Supporting Information

Rhodium-Catalyzed Anti-Markovnikov Hydroamination of Aliphatic and Aromatic Terminal Alkynes with Aliphatic Primary Amines

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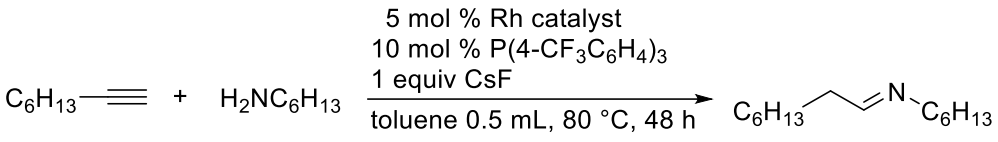
I. Optimization of Reaction Conditions

Table S1. Screening of Rhodium Catalysts for the Reaction of an Alkylacetylene

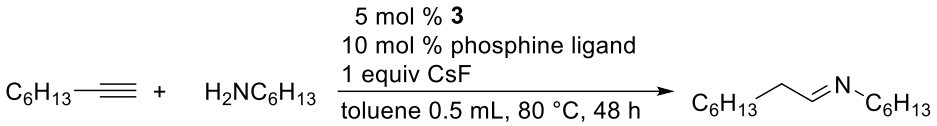


1a **2a** **4aa**

entry	Rh catalyst	NMR yield of **4aa** (%)
1	R = H, L^1 - L^2 = cod (**3**)	72
2	R = H, L^1 = L^2 = CO	15
3	R = Me, L^1 = L^2 = CO	6
4	$[RhCl(cod)]_2$	8
5	$[Rh(OMe)(cod)]_2$	9
6	$RhCl(PPh_3)_3$	8
7	none	not detected

Reaction conditions: **1a** (2 mmol), **2a** (1 mmol).
NMR yield was determined by ^{1}H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.

Table S2. Screening of Phosphine Ligands for the Reaction of an Alkylacetylene

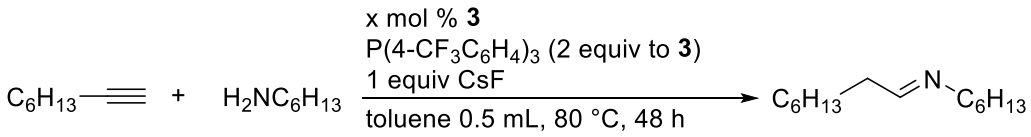


1a **2a** **4aa**

entry	phosphine ligands	NMR yield of **4aa** (%)
1	$P(4\text{-}CF_3C_6H_4)_3$	72
2	$P\{3,5\text{-}(CF_3)_2C_6H_3\}_3$	52
3	$P(3\text{-}FC_6H_4)_3$	55
4	$P(4\text{-}FC_6H_4)_3$	16
5	$PPh_2(C_6F_5)$	10
6	PPh_3	14
7	$P(3\text{-}MeOC_6H_4)_3$	6
8	$P(4\text{-}MeOC_6H_4)_3$	6
9	$P(3\text{-}MeC_6H_4)_3$	5
10	$P(4\text{-}MeC_6H_4)_3$	7
11	$P(OPh)_3$	trace
12	PCy_3	not detected
13	none	not detected

Reaction conditions: **1a** (2 mmol), **2a** (1 mmol).
NMR yield was determined by ^1H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.

Table S3. Optimization of Catalyst Loading for the Reaction of an Alkylacetylene



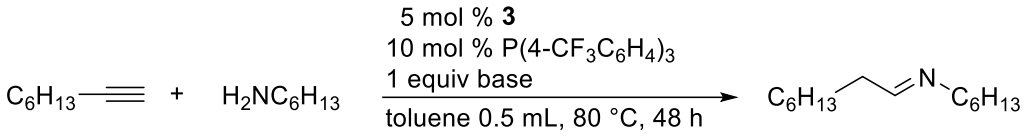
1a **2a** **4aa**

entry	x (mmol)	NMR yield of **4aa** (%)
1	1	9
2	2.5	34
3	5	72
4	7.5	62
5	10	47

Reaction conditions: **1a** (2 mmol), **2a** (1 mmol).
NMR yield was determined by ^{1}H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.

As the catalyst loading was increased from 5 mol %, the amounts of unidentified byproducts were increased and the yield of **4aa** was reduced. Some of the byproducts may be formed via a dimetallic mechanism.

Table S4. Screening of Bases for the Reaction of an Alkylacetylene

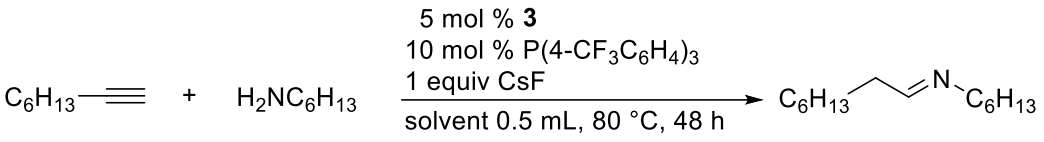


1a **2a** **4aa**

entry	base	NMR yield of **4aa** (%)	entry	base	NMR yield of **4aa** (%)
1	CsF	72	12	K_2CO_3	68
2	CsCl	51	13	Na_2CO_3	64
3	CsBr	63	14	AgF	not detected
4	CsI	64	15	Et_3N	56
5	CsOAc	30	16	pyridine	52
6	$CsHCO_3$	38	17	DABCO	71
7	Cs_2CO_3	33	18	DBU	18
8	LiF	34	19	none	35
9	NaF	64	20	CsF (0.5 equiv)	43
10	KF	47	21	CsF (1.5 equiv)	50
11	TBAF	3	22	CsF (2.0 equiv)	52

Reaction conditions: **1a** (2 mmol), **2a** (1 mmol).
NMR yield was determined by ^{1}H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.

Table S5. Screening of Solvents for the Reaction of an Alkylacetylene

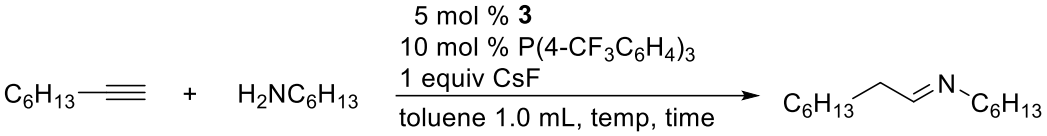


1a **2a** **4aa**

entry	solvent (mL)	NMR yield of **4aa** (%)
1	toluene	72
2	benzene	52
3	THF	64
4	CPME	48
5	1,4-dioxane	45[a]
6	MeCN	17[a]
7	DMA	19
8	toluene (0.75 mL)	82
9	toluene (1.0 mL)	84
10	toluene (1.5 mL)	84

Reaction conditions: **1a** (2 mmol), **2a** (1 mmol).
NMR yield was determined by ^{1}H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.
[a] CsF 1.5 equiv.

Table S6. Optimization of Reaction Temperature and Time for the Reaction of an Alkylacetylene

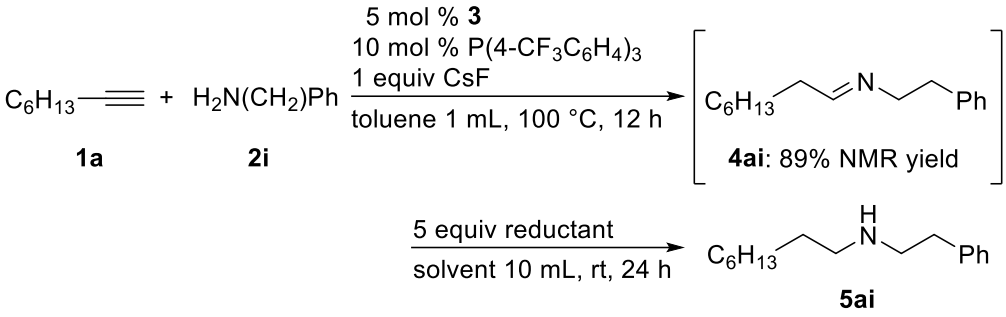


1a **2a** **4aa**

entry	temp	time	NMR yield of **4aa** (%)
1	80 °C	48 h	84
2	70 °C	48 h	64
3	90 °C	48 h	81
4	100 °C	48 h	89
5	120 °C	48 h	89
6	80 °C	24 h	67
7	100 °C	24 h	87
8	120 °C	24 h	86
9	100 °C	12 h	90
10	120 °C	12 h	85
11	100 °C	6 h	77

Reaction conditions: **1a** (2 mmol), **2a** (1 mmol).
NMR yield was determined by ^{1}H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.

Table S7. Screening of Reductants and Solvents for the Reduction of the anti-Markovnikov Hydroamination Product Derived from an Alkylacetylene



entry	reductant	solvent	yield of **5ai** (%)
1	$NaBH_4$	MeOH	70
2	$NaBH_4$	Et_2O	72
3[a]	$NaBH_4$	Et_2O	75
4[b]	$NaBH_4$	Et_2O	55
5	$NaBH_3CN$	MeOH	44
6[c]	$NaBH_3CN$	MeOH	34
7[d]	$LiBH_4$	Et_2O	56
8	LAH	Et_2O	66

Reaction conditions: **1a** (2 mmol), **2i** (1 mmol).

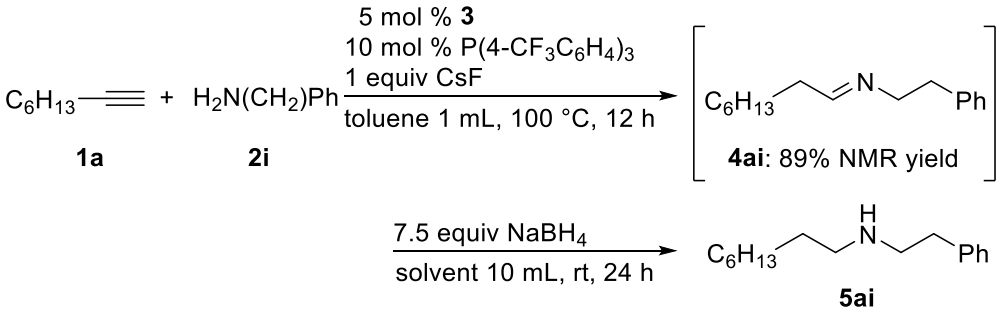
[a] 7.5 equiv of $NaBH_4$

[b] 3.6 equiv of AcOH was added.

[c] 2.3 equiv of $ZnCl_2$ was added.

[d] 7.5 equiv of $LiBH_4$

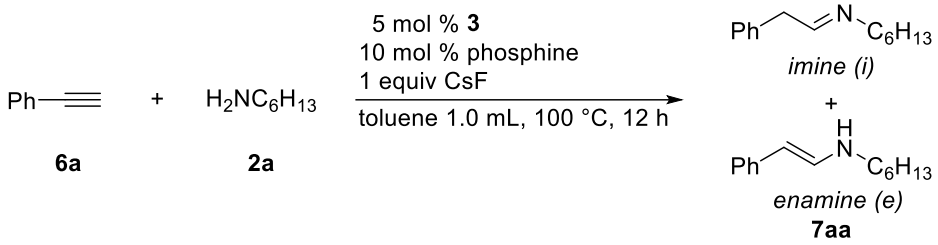
Table S8. Further Screening of Solvents for the Reduction of the anti-Markovnikov Hydroamination Product Derived from an Alkylacetylene



entry	solvent	yield of **5ai** (%)
1	Et_2O	75
2	MeOH 5 mL, Et_2O 5 mL	83
3	MeOH	79
4	DCE	85
5	MeOH 5 mL, Et_2O 5 mL, 3.6 equiv AcOH	70
6	MeOH 5 mL, DCE 5mL	82

Reaction conditions: **1a** (2 mmol), **2i** (1 mmol).

Table S9. Screening of Phosphine Ligands for the Reaction of an Arylacetylene

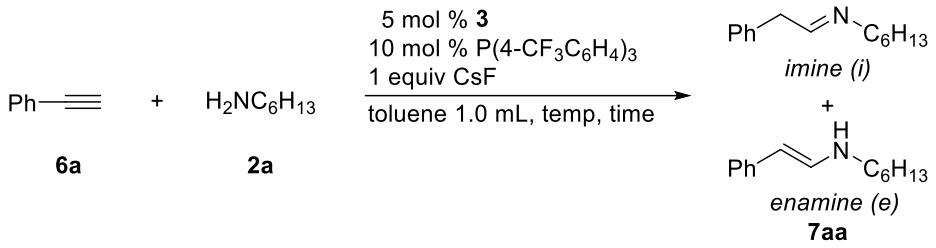


6a **2a** **7aa**

entry	phosphine	NMR yield of **7aa** (%) [i/e][a]
1	$P(4\text{-}CF_3C_6H_4)_3$	64 [52/48]
2	$P(4\text{-}FC_6H_4)_3$	58 [47/53]
3	$P(3\text{-}FC_6H_4)_3$	61 [43/57]
4	$P(3\text{-}ClC_6H_4)_3$	47 [45/55]
5	$P(4\text{-}ClC_6H_4)_3$	57 [53/47]
6	$P\{3,5\text{-}(CF_3)_2C_6H_3\}_3$	not detected
7	PPh_3	43 [51/49]
8	$P(4\text{-}MeOC_6H_4)_3$	28 [57/43]
9	$P(4\text{-}MeC_6H_4)_3$	27 [52/48]
10	PCy_3	8 [50/50]

Reaction conditions: **6a** (2 mmol), **2a** (1 mmol).
NMR yield was determined by ^{1}H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.
[a] Combined yield of aldimine and enamine was shown.

Table S10. Optimization of Reaction Temperature and Time for the Reaction of an Arylacetylene



entry	temp	time	NMR yield of **7aa** (%) [i/e][a]
1	100 °C	12 h	64 [52/48]
2	80 °C	48 h	27 [48/52]
3	60 °C	48 h	38 [53/47]
4	50 °C	48 h	34 [53/47]
5	110 °C	6 h	61 [54/46]
6	120 °C	6 h	61 [56/44]
7	120 °C	12 h	65 [57/43]
8	120 °C	24 h	60 [58/42]
9	120 °C	48 h	41 [59/41]
10 [b]	120 °C	12 h	62 [55/45]

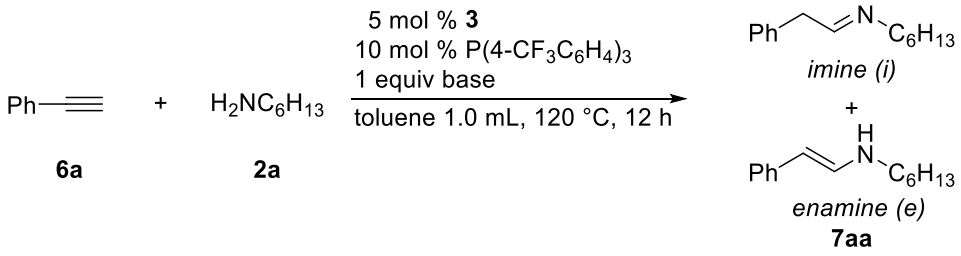
Reaction conditions: **6a** (2 mmol), **2a** (1 mmol).

NMR yield was determined by ^{1}H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.

[a] Combined yield of aldimine and enamine was shown.

[b] 7.5 mol % **3**, 15 mol % P(4-$CF_3C_6H_4$)$_3$.

Table S11. Screening of Bases for the Reaction of an Arylacetylene

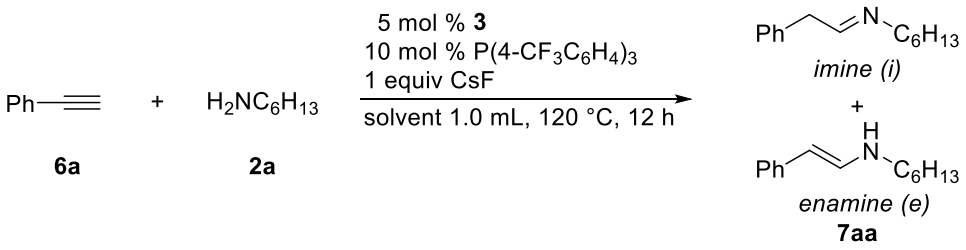


6a **2a** **7aa**

entry	base	NMR yield of **7aa** (%) [i/e][a]
1	CsF	65 [57/43]
2	LiF	35 [49/51]
3	NaF	33 [61/39]
4	KF	35 [51/49]
5	TBAF	not detected
6	K_2CO_3	52 [52/48]
7	Cs_2CO_3	29 [59/41]
8	DABCO	33 [33/67]
9	DMAP	26 [62/38]
10	pyridine	31 [48/52]
11	DBU	3 [0/100]
12	TMG	3 [0/100]
13	TBD	not detected
14	w/o base	24 [67/33]
15	CsF (0.5 eq)	64 [56/44]
16	CsF (2 eq)	62 [56/44]

Reaction conditions: **6a** (2 mmol), **2a** (1 mmol).
NMR yield was determined by ^{1}H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.
[a] Combined yield of aldimine and enamine was shown.

Table S12. Screening of Solvents for the Reaction of an Arylacetylene

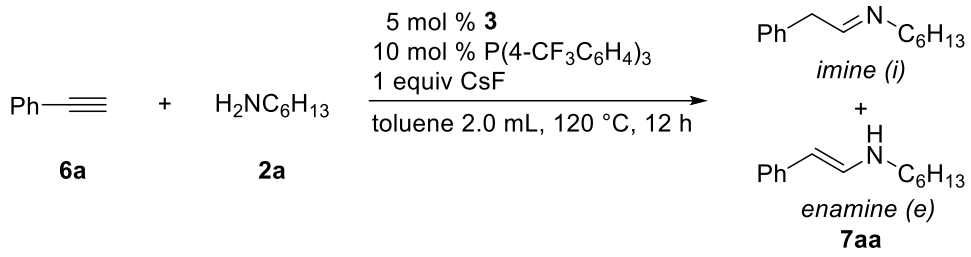


6a **2a** **7aa**

entry	solvent	NMR yield of **7aa** (%) [i/e][a]
1	toluene	65 [57/43]
2	benzene	59 [56/44]
3	p-xylene	58 [55/45]
4	mesitylene	59 [56/44]
5	o-dichloribenzene	59 [53/47]
6	$PhCF_3$	50 [60/40]
7	DMA	not detected
8	DMSO	not detected
9	MeCN	not detected
10	1,4-diaxane	57 [26/74]
11	CPME	62 [48/52]
12[b]	THF	not detected
13[c]	IPA	not detected
14	toluene (0.5 mL)	58 [60/40]
15	toluene (1.5 mL)	65 [57/43]
16	toluene (2.0 mL)	67 [58/42]
17[b]	toluene (2.0 mL)	64 [59/41]
18[b]	toluene (2.5 mL)	65 [58/42]

Reaction conditions: **6a** (2 mmol), **2a** (1 mmol).
NMR yield was determined by ^{1}H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.
[a] Combined yield of aldimine and enamine was shown.
[b] 10 mL Schlenk was used.
[c] 100 °C.

Table S13. Optimization of Equivalent of Phenylacetylene for the Reaction of an Arylacetylene



6a **2a** **7aa**

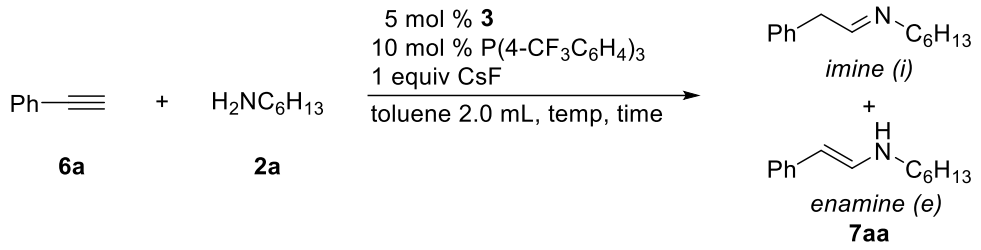
entry	**6a** (equiv)	NMR yield of **7aa** (%) [i/e][a]
1	2	67 [58/42]
2	3	76 [57/43]
3	4	74 [57/43]

Reaction conditions: **2a** (1 mmol).

NMR yield was determined by ^{1}H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.

[a] Combined yield of aldimine and enamine was shown.

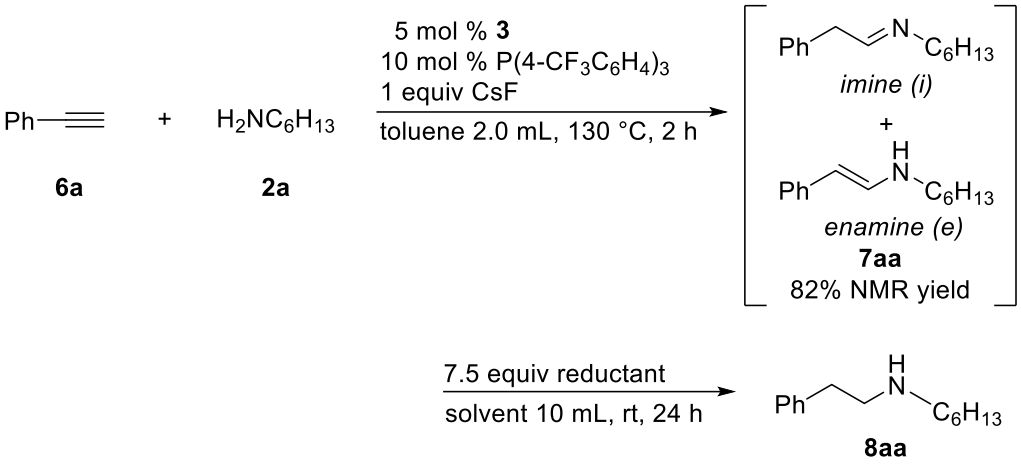
Table S14. Further Optimization of Reaction Temperature and Time for the Reaction of an Arylacetylene



entry	temp	time	NMR yield of **7aa** (%) [i/e][a]
1	120 °C	12 h	76 [57/43]
2	120 °C	6 h	76 [57/43]
3	130 °C	6 h	78 [58/42]
4	130 °C	3 h	79 [58/42]
5	130 °C	2 h	82 [56/44]
6	130 °C	1 h	79 [53/47]
7	100 °C	24 h	73 [55/45]
8	80 °C	24 h	74 [53/47]

Reaction conditions: **6a** (3 mmol), **2a** (1 mmol).
NMR yield was determined by ^{1}H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.
[a] Combined yield of aldimine and enamine was shown.

Table S15. Optimization of Conditions for the Reduction of the anti-Markovnikov Hydroamination Product Derived from an Arylacetylene

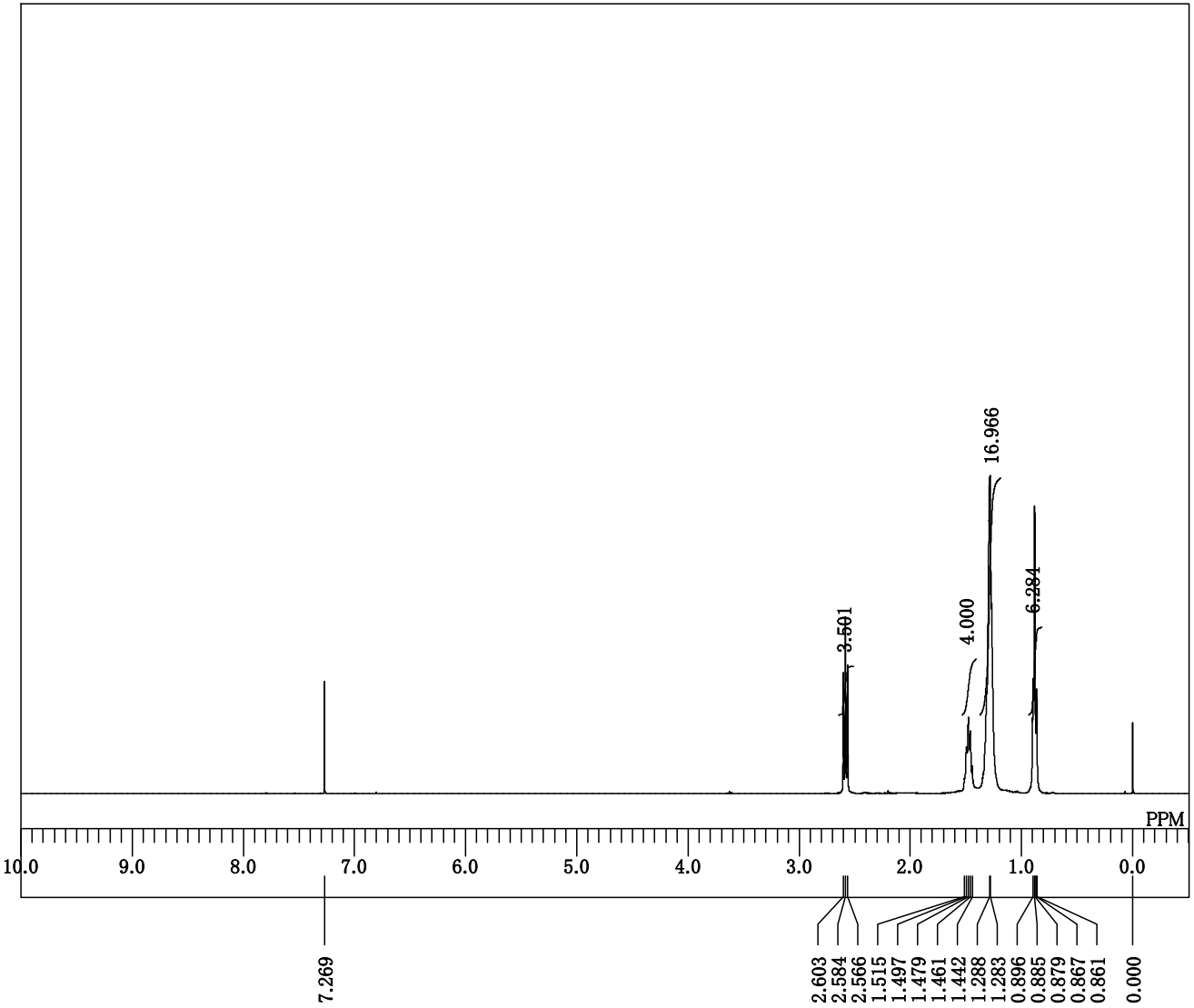


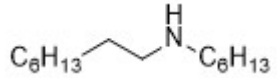
entry	reductant	solvent	NMR yield of **8aa** (%)
1	$NaBH_4$	MeOH	77 (69[a])
2	$NaBH_4$ (10 eq)	MeOH	72
3	$NaBH_4$	Et_2O	57
4	$NaBH_4$	DCE	58
5	$NaBH_3CN$	MeOH	63
6	$NaBH(OAc)_3$	THF	67
7	$LiBH_4$	MeOH	65

Reaction conditions: **6a** (3 mmol), **2a** (1 mmol).
NMR yield was determined by ^1H NMR analysis using 1,3,5 trimethoxybenzene as an internal standard.
[a] Isolated yield.

II. NMR Spectra

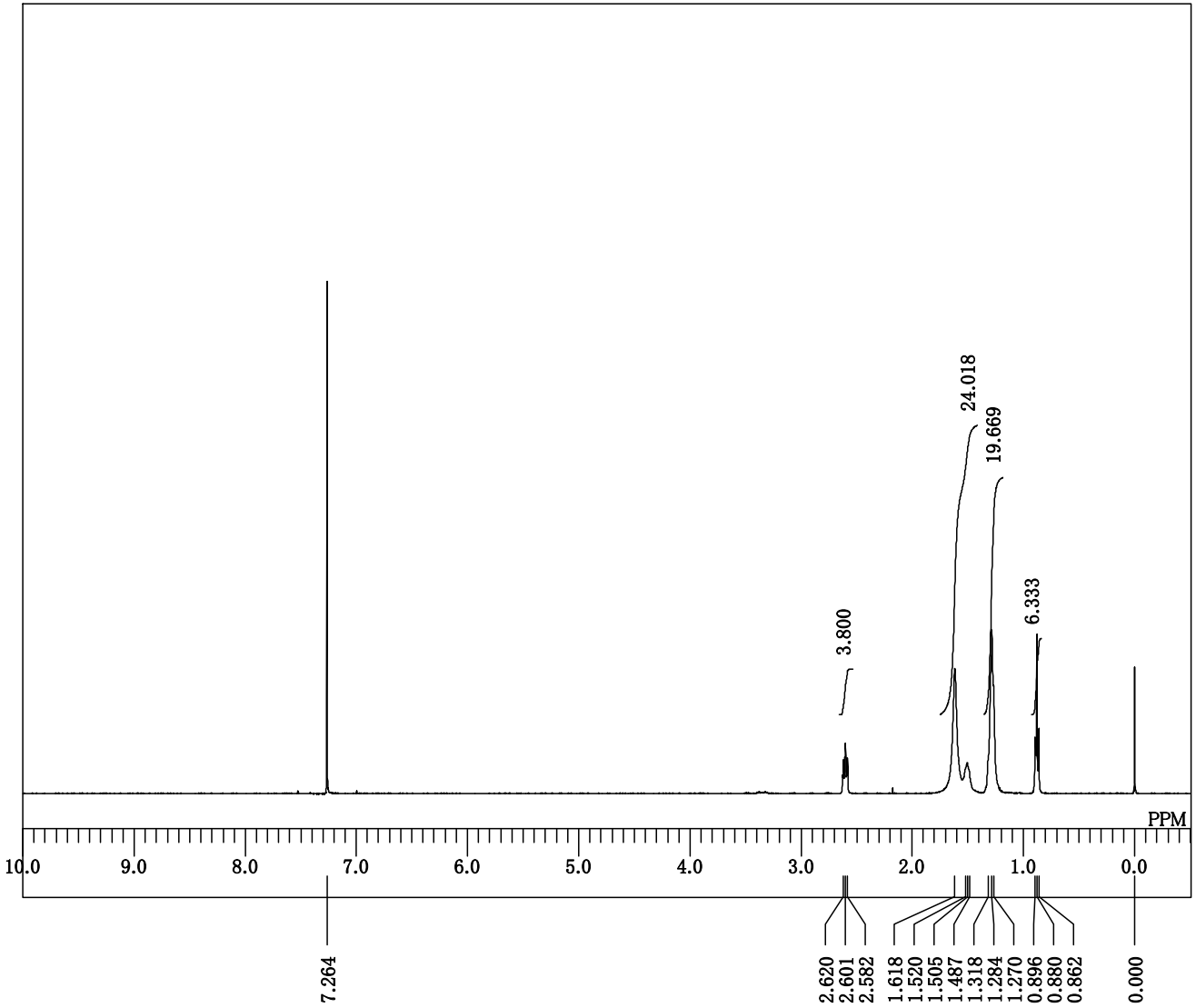
^{1}H NMR (391.78 MHz, $CDCl_3$)

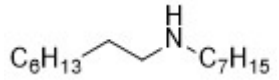




5aa

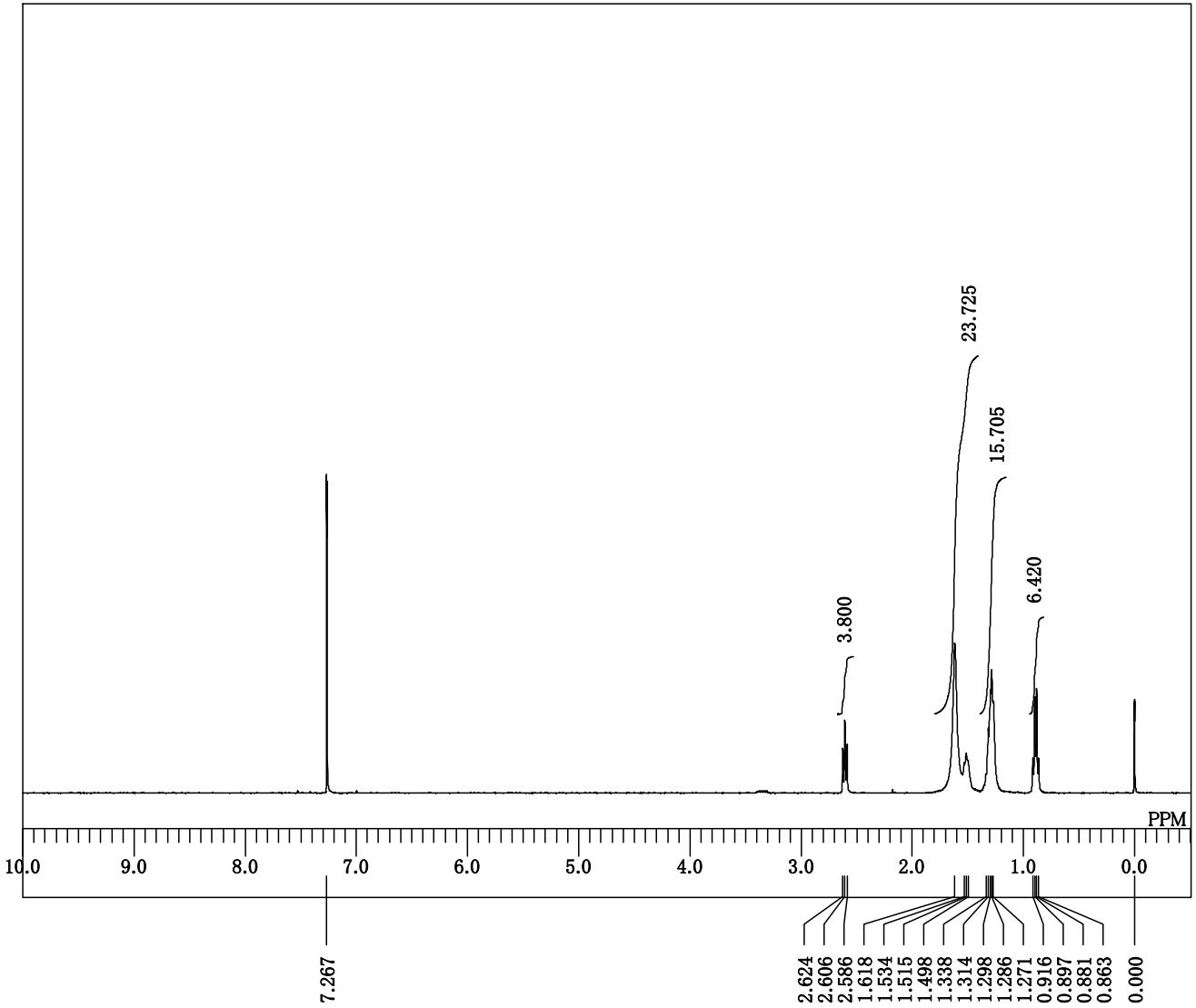
^{1}H NMR (395.88 MHz, $CDCl_3$)

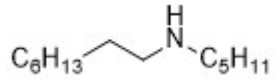




5ab

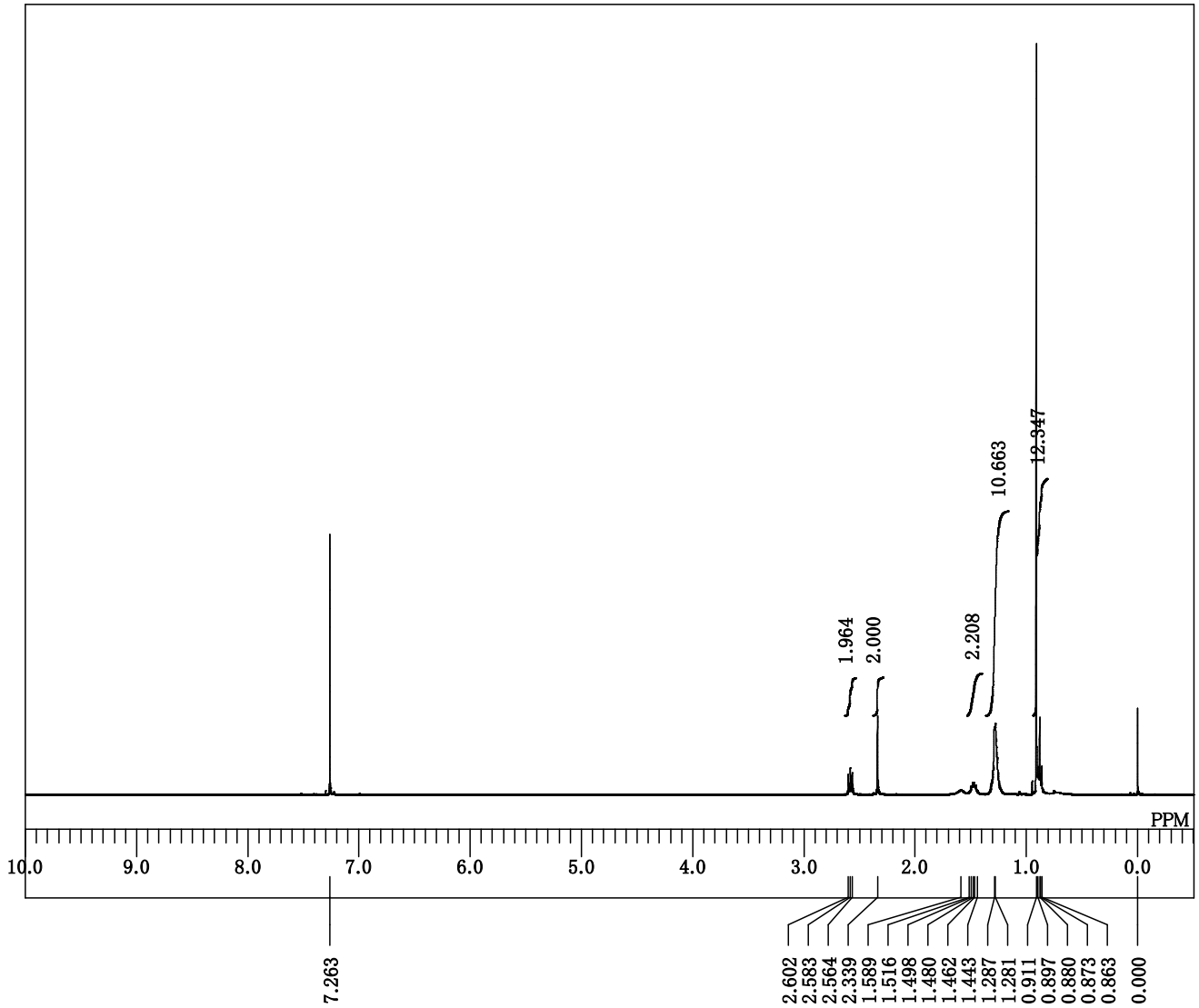
^{1}H NMR (395.88 MHz, $CDCl_3$)

