Electronic Supplementary Information

[Fe^{III}(TF_4DMAP)OTf] Catalysed Anti-Markovnikov Oxidation of Terminal Aryl Alkenes to Aldehydes and Transformation of Methyl Aryl Tertiary Amines to Formamides with H_2O_2 as Terminal Oxidant

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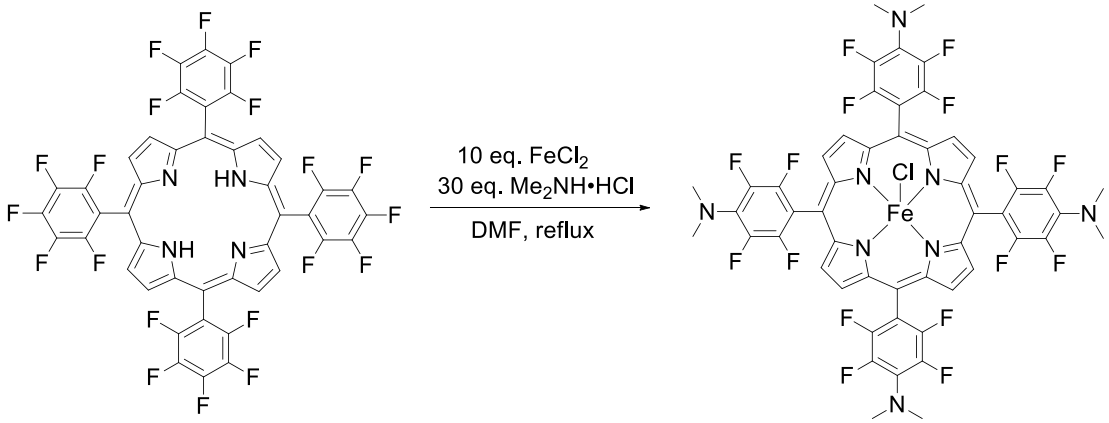
General Experimental: All experiments were performed using standard Schlenk techniques in flame-dried Schlenk tube under an atmosphere of argon unless otherwise specified. Solvents were dried by standard procedures [Dioxane, tetrahydrofuran (THF) and toluene were freshly distilled from Na/benzophenone; Dichloromethane (DCM), Dichloroethane (DCE), Acetonitrile (CH_3CN), *tert*-butyl alcohol (*t*-BuOH) and methanol (MeOH) were distilled from CaH_2] under argon and used immediately. Alkenes were obtained commercially and used directly or filtered through neutral Al_2O_3. ^1H and ^{13}C NMR were recorded on Varian Mercury 300 spectrometer with $CDCl_3$ as solvent (TMS as internal standard). Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet; dt = doublet of triplets, m = multiplet), coupling constants in Hertz (Hz), and integration. EI mass were determined on a HP5989A mass spectrometer. IR spectra (KBr) were measured on Bio-Rad FTS-185 spectrometer. UV-Visible absorption spectra were recorded on a CARY100 spectrophotometer in dichloromethane. GC analyses were performed on a Varian CP-3800, SPB^{TM}-5, FID and *n*-dodecane was used as the internal standard.

