

Supplementary Information

One-pot Nazarov cyclization/oxidative 1,2-carbon rearrangement/Ritter reaction to access 5-quaternary-4-amidocyclopent-2-enones and 2-quaternary-3-amidoindanones

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1. General Information

Unless otherwise stated, all reagents were purchased from commercial sources and were directly used without further purification.

Dichloromethane (DCM) was purified by distillation over the CaH₂ indicated.

Tetrahydrofuran (THF) were dried by distillation over the Na indicated.

All reactions were monitored by thin-layer chromatography (TLC) on silica gel GF₂₅₄ plates using UV light as visualizing agent (if applicable), and a solution of phosphomolybdic acid (50 g/L) in EtOH followed by heating as developing agents. The products were purified by flash column chromatography on silica gel (200-300 meshes) produced by Yantai Xinnuo Chemicals Co., LTD (China).

¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded in CDCl₃ solution on a Bruker AM 400 MHz instrument or 600 MHz NMR instrument. Chemical shifts were denoted in ppm (δ) and calibrated by using residual undeuterated solvent [CDCl₃ (7.26 ppm) or tetramethylsilane (0.00 ppm)] as internal reference for ¹H NMR and the deuterated solvent [CDCl₃ (77.16 ppm) or (CD₃)₂SO (39.52 ppm)] as internal standard for ¹³C NMR. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, br = broad, dd = double doublet, dt = doublet of triplets, m = multiplet.

The high-resolution mass spectral (HRMS) analysis data were measured on Thermo Fisher Orbitrap Elite Mass Spectrometer or a LCT Premier XE (Waters) mass spectrometer (Waters, Milford, MA, U.S.) by means of the ESI technique. Electron ionization mass spectra (EI-MS) were measured on a Shimadzu GCMSQP2010SE spectrometer by direct inlet at 70 eV and the corresponding signals were given in *m/z* with relative intensity (%) in brackets.

Melting points (m.p.) were measured on a Kolfer melting point apparatus (Beijing Tech Instrument Co., LTD) without calibration.

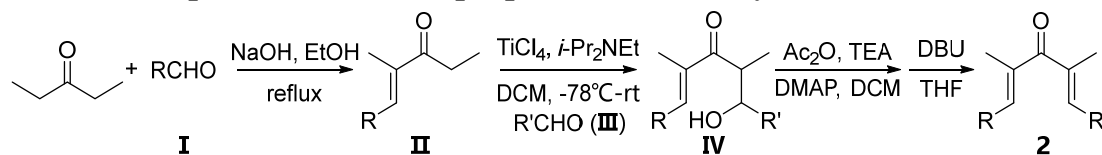
The **IR** spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer.

The **X-ray** single-crystal determination were performed on an Agilent Super Nova single crystal X-ray diffractometer.

2. Preparation of substrates

All the nitrile substrates were commercially available. Substrates **2a**¹, **2b**², **2f**³, **2g**² were synthesized according to the previously reported methods.

2.1 General procedure for the preparation of divinyl ketones.



The aldehyde **I** (10 mmol) and 3-pentanone (40 mmol) were dissolved in EtOH (10 mL) and then NaOH aq. (1.3 mL, 10%) was added dropwise. The mixture was stirred at reflux for 48 h, then it was poured in ice water (100 mL), neutralized with aq. HCl (1 mol/L) and extracted with EtOAc (3 × 25 mL). The combined organic phase was washed with NaHCO₃ aq. (25 mL) and brine (25 mL) dried with Na₂SO₄, filtered, and concentrated. The crude residue was purified by column chromatography to afford the unsaturated ketone **II**.

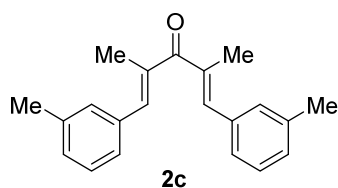
Unsaturated ketone **II** was dissolved in dry CH₂Cl₂ (0.15 M), and then TiCl₄ (1.0 equiv) and *t*Pr₂NEt (1.2 equiv) was sequentially added dropwise at -78 °C. After stirring at -78 °C for 1.5 h, aldehyde **III** (1.5 equiv) was added dropwise. The solution was stirred at -78 °C for 2 h, and then allowed to slowly warm to room temperature until the starting material was disappeared completely (monitored through TLC). The reaction mixture was diluted with DCM and H₂O, and the aqueous layer was extracted with DCM. The combined organic phase was successively washed with water and brine, dried with Na₂SO₄, filtered, and concentrated in vacuum to give the crude product. Purification of the crude product by flash column chromatography with petroleum ether/ethyl acetate as eluent to afford the hydroxy ketones **IV**.

To a solution of hydroxy ketones **IV** in DCM (0.15 M), DMAP (0.1 equiv), TEA (1.5 equiv) and Ac₂O (1.2 equiv) were successively added. The reaction mixture was stirred at room temperature for 1 h and then quenched with 1 mol/L HCl solution. The aqueous layer was extracted with DCM. The organic layers were combined and successively washed with 1 mol/L HCl, water, NaHCO₃ solution, and brine. The organic layer was then filtered and concentrated. The crude material was then purified by flash column

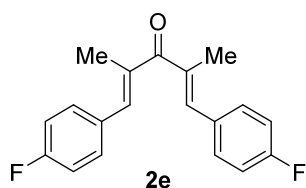
chromatography to afford the corresponding acetates.

DBU (1.5 equiv) was added to a solution of the resulting acetates in THF (0.1 M), and the reaction mixture was stirred at room temperature until the starting material was disappeared completely (monitored through TLC). The reaction was quenched with 1 mol/L HCl solution. The aqueous layer was extracted with EtOAc. The organic layers were combined, successively washed with water and brine, dried with Na₂SO₄. The organic layer was filtered, concentrated in vacuum and purified by column chromatography to yield divinyl ketones **2**.

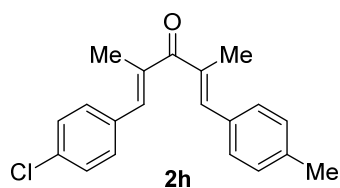
Characterization data of divinyl ketones.



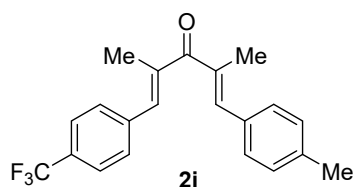
2c: yellowish solid, m.p. = 55.0-57.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.23 (m, 6 H), 7.18 (brs, 2 H), 7.12 (d, *J* = 7.2 Hz, 2 H), 2.36 (s, 6 H), 2.21 (d, *J* = 1.2 Hz, 6 H); ¹³C NMR (100 MHz, CDCl₃): δ 202.2, 139.3, 138.1, 136.8, 136.0, 130.4, 129.1, 128.4, 126.7, 21.5, 15.0; HRMS (ESI) *m/z* calculated for C₂₁H₂₃O [M+H]⁺ 291.1743 found 291.1736; MS (EI) *m/z* (%): 290 (12), 155 (100), 133 (54), 105 (61), 71 (90); IR (KBr plate): 3026, 2959, 1703, 1632, 1451, 1295, 695 cm⁻¹.



2e: white solid, m.p. = 119.0-121.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.43-7.40 (m, 4 H), 7.16-7.08 (m, 6 H), 2.19 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃): δ 201.8, 162.6 (d, *J* = 247 Hz), 137.9, 136.79, 136.78, 132.1 (d, *J* = 4 Hz), 131.6 (d, *J* = 8 Hz), 115.7 (d, *J* = 22 Hz), 15.0; ¹⁹F NMR (376 MHz, CDCl₃): δ -112.30; HRMS (ESI) *m/z* calculated for C₁₉H₁₇F₂O [M+H]⁺ 299.1242 found 299.1234; MS (EI) *m/z* (%): 298 (25), 155 (27), 133 (32), 85 (85), 71 (100); IR (KBr plate): 1608, 1440, 1381, 1097, 784 cm⁻¹.

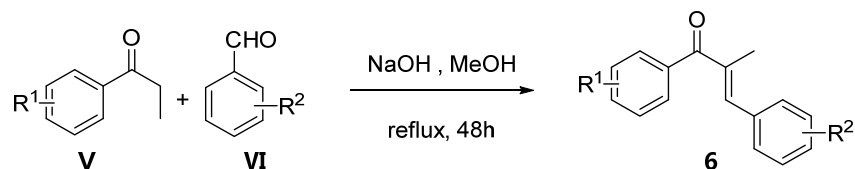


2h: white solid, m.p. = 67.8-69.2 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.38-7.33 (m, 6 H), 7.24-7.21 (m, 3 H), 7.08 (d, $J = 1.2$ Hz, 1 H), 2.38 (s, 3 H), 2.21 (d, $J = 1.2$ Hz, 3 H), 2.18 (d, $J = 1.2$ Hz, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 201.9, 139.9, 138.7, 137.7, 136.9, 136.0, 134.5, 134.1, 133.1, 130.9, 129.8, 129.3, 128.8, 21.4, 15.2, 14.9; **HRMS** (ESI) m/z calculated for $\text{C}_{20}\text{H}_{20}\text{ClO}$ $[\text{M}+\text{H}]^+$ 311.1197 found 311.1190; **MS** (EI) m/z (%): 312 (3), 310 (11), 115 (100), 91 (35); **IR** (KBr plate): 2921, 1635, 1444, 1357, 1044, 736 cm^{-1} .



2i: white solid, m.p. = 39.5-40.2 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.65 (d, $J = 8.4$ Hz, 2 H), 7.51 (d, $J = 8.4$ Hz, 2 H), 7.36 (d, $J = 8.0$ Hz, 2 H), 7.28 (brs, 1 H), 7.23 (d, $J = 8.0$ Hz, 2 H), 7.11 (brs, 1 H), 2.38 (s, 3 H), 2.23 (d, $J = 0.8$ Hz, 3 H), 2.21 (d, $J = 0.8$ Hz, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): 201.6, 140.6, 139.7, 139.3, 138.9, 135.8, 133.0, 129.88 (q, $J = 33$ Hz), 129.89, 129.7, 129.3, 125.4 (q, $J = 4$ Hz), 124.1 (q, $J = 270$ Hz), 21.4, 15.4, 14.7; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -62.56; **HRMS** (ESI) m/z calculated for $\text{C}_{21}\text{H}_{20}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$ 345.1461 found 345.1452; **MS** (EI) m/z (%): 344 (2), 145 (6), 91 (74), 85 (100); **IR** (KBr plate): 2924, 1639, 1390, 1244, 1044, 749 cm^{-1} .

2.2 General procedure for the preparation of chalcone derivatives.

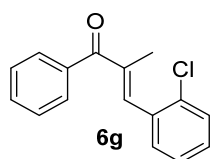


To a stirred solution of ketone **V** (10 mmol) in methanol (5 mL), a solution of sodium hydroxide (13 mmol) in methanol (10 mL) was added dropwise. After stirring at room temperature for 15 minutes, substituted benzaldehydes **VI** (10 mmol) was added and the mixture was heated to reflux for 48 h. The reaction was quenched with water (40

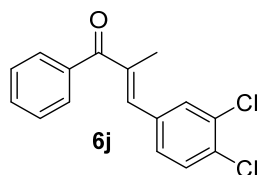
mL) and extracted with ethyl acetate (40 mL×3). The combined organic layer was dried over Na₂SO₄, concentrated, and purified through silica gel column chromatography using a mixture of ethyl acetate and petroleum ether as eluent to afford the corresponding chalcone derivatives **6**.

The NMR spectra data of compound **6a**⁴, **6b**⁴, **6c**⁵, **6d**⁴, **6e**⁴, **6f**⁶, **6h**⁵, **6i**⁴, **6k**⁴, **6m**⁴, **6n**⁷, are consistent with the literatures, respectively.

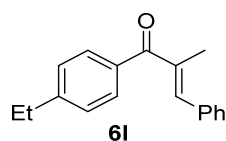
Characterization data of chalcone derivatives.



6g: White solid, m.p. = 43.1-45.0 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.86-7.84 (m, 2 H), 7.58-7.54 (m, 1 H), 7.49-7.39 (m, 4 H), 7.33-7.26 (m, 3 H), 2.13 (d, *J* = 1.6 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 199.2, 138.7, 138.4, 138.0, 134.5, 134.2, 132.2, 130.4, 129.8, 129.72, 129.66, 128.4, 126.7, 14.4; HRMS (ESI) *m/z* calculated for C₁₆H₁₃ClNaO [M+Na]⁺ 279.0547 found 279.0550; MS (EI) *m/z* (%): 256 (4), 221 (83), 115 (49), 105 (100), 77 (85); IR (KBr plate): 2924, 1650, 1468, 1260, 1055, 766 cm⁻¹.



6j: White solid, m.p. = 68.2-70.0 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.74-7.72 (m, 2 H), 7.56-7.52 (m, 1 H), 7.47-7.44 (m, 4 H), 7.23 (dd, *J* = 8.4 Hz, 2.0 Hz, 1 H), 7.02 (s, 1 H), 2.23 (d, *J* = 1.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 198.7, 138.7, 138.5, 137.9, 135.8, 132.7, 132.5, 132.0, 131.3, 130.5, 129.5, 128.8, 128.4, 14.6; HRMS (ESI) *m/z* calculated for C₁₆H₁₃Cl₂O [M+H]⁺ 291.0338 found 291.0333; MS (EI) *m/z* (%): 290 (13), 133 (63), 85 (100), 77 (28); IR (KBr plate): 2961, 1648, 1447, 1261, 1076, 750 cm⁻¹.



6i: Slightly yellow liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.72-7.70 (m, 2 H), 7.43-7.38

(m, 4 H), 7.34-7.30 (m, 1 H), 7.28 (d, $J = 8$ Hz, 2 H), 7.17 (s, 1 H), 2.72 (q, $J = 7.6$ Hz, 2 H), 2.27 (s, 3 H), 1.28 (t, $J = 7.6$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.3, 148.7, 141.4, 137.1, 136.03, 136.60, 130.0, 129.8, 128.6, 127.8, 29.0, 15.4, 14.7; HRMS (ESI) m/z calculated for $\text{C}_{18}\text{H}_{18}\text{ONa}$ $[\text{M}+\text{Na}]^+$ 273.1250 found 273.1249; MS (EI) m/z (%): 250 (21), 127 (68), 105 (11), 85 (100), 71 (82); IR (KBr plate): 2962, 1645, 1450, 1262, 1076, 764 cm^{-1} .

3. Experimental details and characterization data

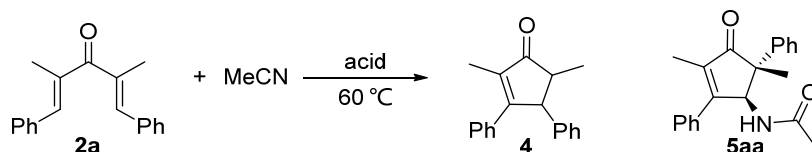
3.1 Construct 2,3-disubstituted-5-quaternary-4-amidocyclopent-2-enones from divinyl ketones

3.1.1 General procedure A

Unless otherwise stated, the general procedure is as follows: to a 10 mL sealed tube containing a magnetic stir bar were added sequentially divinyl ketones (0.2 mmol), *p*-TsOH \cdot H₂O (114.1 mg, 0.6 mmol) and nitrile (1 mL) at room temperature, then the mixture was placed in a preheated oil bath at 60 °C and stirred for the indicated time. After the indicated time, the reaction mixture was cooled down to room temperature, HTIB ([hydroxy(tosyloxy)iodo]benzene, 156.9 mg, 0.4 mmol) was added and the mixture was stirred at 60 °C and stirred for the indicated time. The reaction mixture was cooled to room temperature, diluted with DCM (15.0 mL) and H₂O (15.0 mL), and the aqueous layer was extracted with DCM. The combined organic phase was successively washed with water and brine, dried with Na_2SO_4 , filtered, and concentrated in vacuum. The residues were purified by flash column chromatography on silica gel (DCM/ CH_3OH or petroleum ether/ethyl acetate) to afford the desired product.

3.1.2 The details for the optimization of reaction conditions

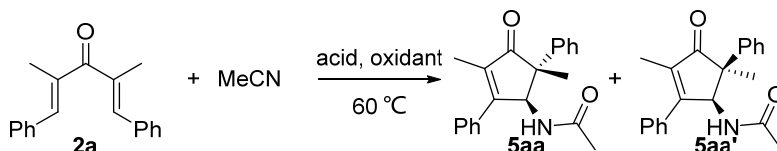
Table S1 The screening of acid^a



Entry	Acid	T/ °C	Solvent	dr of 4	Yield of 4 ^b /%	Yield of 5aa /%
1	<i>p</i> -TsOH	60 (30 min)	CH ₃ CN	6.4:1	93 ^c	ND
2	TfOH	60 (30 min)	CH ₃ CN	5.6:1	40	ND
3	HBF ₄ ·H ₂ O	60 (40 min)	CH ₃ CN	3.7:1	86	ND
4	HCl	60 (30 min)	CH ₃ CN	7.7:1	99	ND
5	H ₂ SO ₄	60 (40 min)	CH ₃ CN	7.7:1	56	ND
6	BF ₃ ·Et ₂ O	60 (2.5 min)	CH ₃ CN		4	ND
7	TMSOTf	60 (30 min)	CH ₃ CN	5.9:1	43	ND
8	Fe(OTf) ₃	60 (24 h)	CH ₃ CN		trace	trace
9	TiCl ₄	60 (40 min)	CH ₃ CN	6.3:1	72	ND

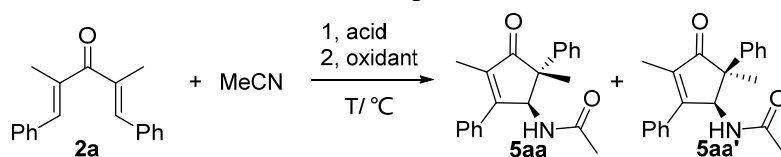
^aOtherwise specified, the reactions were performed using **2a** (0.2 mmol), acid (2.0 equiv.), in 1.0 mL CH₃CN at the noted temperature. ^bNMR yield. ^cIsolated yield.

Table S2 The screening of Oxidant^a



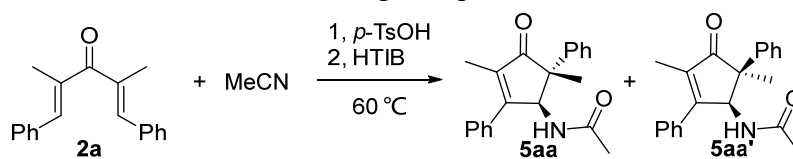
Entry	Acid	T/ °C	Solvent	Oxidant	dr	Yield ^b /%
1	Fe(OTf) ₃	60 (24 h)	CH ₃ CN	Selectfluor		2
2	Fe(OTf) ₃	60 (24 h)	CH ₃ CN	DDQ		decomposition
3	Fe(OTf) ₃	60 (24 h)	CH ₃ CN	PIDA		12
4	Fe(OTf) ₃	60 (24 h)	CH ₃ CN	PhIO		13
5	Fe(OTf) ₃	60 (24 h)	CH ₃ CN	PIFA		12
6	Fe(OTf) ₃	60 (24 h)	CH ₃ CN	HTIB		18
7	HCl	60 (48 h)	CH ₃ CN	HTIB		ND
8	<i>p</i> -TsOH	60 (48 h)	CH ₃ CN	HTIB	4.8:1	31 ^c

^aOtherwise specified, the reactions were performed using **2a** (0.2 mmol), acid (2.0 equiv.) and oxidant (2.0 equiv.) in 1.0 mL CH₃CN at the noted temperature. ^bNMR yield. ^cIsolated yield.

Table S3 The details of the optimal reaction conditions^a

Entry	Acid	T ₁ / °C (time)	Oxidant	T ₂ / °C (time)	dr	Yield ^b /%
1	<i>p</i> -TsOH ^c	60 (20 min)	HTIB	60 (48 h)	5.3:1	60
2	<i>p</i> -TsOH	60 (20 min)	HTIB	60 (48 h)	5.2:1	64
3	<i>p</i> -TsOH	60 (20 min)	PIDA	60 (48 h)	4.9:1	60
4	<i>p</i> -TsOH	60 (20 min)	PhIO	60 (48 h)	6:1	60
5	<i>p</i> -TsOH	60 (20 min)	PIFA	60 (48 h)	5.2:1	63
6	<i>p</i> -TsOH	60 (20 min)	DMP	60 (48 h)	3.8:1	19
7	<i>p</i> -TsOH	60 (20 min)	IBX	60 (48 h)	4.8:1 ^d	12
8	<i>p</i> -TsOH	60 (20 min)	DDQ	60 (48 h)		0
9 ^d	<i>p</i> -TsOH	60 (20 min)	CAN	60 (48 h)		0
10	<i>p</i> -TsOH	60 (20 min)	Oxone	60 (48 h)		4
11	<i>p</i> -TsOH	60 (20 min)	K₂S₂O₈	60 (48 h)		6
12	HBF₄·H₂O	60 (30 min)	HTIB	60 (48 h)	5.3:1	44
13	TfOH	60 (20 min)	HTIB	60 (30 h)	5.0:1	45
14	Cu(OTf)₂	60 (20 min)	HTIB	60 (48 h)		9
15	AlCl₃	60 (7 h)	HTIB	60 (48 h)		0
16	TiCl₄	60 (20 min)	HTIB	60 (48 h)		0
17	<i>p</i> -TsOH	50 (30 min)	HTIB	50 (48 h)	6:1	56
18	<i>p</i> -TsOH	70 (20 min)	HTIB	70 (48 h)	5.1:1	59
19	<i>p</i> -TsOH	80 (20 min)	HTIB	80 (48 h)	4:1	57
20 ^e	<i>p</i> -TsOH	60 (2.5 h)	HTIB	60 (48 h)	5.8:1	51

^aOtherwise specified, reactions were performed using **2a** (0.2 mmol), acid (3.0 eq.), and oxidant (2.0 eq.) in 1.0 mL CH₃CN at the noted temperature in a 10 mL sealed tube. ^bIsolated yield. ^cacids (2.0 eq.). ^ddiastereomeric ratio after isolated. ^eacid (0.2 eq.).

Table S4 The screening of equivalent of CH₃CN ^a

Entry	Acid	T ₁ / °C (time)	Oxidant	T ₂ / °C (time)	Solvent	CH ₃ CN	Yield ^b /%
1	<i>p</i> -TsOH	60 (20 min)	HTIB	60 (48 h)	HFIP	10 eq	trace
2	<i>p</i> -TsOH	60 (20 min)	HTIB	60 (48 h)	HFIP	20 eq	2
3	<i>p</i> -TsOH	60 (20 min)	HTIB	60 (48 h)	HFIP	30 eq	3
4 ^c	<i>p</i> -TsOH	60 (20 min)	HTIB	60 (48 h)	HFIP	0.5 ml	10

^aOtherwise specified, the reactions were performed using **2a** (0.2 mmol), *p*-TsOH·H₂O (3.0 equiv.) and HTIB (2.0 equiv.) in 1.0 mL HFIP at the noted temperature. ^bNMR yield. ^cCH₃CN:HFIP = 0.5mL:0.5mL.

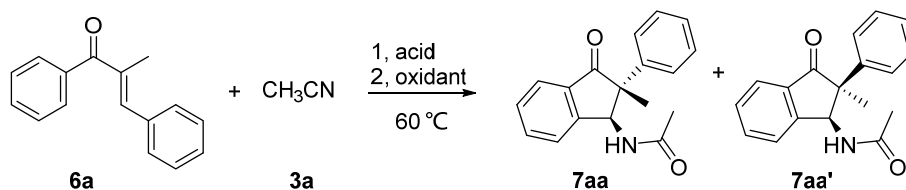
3.2 Construct 2-quaternary-3-amidoindanones from chalcone derivatives

3.2.1 General procedure B

Unless otherwise stated, the general procedure is as follows: to a 10 mL sealed tube containing a magnetic stir bar were added sequentially chalcone derivatives (0.2 mmol), TfOH (53 μ L, 0.6 mmol) and nitrile (1 mL) at room temperature, then the mixture was placed in a preheated oil bath at 60 °C and stirred for the indicated time. After the indicated time, the reaction mixture was cooled down to room temperature, HTIB (156.9 mg, 0.4 mmol) was added and the mixture was stirred at 60 °C for the indicated time. The reaction mixture was cooled to room temperature, diluted with DCM (15.0mL) and H₂O (15.0 mL), and the aqueous layer was extracted with DCM. The combined organic phase was successively washed with water and brine, dried with Na₂SO₄, filtered, and concentrated in vacuum. The residues were purified by flash column chromatography on silica gel (DCM/CH₃OH or petroleum ether/ethyl acetate) to afford the desired product.

3.2.2 The details for the optimization of reaction conditions

Table S5 The details of the optimal reaction conditions^a



Entry	Acid	Oxidant	T ₁ / °C (time)	T ₂ / °C(time)	dr	Yield ^b /%
1	<i>p</i> -TsOH					NR
2 ^c	HBF ₄ ·H ₂ O					NR
3	TiCl ₄					complex
4	Cu(OTf) ₂					NR
5	BF ₃ ·Et ₂ O	HTIB	60 (12 h)	60 (24 h)	11.0:1	51
6	TfOH	HTIB	60 (1.5 h)	60 (8 h)	10.9:1	70
7	TfOH	HTIB	60 (1.5 h)	60 (4 h)	11.8:1	64
8	TfOH	PhIO	60 (1.5 h)	60 (8 h)	12.8:1	40
9	TfOH	PhIO	60 (1.5 h)	60 (3 h)	11.5:1	50
10	TfOH	PhIO	60 (1.5 h)	60 (1.25 h)	12.0:1	41
11	TfOH	PIDA	60 (1.5 h)	60 (8 h)	11.7:1	33
12	TfOH	PIDA	60 (1.5 h)	60 (4 h)	11.0:1	32
13	TfOH	DMP	60 (1.5 h)	60 (3 h)		44
14	TfOH	PIFA	60 (1.5 h)	60		decomposition

^aOtherwise specified, the reactions were performed using **6a** (0.2 mmol), acids (3.0 equiv.), and oxidant (2.0 equiv.) in 1.0 mL CH₃CN at the noted temperature; ^bIsolated yield; ^c50 wt. % in H₂O.

3.3 Some control experiments

3.3.1 Quenching the reaction at different time

Following the general procedure A, quenching the reaction at different times after adding oxidant was performed, and the result was shown in Figure S1. The yields of **4**, **8** and **5aa** were determined by ^1H NMR.

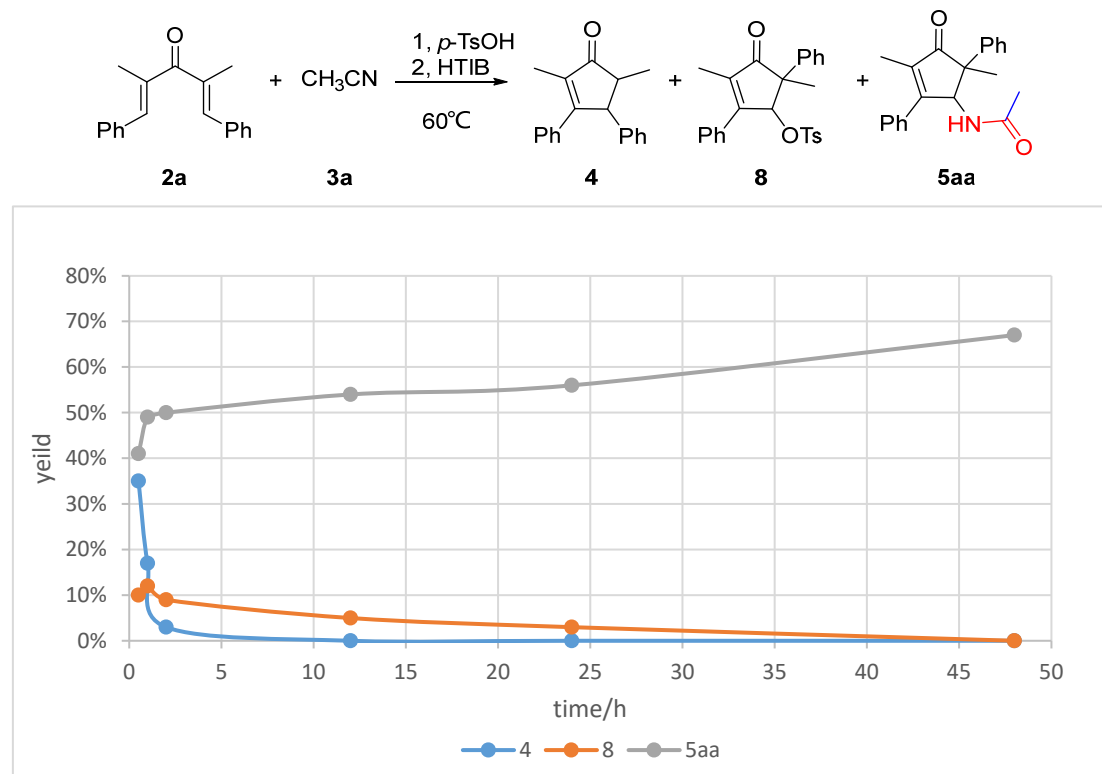
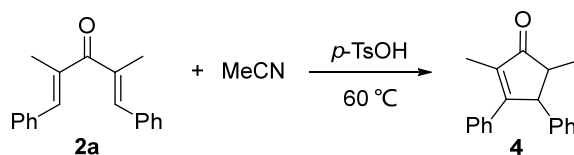


Figure S1 Quenching the reaction at different time

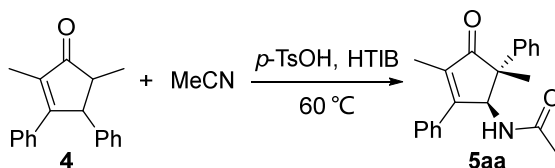
3.3.2 The Nazarov reaction of substrate **2a**



To a 10 mL sealed tube containing a magnetic stir bar were added divinyl ketone **2a** (52.5 mg, 0.2 mmol), *p*-TsOH·H₂O (114.1 mg, 0.6 mmol) and nitrile (1 mL) at room temperature, then the mixture was placed in a preheated oil bath at 60 °C and stirred for the 20 min. The reaction mixture was cooled to room temperature, diluted with DCM (15.0 mL) and H₂O (15.0 mL), and the aqueous layer was extracted with DCM. The combined organic phase was successively washed with water and brine, dried with Na₂SO₄, filtered, and concentrated in vacuum. The residues were purified by flash

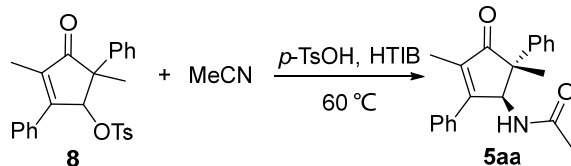
column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to afford the desired compound **4** (48.7 mg, 93%, 6.8:1).

3.3.3 The reaction of compound **4** under standard reaction conditions



compound **4**, *p*-TsOH·H₂O (3 eq.), HTIB (3 eq.) and nitrile (1 mL) were added to a 10 mL sealed tube fitted with a magnetic stirring rod at room temperature, then the mixture was placed in a preheated oil bath at 60 °C and stirred for the 48 h. The reaction mixture was cooled to room temperature, diluted with DCM (15.0 mL) and H₂O (15.0 mL), and the aqueous layer was extracted with DCM. The combined organic phase was successively washed with water and brine, dried with Na₂SO₄, filtered, and concentrated in vacuum. The residues were purified by flash column chromatography on silica gel to afford the desired product **5aa**.

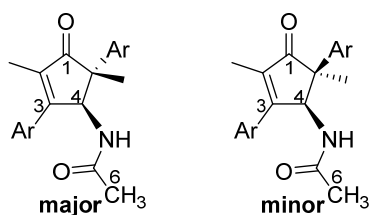
3.3.4 The reaction of byproduct **8** under standard reaction conditions



Byproduct **8** (18 mg, 0.04 mmol), *p*-TsOH·H₂O (23.7 mg, 0.12 mmol), HTIB (32.6 mg, 0.08 mmol) and nitrile (0.4 mL) were added to a 10 mL sealed tube fitted with a magnetic stirring rod at room temperature, then the mixture was placed in a preheated oil bath at 60 °C and stirred for the 50 h. The reaction mixture was cooled to room temperature, diluted with DCM (15.0 mL) and H₂O (15.0 mL), and the aqueous layer was extracted with DCM. The combined organic phase was successively washed with water and brine, dried with Na₂SO₄, filtered, and concentrated in vacuum. The residues were purified by flash column chromatography on silica gel to afford the desired product **5aa** (5.3 mg, 40%).

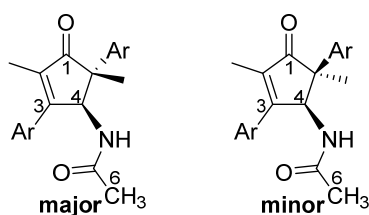
3.4 Explanation of the structure assignment for the two diastereoisomer

Table S6 Comparison of H-4 NMR data of two diastereoisomer

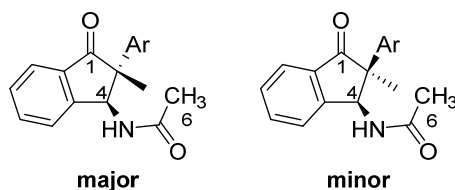


Compounds	Major H-4	Minor H-4	$\Delta\delta$ (ppm)
5aa/5aa'	5.96 (d, $J = 9.6$ Hz)	5.72 (dd, $J = 10.4$ Hz, 2.0 Hz)	0.24
5ba/5ba'	5.89 (d, $J = 9.6$ Hz)	5.68 (dd, $J = 10.4$ Hz, 1.6 Hz)	0.21
5ea/5ea'	5.89 (dd, $J = 10.0$ Hz, 2.0 Hz)	5.67 (dd, $J = 10.4$ Hz, 2.0 Hz)	0.22
5ga/5ga'	5.87 (dd, $J = 9.6$ Hz, 2.0 Hz)	5.67 (dd, $J = 10.0$ Hz, 1.6 Hz)	0.20
5ab/5ab'	5.97 (dd, $J = 9.6$ Hz, 1.6 Hz)	5.73 (dd, $J = 10.0$ Hz, 2.0 Hz)	0.24
5ai/5ai'	6.16 (dd, $J = 9.6$ Hz, 1.6 Hz)	5.95 (dd, $J = 10.2$ Hz, 2.4 Hz)	0.21

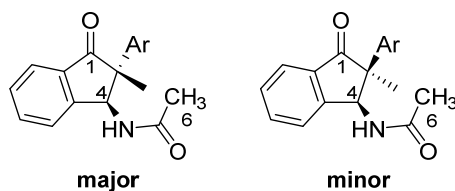
Table S7 Comparison of H-6 NMR data of two diastereoisomer



Compounds	Major H-6	Minor H-6	$\Delta\delta$ (ppm)
5aa/5aa'	1.92 (s)	1.46 (s)	0.46
5ba/5ba'	1.88 (s)	1.49 (s)	0.39
5ca/5ca'	1.89 (s)	1.48 (s)	0.41
5ea/5ea'	1.92 (s)	1.51 (s)	0.41
5fa/5fa'	1.92 (s)	1.53 (s)	0.39
5ga/5ga'	1.92 (s)	1.53 (s)	0.39

Table S8 Comparison of H-4 NMR data of two diastereoisomer

Compounds	Major H-4	Minor H-4	$\Delta\delta$ (ppm)
7da/7da'	5.92 (d, $J = 9.2$ Hz)	5.66 (d, $J = 9.6$ Hz)	0.26
7ea/7ea'	5.92 (d, $J = 9.2$ Hz)	5.66 (d, $J = 9.6$ Hz)	0.26
7ga/7ga'	6.14 (d, $J = 9.2$ Hz)	5.57 (d, $J = 9.2$ Hz)	0.57
7ia/7ia'	5.89 (d, $J = 9.2$ Hz)	5.53 (d, $J = 9.2$ Hz)	0.36
7ja/7ja'	5.89 (d, $J = 9.2$ Hz)	5.66 (d, $J = 9.2$ Hz)	0.23

Table S9 Comparison of H-4 NMR data of two diastereoisomer

Compounds	Major H-6	Minor H-6	$\Delta\delta$ (ppm)
7da/7da'	2.13 (s)	1.75 (s)	0.38
7ea/7ea'	2.13 (s)	1.74 (s)	0.39
7ga/7ga'	2.04 (s)	1.56 (s)	0.48
7ia/7ia'	2.08 (s)	1.55 (s)	0.53
7ja/7ja'	2.13 (s)	1.77 (s)	0.36

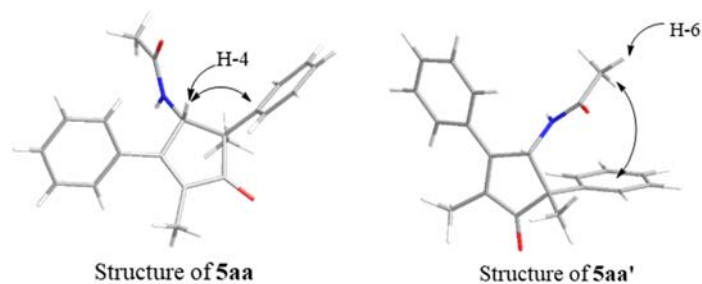


Figure S2 The Chem 3D chemical structure of major product **5aa** and minor product **5aa'**.

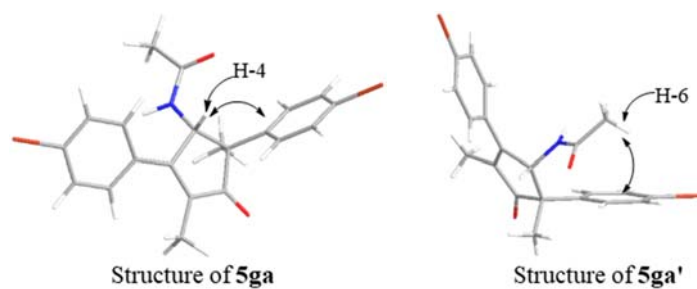


Figure S3 The Chem 3D chemical structure of major major product **5ga** and minor product **5ga'**.

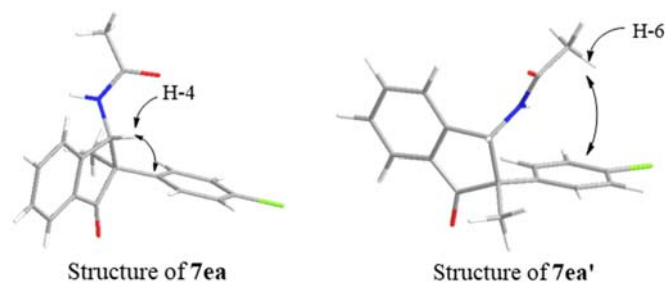


Figure S4 The Chem 3D chemical structure of major major product **7ea** and minor product **7ea'**.

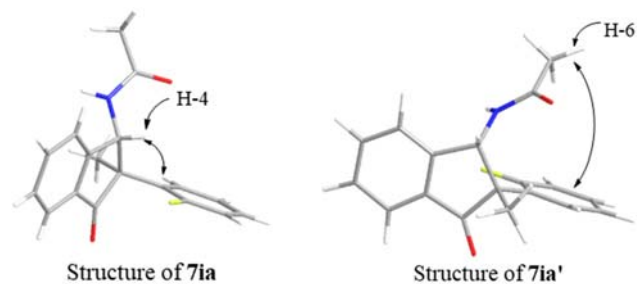
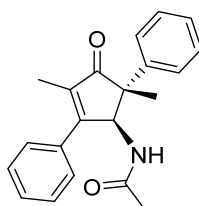


Figure S5 The Chem 3D chemical structure of major major product **7ia** and minor product **7ia'**.

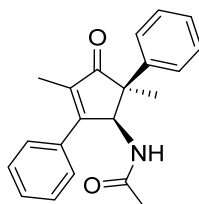
3.5 Characterization data of products



5aa

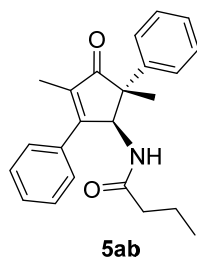
5aa: Following the general procedure A, reaction time: 20 min, 48h; 40.7 mg, 64% yield; dr: 5.2:1.

5aa: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 195.8-197.7 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.52-7.42 (m, 7 H), 7.34 (dd, *J* = 8.0 Hz, 8.0 Hz, 2 H), 7.26-7.22 (m, 1 H), 5.96 (d, *J* = 9.6 Hz, 1 H), 5.38 (d, *J* = 9.6 Hz, 1 H), 2.08 (s, 3 H), 1.92 (s, 3 H), 1.45 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 209.7, 170.1, 162.4, 143.8, 137.0, 133.4, 130.2, 128.9, 128.8, 128.6, 127.0, 126.5, 61.0, 54.7, 23.1, 20.9, 10.6; **HRMS** (ESI) *m/z* calculated for C₂₁H₂₁NO₂Na [M+Na]⁺ 342.1465, found 342.1464; **MS** (EI) *m/z* (%): 319 (100), 276 (15), 261 (28), 260 (71), 107 (6); **IR** (KBr plate): 3293, 2954, 2850, 1700, 1650, 1445, 1278, 1013, 733 cm⁻¹.



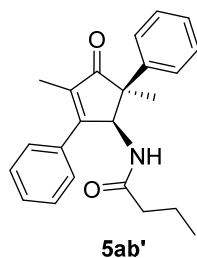
5aa'

5aa': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 201.3-203.2 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.53-7.50 (m, 2 H), 7.48-7.40 (m, 3 H), 7.33-7.29 (m, 2 H), 7.25-7.22 (m, 1 H), 7.15-7.13 (m, 2 H), 5.72 (dd, *J* = 10.4 Hz, 2.0 Hz, 1 H), 4.67 (d, *J* = 10.0 Hz, 1 H), 2.13 (d, *J* = 2.0 Hz, 3 H), 1.78 (s, 3 H), 1.46 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 209.7, 170.0, 163.3, 141.1, 138.2, 133.3, 130.1, 128.8, 128.7, 128.6, 127.5, 127.3, 60.6, 56.0, 23.4, 22.9, 10.6; **HRMS** (ESI) *m/z* calculated for C₂₁H₂₁NO₂Na [M+Na]⁺ 342.1465, found 342.1466; **MS** (EI) *m/z* (%): 319 (32), 262 (29), 261 (9), 107 (9), 57 (100); **IR** (KBr plate): 3292, 2956, 2851, 1736, 1649, 1443, 1262, 1016, 746 cm⁻¹.

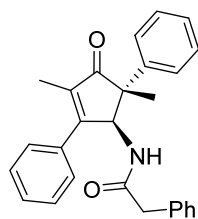


5ab: Following the general procedure A, reaction time: 30 min, 48 h; 32.1 mg, 46% yield; dr: 4.5:1.

5ab: Petroleum ether/ethyl acetate (6:1) as the eluent, white solid, m.p. = 179.0-180.6 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.48 (m, 2 H), 7.45-7.39 (m, 5 H), 7.35-7.31 (m, 2 H), 7.25-7.21 (m, 1 H), 5.97 (dd, *J* = 9.6 Hz, 1.6 Hz, 1 H), 5.47 (d, *J* = 9.6 Hz, 1 H), 2.15-1.99 (m, 5 H), 1.57-1.48 (m, 2 H), 1.44 (s, 3 H), 0.79 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 209.7, 173.0, 162.5, 143.8, 137.0, 133.4, 130.2, 128.9, 128.8, 128.6, 127.0, 126.6, 60.8, 54.6, 38.6, 21.1, 19.2, 13.7, 10.6; HRMS (ESI) *m/z* calculated for C₂₃H₂₅ NO₂Na [M+Na]⁺ 370.1778, found 370.1763; MS (EI) *m/z* (%): 347 (75), 262 (100), 115 (40), 107 (6), 71 (62); IR (KBr plate): 3291, 2956, 2871, 1703, 1642, 1453, 1086, 751 cm⁻¹.



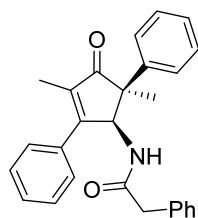
5ab': Petroleum ether/ethyl acetate (6:1) as the eluent, white solid, m.p. = 138.8-140.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.52-7.50 (m, 2 H), 7.47-7.39 (m, 3 H), 7.31-7.28 (m, 2 H), 7.24-7.21 (m, 1 H), 7.15-7.13 (m, 2 H), 5.73 (dd, *J* = 10.0 Hz, 2.0 Hz, 1 H), 4.67 (d, *J* = 10.4 Hz, 1 H), 2.12 (d, *J* = 2.0 Hz, 3 H), 1.78 (s, 3 H), 1.61 (td, *J* = 7.6 Hz, 2.0 Hz, 2 H), 1.23-1.14 (m, 2 H), 0.61 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (150 MHz, CDCl₃): δ 209.8, 172.7, 163.7, 141.1, 138.1, 133.3, 130.1, 128.8, 128.7, 127.5, 127.3, 60.3, 55.9, 38.3, 23.3, 18.7, 13.6, 10.6; HRMS (ESI) *m/z* calculated for C₂₃H₂₅ NO₂Na [M+Na]⁺ 370.1778, found 370.1767; MS (EI) *m/z* (%): 347 (89), 262 (100), 115 (35), 107 (3), 71 (30); IR (KBr plate): 3285, 2958, 1702, 1642, 1460, 1341, 1076, 749 cm⁻¹.



5ac

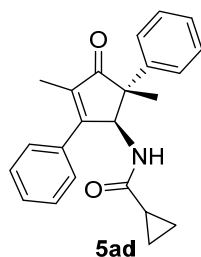
5ac: Following the general procedure A, reaction time: 30 min, 48 h; 37.4 mg, 47% yield; dr: 4.5:1.

5ac: Petroleum ether/ethyl acetate (8:1) as the eluent, white solid, m.p. = 159.0-160.3 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.43-7.36 (m, 7 H), 7.33-7.29 (m, 2 H), 7.24-7.14 (m, 4 H), 6.90-6.88 (m, 2 H), 5.89 (dd, *J* = 9.6 Hz, 2.0 Hz, 1 H), 5.42 (d, *J* = 9.6 Hz, 1 H), 3.48 (d, *J* = 15.6 Hz, 1 H), 3.42 (d, *J* = 15.6 Hz, 1 H), 1.98 (d, *J* = 1.6 Hz, 3 H), 1.27 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 209.4, 170.9, 162.6, 143.6, 136.9, 134.4, 133.3, 130.0, 129.2, 129.1, 128.81, 128.76, 128.4, 127.4, 127.0, 126.5, 61.1, 54.5, 43.7, 20.9, 10.4; **HRMS** (ESI) *m/z* calculated for C₂₇H₂₅NO₂Na [M+Na]⁺ 418.1778, found 418.1764; **MS** (EI) *m/z* (%): 395 (91), 262 (74), 115 (31), 91 (100), 77 (11); **IR** (KBr plate): 3291, 2954, 2851, 1703, 1642, 1452, 1340, 1076, 764 cm⁻¹.



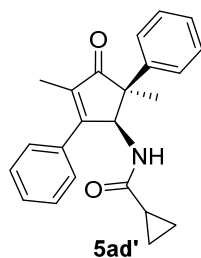
5ac'

5ac': Petroleum ether/ethyl acetate (8:1) as the eluent, white solid, m.p. = 163.6-165.6 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.43-7.36 (m, 5 H), 7.25-7.23 (m, 3 H), 7.11-7.07 (m, 1 H), 7.03-6.99 (m, 4 H), 6.45 (d, *J* = 7.2 Hz, 2 H), 5.64 (dd, *J* = 10.0 Hz, 2.0 Hz, 1 H), 4.59 (d, *J* = 10.0 Hz, 1 H), 3.13 (d, *J* = 16.4 Hz, 1 H), 3.04 (d, *J* = 16.4 Hz, 1 H), 2.04 (d, *J* = 2.0 Hz, 3 H), 1.75 (s, 3 H); ¹³C NMR (150 MHz, CDCl₃): δ 209.5, 170.5, 163.8, 140.9, 138.2, 133.8, 133.2, 129.9, 129.2, 128.8, 128.73, 128.72, 128.5, 127.21, 127.19, 127.1, 60.6, 55.7, 43.4, 23.1, 10.4; **HRMS** (ESI) *m/z* calculated for C₂₇H₂₅NO₂Na [M+Na]⁺ 418.1778, found 418.1761; **MS** (EI) *m/z* (%): 395 (2), 115 (14), 91 (100), 77 (4); **IR** (KBr plate): 3295, 2955, 2853, 1703, 1642, 1442, 1339, 1016, 764 cm⁻¹.

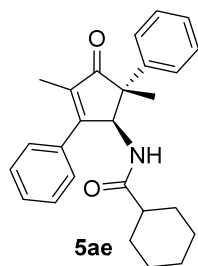


5ad: Following the general procedure A, reaction time: 30 min, 72 h; 32.6 mg, 47% yield; dr: 4.3:1.

5ad: Petroleum ether/ethyl acetate (8:1) as the eluent, white solid, m.p. = 194.6-196.5 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.53-7.51 (m, 2 H), 7.46-7.44 (m, 5 H), 7.32 (dd, $J = 7.6$ Hz, 7.6 Hz, 2 H), 7.24-7.20 (m, 1 H), 5.96 (d, $J = 9.6$ Hz, 1 H), 5.50 (d, $J = 8.8$ Hz, 1 H), 2.10 (s, 3 H), 1.47 (s, 3 H), 1.27-1.22 (m, 1 H), 1.00-0.88 (m, 2 H), 0.75-0.64 (m, 2 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 209.8, 173.8, 162.4, 143.9, 137.0, 133.4, 130.1, 128.83, 128.75, 128.7, 126.9, 126.5, 61.1, 54.9, 20.9, 14.7, 10.7, 7.6, 7.3; **HRMS** (ESI) m/z calculated for $\text{C}_{23}\text{H}_{23}\text{NO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 368.1621, found 368.1606; **MS** (EI) m/z (%): 345 (100), 262 (91), 115 (45), 77 (18), 69 (78); **IR** (KBr plate): 3307, 295, 2851, 1701, 1639, 1446, 1340, 1076, 765 cm^{-1} .

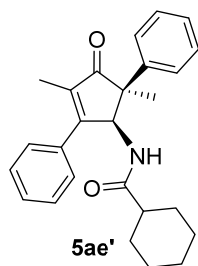


5ad': Petroleum ether/ethyl acetate (8:1) as the eluent, white solid, m.p. = 196.5-198.3 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.53-7.50 (m, 2 H), 7.48-7.40 (m, 3 H), 7.32-7.28 (m, 2 H), 7.25-7.21 (m, 1 H), 7.15-7.13 (m, 2 H), 5.72 (dd, $J = 10.4$ Hz, 2.0 Hz, 1 H), 4.83 (d, $J = 10.4$ Hz, 1 H), 2.13 (d, $J = 2.4$ Hz, 3 H), 1.76 (s, 3 H), 0.76-0.68 (m, 2 H), 0.66-0.61 (m, 1 H), 0.49-0.41 (m, 2 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 209.9, 173.6, 163.6, 141.0, 138.1, 133.3, 130.1, 128.84, 128.77, 128.5, 127.6, 127.2, 60.6, 56.0, 23.3, 14.5, 10.6, 7.4, 6.8; **HRMS** (ESI) m/z calculated for $\text{C}_{23}\text{H}_{23}\text{NO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 368.1621, found 368.1609; **MS** (EI) m/z (%): 345 (100), 262 (85), 115 (43), 77 (17), 69 (72); **IR** (KBr plate): 3311, 2956, 2870, 1701, 1640, 1444, 1339, 1014, 764 cm^{-1} .

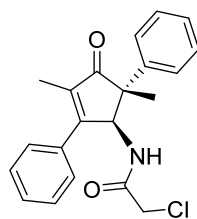


5ae: Following the general procedure A, reaction time: 30 min, 72 h; 34.5 mg, 45% yield; dr: 3.3:1.

5ae: Petroleum ether/ethyl acetate (10:1) as the eluent, white solid, m.p. = 168.5-170.1 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.48 (m, 2 H), 7.46-7.41 (m, 5 H), 7.34-7.30 (m, 2 H), 7.24-7.20 (m, 1 H), 5.94 (dd, *J* = 9.6 Hz, 1.6 Hz, 1 H), 5.42 (d, *J* = 9.6 Hz, 1 H), 2.08 (d, *J* = 1.6 Hz, 3 H), 2.04-1.95 (m, 1 H), 1.76-1.70 (m, 2 H), 1.65-1.52 (m, 3 H), 1.42 (s, 3 H), 1.37-1.23 (m, 2 H), 1.21-1.10 (m, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 209.7, 176.0, 162.5, 143.9, 136.9, 133.4, 130.1, 128.82, 128.78, 128.7, 127.0, 126.6, 60.6, 54.7, 45.5, 29.8, 29.5, 25.71, 25.66 25.6, 21.1, 10.6; HRMS (ESI) *m/z* calculated for C₂₆H₂₉NO₂Na [M+Na]⁺ 410.2091, found 410.2080; MS (EI) *m/z* (%): 387 (89), 276 (21), 262 (100), 115 (30), 77 (10); IR (KBr plate): 3293, 2926, 2853, 1701, 1642, 1447, 1339, 1076, 765 cm⁻¹.



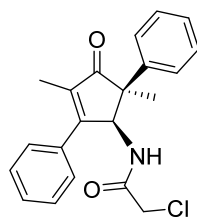
5ae': Petroleum ether/ethyl acetate (10:1) as the eluent, white solid, m.p. = 168.1-169.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.52-7.39 (m, 5 H), 7.33-7.21 (m, 3 H), 7.14-7.12 (m, 2 H), 5.70 (dd, *J* = 10.0 Hz, 2.0 Hz, 1 H), 4.73 (d, *J* = 10.0 Hz, 1 H), 2.13 (d, *J* = 2.0 Hz, 3 H), 1.77 (s, 3 H), 1.57-1.50 (m, 4 H), 1.26-1.14 (m, 2 H), 0.97-0.83 (m, 5 H); ¹³C NMR (100 MHz, CDCl₃): δ 210.0, 175.6, 163.7, 141.1, 137.9, 133.2, 130.1, 128.8, 128.7, 128.6, 127.5, 127.2, 59.9, 55.7, 45.1, 29.1, 29.0, 25.6, 25.5, 25.4, 23.3, 10.6; HRMS (ESI) *m/z* calculated for C₂₆H₂₉NO₂Na [M+Na]⁺ 410.2091, found 410.2090; MS (EI) *m/z* (%): 387 (7), 276 (7), 115 (62), 83 (100), 77 (30); IR (KBr plate): 3336, 2927, 2854, 1699, 1642, 1446, 1340, 1013, 754 cm⁻¹.



5af

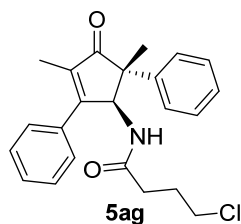
5af: Following the general procedure A, reaction time: 30 min, 48 h; 34.0 mg, 48% yield; dr: 7.7:1.

5af: Petroleum ether/ethyl acetate (7:1) as the eluent, white solid, m.p. = 182.6-185.1 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.48-7.44 (m, 5 H), 7.41-7.39 (m, 2 H), 7.37-7.33 (m, 2 H), 7.27-7.24 (m, 1 H), 6.48 (d, *J* = 9.6 Hz, 1 H), 5.93 (d, *J* = 9.6 Hz, 1 H), 4.06 (d, *J* = 15.2 Hz, 1 H), 3.94 (d, *J* = 15.2 Hz, 1 H), 2.09 (s, 3 H), 1.48 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 209.0, 166.0, 161.9, 143.4, 137.6, 133.1, 130.2, 128.94, 128.88, 128.4, 127.2, 126.4, 61.2, 54.6, 42.5, 20.8, 10.6; HRMS (ESI) *m/z* calculated for C₂₁H₂₀ClNO₂Na [M+Na]⁺ 376.1075, 378.1045, found 376.1058, 378.1021; MS (EI) *m/z* (%): 353 (30), 318 (100), 276 (10), 115 (33), 77 (19); IR (KBr plate): 3285, 2954, 2852, 1702, 1658, 1460, 1377, 1086, 750 cm⁻¹.



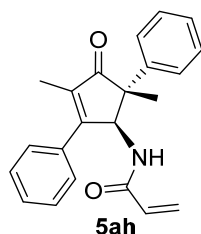
5af'

5af': Petroleum ether/ethyl acetate (7:1) as the eluent, white solid, m.p. = 134.6-136.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.52-7.50 (m, 2 H), 7.48-7.42 (m, 3 H), 7.34-7.30 (m, 2 H), 7.27-7.24 (m, 1 H), 7.16-7.13 (m, 2 H), 5.79 (d, *J* = 10.4 Hz, 1 H), 5.66 (dd, *J* = 10.4 Hz, 2.0 Hz, 1 H), 3.64 (d, *J* = 15.2 Hz, 1 H), 3.52 (d, *J* = 15.2 Hz, 1 H), 2.13 (d, *J* = 2.0 Hz, 3 H), 1.78 (s, 3 H); ¹³C NMR (150 MHz, CDCl₃): δ 209.3, 165.9, 162.8, 140.4, 138.7, 133.1, 130.2, 128.91, 128.89, 128.6, 127.6, 127.3, 60.8, 55.8, 42.2, 23.3, 10.6; HRMS (ESI) *m/z* calculated for C₂₁H₂₀ClNO₂Na [M+Na]⁺ 376.1075, 378.1045, found 376.1060, 378.1035; MS (EI) *m/z* (%): 353 (5), 318 (2), 115 (9), 105 (32), 71 (100); IR (KBr plate): 2955, 2850, 1657, 1452, 1076, 750 cm⁻¹.



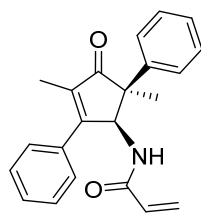
5ag: Following the general procedure A, reaction time: 30 min, 48 h; 34.3 mg, 45% yield; dr: 4.6:1.

5ag: Petroleum ether/ethyl acetate (6:1) as the eluent, white solid, m.p. = 156.8-158.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.50-7.47 (m, 2 H), 7.46-7.40 (m, 5 H), 7.35-7.32 (m, 2 H), 7.26-7.22 (m, 1 H), 5.96 (dd, *J* = 9.6 Hz, 1.6 Hz, 1 H), 5.75 (d, *J* = 9.6 Hz, 1 H), 3.47-3.41 (m, 1 H), 3.35-3.29 (m, 1 H), 2.36-2.29 (m, 1 H), 2.25-2.18 (m, 1 H), 2.06 (d, *J* = 2.0 Hz, 3 H), 2.02-1.95 (m, 2 H), 1.45 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 209.5, 171.7, 162.5, 143.7, 137.1, 133.3, 130.2, 128.93, 128.85, 128.6, 127.1, 126.5, 61.0, 54.6, 44.2, 33.2, 28.0, 21.0, 10.6; HRMS (ESI) *m/z* calculated for C₂₃H₂₄ClNO₂Na [M+Na]⁺ 404.1388, 406.1358, found 404.1370, 406.1340; MS (EI) *m/z* (%): 381 (69), 262 (100), 115 (40), 105 (27), 77 (26); IR (KBr plate): 3291, 2956, 2853, 1703, 1642, 1445, 1340, 1051, 765 cm⁻¹.



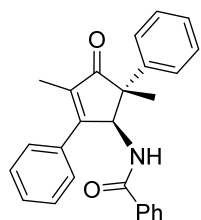
5ah: Following the general procedure A, reaction time: 30 min, 48 h; 36.3 mg, 55% yield; dr: 5.0:1.

5ah: Petroleum ether/ethyl acetate (5:1) as the eluent, white solid, m.p. = 196.4-198.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.49 (m, 2 H), 7.44-7.40 (m, 5 H), 7.35-7.31 (m, 2 H), 7.25-7.22 (m, 1 H), 6.24 (d, *J* = 16.8 Hz, 1 H), 6.03-5.94 (m, 2 H), 5.69 (d, *J* = 9.6 Hz, 1 H), 5.60 (d, *J* = 10.4 Hz, 1 H), 2.08 (d, *J* = 1.6 Hz, 3 H), 1.44 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 209.6, 165.6, 162.1, 143.8, 137.2, 133.2, 130.2, 130.1, 128.9, 128.8, 128.6, 127.7, 127.1, 126.5, 61.1, 54.9, 20.9, 10.7; HRMS (ESI) *m/z* calculated for C₂₂H₂₁NO₂Na [M+Na]⁺ 354.1465, found 354.1450; MS (EI) *m/z* (%): 331 (20), 276 (14), 260 (10), 115 (100), 77 (50); IR (KBr plate): 3275, 2954, 2854, 1702, 1657, 1445, 1340, 1075, 765 cm⁻¹.



5ah'

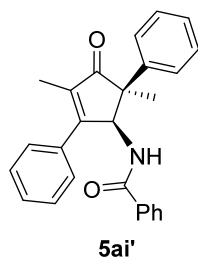
5ah': Petroleum ether/ethyl acetate (5:1) as the eluent, white solid, m.p. = 174.4-176.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.53-7.50 (m, 2 H), 7.46-7.38 (m, 3 H), 7.30-7.26 (m, 2 H), 7.24-7.20 (m, 1 H), 7.15-7.13 (m, 2 H), 5.83-5.78 (m, 2 H), 5.50 (dd, *J* = 17.2 Hz, 10.4 Hz, 1 H), 5.37 (dd, *J* = 10.4 Hz, 1.2 Hz, 1 H), 4.84 (d, *J* = 10.4 Hz, 1 H), 2.14 (d, *J* = 2.0 Hz, 3 H), 1.79 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 209.6, 165.6, 163.3, 140.9, 138.3, 133.2, 130.2, 130.1, 128.8, 128.74, 128.71, 127.40, 127.36, 126.7, 60.3, 56.1, 23.2, 10.6; HRMS (ESI) *m/z* calculated for C₂₂H₂₁NO₂Na [M+Na]⁺ 354.1465, found 354.1451; MS (EI) *m/z* (%): 331 (100), 276 (25), 260 (63), 117 (16), 77 (22); IR (KBr plate): 3311, 2956, 2854, 1702, 1657, 1443, 1339, 1014, 749 cm⁻¹.



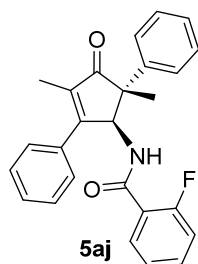
5ai

5ai: Following the general procedure A, reaction time: 30 min, 48 h; 38.2 mg, 50% yield; dr: 4.3:1.

5ai: Petroleum ether/ethyl acetate (8:1) as the eluent, white solid, m.p. = 186.6-187.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.59-7.55 (m, 4 H), 7.50-7.48 (m, 2 H), 7.46-7.34 (m, 8 H), 7.27-7.23 (m, 1 H), 6.16 (dd, *J* = 9.6 Hz, 1.6 Hz, 1 H), 6.09 (d, *J* = 9.6 Hz, 1 H), 2.12 (d, *J* = 1.6 Hz, 3 H), 1.52 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 209.6, 167.7, 162.2, 143.9, 137.4, 134.1, 133.3, 131.9, 130.3, 129.0, 128.9, 128.8, 128.6, 127.1, 127.0, 126.6, 61.6, 55.1, 21.0, 10.8; HRMS (ESI) *m/z* calculated for C₂₆H₂₃NO₂Na [M+Na]⁺ 404.1621, found 404.1608; MS (EI) *m/z* (%): 381 (31), 276 (9), 260 (23), 115 (10), 105 (100), 77 (40); IR (KBr plate): 3310, 2955, 1700, 1639, 1445, 1341, 1076, 696 cm⁻¹.

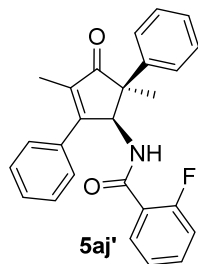


5ai': Petroleum ether/ethyl acetate (8:1) as the eluent, white solid, m.p. = 214.8-216.4 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.59-7.58 (m, 2 H), 7.44-7.42 (m, 2 H), 7.39-7.37 (m, 1 H), 7.33-7.28 (m, 3 H), 7.24-7.20 (m, 3 H), 7.18-7.16 (m, 2 H), 6.95-6.94 (m, 2 H), 5.95 (dd, *J* = 10.2 Hz, 2.4 Hz, 1 H), 5.32 (d, *J* = 10.2 Hz, 1 H), 2.16 (d, *J* = 2.4 Hz, 3 H), 1.85 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 209.6, 167.6, 163.6, 141.2, 138.4, 134.3, 133.2, 131.5, 130.2, 128.94, 128.85, 128.8, 128.4, 127.44, 127.39, 126.6, 60.7, 56.1, 23.3, 10.7; **HRMS** (ESI) *m/z* calculated for C₂₆H₂₄NO₂ [M+H]⁺ 382.1802, found 382.1793; **MS** (EI) *m/z* (%): 381 (1), 260 (1), 115 (16), 105 (100), 77 (79); **IR** (KBr plate): 3322, 2955, 1702, 1640, 1534, 1340, 1016, 748 cm⁻¹.

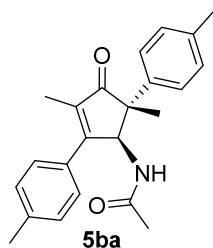


5aj: Following the general procedure A, reaction time: 30 min, 48 h; 43.4 mg, 54% yield; dr: 4.0:1.

5aj: Petroleum ether/ethyl acetate (10:1) as the eluent, white solid, m.p. = 167.3-169.0 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.00 (ddd, *J* = 8.0 Hz, 8.0 Hz, 2 Hz, 1 H), 7.57-7.54 (m, 2 H), 7.51-7.48 (m, 2 H), 7.44-7.33 (m, 6 H), 7.28-7.19 (m, 2 H), 7.01 (ddd, *J* = 12.0 Hz, 8.4 Hz, 0.8 Hz, 1 H), 6.65 (dd, *J* = 12.4 Hz, 9.6 Hz, 1 H), 6.21-6.18 (m, 1 H), 2.10 (d, *J* = 1.6 Hz, 3 H), 1.53 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 209.4, 163.5 (d, *J* = 3 Hz), 162.3, 160.5 (d, *J* = 245 Hz), 143.8, 137.4, 133.7 (d, *J* = 9 Hz), 133.4, 132.1 (d, *J* = 1 Hz), 130.1, 128.9, 128.8, 128.5, 127.0, 126.5, 125.0 (d, *J* = 3 Hz), 120.6 (d, *J* = 12 Hz), 116.1 (d, *J* = 24 Hz), 61.6, 55.0, 20.9, 10.6; ¹⁹F NMR (376 MHz, CDCl₃): δ -113.65; **HRMS** (ESI) *m/z* calculated for C₂₆H₂₂FNO₂Na [M+Na]⁺ 422.1527 found 422.1508; **MS** (EI) *m/z* (%): 399 (1), 123 (100), 115 (22), 95 (34), 77 (14); **IR** (KBr plate): 3326, 2955, 1702, 1640, 1450, 1341, 1076, 757 cm⁻¹.

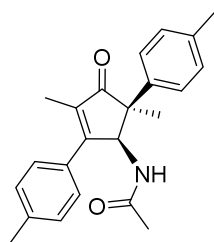


5aj': Petroleum ether/ethyl acetate (10:1) as the eluent, white solid, m.p. = 168.2-170.1 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.71 (ddd, *J* = 7.6 Hz, 7.6 Hz, 1.6 Hz, 1 H), 7.58-7.56 (m, 2 H), 7.45-7.38 (m, 3 H), 7.31-7.28 (m, 1 H), 7.24-7.22 (m, 2 H), 7.19-7.14 (m, 3 H), 7.11-7.08 (m, 1 H), 6.80 (dd, *J* = 12.0 Hz, 8.8 Hz, 1 H), 5.97-5.93 (m, 2 H), 2.14 (s, 3 H), 1.85 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 209.6, 163.7, 163.4 (d, *J* = 3 Hz), 160.3 (d, *J* = 247 Hz), 140.8, 138.5, 133.3 (d, *J* = 1 Hz), 133.2, 131.6 (d, *J* = 1 Hz), 130.1, 128.8, 128.69, 128.68, 127.3, 126.5, 124.6 (d, *J* = 4 Hz), 120.5 (d, *J* = 11 Hz), 116.0 (d, *J* = 24 Hz), 61.2, 56.1, 23.2, 10.6; ¹⁹F NMR (376 MHz, CDCl₃): δ -114.14; HRMS (ESI) *m/z* calculated for C₂₆H₂₃FNO₂ [M+H]⁺ 400.1707 found 400.1698; MS (EI) *m/z* (%): 399 (1), 123 (100), 115 (23), 95 (38), 77 (9); IR (KBr plate): 2955, 2851, 1702, 1641, 1452, 1340, 1015, 753 cm⁻¹.



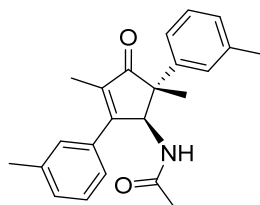
5ba: Following the general procedure A, reaction time: 20 min, 96 h; 29.1 mg, 42% yield; dr: 6.1:1.

5ba: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 181.6-182.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.39 (d, *J* = 8.0 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 5.89 (d, *J* = 9.6 Hz, 1 H), 5.73 (d, *J* = 9.6 Hz, 1 H), 2.38 (s, 3 H), 2.30 (s, 3 H), 2.04 (s, 3 H), 1.88 (s, 3 H), 1.40 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 209.8, 170.1, 162.3, 140.9, 140.5, 136.5, 136.2, 130.5, 129.6, 129.4, 128.6, 126.3, 60.9, 54.3, 23.1, 21.5, 21.0, 20.8, 10.7; HRMS (ESI) *m/z* calculated for C₂₃H₂₅NO₂Na [M+Na]⁺ 370.1778, found 370.1764; MS (EI) *m/z* (%): 347 (43), 289 (15), 107 (9), 91 (22), 57 (100); IR (KBr plate): 3292, 2924, 1701, 1655, 1460, 1121, 1014, 824 cm⁻¹.



5ba'

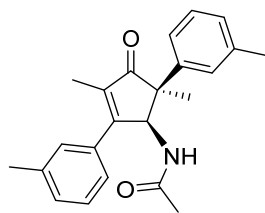
5ba': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 191.9-193.8 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.41 (d, *J* = 8.0 Hz, 2 H), 7.25 (d, *J* = 9.2 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 7.01 (d, *J* = 8.0 Hz, 2 H), 5.68 (dd, *J* = 10.4 Hz, 1.6 Hz, 1 H), 4.67 (d, *J* = 10.4 Hz, 1 H), 2.39 (s, 3 H), 2.30 (s, 3 H), 2.11 (d, *J* = 1.6 Hz, 3 H), 1.73 (s, 3 H), 1.49 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 209.8, 170.0, 163.4, 140.5, 138.1, 137.4, 136.9, 130.5, 129.5, 129.3, 128.8, 127.3, 60.4, 55.7, 23.4, 23.0, 21.6, 21.1, 10.7; **HRMS** (ESI) *m/z* calculated for C₂₃H₂₅NO₂Na [M+Na]⁺ 370.1778, found 370.1764; **MS** (EI) *m/z* (%): 347 (29), 289 (9), 107 (12), 91 (26), 57 (100); **IR** (KBr plate) 3321, 2923, 1701, 1649, 1459, 1376, 1075, 823 cm⁻¹.



5ca

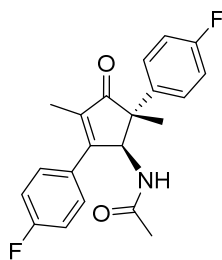
5ca: Following the general procedure A, reaction time: 20 min, 96 h; 27.7 mg, 40% yield; dr: 4.2:1.

5ca: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 137.6-139.3 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.34-7.28 (m, 3 H), 7.24-7.18 (m, 4 H), 7.05-7.03 (m, 1 H), 5.89 (dd, *J* = 9.6 Hz, 1.6 Hz, 1 H), 5.55 (d, *J* = 9.6 Hz, 1 H), 2.38 (s, 3 H), 2.33 (s, 3 H), 2.06 (d, *J* = 1.6 Hz, 3 H), 1.89 (s, 3 H), 1.42 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 209.9, 170.1, 162.7, 143.8, 138.6, 138.3, 136.9, 133.4, 130.9, 129.1, 128.7, 128.6, 127.8, 127.1, 125.7, 123.5, 61.3, 54.6, 23.1, 21.8, 21.6, 20.6, 10.7; **HRMS** (ESI) *m/z* calculated for C₂₃H₂₅NO₂Na [M+Na]⁺ 370.1778, found 370.1766; **MS** (EI) *m/z* (%): 347 (50), 289 (16), 107 (7), 91 (25), 57 (100); **IR** (KBr plate): 3276, 2954, 2853, 1702, 1656, 1460, 1339, 1007, 789 cm⁻¹.



5ca'

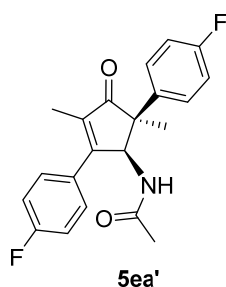
5ca': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 134.9-136.7 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.36-7.29 (m, 3 H), 7.23-7.16 (m, 2 H), 7.04 (d, *J* = 7.2 Hz, 1 H), 6.93-6.91 (m, 2 H), 5.68 (dd, *J* = 10.4 Hz, 2.0 Hz, 1 H), 4.66 (d, *J* = 10.4 Hz, 1 H), 2.40 (s, 3 H), 2.31 (s, 3 H), 2.11 (d, *J* = 2.0 Hz, 3 H), 1.75 (s, 3 H), 1.48 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 209.8, 170.0, 163.7, 141.1, 138.5, 138.2, 138.1, 133.4, 130.8, 129.3, 128.7, 128.5, 128.1, 128.0, 125.8, 124.5, 60.6, 55.9, 23.4, 22.9, 21.8, 21.6, 10.6; **HRMS** (ESI) *m/z* calculated for C₂₃H₂₅NO₂Na [M+Na]⁺ 370.1778, found 370.1762; **MS** (EI) *m/z* (%): 347 (19), 289 (7), 107 (4), 91 (12), 57 (100); **IR** (KBr plate): 3547, 2955, 1656, 1460, 1378, 1076 cm⁻¹.



