Lewis Acid- and Fluoroalcohol-Mediated Nucleophilic Addition to the C2 Position of Indoles

Naoki Morimoto,[a] Kumika Morioku,[b] Hideyuki Suzuki,[c] Yasuo Takeuchi,[a] and Yuta Nishina[c,d]

[a] Graduate School of Medicine, Dentistry, and Pharmaceutical Sciences, Division of Pharmaceutical Sciences, Okayama University, 1-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan.

[b] Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan

[c] Research Core for Interdisciplinary Sciences, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan

[d] Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

E-mail: nisina-y@cc.okayama-u.ac.jp

Homepage: http://www.tt.vbl.okayama-u.ac.jp/

Supplementary information

1. General Information

All chemicals were purchased from Sigma-Aldrich, Tokyo Chemical Industry Co. Ltd., Wako Pure Chemical Industries Ltd. and Apollo Scientific Ltd. used without further purification. Silica gel chromatography was performed using Silica Gel 60N (spherical, neutral) silica gel (40-100 μm). NMR analysis were conducted using Varian NMR System 600. Regioisomer ratios were determined by ^{1}H NMR analysis. Chemical shifts are relative to solvent peaks [chloroform: 7.26 (^{1}H), 77.16 (^{13}C)]. IR spectral data were obtained using SHIMADZU IR Tracer 100. High-resolution mass spectra were measured by JEOL JMS-700.

Synthesis of starting material

1-Acetylindole (**1a**)

Indole (2.3 g, 20 mmol), acetic anhydride (3.9 g, 38 mmol), triethylamine (3.0 g, 30 mmol) and *N*,*N*-dimethyl-4-aminopyridine (464.4 mg, 3.8 mmol) were dissolved in 1,2-dichlororoethane (46 mL). The reaction mixture was stirred at 80 °C overnight under Ar atmosphere. After the reaction, AcOEt and water were added to the reaction mixture. The organic phase was concentrated under reduced pressure and purified by column chromatography (hexane : AcOEt = 10 : 1). The product was obtained as a pale yellow oil (3.0 g, 94%), and exhibited spectral data identical to those reported for 1-acetylindole.[1]

1-Acetyl-2-methylindole (**1b**)

2-Methylindole (1.3 g, 10 mmol), acetyl chloride (2.0 g, 25 mmol), sodium hydroxide (powder) (1.0 g, 25 mmol) and tetrabuthyl ammonium hydrogen sulfate (34 mg, 0.1 mmol) were dissolved in 1,2-dichlororomethane (25 mL) at 0 °C. The reaction mixture was stirred at rt overnight under Ar atmosphere. After the reaction, saturated aq. NH_4Cl and AcOEt were added to the reaction mixture. The organic phase was concentrated under reduced pressure and purified by column chromatography (hexane : AcOEt = 10 : 1). The product was obtained as an orange solid (1.2 g, 69%), and exhibited spectral data identical to those reported for 1-acetyl-2-methylindole.[2]

1-Acetyl-3-methylindole (**1c**)

3-Methylindole (1.3 g, 10 mmol), acetyl chloride (2.0 g, 25 mmol), sodium hydroxide (powder) (1.0 g, 25 mmol) and tetrabuthyl ammonium hydrogen sulfate (34 mg, 0.1 mmol) were dissolved in 1,2-dichlororomethane (25 mL) at 0 °C. The reaction mixture was stirred at rt overnight under Ar atmosphere. After the reaction, saturated aq. NH_4Cl and AcOEt were added to the reaction mixture. The organic phase was concentrated under reduced pressure and purified by column chromatography (hexane : AcOEt = 10 : 1). The product was obtained as a yellow solid (609.5 mg, 35%), and exhibited spectral data identical to those reported for 1-acetyl-3-methylindole.[3]

1-Acetyl-5-methylindole (**1d**)

5-methylindole (655.9 mg, 5.0 mmol), acetic anhydride (969.9 mg, 9.5 mmol), triethylamine (758.9 mg, 7.5 mmol) and *N*,*N*-dimethyl-4-aminopyridine (116.1 mg, 0.95 mmol) were dissolved in 1,2-dichlororoethane (11.5 mL). The reaction mixture was stirred at 80 °C overnight under Ar atmosphere. After the reaction, AcOEt and water were added to the reaction mixture. The organic phase was concentrated under reduced pressure and purified by column chromatography (hexane : AcOEt = 10 : 1). The compound was obtained as a yellow solid (586.9 mg, 68%). The product exhibited spectral data identical to those reported for 1-acetyl-5-methylindole.[4]

1-Acetyl-5-methoxyindole (**1e**)

5-Methoxylindole (735.9 mg, 5.0 mmol), acetic anhydride (969.9 mg, 9.5 mmol), triethylamine (758.9 mg, 7.5 mmol) and *N*,*N*-dimethyl-4-aminopyridine (116.1 mg, 0.95 mmol) were dissolved in 1,2-dichlororoethane (11.5 mL). The reaction mixture was stirred at 80 °C overnight under Ar atmosphere. After the reaction, AcOEt and water were added to the reaction mixture. The organic phase was concentrated under reduced pressure and purified by column chromatography (hexane : AcOEt = 10 : 1). The product was obtained as a pale yellow solid (870.3 mg, 92%), and exhibited spectral data identical to those reported for 1-acetyl-5-methoxyindole.[1]

1-Acetyl-5-chloroindole (**1f**)

5-Chloroindole (758.0 mg, 5.0 mmol), acetic anhydride (969.9 mg, 9.5 mmol), triethylamine (758.9 mg, 7.5 mmol) and *N*,*N*-dimethyl-4-aminopyridine (116.1 mg,

0.95 mmol) were dissolved in 1,2-dichlororoethane (11.5 mL). The reaction mixture was stirred at 80 °C overnight under Ar atmosphere. After the reaction, AcOEt and water were added to the reaction mixture. The organic phase was concentrated under reduced pressure and purified by column chromatography (hexane : AcOEt = 10 : 1). The product was obtained as a pale yellow solid (897.5 mg, 93%), and exhibited spectral data identical to those reported for 1-acetyl-5-chloroindole.[5]

1-Acetyl-5-bromoindole (**1g**)

5-Bromoindole (1.2 g, 10 mmol), acetyl chloride (2.0 g, 25 mmol), sodium hydroxide (powder) (1.0 g, 25 mmol) and tetrabuthyl ammonium hydrogen sulfate (34.0 mg, 0.1 mmol) were dissolved in 1,2-dichlororomethane (25 mL) at 0 °C. The reaction mixture was stirred at rt overnight under Ar atmosphere. After the reaction, saturated aq. NH_4Cl and AcOEt were added to the reaction mixture. The organic phase was concentrated under reduced pressure and purified by column chromatography (hexane : AcOEt = 10 : 1). The product was obtained as a pale yellow solid (1.2 g, 51%), and exhibited spectral data identical to those reported for 1-acetyl-5-bromoindole.[3]

1-Acetyl-5-nitroindole (**1h**)

5-Nitroindole (810.8 mg, 5.0 mmol), acetic anhydride (969.9 mg, 9.5 mmol), triethylamine (758.9 mg, 7.5 mmol) and *N*,*N*-dimethyl-4-aminopyridine (116.1 mg, 0.95 mmol) were dissolved in 1,2-dichlororoethane (11.5 mL). The reaction mixture was stirred at 80 °C overnight under Ar atmosphere. After the reaction, AcOEt and water were added to the reaction mixture. The organic phase was concentrated under reduced pressure and purified by column chromatography (hexane : AcOEt = 10 : 1). The compound was obtained as a pale yellow solid (803.7 mg, 79%). The product exhibited spectral data identical to those reported for 1-acetyl-5-nitroindole[6].

1-(3,4-Dimethoxyphenylacetyl)-indole (**5**)

3,4-Dimethoxyphenylacetic acid (1.96 g, 10 mmol) and thionyl chloride (1.8 g, 15 mmol) were stirred at 80 °C for 2 h. The excess thionyl chloride was evaporated under reduced pressure to obtain 3,4-dimethoxyphenylacetic acid chloride.

Indole (1.2 g, 10 mmol) was dissolved to the solution of THF (20 mL), then 1.6 M *n*-BuLi in hexane (7.5 mL) was added dropwise at -97 °C with stirring. After 10 min,

THF solution (5 mL) of as synthesized 3,4-dimethoxyphenylacetic acid chloride was added, and the reaction temperature was gradually raised to rt and stirred for 30 min. After the reaction, saturated aq. NH_4Cl and AcOEt were added to the reaction mixture. The organic phase was concentrated under reduced pressure and purified by column chromatography (hexane : AcOEt = 5 : 1). The product was obtained as a pale yellow solid (1.3 g, 44%).

Mp: 90-91 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, 1H, *J* = 8.3 Hz), 7.56 (d, 1H, *J* = 7.5 Hz), 7.52 (d, 1H, *J* = 3.7 Hz), 7.36 (ddd, 1H *J* = 8.3, 7.5, 1.2 Hz), 7.28 (ddd, 1H, *J* = 7.5, 7.5, 1.0 Hz), 6.87-6.85 (m, 3H), 6.63 (d, 1H, *J* = 3.7 Hz), 4.20 (s, 2H), 3.87 (s, 3H), 3.87 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.71, 149.37, 148.52, 135.95, 130.44, 125.94, 125.40, 124.97, 123.99, 121.46, 120.96, 116.91, 112.25, 111.56, 109.60, 56.05, 56.05, 42.80

IR (KBr) 3142, 2830, 2604, 2500, 2282, 2203, 2056, 2006, 1950, 1913, 1848, 1805, 1719, 1600, 1535, 1103, 1086, 1016, 961, 930, 910, 868, 826, 752 cm^{-1}

HRMS (FAB+) Calcd for $C_{18}H_{18}NO_3$ (FAB+) 295.1208, Found 295.1218

2. Typical procedure for the investigation to form acyl iminium species (Table 1 and Table S1)

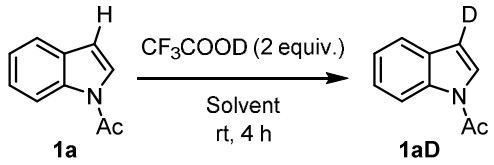
Typical procedure for Table 1.

A solvent (D source, 0.5 mL), **1a** (47.8 mg, 0.3 mmol) and $BF_3 \cdot OEt_2$ (85.2 mg, 0.6 mmol) were mixed under Ar atmosphere, and stirred at rt for 4 h. After the reaction, the reaction mixture was diluted by AcOEt and water. The organic phase was extracted and concentrated under reduced pressure, and analyzed by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Typical procedure for Table S1.

A solvent (0.5 mL), **1a** (47.8 mg, 0.3 mmol) and CF_3COOD (45.9 mg, 0.6 mmol) were mixed under Ar atmosphere, and stirred at rt for 4 h. After the reaction, the reaction mixture was diluted by AcOEt and water. The organic phase was extracted and concentrated under reduced pressure, and analyzed by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Table S1. Investigation of N-acyliminium formation using CF_3COOD as a D source.

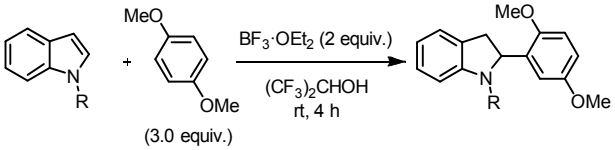


Entry	Solvent	Deuteration ratio (%)
1	MeCN	0
2	CH_2Cl_2	3
3	PhCl	3
4	THF	0
5	DMF	2
6	Hexane	6

Evaluation of substation on nitrogen atom of indole.

$(CF_3)_2CHOH$ (0.5 mL), *N*-substituted indole (0.3 mmol) and $BF_3{\cdot}OEt_2$ (85.2 mg, 0.6 mmol) were added under Ar atmosphere, and stirred at rt for 4 h. The reaction mixture was quenched by AcOEt and water. The organic phase was extracted and concentrated under reduced pressure, and purified by column chromatography (hexane : AcOEt = 2 : 1). Reaction mixtures of entries 2 - 7 were analyzed by GC-MS and TLC.

Table S2. The screening of various *N*-substituted indole.



Entry	R	Yield (%)
1	Ac	79
2	Boc	N.D.
3	Piv	N.D.
4	Ts	N.D.
5	Bz	N.D.
6	Me	N.D.
7	H	N.D.

3. Typical procedure for the optimization of the reaction condition (Table 2)

To the solvent (0.5 mL), **1a** (47.8 mg, 0.3 mmol), **2a** (124.3 mg, 0.9 mmol) and $BF_3 \cdot OEt_2$ (85.2 mg, 0.6 mmol) were added under Ar atmosphere and stirred at rt for 4 h. After the reaction, the reaction mixture was quenched by AcOEt and water. The organic phase was extracted and concentrated under reduced pressure, and purified by column chromatography (hexane : AcOEt = 2 : 1).

4. Typical procedure for the investigation of scope using various *N*-acetylindoles (Table 3)

$(CF_3)_2CHOH$ (0.5 mL), **1** (47.8 mg, 0.3 mmol), **2a** (124.3 mg, 0.9 mmol) and $BF_3 \cdot OEt_2$ (85.2 mg, 0.6 mmol) were added under Ar atmosphere, and stirred at rt for 4 h. After the reaction, the reaction mixture was quenched by AcOEt and water. The organic phase was extracted and concentrated under reduced pressure, and purified by column chromatography (hexane : AcOEt = 2 : 1).

5. Typical procedure for the investigation of scope using various nucleophiles (Table 4)

$(CF_3)_2CHOH$ (0.5 mL), **1a** (47.8 mg, 0.3 mmol), **2** (0.9 mmol) and $BF_3 \cdot OEt_2$ (85.2 mg, 0.6 mmol) were added under Ar atmosphere, and stirred at rt for 4 h. After the reaction, the reaction mixture was quenched by AcOEt and water. The organic phase was extracted and concentrated under reduced pressure, and purified by column chromatography (hexane : AcOEt = 2 : 1). To separate regioisomers, recrystallization was performed using CH_2Cl_2 and hexane.

Table S3. Product yields of Table 4.

Entry	Weight of isolated products (mg)
1[a]	65.7
2	61.8
3[a]	61.5
4[a]	52.9
5[a]	56.1
6	47.7

7	34.2

[a] Yields were measured as mixture of regioisomers before recrystallization.

6. Synthesis of C2 and C3 diaryl substituted indole (Scheme 3.)

Dehydrogenation of 3a

1,2-Dichloroethane (20 mL), **3a** (501.1 mg, 1.7 mmol) and MnO_2 (5.0 g) were added and refluxed for 12 h. After the reaction, the reaction mixture was filtrated using Celite®. The resulting solution was concentrated under reduced pressure and purified by column chromatography (hexane : AcOEt = 5 : 1). The product was obtained as a colorless solid (390.4 mg, 78%).

Bromination of 7

Dichloromethane (5 mL), **7** (147.2 mg, 0.5 mmol) and *N*-Bromosuccinimide (89.0 mg, 0.5 mmol) were added and stirred at rt for 2 h. After the reaction, the reaction mixture was quenched by AcOEt and water. The organic phase was extracted and concentrated under reduced pressure, and purified by column chromatography (hexane : AcOEt = 5 : 1). The product was obtained as a colorless solid (174.2 mg, 93%).

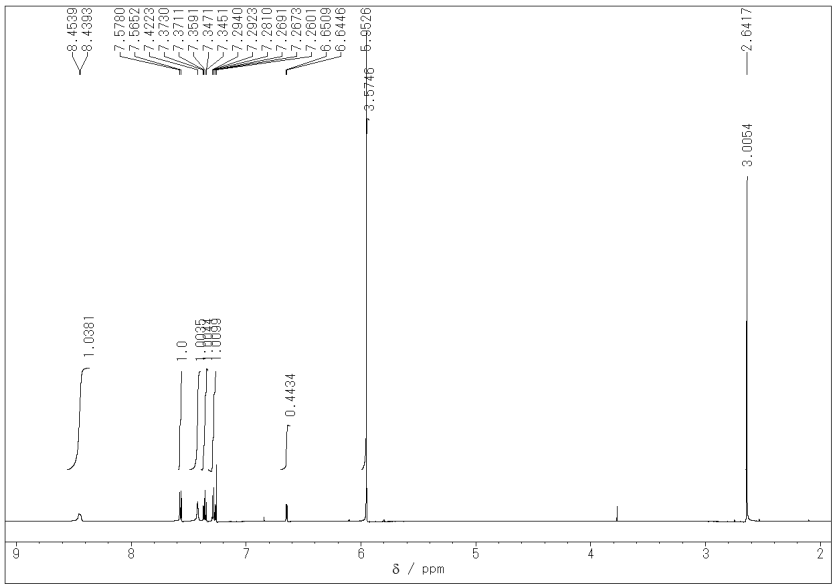
Suzuki-Miyaura coupling reaction of 8

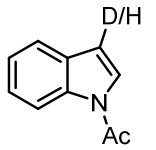
50% aq. dioxane (10 mL), **8** (172.0 mg, 0.46 mmol), phenylboronic acid (67.3 mg, 0.55 mmol), potassium carbonate (190.7 mg, 1.38 mmol) and 10% Pd/C (29.2 mg, Pd: 0.0023 mmol) were added and refluxed overnight. After the reaction, the reaction mixture was quenched by AcOEt and water. The organic phase was extracted and concentrated under reduced pressure, and purified by column chromatography (hexane : AcOEt = 2 : 1). The product was obtained as a colorless solid (120.1 mg, 79%).

7. Typical procedure for the determination of rate determined step (Scheme 4.)

$(CF_3)_2CHOD$ (0.5 mL), **1a** (47.8 mg, 0.3 mmol), **2a** (124.3 mg, 0.9 mmol) and $BF_3 \cdot OEt_2$ (85.2 mg, 0.6 mmol) were added under Ar atmosphere and stirred at rt. The reaction mixture was quenched in 30 min by adding AcOEt and water. The organic phase was extracted and concentrated under reduced pressure, and purified by column chromatography (hexane : AcOEt = 2 : 1). Recovered **1a(D)** and yielded **3a(D)** were calculated from ^{1}H NMR measurement using 1,1,2,2-tetrachloroethane as an internal standard. ^{1}H NMR spectra of **1a(D)** and **3a(D)** were shown below.

^{1}H NMR

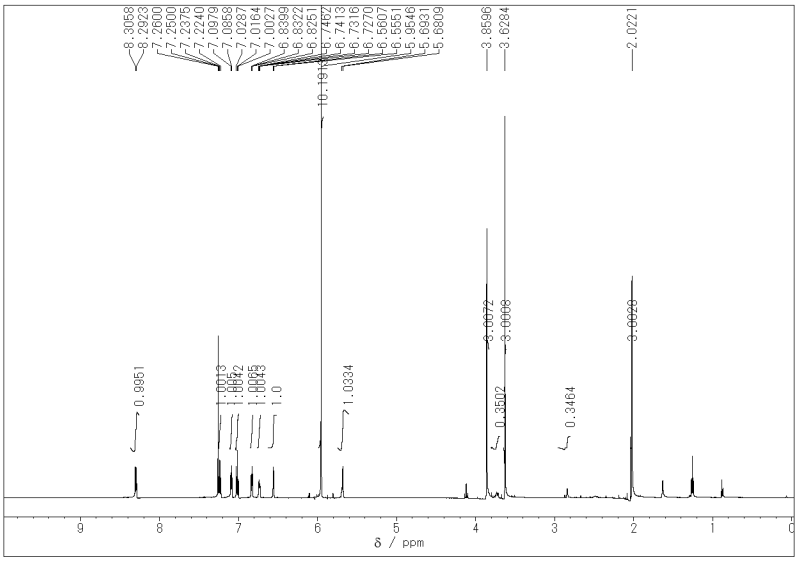


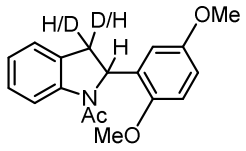


1a(D)

D/H = 56/44

^{1}H NMR





3a(D)

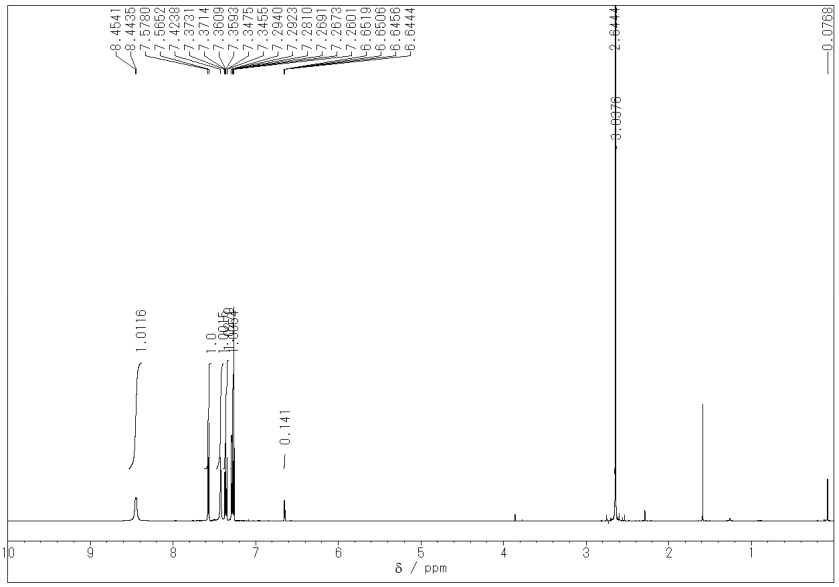
D/H = 35/65

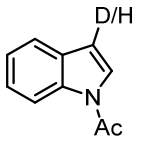
8. The elucidation of the hydrogen source

Synthesis of deuterated *N*-acetylindole (**1a(D)**)

$(CF_3)_2CHOD$ (2.0 mL), *N*-acetylindole (191.0 mg, 1.2 mmol) and $BF_3{\cdot}OEt_2$ (340.6 mg, 2.4 mmol) was added and stirred at rt for 4 h. After the reaction, the reaction mixture was purified by column chromatography (hexane : AcOEt = 5 : 1). The compound was obtained as a pale yellow oil (115.2 mg, 64%). ^{1}H NMR spectra of **1a(D)** was shown below.

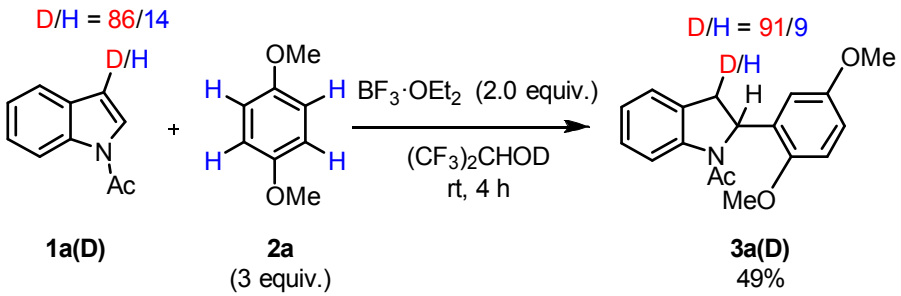
^{1}H NMR





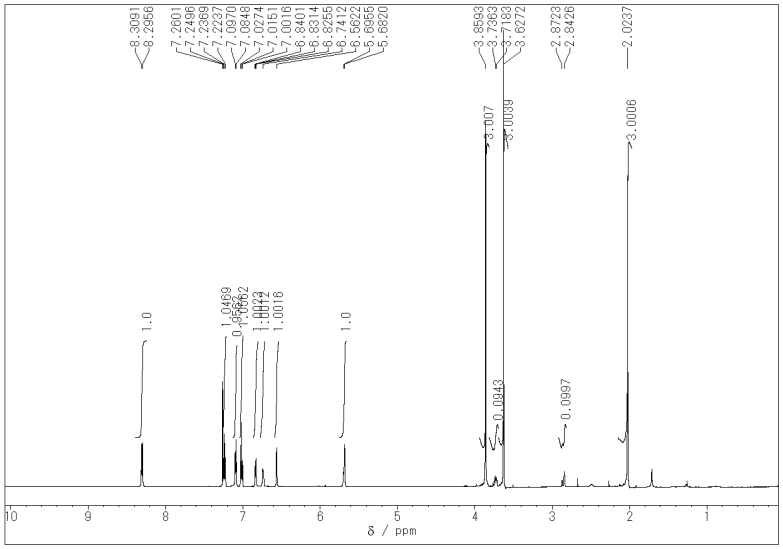
1a(**D**)
D/H = 86/14

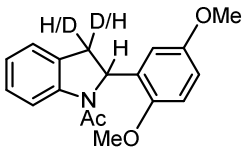
To determine the hydrogen source of C3 position of *N*-acetylindole, the nucleophilic reaction of 1,4-dimethoxybenzene (**2a**) to deuterated *N*-acetylindole (**1a(D)**) was carried out in $(CF_3)_2CHOD$. The deuteration ratio at the C3 position was increased than that of **1a(D)**, therefore, hydrogen at the C3 position did not derive from **2a**. ^{1}H NMR spectra of **3a(D)** was shown below.



1a(D) **2a** (3 equiv.) **3a(D)** 49%

^{1}H NMR





3a(D)
D/H = 91/9

9. Reference

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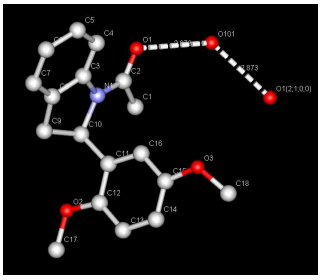
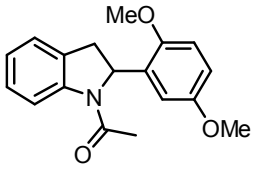
10. Product data

Crystal data and structure refinement





Identification code: **3a**

CCDC number: 1447376

Unit cell parameter

a: 13.341(6)

b: 10.279(5)

c: 22.280(12)

alpha: 90.000

beta: 92.566(8)

gamma: 90.000

volume: 3052(3)

Space group information

symbol: C2/c

number: 15

Z value: 8

formula weight: 300.06

Model refinement

R1 factor[I>2.0sigma(I)]: 0.0677

R factor[all data]: 0.0905

wR factor[all data]: 0.1318

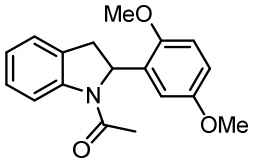
Goodness of fit: 1.182

Experimental condition

radiation: Mo

temperature: -173 °C

1-Acetyl-2-(2,5-dimethoxyphenyl)-2,3-dihydro-indole (**3a**)



Colorless solid. Yield: 70.4 mg, 79%. Mp: 86-89 °C.

