

Supporting Information

Base-Mediated Carboxylation of Unprotected Indole Derivatives with Carbon Dioxide

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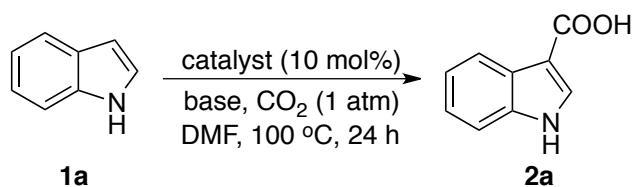
General Information: ^1H and ^{13}C NMR spectra were recorded on a JEOL ECX-500 and a JEOL ECX-600 in CDCl_3 . Chemical shifts were reported in parts per million (ppm) from tetramethylsilane using the solvent resonance as the internal standard. IR spectra were measured on a JASCO FT/IR-610 spectrometer. High-resolution mass spectrometry was carried out using a JEOL JMS-T100TD (DART). Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F from Wako Pure Chemical Industries, Ltd.

Reagents: Unless stated otherwise, commercial reagents were used as received. All organic solvents were purified by distillation under dry argon atmosphere. 7-Bromoindole,¹ 1H-benzo[g]indole, and 4-benzyloxy-1H-indole² were prepared according to literature procedures.

Part I: Optimization of reaction conditions

Previous results using metal as catalyst

Table 1. Screening catalyst and base^a



entry	catalyst	base (equiv)	yield (%) ^b
1	$\text{Pd}(\text{OAc})_2$	Cs_2CO_3 (2)	49
3	$\text{Pd}(\text{OAc})_2$	---	---
4	$\text{Pd}(\text{OAc})_2$	Cs_2CO_3 (1)	16
5	$\text{Pd}(\text{OAc})_2$	Cs_2CO_3 (3)	70
6	$\text{Pd}(\text{OAc})_2$	Cs_2CO_3 (4)	75
7	PdCl_2	Cs_2CO_3 (3)	48
8	$\text{Pd}(\text{acac})_2$	Cs_2CO_3 (3)	52
9	$\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	Cs_2CO_3 (3)	<5
10	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	Cs_2CO_3 (3)	73
11	AgOAc	Cs_2CO_3 (3)	49
12	$\text{Fe}(\text{OAc})_2$	Cs_2CO_3 (3)	51
13 ^c	$\text{Pd}(\text{OAc})_2$	Cs_2CO_3 (3)	---
14	---	Cs_2CO_3 (3)	25
15	---	LiO^tBu (3)	38

^a All the reactions were carried under a balloon pressure of CO_2 in DMF at 100°C for 24 h. ^b Yield based on **1a** and determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as internal standard. ^c Under argon.

Comparison between entry 5 and entry 14, it is clear that $\text{Pd}(\text{OAc})_2$ enhances the direct carboxylation reaction of indoles. However, due to cost and problems of removing trace amounts of palladium from the final product, it is beneficial to perform the reaction under transition metal-free conditions.

We also examined the effect of different solvents in order to improve the yield of the reaction (Table 2).

Table 2. Solvent Screening^a

c1ccc2c(c1)c(c[nH]2)C(=O)O (2a)

entry ^a	solvent	yield (%) ^b
1	DMF	70
2	DMA	45
3	DMSO	34
4	NMP	20
5	toluene	trace
6	1,4-dioxane	trace
7	CPME	trace
8	PhCF ₃	trace

^a All reactions were carried with 0.4 mmol of indole **1a**, 3 equivalence of Cs₂CO₃ and 10 mol% Pd(OAc)₂ under a balloon pressure of CO₂ at 100 °C for 24 h. ^b Yield based on **1a** and determined by ¹H NMR analysis using 1,1,2,2-tetrachloroethane as internal standard

We could not improve the reaction by changing the solvent system. Most of CO₂ fixation reactions were carried in DMF.³

The problem of using 3 equivalence of base was the side reaction (decarboxylation) decreased the conversion of 3-indole carboxylic acid (Table 3).

Table 3. Conversion of Product verses Time^a

c1ccc2c(c1)c(c[nH]2)C(=O)O (2a)

entry	time (h)	conv. (%) ^b
1	4	55
2	8	71
3	9	75
4	10	80
5	15	88
6	24	66

^a All reactions were carried with 0.4 mmol of indole **1a**, 3 equivalence of LiO^tBu and 10 mol% Pd(OAc)₂ under a balloon pressure of CO₂ at 100 °C. ^b Yield based on **1** and determined by ¹H NMR analysis using 1,1,2,2-tetrachloroethane as internal standard

Screening of the reaction **without metal**. Using less base in the reaction (entries 2, 3) gave poor conversion in the desired product after 24 h at 100°C. Low temperatures decrease of yields (entries 4,5). The more suitable solvent was the DMF that has been demonstrated in the previous results with metal.

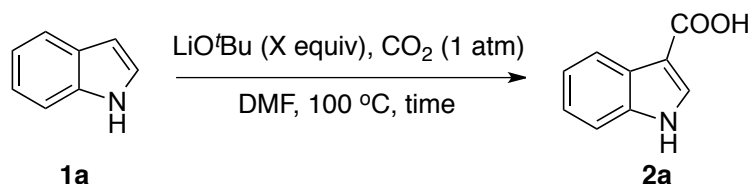


Table 4. Screening of reaction without metal

entry ^a	base (X eq)	solvent	T (°C)	conv.(%) ^b
1	2	DMF	100	36
2	3	DMF	100	47
3	4	DMF	100	60
4	5	DMF	100	99
5	5	DMF	80	80
6	5	DMF	50	10
7	5	THF	60	20
7	5	DMF/H ₂ O (1:1)	---	---

^a All reactions were carried with 0.4 mmol of indole **1a**, X equivalence of LiO^tBu under a balloon pressure of CO₂ at Y °C. ^b Yield based on **1** and determined by ¹H NMR analysis using 1,1,2,2-tetrachloroethane as internal standard

Importance to use excess of base to avoid the side reaction (decarboxylation)

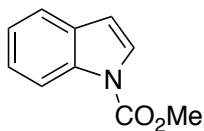
Table 5. Conversion of product versus time

entry ^a	base (X eq)	time (h)	Conv. (%) ^b
1	3	5	40
2	5	5	50
3	3	10	30
4	5	10	80
5	3	24	47
6	5	24	99

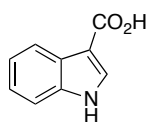
^a All reactions were carried with 0.4 mmol of indole **1a**, X equivalence of LiO^tBu under a balloon pressure of CO₂ at Y °C. ^b Yield based on **1** and determined by ¹H NMR analysis using 1,1,2,2-

Study about mechanism

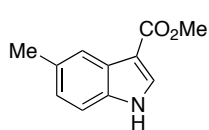
Procedure for the isolation of **methyl indole 1-carboxylate** intermediate in the hypothesized mechanism.



In a dried two-necked test tube was charged with LiO^tBu (160 mg, 2 mmol, 5 equiv) and indole (**1a**) (23.4 mg, 0.4 mmol, 1 equiv). The reaction vessel was evacuated under high vacuum and the atmosphere was replaced with a balloon of CO₂. Then DMF (2 mL) was added. The reaction was run at r.t for 15 hours, then worked up with iodomethane (25 μ L, 1 mmol, 1 eq). The mixture was concentrated under reduced pressure. The residue was extracted with EtOAc and brine (3 times). The combined organic phase was dried over MgSO₄ and concentrated under reduced pressure and the residue was purified by preparative TLC (n-hexane:EtOAc = 7:3) affording the desired product **methyl indole 1-carboxylate** in 15 % yield. ¹H NMR (CD₃Cl, 600 MHz): δ 8.11 (d, 1H, J = 6 Hz), 7.53 (d, 1H, J = 3.4 Hz), 7.50 (d, 1H, J = 7.5 Hz), 7.26 (t, 1H, J = 8.2 Hz), 7.17 (t, 1H, J = 8.2 Hz), 6.53 (d, 1H, J = 3.4 Hz), 3.97 (s, 3H). ¹³C NMR (CD₃Cl, 100 MHz): δ 151.1, 134.8, 130.2, 125.2, 124.0, 122.7, 120.6, 114.8, 107.9, 53.4. This is a known compound reported in the literature.⁴

Part II: Substrate scope for the direct carboxylation of indoles derivatives**General procedure for the direct carboxylation of indole****3-Indole carboxylic acid (2a)**

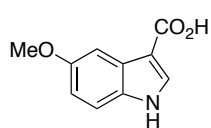
In a dried two-necked test tube was charged with LiO^tBu (160 mg, 2 mmol, 5 equiv) and indole (**1a**) (23.4 mg, 0.4 mmol, 1 equiv). The reaction vessel was evacuated under high vacuum and the atmosphere was replaced with a balloon of CO₂. Then DMF (2 mL) was added and the mixture was stirred for 24 h at 100 °C. Then the reaction mixture was cooled and carefully quenched with a solution of HCl (2 N) and extracted with EtOAc (5x). The combined organic layers were washed with water (2x), brine (1x) and dried over MgSO₄. The dried organics were concentrated under reduced pressure and the residue was purified by preparative TLC (hexane:acetone = 1:1) to afford the desired product **2a** in 95% yield as a white solid. ¹H NMR (DMSO-d₆, 400 MHz): δ 11.87 (bs, 1H), 11.7 (bs, 1H), 7.99-7.92 (m, 2H), 7.43-7.38 (m, 1H), 7.18-7.06 (m, 2H). ¹³C NMR (DMSO-d₆, 100 MHz): δ 165.9, 136.4, 132.2, 125.9, 122.0, 120.9, 120.5, 112.1, 107.3. This is a known compound reported in the literature.⁵

Methyl 5-methyl-3-indolecarboxylate (7a)

The 3-indole carboxylate was generated following the above the general procedure. Isolation of the carboxylic acid was achieved by derivatization to the methyl ester. The crude mixture was diluted with MeOH and cooled to 0 °C. SOCl₂ (1.2 eq, 0.5 mmol) was added and stirred for 3 hours at room temperature. Then MeOH (1 mL) was added and the reaction mixture was heated to reflux for 6 hours. The resulting mixture was quenched with water and extracted with EtOAc (3x). The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. The resulting residue was purified by preparative TLC (hexane:EtOAc = 7:3) to afford the desired product **7a** in 90% yield as a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.68 (bs, 1H), 7.98 (s, 1H), 7.77 (s, 1H), 7.20 (d, 1H, J

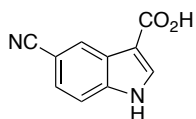
= 6.4 Hz), 6.99 (d, 1H, J = 8.2 Hz), 3.84 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 166.0, 134.3, 131.4, 131.1, 126.1, 124.7, 129.0, 111.1, 108.0, 51.0, 21.5. This is a known compound reported in the literature.⁶

5-Methoxy-1-H-indole-3-carboxylic acid (2c)



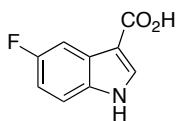
Following the above the general procedure with a slight modification of the purification method. After pouring into a cold solution of HCl (2N), the organic layer was extracted with EtOAc (5x). The combined organic layers were basified with an aqueous solution of NaOH (0.5 M). The aqueous layer was extracted with water and the combined aqueous layers were acidified with a solution of HCl (2N). The desired product **2c** was extracted with EtOAc (5x) and dried over MgSO_4 to afford the desired product **2c** in 92% yield as a white solid. ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 400 MHz): δ 10.86 (bs, 1H), 7.9 (d, 1H, J = 2.7 Hz), 7.63 (d, 1H, J = 3.6 Hz), 7.36 (d, 1H, J = 8.2 Hz), 6.82 (dd, 1H, J = 8.7 Hz, J = 2.7 Hz), 3.79 (s, 3H); ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 100 MHz): δ 167.5, 156.5, 133.3, 132.5, 128.1, 113.6, 113.5, 108.0, 103.4, 55.7. This is a known compound reported in the literature.⁷

5-Cyanoindole-3-carboxylic acid (2d)



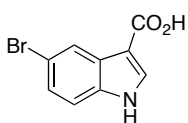
Following the same procedure described for the **2c** afforded the desired product **2d** in 90% yield as a white solid. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz): δ 12.30 (bs, 1H), 12.29 (bs, 1H), 8.35 (s, 1H), 8.18 (s, 1H), 7.64 (d, 1H, J = 7.3 Hz), 7.54 (d, 1H, J = 7.7 Hz); ^{13}C NMR ($\text{DMSO}-d_6$, 100 MHz): δ 165.3, 138.2, 134.6, 125.7, 125.6, 124.9, 120.0, 113.9, 108.0, 103.4. This is a known compound to those reported in the literature.⁸

5-Fluoroindole-3-carboxylic acid (2e)



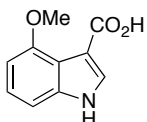
Following the same procedure described for the **2c** afforded the desired product **2e** in 94% yield as a white solid. ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 400 MHz): δ 11.02 (bs, 1H), 8.12 (d, 1H, J = 3.6 Hz), 7.80 (dd, 1H, J = 10.5 Hz, J = 2.8 Hz), 7.51 (dd, 1H, J = 8.7 Hz, J = 8.7 Hz), 7.01 (td, 1H, J = 9.6 Hz, J = 2.7 Hz); ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 100 MHz): δ 166.7, 161.0, 158.6, 134.4 (J = 46.7 Hz), 128.1, 114.1 (J = 9.5 Hz), 111.5 (J = 25.6 Hz), 108.6, 106.6 (J = 24.7 Hz). This is a known compound available from Sigma-Aldrich.

