Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Divergent Reactivity of Sulfoxonium Ylide with Allyl Carbonate and Allyl Carbamate

Vinayak Hanchate, Sudharshan Nagabhushana Reddy, Anil Kumar, and Kandikere Ramaiah Prabhu*

Department of Organic Chemistry,

Indian Institute of Science,

Bangalore 560 012,

Karnataka, India

* E-mail: prabhu@iisc.ac.in

Table of Contents

Note – References are provided in the footnote, wherever applicable.

General Information

All chemicals were purchased from commercial suppliers and used as delivered unless otherwise specified. Reactions were carried out using distilled solvents. NMR spectra were recorded on a BRUKER-AV400 spectrometer in $CDCl_3$ and DMSO-d_6 (400 MHz, ^1H and 100 MHz, ^{13}C). Tetramethylsilane (TMS; $\delta = 0$ ppm) or residual non-deuterated $CDCl_3$ signal ($\delta = 7.27$ ppm); and residual non-deuterated DMSO signal ($\delta = 2.5$ ppm) served as internal standards for 1H NMR. The corresponding residual non-deuterated solvent signals ($CDCl_3$: $\delta = 77.16$ ppm; DMSO: $\delta = 39.50$ ppm) were used as internal standards for ^{13}C NMR. Chemical shifts (δ) are reported in parts per million downfield from the internal reference and coupling constants in Hertz (Hz). IR spectra were measured using a Perkin-Elmer FT-IR Spectrometer. Mass spectra were measured with Micromass Q-TOF (ESI-HRMS). The melting points of the products were determined using a Buchi melting point apparatus. Flash column chromatography was carried out using commercially obtained silica gel, and thin-layer chromatography was carried out using Merck silica gel 60 F_{254} TLC plates. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (230-400 mesh) with solvents distilled prior to use.

No attempts were made to optimize yields for substrate preparation. All spectral data obtained was according to the previously reported. All sulfoxonium ylide derivatives,[1] allyl carbonates derivatives,[2] and allyl carbamates[3] derivatives were prepared according to the reported literature procedure.

[1] (a) Liu, L.; Lin, J.; Pang, M.; Jin, H.; Yu, X.; Wang, S. Photo-Thermo-Mechanochemical Approach to Synthesize Quinolines via Addition/Cyclization of Sulfoxonium Ylides with 2-Vinylanilines Catalyzed by Iron(II) Phthalocyanine. *Org. Lett.* **2022**, *24*, 1146–1151. (b) Zhu, S.; Shi, K.; Zhu, H.; Jia, Z.-K.; Xia, X.-F.; Wang, D.; Zou, L.-H. Copper-Catalyzed Annulation or Homocoupling of Sulfoxonium Ylides: Synthesis of 2,3-Diaroylquinolines or α,α,β-Tricarbonyl Sulfoxonium Ylides. *Org. Lett.* **2020**, *22*, 1504–1509.

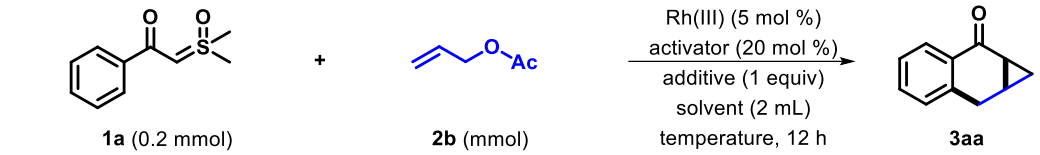
[2] Hoang, G. L.; Yang, Z.-D.; Smith, S. M.; Pal, R.; Miska, J. L.; Pérez, D. E.; Pelter, L. S. W.; Zeng, X. C.; Takacs, J. M. Enantioselective Desymmetrization via Carbonyl-Directed Catalytic Asymmetric Hydroboration and Suzuki–Miyaura Cross-Coupling. *Org. Lett.* **2015**, *17*, 940–943.

[3] Jeschke, S.; Gentschev, A.-C.; Wiemhöfer, H.-D. Disiloxanes with Cyclic or Non-Cyclic Carbamate Moieties as Electrolytes for Lithium-Ion Batteries. *Chem. Commun.* **2013**, *49*, 1190–1192.

Experimental Section

Table ESI – 1. Detail Optimization Studies for (4 + 2) Annulation

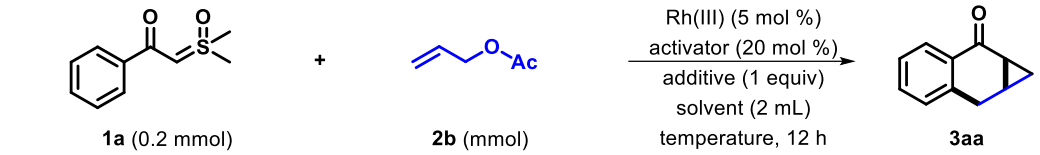
(a) Temperature, Solvent, and Additive Screening



1a (0.2 mmol) + **2b** (mmol) → **3aa**

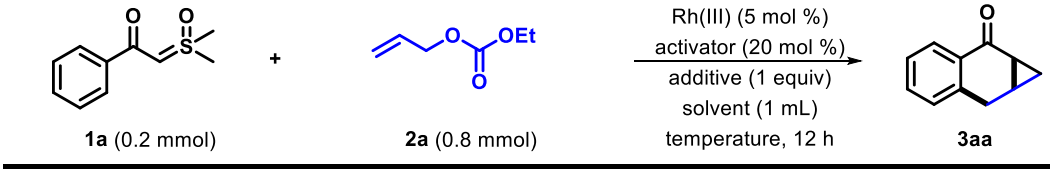
entry	2b (mmol)	temp. (°C)	solvent (2 mL)	additive (1 equiv)	activator (20 mol %)	yield (%)
1	0.4	80	DCE	AcOH	$AgSbF_6$	18
2	0.4	100	DCE	AcOH	$AgSbF_6$	5
3	0.4	60	DCE	AcOH	$AgSbF_6$	14
4	0.4	40	DCE	AcOH	$AgSbF_6$	10
5	0.4	rt	DCE	AcOH	$AgSbF_6$	5
6	0.4	80	TFE	AcOH	$AgSbF_6$	12
7	0.4	80	EtOAc	AcOH	$AgSbF_6$	21
8	0.4	80	1,4-dioxane	AcOH	$AgSbF_6$	21
9	0.4	80	EtOH	AcOH	$AgSbF_6$	00
10	0.4	80	THF	AcOH	$AgSbF_6$	00
11	0.4	80	CH_3CN	AcOH	$AgSbF_6$	38
12	0.4	80	toluene	AcOH	$AgSbF_6$	23
13	0.4	80	HEIP	AcOH	$AgSbF_6$	04
14	0.4	80	DMSO	AcOH	$AgSbF_6$	00
15	0.4	80	CH_3CN	--	$AgSbF_6$	32
16	0.4	80	CH_3CN	NaOAc	$AgSbF_6$	08
17	0.4	80	CH_3CN	AcOH + NaOAc	$AgSbF_6$	16
18	0.4	80	CH_3CN	AcOH (0.5)	$AgSbF_6$	34
19	0.8	80	CH_3CN	AcOH	$AgSbF_6$	42
20	0.4	80	CH_3CN	$Cu(OAc)_2.H_2O$	$AgSbF_6$	--
21	0.8	80	CH_3CN	PivOH	$AgSbF_6$	41
22	0.8	80	CH_3CN	$AdCO_2H$	$AgSbF_6$	51
23	0.8	80	CH_3CN	$ClCH_2CO_2H$	$AgSbF_6$	56
24	0.8	80	CH_3CN	H_2O (10)	$AgSbF_6$	40
25	0.8	80	CH_3CN	$PhCO_2H$	$AgSbF_6$	44
26	0.8	80	CH_3CN	propionic acid	$AgSbF_6$	45
27	0.8	80	CH_3CN	TFA	$AgSbF_6$	--
28	0.8	80	CH_3CN	$Zn(OAc)_2.2H_2O$	$AgSbF_6$	39
29	0.8	80	CH_3CN	Cl_2CHCO_2H	$AgSbF_6$	23
30	0.8	80	CH_3CN	Cl_3CHCO_2H	$AgSbF_6$	07

(b) Other Parameters Screening



entry	2b (mmol)	temp. (°C)	solvent (2 mL)	additive (1 equiv)	activator (20 mol %)	yield (%)
31	0.8	80	CH_3CN	$ClCH_2CO_2H$	$AgBF_4$	42
32	0.8	80	CH_3CN	$ClCH_2CO_2H$	$AgNTf_2$	62
33	0.8	80	CH_3CN	$ClCH_2CO_2H$	$AgPF_6$	57
34	0.8	80	CH_3CN	$ClCH_2CO_2H$ (0.2)	$AgNTf_2$	46
35	0.8	80	CH_3CN	$ClCH_2CO_2H$ (2)	$AgNTf_2$	54
36	0.8	80	CH_3CN (1 mL)	$ClCH_2CO_2H$	$AgNTf_2$	64
37	0.8	80	CH_3CN (4 mL)	$ClCH_2CO_2H$	$AgNTf_2$	46
38	0.8	90	CH_3CN (1 mL)	$ClCH_2CO_2H$	$AgNTf_2$	33
39	0.8	70	CH_3CN (1 mL)	$ClCH_2CO_2H$	$AgNTf_2$	68
40	0.8	60	CH_3CN (1 mL)	$ClCH_2CO_2H$	$AgNTf_2$	62
41	0.6	60	CH_3CN (1 mL)	$ClCH_2CO_2H$	$AgNTf_2$	55
42	1.0	60	CH_3CN (1 mL)	$ClCH_2CO_2H$	$AgNTf_2$	60

(c) Ally carbonate Substrate Screening



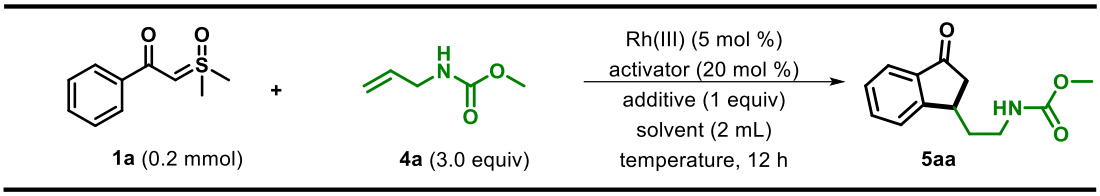
entry	2a (mmol)	temp. (°C)	solvent (1 mL)	additive (1 equiv)	activator (20 mol %)	yield (%)
43	0.8	70	CH_3CN	$ClCH_2CO_2H$	$AgNTf_2$	68
44	0.8	60	CH_3CN	$ClCH_2CO_2H$	$AgNTf_2$	76 (73)
45	0.8	50	CH_3CN	$ClCH_2CO_2H$	$AgNTf_2$	55
46[a]	0.8	50	CH_3CN	$ClCH_2CO_2H$	$AgNTf_2$	56
47[b]	0.8	50	CH_3CN	$ClCH_2CO_2H$	$AgNTf_2$	75
48[c]	0.8	50	CH_3CN	$ClCH_2CO_2H$	$AgNTf_2$	60

[a] 2.5 mol % of catalyst loading. [b] 7.5 mol % of catalyst loading. [c] Under air atmosphere.

Optimization table SI-1, experimentations have been performed as shown in *general experimental procedure A*. In all the cases, the crude products were submitted directly for ^{1}H-NMR analysis for calculating the yields in which 1,3,5-trimethoxybenzene (11.2 mg, 0.0667 mmol) has been used as an internal standard isolated yield in parenthesis. nd = not detected.

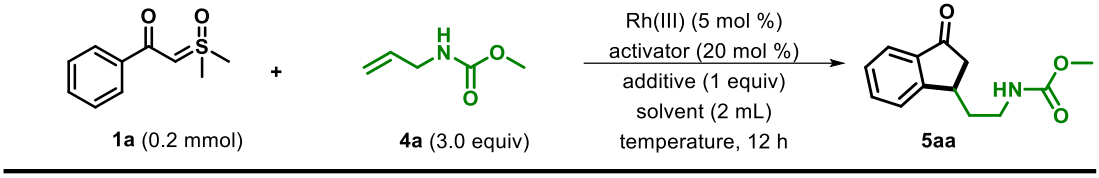
Table ESI – 2. Detail Optimization Studies for (4 + 1) Annulation

(a) Solvent, Temperature, Additive, and Activator Screening



entry	solvent (1 mL)	temp. (°C)	additive (1 equiv)	activator (20 mol %)	yield (%)
1	TFE	80	NaOAc	$AgSbF_6$	30
2	HFIP	80	NaOAc	$AgSbF_6$	48
3	EtOH	80	NaOAc	$AgSbF_6$	nd
4	THF	80	NaOAc	$AgSbF_6$	nd
5	EtOAc	80	NaOAc	$AgSbF_6$	10
6	toluene	80	NaOAc	$AgSbF_6$	trace
7	dioxane	80	NaOAc	$AgSbF_6$	18
8	CH_3CN	80	NaOAc	$AgSbF_6$	10
9	DCE	80	NaOAc	$AgSbF_6$	9
10	HFIP	60	NaOAc	$AgSbF_6$	43
11	HFIP	90	NaOAc	$AgSbF_6$	48
12	HFIP	100	NaOAc	$AgSbF_6$	44
13	HFIP	80	Na_2CO_3	$AgSbF_6$	32
14	HFIP	80	NaOPiv (1 w/w)	$AgSbF_6$	51
15	HFIP	80	HCO_2Na	$AgSbF_6$	nd
16	HFIP	80	CsOAc	$AgSbF_6$	36
17	HFIP	80	F_3CCO_2Na	$AgSbF_6$	25
18	HFIP	80	LiOAc	$AgSbF_6$	35
19	HFIP	80	Cs_2CO_3	$AgSbF_6$	nr
20	HFIP	80	CsOPiv	$AgSbF_6$	42
21	HFIP	80	NaOPiv (2 w/w)	$AgSbF_6$	58
22	HFIP	80	NaOPiv (3 w/w)	$AgSbF_6$	59
23	HFIP	80	NaOPiv (2 w/w)	$AgNTf_2$	58
24	HFIP	80	NaOPiv (2 w/w)	$AgBF_4$	59
25	HFIP	80	NaOPiv (2 w/w)	$AgPF_6$	57

(a) Other Parameters Screening



entry	solvent (1 mL)	temp. (°C)	additive (1 equiv)	activator (20 mol %)	yield (%)
26[a]	HFIP	80	NaOAc	$AgSbF_6$	54
27[b]	HFIP	80	NaOAc	$AgSbF_6$	57
28[c]	HFIP	80	NaOAc	$AgSbF_6$	51
29[d]	HFIP	80	NaOAc	$AgSbF_6$	58
30	HFIP	80	NaOPiv (2 w/w) + 5 equiv H_2O	$AgSbF_6$	35
31	HFIP	80	NaOPiv (2 w/w) + 4 ÅMS (2 w/w)	$AgSbF_6$	73 (71)
32	HFIP	80	NaOPiv (2 w/w) + 4 ÅMS (3 w/w)	$AgSbF_6$	69

[a] 2.0 equiv of allyl methyl carbamate was used. [b] 4.0 equiv of allyl methyl carbamate was used. [c] Solvent HFIP (0.5 mL) used. [d] Solvent HFIP (2.0 mL) used.

Optimization table SI-2, experimentations have been performed as shown in *general experimental procedure B*. In all the cases, the crude products were submitted directly for ^{1}H-NMR analysis for calculating the yields in which 1,3,5-trimethoxybenzene (11.2 mg, 0.0667 mmol) has been used as an internal standard; isolated yield in parenthesis. nd = not detected.

General Procedure

A. Experimental procedure for (4 + 2) annulation

To an oven-dried 8-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with sulfoxonium ylides (0.2 mmol) and allyl carbonate derivatives (0.8 mmol, 4.0 equiv), catalyst $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %, 0.05 equiv), activator $AgNTf_2$ (16 mg, 20 mol %, 0.2 equiv), additive chloroacetic acid (19.0 mg, 0.2 mmol, 1.0 equiv), and acetonitrile solvent (1 mL). The vial was sealed under argon atmosphere with a screw cap and placed in a pre-heated metal block at 60 °C, and the reaction mixture was stirred at the same temperature for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature, filtered through a silica (100-200 mess size) pad using a mixture of EtOAc and petroleum ether (1:1, 100 mL), and concentrated under vacuo. In the optimization Table-1, the crude products were submitted directly for ^{1}H-NMR analysis for calculating the yields wherein 1,3,5-trimethoxybenzene (11.2 mg, 0.0667 mmol) has been used as an internal standard. For the substrate scope (Scheme – 2, left column), the crude product was purified on a silica gel (100-200 mess size) flash column chromatography using EtOAc/ petroleum ether as eluent (1:99 to 3:97 *v/v*) to obtain the desired cyclopropanation product.

B. Experimental procedure for (4 + 1) annulation.

To an oven-dried 8-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with sulfoxonium ylides (0.2 mmol) and allyl carbamate derivatives (0.6 mmol, 3.0 equiv), catalyst $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %, 0.05 equiv), activator $AgSbF_6$ (13.4 mg, 20 mol %, 0.2 equiv), additive sodium pivalate hydrated (2 times w/w), powder molecular sieves 4 A^o (2 times w/w), and HFIP solvent (2 mL). The vial was sealed under argon atmosphere with a screw cap and placed in a pre-heated metal block at 80 °C, and the reaction mixture was stirred at the same temperature for 16 h. After completion of the reaction, the reaction mixture was cooled to room temperature, filtered through a silica (100-200 mess size) pad using a mixture of EtOAc and petroleum ether (1:1, 100 mL), and concentrated under vacuo. In the optimization Table-2, the crude products were submitted directly for ^{1}H-NMR analysis for calculating the yields wherein 1,3,5-trimethoxybenzene (11.2 mg, 0.0667 mmol) has been used as an internal standard. For the substrate scope (Scheme – 2, right column), the crude product was purified on a silica gel (100-200 mess size) flash column chromatography using EtOAc/petroleum ether as eluent (10:90 to 30:90 *v/v*) to obtain the desired indanone product.

C. Experimental procedure for the scale-up reaction of (4 + 2) annulation (3aa).

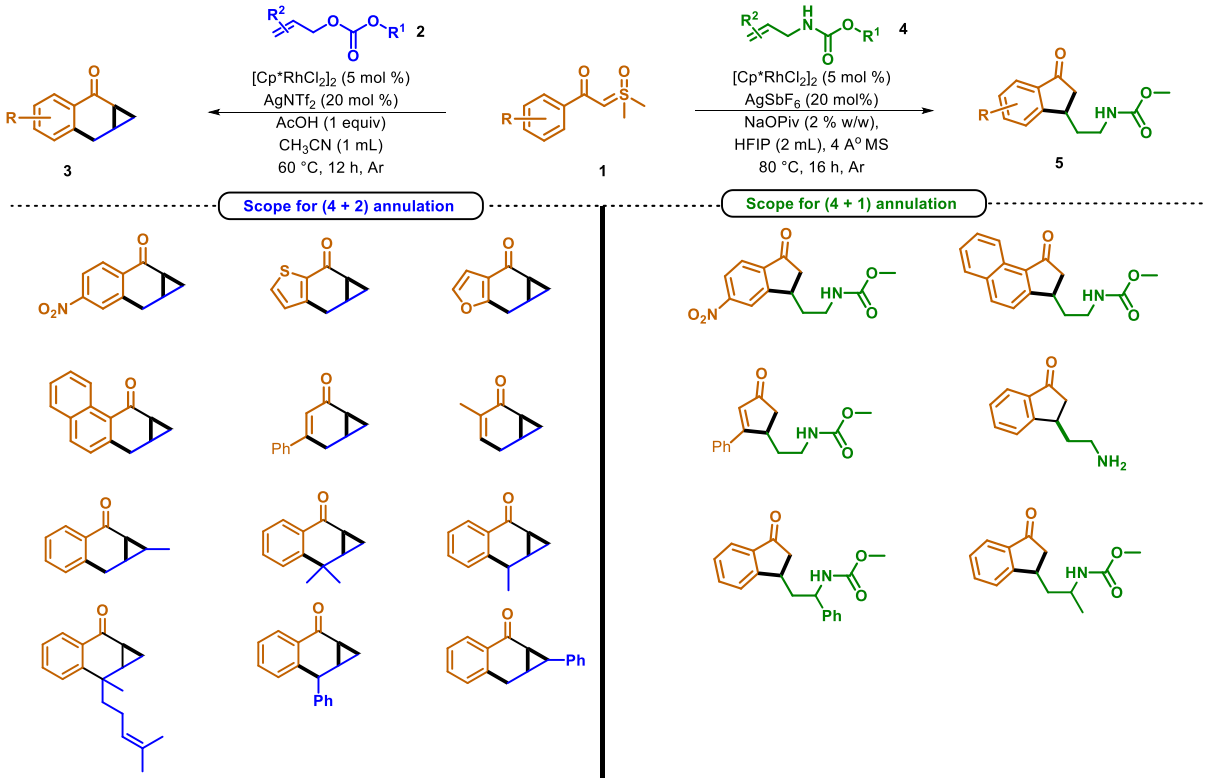
To an oven-dried 50-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with sulfoxonium ylides **1a** (1.0 g, 5.1 mmol) and allyl ethyl carbonate (2.65 g, 20.4 mmol, 4.0 equiv), $[Cp^*RhCl_2]_2$ (0.15 g, 5 mol %, 0.05 equiv), $AgNTf_2$ (0.4 g, 20 mol %, 0.2 equiv), additive chloroacetic acid (0.48 mg, 05.1 mmol, 1.0 equiv), and acetonitrile solvent (20 mL, 0.4 M). The tube was sealed under argon atmosphere with a screw cap and placed in a pre-heated oil bath at 60 °C, and the reaction mixture was stirred at the same temperature for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature, filtered through a silica (100-200 mess size) pad using a mixture of EtOAc and petroleum ether (1:1, 100 mL), and concentrated under vacuo. The crude product was purified on a silica gel (100-200 mess size) flash column chromatography using EtOAc/ petroleum ether as eluent (1:99 to 3:97 *v/v*) to obtain the desired cyclopropanation product in 70% yield (0.565 g).

D. Experimental procedure for the scale-up reaction of (4 + 1) annulation (5aa).

To an oven-dried 50-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with sulfoxonium ylides **1a** (1.0 g, 5.1 mmol) and allyl methyl carbamate (1.75 g, 15.3 mmol, 3.0 equiv), $[Cp^*RhCl_2]_2$ (0.12 g, 5 mol %, 0.05 equiv), $AgSbF_6$ (0.35 g, 20 mol %, 0.2 equiv), additive sodium pivalate hydrated (2.0 g, 2 times w/w), powder molecular sieves 4 Å (2.0 g, 2 times w/w), and HFIP solvent (50 mL, 1M). After completion of the reaction, the reaction mixture was cooled to room temperature, filtered through a silica (100-200 mess size) pad using a mixture of EtOAc and petroleum ether (1:1, 100 mL), and concentrated under vacuo. The crude product was purified on a silica gel (100-200 mess size) flash column chromatography using EtOAc/ petroleum ether as eluent (10:90 to 30:90 *v/v*) to obtain the desired cyclopropanation product in 67% yield (0.802 g).

Unsuccessful Substrates

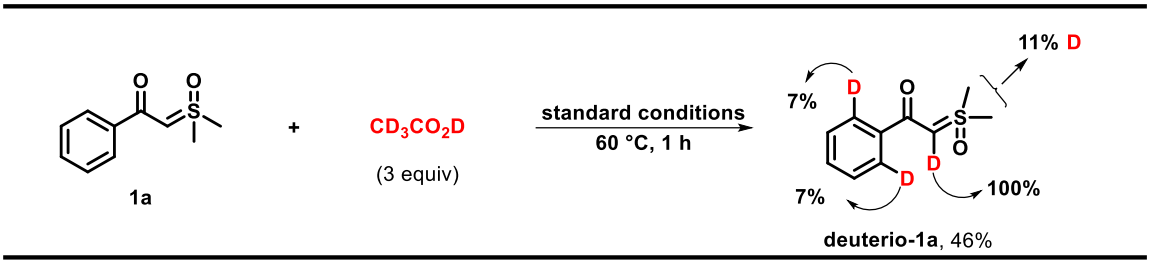
Scheme-ESI-1. Scope for ylides, allyl carbonates, and allyl carbamates.



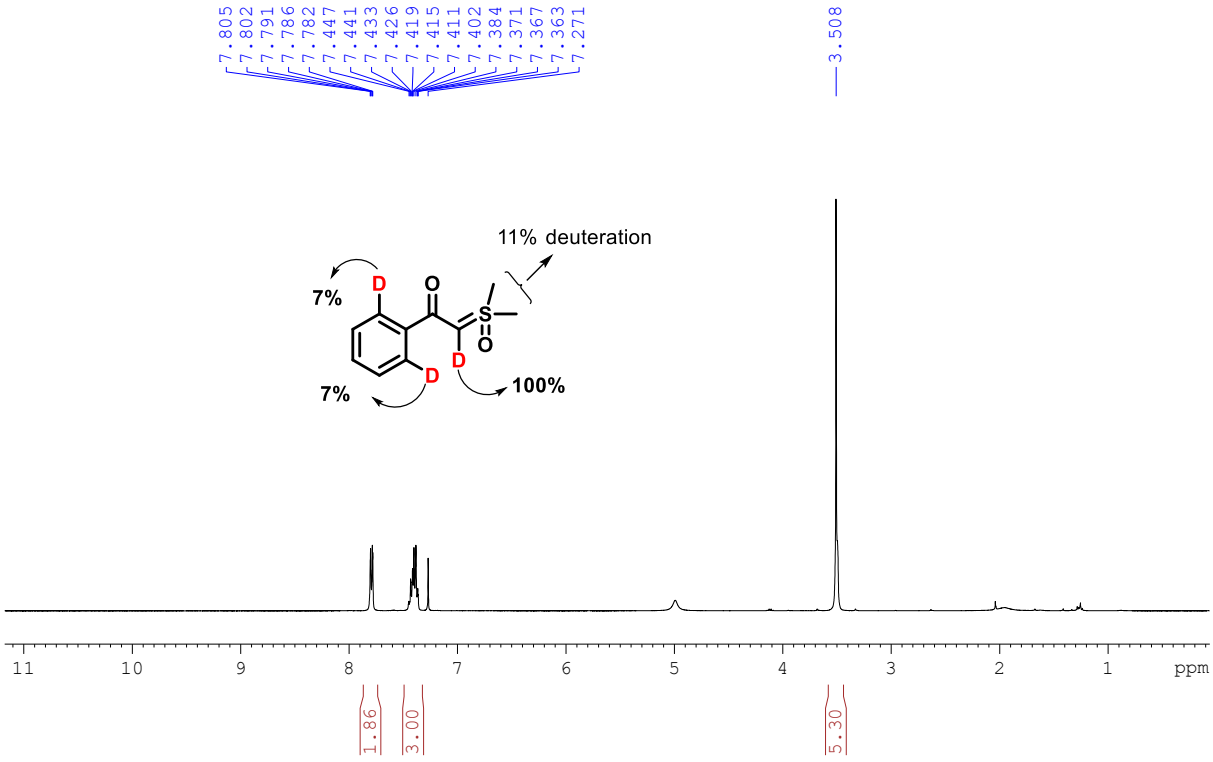
Mechanistic Studies

1. Mechanistic Study for (4 + 2) Annulation

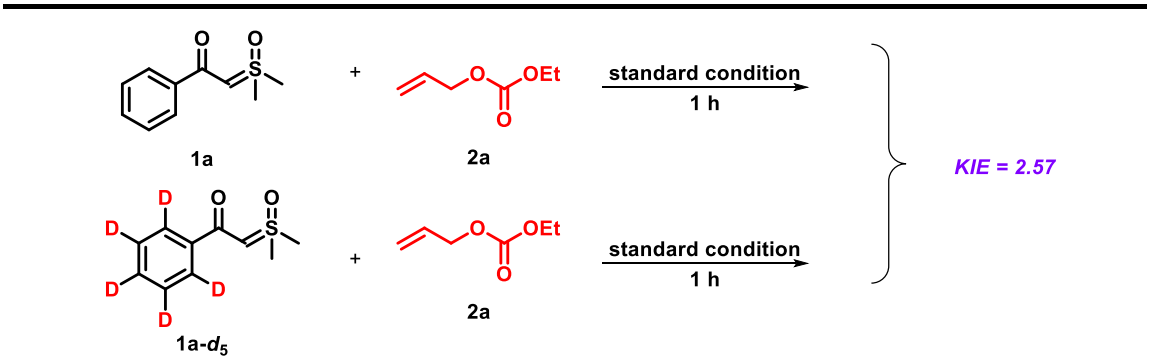
(a) Deuteration incorporation studies



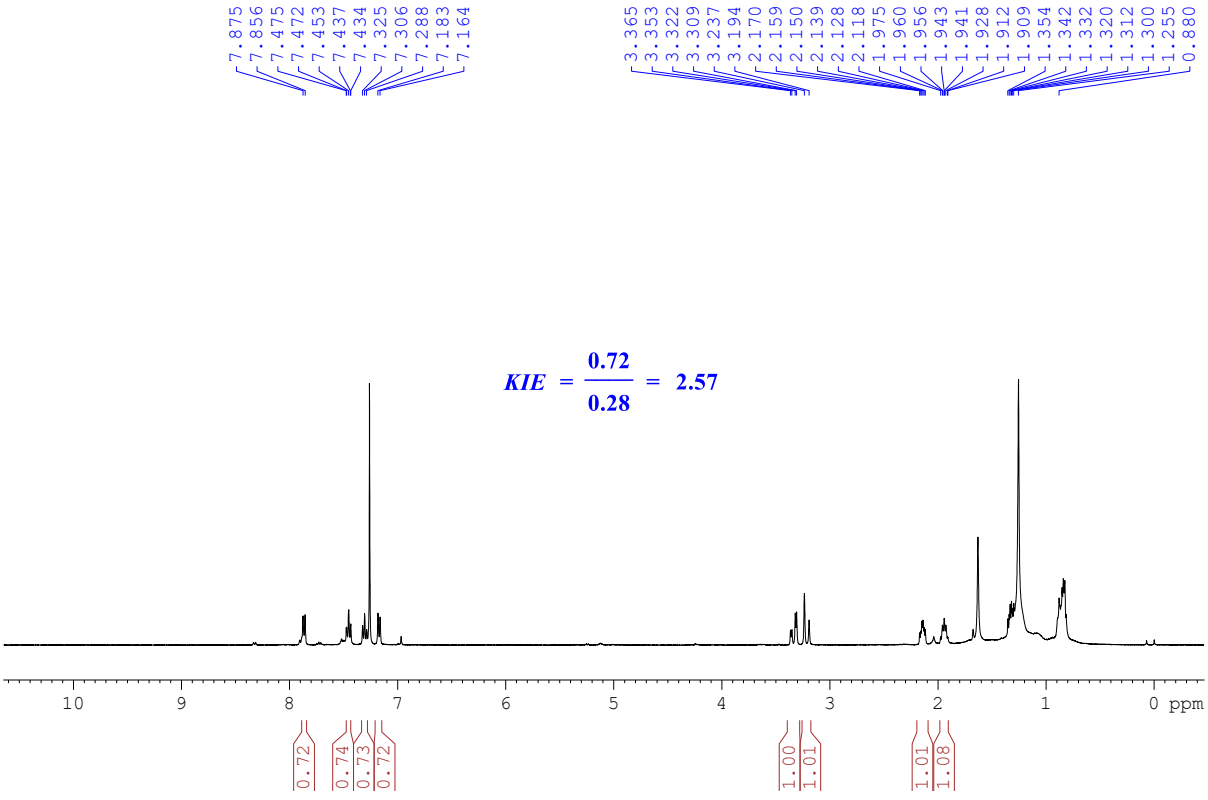
To an oven-dried 8-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with sulfoxonium ylide **1a** (39.3 mg, 0.2 mmol), CD_3CO_2D (38.4 mg, 0.6 mmol, 3.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol%, 0.05 equiv), $AgNTf_2$ (16 mg, 20 mol %, 0.2 equiv), chloroacetic acid (19.0 mg, 0.2 mmol, 1.0 equiv), and acetonitrile solvent (1 mL, 0.5 M). The vial was sealed under argon atmosphere sealed with a screw cap and placed in a pre-heated metal block at 60 °C, and the reaction mixture was stirred at the same temperature for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude reaction mixture was purified on a silica gel column (5% MeOH in EtOAc) to give the desired product **deuterio-1a** in 46% yield. The deuterium incorporation was calculated from ^{1}H-NMR spectroscopy (see the following ^{1}H NMR spectrum).



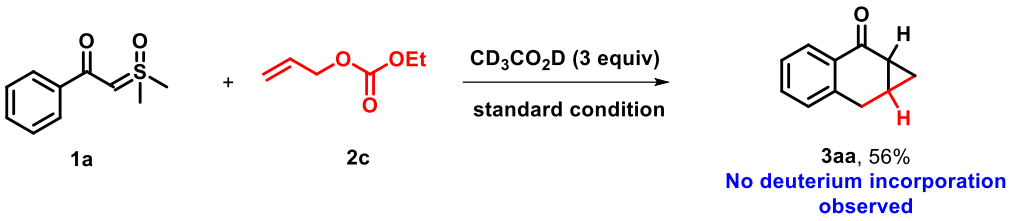
(b) Kinetic isotopic effect studies



Kinetic isotopic effect studies using 1a/1a-d_5 (parallel reactions): Two oven-dried 8-mL screw-cap reaction vials, equipped with a magnetic stir bar was charged with sulfoxonium ylide **1a** (39.3 mg, 0.2 mmol), and **1a-*d*$_5$** (40.3 mg, 0.2 mmol) separately. To each vial were added ethyl allyl carbonate **2c** (26.1 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %, 0.05 equiv), $AgNTf_2$ (16 mg, 20 mol %, 0.2 equiv), chloroacetic acid (19.0 mg, 0.2 mmol, 1.0 equiv), and acetonitrile solvent (1 mL, 0.5 M). The vial was sealed under argon atmosphere sealed with a screw cap and placed in a pre-heated metal block at 60 °C, and the reaction mixture was stirred at the same temperature for 1 h. After that, the reaction mixtures were cooled to 0 °C rapidly and was quenched with pentane. These two reaction mixtures were combined, and the solvent was removed under vacuum. The residue was purified on a silica gel column to obtain a mixture of **3aa** and **3aa-*d*$_4$** as a colorless oil. Based on ^{1}H-NMR analysis, the calculated *KIE* value is 2.57.



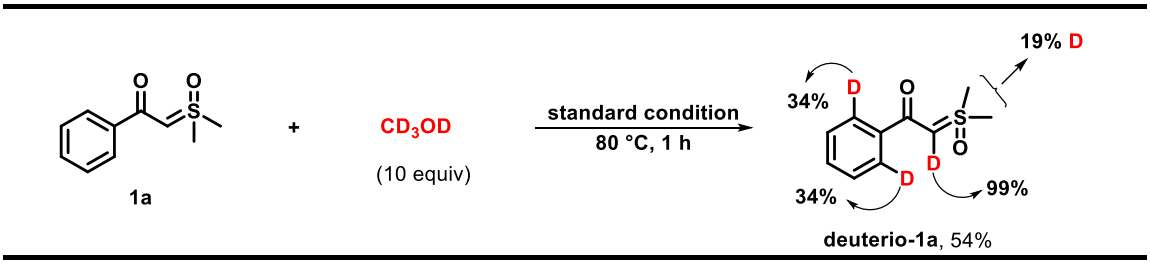
(c) Reaction in the presence of deuterated acetic acid



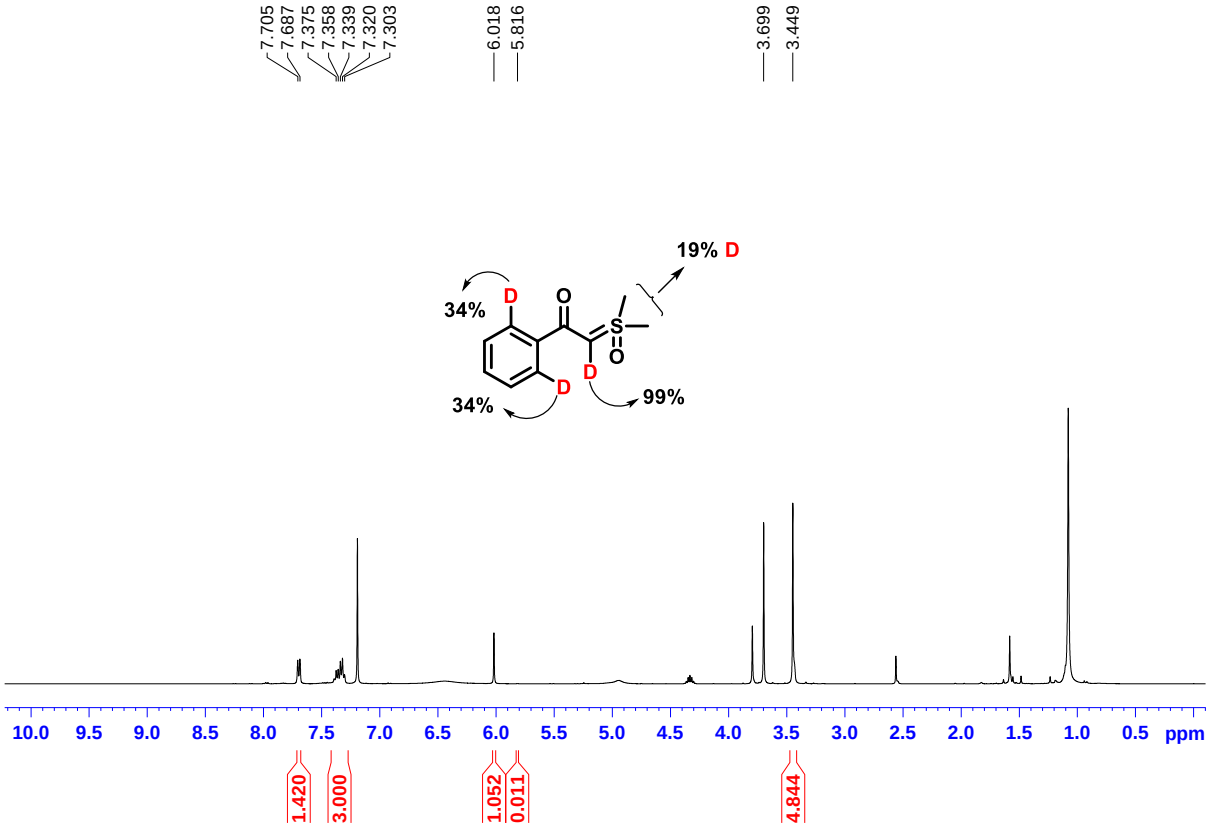
To an oven-dried 8-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with sulfoxonium ylides **1a** (40 mg, 0.2 mmol) and allyl ethyl carbonate **2c** (104 mg, 0.8 mmol), catalyst $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %, 0.05 equiv), $AgNTf_2$ (16 mg, 20 mol %, 0.2 equiv), chloroacetic acid (19.0 mg, 0.2 mmol, 1.0 equiv), and acetonitrile solvent (1 mL, 0.5 M). The vial was sealed under argon atmosphere sealed with a screw cap and placed in a pre-heated metal block at 60 °C, and the reaction mixture was stirred at the same temperature for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature, filtered through a short silica (100-200 mess size) bed using a mixture of EtOAc and petroleum ether (1:1, 100 mL), and concentrated under vacuo. The crude product was purified on a silica gel (100-200 mess size) flash column chromatography using EtOAc/ petroleum ether as eluent (1:99 to 3:97 *v/v*) to obtain the desired cyclopropanation product **3aa** in 56% yield (18 mg). No deuteration incorporation was observed in cyclopropane ring.

2. Mechanistic Study for (4 + 1) Annulation

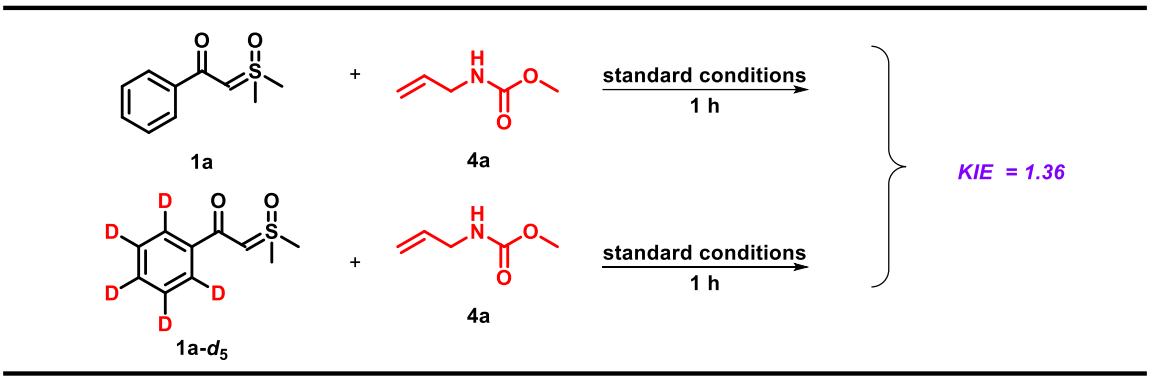
(d) Deuteration incorporation studies



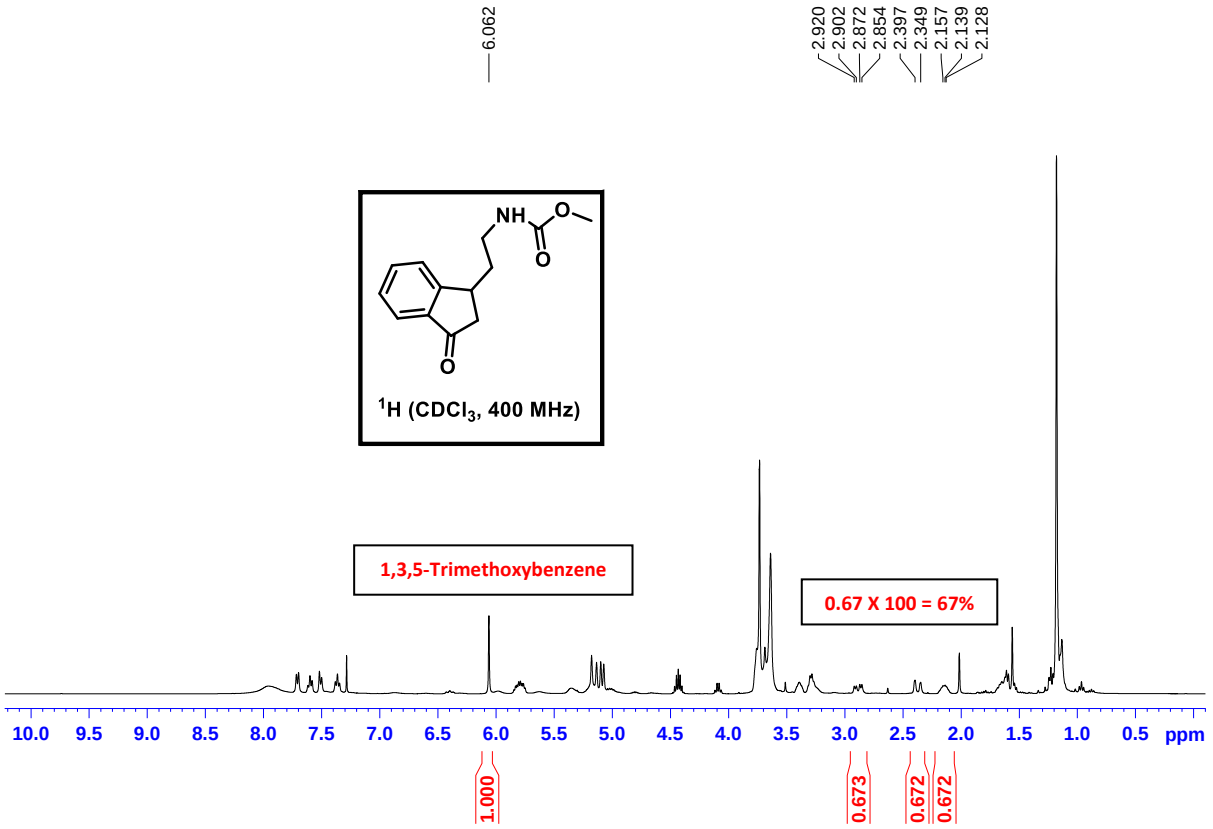
To an oven-dried 8-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with sulfoxonium ylide **1a** (39.3 mg, 0.2 mmol), CD_3OD (72.0 mg, 2.0 mmol, 10.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol%, 0.05 equiv), $AgNTf_2$ (16 mg, 20 mol %, 0.2 equiv), chloroacetic acid (19.0 mg, 0.2 mmol, 1.0 equiv), and acetonitrile solvent (1 mL, 0.5 M). The vial was sealed under argon atmosphere sealed with a screw cap and placed in a pre-heated metal block at 80 °C, and the reaction mixture was stirred at the same temperature for 1 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude reaction mixture was purified on a silica gel column (5% MeOH in EtOAc) to give the desired product **deuterio-1a** in 54% yield. The deuterium incorporation was calculated from ^{1}H-NMR spectroscopy (see the following ^{1}H NMR spectrum).