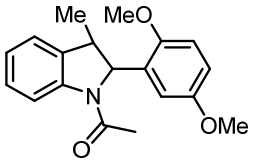
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, 1H, *J* = 7.7 Hz), 7.24 (dd, 1H, *J* = 7.8, 7.7 Hz), 7.09 (d, 1H, *J* = 7.8 Hz), 7.02 (ddd, 1H, *J* = 7.8, 7.8, 0.7 Hz), 6.83 (d, 1H, *J* = 8.8 Hz), 6.74 (dd, 1H, *J* = 8.8, 2.9 Hz), 6.56 (d, 1H, *J* = 2.9 Hz), 5.69 (dd, 1H, *J* = 10.1, 1.8 Hz), 3.86 (s, 3H), 3.74 (dd, 1H, *J* = 16.1, 10.1 Hz), 3.63 (s, 3H), 2.86 (dd, 1H, *J* = 16.1, 1.8 Hz), 2.02 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.64, 154.05, 149.83, 143.40, 132.29, 130.04, 127.75, 125.00, 124.10, 117.27, 112.39, 111.97, 111.46, 58.19, 56.01, 55.71, 37.89, 23.88

IR (KBr) 3200, 3009, 2909, 2841, 2644, 2581, 2521, 2388, 2324, 2245, 2170, 2068, 2004, 1952, 1910, 1869, 1834, 1794, 1744, 1682, 1504, 1288, 1103, 1011, 978, 935, 891, 864, 816, 775, 706 cm^{-1}

HRMS (FAB+) Calcd for $C_{18}H_{20}NO_3$ (FAB+) 298.1443, Found 298.1453

1-Acetyl-2-(2,5-dimethoxy-phenyl)-3-methyl-2,3-dihydro-indole (**3c**)



Pale yellow solid. Yield: 33.6 mg, 36%. Mp: 33-34 °C.

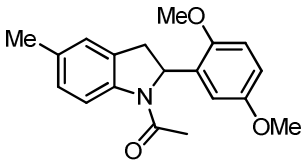
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, 1H, *J* = 8.2 Hz), 7.24 (dd, 1H, *J* = 8.2, 7.2 Hz), 7.07 (d, 1H, *J* = 7.1 Hz), 7.03 (ddd, 1H, *J* = 8.1, 7.2, 0.7 Hz), 6.83 (d, 1H, *J* = 8.9 Hz), 6.72 (dd, 1H, *J* = 8.9, 2.9 Hz), 6.51 (d, 1H, *J* = 2.9 Hz), 5.23 (d, 1H, *J* = 1.7 Hz), 3.88 (s, 3H), 3.62 (s, 3H), 3.08 (dq, 1H, *J* = 7.2, 1.7 Hz), 2.02 (s, 3H), 1.44 (d, 3H, *J* = 7.2 Hz)

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.90, 154.01, 150.21, 142.42, 135.66, 131.81, 127.94, 124.33, 124.22, 117.22, 112.11, 111.82, 111.35, 66.37, 55.99, 55.68, 45.63, 23.87, 22.92

IR (KBr) 2961, 2833, 1659, 1599, 1489, 1391, 1310, 1281, 1242, 1217, 1179, 1157, 1113, 1092, 1047, 1024, 953, 924, 907, 872, 806, 754, 714 cm^{-1}

HRMS (FAB+) Calcd for $C_{19}H_{22}NO_3$ (FAB+) 312.1600, Found 312.1593

1-Acetyl-2-(2,5-dimethoxyphenyl)-5-methyl-2,3-dihydro-indole (**3d**)



Colorless solid. Yield: 72.8 mg, 78%. Mp: 104-105 °C.

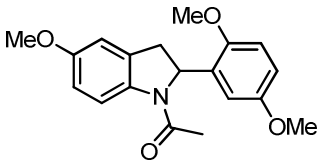
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, 1H, *J* = 8.2 Hz), 7.04 (d, 1H, *J* = 8.2 Hz), 6.90 (s, 1H), 6.83 (d, 1H, *J* = 8.9 Hz), 6.73 (dd, 1H, *J* = 8.9, 3.0 Hz), 6.55 (d, 1H, *J* = 3.0 Hz), 5.67 (dd, 1H, *J* = 10.0, 1.8 Hz), 3.86 (s, 3H), 3.71 (dd, 1H, *J* = 16.1, 10.0 Hz), 3.63 (s, 3H), 2.81 (dd, 1H, *J* = 16.1, 1.8 Hz), 2.28 (s, 3H), 2.01 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.33, 154.03, 149.80, 141.09, 133.71, 132.33, 130.11, 128.18, 125.64, 116.95, 112.32, 111.94, 111.40, 58.27, 55.99, 55.70, 37.83, 23.75, 21.17

IR (KBr) 3302, 3021, 2945, 2839, 2045, 1815, 1659, 1597, 1493, 1437, 1391, 1273, 1223, 1188, 1155, 1136, 1057, 1028, 980, 932, 872, 820, 760, 710 cm^{-1}

HRMS (FAB+) Calcd for $C_{19}H_{22}NO_3$ (FAB+) 312.1600, Found 312.1612

1-Acetyl-2-(2,5-dimethoxyphenyl)-5-methoxy-2,3-dihydro-indole (**3e**)



Pale brown solid. Yield: 9.8 mg, 10%. Mp: 89-91 °C.

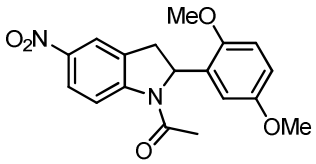
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, 1H, *J* = 8.8 Hz), 6.83 (d, 1H, *J* = 8.8 Hz), 6.76 (dd, 1H, *J* = 8.8, 2.6 Hz), 6.73 (dd, 1H, *J* = 8.8, 3.0 Hz), 6.66 (d, 1H, *J* = 2.6 Hz), 6.55 (d, 1H, *J* = 3.0 Hz), 5.67 (dd, 1H, *J* = 10.0, 1.8 Hz), 3.86 (s, 3H), 3.76 (s, 3H), 3.72 (dd, 1H, *J* = 16.3, 10.0 Hz), 3.63 (s, 3H), 2.82 (dd, 1H, *J* = 16.3, 1.8 Hz), 2.00 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.94, 156.69, 154.02, 149.80, 137.14, 132.19, 131.68, 117.83, 112.36, 112.14, 111.95, 111.41, 111.24, 58.38, 55.97, 55.72, 55.70, 37.97, 23.57

IR (KBr) 3289, 3069, 2953, 2833, 2041, 1815, 1726, 1659, 1589, 1493, 1335, 1310, 1238, 1142, 1107, 1055, 978, 932, 876, 812, 754, 718 cm^{-1}

HRMS (FAB+) Calcd for $C_{19}H_{22}NO_4$ (FAB+) 328.1549, Found 328.1554

1-Acetyl-2-(2,5-dimethoxyphenyl)-5-nitro-2,3-dihydro-indole (**3f**)



Yellow solid. Yield: 30.8 mg, 30%. Mp: 116-118 °C.

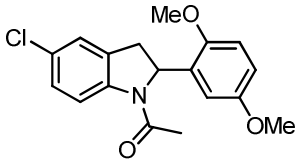
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, 1H, *J* = 8.9 Hz), 8.18 (dd, 1H, *J* = 8.9, 2.4 Hz), 7.97 (s, 1H), 6.86 (d, 1H, *J* = 8.9 Hz), 6.77 (dd, 1H, *J* = 8.9, 3.0 Hz), 6.47 (d, 1H, *J* = 3.0 Hz), 5.80 (d, 1H, *J* = 10.2 Hz), 3.86 (s, 3H), 3.78 (dd, 1H, *J* = 16.6, 10.2 Hz), 3.65 (s, 3H), 2.96 (dd, 1H, *J* = 16.6, 2.2 Hz), 2.07 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 170.45, 154.03, 149.72, 148.80, 144.04, 131.54, 131.01, 124.93, 120.79, 116.44, 112.61, 111.95, 111.73, 59.18, 56.00, 55.74, 37.25, 23.97

IR (KBr) 3096, 2999, 2951, 2833, 2361, 1678, 1599, 1506, 1435, 1385, 1333, 1300, 1263, 1219, 1179, 1150, 1103, 1078, 1055, 1024, 986, 916, 874, 847, 822, 793, 785, 752, 706 cm^{-1}

HRMS (FAB+) Calcd for $C_{18}H_{19}N_2O_5$ (FAB+) 343.1294, Found 343.1293

1-Acetyl-2-(2,5-dimethoxyphenyl)-5-chloro-2,3-dihydro-indole (**3g**)



Colorless solid. Yield: 72.5 mg, 73%. Mp: 92-93 °C.

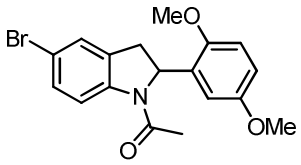
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, 1H, *J* = 8.6 Hz), 7.20 (dd, 1H, *J* = 8.6, 2.0 Hz), 7.06 (d, 1H, *J* = 2.0 Hz), 6.84 (d, 1H, *J* = 8.8 Hz), 6.75 (dd, 1H, *J* = 8.8, 2.9 Hz), 6.51 (d, 1H, *J* = 2.9 Hz), 5.70 (dd, 1H, *J* = 10.2, 2.0 Hz), 3.85 (s, 3H), 3.71 (dd, 1H, *J* = 16.4, 10.2 Hz), 3.64 (s, 3H), 2.84 (dd, 1H, *J* = 16.4, 2.0 Hz), 2.01 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.62, 154.05, 149.76, 142.09, 132.07, 131.73, 128.91, 127.69, 125.15, 118.08, 112.50, 111.92, 111.54, 58.47, 55.99, 55.73, 37.64, 23.73

IR (KBr) 3030, 2671, 2411, 2313, 2037, 1726, 1678, 1599, 1531, 1408, 1346, 1263, 1184, 943, 847, 777 cm^{-1}

HRMS (FAB+) Calcd for $C_{18}H_{19}ClNO_3$ (FAB+) 332.1053, Found 332.1058

1-Acetyl-2-(2,5-dimethoxyphenyl)-5-bromo-2,3-dihydro-indole (**3h**)



Colorless solid. Yield: 92.3 mg, 82%. Mp: 107-110 °C.

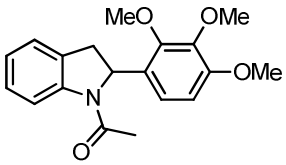
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, 1H, *J* = 8.6 Hz), 7.33 (d, 1H, *J* = 8.6 Hz), 7.19 (s, 1H), 6.83 (d, 1H, *J* = 8.9 Hz), 6.74 (dd, 1H, *J* = 8.9, 2.6 Hz), 6.50 (d, 1H, *J* = 2.6 Hz), 5.68 (d, 1H, *J* = 10.0 Hz), 3.84 (s, 3H), 3.71 (dd, 1H, *J* = 16.4, 10.0 Hz), 3.64 (s, 3H), 2.83 (d, 1H, *J* = 16.4 Hz), 2.00 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.63, 153.97, 149.70, 142.52, 132.45, 131.62, 130.53, 127.98, 118.46, 116.39, 112.41, 111.87, 111.50, 58.36, 55.94, 55.67, 37.51, 23.71

IR (KBr) 3074, 2992, 2930, 2833, 1854, 1659, 1591, 1493, 1385, 1354, 1312, 1285, 1240, 1219, 1165, 1101, 1057, 1024, 980, 928, 893, 870, 812, 760, 737, 714 cm^{-1}

HRMS (FAB+) Calcd for $C_{18}H_{19}BrNO_3$ (FAB+) 375.0470, 377.0450 Found 375.0466, 377.0432

1-Acetyl-2-(2,3,4-trimethoxyphenyl)-2,3-dihydro-indole (**4b**)



Colorless solid. Mp: 117-118 °C.

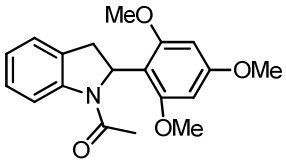
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, 1H, *J* = 7.7 Hz), 7.24 (dd, 1H, *J* = 7.7, 7.7 Hz), 7.11 (d, 1H, *J* = 8.1 Hz), 7.03 (ddd, 1H, *J* = 8.1, 7.7, 0.9 Hz), 6.64 (d, 1H, *J* = 8.6 Hz), 6.51 (d, 1H, *J* = 8.6 Hz), 5.63 (dd, 1H, *J* = 10.1, 1.0 Hz), 3.99 (s, 3H), 3.88 (s, 3H), 3.80 (s, 3H), 3.76 (dd, 1H, *J* = 15.9, 10.1 Hz), 2.87 (dd, 1H, *J* = 15.9, 1.0 Hz), 2.03 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.63, 153.41, 150.08, 143.46, 142.14, 129.81, 128.83, 127.69, 125.03, 124.08, 119.55, 117.10, 107.41, 61.04, 60.93, 58.33, 56.05, 38.56, 23.98

IR (KBr) 1659, 1599, 1479, 1391, 1321, 1281, 1256, 1173, 1126, 1034, 966, 939, 870, 845, 814, 762 cm^{-1}

HRMS (FAB+) Calcd for $C_{19}H_{22}NO_4$ (FAB+) 328.1549, Found 328.1550

1-Acetyl-2-(2,4,6-trimethoxyphenyl)-2,3-dihydro-indole (**4c**)



Colorless solid. Mp: 160-164 °C.

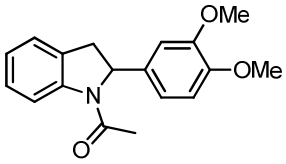
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, 1H, *J* = 8.0 Hz), 7.11 (ddd, 1H, *J* = 8.5, 8.0, 1.1 Hz), 7.03 (dd, 1H, *J* = 7.4, 1.1 Hz), 6.92 (ddd, 1H, *J* = 8.5, 7.4, 1.0 Hz), 6.01 (s, 2H), 5.81 (dd, 1H, *J* = 11.2, 4.4 Hz), 3.73 (s, 3H), 3.56 (dd, 1H, *J* = 16.1, 11.2 Hz), 3.90-3.24 (br, 6H), 2.90 (dd, 1H, *J* = 16.1, 4.4 Hz), 1.90 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.87, 160.95, 144.41, 131.85, 126.84, 123.24, 122.98, 116.68, 111.96, 55.77, 55.44, 54.23, 36.83, 23.45

IR (KBr) 3044, 2940, 2835, 1645, 1601, 1479, 1408, 1296, 1231, 1207, 1163, 1126, 1036, 966, 951, 926, 827, 787, 766 cm^{-1}

HRMS (FAB+) Calcd for $C_{19}H_{22}NO_4$ (FAB+) 328.1549, Found 328.1549

1-Acetyl-2-(3,4-dimethoxyphenyl)-2,3-dihydro-indole (**4d**)



Pale brown solid. Mp: 45-46 °C.

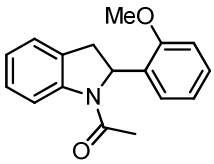
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, 1H, *J* = 7.8 Hz), 7.25 (dd, 1H, *J* = 7.8, 7.7 Hz), 7.13 (d, 1H, *J* = 7.6 Hz), 7.05 (dd, 1H, *J* = 7.7, 7.6 Hz), 6.77 (d, 1H, *J* = 8.2 Hz), 6.70 (dd, 1H, *J* = 8.2, 2.0 Hz), 6.64 (s, 1H), 5.32 (d, 1H, *J* = 9.5 Hz), 3.84 (s, 3H), 3.82-3.70 (m, 4H), 2.97 (dd, 1H, *J* = 16.1, 2.2 Hz), 2.05 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.80, 149.66, 148.66, 143.41, 135.86, 129.34, 127.85, 124.99, 124.18, 117.22, 117.04, 111.57, 108.07, 63.46, 56.03, 55.98, 39.20, 24.29

IR (KBr) 2936, 2835, 2602, 2035, 1667, 1597, 1516, 1310, 1233, 1171, 1136, 1088, 1030, 928, 895, 856, 810, 752 cm^{-1}

HRMS (FAB+) Calcd for $C_{18}H_{20}NO_3$ (FAB+) 298.1443, Found 298.1453

1-Acetyl-2-(2-methoxyphenyl)-2,3-dihydro-indole (**4e**)



Colorless solid. Mp: 89-91 °C.

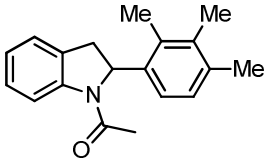
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, 1H, *J* = 8.1 Hz), 7.27-7.21 (m, 2H), 7.10 (d, 1H, *J* = 7.3 Hz), 7.02 (dd, 1H, *J* = 7.4, 7.3 Hz), 6.97 (d, 1H, *J* = 6.7 Hz), 6.91 (d, 1H, *J* = 8.2 Hz), 6.83 (dd, 1H, *J* = 7.5, 7.4 Hz), 5.73 (dd, 1H, *J* = 10.0, 1.6 Hz), 3.91 (s, 3H), 3.75 (dd, 1H, *J* = 16.1, 10.0 Hz), 2.86 (dd, 1H, *J* = 16.1, 1.6 Hz), 2.01 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.74, 155.68, 143.48, 130.99, 130.17, 128.77, 127.69, 125.13, 125.05, 124.08, 121.12, 117.22, 110.53, 58.23, 55.55, 37.86, 23.87

IR (KBr) 2961, 2833, 2043, 1954, 1904, 1854, 1792, 1665, 1599, 1470, 1391, 1273, 1242, 1173, 1105, 1024, 966, 934, 870, 806, 756 cm^{-1}

HRMS (FAB+) Calcd for $C_{17}H_{18}NO_2$ (FAB+) 268.1338, Found 268.1347

1-Acetyl-2-(2,3,4-trimethylphenyl)-2,3-dihydro-indole (**4f**)



Colorless solid. Mp: 121-123 °C.

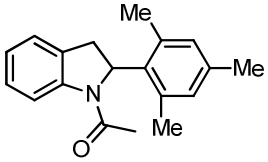
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, 1H, *J* = 8.0 Hz), 7.26 (dd, 1H, *J* = 8.0, 7.4 Hz), 7.08 (d, 1H, *J* = 7.3 Hz), 7.02 (dd, 1H, *J* = 7.4, 7.3 Hz), 6.78 (d, 1H, *J* = 8.0 Hz), 6.75 (d, 1H, *J* = 8.0 Hz), 5.59 (dd, 1H, *J* = 10.2, 1.8 Hz), 3.81 (dd, 1H, *J* = 15.6, 10.2 Hz), 2.84 (dd, 1H, *J* = 15.6, 1.8 Hz), 2.33 (s, 3H), 2.25 (s, 3H), 2.23 (s, 3H), 1.99 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.72, 143.59, 138.64, 136.13, 135.91, 131.83, 129.42, 128.07, 127.82, 125.11, 124.13, 121.14, 117.17, 61.25, 38.10, 23.97, 20.93, 16.02, 15.61

IR (KBr) 3825, 3740, 3667, 2945, 2317, 1655, 1603, 1483, 1391, 1281, 1256, 1221, 1173, 1126, 1098, 1034, 966, 939, 872, 845, 814, 762 cm^{-1}

HRMS (FAB+) Calcd for $C_{19}H_{22}NO$ (FAB+) 280.1701, Found 280.1706

1-Acetyl-2-(2,4,6-trimethylphenyl)-2,3-dihydro-indole (**4g**)



Colorless solid. Mp: 126-128 °C.

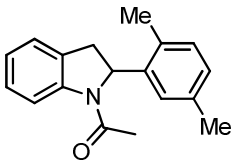
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, 1H, *J* = 7.0 Hz), 7.25 (dd, 1H, *J* = 7.0 Hz), 7.15 (d, 1H, *J* = 7.0 Hz), 7.06 (dd, 1H, *J* = 7.0 Hz), 6.87 (s, 1H), 6.83 (s, 1H), 5.85-5.65 (m, 1H), 3.76 (dd, 1H, *J* = 15.8, 12.1 Hz), 3.03 (dd, 1H, *J* = 15.8, 6.1 Hz), 2.41 (s, 3H), 2.26 (s, 3H), 1.99 (s, 3H), 1.84 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 170.17, 144.06, 137.04, 136.44, 135.95, 134.61, 132.08, 130.10, 129.61, 127.98, 124.02, 123.88, 117.62, 59.86, 36.65, 23.86, 20.84, 20.82, 20.55

IR (KBr) 3292, 2967, 1962, 1913, 1663, 1477, 1312, 1285, 1252, 1219, 1159, 1115, 1084, 1018, 957, 920, 854, 762 cm^{-1}

HRMS (FAB+) Calcd for $C_{19}H_{22}NO$ (FAB+) 280.1701, Found 280.1706

1-Acetyl-2-(2,5-dimethylphenyl)-2,3-dihydro-indole (**4h**)



Colorless solid. Mp: 210-211 °C.

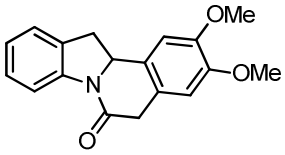
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, 1H, *J* = 8.0 Hz), 7.28 (dd, 1H, *J* = 8.0, 7.7 Hz), 7.14-7.07 (m, 2H), 7.05 (d, 1H, *J* = 7.7, 7.4 Hz), 6.97 (d, 1H, *J* = 7.5 Hz), 6.78 (s, 1H), 5.52 (dd, 1H, *J* = 10.4, 1.7 Hz), 3.81 (dd, 1H, *J* = 15.8, 10.4 Hz), 2.86 (dd, 1H, *J* = 15.8, 1.7 Hz), 2.36 (s, 3H), 2.18 (s, 3H), 1.97 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.73, 143.60, 141.05, 136.66, 130.95, 130.29, 129.33, 128.37, 127.91, 125.08, 124.48, 124.18, 117.21, 60.56, 37.71, 24.01, 21.32, 19.03

IR (KBr) 2947, 1661, 1597, 1481, 1462, 1398, 1360, 1341, 1279, 1209, 1169, 1132, 1090, 1020, 930, 883, 812, 762 cm^{-1}

HRMS (FAB+) Calcd for $C_{18}H_{20}NO$ (FAB+) 265.1467, Found 265.1473

2,3-Dimethoxy-12,12a-dihydro-5*H*-indolo[2,1-α]isoquinolin-6-one (**6**)



Colorless solid. Mp: 142-143 °C.

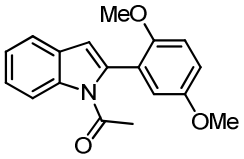
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, 1H, *J* = 7.9 Hz), 7.29-7.22 (m, 2H), 7.07 (ddd, 1H, *J* = 8.5, 7.5, 1.1 Hz), 6.77 (s, 1H), 6.73 (s, 1H), 5.43-5.37 (m, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.77 (dd, 1H, *J* = 18.5, 3.5 Hz), 3.67-3.60 (m, 2H), 3.45 (dd, 1H, *J* = 14.9, 10.9 Hz)

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.14, 148.96, 148.32, 142.03, 129.99, 128.00, 127.48, 125.27, 124.65, 124.30, 116.65, 110.52, 107.78, 61.50, 56.39, 56.24, 39.70, 34.67

IR (KBr) 2920, 2621, 2361, 2035, 1950, 1888, 1775, 1651, 1483, 1300, 1254, 1219, 1119, 1086, 1030, 1003, 974, 922, 883, 847, 772, 748, 719 cm^{-1}

HRMS (FAB+) Calcd for $C_{18}H_{18}NO_3$ (FAB+) 295.1208, Found 295.1217

1-Acetyl-2-(2,5-dimethoxyphenyl)-indole (**7**)



Colorless solid. Mp: 42-47 °C.

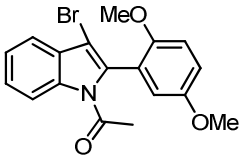
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, 1H, *J* = 8.3 Hz), 7.56 (d, 1H, *J* = 7.3 Hz), 7.34 (ddd, 1H, *J* = 8.3, 7.3, 1.3 Hz), 7.27-7.24 (m, 1H), 7.03 (d, 1H, *J* = 3.1 Hz), 6.95 (dd, 1H, *J* = 8.9, 3.1 Hz), 6.88 (d, 1H, *J* = 8.9 Hz), 6.57 (s, 1H), 3.83 (s, 3H), 3.73 (s, 3H), 2.15 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 171.46, 153.92, 151.28, 137.48, 136.35, 129.13, 125.03, 124.35, 123.35, 120.44, 116.71, 116.21, 114.93, 111.51, 56.06, 55.95, 25.95

IR (KBr) 3063, 3011, 2930, 2841, 2484, 2349, 2052, 2004, 1975, 1937, 1913, 1881, 1842, 1788, 1715, 1609, 1557, 1470, 1366, 1315, 1180, 1113, 1092, 1047, 978, 935, 907, 856, 824, 804, 758 cm^{-1}

HRMS (FAB+) Calcd for $C_{18}H_{18}NO_3$ (FAB+) 296.1287, Found 296.1283

1-Acetyl-2-(2,5-dimethoxyphenyl)-3-bromoindole (**8**)



Colorless solid. Mp: 84-85 °C.