5-Bromoindole-3-carboxylic acid (2f)



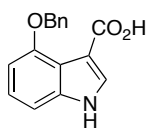
Following the same procedure described for the **2c** afforded the desired product **2f** in 96% yield as a brown solid. ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 400 MHz): δ 11.08 (bs, 1H), 8.31 (d, 1H, J = 2.3 Hz), 8.09 (d, 1H, J = 3.2 Hz), 7.48 (d, 1H, J = 7.3 Hz), 7.33 (d, 1H, J = 8.2 Hz, J = 1.3 Hz); ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 100 MHz): δ 166.1, 136.3, 134.2, 129.0, 126.2, 124.3, 115.3, 114.8, 108.2. This is a known compound reported in the literature.⁹

4-Methoxy-1H-indole-3-carboxylic acid (2g)

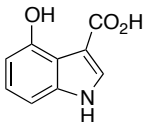


Following the same procedure described for the **2a**. The desired product was isolated by preparative TLC ($\text{DCM}:\text{MeOH}$ = 9:1) to afford the desired product **2g** in 30% yield. ^1H NMR (CD_3CN , 400 MHz): δ 11.57 (bs, 1H), 10.08 (bs, 1H), 7.97 (d, 1H, J = 3.2 Hz), 7.22 (d, 2H, J = 3.6 Hz), 6.81 (d, 1H, J = 4.1 Hz), 4.08 (s, 3H). ^{13}C NMR (CD_3CN , 100 MHz): δ 164.5, 151.7, 139.1, 134.6, 125.0, 114.4, 108.9, 108.1, 103.5, 57.3. This is a known compound reported in the literature.¹⁰

4-(Benzyloxy)-1H-indole-3-carboxylate (2h)

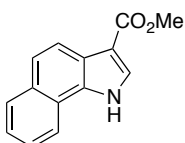


Following the same procedure described for the **2a**. The product was isolated by preparative TLC (DCM:MeOH = 9:1) to afford **2h** in 19% yield as white solid. ¹H NMR (DMSO-*d*₆, 400 MHz): δ 11.89 (bs, 1H), 11.6 (bs, 1H), 7.94 (s, 1H), 7.63 (d, 2H, *J* = 6.8 Hz), 7.40-7.30 (m, 3H), 7.15-7.09 (m, 2H), 6.82 (1H, dd, *J* = 6.4 Hz, *J* = 2.3 Hz), 5.2 (s, 2H). ¹³C NMR (DMSO-*d*₆, 100 MHz): δ 164.3, 151.3, 138.5, 136.7, 132.7, 128.2, 127.6, 127.5 (2C), 123.2, 114.6, 107.8, 106.2, 103.6, 70.0 (2C). This is a known compound reported in the literature.¹¹



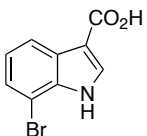
4-Hydroxy-indole-3-carboxylic acid (2i)

Following the same procedure described for the **2c** affording the desired product **2i** in 83% yield as a brown solid. ¹H NMR ((CD₃)₂CO, 400 MHz): δ 12.10 (s, 1H), 11.4 (s, 1H), 7.45 (1H, d, *J* = 9.1 Hz), 7.28-7.27 (m, 1H), 6.91 (1H, d, *J* = 8.2 Hz), 6.56-6.54 (1H, m); ¹³C NMR ((CD₃)₂CO, 100 MHz): δ 173.8, 159.3, 141.5, 125.4, 123.7, 118.3, 104.8, 102.3, 101.5. This is a known compound reported in the literature.¹²



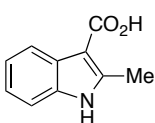
Methyl benzo[g]indole-3-indolecarboxylate (7b)

Following the same procedure described for the **2b**. The product was isolated by preparative TLC (hexane: EtOAc = 7:3) to afford **2j** in 51% yield as a white solid. ¹H NMR ((CD₃)₂CO, 500 MHz): δ 11.8 (bs, 1H), 8.36 (d, 1H, *J* = 9.7 Hz), 8.25 (d, 1H, *J* = 9.2 Hz), 8.05 (d, 1H, *J* = 2.3 Hz), 7.97 (d, 1H, *J* = 8.05), 7.66 (d, 1H, *J* = 6.4 Hz) 7.56 (t, 1H, *J* = 6.9 Hz), 7.46 (t, 1H, *J* = 7.4 Hz), 3.90 (s, 3H). ¹³C NMR ((CD₃)₂CO, 125 MHz): δ 165.7, 132.3, 131.5, 130.1, 129.4 (2C), 126.7, 125.2, 123.4, 123.0, 121.3, 121.1, 110.2, 51.1 This is a known compound reported in the literature.¹³



7-Bromo-1H-indole-3-carboxylic acid (2k)

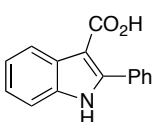
Following the same procedure described for the **2c** afforded the desired product **2k** in 88% yield as a black solid (mp = 215-217 °C). ¹H NMR ((CD₃)₂CO, 400 MHz): δ 11.07 (bs, 1H), 8.14 (d, 1H, *J* = 7.3 Hz), 8.07 (s, 1H), 7.43 (d, 1H, *J* = 7.3 Hz), 7.15 (t, 1H, *J* = 7.7 Hz); ¹³C NMR ((CD₃)₂CO, 100 MHz): δ 165.8, 136.1, 133.5, 128.8, 126.0, 123.5, 121.4, 110.0, 105.4. IR (cm⁻¹): 3421 (O-H, strong broad), 1648 (C=O, strong stretch), 1444 (C=C, stretch band). HMRS calcd for C₉H₇BrNO₂ [(M+H)]: 239.96602, found: 239.96552.



2-Methyl-1H-indole-3-carboxylic acid (2l)

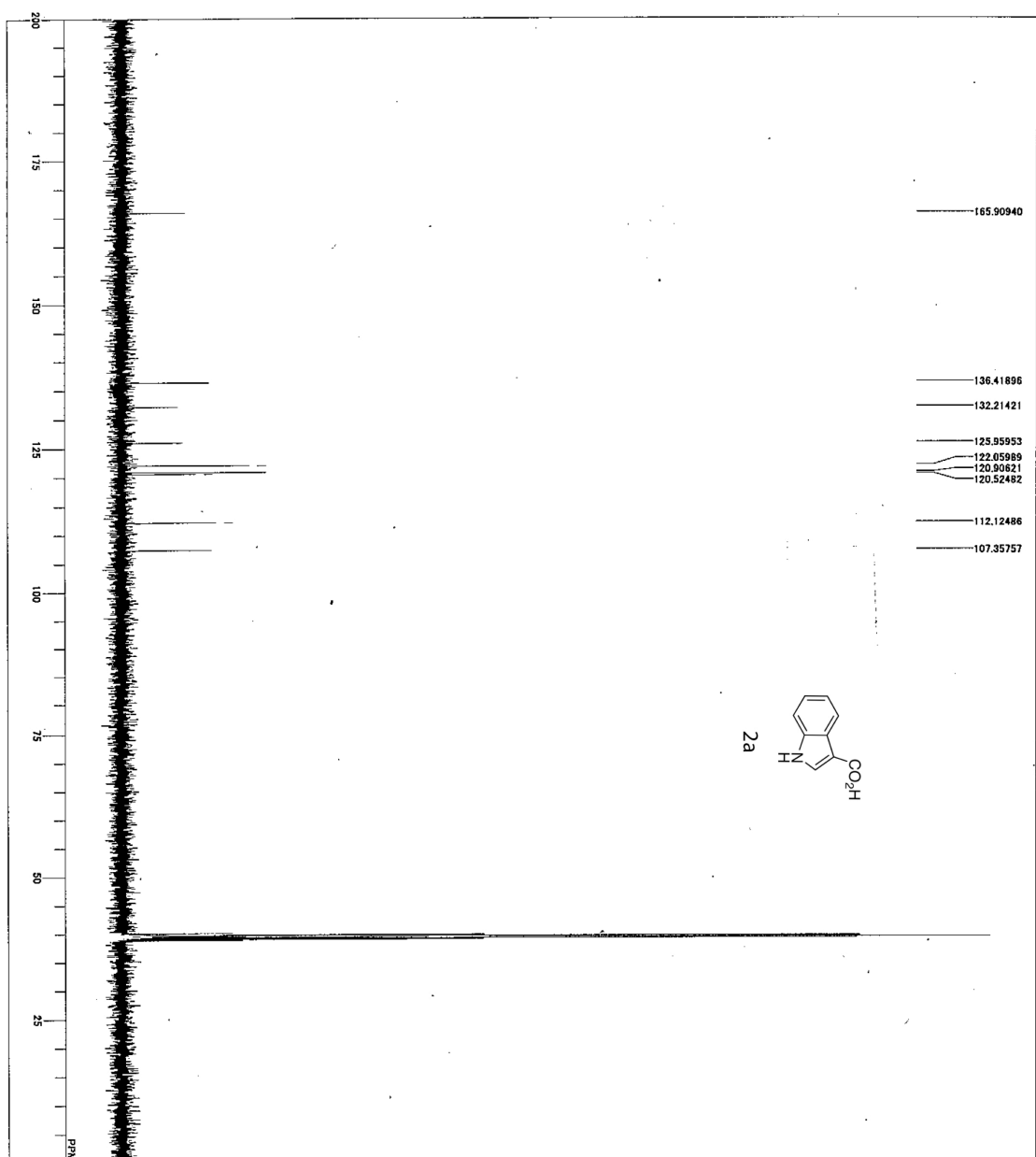
Following the same procedure described for the **2c** afforded the desired product **2l** in 80% yield as a white solid. ¹H NMR ((CD₃)₂CO, 400 MHz): δ 10.7 (bs, 1H), 8.08-8.06 (m, 1H), 7.36-7.34 (m, 1H), 7.12-7.10 (m, 2H), 2.73 (s, 3H); ¹³C NMR ((CD₃)₂CO, 100 MHz): δ 168.2, 145.6, 136.2, 129.0, 122.5, 121.9 (2C), 111.6, 104.4, 14.0. This is a known compound reported in the literature.¹⁴

2-Phenyl-indole-3-carboxylic acid (2m)

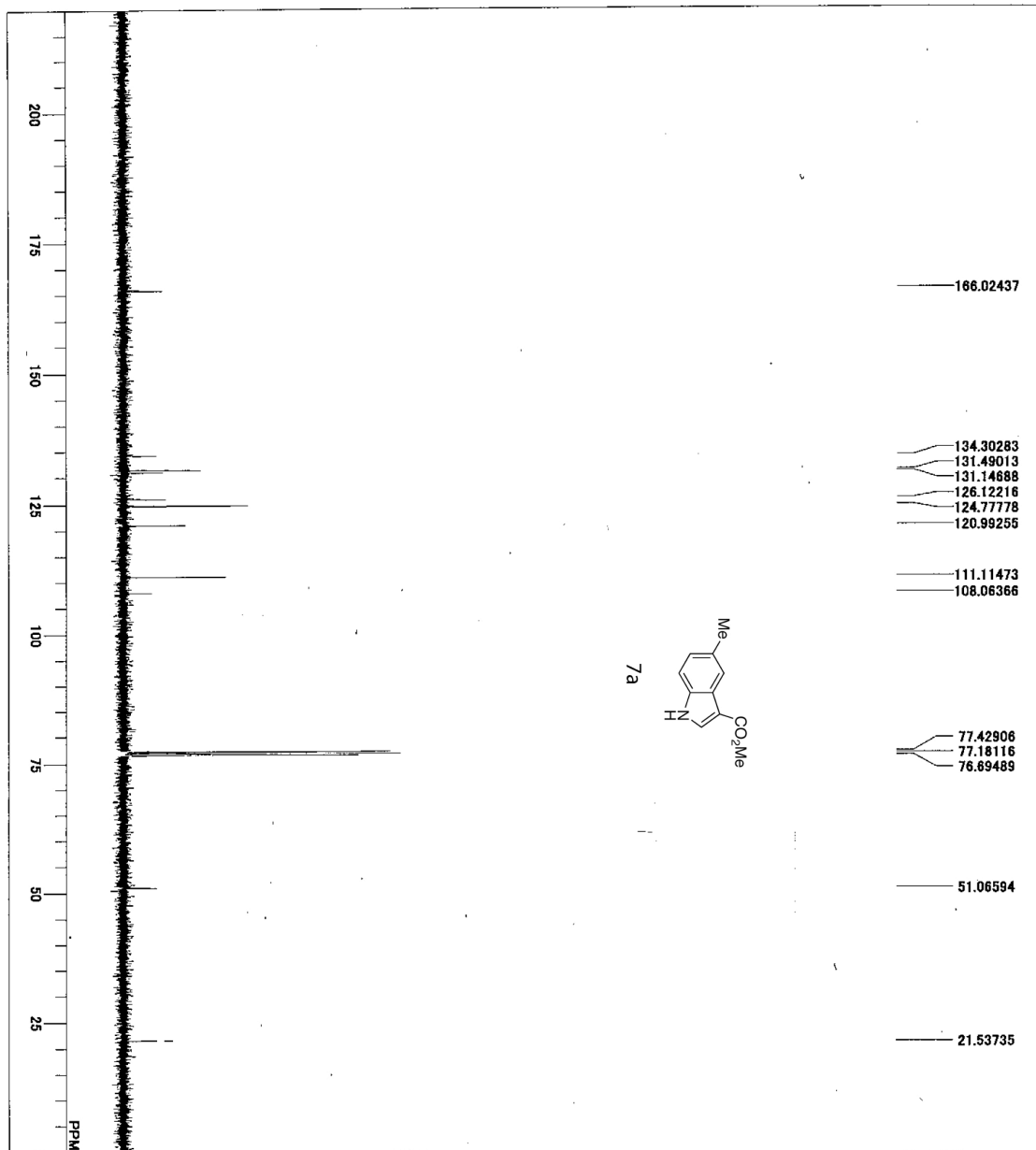


Following the same procedure described for the **2c** afforded the desired product **2m** in 31% yield as a yellow solid. ¹H NMR ((CD₃)₂CO, 400 MHz): δ 10.9 (bs, 1H), 8.22- 8.21 (1H, m), 7.74- 7.72 (2H, m), 7.47-7.39 (4H, m), 7.20-7.16 (2H, m). ¹³C NMR ((CD₃)₂CO, 100 MHz): δ 167.2, 145.8, 136.7, 133.3, 130.7, 129.6, 129.1, 128.7, 125.9, 123.5, 122.8, 122.3, 104.4, 99.5. This is a known compound reported in the literature.¹⁵

