Electronic Supplementary Material (ESI) for Chemical Communications

Unexpected dehomologation of primary alcohols to one-carbon shorter carboxylic acids using *o*-iodoxybenzoic acid (IBX)

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1. General Information

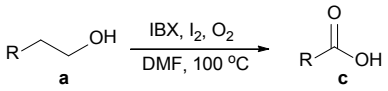
Reagents were used as received from commercial suppliers unless otherwise indicated. THF, toluene, MeCN were purchased as dehydrated solvent. All solvents for work-up procedure were used as received.

Column chromatography was performed with silica gel 60N (Kanto Chemical). Analytical thin-layer chromatography (TLC) was performed with glass TLC plates (Merck 0.25 mm coated silica gel $60F_{254}$ plates). Visualization was accomplished with UV light, or phosphomolybdic acid and subsequent heating.

Melting points were uncorrected and measured with a Yanako MP-J3 melting point apparatus. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Gas chromatography – mass spectrometric (GC-MS) analysis was carried out on a SHIMADZU GCMS-QP5050 spectrometer. Proton nuclear magnetic resonance (^{1}H-NMR) data were acquired at 600 MHz on JEOL ECA600. Carbon nuclear magnetic resonance (^{13}C-NMR) data were acquired at 150 MHz on JEOL ECA600. Data for ^{1}H NMR spectra are reported in the following format: chemical shift (multiplicity, coupling constant, number of atoms, position of atoms). Chemical shifts are indicated in parts per million (ppm) downfield from tetramethylsilane (TMS, $\delta = 0.00$). Multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or combinations of those. Coupling constants (J) are in hertz. Mass spectra are electron ionization (EI) or fast atom bombardment (FAB). EIMS and FABMS were recorded on a JEOL JMS-700 spectrometer. The matrix used in HRFABMS analysis was *m*-nitrobenzyl alcohol (NBA).

2. Experimental Procedures

General procedure for the dehomologation of primary alcohols**:**



A mixture of primary alcohol (**a**, 0.25 mmol), IBX (560 mg, 2.0 mmol), and I_2 (102 mg, 0.40 mmol) in DMF (3.6 mL) was heated at 100°C under the O_2 atmosphere. The reaction was monitored by GC-MS. After the reaction finished, the reacting mixture was cooled to room temperature. *n*-Nonanoic acid (43.7 μL, 0.25 mmol) was added as the internal standard, and the mixture was analyzed by GC-MS. The yield of the reaction was determined by calculating the ratio of the peak areas of product **c** and *n*-nonanoic acid in GC-MS spectrum, and comparison that with the calibration line measured using the authentic sample of product **c** and *n*-nonanoic acid.

Note:

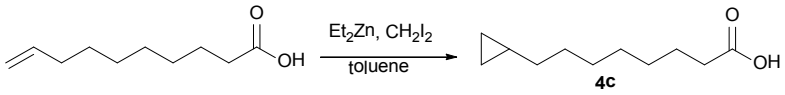
(1) IBX was prepared from *o*-iodobenzoic acid and Oxone® according to the literature procedure[1] and the purity was > 95% determined by ^{1}H-NMR in D_6-DMSO.

(2) DMF (JIS special grade) was purchased from Wako Pure Chemical Industries, Ltd., and used as received. The dehydrated DMF has also been tested, and gave almost the same result of yield and selectivity for the reaction.

(3) Alcohols **2a**, **3a**, **5a-14a** and authentic carboxylic acids of **2c**, **3c**, **5c-14c** were purchased from commercial suppliers and used as received. Alcohols **4a**,[2] **15a**,[3] and carboxylic acid **15c**[4] were prepared according to the literature procedure. Carboxylic acid **4c** and ^{13}C-labelled alcohol **5a** was synthesized as following.

[1] M. Frigerio, M. Santagostino and S. Sputore, *J. Org. Chem.*, 1999, **64**, 4537-4538.
[2] C. A. Henrick and G. B. Staal, US 3948961, April 6, 1976.
[3] T. D. Beeson, A. Mastracchio, J. -B. Hong, K. Ashton, and D. W. C. MacMillan, *Science*, 2007, **316**, 582-585.
[4] K. Wada, T. Chiba, Y. Takei, H..Ishihara, H. Hayashi and K. Onozaki, *J. Carbohydr. Chem.*, 1994, **13**, 941-965.

Synthesis of 8-cyclopropyloctanoic acid (**4c**):



4c

To a mixture of Et_2Zn solution in toluene (1.1 M, 8.7 mL, 9.6 mmol) and 9-decenoic acid (0.93 mL, 5.0 mmol) was added dropwise CH_2I_2 (0.60 mL, 7.5 mmol) at room temperature under Ar atmosphere. The reaction mixture was stirred at room temperature for 19 hours. More CH_2I_2 (0.60 mL, 7.5 mmol) and Et_2Zn solution in toluene (1.1 M, 4.5 mL, 5.0 mmol) was added, and then the mixture was further stirred at room temperature for 23 hours. Then, more CH_2I_2 (0.60 mL, 7.5 mmol) and Et_2Zn solution in toluene (1.1 M, 2.25 mL, 2.5 mmol) was added, and then the mixture was further stirred at room temperature for 6 hours. Aqueous HCl (1 M, 50 mL) and CH_2Cl_2 (50 mL) were added at 0°C. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic phase was concentrated under vacuum. The residue was filtered through a pad of celite eluted with CH_2Cl_2 to remove the Zinc salt. Aqueous NaOH (1 M, 50 mL) was added to the filtrate. The layers were separated to remove the methyl ester byproduct and the aqueous layer was neutralized with aqueous HCl (1 M, 50 mL) to pH = 1. CH_2Cl_2 (50 mL) were added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic phase was dried over Na_2SO_4 and concentrated under vacuum to afford **4c** (0.709 g, 77%) as a colorless oil.

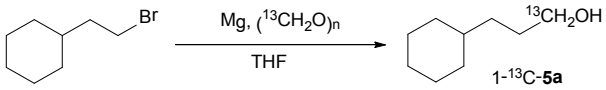
IR ν_{max}(neat)/cm^{-1} 3074, 3000, 2918, 2850, 1697, 1466, 1409, 1299, 935 and 544;

^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ = 7.26) δ 10.29 (br, 1H, CO_2H), 2.35 (d, J = 7.6 Hz, 2H), 1.63 (m, 2H), 1.39-1.30 (m, 8H), 1.17 (m, 2H), 0.64 (m, 1H), 0.38 (m, 2H), -0.18 (m, 2H);

^{13}C NMR (150 MHz, $CDCl_3$, $CDCl_3$ = 77.0) δ 180.4, 34.7, 34.1, 29.5, 29.3 (two overlapped carbon), 29.0, 24.7, 10.9, 4.3;

HRMS (FAB) calcd for $C_{11}H_{20}NaO_2^+$ $[M+Na]^+$ 207.1356, found 207.1358.

Synthesis of 1-^{13}C-3-cyclohexyl-1-propanol (1-^{13}C-**5a**):



1-^{13}C-**5a**

To a mixture of Mg turnings (0.021 g, 8.8 mmol) and ^{13}C-paraformaldehyde (0.186 g, 6.2 mmol) in THF (5 mL) was added 1-bromo-2-cyclohexylethane (0.63 mL, 4.0 mmol) at room temperature under Ar atmosphere. The reaction mixture was stirred at room temperature for 17 hours. Aqueous HCl (1 M, 20 mL) and $CHCl_3$ (20 mL) were added at 0°C. The layers were separated and the aqueous layer was extracted with $CHCl_3$ (2 x 20 mL). The combined organic phase was washed with brine (40 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (EtOAc/hexanes = 0:10 to 1:10) to afford 1-^{13}C-**5a** (0.282 g, 49%) as a colorless oil.

R_f = 0.14 (EtOAc/hexanes = 1:10);

IR ν_{max}(neat)/cm^{-1} 3316, 2921, 2849, 1447, 1035 and 1000;

^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ = 7.26)
δ 3.62 (ddd, J = 141, 10.3, 6.5 Hz, 2H, $^{13}CH_2$), 1.72-1.68 (m, 4H), 1.64 (m, 1H), 1.57 (m, 2H), 1.26-1.10 (m, 7H), 0.88 (m, 2H);

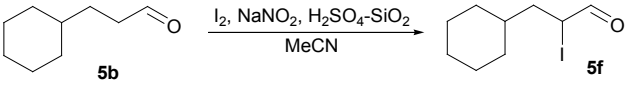
^{13}C NMR (150 MHz, $CDCl_3$, $CDCl_3$ = 77.0)
δ 63.5 (^{13}C), 37.5 (d, J = 4.3 Hz), 33.4, 33.3, 30.1 (d, J = 37.4 Hz), 26.7, 26.4;

^{1}H NMR (600 MHz, D_7-DMF, solvent residual peak = 2.75)
δ 4.35 (dt, J = 2.8, 5.2 Hz, 1H, OH), 3.48 (ddt, J = 138, 5.2, 5.9 Hz, 2H, $^{13}CH_2$), 1.69 (m, 2H), 1.66 (m, 2H), 1.62 (m, 1H), 1.49 (m, 2H), 1.25-1.10 (m, 6H), 0.86 (m, 2H);

^{13}C NMR (150 MHz, D_7-DMF, D_7-DMF = 29.76)
δ 62.1 (^{13}C), 37.8 (d, J = 2.2 Hz), 34.0, 33.6, 30.6 (d, J = 37.4 Hz), 26.8, 26.5;

HRMS (EI) calcd for $C_8{}^{13}CH_{18}O^+$ $[M]^+$ 143.1391, found 143.1389.

Synthesis of 3-cyclohexyl-2-iodopropanal (**5f**):[5]



To a mixture of aldehyde **5b** (129.8 mg, 0.926 mmol) in dry acetonitrile (2 mL) was added I_2 (120.0 mg, 0.473mmol, 0.51 eq), $NaNO_2$ (1.9 mg, 0.0275 mmol, 0.03 eq), and H_2SO_4–silica[6] (20 mg). The reaction mixture was stirred at room temperature under air atmosphere for 30 hours (monitored by TLC until complete conversion of the starting material). The reaction mixture was diluted with hexane/EtOAc (20 ml, 9:1), discolored by adding a few drops of 37% aqueous $NaHSO_3$, neutralized by the addition of solid $NaHCO_3$, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/toluene = 12:1) to afford α-iodoaldehyde **5f** (78.6 mg, 32%) as colorless oil.

R_f = 0.56 (toluene/hexanes = 1/1);

IR ν_{max}(neat)/cm^{-1} 2921, 2848, 1714, 1446, 1080, 1038, 914, 891, 458 and 433;

^{1}H NMR (600 MHz, $CDCl_3$, TMS = 0.00)

[5] The enantiomer-enriched **5f** has been reported: T. Kano, M. Ueda, and K. Maruoka *J. Am. Chem. Soc.*, 2008, **130**, 3728-3729.
[6] Preparation of H_2SO_4 immobilized on silica gel: silica gel (2.4 g) and conc. H_2SO_4 (1.2 g) was well mixed in a mortar, and then laid in a 100°C oven for 13 hours. After cooled to room temperature, the mixture was stored in a desiccator for further use.

δ9.25 (d, J = 3.7 Hz, 1H), 4.56 (ddd, J = 8.3, 7.4, 3.7 Hz, 1H), 1.91-1.80 (m, 2H), 1.73-1.69 (m, 4H), 1.66 (m, 1H), 1.41 (m, 1H), 1.28-1.21 (m ,2H), 1.14 (m, 1H), 1.01 (m, 1H), 0.86 (m, 1H);

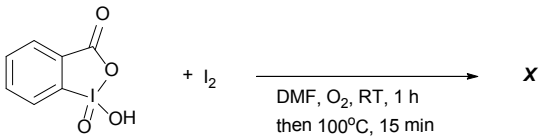
^{13}C NMR (150 MHz, $CDCl_3$, $CDCl_3$ = 77.0)
δ191.8, 39.4, 37.6, 35.0, 32.9, 32.2, 26.2, 25.95, 25.85;

^{1}H NMR (600 MHz, D_7-DMF, solvent residual peak = 2.75)
δ9.33 (d, J = 2.3 Hz, 1H), 4.91 (ddd, J = 8.9, 7.8, 2.3 Hz, 1H), 1.88-1.80 (m, 2H), 1.75-1.72 (m, 2H), 1.69-1.67 (m, 2H), 1.63-1.60 (m, 2H), 1.40 (m, 1H), 1.27-1.10 (m, 4H), 1.02 (m, 1H), 0.88 (m, 1H);

^{13}C NMR (150 MHz, D_7-DMF, D_7-DMF = 29.76)
δ193.27, 39.4, 38.0, 35.7, 33.1, 32.2, 26.5, 26.2, 26.1;

LRMS (EI) calcd for $C_9H_{15}IO^+$ $[M]^+$ 266, found 266.

Preparation of ***X***:



A mixture of IBX (15.6 g, 55.5 mmol), and I_2 (2.82 mg, 11.1 mmol) in DMF (100 mL) was stirred at room temperature under the O_2 atmosphere for 1 hour, and then at 100°C for 15 minutes. The reaction mixture was cooled to room temperature and filtered. The residue was washed with benzene (180 mL x 4) and CH_2Cl_2 (180 mL x 4) and then dried under vacuum for 18 hours to afford a colorless solid (12.2 g).

m.p. 238-240°C (dec.);

IR ν_{max}(Nujor)/cm^{-1} 1682, 1638, 1287, 1122, 782, 740 and 585;

^{1}H NMR (600 MHz, D_7-DMF, room temperature, solvent residual peak = 2.75)
δ8.13 (dd, J = 7.8, 1.4 Hz, 1H, H-6), 8.05 (ddd, J = 7.8, 7.8, 1.4 Hz, 1H, H-4), 7.82 (dd, J = 7.8, 7.8 Hz, 1H, H-5);

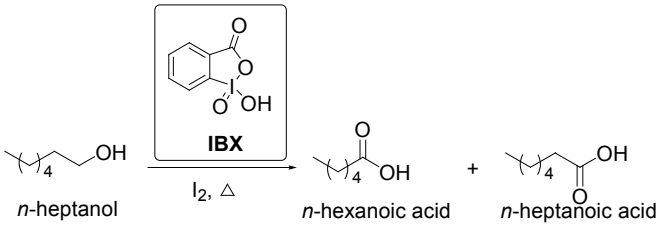
^{1}H NMR (600 MHz, D_7-DMF, 80°C, solvent residual peak = 2.75)
δ8.16 (br d, J = 7.8 Hz, 1H, H-3), 8.09 (dd, J = 7.3, 1.4 Hz, 1H, H-6), 7.98 (ddd, J = 7.3, 7.3, 1.4 Hz, 1H, H-4), 7.75 (dd, J = 7.3, 7.3 Hz, 1H, H-5);

^{13}C NMR (150 MHz, D_7-DMF, room temperature, D_7-DMF = 29.76)
δ168.2 (C-7), 135.2 (C-5), 131.5 (C-6), 130.9 (C-4), 127.9 (br, C-3), 121.4 (br, C-1);

^{13}C NMR (150 MHz, D_7-DMF, 80°C, D_7-DMF = 29.76)
δ167.8 (C-7), 134.8 (C-5), 131.4 (C-6), 130.7 (C-4), 127.5 (C-3), 120.9 (C-1);

3. Optimization of the reaction condition

Table S1. optimization of the IBX dehomologation of *n*-heptanol (**2a**)[a]

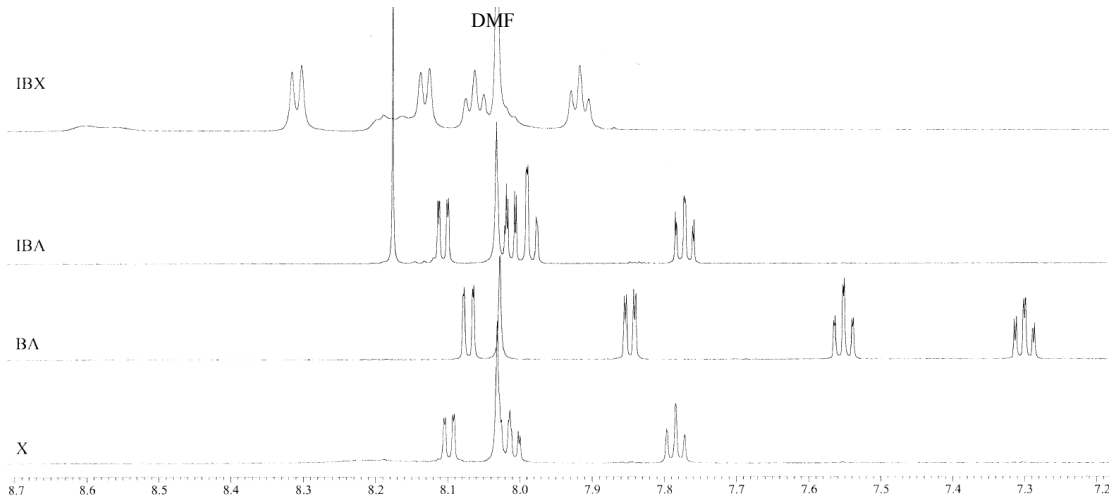


Entry	IBX (eq.)	I_2 (eq.)	Environment[b]	Solvent	Time (h)	**2c**/**2d**[c]	Yield of **2c**[d] (%)
1	6	0	Ar	EtOAc	28	0.21	nd
2	6	0.5	Ar	EtOAc	21	0.35	nd
3	6	0.5	O_2, H_2SO_4	EtOAc	49	0.80	nd
4	6	0.5	O_2, H_2SO_4	acetone	69	0	nd
5	6	0.5	O_2, H_2SO_4	MeCN	49	0.64	nd
6	6	0.5	O_2, H_2SO_4	DMSO	46	6.4	nd
7	6	0.5	O_2, H_2SO_4	DMF	7	16	7
8	6	0	O_2, H_2SO_4	DMF	7	0.19	3
9	0	0.5	O_2, H_2SO_4	DMF	48	-	nr
10	6	0.5	O_2	DMF	7	2.5	15
11	6	1.2	Ar	DMF	3	**2c** only	50
12	6	1.2	air	DMF	3	**2c** only	60
13	6	1.2	O_2	DMF	3	8.5	62
14	**8**	**1.6**	**O_2**	**DMF**	**4**	**2c** only	**74**
15	8	2.0	O_2	DMF	3	25	56
16	10	2.0	O_2	DMF	4	9	57

[a] Reaction conditions: a mixture of **2a** (0.25 mmol) and other reagents in solvent (3.6 mL) was heated at an elevated temperature for the indicated time. For solvents other than DMSO and DMF, the reaction was refluxed. For DMSO and DMF, the reaction was carried out at 100 °C. [b] For H_2SO_4, 0.1 mL of a 10 mM aqueous solution was added. [c] The ratio of **2c** and **2d** was determined by GC–MS. [d] The yield of **2c** was determined by GC–MS with added *n*-nonanoic acid (0.25 mmol) as an internal standard after completion of the reaction. nd: not determined. nr: no reaction.

4. Comparison of ^{1}H- and ^{13}C-NMR spectra of *X*, IBX, IBA and BA

(a) ^{1}H-NMR (D_7-DMF, 600 MHz)



(b) ^{13}C-NMR (D_7-DMF, 150 MHz)

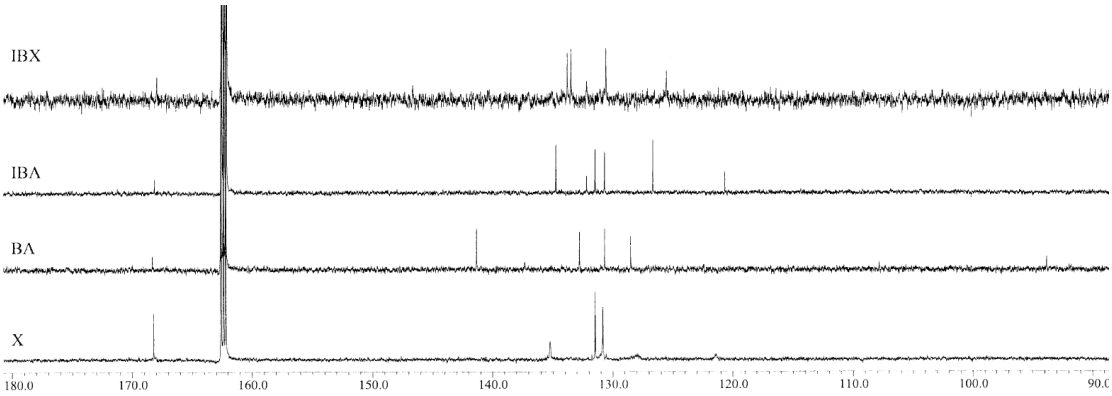


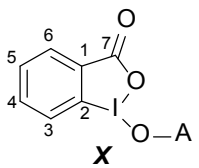
Fig. S1 Comparison of ^{1}H- and ^{13}C-NMR spectra of ***X***, IBX, IBA and BA. All the spectra were measured in D_7-DMF at room temperature. The spectra of ***X*** are very different from those of IBX and BA, but similar with those of IBA, suggesting that ***X*** contains the same iodine-substituted benzoic acid fragment as that of IBA.