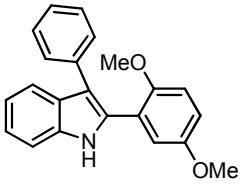
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (ddd, 1H, *J* = 8.3, 0.7, 0.7 Hz), 7.58 (ddd, 1H, *J* = 7.7, 1.3, 0.7 Hz), 7.42 (ddd, 1H, *J* = 8.3, 7.3, 1.3 Hz), 7.38-7.34 (m, 1H), 7.04-7.00 (m, 2H), 6.94 (d, 1H, *J* = 8.6 Hz), 3.83 (s, 3H), 3.74 (s, 3H), 2.10 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 170.61, 153.74, 151.79, 136.11, 132.97, 128.62, 126.30, 123.98, 121.90, 119.48, 117.86, 116.52, 116.12, 112.41, 102.71, 56.21, 55.97, 25.93

IR (KBr) 3071, 2995, 2940, 2835, 2492, 2062, 1711, 1609, 1589, 1493, 1443, 1369, 1312, 1200, 1146, 1111, 1043, 1018, 991, 932, 899, 878, 866, 808, 739 cm^{-1}

HRMS (FAB+) Calcd for $C_{18}H_{17}BrNO_3$ (FAB+) 374.0392, 376.0371 Found 374.0391, 376.0365

2-(2,5-dimethoxyphenyl)-3-phenylindole (**9**)



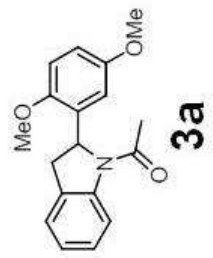
Colorless solid. Mp: 26-27 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.27 (s, 1H), 7.66 (dd, 1H, *J* = 7.9, 0.9 Hz), 7.49-7.46 (m, 2H), 7.45 (ddd, 1H, *J* = 8.2, 1.7, 0.8 Hz), 7.42-7.38 (m, 2H), 7.29 (ddd, 1H, *J* = 8.7, 7.1, 1.3 Hz), 7.24 (ddd, 1H, *J* = 8.2, 7.0, 1.1 Hz), 7.13 (ddd, 1H, *J* = 8.2, 7.0, 1.1 Hz), 6.94 (d, 1H, *J* = 8.8 Hz), 6.82 (d, 1H, *J* = 3.2 Hz), 6.79 (dd, 1H, *J* = 8.8, 3.2 Hz), 3.86 (s, 3H), 3.39 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 153.53, 150.96, 136.10, 135.45, 131.13, 130.53(2C), 128.73(2C), 128.07, 126.37, 122.65, 121.47, 120.05, 119.51, 116.09, 116.03, 115.30, 113.48, 110.93, 56.67, 55.36

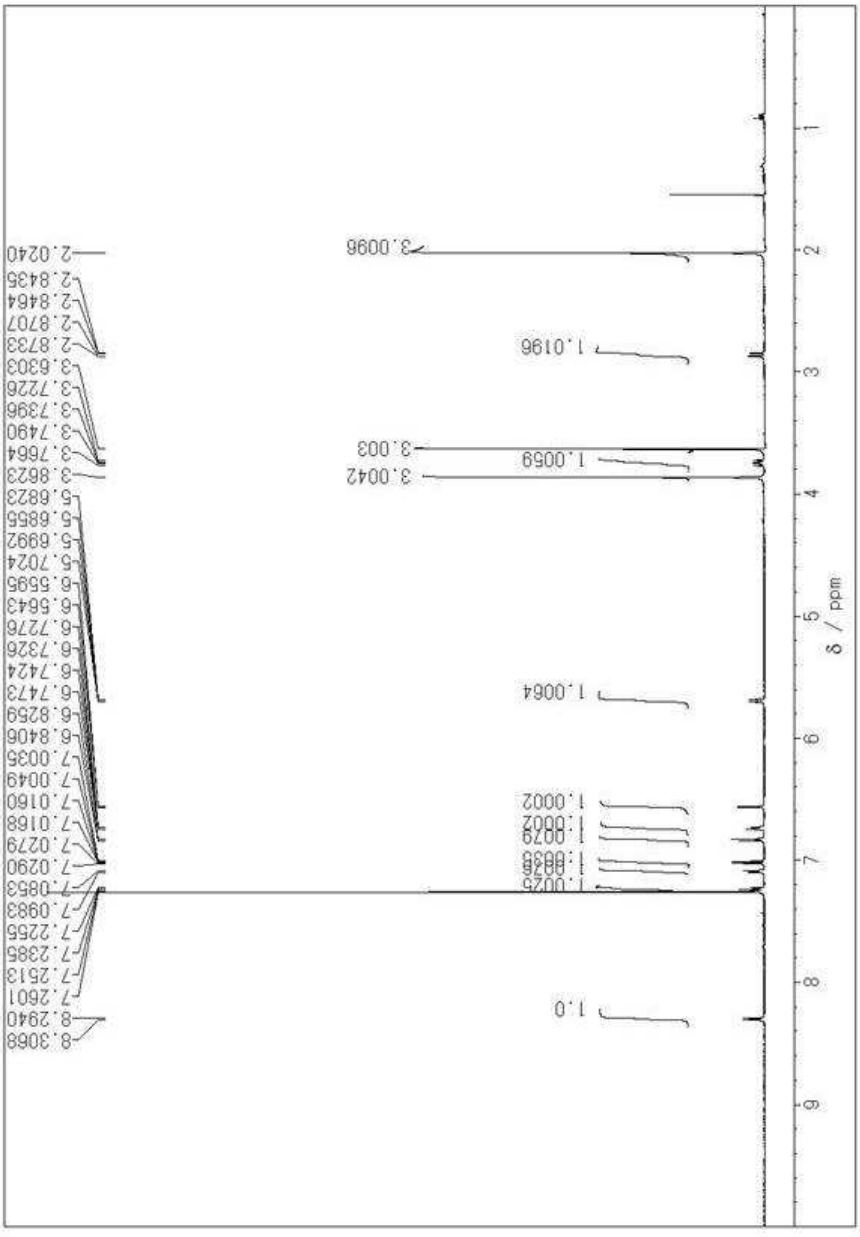
IR 3048, 2936, 2832, 2317, 2245, 1599, 1549, 1476, 1362, 1333, 1275, 1223, 1177, 1148, 1086, 1042, 974, 930, 908, 864, 802, 773, 748 cm^{-1}

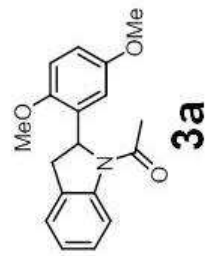
HRMS (FAB+) Calcd for $C_{22}H_{20}NO_2$ (FAB+) 330.1494, Found 330.1502



3a

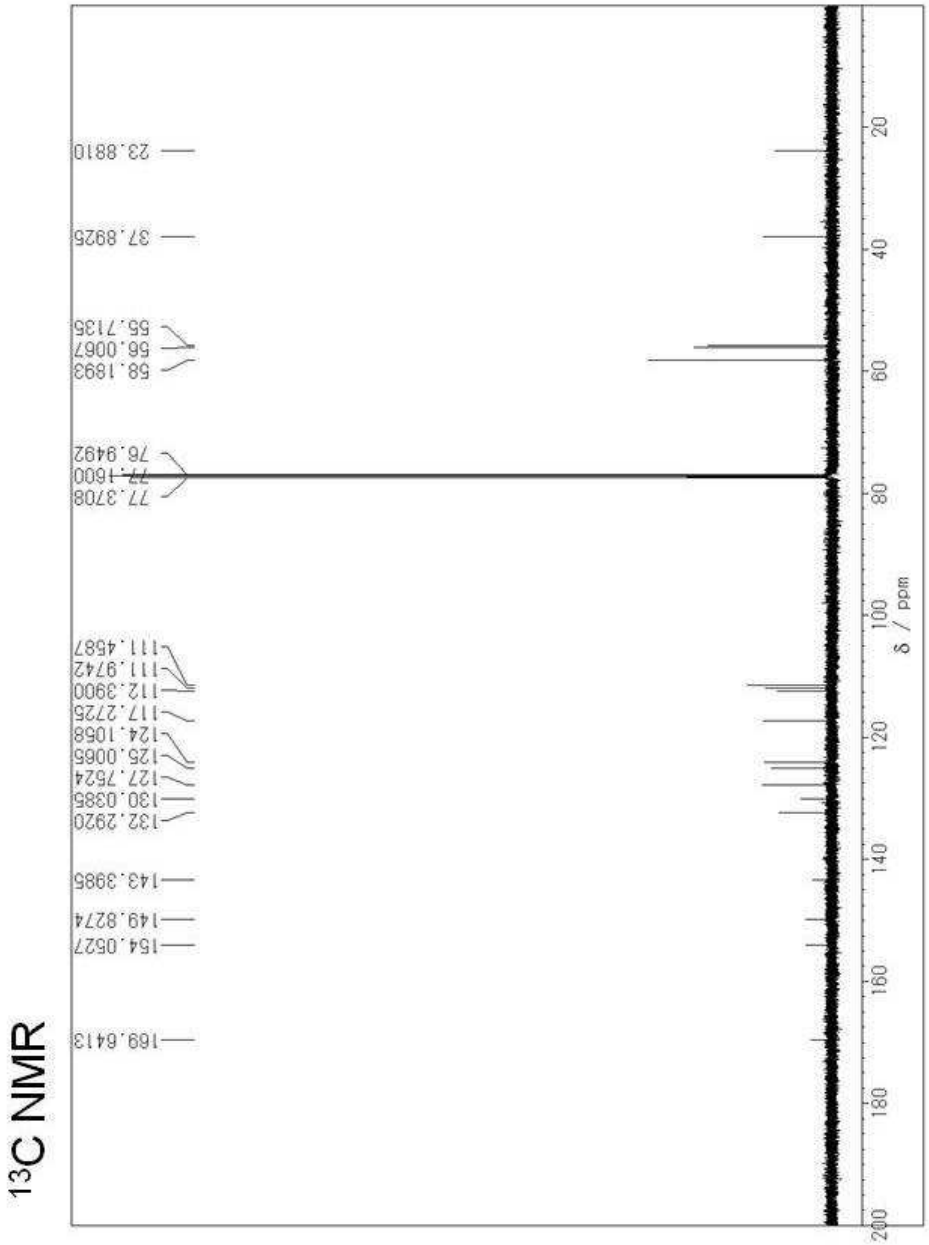
^{1}H NMR

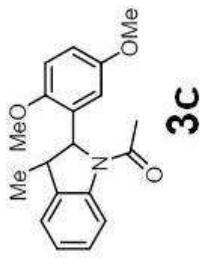



MeO
OMe
N
O

3a

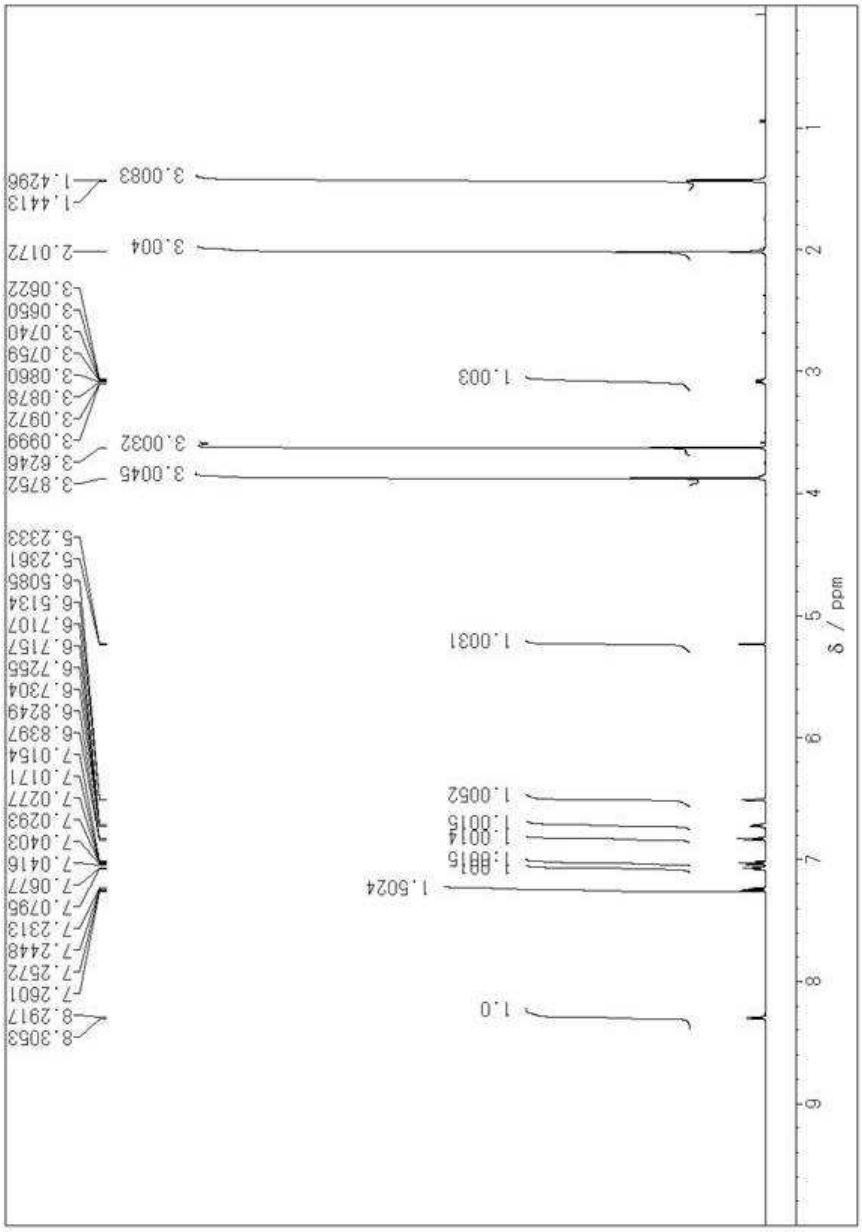
^{13}C NMR

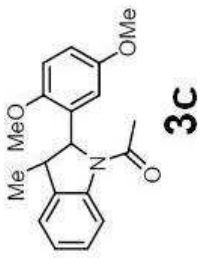

23.8810
37.8925
55.7135
56.0067
58.1893
76.9492
77.1600
77.3708
111.4587
111.9742
112.3900
117.2725
124.1058
125.0065
127.7624
130.0385
132.2920
143.3985
149.8274
154.0627
169.6413
20
40
60
80
100
120
140
160
180
200
δ / ppm


OMe
MeO
Me
N
O

3c

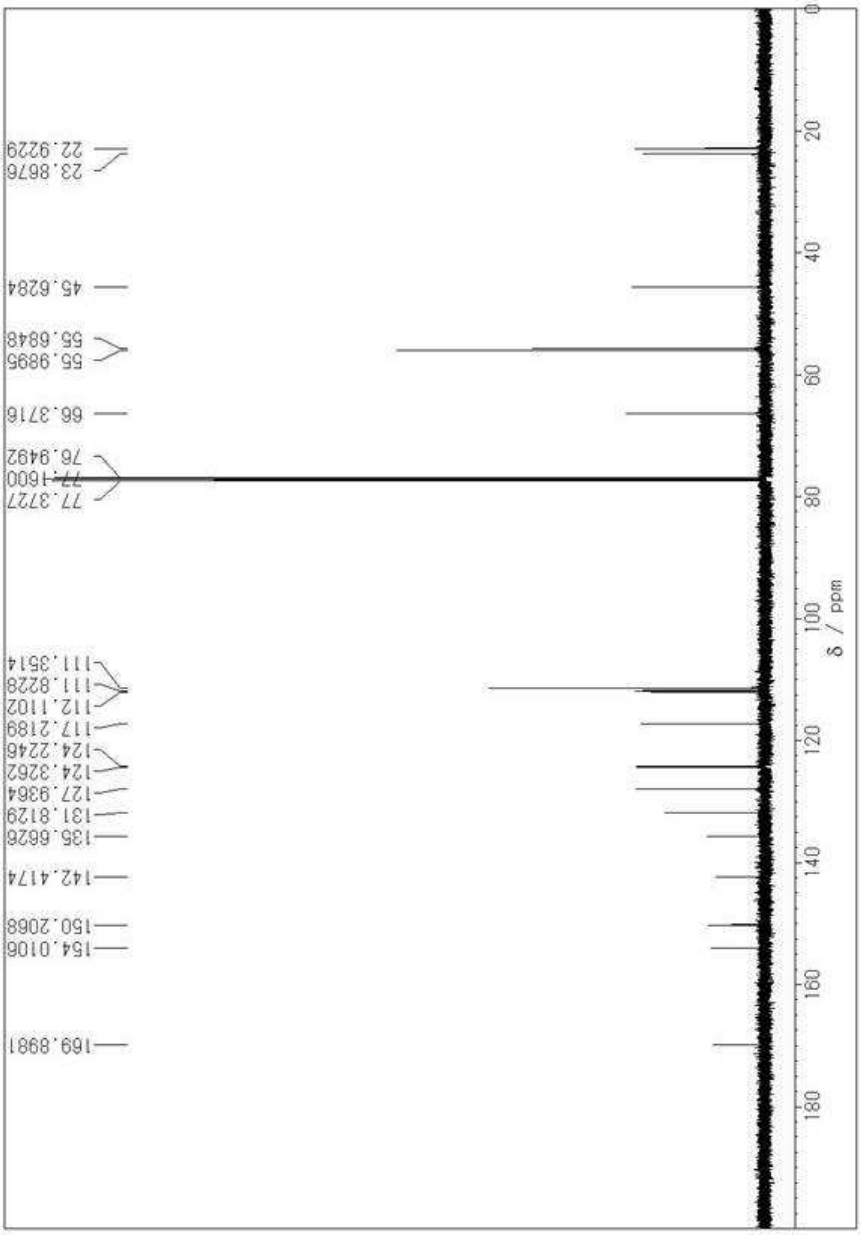
^{1}H NMR

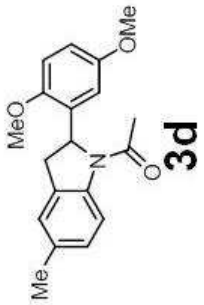

8.3053
8.2917
7.2601
7.2572
7.2448
7.2313
7.0795
7.0677
7.0416
7.0403
7.0293
7.0277
7.0171
7.0154
6.8397
6.8249
6.7304
6.7255
6.7157
6.7107
6.5134
6.5085
5.2361
5.2333
3.8752
3.6246
3.0999
3.0972
3.0878
3.0860
3.0759
3.0740
3.0650
3.0622
2.0172
1.4413
1.4296
3.0045
3.0032
3.004
3.0083
1.0031
1.003
1.0
1.5024
1.0052
1.0015
1.0014
1.0015
δ / ppm


OMe
MeO
Me
N
O

3c

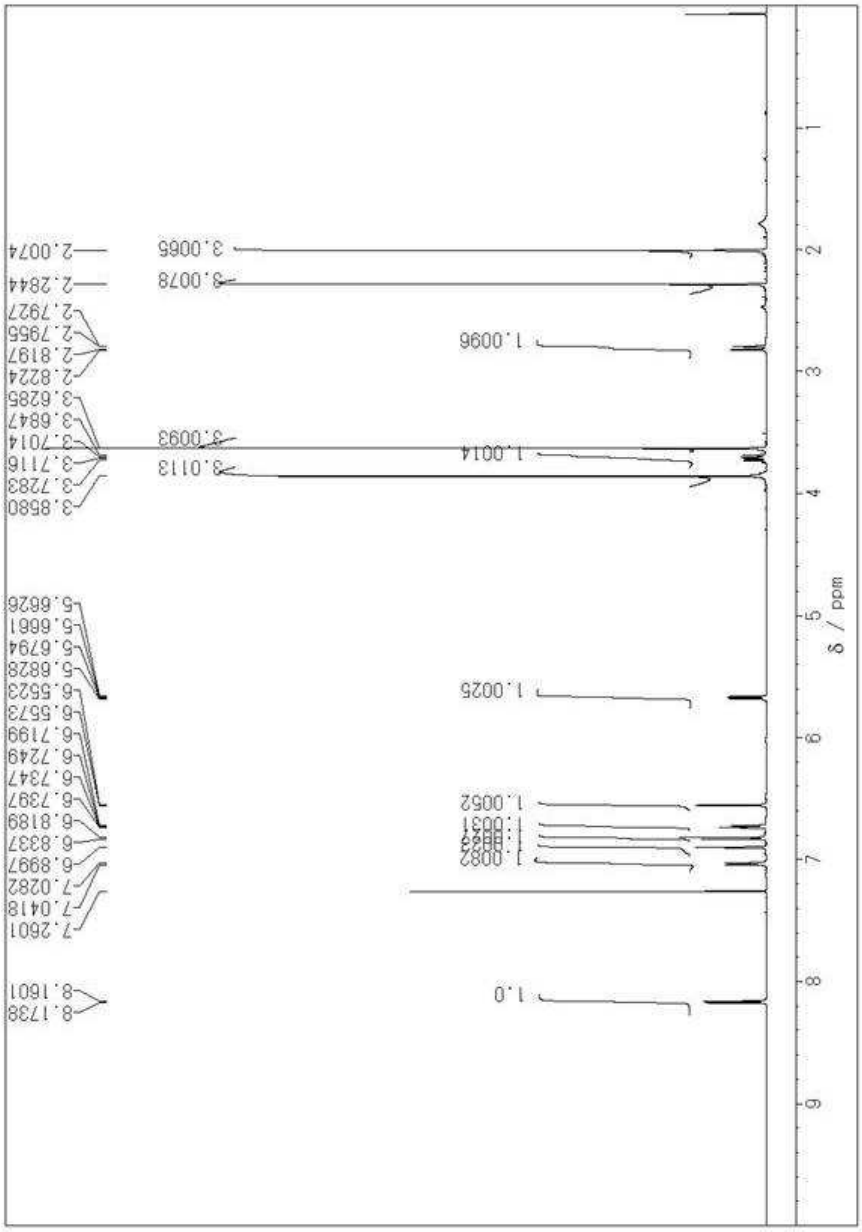
^{13}C NMR

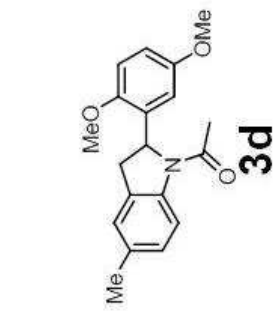

22.9229
23.8676
45.6284
55.6848
55.9895
66.3716
76.9492
77.1600
77.3727
111.3514
111.8228
112.1102
117.2189
124.2246
124.3262
127.9364
131.8129
135.6626
142.4174
150.2068
154.0106
169.8981
20
40
60
80
100
120
140
160
180
δ / ppm