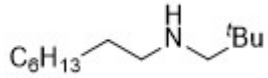




5ac

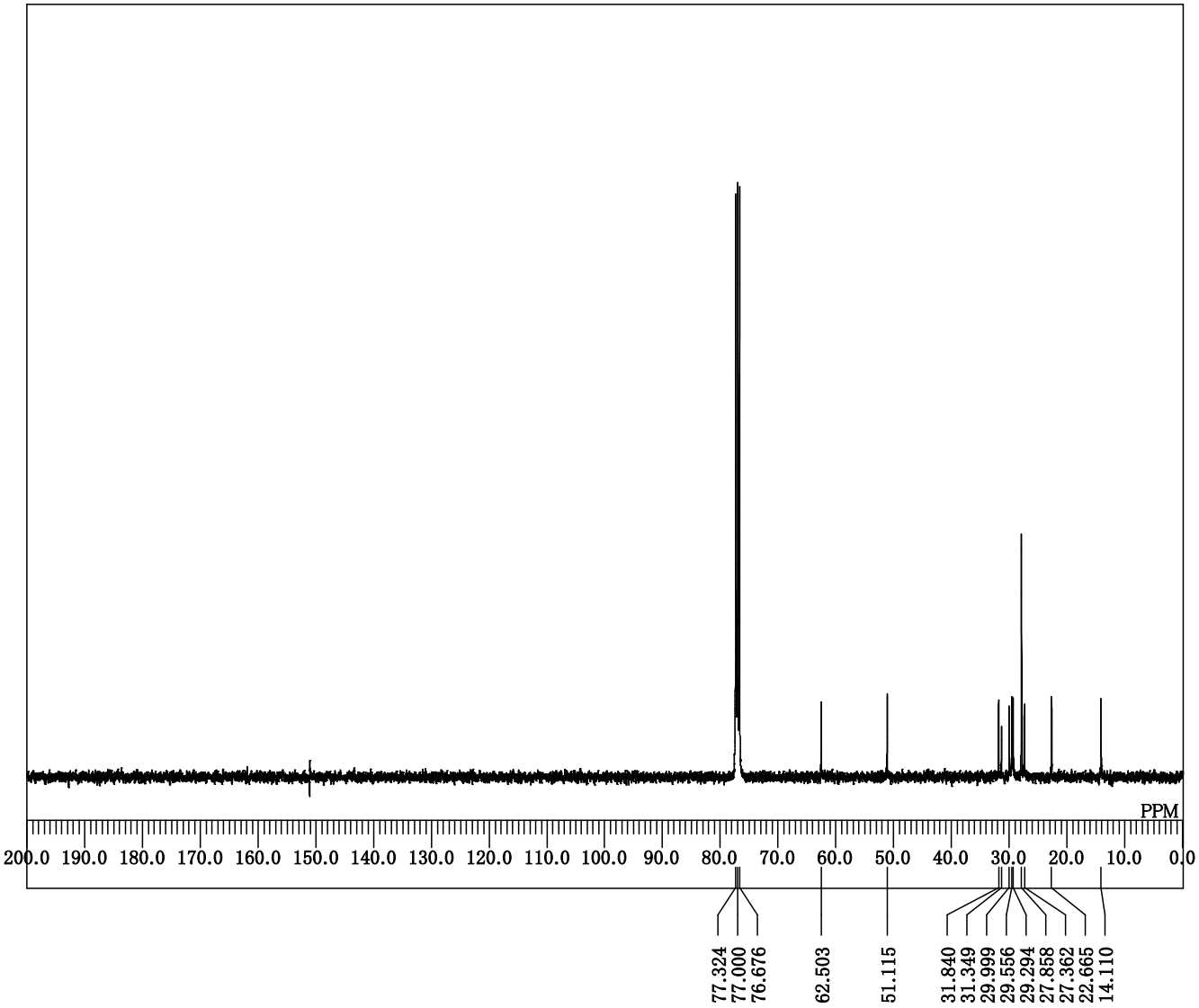
^{1}H NMR (395.88 MHz, $CDCl_3$)

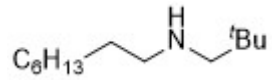




5ad

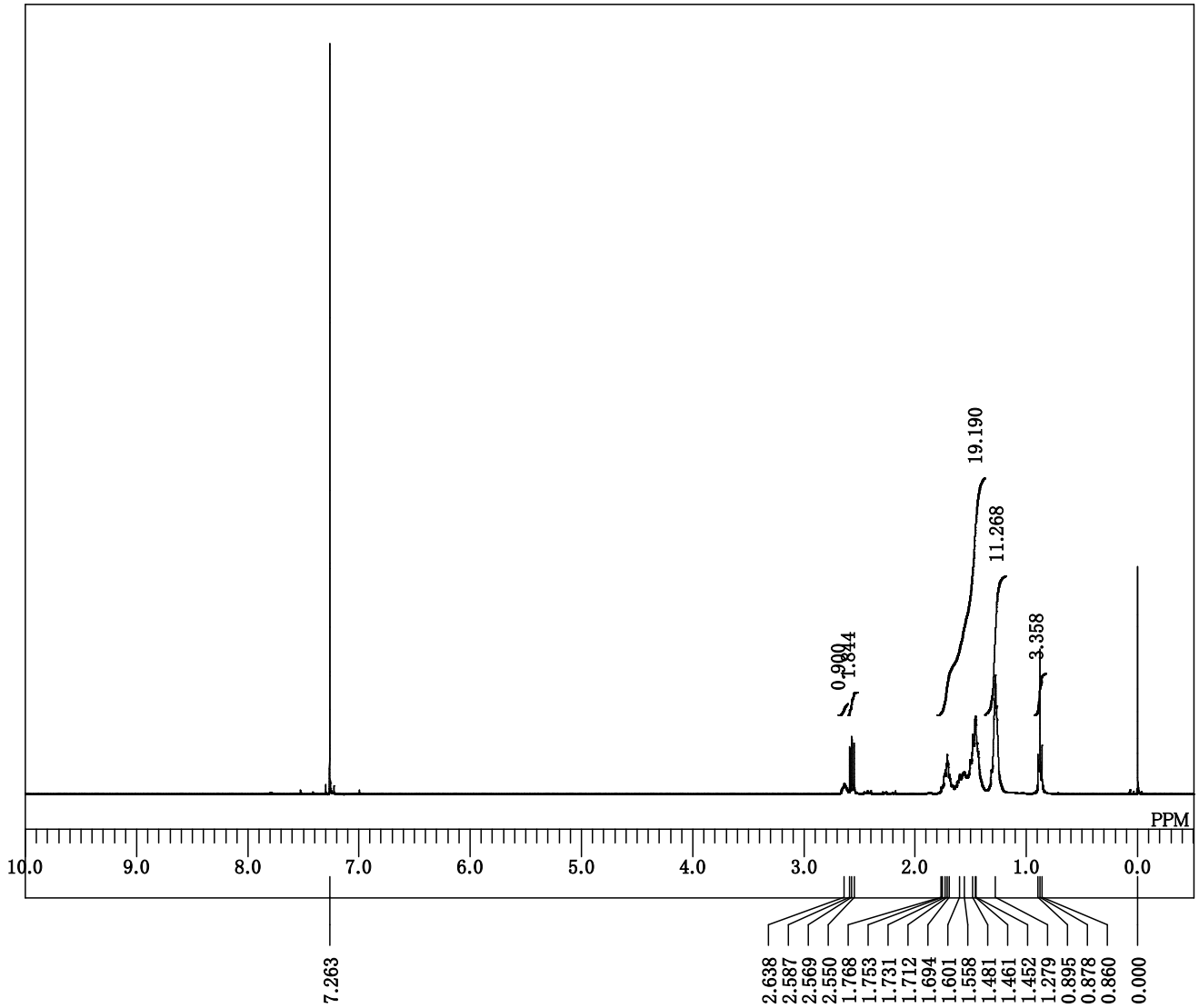
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

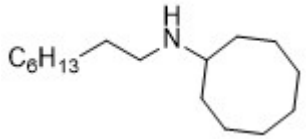




5ad

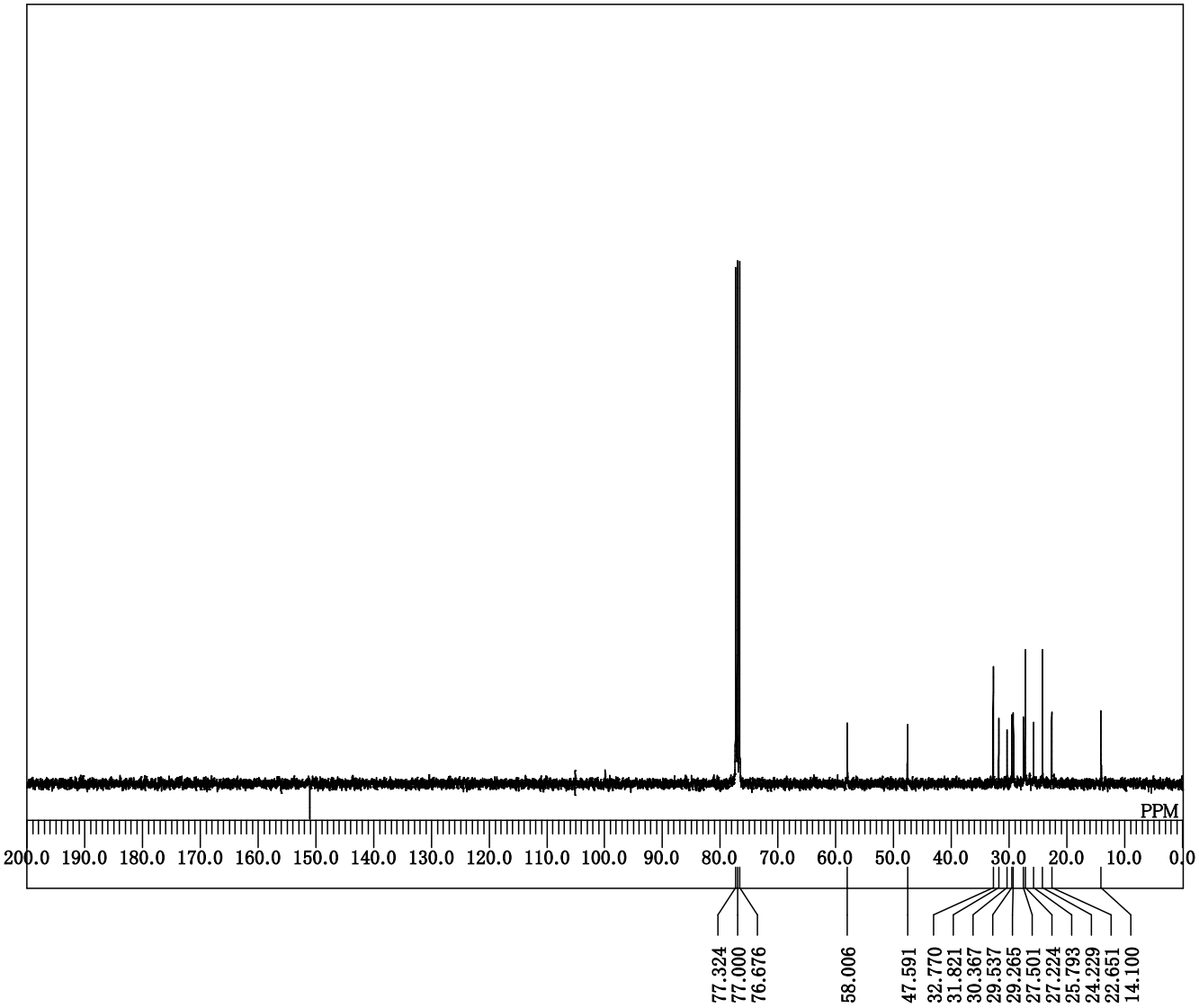
^{1}H NMR (395.88 MHz, $CDCl_3$)

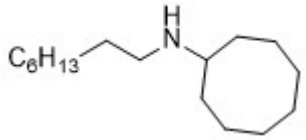




5ae

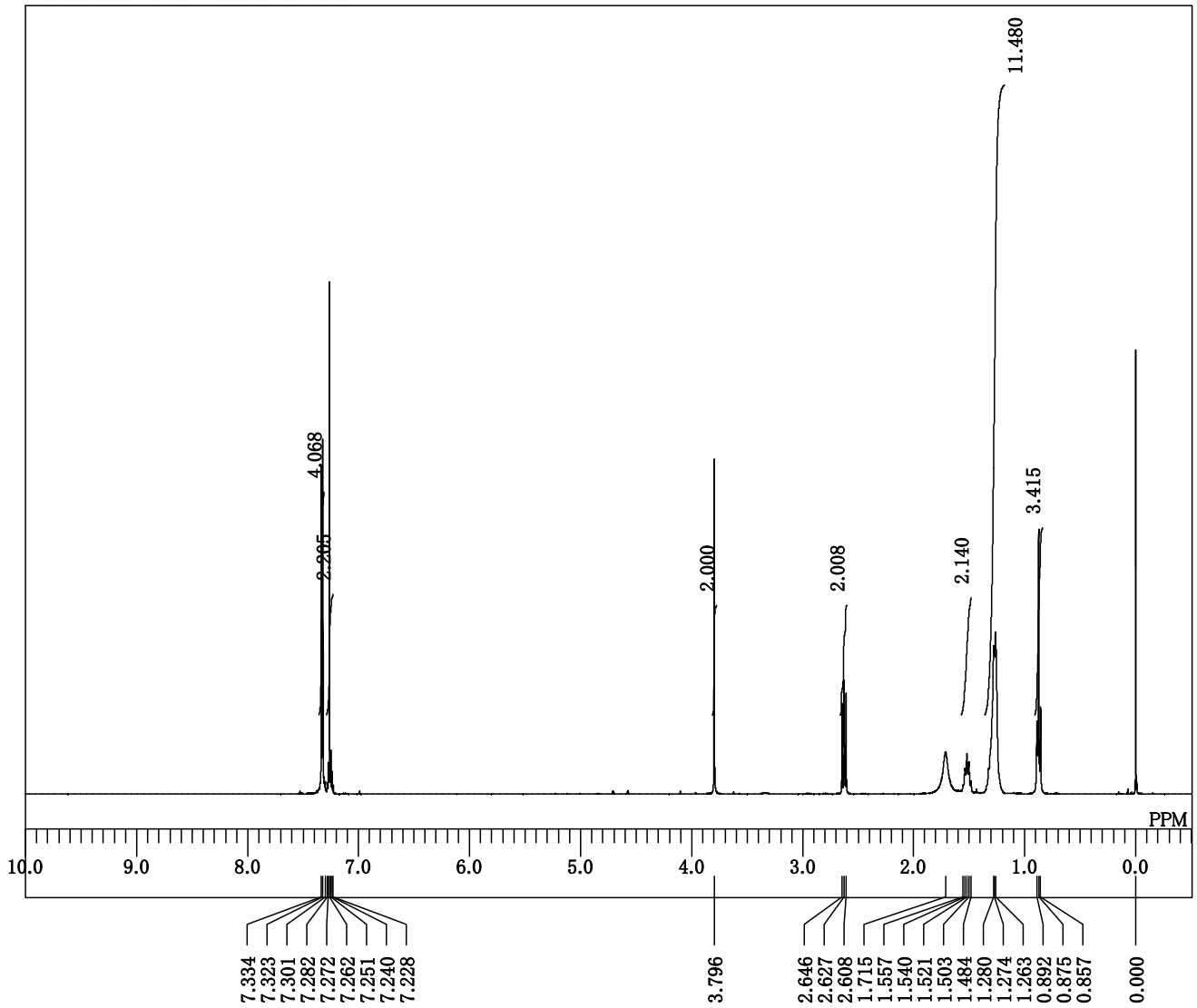
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

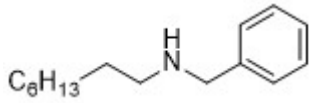




5ae

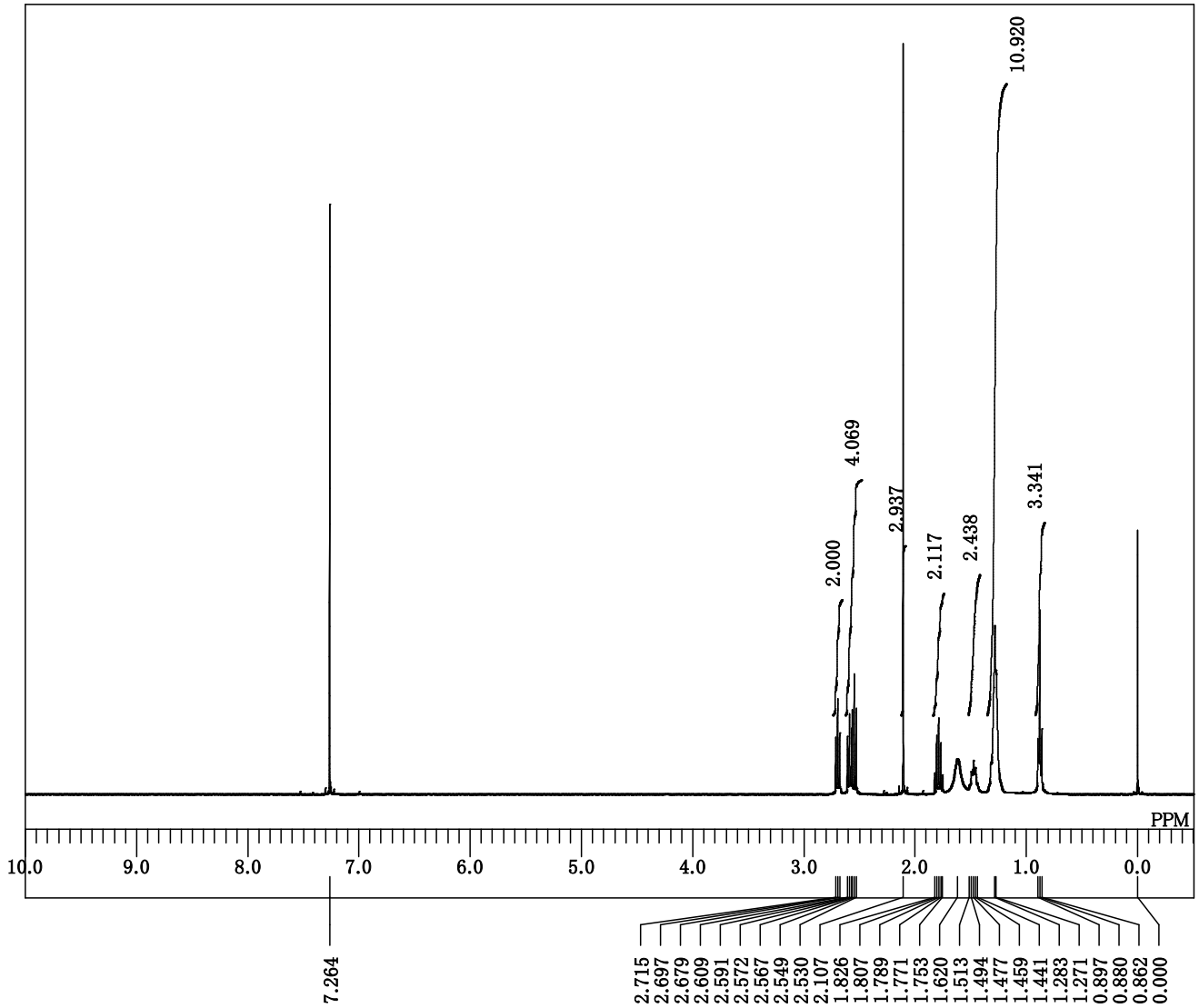
^{1}H NMR (391.78 MHz, $CDCl_3$)

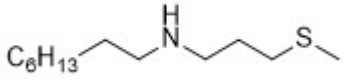




5af

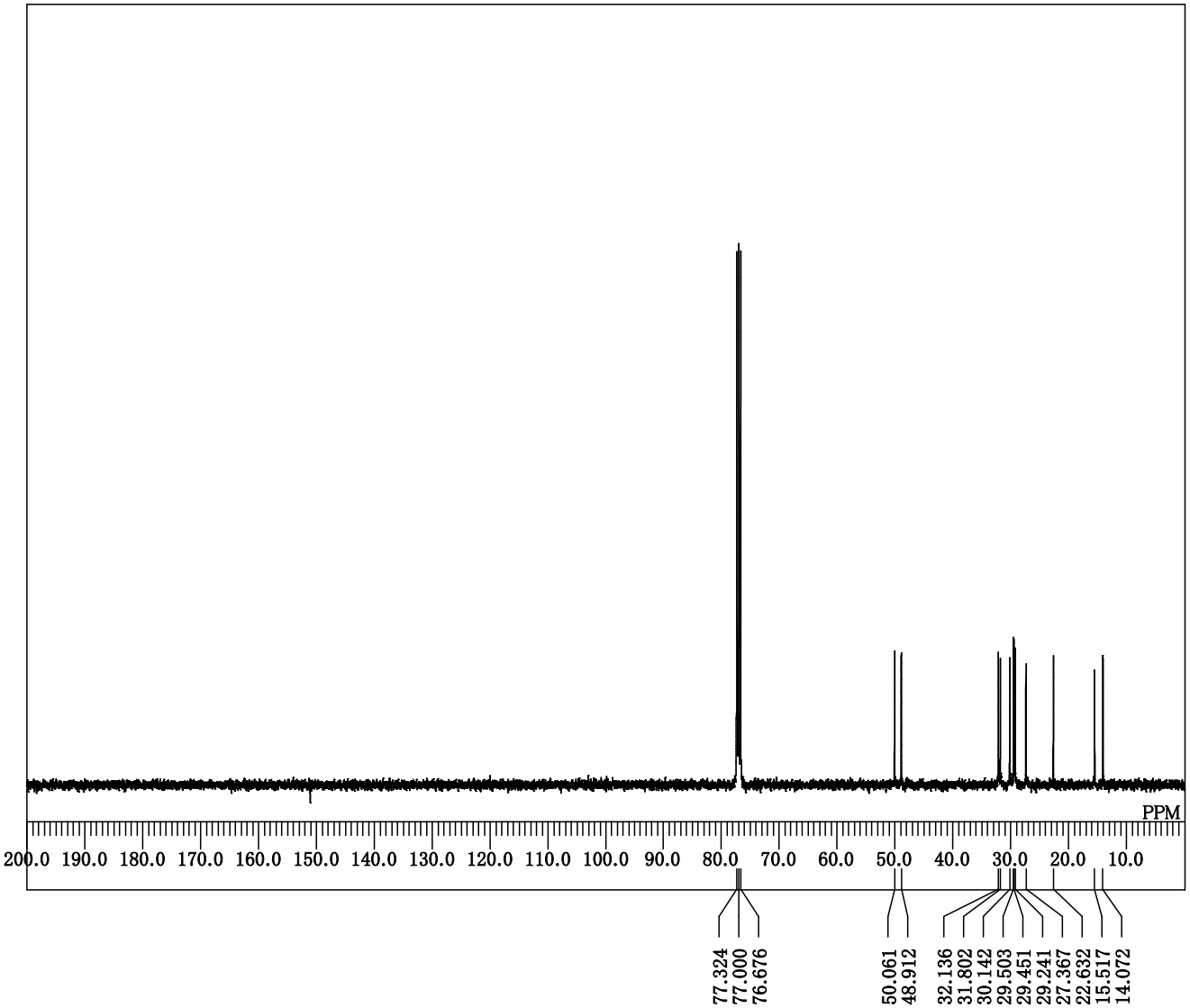
^{1}H NMR (395.88 MHz, $CDCl_3$)

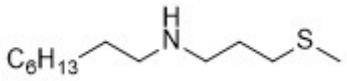




5ag

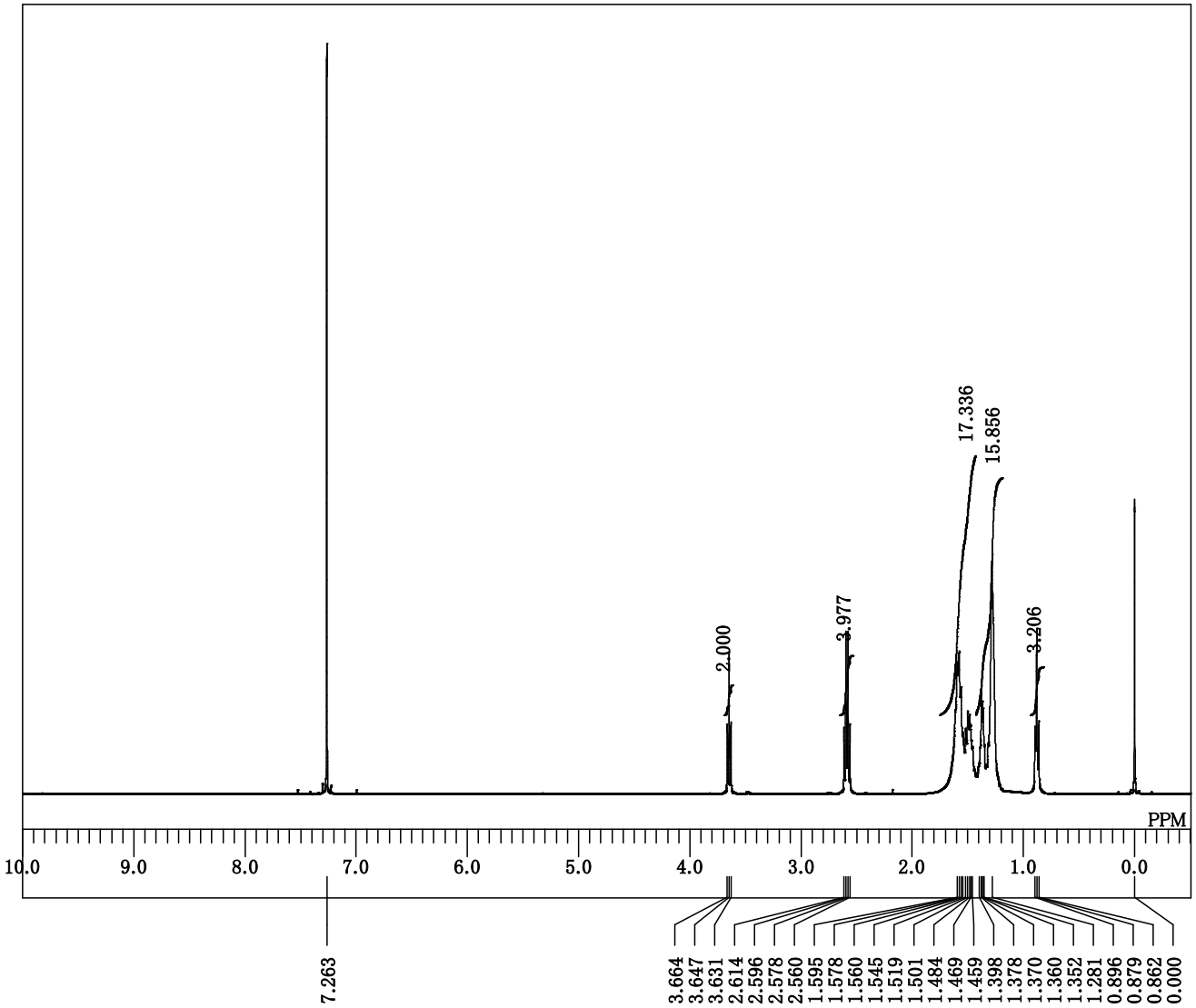
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)





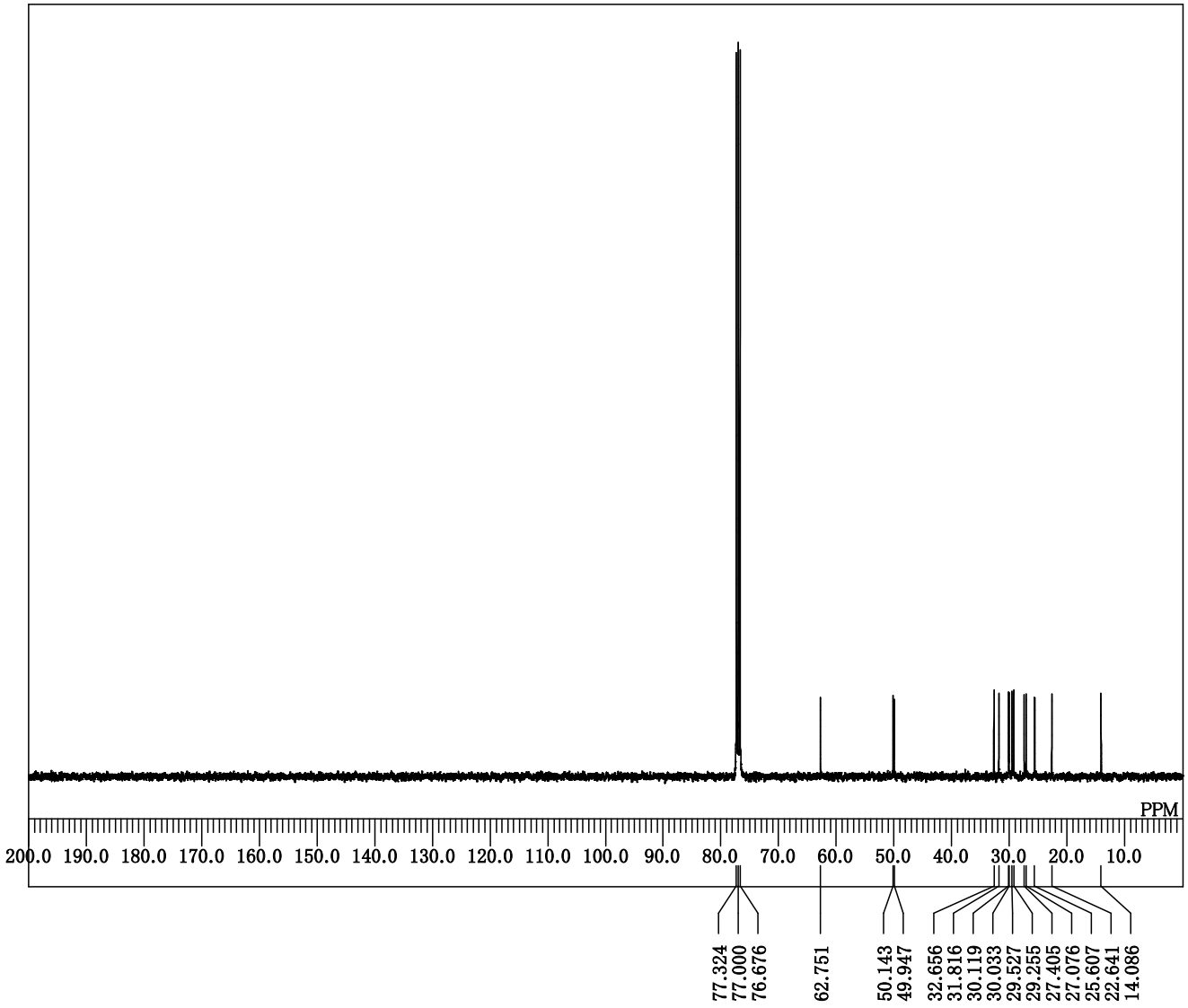
5ag

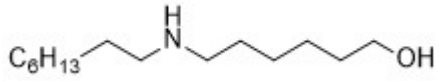
^{1}H NMR (395.88 MHz, $CDCl_3$)



5ah

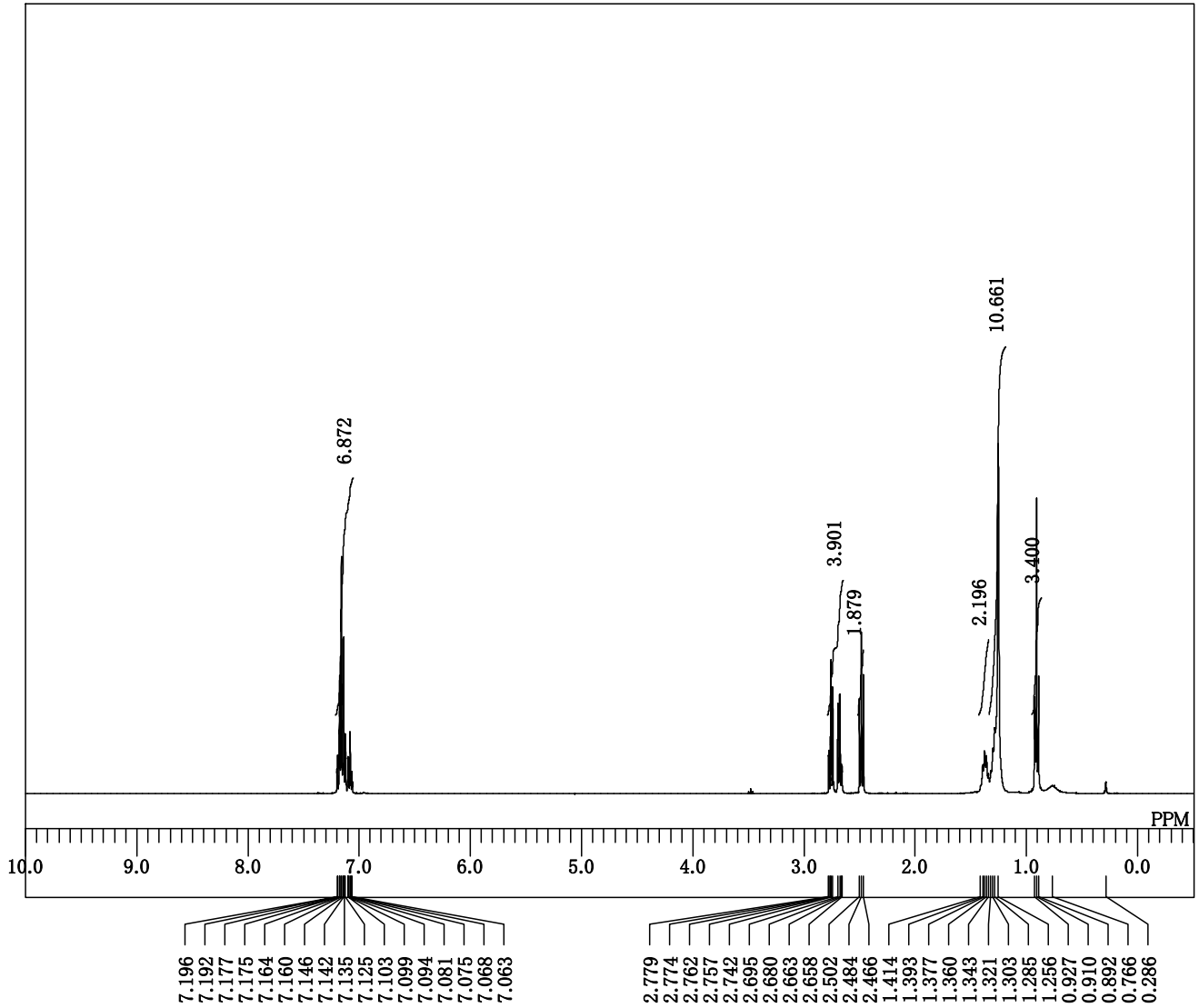
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

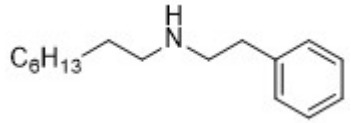




5ah

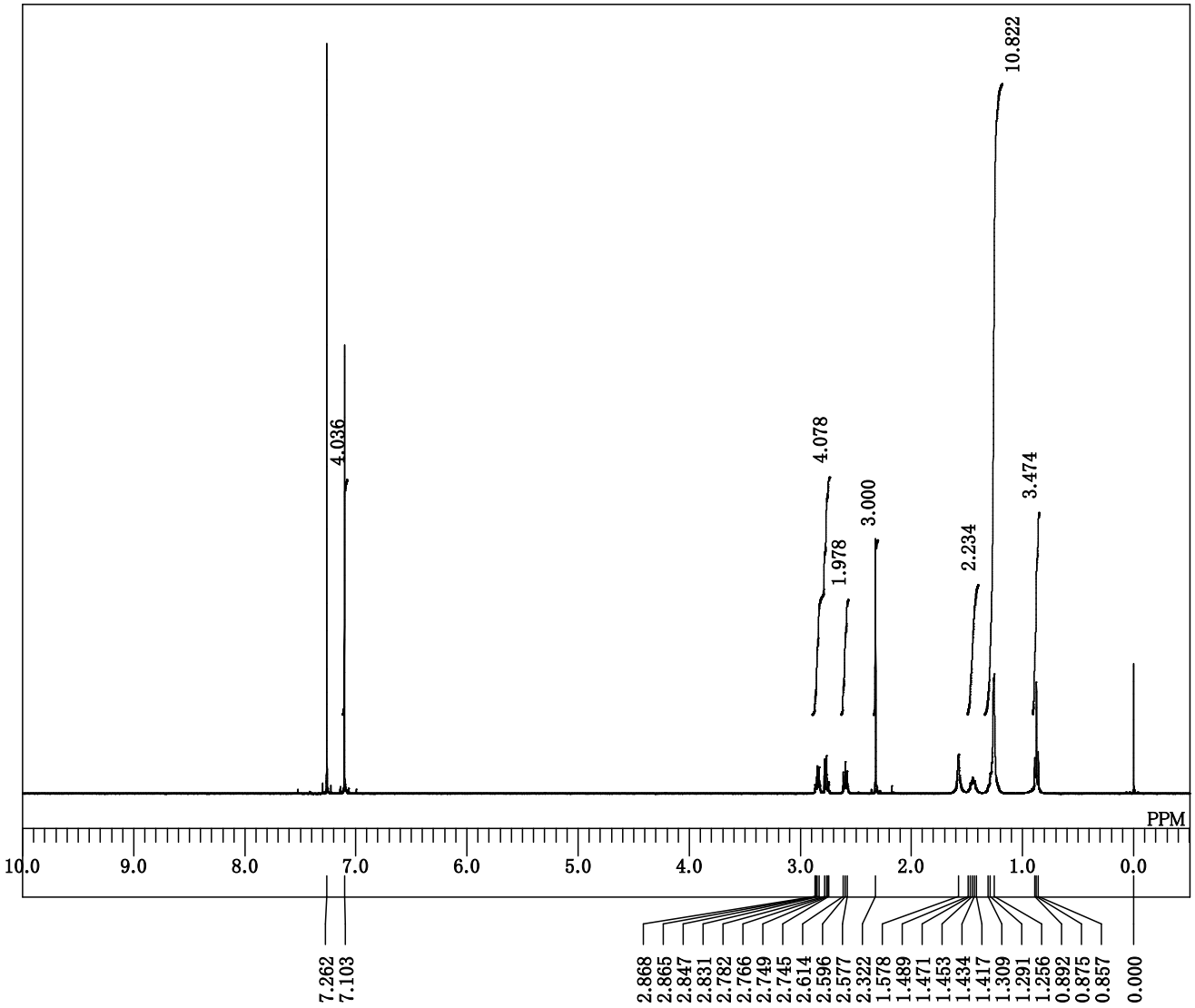
^{1}H NMR (391.78 MHz, C_6D_6)