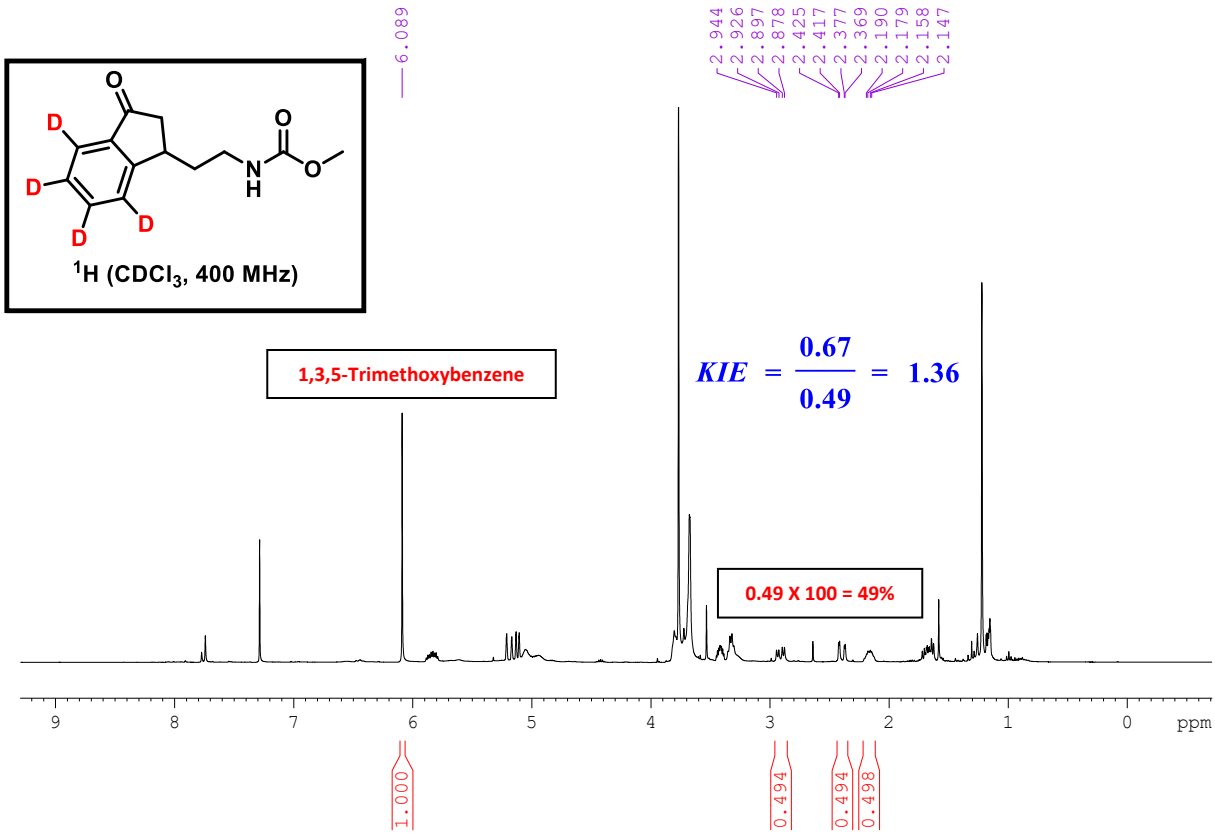


(e) Kinetic isotopic effect studies

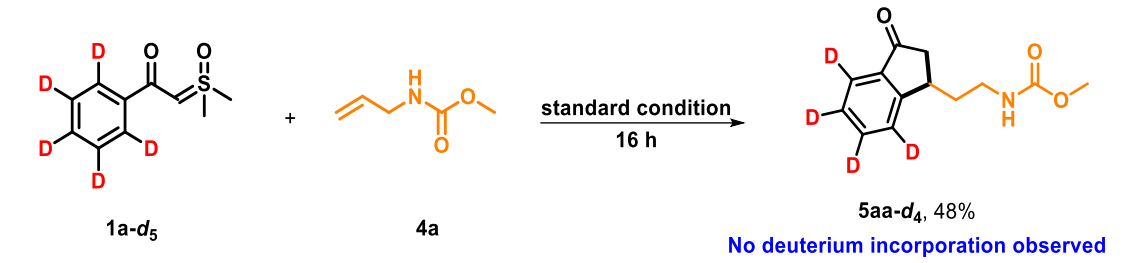


Kinetic isotopic effect studies using 1a/1a-d_5 (parallel reactions): Two oven-dried 8-mL screw-cap reaction vials, equipped with a magnetic stir bar was charged with sulfoxonium ylide **1a** (39.3 mg, 0.2 mmol), and **1a-*d*$_5$** (40.3 mg, 0.2 mmol) separately. To each vial were added allyl methyl carbamate **4a** (23.1 mg, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %, 0.05 equiv), $AgSbF_6$ (13.4 mg, 20 mol %, 0.2 equiv), sodium pivalate hydrated (80 mg, 2 times w/w), powder molecular sieves 4 A^o (80 mg, 2 times w/w), and HFIP solvent (2 mL, 1M). The vial was sealed under argon atmosphere sealed with a screw cap and placed in a pre-heated metal block at 80 °C, and the reaction mixture was stirred at the same temperature for 1 h. After that, the reaction mixtures were cooled to 0 °C rapidly and was quenched with pentane. After that, the crude products were directly submitted for ^{1}H–NMR analysis for calculating the yield, wherein 1,3,5-trimethoxybenzene (11.2 mg, 0.667 mmol) has been used as an internal standard. The calculated yield for substrate **1a** is 67%, whereas for substrate **1a–*d*$_5$** is 49%. Based on observed yields, the calculated *KIE* value is 1.36.

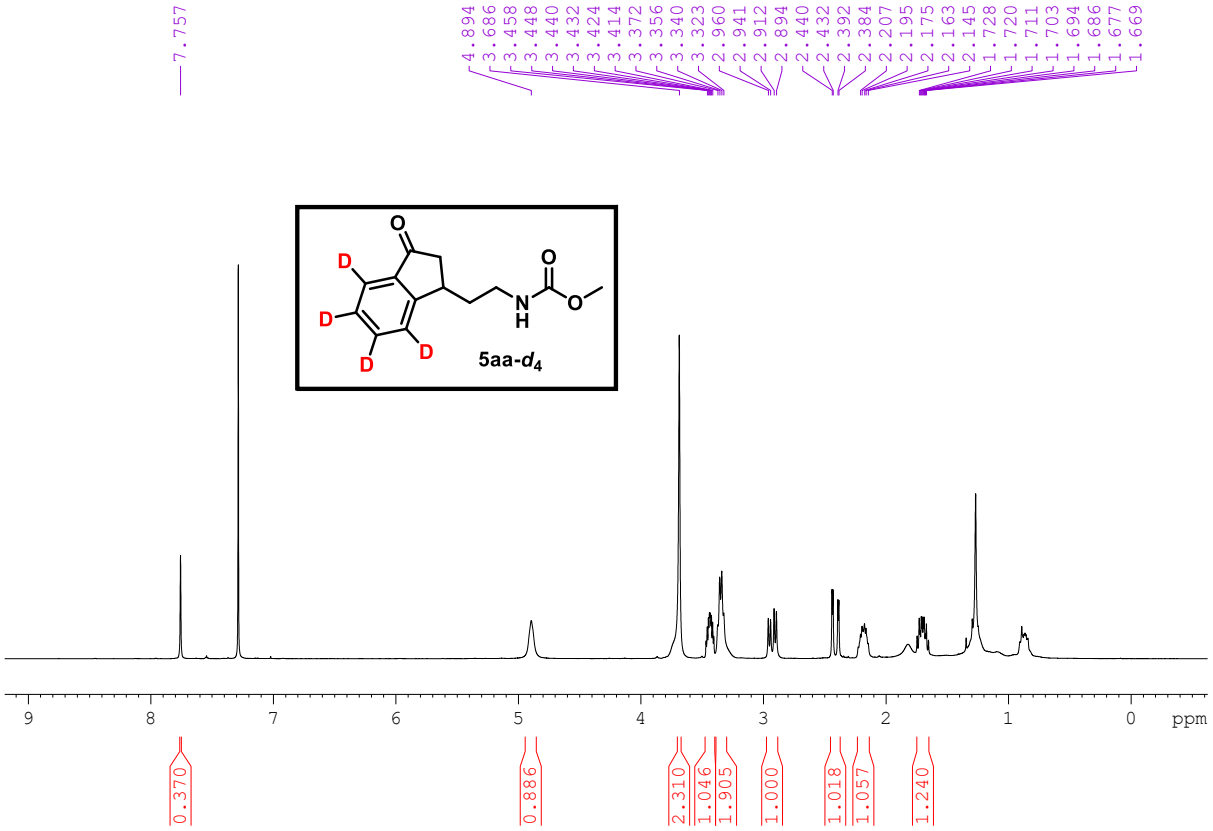

6.062
2.920
2.902
2.872
2.854
2.397
2.349
2.157
2.139
2.128
NH
O
O
O
^{1}H (CDCl$_3$, 400 MHz)
1,3,5-Trimethoxybenzene
0.67 X 100 = 67%
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
0.673
0.672
0.672


6.089
2.944
2.926
2.897
2.878
2.425
2.417
2.377
2.369
2.190
2.179
2.158
2.147
D
D
D
D
O
O
N
H
O
^{1}H (CDCl$_3$, 400 MHz)
1,3,5-Trimethoxybenzene
KIE = 0.67 / 0.49 = 1.36
0.49 X 100 = 49%
9 8 7 6 5 4 3 2 1 0 ppm
1.000
0.494
0.494
0.498

(f) Reaction in the presence of deuterated sulfoxonium ylides

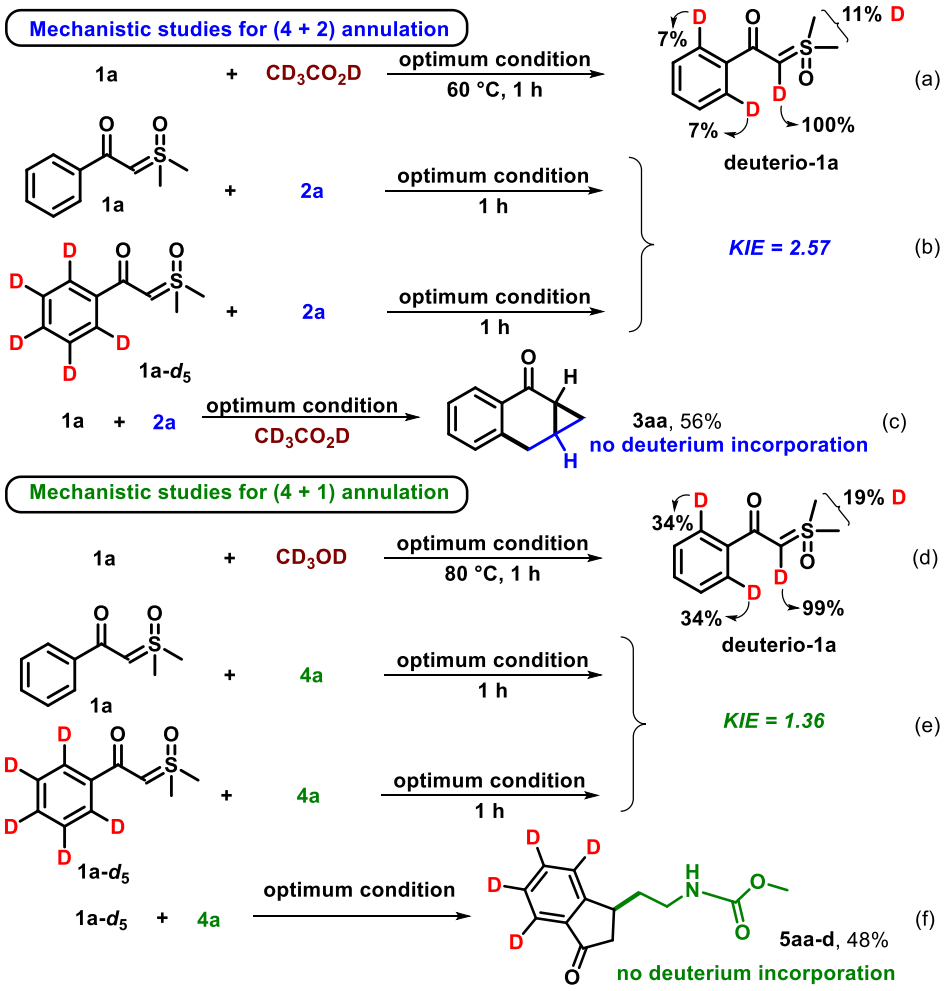


To an oven-dried 8-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with deuterated sulfoxonium ylides **1a–d$_5$** (40.3 mg, 0.2 mmol) and allyl methyl carbamate **4a** (69.1 mg, 0.6 mmol, 3.0 equiv), [Cp*RhCl$_2$]$_2$ (6.2 mg, 5 mol %, 0.05 equiv), AgSbF$_6$ (13.7 mg, 20 mol %, 0.2 equiv), sodium pivalate hydrated (80 mg, 2 times w/w), powder molecular sieves 4A^o (80 mg, 2 times w/w), and HFIP solvent (2 mL, 1 M). The vial was sealed under argon atmosphere sealed with a screw cap and placed in a pre-heated metal block at 80 °C, and the reaction mixture was stirred at the same temperature for 16 h. After completion of the reaction, the reaction mixture was cooled to room temperature and the crude product was purified on a silica gel (100-200 mess size) flash column chromatography using EtOAc/ petroleum ether as eluent (10:90 to 30:70 *v/v*) to obtain the desired product **5aa-d$_4$** in 48% yield (28.1 mg). No deuteration incorporation was observed in aliphatic regions.



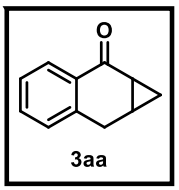
(g) Control studies.

Deuterium labeling experiments of sulfoxonium ylide **1a** were conducted to gain insights into the reaction mechanism (Scheme 4). Deuteration of sulfoxonium ylide under both annulation conditions revealed that C-H activation is reversible, and α-carbon is involved in the metallacycle (Schemes 4a and 4d). The kinetic isotopic effect for both reactions was calculated by parallel reactions of undeuterated sulfoxonium ylide **1a** and pentadeuterated sulfoxonium ylide **1a-*d*$_5$** with allyl carbonate (**2a**) and allyl carbamate (**4a**) under their respective optimal conditions for 1 h. The KIE value of 2.57 was observed for (4+2) annulation, suggesting that the C–H activation step may be the rate-determining in the catalytic cycle, whereas the KIE value of 1.36 was observed for (4+1) annulation, suggesting that the C–H activation step may not be the rate-determining step (Scheme 4b and 4e). The reaction of **1a** with **2a** in the presence of deuterated acetic acid resulted in the formation of the undeuterated product **3aa**, suggesting that the reaction does not involve the regeneration of the catalyst by protodemetallation (Scheme 4c). When the deuterated sulfoxonium ylides **1a- *d*$_5$** were reacted with **4a**, no deuterium incorporation was observed in the aliphatic regions of the product (Scheme 4f).



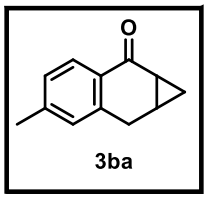
Characterization Data

1,1a,7,7a-Tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3aa).



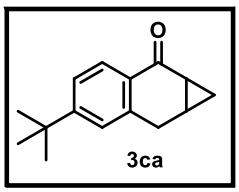
Prepared as shown in *general experimental procedure A*. **Yield** = 73% (42.2 mg); **Appearance** - Yellow Liquid; R_f = 0.7 (10% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 7.3 Hz, 1H), 7.45 (td, *J* = 7.5, 1.1 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 3.33 (dd, *J* = 17.4, 4.9 Hz, 1H), 3.21 (d, *J* = 17.4 Hz, 1H), 2.14 (td, *J* = 8.2, 4.2 Hz, 1H), 2.02 – 1.89 (m, 1H), 1.32 (td, *J* = 8.5, 4.9 Hz, 1H), 0.83 (dd, *J* = 10.6, 4.7 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 198.4, 138.6, 133.2, 131.3, 129.1, 127.2, 127.1, 28.1, 25.5, 14.1, 13.0; **FT-IR (cm^{-1})** 2922, 1670, 1601; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{11}H_{10}OH$ 159.0810; Found 159.0815.

5-Methyl-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3ba).



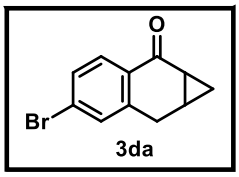
Prepared as shown in *general experimental procedure A*. Yield = 70% (42.2 mg); Appearance – Pale Yellow Liquid; R_f = 0.60 (10% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (s, 1H), 7.27 (t, *J* = 3.1 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 3.28 (dd, *J* = 17.3, 4.8 Hz, 1H), 3.17 (d, *J* = 17.2 Hz, 1H), 2.34 (s, 3H), 2.12 (td, *J* = 8.0, 4.3 Hz, 1H), 1.92 (tt, *J* = 7.7, 3.8 Hz, 1H), 1.34 – 1.27 (m, 1H), 0.81 (dd, *J* = 10.6, 4.6 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 198.8, 136.9, 135.7, 134.1, 131.0, 128.9, 127.2, 27.7, 25.5, 21.0, 14.2, 13.0; **FT-IR (cm^{-1})** 2119, 1671, 1612; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{12}H_{12}OH$ 173.0966; Found 173.0966.

5-(tert-Butyl)-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3ca).



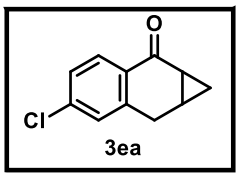
Prepared as shown in *general experimental procedure A*. **Yield** = 55% (42.2 mg); **Appearance** – Yellow Liquid; R_f = 0.7 (10% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.15 (s, 1H), 3.33 (dd, *J* = 17.3, 4.9 Hz, 1H), 3.19 (d, *J* = 17.4 Hz, 1H), 2.10 (td, *J* = 8.4, 4.3 Hz, 1H), 1.96 – 1.86 (m, 1H), 1.71 (s, 1H), 1.31 (s, 9H), 0.83 (dd, *J* = 10.5, 4.7 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 198.2, 156.8, 138.5, 128.7, 127.0, 125.7, 124.5, 35.1, 31.2, 28.3, 25.3, 14.1, 13.0. **FT-IR (cm^{-1})** 2962, 1671, 1606; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{15}H_{18}OH$ 215.1436; Found 215.1437.

5-Bromo-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3da).



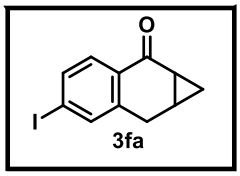
Prepared as shown in *general experimental procedure A*. **Yield** = 61% (42.2 mg); **Appearance** – Yellow Liquid; R_f = 0.70 (10% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.3 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.36 (s, 1H), 3.32 (dd, *J* = 17.6, 4.9 Hz, 1H), 3.18 (d, *J* = 17.5 Hz, 1H), 2.14 (td, *J* = 8.4, 4.3 Hz, 1H), 1.94 (tt, *J* = 7.6, 3.8 Hz, 1H), 1.35 (td, *J* = 8.5, 5.0 Hz, 1H), 0.82 (dd, *J* = 10.6, 4.8 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 197.4, 140.4, 131.9, 130.6, 130.1, 128.9, 128.1, 27.8, 25.3, 14.1, 12.9;**FT-IR (cm^{-1})** 2922, 1671, 1587; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{11}H_9BrOH$ 236.9915; Found 236.9915.

5-Chloro-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3ea).



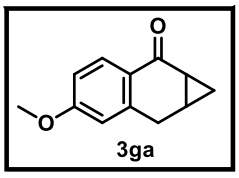
Prepared as shown in *general experimental procedure A*. **Yield** = 55% (42.2 mg); **Appearance** – Yellow Liquid; R_f = 0.60 (10% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.18 (s, 1H), 3.32 (dd, *J* = 17.6, 5.0 Hz, 1H), 3.19 (d, *J* = 17.5 Hz, 1H), 2.14 (td, *J* = 8.0, 4.3 Hz, 1H), 2.00 – 1.90 (m, 1H), 1.39 – 1.32 (m, 1H), 0.82 (dd, *J* = 10.7, 4.8 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 197.2, 140.3, 139.4, 129.7, 128.9, 128.8, 127.7, 27.9, 25.3, 14.1, 12.9; **FT-IR (cm^{-1})** 2923, 1673, 1592; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{11}H_9ClOH$ 193.0420; Found 193.0422.

5-Iodo-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3fa).



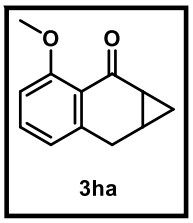
Prepared as shown in *general experimental procedure A*. **Yield** = 69% (39 mg); **Appearance** – Yellow Liquid; R_f = 0.60 (10% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.47 (m, 2H), 3.30 (dd, *J* = 17.6, 5.0 Hz, 1H), 3.16 (d, *J* = 17.5 Hz, 1H), 2.14 (td, *J* = 8.3, 4.3 Hz, 1H), 2.01 – 1.89 (m, 1H), 1.35 (td, *J* = 8.5, 5.0 Hz, 1H), 0.82 (dd, *J* = 10.7, 4.8 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.7, 140.3, 137.9, 136.5, 130.6, 128.6, 100.9, 27.6, 25.3, 14.1, 12.9; **FT-IR (cm^{-1})** 2922, 1668, 1581; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{11}H_9IOH$ 284.9776; Found 284.9779.

5-Methoxy-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3ga).



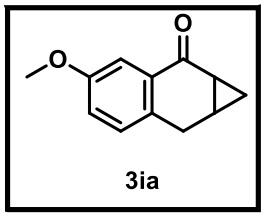
Prepared as shown in *general experimental procedure A*. **Yield** = 42% (42.2 mg); **Appearance** – Yellow Liquid; R_f = 0.60 (20% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.7 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.63 (s, 1H), 3.83 (s, 3H), 3.31 (dd, *J* = 17.4, 5.1 Hz, 1H), 3.17 (d, *J* = 17.4 Hz, 1H), 2.08 (td, *J* = 8.3, 4.3 Hz, 1H), 1.89 (dt, *J* = 12.8, 6.4 Hz, 1H), 1.34 – 1.27 (m, 1H), 0.79 (dd, *J* = 10.6, 4.6 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 197.4, 163.6, 141.0, 129.4, 124.4, 113.3, 113.2, 55.5, 28.4, 24.9, 13.9, 13.1; **FT-IR (cm^{-1})** 2839, 1662, 1601; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{12}H_{12}O_2H$ 189.0916; Found 189.0919.

3-Methoxy-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3ha).



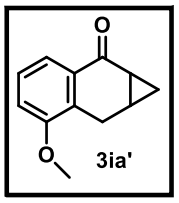
Prepared as shown in *general experimental procedure A*. Yield = 58% (42.2 mg); Appearance – Yellow Liquid; R_f = 0.60 (20% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 3.86 (s, 3H), 3.28 (dd, *J* = 17.0, 4.4 Hz, 1H), 3.13 (d, *J* = 16.9 Hz, 1H), 2.14 (td, *J* = 8.3, 4.3 Hz, 1H), 1.92 – 1.86 (m, 1H), 1.25 – 1.19 (m, 1H), 0.88 (dd, *J* = 10.6, 4.7 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$** δ 198.4, 158.8, 140.7, 133.2, 121.2, 121.0, 110.4, 56.1, 29.2, 27.8, 14.5, 13.3; **FT-IR (cm^{-1})** 2882, 1669, 1265; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{12}H_{12}O_2Na$ 189.0916; Found 189.0922.

4-Methoxy-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one(3ia).



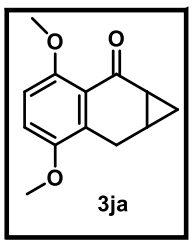
Prepared as shown in *general experimental procedure A*. **Yield** = 32% (42.2 mg); **Appearance** – Yellow Liquid; R_f = 0.6 (10% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 (d, *J* = 2.7 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.03 (dd, *J* = 8.4, 2.7 Hz, 1H), 3.82 (s, 3H), 3.26 (dd, *J* = 17.1, 4.9 Hz, 1H), 3.16 (d, *J* = 17.2 Hz, 1H), 2.13 (td, *J* = 8.2, 4.3 Hz, 1H), 1.93 (dt, *J* = 12.6, 6.3 Hz, 1H), 1.34 – 1.29 (m, 1H), 0.82 (dd, *J* = 10.6, 4.6 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 198.4, 158.8, 132.0, 130.9, 130.2, 121.3, 109.5, 55.6, 27.3, 25.3, 14.3, 13.0; **FT-IR (cm^{-1})** 2838, 1668, 1608; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calculated for $C_{12}H_{12}O_2H$ 189.0916; Found 189.0920.

6-Methoxy-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3ia').



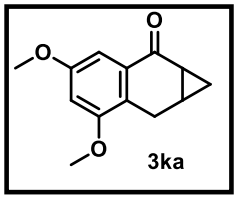
Prepared as shown in *general experimental procedure A*. **Yield** = 60% (42.2 mg); **Appearance** – Yellow Liquid; R_f = 0.6 (10% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 3.85 (s, 3H), 3.49 (d, *J* = 18.4 Hz, 1H), 2.89 (dd, *J* = 18.4, 5.4 Hz, 1H), 2.17 – 2.08 (m, 1H), 2.04 – 1.89 (m, 1H), 1.37 – 1.28 (m, 1H), 0.81 (dd, *J* = 10.6, 4.6 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 198.6, 157.0, 132.1, 127.9, 127.2, 118.9, 114.1, 55.7, 25.3, 21.3, 14.5, 12.9; **FT-IR (cm^{-1})** 2930, 1672, 1581; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{12}H_{12}O_2H$ 189.0916; Found 189.0921.

3,6-Dimethoxy-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3ja).



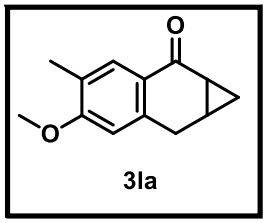
Prepared as shown in *general experimental procedure A*. Yield = 71% (42.2 mg); Appearance – Yellow Liquid; R_f = 0.5 (20% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.92 (d, *J* = 9.0 Hz, 1H), 6.78 (d, *J* = 9.1 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.51 (d, *J* = 18.0 Hz, 1H), 2.82 (dd, *J* = 18.0, 4.8 Hz, 1H), 2.13 (td, *J* = 8.3, 4.2 Hz, 1H), 2.02 – 1.83 (m, 1H), 1.21 (td, *J* = 8.1, 5.0 Hz, 1H), 0.87 (dd, *J* = 10.5, 4.8 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$**) δ 198.7, 152.7, 150.6, 129.3, 122.3, 114.5, 110.4, 56.6, 56.1, 27.8, 21.9, 15.0, 13.1; **FT-IR (cm^{-1})** 2927, 1669, 1134; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{13}H_{14}O_3Na$ 241.0841; Found 241.0837.

4,6-Dimethoxy-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3ka).



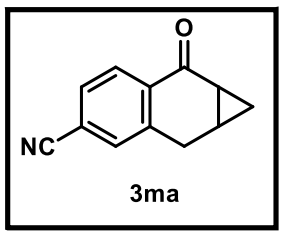
Prepared as shown in *general experimental procedure A*. Yield = 64% (42.2 mg); Appearance – Yellow Liquid; R_f = 0.60 (20% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.98 (d, *J* = 2.4 Hz, 1H), 6.60 (d, *J* = 2.4 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.39 (d, *J* = 18.2 Hz, 1H), 2.83 (dd, *J* = 18.2, 5.5 Hz, 1H), 2.11 (ddd, *J* = 6.0, 5.2, 2.6 Hz, 1H), 2.00 – 1.89 (m, 1H), 1.30 (td, *J* = 8.8, 4.7 Hz, 1H), 0.79 (dd, *J* = 10.5, 4.5 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$** δ 198.5, 159.2, 158.2, 132.3, 120.9, 103.7, 100.3, 55.7, 55.6, 25.3, 21.0, 14.5, 13.0; **FT-IR (cm^{-1})** 2927, 1669, 1608; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{13}H_{14}O_3H$ 219.1021; Found 219.1023.

5-Methoxy-4-methyl-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3la).



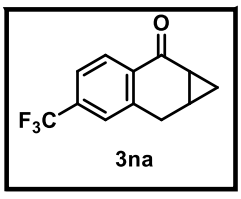
Prepared as shown in *general experimental procedure A*. Yield = 67% (42.2 mg); Appearance – Yellow liquid; R_f = 0.5 (20%EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (s, *J* = 8.1 Hz, 1H), 6.53 (s, *J* = 8.1 Hz, 1H), 3.85 (s, 3H), 3.30 (dd, *J* = 17.4, 5.1 Hz, 1H), 3.15 (d, *J* = 17.4 Hz, 1H), 2.18 (s , *J* = 8.4, 4.3 Hz, 3H), 2.10 – 2.01 (m, 1H), 1.87 (dt, J=12.9, 6.4 Hz 1H), 1.28 (dd, *J* = 8.6, 3.8 Hz, 1H),0.77(dd, J=10.5, 4.6Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 197.6, 161.9, 138.7, 129.4, 126.0, 123.6, 109.2, 55.6, 28.2, 24.8, 15.9, 13.8, 13.1; **FT-IR (cm^{-1})** 2923, 1658, 1607; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{13}H_{14}O_2H$ 203.1072; Found 203.1073.

7-Oxo-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalene-4-carbonitrile (3ma).



Prepared as shown in *general experimental procedure A*. Yield = 32% (42.2 mg); Appearance – Pale Yellow Liquid; R_f = 0.4 (10% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.52 (s, 1H), 3.37 (dd, *J* = 17.6, 4.8 Hz, 1H), 3.28 (d, *J* = 17.6 Hz, 1H), 2.22 (td, *J* = 8.3, 4.3 Hz, 1H), 2.10 – 1.97 (m, 1H), 1.42 (ddd, *J* = 9.1, 8.1, 5.3 Hz, 1H), 0.84 (dd, *J* = 10.7, 5.1 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.7, 139.4, 134.5, 132.9, 130.6, 128.0, 118.1, 116.5, 27.9, 25.7, 14.4, 12.9; **FT-IR (cm^{-1})** 2926, 2229, 1669; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{12}H_9NOH$ 184.0762; Found 184.07766.

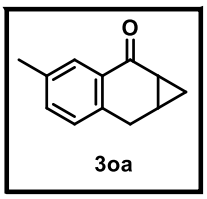
5-(Trifluoromethyl)-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3na).



Prepared as shown in *general experimental procedure A*. Yield = 49% (42.2 mg); Appearance – Pale Yellow Liquid; R_f = 0.60 (10% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.46 (s, 1H), 3.39 (dd, *J* = 17.6, 4.7 Hz, 1H), 3.30 (d, *J* = 17.5 Hz, 1H), 2.21 (td, *J* = 8.4, 4.3 Hz, 1H), 2.08 – 1.95 (m, 1H), 1.44 – 1.36 (m, 1H), 0.85 (dd, *J* = 10.7, 4.9 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.2, 139.2, 134.6 (q, $J_{C\text{-}F}$ = 32.6 Hz), 134.0, 127.9, 126.1 (q, $J_{C\text{-}F}$ = 3.5 Hz), 124.0 (q, $J_{C\text{-}F}$ =

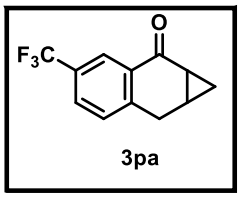
3.6 Hz), 123.7 (q, $J_{C\text{-}F}$ = 272.9 Hz), 28.1, 25.6, 14.4, 12.9; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -63.16. **FT-IR (cm^{-1})** 2926, 1678, 1329; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{12}H_9F_3OH$ 227.0684; Found 227.0686.

4-Methyl-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3oa).



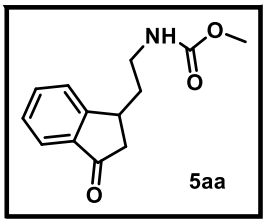
Prepared as shown in *general experimental procedure A*. Yield = 78% (42.2 mg); Appearance – Colourless Liquid; R_f = 0.6 (10% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (s, 1H), 7.26 (d, *J* = 4.5 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 3.28 (dd, *J* = 17.4, 4.7 Hz, 1H), 3.17 (d, *J* = 17.2 Hz, 1H), 2.34 (s, 3H), 2.12 (td, *J* = 8.4, 4.3 Hz, 1H), 1.93 (dd, *J* = 12.7, 6.3 Hz, 1H), 1.34 – 1.28 (m, 1H), 0.81 (dd, *J* = 10.6, 4.6 Hz, 1H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$** δ 198.8, 136.9, 135.7, 134.1, 131.0, 128.9, 127.2, 27.7, 25.5, 21.0, 14.2, 13.0; **FT-IR (cm^{-1})** 2921, 1671, 1611; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{12}H_{12}OH$ 173.0966; Found 173.0965.

4-(Trifluoromethyl)-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]naphthalen-2-one (3pa).



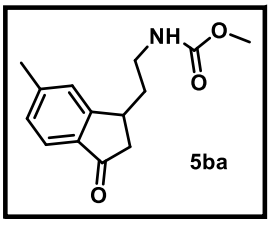
Prepared as shown in *general experimental procedure A*. Yield = 40% (42.2 mg); Appearance – Pale Yellow Liquid; R_f = 0.7 (10% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (s, 1H), 7.69 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 3.38 (dd, *J* = 18.0, 4.6 Hz, 1H), 3.30 (d, *J* = 17.7 Hz, 1H), 2.20 (td, *J* = 8.3, 4.3 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.45 – 1.35 (m, 1H), 0.84 (dd, *J* = 10.7, 5.0 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$** δ 196.9, 142.3, 131.6, 130.1, 129.8, 129.4 (dd, $J_{C\text{-}H}$ = 3.3 Hz), 124.4 (q, $J_{C\text{-}H}$ = 3.8 Hz), 123.9 (q, $J_{C\text{-}H}$ = 272.2 Hz), 28.1, 25.4, 14.3, 12.9; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -62.74; **FT-IR (cm^{-1})** 2926, 1676, 1616; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{12}H_9F_3OH$ 227.0684; Found 227.0686.

Methyl (2-(3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5aa)



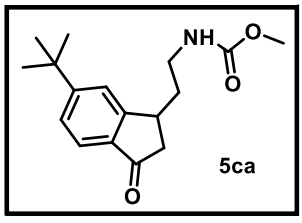
Prepared as shown in *general experimental procedure B*. **Yield** = 71% (66.1mg); **Appearance** – Yellow Oil; R_f = 0.40 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 4.83 (s, 1H), 3.60 (s, 3H), 3.32 (ddd, *J* = 30.2, 16.9, 5.1 Hz, 3H), 2.84 (dd, *J* = 19.0, 7.5 Hz, 1H), 2.33 (dd, *J* = 19.0, 3.3 Hz, 1H), 2.10 (dd, *J* = 12.9, 4.8 Hz, 1H), 1.61 (ddt, *J* = 13.5, 9.9, 6.7 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 205.6, 157.8, 157.0, 136.6, 134.8, 127.7, 125.5, 123.6, 52.0, 42.9, 39.5, 36.4, 35.7; **FT-IR (cm^{-1})** 3342 , 2947, 1710, 1534, 1023, 763; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{13}H_{15}NO_3Na$ 256.0950; Found 256.0950.

Methyl (2-(6-methyl-3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5ba).



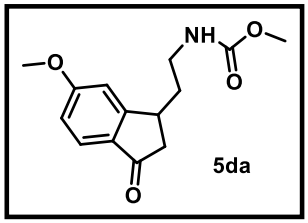
Prepared as shown in *general experimental procedure B*. **Yield** = 68% (67.1 mg); **Appearance** – Yellow Oil; R_f = 0.45(40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 8.5 Hz, 1H), 7.02 – 6.88 (m, 2H), 4.89 (s, 1H), 3.91 (s, 3H), 3.70 (s, 3H), 3.35 (d, *J* = 6.6 Hz, 3H), 2.90 (dd, *J* = 18.7, 7.5 Hz, 1H), 2.39 (dd, *J* = 18.8, 3.2 Hz, 1H), 2.18 (d, *J* = 7.6 Hz, 1H), 1.69 (ddt, *J* = 13.5, 10.0, 6.7 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 205.8, 157.0, 155.2, 137.7, 136.7, 136.0, 125.1, 123.5, 52.0, 43.2, 39.5, 36.5, 35.3, 21.0; **FT-IR (cm^{-1})** 2922, 2853, 2363, 1701, 1614, 1533, 1252, 1022; **HRMS (ESI-TOF) m/z** [M + Na] Calcd for $C_{14}H_{17}NO_3Na$ 270.1106; Found 270.1106.

Methyl (2-(6-(tert-butyl)-3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5ca).



Prepared as shown in *general experimental procedure B*. **Yield** = 65% (75.1 mg); **Appearance** – Yellow Oil; R_f = 0.40 (20% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 8.1 Hz, 1H), 7.43 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 4.99 (s, 1H), 3.59 (s, 3H), 3.35 – 3.20 (m, 3H), 2.81 (dd, *J* = 18.9, 7.4 Hz, 1H), 2.31 (dd, *J* = 18.9, 3.1 Hz, 1H), 2.19 – 2.01 (m, 1H), 1.59 (dd, *J* = 17.3, 13.5, 6.7 Hz, 1H), 1.28 (s, 9H) ;**^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 203.9, 165.3, 160.9, 157.1, 129.8, 125.2, 115.5, 108.7, 55.6, 52.0, 43.0, 39.4, 36.3, 35.6 ;**FT-IR (cm^{-1})** 3342, 2961, 1699, 1533, 1255, 756; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{17}H_{23}NO_3Na$ 312.1576; Found 312.1574.

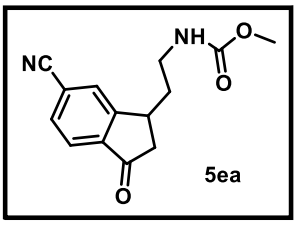
Methyl (2-(6-methoxy-3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5da).



Prepared as shown in *general experimental procedure B*. **Yield** = 67% (70.0 mg); **Appearance** – Yellow Oil; R_f = 0.40 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 8.5 Hz, 1H), 6.91 (dd, *J* = 14.2, 5.7 Hz, 2H), 5.03 (s, 1H), 3.90 (d, *J* = 6.8 Hz, 3H), 3.67 (s, 3H), 3.39 – 3.26 (m, 3H), 2.87 (dd, *J* = 18.8, 7.5 Hz, 1H), 2.37 (dd, *J* = 18.8, 3.3 Hz, 1H), 2.22 – 2.08 (m, 1H), 1.66 (ddt, *J* = 13.4, 10.1, 6.7 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 203.9, 165.3, 160.9,

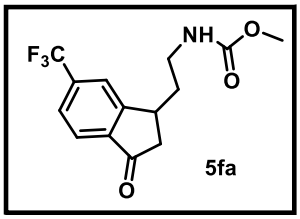
157.1, 129.8, 125.2, 115.5, 108.7, 55.6, 52.5, 43.0, 39.4, 36.3, 35.6;**FT-IR (cm^{-1})** 3338, 2943, 1698, 1599,1193 ; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{14}H_{17}NO_4Na$ 286.1055; Found 286.1053.

Methyl (2-(6-cyano-3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5ea).



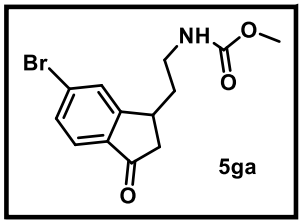
Prepared as shown in *general experimental procedure B*. **Yield** = 46% (47.4 mg); **Appearance** – Yellow Oil; R_f = 0.35 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 – 7.79 (m, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 4.88 (s, 1H), 3.68 (s, 3H), 3.49 (dd, *J* = 10.1, 7.4 Hz, 2H), 3.35 (d, *J* = 6.3 Hz, 1H), 3.00 (dd, *J* = 19.3, 7.6 Hz, 1H), 2.49 (dd, *J* = 19.3, 3.2 Hz, 1H), 1.81 – 1.59 (m, 2H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 203.9, 157.7, 157.1, 139.5, 131.4, 129.8, 124.4, 117.9, 117.8, 76.6, 52.2, 42.8, 39.2, 36.4, 35.7; **FT-IR (cm^{-1})** 3351, 1718, 1531, 1255, 1192, 1037; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{14}H_{14}N_2O_3Na$ 281.0902; Found 281.0900.

Methyl (2-(3-oxo-6-(trifluoromethyl)-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5fa).



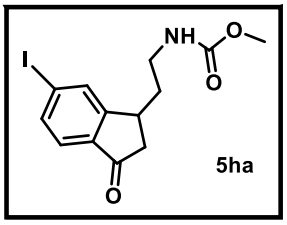
Prepared as shown in *general experimental procedure B*. **Yield** = 48% (57.4mg); **Appearance** – Yellow Oil; R_f = 0.50 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 – 7.78 (m, 2H), 7.66 (d, *J* = 7.9 Hz, 1H), 4.87 (s, 1H), 3.68 (s, 3H), 3.49 (d, *J* = 3.2 Hz, 1H), 3.35 (s, 2H), 3.00 (dd, *J* = 19.2, 7.5 Hz, 1H), 2.49 (dd, *J* = 19.2, 3.3 Hz, 1H), 2.31 – 2.15 (m, 1H), 1.79 – 1.63 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 204.5, 158.0, 157.2, 139.2, 136.3, 136.0, 124.9, 124.3, 122.7, 52.2, 43.0, 39.4, 36.5, 35.8; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -62.78; **FT-IR (cm^{-1})** 3346, 1718, 1534, 1329, 1272, 1061; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{14}H_{14}F_3NO_3Na$ 324.0823; Found 324.0824.

Methyl (2-(6-bromo-3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5ga).



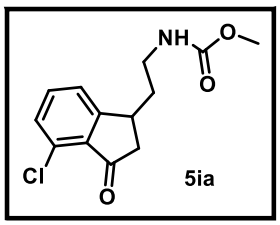
Prepared as shown in *general experimental procedure B*. **Yield** = 53% (65.9mg); **Appearance** –Yellow Oil; R_f = 0.50 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (s, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 5.07 (s, 1H), 3.66 (s, 3H), 3.41 (ddd, *J* = 14.1, 7.5, 3.6 Hz, 1H), 3.32 (dd, *J* = 13.2, 6.5 Hz, 2H), 2.90 (dd, *J* = 19.1, 7.5 Hz, 1H), 2.39 (dd, *J* = 19.1, 3.3 Hz 1H), 2.22 – 2.10 (m, 1H), 1.66 (ddt, *J* = 13.4, 10.4, 6.5 Hz, 1H): **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 204.3, 159.5, 157.0, 135.3, 131.3, 130.1, 128.8, 124.8, 52.0, 42.7, 39.3, 36.2, 35.5 ; **FT-IR (cm^{-1})** 3337, 2922, 2363, 1716, 1594, 1533, 1443, 1264, 1026; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{13}H_{14}BrNO_3Na$ 334.0055; Found 334.0053.

Methyl (2-(6-iodo-3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5ha).



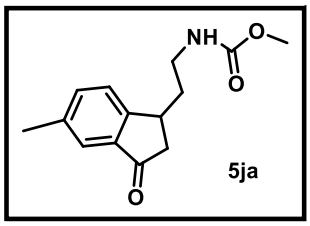
Prepared as shown in *general experimental procedure B.* **Yield** = 40% (57.2mg); **Appearance** – Yellow Oil; R_f = 0.4 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 5.08 (s, 1H), 3.67 (s, 3H), 3.39 (dd, *J* = 10.1, 7.3 Hz, 1H), 3.32 (d, *J* = 6.2 Hz, 2H), 2.87 (dd, *J* = 19.1, 7.5 Hz, 1H), 2.37 (dd, *J* = 19.1, 3.1 Hz, 1H), 2.16 (d, *J* = 7.6 Hz, 1H), 1.66 (ddd, *J* = 16.8, 13.3, 6.5 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 204.6, 159.8, 157.0, 137.0, 135.8, 135.0, 124.7, 103.2, 52.0, 42.5, 39.3, 36.2, 35.4; **FT-IR (cm^{-1})** 3335, 2922, 2363, 2331, 1710, 1588, 1533, 1263, 1193, 1023; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{13}H_{14}NO_3INa$ 381.9916; Found 381.9913.

Methyl (2-(4-chloro-3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5ia).



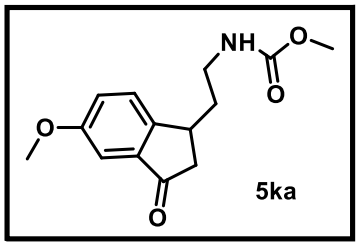
Prepared as shown in *general experimental procedure B.* **Yield** = 58% (61.9 mg); **Appearance** – Yellow Oil; R_f = 0.40 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (t, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 4.86 (s, 1H), 3.68 (s, 3H), 3.42 – 3.24 (m, 3H), 2.95 (dd, *J* = 18.9, 7.7 Hz, 1H), 2.45 (dd, *J* = 18.9, 3.5 Hz, 1H), 2.23 – 2.07 (m, 1H), 1.67 (m, *J* = 13.5, 10.1, 6.7 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 202.4, 160.2, 157.0, 135.1, 132.4, 131.8, 129.4, 123.9, 52.1, 43.5, 39.3, 36.5, 34.9; **FT-IR (cm^{-1})** 3342, 1715, 1591, 1458, 1235, 1136, 1025; **HRMS (ESI-TOF) m/z** [M + Na] Calcd for $C_{13}H_{14}ClNO_3Na$ 290.0560; Found 290.0560.

Methyl (2-(5-methyl-3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate(5ja).



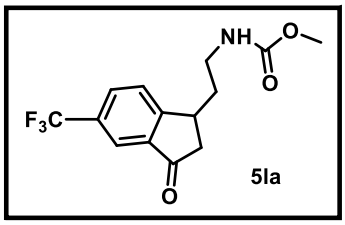
Prepared as shown in *general experimental procedure B.* **Yield** = 72% (71.1 mg); **Appearance** – Yellow Oil; R_f = 0.60 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (s, 1H), 7.44 (q, *J* = 8.2 Hz, 2H), 4.91 (s, 1H), 3.69 (s, 3H), 3.35 (dd, *J* = 15.2, 8.5 Hz, 3H), 2.91 (dd, *J* = 18.9, 7.3 Hz, 1H), 2.39 (d, *J* = 19.2 Hz, 4H), 2.20 – 2.09 (m, 1H), 1.68 (tt, *J* = 16.8, 6.9 Hz, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 205.8, 157.0, 155.2, 137.7, 136.7, 136.0, 125.1, 123.5, 77.3, 77.2, 77.0, 76.6, 52.0, 43.2, 39.5, 36.5, 35.3, 21.0; **FT-IR (cm^{-1})** 2961,2872, 1714, 1622, 1266, 1006; **HRMS (ESI-TOF) m/z** [M + Na] Calcd for $C_{14}H_{17}NO_3Na$ 270.1106; Found 270.1103.

Methyl (2-(3-oxo-5-(trifluoromethyl)-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5ka).



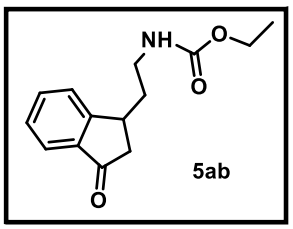
Prepared as shown in *general experimental procedure B*. **Yield** = 68% (71.5 mg); **Appearance** – Yellow Oil; R_f = 0.40 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 –7.32 (m, 2H), 7.06 (dd, *J* = 6.9, 1.4 Hz, 1H), 4.79 (s, 1H), 3.91 (s, 3H), 3.66 (s, 3H), 3.50 (s, 1H), 3.25 (d, *J* = 40.3 Hz, 2H), 2.86 (dd, *J* = 19.1, 7.5 Hz, 1H), 2.44 (d, *J* = 18.9 Hz, 1H), 2.28 (s, 1H), 1.62 (dt, *J* = 13.7, 7.9 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 205.9, 157.1, 156.9, 145.8, 138.3, 129.3, 115.4, 115.4, 77.3, 55.5, 55.4, 52.0, 43.1, 39.5, 34.6, 33.8; **FT-IR (cm^{-1})** 3341, 1710, 1599, 1265, , 1063, 1035; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{14}H_{17}NO_4Na$ 286.1055; Found 286.1053.

Methyl (2-(3-oxo-5-(trifluoromethyl)-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5la).



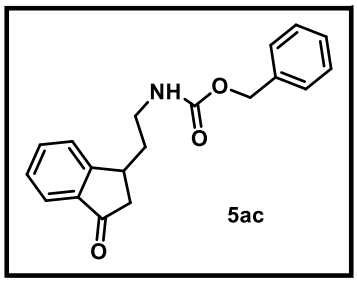
Prepared as shown in *general experimental procedure B*. **Yield** = 43% 51.7 mg); **Appearance** – Yellow Oil; R_f = 0.40 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 5.07 (s, 1H), 3.67 (s, 3H), 3.51 (s, 1H), 3.36 (d, *J* = 6.3 Hz, 2H), 2.99 (dd, *J* = 19.2, 7.6 Hz, 1H), 2.49 (dd, *J* = 19.2, 3.2 Hz, 1H), 2.21 (dt, *J* = 11.9, 7.4 Hz, 1H), 1.81 – 1.64 (m, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 204.23, 161.0, 157.1, 137.0, 131.3, 131.2, 126.3, 120.9, 120.88, 52.1, 42.9, 39.3, 36.2, 35.8; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -62.78; **FT-IR (cm^{-1})** 3349, 1712, 1534, 1262, 1167, 1024; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{14}H_{14}F_3NO_3Na$ 324.0823; Found 324.0820.

Ethyl (2-(3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5ab).



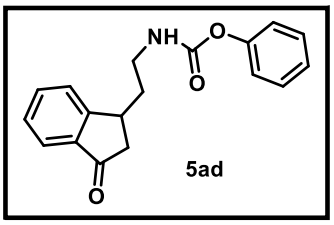
Prepared as shown in *general experimental procedure B*. **Yield** = 69% (68.2mg); **Appearance** – Yellowish Oil; R_f = 0.45(40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 4.76 (s, 1H), 4.05 (dd, *J* = 13.9, 6.9 Hz, 2H), 3.39 – 3.17 (m, 3H), 2.84 (dd, *J* = 19.0, 7.5 Hz, 1H), 2.33 (dd, *J* = 19.0, 3.3 Hz, 1H), 2.10 (dd, *J* = 13.0, 4.7 Hz, 1H), 1.61 (ddt, *J* = 13.6, 10.1, 6.8 Hz, 1H), 1.17 (t, *J* = 6.9 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 205.7, 157., 156.6, 136.6, 134.8, 127.7, 125.5, 123.6, 60.8, 42.9, 39.4, 36.4, 35.7, 14.6; **FT-IR (cm^{-1})** 3349, 1711, 1603, 1255,1041; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{14}H_{17}NO_3Na$ 270.1106; Found 270.1104.

