Supporting Information for

Cu-catalyzed aerobic oxidative dehydrogenation of tertiary indolines to indoles using azo/hydrazide redox

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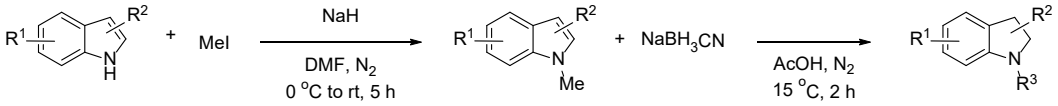
1. General Considerations

All commercially available compounds and solvents were purchased and used as received unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm) and treatment with phosphomolybdic acid, *p*-anisaldehyde, $KMnO_4$, or Vanillin stain followed by heating. Flash chromatography was performed using silica gel (particle size 40−63 μm, 230−400 mesh). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on 300 MHz NMR (300 MHz for ^{1}H, 75 MHz for ^{13}C, 282 MHz for ^{19}F), 400 MHz NMR (400 MHz for ^{1}H, 101 MHz for ^{13}C), or 850 MHz NMR (850 MHz for ^{1}H, 214 MHz for ^{13}C). Chemical shift values are given in parts per million relative to internal TMS (0.00 ppm for ^{1}H) or $CDCl_3$ (77.06 ppm for ^{13}C). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = double of doublet, dt = double of triplet, td = triple of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). High-resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using EI method and magnetic sector mass analyzer. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected.

2. Preparation of indolines (starting materials)

Synthesis of 4a–4v

Indolines **4a**–**4v** were prepared by methylation[1] of indole followed by reduction.[2]

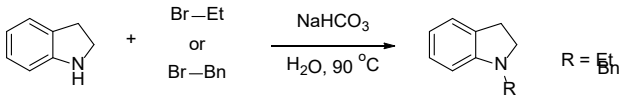


Methylation A 50 mL flame-dried round-bottom flask, which was equipped with a magnetic stir bar and charged with NaH (6.0 mmol, 60% suspension in mineral oil), was evacuated and backfilled with nitrogen (this process was repeated three times). After DMF (10 mL) was added at 0 ℃, indole (5.0 mmol) in DMF (5.0 ml) was added dropwise. After the reaction mixture was stirred at room temperature for 1 h, MeI (6.0 mmol) was added dropwise to the mixture at 0 ℃. Then, the reaction mixture was stirred at room temperature for 4 h. After the reaction was completed, ice water was added. The reaction mixture was extracted with EtOAc. The combined organic layers were washed with water and brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel to give *N*-methyl indoles.

Reduction A 50 mL flame-dried round-bottom flask, which was equipped with a magnetic stir bar, was evacuated and backfilled with nitrogen (this process was repeated three times). After $NaBH_3CN$ (20 mmol) in acetic acid (10 mL) was added to the flask at 15 ℃, the synthesized *N*-methyl indoles (4.0 mmol) in acetic acid (5.0 mL) was added dropwise. The reaction mixture was stirred at room temperature for 2 h. After the reaction was completed, most of the acetic acid was removed by a rotary evaporator. Then, 10 M NaOH aqueous solution was added to make pH = 9, and the reaction mixture was extracted with Et_2O. The combined organic layers were washed with water and brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel to give *N*-methyl indolines **4a**–**4v**.

Synthesis of 4w and 4x

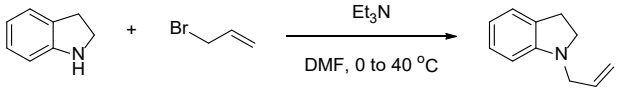
Indolines **4w** and **4x** were prepared by the known procedure.[2]



To a 50 mL round-bottom flask, which was equipped with a magnetic stir bar, $NaHCO_3$ (6.25 mmol) in 3 mL of H_2O was added. After indoline (5.0 mmol) was added dropwise, the reaction mixture was stirred at 90 °C. After bromoethane (5.0 mmol) for **4w** or benzylbromide (5.0 mmol) for **4x** was added dropwise for 1.5 h, the mixture was stirred for an additional 3.5 h. Then, water was added and the mixture was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel (EtOAc/Hx=1:10) to give the desired indolines.

Synthesis of 4y

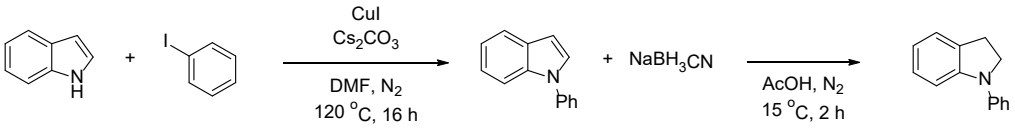
Indoline **4y** was prepared by the known procedure.[3]



A 50 mL flame-dried round-bottom flask, which was equipped with a magnetic stir bar, was evacuated and backfilled with nitrogen (this process was repeated three times). Then, indoline (5.0 mmol), DMF (4.0 mL), and triethyl amine (7.5 mmol) were added sequentially at 0 ℃. After allyl bromide (7.5 mmol) was added dropwise, the reaction mixture was stirred at 40 ℃ for 14 h. After completion of the reaction, ice-cold water was added, and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel (EtOAc/Hx=1:10) to give a desired 1-allylindoline **4y**.

Synthesis of 4z

Indoline **4z** was prepared by C-N cross coupling[4] of indole followed by reduction.

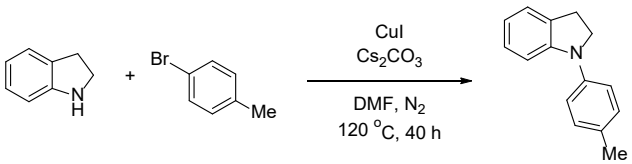


C-N cross coupling A 50 mL flame-dried round-bottom flask, which was equipped with a magnetic stir bar and charged with indole (10.0 mmol), CuI (2.0 mmol), and Cs_2CO_3 (20 mmol) was evacuated and backfilled with nitrogen (this process was repeated three times). Phenyliodide (7.1 mmol) in DMF (18 mL) was added, then the reaction mixture was vigorously stirred at 120 ℃ for 16 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with EtOAc. The combined organic layers were washed with water and brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The crude product was purified by flash column chromatography on silica gel (pure PE) to give 1-phenylindole as a colorless oil.

Reduction See the reduction procedure in the **Synthesis of 4a–4v**.

Synthesis of 4aa

Indolines **4aa** was prepared by the known procedure.[5]

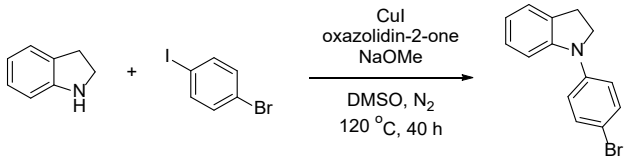


A 50 mL flame-dried round-bottom flask, which was eqipped with a magnetic stirring bar and charged CuI (1.4 mmol) and Cs_2CO_3 (14.3 mmol), was evacuated and backfilled with nitrogen (this process was

repeated three times). Indoline (10.0 mmol), 1-bromo-4-methylbenzene (7.1 mmol), and DMF (15 mL) were added, and the reaction mixture was stirred at room temperature for 0.5 h, then heated at 120 ℃. After 40 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered through a plug of silica gel, and washed with EtOAc. The filtrate was concentrated on a rotary evaporator, and the resulting residue was purified by column chromatography on silica gel (EtOAc/Hx=1:10) to provide the desired indoline **4aa**.

Synthesis of 4ab

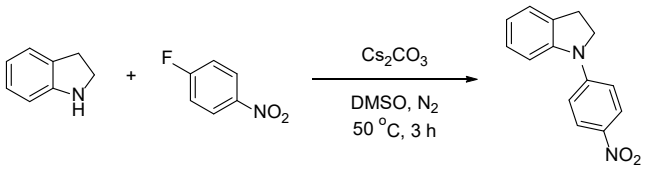
Indolines **4ab** was prepared by the known procedure.[6]



A 50 mL flame-dried round-bottom flask, which was equipped with a magnetic stirring bar and charged with CuI (0.5 mmol), oxazolidin-2-one (1.0 mmol), and NaOMe (15 mmol), was evacuated, and backfilled with nitrogen (this process was repeated three times). DMSO (20 mL) was added, and the reaction mixture was stirred at room temperature for 0.5 h. Then, indoline (10 mmol) and 1-bromo-4-iodobenzene (15 mmol) were added. After the reaction mixture was stirred at 120 °C for 40 h, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel (EtOAc/Hx=1:10) to give a desired indoline **4ab**.

Synthesis of 4ac

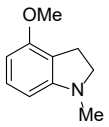
Indolines **4ac** was prepared by the known procedure.[7]



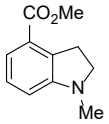
A 50 mL flame-dried round-bottom flask, which was equipped with a magnetic stir bar and charged with Cs_2CO_3 (20 mmol), was evacuated and backfilled with nitrogen (this process was repeated three times). After DMSO (12 mL), indoline (10.0 mmol), and 1-fluoro-4-nitrobenzene (8.8 mmol) were added, the reaction mixture was stirred at 50 ℃ for 3 h. Then, cold water was added, and the reaction mixture was extracted with EtOAc. The combined organic layers were washed with water and brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The crude product was purified by flash column chromatography on silica (EtOAc/Hx=1:10) to give indoline **4ac**.

3. Charaterizations of newly synthesized indolines

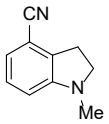
The characterizations of newly synthesized indolines were provided below.



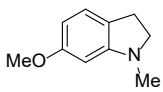
4-methoxy-1-methylindoline (4i): yellow oil, EtOAc/Hx=1:10, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 – 7.02 (m, 1H), 6.28 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.18 (dd, *J* = 7.9, 2.5 Hz, 1H), 3.79 (s, 3H), 3.29 (t, *J* = 7.2 Hz, 2H), 2.90 (t, *J* = 6.9, 2H), 2.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0, 155.1, 128.7, 116.2, 101.3, 101.2, 56.3, 55.2, 36.4, 25.7; HRMS (EI) m/z calcd. For $C_{10}H_{13}NO$ $[M]^+$: 163.0997, found 163.0995.



methyl 1-methylindoline-4-carboxylate (4l): yellow oil, EtOAc/Hx=1:60, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.58 (dd, *J* = 7.8, 1.0 Hz, 1H), 3.87 (s, 3H), 3.37 – 3.33 (m, 2H), 3.32 – 3.27 (m, 2H), 2.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 154.0, 133.4, 127.5, 126.2, 118.8, 110.5, 55.7, 51.7, 36.0, 29.8; HRMS (EI) m/z calcd. For $C_{11}H_{13}NO$ $[M]^+$: 191.0946, found 191.0947.



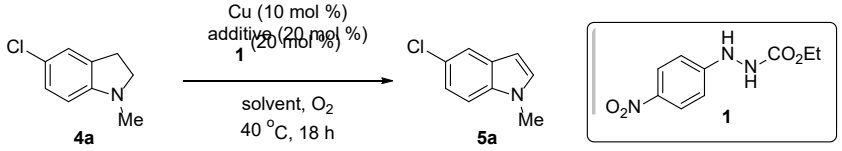
1-methylindoline-4-carbonitrile (4m): yellow oil, EtOAc/PE=1:5, ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71 – 5.65 (m, 1H), 5.42 (dd, *J* = 7.8, 0.9 Hz, 1H), 5.13 (dd, *J* = 8.0, 0.8 Hz, 1H), 1.99 (t, *J* = 8.2 Hz, 2H), 1.70 (t, *J* = 8.3 Hz, 2H), 1.35 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 134.8, 128.4, 119.7, 118.0, 110.1, 108.3, 55.3, 35.4, 28.2; HRMS (EI) m/z calcd. For $C_{10}H_{10}N_2$ $[M]^+$: 158.0844, found 158.0842.



6-methoxy-1-methylindoline (4n): yellow oil, EtOAc/Hx=1:40, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 – 6.93 (m, 1H), 6.19 (dd, *J* = 8.0, 2.3 Hz, 1H), 6.08 (s, 1H), 3.76 (s, 3H), 3.29 (t, *J* = 8.1 Hz, 2H), 2.86 (t, *J* = 7.9 Hz, 2H), 2.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 154.6, 124.2, 122.7, 101.8, 95.0, 56.7, 55.3, 36.0, 27.9. HRMS (EI) m/z calcd. For $C_{10}H_{13}NO$ $[M]^+$: 163.0997, found 163.0996.

4. Optimization of aerobic oxidative dehydrogenation of tertiary indolines

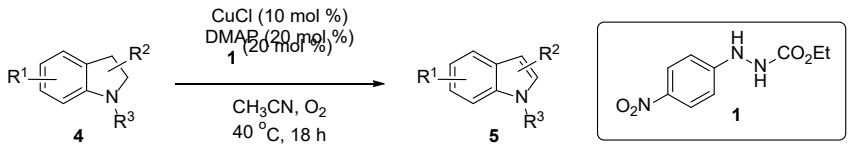
A 10 mL flame-dried test tube, which was equipped with a magnetic stir bar and charged with catalyst (0.1 equiv., 0.05 mmol), additives (0.2 equiv., 0.10 mmol), and **1** (0.2 equiv., 0.10 mmol), was evacuated and backfilled with oxygen (this process was repeated three times). After 0.3 mL of solvent was added, 5-chloro-1-methylindoline **4a** (0.5 mmol) and 0.7 mL of the solvent were added in sequence. The reaction mixture was stirred at 40 °C for 18 h. The reaction was quenched with saturated aqueous NH_4Cl solution, washed with water, and extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel (EtOAc/Hx=1:10) to give the desired indole **5a**.



Entry	Cu	Additive	Solvent	Yield (%)[a]
1	$Cu(acac)_2$	DMAP	CH_3CN	24
2	$Cu(OAc)_2$	DMAP	CH_3CN	37
3	$Cu(OH)_2$	DMAP	CH_3CN	30
4	$Cu(NO_3)_2$	DMAP	CH_3CN	74
5	$Cu(OTf)_2$	DMAP	CH_3CN	74
8	$Cu(CH_3CN)_4PF_6$	DMAP	CH_3CN	67
9	$CuBr_2$	DMAP	CH_3CN	55
10	CuBr	DMAP	CH_3CN	70
11	CuI	DMAP	CH_3CN	60
12	**CuCl**	**DMAP**	**CH_3CN**	**82**
13	CuCl	pyridine	CH_3CN	20
14	CuCl	2,2'-bipyridine	CH_3CN	19
15	CuCl	DMAP	THF	7
16	CuCl	DMAP	DMSO	41
17	CuCl	DMAP	toluene	15
18	-	DMAP	CH_3CN	-
19	CuCl	-	CH_3CN	14
20[b]	CuCl	DMAP	CH_3CN	9
21[c]	CuCl	DMAP	CH_3CN	5
22[d]	CuCl	DMAP	CH_3CN	27

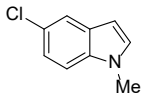
[a] Isolated yields. [b] No **1** was used. [c] Under N_2. [d] At room temperature

5. General procedure for Cu-catalyzed dehydrogenation of tertiary indolines

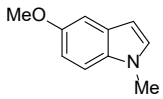


A 10 mL flame-dried test tube, which was equipped with a magnetic stir bar and charged with CuCl (0.1 equiv., 0.05 mmol), DMAP (0.2 equiv., 0.10 mmol), and **1** (0.2 equiv., 0.10 mmol), was evacuated and backfilled with oxygen (this process was repeated three times). After 0.3 mL of acetonitrile was

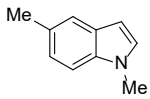
added, indolines **4** (0.5 mmol) and 0.7 mL of acetonitrile were added in sequence. The reaction mixture was stirred at 40 °C for 18 h. The reaction was quenched with saturated aqueous NH_4Cl solution, washed with water, and extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel to give the desired indole **5**.



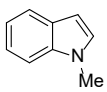
5-chloro-1-methyl-1*H*-indole[8] (5a); light yellow liquid, EtOAc/Hx=1:10, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 1.9 Hz, 1H), 7.22 (d, *J* = 8.7 Hz, 1H), 7.16 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.06 (d, *J* = 3.0 Hz, 1H), 6.41 (d, *J* = 3.0 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 130.1, 129.5, 125.1, 121.8, 120.2, 110.2, 100.6, 33.0.



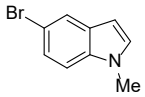
5-methoxy-1-methyl-1*H*-indole[8] (5b); brown solid, EtOAc/Hx=1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 2.1 Hz, 1H), 7.01 (d, *J* = 2.9 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.39 (d, *J* = 2.7 Hz, 1H), 3.85 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 132.1, 129.3, 128.8, 111.9, 109.9, 102.5, 100.4, 55.9, 33.0.



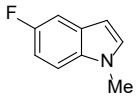
1,5-dimethyl-1*H*-indole[1] (5c); yellow liquid, EtOAc/Hx=1:10, 1H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.38 (d, *J* = 2.8 Hz, 1H), 3.74 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 128.8, 128.7, 128.4, 123.1, 120.5, 108.9, 100.3, 32.8, 21.4.



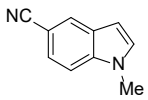
1-methyl-1*H*-indole[8] (5d); light yellow liquid, EtOAc/Hx=1:10, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.14 – 7.07 (m, 1H), 7.04 (d, *J* = 3.1 Hz, 1H), 6.48 (d, *J* = 3.1 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 128.8, 128.5, 121.5, 120.9, 119.3, 109.2, 100.9, 32.8.



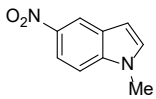
5-bromo-1-methyl-1*H*-indole[1] (5e); light yellow solid, EtOAc/Hx=1:10, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.6, 1H), 7.28 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 3.0 Hz, 1H), 6.40 (d, *J* = 2.6 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4, 130.1, 130.0, 124.3, 123.3, 112.6, 110.7, 100.5, 33.0.



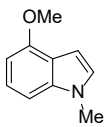
5-fluoro-1-methyl-1*H*-indole[8] (5f); yellow solid, EtOAc/Hx=1:40, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 9.7, 2.5 Hz, 1H), 7.17 (dd, *J* = 8.9, 4.3 Hz, 1H), 7.03 (d, *J* = 3.1 Hz, 1H), 6.94 (td, *J* = 9.1, 2.5 Hz, 1H), 6.41 (dd, *J* = 3.0, 0.9 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9 (d, *J* = 232.5 Hz), 133.4, 130.4, 128.7 (d, *J* = 10.3 Hz), 109.9 (d, *J* = 15 Hz), 109.7, 105.6 (d, *J* = 23.2 Hz), 100.9 (d, *J* = 4.7 Hz), 33.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -127.6.



1-methyl-1*H*-indole-5-carbonitrile[9] (5g); white solid, EtOAc/Hx=1:10, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.44 (dt, *J* = 8.4, 1.2 Hz,1H), 7.36 (d, *J* = 8.4, Hz 1H), 7.17 (d, *J* = 3.2 Hz, 1H), 6.57 (d, *J* = 3.2, Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 131.1, 128.2, 126.5, 124.5, 120.9, 110.1, 102.4, 102.2, 33.1.

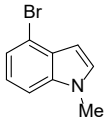


1-methyl-5-nitro-1*H*-indole[8] (5h); brown solid, MC/Hx=1:2, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, *J* = 2.3 Hz, 1H), 8.12 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.33 (d, *J* = 9.1 Hz, 1H), 7.21 (d, *J* = 3.3 Hz, 1H), 6.67 (d, *J* = 3.3 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.6, 139.4, 132.1, 127.6, 118.2, 117.2, 109.1, 103.9, 33.3.

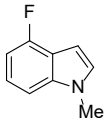


4-methoxy-1-methyl-1*H*-indole[1] (5i); colorless solid, EtOAc/Hx=1:60, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (t, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 6.0, 2.9 Hz, 2H), 6.57 (dd, *J* = 3.1, 0.9 Hz, 1H), 6.49 (d, *J* = 8.4,

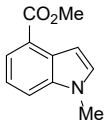
1H), 3.91 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 138.2, 127.3, 122.3, 119.0, 102.7, 99.2, 98.2, 55.3, 33.0.



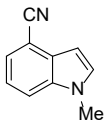
4-bromo-1-methyl-1*H*-indole[8] (5j); light yellow oil, EtOAc/PE=1:20, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 2H), 7.06 – 7.01 (m, 2H), 6.50 (d, *J* = 3.1, Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 129.4, 129.1, 122.3, 122.2, 114.8, 108.4, 101.2, 33.1.



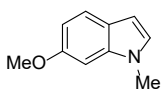
4-fluoro-1-methyl-1*H*-indole[8] (5k); yellow oil, EtOAc/Hx=1:40, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 – 6.94 (m, 2H), 6.85 (d, *J* = 3.2 Hz, 1H), 6.77 – 6.71 (m, 1H), 6.51 (d, *J* = 3.2, Hz, 1H), 3.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4 (d, *J* = 244.9 Hz), 139.4 (d, *J* = 11.6 Hz), 128.7, 121.9 (d, *J* = 7.7 Hz), 117.4 (d, *J* = 22.2 Hz), 105.4 (d, *J* = 3.5 Hz), 104.0 (d, *J* = 19.0 Hz), 96.9, 32.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -124.0.



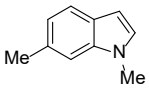
methyl 1-methyl-1*H*-indole-4-carboxylate[8] (5l); yellow oil, MC/Hx=1:2, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.17 (d, *J* = 3.1 Hz, 1H), 7.10 (d, *J* = 3.1 Hz, 1H), 3.97 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 137.5, 130.9, 128.0, 123.0, 121.5, 120.6, 114.0, 102.2, 51.7, 33.0.



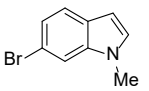
1-methyl-1*H*-indole-4-carbonitrile[9] (5m); white solid, EtOAc/PE=1:5, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 1H), 7.44 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.25 – 7.20 (m, 2H), 6.66 (dd, *J* = 3.1, 0.7 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3, 131.5, 129.6, 124.7, 121.0, 118.8, 114.0, 102.9, 100.0, 33.0.



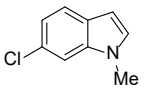
6-methoxy-1-methyl-1*H*-indole[4] (5n); orange oil, EtOAc/Hx=1:40, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 1H), 7.01 (d, *J* = 3.2 Hz, 1H), 6.89 – 6.85 (m, 2H), 6.51 – 6.48 (m, 1H), 3.96 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 137.3, 127.7, 122.6, 121.3, 109.2, 100.7, 92.6, 55.6, 32.6.



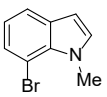
1,6-dimethyl-1*H*-indole[8] (5o); yellow oil, EtOAc/Hx=1:40, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 6.94 – 6.92 (m, 2H), 6.41 (d, *J* = 3.0 Hz, 1H), 3.71 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1, 131.3, 128.2, 126.3, 121.1, 120.5, 109.2, 100.7, 32.7, 21.9.



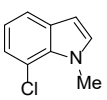
6-bromo-1-methyl-1*H*-indole[9] (5p); yellow oil, EtOAc/Hx=1:7, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H), 7.19 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.00 (d, *J* = 3.1 Hz, 1H), 6.44 (dd, *J* = 3.1, 0.9 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 129.5, 127.3, 122.5, 122.1, 115.2, 112.3, 101.2, 32.9.



6-chloro-1-methyl-1*H*-indole[1] (5q); yellow oil, EtOAc/Hx=1:60, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.05 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.98 (d, *J* = 3.1 Hz, 1H), 6.43 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1, 129.5, 127.5, 127.0, 121.7, 119.9, 109.2, 101.1, 32.8.

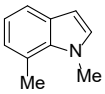


7-bromo-1-methyl-1*H*-indole[9] (5r); yellow oil, MC/Hx=1:5, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.34 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.00 (d, *J* = 3.2, 1H), 6.91 (t, *J* = 7.7 Hz, 1H), 6.46 (d, *J* = 3.3, Hz, 1H), 4.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.04, 131.8, 131.7, 126.5, 120.5, 120.4, 103.9, 101.2, 36.9.

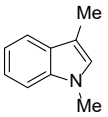


7-chloro-1-methyl-1*H*-indole (5s); yellow oil, EtOAc/Hx=1:10, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.12 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.98 – 6.93 (m, 2H), 6.45 (d, *J* = 3.1 Hz, 1H),

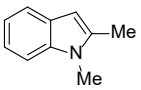
4.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.0, 131.7, 131.5, 123.0, 120.1, 119.7, 117.0, 101.3, 36.8. HRMS (EI) m/z calcd. For C_9H_8NCl $[M]^+$: 165.0345, found 165.0343.



1,7-dimethyl-1*H*-indole[1] (5t); colorless solid, MC/Hx=1:7, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.03 – 6.93 (m, 3H), 6.47 (d, *J* = 3.1 Hz, 1H), 4.10 (s, 3H), 2.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 130.4, 129.6, 124.1, 121.2, 119.6, 119.1, 100.9, 36.8, 19.7.

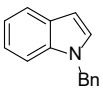


1,3-dimethyl-1*H*-indole[8] (5u); light yellow liquid, MC/Hx=1:2, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.80 (s, 1H), 3.70 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 128.7, 126.5, 121.4, 119.0, 118.5, 110.1, 109.0, 32.5, 9.6.



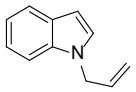
1,2-dimethyl-1*H*-indole[8] (5v); yellow solid, EtOAc/Hx=1:2, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 8.8 Hz, 1H), 7.14 (t, *J* = 7.1 Hz, 1H), 7.05 (t, *J* = 6.9 Hz, 1H), 6.23 (s, 1H), 3.63 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 136.8, 127.9, 120.4, 119.6, 119.2, 108.7, 99.5, 29.4, 12.8.

1-ethyl-1*H*-indole[10] (5w); colorless liquid, EtOAc/Hx=1:10, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 3.6 Hz, 1H), 4.12 (q, *J* = 6.9 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 128.6, 127.0, 121.3, 121.0, 119.2, 109.3, 101.0, 40.9, 15.5.

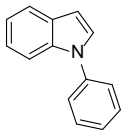


1-benzyl-1*H*-indole[10] (5x); white solid, MC/Hx=1:4, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.21 (m, 4H), 7.16 (td, *J* = 7.5, 0.8 Hz, 1H), 7.14 – 1.09 (m, 4H), 6.55 (d, *J* = 3.0 Hz, 1H),

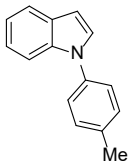
5.30 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 136.3, 129.6, 128.8, 128.3, 127.6, 126.8, 121.7, 121.0, 119.6, 109.7, 101.7, 50.1.



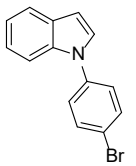
1-allyl-1*H*-indole[10] (5y); colorless oil, MC/Hx=1:7, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.12 – 7.06 (m, 2H), 6.50 (dd, *J* = 3.1, 0.7 Hz, 1H), 6.01 – 5.90 (m, 1H), 5.18 – 5.14 (m, 1H), 5.09 – 5.02 (m, 1H), 4.70 – 4.67 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 133.5, 128.7, 127.8, 121.5, 121.0, 119.4, 117.2, 109.6, 101.4, 48.8.



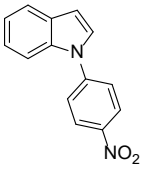
1-phenyl-1*H*-indole[10] (5z); white solid, PE/Hx=1:1, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.8, 1.9 Hz, 1H), 7.55 (d, *J* = 7.6, 1H), 7.47 – 7.45 (m, 4H), 7.33 – 7.20 (m, 2H), 7.19 – 7.15 (m, 2H), 6.67 (q, *J* = 3.0, 0.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.8, 135.8, 129.6, 129.3, 127.9, 126.4, 124.3, 122.4, 121.1, 120.4, 110.5, 103.6.



1-(*p*-tolyl)-1*H*-indole[11] (5aa); yellow oil, EtOAc/Hx=1:10, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.22 – 7.11 (m, 2H), 6.65 (d, *J* = 3.2 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 136.3, 136.0, 130.1, 129.2, 128.1, 124.3, 122.2, 121.1, 120.2, 110.5, 103.2, 21.0.



1-(4-bromophenyl)-1*H*-indole[12] (5ab); yellow oil, EtOAc/Hx=1:10, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 1H), 7.61 – 7.51 (m, 2H), 7.51 – 7.49 (m, 1H), 7.35 – 7.33 (m, 2H), 7.25 – 7.17 (m, 3H), 6.67 (d, *J* = 2.8 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 135.6, 132.7, 129.4, 127.6, 125.7, 122.6, 121.3, 120.6, 119.7, 110.3, 104.2.



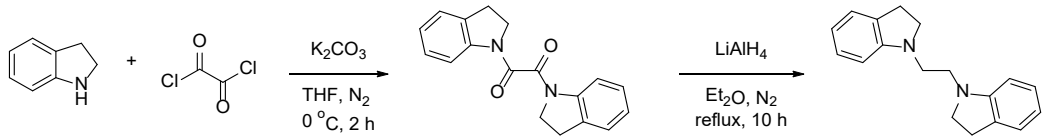
1-(4-nitrophenyl)-1*H*-indole[13] (5ac); yellow solid, EtOAc/Hx=1:10, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 9.0 Hz, 2H), 7.71 – 7.63 (m, 4H), 7.36 (d, *J* = 3.4 Hz, 1H), 7.31 – 7.21 (m, 2H), 6.76 (d, *J* = 3.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 145.0, 135.3, 130.1, 127.1, 125.5, 123.4, 123.3, 121.7, 121.6, 110.5, 106.2.

6. Scale-up process for 5-methoxy-1-methyl-1*H*-indole

A 250 mL round-bottle flask, which was equipped with a magnetic stir bar and charged with CuCl (0.1 equiv., 0.7 mmol), DMAP (0.2 equiv., 1.4 mmol), and **1** (0.2 equiv., 1.4 mmol), was evacuated and backfilled with oxygen (this process was repeated three times). After 4.0 mL of acetonitrile was added, 5-methoxy-1-methylindoline **4b** (7.0 mmol) and 10 mL of acetonitrile were added in sequence. The reaction mixture was stirred at 40 °C for 18 h. The reaction was quenched with saturated aqueous NH_4Cl solution, washed with water, and extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel (EtOAc/Hx=1:5) to give the desired indole **5b**.

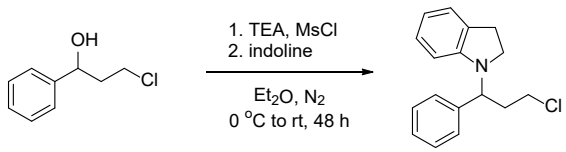
7. Synthesis of indolines 4af and 4ag for the synthesis of biologically active compounds

Synthesis of 4af



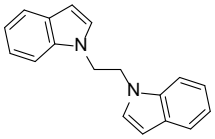
Indoline **4af** was prepared by the known procedure.[14]

Synthesis of 4ag

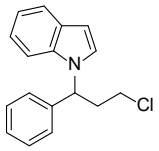


Indoline **4ag** was prepared by the known procedure.[15]

8. Charaterizations of 5af and 5ag



1,2-di(1*H*-indol-1-yl)ethane[14] (5af); colorless oil, EtOAc/Hx=1:10, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 2H), 7.17 – 7.15 (m, 4H), 7.10 (t, *J* = 6.5 Hz, 2H), 6.50 (d, *J* = 3.2 Hz, 2H), 6.35 (d, *J* = 3.2 Hz, 2H), 4.34 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 128.8, 128.0, 121.7, 121.2, 119.7, 108.7, 101.8, 46.1.



1-(3-chloro-1-phenylpropyl)-1*H*-indole[15] (5ag); colorless liquid, EtOAc/Hx=1:10, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.07 (m, 9H), 6.57 (d, *J* = 3.2 Hz, 1H), 5.81 (dd, *J* = 9.3, 5.9 Hz, 1H), 3.48 (dt, *J* = 11.2, 5.6 Hz, 1H), 3.37 – 3.30 (m, 1H), 2.80 – 2.73 (m, 1H), 2.70 – 2.63 (m, 1H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 136.3, 128.9, 128.7, 127.9, 126.4, 124.9, 121.8, 121.0, 119.8, 110.0, 102.5, 56.3, 41.5, 37.5.

