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Electronic Supplementary Information

Rh(III)-Catalyzed *ortho*-C-(sp2)-H Amidation of Ketone and Aldehyde by Virtue of Synergistic Ligand Accelerated Catalysis

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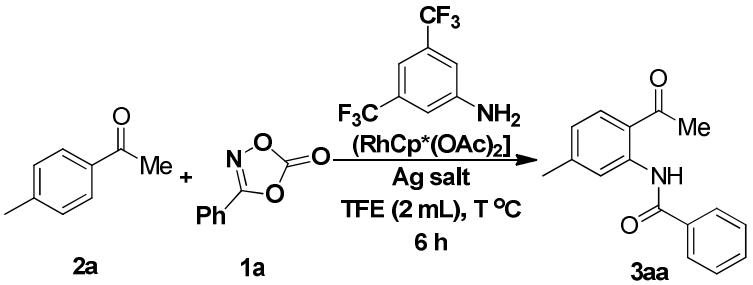
Contents

General experimental

NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$, Tetramethylsilane (TMS; δ = 0.00 ppm) served as an internal standard for ^1H NMR. The corresponding residual nondeuterated solvent signal ($CDCl_3$; δ = 77.16 ppm) was used as internal standard for ^{13}C NMR (100 MHz). IR spectra were measured using a FT-IR spectrometer. Mass spectra were obtained with a Q-TOF Mass Spectrometer (ESI-HRMS). Flash column chromatography was carried out by packing glass columns with commercial silica gel 100-200 mesh (commercial suppliers) and thin-layer chromatography was carried out using silica gel GF-254. All catalysts $[RhCp^*Cl_2]_2$, $[RhCp^*(OAc)_2]$, $[RhCp^*(CH_3CN)_3](SbF_6)_2$, and $[Cp^*Co(CO)I_2]$ were prepared according to literature procedure.[1-2] Reagents and reactants were procured from commercial suppliers. Trifluoroethanol solvent was purchased from commercial suppliers and used for all procedures. Other solvents, used for work up and chromatographic procedures were purchased from commercial suppliers and used without any further purification. All the aldehydes were freshly distilled under Argon atmosphere or washed with saturated aq. solution of $NaHCO_3$ before use. Dioxazolones were prepared according to the literature procedure.[3]

Table 1: Detailed optimization of reaction conditions for Rh(III) catalyzed C-H amidation of ketones:[a]



entry	silver salt (equiv)	temp (°C)	additives (mol %)	yield (%)[b]
1	$AgSbF_6$	rt	none	nd
2	$AgSbF_6$	50	none	nd
3	$AgSbF_6$	80	none	13
4	$AgSbF_6$	120	none	25
5	$AgSbF_6$	100	none	9
6[c]	$AgSbF_6$	100	none	45
7	$AgPF_6$	100	AcOH	43
8	$AgPF_6$	100	Cl_3CCO_2H	21
9	$AgPF_6$	100	NaOAc	18
10	$AgPF_6$	100	AgOAc	35
11	$AgPF_6$	100	H_2O	40
12	$AgPF_6$	100	$(C_6H_5)_3B$	9
13[d]	$AgPF_6$	100	none	13

[a] Reaction conditions: Unless otherwise noted all reactions were carried out using **1a** (0. 24 mmol), **2a** (0.2 mmol), Ligand **L11** (0.04 mol%), Catalyst (0.01 mmol), Ag salt (0.04 mmol), Additive (0.02 mmol), TFE (2 mL) as solvent at 100 °C over 6 h. [b] NMR yield. [c] Reaction was continued over 20 h. [d] 3 mL of TFE solvent was used.

Table 2: Ligand screening for the amidation reaction for o*rtho* C-H amidation of 4-methylacetophenone **2a** with 3-phenyl-1,4,2-dioxazol-5-one **1a.**

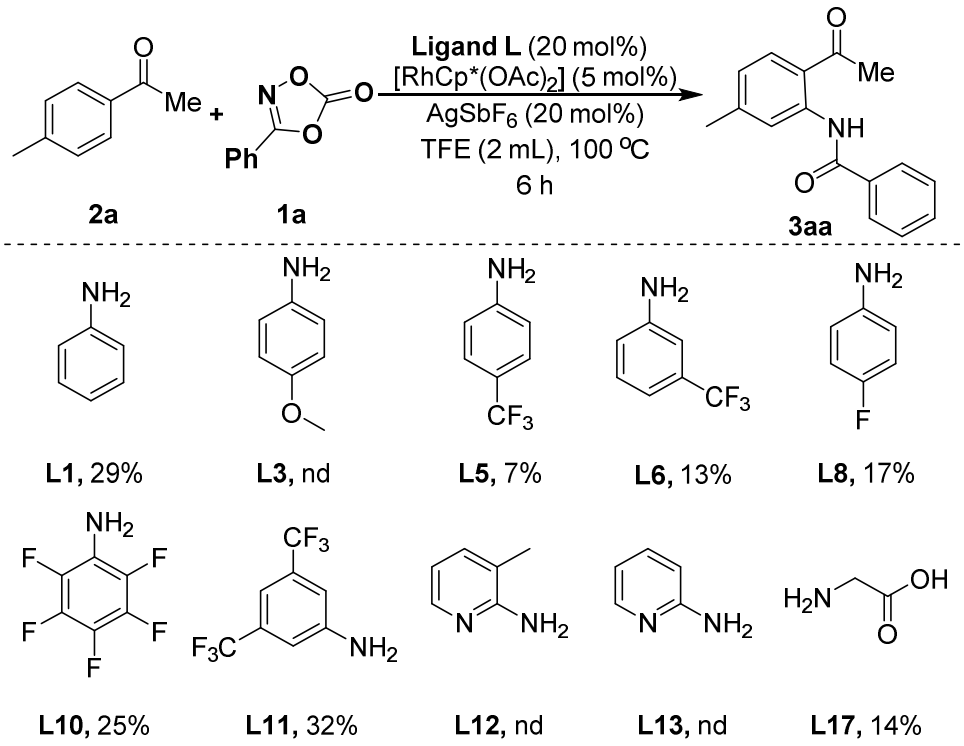
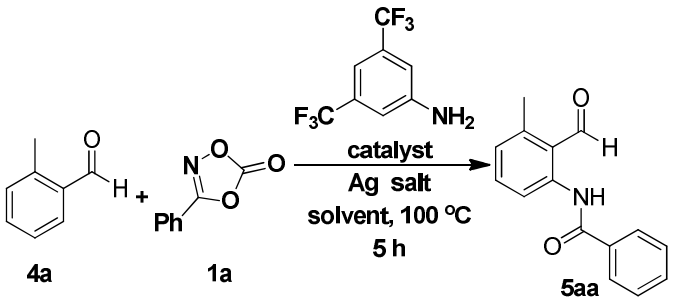


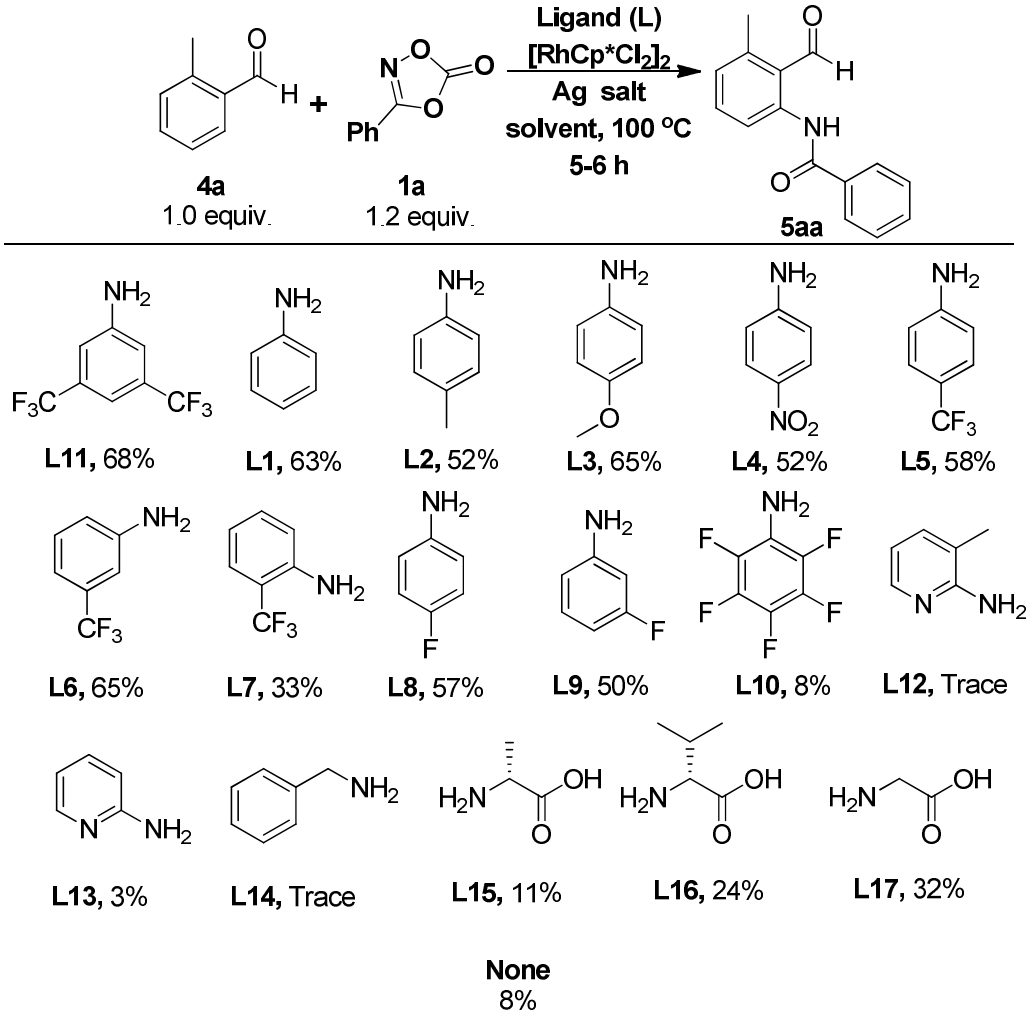
Table 3: Optimization of reaction conditions for Rh(III) catalyzed C-H amidation of aldehydes:



entry	catalyst(equiv)	Ag- salt (equiv)	additives (mol %)	yield [b] %)
1	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$	none	nd
2[c]	[RhCp*Cl_2]$_2$	$AgSbF_6$	none	60
3	[Cp*Co(CO)I_2]	$AgSbF_6$	none	nd
4 [d]	[RhCp*Cl_2]$_2$	$AgSbF_6$	none	Trace
5[e]	[RhCp*Cl_2]$_2$	$AgSbF_6$	none	9
6[f]	[RhCp*Cl_2]$_2$	$AgSbF_6$	none	56
7 [g]	[RhCp*Cl_2]$_2$	$AgSbF_6$	none	64
8	[RhCp*Cl_2]$_2$	$AgNTf_2$	none	53
9	[RhCp*Cl_2]$_2$	$AgBF_4$	none	52
10	[RhCp*Cl_2]$_2$	AgOAc	none	Trace
11	[RhCp*Cl_2]$_2$	$AgPF_6$	none	55
12	[RhCp*Cl_2]$_2$	$AgPF_6$	AcOH	55
13	[RhCp*Cl_2]$_2$	$AgSbF_6$	PivOH	57
15	[RhCp*Cl_2]$_2$	$AgSbF_6$	NaOAc	10
17	[RhCp*Cl_2]$_2$	$AgSbF_6$	CsOAc	nd
18	[RhCp*Cl_2]$_2$	$AgSbF_6$	4 Å MS	9
19 [i]	[RhCp*Cl_2]$_2$	$AgSbF_6$	none	70
20 [j]	[RhCp*Cl_2]$_2$	$AgSbF_6$	none	75
21 [h]	[RhCp*Cl_2]$_2$	$AgSbF_6$	none	74
22 [k]	[RhCp*Cl_2]$_2$	$AgSbF_6$	none	79
23 [l]	**[RhCp*Cl_2]$_2$**	**$AgSbF_6$**	**none**	**83**
24 [m]	[RhCp*Cl_2]$_2$	$AgSbF_6$	none	40
25 [n]	[RhCp*Cl_2]$_2$	$AgSbF_6$	none	76
26 [o]	[RhCp*Cl_2]$_2$	$AgSbF_6$	none	8

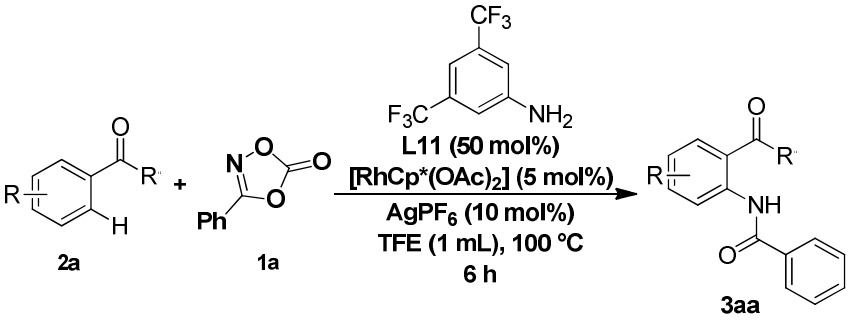
[a] Reaction conditions: Unless otherwise noted all reactions were carried out using **1a** (0. 24 mmol), **4a** (0.2 mmol), Ligand **L11** (0.04 mol%), Catalyst (0.01 mmol), Ag salt (0.04 mmol), Additive (0.04 mmol), TFE (2 mL) as solvent, entry 1-18 at 100 °C over 5 h, entry 19-25 at rt over 24 h. [b] NMR yield. [c]DCE as solvent. [e] Toluene as solvent.[f]THF as solvent.[g] DCM as solvent. [h] Reversing the equiv. of **1a** and **4a**. [i] Reaction was carried out at 50°C [j] Reaction was continued for 24 h. [k] for 48 h. [l] Catalyst (0.015 mmol), Ag salt (0.06 mmol), Additive (0.04 mmol), TFE (2 mL) as solvent, at rt over 48 h. [m] 10 mol% of 3,5- bis(trifluoromethyl)aniline. [n] 40 mol% of 3,5-bis(trifluoromethyl)aniline. [o] In the absence of aniline.

Table 4: Ligand screening for the amidation reaction for o*rtho* C-H amidation of 2-methylbenzaldehyde **4a** with3-phenyl-1,4,2-dioxazol-5-one **1a.**



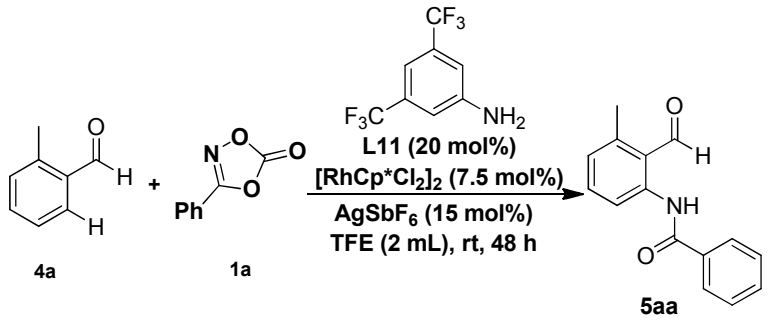
Reaction conditions: **1a** (0.24 mmol), **4a** (0.2 mmol), ligand **L** (20 mol%), $[RhCp^*Cl_2]_2$ (0.01 mmol), $AgSbF_6$ (0.04 mmol), TFE (2 mL) as solvent.

Typical experimental procedure for Rh(III) catalyzed C-H amidation of ketones:



A suspension of 4-methylacetophenone **2a** (27.0 mg, 0.2 mmol, 1.0 equiv), 3-phenyl-1, 4, 2-dioxazol-5-one **1a** (40.0 mg, 0.24 mmol, 1.2 equiv)**,** 3,5-bis(trifluoromethyl)aniline **L11** (22.9 mg, 0.04 mmol, 0.5 equiv)**,** [RhCp*$(OAc)_2$] (3.6 mg, 0.01 mmol, 0.05 equiv), and $AgPF_6$ (5.1 mg, 0.02 mmol, 0.1 equiv) in anhydrous TFE was stirred at 100 °C temperature for 6 h. At ambient temperature the solvent was evaporated on vacuo and the resulting crude reaction mixture was purified on a silica gel column using a flash column.

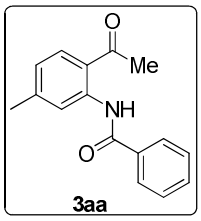
Typical experimental procedure for Rh(III) catalyzed C-H amidation of aldehyde:



A suspension of 2-methylbenzaldehyde **4a** (24.0 mg, 0.2 mmol, 1.0 equiv)**,** 3-phenyl-1, 4, 2-dioxazol-5-one **1a** (40.0 mg, 0.24 mmol, 1.2 equiv)**,** 3,5-bis(trifluoromethyl) aniline **L11** (9.2 mg, 0.04 mmol, 0.2 equiv)**,** [RhCp*Cl_2]$_2$ (9.3 mg, 0.015 mmol, 0.075 equiv), and $AgSbF_6$ (20.6 mg, 0.06 mmol, 0.3 equiv.) in anhydrous TFE was stirred at room temperature, until completion of reaction indicated by TLC. At ambient temperature the solvent was evaporated on vacuo and the resulting crude reaction mixture was purified on a silica gel column using a flash column.

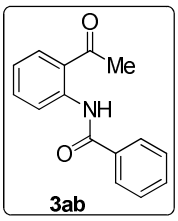
Characterization data for amidation of ketones:

***N*-(2-Acetyl-5-methylphenyl) benzamide 3aa:**



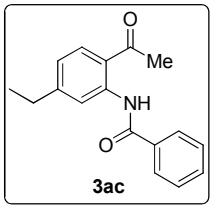
Purified by silica gel (230-400) flash column chromatography (8-10% EtOAc in petroleum ether); white solid (32 mg, 0.126 mmol, 64% yield); R_f = 0.2; m.p. 127-129 °C; **FT-IR (Thin film):** 2917 (m), 1645 (m), 1581 (s), 1536 (s), 1451 (s), 1248 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.76 (s, 1H), 8.84 (s, 1H), 8.07 (d, *J* = 7.17 Hz, 2H), 7.83 (d, *J* = 8.07 Hz, 1H), 7.50-7.56 (m, 3H), 6.96 (d, *J* = 7.91 Hz, 1H), 2.68 (s, 3H), 2.44 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 202.9, 166.3, 147.0, 141.6, 135.0, 132.1, 132.0, 128.9, 127.6, 123.6, 121.2, 119.8, 28.6, 22.4; **HRMS (ESI+):** Calcd. for $C_{16}H_{15}NO_2Na$ ($[M+Na]^+$): 276.1000, Found: 276.1000

***N*-(2-Acetylphenyl) benzamide 3ab:**



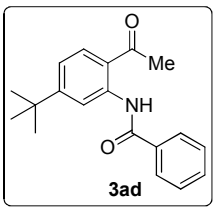
Purified by silica gel (230-400) flash column chromatography (6-8% EtOAc in petroleum ether); yellow solid (30 mg, 0.124 mmol, 62% yield); R_f = 0.2; m.p. 92-94 °C; **FT-IR (Thin film):** 3226 (broad), 2925 (m), 1679 (m), 1650 (s), 1584 (s), 1525 (s), 1249 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.71 (s, 1H), 8.98 (d, *J* = 8.62 Hz, 1H), 8.07 (d, *J* = 7.60 Hz, 2H), 7.95 (d, *J* = 7.83 Hz, 1H), 7.50-7.64 (m, 4H), 7.15 (t, *J* = 7.73 Hz, 1H), 2.71 (s, 3H),); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.4, 166.3, 141.5 135.5, 134.9, 132.1, 132.0, 128.9, 127.6, 122.6, 122.1, 120.9; **HRMS (ESI+):** Calcd. for $C_{15}H_{13}NO_2Na$ ($[M+Na]^+$): 262.0844, Found: 262.0845

***N*-(2-Acetyl-5-methylphenyl) benzamide 3ac:**



Purified by silica gel (230-400) flash column chromatography (4-5% EtOAc in petroleum ether); off white solid 33 mg, 0.122 mmol, 61% yield); R_f = 0.5; m.p. 138-140 °C; **FT-IR (Thin film):** 3438 (broad), 2925 (m), 1671 (m), 1644 (s), 1579 (s), 1454 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.78 (s, 1H), 8.87 (s, 1H), 8.07-8.09 (m, 2H), 7.86 (d, *J* = 8.19 Hz, 1H),7.50-7.56 (m, 3H), 6.99 (d, *J* = 8.19 Hz, 1H), 2.74 (q, *J* = 7.54 Hz, 2H), 2.68 (s, 3H), 1.29 (t, *J* = 7.64 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 202.9, 166.3, 153.1, 141.8, 135.0, 132.2, 132.1, 128.9, 127.6, 122.4, 120.1, 120.0, 29.6, 28.6, 15.2; **HRMS (ESI+):** Calcd. for $C_{17}H_{17}NO_2Na$ ($[M+Na]^+$): 268.1157, Found: 268.1154

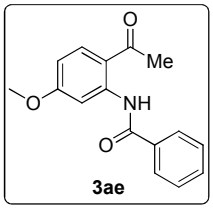
***N*-(2-Propionylphenyl) benzamide 3ad:**



Purified by silica gel (230-400) flash column chromatography (5-6% EtOAc in petroleum ether); off white solid (36 mg, 0.122 mmol, 62% yield); R_f = 0.5; m.p. 154-156 °C; **FT-IR (Thin film):** 3429 (broad), 2964 (s), 1669 (s), 1651(s), 1577 (s), 1447 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.76 (s, 1H), 9.11 (s, 1H), 8.08 (d, *J* = 7.48 Hz, 2H), 7.89 (dd, *J* = 8.32 Hz & 1.12 Hz, 1H), 7.50-7.57 (m, 3H), 7.18 (d, *J* = 8.40 Hz, 1H), 2.68 (s, 3H), 1.38 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 202.9, 166.4, 159.9, 141.7, 135.1, 132.1, 131.9, 128.9, 127.6,

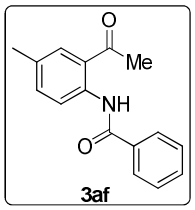
119.9, 119.8, 117.9, 35.8, 31.1, 28.6; **HRMS (ESI+):** Calcd. for $C_{19}H_{21}NO_2Na$ ($[M+Na]^+$): 318.1468, Found: 318.1470

***N*-(2-Acetyl-5-methylphenyl) benzamide 3ae:**



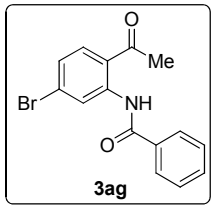
Purified by silica gel (230-400) flash column chromatography (10-12% EtOAc in petroleum ether); off white solid (31 mg, 0.116 mmol, 58% yield); R_f = 0.2; m.p. 125-127 °C; **FT-IR (Thin film):** 3399 (broad), 2964 (m), 1674 (s), 1638 (s), 1530 (s), 1261 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 13.09 (s, 1H), 8.66 (s, 1H), 8.08 (d, *J* = 7.30 Hz, 2H), 7.86 (d, *J* = 8.92 Hz, 1H), 7.50-7.56 (m, 3H), 6.65 (d, *J* = 8.74 Hz, 1H), 3.93 (s, 3H), 2.64 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 201.6, 166.6, 165.1, 144.3, 134.8, 133.9, 132.2, 129.0, 127.6, 115.6, 110.1, 104.0, 55.8, 28.4; **HRMS (ESI+):** Calcd. for $C_{16}H_{15}NO_3Na$ ($[M+Na]^+$): 292.0950, Found: 292.0953

***N*-(2-acetyl-4-methylphenyl) benzamide 3af:**



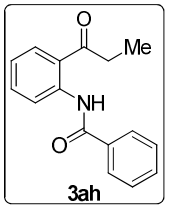
Purified by silica gel (230-400) flash column chromatography (5-6% EtOAc in petroleum ether); off white solid (22 mg, 0.087 mmol, 44% yield); R_f = 0.4; m.p. 123-125°C; **FT-IR (Thin film):** 3431 (s), 2361 (m), 1649 (s), 1532 (s); **^{1}H-NMR(400 MHz, $CDCl_3$):** δ 12.59 (s, 1H), 8.86 (d, *J* = 8.65 Hz, 1H), 8.06 (d, *J* = 7.73 Hz, 2H), 7.73 (s, 1H), 7.50-7.55 (m, 3H), 7.43 (d, *J* = 8.63 Hz, 1H), 7.26 (s, 1H), 2.70 (s, 3H), 2.39 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.4, 166.1, 139.2, 136.3, 135.0, 132.1, 132.0, 128.9, 127.6, 122.1, 120.9, 28.8, 21.0; **HRMS (ESI+):** Calcd. for $C_{16}H_{15}NO_2H$ ($[M+H]^+$): 254.1181, Found: 254.1181

***N*-(2-acetyl-5-bromophenyl) benzamide 3ag:**



Purified by silica gel (230-400) flash column chromatography (6-8% EtOAc in petroleum ether); white solid (24 mg, 0.075 mmol, 38% yield); R_f = 0.2; m.p. 166-168 °C; **FT-IR (Thin film):** 3398 (broad), 2919 (m), 1677 (s), 1647 (s), 1574 (s), 1233 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.74 (s, 1H), 9.26 (s, 1H), 8.05 (d, *J* = 7.80 Hz, 2H), 7.79 (d, *J* = 8.45 Hz, 1H), 7.51-7.58 (m, 3H), 7.28 (d, *J* = 8.56 Hz, 1H), 2.69 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 202.7, 166.3, 142.4, 134.4, 132.9, 132.4, 130.6, 129.0, 127.6, 125.8, 123.8, 120.6, 28.8; **HRMS (ESI+):** Calcd. for $C_{15}H_{12}BrNO_2Na$;($[M+Na]^+$): 339.9949, Found: 339.9992

***N*-(2-Propionylphenyl) benzamide 3ah:**

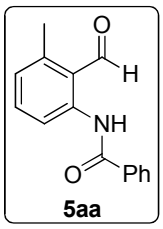


Purified by silica gel (230-400) flash column chromatography (8-10% EtOAc in petroleum ether); off white solid (23 mg, 0.920 mmol, 46% yield); R_f = 0.2; m.p. 127-129 °C; **FT-IR (Thin film):** 3445 (s), 2096 (m), 1644 (s), 1210 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.74 (s, 1H), 8.97 (d, *J* = 8.55 Hz, 1H), 8.07-8.09 (m, 2H), 7.99 (d, *J* = 8.05 Hz, 1H), 7.52-7.63 (m, 4H), 7.16 (t, *J* = 7.93 Hz, 1H), 3.11 (q, *J* = 7.26 Hz, 2H), 1.26 (t, *J* = 7.17 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 205.9, 166.3, 141.4, 135.1, 135.0, 132.1, 130.9, 129.0, 127.6,

122.6, 121.9, 121.1, 33.4, 8.8; **HRMS (ESI+):** Calcd. for $C_{16}H_{15}NO_2Na$ ($[M+Na]^+$): 276.1000, Found: 276.1003

Characterization data for amidation of aldehyde:

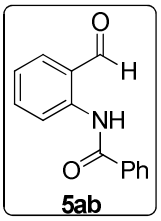
***N*-(2-Formyl-3-methylphenyl) benzamide 5aa:**



5aa

Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); white solid (37 mg, 0.154 mmol, 77% yield): R_f = 0.3, m.p. 108-110 °C; **FT-IR (Thin film):** 3250 (broad), 2917 (m), 2338 (m), 1658 (s), 1536 (s), 1464 (s), 1396 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.55 (s, 1H), 10.52 (bs, 1H), 8.82 (d, *J* = 8.49 Hz, 1H), 8.08 (d, *J* = 7.17 Hz, 2H), 7.51-7.57 (m, 4H), 6.96 (d, *J* = 7.39 Hz, 1H), 2.70 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.9, 166.4, 143.5, 142.2, 136.8, 134.8, 132.2, 129.0, 127.7, 126.1, 119.7, 118.7, 19.4; **HRMS (ESI+):** calcd. for $C_{15}H_{13}NO_2Na$ ($[M+Na]^+$): 262.0844, found: 262.0841

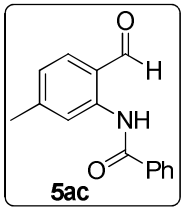
***N*-(2-Formylphenyl) benzamide 5ab:**



5ab

Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); white solid (34 mg, 0.150 mmol, 75% yield): R_f = 0.3, m.p. 110-112 °C; **FT-IR (Thin film):** 3401 (broad), 2339 (m), 1653 (s), 1588 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.0 (bs, 1H), 9.90 (s, 1H), 8.87 (d, *J* = 8.15 Hz, 1H), 7.97-7.99 (m, 2H), 7.56-7.64 (m, 2H), 7.43-7.49 (m, 3H), 7.17 (t, *J* = 7.45 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 196.0, 166.3, 141.3, 136.5, 136.3, 134.4, 132.3, 129.0, 127.6, 123.2, 122.1, 120.0; **HRMS (ESI+):** calcd. for $C_{14}H_{11}NO_2Na$ ($[M+Na]^+$): 248.0687, found: 248.0688

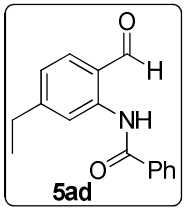
***N*-(2-Formyl-5-methylphenyl) benzamide 5ac:**



5ac

Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); off white solid (34 mg, 0.142 mmol, 71% yield); R_f = 0.3, m.p. 135-137 °C; **FT-IR (Thin film):** 3241 (broad), 2852 (m), 1681 (s), 1659 (s), 1620 (s), 1578 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.11 (bs, 1H), 9.92 (s, 1H), 8.80 (s, 1H), 8.07 (d, *J* = 6.86 Hz, 2H), 7.51-7.60 (m, 4H), 7.06 (d, *J* = 7.77 Hz, 1H), 2.47 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.4, 166.3, 148.4, 141.3, 136.4, 134.5, 132.3, 129.0, 127.6, 124.2, 120.5, 120.1, 22.7; **HRMS (ESI+):** calcd. for $C_{15}H_{13}NO_2Na$ ($[M+Na]^+$): 262.0844, found: 262.0848

***N*-(5-Ethyl-2-formylphenyl) benzamide 5ad:**

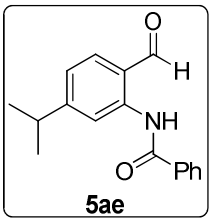


5ad

Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); off white solid (36 mg, 0.142 mmol, 71% yield); R_f = 0.3, m.p. 56-58 °C; **FT-IR (Thin film):** 2930 (m), 1663 (s), 1578 (s), 1533 (s), 1440 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.13 (bs, 1H), 9.93 (s, 1H), 8.84 (s, 1H), 8.06-8.09 (m, 2H), 7.62 (d, *J* = 7.77 Hz, 1H), 7.51-7.58 (m, 3H), 7.08-7.11 (m, 1H), 2.76 (q, *J* = 7.73Hz, 2H), 1.30 (t, *J* = 7.62 Hz, 3H)**: ^{13}C-NMR (100 MHz,**

$CDCl_3$): δ 195.4, 166.3, 154.4, 141.5, 136.5, 134.5, 129.0, 127.6, 123.0, 120.3, 119.4, 29.9, 15.2; **HRMS (ESI+):** calcd. for $C_{16}H_{15}NO_2Na$ ($[M+Na]^+$): 276.1000, found: 276.1002

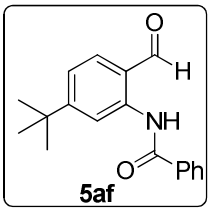
***N*-(2-Formyl-5-isopropylphenyl) benzamide 5ae:**



5ae

Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); yellow oil (38 mg, 0.142 mmol, 72% yield): R_f = 0.5; **FT-IR (thin film):** 3278 (broad), 2963 (m), 2336 (m), 1662 (s), 1617 (m), 1577 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.14 (bs, 1H), 9.94 (s, 1H), 8.88 (s, 1H), 8.08 (d, *J* = 6.95 Hz, 2H), 7.65 (d, *J* = 7.87 Hz, 1H), 7.52-7.58 (m, 3H), 7.14 (d, J = 7.83 Hz, 1H), 3.04 (m, 1H), 1.31-1.33 (m, 6H)**: ^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.4, 159.0, 141.7, 136.6, 134.6, 132.3, 129.0, 127.7, 121.6, 120.6, 118.3, 35.2, 29.8, 23.6; **HRMS (ESI+):** calcd. for $C_{17}H_{17}NO_2Na$ ($[M+Na]^+$): 290.1157, found: 290.1155

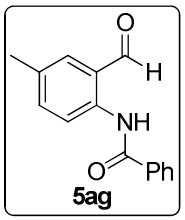
***N*-(5-(Tert-butyl)-2-formylphenyl) benzamide 5af:**



5af

Purified by silica gel flash column chromatography (3-4% EtOAc in petroleum ether); off white solid (36 mg, 0.128 mmol, 64% yield); R_f = 0.4,m.p. 110-112 °C; **FT-IR (Thin film):** 3278 (broad), 2962 (m), 1726 (m), 1664 (s), 1577 (s), 1271 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.12 (s, 1H), 9.95 (s, 1H), 9.09 (s, 1H), 8.08-8.09 (m, 2H), 7.65 (d, *J* = 7.96 Hz, 1H), 7.54-7.55 (m, 3H), 7.29 (d, *J* = 7.66 Hz, 1H), 1.40 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.4, 166.6, 161.2, 141.4, 136.2, 134.6, 132.3, 129.0, 127.6, 120.6, 120.1, 117.3, 36.0, 31.1; **HRMS (ESI+):** calcd. for $C_{18}H_{19}NO_2Na$ ($[M+Na]^+$): 304.1313, found: 304.1314

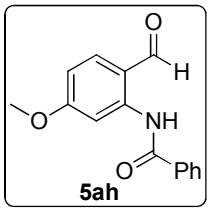
***N*-(2-Formyl-4-methylphenyl) benzamide 5ag:**



5ag

Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); off white solid (31 mg, 0.13 mmol, 65% yield); R_f = 0.3, m.p. 120-122 °C; **FT-IR (Thin film):** 2870 (m), 1663 (s), 1599 (s), 1532 (m), 1152 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 11.99 (bs, 1H), 9.95 (s, 1H), 8.84 (d, *J* = 8.52 Hz, 1H), 8.05-8.07 (m, 2H), 7.47-7.59 (m, 5H), 2.41 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 196.1, 166.1, 139.0, 137.3, 136.5, 134.5, 132.9, 132.2, 129.0, 127.6, 122.1, 120.1, 20.7; **HRMS (ESI+):** calcd. for $C_{15}H_{13}NO_2Na$ ($[M+Na]^+$): 262.0844, found: 262.0843

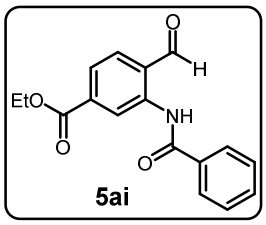
***N*-(2-Formyl-5-methoxyphenyl) benzamide 5ah:**



5ah

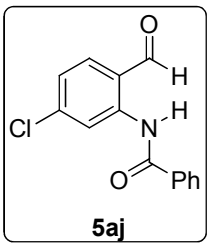
Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); off white solid (29 mg, 0.114 mmol, 57% yield): R_f = 0.2, m.p. 119-121 °C; **FT-IR (Thin film):** 3222 (broad), 1656 (m), 1618 (s), 1579 (m), 1268 (m), 1209 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.39 (bs, 1H), 9.82 (s, 1H), 8.60 (s, 1H), 8.07-8.08 (m, 2H),7.54-7.60 (m, 4H), 6.75 (d, *J* = 7.84 Hz, 1H), 3.95 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.0, 166.6, 166.2, 143.9, 138.2, 134.3, 132.4, 129.0, 127.7 116.2, 110.7, 103.8, 56.0; **HRMS (ESI+):** calcd. for $C_{15}H_{13}NO_3Na$ ($[M+Na]^+$): 278.0793, found: 278.0790

Ethyl 3-benzamido-4-formylbenzoate 5ai:



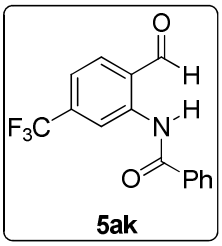
Purified by silica gel flash column chromatography (6-8% EtOAc in petroleum ether); white solid (35 mg, 0.118 mmol, 59% yield); R_f = 0.2, m.p. 98-100 °C; **FT-IR (Thin film):** 3436 (broad), 1712 (s), 1662 (s), 1579 (s), 1405 (s); **^{1}H-NMR (400 MHz, ($CDCl_3$):** δ 12.02 (bs, 1H), 10.07 (s, 1H), 9.55(s, 1H), 8.05-8.07 (m, 2H), 7.91 (dd, *J* = 7.94 & 1.35 Hz, 1H), 7.81 (d, *J* = 8.01, 1H), 7.52-7.61 (m, 3H), 4.43 (q, *J* = 7.07 Hz, 2H), 1.43 (t, J = 7.34 Hz, 3H); **^{13}C-NMR (100 MHz, ($CDCl_3$):** δ 195.8, 166.2, 165.5, 141.3, 137.2, 136.0, 134.1, 132.5, 129.1, 127.6, 124.2, 123.9, 121.1, 62.0, 14.4; **HRMS (ESI+):** calcd. for $C_{17}H_{15}NO_4Na$ ($[M+Na]^+$): 320.0899, found: 320.0898

***N*-(5-Chloro-2-formylphenyl) benzamide 5aj:**



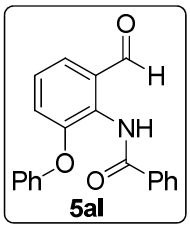
Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); white solid (25 mg, 0.098 mmol, 48% yield): R_f = 0.3,m.p. 158-160 °C; **FT-IR (Thin film):** 3457 (broad), 2854 (m), 2336 (m), 1665 (s), 1610 (s), 1577 (s), 1271 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.15 (s, 1H), 9.95 (s, 1H), 9.05 (s, 1H), 8.06 (d, *J* = 6.88 Hz, 2H), 7.55-7.66 (m, 4H), 7.22-7.26 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.9, 166.3, 143.3, 142.2, 137.2, 134.0, 132.6, 129.1, 127.7, 123.5, 120.4, 120.3; **HRMS (ESI+):** calcd. for $C_{14}H_{10}ClNO_2Na$ ($[M+Na]^+$): 282.0298, found: 282.0313

***N*-(2-Formyl-5-(trifluoromethyl)phenyl) benzamide 5ak:**



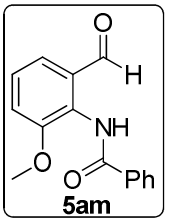
Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); white solid (33 mg, 0.115 mmol, 57% yield); R_f = 0.3, m.p. 124-126 °C; **FT-IR (Thin film):** 2923 (s), 1670 (s), 1587 (s), 1332 (s), 1126 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.13 (s, 1H), 10.09 (s, 1H), 9.33 (s, 1H), 8.07 (d, *J* = 7.27 Hz, 2H), 7.88 (d, *J* = 8.00 Hz, 1H), 7.51-7.62 (m, 4H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.5, 166.4, 141.7, 137.6, 137.3, 136.6, 133.9, 132.8, 129.2, 127.7, 123.7, 119.6, 117.5; **HRMS (ESI+):** calcd. for $C_{15}H_{10}F_3NO_2Na$ ($[M+Na]^+$): 316.0561, found: 316.0562

***N*-(2-Formyl-4-phenoxyphenyl) benzamide 5al:**



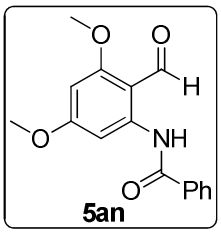
Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); light yellow solid (38 mg, 0.120 mmol, 60% yield): R_f = 0.3,m.p. 136-138 °C; **FT-IR (Thin film):** 3401 (m), 1665 (s), 1590 (s), 1529 (s), 1257 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 11.94 (bs, 1H), 9.89 (s, 1H), 8.97 (d, *J* = 7.65 Hz, 1H), 8.06 (d, *J* = 7.07 Hz, 2H), 7.52-7.60 (m, 3H), 7.36-7.40 (m, 4H), 7.15 (t, *J* = 7.28 Hz, 1H), 7.03 (d, *J* = 7.83 Hz, 2H)**: ^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.3, 166.0, 157.0, 152.6, 137.0, 134.4, 132.3, 130.1, 129.0, 127.6, 127.3, 125.2, 123.9, 123.1, 122.0, 118.8; **HRMS (ESI+):** calcd. for $C_{20}H_{15}NO_3Na$ ($[M+Na]^+$): 340.0950, found: 340.0948

***N*-(2-Formyl-4-methoxyphenyl) benzamide 5am:**



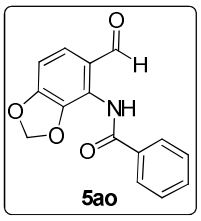
Purified by silica gel flash column chromatography (7% EtOAc in petroleum ether); light yellow solid (35 mg, 0.137 mmol, 69% yield); R_f = 0.2, m.p. 130-132 °C; **FT-IR (Thin film):** 3303 (broad), 1668 (s), 1600 (s), 1542 (s), 1285 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 11.84 (bs, 1H), 9.96 (s, 1H), 8.91 (d, *J* = 8.92 Hz, 1H), 8.05 (d, *J* = 8.92 Hz, 2H), 7.53-7.55 (m, 3H), 7.21-7.26 (m, 2H), 3.88 (s, 3H)**: ^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.7, 165.9, 155.3, 135.0, 134.6, 132.2, 129.0, 127.5, 122.9, 122.4, 121.8, 119.9, 55.9; **HRMS (ESI+):** calcd. for $C_{15}H_{13}NO_3Na$ ($[M+Na]^+$): 278.0793, found: 278.0795

***N*-(2-Formyl-3,5-dimethoxyphenyl) benzamide 5an:**



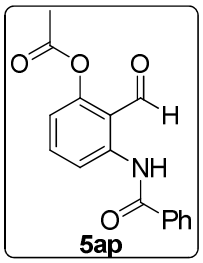
Purified by silica gel flash column chromatography (5-6% EtOAc in petroleum ether); off white solid (33 mg, 0.116 mmol, 58% yield): R_f = 0.3, m.p. 109-111 °C; **FT-IR (Thin film):** 3444 (broad), 2335 (s), 1680 (m), 1637 (s), 1578 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.97 (bs, 1H), 10.32 (s, 1H), 8.21 (s, 1H), 8.07-8.08 (m, 2H), 7.51-7.53 (m, 3H), 6.14 (s, 1H), 3.92 (s, 3H), 3.86 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 191.6, 167.7, 166.7, 164.7, 145.2, 134.5, 132.3, 128.9, 127.7, 106.1, 95.8, 93.8, 55.9, 55.9; **HRMS (ESI+):** calcd. for $C_{16}H_{15}NO_4Na$ ($[M+Na]^+$): 308.0899, found: 308.0899

***N*-(6-Formylbenzo[d][1,3]dioxol-5-yl) benzamide 5ao:**



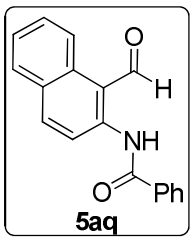
Purified by silica gel flash column chromatography (10-15% EtOAc in petroleum ether); yellow solid (23 mg, 0.086 mmol, 43% yield); R_f = 0.1; m.p. 117-119 °C; **FT-IR (Thin film):** 3289 (broad), 2917 (m), 1669 (m), 1464 (s), 1266 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 10.88 (s, 1H), 9.80 (s, 1H), 8.04 (d, *J* = 7.19 Hz, 2H), 7.57 (t, *J* = 7.13 Hz, 1H), 7.51 (t, *J* = 6.98 Hz, 2H), 7.32 (d, *J* = 8.09 Hz, 1H), 6.83 (d, *J* = 8.11 Hz, 1H), 6.19 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.4, 164.5, 154.8, 140.3, 133.3, 133.0, 132.3, 128.7, 127.9, 122.2, 121.7, 104.9, 102.6; **HRMS (ESI+):** Calcd. for $C_{15}H_{11}NO_4Na$ ($[M+Na]^+$): 292.0586, Found: 292.0589

3-Benzamido-2-formylphenyl acetate 5ap:



Purified by silica gel flash column chromatography (7-8% EtOAc in petroleum ether); off white solid (28 mg, 0.099 mmol, 50% yield): R_f = 0.2, m.p. 130-132 °C; **FT-IR (Thin film):** 3296 (broad), 2335 (m), 1762 (s), 1656 (s), 1464 (s), 1203 (s);**^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.35 (bs, 1H), 10.29 (s, 1H), 8.86 (d, *J* = 8.46 Hz, 1H), 8.06 (d, *J* = 7.35 Hz, 2H), 7.67 (t, *J* = 8.15 Hz, 1H), 7.52-7.59 (m, 3H), 6.91 (d, *J* = 8.11 Hz, 1H), 2.41 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 192.1, 169.0, 166.4, 154.6, 142.7, 137.5, 134.4, 132.5, 129.0, 127.7, 118.0, 117.1, 114.3, 21.0; **HRMS (ESI+):** calcd. for $C_{16}H_{13}NO_4Na$ ($[M+Na]^+$): 306.0742, found: 306.0744

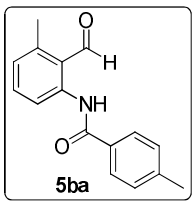
***N*-(1-Formylnaphthalen-2-yl) benzamide 5aq:**



5aq

Purified by silica gel flash column chromatography (3-4% EtOAc in petroleum ether); yellow solid (43 mg, 0.156 mmol, 78% yield); R_f = 0.4, m.p. 204-206 °C; **FT-IR (Thin film):** 3402 (broad), 2361 (m), 1679 (s), 1647 (s), 1590 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 13.14 (s, 1H), 11.08 (s, 1H), 9.16 (d, *J* = 9.22 Hz, 1H), 8.48 (d, *J* = 8.64 Hz, 1H), 8.11-8.15 (m, 3H), 7.87 (d, *J* = 8.09 Hz, 1H), 7.48-7.66 (m, 5H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.2, 166.8, 143.2, 138.0, 134.5, 133.8, 132.5, 129.7, 129.6, 129.2, 129.1, 127.9, 125.4, 119.9, 119.3, 113.0; **HRMS (ESI+):** calcd. for $C_{18}H_{13}NO_2Na$ ($[M+Na]^+$): 298.0844, found: 298.0845

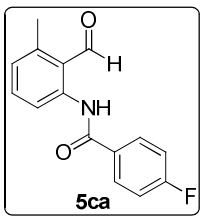
***N*-(2-Formyl-3-methylphenyl)-4-methylbenzamide 5ba:**



5ba

Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); white solid (29 mg, 0.115 mmol, 57% yield); R_f = 0.3, m.p. 115-117 °C; **FT-IR (Thin film):** 3423 (broad), 2336 (m), 1655 (s), 1608 (s), 1463 (s), 1395 (s), 1271 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.52 (bs, 1H), 10.51 (s, 1H), 8.82 (d, *J* = 8.51 Hz, 1H), 7.97 (d, *J* = 8.13 Hz, 2H), 7.51 (t, *J* = 7.82 Hz, 1H), 7.32 (d, *J* = 8.21 Hz, 2H), 6.95 (d, *J* = 7.46 Hz, 1H), 2.69 (s, 3H), 2.43 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.9, 166.4, 143.4, 142.8, 142.3, 136.7, 131.9, 129.6, 127.7, 125.9, 119.6, 118.6, 21.7, 19.4; **HRMS (ESI+):** calcd. for $C_{16}H_{15}NO_2Na$ ($[M+Na]^+$): 276.1000, Found: 276.1000

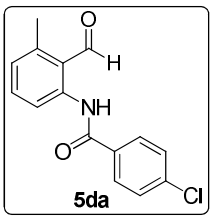
4-Fluoro-*N*-(2-formyl-3-methylphenyl) benzamide 5ca:



5ca

Purified by silica gel flash column chromatography (3-4% EtOAc in petroleum ether); yellow solid (32 mg, 0.125 mmol, 62% yield); R_f = 0.4, m.p. 135-137 °C; **FT-IR (Thin film):** 1650 (s), 1600 (s), 1500 (s), 1457 (s), 1389 (s); **^{1}H-NMR (400 MHz, ($CDCl_3$):** δ 12.54 (bs, 1H), 10.51 (s, 1H), 8.78 (d, *J* = 7.57 Hz, 1H), 8.07-8.10 (m, 2H), 7.53 (t, *J* = 8.49 Hz, 1H), 7.20 (t, *J* = 8.41 Hz, 2H), 6.97 (d, *J* = 7.37 Hz, 1H), 2.70 (s, 3H); **^{13}C-NMR (100 MHz, ($CDCl_3$):** δ 195.0, 166.5, 165.2, 164.0, 143.6, 142.2, 136.8, 131.0, 131.0, 130.2, 130.1, 130.1, 126.2, 119.7, 118.6, 116.1, 115.9, 19.4; **HRMS (ESI+):** calcd. for $C_{15}H_{12}FNO_2Na$ ($[M+Na]^+$): 280.0750, found: 280.0752

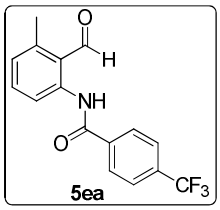
4-Chloro-*N*-(2-formyl-3-methylphenyl) benzamide 5da:



5da

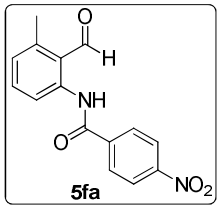
Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); white solid (33 mg, 0.122 mmol, 61% yield); R_f = 0.3, m.p. 136-138 °C; **FT-IR (Thin film):** 2925 (w), 2362 (w), 1680 (s), 1609 (s), 1463 (s), 1190 (s); **^{1}H-NMR (400 MHz, ($CDCl_3$):** δ 12.56 (bs, 1H), 10.50 (s, 1H), 8.78 (d, *J* = 8.60 Hz, 1H), 8.00 (d, *J* = 8.61 Hz, 2H), 7.47-7.54 (m, 3H), 6.97 (d, *J* = 7.51 Hz, 1H), 2.70 (s, 3H); **^{13}C-NMR (100 MHz, ($CDCl_3$):** δ 195.0, 165.2, 143.6, 142.0, 138.6, 136.8, 133.1, 129.2, 129.1, 126.3, 119.7, 118.6, 19.4; **HRMS (ESI+):** calcd. for $C_{15}H_{12}ClNO_2Na$ ($[M+Na]^+$): 296.0454, found: 296.0457

***N*-(2-Formyl-3-methylphenyl)-4-(trifluoromethyl) benzamide 5ea:**



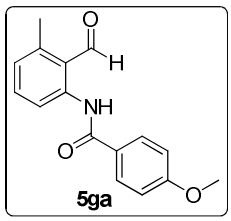
Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); off white solid (45 mg, 0.147 mmol, 73% yield); m.p. 142-144 °C; **FT-IR (Thin film):** 1678 (s), 1608 (w), 1575 (s), 1462 (s), 1116 (s); **^{1}H-NMR: (400 MHz, $CDCl_3$):** δ 12.65 (bs, 1H), 10.50 (s, 1H), 8.78 (d, *J* = 8.33 Hz, 1H), 8.17 (d, *J* = 7.31 Hz, 2H), 7.78 (d, *J* = 7.93 Hz, 2H), 7.52-7.56 (m, 1H), 6.99-7.00 (m, 1H), 2.71 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.1, 164.9, 143.7, 141.8, 138.0, 136.9, 133.9, 133.6, 128.1, 126.6, 126.0, 126.0, 125.2, 122.4, 119.7, 118.7, 19.4; **HRMS (ESI+):** calcd. for $C_{16}H_{12}F_3NO_2Na$ ($[M+Na]^+$): 330.0718, found: 330.0718

***N*-(2-Formyl-3-methylphenyl)-4-nitrobenzamide 5fa:**



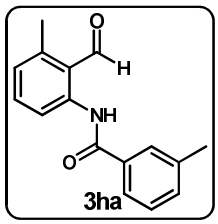
Purified by silica gel flash column chromatography (8-10% EtOAc in petroleum ether); yellow solid (44 mg, 0.155 mmol, 77% yield); R_f = 0.1; m.p. 212-214 °C; **FT-IR (Thin film):** 3398 (m), 2920 (s), 1650 (s), 1542 (s), 1344; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.73 (bs, 1H), 10.53 (s, 1H), 8.77 (s, 1H), 8.36 (s, 2H), 8.23 (s, 2H), 7.56 (s, 1H), 7.03 (s, 1H), 2.73 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.3, 164.1, 150.0, 143.8, 141.6, 140.2, 137.0, 128.8, 126.9, 124.2, 119.8, 118.7, 19.4; **HRMS (ESI+):** calcd. for $C_{15}H_{12}N_2O_4Na$ ($[M+Na]^+$): 307.0695, found: 307.0698

***N*-(2-Formyl-3-methylphenyl)-4-methoxybenzamide 5ga:**



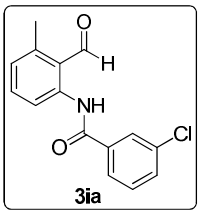
Purified by silica gel flash column chromatography (8-10% EtOAc in petroleum ether); yellow semisolid (5 mg, 0.019 mmol, 9% yield); R_f = 0.1; 3426 (broad), 2923 (m), 2363 (s), 1644 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.51 (bs, 1H), 10.53 (s, 1H), 8.82 (d, *J* = 8.69 Hz, 1H), 8.06 (d, *J* = 8.68 Hz, 2H), 7.52 (t, *J* = 8.06 Hz, 1H), 7.02 (d, *J* = 8.59 Hz, 2H), 6.96 (d, *J* = 7.66 Hz, 1H), 3.89 (s, 3H), 2.71 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.9, 166.0, 162.9, 143.5, 142.6, 136.8, 129.7, 127.2, 125.8, 119.7, 118.7, 114.2, 55.6, 29.9; **HRMS (ESI+):** calcd. for $C_{16}H_{15}NO_3Na$ ($[M+Na]^+$): 292.0950, found: 292.0953.