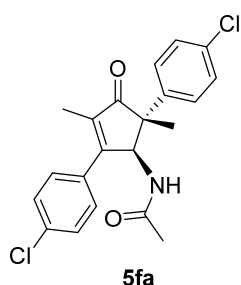
5ea

5ea: Following the general procedure A, reaction time: 20 min, 48h; 41.6 mg, 59% yield; dr: 4.7:1.

5ea: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 176.6-178.5 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.51-7.48 (m, 2 H), 7.41-7.38 (m, 2 H), 7.17-7.12 (m, 2 H), 7.03-6.99 (m, 2 H), 5.89 (dd, *J* = 10.0 Hz, 2.0 Hz, 1 H), 5.57 (d, *J* = 10.0 Hz, 1 H), 2.05 (d, *J* = 1.6 Hz, 3 H), 1.92 (s, 3 H), 1.41 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 209.1, 170.2, 163.6 (d, *J* = 250 Hz), 161.8 (d, *J* = 244 Hz), 161.2, 139.3 (d, *J* = 3 Hz), 136.7, 130.7 (d, *J* = 8 Hz), 129.2 (d, *J* = 4 Hz), 128.3 (d, *J* = 8 Hz), 116.2 (d, *J* = 22 Hz), 115.6 (d, *J* = 21 Hz), 60.8, 54.1, 23.2, 21.5, 10.6; **¹⁹F NMR** (376 MHz, CDCl₃): δ -109.04, -115.91; **HRMS** (ESI) *m/z* calculated for C₂₁H₁₉F₂NO₂Na [M+Na]⁺ 378.1276, found 378.1263; **MS** (EI) *m/z* (%): 355 (59), 298 (100), 268 (60), 259 (18), 107 (7); **IR** (KBr plate): 3275, 2955, 2851, 1703, 1656, 1461, 1234, 1014, 841 cm⁻¹.

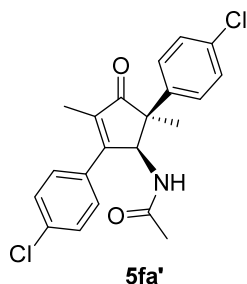


5ea': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 219.9-221.7 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.54-7.50 (m, 2 H), 7.17-7.10 (m, 4 H), 7.02-6.98 (m, 2 H), 5.67 (dd, *J* = 10.4 Hz, 2.0 Hz, 1 H), 4.68 (d, *J* = 10.0 Hz, 1 H), 2.11 (d, *J* = 1.6 Hz, 3 H), 1.74 (s, 3 H), 1.51 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 209.4, 170.0, 163.6 (d, *J* = 250 Hz), 161.86 (d, *J* = 245 Hz), 161.90, 137.7, 136.7 (d, *J* = 3 Hz), 130.8 (d, *J* = 8 Hz), 129.3 (d, *J* = 7 Hz), 129.2 (d, *J* = 3 Hz), 116.1 (d, *J* = 21 Hz), 115.4 (d, *J* = 21 Hz), 60.5, 55.3, 24.2, 22.9, 10.7; **¹⁹F NMR** (376 MHz, CDCl₃): δ -109.11, -114.92; **HRMS** (ESI) *m/z* calculated for C₂₁H₁₉ F₂NO₂Na [M+Na]⁺ 378.1276, found 378.1263; **MS** (EI) *m/z* (%): 355 (61), 298 (100), 268 (60), 259 (20), 107 (12); **IR** (KBr plate): 2955, 2851, 1701, 1656, 1460, 1234, 1015, 839 cm⁻¹.

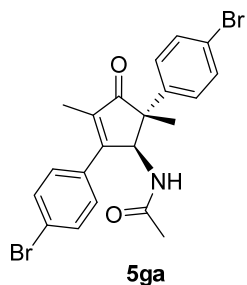


5fa: Following the general procedure A, reaction time: 20 min, 48h; 38.1 mg, 49% yield; dr: 4.7:1.

5fa: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 167.8-169.6 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.42 (brs, 4 H), 7.37-7.35 (m, 2 H), 7.30-7.27 (m, 2 H), 5.88 (d, *J* = 10.0 Hz, 1 H), 5.57 (d, *J* = 9.6 Hz, 1 H), 2.04 (s, 3 H), 1.92 (s, 3 H), 1.41 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 208.8, 170.2, 161.1, 142.0, 137.2, 136.4, 133.0, 131.5, 129.9, 129.3, 128.9, 128.1, 60.5, 54.3, 23.2, 21.3, 10.6; **HRMS** (ESI) *m/z* calculated for C₂₁H₁₉ Cl₂NO₂Na [M+Na]⁺ 410.0685, found 410.0665; **MS** (EI) *m/z* (%): 387 (54), 330 (100), 115 (59), 111 (15), 107 (8); **IR** (KBr plate): 3276, 2925, 1703, 1651, 1456, 1338, 1011, 736 cm⁻¹.

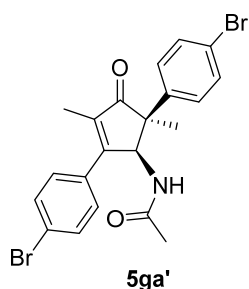


5fa': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 226.2–228.1 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.44 (brs, 4 H), 7.30–7.27 (m, 2 H), 7.09–7.07 (m, 2 H), 5.68 (dd, *J* = 10.4 Hz, 2.0 Hz, 1 H), 4.66 (d, *J* = 10.4 Hz, 1 H), 2.10 (d, *J* = 1.6 Hz, 3 H), 1.73 (s, 3 H), 1.53 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 209.0, 170.0, 161.8, 139.3, 138.3, 136.4, 133.3, 131.5, 130.0, 129.2, 129.0, 128.7, 60.3, 55.5, 24.0, 22.9, 10.6; **HRMS** (ESI) *m/z* calculated for C₂₁H₁₉ Cl₂NO₂Na [M+Na]⁺ 410.0685, found 410.0669; **MS** (EI) *m/z* (%): 387 (65), 330 (100), 115 (56), 111 (10), 107 (8); **IR** (KBr plate): 3350, 2955, 2851, 1695, 1462, 1377, 1094 cm⁻¹.

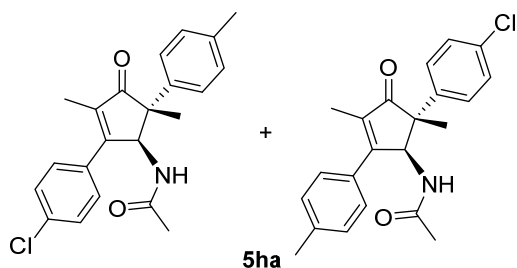


5ga: Following the general procedure A, reaction time: 20 min, 48h; 43.5 mg, 46% yield; dr: 4.4:1.

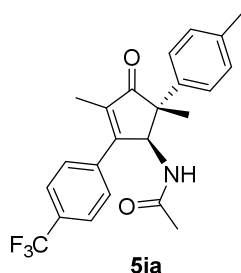
5ga: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 165.4–167.2 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.58 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 5.87 (dd, *J* = 9.6 Hz, 2.0 Hz, 1 H), 5.54 (d, *J* = 10.0 Hz, 1 H), 2.03 (d, *J* = 1.6 Hz, 3 H), 1.92 (s, 3 H), 1.40 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 208.7, 170.2, 161.1, 142.5, 137.3, 132.3, 132.0, 131.9, 130.1, 128.4, 124.8, 121.2, 60.4, 54.3, 23.2, 21.3, 10.6; **HRMS** (ESI) *m/z* calculated for C₂₁H₁₉ Br₂NO₂Na [M+Na]⁺ 497.9675, found 497.9642; **MS** (EI) *m/z* (%): 477 (82), 475 (42), 420 (100), 154 (8), 115 (94); **IR** (KBr plate): 3449, 2955, 1701, 1655, 1490, 1076 cm⁻¹.



5ga': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 233.2–234.7 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.59 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.8 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 5.67 (dd, *J* = 10.0 Hz, 1.6 Hz, 1 H), 4.70 (d, *J* = 10.4 Hz, 1 H), 2.09 (d, *J* = 1.2 Hz, 3 H), 1.73 (s, 3 H), 1.53 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 208.9, 170.0, 161.9, 139.9, 138.4, 132.2, 131.9, 131.7, 130.2, 129.4, 124.8, 121.4, 60.2, 55.6, 23.9, 22.9, 10.6; **HRMS** (ESI) *m/z* calculated for C₂₁H₁₉Br₂NO₂Na [M+Na]⁺ 497.9675, found 497.9661; **MS** (EI) *m/z* (%): 477 (84), 475 (42), 420 (99), 154 (8), 115 (100); **IR** (KBr plate): 3276, 2958, 1700, 1655, 1491, 1336, 1076, 731 cm⁻¹.

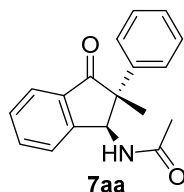


5ha: Following the general procedure A, reaction time: 20 min, 48h; mixture, 49% yield. **5ha**: DCM/MeOH (300:1–150:1) as the eluent, **¹H NMR** (400 MHz, CDCl₃): δ 7.45–7.35 (m, 7.4 H), 7.29–7.24 (m, 5.7 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 5.91 (dd, *J* = 10.0, 2.0 Hz, 1 H), 5.85 (dd, *J* = 9.6 Hz, 2.0 Hz, 0.8 H), 5.52 (s, 1 H), 5.49 (s, 0.7 H), 2.40 (s, 2.4 H), 2.31 (s, 3 H), 2.06 (d, *J* = 1.6 Hz, 2.3 H), 2.04 (d, *J* = 1.6 Hz, 3 H), 1.92 (s, 5.3 H), 1.41 (d, *J* = 4.0 Hz, 5.3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 209.5, 209.1, 170.2, 170.1, 162.4, 160.9, 142.3, 140.8, 140.6, 137.3, 136.7, 136.3, 136.2, 132.9, 131.8, 130.2, 129.9, 129.7, 129.5, 129.2, 128.9, 128.6, 128.1, 126.3, 60.7, 54.4, 54.3, 23.23, 23.19, 21.6, 21.08, 21.05, 10.8, 10.7.



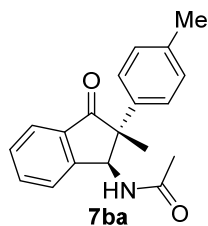
5ia: Following the general procedure A, reaction time: 20 min, 72h; 27.9 mg, 35% yield; dr: 6.7:1.

5ia: DCM/MeOH (300:1–150:1) as the eluent, a pale yellow amorphous solid. **¹H NMR** (600 MHz, CDCl₃): δ 7.68 (d, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 5.96 (dd, *J* = 10.2 Hz, 1.8 Hz, 1 H), 5.73 (d, *J* = 10.2 Hz, 1 H), 2.31 (s, 3 H), 2.03 (d, *J* = 1.8 Hz, 3 H), 1.88 (s, 3 H), 1.42 (s, 3 H); **¹³C NMR** (150 MHz, CDCl₃): δ 209.4, 170.1, 160.8, 140.4, 138.4, 137.0, 136.8, 131.7 (q, *J* = 33 Hz), 129.6, 128.8, 126.3, 125.8 (q, *J* = 4.5 Hz), 123.8 (q, *J* = 270 Hz), 60.8, 54.4, 23.1, 21.0, 10.5; **¹⁹F NMR** (376 MHz, CDCl₃): δ -62.89; **HRMS** (ESI) *m/z* calculated for C₂₃H₂₃F₃NO₂ [M+H]⁺ 402.1675, found 402.1667; **MS** (EI) *m/z* (%): 401 (9), 256 (33), 115 (57), 91 (100); **IR** (KBr plate): 2925, 1707, 1652, 1537, 1324, 1068, 749 cm⁻¹.



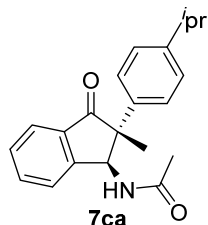
7aa: Following the general procedure B, reaction time: 1.5 h, 8 h; 39.1 mg, 70% yield; dr: 10.9:1.

7aa: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 213.4–215.4 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.83 (d, *J* = 7.6 Hz, 1 H), 7.71–7.67 (m, 1 H), 7.55–7.49 (m, 2 H), 7.39–7.37 (m, 2 H), 7.32–7.28 (m, 2 H), 7.23–7.20 (m, 1 H), 5.96 (d, *J* = 9.2 Hz, 1 H), 5.88 (d, *J* = 9.2 Hz, 1 H), 2.08 (s, 3 H), 1.48 (s, 3 H); **¹³C NMR** (150 MHz, CDCl₃): δ 207.0, 170.2, 151.6, 143.2, 135.9, 135.6, 129.7, 128.8, 127.1, 126.6, 126.3, 124.3, 59.5, 57.5, 23.2, 20.3; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₇NO₂Na [M+Na]⁺ 302.1151, found 302.1138; **MS** (EI) *m/z* (%): 279 (29), 236 (14), 222 (100), 159 (6), 77 (48); **IR** (KBr plate): 3245, 2956, 2851, 1714, 1650, 1463, 1274, 1076, 757 cm⁻¹.



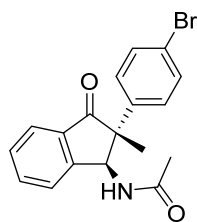
7ba: Following the general procedure B, reaction time: 0.5 h, 4 h; 34.3 mg, 58% yield; dr: 20:1.

7ba: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 208.6-209.9 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.79 (d, *J* = 7.6 Hz, 1 H), 7.66 (ddd, *J* = 7.6 Hz, 7.6 Hz, 0.8 Hz, 1 H), 7.53-7.47 (m, 2 H), 7.26-7.24 (m, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 5.98 (d, *J* = 9.6 Hz, 1 H), 5.92 (d, *J* = 9.2 Hz, 1 H), 2.29 (s, 3 H), 2.05 (s, 3 H), 1.45 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 207.1, 170.1, 151.6, 140.2, 136.7, 135.9, 135.6, 129.7, 129.5, 126.5, 126.2, 124.3, 59.6, 57.3, 23.3, 21.1, 20.3; **HRMS** (ESI) *m/z* calculated for C₁₉H₁₉NO₂Na [M+Na]⁺ 316.1308, found 316.1297; **MS** (EI) *m/z* (%): 293 (60), 236 (100), 234 (93), 174 (2), 77 (18); **IR** (KBr plate): 3525, 2954, 2869, 1719, 1650, 1461, 1274, 1076, 751 cm⁻¹.



7ca: Following the general procedure B, reaction time: 1 h, 8 h; 43.0 mg, 67% yield; dr: 16.9:1.

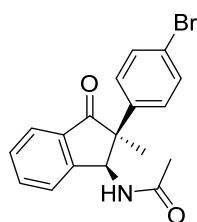
7ca: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 170.8-172.5 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.73 (d, *J* = 7.6 Hz, 1 H), 7.62 (ddd, *J* = 7.6 Hz, 7.6 Hz, 0.8 Hz, 1 H), 7.49-7.42 (m, 2 H), 7.25-7.23 (m, 2 H), 7.15-7.12 (m, 2 H), 6.39 (d, *J* = 9.6 Hz, 1 H), 5.87 (d, *J* = 9.6 Hz, 1 H), 2.90-2.79 (m, 1 H), 1.96 (s, 3 H), 1.41 (s, 3 H), 1.21 (s, 3 H), 1.19 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 207.3, 170.3, 151.8, 147.4, 140.5, 135.8, 135.5, 129.5, 126.7, 126.4, 126.3, 124.2, 59.4, 57.2, 33.7, 24.0, 23.1, 20.2; **HRMS** (ESI) *m/z* calculated for C₂₁H₂₃NO₂Na [M+Na]⁺ 344.1621, found 344.1606; **MS** (EI) *m/z* (%): 321 (89), 264 (100), 160 (29), 119 (3), 77 (17); **IR** (KBr plate): 3275, 2960, 2870, 1716, 1654, 1464, 1269, 960, 761 cm⁻¹.



7da

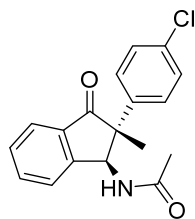
7da: Following the general procedure B, reaction time: 1.5 h, 8 h; 45.9 mg, 64% yield; dr: 6.4:1. white solid, m.p. = 231.2-233.1 °C. 167.0-168.9 °C.

7da: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 231.2-233.1 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 8.0 Hz, 1 H), 7.74-7.70 (m, 1 H), 7.57-7.52 (m, 2 H), 7.45-7.31 (m, 2 H), 7.31-7.28 (m, 2 H), 5.92 (d, *J* = 9.2 Hz, 1 H), 5.75 (d, *J* = 9.2 Hz, 1 H), 2.13 (s, 3 H), 1.47 (s, 3 H); ¹³C NMR (100 MHz, (CD₃)₂SO): δ 206.2, 169.7, 152.2, 143.2, 136.1, 134.5, 131.3, 129.6, 128.8, 126.5, 123.6, 119.9, 58.8, 56.8, 22.5, 19.4; HRMS (ESI) *m/z* calculated for C₁₈H₁₆BrNO₂Na [M+Na]⁺ 380.0257, 382.0236, found 380.0249, 382.0217; MS (EI) *m/z* (%): 359 (22), 357 (22), 300 (100), 160 (40), 77 (25); IR (KBr plate): 3256, 2955, 2851, 1720, 1650, 1462, 1376, 1077, 759 cm⁻¹.



7da'

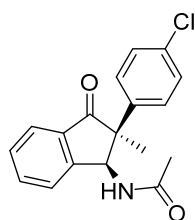
7da': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 167.0-168.9 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.91-7.89 (m, 1 H), 7.75-7.71 (m, 1 H), 7.58-7.54 (m, 2 H), 7.42-7.39 (m, 2 H), 6.97-6.93 (m, 2 H), 5.66 (d, *J* = 9.6 Hz, 1 H), 5.18 (d, *J* = 9.2 Hz, 1 H), 1.78 (s, 3 H), 1.75 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 206.6, 170.2, 151.7, 139.6, 136.4, 136.3, 131.7, 129.9, 129.4, 126.2, 124.4, 121.5, 59.4, 58.4, 23.11, 23.09; HRMS (ESI) *m/z* calculated for C₁₈H₁₆BrNO₂Na [M+Na]⁺ 380.0257, 382.0236, found 380.0241, 382.0219; MS (EI) *m/z* (%): 359 (22), 357 (23), 300 (100), 160 (43), 77 (32); IR (KBr plate): 3273, 2956, 2851, 1716, 1651, 1490, 1276, 1088, 760 cm⁻¹.



7ea

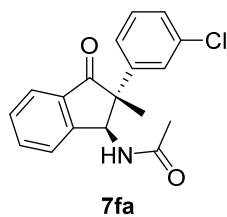
7ea: Following the general procedure B, reaction time: 1.5 h, 8 h; 43.2 mg, 69% yield; dr: 7.3:1.

7ea: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 229.4–231.1 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.85 (d, *J* = 7.6 Hz, 1 H), 7.74–7.70 (m, 1 H), 7.57–7.52 (m, 2 H), 7.37–7.34 (m, 2 H), 7.29–7.26 (m, 2 H), 5.92 (d, *J* = 9.2 Hz, 1 H), 5.74 (d, *J* = 9.6 Hz, 1 H), 2.13 (s, 3 H), 1.47 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.3, 170.1, 151.3, 141.7, 136.2, 135.5, 133.1, 130.0, 128.9, 128.3, 126.2, 124.6, 59.5, 57.2, 23.4, 20.6; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₆ClNO₂Na [M+Na]⁺ 336.0762, 338.0732, found 336.0751, 338.0722; **MS** (EI) *m/z* (%): 315 (11), 313 (30), 256 (100), 160 (35), 132 (21), 77 (19); **IR** (KBr plate): 3247, 2955, 2851, 1721, 1650, 1461, 1276, 1014, 760 cm⁻¹.



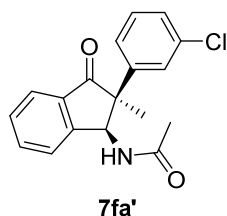
7ea'

7ea': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 159.3–160.8 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.91–7.89 (m, 1 H), 7.75–7.71 (m, 1 H), 7.58–7.54 (m, 2 H), 7.27–7.24 (m, 2 H), 7.03–6.99 (m, 2 H), 5.66 (d, *J* = 9.6 Hz, 1 H), 5.17 (d, *J* = 9.6 Hz, 1 H), 1.79 (s, 3 H), 1.74 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.7, 170.2, 151.7, 139.0, 136.34, 136.25, 133.4, 129.8, 129.0, 128.7, 126.2, 124.4, 59.4, 58.3, 23.2, 23.1; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₆ClNO₂Na [M+Na]⁺ 336.0762, 338.0732, found 336.0745, 338.0711; **MS** (EI) *m/z* (%): 315 (11), 313 (30), 256 (100), 160 (35), 132 (22), 77 (22); **IR** (KBr plate): 3276, 2956, 2850, 1712, 1656, 1461, 1276, 1014, 764 cm⁻¹.

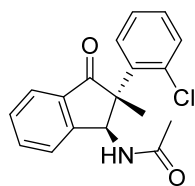


7fa: Following the general procedure B, reaction time: 1.5 h, 10 h; 29.8 mg, 47% yield; dr: 4.8:1. white solid, m.p. = 170.9-171.9 °C. 61.5-62.6 °C.

7fa: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 170.9-171.9 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.82 (d, *J* = 7.6 Hz, 1 H), 7.70 (ddd, *J* = 7.6 Hz, 7.6 Hz, 1.2 Hz, 1 H), 7.55-7.50 (m, 2 H), 7.362-7.359 (m, 1 H), 7.28-7.19 (m, 3 H), 6.02 (d, *J* = 9.2 Hz, 1 H), 5.87 (d, *J* = 9.2 Hz, 1 H), 2.07 (s, 3 H), 1.45 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.2, 170.2, 151.4, 145.2, 136.2, 135.3, 134.6, 130.0, 129.9, 127.4, 127.0, 126.2, 125.0, 124.5, 59.5, 57.3, 23.2, 20.3; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₆ClNO₂Na [M+Na]⁺ 336.0762, 338.0732, found 336.0746, 338.0723; **MS** (EI) *m/z* (%): 315 (10), 313 (29), 256 (100), 160 (47), 132 (22), 77 (18); **IR** (KBr plate): 3272, 2955, 2870, 1715, 1656, 1462, 1288, 1092, 761 cm⁻¹.



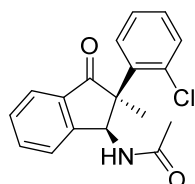
7fa': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 61.5-62.6 °C. **¹H NMR** (600 MHz, CDCl₃): δ 7.90 (d, *J* = 7.8 Hz, 1 H), 7.75-7.72 (m, 1 H), 7.58-7.56 (m, 2 H), 7.24-7.20 (m, 2 H), 7.059-7.056 (m, 1 H), 6.97-6.96 (m, 1 H), 5.67 (d, *J* = 10.2 Hz, 1 H), 5.20 (d, *J* = 9.6 Hz, 1 H), 1.80 (s, 3 H), 1.74 (s, 3 H); **¹³C NMR** (150 MHz, CDCl₃): δ 206.4, 170.2, 151.6, 142.6, 136.31, 136.29, 134.6, 129.9, 129.8, 127.9, 127.7, 126.2, 125.8, 124.5, 59.4, 58.6, 23.1, 23.0; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₆ClNO₂Na [M+Na]⁺ 336.0762, 338.0732, found 336.0746, 338.0740; **MS** (EI) *m/z* (%): 315 (11), 313 (31), 256 (100), 160 (52), 132 (29), 77 (31); **IR** (KBr plate): 3275, 2957, 2851, 1714, 1657, 1463, 1265, 1087, 746 cm⁻¹.



7ga

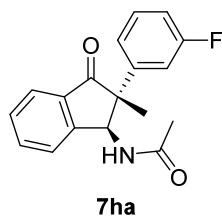
7ga: Following the general procedure B, reaction time: 2 h, 10 h; 26.0 mg, 41% yield; dr: 2.8:1. white solid, m.p. = 238.5-240.2 °C. 55.1-57.0 °C.

7ga: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 238.5-240.2 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.88-7.86 (m, 1 H), 7.70 (ddd, *J* = 7.6 Hz, 7.6 Hz, 0.8 Hz, 1 H), 7.55-7.51 (m, 2 H), 7.40 (dd, *J* = 7.6 Hz, 1.6 Hz, 1 H), 7.36 (dd, *J* = 7.6 Hz, 1.6 Hz, 1 H), 7.32-7.23 (m, 2 H), 6.14 (d, *J* = 9.2 Hz, 1 H), 5.85 (d, *J* = 9.2 Hz, 1 H), 2.04 (s, 3 H), 1.43 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 204.9, 170.0, 150.4, 139.2, 135.3, 135.2, 133.2, 130.7, 129.5, 129.4, 129.1, 127.1, 125.1, 124.5, 57.6, 57.4, 23.3, 19.5; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₆ClNO₂Na [M+Na]⁺ 336.0762, 338.0732, found 336.0756, 338.0725; **MS** (EI) *m/z* (%): 313 (42), 315 (14), 256 (100), 160 (57), 132 (25), 77 (25); **IR** (KBr plate): 2954, 2851, 1720, 1656, 1461, 1268, 1075, 765 cm⁻¹.



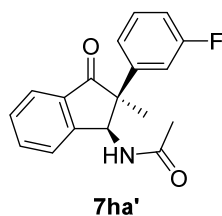
7ga'

7ga': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 55.1-57.0 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.89 (d, *J* = 7.6 Hz, 1 H), 7.74-7.70 (m, 1 H), 7.63 (dd, *J* = 8.0 Hz, 1.6 Hz, 1 H), 7.58-7.54 (m, 2 H), 7.37-7.23 (m, 3 H), 6.02 (d, *J* = 7.6 Hz, 1 H), 5.57 (d, *J* = 9.2 Hz, 1 H), 1.79 (s, 3 H), 1.56 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.1, 170.0, 149.9, 137.8, 136.1, 135.5, 133.7, 131.5, 129.9, 129.8, 129.2, 127.5, 126.2, 124.6, 60.4, 58.2, 25.1, 22.6; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₆ClNO₂Na [M+Na]⁺ 336.0762, 338.0732, found 336.0758, 338.0727; **MS** (EI) *m/z* (%): 313 (7), 256 (4), 160 (2), 132 (5), 71 (100); **IR** (KBr plate): 2955, 2851, 1720, 1656, 1461, 1376, 753 cm⁻¹.

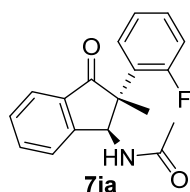


7ha: Following the general procedure B, reaction time: 2 h, 10 h; 26.5 mg, 45% yield; dr: 5.6:1.

7ha: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 200.6-202.1 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.83 (d, *J* = 7.6 Hz, 1 H), 7.73-7.69 (m, 1 H), 7.56-7.50 (m, 2 H), 7.30-7.24 (m, 1 H), 7.16-7.10 (m, 2 H), 6.94-6.90 (m, 1 H), 5.94-5.89 (m, 2 H), 2.09 (s, 3 H), 1.46 (s, 3 H); **¹³C NMR** (150 MHz, CDCl₃): δ 206.2, 170.2, 163.0 (d, *J* = 244.5 Hz), 151.4, 145.7 (d, *J* = 7.5 Hz), 136.2, 135.4 130.3 (d, *J* = 9 Hz), 129.9, 126.2, 124.6, 122.4 (d, *J* = 1.5 Hz), 114.10 (d, *J* = 19.5 Hz), 114.06 (d, *J* = 22.5 Hz), 59.5, 57.3, 23.3, 20.3; **¹⁹F NMR** (376 MHz, CDCl₃): δ -112.22; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₇FNO₂ [M+H]⁺ 298.1238, found 298.1233; **MS** (EI) *m/z* (%): 297 (36), 240 (100), 160 (40), 132 (19), 77 (13); **IR** (KBr plate): 3245, 2955, 2851, 1719, 1650, 1462, 1249, 1076, 751 cm⁻¹.

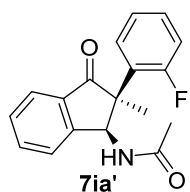


7ha': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 132.9-134.5 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.91 (d, *J* = 7.6 Hz, 1 H), 7.76-7.72 (m, 1 H), 7.58-7.55 (m, 2 H), 7.29-7.23 (m, 1 H), 6.98-6.93 (m, 1 H), 6.85-6.78 (m, 2 H), 5.68 (d, *J* = 9.6 Hz, 1 H), 5.16 (d, *J* = 9.6 Hz, 1 H), 1.81 (s, 3 H), 1.74 (s, 3 H); **¹³C NMR** (150 MHz, CDCl₃): δ 206.4, 170.2, 162.9 (d, *J* = 246 Hz), 151.8, 143.1 (d, *J* = 6 Hz), 136.3 (d, *J* = 16.5 Hz), 130.2 (d, *J* = 9 Hz), 129.9, 126.2, 124.5, 123.2 (d, *J* = 3 Hz), 114.8 (d, *J* = 21 Hz), 114.4 (d, *J* = 21 Hz), 59.4, 58.5, 23.1, 22.9; **¹⁹F NMR** (376 MHz, CDCl₃): δ -111.74; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₇FNO₂ [M+H]⁺ 298.1238, found 298.1232; **MS** (EI) *m/z* (%): 297 (16), 240 (47), 160 (17), 132 (12), 71 (100); **IR** (KBr plate): 3275, 2956, 2850, 1714, 1657, 1462, 1265, 1087, 754 cm⁻¹.

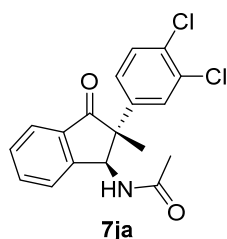


7ia: Following the general procedure B, reaction time: 1.5 h, 8 h; 26.3 mg, 44% yield; dr: 2.2:1.

7ia: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 216.8–218.7 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.89–7.87 (m, 1 H), 7.72 (ddd, *J* = 7.2 Hz, 7.2 Hz, 0.8 Hz, 1 H), 7.56–7.52 (m, 2 H), 7.35 (ddd, *J* = 8 Hz, 8 Hz, 1.6 Hz, 1 H), 7.31–7.25 (m, 1 H), 7.16 (ddd, *J* = 7.6 Hz, 7.6 Hz, 1.2 Hz, 1 H), 7.01 (ddd, *J* = 11.6 Hz, 8.4 Hz, 1.2 Hz, 1 H), 5.89 (d, *J* = 9.2 Hz, 1 H), 5.79 (d, *J* = 9.2 Hz, 1 H), 2.08 (s, 3 H), 1.44 (s, 3 H); ¹³C NMR (150 MHz, CDCl₃): δ 205.6, 170.0, 160.4 (d, *J* = 244.5 Hz), 150.9, 135.7, 134.4, 129.8 (d, *J* = 13.5 Hz), 129.6, 129.4 (d, *J* = 9 Hz), 128.6 (d, *J* = 4.5 Hz), 125.3, 124.7, 124.4 (d, *J* = 3 Hz), 115.9 (d, *J* = 22.5 Hz), 58.7 (d, *J* = 3 Hz), 54.9, 23.3, 18.0; ¹⁹F NMR (376 MHz, CDCl₃): δ -110.89; HRMS (ESI) *m/z* calculated for C₁₈H₁₆FNO₂Na [M+Na]⁺ 320.1057, found 320.1047; MS (EI) *m/z* (%): 297 (30), 240 (100), 160 (38), 132 (17), 77 (15); IR (KBr plate): 2955, 2851, 1717, 1654, 1457, 1088, 747 cm⁻¹.

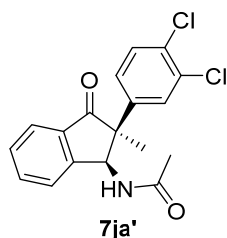


7ia': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 145.9–147.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, *J* = 7.6 Hz, 1 H), 7.73 (ddd, *J* = 8.0 Hz, 8.0 Hz, 0.8 Hz, 1 H), 7.59–7.54 (m, 2 H), 7.50 (ddd, *J* = 7.6 Hz, 7.6 Hz, 1.6 Hz, 1 H), 7.31–7.26 (m, 1 H), 7.20 (ddd, *J* = 7.6 Hz, 7.6 Hz, 1.2 Hz, 1 H), 6.94 (ddd, *J* = 11.2 Hz, 8.0 Hz, 1.2 Hz, 1 H), 5.70 (d, *J* = 9.2 Hz, 1 H), 5.53 (d, *J* = 9.2 Hz, 1 H), 1.77 (s, 3 H), 1.55 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 206.6 (d, *J* = 2 Hz), 170.0, 160.4 (d, *J* = 241 Hz), 150.2, 135.7, 135.2 (d, *J* = 2 Hz), 130.3 (d, *J* = 5 Hz), 129.8, 129.5 (d, *J* = 8 Hz), 127.2 (d, *J* = 15 Hz), 126.4, 124.74, 124.71, 114.8 (d, *J* = 22 Hz), 59.8, 56.0 (d, *J* = 2 Hz), 23.1, 22.5; ¹⁹F NMR (376 MHz, CDCl₃): δ -105.59; HRMS (ESI) *m/z* calculated for C₁₈H₁₆FNO₂Na [M+Na]⁺ 320.1057, found 320.1059; MS (EI) *m/z* (%): 297 (33), 240 (100), 160 (42), 132 (20), 77 (18); IR (KBr plate): 3276, 2958, 2851, 1721, 1657, 1490, 1266, 1090, 757 cm⁻¹.

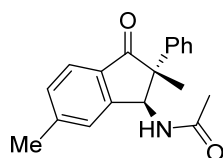


7ja: Following the general procedure B, reaction time: 1.5 h, 8 h; 27.8 mg, 40% yield; dr: 3.8:1.

7ja: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 189.1-190.4 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.86 (d, *J*=7.6 Hz, 1 H), 7.76-7.72 (m, 1 H), 7.58-7.54 (m, 2 H), 7.51 (d, *J* = 2.4 Hz, 1 H), 7.38 (d, *J* = 8.4 Hz, 1 H), 7.29-7.26 (m, 1 H), 5.89 (d, *J* = 9.2 Hz, 1 H), 5.76 (d, *J* = 9.2 Hz, 1 H), 2.13 (s, 3 H), 1.46 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 205.7, 170.2, 151.1, 143.4, 136.4, 135.2, 132.8, 131.4, 130.7, 130.1, 129.0, 126.5, 126.1, 124.7, 59.4, 57.1, 23.3, 20.6; **MS** (EI) *m/z* (%): 347 (19), 290 (100), 132 (28), 77 (16), 71 (16); **HRMS** (ESI) *m/z* calculated for C₁₈H₁₅Cl₂NO₂Na [M+Na]⁺ 370.0372, found 370.0363; **IR** (KBr plate): 2955, 2851, 1717, 1656, 1463, 1275, 1076, 763 cm⁻¹.



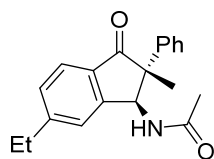
7ja': DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 160.6-162.4 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.90 (d, *J*=7.2 Hz, 1 H), 7.77-7.73 (m, 1 H), 7.59-7.56 (m, 2 H), 7.35 (d, *J* = 8.4 Hz, 1 H), 7.17 (d, *J* = 2.4 Hz, 1 H), 6.94 (dd, *J* = 8.4 Hz, 2.0 Hz, 1 H), 5.66 (d, *J* = 9.2 Hz, 1 H), 5.27 (d, *J* = 9.2 Hz, 1 H), 1.78 (s, 3 H), 1.77 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.1, 170.2, 151.3, 140.8, 136.5, 136.1, 132.7, 131.6, 130.4, 130.0, 129.9, 127.2, 126.2, 124.6, 59.5, 58.3, 23.5, 23.1; **MS** (EI) *m/z* (%): 347 (17), 290 (82), 132 (31), 77 (20), 71 (100); **HRMS** (ESI) *m/z* calculated for C₁₈H₁₅Cl₂NO₂Na [M+Na]⁺ 370.0372, found 370.0359; **IR** (KBr plate): 2955, 2852, 1716, 1654, 1457, 1261, 1088, 750 cm⁻¹.



7ka

7ka: Following the general procedure B, reaction time: 0.5 h, 4 h; 35.2 mg, 60% yield; dr: 10.5:1.

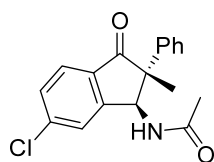
7ka: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 228.5-230.5 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.71 (d, *J* = 7.6 Hz, 1 H), 7.38-7.35 (m, 2 H), 7.33-7.26 (m, 4 H), 7.23-7.18 (m, 1 H), 5.91-5.85 (m, 2 H), 2.46 (s, 3 H), 2.09 (s, 3 H), 1.47 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.4, 170.1, 152.1, 147.4, 143.4, 133.4, 131.0, 128.8, 127.0, 126.6, 126.5, 124.3, 59.5, 57.7, 23.4, 22.3, 20.3; **HRMS** (ESI) *m/z* calculated for C₁₉H₁₉NO₂Na [M+Na]⁺ 316.1308, found 316.1298; **MS** (EI) *m/z* (%): 293 (52), 236 (96), 234 (100), 174 (27), 77 (12); **IR** (KBr plate): 3233, 2955, 2852, 1708, 1657, 1461, 1276, 1076, 750 cm⁻¹.



7la

7la: Following the general procedure B, reaction time: 1 h, 4 h; 38.2 mg, 62% yield; dr: 9.3:1.

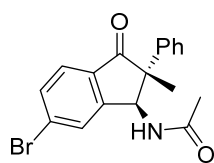
7la: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 182.5-183.8 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.4 Hz, 1 H), 7.39-7.28 (m, 6 H), 7.23-7.19 (m, 1 H), 5.92 (d, *J* = 9.6 Hz, 1 H), 5.82 (d, *J* = 9.2 Hz, 1 H), 2.75 (q, *J* = 7.6 Hz, 2 H), 2.11 (s, 3 H), 1.48 (s, 3 H), 1.28 (t, *J* = 7.6 Hz, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 206.6, 170.2, 153.6, 152.2, 143.5, 133.5, 129.8, 128.7, 127.0, 126.6, 125.3, 124.3, 59.5, 57.7, 29.5, 23.2, 20.2, 15.4; **HRMS** (ESI) *m/z* calculated for C₂₀H₂₁NO₂Na [M+Na]⁺ 330.1465, found 330.1452; **MS** (EI) *m/z* (%): 307 (46), 248 (100), 236 (5), 160 (14), 77 (12); **IR** (KBr plate): 3273, 2965, 2871, 1712, 1655, 1444, 1275, 1097, 764 cm⁻¹.



7ma

7ma: Following the general procedure B, reaction time: 2 h, 8 h; 26.5 mg, 42% yield; dr: 10.2:1.

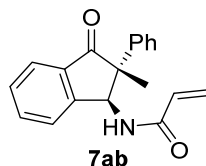
7ma: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 224.5-226.1 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.4 Hz, 1 H), 7.530-7.526 (m, 1 H), 7.47 (dd, *J* = 8.4 Hz, 1.6 Hz, 1 H), 7.36-7.29 (m, 4 H), 7.25-7.21 (m, 1 H), 5.98 (d, *J* = 9.2 Hz, 1 H), 5.93 (d, *J* = 9.2 Hz, 1 H), 2.08 (s, 3 H), 1.47 (s, 3 H); **¹³C NMR** (100 MHz, CDCl₃): δ 205.5, 170.2, 153.2, 142.7, 142.5, 133.9, 130.5, 128.9, 127.3, 126.6, 126.5, 125.6, 59.1, 57.7, 23.3, 20.4; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₆ClNO₂Na [M+Na]⁺ 336.0762, 338.0732, found 336.0747, 338.0722; **MS** (EI) *m/z* (%): 315 (13), 313 (34), 258 (28), 256 (100), 77 (15); **IR** (KBr plate): 3461, 2955, 2851, 1716, 1650, 1274, 1076, 750 cm⁻¹.



7na

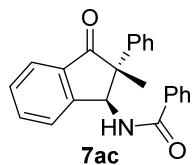
7na: Following the general procedure B, reaction time: 2 h, 10 h; 31.1 mg, 43% yield; dr: 11.2:1.

7na: DCM/MeOH (300:1–150:1) as the eluent, white solid, m.p. = 229.0-230.9 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.71-7.63 (m, 3 H), 7.36-7.29 (m, 4 H), 7.25-7.21 (m, 1 H), 5.96-5.91 (m, 2 H), 2.09 (s, 3 H), 1.48 (s, 3 H); **¹³C NMR** (150 MHz, CDCl₃): δ 205.7, 170.1, 153.2, 142.6, 134.3, 133.4, 131.3, 129.6, 128.9, 127.3, 126.6, 125.6, 59.0, 57.7, 23.4, 20.4; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₆BrNO₂Na [M+Na]⁺ 380.0257, found 380.0239; **MS** (EI) *m/z* (%): 359 (25), 357 (25), 300 (100), 235 (2), 77 (16); **IR** (KBr plate): 3256, 2955, 2869, 1719, 1656, 1460, 1274, 1054, 750 cm⁻¹.



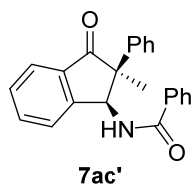
7ab: Following the general procedure B, reaction time: 1.5 h, 8 h; 35.0 mg, 60% yield; dr: 10.0:1.

7ab: Petroleum ether/ethyl acetate (5:1) as the eluent, white solid, m.p. = 156.9-158.7 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.86 (d, *J* = 7.2 Hz, 1 H), 7.71-7.68 (m, 1 H), 7.56 (d, *J* = 7.8 Hz, 1 H), 7.53 (dd, *J* = 7.8 Hz, 7.8 Hz, 1 H), 7.43-7.41 (m, 2 H), 7.33-7.30 (m, 2 H), 7.24-7.21 (m, 1 H), 6.41 (dd, *J* = 16.8 Hz, 1.2 Hz, 1 H), 6.18 (dd, *J* = 17.4 Hz, 10.8 Hz, 1 H), 6.06 (d, *J* = 9.6 Hz, 1 H), 5.83 (d, *J* = 9.6 Hz, 1 H), 5.76 (dd, *J* = 10.2 Hz, 1.2 Hz, 1 H), 1.51 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 207.1, 165.7, 151.5, 143.2, 135.8, 135.4, 130.1, 129.6, 128.7, 127.6, 127.0, 126.5, 126.3, 124.1, 59.5, 57.6, 20.2; HRMS (ESI) *m/z* calculated for C₁₉H₁₈NO₂ [M+H]⁺ 292.1332, found 292.1329; MS (EI) *m/z* (%): 291 (65), 178 (73), 130 (42), 103 (95), 77 (100); IR (KBr plate): 3276, 3056, 2930, 1716, 1658, 1464, 1231, 1076, 759 cm⁻¹.

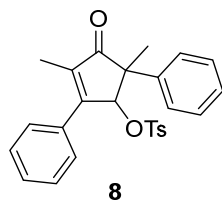


7ac: Following the general procedure B, reaction time: 1.5 h, 8 h; 48.5 mg, 71% yield; dr: 7.5:1.

7ac: Petroleum ether/ethyl acetate (7:1) as the eluent, white solid, m.p. = 193.2-195.0 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.86 (d, *J* = 7.8 Hz, 1 H), 7.81 (d, *J* = 7.8 Hz, 2 H), 7.69 (dd, *J* = 7.8 Hz, 7.8 Hz, 1 H), 7.59 (d, *J* = 7.8 Hz, 1 H), 7.55-7.51 (m, 2 H), 7.46-7.43 (m, 4 H), 7.32 (dd, *J* = 7.8 Hz, 7.8 Hz, 2 H), 7.23 (dd, *J* = 7.2 Hz, 7.2 Hz, 1 H), 6.52 (d, *J* = 9.0 Hz, 1 H), 6.16 (d, *J* = 9.6 Hz, 1 H), 1.57 (s, 3 H); ¹³C NMR (150 MHz, CDCl₃): δ 207.0, 167.5, 151.5, 143.3, 136.1, 135.8, 133.9, 132.2, 129.9, 128.9, 128.8, 127.2, 126.7, 126.4, 124.5, 60.0, 57.9, 20.4; HRMS (ESI) *m/z* calculated for C₂₃H₂₀NO₂ [M+H]⁺ 342.1489, found 342.1483; MS (EI) *m/z* (%): 341 (3), 220 (4), 130 (4), 105 (100), 77 (54); IR (KBr plate): 3293, 3056, 2977, 1714, 1640, 1490, 1267, 757 cm⁻¹.



7ac': Petroleum ether/ethyl acetate (7:1) as the eluent, white solid, m.p. = 156.9-158.7 °C. **¹H NMR** (600 MHz, CDCl₃): δ 7.95 (d, *J* = 7.8 Hz, 1 H), 7.72 (dd, *J* = 7.2 Hz, 7.2 Hz, 1 H), 7.63 (d, *J* = 7.8 Hz, 1 H), 7.57 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1 H), 7.42 (dd, *J* = 7.2 Hz, 7.2 Hz, 1 H), 7.30-7.27 (m, 5 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 7.13 (d, *J* = 7.2 Hz, 2 H), 5.90 (d, *J* = 9.6 Hz, 1 H), 5.78 (d, *J* = 9.0 Hz, 1 H), 1.98 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃): δ 207.0, 167.6, 152.3, 140.6, 136.7, 136.2, 134.1, 131.8, 129.7, 129.1, 128.6, 127.7, 127.4, 126.7, 126.5, 124.3, 59.5, 58.7, 22.6; **HRMS** (ESI) *m/z* calculated for C₂₃H₂₀NO₂ [M+H]⁺ 342.1489, found 342.1484; **MS** (EI) *m/z* (%): 341 (2), 155 (100), 127 (63), 105 (17), 77 (32); **IR** (KBr plate): 3309, 3057, 2913, 1713, 1641, 1489, 1266, 754 cm⁻¹.



8: Petroleum ether/ethyl acetate (15:1) as the eluent, a pale yellow amorphous solid. **¹H NMR** (600 MHz, CDCl₃): δ 7.37-7.33 (m, 5 H), 7.31-7.28 (m, 3 H), 7.24-7.23 (m, 2 H), 7.21-7.20 (m, 2 H), 7.06 (d, *J* = 8.4 Hz, 2 H), 6.08 (d, *J* = 1.2 Hz, 1 H), 2.38 (s, 3H), 1.96 (d, *J* = 1.2 Hz, 3 H), 1.60 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃): δ 207.4, 160.5, 144.7, 142.3, 140.3, 133.6, 132.7, 129.7, 129.5, 129.0, 128.6, 128.1, 127.8, 127.4, 126.5, 88.9, 54.8, 21.7, 19.2, 10.1; **HRMS** (ESI) *m/z* calculated for C₂₆H₂₄O₄SNa [M+Na]⁺ 455.1288, found 455.1281; **MS** (EI) *m/z* (%): 432 (5), 262 (22), 235 (100), 105 (96), 77 (26).

4. X-Ray crystallography Data

4.1 X-Ray crystallography of compound 5aa

The crystal of compound **5aa** for X-ray diffraction study was obtained through the dissolving of compound in ethyl acetate and petroleum ether, followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in an Agilent Super Nova.

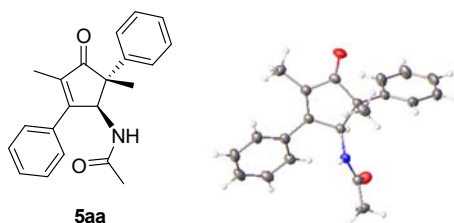


Figure S1. X-Ray coordinate of precursor **5aa** (CCDC 2408876). Displacement ellipsoids are scaled to the 30% probability level.

Identification code	huyuehong_0707_auto
Empirical formula	C ₂₁ H ₂₁ NO ₂
Formula weight	319.39
Temperature/K	149.98(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	9.38050(10)
b/Å	17.9125(3)
c/Å	20.6371(3)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	3467.61(9)
Z	8
ρ _{calc} /cm ³	1.224
μ/mm ⁻¹	0.619
F(000)	1360.0
Crystal size/mm ³	0.15 × 0.03 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	8.57 to 152.162
Index ranges	-4 ≤ h ≤ 11, -22 ≤ k ≤ 19, -25 ≤ l ≤ 19
Reflections collected	13330
Independent reflections	3472 [R _{int} = 0.0307, R _{sigma} = 0.0293]
Data/restraints/parameters	3472/0/220
Goodness-of-fit on F ²	1.032
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0393, wR ₂ = 0.0998
Final R indexes [all data]	R ₁ = 0.0464, wR ₂ = 0.1042
Largest diff. peak/hole / e Å ⁻³	0.26/-0.23

4.2 X-Ray crystallography of compound 5ea

The crystal of compound **5ea** for X-ray diffraction study was obtained through the dissolving of compound in ethyl acetate and petroleum ether, followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in an Agilent Super Nova.

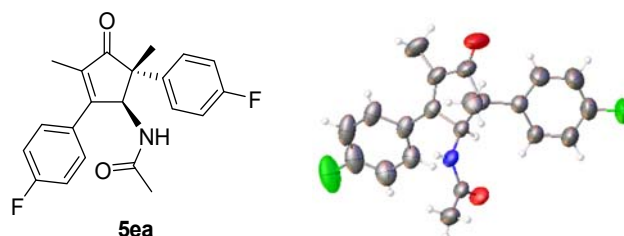


Figure S2. X-Ray coordinate of precursor **5ea** (CCDC 2408879). Displacement ellipsoids are scaled to the 30% probability level.

Identification code	huyuehong1-zhfm_0426_auto
Empirical formula	C ₂₁ H ₁₉ F ₂ NO ₂
Formula weight	355.37
Temperature/K	271.8(9)
Crystal system	monoclinic
Space group	Ia
a/Å	9.7705(2)
b/Å	13.1781(3)
c/Å	14.4870(4)
α/°	90
β/°	103.850(2)
γ/°	90
Volume/Å ³	1811.06(8)
Z	4
ρ _{calc} /cm ³	1.303
μ/mm ⁻¹	0.812
F(000)	744.0
Crystal size/mm ³	0.11 × 0.07 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	9.196 to 155.122
Index ranges	-11 ≤ h ≤ 8, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18
Reflections collected	12116
Independent reflections	2762 [R _{int} = 0.0321, R _{sigma} = 0.0193]
Data/restraints/parameters	2762/2/238
Goodness-of-fit on F ²	1.103
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0372, wR ₂ = 0.1048
Final R indexes [all data]	R ₁ = 0.0406, wR ₂ = 0.1082
Largest diff. peak/hole / e Å ⁻³	0.13/-0.17
Flack parameter	-0.08(11)

4.3 X-Ray crystallography of compound 5ga'

The crystal of compound 5ga' for X-ray diffraction study was obtained through the dissolving of compound in ethyl acetate and chloroform, followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in an Agilent Super Nova.

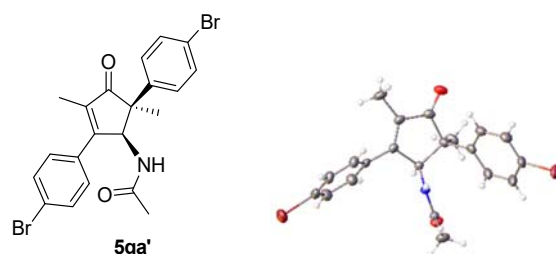


Figure S3. X-Ray coordinate of precursor 5ga' (CCDC 2410041). Displacement ellipsoids are scaled to the 30% probability level.

Identification code	huyh 1211 auto
Empirical formula	C ₂₁ H ₁₉ Br ₂ NO ₂
Formula weight	477.19
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	I2/a
a/Å	16.9874(2)
b/Å	9.81932(13)
c/Å	24.6758(3)
α /°	90
β /°	109.0437(14)
γ /°	90
Volume/Å ³	3890.75(10)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.629
μ/mm^{-1}	5.404
F(000)	1904.0
Crystal size/mm ³	0.25 × 0.12 × 0.04
Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/°	7.58 to 152.192
Index ranges	-21 ≤ h ≤ 16, -11 ≤ k ≤ 12, -25 ≤ l ≤ 31
Reflections collected	12974
Independent reflections	3856 [R _{int} = 0.0367, R _{sigma} = 0.0253]
Data/restraints/parameters	3856/0/243
Goodness-of-fit on F ²	1.038
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0394, wR ₂ = 0.1026
Final R indexes [all data]	R ₁ = 0.0414, wR ₂ = 0.1044
Largest diff. peak/hole / e Å ⁻³	1.77/-1.18

4.4 X-Ray crystallography of compound 7ea

The crystal of compound 7ea for X-ray diffraction study was obtained through the dissolving of compound in ethyl acetate and petroleum ether, followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in an Agilent Super Nova.

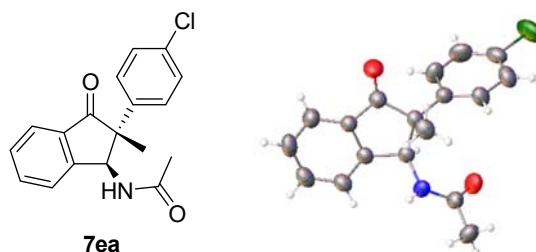


Figure S4. X-Ray coordinate of precursor 7ea (CCDC 2408878). Displacement ellipsoids are scaled to the 30% probability level.

Identification code	huvuehong_0831_auto
Empirical formula	C ₃₆ H ₃₂ Cl ₂ N ₂ O ₄
Formula weight	627.53
Temperature/K	301.46(10)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	9.74490(10)
b/Å	12.6197(3)
c/Å	12.8104(2)
α/°	90
β/°	91.761(2)
γ/°	90
Volume/Å ³	1574.65(5)
Z	2
ρ _{calc} /cm ³	1.324
μ/mm ⁻¹	2.197
F(000)	656.0
Crystal size/mm ³	0.16 × 0.16 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.904 to 155.844
Index ranges	-12 ≤ h ≤ 8, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	11508
Independent reflections	5451 [R _{int} = 0.0502, R _{sigma} = 0.0480]
Data/restraints/parameters	5451/1/410
Goodness-of-fit on F ²	1.097
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0449, wR ₂ = 0.1198
Final R indexes [all data]	R ₁ = 0.0513, wR ₂ = 0.1306
Largest diff. peak/hole / e Å ⁻³	0.25/-0.30
Flack parameter	0.268(10)

4.5 X-Ray crystallography of compound 7ia

The crystal of compound **7ia** for X-ray diffraction study was obtained through the dissolving of compound in dichloromethane, followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in an Agilent Super Nova.

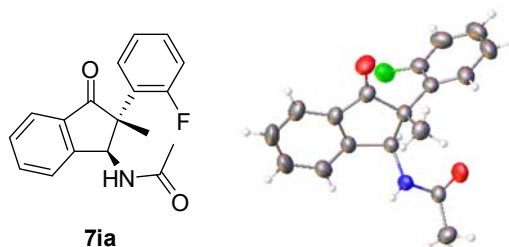


Figure S5. X-Ray coordinate of precursor **7ia** (CCDC 2408877). Displacement ellipsoids are scaled to the 30% probability level.

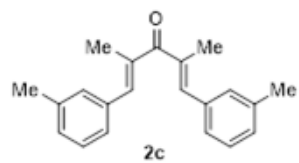
Identification code	huvuehong2-zhfm_0426_auto
Empirical formula	C ₁₈ H ₁₆ FNO ₂
Formula weight	297.32
Temperature/K	271.7(3)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	8.35635(9)
b/Å	20.16774(19)
c/Å	9.47069(10)
α/°	90
β/°	111.5299(12)
γ/°	90
Volume/Å ³	1484.72(3)
Z	4
ρ _{calc} /cm ³	1.330
μ/mm ⁻¹	0.783
F(000)	624.0
Crystal size/mm ³	0.11 × 0.08 × 0.06
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	12.108 to 154.988
Index ranges	-10 ≤ h ≤ 10, -25 ≤ k ≤ 24, -11 ≤ l ≤ 11
Reflections collected	19065
Independent reflections	3061 [R _{int} = 0.0223, R _{sigma} = 0.0123]
Data/restraints/parameters	3061/0/201
Goodness-of-fit on F ²	1.084
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0451, wR ₂ = 0.1199
Final R indexes [all data]	R ₁ = 0.0467, wR ₂ = 0.1214
Largest diff. peak/hole / e Å ⁻³	0.27/-0.27

5. References

- 1) Z. Daneshfara and A. Rostami, *RSC Adv.*, 2015, **5**, 104695.
- 2) S. Gelozia, Y. Kwon, R. McDonald and F. G. West, *Chem. Eur. J.* 2018, **24**, 6052.
- 3) C. J. Rieder, K. J. Winberg and F. G. West, *J. Org. Chem.* 2011, **76**, 50.
- 4) Y. Wei, J. Tang, X. Cong and X. Zeng, *Green Chem.*, 2013, **15**, 3165.
- 5) B. K. Pandia, S. Pattanaik and C. Gunanathan, *Tetrahedron* 2021, **101**, 132472.
- 6) C. D. Smith, G. Rosocha, L. Mui and R. A. Batey, *J. Org. Chem.* 2010, **75**, 4716
- 7) Z. Han, X. Feng and H. Du, *J. Org. Chem.* 2023, **88**, 16038.

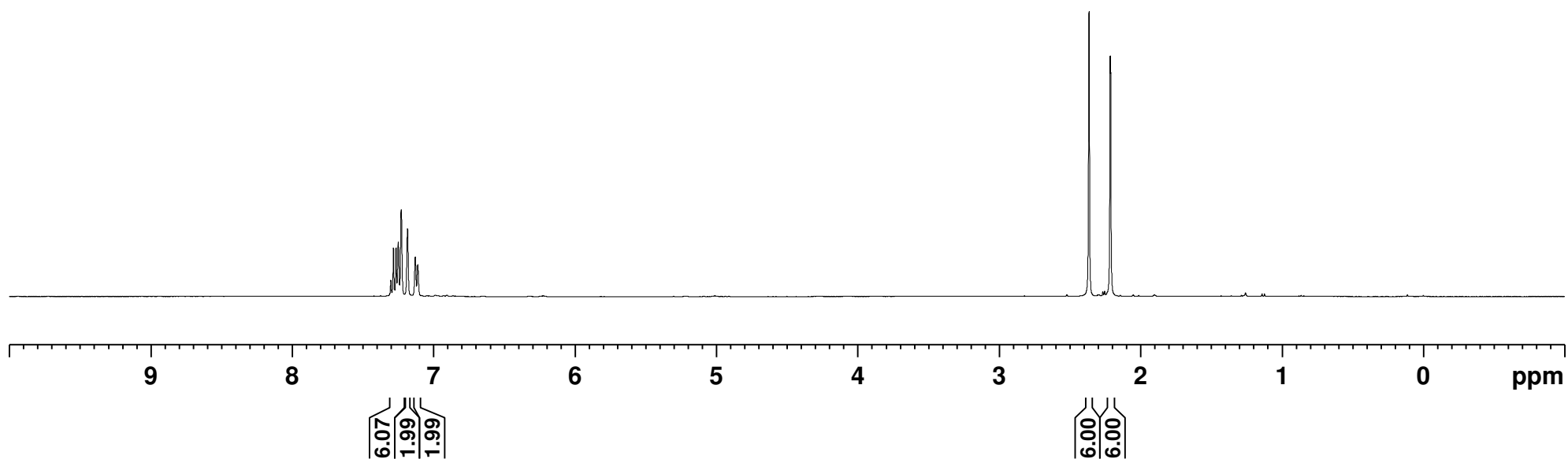
6. Copies of ^1H and ^{13}C NMR spectra of products

^1H NMR (400 MHz, CDCl_3)

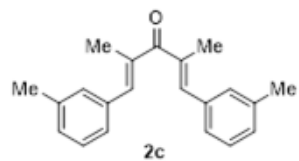


7.301
7.283
7.264
7.249
7.227
7.183
7.128
7.110

2.363
2.214
2.211



¹³C NMR (100 MHz, CDCl₃)



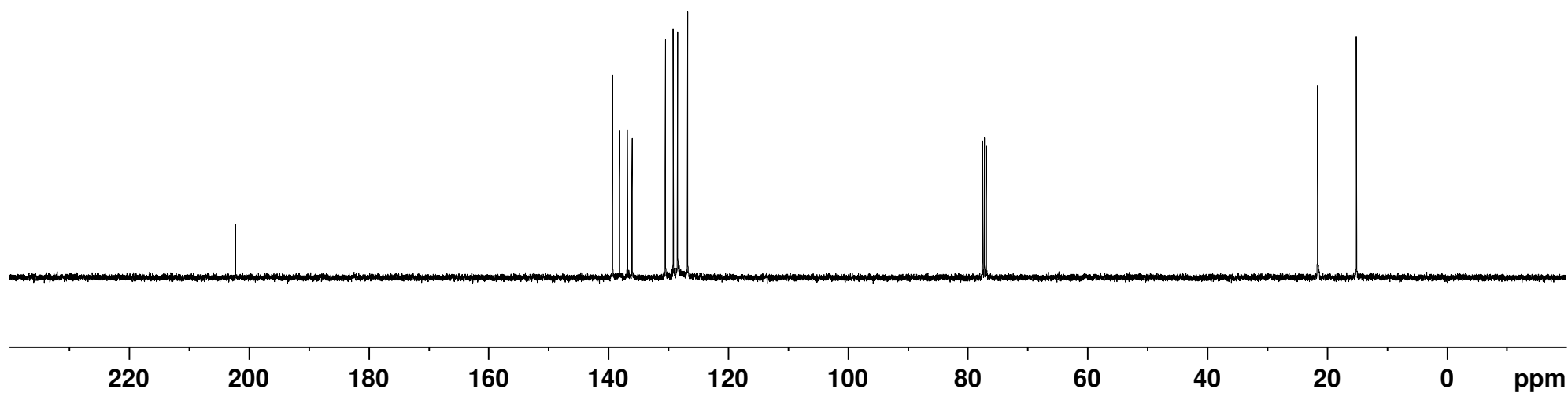
202.21

139.26
138.10
136.78
135.99
130.44
129.12
128.40
126.72

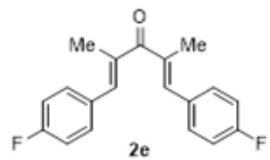
77.47
77.16
76.84

21.49

15.02



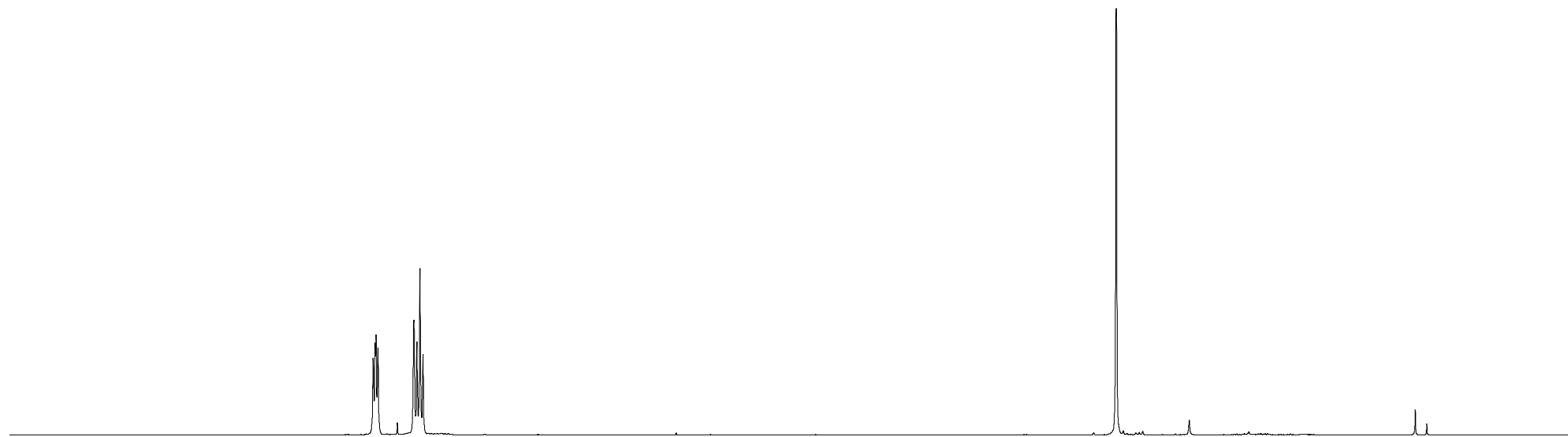
^1H NMR (400 MHz, CDCl_3)



7.433
7.419
7.412
7.398
7.262
7.145
7.124
7.102
7.081

2.189

0.081
-0.000



9

8

6

5

4

3

2

1

0

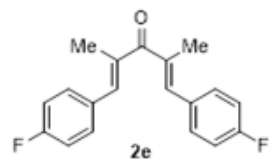
ppm

4.03

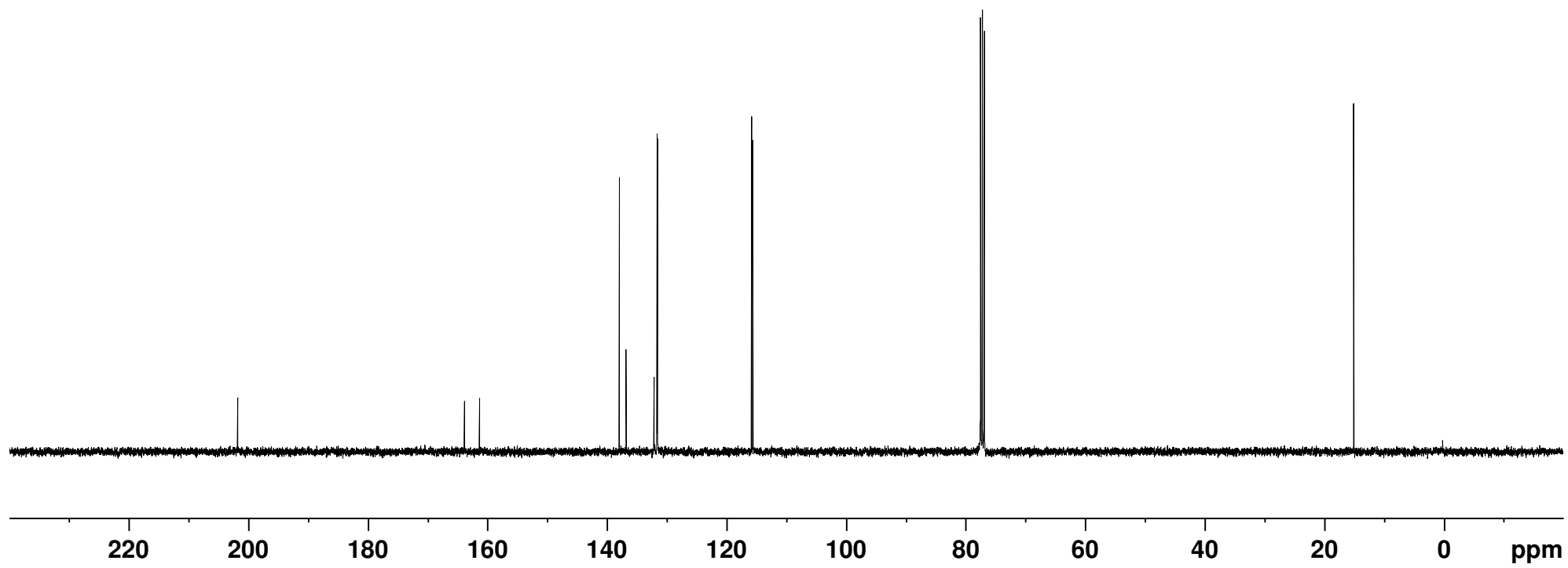
6.03

6.00

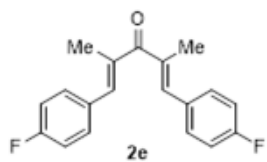
¹³C NMR (100 MHz, CDCl₃)



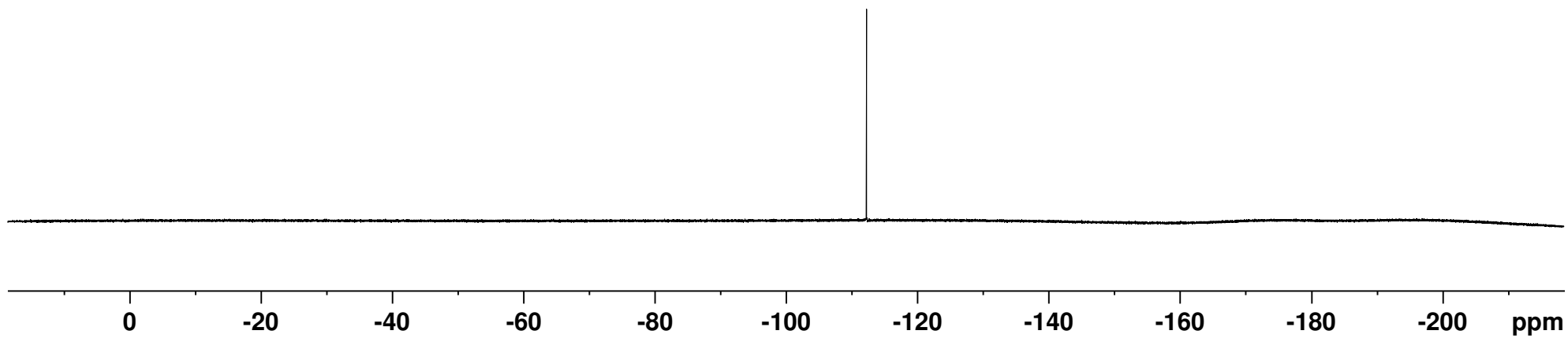
201.79
163.80
161.33
137.91
136.79
136.78
132.11
132.07
131.61
131.53
115.79
115.57
77.47
77.16
76.84
15.01



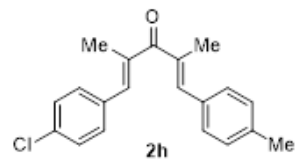
^{19}F NMR (376 MHz, CDCl_3)



— -112.301



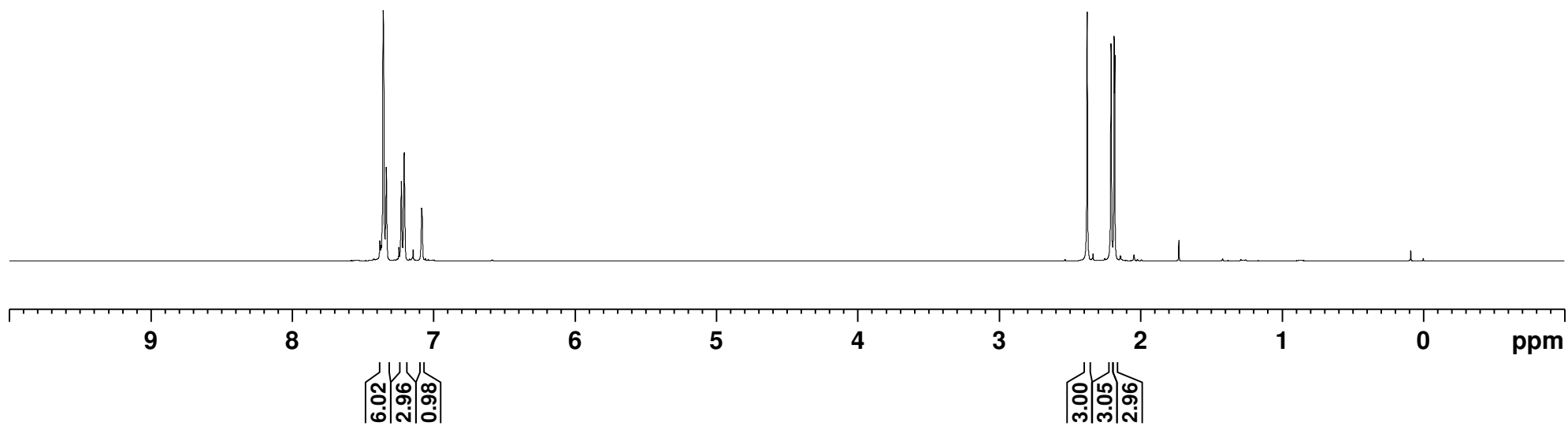
^1H NMR (400 MHz, CDCl_3)



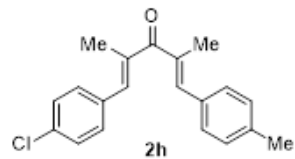
7.379
7.371
7.356
7.352
7.333
7.244
7.227
7.207
7.083
7.080

2.376
2.208
2.205
2.185
2.182

0.088
-0.000



¹³C NMR (100 MHz, CDCl₃)

