

Mechanistic Study of SmI₂/H₂O and SmI₂/Amine/H₂O-Promoted Chemoselective Reduction of Aromatic Amides (Primary, Secondary, Tertiary) to Alcohols via Aminoketyl Radicals

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Chart SI-1. Electronic Influence on the Relative Rates in the Reduction of Primary Amides using $\text{SmI}_2\text{--H}_2\text{O}$.^a

entry	X	k_X/k_H^a	$\log(k_X/k_H)$	Hammett σ constant
1	MeO	0.04	-1.35	-0.27
2	CF_3	60.7	1.78	0.54
3	F	0.64	-0.20	0.06
4	Cl	7.57	0.88	0.23
5	H	1	0	0

^aRelative reactivity values determined from product distribution by ^1H NMR and/or GC of crude reaction mixtures. Relative reactivity rates were obtained by intermolecular competition experiments using concentrations of starting materials. k_{rel} were determined by the following equation: $k_{\text{rel}} = \ln(1/\%\text{SM}_A)/\ln(1/\%\text{SM}_B)$. Intermolecular competition experiments were carried out using an equimolar ratio of the parent amide and the 4-substituted amide.

Chart SI-2. Electronic Influence on the Relative Rates in the Reduction of Secondary Amides using $\text{SmI}_2\text{--H}_2\text{O}$.^a

entry	X	k_X/k_H^a	$\log(k_X/k_H)$	Hammett σ constant
1	MeO	0.02	-1.74	-0.27
2	CF_3	67.0	1.83	0.54
3	F	0.32	-0.50	0.06
4	Cl	5.43	0.74	0.23
5	H	1	0	0

^aSee Chart SI-1.

Chart SI-3. Electronic Influence on the Relative Rates in the Reduction of Tertiary Amides using $\text{SmI}_2\text{--H}_2\text{O}$.^a

entry	X	k_X/k_H^a	$\log(k_X/k_H)$	Hammett σ constant
1	MeO	0.08	-1.12	-0.27
2	CF_3	67.0	1.83	0.54
3	F	0.55	-0.26	0.06
4	Cl	6.75	0.83	0.23
5	H	1	0	0

^aSee Chart SI-1.**Chart SI-4.** Electronic Influence on the Relative Rates in the Reduction of Primary Amides using $\text{SmI}_2\text{--Et}_3\text{N--H}_2\text{O}$.^a

entry	X	k_X/k_H^a	$\log(k_X/k_H)$	Hammett σ constant
1	MeO	0.24	-0.62	-0.27
2	CF_3	4.84	0.69	0.54
3	F	1.05	0.02	0.06
4	Cl	nd	nd	0.23
5	H	1	0	0

^aSee Chart SI-1. nd = not determined, dearomatization of the aromatic ring was observed.

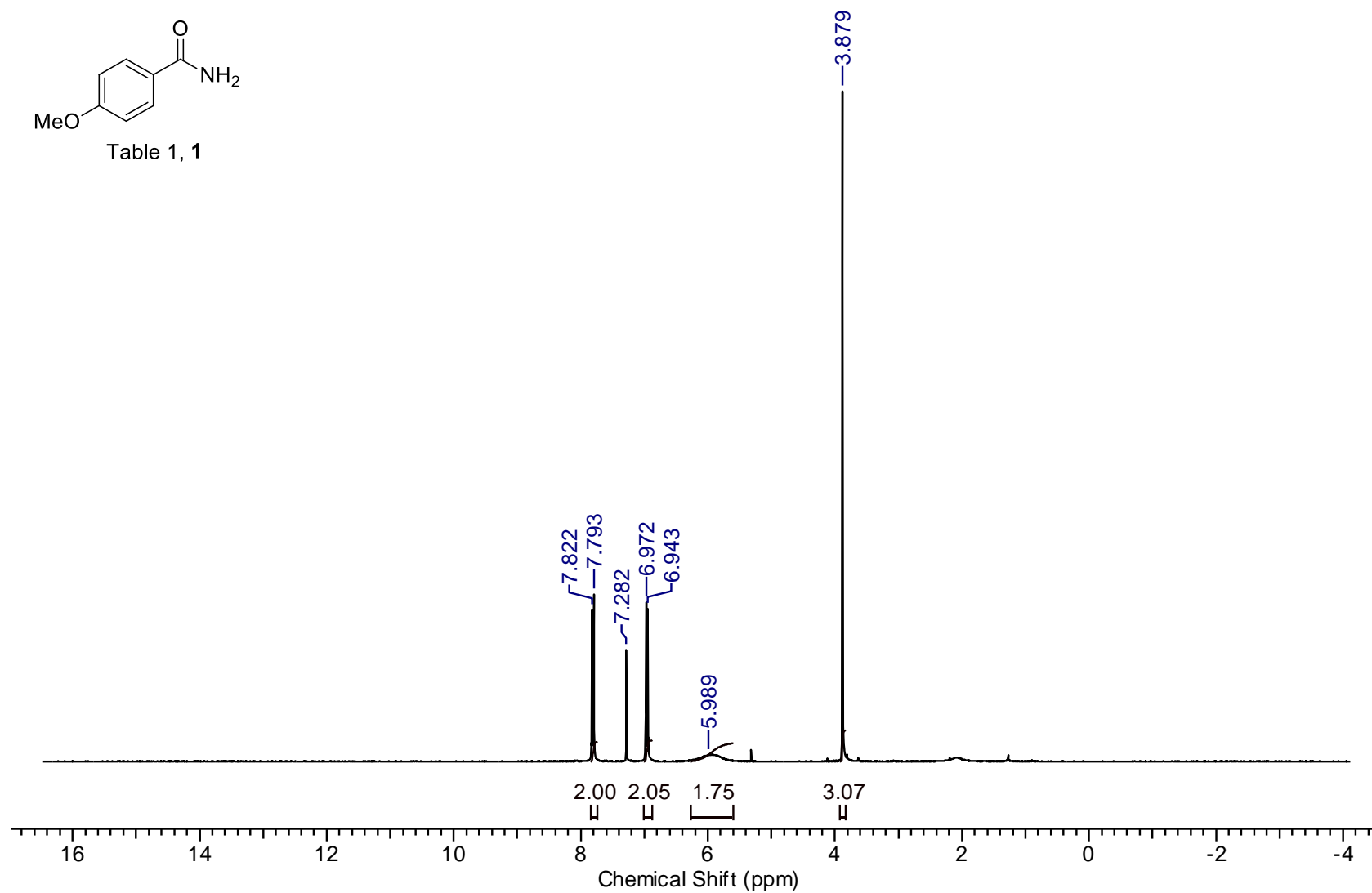
Chart SI-5. Electronic Influence on the Relative Rates in the Reduction of Secondary Amides using SmI₂–Et₃N–H₂O.^a

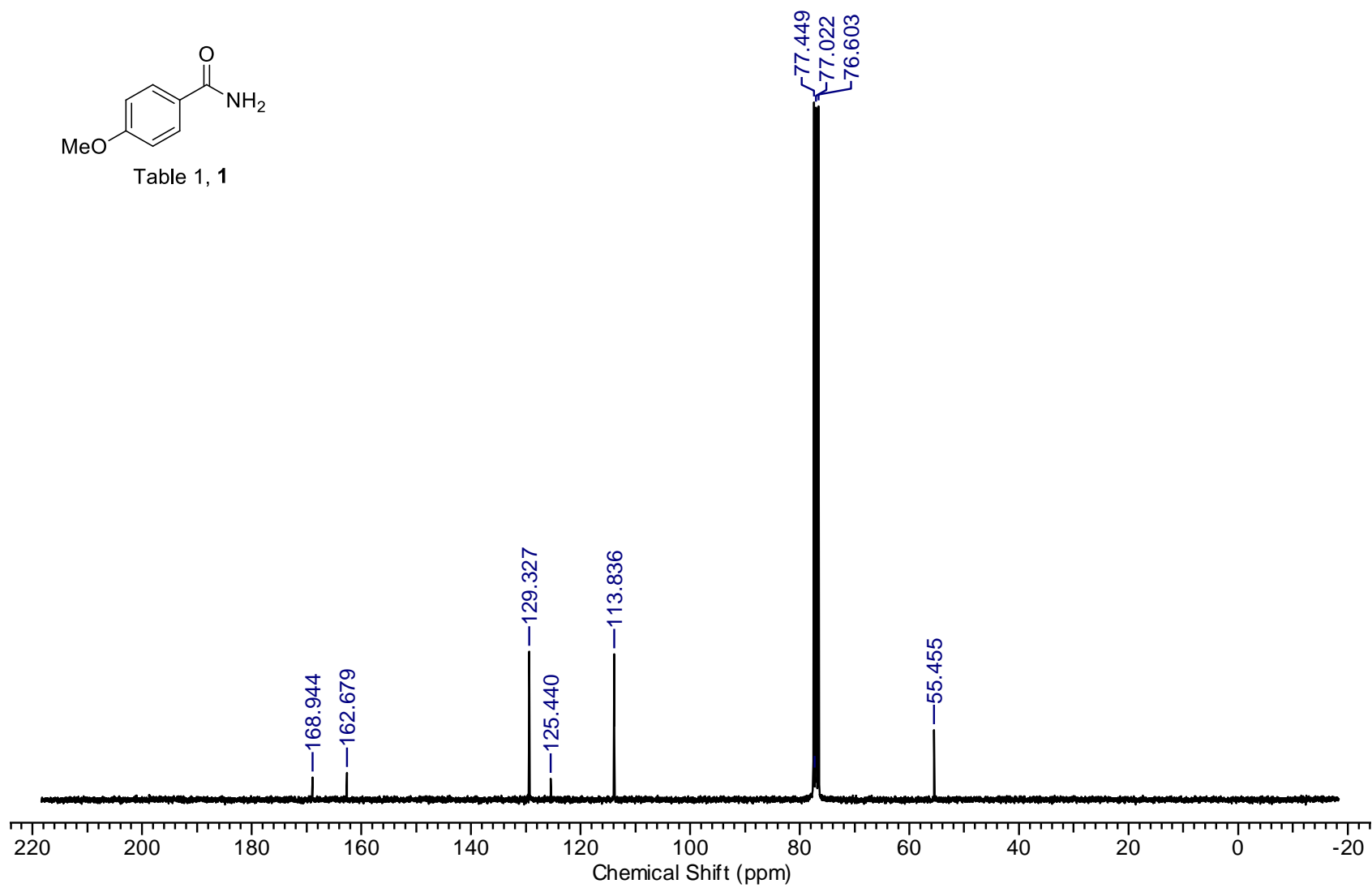
entry	X	k_X/k_H^a	$\log(k_X/k_H)$	Hammett σ constant
1	MeO	0.12	-0.93	-0.27
2	CF ₃	67.0	1.83	0.54
3	F	0.63	-0.20	0.06
4	Cl	7.57	0.88	0.23
5	H	1	0	0