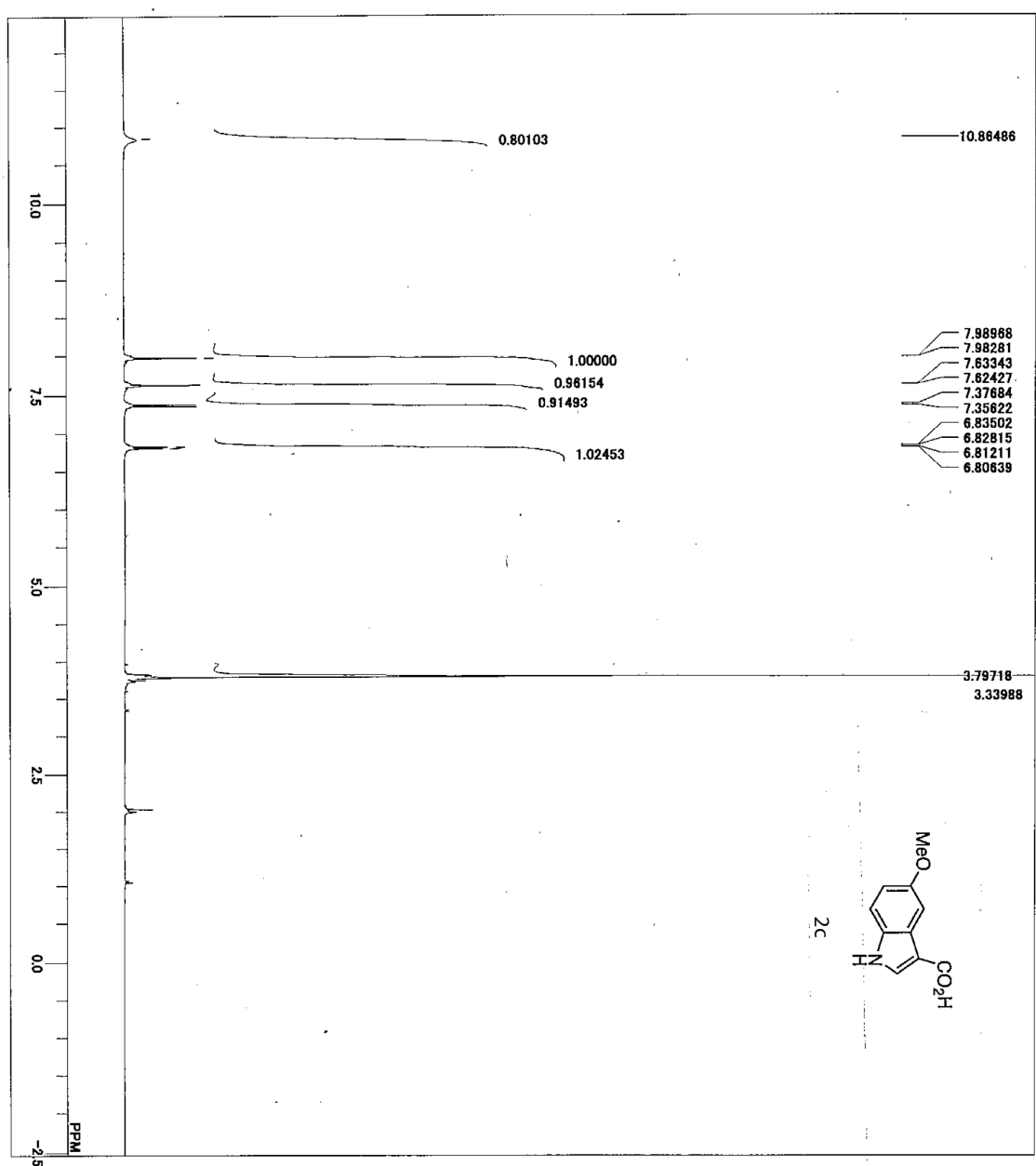
Part III: ^1H and ^{13}C NMR Spectra of 2a-m



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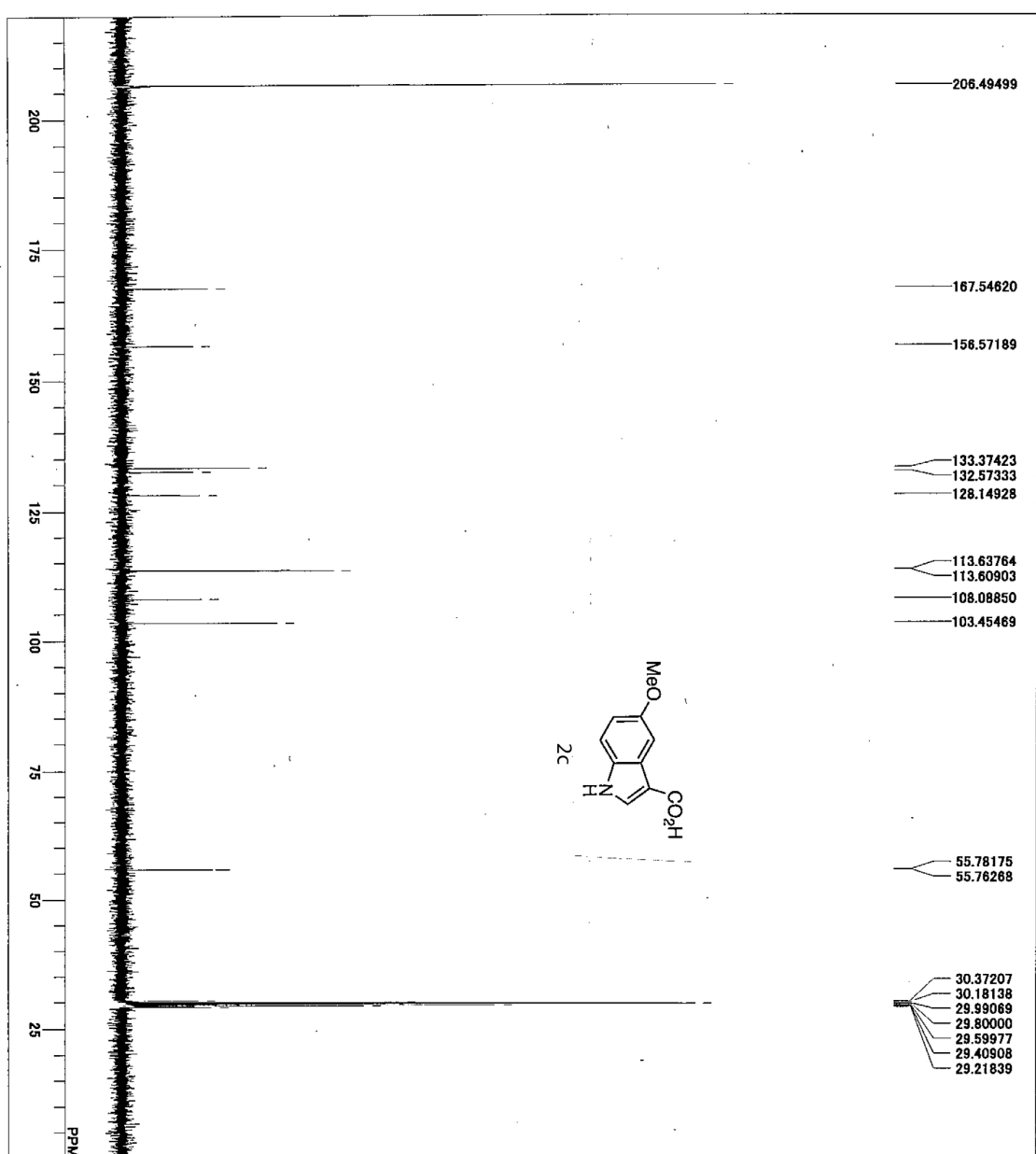


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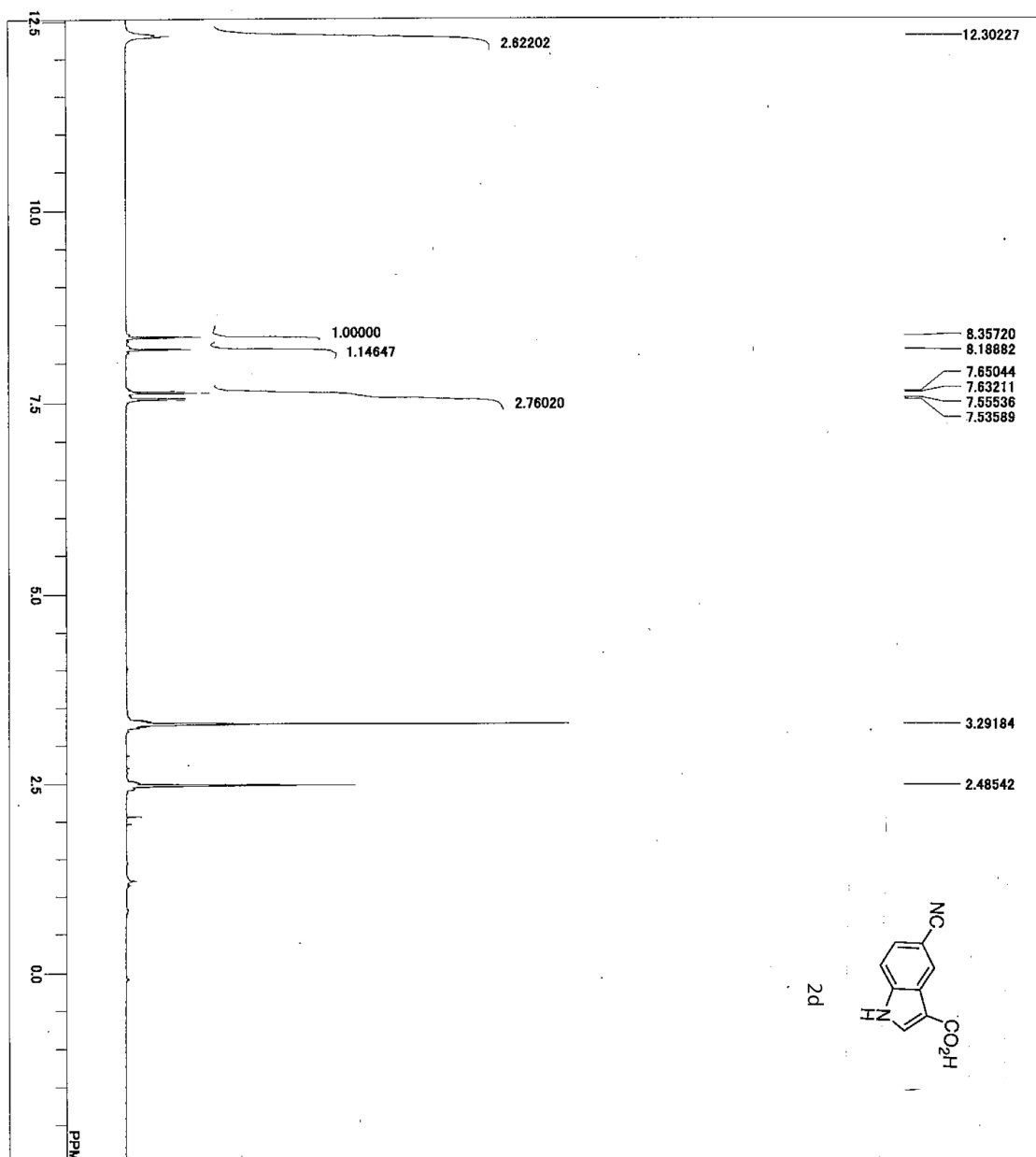
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 0.12 Hz
 32

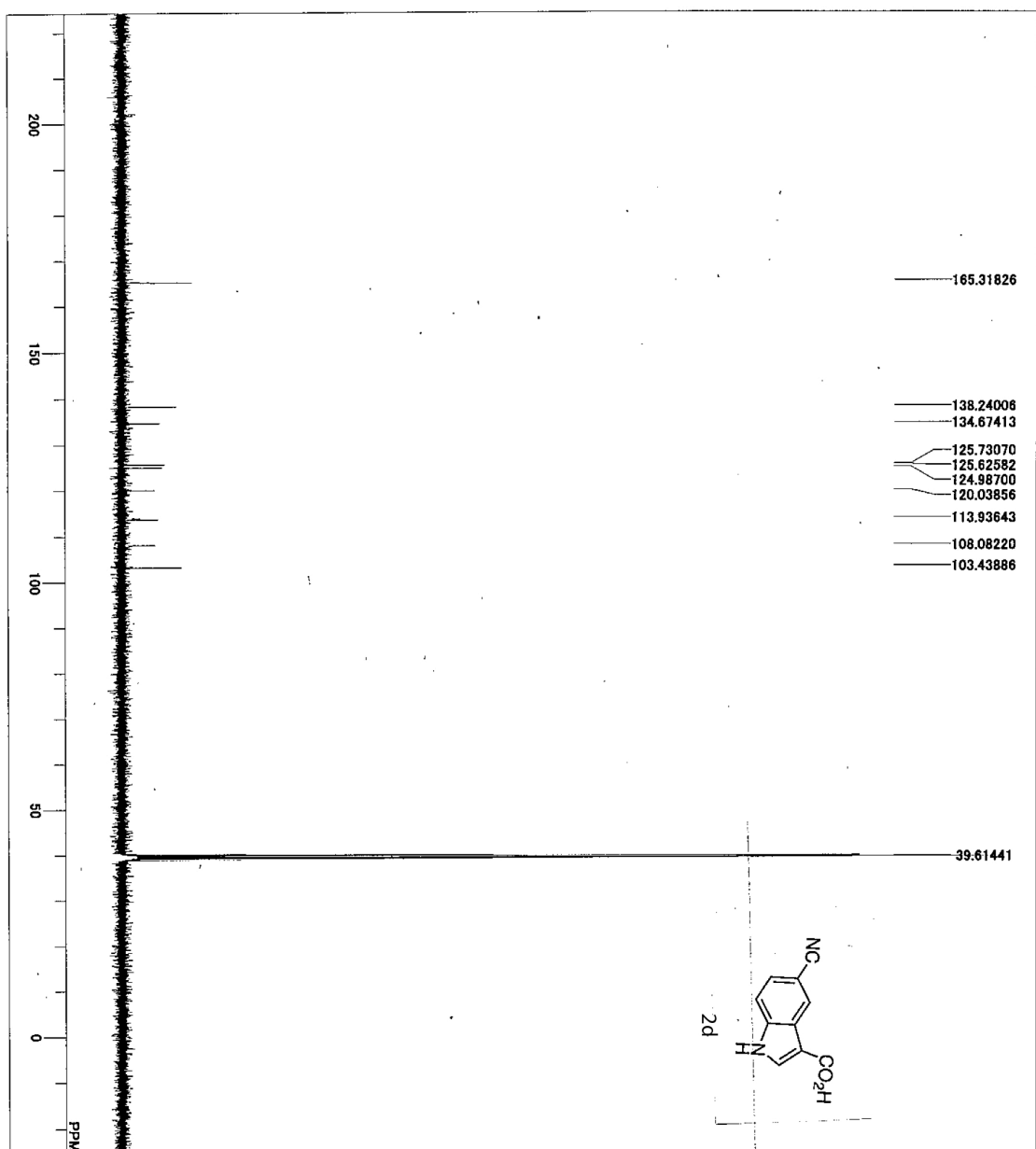


DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFREQ
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PWI
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