***N*-(2-Formyl-3-methylphenyl)-3-methylbenzamide 5ha:**



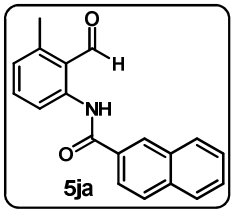
Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); white solid (30 mg, 0.118 mmol, 59% yield); R_f = 0.3, m.p. 124-126 °C; **FT-IR (Thin film):** 3424 (s), 2918 (m), 1648 (s), 1604 (s), 1270 (s), 1165 (s); **^{1}H-NMR (400 MHz, ($CDCl_3$):** δ 12.52 (bs, 1H), 10.52 (s, 1H), 8.82 (d, *J* = 8.61 Hz 1H), 7.85-7.88 (m, 2H), 7.52 (t, *J* = 7.92 Hz, 1H), 7.37-7.44 (m, 2H), 6.96 (d, *J* = 7.35 Hz, 1H), 2.70 (s, 3H), 2.46 (s, 3H); **^{13}C-NMR (100 MHz, ($CDCl_3$):** δ 194.8, 166.7, 143.5, 142.3, 138.8, 136.7, 134.8, 133.0, 128.8, 128.5, 126.0, 124.6, 119.7, 118.7, 21.6, 19.4; **HRMS (ESI+):** calcd. for $C_{16}H_{15}NO_2Na$ ($[M+Na]^+$): 276.1000, found: 276.1003

3-Chloro-*N*-(2-formyl-3-methylphenyl) benzamide 5ia:



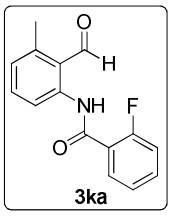
Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); white solid (35 mg, 0.128 mmol, 65% yield); R_f = 0.3; m.p. 142-144 °C; **FT-IR (Thin film):** 3583 (broad), 2920 (m), 1672 (s), 1607 (s), 1572 (s), 1258 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.56 (s, 1H), 10.51 (s, 1H), 8.77 (d, *J* = 8.50 Hz, 1H), 8.05 (s, 1H), 7.93 (d, *J* = 7.58 Hz, 1H), 7.52 (t, *J* = 7.54 Hz, 2H), 7.46 (t, *J* = 7.90 Hz, 1H), 6.98 (d, *J* = 7.47 Hz, 1H), 2.70 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.9, 164.9, 143.6, 141.9, 136.8, 136.5, 135.2, 132.2, 130.2, 128.3, 126.4, 125.4, 119.7, 118.7, 19.4; **HRMS (ESI+):** Calcd. for $C_{15}H_{12}ClNO_2Na$ ($[M+Na]^+$): 296.0453, Found: 296.0454

***N*-(2-Formyl-3-methylphenyl)-2-naphthamide 5ja:**



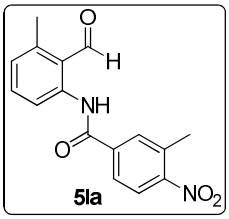
Purified by silica gel flash column chromatography (4-6% EtOAc in petroleum ether); white solid (21 mg, 0.158 mmol, 36% yield); R_f = 0.4; m.p. 150-152 °C; **FT-IR (Thin film):** 3203 (broad),3055 (s), 1676 (s), 1609 (s), 1576 (s), 1462 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.74 (s, 1H), 10.55 (s, 1H), 8.88 (d,*J* = 8.61 Hz, 1H), 8.61 (bs, 1H), 8.13 (d, J = 8.73 Hz, 1H), 8.04 (d, *J* = 7.83 Hz, 1H), 7.98 (d, J = 8.53 Hz, 1H), 7.91 (d, J = 7.50 Hz, 1H), 7.54-7.62 (m, 3H), 6.99 (d, *J* = 7.83 Hz, 1H), 2.72 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.0, 166.5, 143.5, 142.3, 136.8, 135.2, 132.9, 132.0, 129.6, 128.9, 128.7, 128.2, 127.9, 126.9, 126.1, 123.9, 119.7, 118.8, 19.5; **HRMS (ESI+):** calcd. for $C_{19}H_{15}NO_2Na$ ($[M+Na]^+$): 312.1000, found: 312.1008

2-Fluoro-*N*-(2-formyl-3-methylphenyl) benzamide 5ka:



Purified by silica gel flash column chromatography (3-4% EtOAc in petroleum ether); white solid (32 mg, 0.125 mmol, 62% yield); R_f = 0.3; m.p. 126-128 °C; **FT-IR (Thin film):** 3439 (broad), 2932 (m), 1651 (s), 1541 (s),1273 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):**12.56 (s, 1H), 10.51 (s, 1H), 8.78 (d, *J* = 7.83 Hz, 1H), 7.84 (d, *J* = 6.92 Hz, 1H), 7.77 (d, *J* = 8.41 Hz, 1H), 7.51-7.54 (m, 2H), 7.26 (s, 1H), 6.98 (d, *J* = 6.25 Hz, 1H), 2.70 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.9, 164.9, 163.1 (d, *J* = 248 Hz), 143.6, 141.9, 137.1 (d, *J* = 6.8 Hz), 136.8, 130.6 (d, *J* = 7.7 Hz), 126.3, 122.9 (d, *J* = 2.9 Hz), 119.7, 119.2 (d, *J* = 22 Hz), 118.7, 115.2, 115.0, 19.3; **HRMS (ESI+):** Calcd. for $C_{15}H_{12}FNO_2Na$ ($[M+Na]^+$): 280.0751, Found: 280.0751

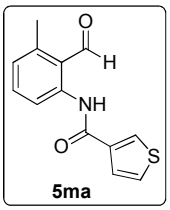
***N*-(2-Formyl-3-methylphenyl)-3-methyl-4-nitrobenzamide 5la:**



Purified by silica gel flash column chromatography (8-10% EtOAc in petroleum ether); yellow solid (46 mg, 0.155 mmol, 77% yield); R_f = 0.1; m.p. 203-205 °C; **FT-IR (Thin film):** 2927 (m), 1680 (s), 1612 (s), 1523 (s), 1194; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.66 (bs, 1H), 10.52 (s, 1H), 8.76 (d, *J* = 8.34, 1H),7.98-8.09 (m, 3H), 7.55 (t, *J* = 8.24 Hz, 1H), 7.02 (d, *J* = 7.17 Hz, 1H), 2.69-2.72 (m, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 195.1,

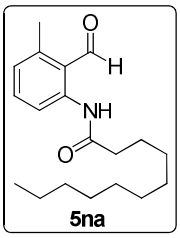
164.3, 151.2, 143.8, 141.6, 138.5, 136.9, 134.3, 132.4, 126.8, 125.9, 125.3, 119.8, 118.7, 20.6, 19.4; **HRMS (ESI+):** calcd. for $C_{16}H_{14}N_2O_4Na$ ($[M+Na]^+$): 321.0847, found: 321.0851

***N*-(2-Formyl-3-methylphenyl) thiophene-3-carboxamide 5ma:**



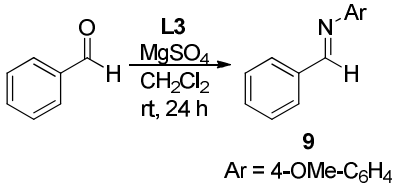
Purified by silica gel (230-400) flash column chromatography (10-12% EtOAc in petroleum ether); white solid (19 mg, 0.078 mmol, 39% yield); R_f = 0.2, m.p. 134-136 °C; **FT-IR (Thin film):** 2917 (s), 1661 (m), 1609 (s), 1541 (s), 1268 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.44 (s, 1H), 10.49 (s, 1H), 8.75 (d, *J* = 8.67 Hz, 1H), 8.16 (s, 1H), 7.68-7.69 (m, 1H), 7.48-7.52 (m, 1H), 7.39-7.41 (m, 1H), 6.94 (d, *J* = 7.51 Hz, 1H), 2.68 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.9, 161.8, 143.5, 142.2, 138.3, 136.8, 129.8, 126.9, 126.6, 125.9, 119.4, 118.5, 19.4; **HRMS (ESI+):** Calcd. for $C_{13}H_{11}NO_2SNa$ ($[M+Na]^+$): 268.0415, Found: 268.0408

***N*-(2-Formyl-3-methylphenyl) undecanamide 5na:**



Purified by silica gel flash column chromatography (2-3% EtOAc in petroleum ether); yellow oil (45 mg, 0.149 mmol, 75% yield); R_f = 0.5; **FT-IR (Thin film):** 3260 (broad), 2925 (s), 1702 (m), 1659 (s), 1606 (s), 1578 (s), 1465 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 11.61 (s, 1H), 10.43 (s, 1H), 8.61 (d, *J* = 8.46 Hz, 1H), 7.44 (t, *J* = 8.22 Hz, 1H), 6.90 (d, *J* = 7.51 Hz, 1H), 2.65 (s, 3H), 2.43 (t, *J* = 7.81 Hz, 2H), 1.74 (q, *J* = 7.51 Hz, 2H), 1.24-1.37 (m, 12H), 0.84-0.88 (m, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 194.5, 173.1, 143.2, 142.0, 136.5, 125.7, 119.2, 118.5, 38.9, 32.0, 29.5, 29.4, 29.4, 29.3, 25.6, 22.8, 19.3, 14.2; **HRMS (ESI+):** Calcd. for $C_{18}H_{27}NO_2Na$ ($[M+Na]^+$): 312.1939, Found: 312.1937

Experimental procedure for the synthesis of imine (E)-1-(4-methoxystyryl)-2-methylbenzene 9:[4]

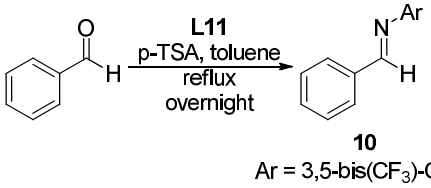


9

Ar = 4-OMe-C_6H_4

In an oven and vaccum dried 50 mL single neck round bottom flask, 2-methyl benzaldehyde (0.6 g, 4.99 mmol, 1.0 equiv) and 4-methoxy aniline **L3** (0.61 g, 4.99 mmol, 1.0 equiv) were taken in 15 mL of dichloromethane in an argon atmosphere. To this 1.0 g of $MgSO_4$ was added and resulting reaction mixture was allowed to stir overnight at rt in an argon atmosphere. Reaction mixture was filtered through a Celite pad and resulting reaction mixture was purified by deactivated silica gel column chromatography. (10-12% EtOAc in petroleum ether); **9** yellow solid (1.06 g, 1.12 mmol, 95% yield); R_f = 0.5; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.75 (s, 1H), 8.06 (d, *J* = 7.73 Hz, 1H), 7.26-7.34 (m, 2H), 7.20-7.22 (m, 3H), 6.92 (d, *J* = 8.47 Hz, 2H), 3.81 (s, 3H), 2.56 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 158.3, 157.2, 145.7, 138.4, 134.4, 131.0, 130.8, 127.6, 126.4, 122.3, 114.5, 55.6, 19.5

Experimental procedure for the synthesis of imine (*E*)-1-(2-methylstyryl)-3,5-bis(trifluoromethyl)benzene 10:[4]



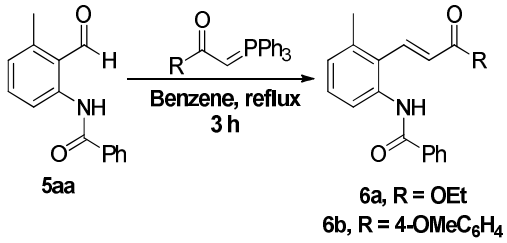
10

Ar = 3,5-bis(CF_3)-C_6H_3

In an oven and vaccum dried 25 mL single neck round bottom flask, 2-methyl benzaldehyde (0.5 g, 4.16 mmol, 1.0 equiv) and **L11** (0.95 g, 4.16 mmol, 1.0 equiv) were taken in 10 mL of toluene in an Argon atmosphere. To this 4-methylbenzenesulfonic acid (15.0 mg, 0.085 mmol, 0.02 equiv) was added and the resulting reaction mixture was allowed to reflux overnight in an argon atmosphere. Reaction mixture was cooled to room temperature and hexane was added to it, filtered through a Celite pad and the filtrate was evaporated on vacuo. Recrystalisation with hexane/dichloromethane (50:1) afforded **10** as a grey solid (1.06 g, 1.12 mmol, 95% yield); R_f = 0.8 (10% EtOAc/petroleum ether); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.72 (s, 1H), 8.04 (d, *J* = 7.71 Hz, 1H), 7.72(s, 1H), 7.57 (s, 2H), 7.40 (t, *J* = 7.39 Hz, 1H), 7.31 (t, *J* = 7.62 Hz, 1H), 7.23-7.26 (m, 1H), 2.61 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.1, 154.1, 139.5, 133.3, 133.2, 132.8, 132.5, 132.2, 131.5, 128.7, 126.7, 124.8, 122.0, 121.2, 119.1, 19.7

Synthetic utility of the amidated product:

Experimental procedure for synthesis of olefinated compounds:



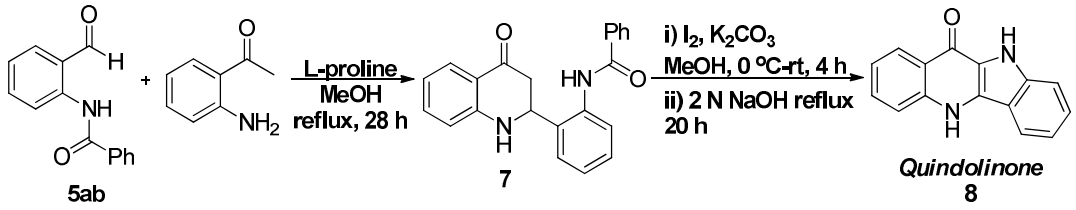
In an oven and vaccum dried 10 mL single neck round bottom, flask *N*-(2-formyl-3-methylphenyl) benzamide **5aa** (13.0 mg, 0.054 mmol, 1.0 equiv), stabilized wittig ylide (21.0 mg, 0.06 mmol, 1.1 equiv) in anhydrous benzene (3 mL) equipped with a reflux condenser was allowed to reflux for 3 h. After the completion of reaction, the solvent was evaporated on vacuo and the resulting crude reaction mixture was purified on a silica gel column (100-200) to obtain (*E*)-Ethyl 3-(2-benzamido-6-methylphenyl) acrylate **6**.

Spectral data for compounds 6a and 6b:

(E)-Ethyl 3-(2-benzamido-6-methylphenyl) acrylate 6a: Purified by silica gel (100-200) flash column chromatography (12-14% EtOAc in petroleum ether); white solid (14 mg, 0.0453 mmol, 84% yield); R_f = 0.1; m.p. 158-160 °C; **FT-IR (Thin film):** 1644 (s), 2101 (s), 2362 (s), 3449 (broad); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.10 (d, *J* = 8.25 Hz, 1H), 8.00 (bs, 1H), 7.79-7.84 (m, 3H), 7.55 (t, *J* = 6.82 Hz, 1H), 7.48 (t, *J* = 7.87 Hz, 2H), 7.30 (t, *J* = 7.72 Hz, 1H), 7.06 (d, *J* = 7.55 Hz, 1H), 6.25 (d, *J* = 16.52 Hz, 1H), 4.28 (q, *J* = 7.07 Hz, 2H), 2.35 (s, 3H), 1.33 (t, *J* = 7.07 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 166.1, 165.6, 140.8, 137.5, 135.3, 134.9, 132.1, 129.5, 129.0, 127.2, 127.0, 126.3, 125.7, 120.6, 61.0, 20.9, 14.4; **HRMS (ESI+):** Calcd. for $C_{19}H_{19}NO_3Na$ ($[M+Na]^+$): 332.1263, found: 332.1264

(E)-*N*-(2-(3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)-3-methylphenyl)benzamide 6b: Purified by silica gel (100-200) flash column chromatography (25-30% EtOAc in petroleum ether); off white solid (155 mg, 0.418 mmol, 83% yield); R_f = 0.2; m.p. 154-156 °C; **FT-IR (Thin film):** 3300 (broad), 2923 (m), 2392 (m), 1654 (s), 1602 (s), 1515 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.15 (bs, 1H), 8.10 (d, *J* = 8.15 Hz, 1H), 7.83-7.91 (m, 5H), 7.51 (t, *J* = 7.31 Hz, 1H), 7.29-7.42 (m, 4H), 7.08 (d, *J* = 7.53 Hz, 1H), 6.87 (d, *J* = 8.83 Hz, 2H), 3.86 (s, 3H), 2.38 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 187.9, 165.6, 163.9, 139.6, 138.0, 135.4, 134.7, 132.1, 131.0, 130.4, 129.5, 129.0, 128.9, 127.2, 127.2, 127.1, 121.0, 114.1, 55.7, 20.9; **HRMS (ESI+):** Calcd. for $C_{24}H_{21}NO_3Na$ ($[M+Na]^+$): 394.1419, found: 394.1416

Experimental procedure for the synthesis of *Quindolinone* natural product:



In an oven and vaccum dried 25 mL single neck round bottom flask, 1-(2-aminophenyl) ethanone (128 mg, 0.948 mmol, 1.2 equiv) was dissolved in 4.0 mL methanol equipped with a reflux condenser in an argon atmosphere. To this was added **3aa** (178 mg, 0.790 mmol, 1.2 equiv). Subsequently L-proline (82 mg, 0.711 mmol, 0.9 equiv) was added portion wise over 2 batches and the resulting reaction mixture was allowed to reflux for 30 h. The reaction was monitored by TLC, cooled it to room temperature. The solvent was evaporated on vacuo and the resulting reaction mixture was quenched with saturated aq. NH_4Cl and extracted with EtOAc (15x3 mL). Combined organic layer was evaporated on vacuo and resulting crude reaction mixture was purified on a silica gel column (100-200) (30-35% EtOAc in petroleum ether); **7** yellow solid (121 mg, 0.353 mmol, 37% yield); R_f = 0.2; m.p. 92-94 °C; **FT-IR (Thin film):** 3397 (broad), 3063 (m), 1653 (s), 1520 (s), 1155 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.85 (bs, 1H), 8.16 (d, *J* = 7.83 Hz, 1H), 7.88 (d, *J* = 7.78 Hz, 1H), 7.80 (d, *J* = 7.43 Hz, 2H), 7.29-7.47 (m, 7H), 7.17 (t, *J* = 7.65 Hz, 1H), 6.85-6.92 (m, 2H), 5.10 (bs, 1H), 4.88 (d, *J* = 14.69 Hz, 1H), 3.09 (t, *J* = 17.06 Hz, 1H), 2.68 (d, *J* = 16.63 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 193.3, 165.6, 151.0, 136.8, 135.7, 134.2, 132.1, 130.3, 129.6, 128.9, 128.8, 127.9, 127.1, 125.6, 124.0, 120.2, 120.0, 116.9, 58.1, 43.4; **HRMS (ESI+):** Calcd. for $C_{22}H_{18}N_2O_2Na$ ($[M+Na]^+$): 365.1266, found: 365.1262

In an oven and vaccum dried 25 mL single neck round bottom flask, *N*-(2-(4-oxo-1,2,3,4-tetrahydroquinolin-2-yl)phenyl) benzamide **6** (75 mg, 0.219 mmol, 1.0 equiv) and K_2CO_3 (67 mg, 0.482 mmol, 2.2 equiv.) were taken in 4 mL MeOH under in an argon atmosphere and cooled it to 0 °C. To this was added I_2 (83 mg, 0.657 mmol, 3.0 equiv.) directly and the resulting reaction mixture was slowly warmed to room temperature and stirred at rt for 4 h. To this aq. 2 N NaOH (until the pH of the solution in range of 7-8) was added and resulting reaction mixture was allowed to reflux overnight. The reaction mixture was cooled to rt and the methanol was evaporated on vacuo. The reaction mixture was quenched with saturated aq. $Na_2S_2O_3$ and extracted with EtOAc (10x3 mL), the combined organic layer was evaporated on vacuo and the crude reaction mixture was purified on a silica gel column. (100-200) (78% EtOAc + 2% MeOH in petroleum ether); **8** yellow solid (34 mg, 0.145 mmol, 66% yield); R_f = 0.1 (50% EtOAc in petroleum ether); m.p. >250 °C; **FT-IR (Thin film):** 3399 (broad), 2875 (m), 2336 (m), 1628 (s), 1581 (s); **^{1}H-NMR (400 MHz, DMSO-d_6):** δ 12.48(s, 1H), 11.72 (s, 1H), 8.37 (d, *J* = 7.34 Hz, 1H), 8.20 (d, *J* = 6.97 Hz, 1H), 7.68-7.74 (m, 2H), 7.47-7.54 (m, 2H), 7.29 (s, 1H), 7.20 (s, 1H):

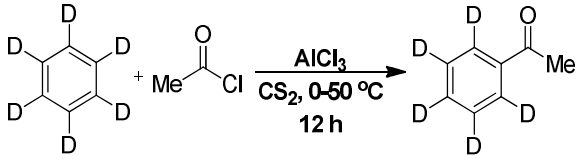
^{13}C-NMR (100 MHz, DMSO-d_6): δ 167.4, 139.1, 138.6, 130.7, 128.9, 127.4, 125.2, 123.1, 122.9, 120.9, 120.5, 118.9, 117.8, 115.9, 112.6; **HRMS (ESI+):** Calcd. for $C_{15}H_{10}N_2OH([M+Na]^+)$: 235.0871, found: 235.0875

Mechanistic studies:

Intramolecular competitive reaction of aldehyde with anilines:

In a 8 mL screw-cap reaction vial, benzaldehyde (61 mg, 0.5 mmol, 1.0 equiv), **L3** (61 mg, 0.5 mmol, 1.0 equiv) and **L11 (**61 mg, 0.5 mmol, 1.0 equiv) were taken in 2.0 mL TFE solvent and allowed to stir at rt for 24 h. The reaction mixture was filtered through a Celite pad, the filtrate was evaporated on vacuo. The ratio of the imine formation was determined by crude ^{1}H NMR analysis (see ^{1}H NMR spectrum SI-113).

Synthesis of pentadeutero-acetophenone (deutrio 2b):



In an oven and vaccum dried 25 mL single neck round bottom flask, benzene-d_6 (0.5 mL, 5.65 mmol, 1.0 equiv) and $AlCl_3$ (0.95 g, 7.85 mmol, 1.4 equiv) were taken in 2 mL of CS_2 as solvent and cooled the reaction mixture to 0 °C. To this solution, acetyl chloride in 3 mL CS_2 was added drop wise, and the resulting reaction mixture was allowed to stir at rt for 4 h, and subsequently at 50 °C over 6 h. The reaction mixture was cooled to rt and quenched with ice water and extracted with dichloromethane. Combined organic layer was washed with saturated aqueous solution of Na_2CO_3 followed by brine. Dried over anhy. Na_2SO_4 and evaporated on the vacuo and the crude reaction mixture was purified on silica column (2% EtOAc in petroleum ether) to get pentadeuterated acetophenone **deutrio 2b** as an yellow oil (0.49 g, 3.92 mmol, 69% yield).

Mechanistic investigation (H/D) exchange reaction:

Deuterium incorporation:

In a 8-mL screw cap reaction vial, acetophenone **2b** (0.2 mmol), CD_3CO_2D (10 equiv), [RhCp*$(OAc)_2$] catalyst (5.0 mol %), $AgPF_6$ (10 mol %), and **L11** (50 mol %) were added in TFE (1 mL) as solvent. This vial was sealed with a screw cap, stirred it at 100 °C for 24 h, concentrated under vacuo. The yield of starting material was determined by crude ^{1}H NMR analysis (see the Supporting Information for ^{1}H NMR spectra SI-116). The crude product was purified on a silica gel column using EtOAc/petroleum etherto give Deuterium enriched mixture of products **2b** and **deutrio-2b** in 98% yield. The 11% deuterium incorporation was calculated by ^{1}H NMR spectroscopy (See the Supporting Information for ^{1}H NMR spectra SI-114).

Competitive experiment:

In a 8 mL screw cap reaction vial, acetophenone (**2b**, 0.096 mmol), pentadeuterated acetophenone (**deutrio-2b**, 100% D, 0.096 mmol), dioxazolone **1a** (0.23 mmol), [RhCp*$(OAc)_2$] catalyst (5.0 mol %), $AgPF_6$ (10 mol %),and **L11** (50 mol %) were added followed by the addition of TFE (1.91 mL). Thevial was sealed with a screw cap, stirred it at 100 °C for 6 h, filtered over a Celite pad. The solvent, EtOAc, was evaporated on vacuo. Product yield was calculated by crude ^{1}H NMR spectral analysis using 2,4,6-trimethoxy benzene as an internal standard. The product ratio (**3ab**/**deutrio-3ab** = 2.2:1) was determined by ^{1}H NMR spectral analysis after the purification (see the Supporting Information for ^{1}H NMR spectra SI-115, 116).

References:

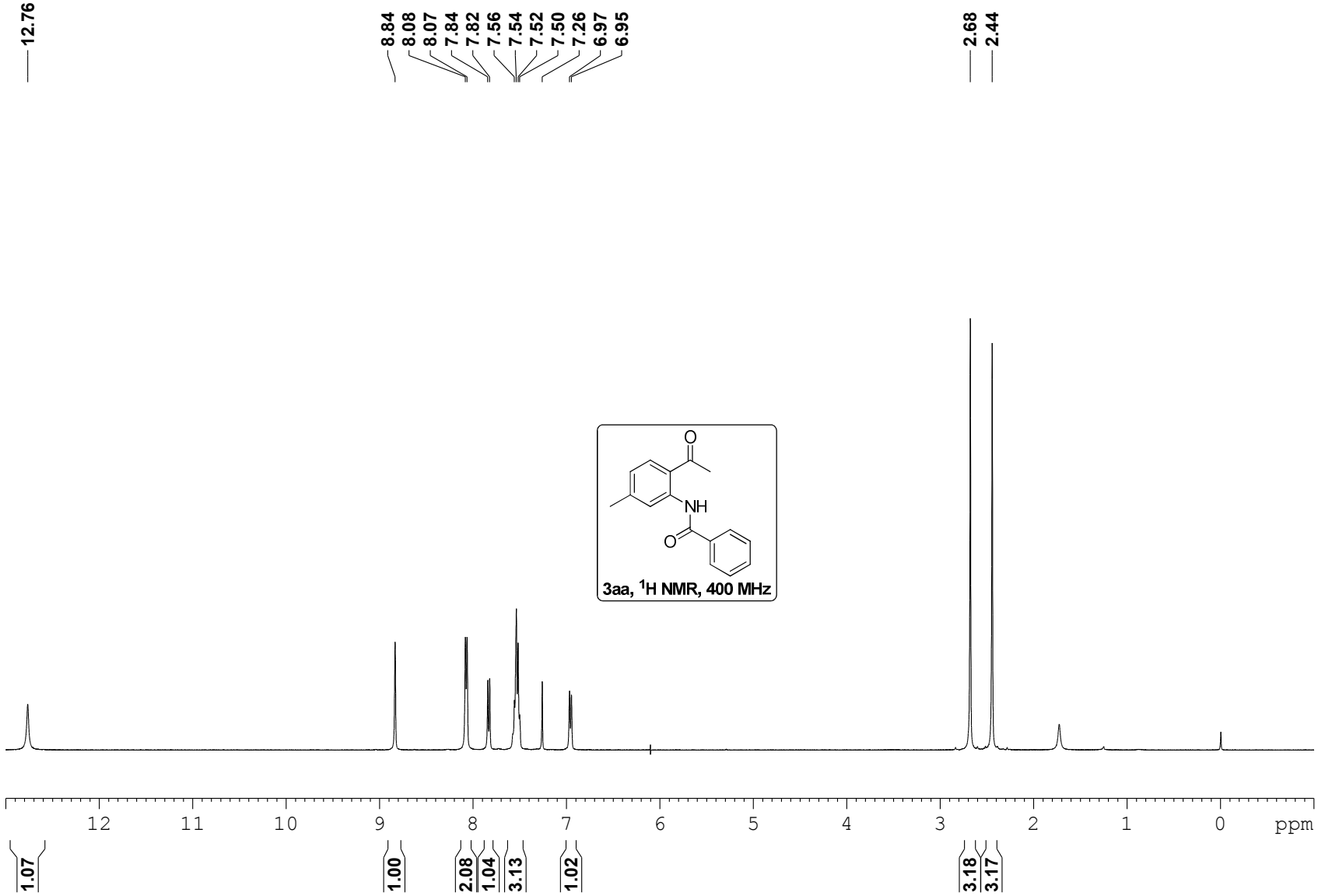
1. F. Romanov-Michailidis, K. F. Sedillo, J. M. Neely and T. Rovis, *J. Am. Chem. Soc.* 2015, **137**, 8892-8895.

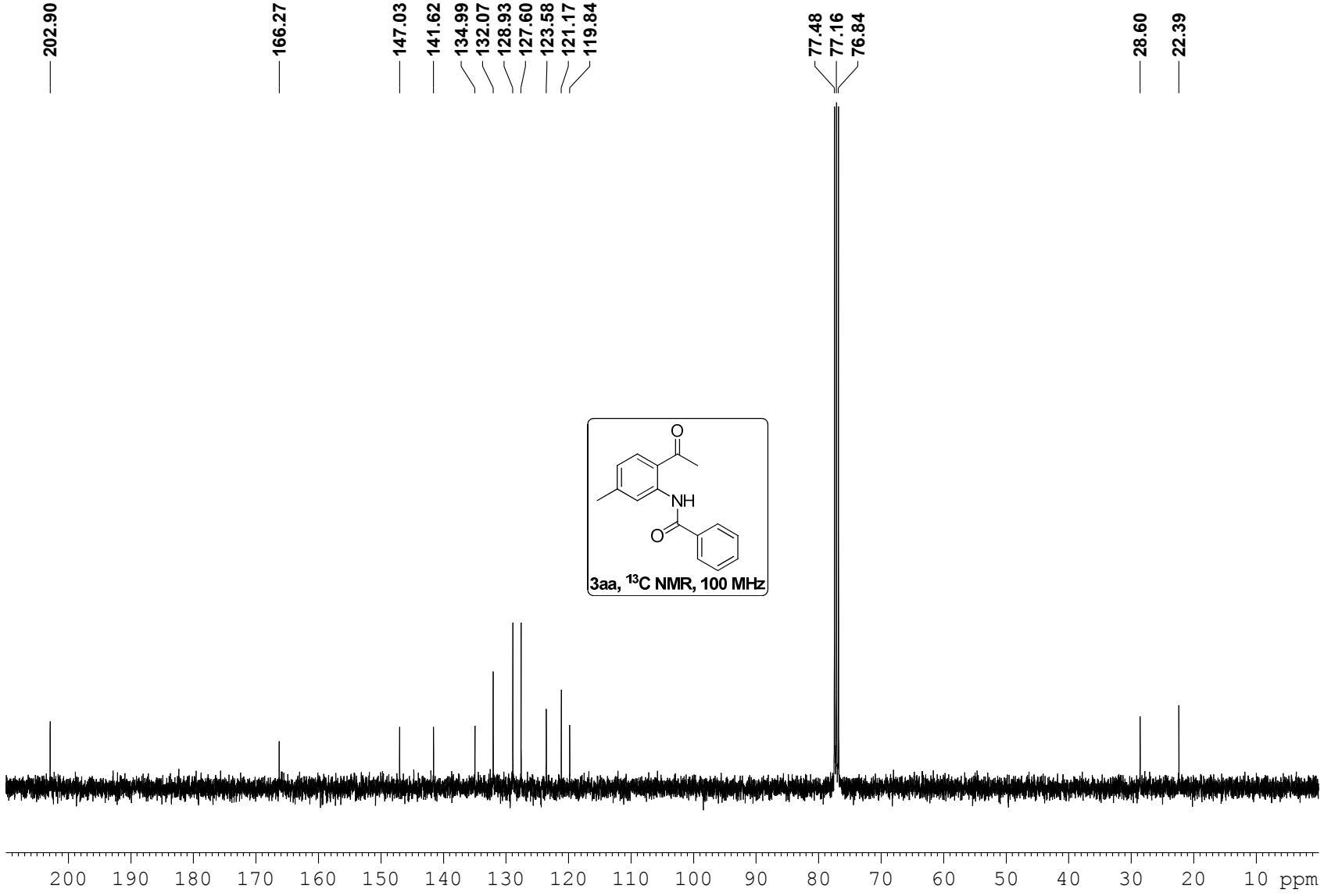
2. M. P. Huestis, *J. Org. Chem.* 2016, **81**, 12545-12552.