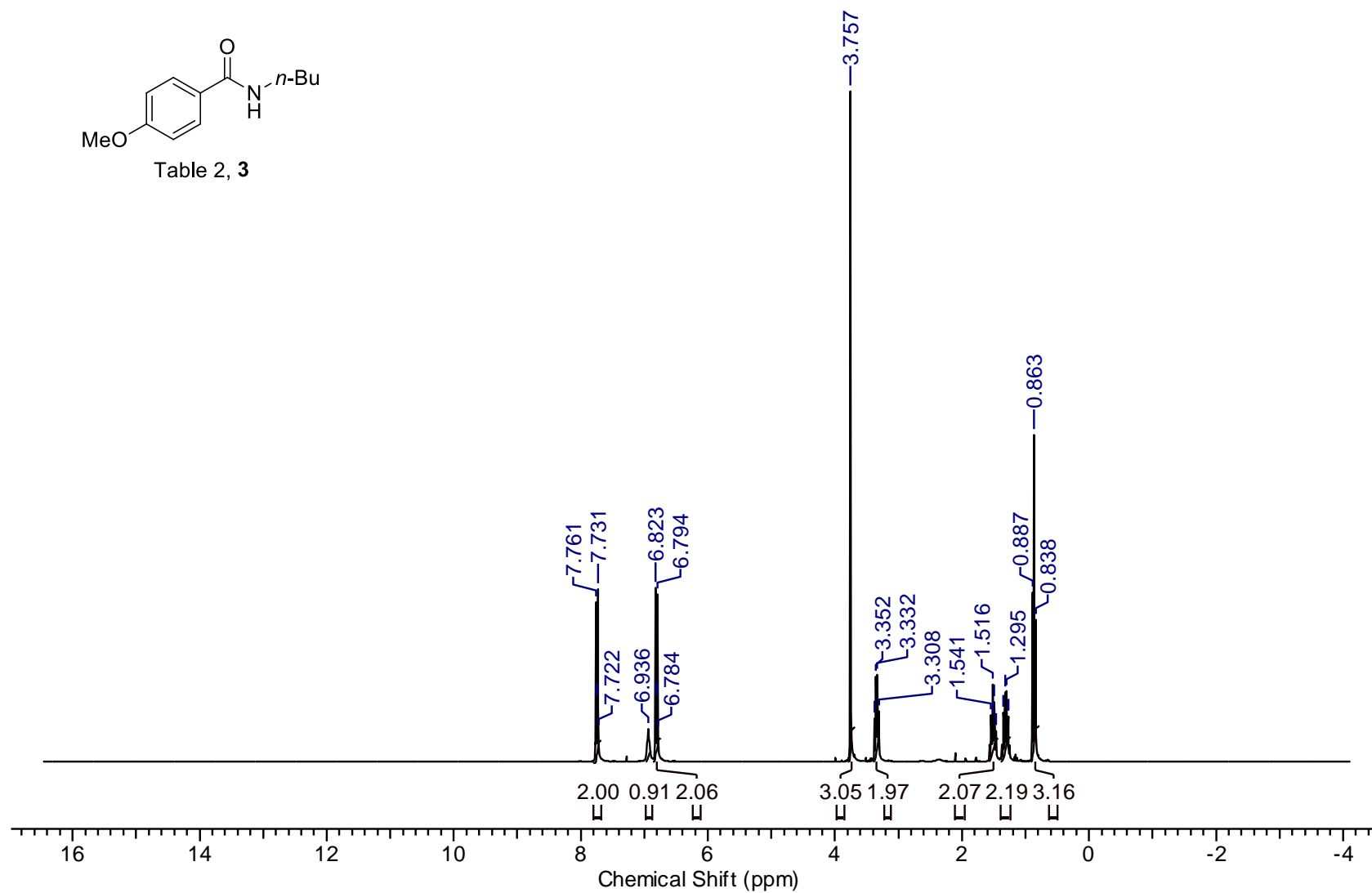
^aSee Chart SI-1.**Chart SI-6.** Electronic Influence on the Relative Rates in the Reduction of Tertiary Amides using SmI₂–Et₃N–H₂O.^a

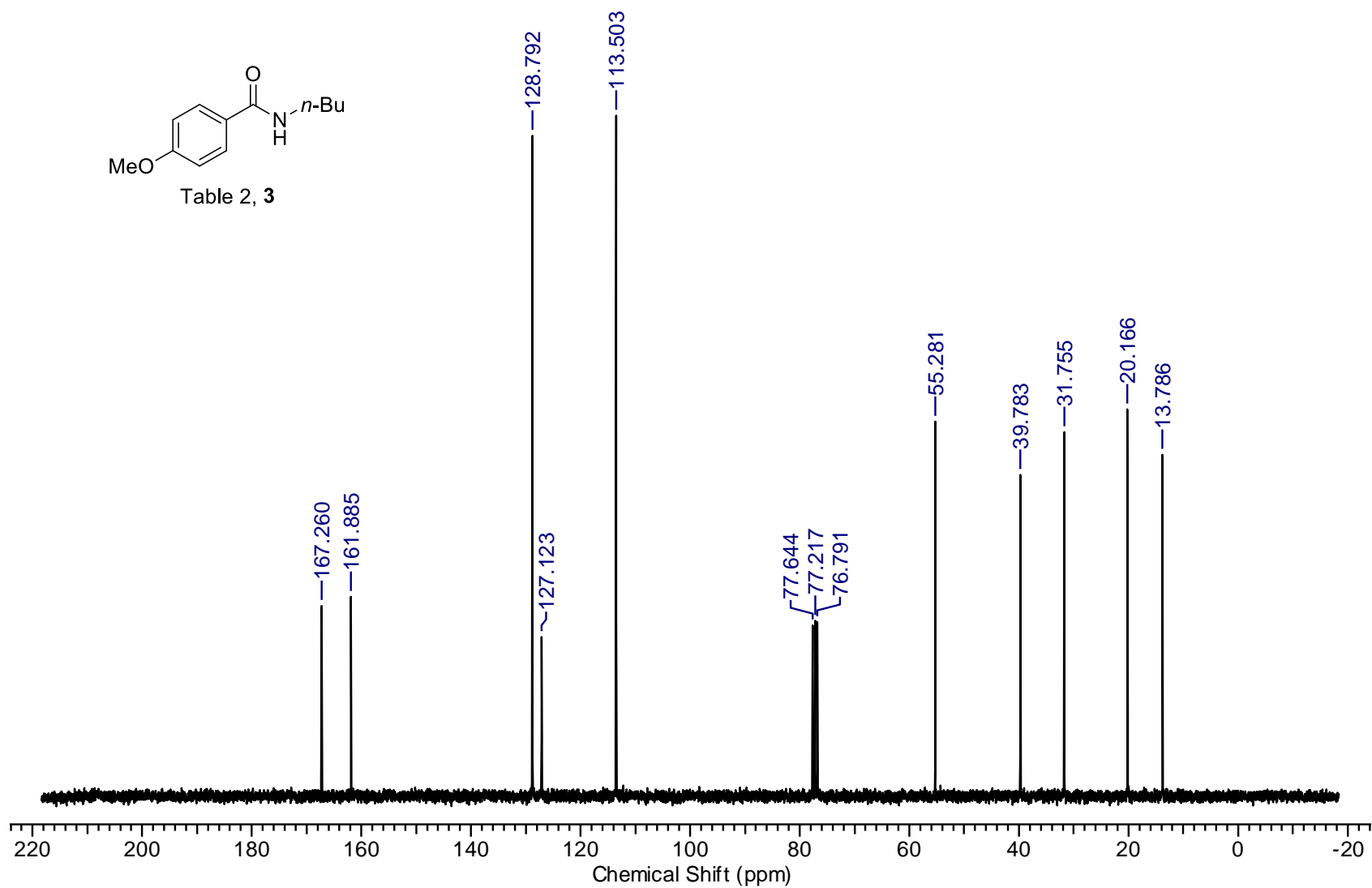
entry	X	k_X/k_H^a	$\log(k_X/k_H)$	Hammett σ constant
1	MeO	0.17	-0.79	-0.27
2	CF ₃	41.0	1.61	0.54
3	F	0.69	-0.16	0.06
4	Cl	3.24	0.51	0.23
5	H	1	0	0

^aSee Chart SI-1.









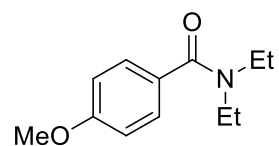
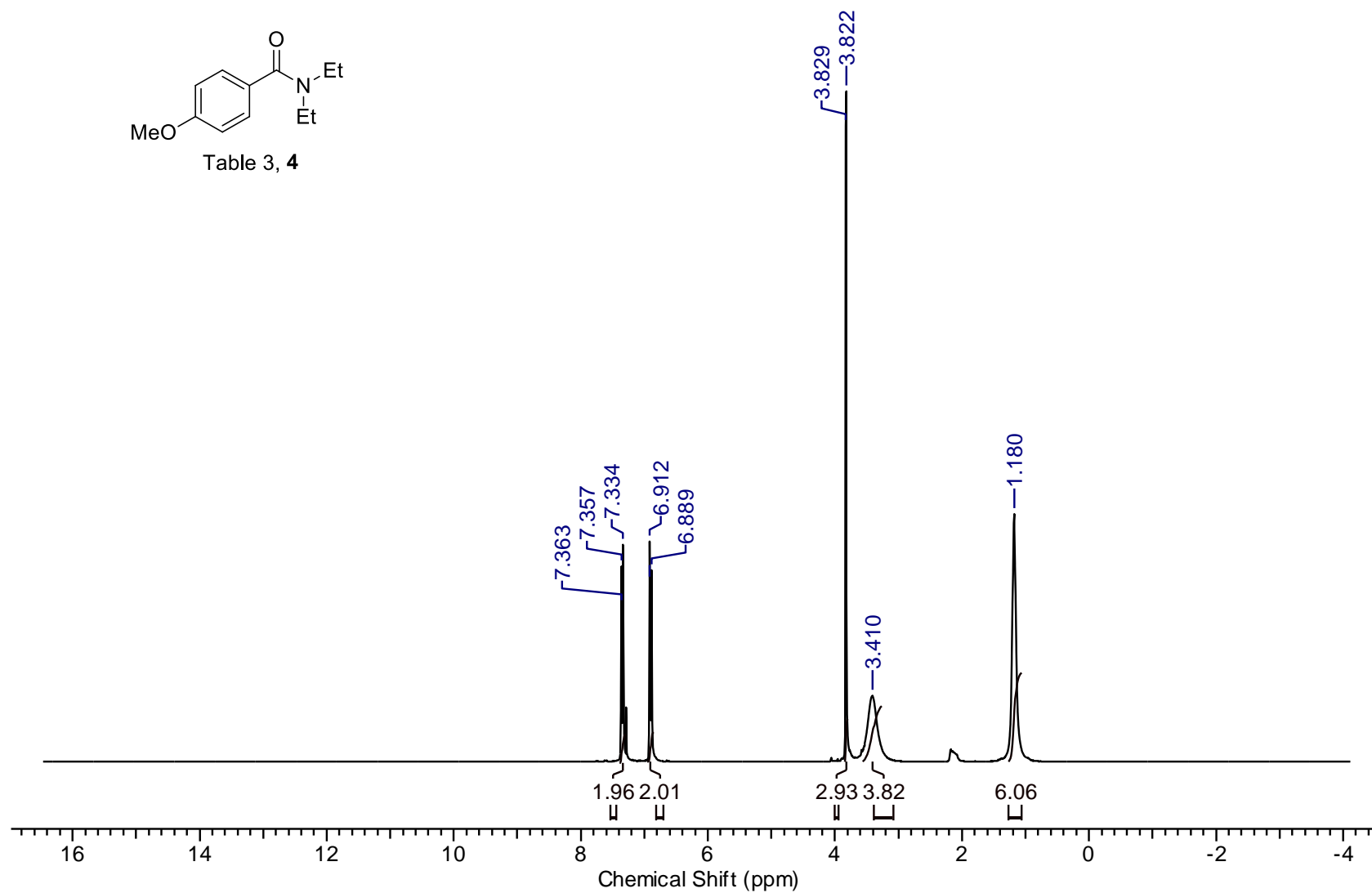
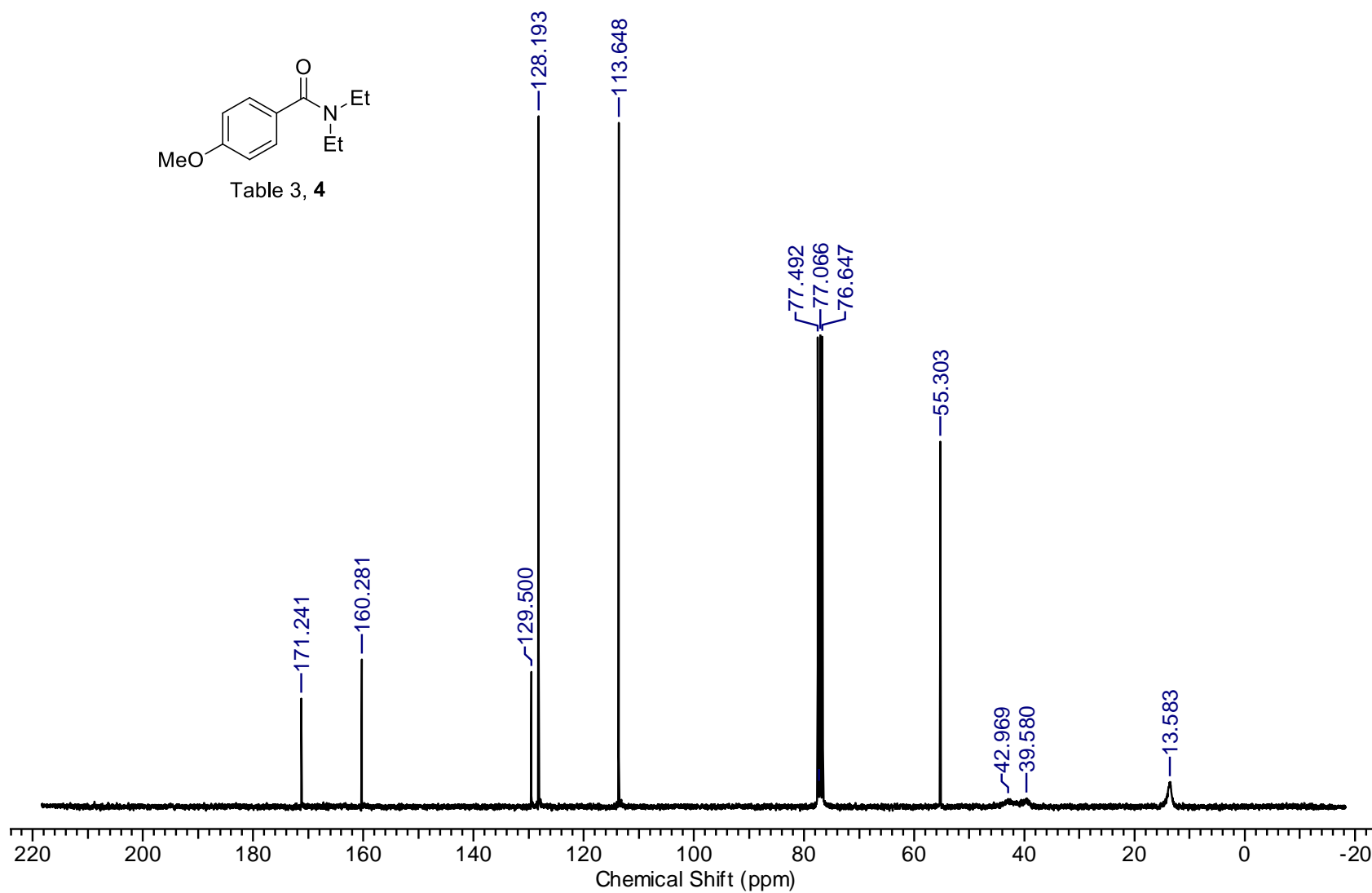