(a) Comparison of ^{1}H-NMR spectra (7.2 to 8.7 ppm) of ***X***, IBX, IBA and BA.

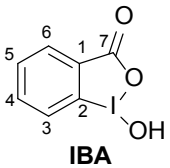
(b) Comparison of ^{13}C-NMR spectra (90 to 180 ppm) of ***X***, IBX, IBA and BA.

The full-area spectra are in page S18-S25.

Table S2. Comparison of the NMR data of ***X*** and IBA (D_7-DMF)



X



IBA

position	^{13}C-NMR of ***X***	^{13}C-NMR of IBA	^{1}H-NMR of ***X***	^{1}H-NMR of IBA
1	nd	132.2	-	-
2	121.4 (br)	120.7	-	-
3	127.9 (br)	126.7	nd	7.98 (dd, *J* = 0.9, 7.7 Hz)
4	135.2	134.7	8.05 (ddd, *J* = 1.4, 6.9, 8.3 Hz)	8.02 (ddd, *J* = 1.4, ?, 9.7 Hz)
5	130.9	130.7	7.82 (dd, *J* = 7.8, 7.8 Hz)	7.77 (ddd, *J* = 1.4, 7.3, 7.3 Hz)
6	131.5	131.5	8.13 (dd, *J* = 1.4, 7.8 Hz)	8.11 (dd, *J* = 1.4, 7.8 Hz)
7	168.2	168.2	-	-
OH	-	-	-	8.18 (s)

Table S3. Comparison of the chemical shifts of ^{1}H-NMR of ***X***, IBX, IBA and BA (D_7-DMF, 600 MHz)

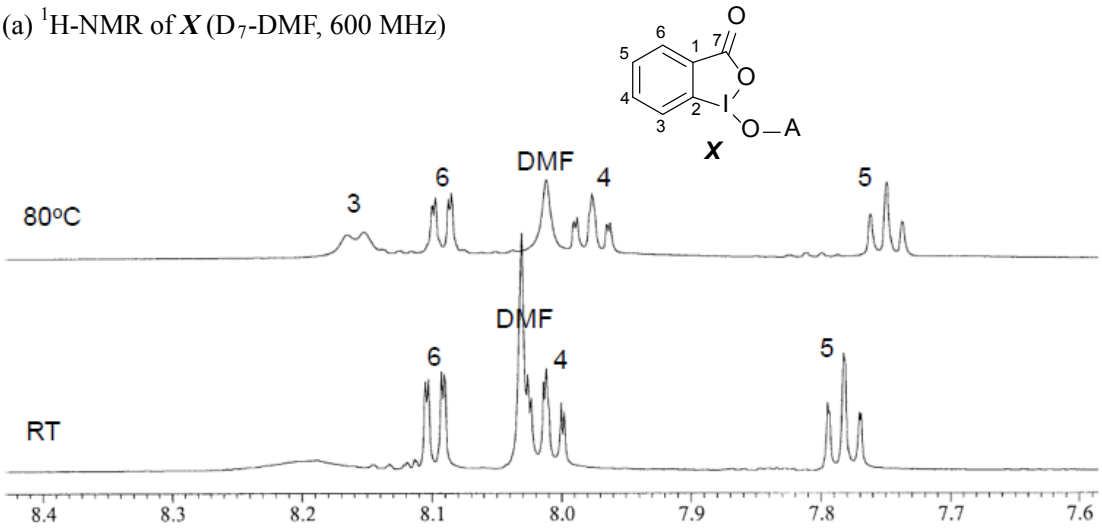
	H-3	H-4	H-5	H-6
δ(***X***)	nd	8.05	7.82	8.13
δ(IBX)	8.31	7.91	8.06	8.13
δ(IBA)	7.98	8.02	7.77	8.11
δ(BA)	8.07	7.30	7.55	7.86
Δδ(IBX-***X***)	-	-0.14	0.24	0
Δδ(IBA-***X***)	-	-0.03	-0.05	-0.02
Δδ(BA-***X***)	-	-0.75	-0.27	-0.27

Table S4. Comparison of the chemical shifts of ^{13}C-NMR of ***X***, IBX, IBA and BA (D_7-DMF, 150 MHz)

	C-1	C-2	C-3	C-4	C-5	C-6	C-7
δ(***X***)	nd	121.4 (br)	127.9 (br)	135.2	130.9	131.5	168.2
δ(IBX)	146.7	132.1	125.6	133.5	133.8	130.6	168.0
δ(IBA)	132.2	120.7	126.7	132.7	130.7	131.5	168.2
δ(BA)	137.3	93.9	141.4	132.8	130.7	128.5	168.3
Δδ(IBX-***X***)	-	10.7	-2.3	-1.7	2.9	-0.9	-0.2
Δδ(IBA-***X***)	-	-0.7	-1.2	-2.5	-0.2	0	0
Δδ(BA-***X***)	-	-27.5	13.5	-2.4	-0.2	-3	0.1

5. Comparison of ^{1}H- and ^{13}C-NMR spectra of *X* at room temperature and 80°C

(a) ^{1}H-NMR of ***X*** (D_7-DMF, 600 MHz)



(b) ^{13}C-NMR of ***X*** (D_7-DMF, 150 MHz)

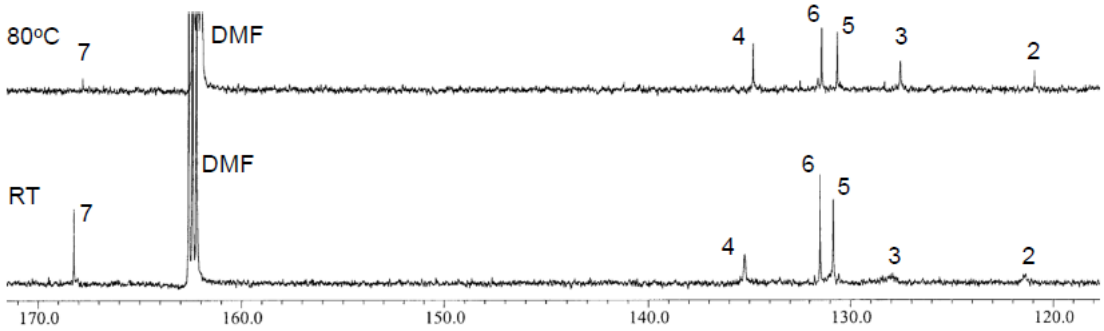


Fig. S2 Comparison of ^{1}H- and ^{13}C-NMR spectra of ***X*** at room temperature and 80°C. At room temperature, the H-3 and C-1 signals were lost in ^{1}H- and ^{13}C-NMR spectra, and the C-2 and C-3 signals were broadened in ^{13}C-NMR spectrum, while at 80°C, H-3 signal appeared (broad doublet) and C-2 and C-3 signals became sharp.

(a) Comparison of ^{1}H-NMR spectra (7.6 to 8.4 ppm) of ***X*** at room temperature and 80°C.

(b) Comparison of ^{13}C-NMR spectra (120 to 170 ppm) of ***X*** at room temperature and 80°C.

The full-area spectra are in page S18-19 and S26-S34, including the HMQC and HMBC spectra of ***X*** at room temperature and 80°C.

6. Detection of CO_2 as a product of dehomologation using ^{13}C-labelled substrate 5a

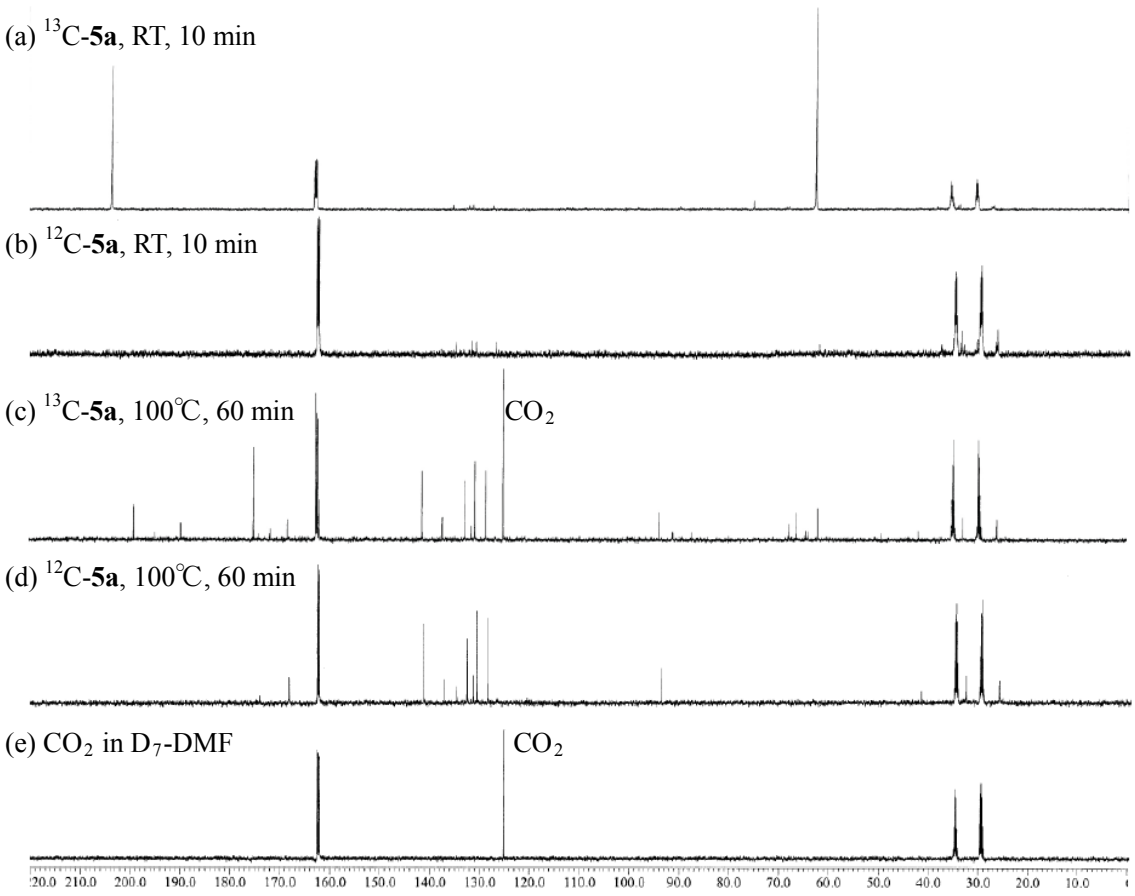


Fig. S3 Comparison of the ^{13}C-NMR spectra of dehomologation of ^{13}C-**5a** and ^{12}C-**5a** in D_7-DMF (150 MHz). The difference in (c) and (d) showed clearly that the ^{13}C-labelled carbon changed to $^{13}CO_2$ during the reaction.

(a) ^{13}C-NMR spectrum of the mixture of ^{13}C-**5a**, IBX, I_2 and D_7-DMF in a NMR tube after shaken at room temperature for 10 minute;

(b) ^{13}C-NMR spectrum of the mixture of ^{12}C-**5a**, IBX, I_2 and D_7-DMF in a NMR tube after shaken at room temperature for 10 minute;

(c) ^{13}C-NMR spectrum of the mixture of (a) after standing in a 100℃ oil bath for 60 min;

(d) ^{13}C-NMR spectrum of the mixture of (b) after standing in a 100℃ oil bath for 60 min;

(e) ^{13}C-NMR spectrum of the solution of a small piece of dry ice (CO_2) in D_7-DMF.

7. Proposed mechanism for the IBX-I_2 dehomologation of alcohols.

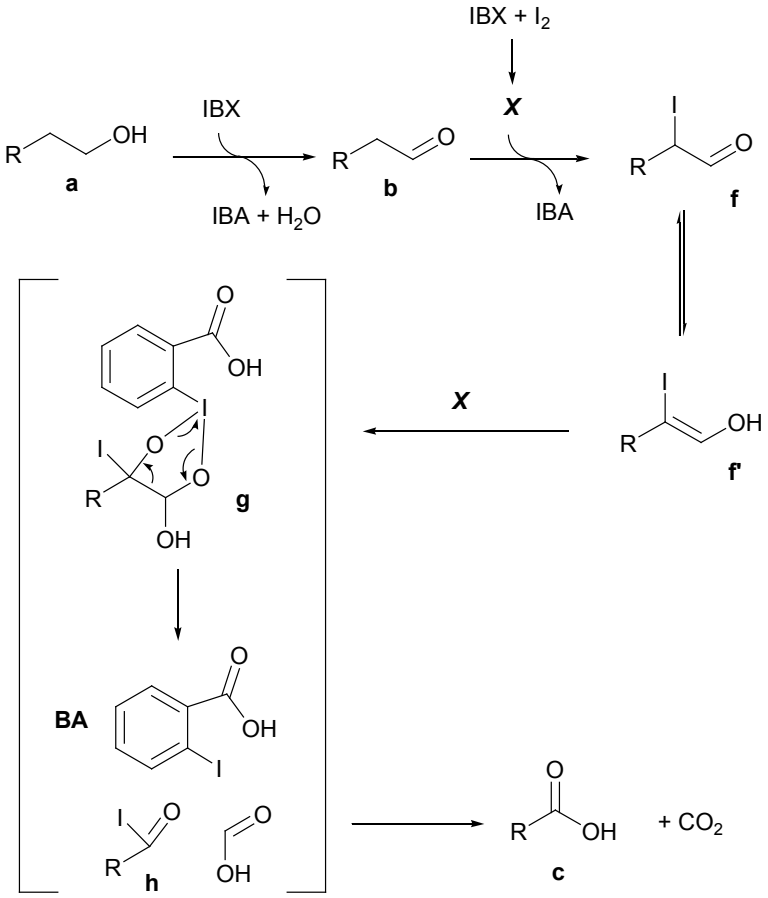
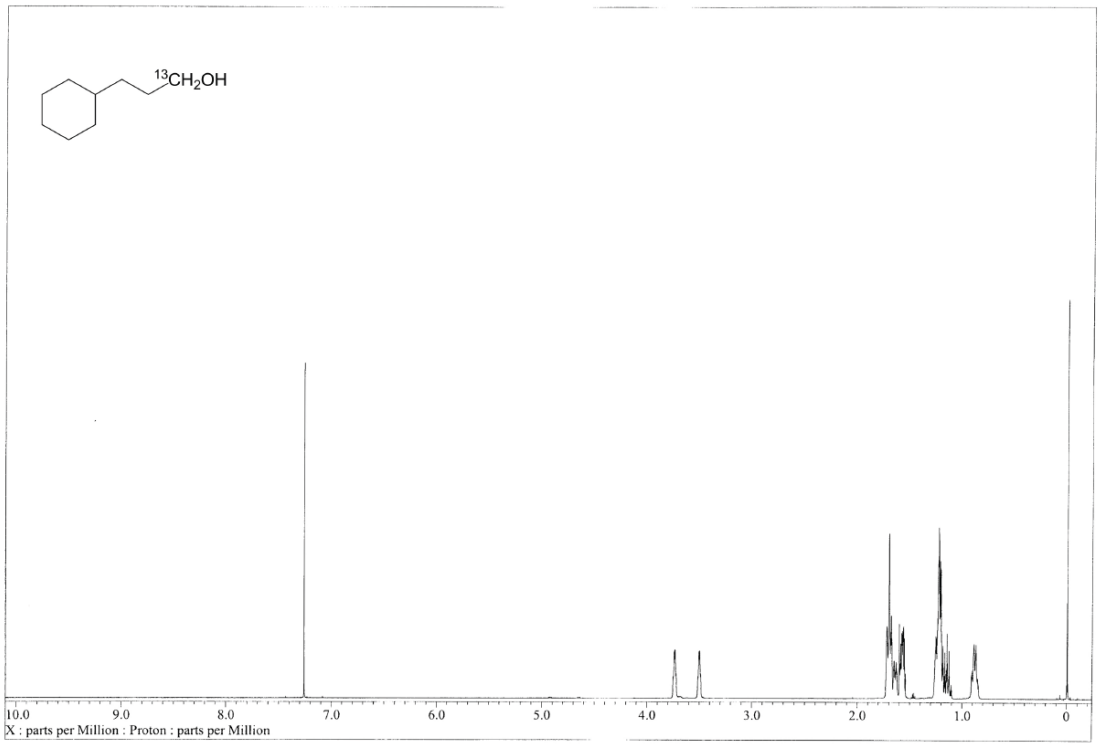
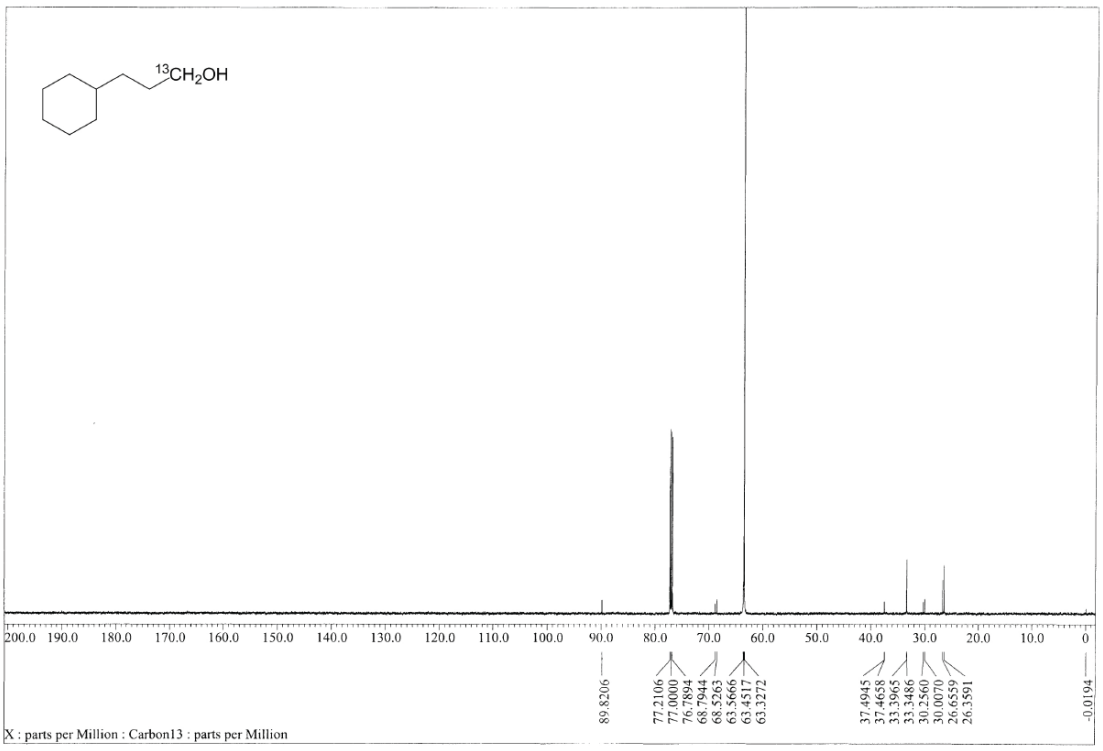


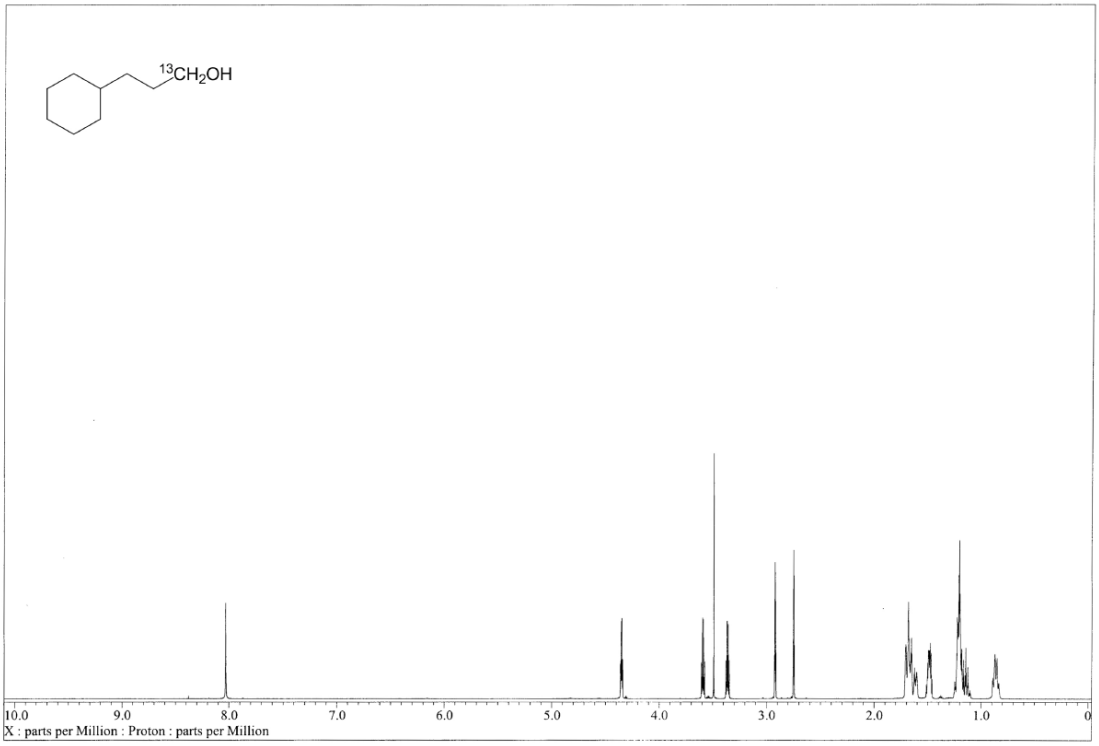
Fig. S4 The reaction mechanism we thus propose is outlined. After iodonation of aldehyde **b** by ***X***, the enol form **f′** of iodoaldehyde **f** is assumed to react with ***X*** to form a five-membered cyclic intermediate **g**. Carbon–carbon bond cleavage and ring-opening of intermediate **g** lead to dehomologated carbonyl iodide **h**, along with BA and formic acid. Five-membered ring intermediates similar to **g** have been proposed for other hypervalent iodine reactions of carbonyl compounds. The iodine substituent in the five-membered ring of **g** does not make the cleavage product **h** an aldehyde, thus possibly preventing further dehomologation. Finally, hydrolysis of **h** affords dehomologated carboxylic acid **c**, while formic acid is oxidized to CO_2.