3. A. E. Hande and K. R. Prabhu, *J. Org. Chem.,* 2017, **82**, 13405-13413.

4. D. Mu, X. Wang, G. Chen and G. He, *J. Org. Chem.* 2017, **82**, 4497-4503.

^{1}H NMR and ^{13}C NMR spectra for all compounds

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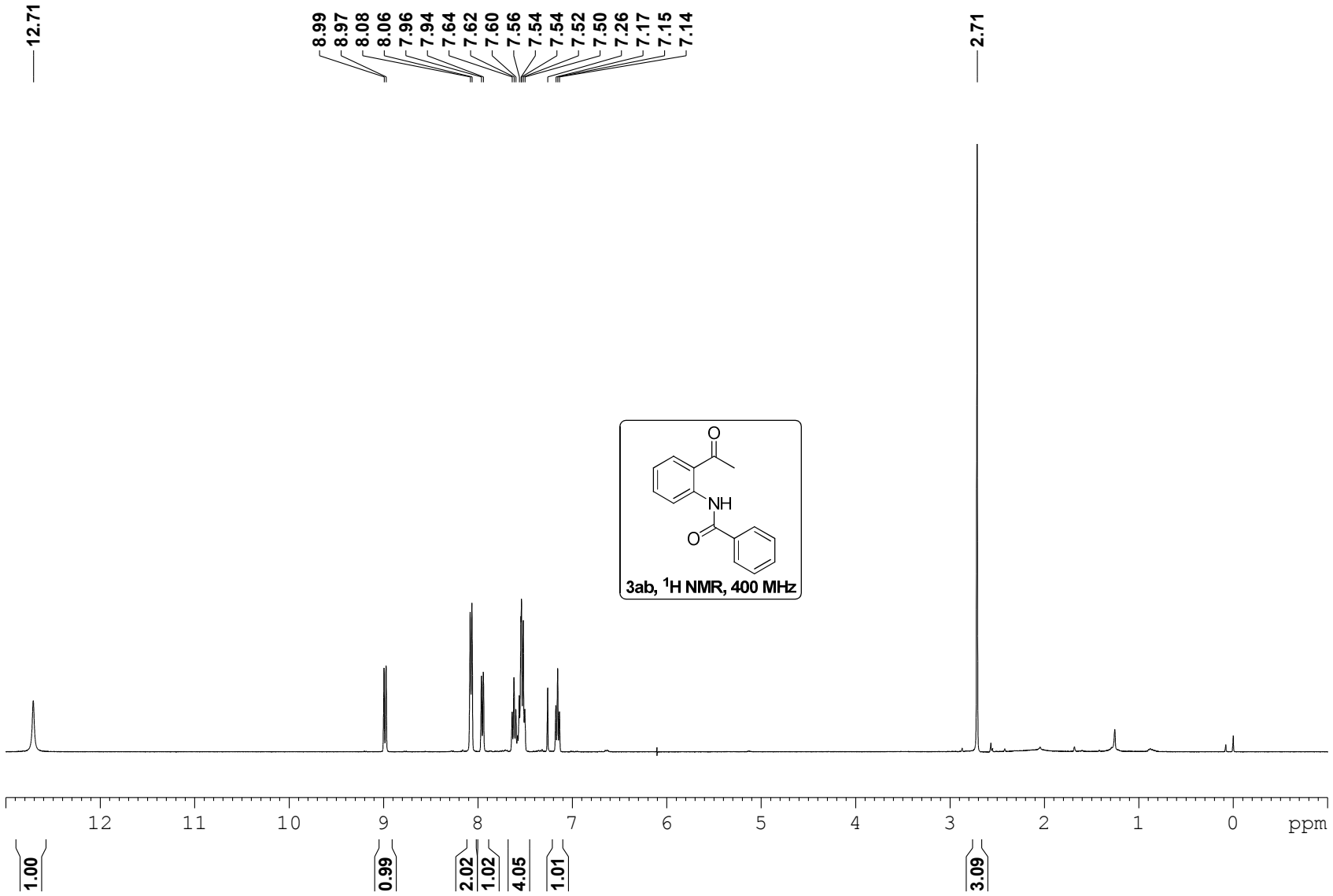
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7.50
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O
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12
11
10
9
8
7
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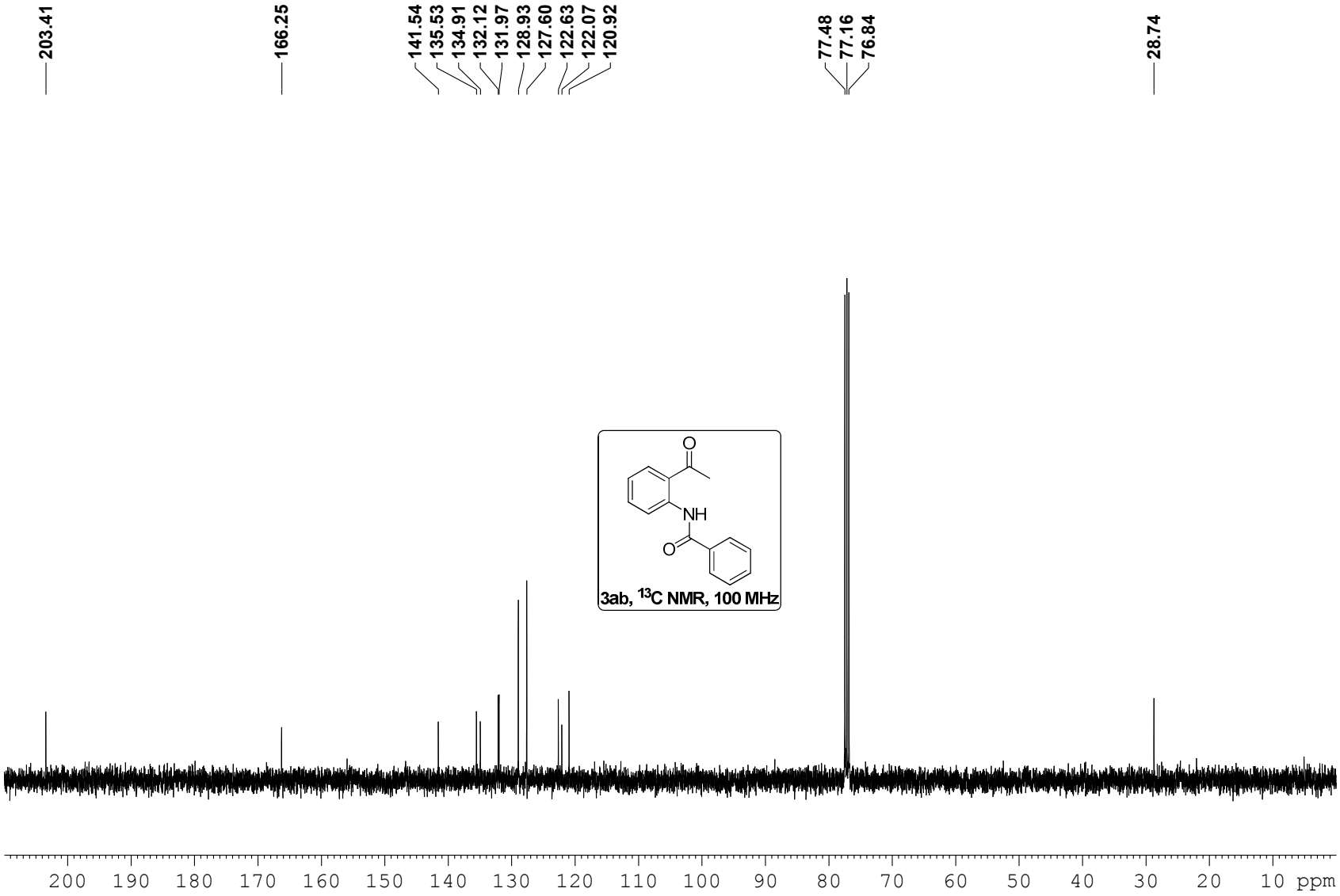
1.01
3.09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O
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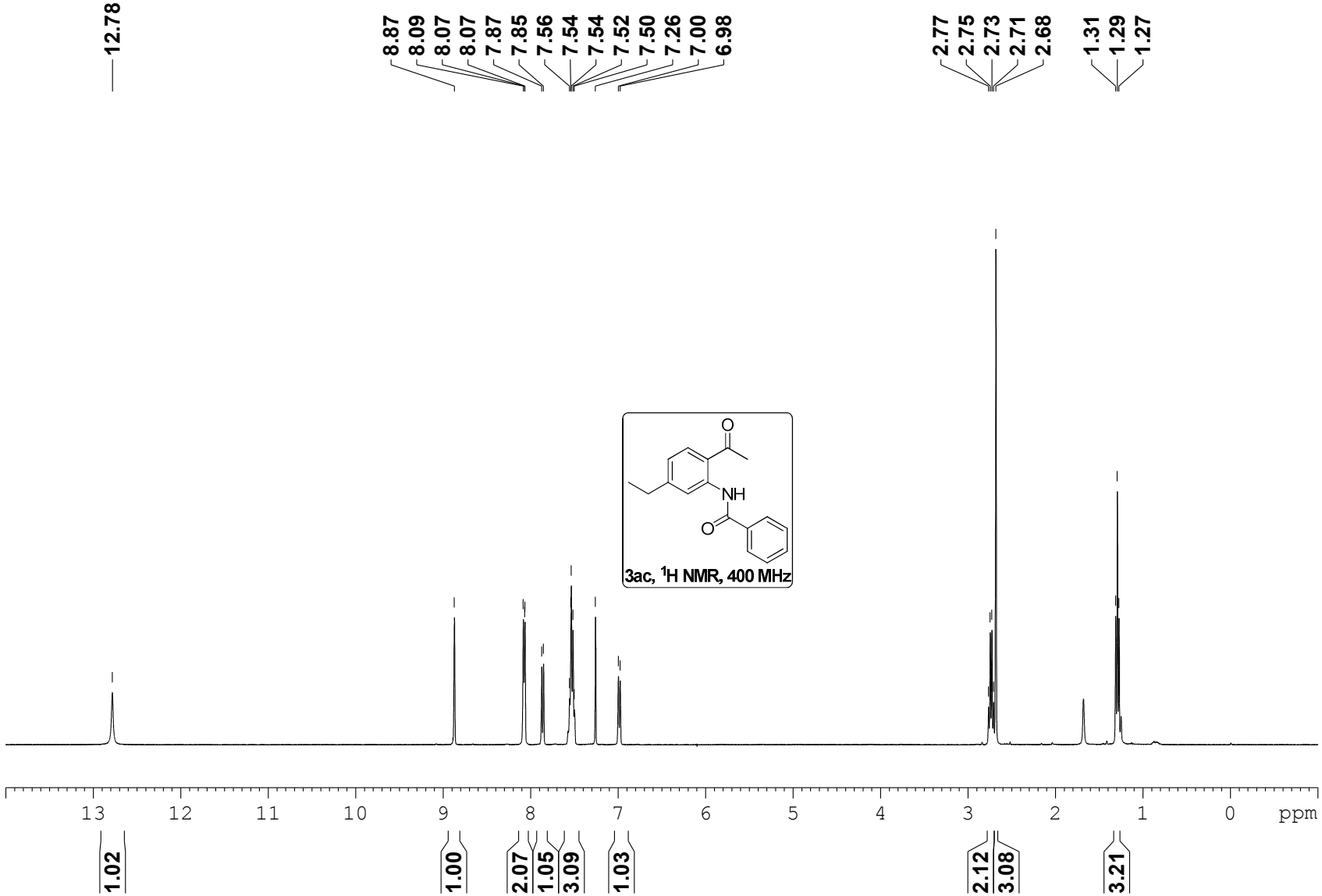
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O
NH
O
3ac, 1H NMR, 400 MHz
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12
11
10
9
8
7
6
5
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3.09
1.03
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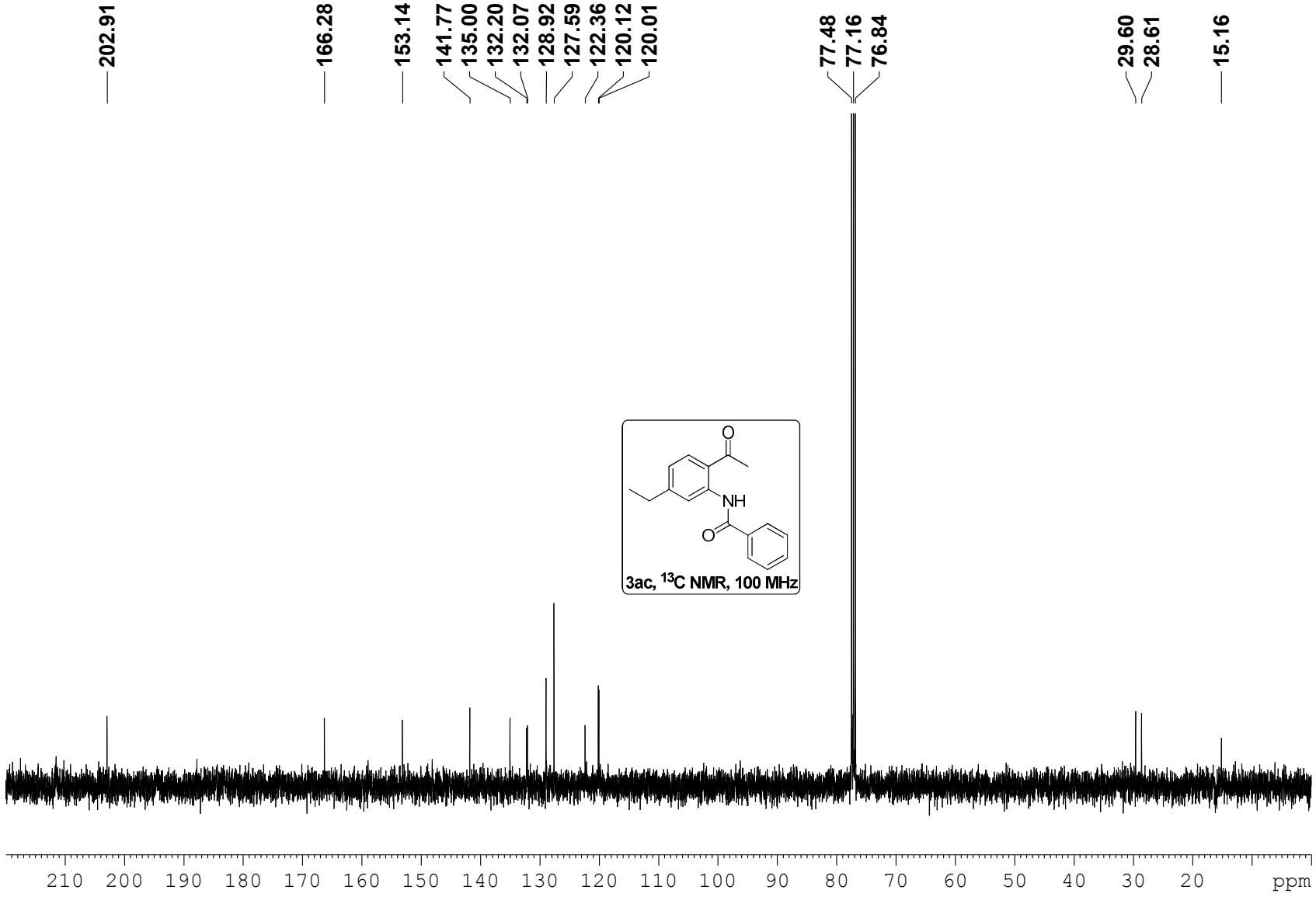
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O
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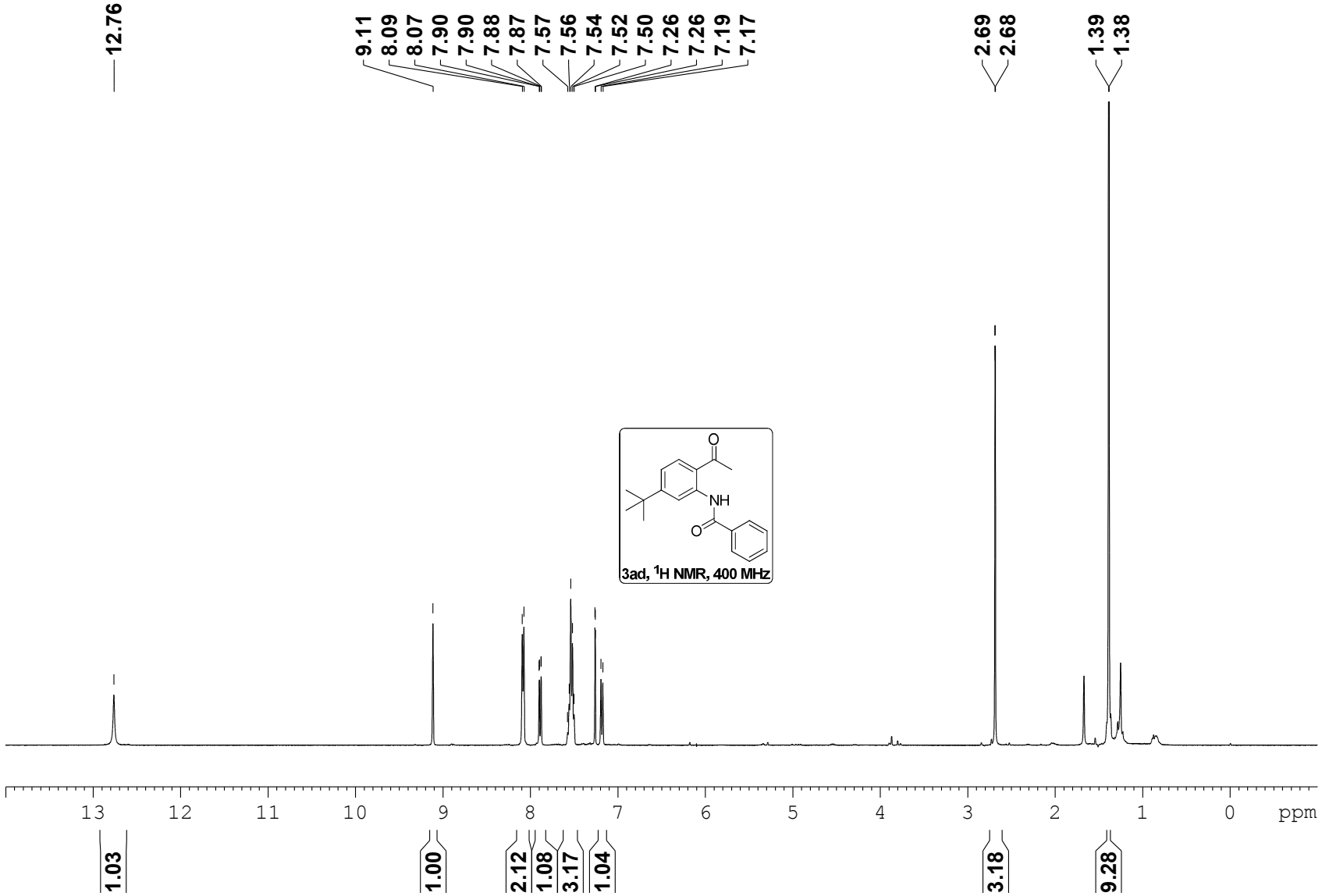
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7.19
7.17
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1.38
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NH
O
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12
11
10
9
8
7
6
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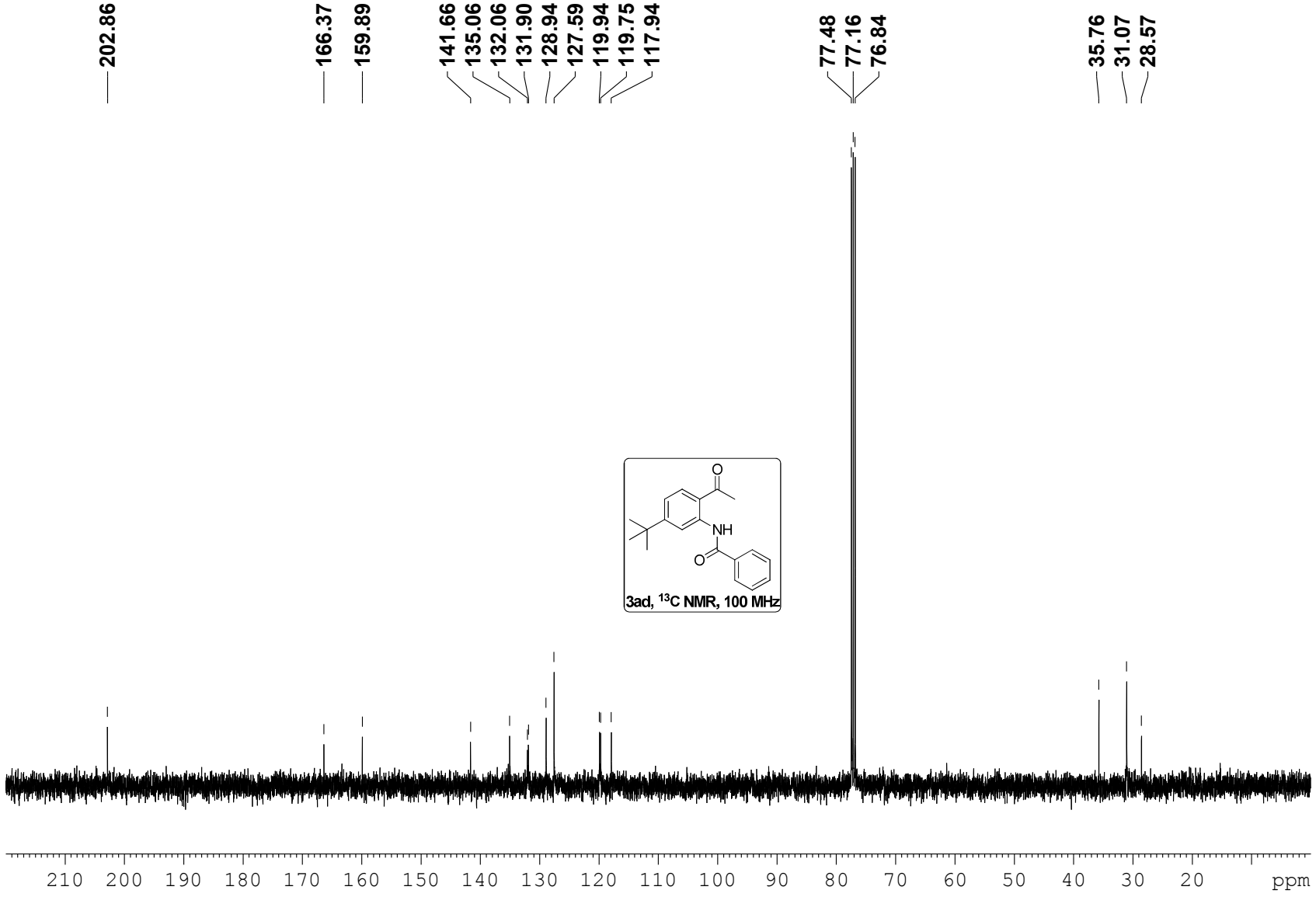
1.04
3.18
9.28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77.16
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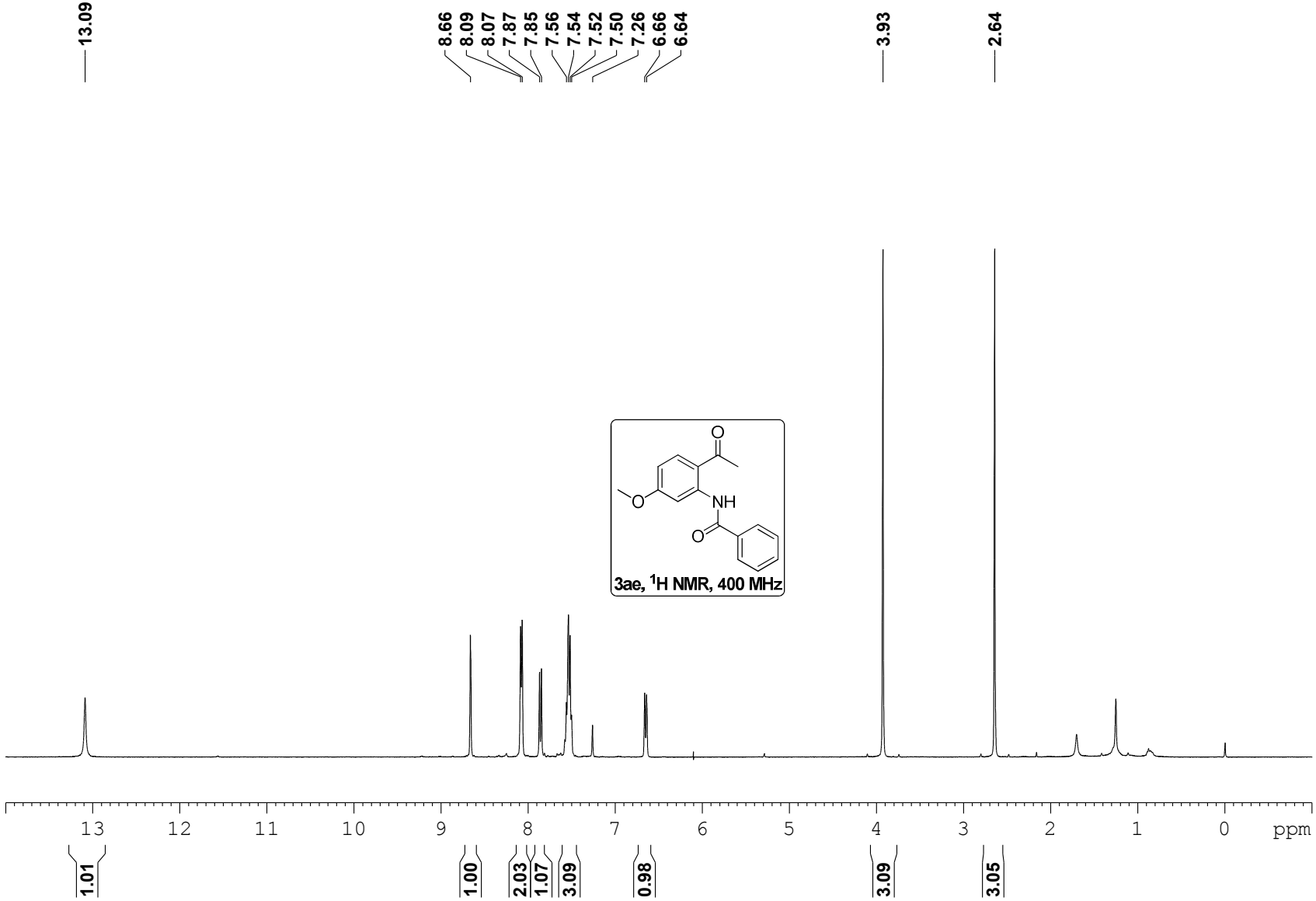
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O
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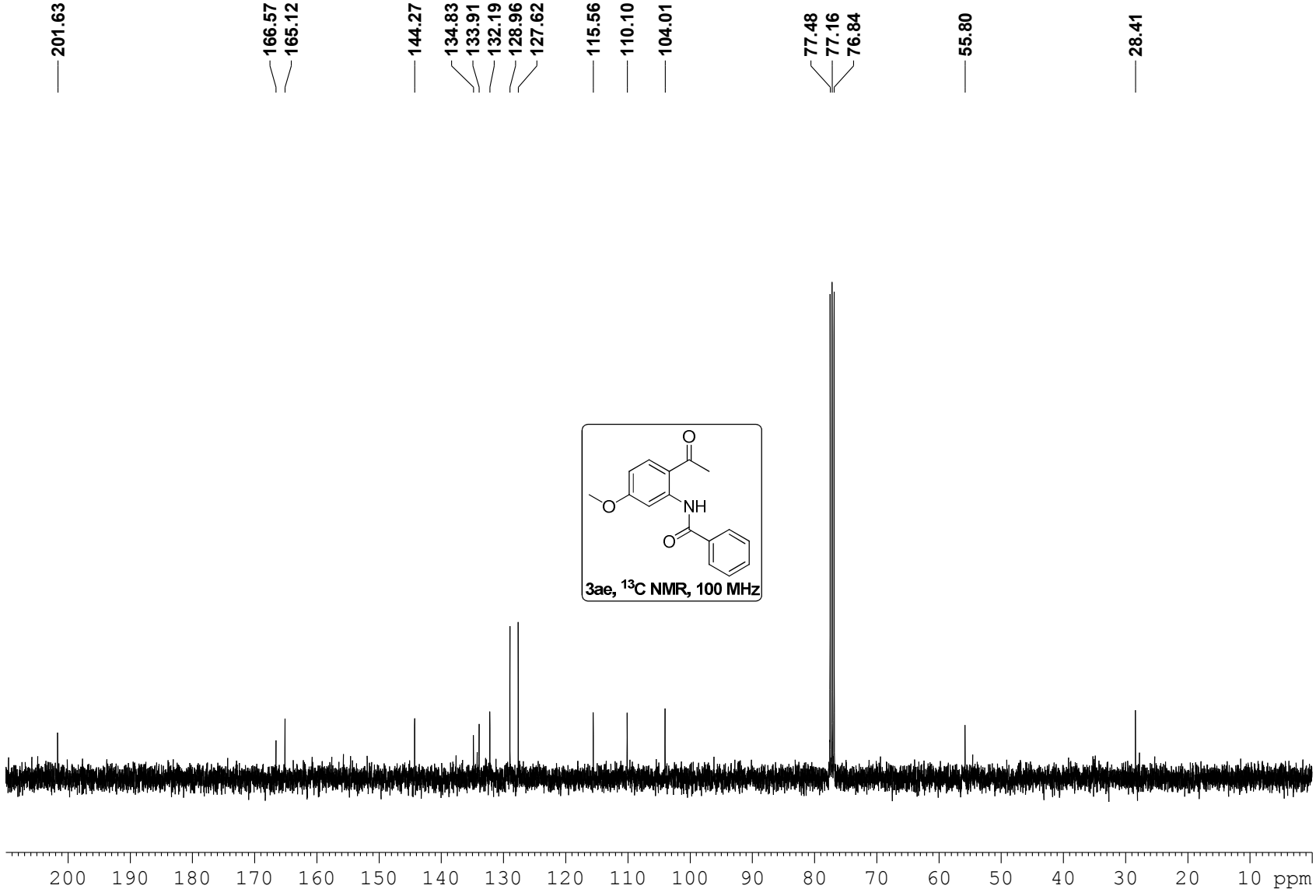
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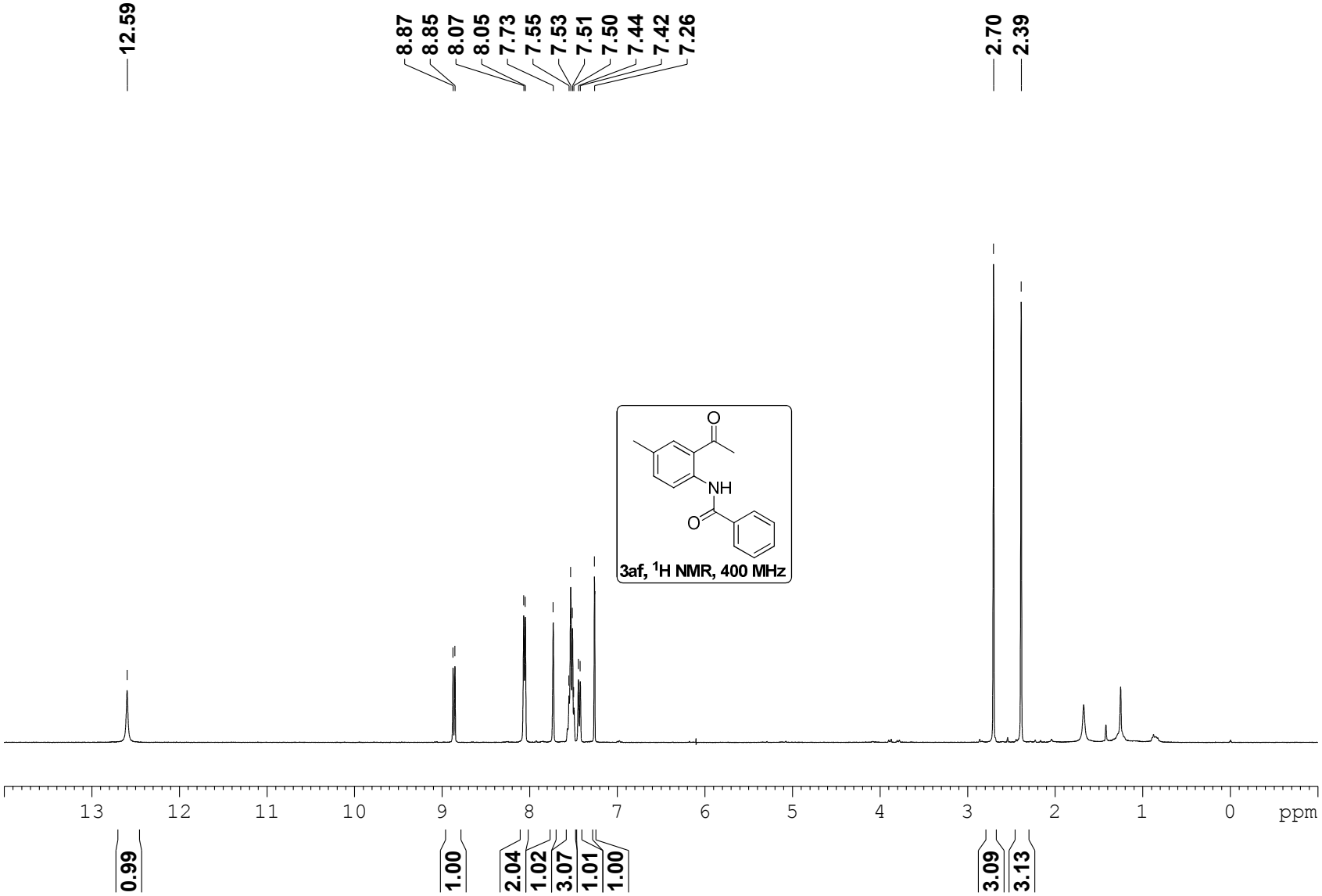
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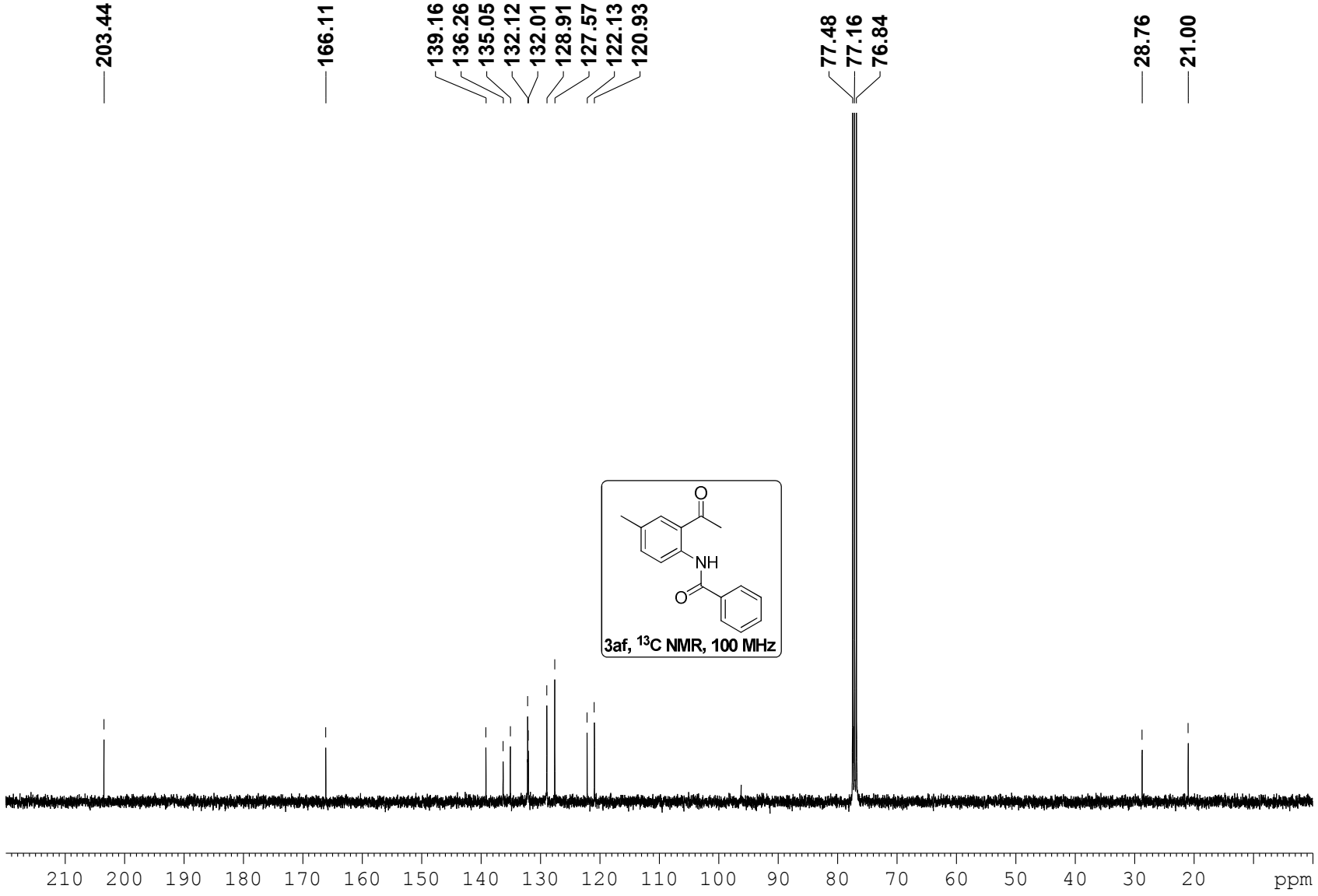
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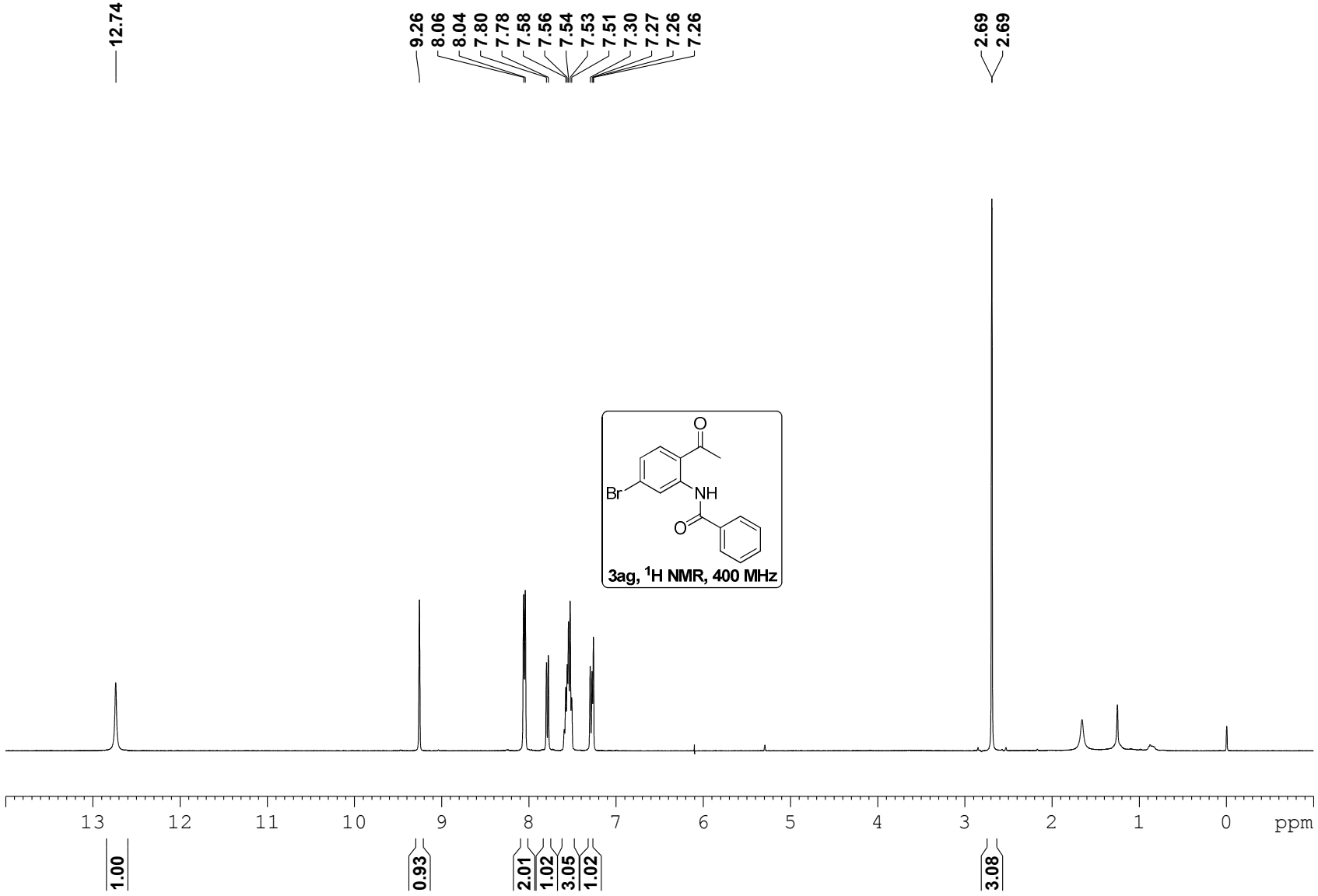
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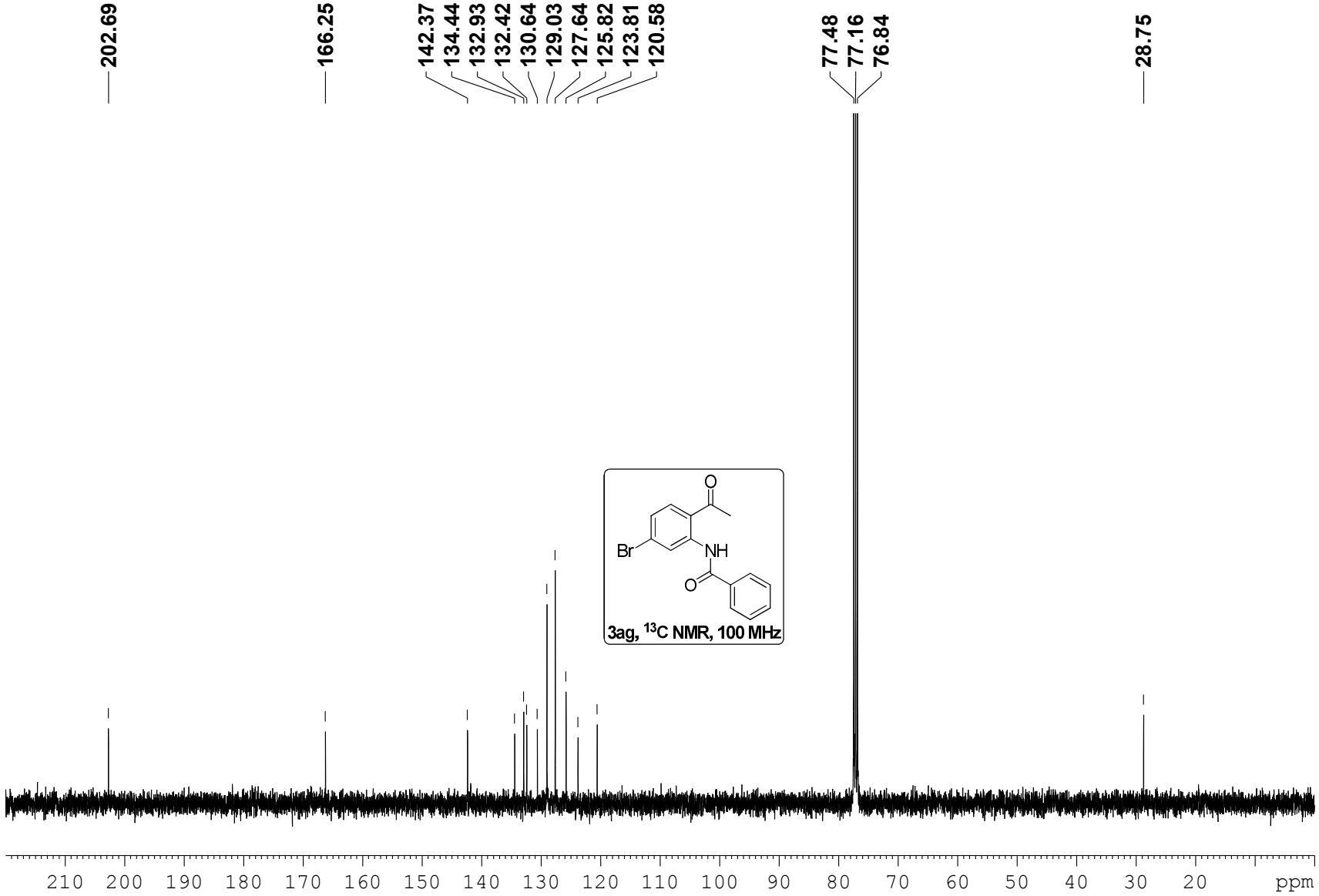
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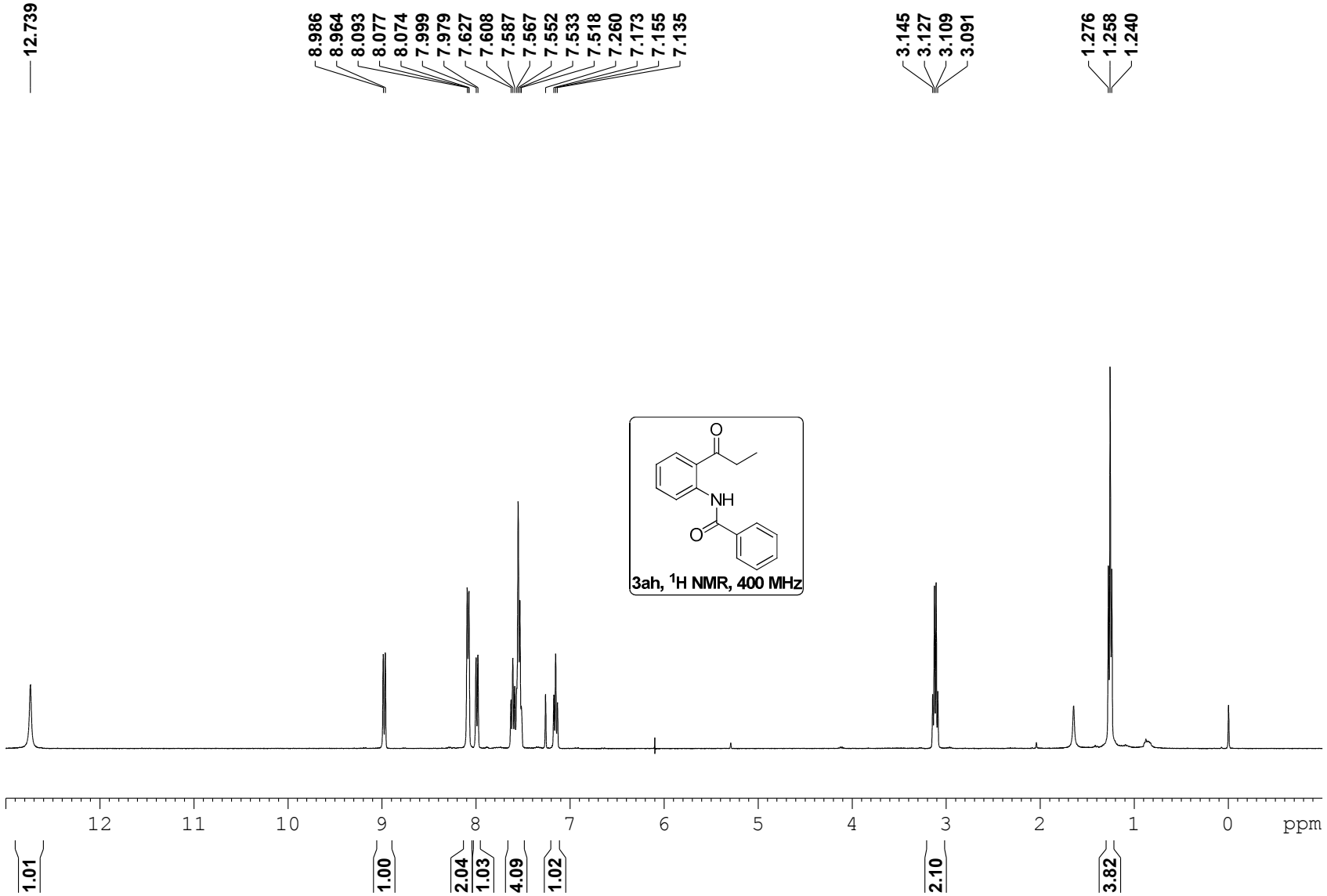
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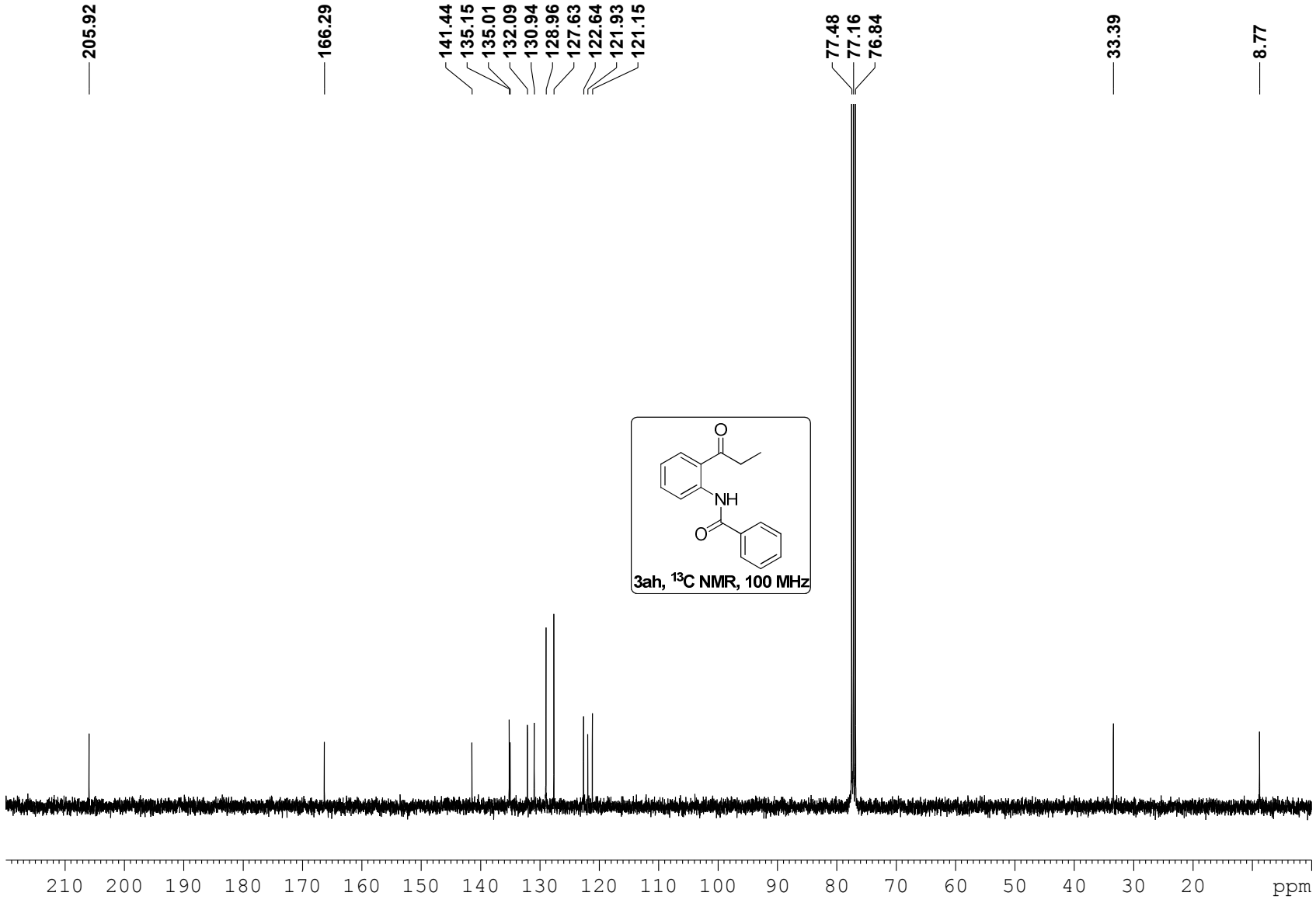
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77.16
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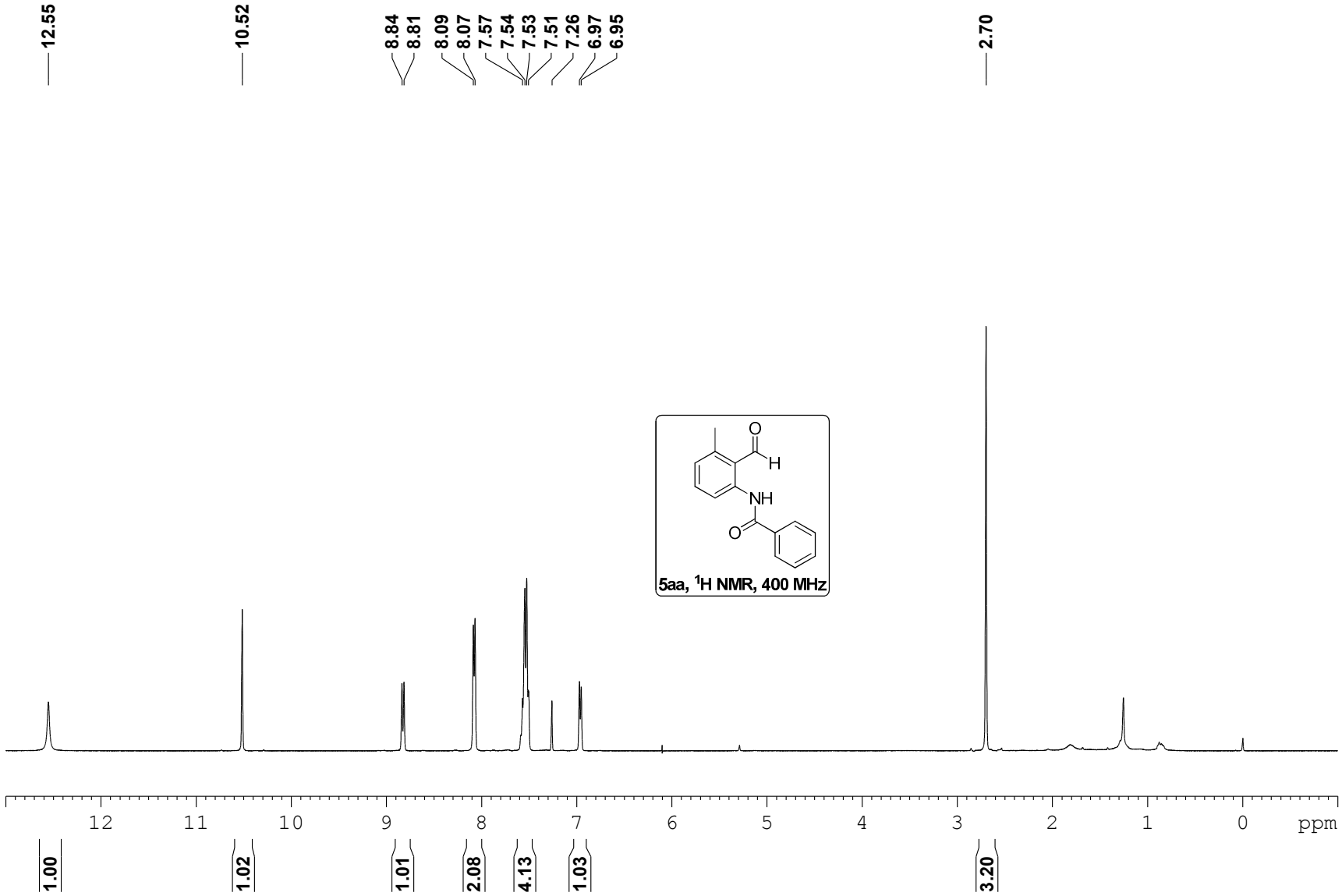
33.39
8.77
O
NH
O
3ah, 13C NMR, 100 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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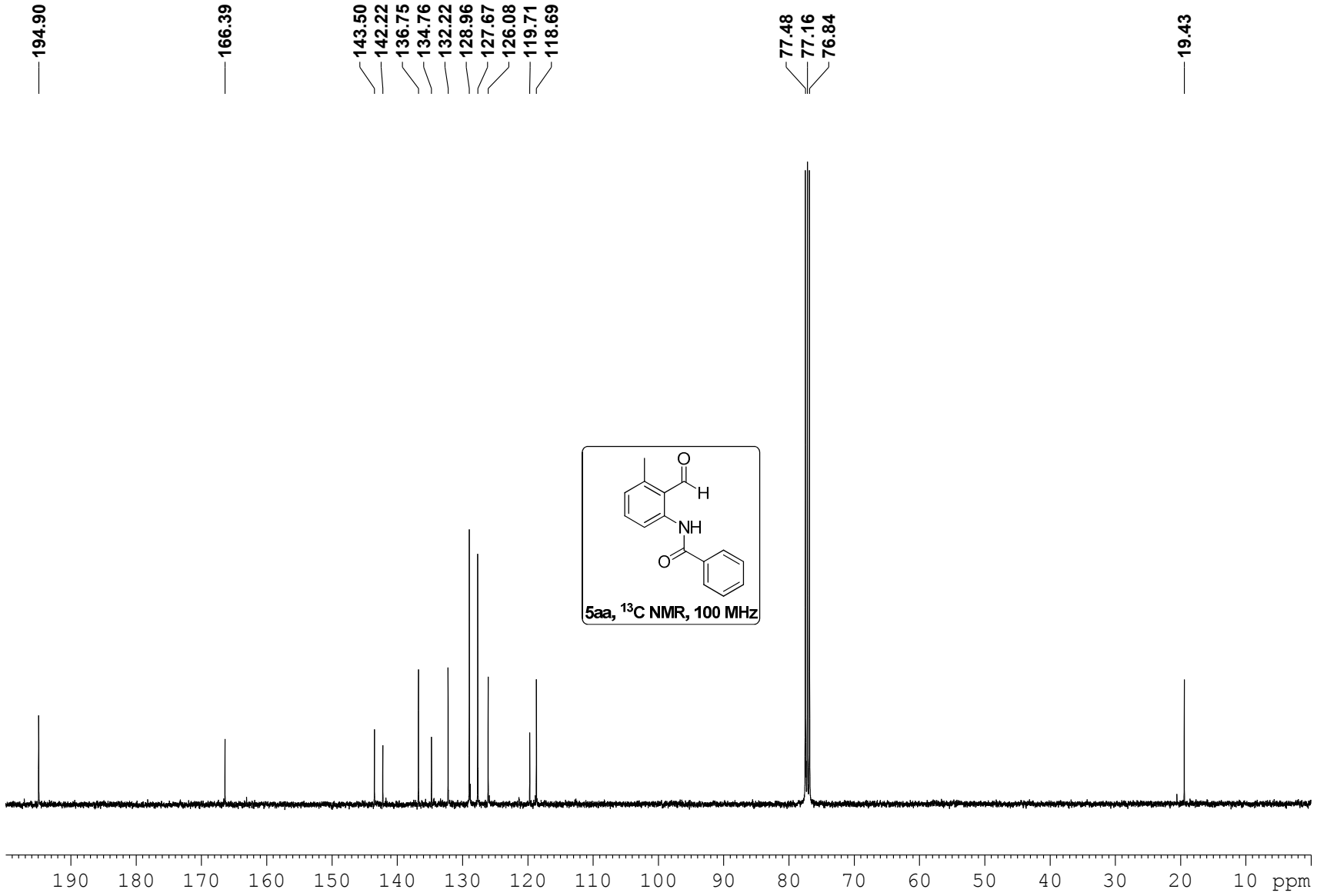
10.52
8.84
8.81
8.09
8.07
7.57
7.54
7.53
7.51
7.26
6.97
6.95
2.70
O
H
NH
O
5aa, ^{1}H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
1.01
2.08
4.13
1.03
3.20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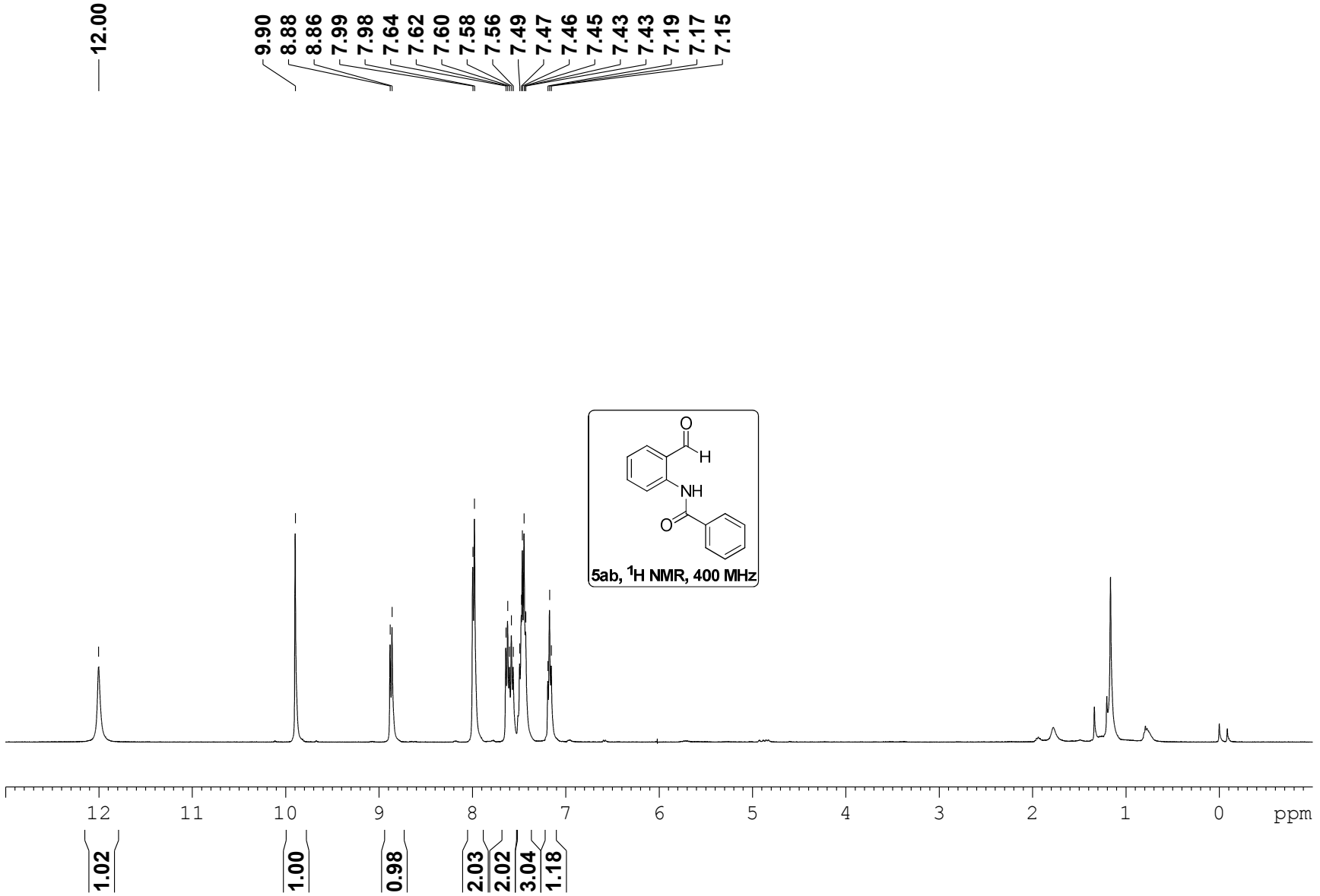
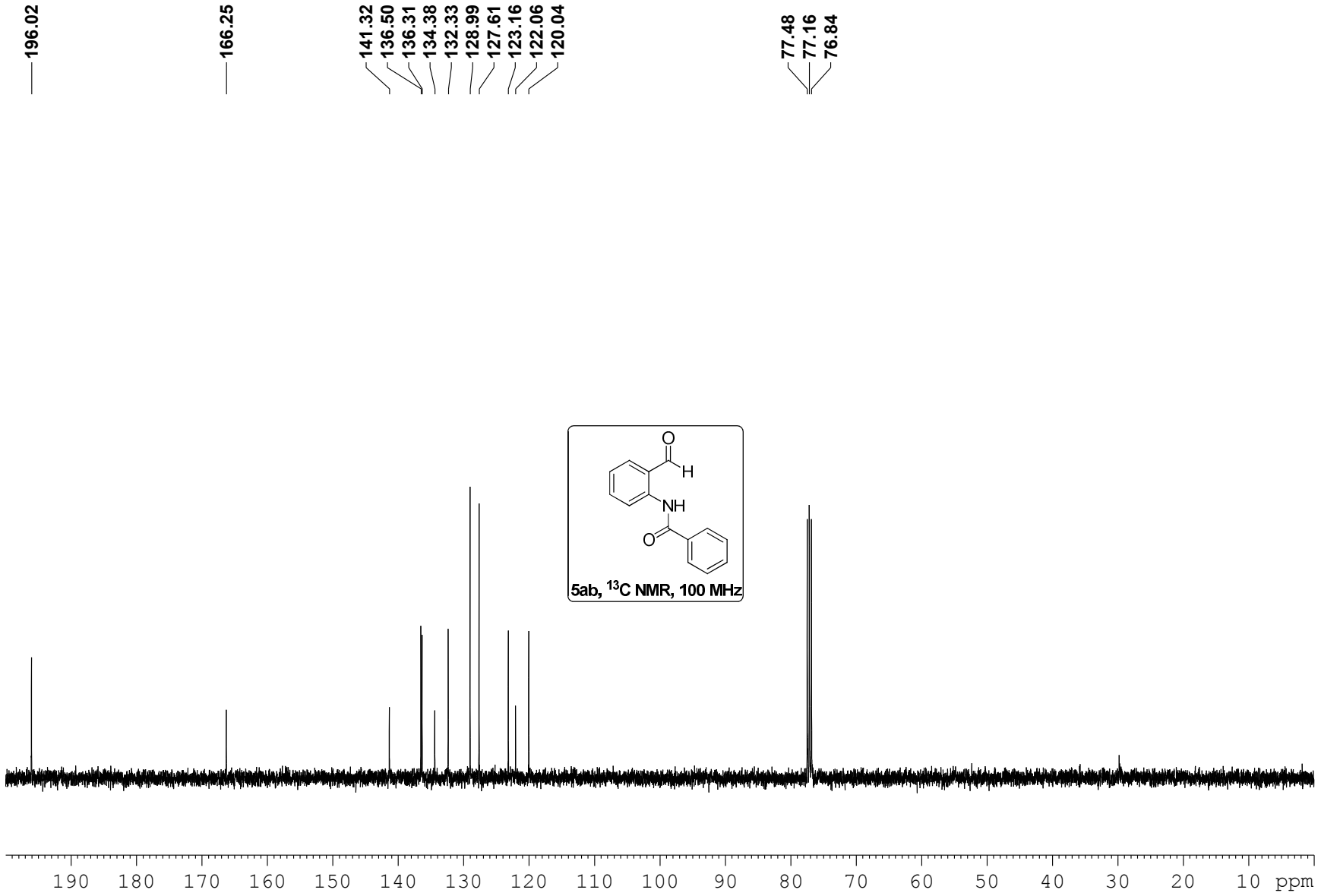
166.39
143.50
142.22
136.75
134.76
132.22
128.96
127.67
126.08
119.71
118.69
77.48
77.16
76.84
19.43
O
H
NH
O
5aa, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


12.00
9.90
8.88
8.86
7.99
7.98
7.64
7.62
7.60
7.58
7.56
7.49
7.47
7.46
7.45
7.43
7.43
7.19
7.17
7.15
O
H
NH
O
5ab, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.00
0.98
2.03
2.02
3.04
1.18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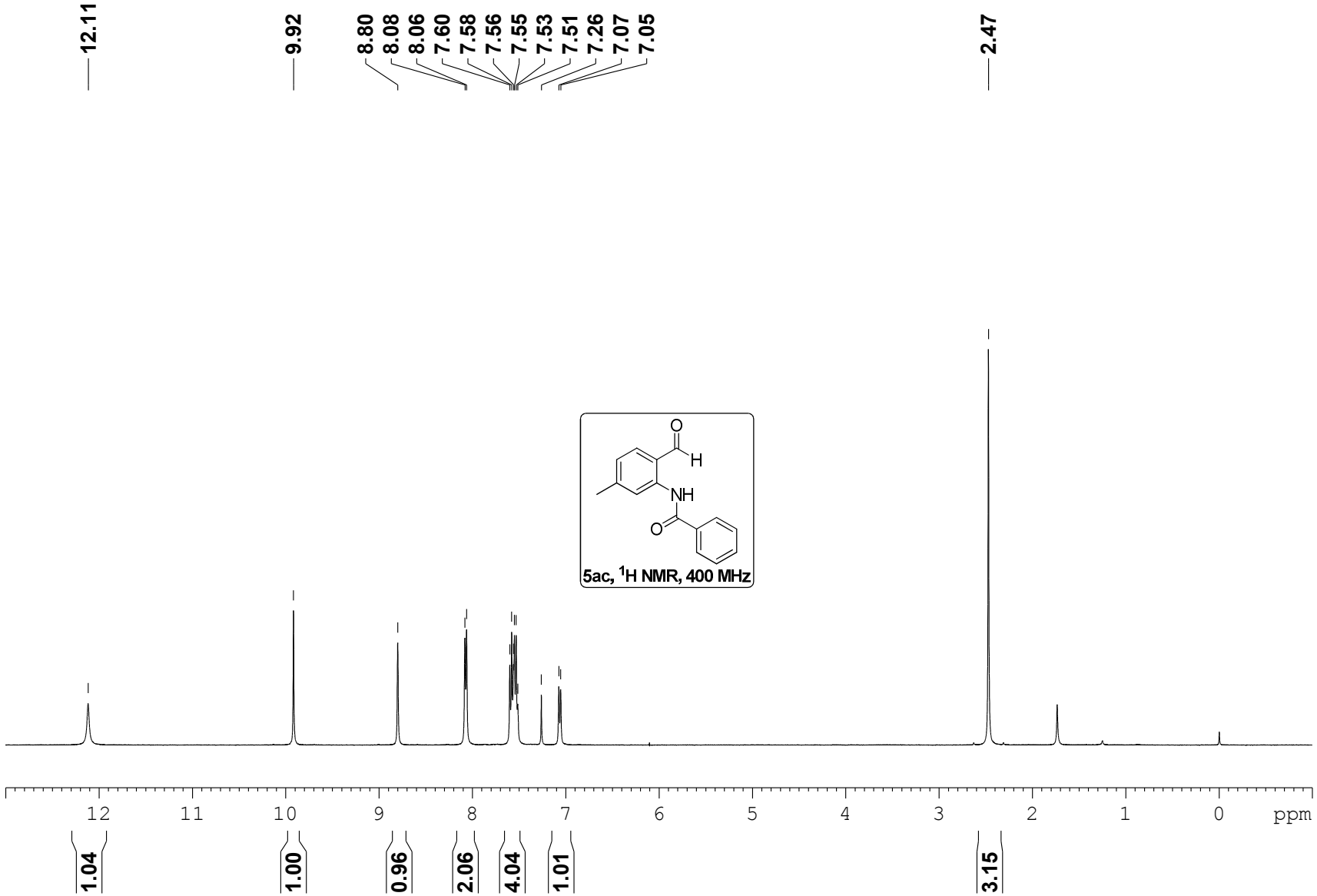
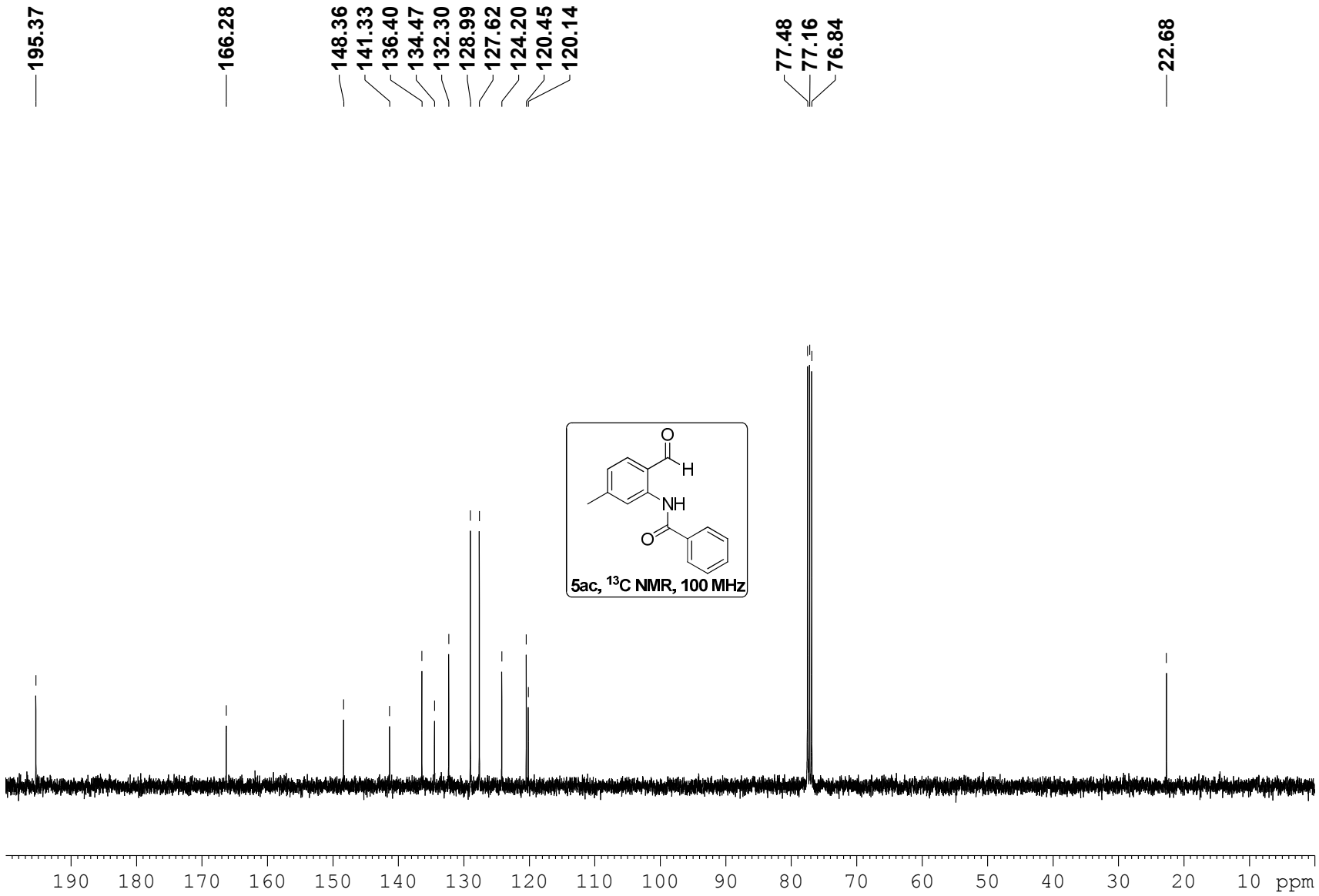
166.25
141.32
136.50
136.31
134.38
132.33
128.99
127.61
123.16
122.06
120.04
77.48
77.16
76.84
O
H
NH
O
5ab, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


12.11
9.92
8.80
8.08
8.06
7.60
7.58
7.56
7.55
7.53
7.51
7.26
7.07
7.05
2.47
O
H
NH
O
5ac, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.00
0.96
2.06
4.04
1.01
3.15