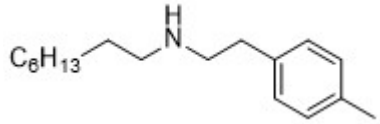




5ai

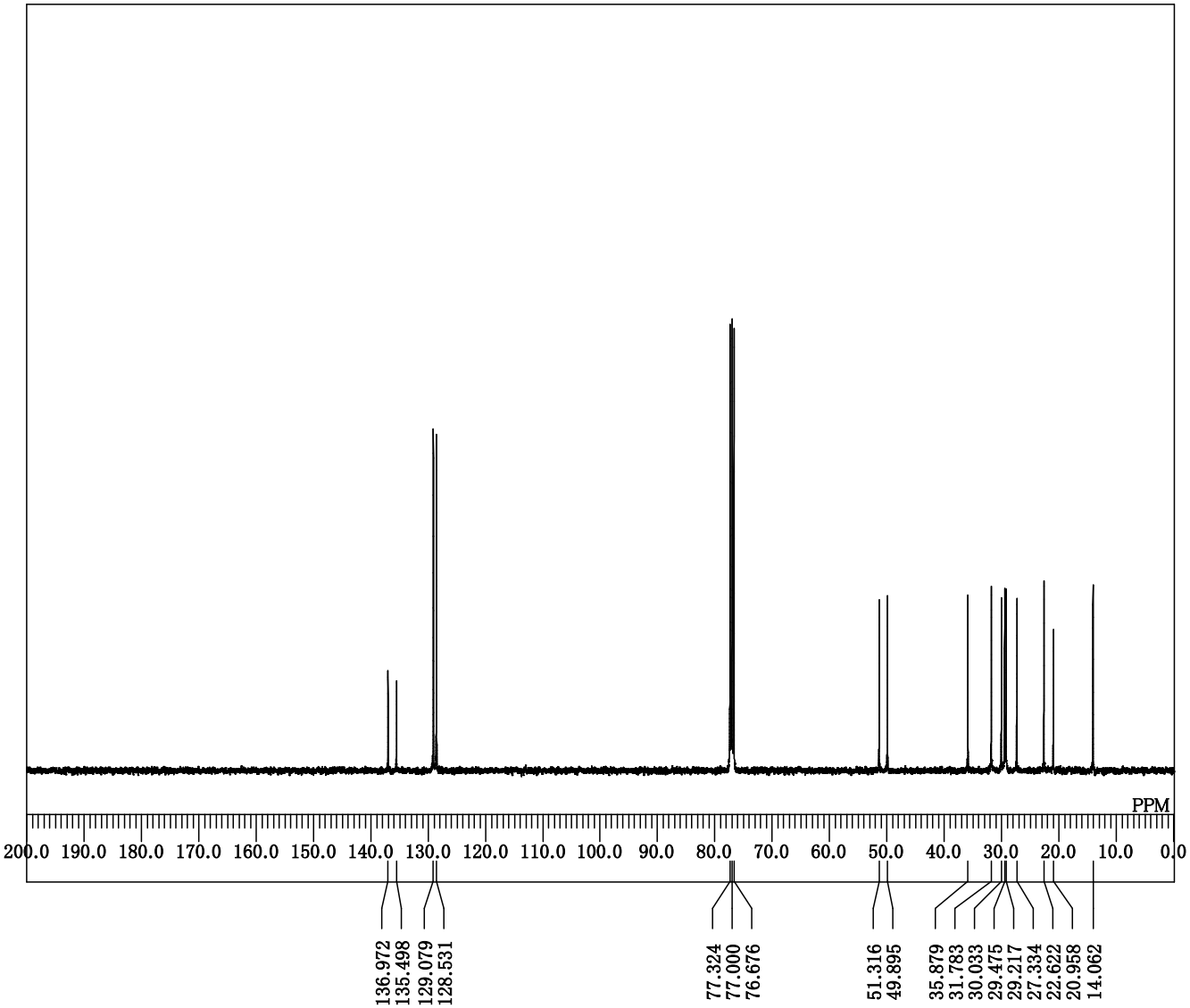
^{1}H NMR (395.88 MHz, $CDCl_3$)

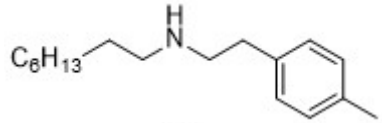




5aj

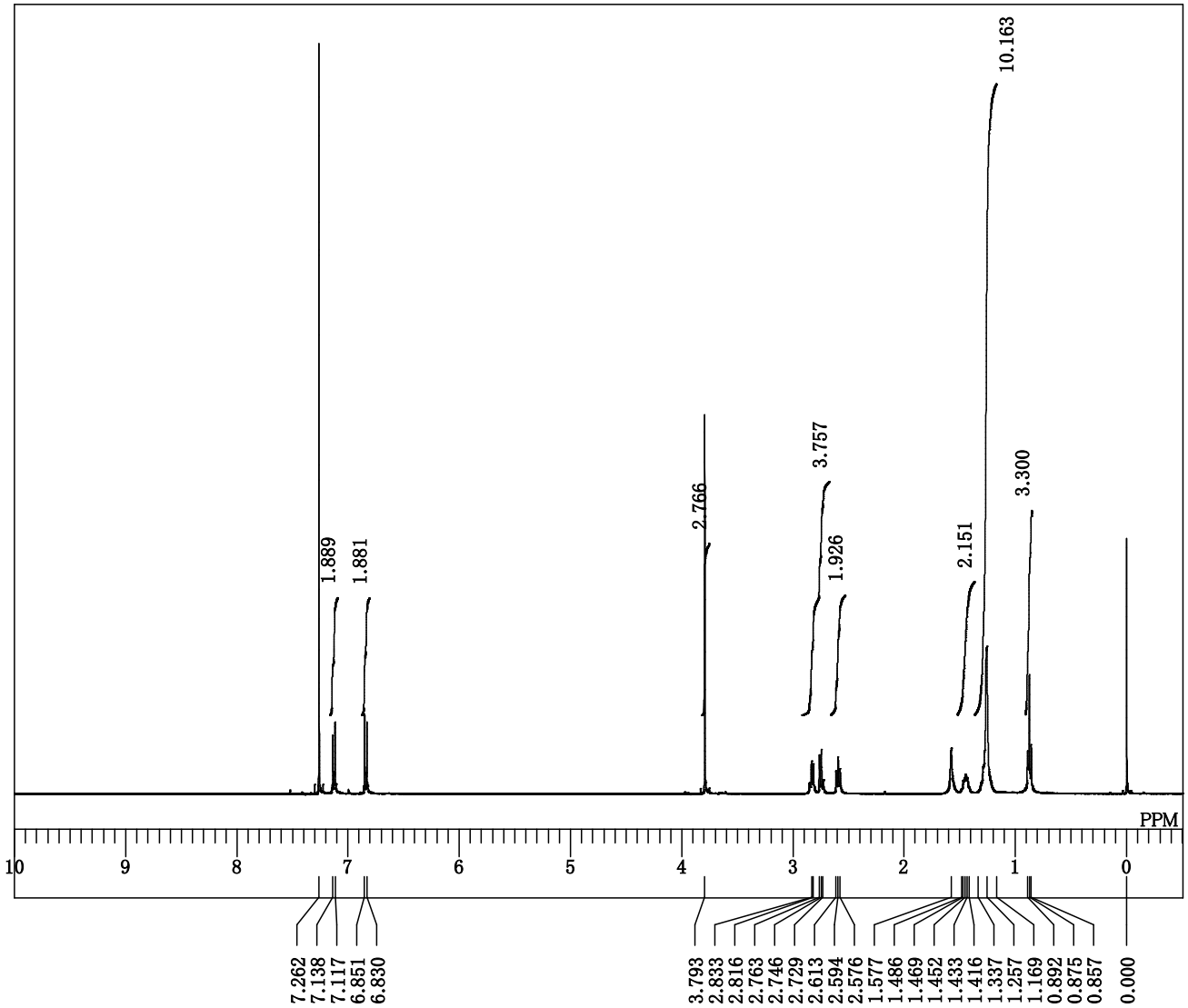
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

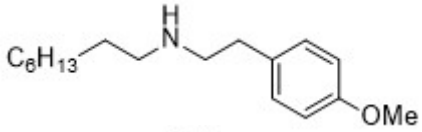




5aj

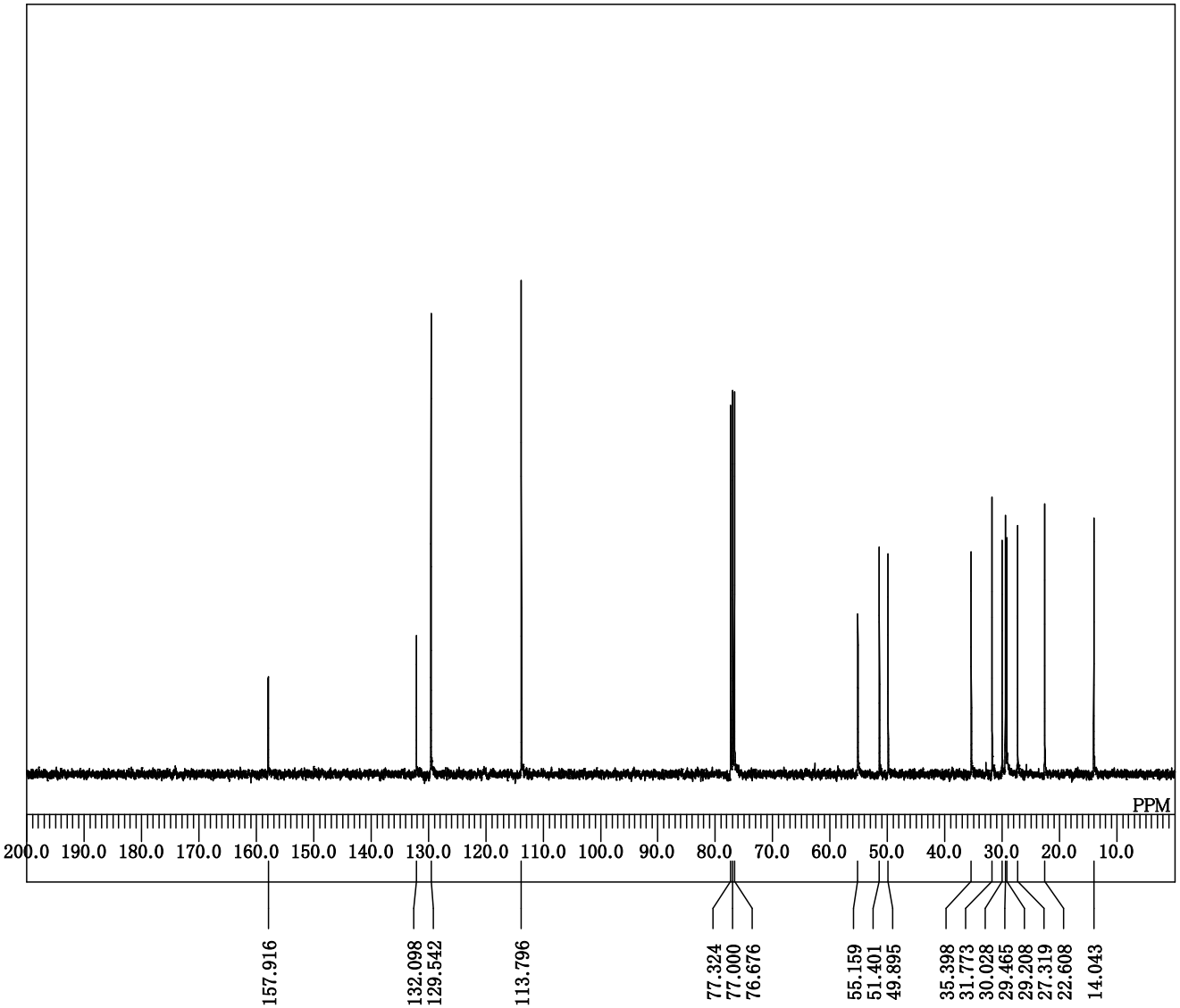
^{1}H NMR (395.88 MHz, $CDCl_3$)

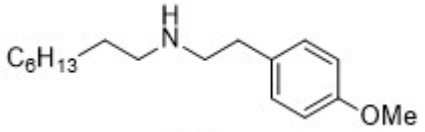




5ak

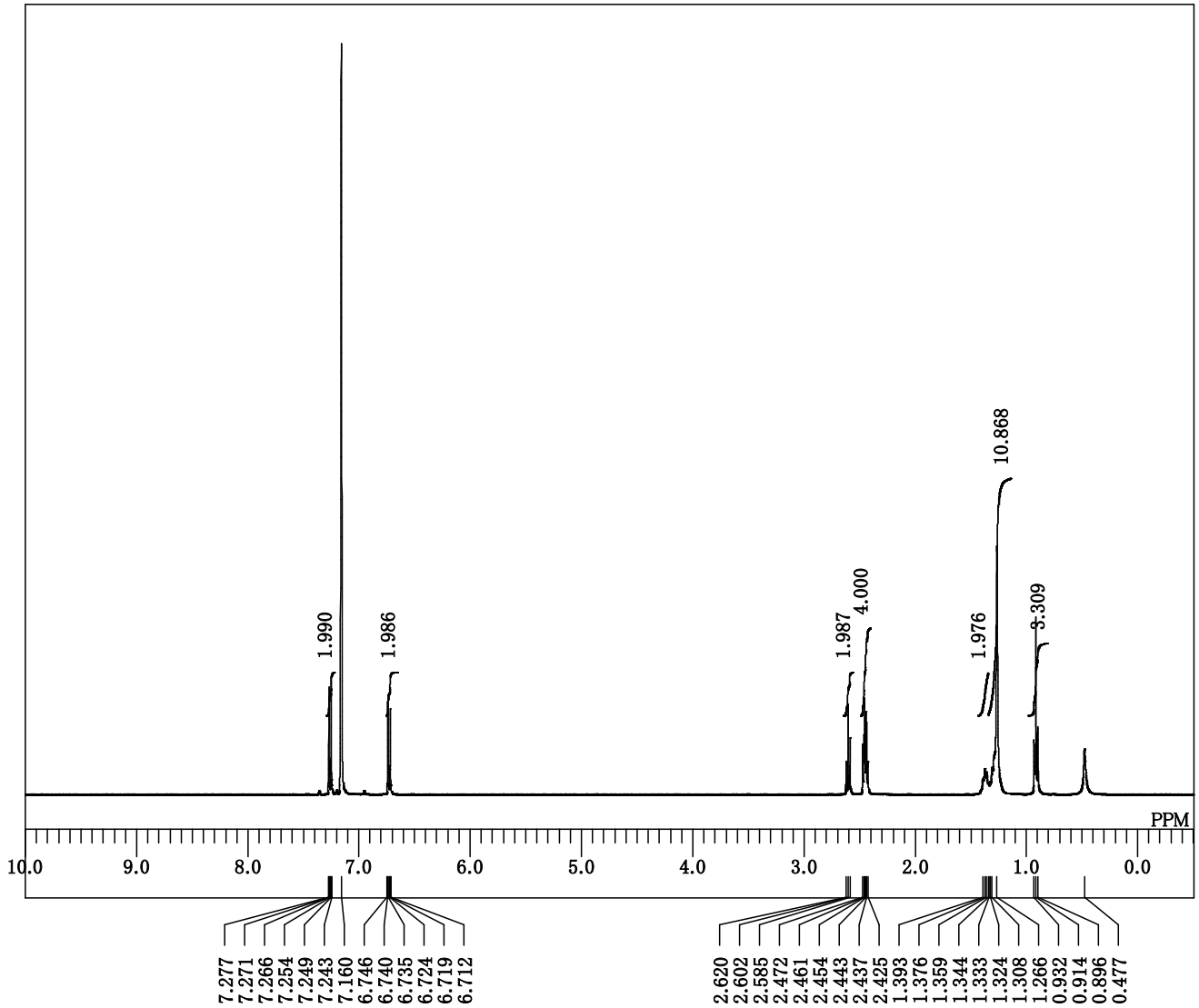
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

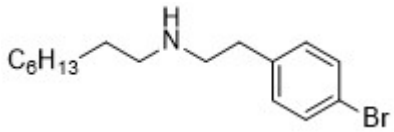




5ak

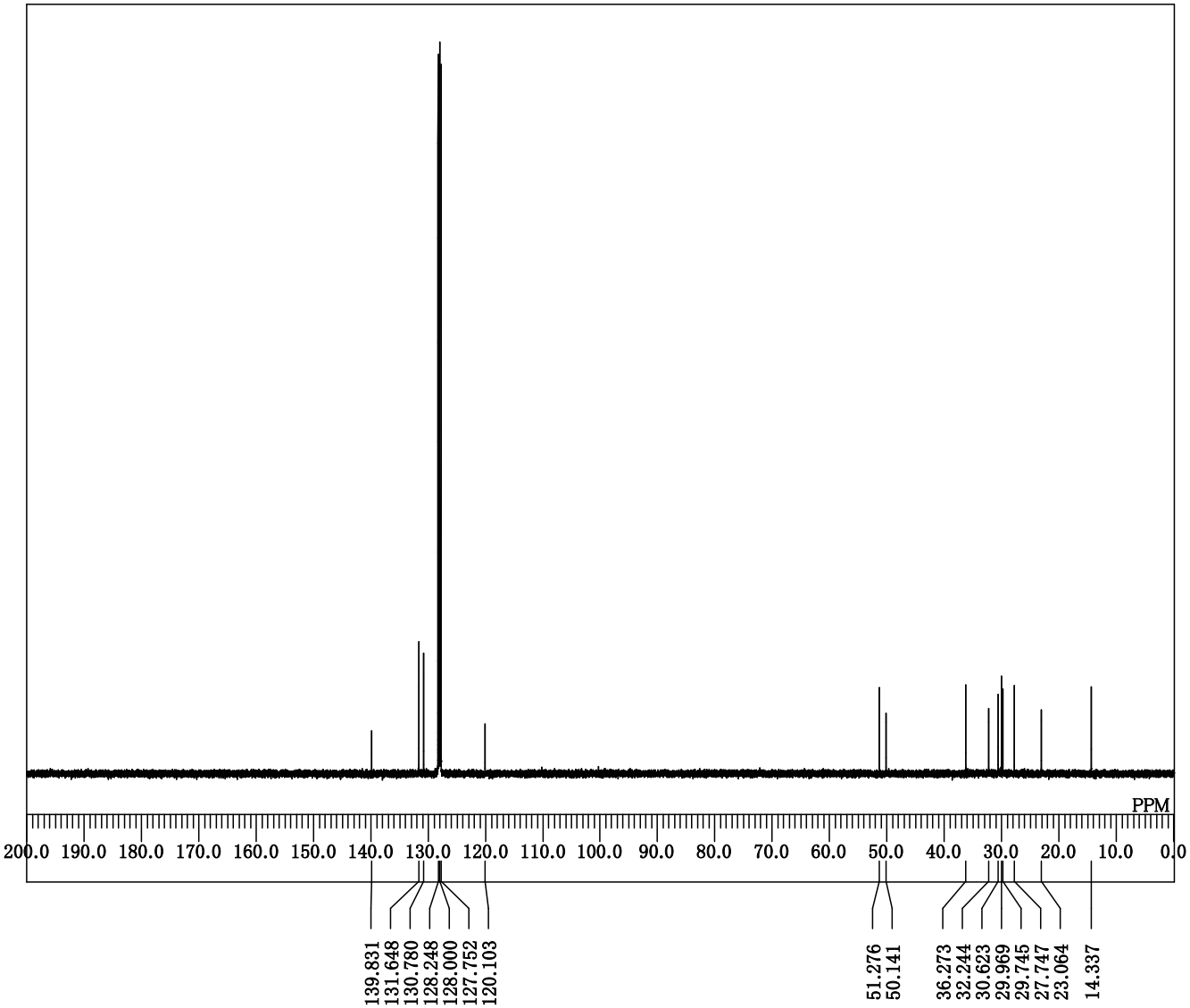
^{1}H NMR (391.78 MHz, C_6D_6)

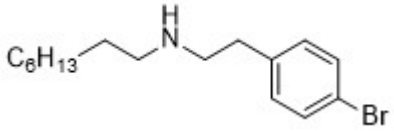




5al

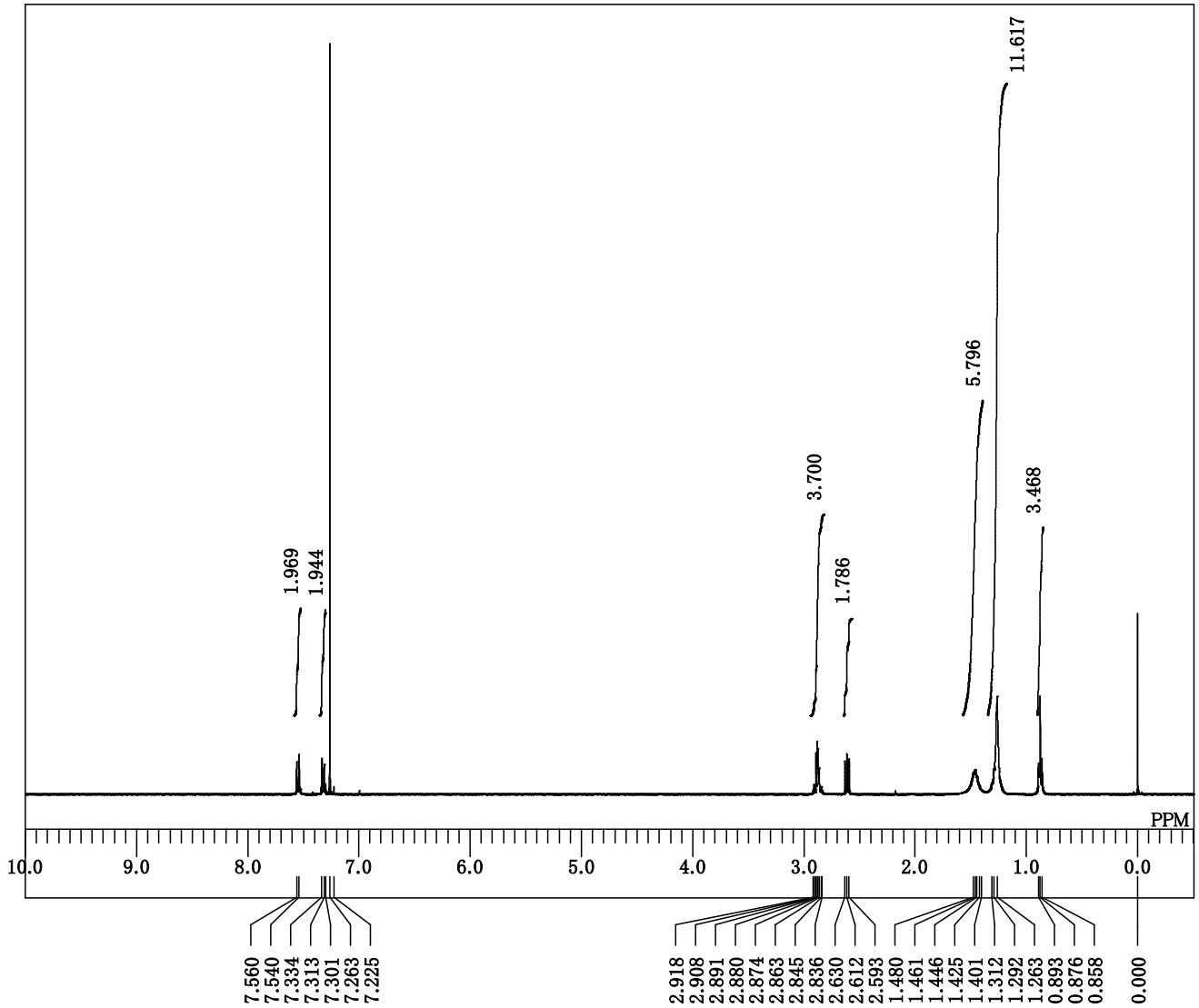
^{13}C {^{1}H} NMR (98.52 MHz, C_6D_6)

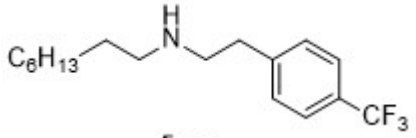




5al

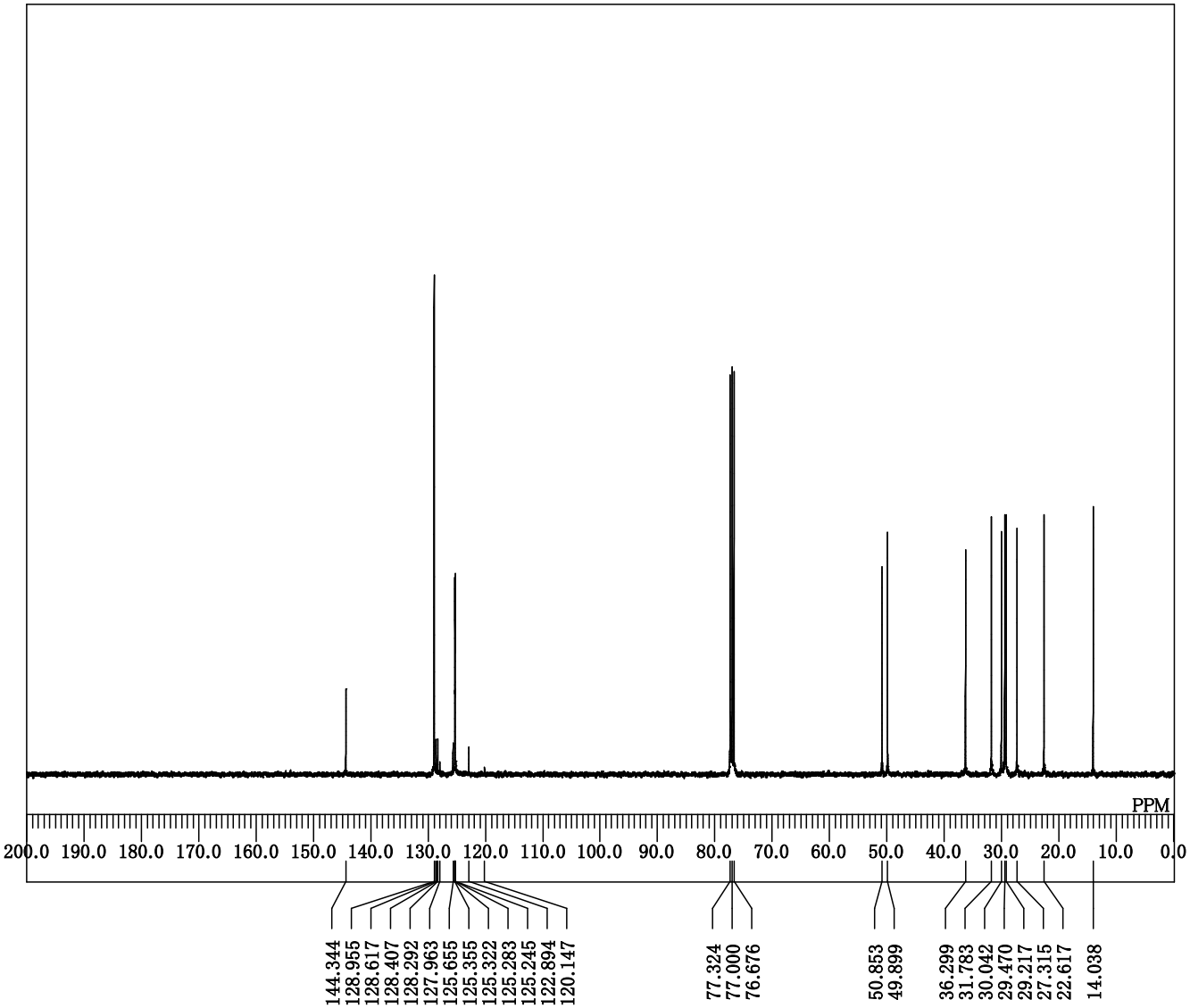
^{1}H NMR (395.88 MHz, $CDCl_3$)

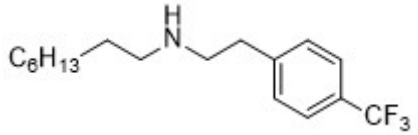




5am

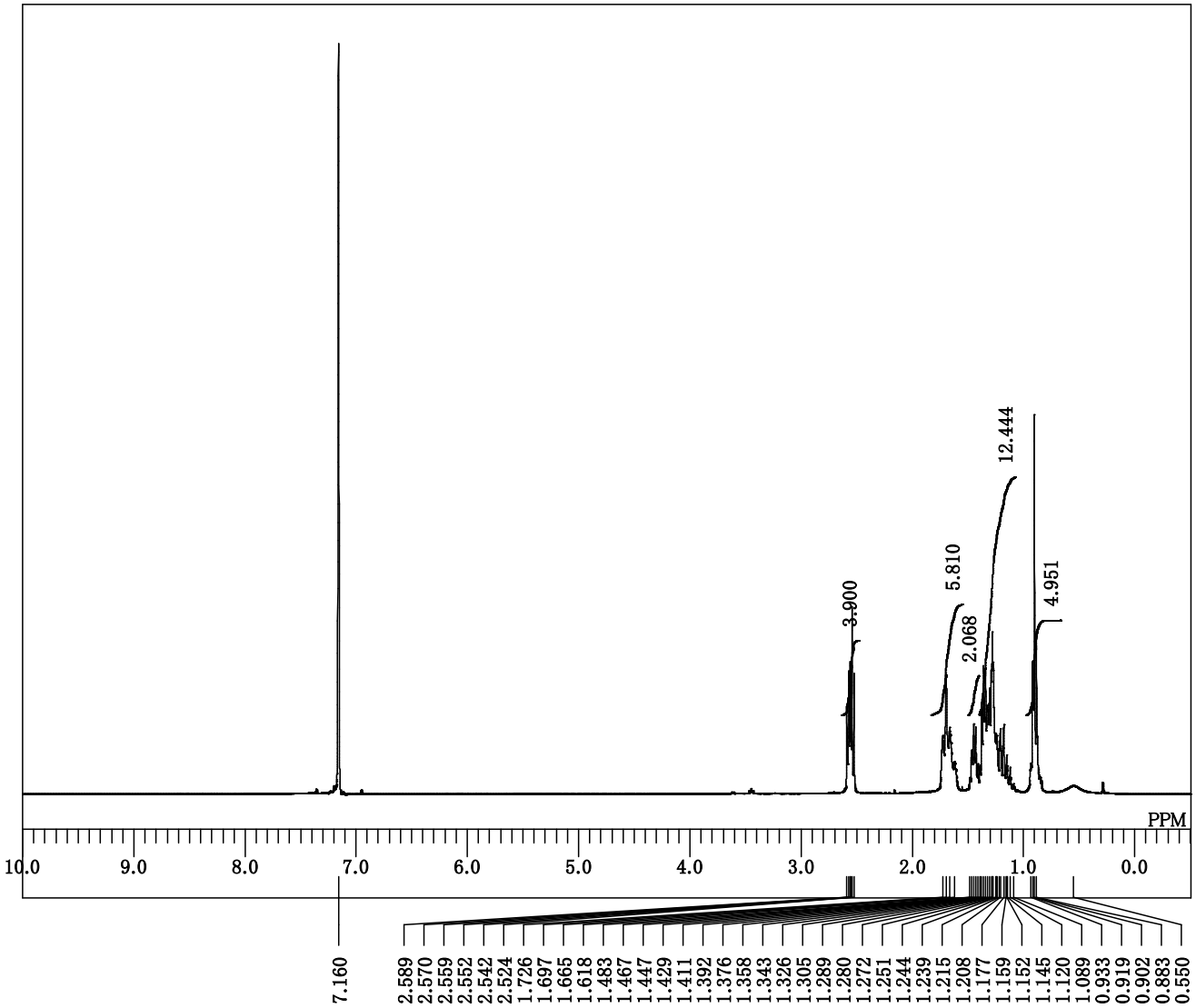
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

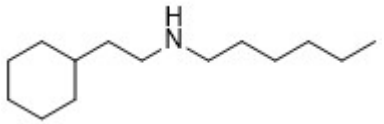




5am

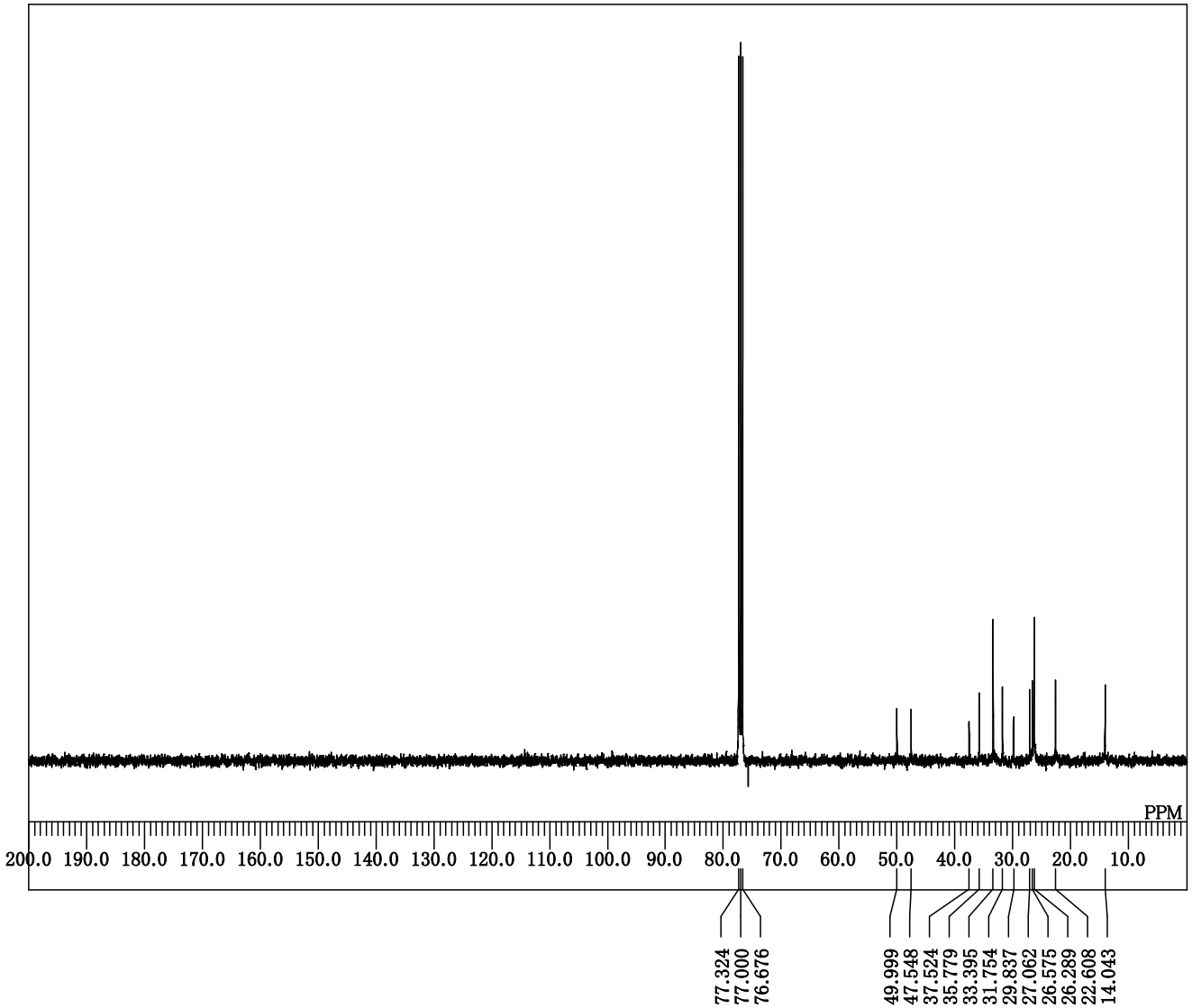
^{1}H NMR (391.78 MHz, C_6D_6)

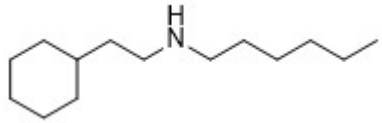




5ba

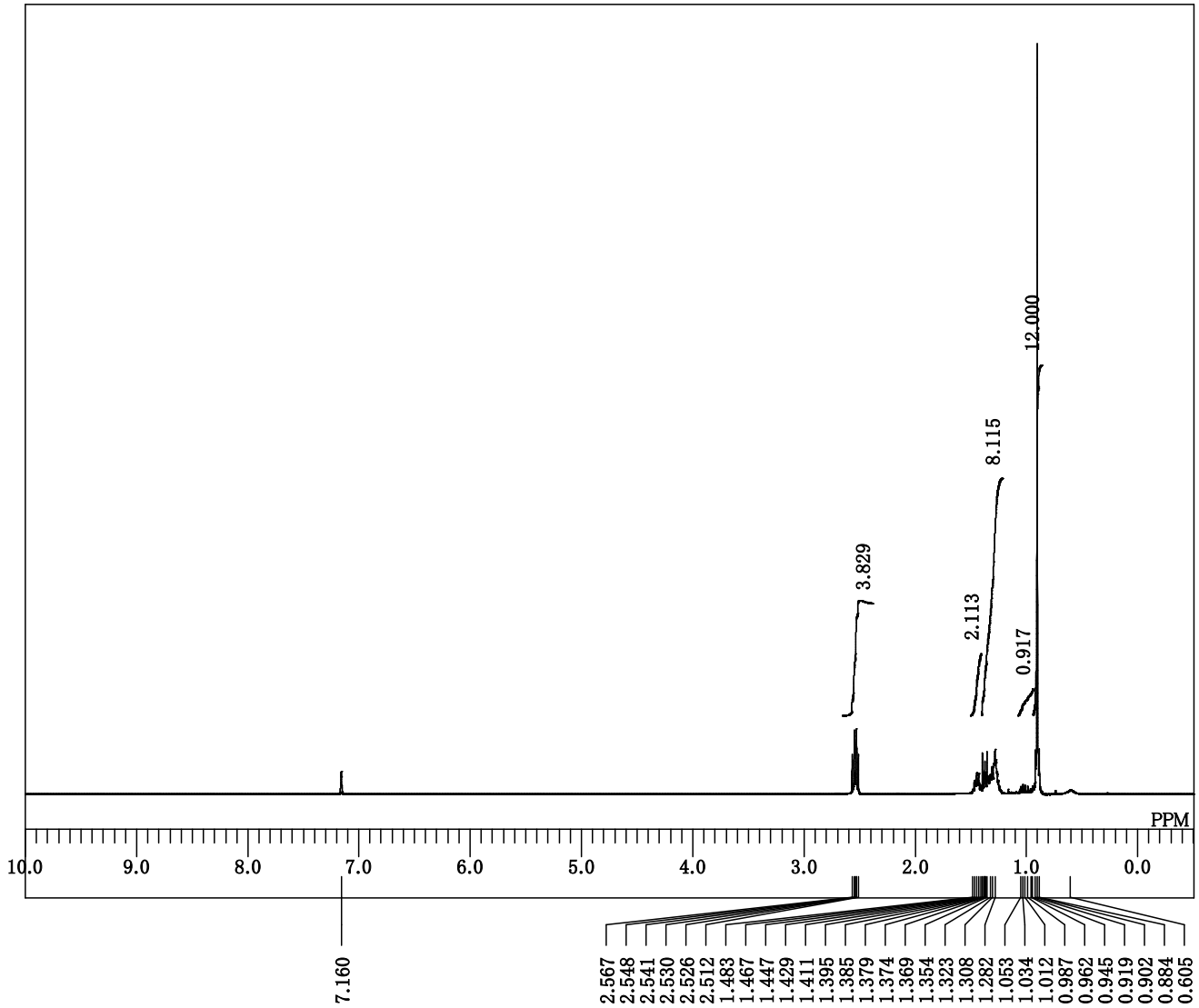
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

