

REFERENCES

- [1] Office of the Forest Herbarium, National Park, Wildlife and Plant Conservation Department, Thailand [Online]. Available from: www.dnp.go.th [2007; Dec 7].
- [2] Singh, V.; Singh, J.; Sharma, J. P. Antraquinones from *Cassia siamea*. *Phytochemistry* 31(1992): 2176 – 2177.
- [3] Koyama, J.; Morita, I.; Tagahara, K.; Aqil, M. Biantraquinones from *Cassia siamea*. *Phytochemistry* 56(2001): 849 – 851.
- [4] El-Sayyad, S. M.; Ross, S. A.; Sayed, H. M. New isoquinolone alkaloids from the leaves of *Cassia siamea*. *Journal of Natural Products* 47(1984): 708 – 719.
- [5] Arora, S.; Deymann, H.; Tiwari, R. D.; Winterfeldt, E. A new chromone from *Cassia siamea*. *Tetrahedron* 27(1971): 981 – 984.
- [6] Biwas, K. M.; Mallik, H. Cassiadinine, a chromone alkaloid and (+)-6-hydroxymellein, a dihydroisocoumarin from *Cassia siamea*. *Phytochemistry* 25(1986): 1727 – 1730.
- [7] Hassanali, A.; King, T. J.; Wallwork, S. C. Barakol, a novel dioxaphenalene derivative from *Cassia siamea*. *Chemical Communications* 12(1969): 678.
- [8] Bycroft, B. W.; Hassanali-Walji, A.; Johnson, A. W.; King, T. J. The structure and synthesis of barakol: a novel dioxaphenalene derivative from *Cassia siamea* Lamk. *Journal of Chemical Society C* 12(1970): 1686 – 1689.
- [9] Sukma, M.; Chaichantipyuth, C.; Murakami, Y.; Tohda, M.; Matsumoto, K.; Watanabe, H. CNS inhibitory effects of barakol, a constituent of *Cassia siamea* Lamk. *Journal of Ethnopharmacology* 83(2002): 87 – 94.
- [10] Deachapunya, C.; Poonyachoti, S.; Thongsard, W.; Krishnamra, N. Barakol extracted from *Cassia siamea* stimulates chloride secretion in rat colon. *Journal of Pharmacology and Experimental Therapeutics* 314(2005): 732 – 737.

- [11] Deachapunya, C.; Thongsaard, W.; Poonyachoti, S. Barakol suppresses norepinephrine-induced inhibition of spontaneous longitudinal smooth muscle contractions in isolated rat small intestine. *Journal of Ethnopharmacology* 101(2005): 227 – 232.
- [12] Morita, H.; Oshimi, S.; Hirasawa, Y.; Koyama, K.; Honda, T.; Ekasari, W.; Indrayanto, G.; Zaini, N. C. Cassiarins A and B, novel antiplasmodial alkaloids from *Cassia siamea*. *Organic Letters* 9(2007): 3691 – 3693.
- [13] Rudyanto, M.; Tomizawa, Y.; Morita, H.; Honda, T. First total synthesis of Cassiarin A, a naturally occurring potent antiplasmodial alkaloid. *Organic Letters* 10(2008): 1921 – 1689.
- [14] Yao, Y.-S.; Yao, Z.-J. Biomimetic total syntheses of cassiarins A and B. *Journal of Organic Chemistry* 73(2008): 5221 – 5225.
- [15] Zappalà, M.; Grasso, S.; Micale, N.; Polimeni, S.; Micheli, C. D. A simple and efficient synthesis of GYKI 52466 and GYKI 52895. *Synthetic Communications* 32(2002): 527 – 533.
- [16] Deady, L. W.; Smith, C. L. Tetracycle formation from the reaction of acetophenones with 1-aminoantraquinone, and further annulation of pyridine and diazepine rings. *Australian Journal of Chemistry* 56(2003): 1219 – 1224.
- [17] Kibalny, A. V.; Afonin, A. A.; Dulenko, V. I. Synthesis and reactions of 1-(3-chloropropyl)-6,7-dimethoxy-3-methylbenzo[*c*]pyrylium perchlorate. *Chemistry of Heterocyclic Compounds* 40(2004): 1131 – 1136.
- [18] Nenajdenko, V. G.; Druzhinin, S. V.; Balenkova, E. S. Efficient route to 6-CF₃-substituted nicotinic acid derivatives. *Journal of Fluorine Chemistry* 127(2006): 865 – 873.
- [19] Ponte-Sucre, A.; Faber, J. H.; Gulder, T.; Kajahn, I.; Pedersen, S. E. H.; Schultheis, M.; Bringmann, G.; Moll, H. Activities of naphthylisoquinoline alkaloids and synthetic analogs against *Leishmania major*. *Antimicrobial Agents and Chemotherapy* 51(2007): 188 – 194.

- [20] Tolkunov, S. V.; Kryuchkov, M. A.; Tolkunov, V. S.; Dulenko, V. I. Reaction of 1,3-substituted benzothieno[2,3-*c*]pyrylium salts with primary amines. *Chemistry of Heterocyclic Compounds* 40(2004): 1082 – 1086.
- [21] Trager, W.; Jensen, J. B. Human malaria parasites in continuous culture. *Science* 193(1976): 673 – 675.
- [22] Desjardins, R. E.; Canfield, C. J.; Haynes, J. D. Quantitative assessment of antimalarial activity *in vitro* by a semiautomated microdilution technique. *Antimicrobial Agents and Chemotherapy* 16(1979): 710 – 718.
- [23] Twentyman, P. R.; Luscombe, M. A study of some variables in a tetrazolium dye (MTT) based assay for cell growth and chemosensitivity. *British Journal of Cancer* 56(1987): 279 – 285.
- [24] Carmichael, J.; DeGraff, W. G.; Gazdar, A. F.; Minna, J. D.; Mitchell, J. B. Evaluation of a tetrazolium-based semiautomated colorimetric assay: Assessment of chemosensitivity testing. *Cancer Reserch* 47(1987): 936 – 942.

APPENDICES

APPENDIX A

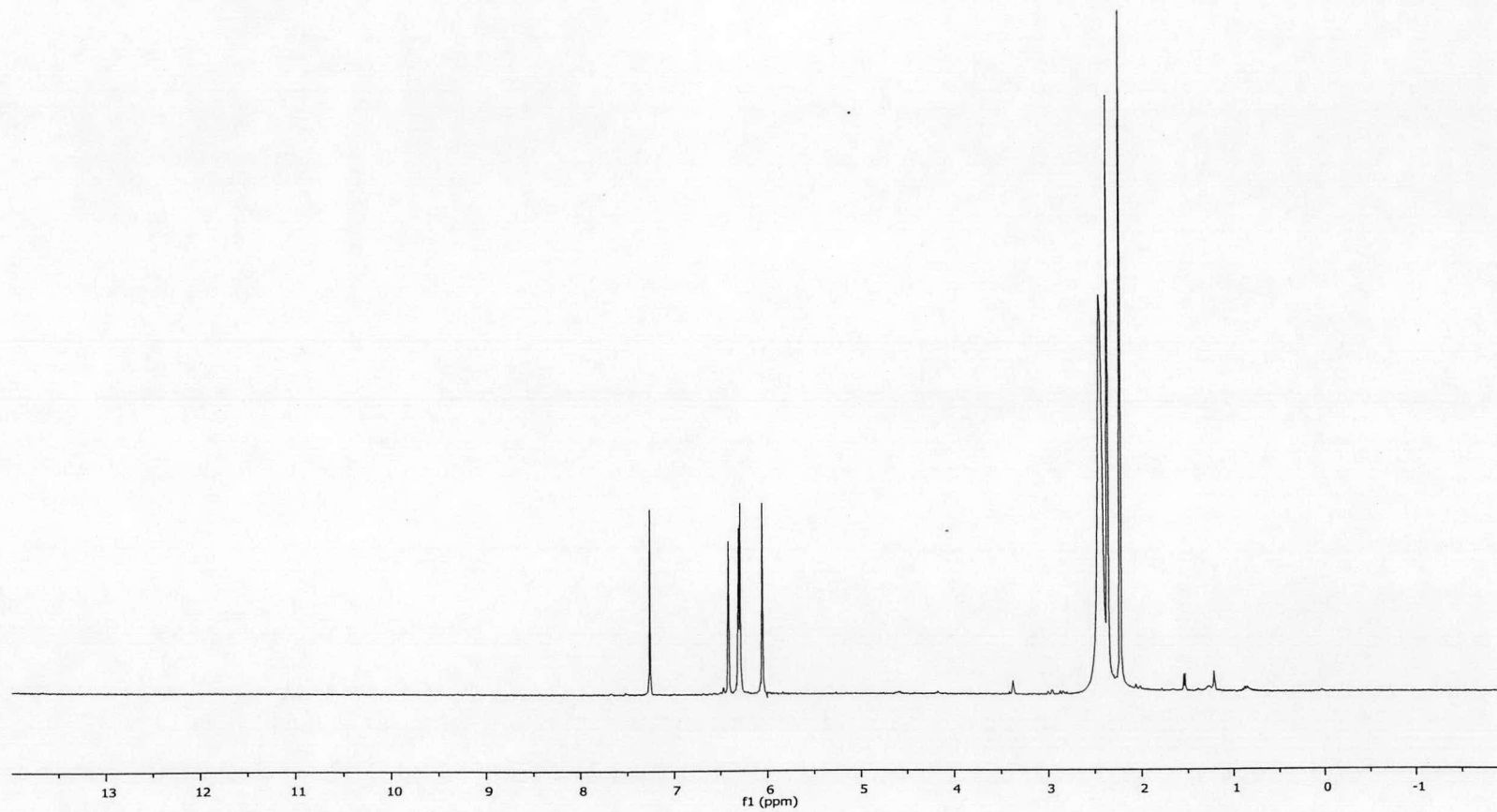


Figure A-1 $^1\text{H-NMR}$ spectrum of barakol obtained in CDCl_3 (Compound **1**)

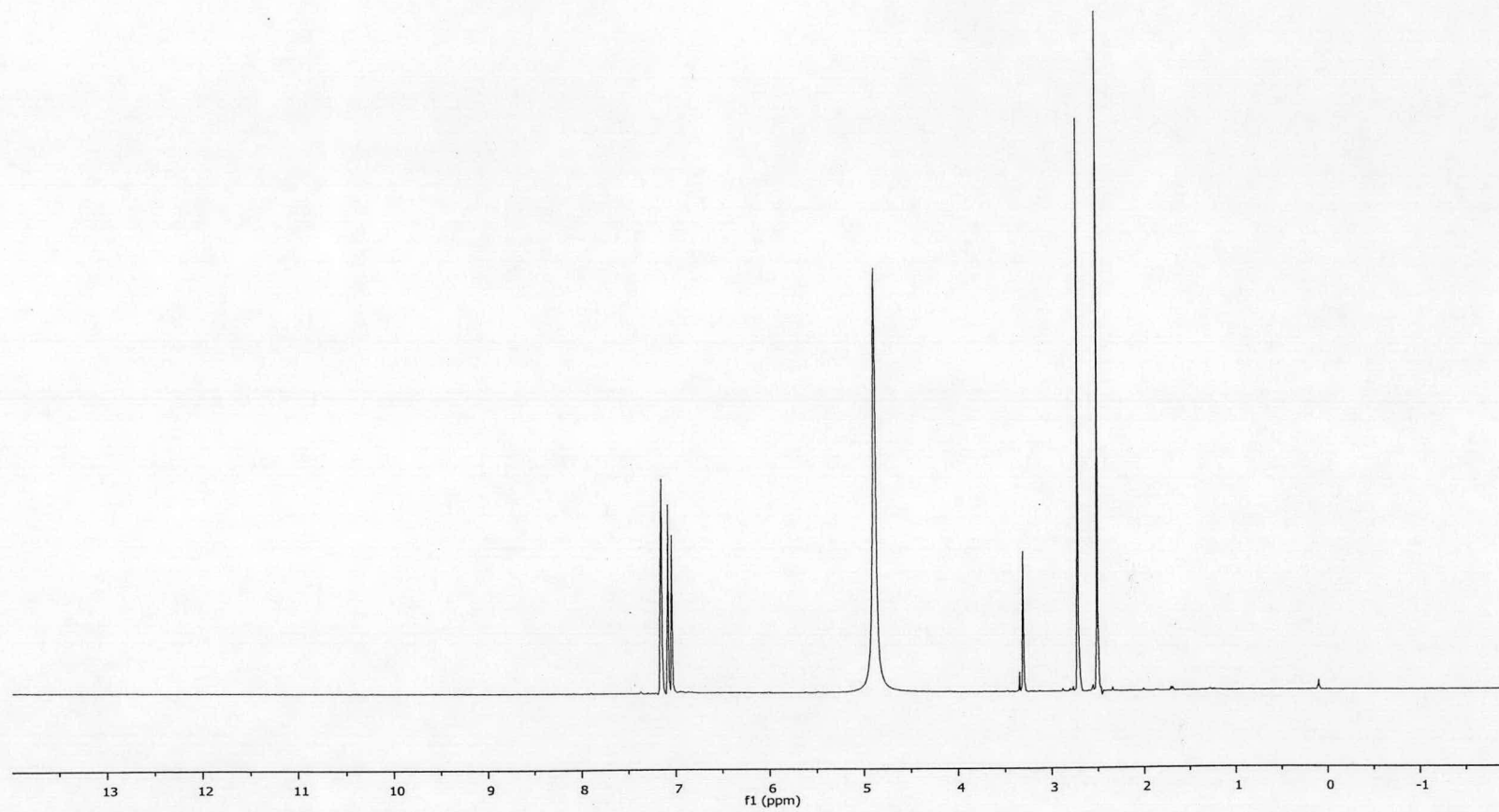


Figure A-2 ^1H -NMR spectrum of anhydrobarakol chloride obtained in CD_3OD (Compound **3**)

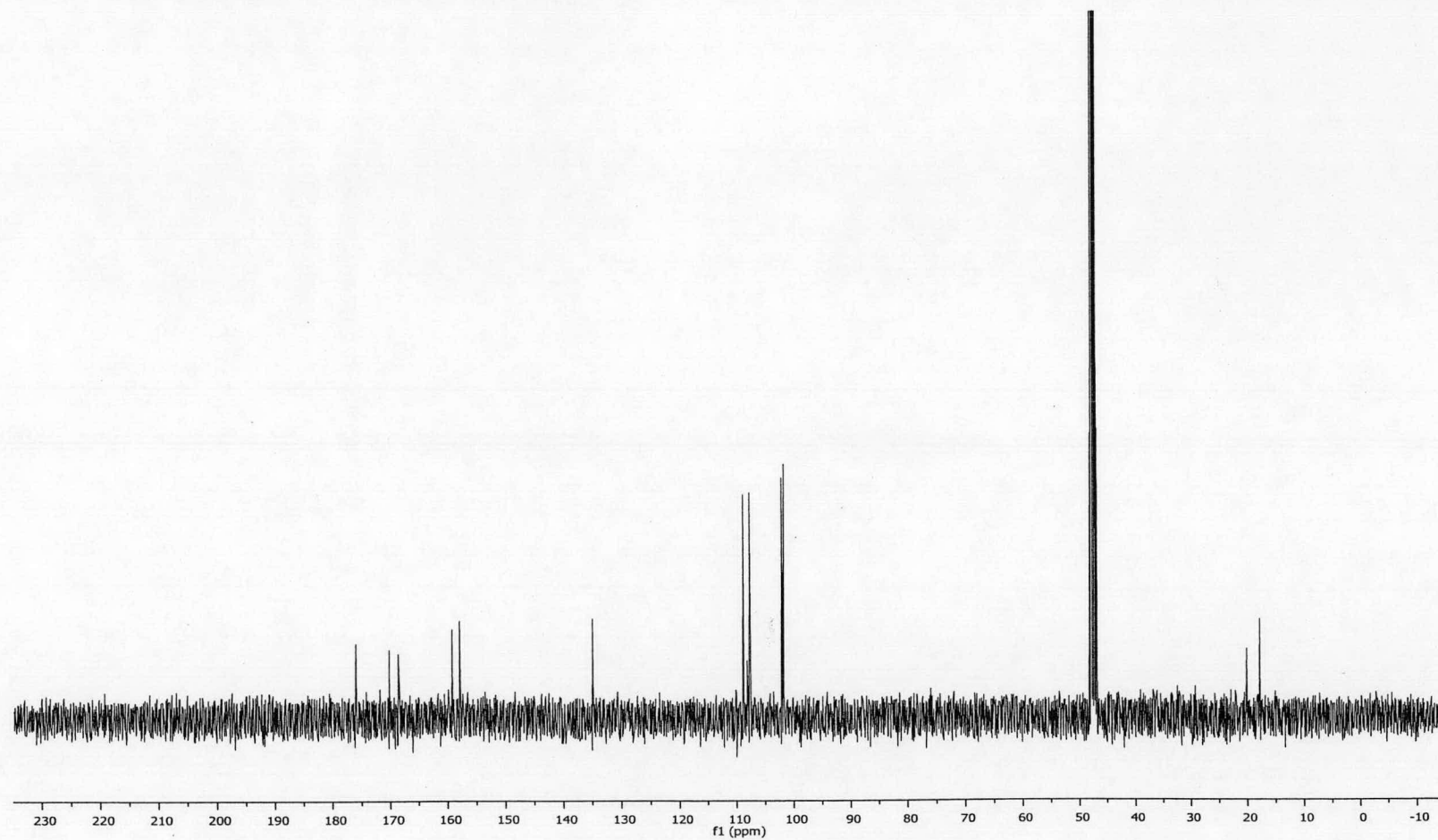


Figure A-3 ^{13}C -NMR spectrum of anhydrobarakol chloride obtained in CD_3OD (Compound 3)

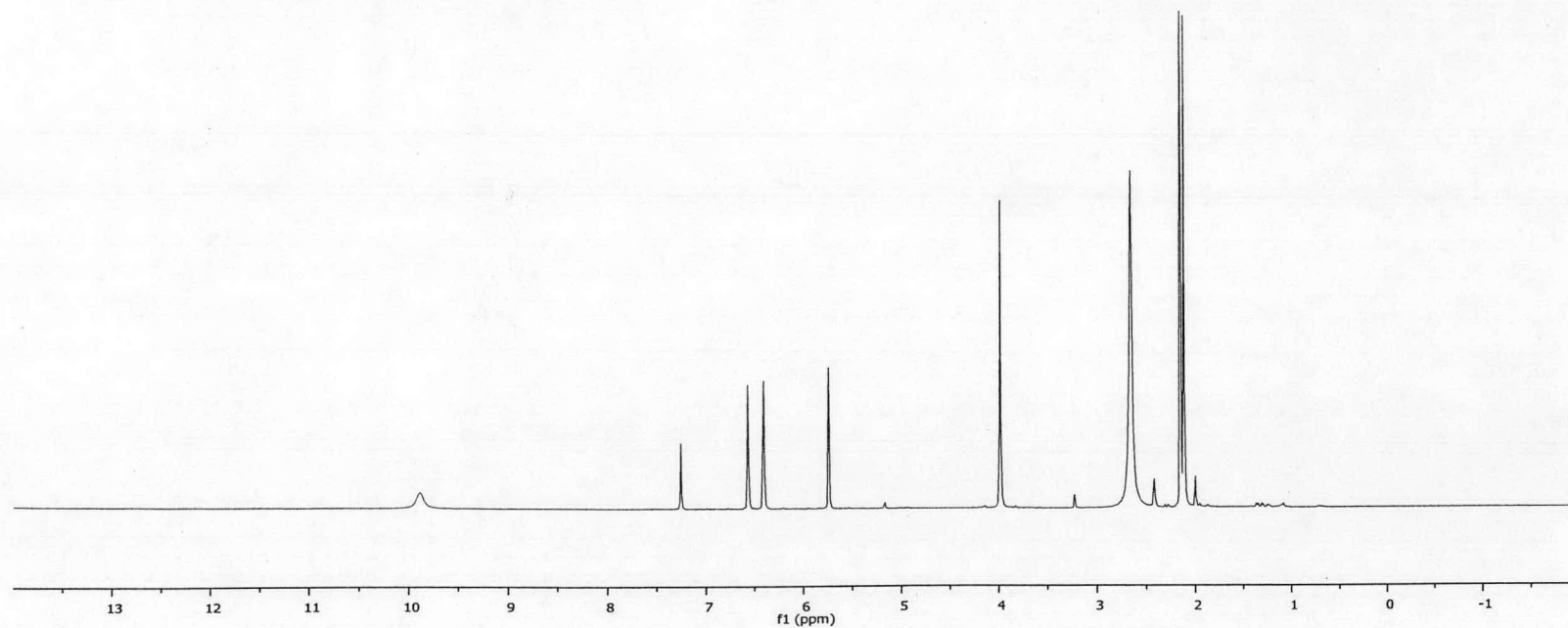


Figure A-4 ¹H-NMR spectrum of 5-acetyl-7-hydroxy-2-methyl chromone obtained in CDCl₃/DMSO-*d*₆ (9:1) (Compound 27)

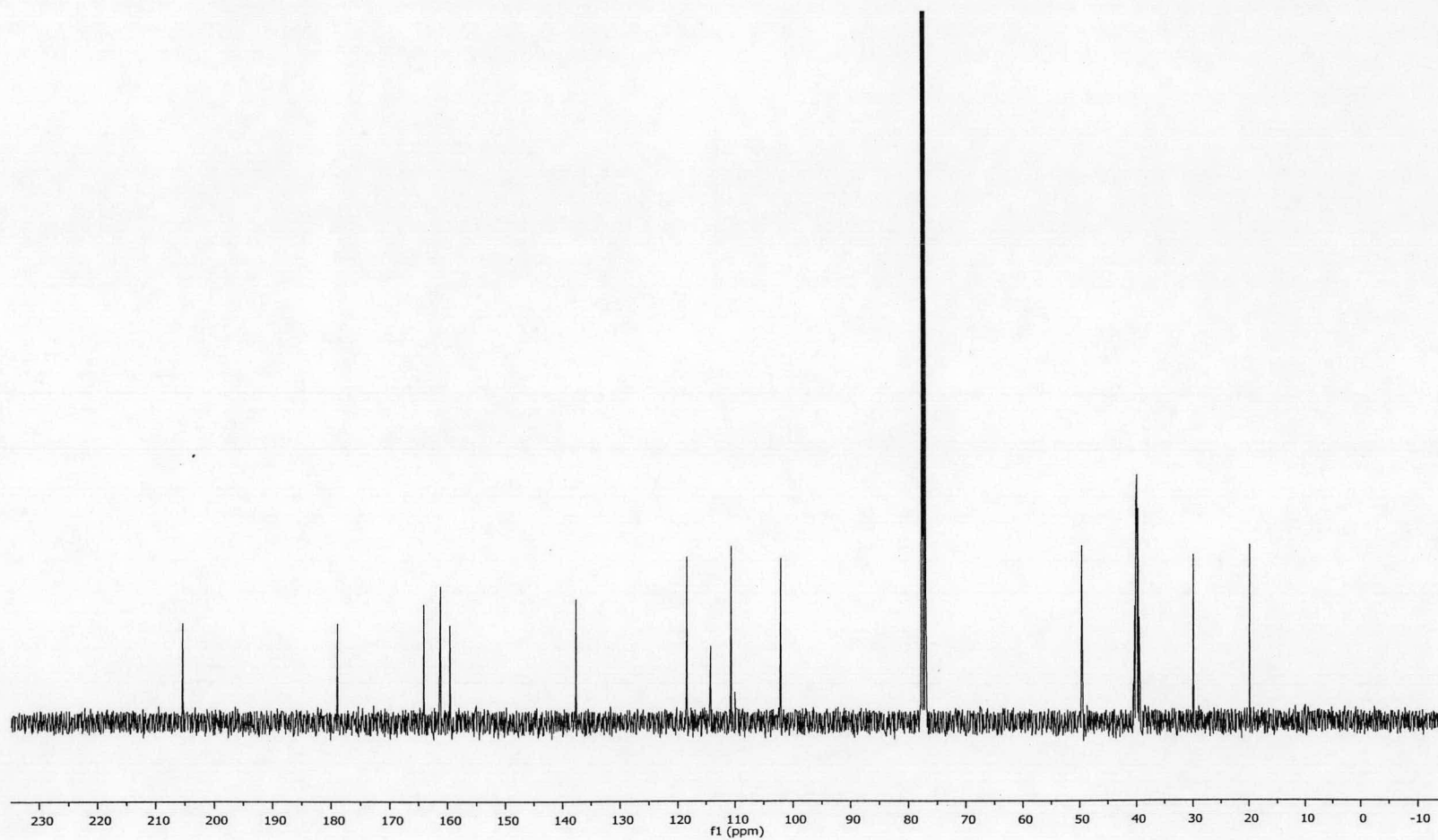


Figure A-5 ^{13}C -NMR spectrum of 5-acetyl-7-hydroxy-2-methyl chromone obtained in $\text{CDCl}_3/\text{DMSO}-d_6$ (9:1) (Compound 27)

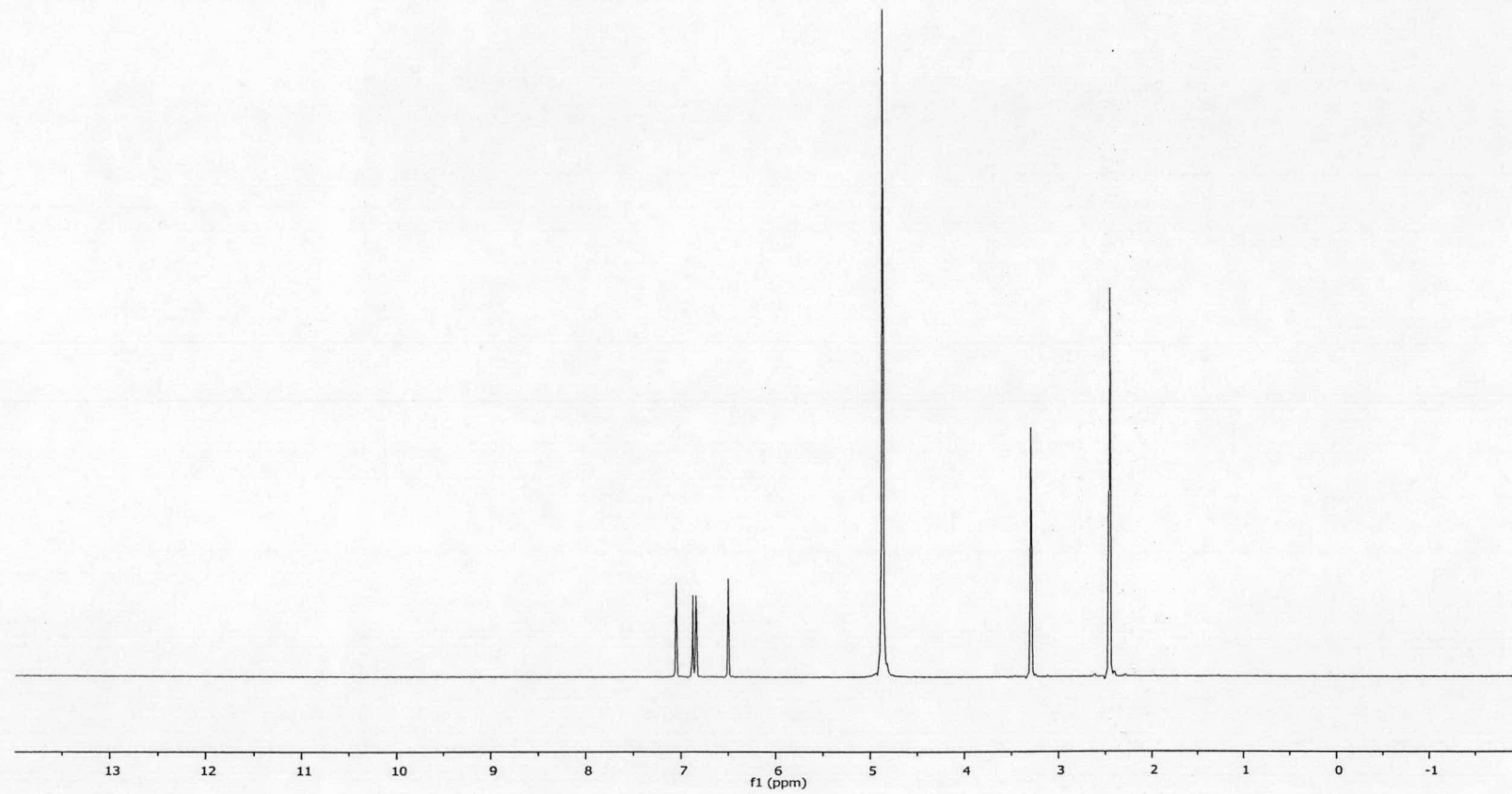


Figure A-6 ¹H-NMR spectrum of cassiarin A hydrochloride obtained in CD₃OD (Compound **4a**)