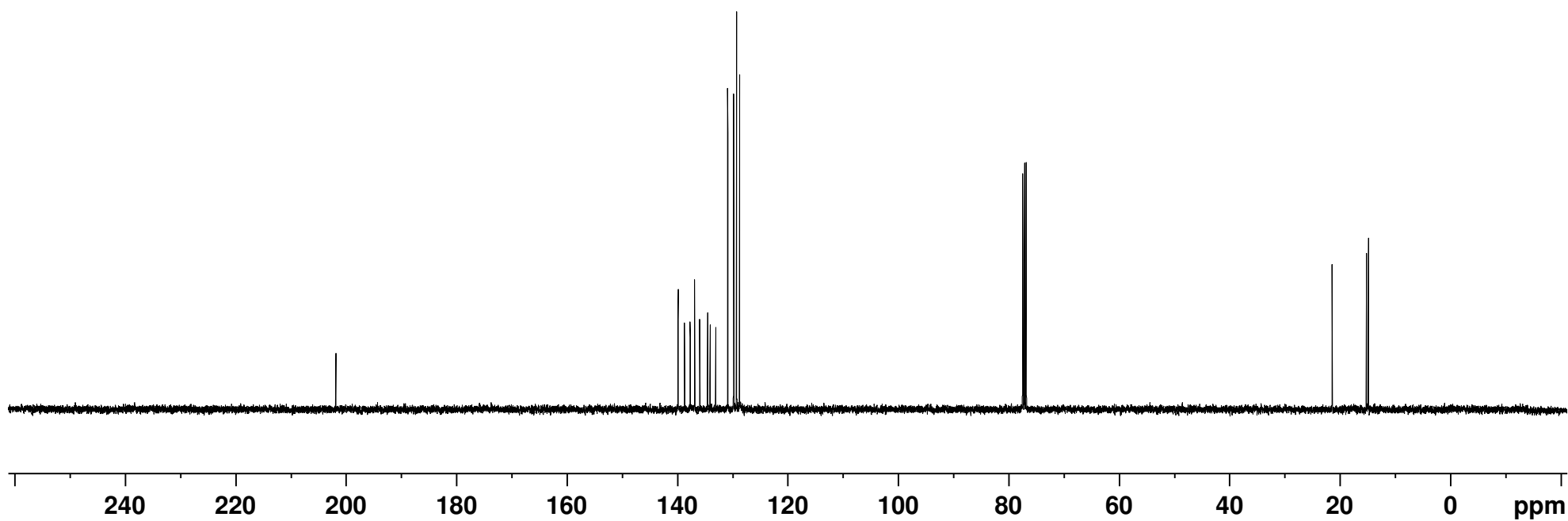


— 201.87

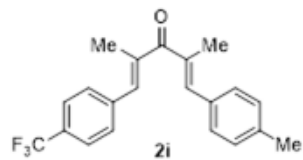
139.90
138.72
137.70
136.89
135.96
134.52
134.11
133.07
130.90
129.83
129.31
128.75

77.48
77.16
76.84

21.44
15.23
14.88



^1H NMR (400 MHz, CDCl_3)



7.660
7.639
7.521
7.500
7.374
7.354
7.279
7.239
7.219
7.106

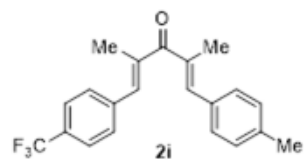
2.381
2.226
2.224
2.207
2.205



1.96
2.00
1.99
1.01
1.99
0.97

3.00
3.04
2.89

¹³C NMR (100 MHz, CDCl₃)

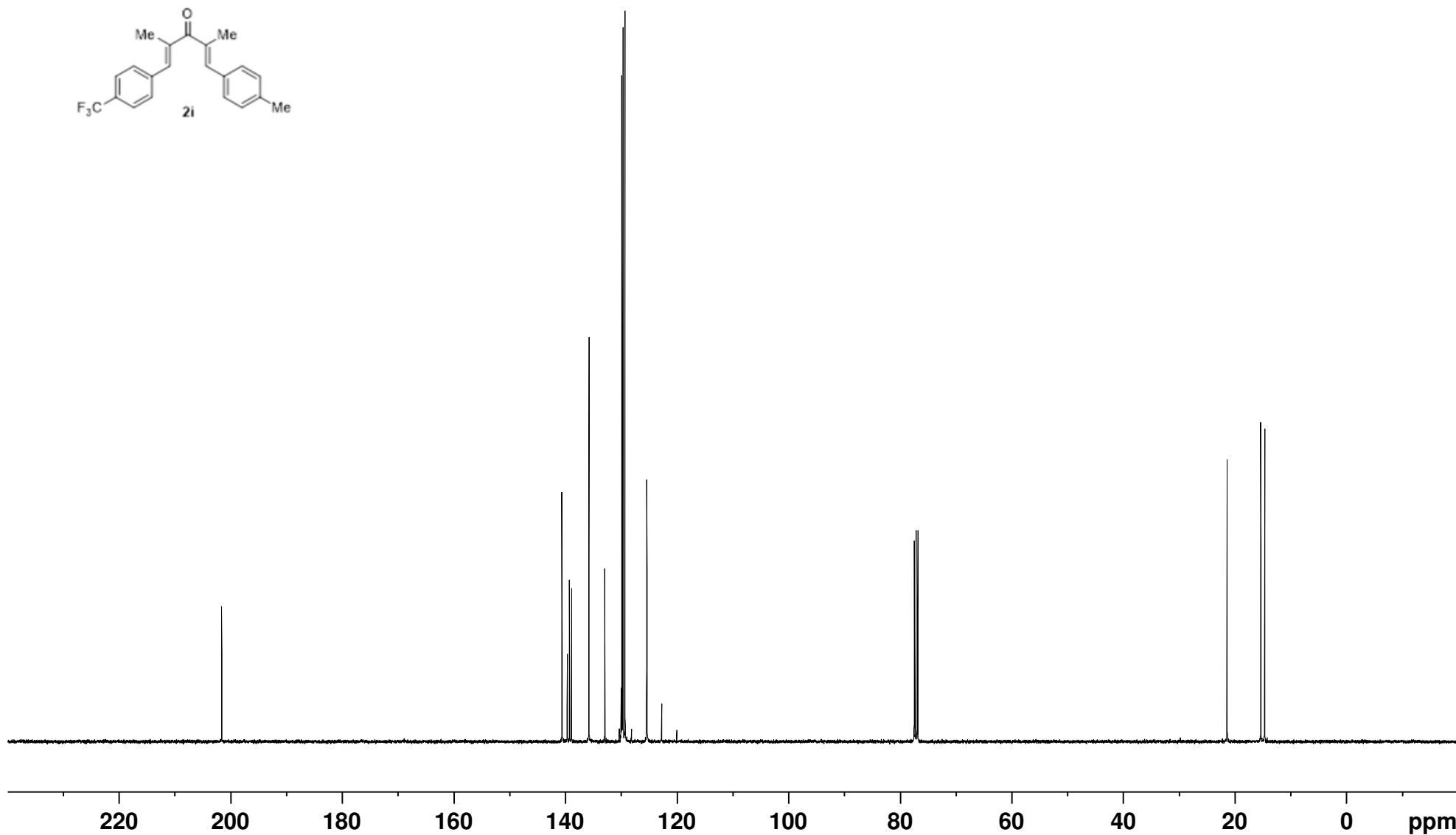


— 201.61

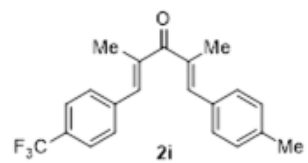
140.63
139.67
139.28
138.91
135.80
132.96
130.36
130.03
129.89
129.70
129.39
129.34
128.17
125.47
125.43
125.40
125.36
122.76
120.06

77.47
77.16
76.84

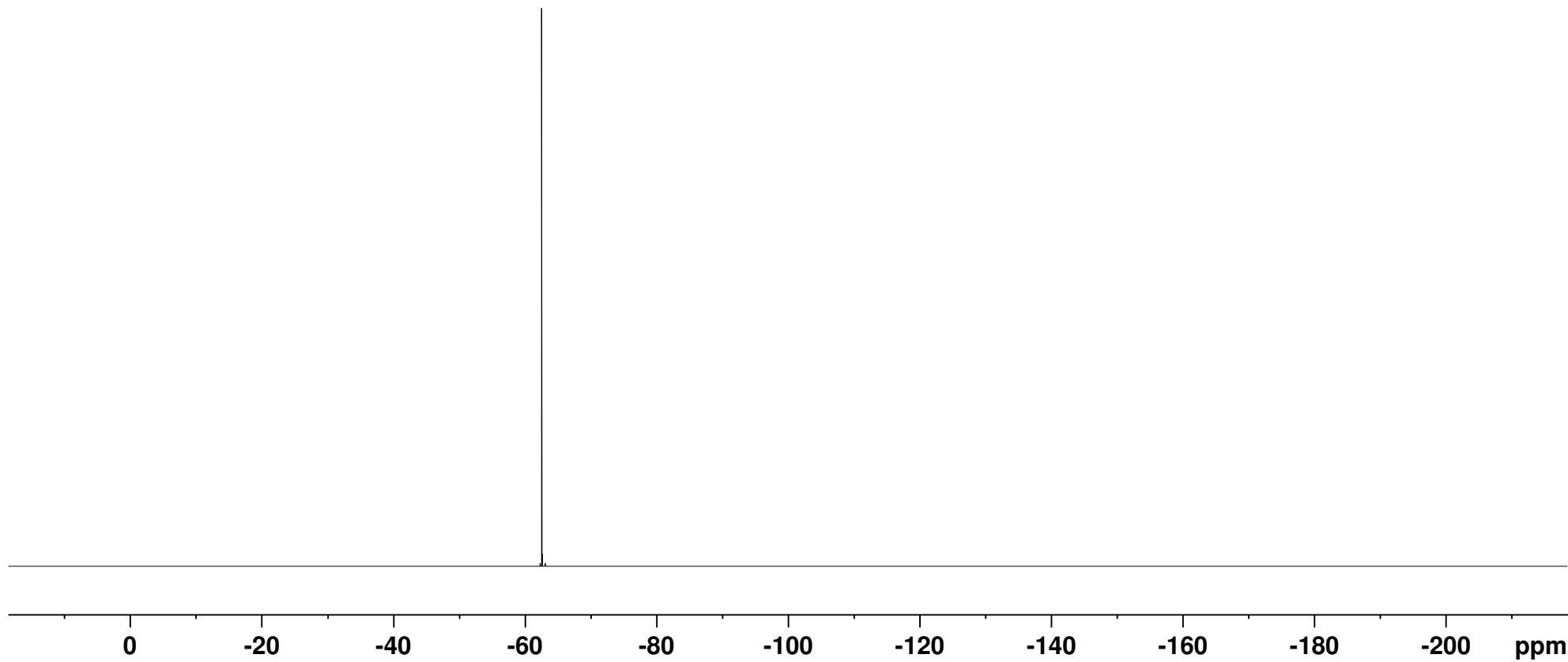
21.41
15.36
14.67



^{19}F NMR (376 MHz, CDCl_3)



— -62.564

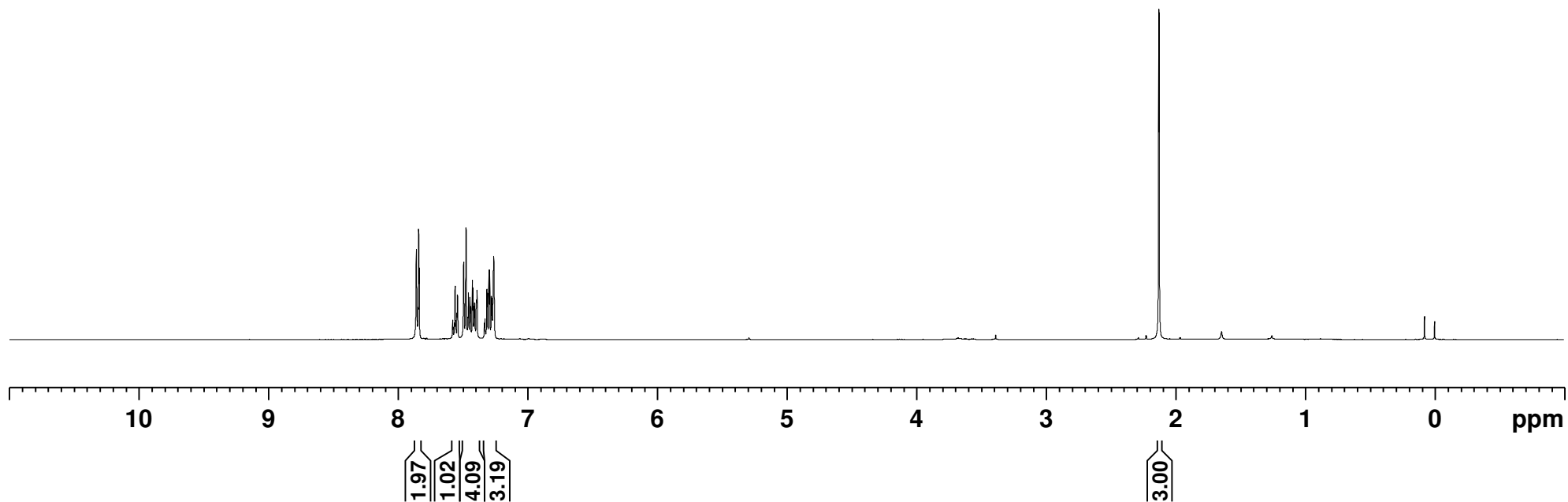
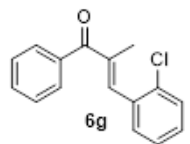


^1H NMR (400 MHz, CDCl_3)

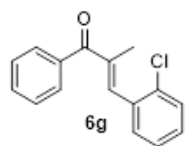
7.860
7.857
7.854
7.845
7.840
7.836
7.580
7.577
7.574
7.564
7.559
7.553
7.543
7.540
7.537
7.493
7.489
7.477
7.474
7.460
7.456
7.453
7.444
7.426
7.413
7.389
7.332
7.329
7.314
7.297
7.292
7.274
7.261
7.258

2.129
2.125

0.077
-0.000



¹³C NMR (100 MHz, CDCl₃)

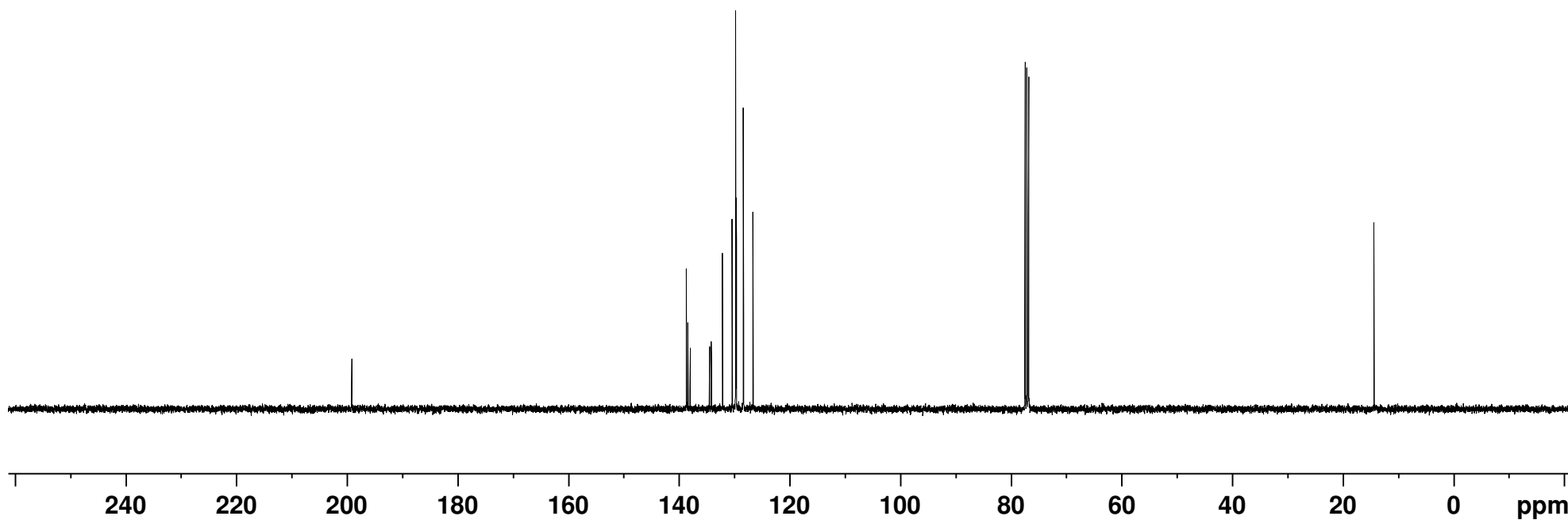


— 199.16

138.70
138.41
138.02
134.50
134.17
132.16
130.43
129.81
129.72
129.66
128.39
126.65

77.48
77.16
76.84

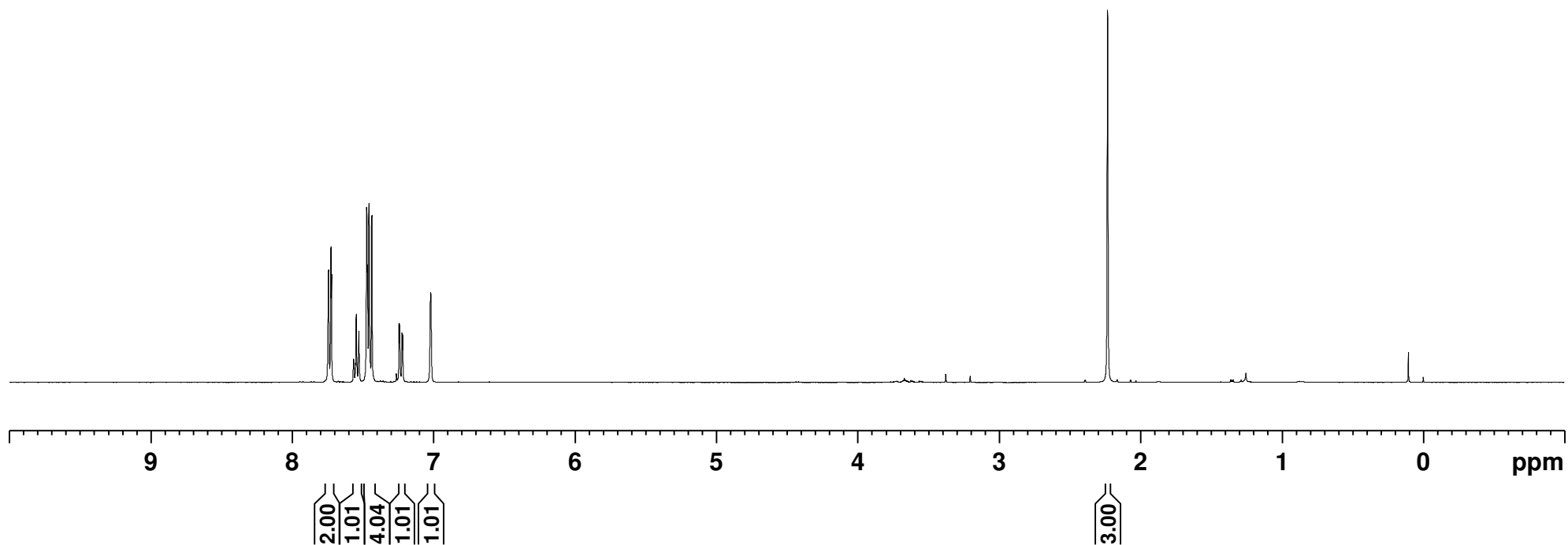
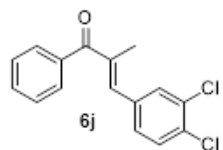
— 14.41



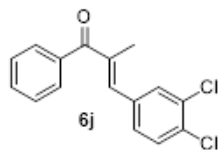
¹H NMR (400 MHz, CDCl₃)

7.742
7.729
7.724
7.721
7.567
7.564
7.561
7.551
7.545
7.541
7.530
7.527
7.524
7.472
7.466
7.456
7.454
7.435
7.262
7.243
7.238
7.222
7.217
7.019

2.233
2.230



¹³C NMR (100 MHz, CDCl₃)

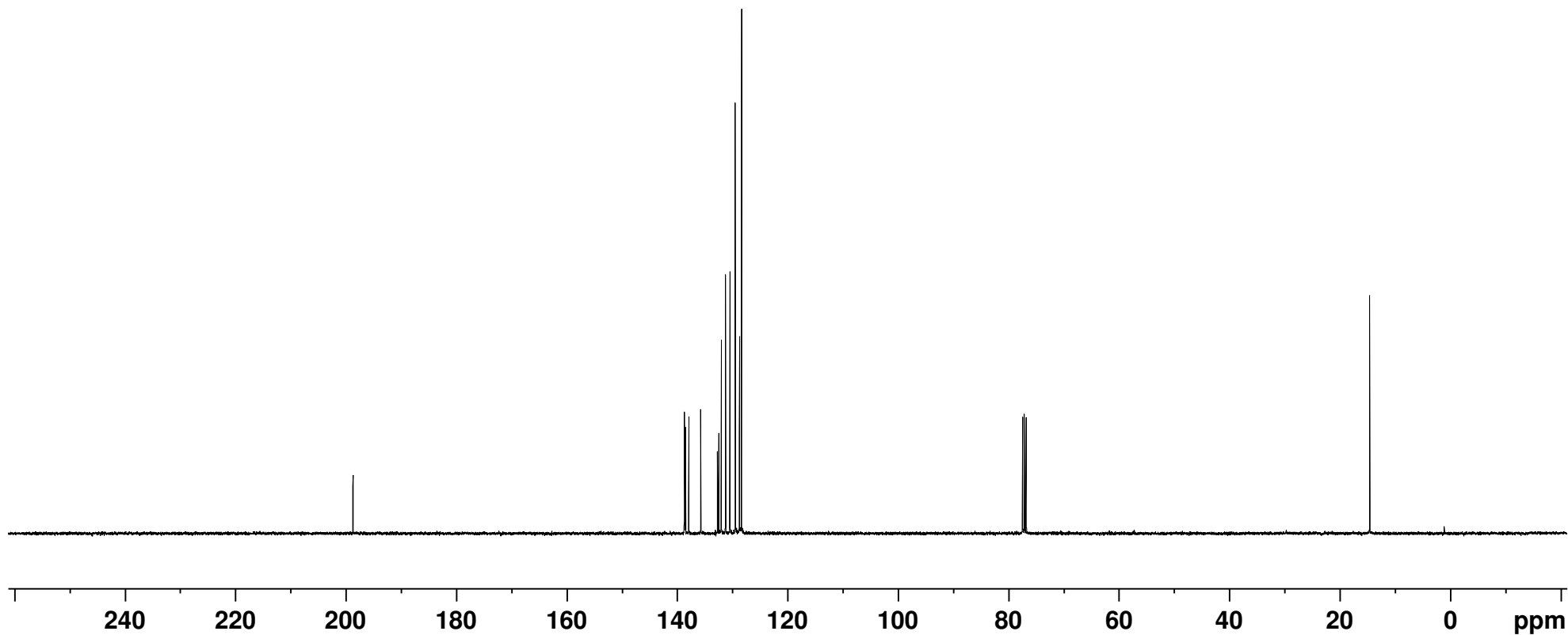


— 198.74

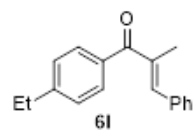
138.69
138.52
137.94
135.78
132.73
132.51
132.04
131.27
130.48
129.51
128.75
128.37

77.48
77.16
76.84

— 14.60



¹H NMR (400 MHz, CDCl₃)

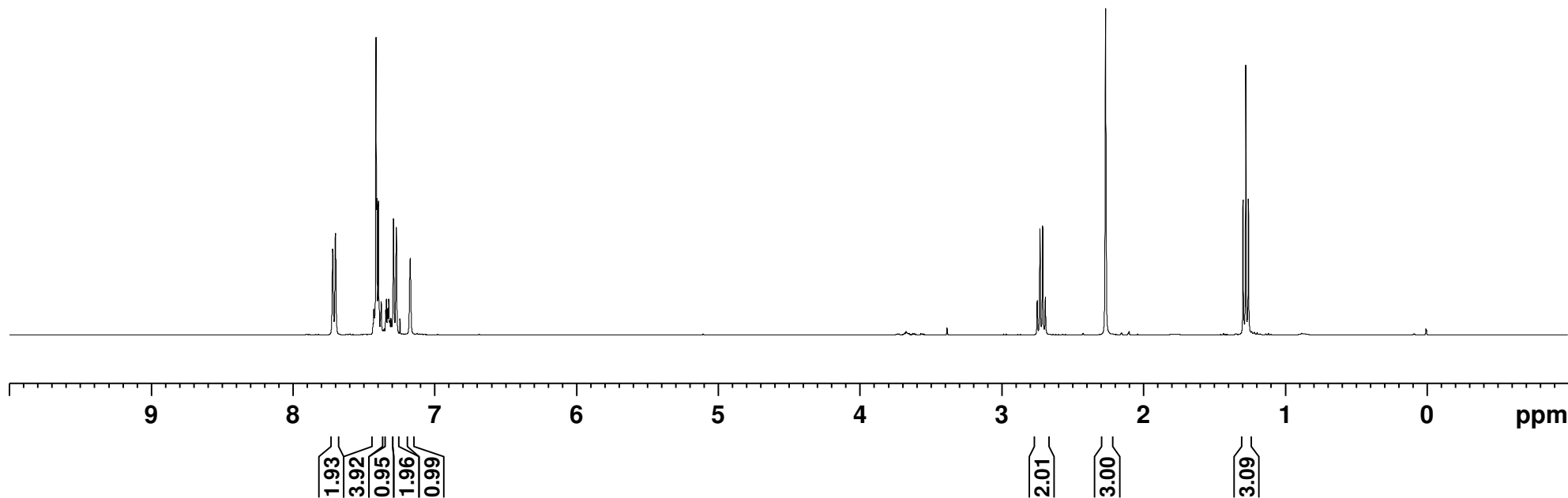


7.719
7.698
7.433
7.427
7.412
7.407
7.395
7.390
7.380
7.375
7.344
7.338
7.330
7.322
7.314
7.312
7.306
7.301
7.289
7.269
7.243
7.170

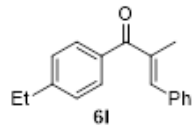
2.746
2.727
2.707
2.688
2.266

1.294
1.275
1.256

0.003
-0.000



¹³C NMR (100 MHz, CDCl₃)



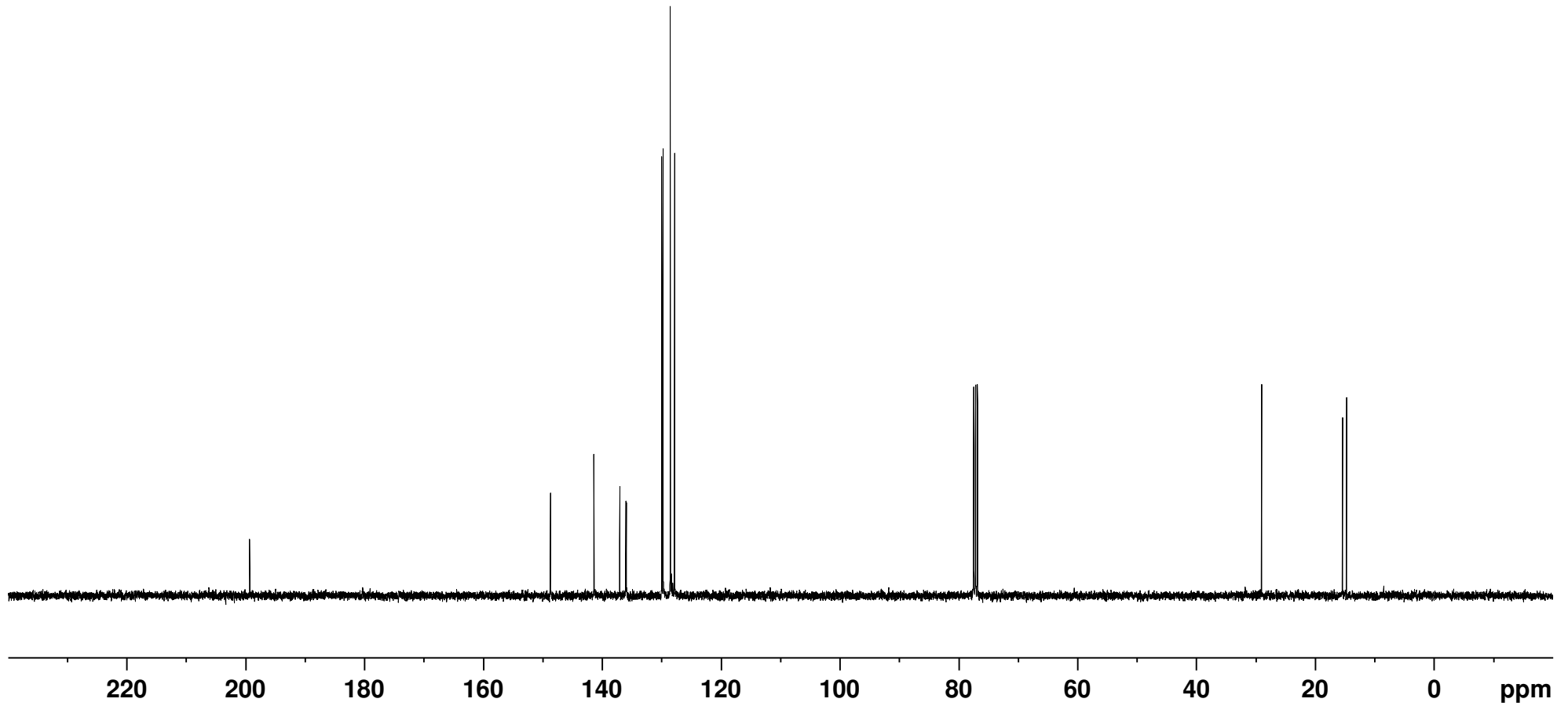
— 199.34

148.71
141.40
137.06
136.03
135.95
129.97
129.76
128.55
127.83

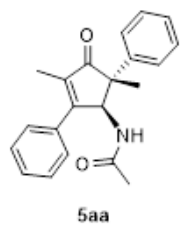
77.48
77.16
76.84

— 29.01

15.40
14.72



¹H NMR (400 MHz, CDCl₃)

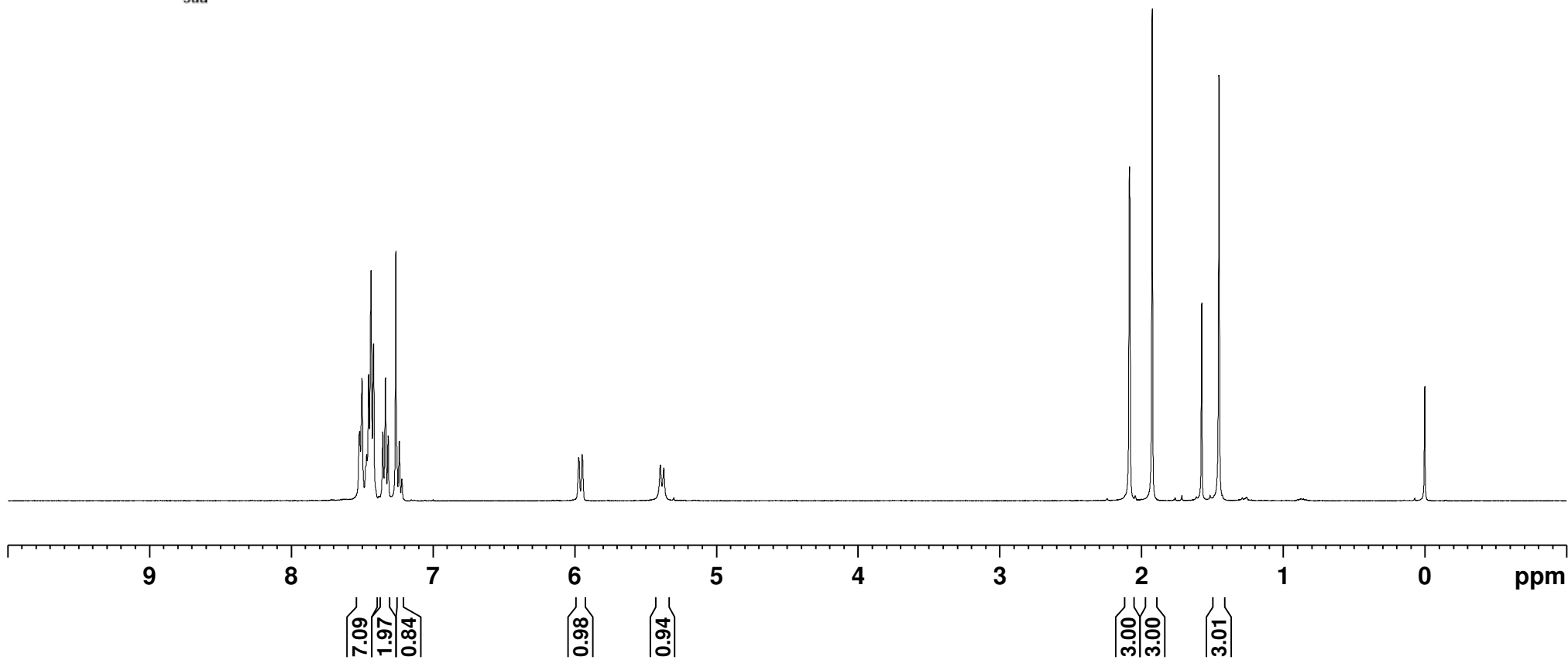


7.516
7.500
7.474
7.467
7.453
7.436
7.418
7.353
7.335
7.315
7.261
7.237
7.219
5.971
5.947
5.395
5.371

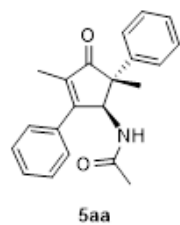
2.084
1.923

1.452

-0.000



¹³C NMR (100 MHz, CDCl₃)



— 209.65

— 170.09

— 162.43

— 143.77

— 136.98

— 133.36

— 130.15

— 128.89

— 128.79

— 128.58

— 127.01

— 126.49

— 77.47

— 77.16

— 76.84

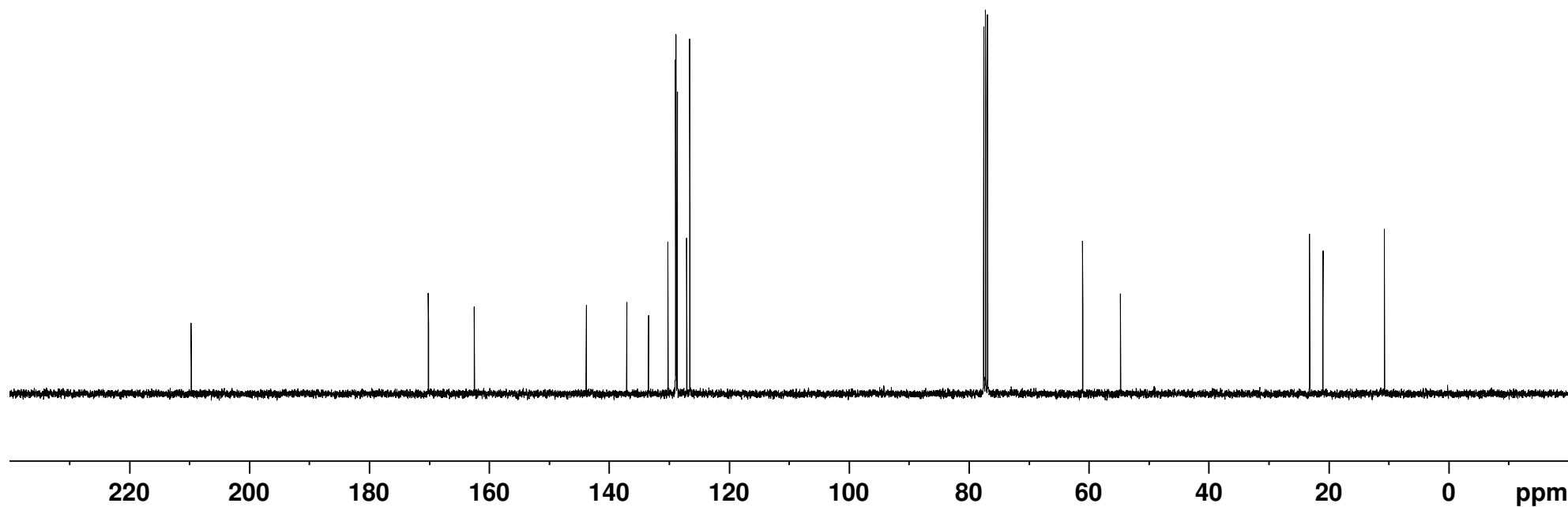
— 60.97

— 54.67

— 23.14

— 20.90

— 10.64

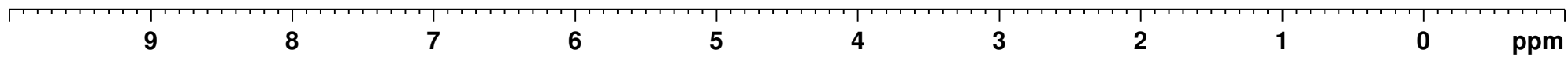
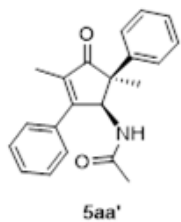


¹H NMR (400 MHz, CDCl₃)

7.526
7.522
7.506
7.502
7.477
7.471
7.466
7.455
7.436
7.432
7.428
7.423
7.415
7.401
7.397
7.325
7.308
7.288
7.264
7.254
7.241
7.236
7.230
7.218
7.152
7.149
7.131
5.737
5.732
5.711
5.706
4.679
4.654

2.130
2.125
1.775
1.462

0.071
-0.000



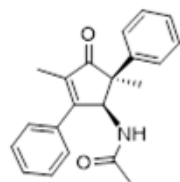
2.05
3.17
2.13
1.04
2.01

1.03

0.95

3.00
2.98
3.01

¹³C NMR (100 MHz, CDCl₃)



— 209.73

— 170.04

— 163.30

141.12

138.17

133.28

130.11

128.83

128.73

128.63

127.46

127.32

77.47

77.16

76.84

— 60.56

— 55.97

23.40

22.89

— 10.61

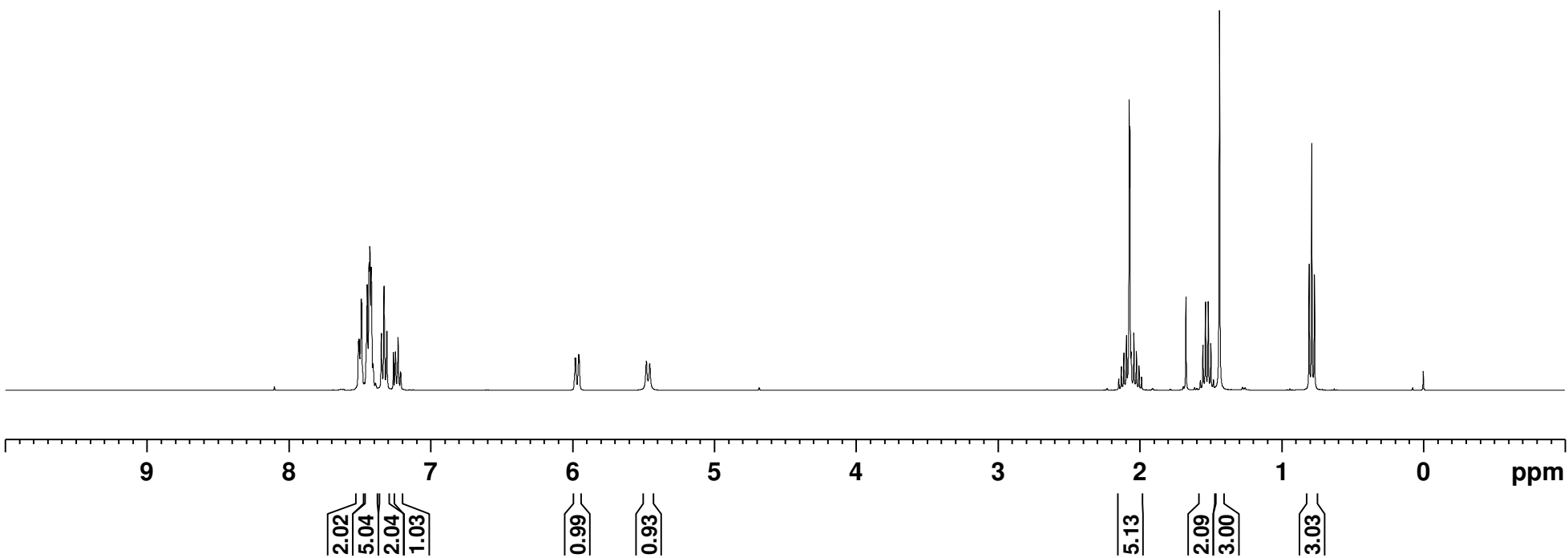
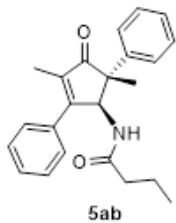


220 200 180 160 140 120 100 80 60 40 20 0 ppm

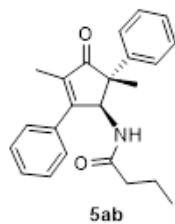
¹H NMR (400 MHz, CDCl₃)

7.509
7.504
7.489
7.485
7.479
7.447
7.434
7.429
7.419
7.416
7.406
7.403
7.390
7.386
7.346
7.342
7.328
7.308
7.262
7.248
7.229
7.211
5.981
5.977
5.957
5.952
5.478
5.454

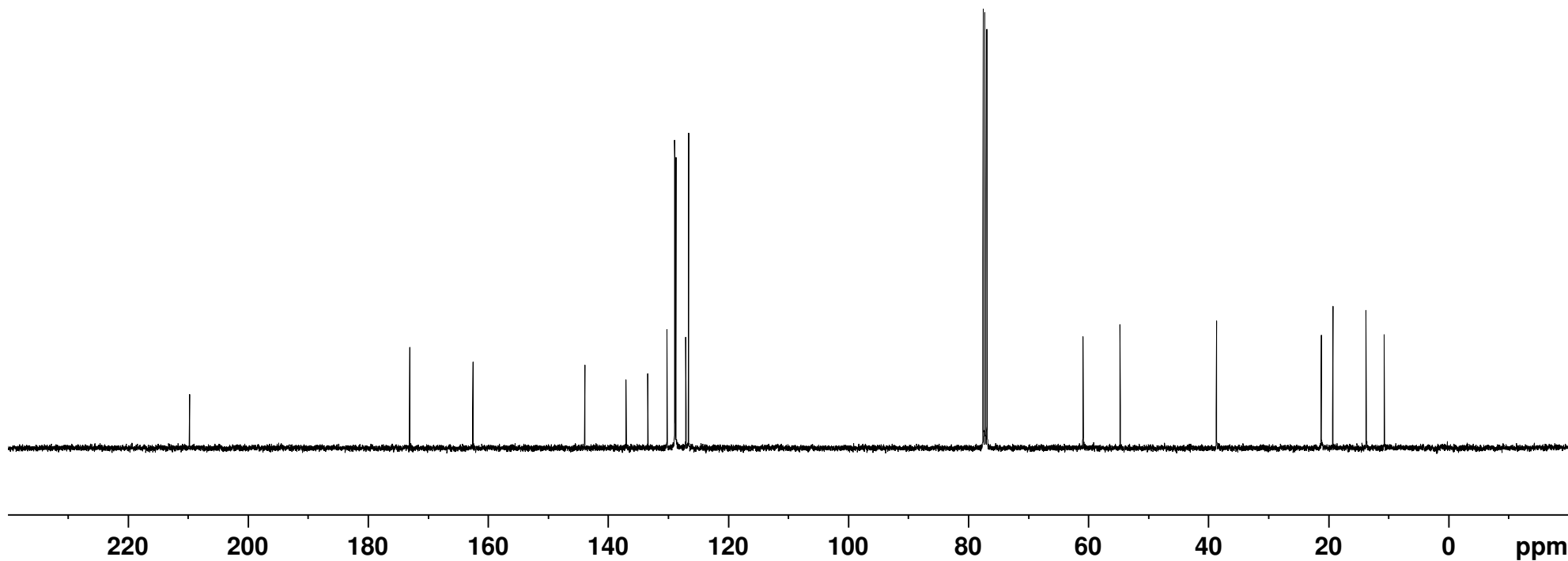
2.147
2.128
2.110
2.092
2.073
2.069
2.059
2.041
2.023
2.005
1.986
1.572
1.553
1.535
1.516
1.498
1.480
1.437
0.804
0.786
0.767
0.073
-0.000



^{13}C NMR (100 MHz, CDCl_3)



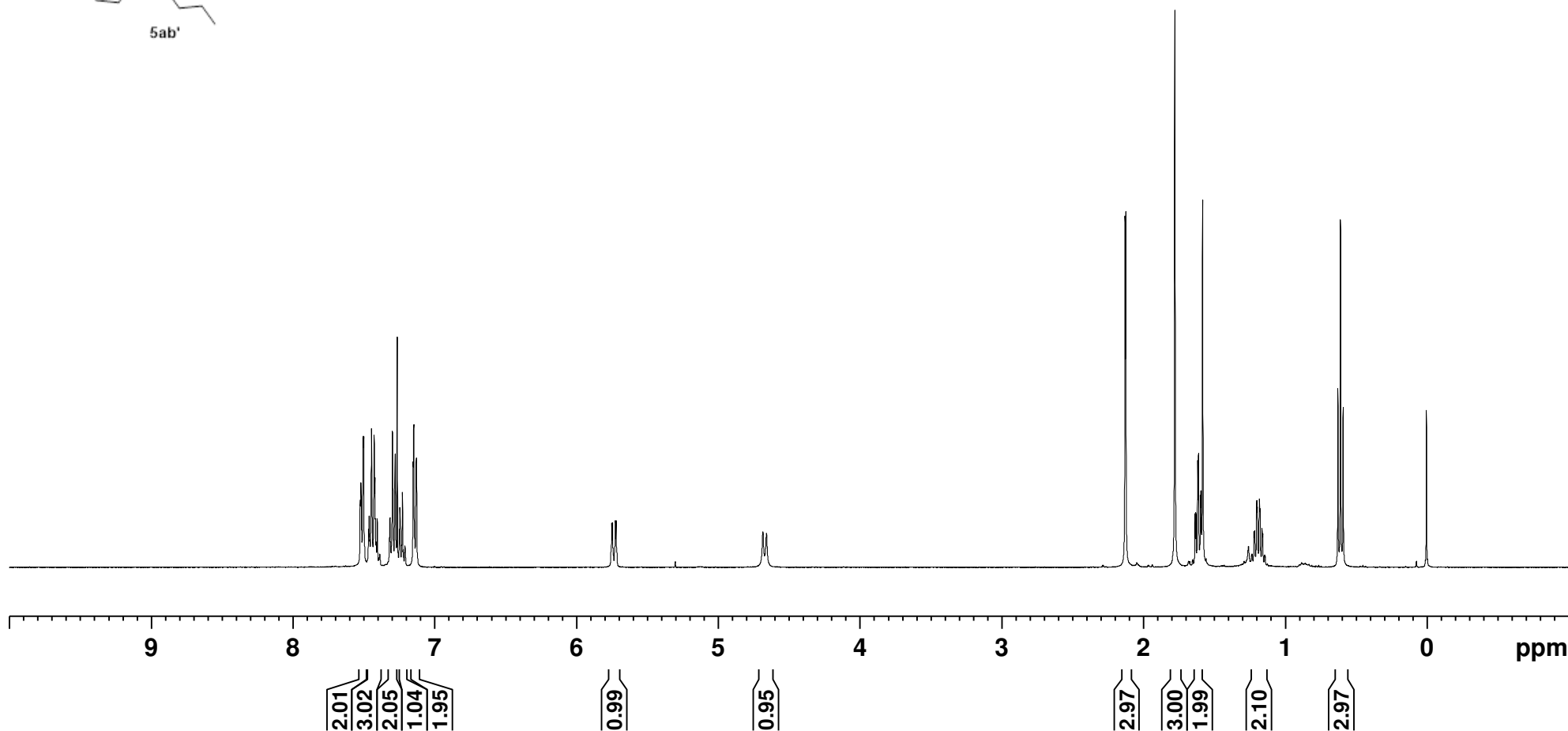
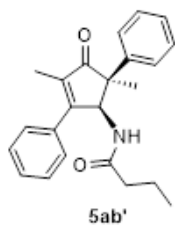
- 209.69
- 173.00
- 162.50
- 143.84
- 136.96
- 133.35
- 130.15
- 128.87
- 128.80
- 128.64
- 127.00
- 126.55
- 77.48
- 77.16
- 76.84
- 60.83
- 54.64
- 38.60
- 21.11
- 19.20
- 13.66
- 10.64



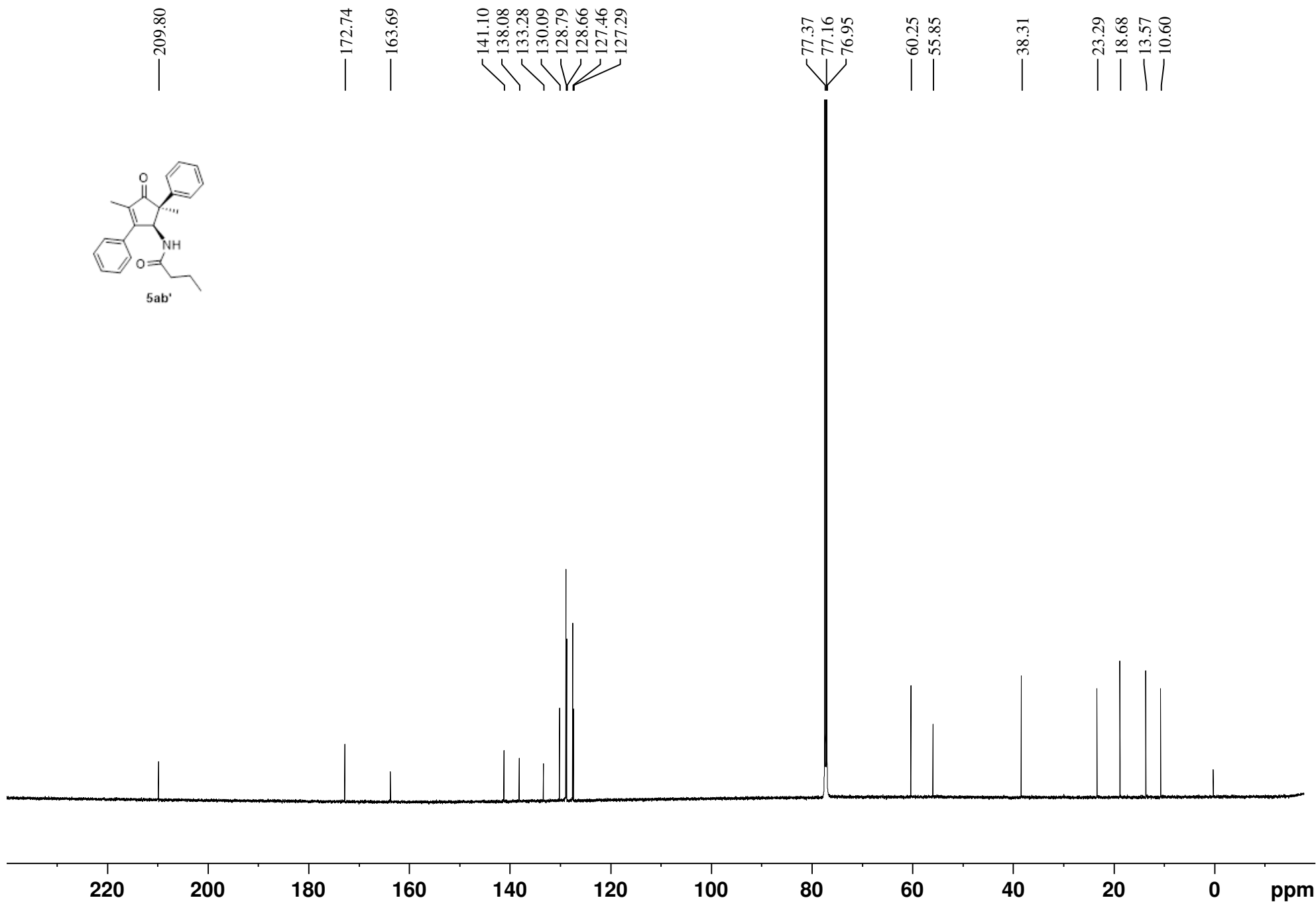
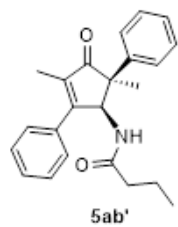
¹H NMR (400 MHz, CDCl₃)

7.522
7.518
7.502
7.499
7.465
7.460
7.420
7.403
7.393
7.385
7.313
7.296
7.276
7.262
7.244
7.230
7.226
7.220
7.207
7.149
7.145
7.127
5.748
5.743
5.723
5.718
5.713
4.682
4.656

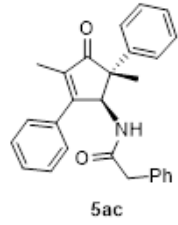
2.126
2.121
1.775
1.632
1.626
1.613
1.608
1.594
1.590
1.234
1.230
1.215
1.141
1.137
0.624
0.606
0.587
0.070
-0.000



¹³C NMR (150 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)



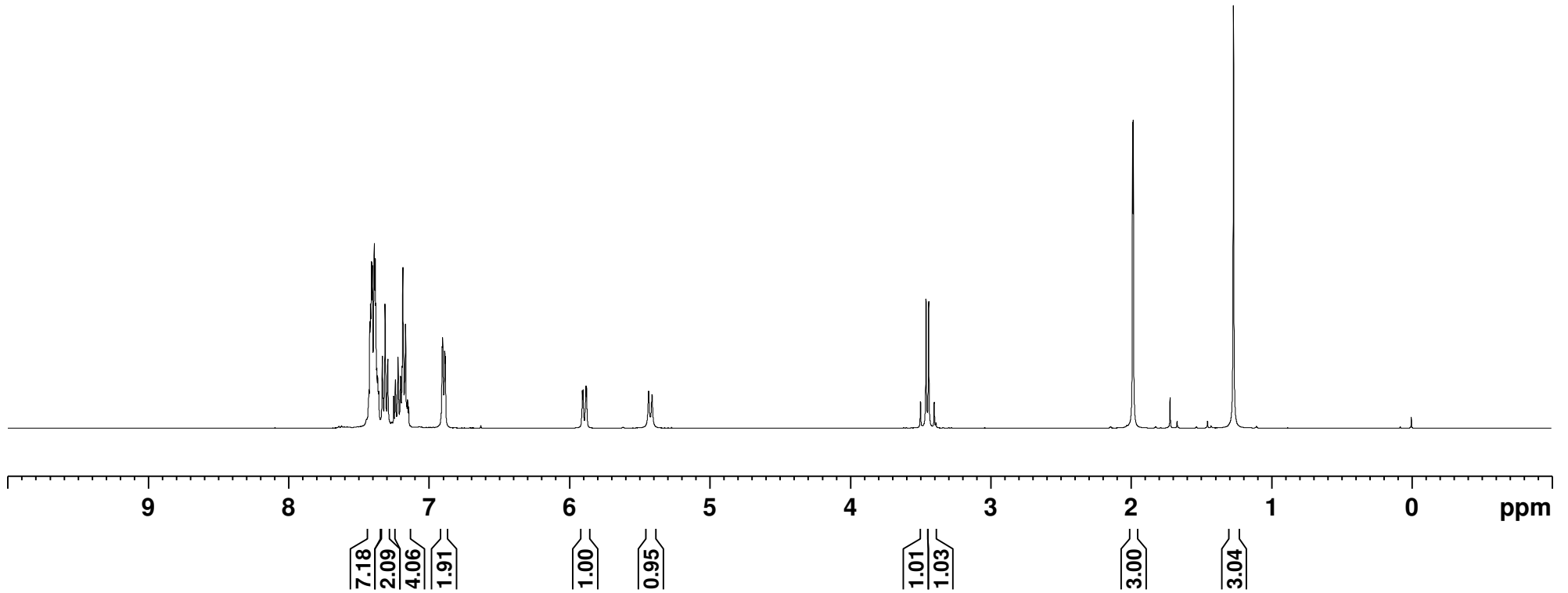
7.426
7.420
7.415
7.364
7.360
7.356
7.329
7.324
7.311
7.291
7.249
7.237
7.234
7.184
7.165
7.155
7.150
7.143
6.904
6.901
6.886
6.881
5.905
5.900
5.881
5.876
5.433
5.409

3.496
3.457
3.438
3.399

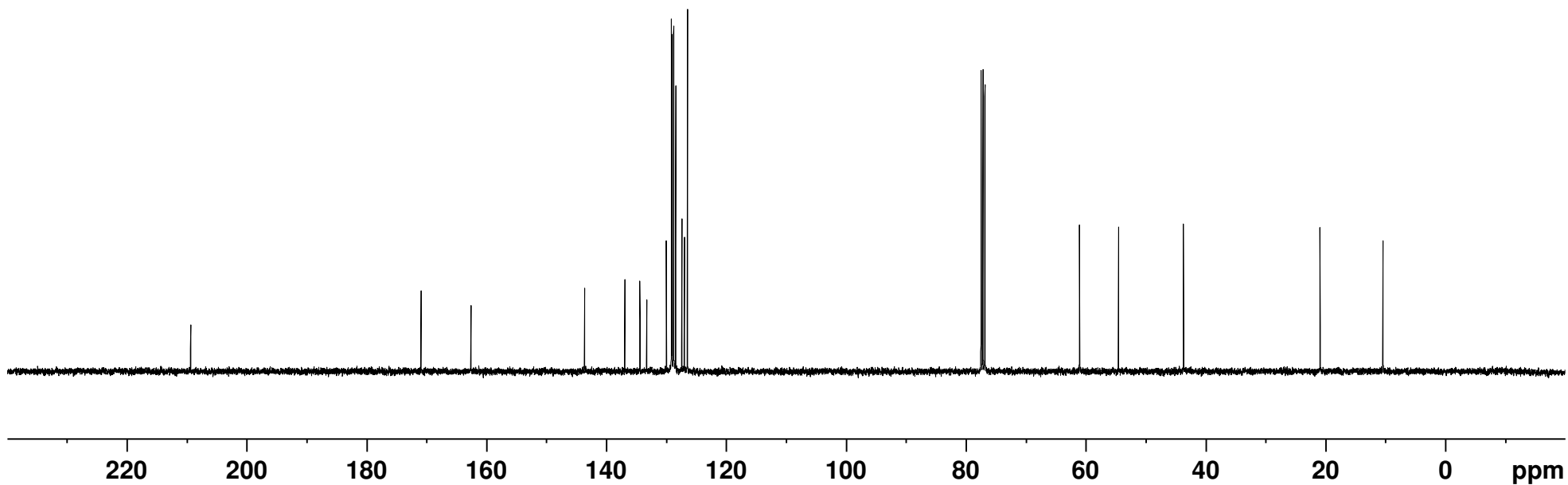
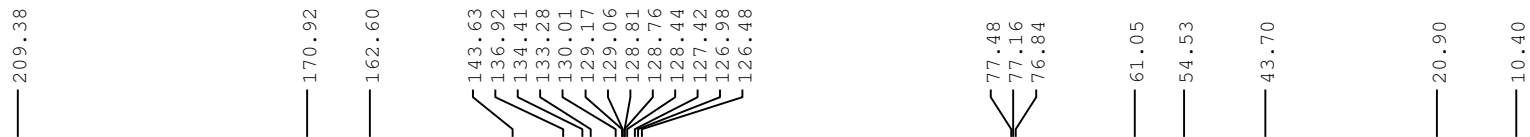
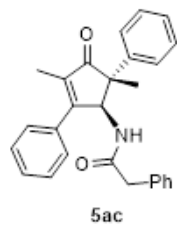
1.985
1.981

1.267

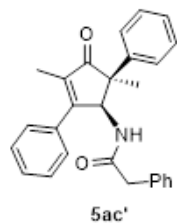
0.078
-0.000



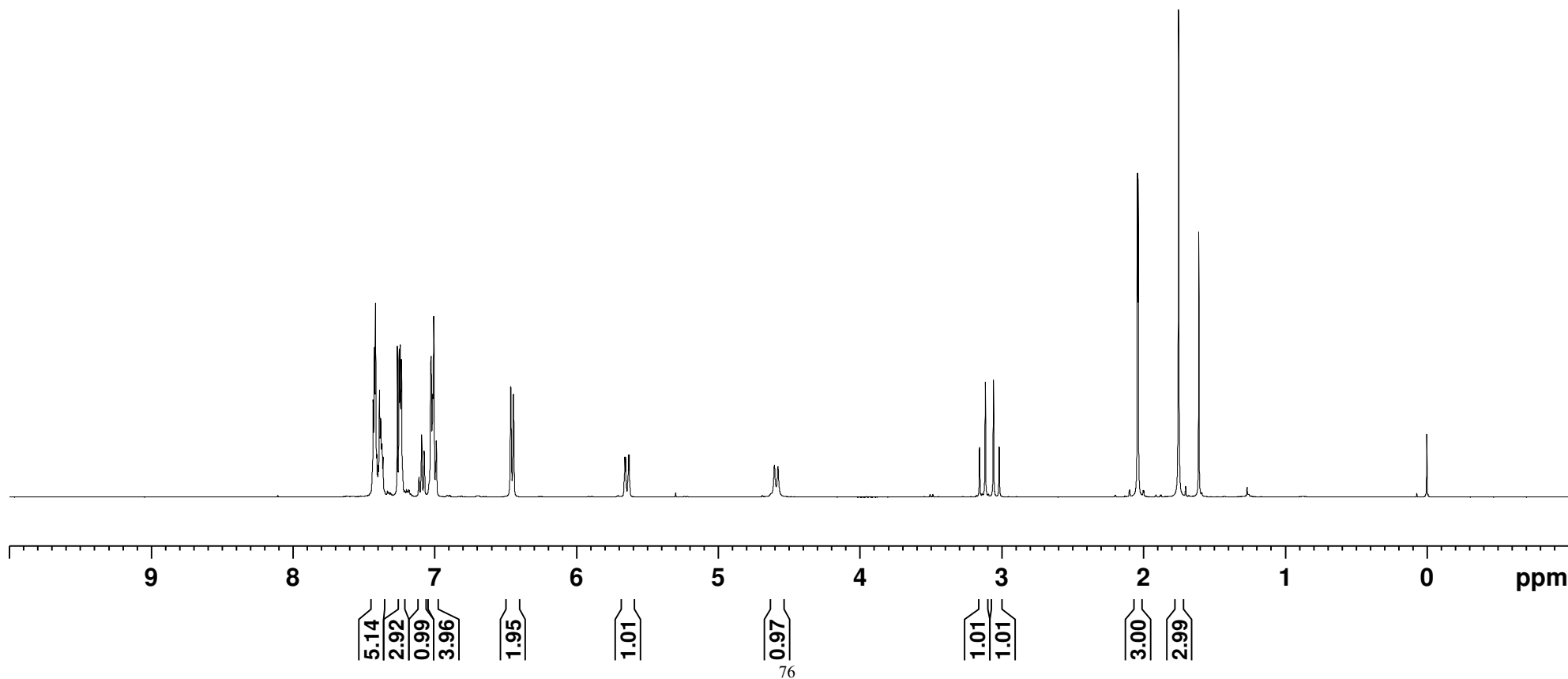
¹³C NMR (100 MHz, CDCl₃)



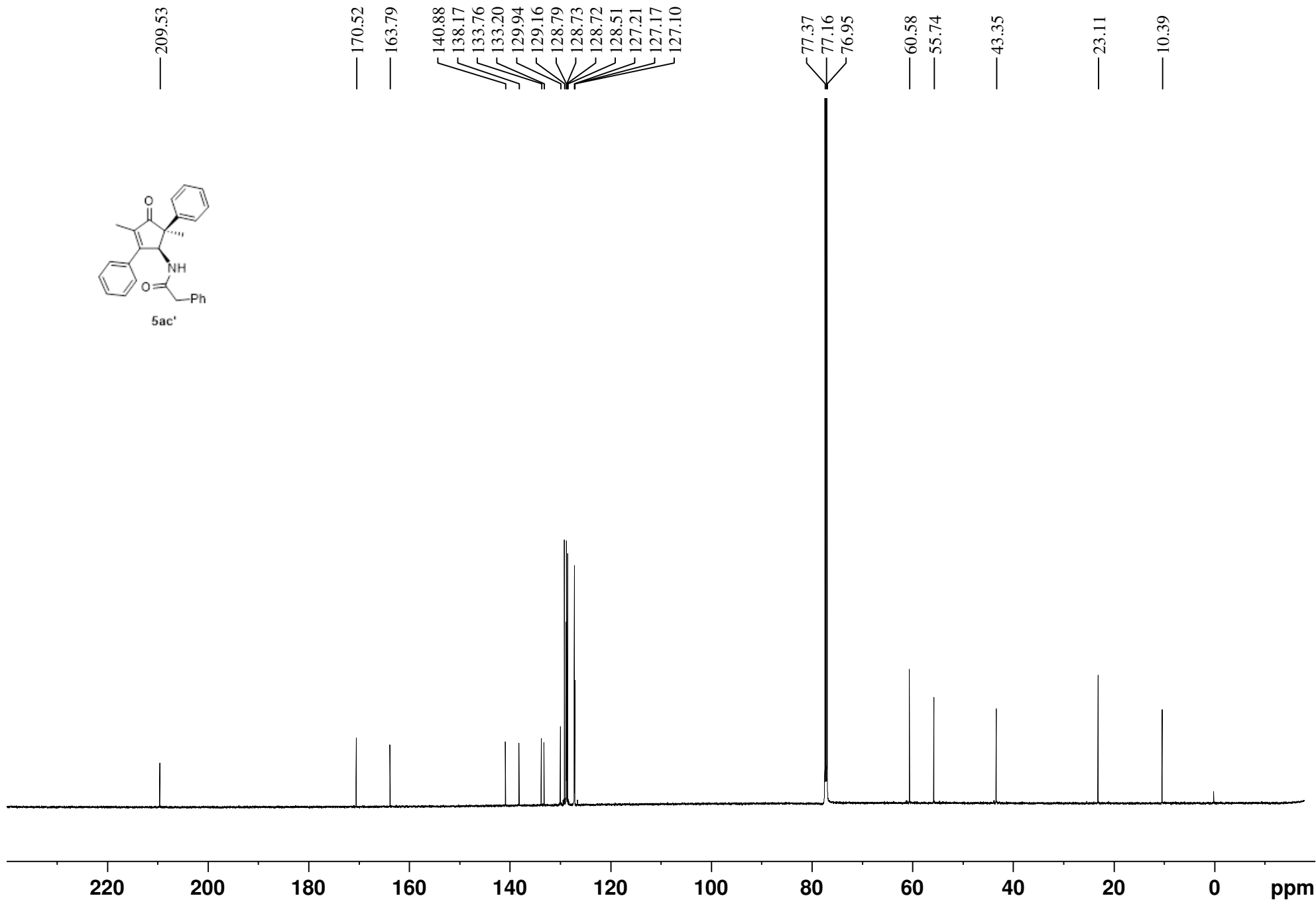
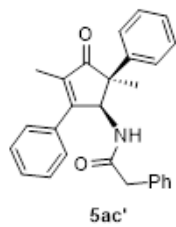
¹H NMR (400 MHz, CDCl₃)



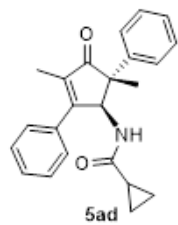
7.432
7.423
7.370
7.363
7.262
7.250
7.242
7.233
7.109
7.091
7.072
7.025
7.017
6.988
6.462
6.444
5.657
5.652
5.632
5.627
4.602
4.577
3.155
3.114
3.057
3.016
2.041
2.036
1.751
-0.000



¹³C NMR (150 MHz, CDCl₃)

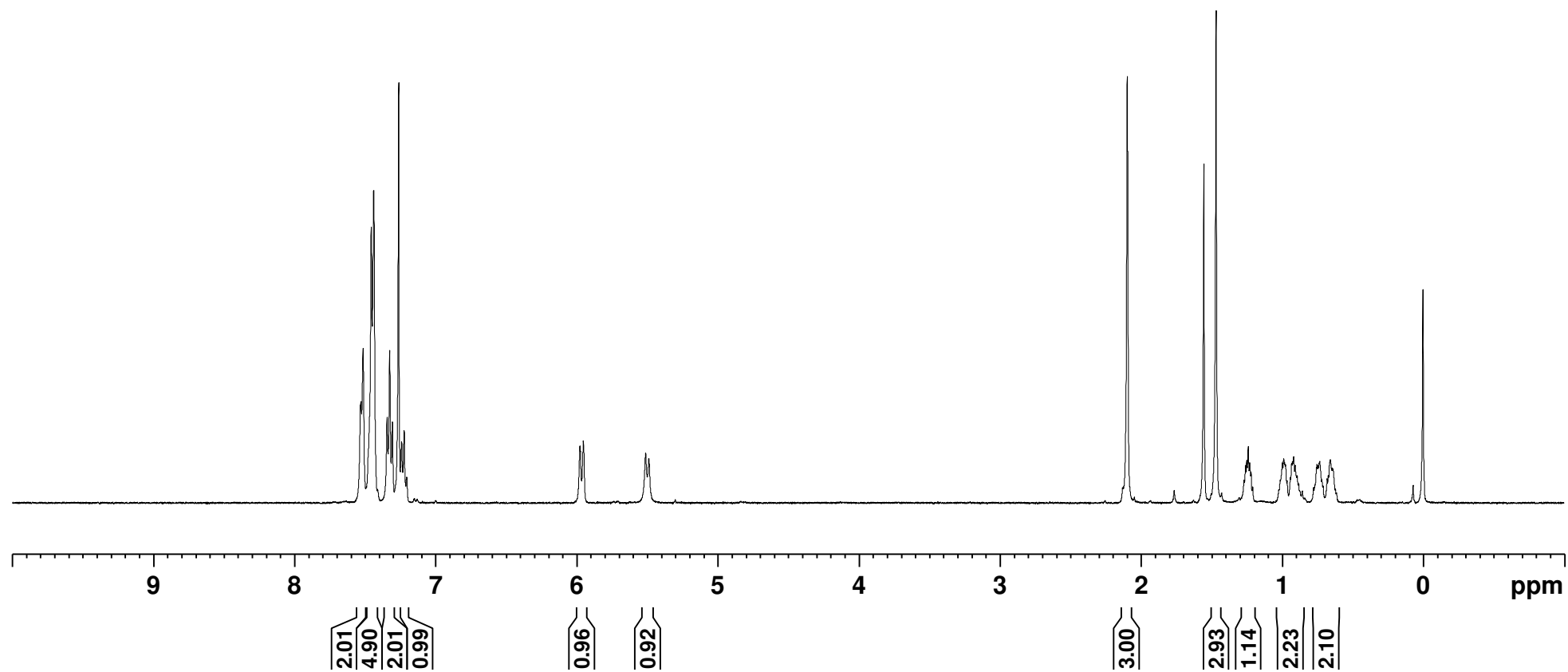


^1H NMR (400 MHz, CDCl_3)

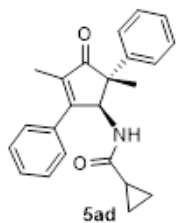


7.533
7.528
7.513
7.456
7.438
7.343
7.324
7.305
7.261
7.240
7.222
7.203
5.976
5.952
5.510
5.488

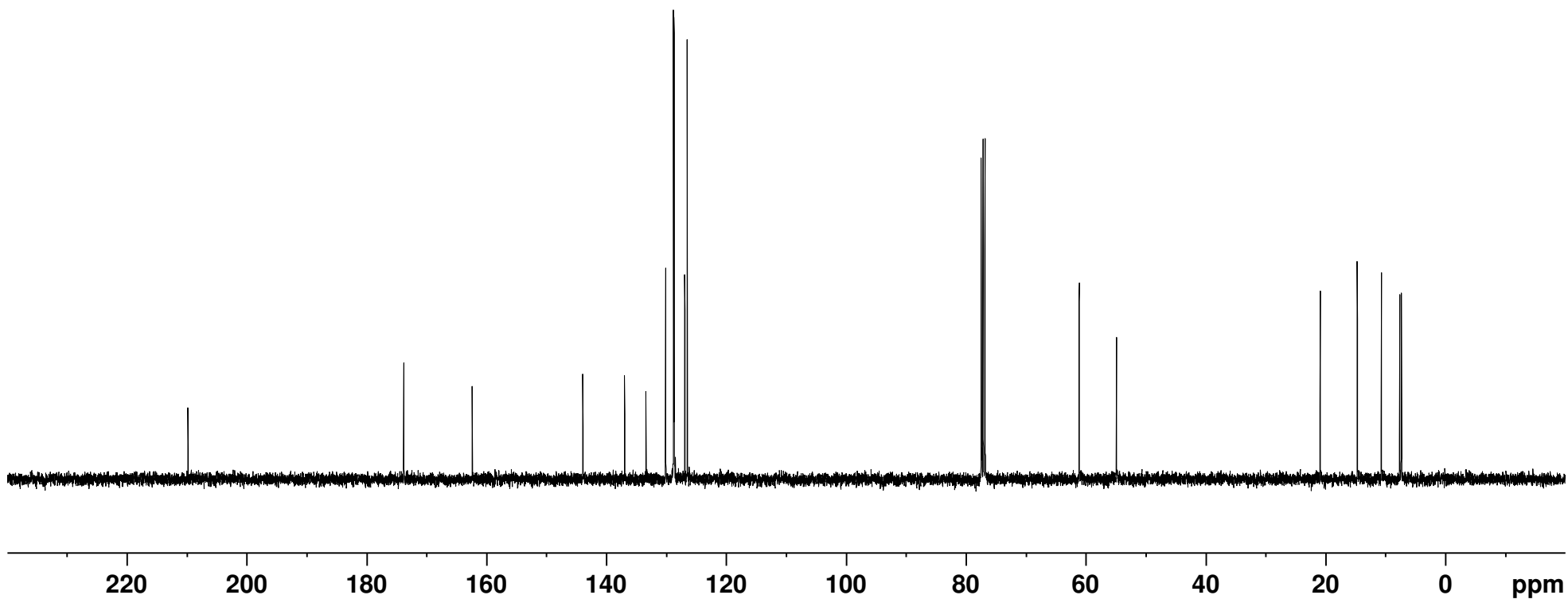
2.097
1.467
1.269
1.249
1.238
1.219
0.998
0.982
0.963
0.930
0.893
0.882
0.752
0.732
0.680
0.657
0.638
0.070
-0.000



¹³C NMR (100 MHz, CDCl₃)