9. References

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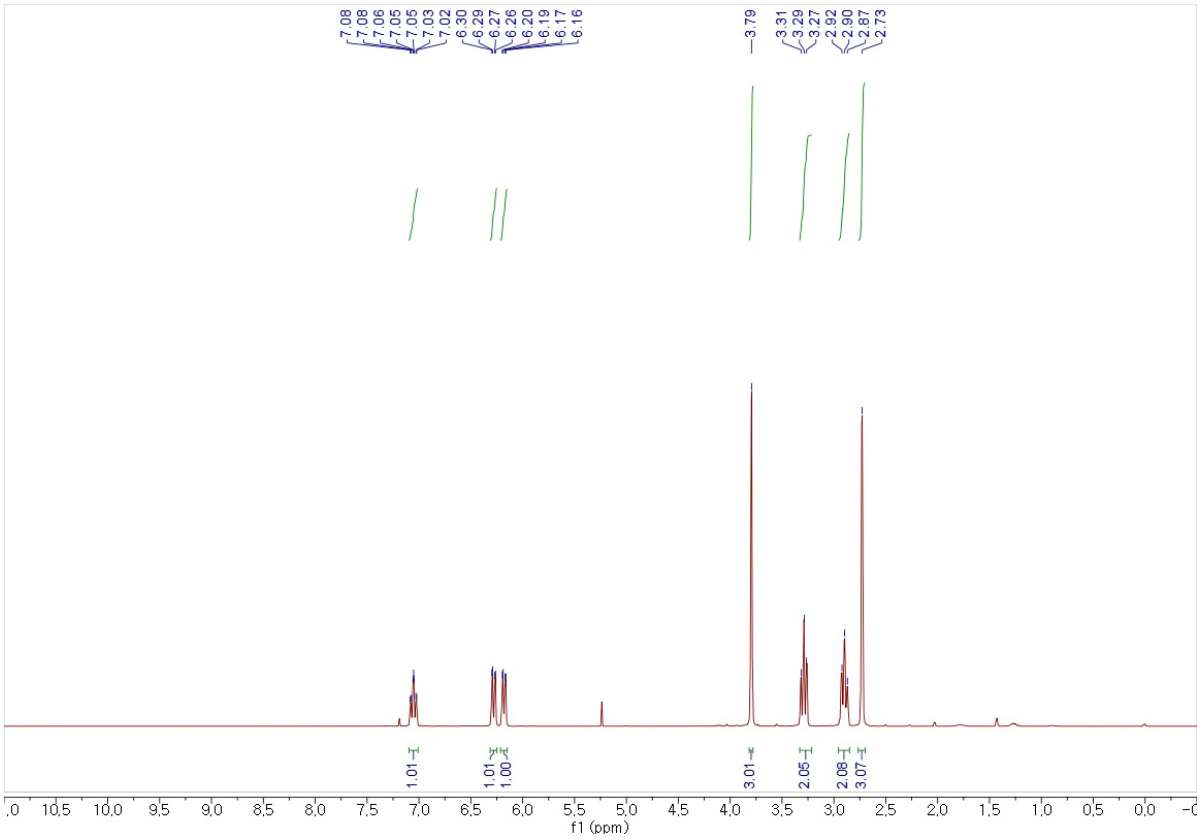
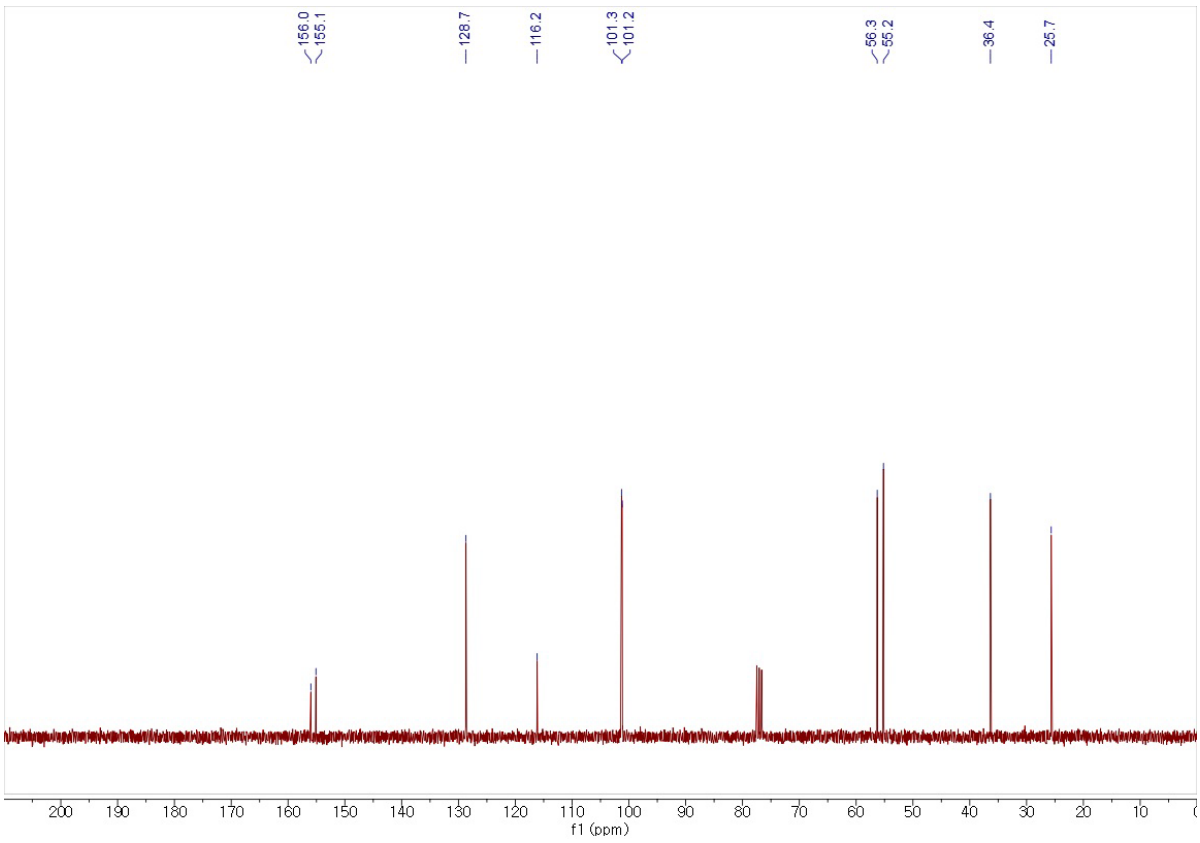
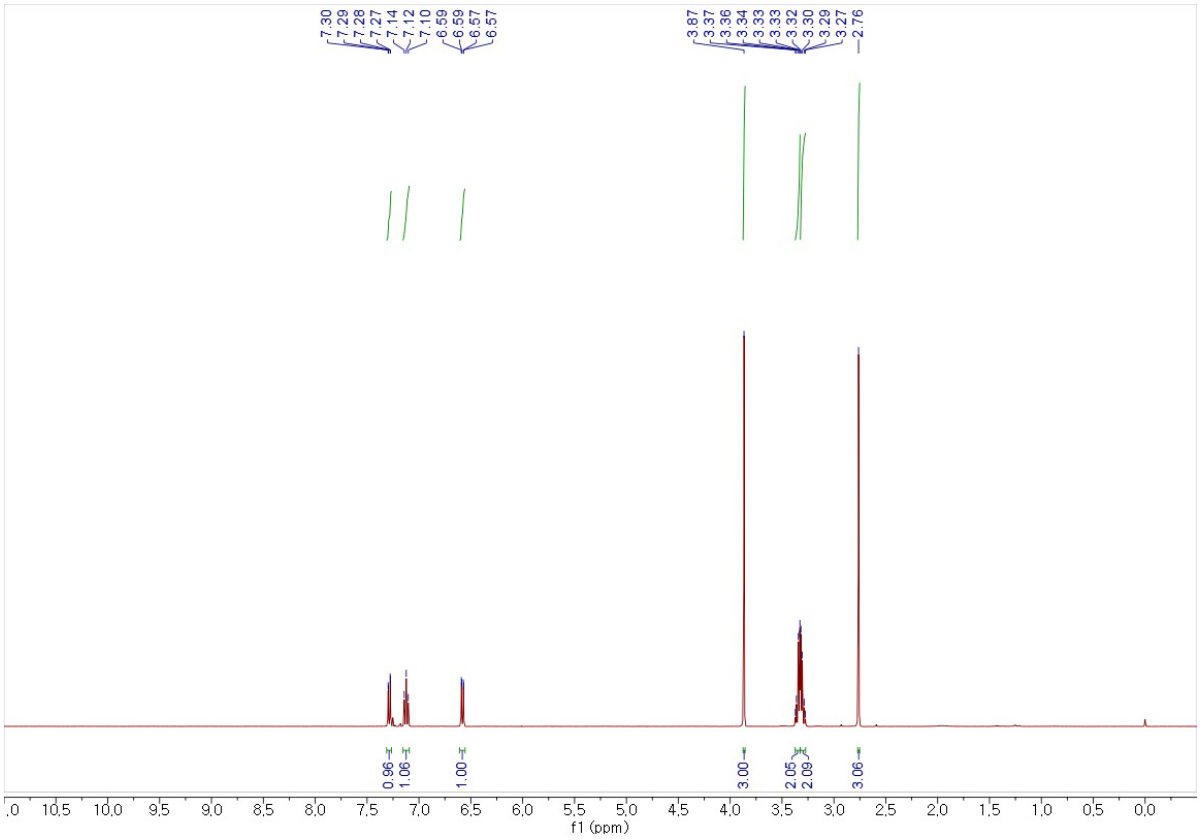
10. ^{1}H, ^{13}C, and ^{19}F NMR spectra

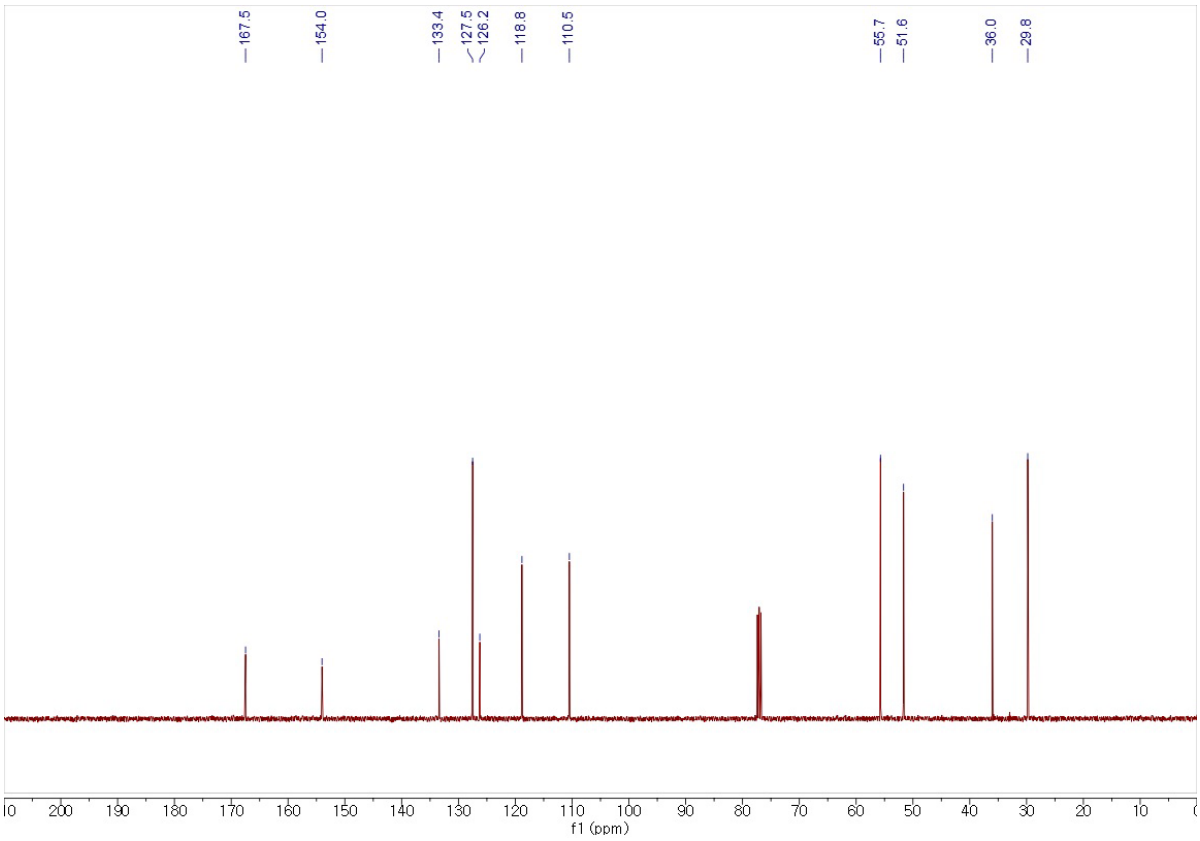
4-methoxy-1-methylindoline (4i)



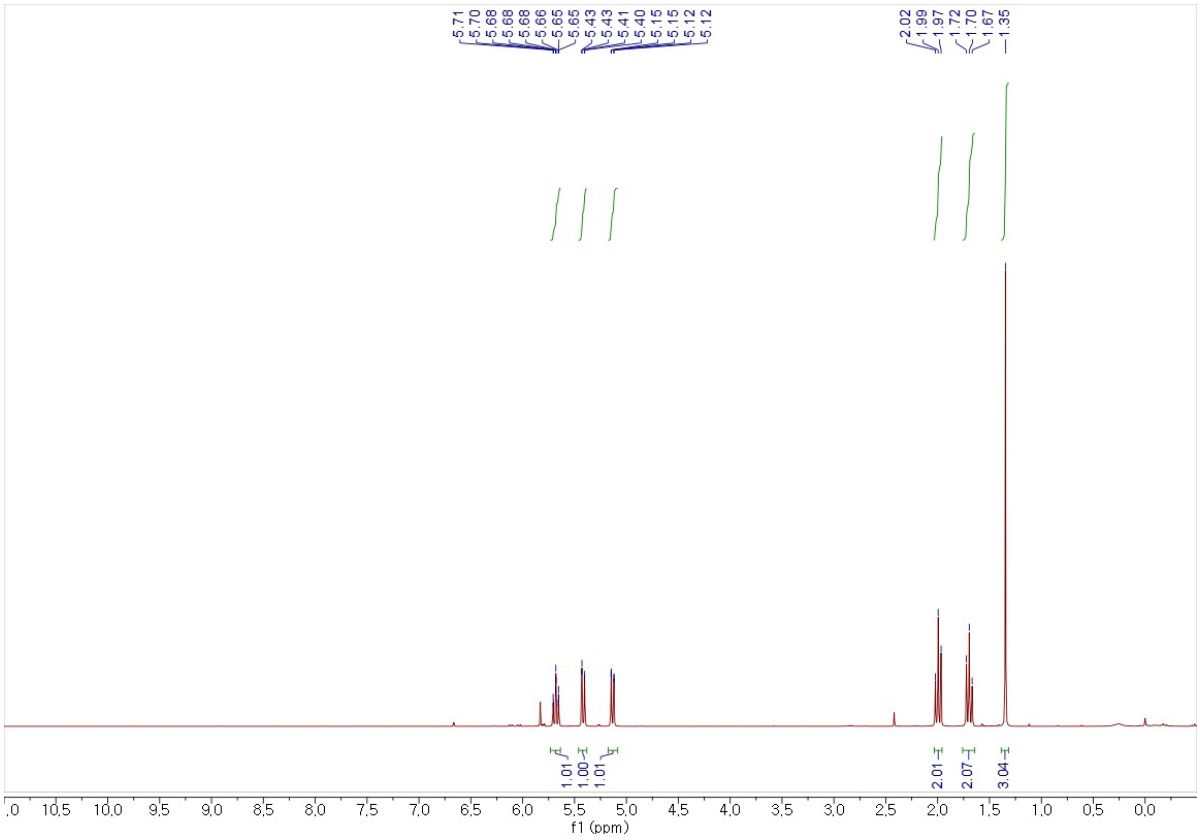


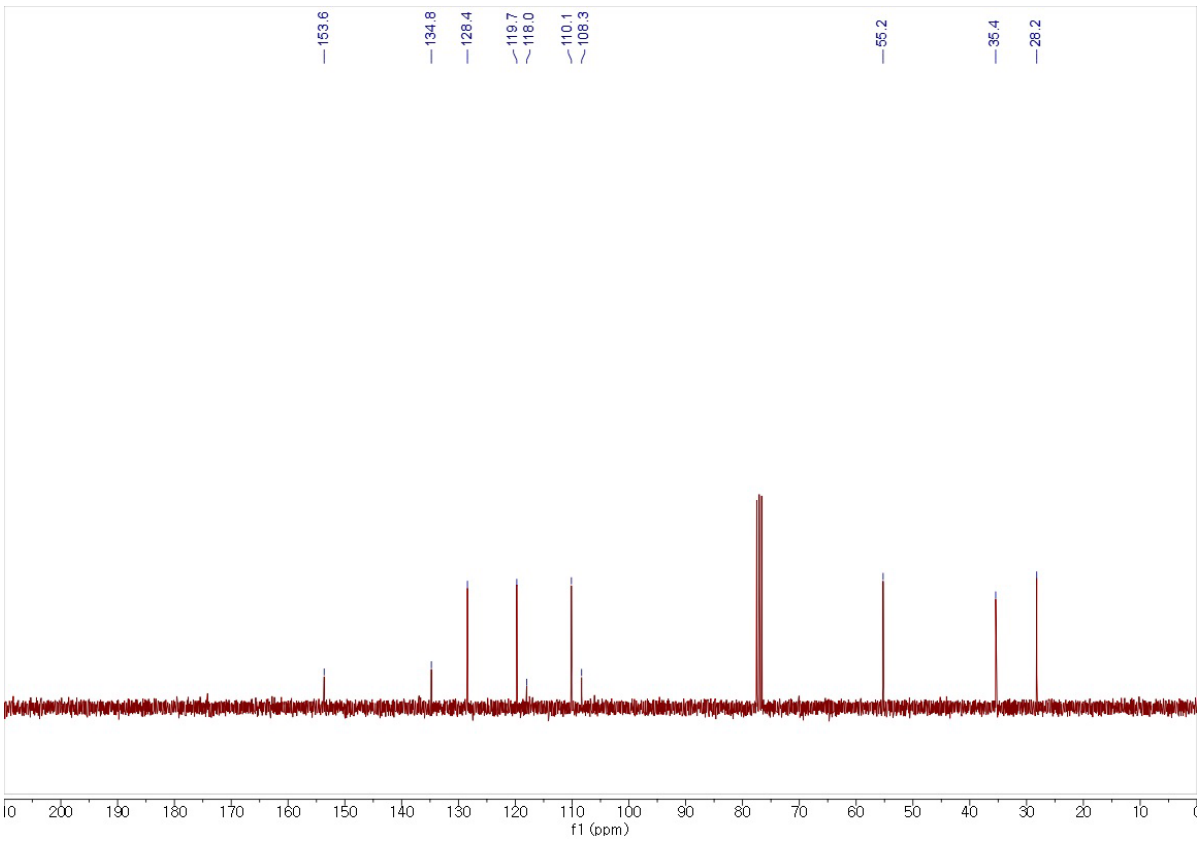
methyl-1-methylindoline-4-carboxylate (4l)





1-methylindoline-4-carbonitrile (4m)





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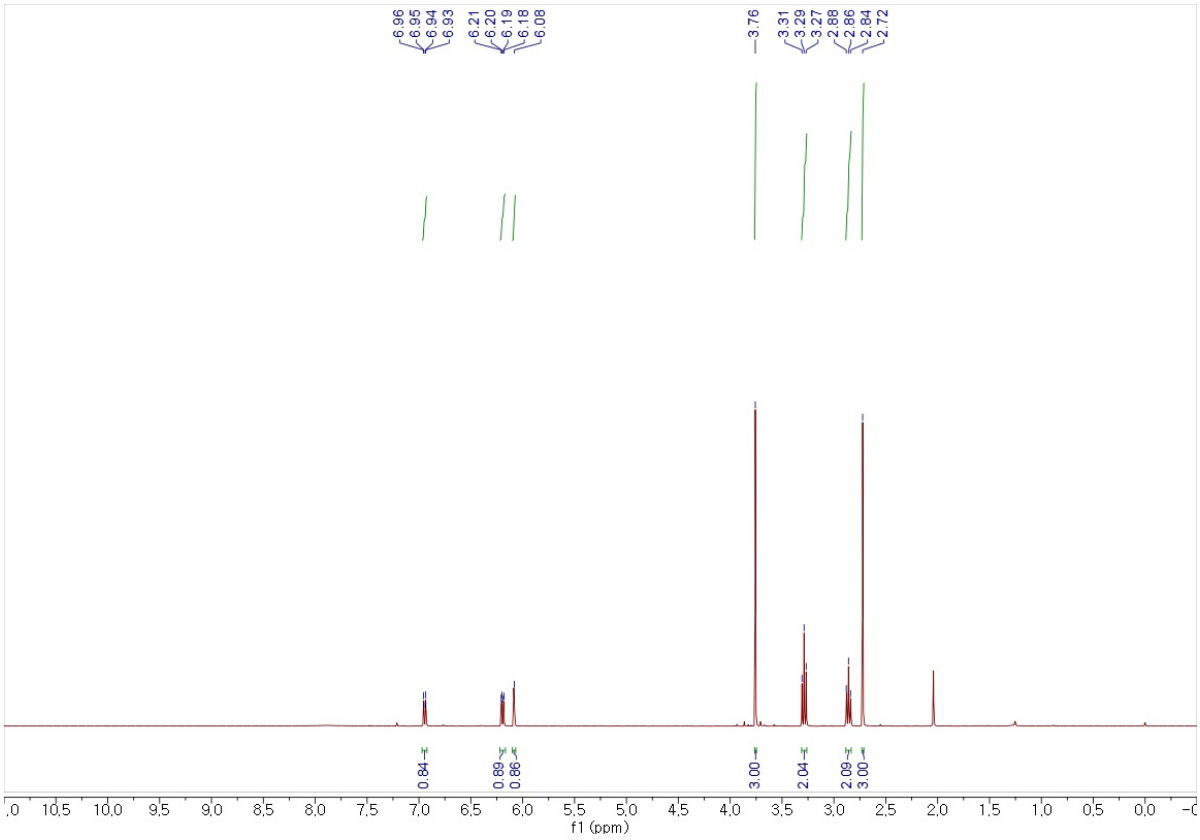
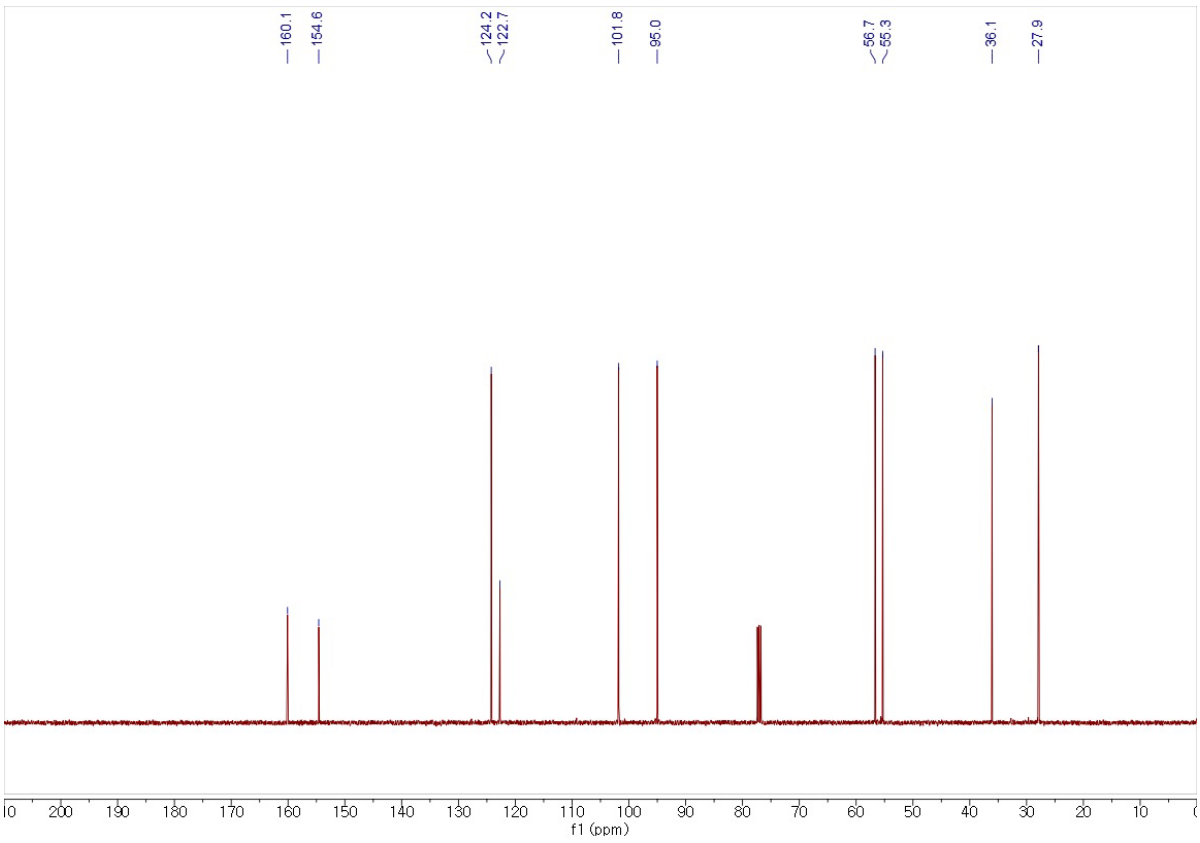
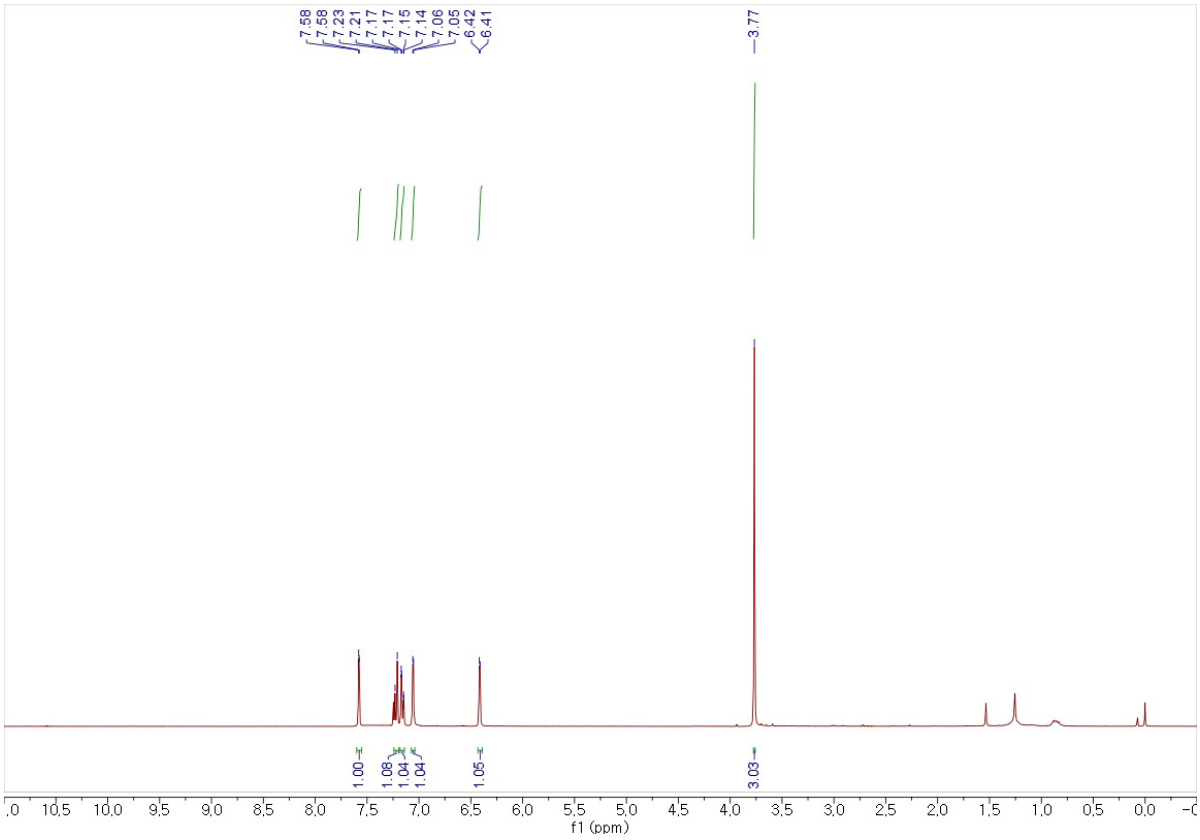
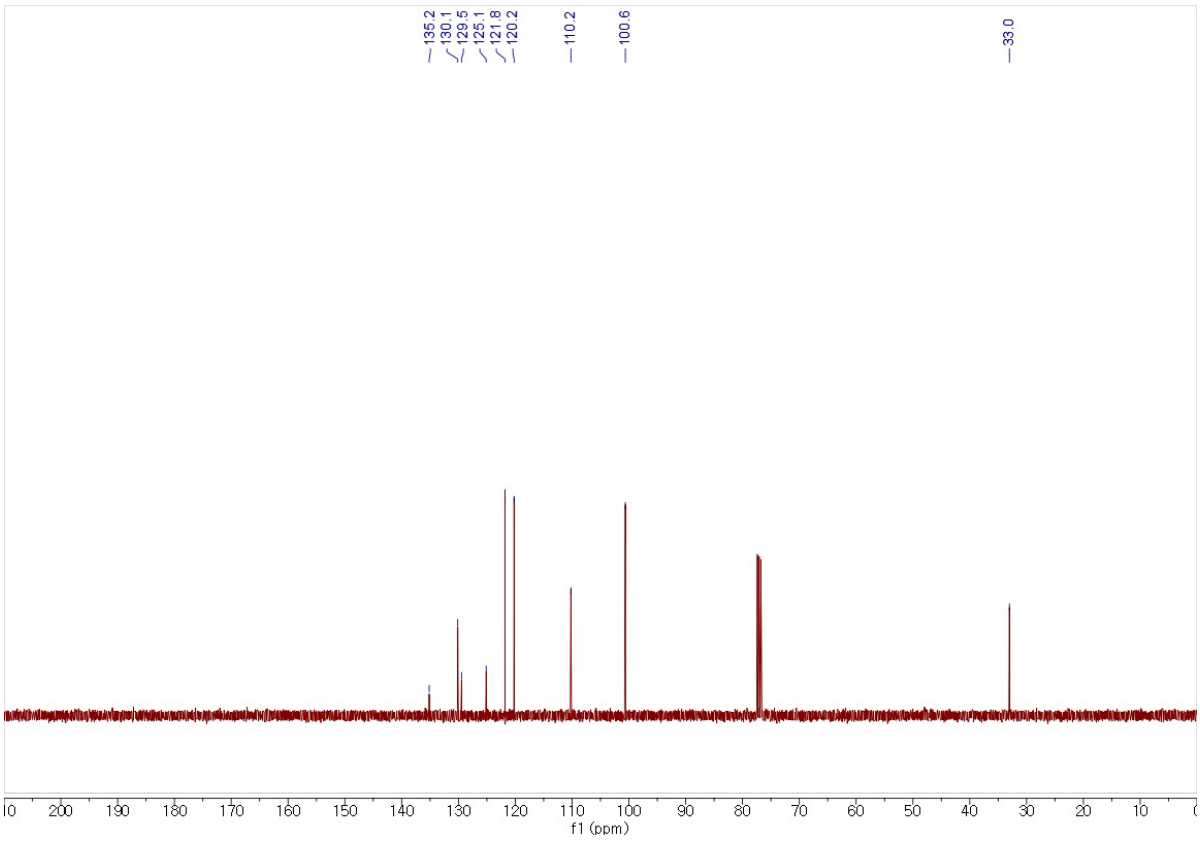