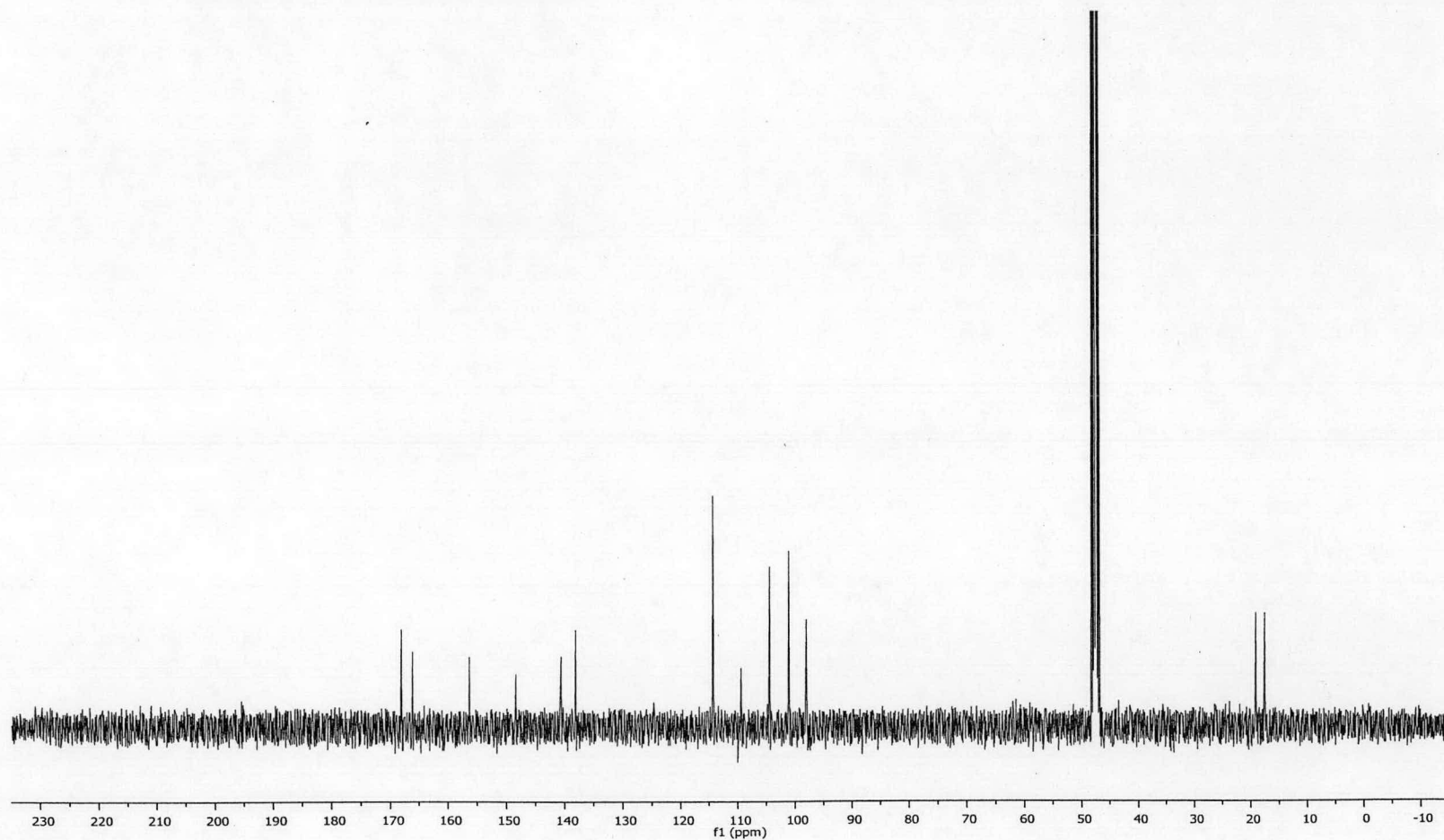


Figure A-7 ^{13}C -NMR spectrum of cassiarin A hydrochloride obtained in CD_3OD (Compound 4a)

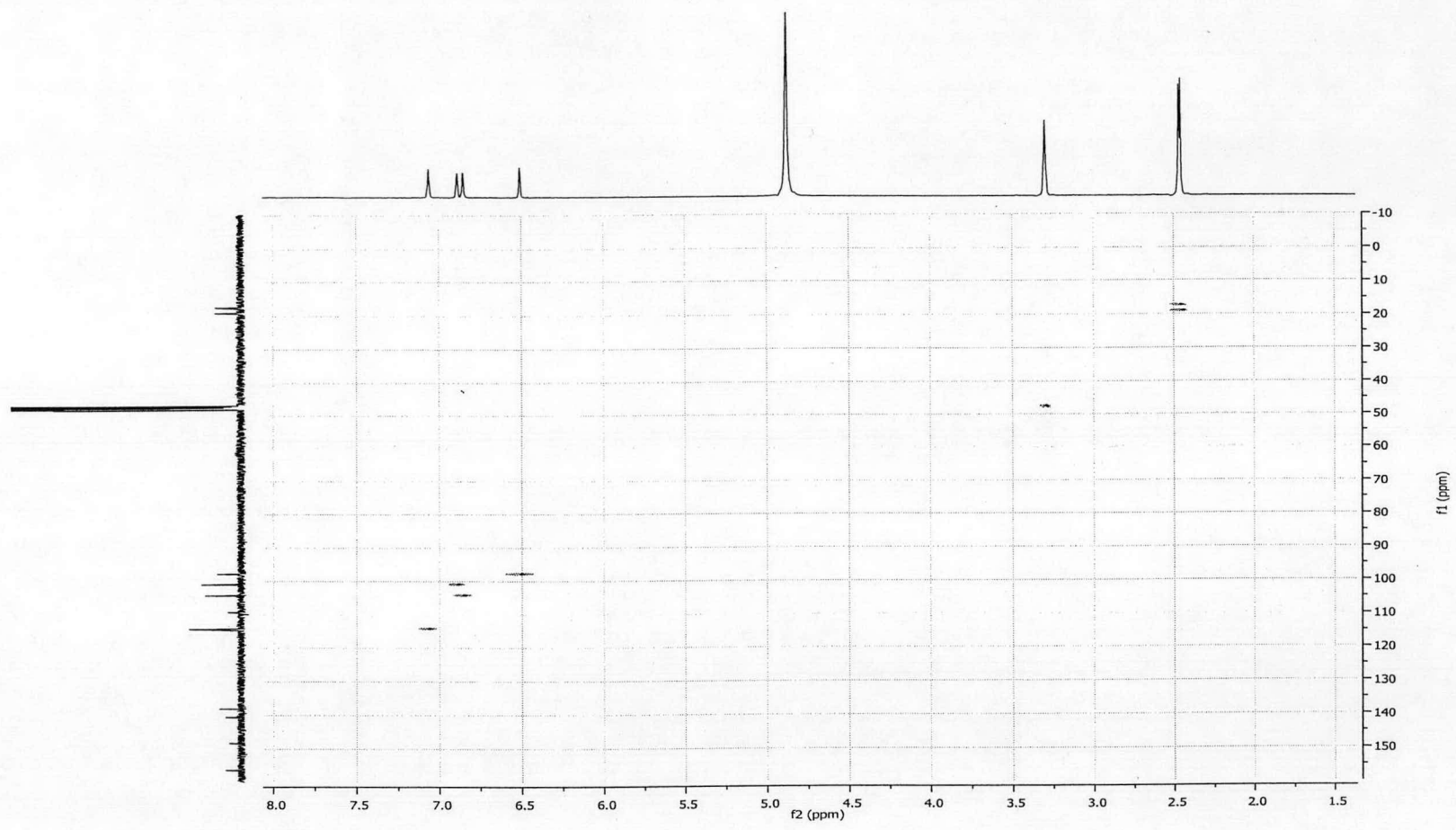


Figure A-8 HSQC spectrum of cassiarin A hydrochloride obtained in CD₃OD (Compound 4a)

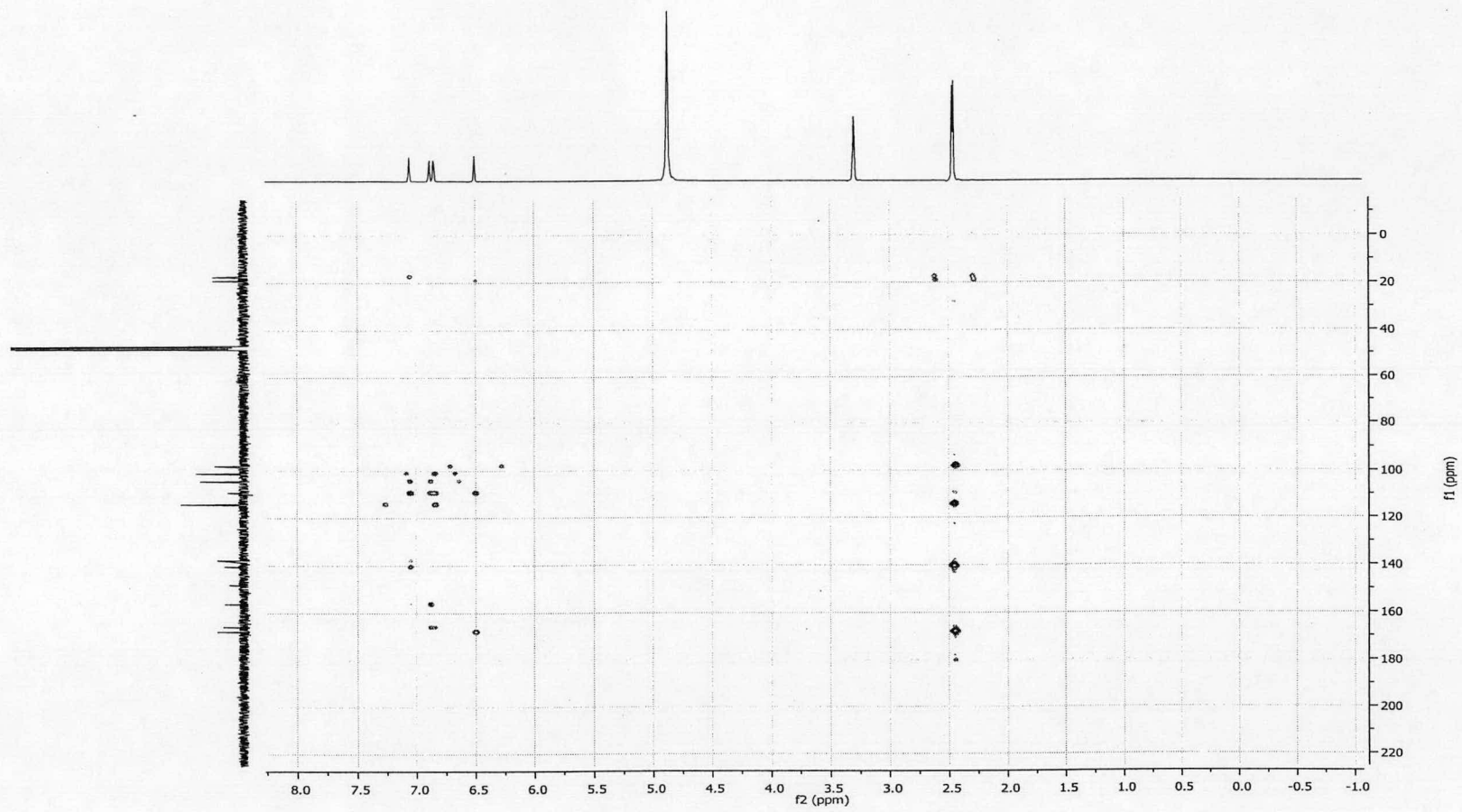


Figure A-9 HMBC spectrum of cassiarin A hydrochloride obtained in CD₃OD (Compound 4a)

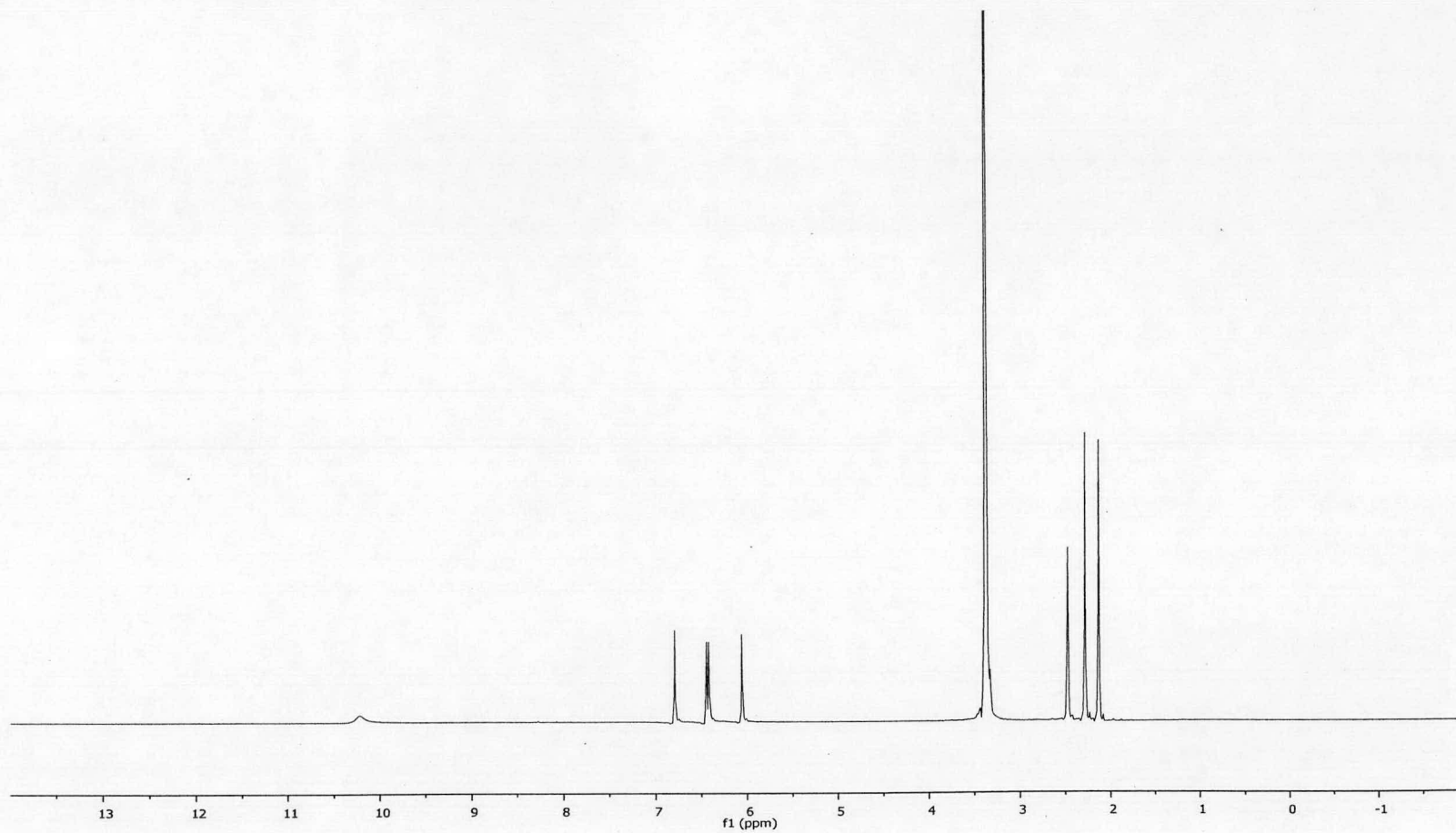


Figure A-10 $^1\text{H-NMR}$ spectrum of cassiarin A obtained in $\text{DMSO-}d_6$ (Compound 4)

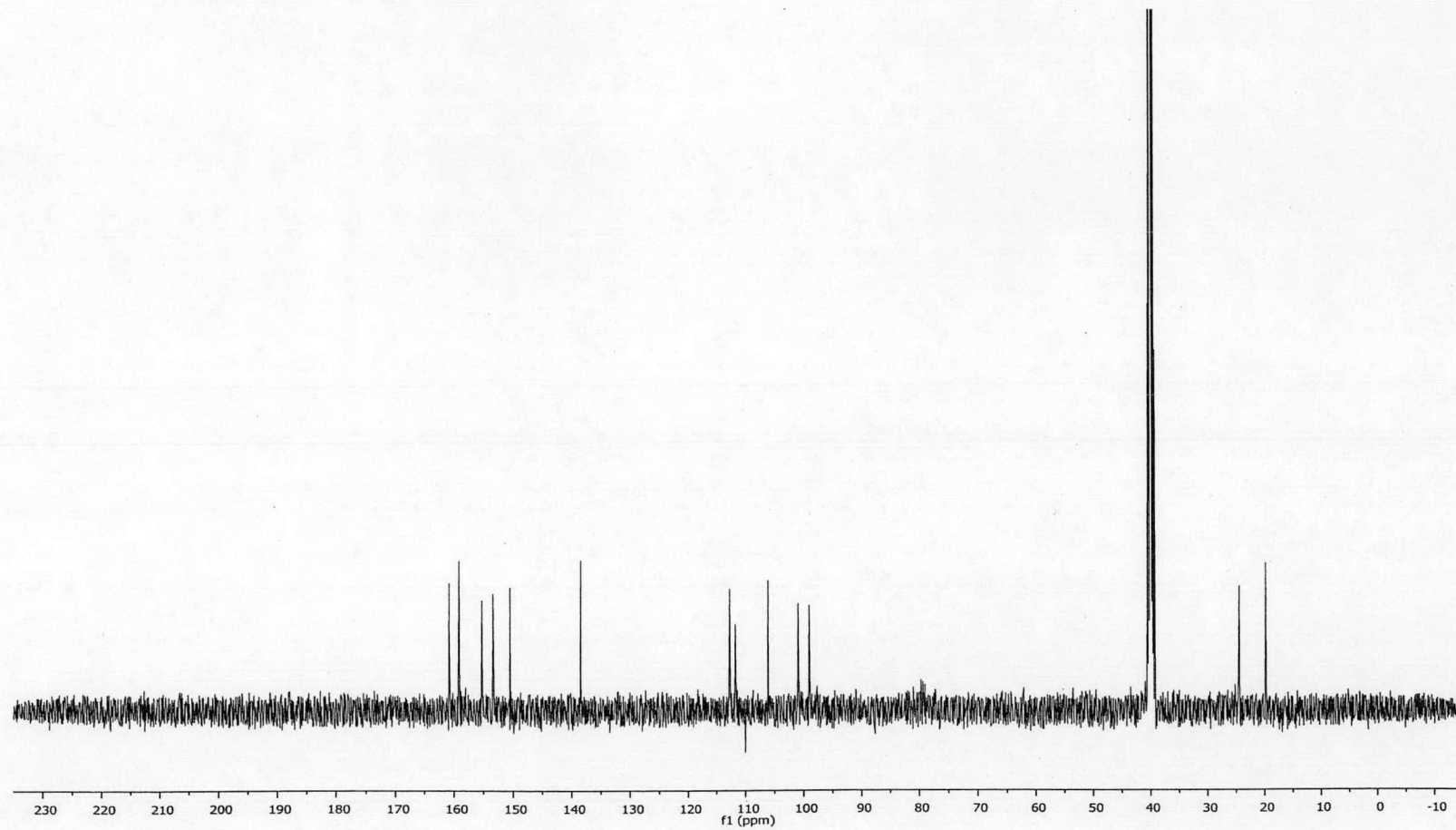


Figure A-11 ^{13}C -NMR spectrum of cassiarin A obtained in $\text{DMSO-}d_6$ (Compound 4)

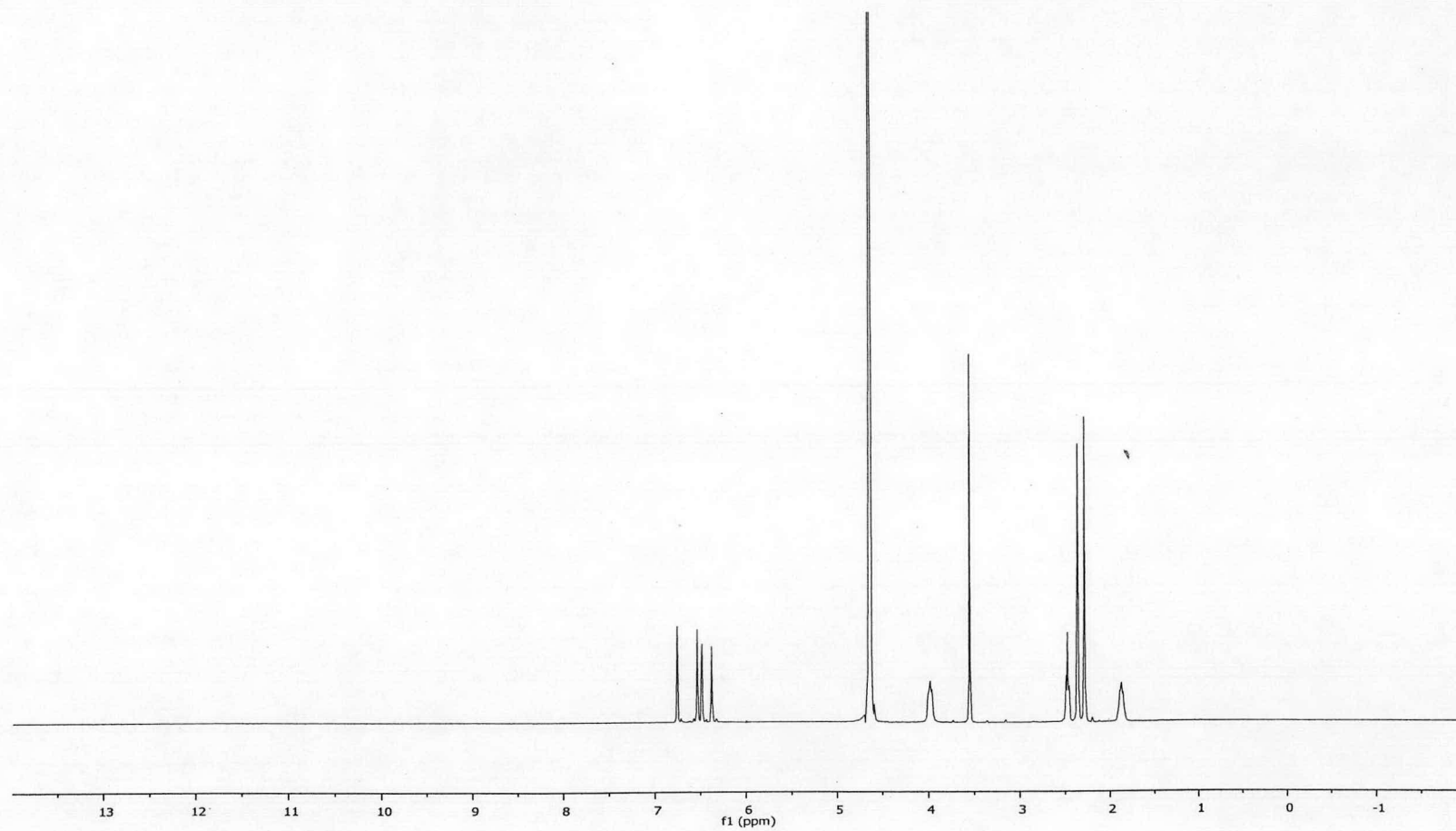


Figure A-12 ¹H-NMR spectrum of *N*-4-methoxy-4-oxobutyl cassiarin A chloride obtained in D₂O/DMSO-*d*₆ (9.5:0.5) (Compound **5a**)

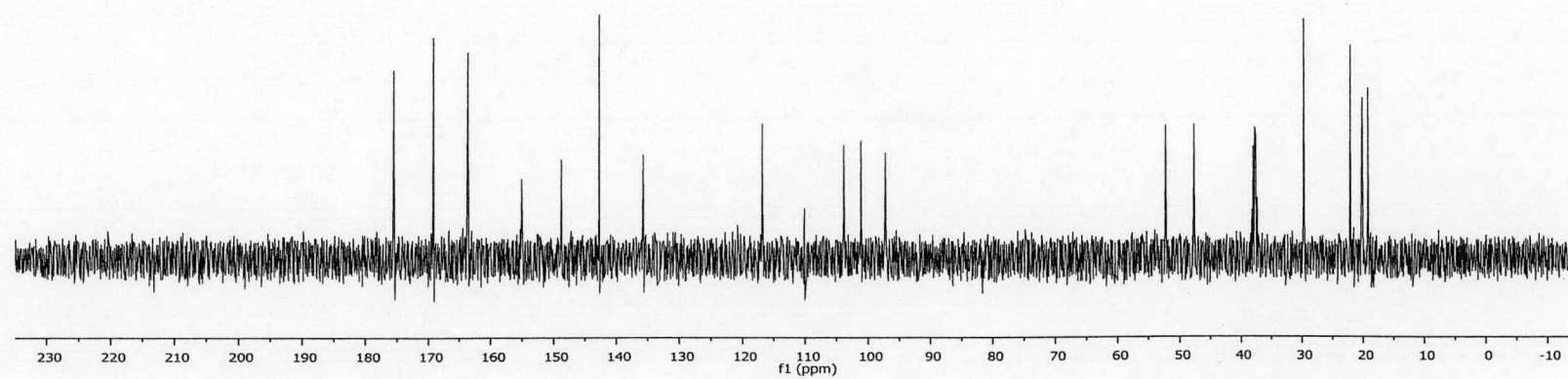


Figure A-13 ^{13}C -NMR spectrum of *N*-4-methoxy-4-oxobutyl cassiarin A chloride obtained in $\text{D}_2\text{O}/\text{DMSO}-d_6$ (9.5:0.5) (Compound **5a**)

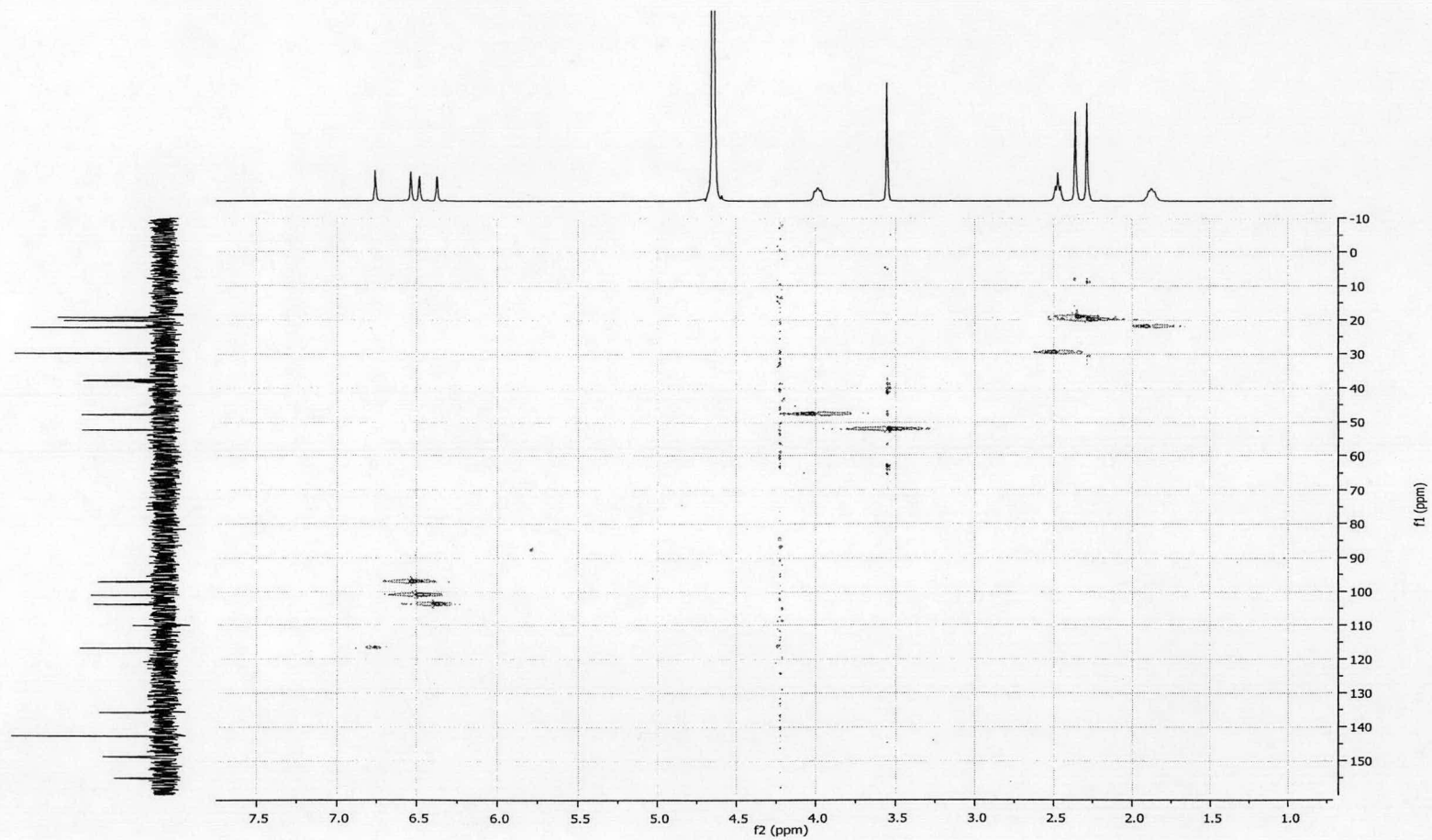


Figure A-14 HSQC spectrum of *N*-4-methoxy-4-oxobutyl cassiarin A chloride obtained in D₂O/DMSO-*d*₆ (9.5:0.5) (Compound **5a**)