Benzyl (2-(3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5ac).



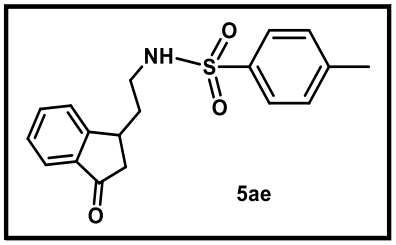
Prepared as shown in *general experimental procedure B*. **Yield** = 66% (50.3 mg); **Appearance** – Colourless Oil; R_f = 0.50 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.44 – 7.30 (m, 6H), 5.12 (s, 3H), 3.37 (dd, *J* = 16.4, 9.4 Hz, 3H), 2.91 (dd, *J* = 19.0, 7.3 Hz, 1H), 2.40 (d, *J* = 19.1 Hz, 1H), 2.18 (d, *J* = 7.5 Hz, 1H). 1.76 – 1.59 (m, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 205.6, 157.8, 156.3, 136.5, 136.3, 134.7, 128.4, 128.0, 127.9, 127.6, 125.4, 123.5, 66.6, 42.8, 39.4, 36.3, 35.6; **FT-IR (cm^{-1})** 3339, 2931, 1710, 1250, 1015, 769; **HRMS (ESI-TOF) m/z** $[M + Na]^+$ Calcd for $C_{19}H_{19}NO_3Na$ 332.1263; Found 332.1262.

Phenyl (2-(3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)carbamate (5ad).



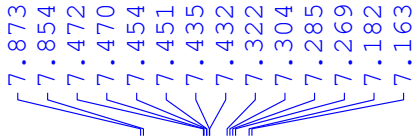
Prepared as shown in *general experimental procedure B*. **Yield** = 62% (52.1 mg); **Appearance** – Colourless Oil; R_f = 0.5 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.41 (dt, *J* = 15.7, 7.6 Hz, 3H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 5.20 (s, 1H), 3.55 – 3.38 (m, 3H), 2.97 (dd, *J* = 19.0, 7.6 Hz, 1H), 2.45 (dd, *J* = 19.0, 3.3 Hz, 1H), 2.28 (ddd, *J* = 20.8, 7.6, 4.4 Hz, 1H), 1.79 (ddd, *J* = 16.8, 13.7, 7.0 Hz, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 205.6, 157.7, 154.7, 150.8, 136.6, 134.9, 129.3, 127.8, 125.5, 125.4, 123.7, 121.5, 42.9, 39.7, 36.2, 35.7; **FT-IR (cm^{-1})** 3331, 2931, 1712, 1490, 1206, 761;**HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{15}H_{15}NO_3H$ 318.1106; Found 318.1103.

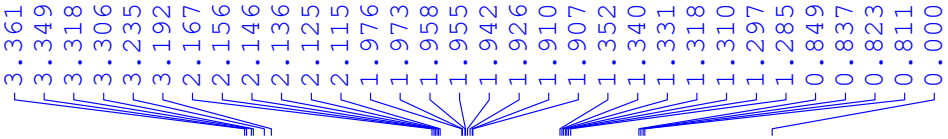
4-Methyl-N-(2-(3-oxo-2,3-dihydro-1H-inden-1-yl)ethyl)benzenesulfonamide (5ae).

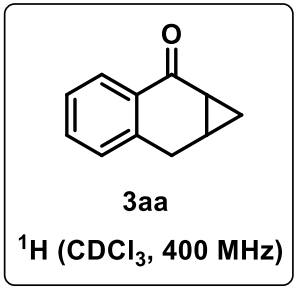


Prepared as shown in *general experimental procedure B*. **Yield** = 47% (31.1 mg); **Appearance** – Yellow Oil; R_f = 0.35 (40% EtOAc /Hexane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.58 (dd, *J* = 10.5, 4.4 Hz, 1H), 7.45 – 7.34 (m, 2H), 7.34 – 7.28 (m, 2H), 5.43 (d, *J* = 6.0 Hz, 1H), 3.43 (s, 1H), 3.15 – 2.98 (m, 2H), 2.81 (ddd, *J* = 19.0, 7.5, 1.0 Hz, 1H), 2.43 (s, 3H), 2.26 (dd, *J* = 19.0, 2.3 Hz, 1H), 2.14 (dt, *J* = 12.1, 7.5 Hz, 1H), 1.68 – 1.57 (m, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 205.6, 157.6, 143.5, 136.6, 136.4, 134.8, 129.7, 127.7, 127.0, 125.5, 123.5, 42.6, 41.5, 35.9, 35.2, 21.4; **FT-IR (cm^{-1})** 3273, 2926, 1706, 1326, 1157, 762; **HRMS (ESI-TOF) m/z** $[M + H]^+$ Calcd for $C_{15}H_{15}NO_3H$ 330.1164; Found 330.1163.

^{1}H and ^{13}C NMR Spectra

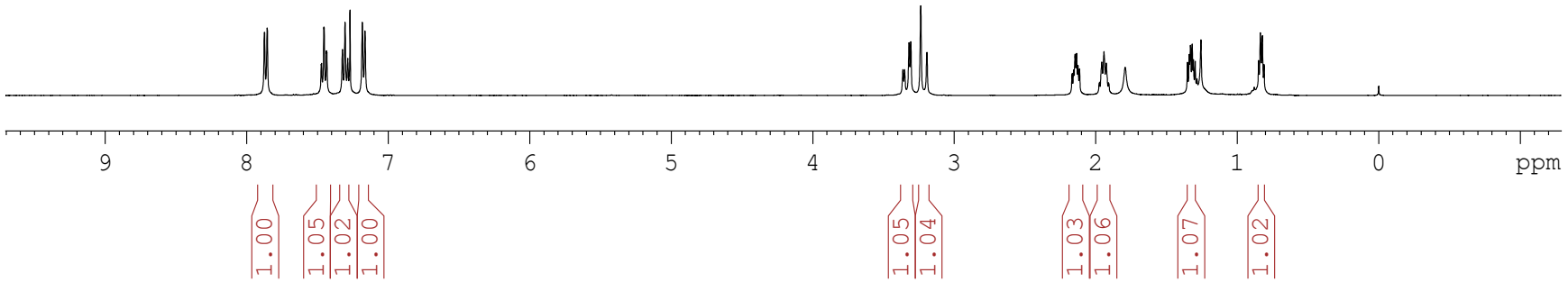


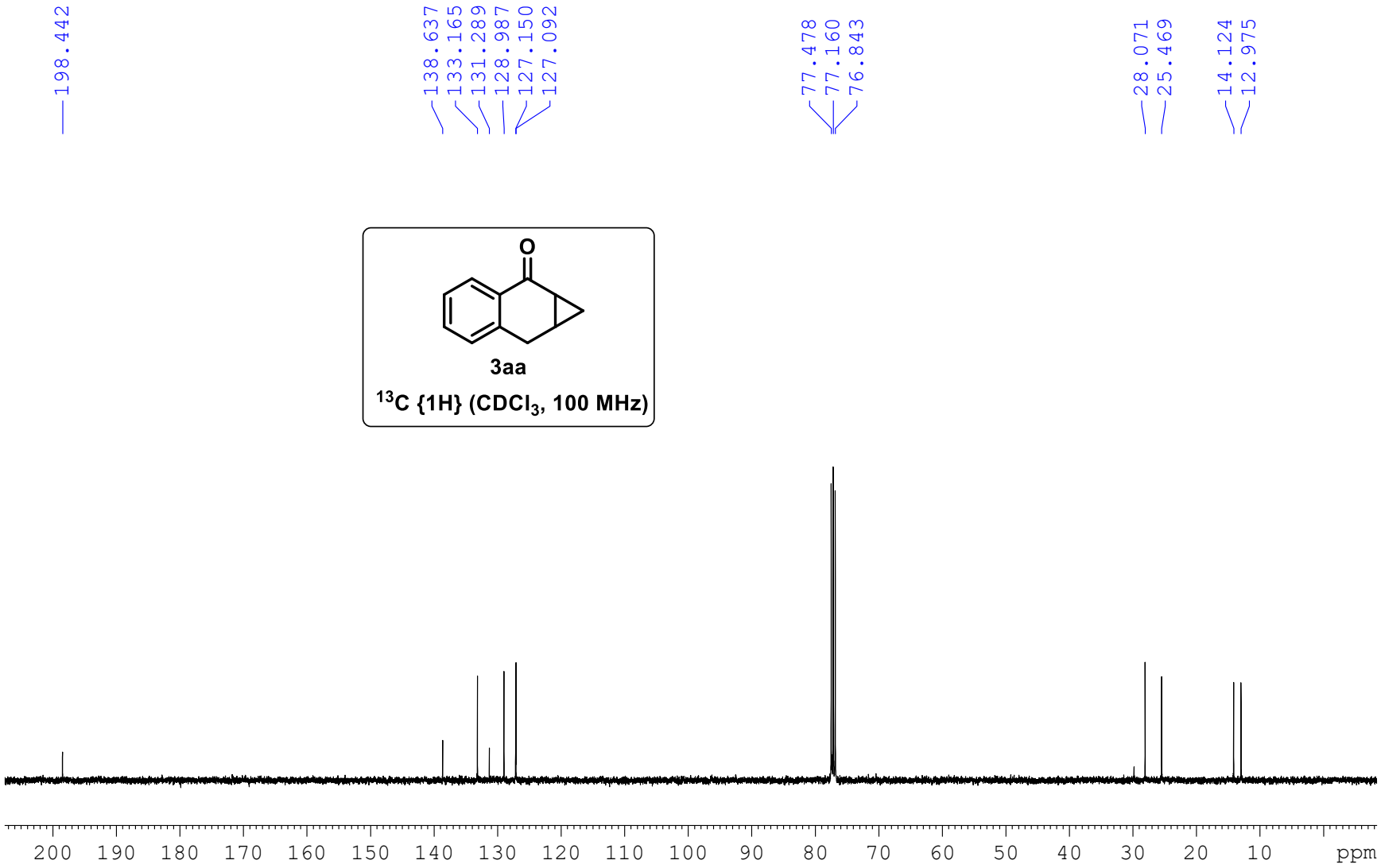


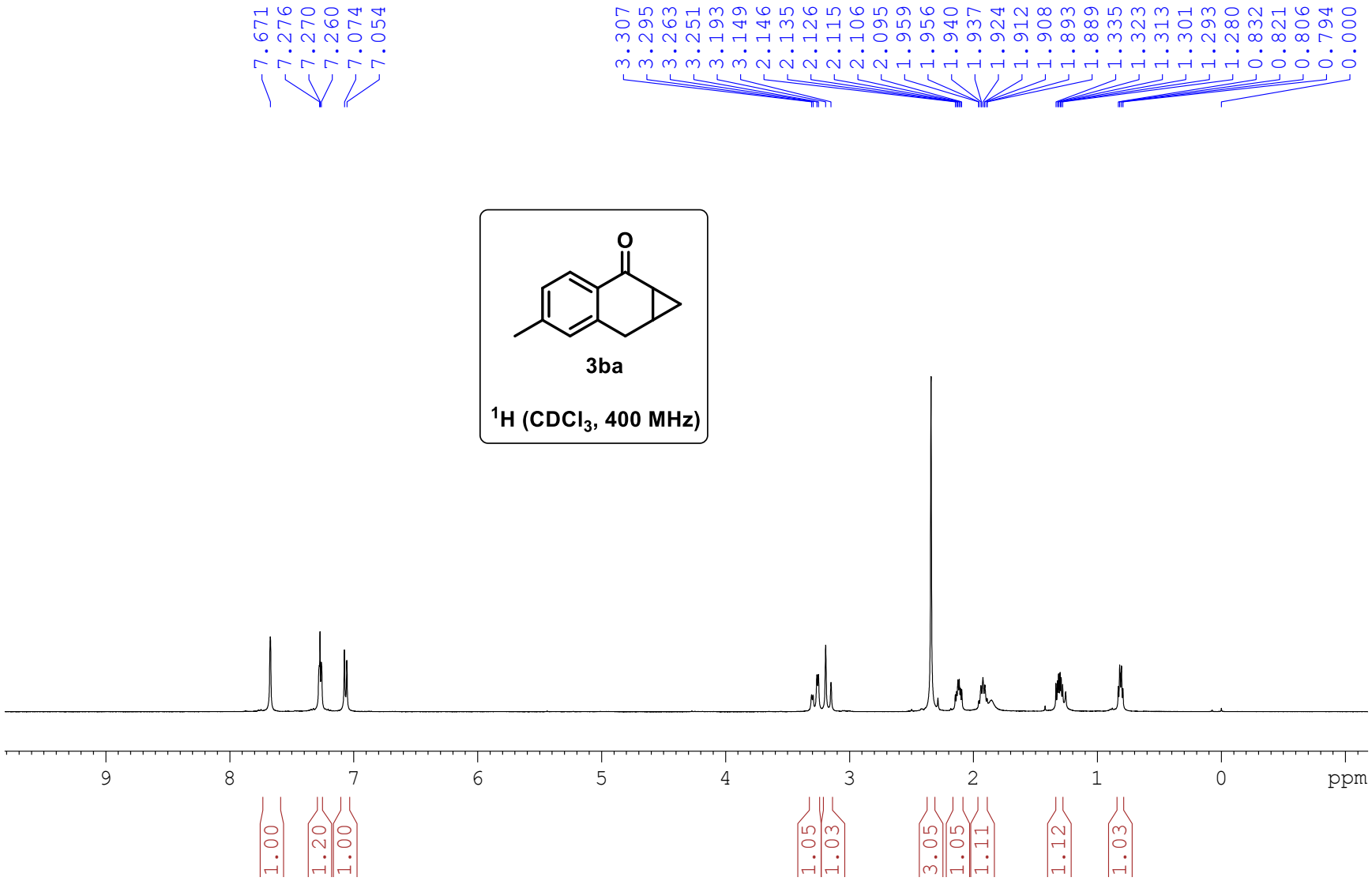


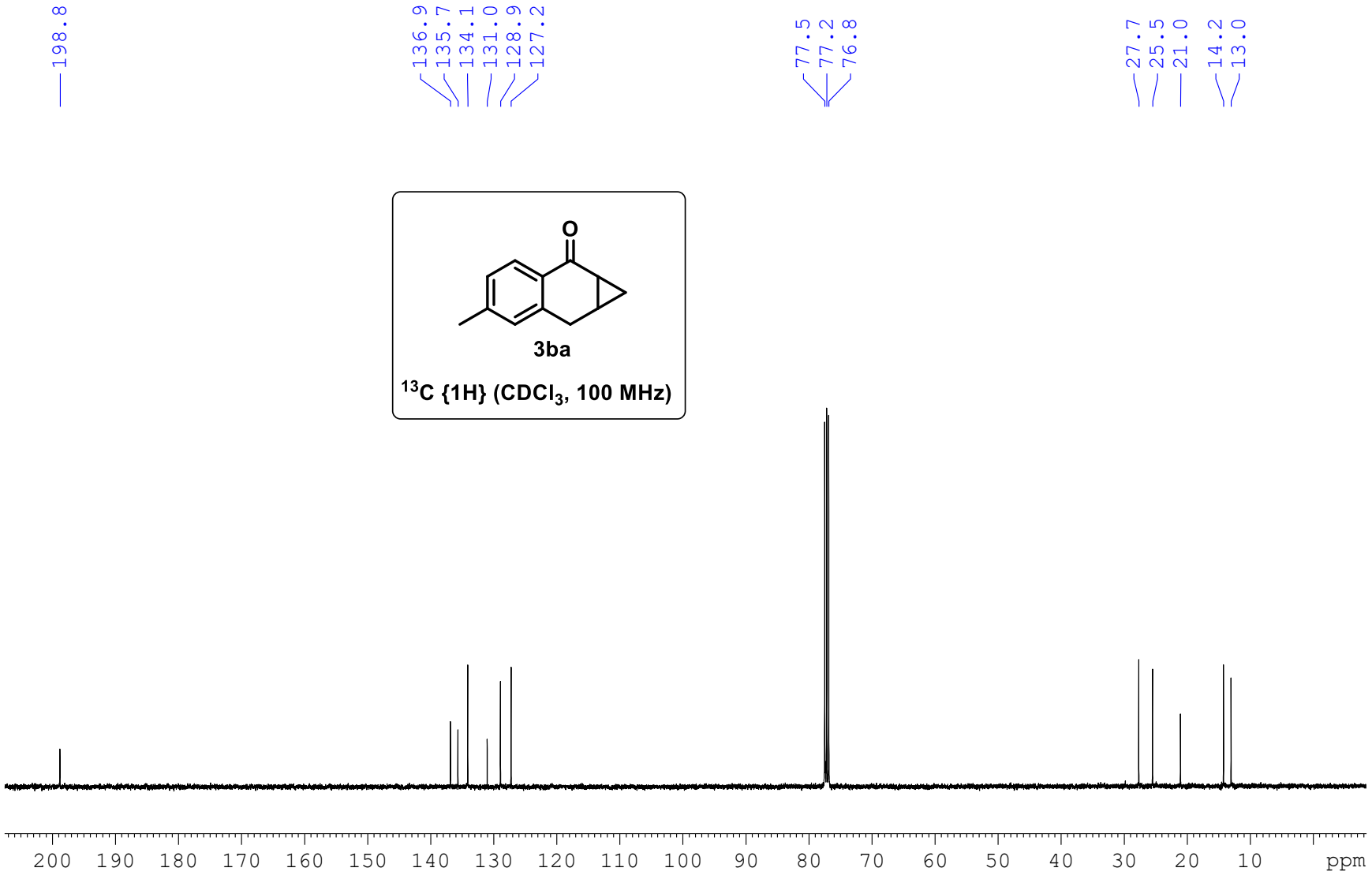
3aa

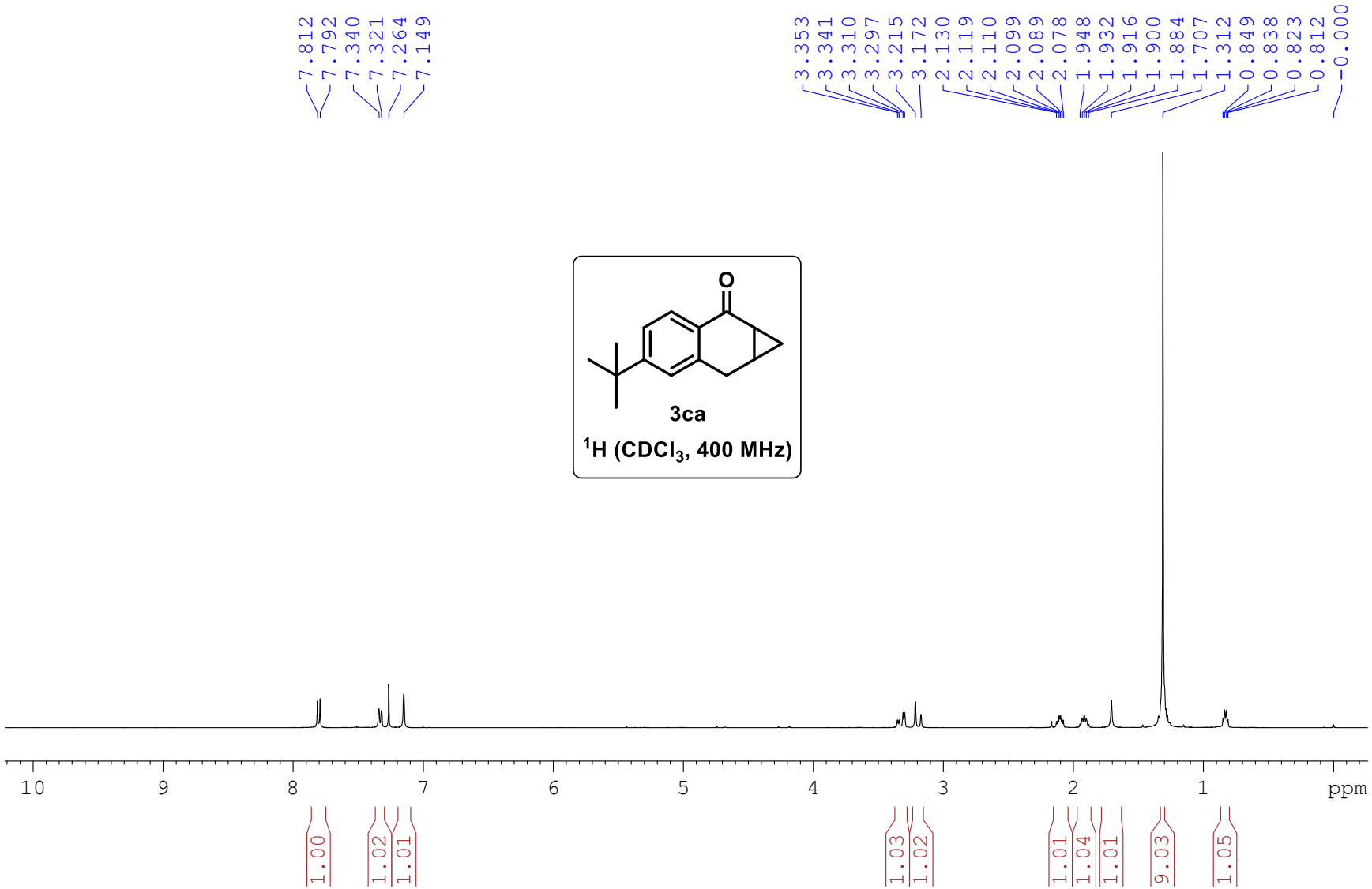
^{1}H ($CDCl_3$, 400 MHz)

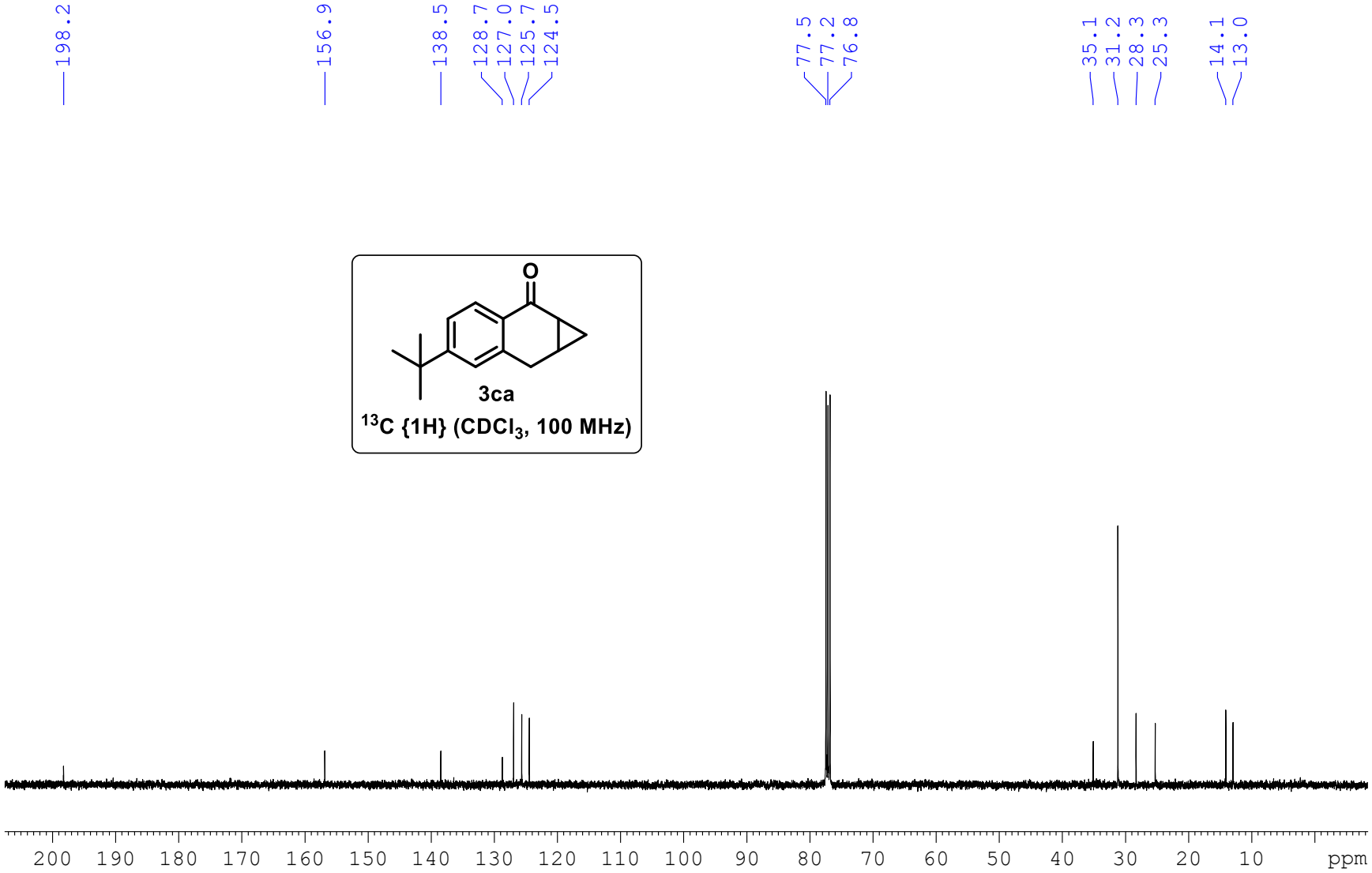


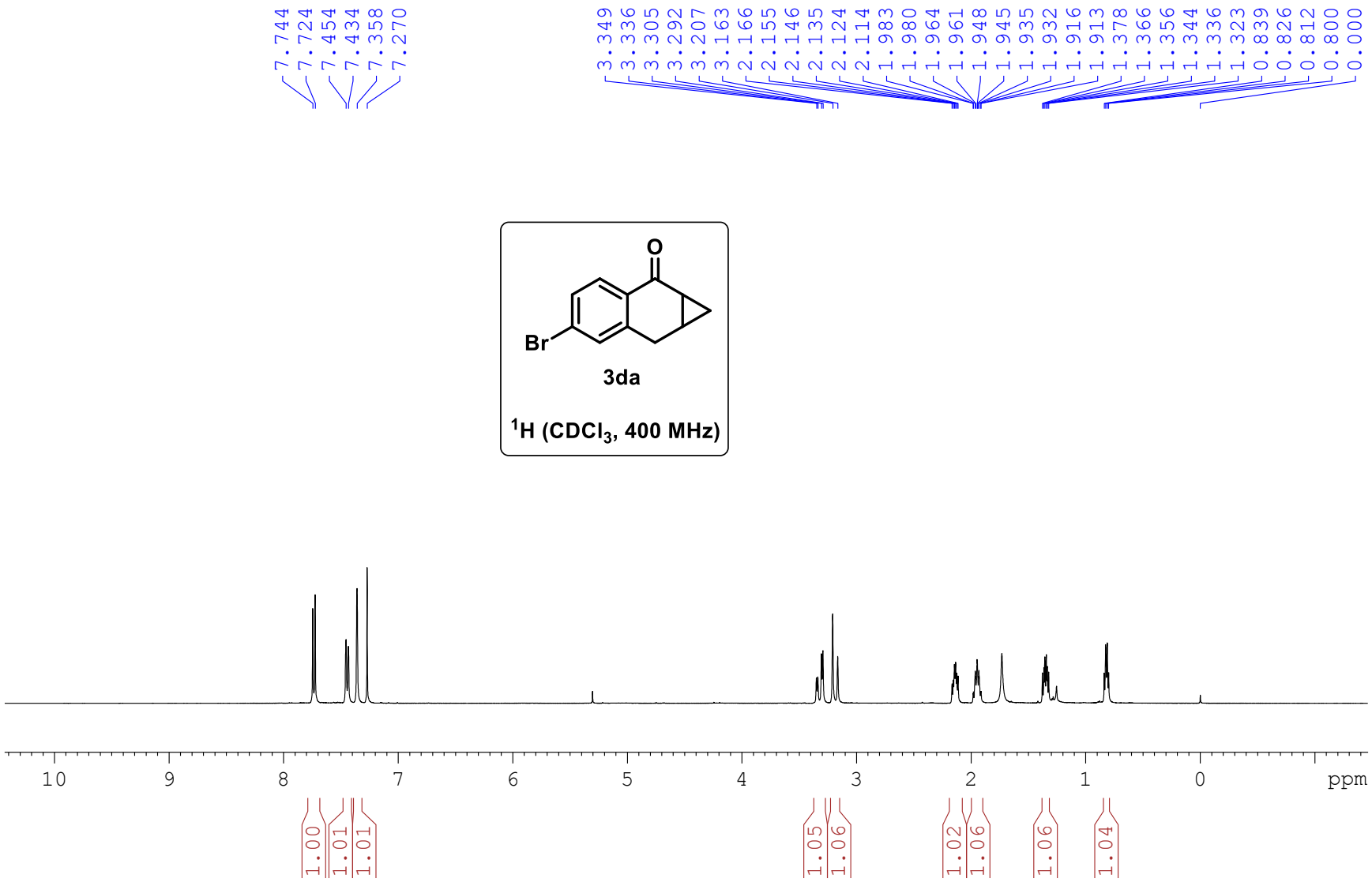

198.442
138.637
133.165
131.289
128.987
127.150
127.092
77.478
77.160
76.843
28.071
25.469
14.124
12.975
O
3aa
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

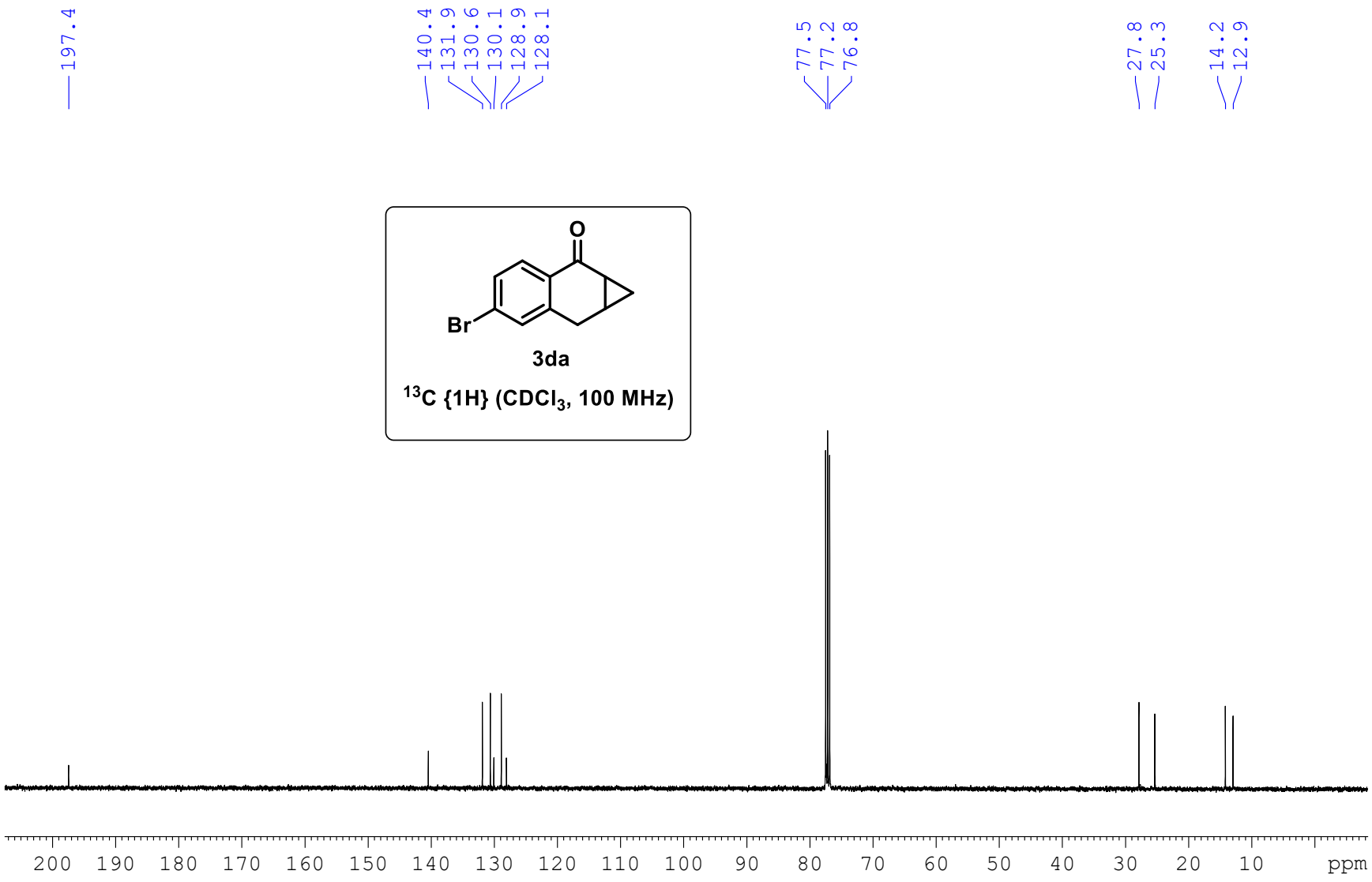

7.671
7.276
7.270
7.260
7.074
7.054
3.307
3.295
3.263
3.251
3.193
3.149
2.146
2.135
2.126
2.115
2.106
2.095
1.959
1.956
1.940
1.937
1.924
1.912
1.908
1.893
1.889
1.335
1.323
1.313
1.301
1.293
1.280
0.832
0.821
0.806
0.794
0.000
O
3ba
^{1}H (CDCl$_3$, 400 MHz)
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.20
1.00
1.05
1.03
3.05
1.05
1.11
1.12
1.03

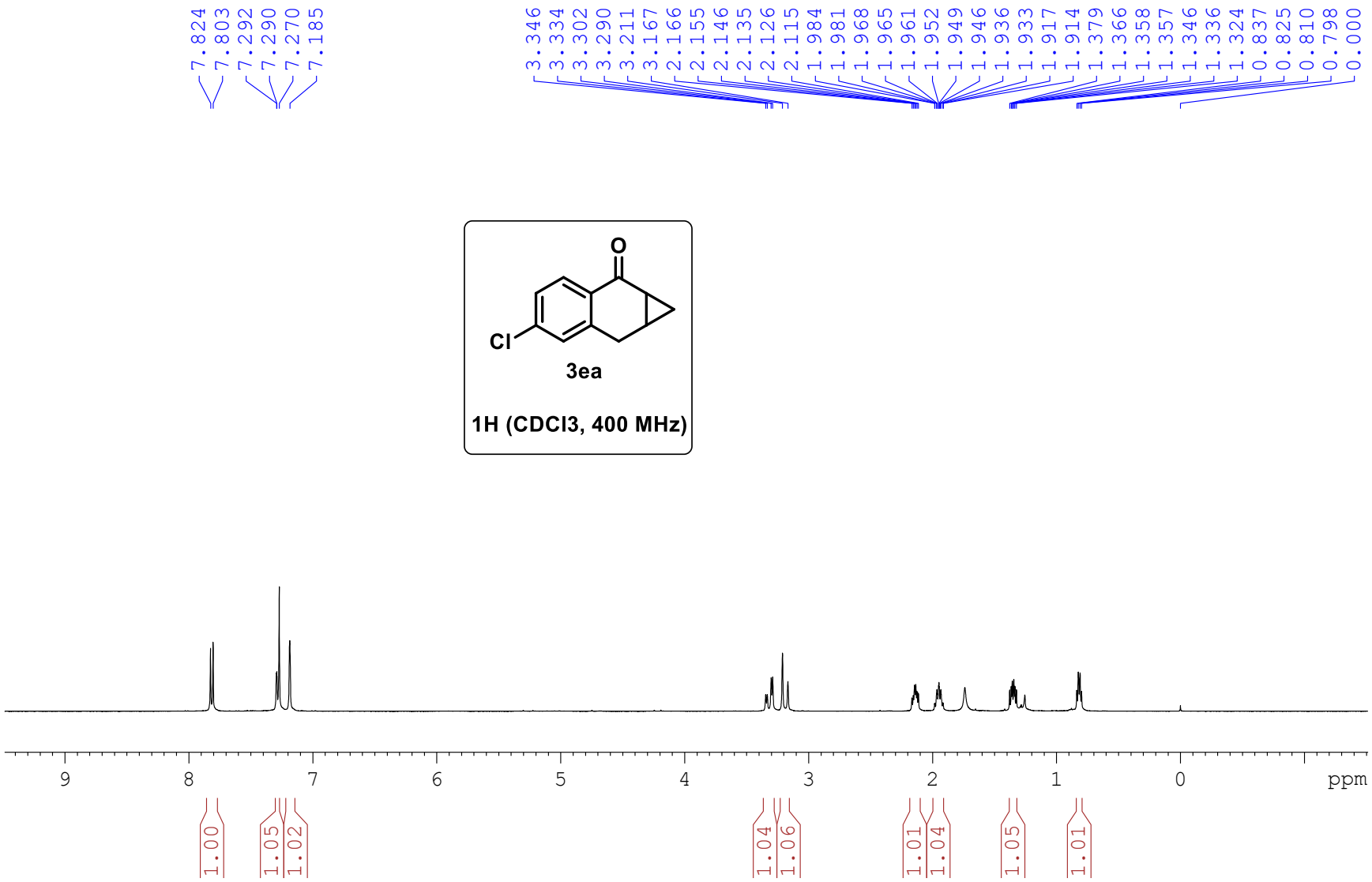

198.8
136.9
135.7
134.1
131.0
128.9
127.2
77.5
77.2
76.8
27.7
25.5
21.0
14.2
13.0
O
3ba
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

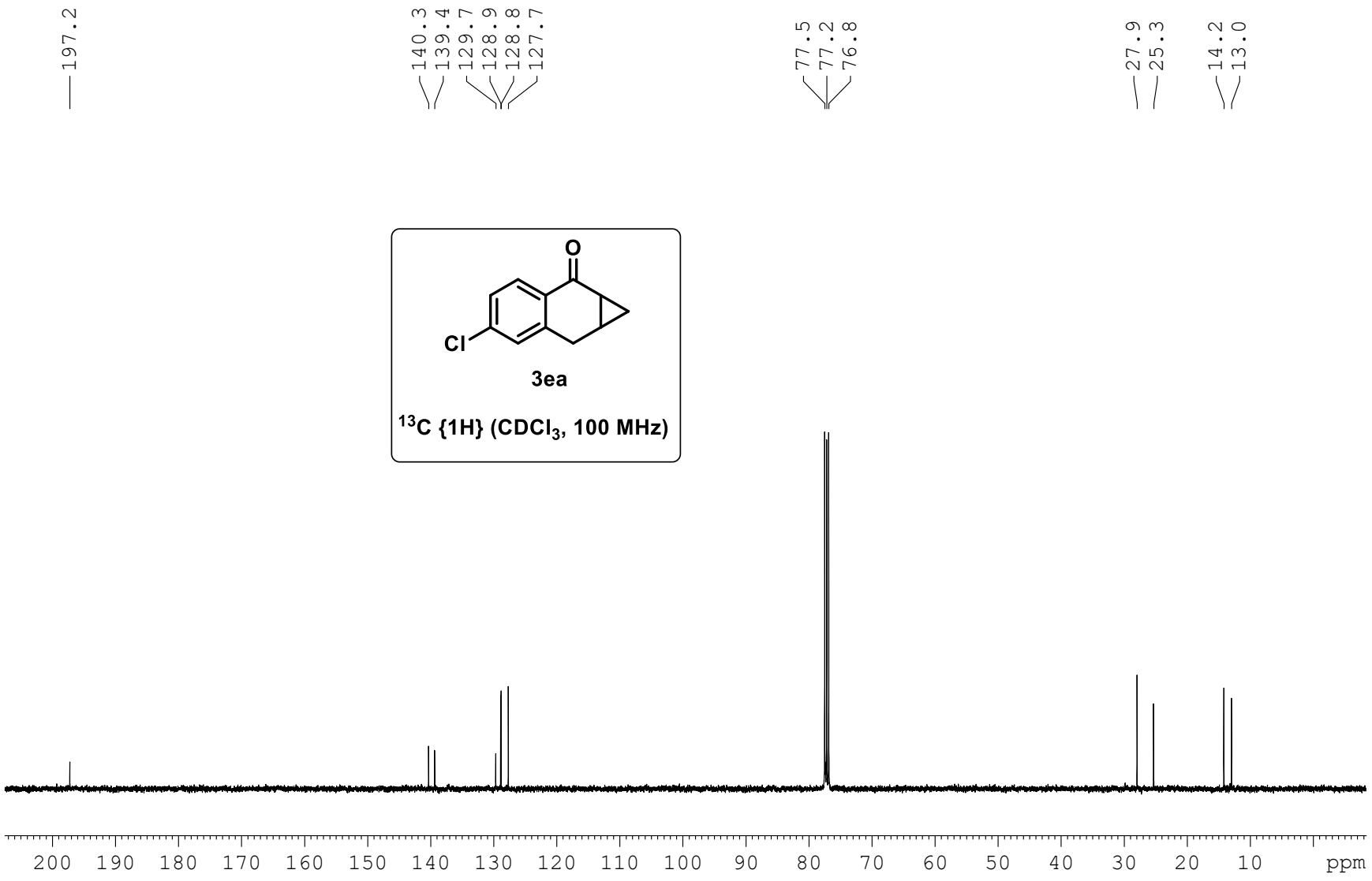

7.812
7.792
7.340
7.321
7.264
7.149
3.353
3.341
3.310
3.297
3.215
3.172
2.130
2.119
2.110
2.099
2.089
2.078
1.948
1.932
1.916
1.900
1.884
1.707
1.312
0.849
0.838
0.823
0.812
-0.000
O
3ca
^{1}H (CDCl$_3$, 400 MHz)
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.01
1.03
1.02
1.01
1.04
1.01
9.03
1.05

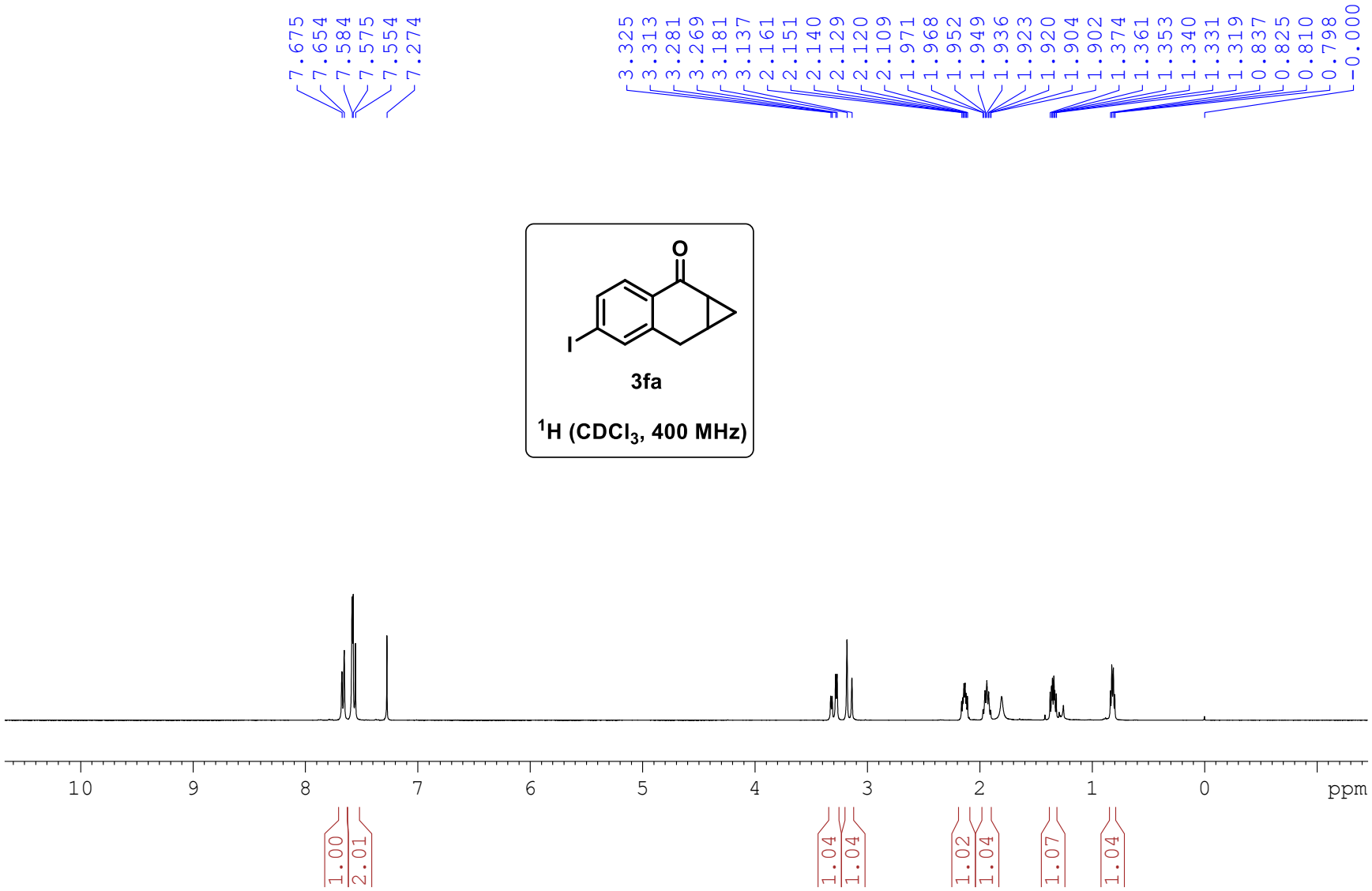

198.2
156.9
138.5
128.7
127.0
125.7
124.5
77.5
77.2
76.8
35.1
31.2
28.3
25.3
14.1
13.0
O
3ca
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

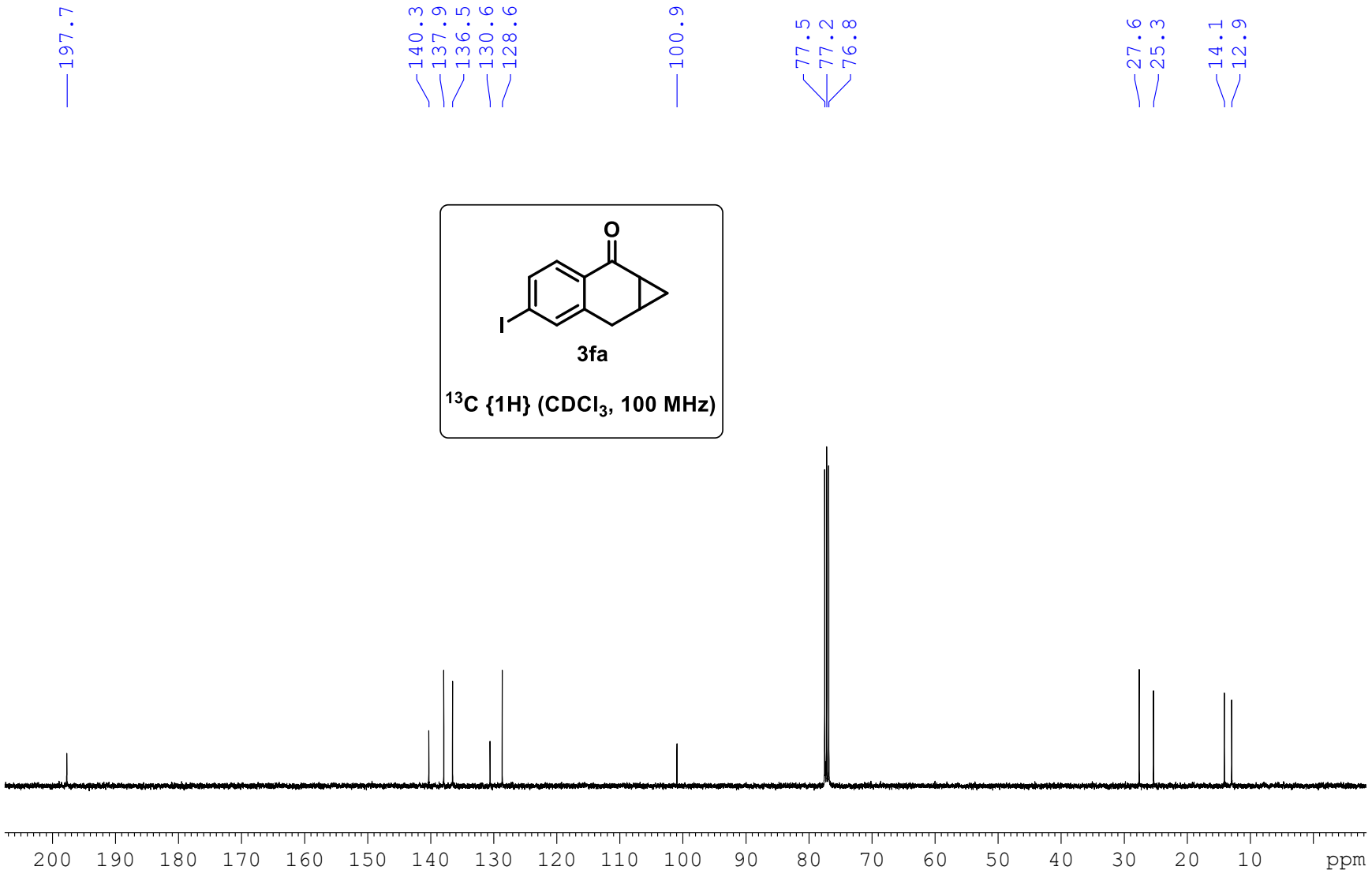

7.744
7.724
7.454
7.434
7.358
7.270
3.349
3.336
3.305
3.292
3.207
3.163
2.166
2.155
2.146
2.135
2.124
2.114
1.983
1.980
1.964
1.961
1.948
1.945
1.935
1.932
1.916
1.913
1.378
1.366
1.356
1.344
1.336
1.323
0.839
0.826
0.812
0.800
0.000
O
Br
3da
^{1}H (CDCl$_3$, 400 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.01
1.05
1.06
1.02
1.06
1.06
1.04