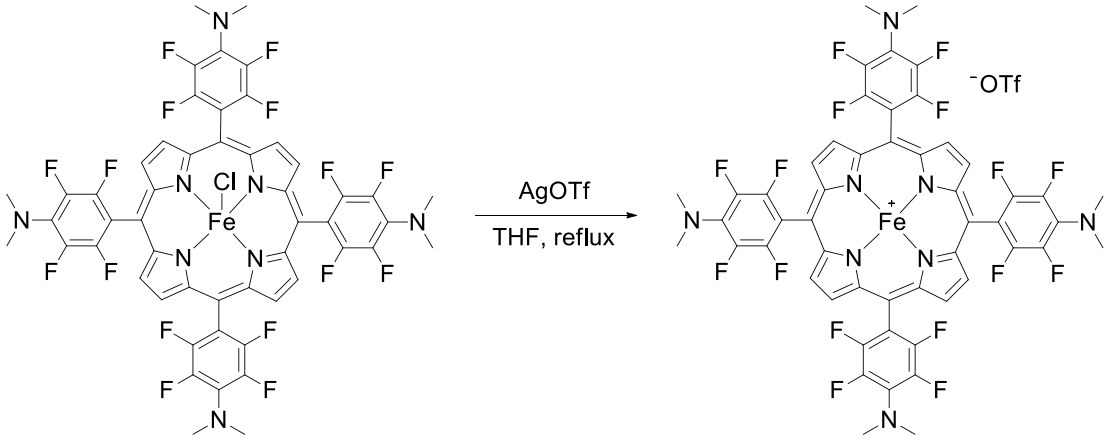
Preparation of Fe(TF$_4$DMAP)Cl



A mixture of H_2F_{20}TPP (380 mg, 0.39 mmol), $FeCl_2$ (494 mg, 3.9 mmol), and $(CH_3)_2NH{\cdot}HCl$ (954 mg, 11.7 mmol) in DMF (120 mL) was refluxed under argon for 12 h. Then the solvent was removed under reduced pressure and the residue was purified by chromatography on a neutral alumina column with CH_2Cl_2/PE 1:1 ~ CH_2Cl_2 as eluting solvent to give the desired product as a dark purple solid in 97% yield.

MS (MALDI) *m/z*: 1128.3 (100), 1129.4 (60); IR (KBr): ν_{max} 3446, 2892, 2812, 1682, 1647, 1538, 1506, 1479, 1436, 1419, 1334, 1209, 1075, 1048, 1002, 976, 948, 806, 771, 756, 707 cm^{-1}; UV-Vis (CH_2Cl_2, nm): λ_{max} = 347, 416, 505, 581, 635.

Preparation of Fe(TF$_4$DMAP)OTf



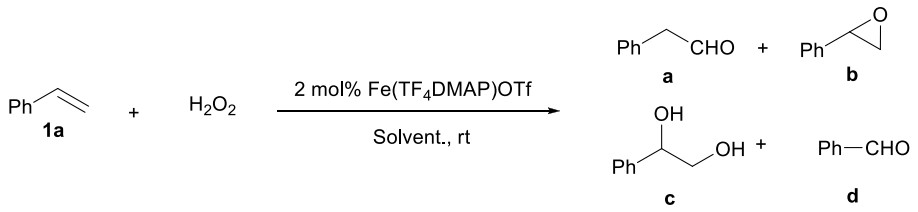
A mixture of [Fe(TF$_4$DMAP)Cl] (116 mg, 0.1 mmol) and AgOTf (26 mg, 0.1 mmol) in THF (6 mL) was refluxed gently under argon for 5 h. Upon cooling to room temperature, the reaction mixture was filtered through a pad of Celite under argon and then dried under vacuum to give the desired product.

HR-MS (MALDI) *m/z*: $[C_{52}H_{32}N_8F_{16}Fe]^+$ cacld 1128.1838, found 1128.1901. IR (KBr): ν_{max} 3447, 2933, 2813, 1647, 1480, 1436, 1419, 1333, 1259, 1227, 1168, 1076, 1048, 1027, 975, 950, 807, 772, 756, 708, 636, 517 cm^{-1}; UV-Vis (CH_2Cl_2, nm): λ_{max} = 335, 409, 517, 646.

Preparation of Fe(TF$_4$DMAP)X (in situ, Table 1)

Fe(TF$_4$DMAP)Cl (4.65 mg, 0.004 mmol) and AgX or NaBArF (0.004 mmol) were added to 1.5 mL of dioxane and further stirred at room temperature under argon for 0.5 h. After adding styrene (0.2 mmol) to the mixture, H_2O_2 (0.4 mmol) diluted in dioxane (0.5 mL) was added via syringe pump.