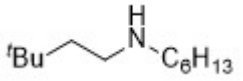




5ba

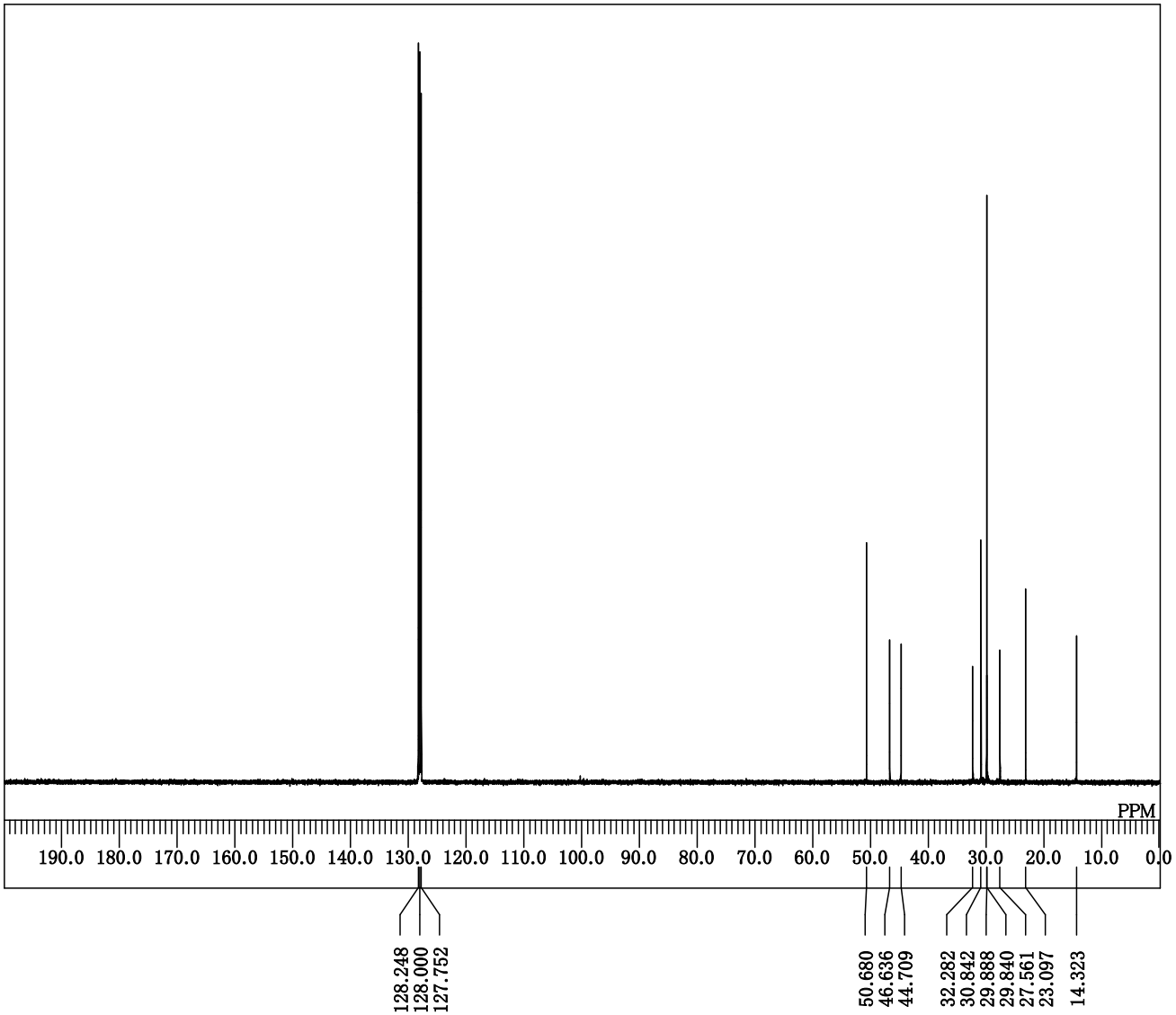
^{1}H NMR (391.78 MHz, C_6D_6)

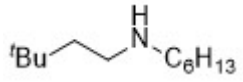




5ca

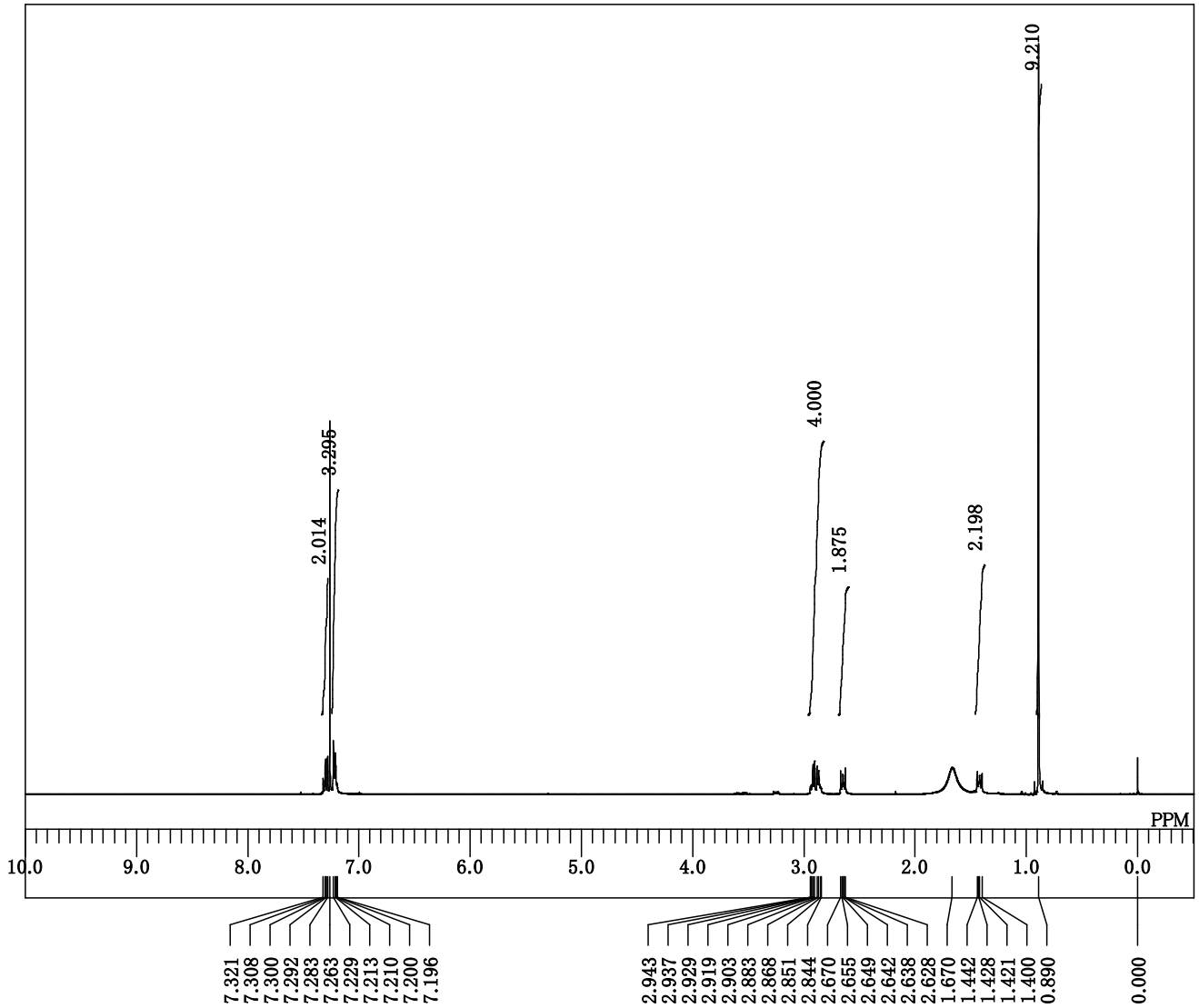
^{13}C {^{1}H} NMR (98.52 MHz, C_6D_6)

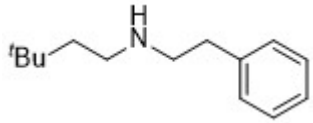




5ca

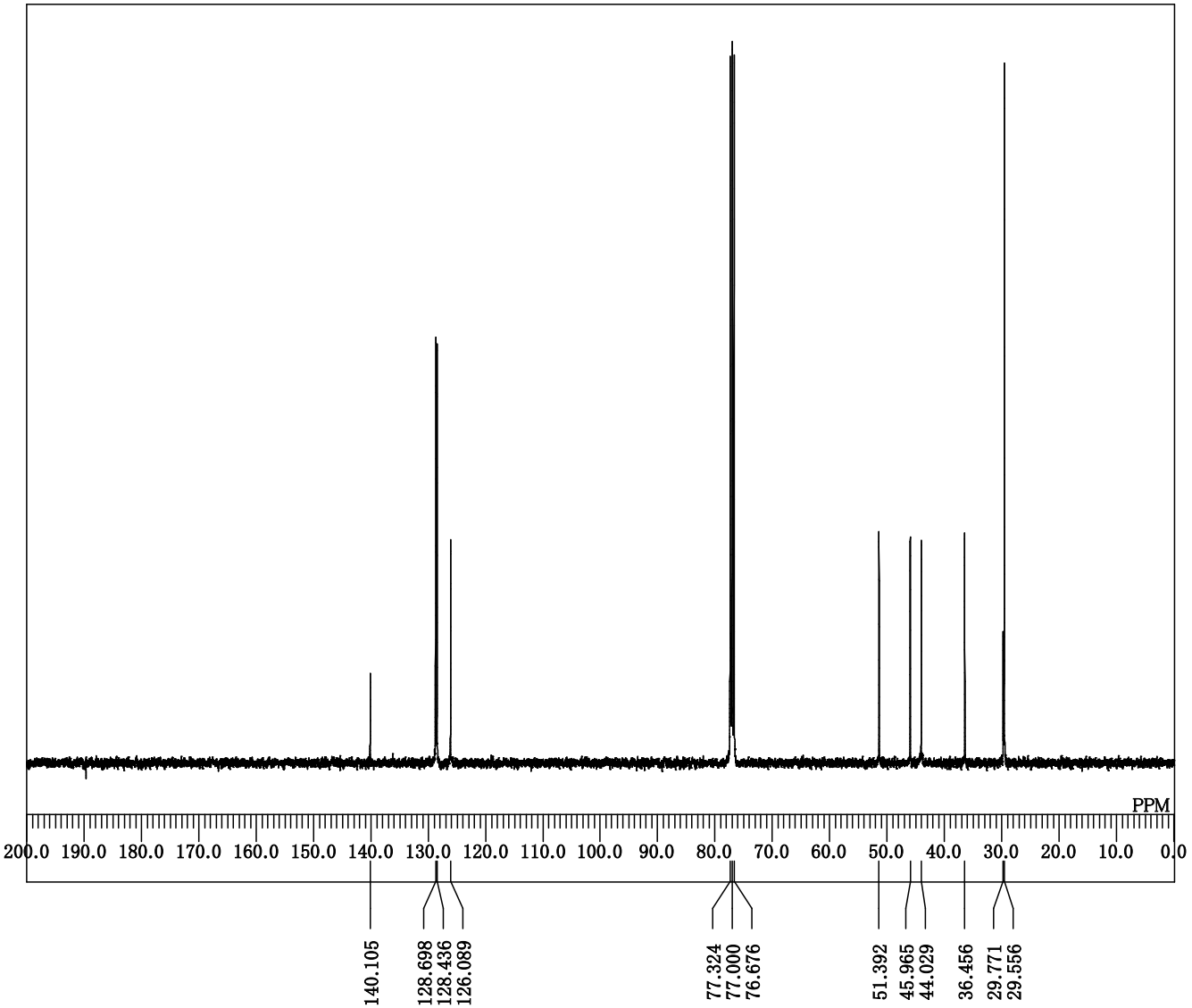
^{1}H NMR (395.88 MHz, $CDCl_3$)

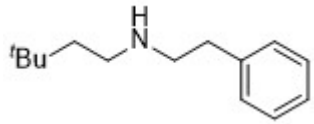




5ci

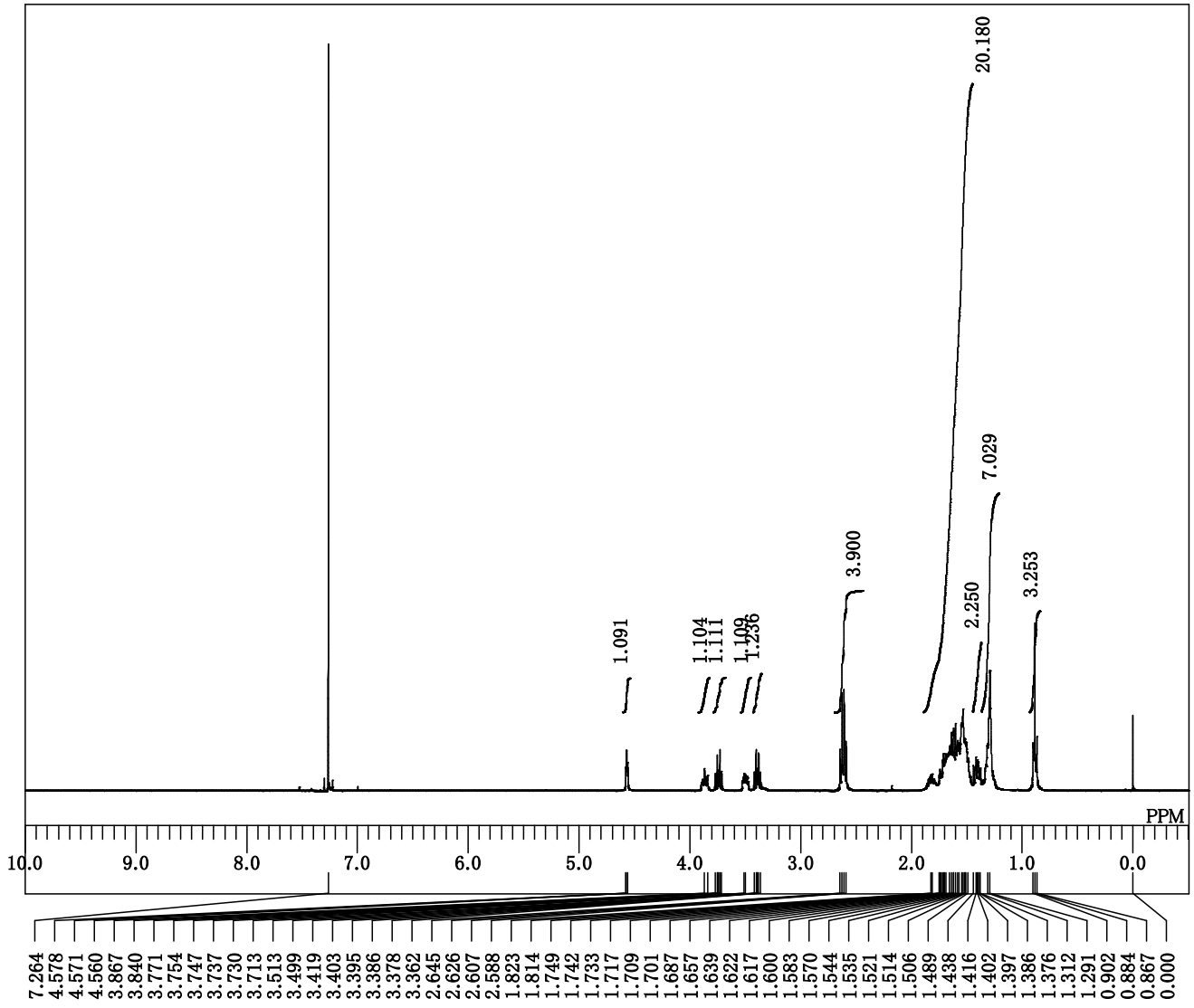
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

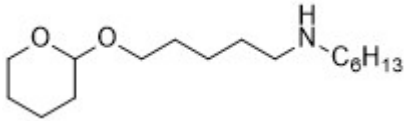




5ci

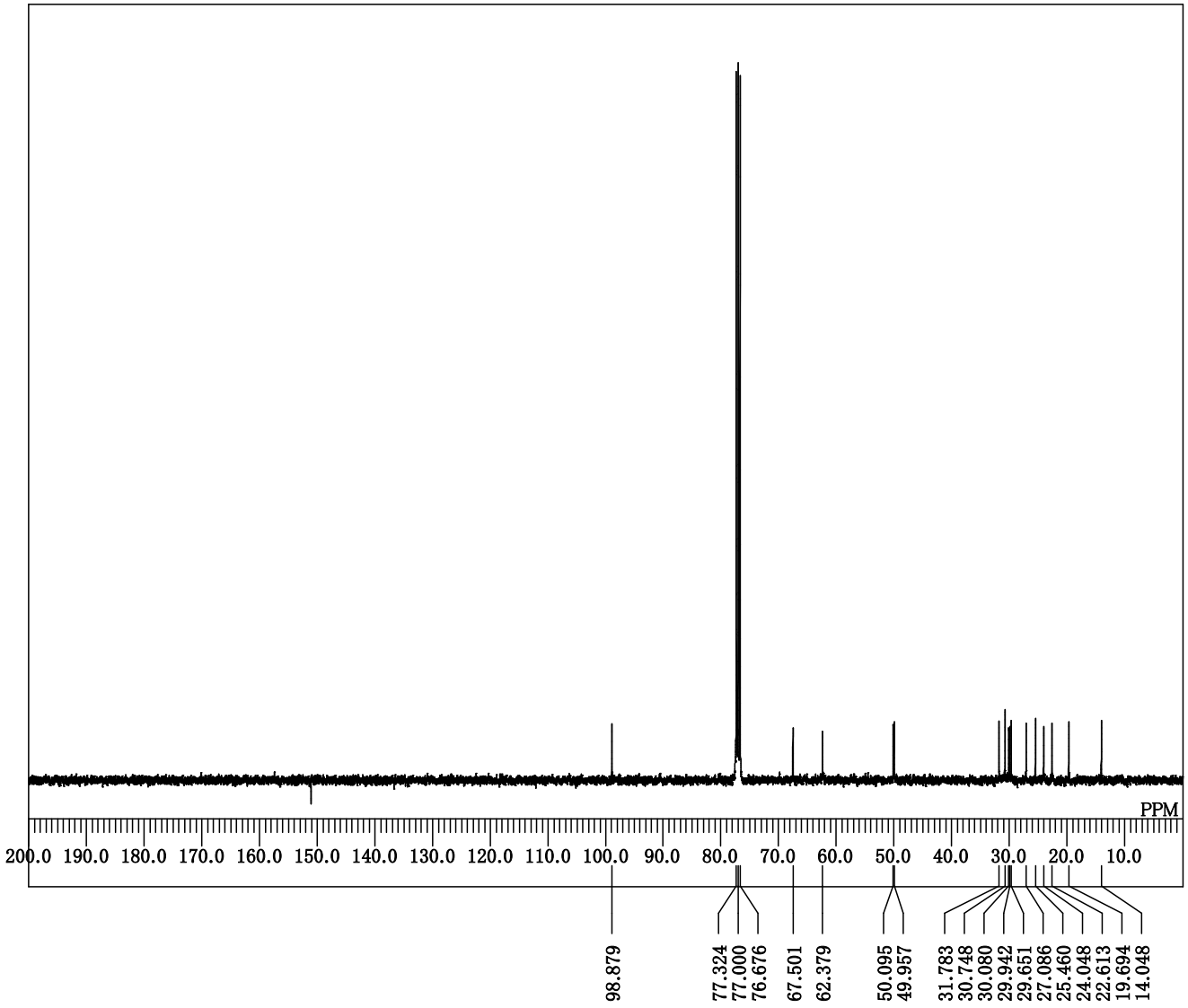
^{1}H NMR (395.88 MHz, $CDCl_3$)

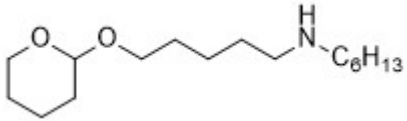




5da

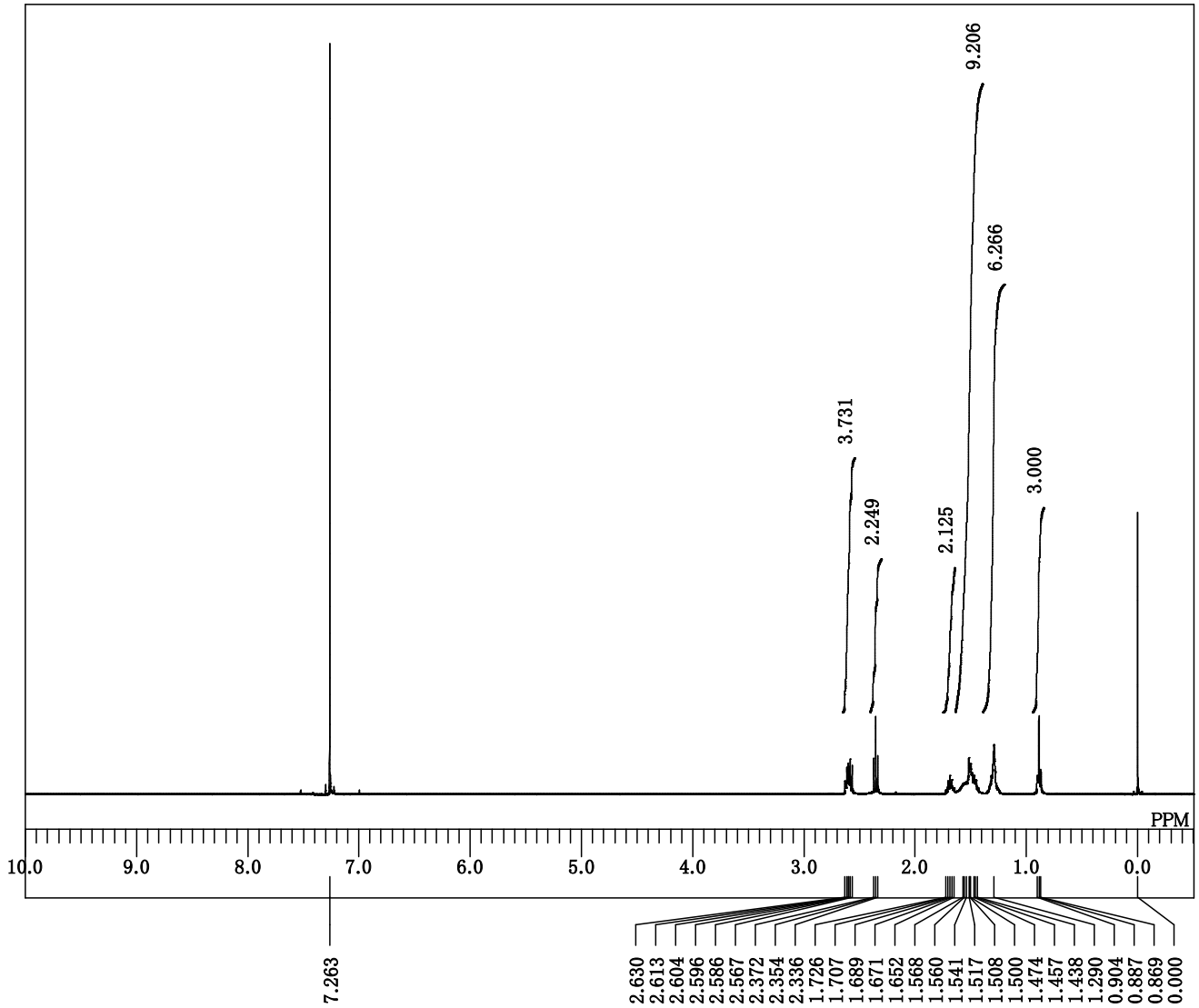
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

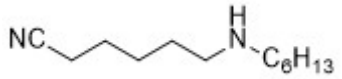




5da

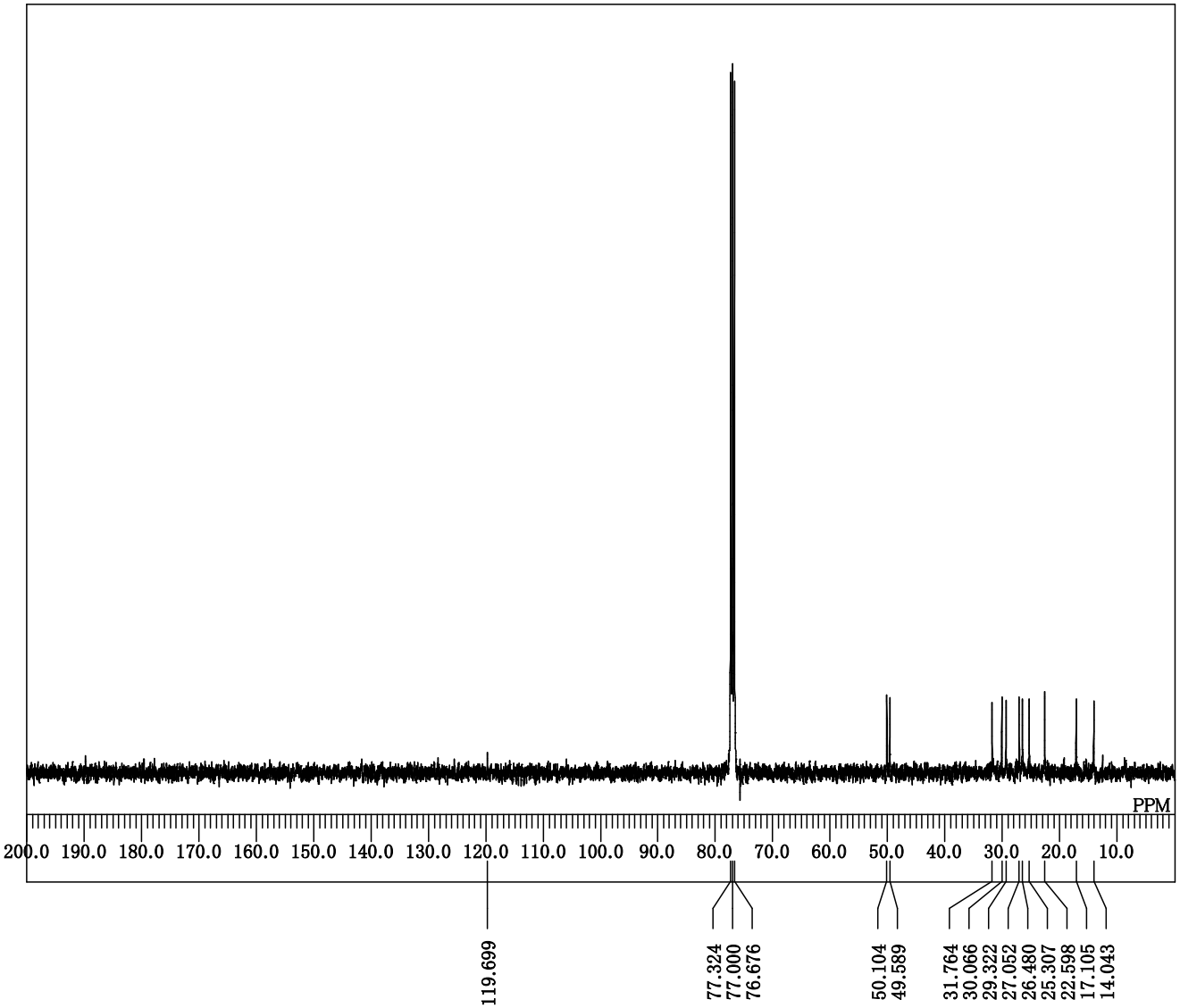
^{1}H NMR (395.88 MHz, $CDCl_3$)

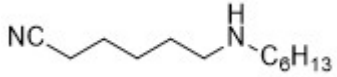




5ea

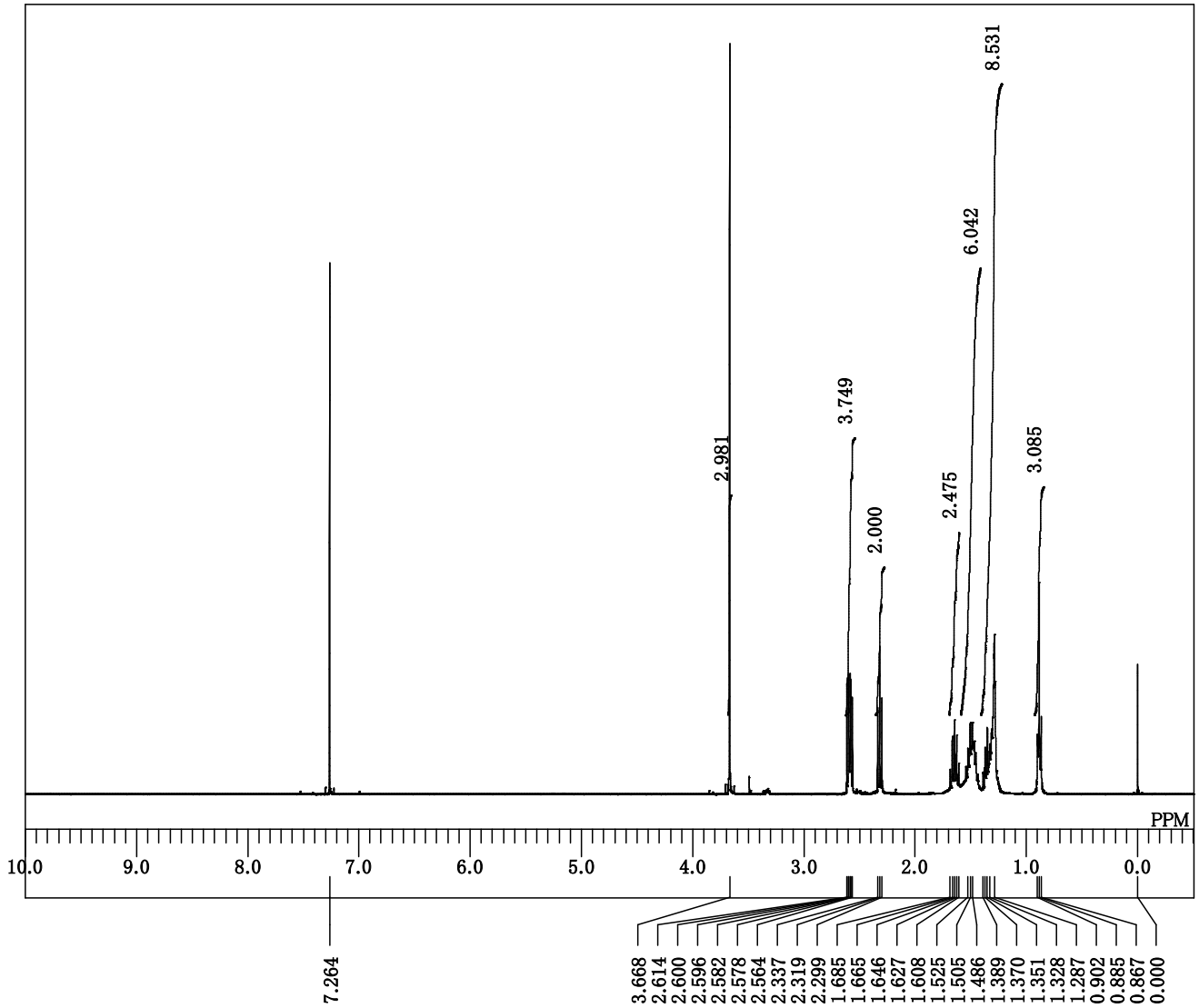
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

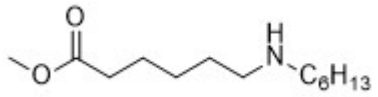




5ea

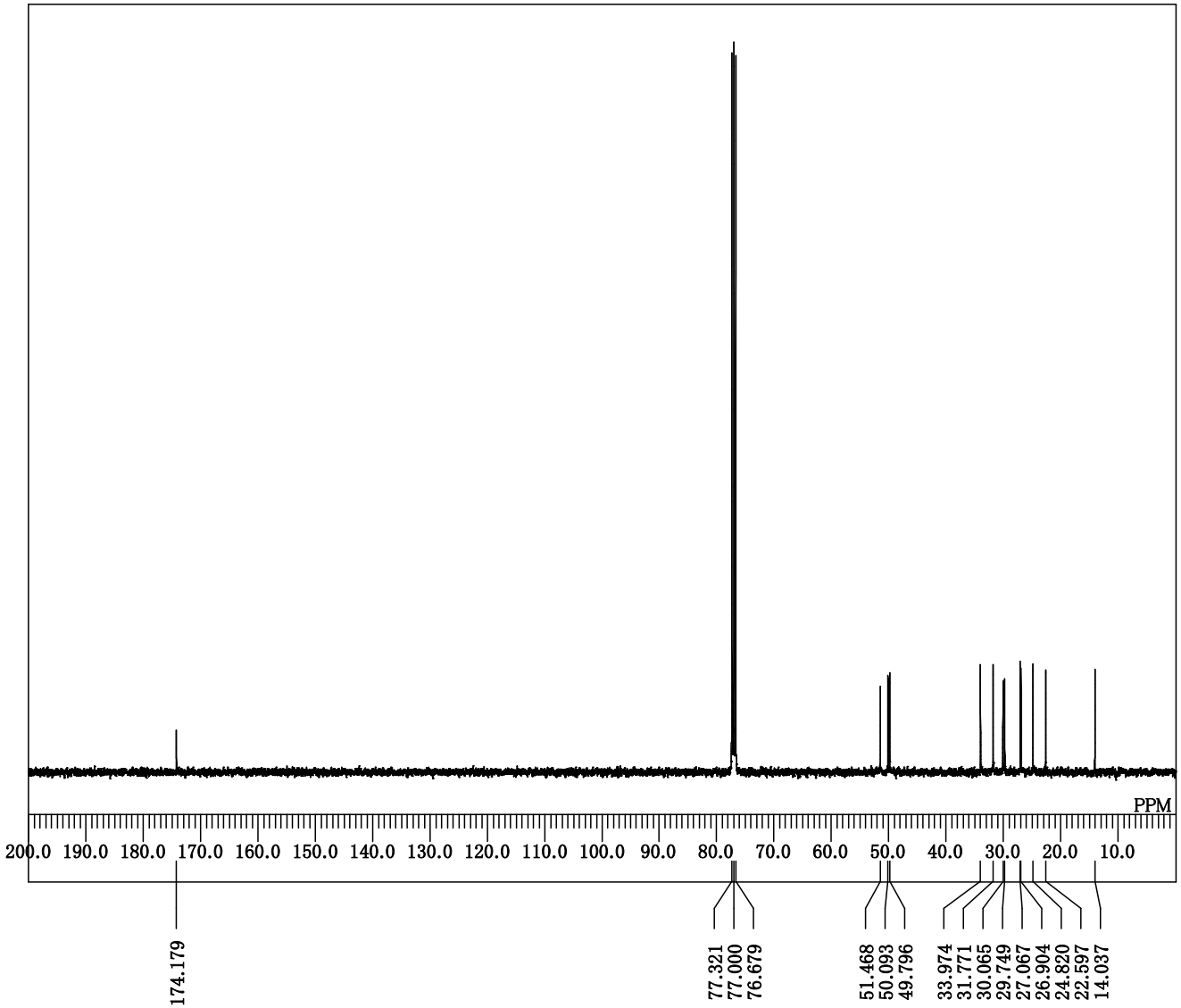
^{1}H NMR (395.88 MHz, $CDCl_3$)

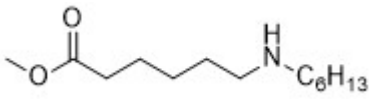




5fa

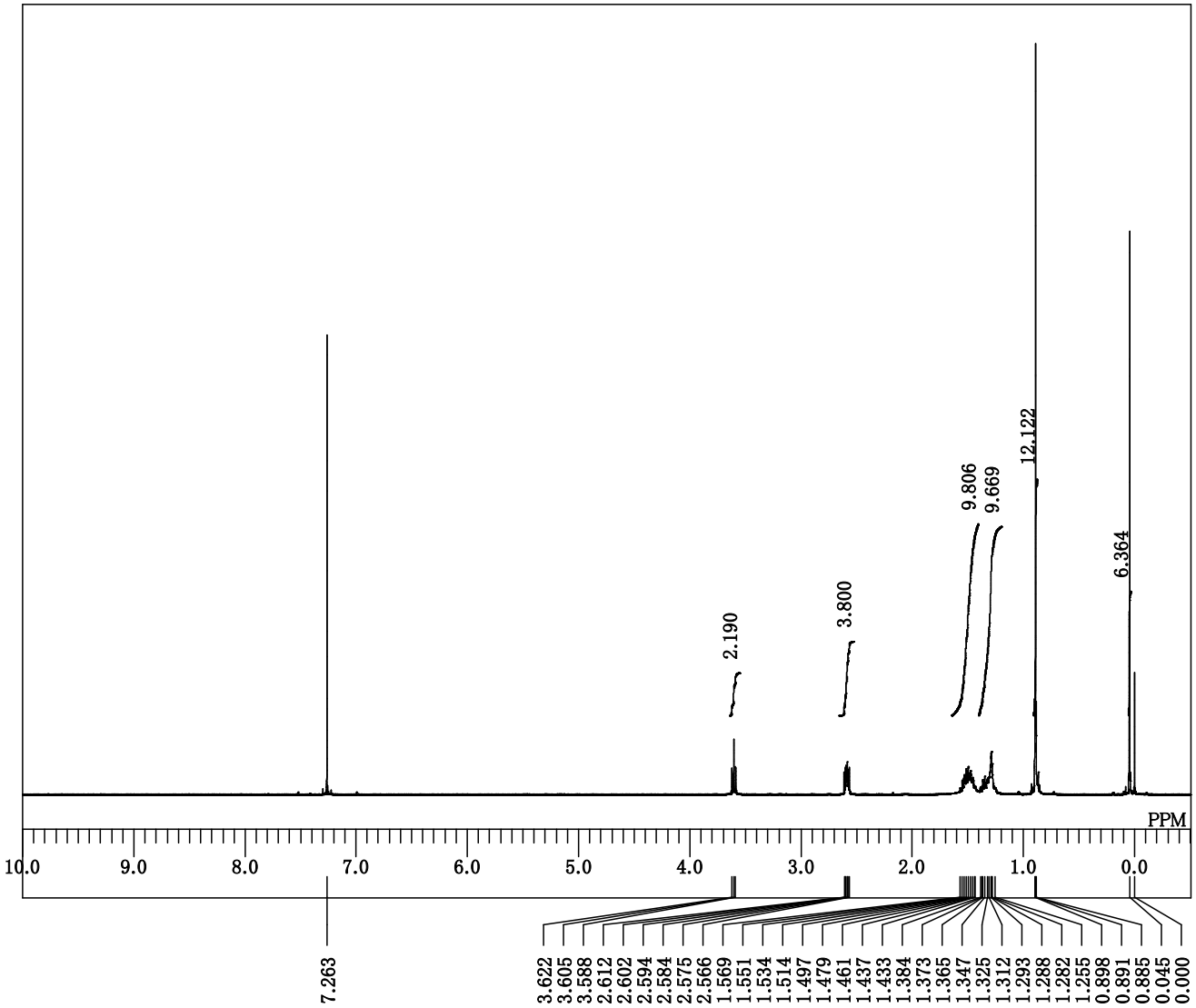
^{13}C {^{1}H} NMR (99.55 MHz, $CDCl_3$)