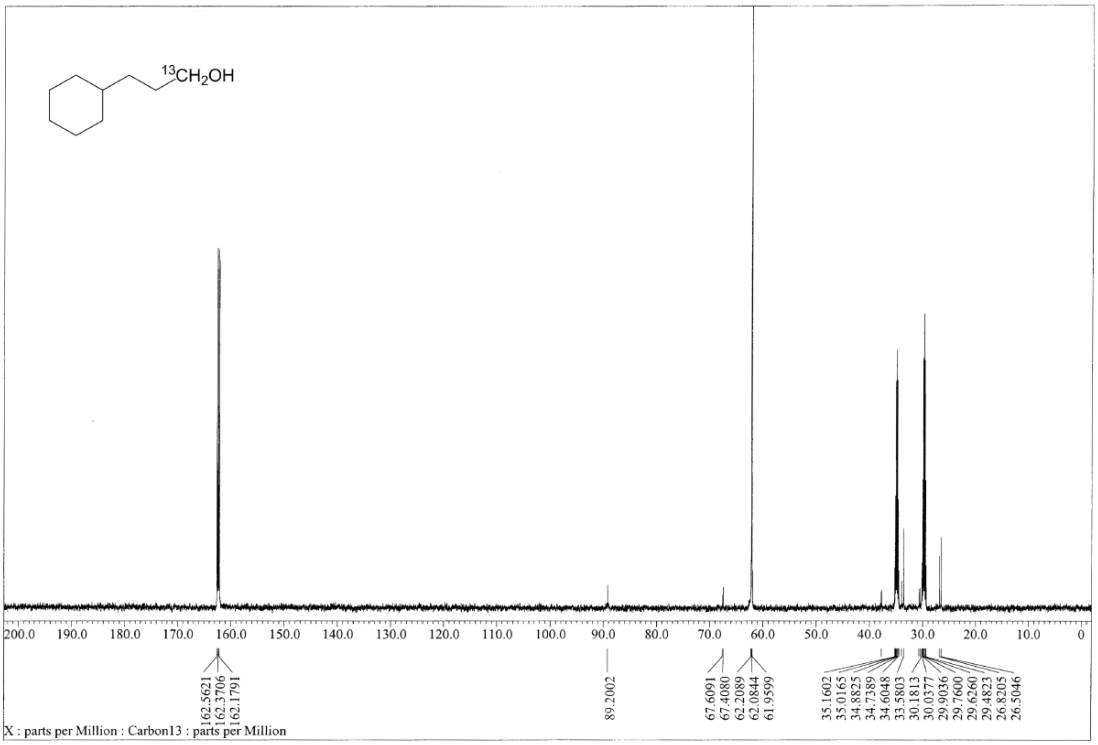
8. ^{1}H NMR and ^{13}C NMR spectra of 1-^{13}C-5a





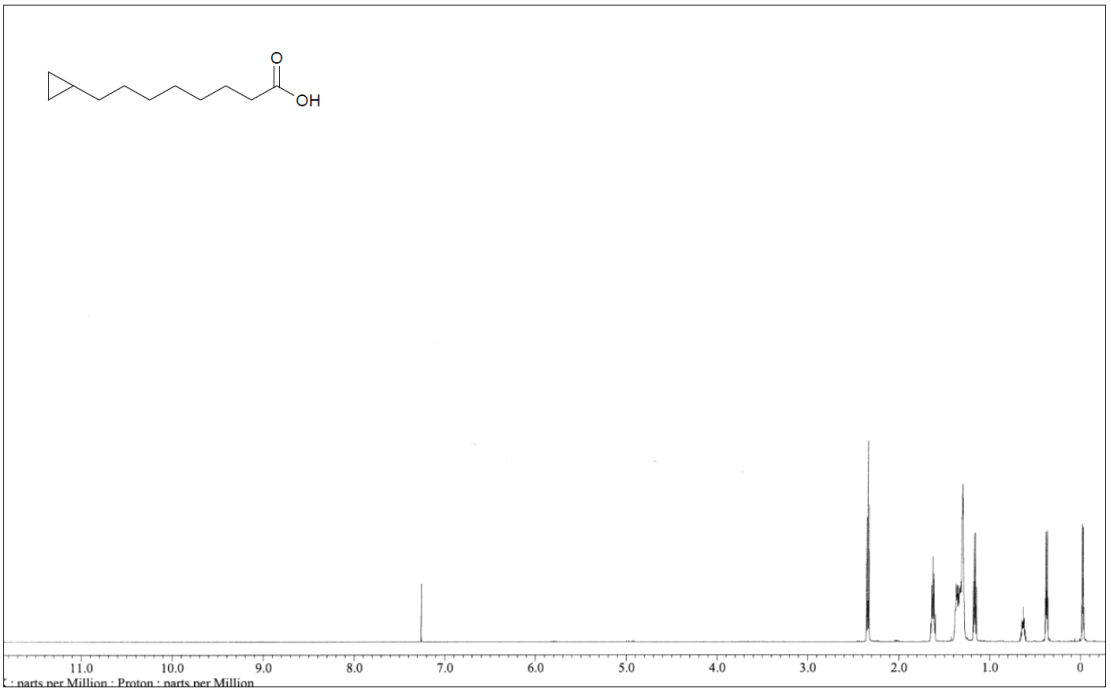
^{1}H-NMR ($CDCl_3$, 600 MHz) and ^{13}C-NMR ($CDCl_3$, 150 MHz) spectra of 1-^{13}C-**5a**

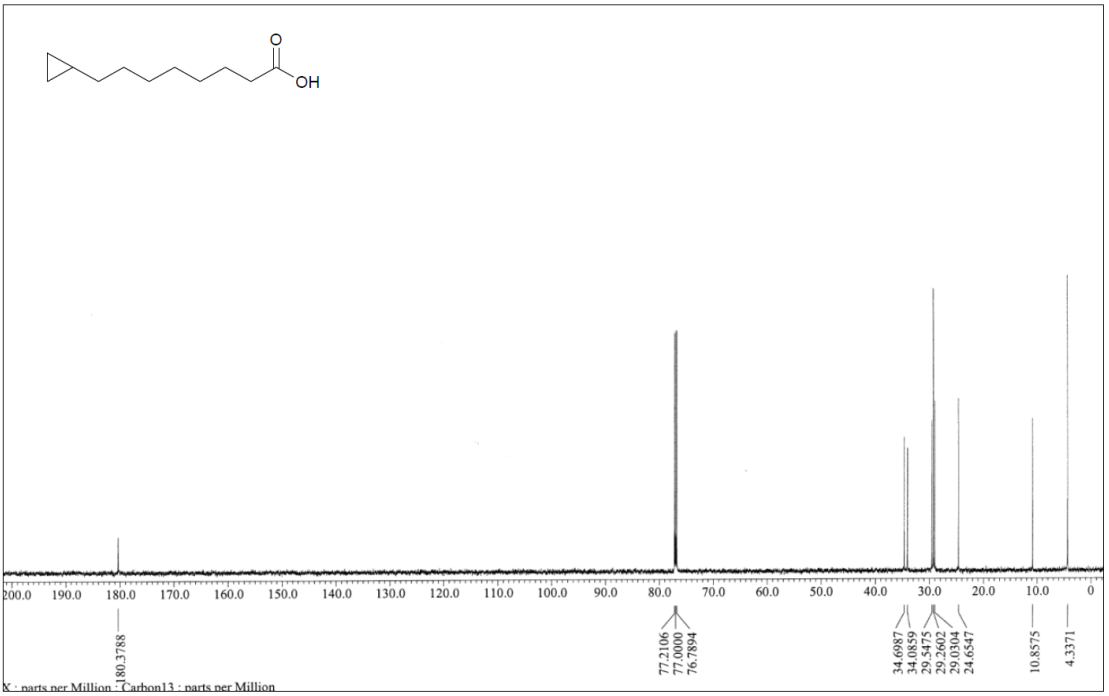




^{1}H-NMR (D_7-DMF, 600 MHz) and ^{13}C-NMR (D_7-DMF, 150 MHz) spectra of 1-^{13}C-**5a**

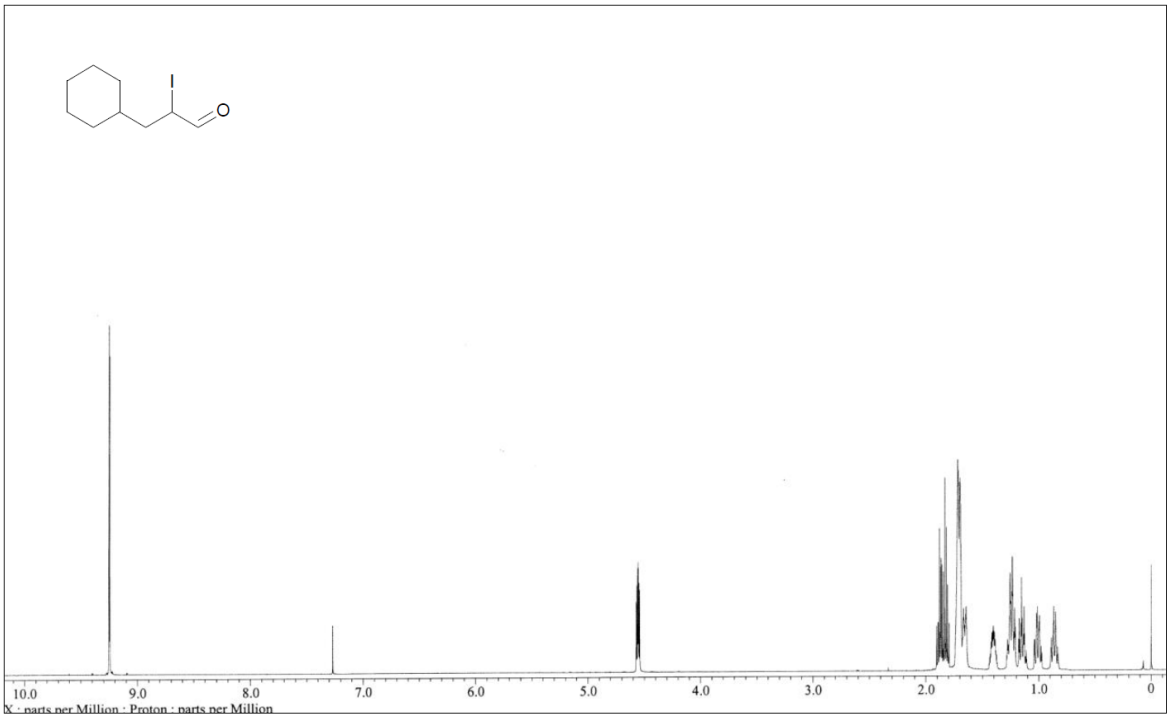
9. ^{1}H NMR and ^{13}C NMR spectra of 4c

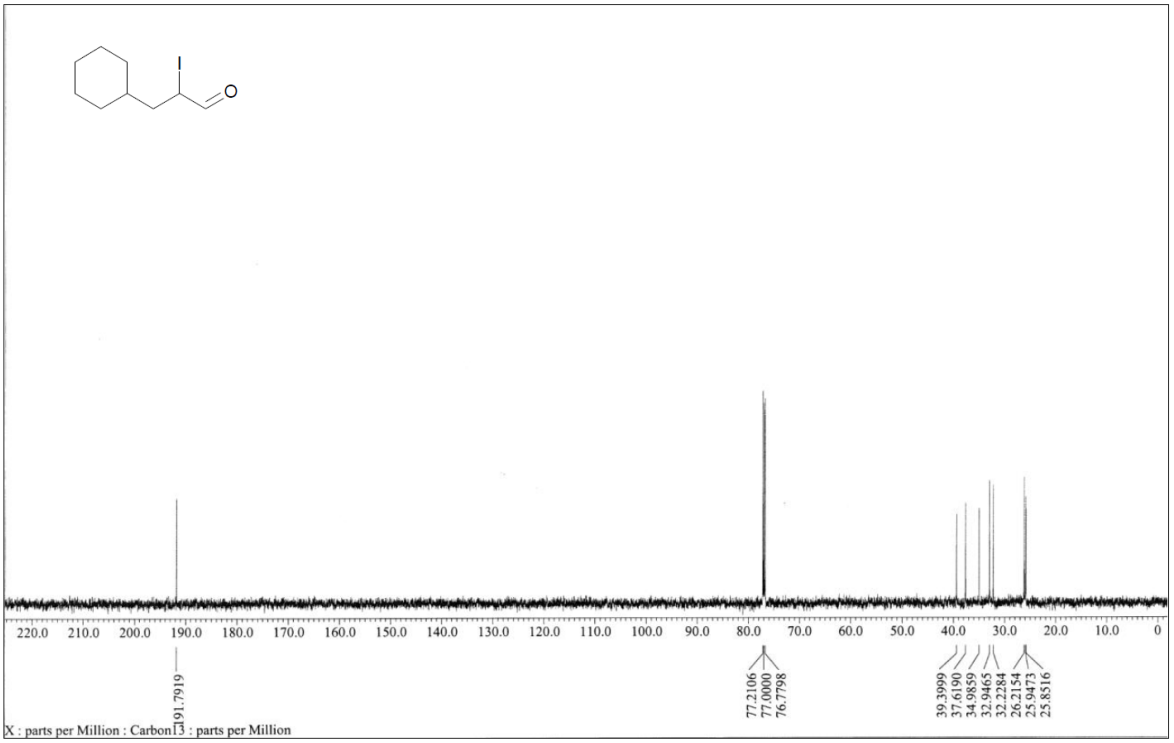




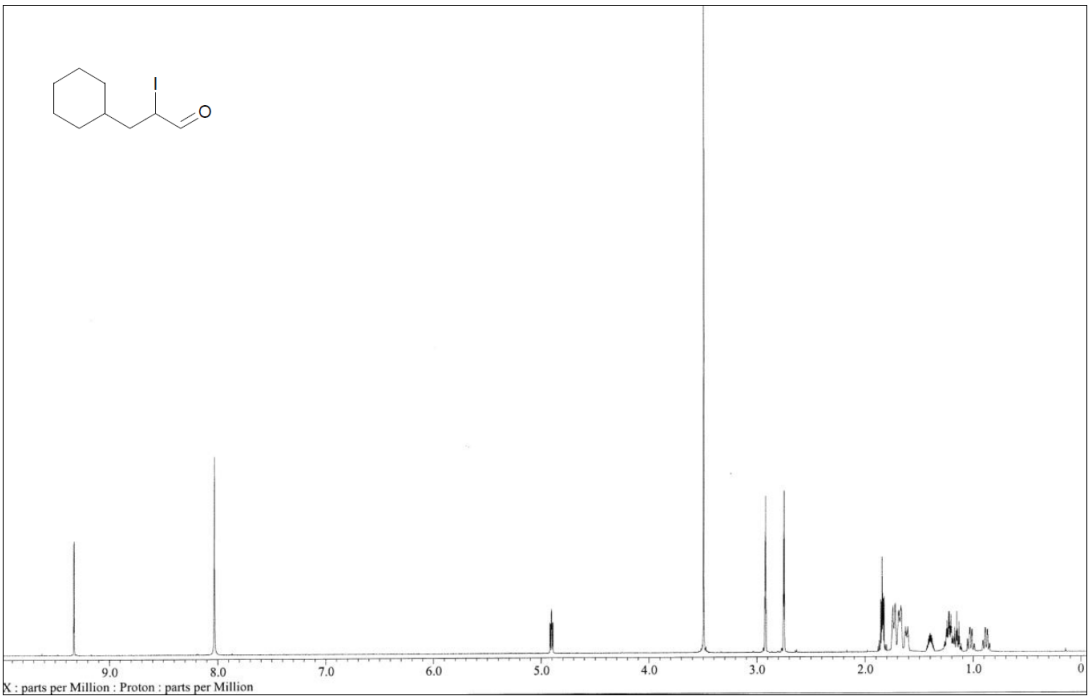
^{1}H-NMR ($CDCl_3$, 600MHz) and ^{13}C-NMR ($CDCl_3$, 150MHz) spectra of **4c**

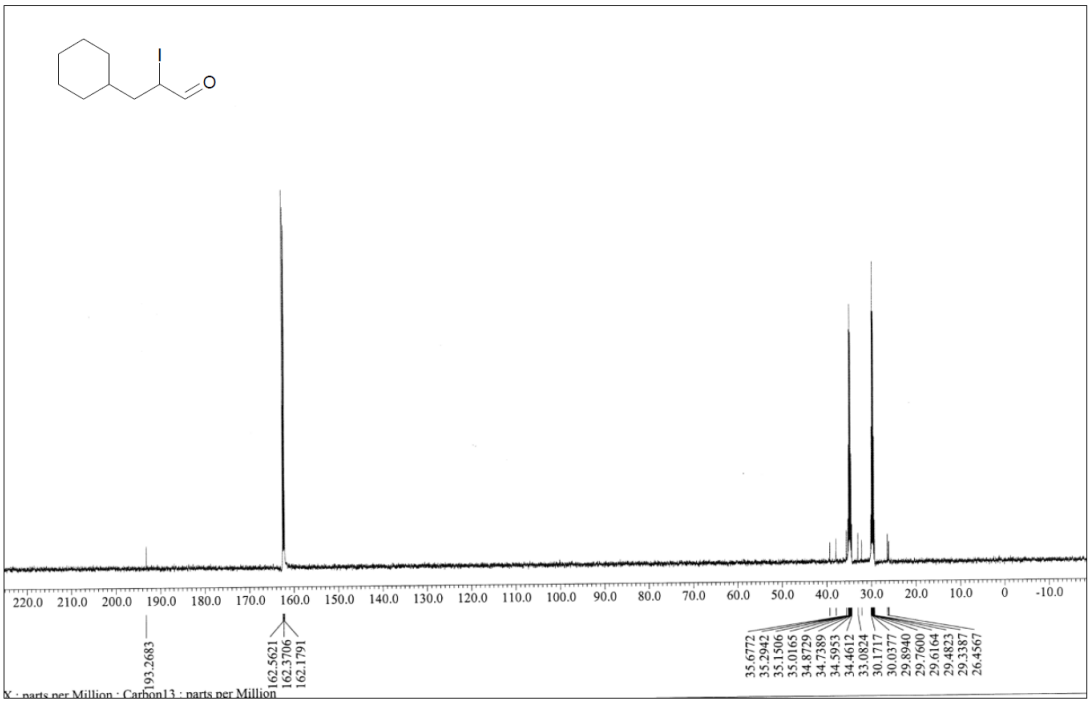
10. ^{1}H NMR and ^{13}C NMR spectra of 5f



