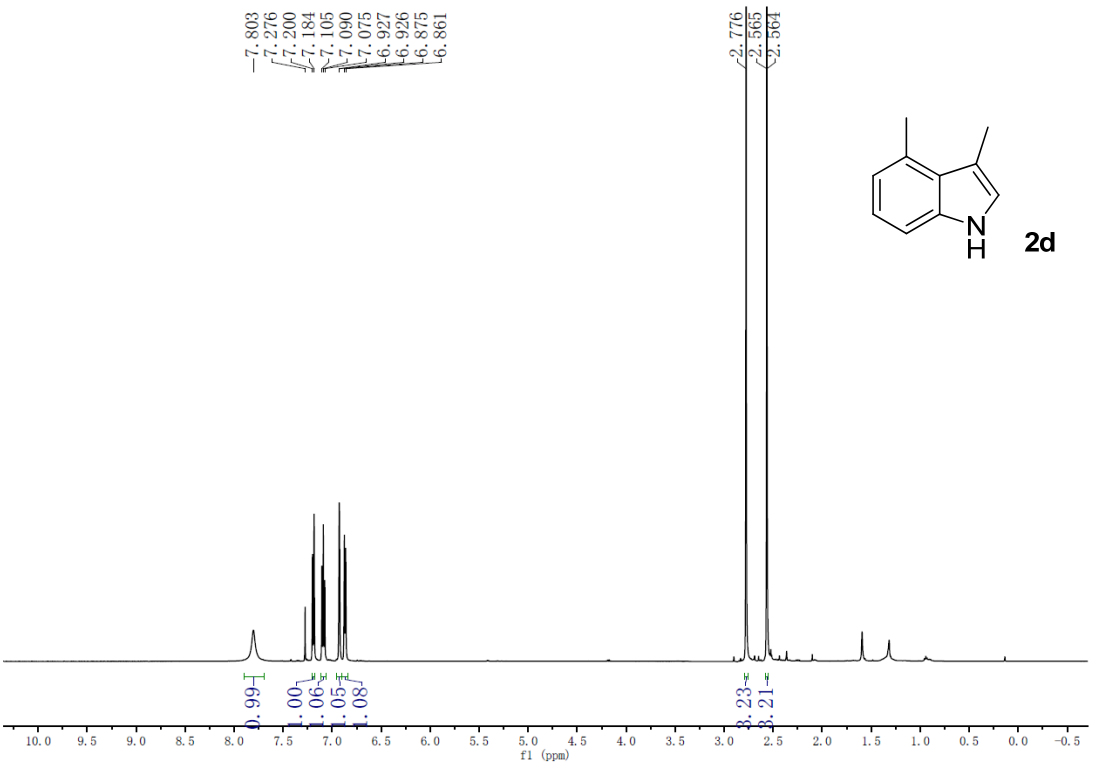
3-Methyl-2-phenyl-1*H*-indole (**2c**, ^{1}H NMR, $CDCl_3$, 500 MHz)



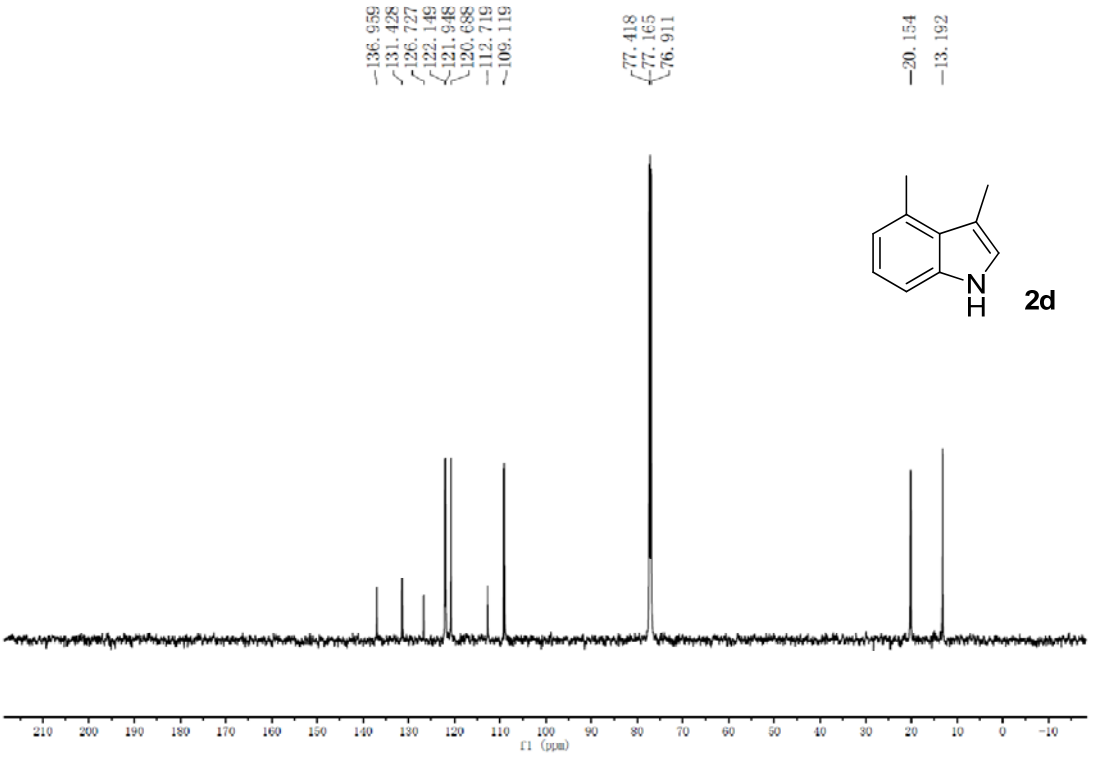
3-Methyl-2-phenyl-1*H*-indole (**2c**, ^{13}C NMR, $CDCl_3$, 125 MHz)



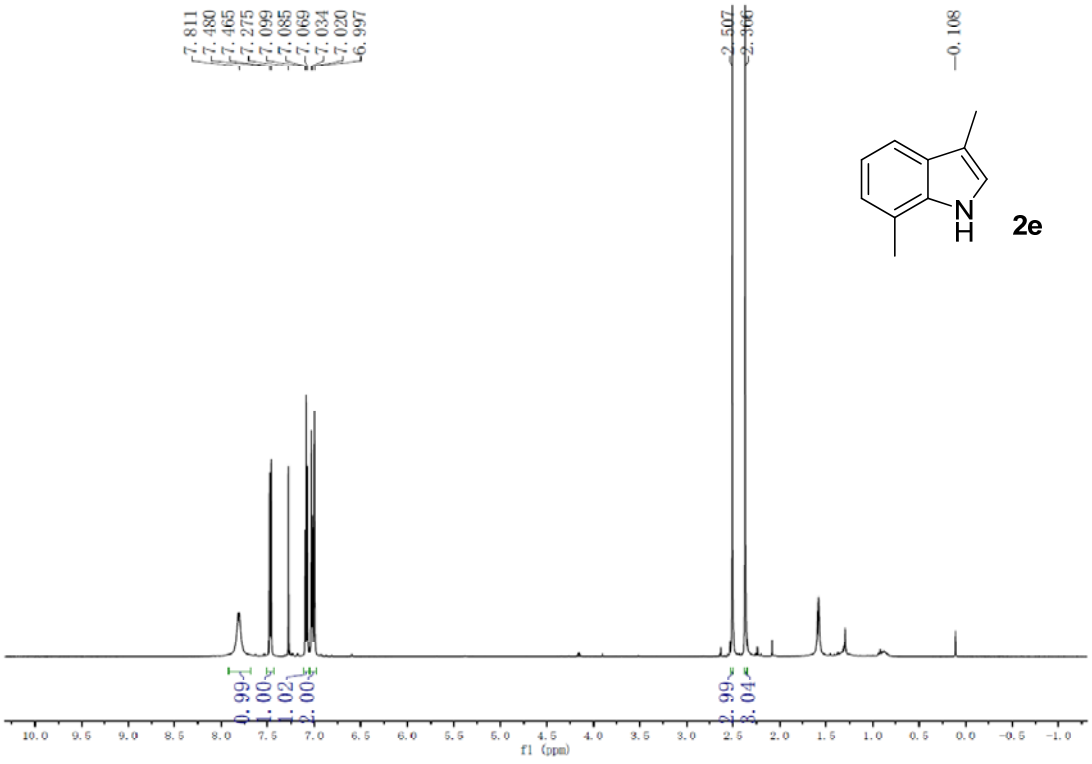
3,4-Dimethyl-1*H*-indole (**2d**, ^{1}H NMR, $CDCl_3$, 500 MHz)



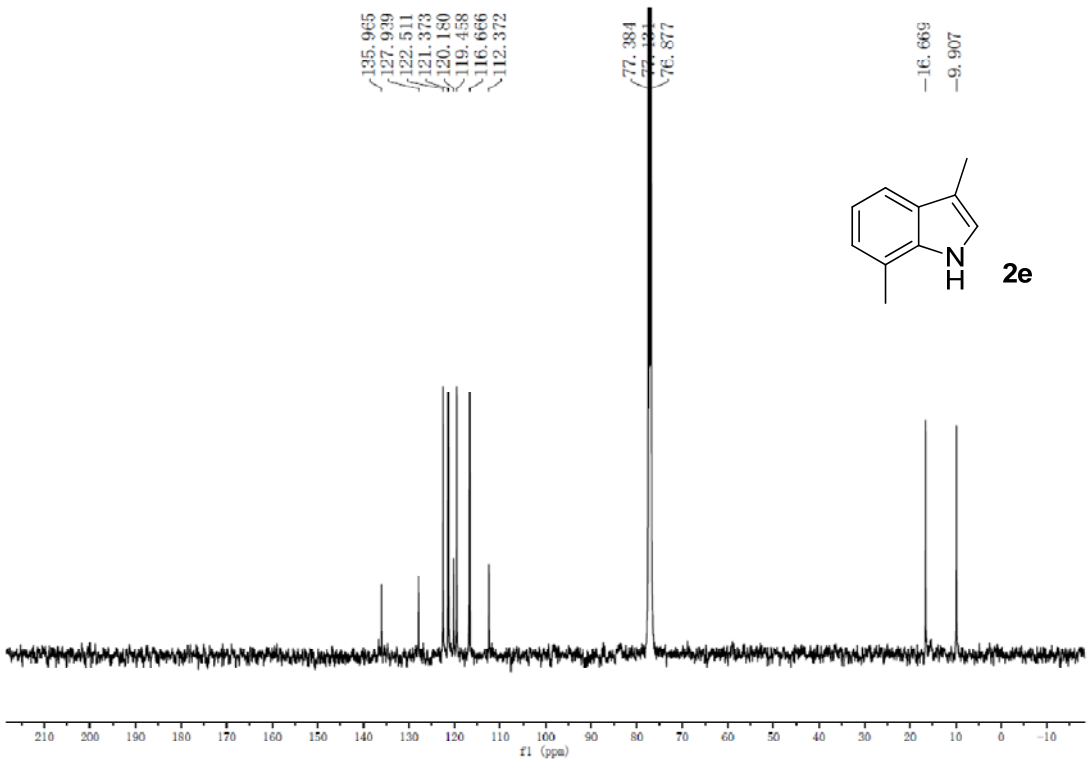
3,4-Dimethyl-1*H*-indole (**2d**, ^{13}C NMR, $CDCl_3$, 125 MHz)