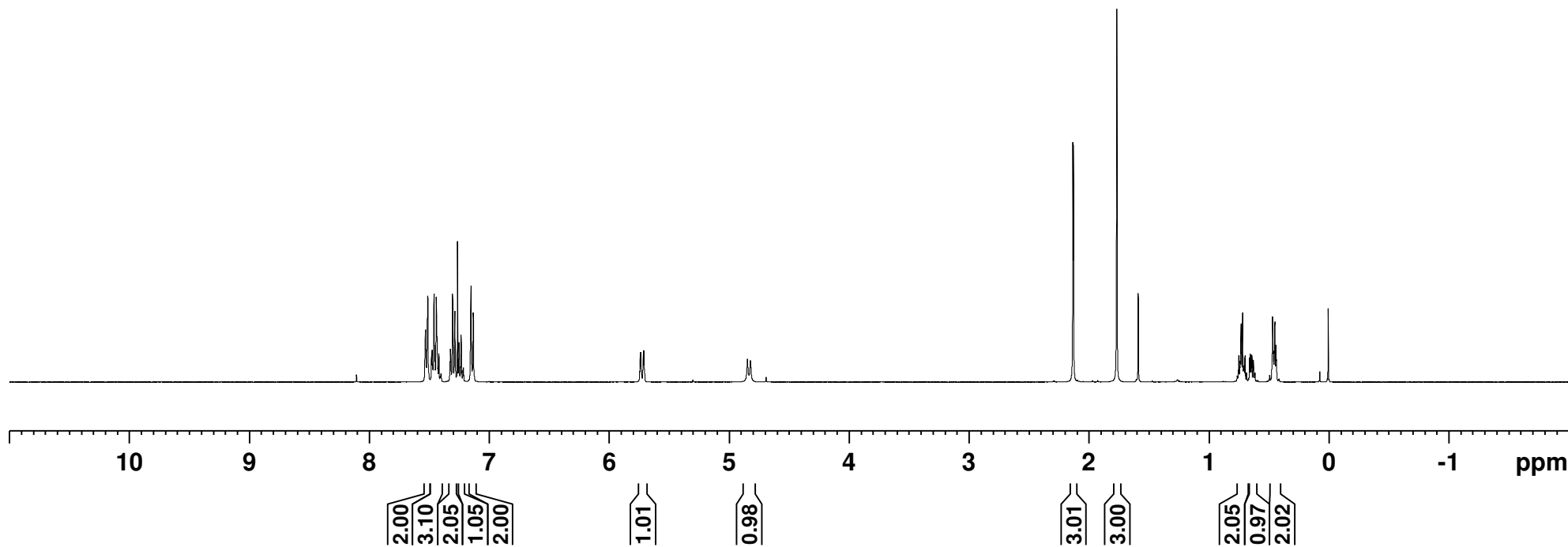
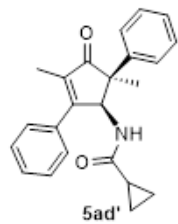
- 209.83
- 173.82
- 162.41
- 143.93
- 136.96
- 133.40
- 130.13
- 128.83
- 128.75
- 128.70
- 126.93
- 126.52
- 77.48
- 77.16
- 76.84
- 61.11
- 54.89
- 20.89
- 14.69
- 10.68
- 7.61
- 7.34



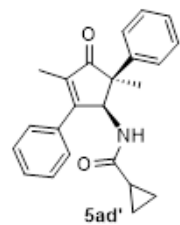
^1H NMR (400 MHz, CDCl_3)

7.532
7.528
7.523
7.511
7.508
7.502
7.478
7.473
7.468
7.457
7.438
7.403
7.399
7.323
7.320
7.303
7.299
7.284
7.262
7.252
7.249
7.231
7.216
7.213
7.152
7.148
7.143
7.131
5.737
5.732
5.711
5.706
4.844
4.818

2.130
2.124
1.763
0.760
0.745
0.727
0.714
0.703
0.694
0.682
0.656
0.648
0.636
0.625
0.610
0.488
0.464
0.445
0.437
0.433
0.414
0.410
0.070
-0.000



¹³C NMR (100 MHz, CDCl₃)



— 209.86

— 173.57

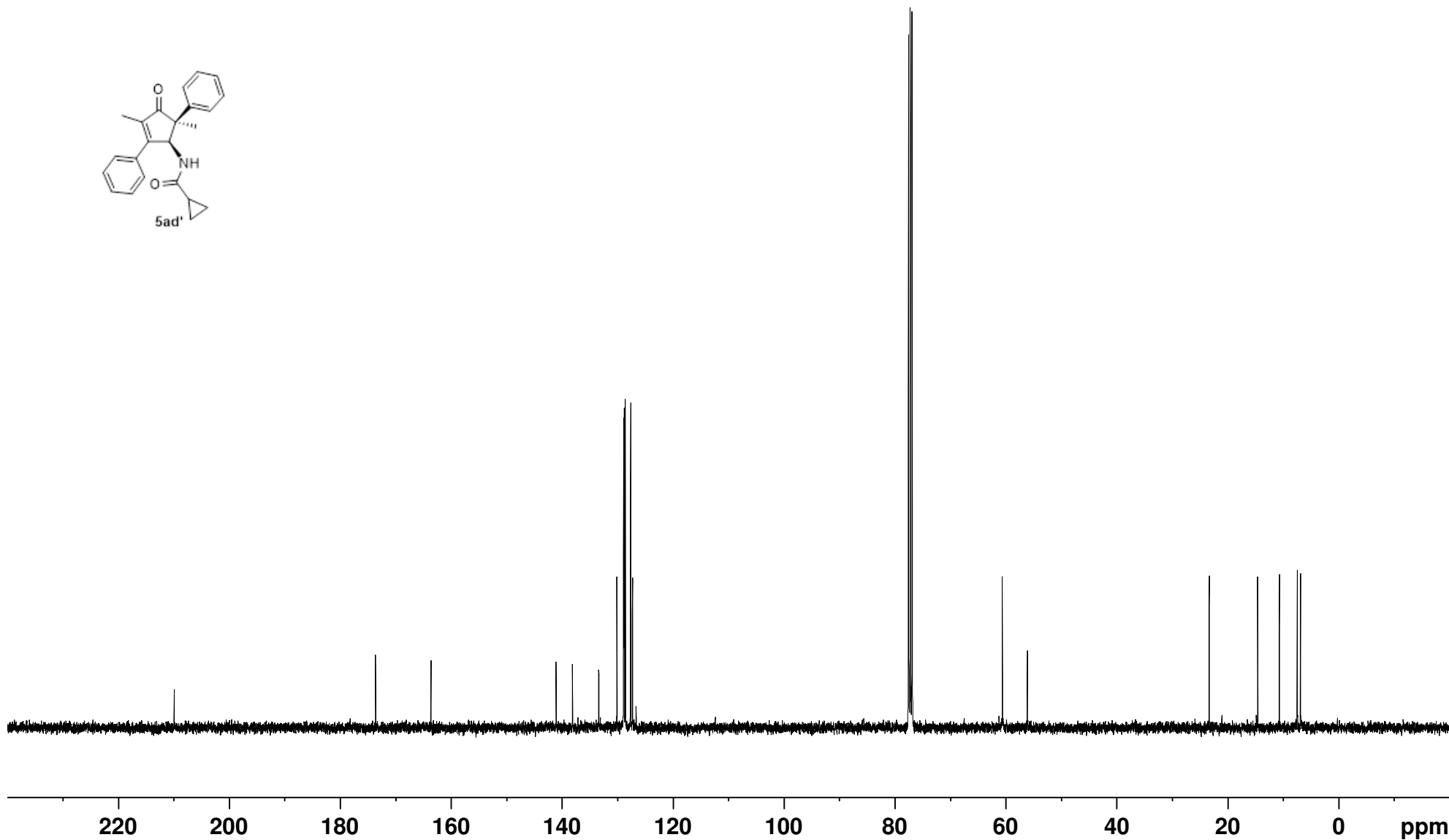
— 163.56

141.04
138.07
133.32
130.06
128.84
128.77
128.53
127.59
127.24

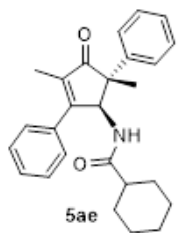
77.48
77.16
76.84

— 60.56
— 56.03

— 23.26
14.53
10.61
7.38
6.78

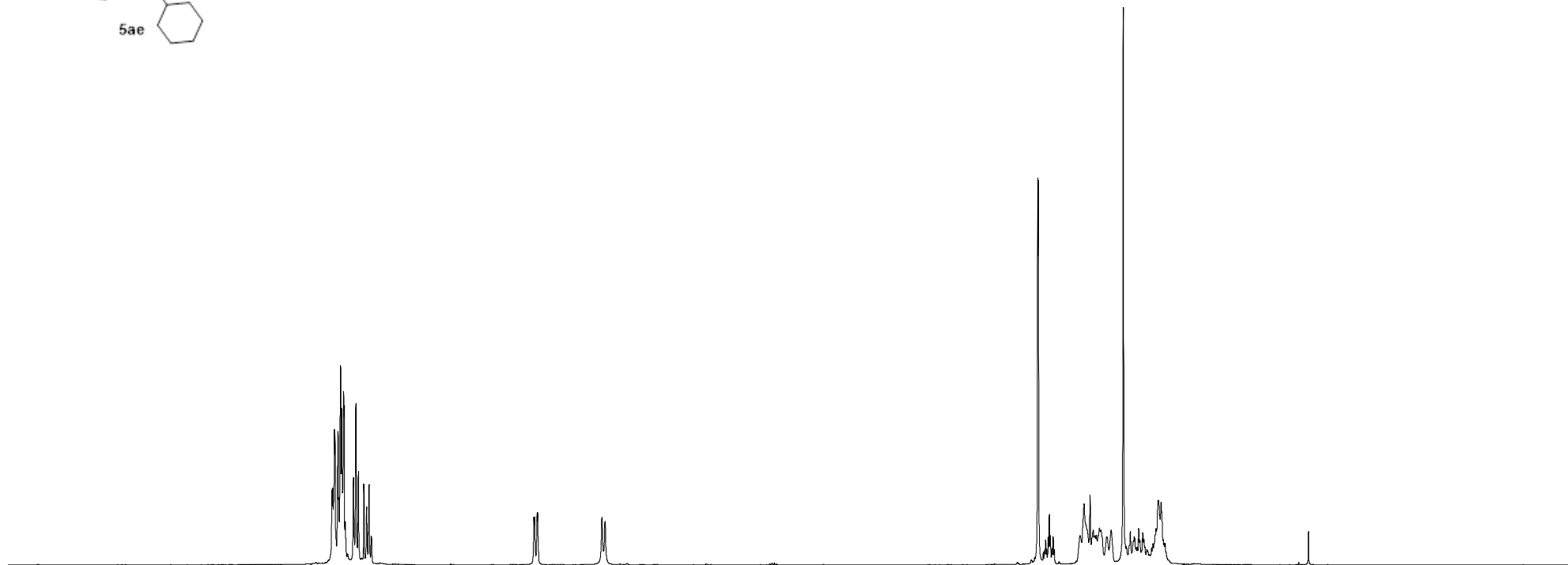


¹H NMR (400 MHz, CDCl₃)



7.507
7.502
7.487
7.483
7.460
7.440
7.417
7.413
7.405
7.341
7.323
7.303
7.262
7.240
7.222
7.203
5.953
5.949
5.929
5.925
5.431
5.407

2.080
2.076
2.038
2.029
2.021
1.971
1.963
1.954
1.757
1.725
1.700
1.695
1.654
1.639
1.630
1.606
1.594
1.549
1.516
1.423
1.369
1.345
1.339
1.305
1.295
1.274
1.242
1.237
1.226
1.205
1.195
1.172
1.132
1.108
1.102
0.074
-0.000



9

8

2.04
5.01
2.12
1.03

6

1.00

5

0.95

4

3

3.00
1.12
2.07
3.28
3.06
2.21
3.03

2

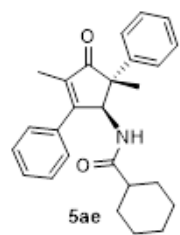
1

0

-1

ppm

^{13}C NMR (100 MHz, CDCl_3)



— 209.72 — 176.03 — 162.49

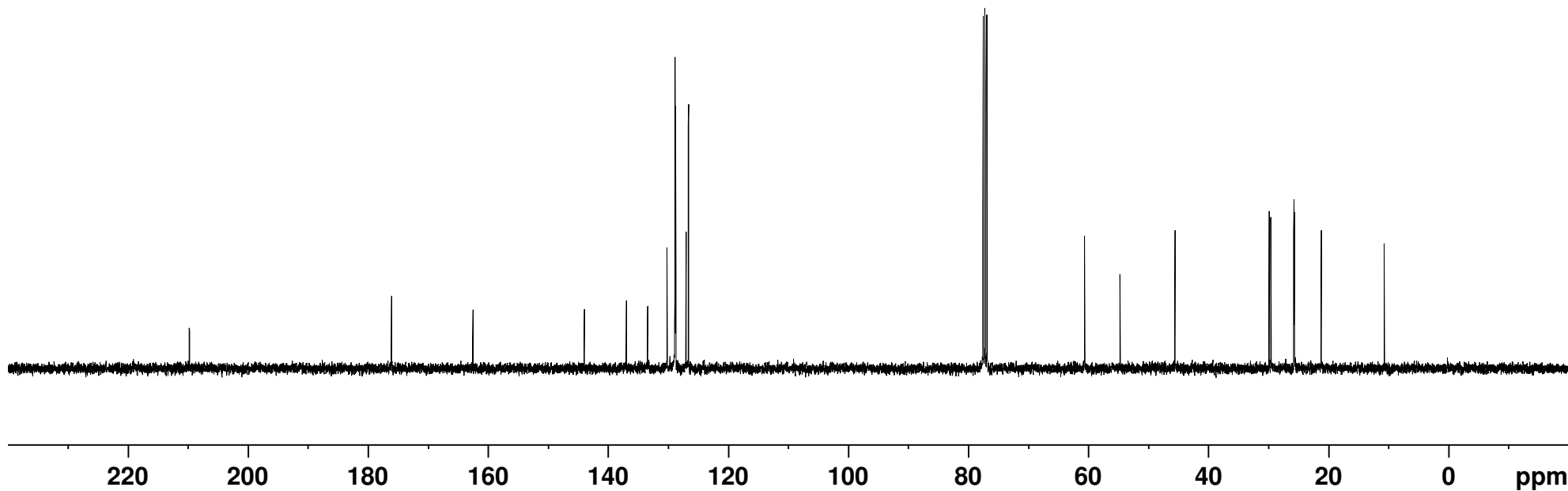
143.93 136.91 133.35 130.14 128.82 128.78 128.69 126.96 126.57

77.47 77.16 76.84

— 60.58 — 54.66 — 45.50

29.81 29.51 25.71 25.66 25.61 21.13

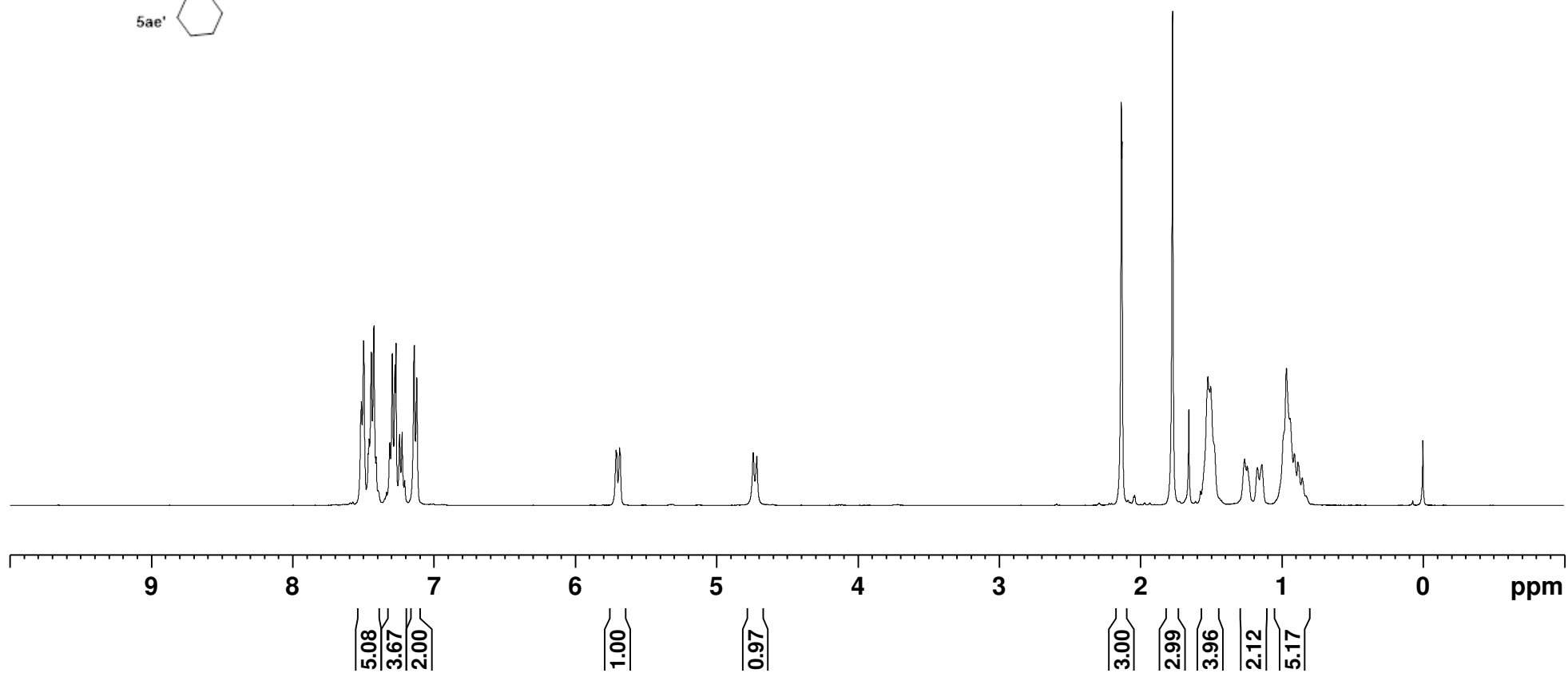
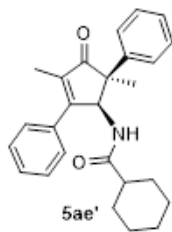
— 10.64



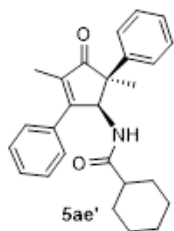
¹H NMR (400 MHz, CDCl₃)

7.516
7.512
7.496
7.464
7.457
7.442
7.423
7.408
7.395
7.392
7.389
7.334
7.311
7.293
7.274
7.266
7.241
7.223
7.205
7.141
7.138
7.120
5.710
5.706
5.685
5.680
4.739
4.714

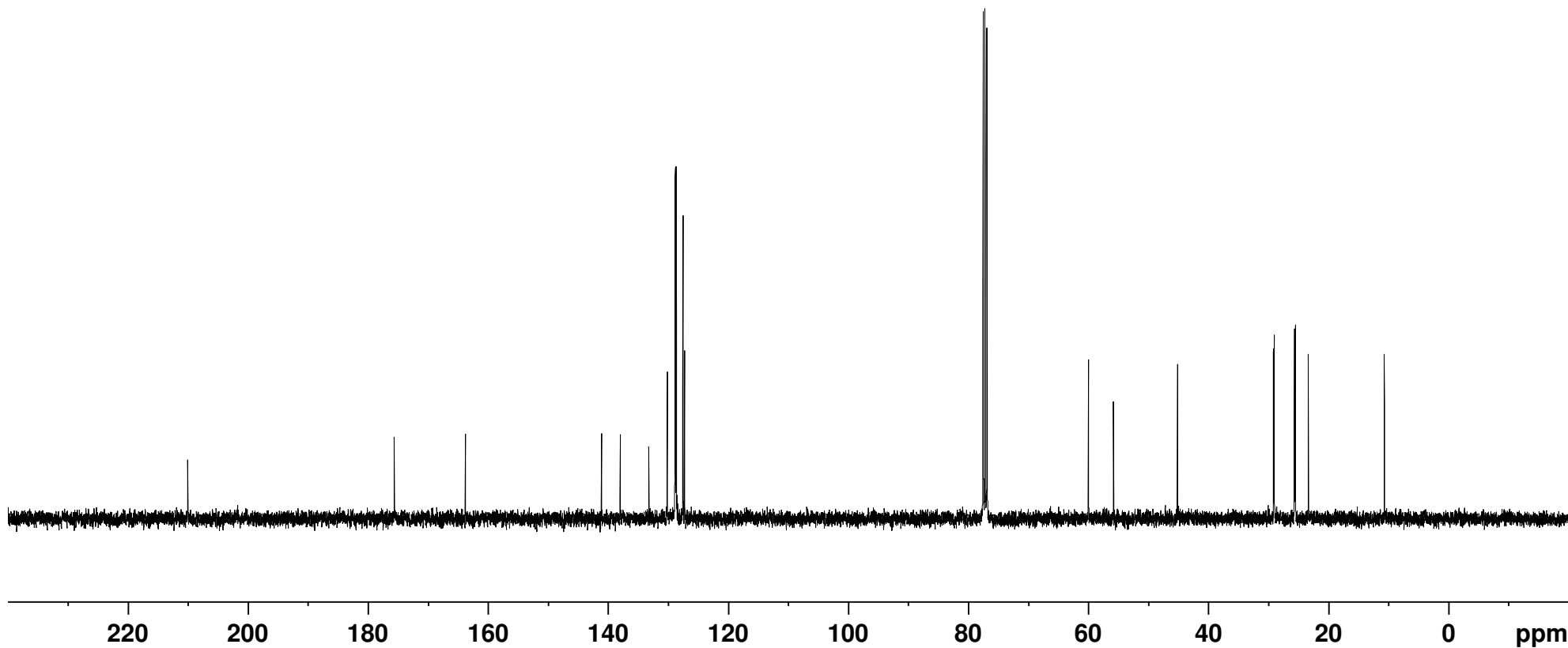
2.134
2.129
1.771
1.574
1.521
1.502
1.260
1.242
1.171
1.140
0.966
0.939
0.909
0.884
0.854
0.825
0.071
-0.000



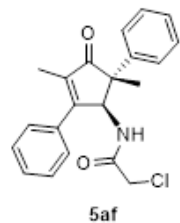
¹³C NMR (100 MHz, CDCl₃)



- 210.00
- 175.60
- 163.73
- 141.07
- 137.94
- 133.19
- 130.10
- 128.81
- 128.71
- 128.60
- 127.49
- 127.21
- 77.47
- 77.16
- 76.84
- 59.91
- 55.74
- 45.08
- 29.08
- 28.97
- 25.60
- 25.49
- 25.45
- 23.29
- 10.61



¹H NMR (400 MHz, CDCl₃)



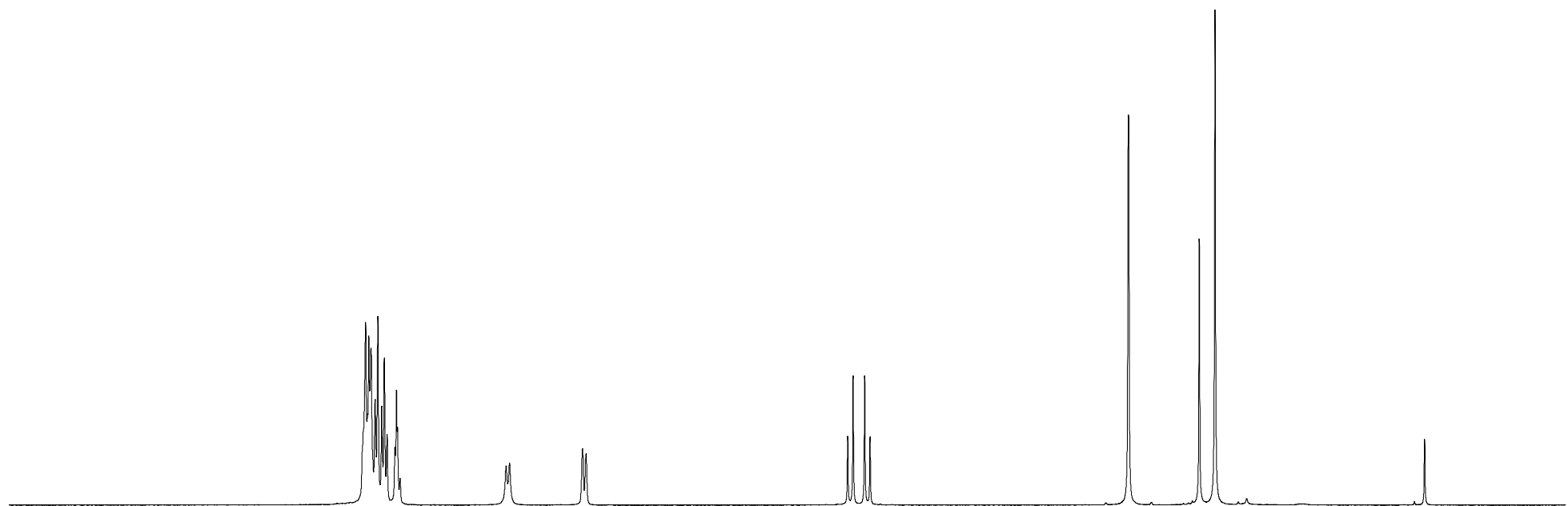
7.479
7.465
7.457
7.441
7.412
7.392
7.365
7.347
7.327
7.271
7.261
7.254
7.236
6.487
6.463
5.946
5.922

4.074
4.036
3.954
3.916

— 2.090

— 1.480

0.071
-0.000



5.11
2.10
2.02
1.42

0.96

1.00

1.01
1.00

3.00

3.01

¹³C NMR (100 MHz, CDCl₃)

— 208.97

— 166.04
— 161.90

143.37
137.55
133.07
130.24
128.94
128.88
128.41
127.17
126.40

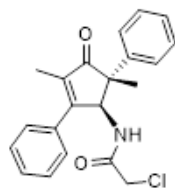
77.48
77.16
76.84

— 61.22
— 54.59

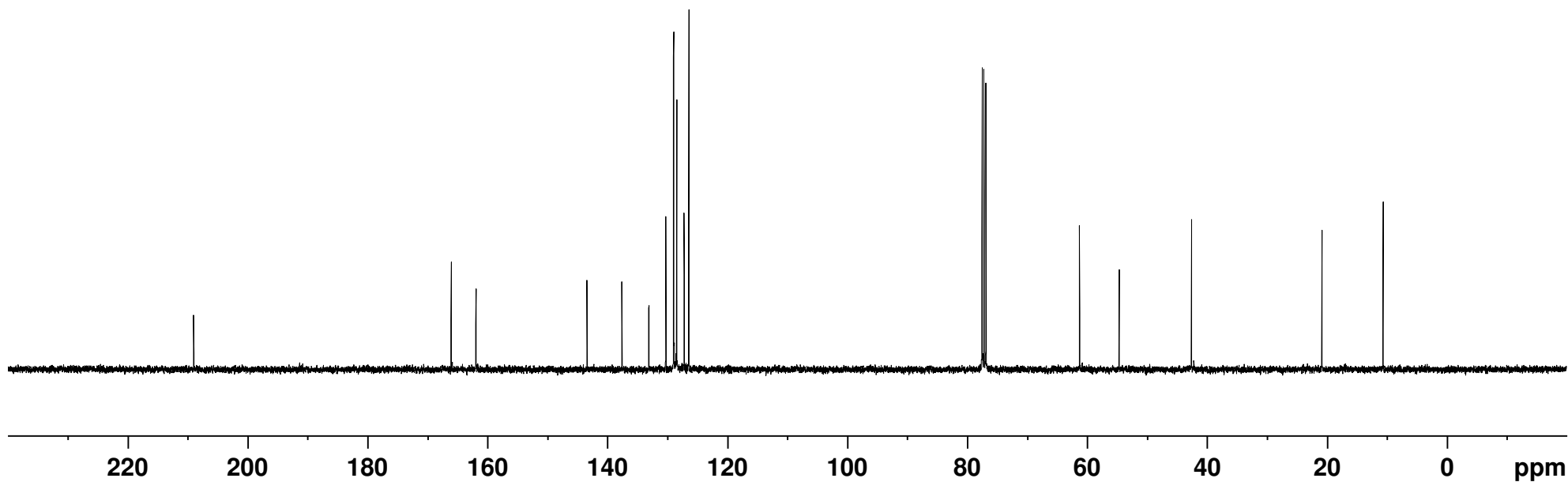
— 42.54

— 20.78

— 10.60



5af



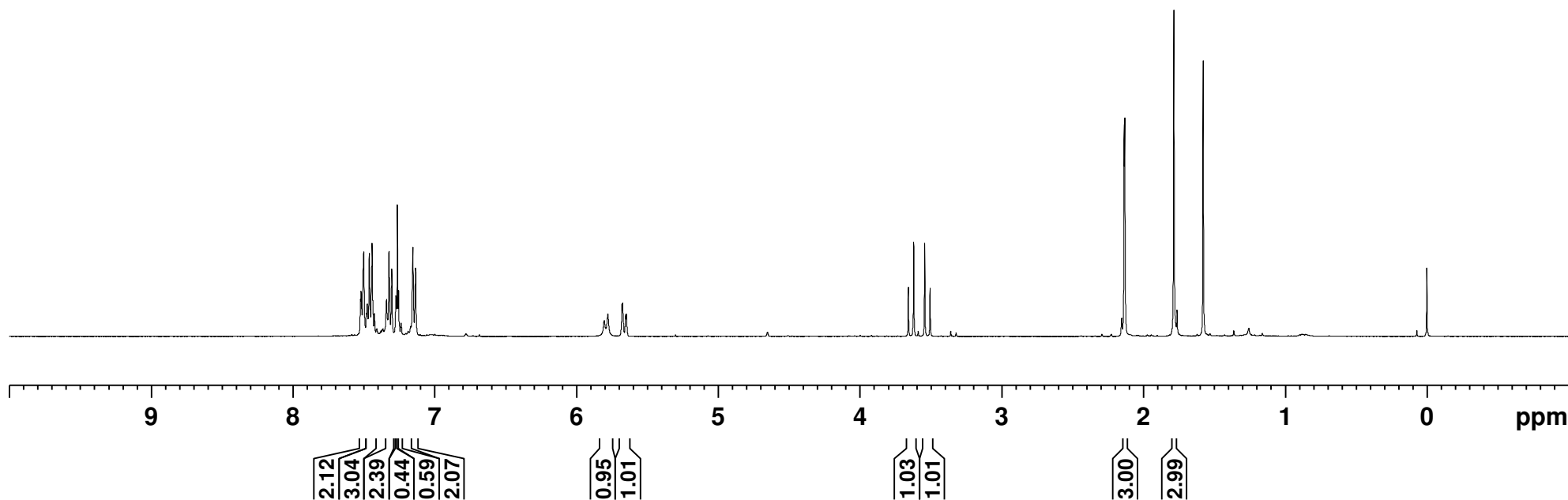
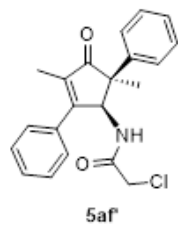
¹H NMR (400 MHz, CDCl₃)

7.522
7.518
7.502
7.498
7.481
7.474
7.460
7.440
7.423
7.339
7.321
7.302
7.272
7.262
7.254
7.247
7.235
7.155
7.152
7.134
5.803
5.777
5.677
5.672
5.651
5.646

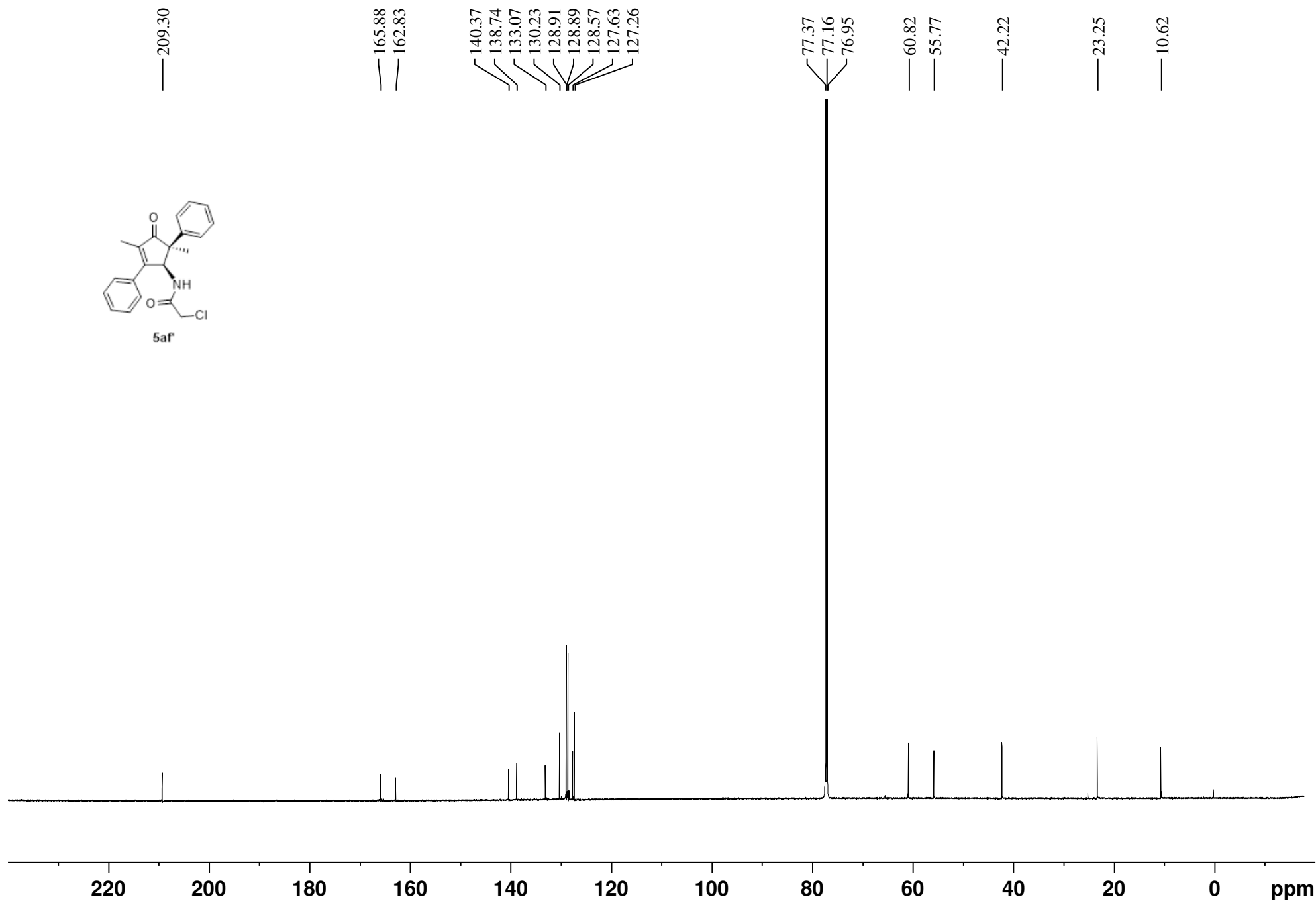
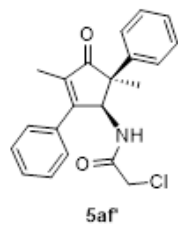
3.657
3.619
3.542
3.504

2.135
2.130
1.784

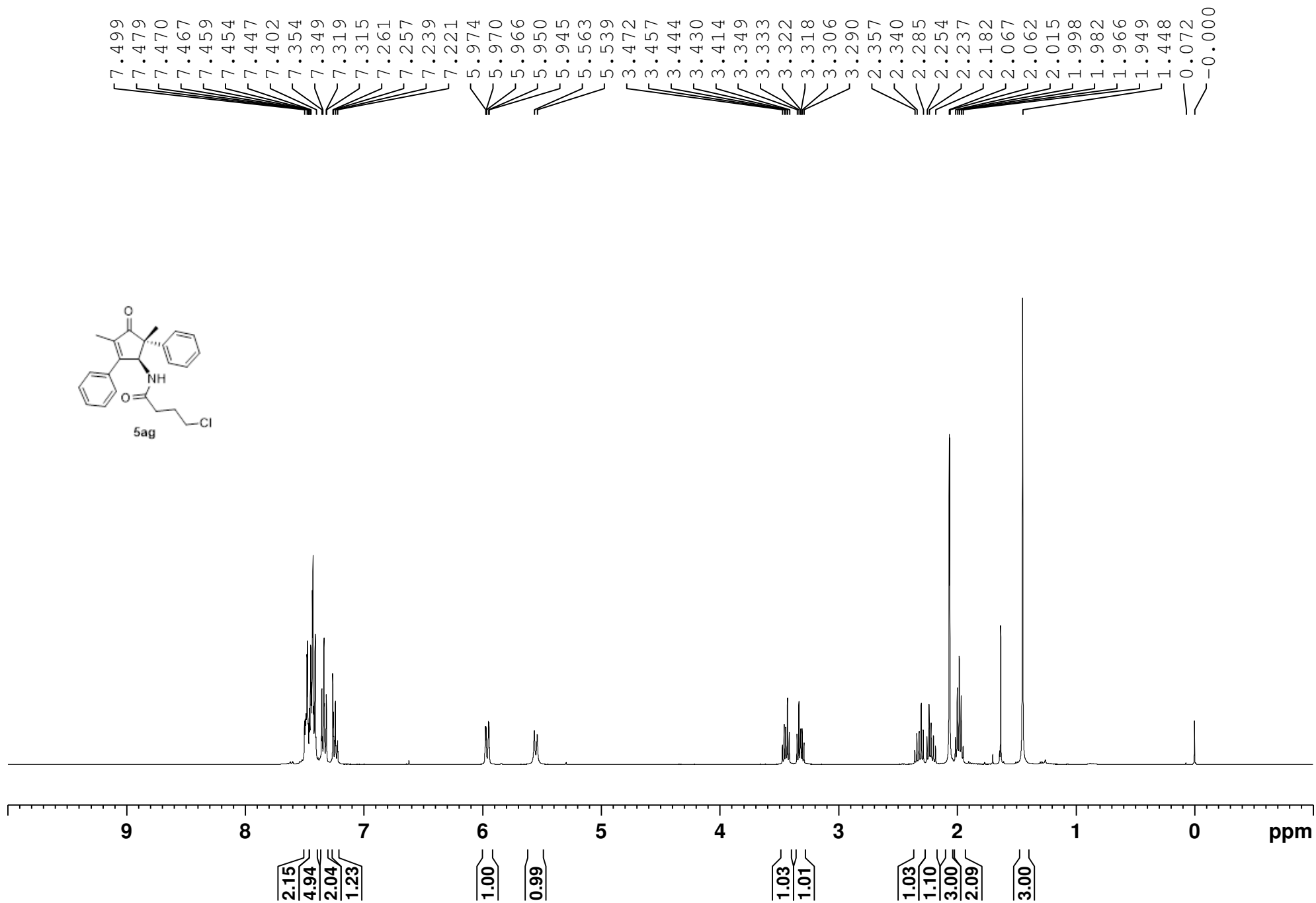
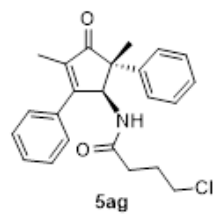
0.070
-0.000



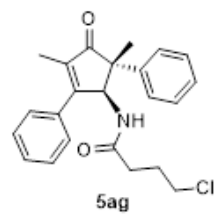
¹³C NMR (150 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)



— 209.47

— 171.73

— 162.47

— 143.70
— 137.11
— 133.32
— 130.23
— 128.93
— 128.85
— 128.55
— 127.08
— 126.48

— 77.48
— 77.16
— 76.84

— 61.02

— 54.57

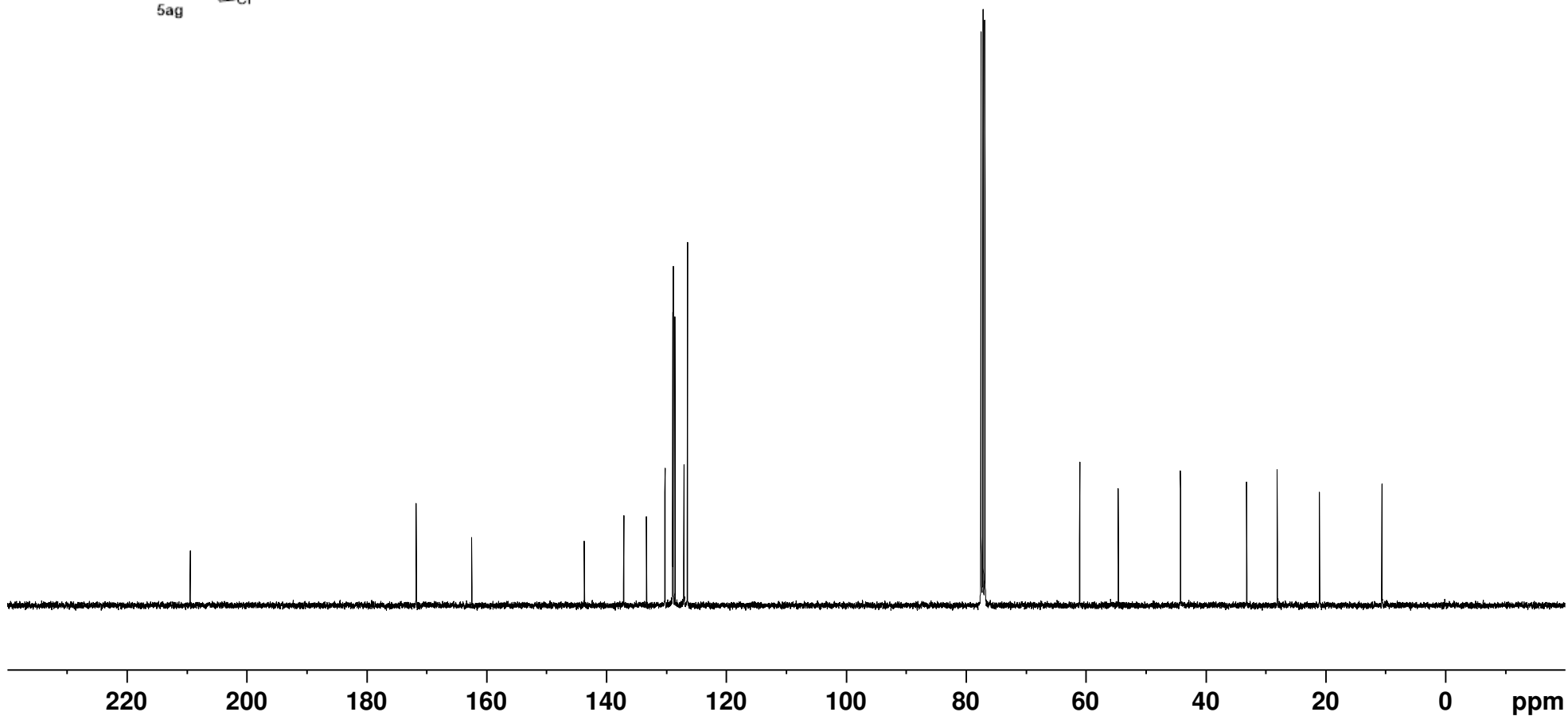
— 44.19

— 33.15

— 28.04

— 21.01

— 10.58



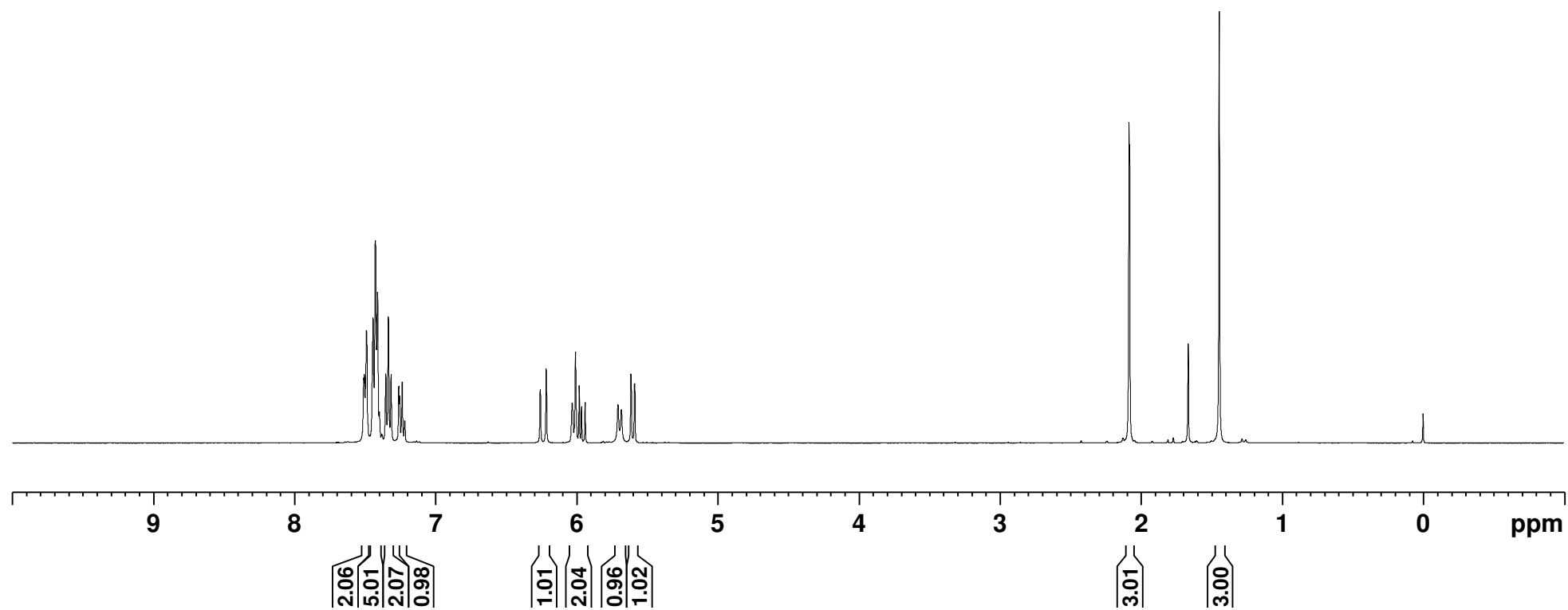
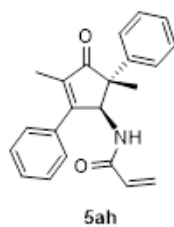
¹H NMR (400 MHz, CDCl₃)

7.509
7.505
7.489
7.486
7.442
7.427
7.425
7.411
7.398
7.352
7.334
7.314
7.261
7.254
7.236
7.217
6.258
6.216
6.032
6.028
6.007
5.981
5.964
5.939
5.706
5.682
5.615
5.589

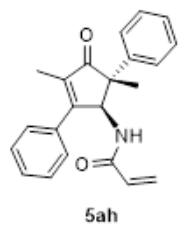
2.084
2.080

1.444

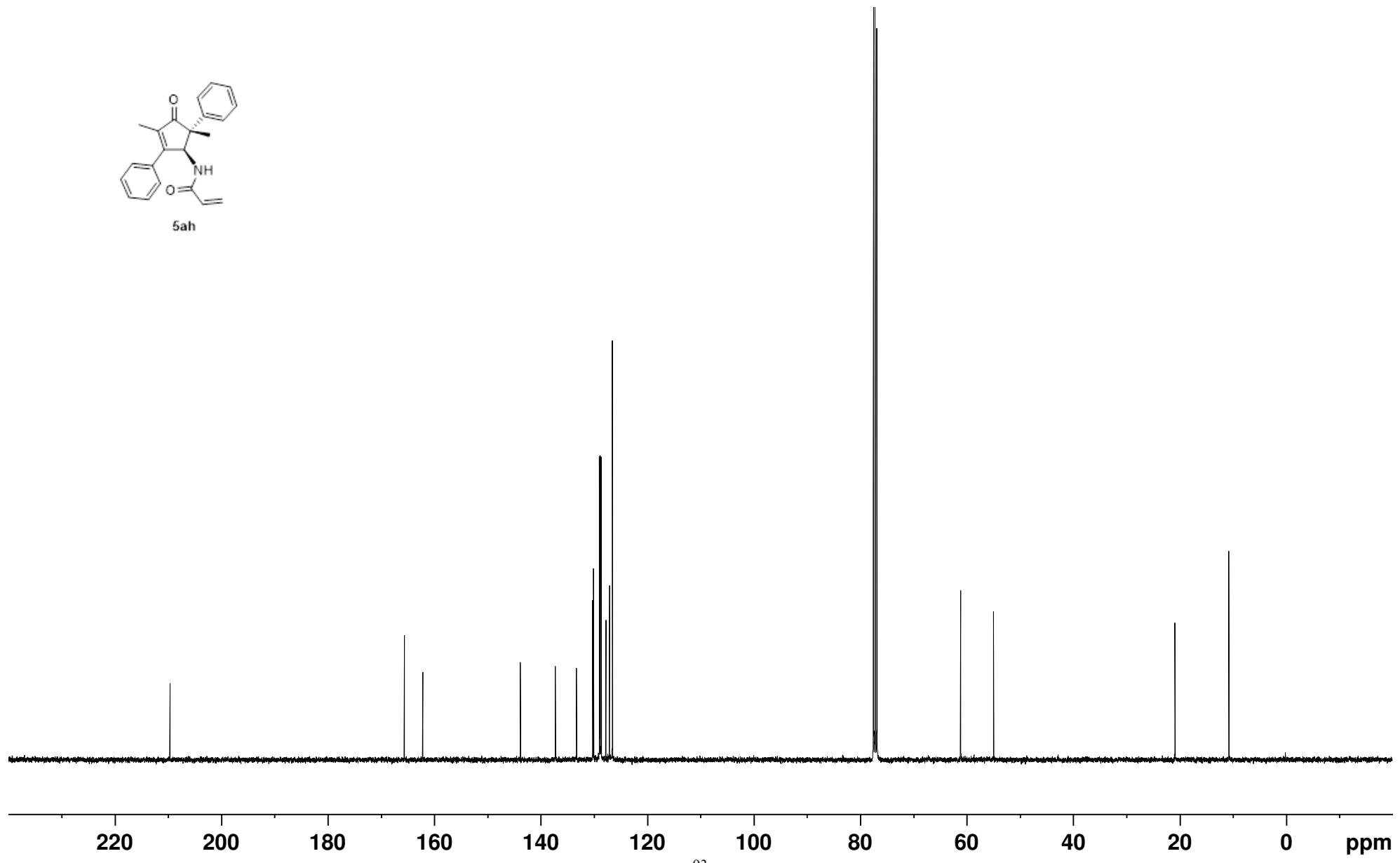
0.074
-0.000



¹³C NMR (100 MHz, CDCl₃)



- 209.63
- 165.59
- 162.12
- 143.78
- 137.23
- 133.24
- 130.23
- 130.06
- 128.94
- 128.84
- 128.61
- 127.72
- 127.06
- 126.52
- 77.47
- 77.16
- 76.84
- 61.10
- 54.93
- 20.86
- 10.73

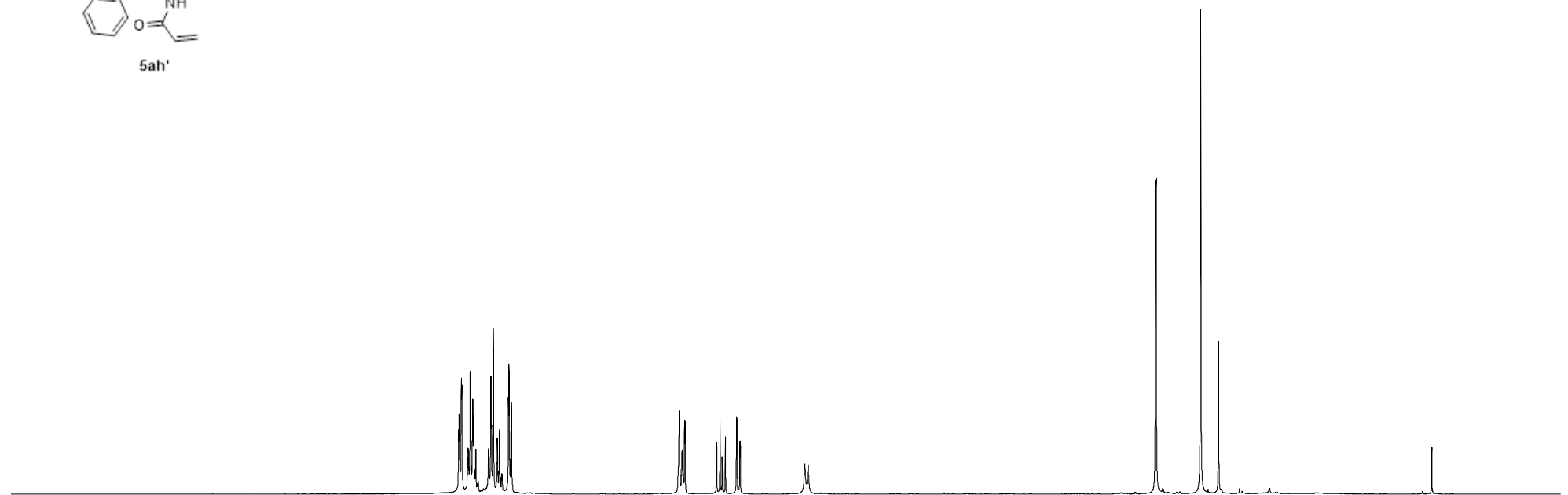
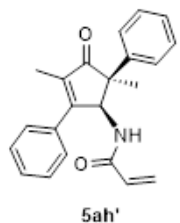


¹H NMR (400 MHz, CDCl₃)

7.533
7.528
7.523
7.512
7.509
7.502
7.464
7.459
7.442
7.423
7.417
7.400
7.385
7.382
7.303
7.300
7.283
7.279
7.264
7.237
7.234
7.216
7.201
7.198
7.195
7.147
7.143
7.138
7.125
5.834
5.826
5.823
5.803
5.798
5.784
5.780
5.536
5.510
5.493
5.467
5.382
5.379
5.356
5.353
4.853
4.827

2.138
2.133
1.789

-0.000

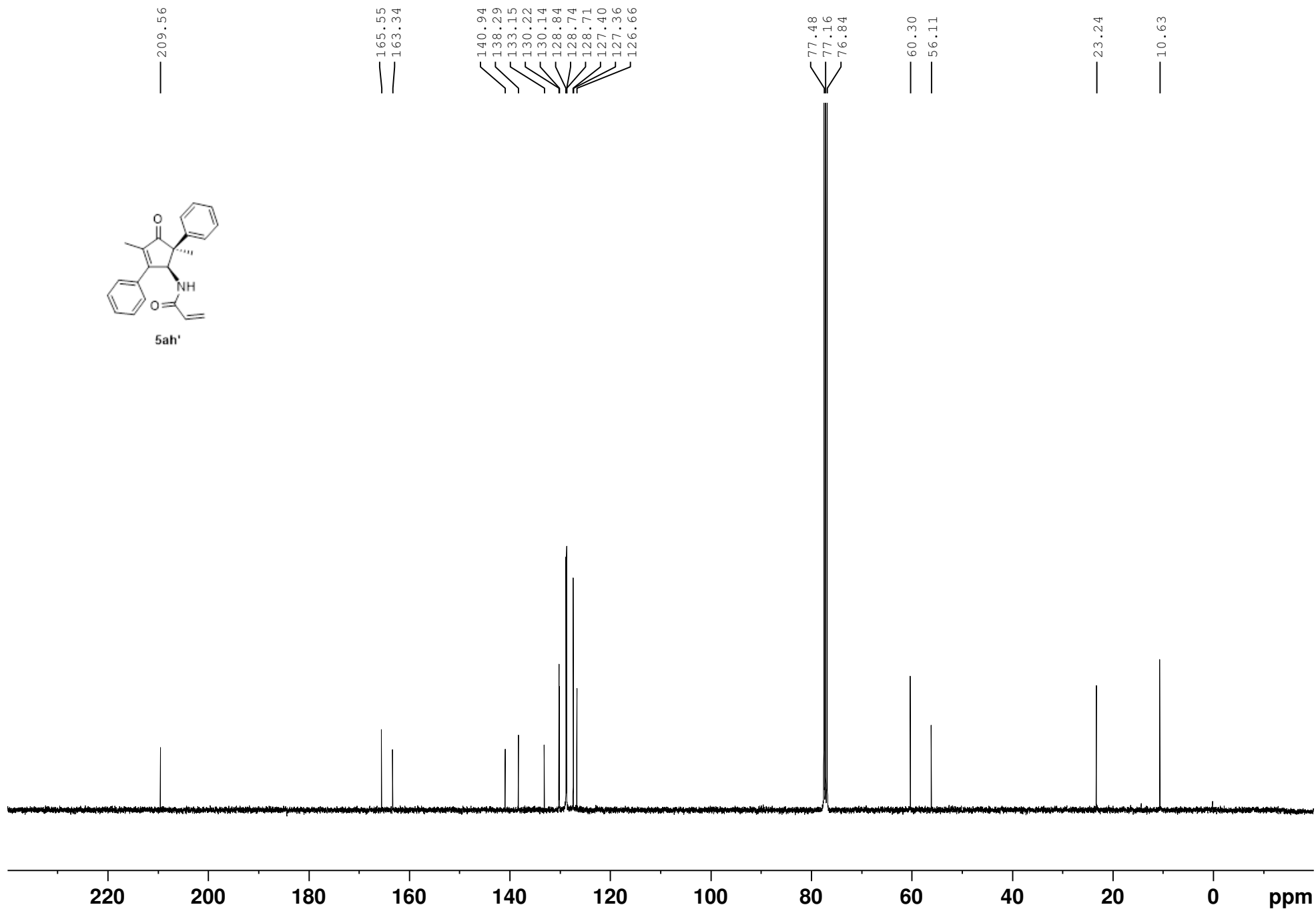
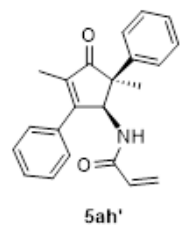


2.05
3.29
2.44
1.13
2.04

2.08
1.02
1.03
0.98

3.00
3.00

¹³C NMR (100 MHz, CDCl₃)



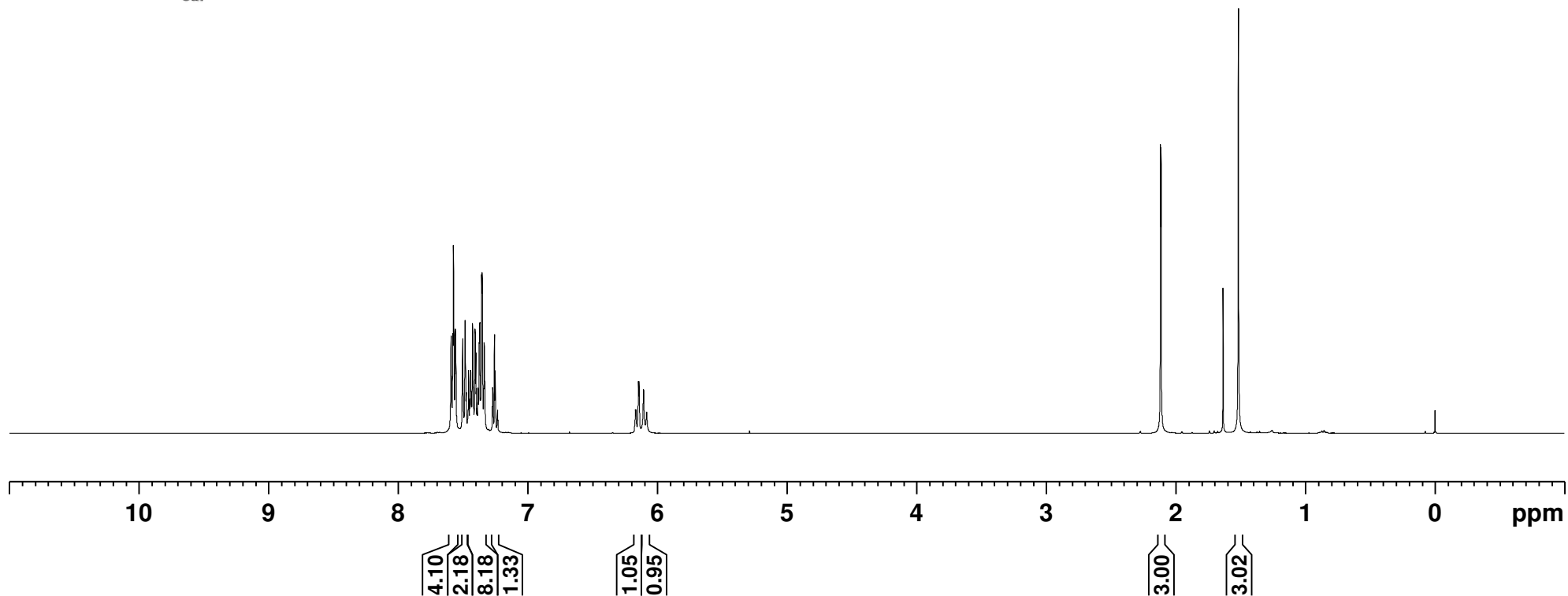
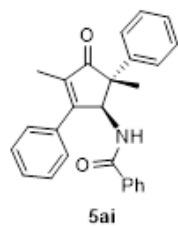
¹H NMR (400 MHz, CDCl₃)

7.590
7.578
7.573
7.554
7.547
7.504
7.501
7.483
7.480
7.475
7.461
7.456
7.438
7.405
7.370
7.354
7.351
7.339
7.335
7.272
7.269
7.256
7.251
7.233
7.230
6.169
6.165
6.145
6.141
6.106
6.082

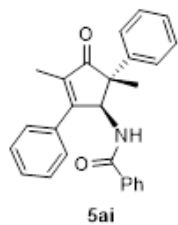
< 2.117
< 2.113

— 1.516

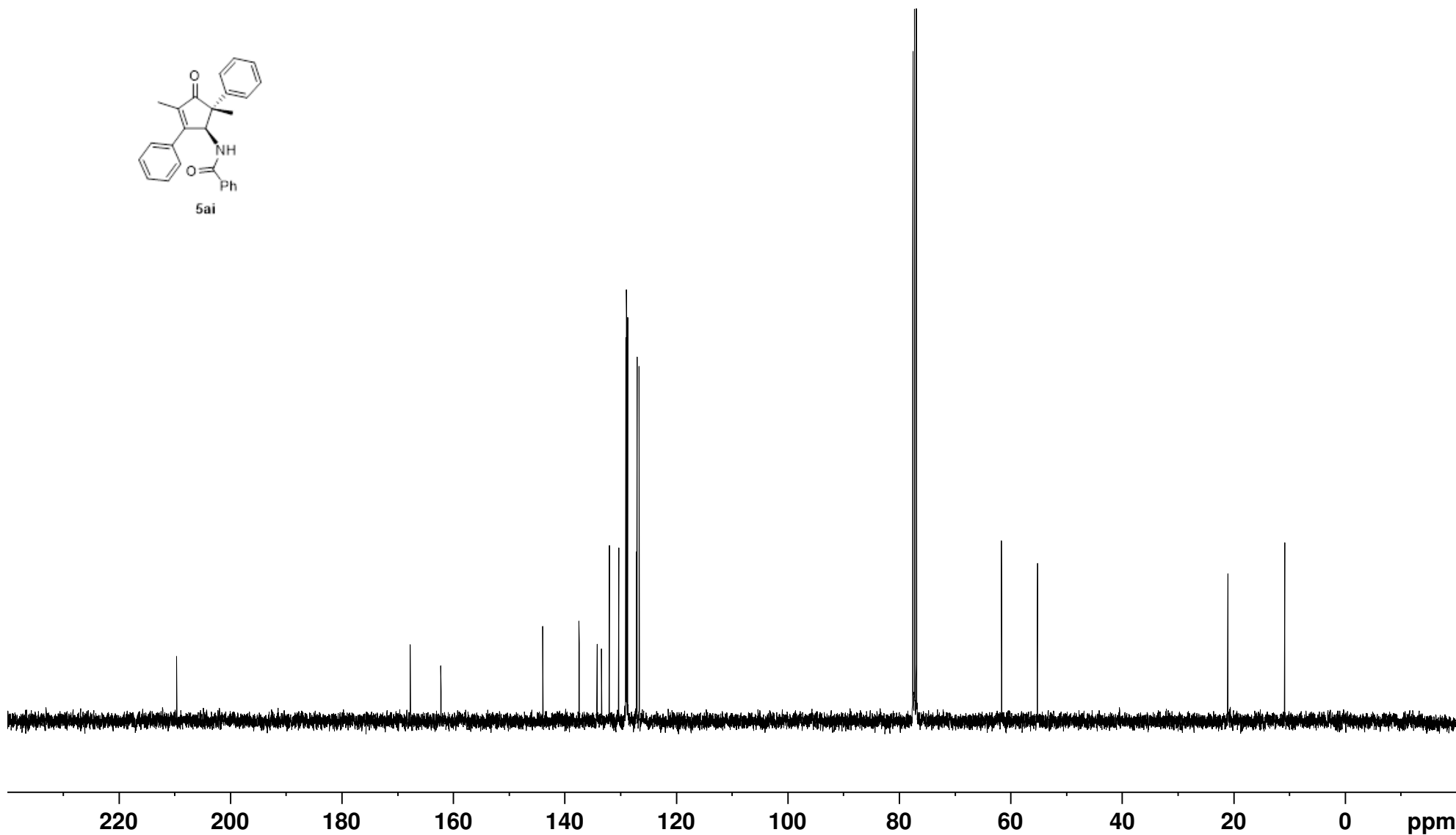
< 0.075
< -0.000



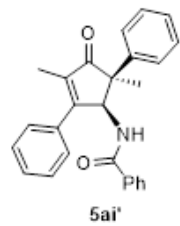
¹³C NMR (100 MHz, CDCl₃)



- 209.60
- 167.68
- 162.17
- 143.88
- 137.37
- 134.14
- 133.34
- 131.93
- 130.25
- 128.99
- 128.88
- 128.81
- 128.64
- 127.09
- 126.98
- 126.59
- 77.48
- 77.16
- 76.85
- 61.56
- 55.13
- 20.96
- 10.75



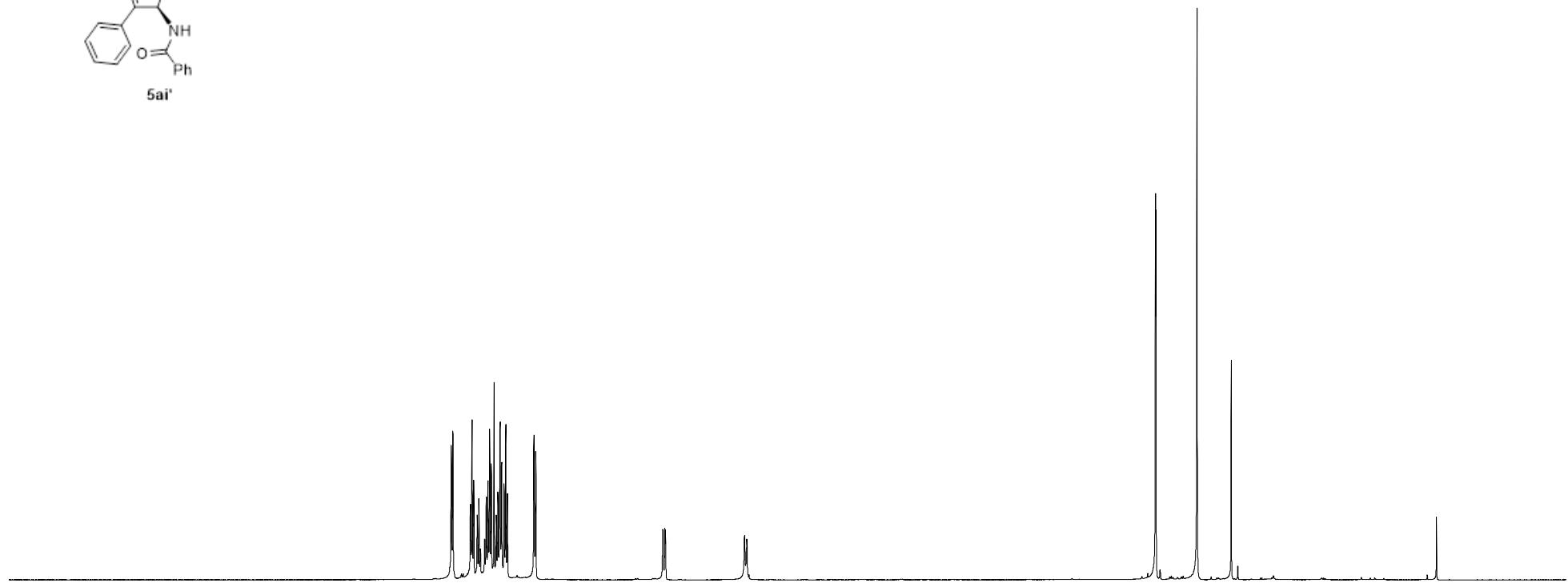
¹H NMR (600 MHz, CDCl₃)



7.592
7.590
7.578
7.442
7.430
7.417
7.390
7.378
7.365
7.333
7.321
7.308
7.295
7.282
7.260
7.243
7.231
7.216
7.214
7.202
7.183
7.170
7.157
6.952
6.940
6.938
5.961
5.957
5.944
5.940
5.331
5.314

< 2.165
2.161
— 1.845

— -0.000



10 9 8 7 6 5 4 3 2 1 0 ppm

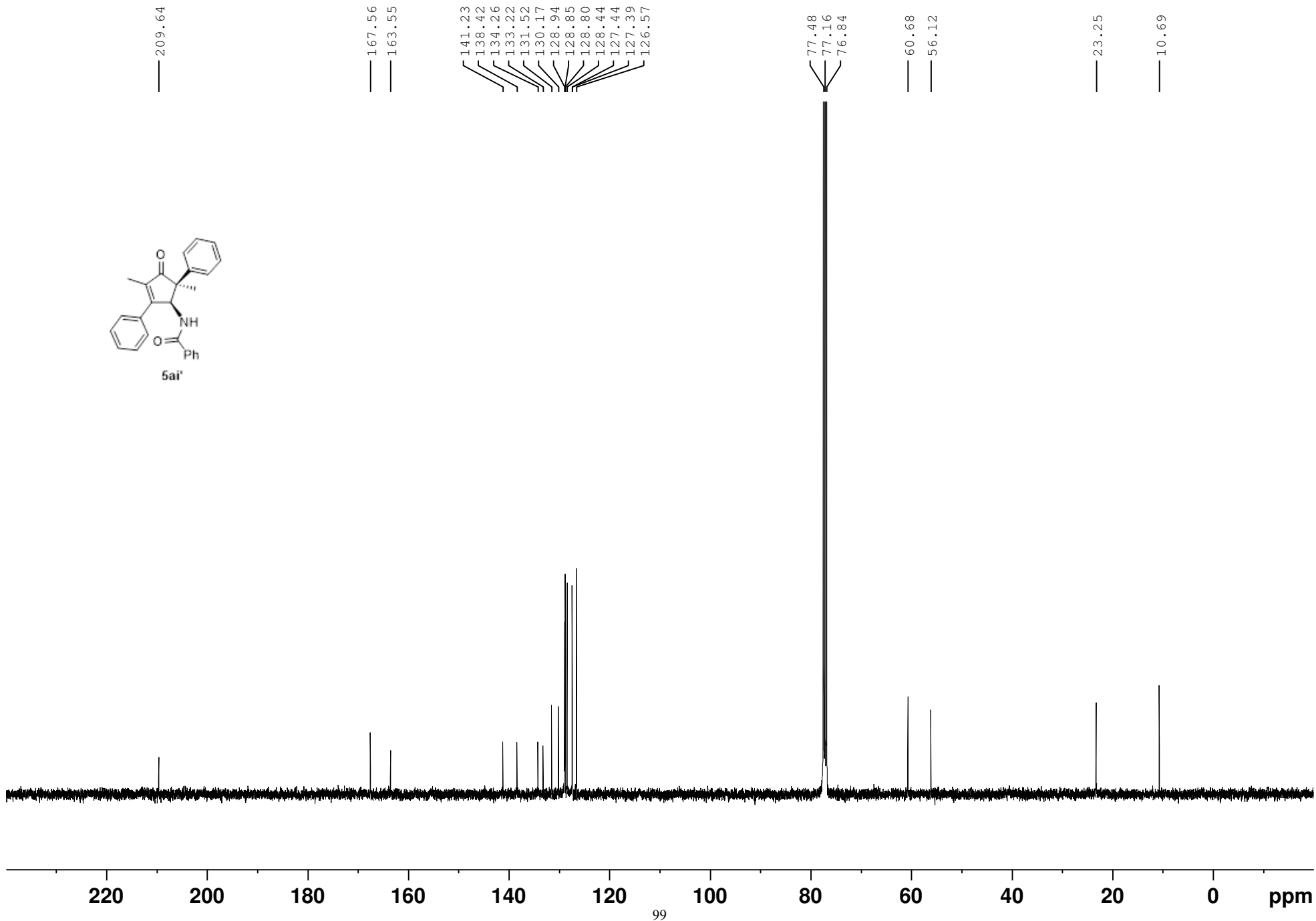
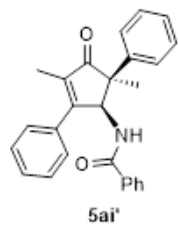
2.12
2.17
1.14
3.28
3.19
1.98
1.97