195.37
166.28
148.36
141.33
136.40
134.47
132.30
128.99
127.62
124.20
120.45
120.14
77.48
77.16
76.84
22.68
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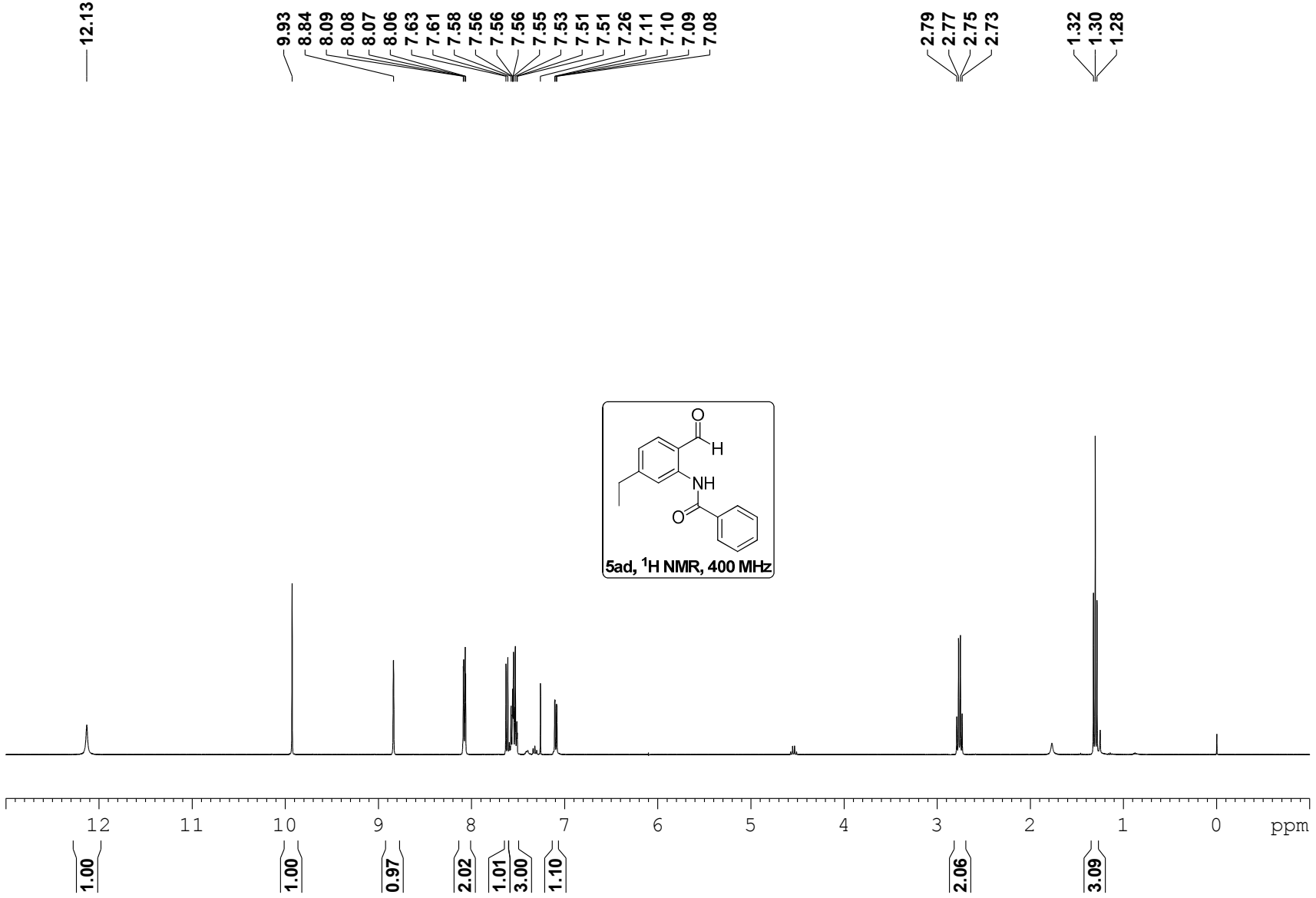
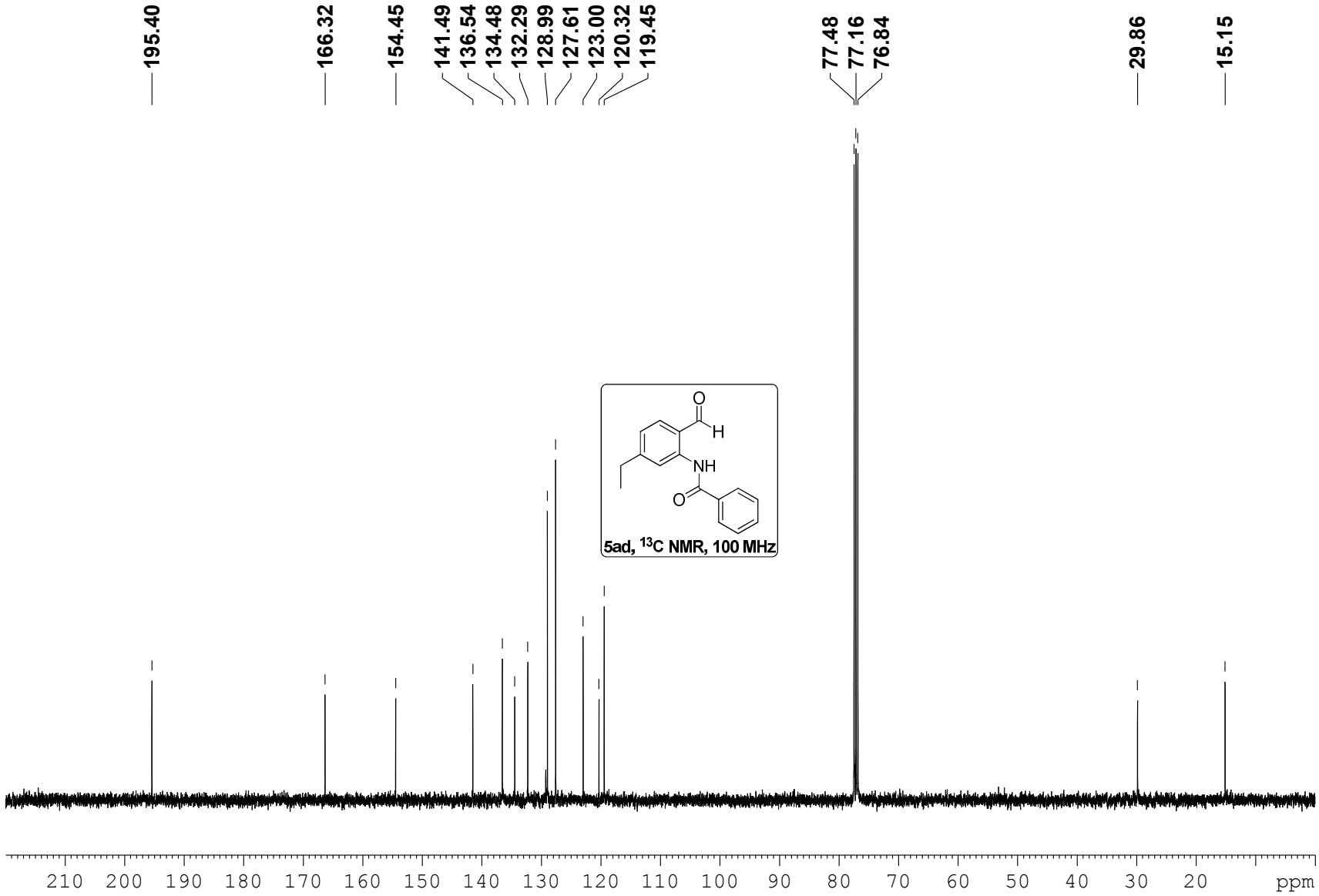
H
NH
O
5ac, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


12.13
9.93
8.84
8.09
8.08
8.07
8.06
7.63
7.61
7.58
7.56
7.56
7.56
7.55
7.53
7.51
7.51
7.26
7.11
7.10
7.09
7.08
2.79
2.77
2.75
2.73
1.32
1.30
1.28
O
H
NH
O
5ad, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
0.97
2.02
1.01
3.00
1.10
2.06
3.09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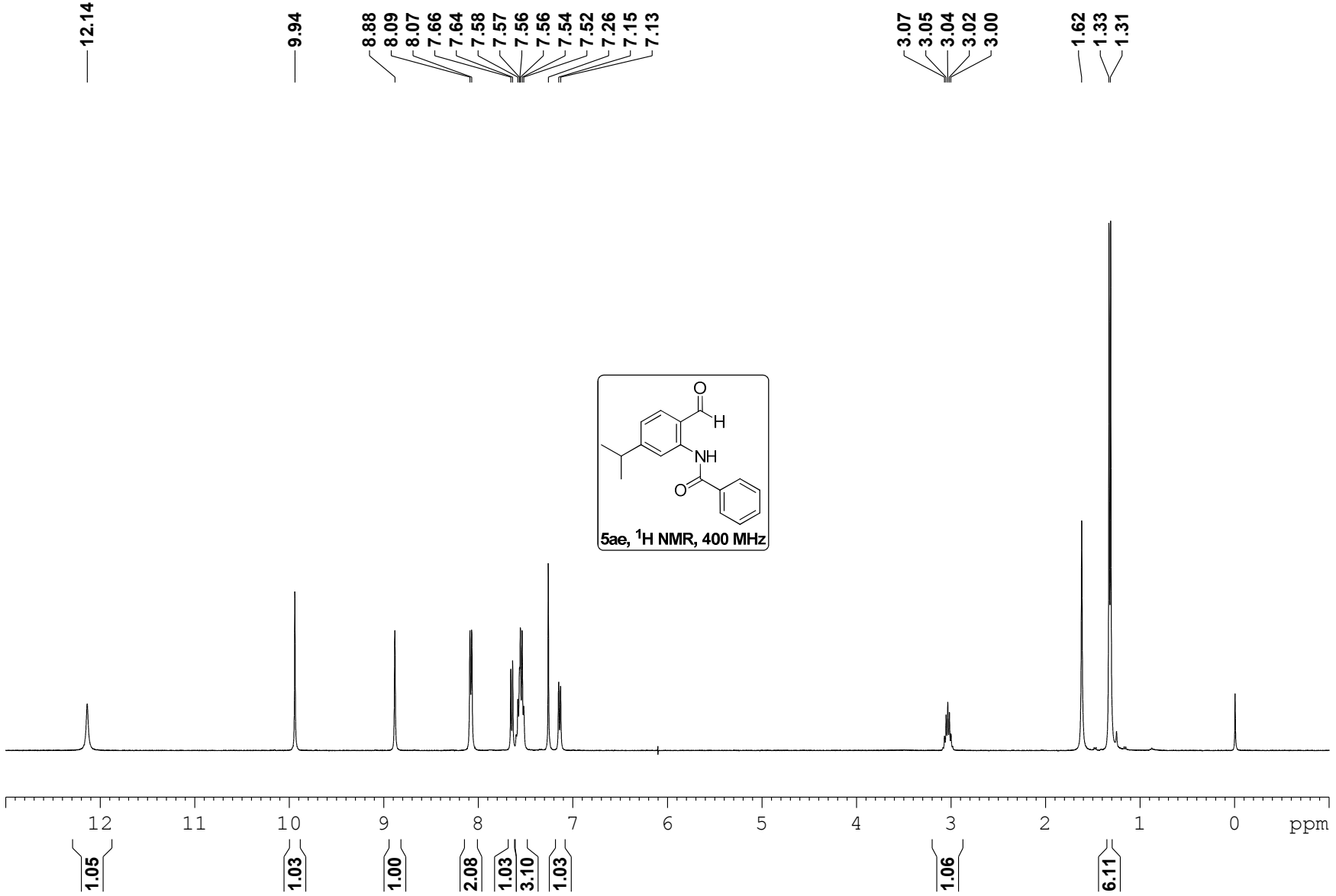
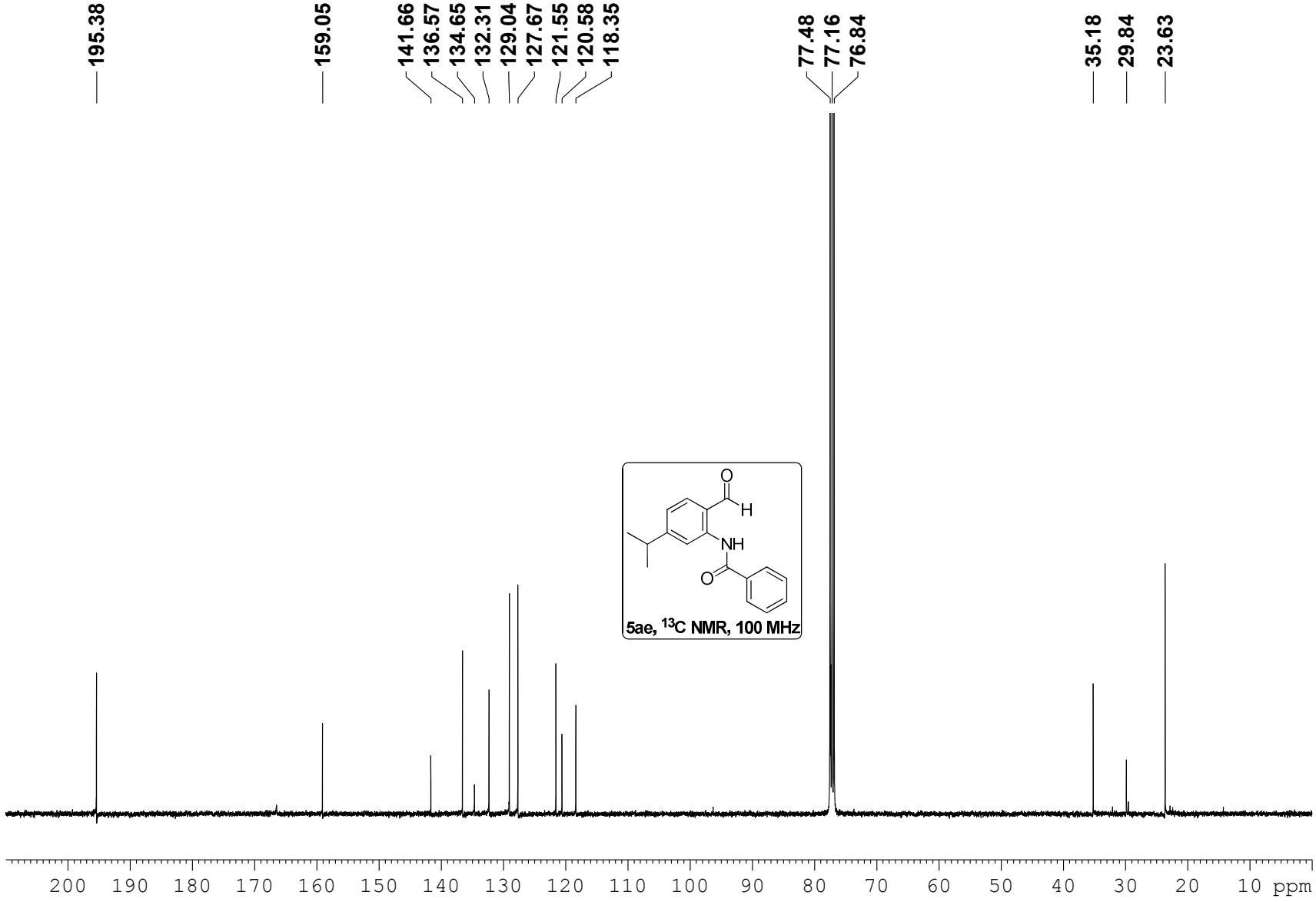
166.32
154.45
141.49
136.54
134.48
132.29
128.99
127.61
123.00
120.32
119.45
77.48
77.16
76.84
29.86
15.15
O
H
NH
O
5ad, 13C NMR, 100 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


12.14
9.94
8.88
8.09
8.07
7.66
7.64
7.58
7.57
7.56
7.56
7.54
7.52
7.26
7.15
7.13
3.07
3.05
3.04
3.02
3.00
1.62
1.33
1.31
O
H
NH
O
5ae, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.05
1.03
1.00
2.08
1.03
3.10
1.03
1.06
6.11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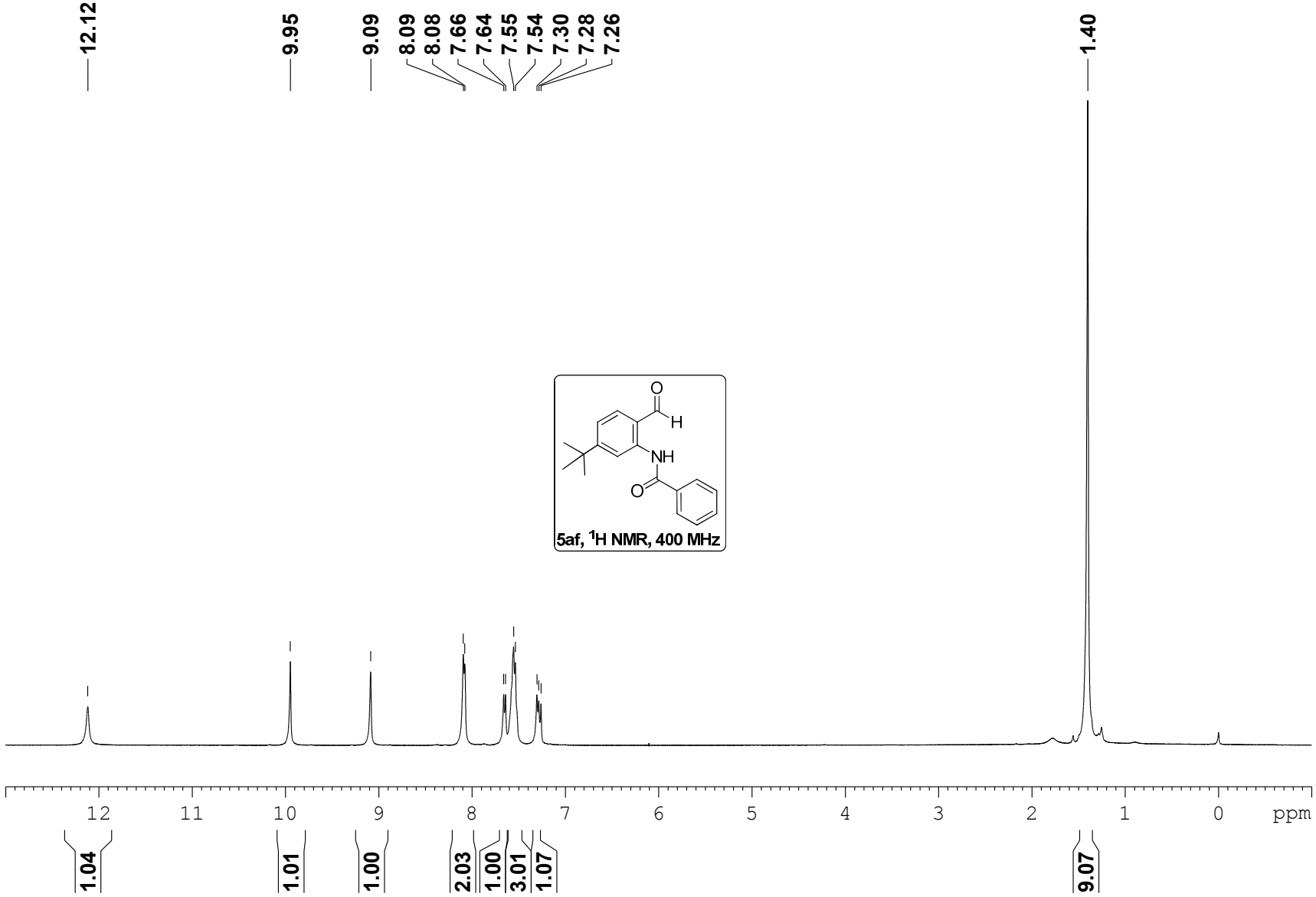
159.05
141.66
136.57
134.65
132.31
129.04
127.67
121.55
120.58
118.35
77.48
77.16
76.84
35.18
29.84
23.63
O
H
NH
O
5ae, 13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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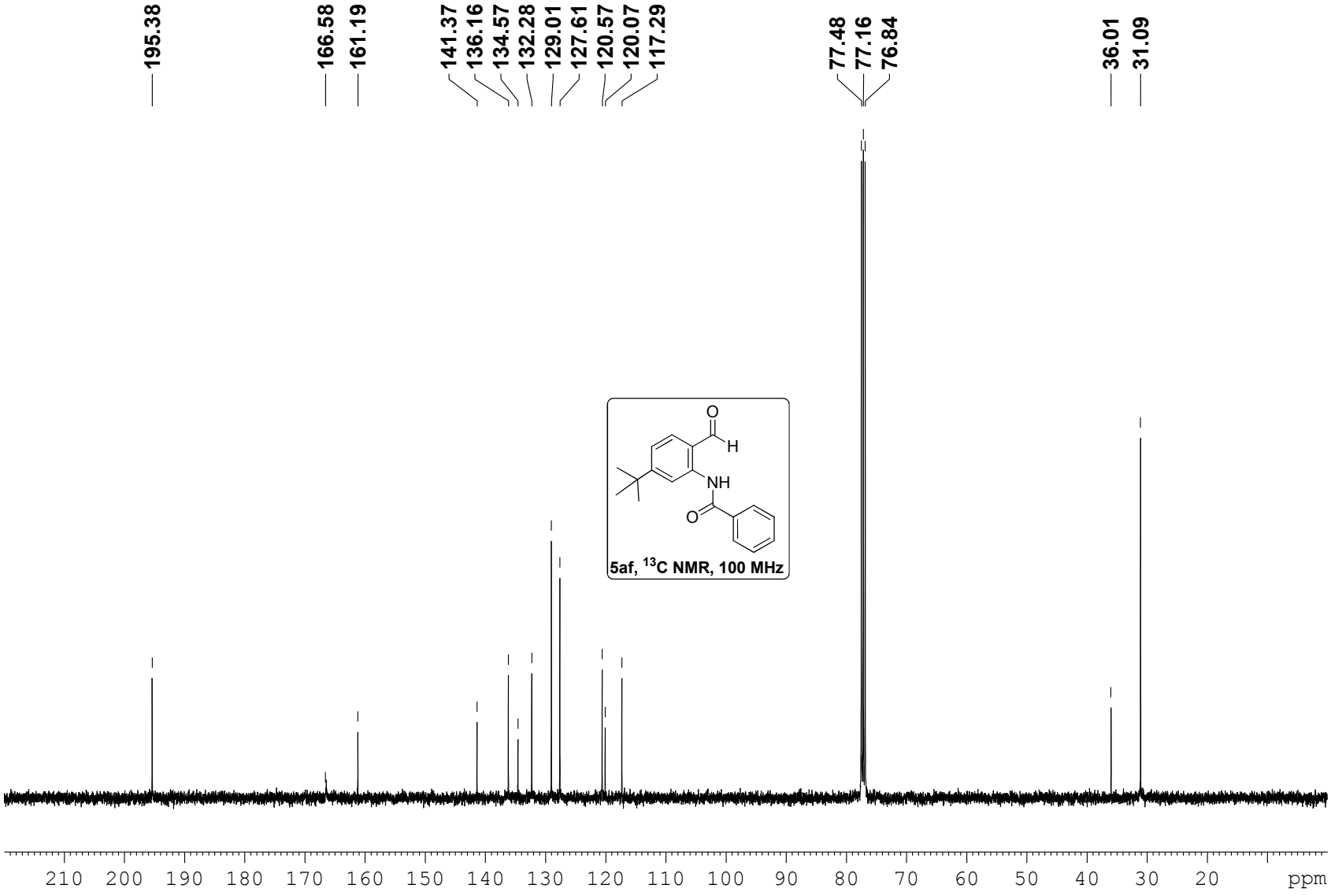
9.95
9.09
8.09
8.08
7.66
7.64
7.55
7.54
7.30
7.28
7.26
1.40
O
H
NH
O
5af, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.01
1.00
2.03
1.00
3.01
1.07
9.07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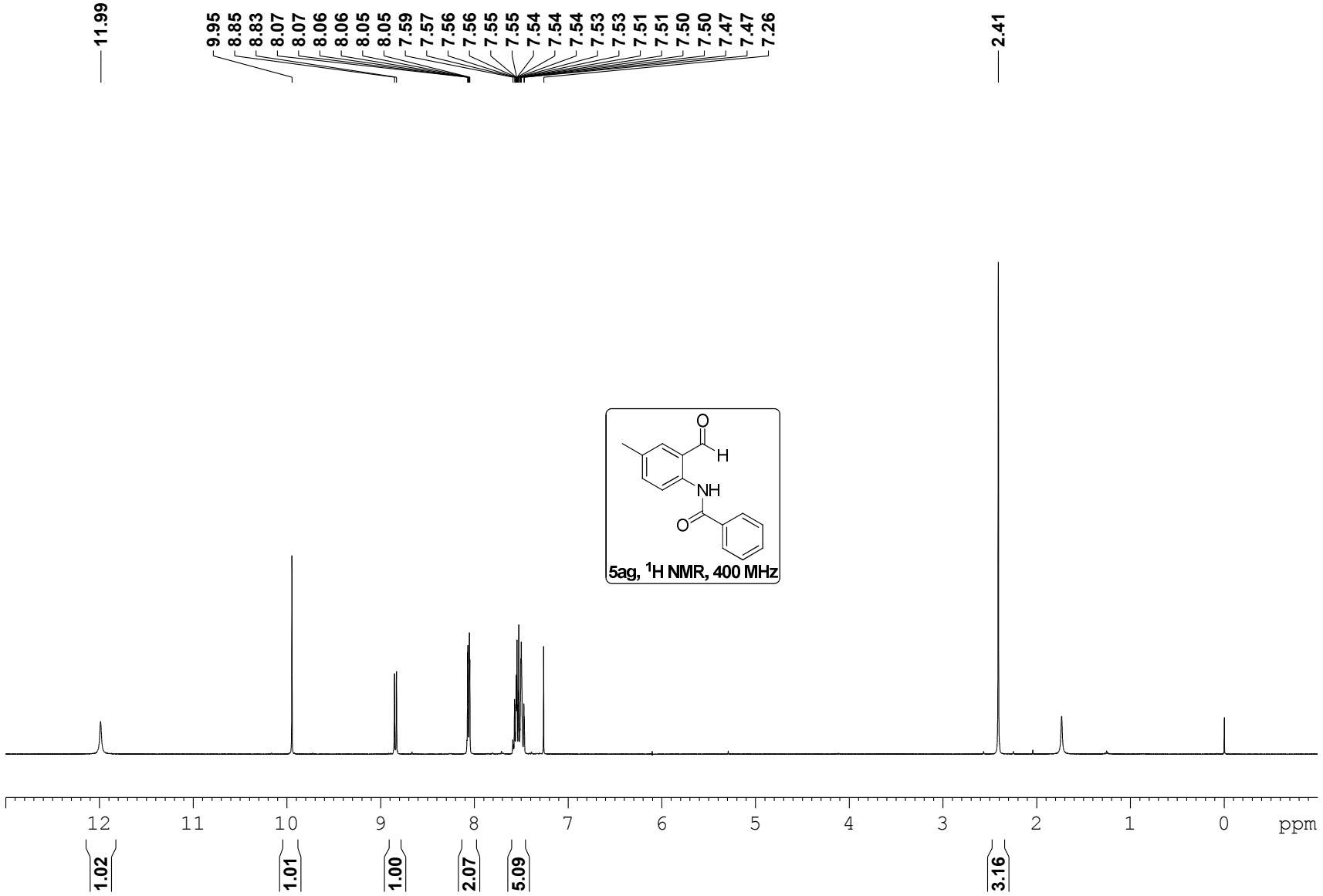
166.58
161.19
141.37
136.16
134.57
132.28
129.01
127.61
120.57
120.07
117.29
77.48
77.16
76.84
36.01
31.09
O
H
NH
O
5af, 13C NMR, 100 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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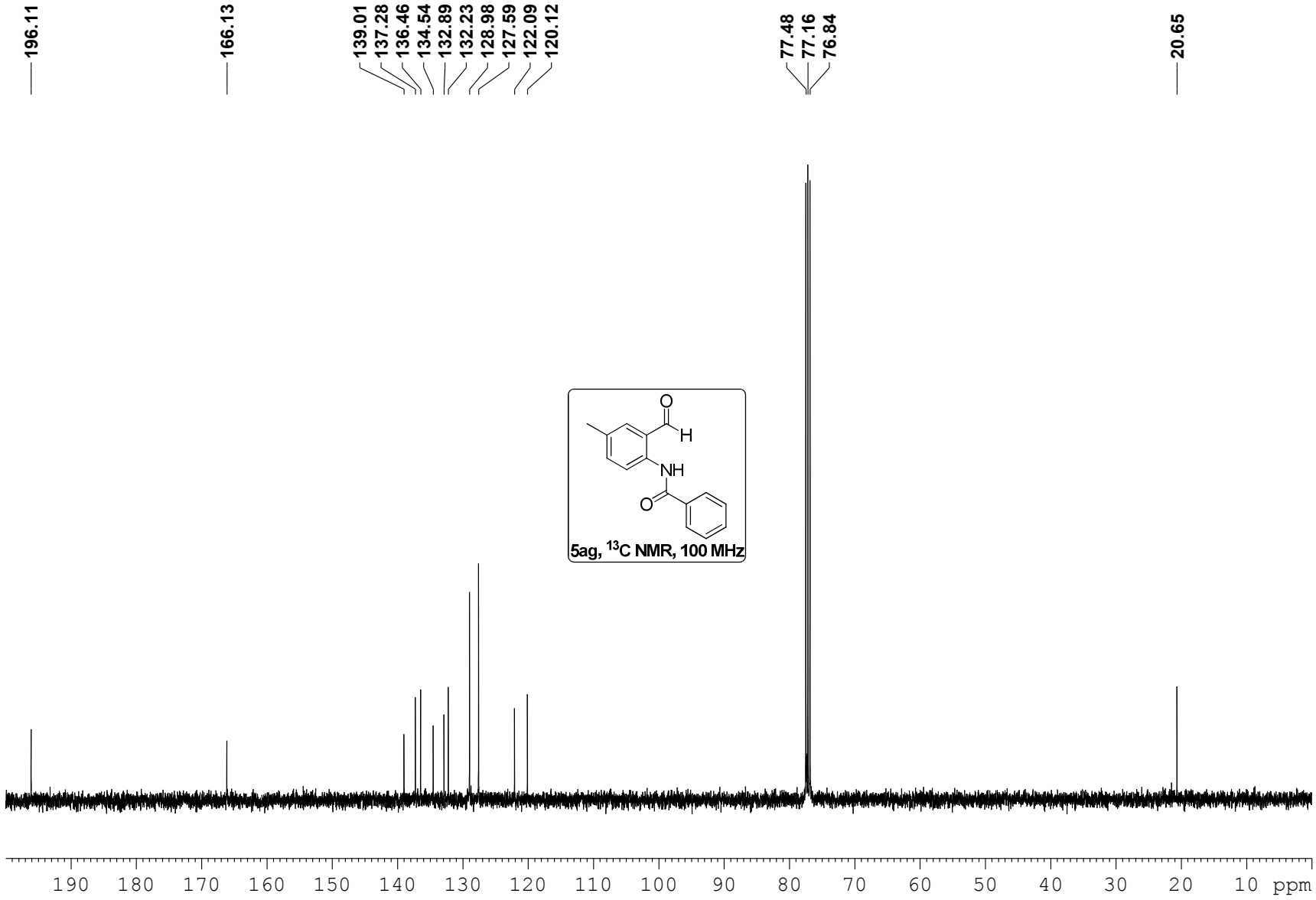
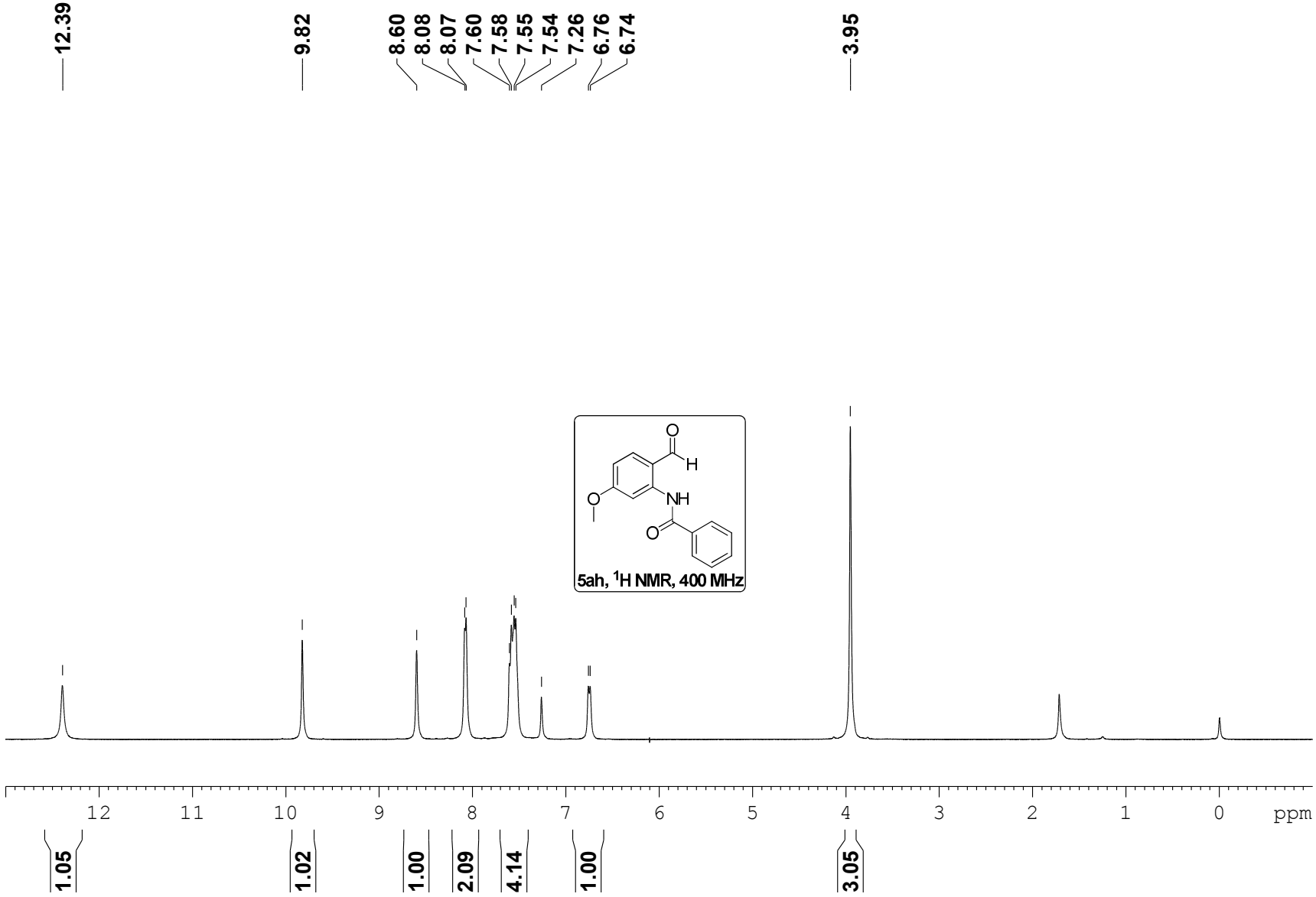
9.95
8.85
8.83
8.07
8.07
8.06
8.06
8.05
8.05
7.59
7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.54
7.53
7.53
7.51
7.51
7.50
7.50
7.47
7.47
7.26
2.41
O
H
NH
O
5ag, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.01
1.00
2.07
5.09
3.16


196.11
166.13
139.01
137.28
136.46
134.54
132.89
132.23
128.98
127.59
122.09
120.12
77.48
77.16
76.84
20.65
O
H
NH
O
5ag, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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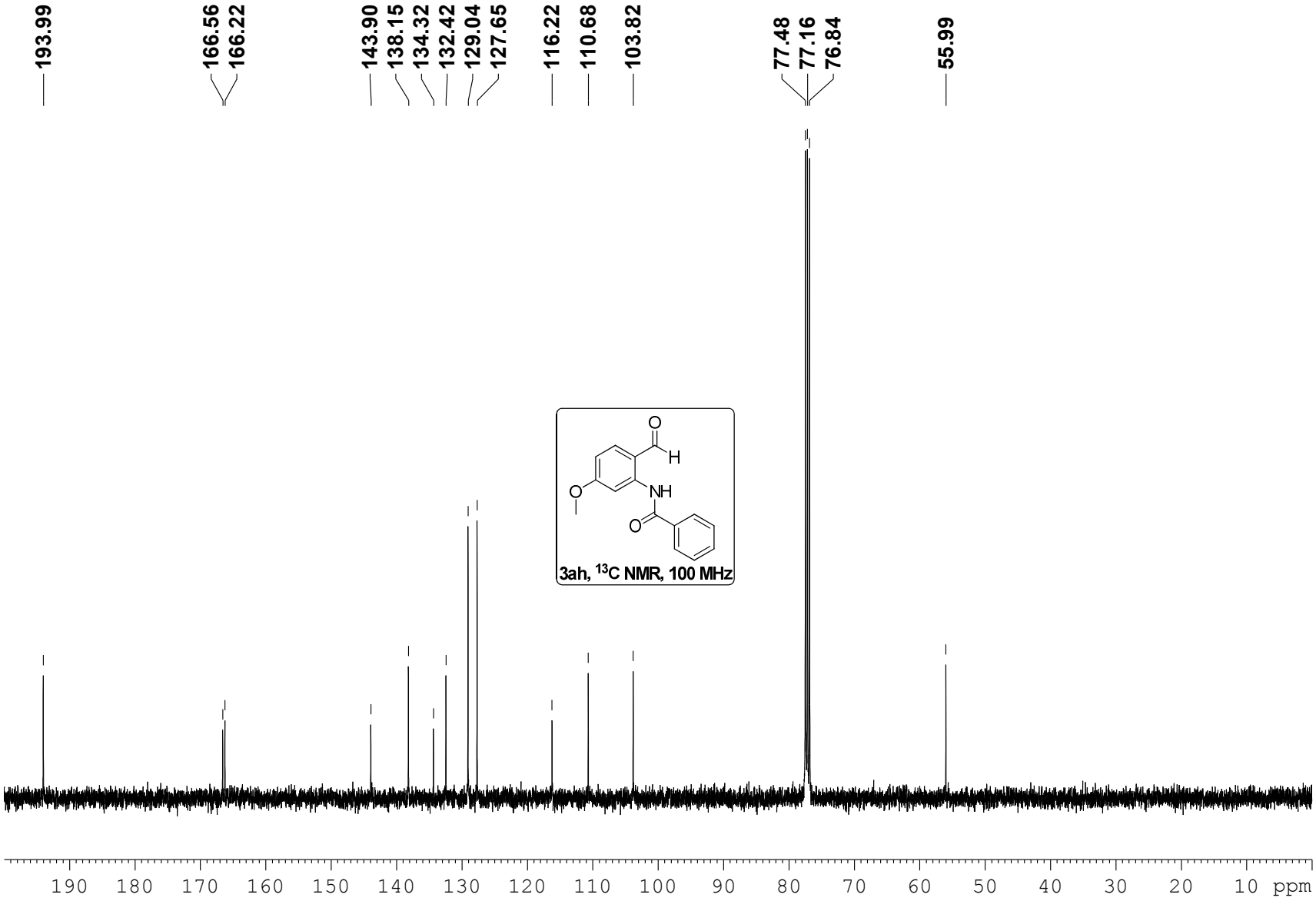
9.82
8.60
8.08
8.07
7.60
7.58
7.55
7.54
7.26
6.76
6.74
3.95
O
H
NH
O
O
5ah, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.05
1.02
1.00
2.09
4.14
1.00
3.05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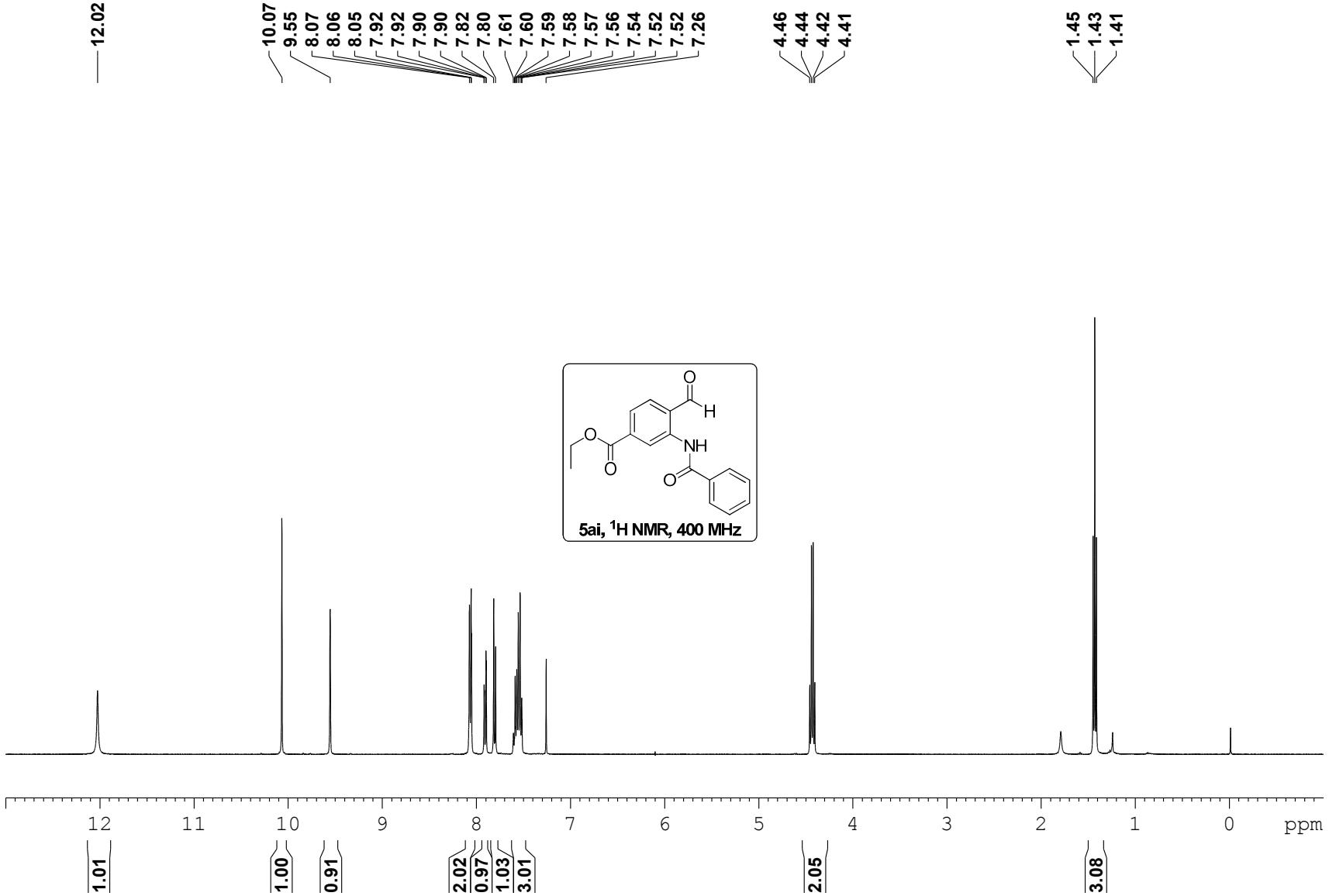
166.56
166.22
143.90
138.15
134.32
132.42
129.04
127.65
116.22
110.68
103.82
77.48
77.16
76.84
55.99
O
H
O
NH
O
3ah, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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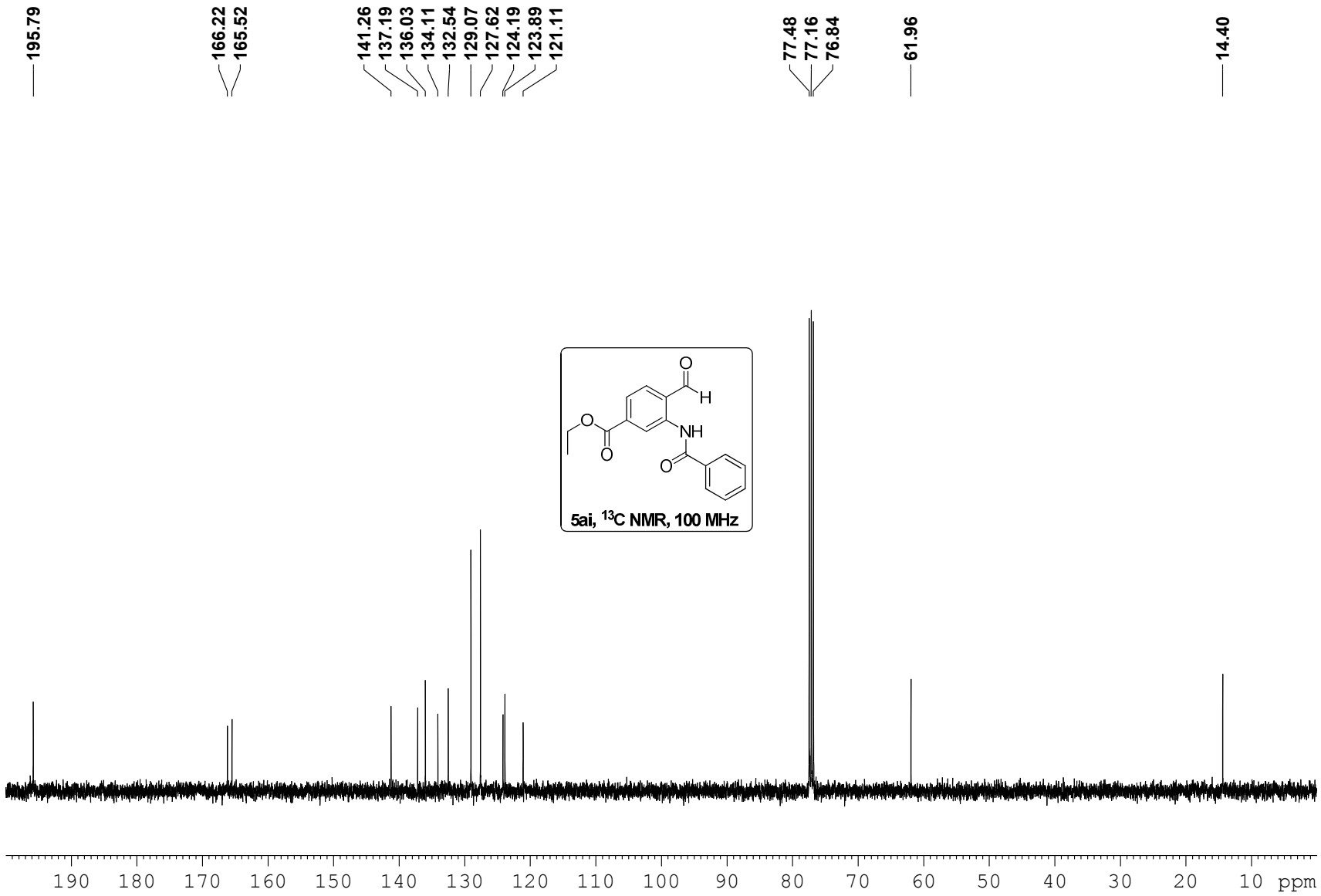
10.07
9.55
8.07
8.06
8.05
7.92
7.92
7.90
7.90
7.82
7.80
7.61
7.60
7.59
7.58
7.57
7.56
7.54
7.52
7.52
7.26
4.46
4.44
4.42
4.41
1.45
1.43
1.41
O
H
O
NH
O
O
5ai, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.00
0.91
2.02
0.97
1.03
3.01
2.05
3.08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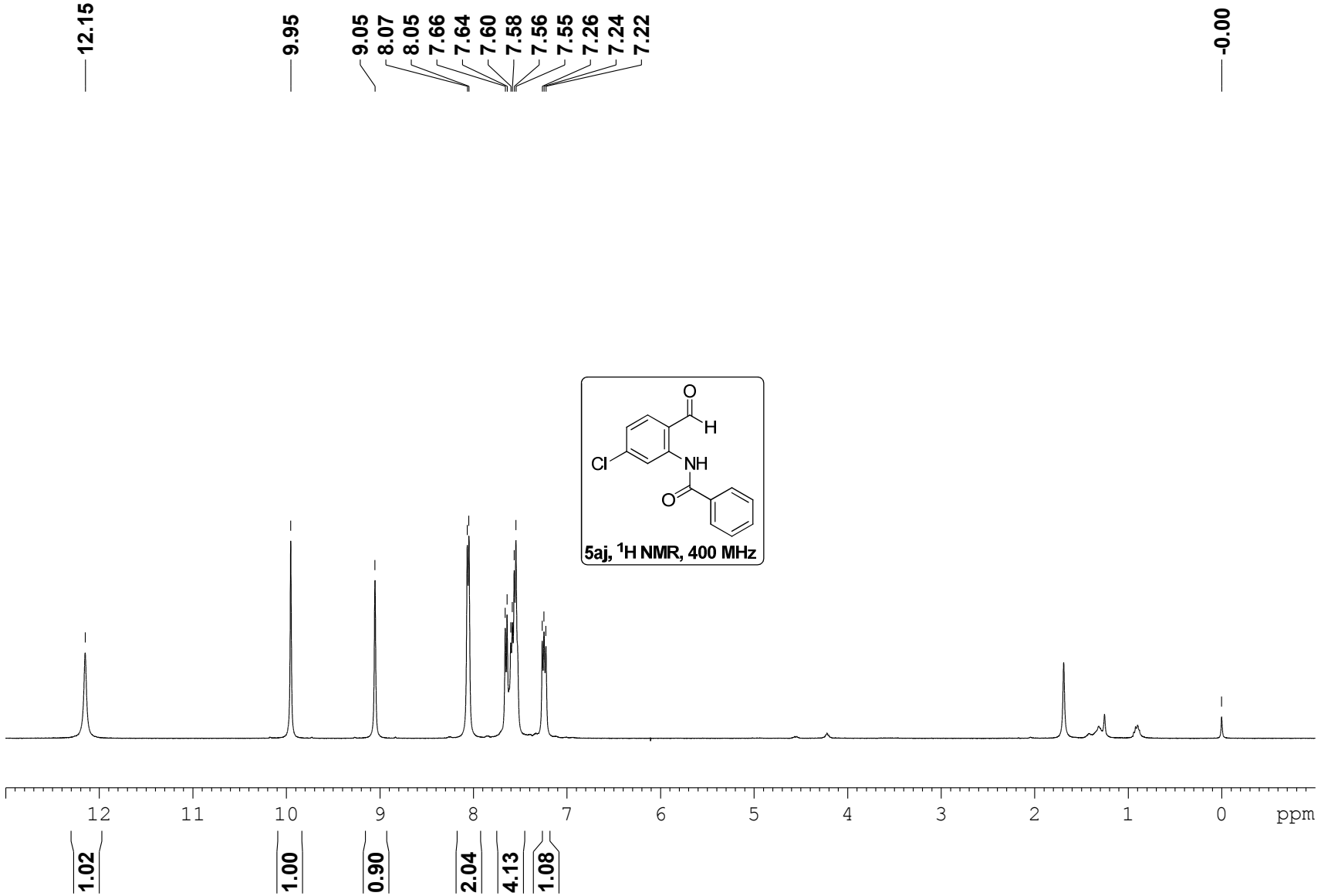
165.52
141.26
137.19
136.03
134.11
132.54
129.07
127.62
124.19
123.89
121.11
77.48
77.16
76.84
61.96
14.40
O
H
O
NH
O
O
5ai, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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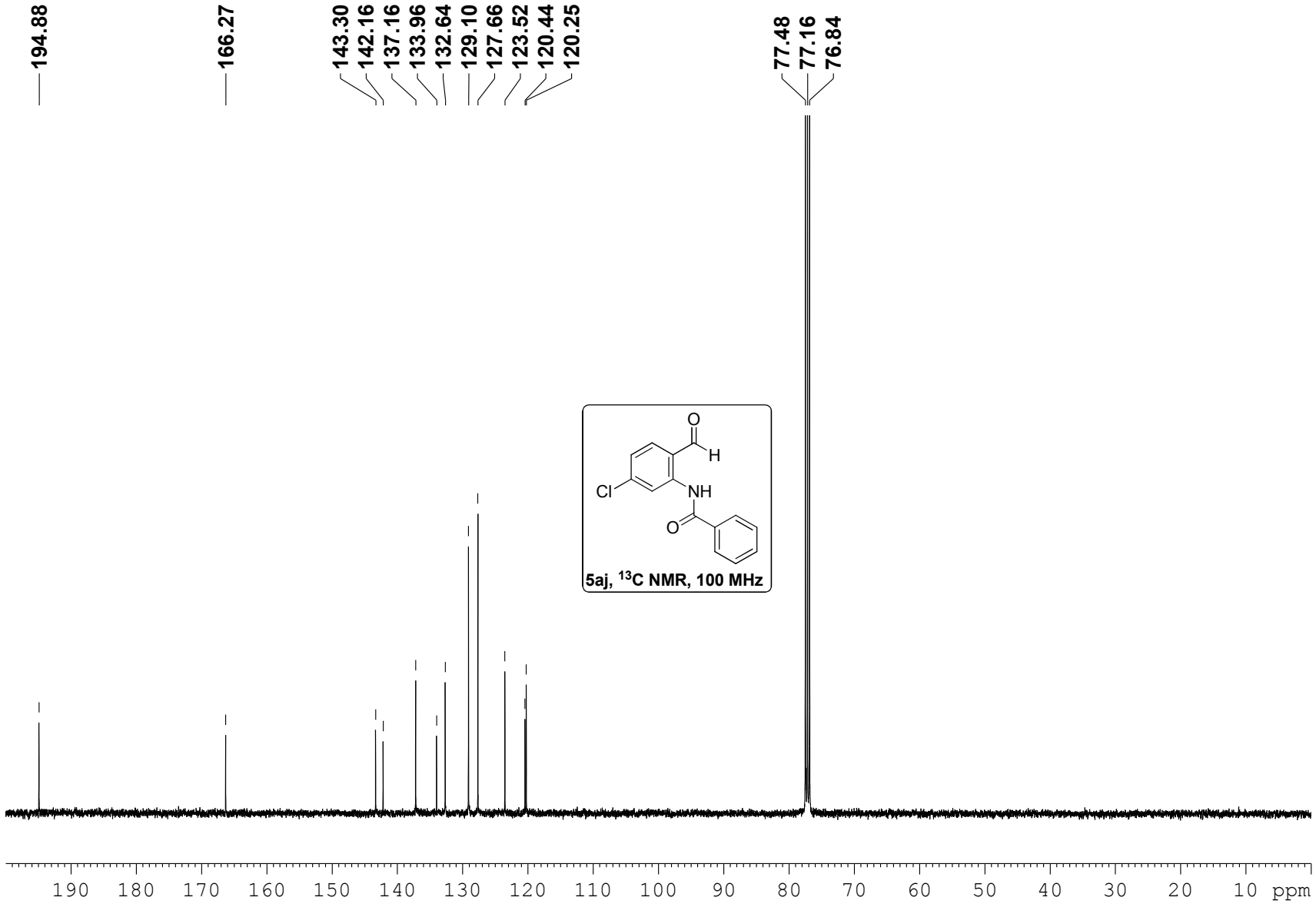
9.95
9.05
8.07
8.05
7.66
7.64
7.60
7.58
7.56
7.55
7.26
7.24
7.22
-0.00
O
H
Cl
NH
O
5aj, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.00
0.90
2.04
4.13
1.08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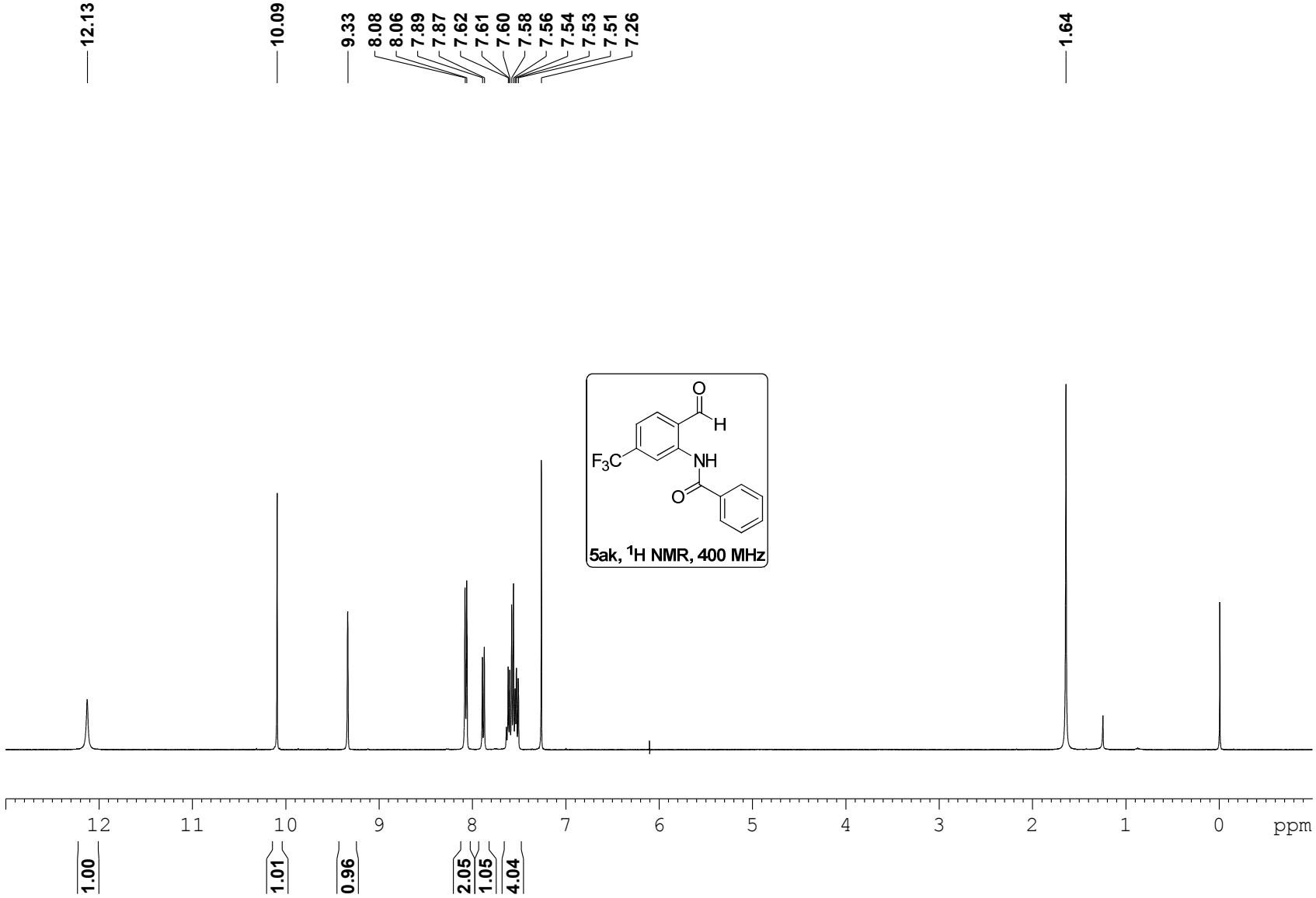
142.16
137.16
133.96
132.64
129.10
127.66
123.52
120.44
120.25
77.48
77.16
76.84
O
H
Cl
NH
O
5aj, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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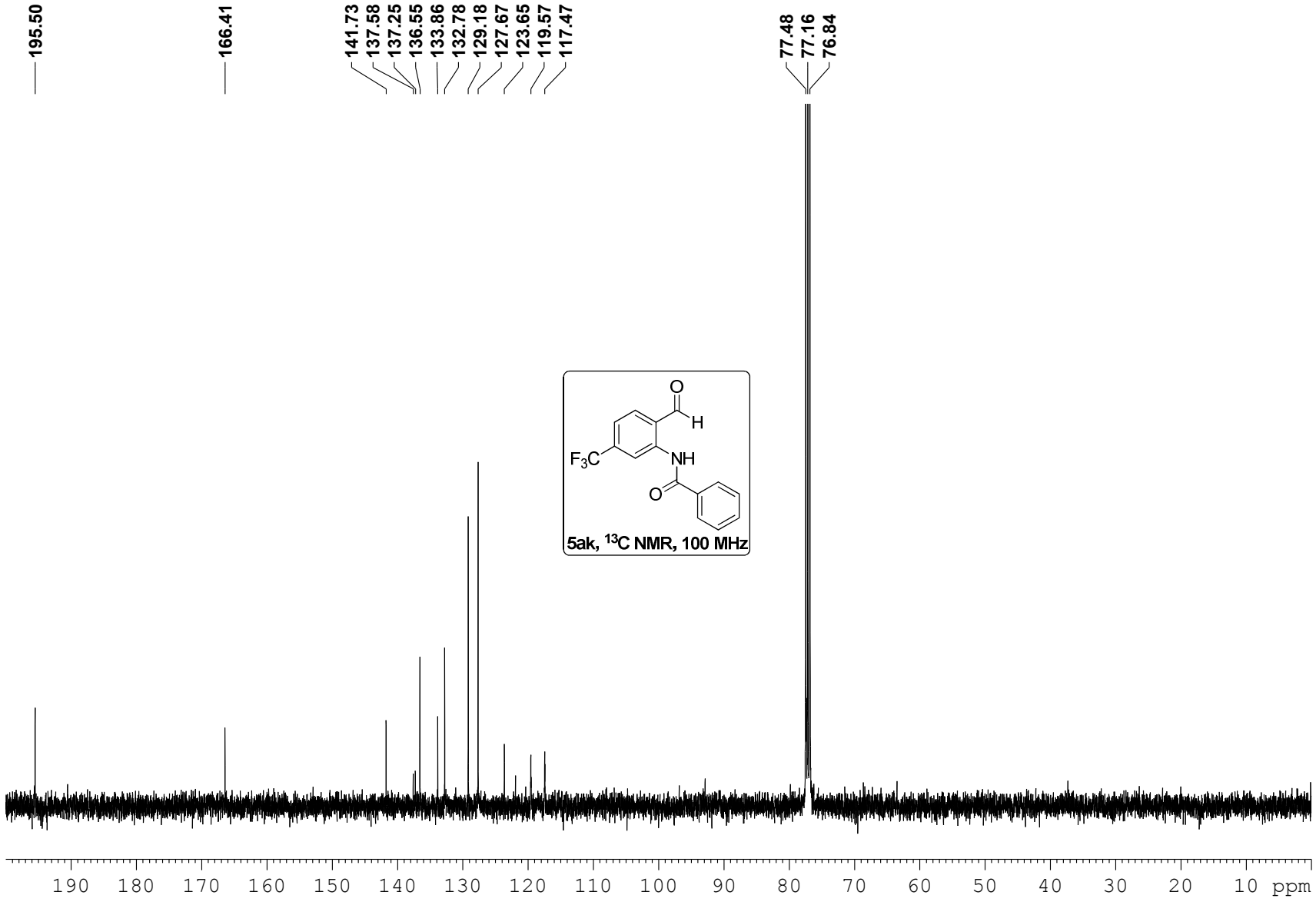
10.09
9.33
8.08
8.06
7.89
7.87
7.62
7.61
7.60
7.58
7.56
7.54
7.53
7.51
7.26
1.64
O
H
F3C
NH
O
5ak, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
0.96
2.05
1.05
4.04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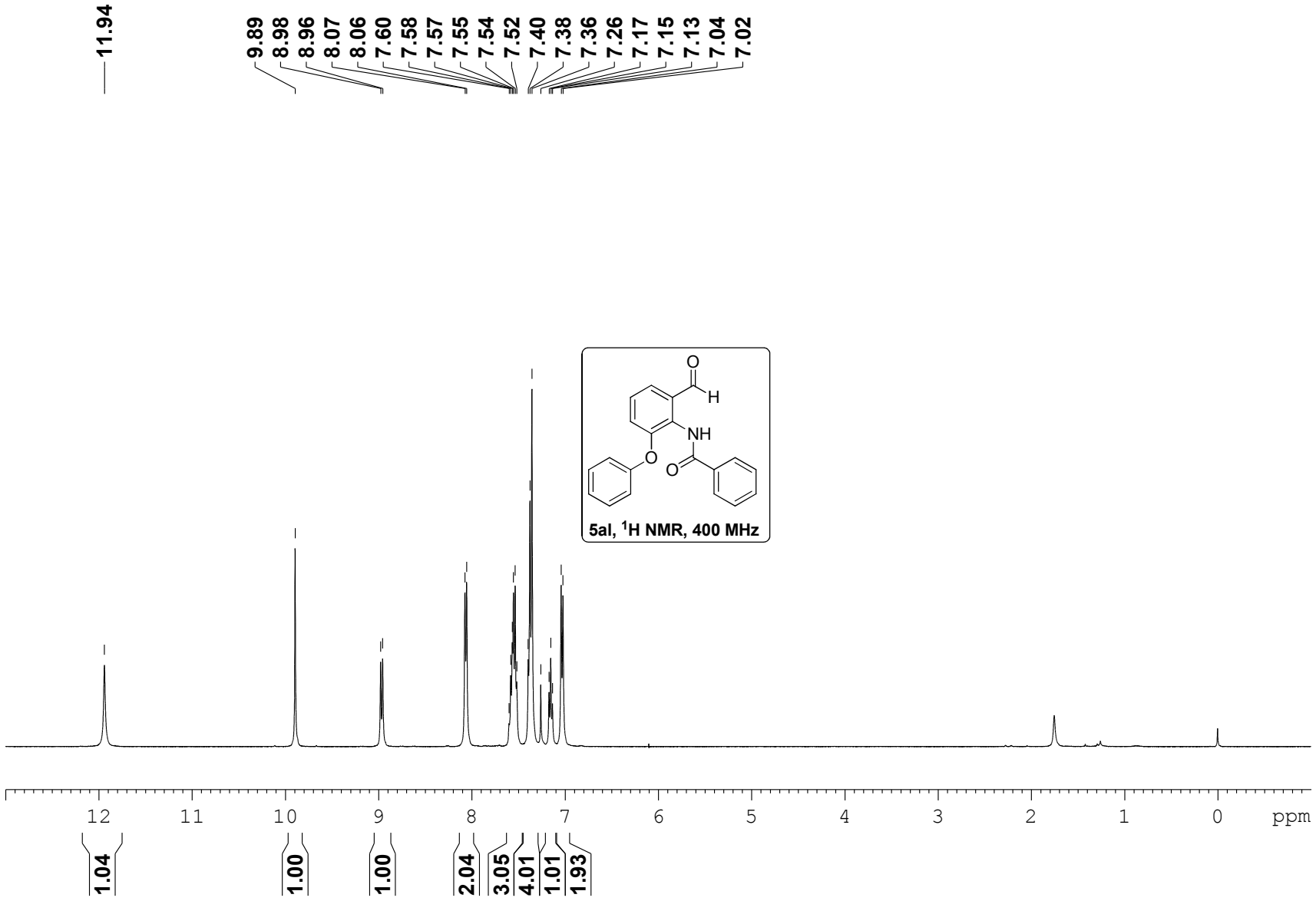
166.41
141.73
137.58
137.25
136.55
133.86
132.78
129.18
127.67
123.65
119.57
117.47
77.48
77.16
76.84
O
H
F3C
NH
O
5ak, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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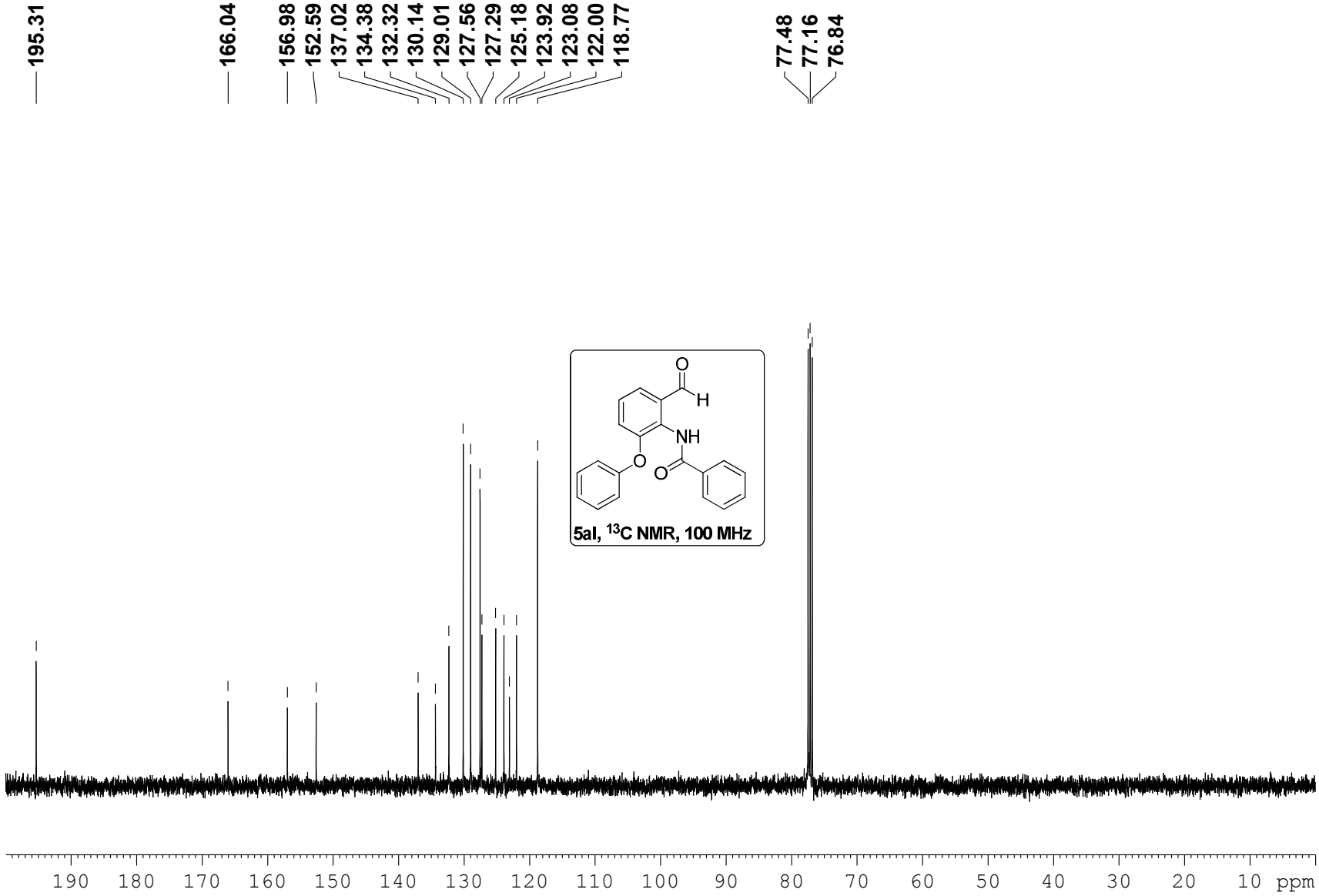
9.89
8.98
8.96
8.07
8.06
7.60
7.58
7.57
7.55
7.54
7.52
7.40
7.38
7.36
7.26
7.17
7.15
7.13
7.04
7.02
O
H
NH
O
O
5al, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.00
1.00
2.04
3.05
4.01
1.01
1.93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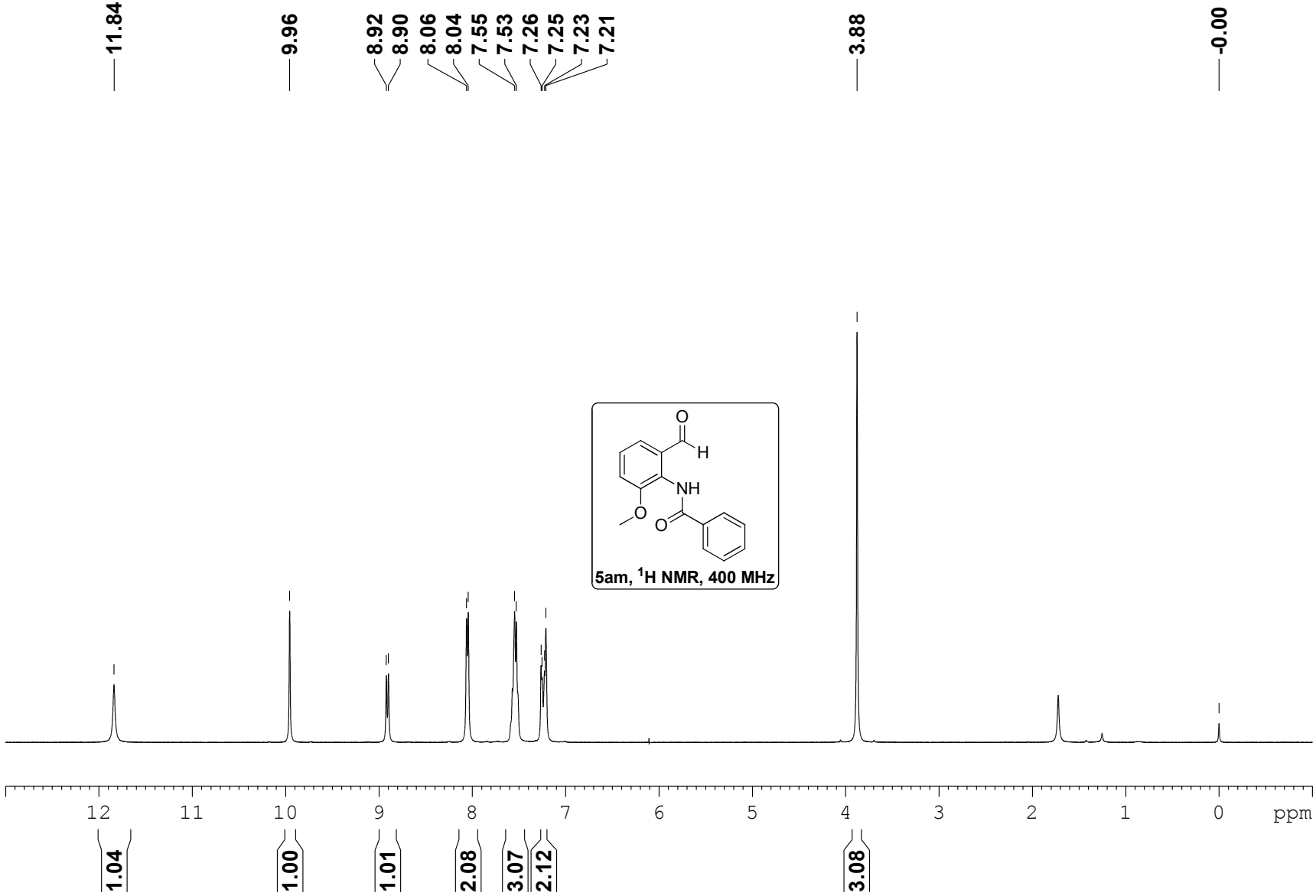
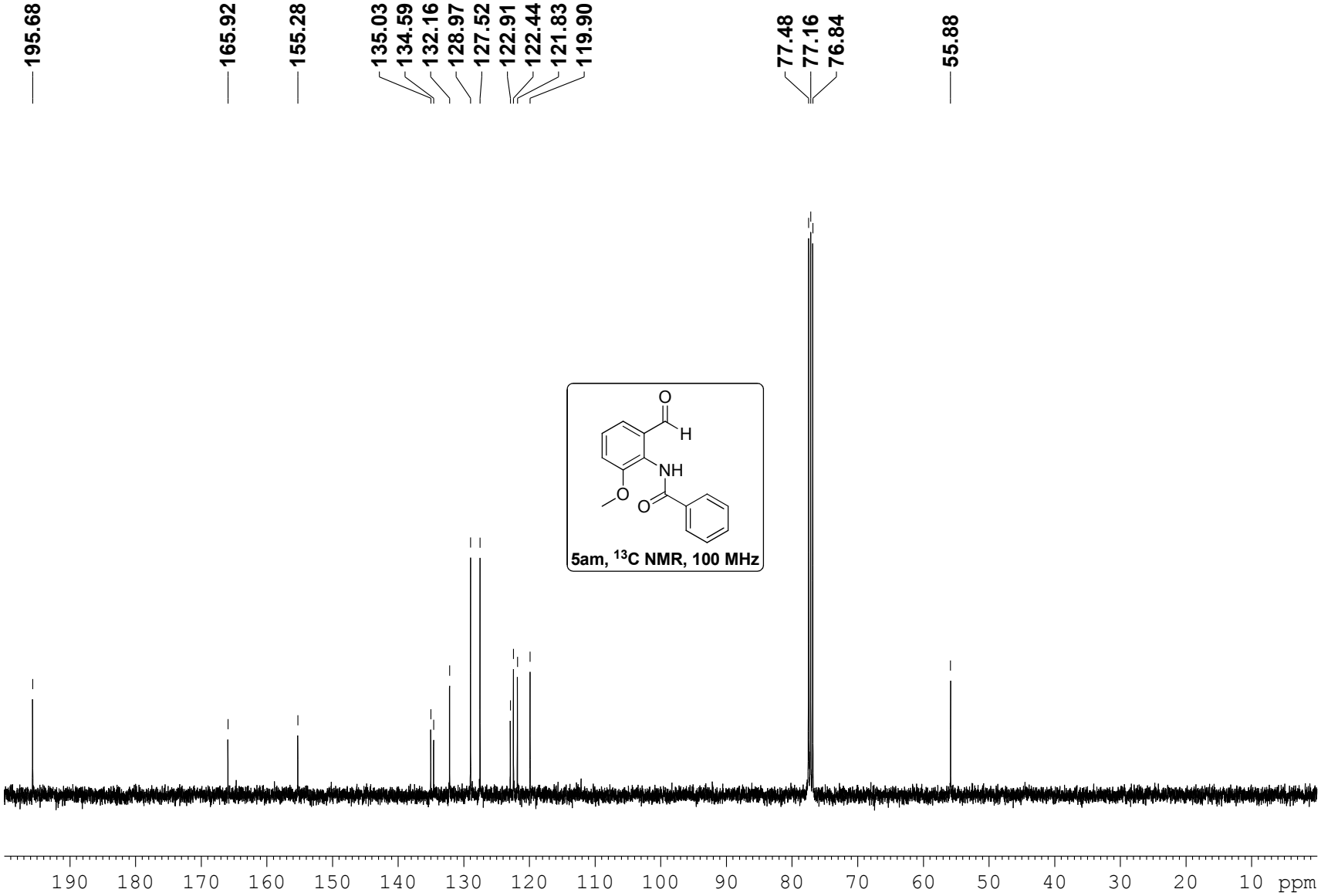
166.04
156.98
152.59
137.02
134.38
132.32
130.14
129.01
127.56
127.29
125.18
123.92
123.08
122.00
118.77
77.48
77.16
76.84
O
H
NH
O
O
5al, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