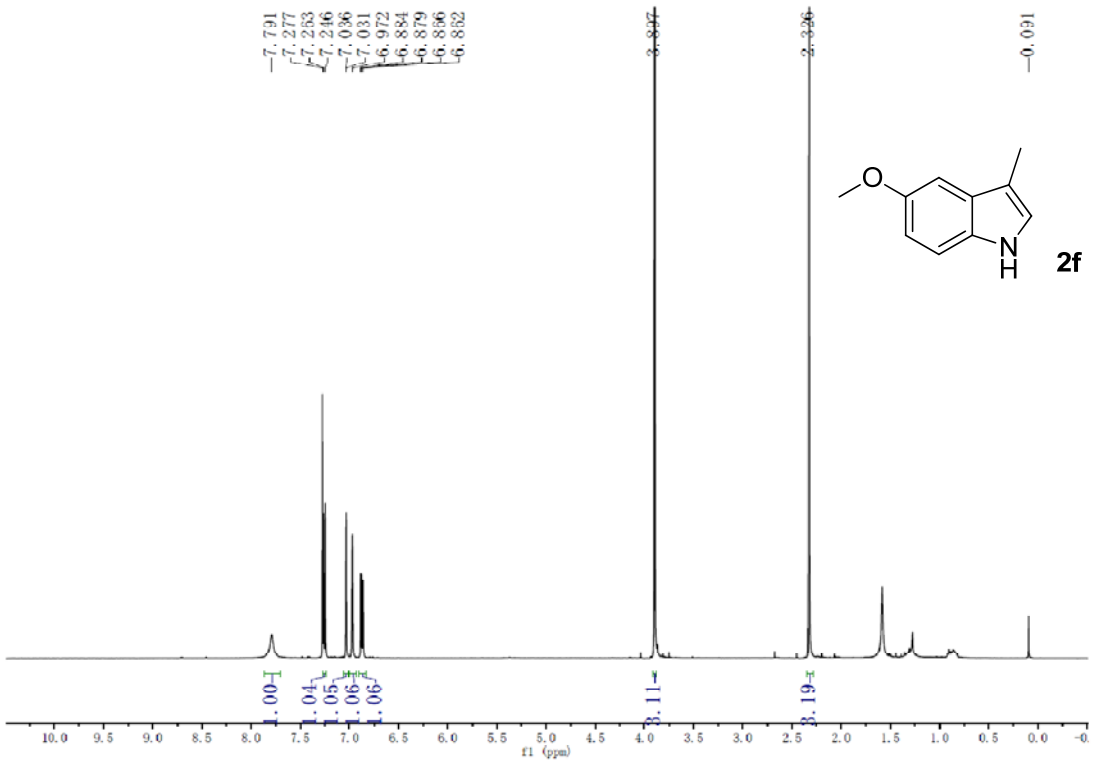
3,7-Dimethyl-1*H*-indole (**2e**, ^{1}H NMR, $CDCl_3$, 500 MHz)



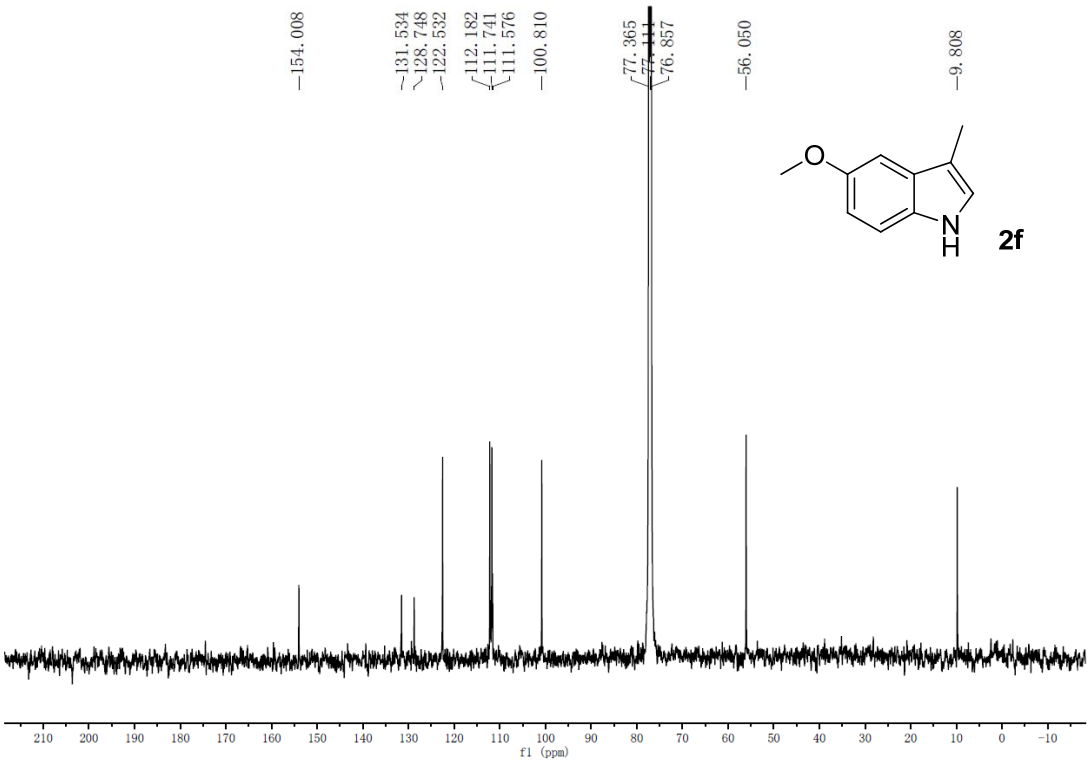
3,7-Dimethyl-1*H*-indole (**2e**, ^{13}C NMR, $CDCl_3$, 125 MHz)



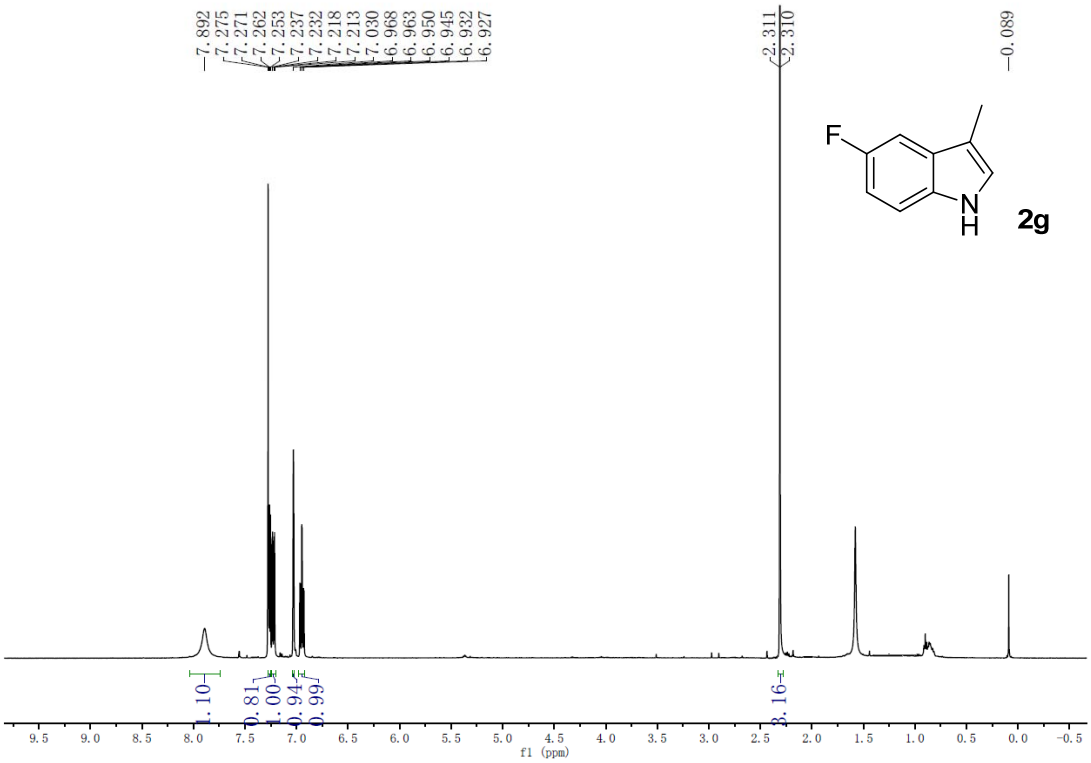
5-Methoxy-3-methyl-1*H*-indole (**2f**, ^{1}H NMR, $CDCl_3$, 500 MHz)



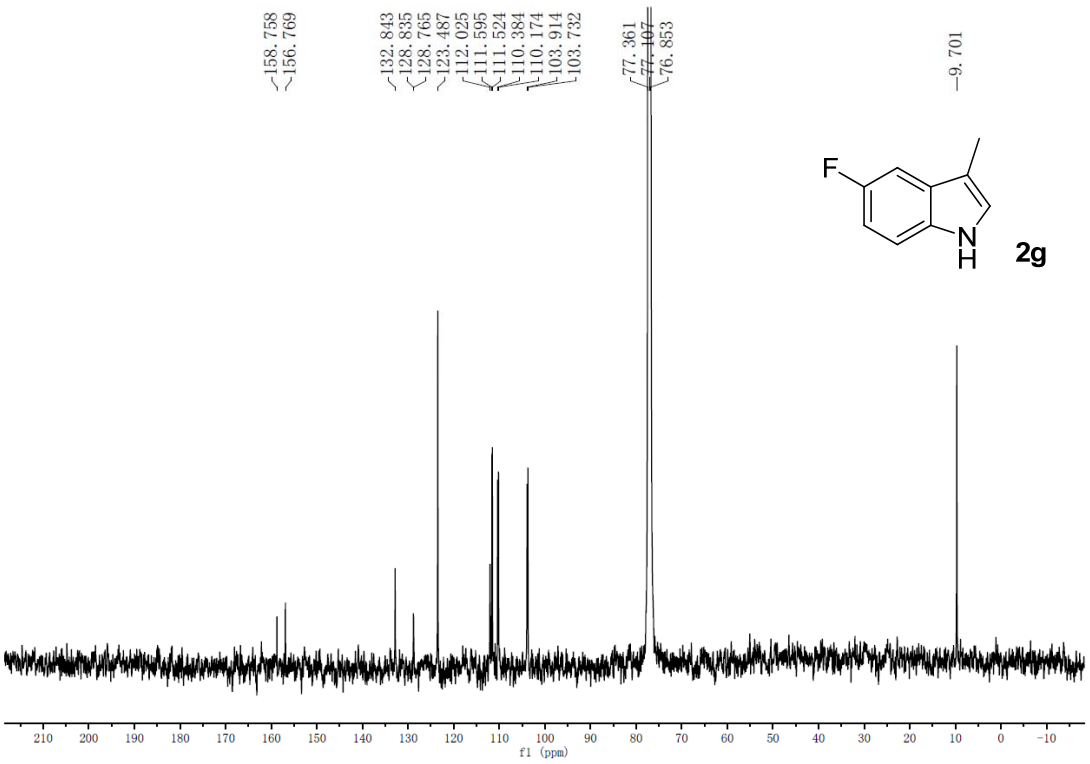
5-Methoxy-3-methyl-1*H*-indole (**2f**, ^{13}C NMR, $CDCl_3$, 125 MHz)



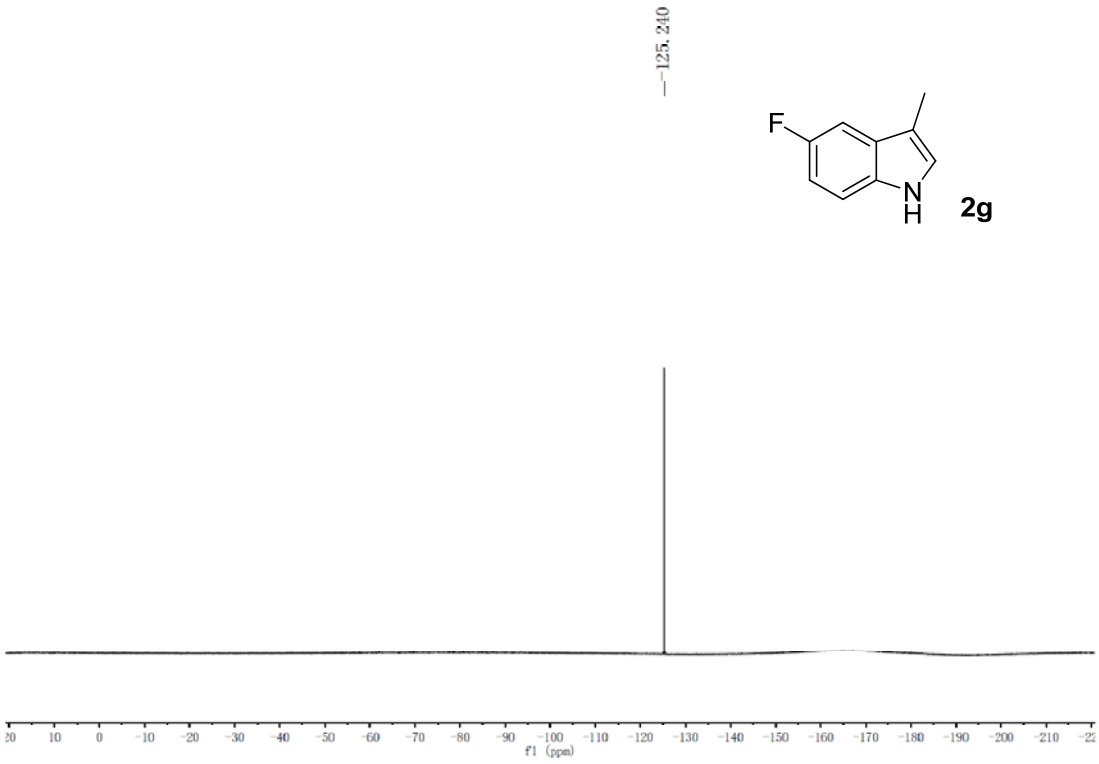
5-Fluoro-3-methyl-1*H*-indole (**2g**, ^{1}H NMR, $CDCl_3$, 500 MHz)