1.01

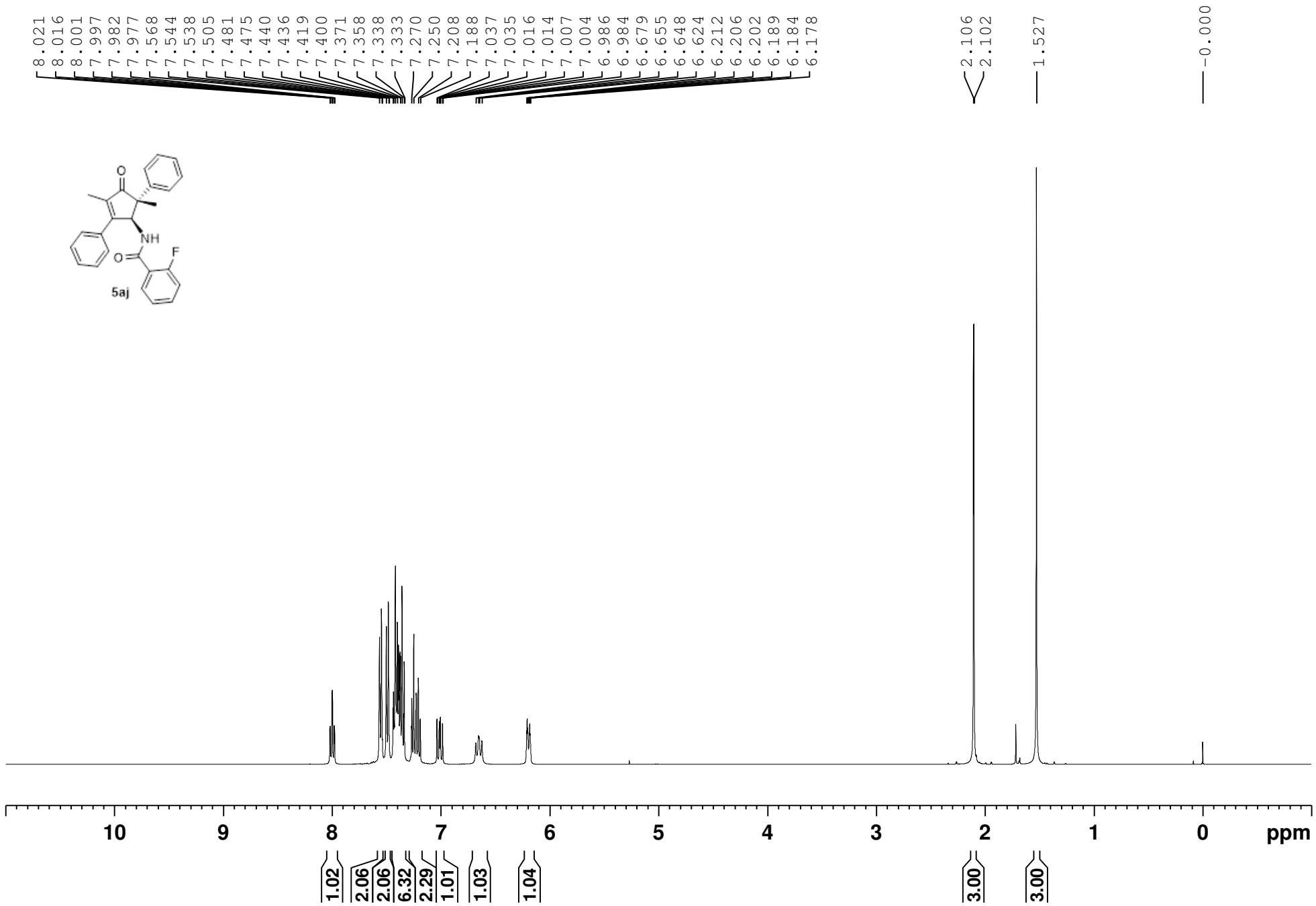
0.97

2.97
3.00

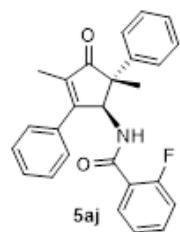
¹³C NMR (100 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)



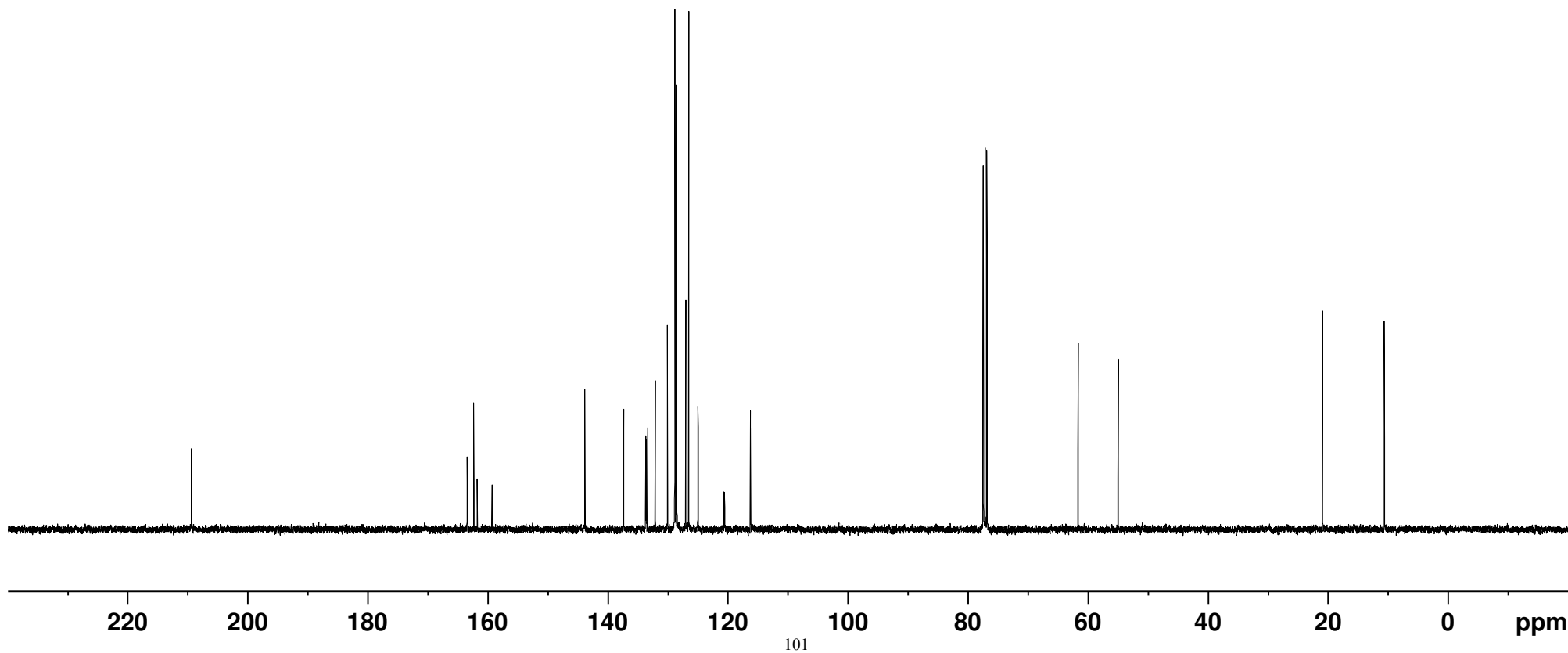
209.41

163.48
163.45
162.34
161.77
159.32
143.84
137.36
133.71
133.62
133.38
132.11
132.10
130.08
128.87
128.83
128.53
127.03
126.54
125.01
124.98
120.68
120.56
116.26
116.02

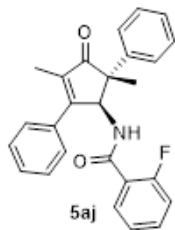
77.48
77.16
76.84

61.65
54.98

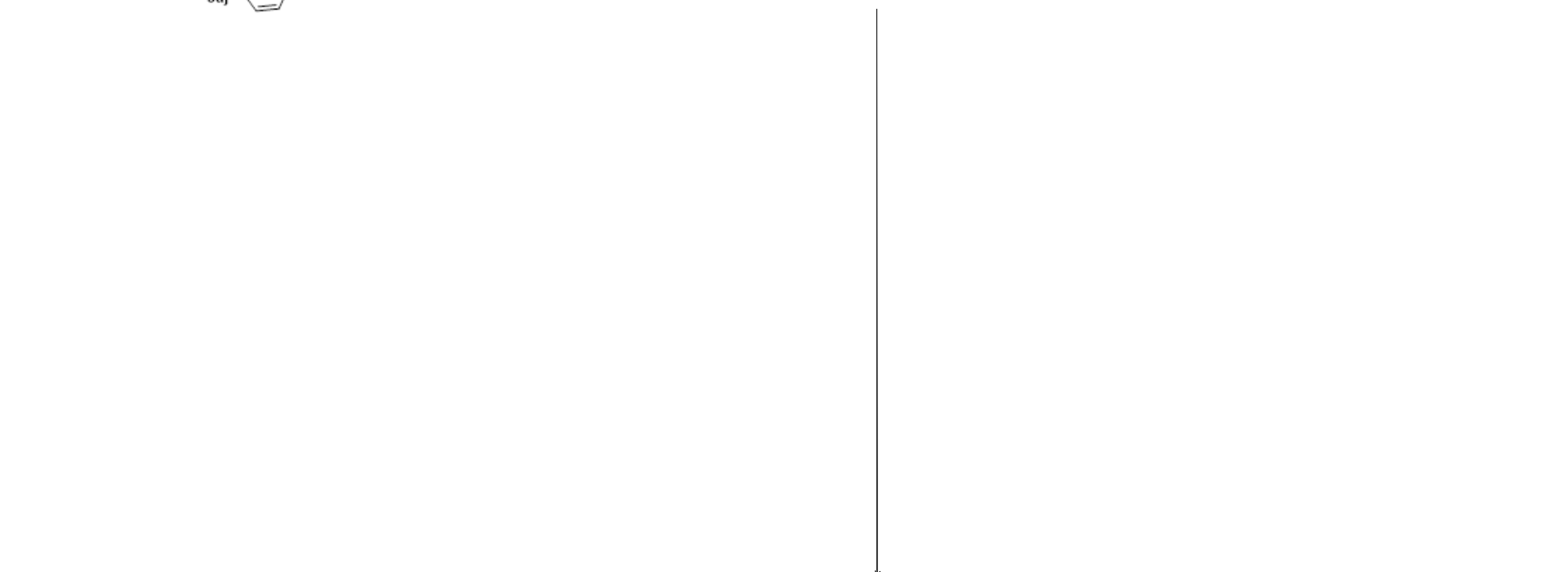
20.93
10.62



¹⁹F NMR (376 MHz, CDCl₃)



— -113.651



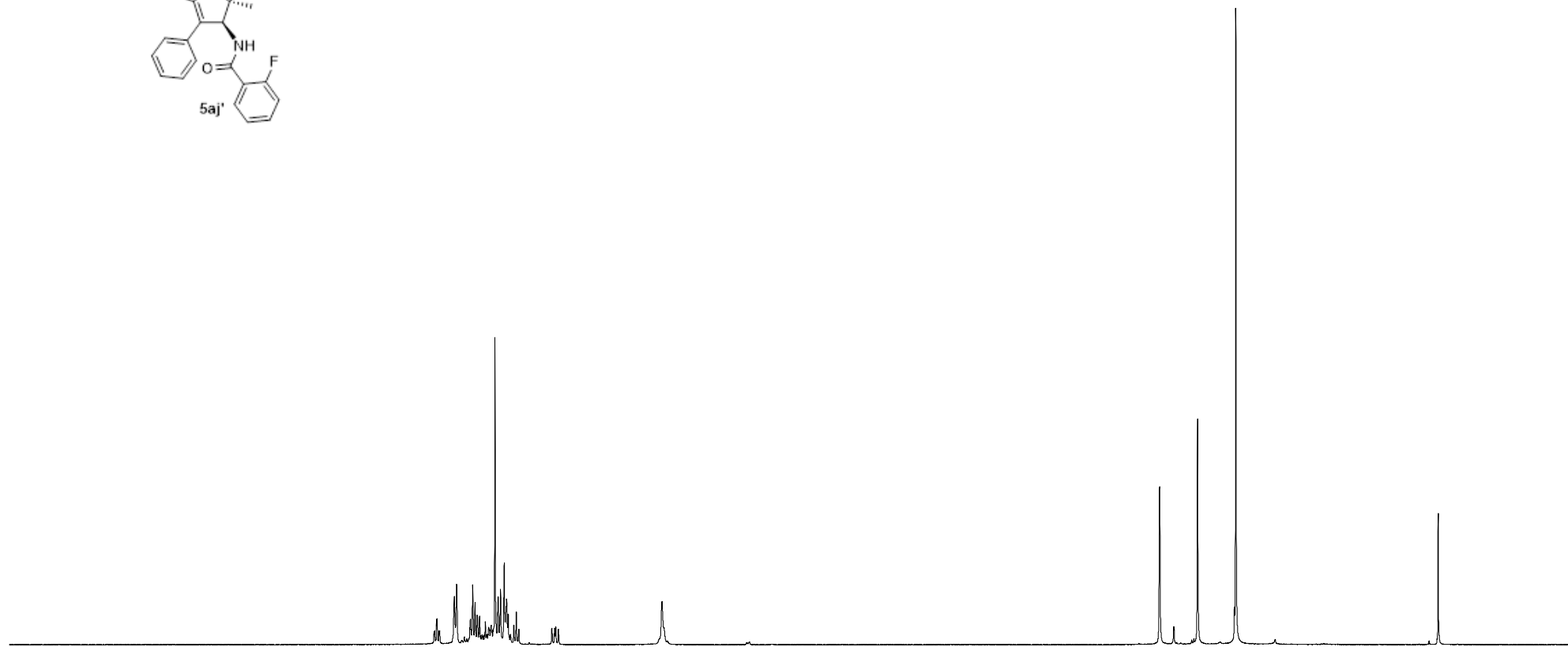
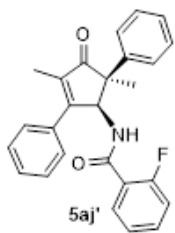
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

¹H NMR (400 MHz, CDCl₃)

7.729
7.725
7.710
7.705
7.690
7.686
7.577
7.573
7.556
7.450
7.432
7.378
7.314
7.289
7.284
7.261
7.236
7.218
7.189
7.158
7.141
7.114
7.097
7.076
6.823
6.801
6.793
6.772
5.974
5.959
5.933

— 2.144
— 1.852

— -0.000

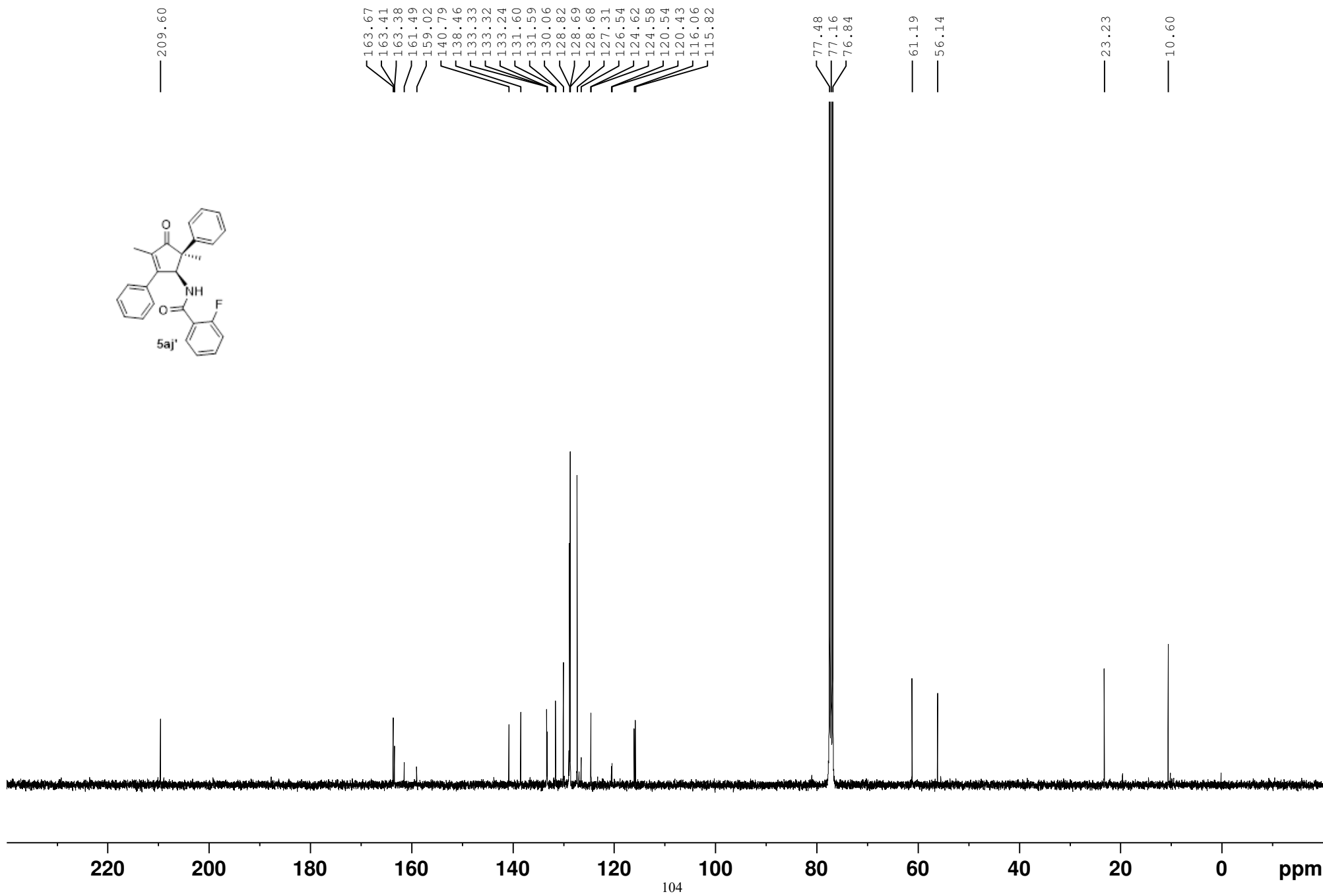
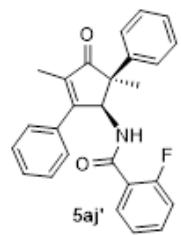


1.10
2.39
3.23
1.03
1.91
3.15
1.06
1.02

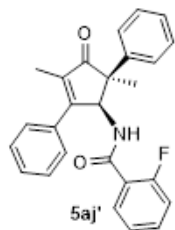
1.92

3.00
2.99

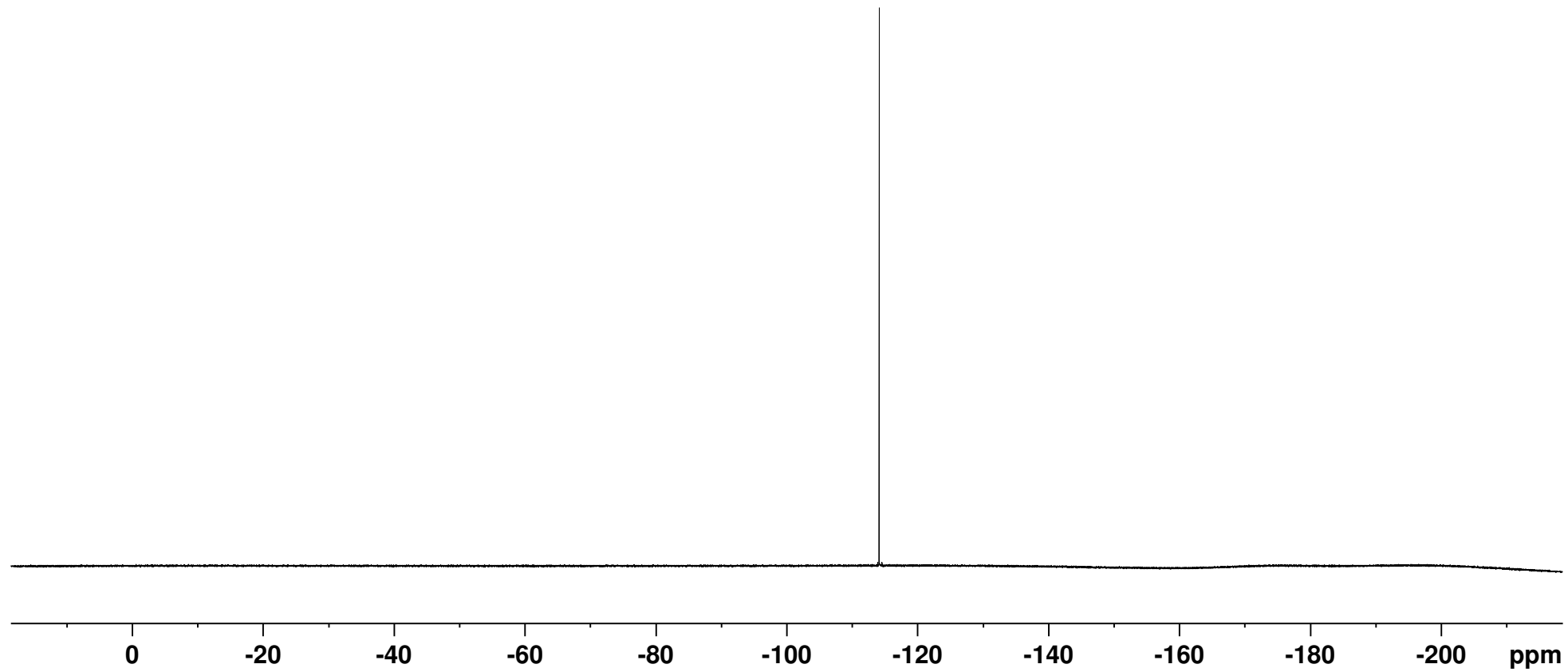
¹³C NMR (100 MHz, CDCl₃)



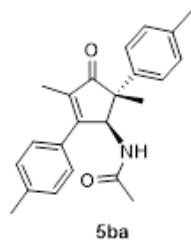
¹⁹F NMR (376 MHz, CDCl₃)



— -114.140



¹H NMR (400 MHz, CDCl₃)



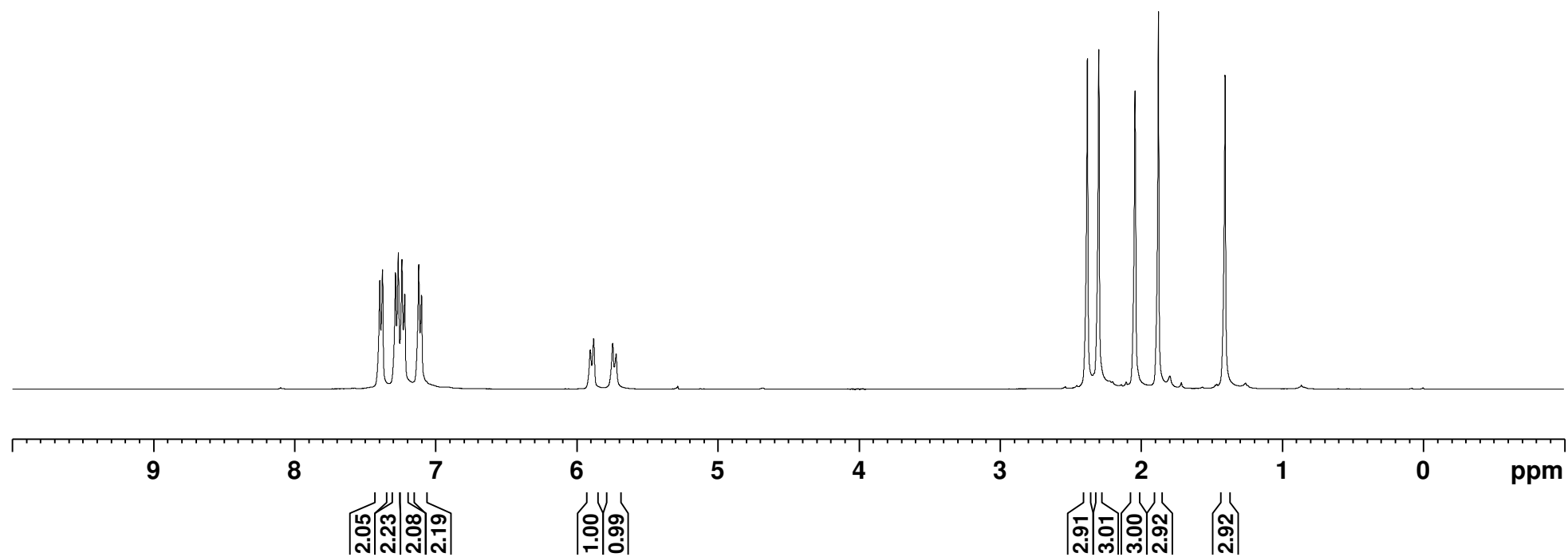
7.395
7.375
7.283
7.263
7.238
7.218
7.119
7.099

5.903
5.879
5.743
5.719

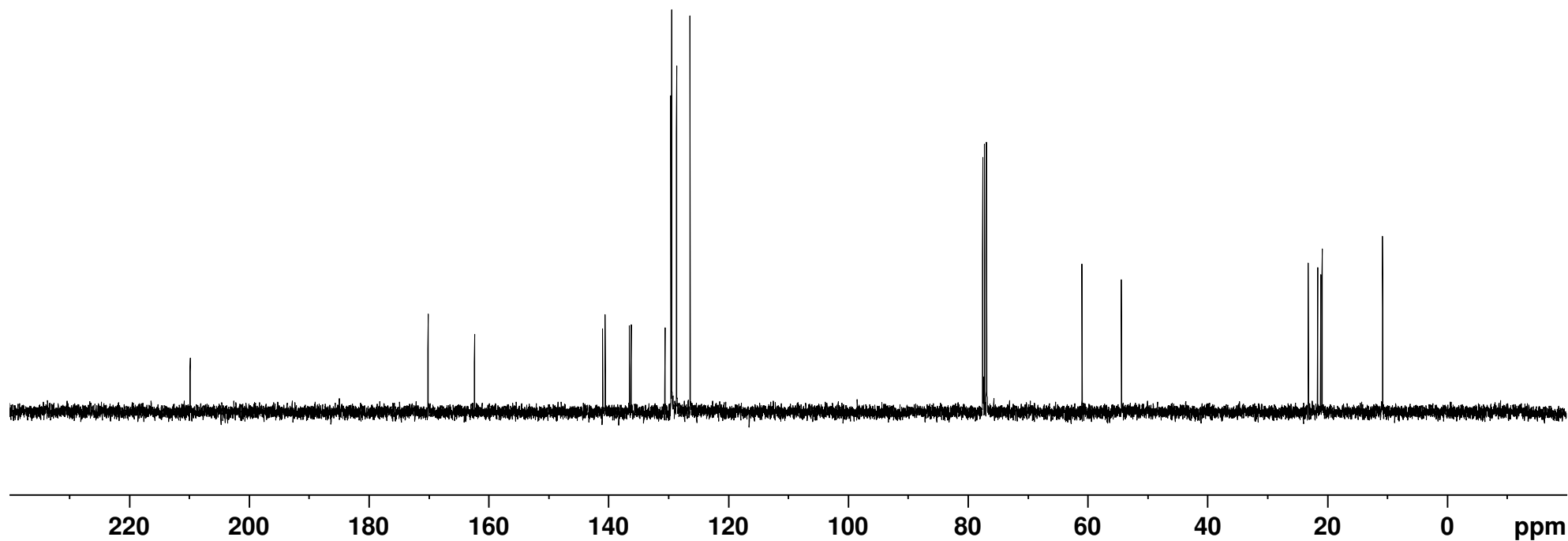
2.379
2.298
2.042
1.875

1.403

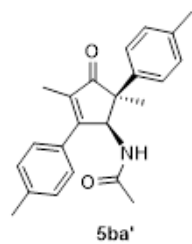
0.077
-0.000



¹³C NMR (100 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)



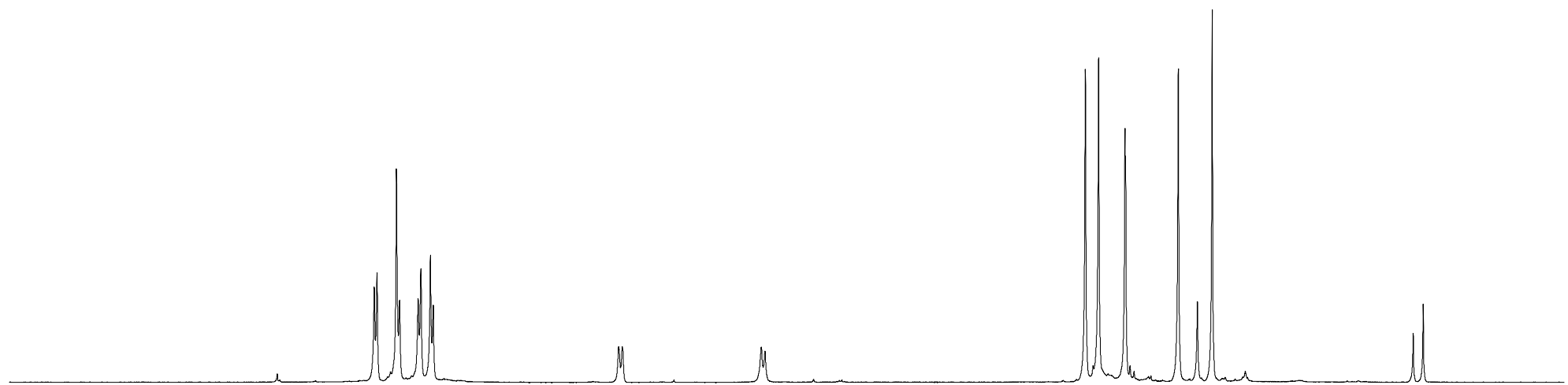
7.418
7.398
7.262
7.239
7.108
7.088
7.021
7.001

5.690
5.686
5.665
5.660

4.681
4.655

2.389
2.295
2.109
2.105
1.732
1.492

0.070
-0.000



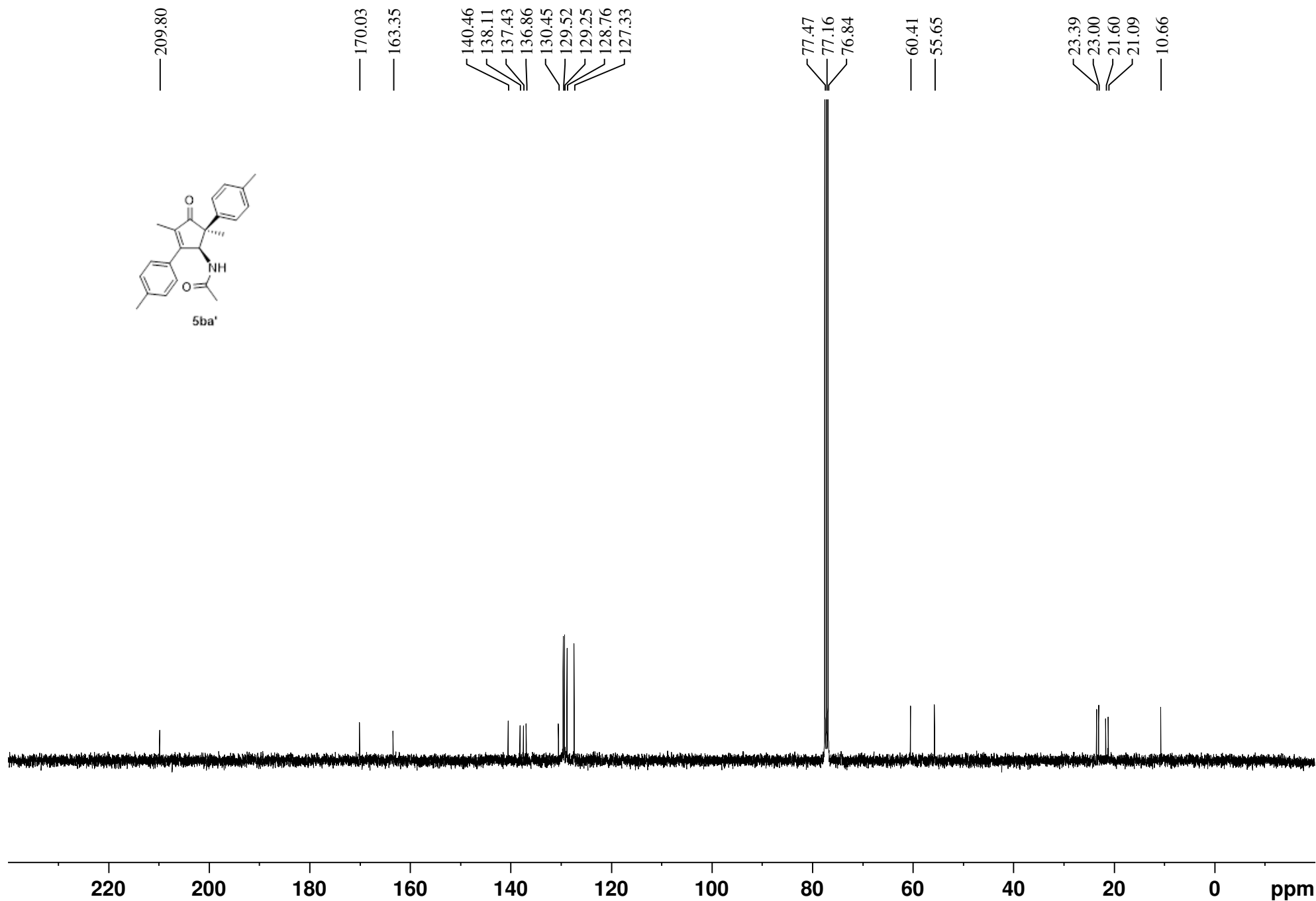
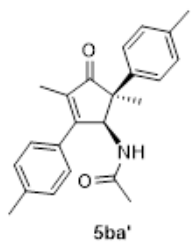
2.10
2.01
2.18
2.15

0.99

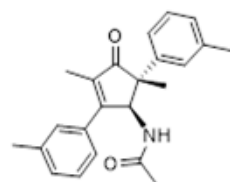
1.05

3.12
3.20
3.10
3.00
3.00

^{13}C NMR (100 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)

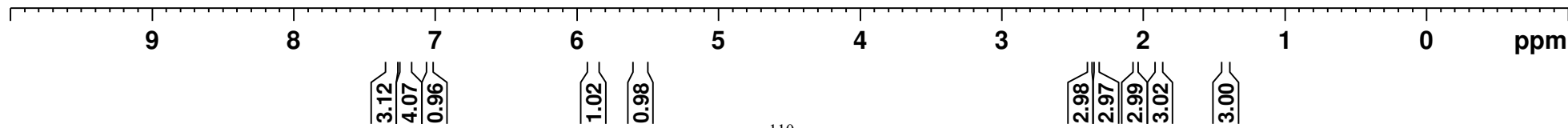
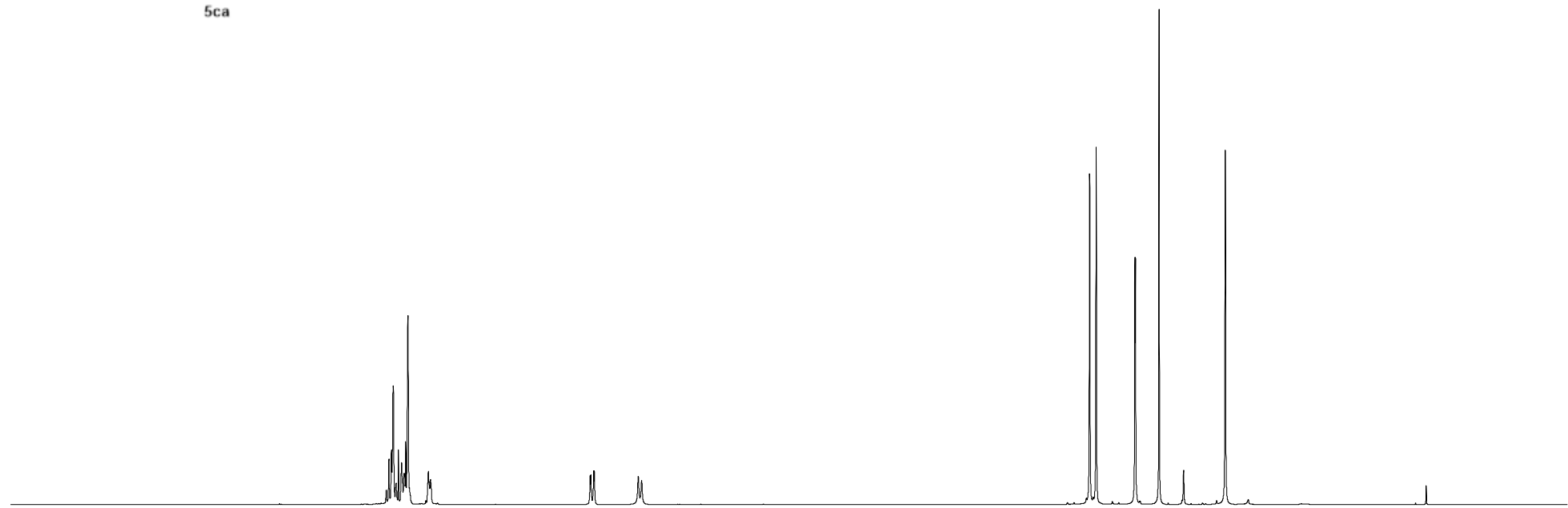


5ca

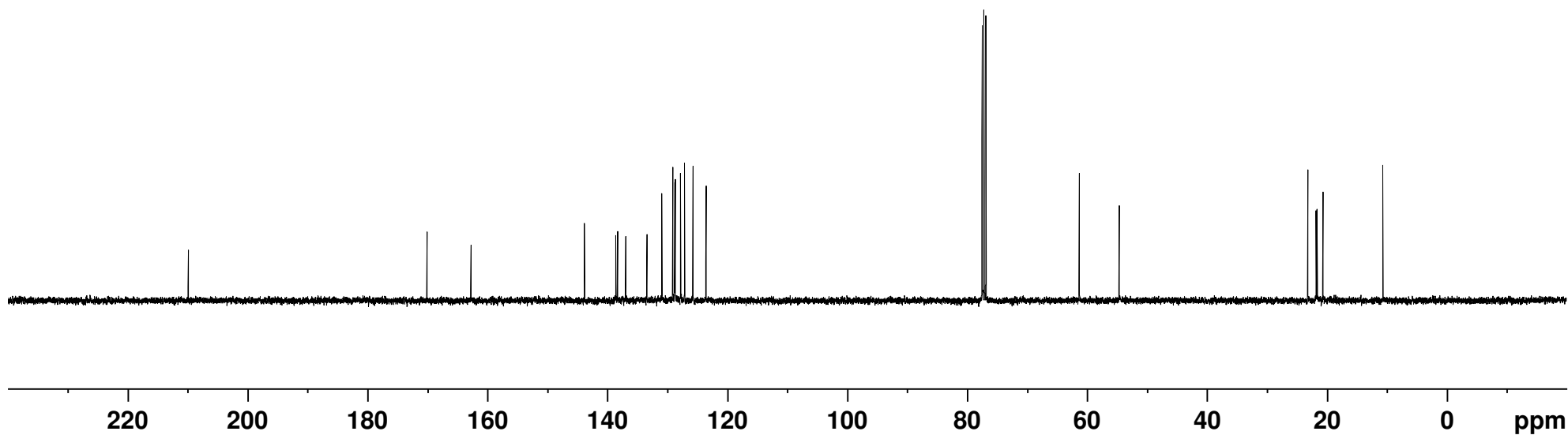
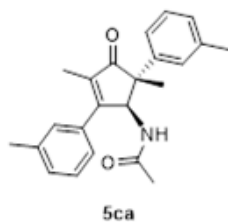
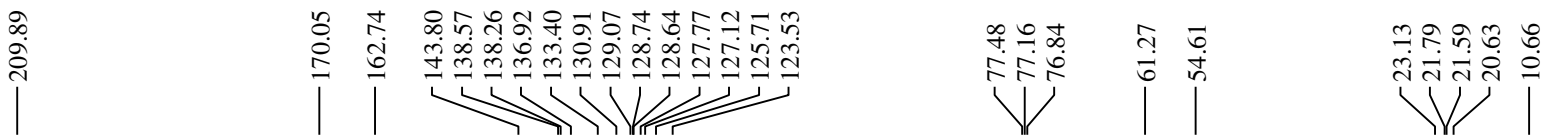
7.344
7.326
7.307
7.295
7.275
7.259
7.236
7.218
7.208
7.192
7.180
7.047
7.042
7.039
7.031
5.904
5.900
5.880
5.875
5.565
5.541

2.377
2.331
2.057
2.053
1.886
1.419

0.075
-0.000



^{13}C NMR (100 MHz, CDCl_3)

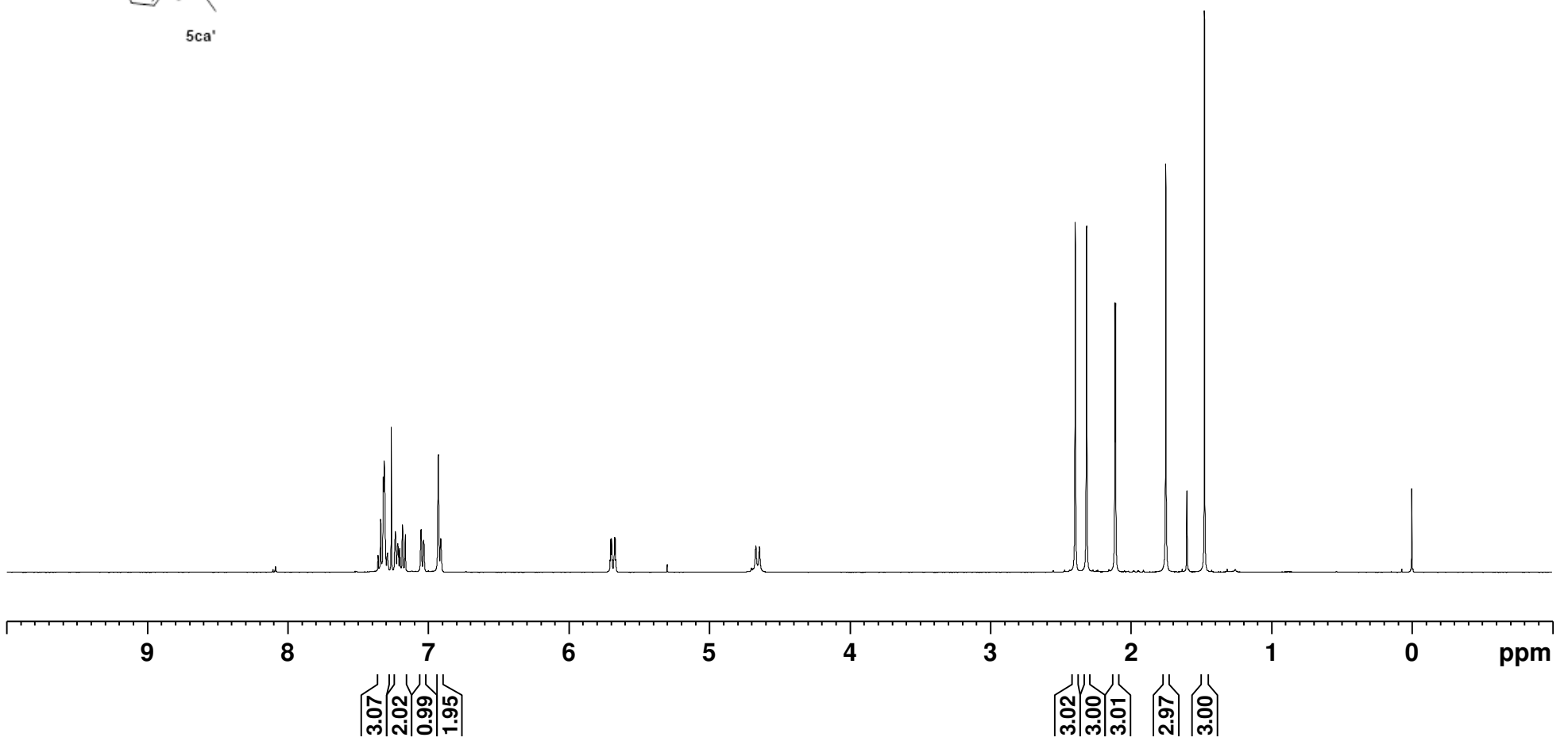
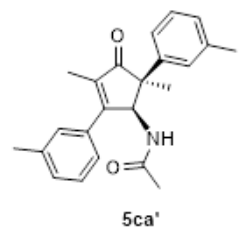


¹H NMR (400 MHz, CDCl₃)

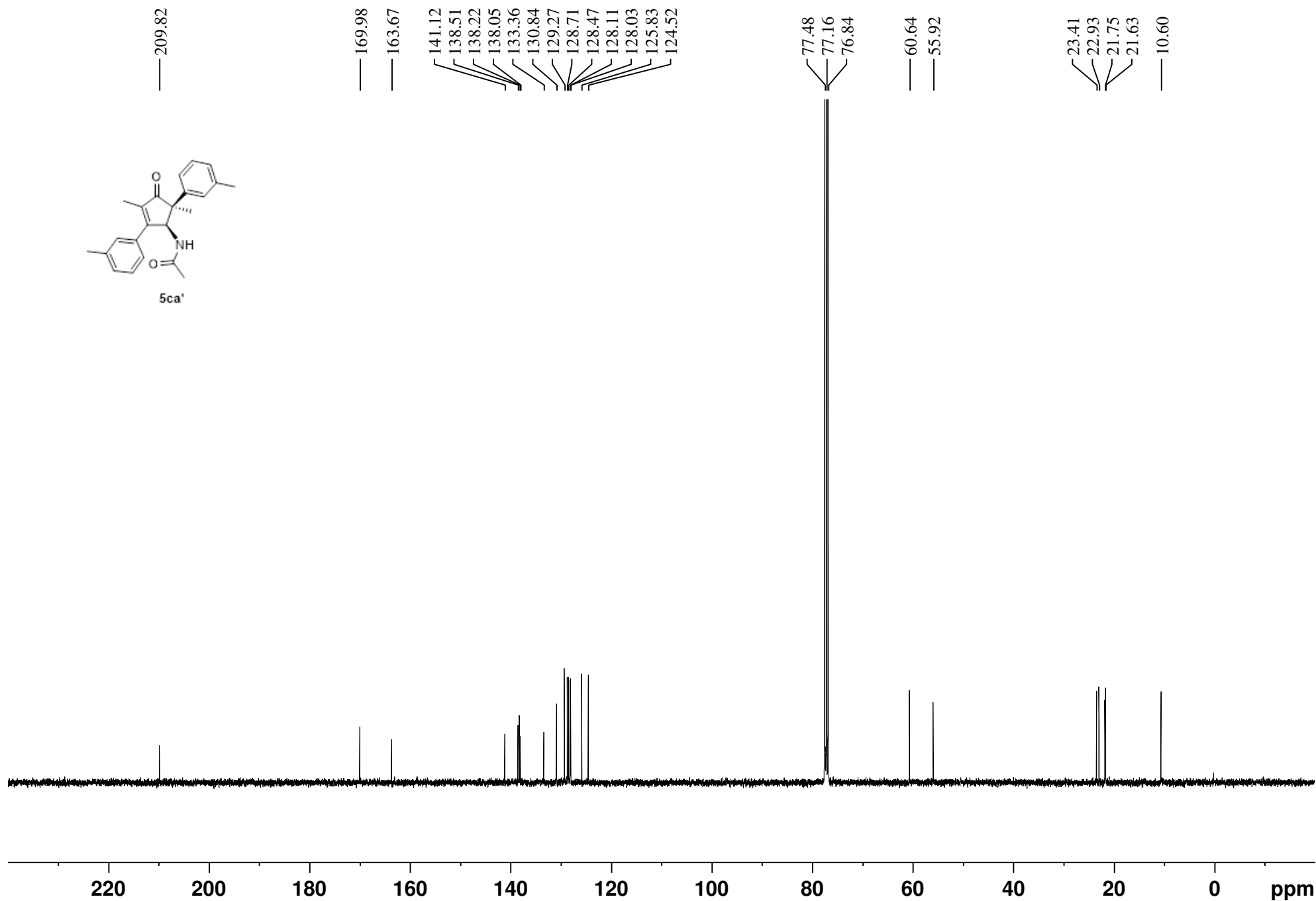
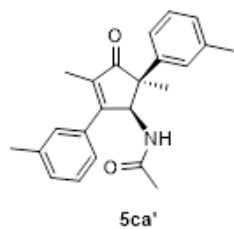
7.356
7.338
7.319
7.313
7.292
7.289
7.262
7.234
7.216
7.202
7.199
7.183
7.162
7.050
7.032
6.928
6.911
5.700
5.695
5.674
5.669
4.668
4.642

2.395
2.314
2.113
2.108
1.750
1.475

0.071
0.008
-0.000
-0.008



^{13}C NMR (100 MHz, CDCl_3)



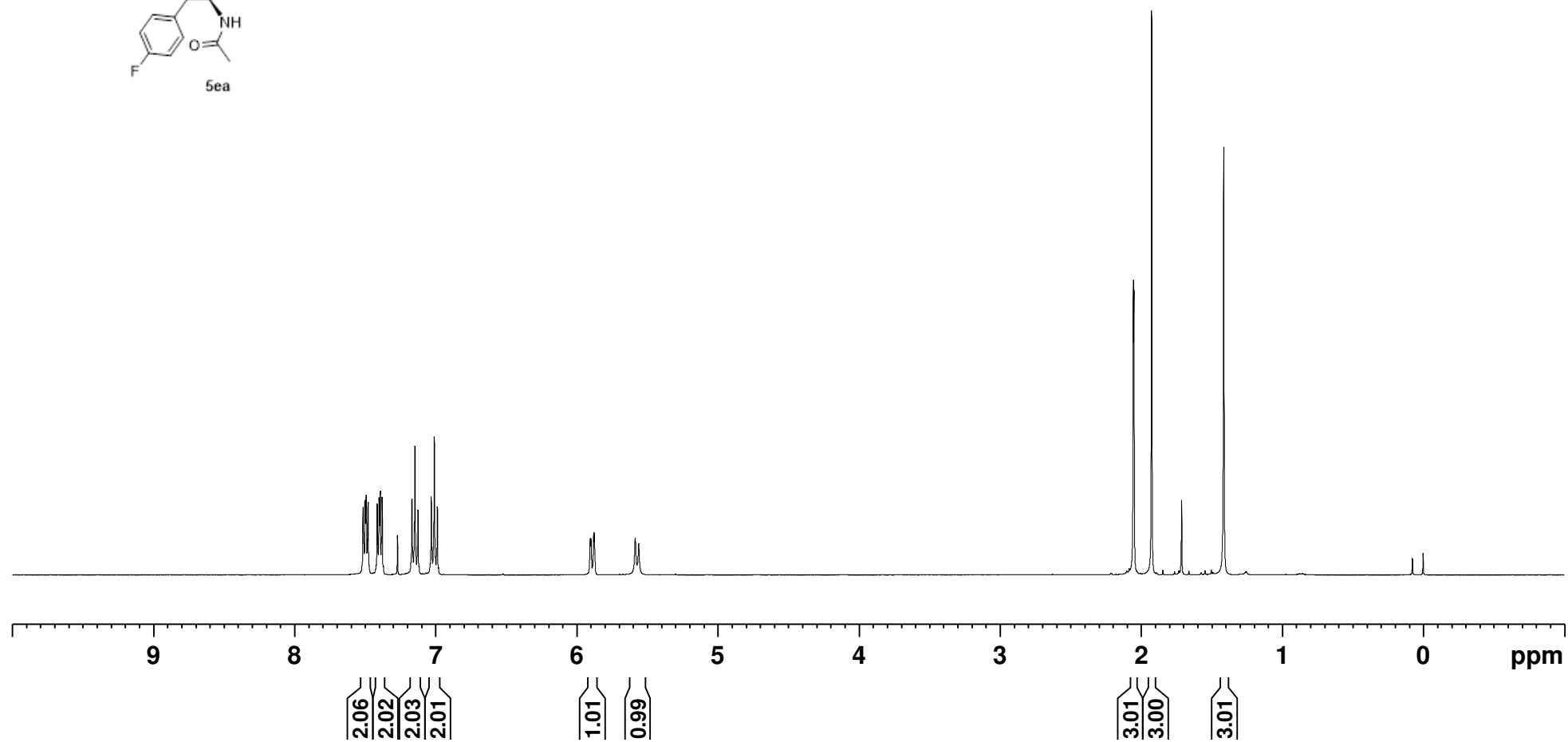
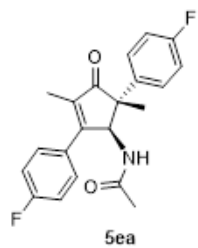
¹H NMR (400 MHz, CDCl₃)

7.513
7.508
7.500
7.491
7.483
7.478
7.413
7.408
7.400
7.395
7.391
7.383
7.378
7.269
7.167
7.162
7.146
7.129
7.124
7.030
7.025
7.008
6.992
6.986
5.903
5.898
5.878
5.874
5.584
5.559

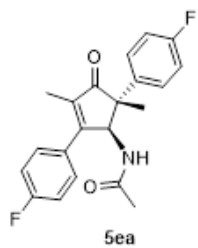
2.053
2.049
1.924

1.413

0.075
-0.000



¹³C NMR (100 MHz, CDCl₃)



— 209.11

170.18
164.88
163.03
162.38
161.20
160.59

139.33
139.30
136.67
130.77
130.69
129.29
129.25
128.32
128.24
116.30
116.08
115.68
115.47

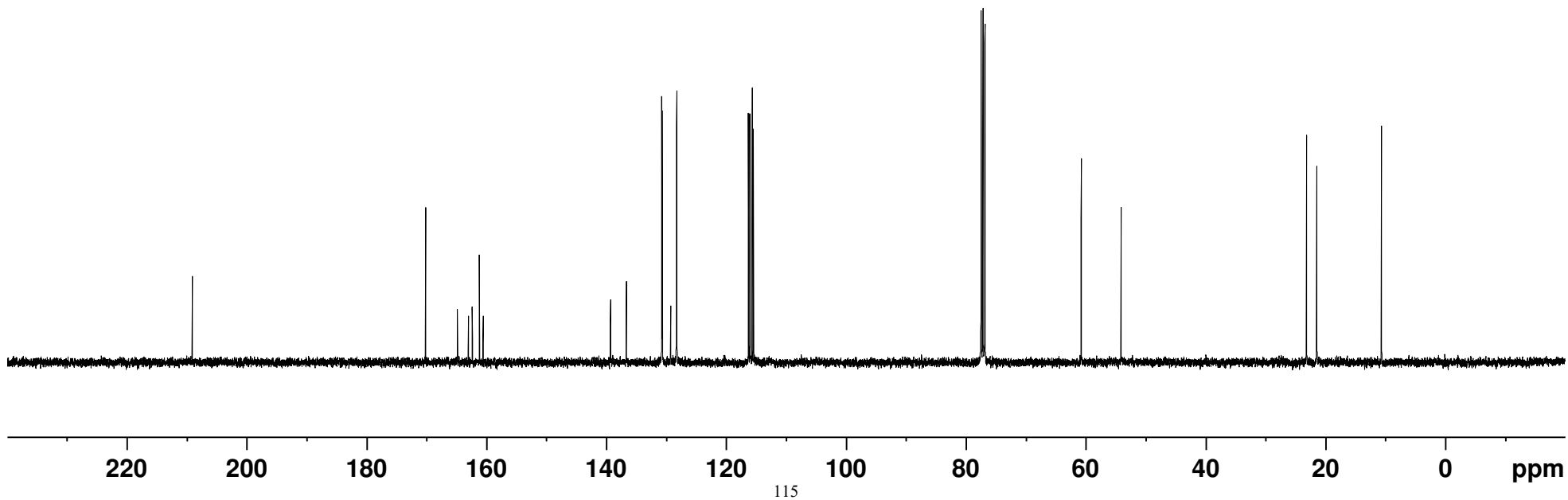
77.48
77.16
76.84

— 60.77

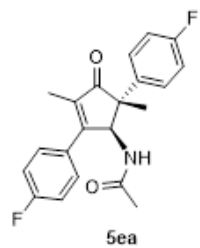
— 54.10

23.16
21.45

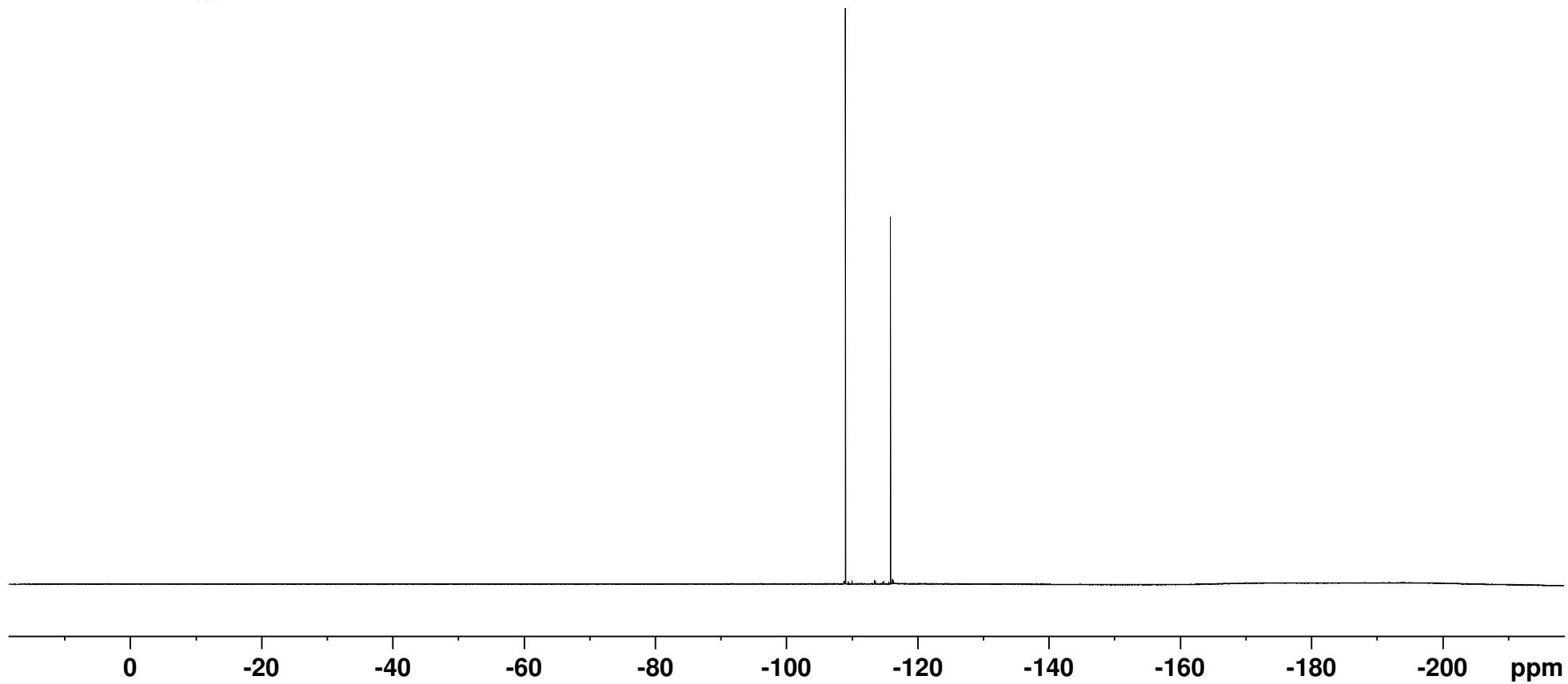
— 10.64



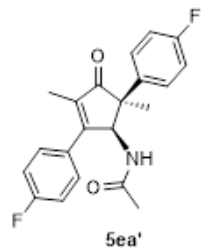
¹⁹F NMR (376 MHz, CDCl₃)



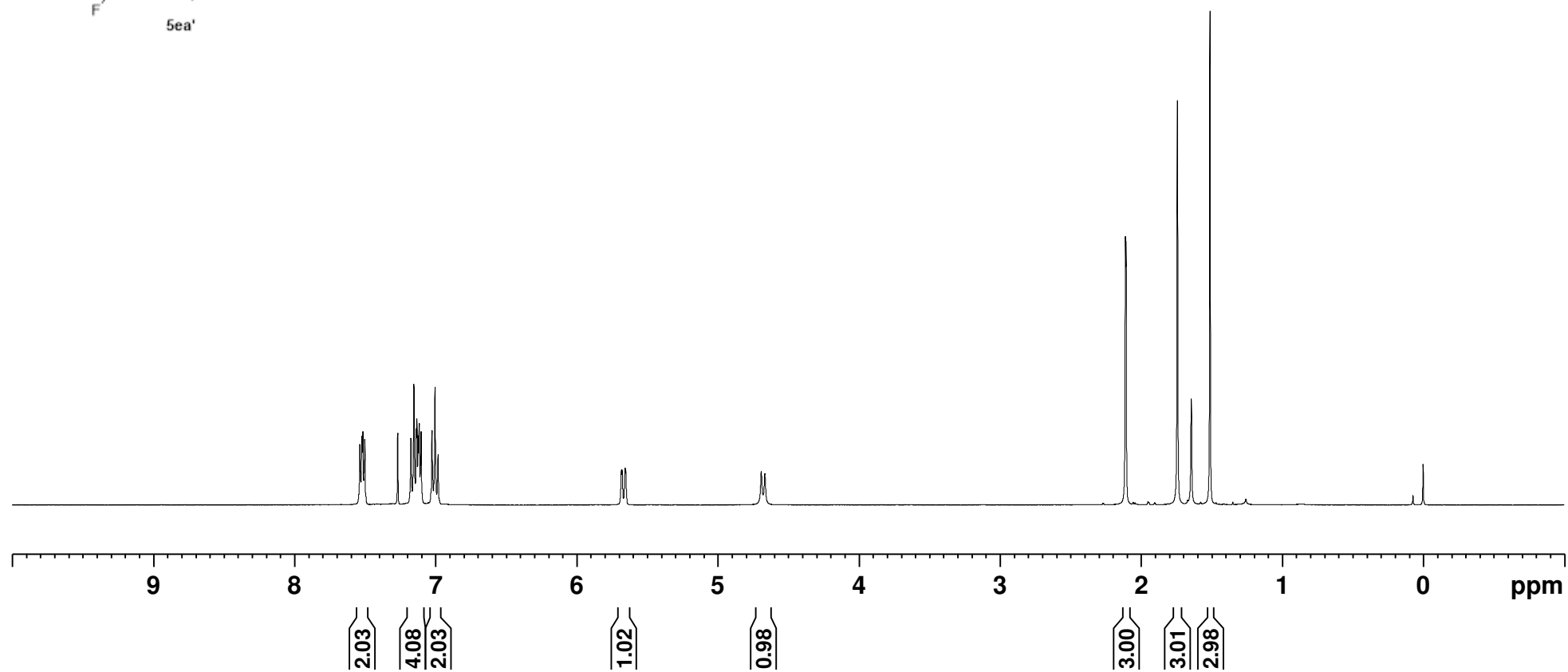
— -109.041
— -115.913



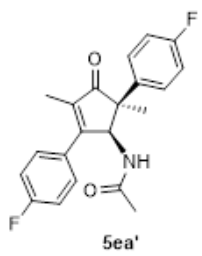
¹H NMR (400 MHz, CDCl₃)



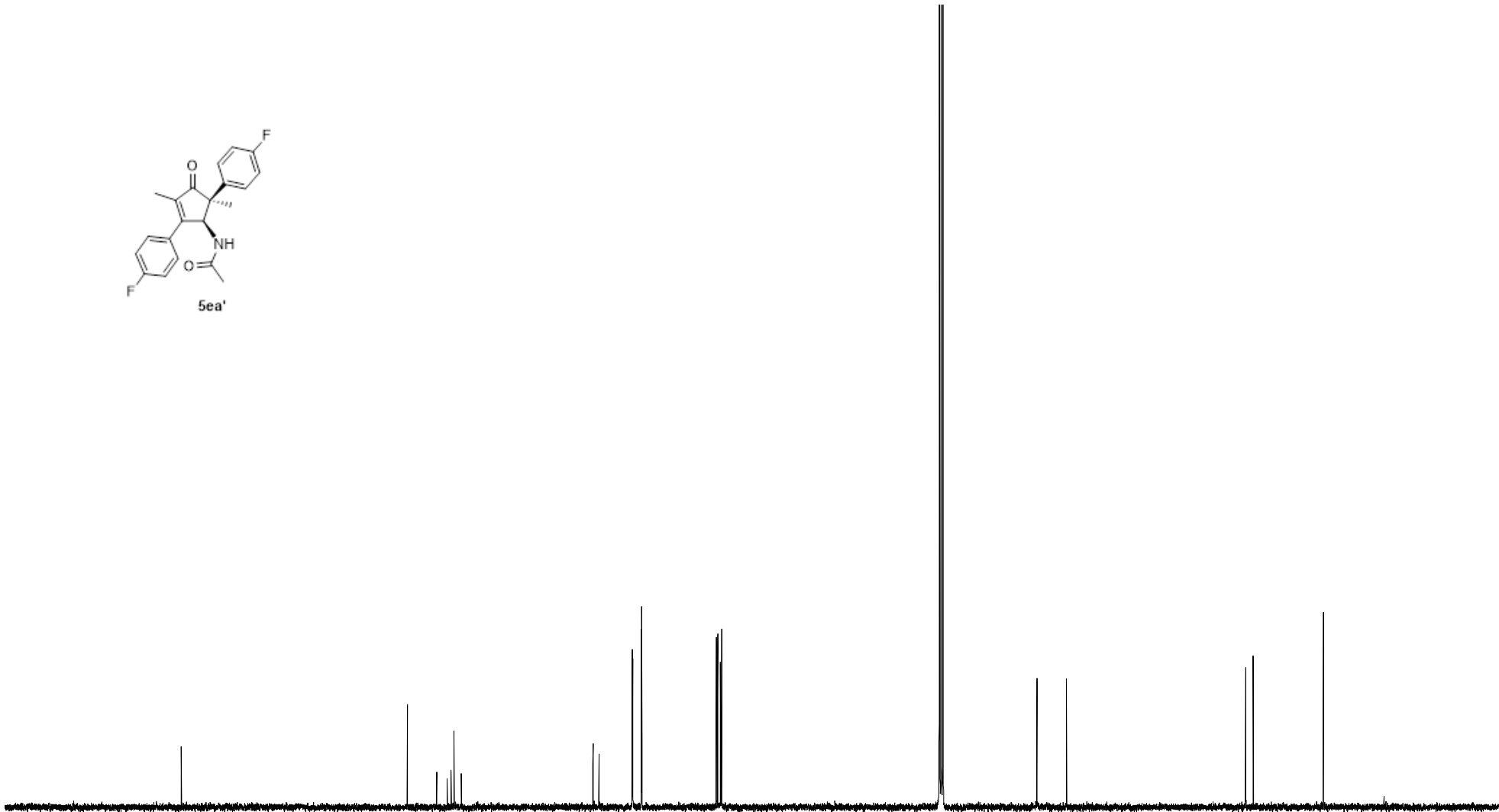
7.536
7.523
7.514
7.501
7.268
7.174
7.153
7.137
7.132
7.124
7.115
7.102
7.025
7.003
6.981
5.682
5.677
5.656
5.652
4.690
4.665
2.110
2.106
1.741
1.510
0.072
-0.000



¹³C NMR (100 MHz, CDCl₃)

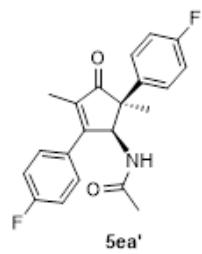


- 209.35
- 169.99
- 164.90
- 163.08
- 162.39
- 161.90
- 160.63
- 137.71
- 136.68
- 136.65
- 130.88
- 130.80
- 129.31
- 129.24
- 129.21
- 116.25
- 116.04
- 115.54
- 115.33
- 77.47
- 77.16
- 76.84
- 60.48
- 55.34
- 24.18
- 22.86
- 10.65

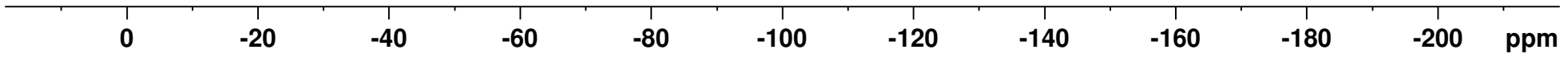
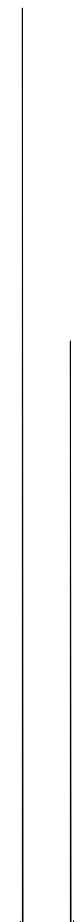


220 200 180 160 140 120 100 80 60 40 20 0 ppm

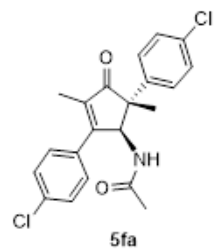
¹⁹F NMR (376 MHz, CDCl₃)



— -109.113
— -114.920



¹H NMR (400 MHz, CDCl₃)



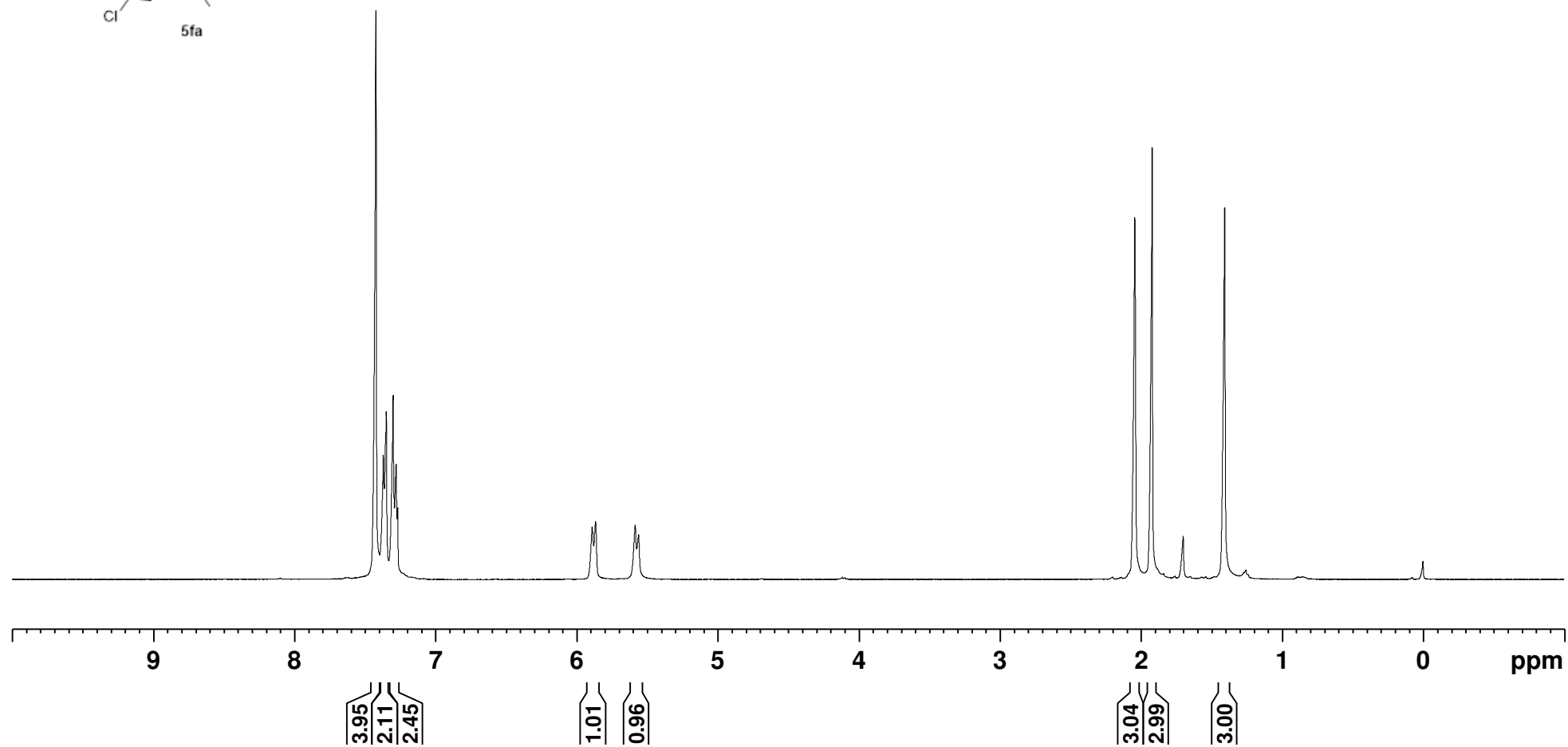
7.422
7.370
7.354
7.349
7.300
7.284
7.279
7.268

5.890
5.865
5.584
5.560

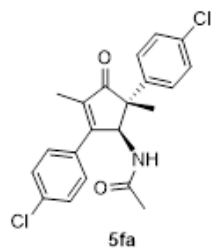
2.043
1.920

1.406

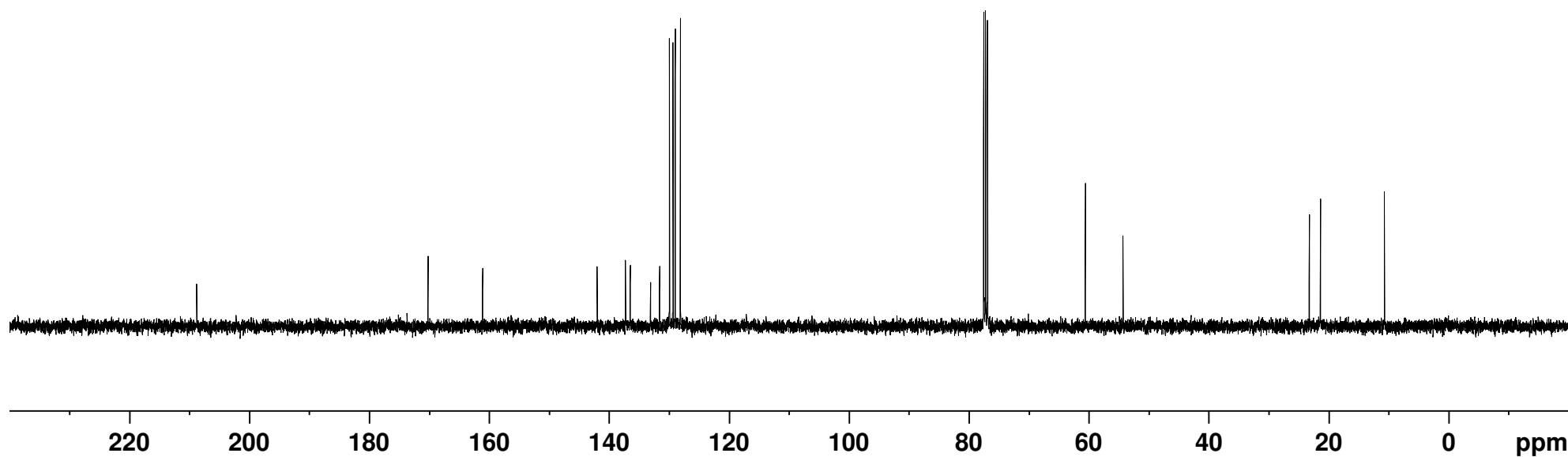
0.075
-0.000



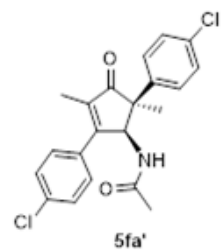
¹³C NMR (100 MHz, CDCl₃)