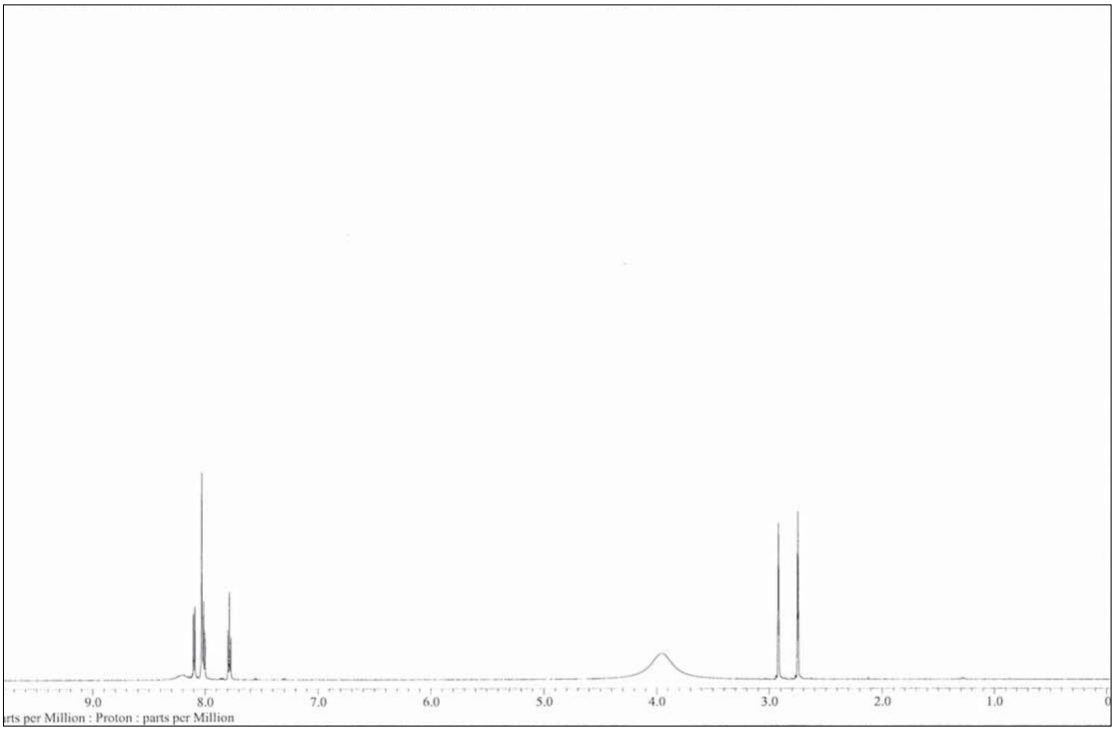


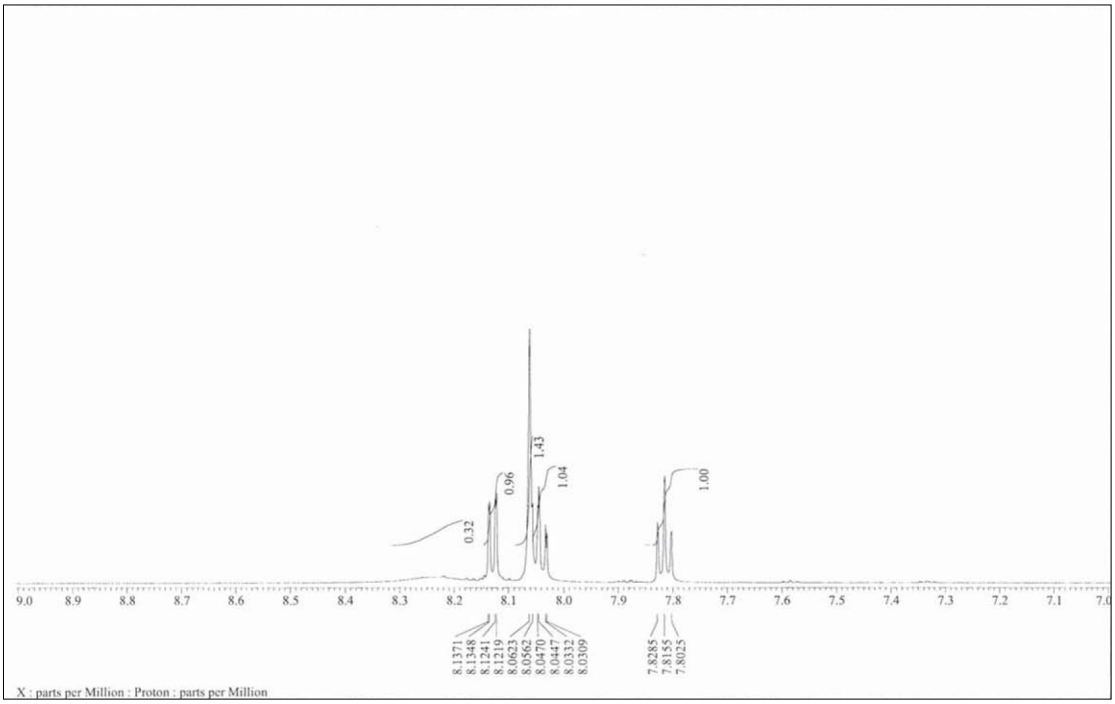
^{1}H-NMR ($CDCl_3$, 600MHz) and ^{13}C-NMR ($CDCl_3$, 150MHz) spectra of **5f**





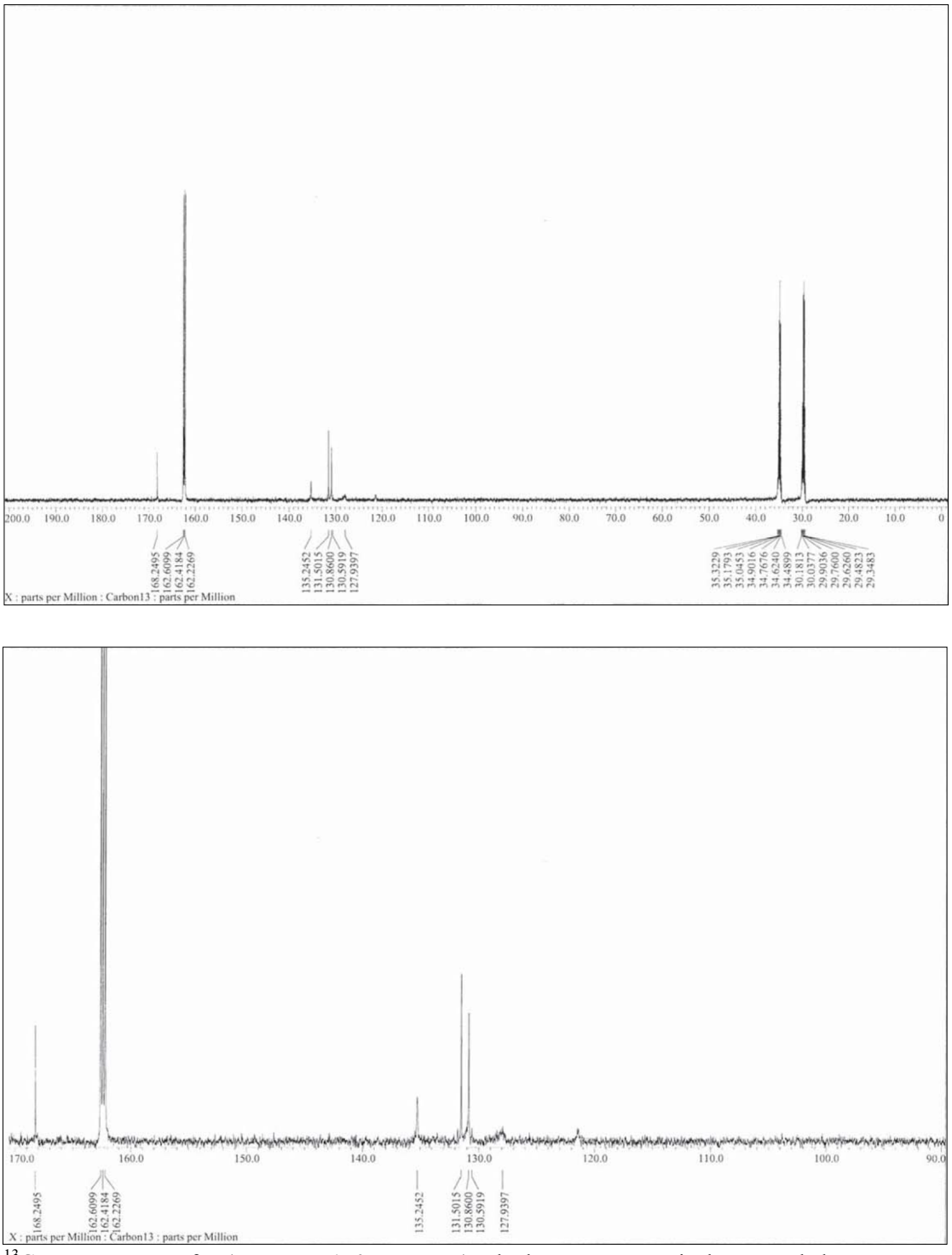
^{1}H-NMR (D_7-DMF, 600MHz) and ^{13}C-NMR (D_7-DMF, 150MHz) spectra of **5f**



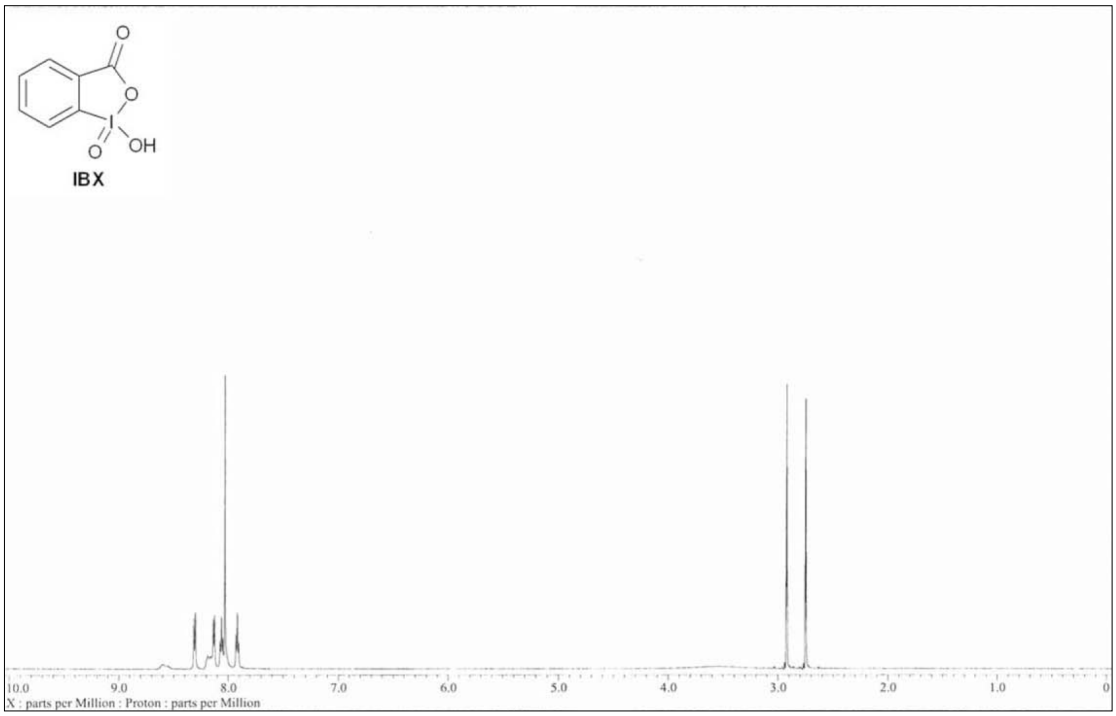


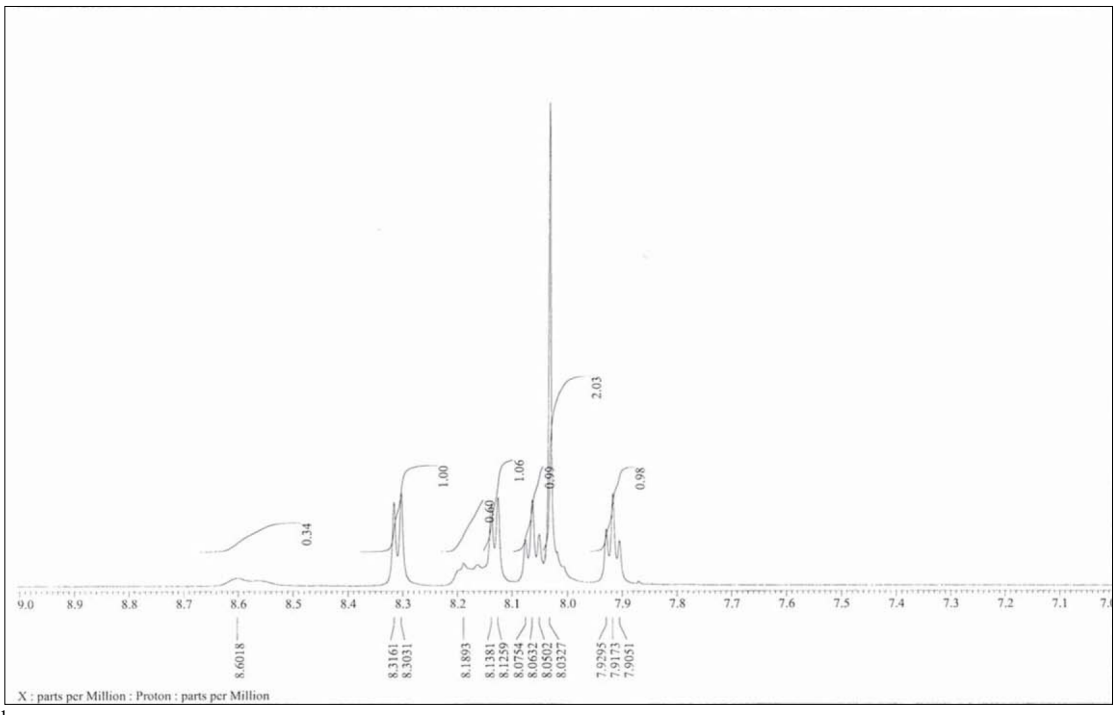
11. ^{1}H NMR and ^{13}C NMR spectra (RT) of *X*, IBX, IBA and BA

^{1}H-NMR spectra of ***X*** (D_7-DMF, 600 MHz, RT). The lower spectrum is the expanded one.

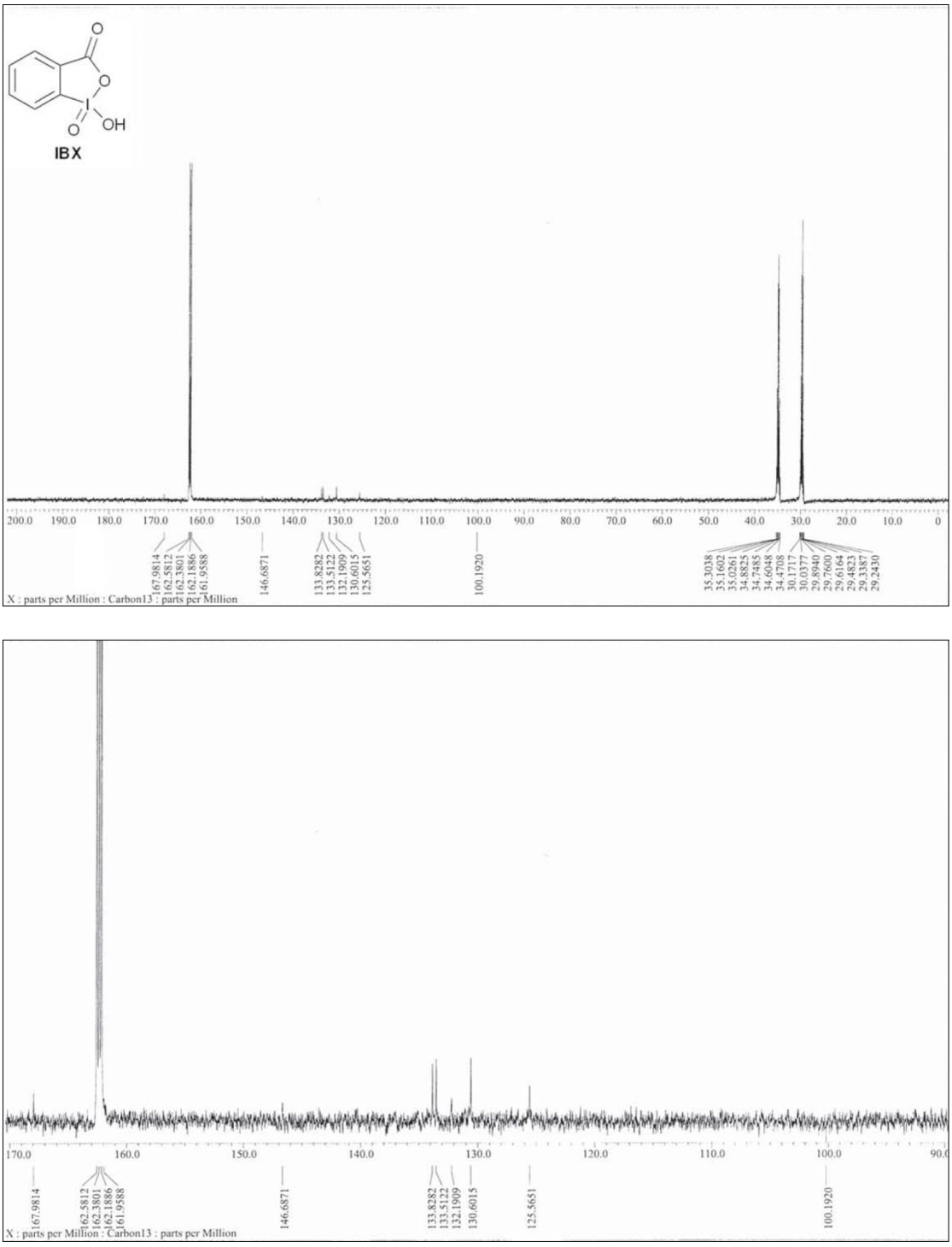


^{13}C-NMR spectra of ***X*** (D_7-DMF, 150 MHz, RT). The lower spectrum is the expanded one.

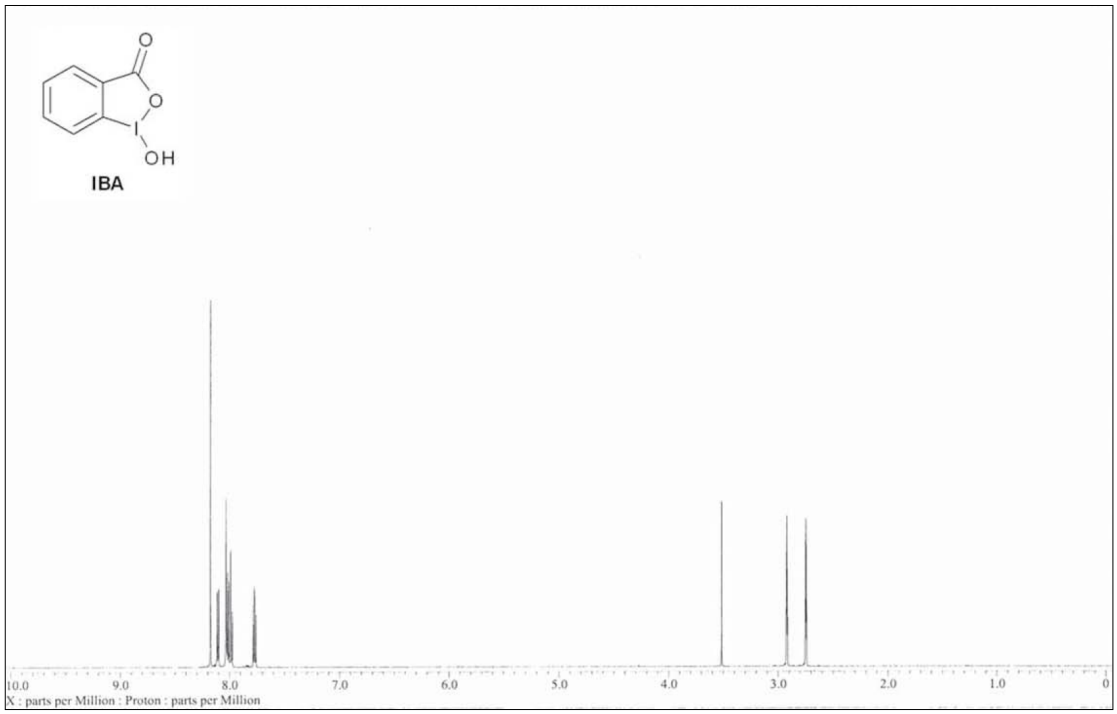


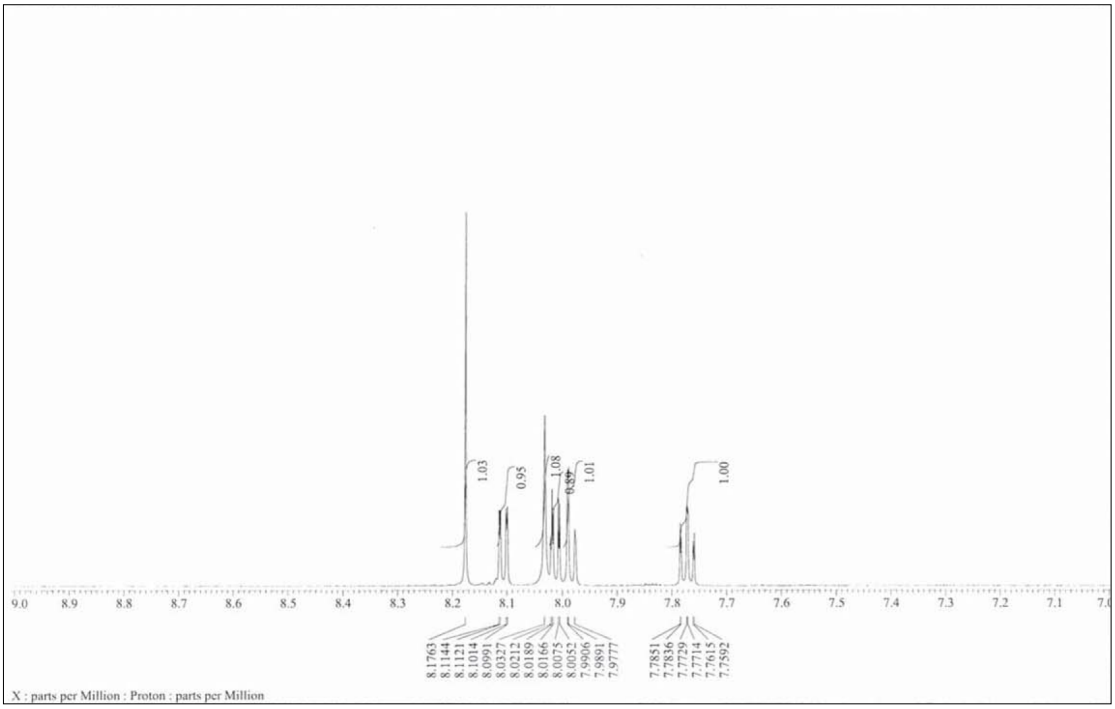


^{1}H-NMR spectra of IBX (D_7-DMF, 600 MHz, RT). The lower spectrum is the expanded one.