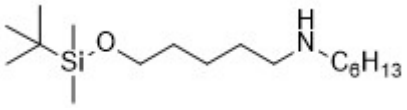




5fa

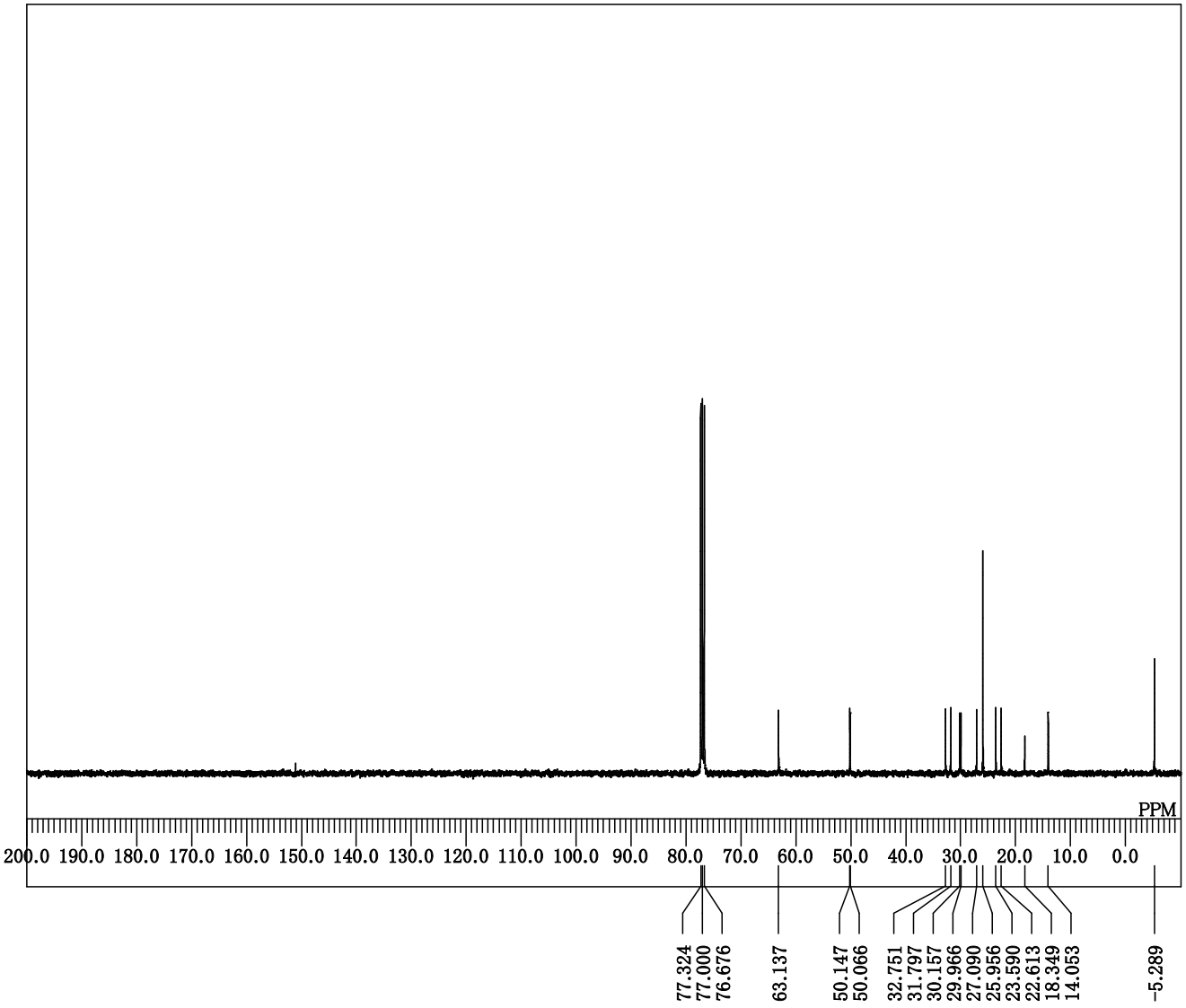
^{1}H NMR (395.88 MHz, $CDCl_3$)

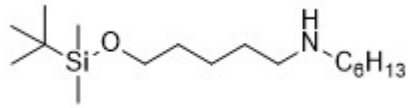




5ga

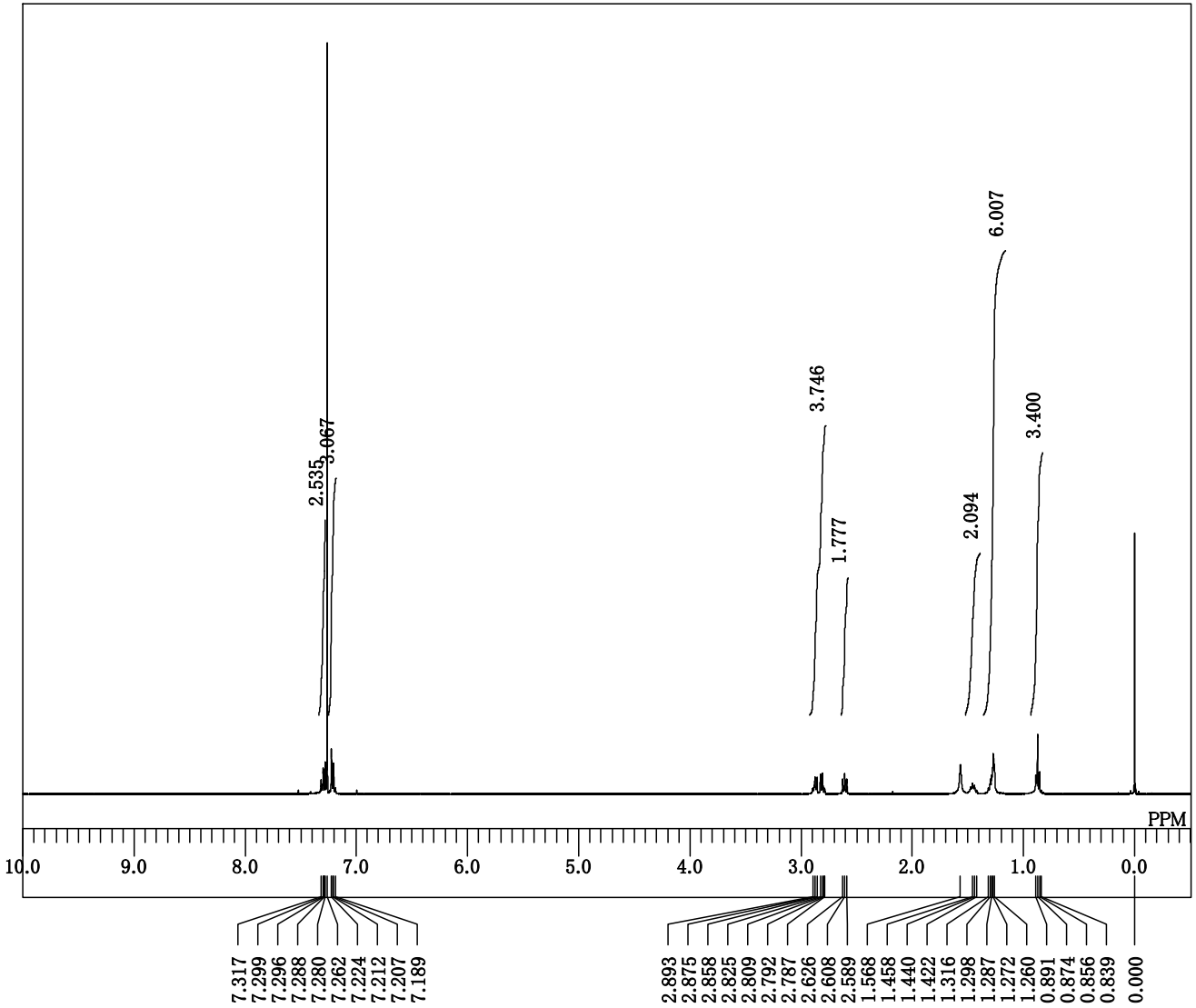
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

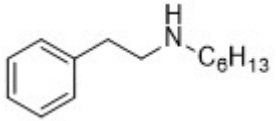




5ga

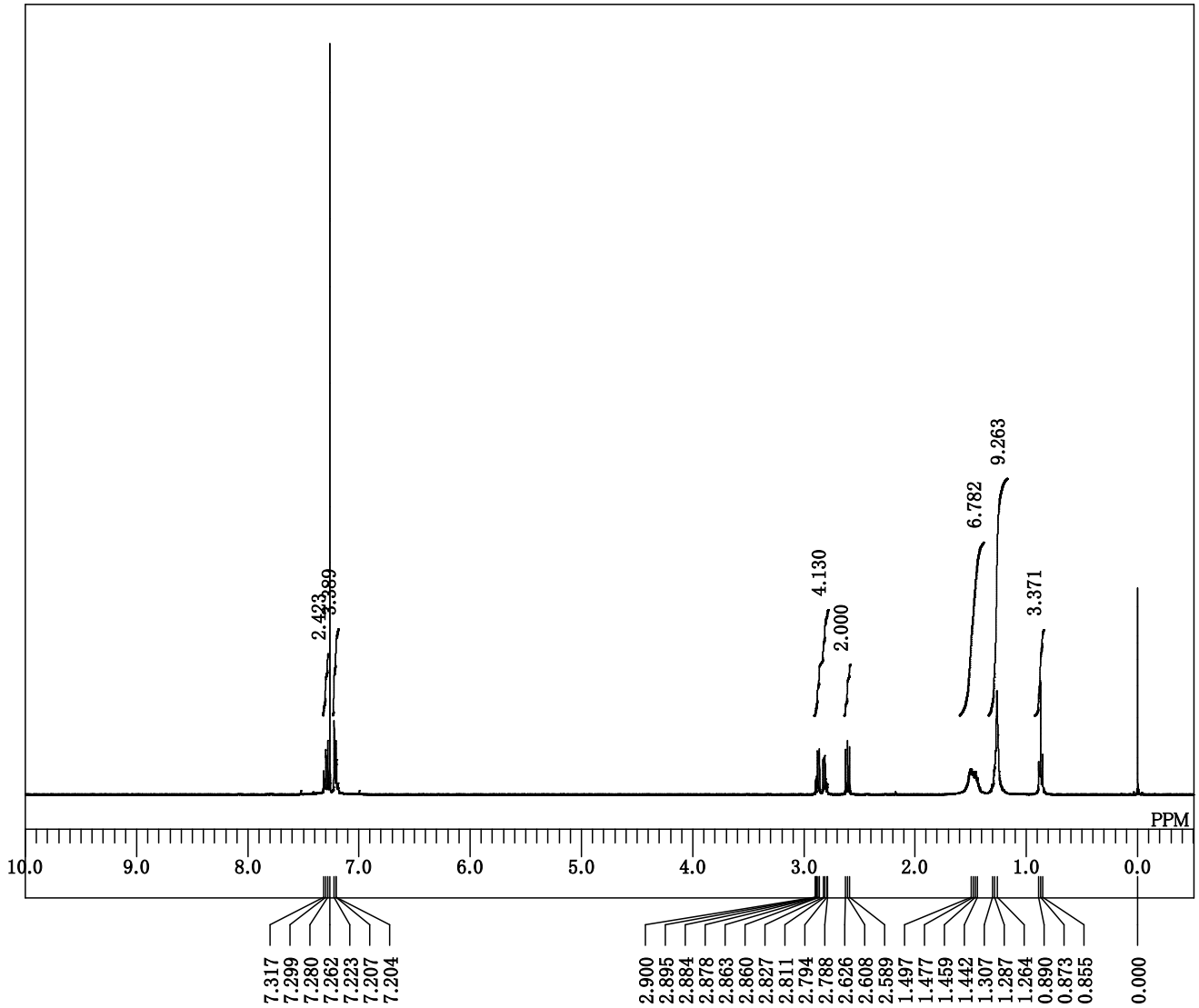
^{1}H NMR (395.88 MHz, $CDCl_3$)

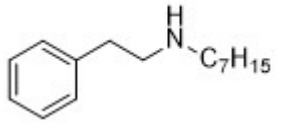




8aa

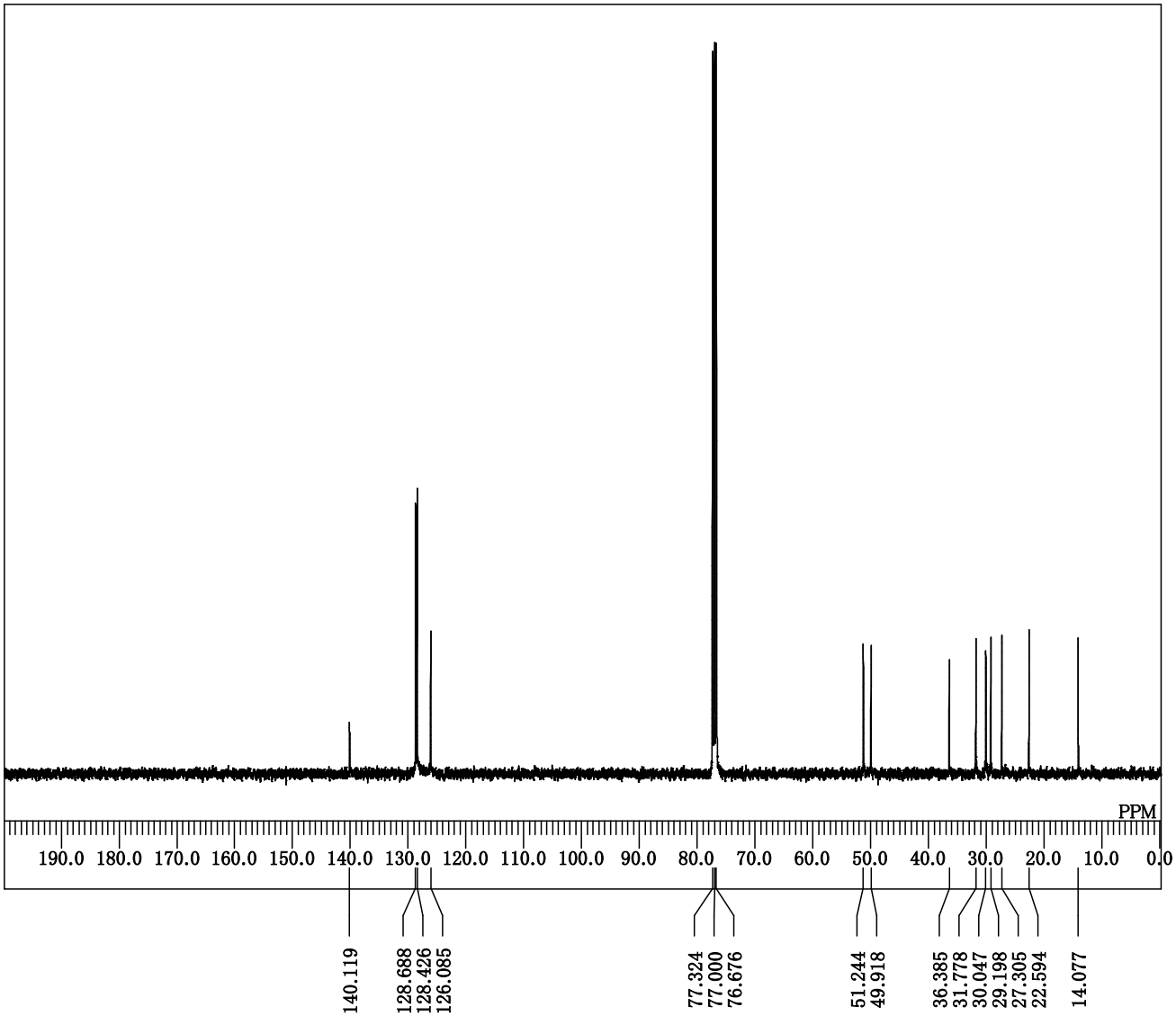
^{1}H NMR (395.88 MHz, $CDCl_3$)

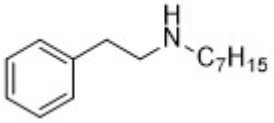




8ab

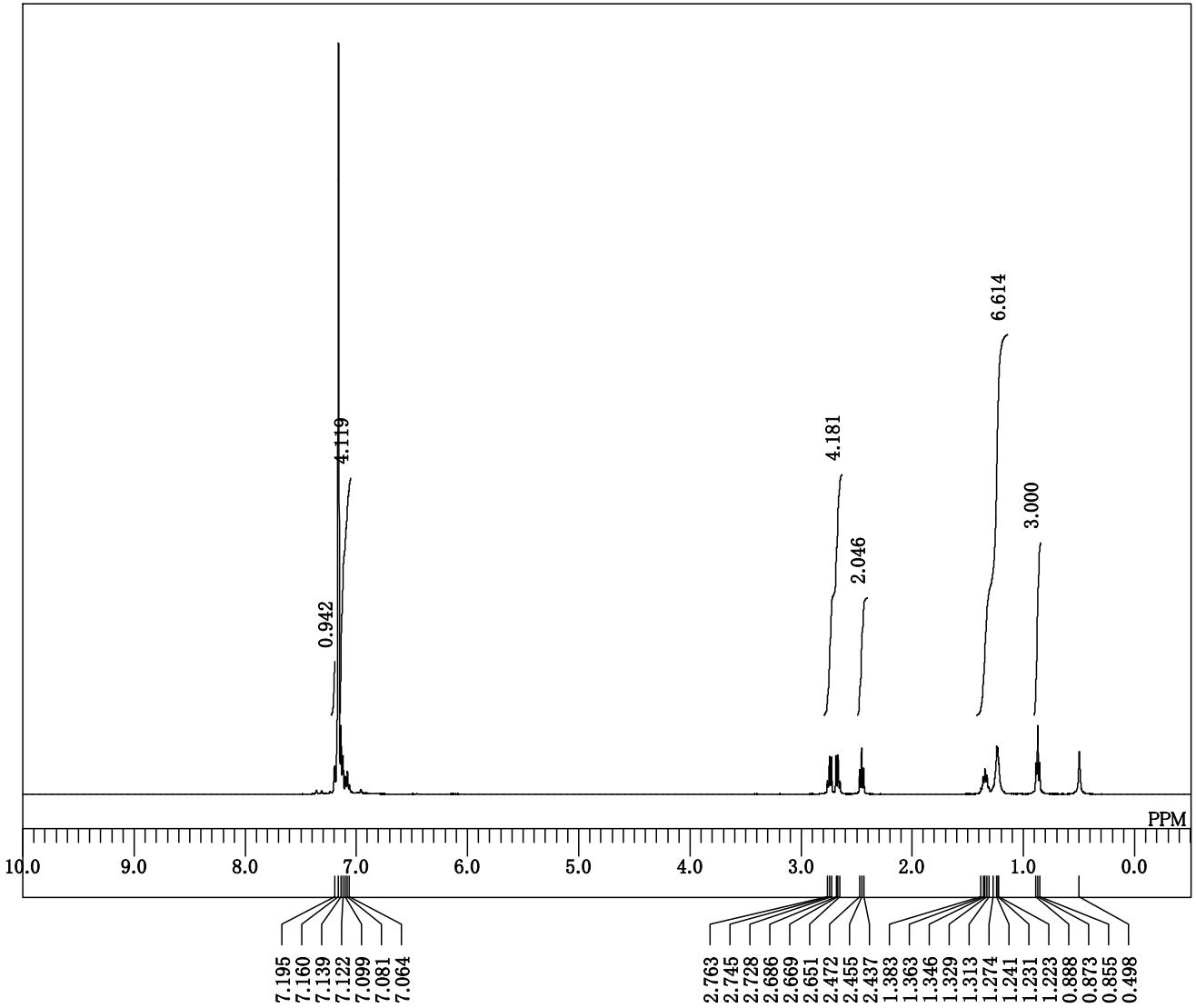
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

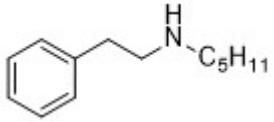




8ab

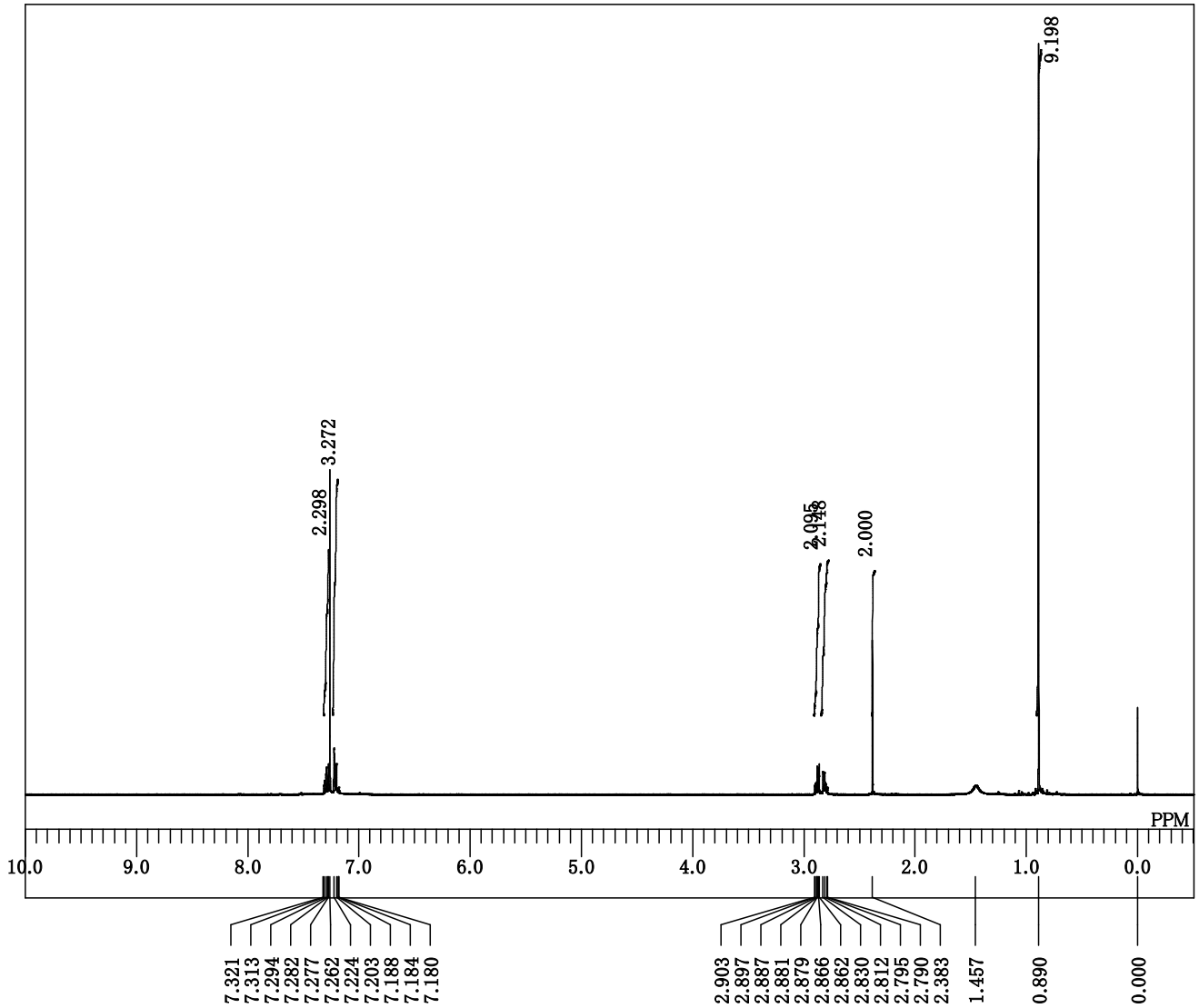
^{1}H NMR (395.88 MHz, C_6D_6)

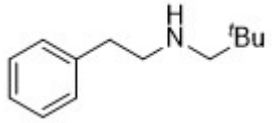




8ac

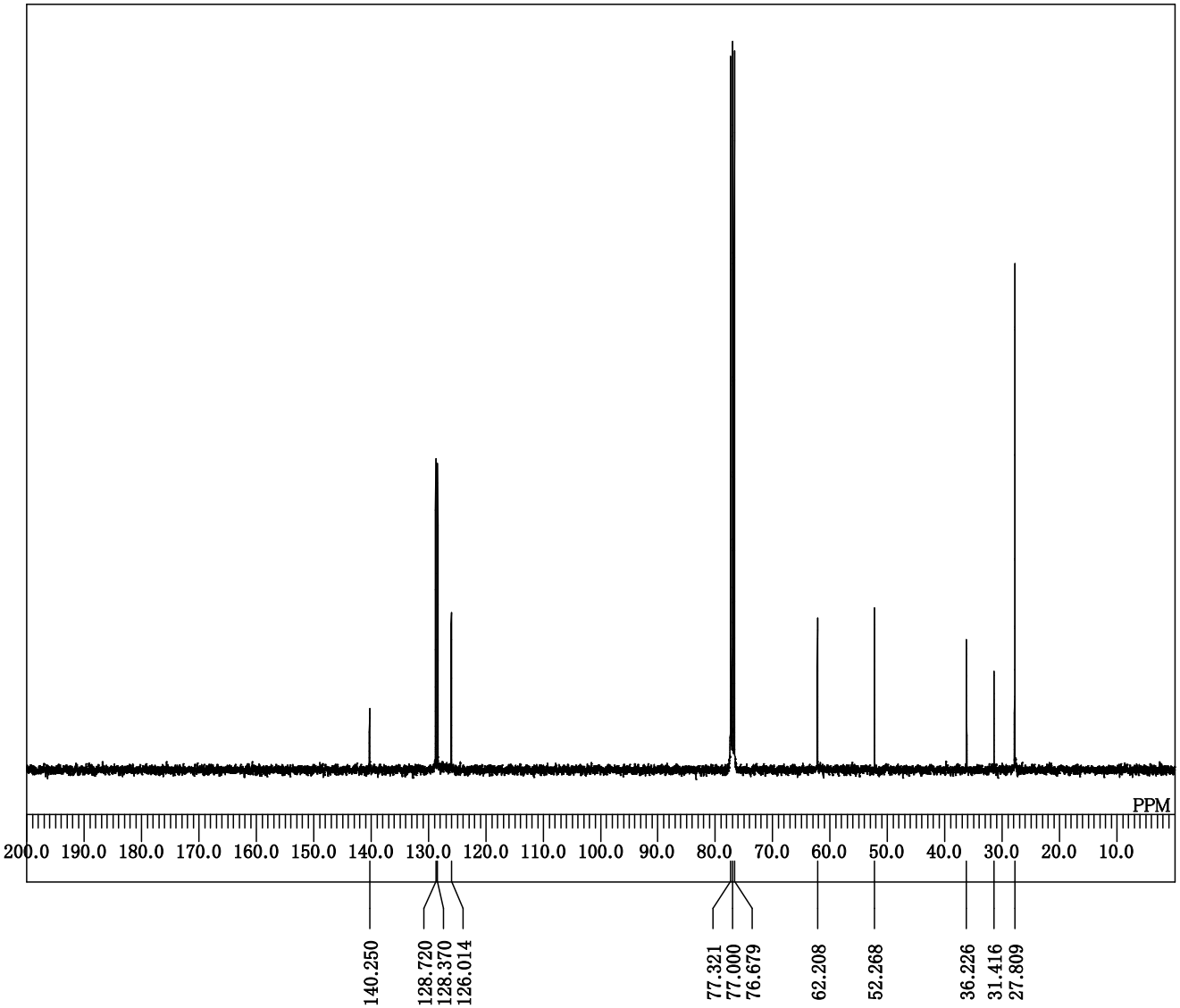
^{1}H NMR (395.88 MHz, $CDCl_3$)

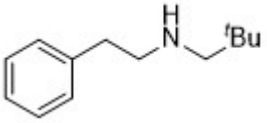




8ad

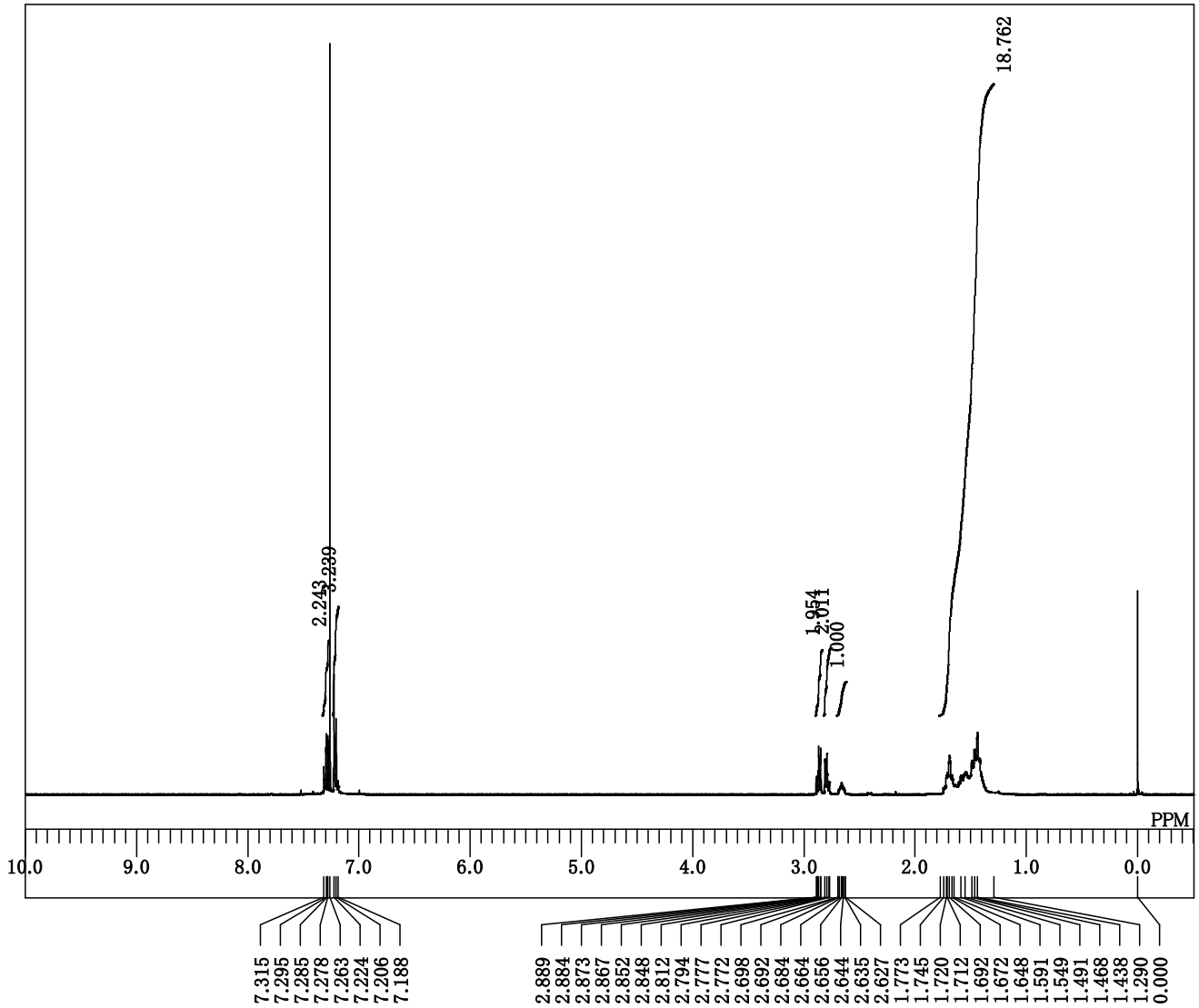
^{13}C {^{1}H} NMR (99.55 MHz, $CDCl_3$)

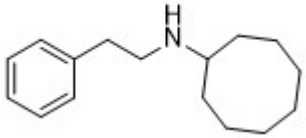




8ad

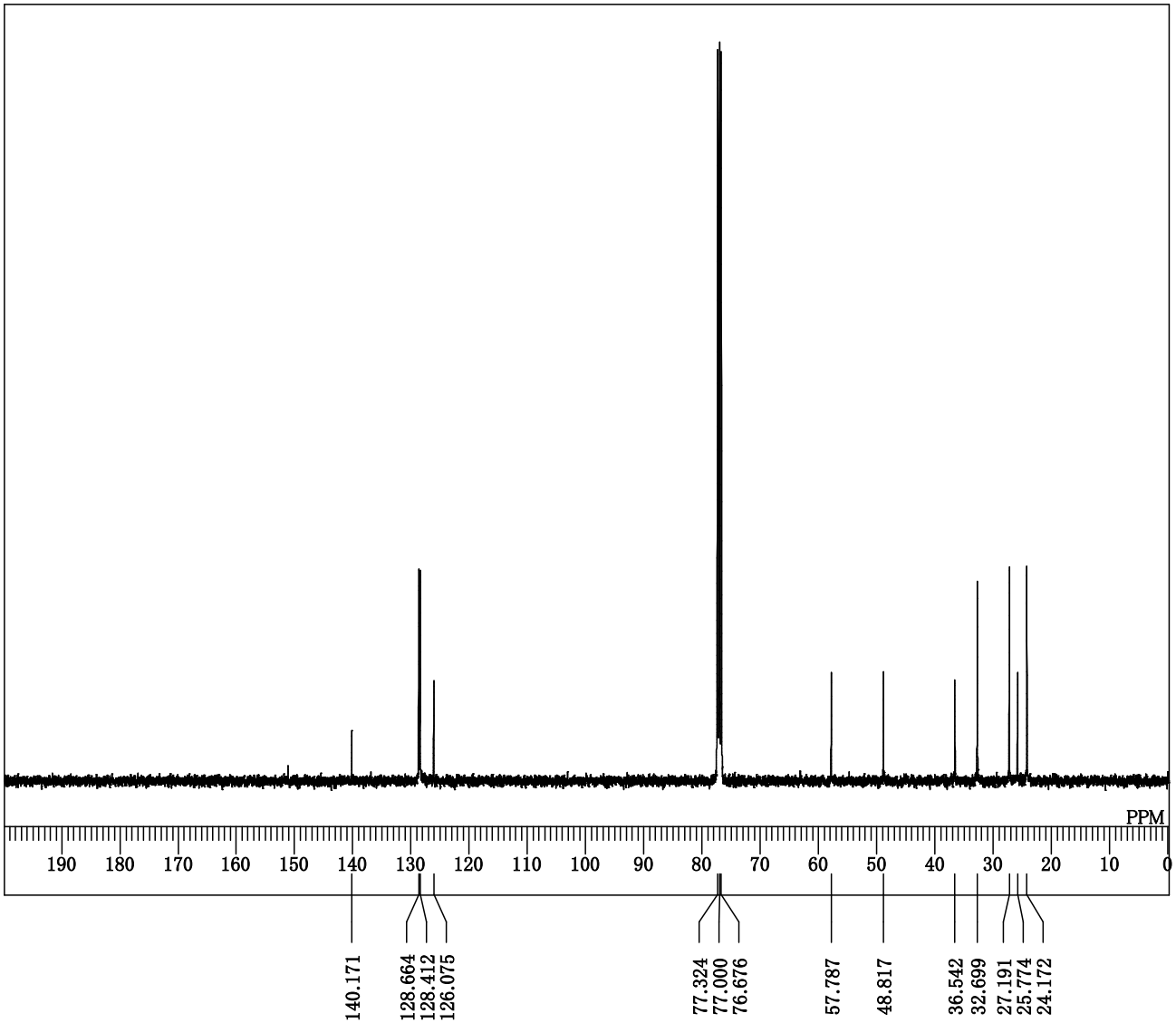
^{1}H NMR (395.88 MHz, $CDCl_3$)

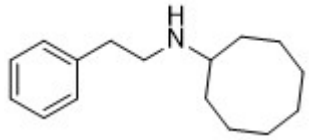




8ae

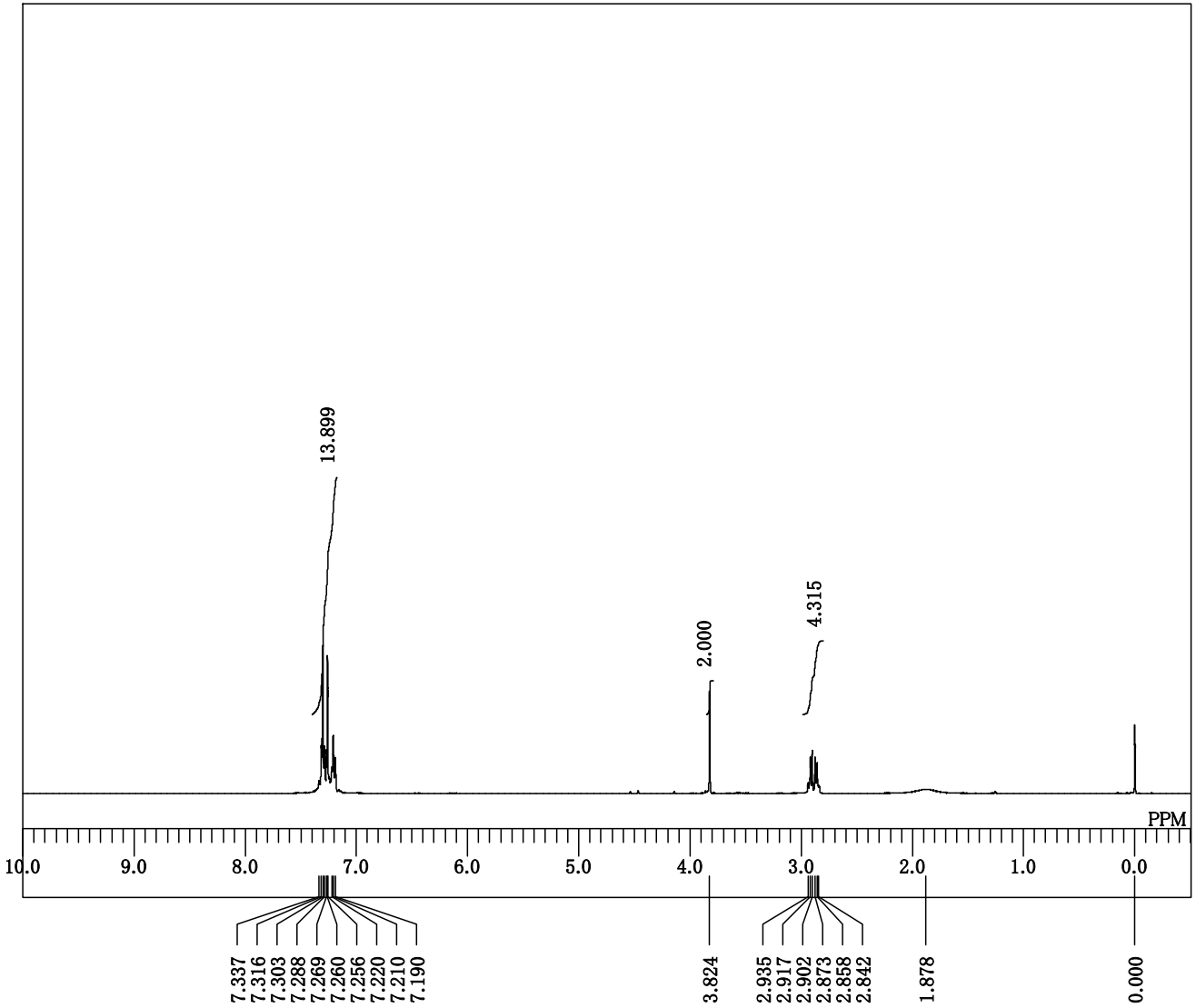
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