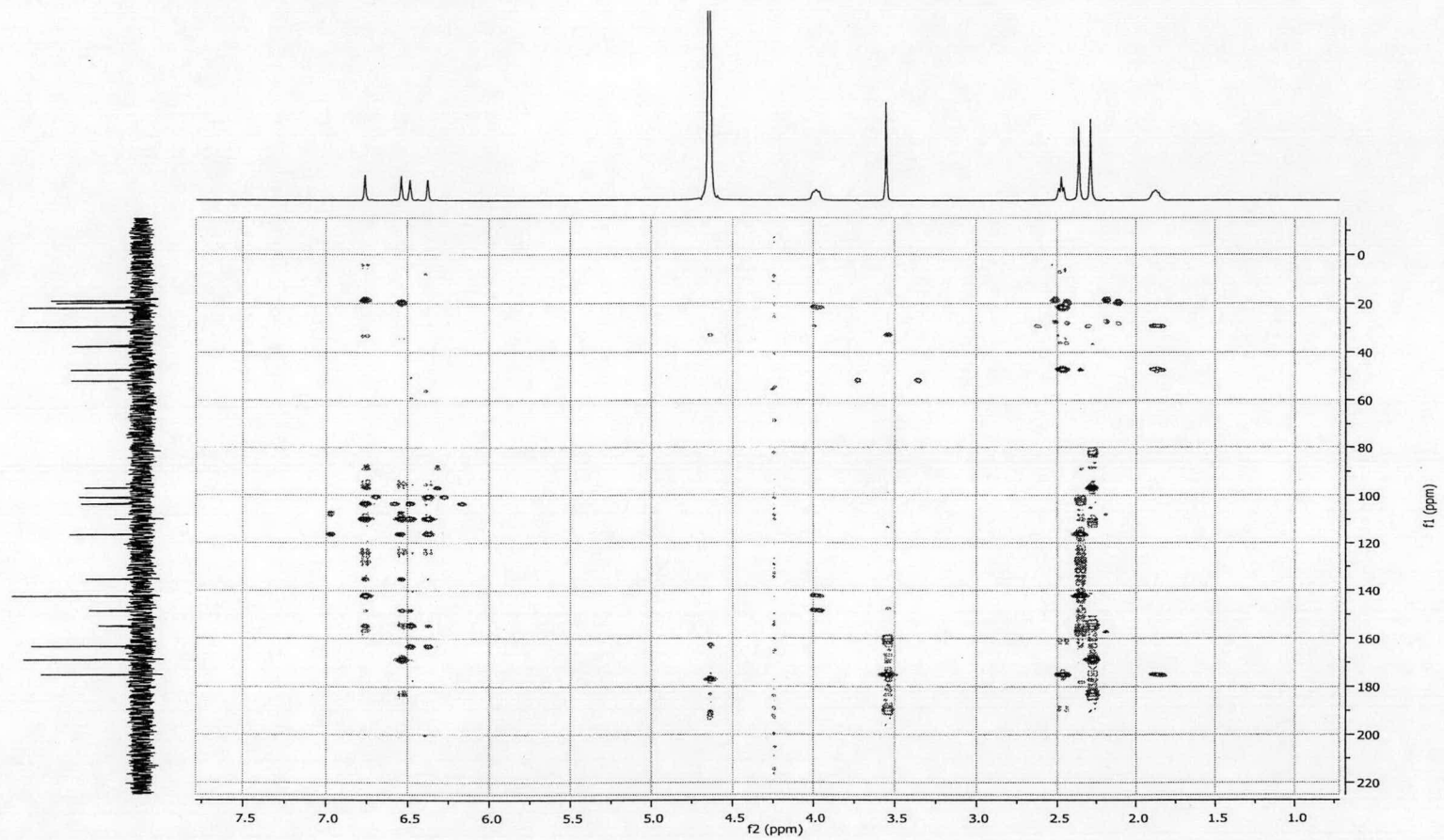


Figure A-15 HMBC spectrum of *N*-4-methoxy-4-oxobutyl cassiarin A chloride obtained in D₂O/DMSO-*d*₆ (9.5:0.5) (Compound **5a**)

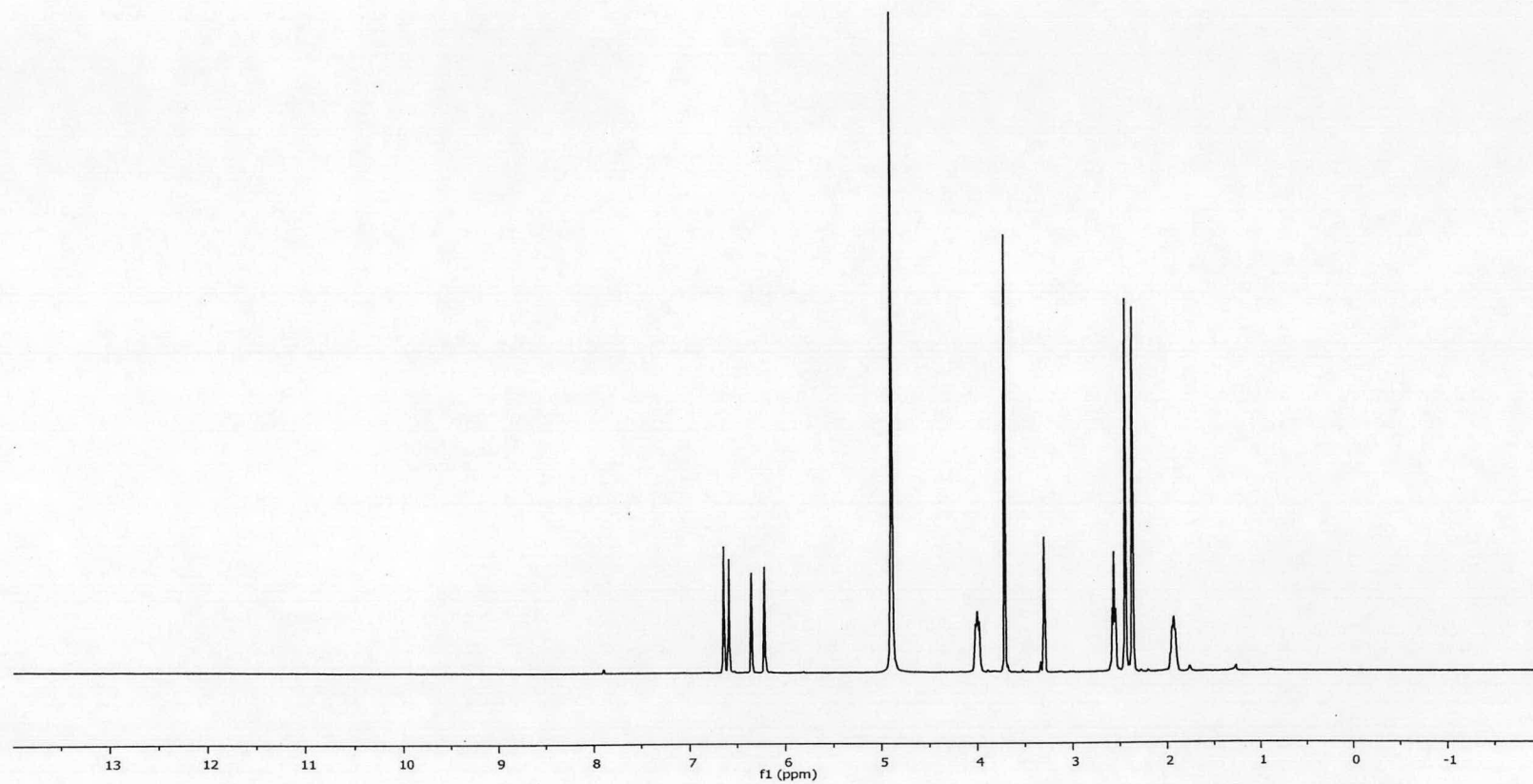


Figure A-16 $^1\text{H-NMR}$ spectrum of cassairin B obtained in CD_3OD (Compound 5)

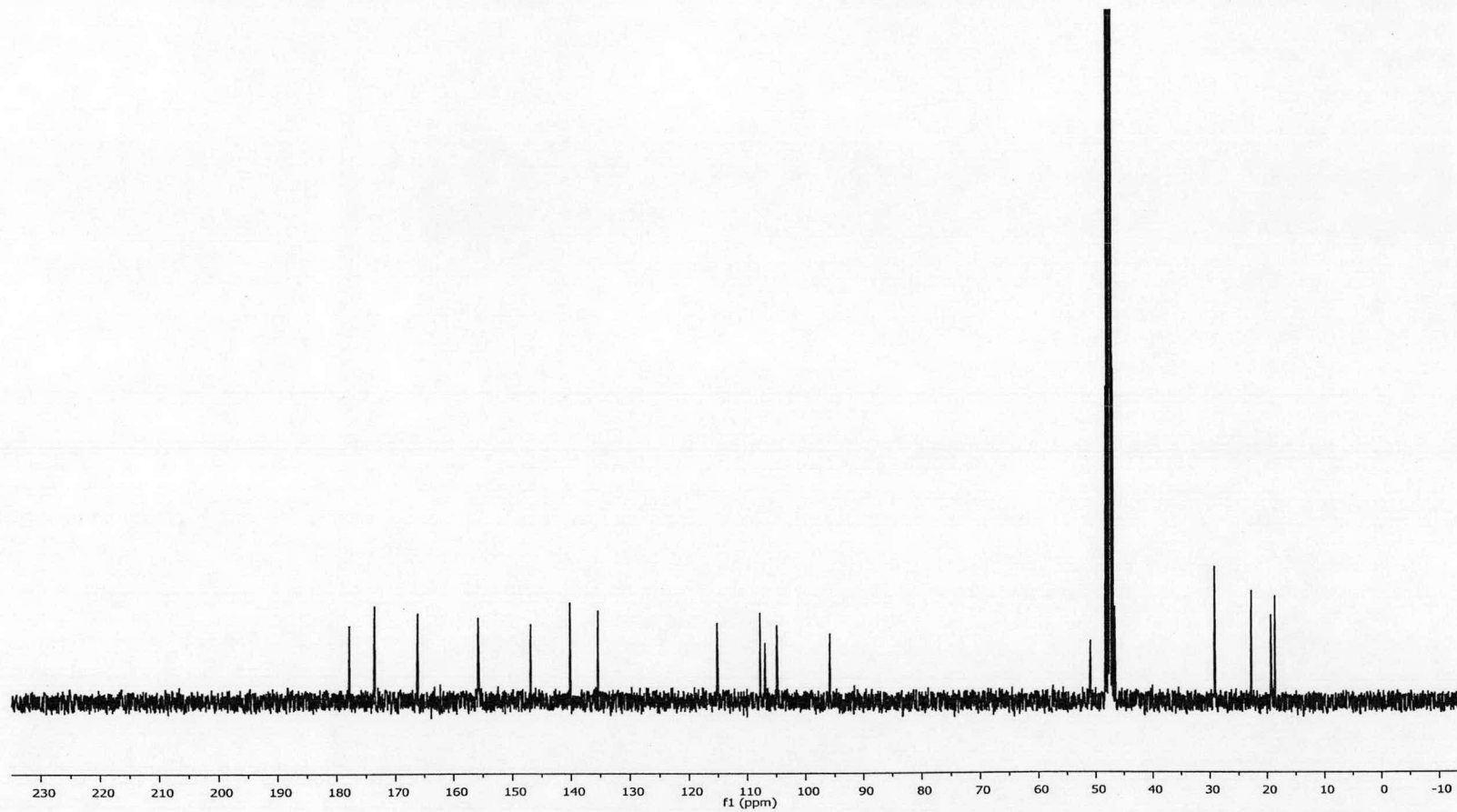


Figure A-17 ^{13}C -NMR spectrum of cassairin B obtained in CD_3OD (Compound 5)

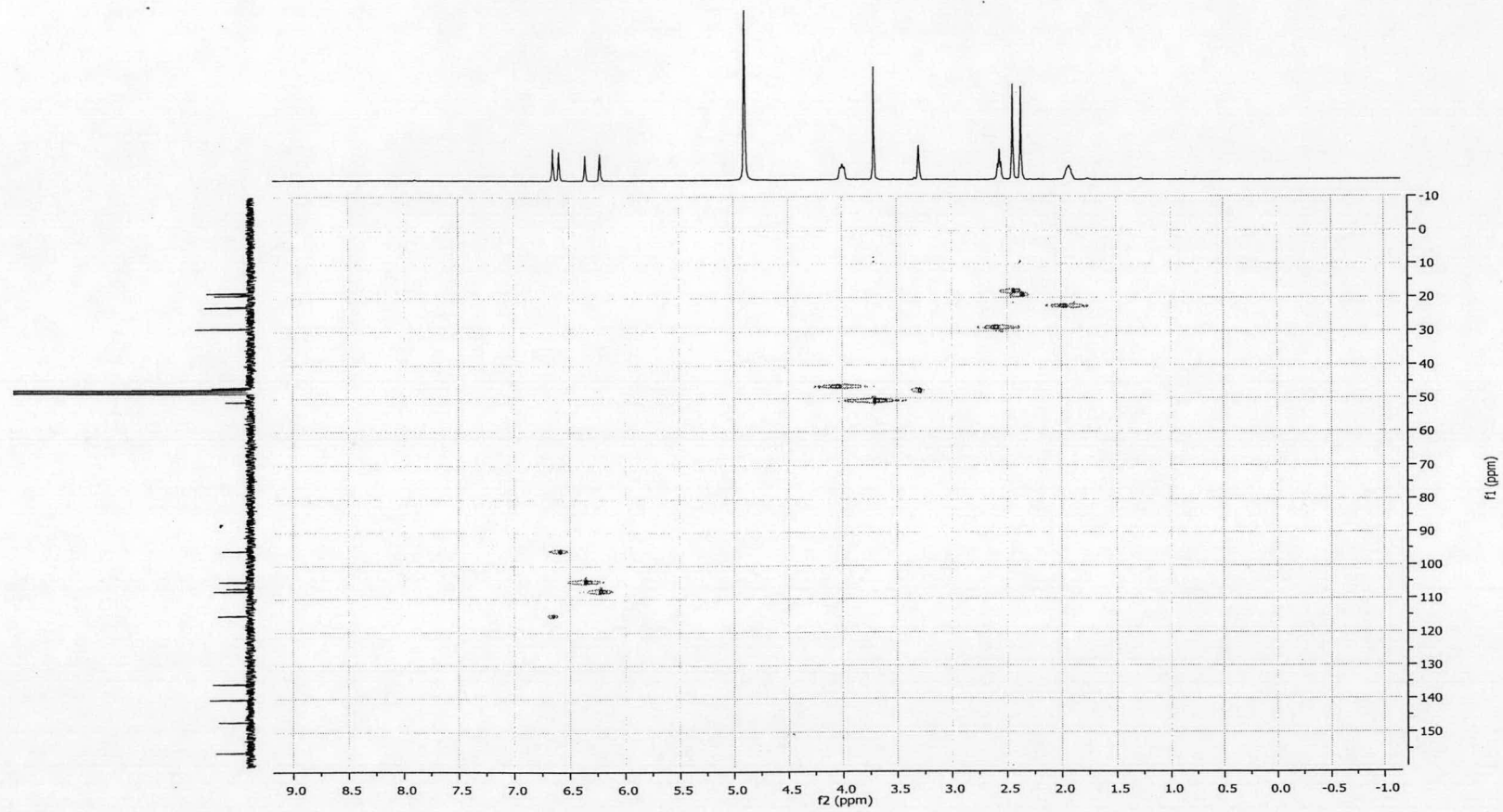


Figure A-18 HSQC spectrum of cassairin B obtained in CD₃OD (Compound 5)

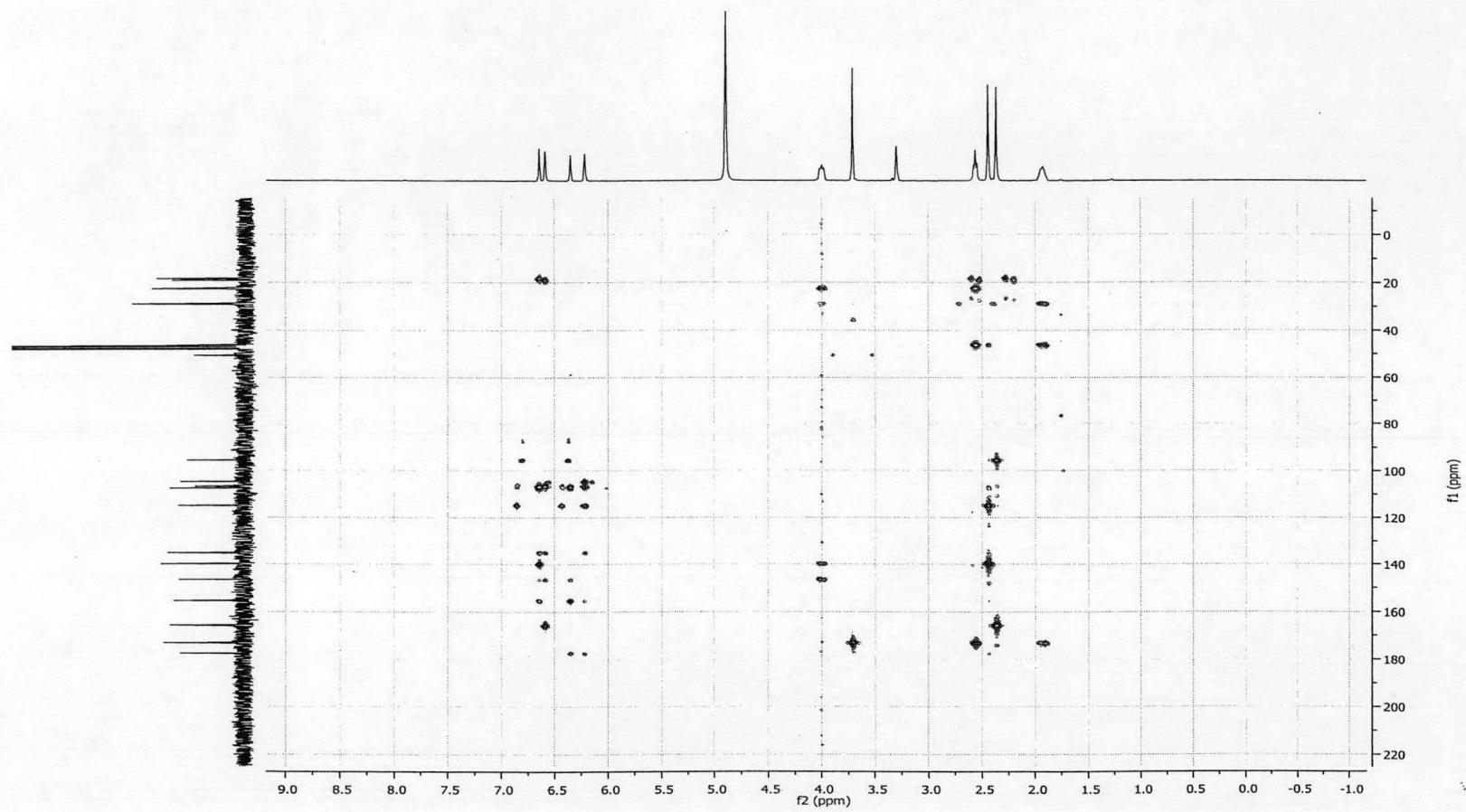


Figure A-19 HMBC spectrum of cassairin B obtained in CD₃OD (Compound 5)

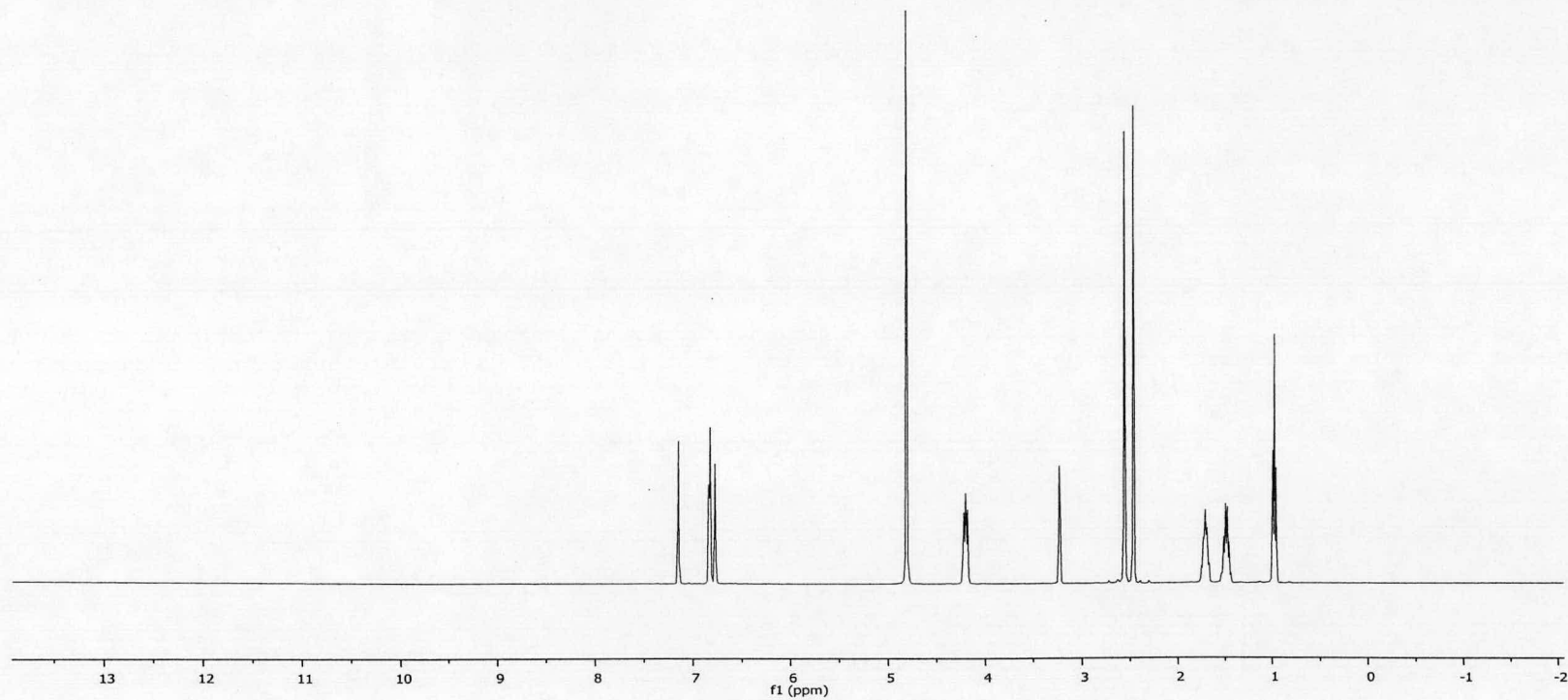


Figure A-20 ^1H -NMR spectrum of *N*-butyl cassiarin A chloride obtained in CD_3OD (Compound **28a**)

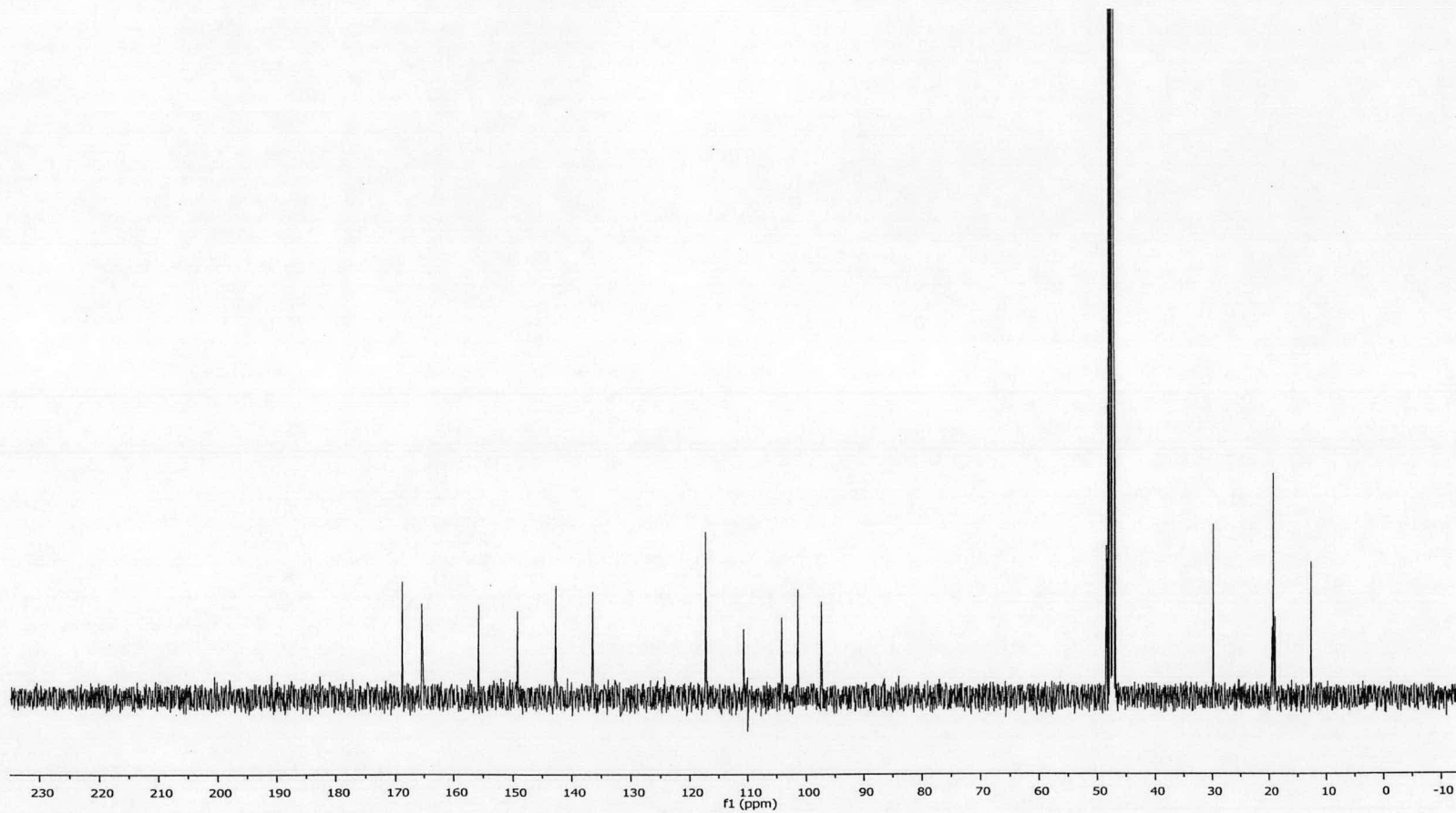


Figure A-21 ^{13}C -NMR spectrum of *N*-butyl cassiarin A chloride obtained in CD_3OD (Compound **28a**)

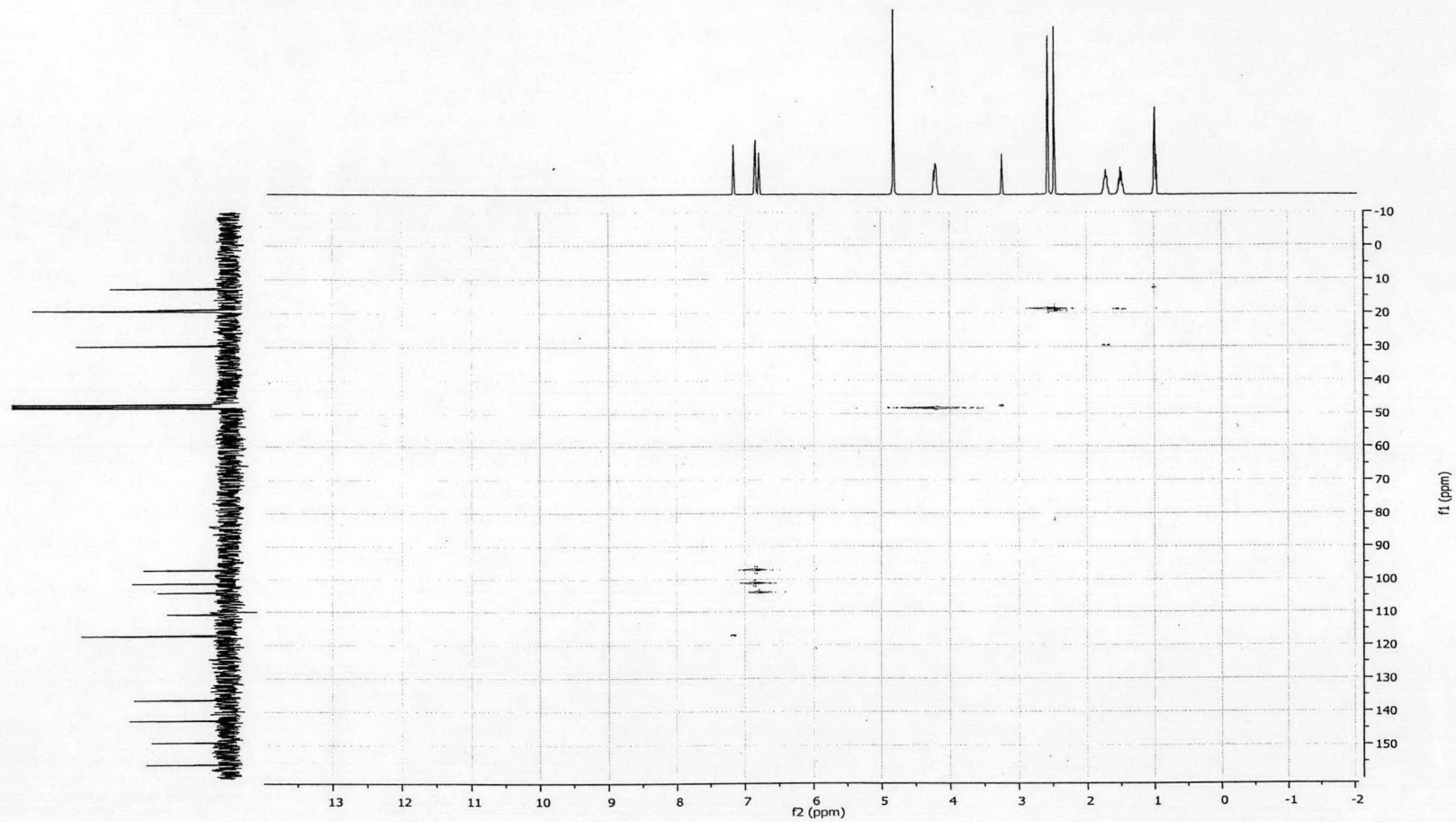


Figure A-22 HSQC spectrum of *N*-butyl cassiarin A chloride obtained in CD_3OD (Compound **28a**)