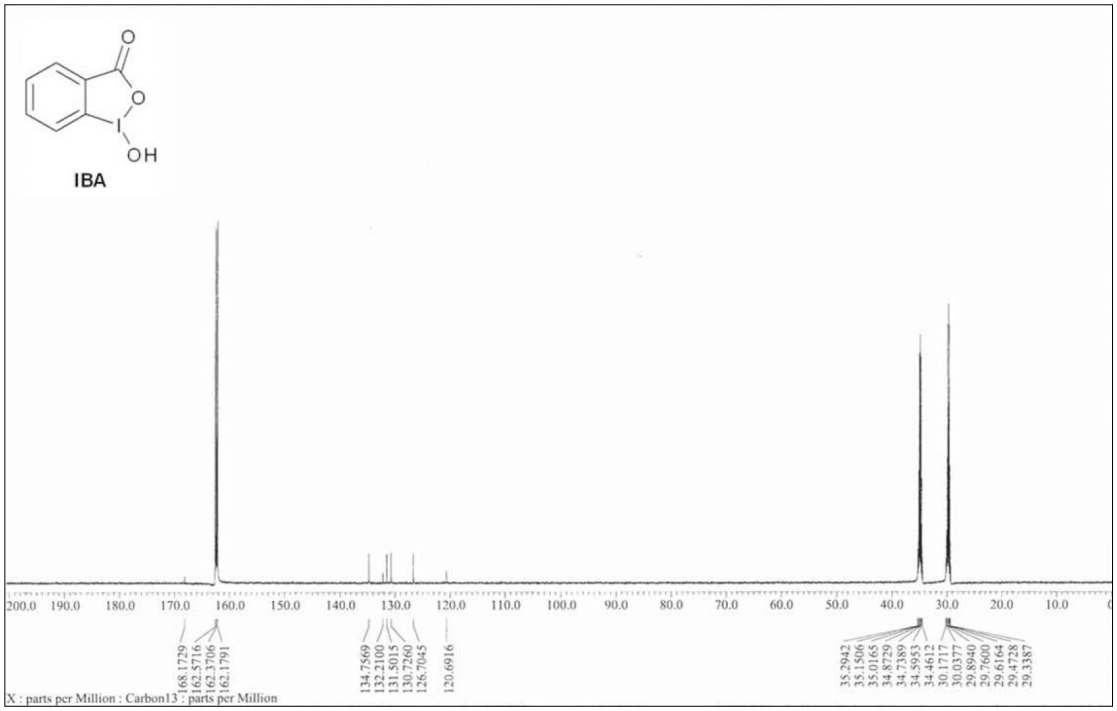


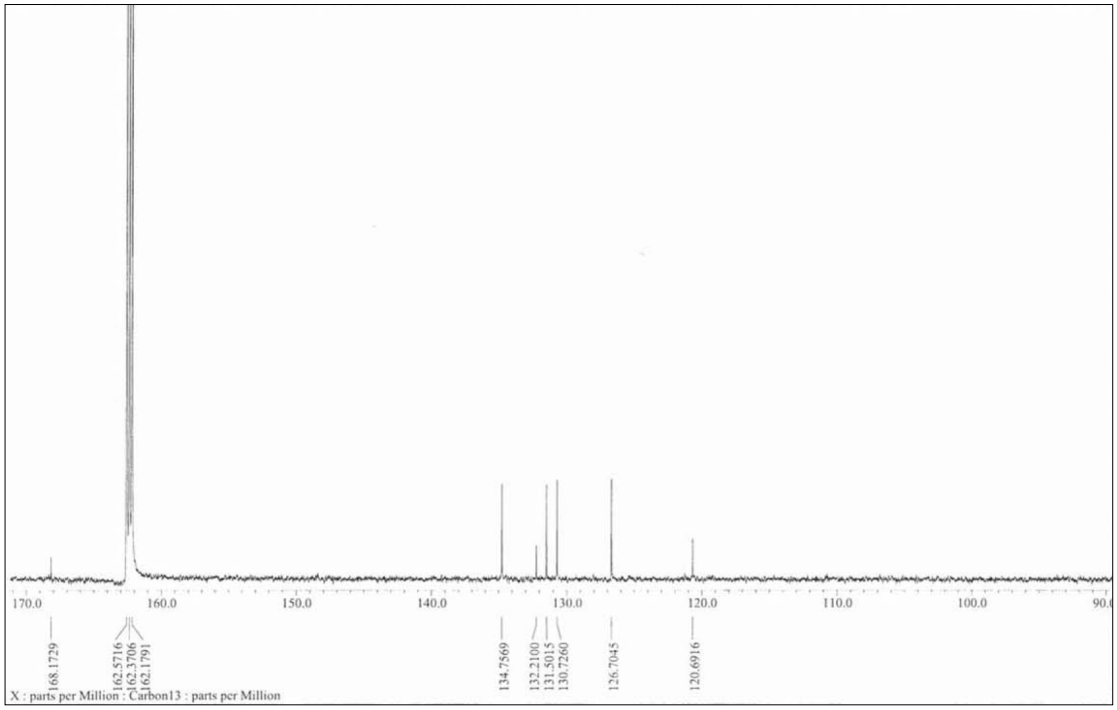
^{13}C-NMR spectra of IBX (D_7-DMF, 150 MHz, RT). The lower spectrum is the expanded one.



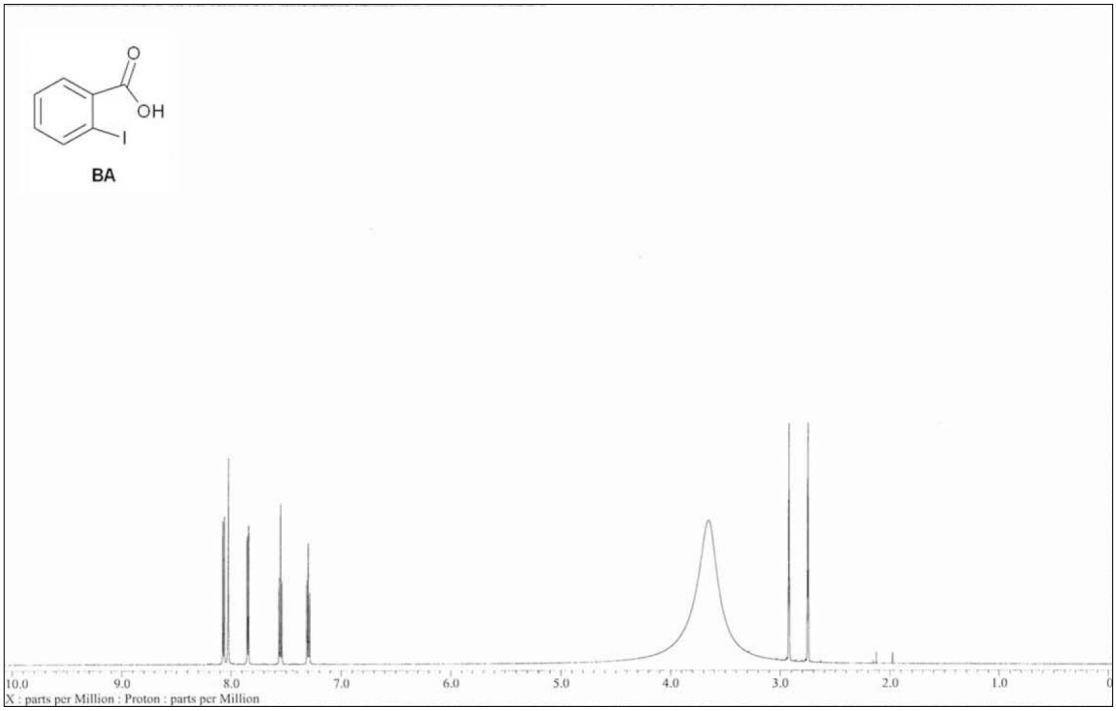


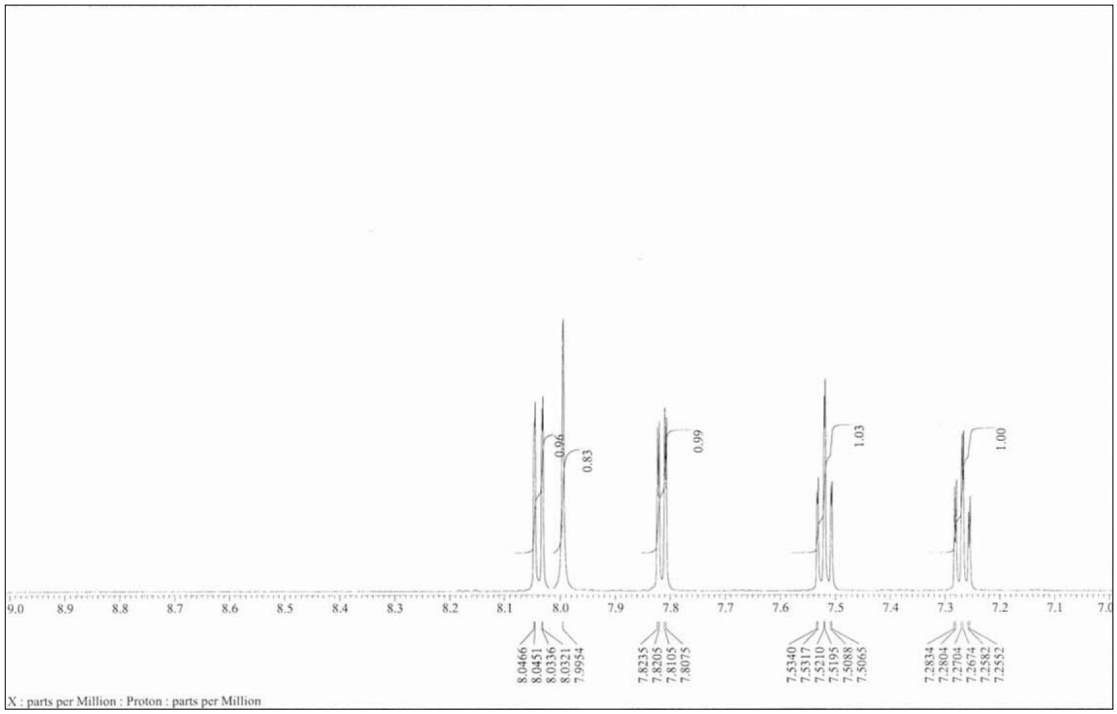
^{1}H-NMR spectra of IBA (D_7-DMF, 600 MHz, RT). The lower spectrum is the expanded one.



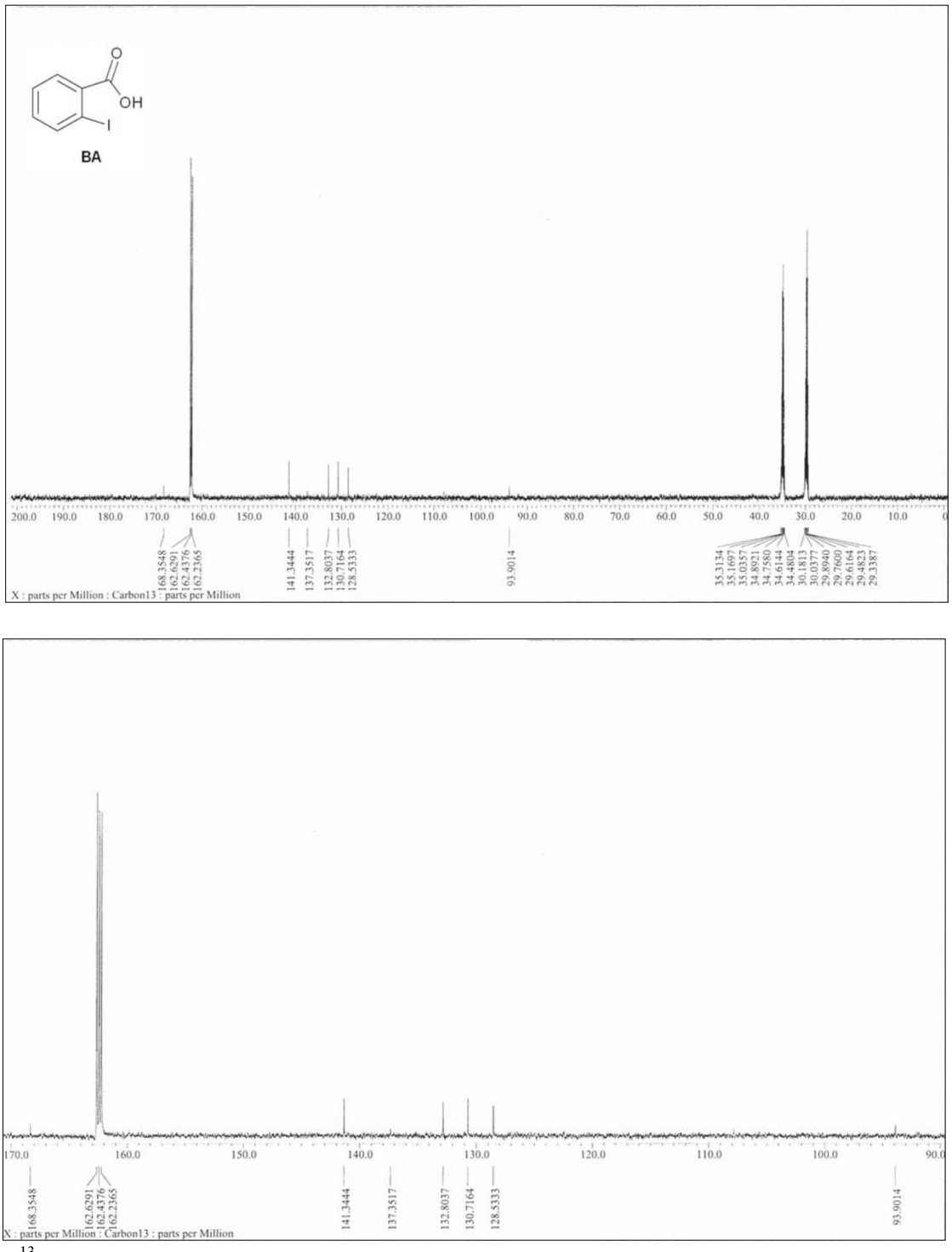


^{13}C-NMR spectra of IBA (D_7-DMF, 150 MHz, RT). The lower spectrum is the expanded one.



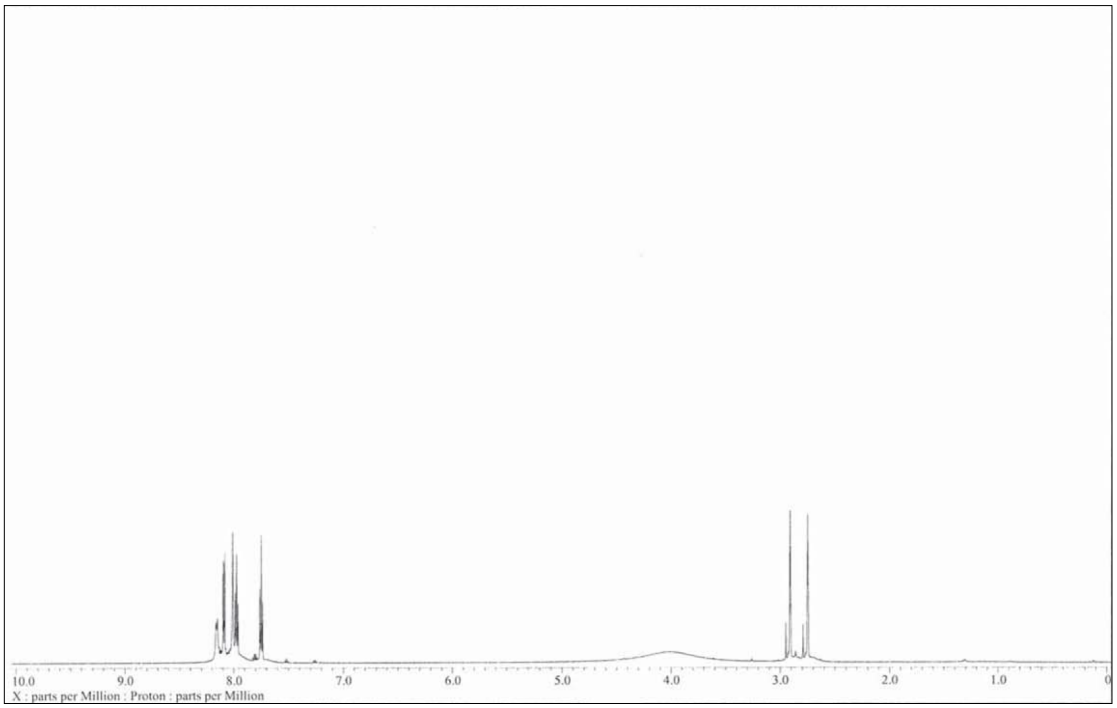


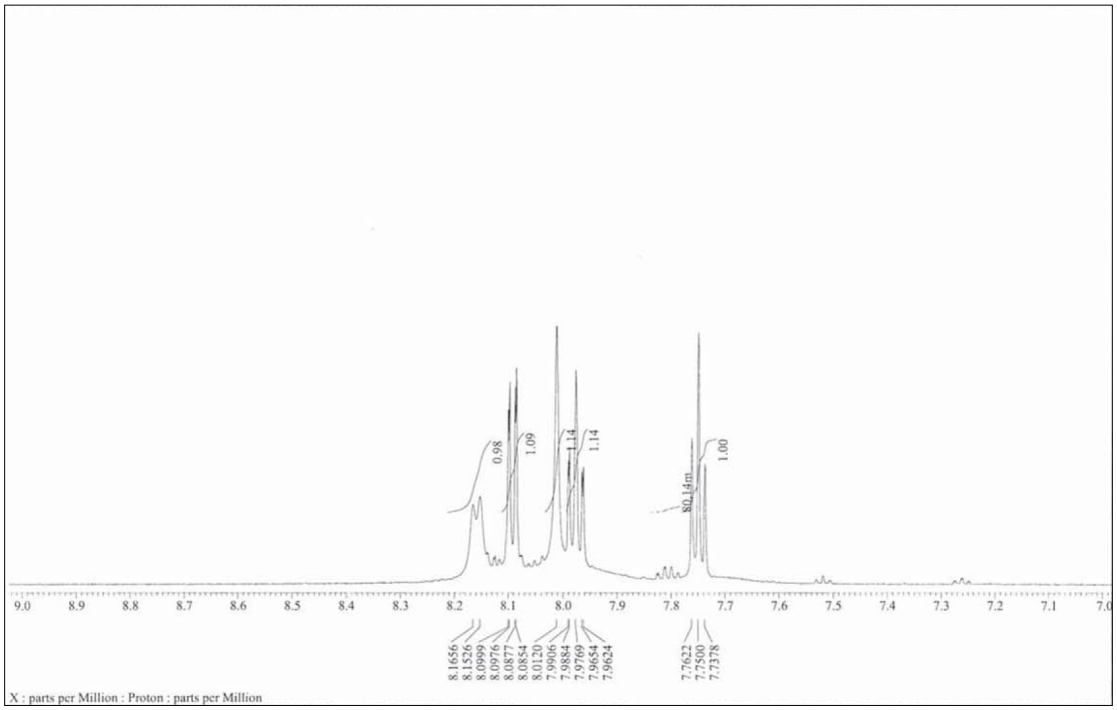
^{1}H-NMR spectra of BA (D_7-DMF, 600 MHz, RT). The lower spectrum is the expanded one.