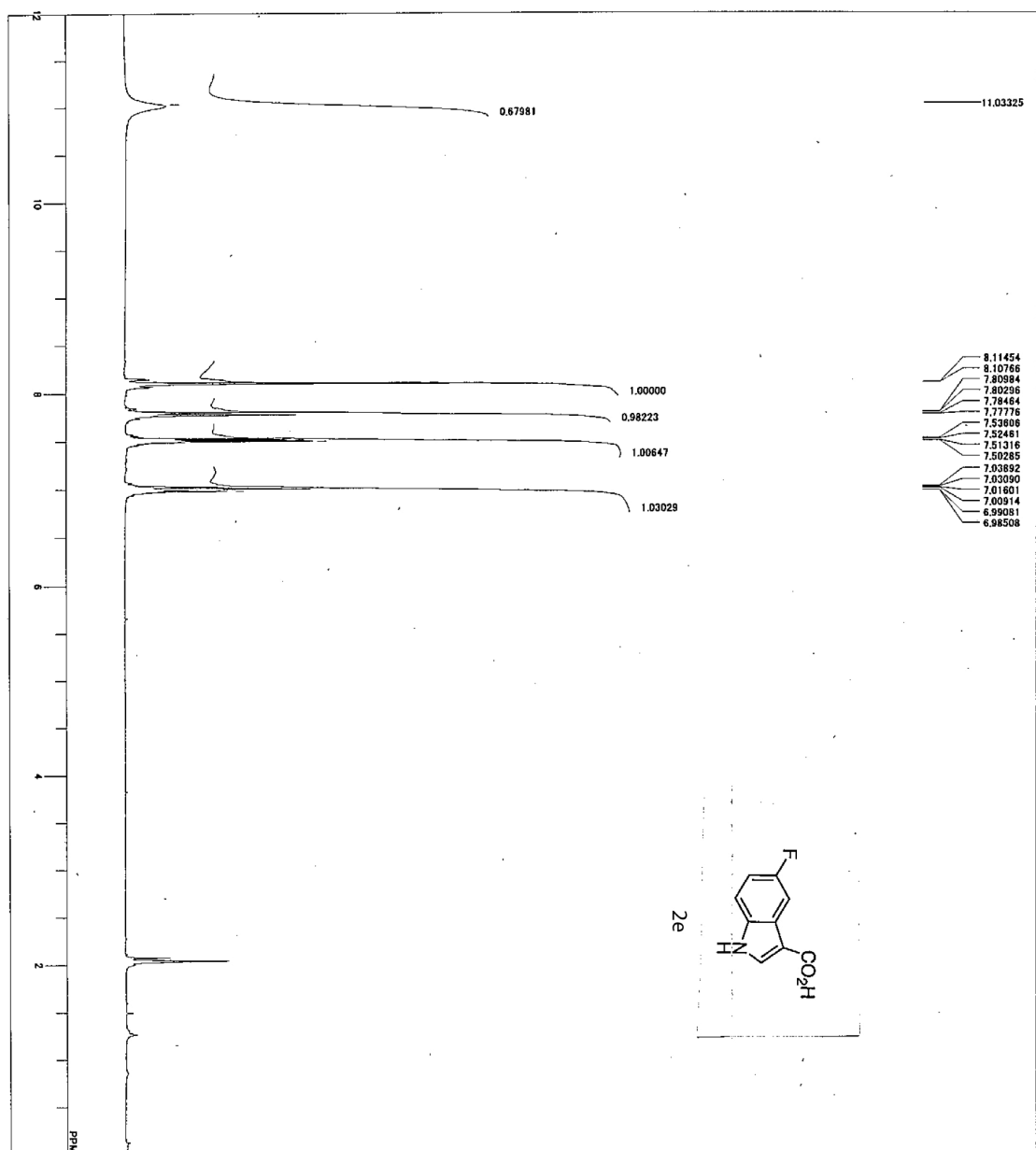
C:\Documents and Settings\delia\F5スクリーンショット\F5meth
01-08-2012 14:57:49
13C
single, pulse, dec
100.53 MHz
5.35 KHz
5.68 Hz
32768
31407.03 Hz
30
1.0433 sec
2.0000 sec
3.50 usec
409.3 c
ACETN
29.80 ppm
0.12 Hz
56



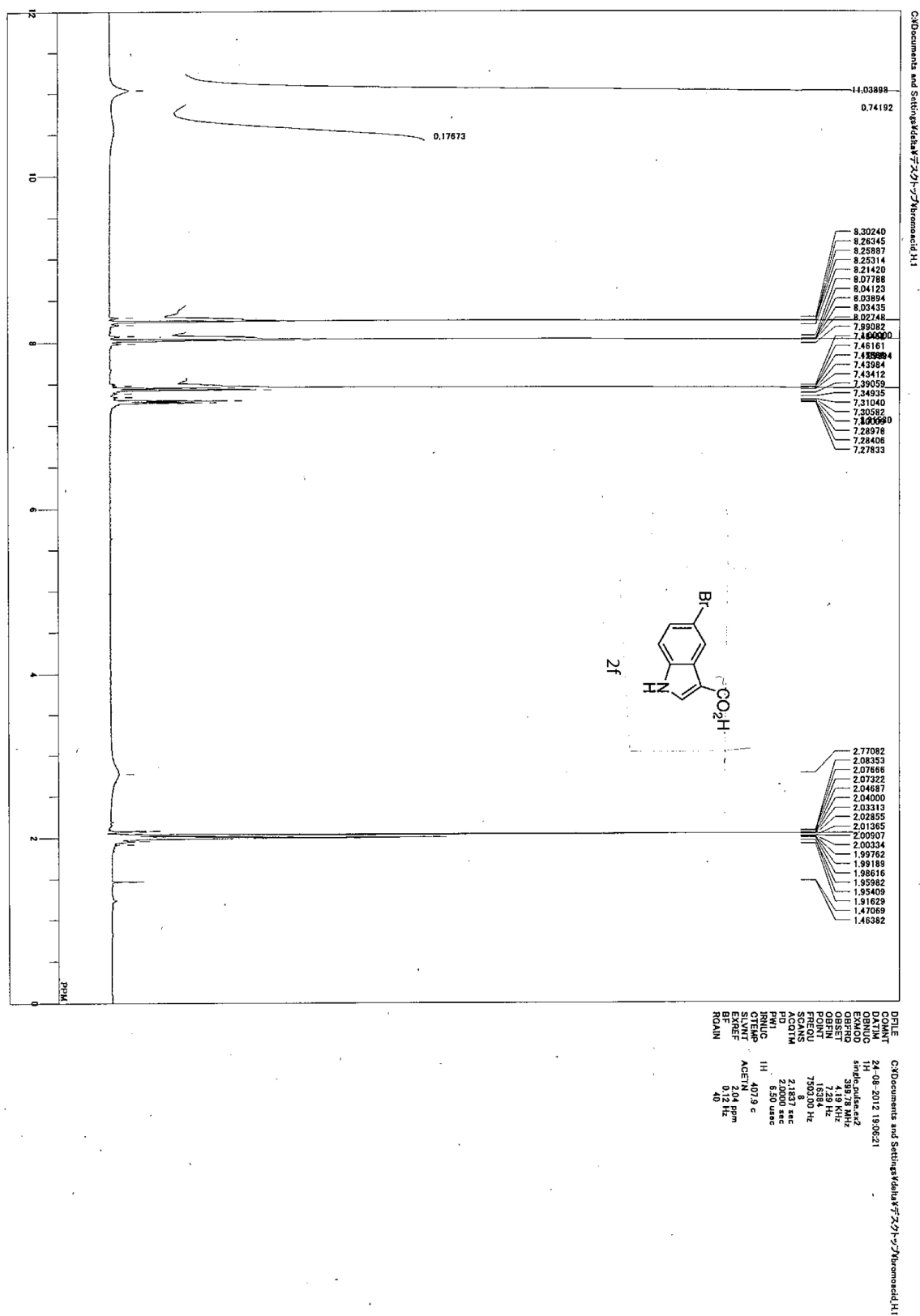
DFLE
 COMNT
 DATM 30-07-2012 19:15:22
 OBNUC 1H
 EXMOD single.pulse.ac2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 16384
 FREQU 7503.00 Hz
 SCANS 8
 ACQTM
 PD 2.1837 sec
 PW 2.0000 sec
 IRNUC 6.50 usec
 CTENP 1H
 SLVNT 408.5 c
 EXREF DMSO
 BF 2.49 ppm
 RGAIN 0.12 Hz
 38

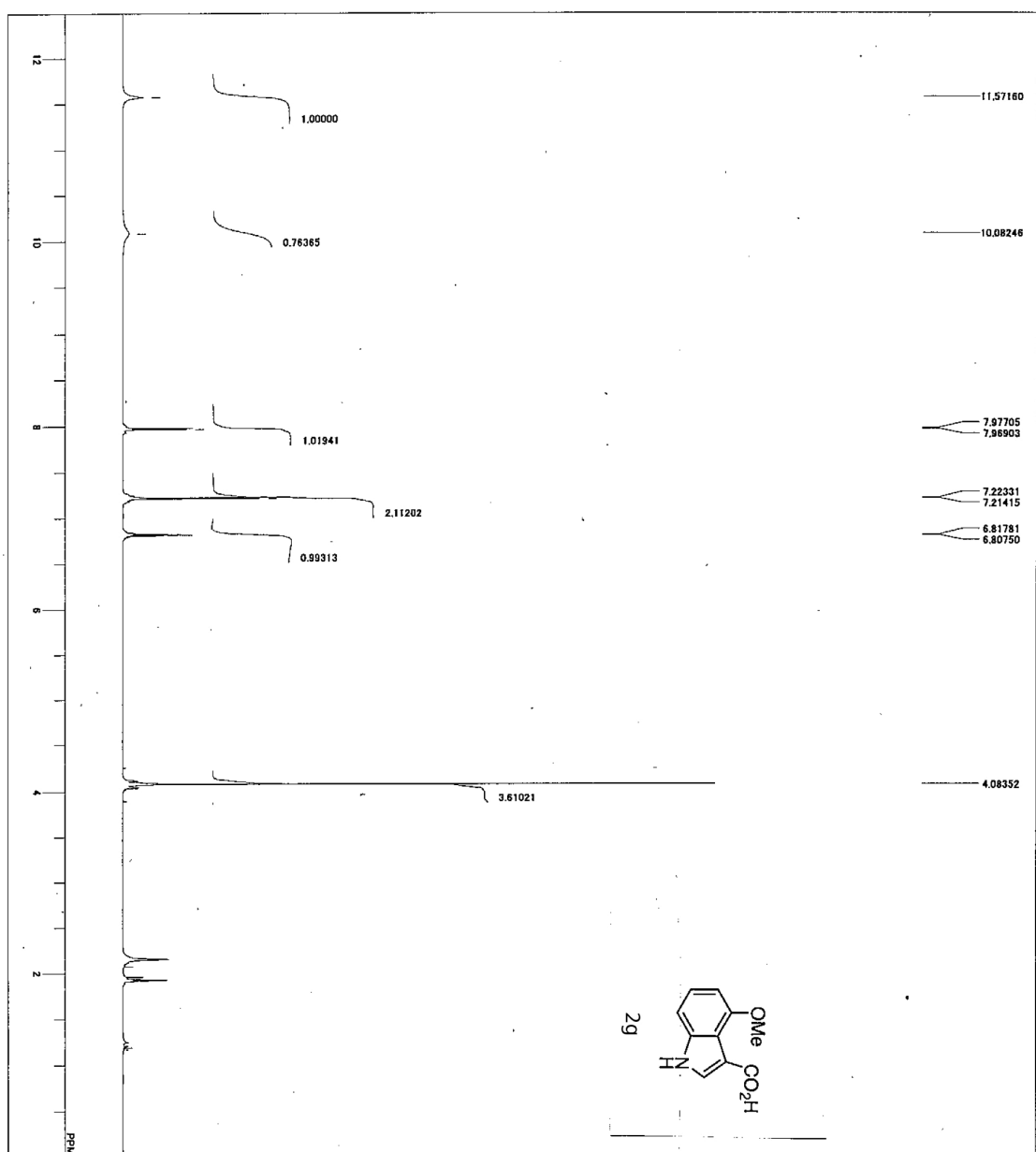


DFILE 31-07-2012 08:34:28
 COUNT 13C
 DATIM single pulse dec
 OBNUC 100.53 MHz
 EXMOD 5.35 KHz
 OBSFQ 5.86 Hz
 OBSFQ 32768
 POINT 31407.03 Hz
 FREQ 248
 SCANS 248
 ACOPT 1.0433 sec
 PD 2.0000 sec
 PW1 3.50 usec
 IRNUC 1H
 CTEMP 408.6 c
 SYNT DMSO
 EXREF 39.50 ppm
 BF 0.12 Hz
 RGAIN 60