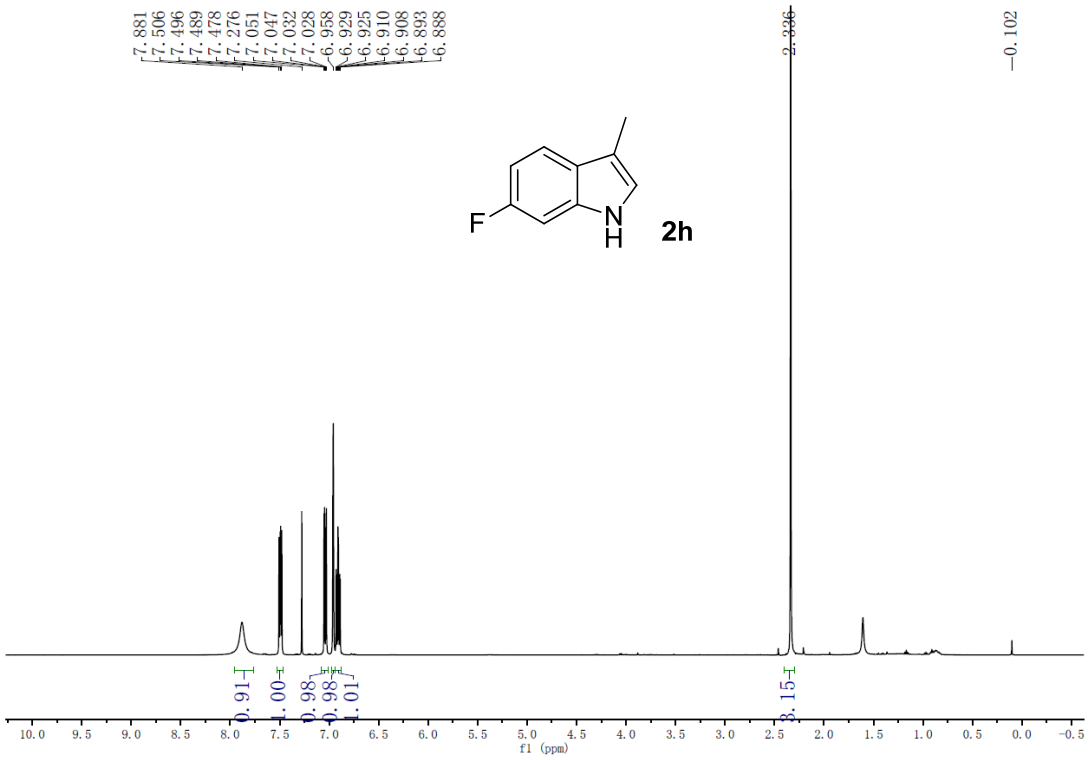
5-Fluoro-3-methyl-1*H*-indole (**2g**, ^{13}C NMR, $CDCl_3$, 125 MHz)



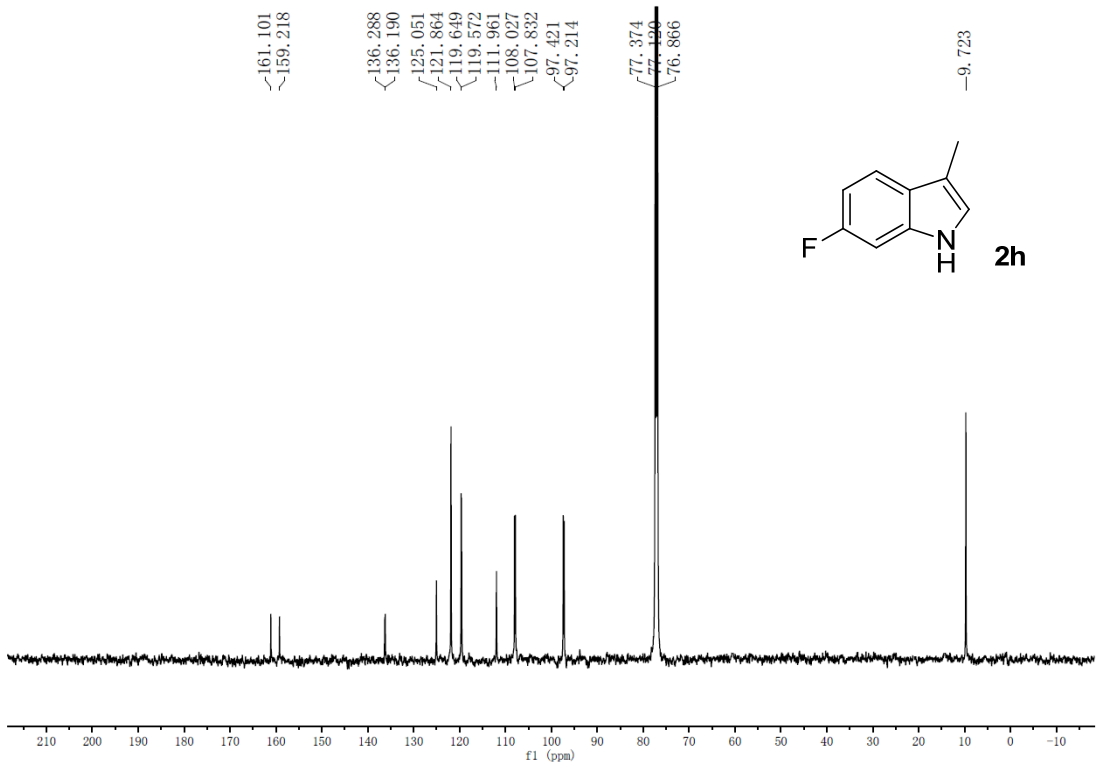
5-Fluoro-3-methyl-1*H*-indole (**2g**, ^{19}F NMR, $CDCl_3$, 470 MHz)



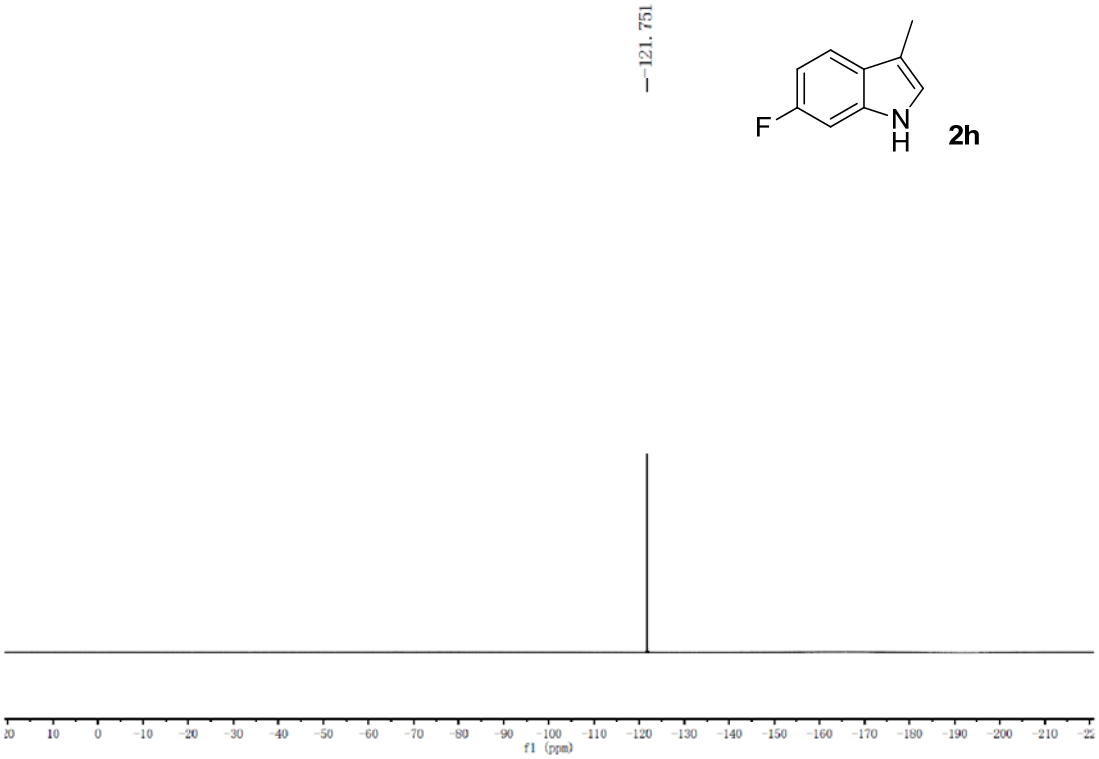
6-Fluoro-3-methyl-1*H*-indole (**2h**, ^{1}H NMR, $CDCl_3$, 500 MHz)



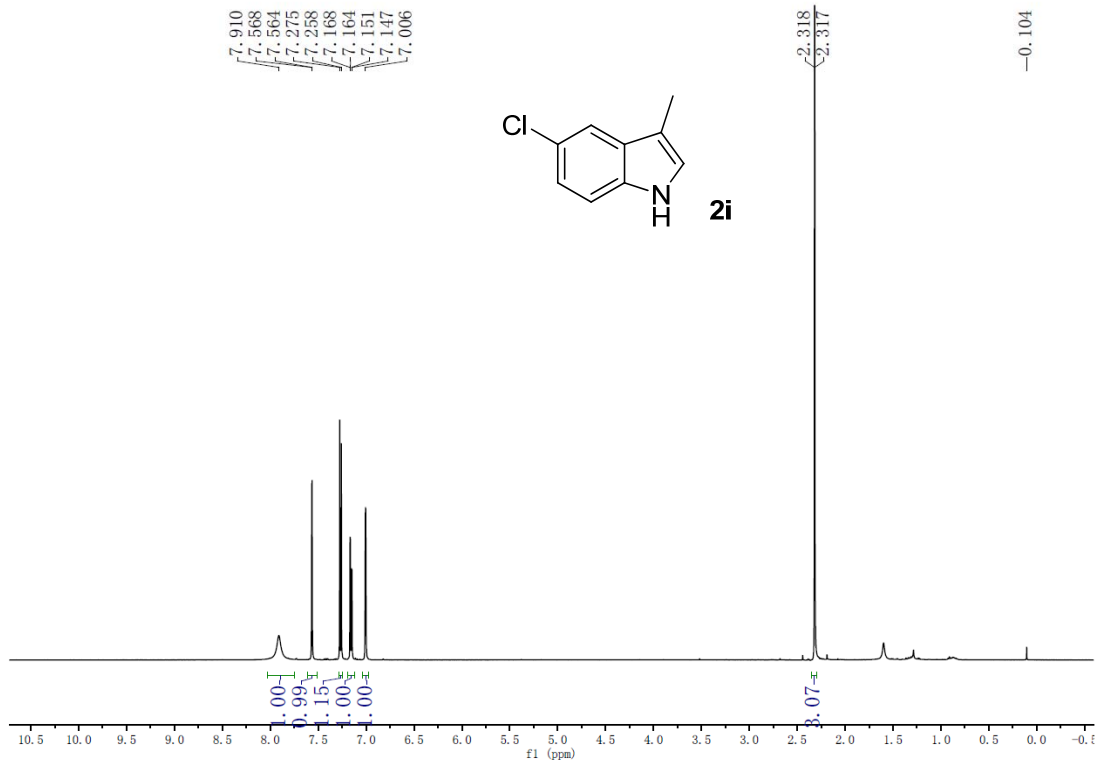
6-Fluoro-3-methyl-1*H*-indole (**2h**, ^{13}C NMR, $CDCl_3$, 125 MHz)