— 208.75
— 170.15
— 161.05
141.97
137.23
136.43
133.04
131.54
129.89
129.29
128.93
128.06
77.48
77.16
76.84
60.52
54.25
23.16
21.30
10.63



^1H NMR (400 MHz, CDCl_3)



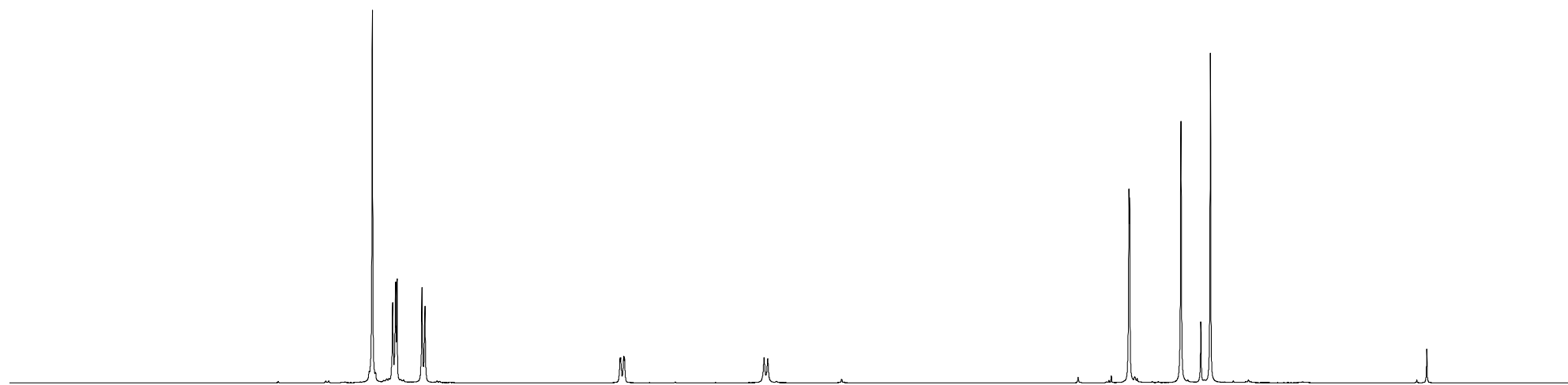
7.438
7.296
7.274
7.264
7.088
7.067

5.691
5.686
5.665
5.660

4.675
4.649

2.101
2.097
1.734
1.527

0.071



4.08
2.02
2.05

3.00
3.00
3.02

^{13}C NMR (100 MHz, CDCl_3)

— 209.02

— 170.01

— 161.77

139.33

138.26

136.39

133.30

131.47

130.00

129.24

129.02

128.69

77.48

77.16

76.84

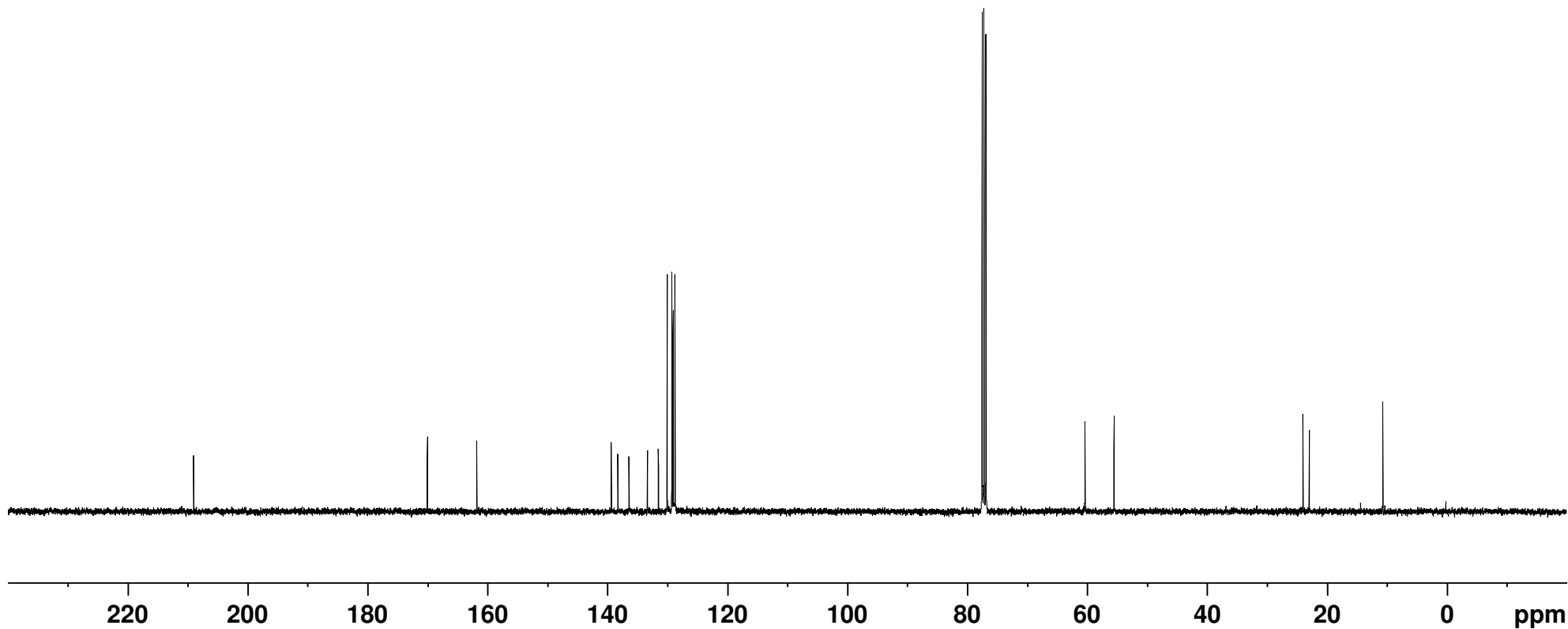
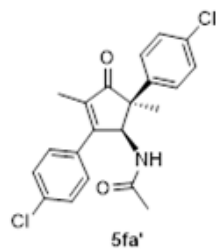
— 60.31

— 55.48

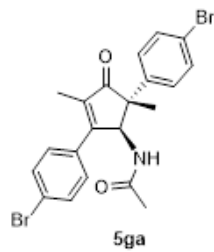
23.97

22.90

— 10.63



¹H NMR (400 MHz, CDCl₃)



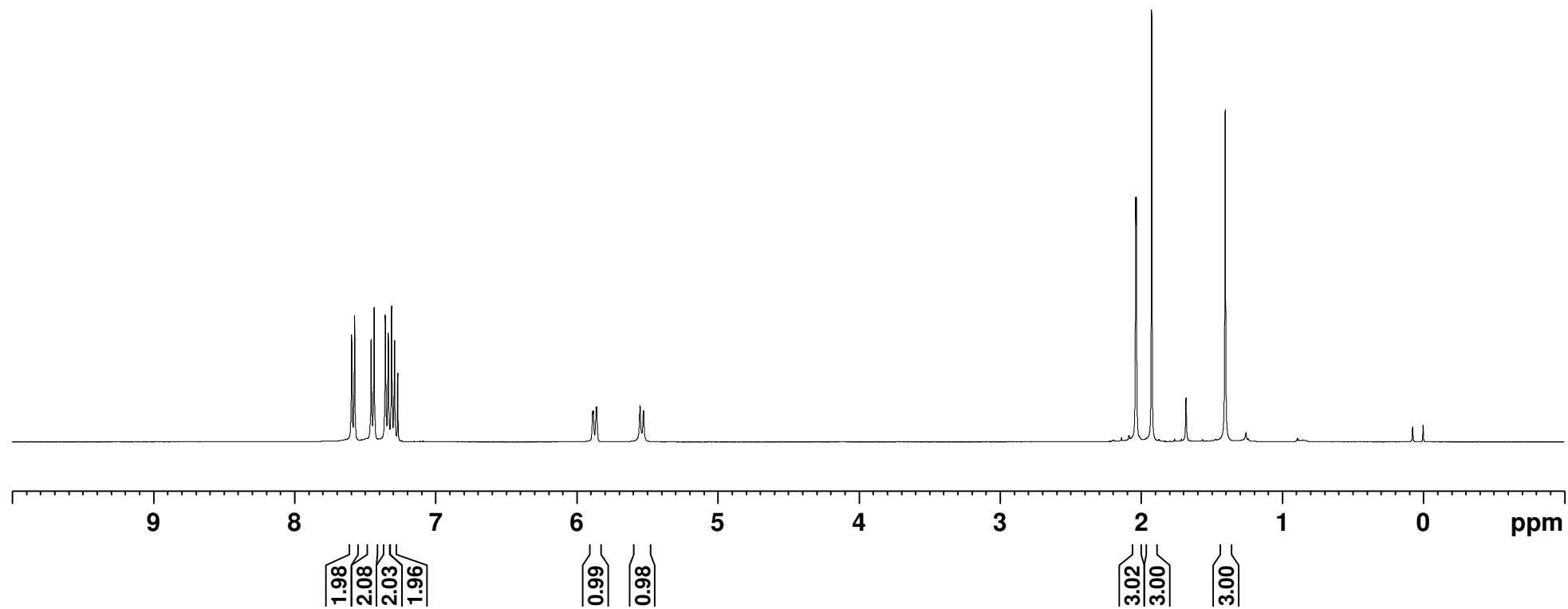
7.594
7.573
7.456
7.435
7.355
7.334
7.311
7.290
7.267

5.886
5.881
5.861
5.857
5.550
5.525

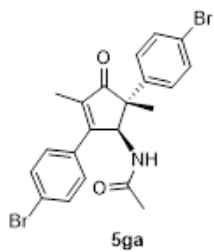
2.036
2.032
1.924

1.402

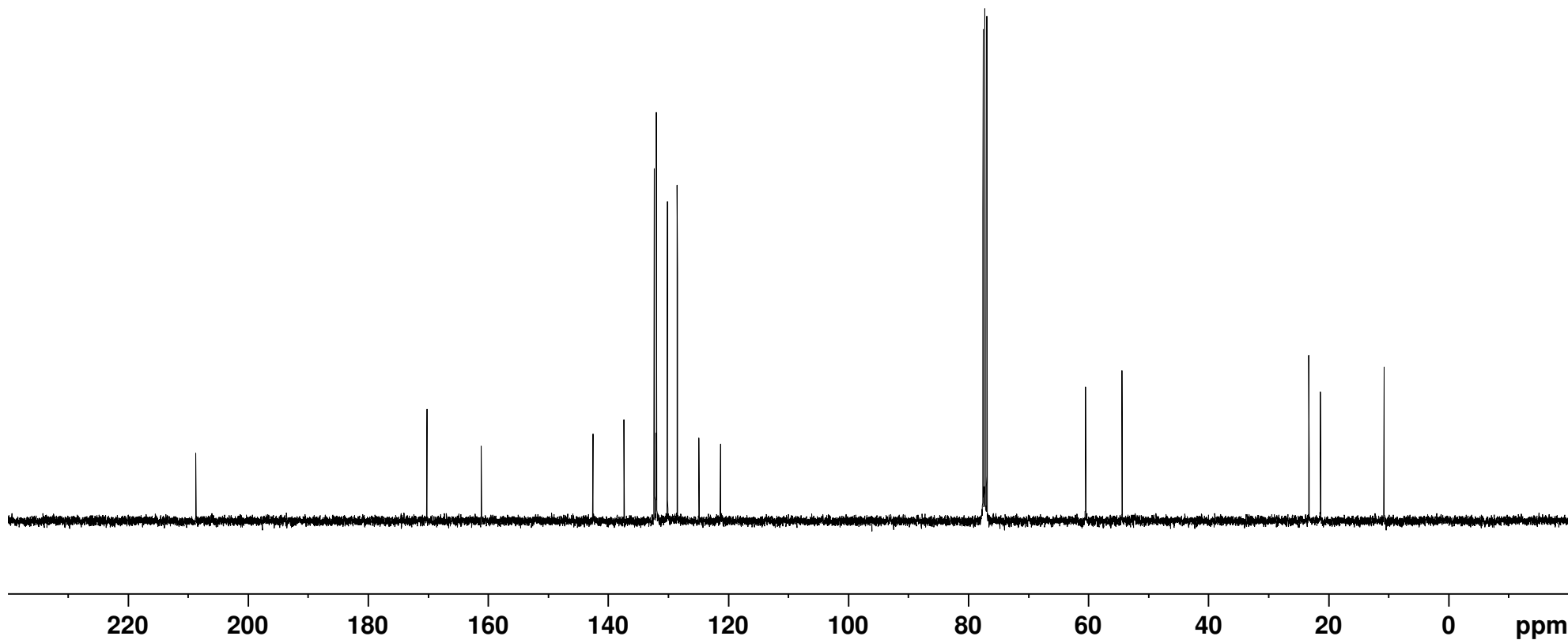
0.073
-0.000



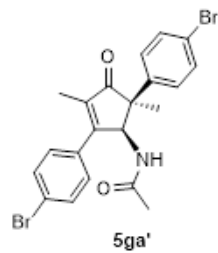
¹³C NMR (100 MHz, CDCl₃)



208.67
170.15
161.11
142.48
137.31
132.27
131.98
131.90
130.08
128.43
124.82
121.24
77.48
77.16
76.84
60.40
54.33
23.18
21.26
10.64



¹H NMR (400 MHz, CDCl₃)



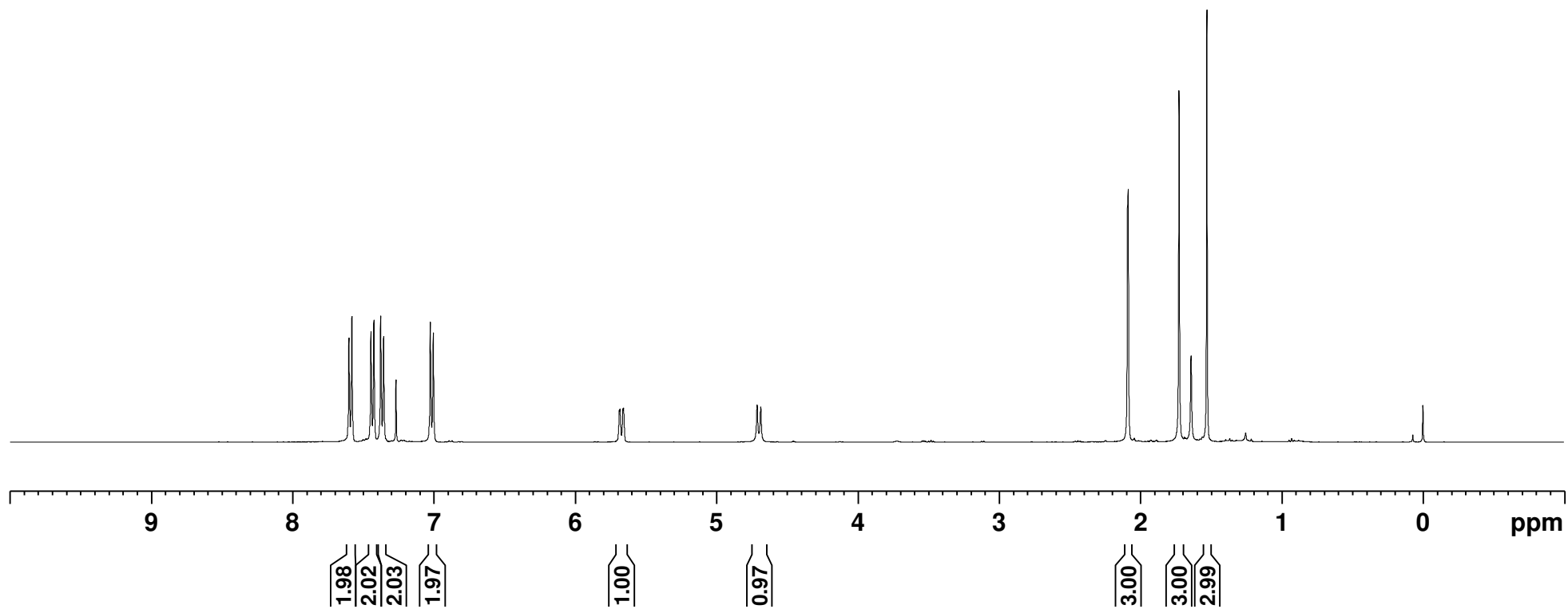
7.600
7.579
7.445
7.423
7.376
7.355
7.267
7.024
7.003

5.686
5.682
5.661
5.657

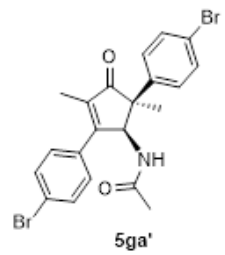
4.712
4.686

2.089
2.086
1.726
1.529

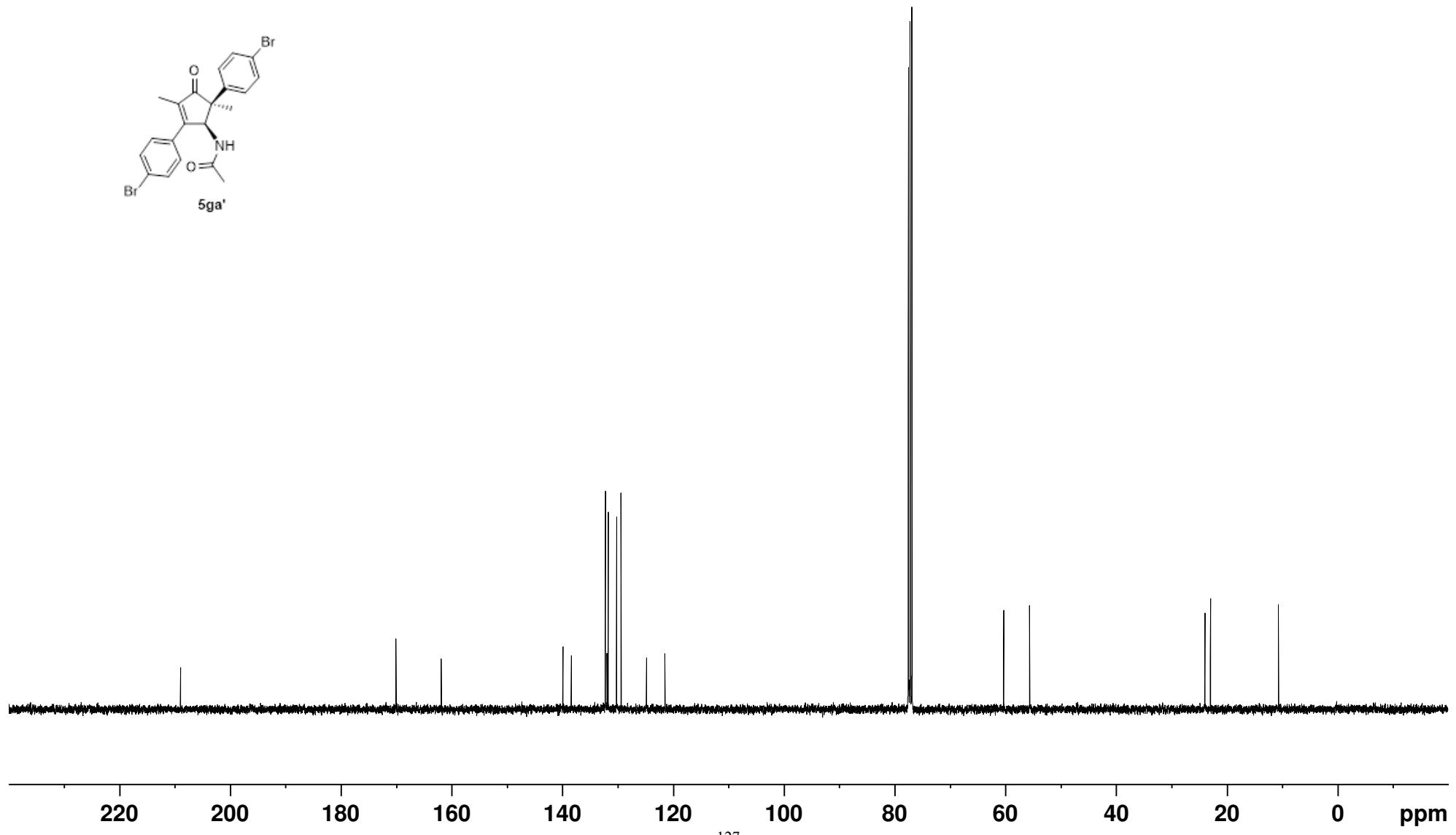
0.071
-0.000



¹³C NMR (100 MHz, CDCl₃)



— 208.94
— 170.04
— 161.85
139.85
138.35
132.21
131.92
131.67
130.18
129.37
124.78
121.44
77.48
77.16
76.84
60.24
55.58
23.90
22.92
10.63

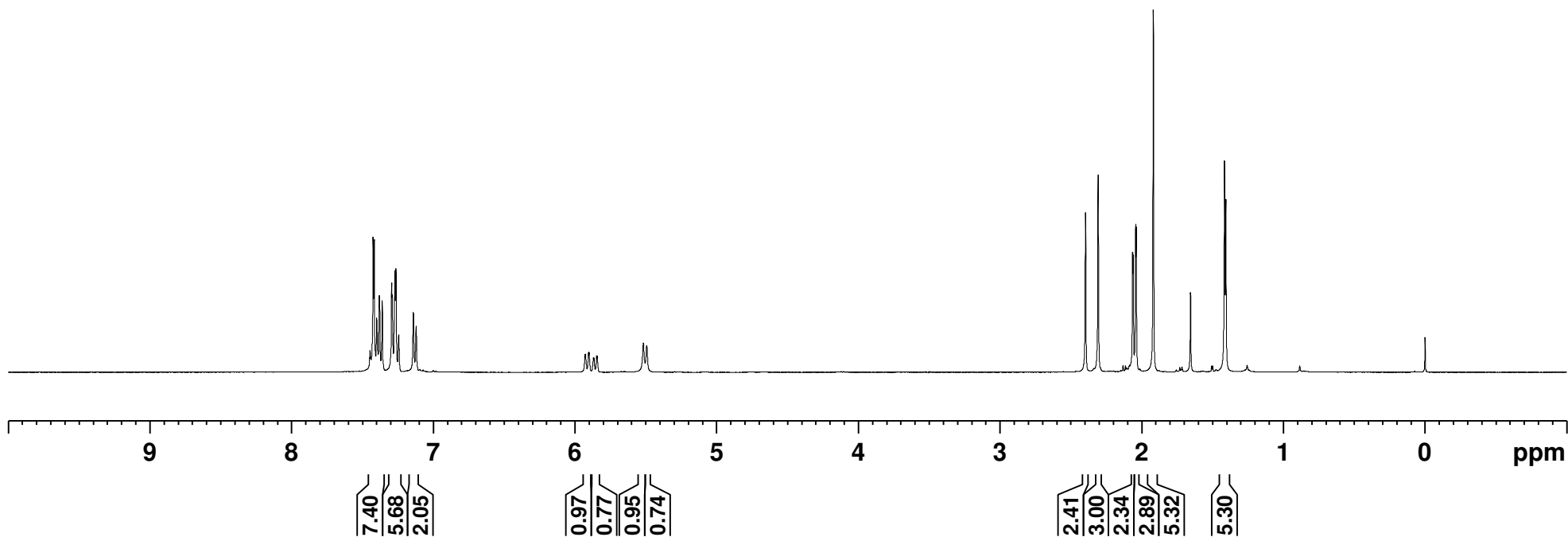
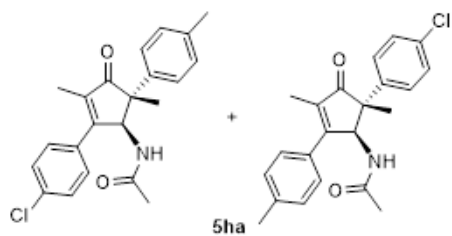


¹H NMR (400 MHz, CDCl₃)

7.447
7.441
7.425
7.417
7.410
7.400
7.381
7.380
7.365
7.360
7.354
7.294
7.290
7.270
7.263
7.244
7.141
7.121
5.929
5.924
5.904
5.900
5.871
5.866
5.847
5.842
5.518
5.493

2.396
2.307
2.064
2.060
2.042
2.038
1.918
1.416
1.406

— -0.000



¹³C NMR (100 MHz, CDCl₃)

209.45
209.12

170.16
170.05

162.35
160.89

142.34
140.84
140.55
137.26
136.73
136.29
136.20
132.87
131.80
130.21
129.93
129.70
129.54
129.20
128.85
128.62
128.12
126.33

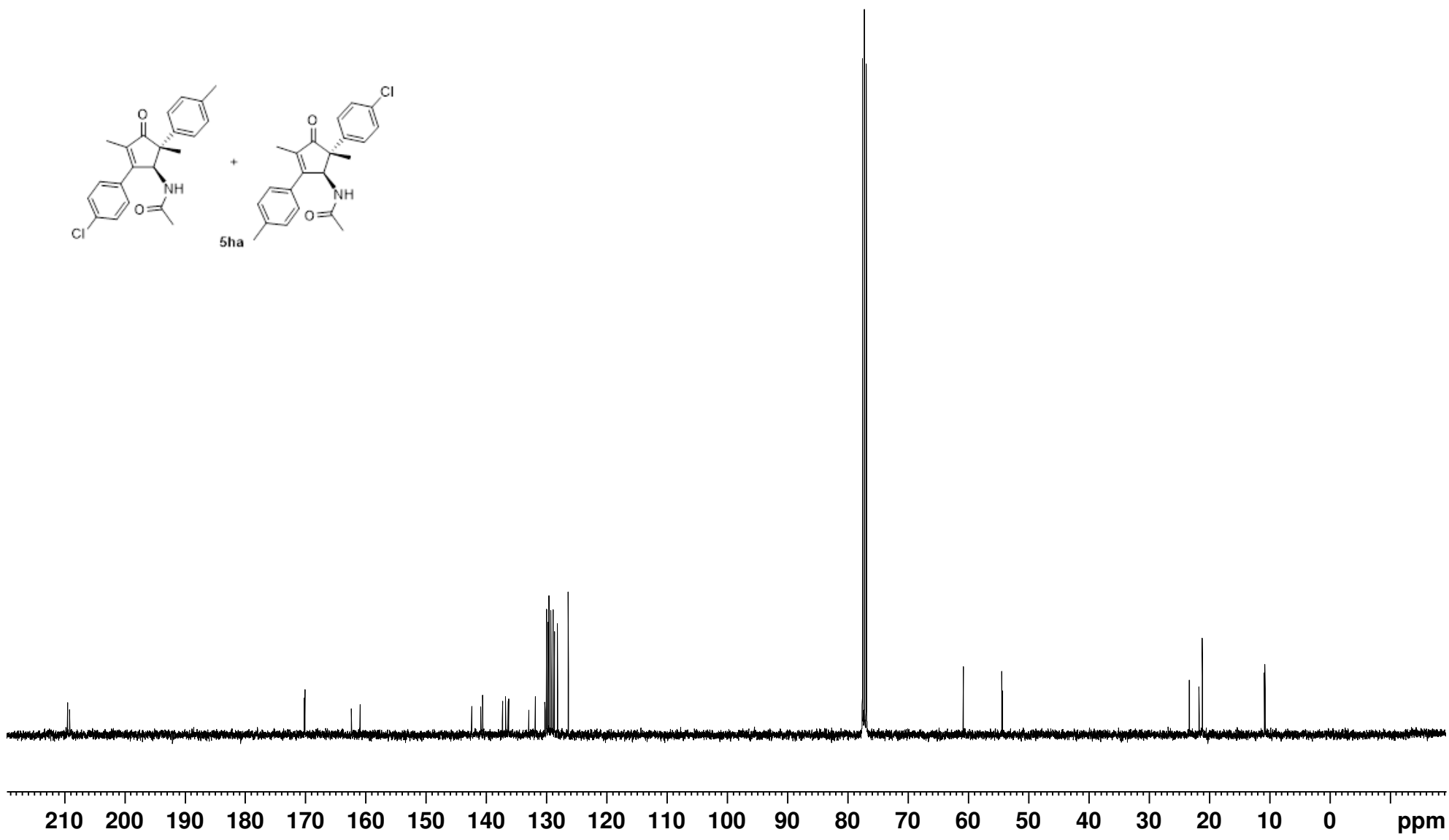
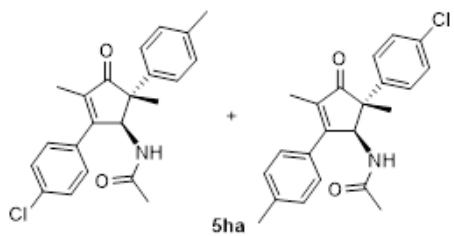
77.47
77.16
76.84

60.74

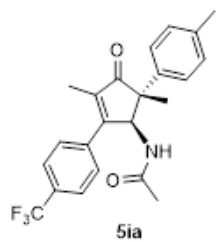
54.36
54.25

23.23
23.19
21.61
21.08
21.05

10.75
10.67

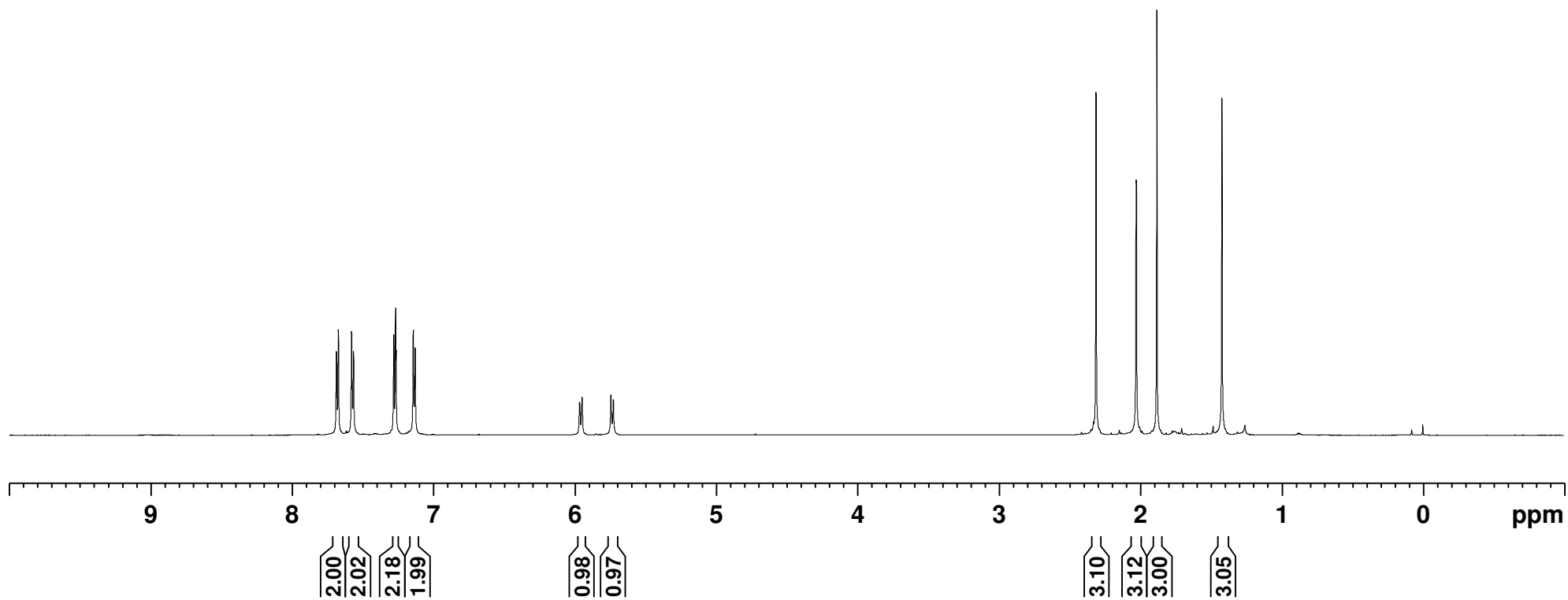


^1H NMR (600 MHz, CDCl_3)

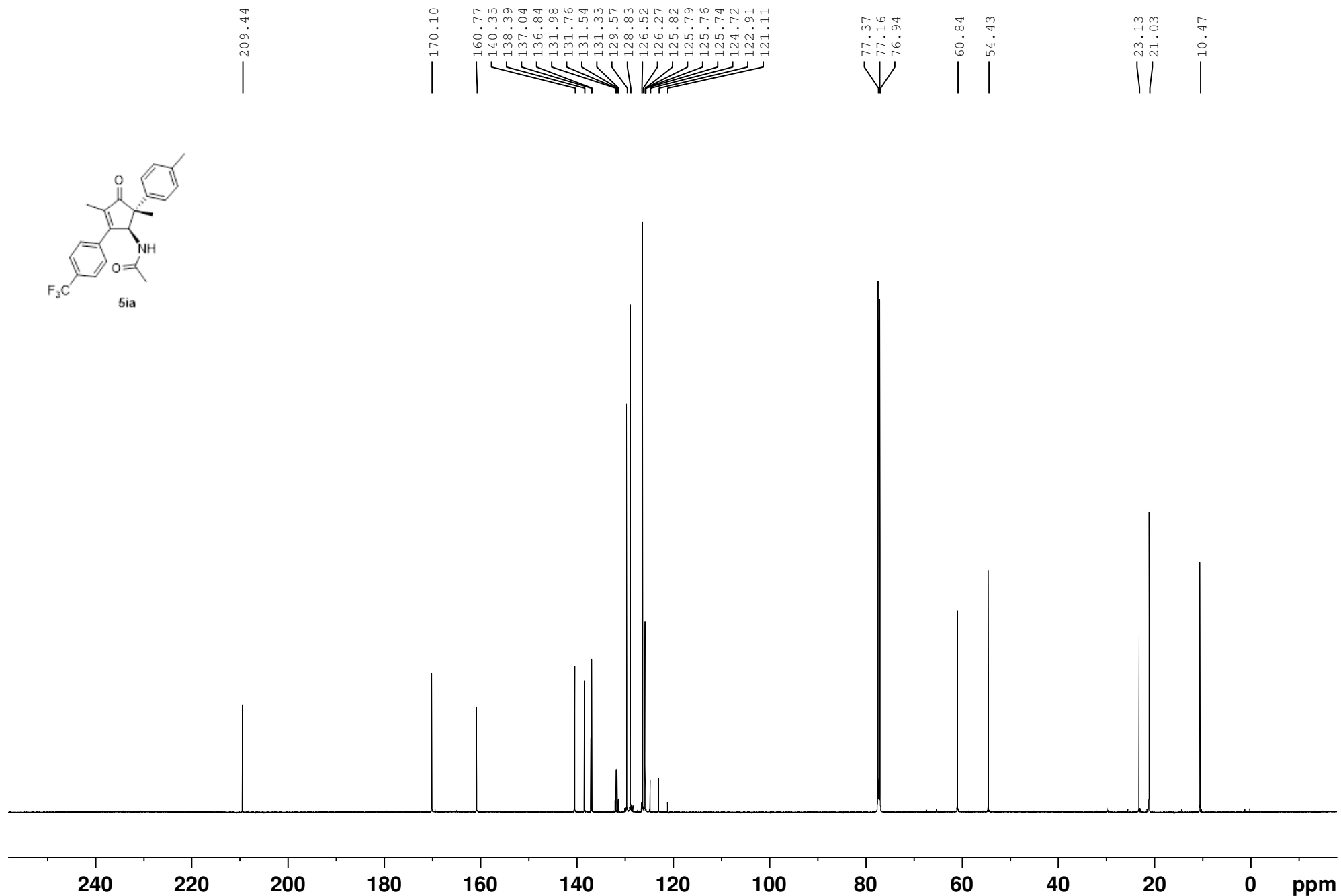
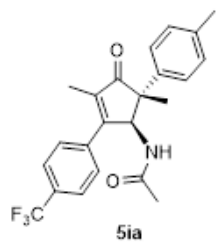


7.685
7.671
7.578
7.564
7.280
7.266
7.262
7.141
7.128
5.966
5.963
5.949
5.946
5.743
5.726

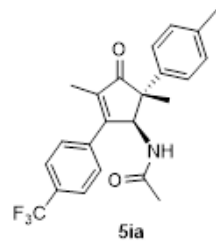
2.311
2.028
2.025
1.881
1.420



¹³C NMR (150 MHz, CDCl₃)



¹⁹F NMR (376 MHz, CDCl₃)

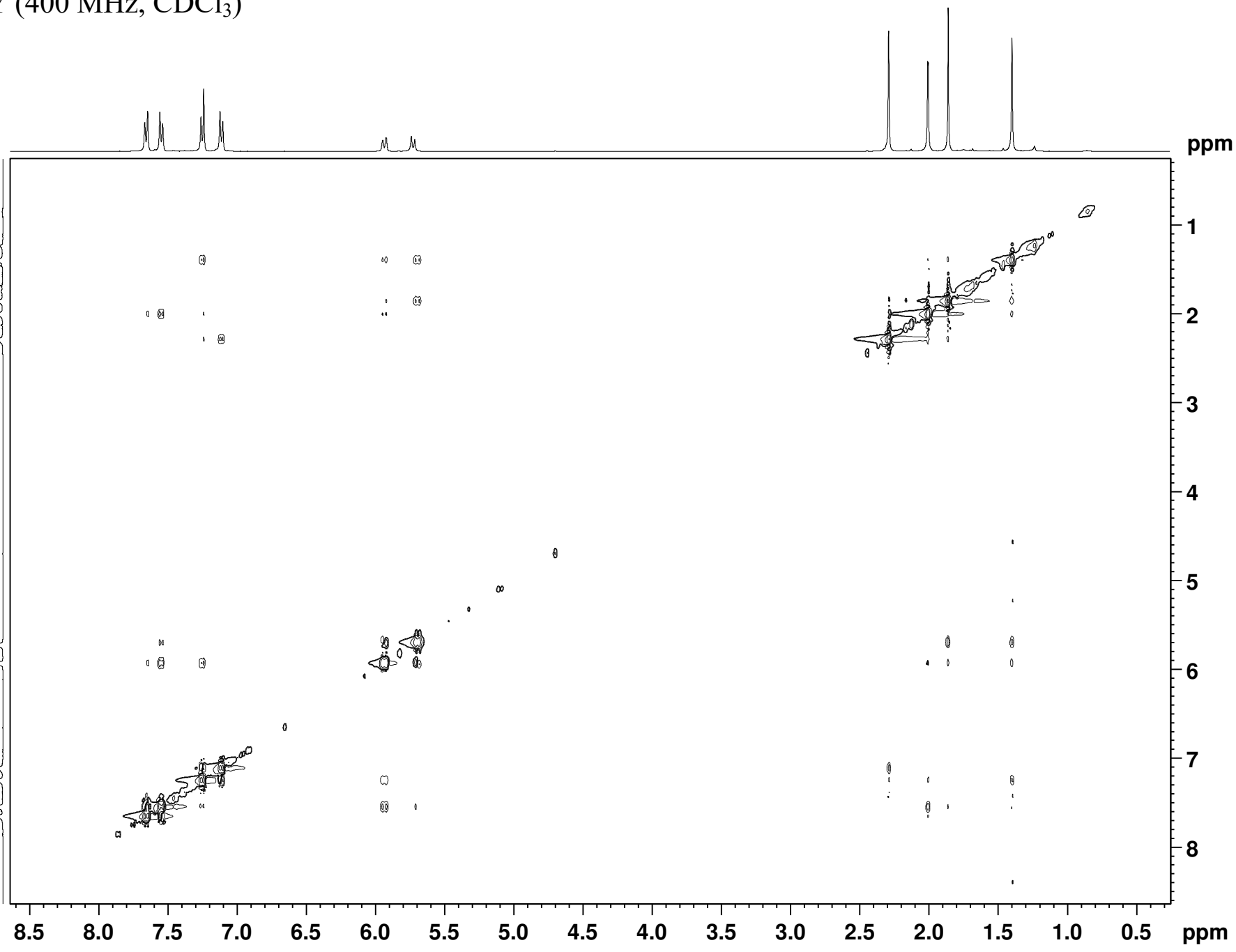
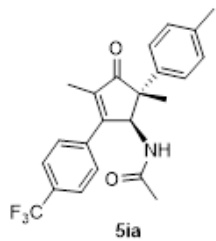


-62.889



0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

NOESY (400 MHz, CDCl₃)



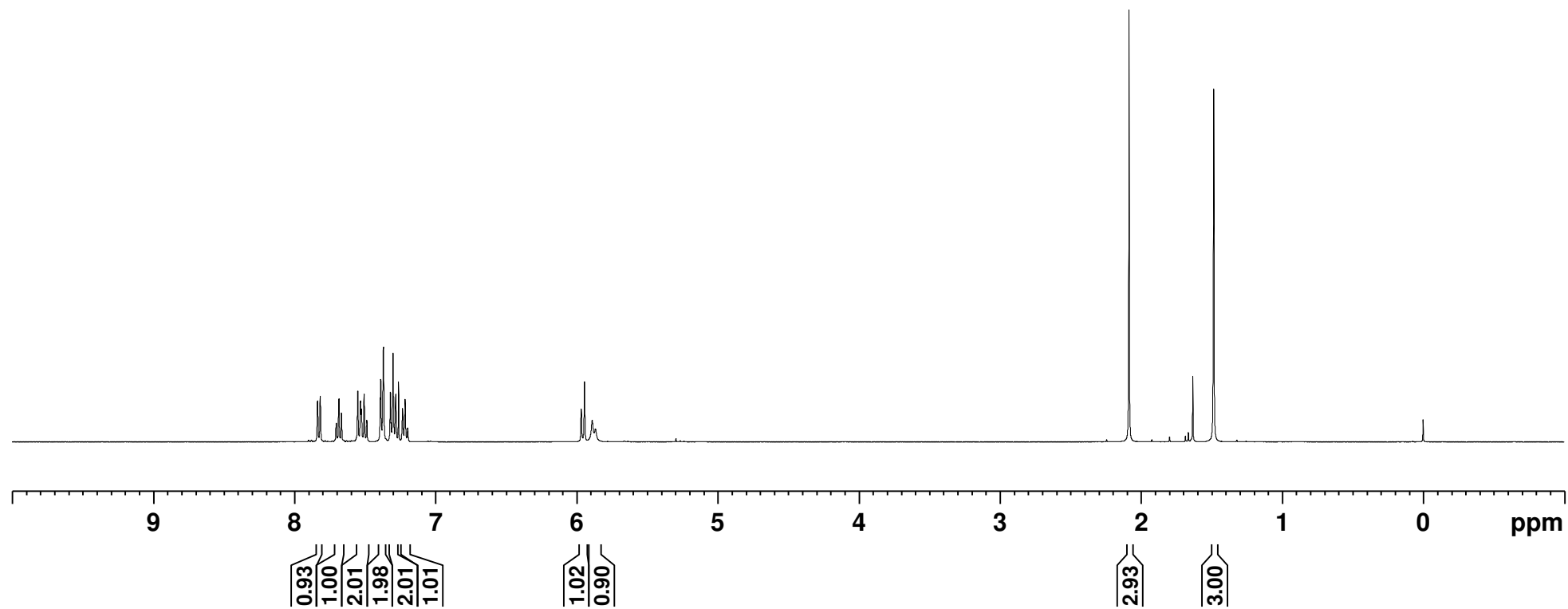
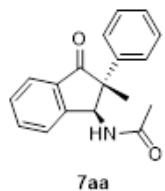
¹H NMR (400 MHz, CDCl₃)

7.836
7.817
7.705
7.702
7.684
7.667
7.665
7.550
7.531
7.524
7.505
7.487
7.391
7.388
7.368
7.319
7.314
7.301
7.281
7.262
7.233
7.220
7.215
7.197
5.967
5.944
5.889
5.866

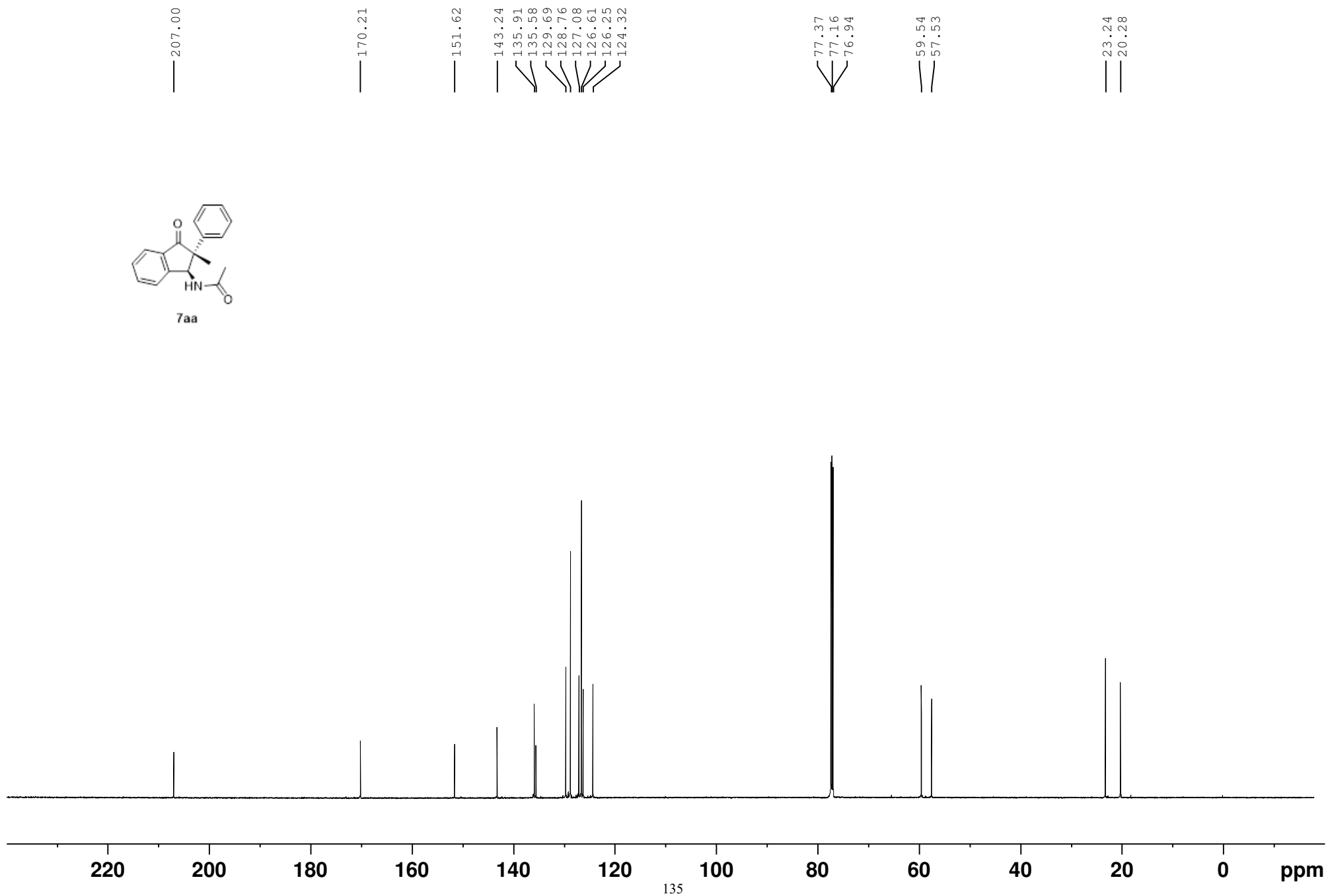
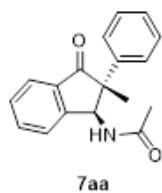
— 2.084

— 1.484

— 0.000



¹³C NMR (150 MHz, CDCl₃)



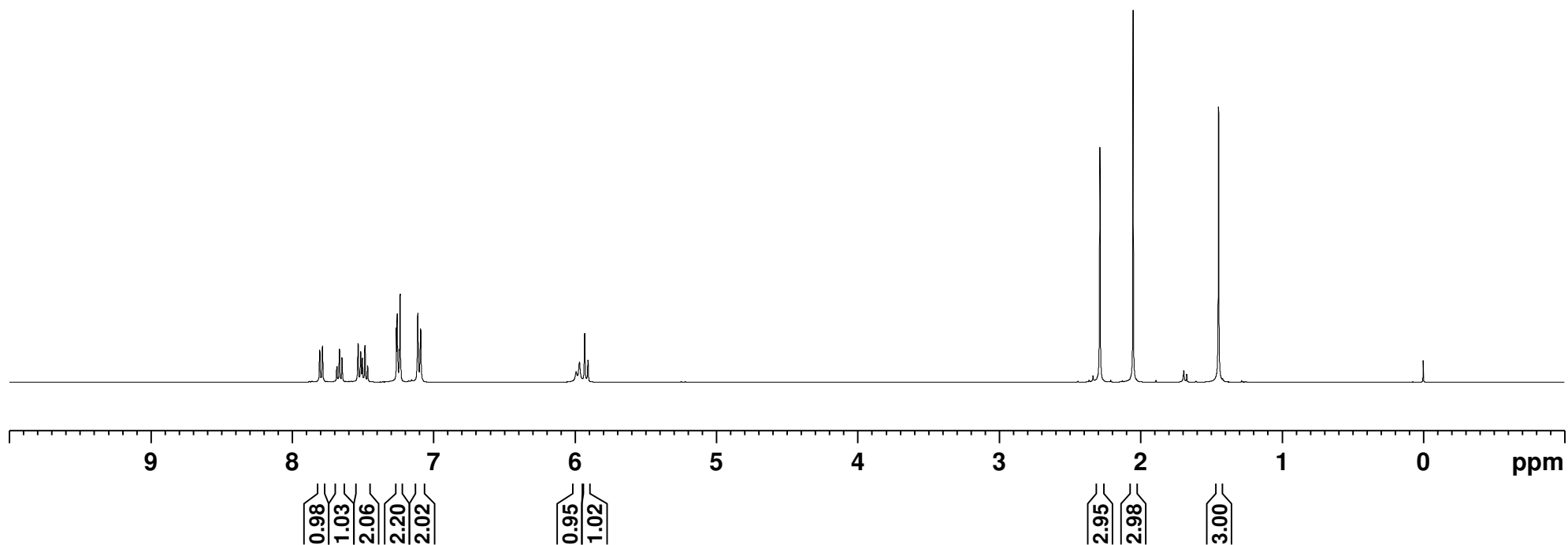
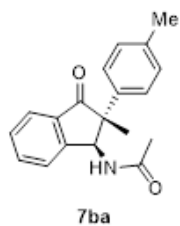
¹H NMR (400 MHz, CDCl₃)

7.804
7.785
7.684
7.682
7.665
7.663
7.647
7.644
7.534
7.532
7.514
7.513
7.503
7.484
7.465
7.261
7.256
7.252
7.240
7.235
7.110
7.090
5.991
5.967
5.930
5.907

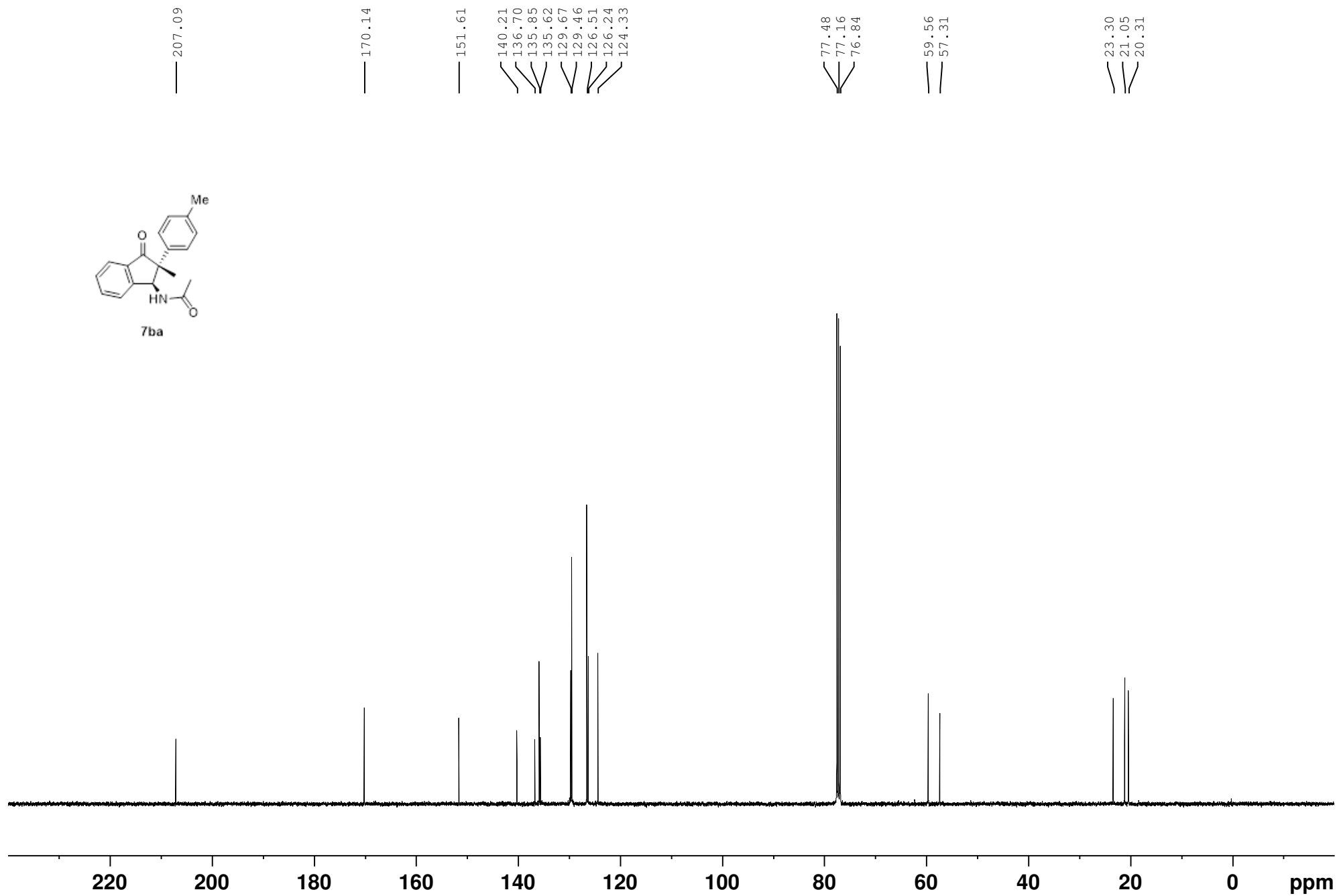
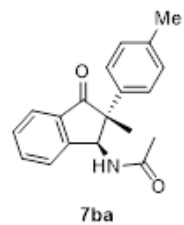
— 2.286
— 2.051

— 1.447

— 0.073
— -0.000



¹³C NMR (100 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)

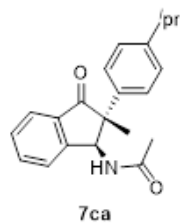
7.737
7.718
7.644
7.642
7.625
7.624
7.607
7.605
7.491
7.473
7.472
7.461
7.442
7.423
7.263
7.250
7.229
7.145
7.124
6.402
6.378
5.880
5.856

2.896
2.879
2.861
2.844
2.827
2.810
2.792

1.956

1.413
1.208
1.190

0.081
-0.000



9

8

7

6

5

4

3

2

1

0

ppm

0.98
1.01
2.05
1.98
1.98

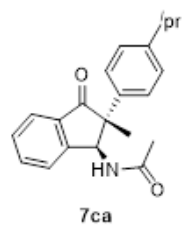
0.98
0.98

1.03

2.96

3.00
2.99
2.92

^{13}C NMR (100 MHz, CDCl_3)



— 207.26

— 170.26

— 151.76

— 147.44

— 140.49

— 135.76

— 135.53

— 129.51

— 126.73

— 126.43

— 126.25

— 124.15

— 77.47

— 77.16

— 76.84

— 59.39

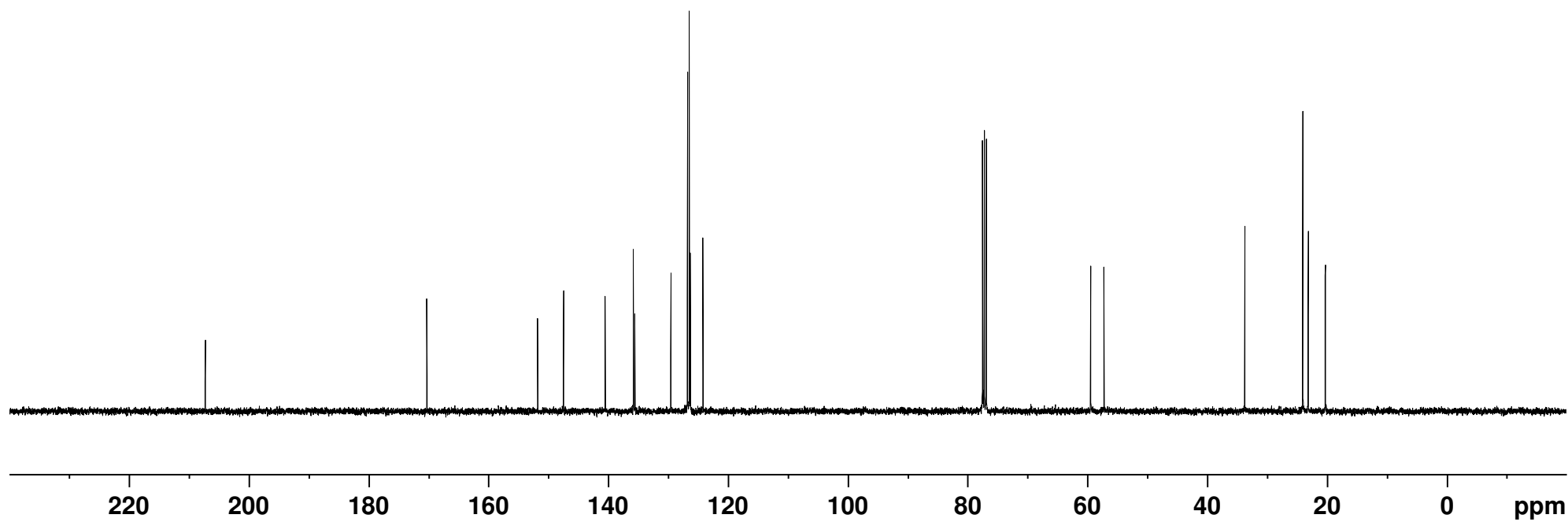
— 57.19

— 33.65

— 23.97

— 23.08

— 20.22



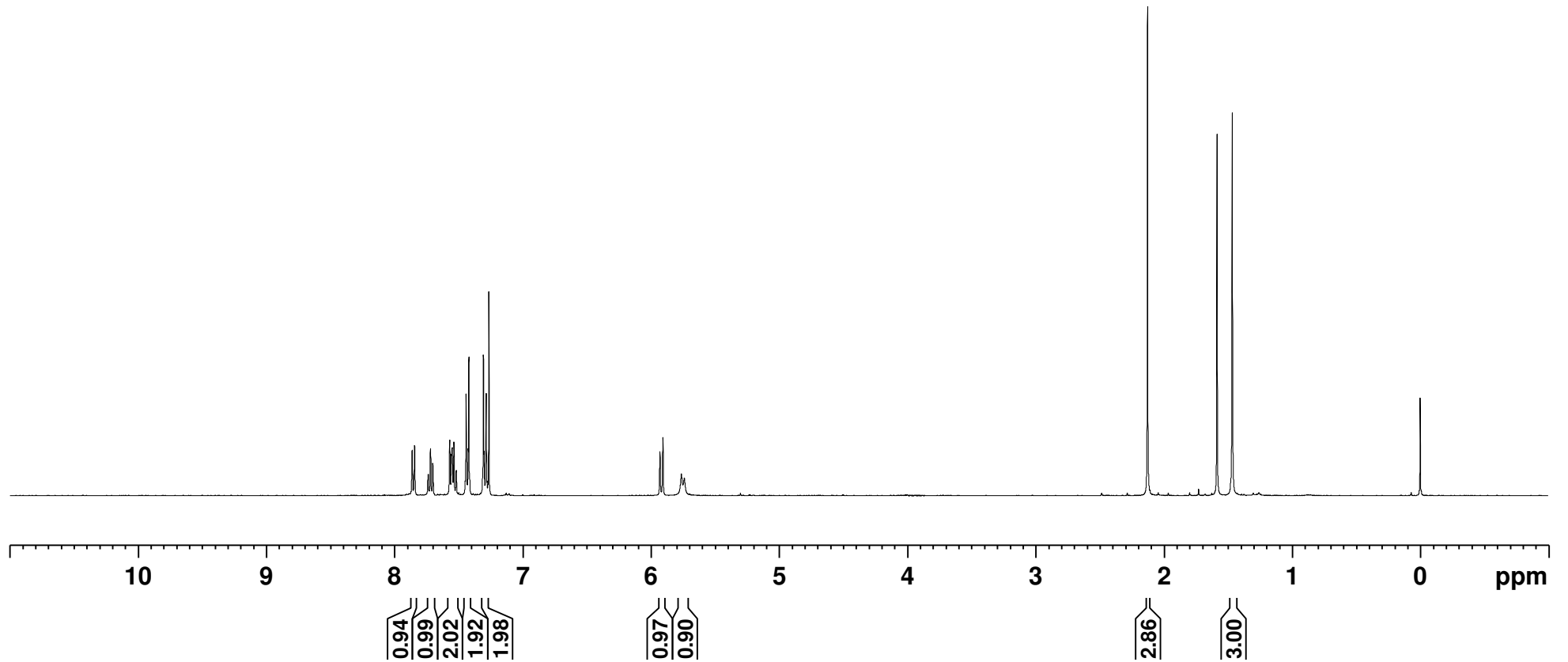
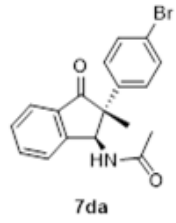
^1H NMR (400 MHz, CDCl_3)

7.862
7.842
7.738
7.736
7.719
7.701
7.698
7.567
7.554
7.550
7.536
7.518
7.448
7.441
7.436
7.424
7.420
7.413
7.312
7.305
7.301
7.288
7.284
7.277
7.263
5.929
5.906
5.762
5.739

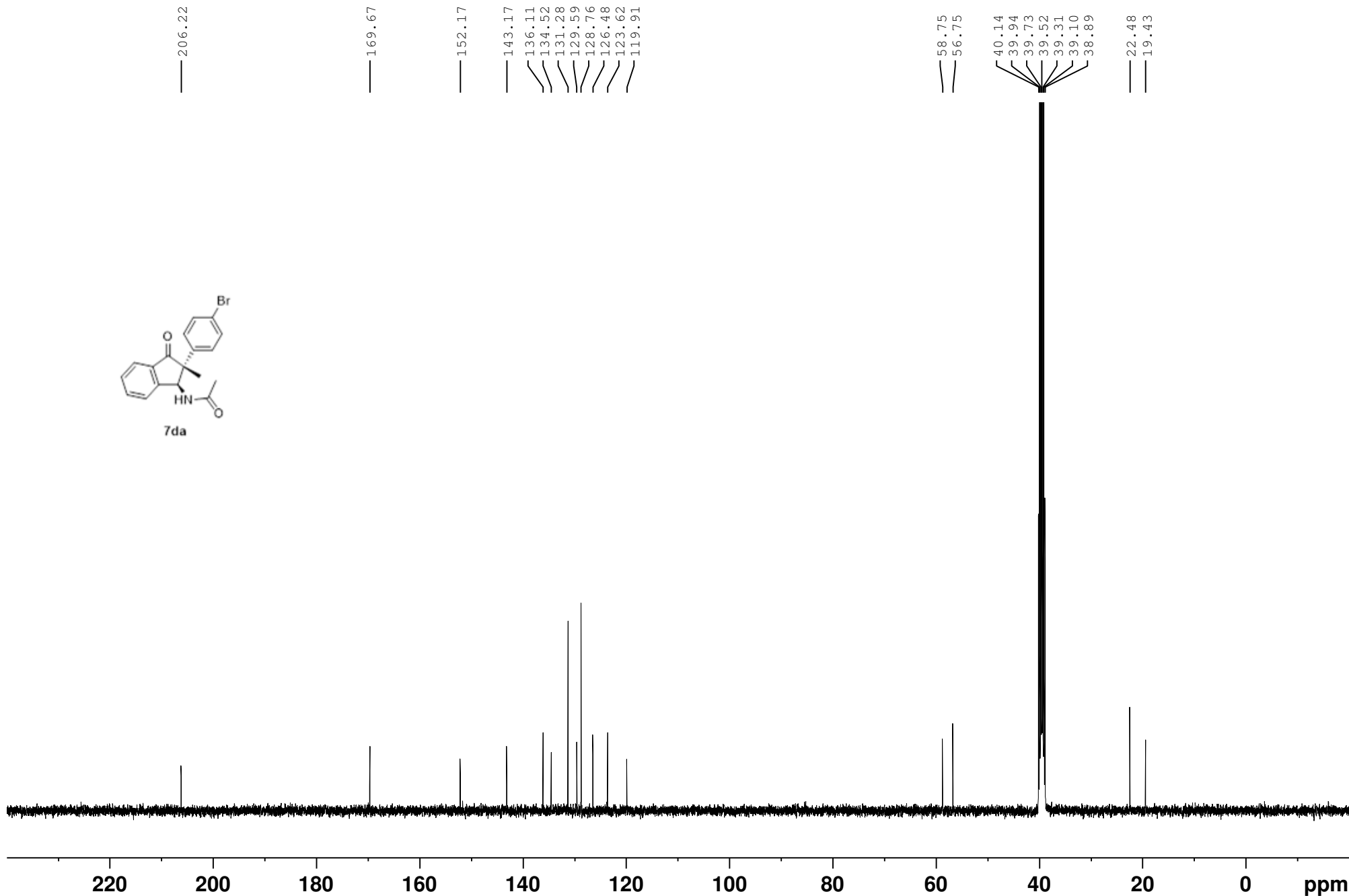
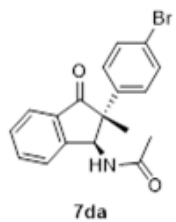
— 2.126

— 1.465

— -0.000



¹³C NMR (100 MHz, (CD₃)₂SO)

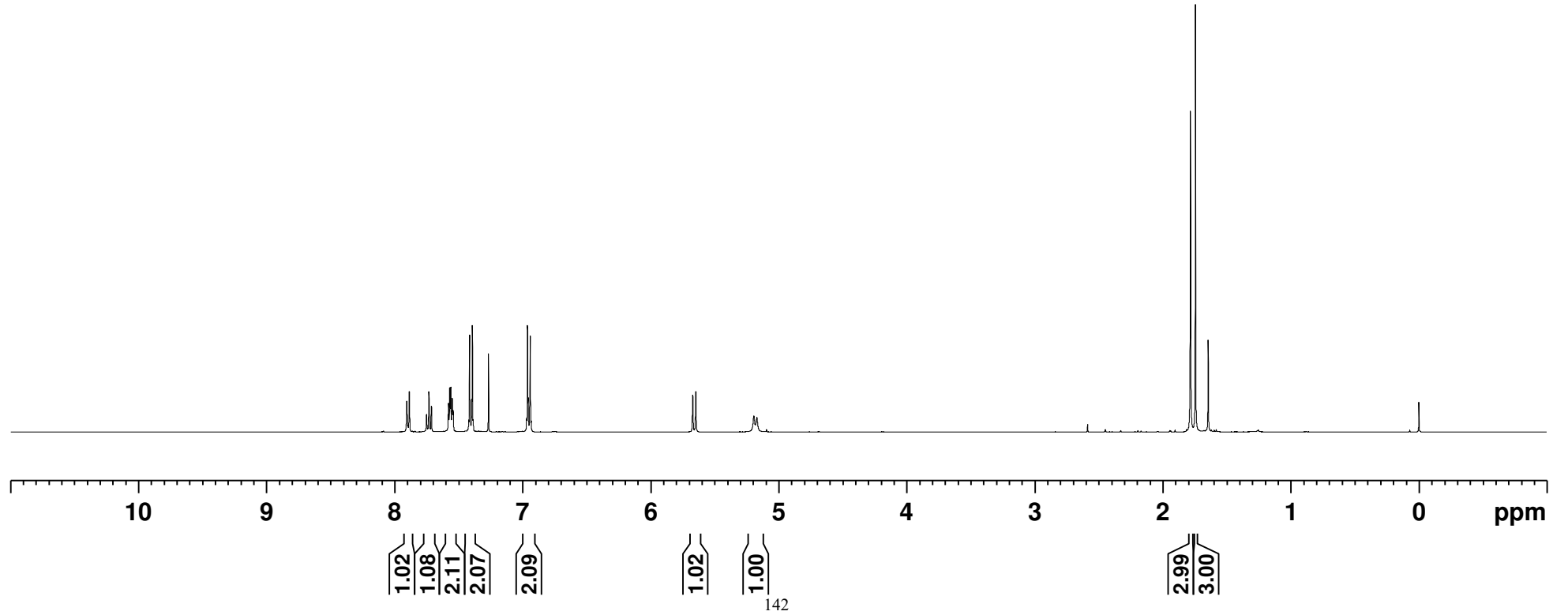
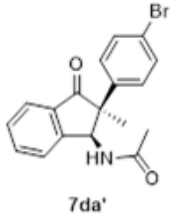


¹H NMR (400 MHz, CDCl₃)

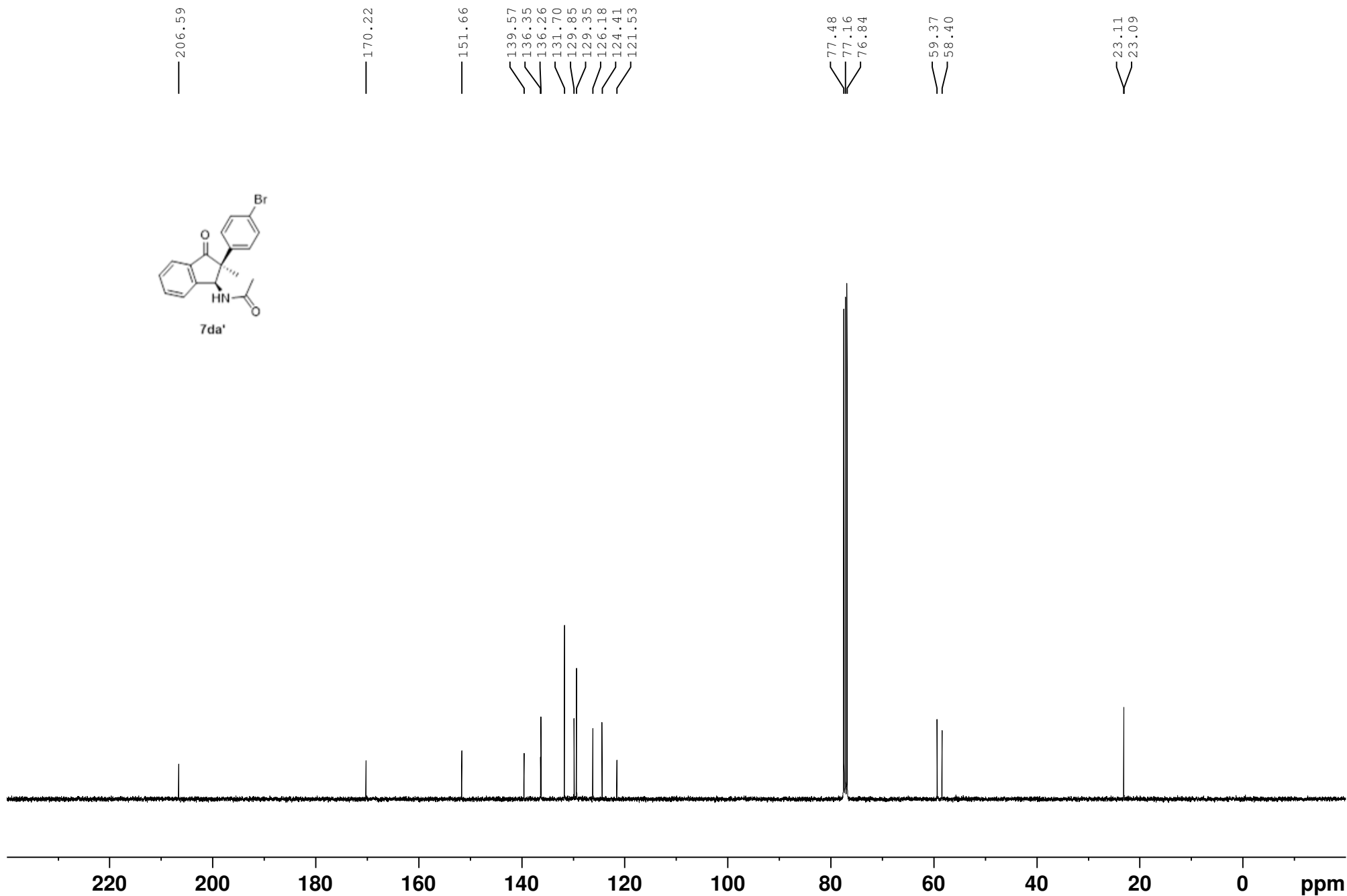
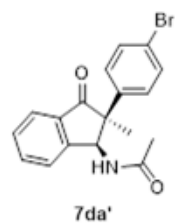
7.906
7.905
7.885
7.752
7.749
7.733
7.715
7.712
7.580
7.570
7.561
7.551
7.550
7.544
7.543
7.421
7.414
7.410
7.398
7.393
7.386
7.267
6.969
6.962
6.957
6.945
6.940
6.933
5.672
5.648
5.194
5.171