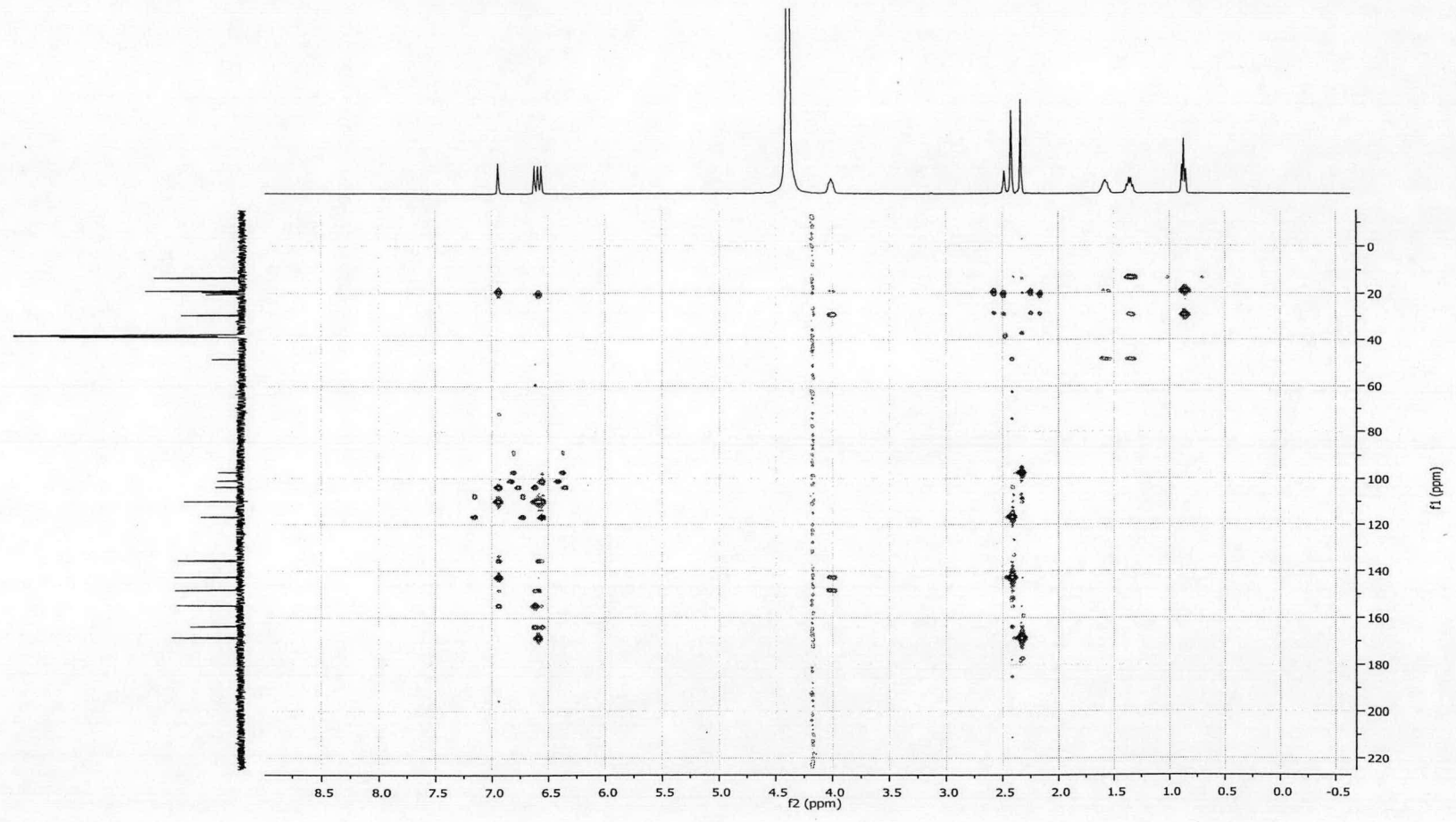


Figure A-23 HMBC spectrum of *N*-butyl cassiarin A chloride obtained in DMSO-*d*₆ (Compound 28a)

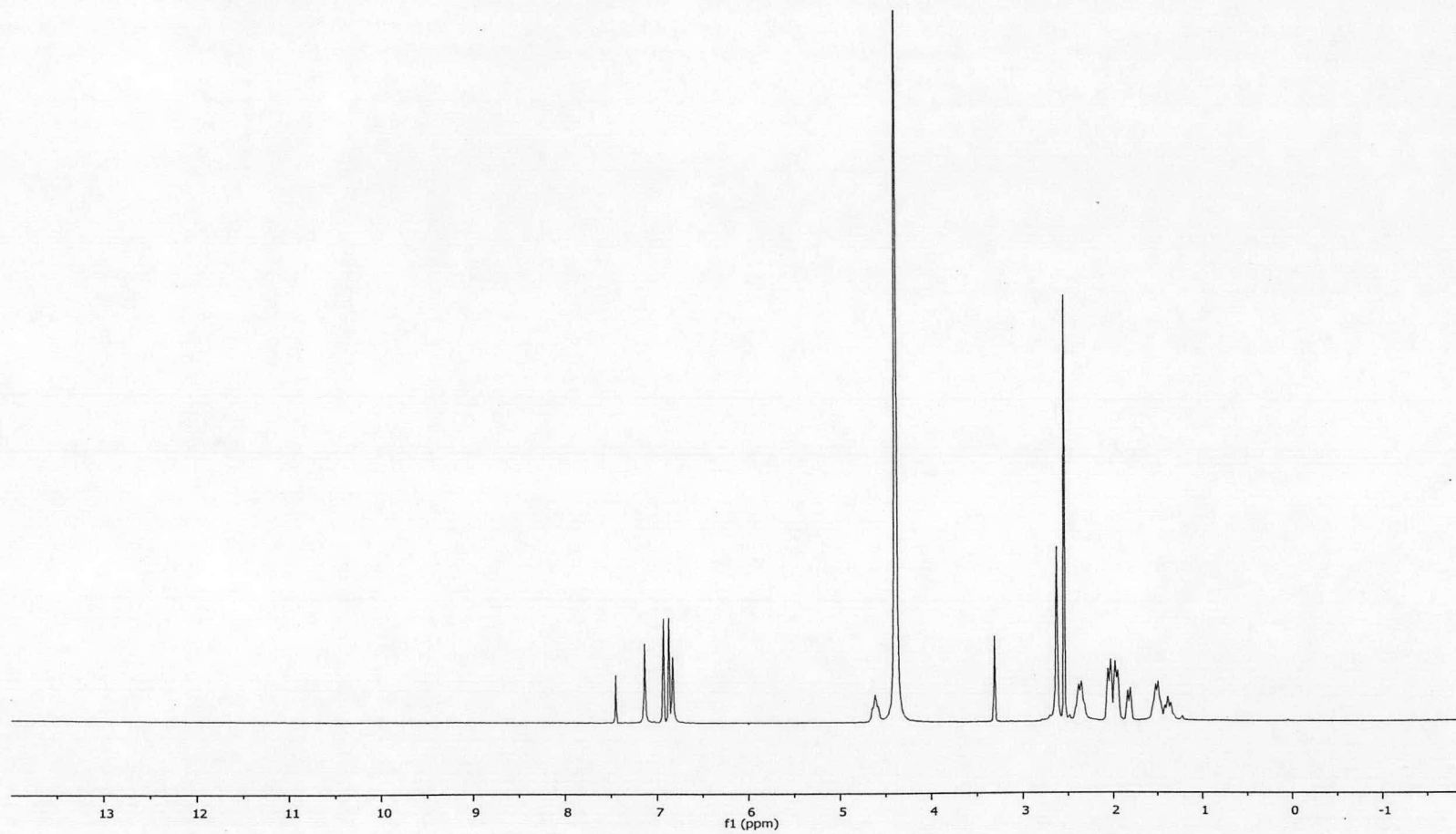


Figure A-24 ¹H-NMR spectrum of *N*-cyclohexyl cassiarin A chloride obtained in CD₃OD/CDCl₃ (1:4) (Compound **29a**)

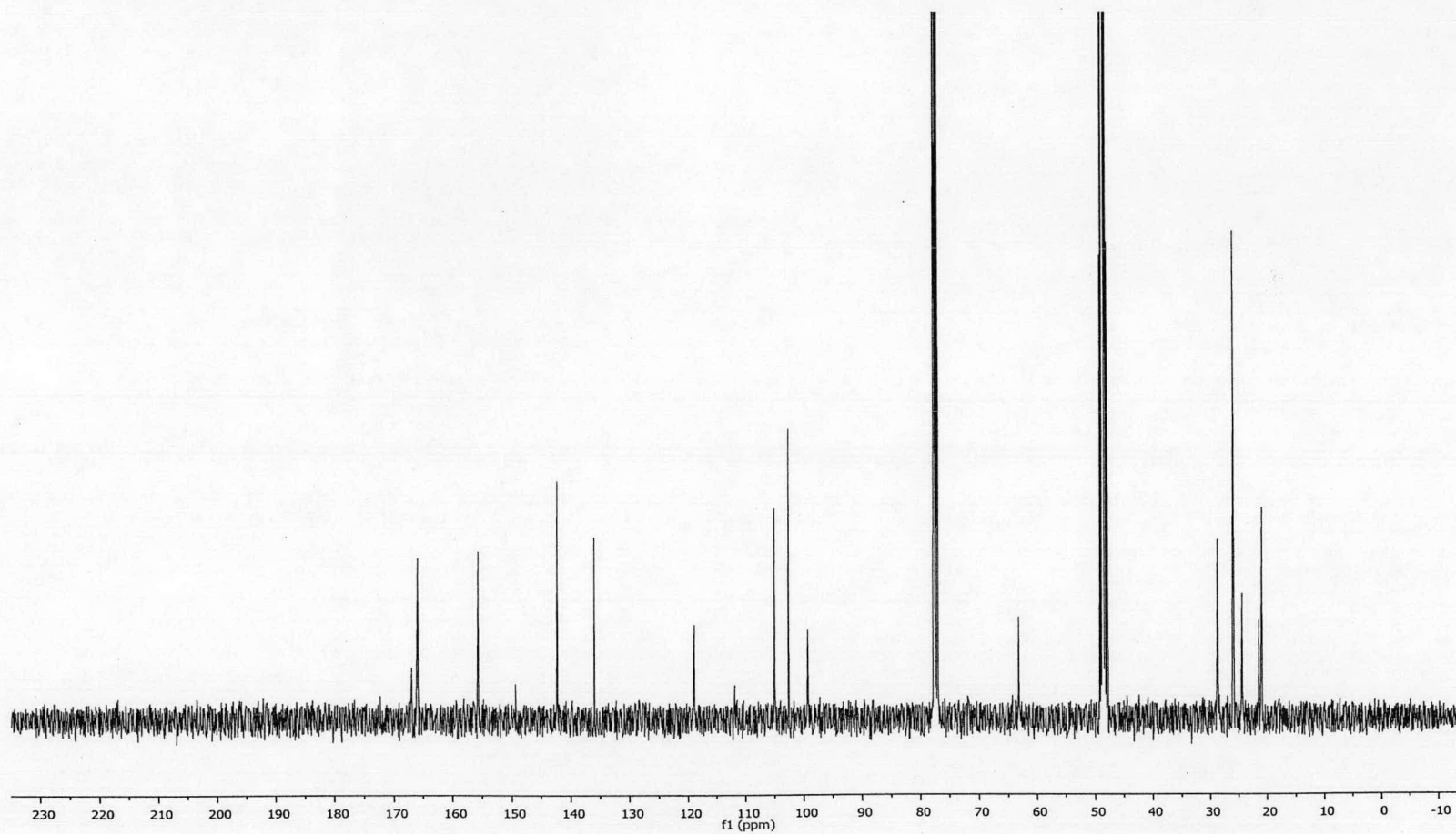


Figure A-25 ^{13}C -NMR spectrum of *N*-cyclohexyl cassiarin A chloride obtained in $\text{CD}_3\text{OD}/\text{CDCl}_3$ (1:4) (Compound **29a**)

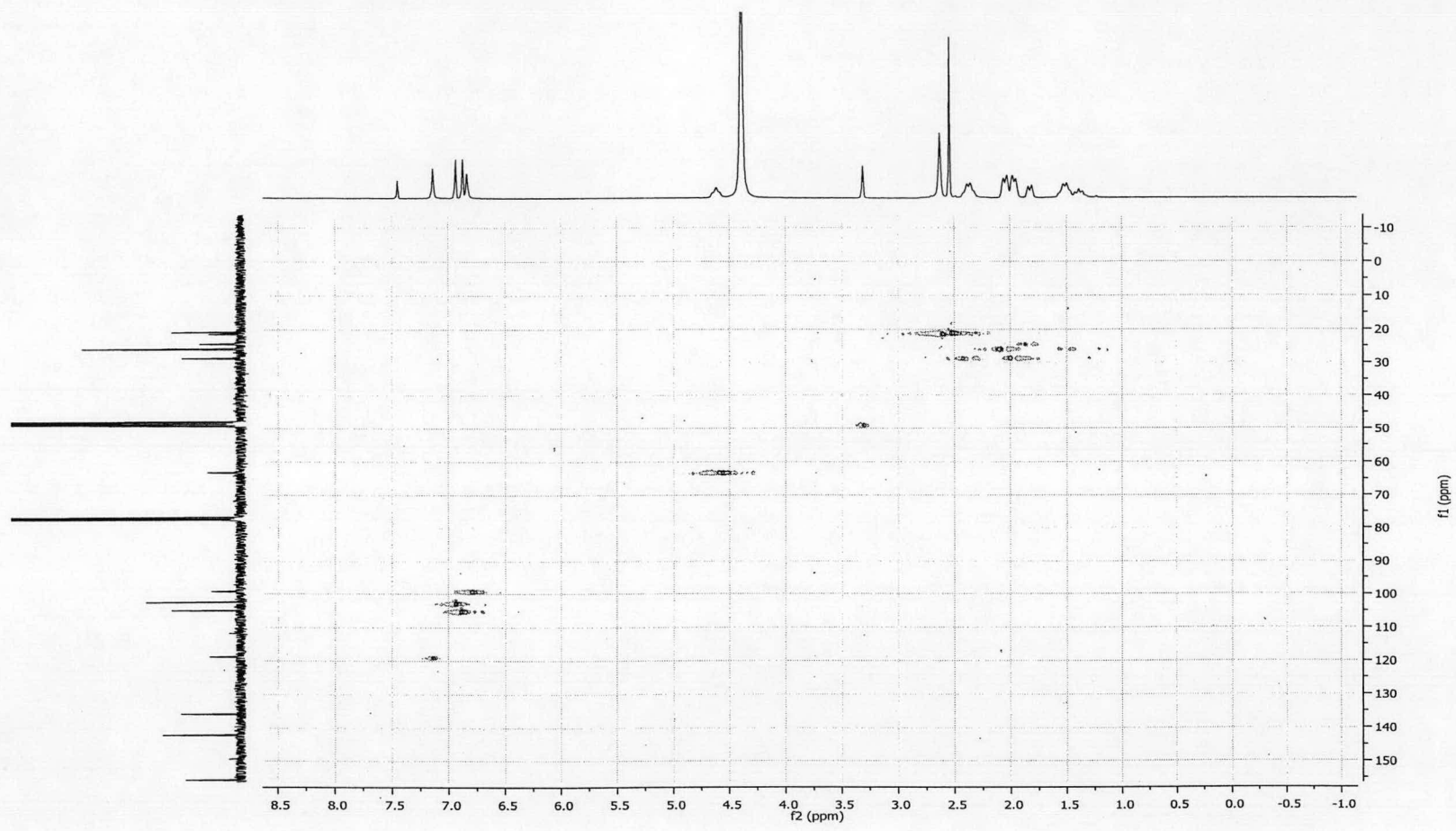


Figure A-26 HSQC NMR spectrum of *N*-cyclohexyl cassiarin A chloride obtained in CD₃OD/CDCl₃ (1:4) (Compound 29a)

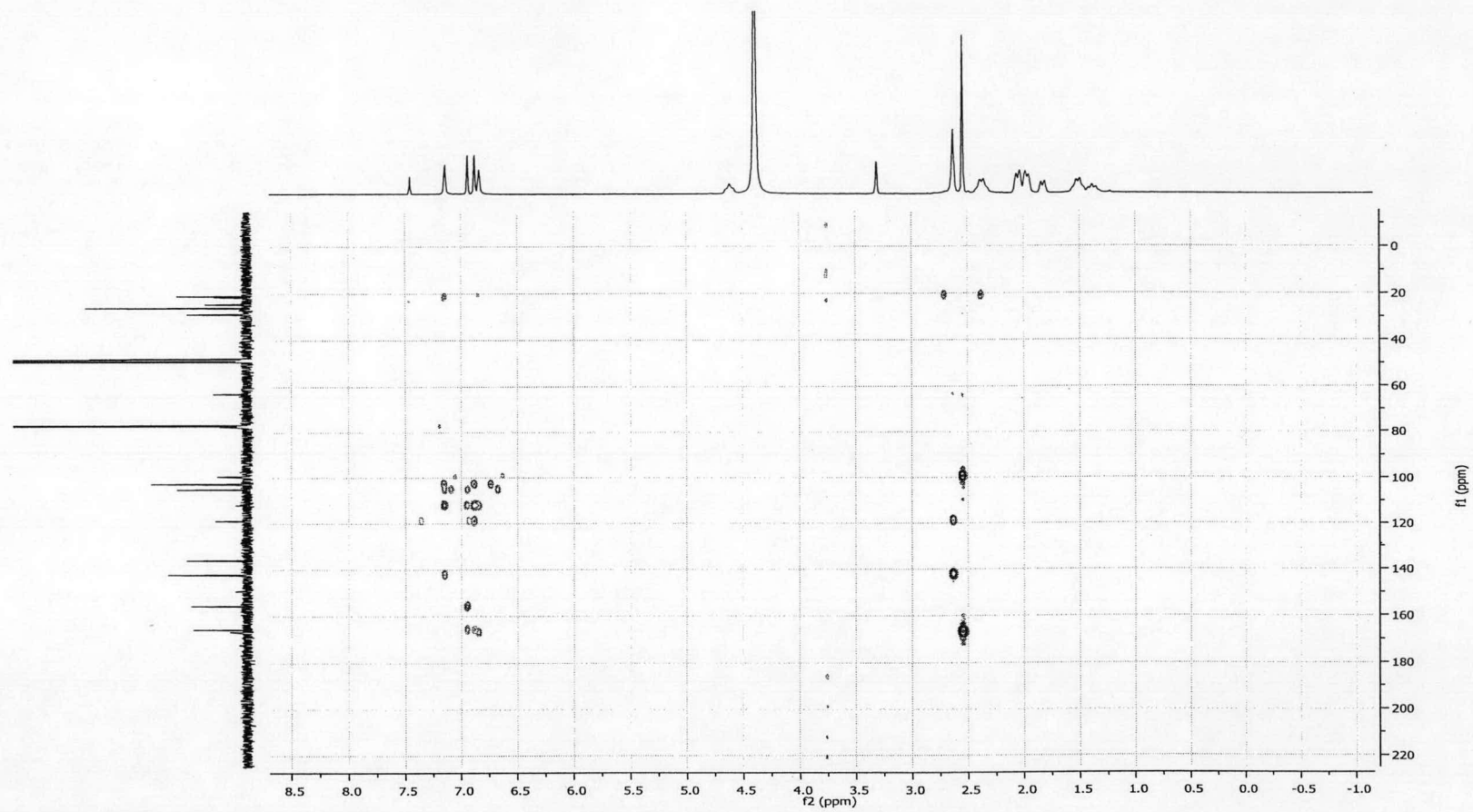


Figure A-27 HMBC NMR spectrum of *N*-cyclohexyl cassiarin A chloride obtained in CD₃OD/CDCl₃ (1:4) (Compound **29a**)

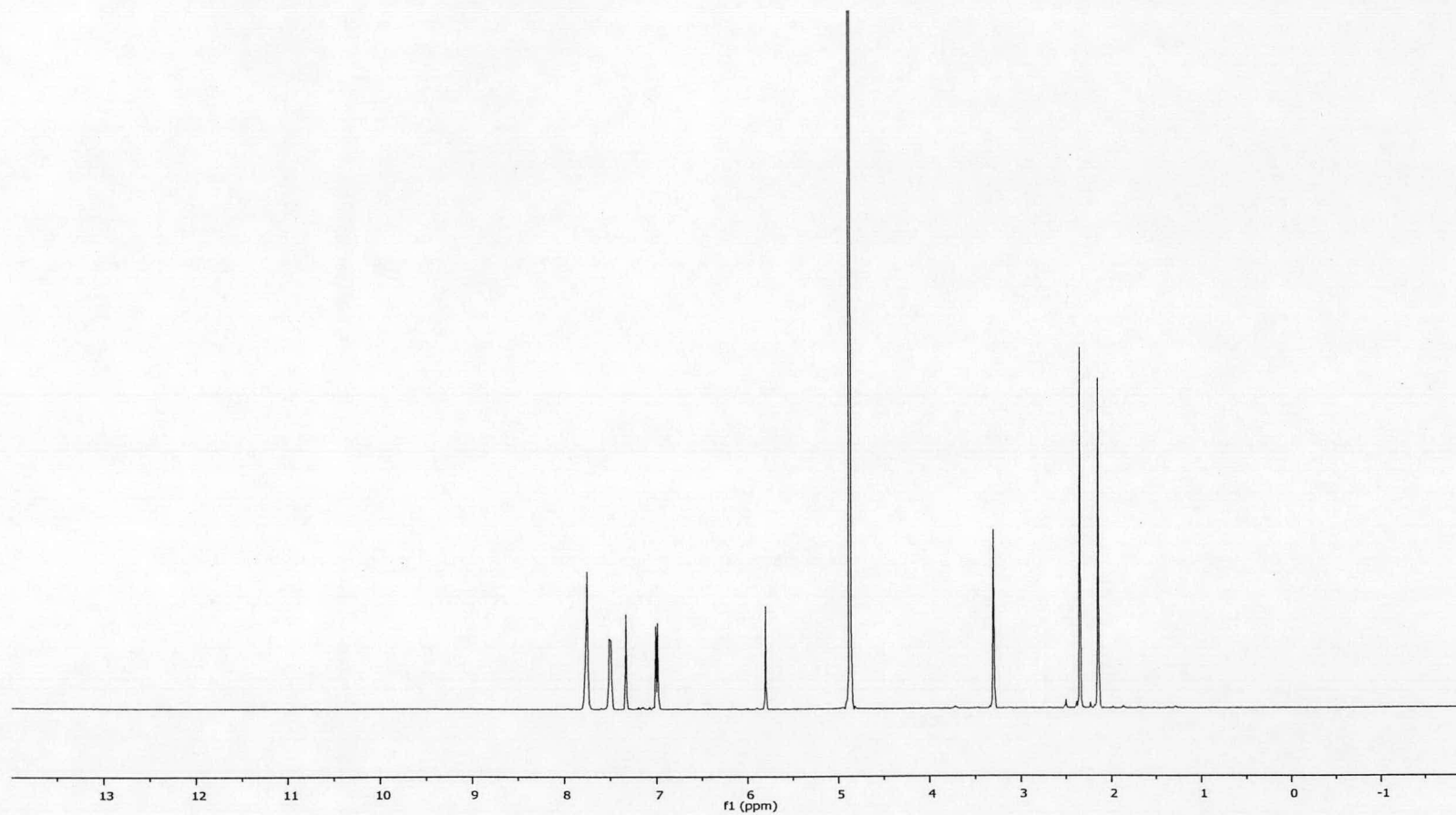


Figure A-28 ¹H-NMR spectrum of *N*-phenyl cassiarin A chloride obtained in CD₃OD (Compound **30a**)

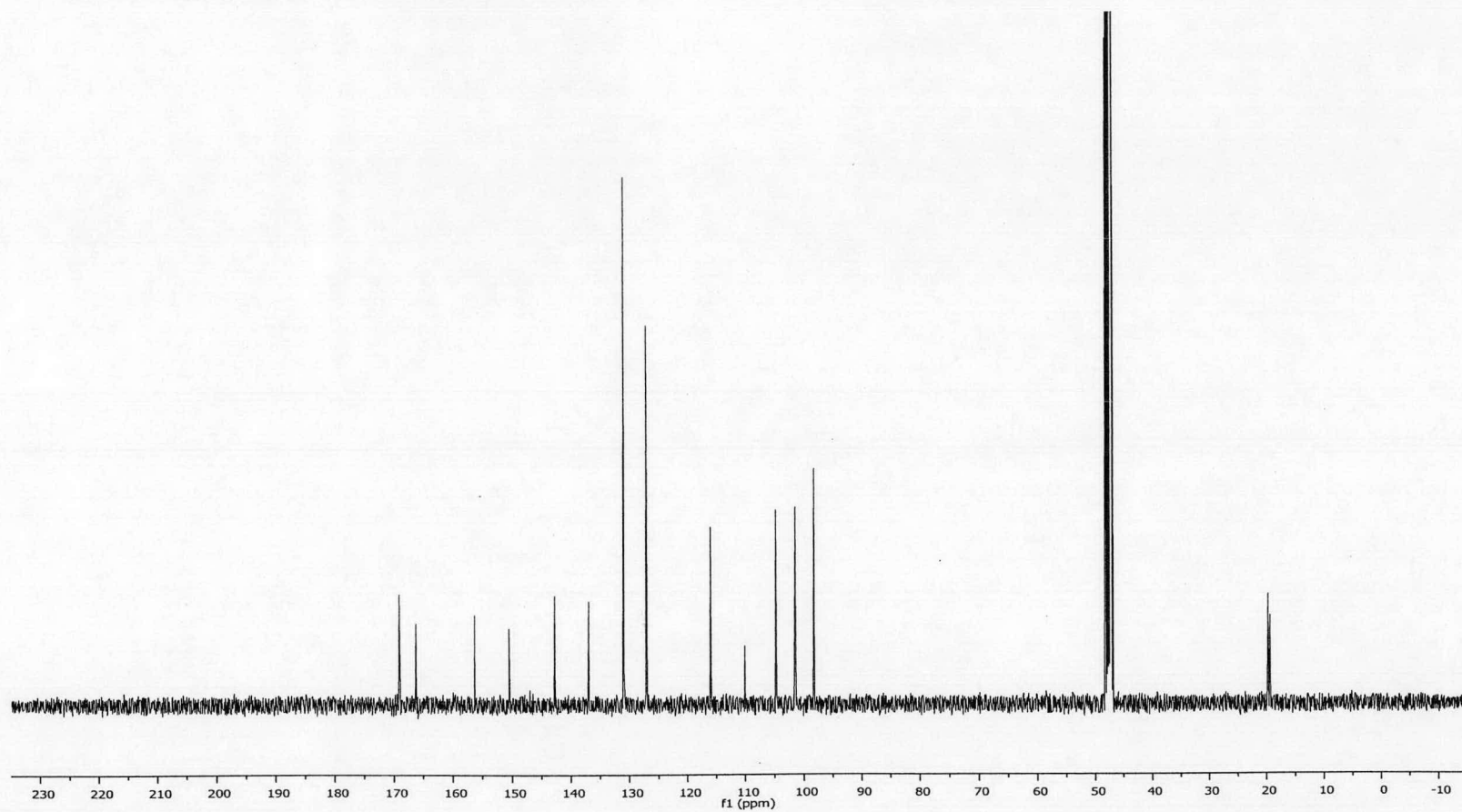


Figure A-29 ^{13}C -NMR spectrum of *N*-phenyl cassiarin A chloride obtained in CD_3OD (Compound **30a**)

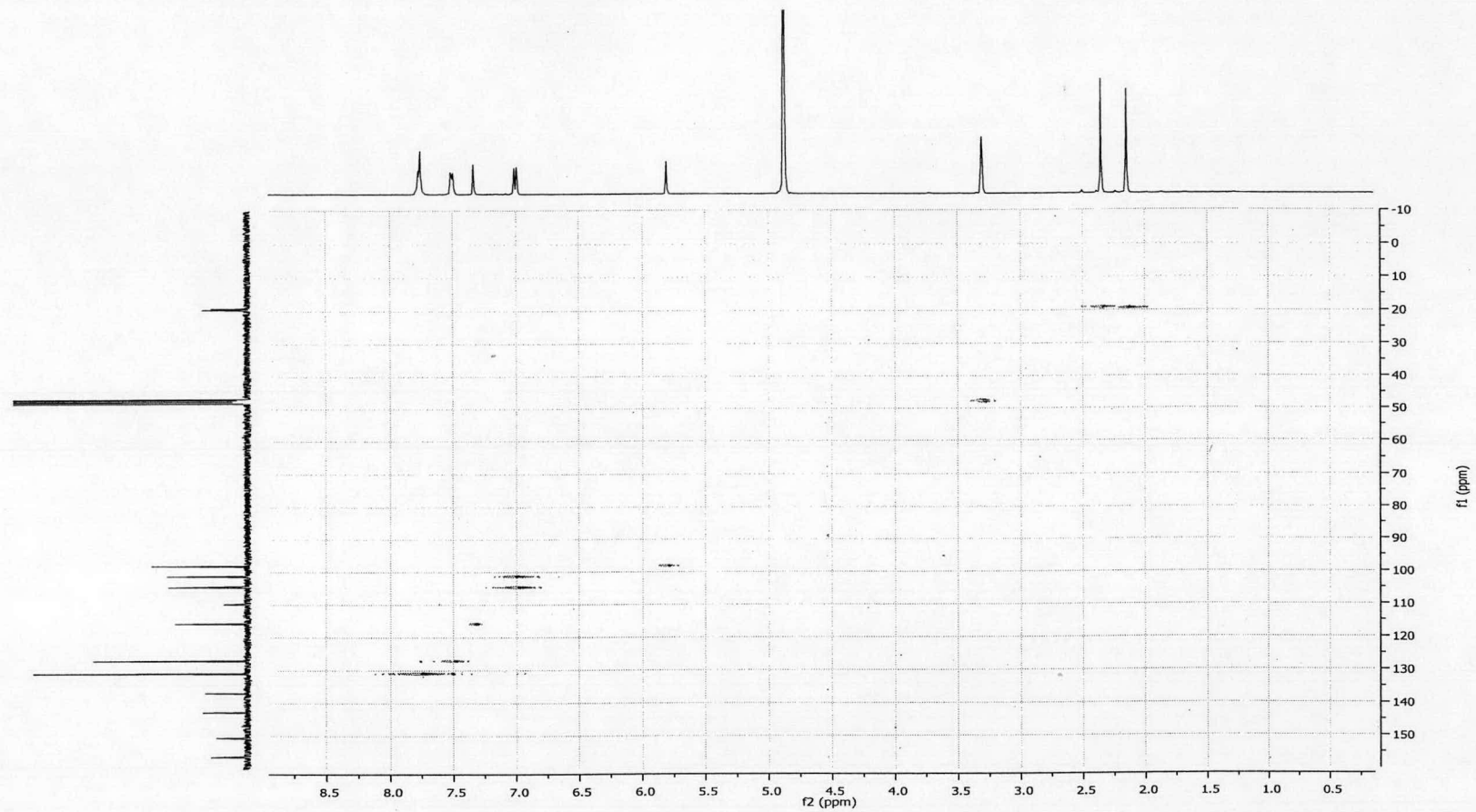


Figure A-30 HSQC spectrum of *N*-phenyl cassiarin A chloride obtained in CD₃OD (Compound 30a)