3d

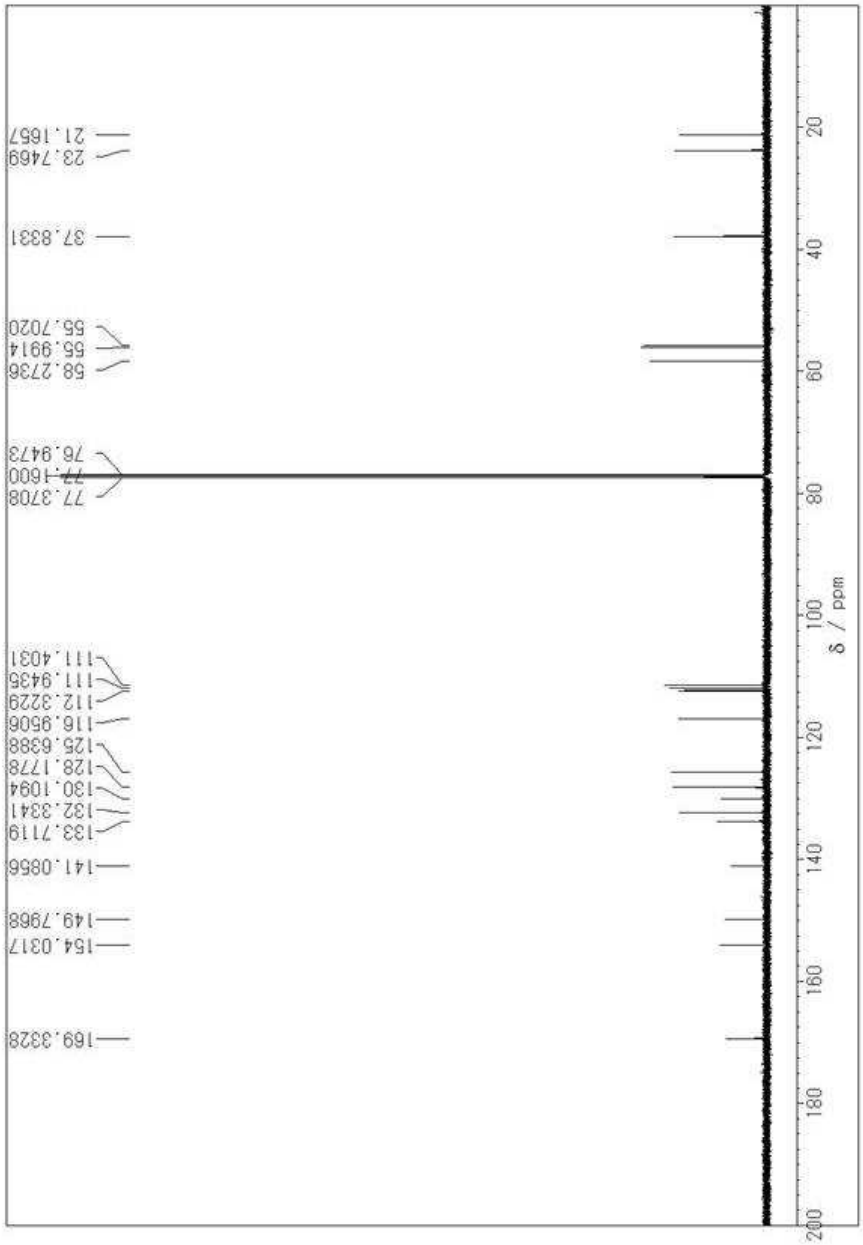
^{1}H NMR

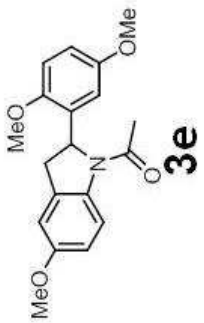



MeO
OMe
N
O
Me

3d

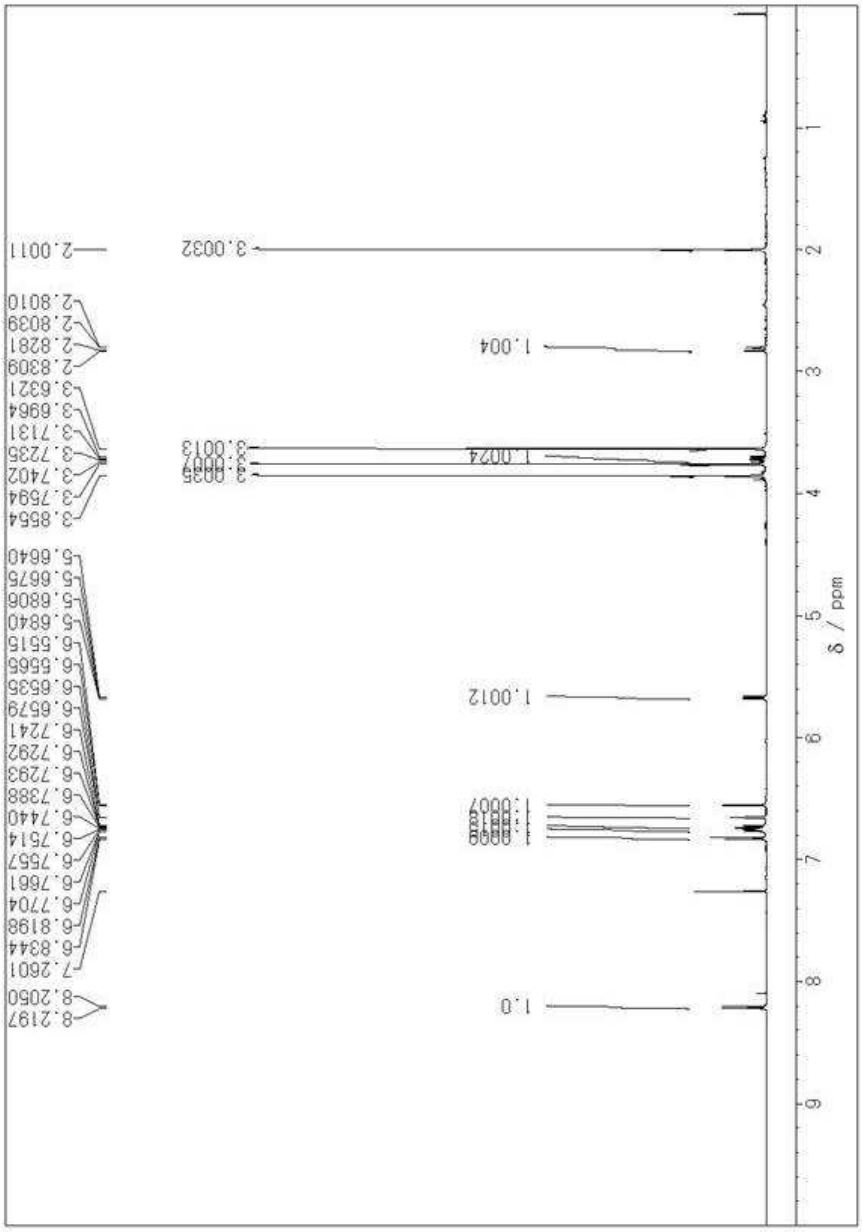
^{13}C NMR

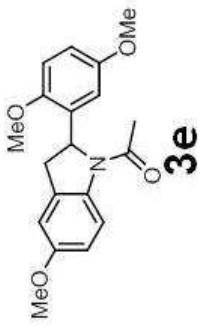

21.1657
23.7469
37.8331
55.7020
55.9914
58.2736
76.9473
77.1600
77.3708
111.4031
111.9435
112.3229
116.9506
125.6388
128.1778
130.1094
132.3341
133.7119
141.0856
149.7968
154.0317
169.3328
20
40
60
80
100
120
140
160
180
200
δ / ppm



3e

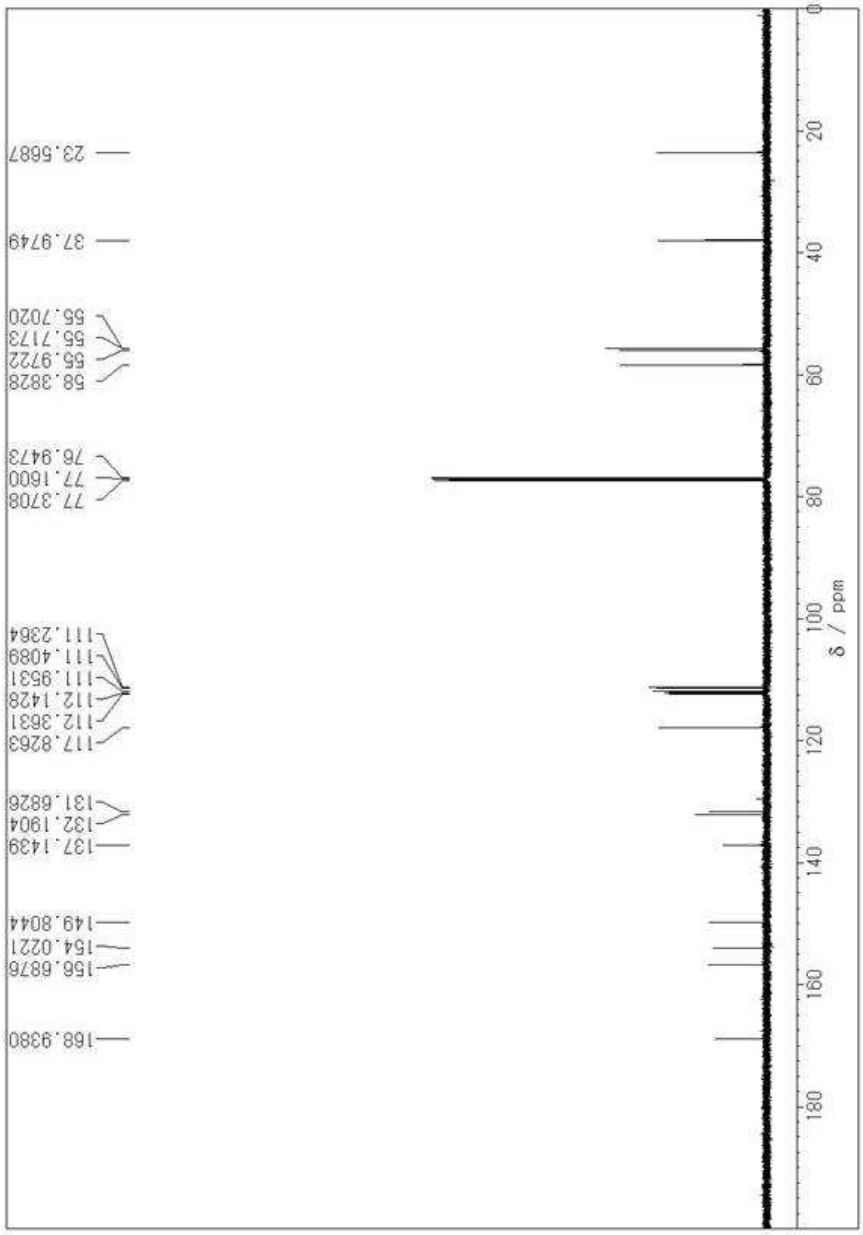
^{1}H NMR




MeO
OMe
MeO
N
O

3e

^{13}C NMR


23.5687
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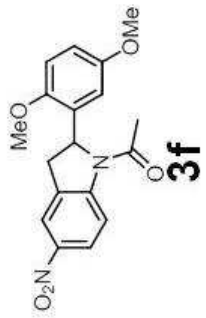
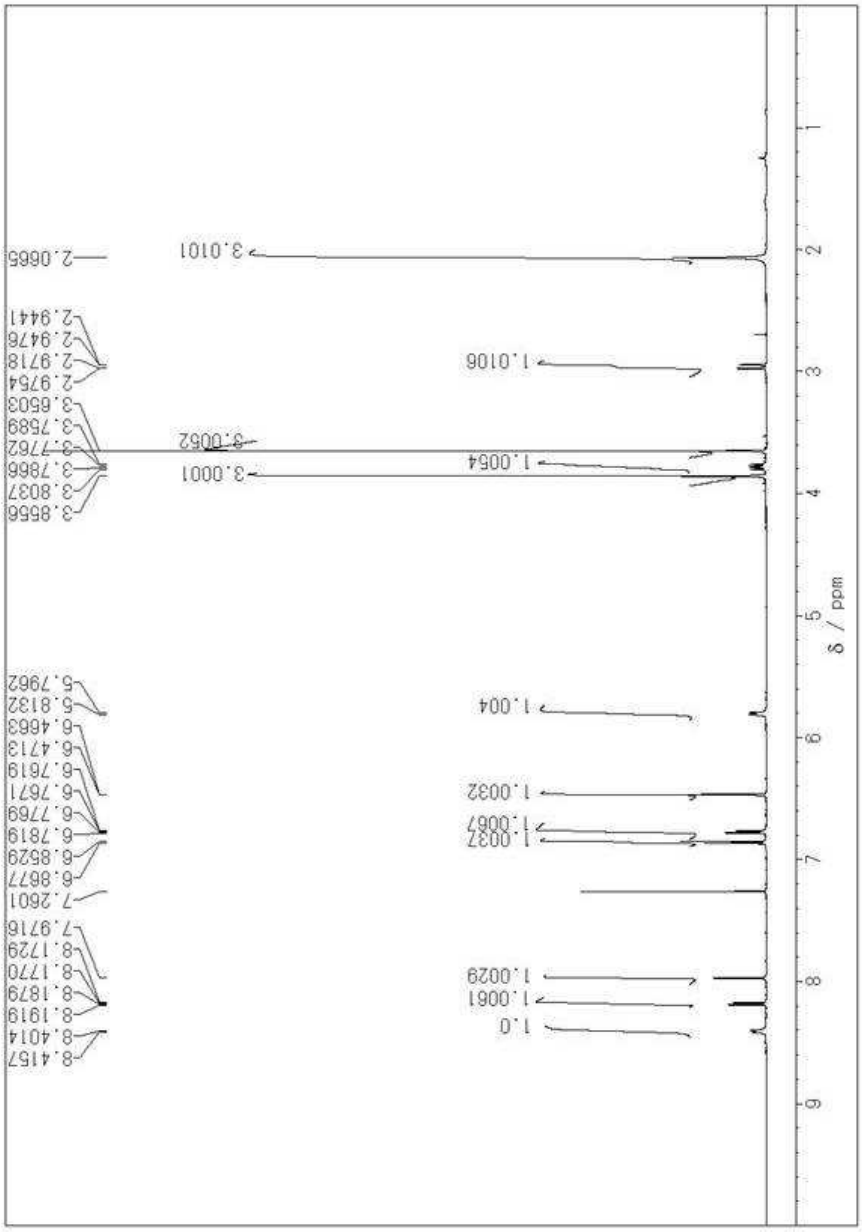
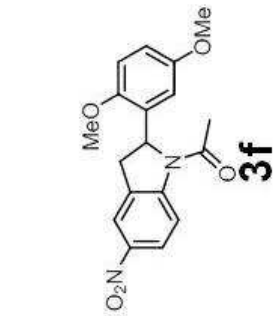
55.7020
55.7173
55.9722
58.3828
76.9473
77.1600
77.3708
111.2364
111.4089
111.9531
112.1428
112.3631
117.8263
131.6826
132.1904
137.1439
149.8044
154.0221
156.6876
168.9380
0
20
40
60
80
100
120
140
160
180
δ / ppm



3f

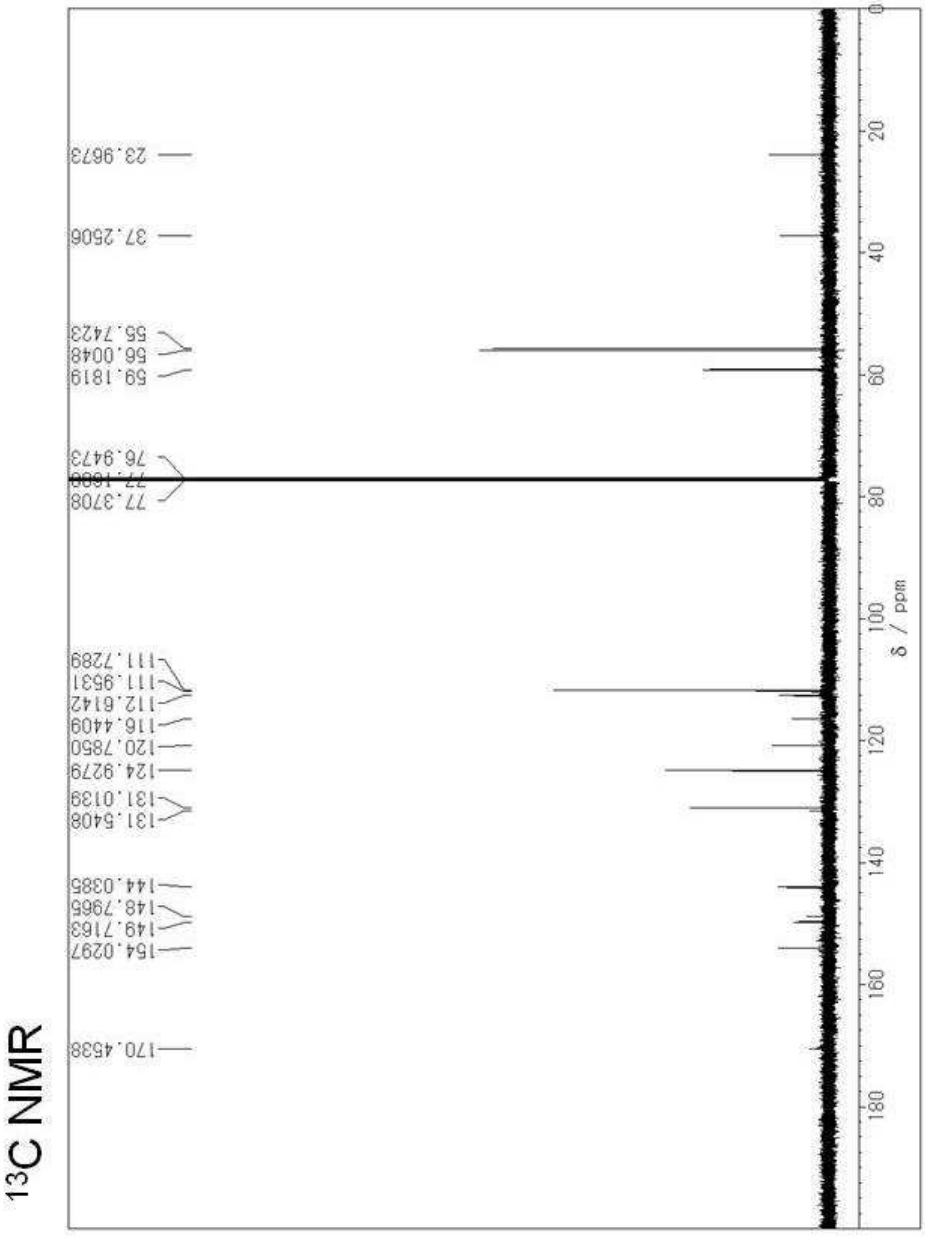
^{1}H NMR




MeO
OMe
N
O
O2N

3f

^{13}C NMR


23.9673
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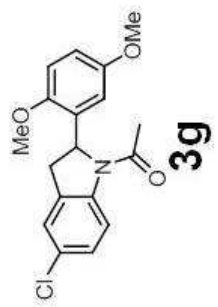
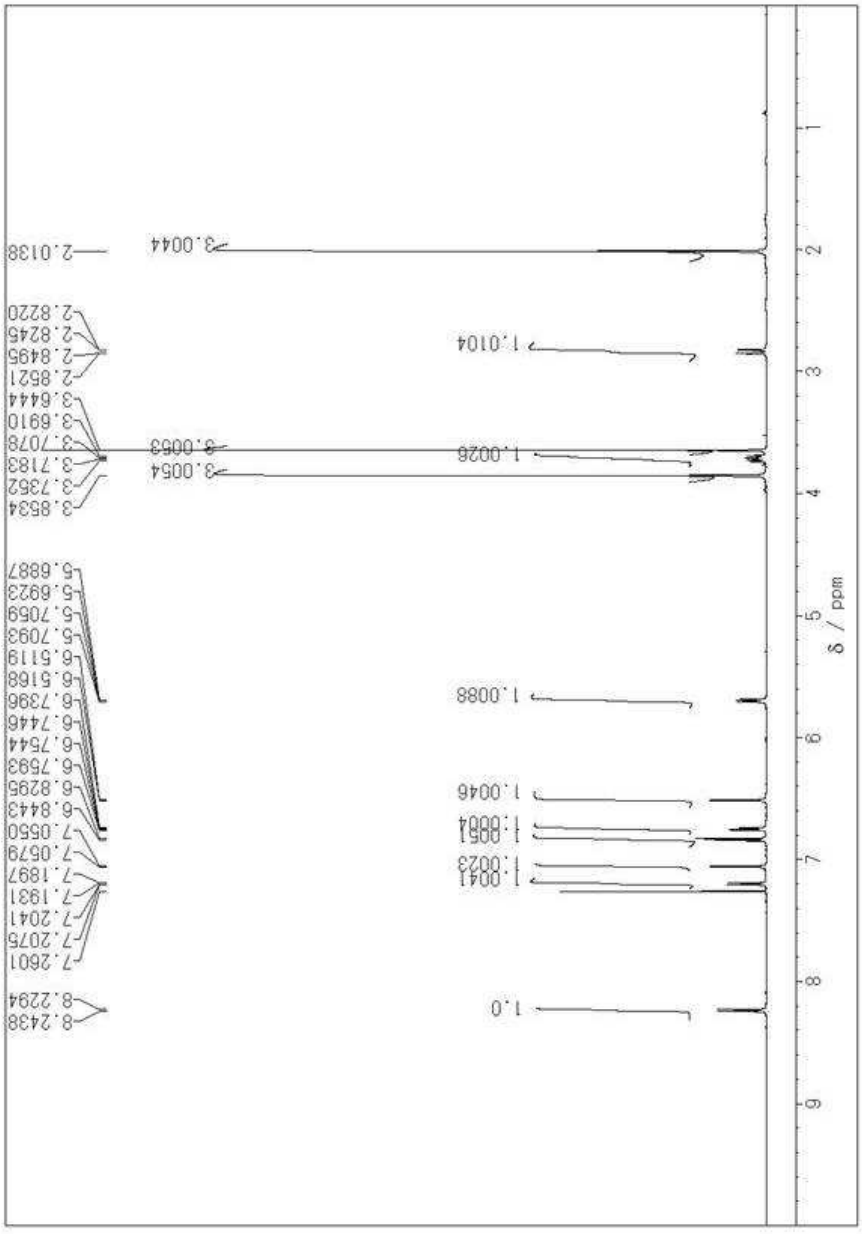
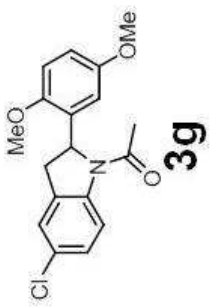
55.7423
56.0048
59.1819
76.9473
77.1808
77.3708
111.7289
111.9531
112.6142
116.4409
120.7850
124.9279
131.0139
131.5408
144.0385
148.7965
149.7163
154.0297
170.4538
0
20
40
60
80
100
120
140
160
180
δ / ppm



3g

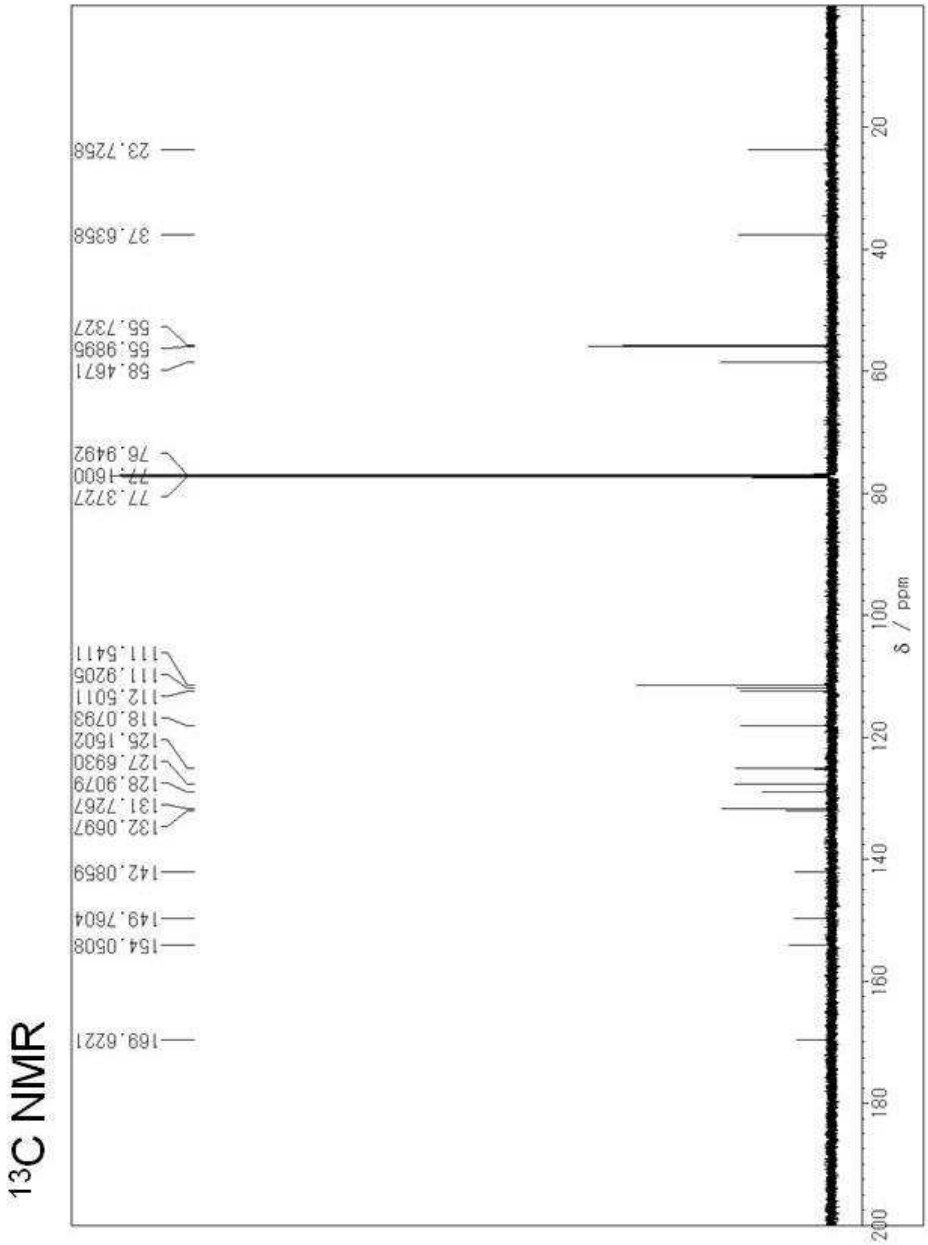
^{1}H NMR

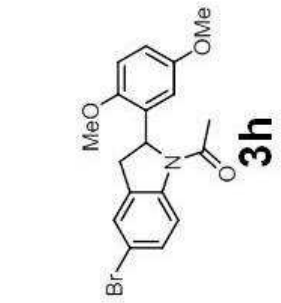



MeO
OMe
N
O
Cl

3g

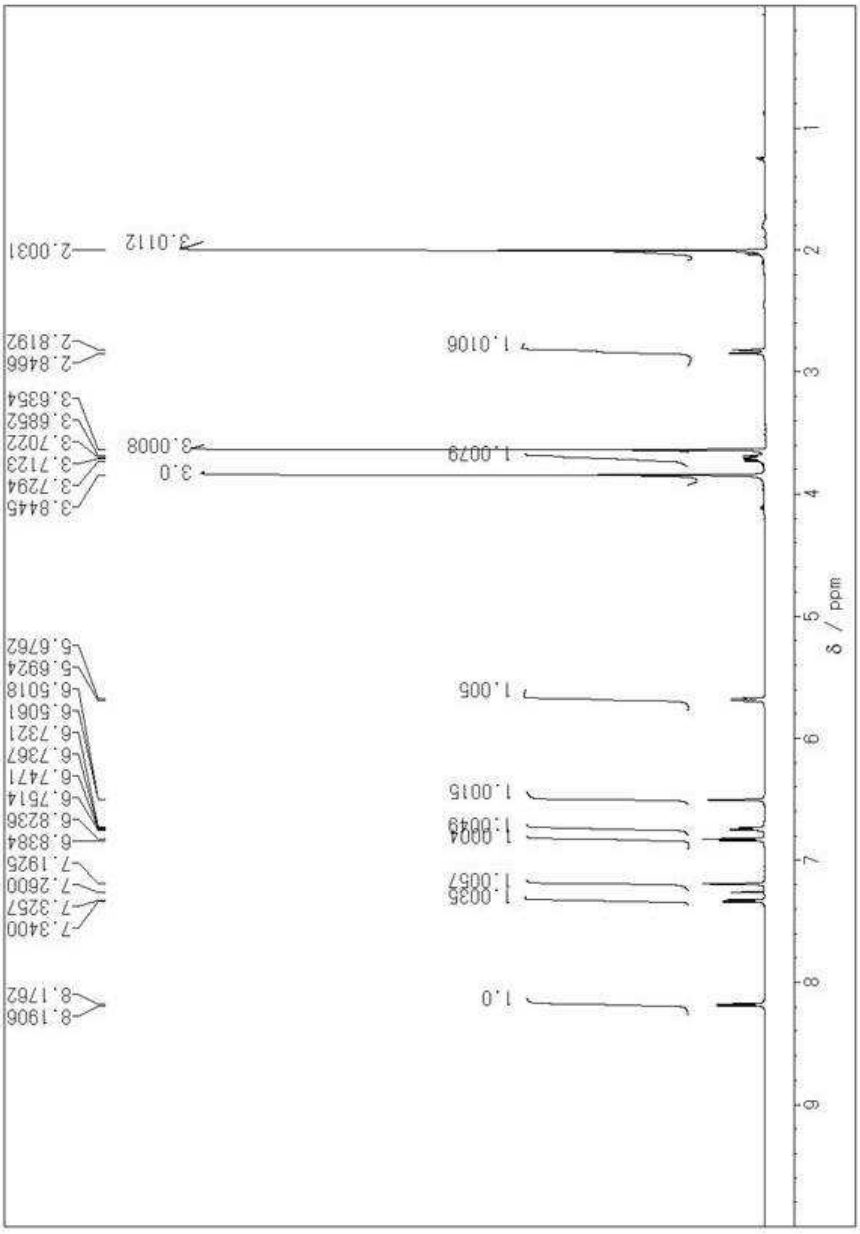
^{13}C NMR

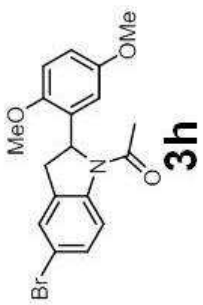

23.7258
37.6358
55.7327
55.9895
58.4671
76.9492
77.1600
77.3727
111.5411
111.9205
112.5011
118.0793
125.1502
127.6930
128.9079
131.7267
132.0697
142.0859
149.7604
154.0508
169.6221
20
40
60
80
100
120
140
160
180
200
δ / ppm