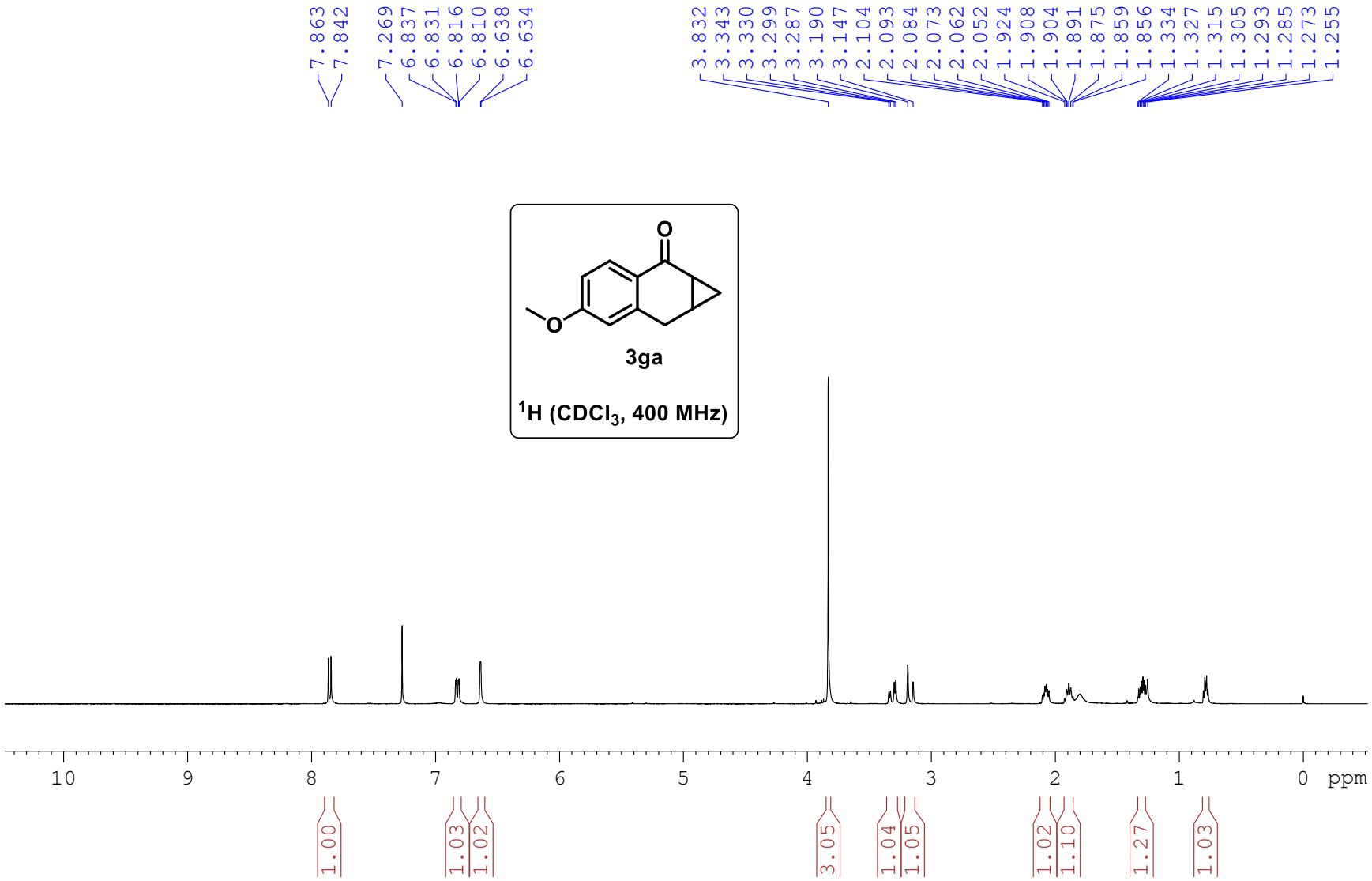

197.4
140.4
131.9
130.6
130.1
128.9
128.1
77.5
77.2
76.8
27.8
25.3
14.2
12.9
O
Br
3da
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

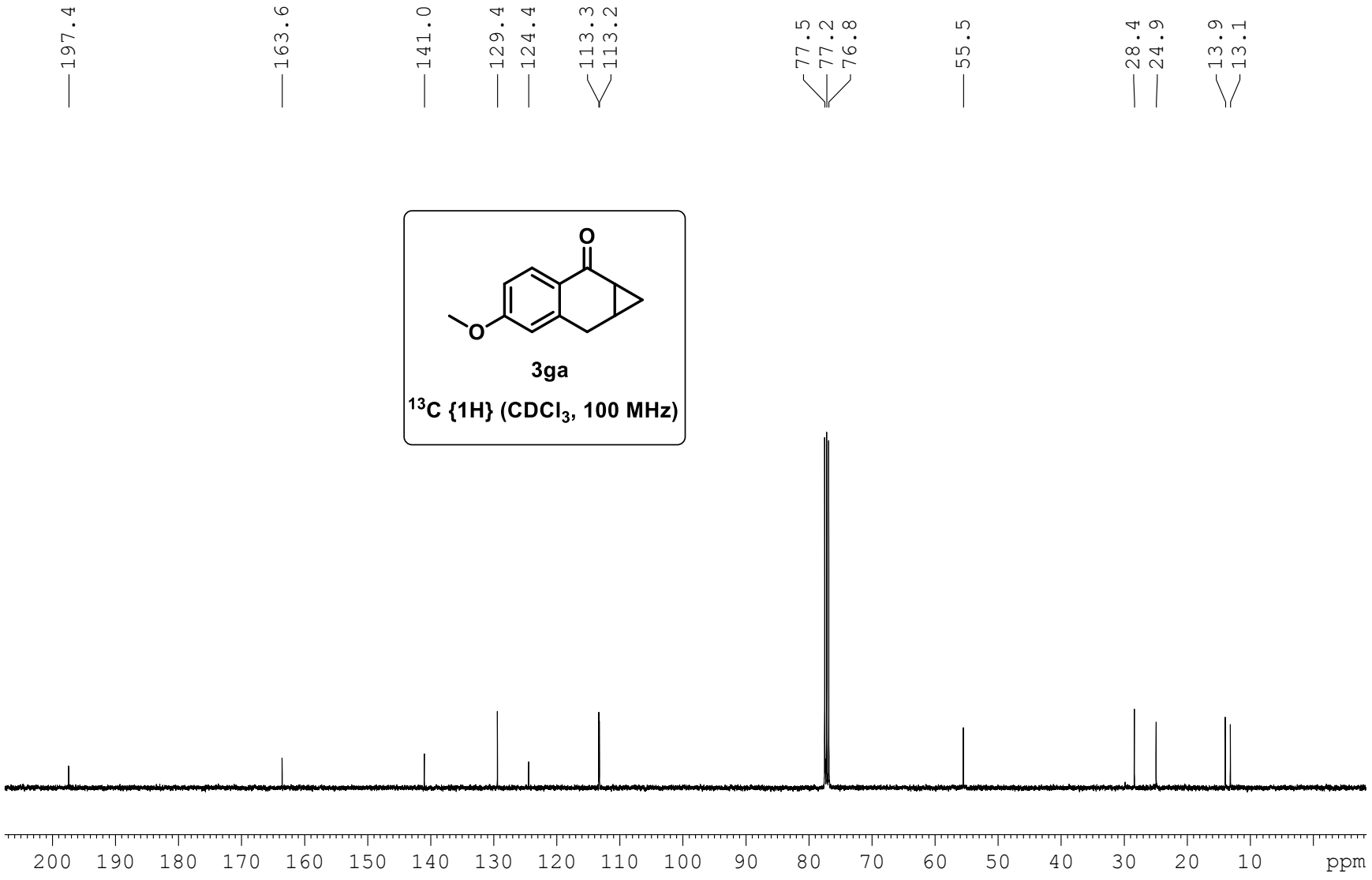

7.824
7.803
7.292
7.290
7.270
7.185
3.346
3.334
3.302
3.290
3.211
3.167
2.166
2.155
2.146
2.135
2.126
2.115
1.984
1.981
1.968
1.965
1.961
1.952
1.949
1.946
1.936
1.933
1.917
1.914
1.379
1.366
1.358
1.357
1.346
1.336
1.324
0.837
0.825
0.810
0.798
0.000
O
Cl
3ea
1H (CDCl3, 400 MHz)
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
1.02
1.04
1.06
1.01
1.04
1.05
1.01

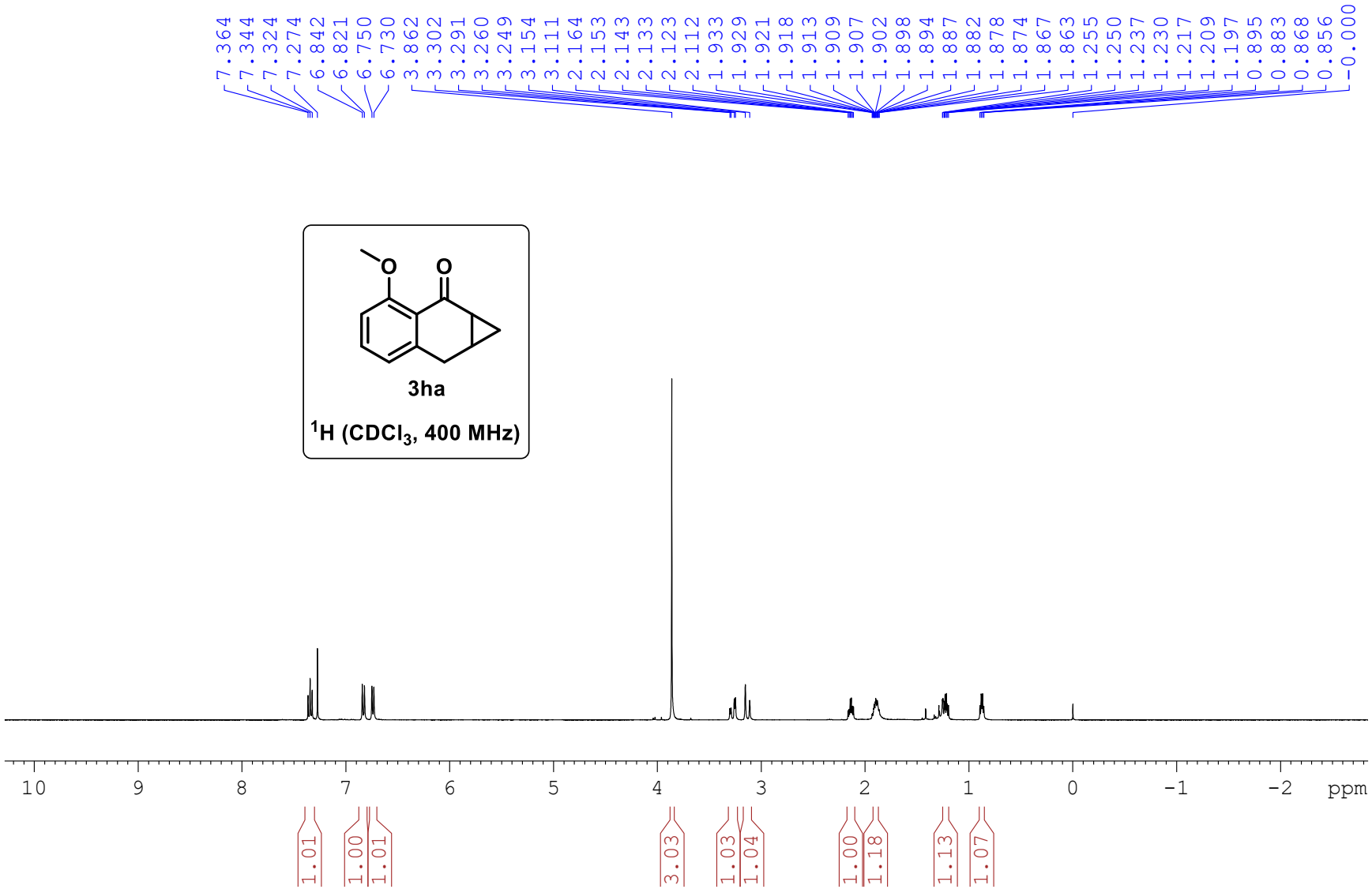

197.2
140.3
139.4
129.7
128.9
128.8
127.7
77.5
77.2
76.8
27.9
25.3
14.2
13.0
O
Cl
3ea
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

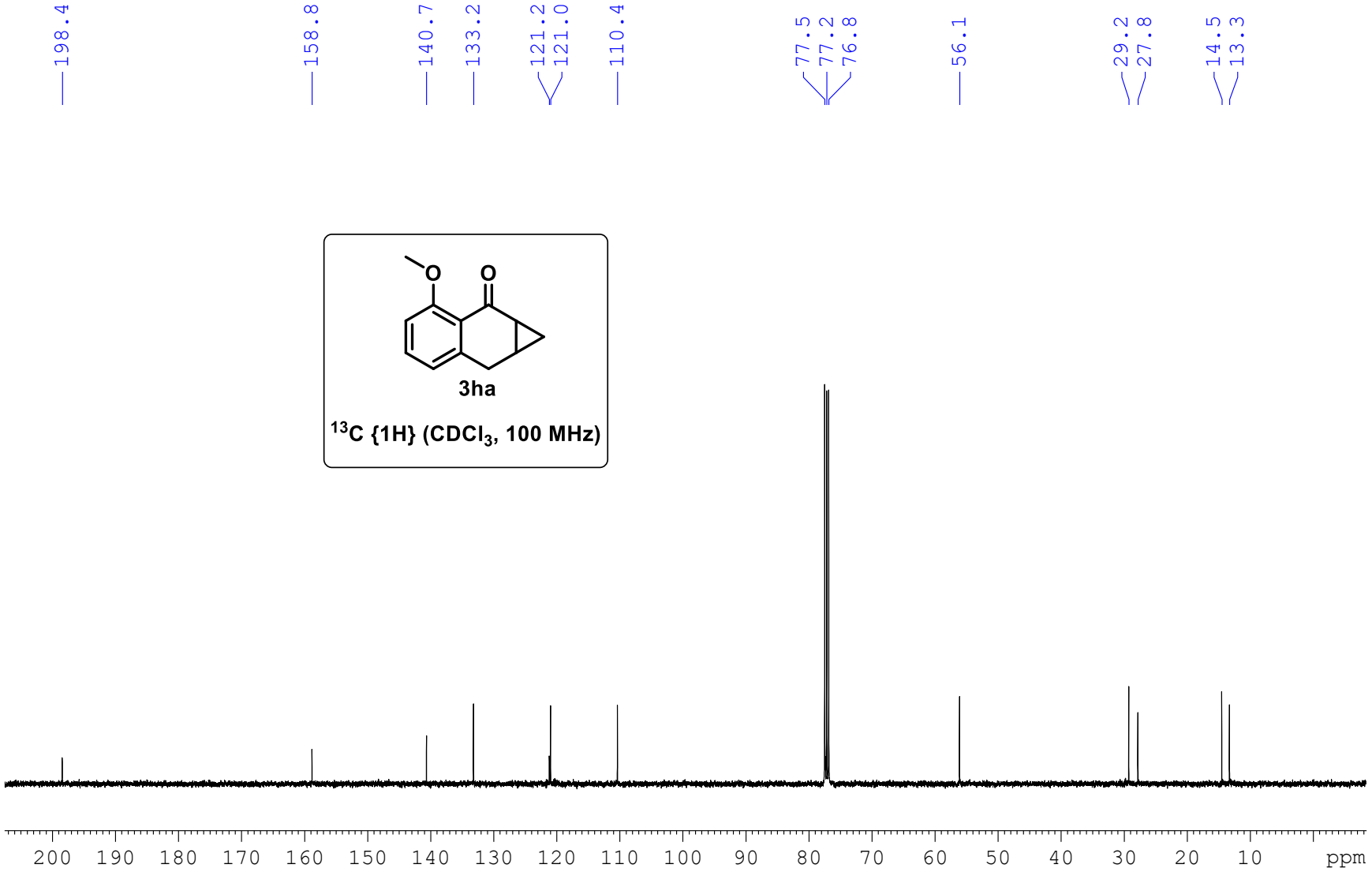

7.675
7.654
7.584
7.575
7.554
7.274
3.325
3.313
3.281
3.269
3.181
3.137
2.161
2.151
2.140
2.129
2.120
2.109
1.971
1.968
1.952
1.949
1.936
1.923
1.920
1.904
1.902
1.374
1.361
1.353
1.340
1.331
1.319
0.837
0.825
0.810
0.798
-0.000
O
I
3fa
^{1}H (CDCl$_3$, 400 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.01
1.04
1.04
1.02
1.04
1.07
1.04

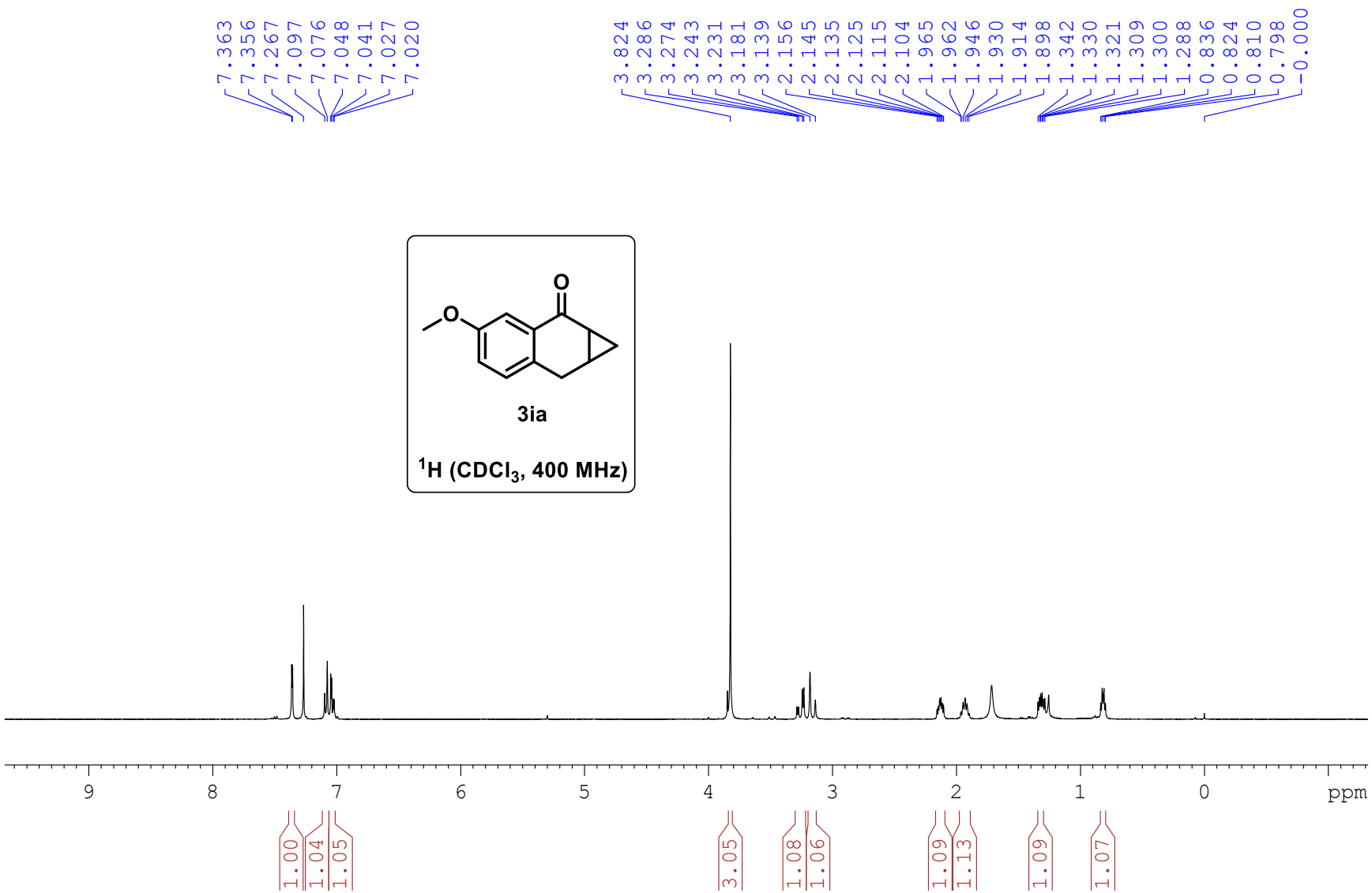

197.7
140.3
137.9
136.5
130.6
128.6
100.9
77.5
77.2
76.8
27.6
25.3
14.1
12.9
O
I
3fa
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

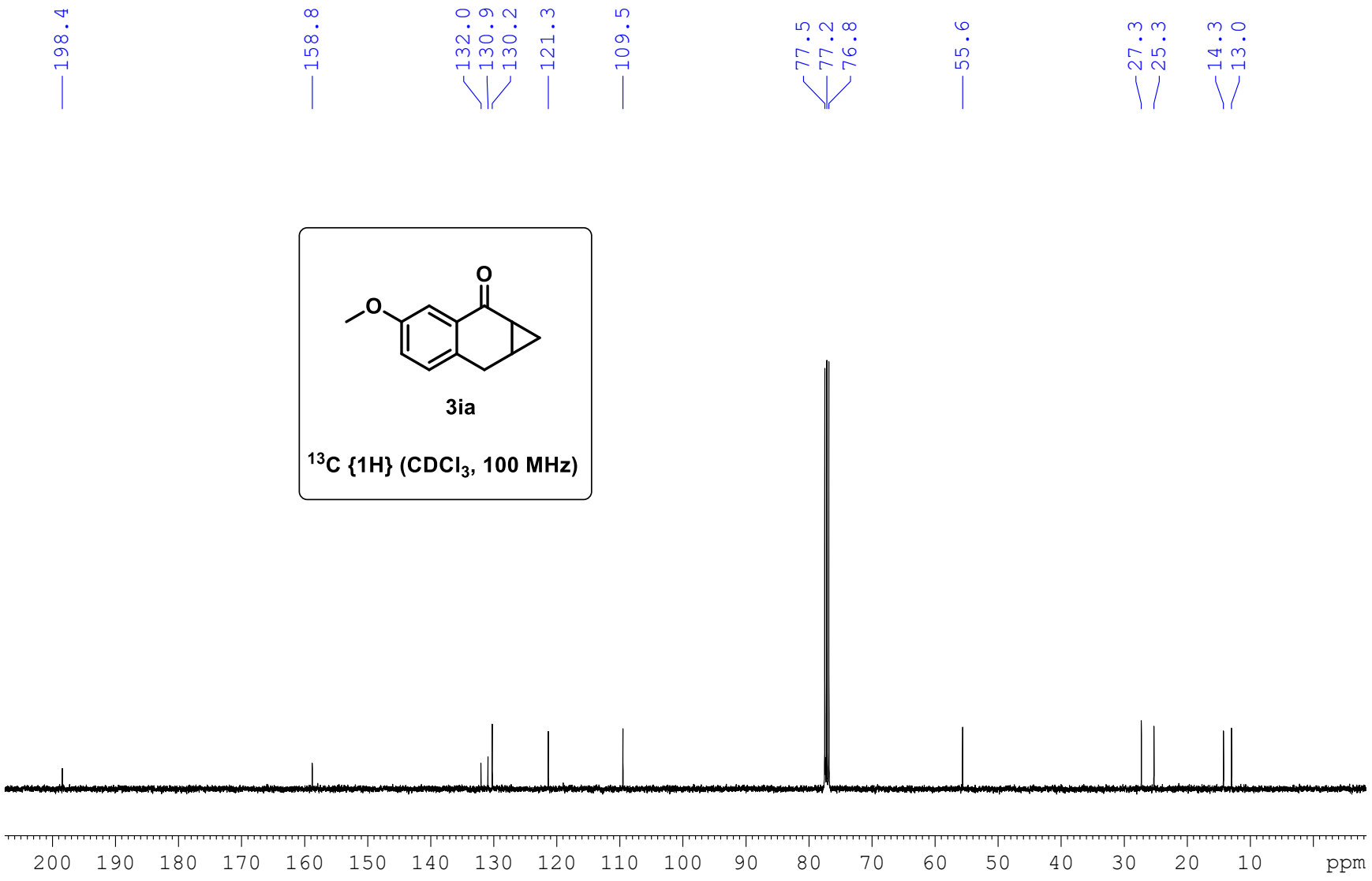

7.863
7.842
7.269
6.837
6.831
6.816
6.810
6.638
6.634
3.832
3.343
3.330
3.299
3.287
3.190
3.147
2.104
2.093
2.084
2.073
2.062
2.052
1.924
1.908
1.904
1.891
1.875
1.859
1.856
1.334
1.327
1.315
1.305
1.293
1.285
1.273
1.255
O
O
3ga
^{1}H ($CDCl_3$, 400 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
1.02
3.05
1.04
1.05
1.02
1.10
1.27
1.03

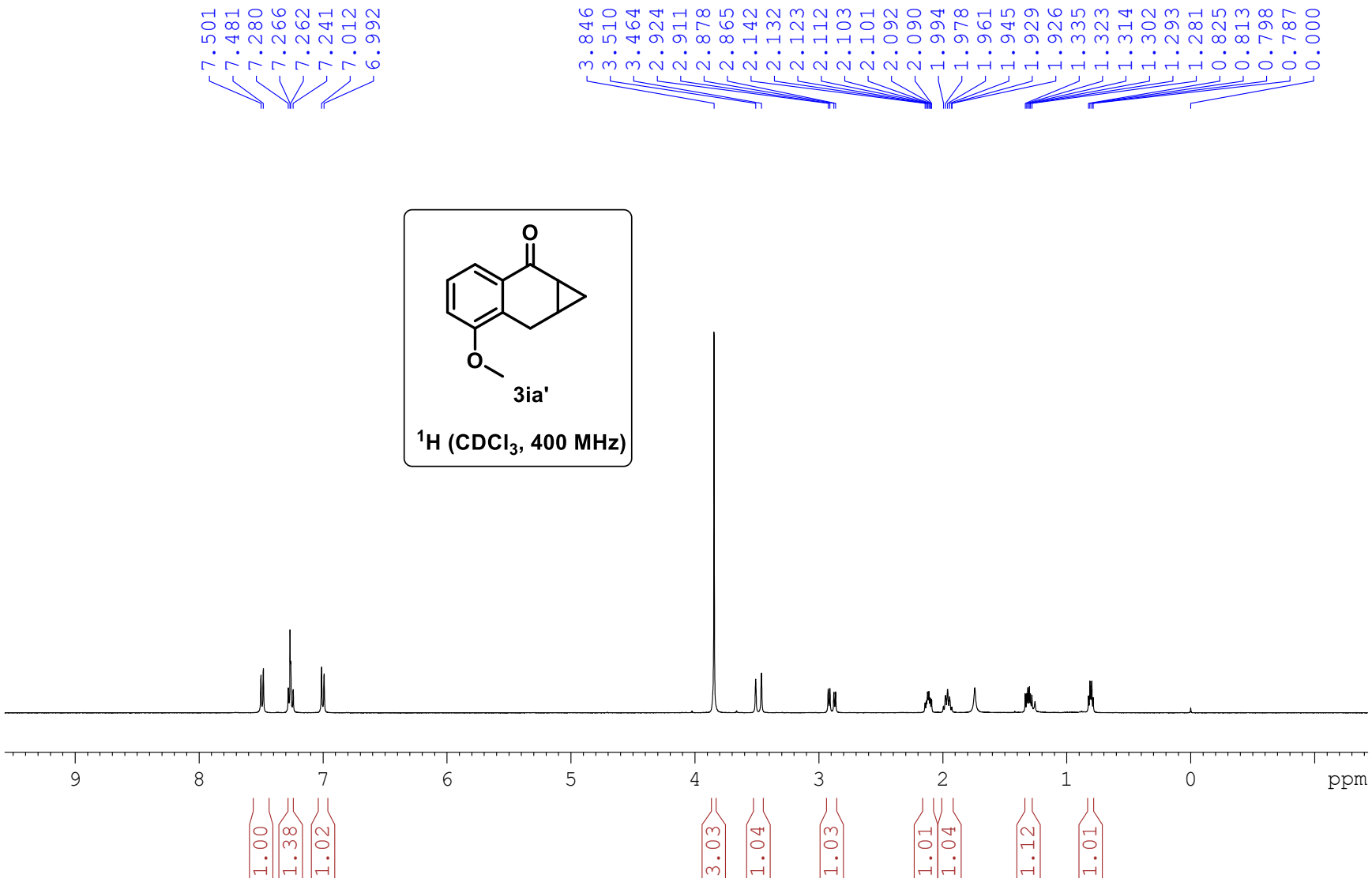

197.4
163.6
141.0
129.4
124.4
113.3
113.2
77.5
77.2
76.8
55.5
28.4
24.9
13.9
13.1
O
O
3ga
^{13}C {1H} ($CDCl_3$, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

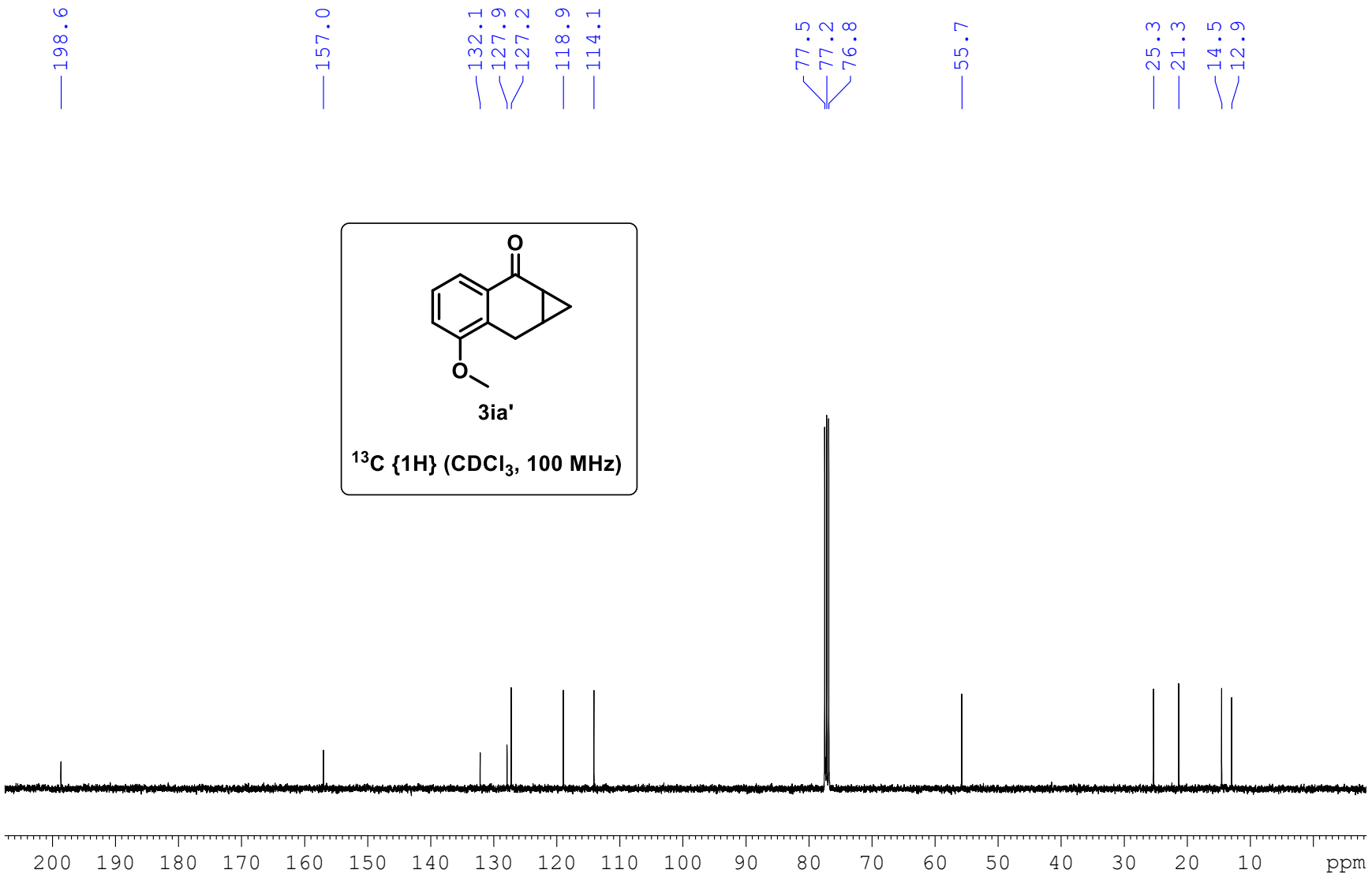

7.364
7.344
7.324
7.274
6.842
6.821
6.750
6.730
3.862
3.302
3.291
3.260
3.249
3.154
3.111
2.164
2.153
2.143
2.133
2.123
2.112
1.933
1.929
1.921
1.918
1.913
1.909
1.907
1.902
1.898
1.894
1.887
1.882
1.878
1.874
1.867
1.863
1.255
1.250
1.237
1.230
1.217
1.209
1.197
0.895
0.883
0.868
0.856
-0.000
O
O
3ha
^{1}H (CDCl$_3$, 400 MHz)
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
1.01
1.00
1.01
3.03
1.03
1.04
1.00
1.18
1.13
1.07

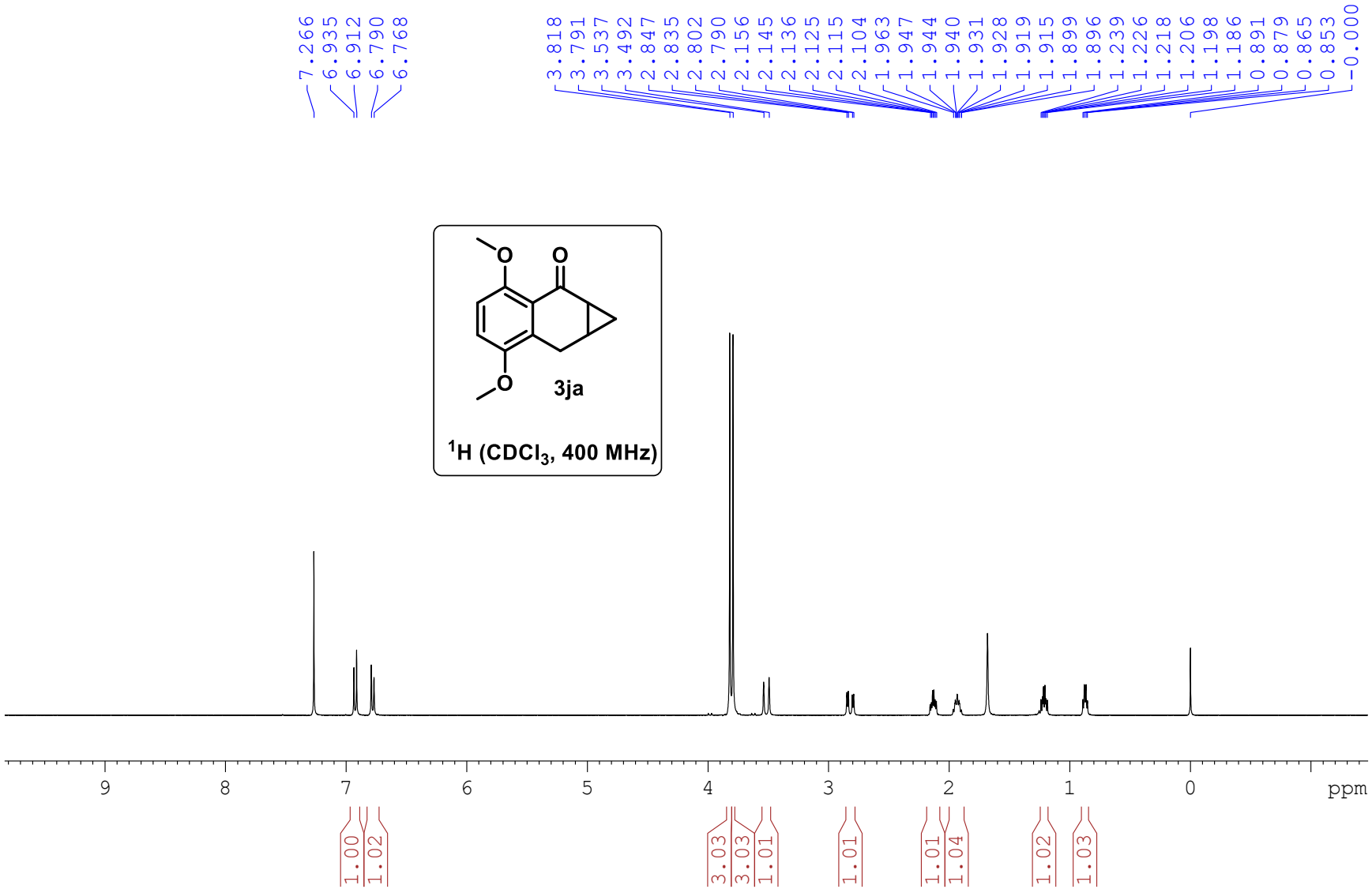

198.4
158.8
140.7
133.2
121.2
121.0
110.4
77.5
77.2
76.8
56.1
29.2
27.8
14.5
13.3
O
O
3ha
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.363
7.356
7.267
7.097
7.076
7.048
7.041
7.027
7.020
3.824
3.286
3.274
3.243
3.231
3.181
3.139
2.156
2.145
2.135
2.125
2.115
2.104
1.965
1.962
1.946
1.930
1.914
1.898
1.342
1.330
1.321
1.309
1.300
1.288
0.836
0.824
0.810
0.798
-0.000
O
O
3ia
^{1}H (CDCl$_3$, 400 MHz)
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
1.05
3.05
1.08
1.06
1.09
1.13
1.09
1.07

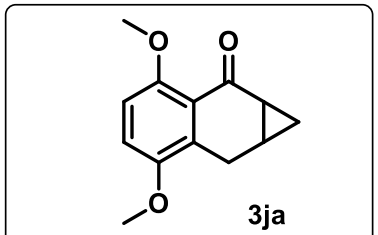

198.4
158.8
132.0
130.9
130.2
121.3
109.5
77.5
77.2
76.8
55.6
27.3
25.3
14.3
13.0
O
O
3ia
^{13}C {1H} (CDCl$_3$, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.501
7.481
7.280
7.266
7.262
7.241
7.012
6.992
3.846
3.510
3.464
2.924
2.911
2.878
2.865
2.142
2.132
2.123
2.112
2.103
2.101
2.092
2.090
1.994
1.978
1.961
1.945
1.929
1.926
1.335
1.323
1.314
1.302
1.293
1.281
0.825
0.813
0.798
0.787
0.000
O
O
3ia'
1H (CDCl3, 400 MHz)
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.38
1.02
3.03
1.04
1.03
1.01
1.04
1.12
1.01


198.6
157.0
132.1
127.9
127.2
118.9
114.1
77.5
77.2
76.8
55.7
25.3
21.3
14.5
12.9
O
O
3ia'
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

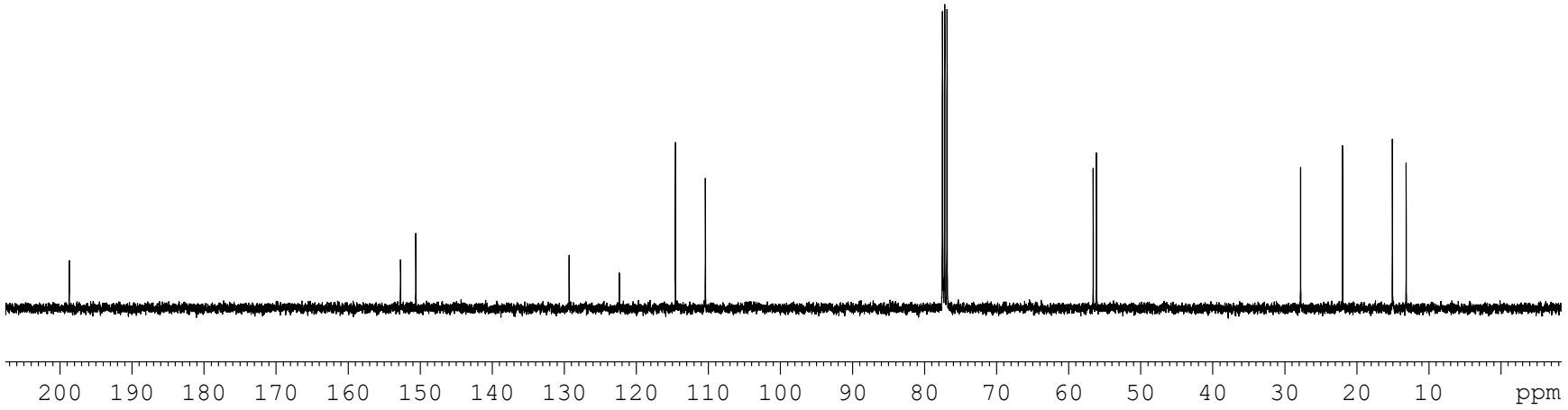

7.266
6.935
6.912
6.790
6.768
3.818
3.791
3.537
3.492
2.847
2.835
2.802
2.790
2.156
2.145
2.136
2.125
2.115
2.104
1.963
1.947
1.944
1.940
1.931
1.928
1.919
1.915
1.899
1.896
1.239
1.226
1.218
1.206
1.198
1.186
0.891
0.879
0.865
0.853
0.000
O
O
O
3ja
^{1}H (CDCl$_3$, 400 MHz)
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
3.03
3.03
1.01
1.01
1.01
1.04
1.02
1.03

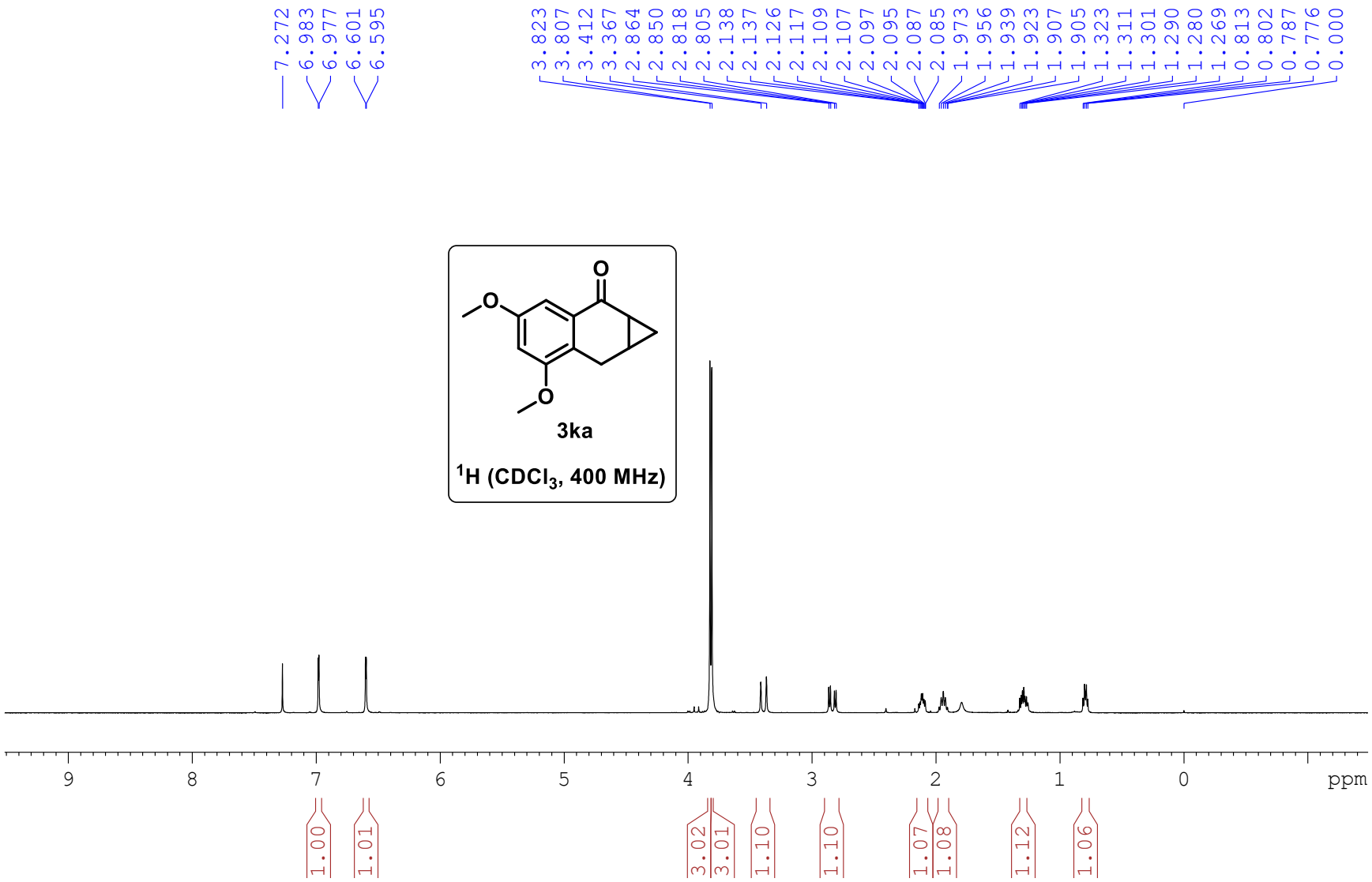
198.7
152.7
150.6
129.3
122.3
114.5
110.4
77.5
77.2
76.8
56.6
56.1
27.8
21.9
15.0
13.1