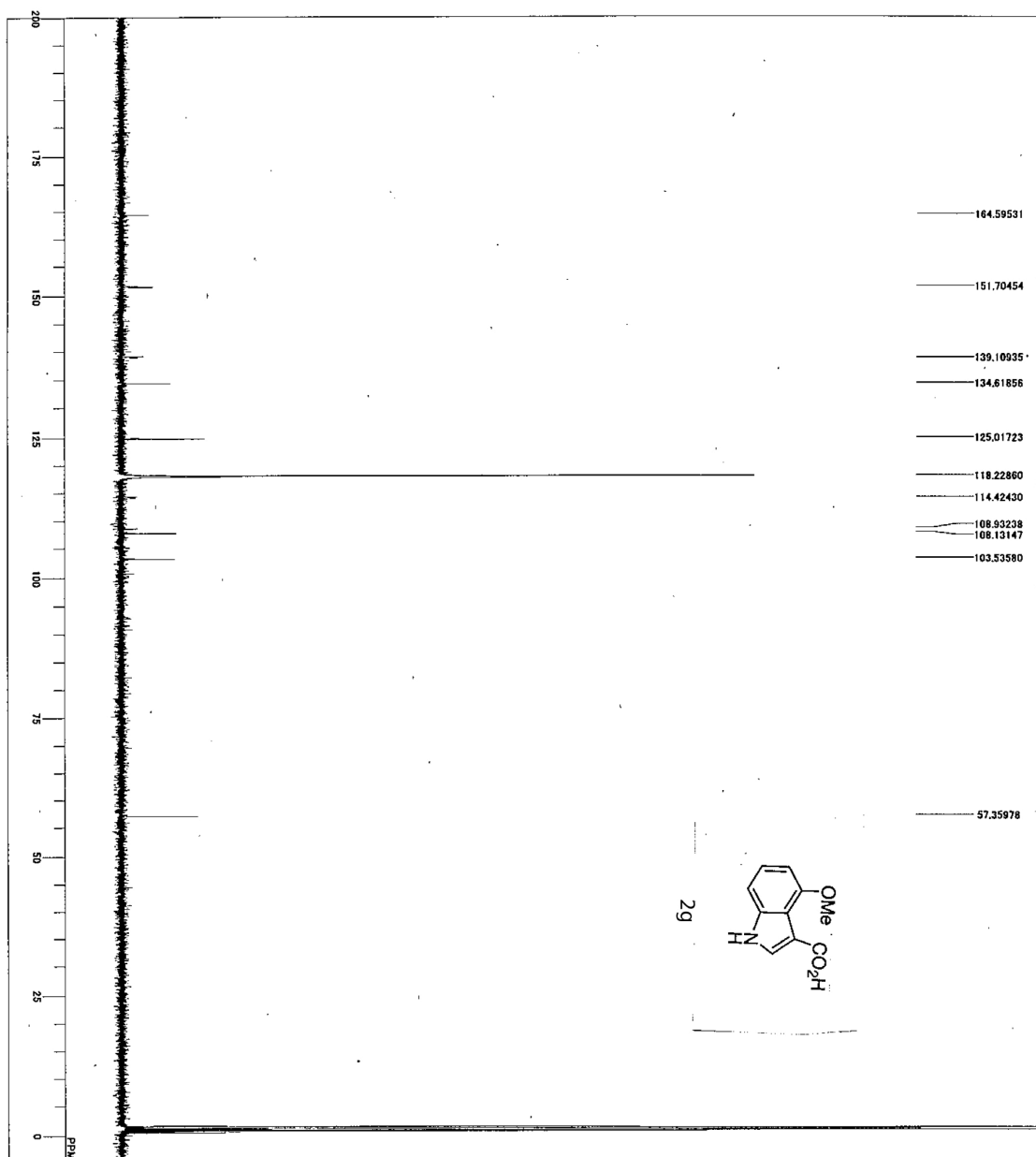


FILE C:\Documents and Settings\Kishiyama\My Documents\100s_H1
 COUNT 35
 ONNO 35-08-2012 13:00:45
 NAME single pulse
 EPROG 399.78 MHz
 OBSFQ 400.13 MHz
 OBSFN 7.29 Hz
 POINT 16384
 PULPROG zgpg30
 SCANS 5
 ACQTM 7500.00 Hz
 PD 2.1837 sec
 PDI 2.0000 sec
 INUG 6.30 usec
 STW 1H
 CTEMP 409.2 c
 SLVST ACETN
 SLEST 125.4 ppm
 BR 0.12 Hz
 RGAIN 38

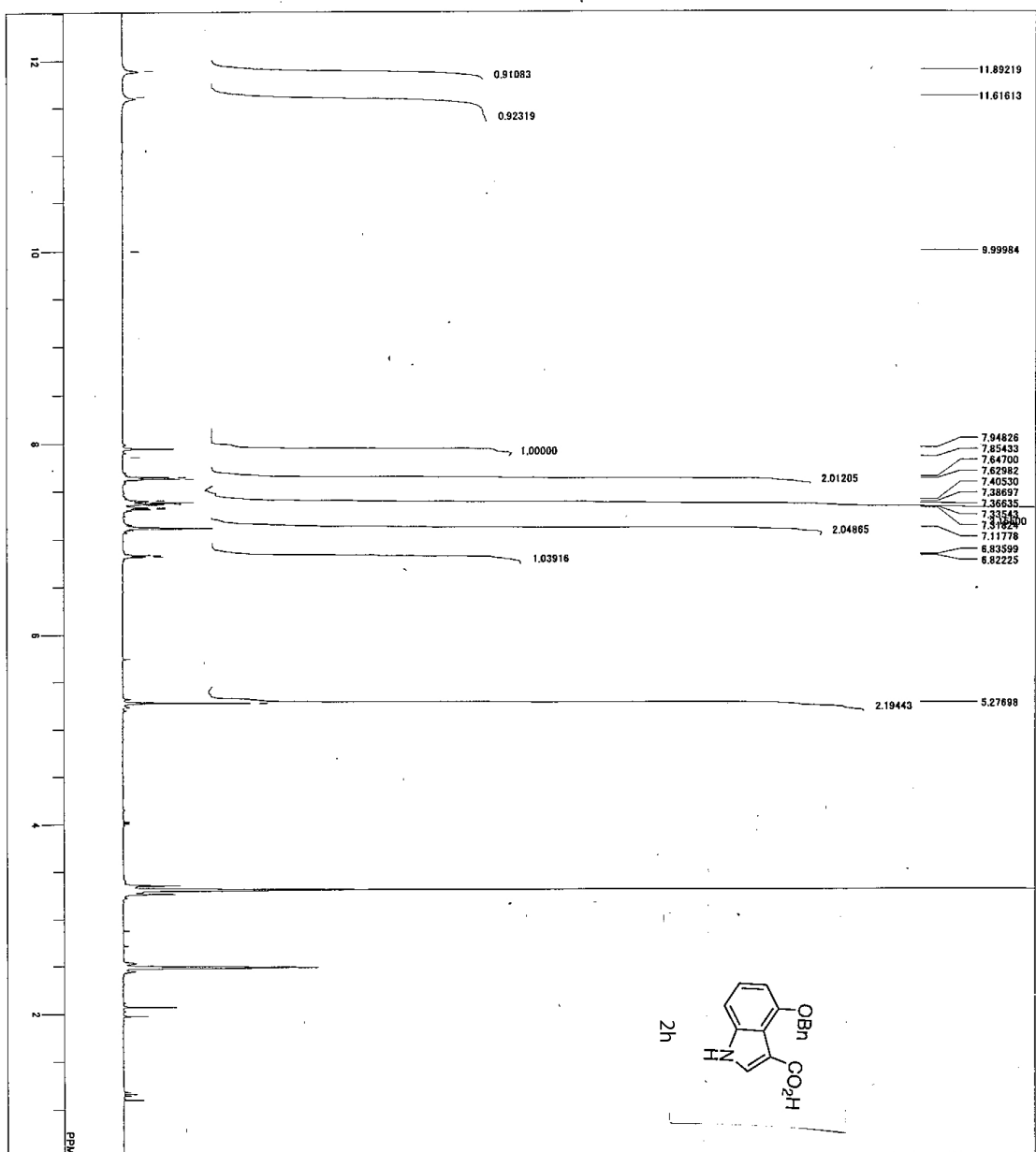




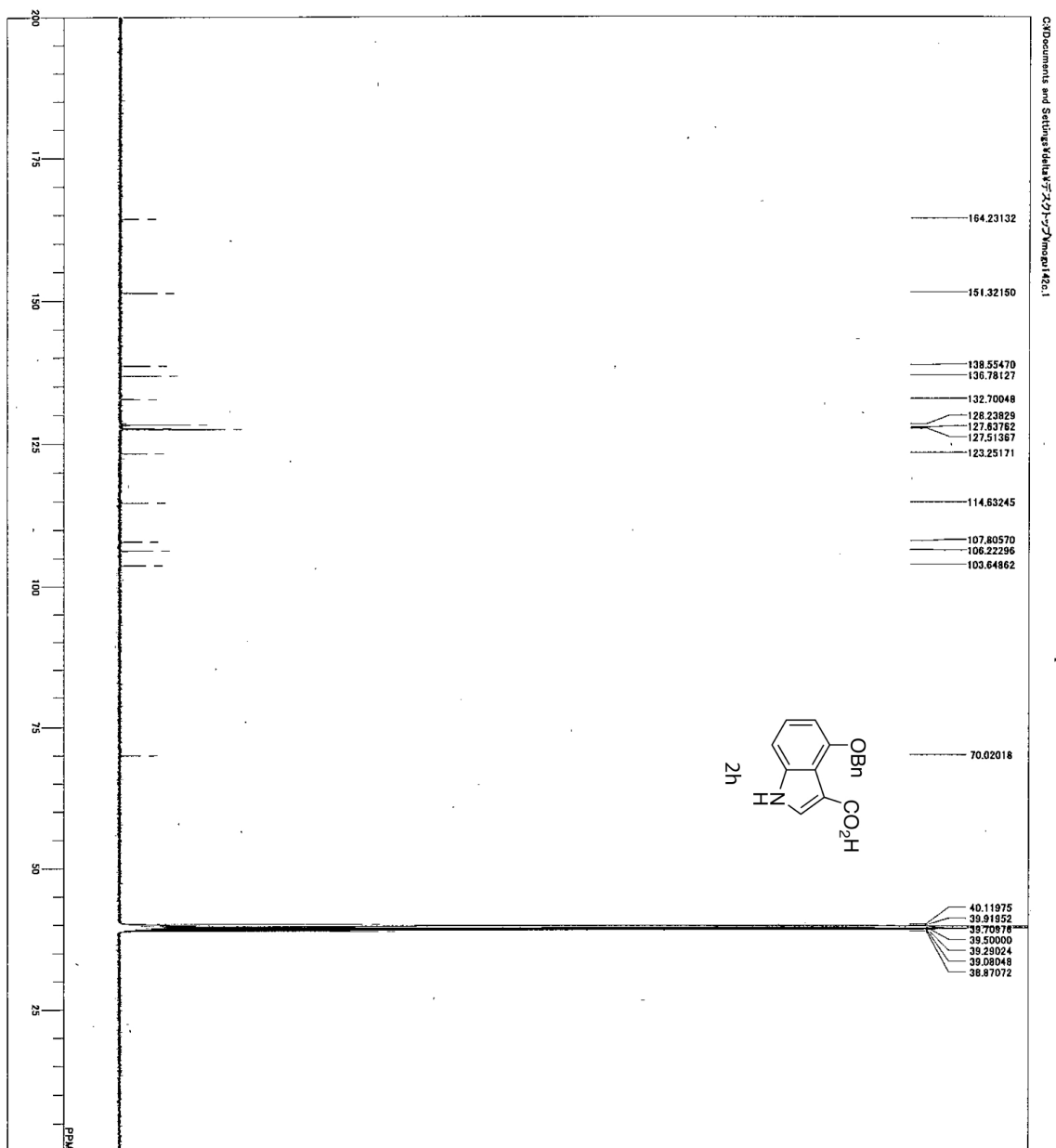
FILE C:\Documents and Settings\Kishiyu\デスクトップ\2-Methoxyindol-3-yl
 NAME 2g
 DATE 2012-08-24
 TIME 17:04:56
 INSTR single pulse as2
 EXPRO 399.78 MHz
 OBSFQ 399.78 MHz
 OBSN 7.28 Hz
 POINT 16384
 PREOU 7500.00 Hz
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PULP 6.50 usec
 PRNUC 408.1 c
 SLEW 408.1 c
 CTEMP 30.00 Hz
 CDON 0.12 Hz
 SLEW 0.12 Hz
 RF 38
 RAIN 38