MeO
OMe
N
O
Br

3h

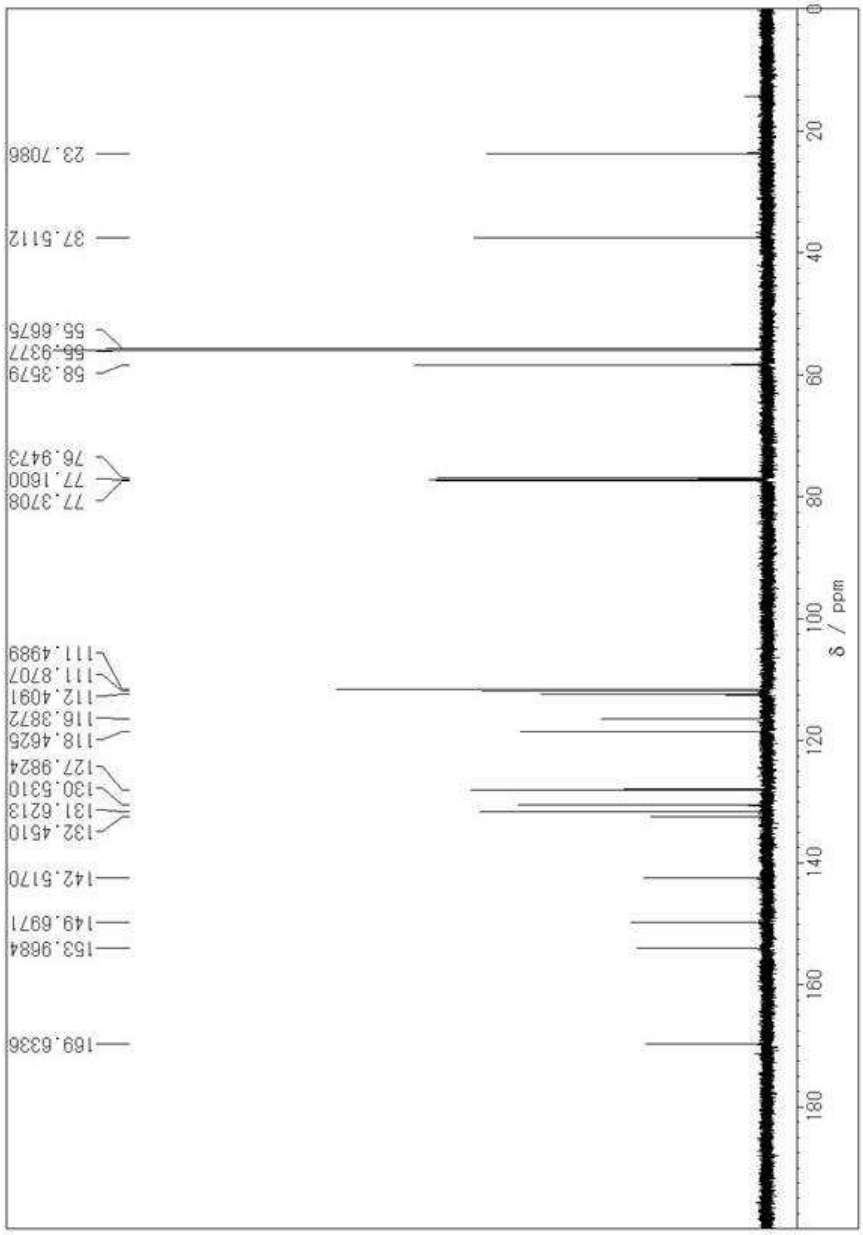
^{1}H NMR

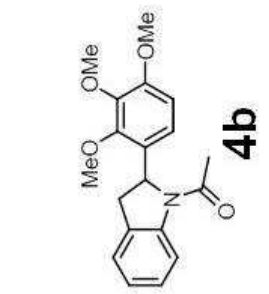

8.1906
8.1762
7.3400
7.3257
7.2600
7.1925
6.8384
6.8236
6.7514
6.7471
6.7367
6.7321
6.6061
6.6018
6.5924
6.5762
3.8445
3.7294
3.7123
3.7022
3.6852
3.6554
2.8466
2.8192
2.0031
1.0
1.005
1.0015
1.0024
1.0049
1.0035
1.0057
1.0106
3.0
3.0008
3.0112
1.0079
δ / ppm


MeO
OMe
N
O
Br

3h

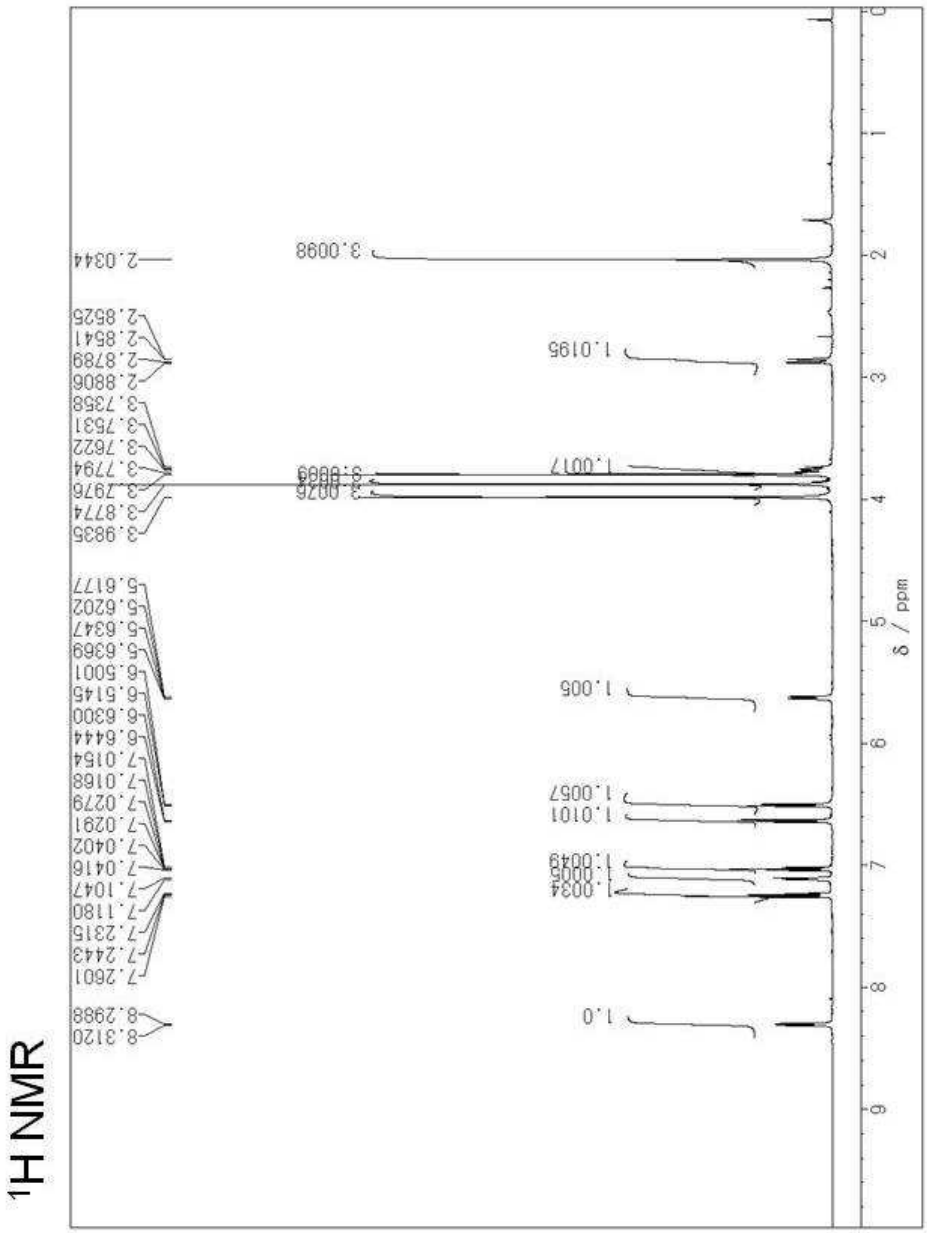
^{13}C NMR

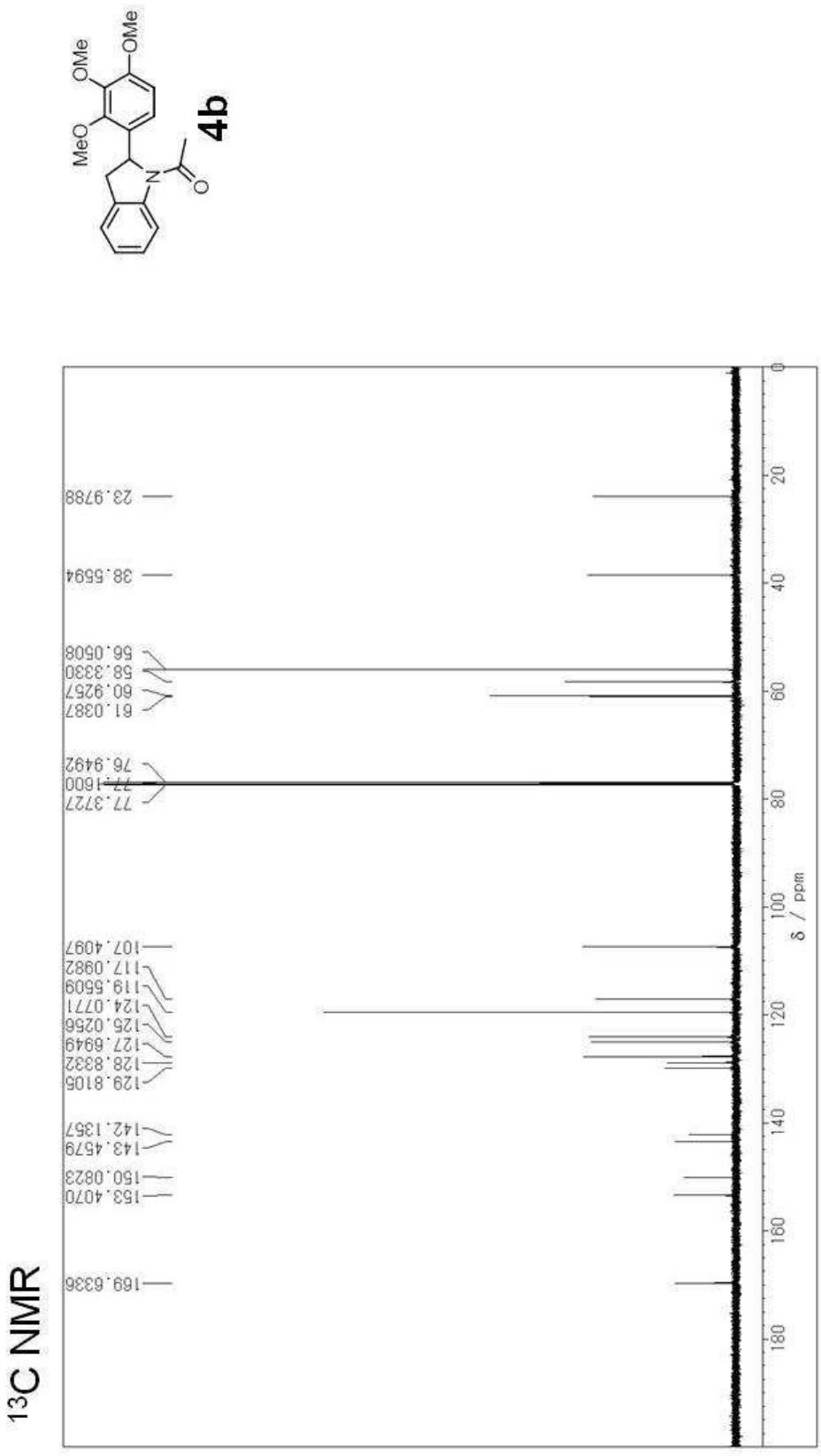

23.7086
37.5112
55.6675
56.9377
58.3579
76.9473
77.1600
77.3708
111.4989
111.8707
112.4091
116.3872
118.4625
127.9824
130.5310
131.6213
132.4510
142.5170
149.6971
153.9684
169.6336
0
20
40
60
80
100
120
140
160
180
δ / ppm

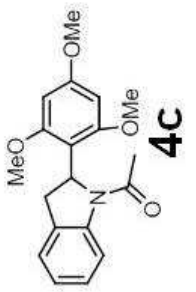


4b

^{1}H NMR

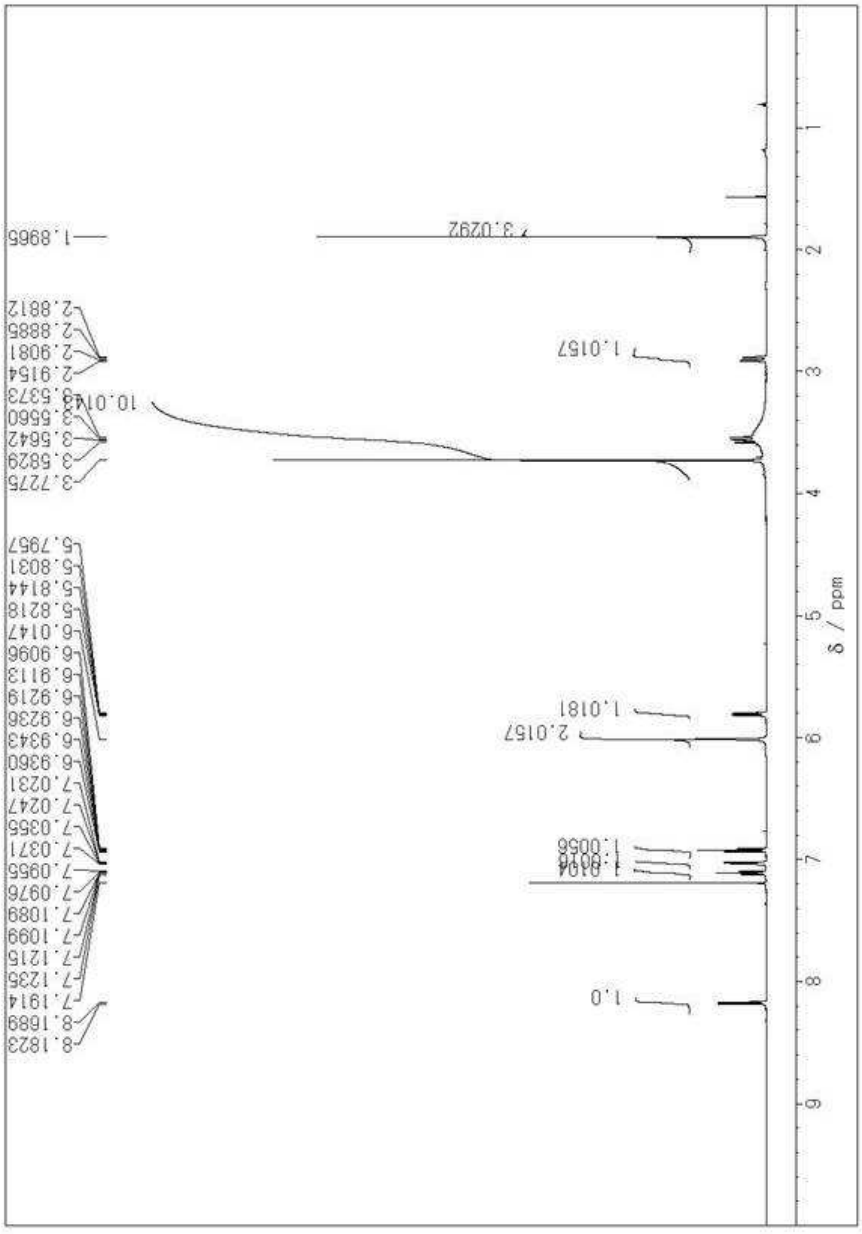


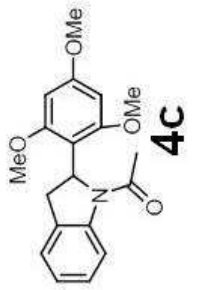

OMe
OMe
MeO
N
O
4b
^{13}C NMR
23.9788
38.5594
56.0508
58.3330
60.9257
61.0387
76.9492
77.1600
77.3727
107.4097
117.0982
119.5509
124.0771
125.0256
127.6949
128.8332
129.8105
142.1357
143.4579
150.0823
153.4070
169.6336
δ / ppm



4c

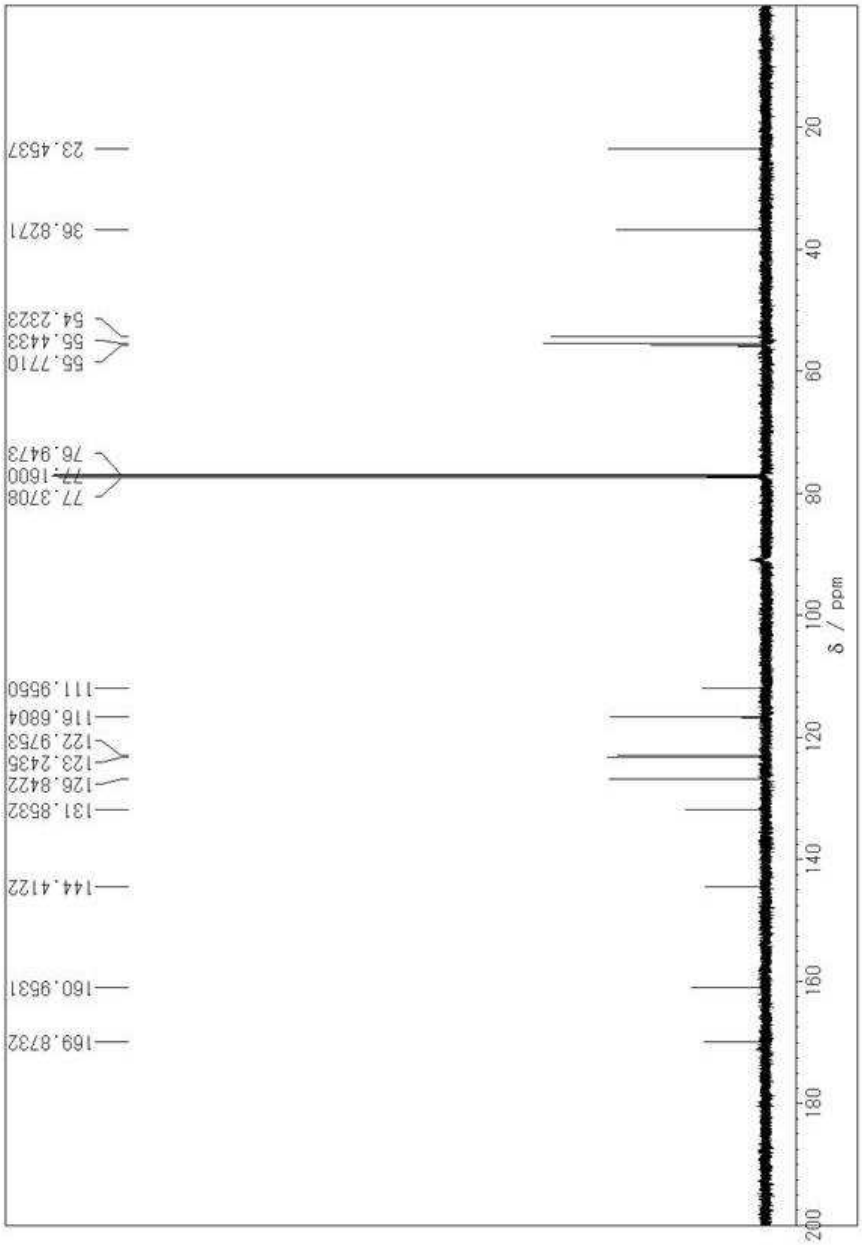
^{1}H NMR

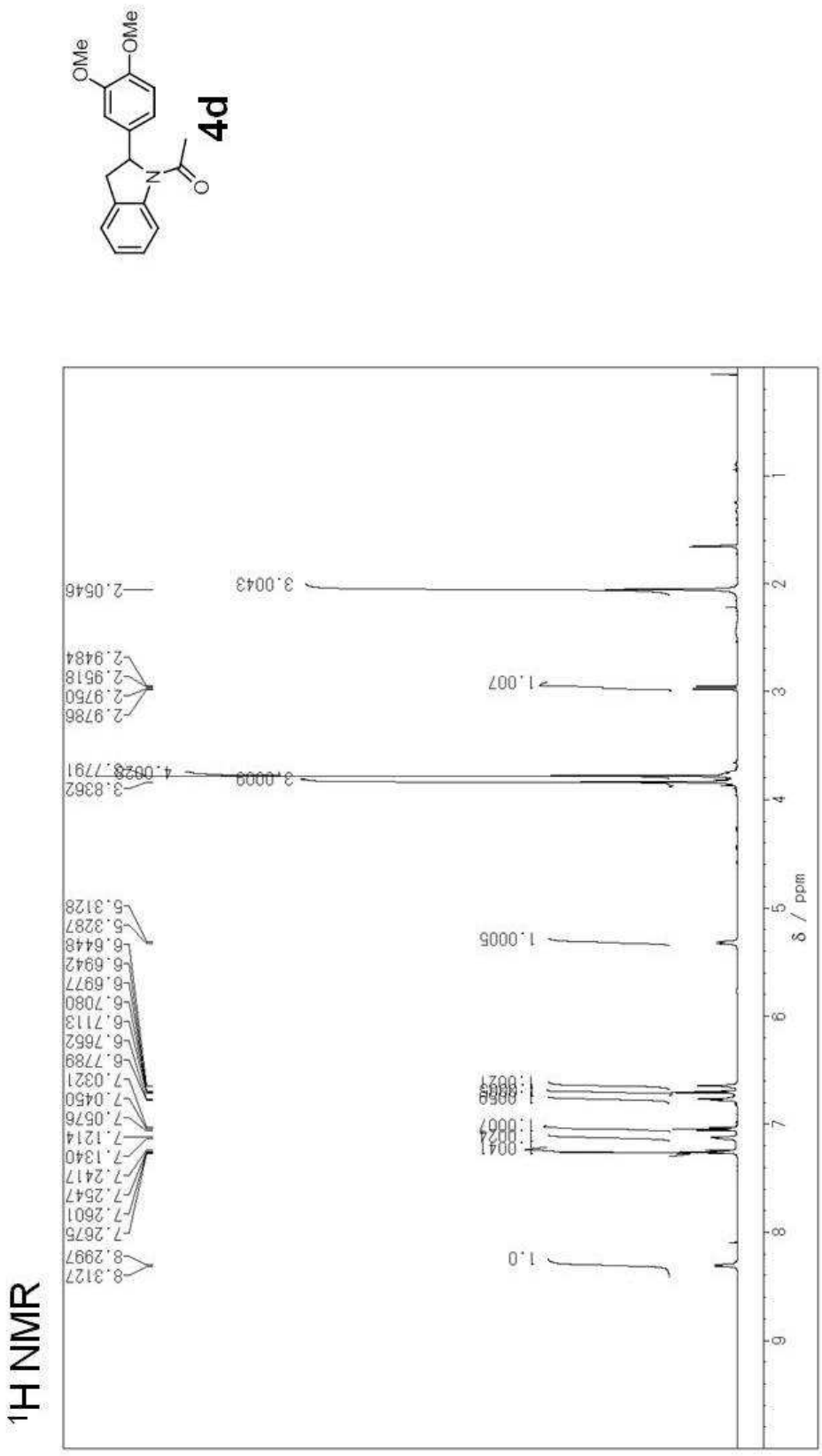


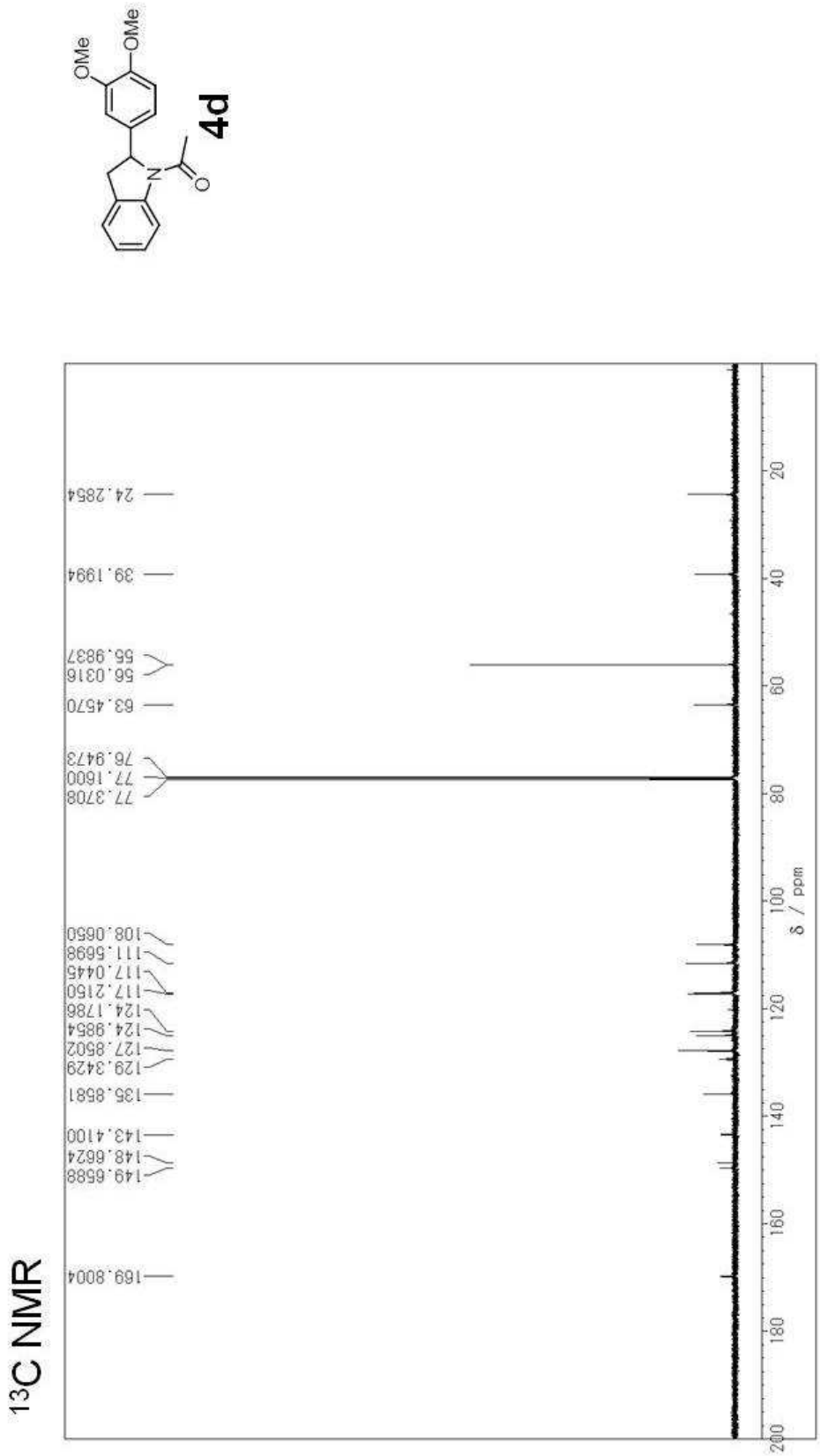

OMe
OMe
MeO
N
O

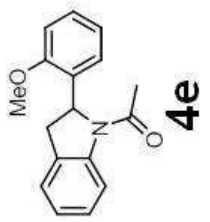
4c

^{13}C NMR


23.4537
36.8271
54.2323
55.4433
55.7710
76.9473
77.1600
77.3708
111.9550
116.6804
122.9753
123.2435
126.8422
131.8532
144.4122
160.9531
169.8732
20
40
60
80
100
120
140
160
180
200
δ / ppm