Table 3, 4





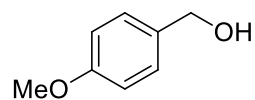
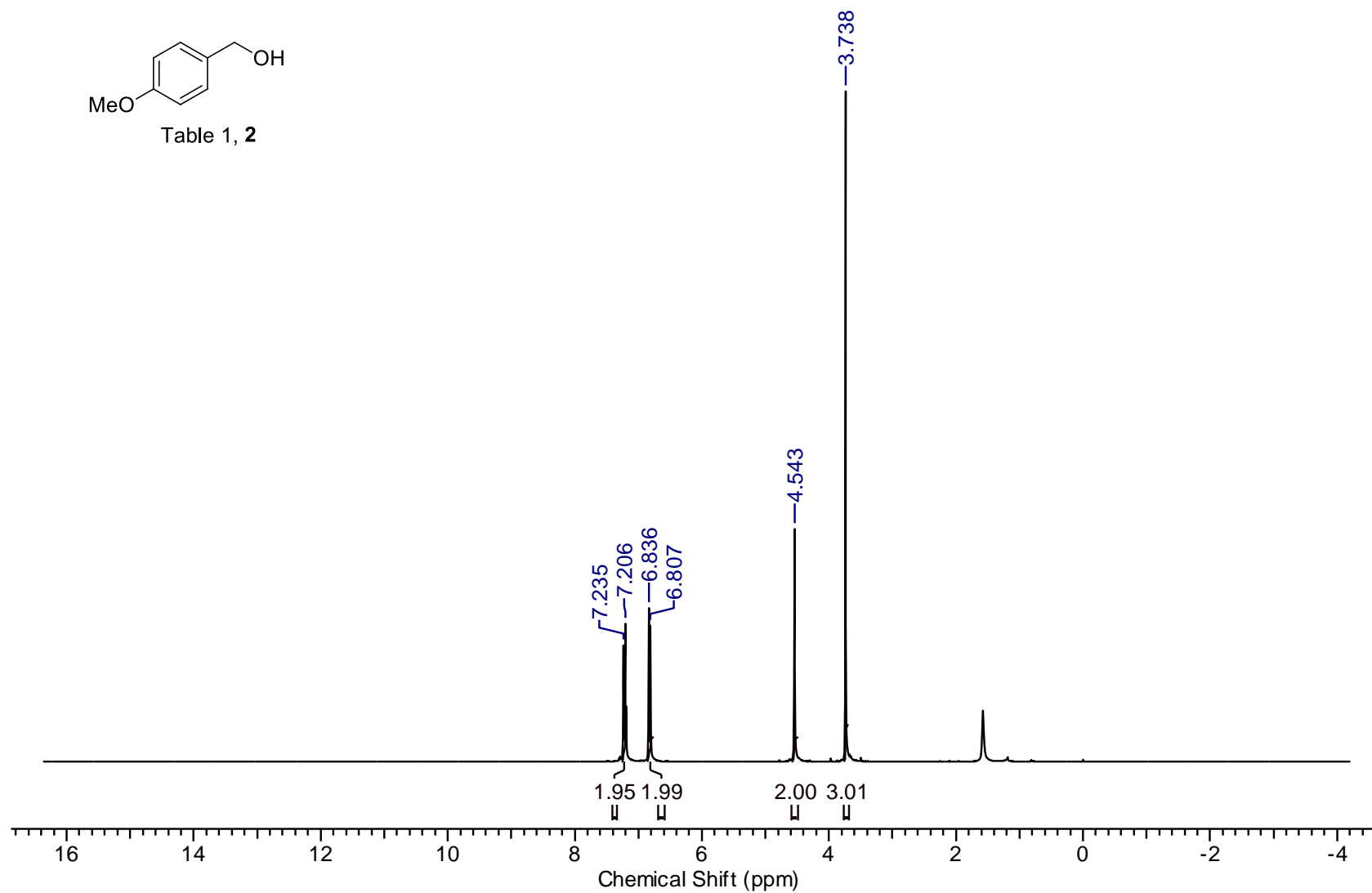
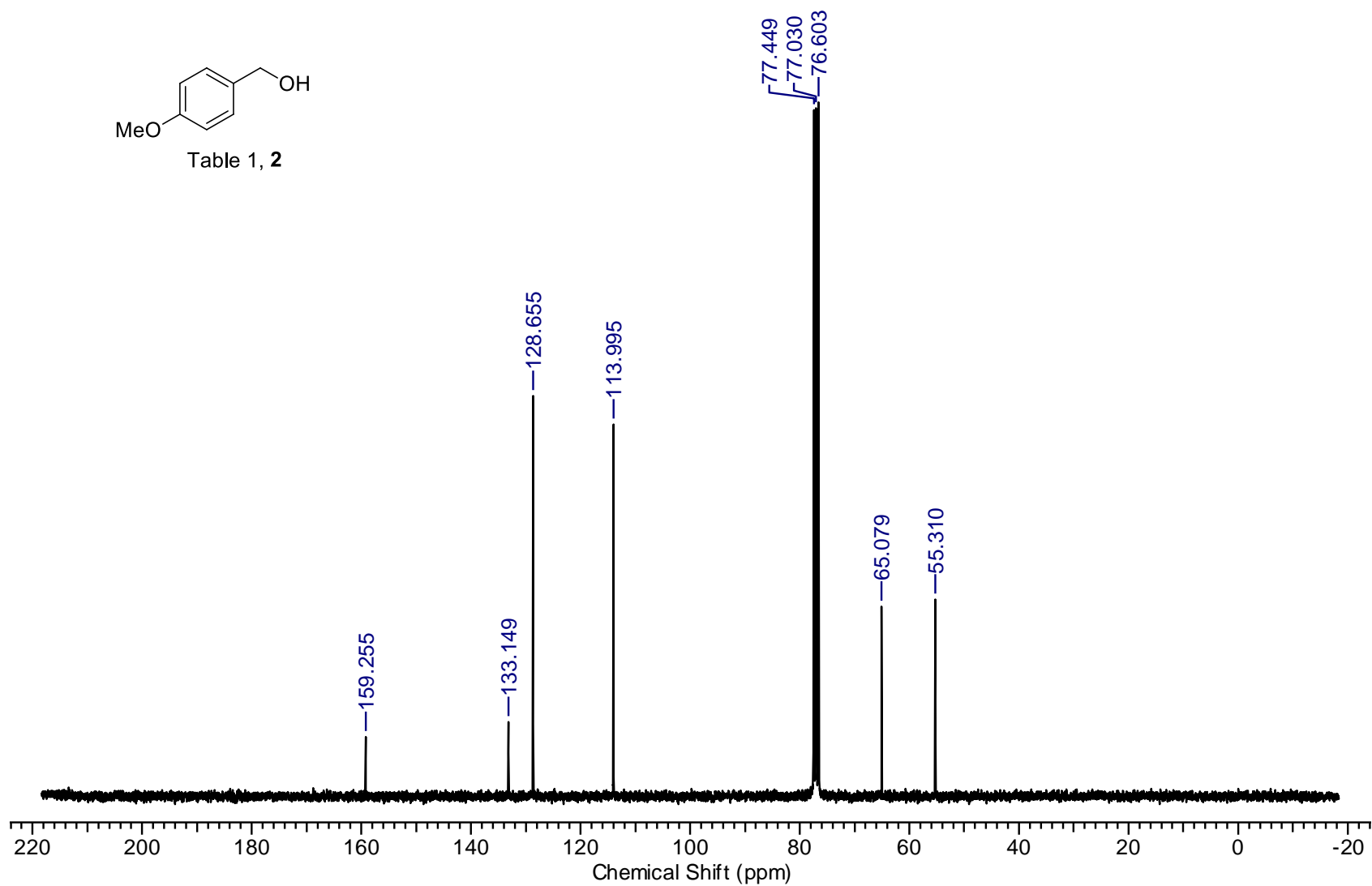


Table 1, 2





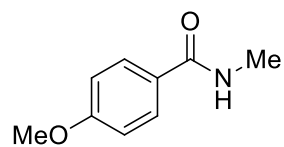
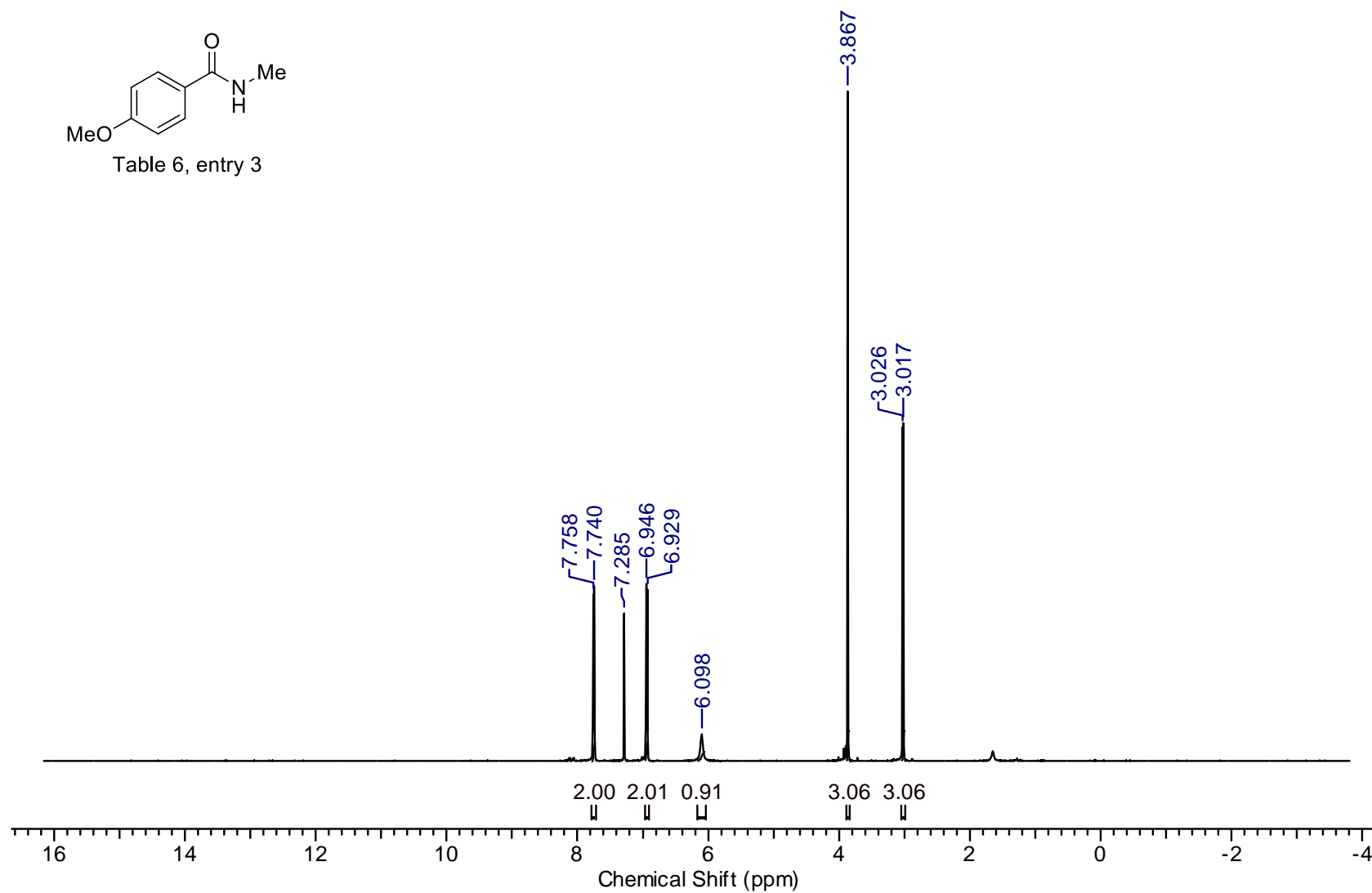