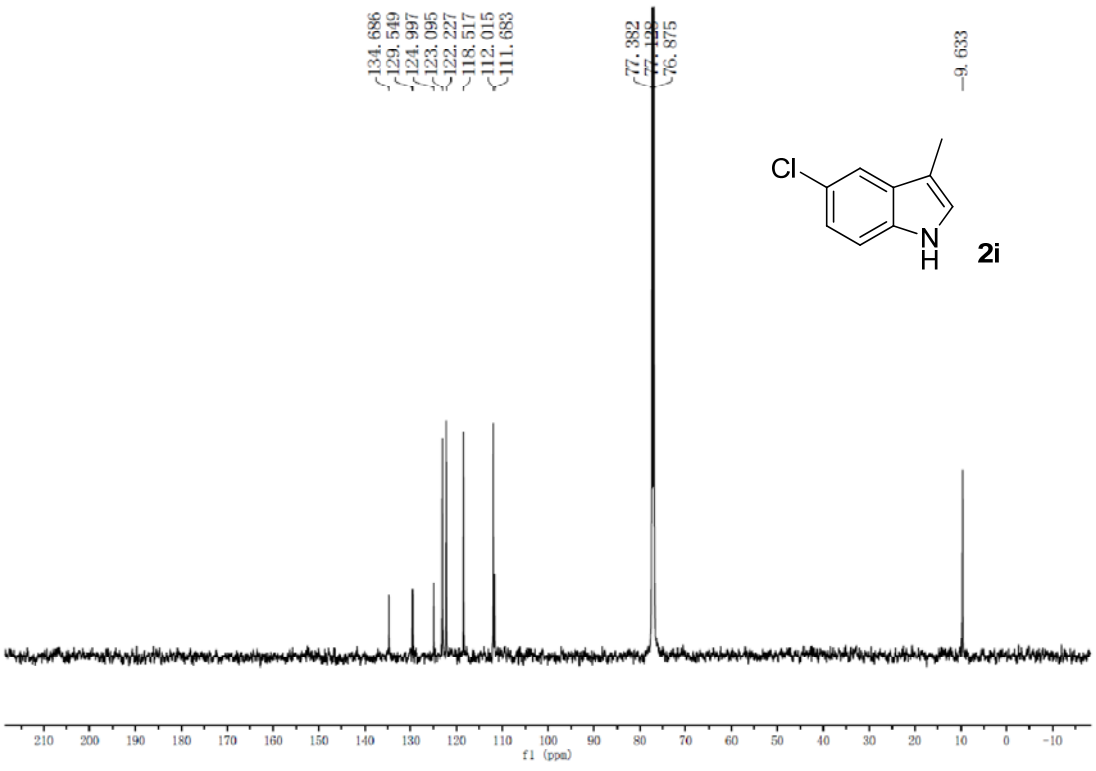
6-Fluoro-3-methyl-1*H*-indole (**2h**, ^{19}F NMR, $CDCl_3$, 470 MHz)



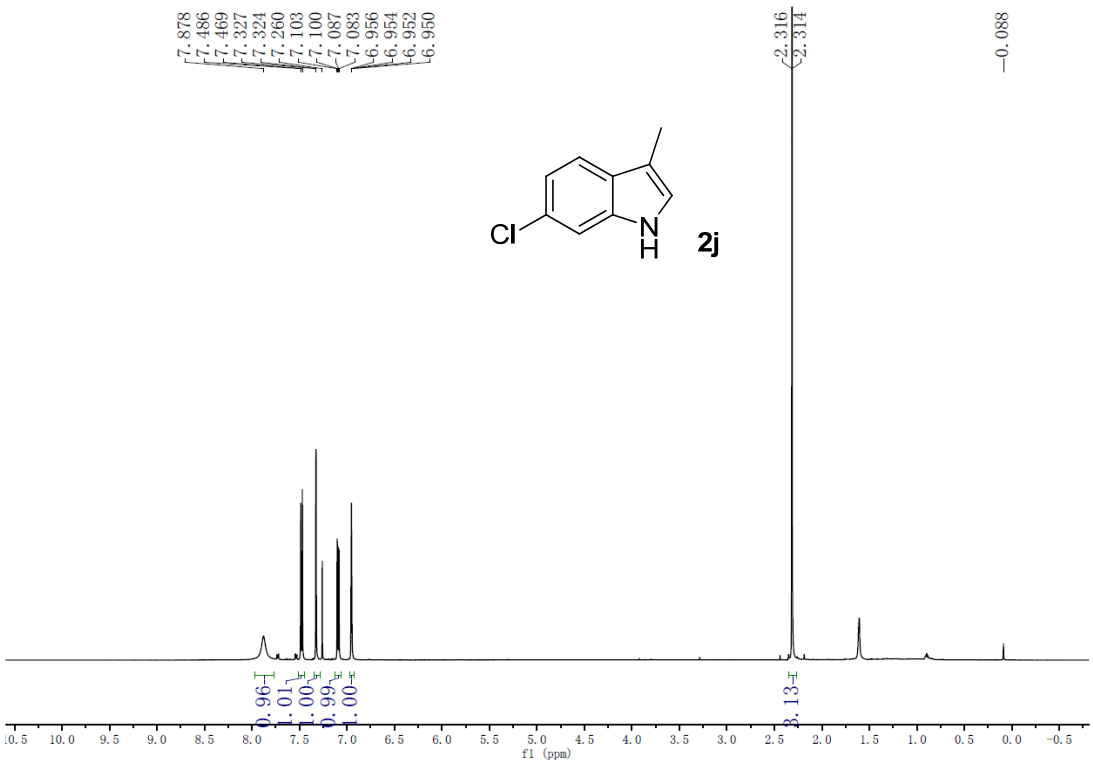
5-Chloro-3-methyl-1*H*-indole (**2i**, ^{1}H NMR, $CDCl_3$, 500 MHz)



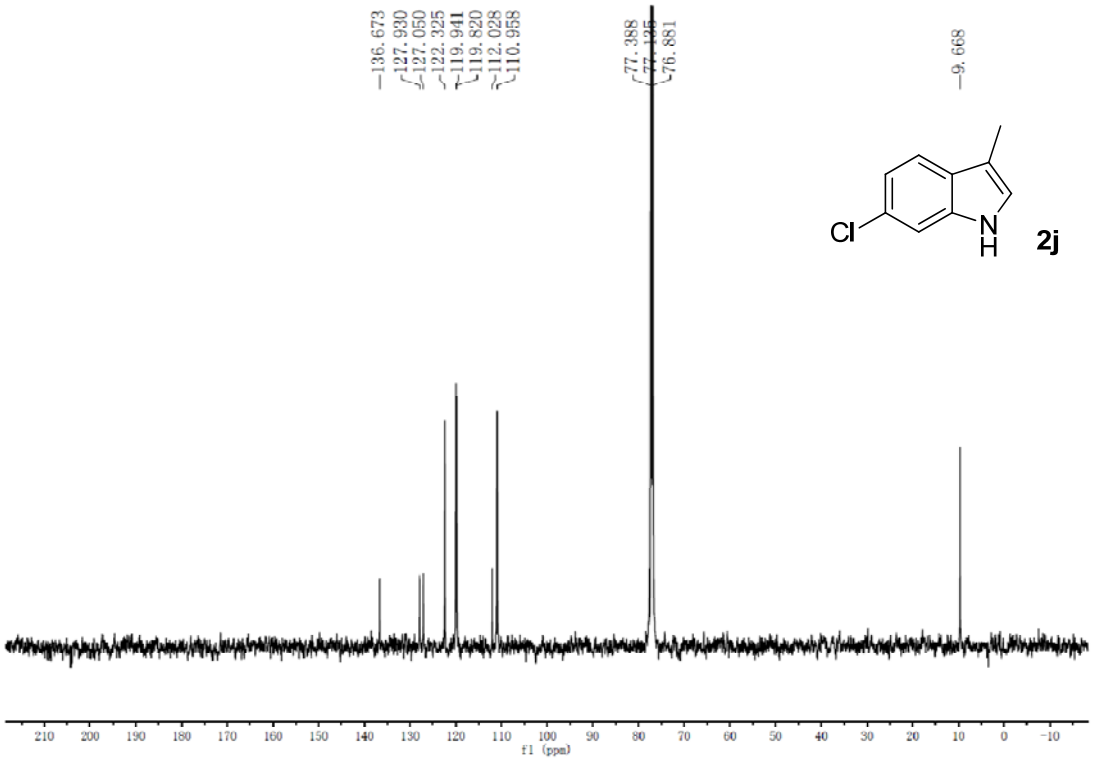
5-Chloro-3-methyl-1*H*-indole (**2i**, ^{13}C NMR, $CDCl_3$, 125 MHz)



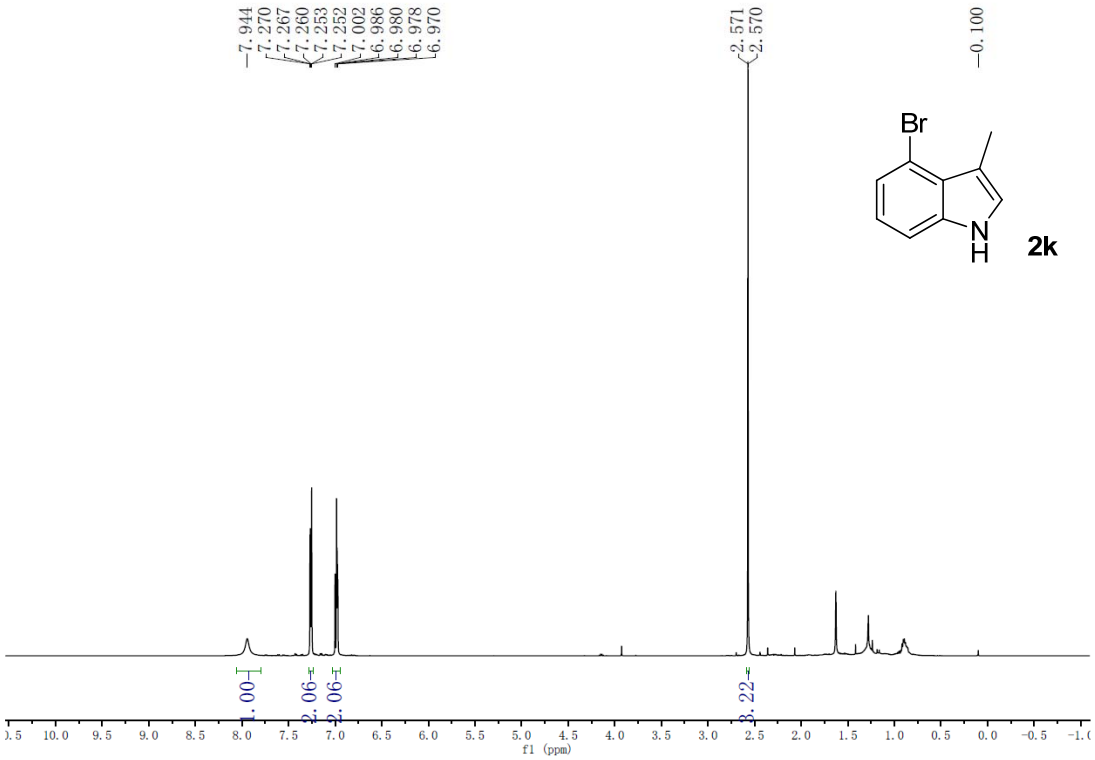
6-Chloro-3-methyl-1*H*-indole (**2j**, ^{1}H NMR, $CDCl_3$, 500 MHz)



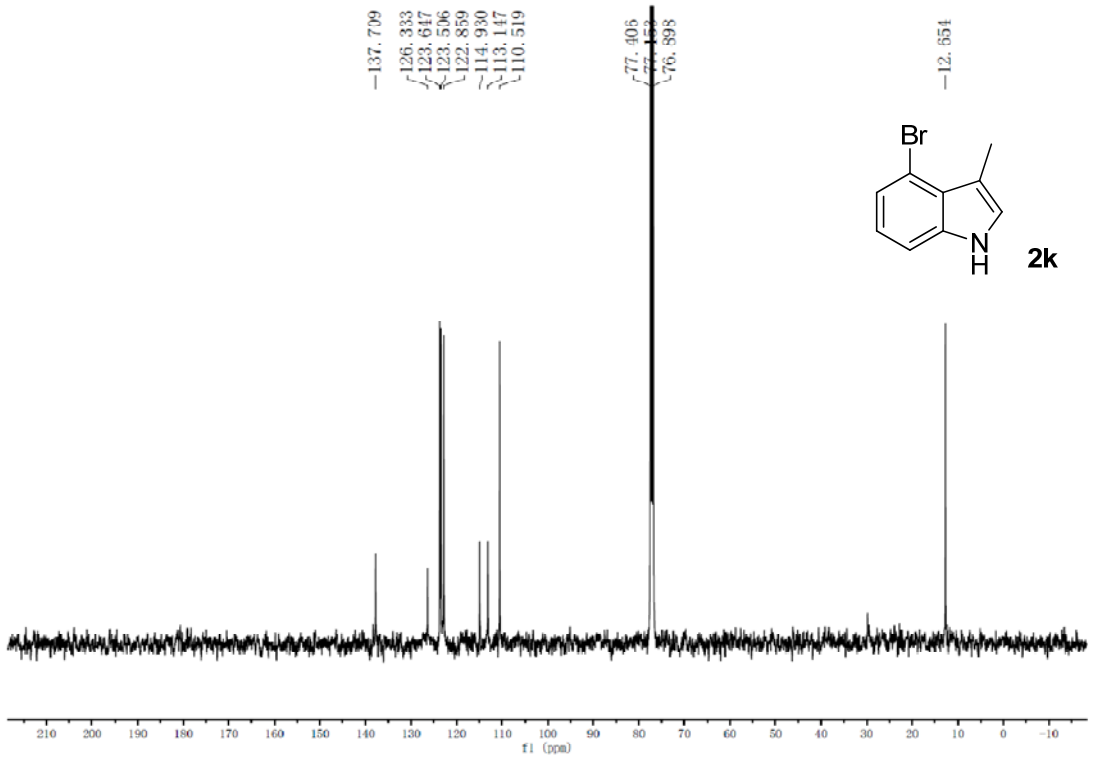
6-Chloro-3-methyl-1*H*-indole (**2j**, ^{13}C NMR, $CDCl_3$, 125 MHz)