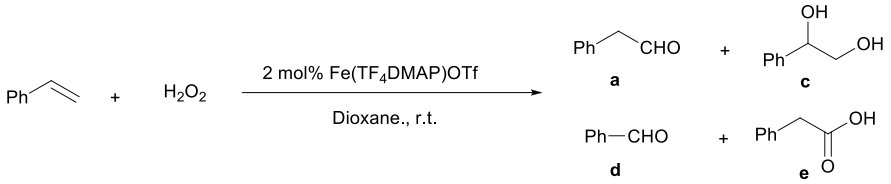
Table S1 Solvent Effect of [Fe(TF$_4$DMAP)OTf] Catalysed E–I Reaction[a]



Entry	solvent	conversion (%)[b]	Yield (%)[b]			
			a	**b**	**c**	**d**
1	Dioxane	100	84	0	5	11
2	THF[c]	30	11	0	0	3
3	Toluene[c]	31	5	0	0	3
4	CH_3CN	23	1	18	0	3
5	Et_2O	42	13	0	25	2
6	MTBE[d]	96	28	18	25	6
7	CH_3OH/CH_2Cl_2[e]	21	2	9	0	1
8	DME	100	47	0	38	10
9	^{t}BuOH	100	-	70[f]	0	-
10	MeOH	100	65[g]	0	0	25[g]
11	acetone	80	5	0	70[g]	5

[a] H_2O_2 (0.4 mmol, diluted in 0.5 mL solvent) was added to a mixture of styrene (0.2 mmol) and catalyst (2 mol%) in solvent (1.5 mL) at room temperature via syringe pump for 5 h, and then the mixture was further stirred for additional 15 h; [b] determined by GC; [c] the solvent itself was oxidized; [d] 5% (dimethoxymethyl)benzene and 3% 2-tert-butoxy-2-phenylethanol were also obtained; [e] CH_3OH/CH_2Cl_2 = 3/1, 0.05 mol% catalyst was used with 2.5 mmol of styrene; [f] ring-opening product 2-tert-butoxy-2-phenylethanol was obtained; [g] the products existed in the form of acetals. THF = tetrahydrofuran, MTBE = methyl *tert*-butyl ether, DME = 1,2-dimethoxyethane.

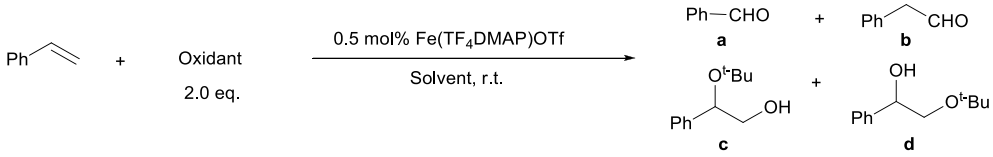
Table S2 The influence of the amount of H_2O_2



Entry[a]	H_2O_2 /eq.	Conversion (%)[b]	Yield (%)[b]			
			a	**c**	**d**	**e**
1	1.2	40	28	6	5	-
2	5.0	100	41	15	11	28

[a] H_2O_2 (diluted in 0.5 mL of dioxane) was added to a mixture of styrene (0.2 mmol) and catalyst (2 mol%) in 1.5 mL of dioxane via syringe pump for 5 h; [b] determined by GC.

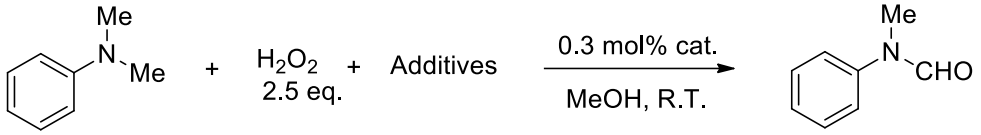
Table S3 Other Oxidants:



Entry [a]	Oxidant	Solvent	Conversion (%)[b]	Yield (%)[b]			
				a	**b**	**c**	**d**
1	^{t}BuOOBu^t	dioxane	1	0.2	0.5	-	-
2[c]	^{t}BuOOH	dioxane	<2	trace	trace	-	-
3[c]	^{t}BuOOH	^{t}BuOH	84	4	5	22[d]	-
4	H_2O_2	^{t}BuOH	100	trace	trace	70[d]	-

[a] Oxidant (dissolved in 0.5 mL of solvent) was added to a mixture of styrene (0.2 mmol) and catalyst (0.5 mol%) in 1.5 mL of solvent via syringe pump for 5 h; [b] determined by GC; [c] one undefined structure with *m/z* = 142 was obtained; [d] determined by ^{1}H NMR with PhTMS as internal standard.