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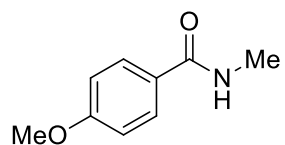
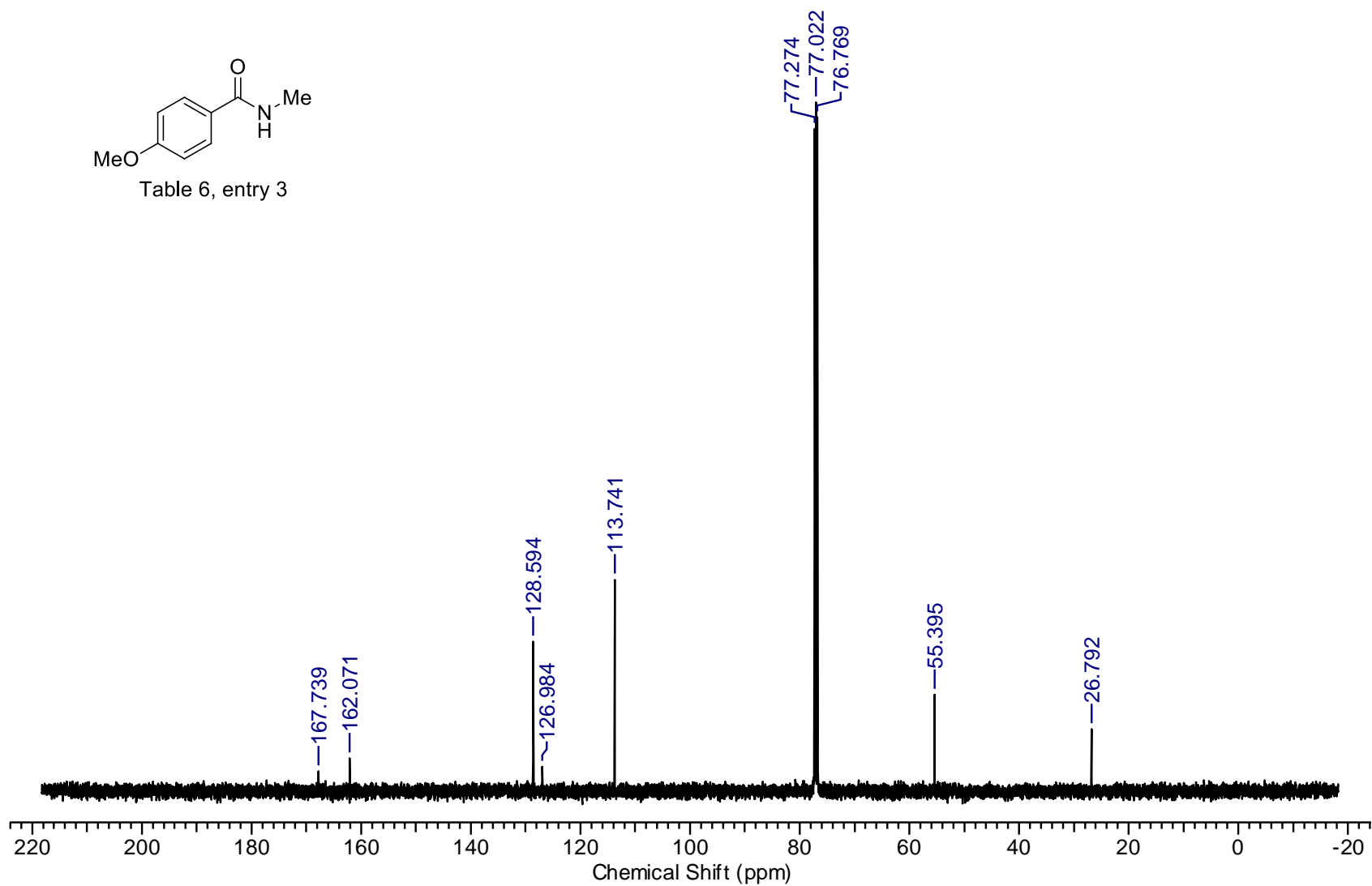


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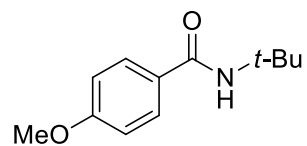
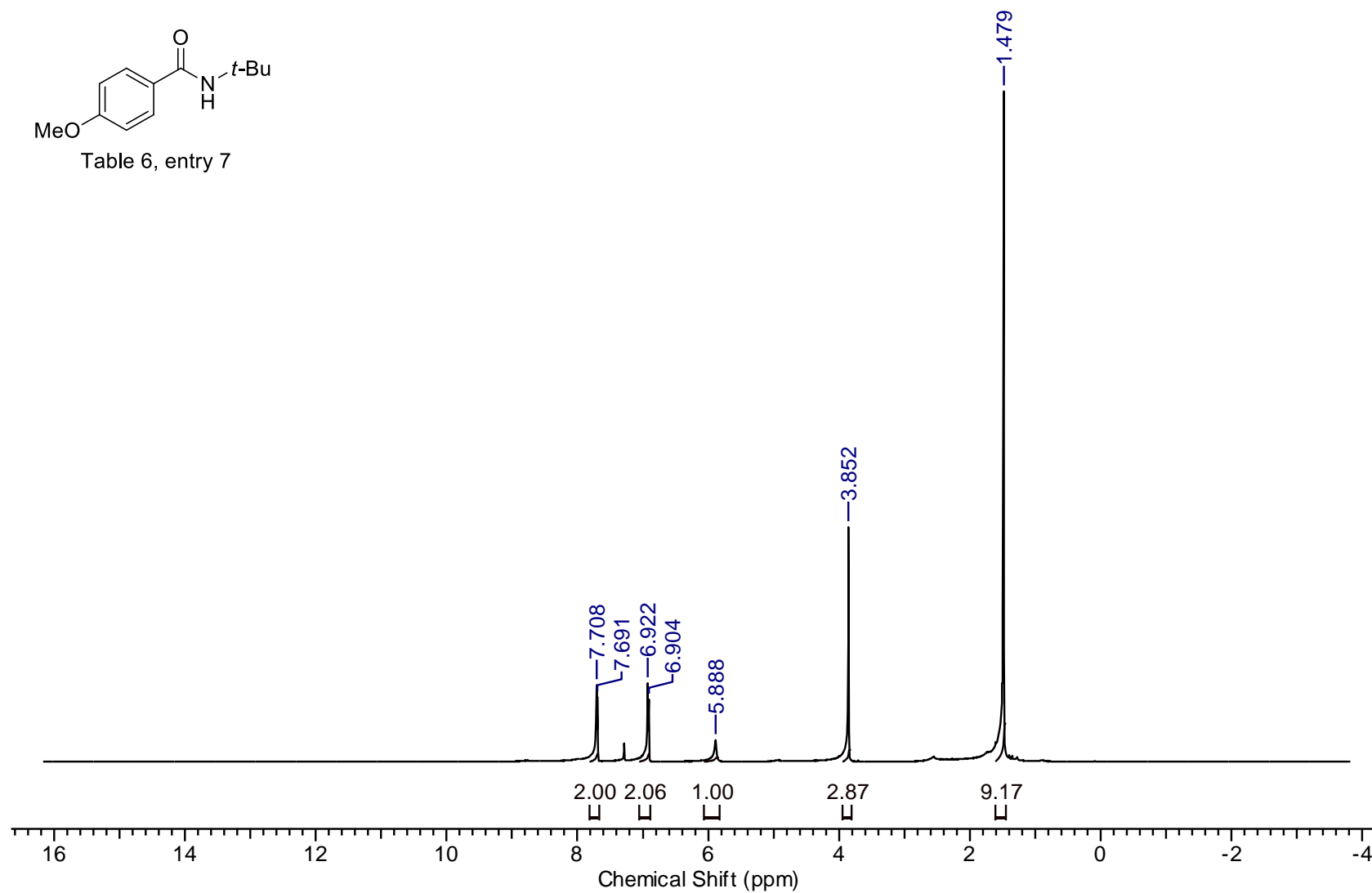
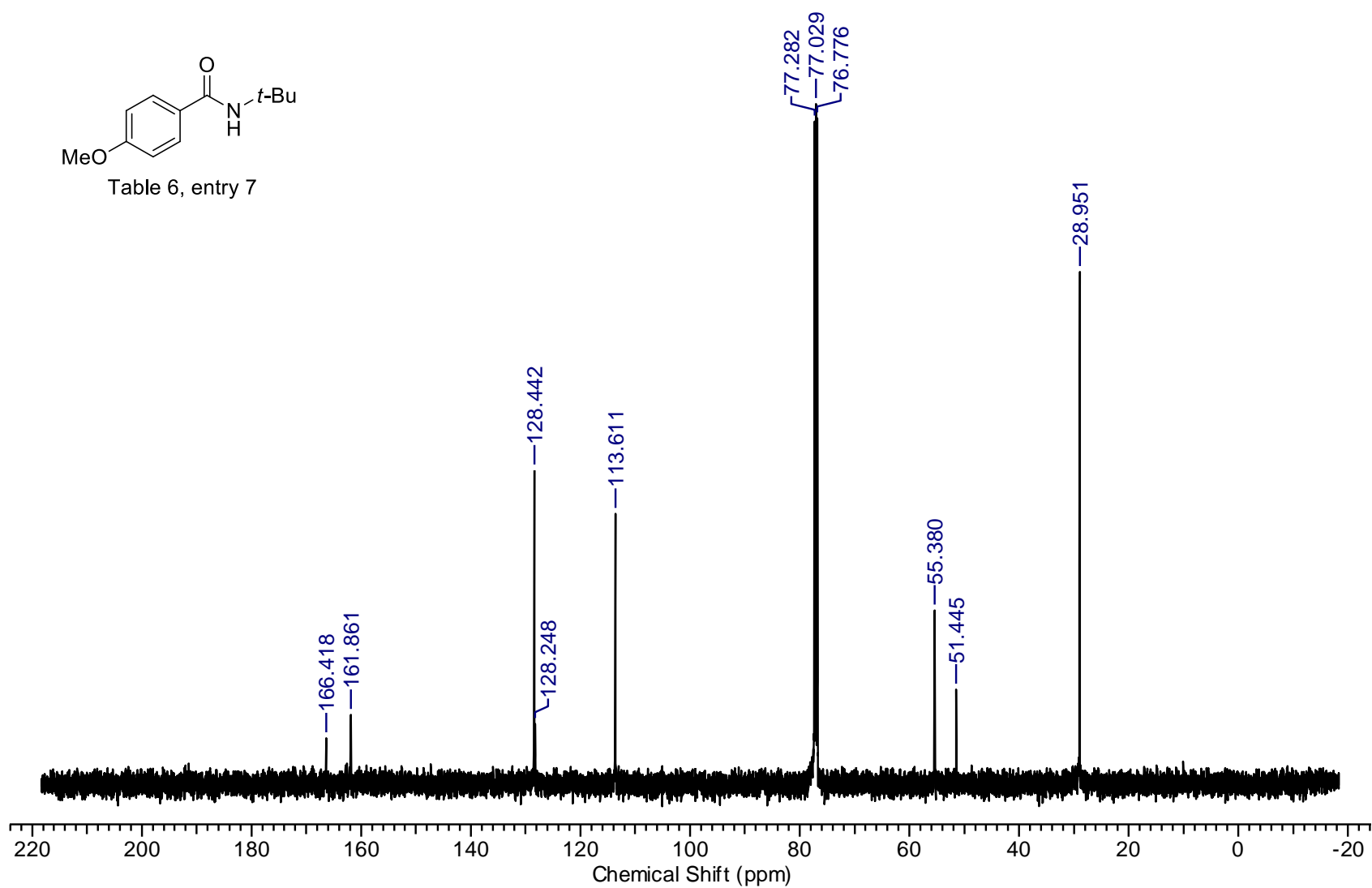
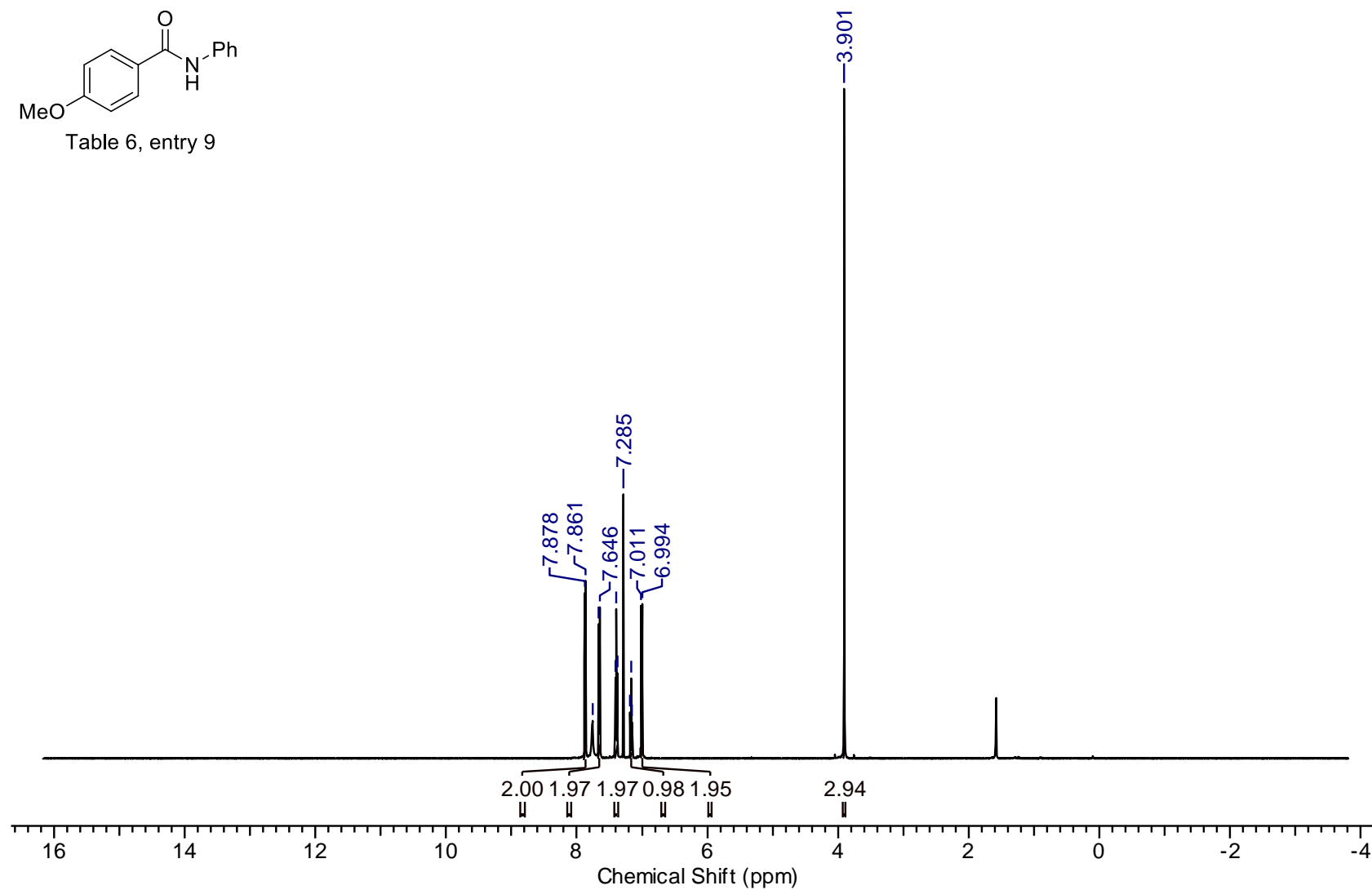
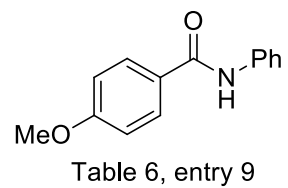
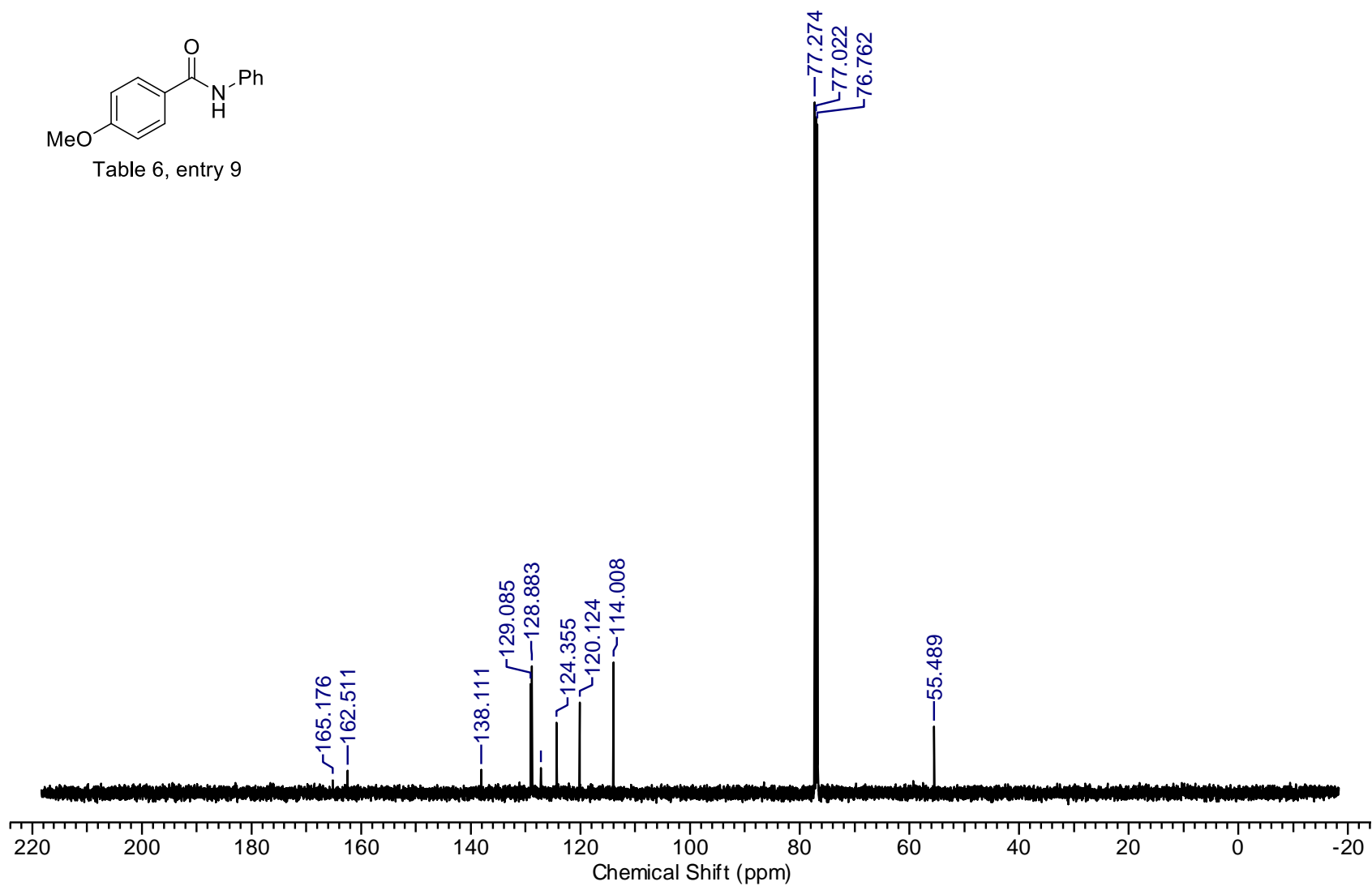