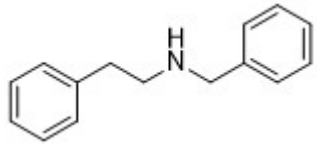




8ae

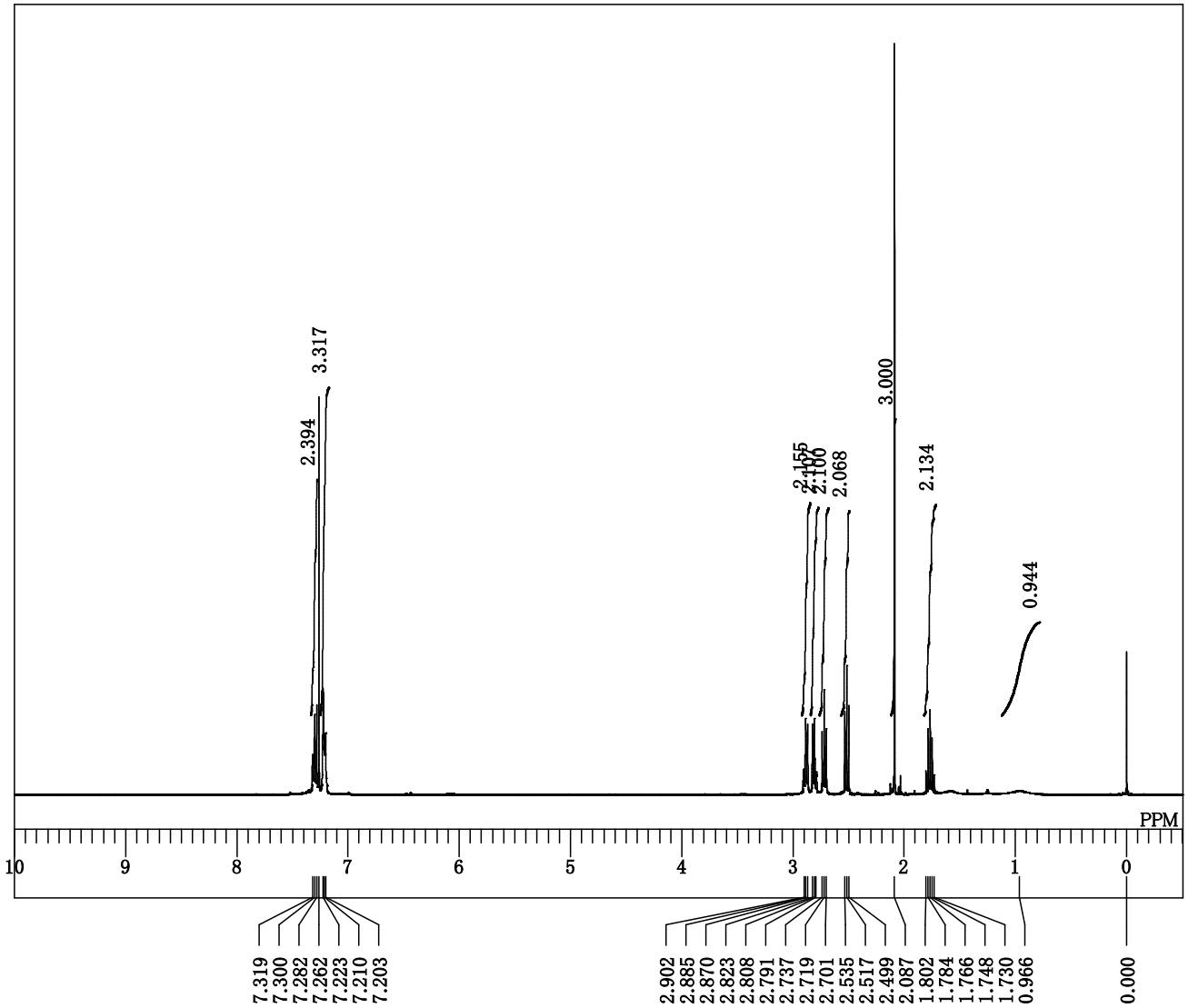
^{1}H NMR (395.88 MHz, $CDCl_3$)

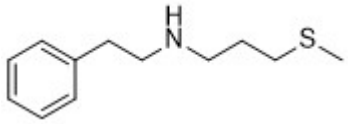




8af

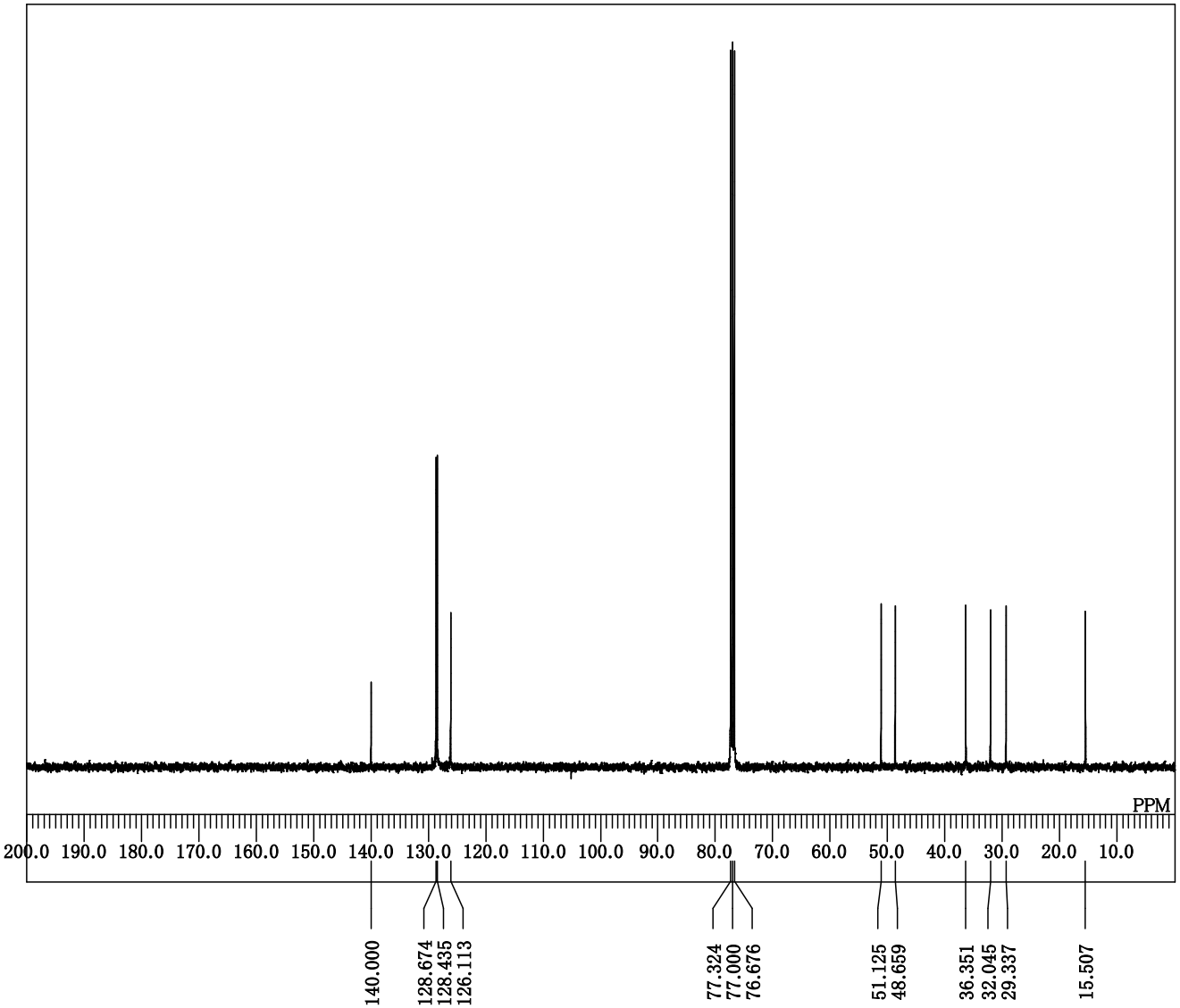
^{1}H NMR (395.88 MHz, $CDCl_3$)

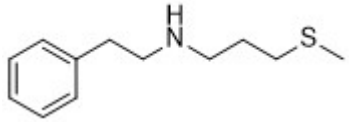




8ag

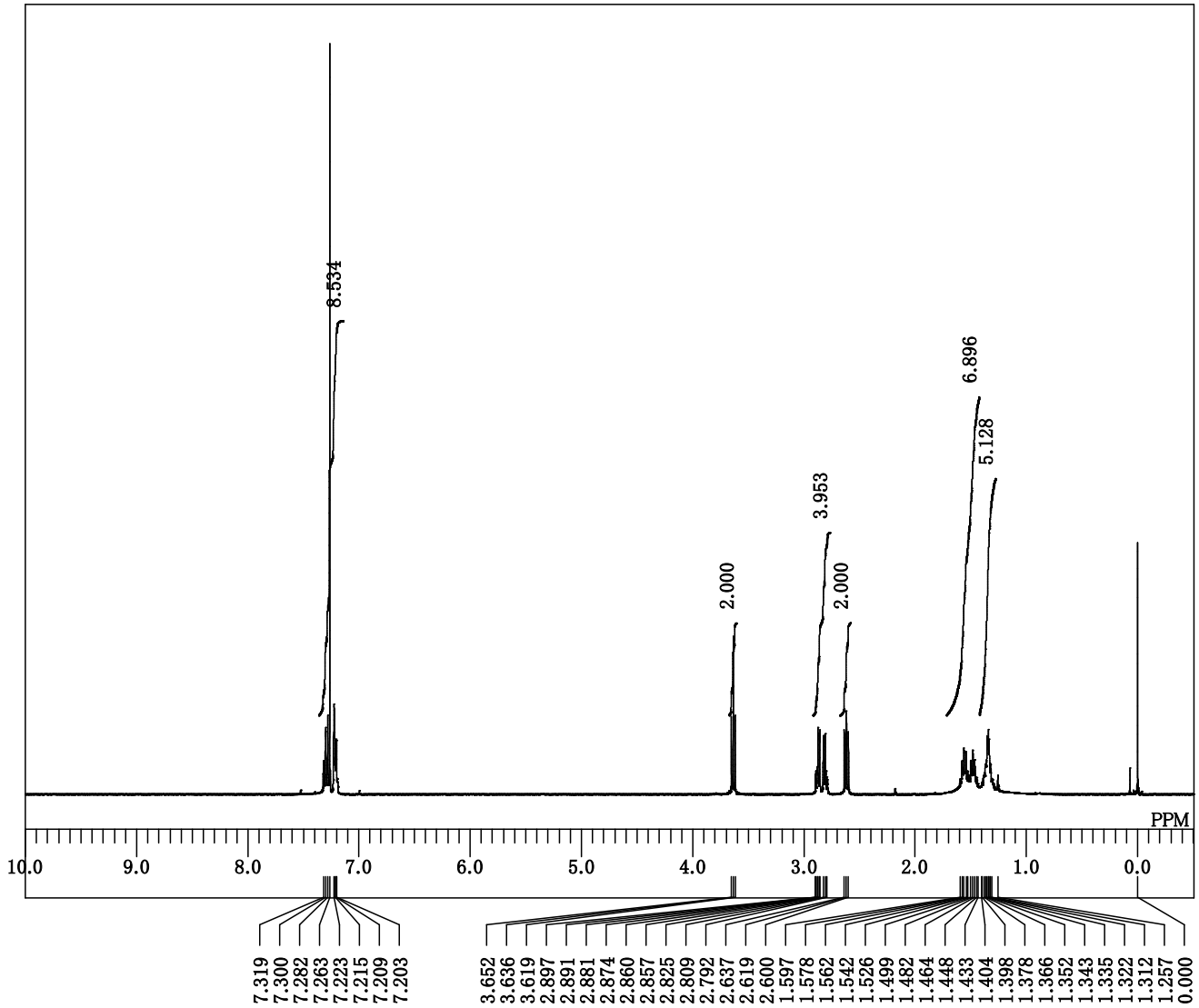
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

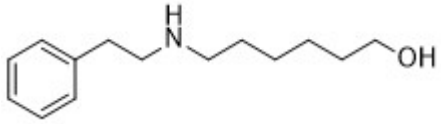




8ag

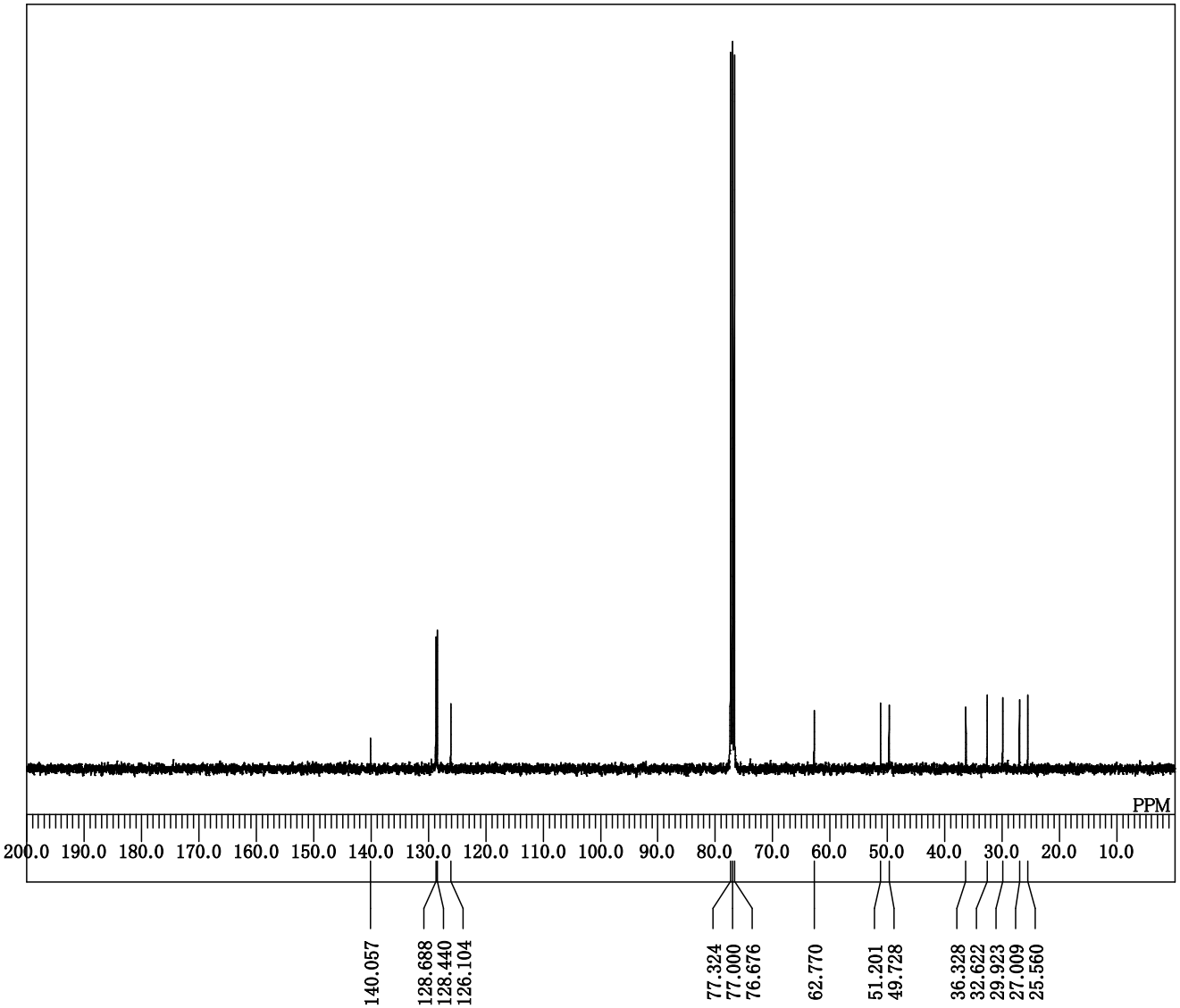
^{1}H NMR (395.88 MHz, $CDCl_3$)

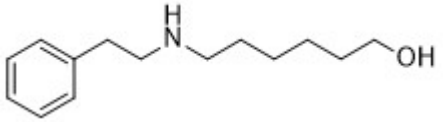




8ah

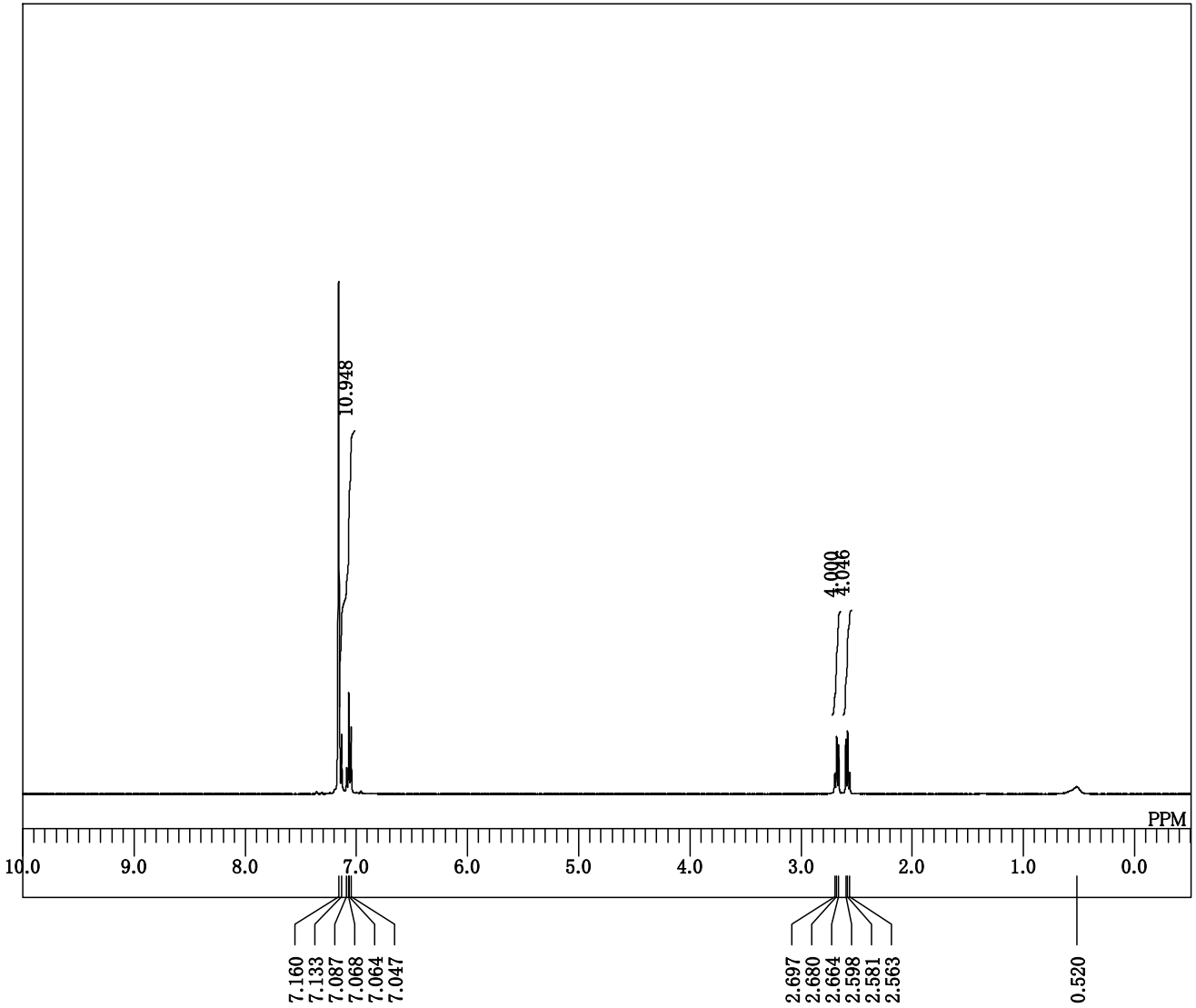
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

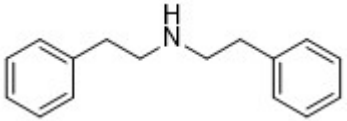




8ah

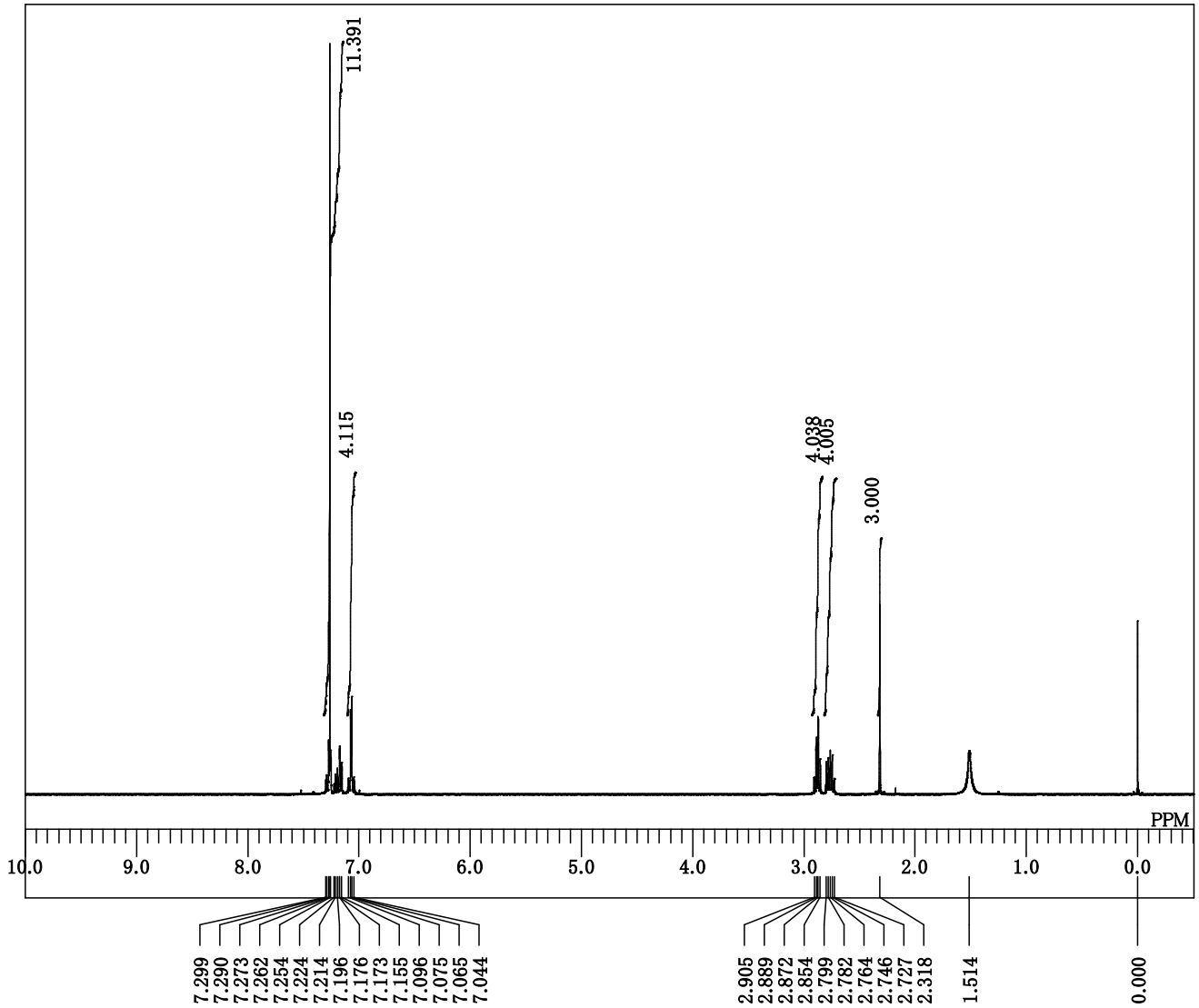
^{1}H NMR (395.88 MHz, C_6D_6)

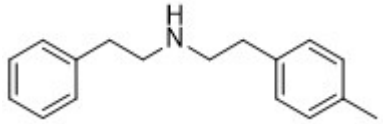




8ai

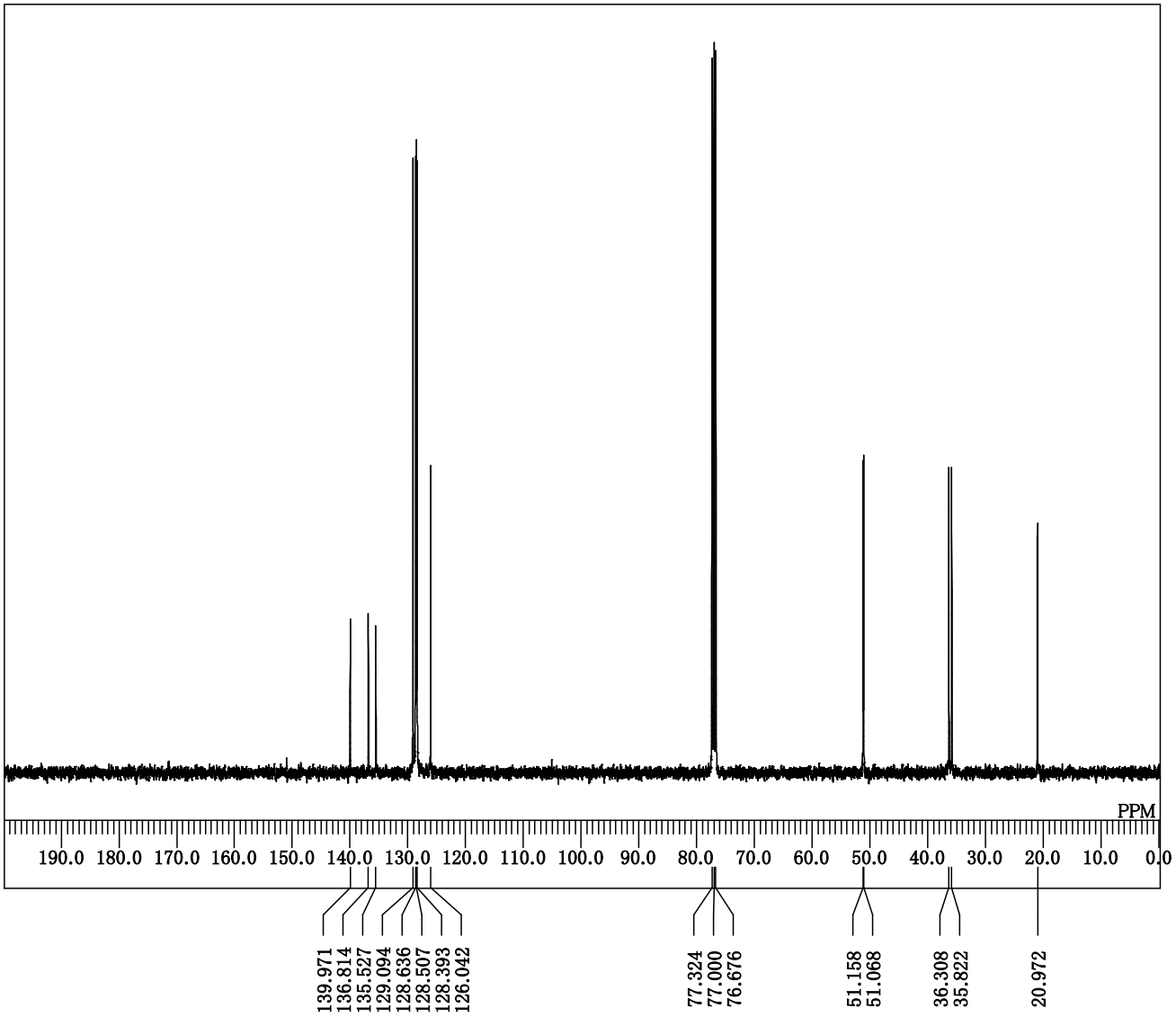
^{1}H NMR (395.88 MHz, $CDCl_3$)

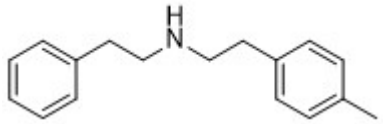




8aj

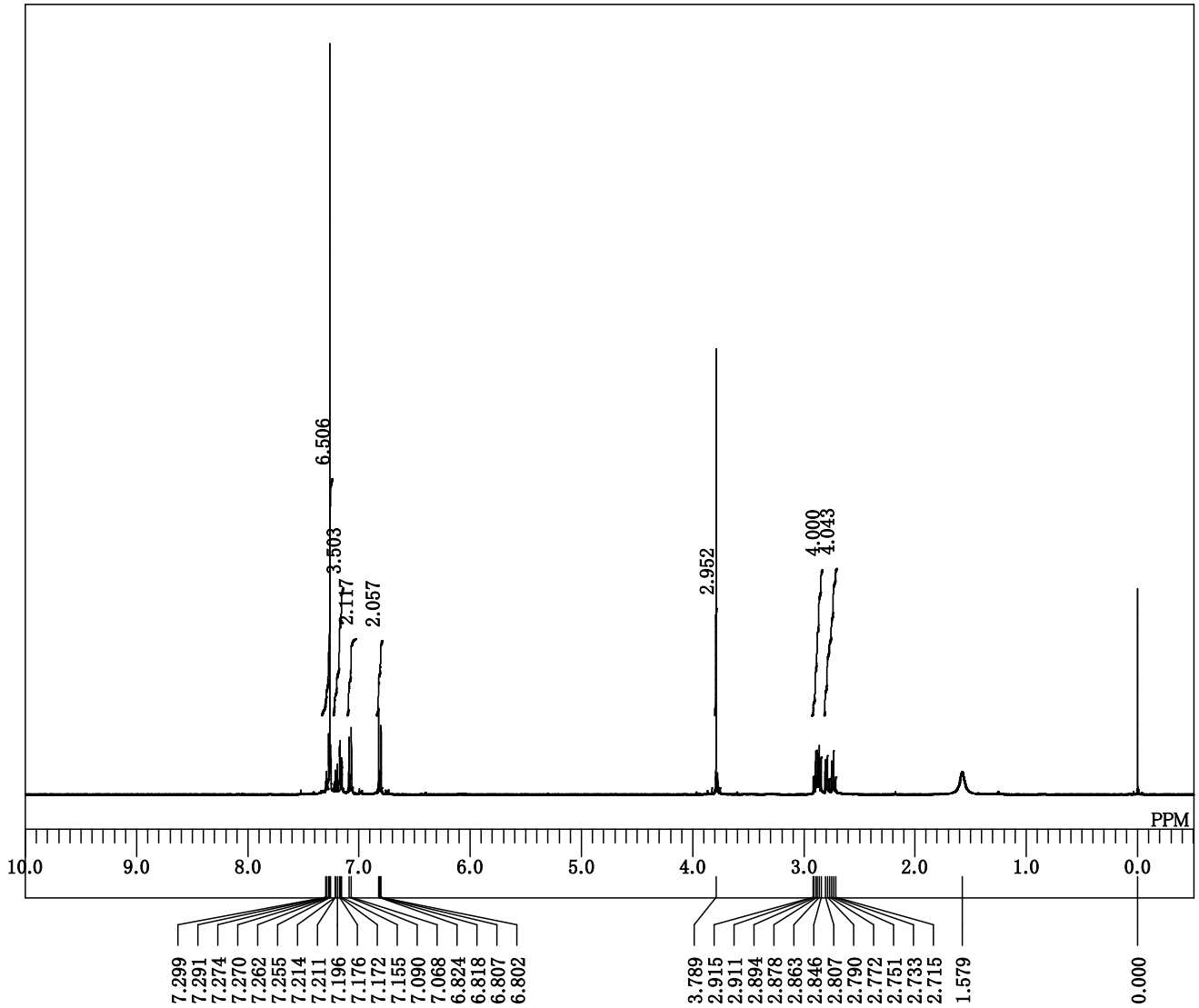
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

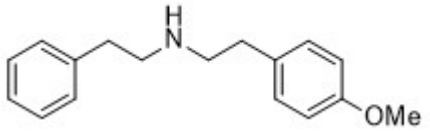




8aj

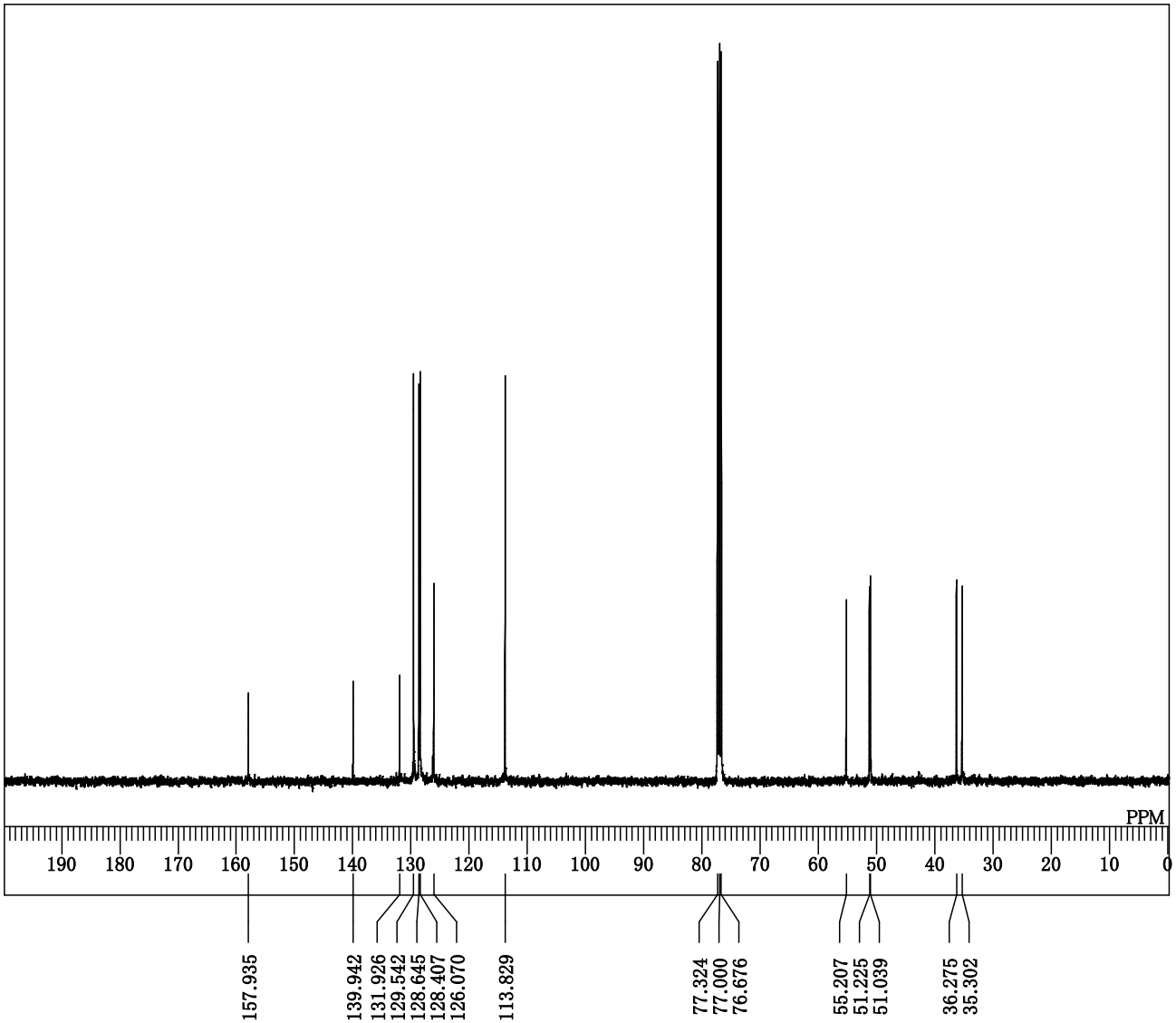
^{1}H NMR (395.88 MHz, $CDCl_3$)

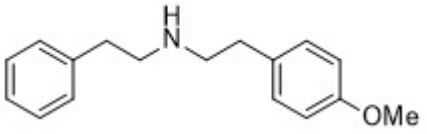




8ak

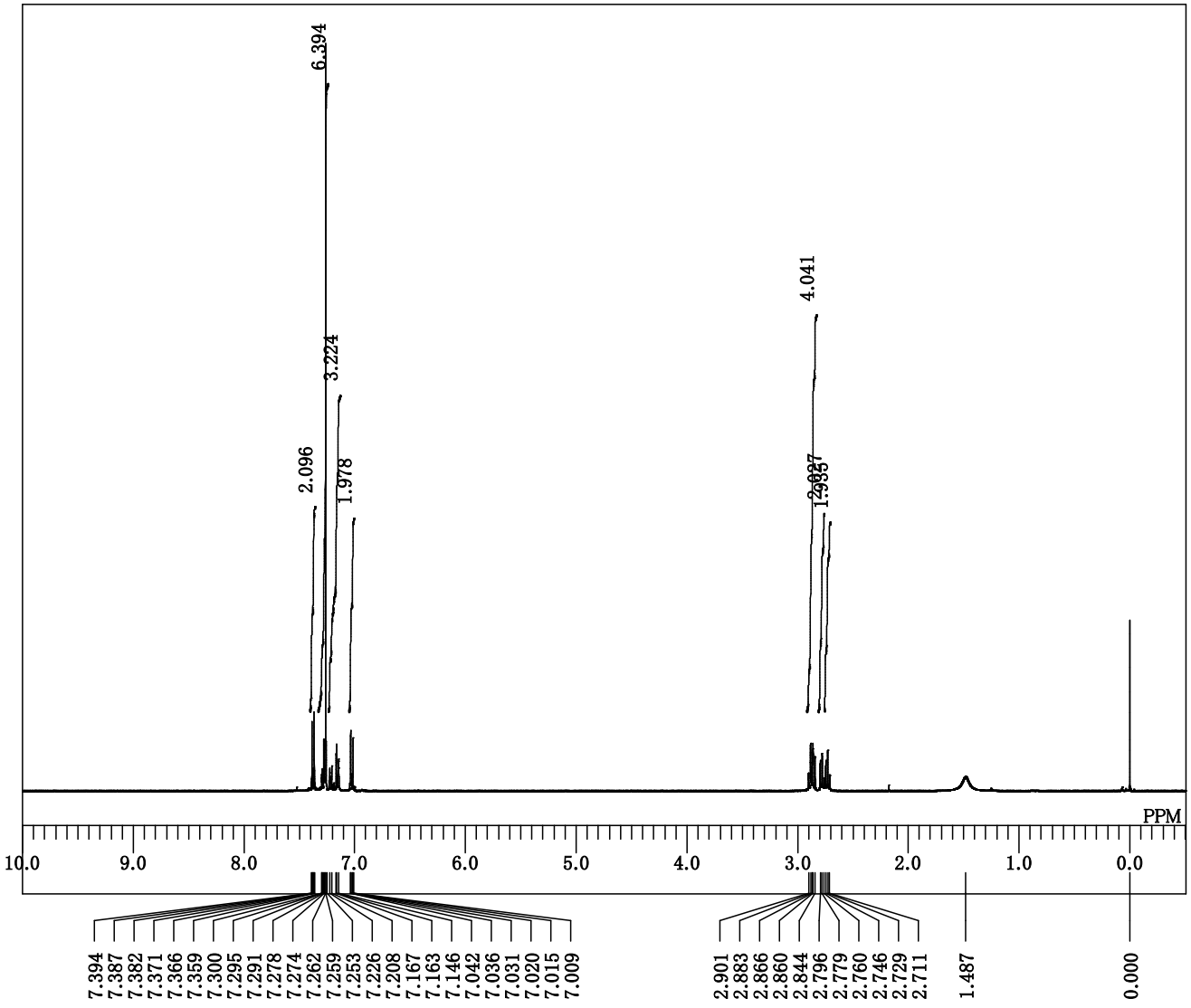
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