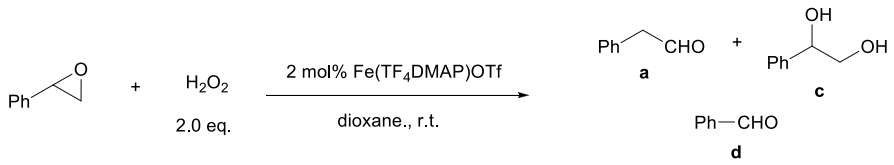
Table S4 Additive effect in iron porphyrin catalyzed formamide formation reactions



Entry [a]	Add. (eq.)	Cat.	Convn. (%)[b]	Yield (%)[c]
1	$TMSCF_3$ (1.2), AcOH (6)	$RuCl_3$ (5%)	100	32
2	$TMSCF_3$ (1.2), AcOH (6)	Fe(TDCDMAP)OTf	100	98
3	-	Fe(TDCDMAP)OTf	65	95
4	AcOH (1)	Fe(TPFPP)OTf	99.5	100
5	AcOH (1)	Fe(TF_4DMAP)OTf	91	100
6	AcOH (1)	Fe(TDCDMAP)OTf	100	96 (80)
7	AcOH (0.2)	Fe(TF_4DMAP)OTf	80	87
8	AcOH (0.2)	Fe(TDCDMAP)OTf	82	86
9	AcOH (1)	$FeCl_3$ (5%)	47	49
10	AcOH (1)	$FeCl_2$ (5%)	19	37

[a] Fe(Por)OTf (3 μmol), substrate (1.0 mmol), and the additive were added successively to 1.2 mL of MeOH, and the mixture was stirred under argon at room temperature. H_2O_2 (283.5 mg, 2.5 mmol) were added via syringe pump over 1 h. [b] Analysed by GC and GC-MS. [c] Determined by GC and GC-MS based on conversions, and the isolated yields were shown in brackets.

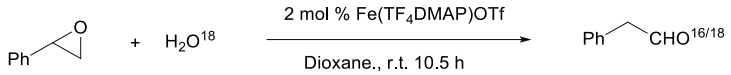
Mechanism A) Control experiments:



Entry [a]	time (h)	Conversion (%)[b]	Yield (%)[b]		
			a	**c**	**d**
1	6	98	75	13	9
2	43	100	71	19	10

[a] H_2O_2 (0.4 mmol, diluted in 0.5 mL dioxane) was added to a mixture of styrene oxide (0.2 mmol) and catalyst (2 mol%) in 1.5 mL of dioxane via syringe pump for 5 h; [b] determined by GC.

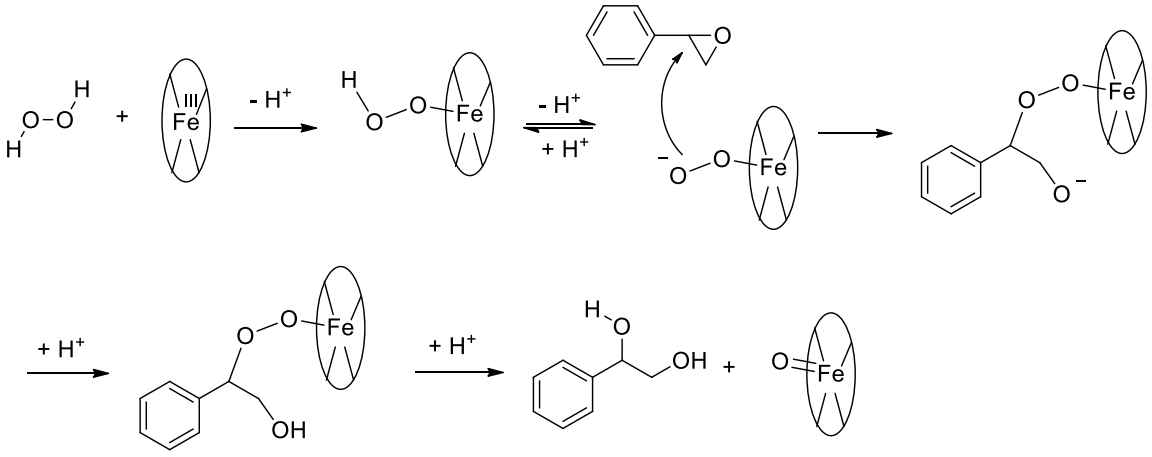
B) ^{18}O-Labelling:



^{18}O-H_2O (35 mg, diluted in 0.5 mL of dioxane) was added to a mixture of styrene oxide (0.2 mmol) and catalyst (2 mol%) in 1.5 mL of dioxane via syringe pump for 5 h. After stirring for another 5 h, the reaction mixture was analysed by GC-MS. No diol was obtained.