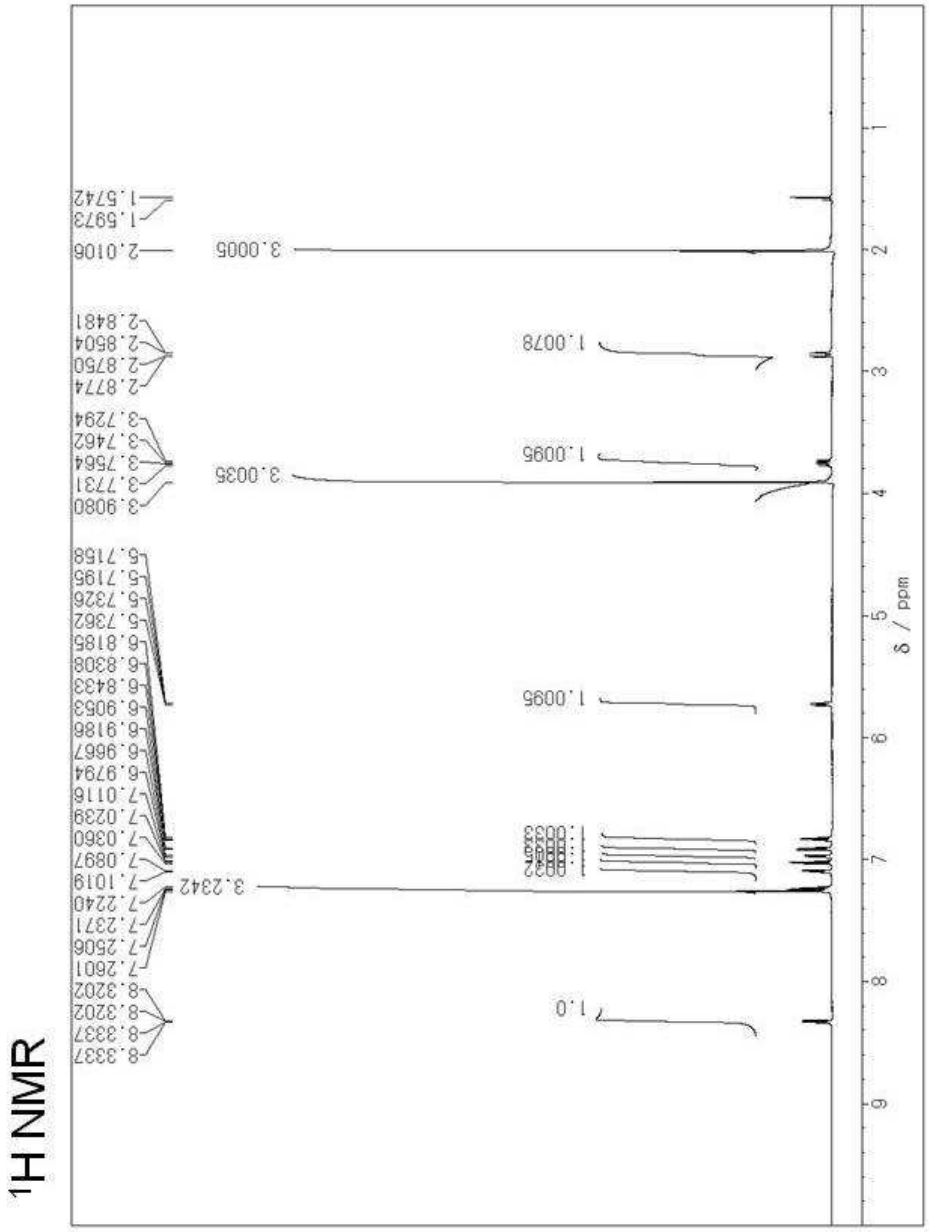

OMe
OMe
N
O
4d
^{1}H NMR
δ / ppm

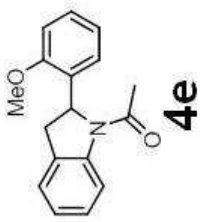

4d
OMe
OMe
N
O
^{13}C NMR
24.2854
39.1994
55.9837
56.0316
63.4570
76.9473
77.1600
77.3708
108.0650
111.5698
117.0445
117.2150
124.1786
124.9854
127.8502
129.3429
135.8581
143.4100
148.6624
149.6588
169.8004
δ / ppm


MeO
N
O

4e

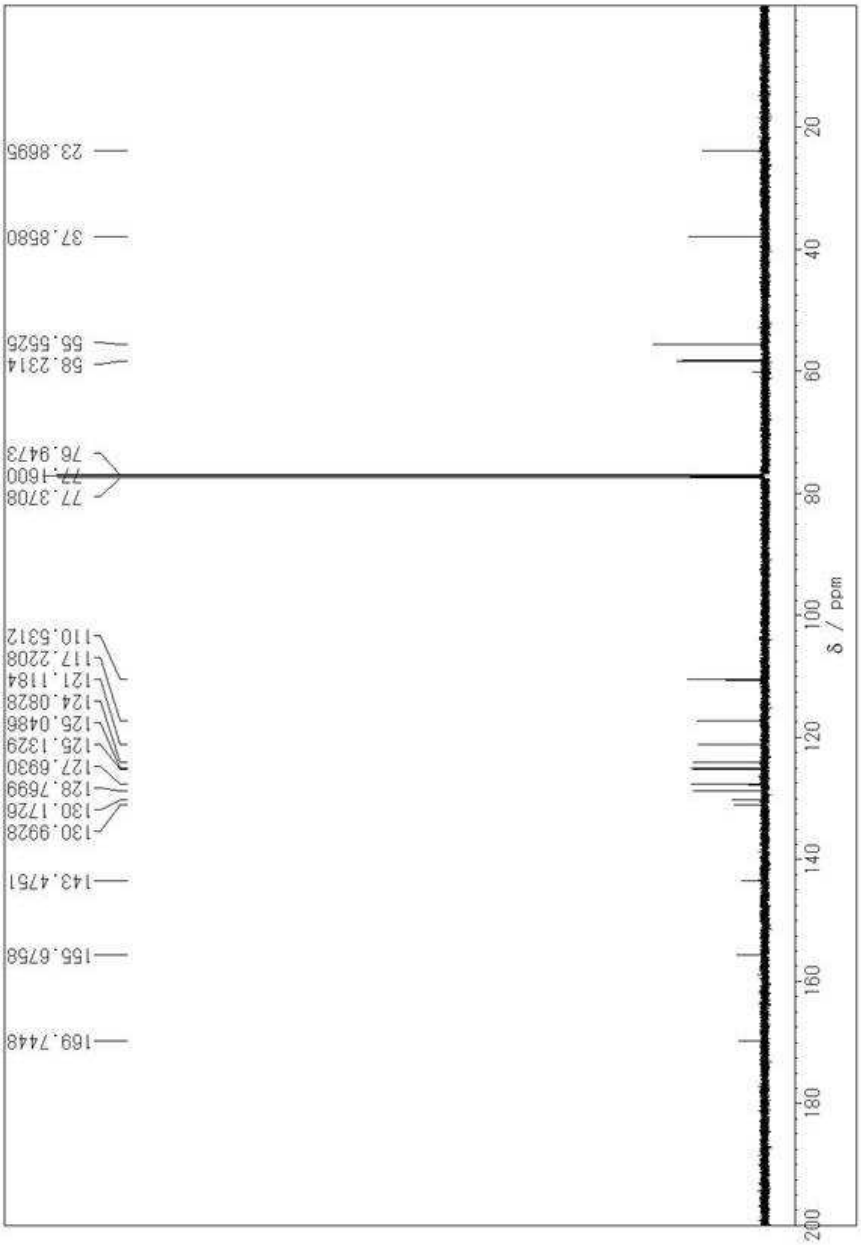
^{1}H NMR

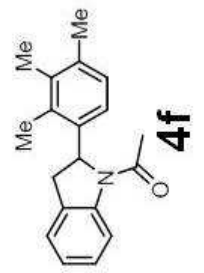

8.3337
8.3302
8.3302
8.3337
7.2601
7.2506
7.2371
7.2240
7.1019
7.0897
7.0360
7.0239
7.0116
6.9794
6.9667
6.9186
6.9053
6.8433
6.8308
6.8185
5.7362
5.7326
5.7195
5.7158
3.9080
3.7731
3.7564
3.7462
3.7294
2.8774
2.8750
2.8504
2.8481
1.5973
1.5742
3.2342
3.0035
3.0005
2.0106
1.0095
1.0095
1.0078
1.0
δ / ppm


MeO
N
O

4e

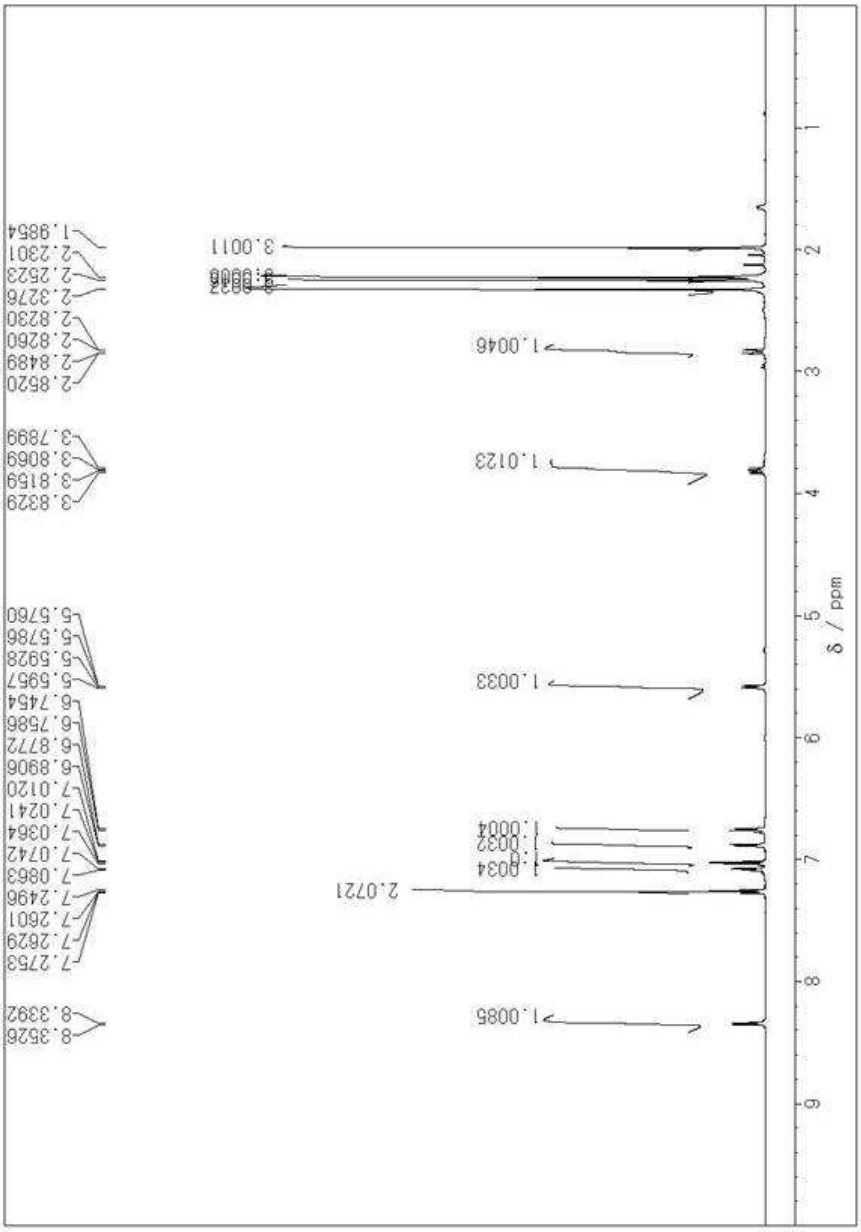
^{13}C NMR

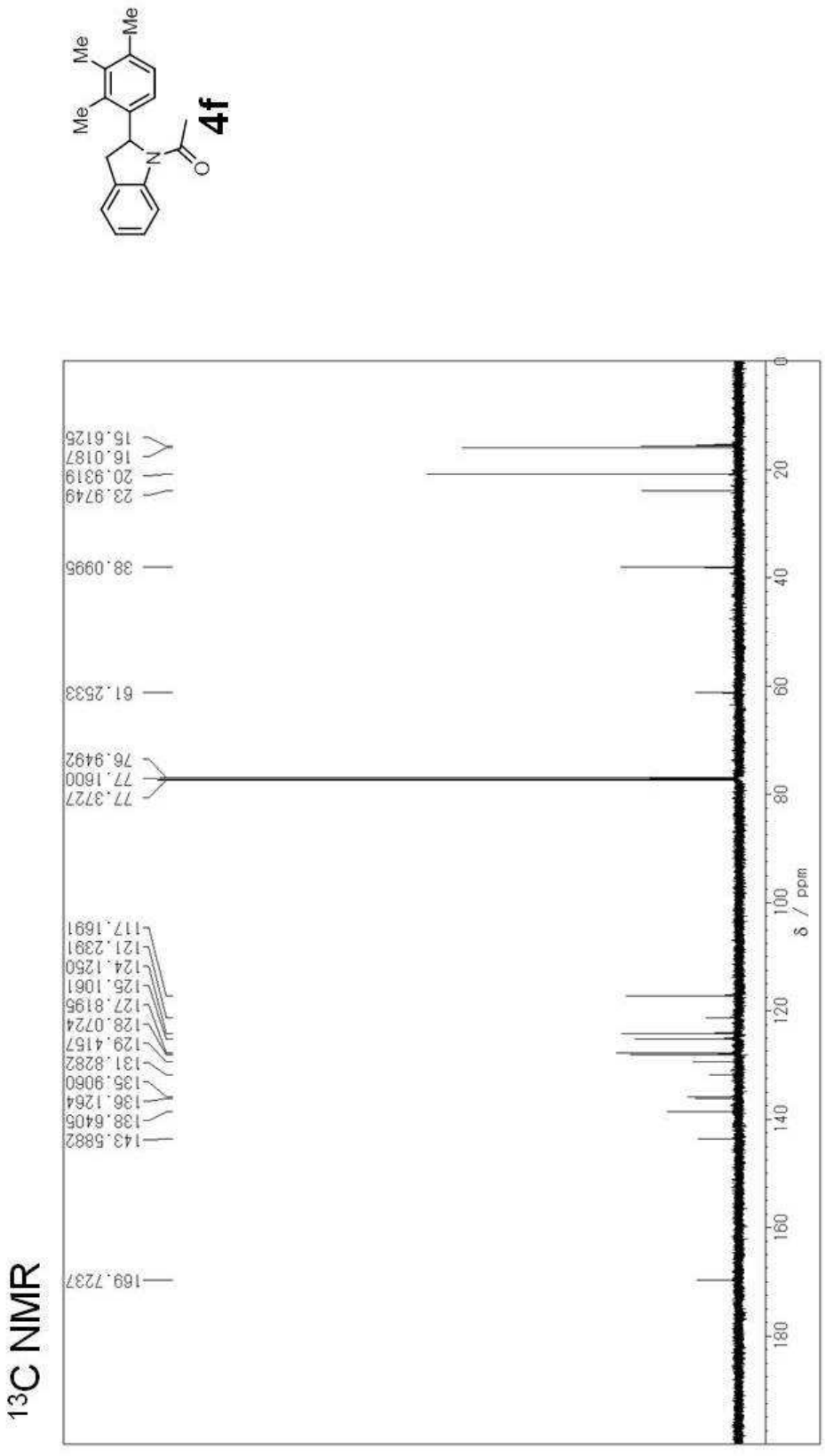

23.8695
37.8580
55.5525
58.2314
76.9473
77.1600
77.3708
110.5312
117.2208
121.1184
124.0828
125.0486
125.1329
127.6930
128.7699
130.1726
130.9928
143.4751
155.6758
169.7448
δ / ppm

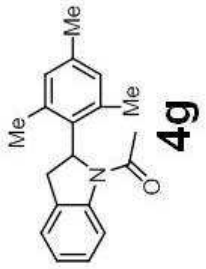

Me
Me
Me
N
O

4f

^{1}H NMR

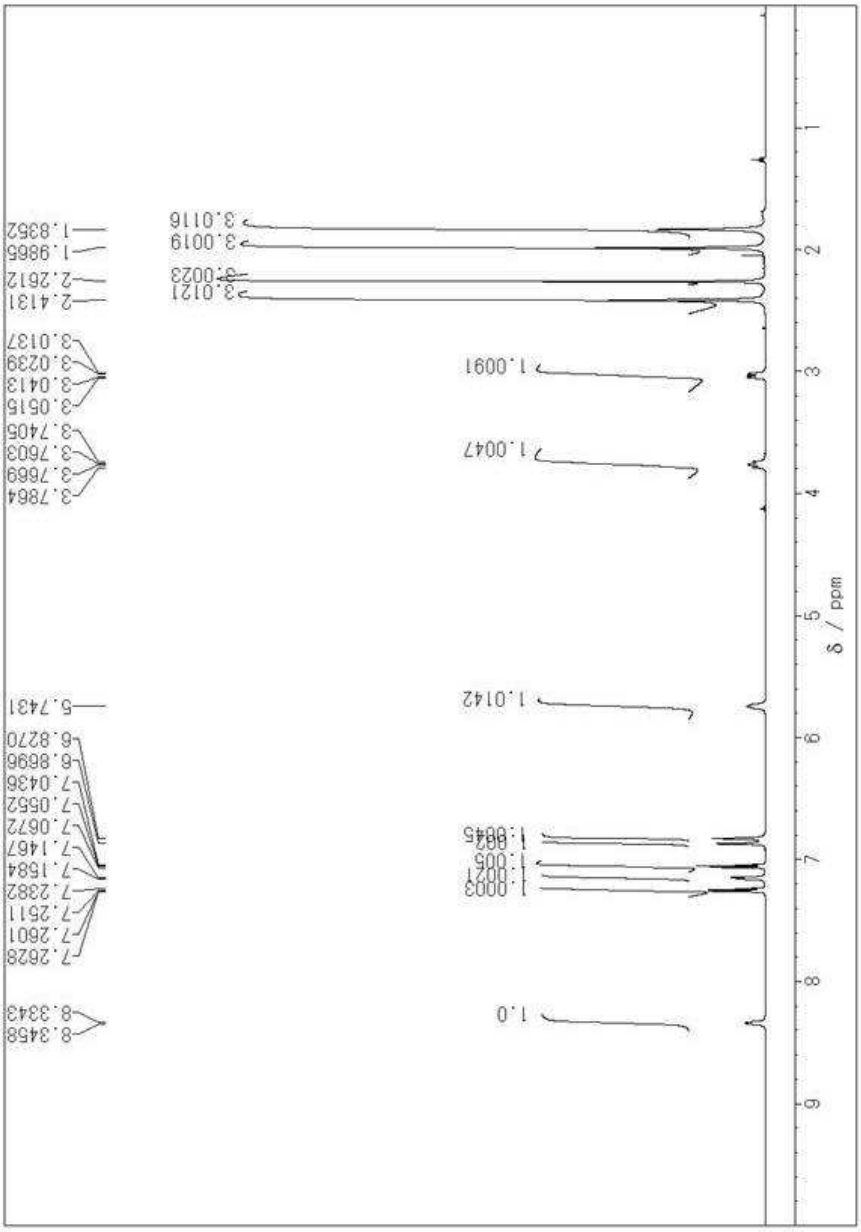

8.3526
8.3392
7.7753
7.7629
7.7601
7.7496
7.7483
7.7363
7.7242
7.7064
7.7041
7.6920
7.6772
7.6586
7.6454
5.6957
5.6928
5.6786
5.6760
3.8329
3.8159
3.8069
3.7899
2.8520
2.8489
2.8260
2.8230
2.3276
2.2623
2.2301
1.9854
1.0085
2.0721
1.0034
1.0032
1.0004
1.0033
1.0123
1.0046
3.0011
δ / ppm

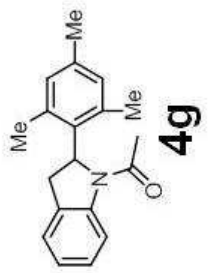

Me
Me
Me
N
O
4f
^{13}C NMR
169.7237
143.5882
138.6405
136.1264
135.9060
131.8282
129.4157
128.0724
127.8195
125.1061
124.1250
121.2391
117.1691
77.3727
77.1600
76.9492
61.2533
38.0995
23.9749
20.9319
16.0187
15.6125
δ / ppm