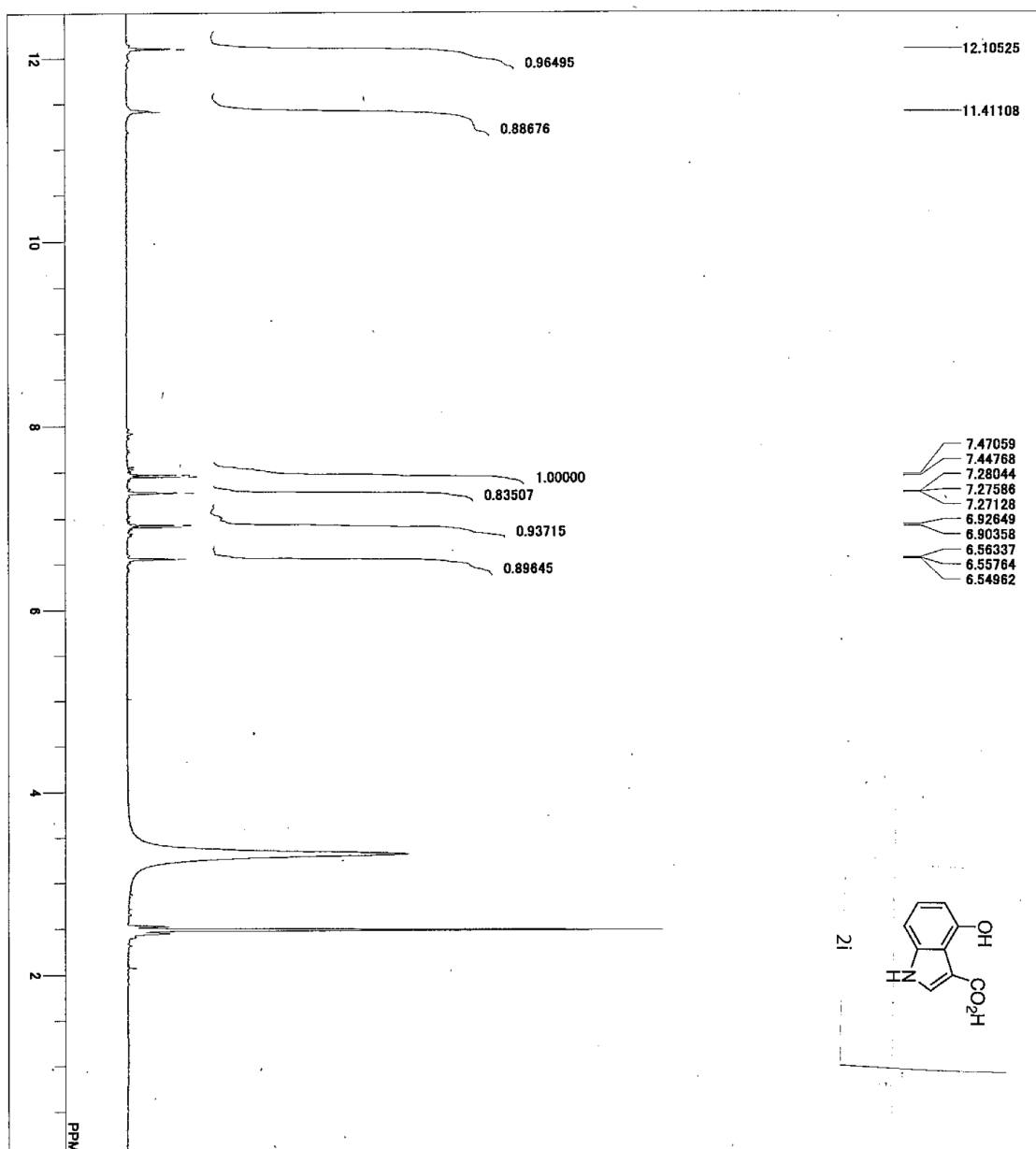
FILE C:\Documents and Settings\Kobayashi\My Documents\29g\29g.mxd
 NAME 29g
 DATE 2012-08-24
 TIME 18:22:28
 INSTR EPR
 PULPROG zgpg30
 PROCNO 1
 F2 100.625 MHz
 F1 125.761 MHz
 SFO 100.625 MHz
 AQ 1.00000000
 ACQ 1.00000000
 PD 1.00000000
 P1 1.00000000
 PR 1.00000000
 IRNUC 13C
 QTEMP 407.9 K
 SLOWT 1.00000000
 ST 1.00000000
 B1 1.00000000
 RGAIN 58



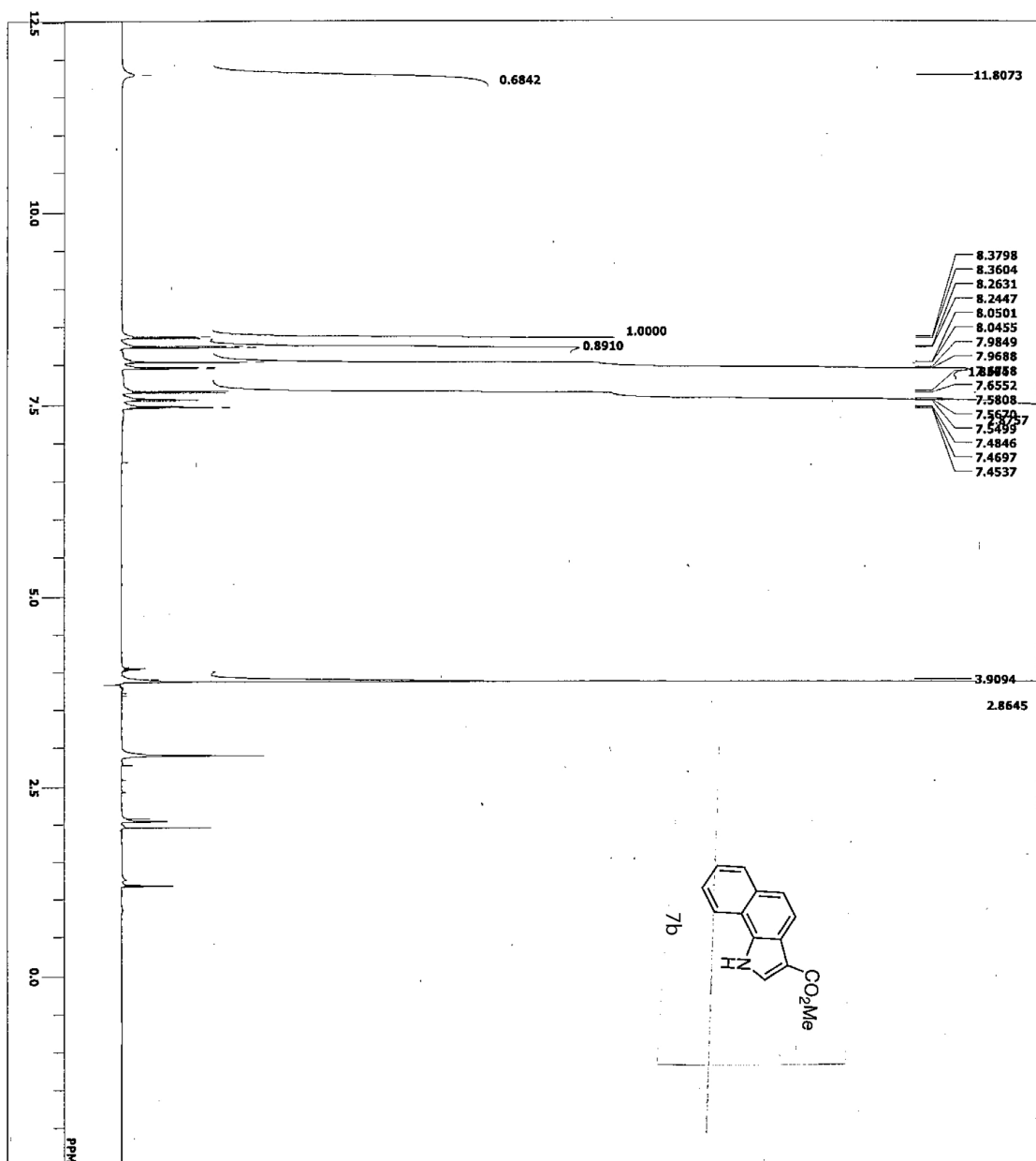
DFILE C:\Documents and Settings\Kakey\My Documents\18ap0118ap01
 COUNT 32
 DATE 23-08-2012 19:48:23
 NAME 18ap0118ap01
 EXMODE 18ap0118ap01
 OBERFO 399.78 MHz
 OBERFO 125.76 MHz
 OBERFO 7.28 Hz
 POINT 16384 Hz
 FREQU 7503.00 Hz
 ACQTIME 2.1837 sec
 PD 2.0800 sec
 PULPROG 630 usec
 INVERT 1H
 CTXPRG 407.5 e
 SLVNT DMSO
 SLSMNT 2.08 sec
 BF 612 Hz
 RGAIN 38



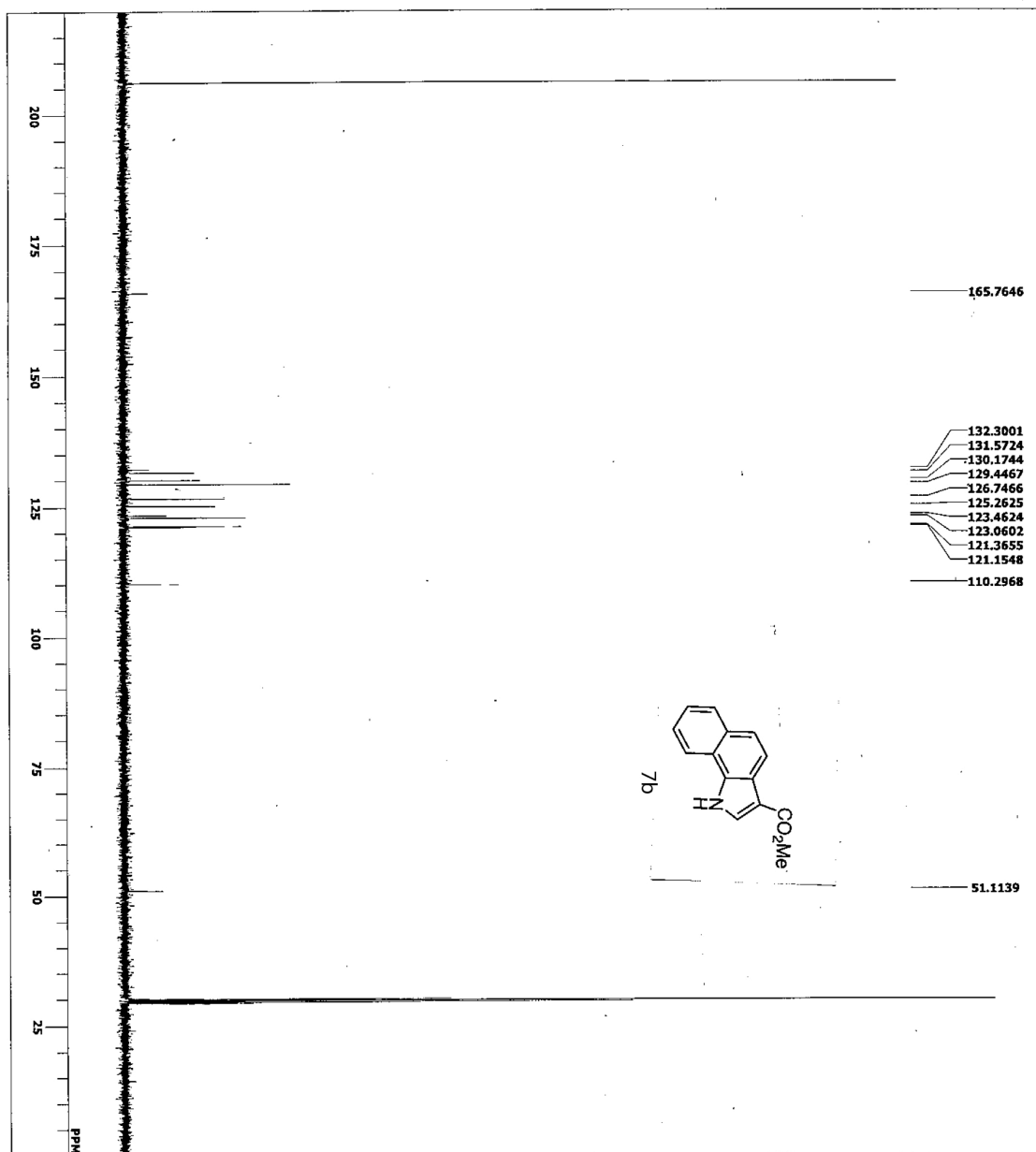
DFILE C:\Documents and Settings\Kaliya\F2h1-F2hmg0142c.1
 COUNT 32
 ORNUC 13C
 EXMRO simple_pulse_dac
 OBPRQ 100.53 MHz
 OBRF 125.754 MHz
 OBFN 5.88 Hz
 POINT 3140.00 Hz
 FREQD 3140.00 Hz
 SFO 141.00 MHz
 ACQTM 1.6433 sec
 PD 2.0000 sec
 PDI 3.50 usec
 IRNUC 1H
 CTENP 408.7 c
 SLVNT DMSO
 SLSOLV 300.00 MHz
 SFT 125.754 MHz
 BF 0.12 Hz
 RGAIN 56