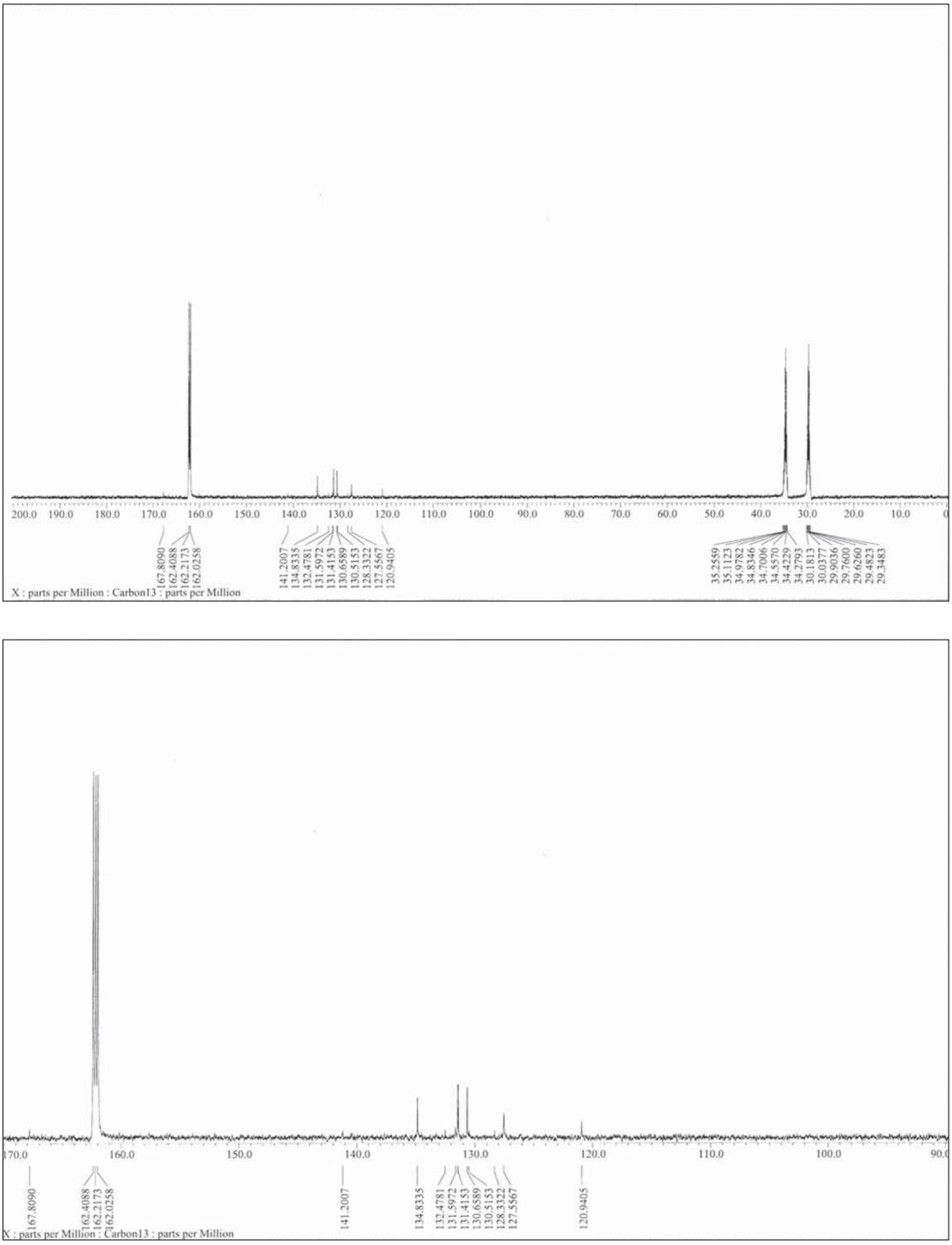
^{13}C-NMR spectra of BA (D_7-DMF, 150 MHz, RT). The lower spectrum is the expanded one.

12. ^{1}H NMR and ^{13}C NMR spectra (80°C) of *X*



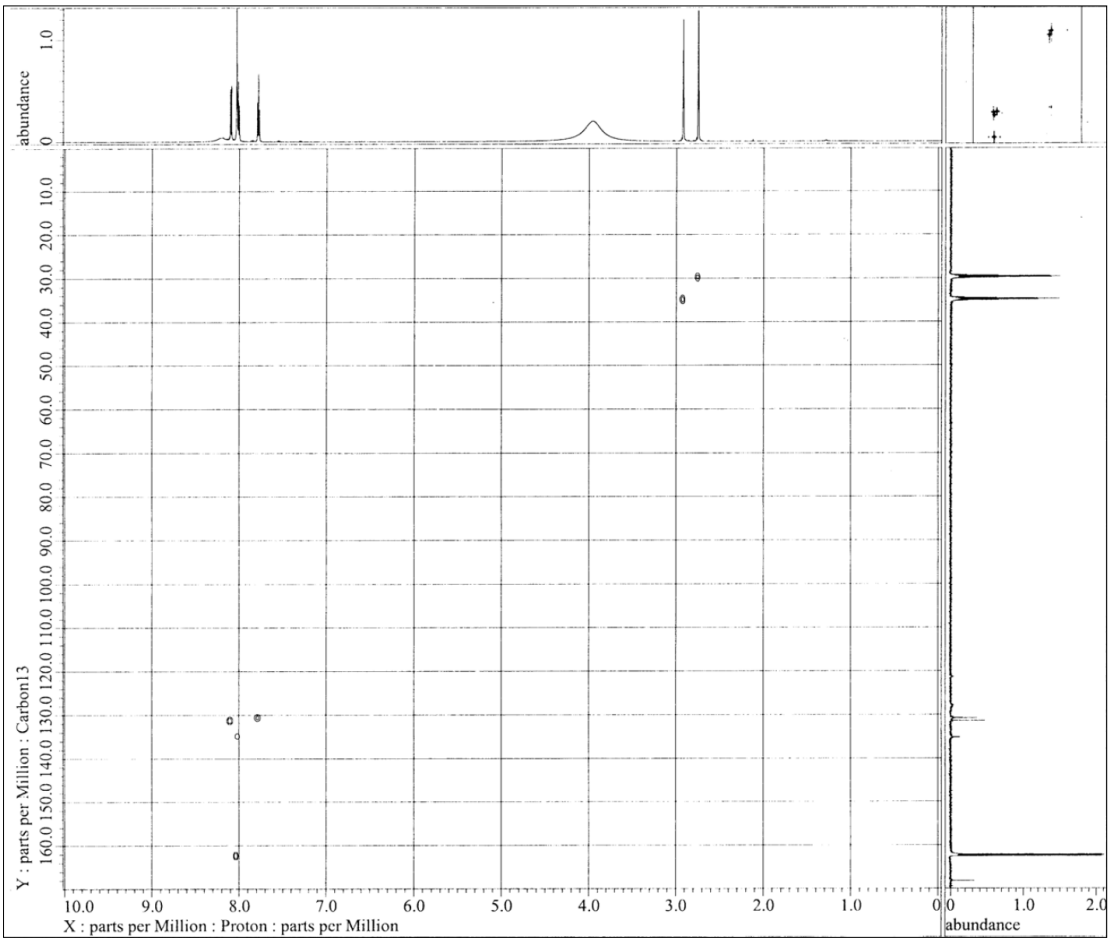


^{1}H-NMR spectra of ***X*** (D_7-DMF, 600 MHz, 80°C). The lower spectrum is the expanded one.

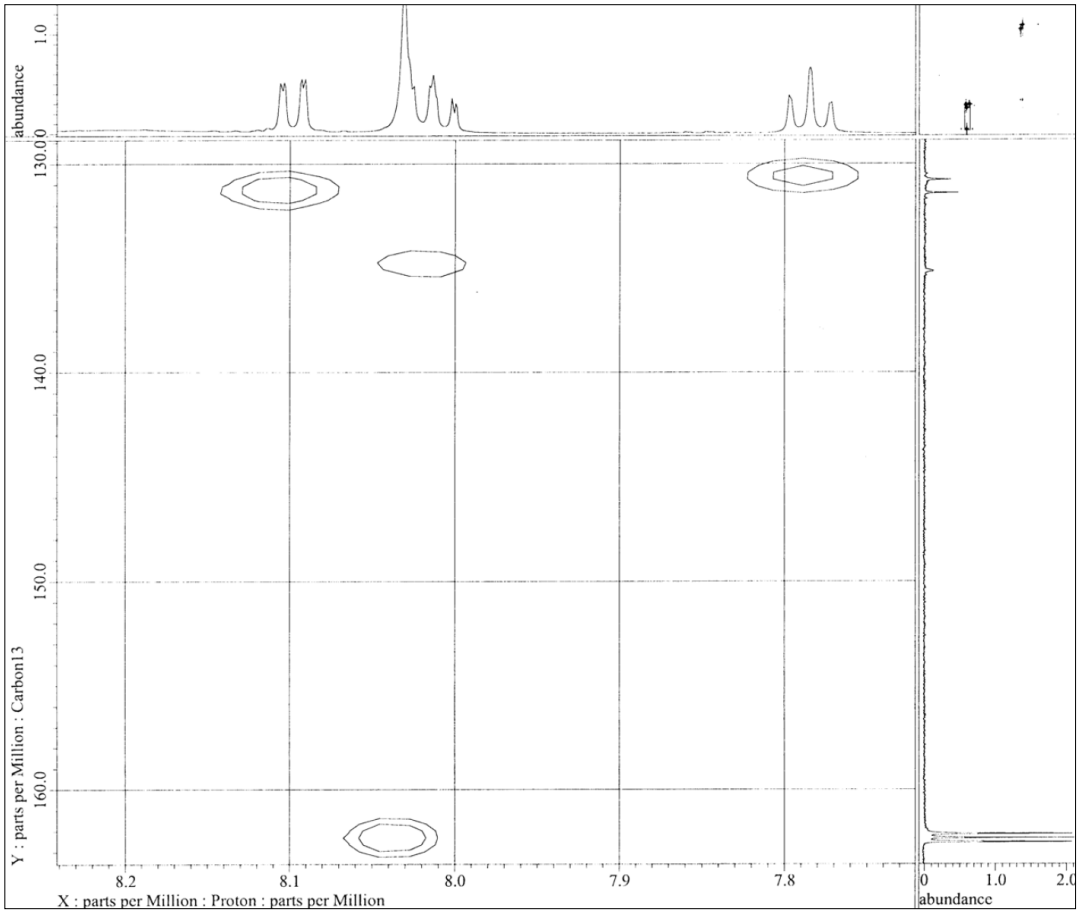


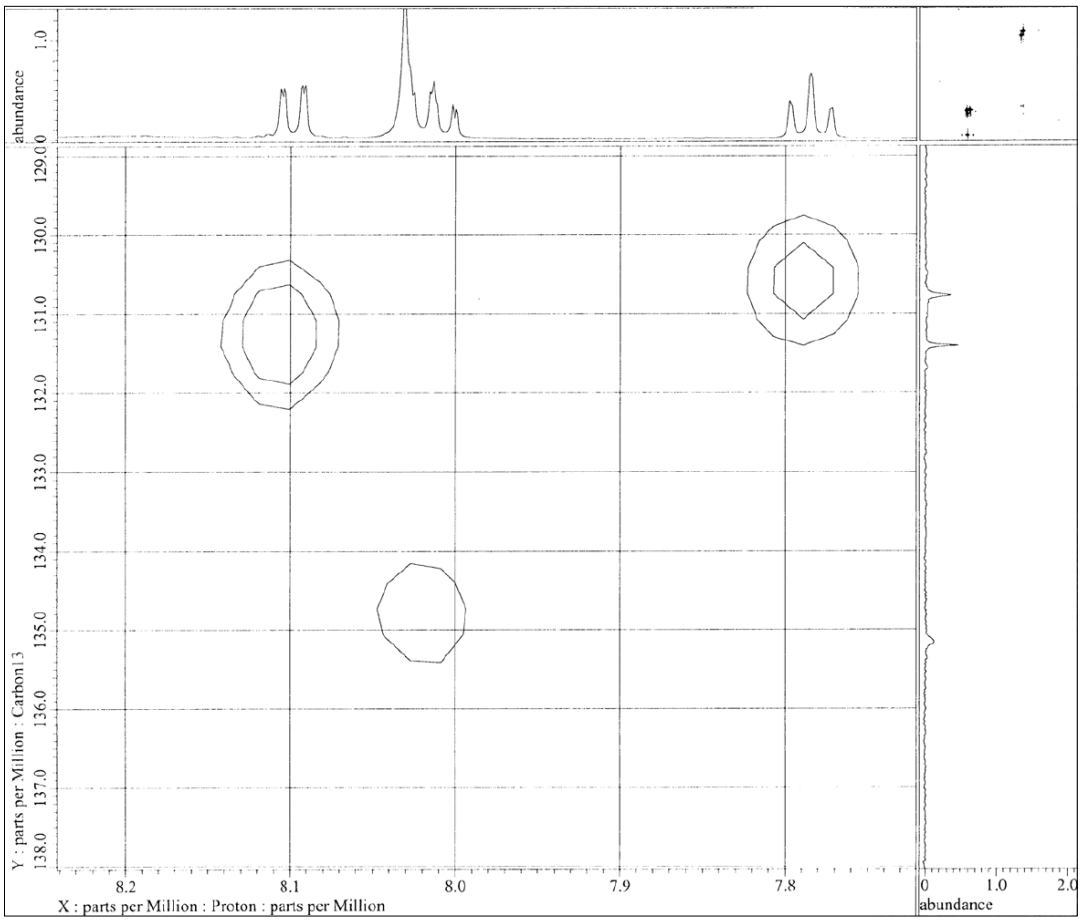
^{13}C-NMR spectra of ***X*** (D_7-DMF, 150 MHz, 80 °C). The lower spectrum is the expanded one.

13. HMQC, HMBC of *X* (RT)

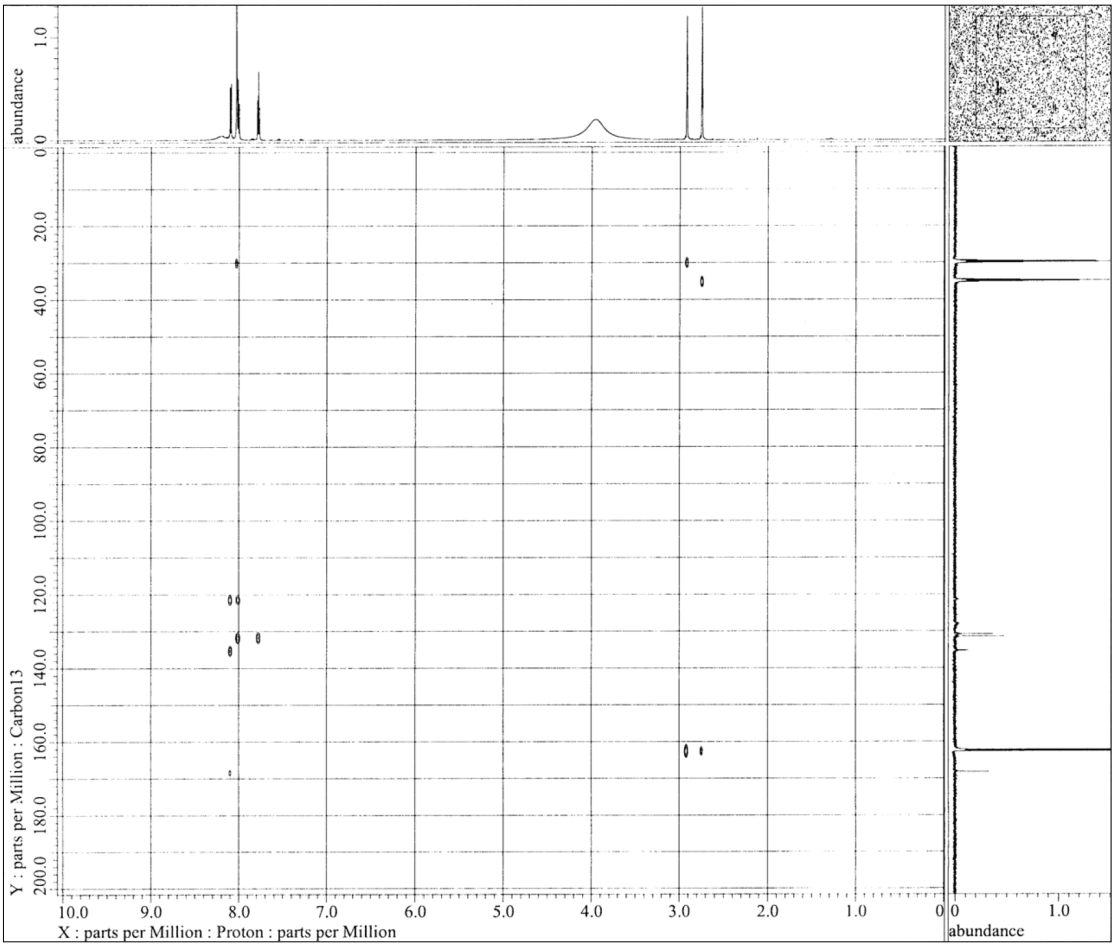


HMQC of ***X*** (D_7-DMF, 600 MHz, RT).