11.84
9.96
8.92
8.90
8.06
8.04
7.55
7.53
7.26
7.25
7.23
7.21
3.88
-0.00
O
H
NH
O
O
5am, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.00
1.01
2.08
3.07
2.12
3.08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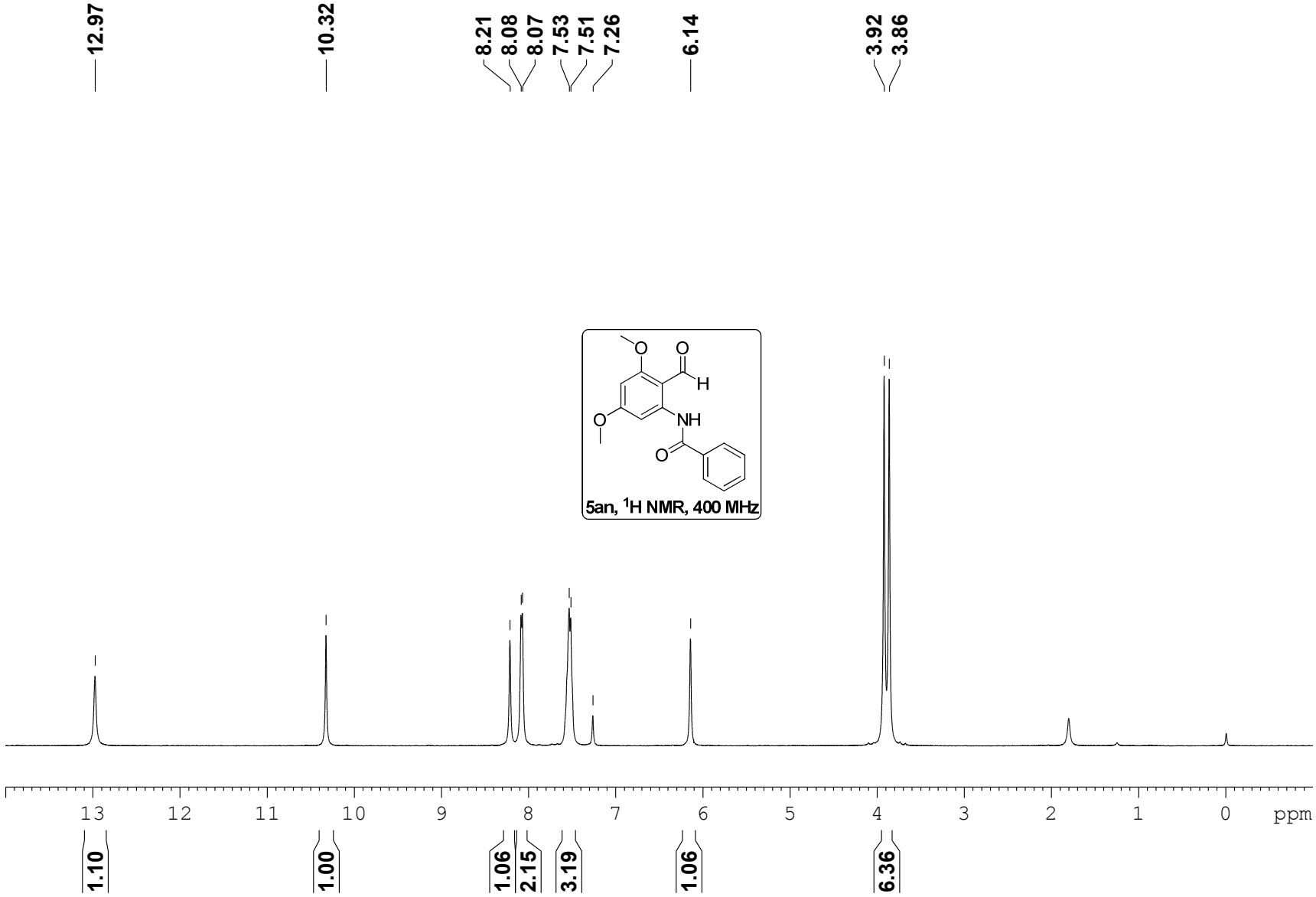
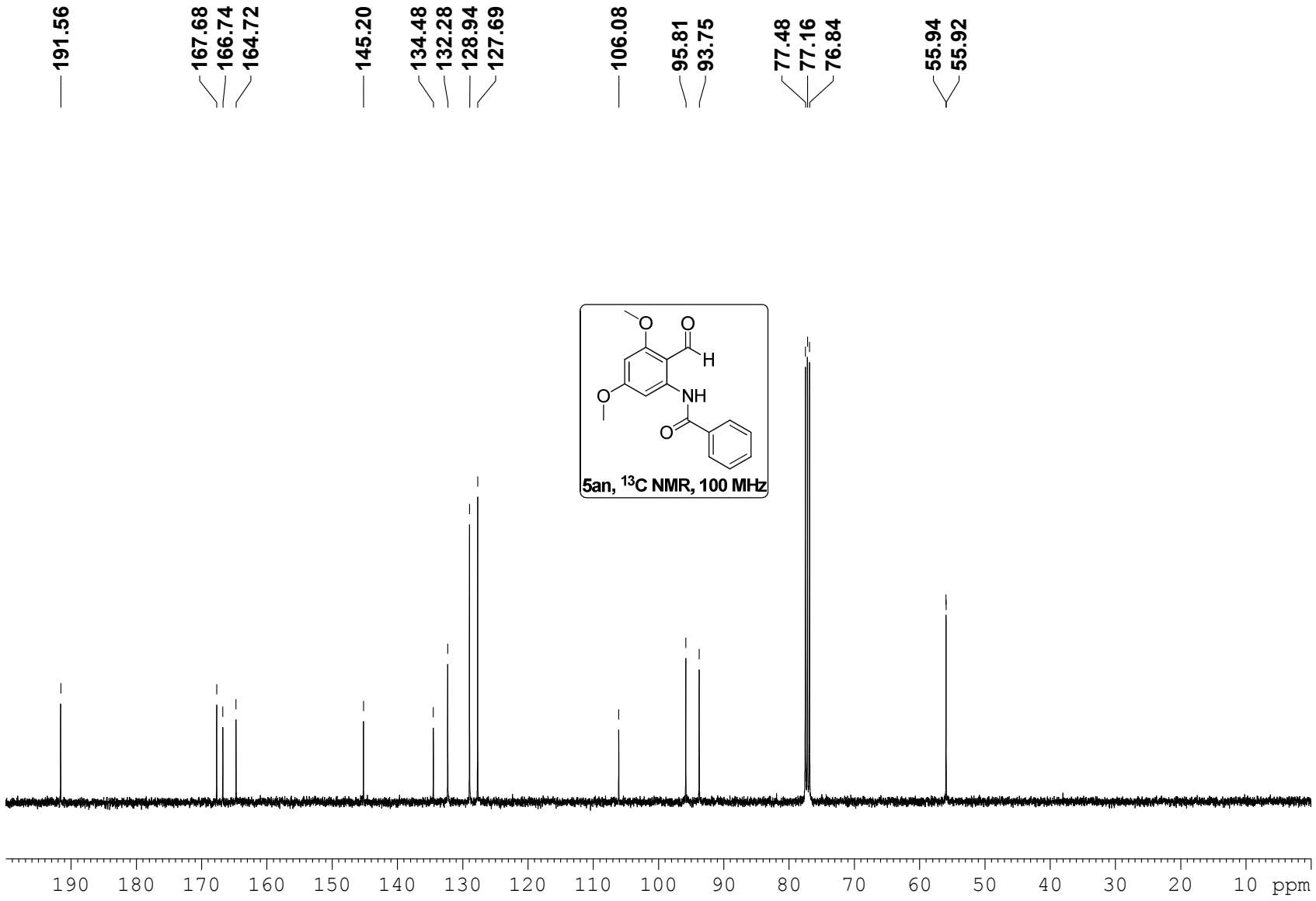
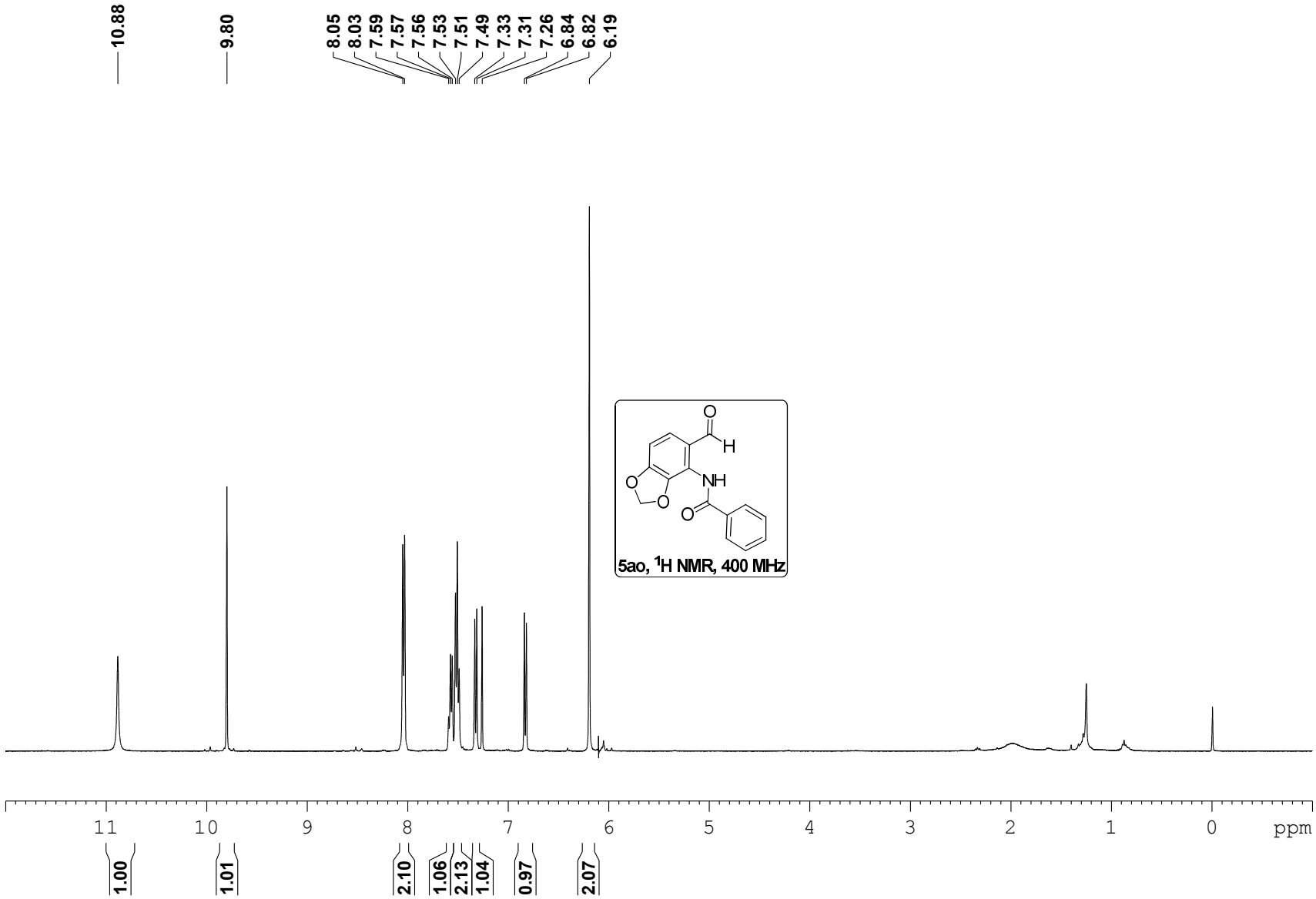
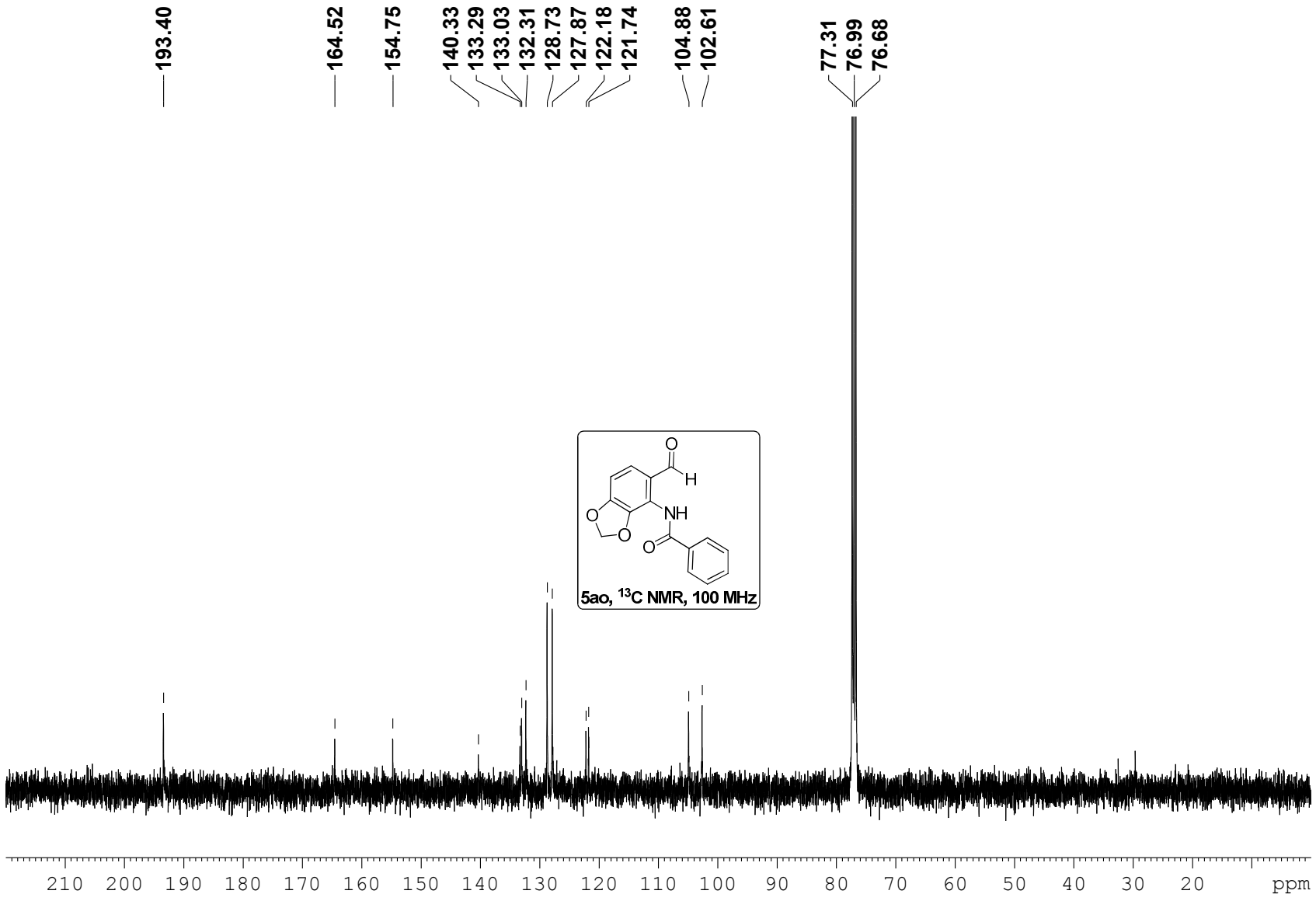
165.92
155.28
135.03
134.59
132.16
128.97
127.52
122.91
122.44
121.83
119.90
77.48
77.16
76.84
55.88
O
H
NH
O
O
5am, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


12.97
10.32
8.21
8.08
8.07
7.53
7.51
7.26
6.14
3.92
3.86
O
O
H
O
NH
O
5an, 1H NMR, 400 MHz
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.10
1.00
1.06
2.15
3.19
1.06
6.36


191.56
167.68
166.74
164.72
145.20
134.48
132.28
128.94
127.69
106.08
95.81
93.75
77.48
77.16
76.84
55.94
55.92
5an, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


10.88
9.80
8.05
8.03
7.59
7.57
7.56
7.53
7.51
7.49
7.33
7.31
7.26
6.84
6.82
6.19
O
H
NH
O
O
O
5ao, 1H NMR, 400 MHz
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
2.10
1.06
2.13
1.04
0.97
2.07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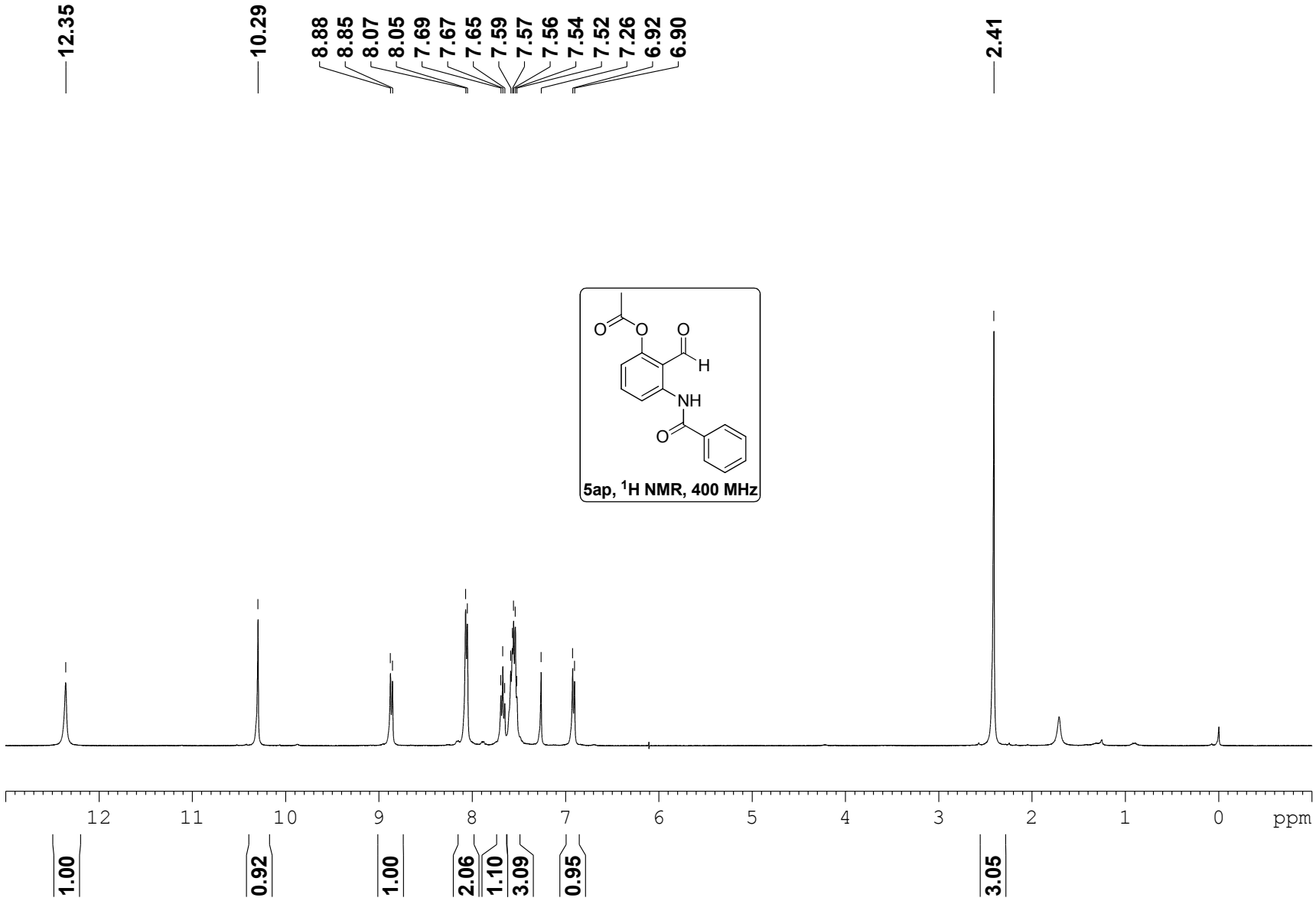
164.52
154.75
140.33
133.29
133.03
132.31
128.73
127.87
122.18
121.74
104.88
102.61
77.31
76.99
76.68
O
H
NH
O
O
O
5ao, 13C NMR, 100 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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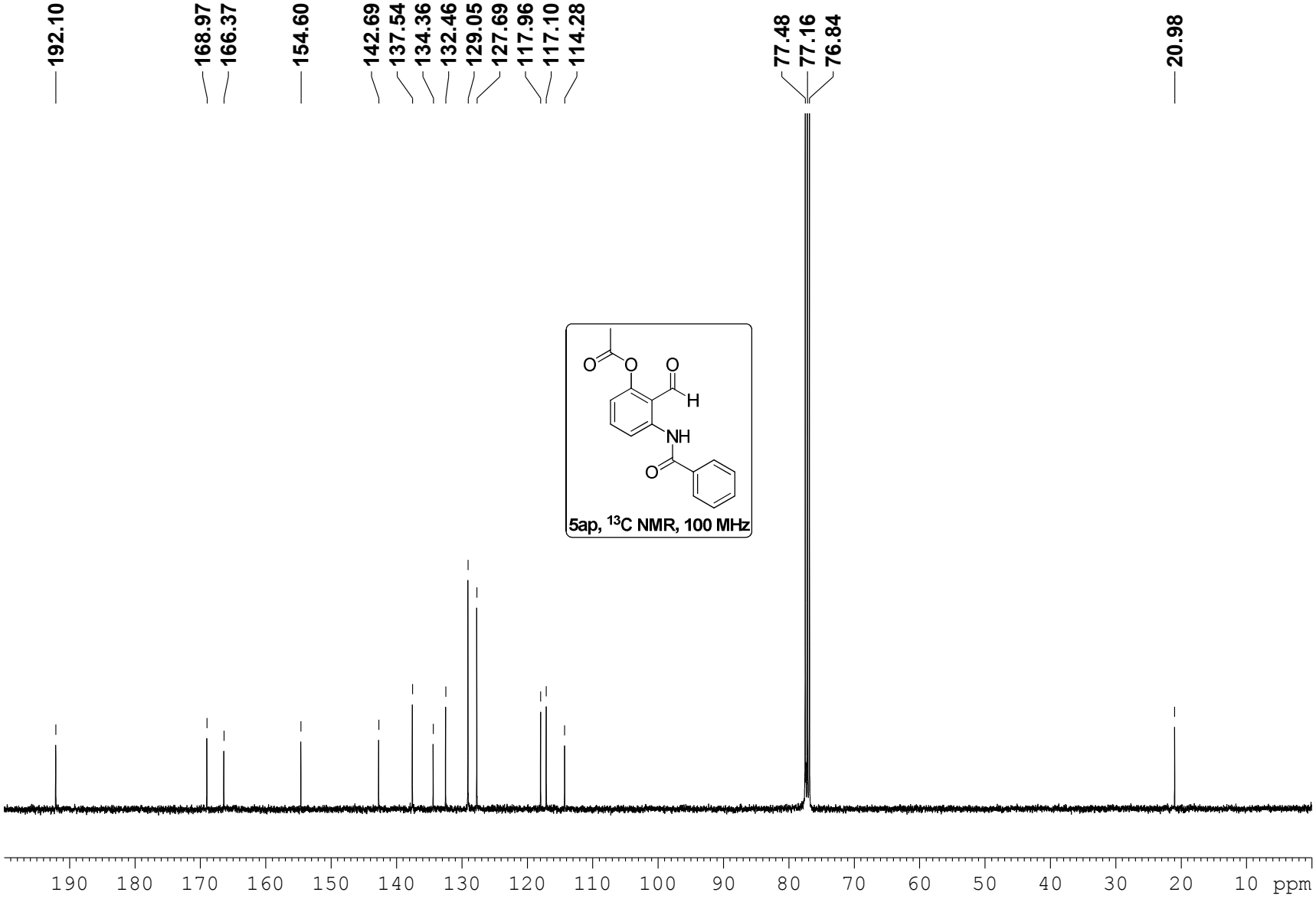
10.29
8.88
8.85
8.07
8.05
7.69
7.67
7.65
7.59
7.57
7.56
7.54
7.52
7.26
6.92
6.90
2.41
O
O
O
H
NH
O
5ap, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.92
1.00
2.06
1.10
3.09
0.95
3.05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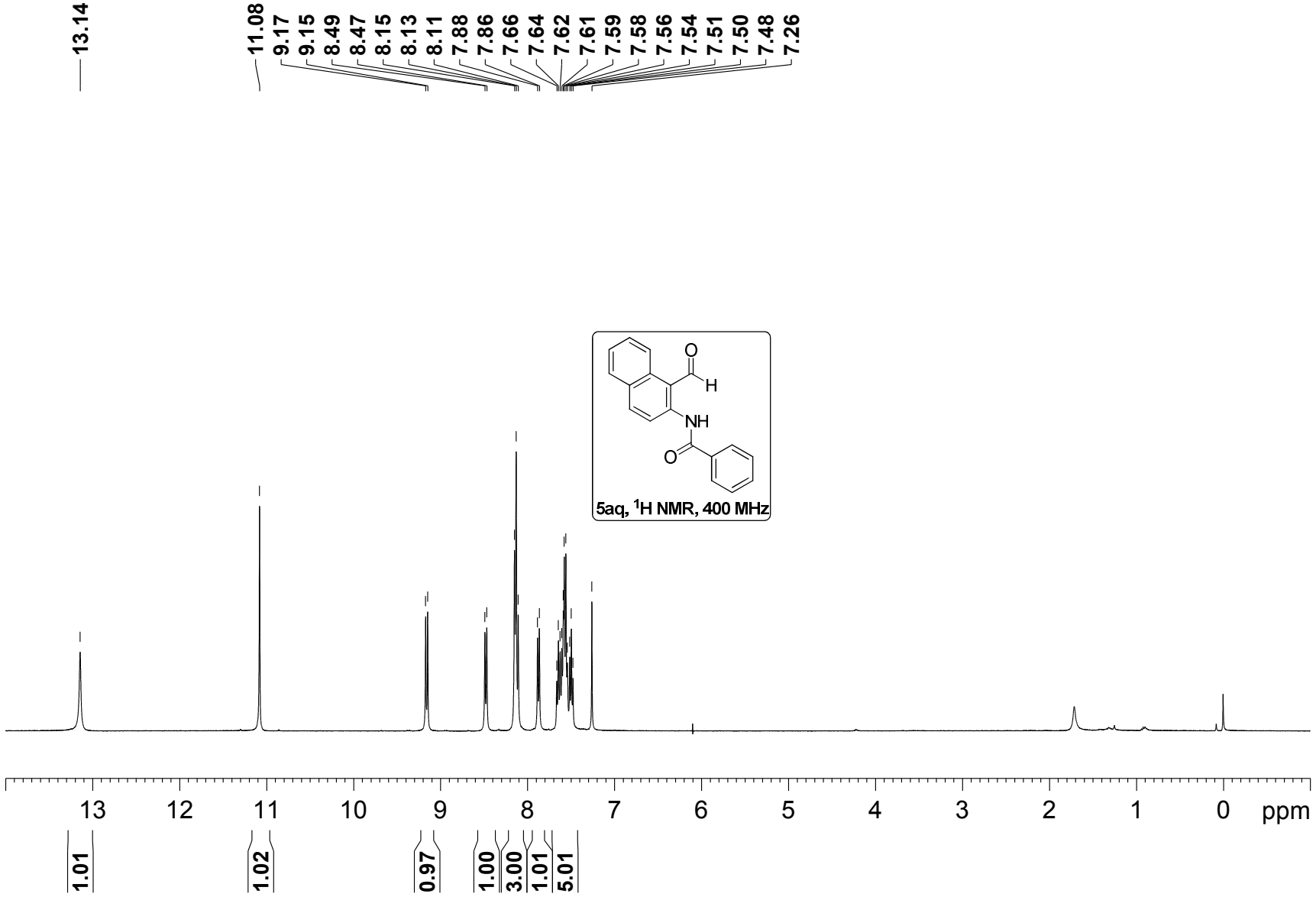
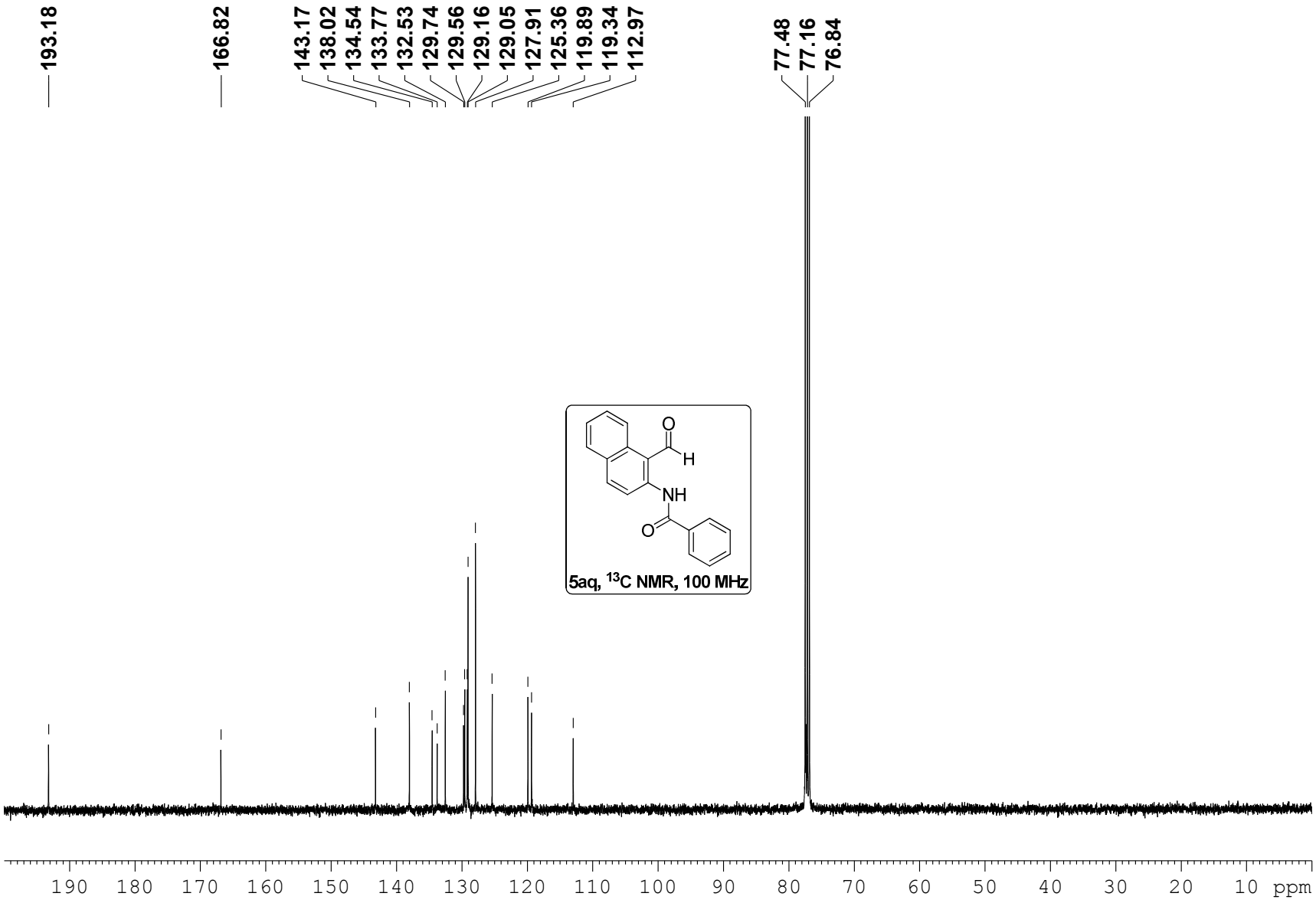
168.97
166.37
154.60
142.69
137.54
134.36
132.46
129.05
127.69
117.96
117.10
114.28
77.48
77.16
76.84
20.98
O
O
O
H
NH
O
5ap, 13C NMR, 100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