Me
Me
Me
N
O

4g

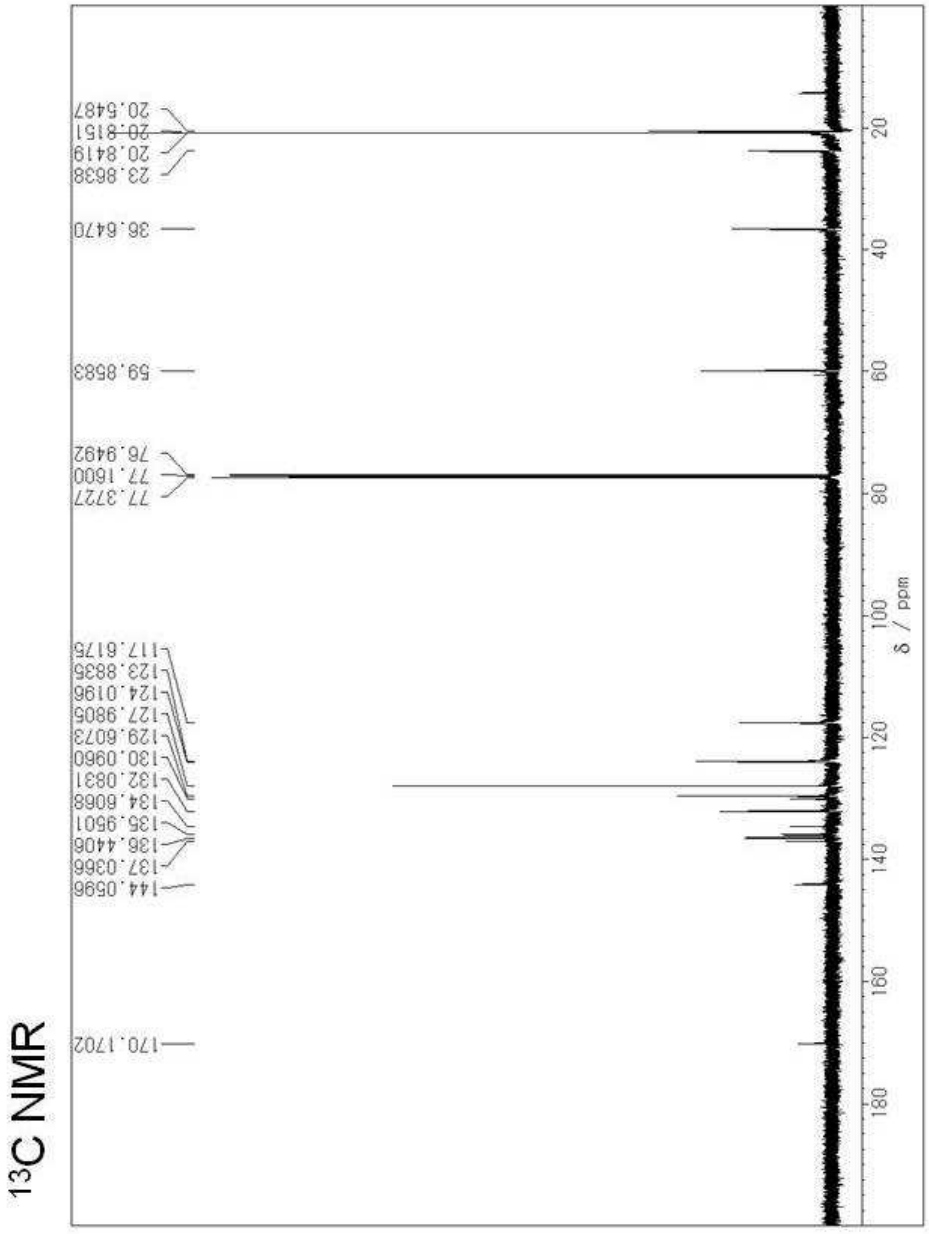
^{1}H NMR

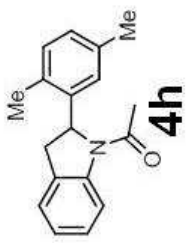

8.3458
8.3343
7.2628
7.2601
7.2511
7.2382
7.1584
7.1467
7.0672
7.0552
7.0436
6.8696
6.8270
5.7431
3.7864
3.7669
3.7603
3.7405
3.0515
3.0413
3.0239
3.0137
2.4131
2.2612
3.0121
3.0023
3.0019
3.0116
1.9865
1.8352
1.0
1.0045
1.0027
1.0093
1.0142
1.0047
1.0091
δ / ppm


Me
Me
Me
N
O

4g

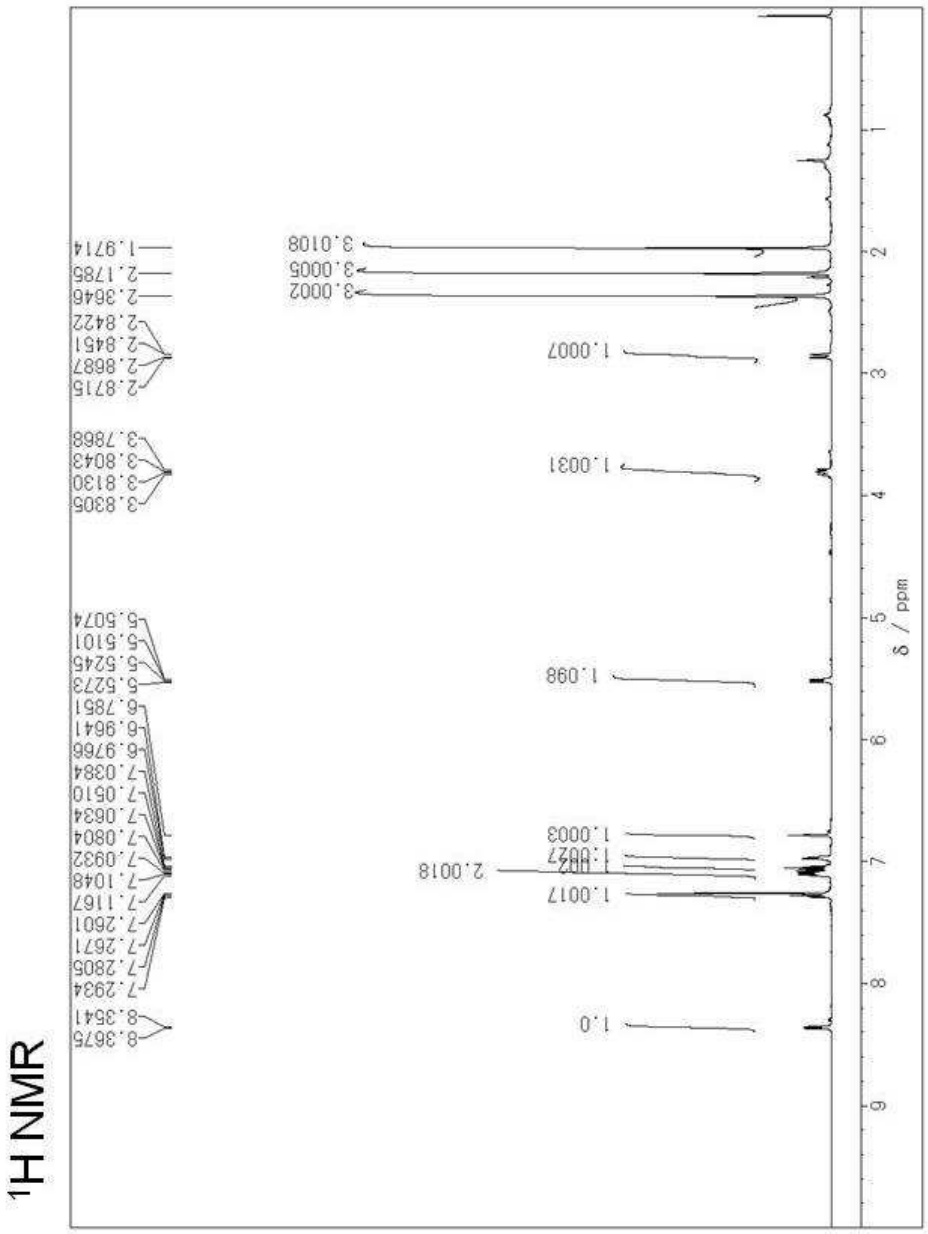
^{13}C NMR

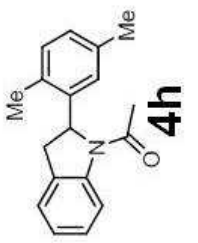

20.5487
20.8151
20.8419
23.8638
36.6470
59.8583
76.9492
77.1600
77.3727
117.6175
123.8835
124.0196
127.9805
129.6073
130.0960
132.0831
134.6068
135.9601
136.4406
137.0366
144.0596
170.1702
20
40
60
80
100
120
140
160
180
δ / ppm


Me
Me
N
O

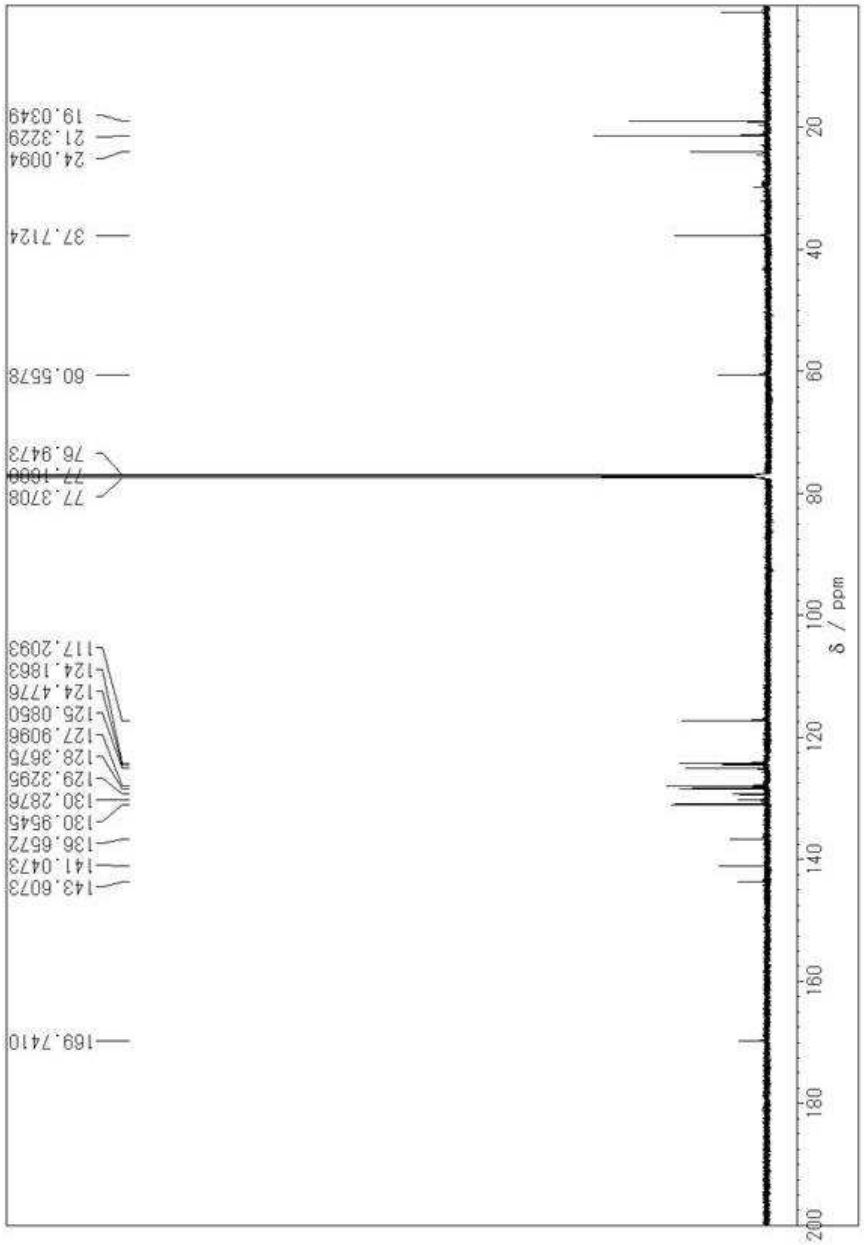
4h

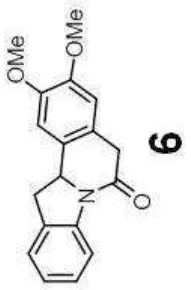
^{1}H NMR


8.3675
8.3541
7.2934
7.2805
7.2671
7.2601
7.1167
7.1048
7.0932
7.0804
7.0634
7.0510
7.0384
6.9766
6.9641
6.7851
5.5273
5.5245
5.5101
5.5074
3.8305
3.8130
3.8043
3.7868
2.8715
2.8687
2.8451
2.8422
2.3646
2.1785
1.9714
3.0108
3.0005
3.0002
1.0007
1.0031
1.098
1.0003
1.0027
2.0018
1.0017
1.0
δ / ppm


Me
Me
4h

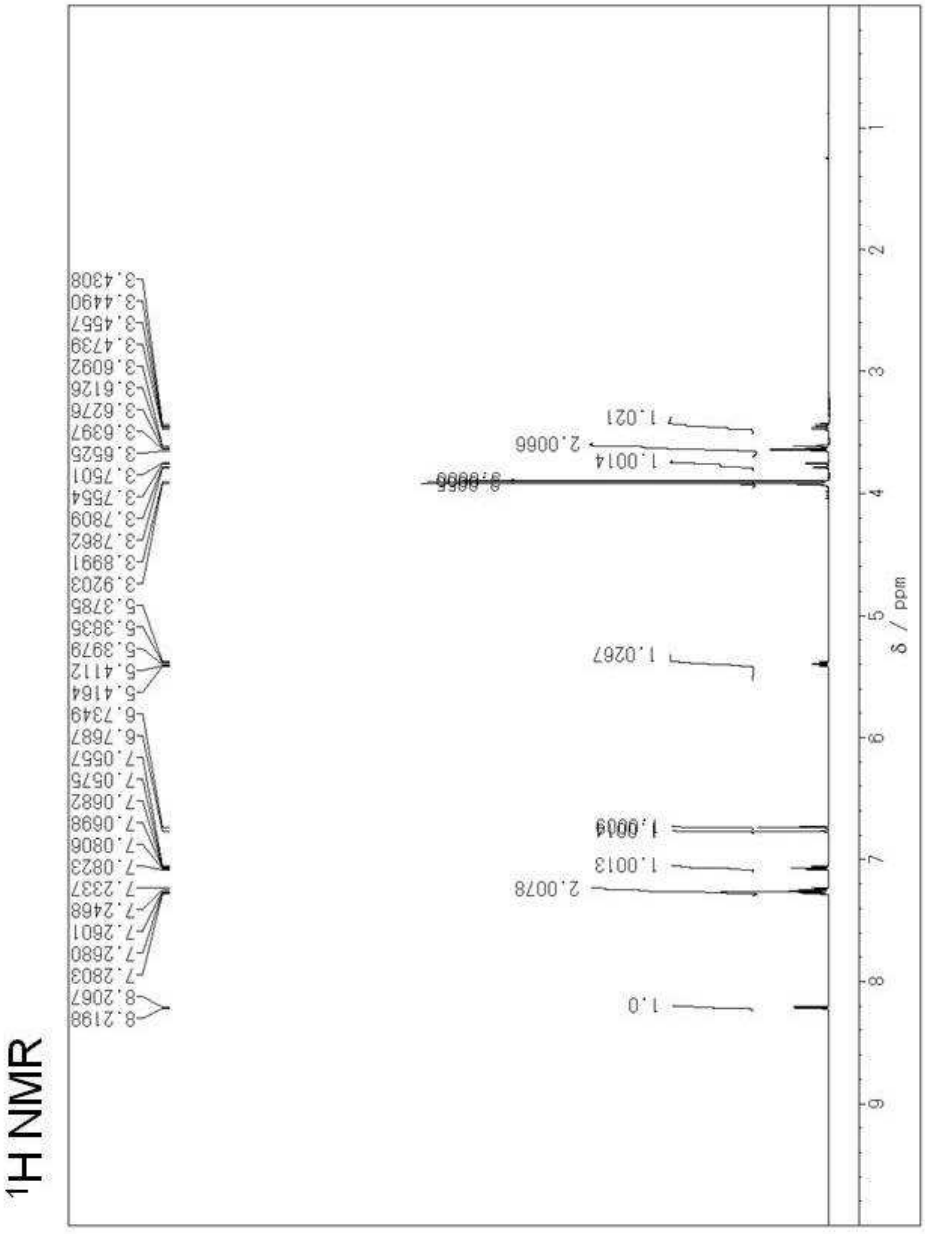
^{13}C NMR

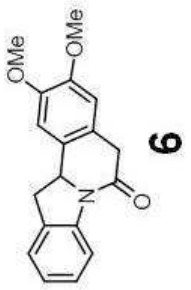

19.0349
21.3229
24.0094
37.7124
60.5578
76.9473
77.1600
77.3708
117.2093
124.1863
124.4776
125.0850
127.9096
128.3675
129.3295
130.2876
130.9545
136.6572
141.0473
143.6073
169.7410
20
40
60
80
100
120
140
160
180
200
δ / ppm


OMe
OMe
N
O

6

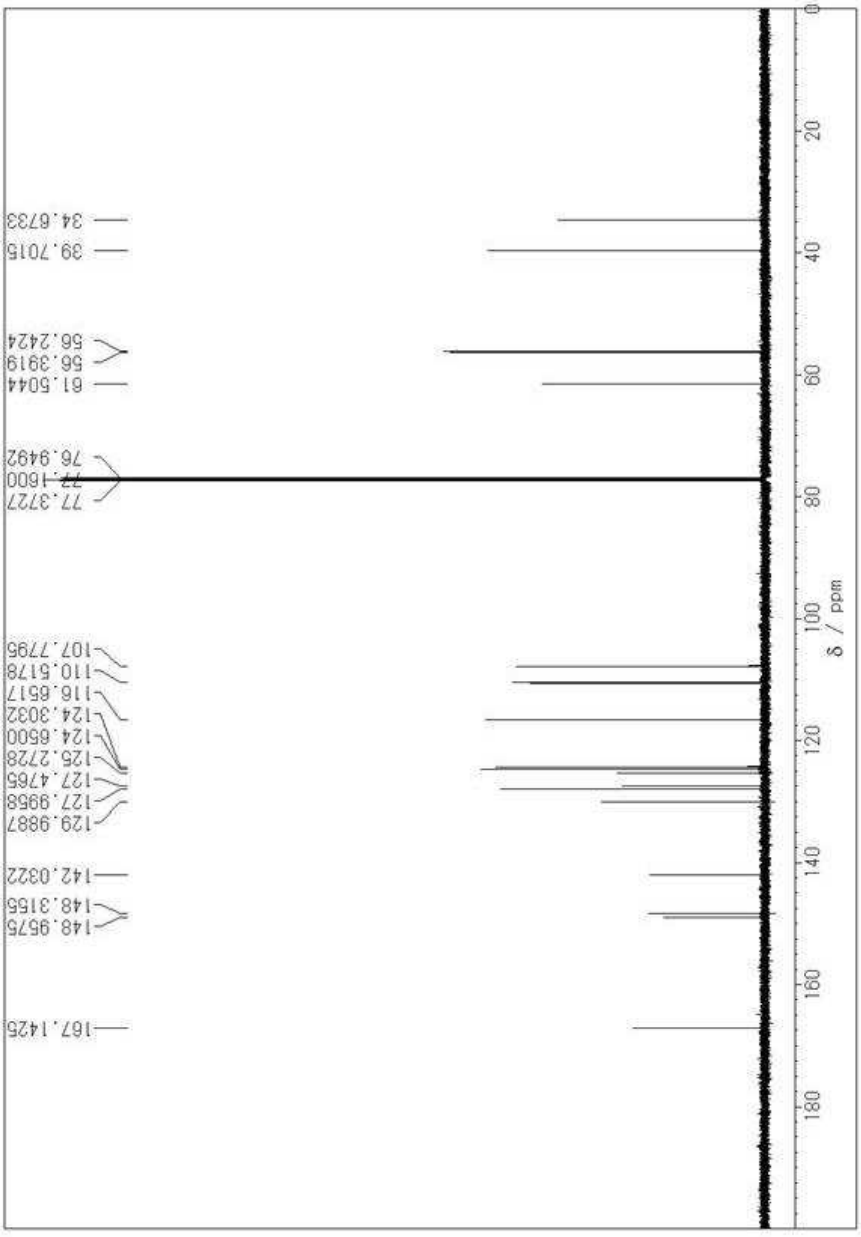
^{1}H NMR

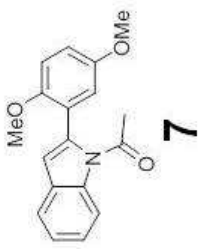

8.2198
8.2067
7.2803
7.2680
7.2601
7.2468
7.2337
7.0823
7.0806
7.0698
7.0682
7.0575
7.0575
6.7687
6.7349
5.4164
5.4112
5.3979
5.3835
5.3785
3.9203
3.8991
3.7862
3.7809
3.7554
3.7501
3.6525
3.6397
3.6276
3.6126
3.6092
3.4739
3.4657
3.4490
3.4308
1.021
2.0066
1.0014
1.0267
1.0014
1.0013
2.0078
1.0
δ / ppm


OMe
OMe
O
N

6

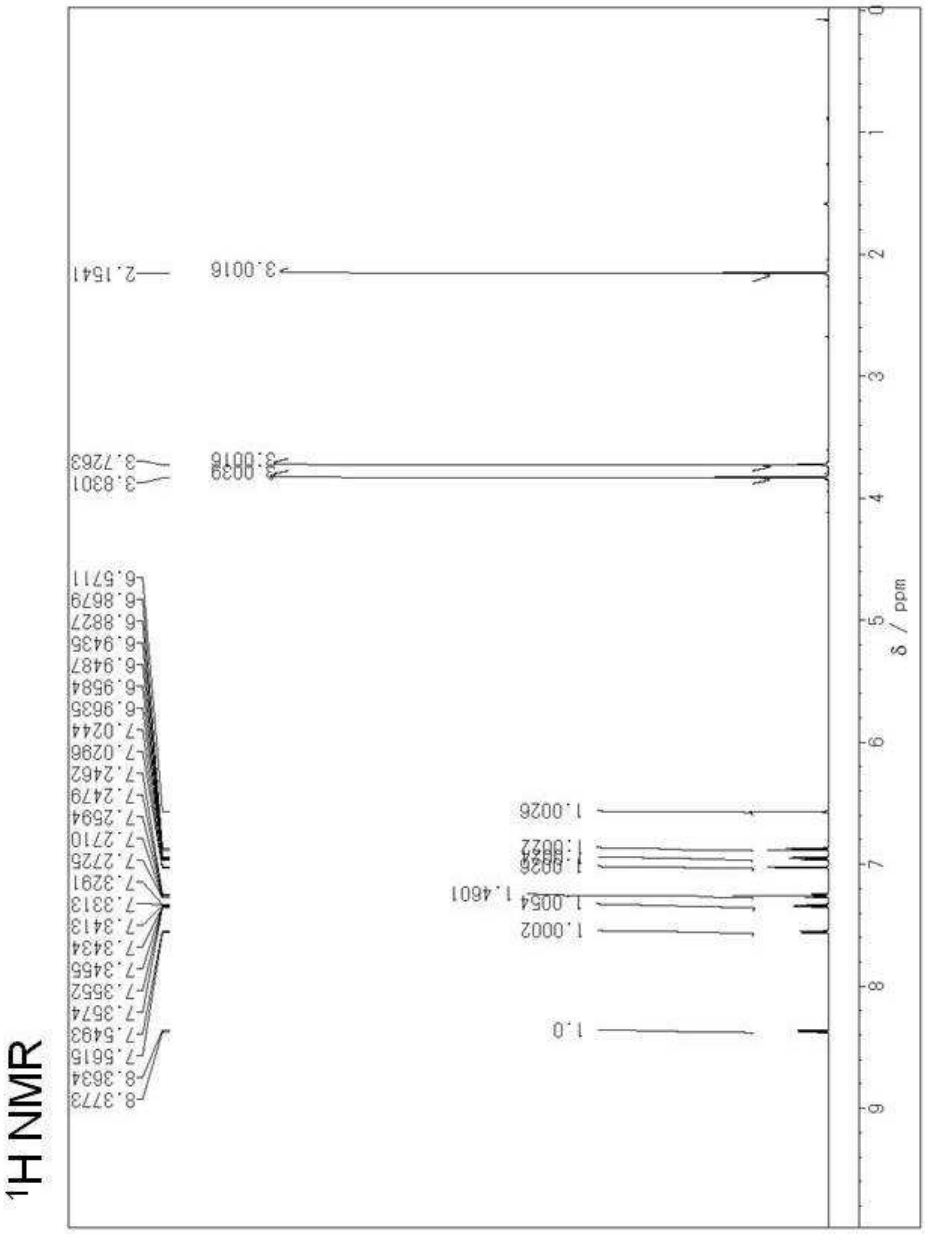
^{13}C NMR

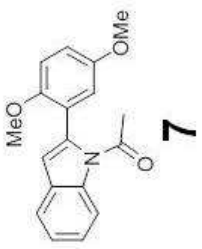

34.6733
39.7015
56.2424
56.3919
61.5044
76.9492
77.1600
77.3727
107.7795
110.5178
116.6517
124.3032
124.6500
125.2728
127.4765
127.9958
129.9887
142.0322
148.3155
148.9575
167.1425
0
20
40
60
80
100
120
140
160
180
δ / ppm


MeO
OMe
N
O

7

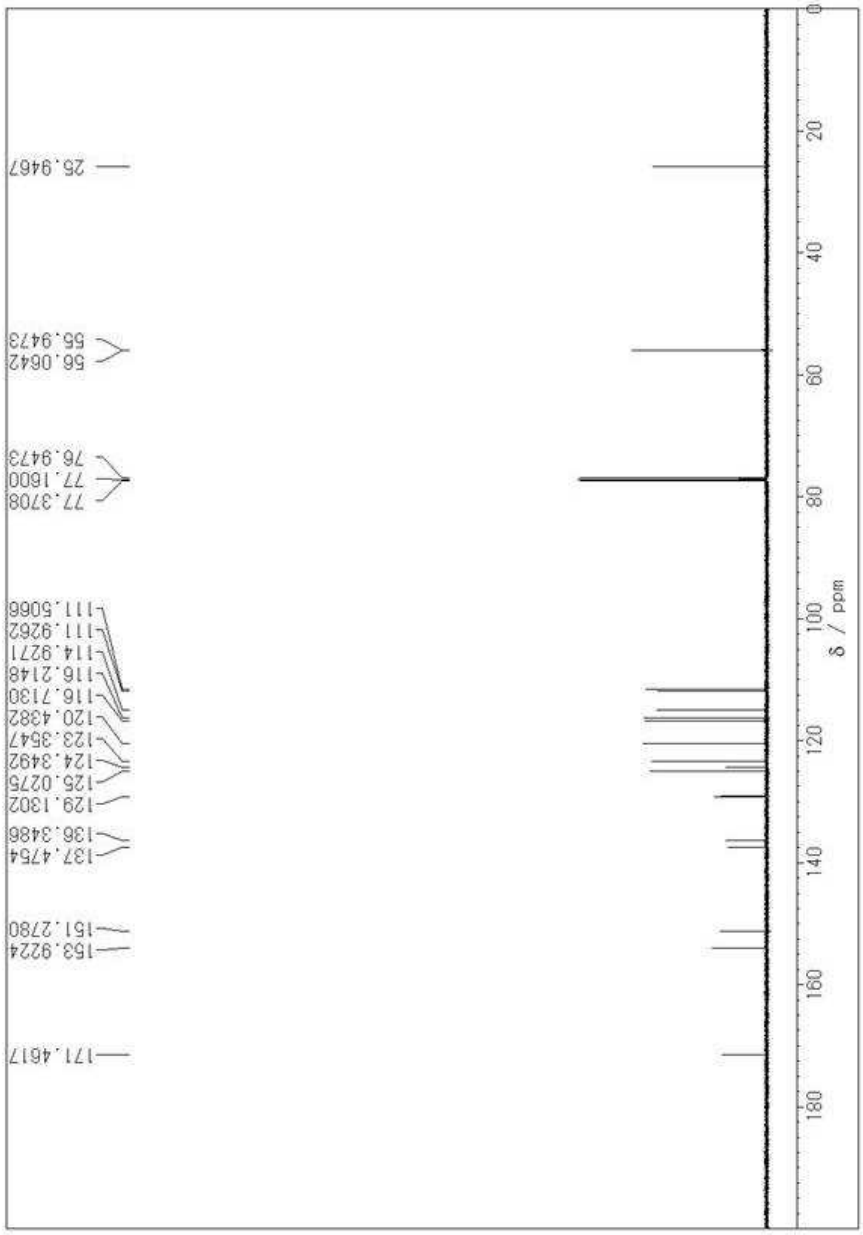
^{1}H NMR

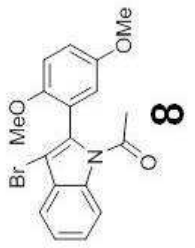

8.3773
8.3634
7.5615
7.5493
7.3574
7.3552
7.3455
7.3434
7.3413
7.3313
7.3291
7.2725
7.2710
7.2694
7.2479
7.2462
7.0296
7.0244
6.9835
6.9584
6.9487
6.9435
6.8827
6.8679
6.5711
3.7263
3.8301
2.1541
1.0026
1.0022
1.0025
1.4601
1.0054
1.0002
1.0
3.0016
3.0039
3.0016
δ / ppm