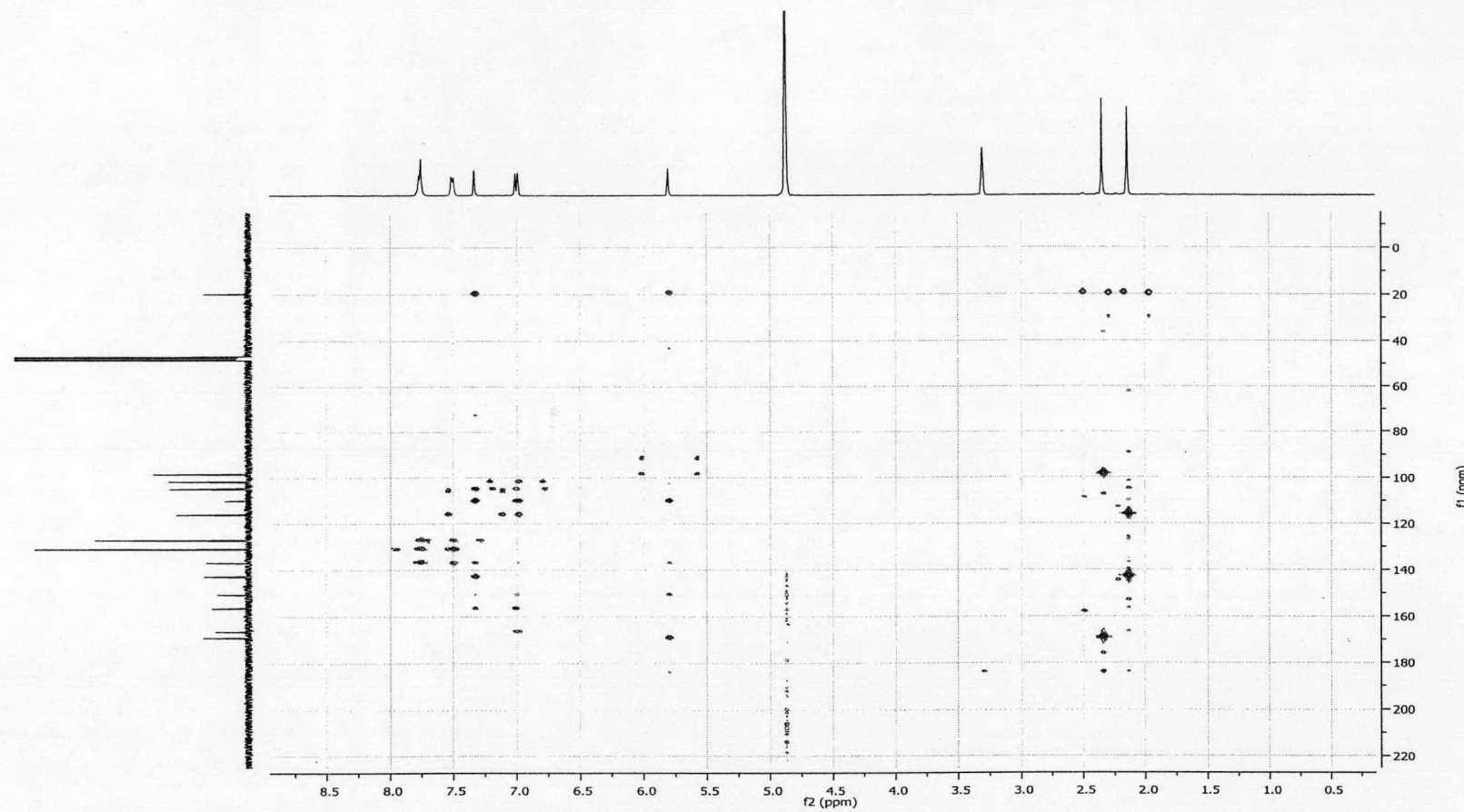


Figure A-31 HMBC spectrum of *N*-phenyl cassiarin A chloride obtained in CD₃OD (Compound 30a)

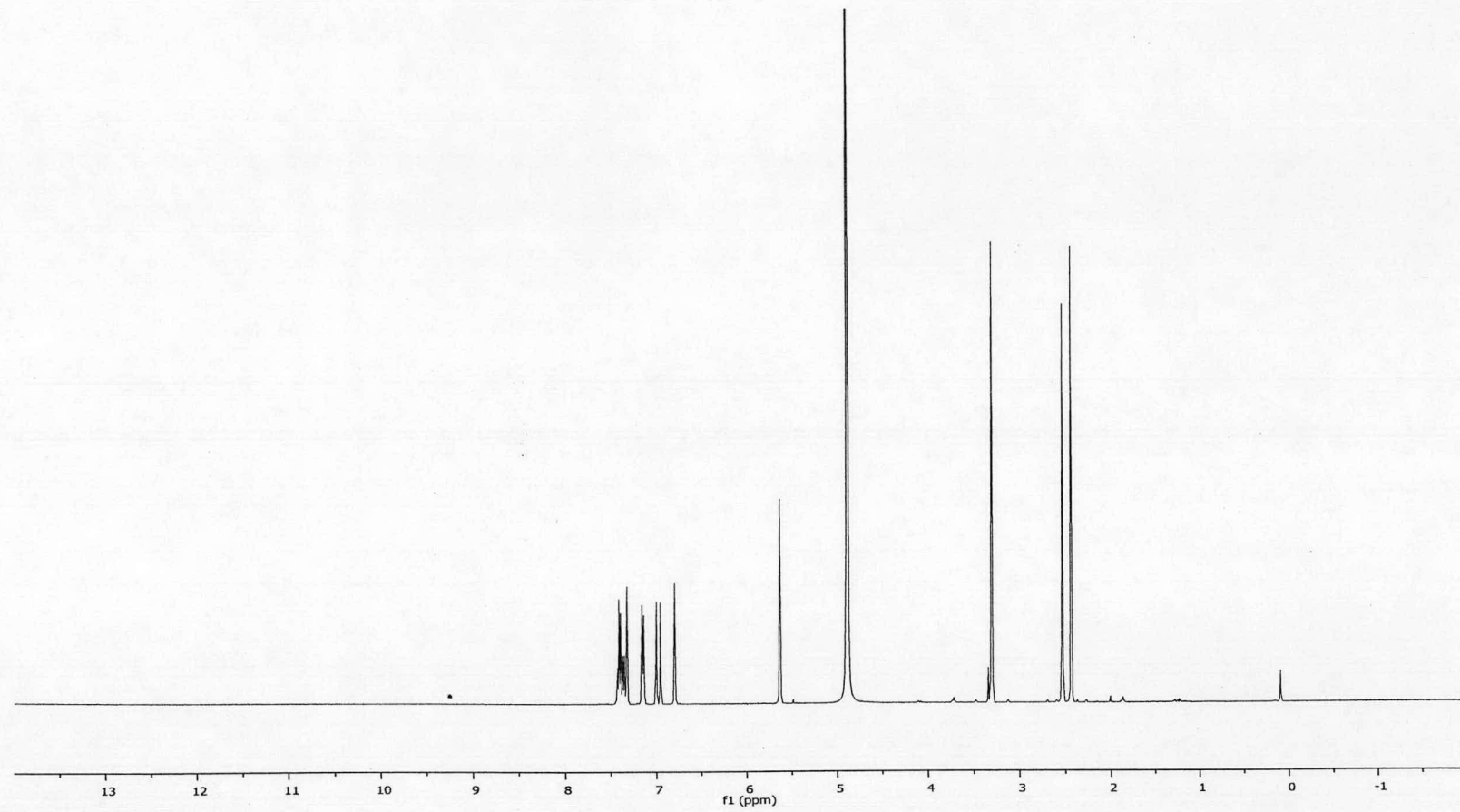


Figure A-32 $^1\text{H-NMR}$ spectrum of *N*-benzyl cassiarin A chloride obtained in CD_3OD (Compound **31a**)

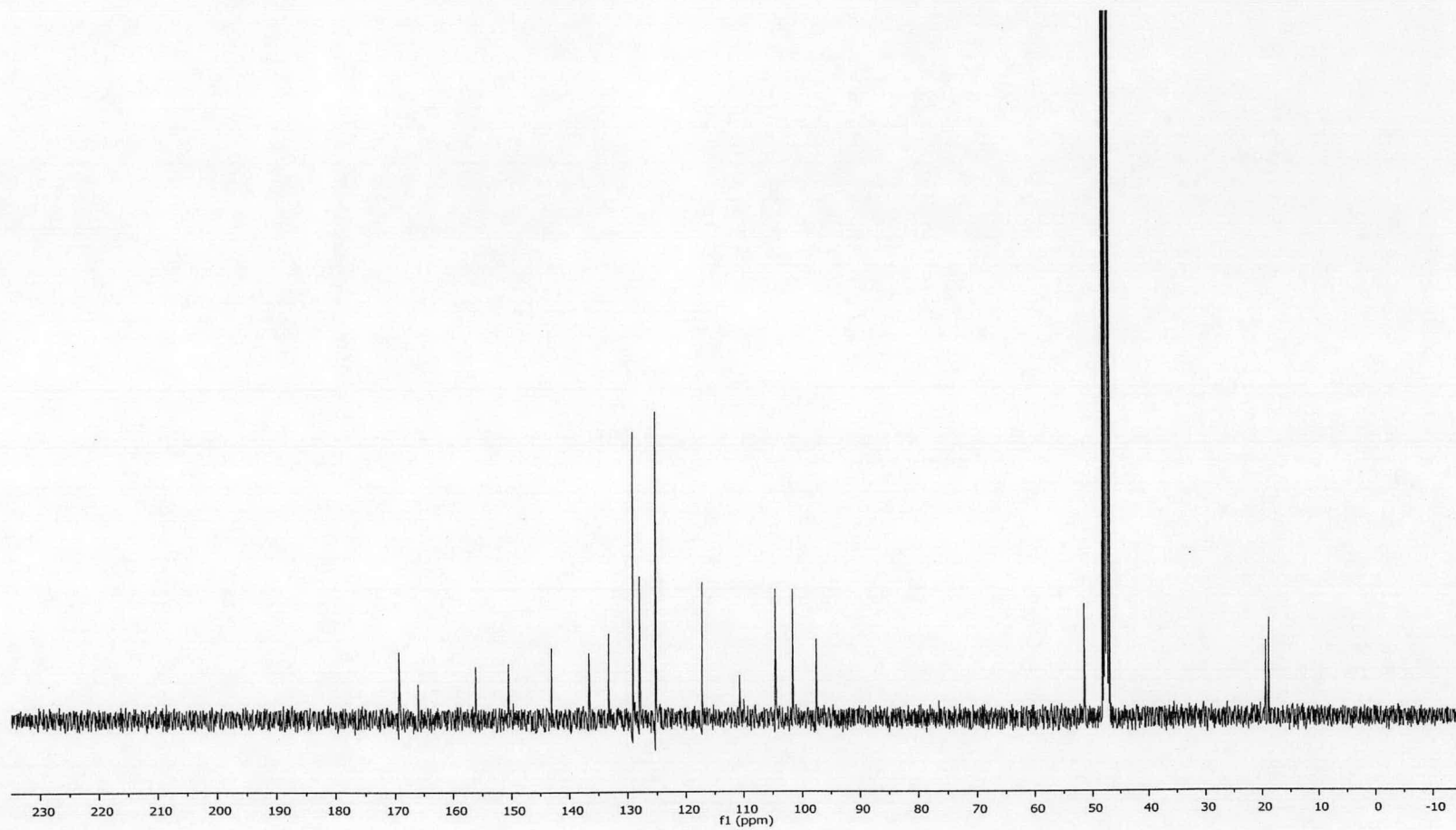


Figure A-33 ^{13}C -NMR spectrum of *N*-benzyl cassiarin A chloride obtained in CD_3OD (Compound **31a**)

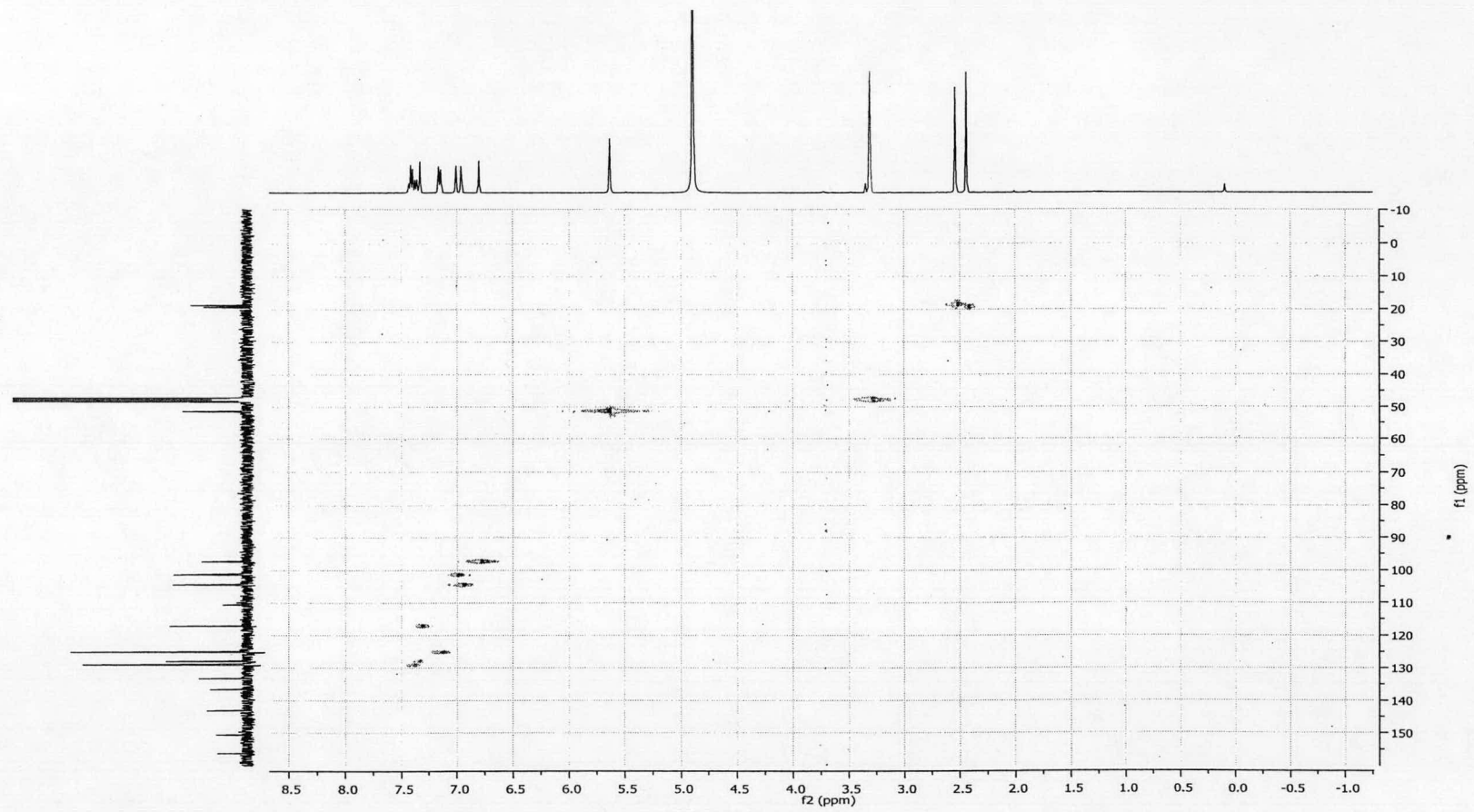


Figure A-34 HSQC spectrum of *N*-benzyl cassiarin A chloride obtained in CD₃OD (Compound 31a)

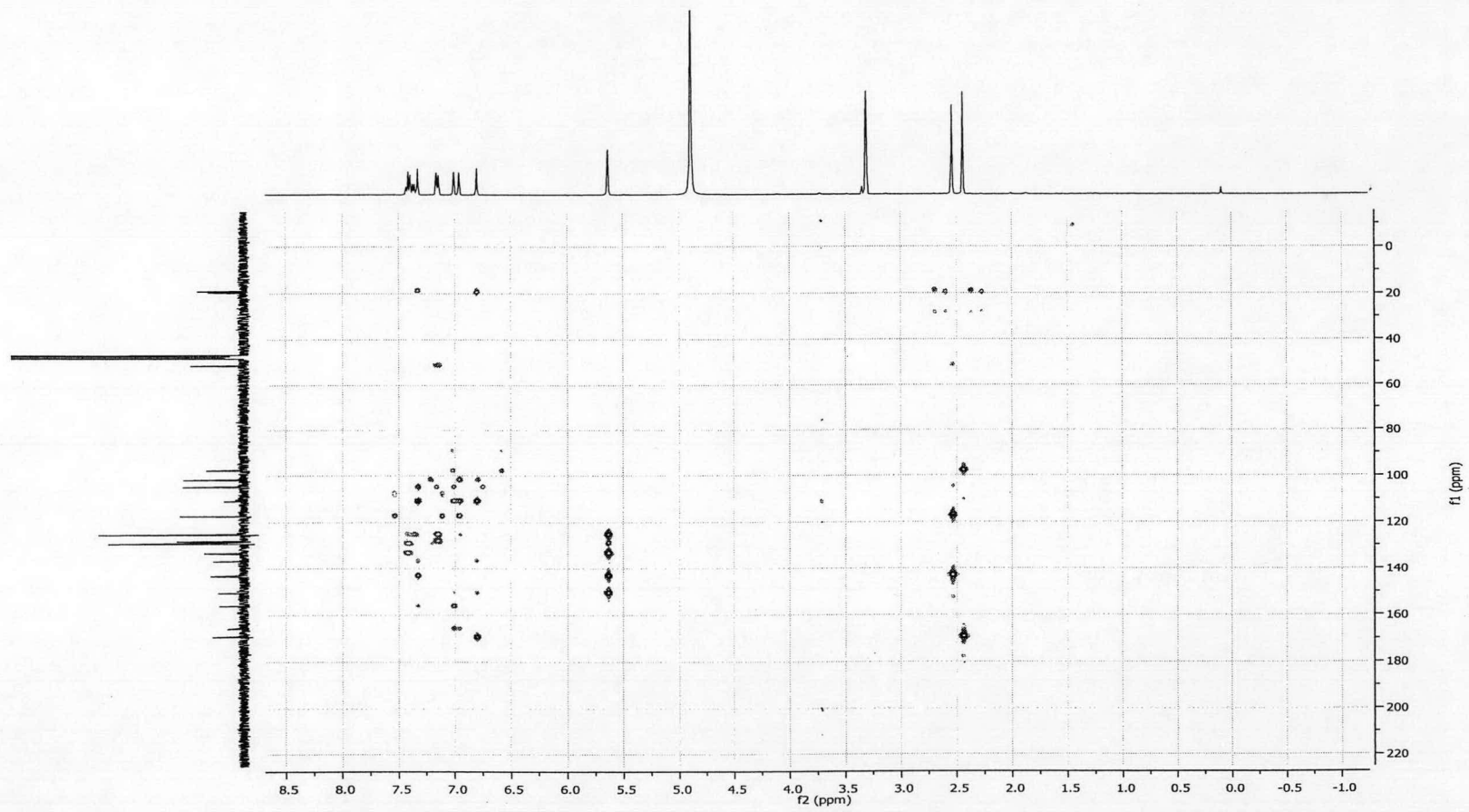


Figure A-35 HMBC spectrum of *N*-benzyl cassiarin A chloride obtained in CD₃OD (Compound 31a)

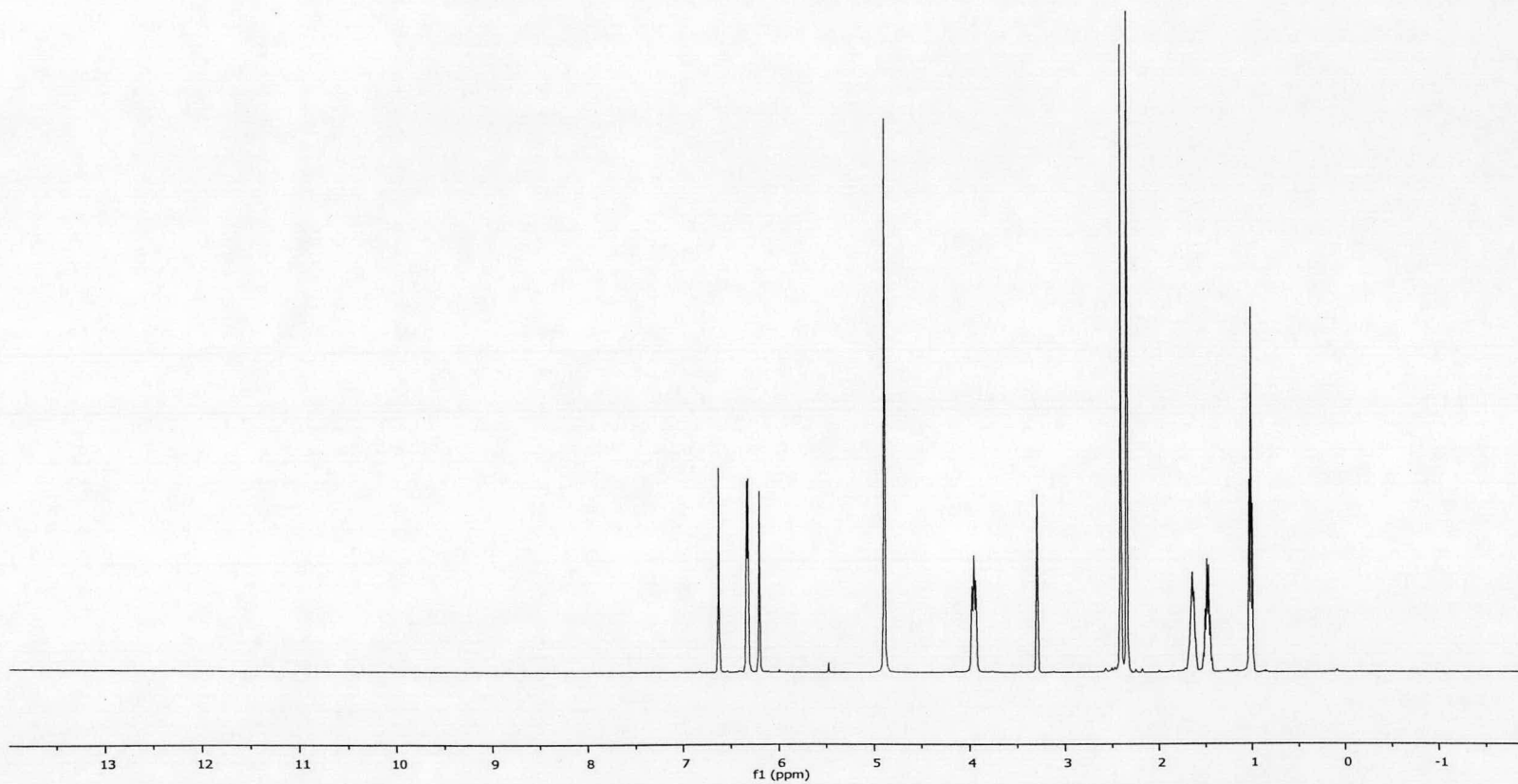


Figure A-36 $^1\text{H-NMR}$ spectrum of *N*-butyl cassiarin B (Compound 28b)

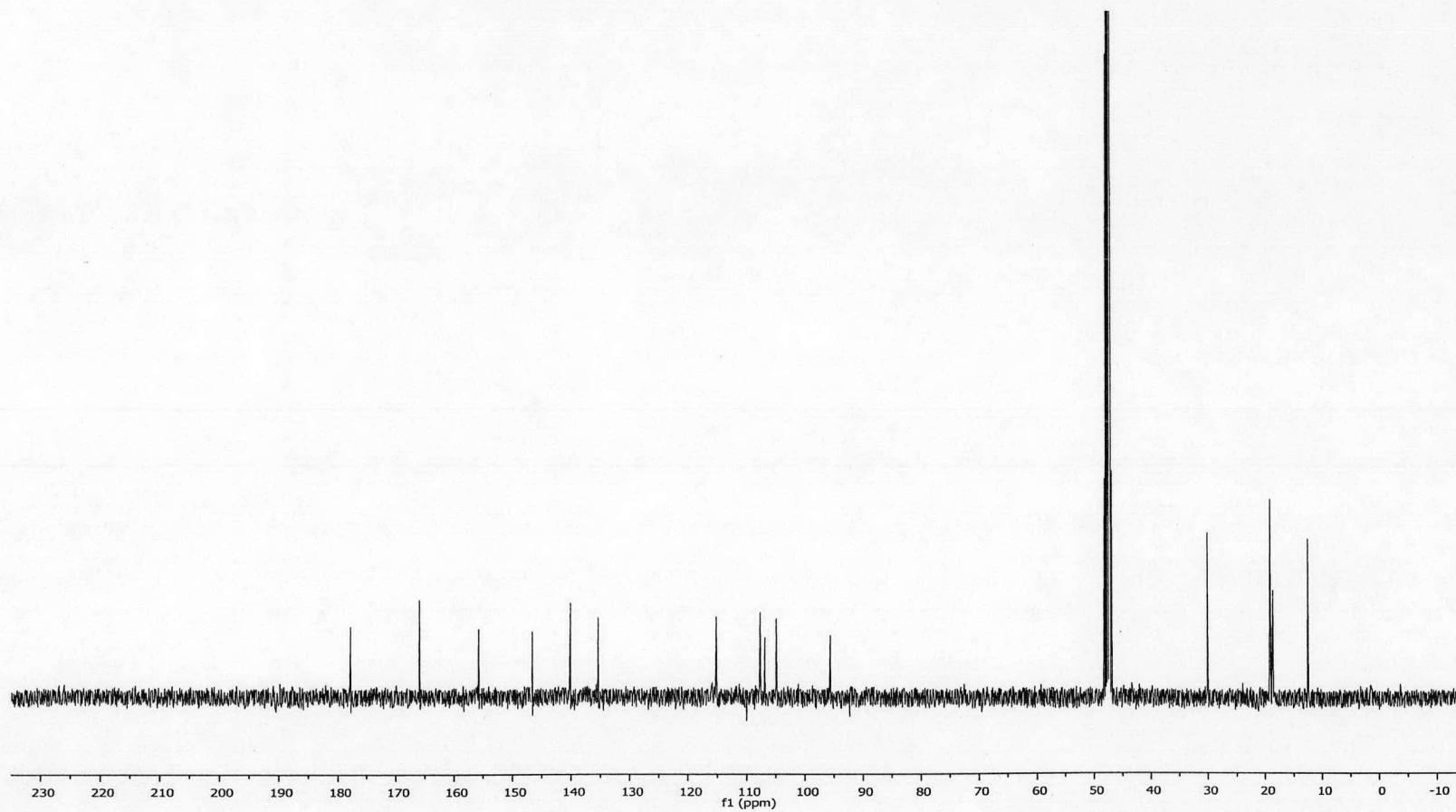


Figure A-37 ^{13}C -NMR spectrum of *N*-butyl cassiarin B (Compound 28b)

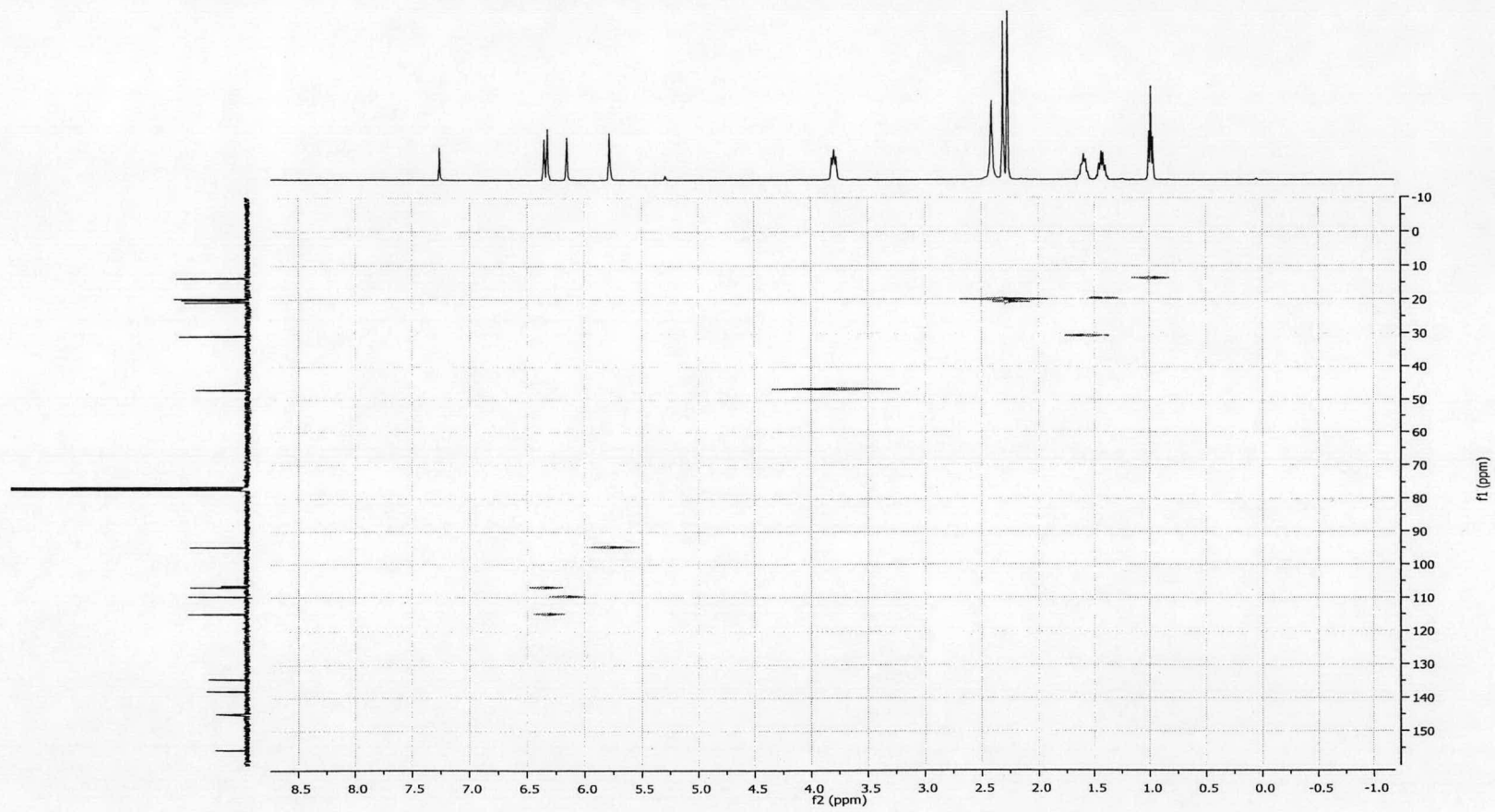


Figure A-38 HSQC spectrum of *N*-butyl cassiarin B (Compound 28b)