1.784
1.745

-0.000

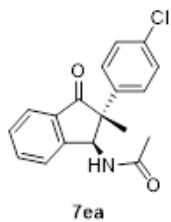


¹³C NMR (100 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)

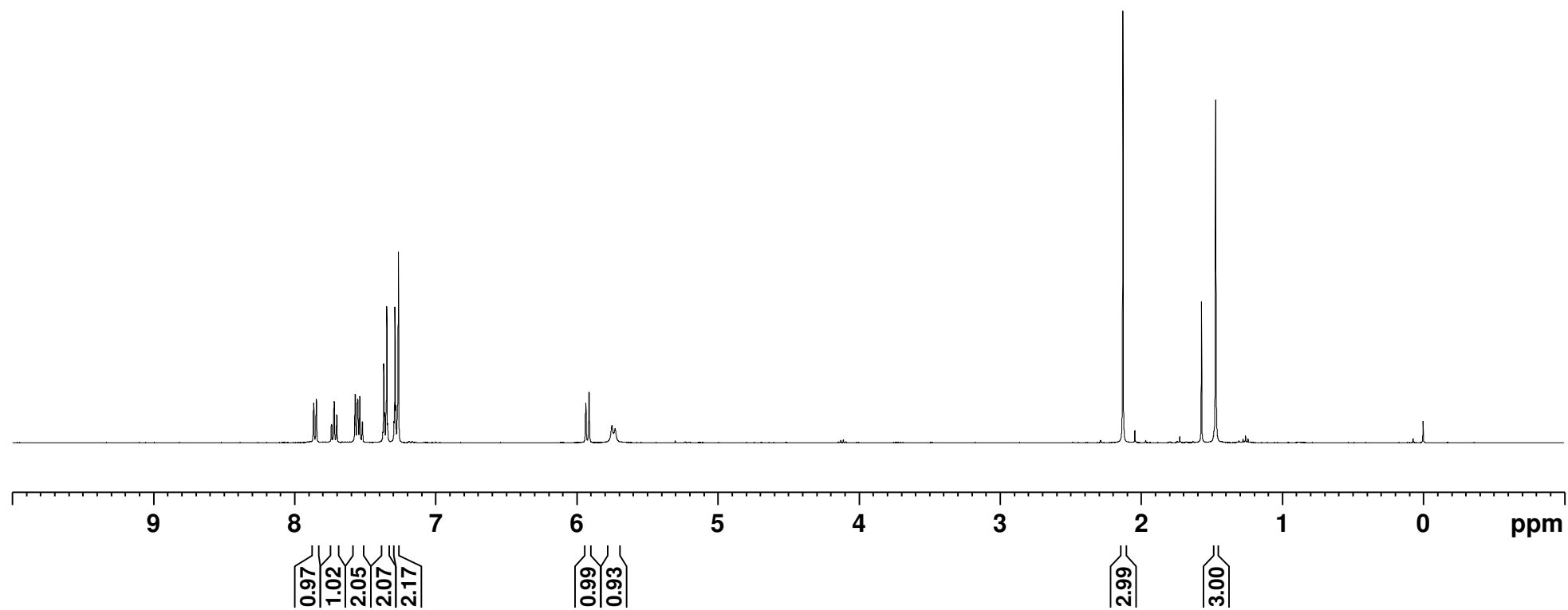
7.863
7.844
7.738
7.736
7.718
7.701
7.698
7.569
7.551
7.536
7.518
7.373
7.367
7.362
7.350
7.345
7.338
7.293
7.287
7.282
7.270
7.262
5.934
5.911
5.750
5.726



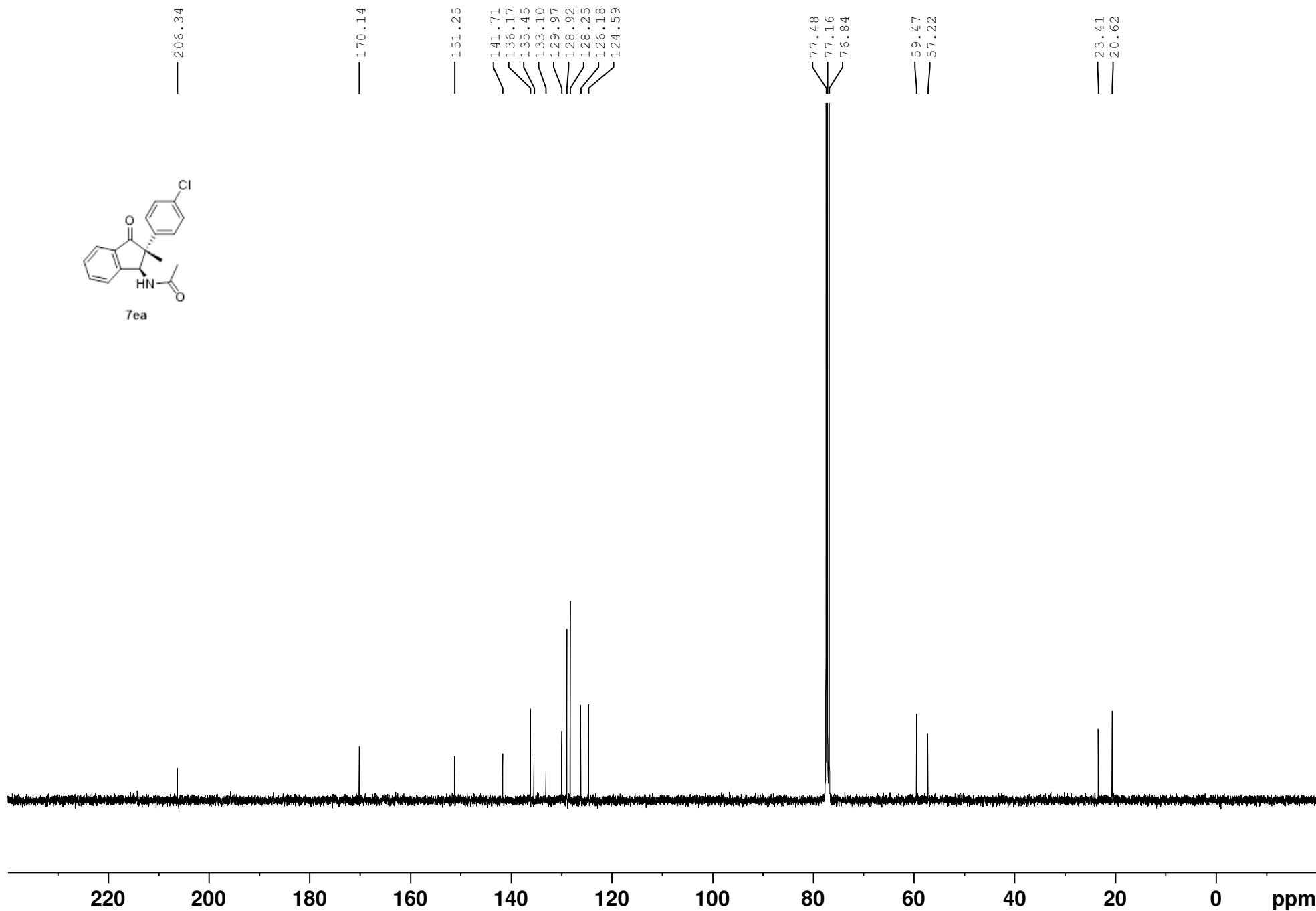
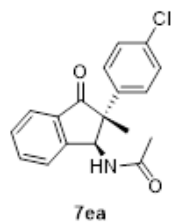
— 2.127

— 1.470

< 0.070
< -0.000



¹³C NMR (100 MHz, CDCl₃)

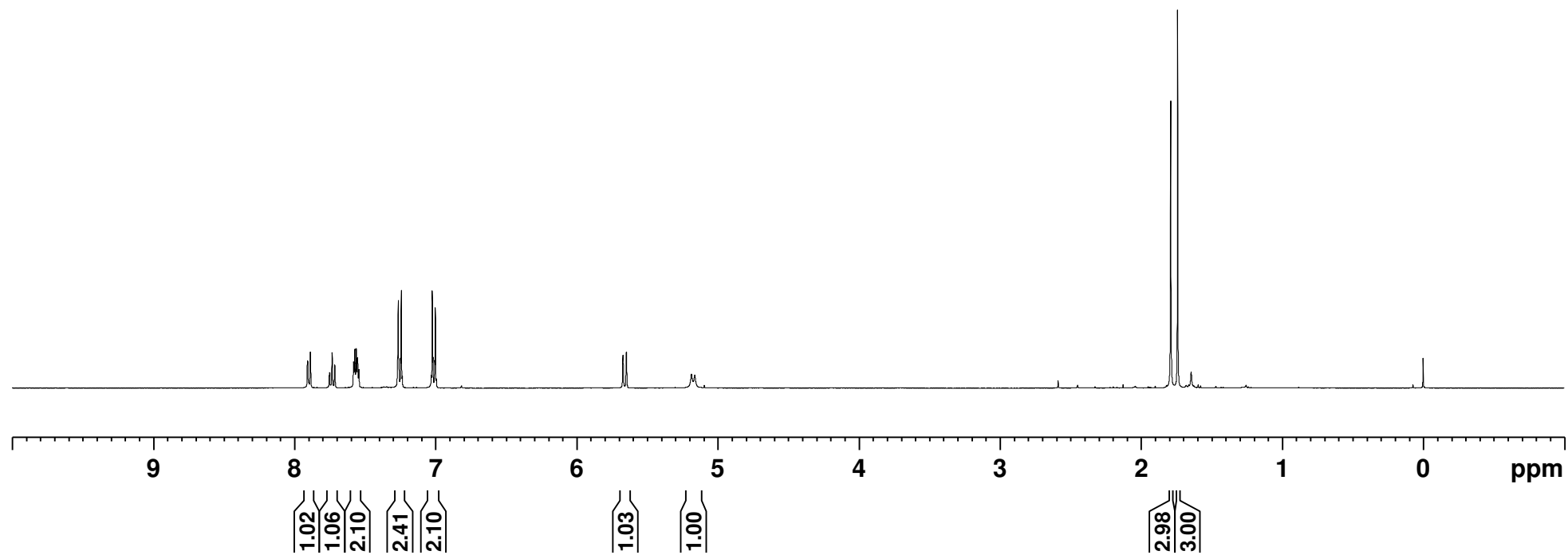
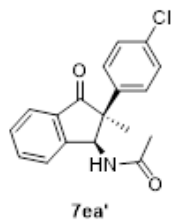


¹H NMR (400 MHz, CDCl₃)

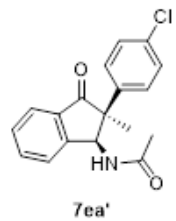
7.907
7.906
7.887
7.752
7.750
7.734
7.732
7.715
7.712
7.580
7.579
7.572
7.561
7.553
7.551
7.543
7.267
7.264
7.259
7.247
7.242
7.235
7.029
7.023
7.018
7.006
7.001
6.994
5.671
5.647
5.186
5.162

1.788
1.740

— 0.000



¹³C NMR (100 MHz, CDCl₃)



206.67

170.21

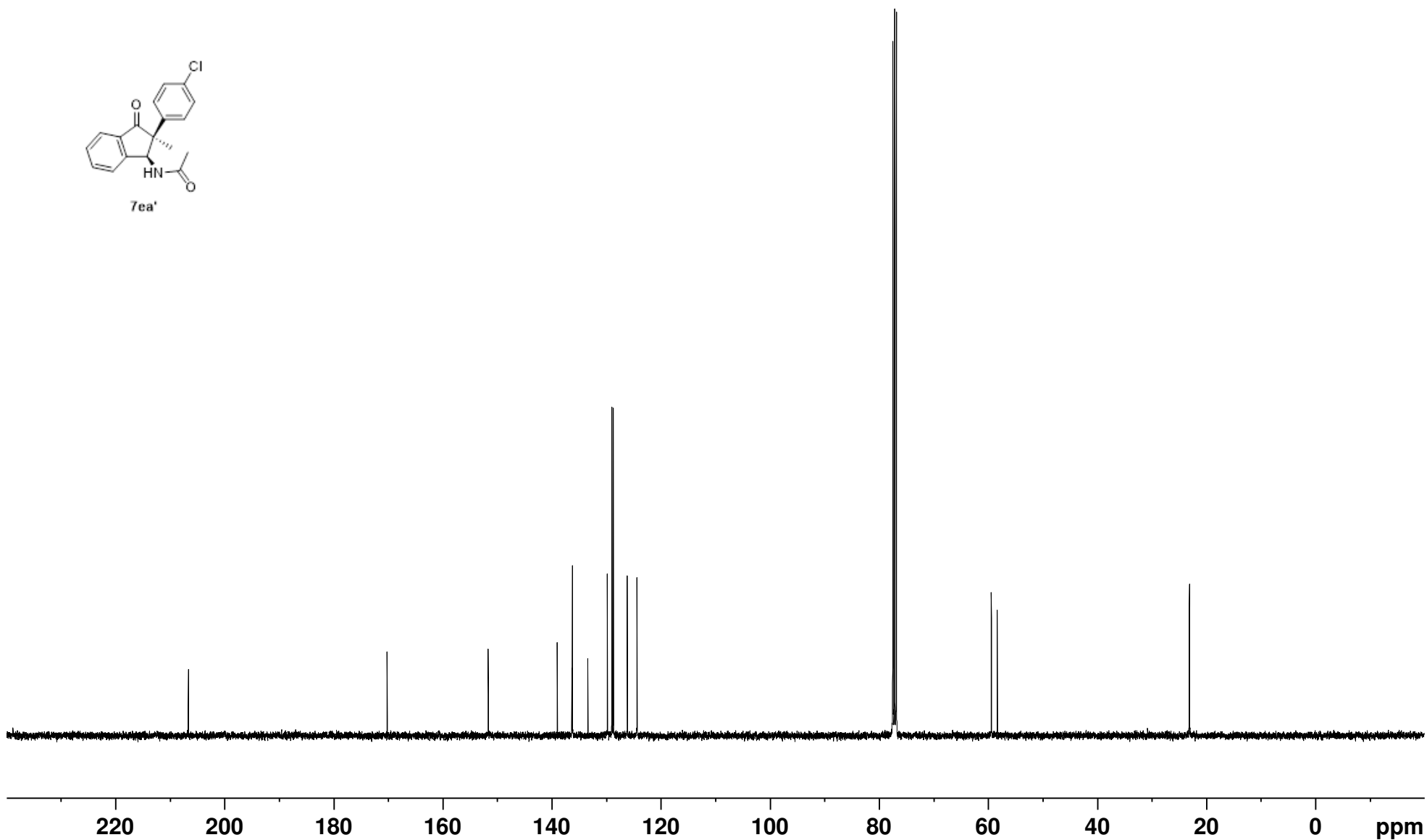
151.67

139.03
136.34
136.25
133.39
129.83
129.00
128.74
126.20
124.40

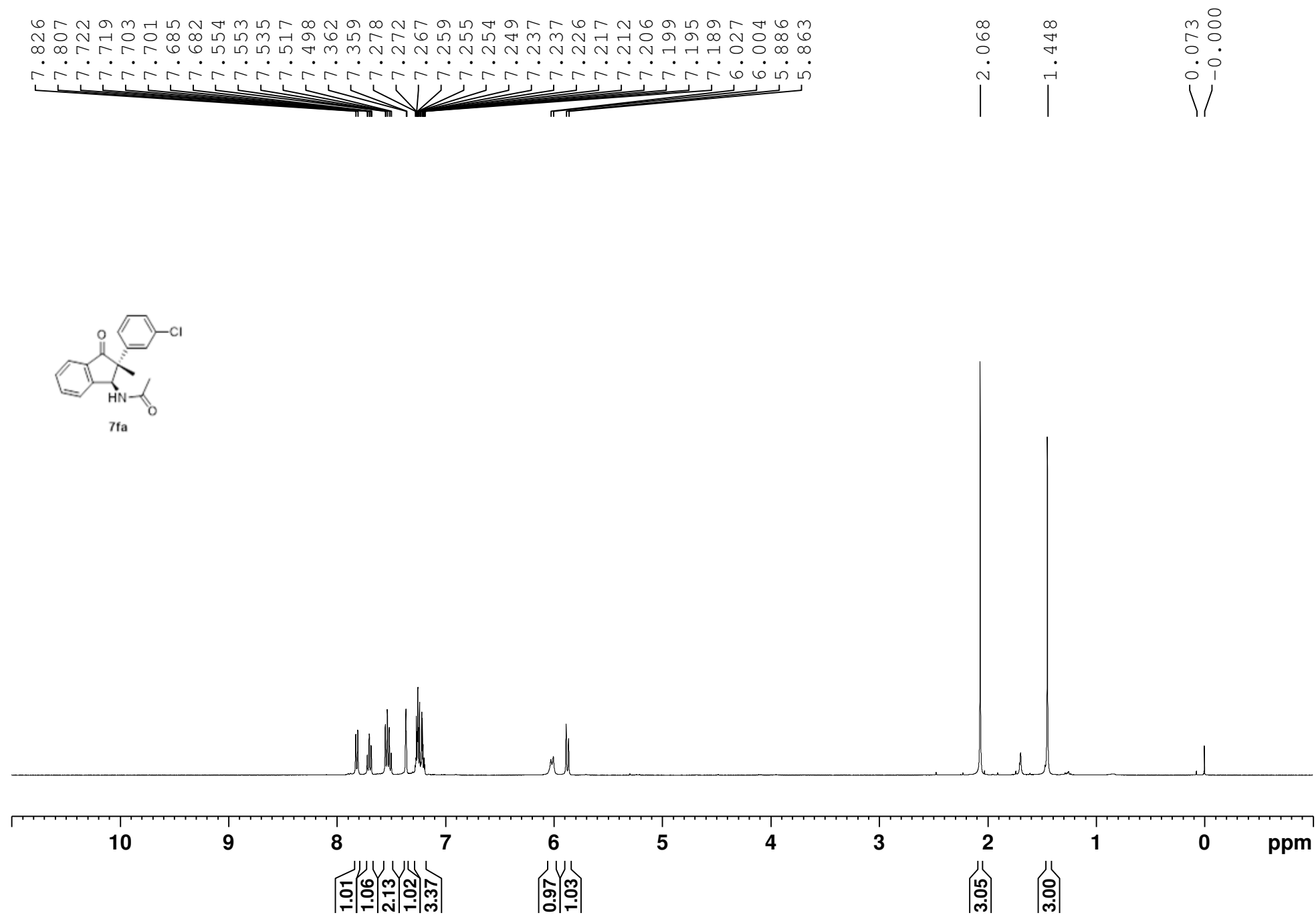
77.48
77.16
76.84

59.41
58.32

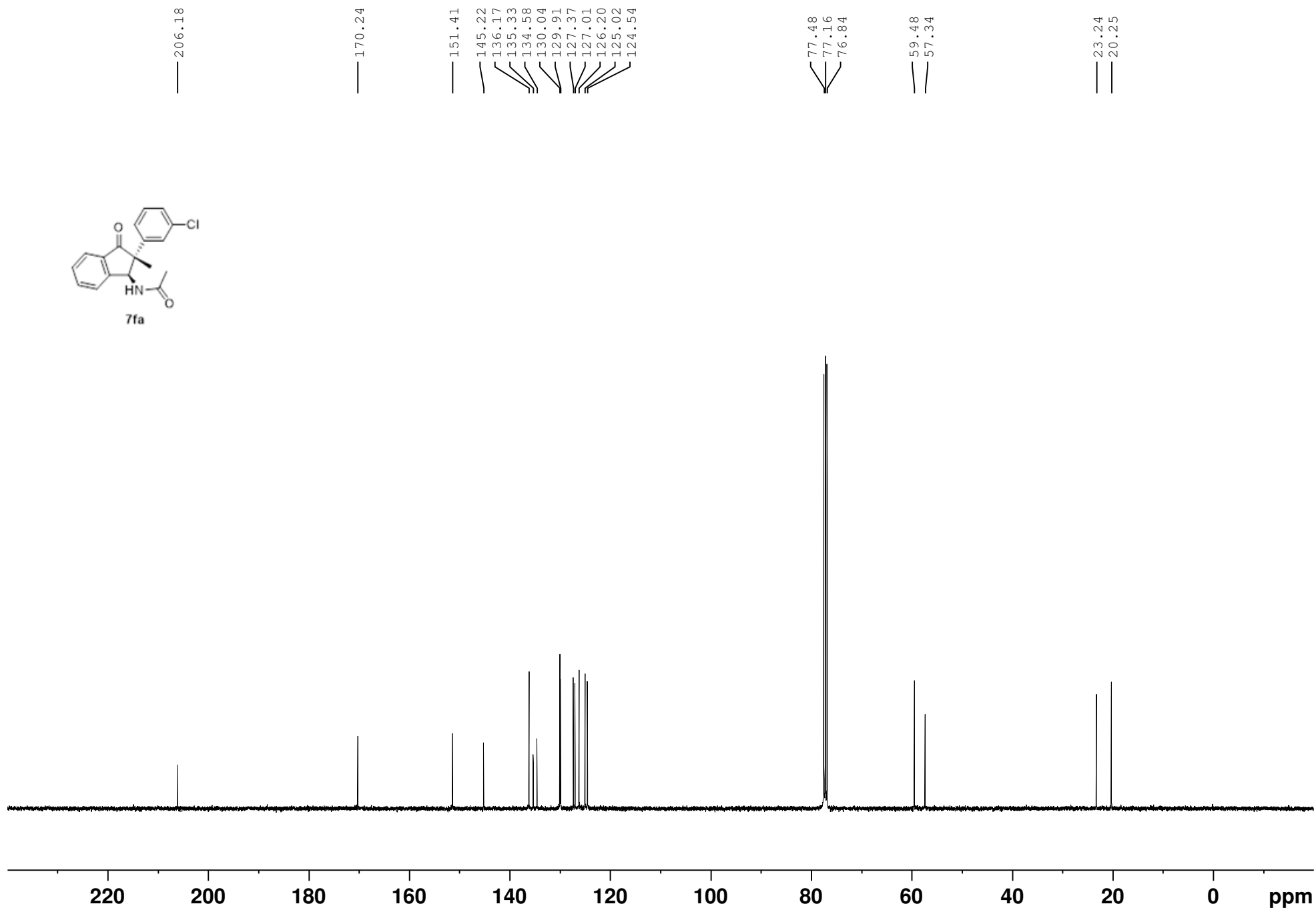
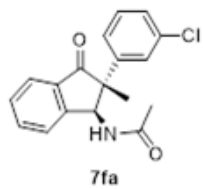
23.15
23.09



¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)

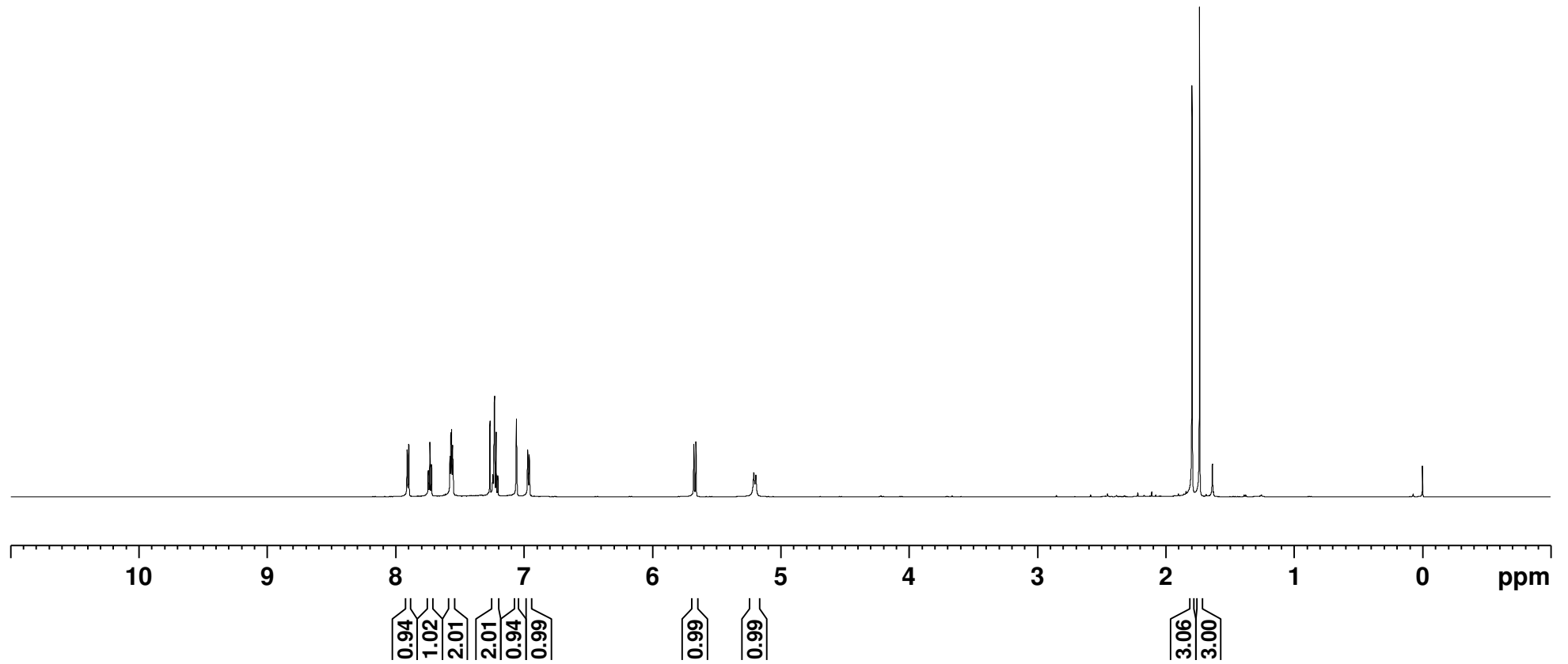
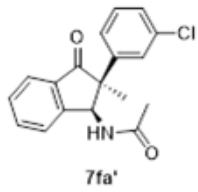


¹H NMR (600 MHz, CDCl₃)

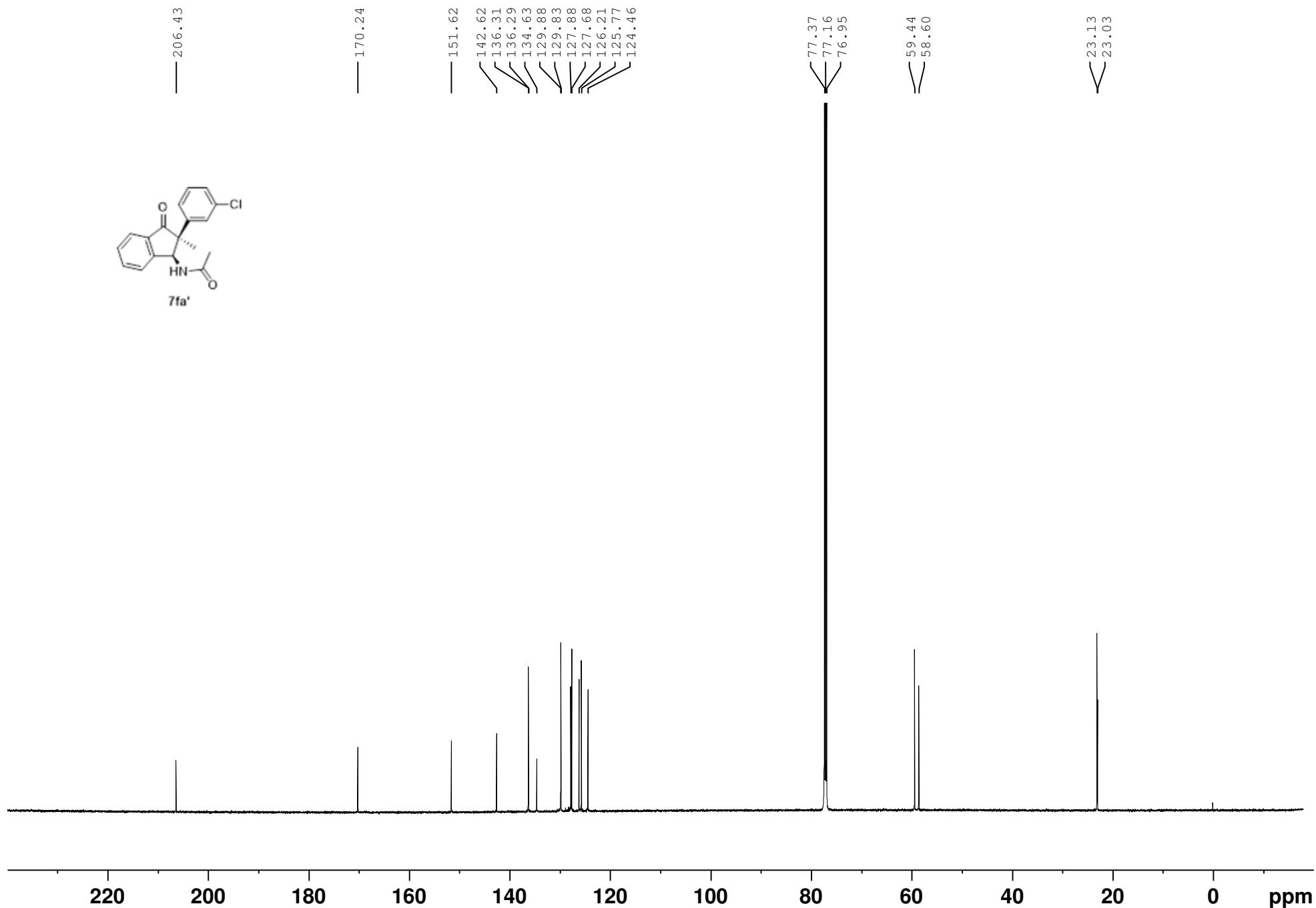
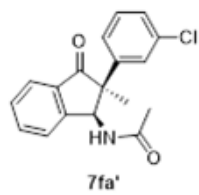
7.911
7.898
7.747
7.745
7.734
7.722
7.720
7.577
7.569
7.565
7.556
7.266
7.244
7.241
7.234
7.231
7.228
7.217
7.203
7.059
7.056
6.973
6.970
6.967
6.961
6.959
6.956
5.677
5.660
5.210
5.194

1.795
1.736

0.072
-0.000

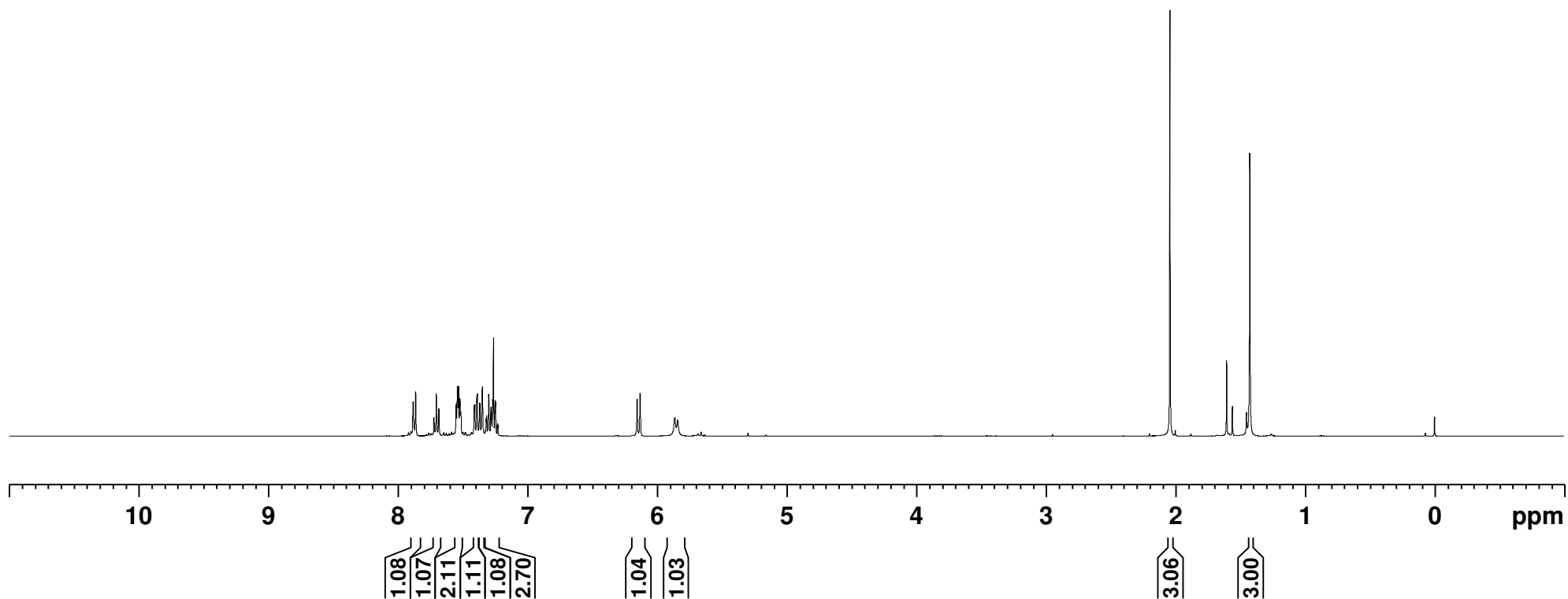
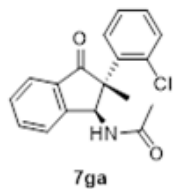


¹³C NMR (150 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)

7.883
7.864
7.723
7.720
7.704
7.702
7.685
7.683
7.551
7.541
7.532
7.522
7.521
7.516
7.514
7.410
7.406
7.391
7.387
7.370
7.366
7.351
7.347
7.319
7.315
7.301
7.297
7.282
7.277
7.269
7.262
7.250
7.246
7.231
7.227
6.154
6.131
5.864
5.841

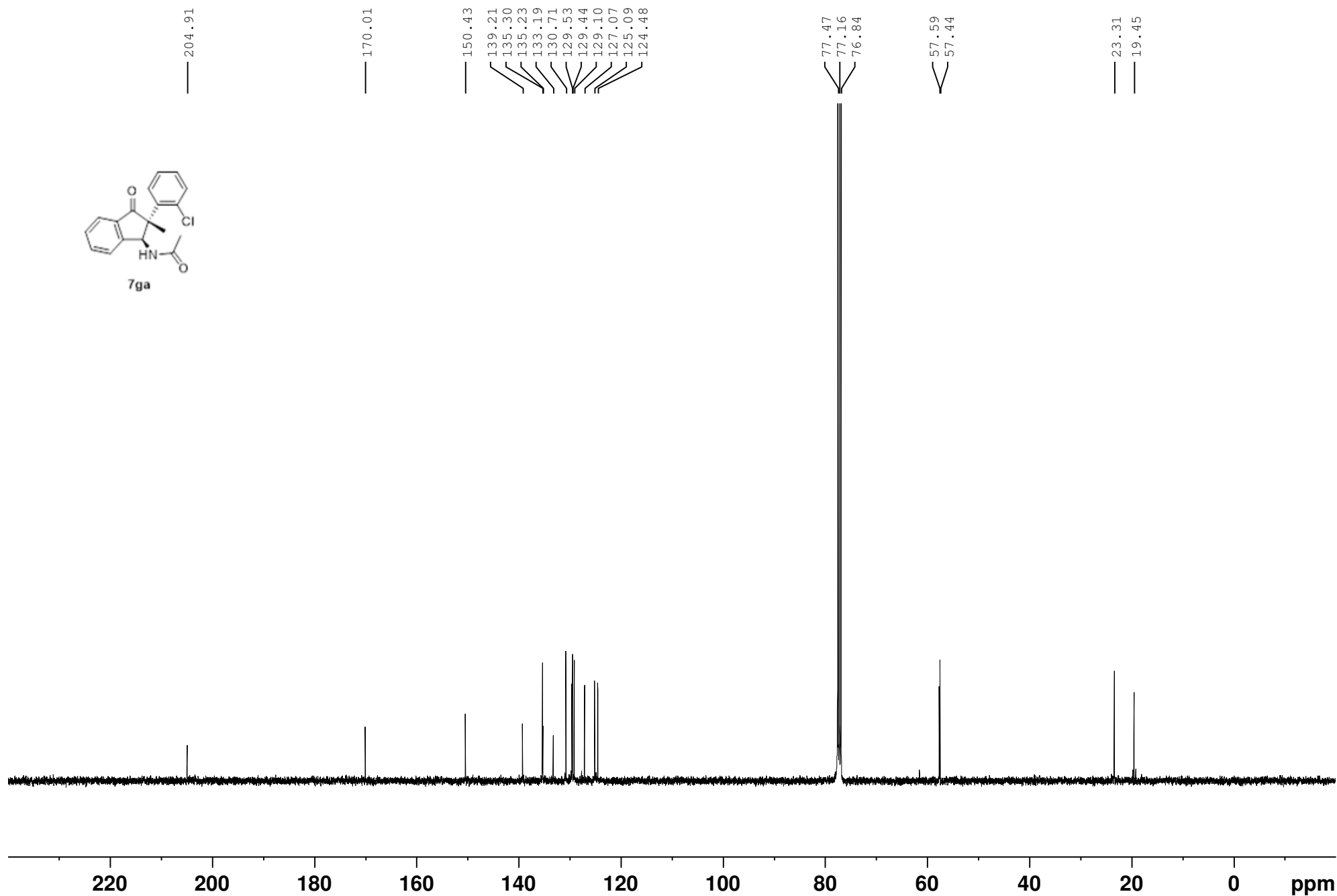
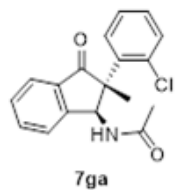


— 2.042

— 1.426

0.071
-0.000

¹³C NMR (100 MHz, CDCl₃)

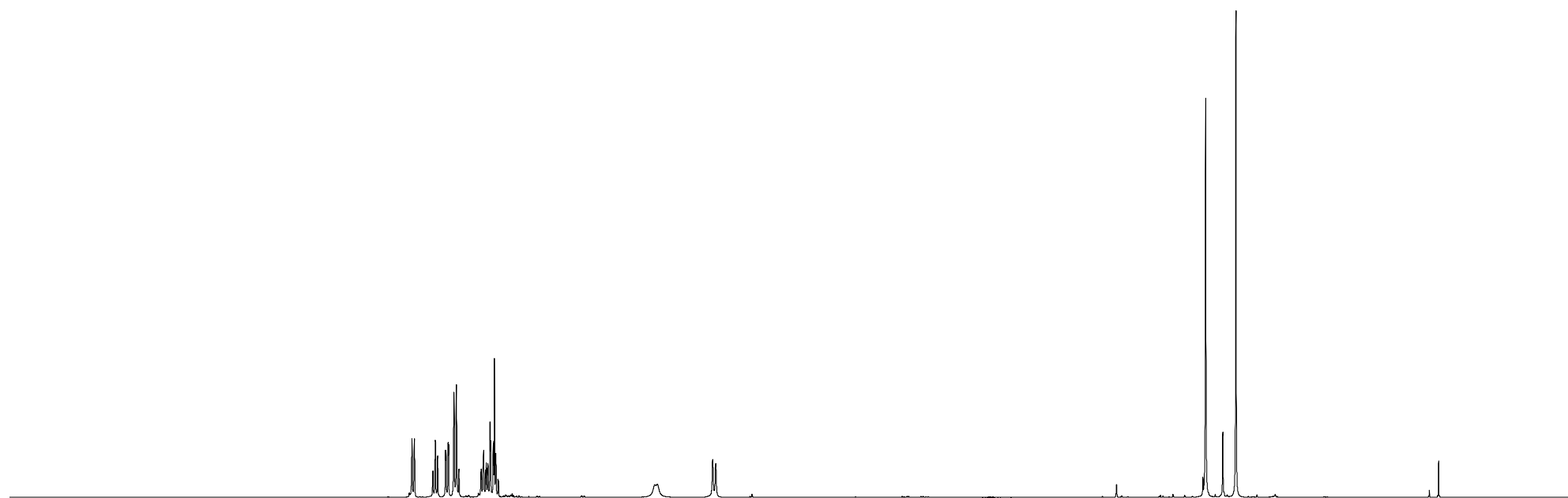
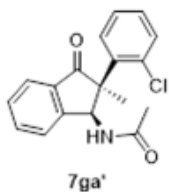


¹H NMR (400 MHz, CDCl₃)

7.901
7.882
7.741
7.739
7.720
7.704
7.701
7.643
7.639
7.623
7.619
7.578
7.558
7.539
7.371
7.367
7.353
7.349
7.334
7.329
7.320
7.316
7.300
7.296
7.276
7.272
7.266
7.258
7.256
7.254
7.238
7.234
6.032
6.013
5.586
5.563

— 1.793
— 1.560

< 0.071
< -0.000

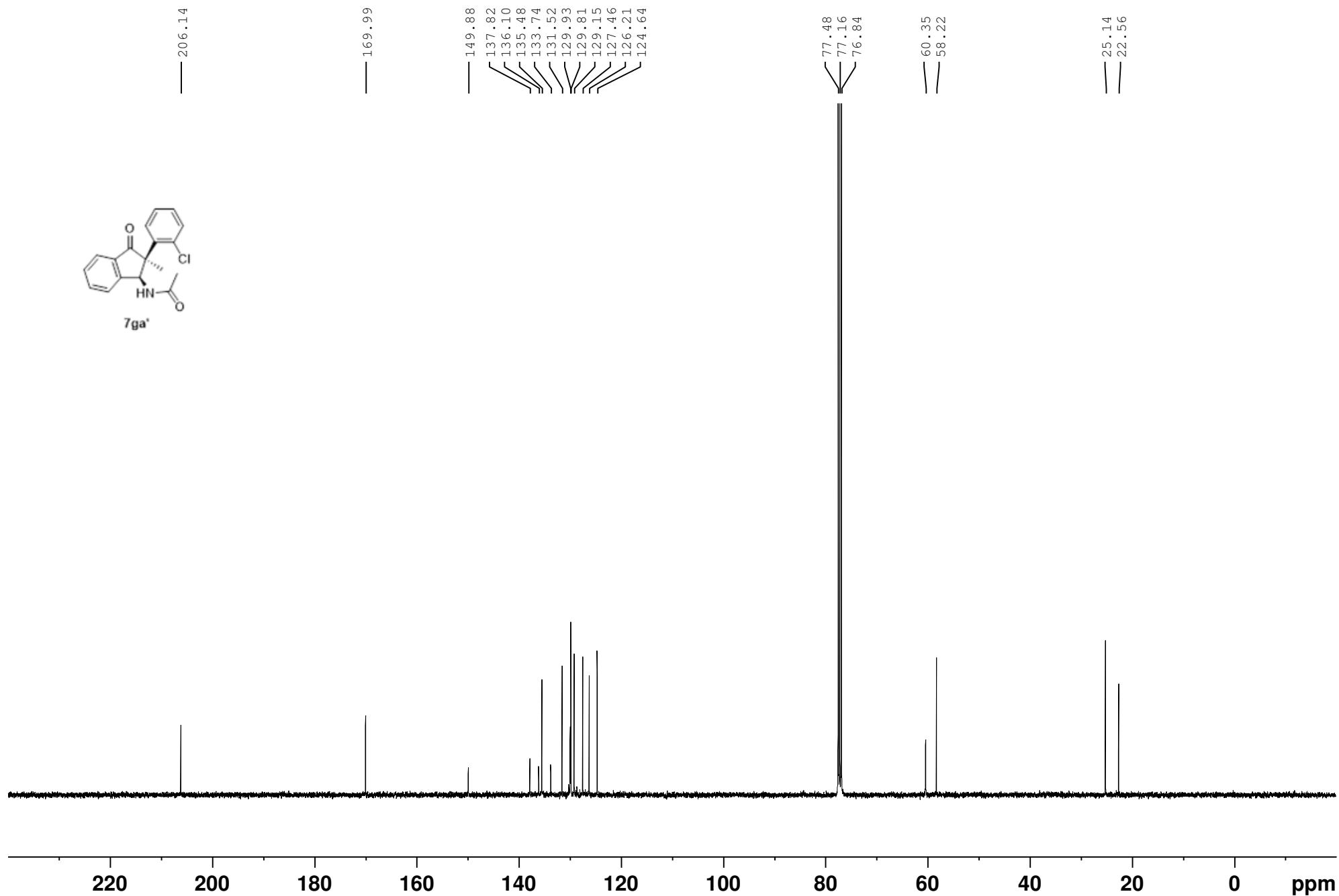
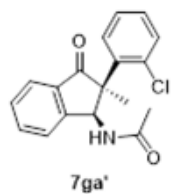


1.07
1.06
1.05
2.05
3.64

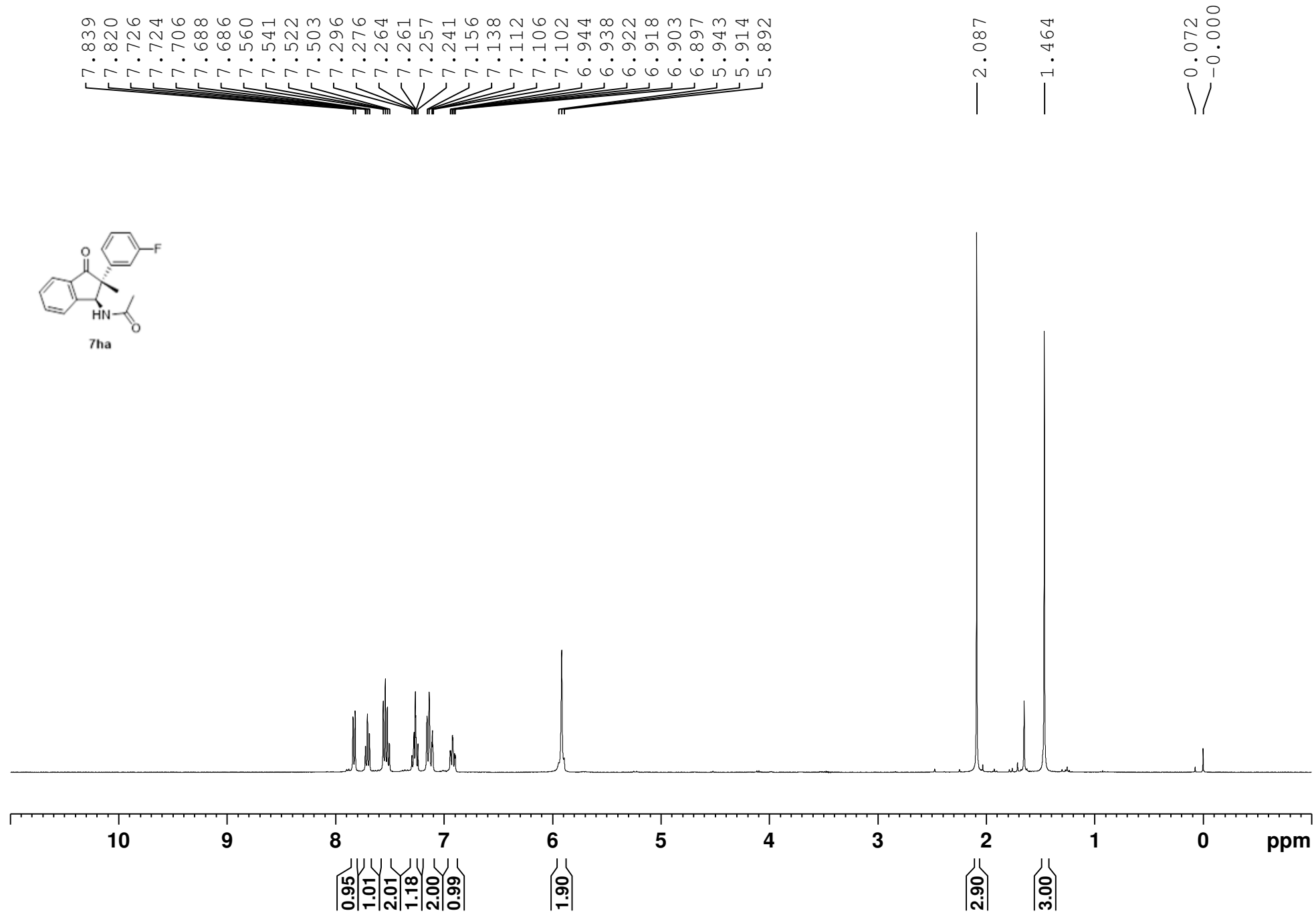
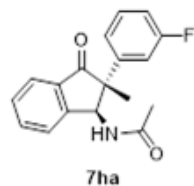
0.90
1.03

2.97
3.00

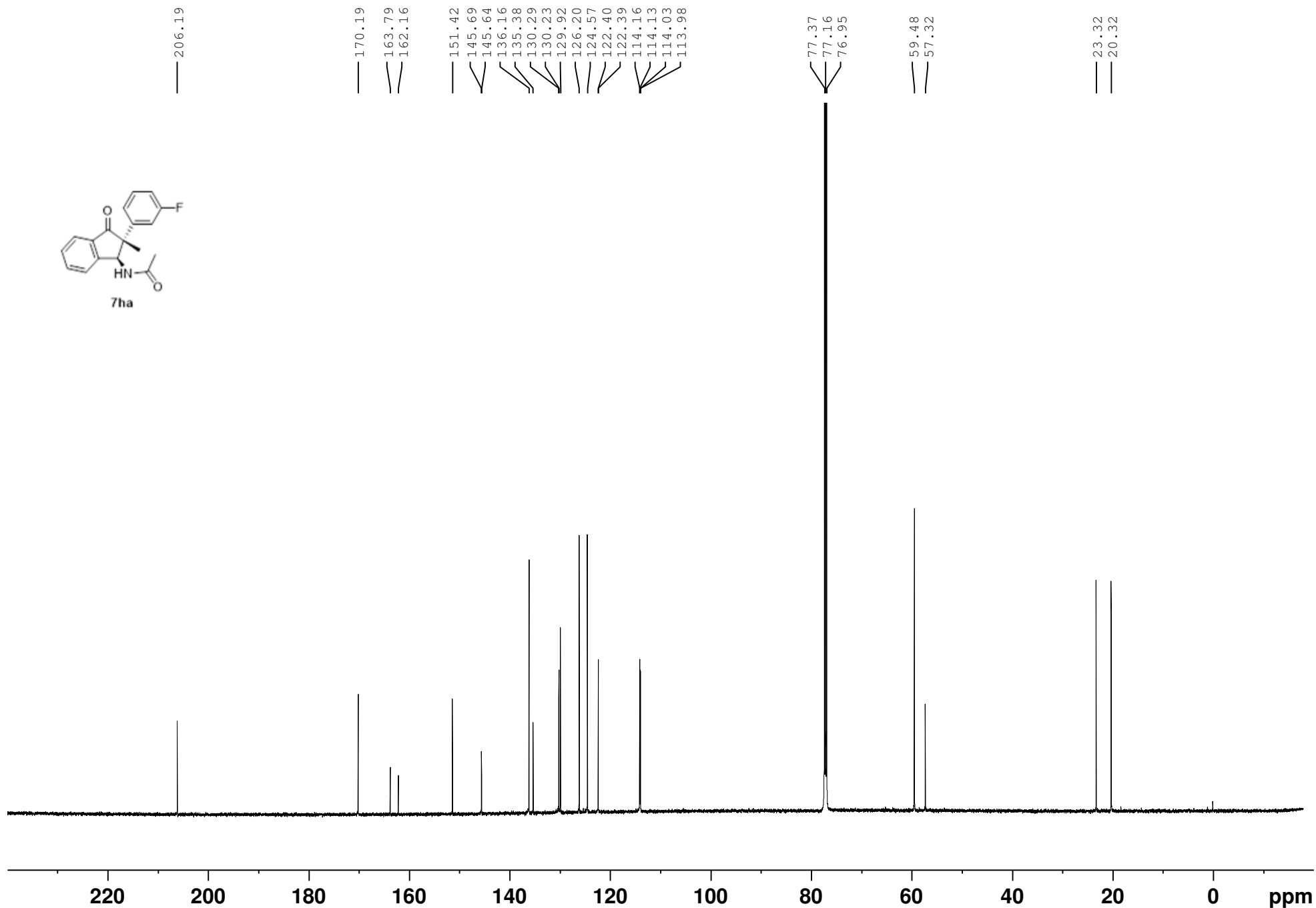
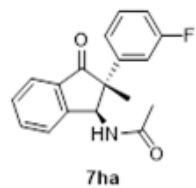
¹³C NMR (100 MHz, CDCl₃)



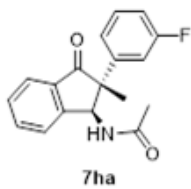
¹H NMR (400 MHz, CDCl₃)



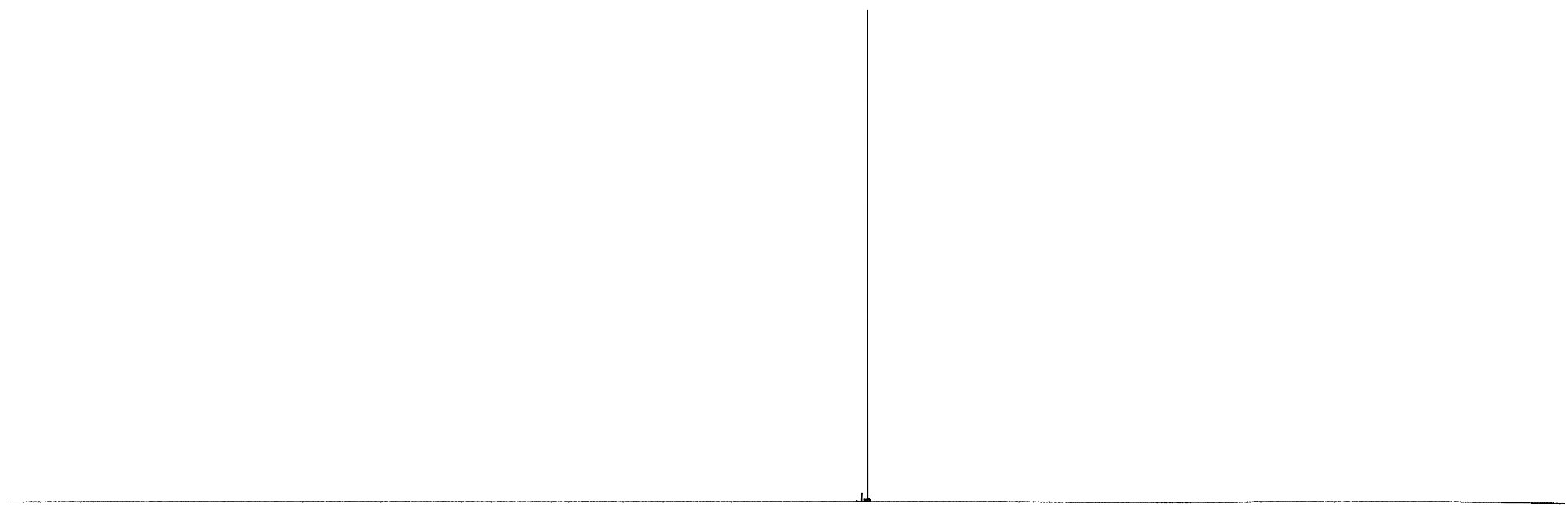
¹³C NMR (150 MHz, CDCl₃)



¹⁹F NMR (376 MHz, CDCl₃)

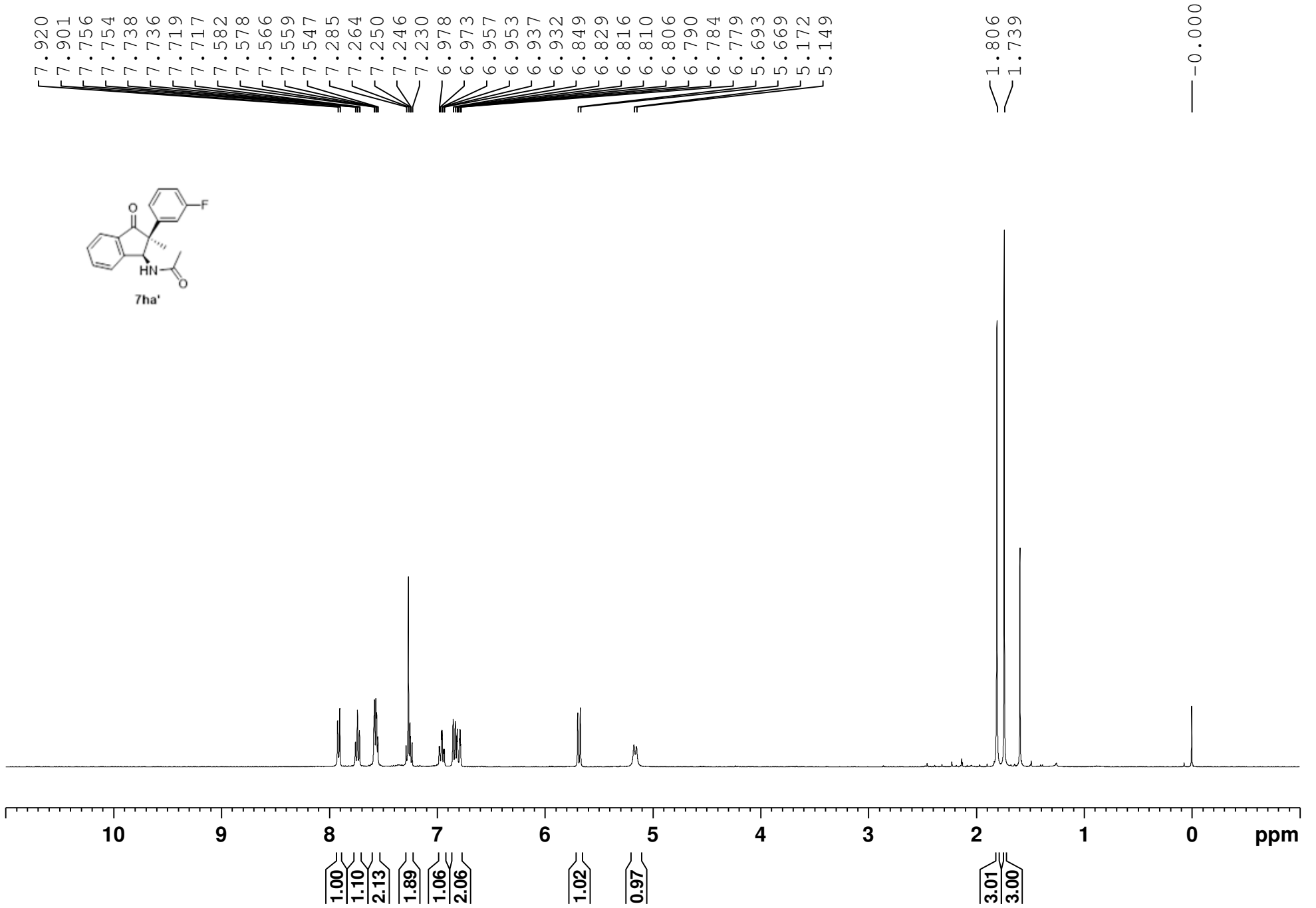


— -112.222

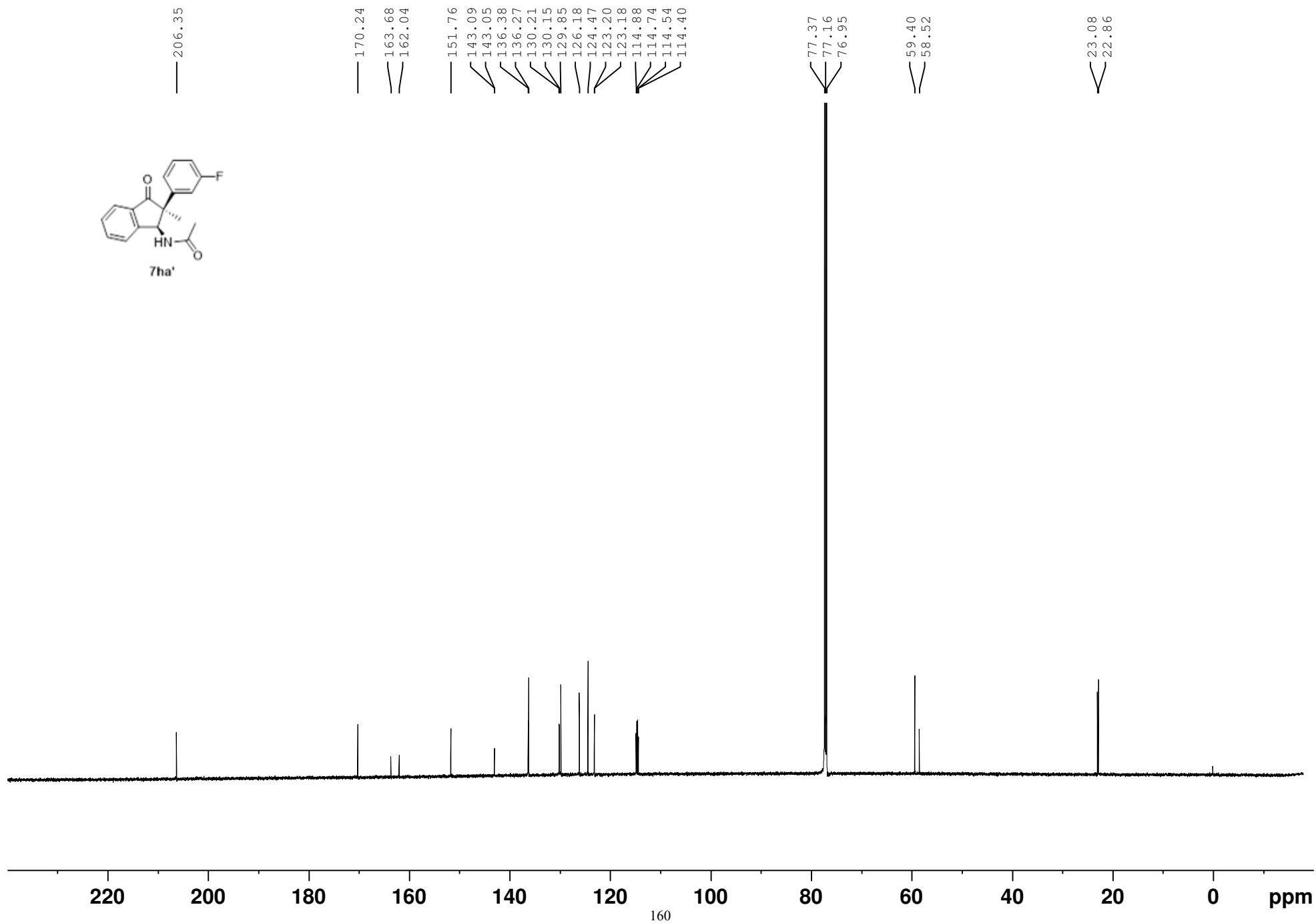
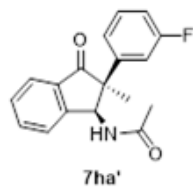


0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

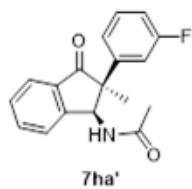
¹H NMR (400 MHz, CDCl₃)



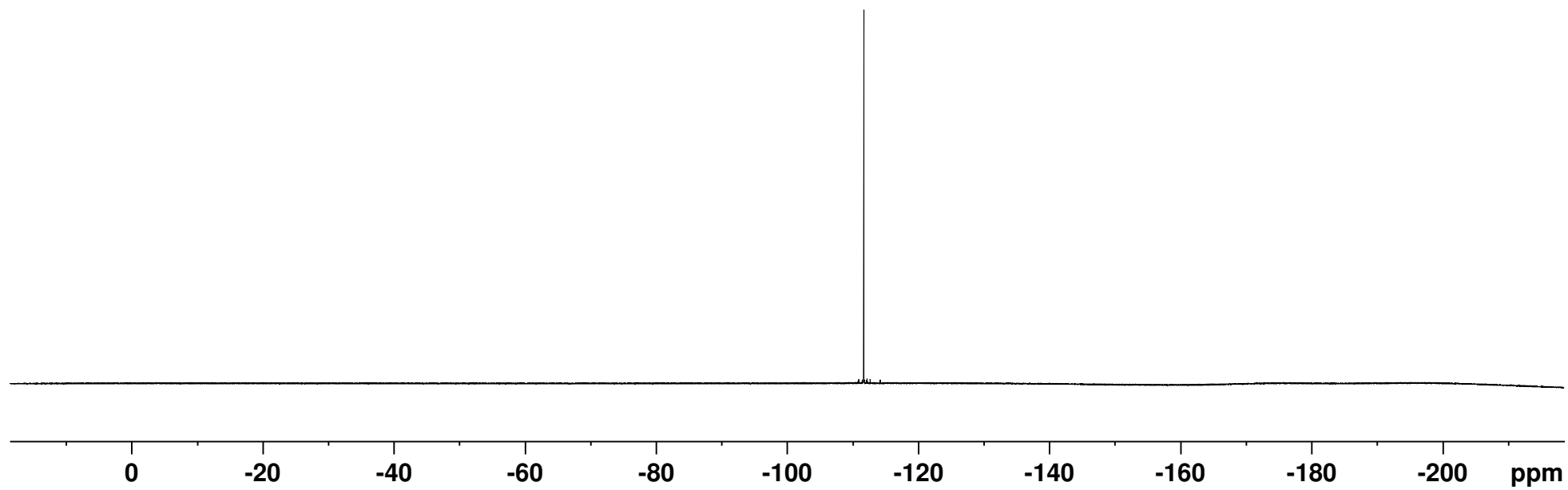
¹³C NMR (150 MHz, CDCl₃)



^{19}F NMR (376 MHz, CDCl_3)



— -111.740



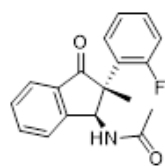
¹H NMR (400 MHz, CDCl₃)

7.887
7.884
7.866
7.737
7.735
7.718
7.716
7.700
7.698
7.555
7.536
7.518
7.373
7.369
7.353
7.350
7.334
7.330
7.306
7.287
7.283
7.267
7.250
7.184
7.181
7.165
7.162
7.146
7.143
7.030
7.027
7.009
7.007
7.001
6.998
6.981
6.978
5.904
5.881
5.800
5.777

— 2.076

— 1.440

0.070
-0.000



7ia



10 9 8 7 6 5 4 3 2 1 0 ppm

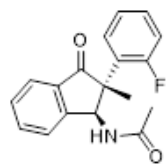
0.96
1.00
1.98
1.08
0.78
0.23
0.98
0.96

1.02
0.93

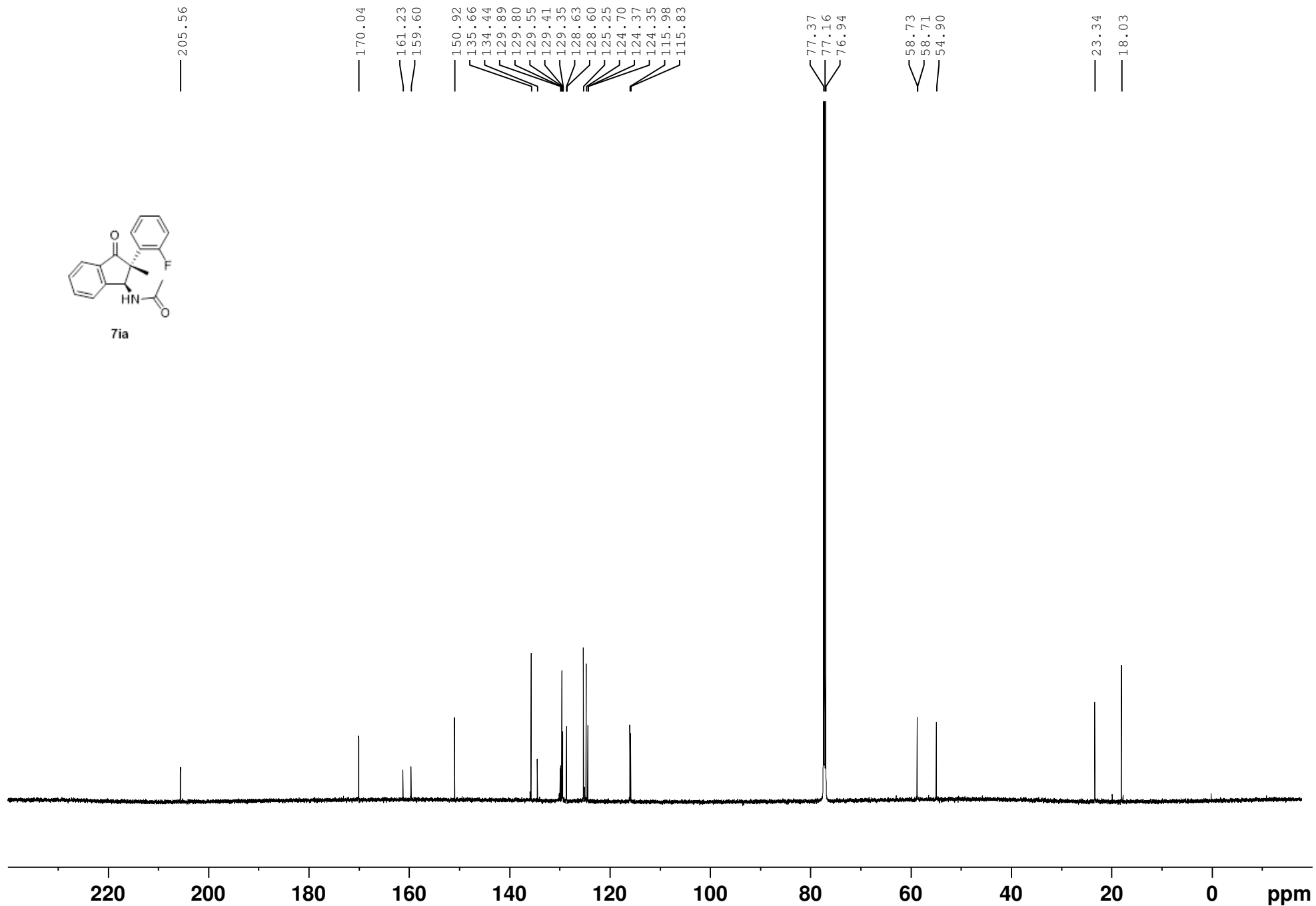
2.98

3.00

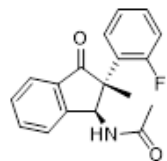
¹³C NMR (150 MHz, CDCl₃)



7ia

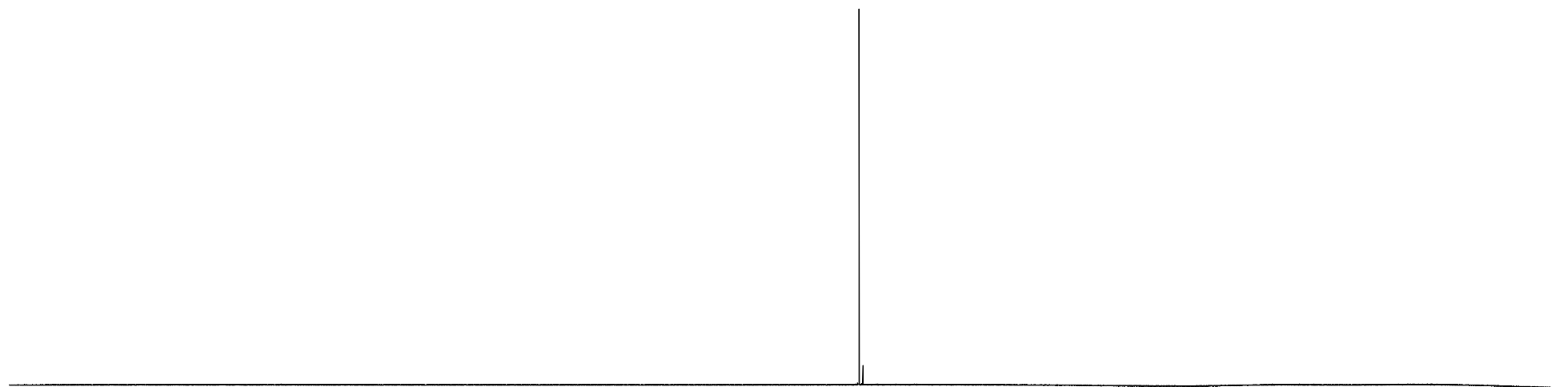


^{19}F NMR (376 MHz, CDCl_3)