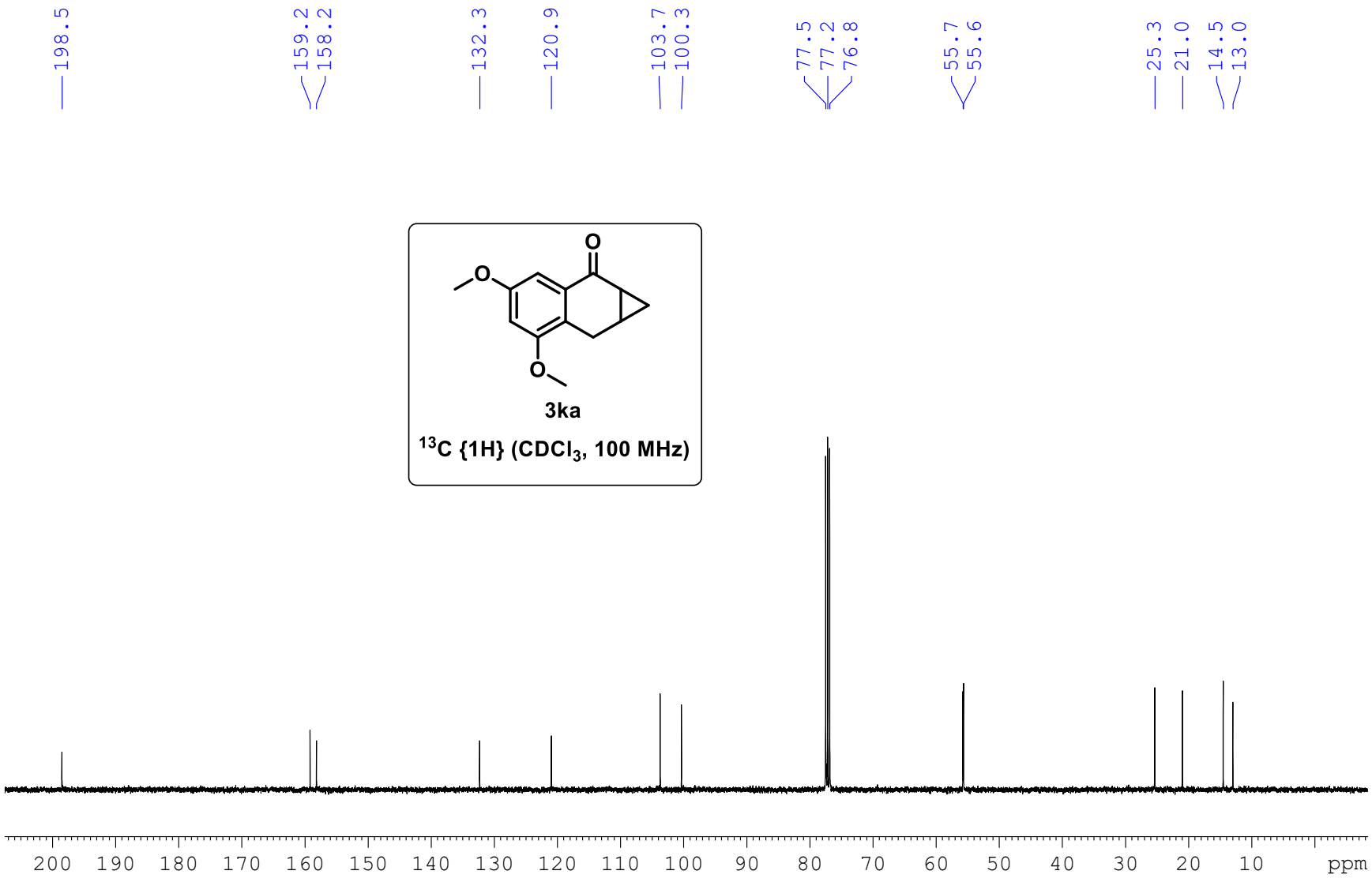


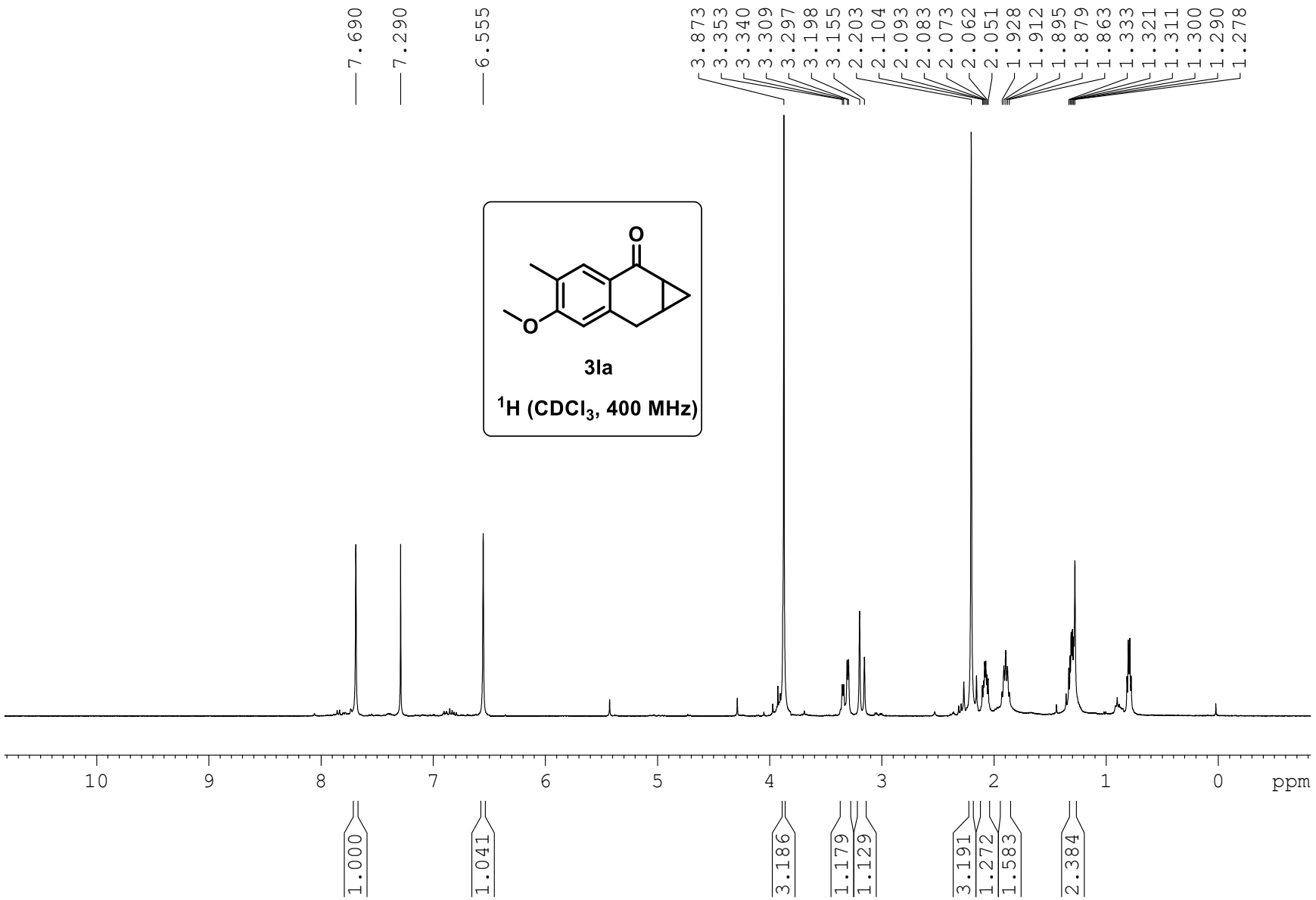
3ja

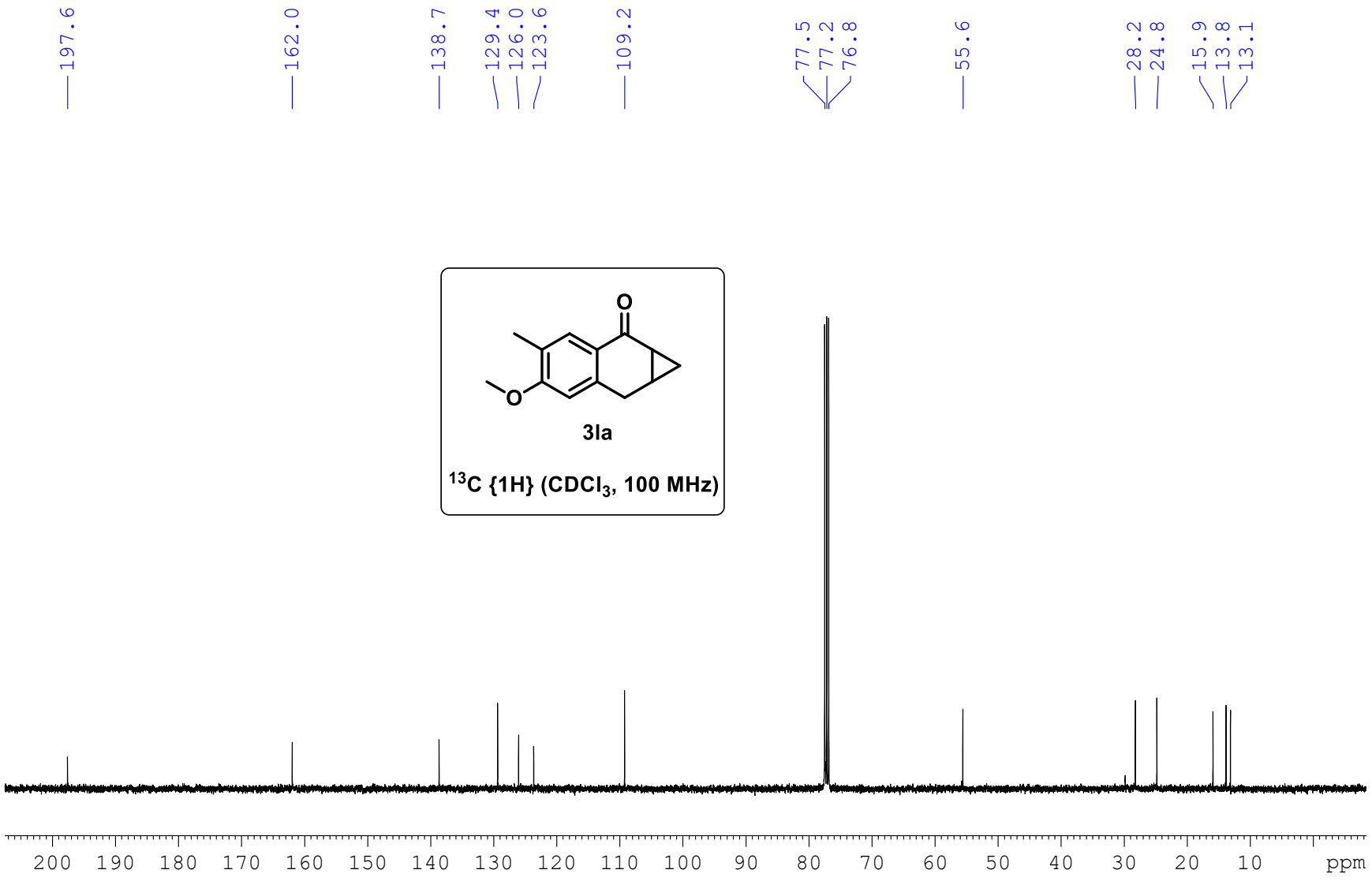
^{13}C {1H} ($CDCl_3$, 100 MHz)

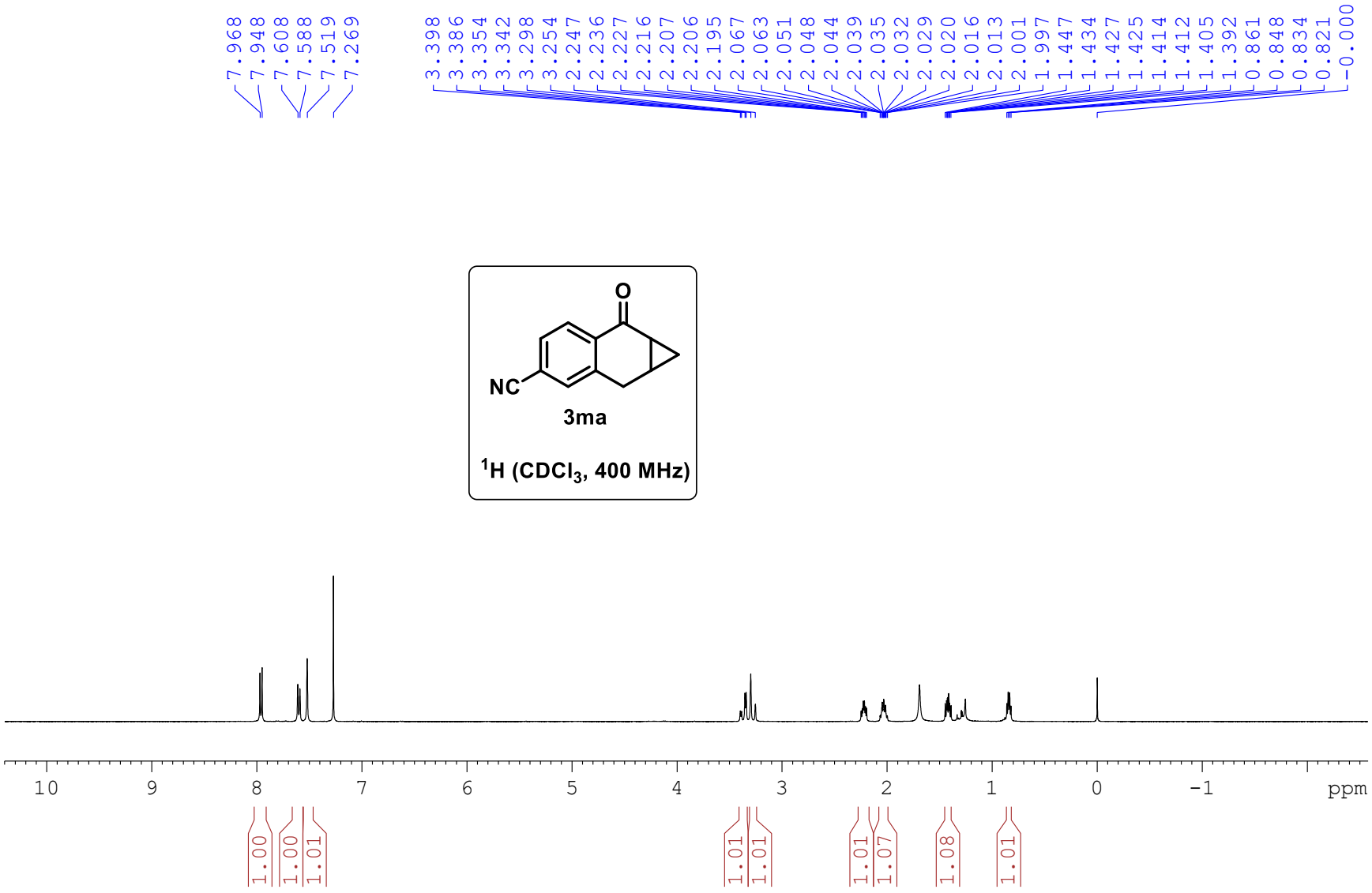


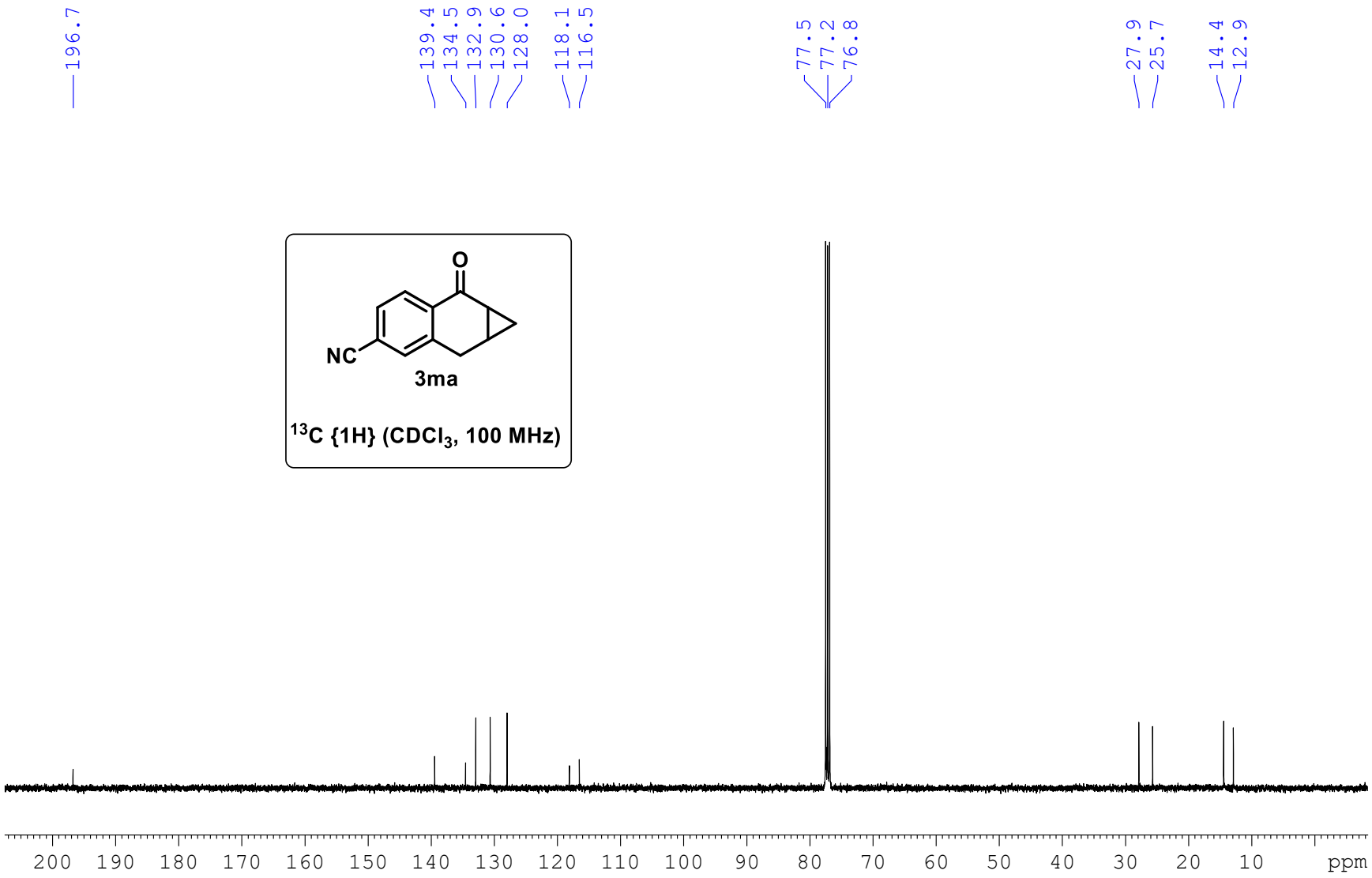

7.272
6.983
6.977
6.601
6.595
3.823
3.807
3.412
3.367
2.864
2.850
2.818
2.805
2.138
2.137
2.126
2.117
2.109
2.107
2.097
2.095
2.087
2.085
1.973
1.956
1.939
1.923
1.907
1.905
1.323
1.311
1.301
1.290
1.280
1.269
0.813
0.802
0.787
0.776
0.000
O
O
O
3ka
^{1}H (CDCl$_3$, 400 MHz)
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
3.02
3.01
1.10
1.10
1.07
1.08
1.12
1.06

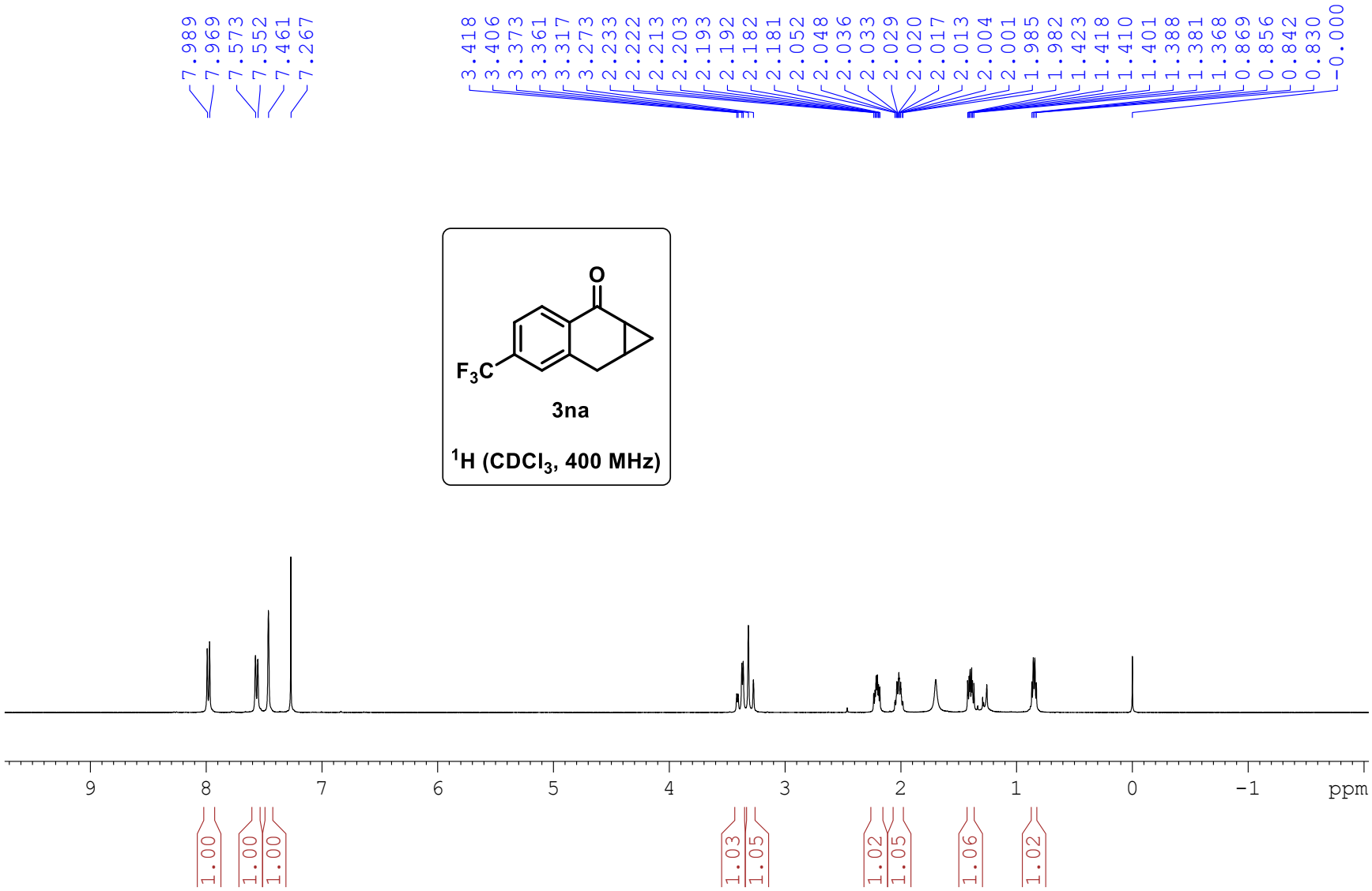

198.5
159.2
158.2
132.3
120.9
103.7
100.3
77.5
77.2
76.8
55.7
55.6
25.3
21.0
14.5
13.0
O
O
O
3ka
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

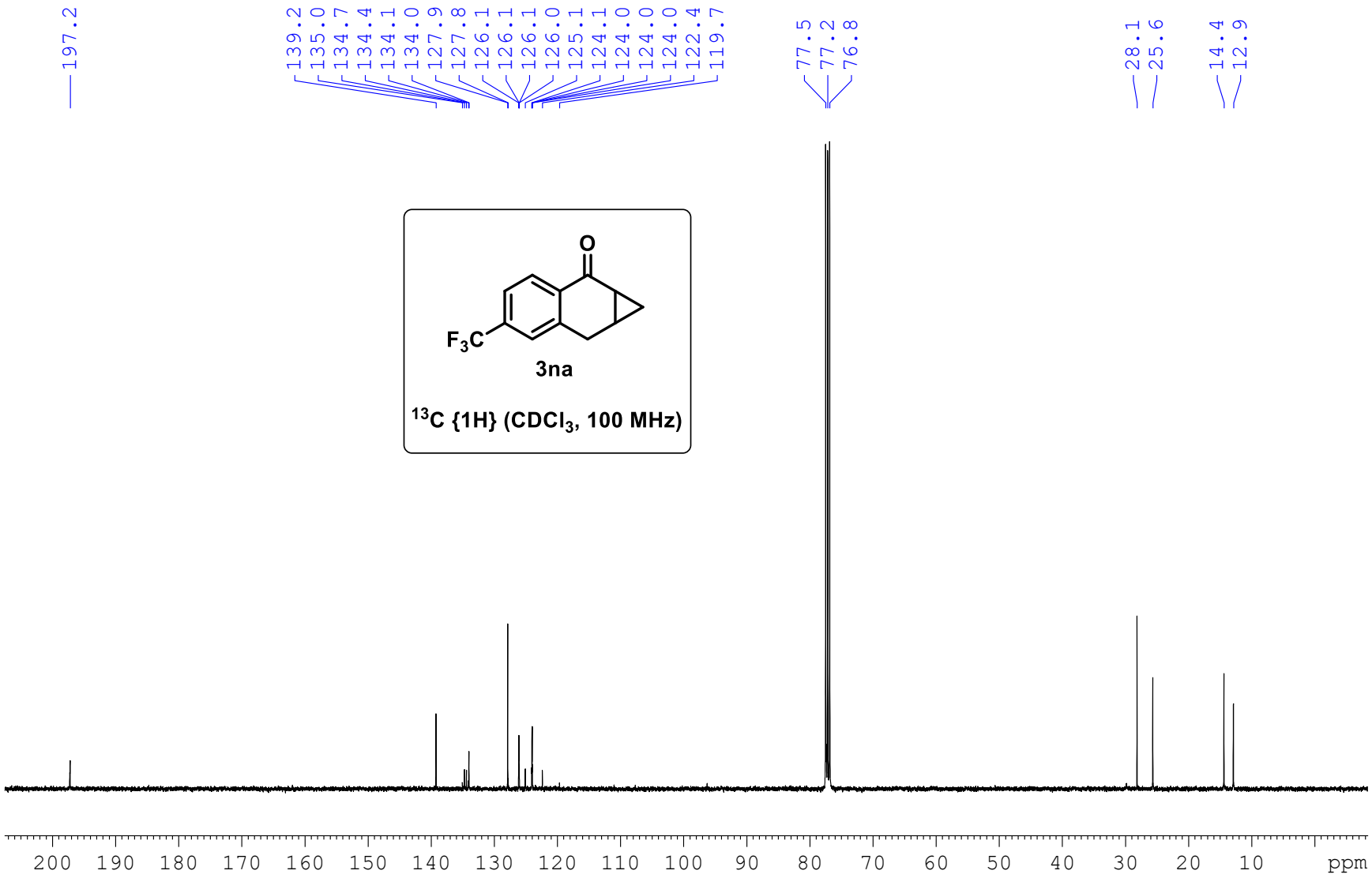

7.690
7.290
6.555
3.873
3.353
3.340
3.309
3.297
3.198
3.155
2.203
2.104
2.093
2.083
2.073
2.062
2.051
1.928
1.912
1.895
1.879
1.863
1.333
1.321
1.311
1.300
1.290
1.278
O
O
3Ia
^{1}H (CDCl$_3$, 400 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.041
3.186
1.179
1.129
3.191
1.272
1.583
2.384

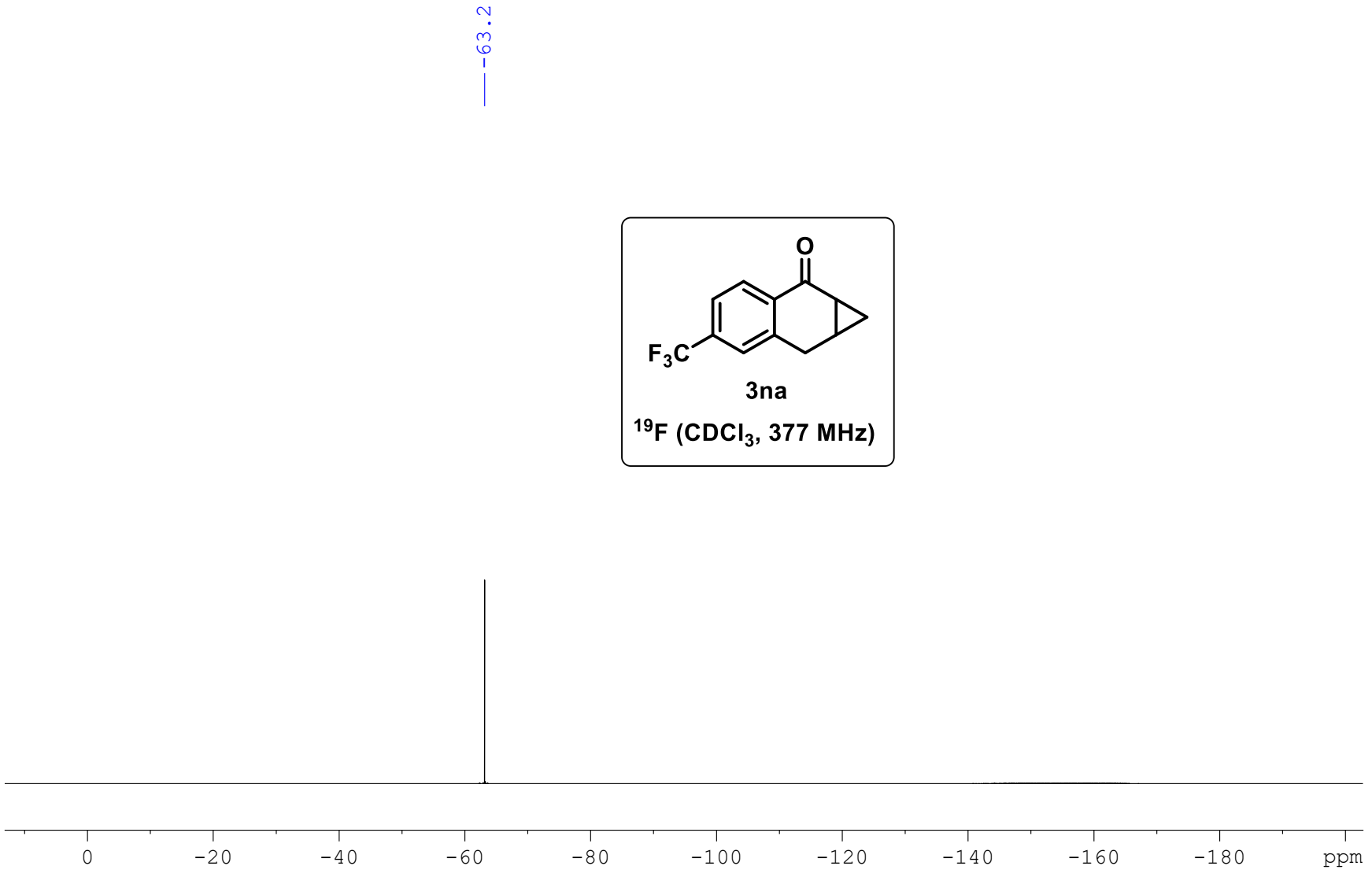

197.6
162.0
138.7
129.4
126.0
123.6
109.2
77.5
77.2
76.8
55.6
28.2
24.8
15.9
13.8
13.1
O
O
3la
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

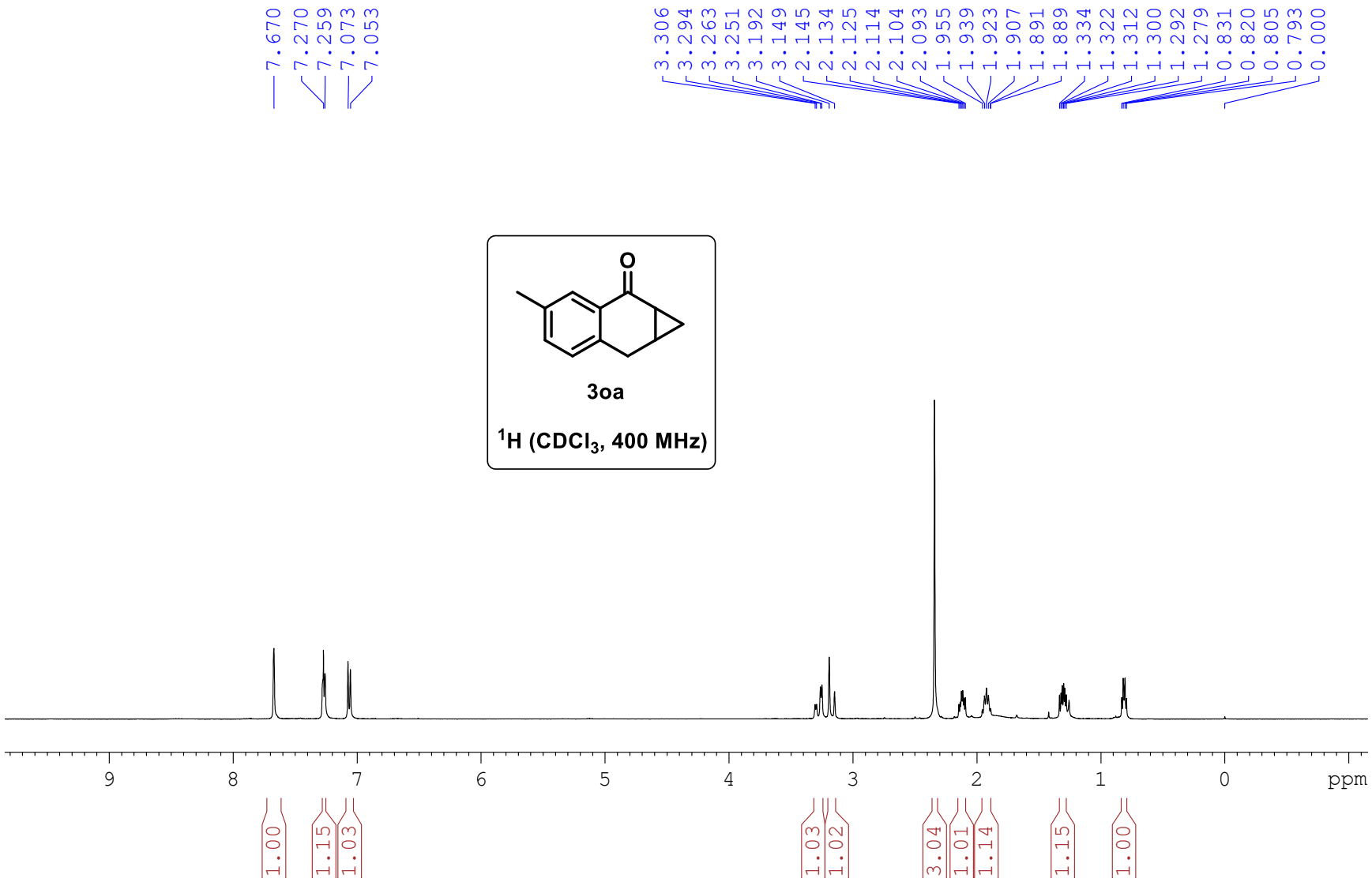

7.968
7.948
7.608
7.588
7.519
7.269
3.398
3.386
3.354
3.342
3.298
3.254
2.247
2.236
2.227
2.216
2.207
2.206
2.195
2.067
2.063
2.051
2.048
2.044
2.039
2.035
2.032
2.029
2.020
2.016
2.013
2.001
1.997
1.447
1.434
1.427
1.425
1.414
1.412
1.405
1.392
0.861
0.848
0.834
0.821
-0.000
O
NC
3ma
1H (CDCl3, 400 MHz)
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.00
1.01
1.01
1.01
1.01
1.07
1.08
1.01

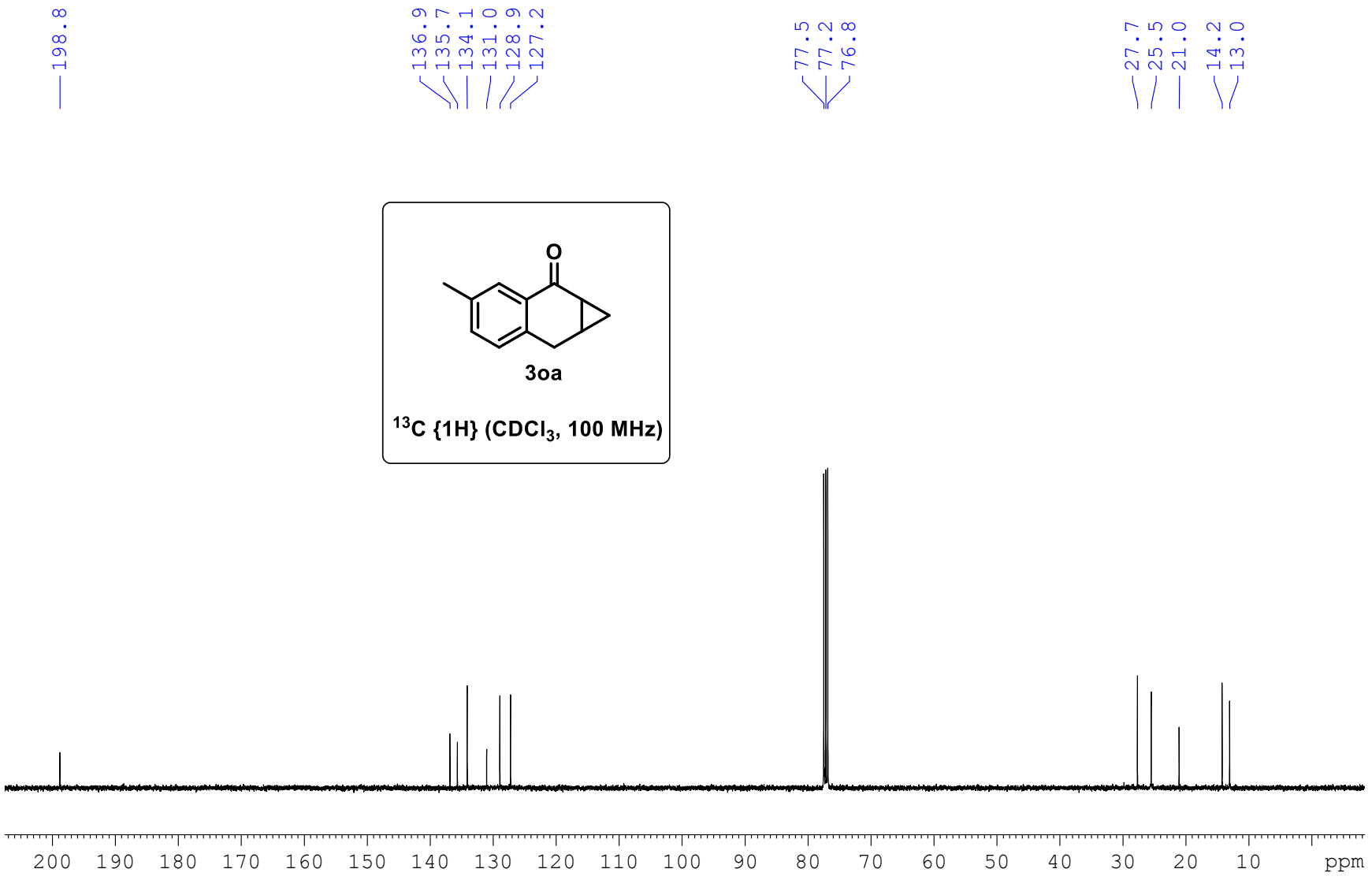

196.7
139.4
134.5
132.9
130.6
128.0
118.1
116.5
77.5
77.2
76.8
27.9
25.7
14.4
12.9
O
NC
3ma
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

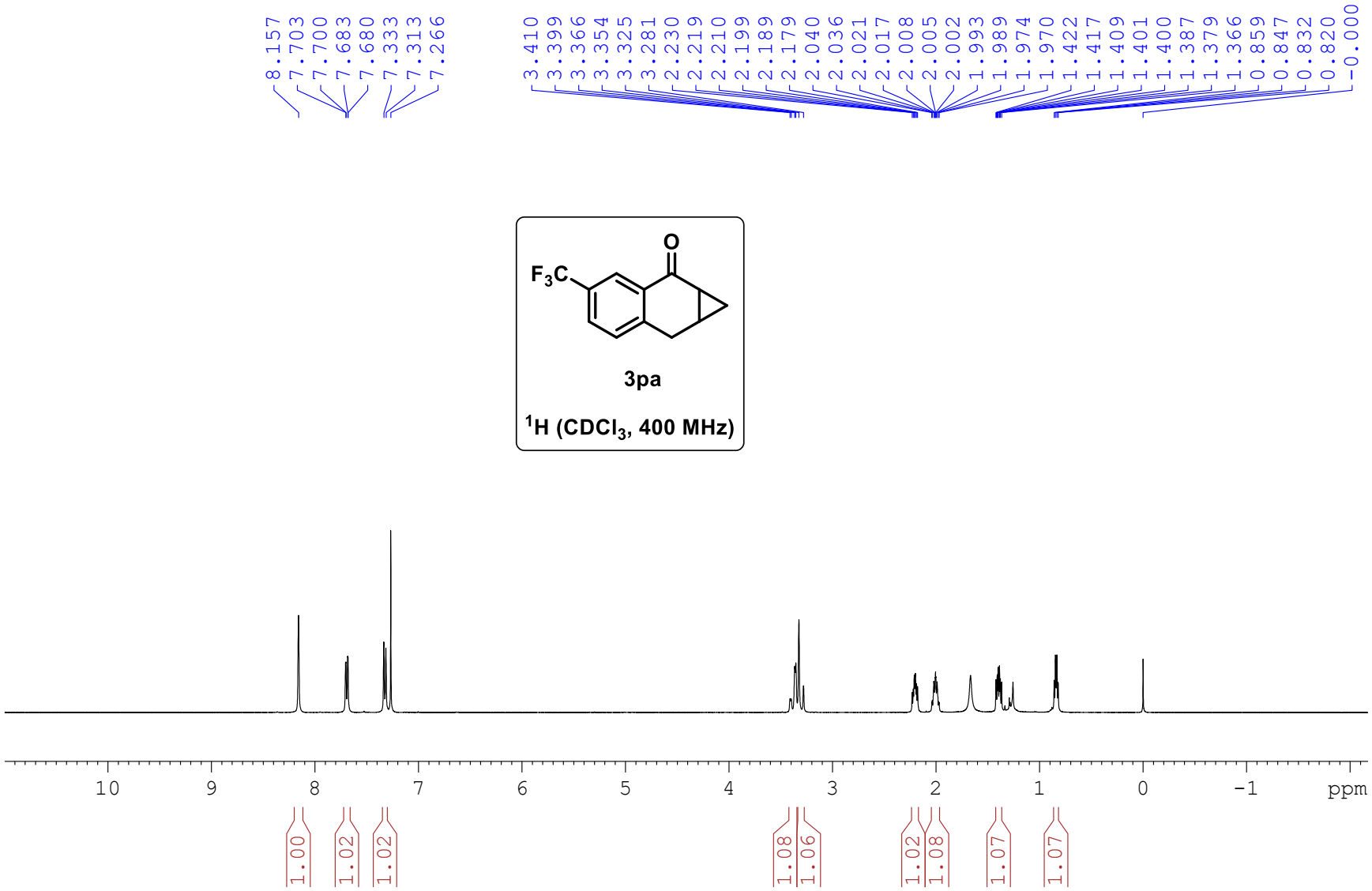

7.989
7.969
7.573
7.552
7.461
7.267
3.418
3.406
3.373
3.361
3.317
3.273
3.233
2.222
2.213
2.203
2.193
2.192
2.182
2.181
2.052
2.048
2.036
2.033
2.029
2.020
2.017
2.013
2.004
2.001
1.985
1.982
1.423
1.418
1.410
1.401
1.388
1.381
1.368
0.869
0.856
0.842
0.830
-0.000
O
F3C
3na
1H (CDCl3, 400 MHz)
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.00
1.00
1.03
1.05
1.02
1.05
1.06
1.02

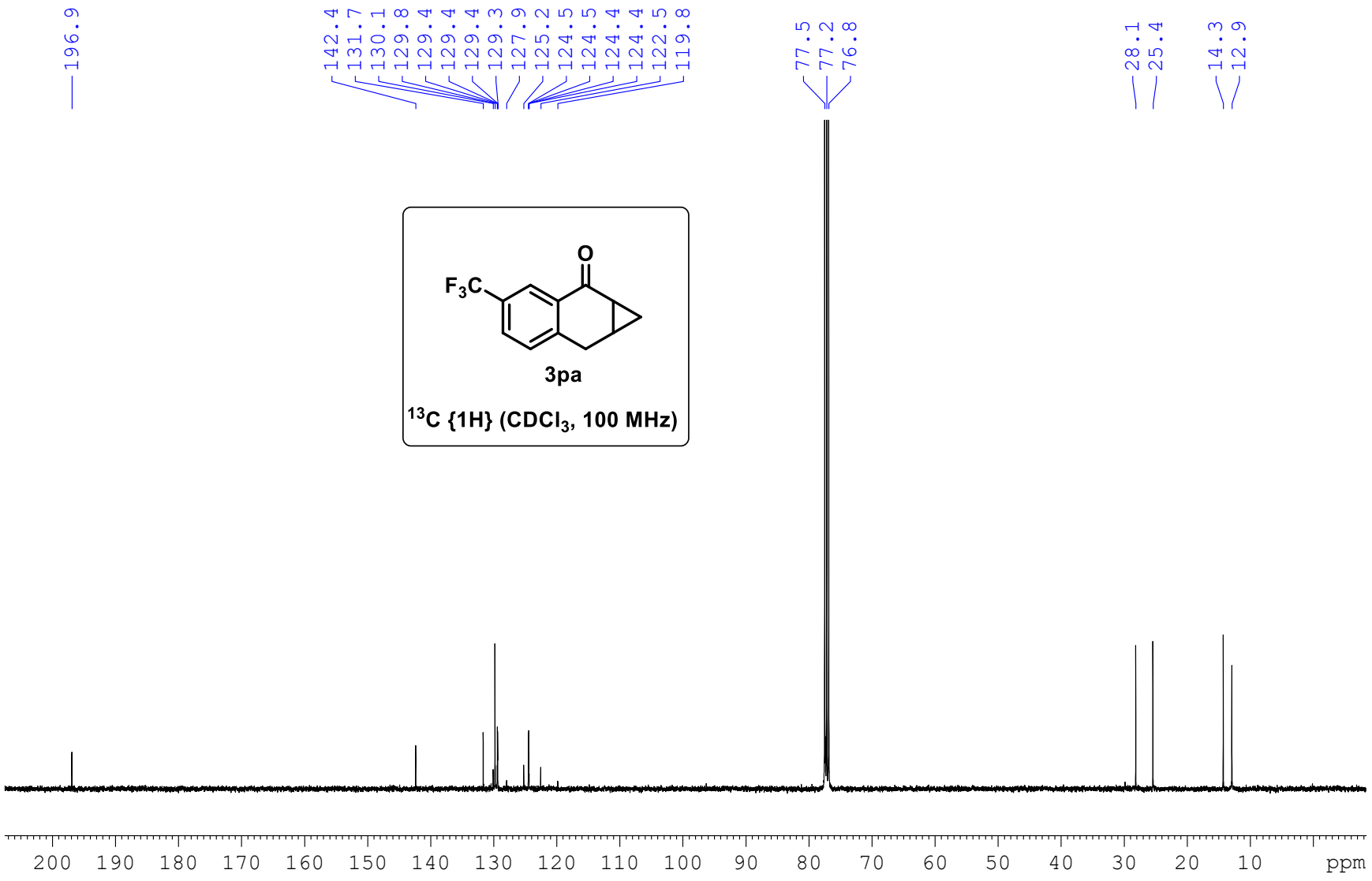

197.2
139.2
135.0
134.7
134.4
134.1
134.0
127.9
127.8
126.1
126.1
126.1
126.0
125.1
124.1
124.0
124.0
124.0
122.4
119.7
77.5
77.2
76.8
28.1
25.6
14.4
12.9
O
F3C
3na
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