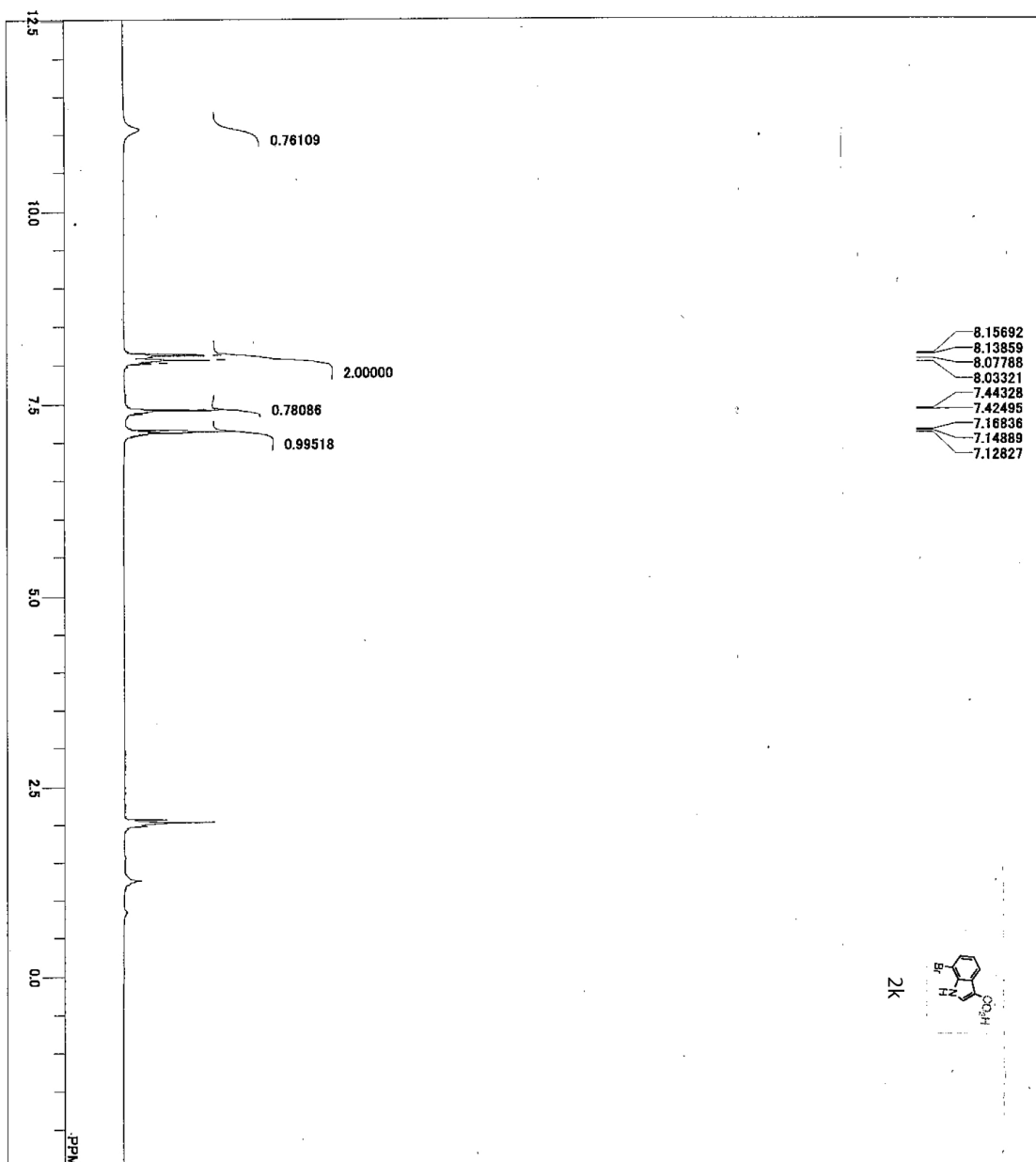
FILE C:\Documents and Settings\delav\デスクトップ\Xmogu1
 COUNT 02-08-2012 08:55:20
 DATUM 1H
 OBNUC single pulse ex2
 EXMOD 399.78 MHz
 OBSRO 4.19 KHz
 OBSRT 7.29 Hz
 POINT 16384
 FREQU 7503.00 Hz
 SCANS 8
 ACQTM
 PD 2.1837 sec
 PW 2.0000 sec
 IRNUC 6.50 usec
 CTMP 1H
 SLVNT 403.2 c
 EXREF DMSO
 BF 2.49 ppm
 RGAIN 0.12 Hz
 40



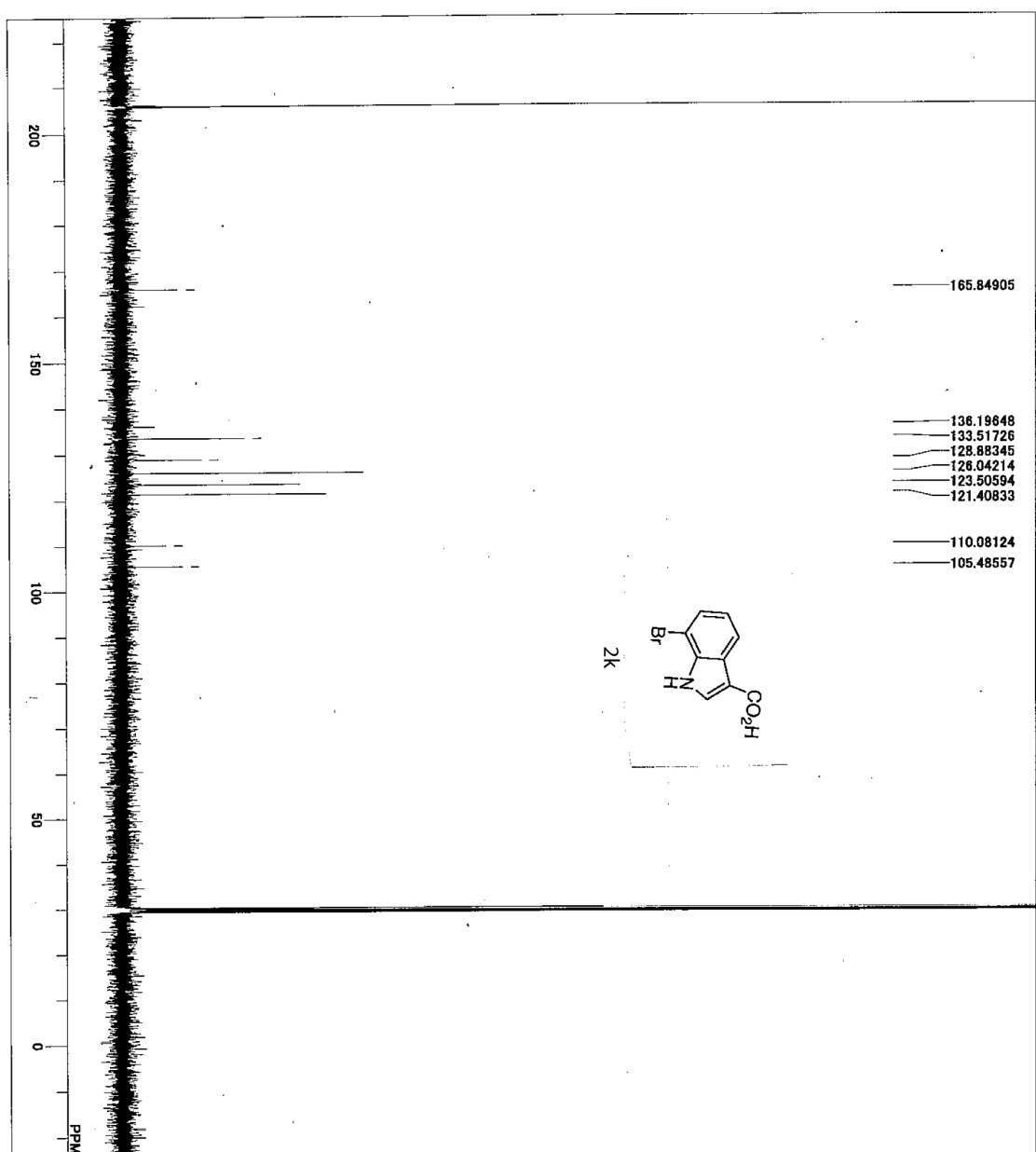
D:\Documents and Settings\Kobayashilab\Desktop\imgu2
 DFILE
 COUNT 05-08-2012 10:23:57
 DATIN 1H
 OBNUC 1H NMR.ex2
 EXMOD 495.13 MHz
 OBFREQ 4.38 kHz
 OBSET 9.64 Hz
 OBEIN 16384
 POINT 9286.78 Hz
 FREQU 8
 SCANS 1.7642 sec
 ACQTM 5.0000 sec
 PD 3.65 usec
 PUL 1H
 INTRUC 30.9 c
 CTEMP ACETN
 SLVT 2.04 ppm
 EXMT 0.12 Hz
 EXNER 34
 RGAIN



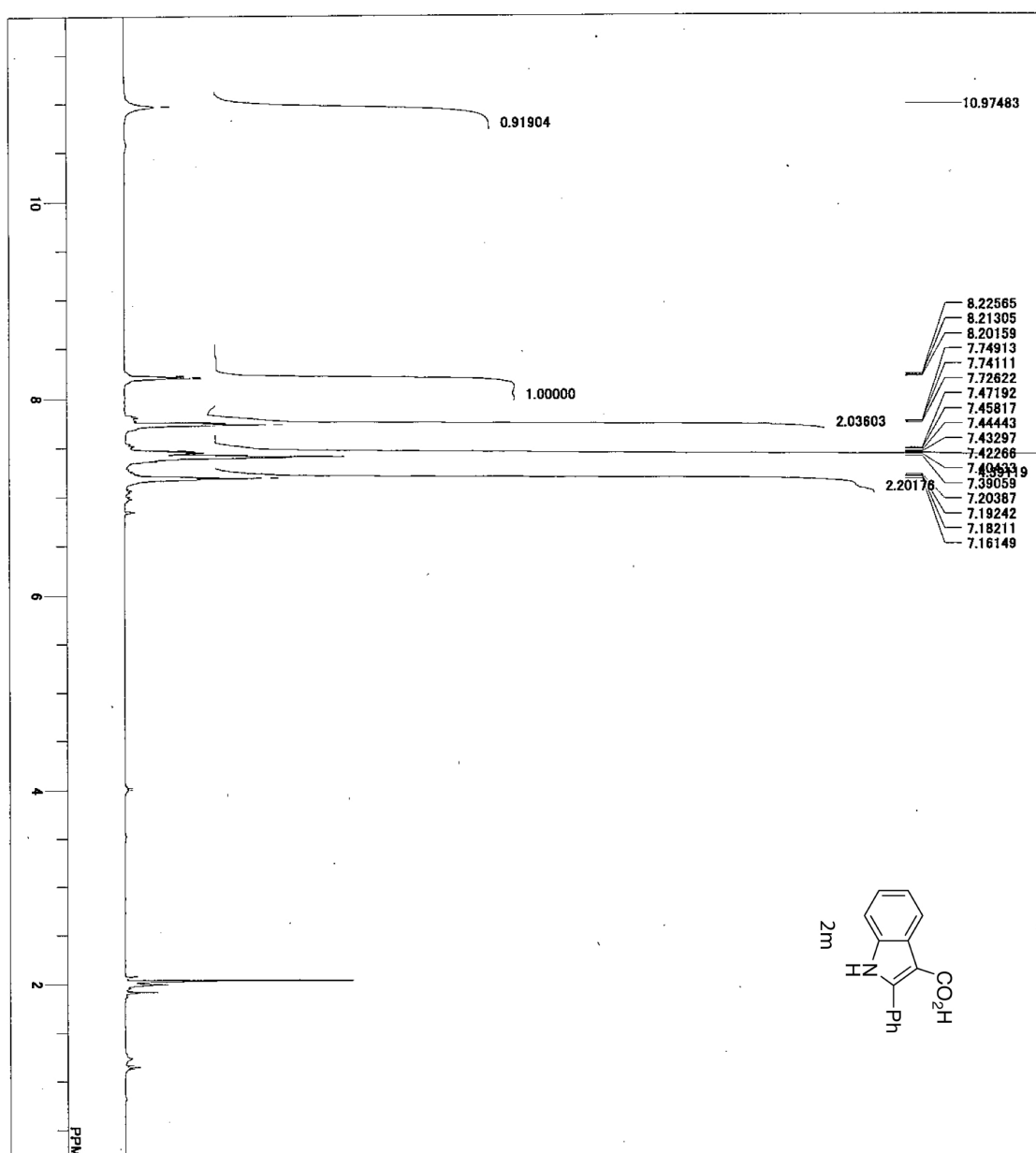
D:\Documents and Settings\Kobayashi\lab\Desktop\imgu12
 FILE
 COUNT 05-08-2012 10:28:56
 DATE 13C
 OBNUC 13C NMR-EX2
 EXMOD 124.51 MHz
 OBFREQ 3.45 kHz
 OBFET 6.00 Hz
 OBFIN 32768
 POINT 39062.50 Hz
 FREOU 84
 SCANS
 ACQTM 0.8389 sec
 PD 2.0000 sec
 PUL 3.42 usec
 INPUC 1H
 CTEMP 31.1 c
 SUMP
 SUMP 20.80 ppm
 EXNER 0.12 Hz
 RGAIN 58