5-chloro-1-methyl-1*H*-indole (5a)





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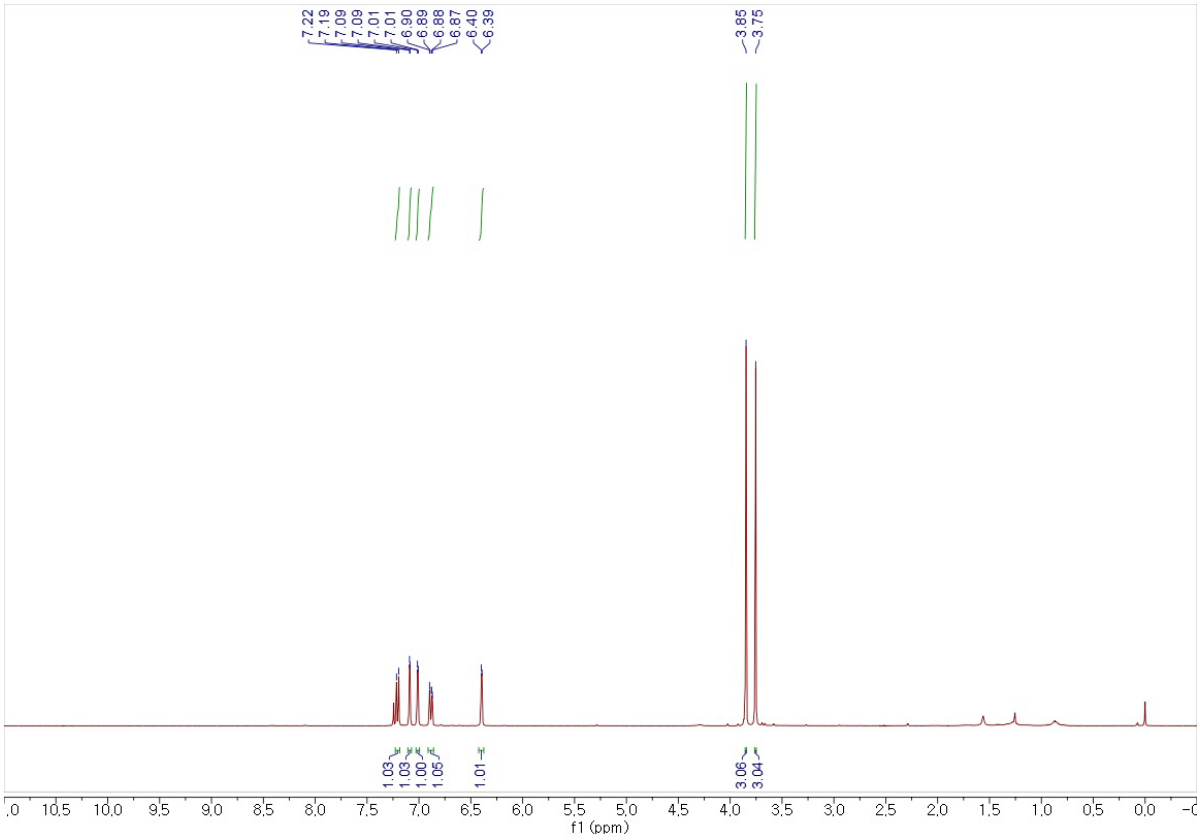
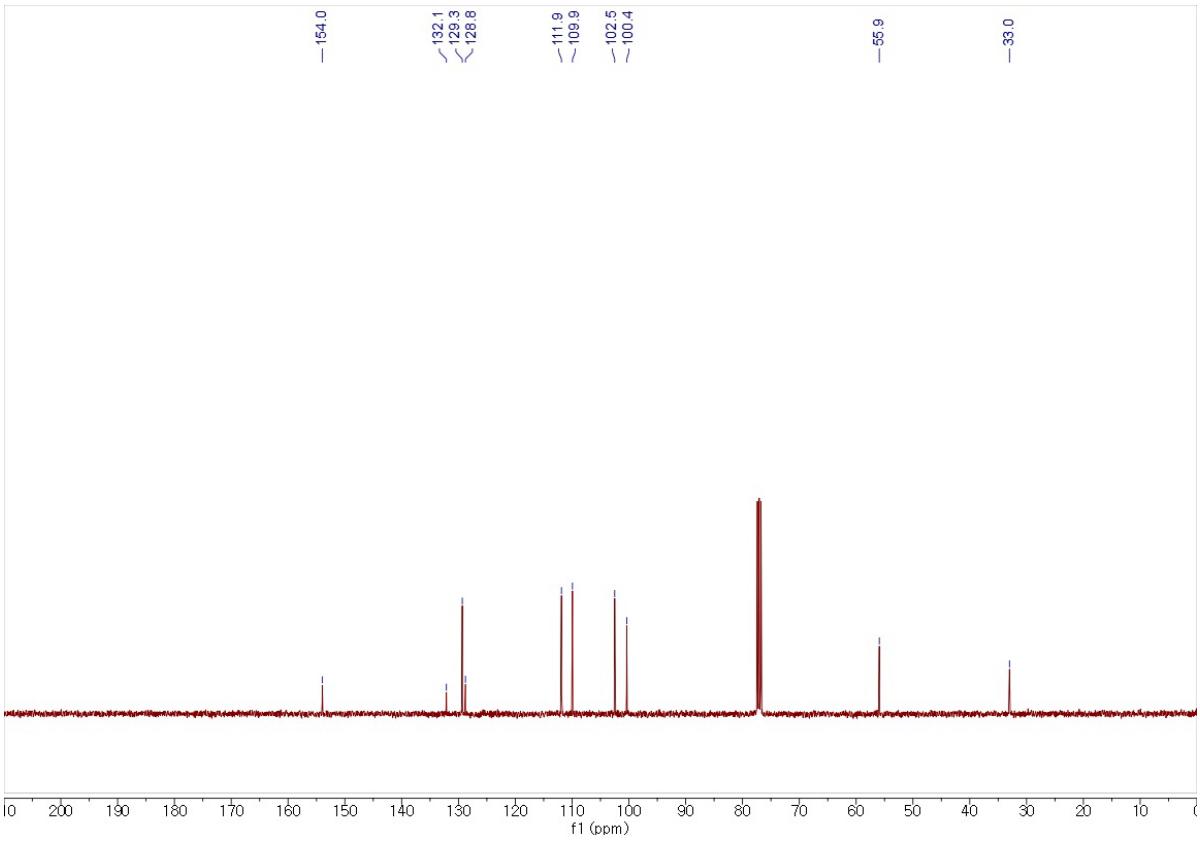
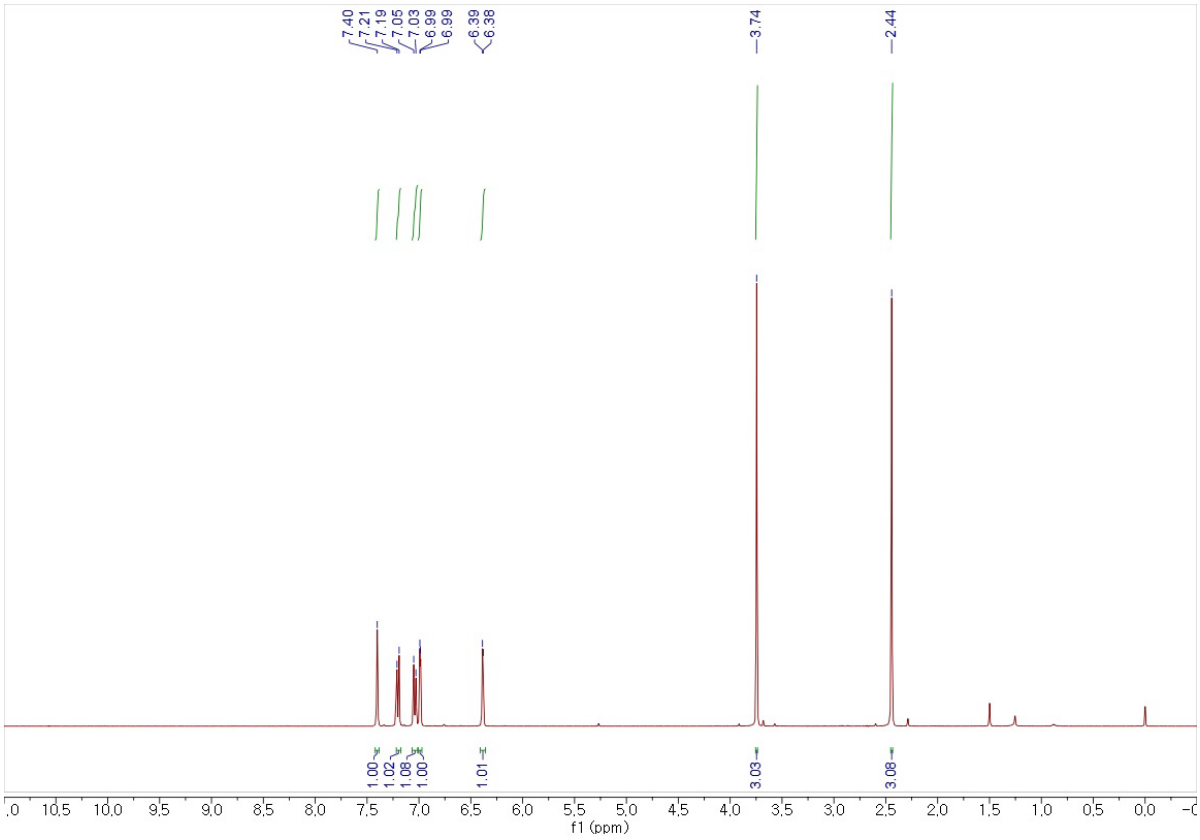
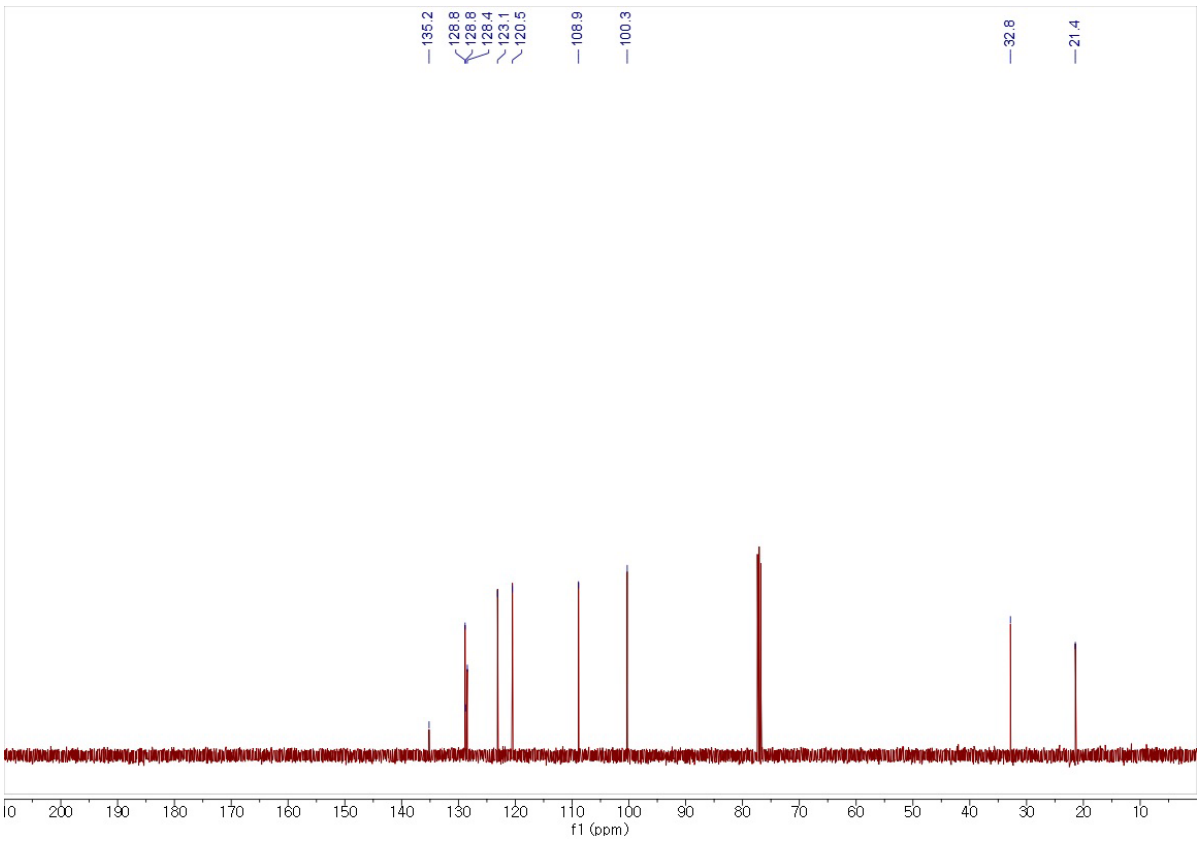




1,5-dimethyl-1*H*-indole (5c)





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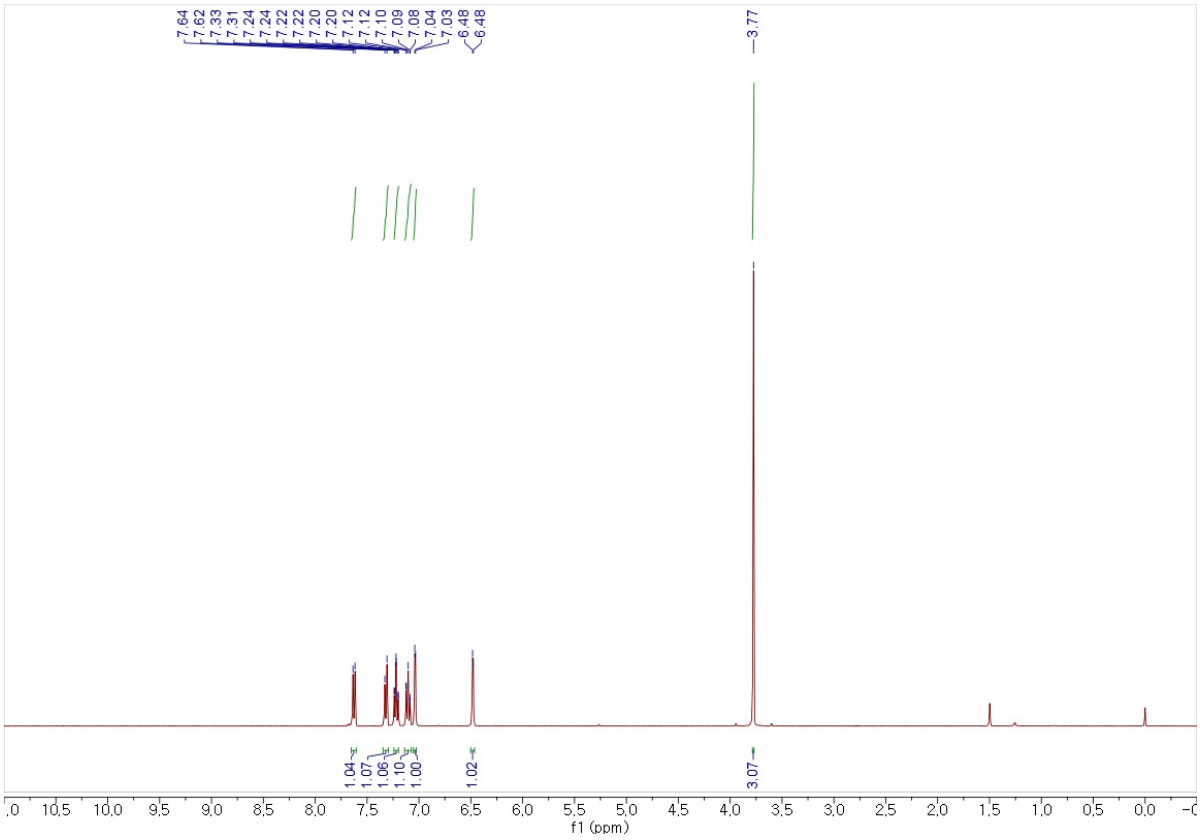

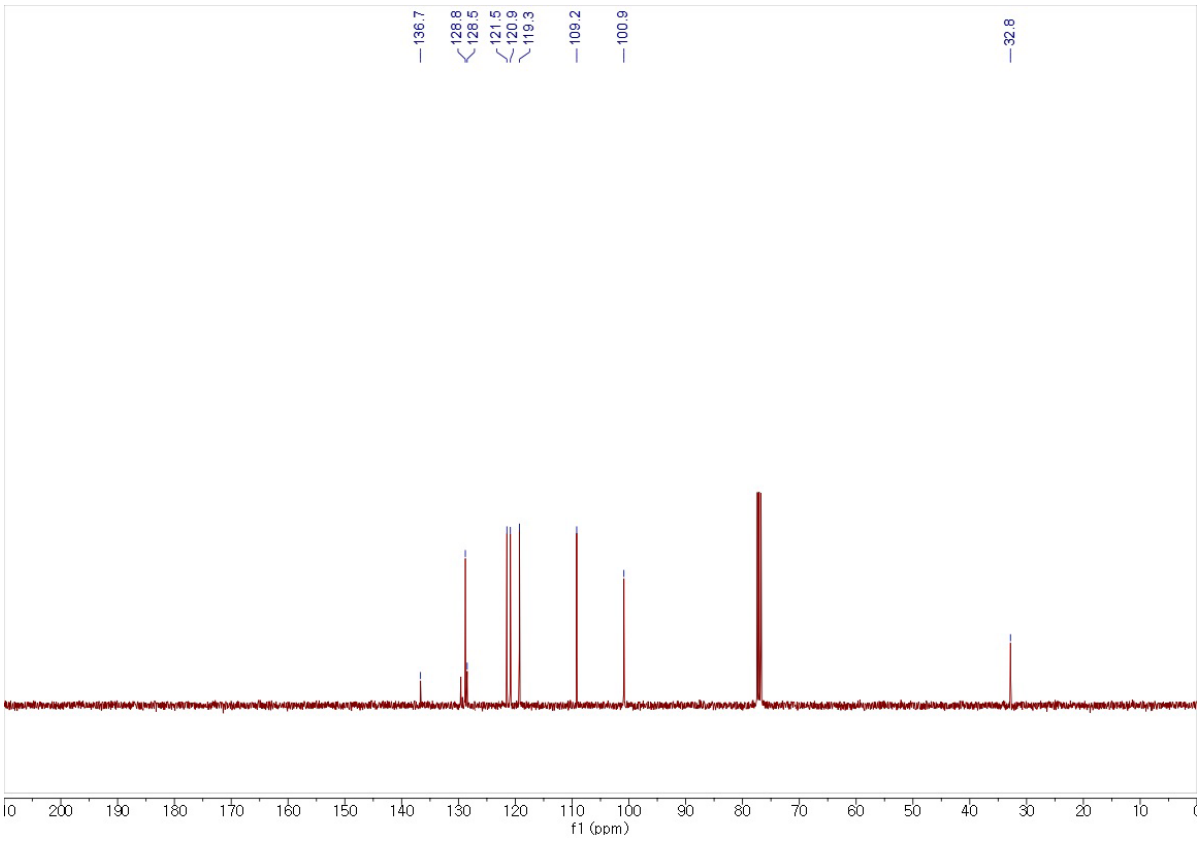

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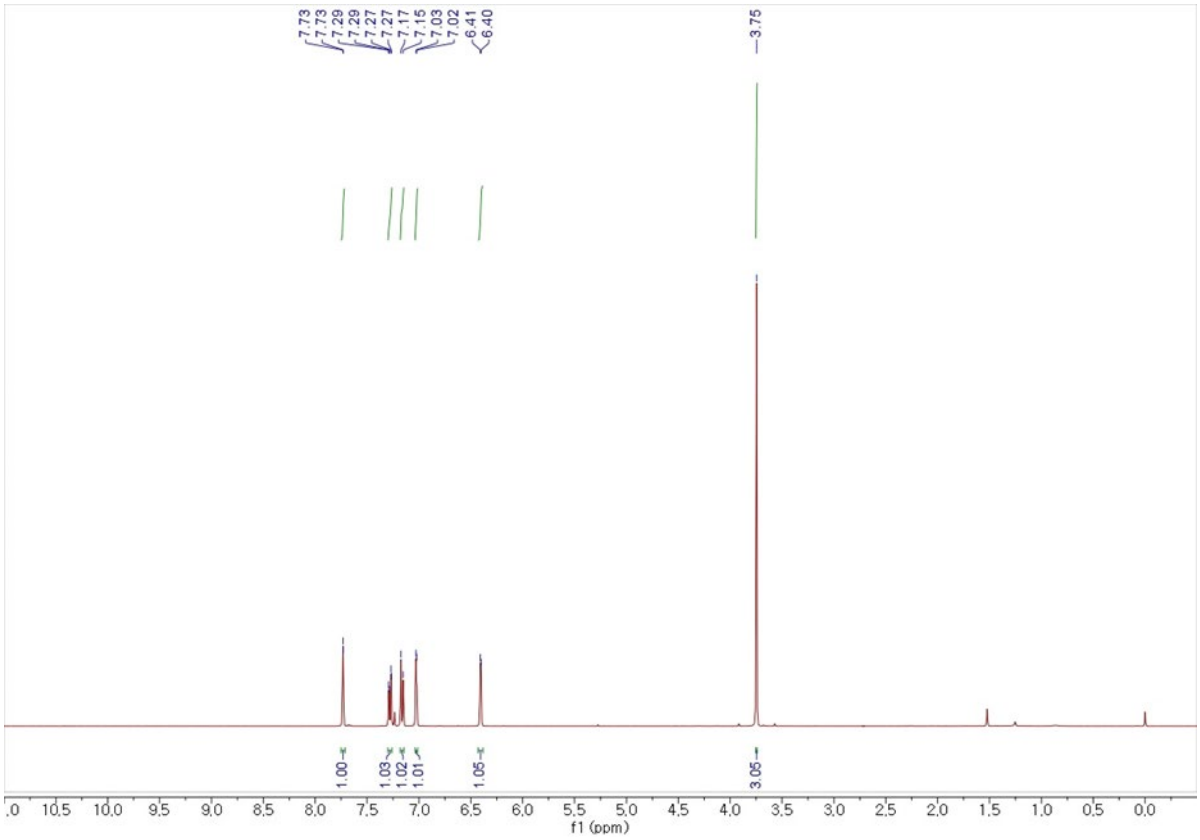

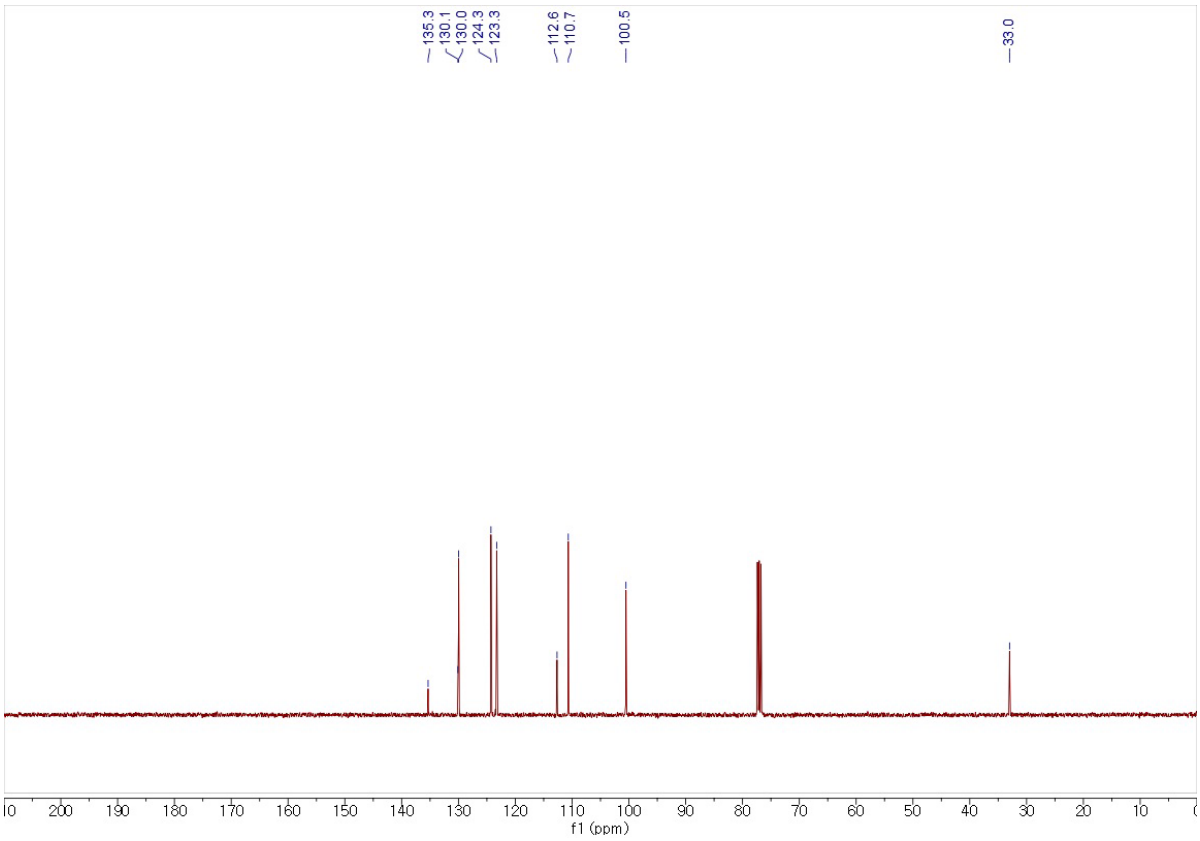

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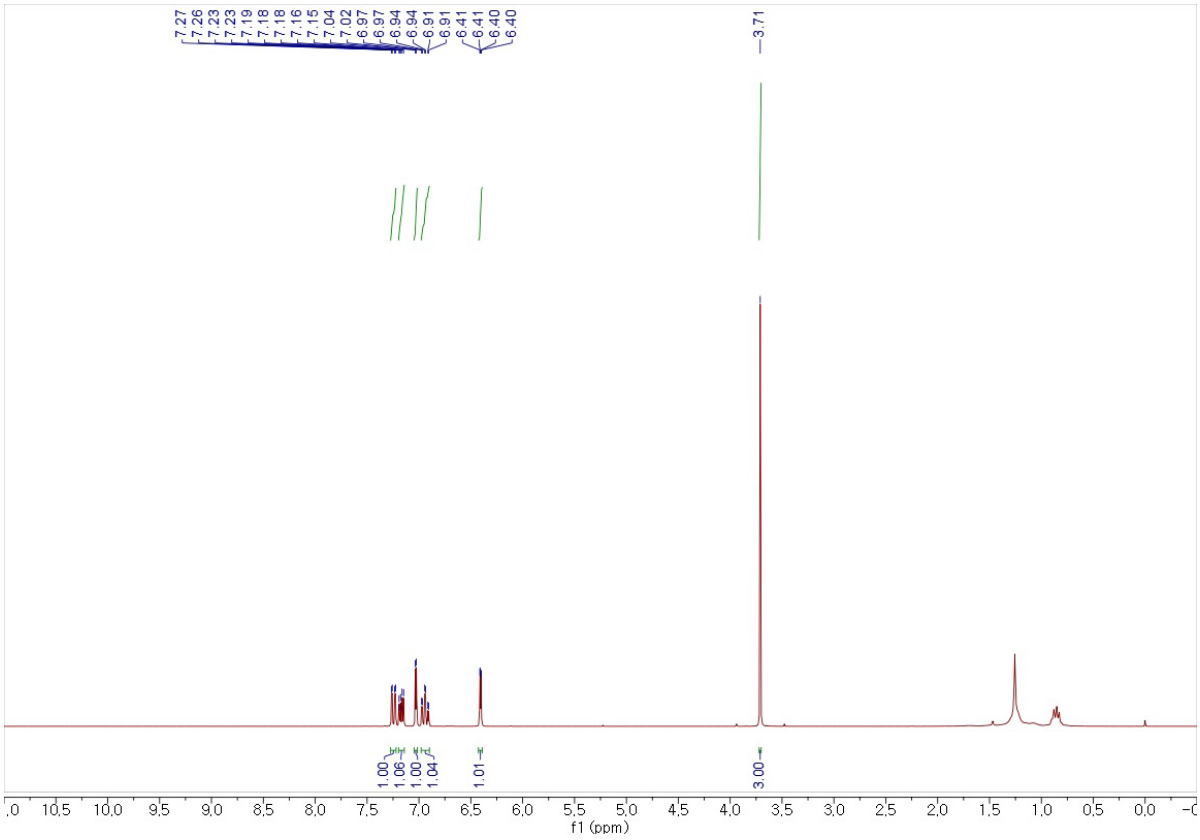