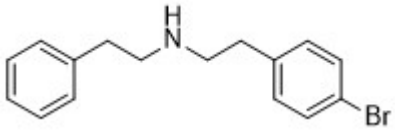




8ak

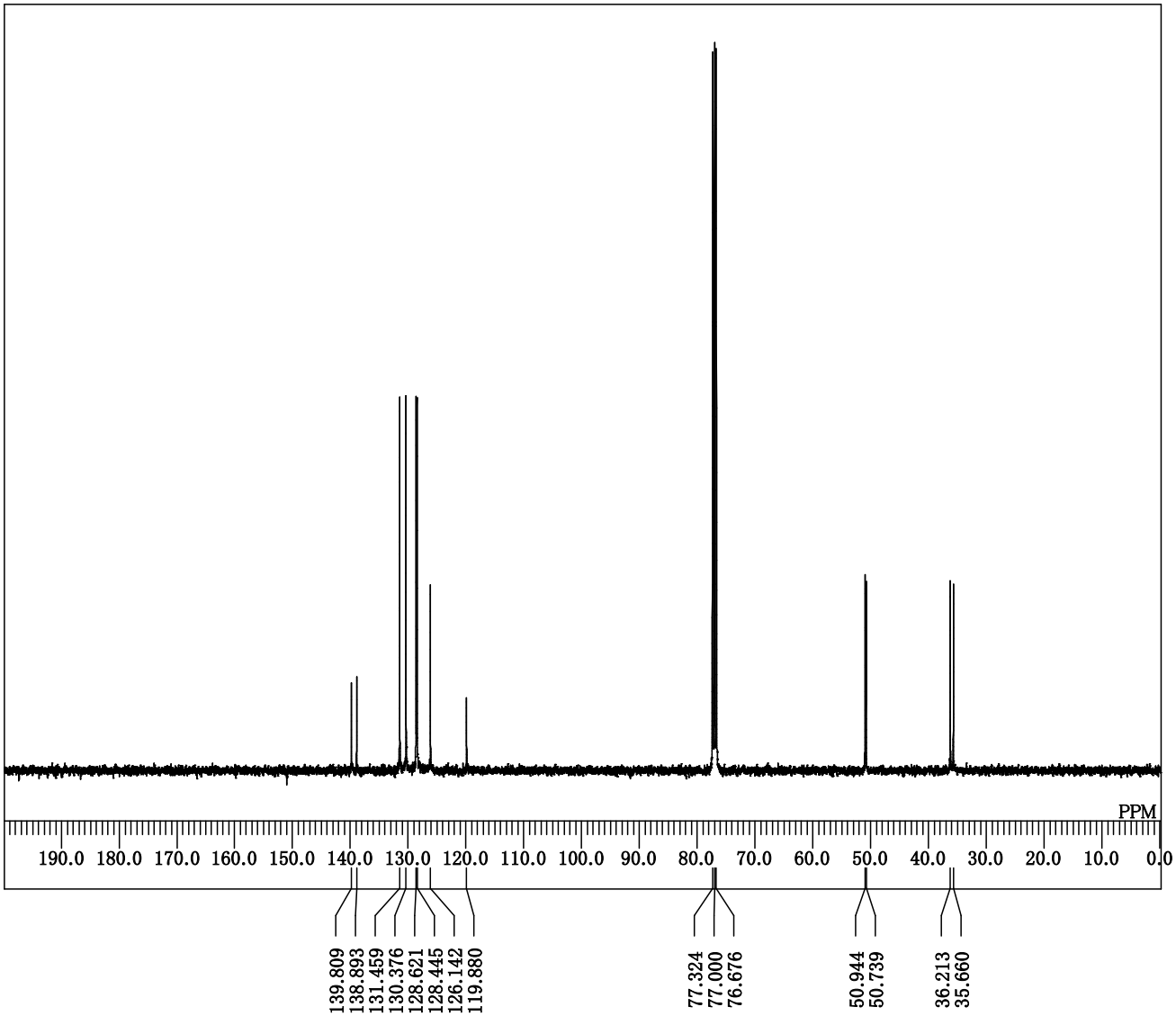
^{1}H NMR (395.88 MHz, $CDCl_3$)

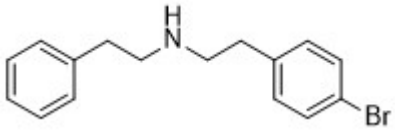




8al

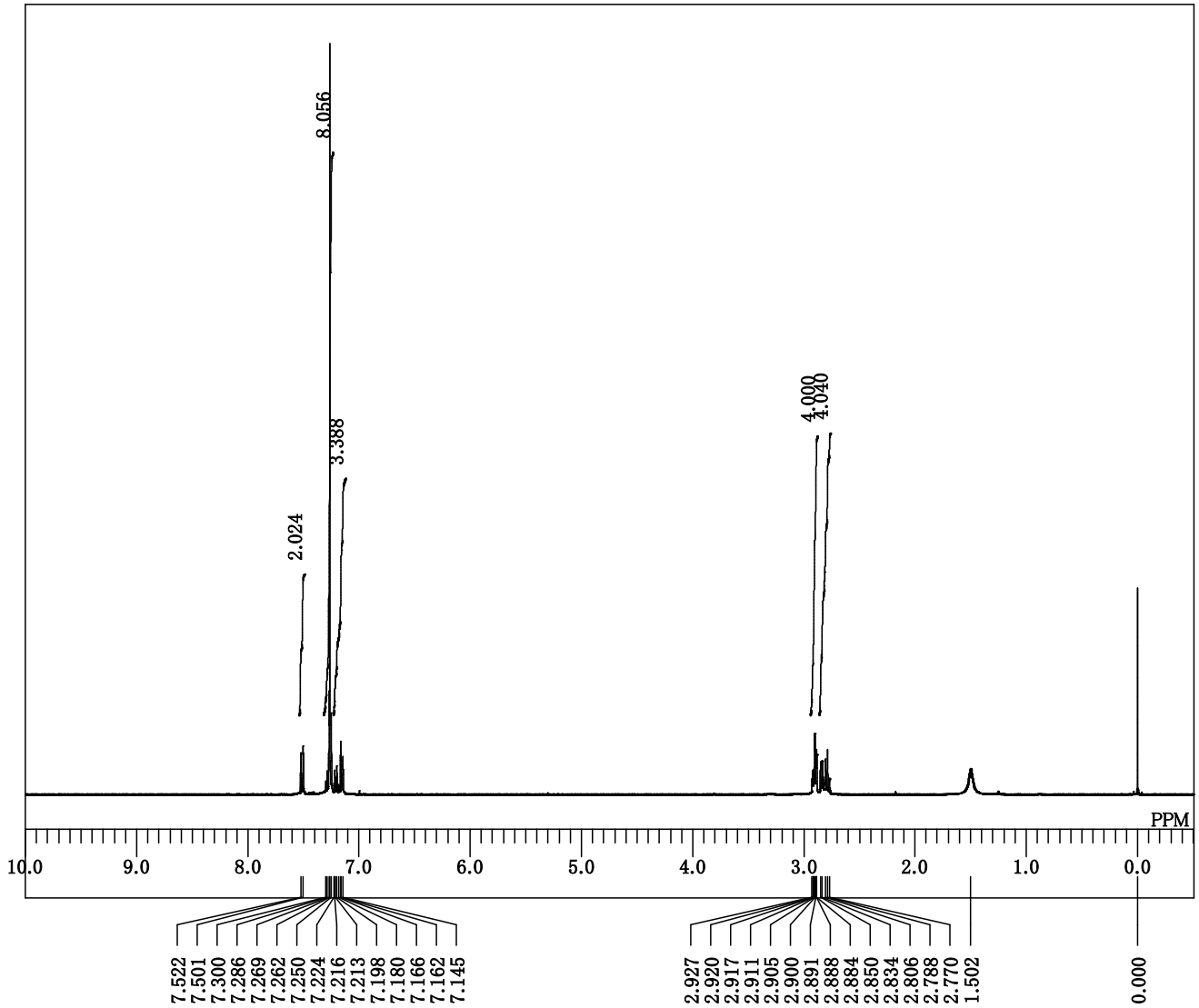
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

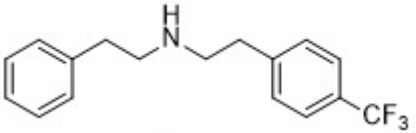




8al

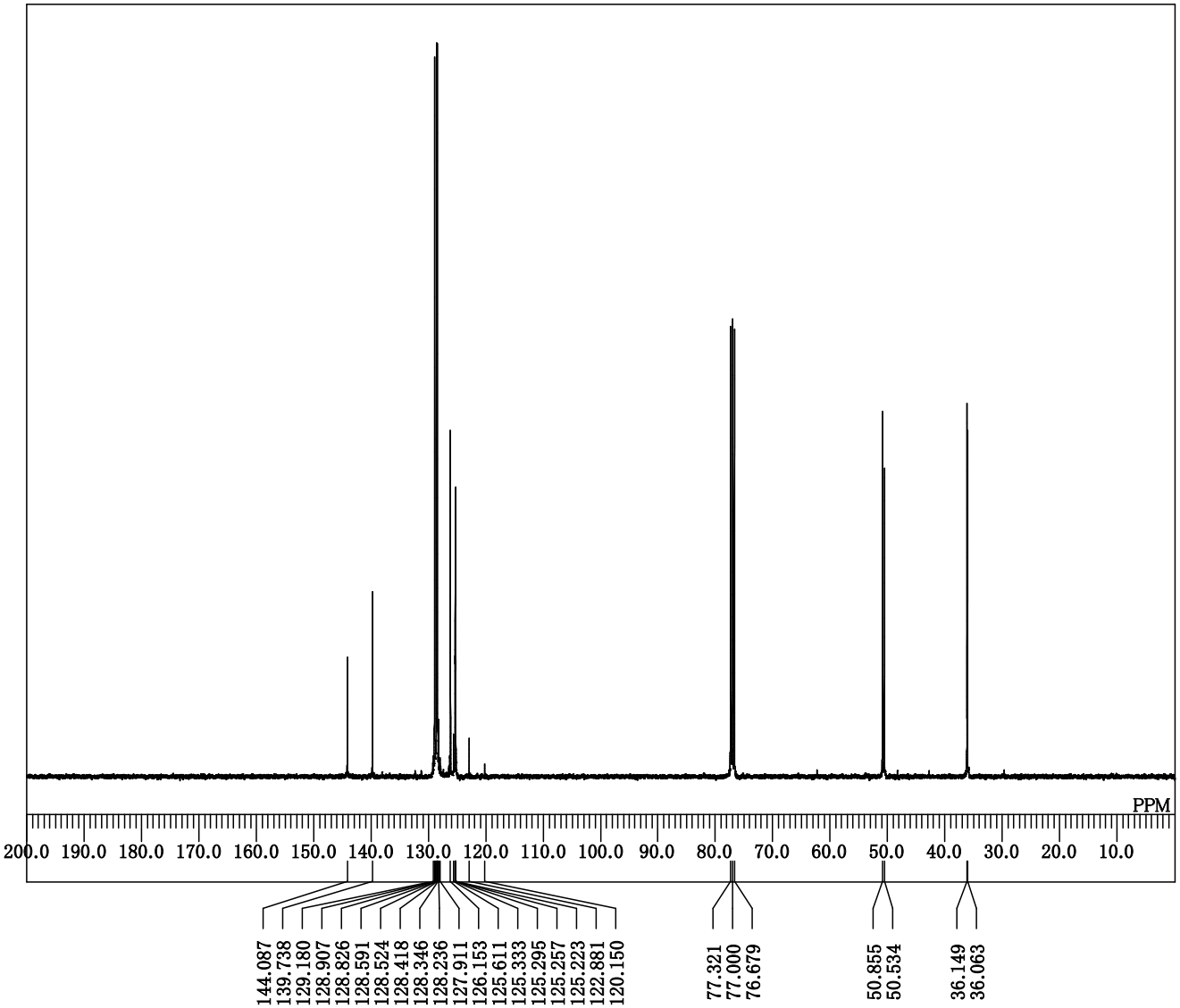
^{1}H NMR (395.88 MHz, $CDCl_3$)

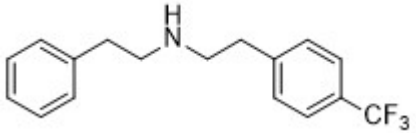




8am

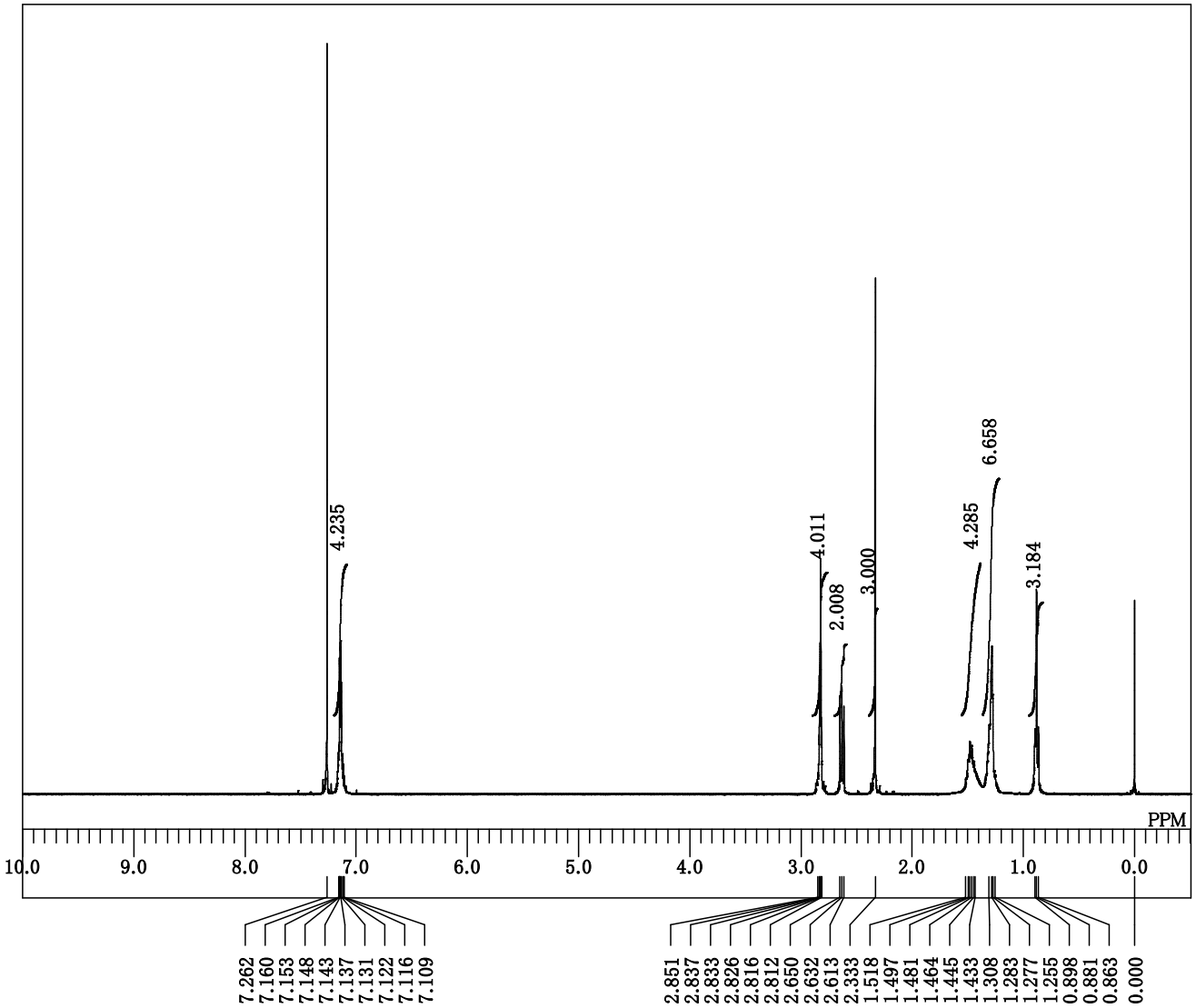
^{13}C {^{1}H} NMR (99.55 MHz, $CDCl_3$)

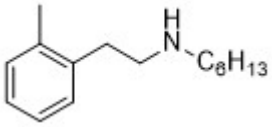




8am

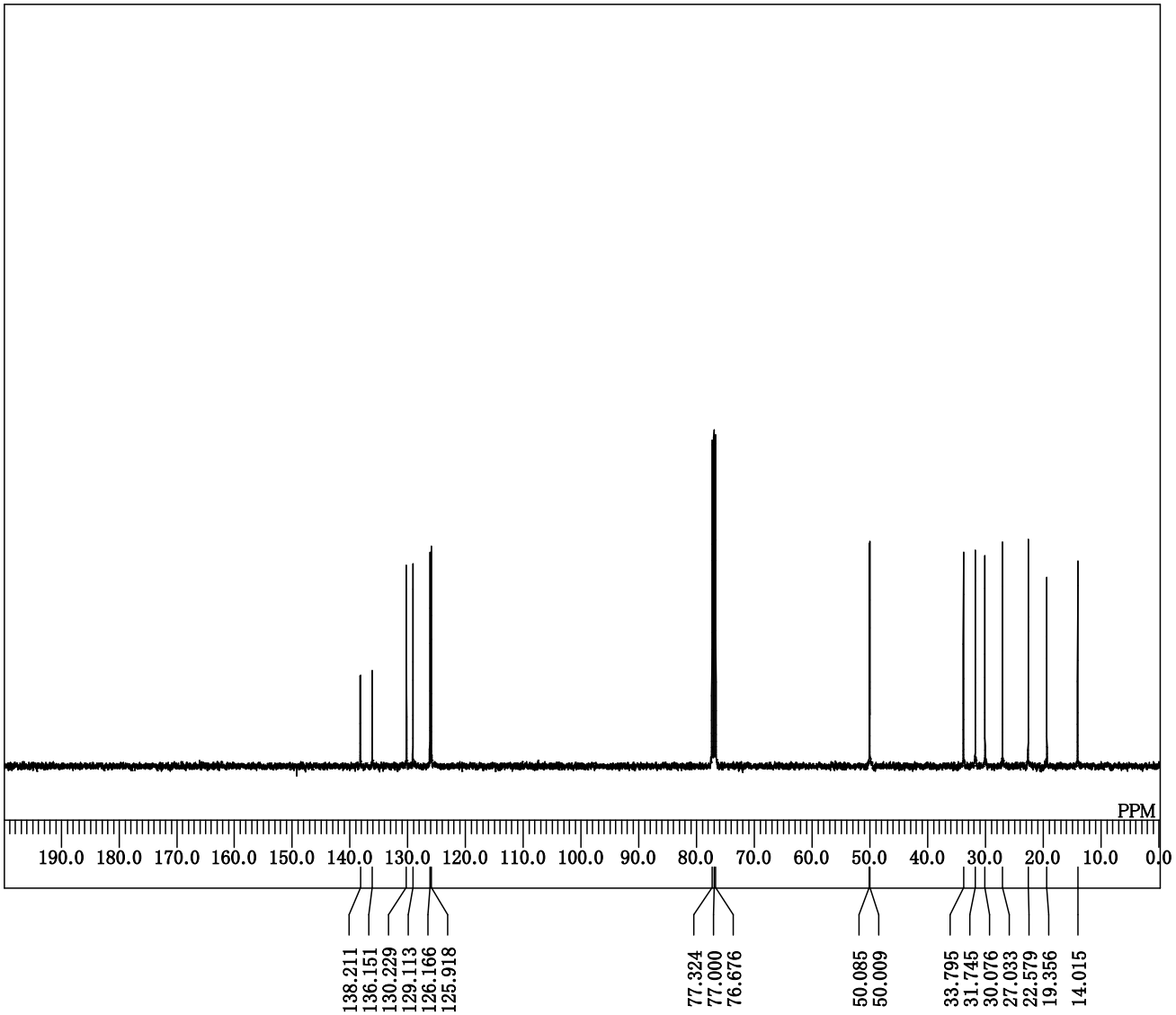
^{1}H NMR (395.88 MHz, $CDCl_3$)

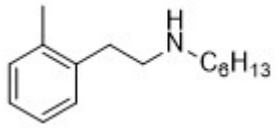




8ba

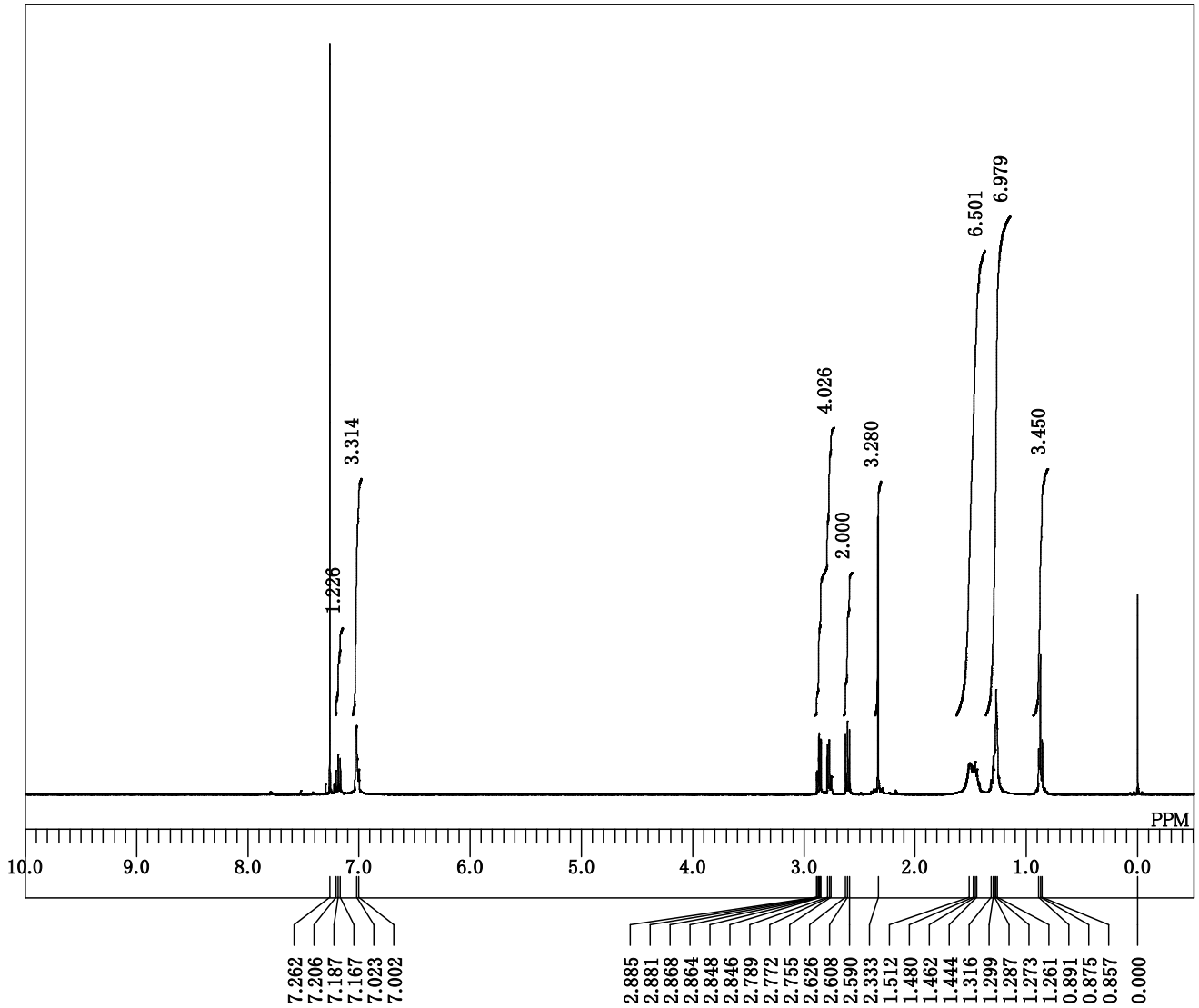
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

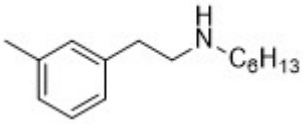




8ba

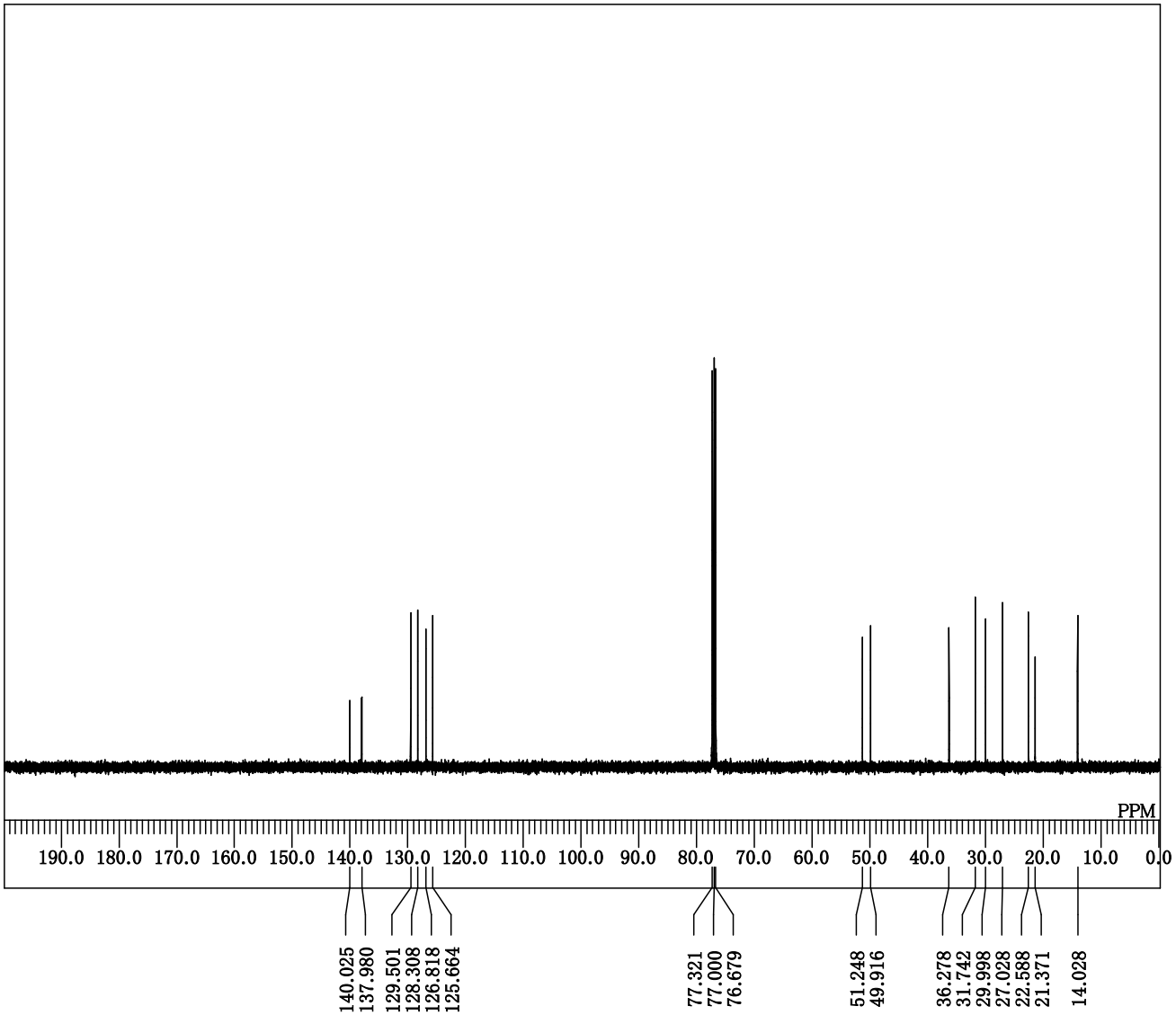
^{1}H NMR (395.88 MHz, $CDCl_3$)

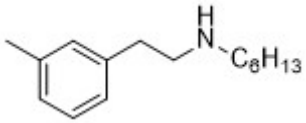




8ca

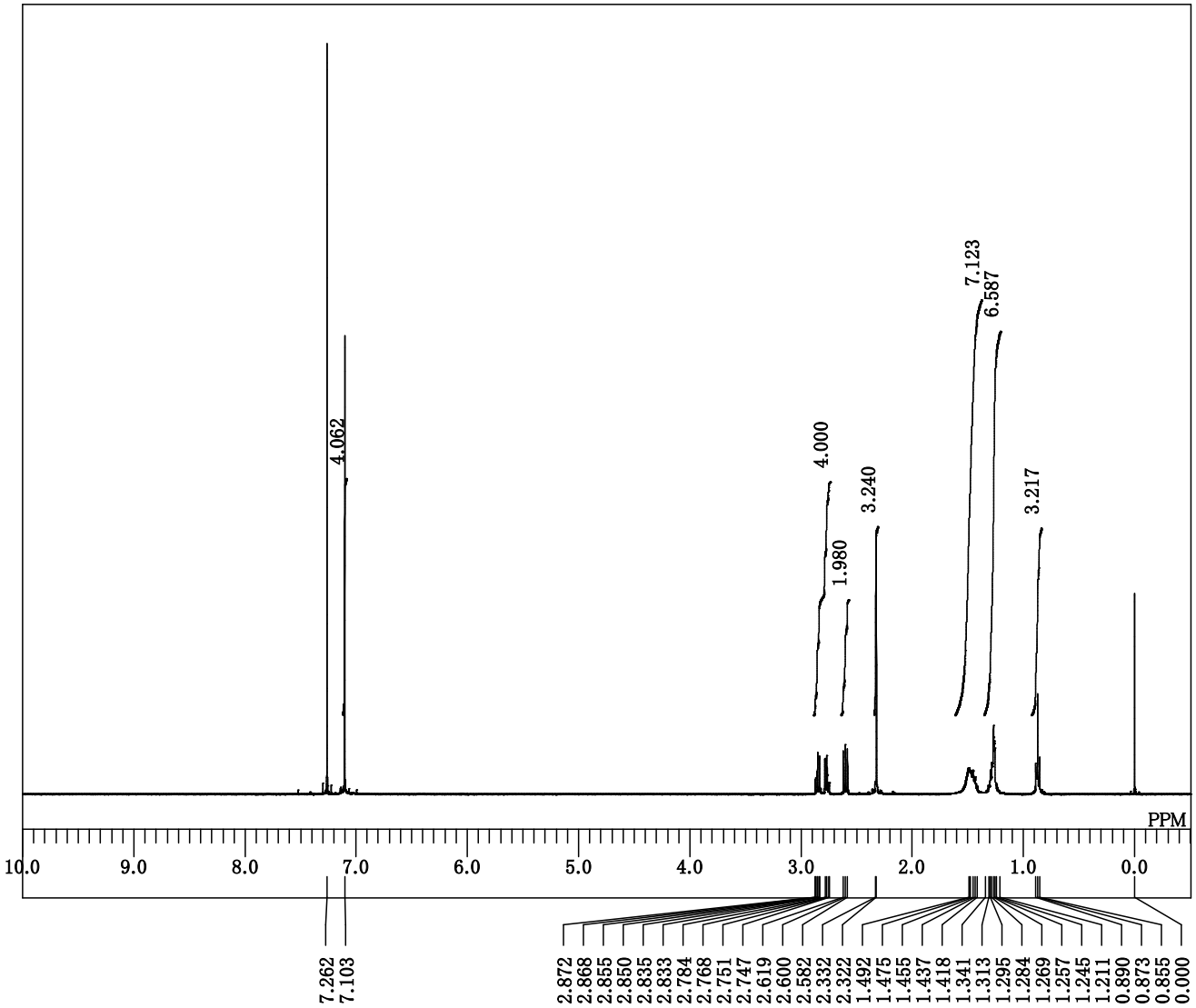
^{13}C {^{1}H} NMR (99.55 MHz, $CDCl_3$)

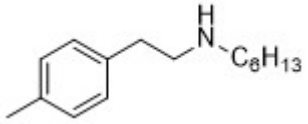




8ca

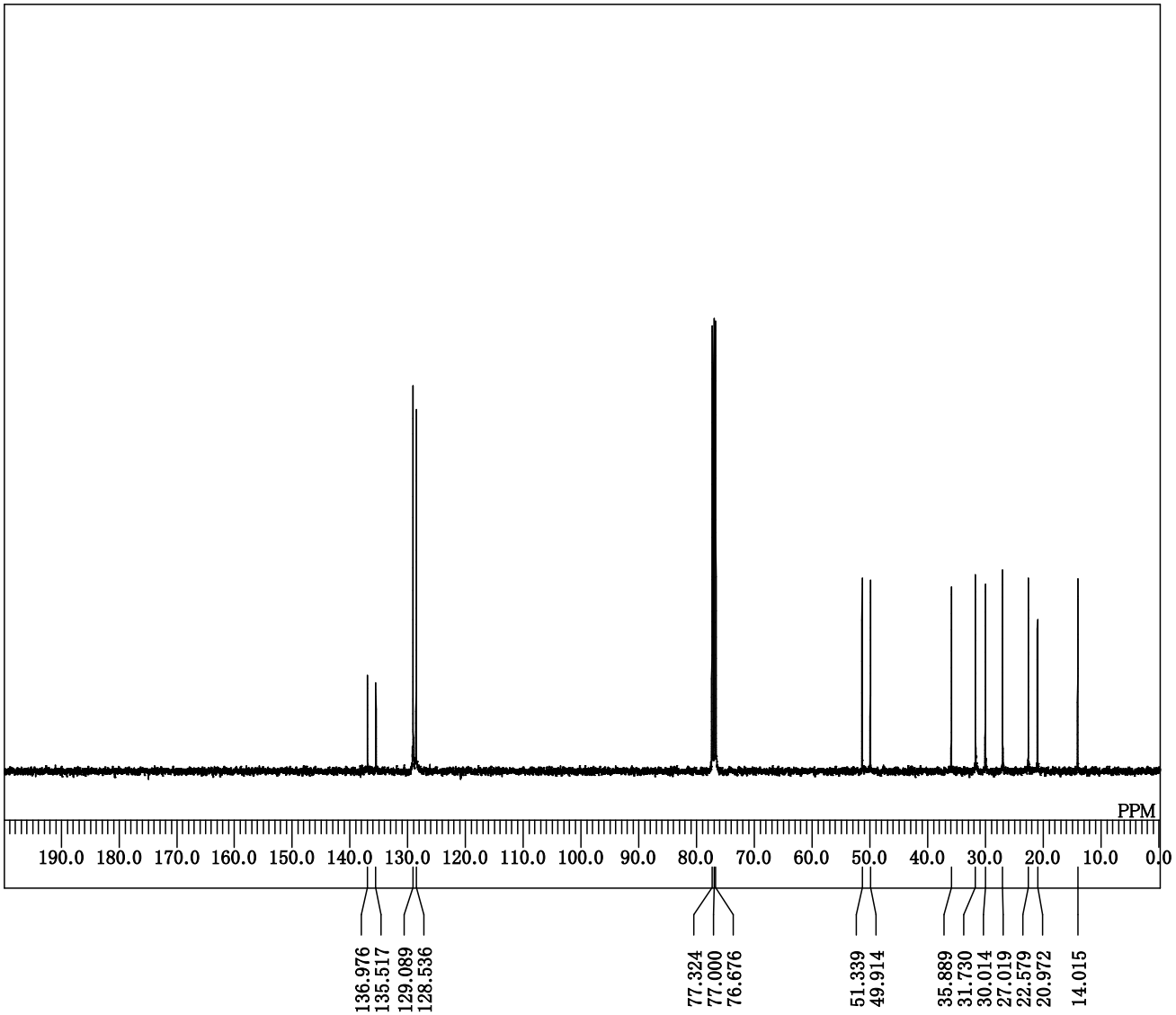
^{1}H NMR (395.88 MHz, $CDCl_3$)

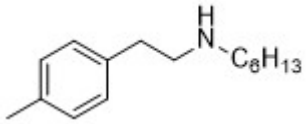




8da

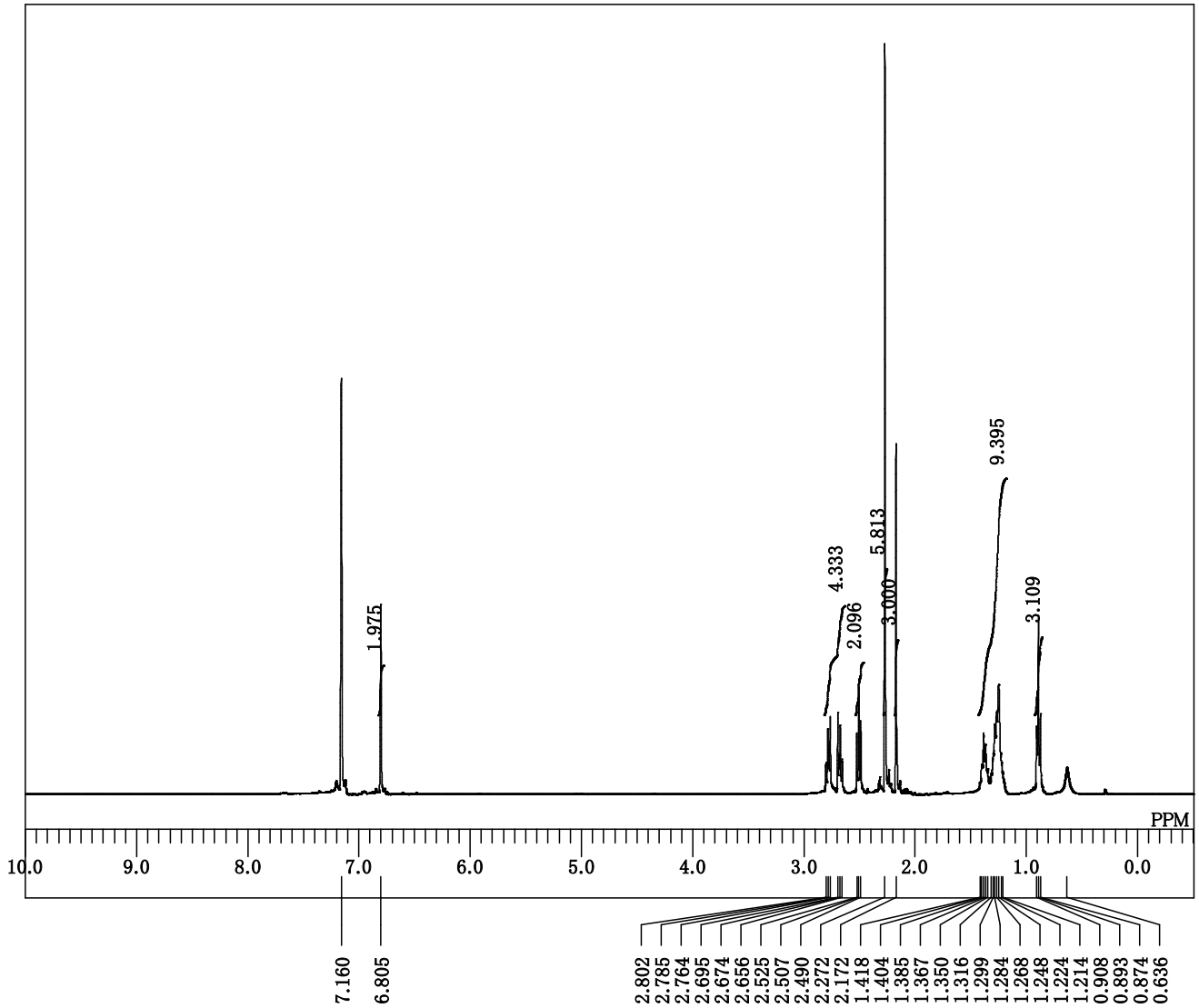
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

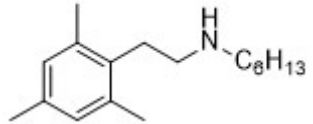




8da

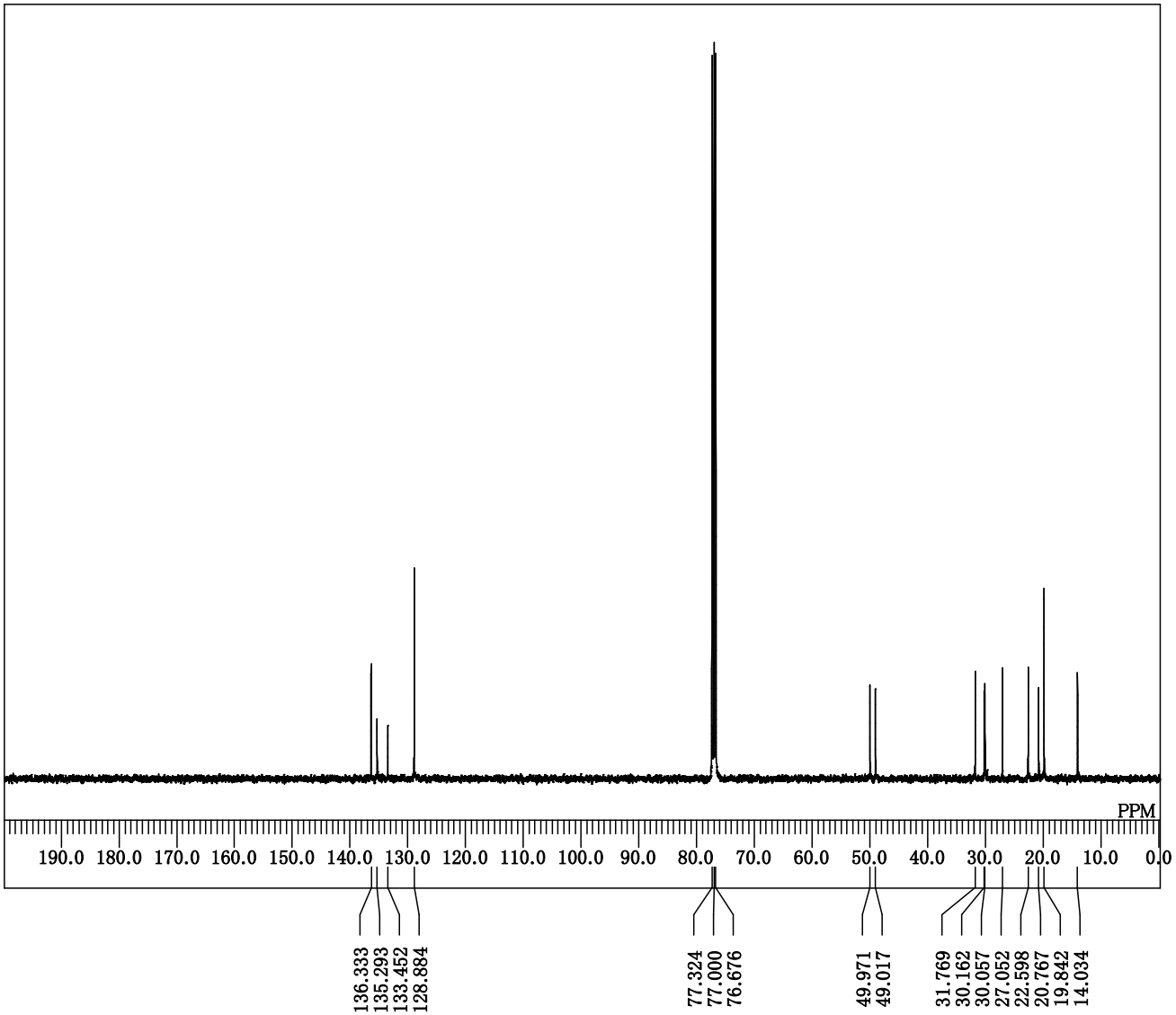
^{1}H NMR (391.78 MHz, C_6D_6)

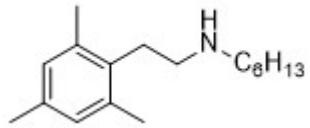




8ea

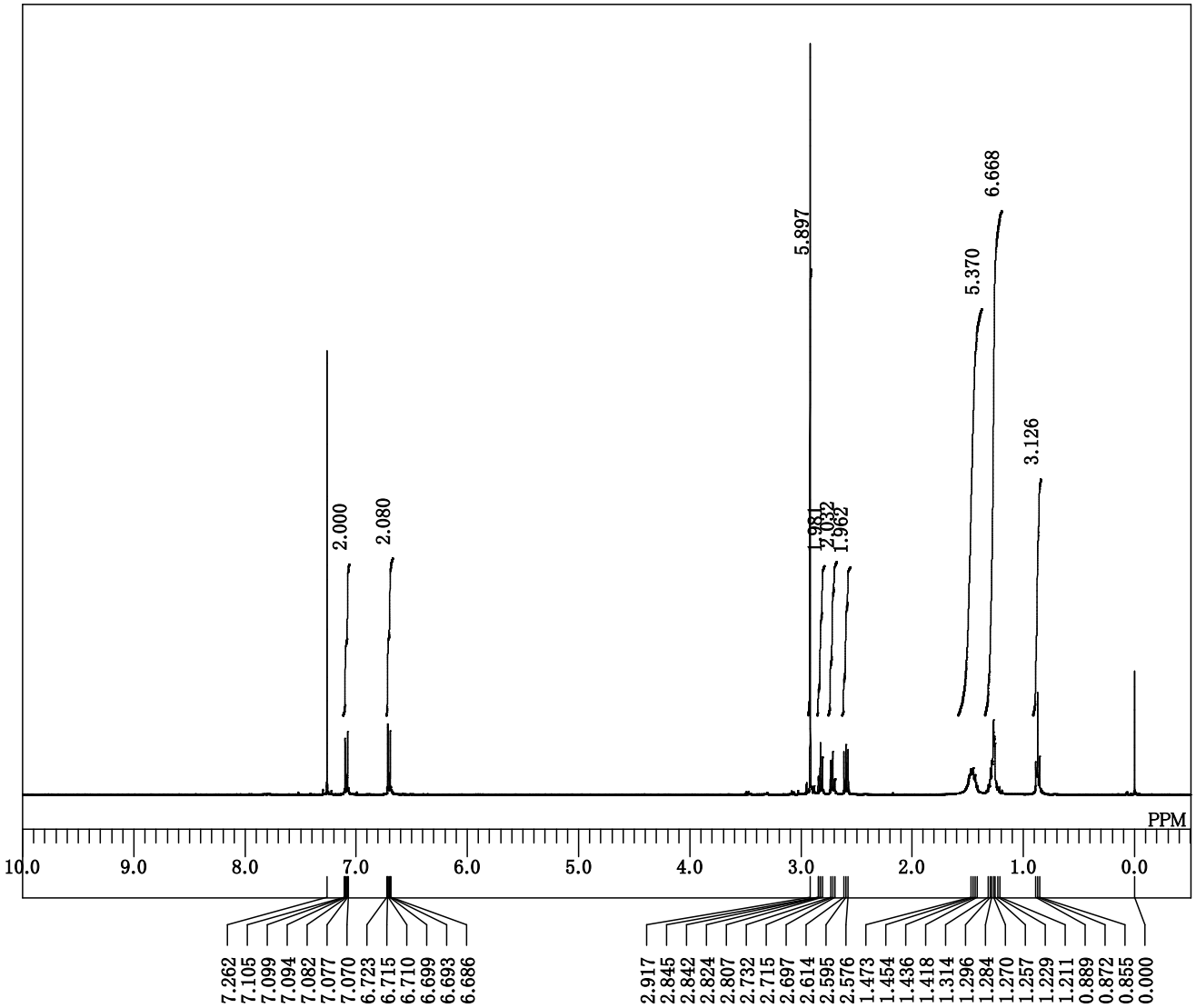
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

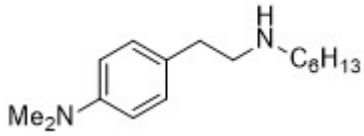




8ea

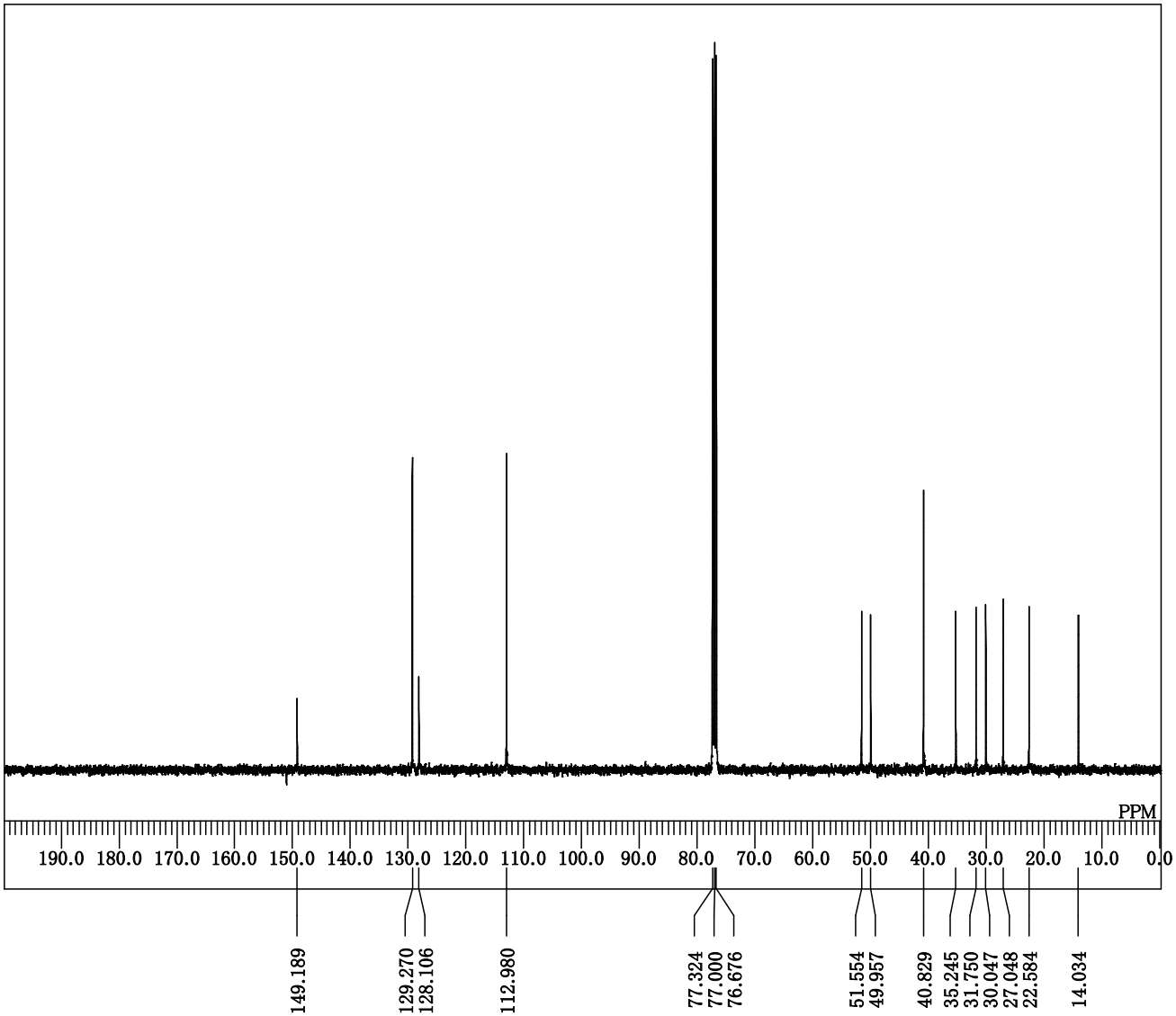
^{1}H NMR (395.88 MHz, $CDCl_3$)

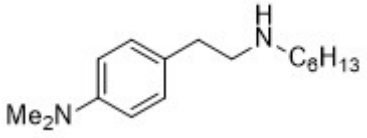




8fa

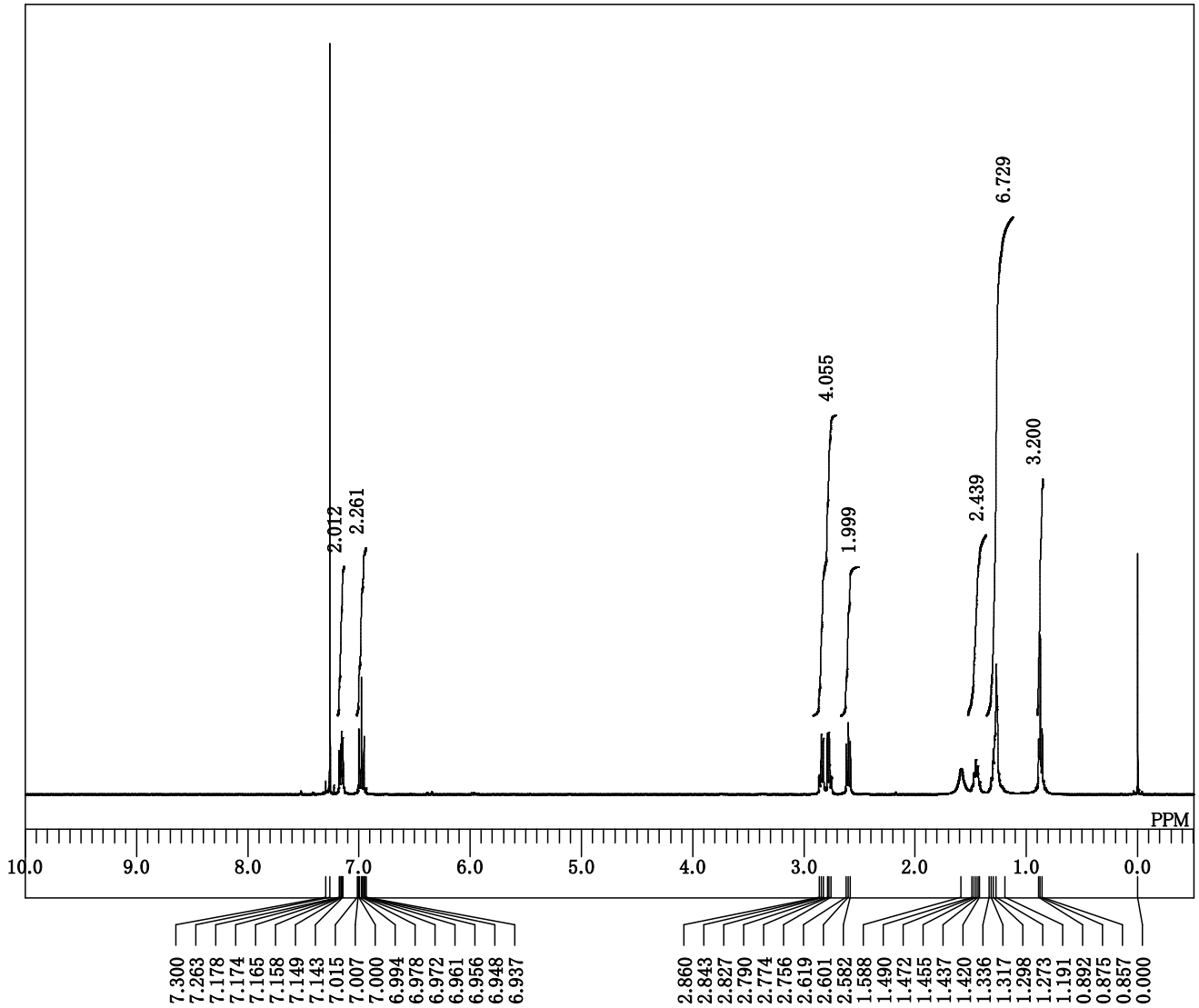
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

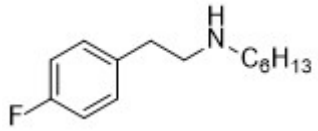




8fa

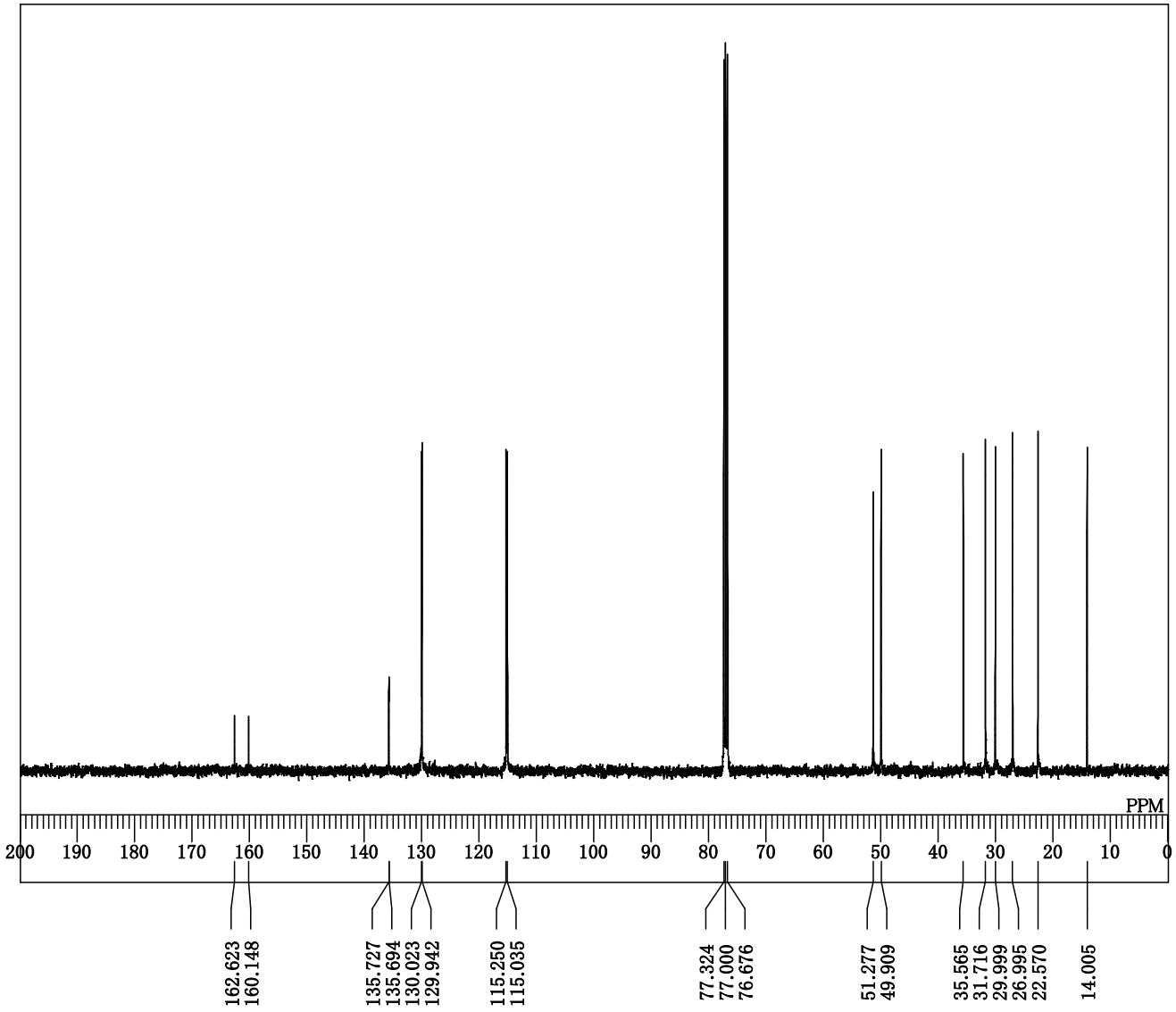
^{1}H NMR (395.88 MHz, $CDCl_3$)

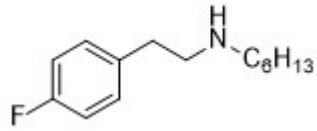




8ga

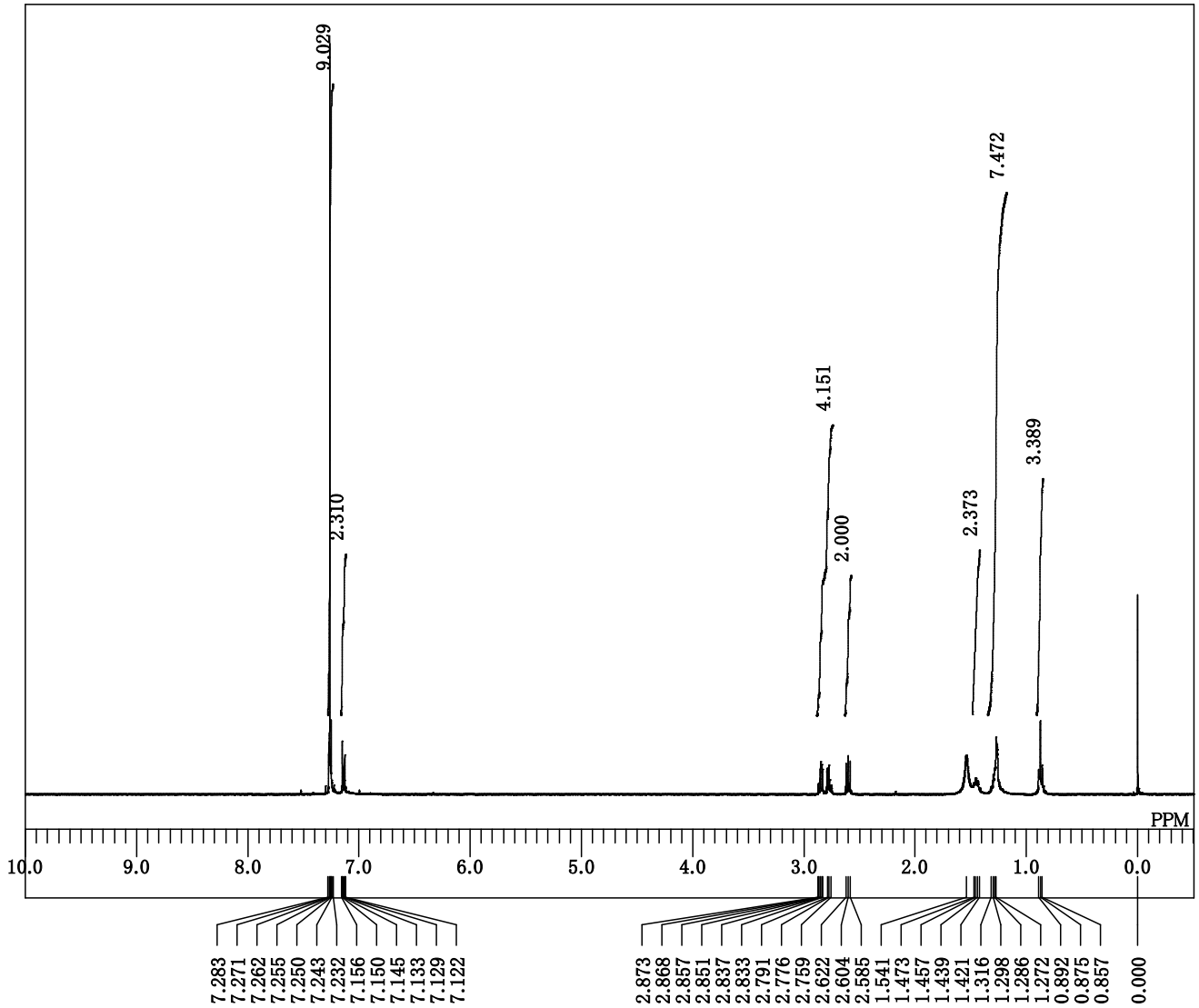
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

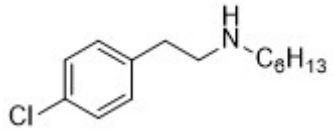




8ga

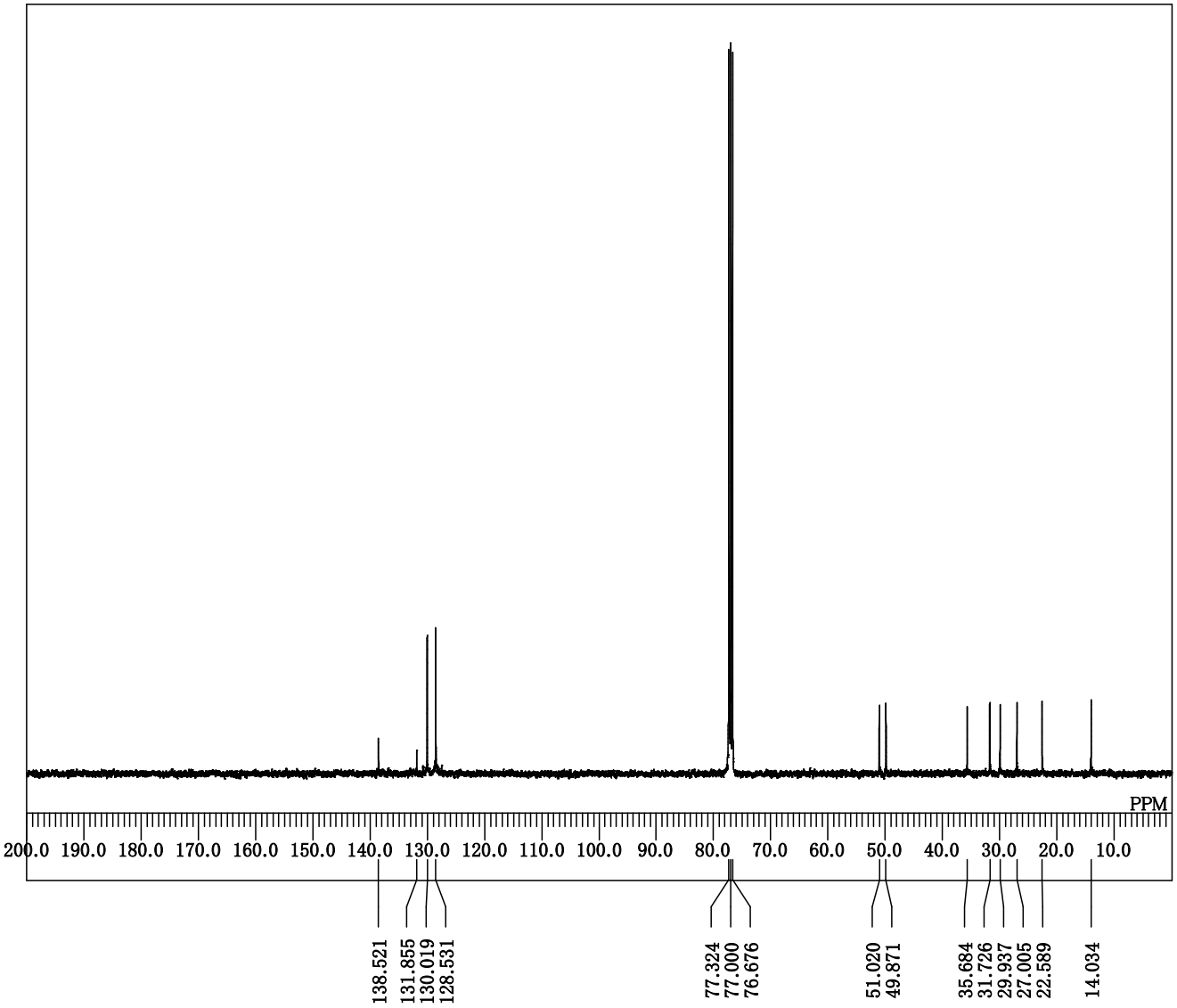
^{1}H NMR (395.88 MHz, $CDCl_3$)

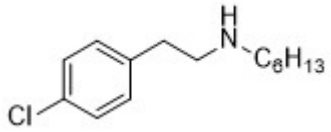




8ha

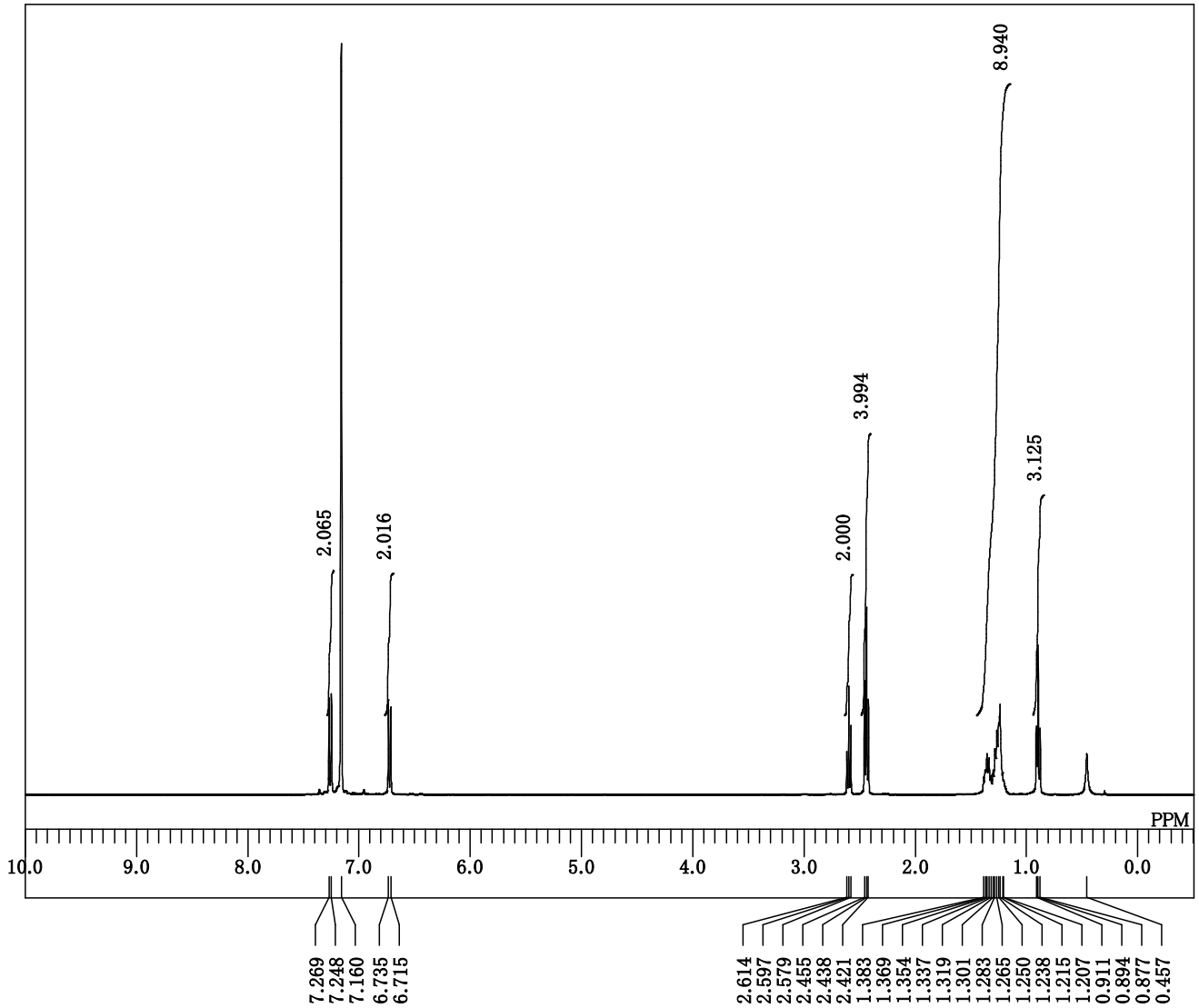
^{13}C {^{1}H} NMR (98.52 MHz, $CDCl_3$)

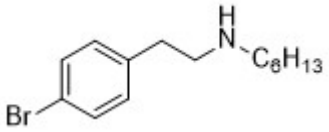




8ha

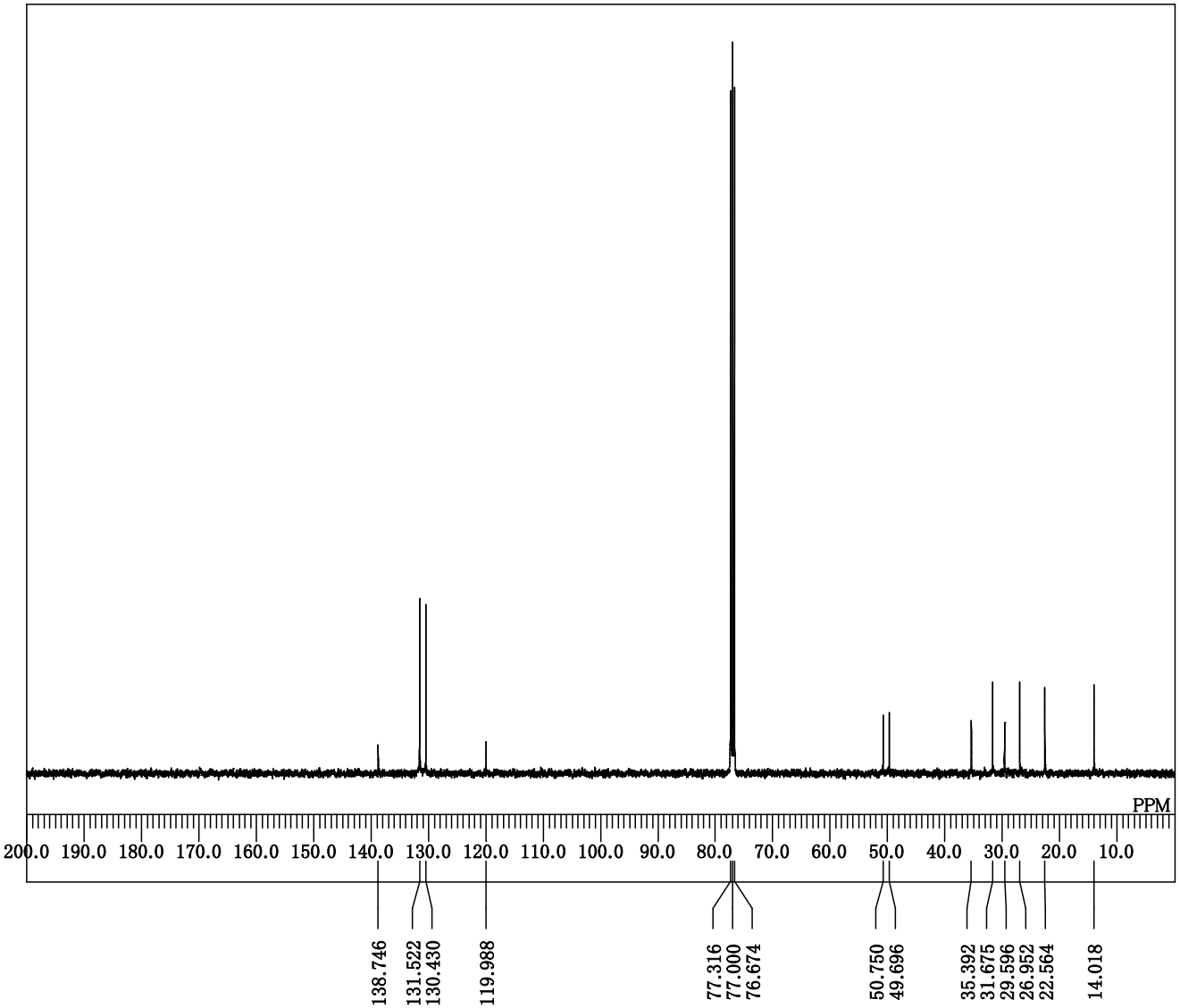
^{1}H NMR (395.88 MHz, C_6D_6)

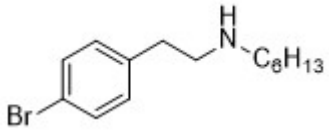




8ia

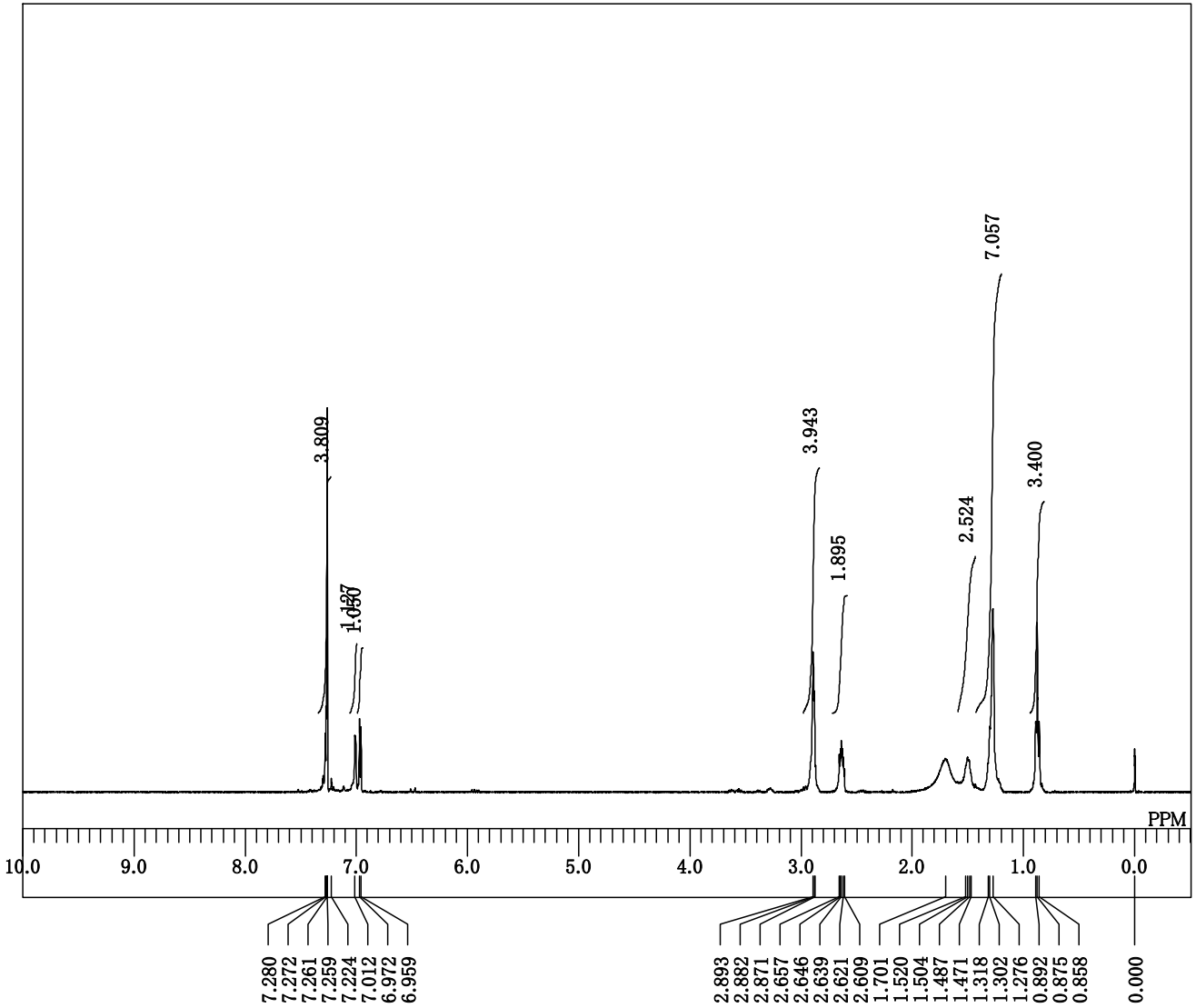
^{13}C {^{1}H} NMR (99.55 MHz, $CDCl_3$)

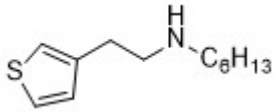




8ia

^{1}H NMR (395.88 MHz, $CDCl_3$)





8ja