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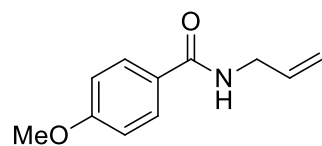
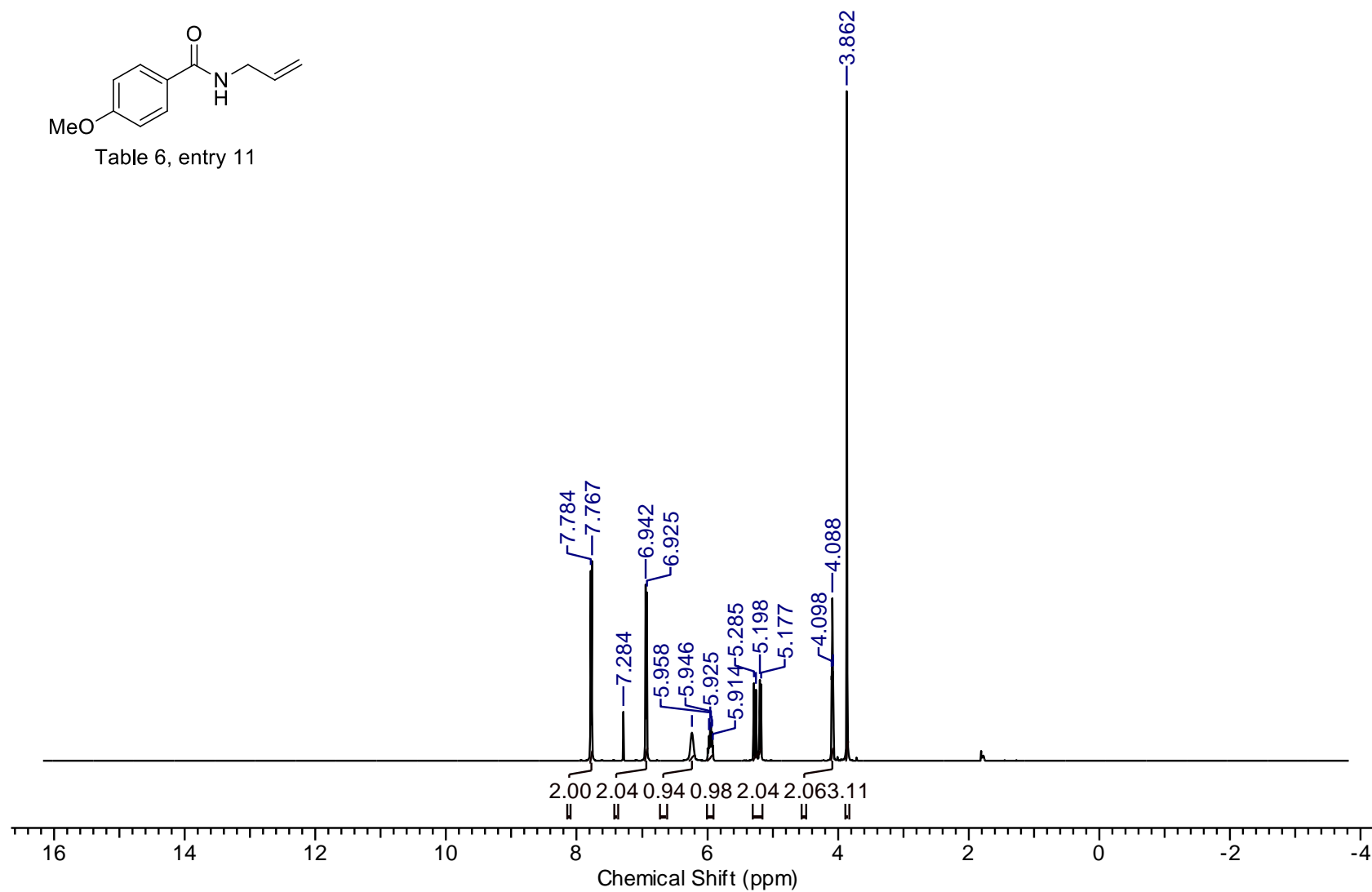