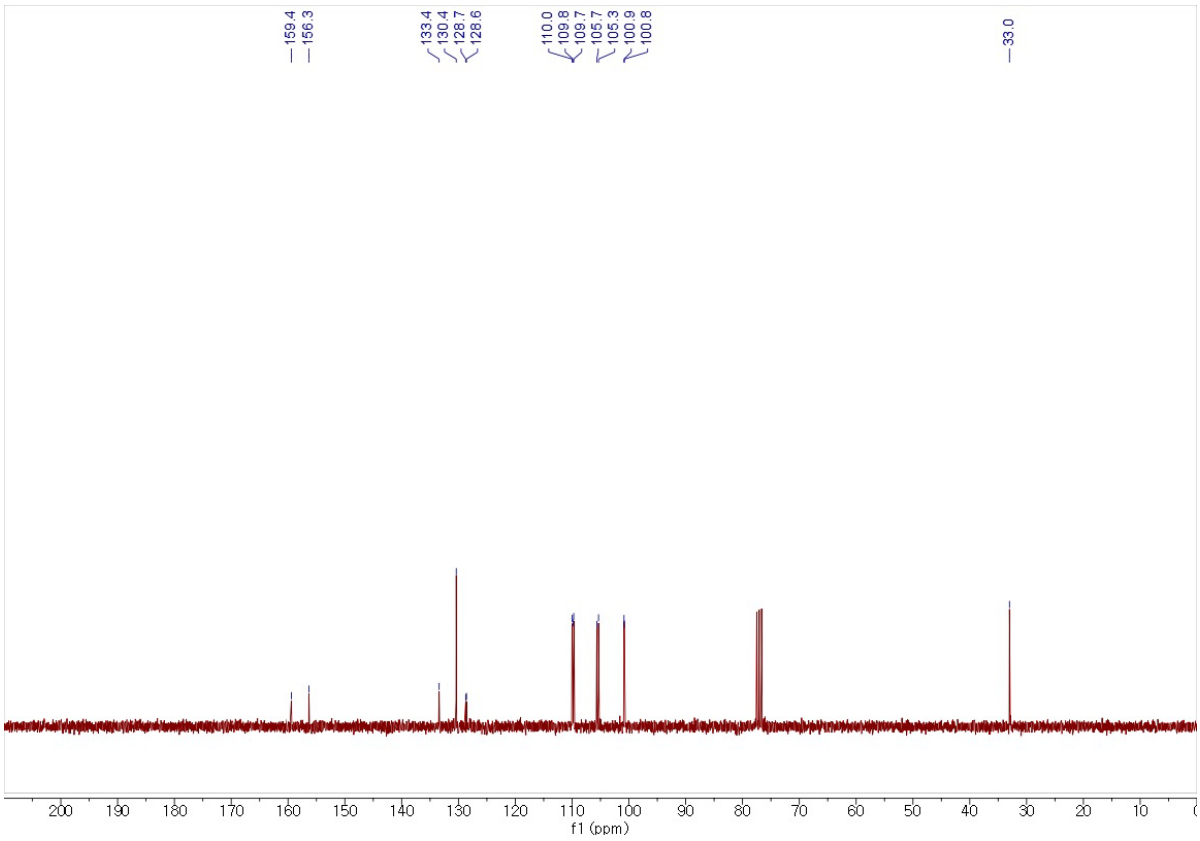

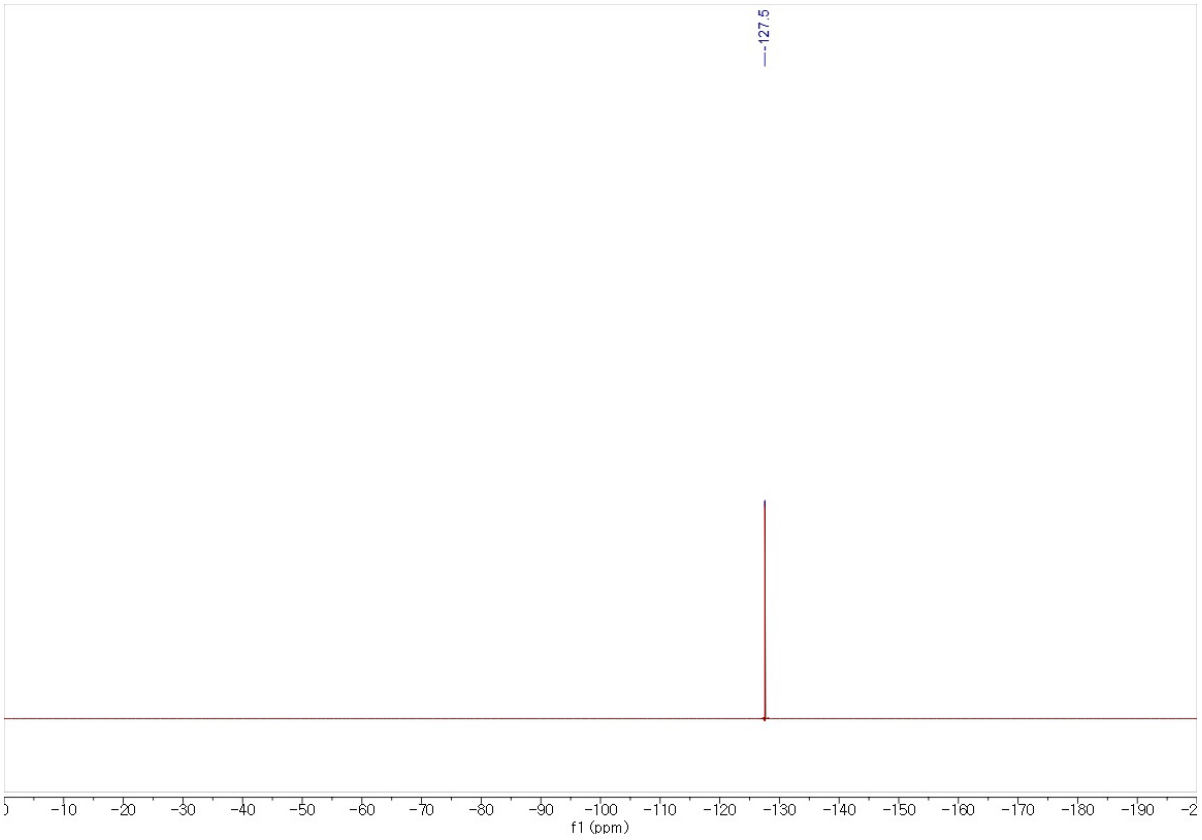
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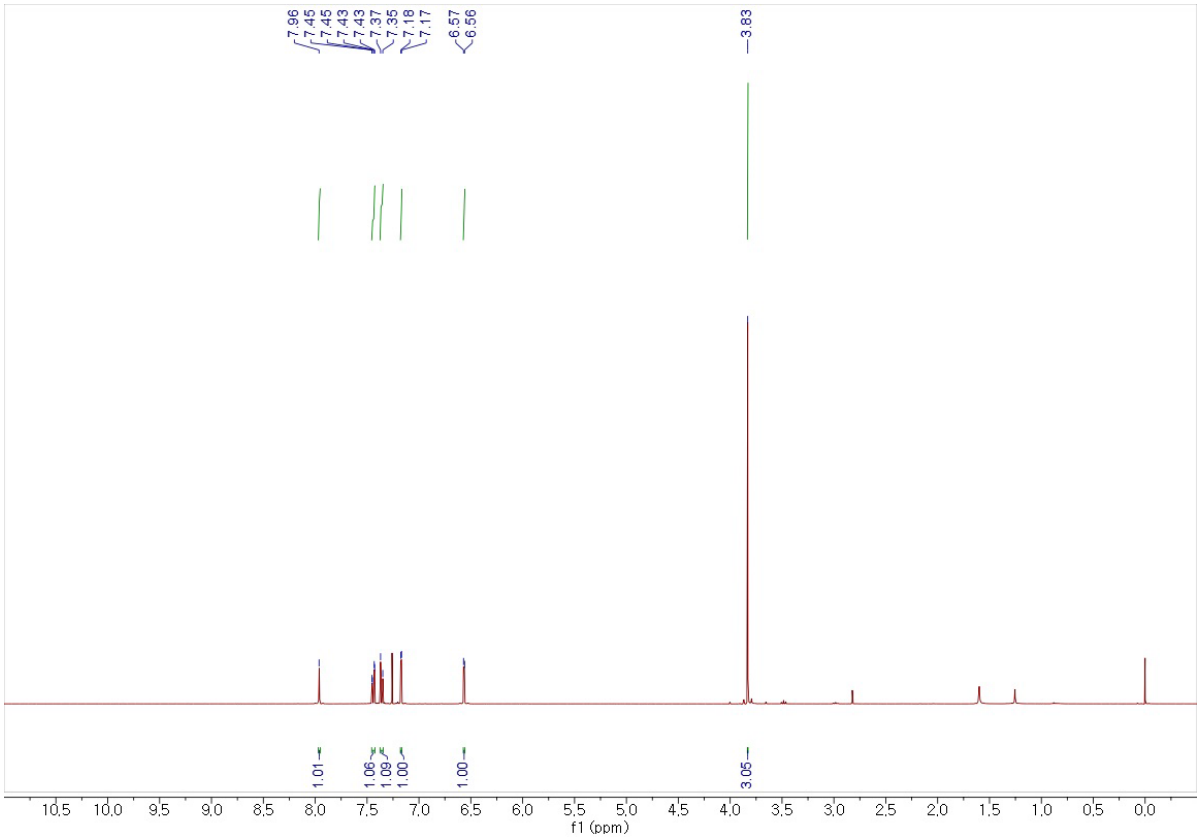
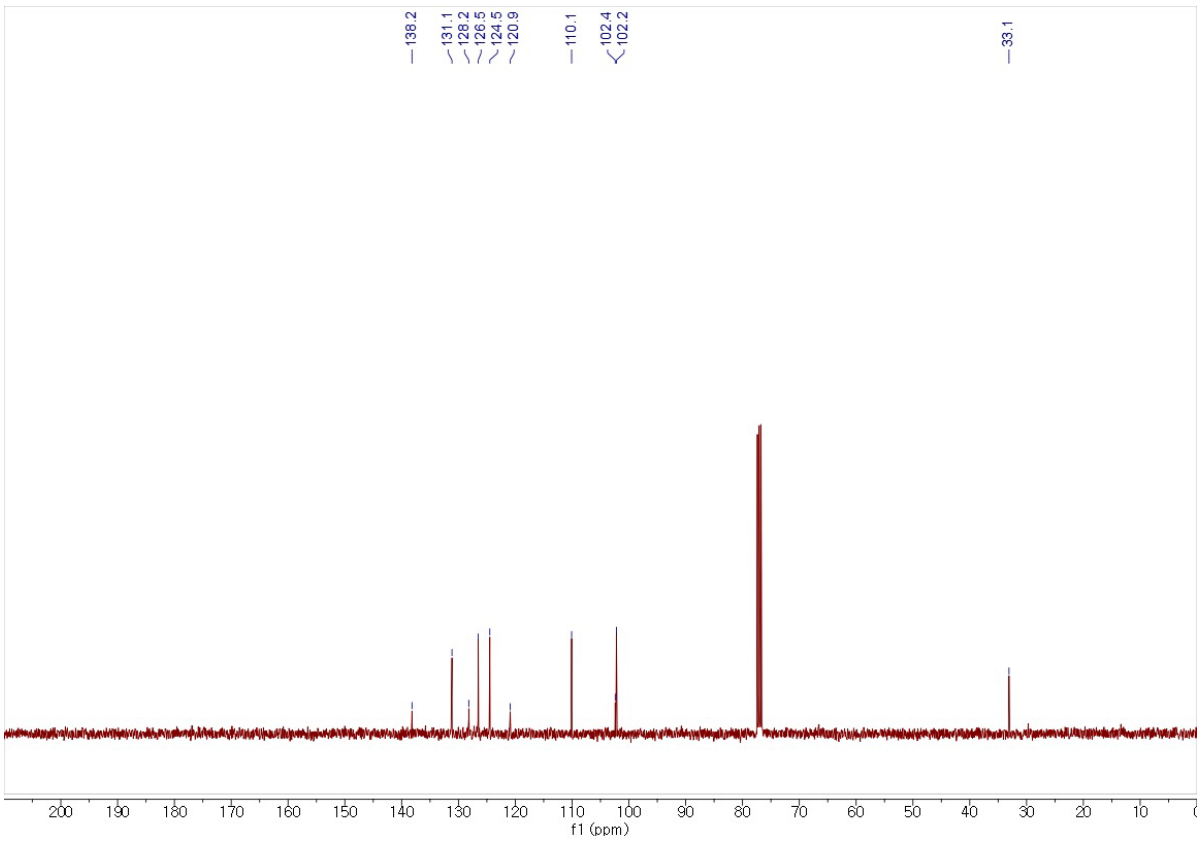
f1 (ppm)

1-methyl-1*H*-indole-5-carbonitrile (5g)





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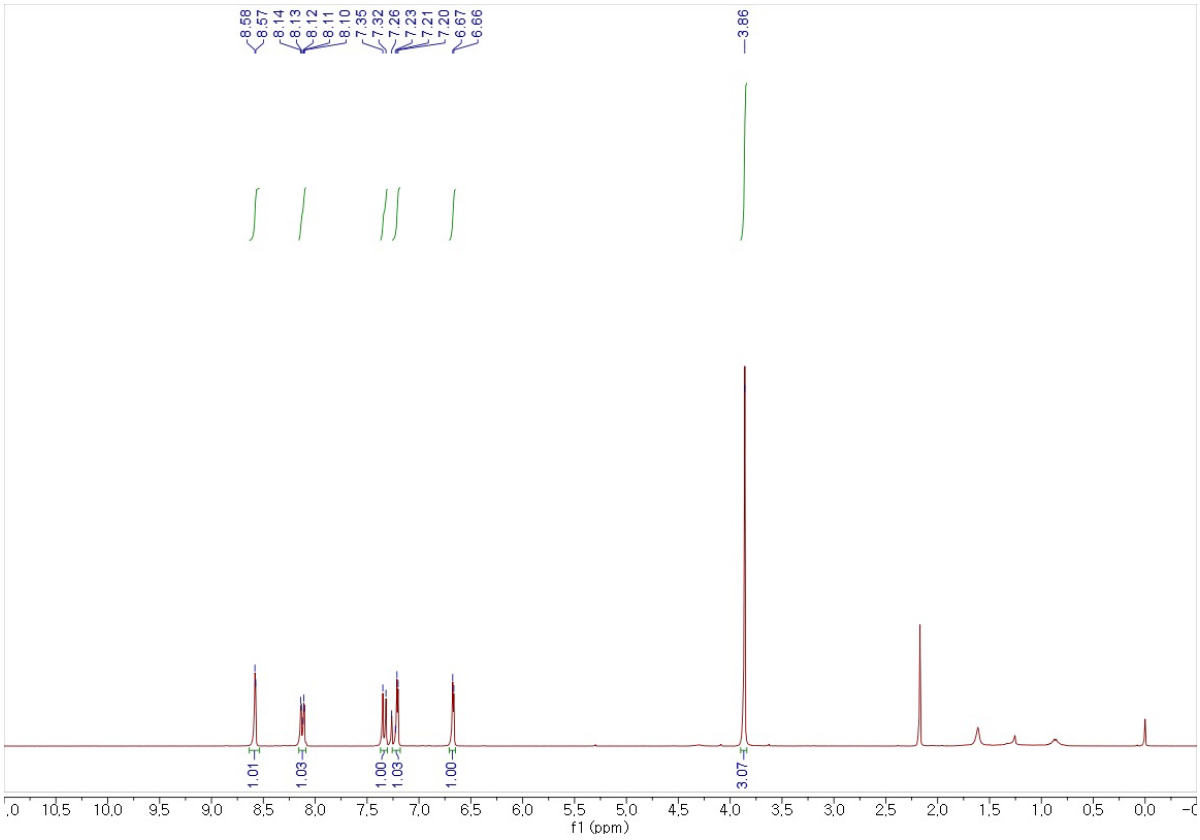

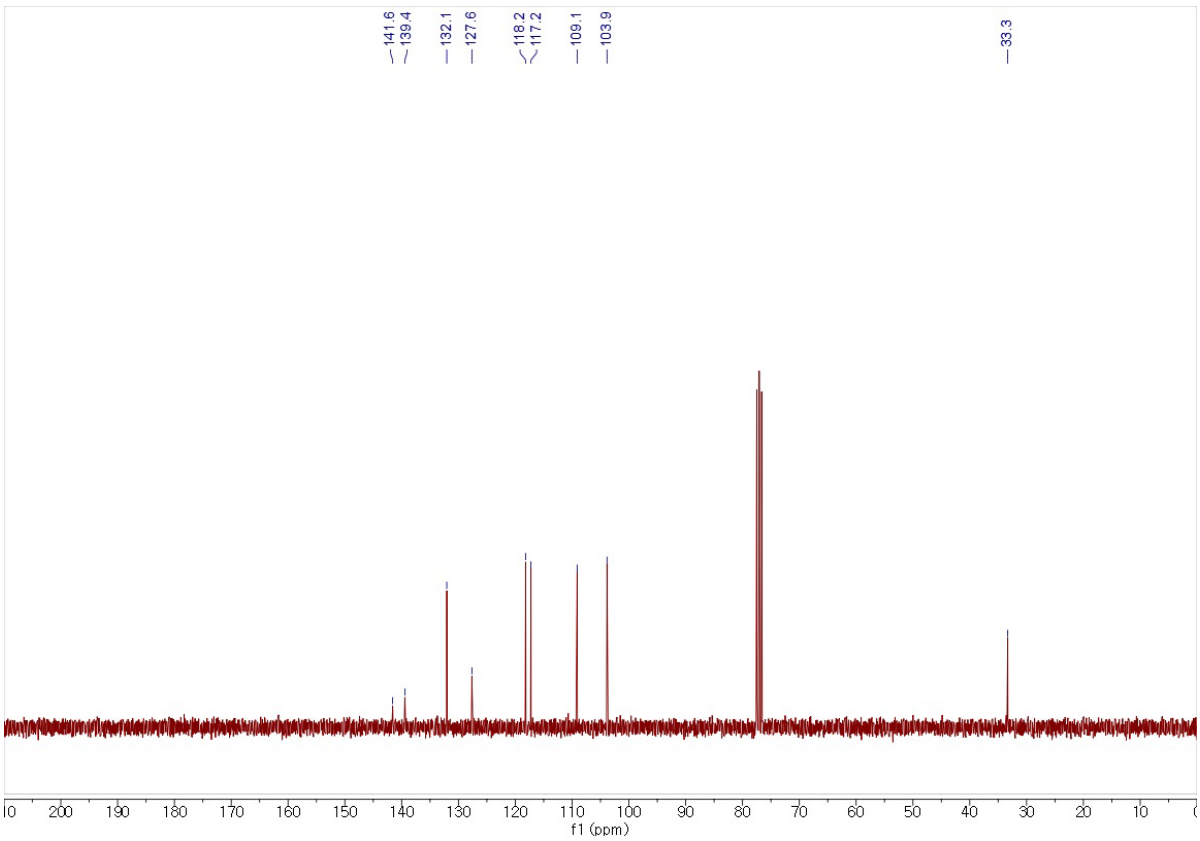

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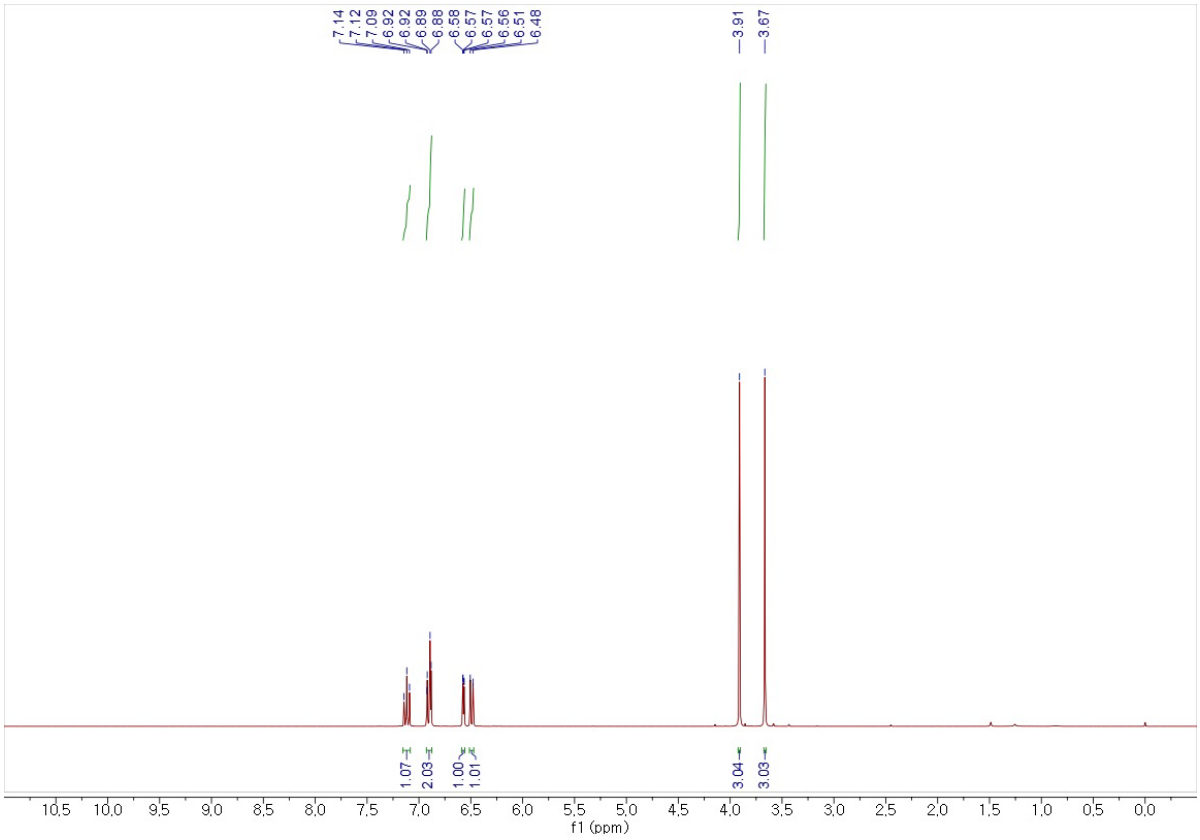

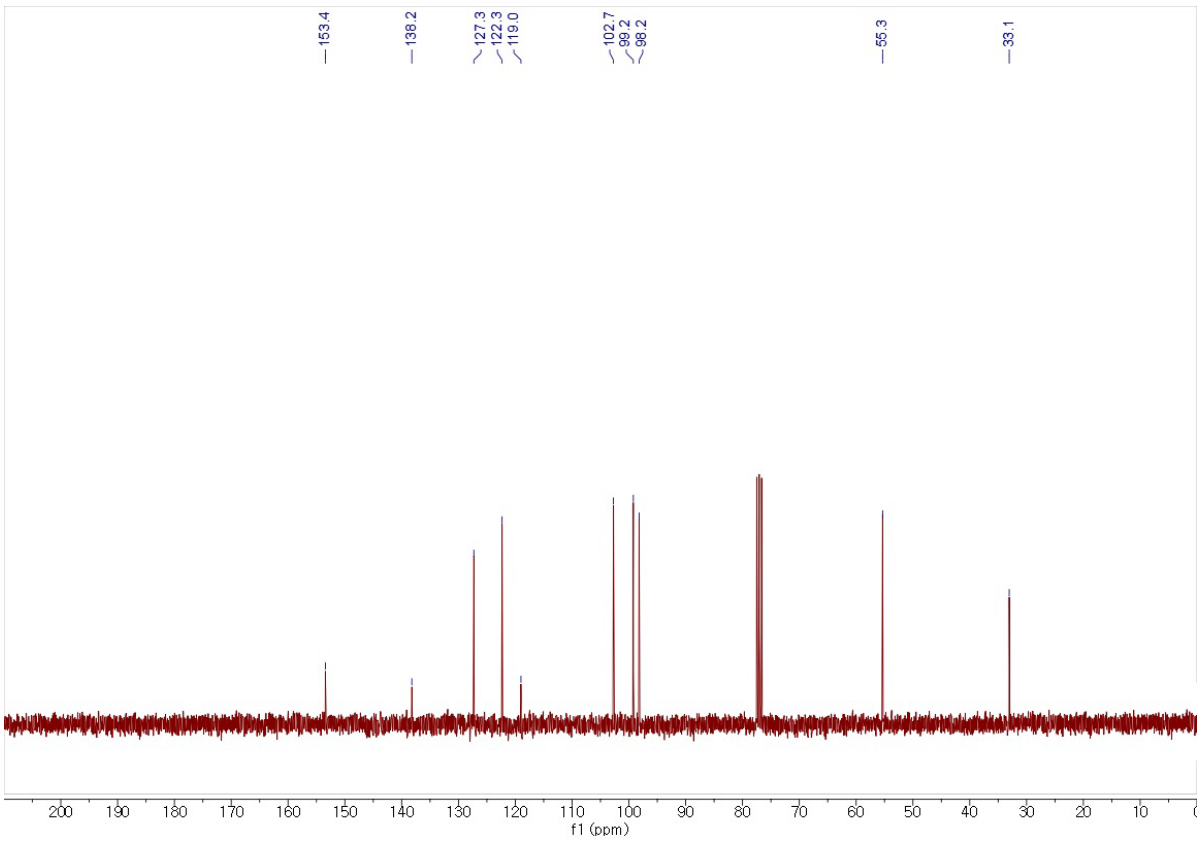

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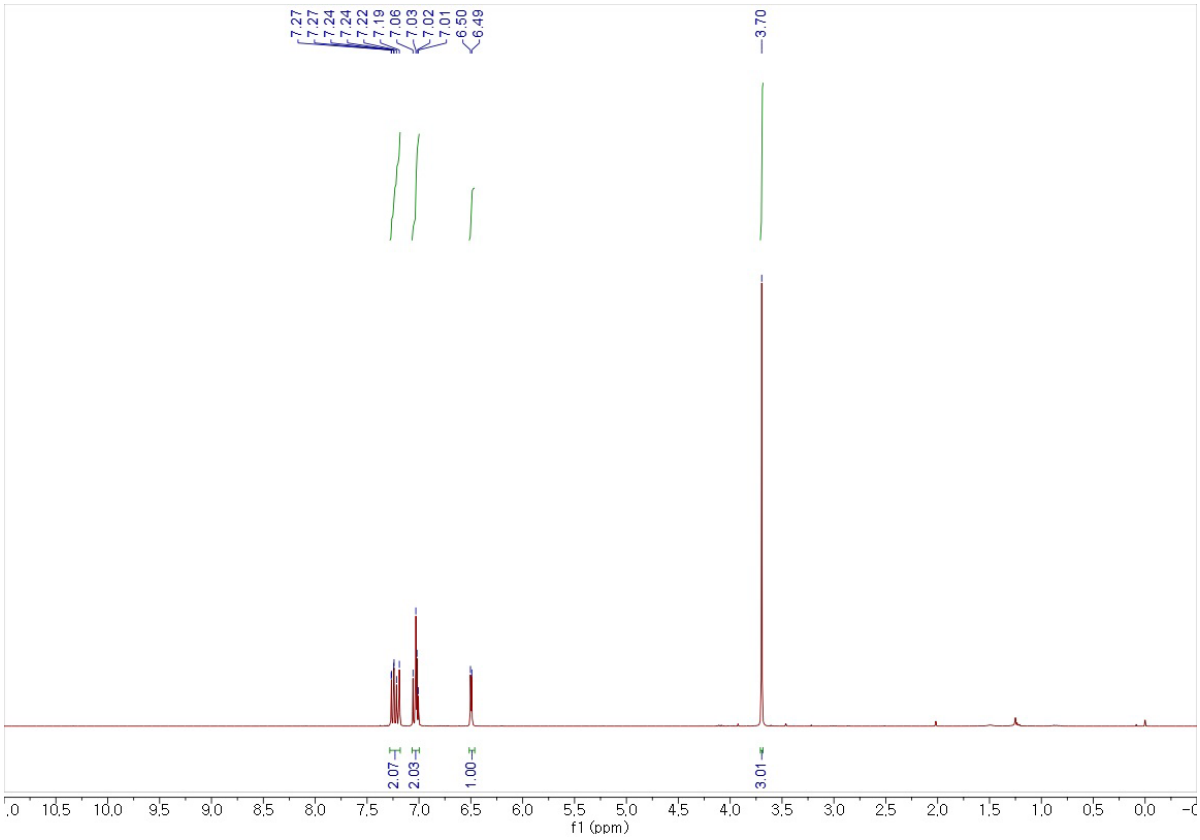

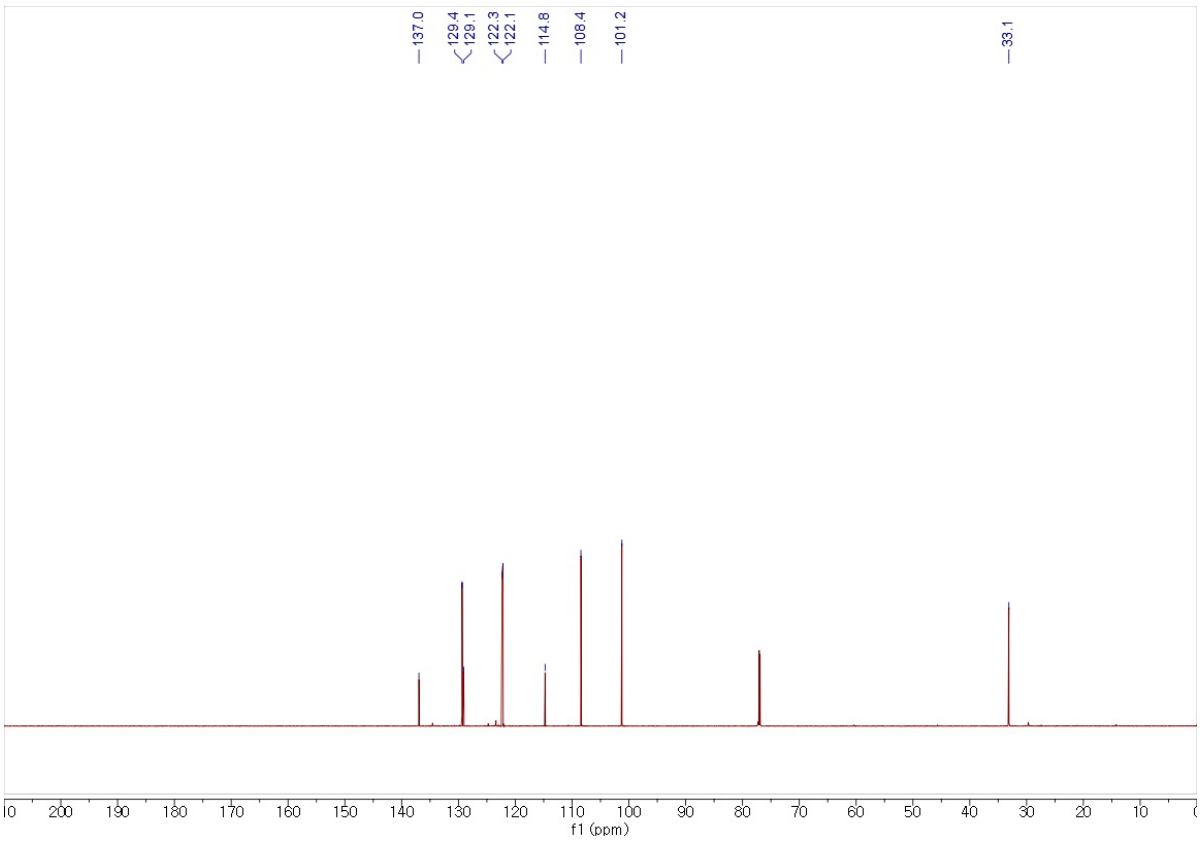

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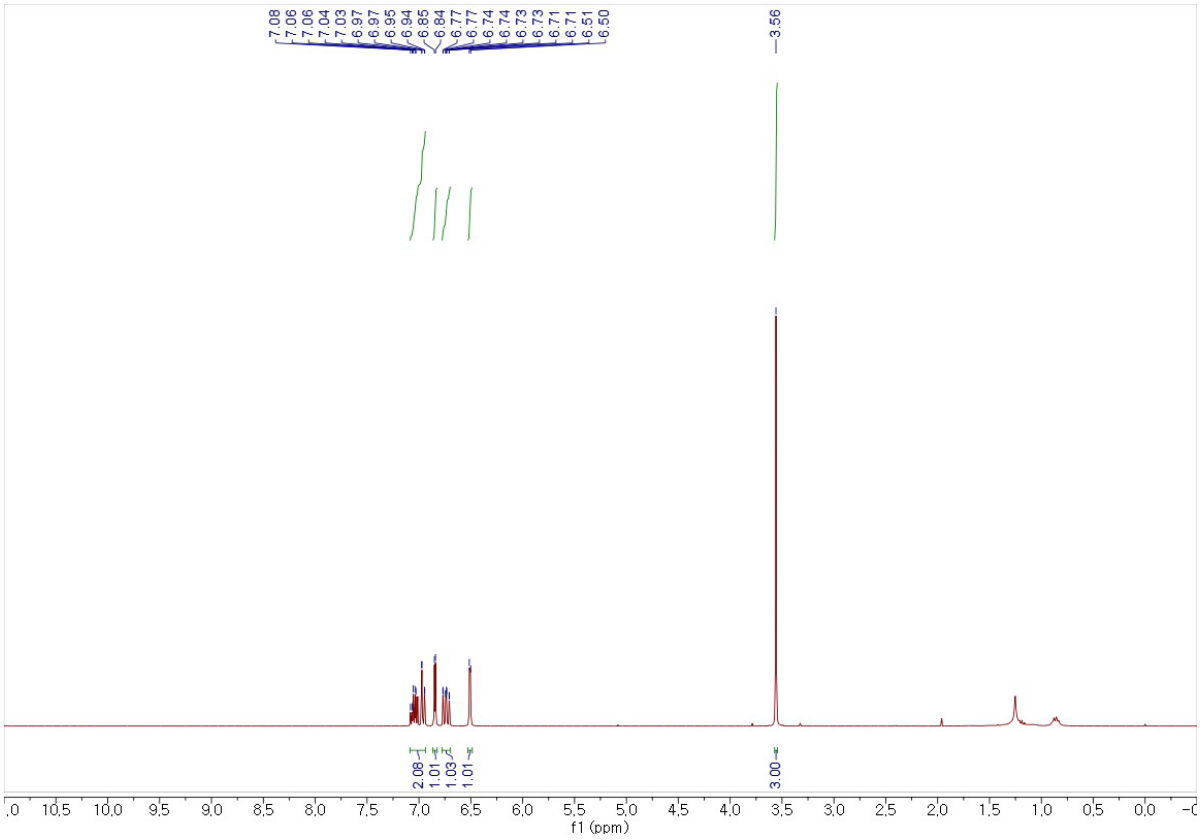