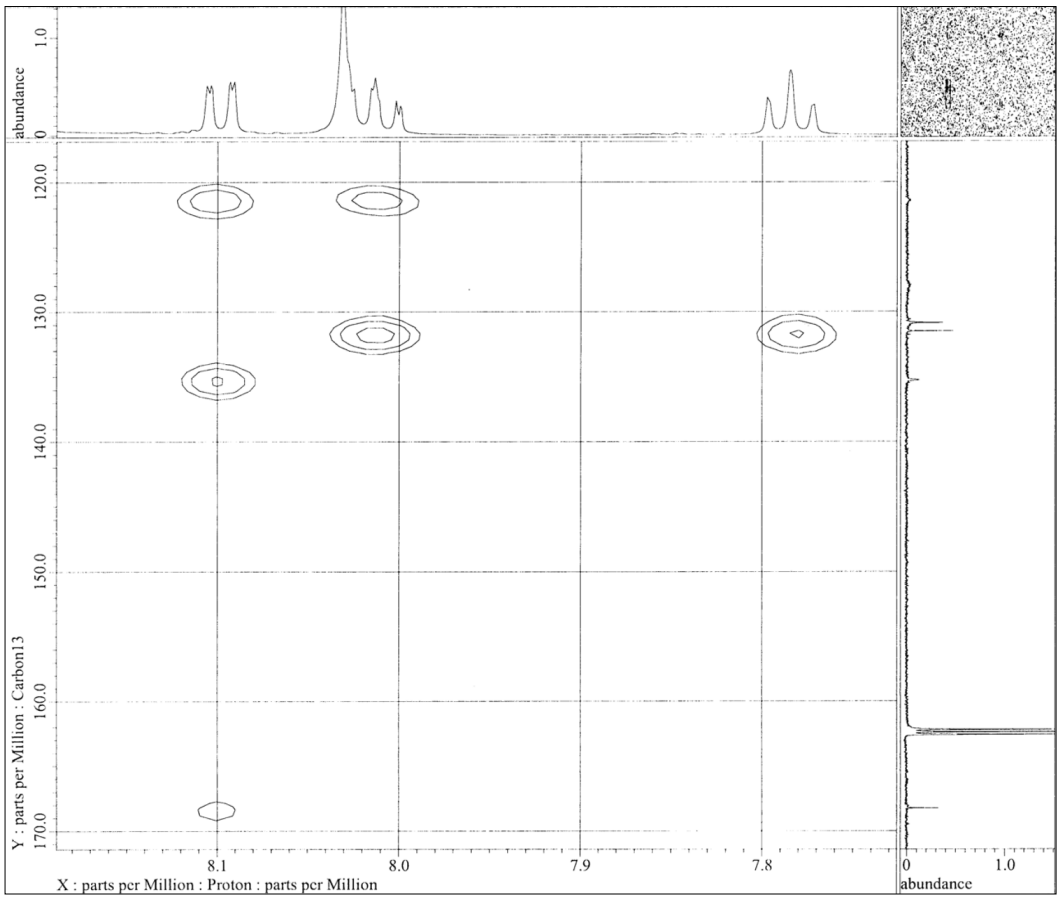


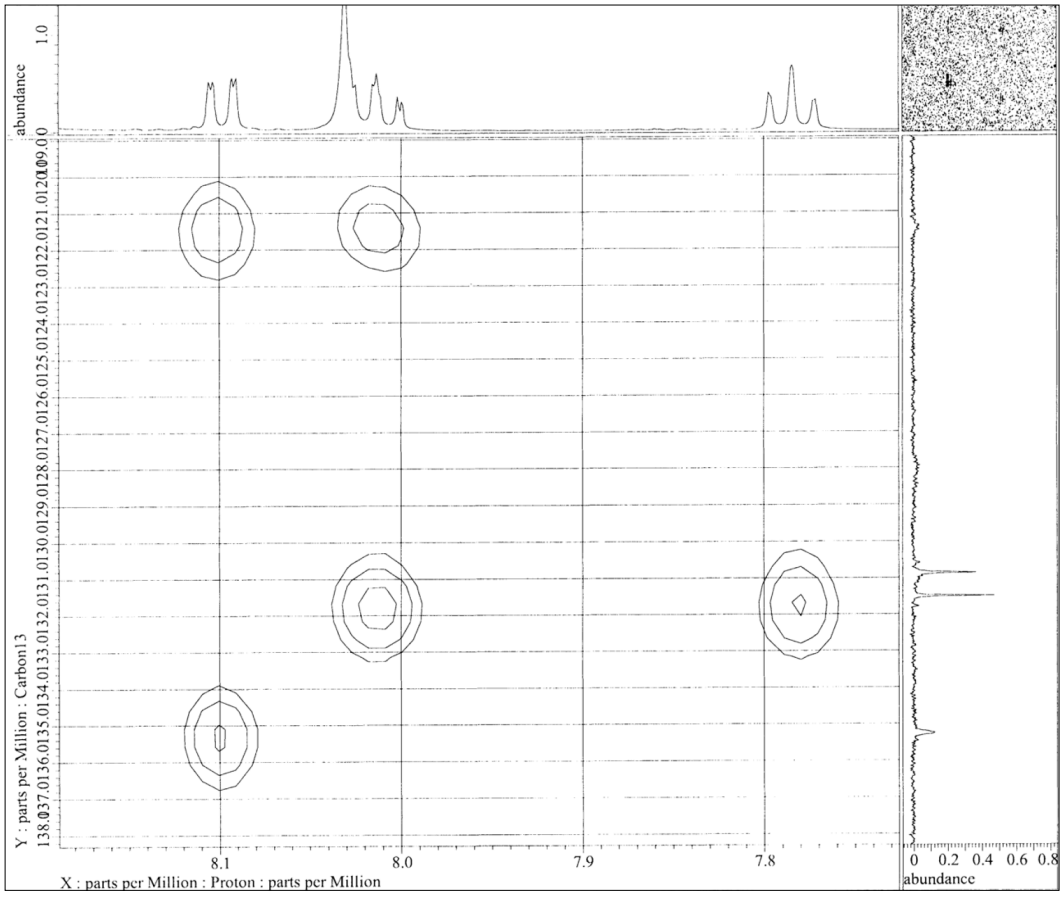


Expanded HMQC of ***X*** (D_7-DMF, 600 MHz, RT).



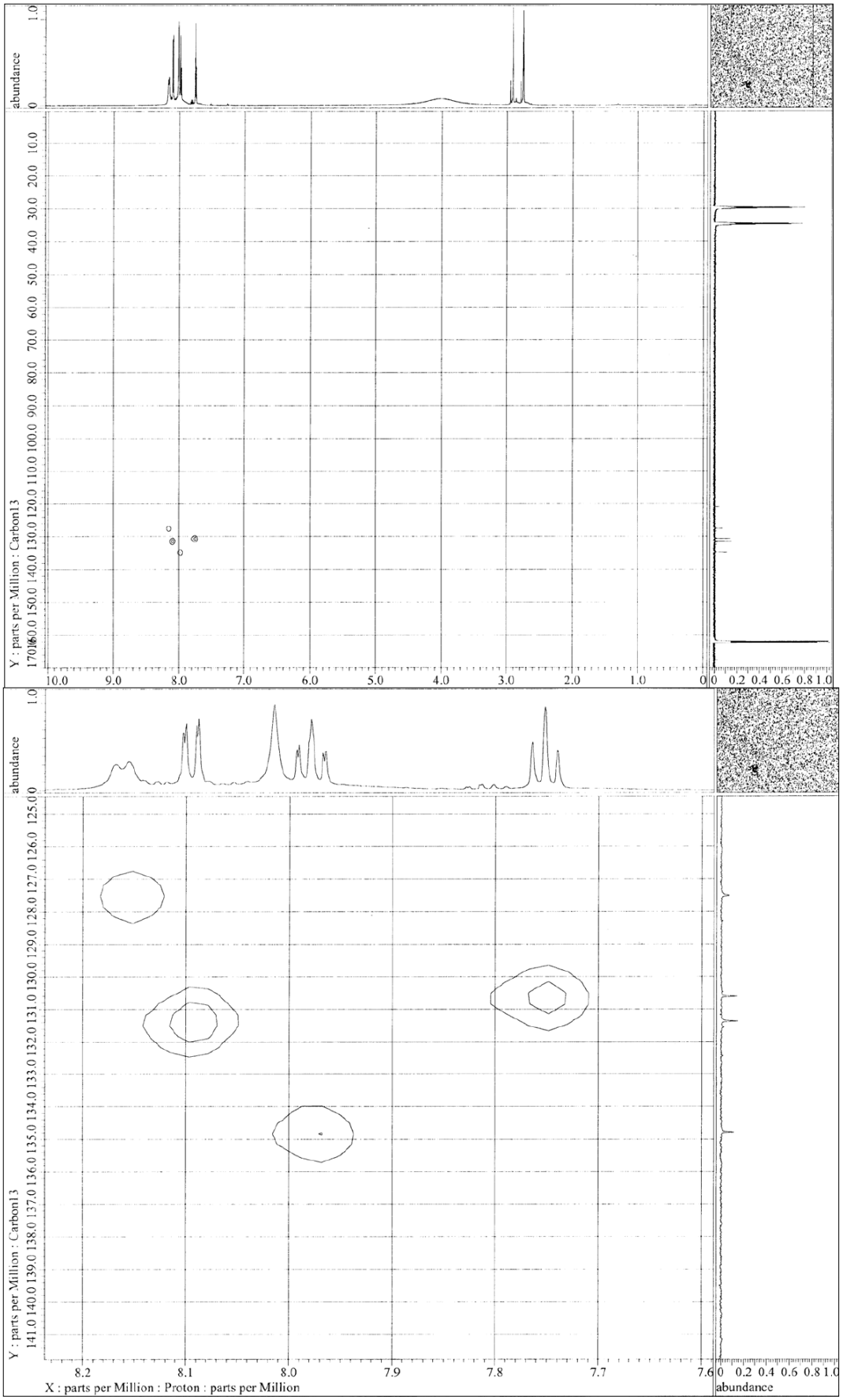
HMBC of ***X*** (D_7-DMF, 600 MHz, RT).



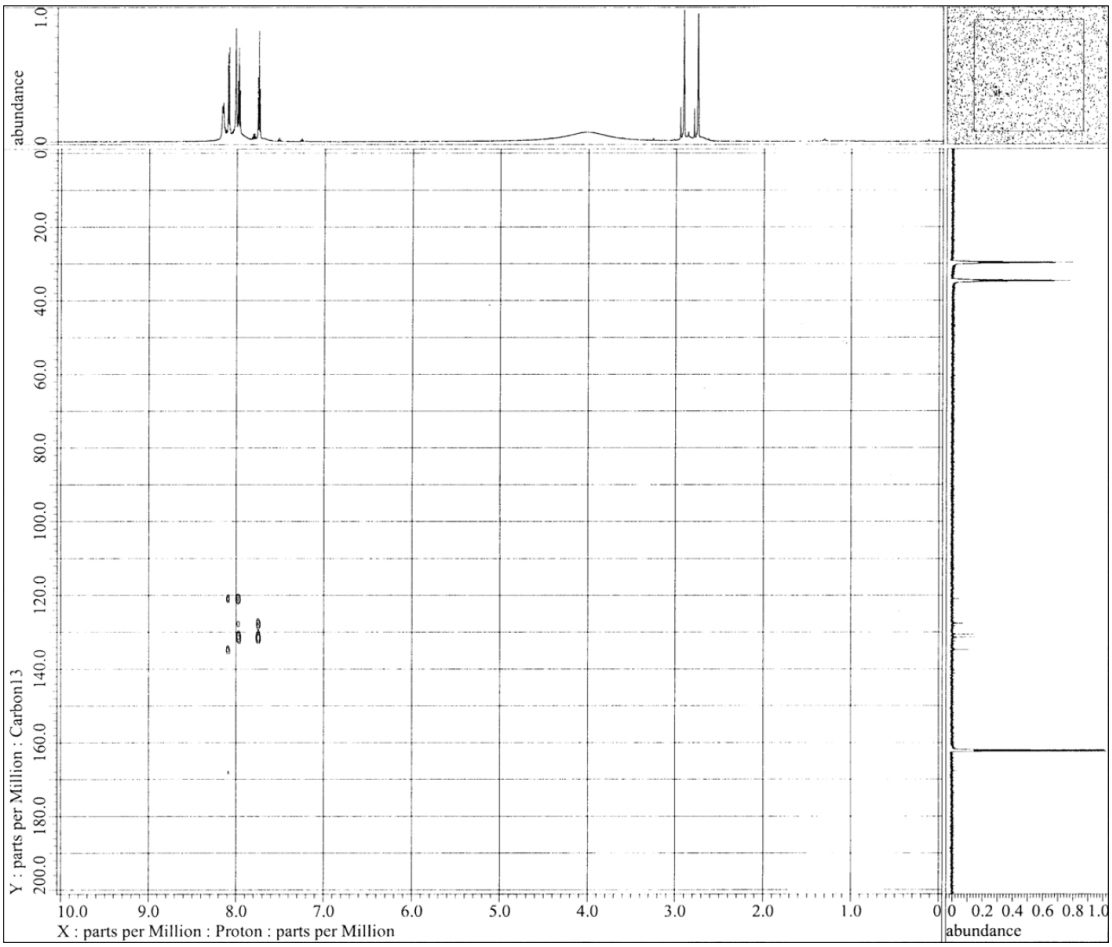


Expanded HMBC of ***X*** (D_7-DMF, 600 MHz, RT).

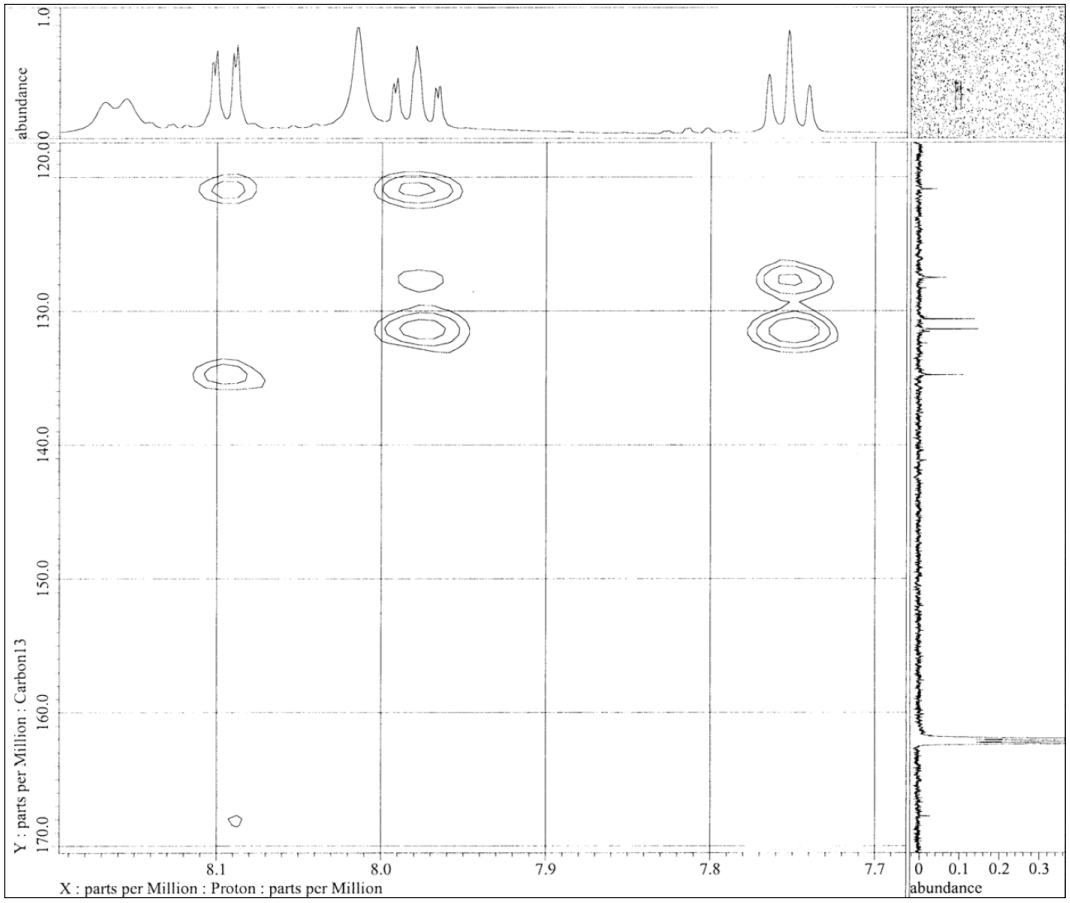
14. HMQC, HMBC of *X* (80°C)

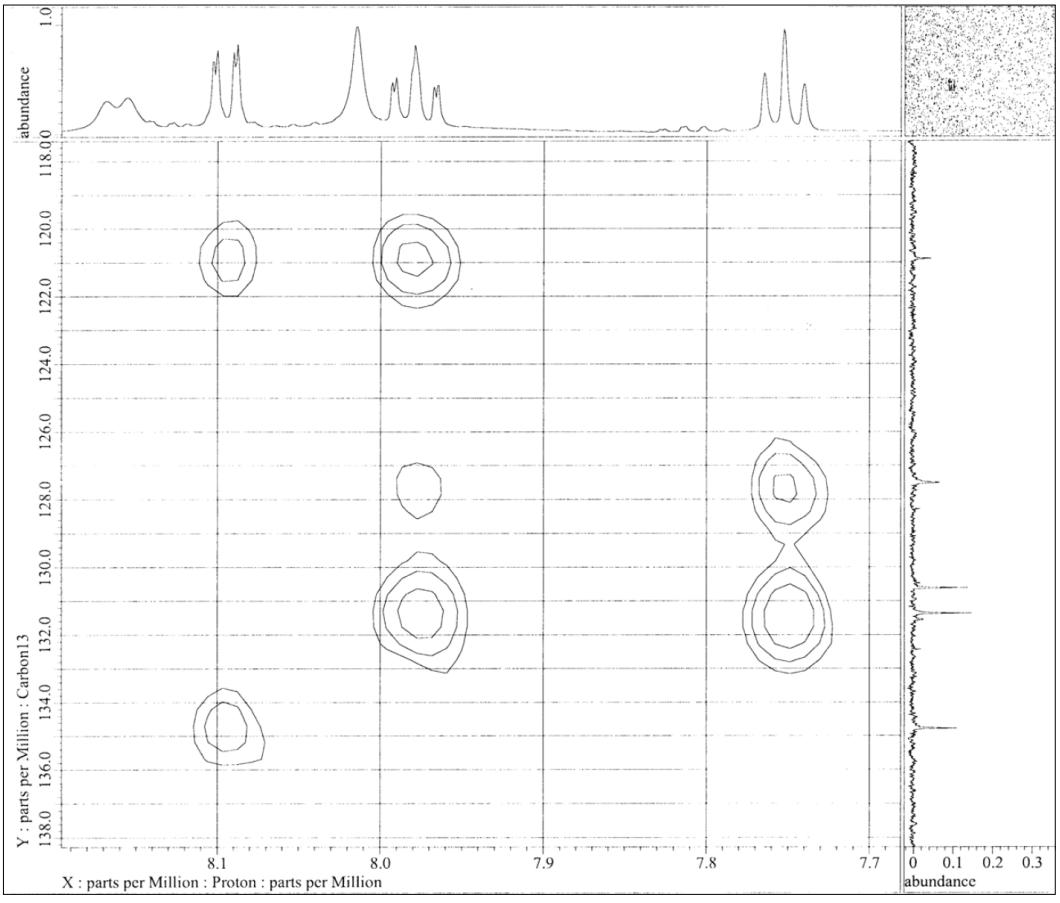


HMQC of ***X*** (D_7-DMF, 600 MHz, 80°C). The lower spectrum is the expanded one.



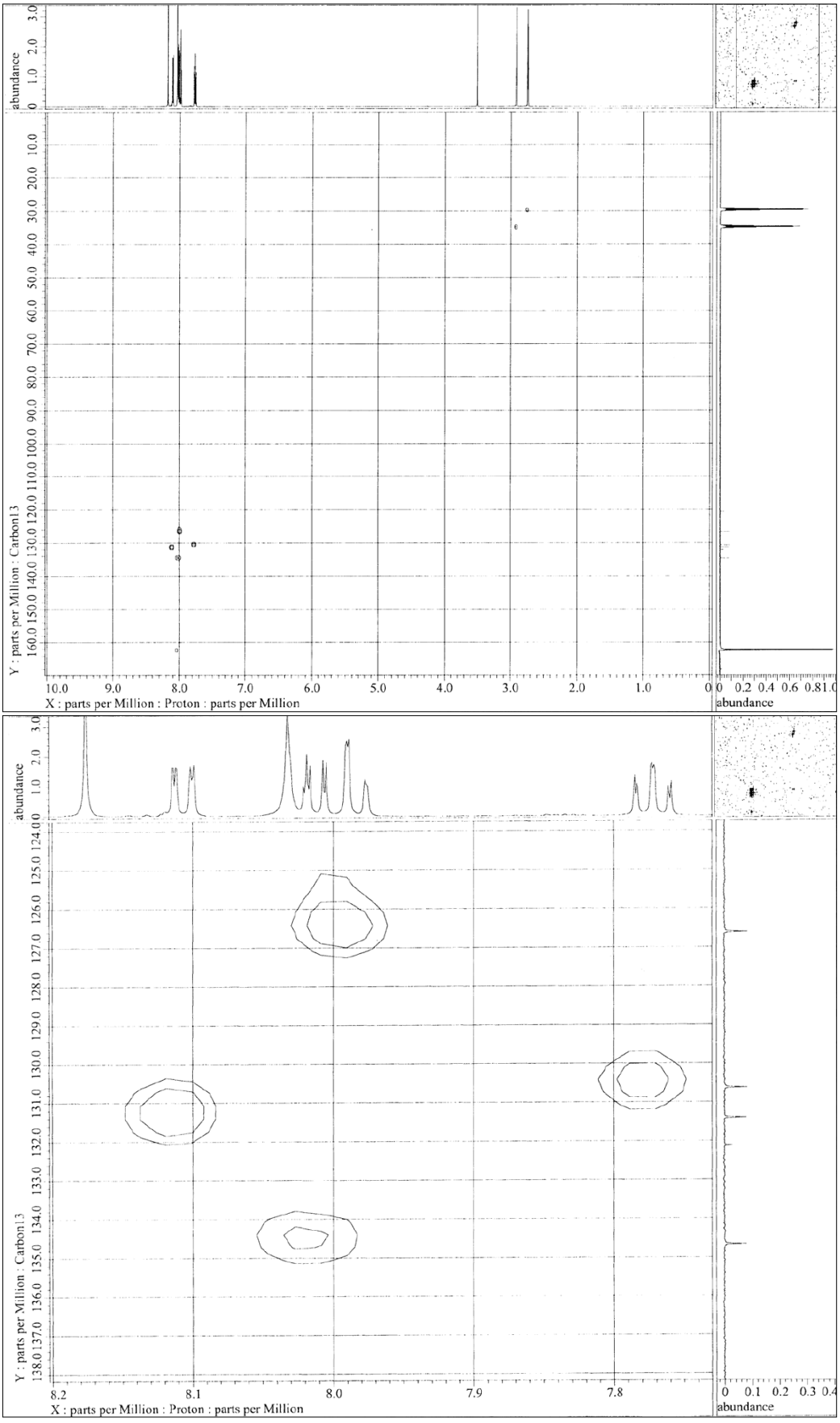
HMBC of ***X*** (D_7-DMF, 600 MHz, 80°C).