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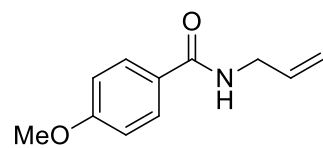
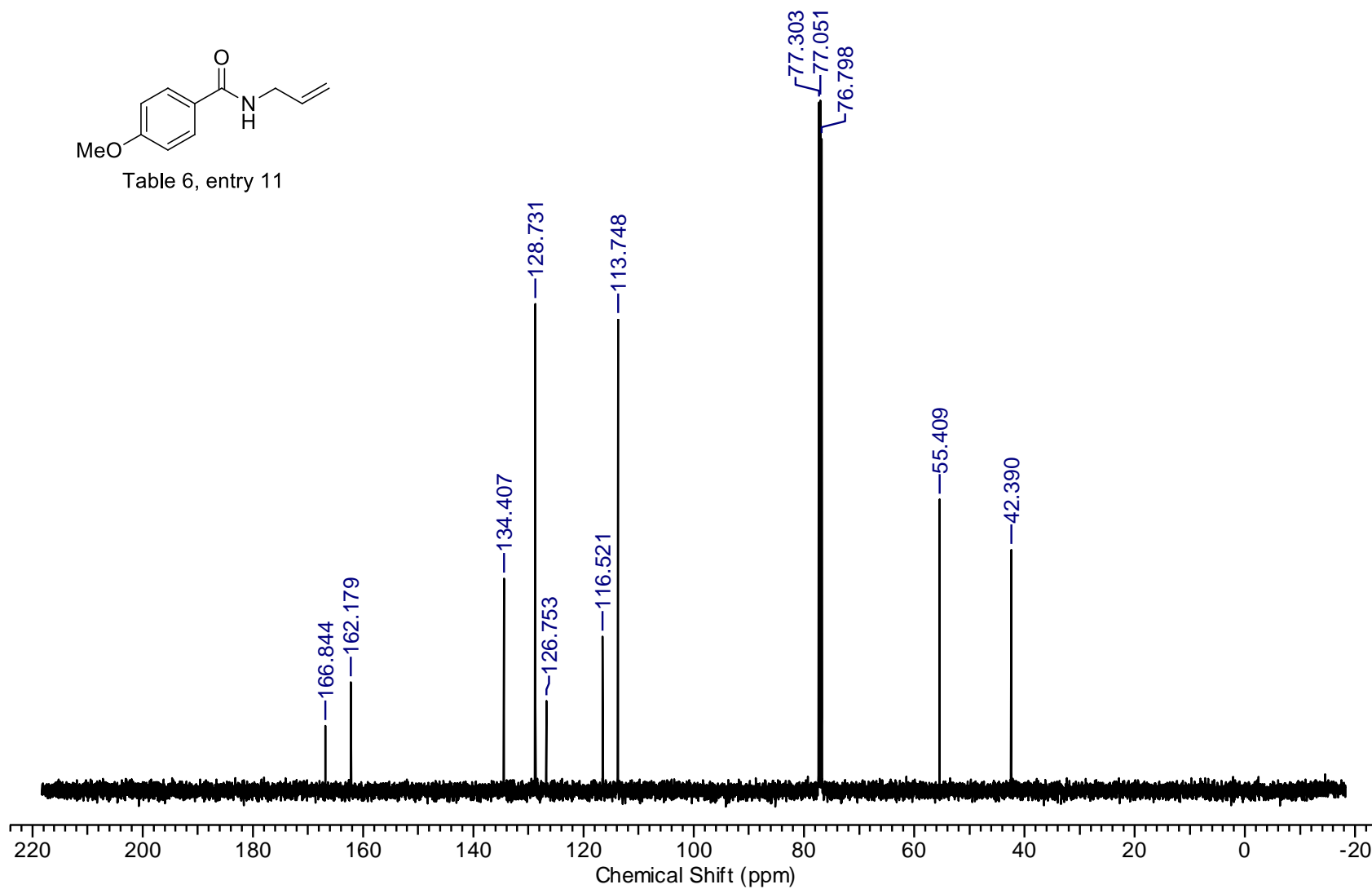


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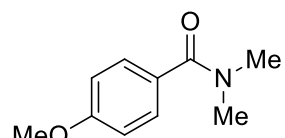
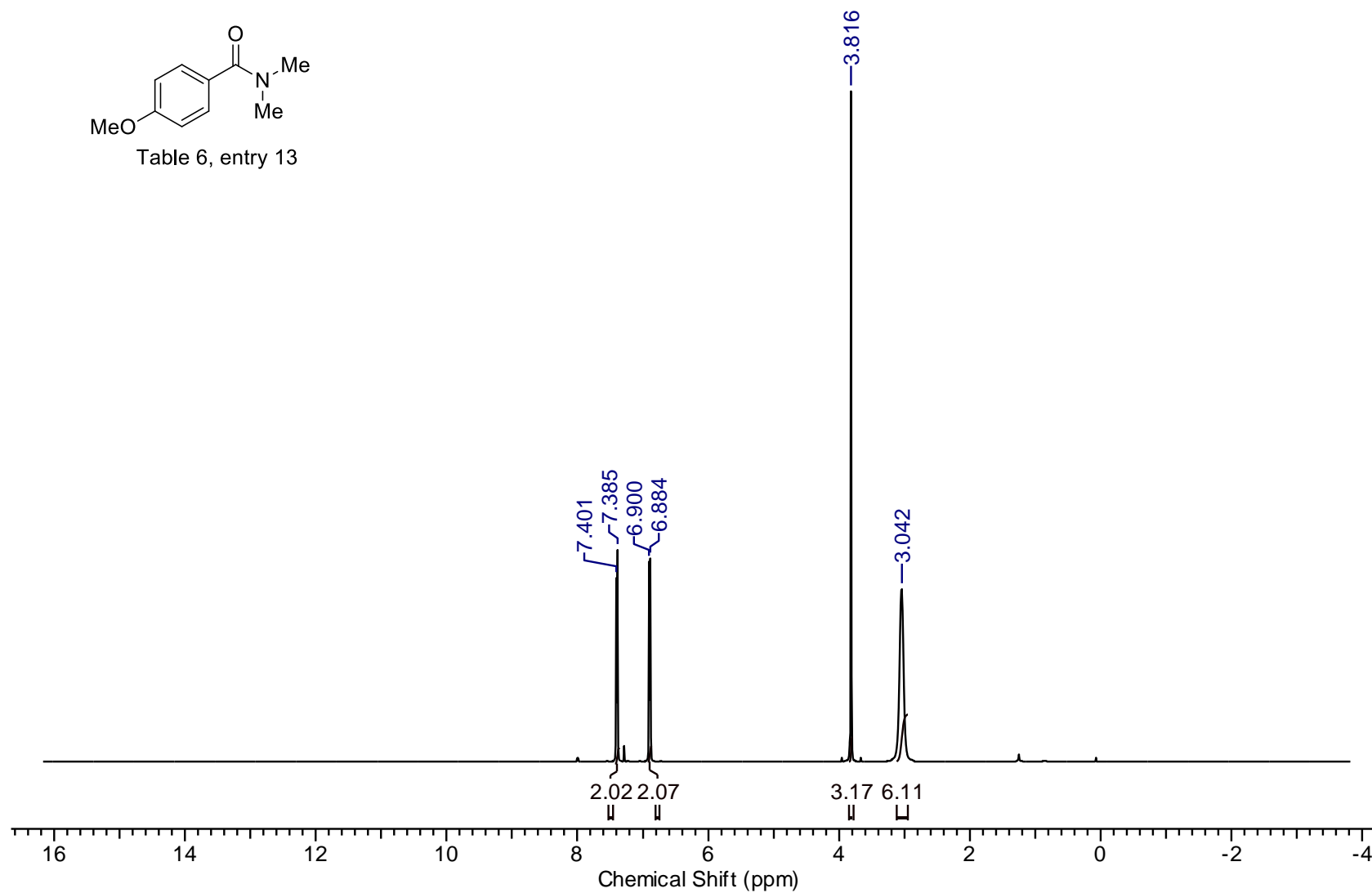
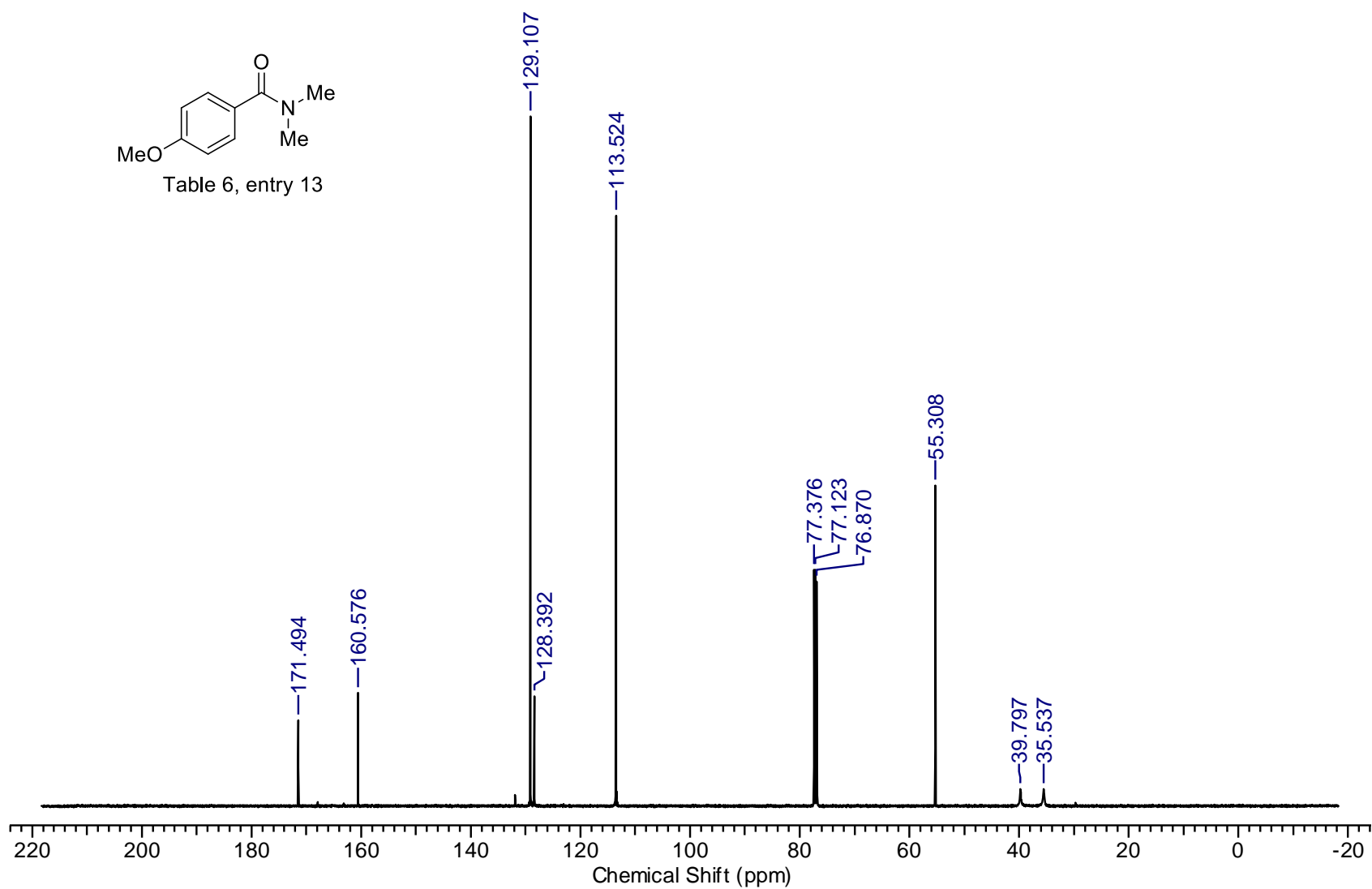
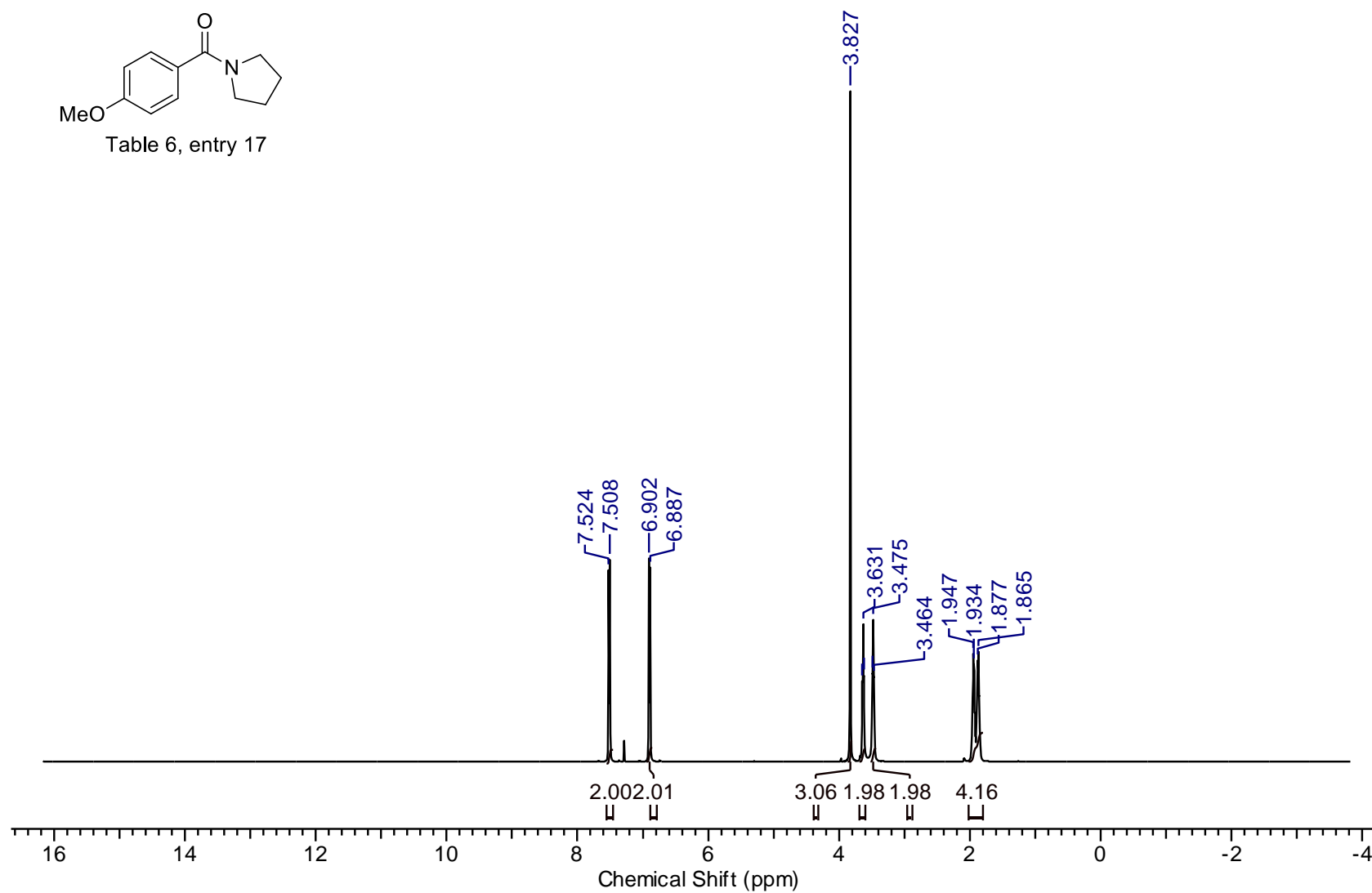
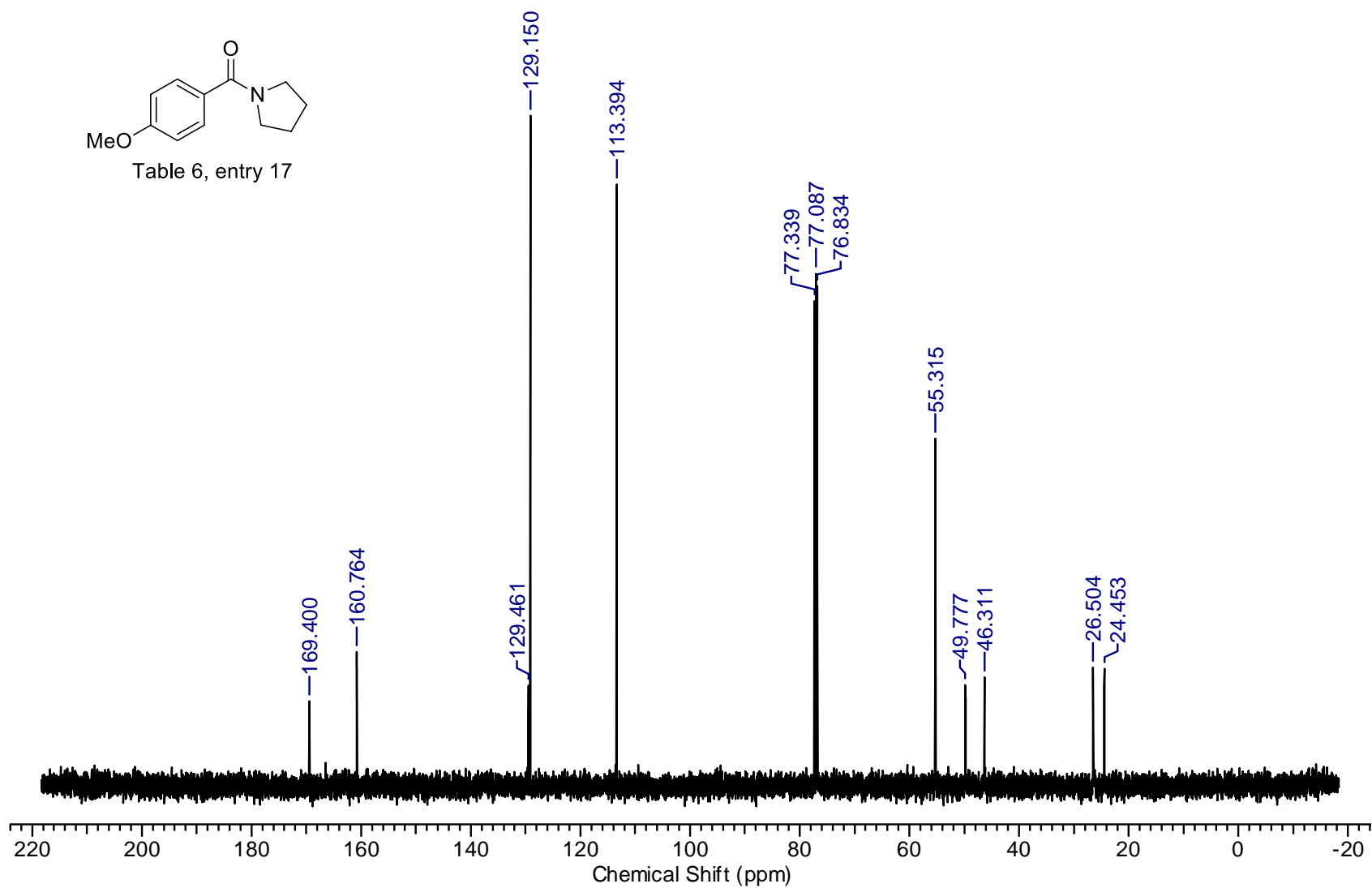