13.14
11.08
9.17
9.15
8.49
8.47
8.15
8.13
8.11
7.88
7.86
7.66
7.64
7.62
7.61
7.59
7.58
7.56
7.54
7.51
7.50
7.48
7.26
O
H
NH
O
5aq, 1H NMR, 400 MHz
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.02
0.97
1.00
3.00
1.01
5.01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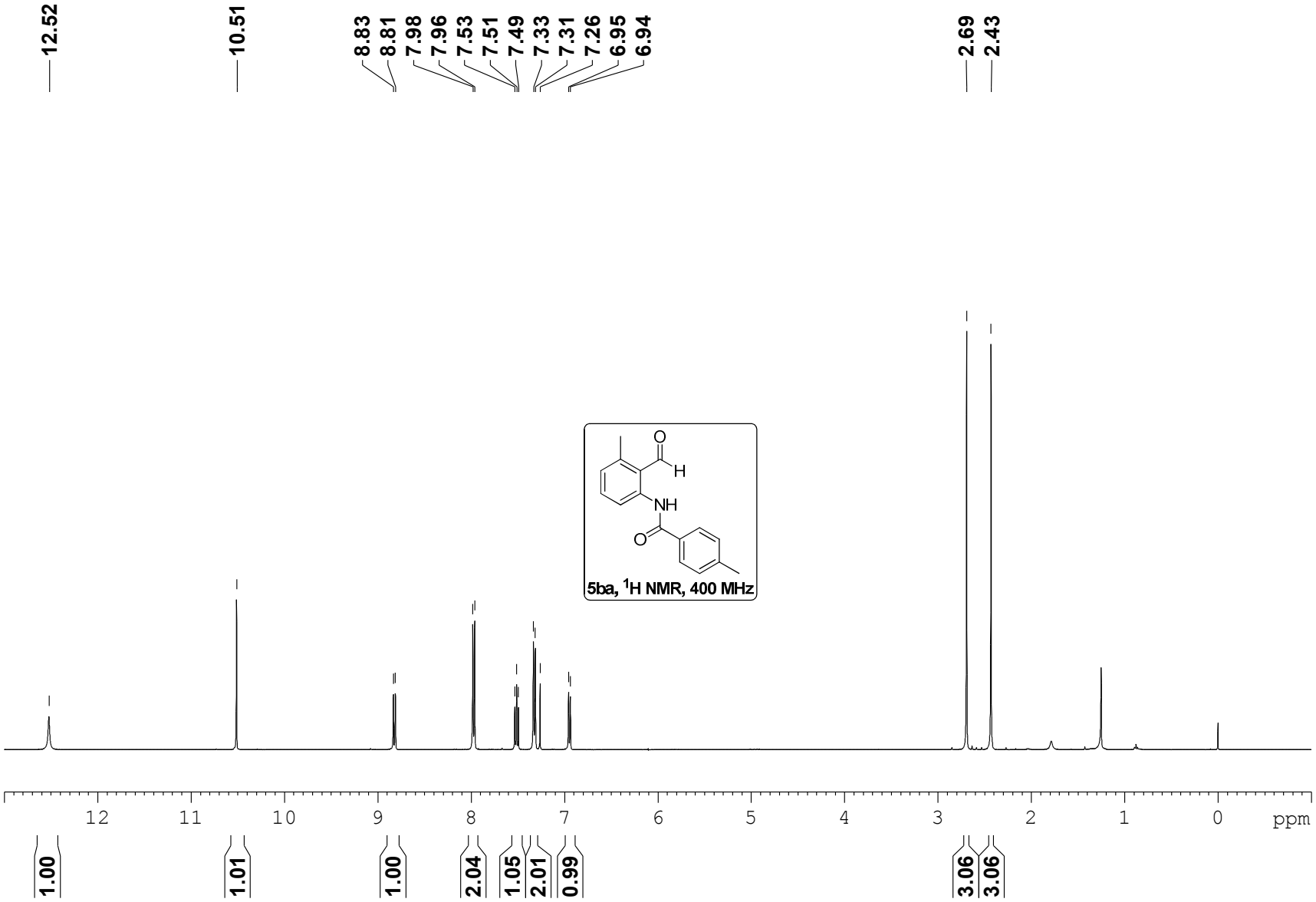
166.82
143.17
138.02
134.54
133.77
132.53
129.74
129.56
129.16
129.05
127.91
125.36
119.89
119.34
112.97
77.48
77.16
76.84
O
H
NH
O
5aq, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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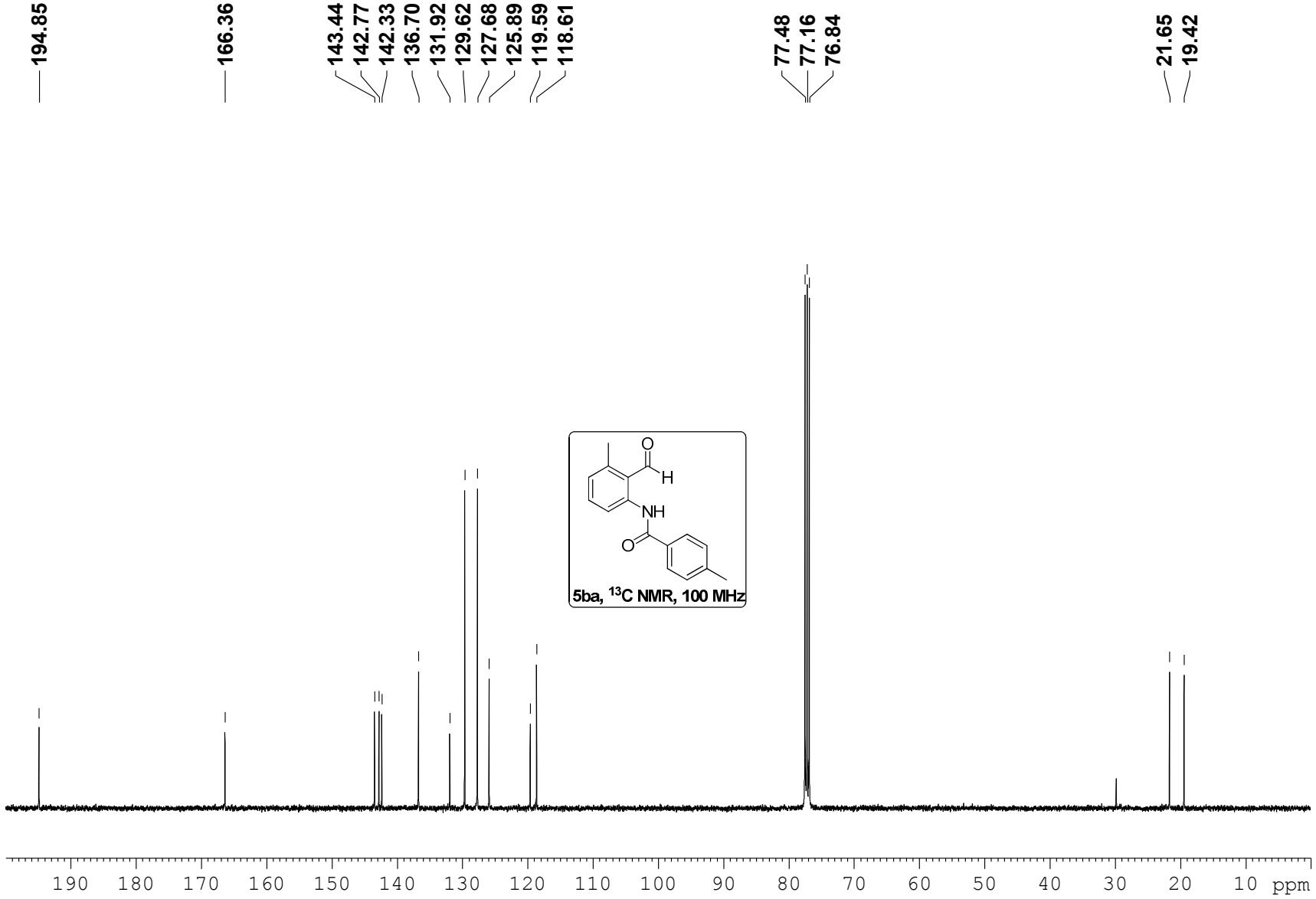
10.51
8.83
8.81
7.98
7.96
7.53
7.51
7.49
7.33
7.31
7.26
6.95
6.94
2.69
2.43
O
H
NH
O
5ba, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.00
2.04
1.05
2.01
0.99
3.06
3.06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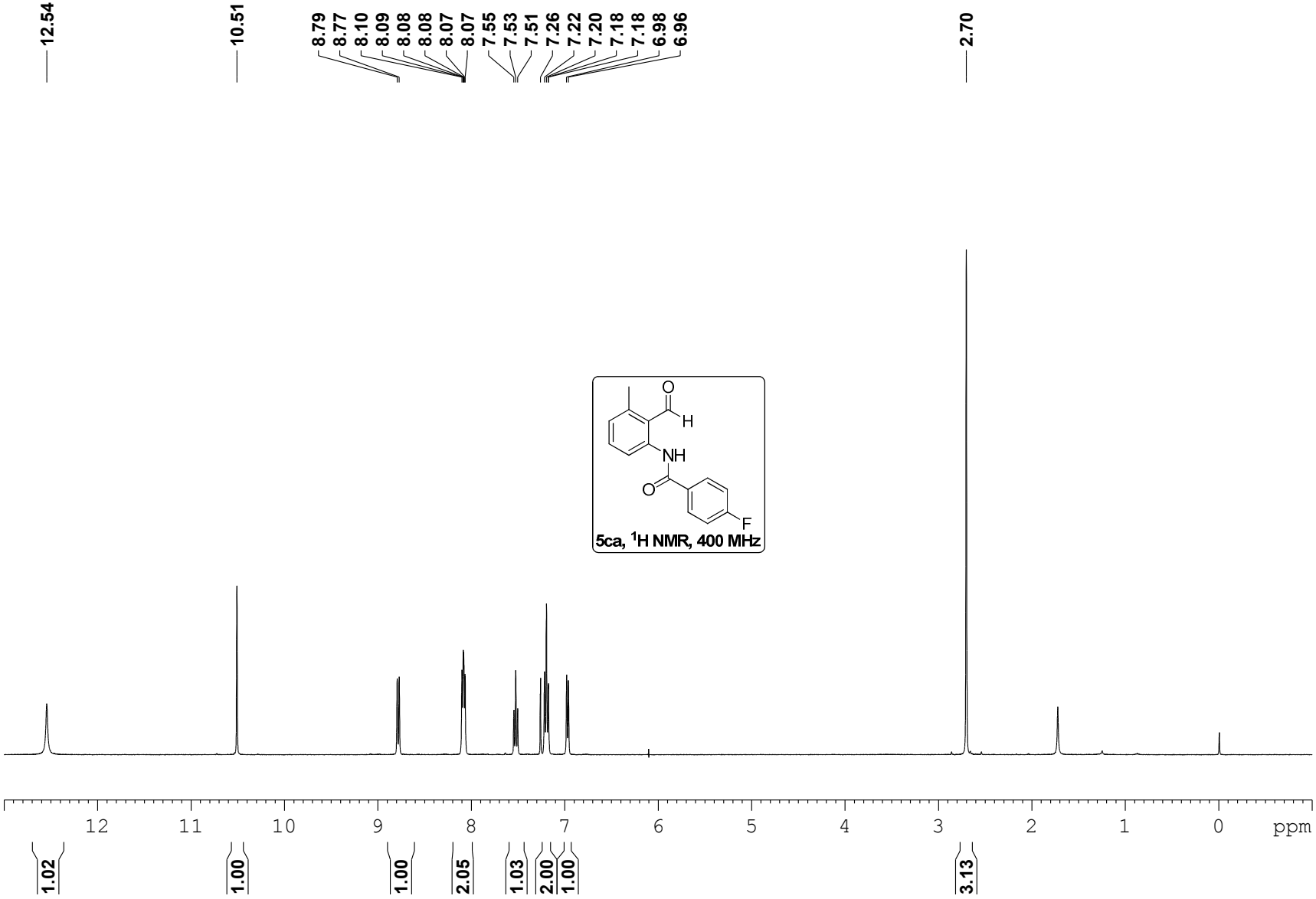
166.36
143.44
142.77
142.33
136.70
131.92
129.62
127.68
125.89
119.59
118.61
77.48
77.16
76.84
21.65
19.42
O
H
NH
O
5ba, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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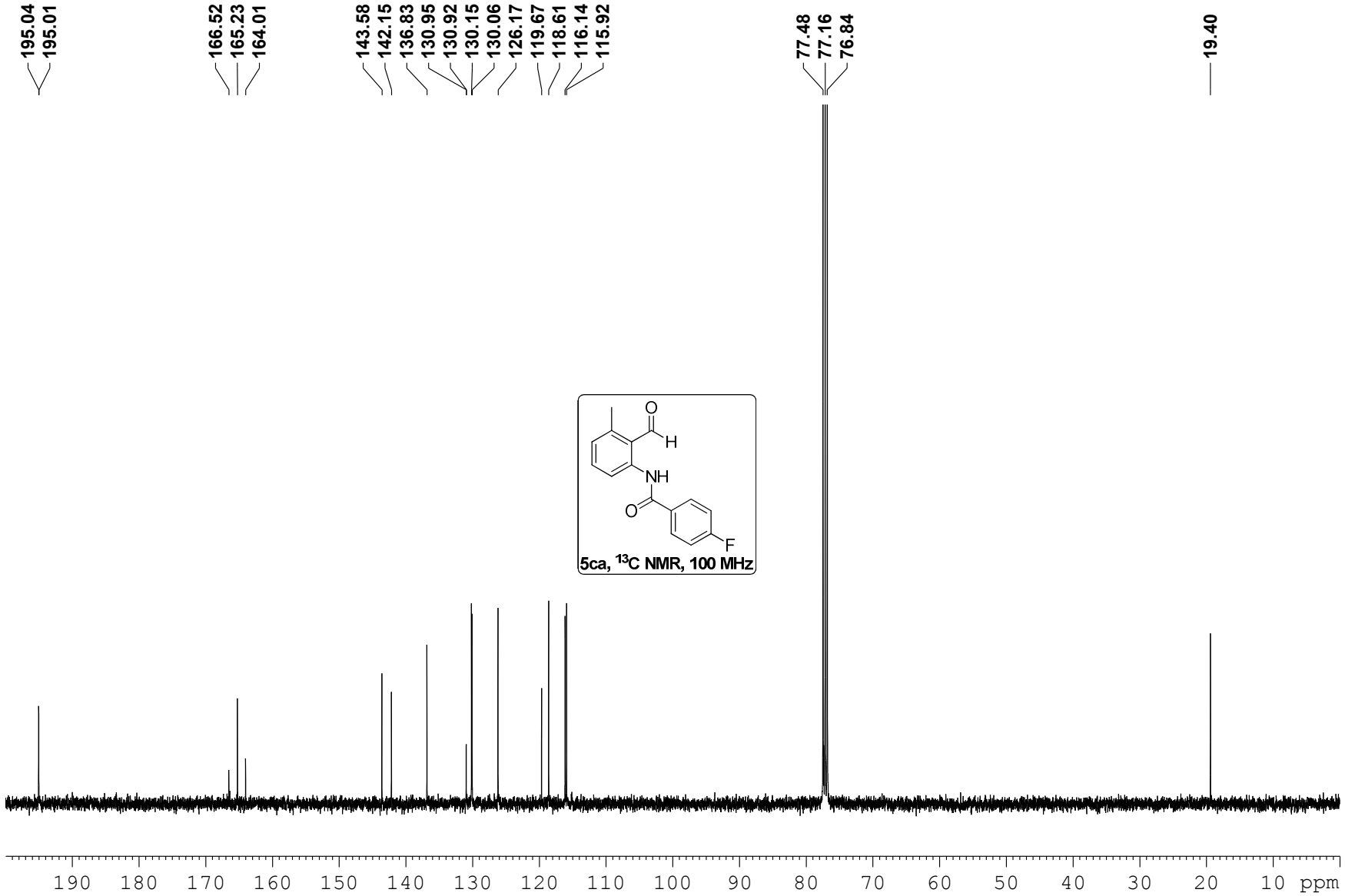
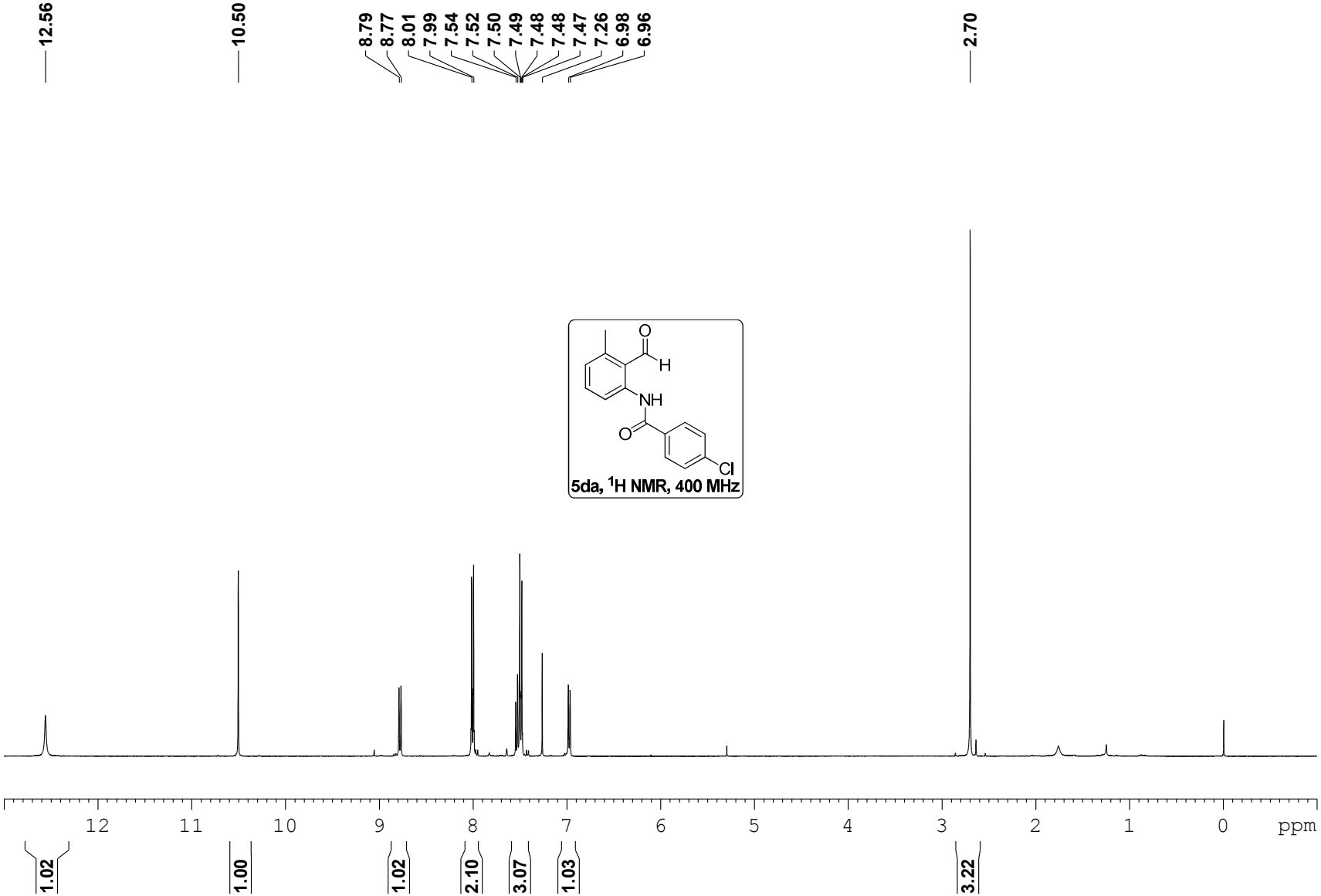
10.51
8.79
8.77
8.10
8.09
8.08
8.08
8.07
8.07
7.55
7.53
7.51
7.26
7.22
7.20
7.18
7.18
6.98
6.96
2.70
O
H
NH
O
F
5ca, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.00
1.00
2.05
1.03
2.00
1.00
3.13


195.04
195.01
166.52
165.23
164.01
143.58
142.15
136.83
130.95
130.92
130.15
130.06
126.17
119.67
118.61
116.14
115.92
77.48
77.16
76.84
19.40
O
H
NH
O
F
5ca, 13C NMR, 100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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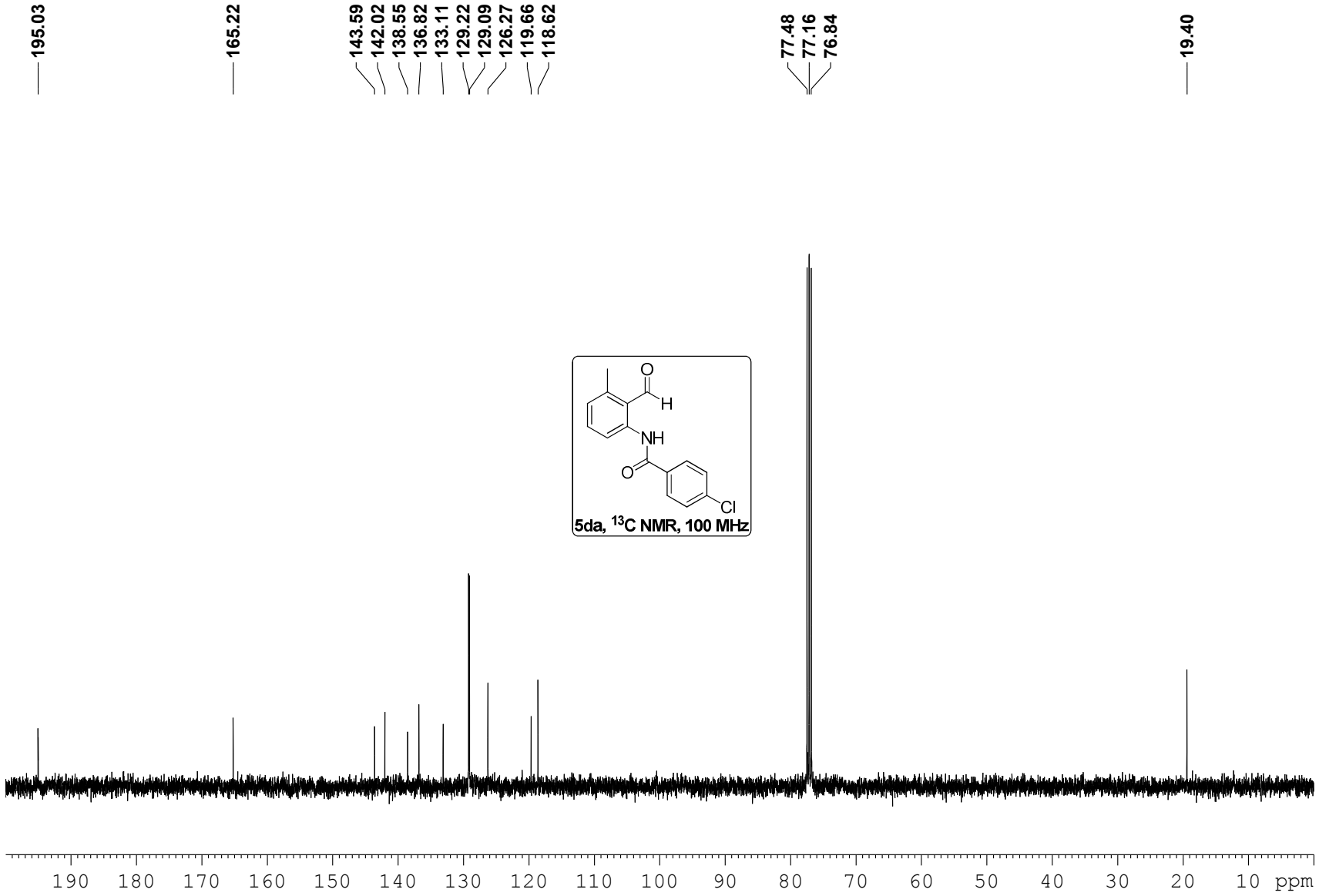
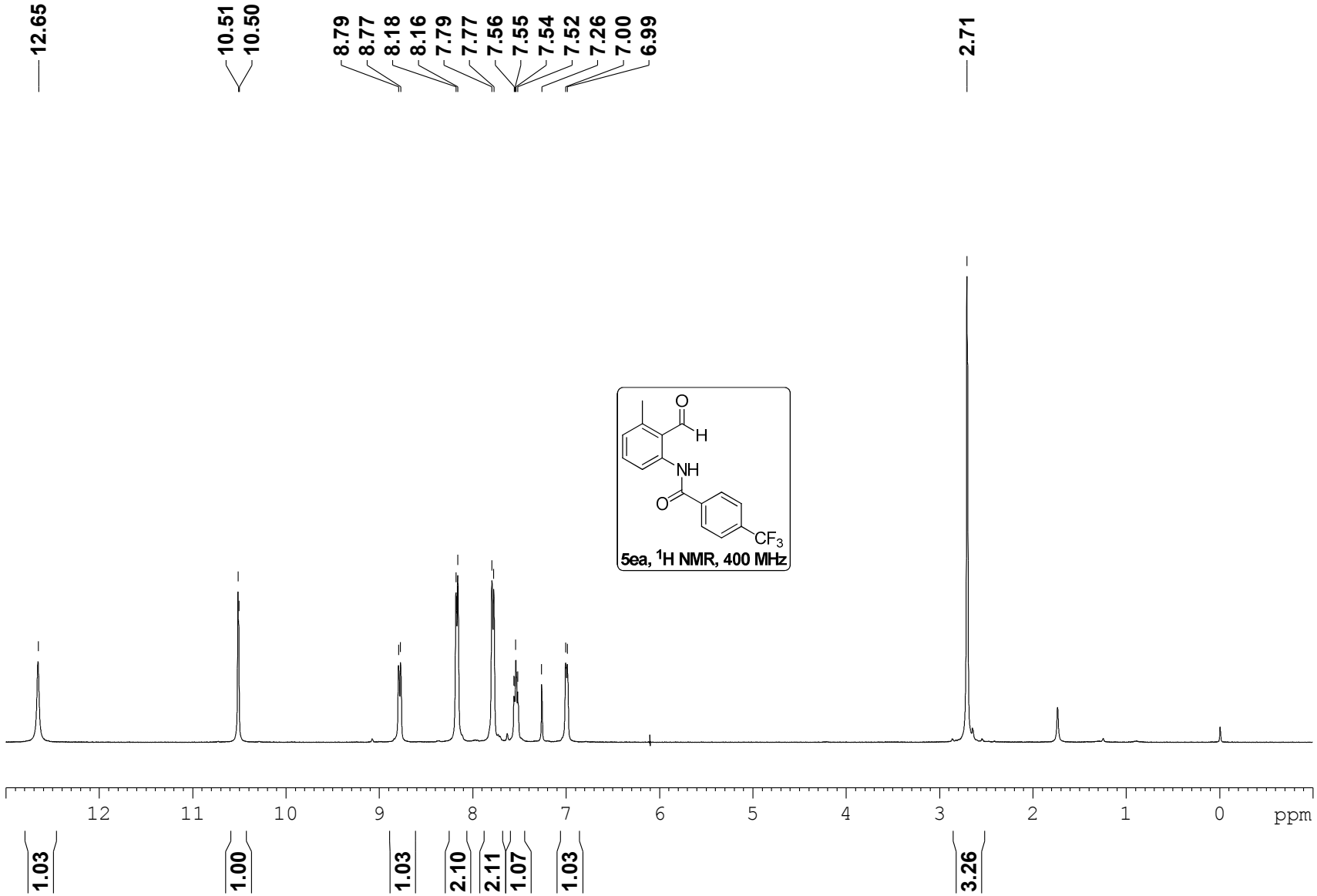
10.50
8.79
8.77
8.01
7.99
7.54
7.52
7.50
7.49
7.48
7.48
7.47
7.26
6.98
6.96
2.70
O
H
NH
O
Cl
5da, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.00
1.02
2.10
3.07
1.03
3.22


195.03
165.22
143.59
142.02
138.55
136.82
133.11
129.22
129.09
126.27
119.66
118.62
77.48
77.16
76.84
19.40
O
H
NH
O
Cl
5da, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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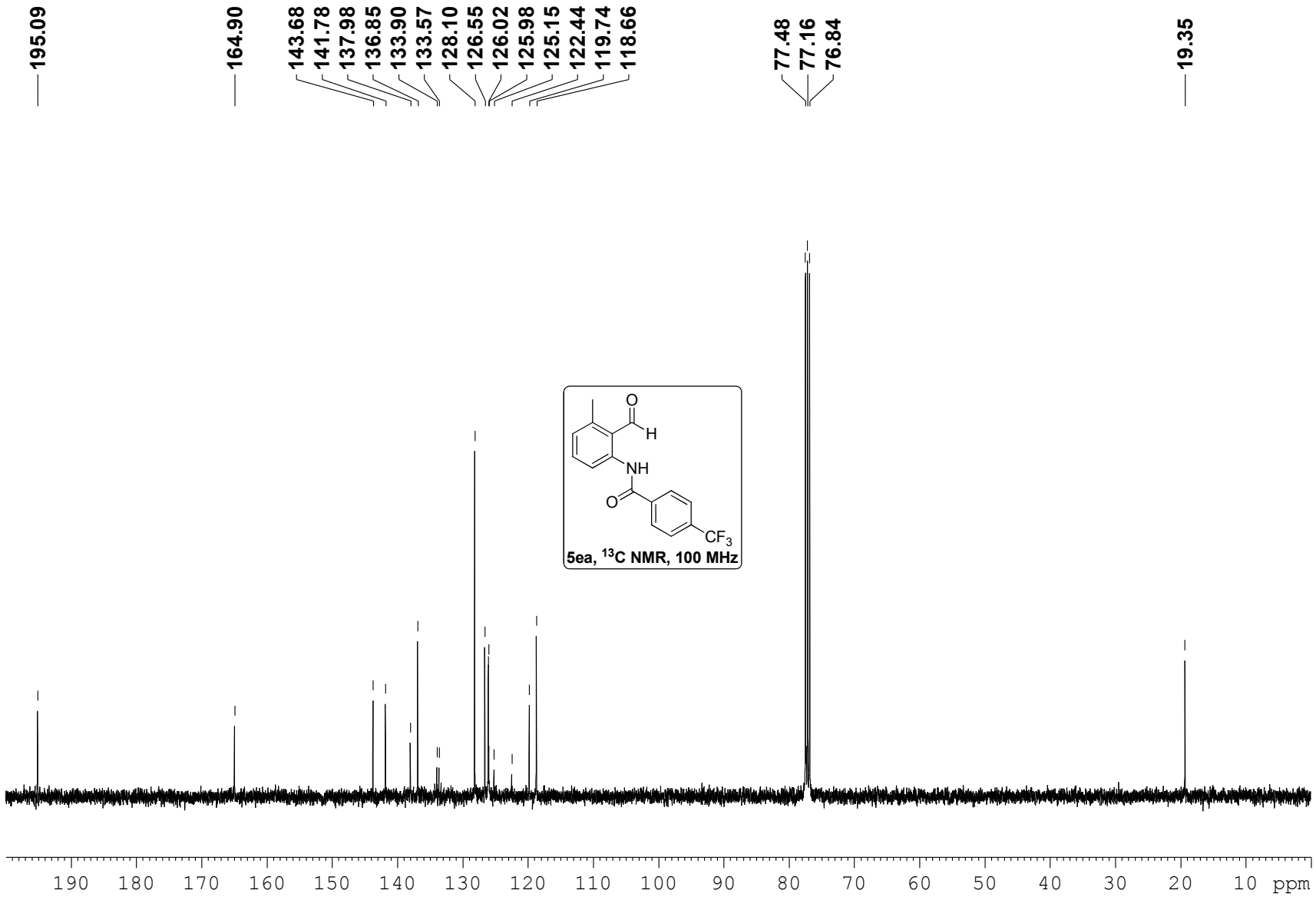
10.51
10.50
8.79
8.77
8.18
8.16
7.79
7.77
7.56
7.55
7.54
7.52
7.26
7.00
6.99
2.71
O
H
NH
O
CF3
5ea, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.03
1.00
1.03
2.10
2.11
1.07
1.03
3.26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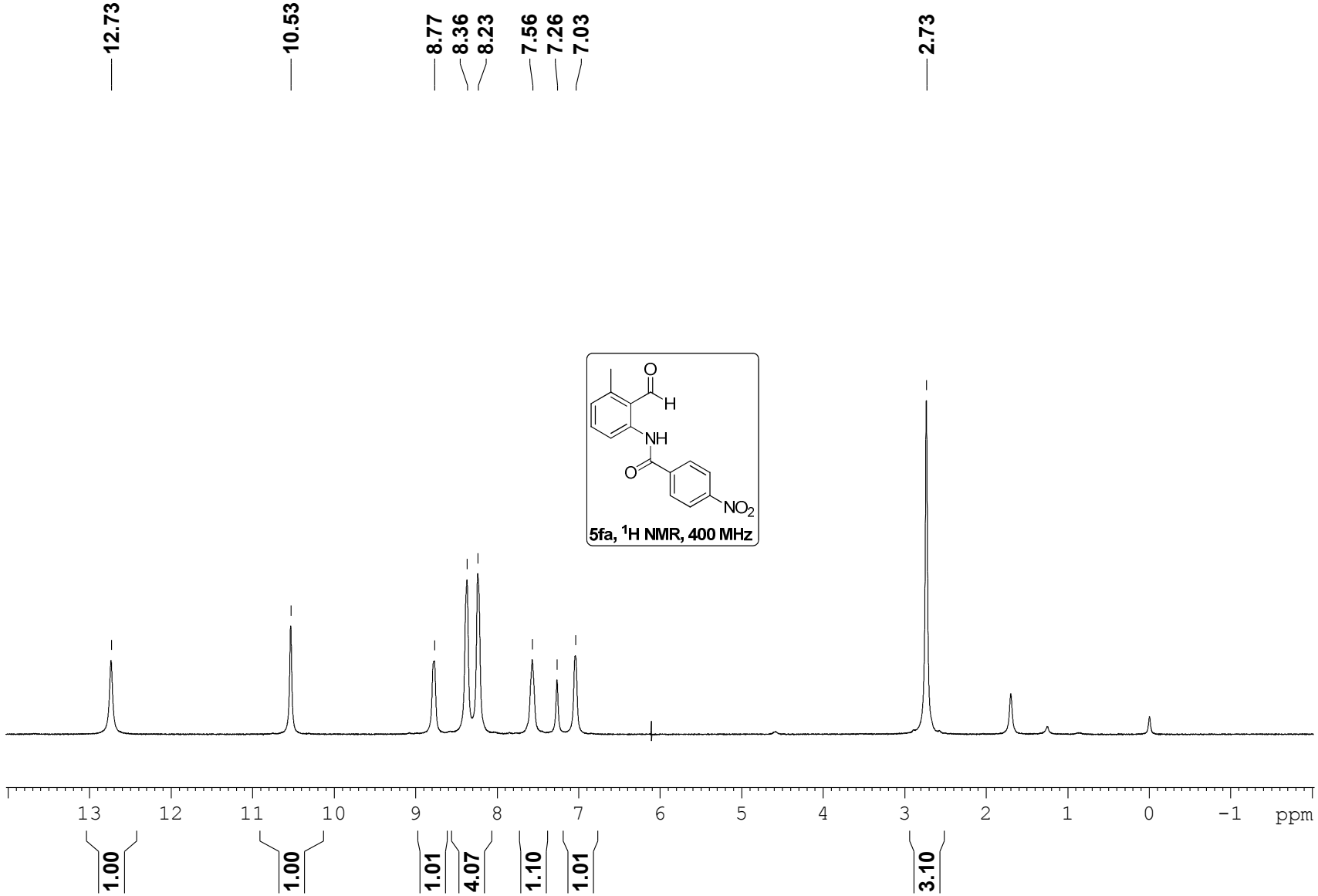
164.90
143.68
141.78
137.98
136.85
133.90
133.57
128.10
126.55
126.02
125.98
125.15
122.44
119.74
118.66
77.48
77.16
76.84
19.35
O
H
NH
O
CF3
5ea, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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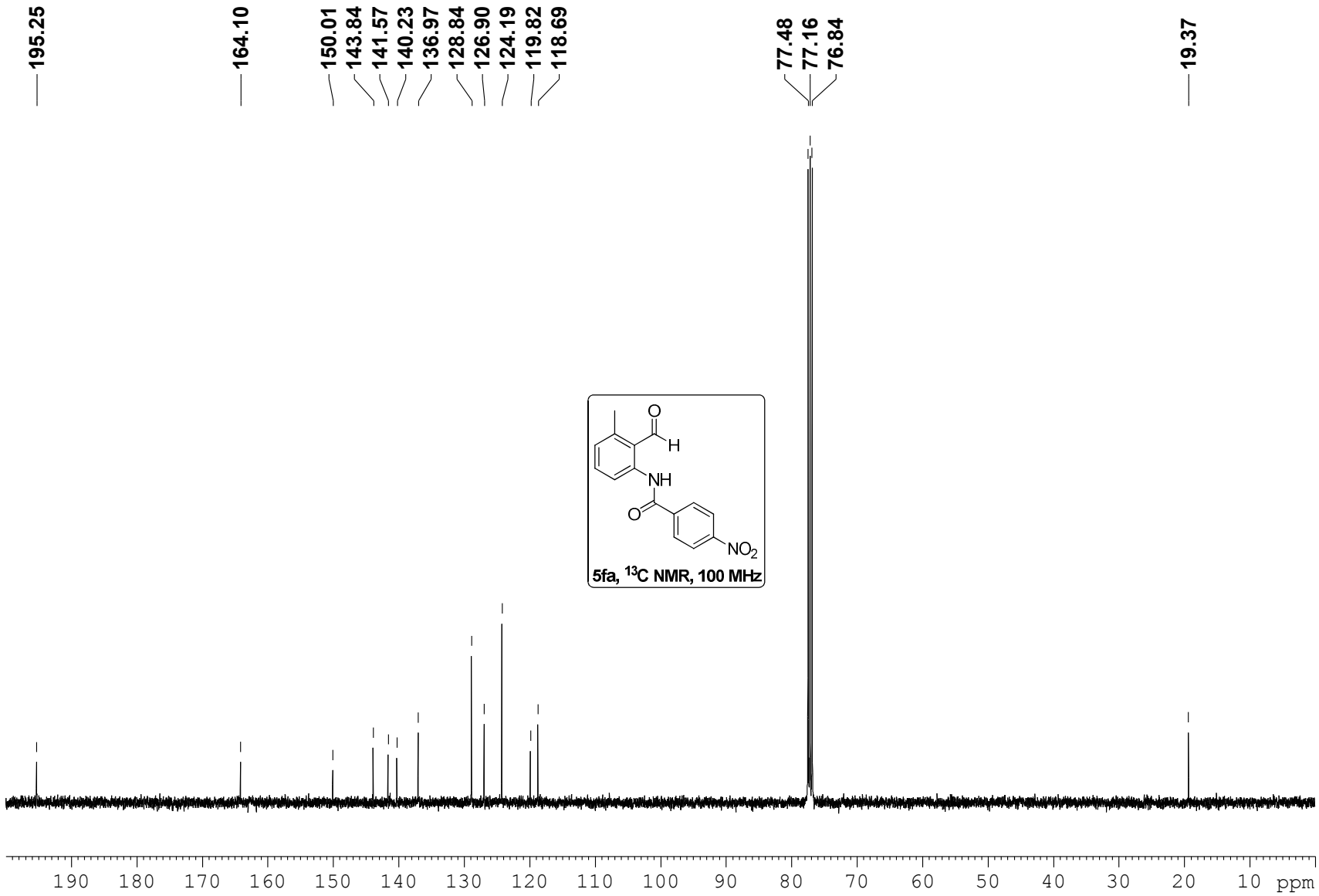
10.53
8.77
8.36
8.23
7.56
7.26
7.03
2.73
O
H
NH
O
NO2
5fa, 1H NMR, 400 MHz
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.00
1.01
4.07
1.10
1.01
3.10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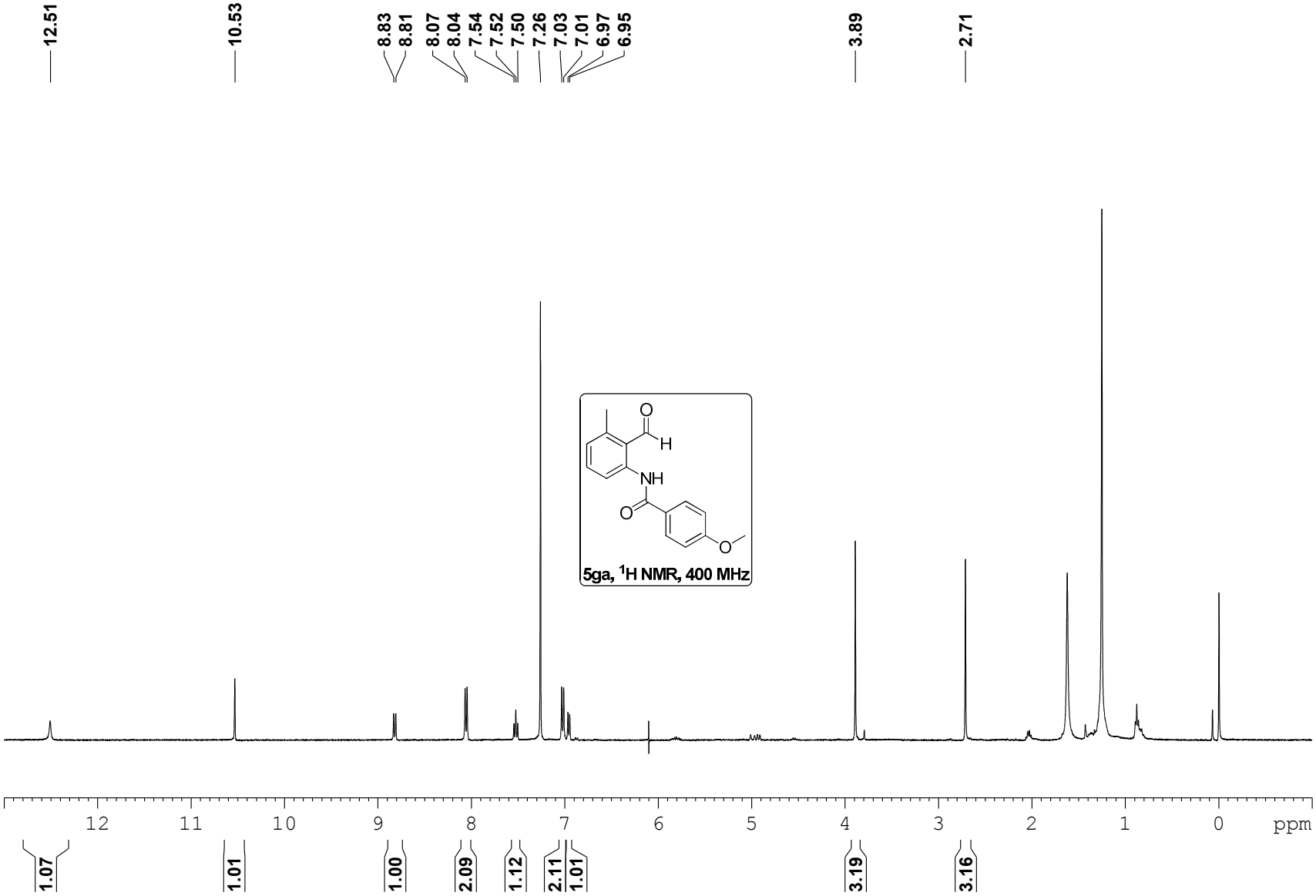
164.10
150.01
143.84
141.57
140.23
136.97
128.84
126.90
124.19
119.82
118.69
77.48
77.16
76.84
19.37
O
H
NH
O
NO2
5fa, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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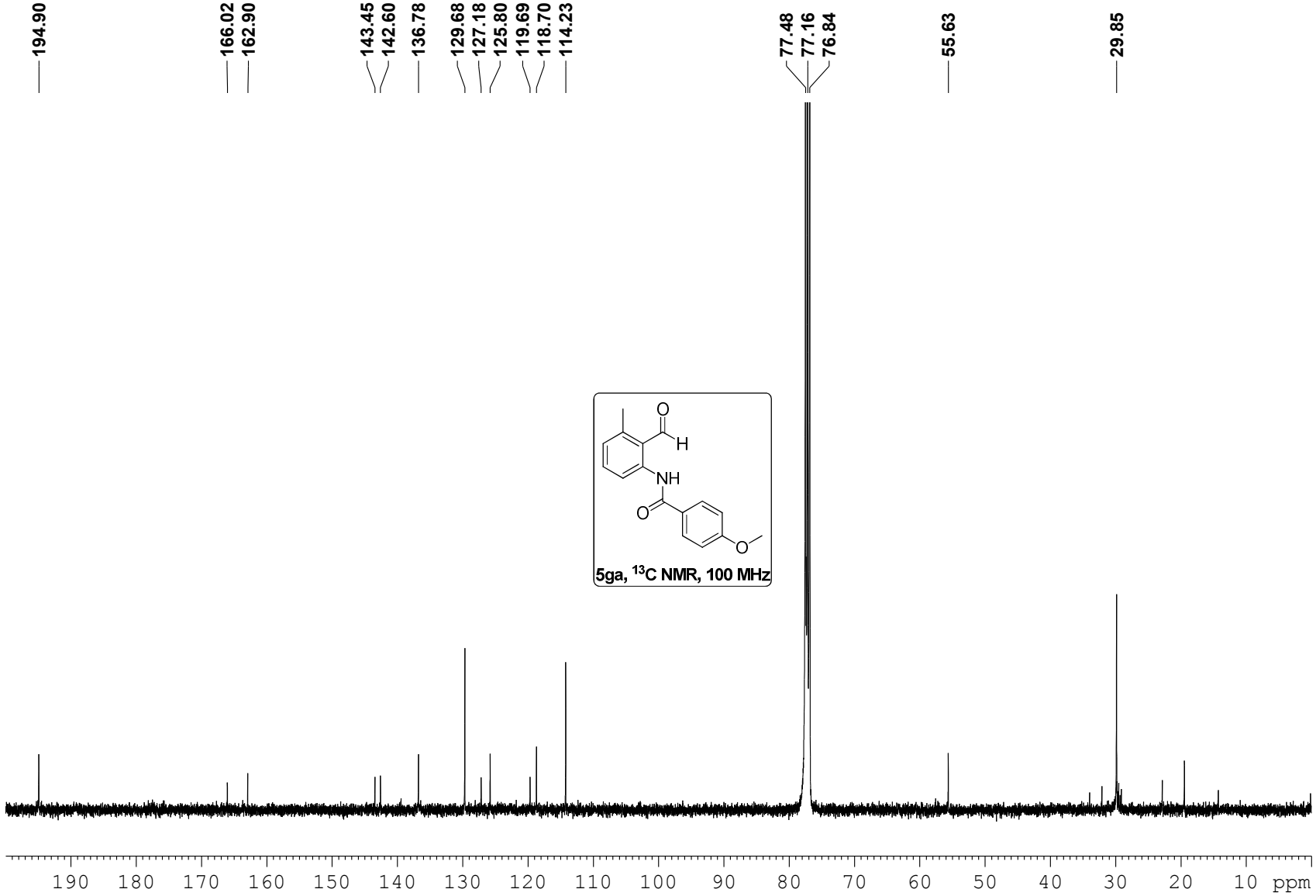
10.53
8.83
8.81
8.07
8.04
7.54
7.52
7.50
7.26
7.03
7.01
6.97
6.95
3.89
2.71
O
H
NH
O
O
5ga, ^{1}H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.07
1.01
1.00
2.09
1.12
2.11
1.01
3.19
3.16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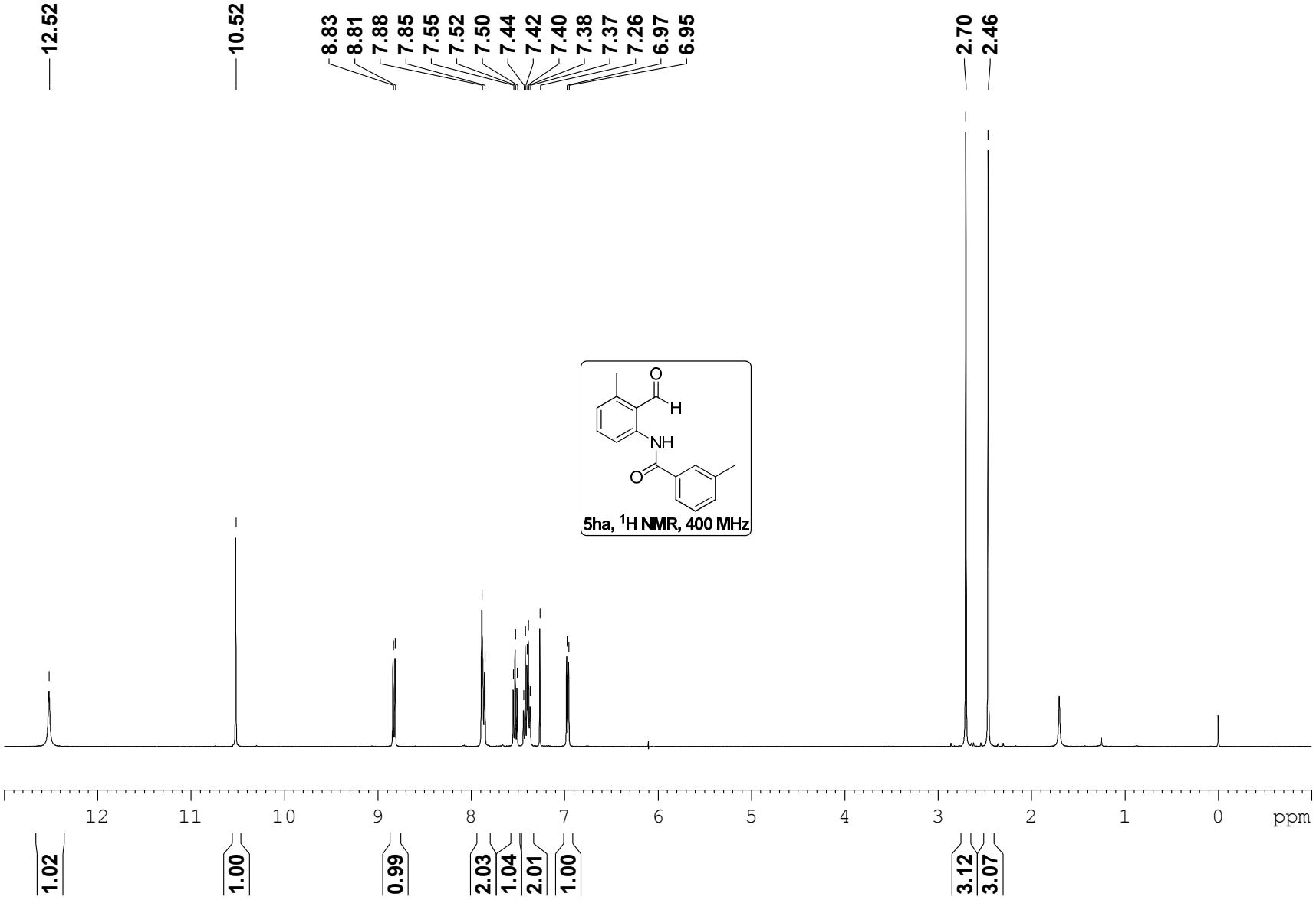
166.02
162.90
143.45
142.60
136.78
129.68
127.18
125.80
119.69
118.70
114.23
77.48
77.16
76.84
55.63
29.85
O
H
NH
O
O
5ga, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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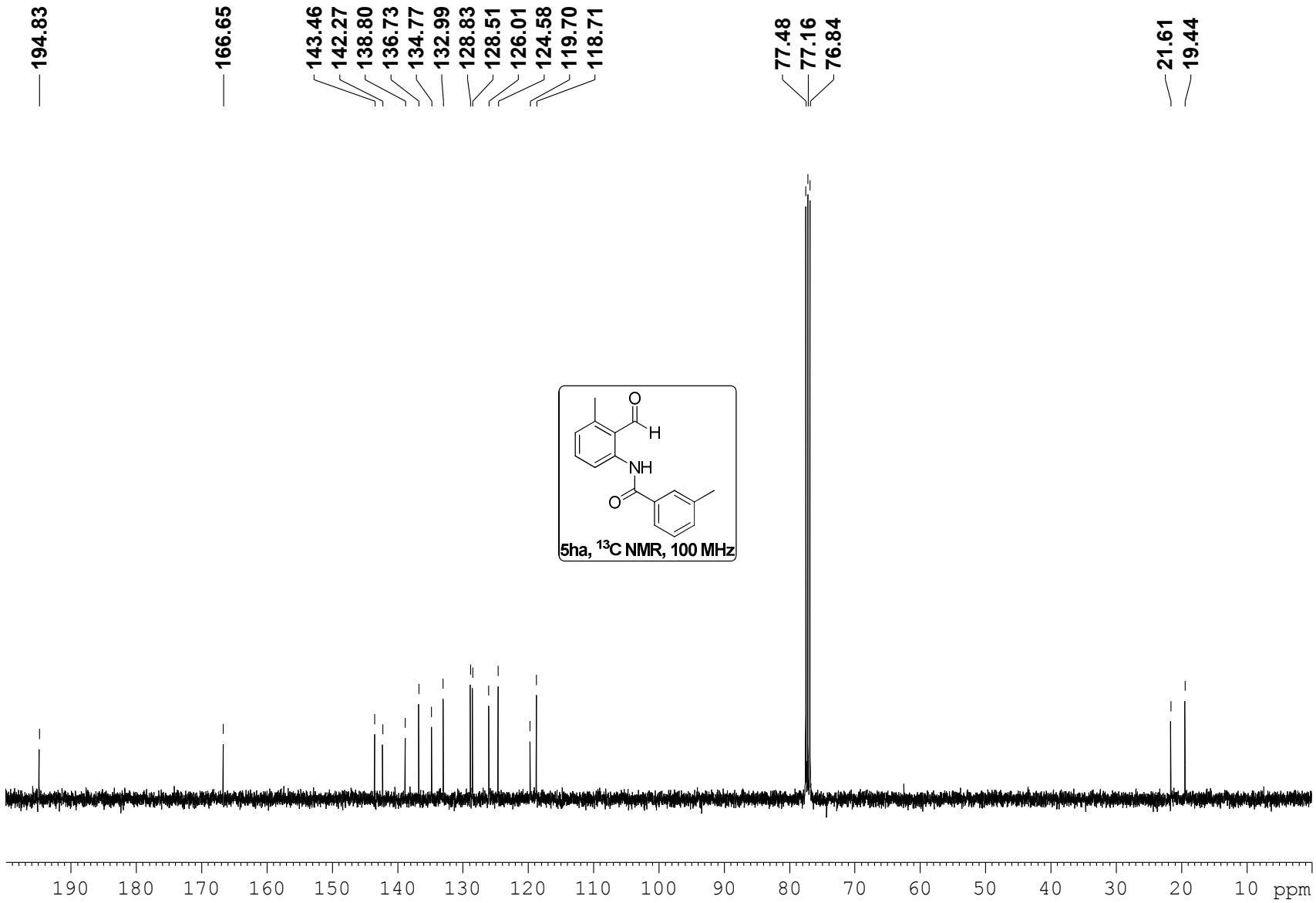
10.52
8.83
8.81
7.88
7.85
7.55
7.52
7.50
7.44
7.42
7.40
7.38
7.37
7.26
6.97
6.95
2.70
2.46
O
H
NH
O
5ha, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.00
0.99
2.03
1.04
2.01
1.00
3.12
3.07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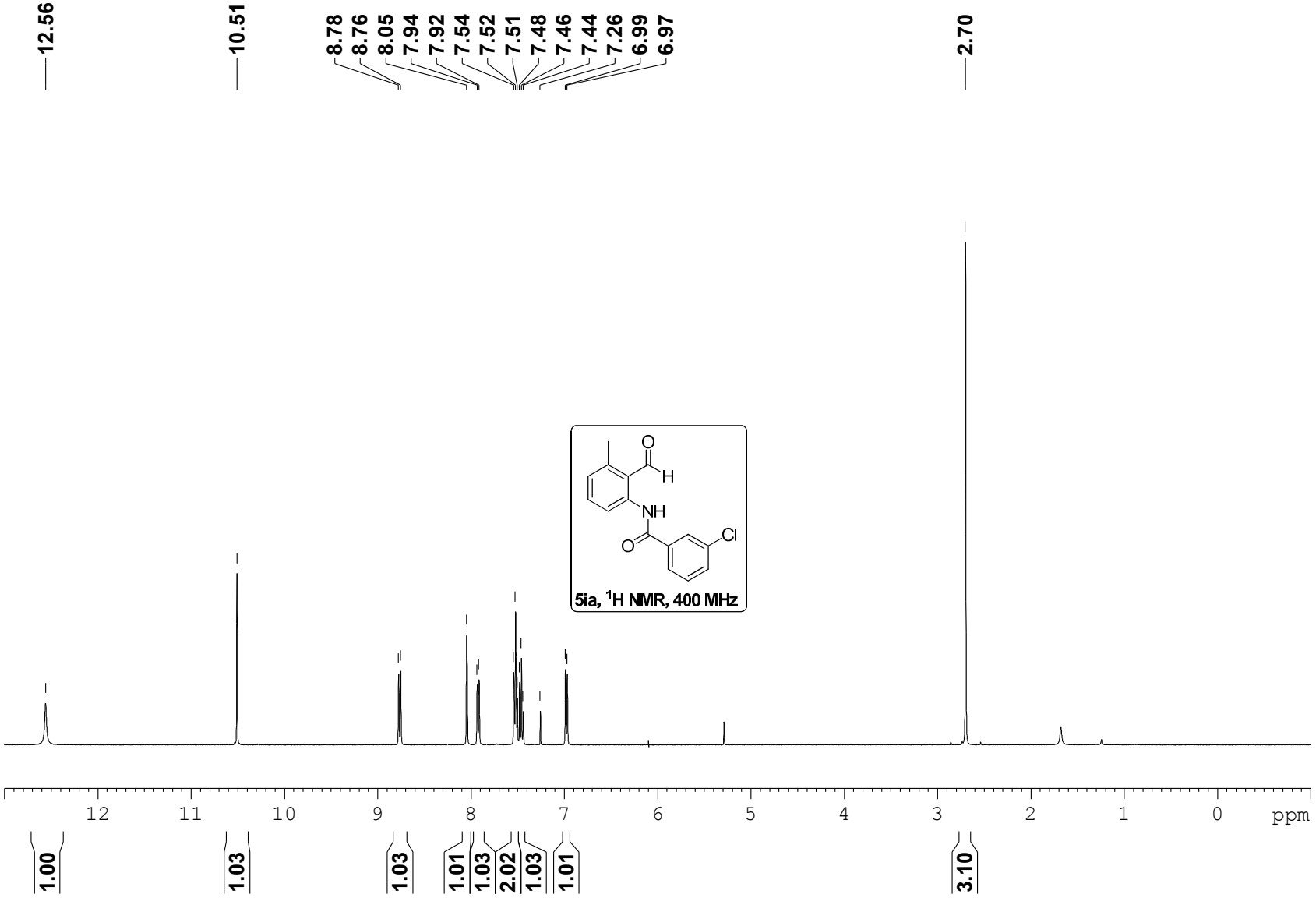
166.65
143.46
142.27
138.80
136.73
134.77
132.99
128.83
128.51
126.01
124.58
119.70
118.71
77.48
77.16
76.84
21.61
19.44
O
H
NH
O
5ha, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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10.51
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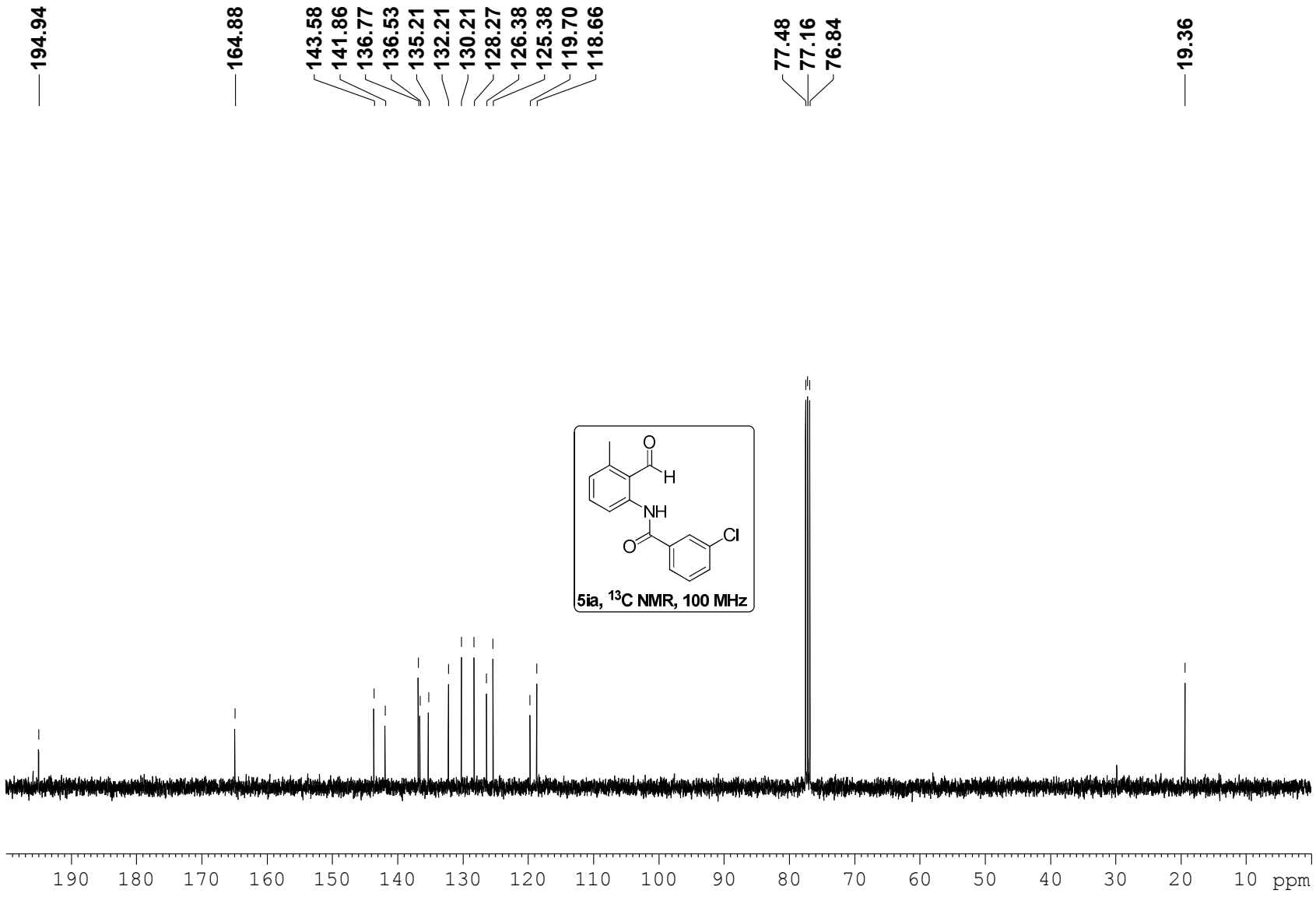
8.76
8.05
7.94
7.92
7.54
7.52
7.51
7.48
7.46
7.44
7.26
6.99
6.97
2.70
O
H
NH
O
Cl
5ia, ^{1}H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
1.03
1.01
1.03
2.02
1.03
1.01
3.10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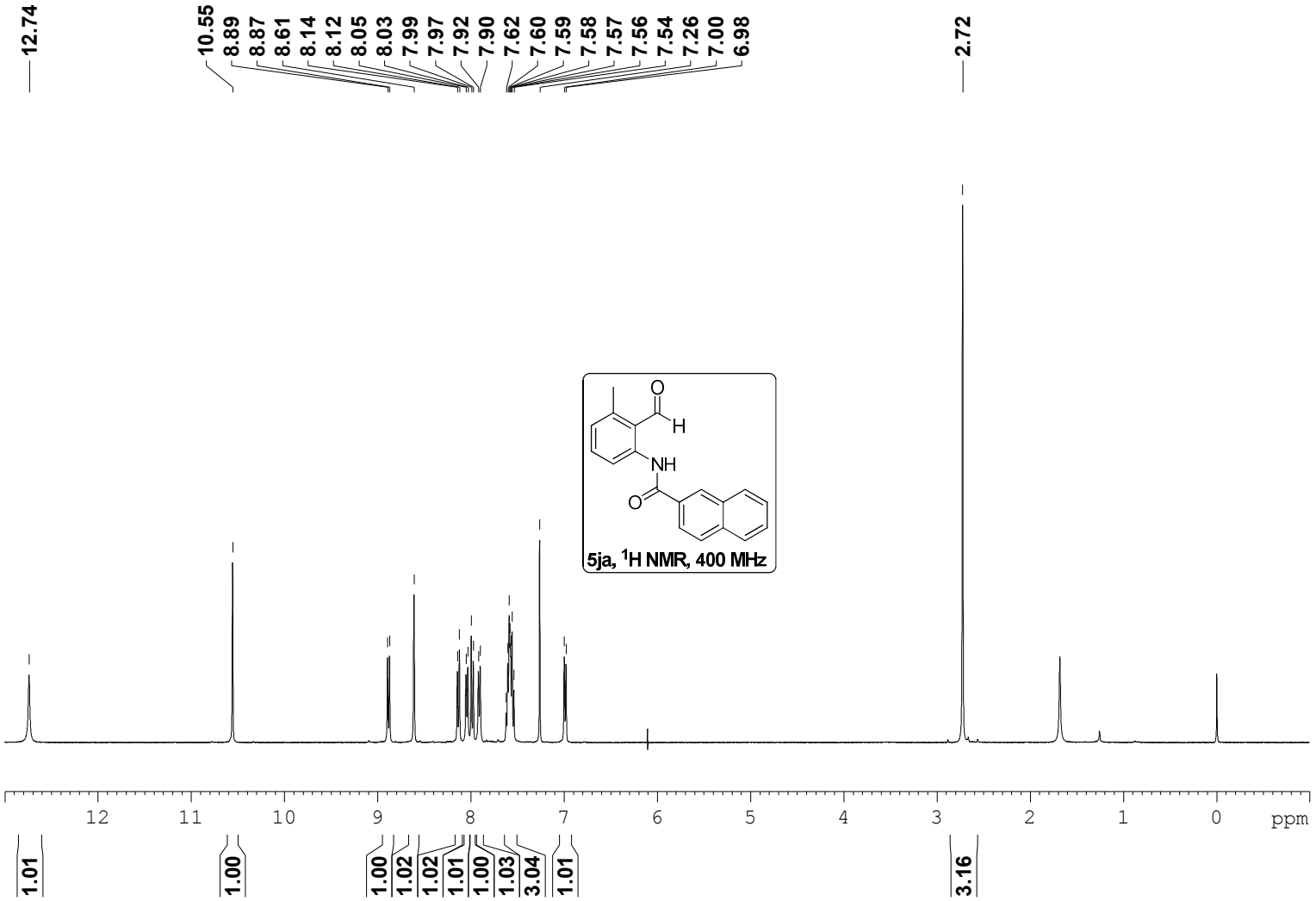
143.58
141.86
136.77
136.53
135.21
132.21
130.21
128.27
126.38
125.38
119.70
118.66
77.48
77.16
76.84
19.36
O
H
NH
O
Cl
5ia, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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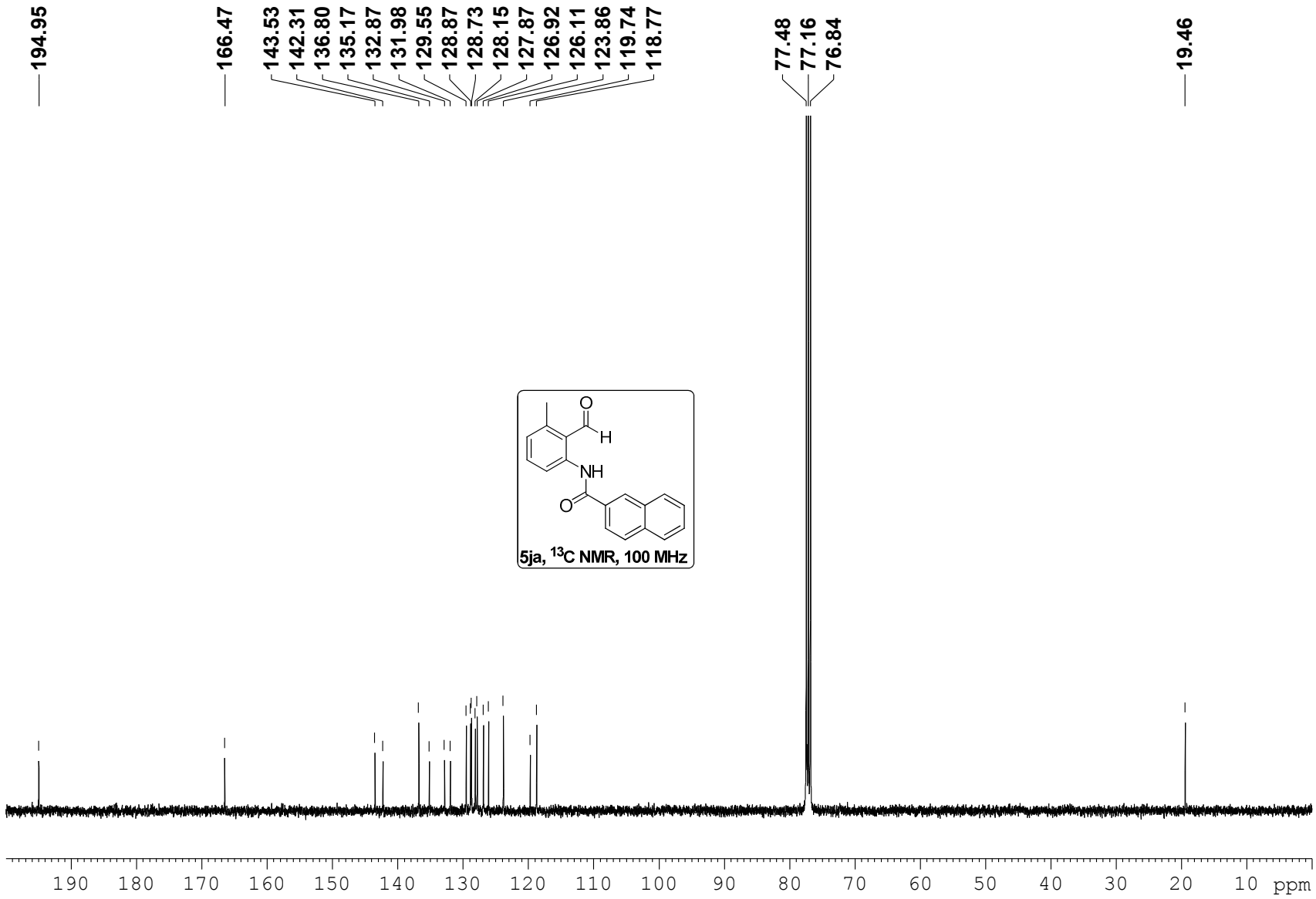
8.61
8.14
8.12
8.05
8.03
7.99
7.97
7.92
7.90
7.62
7.60
7.59
7.58
7.57
7.56
7.54
7.26
7.00
6.98
2.72
O
H
NH
O
5ja, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.00
1.00
1.02
1.02
1.01
1.00
1.03
3.04
1.01
3.16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166.47
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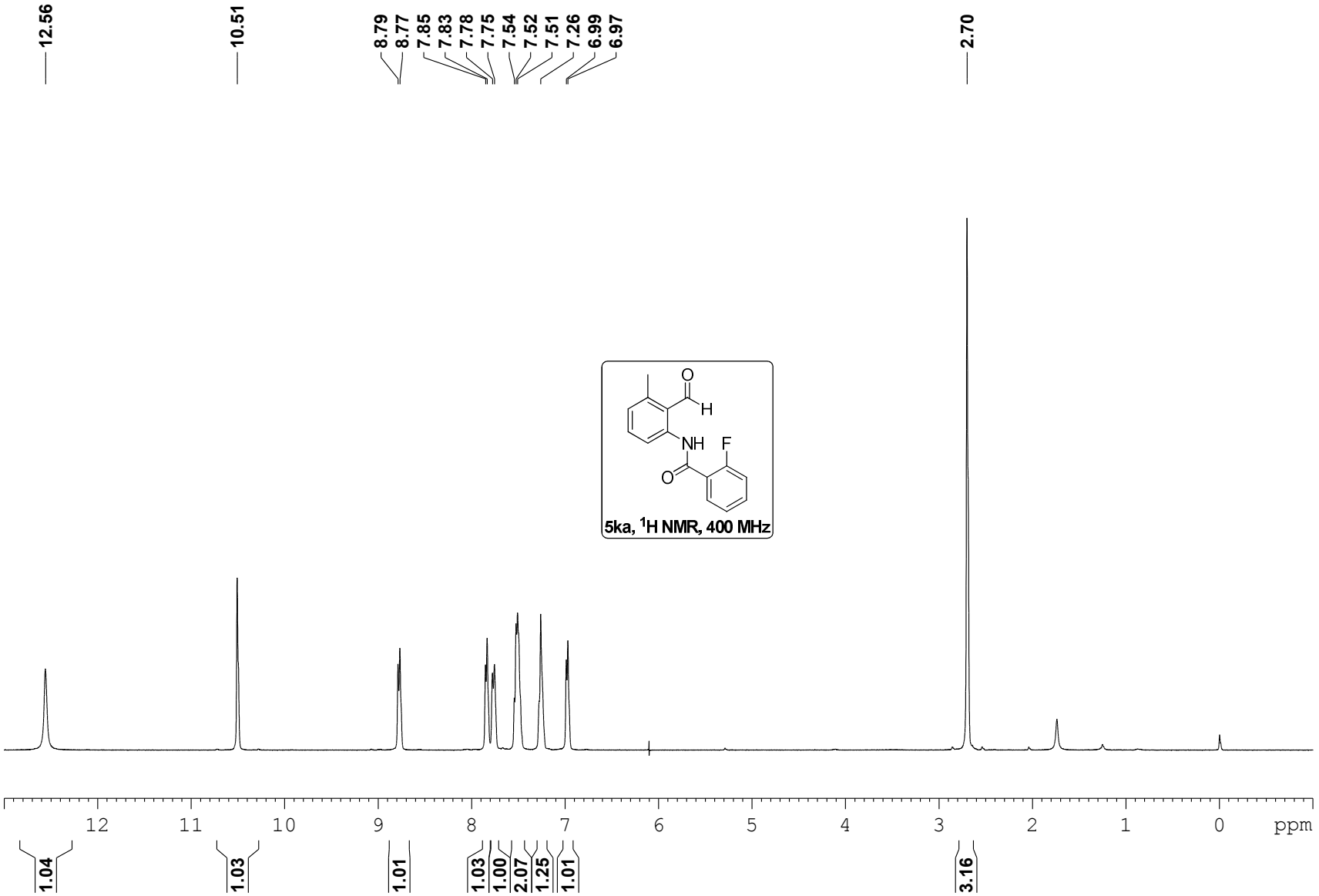
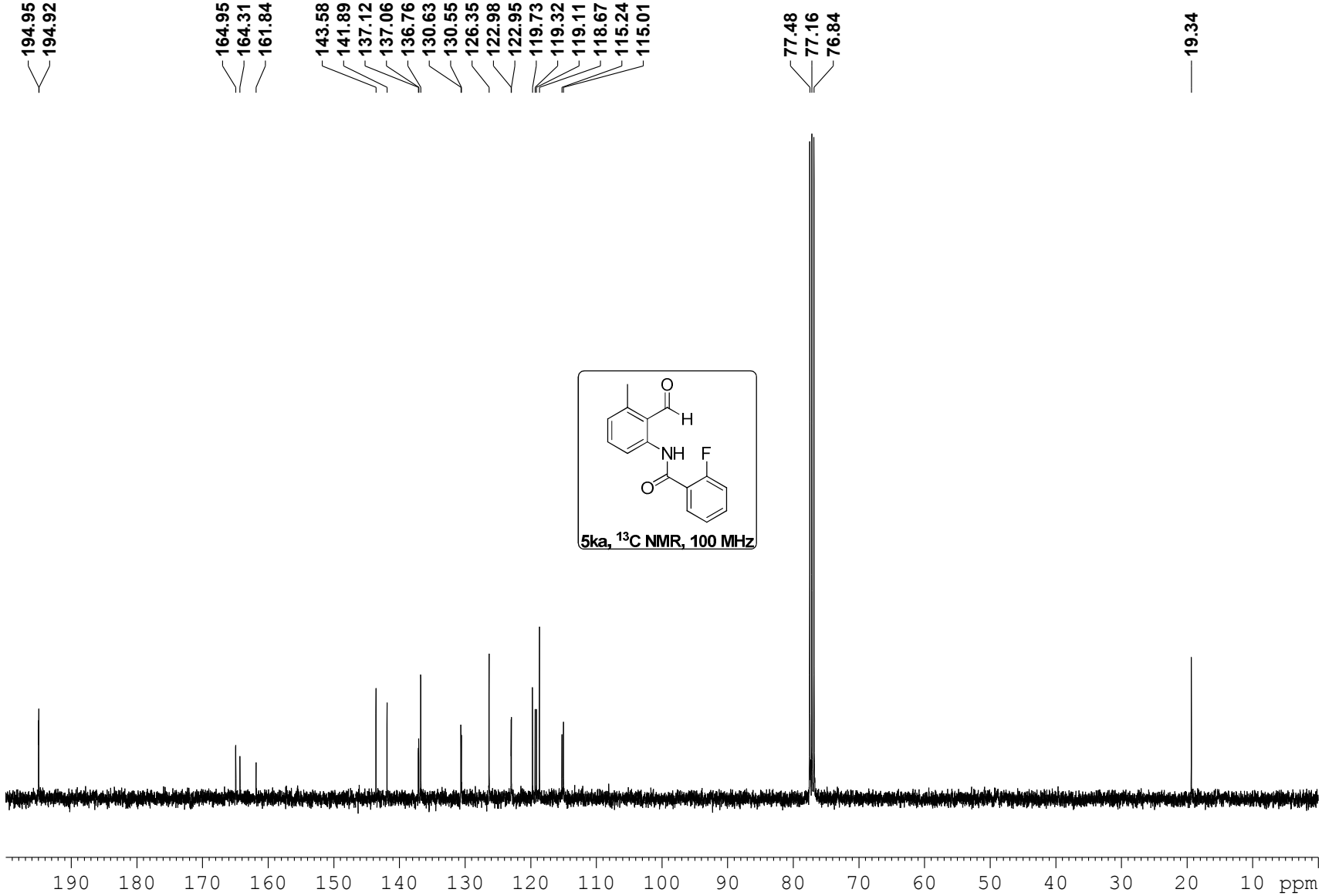
142.31
136.80
135.17
132.87
131.98
129.55
128.87
128.73
128.15
127.87
126.92
126.11
123.86
119.74
118.77
77.48
77.16
76.84
19.46
O
H
NH
O
5ja, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