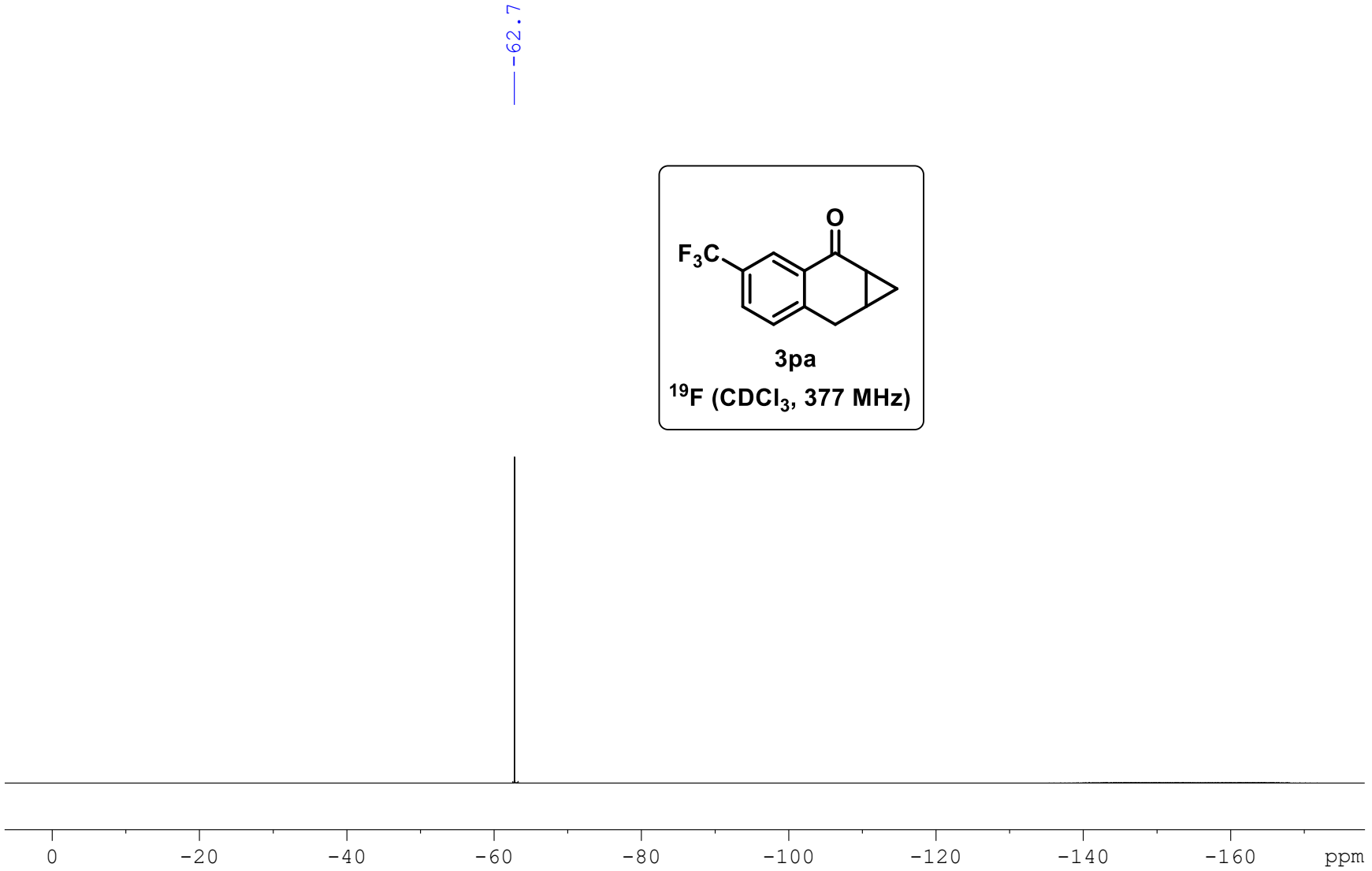

-63.2
O
F3C
3na
19F (CDCl3, 377 MHz)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

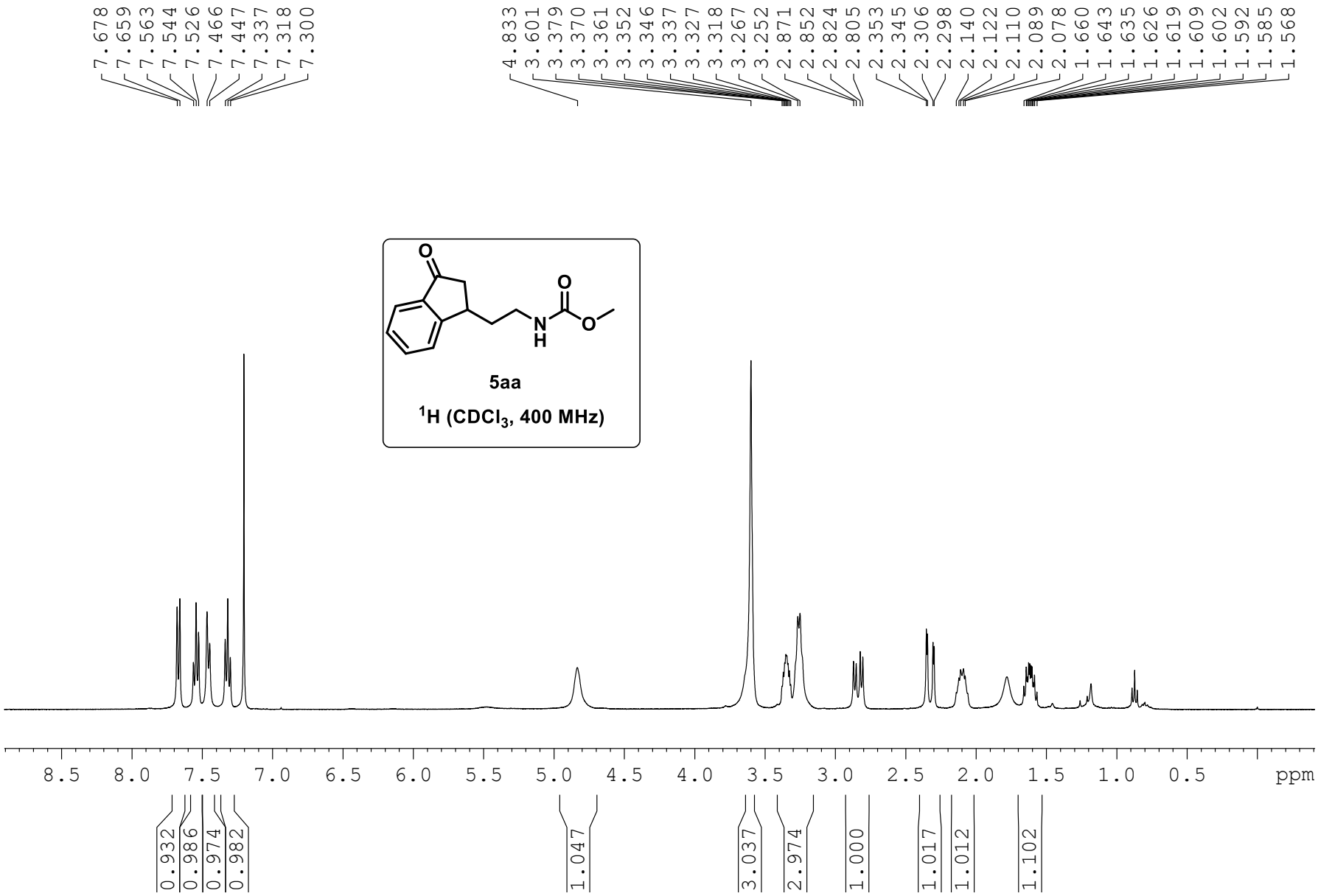

7.670
7.270
7.259
7.073
7.053
3.306
3.294
3.263
3.251
3.192
3.149
2.145
2.134
2.125
2.114
2.104
2.093
1.955
1.939
1.923
1.907
1.891
1.889
1.334
1.322
1.312
1.300
1.292
1.279
0.831
0.820
0.805
0.793
0.000
O
3oa
^{1}H ($CDCl_3$, 400 MHz)
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.15
1.03
1.03
1.02
3.04
1.01
1.14
1.15
1.00

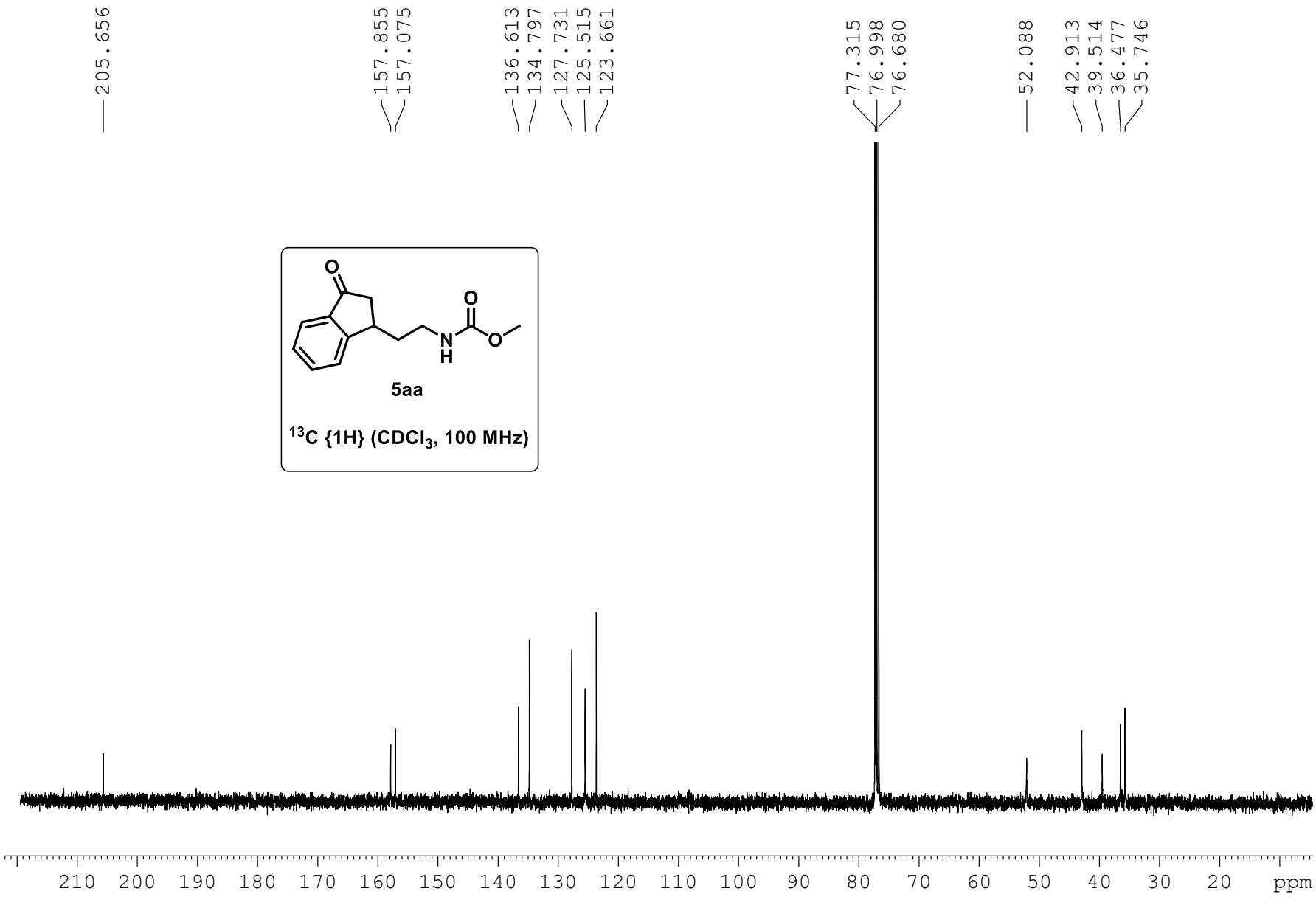

198.8
136.9
135.7
134.1
131.0
128.9
127.2
77.5
77.2
76.8
27.7
25.5
21.0
14.2
13.0
O
3oa
^{13}C {1H} ($CDCl_3$, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

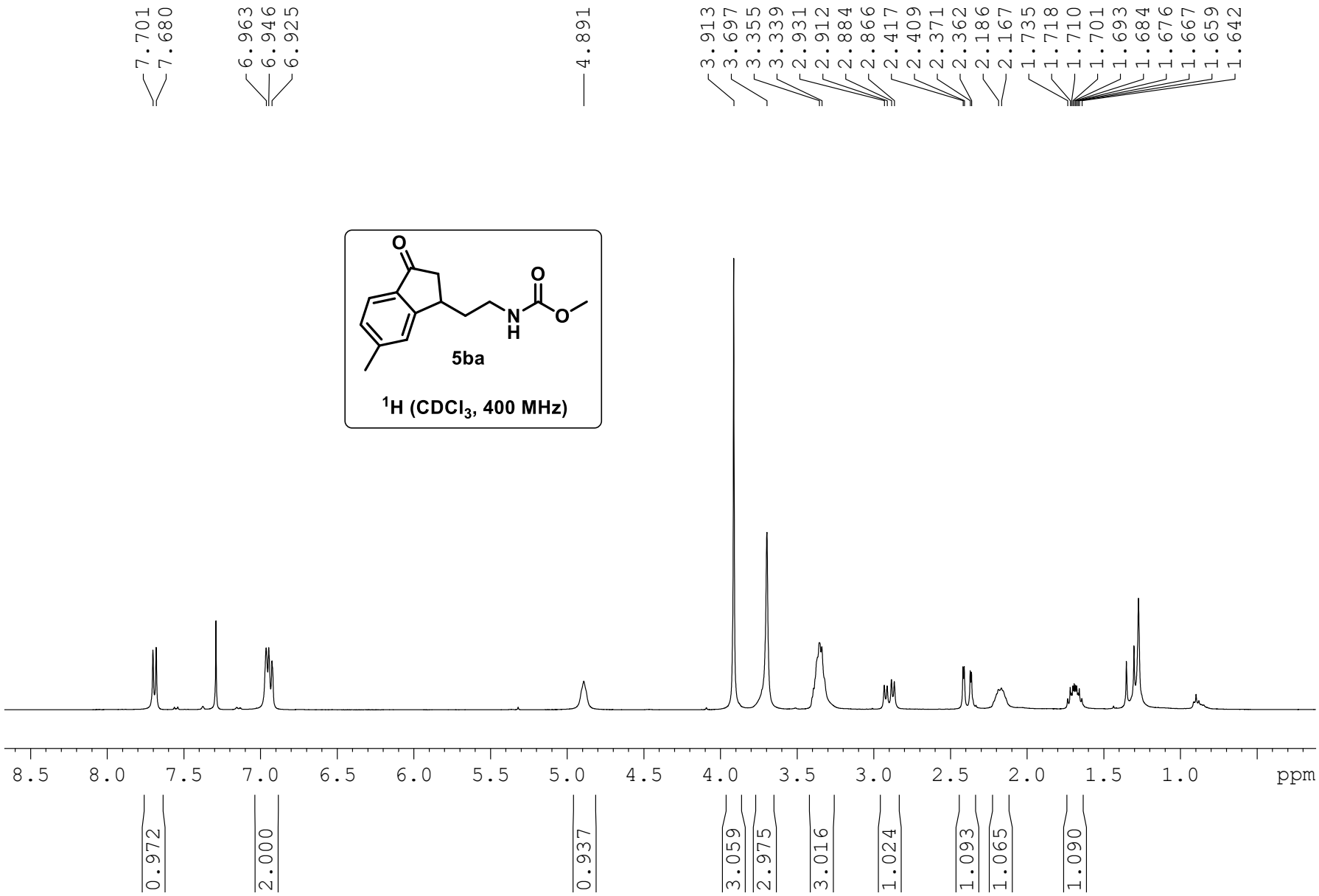

8.157
7.703
7.700
7.683
7.680
7.333
7.313
7.266
3.410
3.399
3.366
3.354
3.325
3.281
2.230
2.219
2.210
2.199
2.189
2.179
2.040
2.036
2.021
2.017
2.008
2.005
2.002
1.993
1.989
1.974
1.970
1.422
1.417
1.409
1.401
1.400
1.387
1.379
1.366
0.859
0.847
0.832
0.820
0.000
O
F3C
3pa
1H (CDCl3, 400 MHz)
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.02
1.02
1.08
1.06
1.02
1.08
1.07
1.07

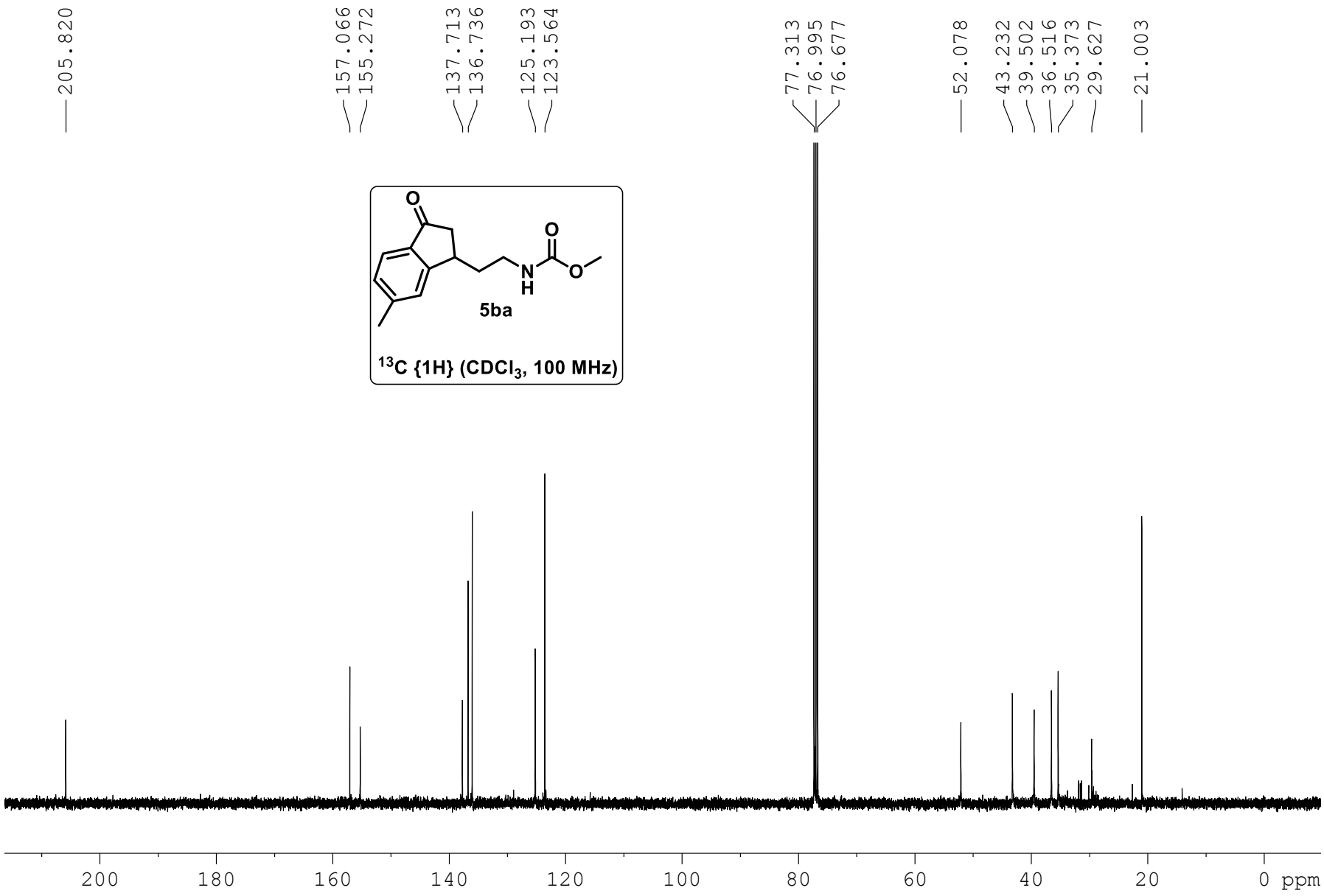

196.9
142.4
131.7
130.1
129.8
129.4
129.4
129.4
129.3
127.9
125.2
124.5
124.5
124.4
124.4
122.5
119.8
77.5
77.2
76.8
28.1
25.4
14.3
12.9
O
F3C
3pa
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

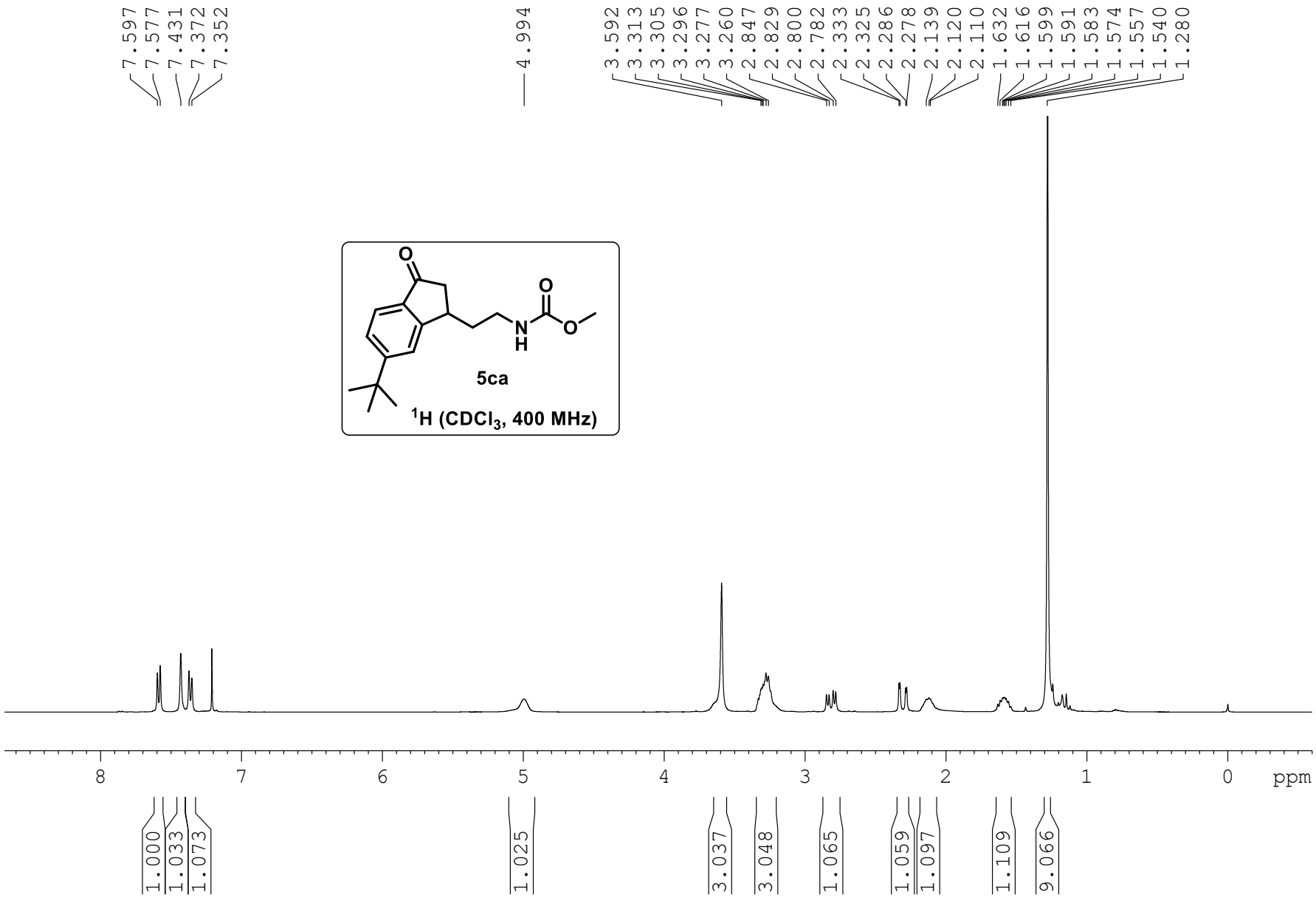

-62.7
O
F3C
3pa
19F (CDCl3, 377 MHz)
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm

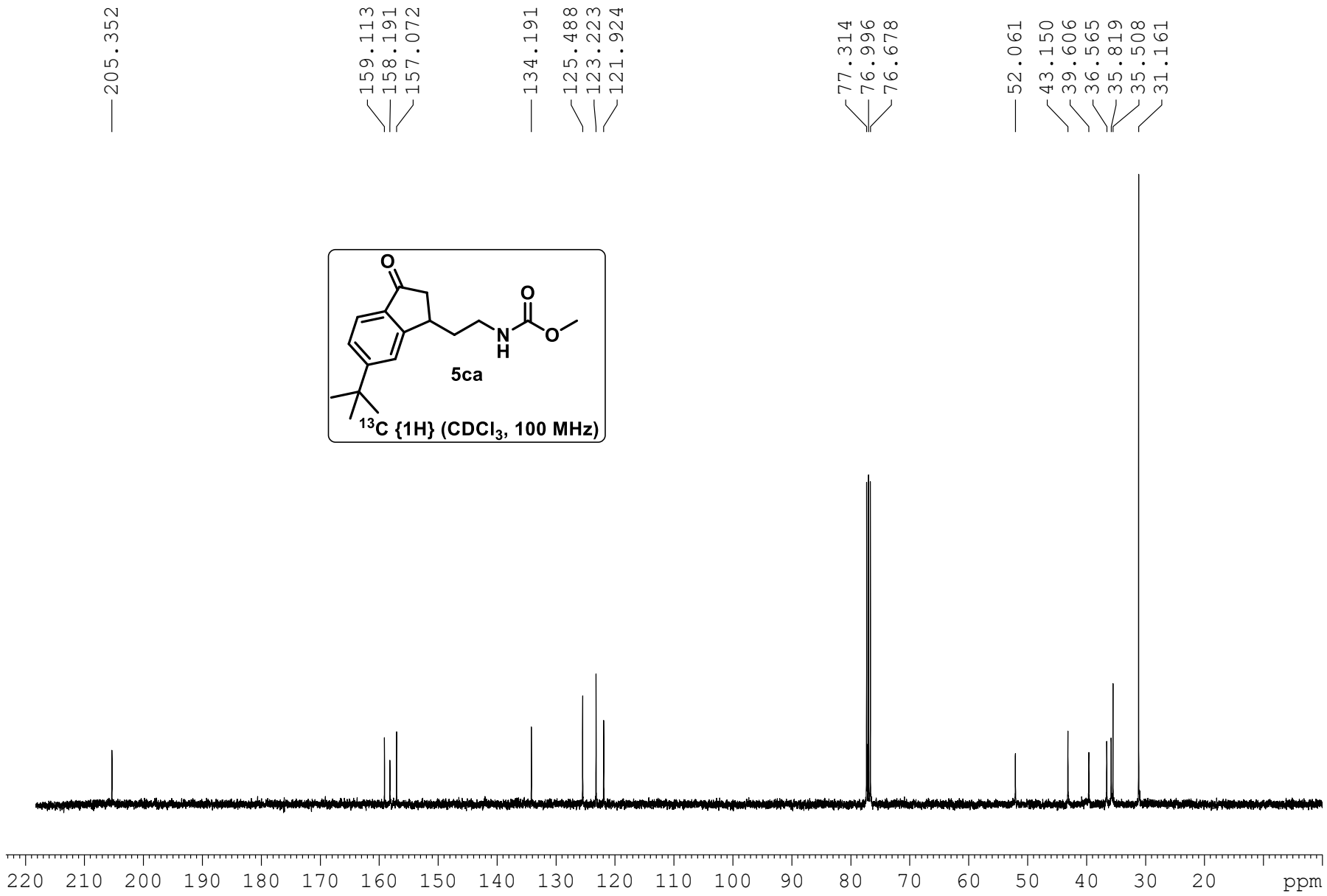

7.678
7.659
7.563
7.544
7.526
7.466
7.447
7.337
7.318
7.300
4.833
3.601
3.379
3.370
3.361
3.352
3.346
3.337
3.327
3.318
3.267
3.252
2.871
2.852
2.824
2.805
2.353
2.345
2.306
2.298
2.140
2.122
2.110
2.089
2.078
1.660
1.643
1.635
1.626
1.619
1.609
1.602
1.592
1.585
1.568
O
O
N
H
O
5aa
1H (CDCl3, 400 MHz)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.932
0.986
0.974
0.982
1.047
3.037
2.974
1.000
1.017
1.012
1.102

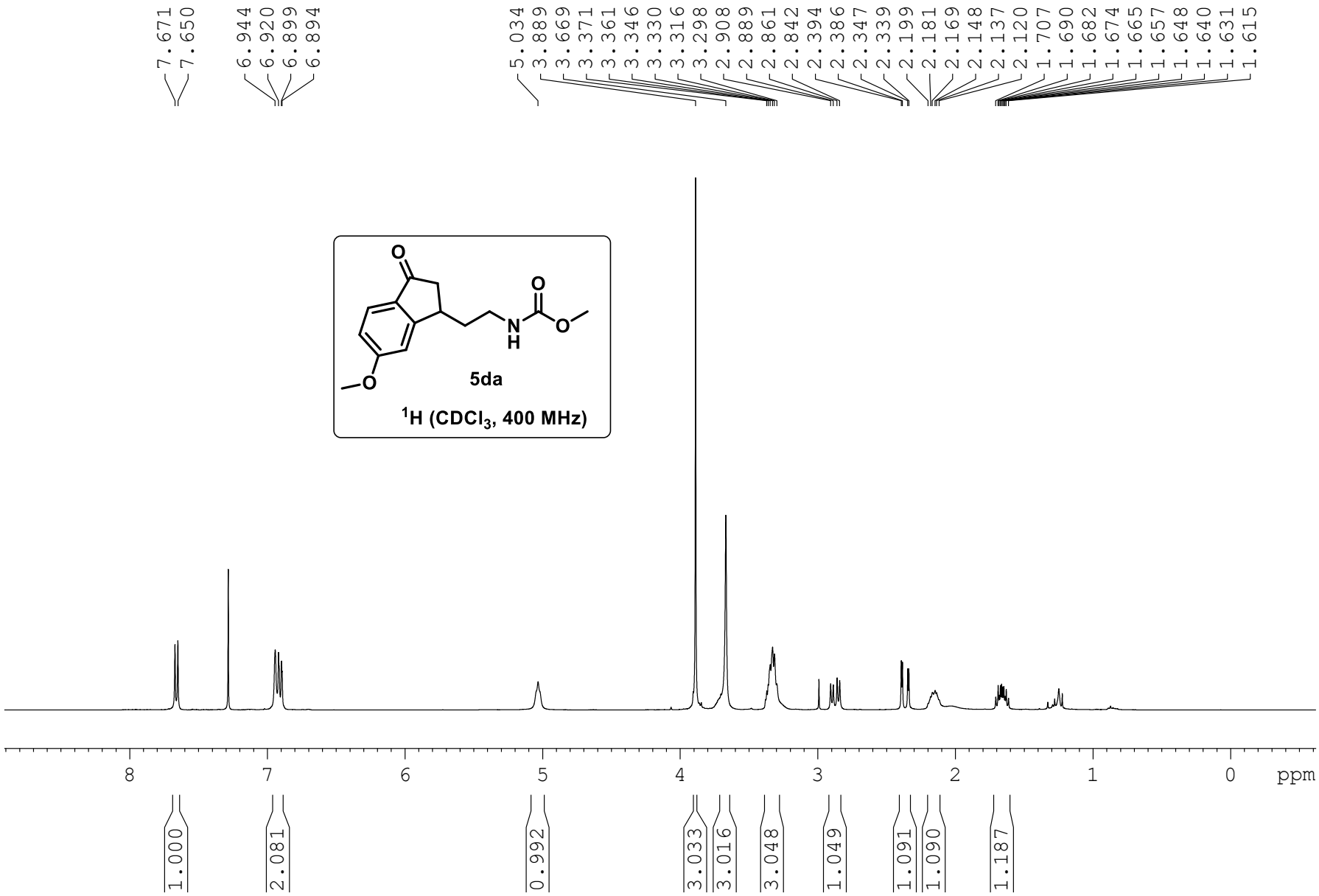

205.656
157.855
157.075
136.613
134.797
127.731
125.515
123.661
77.315
76.998
76.680
52.088
42.913
39.514
36.477
35.746
O
O
N
H
O
5aa
13C {1H} (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

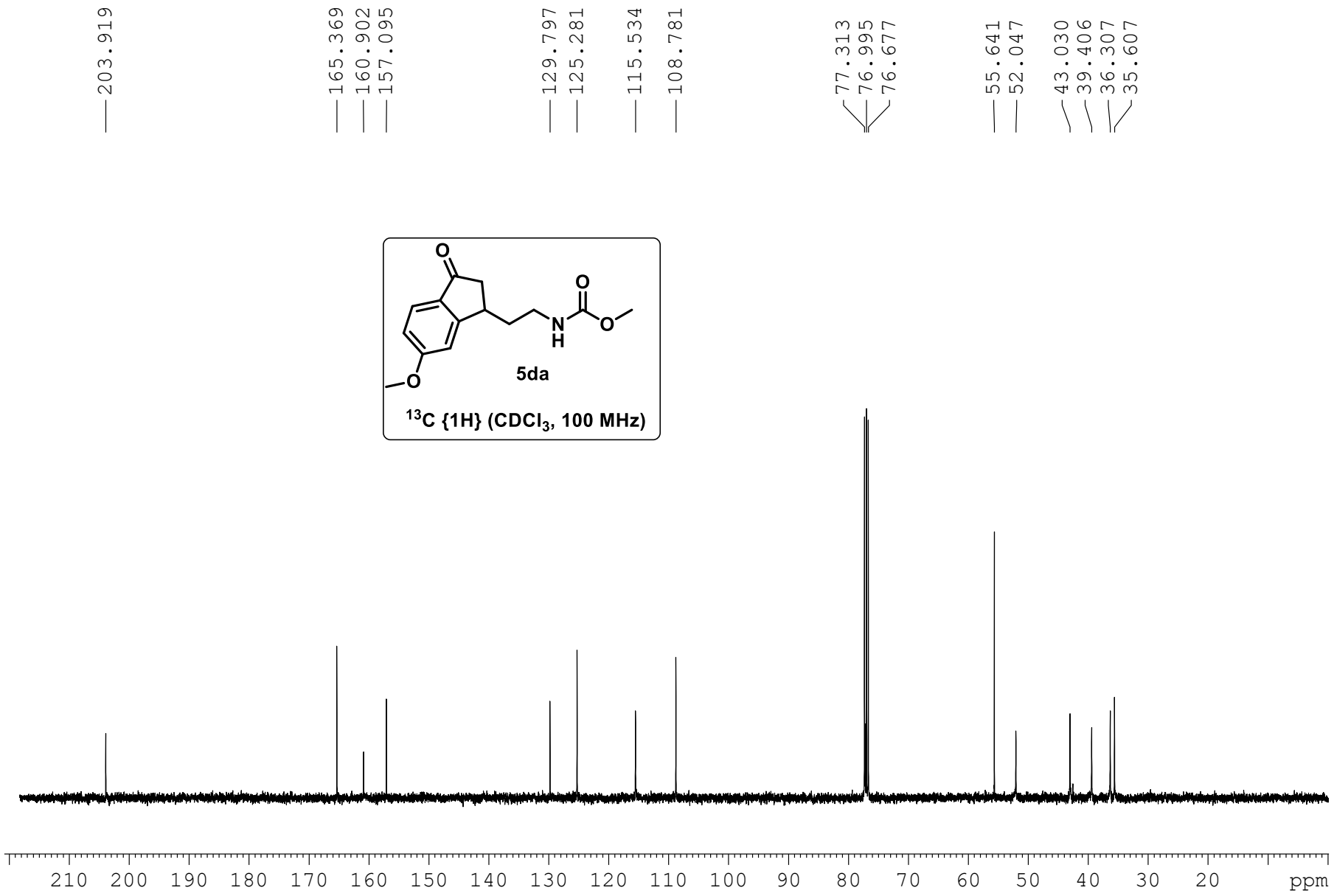

7.701
7.680
6.963
6.946
6.925
4.891
3.913
3.697
3.355
3.339
2.931
2.912
2.884
2.866
2.417
2.409
2.371
2.362
2.186
2.167
1.735
1.718
1.710
1.701
1.693
1.684
1.676
1.667
1.659
1.642
O
O
N
H
O
5ba
1H (CDCl3, 400 MHz)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.972
2.000
0.937
3.059
2.975
3.016
1.024
1.093
1.065
1.090

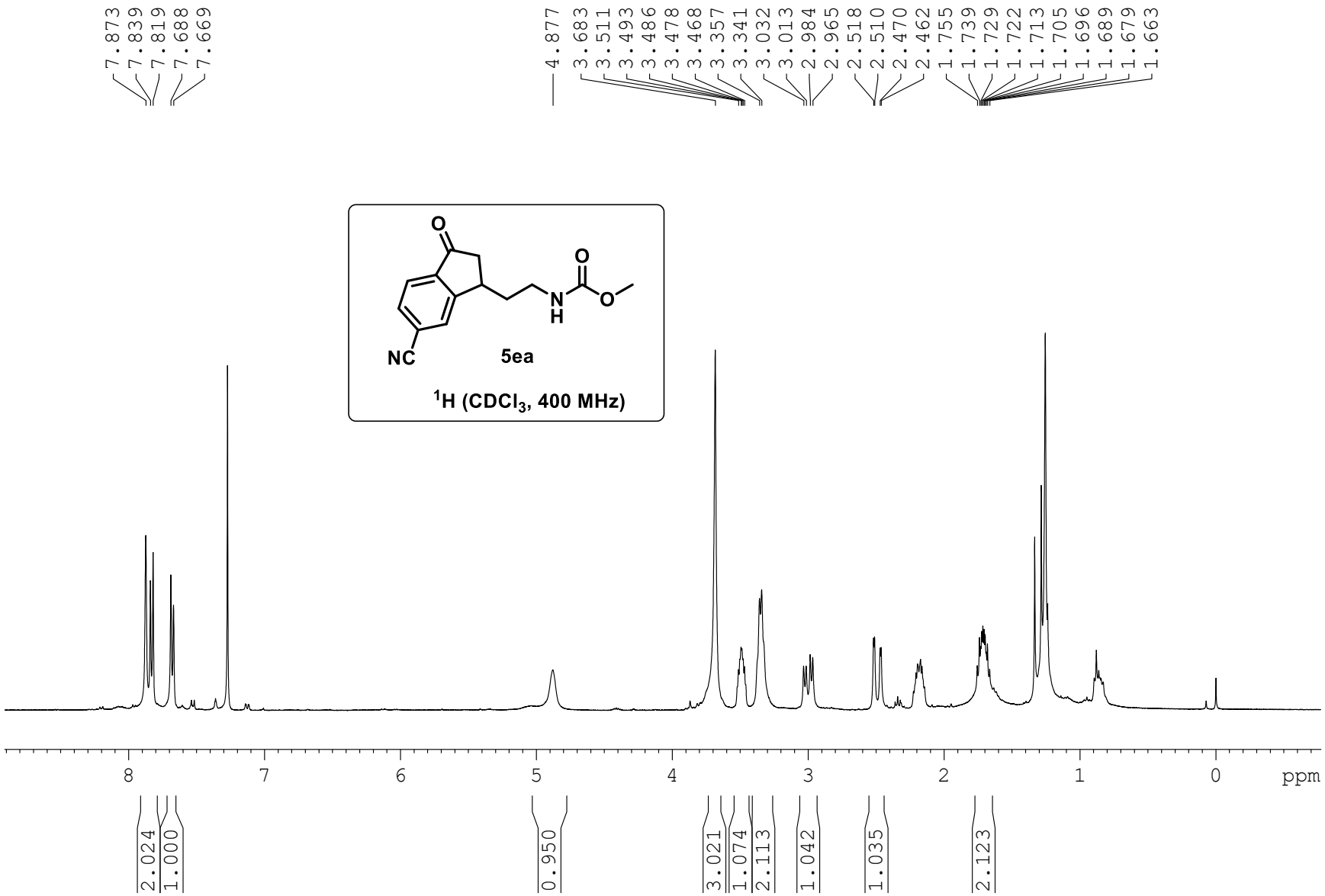

205.820
157.066
155.272
137.713
136.736
125.193
123.564
77.313
76.995
76.677
52.078
43.232
39.502
36.516
35.373
29.627
21.003
O
O
N
H
O
5ba
13C {1H} (CDCl3, 100 MHz)
200
180
160
140
120
100
80
60
40
20
0 ppm

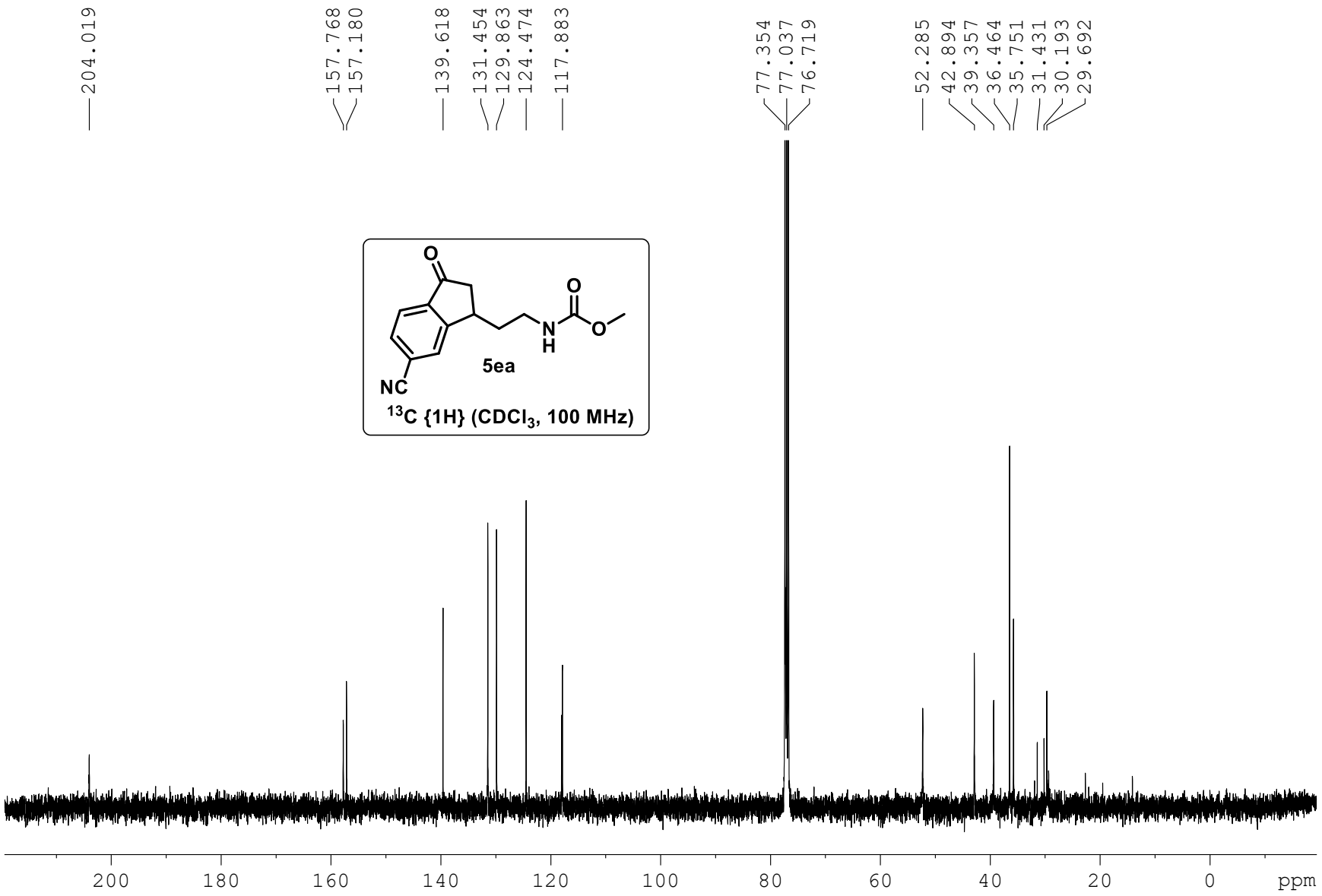

7.597
7.577
7.431
7.372
7.352
4.994
3.592
3.313
3.305
3.296
3.277
3.260
2.847
2.829
2.800
2.782
2.333
2.325
2.286
2.278
2.139
2.120
2.110
1.632
1.616
1.599
1.591
1.583
1.574
1.557
1.540
1.280
5ca
1H (CDCl3, 400 MHz)
8
7
6
5
4
3
2
1
0
ppm
1.000
1.033
1.073
1.025
3.037
3.048
1.065
1.059
1.097
1.109
9.066

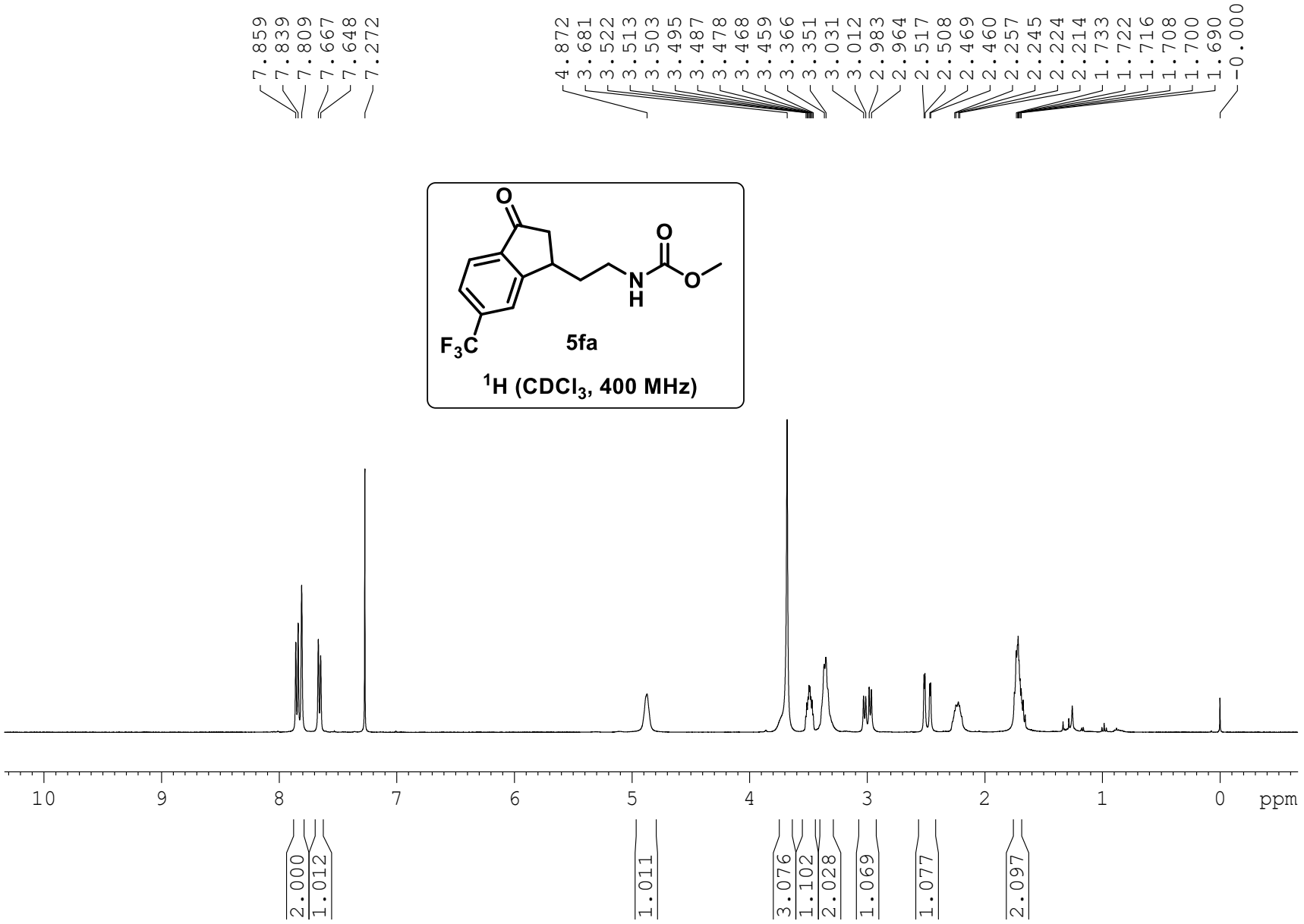

205.352
159.113
158.191
157.072
134.191
125.488
123.223
121.924
77.314
76.996
76.678
52.061
43.150
39.606
36.565
35.819
35.508
31.161
O
O
N
H
O
5ca
13C {1H} (CDCl3, 100 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