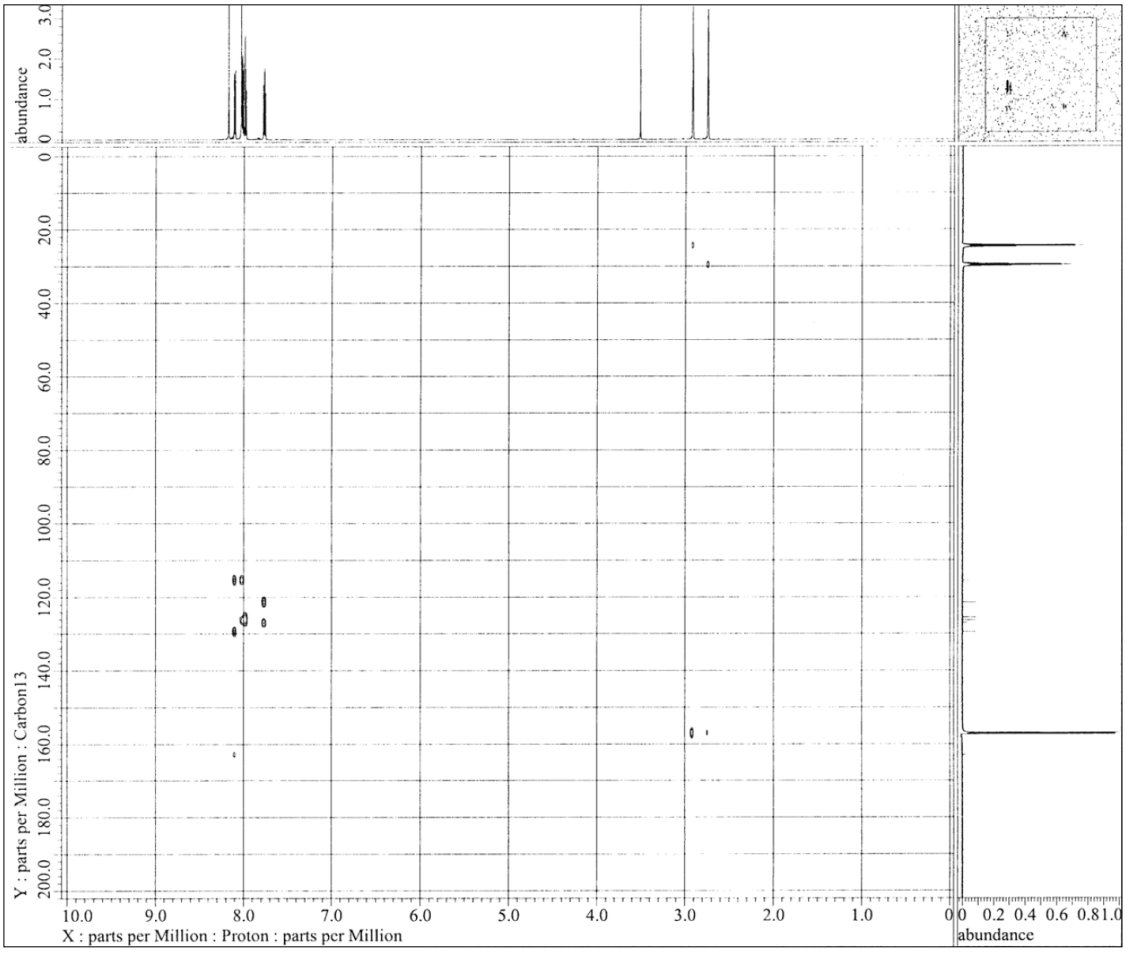


Expanded HMBC of ***X*** (D_7-DMF, 600 MHz, 80°C)

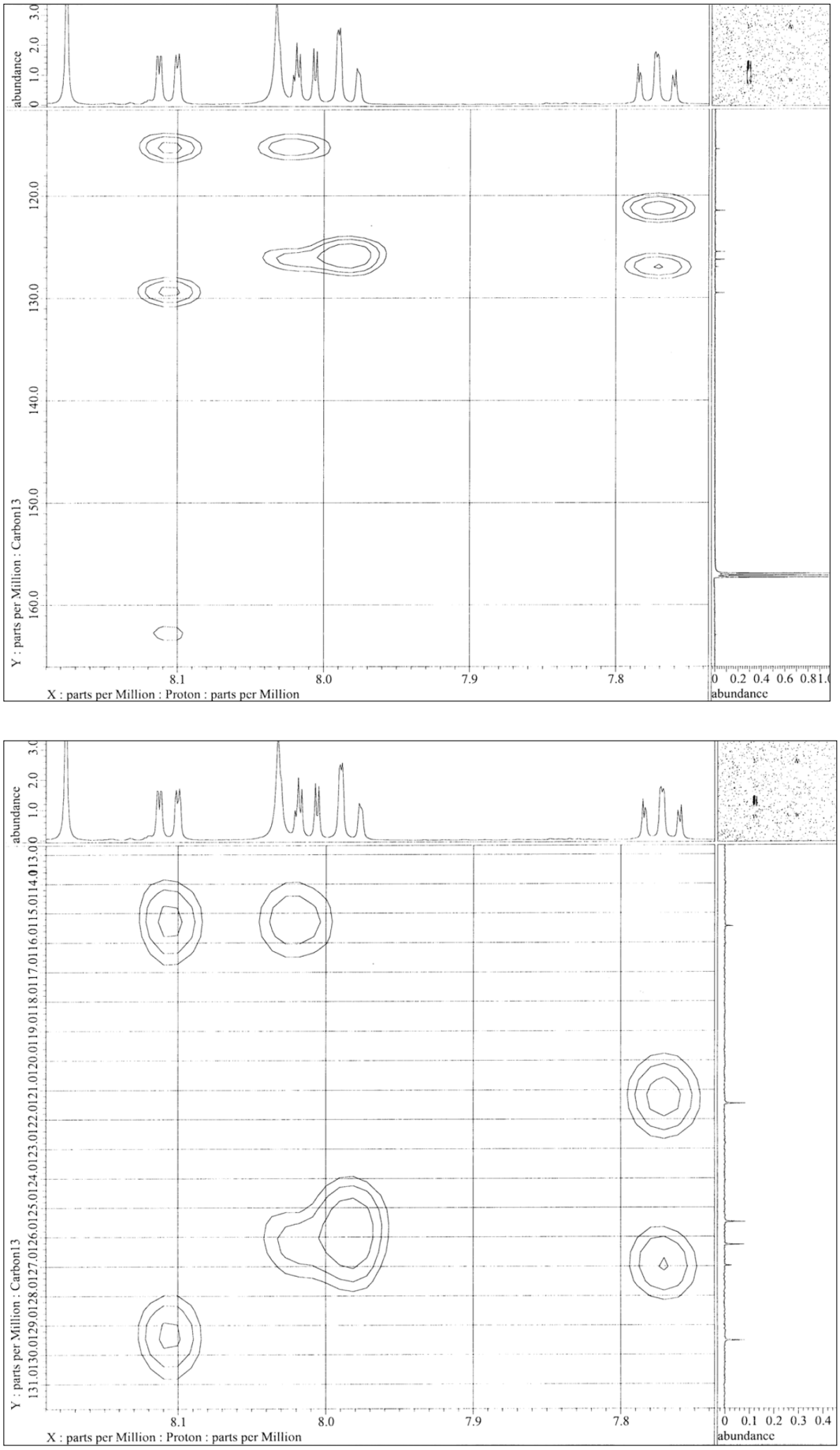
15. HMQC, HMBC of IBA (RT)



HMQC of IBA (D_7-DMF, 600 MHz, RT). The lower spectrum is the expanded one.

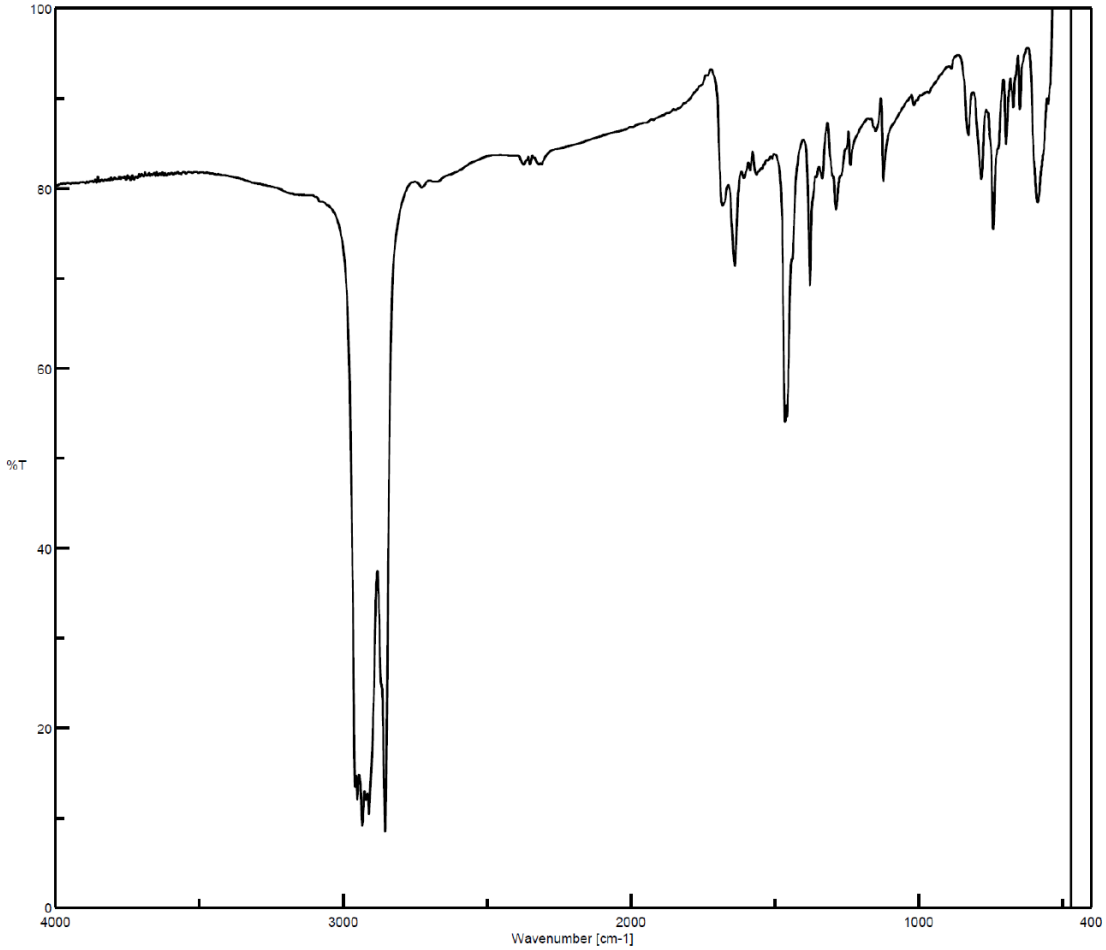


HMBC of IBA (D_7-DMF, 600 MHz, RT).

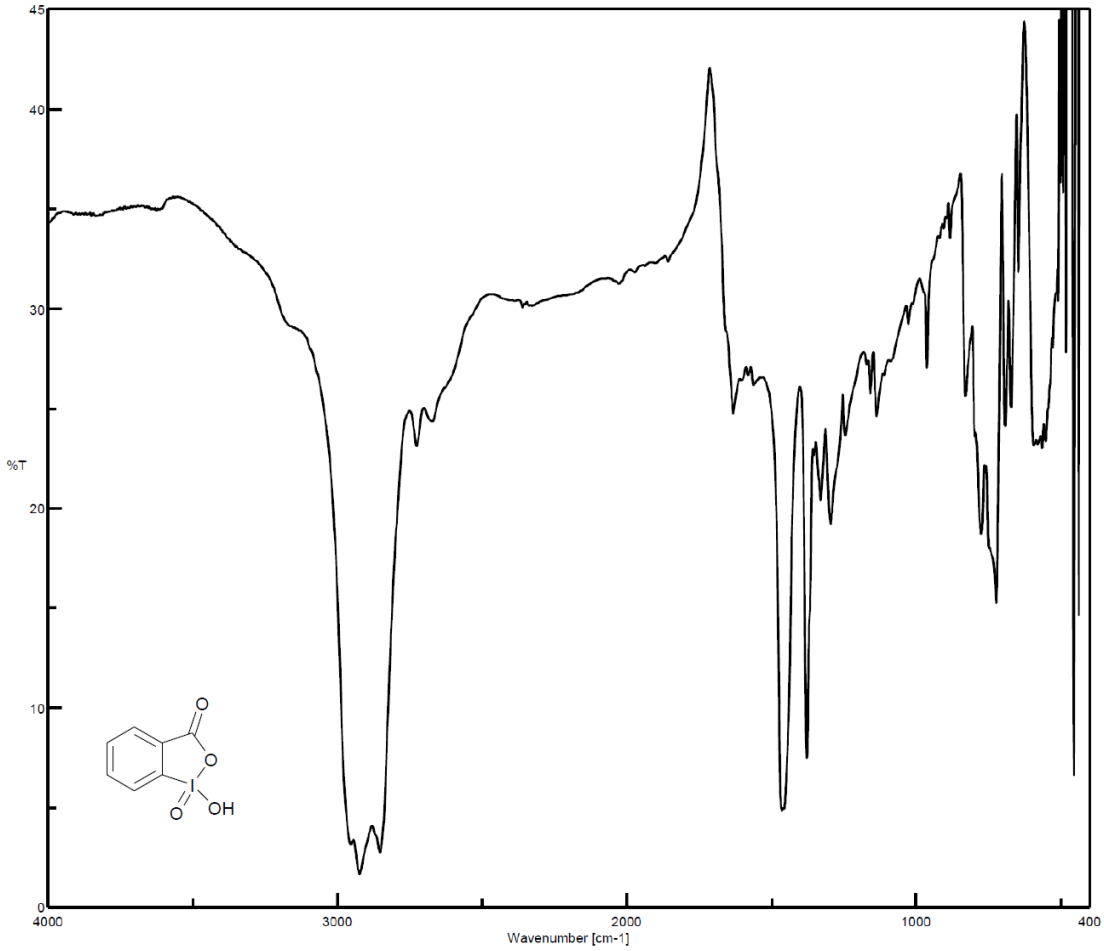


Expanded HMBC of IBA (D_7-DMF, 600 MHz, RT).

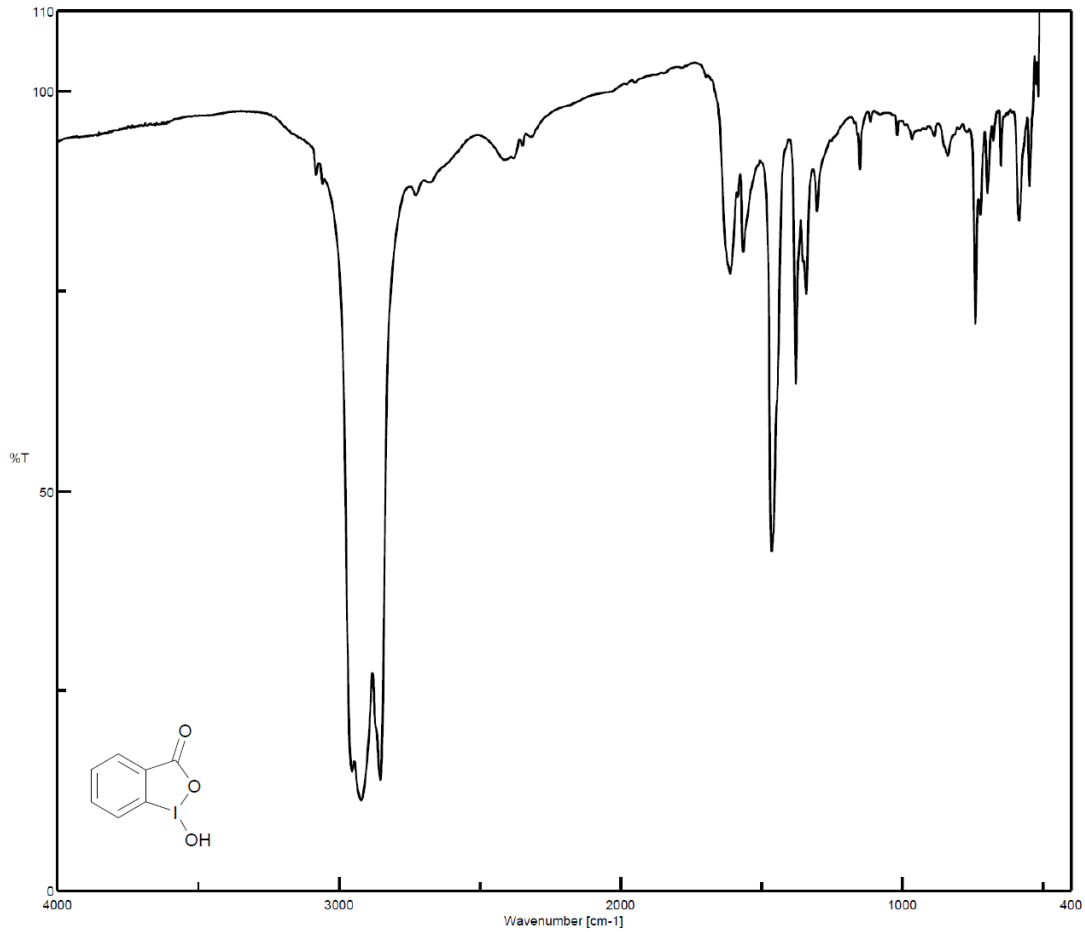
16. IR spectra of *X*, IBX, IBA and BA



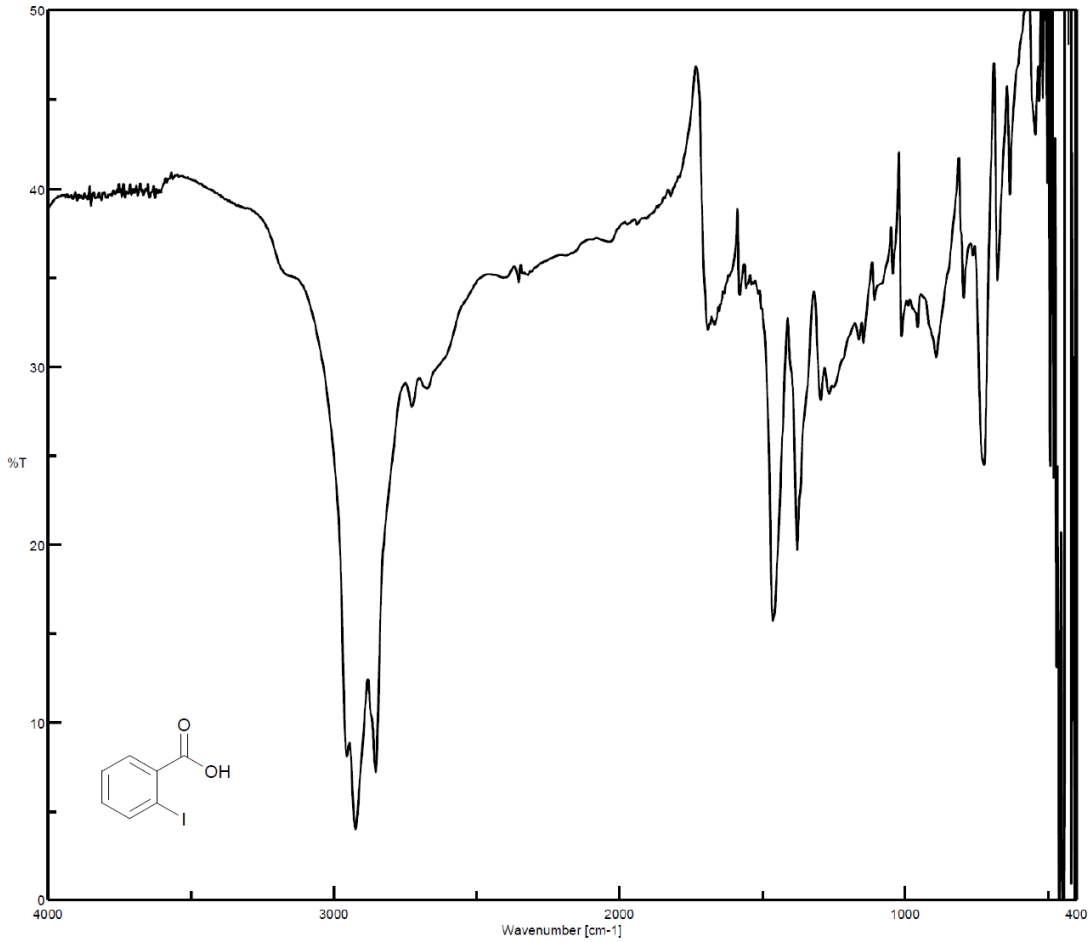
IR spectra (Nujol) of ***X***



IR spectra (Nujol) of *o*-iodoxybenzoic acid (IBX)



IR spectra (Nujol) of *o*-iodosobenzoic acid (IBA)



IR spectra (Nujol) of iodobenzoic acid (BA)