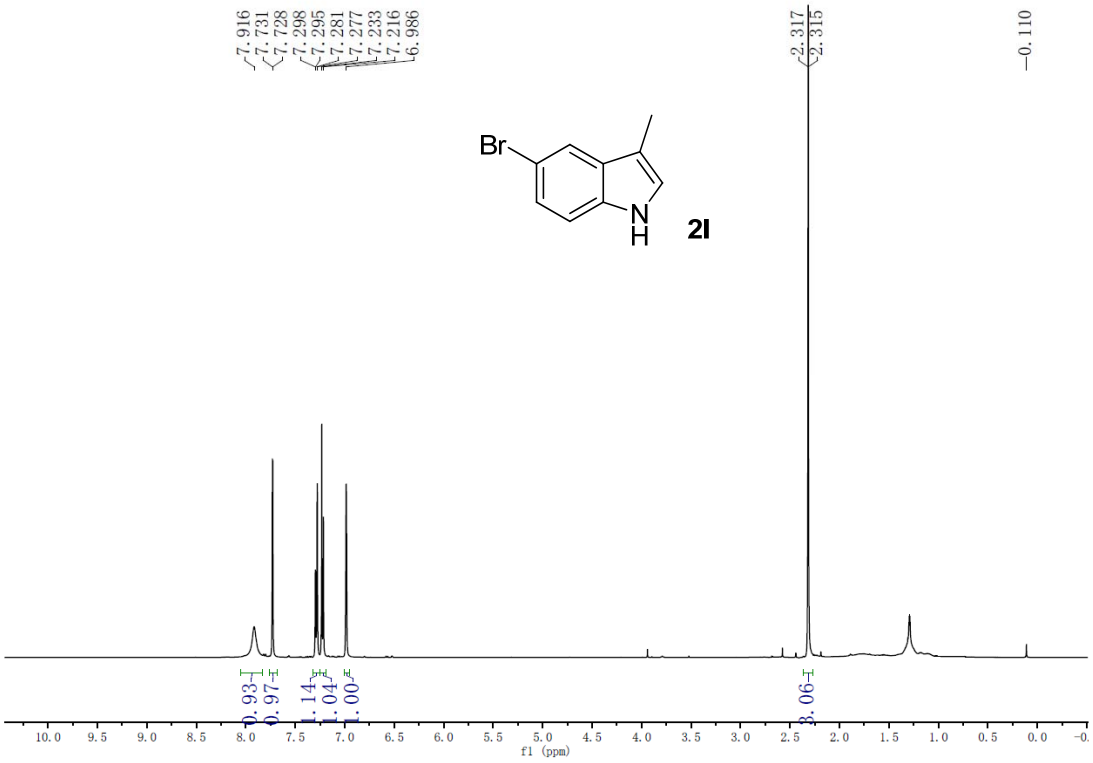
4-Bromo-3-methyl-1*H*-indole (**2k**, ^{1}H NMR, $CDCl_3$, 500 MHz)



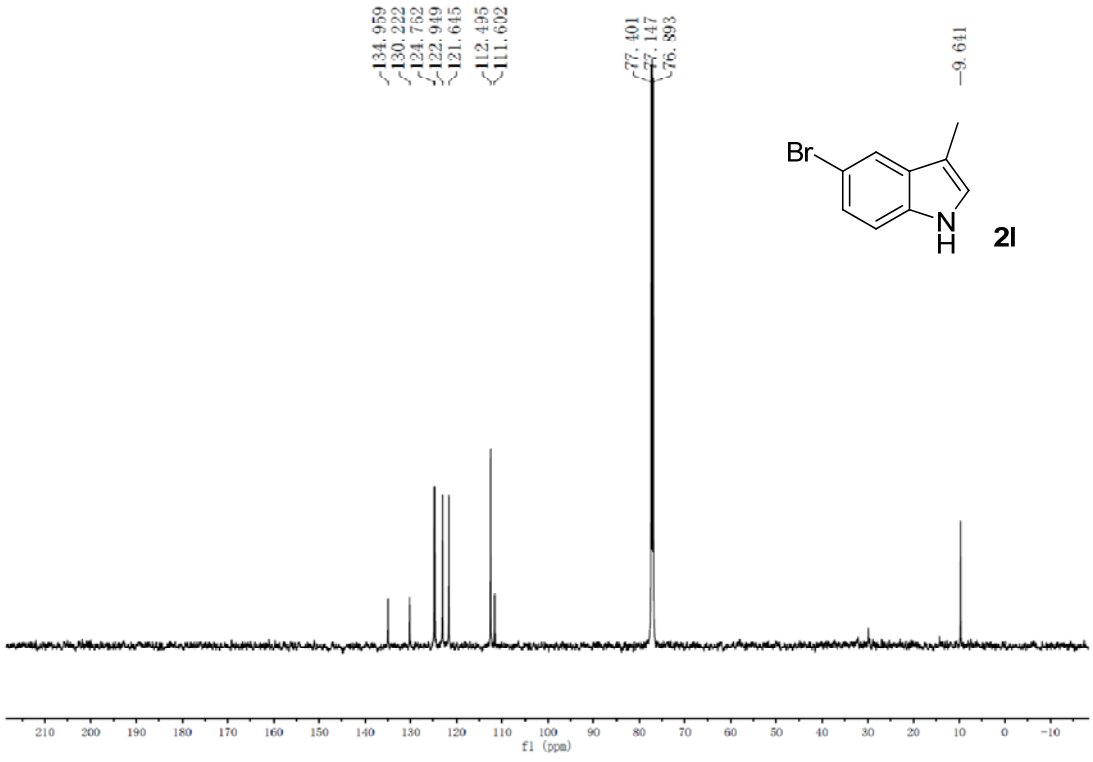
4-Bromo-3-methyl-1*H*-indole (**2k**, ^{13}C NMR, $CDCl_3$, 125 MHz)



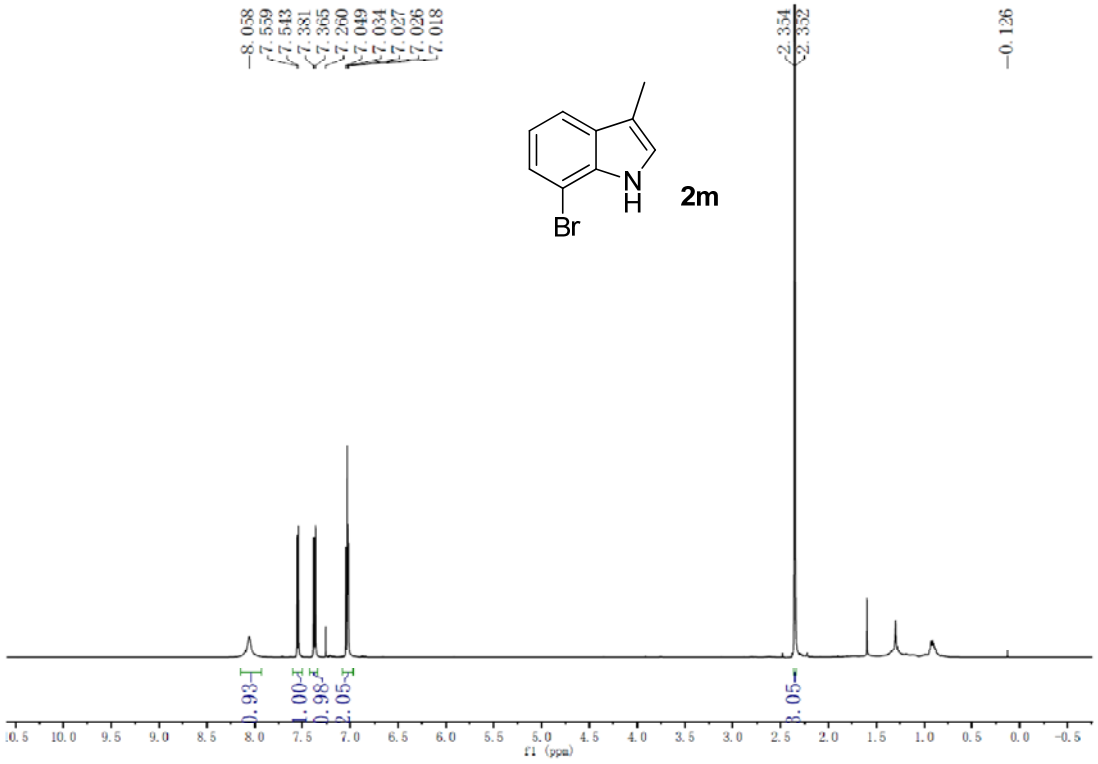
5-Bromo-3-methyl-1*H*-indole (**2l**, ^{1}H NMR, $CDCl_3$, 500 MHz)



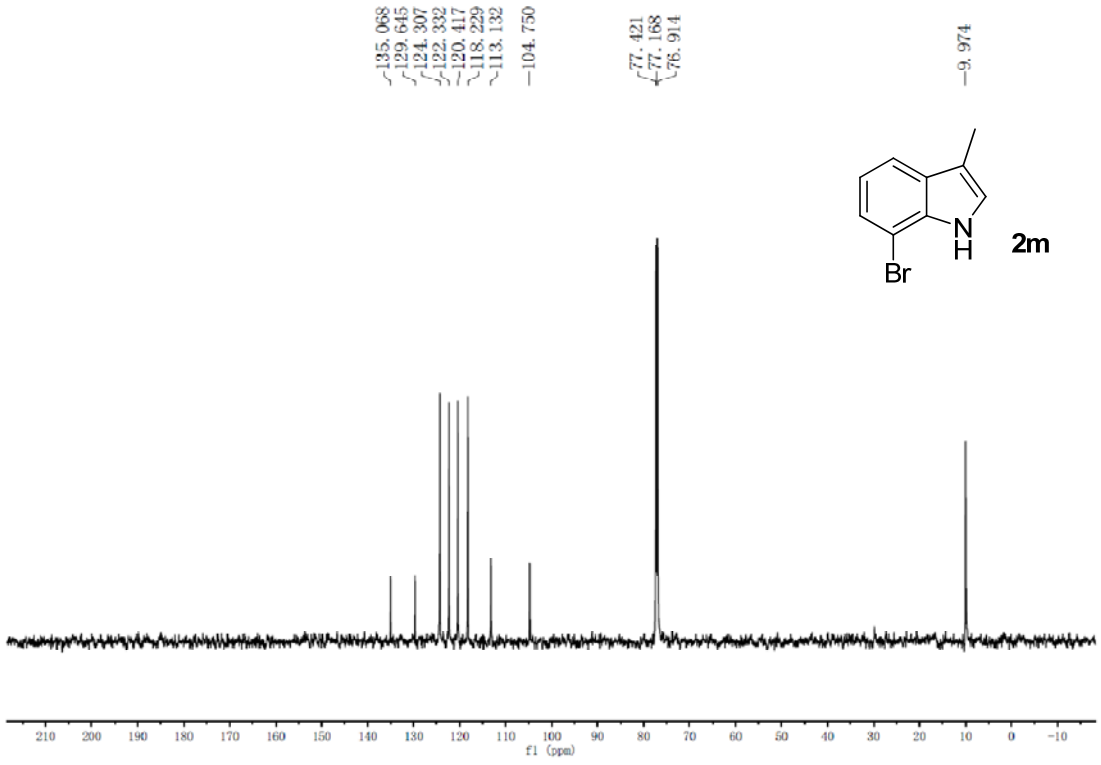
5-Bromo-3-methyl-1*H*-indole (**2l**, ^{13}C NMR, $CDCl_3$, 125 MHz)