MeO
OMe
N
O

7

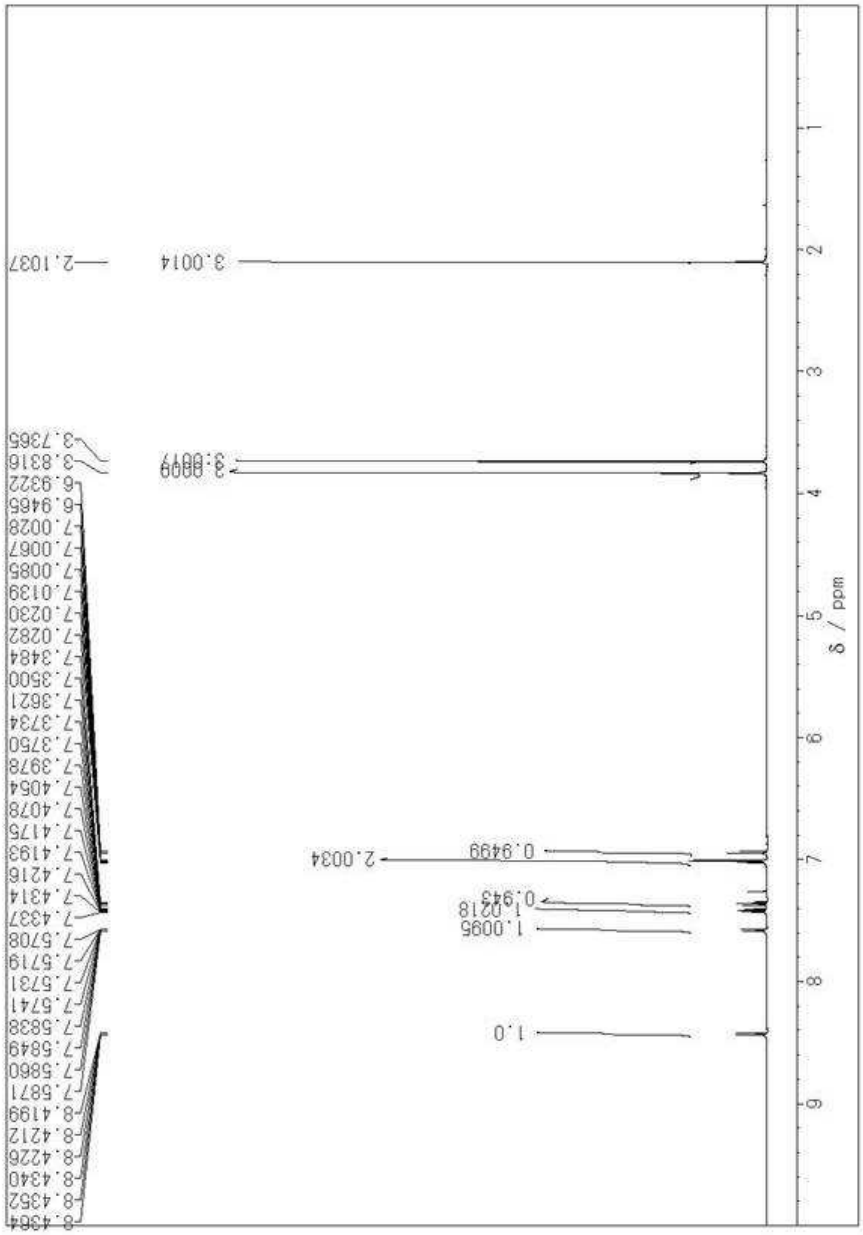
^{13}C NMR

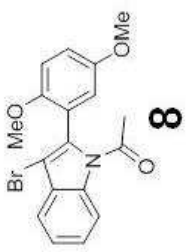

171.4617
153.9224
151.2780
137.4754
136.3486
129.1302
125.0275
124.3492
123.3547
120.4382
116.7130
116.2148
114.9271
111.9262
111.5066
77.3708
77.1600
76.9473
56.0642
55.9473
25.9467
0
20
40
60
80
100
120
140
160
180
δ / ppm


OMe
MeO
Br
N
O

8

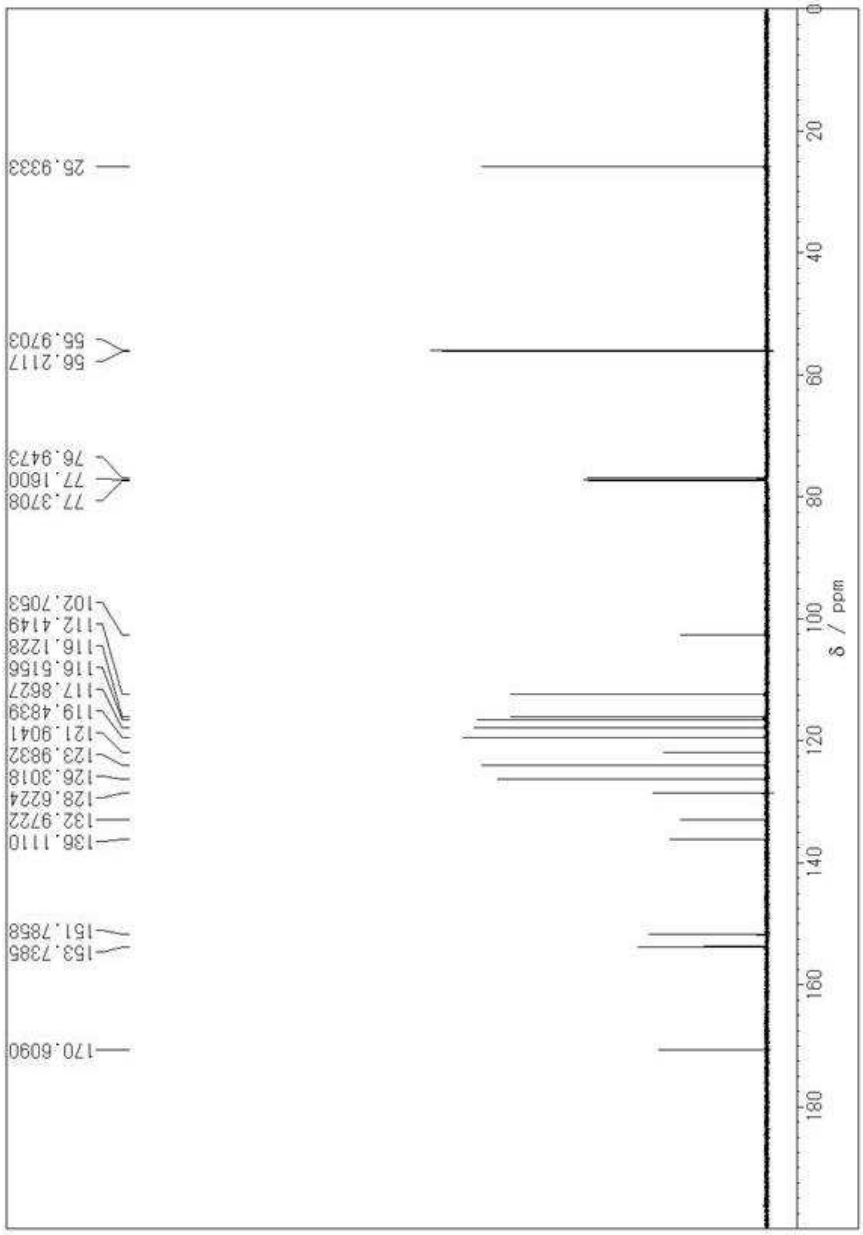
^{1}H NMR

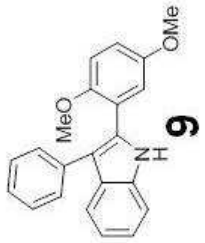

8.4364
8.4352
8.4340
8.4226
8.4212
8.4199
7.5871
7.5860
7.5849
7.5838
7.5741
7.5731
7.5719
7.5708
7.4337
7.4314
7.4216
7.4193
7.4175
7.4078
7.4054
7.3978
7.3750
7.3734
7.3621
7.3500
7.3484
7.0282
7.0230
7.0139
7.0085
7.0067
7.0028
6.9465
6.9322
3.7365
3.8316
3.8099
3.8017
2.1037
3.0014
2.0034
0.9499
0.943
1.0218
1.0095
1.0
δ / ppm


OMe
MeO
Br
N
O

8

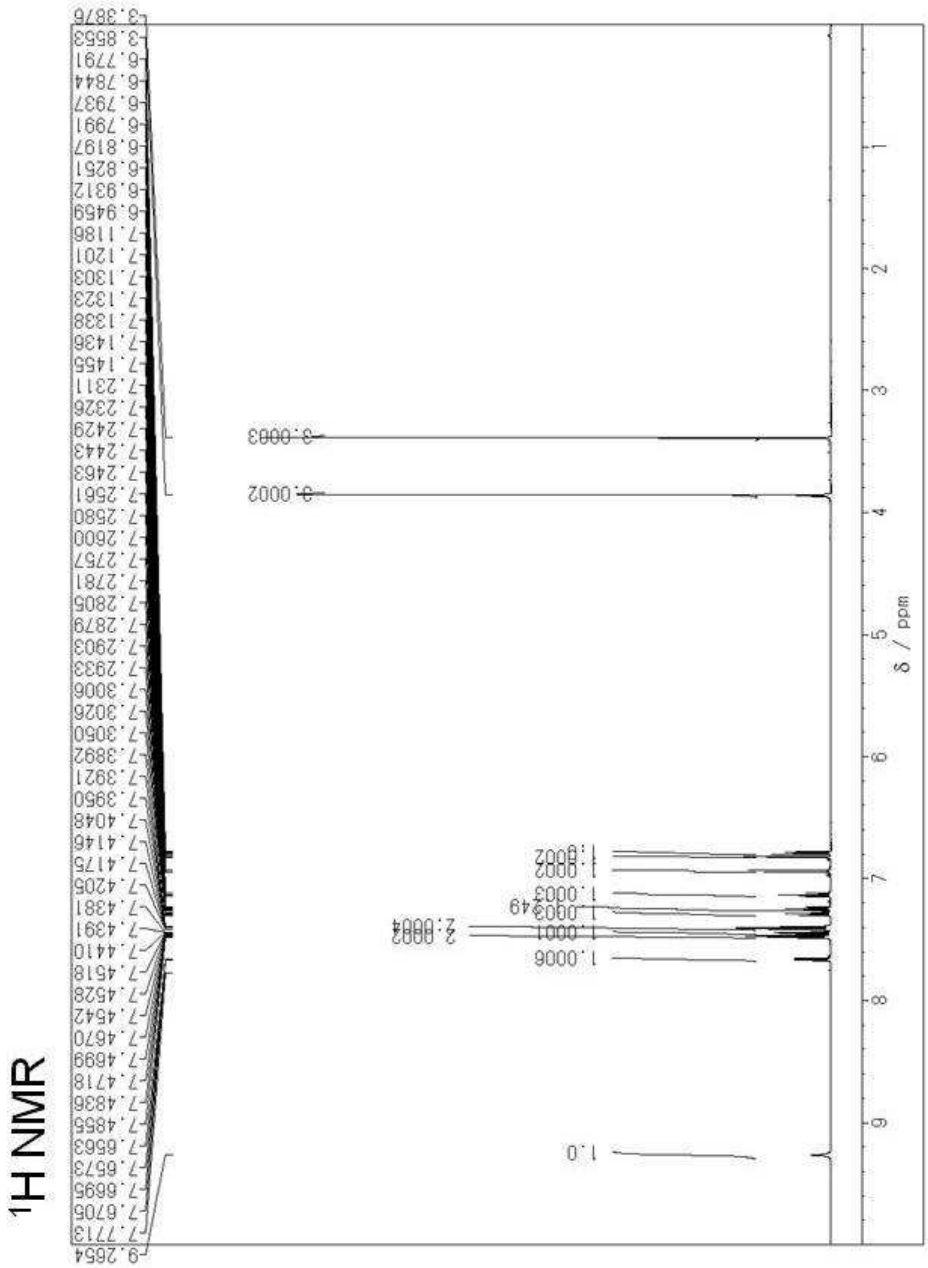
^{13}C NMR

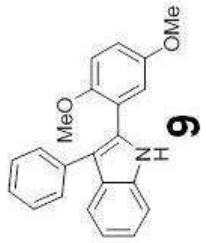

170.6090
153.7385
151.7858
136.1110
132.9722
128.6224
126.3018
123.9832
121.9041
119.4839
117.8627
116.5156
116.1228
112.4149
102.7053
77.3708
77.1600
76.9473
56.2117
55.9703
25.9333
δ / ppm



9

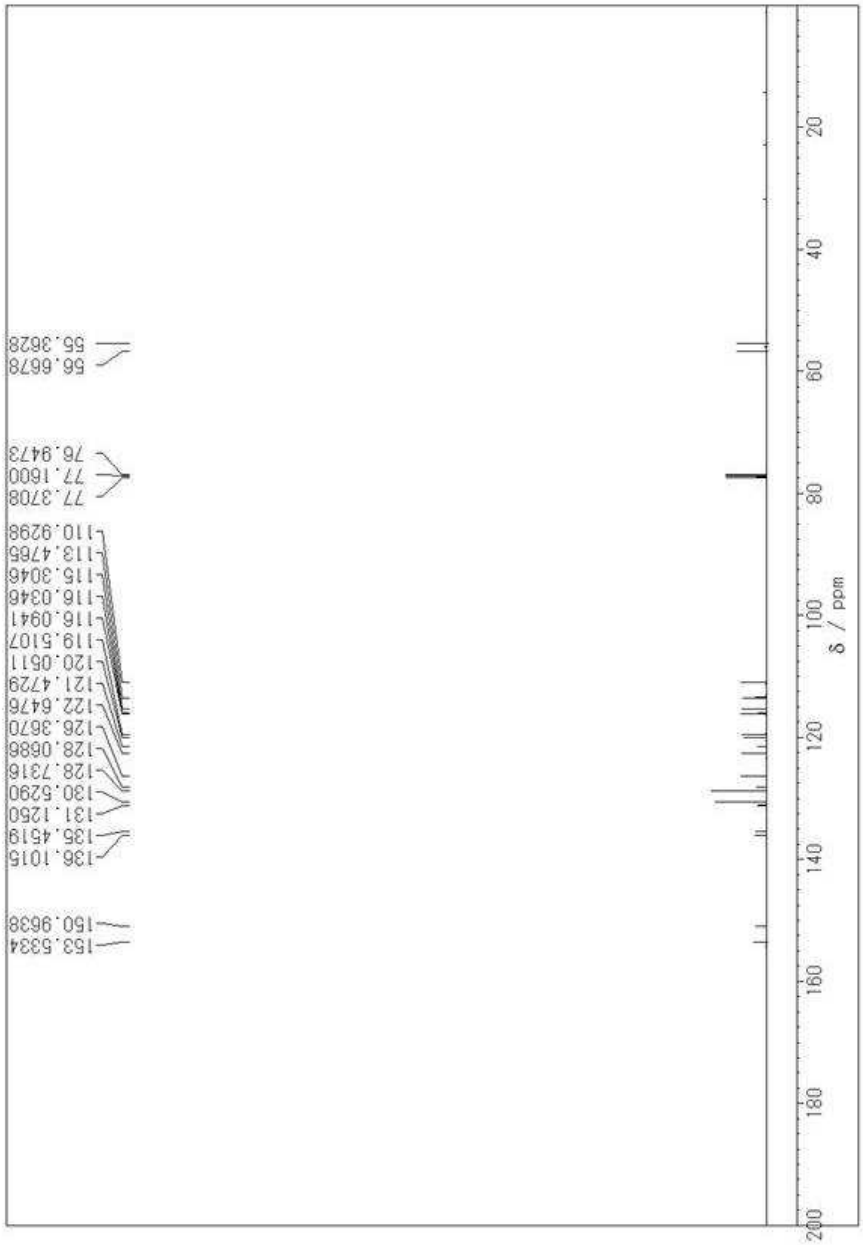
^{1}H NMR

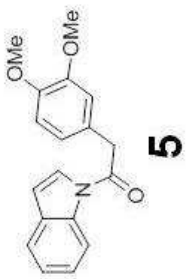



MeO
OMe
NH

9

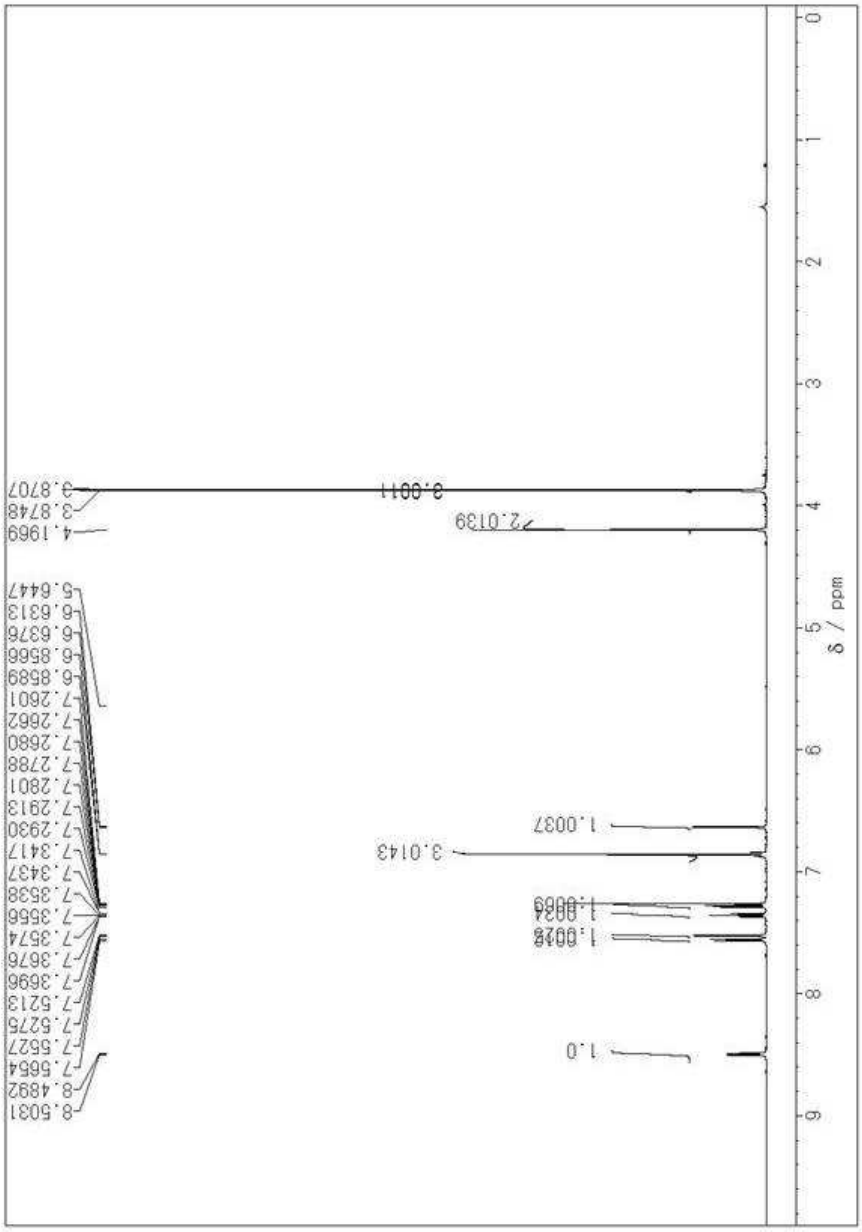
^{13}C NMR

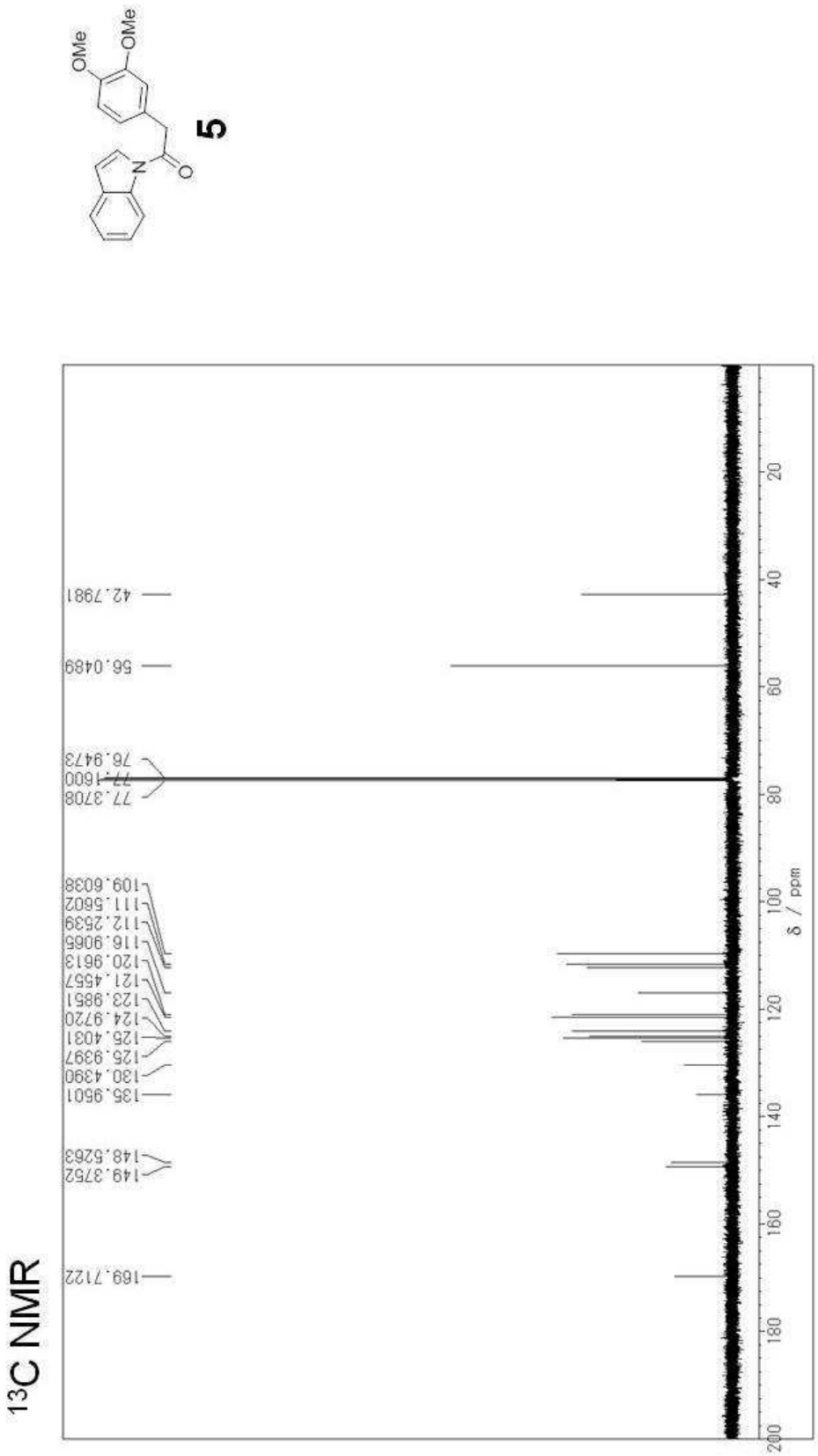

55.3628
56.6678
76.9473
77.1600
77.3708
110.9298
113.4765
115.3046
116.0346
116.0941
119.5107
120.0511
121.4729
122.6476
126.3670
128.0686
128.7316
130.5290
131.1250
135.4519
136.1015
150.9638
153.5334
20
40
60
80
100
120
140
160
180
200
δ / ppm


OMe
OMe
N
O

5

^{1}H NMR


8.5031
8.4892
7.5654
7.5527
7.5275
7.5213
7.3696
7.3676
7.3574
7.3556
7.3538
7.3437
7.3417
7.2930
7.2913
7.2801
7.2788
7.2680
7.2662
7.2601
6.8589
6.8566
6.6376
6.6313
5.6447
4.1969
3.8748
3.8707
2.0139
3.0011
1.0037
3.0143
1.0
δ / ppm


OMe
OMe
N
O
5
^{13}C NMR
169.7122
149.3752
148.5263
135.9601
130.4390
125.9397
125.4031
124.9720
123.9851
121.4557
120.9613
116.9065
112.2539
111.5602
109.6038
77.3708
77.1600
76.9473
56.0489
42.7981
δ / ppm