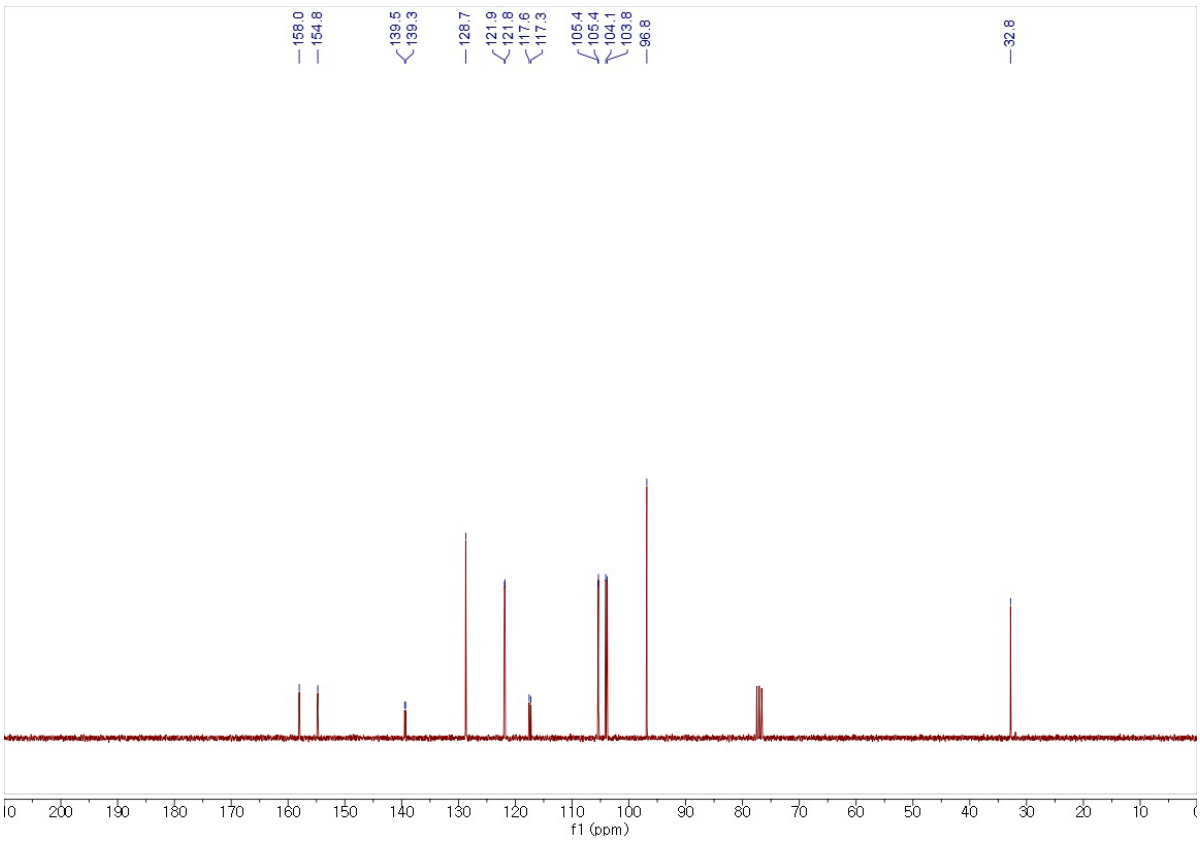

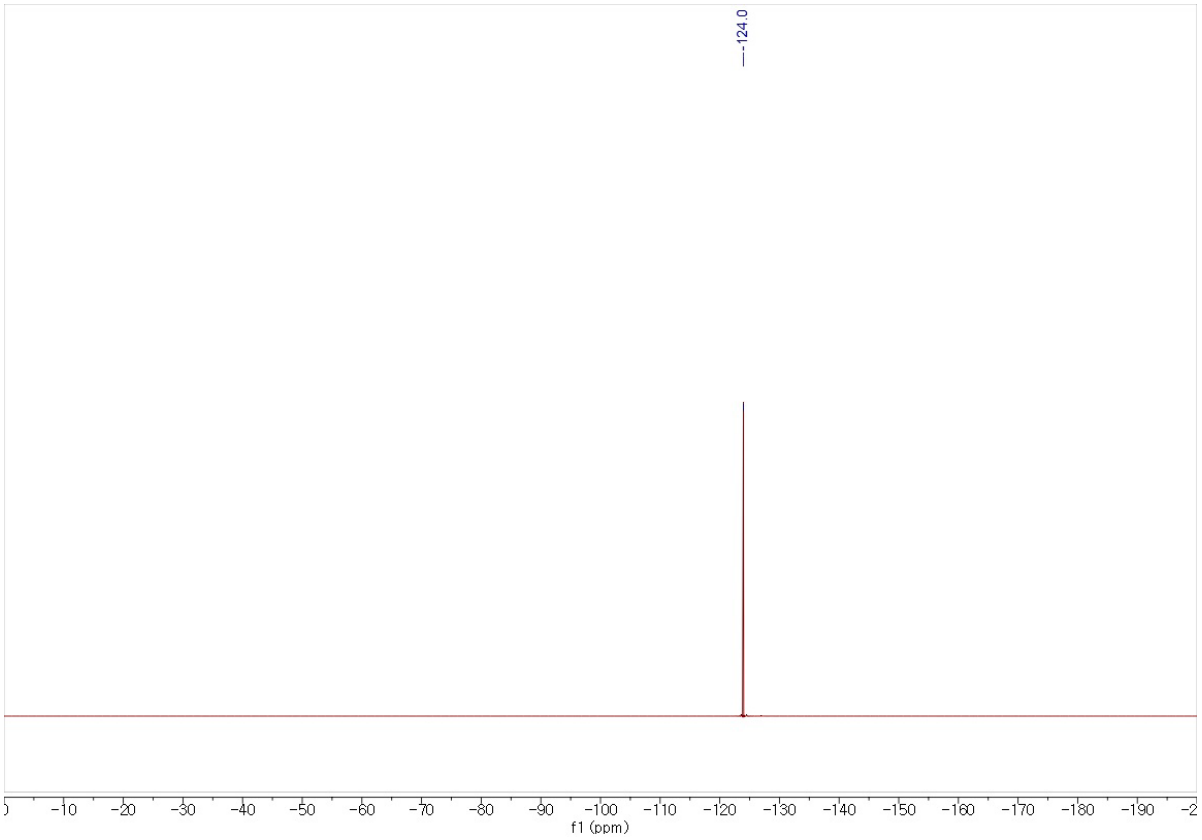
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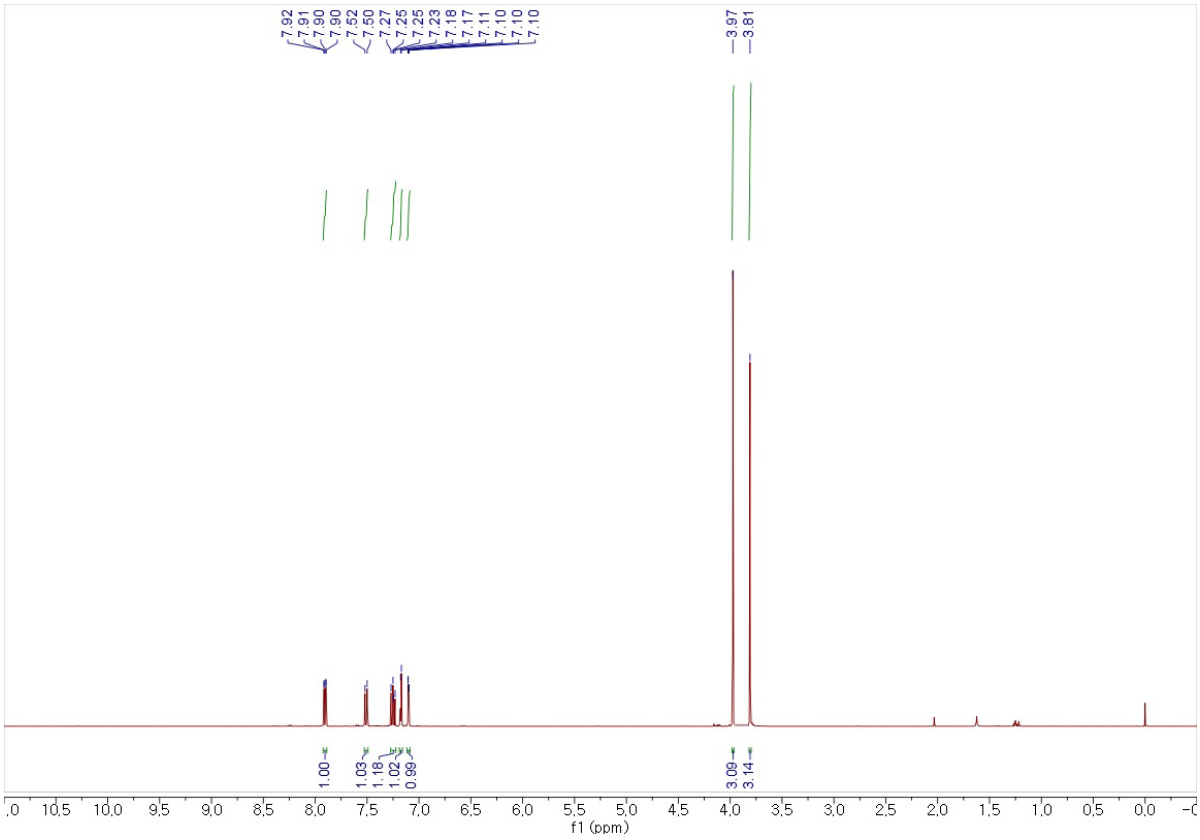
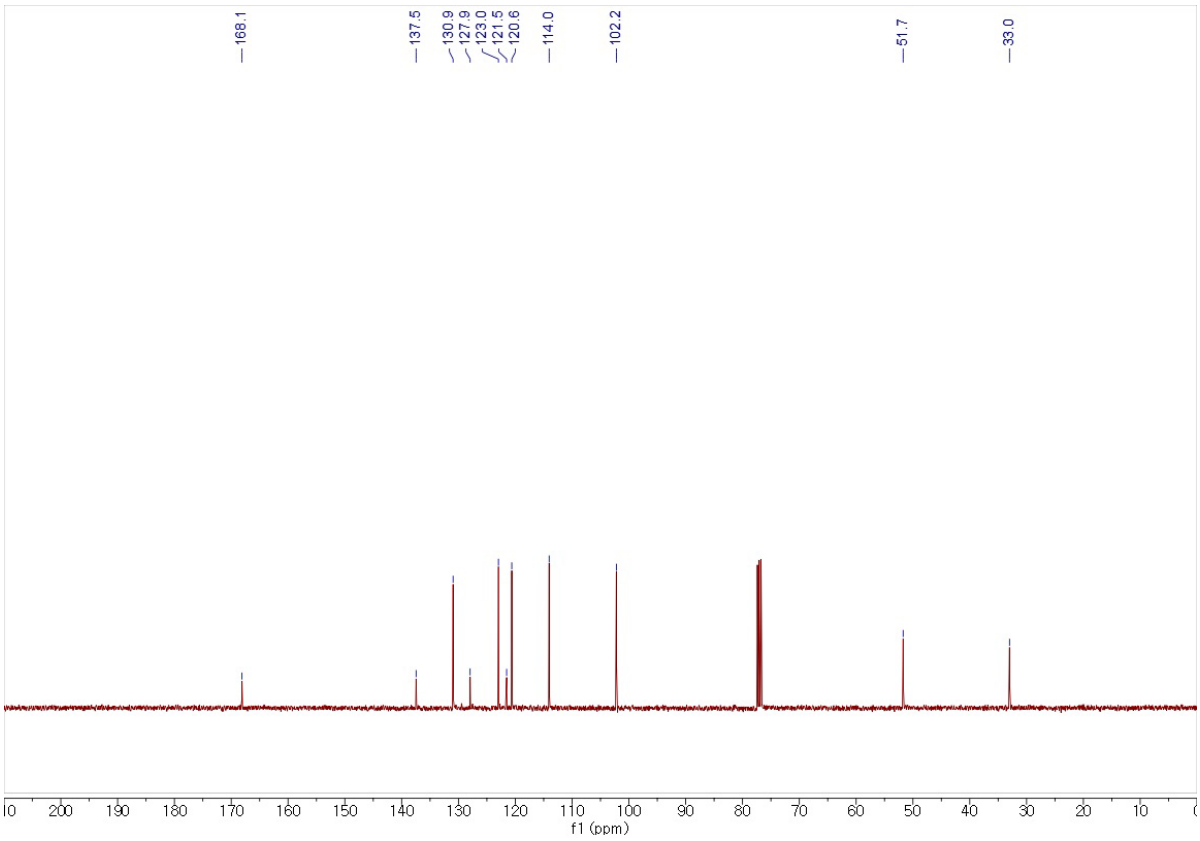
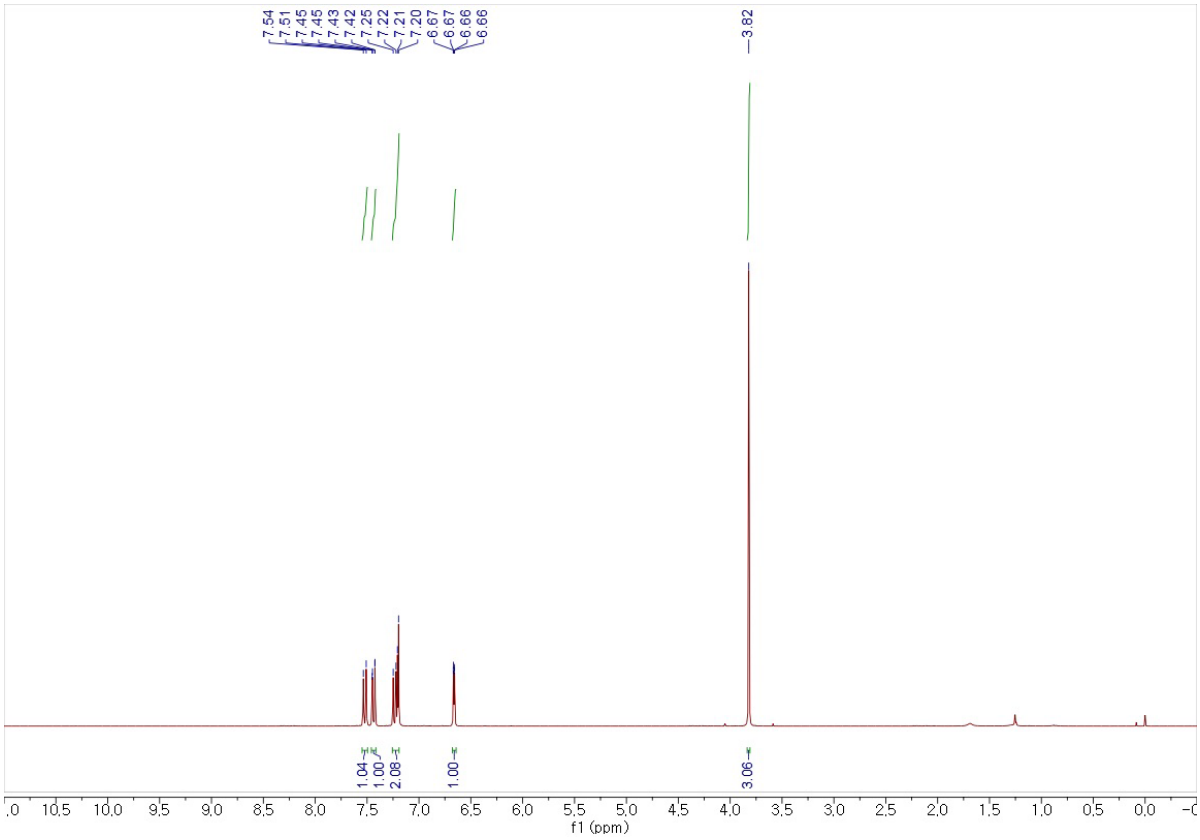
f1 (ppm)

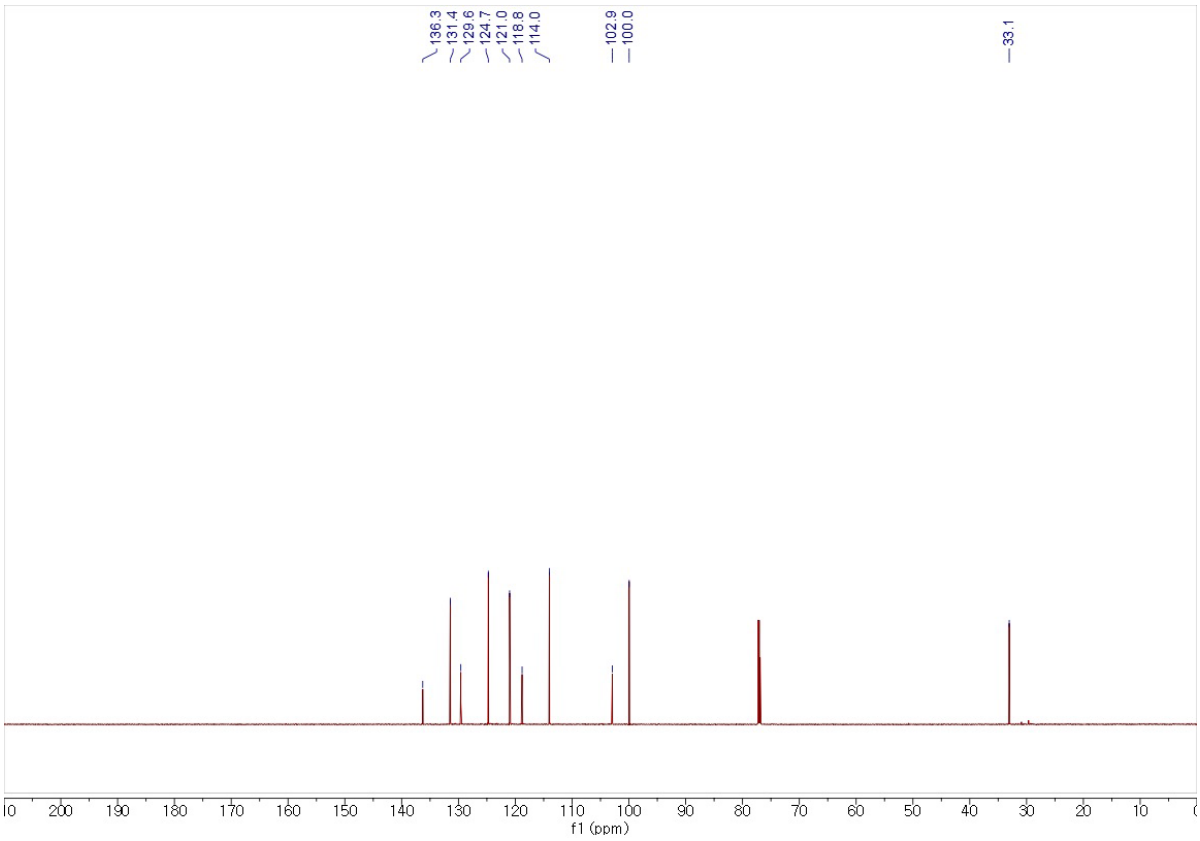
methyl 1-methyl-1*H*-indole-4-carboxylate (5l)



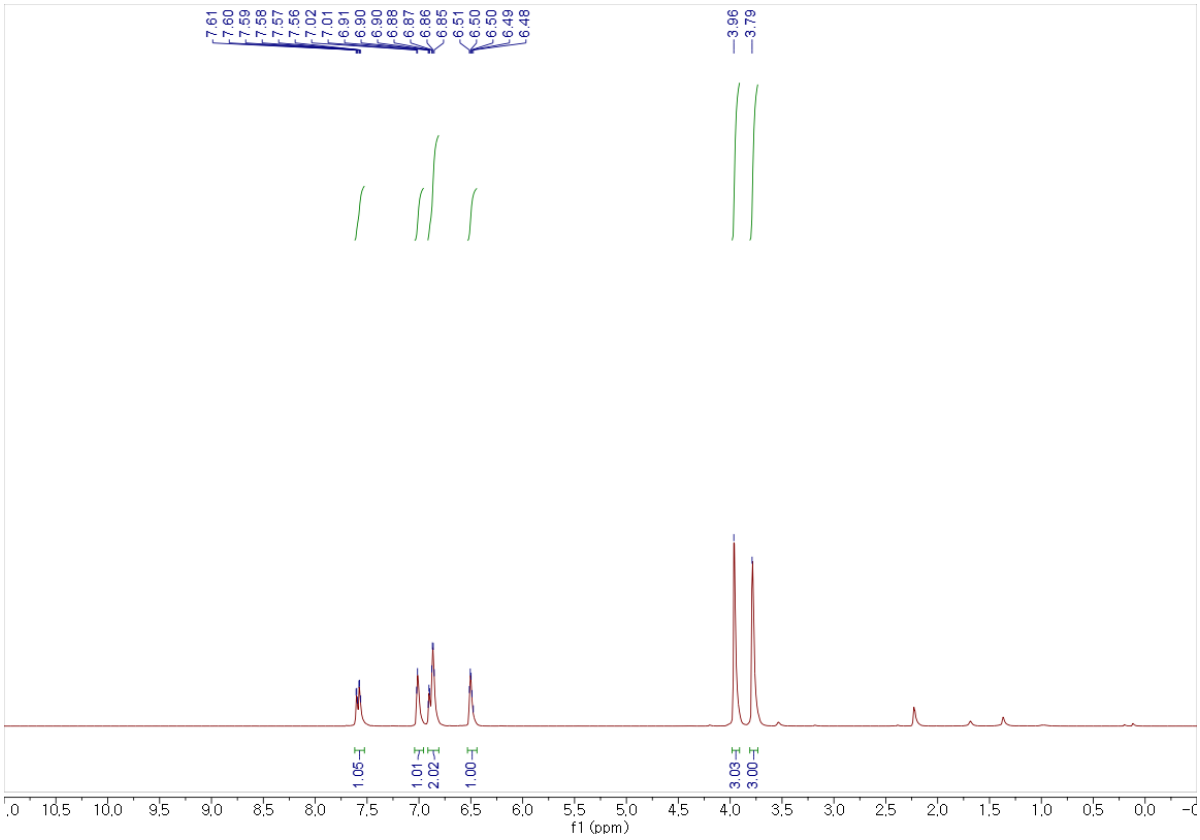


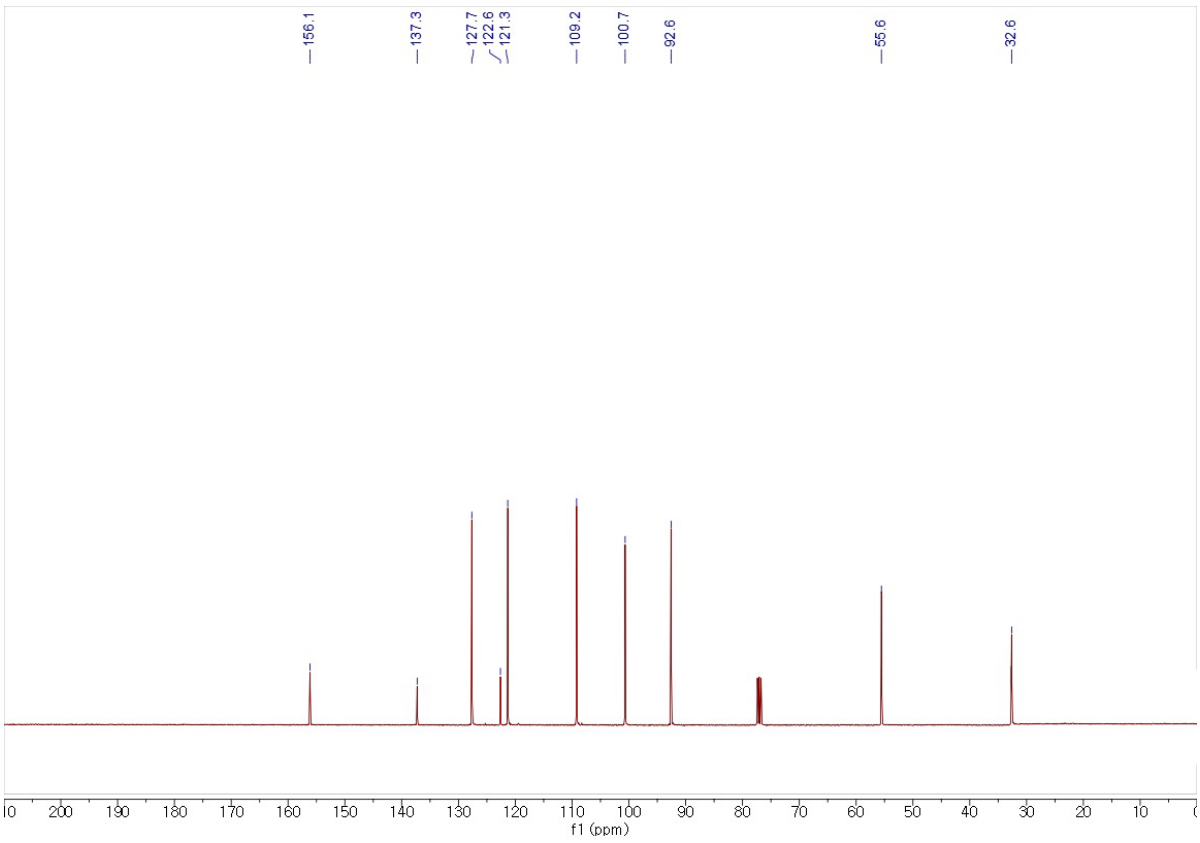
1-methyl-1*H*-indole-4-carbonitrile (5m)



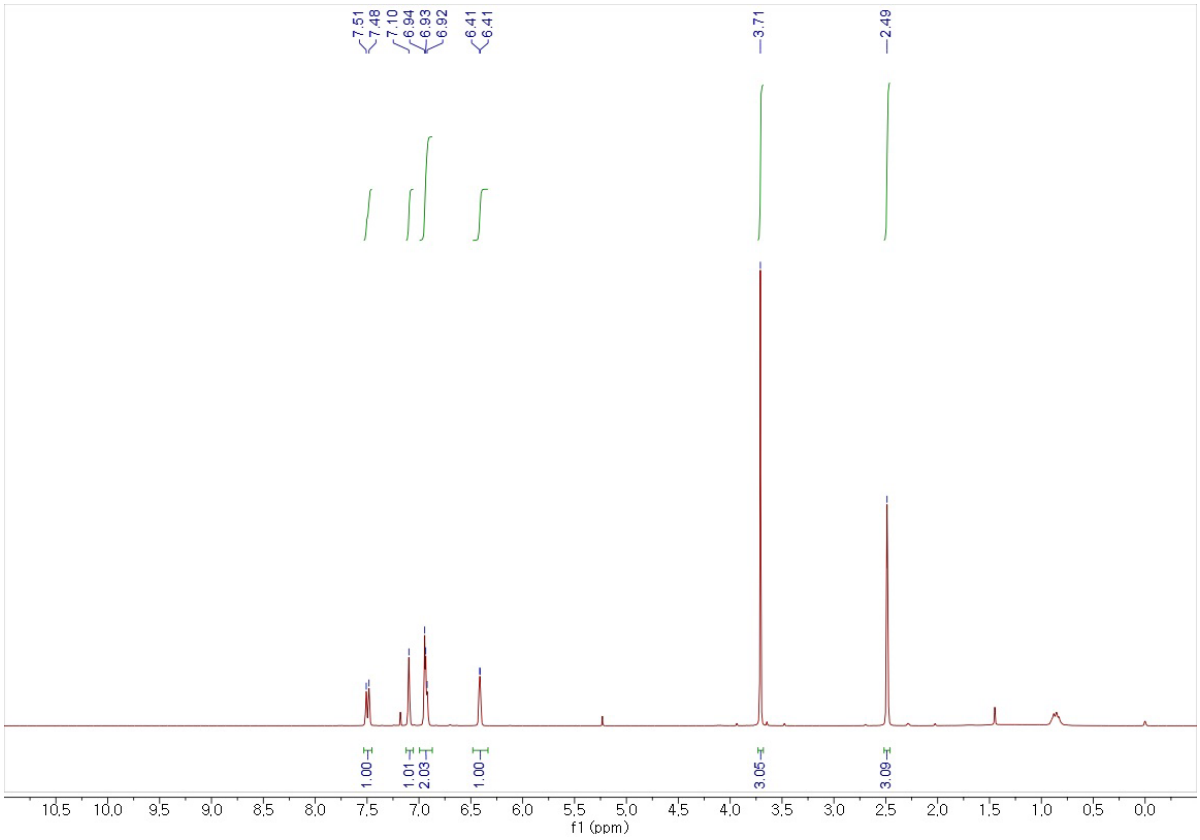


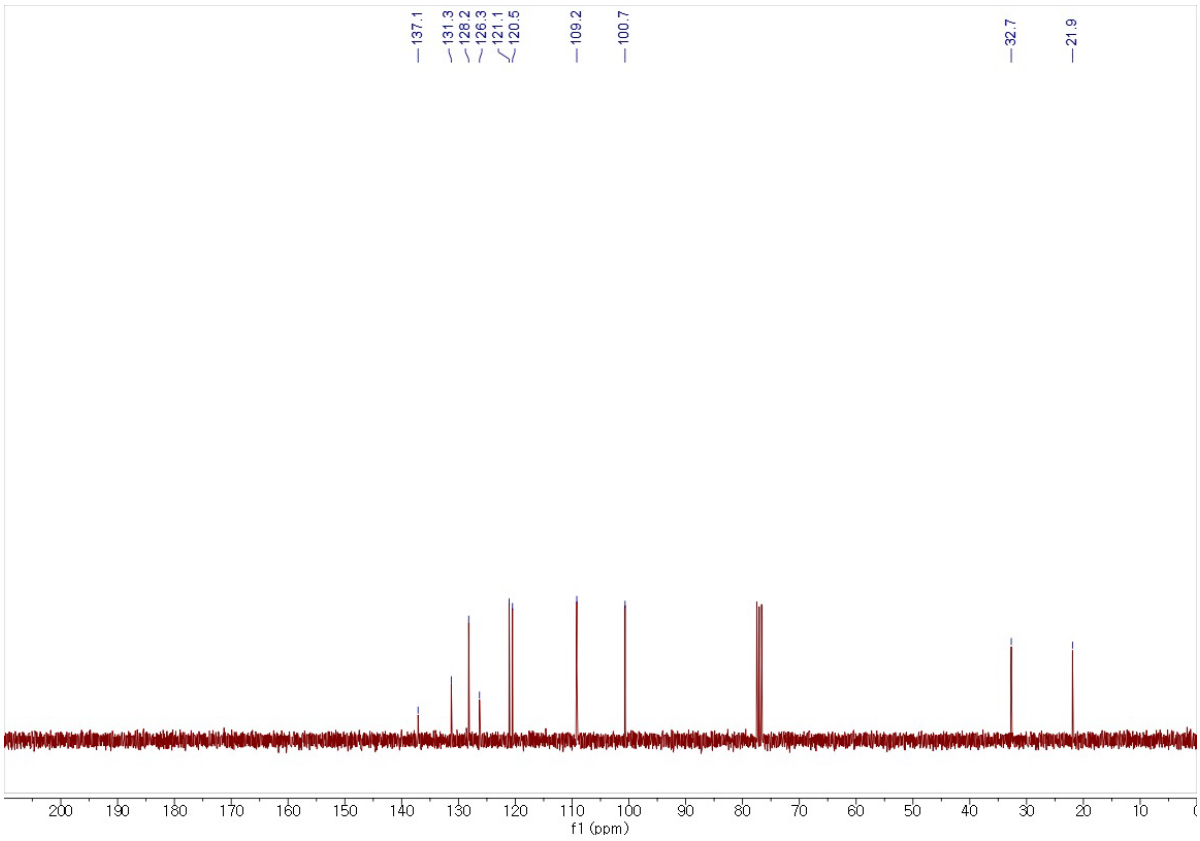
6-methoxy-1-methyl-1*H*-indole (5n)