12.56
10.51
8.79
8.77
7.85
7.83
7.78
7.75
7.54
7.52
7.51
7.26
6.99
6.97
2.70
O
H
NH
F
O
5ka, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.03
1.01
1.03
1.00
2.07
1.25
1.01
3.16


194.95
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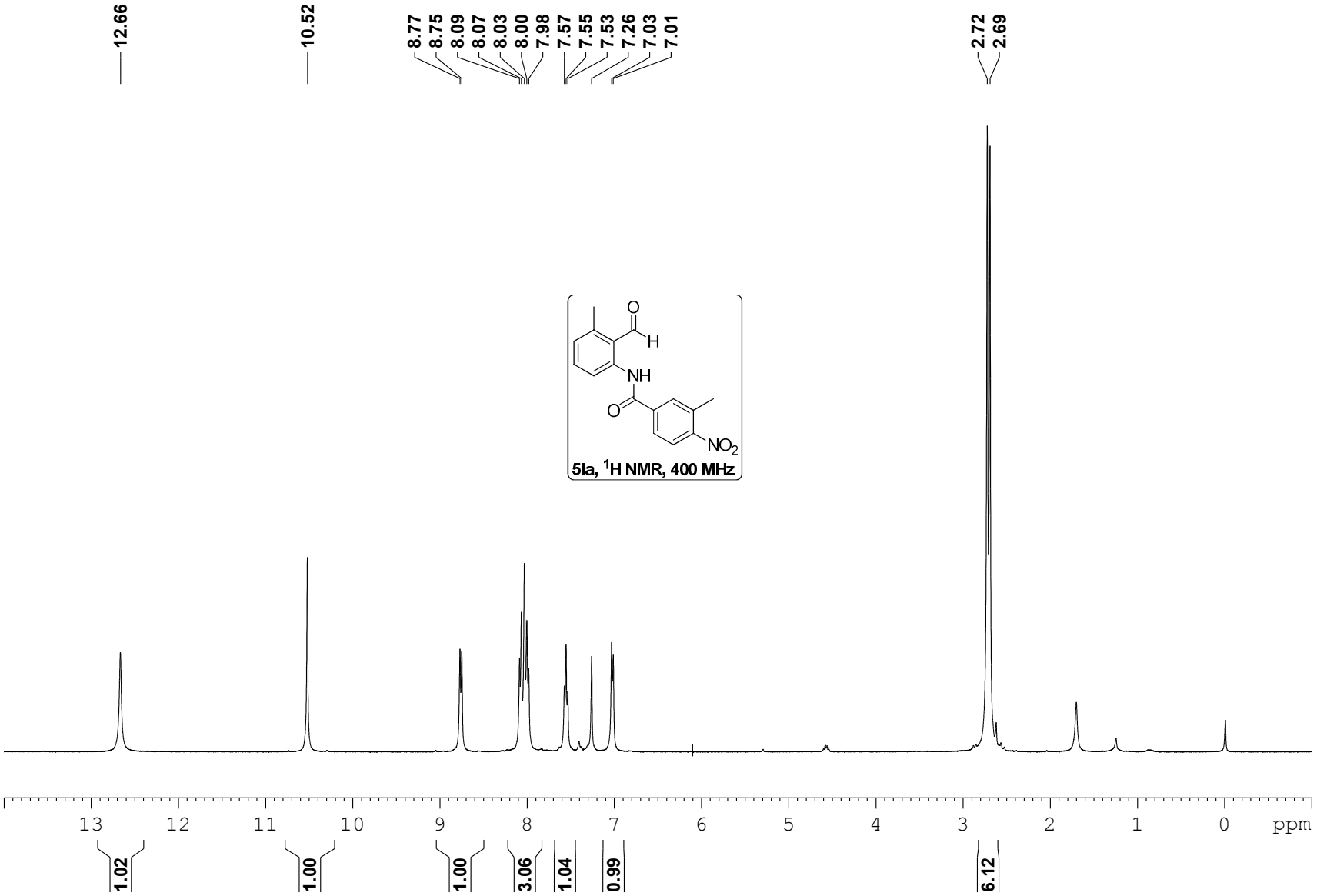
164.95
164.31
161.84
143.58
141.89
137.12
137.06
136.76
130.63
130.55
126.35
122.98
122.95
119.73
119.32
119.11
118.67
115.24
115.01
77.48
77.16
76.84
19.34
O
H
NH
F
O
5ka, 13C NMR, 100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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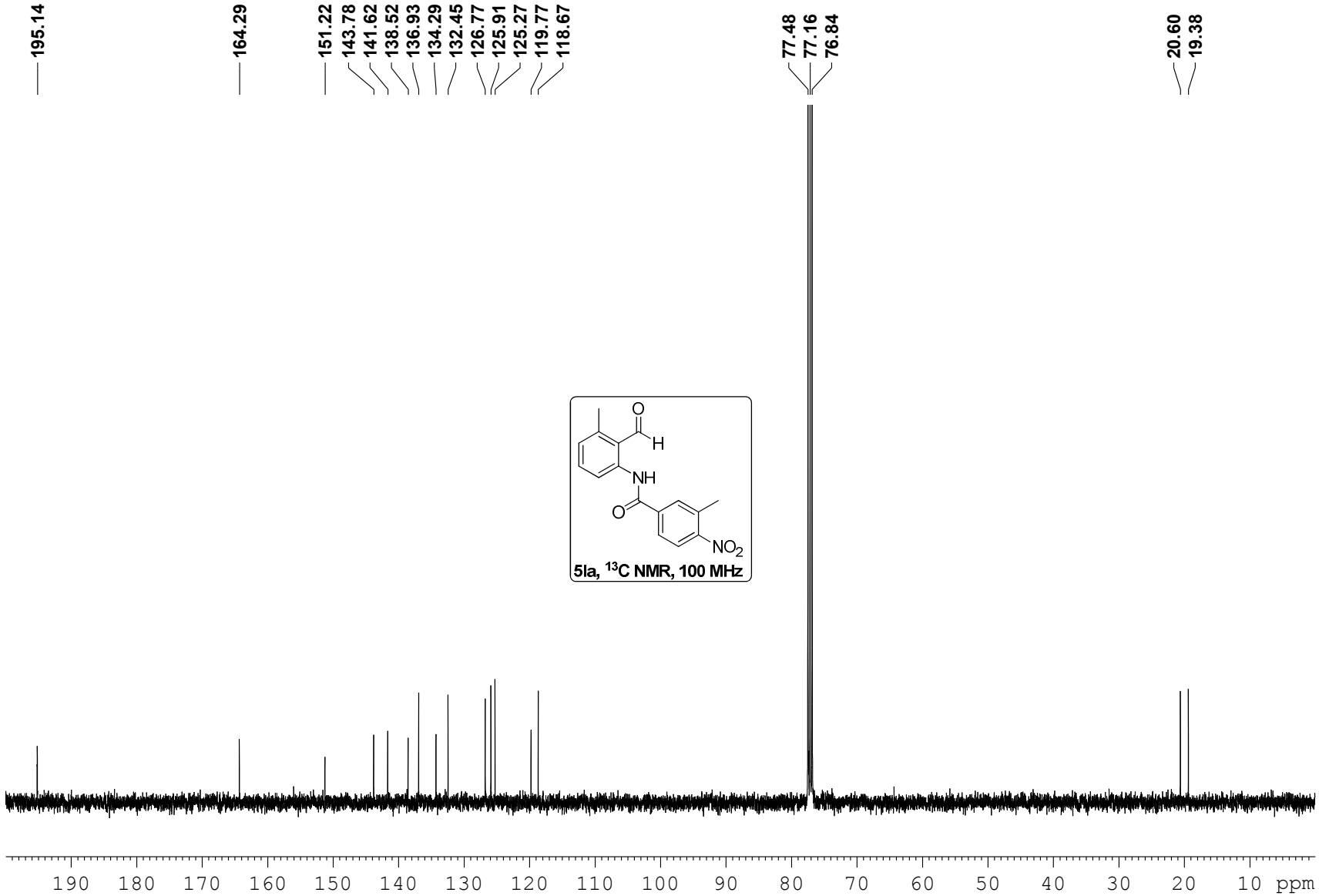
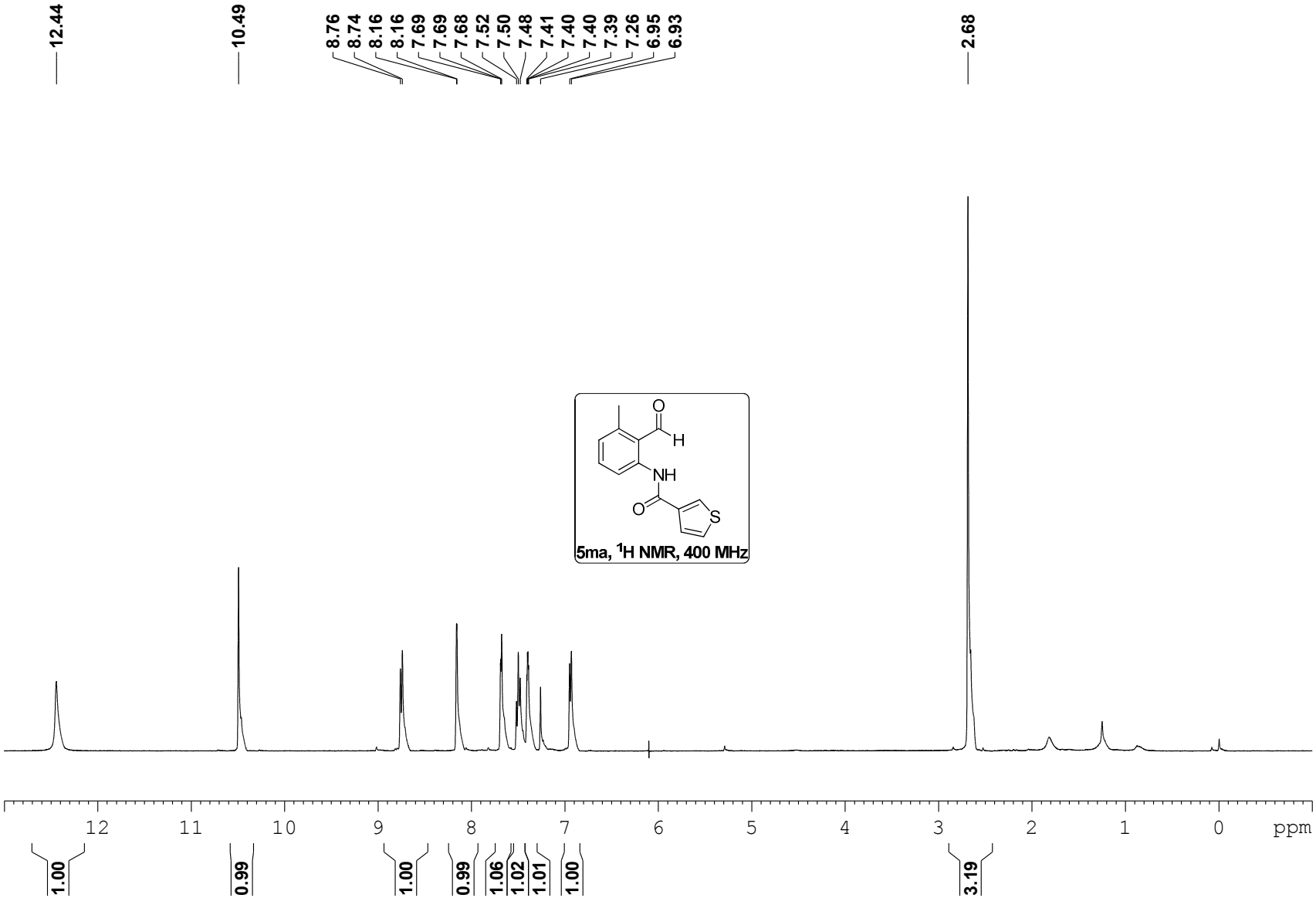
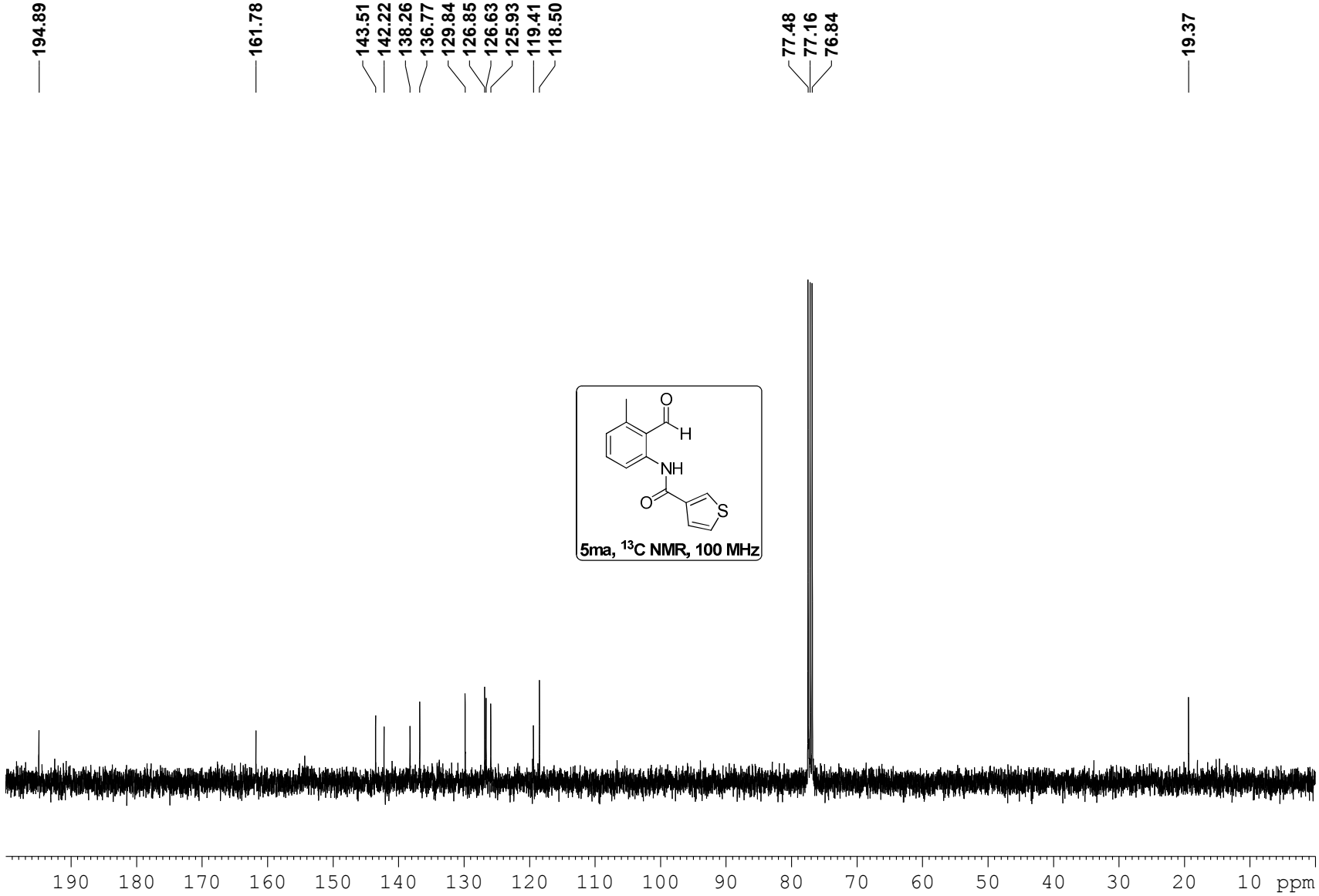
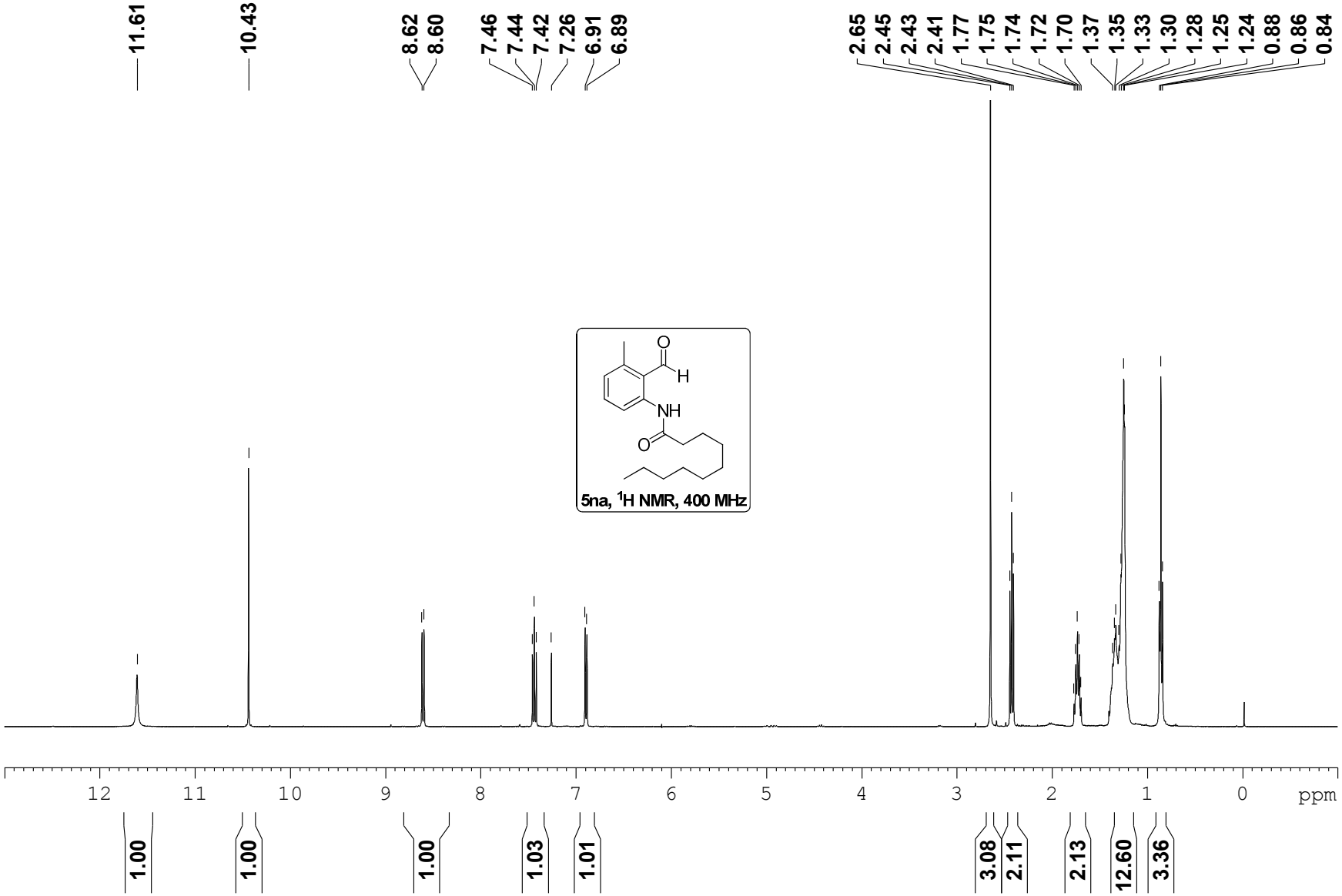
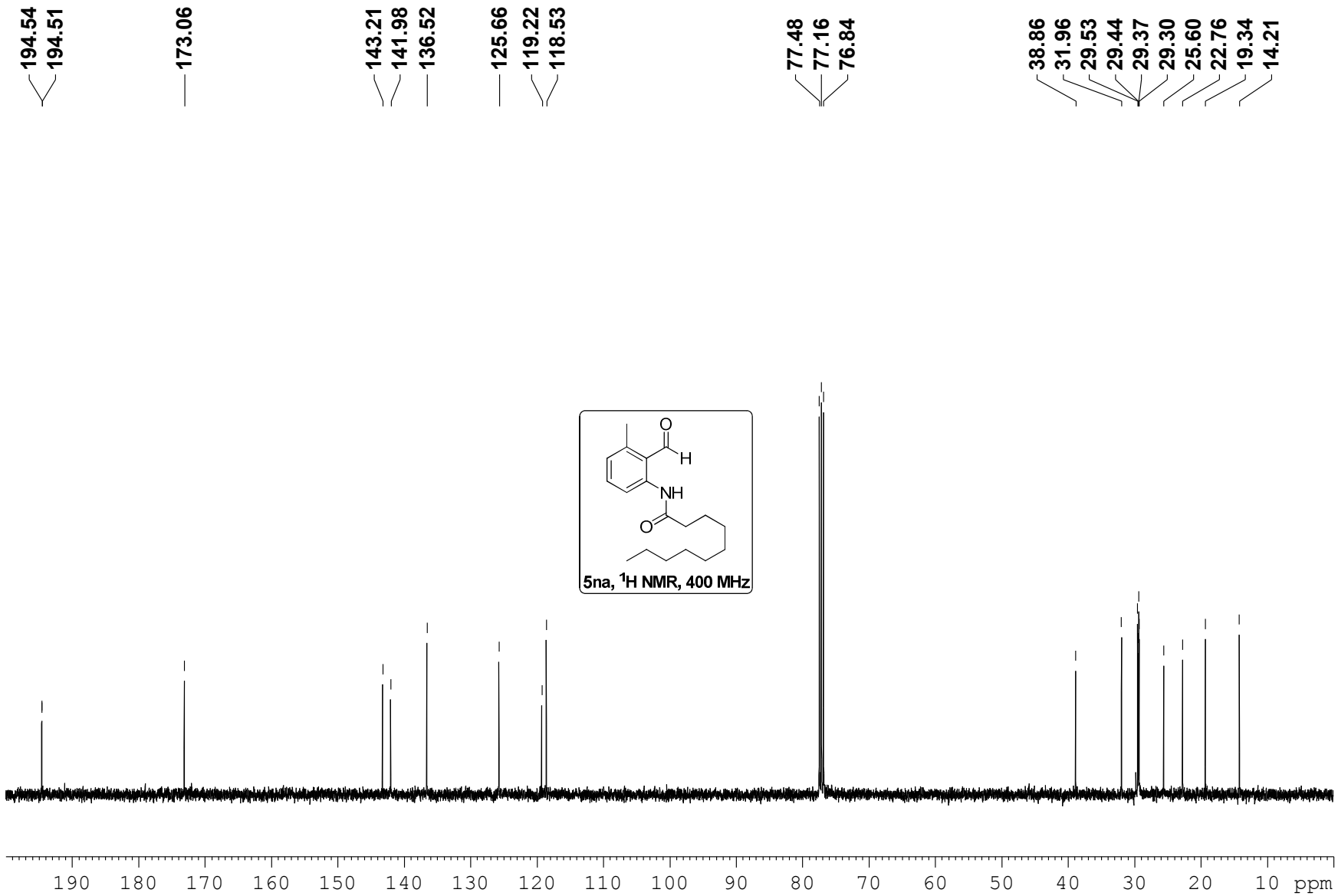
10.52
8.77
8.75
8.09
8.07
8.03
8.00
7.98
7.57
7.55
7.53
7.26
7.03
7.01
2.72
2.69
O
H
NH
O
NO2
5Ia, 1H NMR, 400 MHz
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.00
1.00
3.06
1.04
0.99
6.12

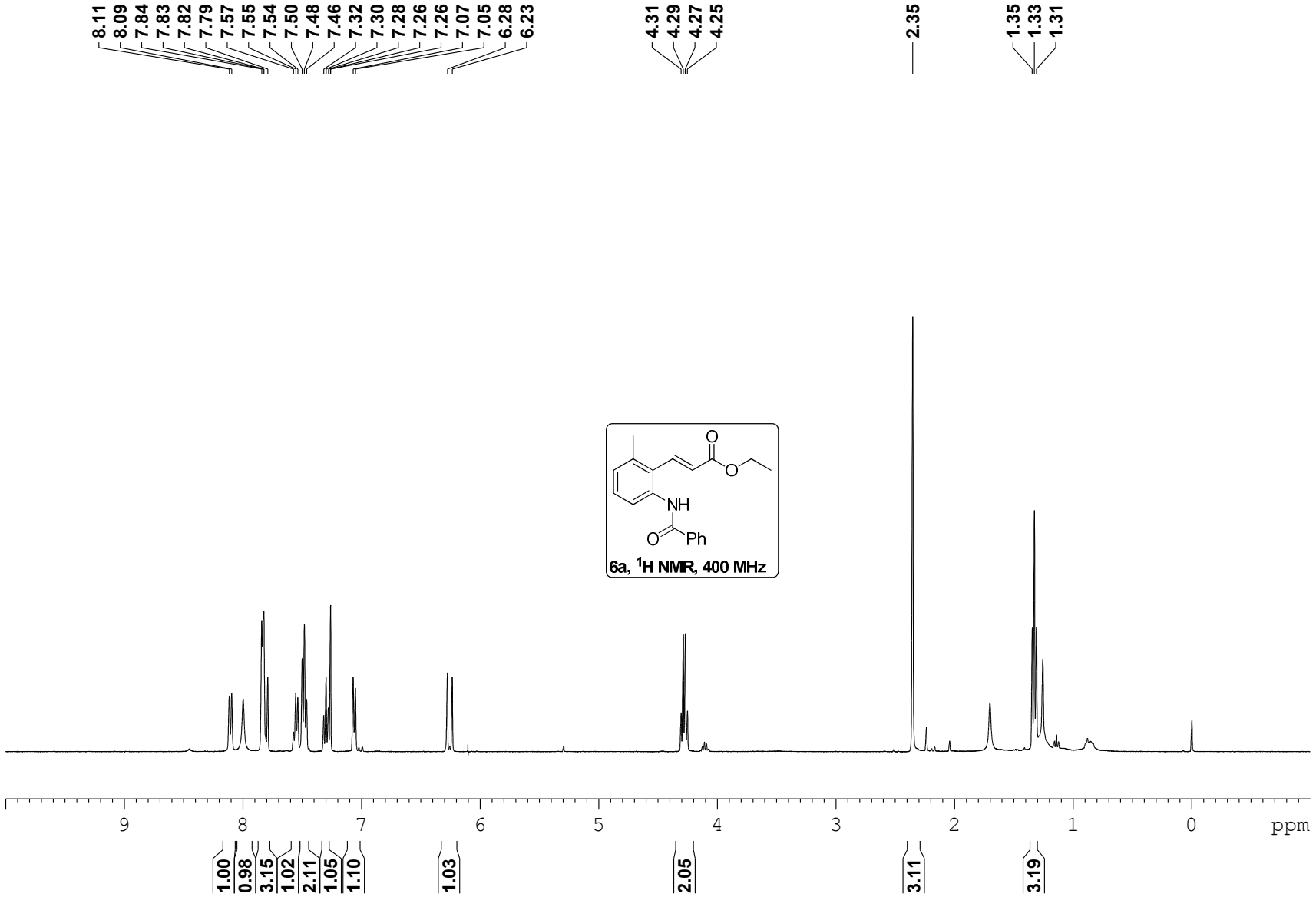

195.14
164.29
151.22
143.78
141.62
138.52
136.93
134.29
132.45
126.77
125.91
125.27
119.77
118.67
77.48
77.16
76.84
20.60
19.38
O
H
NH
O
NO2
5ia, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

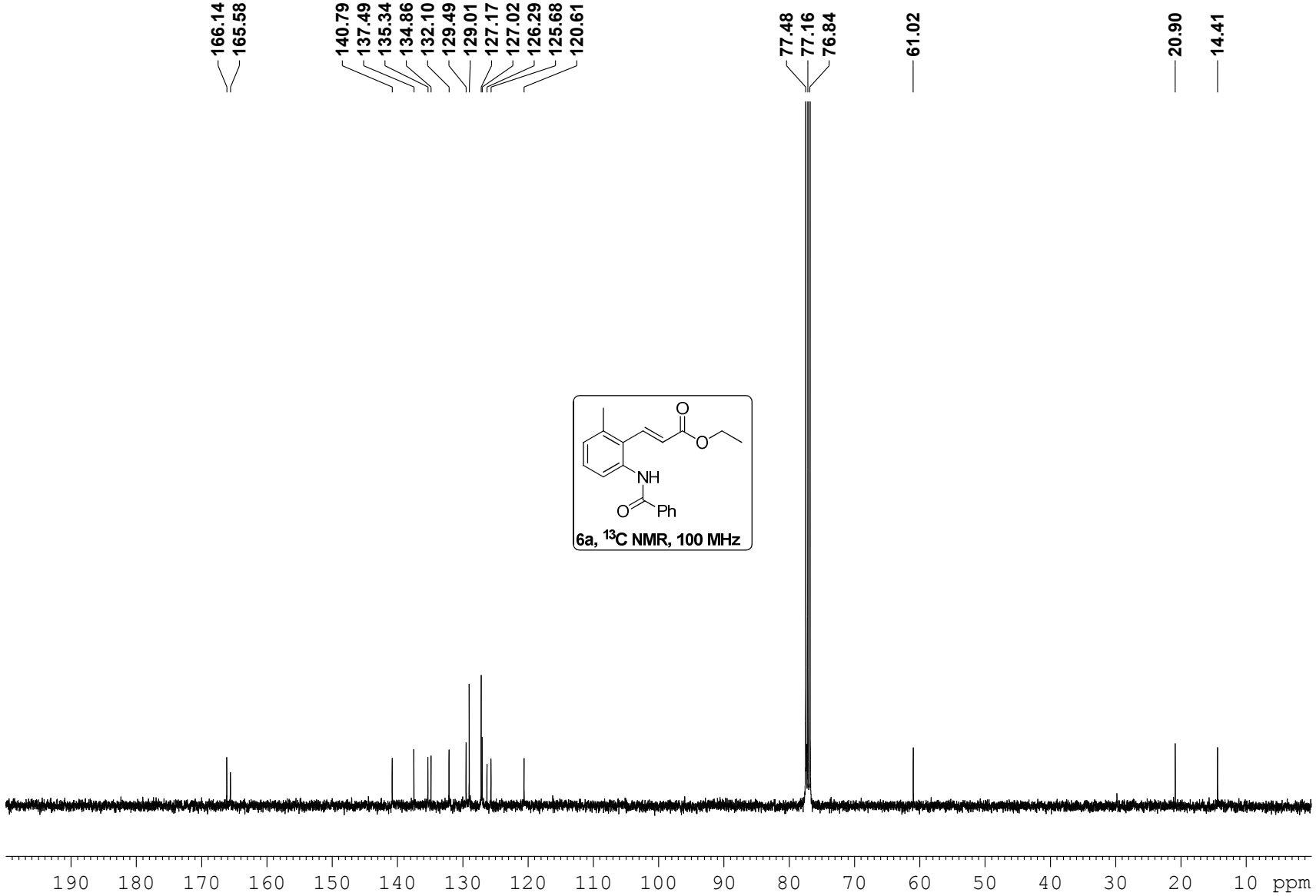

12.44
10.49
8.76
8.74
8.16
8.16
7.69
7.69
7.68
7.52
7.50
7.48
7.41
7.40
7.40
7.39
7.26
6.95
6.93
2.68
O
H
NH
O
S
5ma, ^{1}H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.00
0.99
1.06
1.02
1.01
1.00
3.19

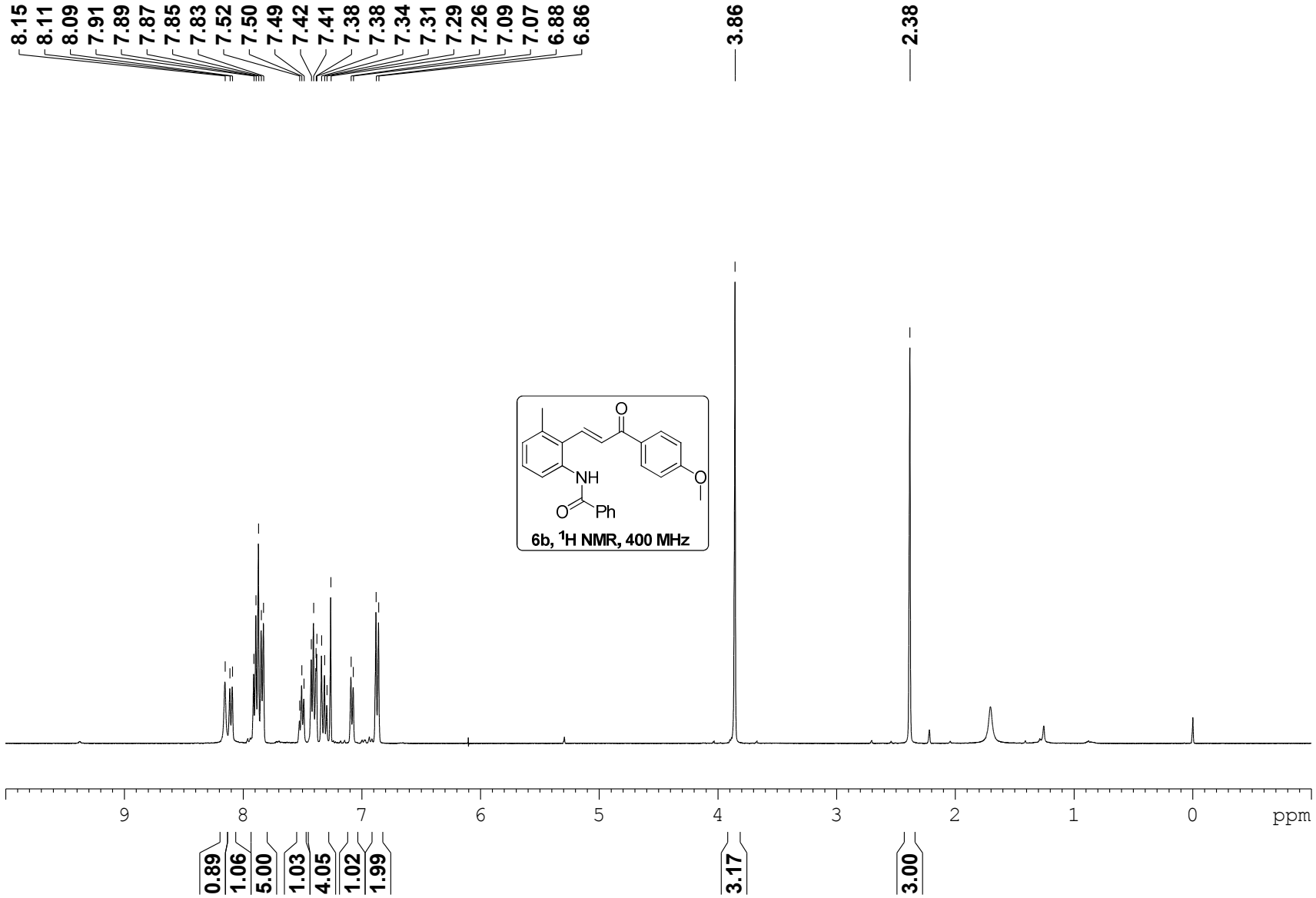

194.89
161.78
143.51
142.22
138.26
136.77
129.84
126.85
126.63
125.93
119.41
118.50
77.48
77.16
76.84
19.37
O
H
NH
O
S
5ma, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