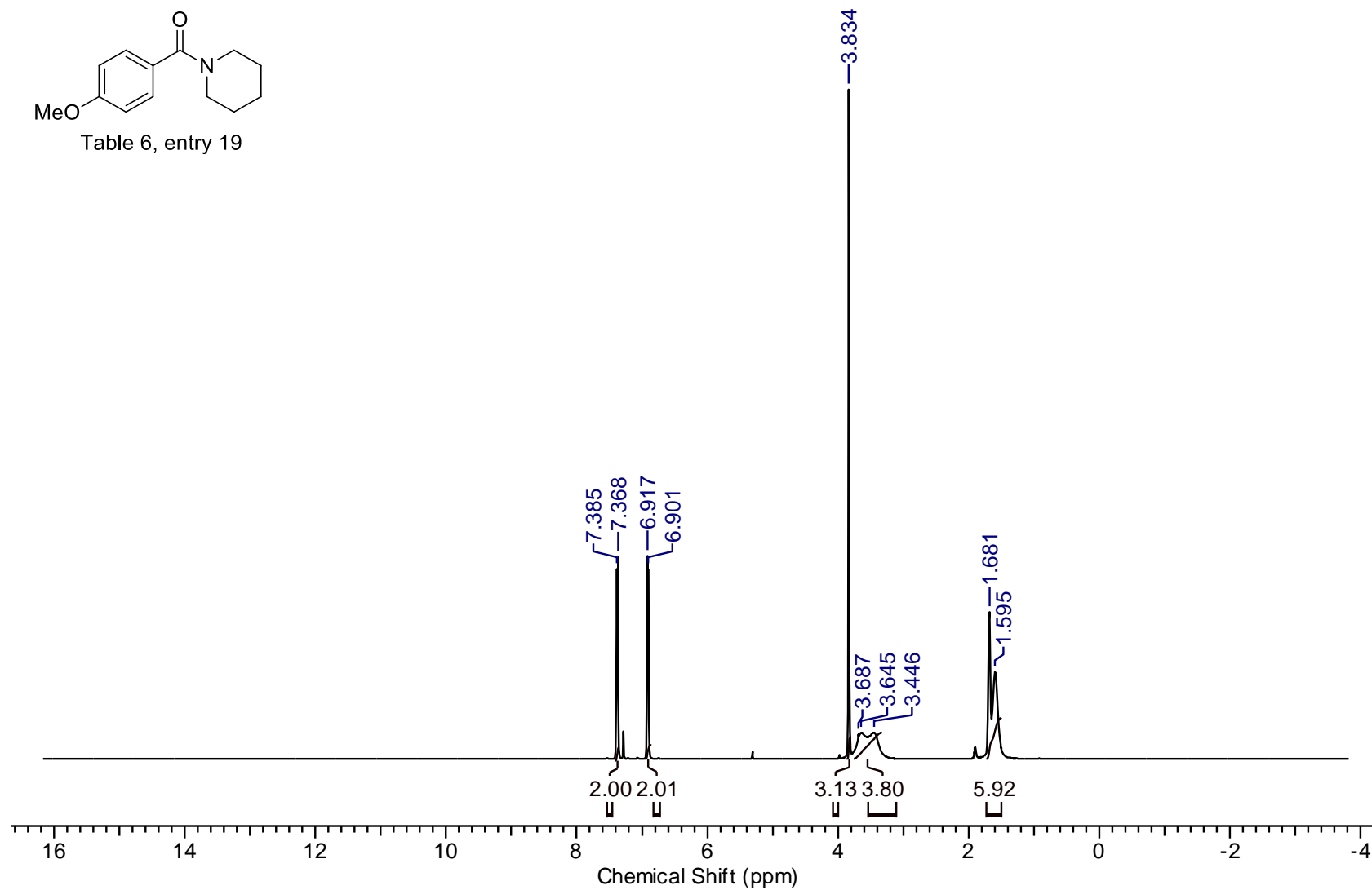
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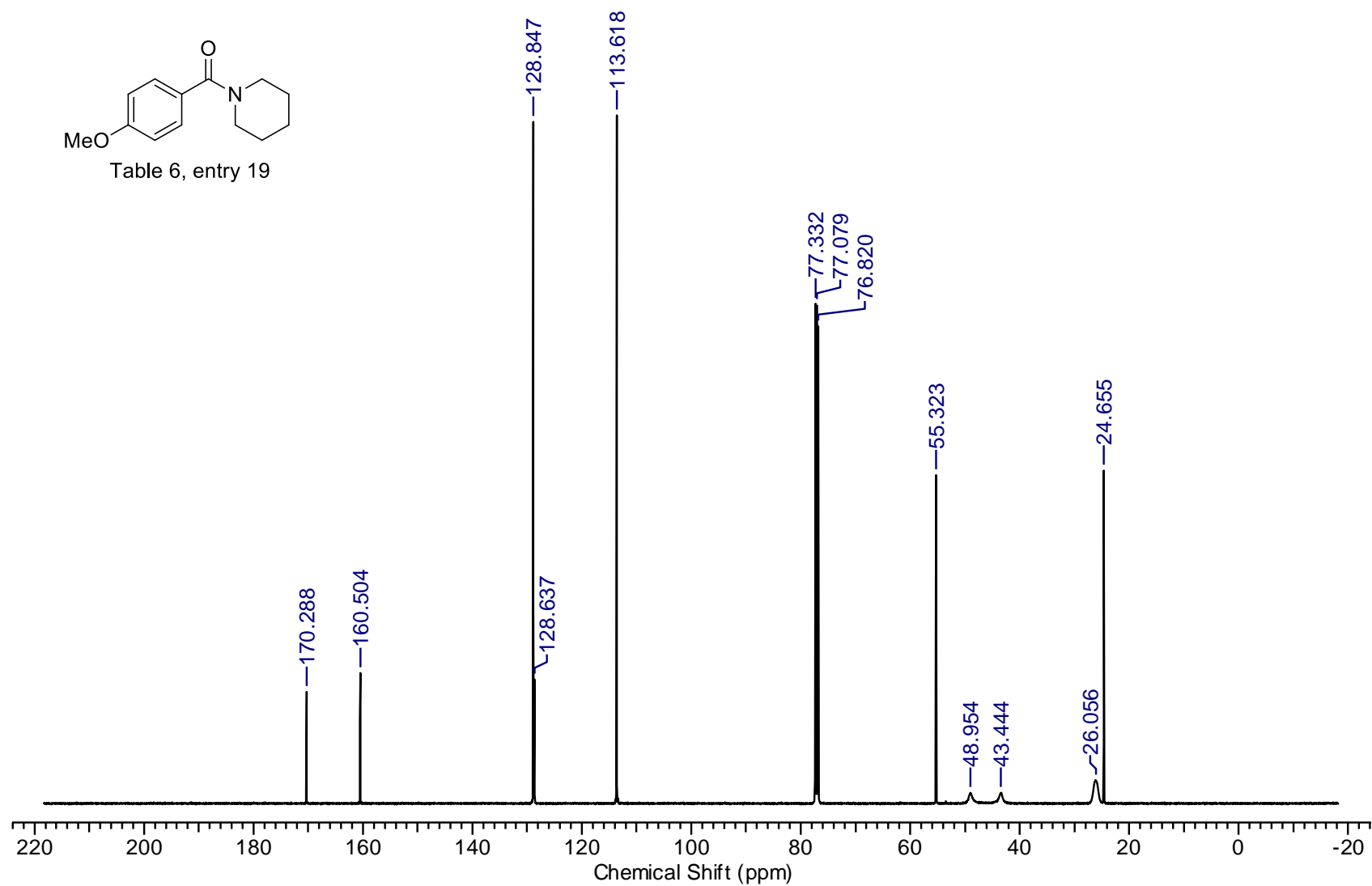