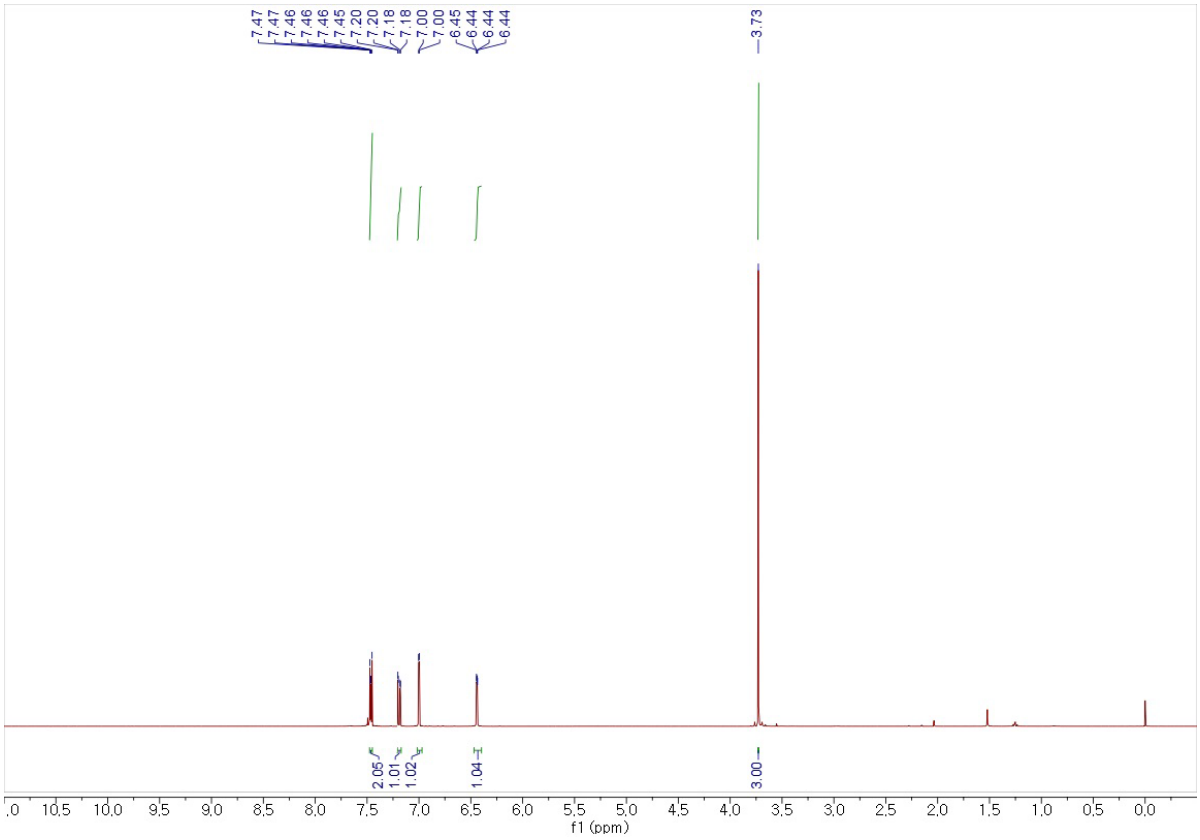


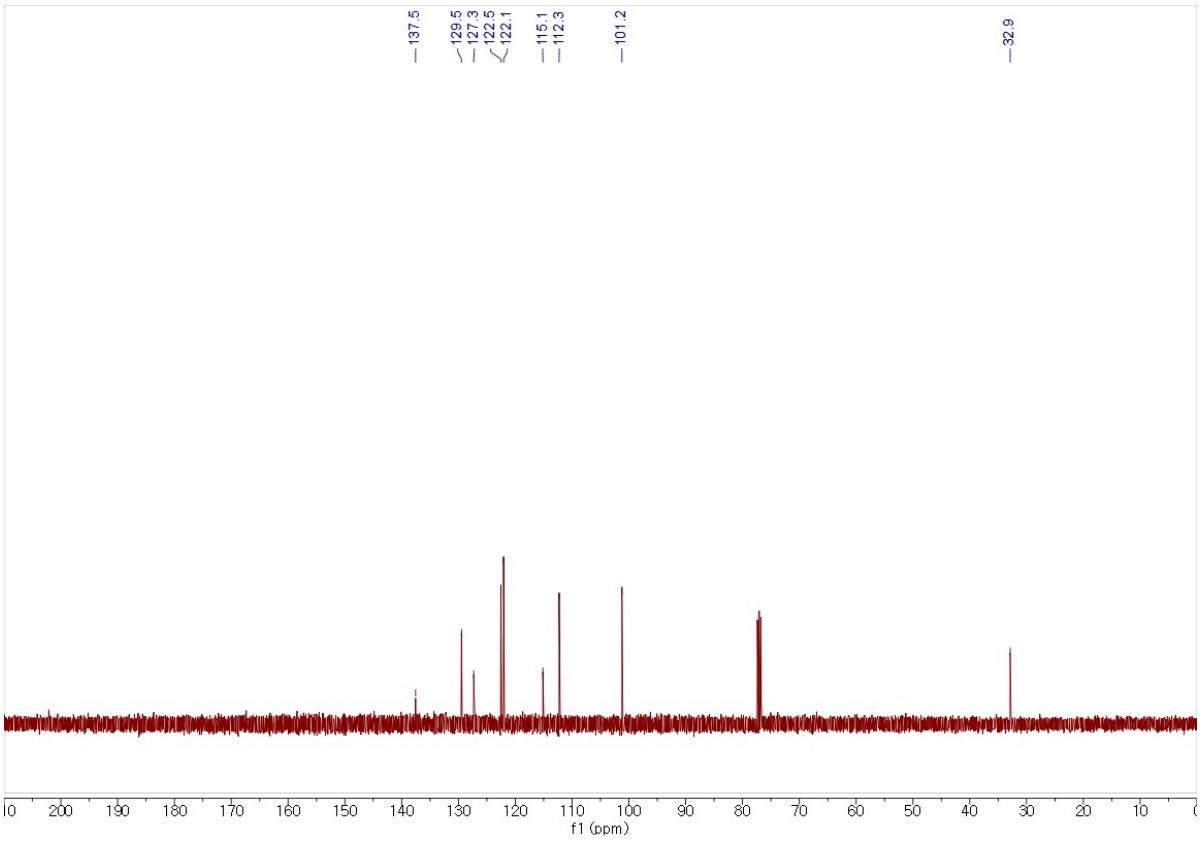
1,6-dimethyl-1*H*-indole (5o)



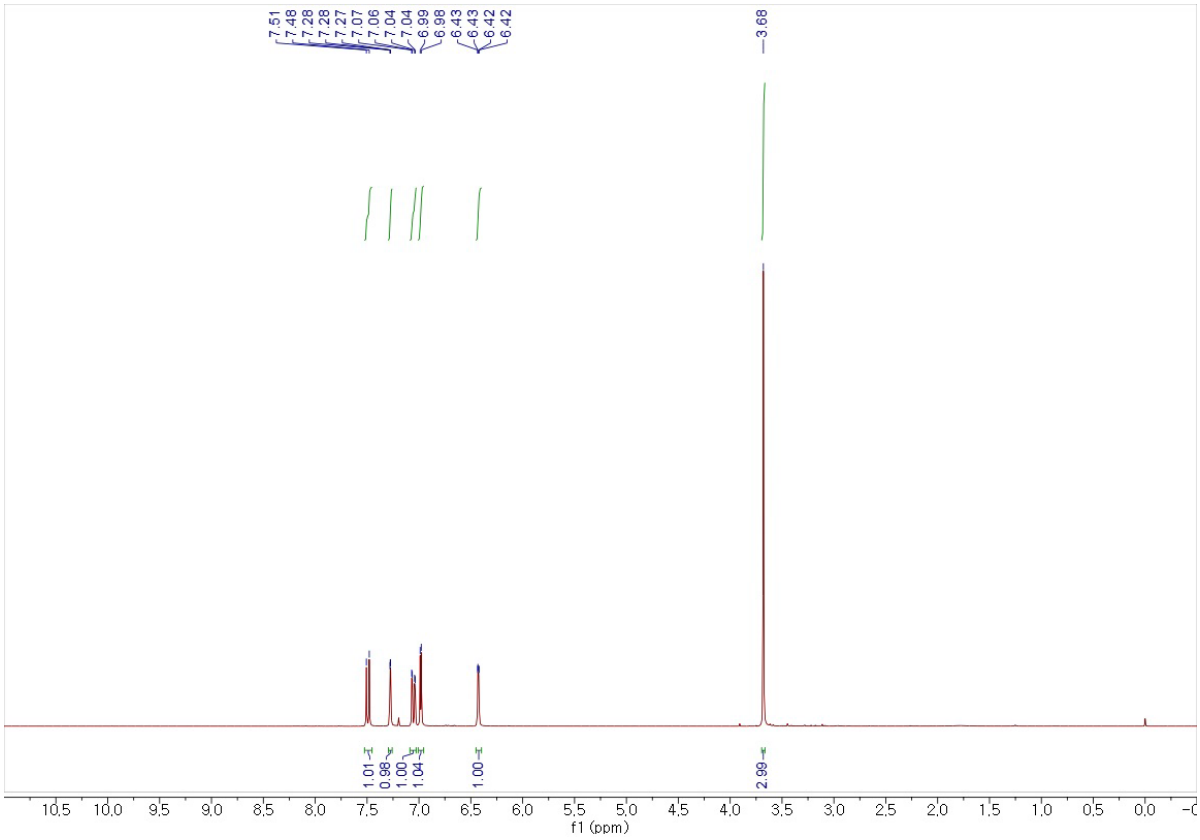


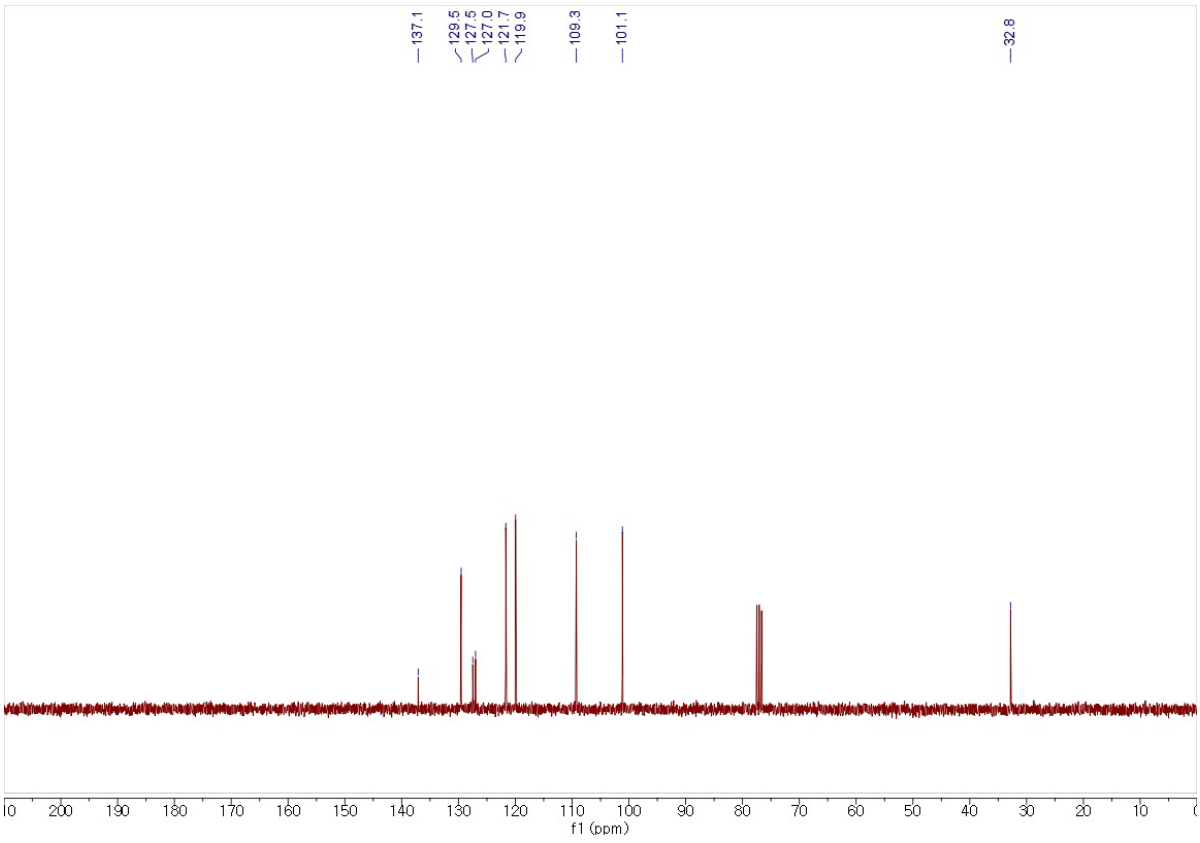
6-bromo-1-methyl-1*H*-indole (5p)



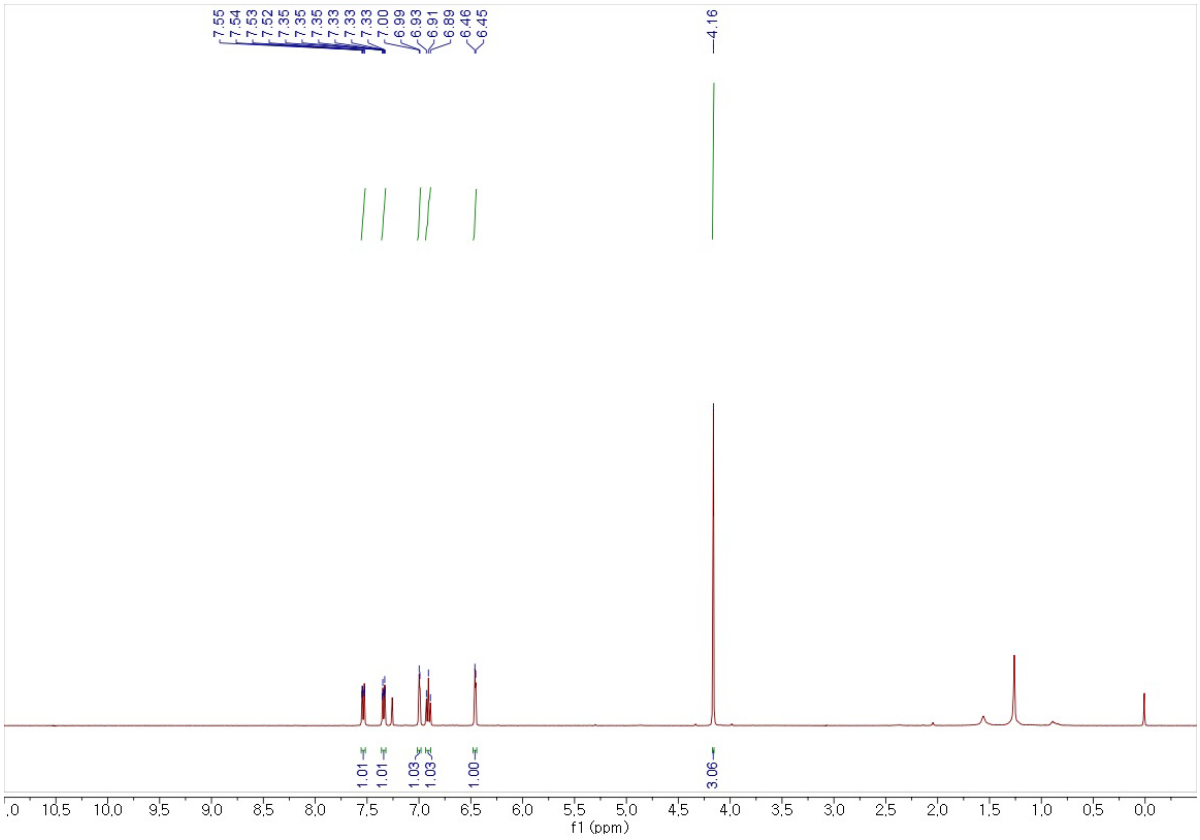


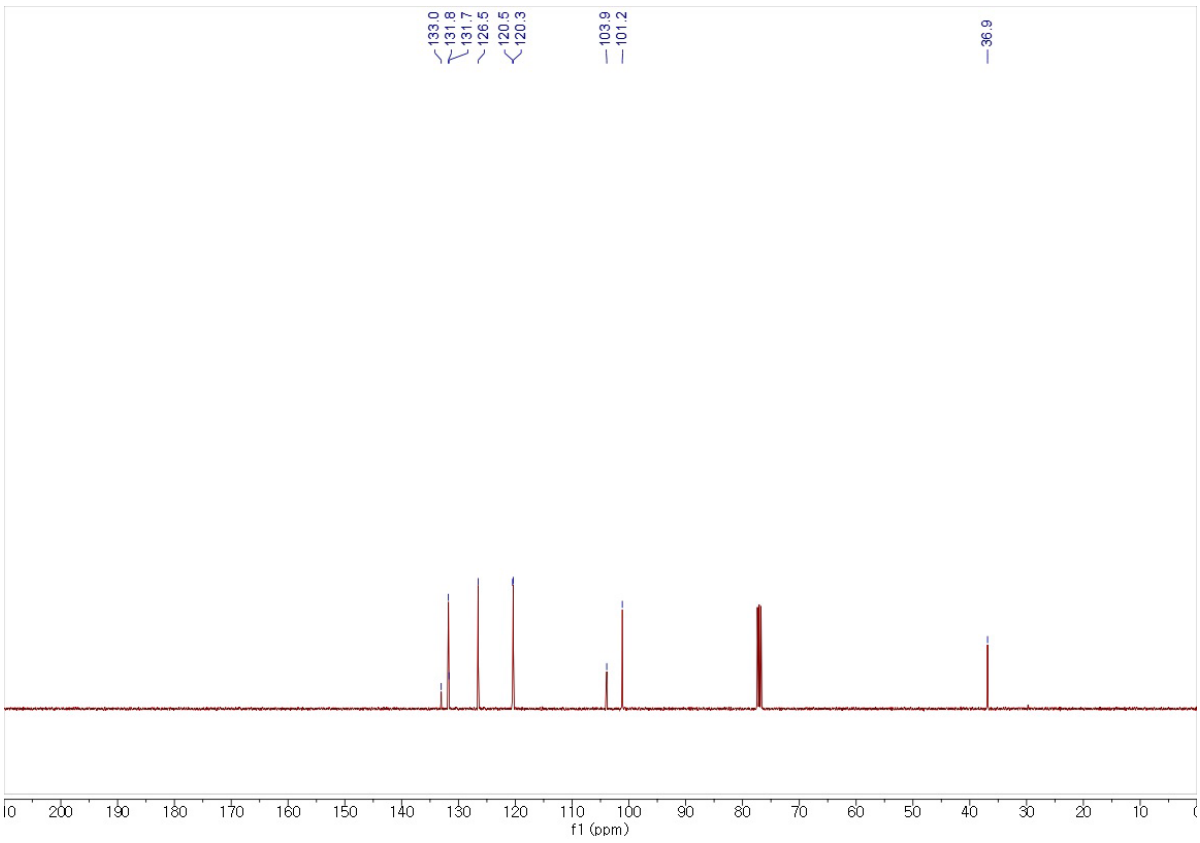
6-chloro-1-methyl-1*H*-indole (5q)



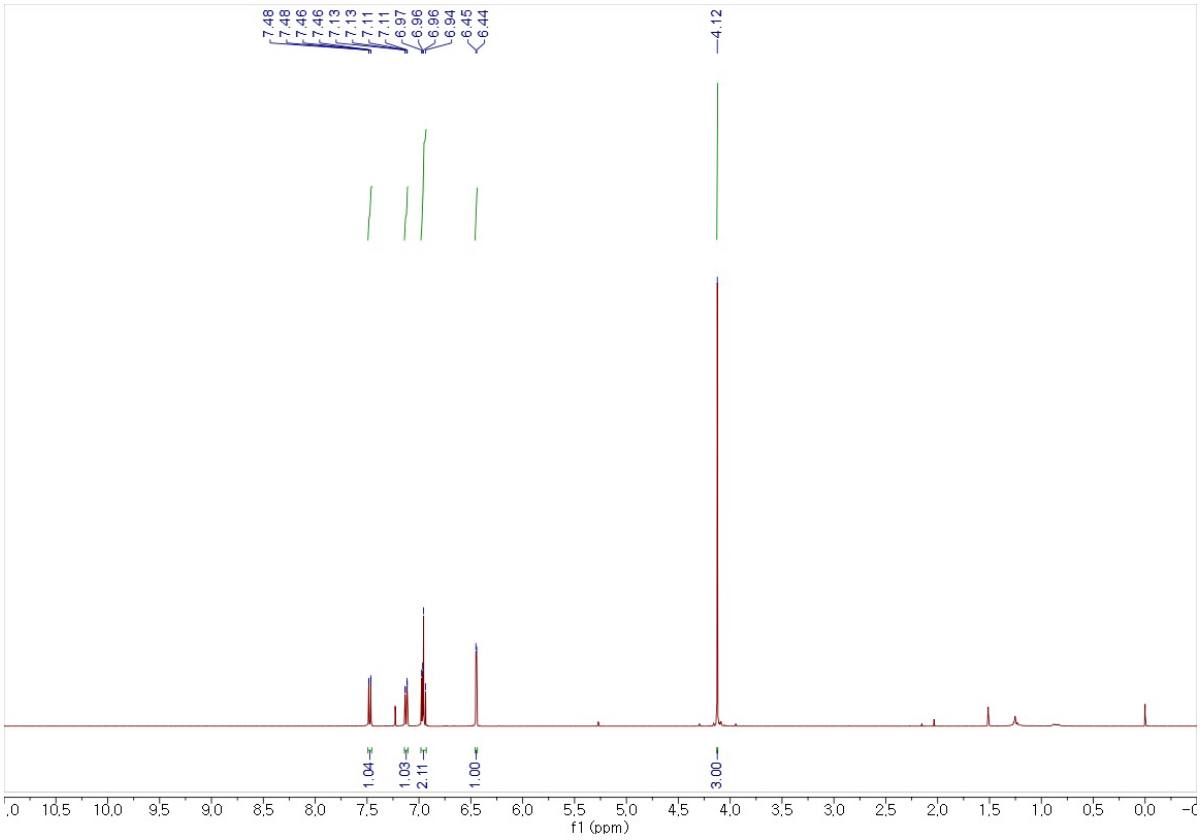


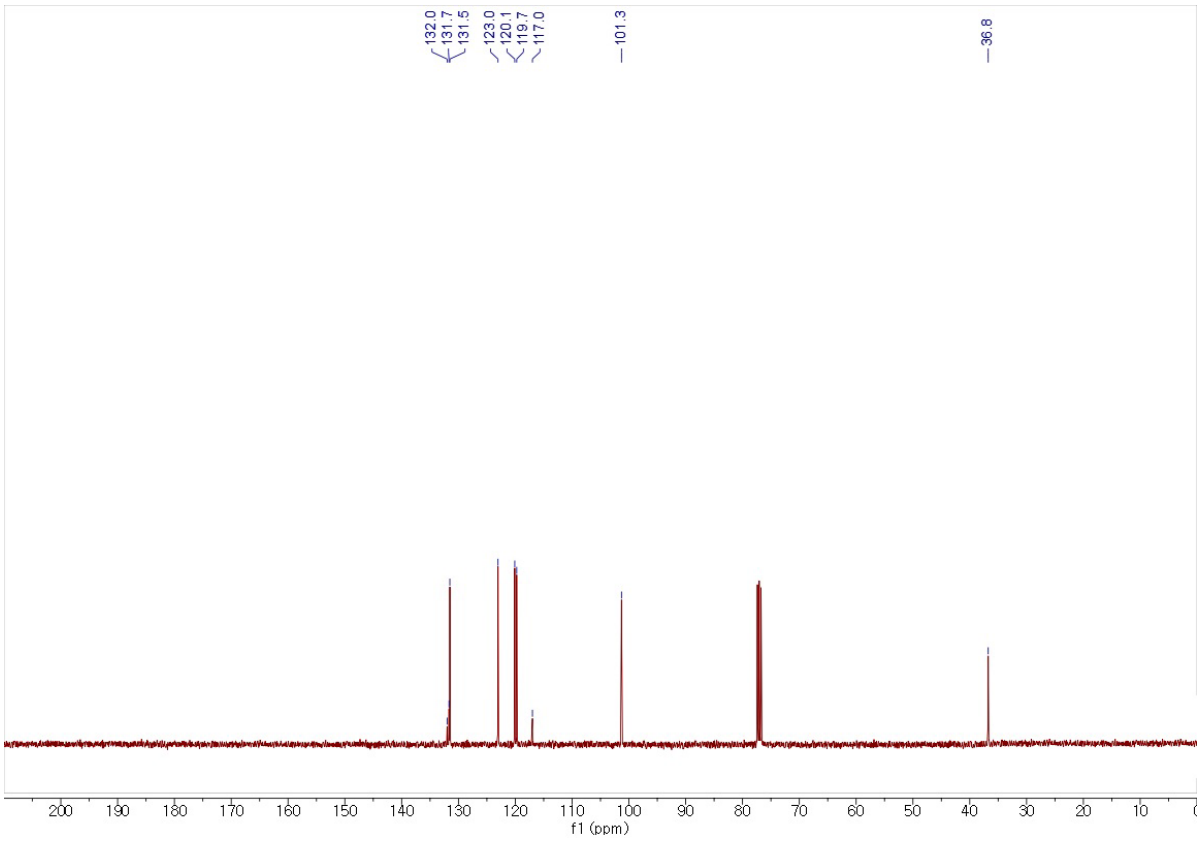
7-bromo-1-methyl-1*H*-indole (5r)



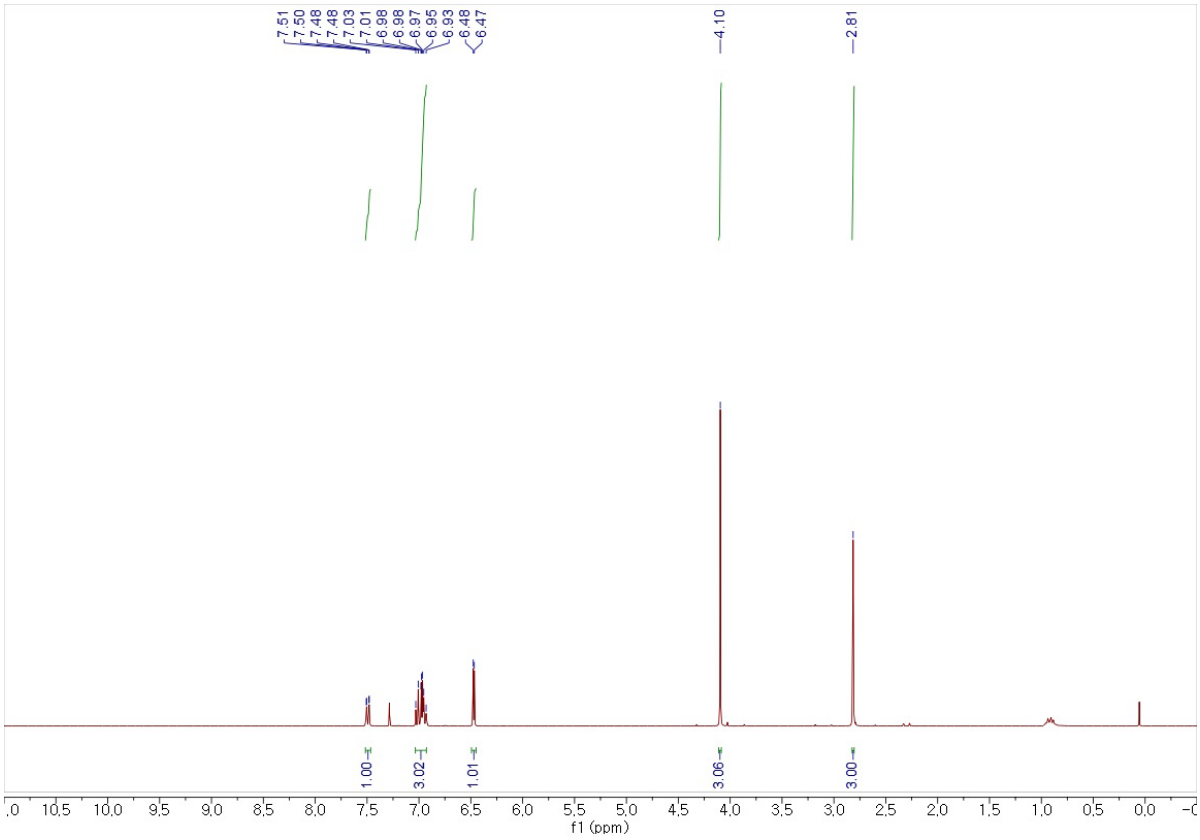


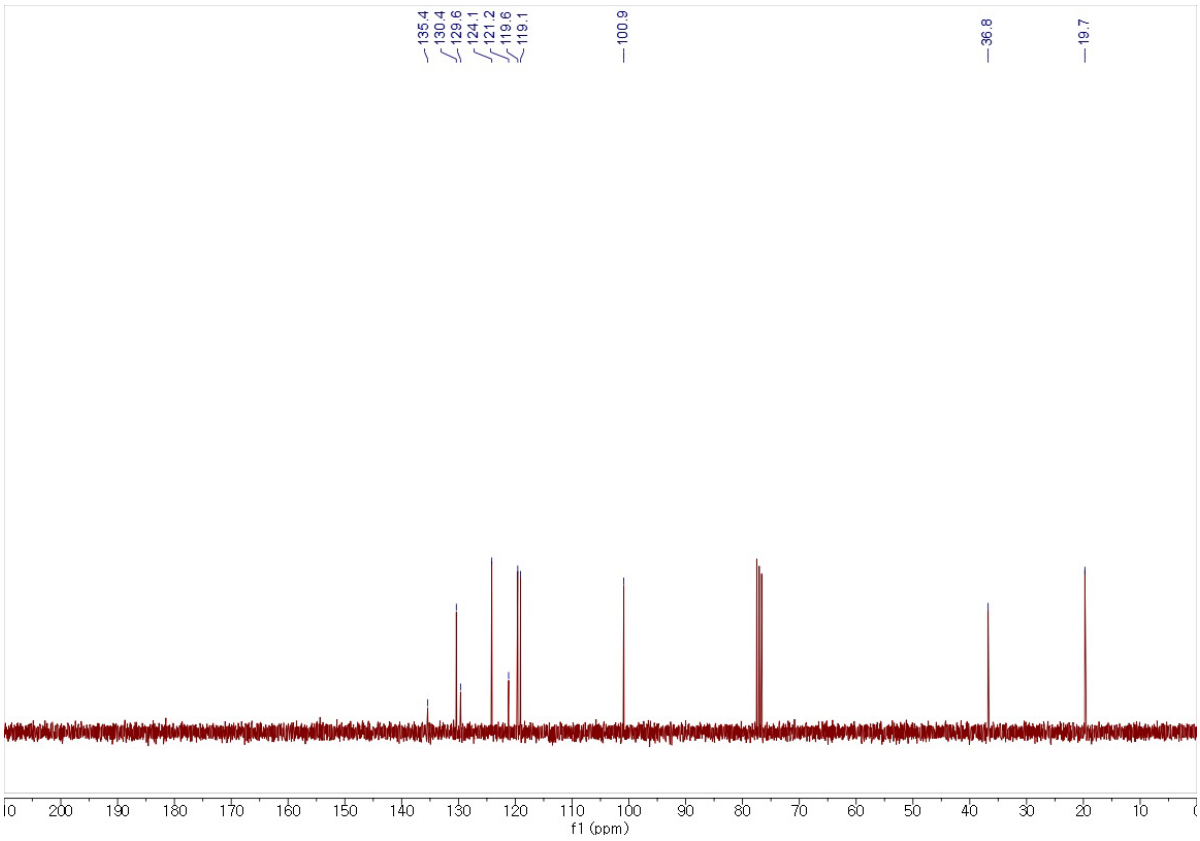
7-chloro-1-methyl-1*H*-indole (5s)