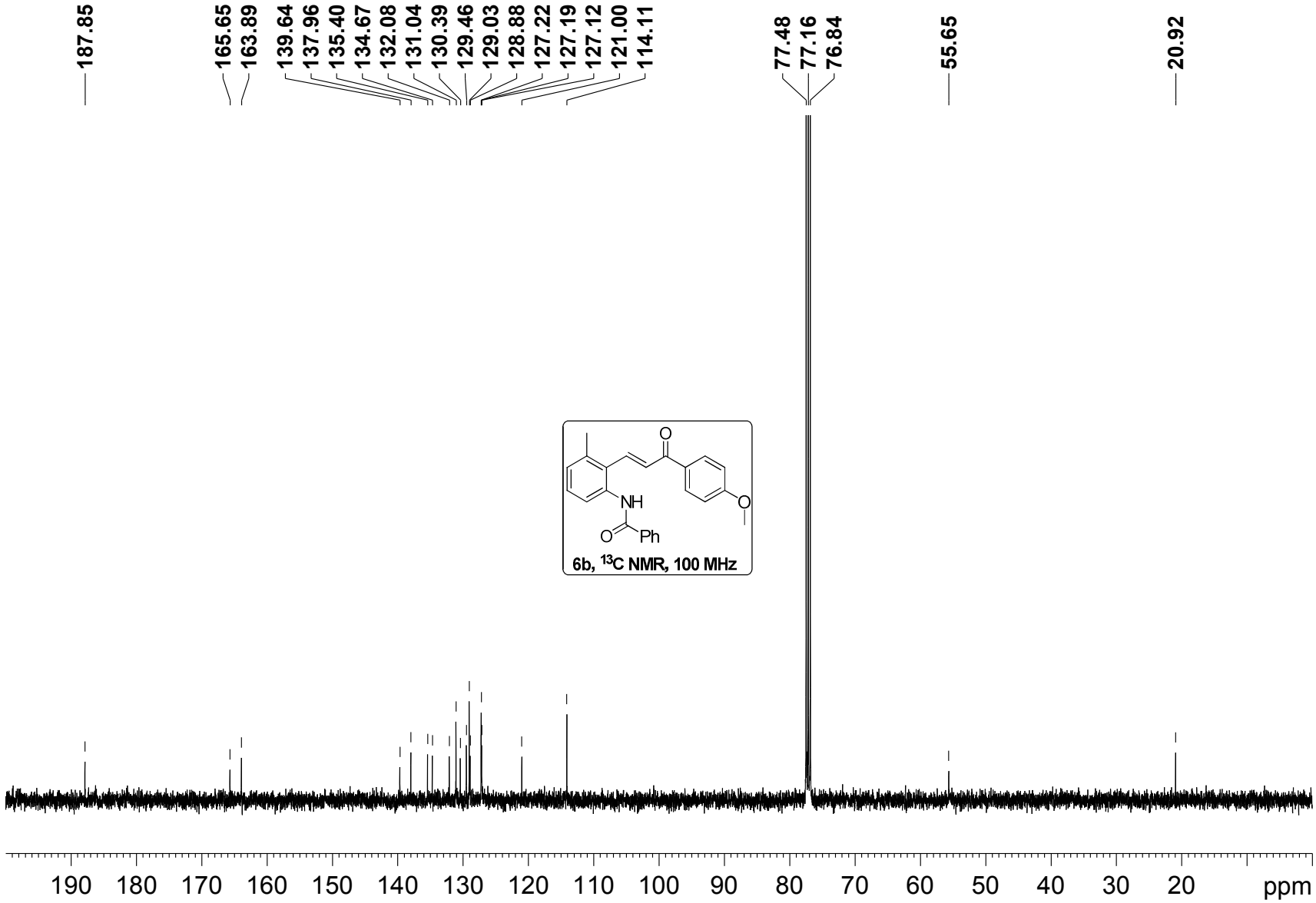

11.61
10.43
8.62
8.60
7.46
7.44
7.42
7.26
6.91
6.89
2.65
2.45
2.43
2.41
1.77
1.75
1.74
1.72
1.70
1.37
1.35
1.33
1.30
1.28
1.25
1.24
0.88
0.86
0.84
O
H
NH
O
5na, 1H NMR, 400 MHz
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.00
1.03
1.01
3.08
2.11
2.13
12.60
3.36

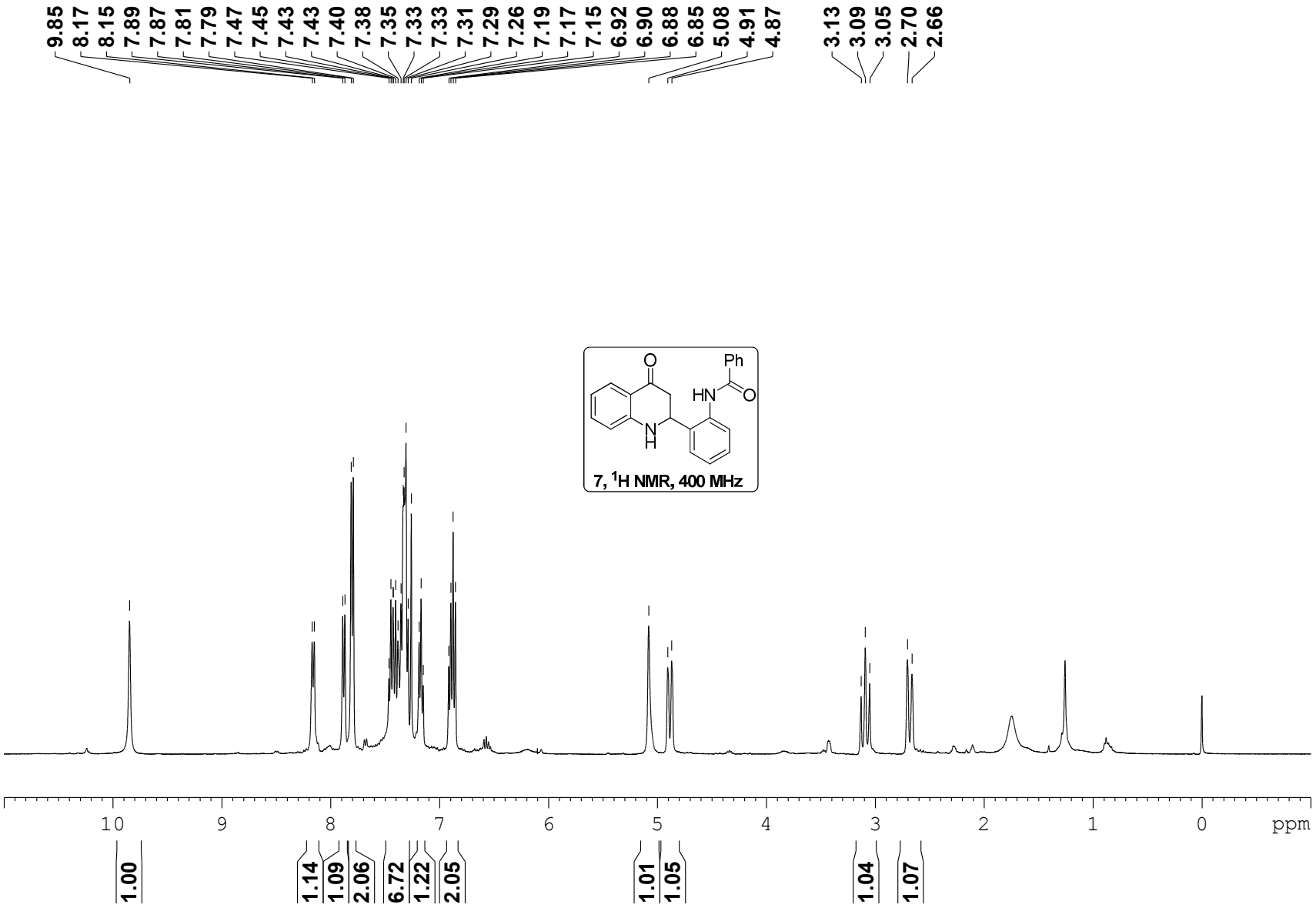

194.54
194.51
173.06
143.21
141.98
136.52
125.66
119.22
118.53
77.48
77.16
76.84
38.86
31.96
29.53
29.44
29.37
29.30
25.60
22.76
19.34
14.21
O
H
NH
O
5na, 1H NMR, 400 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

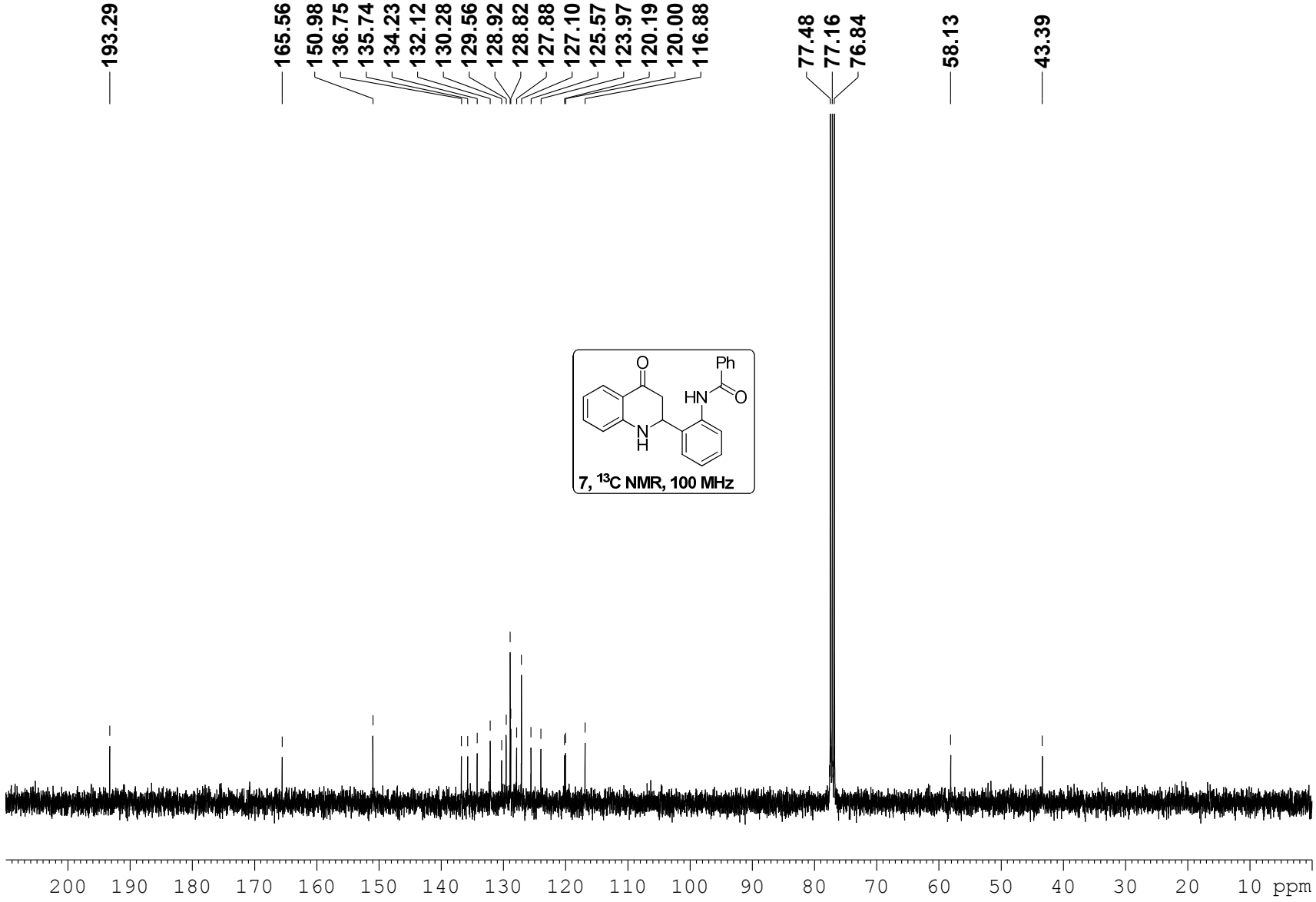

8.11
8.09
7.84
7.83
7.82
7.79
7.57
7.55
7.54
7.50
7.48
7.46
7.32
7.30
7.28
7.26
7.26
7.07
7.05
6.28
6.23
4.31
4.29
4.27
4.25
2.35
1.35
1.33
1.31
NH
O
Ph
6a, 1H NMR, 400 MHz
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.98
3.15
1.02
2.11
1.05
1.10
1.03
2.05
3.11
3.19

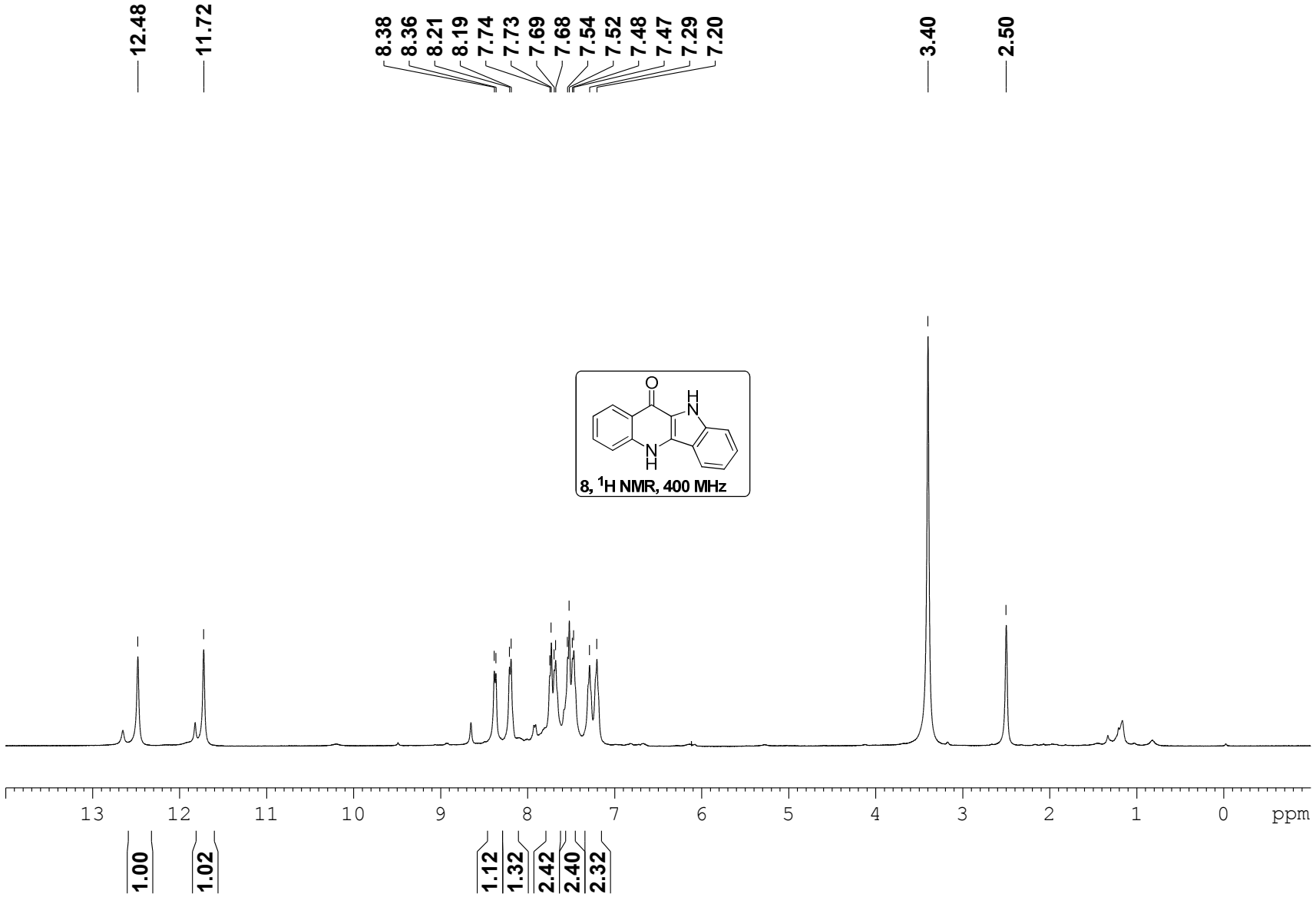

166.14
165.58
140.79
137.49
135.34
134.86
132.10
129.49
129.01
127.17
127.02
126.29
125.68
120.61
77.48
77.16
76.84
61.02
20.90
14.41
O
O
NH
O
Ph
6a, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

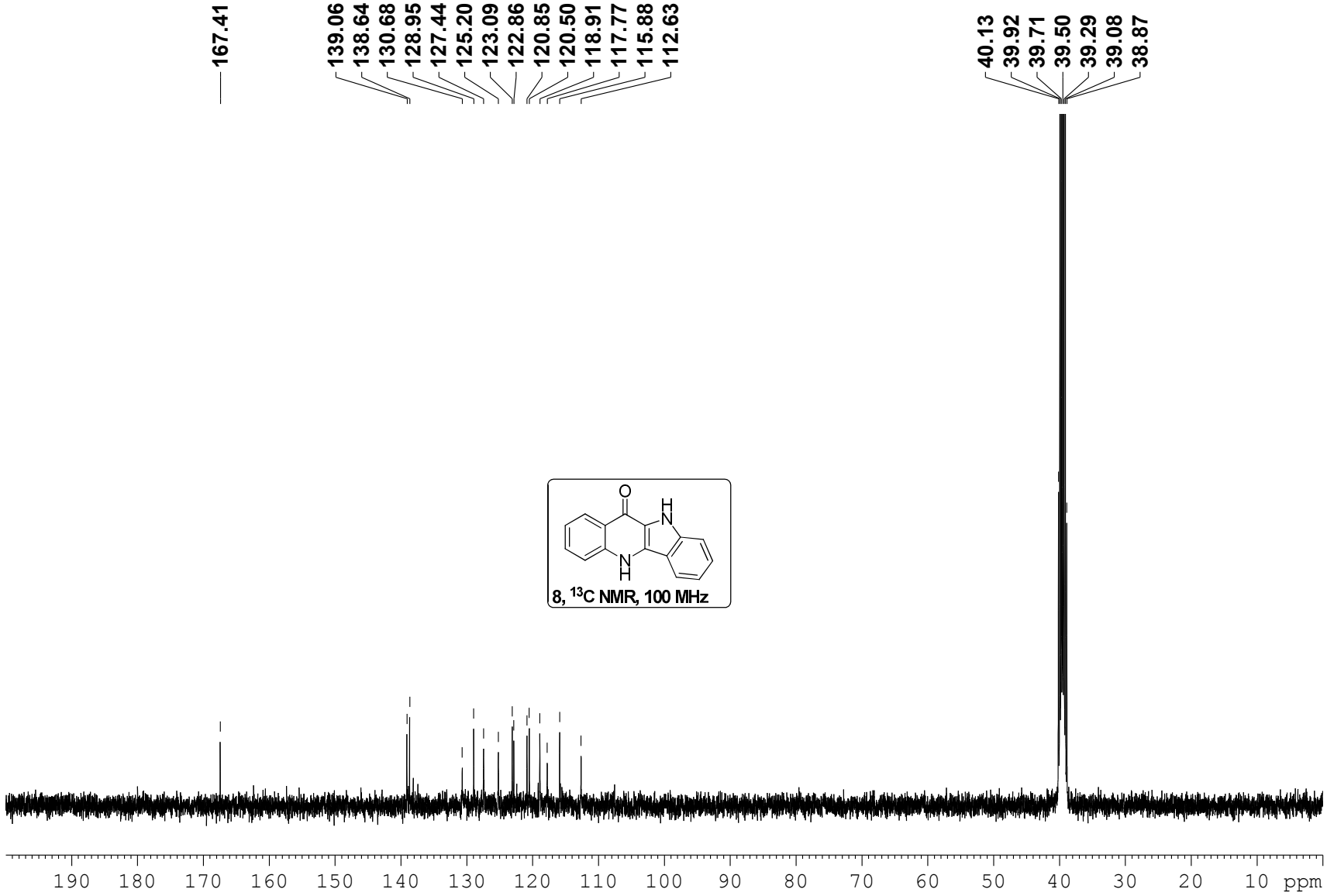

8.15
8.11
8.09
7.91
7.89
7.87
7.85
7.83
7.52
7.50
7.49
7.42
7.41
7.38
7.38
7.34
7.31
7.29
7.26
7.09
7.07
6.88
6.86
3.86
2.38
NH
O
Ph
O
O
6b, 1H NMR, 400 MHz
9
8
7
6
5
4
3
2
1
0
ppm
0.89
1.06
5.00
1.03
4.05
1.02
1.99
3.17
3.00


187.85
165.65
163.89
139.64
137.96
135.40
134.67
132.08
131.04
130.39
129.46
129.03
128.88
127.22
127.19
127.12
121.00
114.11
77.48
77.16
76.84
55.65
20.92
NH
O
Ph
O
O
6b, 13C NMR, 100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

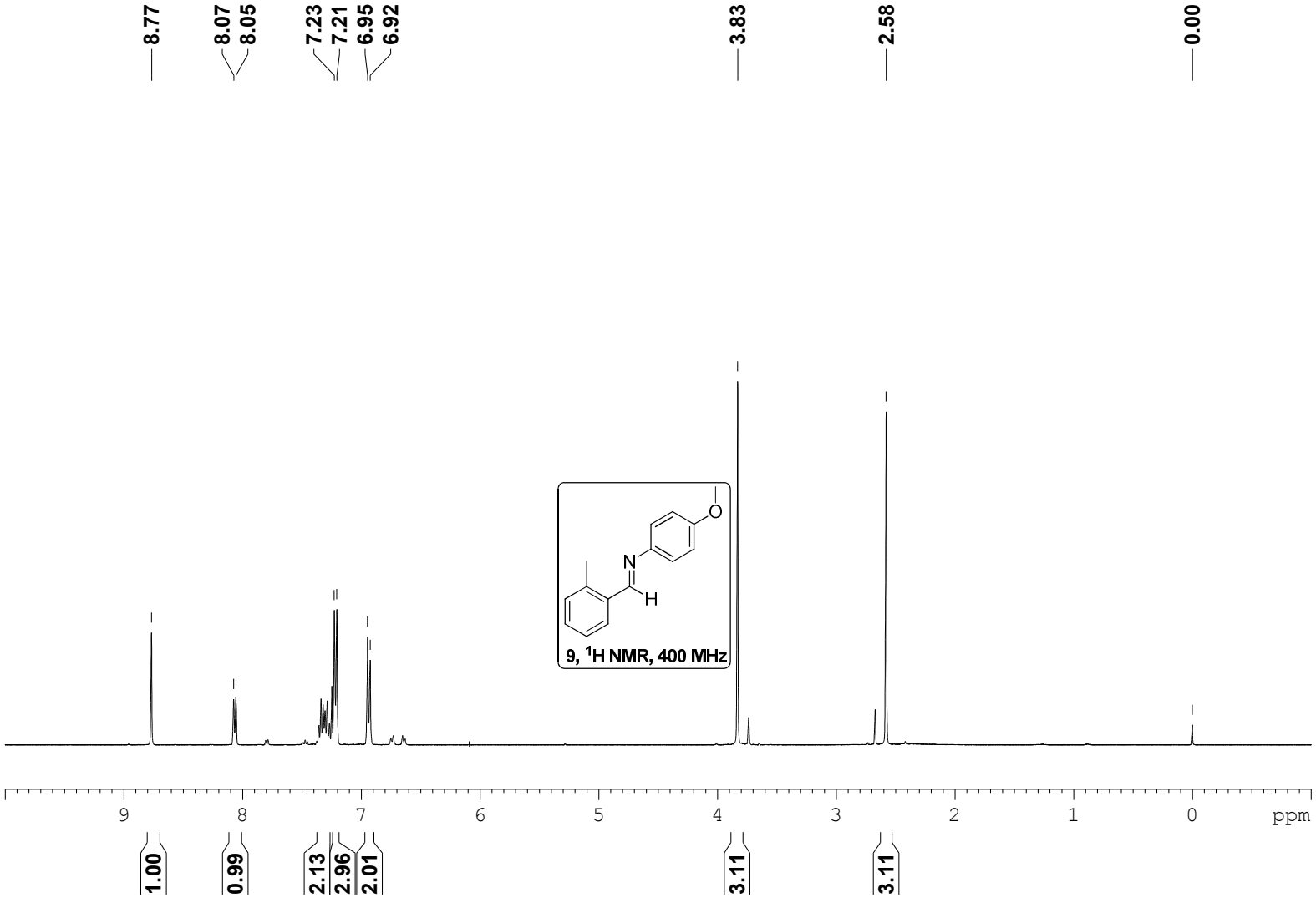

9.85
8.17
8.15
7.89
7.87
7.81
7.79
7.47
7.45
7.43
7.43
7.40
7.38
7.35
7.33
7.33
7.31
7.29
7.26
7.19
7.17
7.15
6.92
6.90
6.88
6.85
5.08
4.91
4.87
3.13
3.09
3.05
2.70
2.66
O
Ph
HN
O
N
H
7, 1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.14
1.09
2.06
6.72
1.22
2.05
1.01
1.05
1.04
1.07

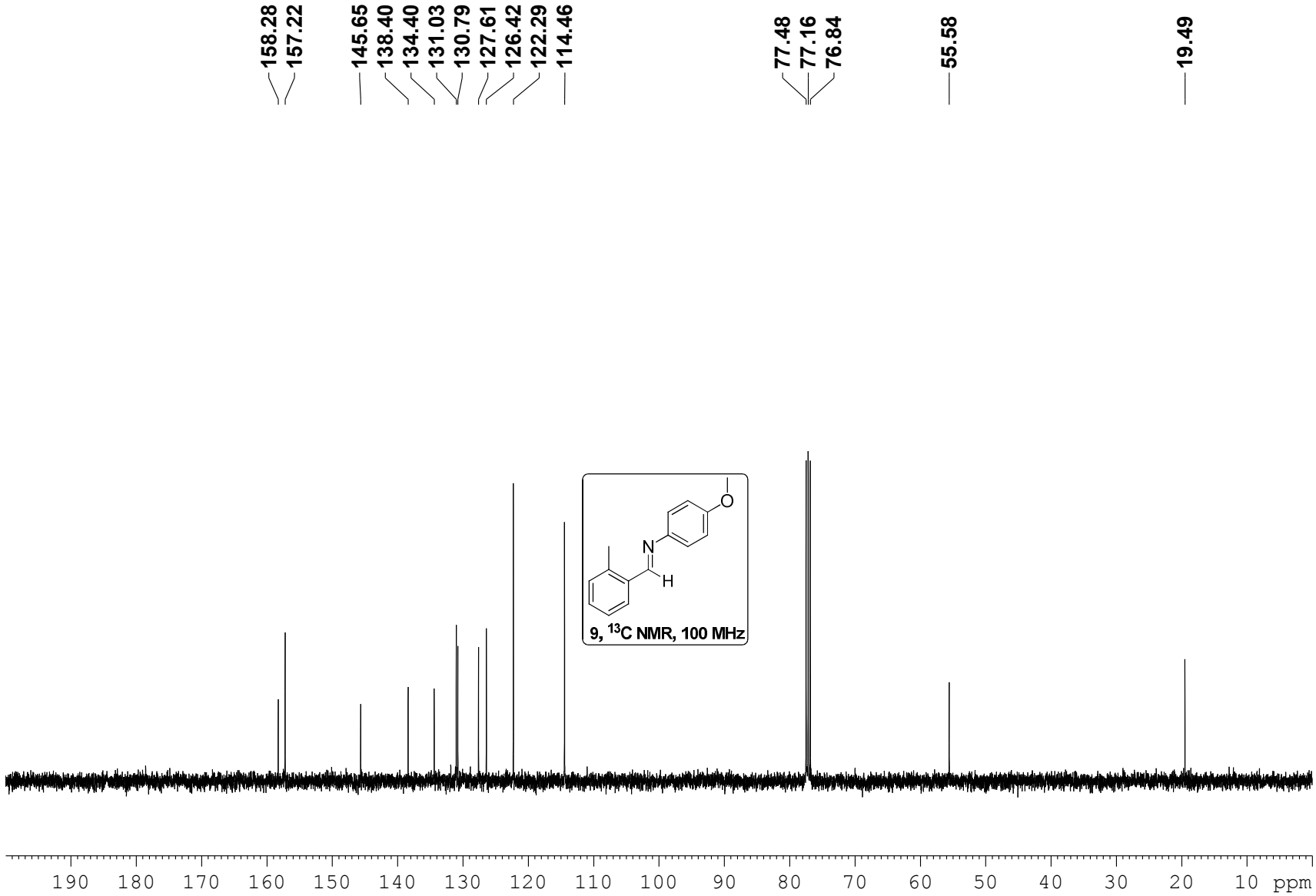

193.29
165.56
150.98
136.75
135.74
134.23
132.12
130.28
129.56
128.92
128.82
127.88
127.10
125.57
123.97
120.19
120.00
116.88
77.48
77.16
76.84
58.13
43.39
O
Ph
HN
O
N
H
7, 13C NMR, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

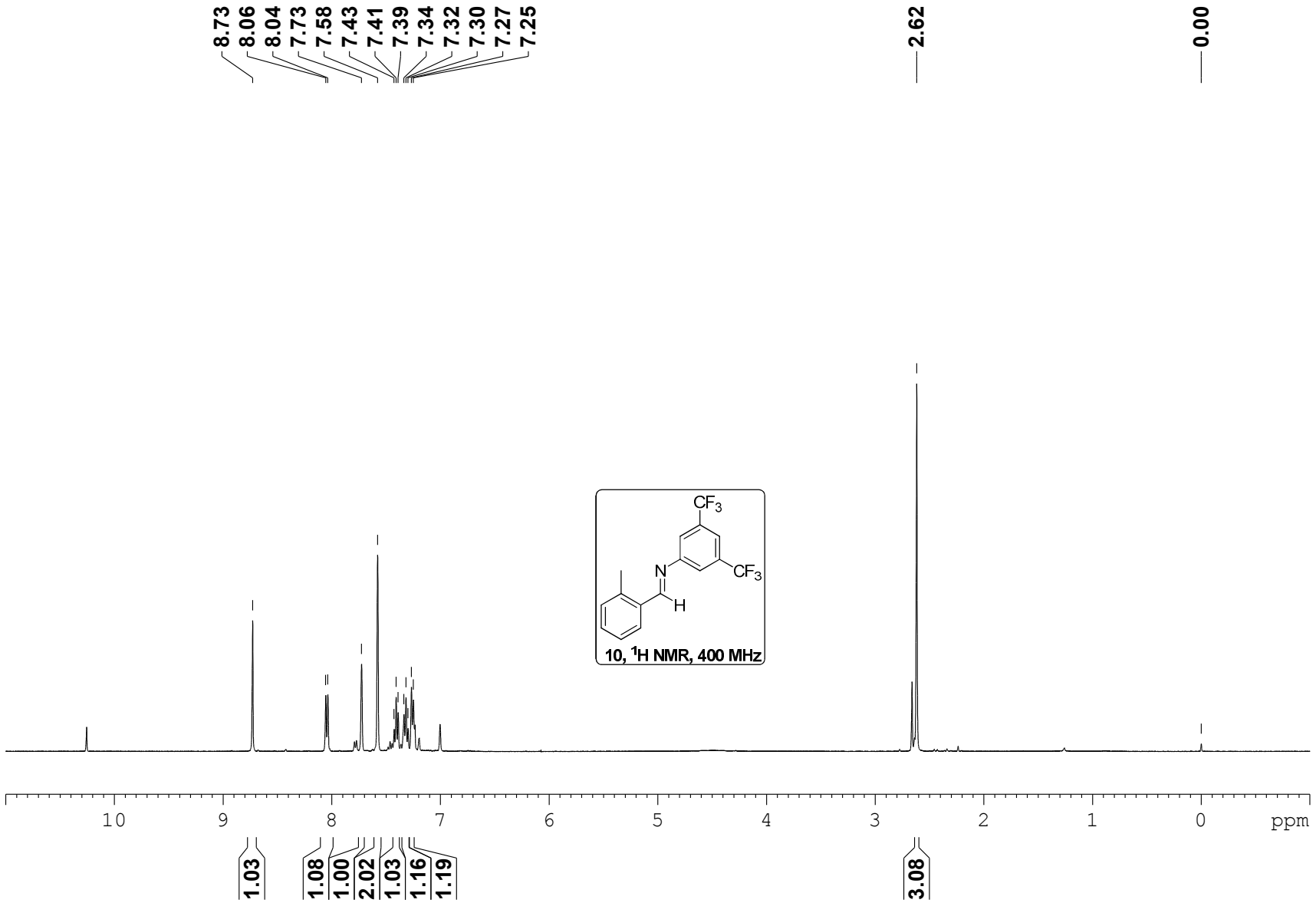

12.48
11.72
8.38
8.36
8.21
8.19
7.74
7.73
7.69
7.68
7.54
7.52
7.48
7.47
7.29
7.20
3.40
2.50
8, ^{1}H NMR, 400 MHz
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
1.12
1.32
2.42
2.40
2.32

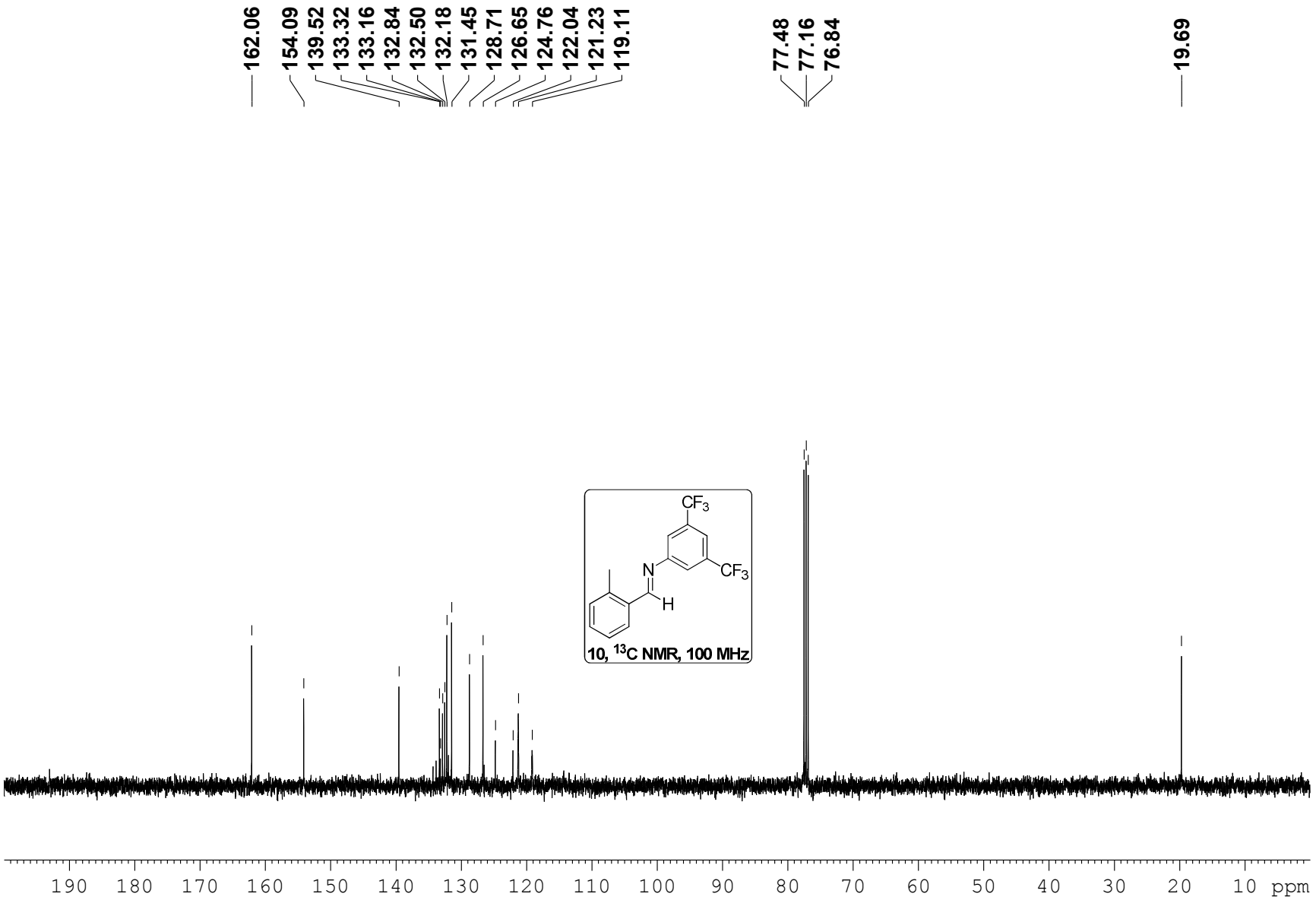

167.41
139.06
138.64
130.68
128.95
127.44
125.20
123.09
122.86
120.85
120.50
118.91
117.77
115.88
112.63
40.13
39.92
39.71
39.50
39.29
39.08
38.87
O
H
N
N
H
8, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

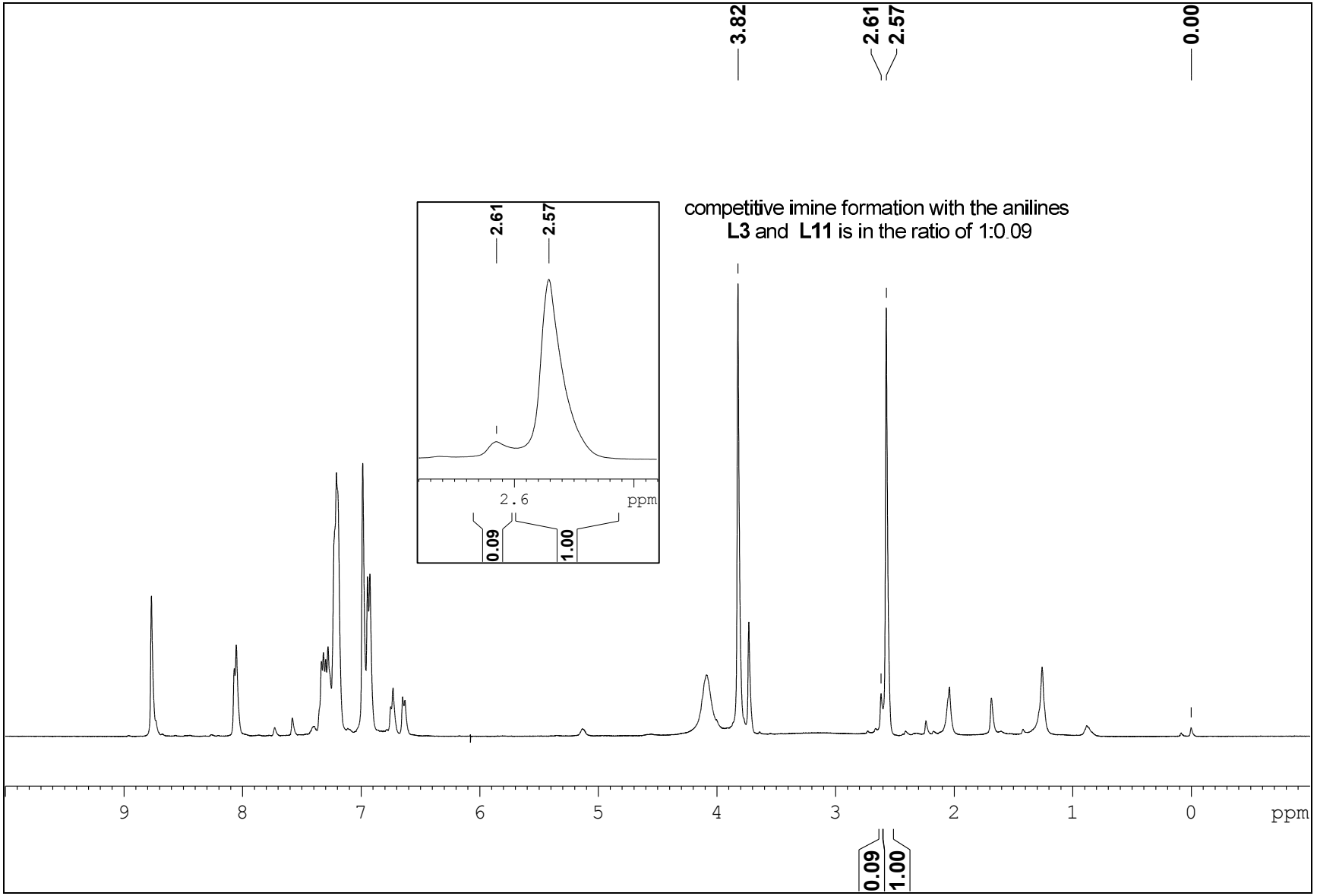
Spectral analysis for the mechanistic studies:

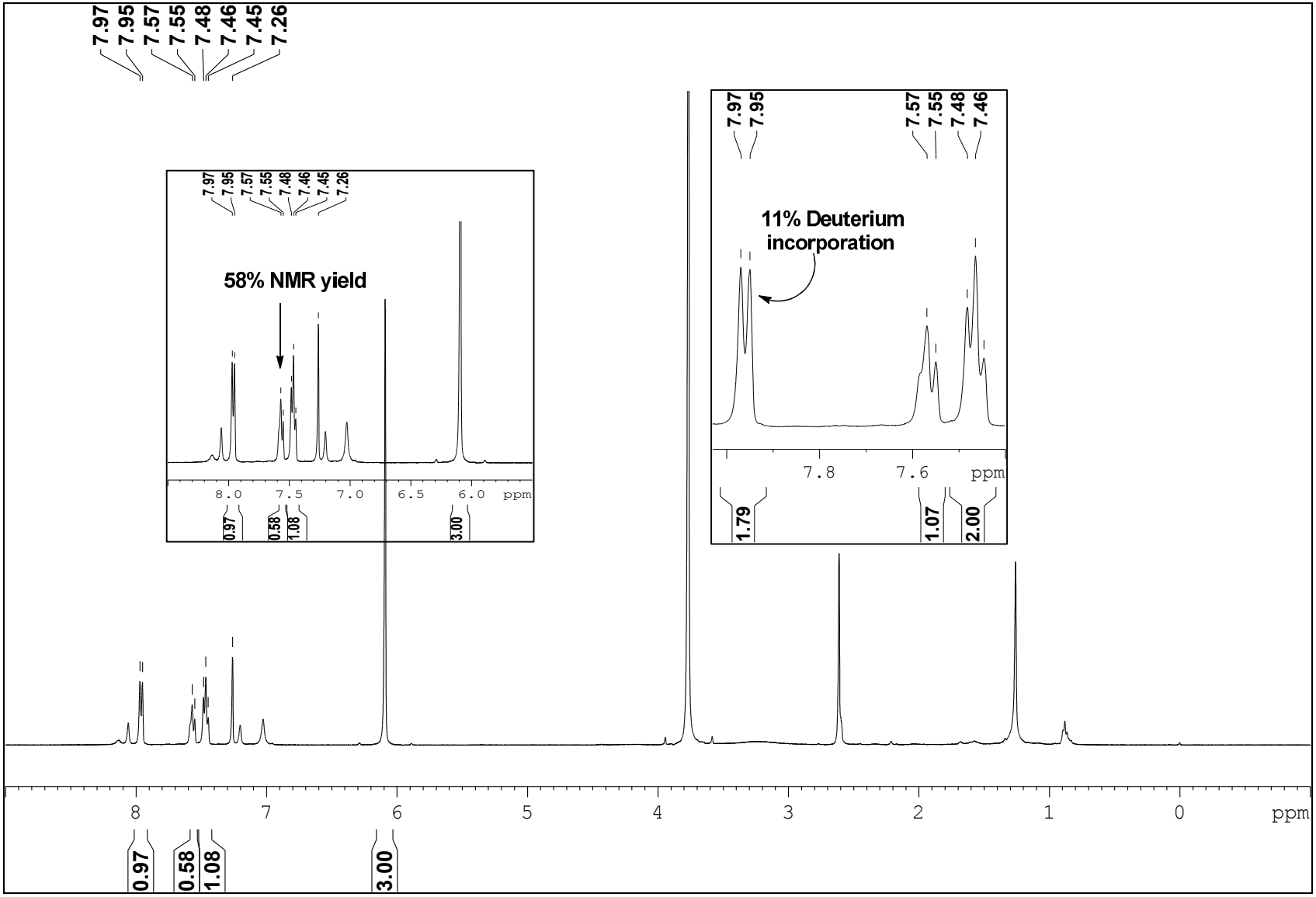


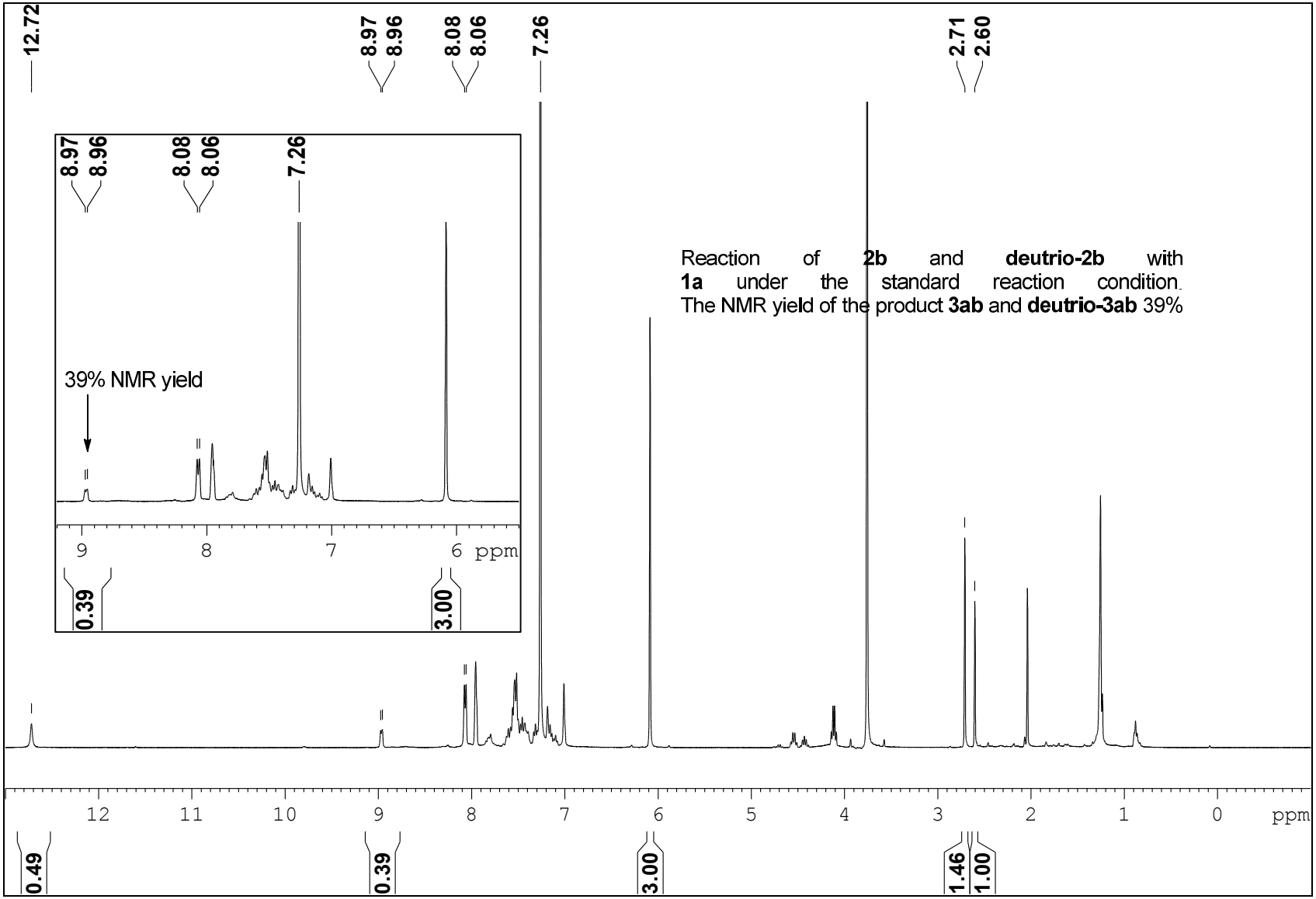

158.28
157.22
145.65
138.40
134.40
131.03
130.79
127.61
126.42
122.29
114.46
77.48
77.16
76.84
55.58
19.49
O
N
H
9, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

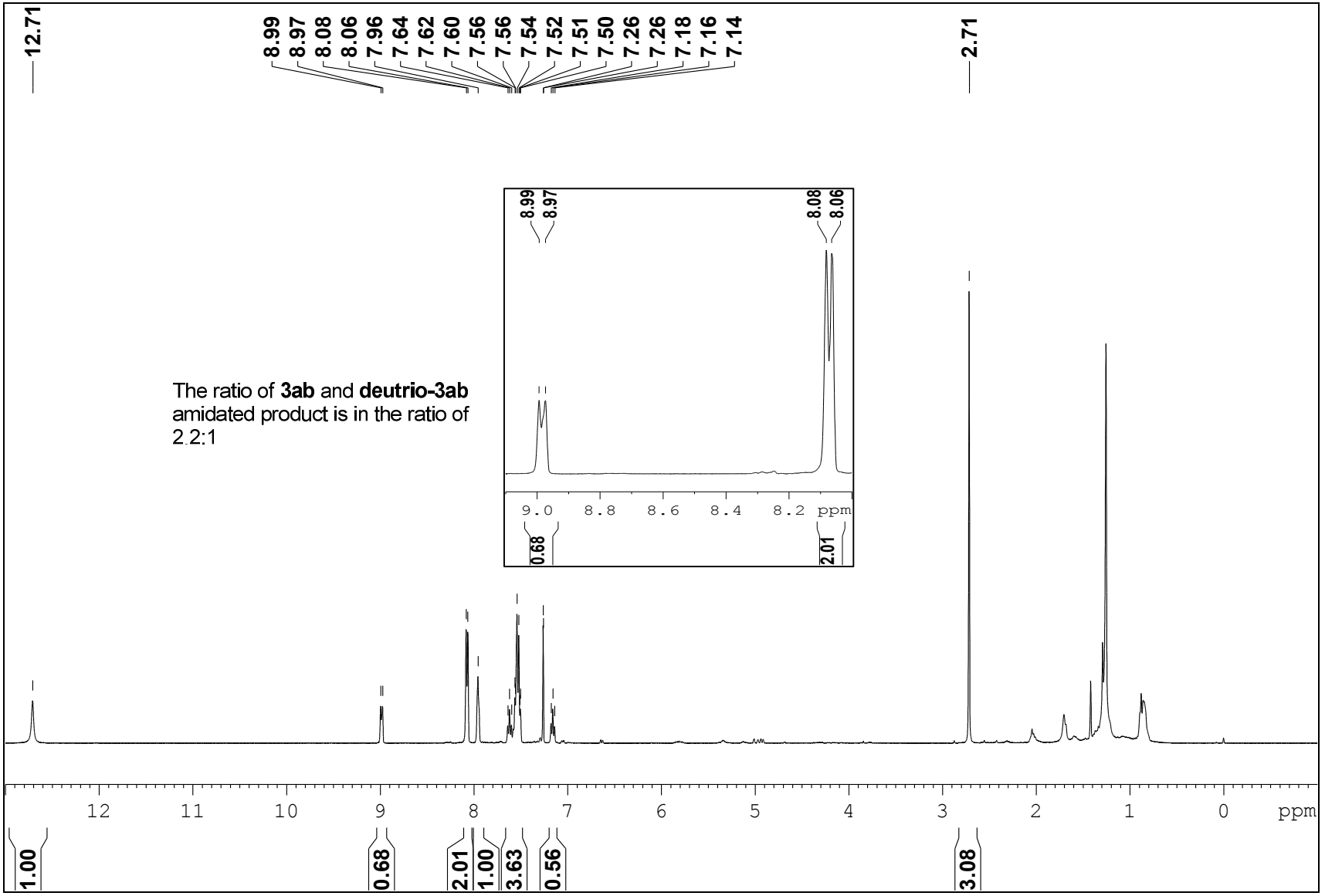

8.73
8.06
8.04
7.73
7.58
7.43
7.41
7.39
7.34
7.32
7.30
7.27
7.25
2.62
0.00
CF3
CF3
N
H
10, 1H NMR, 400 MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
1.03
1.08
1.00
2.02
1.03
1.16
1.19
3.08


162.06
154.09
139.52
133.32
133.16
132.84
132.50
132.18
131.45
128.71
126.65
124.76
122.04
121.23
119.11
77.48
77.16
76.84
19.69
CF3
CF3
N
H
10, 13C NMR, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


3.82
2.61
2.57
0.00
competitive imine formation with the anilines
L3 and L11 is in the ratio of 1:0.09
2.61
2.57
2.6
ppm
0.09
1.00
9
8
7
6
5
4
3
2
1
0
ppm
0.09
1.00


7.97
7.95
7.57
7.55
7.48
7.46
7.45
7.26
58% NMR yield
11% Deuterium incorporation
8.0
7.5
7.0
6.5
6.0
ppm
7.8
7.6
0.97
0.58
1.08
3.00
1.79
1.07
2.00
8
7
6
5
4
3
2
1
0


12.72
8.97
8.96
8.08
8.06
7.26
2.71
2.60
Reaction of 2b and deutrio-2b with 1a under the standard reaction condition.
The NMR yield of the product 3ab and deutrio-3ab 39%
39% NMR yield
9
8
7
6 ppm
0.39
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.49
0.39
3.00
1.46
1.00


12.71
8.99
8.97
8.08
8.06
7.96
7.64
7.62
7.60
7.56
7.56
7.54
7.52
7.51
7.50
7.26
7.26
7.18
7.16
7.14
2.71
The ratio of 3ab and deutrio-3ab amidated product is in the ratio of 2.2:1
8.99
8.97
8.08
8.06
9.0
8.8
8.6
8.4
8.2
ppm
0.68
2.01
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.68
2.01
1.00
3.63
0.56
3.08