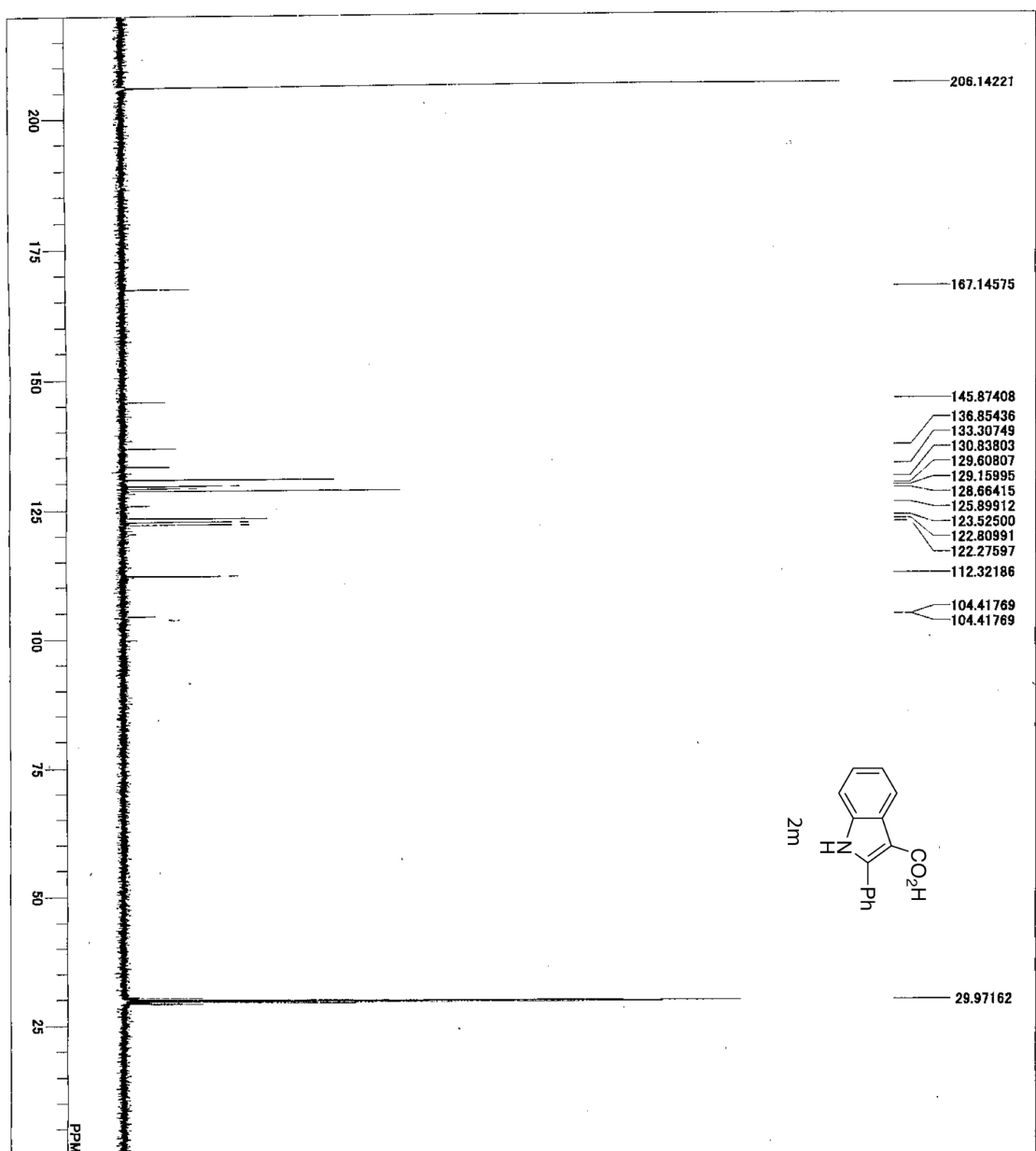
DFILE C:\Documents and Settings\delia\Fractions\Xmogu1
 COUNT 10-08-2012 14:16:44
 DATIM 1H
 OBNUC single, pulse ex2
 EXMOD 399.76 MHz
 OBSFQ 4.19 KHz
 OBSSET 7.29 Hz
 OBSFN 16384
 POINT 7503.00 Hz
 FREQU 8
 SCANS 2.1837 sec
 ACQTM 2.0000 sec
 PD 6.50 usec
 PWT 1H
 IRNUC 408.2 c
 CTEMP ACETN
 SLVNT 204 ppm
 EXREF 0.12 Hz
 RGAIN 38



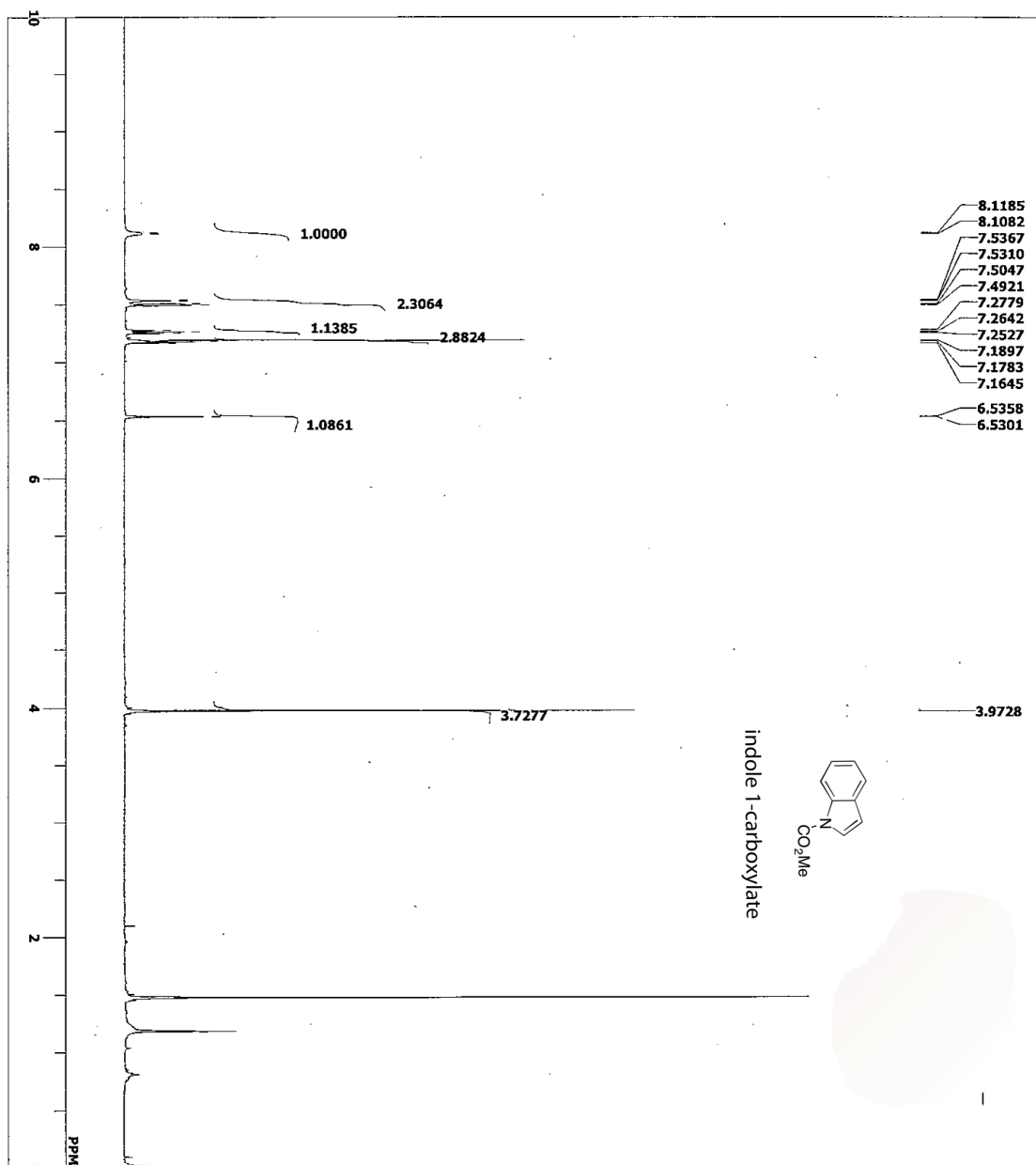
DFILE
 COUNT 10-08-2012 18:38:13
 DATUM 13C
 OBNUC single pulse dec
 EXMOD 100.53 MHz
 OBFREQ 5.35 KHz
 OBSSET 5.86 Hz
 OBRFN 32768
 POINT 31407.03 Hz
 FREOU 353
 SCANS
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.50 usec
 IRNUC 1H
 CTEMP 407.8 c
 SLVNT ACETN
 EXREF 29.80 ppm
 BF 0.12 Hz
 RGAIN 56



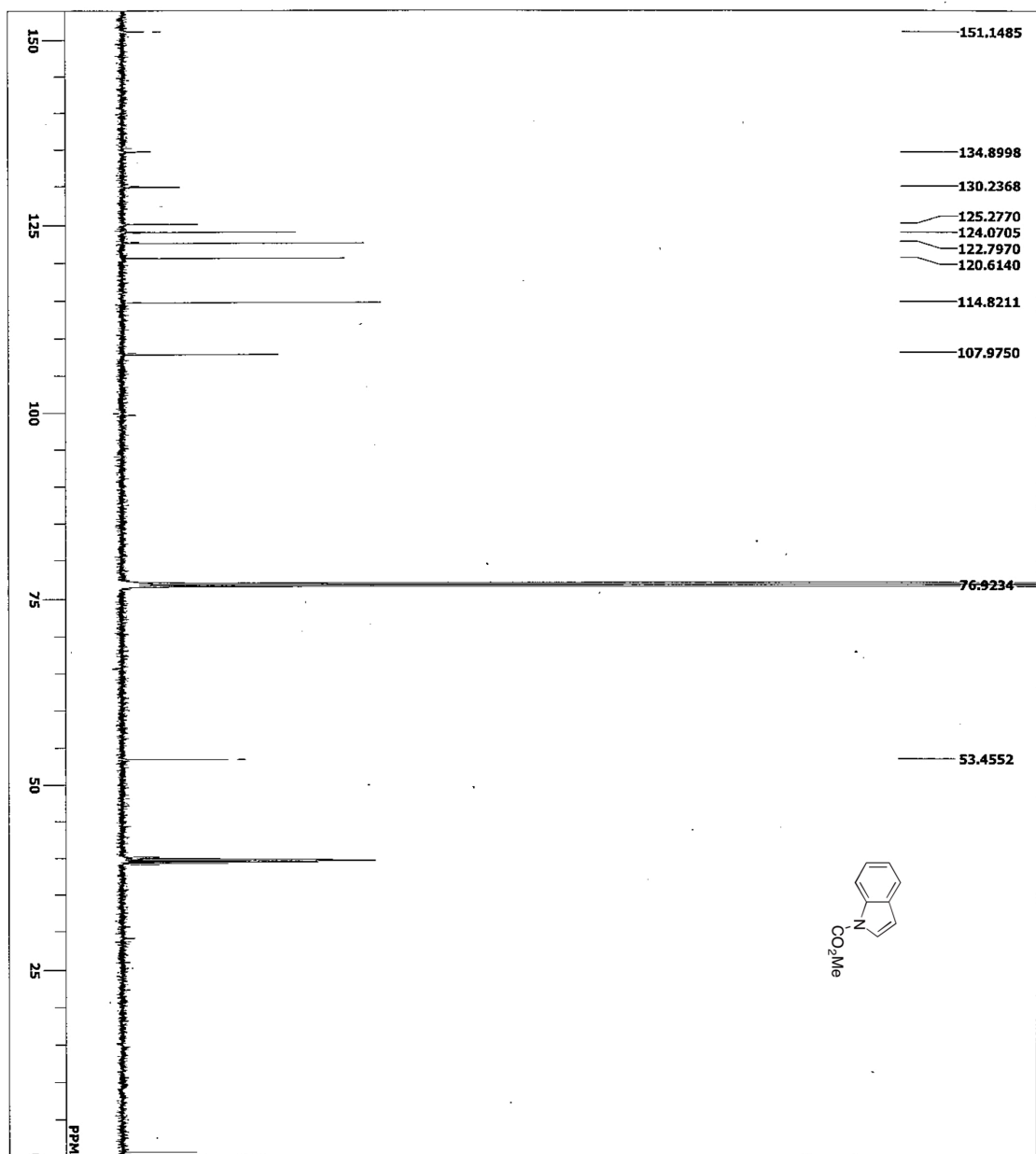
FILE C:\Documents and Settings\delav\デスクトップ\Xmogu\
 COUNT 07-08-2012 21:58:25
 DATUM 1H
 OBNUC single-pulse ex2
 EXMUD 399.78 MHz
 OBFREQ 4.19 KHz
 OBSET 7.29 Hz
 POINT 16384
 FREQ 7503.00 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PWT 6.50 usec
 IRNUC 1H
 CTMPC 408.9 c
 SLYNT ACETN
 EXREF 2.04 ppm
 BF 0.12 Hz
 RGAIN 34



FILE C:\Documents and Settings\delany\デスクトップ\Xmogu1
 COMMENT 07-08-2012 22:08:28
 DATE 13C
 EXPT single-pulse, dac
 EXMOD 100.63 MHz
 OBSFQ 338.142 MHz
 OBSRT 3.58 Hz
 PBRN 327.6 Hz
 PRCAL 31407.03 Hz
 SCANS 1420
 ACQTM 1.063 sec
 PULP 2.000 sec
 PM1 3.50 usec
 PRNUC 1H 408.9 c
 CTEMP ACETN
 SLEWT 29.80 ppm
 EXREF 0.12 Hz
 BT 56
 RGAIN



FILE D:\Documents and Settings\Kobayashilab\Desktop\
 CONNT single_pulse
 DATIM 09-09-2012 19:59:55
 OBNUC 1H
 EKHOD single_pulse.ex2
 OBFRO 600.17 MHz
 OBFRO 5.30 KHz
 OBFRO 5.47 Hz
 POINT 16384
 FREQU 11261.26 Hz
 SCANS 8
 ACQTM 1.4549 sec
 PD 2.0000 sec
 PW1 6.50 usec
 TRNUC 1H
 CTMP 27.5 c
 SLVT CDCl₃
 EXREF 0.00 ppm
 BF 0.52 Hz
 RGAIN 44



FILE D:\Documents and Settings\Kobayashilab\Desktop\
 COMNT 11-09-2012 07:33:08
 DATIM 13C
 DBNUC 13C
 EXMOD 13C NMR,ex2
 OBFRQ 124.51 MHz
 OBSET 3.45 KHz
 OFEIN 6.00 Hz
 POINT 32768
 FREOU 39062.50 Hz
 SCANS 11981
 ACQTM 0.8389 sec
 PD 2.0000 sec
 PW1 3.42 usec
 IRNUC 1H
 CTMP 29.6 c
 SLYNT CDCl3
 EXREF 77.00 ppm
 B1 0.52 Hz
 RGAIN 50

Part IV: References

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