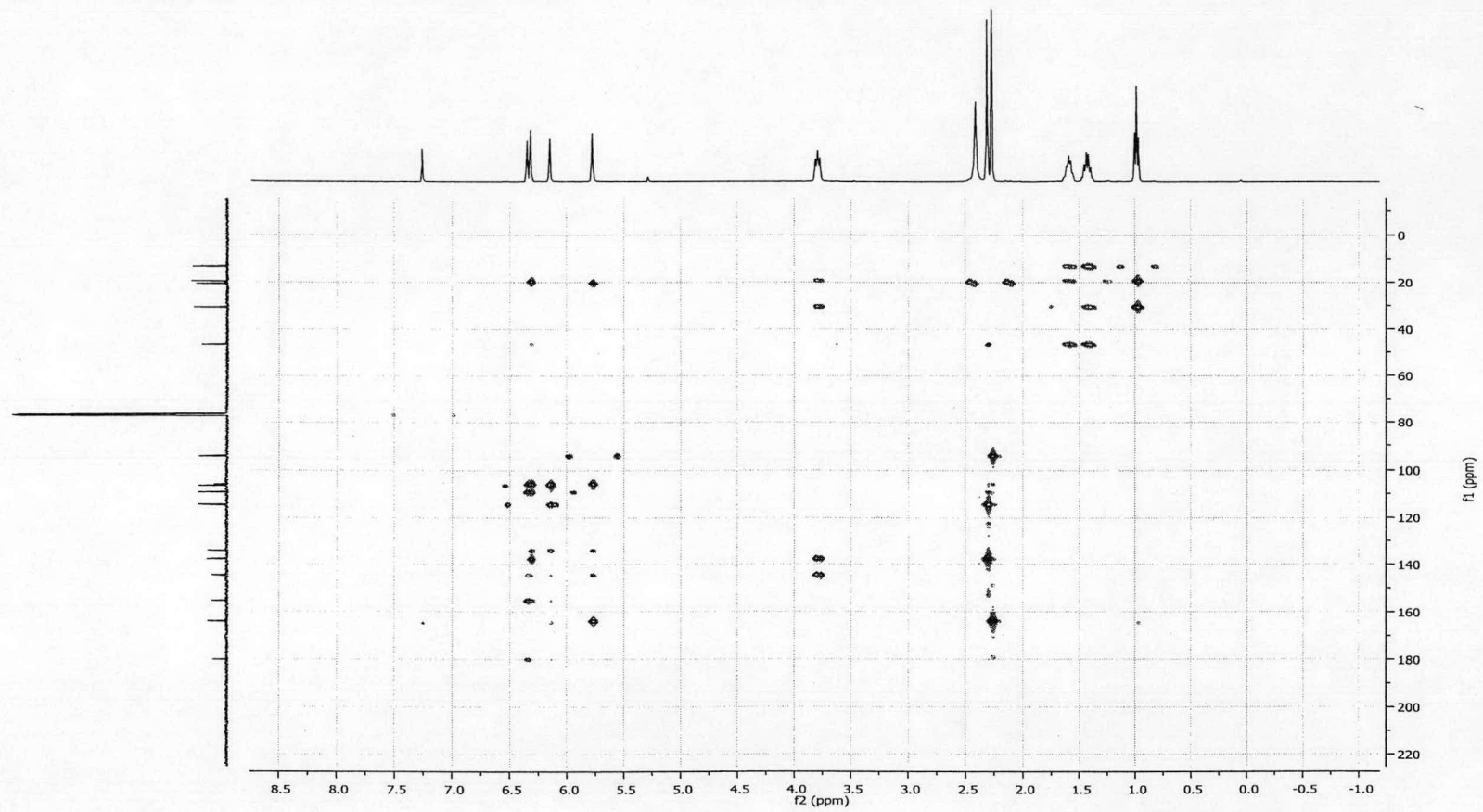


Figure A-39 HMBC spectrum of *N*-butyl cassiarin B (Compound 28b)

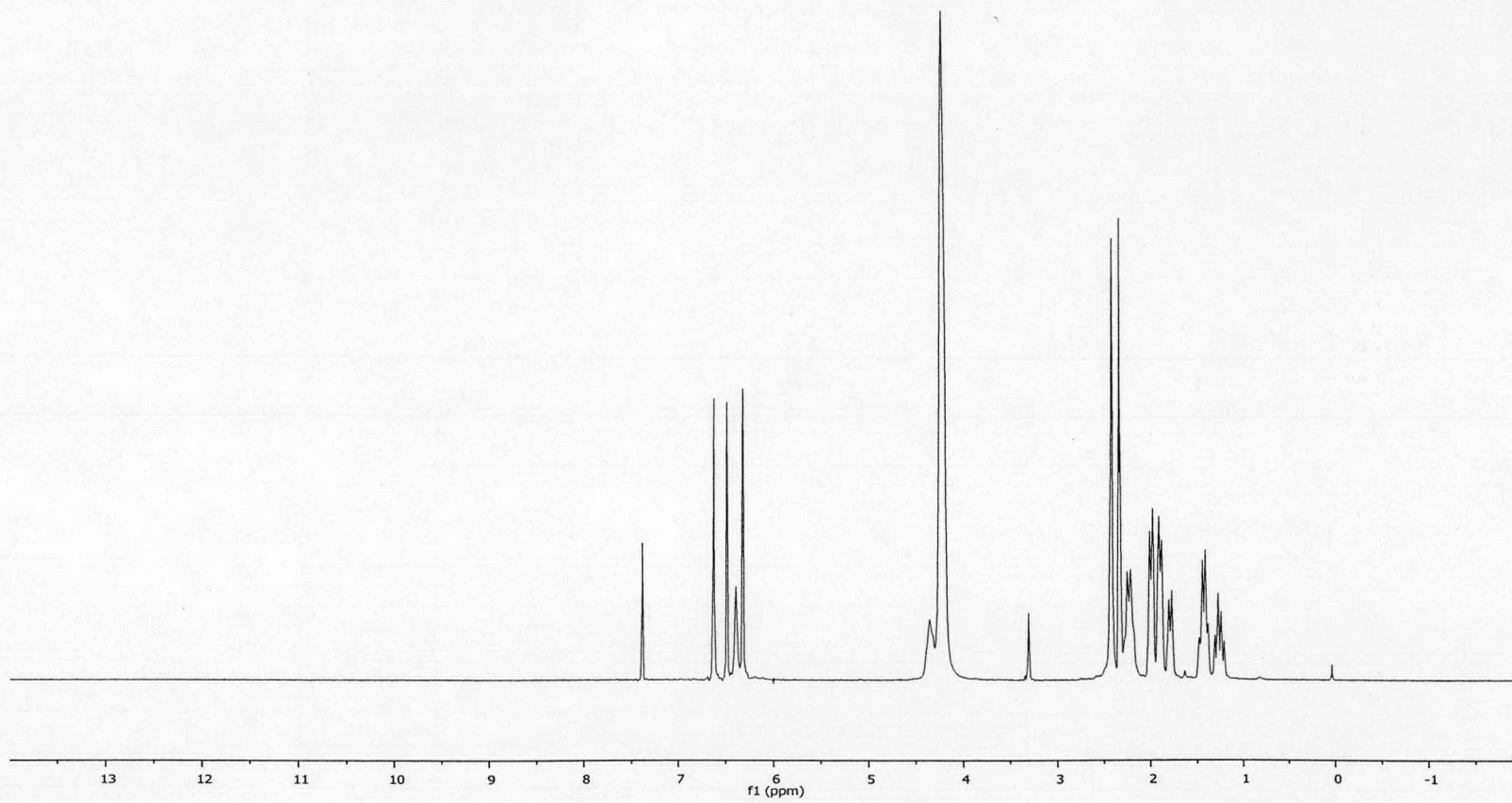


Figure A-40 $^1\text{H-NMR}$ spectrum of *N*-cyclohexyl cassiarin B (Compound **29b**)

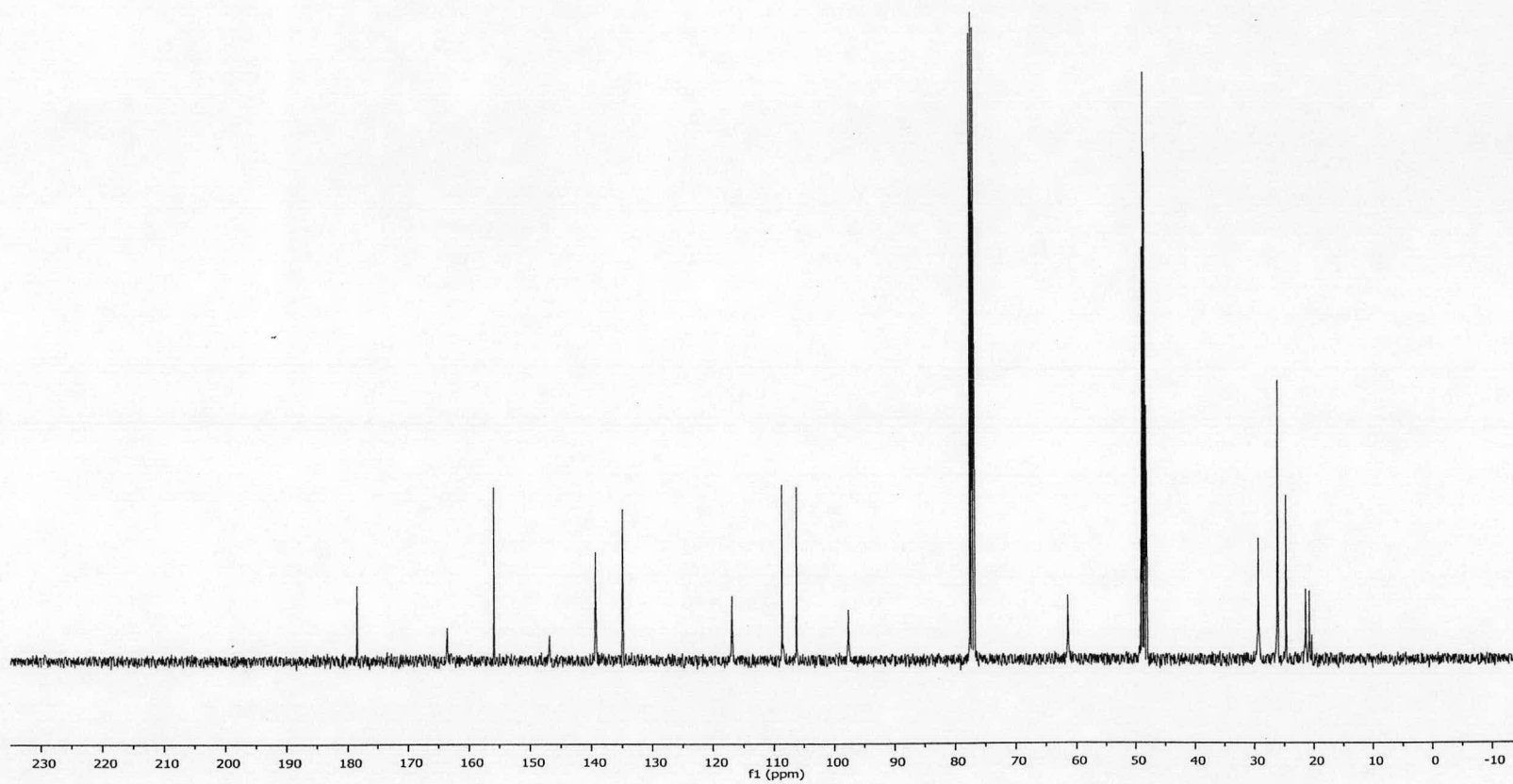


Figure A-41 ^{13}C -NMR spectrum of *N*-cyclohexyl cassiarin B (Compound 29b)

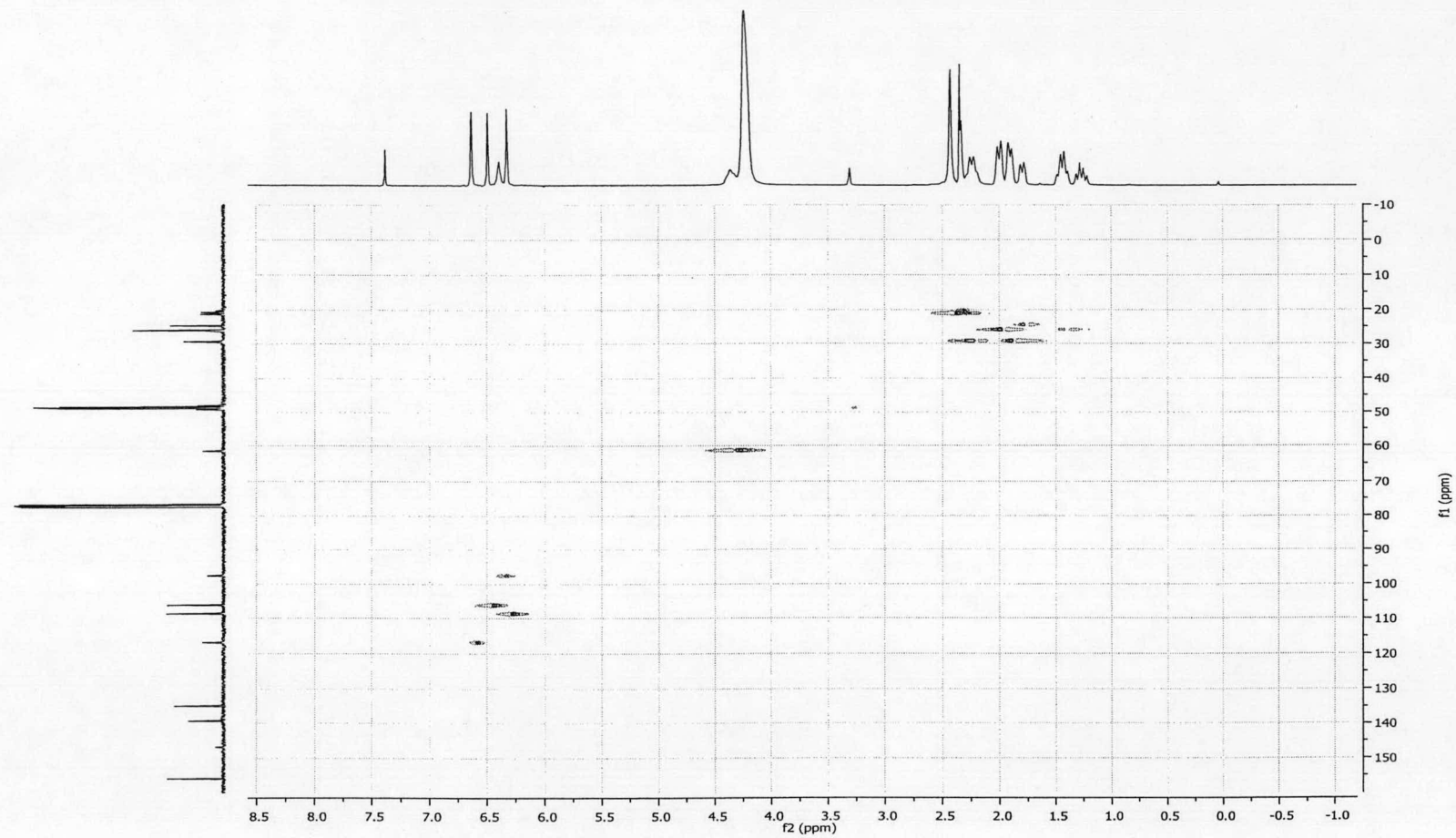


Figure A-42 HSQC spectrum of *N*-cyclohexyl cassiarin B (Compound 29b)

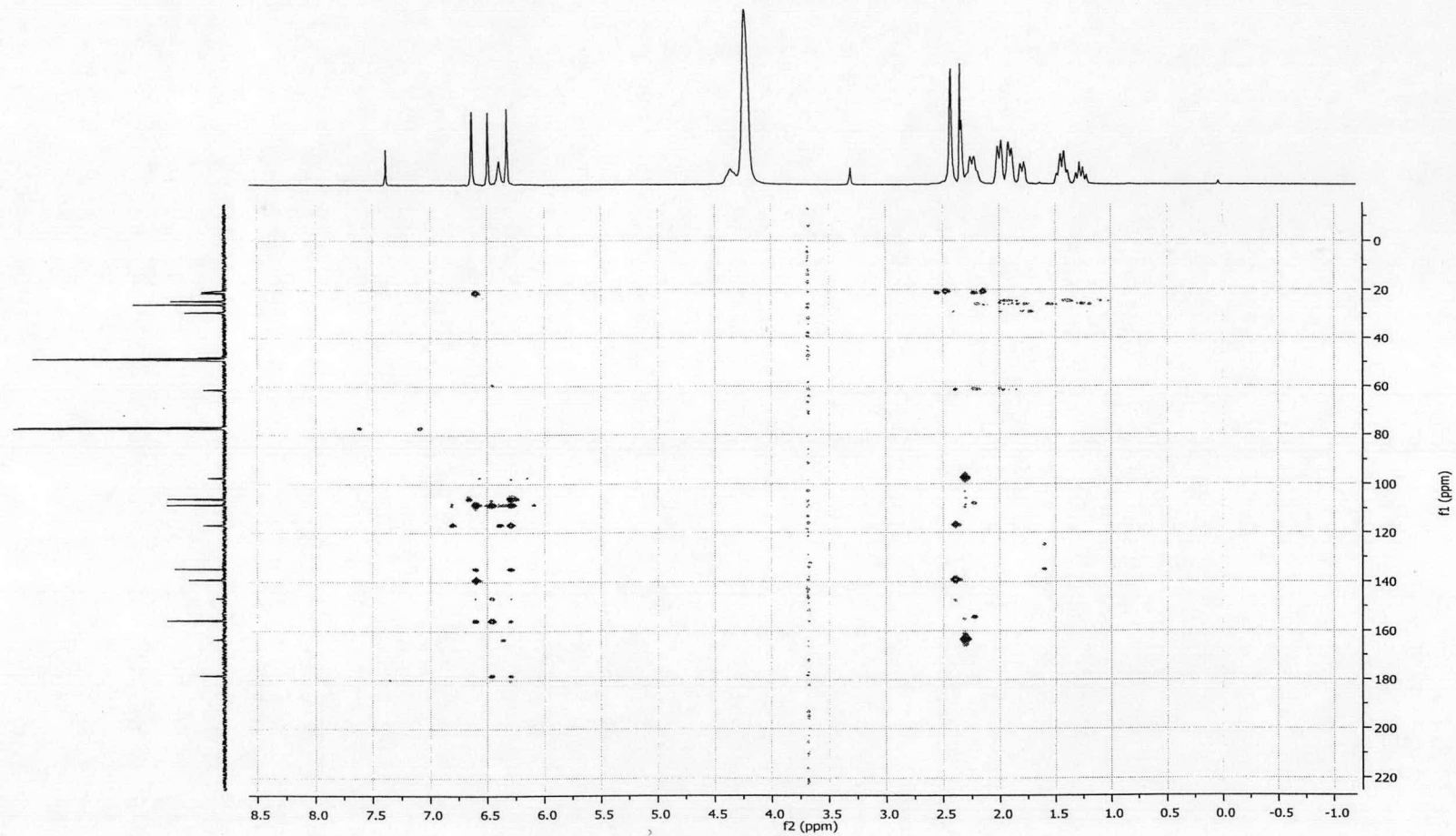


Figure A-43 HMBC spectrum of *N*-cyclohexyl cassiarin B (Compound 29b)

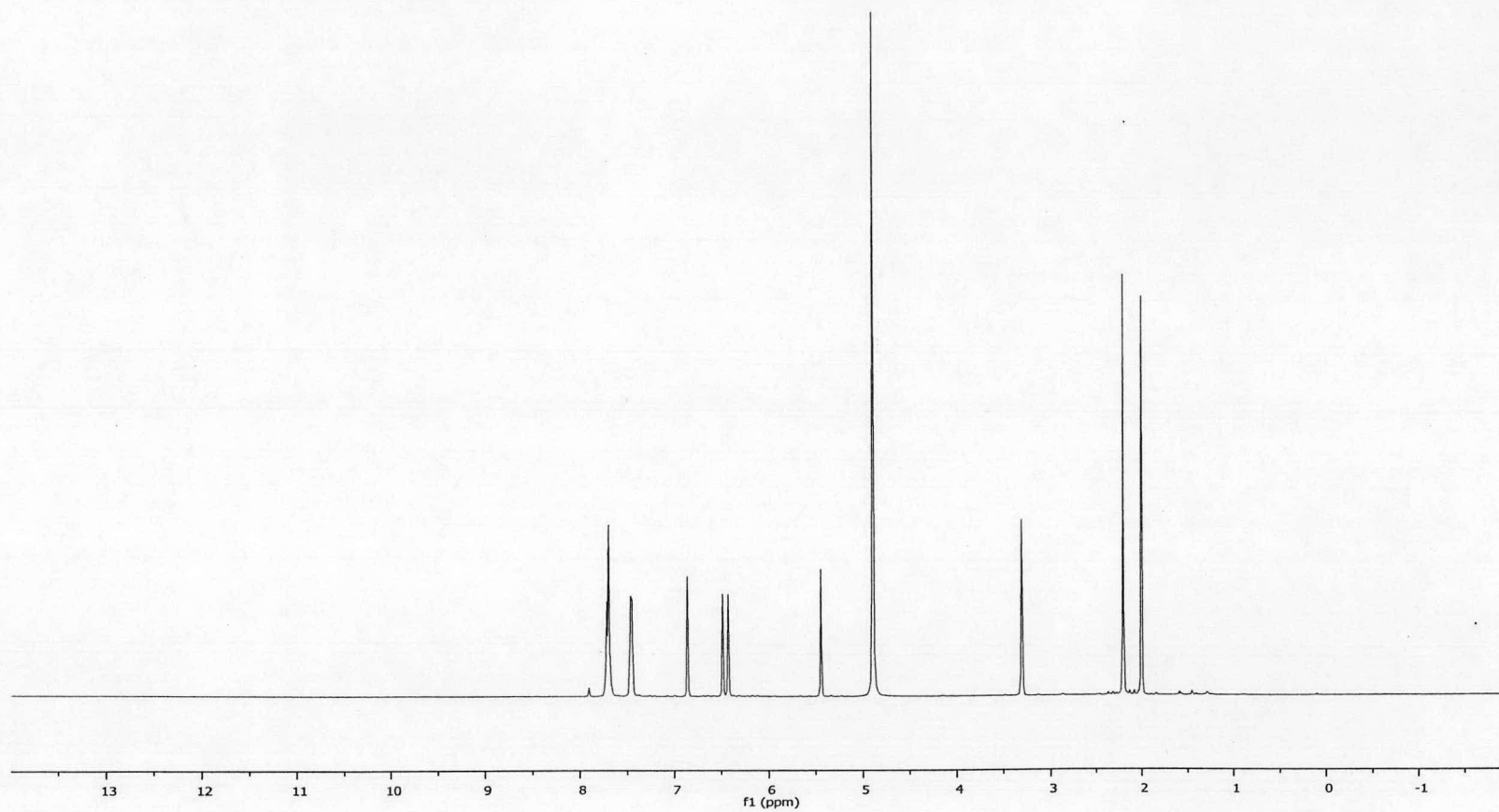


Figure A-44 ¹H-NMR spectrum of *N*-phenyl cassiarin B (Compound 30b)

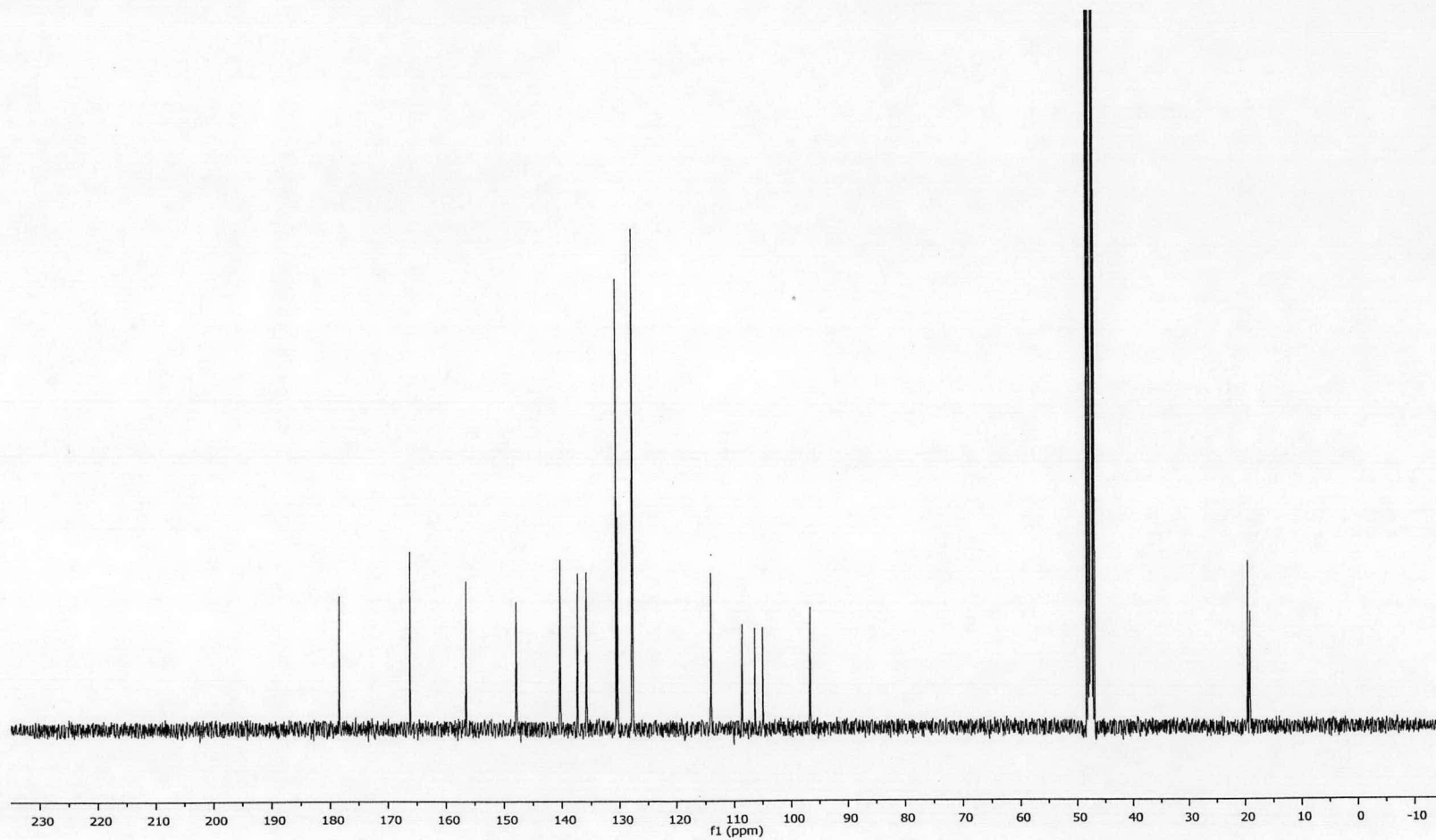


Figure A-45 ^{13}C -NMR spectrum of *N*-phenyl cassiarin B (Compound 30b)