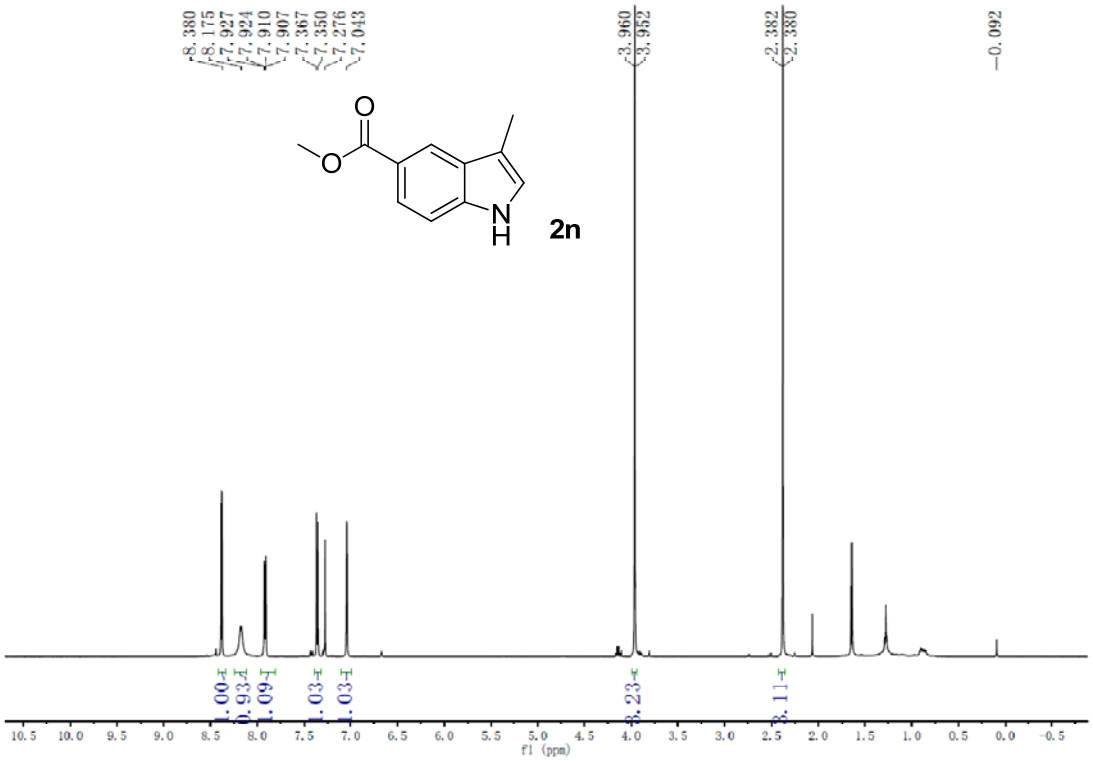
7-Bromo-3-methyl-1*H*-indole (**2m**, ^{1}H NMR, $CDCl_3$, 500 MHz)



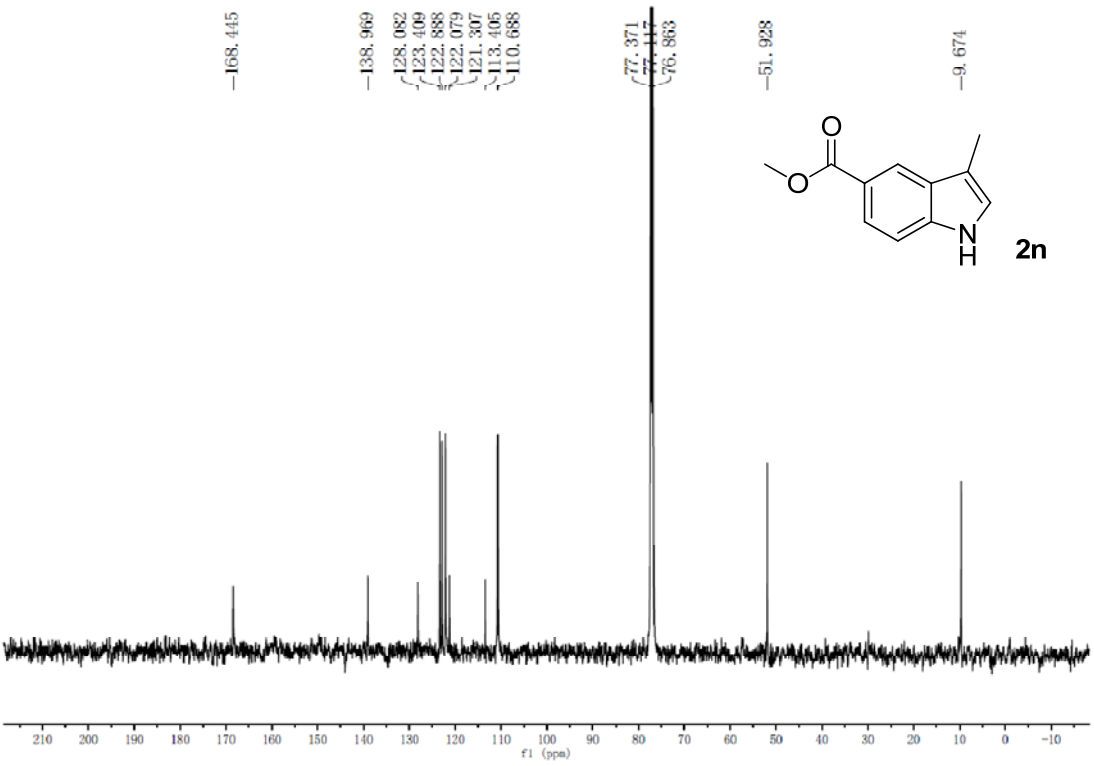
7-Bromo-3-methyl-1*H*-indole (**2m**, ^{13}C NMR, $CDCl_3$, 125 MHz)



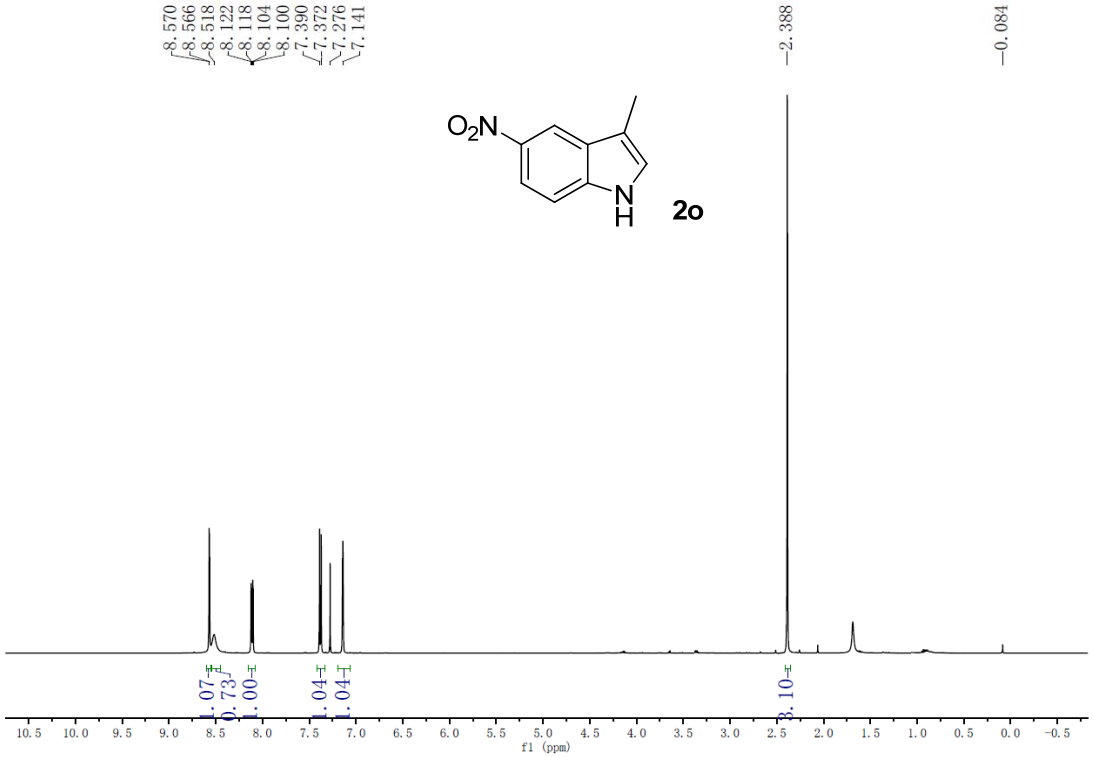
Methyl 3-methyl-1*H*-indole-5-carboxylate (**2n**, ^{1}H NMR, $CDCl_3$, 500 MHz)



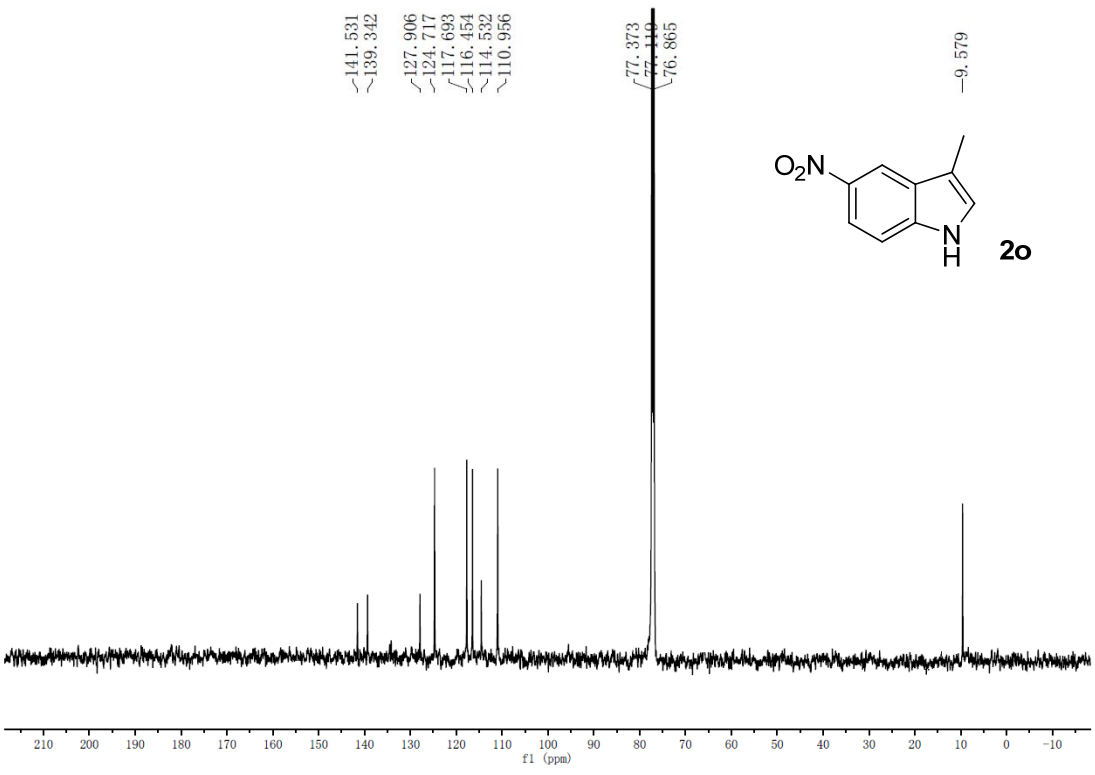
Methyl 3-methyl-1*H*-indole-5-carboxylate (**2n**, ^{13}C NMR, $CDCl_3$, 125 MHz)