7ia

— -110.894



0

-20

-40

-60

-80

-100

-120

-140

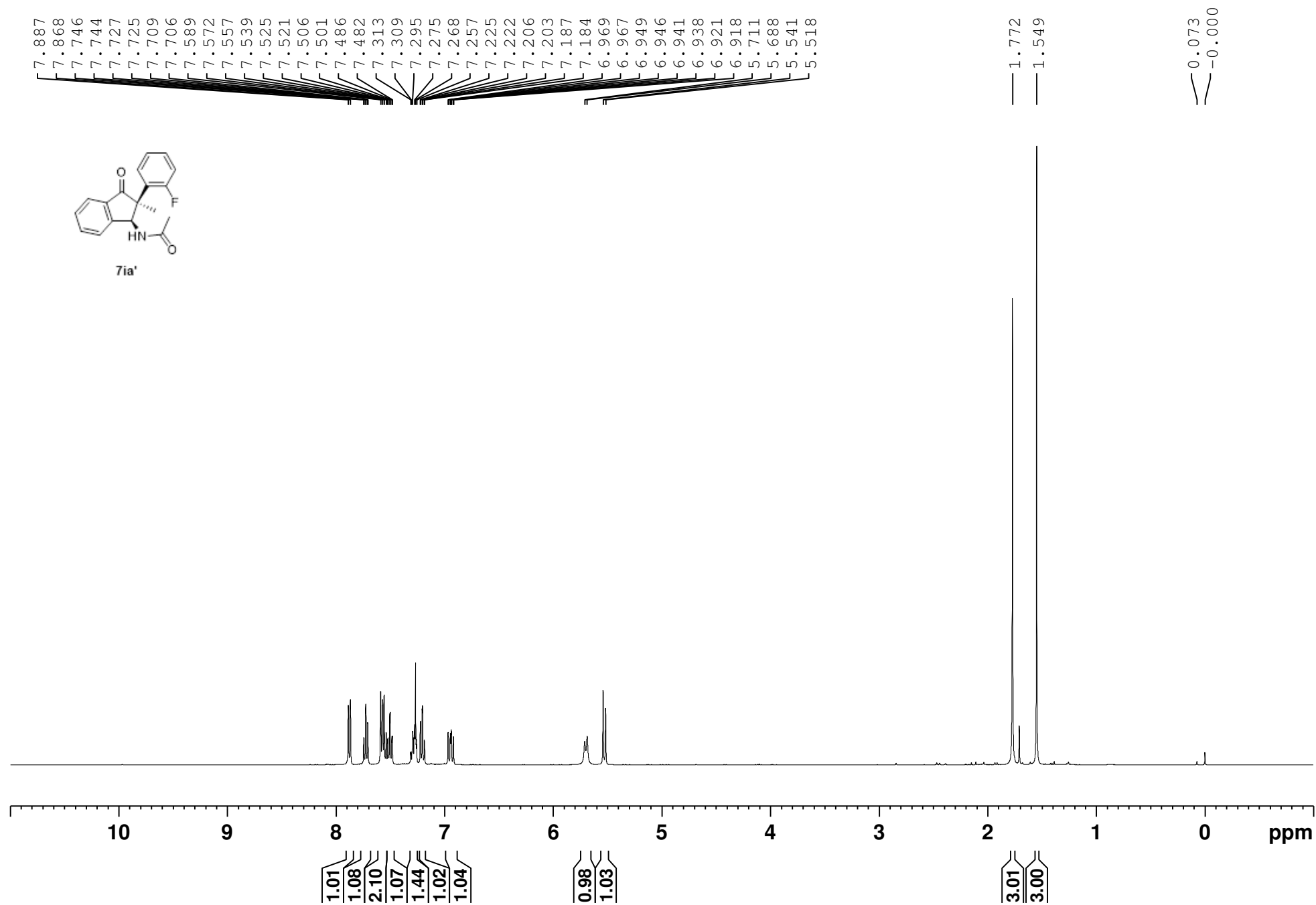
-160

-180

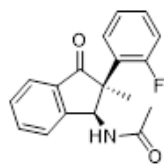
-200

ppm

¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)



7ia'

206.62
206.60

169.97

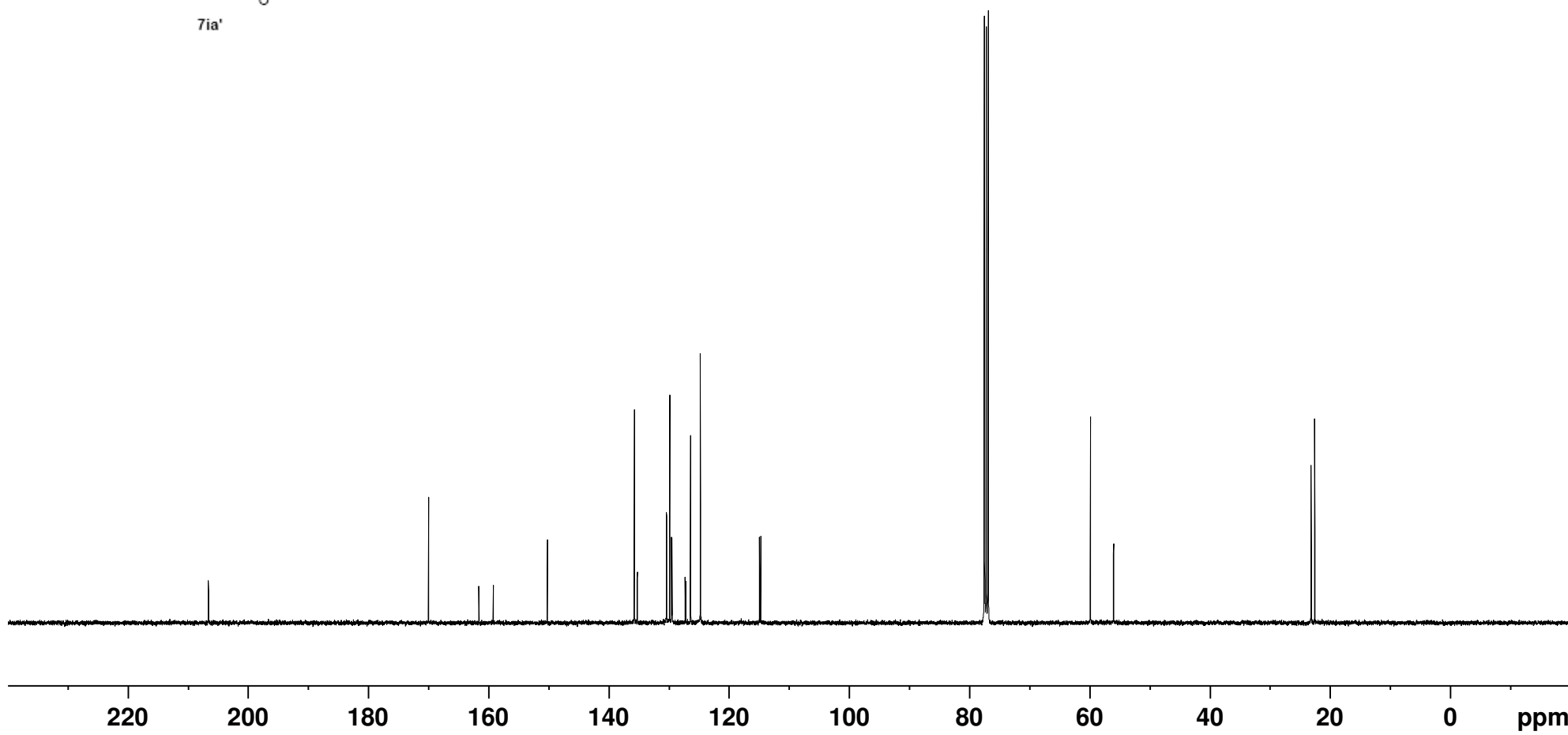
161.62
159.21

150.19
135.71
135.25
135.23
130.36
130.31
129.83
129.54
129.46
127.29
127.14
126.36
124.74
124.72
114.92
114.70

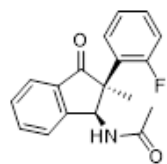
77.48
77.16
76.84

59.84
55.98
55.96

23.09
22.49

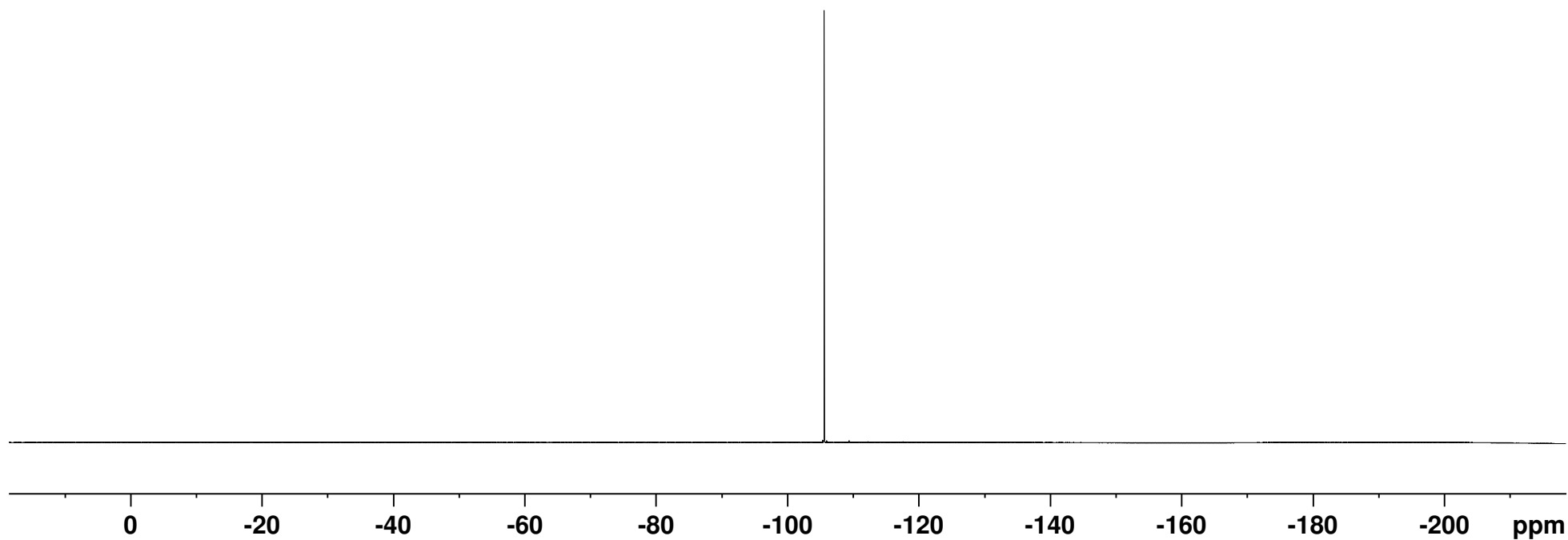


^{19}F NMR (376 MHz, CDCl_3)



7ia'

— -105.586



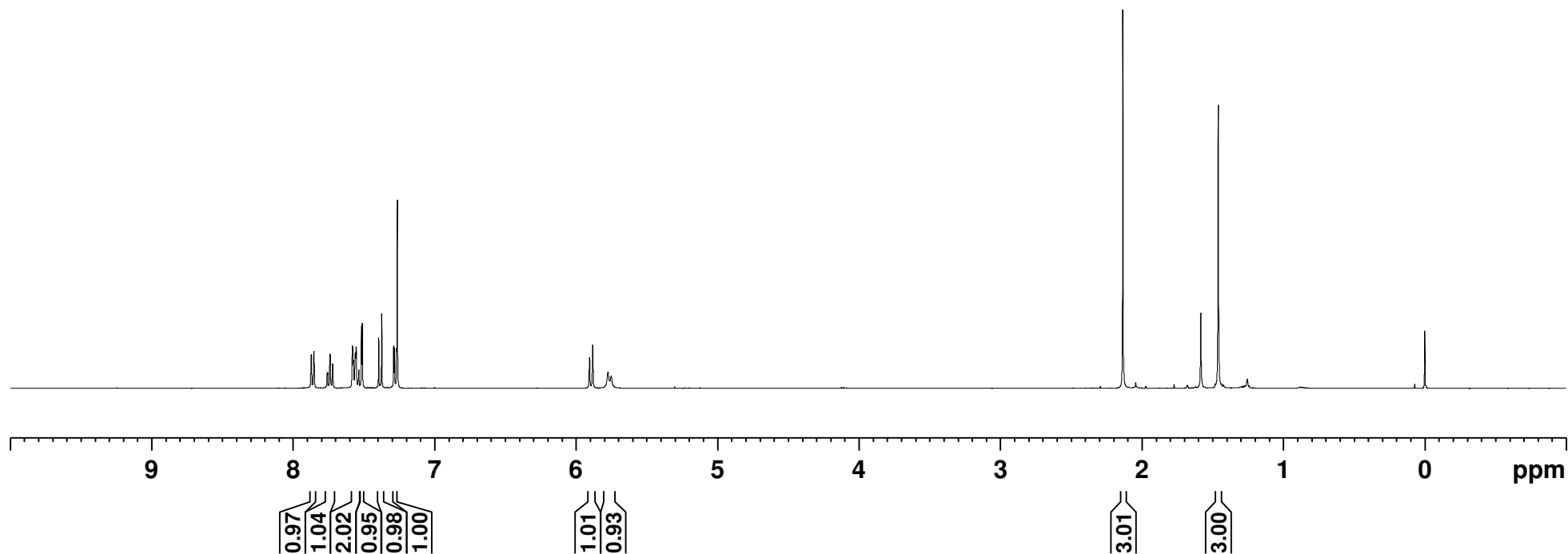
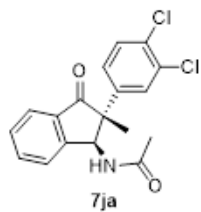
¹H NMR (400 MHz, CDCl₃)

7.872
7.853
7.760
7.757
7.739
7.722
7.719
7.580
7.574
7.562
7.561
7.555
7.536
7.517
7.511
7.395
7.374
7.290
7.284
7.268
7.264
5.905
5.882
5.775
5.752

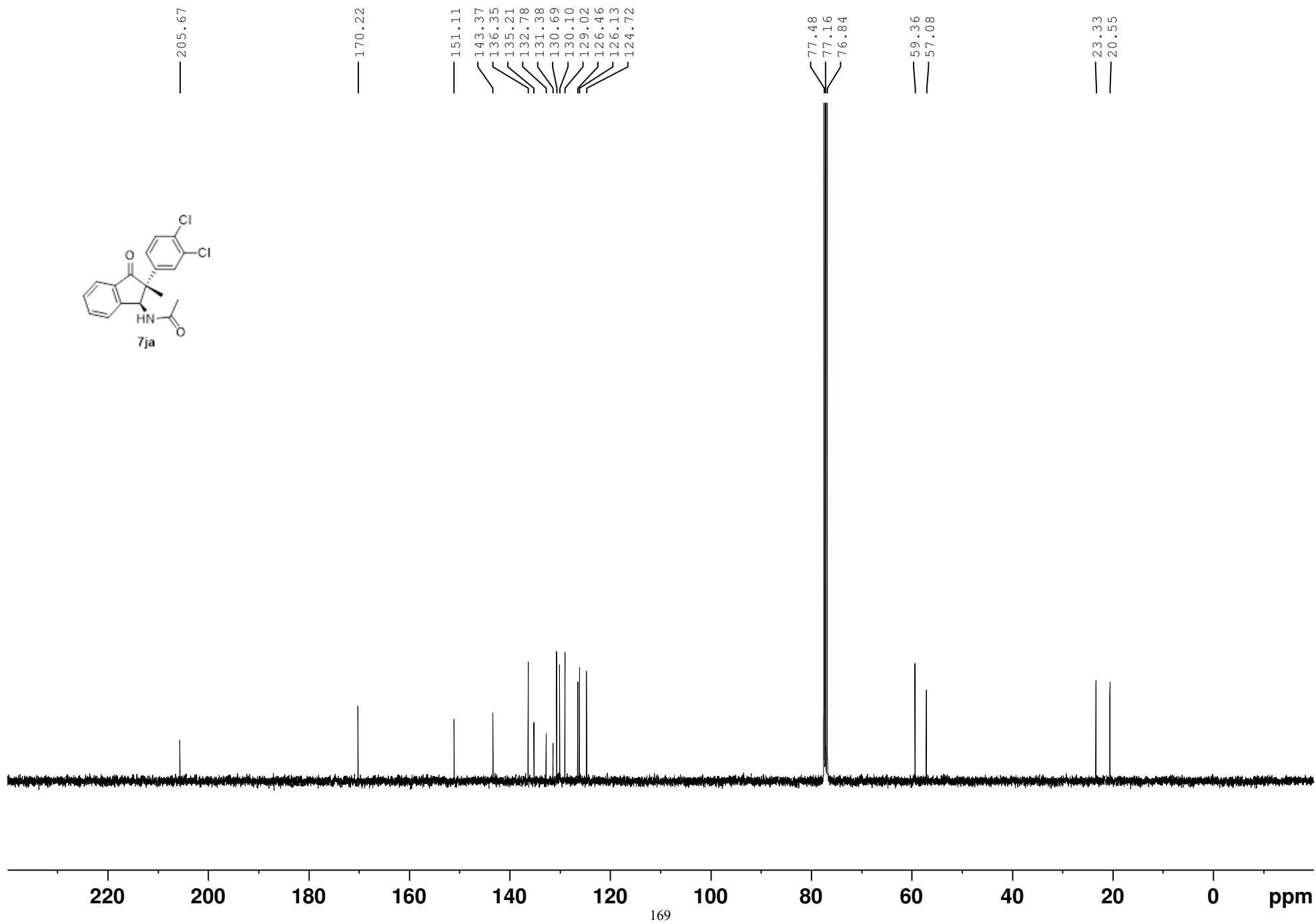
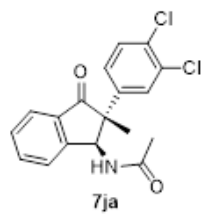
— 2.134

— 1.460

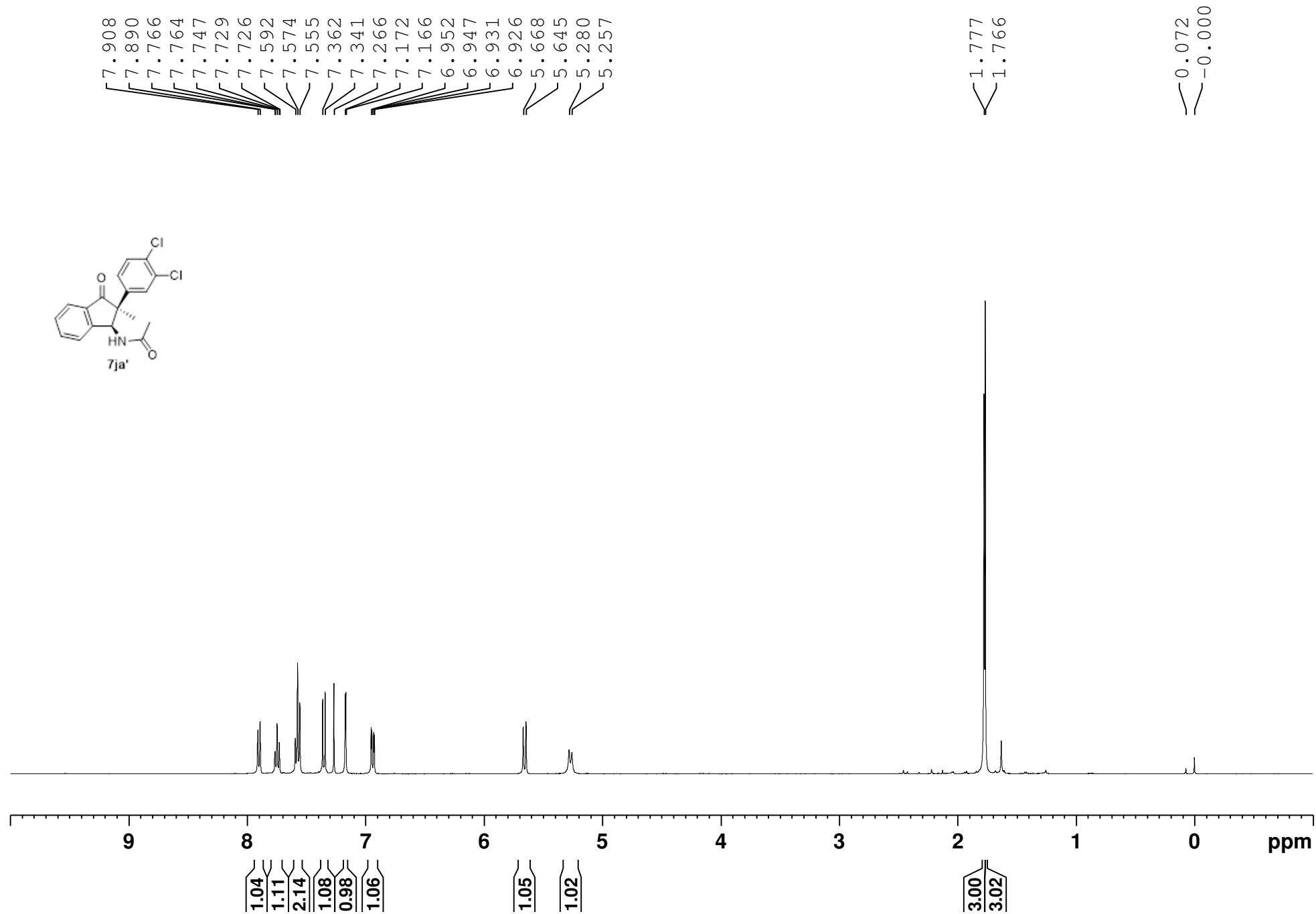
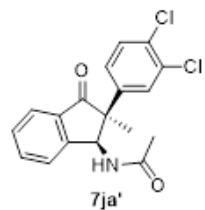
< 0.070
< -0.000



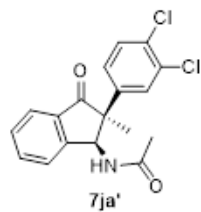
¹³C NMR (100 MHz, CDCl₃)



^1H NMR (400 MHz, CDCl_3)



¹³C NMR (100 MHz, CDCl₃)



206.07

170.18

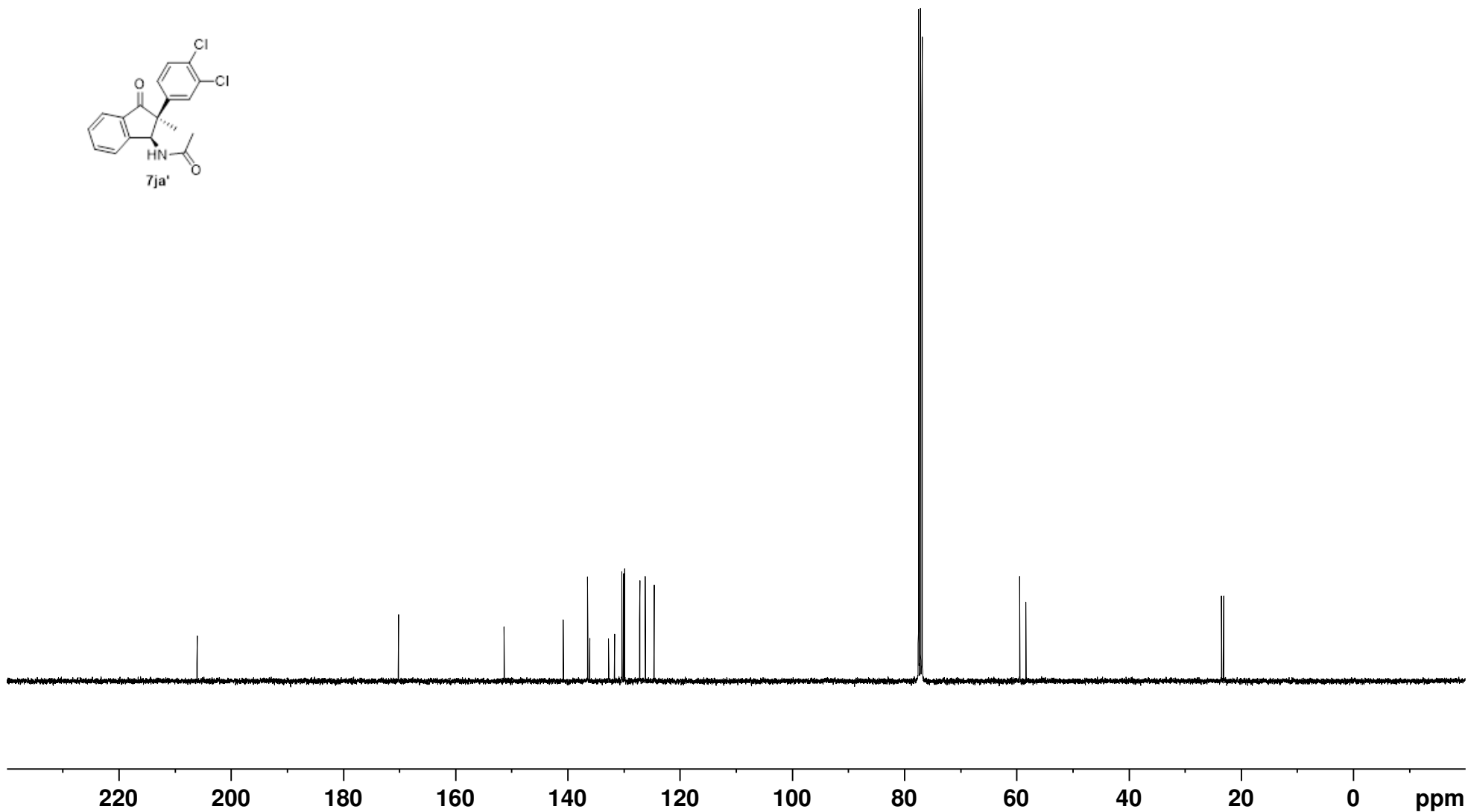
151.33

140.80
136.45
136.09
132.71
131.63
130.35
130.03
129.86
127.17
126.20
124.58

77.47
77.16
76.84

59.45
58.34

23.46
23.06

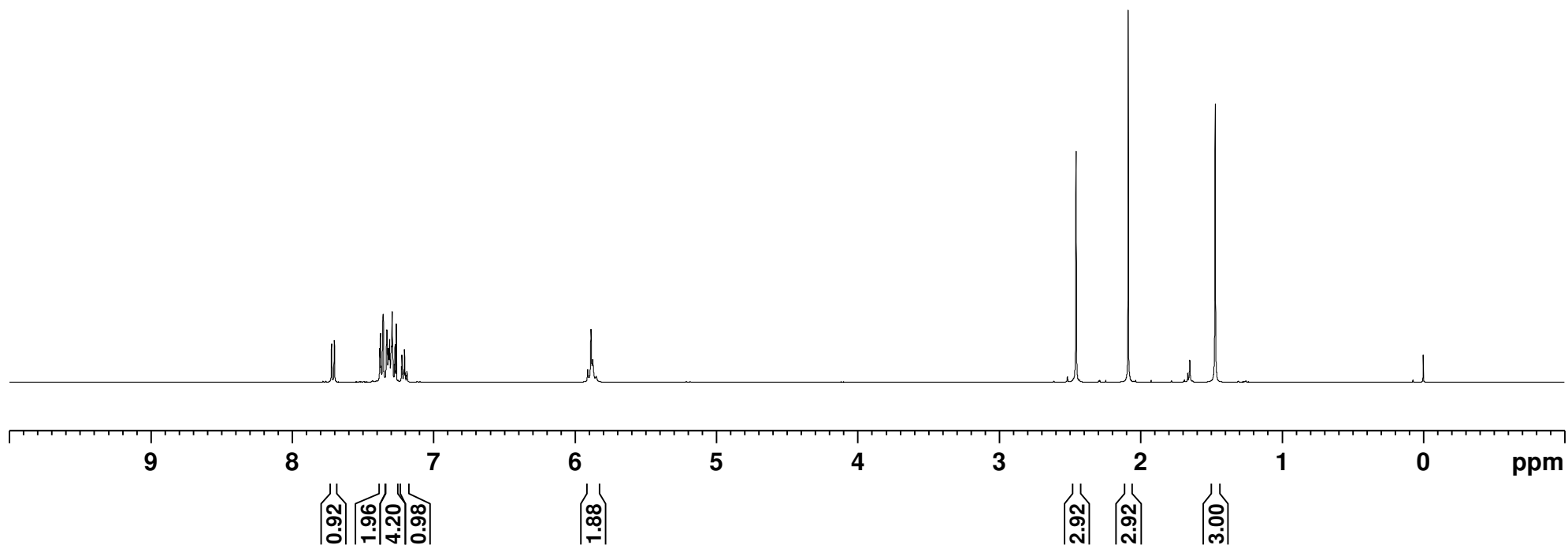
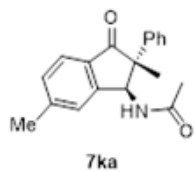


¹H NMR (400 MHz, CDCl₃)

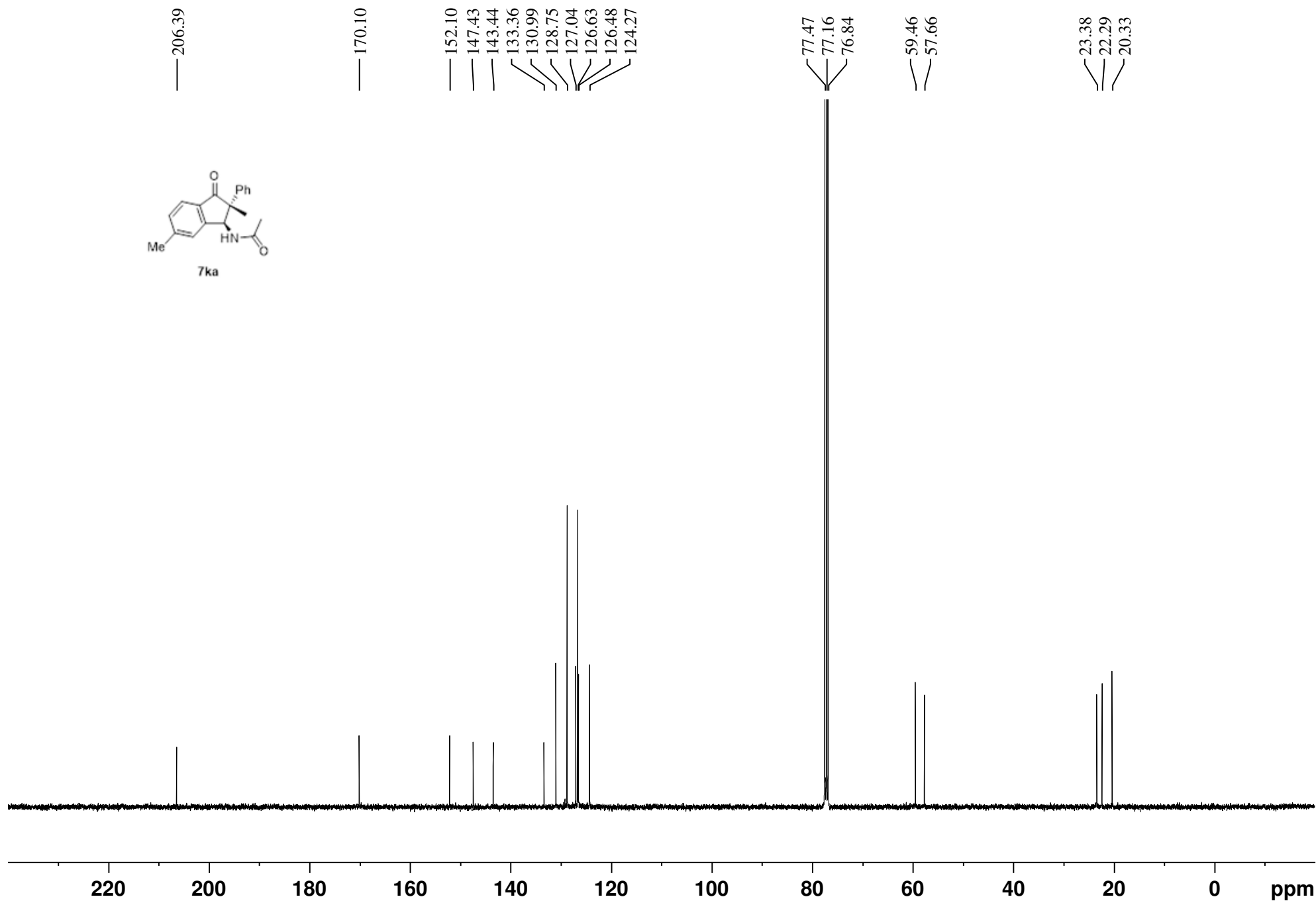
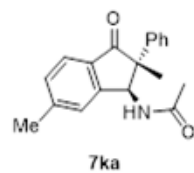
7.720
7.701
7.378
7.375
7.370
7.357
7.355
7.349
7.329
7.319
7.309
7.291
7.271
7.262
7.226
7.223
7.220
7.210
7.205
7.199
7.190
7.187
7.184
5.909
5.886
5.873
5.849

— 2.455
— 2.086
— 1.471

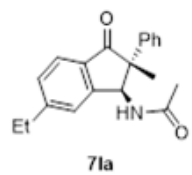
0.072
-0.000



¹³C NMR (100 MHz, CDCl₃)



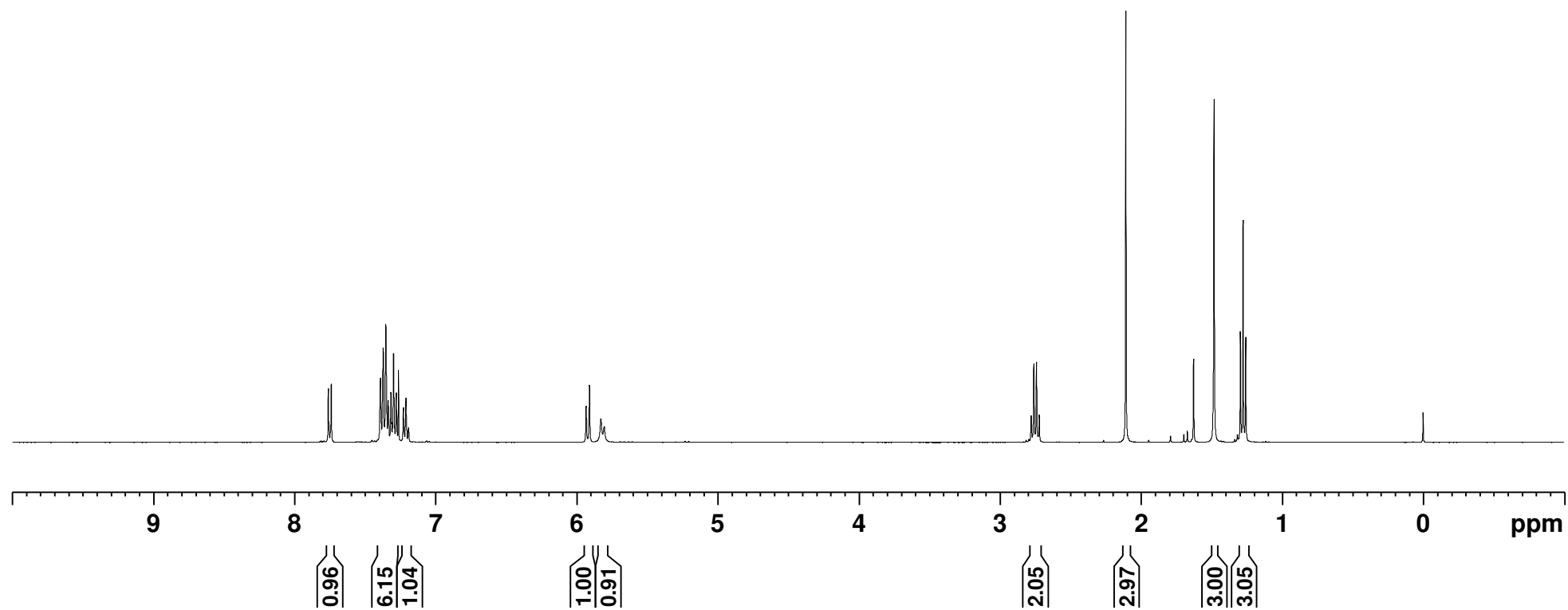
¹H NMR (400 MHz, CDCl₃)



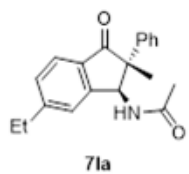
7.759
7.738
7.393
7.390
7.371
7.352
7.335
7.315
7.310
7.297
7.277
7.262
7.227
7.209
7.191
5.932
5.908
5.827
5.804

2.778
2.759
2.740
2.721
2.106
1.481
1.295
1.276
1.257

— -0.000



¹³C NMR (100 MHz, CDCl₃)



— 206.57

— 170.22

— 153.58

— 152.19

— 143.50

— 133.51

— 129.83

— 128.68

— 126.97

— 126.58

— 125.26

— 124.26

— 77.48

— 77.16

— 76.84

— 59.49

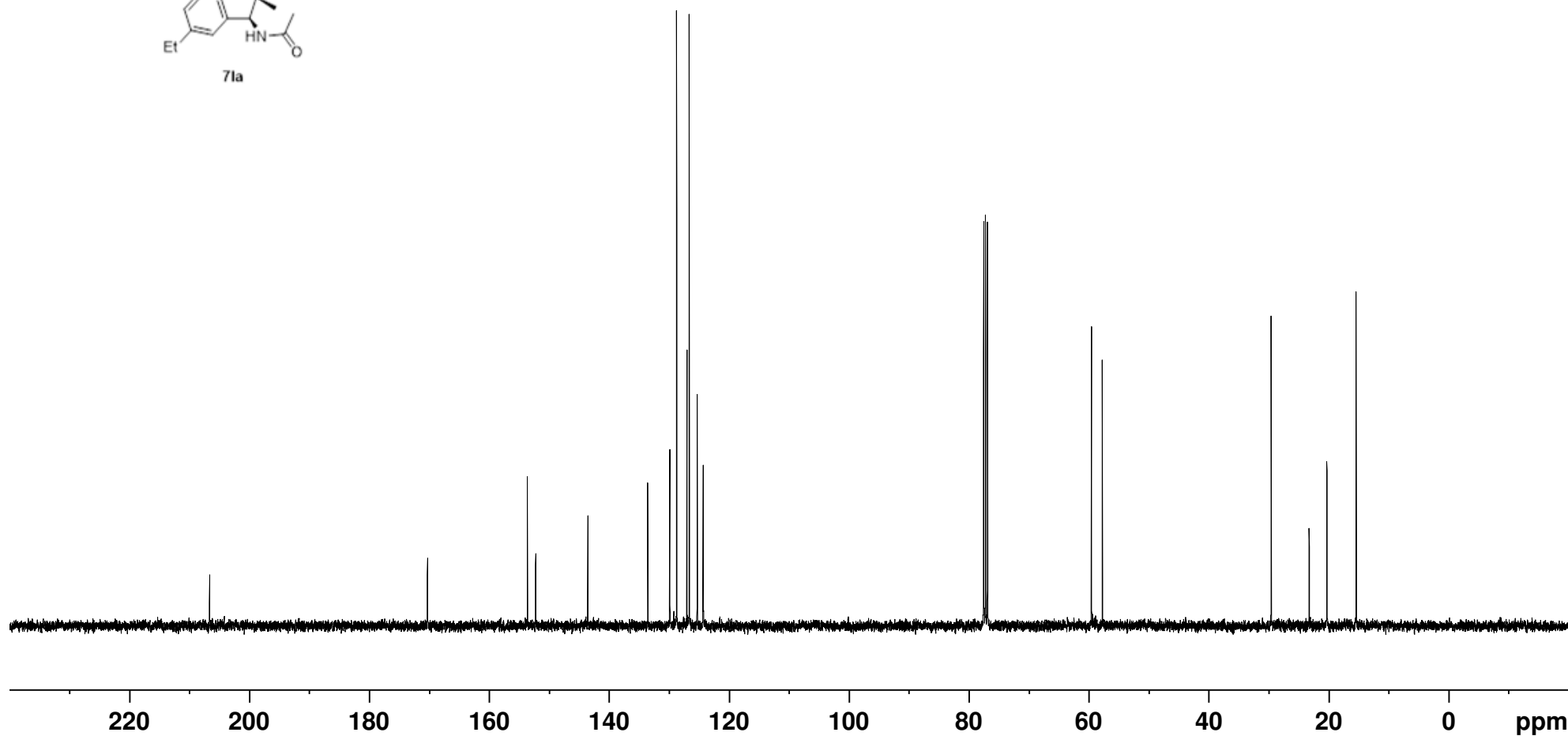
— 57.68

— 29.53

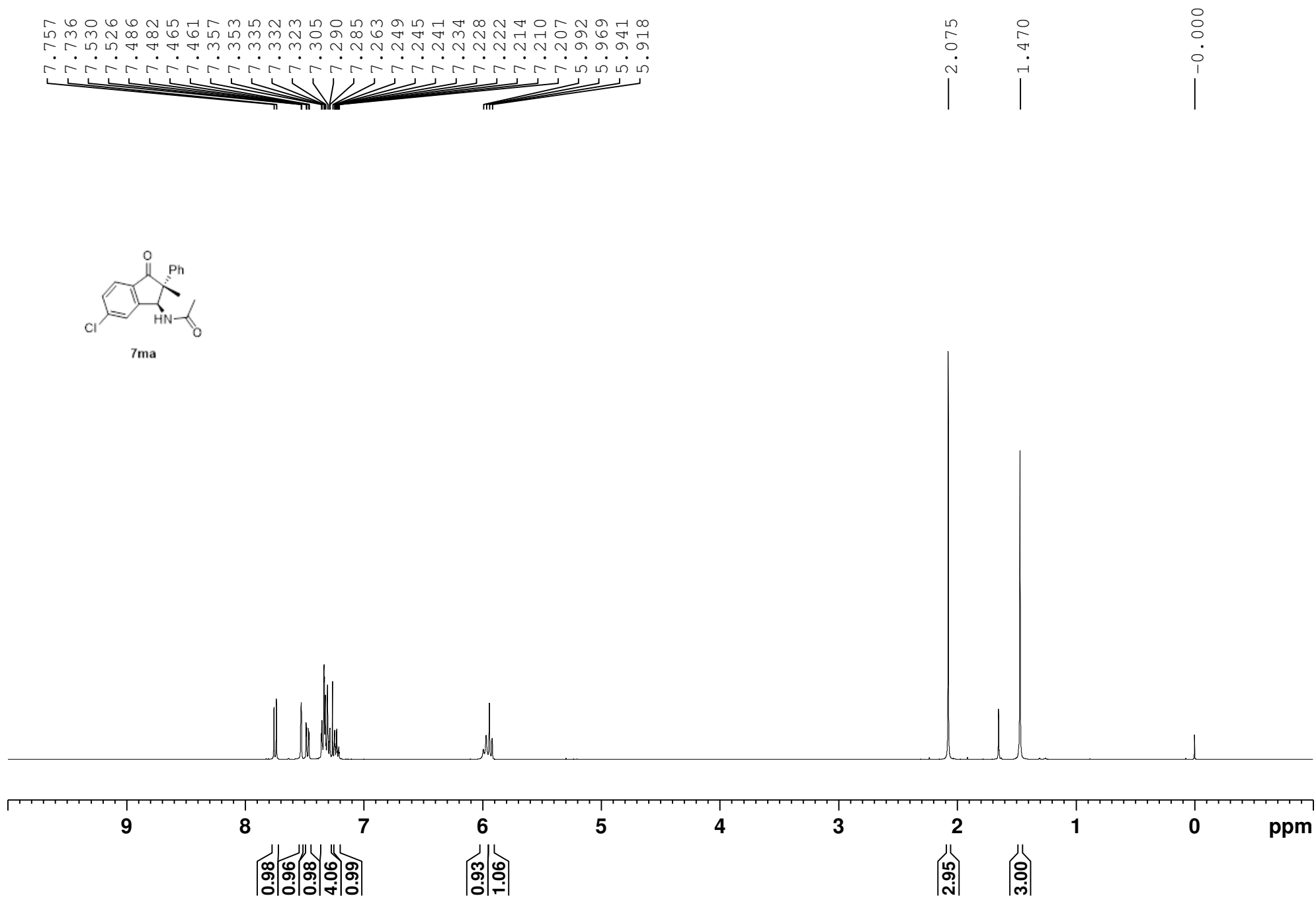
— 23.22

— 20.23

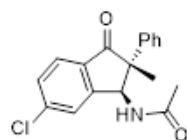
— 15.35



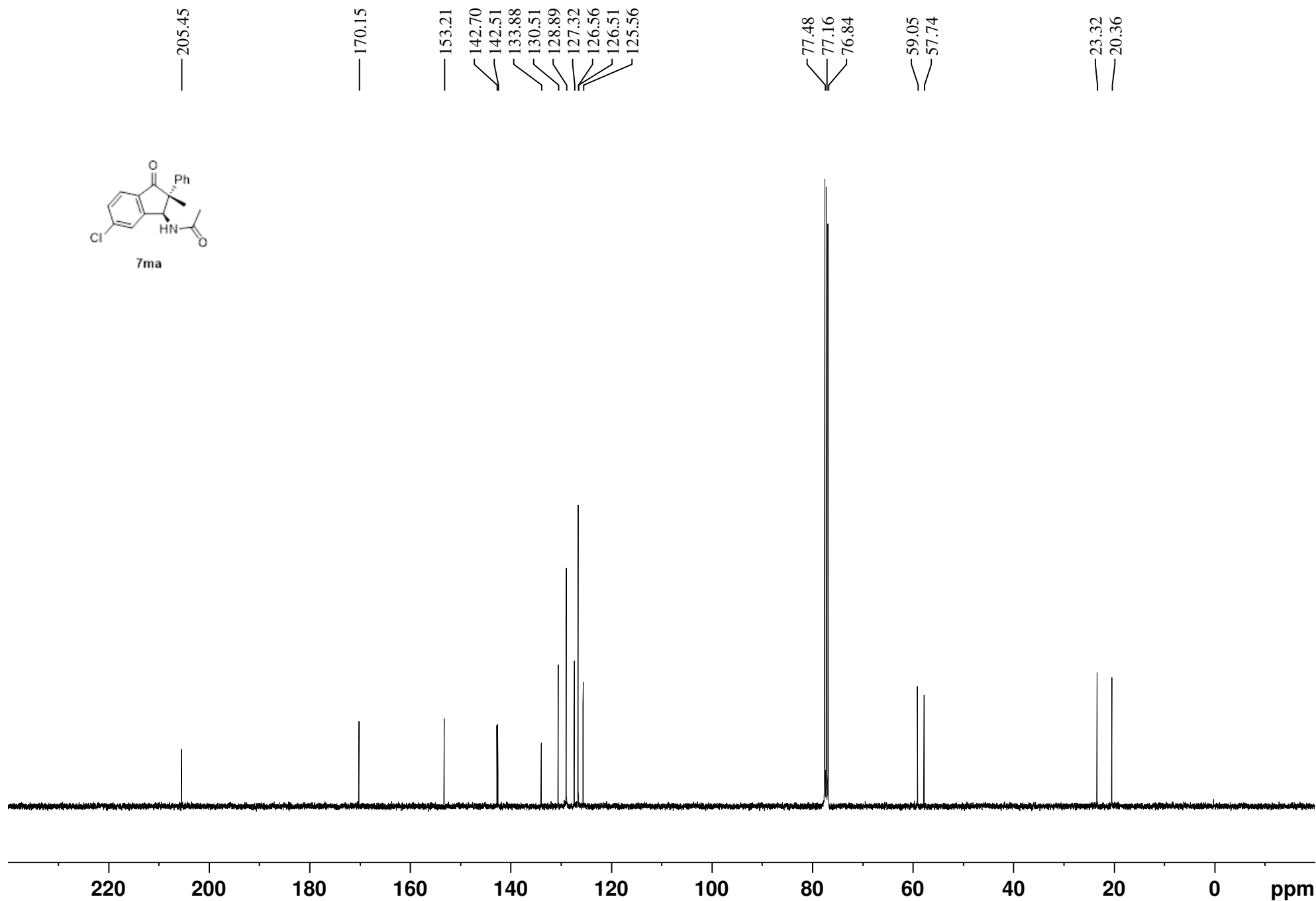
^1H NMR (400 MHz, CDCl_3)



¹³C NMR (100 MHz, CDCl₃)

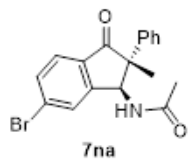


7ma



^1H NMR (400 MHz, CDCl_3)

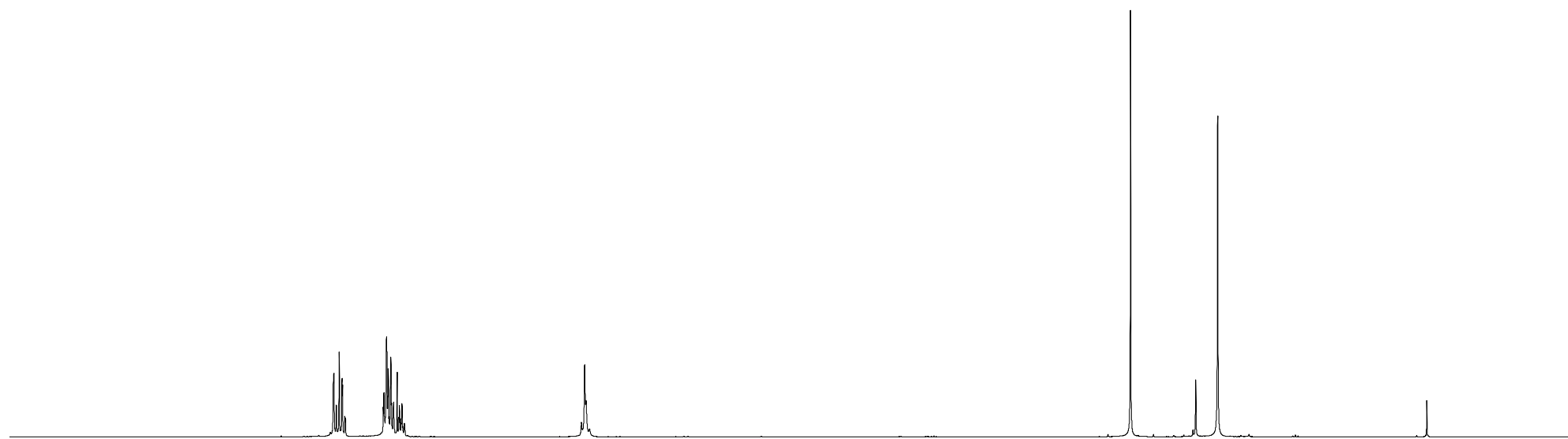
7.711
7.710
7.693
7.672
7.653
7.649
7.632
7.629
7.361
7.357
7.339
7.326
7.308
7.304
7.292
7.288
7.263
7.251
7.247
7.243
7.235
7.230
7.224
7.216
7.212
7.208
5.964
5.941
5.931
5.907



— 2.090

— 1.475

— -0.000



9 8 7 6 5 4 3 2 1 0 ppm

3.00

4.12

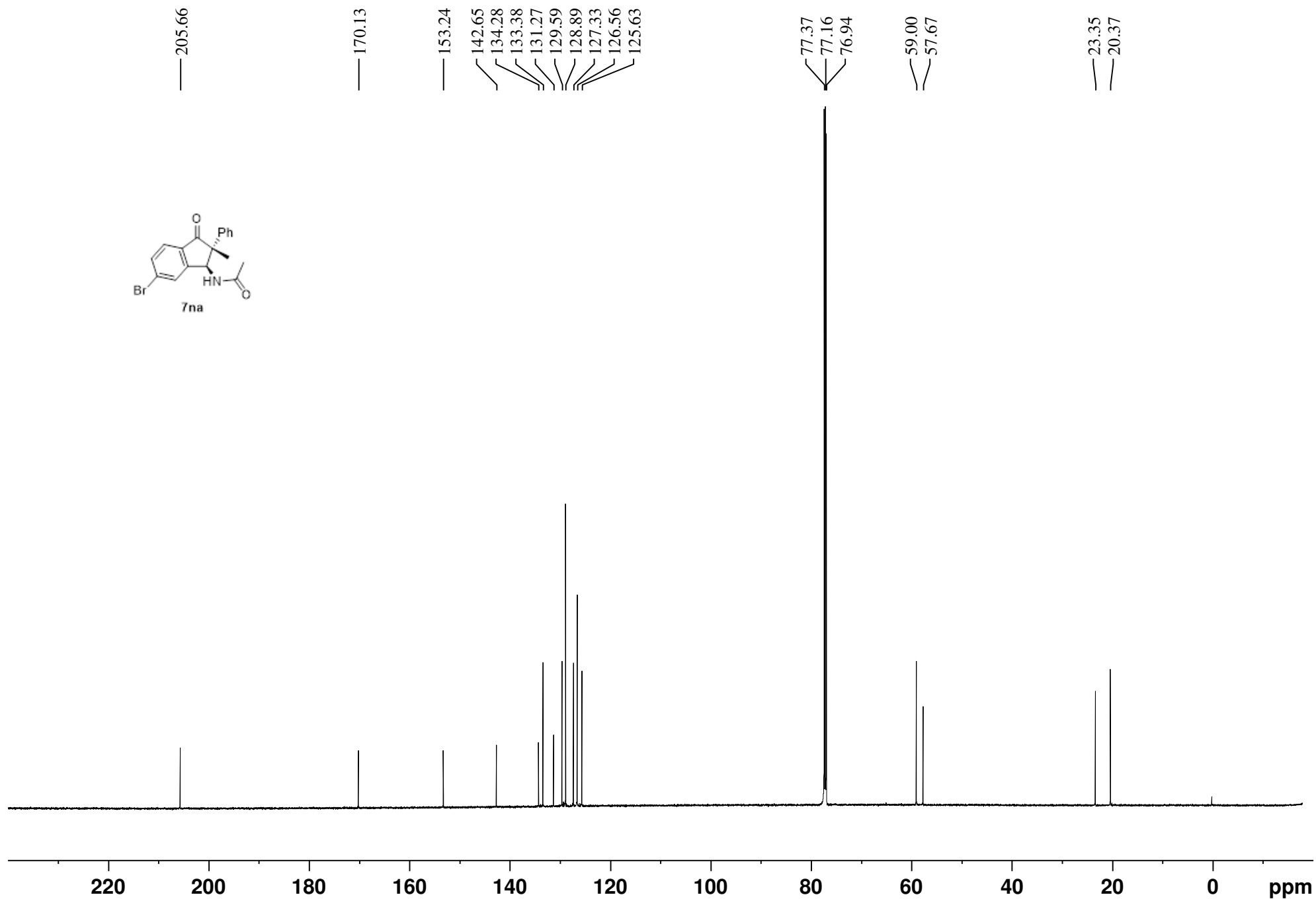
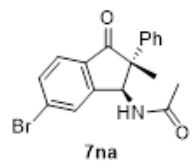
0.98

1.98

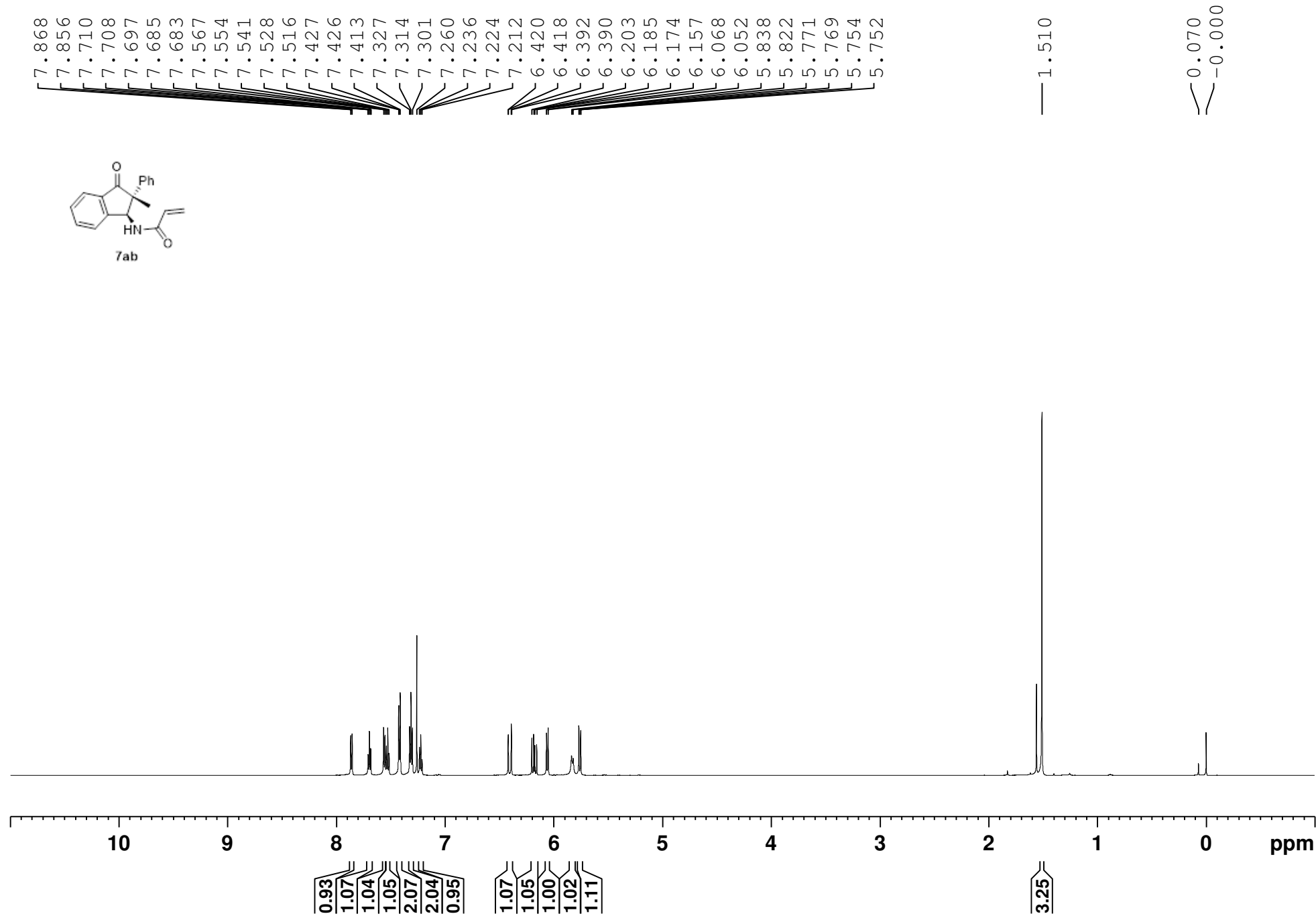
2.95

3.00

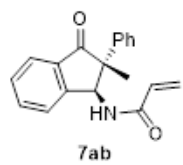
¹³C NMR (150 MHz, CDCl₃)



¹H NMR (600 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)



— 207.08

— 165.74

— 151.46

143.19

135.84

135.42

130.13

129.55

128.69

127.61

127.03

126.51

126.28

124.14

77.47

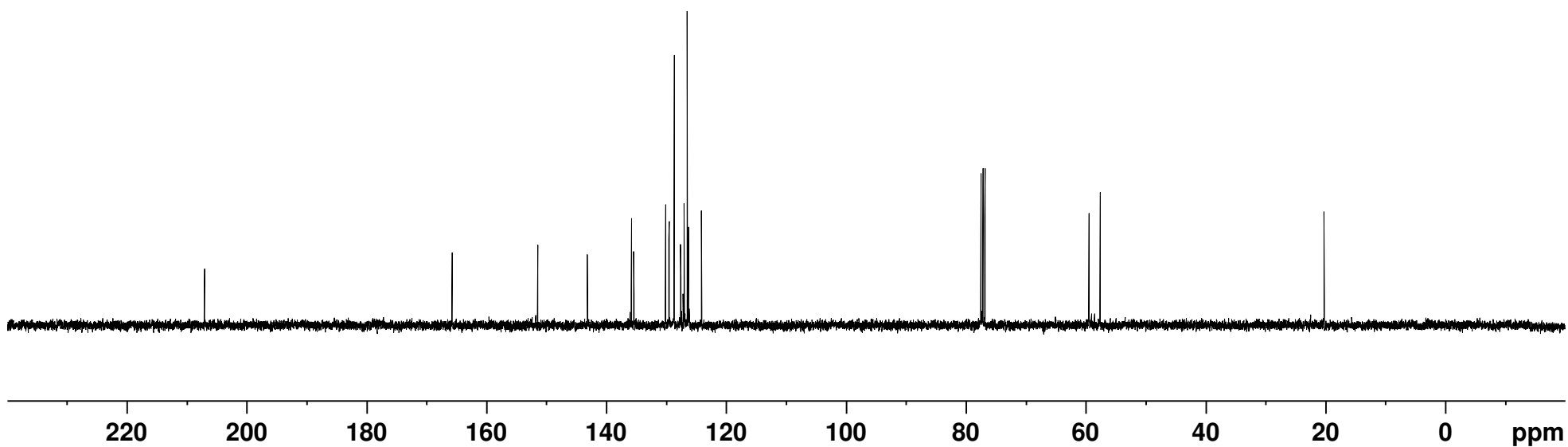
77.16

76.84

59.45

57.61

— 20.22

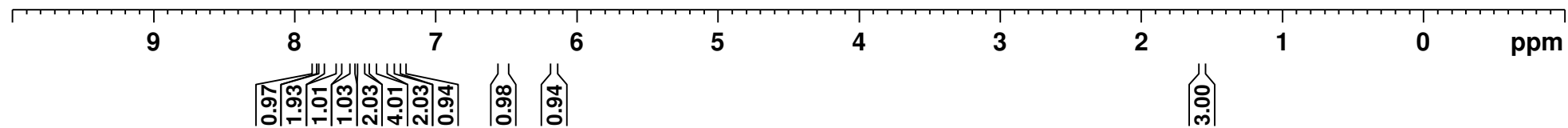
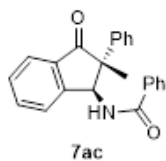


¹H NMR (600 MHz, CDCl₃)

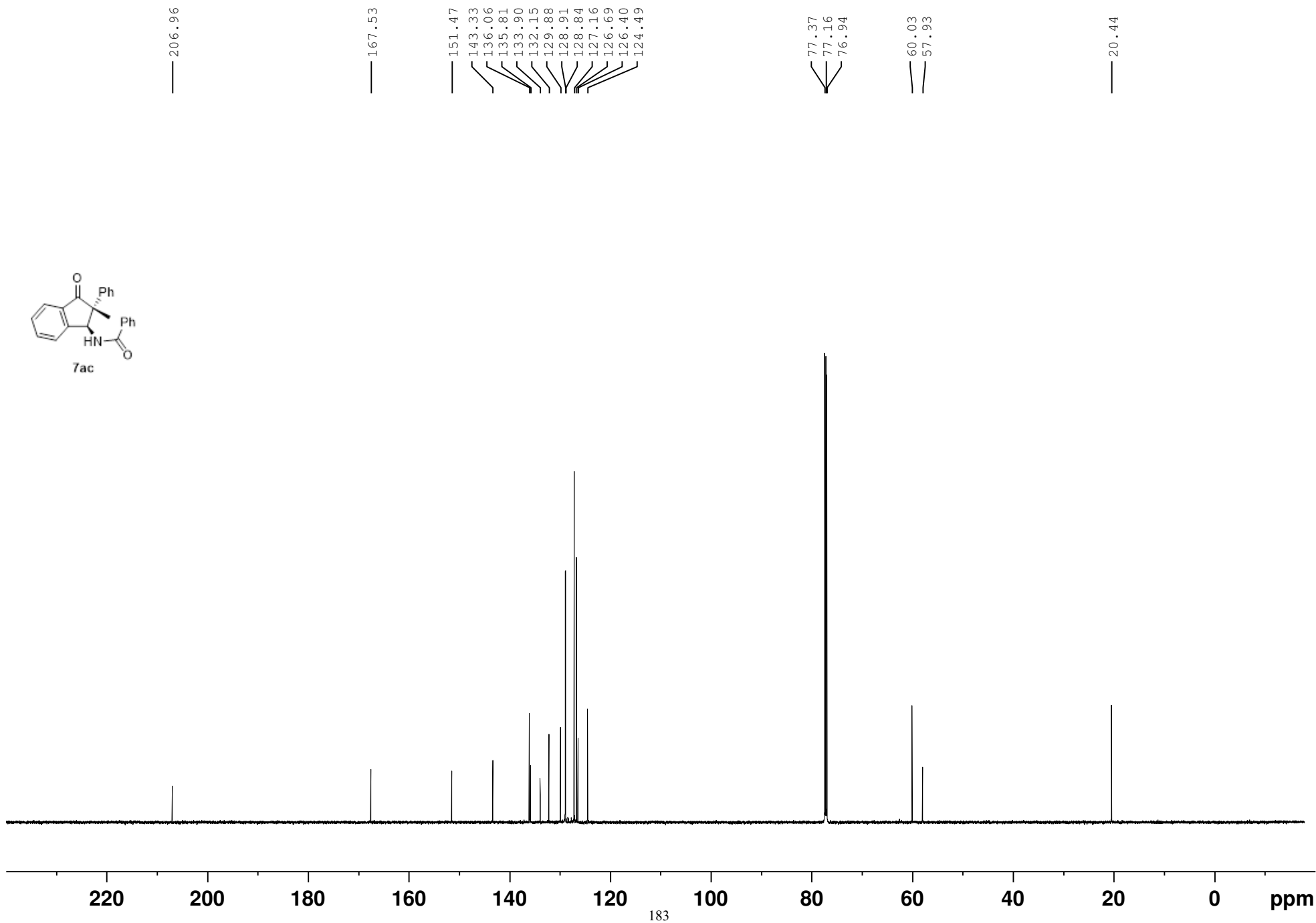
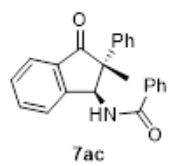
7.864
7.851
7.817
7.804
7.701
7.688
7.676
7.595
7.582
7.548
7.536
7.523
7.511
7.459
7.447
7.434
7.332
7.319
7.306
7.259
7.243
7.231
7.219
6.526
6.511
6.172
6.156

— 1.567

< 0.075
< -0.000

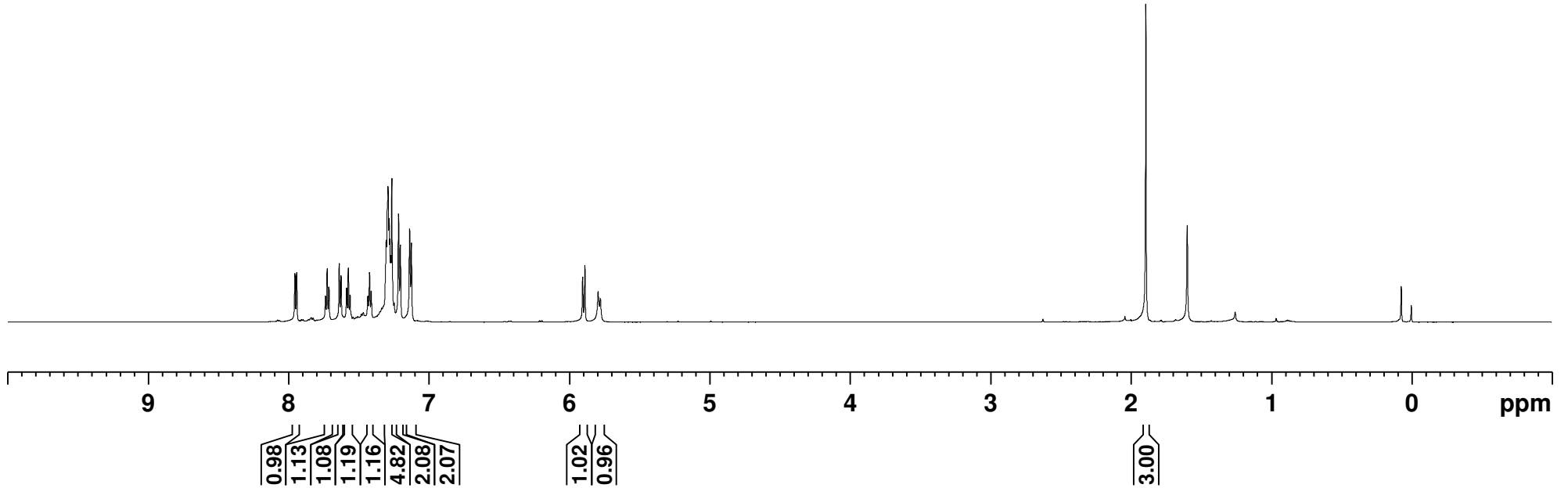
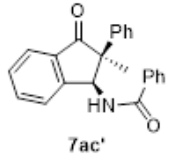


¹³C NMR (150 MHz, CDCl₃)

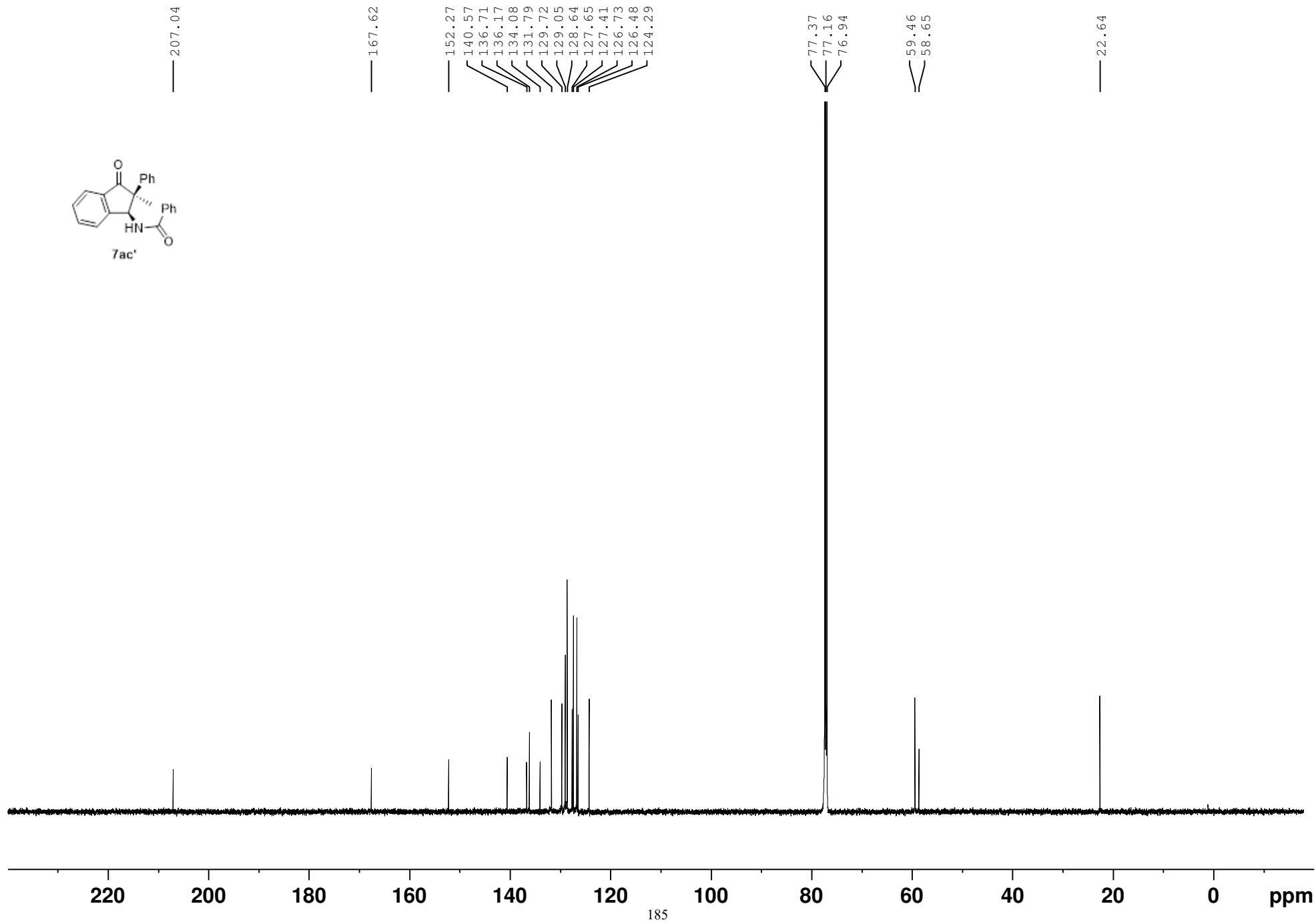
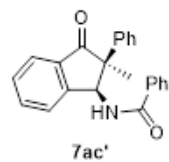


¹H NMR (600 MHz, CDCl₃)

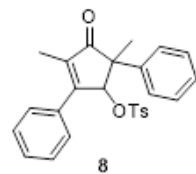
7.953
7.940
7.735
7.723
7.710
7.637
7.624
7.584
7.572
7.560
7.433
7.421
7.409
7.302
7.294
7.290
7.282
7.277
7.269
7.262
7.215
7.202
7.135
7.123
5.903
5.887
5.792
5.777



¹³C NMR (150 MHz, CDCl₃)



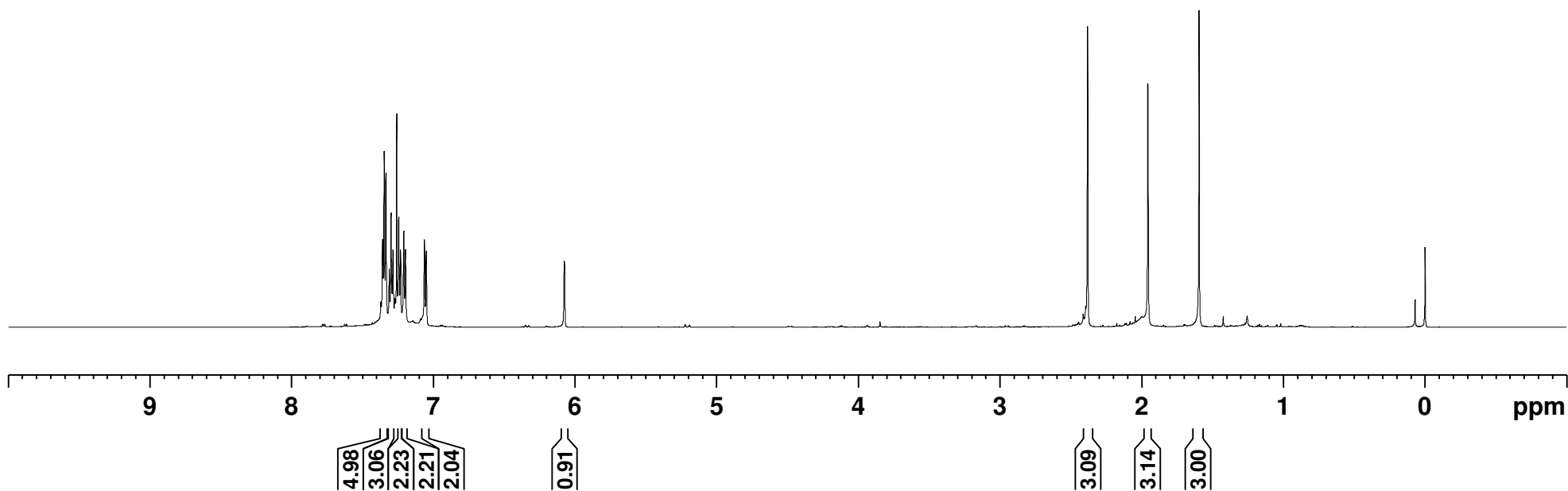
^1H NMR (600 MHz, CDCl_3)



7.370
7.358
7.346
7.334
7.311
7.298
7.286
7.284
7.259
7.244
7.232
7.209
7.196
7.063
7.049
6.076
6.074

— 2.382
∨ 1.957
— 1.955
— 1.595

∨ 0.070
∨ -0.000



¹³C NMR (150 MHz, CDCl₃)