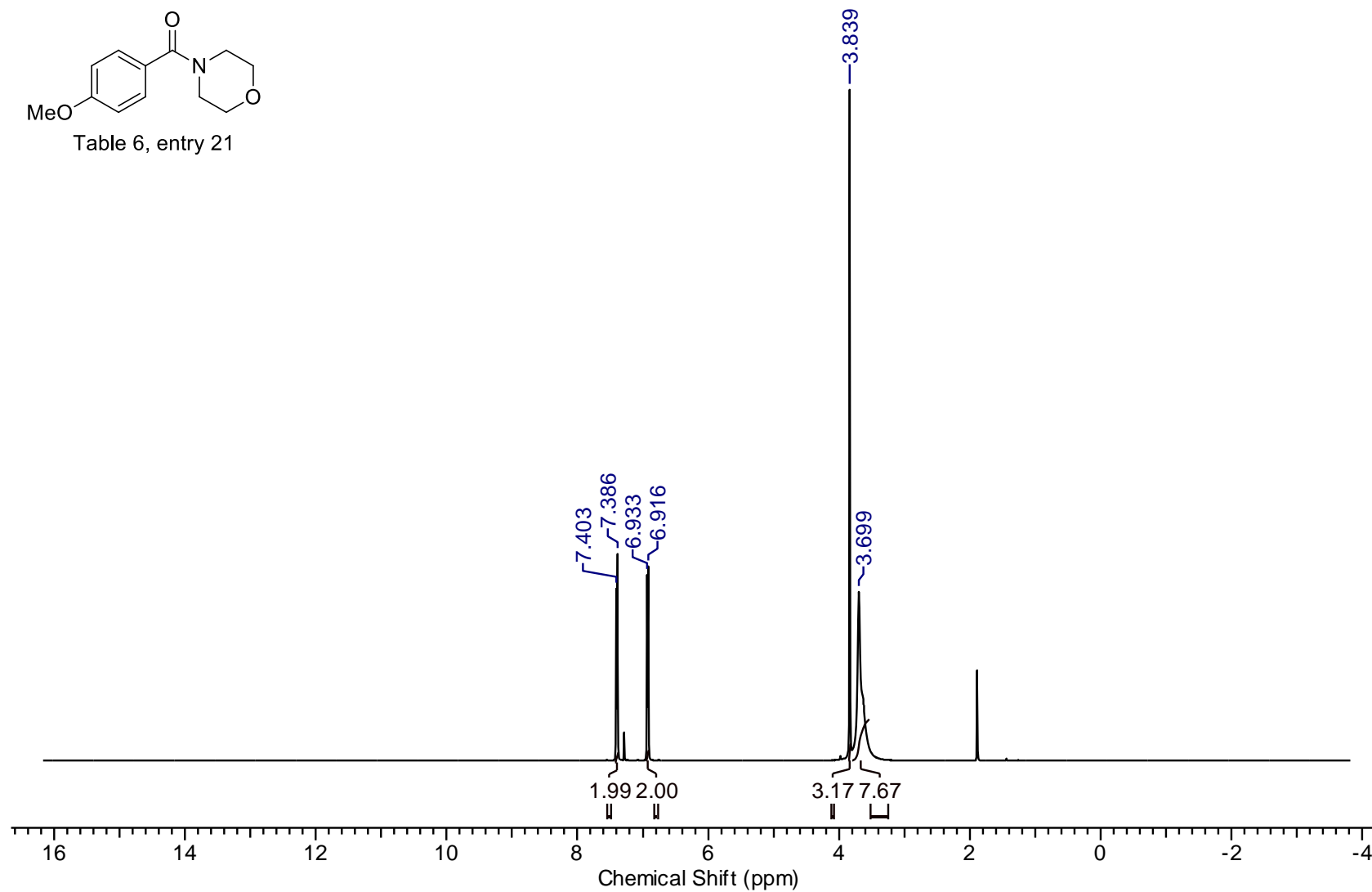
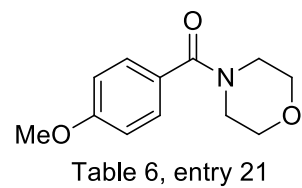


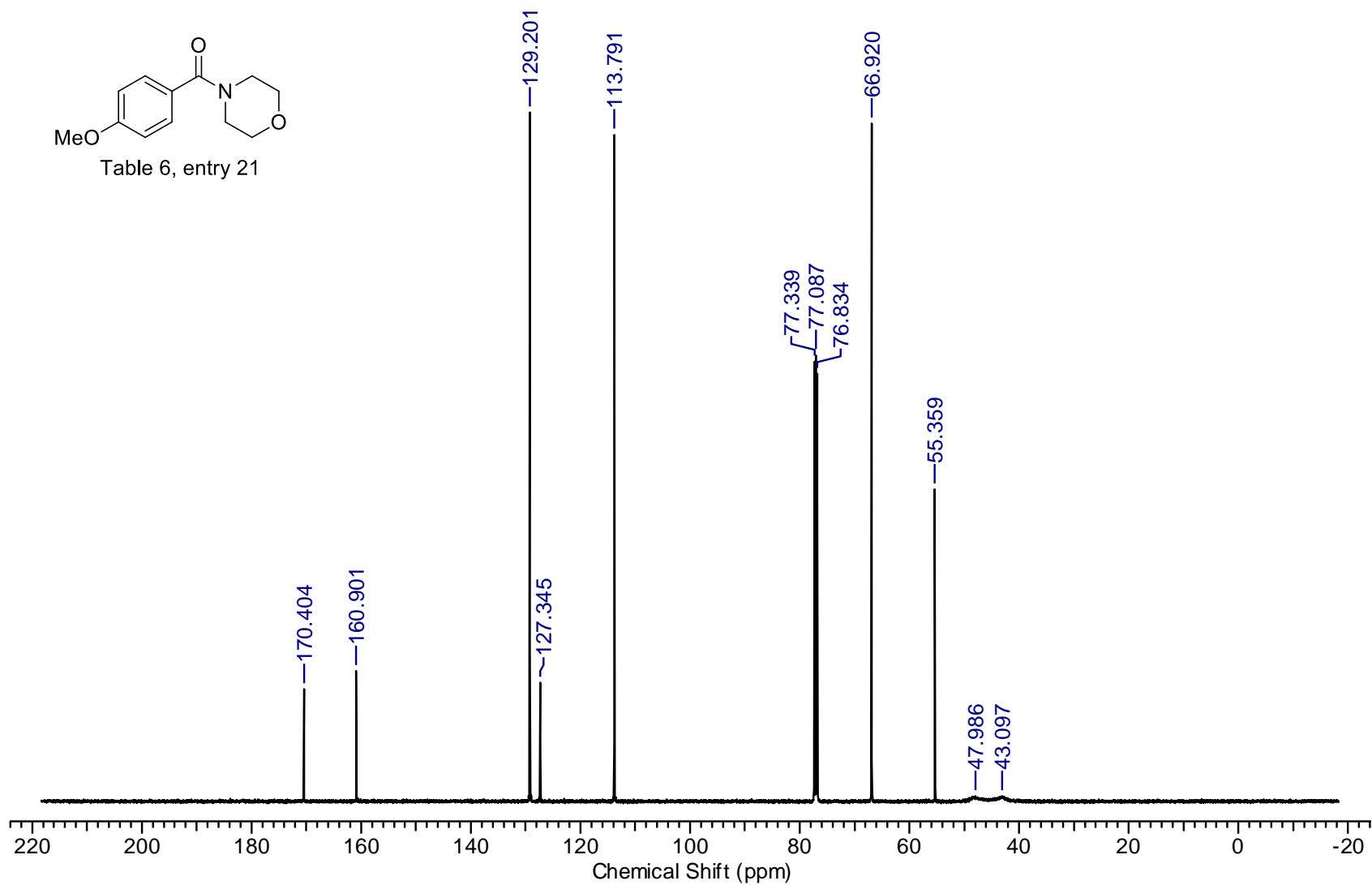


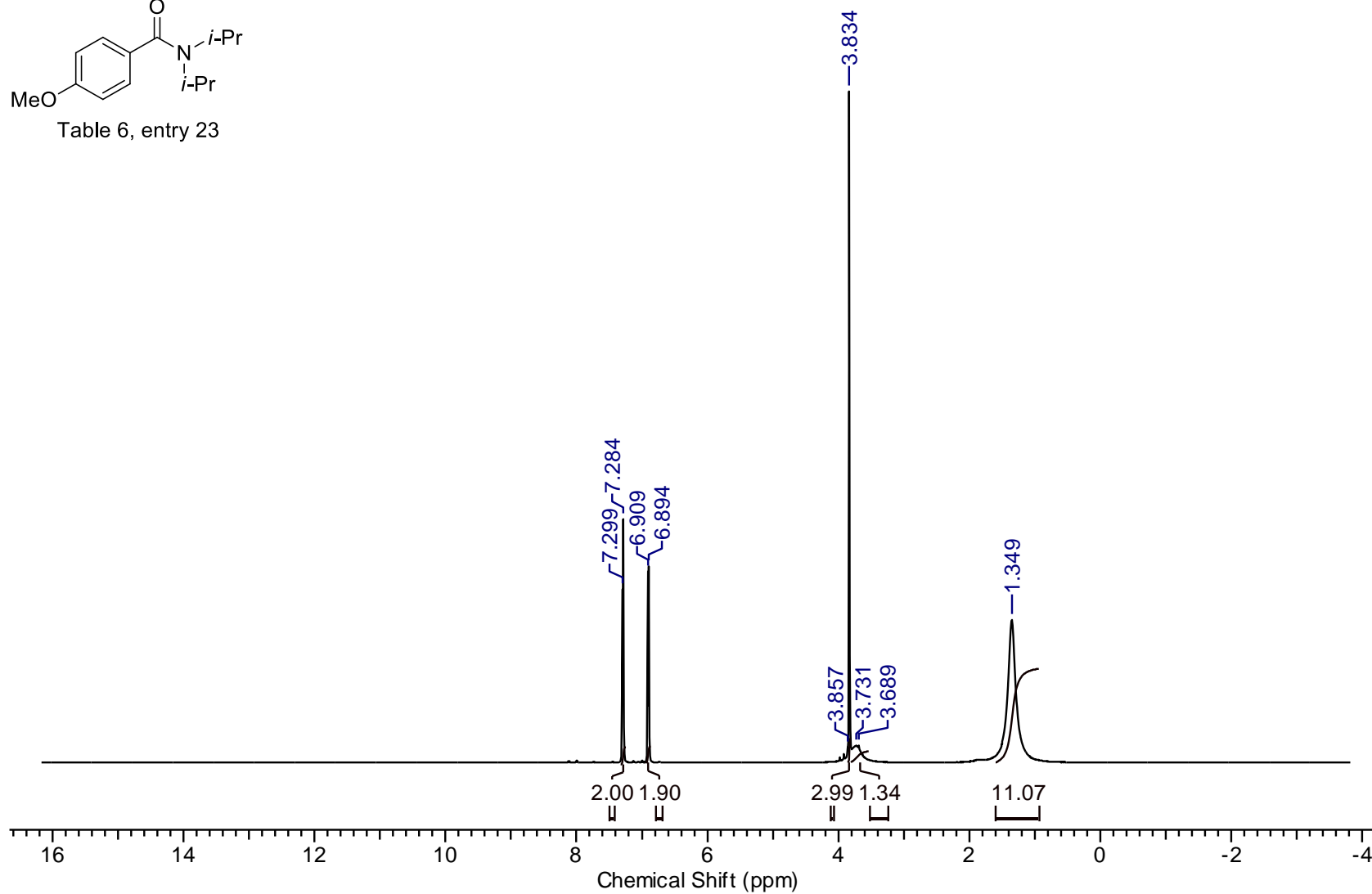
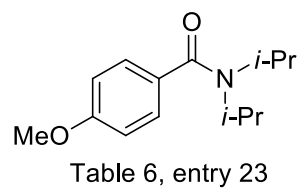












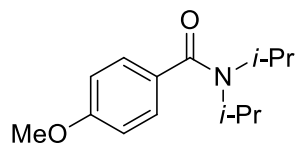


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