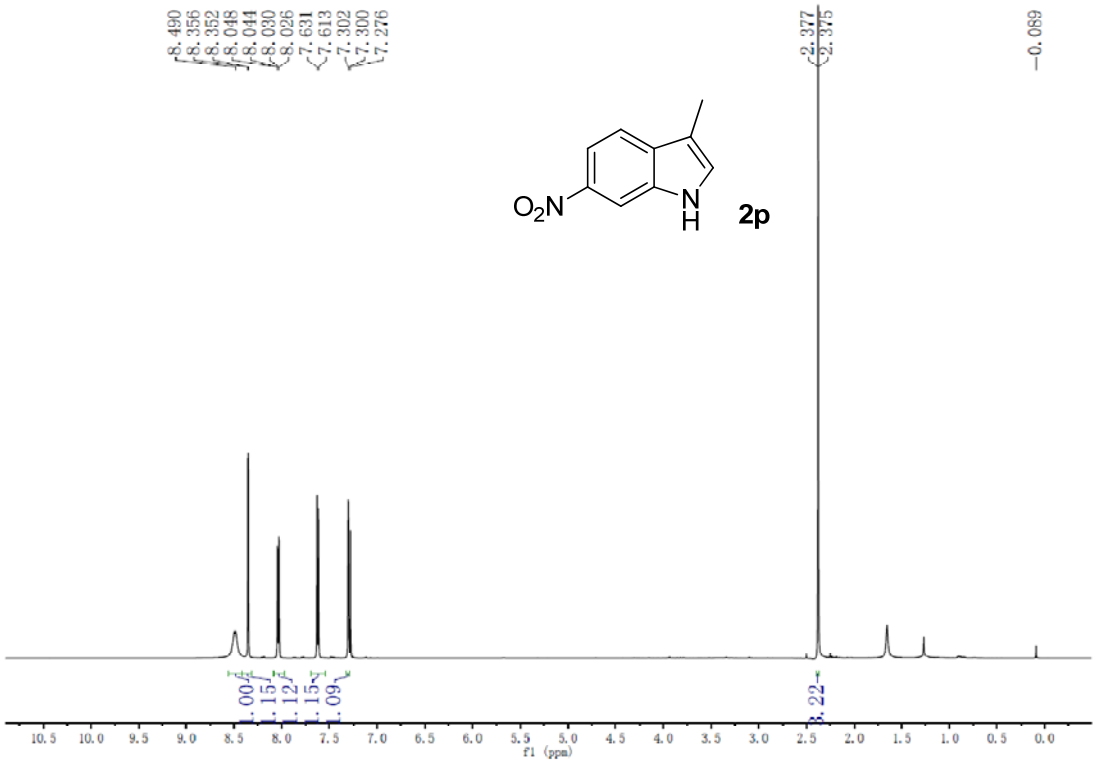
3-Methyl-5-nitro-1*H*-indole (**2o**, ^{1}H NMR, $CDCl_3$, 500 MHz)



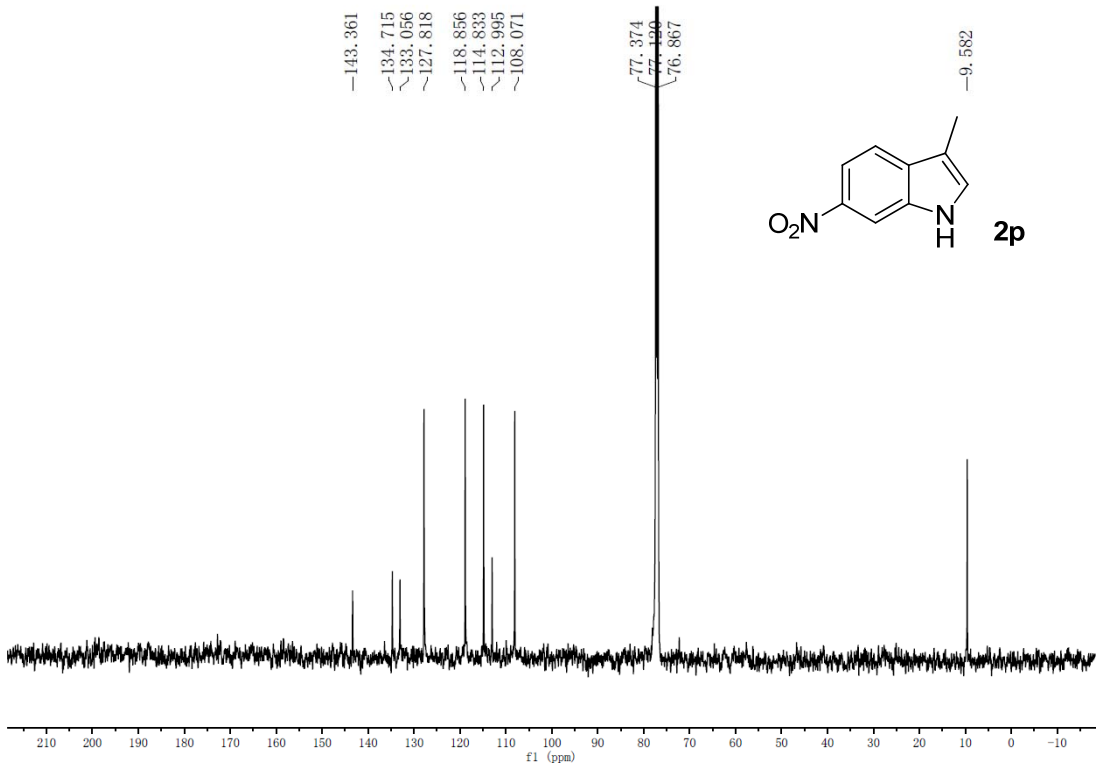
3-Methyl-5-nitro-1*H*-indole (**2o**, ^{13}C NMR, $CDCl_3$, 125 MHz)



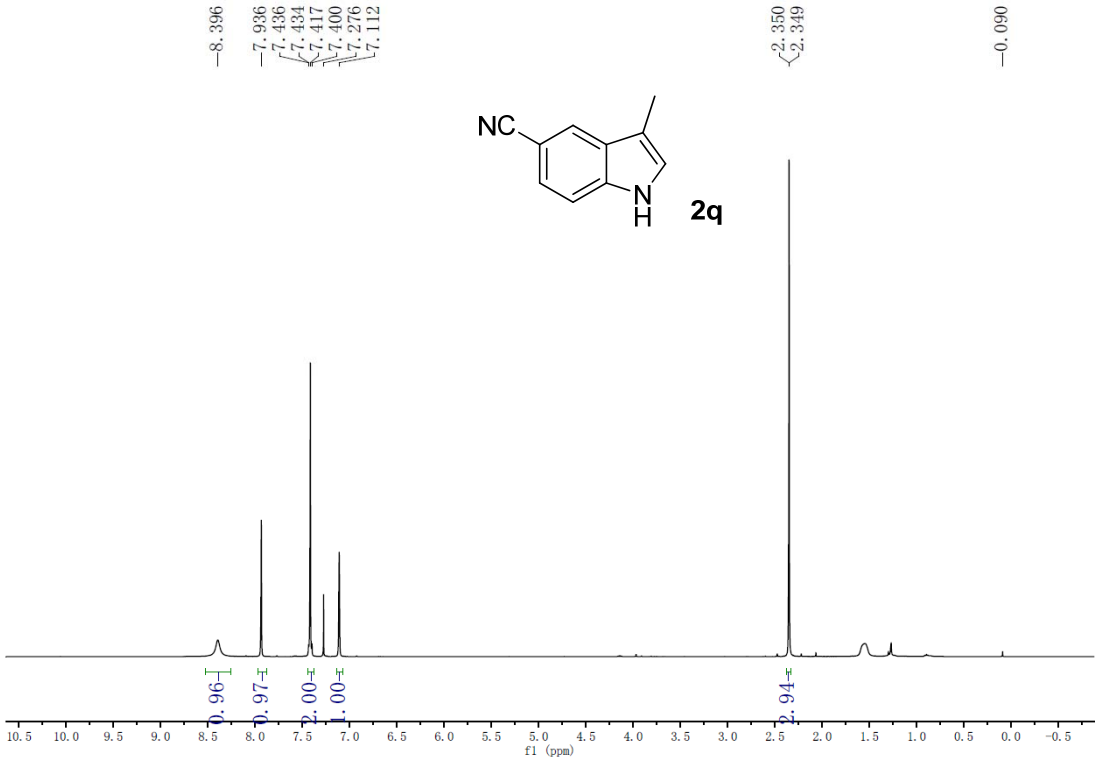
3-Methyl-6-nitro-1*H*-indole (**2p**, ^{1}H NMR, $CDCl_3$, 500 MHz)



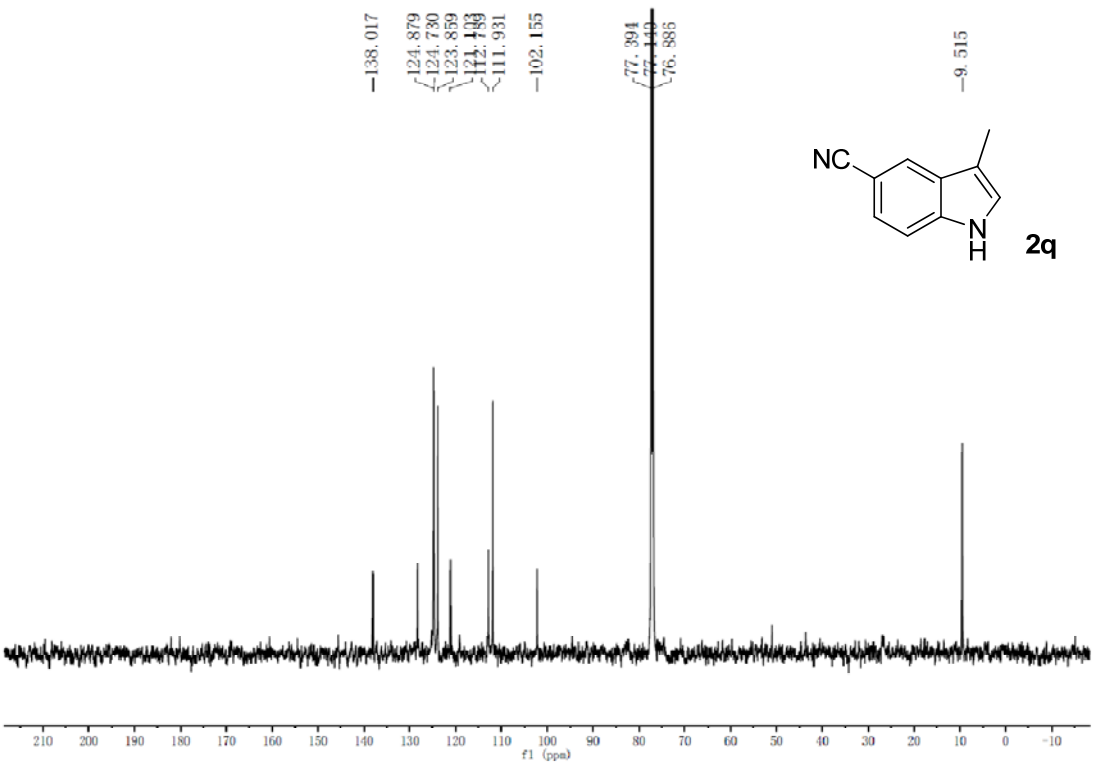
3-Methyl-6-nitro-1*H*-indole (**2p**, ^{13}C NMR, $CDCl_3$, 125 MHz)



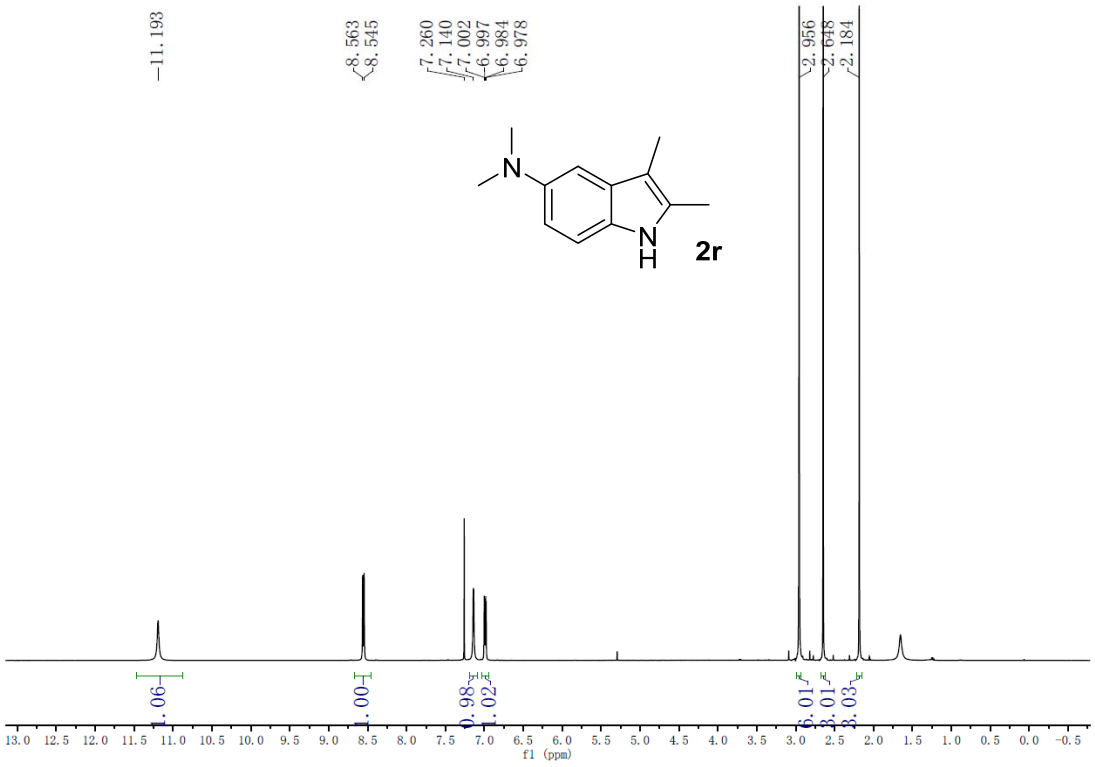
3-Methyl-1*H*-indole-5-carbonitrile (**2q**, ^{1}H NMR, $CDCl_3$, 500 MHz)