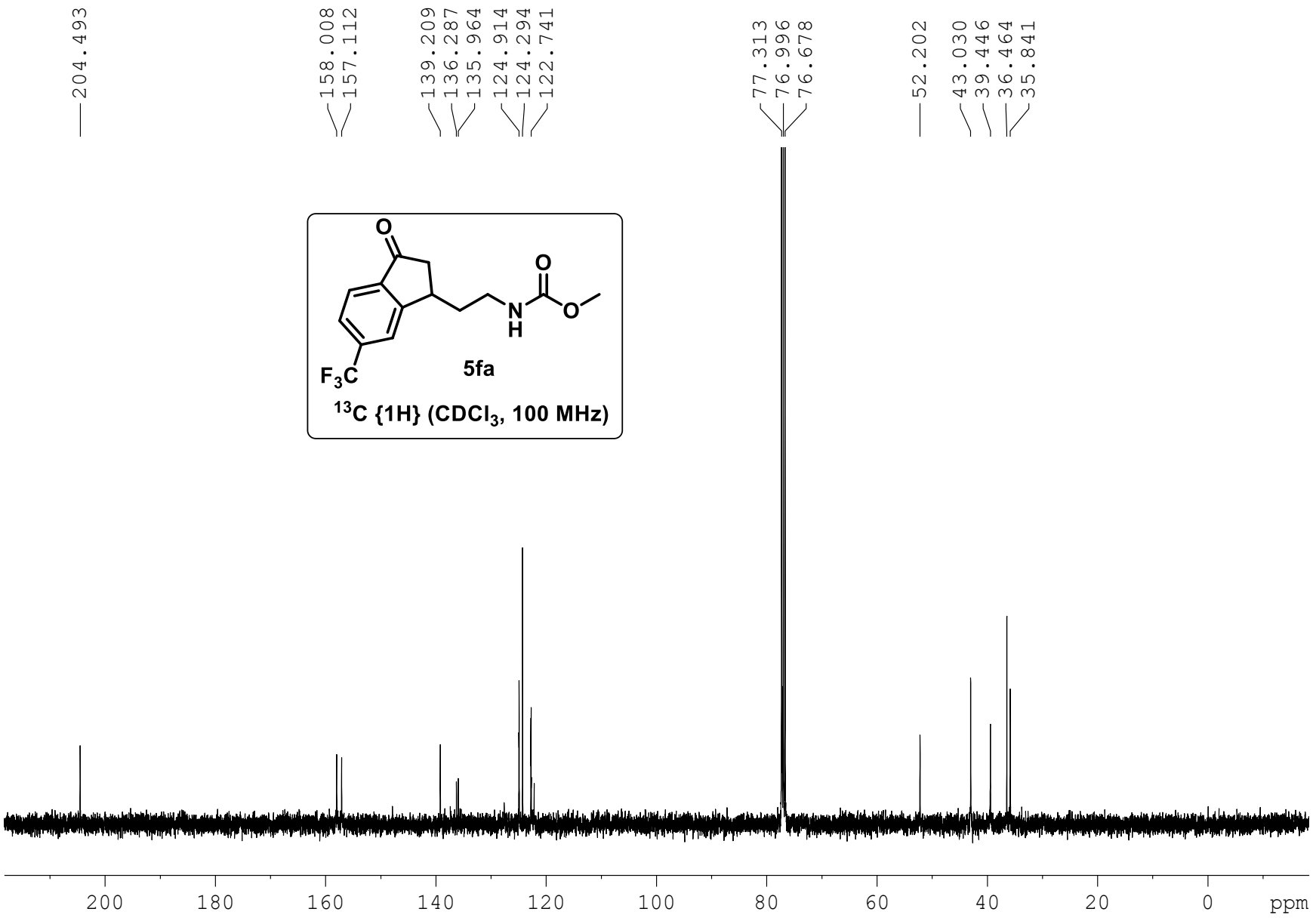

7.671
7.650
6.944
6.920
6.899
6.894
5.034
3.889
3.669
3.371
3.361
3.346
3.330
3.316
3.298
2.908
2.889
2.861
2.842
2.394
2.386
2.347
2.339
2.199
2.181
2.169
2.148
2.137
2.120
1.707
1.690
1.682
1.674
1.665
1.657
1.648
1.640
1.631
1.615
O
O
N
H
O
O
5da
1H (CDCl3, 400 MHz)
8
7
6
5
4
3
2
1
0
ppm
1.000
2.081
0.992
3.033
3.016
3.048
1.049
1.091
1.090
1.187

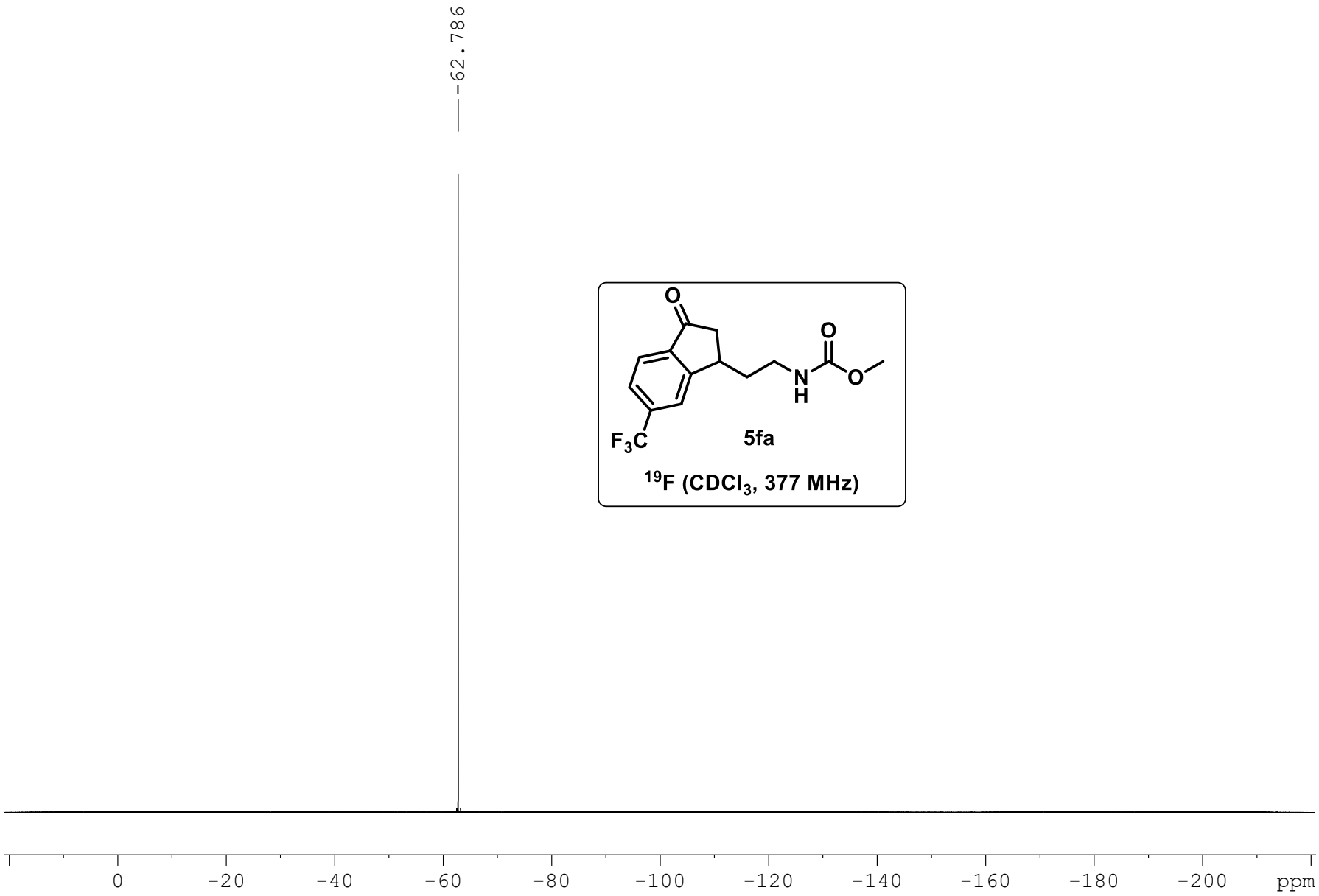

203.919
165.369
160.902
157.095
129.797
125.281
115.534
108.781
77.313
76.995
76.677
55.641
52.047
43.030
39.406
36.307
35.607
O
O
N
H
O
O
5da
13C {1H} (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

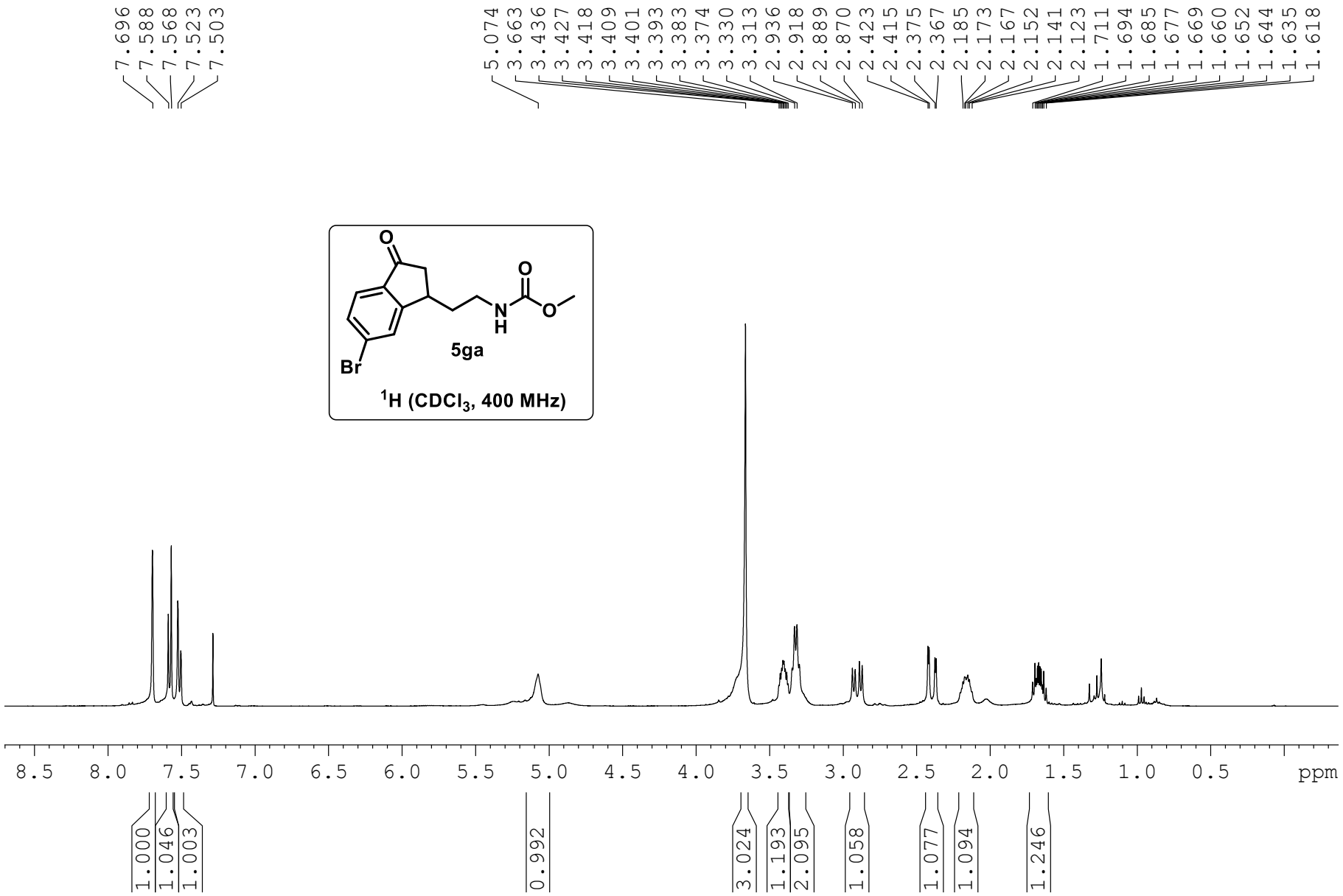

7.873
7.839
7.819
7.688
7.669
4.877
3.683
3.511
3.493
3.486
3.478
3.468
3.357
3.341
3.032
3.013
2.984
2.965
2.518
2.510
2.470
2.462
1.755
1.739
1.729
1.722
1.713
1.705
1.696
1.689
1.679
1.663
O
O
N
H
O
NC
5ea
^{1}H (CDCl$_3$, 400 MHz)
8
7
6
5
4
3
2
1
0
ppm
2.024
1.000
0.950
3.021
1.074
2.113
1.042
1.035
2.123

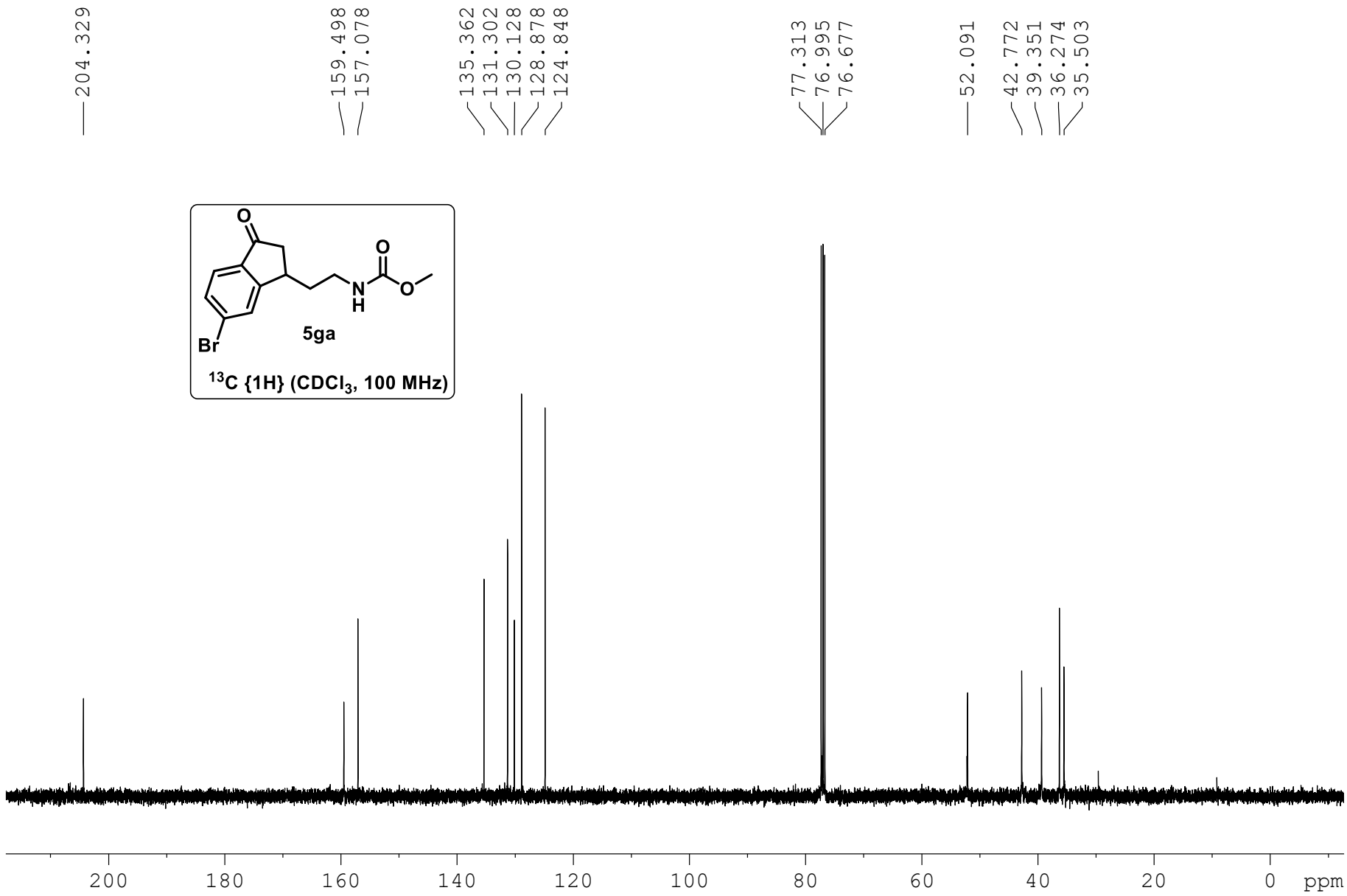

204.019
157.768
157.180
139.618
131.454
129.863
124.474
117.883
77.354
77.037
76.719
52.285
42.894
39.357
36.464
35.751
31.431
30.193
29.692
O
O
N
H
O
NC
5ea
^{13}C {1H} ($CDCl_3$, 100 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

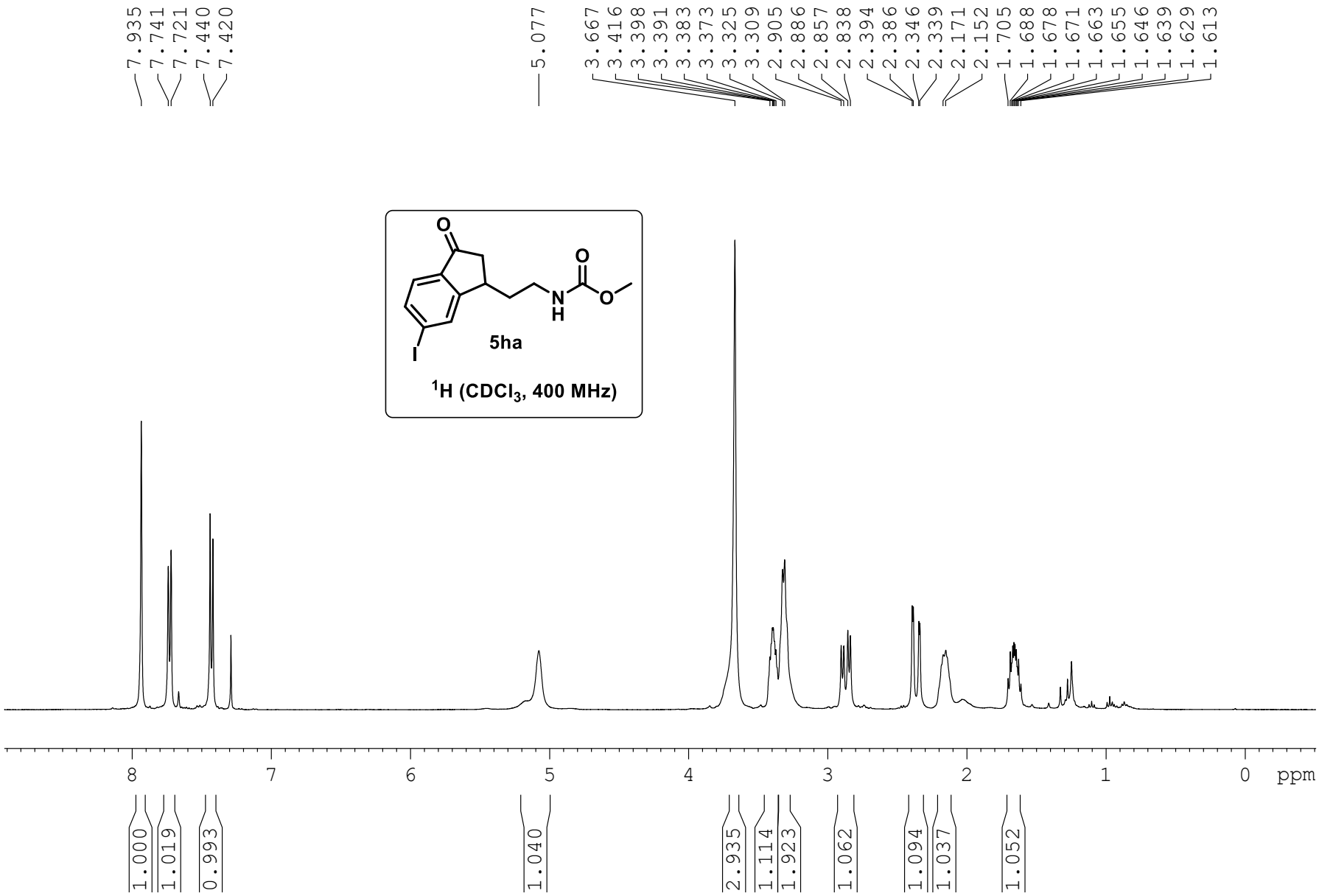

7.859
7.839
7.809
7.667
7.648
7.272
4.872
3.681
3.522
3.513
3.503
3.495
3.487
3.478
3.468
3.459
3.366
3.351
3.031
3.012
2.983
2.964
2.517
2.508
2.469
2.460
2.257
2.245
2.224
2.214
1.733
1.722
1.716
1.708
1.700
1.690
-0.000
O
O
N
H
O
F3C
5fa
1H (CDCl3, 400 MHz)
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
1.012
1.011
3.076
1.102
2.028
1.069
1.077
2.097

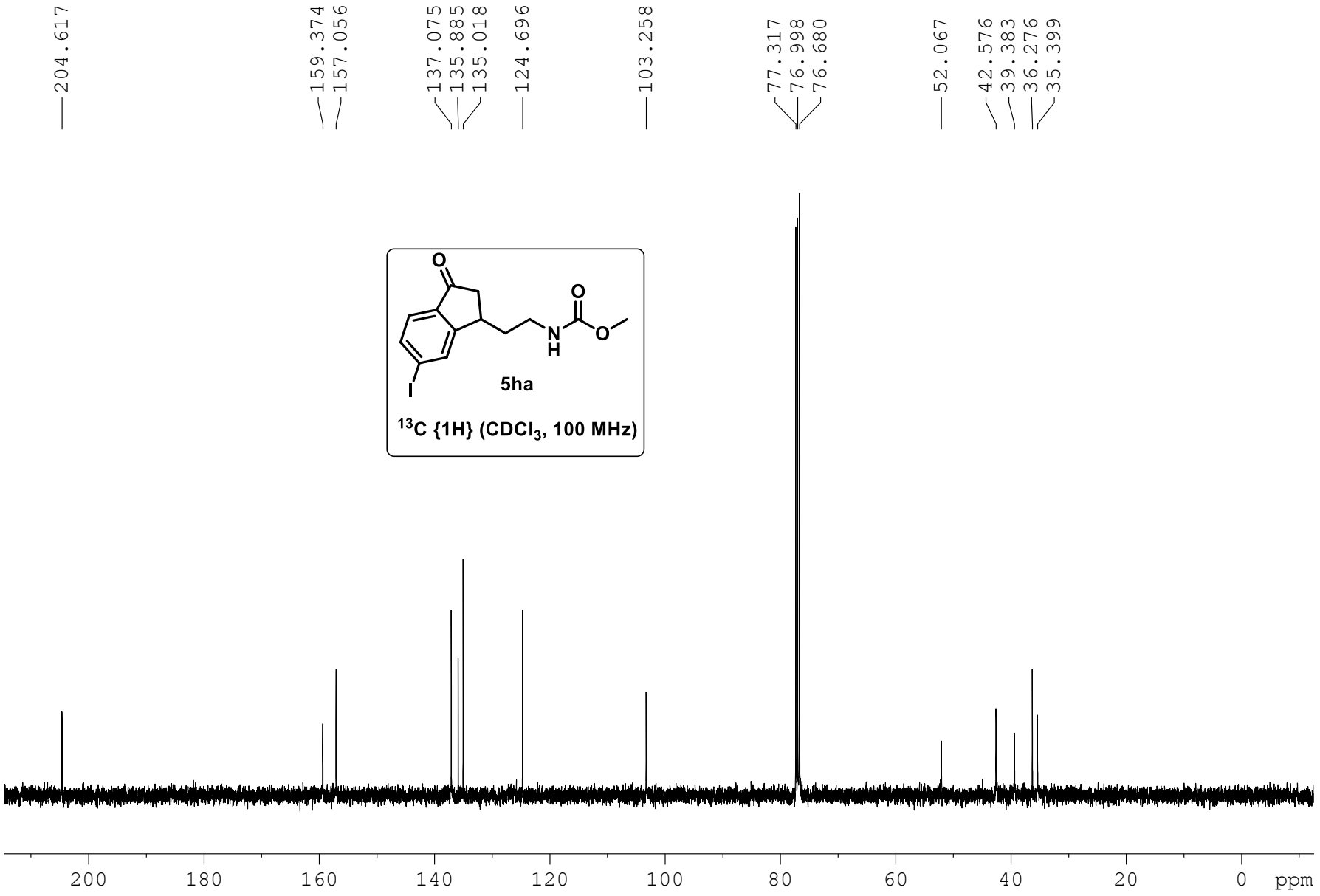

204.493
158.008
157.112
139.209
136.287
135.964
124.914
124.294
122.741
77.313
76.996
76.678
52.202
43.030
39.446
36.464
35.841
O
O
N
H
O
F3C
5fa
13C {1H} (CDCl3, 100 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

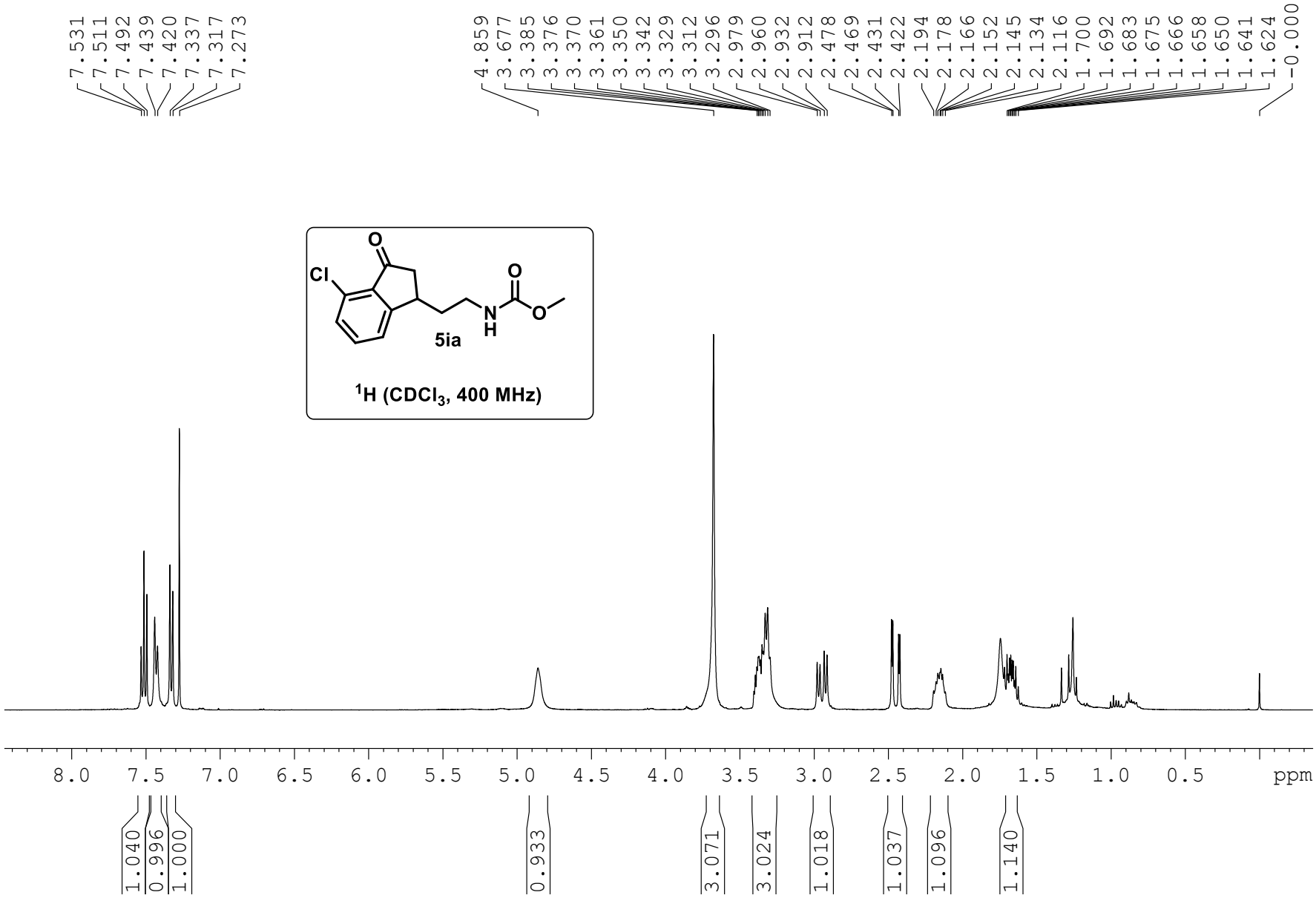

-62.786
O
O
N
H
O
F3C
5fa
19F (CDCl3, 377 MHz)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

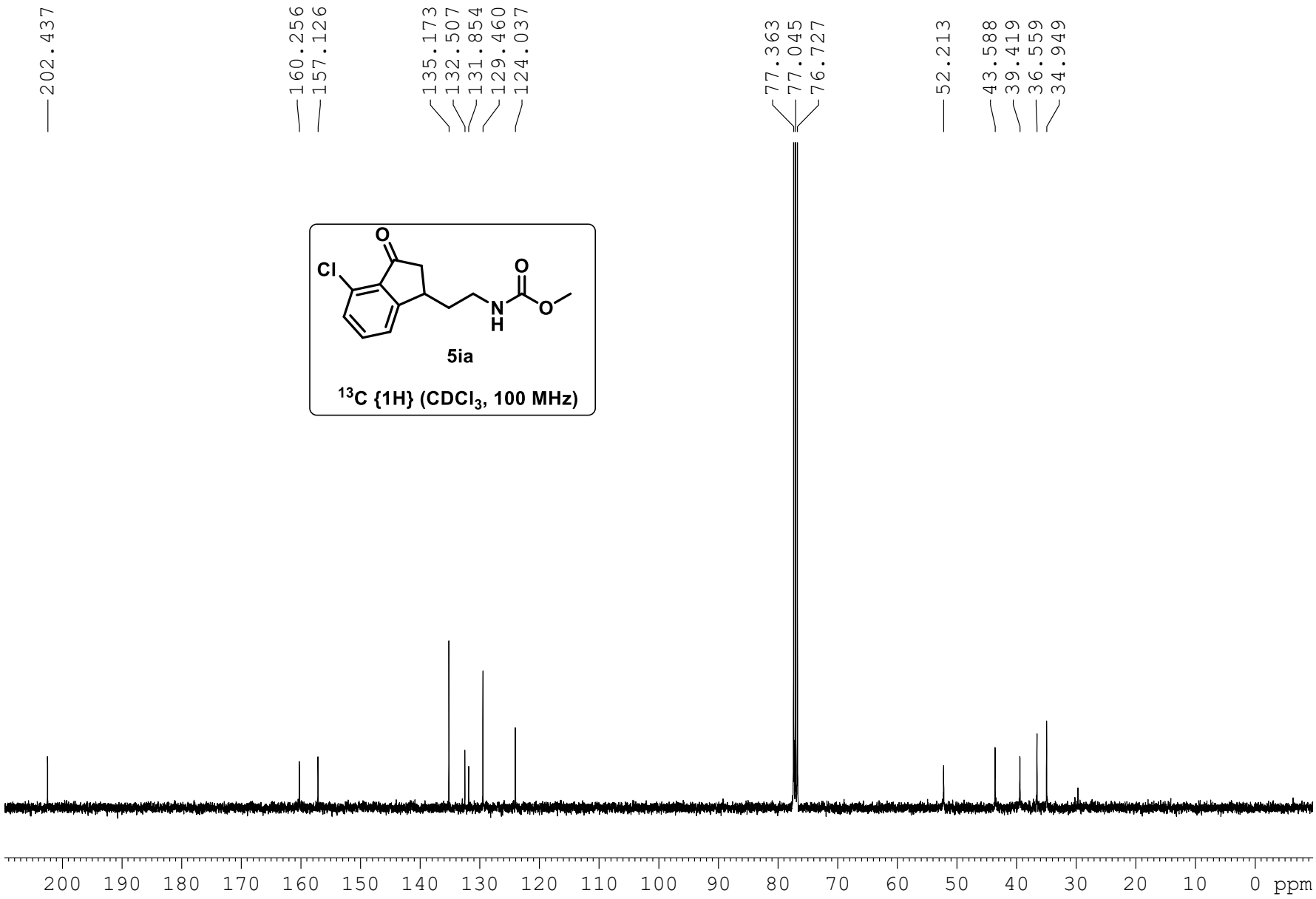

7.696
7.588
7.568
7.523
7.503
5.074
3.663
3.436
3.427
3.418
3.409
3.401
3.393
3.383
3.374
3.330
3.313
2.936
2.918
2.889
2.870
2.423
2.415
2.375
2.367
2.185
2.173
2.167
2.152
2.141
2.123
1.711
1.694
1.685
1.677
1.669
1.660
1.652
1.644
1.635
1.618
O
O
N
H
O
Br
5ga
1H (CDCl3, 400 MHz)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.046
1.003
0.992
3.024
1.193
2.095
1.058
1.077
1.094
1.246

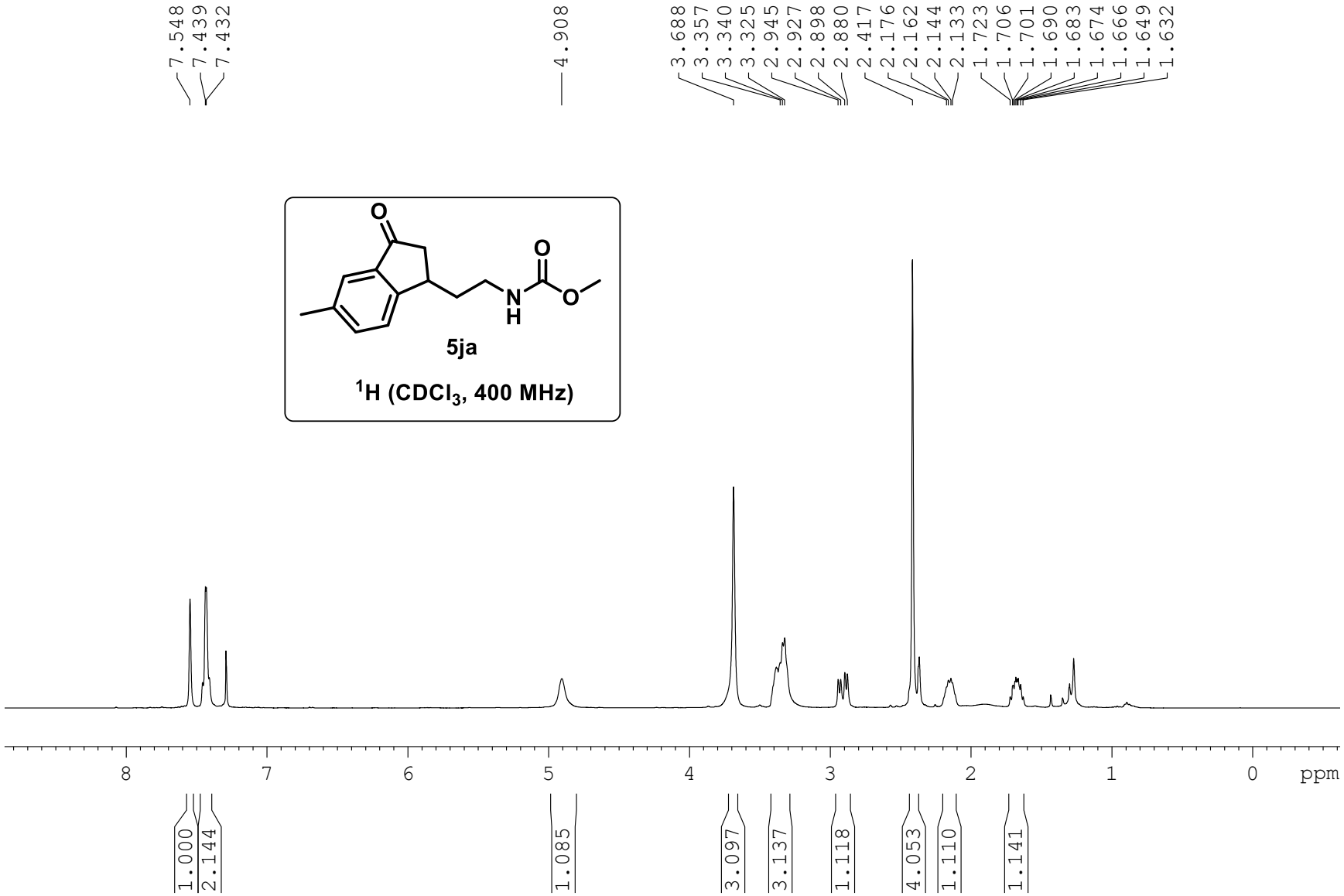

204.329
159.498
157.078
135.362
131.302
130.128
128.878
124.848
77.313
76.995
76.677
52.091
42.772
39.351
36.274
35.503
O
O
N
H
O
Br
5ga
^{13}C {1H} (CDCl$_3$, 100 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

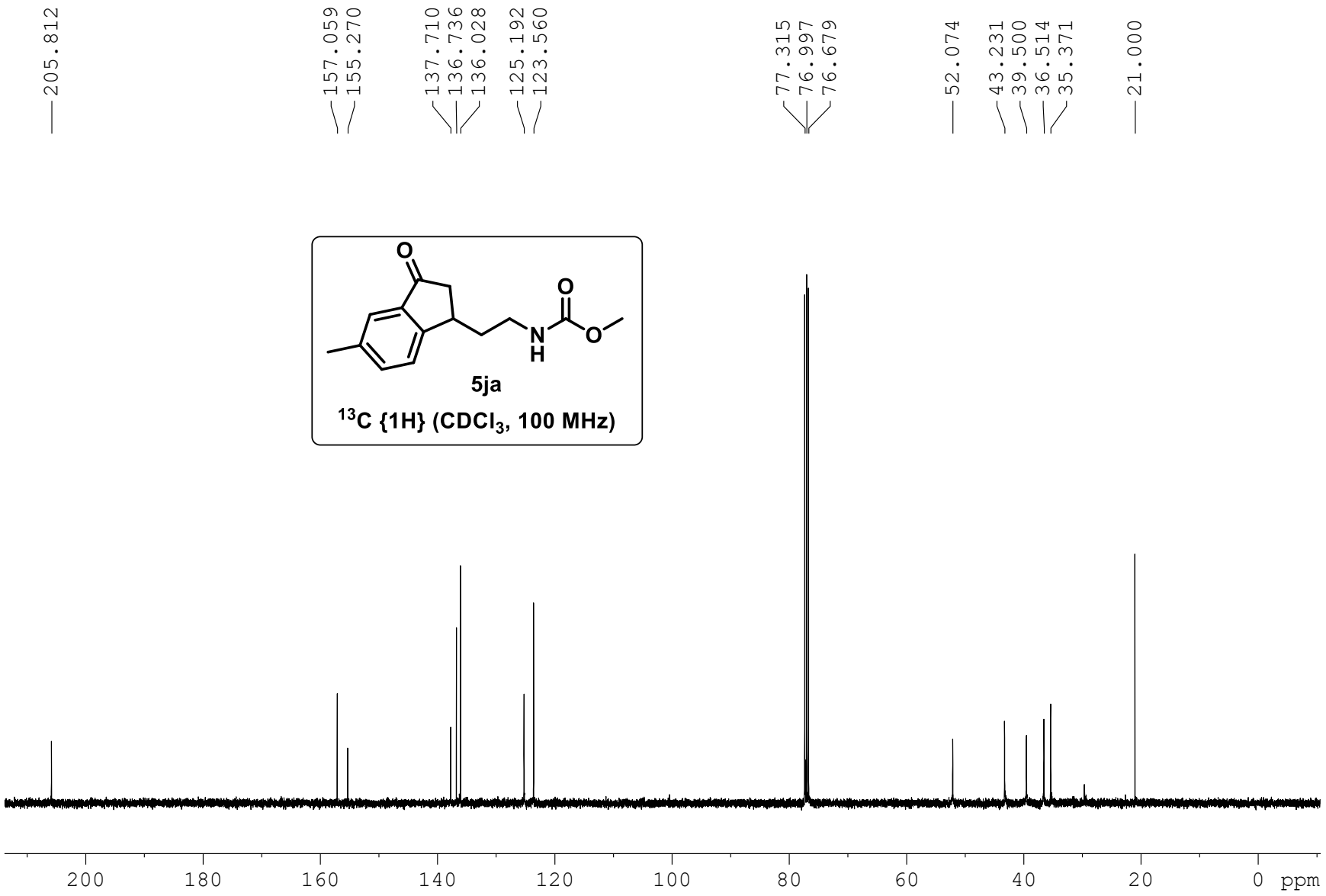

7.935
7.741
7.721
7.440
7.420
5.077
3.667
3.416
3.398
3.391
3.383
3.373
3.325
3.309
2.905
2.886
2.857
2.838
2.394
2.386
2.346
2.339
2.171
2.152
1.705
1.688
1.678
1.671
1.663
1.655
1.646
1.639
1.629
1.613
O
O
N
H
O
I
5ha
1H (CDCl3, 400 MHz)
8
7
6
5
4
3
2
1
0
ppm
1.000
1.019
0.993
1.040
2.935
1.114
1.923
1.062
1.094
1.037
1.052

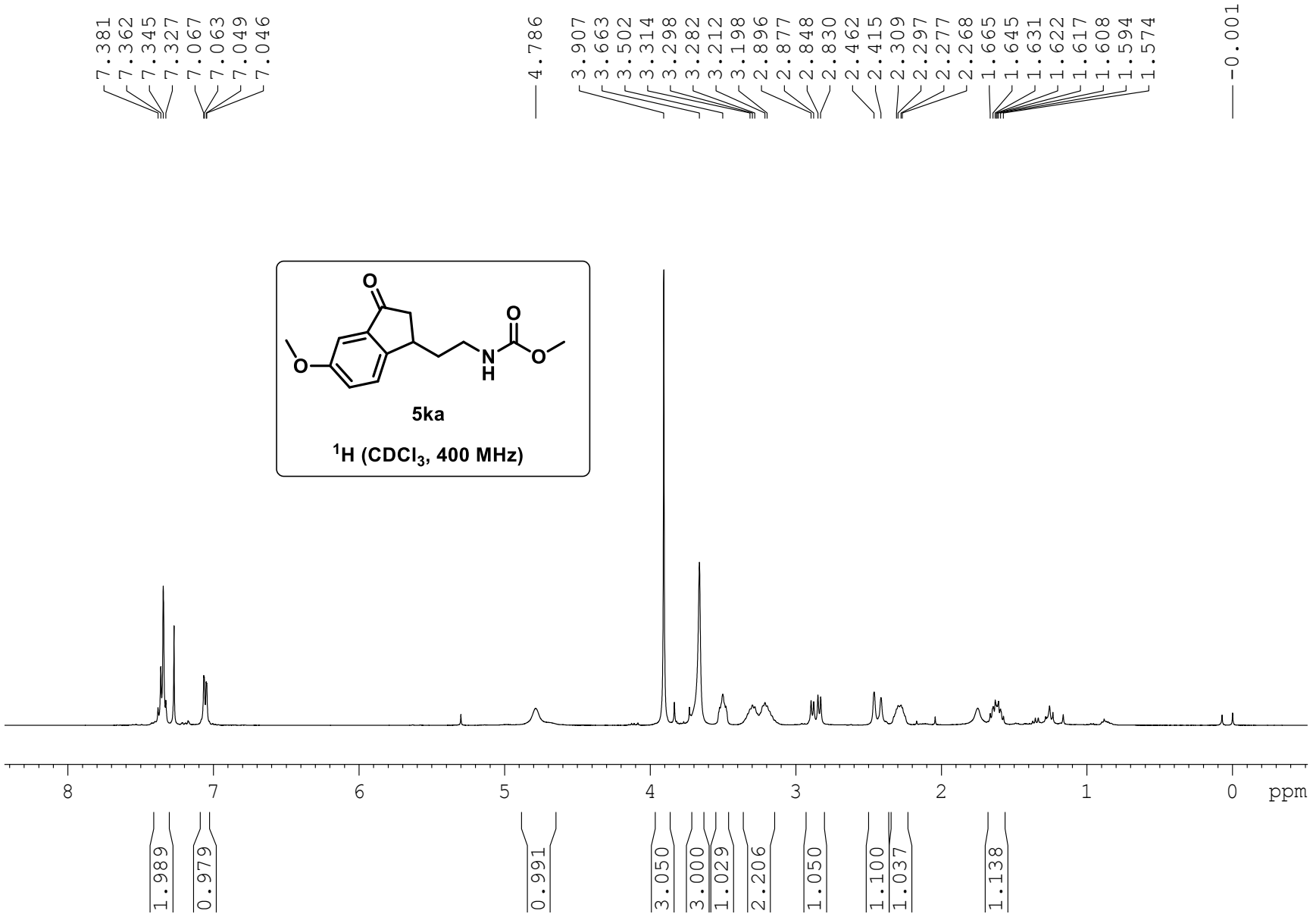

204.617
159.374
157.056
137.075
135.885
135.018
124.696
103.258
77.317
76.998
76.680
52.067
42.576
39.383
36.276
35.399
O
O
N
H
O
I
5ha
13C {1H} (CDCl3, 100 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

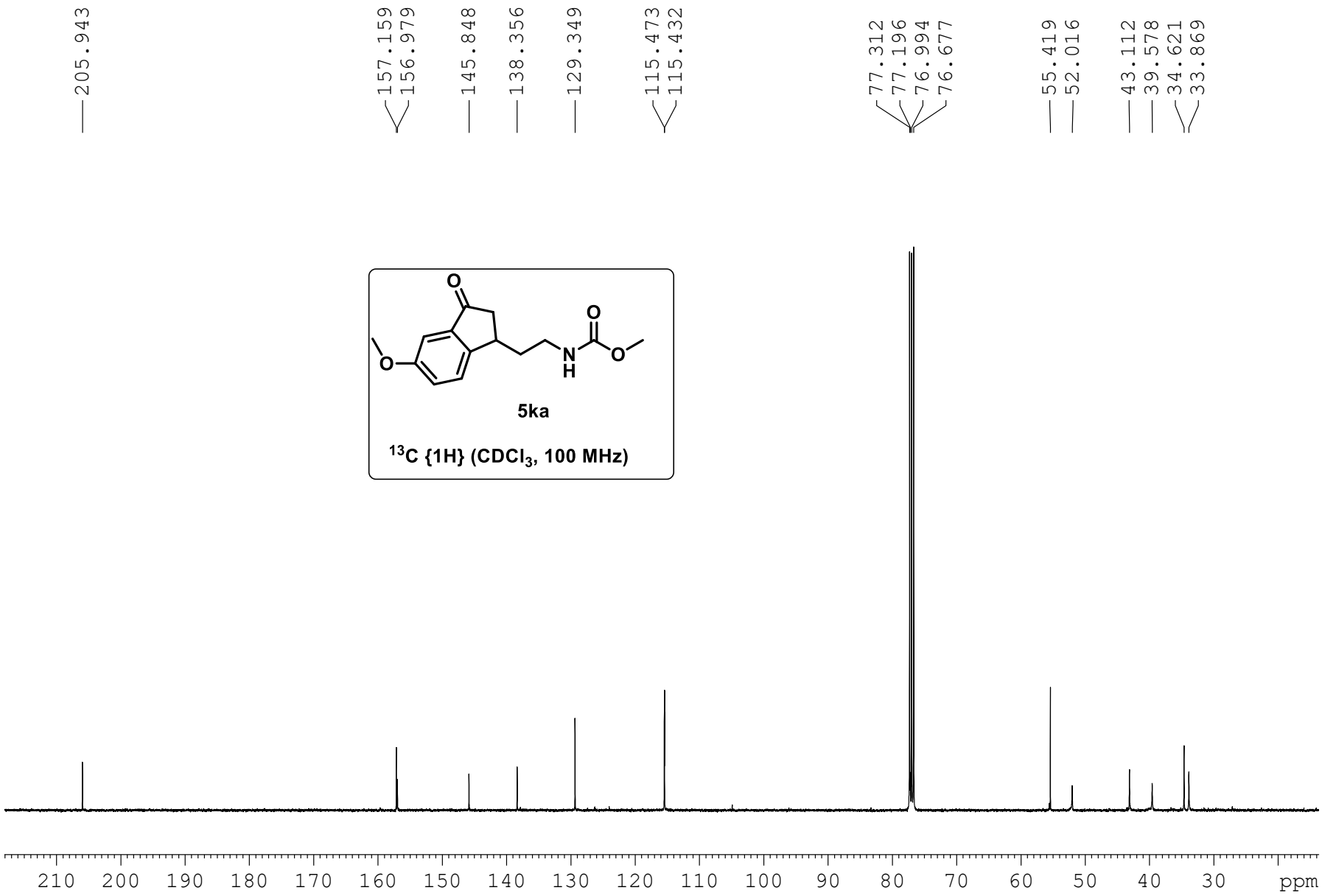

7.531
7.511
7.492
7.439
7.420
7.337
7.317
7.273
4.859
3.677
3.385
3.376
3.370
3.361
3.350
3.342
3.329
3.312
3.296
2.979
2.960
2.932
2.912
2.478
2.469
2.431
2.422
2.194
2.178
2.166
2.152
2.145
2.134
2.116
1.700
1.692
1.683
1.675
1.666
1.658
1.650
1.641
1.624
-0.000
O
Cl
O
N
H
O
5ia
^{1}H (CDCl$_3$, 400 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.040
0.996
1.000
0.933
3.071
3.024
1.018
1.037
1.096
1.140