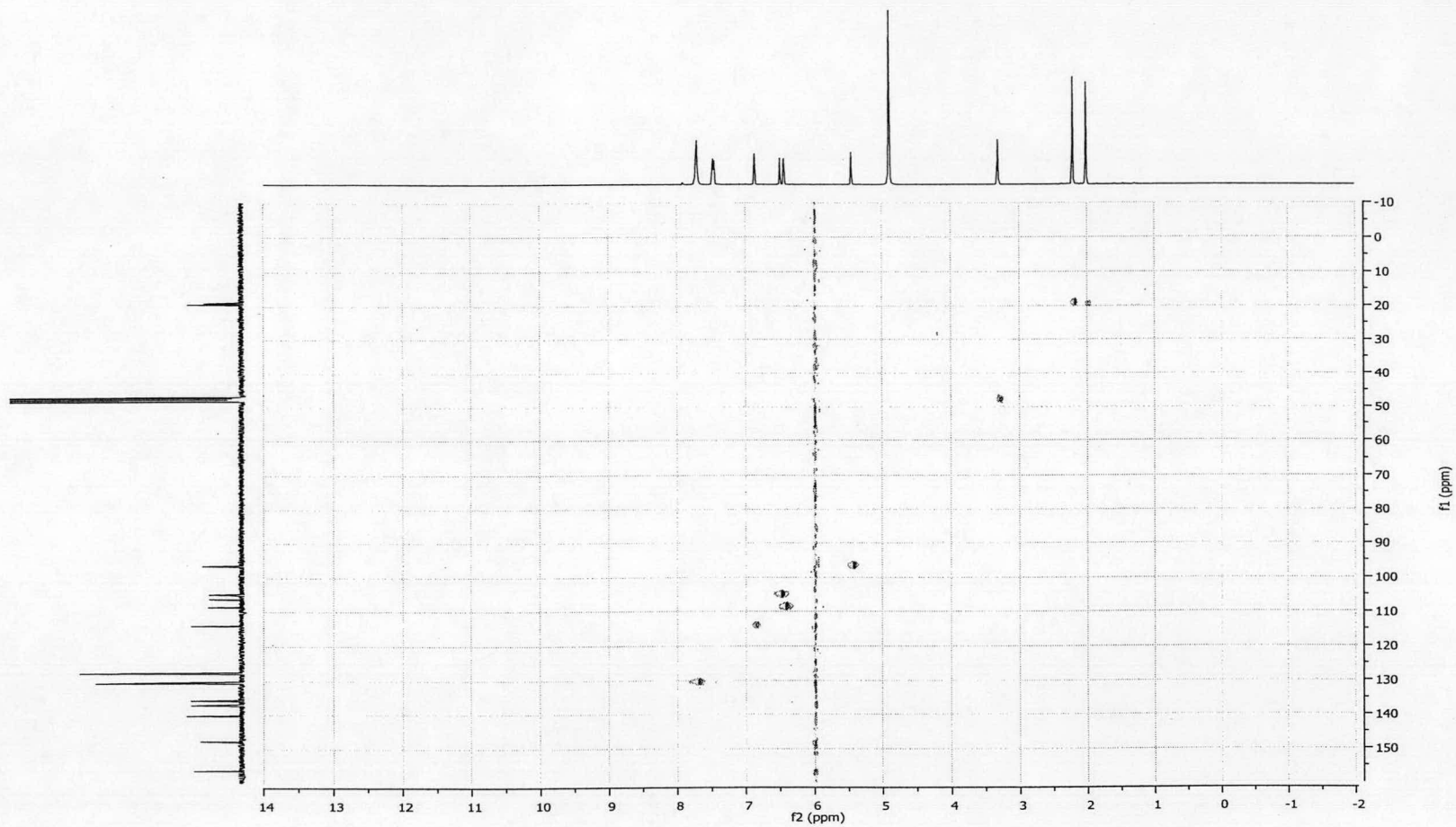


Figure A-46 HSQC spectrum of *N*-phenyl cassiarin B (Compound 30b)

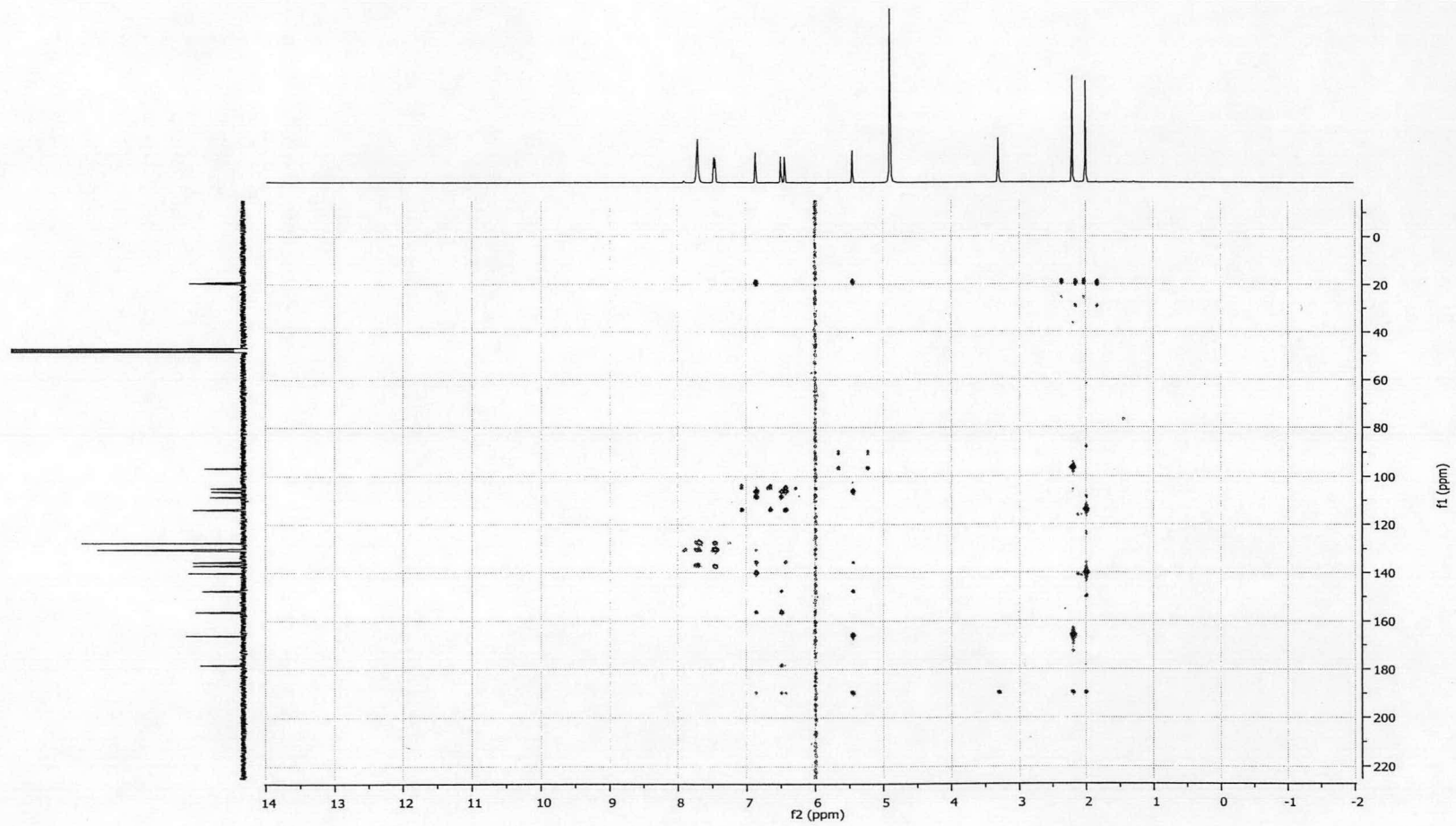


Figure A-47 HMBC spectrum of *N*-phenyl cassiarin B (Compound 30b)

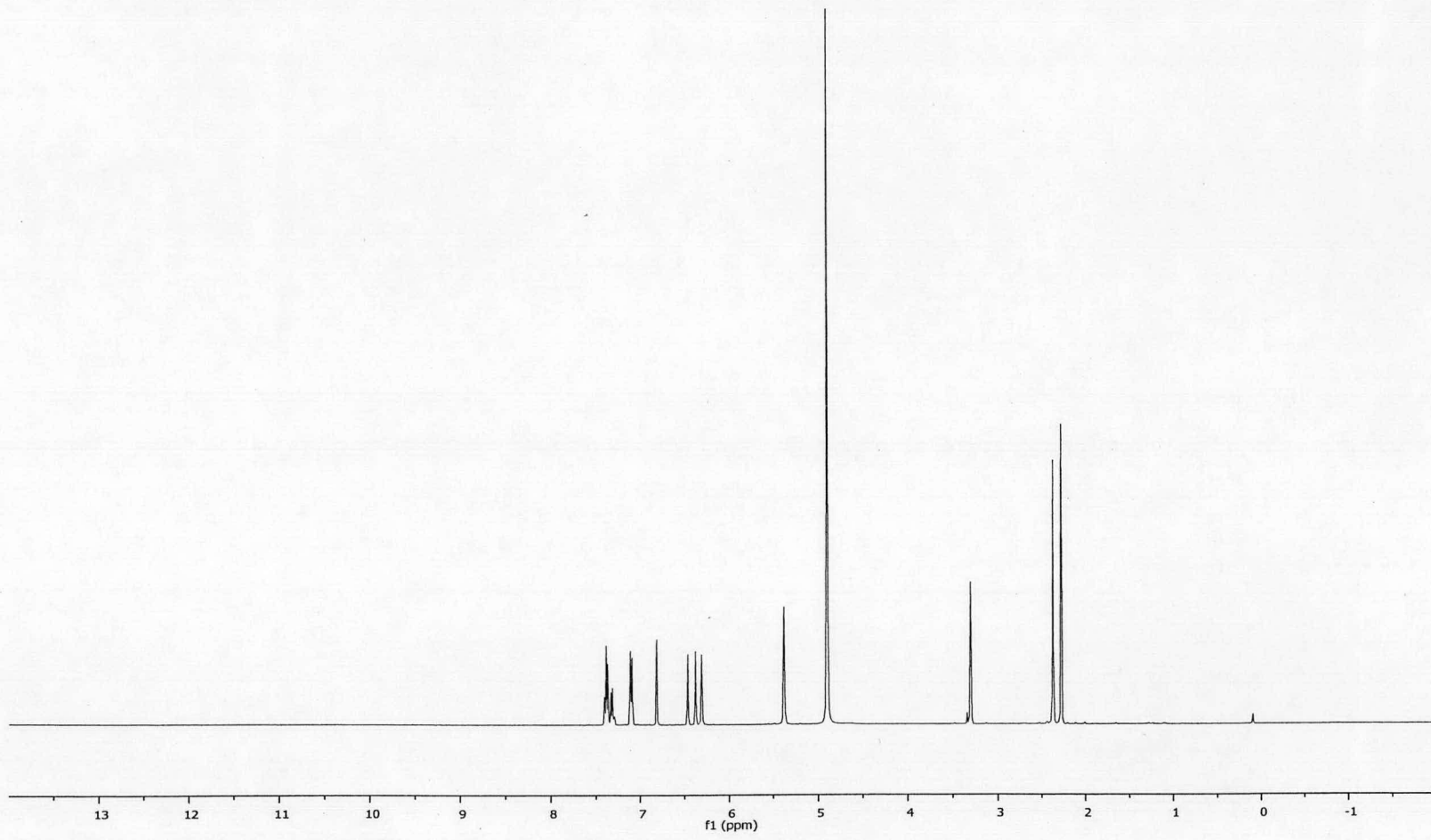


Figure A-48 ¹H-NMR spectrum of *N*-benzyl cassiarin B (Compound 31b)

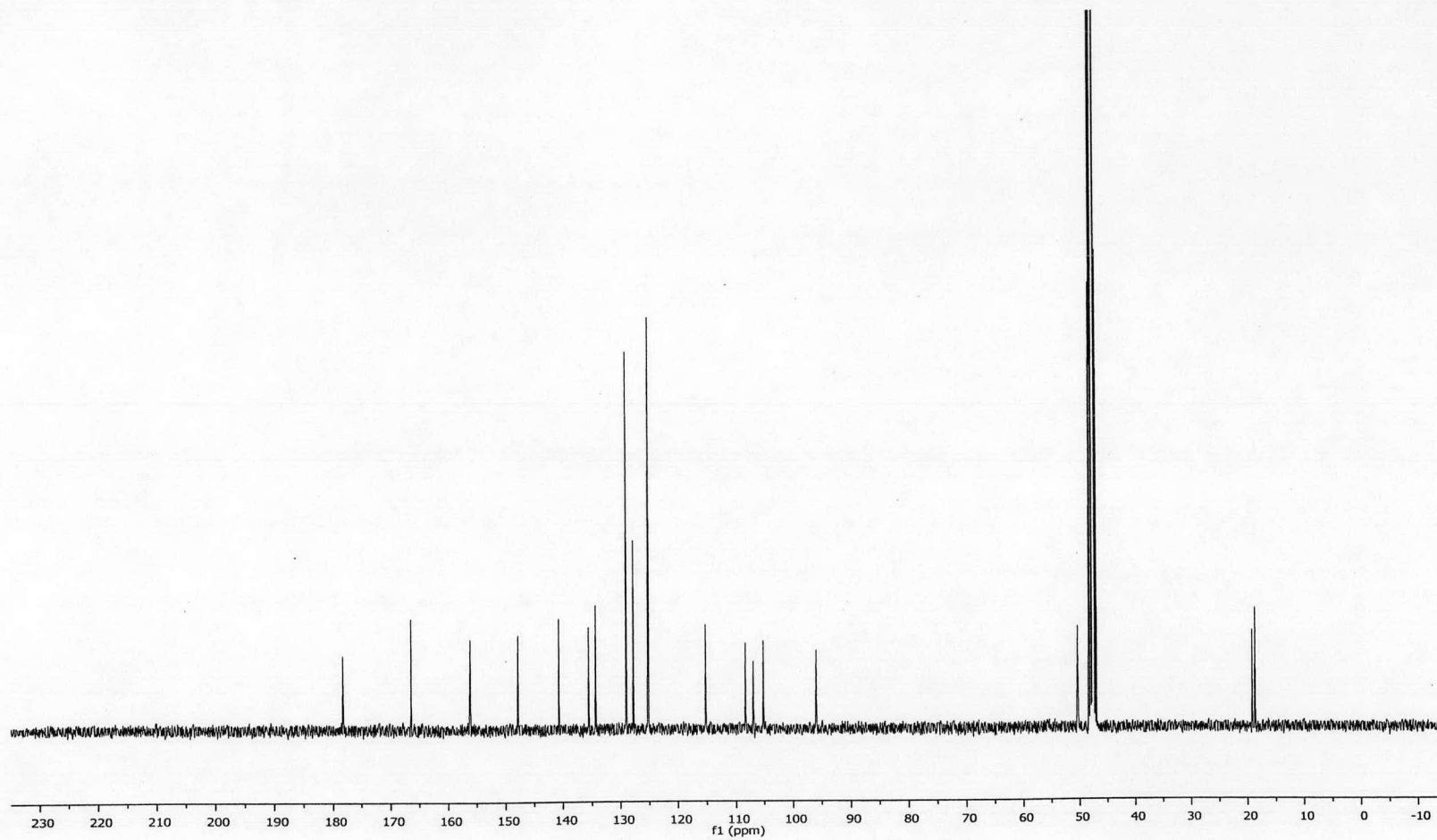


Figure A-49 ^{13}C -NMR spectrum of *N*-benzyl cassiarin B (Compound 31b)

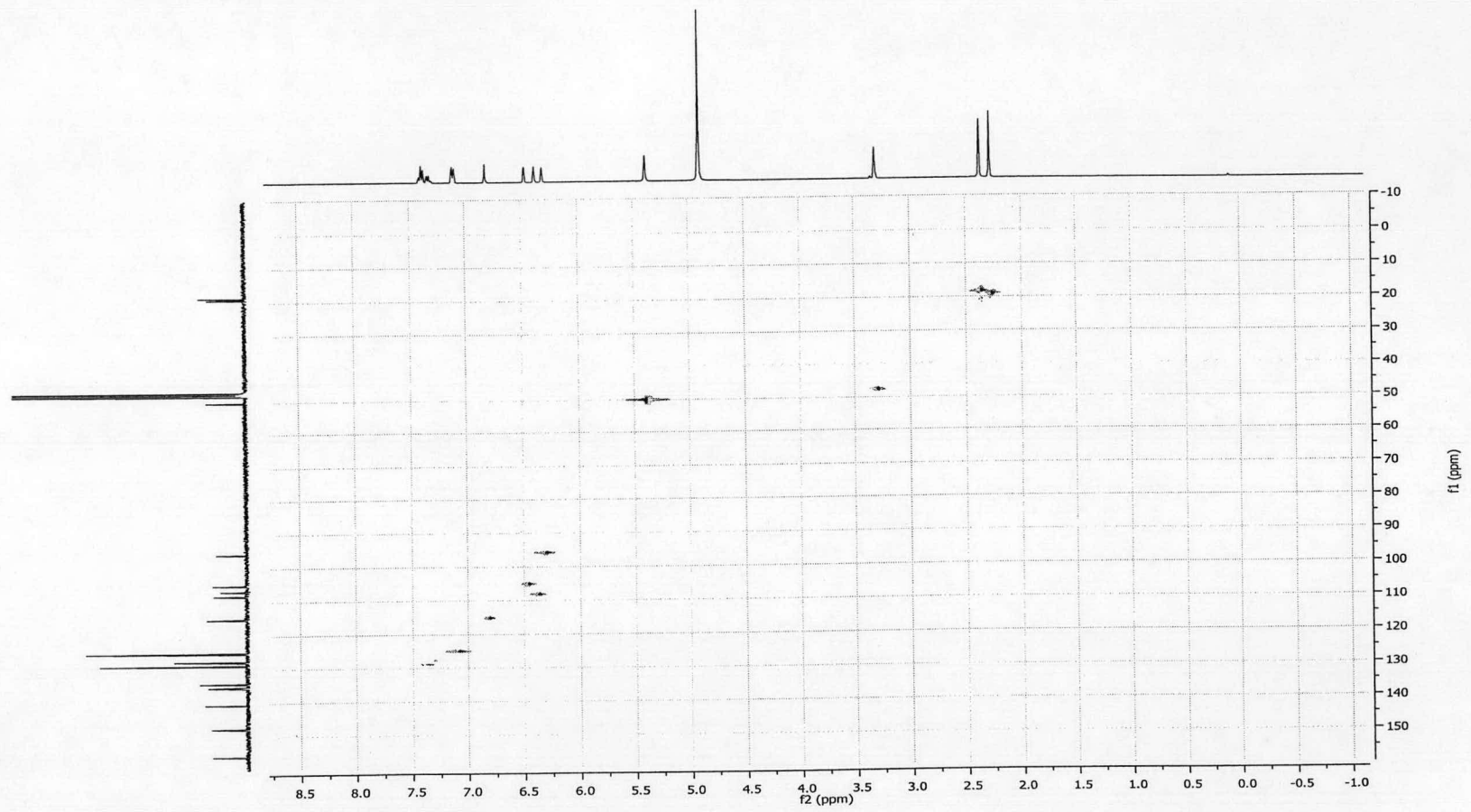


Figure A-50 HSQC spectrum of *N*-benzyl cassiarin B (Compound 31b)

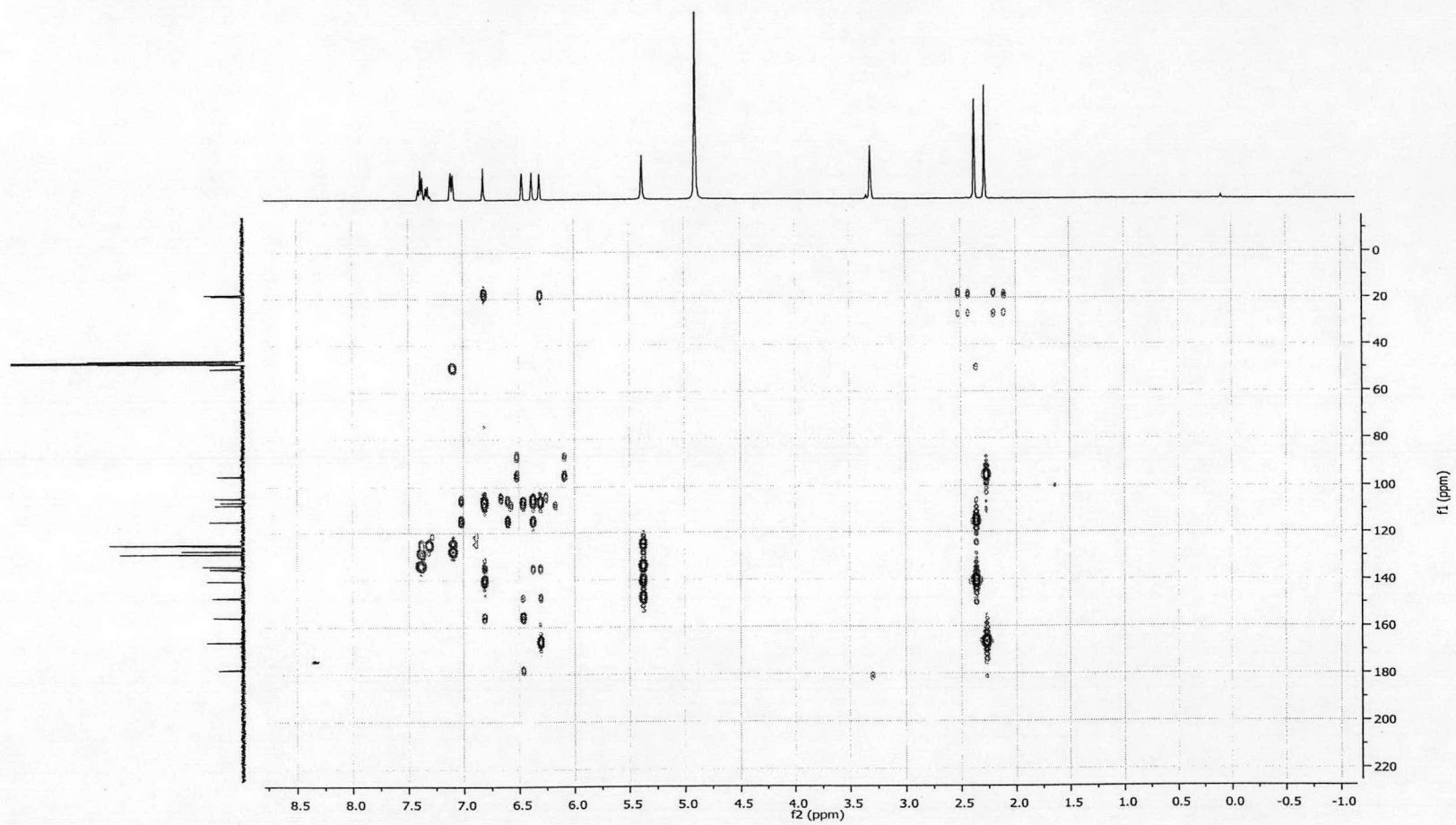


Figure A-51 HMBC spectrum of *N*-benzyl cassiarin B (Compound 31b)

APPENDIX B

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	47 V
Scan Range	n/a	Capillary Exit	140.0 V	Set Pulsar Pull	394 V
Scan Begin	50 m/z	Hexapole RF	150.0 V	Set Pulsar Push	394 V
Scan End	3000 m/z	Skimmer 1	30.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

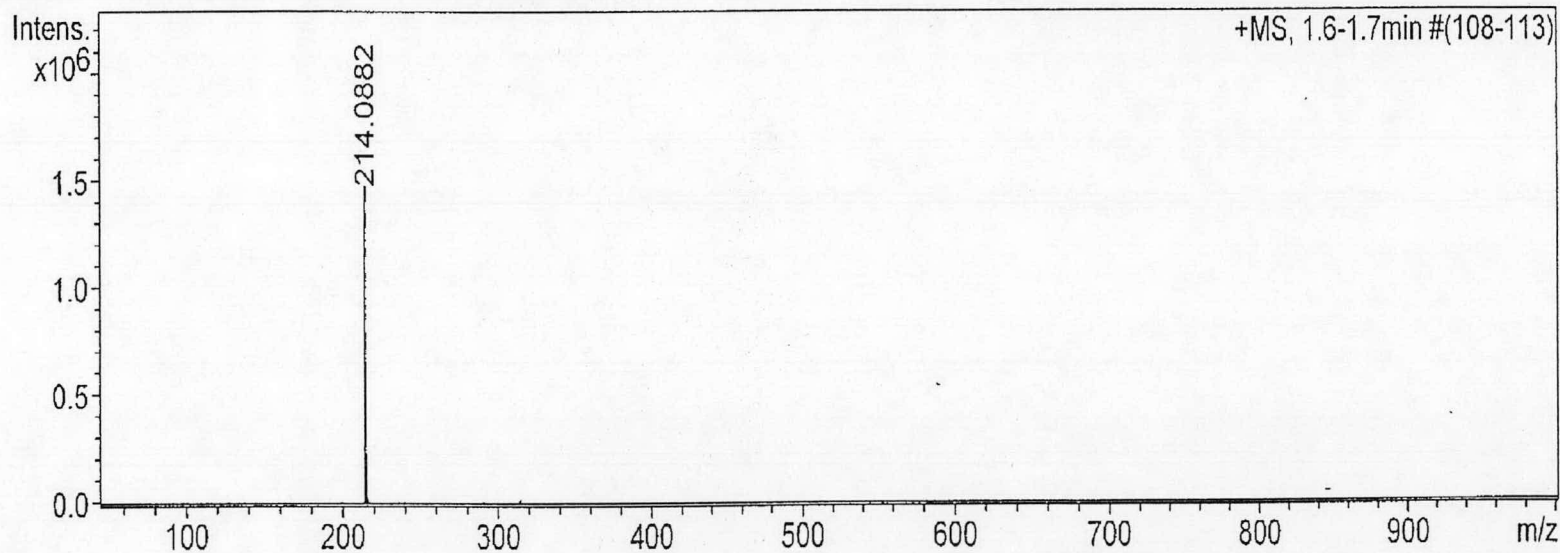


Figure B-1 Mass spectrum of cassiarin A hydrochloride (Compound **4a**)

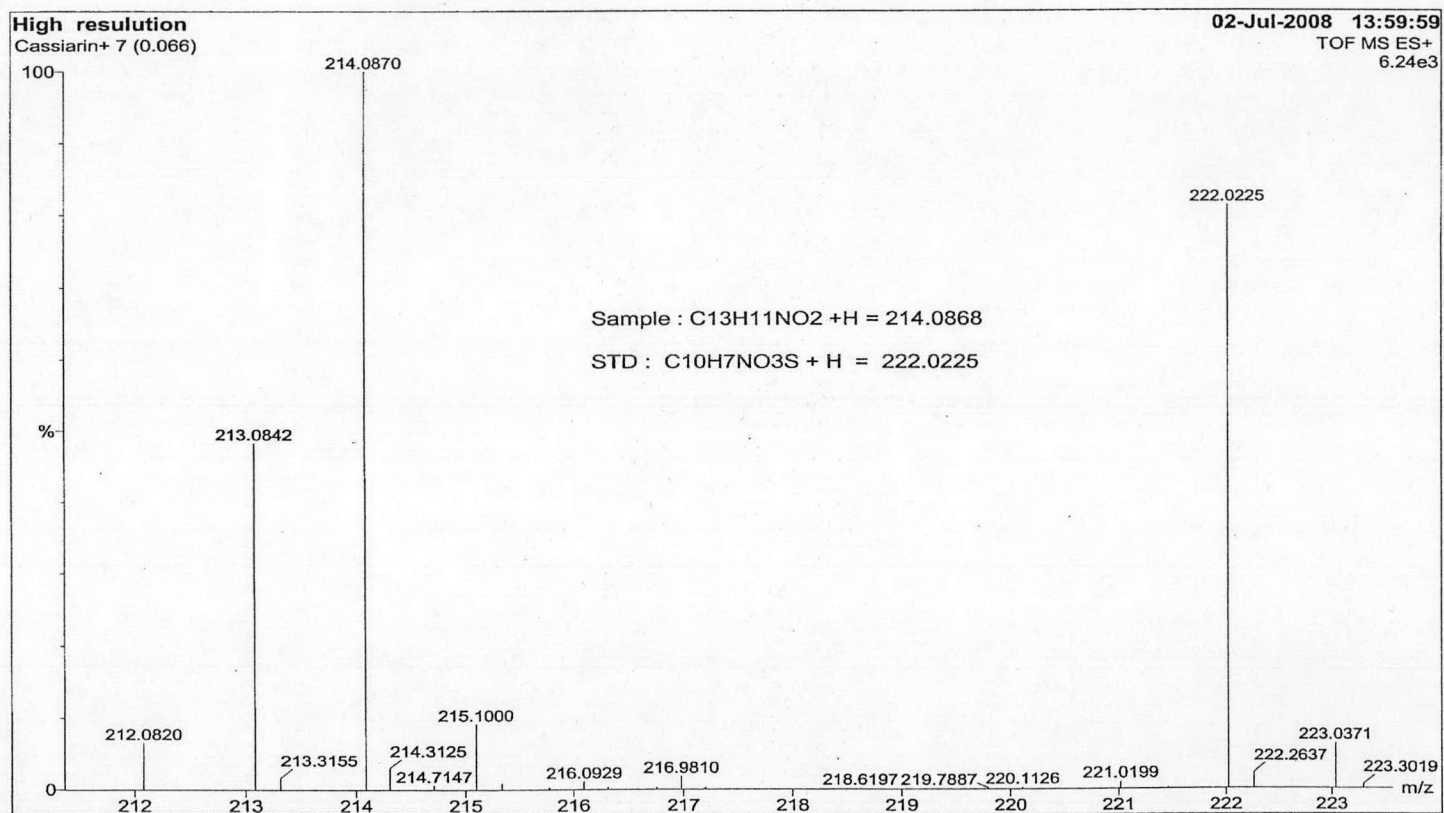


Figure B-2 Mass spectrum of cassiarin A (Compound 4)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	47 V
Scan Range	n/a	Capillary Exit	140.0 V	Set Pulsar Pull	394 V
Scan Begin	50 m/z	Hexapole RF	150.0 V	Set Pulsar Push	394 V
Scan End	3000 m/z	Skimmer 1	30.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