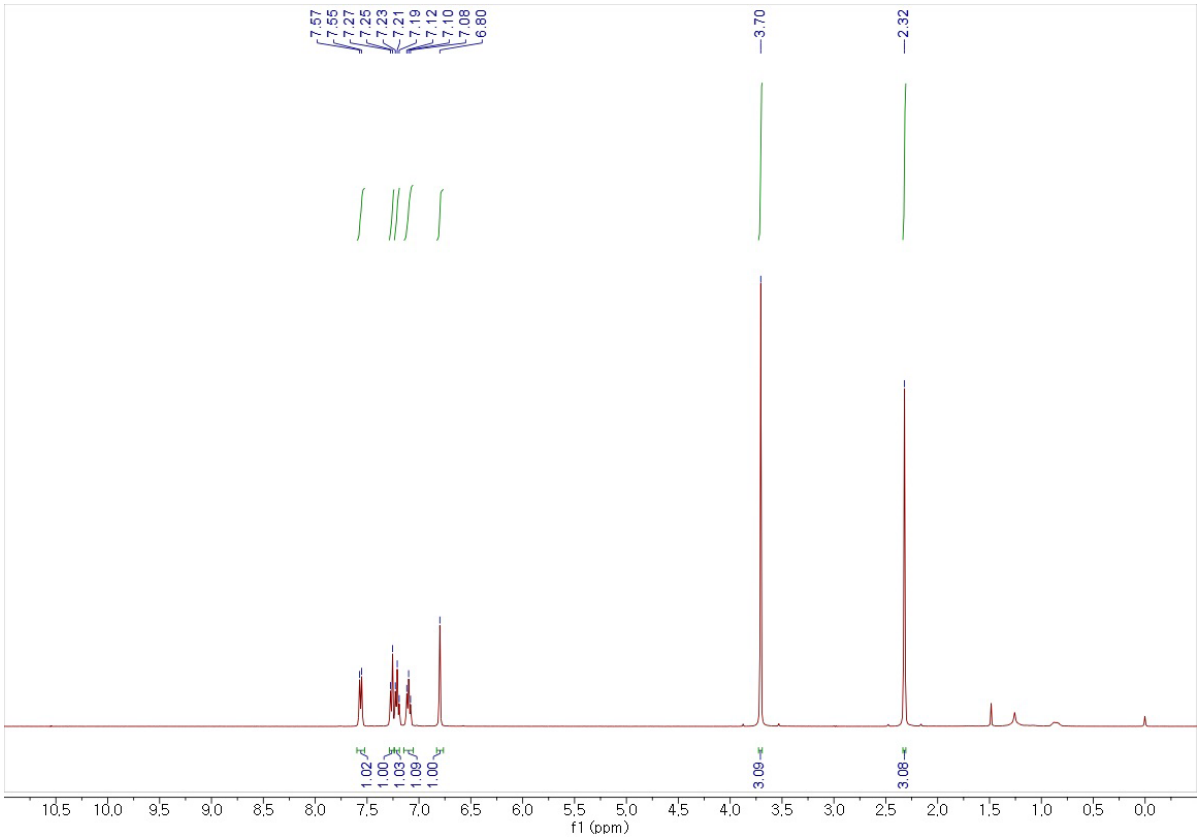


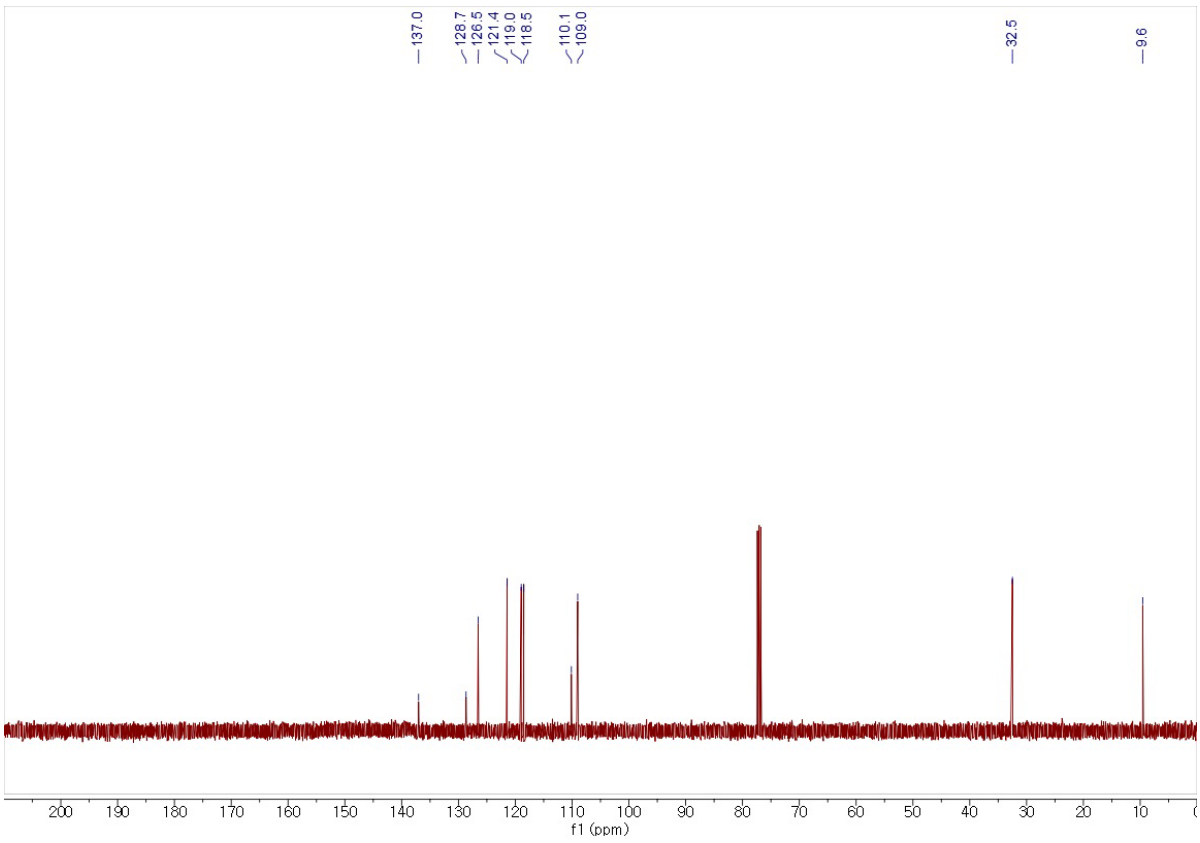
1,7-dimethyl-1*H*-indole (5t)



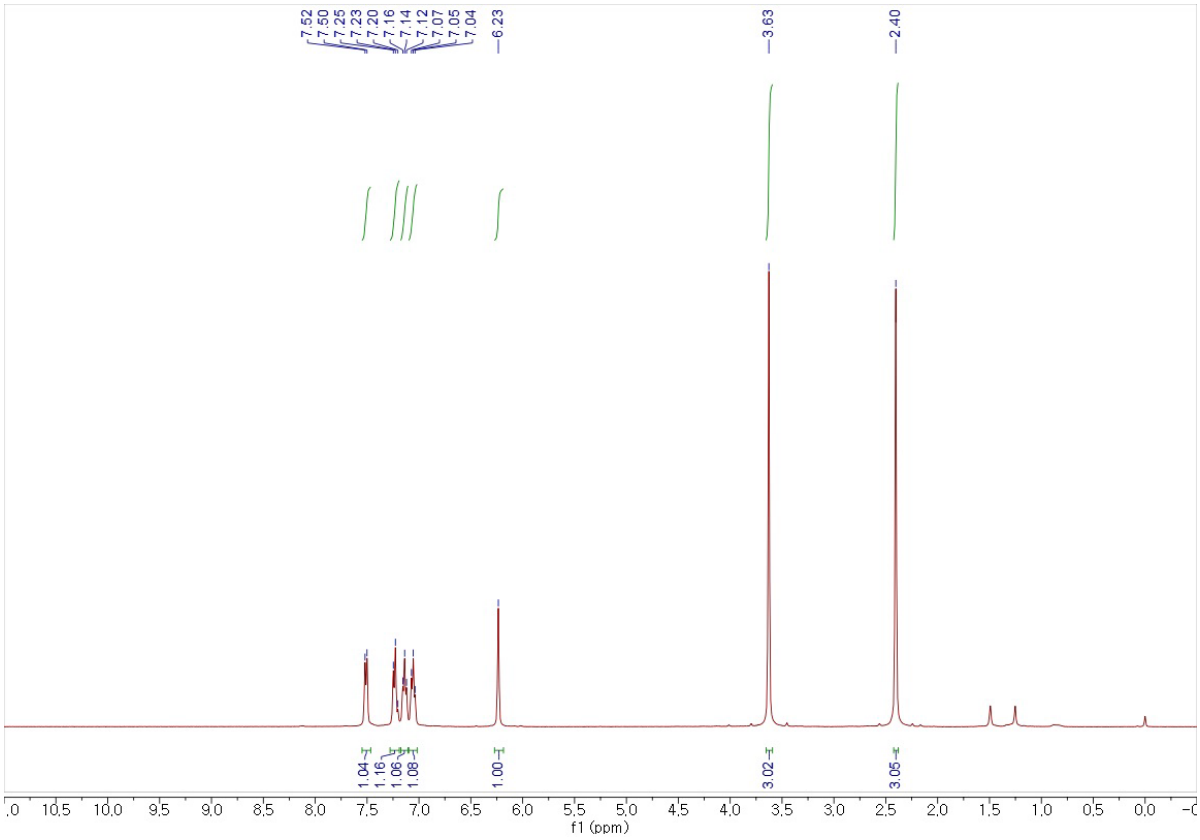


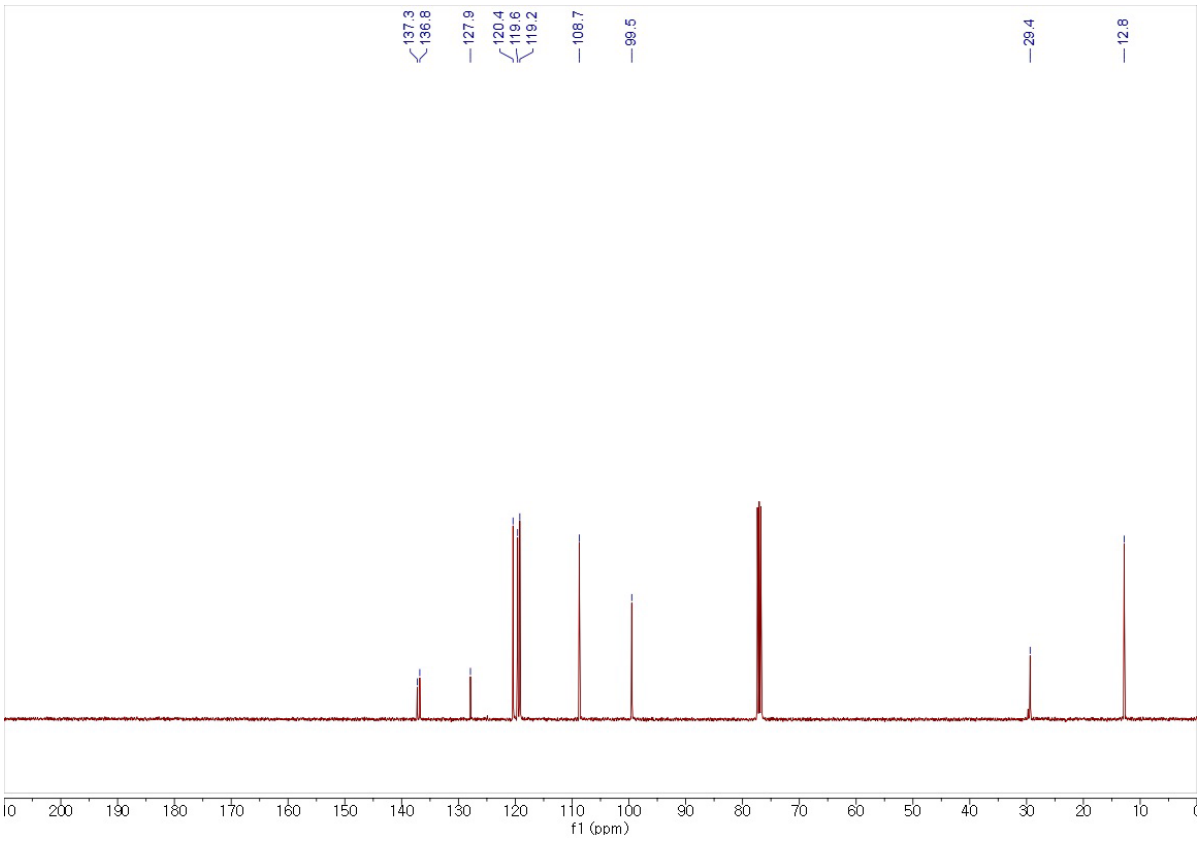
1,3-dimethyl-1*H*-indole (5u)



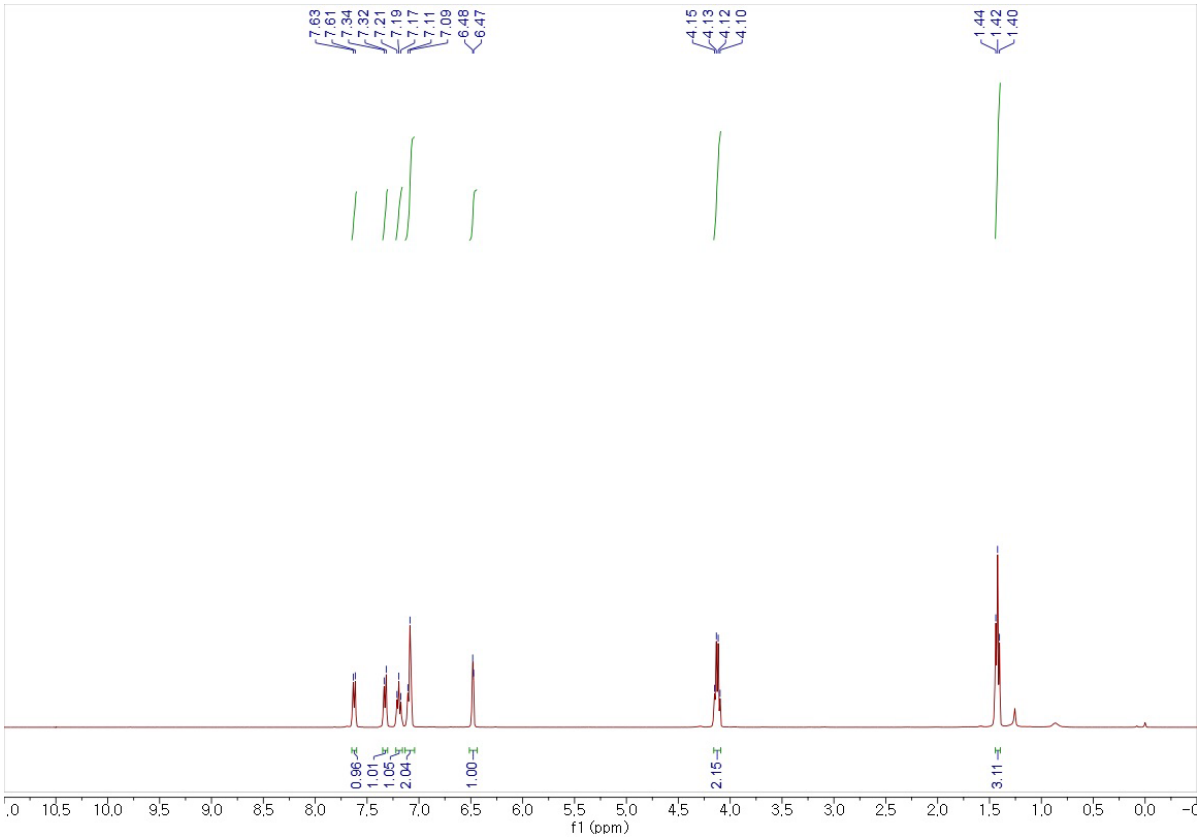


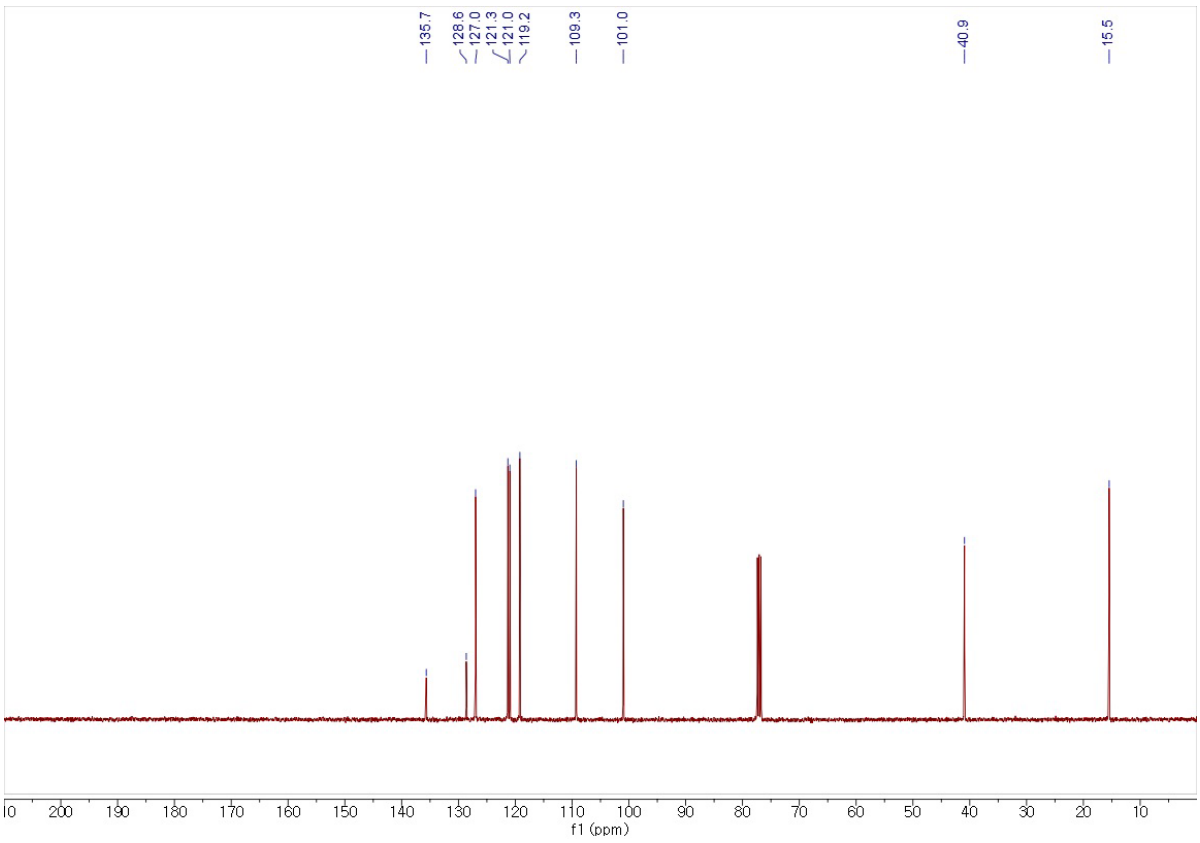
1,2-dimethyl-1*H*-indole (5v)



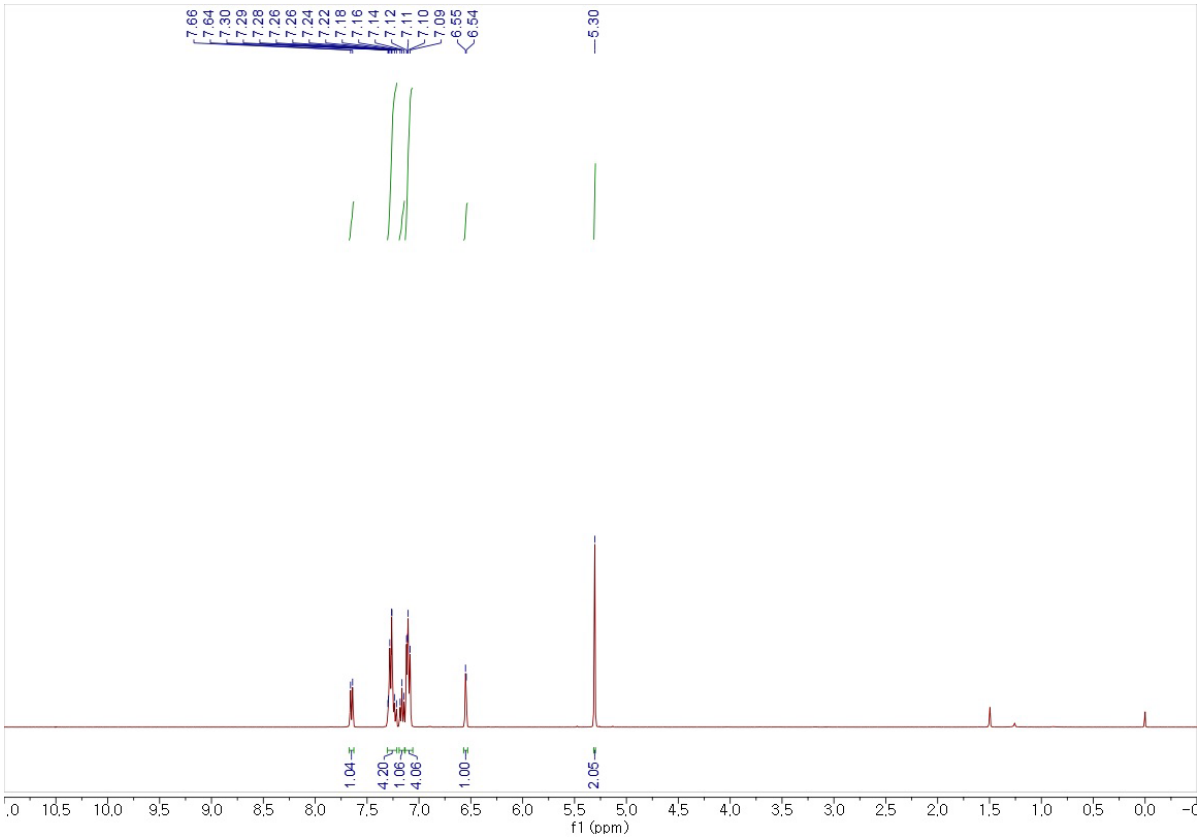


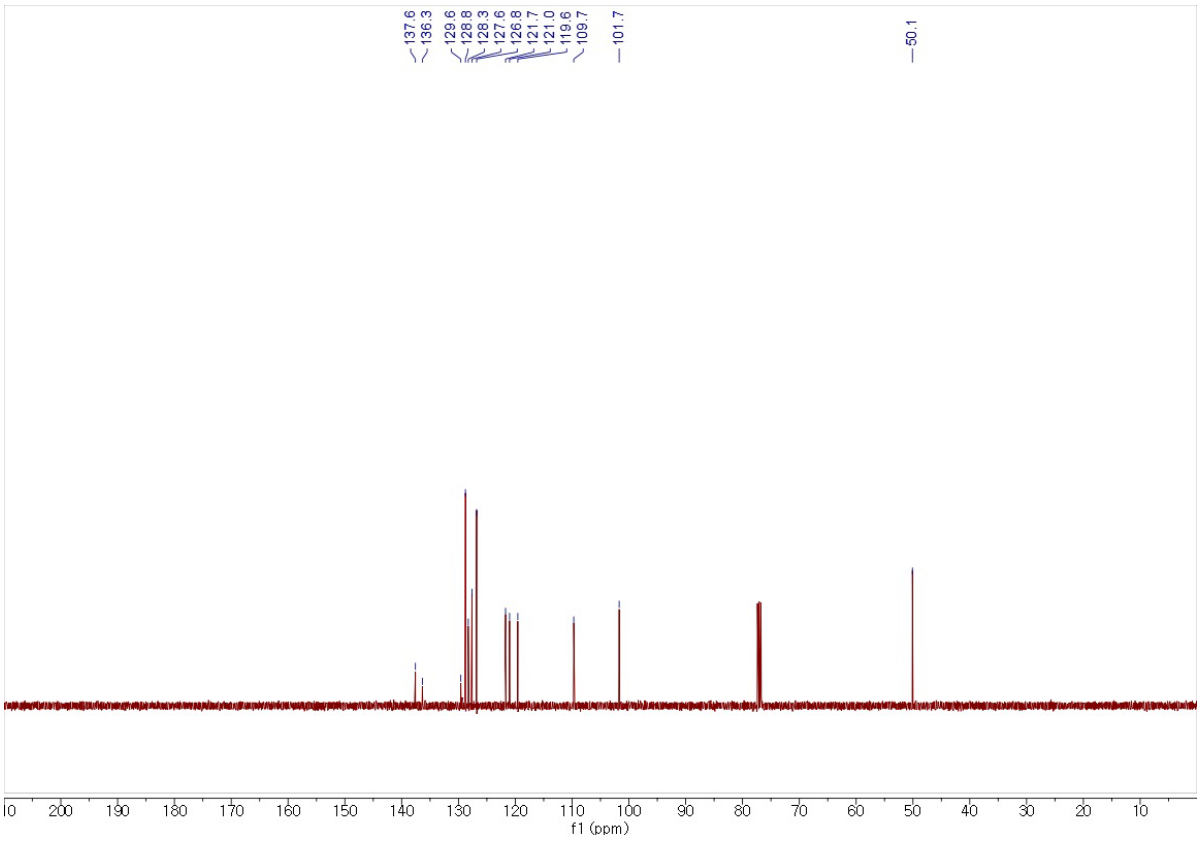
1-ethyl-1*H*-indole (5w)



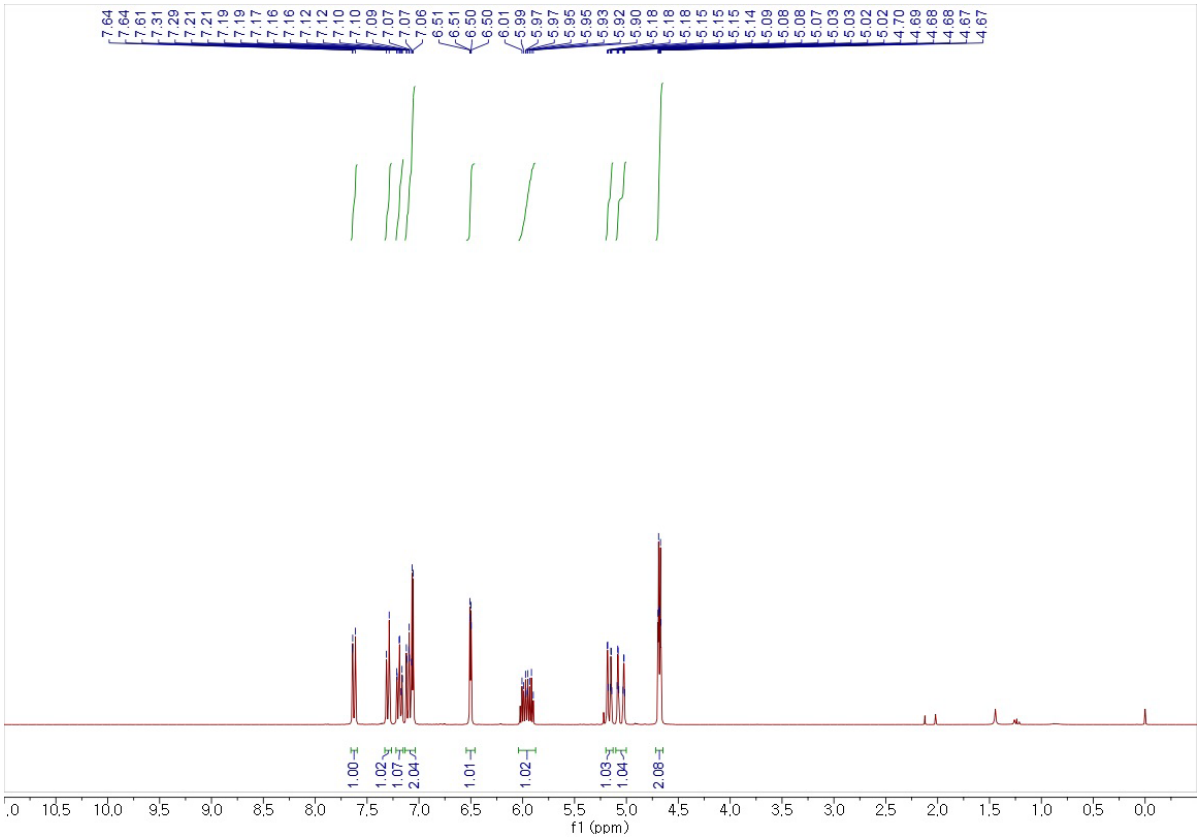


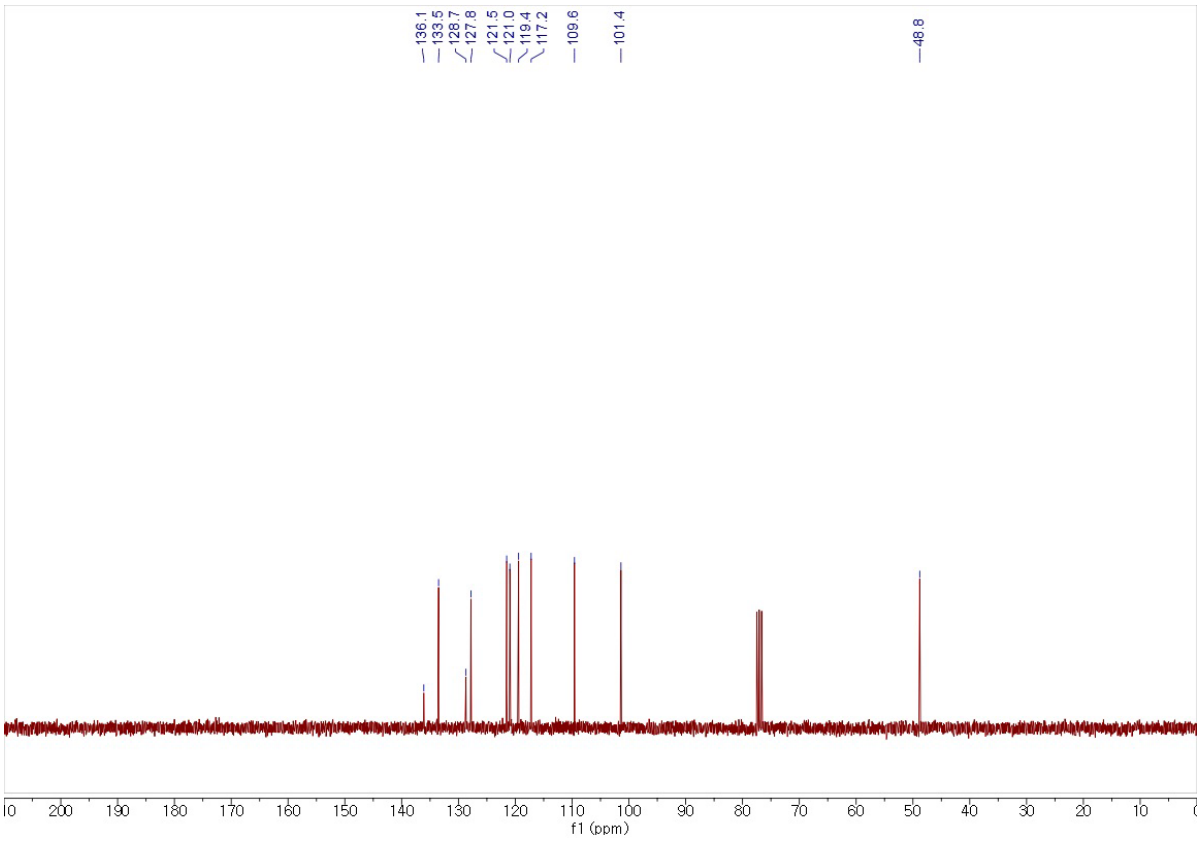
1-benzyl-1*H*-indole (5x)