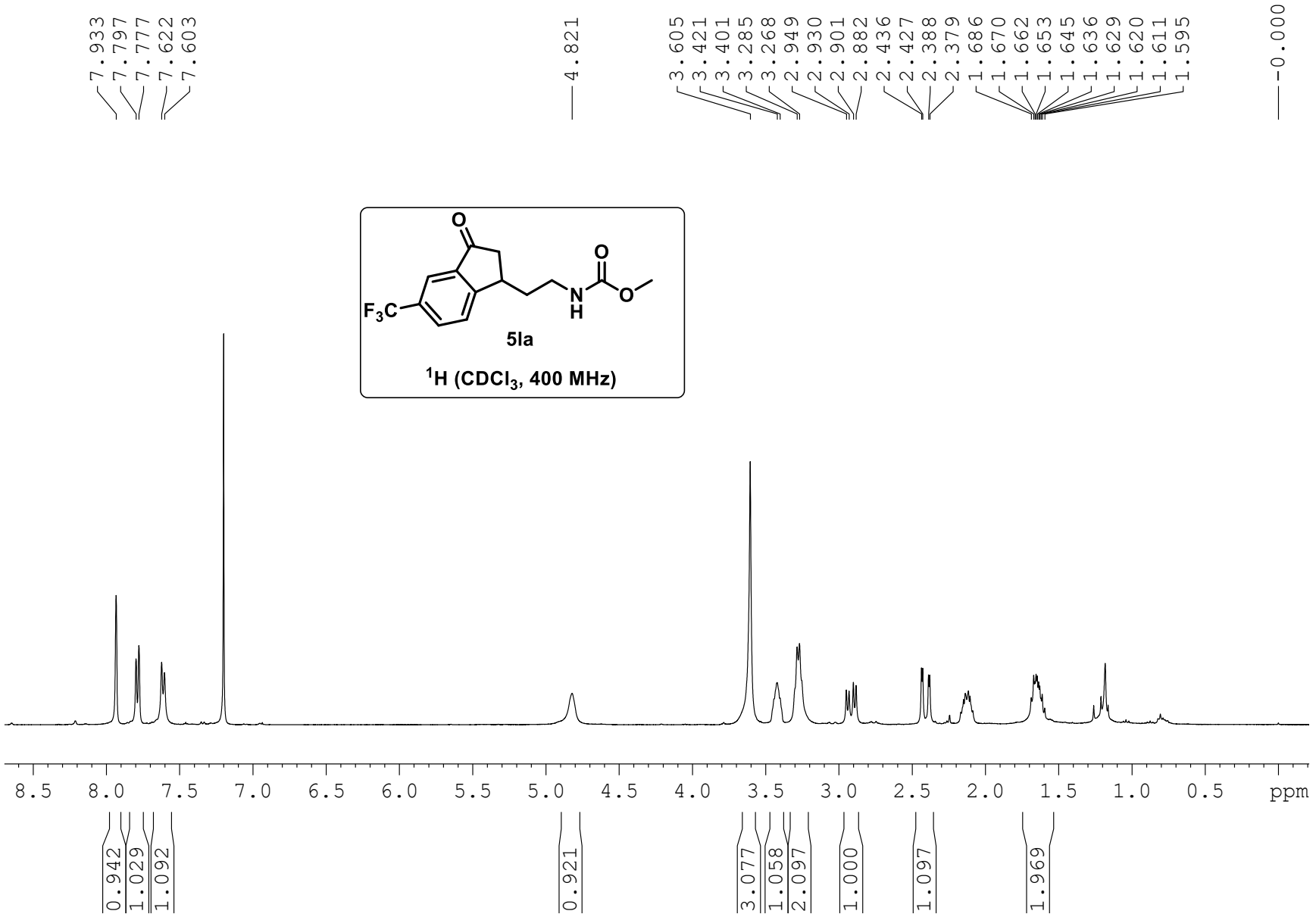

202.437
160.256
157.126
135.173
132.507
131.854
129.460
124.037
77.363
77.045
76.727
52.213
43.588
39.419
36.559
34.949
Cl
O
O
N
H
O
5ia
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

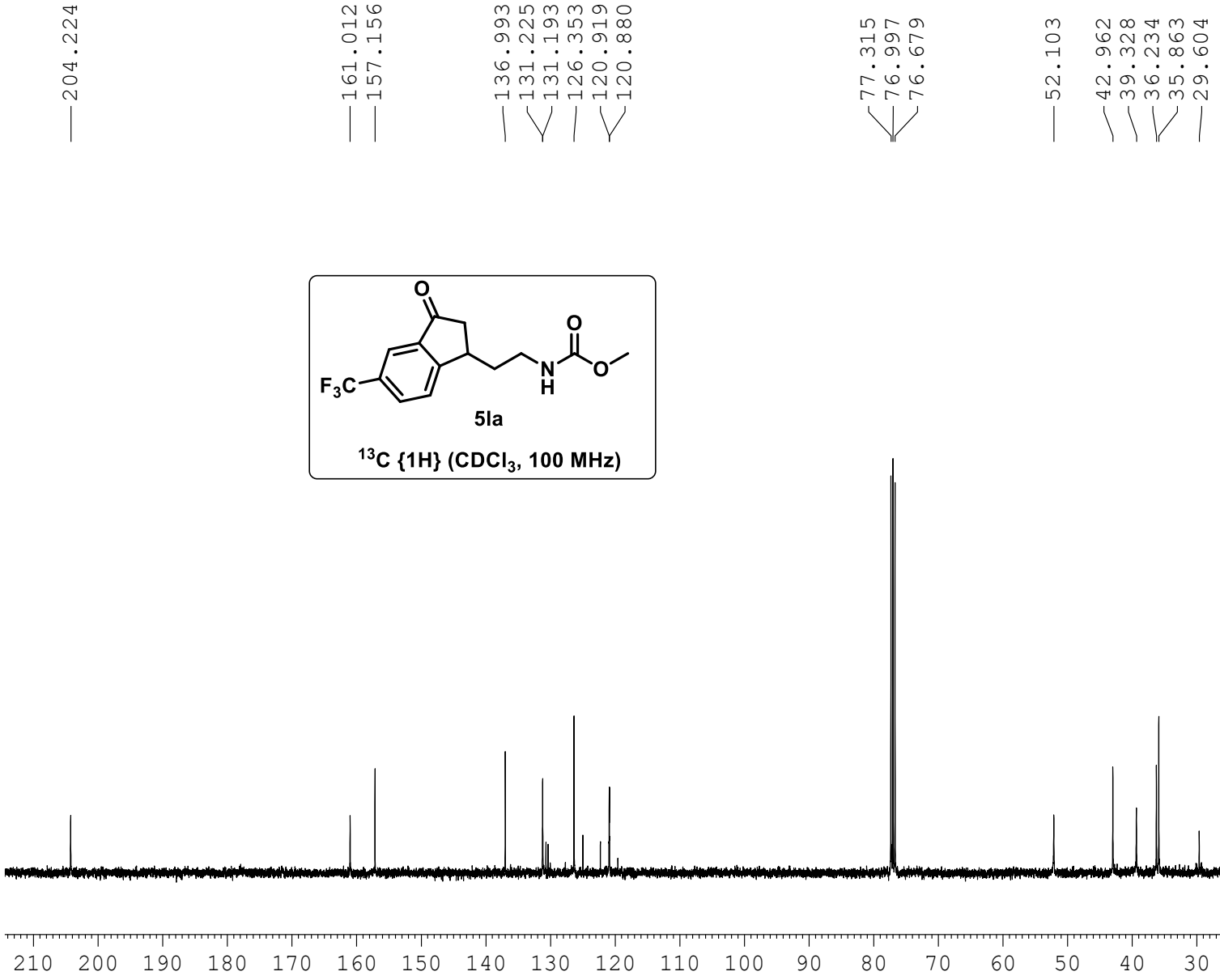

7.548
7.439
7.432
4.908
3.688
3.357
3.340
3.325
2.945
2.927
2.898
2.880
2.417
2.176
2.162
2.144
2.133
1.723
1.706
1.701
1.690
1.683
1.674
1.666
1.649
1.632
O
O
N
H
O
5ja
^{1}H (CDCl$_3$, 400 MHz)
8
7
6
5
4
3
2
1
0
ppm
1.000
2.144
1.085
3.097
3.137
1.118
4.053
1.110
1.141

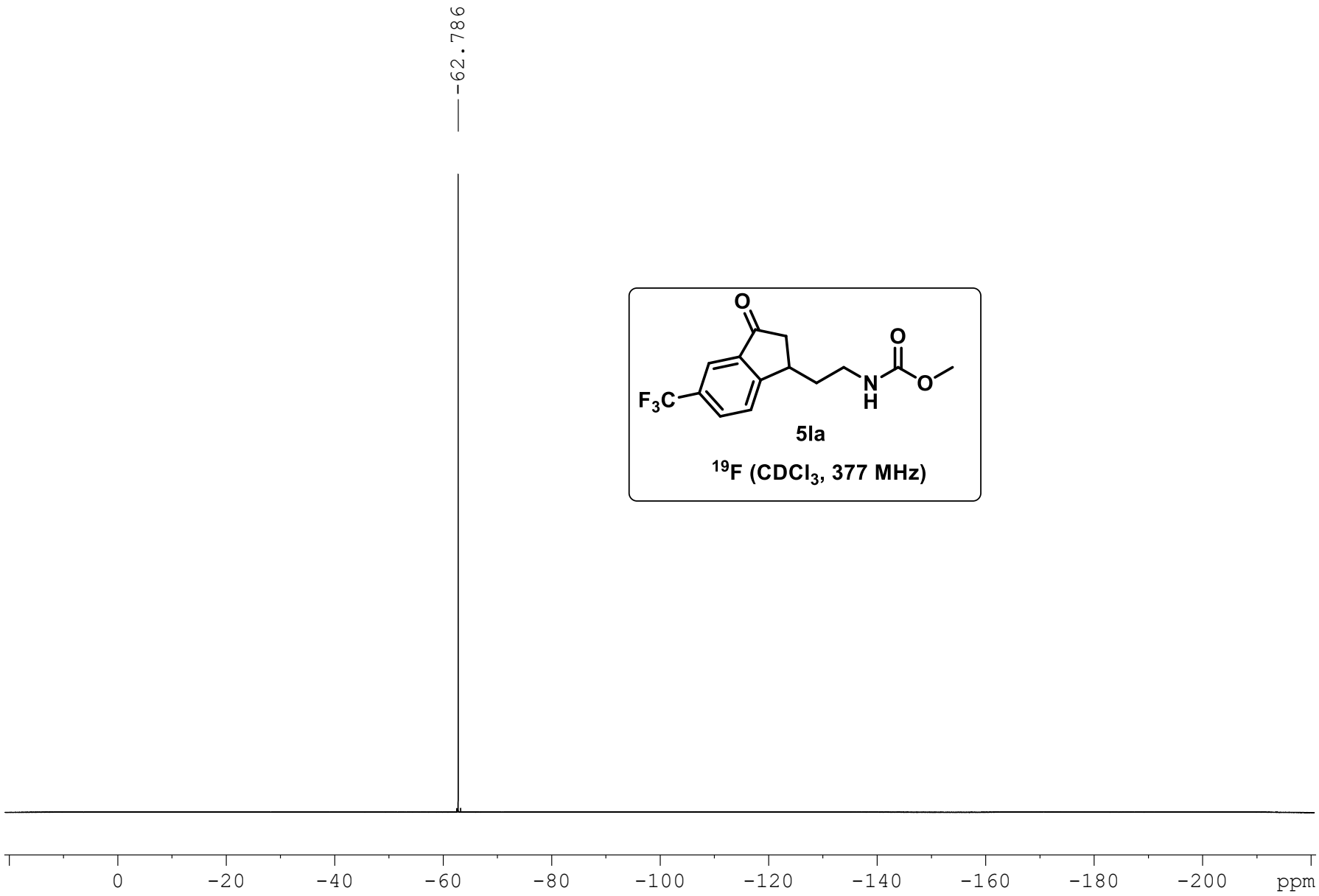

205.812
157.059
155.270
137.710
136.736
136.028
125.192
123.560
77.315
76.997
76.679
52.074
43.231
39.500
36.514
35.371
21.000
O
O
N
H
O
5ja
13C {1H} (CDCl3, 100 MHz)
200
180
160
140
120
100
80
60
40
20
0 ppm

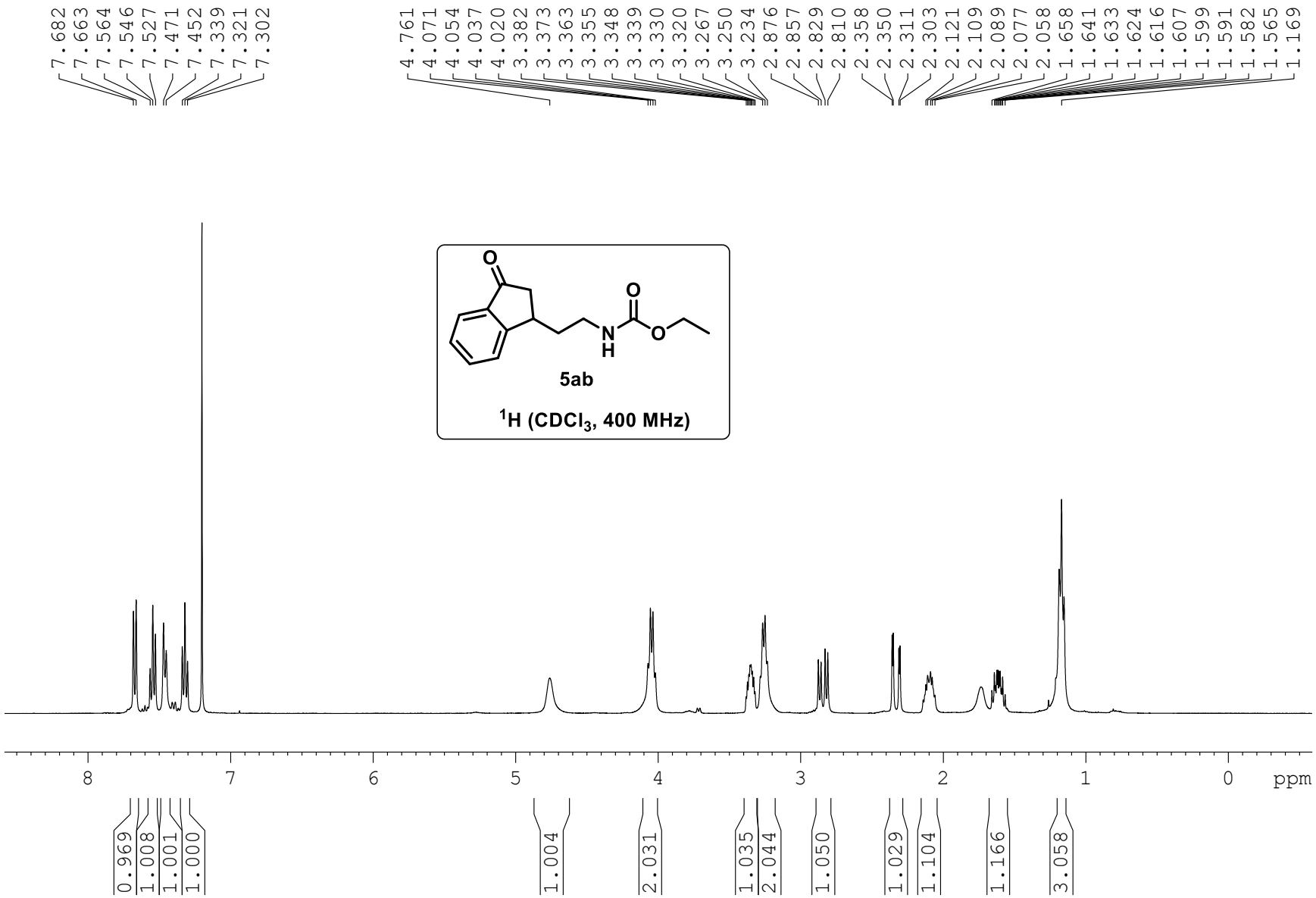

7.381
7.362
7.345
7.327
7.067
7.063
7.049
7.046
4.786
3.907
3.663
3.502
3.314
3.298
3.282
3.212
3.198
2.896
2.877
2.848
2.830
2.462
2.415
2.309
2.297
2.277
2.268
1.665
1.645
1.631
1.622
1.617
1.608
1.594
1.574
-0.001
5ka
1H (CDCl3, 400 MHz)
8
7
6
5
4
3
2
1
0
ppm
1.989
0.979
0.991
3.050
3.000
1.029
2.206
1.050
1.100
1.037
1.138

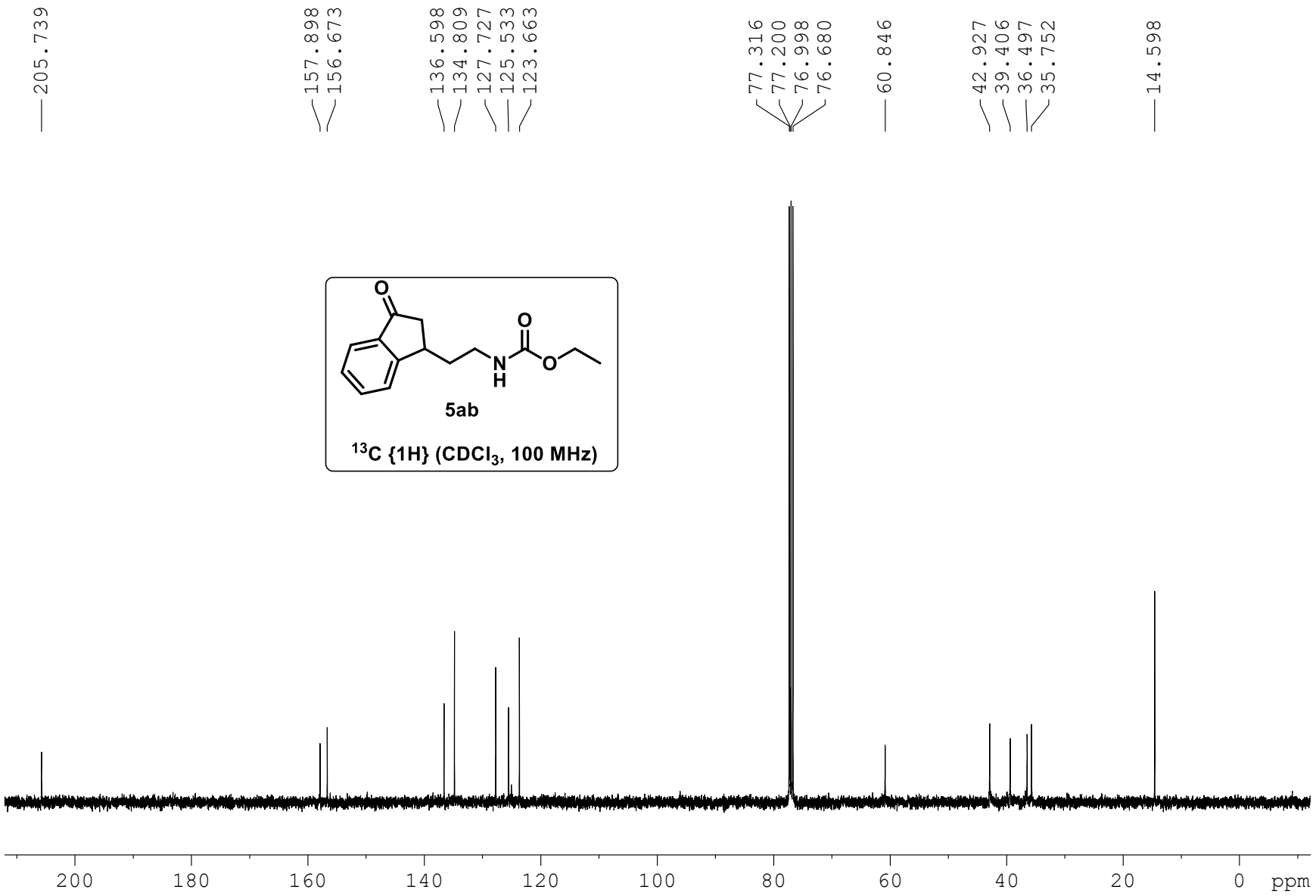

205.943
157.159
156.979
145.848
138.356
129.349
115.473
115.432
77.312
77.196
76.994
76.677
55.419
52.016
43.112
39.578
34.621
33.869
O
O
O
N
H
O
5ka
13C {1H} (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

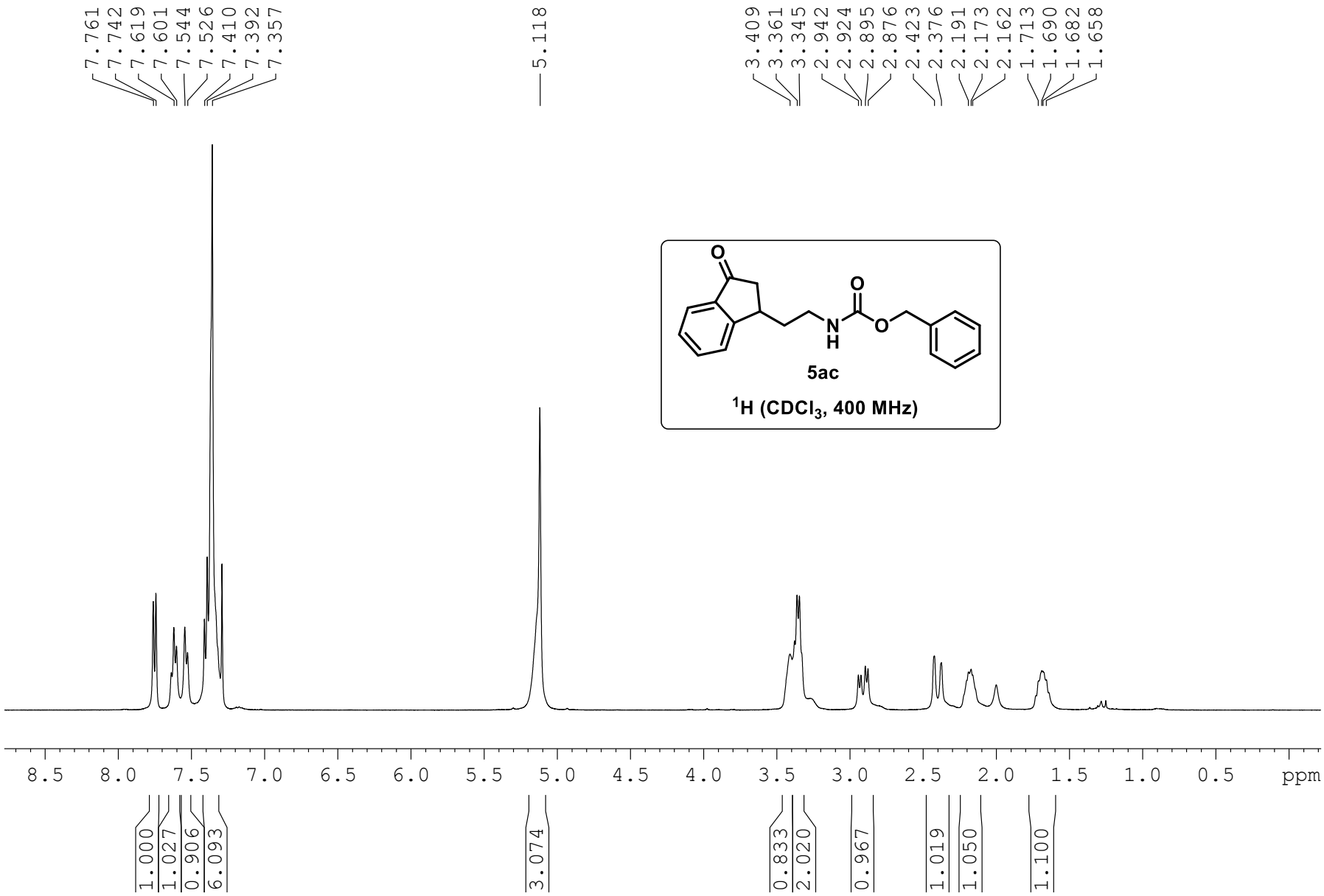

7.933
7.797
7.777
7.622
7.603
4.821
3.605
3.421
3.401
3.285
3.268
2.949
2.930
2.901
2.882
2.436
2.427
2.388
2.379
1.686
1.670
1.662
1.653
1.645
1.636
1.629
1.620
1.611
1.595
0.000
O
O
N
H
O
F3C
5Ia
1H (CDCl3, 400 MHz)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.942
1.029
1.092
0.921
3.077
1.058
2.097
1.000
1.097
1.969

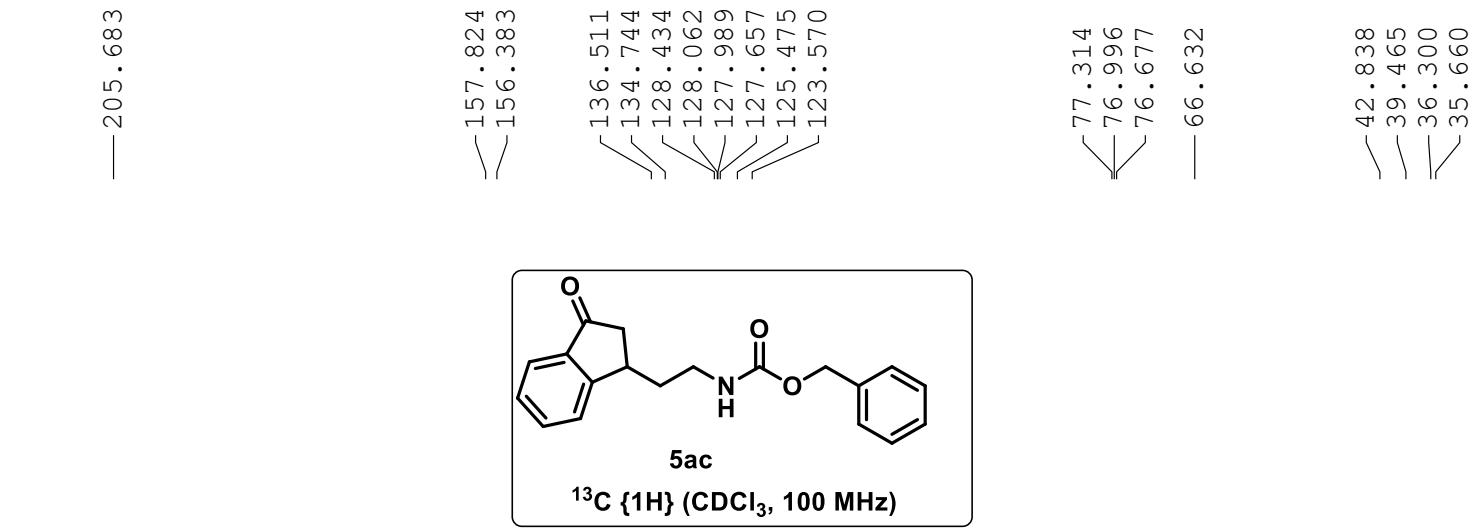

204.224
161.012
157.156
136.993
131.225
131.193
126.353
120.919
120.880
77.315
76.997
76.679
52.103
42.962
39.328
36.234
35.863
29.604
O
O
N
H
O
F3C
5la
13C {1H} (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

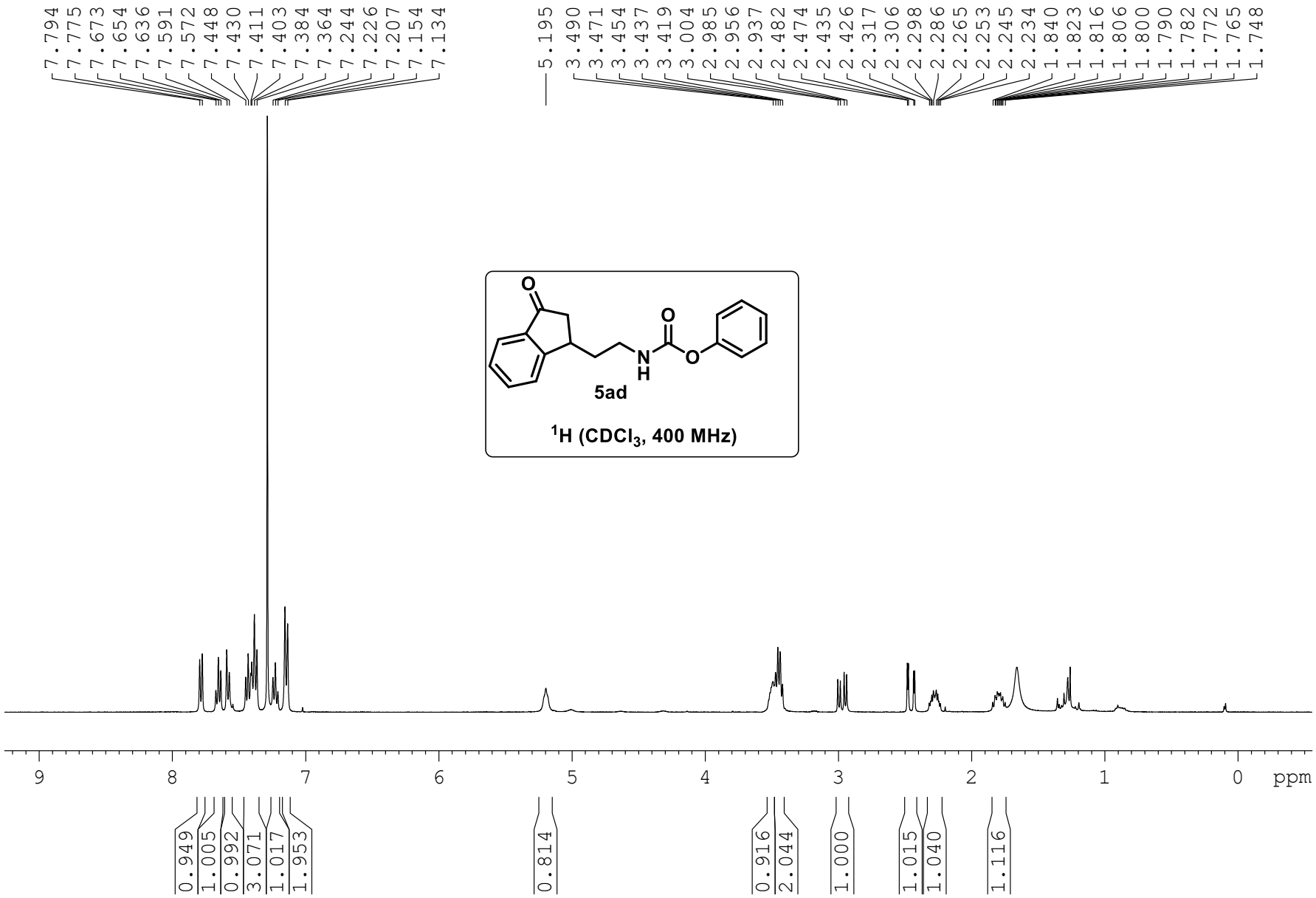

-62.786
O
O
N
H
O
F3C
5la
19F (CDCl3, 377 MHz)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

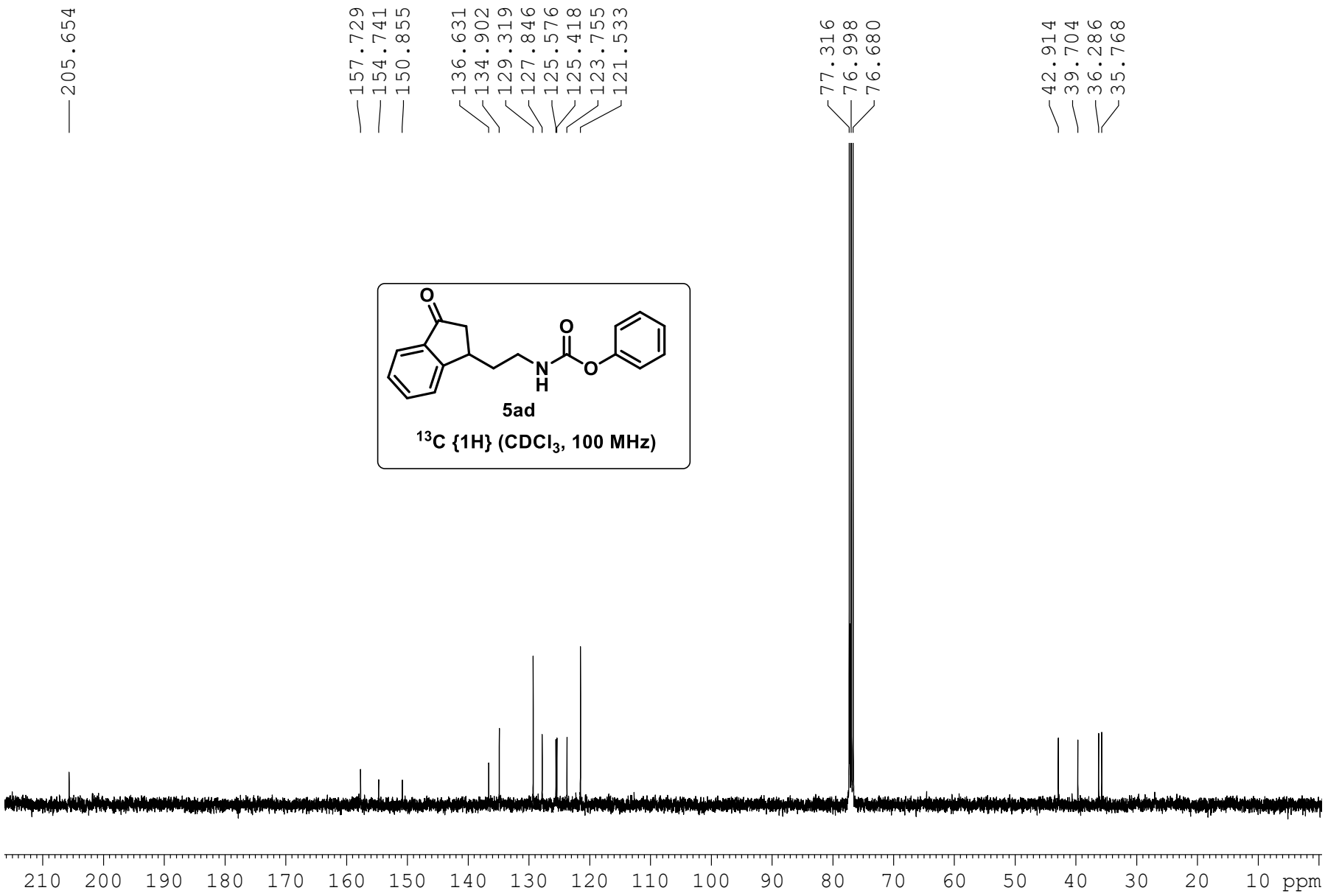

7.682
7.663
7.564
7.546
7.527
7.471
7.452
7.339
7.321
7.302
4.761
4.071
4.054
4.037
4.020
3.382
3.373
3.363
3.355
3.348
3.339
3.330
3.320
3.267
3.250
3.234
2.876
2.857
2.829
2.810
2.358
2.350
2.311
2.303
2.121
2.109
2.089
2.077
2.058
1.658
1.641
1.633
1.624
1.616
1.607
1.599
1.591
1.582
1.565
1.169
O
O
N
H
O
5ab
1H (CDCl3, 400 MHz)
8
7
6
5
4
3
2
1
0
ppm
0.969
1.008
1.001
1.000
1.004
2.031
1.035
2.044
1.050
1.029
1.104
1.166
3.058

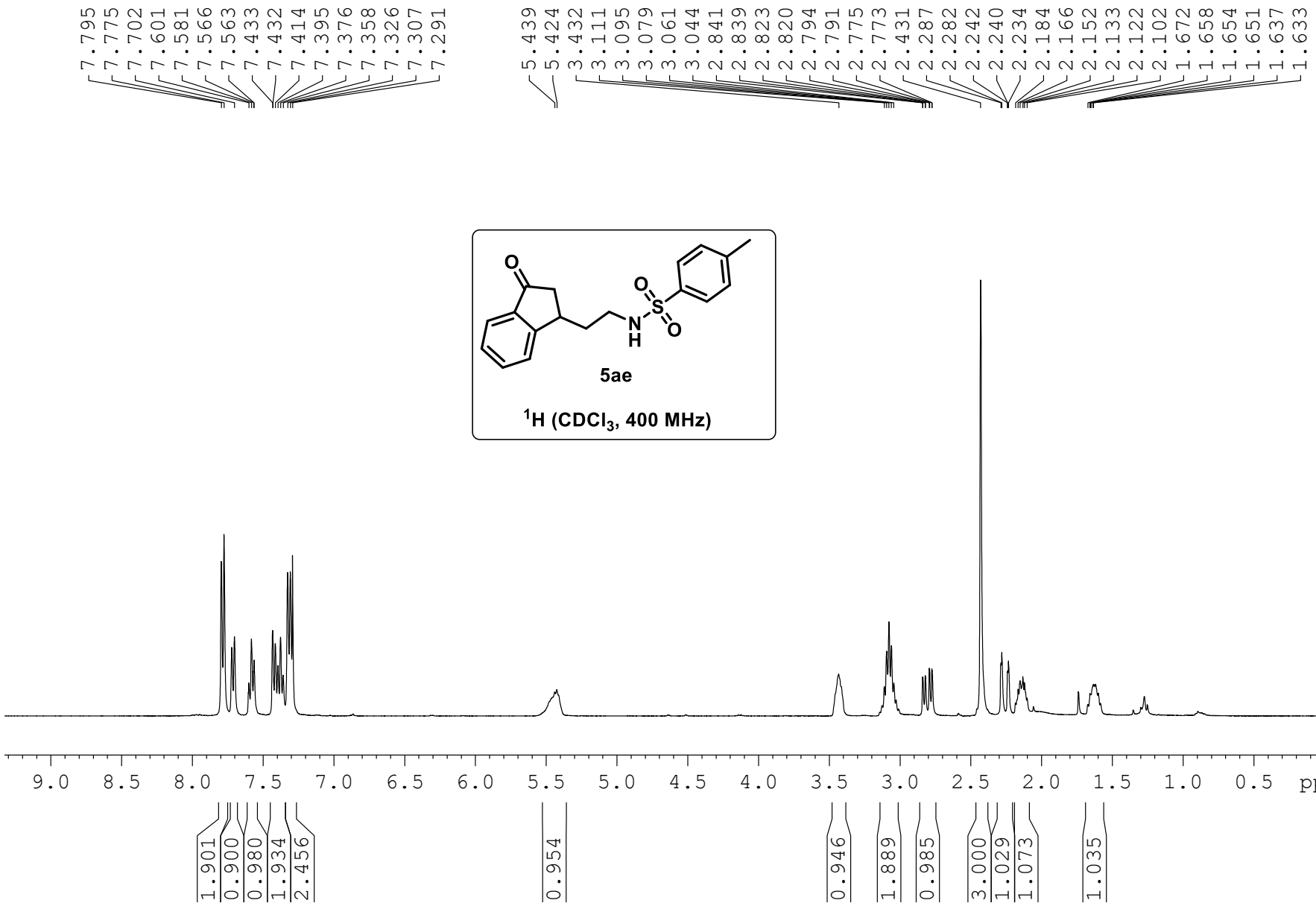

205.739
157.898
156.673
136.598
134.809
127.727
125.533
123.663
77.316
77.200
76.998
76.680
60.846
42.927
39.406
36.497
35.752
14.598
O
O
N
H
O
5ab
13C {1H} (CDCl3, 100 MHz)
200
180
160
140
120
100
80
60
40
20
0
ppm

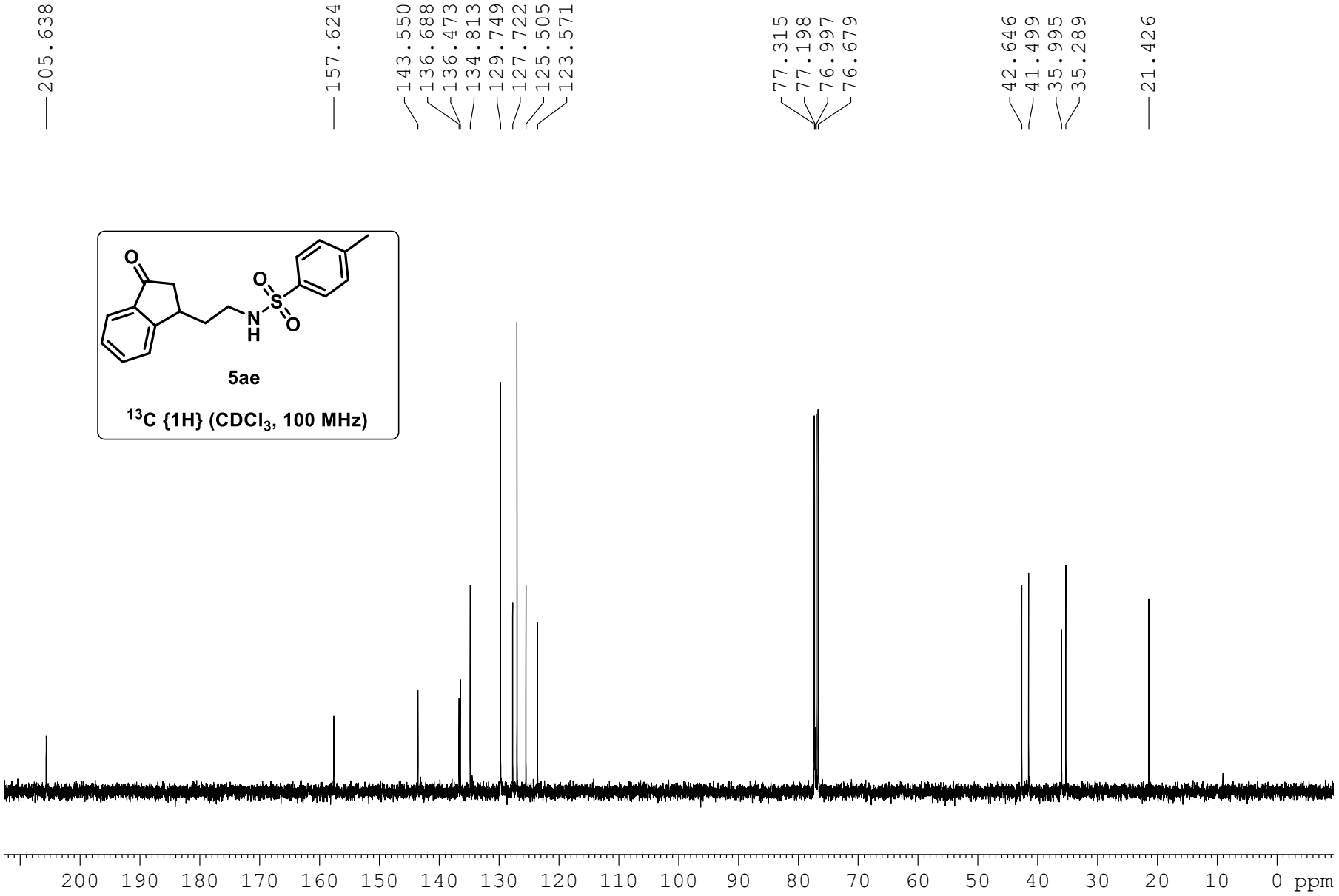

7.761
7.742
7.619
7.601
7.544
7.526
7.410
7.392
7.357
5.118
3.409
3.361
3.345
2.942
2.924
2.895
2.876
2.423
2.376
2.191
2.173
2.162
1.713
1.690
1.682
1.658
O
O
N
H
O
5ac
1H (CDCl3, 400 MHz)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.027
0.906
6.093
3.074
0.833
2.020
0.967
1.019
1.050
1.100


205.683
157.824
156.383
136.511
134.744
128.434
128.062
127.989
127.657
125.475
123.570
77.314
76.996
76.677
66.632
42.838
39.465
36.300
35.660
O
O
N
H
O
5ac
13C {1H} (CDCl3, 100 MHz)
200
180
160
140
120
100
80
60
40
20
0 ppm


7.794
7.775
7.673
7.654
7.636
7.591
7.572
7.448
7.430
7.411
7.403
7.384
7.364
7.244
7.226
7.207
7.154
7.134
5.195
3.490
3.471
3.454
3.437
3.419
3.004
2.985
2.956
2.937
2.482
2.474
2.435
2.426
2.317
2.306
2.298
2.286
2.265
2.253
2.245
2.234
1.840
1.823
1.816
1.806
1.800
1.790
1.782
1.772
1.765
1.748
O
O
N
H
O
5ad
1H (CDCl3, 400 MHz)
9
8
7
6
5
4
3
2
1
0
ppm
0.949
1.005
0.992
3.071
1.017
1.953
0.814
0.916
2.044
1.000
1.015
1.040
1.116


205.654
157.729
154.741
150.855
136.631
134.902
129.319
127.846
125.576
125.418
123.755
121.533
77.316
76.998
76.680
42.914
39.704
36.286
35.768
O
O
N
H
O
5ad
13C {1H} (CDCl3, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.795
7.775
7.702
7.601
7.581
7.566
7.563
7.433
7.432
7.414
7.395
7.376
7.358
7.326
7.307
7.291
5.439
5.424
5.432
3.111
3.095
3.079
3.061
3.044
2.841
2.839
2.823
2.820
2.794
2.791
2.775
2.773
2.431
2.287
2.282
2.242
2.240
2.234
2.184
2.166
2.152
2.133
2.122
2.102
1.672
1.658
1.654
1.651
1.637
1.633
O
O
S
O
N
H
5ae
1H (CDCl3, 400 MHz)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.901
0.900
0.980
1.934
2.456
0.954
0.946
1.889
0.985
3.000
1.029
1.073
1.035


205.638
157.624
143.550
136.688
136.473
134.813
129.749
127.722
125.505
123.571
77.315
77.198
76.997
76.679
42.646
41.499
35.995
35.289
21.426
O
O
S
O
N
H
5ae
13C {1H} (CDCl3, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm