Electronic Supplementary Information (ESI)

For *Org. Biomol. Chem.*

K_2CO_3-Promoted formation of aryl esters from primary aryl amides by acyl-acyl exchange process

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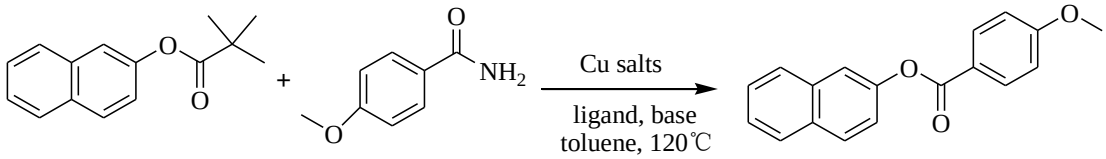
Supporting information

Part Ⅰ Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker ARX-300 or 500 MHz spectrometer with TMS as internal standard. Toluene and THF were distilled over sodium. 1,2-dichloroethane (DCE) and CH_3CN were distilled over calcium hydride. Other solvents were distilled under nitrogen. All bases were commercially available and used as received.

1. Table 1. Optimization of The Acyl-Acyl Exchange Reaction Conditions In the Presence of Copper Salts.[a]

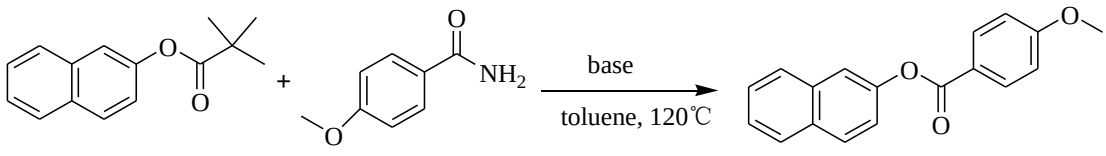


1a **2a** **3aa**

Entry	[Cu](10 mol %)	Ligand	Base	Yield (%)[b]
1	CuI	1,10-phenanthroline	$K_3PO_4 \cdot 3H_2O$	16
2	CuBr	1,10-phenanthroline	$K_3PO_4 \cdot 3H_2O$	23
3	CuCl	1,10-phenanthroline	$K_3PO_4 \cdot 3H_2O$	trace
4	$Cu(OTf)_2$	1,10-phenanthroline	$K_3PO_4 \cdot 3H_2O$	trace
5	$Cu(acac)_2$	1,10-phenanthroline	$K_3PO_4 \cdot 3H_2O$	7
6	$CuCl_2$	1,10-phenanthroline	$K_3PO_4 \cdot 3H_2O$	10
7	$Cu(OAc)_2$	1,10-phenanthroline	$K_3PO_4 \cdot 3H_2O$	<5
8	$CuSO_4$	1,10-phenanthroline	$K_3PO_4 \cdot 3H_2O$	11
9	CuI	2,2′-dipyridyl	$K_3PO_4 \cdot 3H_2O$	15
10	CuI	1,10-phenanthroline	K_2CO_3	58
11	-	-	-	0
12	CuI	1,10-phenanthroline	-	0
13	-	-	K_2CO_3	60

[a] Conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), [Cu] (0.025 mmol), ligand (0.05 mmol), base (2 equiv), 120℃ for 12 h in toluene, unless otherwise noted. [b] Isolated yield..

2.Table 2. Screening of Various Bases for This Acyl-Acyl Exchange Reaction without the Transition Metal [a]



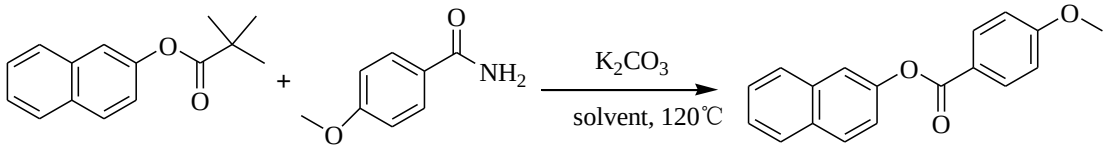
1a **2a** **3aa**

Entry	Base	Yield (%)[b]
1	$K_3PO_4 \cdot 3H_2O$	18
2	*t*-BuOK	33
3	LiOAc	trace

4	NaOAc	0
5	Cs_2CO_3	43 [c]
6	KF	0
7	CsF	trace
8	NaOTf	0
9	DBU	0
10	$NaCO_3$	0
11	KOH	33
12	*t*-BuOLi	52
13	CsOH	50
14	Ag_2CO_3	0
15	K_2CO_3	60
16	K_2CO_3	72 [d]
17	K_2CO_3	79 [e]
18	K_2CO_3	82 [f]

[a] Conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), base (2 equiv), 120℃ for 12 h in toluene, unless otherwise noted. [b] Isolated yield. [c] 1 equiv of Cs_2CO_3 was used. [d] 1 equiv of K_2CO_3 was used. [e] 0.5 equiv of K_2CO_3 was used. [f] 20 mol% of K_2CO_3 was used

3. Table 3. Screening of Various Solvents for This Acyl-Acyl Exchange Reaction without the Transition Metal [a]

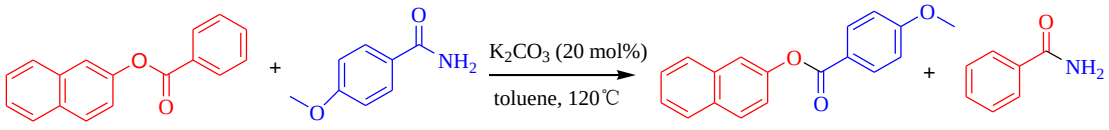


1a **2a** **3aa**

Entry	Solvent	Yield (%)[b]
1	toluene	82
2	1,4-dioxane	trace
3	DCE	0
4	CH_3CN	0
5	THF	0
6	DMF	<5
7	anisole	0
8	DMAc	0
9	DMSO	0

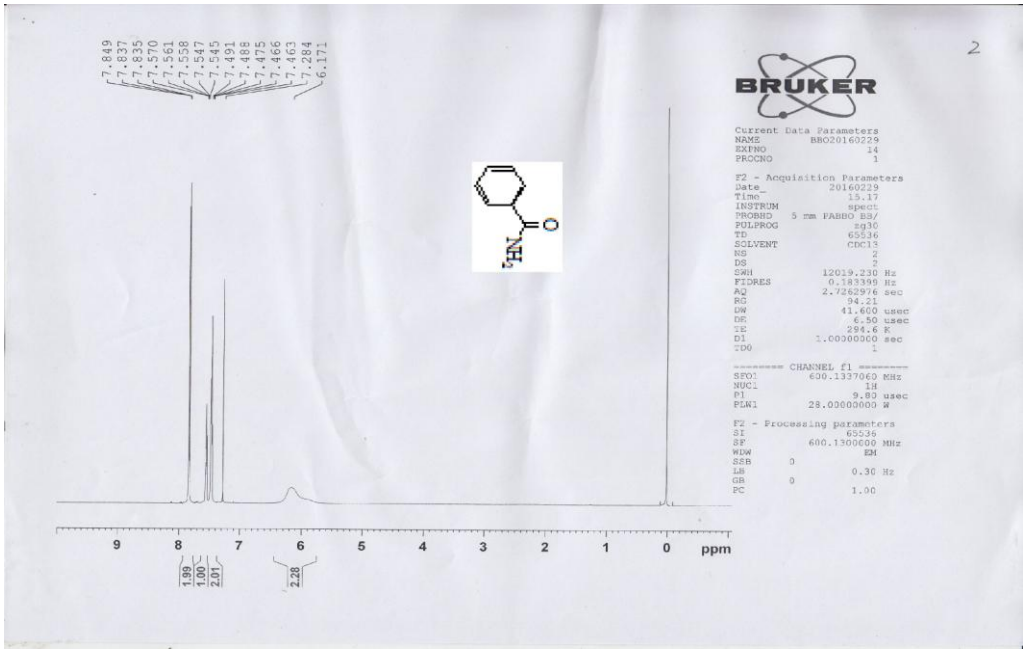
[a] Conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), K_2CO_3 (20 mol%), 120℃ for 12 h in solvent, unless otherwise noted. [b] Isolated yield.

4. Isolation of the primary amide products for the evidence of the proposed acyl-acyl exchange reaction.

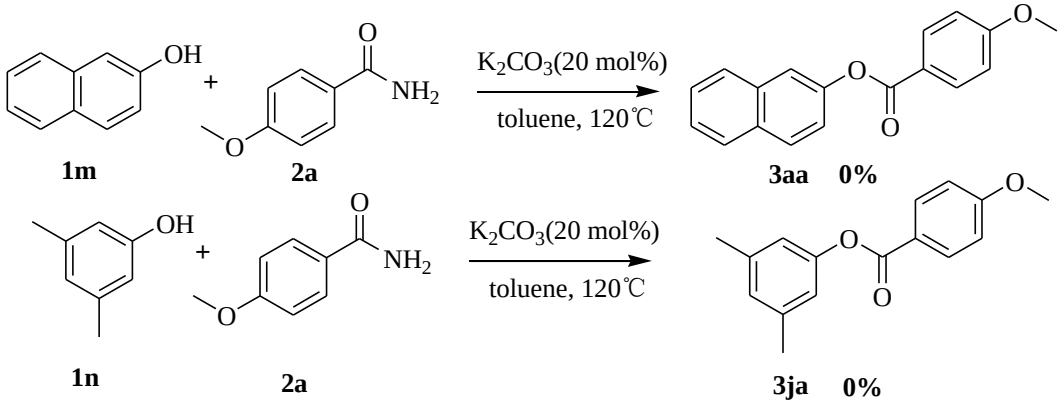


1C **2a** **3aa** **4**

A mixture of 2-naphthyl benzoate 1C (0.25 mmol), 4-methoxybenzamide **2a** (0.5 mmol) and K_2CO_3 (20 mol%) in toluene was stirred at 120 ℃ for 12 h. After the reaction was achieved, the primary benzamide product **4** was isolated by preparative TLC (silica gel, EtOAc as eluent) in 33% yield (10 mg) as a white solid**:** R_f = 0.56 (in EtOAc); ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm): 7.84 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 6.17 (s, 2H).



5. The reaction of unprotected 2-naphthol with 4-methoxybenzamide

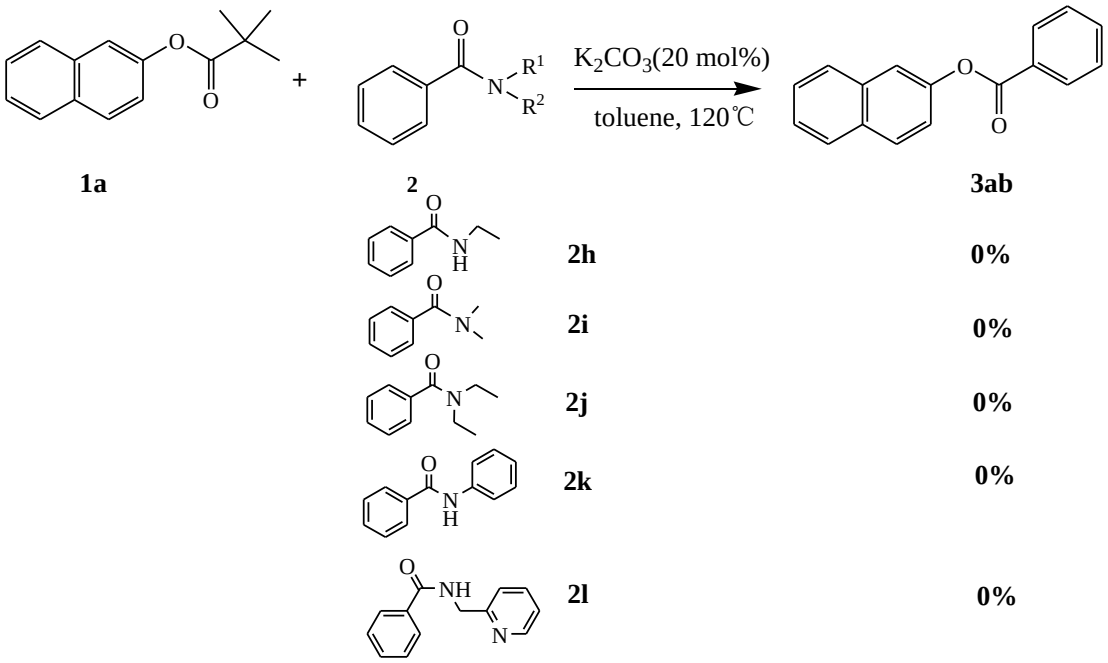


1m **2a** **3aa** **0%**

1n **2a** **3ja** **0%**

Scheme 1. The unprotected 2-naphthol and 3, 5-dimethylphenol was tried for this reaction. A mixture of 1m or 1n (0.25 mmol), 4-methoxybenzamide 2a (0.50 mmol) and K_2CO_3 (20 mol%) in toluene was stirred at 120℃ for 12 h;

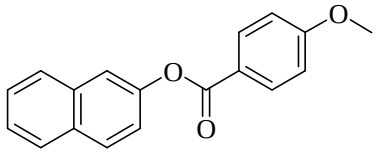
6. The reaction of secondary and tertiary amides with 2-naphthyl pivalate



Scheme 2. Several secondary and tertiary amides were tried for this reaction under the standard condition.

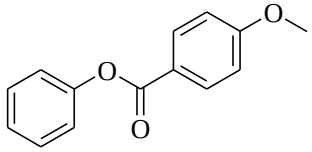
General Procedure for This Acyl-Acyl Exchange Reaction of esters with primary amides: A mixture of esters **1** (0.25 mmol), primary amides **2** (0.5 mmol) and K_2CO_3 (20 mol%) in toluene was stirred in a sealed tube under air without a reflux condenser attached at 120 ℃ for 12 h. After the reaction was achieved, the crude mixture was purified by column chromatography (silica gel, EtOAc / petroleum ether) to afford the desired products **3.** All products have been reported previously and identical with that described in literature.

naphthalen-6-yl 4-methoxybenzoate **3aa** [1]



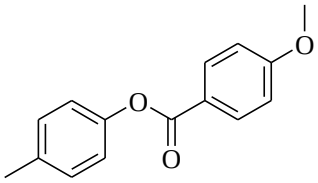
The general procedure was followed with 2-naphthyl pivalate (0.25 mmol), 4-methoxybenzamide (0.5 mmol) and K_2CO_3 (20 mol%); Yield: 57 mg, 82%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.22 (d, *J* = 8.7 Hz, 2H), 7.92-7.83 (m, 3 H), 7.69 (d, *J* = 1.5 Hz, 1 H), 7.54-7.47 (m, 2 H), 7.38-7.35 (m, 1 H) 7.02 (d, *J* = 8.7 Hz, 2 H), 3.92 (s, 3H); MS (EI) m/z (%) 278.1 (M+, 17.5),135.0(100), 107.0 (26.8), 77.0 (31.0).

phenyl 4-methoxybenzoate **3ba** [2]



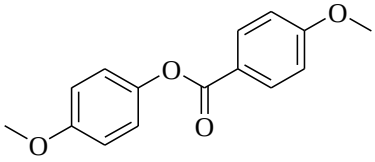
Yield: 41.6 mg, 73%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.19-8.15 (m, 2 H), 7.46-7.41 (m, 2 H), 7.30-7.20 (m, 3 H), 7.02-6.98 (m, 2 H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 164.8, 163.9, 150.9, 132.2, 129.5, 125.6, 121.8, 121.7, 113.8, 55.4.

p-tolyl 4-methoxybenzoate **3ca** [3]



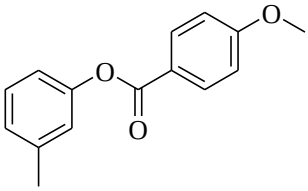
Yield: 44.7 mg, 74%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.19-8.14 (m, 2 H), 7.21 (d, *J* = 8.4Hz, 2 H), 7.10 (d, *J* = 8.4Hz, 2 H), 7.03-7.01 (m, 2 H), 3.91 (s, 3H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 165.0, 163.8, 148.8, 135.0, 132.2, 130.0, 122.2, 121.5, 113.9, 55.4, 20.9.

4-methoxyphenyl 4-methoxybenzoate **3da** [4]



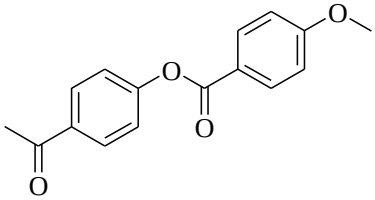
Yield: 48.3 mg, 75%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.17-8.14 (m, 2 H), 7.14-7.10 (m, 2 H), 7.00-6.91 (m, 4 H), 3.90 (s, 3H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 165.3, 163.8, 157.2, 144.5, 132.2, 122.5, 122.0, 114.5, 113.8, 55.6, 55.5.

m-tolyl 4-methoxybenzoate **3ea** [3]



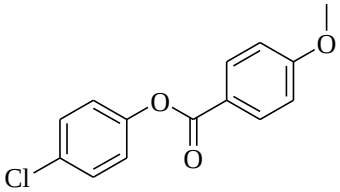
Yield: 36.7 mg, 61%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.19-8.14 (m, 2 H), 7.34-7.27 (m, 1 H),, 7.10-6.97 (m, 5 H), 3.90 (s, 3H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 165.1, 163.9, 151.0, 139.6, 132.3, 129.2, 126.6, 122.4, 122.0, 118.8, 113.8, 55.5, 21.4.

4-acetylphenyl 4-methoxybenzoate **3fa** [5]



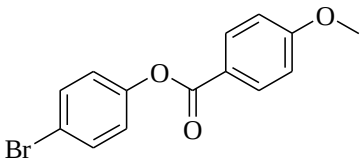
Yield: 26 mg, 39%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.16 (d, *J* = 8.4Hz, 2 H), 8.03 (d, *J* = 8.1Hz, 2 H), 7.32 (d, *J* = 8.4Hz, 2 H), 7.00 (d, *J* = 8.1Hz, 2 H), 3.91 (s, 3H), 2.63 (s, 3H); MS (EI) m/z (%) 270.0 (M^+, 0.15),135.9(6), 134.9 (100), 120.9(8), 106.9(6).

4-chlorophenyl 4-methoxybenzoate **3ga** [2]



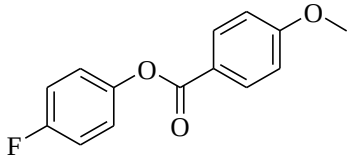
Yield: 49.4 mg, 76%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.17-8.12 (m, 2 H), 7.40 (d, *J* = 8.8 Hz, 2 H), 7.15 (d, *J* = 8.8 Hz, 2 H), 7.03-6.96 (m, 2 H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 163.9, 149.5, 132.2, 131.0, 129.4, 123.0, 121.3, 113.8, 55.4.

4-bromophenyl 4-methoxybenzoate **3ha** [6]



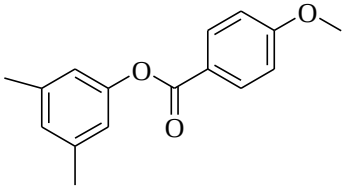
Yield: 55.8 mg, 73%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.17-8.12 (m, 2 H), 7.56-7.51 (m, 2 H), 7.13-7.08 (m, 2 H), 7.02-6.97 (m, 2 H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 164.6, 164.1, 150.1, 132.5, 132.3, 123.6, 121.4, 118.8, 113.9, 55.5.

4-fluorophenyl 4-methoxybenzoate **3ia** [7]



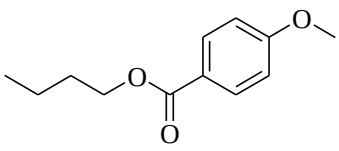
Yield: 44 mg, 72%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.17-8.13 (m, 2 H), 7.20-7.08 (m, 4 H),, 7.01-6.97 (m, 2 H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 164.9, 164.0, 160.1 (d, *J* = 243.0 Hz), 146.8, 132.2, 123.1, 121.4, 115.9 (d, *J* = 23.3 Hz), 113.8, 55.4.

3, 5-dimethylphenyl 4-methoxybenzoate **3ja** [8]



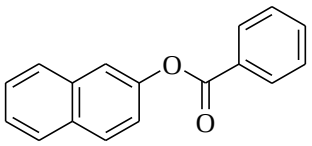
Yield: 34.4 mg, 54%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.18-8.13 (m, 2 H),7.01-6.96 (m, 2 H), 6.90 (s, 1H), 6.83 (s, 2H),3.90 (s, 3H), 2.35 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 165.2, 163.8, 151.0, 139.3, 132.3, 127.5, 122.1, 119.4, 113.8, 55.5, 21.3.

butyl 4-methoxybenzoate **3la** [9]



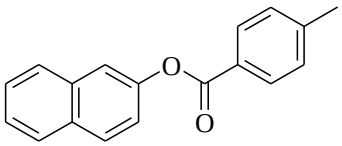
Yield: 38.2 mg, 74%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.01-7.98 (m, 2 H), 6.92 (d, *J* = 8.7Hz, 2 H),, 4.29 (t, *J* = 6.6Hz, 2H) 3.86 (s, 3H),1.78-1.69 (m, 2 H), 1.54-1.41 (m, 2 H), 0.98 (t, *J* = 7.5Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 166.4, 163.3, 131.5, 123.0, 113.5, 64.5, 55.3, 31.0, 19.3, 13.8.

naphthalen-6-yl benzoate **3ab** [10]



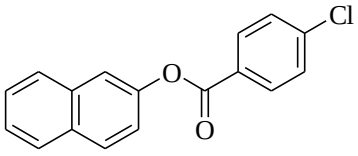
Yield: 50 mg, 81%; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 8.69 (s, 1H), 8.08 (d, J = 8.6 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.86-7.79 (m, 2H), 7.55-7.46 (m,2H), 7.39-7.36 (m, 2H), 7.21-7.11 （m, 3H）; ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 165,3, 151.0, 135.8, 132.5, 131.9, 129.6, 129.5, 128.7, 128.4, 127.8, 126.8, 126.0, 125.4, 121.7.

naphthalen-6-yl 4-methylbenzoate **3ac** [2]



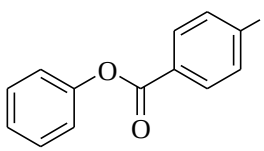
Yield: 54 mg, 82%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.16 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.93-7.83 (m, 3 H), 7.70 (d, *J* = 2.4 Hz, 1 H), 7.55-7.47 (m, 2 H), 7.38-7.33 (m, 3 H) , 2.48 (s, 3H); MS (EI) m/z (%) 278.1 (M^+, 19.9), 119.0 (100), 91.0 (42.8).

naphthalen-3-yl 4-chlorobenzoate **3ad** [2]



The general procedure was followed with 2-naphthyl pivalate (0.25 mmol), 4-chlorobenzamide (0.5 mmol) and K_2CO_3 (20 mol%); Yield: 56 mg, 80%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.20 (d, *J* = 8.7Hz, 2 H), 7.94-7.84 (m, 3 H), 7.71 (d, *J* = 1.8Hz, 1 H), 7.56-7.48 (m, 4 H), 7.37 (dd, *J* = 8.4, 2.4Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 164.6, 148.4, 140.2, 133.8, 131.63, 131.60, 129.6, 129.0, 128.1, 128.0,127.7, 126.7, 125.9,121.1,118.7.

phenyl 4-bromobenzoate **3be** [11]



Yield: 49.4 mg, 72%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 8.08 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.48 -7.42 (m, 2H), 7.32-7.28 (m, 1H), 7.23 -7.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 164.5, 150.7, 131.9, 131.6, 129.5, 128.8, 128.5,126.0, 121.6.

Reference

[1] Rosa, J. N.; Reddy, S.; Candeias, N. R.; Cal, P. M. S. D.; Gois, P. M. P. *Org. Lett*, 2010, **12,** 2686.

[2] Arde, P.; Ramanjaneyulu, B. T.; Reddy, V.; Saxena, A.; Anand, R. V. *Org. Biomol. Chem*., 2012, **10**, 848-851.

[3] He, H. Q.; Chang, Y. W.; Xu, W. M. *Lett. Org. Chem*, 2015, **12,** 280.

[4] Fitzjarrald, V. P.; Pongdee, R. *Tetrahedron Lett*, 2007, **48**, 3553

[5] Bao, Y.-S.; Chen, C.-Y.; Huang, Z.-Z. *J. Org.Chem.* 2012, **77**, 8344.

[6] Helmi, N.; Kari, N.; Paavo, P. *J. Org.Chem.* 2004, **69**, 3794.

[7] K. C. Joshi.; S. C. Bahel.; J. Indian Chem. Soc., 1960, **37**, 687

[8] Shintou, T.; Fukumoto, K.; Mukaiyama, *T. B Chem Soc Jpn.* 2004, **77**, 1569.

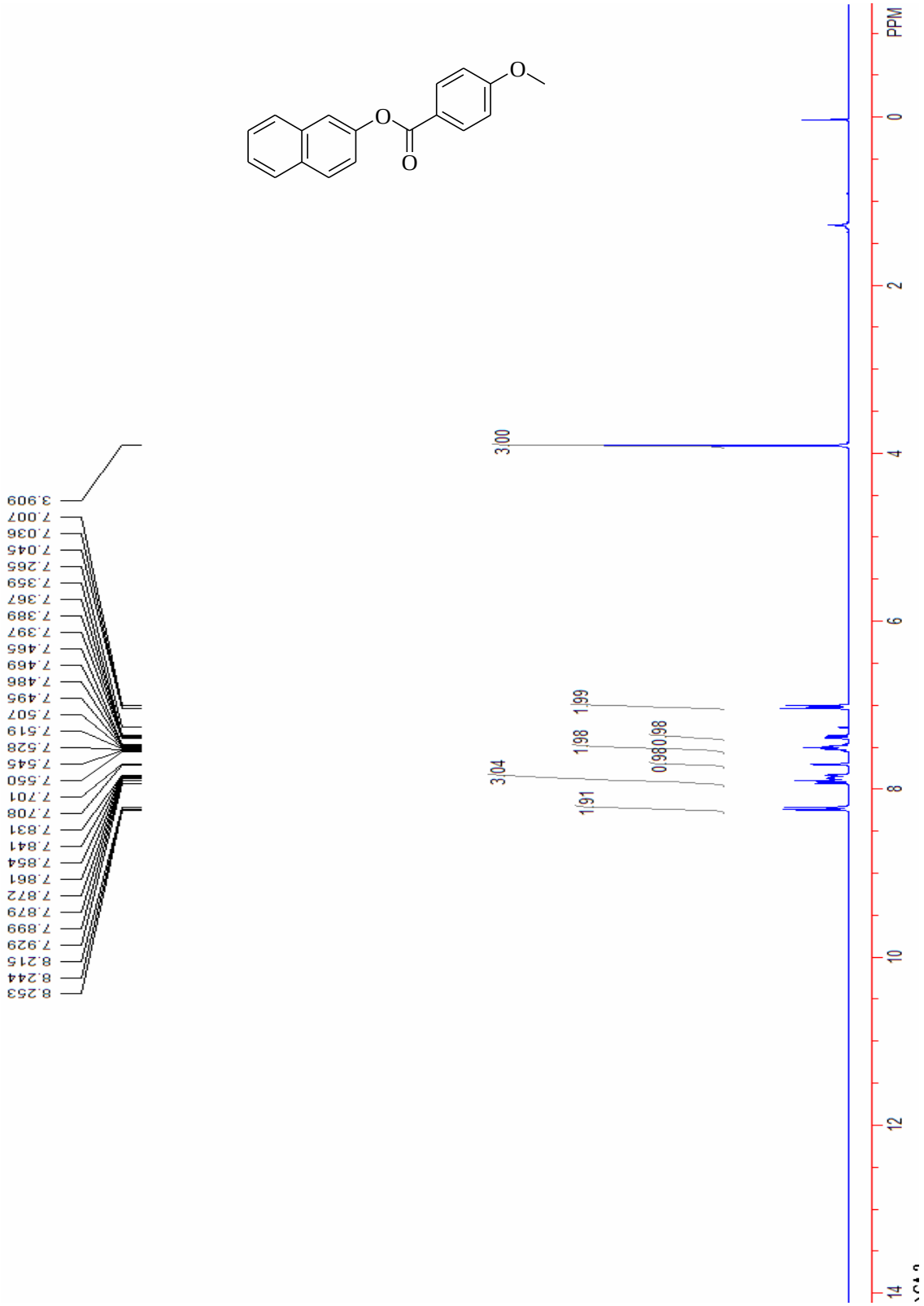
[9] Ma, G..-Z.; Leng, Y.-T.; Qiao, H.-J.; Yang, F.; Wang, S.-W.; Wu, Y.-J. *Appl. Organomet. Chem.*, 2014, **28**, 44.

[10] Chen, J. X.; Peng, Y.; Liu, M. C.; Ding, J. C.; Su, W. K.; Wu, H. Y. *Adv. Synth. Catal.* 2012, **354**, 2117.

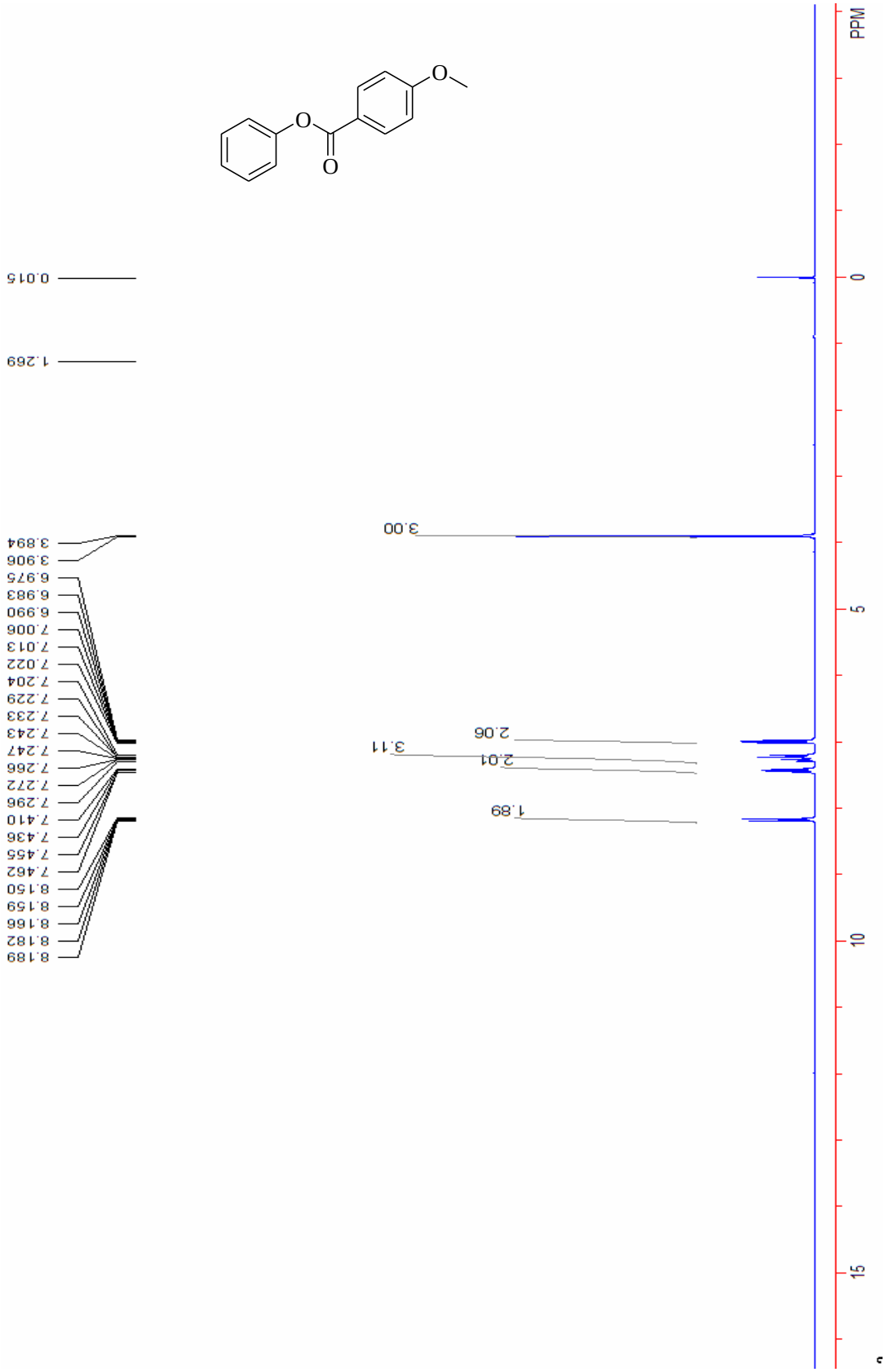
[11] Luo, F.; Pan, C. D.; Qian, P. C.; Cheng, J. *Synthesis.* 2010, **12**, 2005.

Part II ^{1}H NMR and ^{13}C NMR

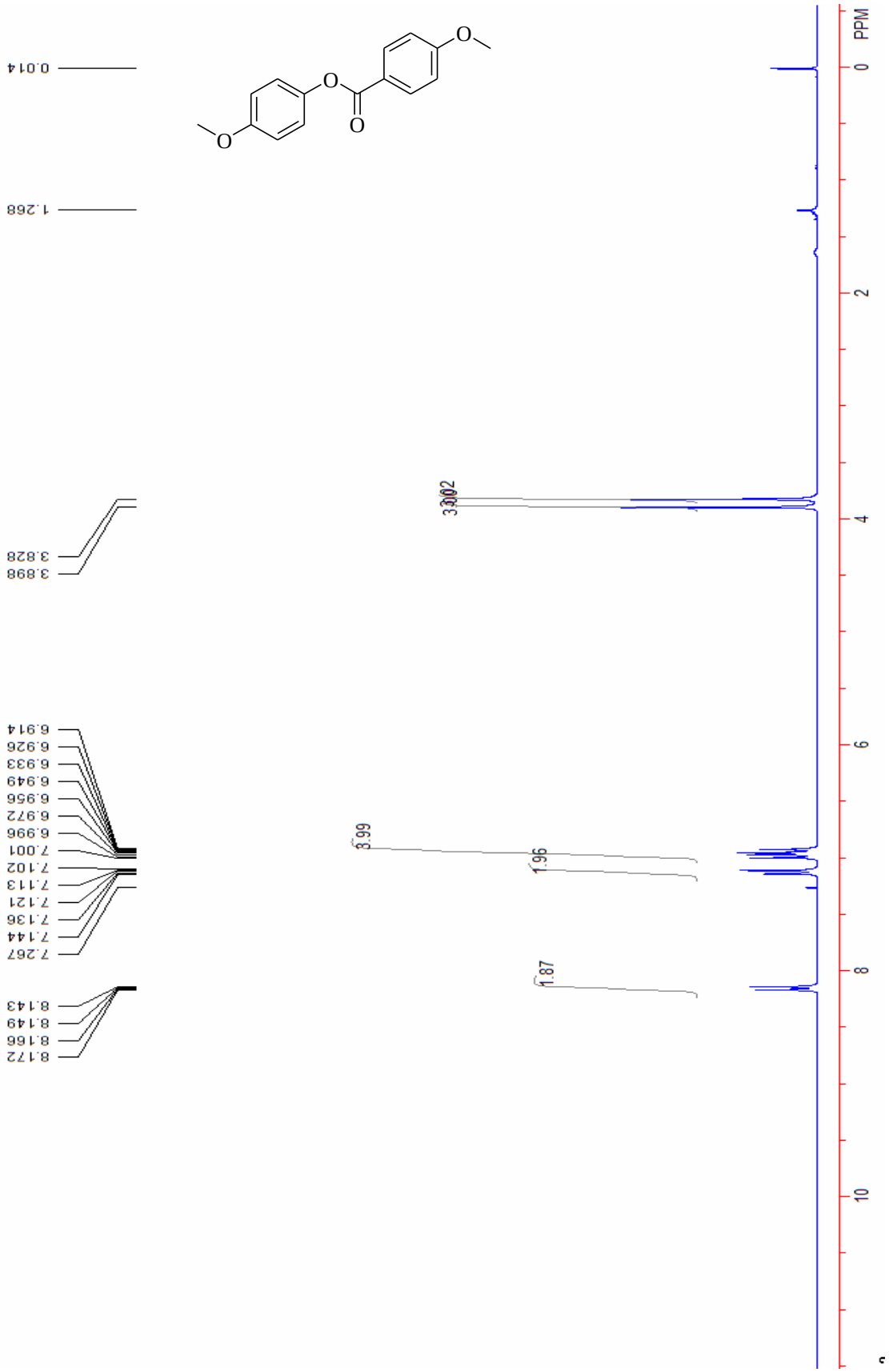
^{1}H NMR of naphthalen-6-yl 4-methoxybenzoate **3aa**



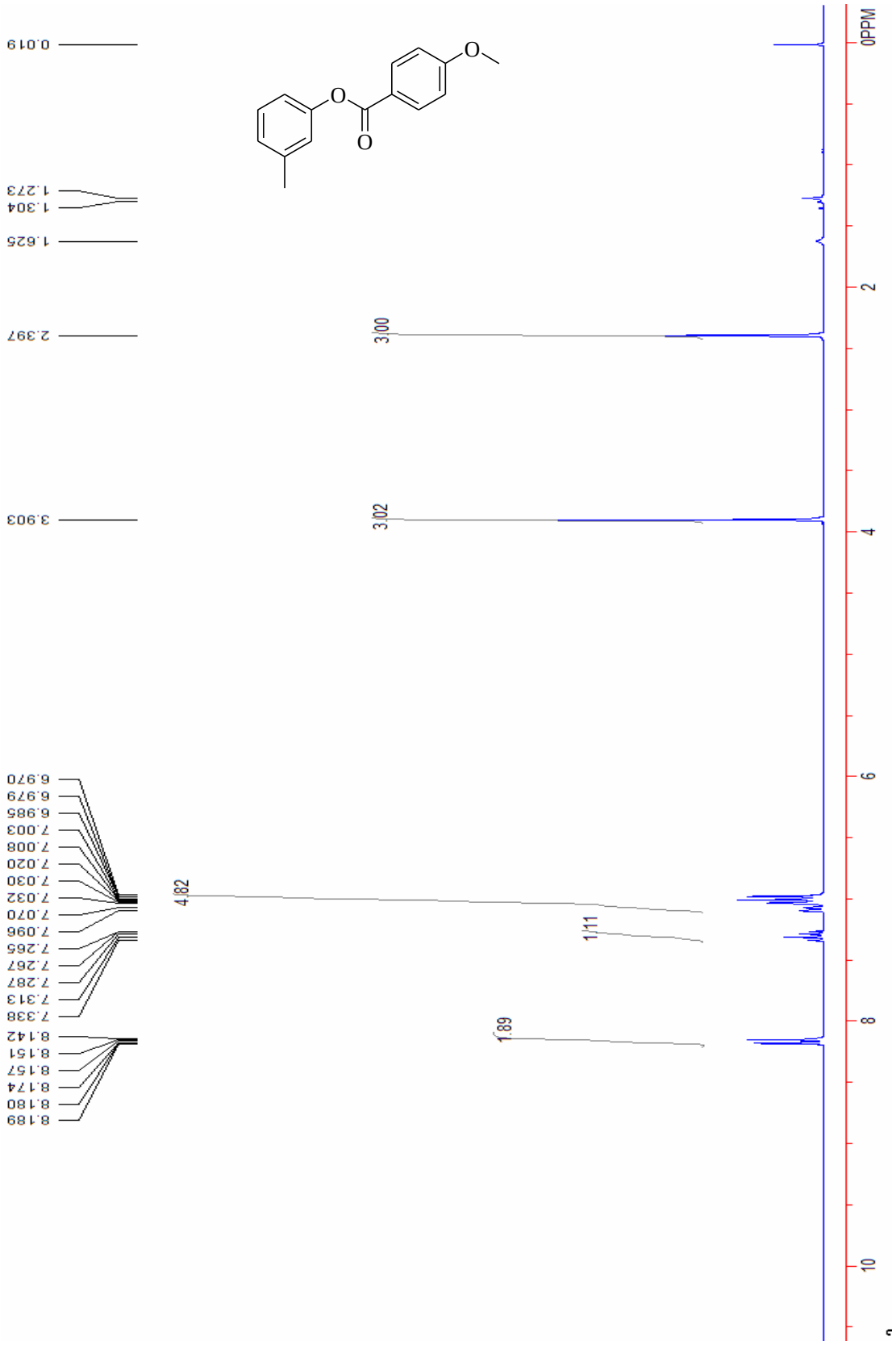
^{1}H NMR of phenyl 4-methoxybenzoate **3ba**



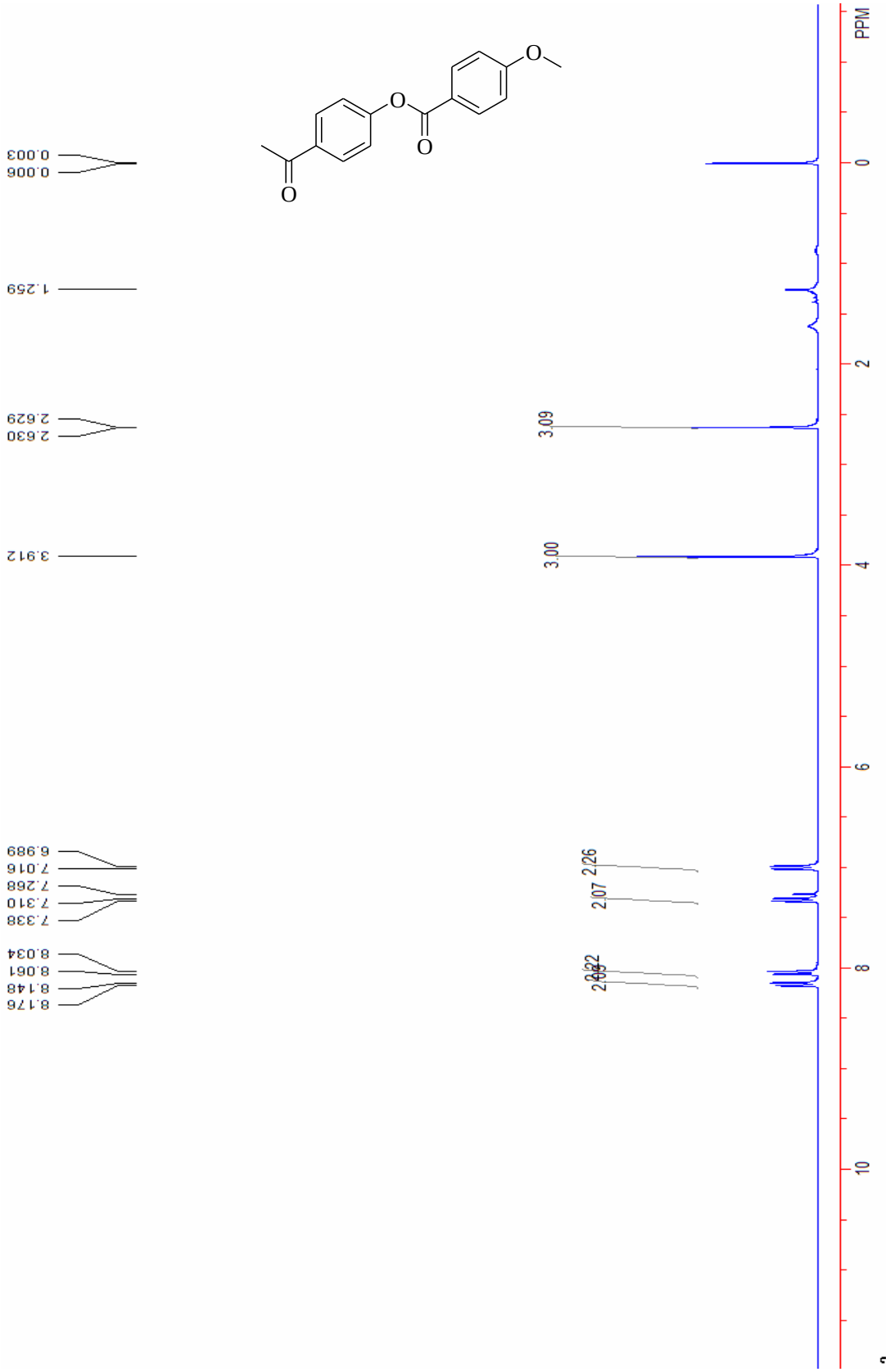
^{1}H NMR of 4-methoxyphenyl 4-methoxybenzoate **3da**



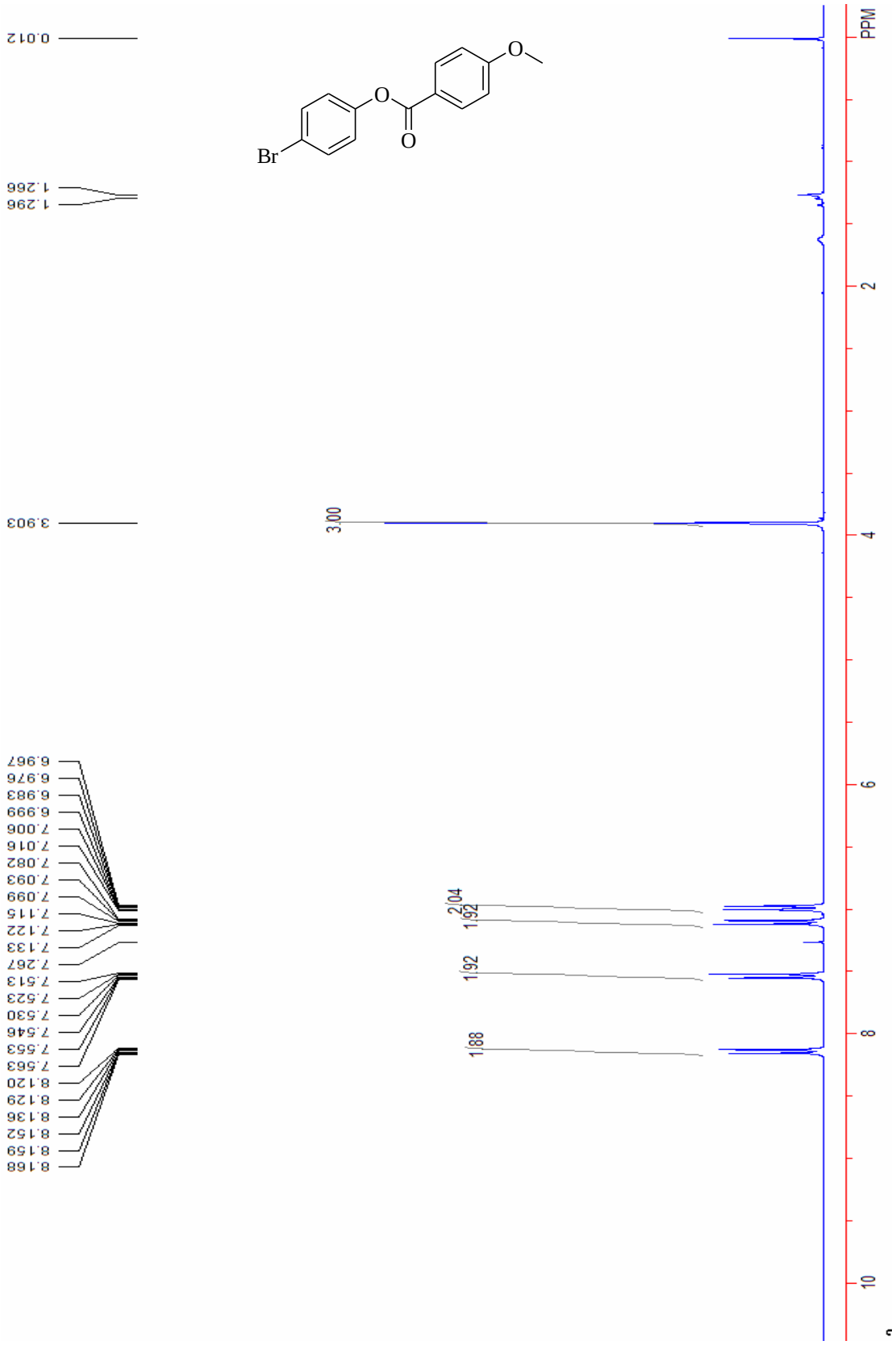
^{1}H NMR of m-tolyl 4-methoxybenzoate **3ea**



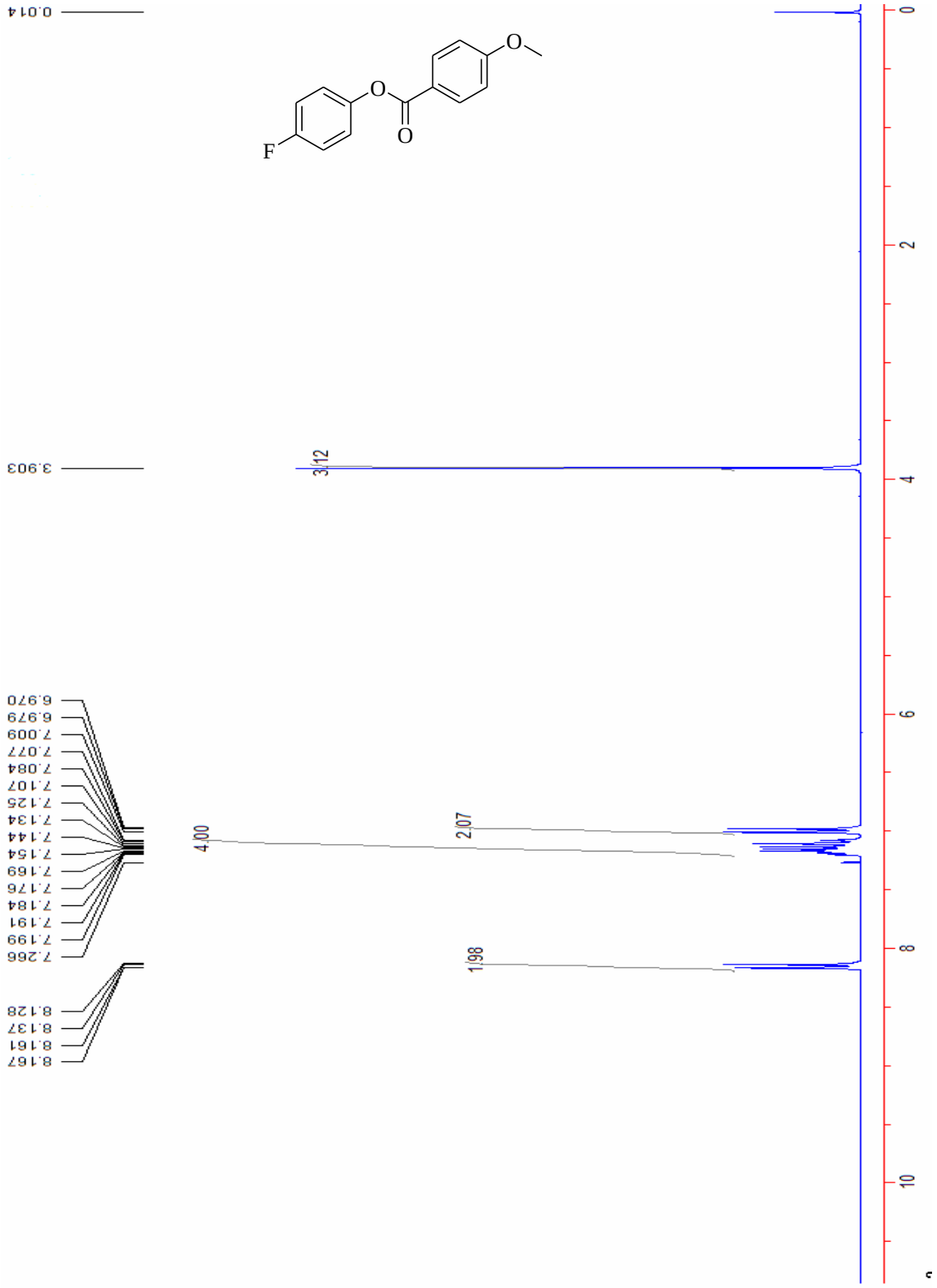
^{1}H NMR of 4-acetylphenyl 4-methoxybenzoate **3fa**



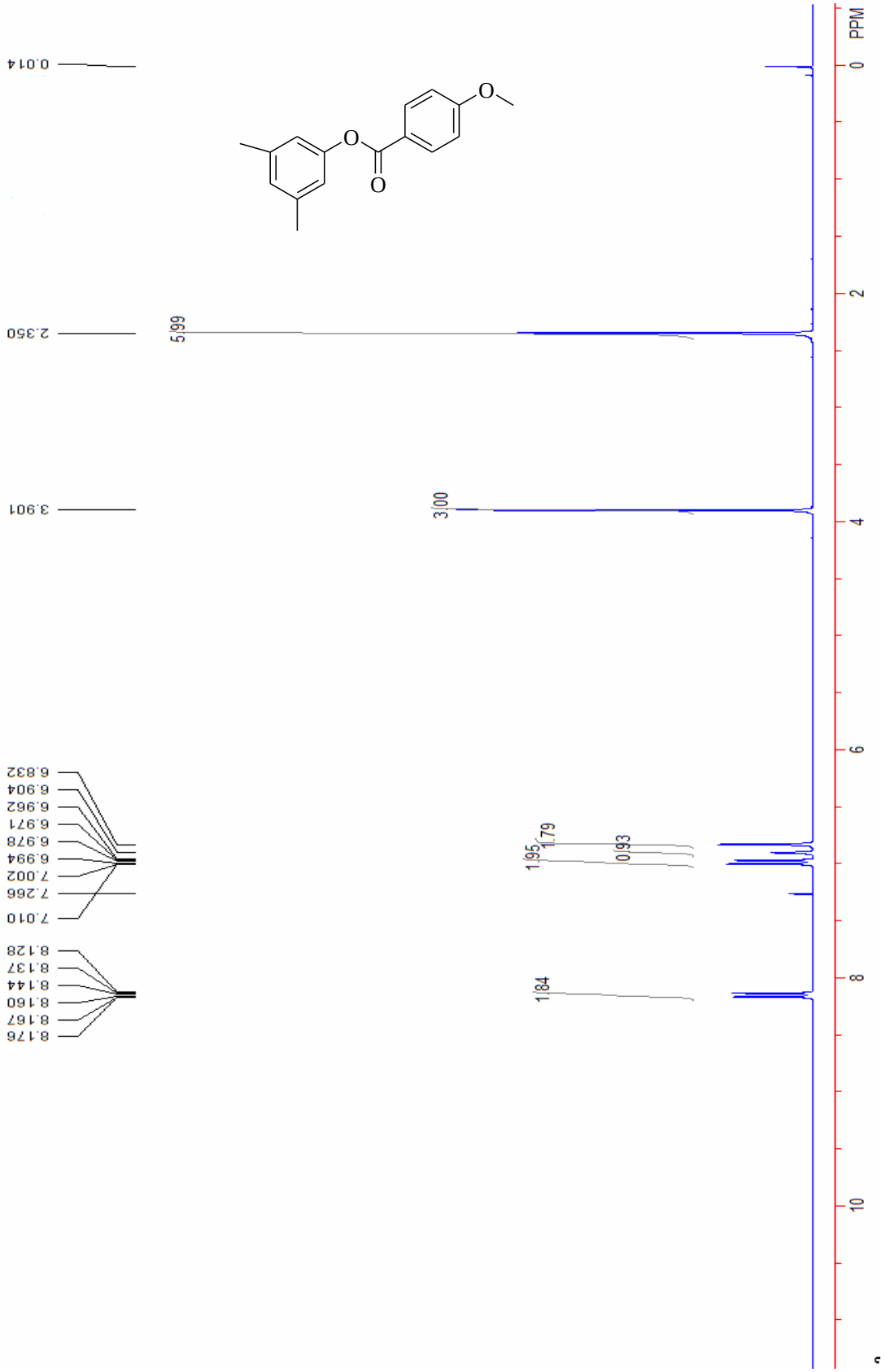
^{1}H NMR of 4-bromophenyl 4-methoxybenzoate **3ha**



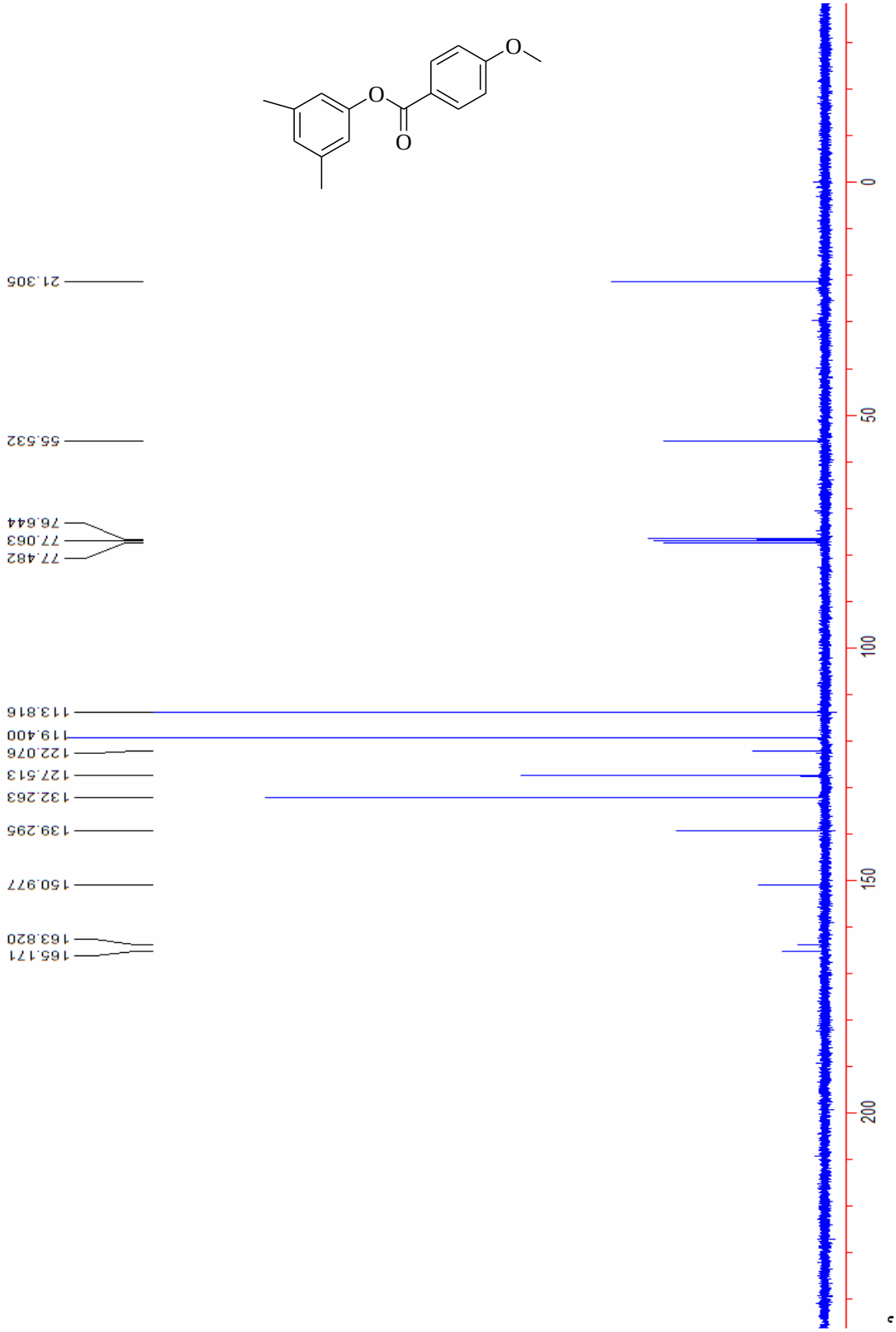
^{1}H NMR of 4-fluorophenyl 4-methoxybenzoate **3ia**



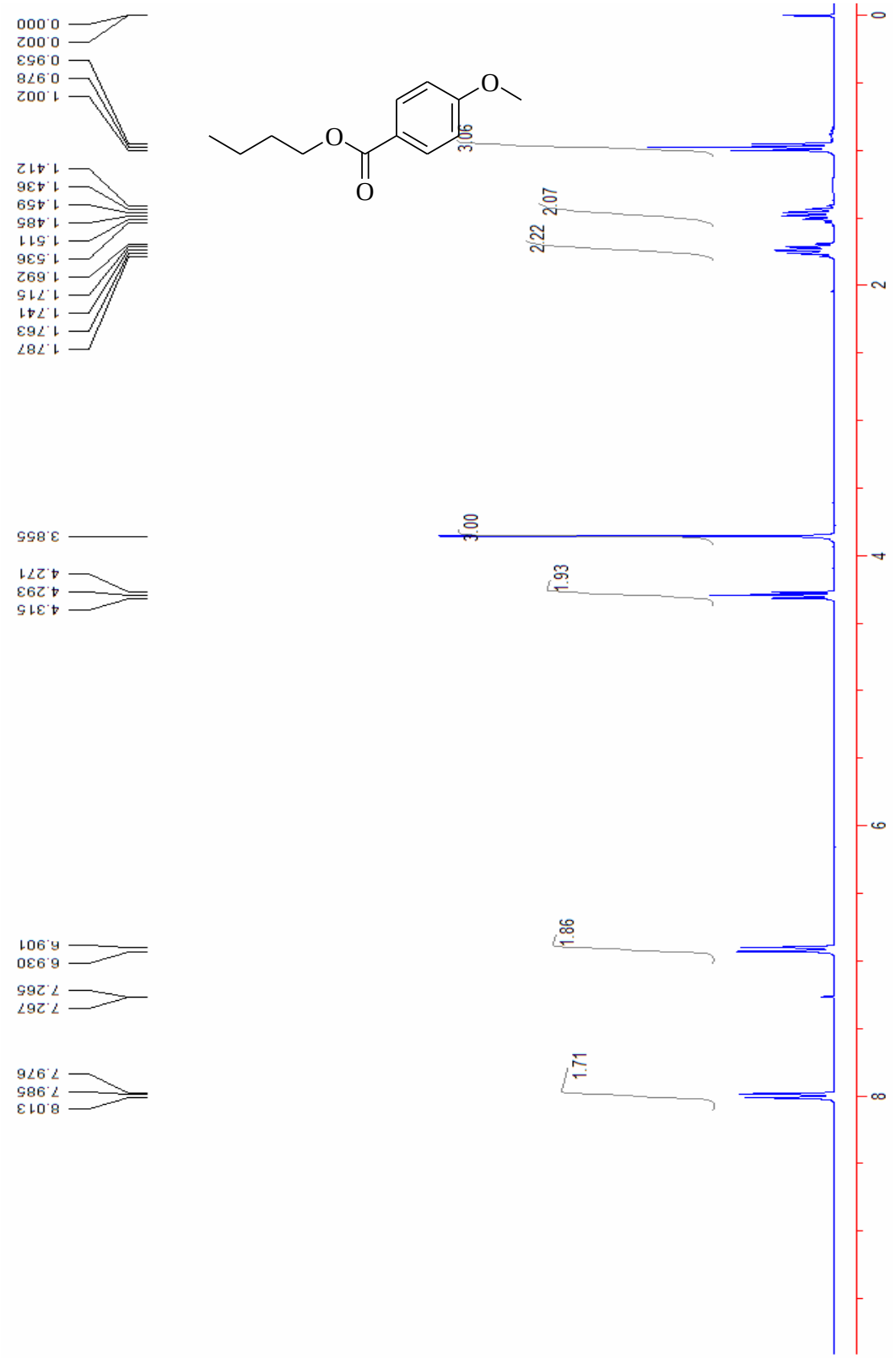
^{1}H NMR of 3,5-dimethylphenyl 4-methoxybenzoate **3ja**



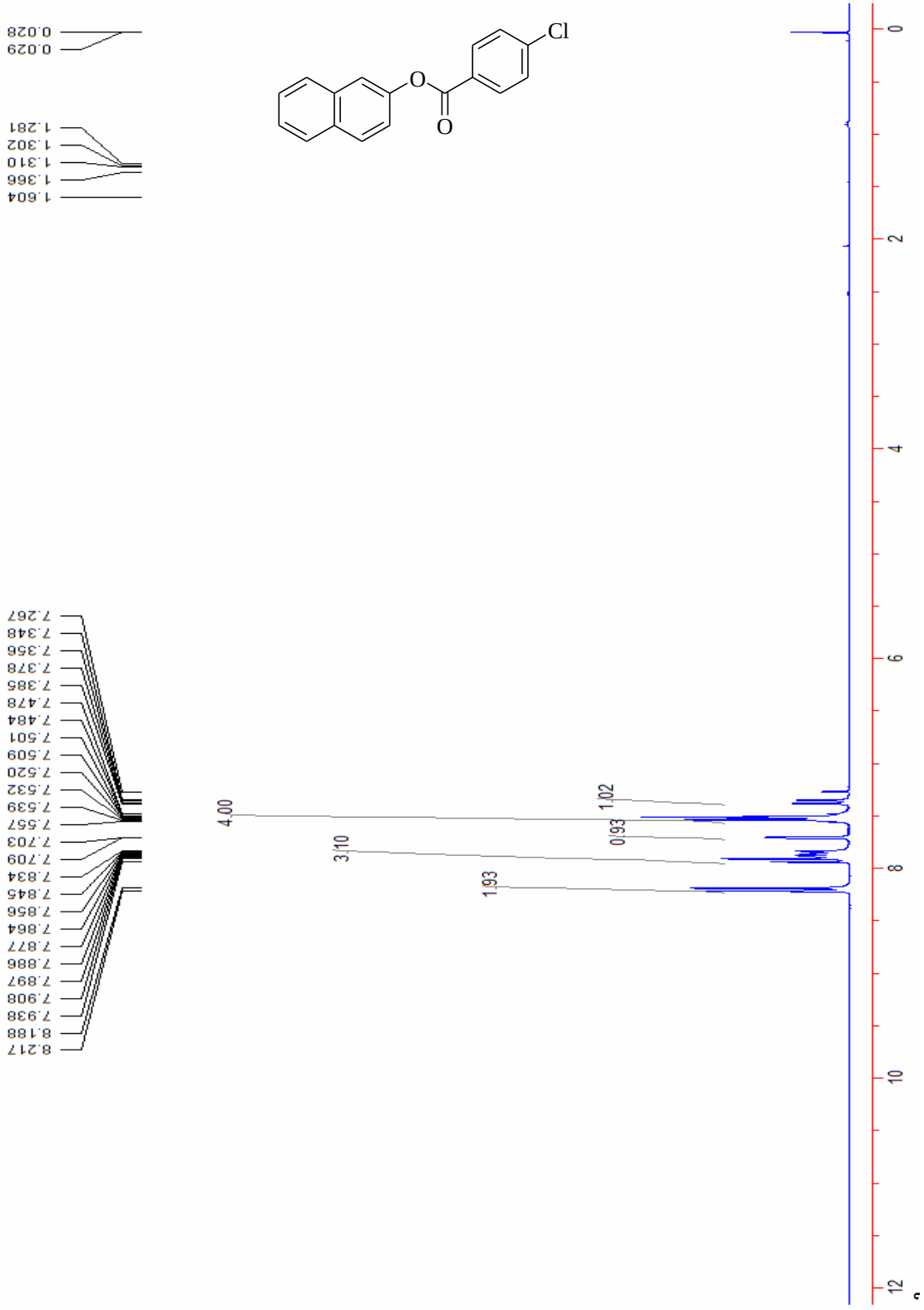
^{13}C NMR of 3,5-dimethylphenyl 4-methoxybenzoate **3ja**



^{1}H NMR of butyl 4-methoxybenzoate **3la**



^{1}H NMR of naphthalen-3-yl 4-chlorobenzoate **3ad**



^{1}H NMR of naphthalen-6-yl 4-methylbenzoate **3ac**