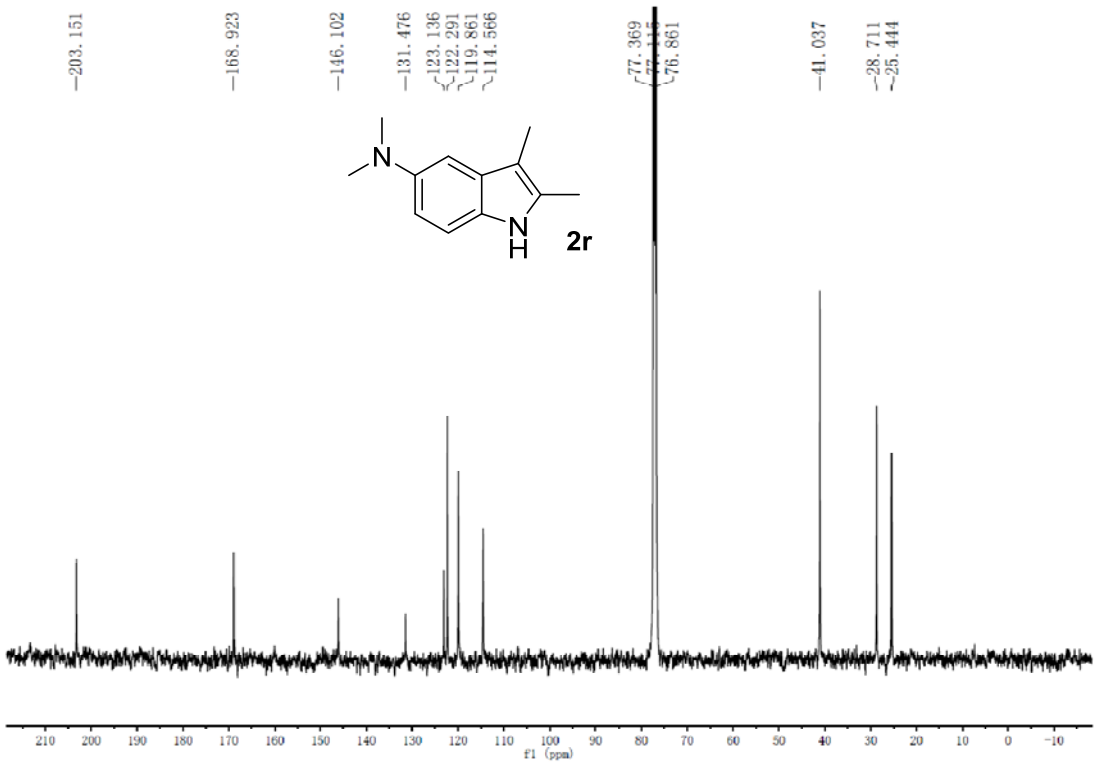
3-Methyl-1*H*-indole-5-carbonitrile (**2q**, ^{13}C NMR, $CDCl_3$, 125 MHz)



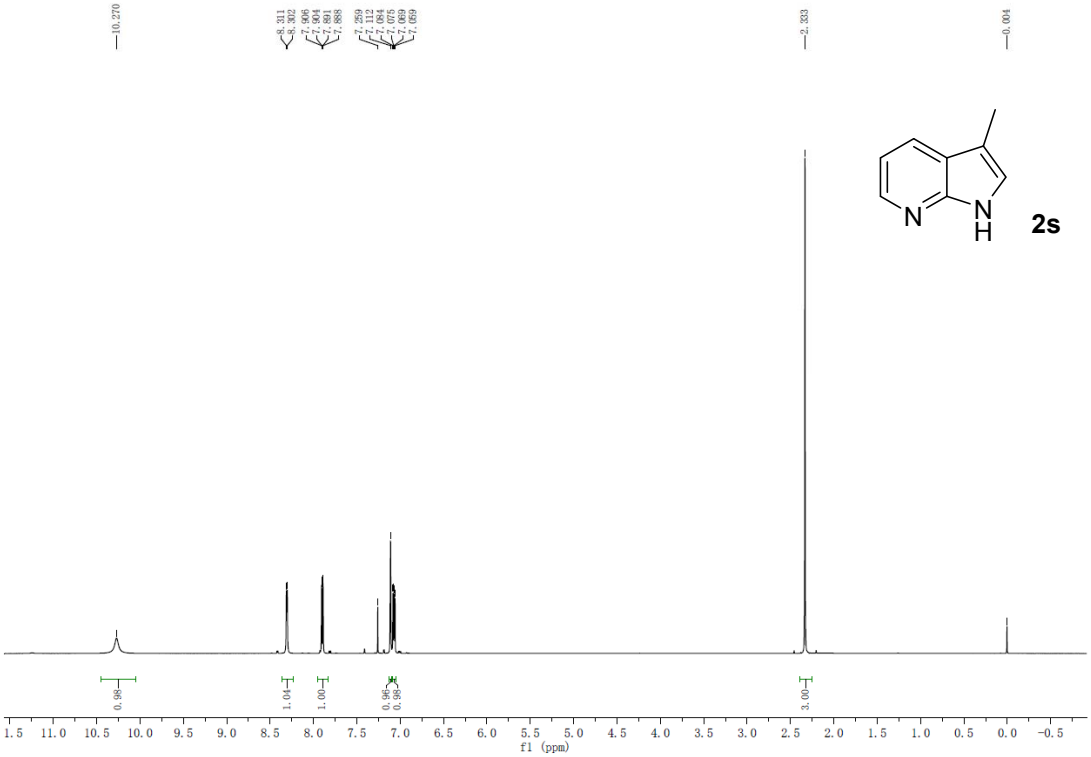
N,*N*,2,3-tetramethyl-1*H*-indol-5-amine (**2r**, ^{1}H NMR, $CDCl_3$, 500 MHz)



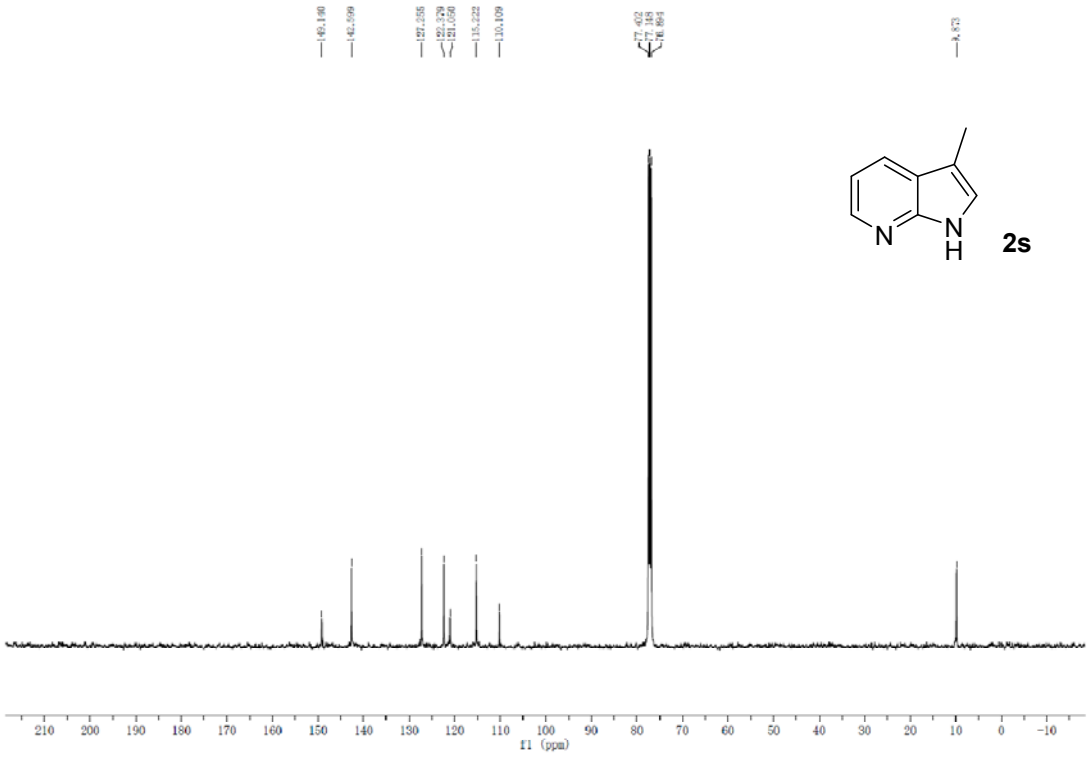
N,*N*,2,3-tetramethyl-1*H*-indol-5-amine (**2r**, ^{13}C NMR, $CDCl_3$, 125 MHz)



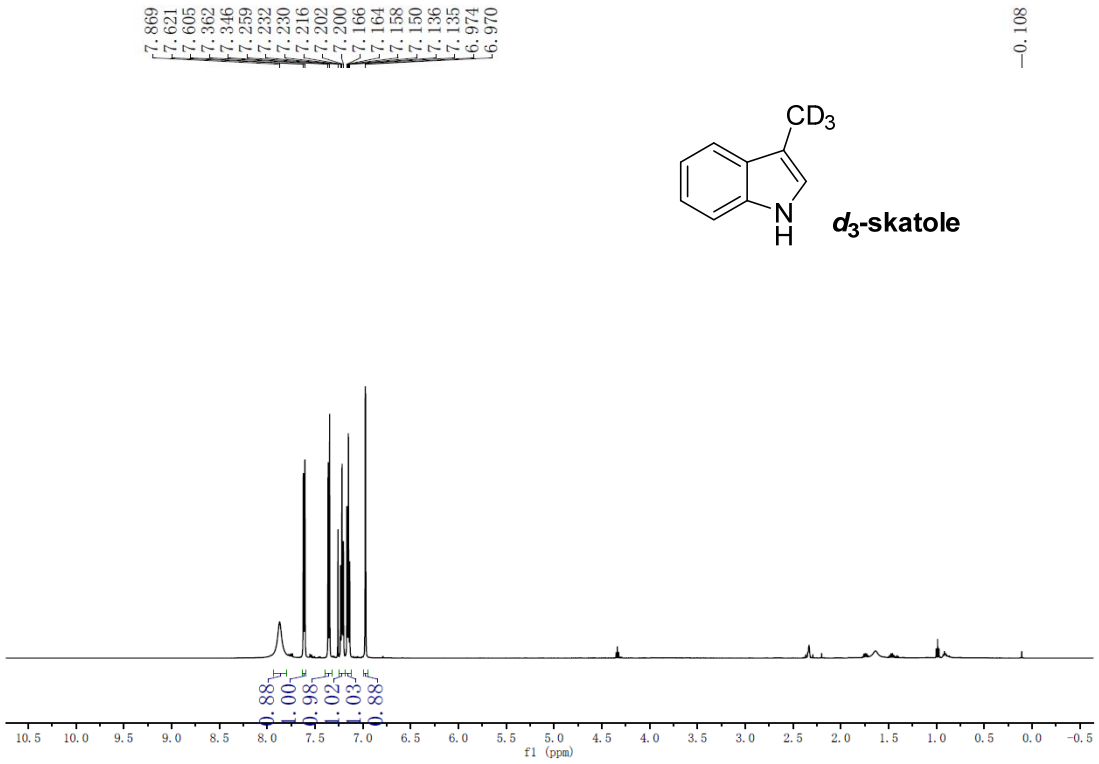
3-Methyl-1*H*-pyrrolo[2,3-*b*]pyridine (**2s**, ^{1}H NMR, $CDCl_3$, 500 MHz)



3-Methyl-1*H*-pyrrolo[2,3-*b*]pyridine (**2s**, ^{13}C NMR, $CDCl_3$, 125 MHz)



***d*$_3$-skatole** (^{1}H NMR, $CDCl_3$, 500 MHz)



***d*$_3$-skatole** (^{13}C NMR, $CDCl_3$, 125 MHz)