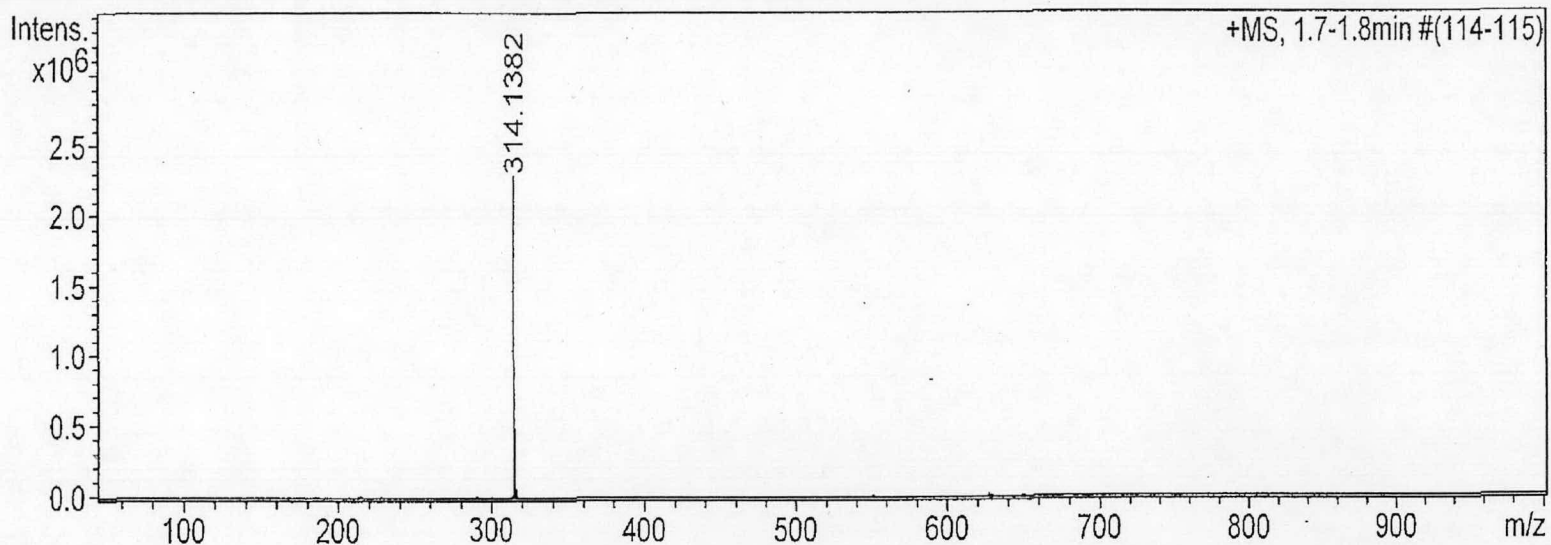


Figure B-3 Mass spectrum of *N*-4-methoxy-4-oxobutyl cassiarin A chloride (Compound **5a**)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	47 V
Scan Range	n/a	Capillary Exit	120.0 V	Set Pulsar Pull	394 V
Scan Begin	50 m/z	Hexapole RF	160.0 V	Set Pulsar Push	394 V
Scan End	3000 m/z	Skimmer 1	40.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

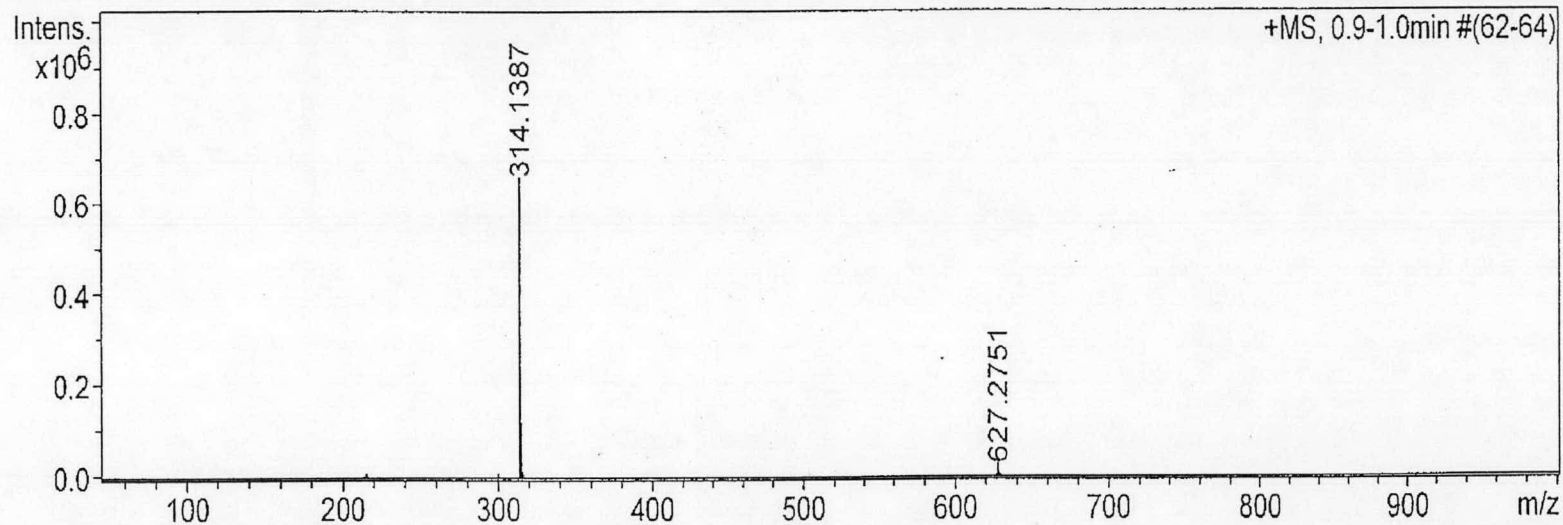


Figure B-4 Mass spectrum of cassairin B (Compound 5)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	47 V
Scan Range	n/a	Capillary Exit	140.0 V	Set Pulsar Pull	394 V
Scan Begin	50 m/z	Hexapole RF	250.0 V	Set Pulsar Push	394 V
Scan End	3000 m/z	Skimmer 1	40.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

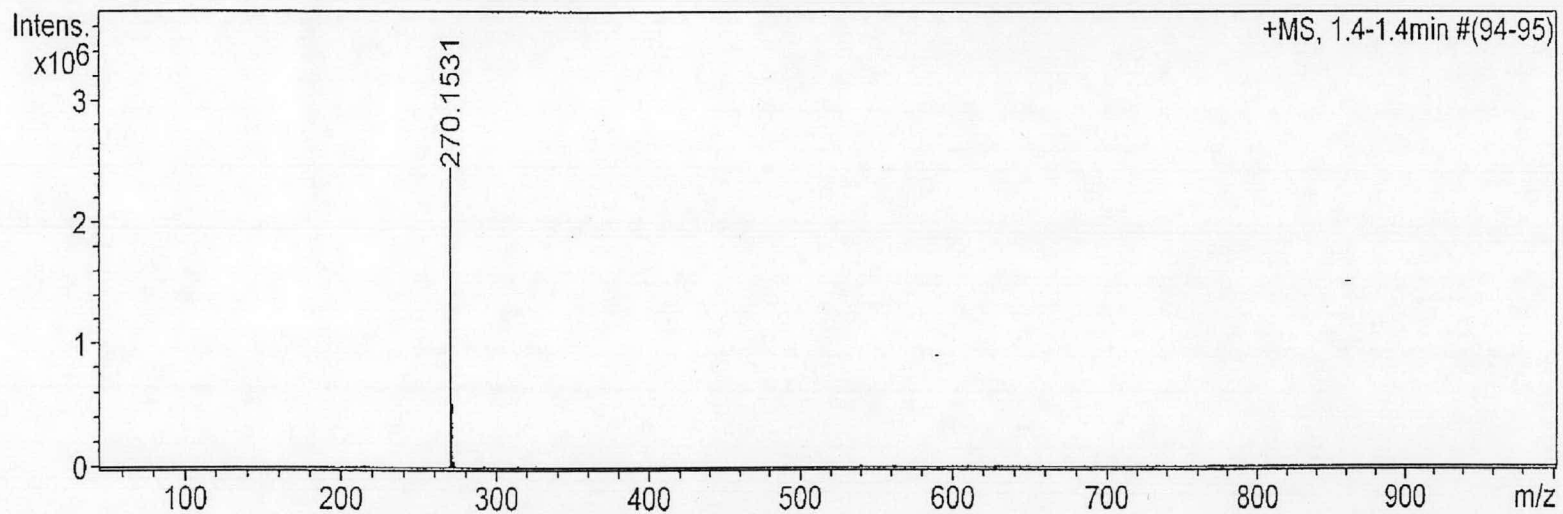


Figure B-5 Mass spectrum of *N*-butyl cassiarin A chloride (Compound **28a**)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	47 V
Scan Range	n/a	Capillary Exit	140.0 V	Set Pulsar Pull	394 V
Scan Begin	50 m/z	Hexapole RF	250.0 V	Set Pulsar Push	394 V
Scan End	3000 m/z	Skimmer 1	40.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

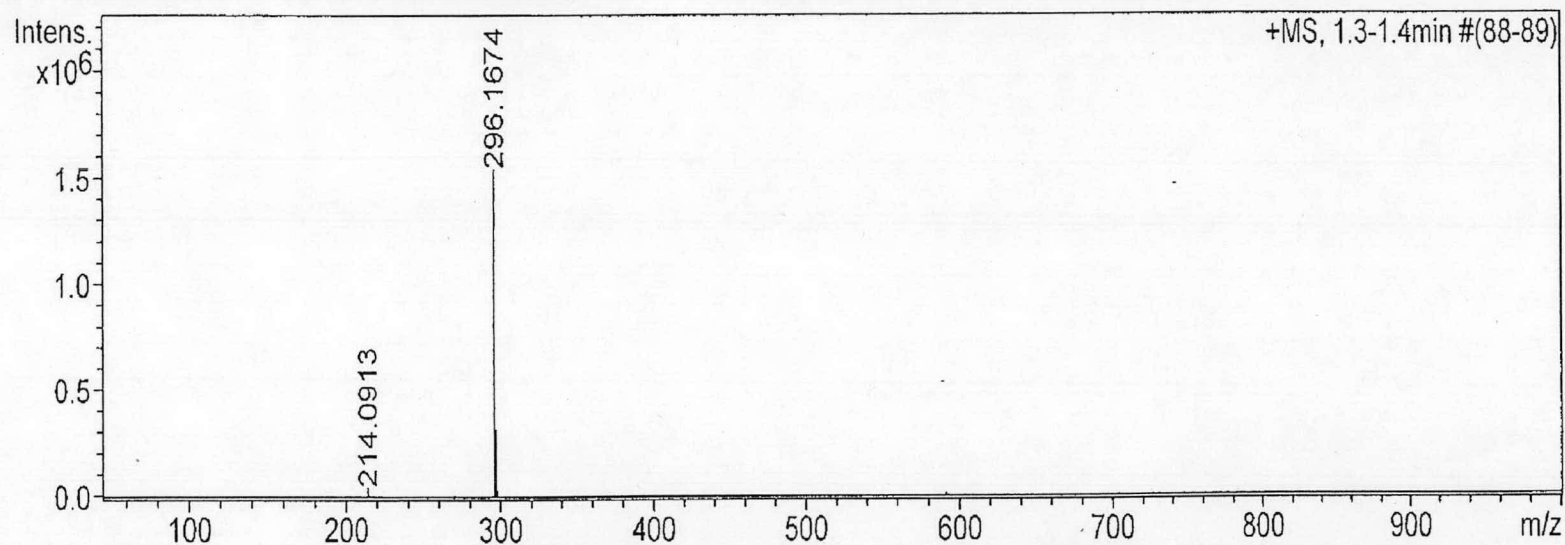


Figure B-6 Mass spectrum of *N*-cyclohexyl cassiarin A chloride (Compound **29a**)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	47 V
Scan Range	n/a	Capillary Exit	150.0 V	Set Pulsar Pull	394 V
Scan Begin	50 m/z	Hexapole RF	200.0 V	Set Pulsar Push	394 V
Scan End	3000 m/z	Skimmer 1	40.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

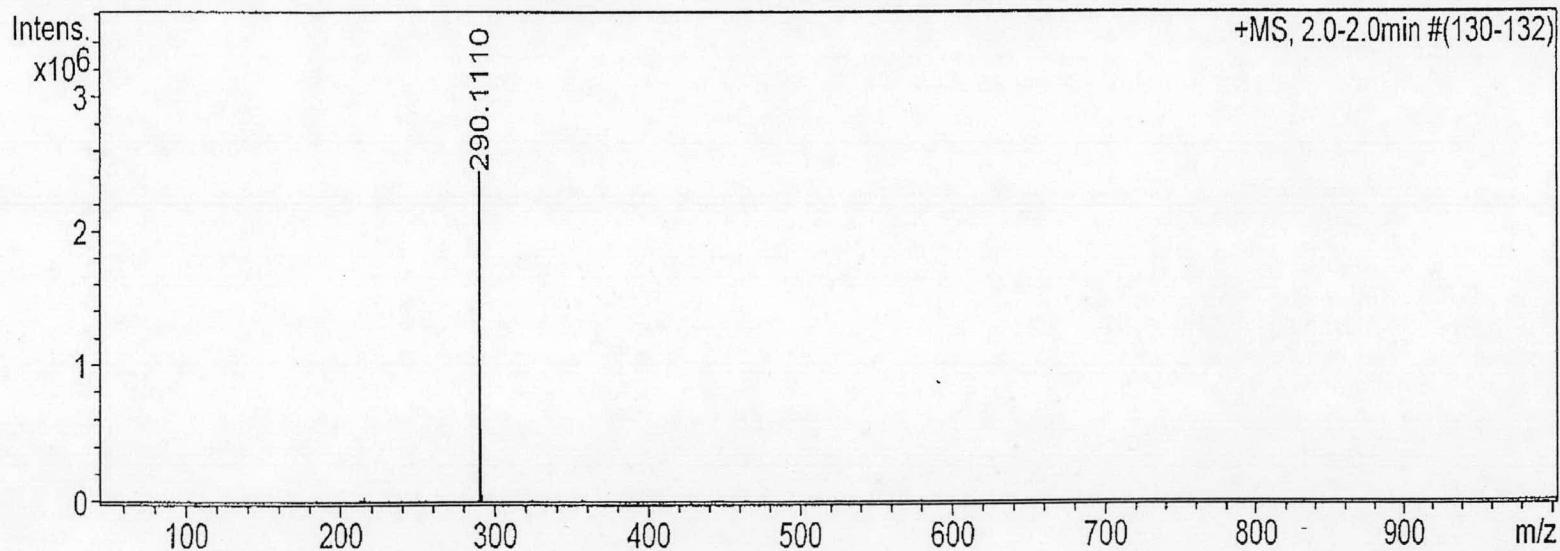


Figure B-7 Mass spectrum of *N*-phenyl cassiarin A chloride (Compound **30a**)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	47 V
Scan Range	n/a	Capillary Exit	160.0 V	Set Pulsar Pull	394 V
Scan Begin	50 m/z	Hexapole RF	200.0 V	Set Pulsar Push	394 V
Scan End	2000 m/z	Skimmer 1	60.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

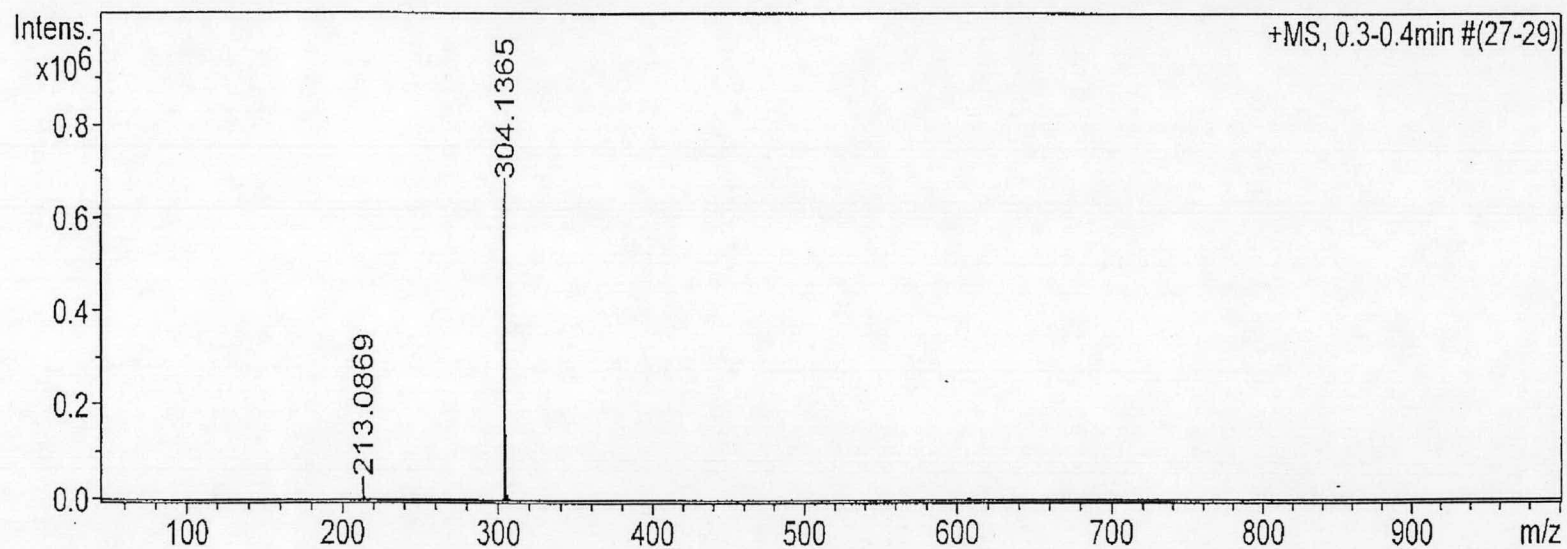


Figure B-8 Mass spectrum of *N*-benzyl cassiarin A chloride (Compound **31a**)

Acquisition Parameter

Source Type ESI
Scan Range n/a
Scan Begin 50 m/z
Scan End 3000 m/z

Ion Polarity Positive
Capillary Exit 140.0 V
Hexapole RF 150.0 V
Skimmer 1 30.0 V
Hexapole 1 23.0 V

Set Corrector Fill 47 V
Set Pulsar Pull 394 V
Set Pulsar Push 394 V
Set Reflector 1300 V
Set Flight Tube 9000 V
Set Detector TOF 2150 V

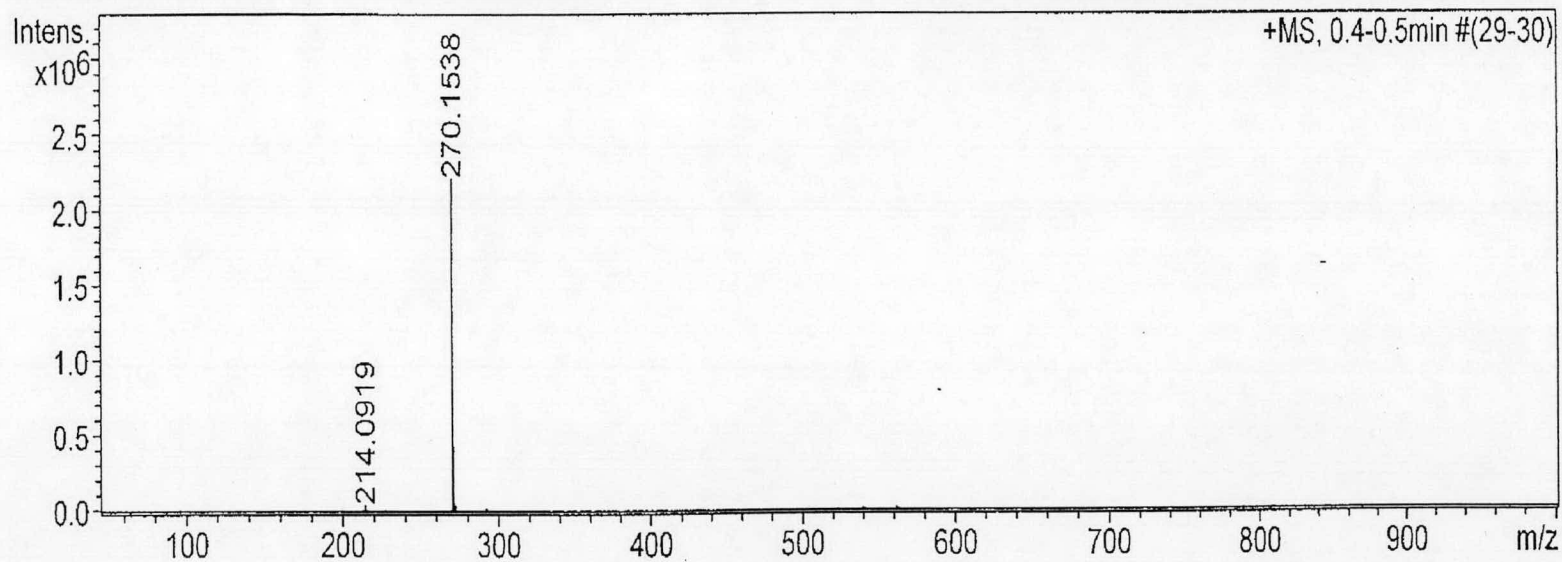


Figure B-9 Mass spectrum of *N*-butyl cassiarin B (Compound **28b**)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	47 V
Scan Range	n/a	Capillary Exit	140.0 V	Set Pulsar Pull	394 V
Scan Begin	50 m/z	Hexapole RF	250.0 V	Set Pulsar Push	394 V
Scan End	3000 m/z	Skimmer 1	40.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

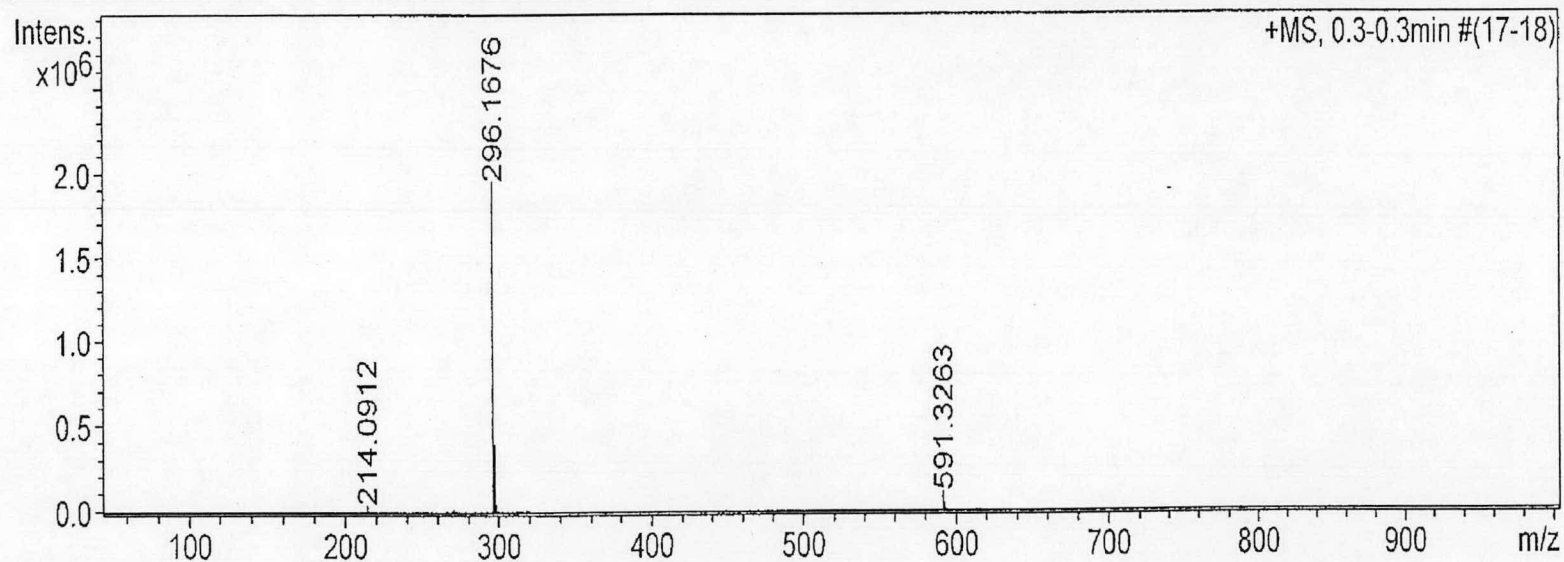


Figure B-10 Mass spectrum of *N*-cyclohexyl cassiarin B (Compound 29b)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	47 V
Scan Range	n/a	Capillary Exit	150.0 V	Set Pulsar Pull	394 V
Scan Begin	50 m/z	Hexapole RF	200.0 V	Set Pulsar Push	394 V
Scan End	3000 m/z	Skimmer 1	40.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

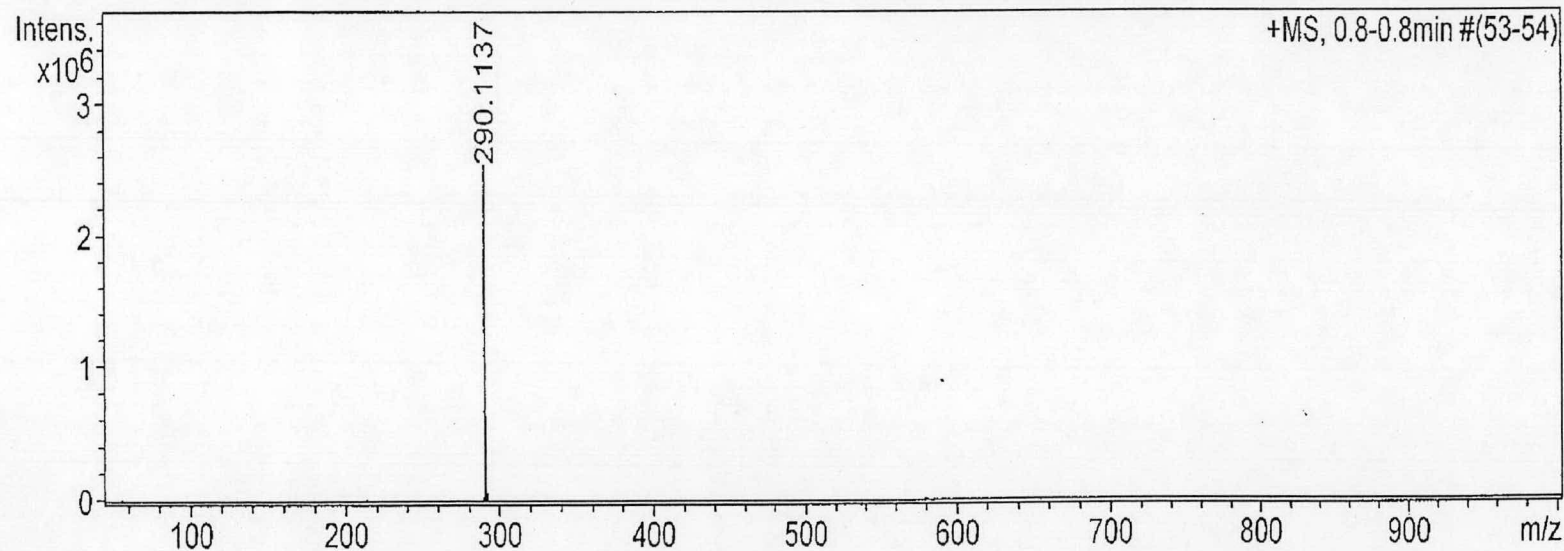


Figure B-11 Mass spectrum of *N*-phenyl cassiarin B (Compound **30b**)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	47 V
Scan Range	n/a	Capillary Exit	160.0 V	Set Pulsar Pull	394 V
Scan Begin	50 m/z	Hexapole RF	200.0 V	Set Pulsar Push	394 V
Scan End	2000 m/z	Skimmer 1	60.0 V	Set Reflector	1300 V
		Hexapole 1	23.0 V	Set Flight Tube	9000 V
				Set Detector TOF	2150 V

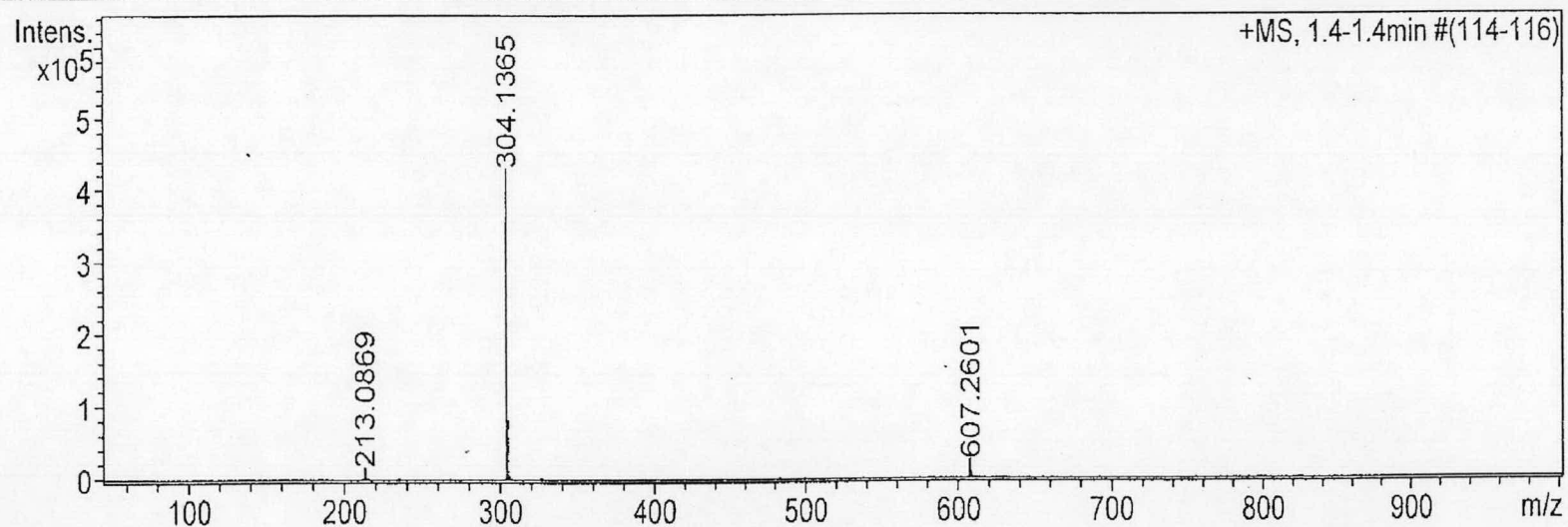


Figure B-12 Mass spectrum of *N*-benzyl cassiarin B (Compound **31b**)

VITA

Mr. Sarawut Kanputhorn was born on March 8, 1981 in Bangkok, Thailand. He got a Diploma in Analytical Chemistry from Institute of Analytical Chemistry Training, which affiliated institute of Chulalongkorn University in 2003 and continued a Bachelor Degree of Science in Chemistry at Chulalongkorn University in 2005. Then, he started experienced work in Research and Development Staff at Max Development International Co., Ltd. for 12 months. After that, he admitted into a Master Degree of Science program in Chemistry at Chulalongkorn University in 2006 and completed the program in 2008.