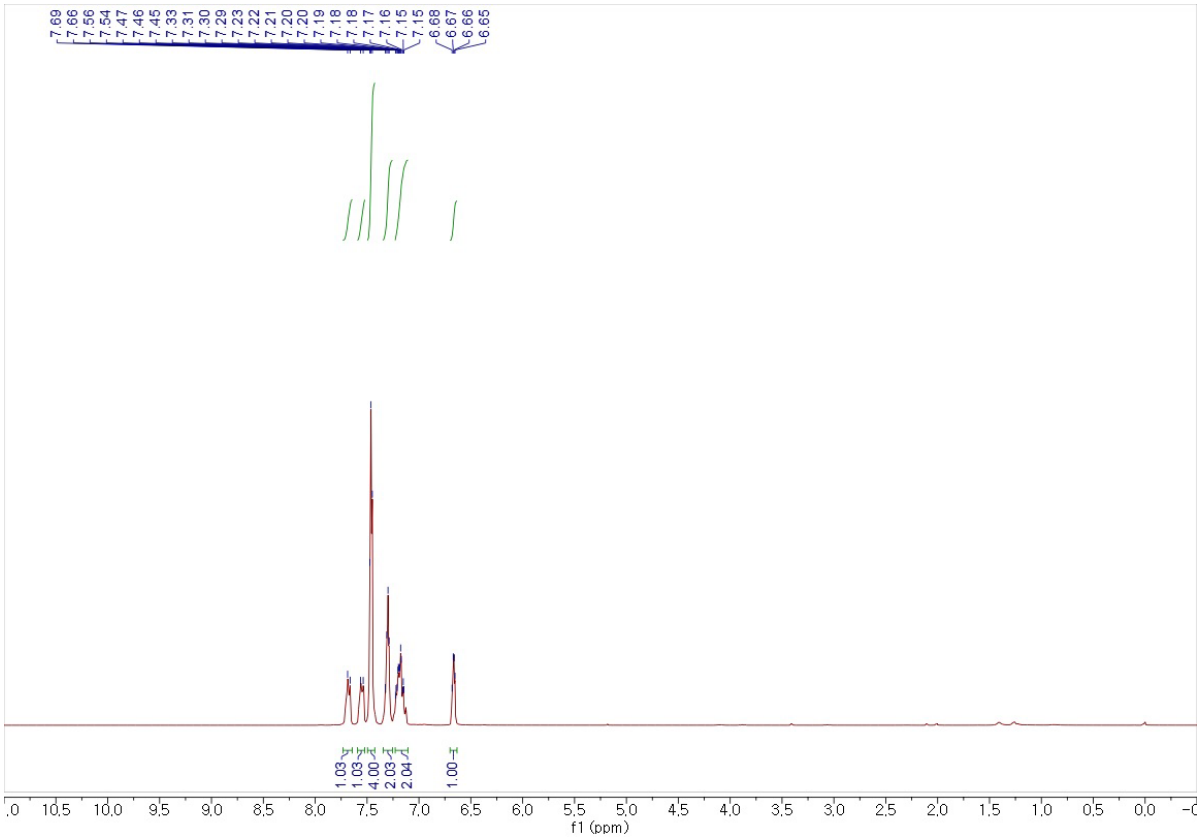


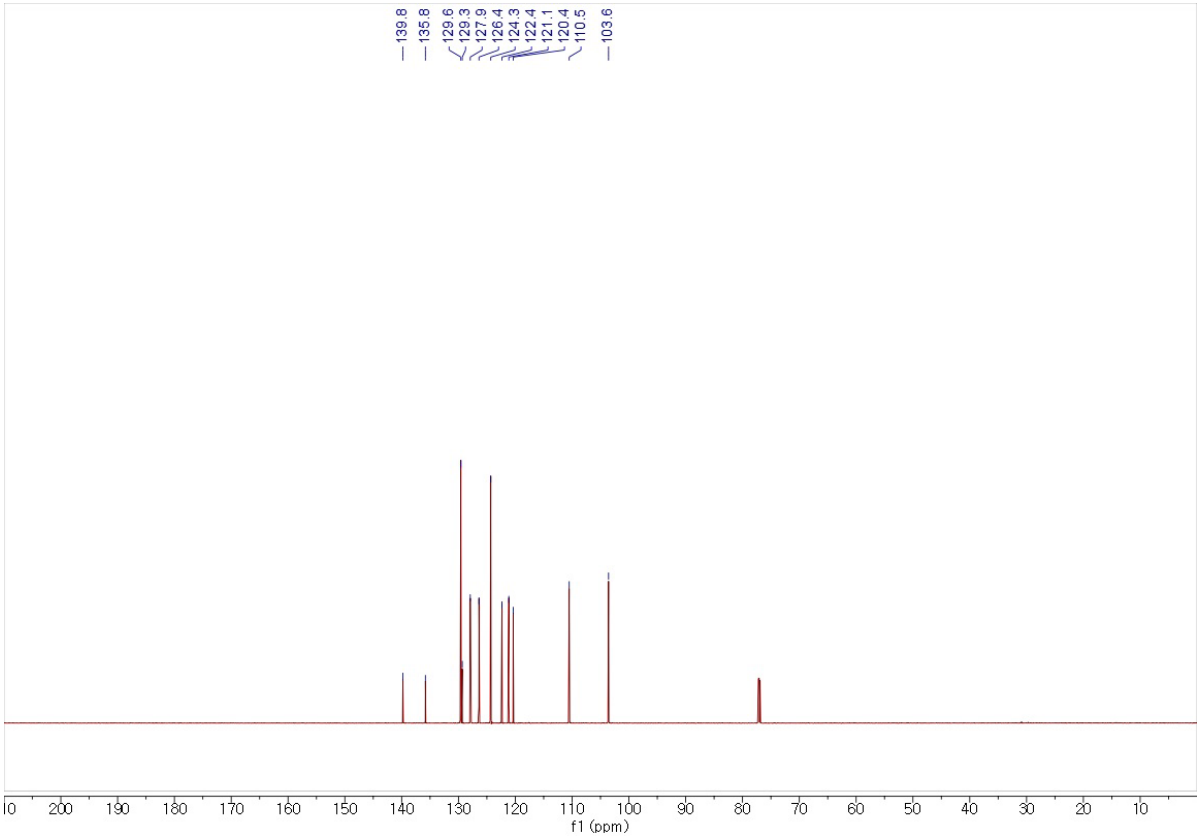
1-allyl-1*H*-indole (5y)



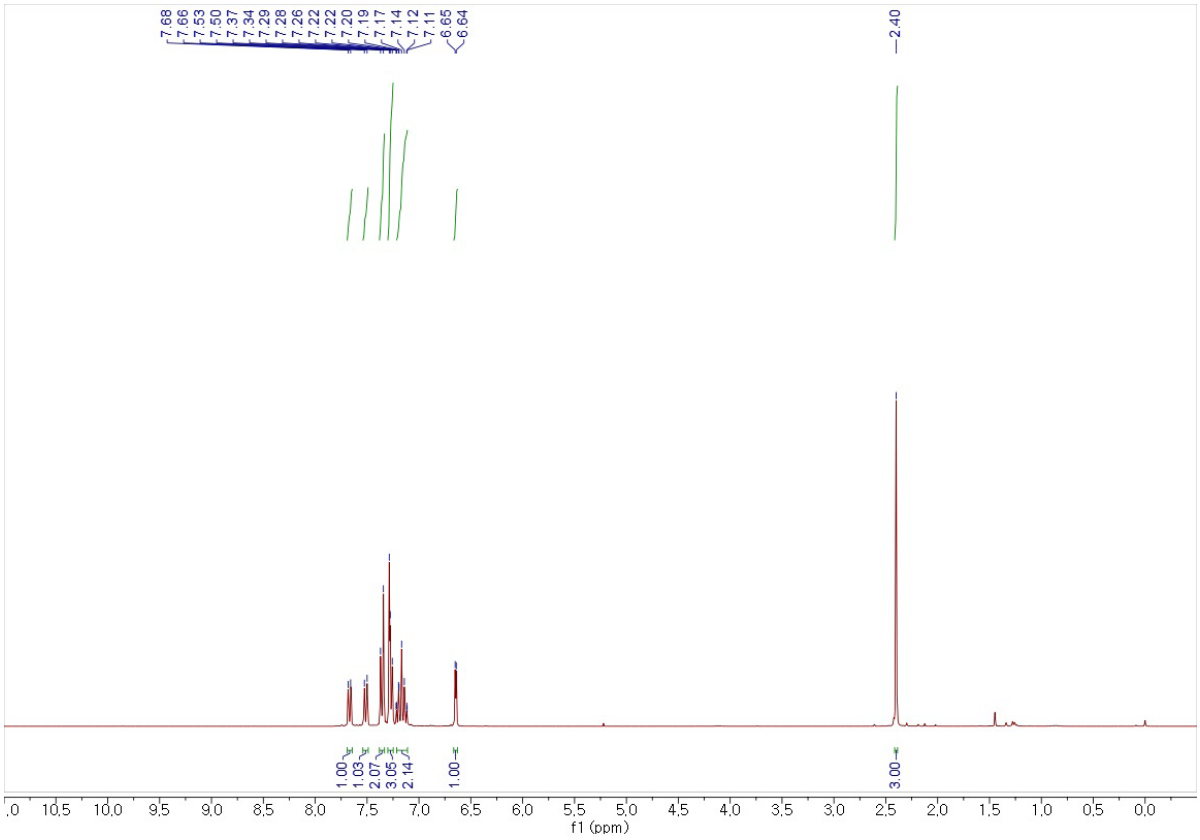


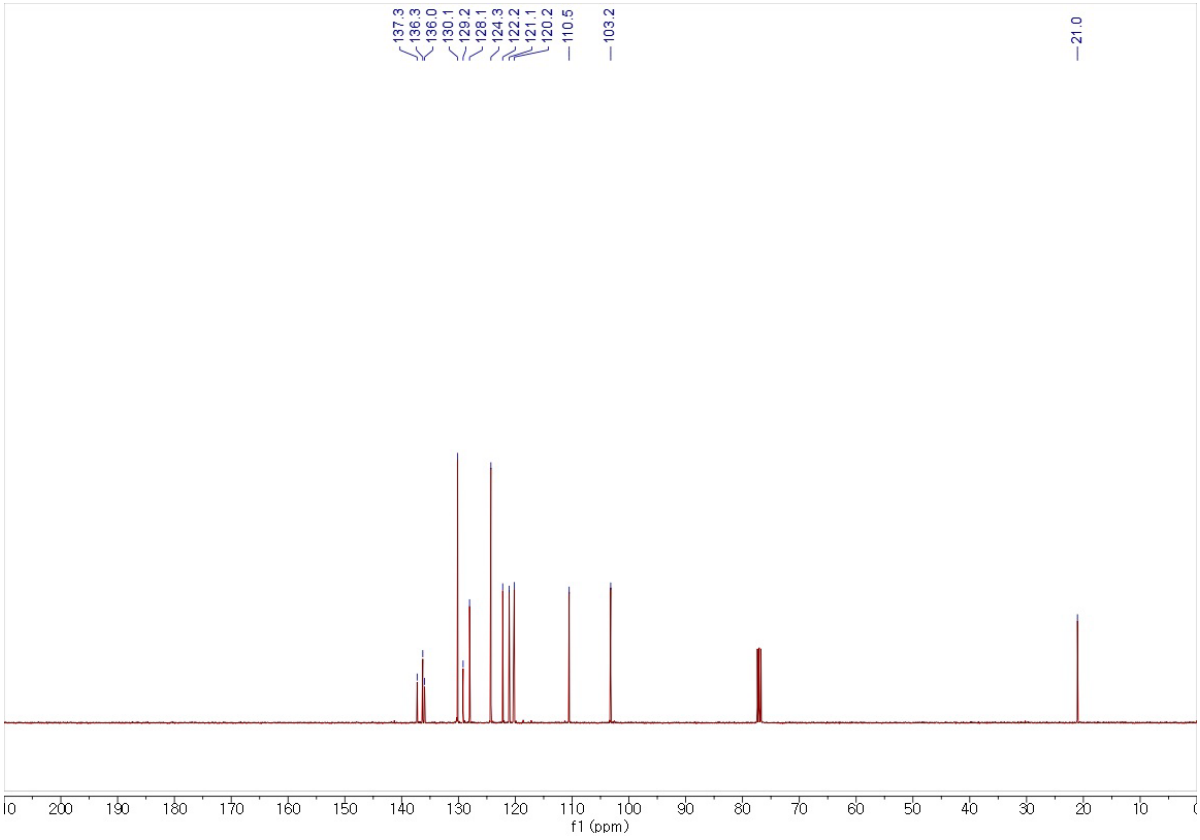
1-phenyl-1*H*-indole (5z)



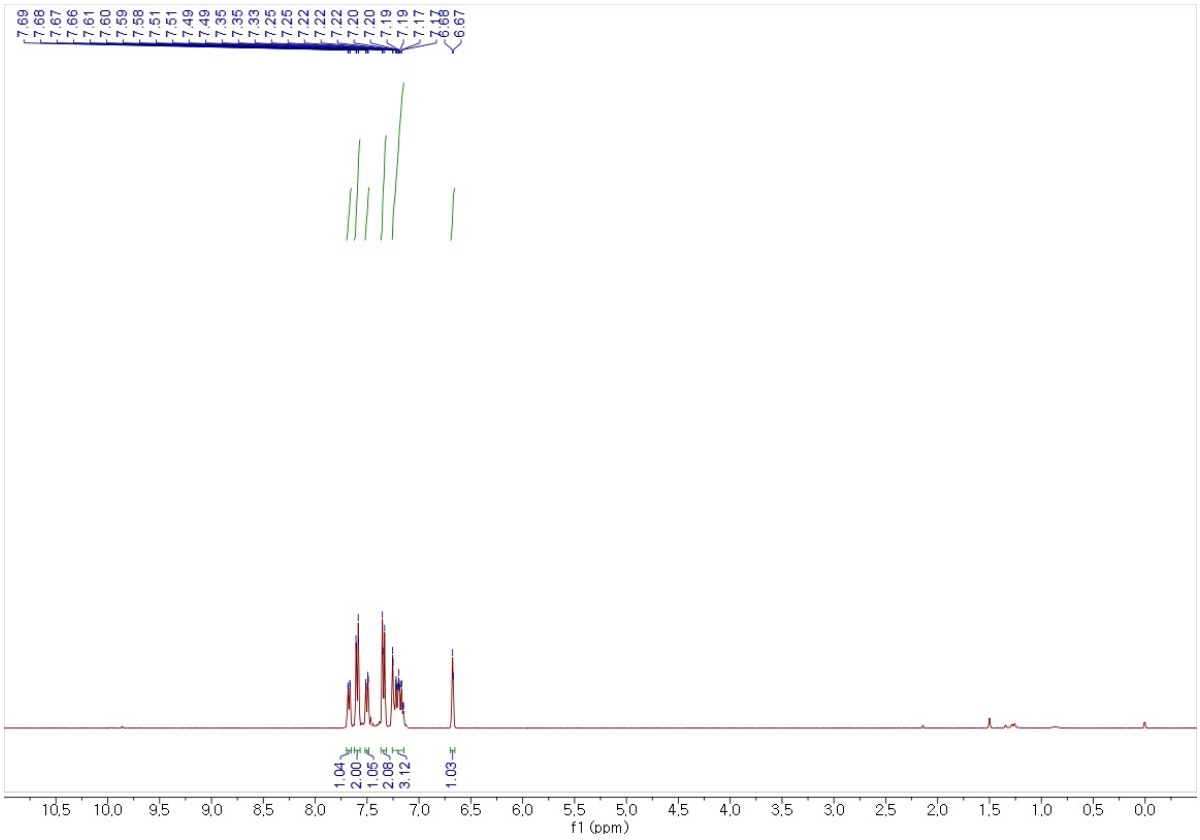


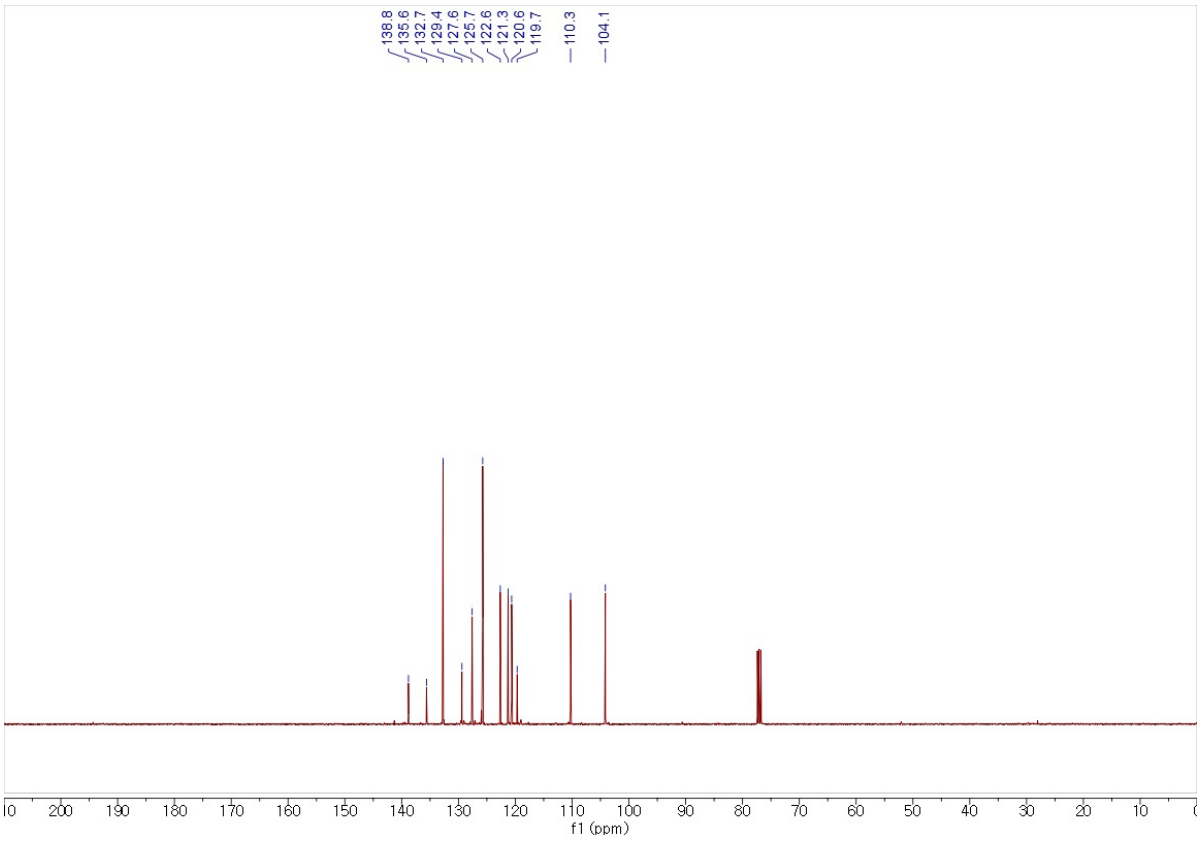
1-(*p*-tolyl)-1*H*-indole (5aa)



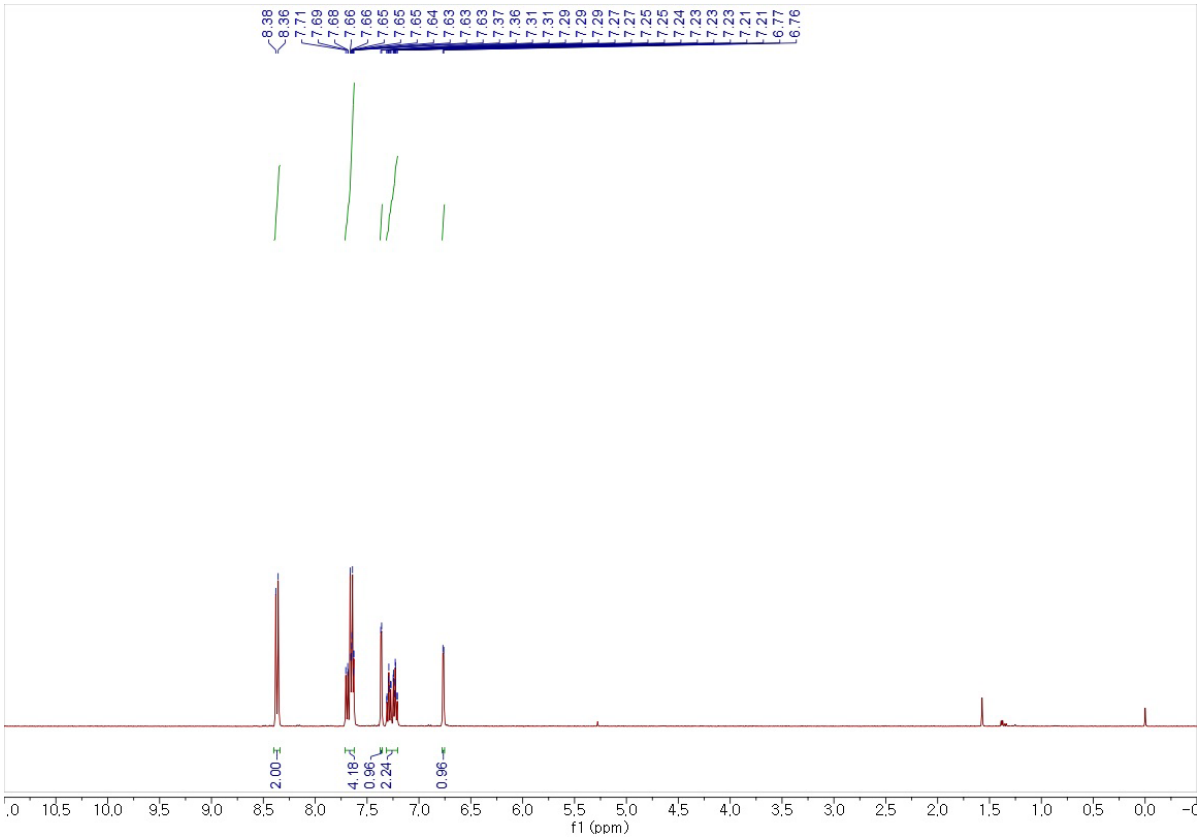


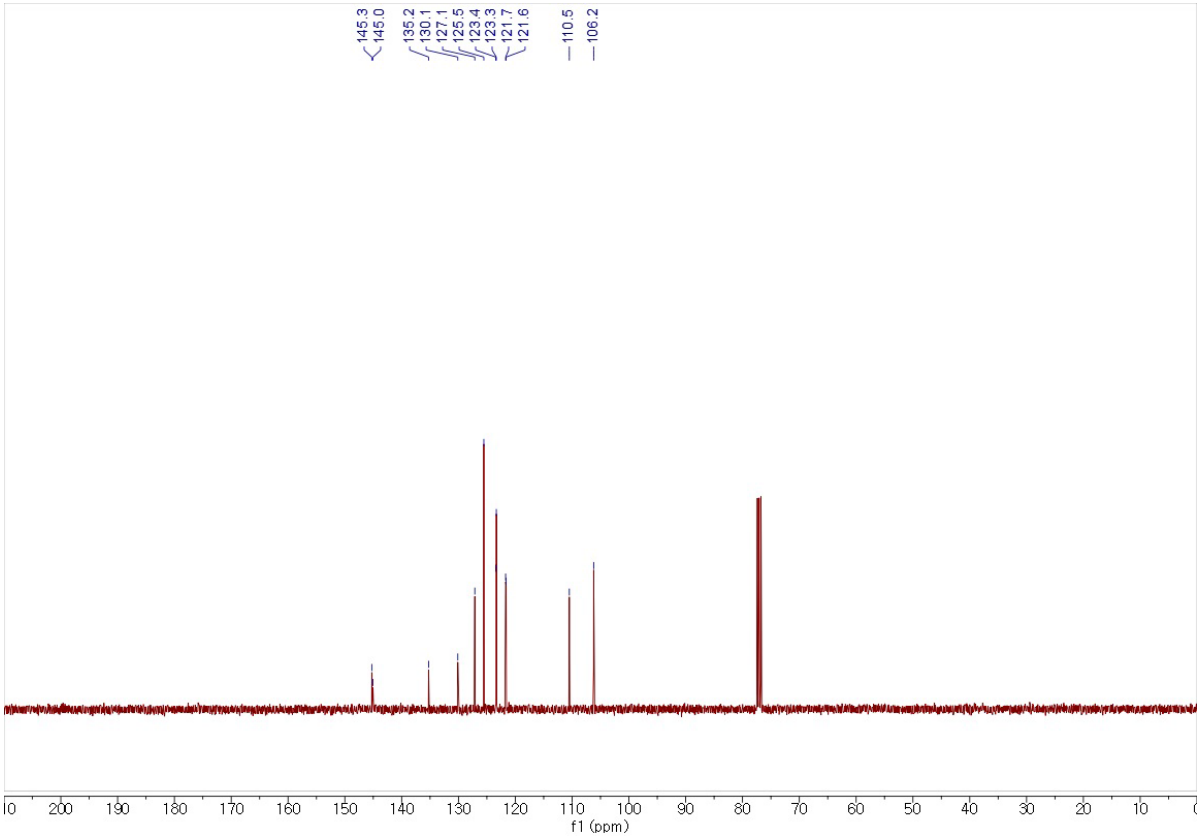
1-(4-bromophenyl)-1*H*-indole (5ab)



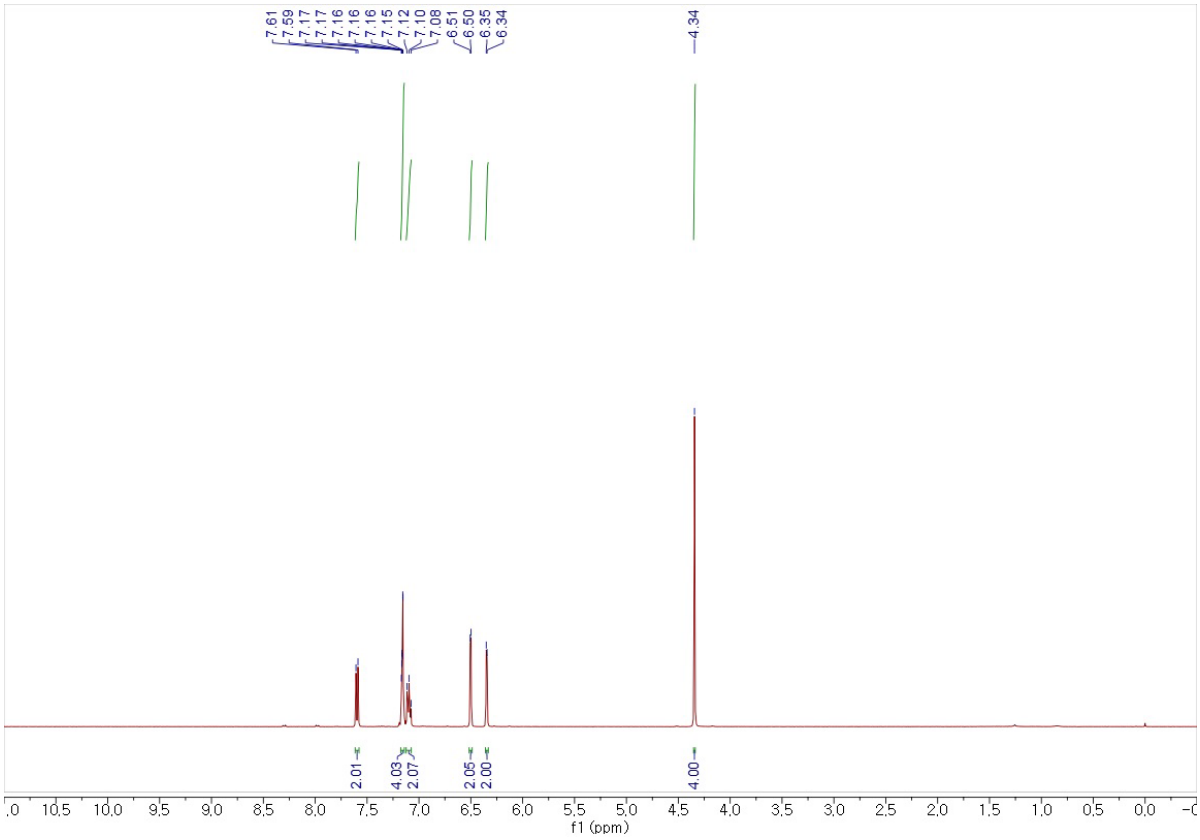


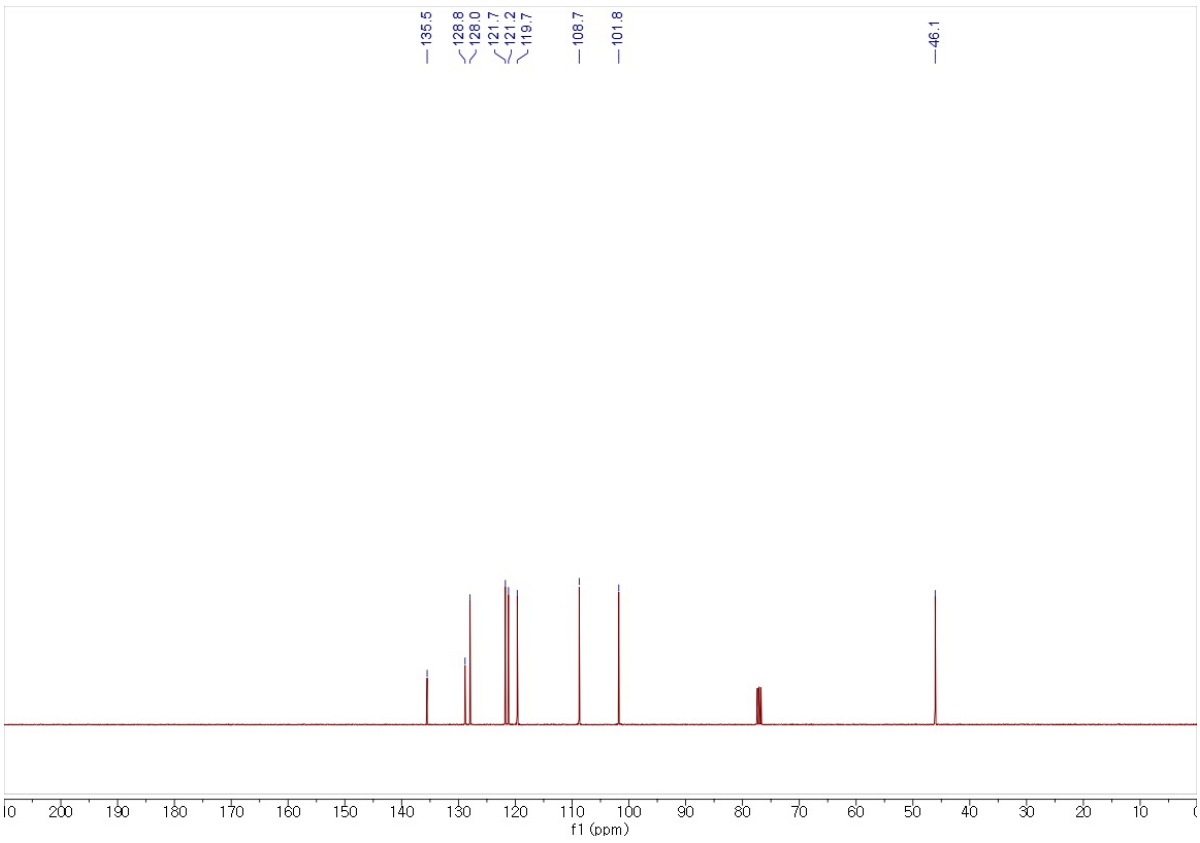
1-(4-nitrophenyl)-1*H*-indole (5ac)





1,2-di(1*H*-indol-1-yl)ethane (5af)





1-(3-chloro-1-phenylpropyl)-1*H*-indole (5ag)