Phenylacetaldehyde: EI-MS *m/z* (relative intensity): 120(M^+, 18), 122(^{18}O-M^+, 6), 91 (100), 92 (31), 65 (27); **Styrene oxide**: EI-MS *m/z* (relative intensity):119(M-1, 54), 120(31), 121 (^{18}OM-1, 3), 91 (100), 89 (84), 90 (67), 92 (37), 63 (28), 51 (24), 65 (21).

The speculative mechanism on formation of diol:



Mass spectrometry analysis

Positive-ion ESI mass spectra were obtained on a Waters Micromass Q-Tof Premier quadrupole time-of-flight tandem mass spectrometer. Typically, [Fe^{III}(Por)(OTf)] (5×10^{-4} M) was treated with H_2O_2 (5 equiv.) in acetonitrile. After reacting at room temperature for 30 s, the reaction mixture was introduced into the ESI source by a syringe pump operating at 5 μL min^{-1}.

For accurate mass measurements, sodium formate was used as calibration reference. The mass resolution was fixed at about 8000 (full width at half-height) with mass accuracy limited within 10 ppm.

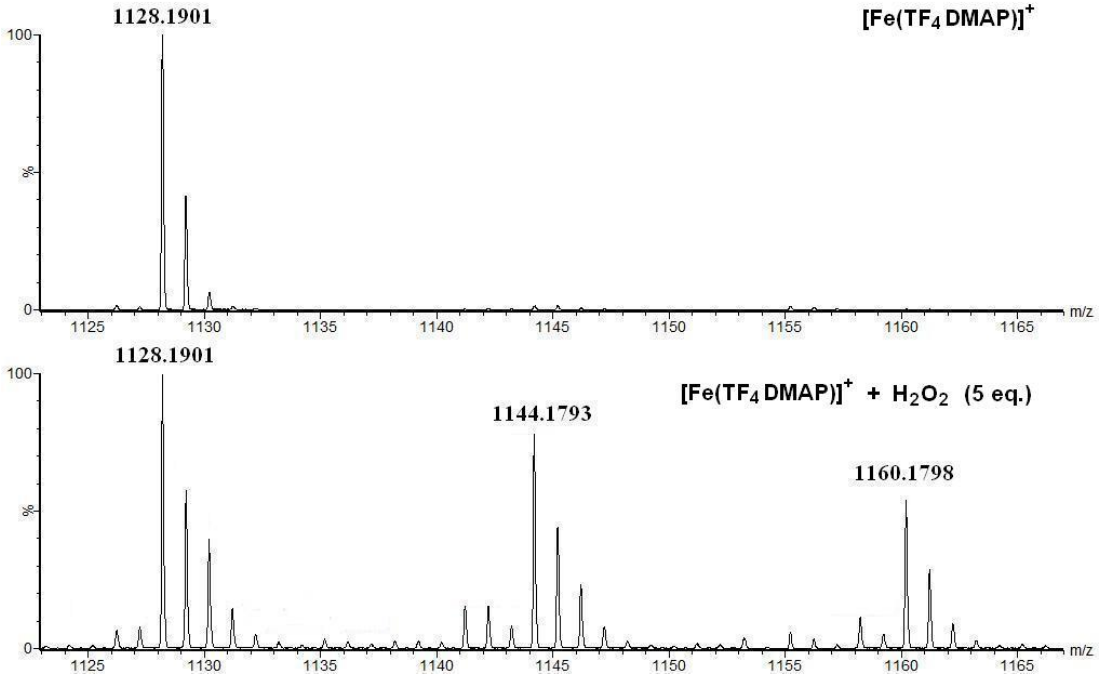


Fig. S1 ESI-MS spectrum of the reaction mixture of [Fe^{III}(TF_4DMAP)(OTf)] (5 × 10^{-4} M in acetonitrile) with H_2O_2 (5 equiv.)

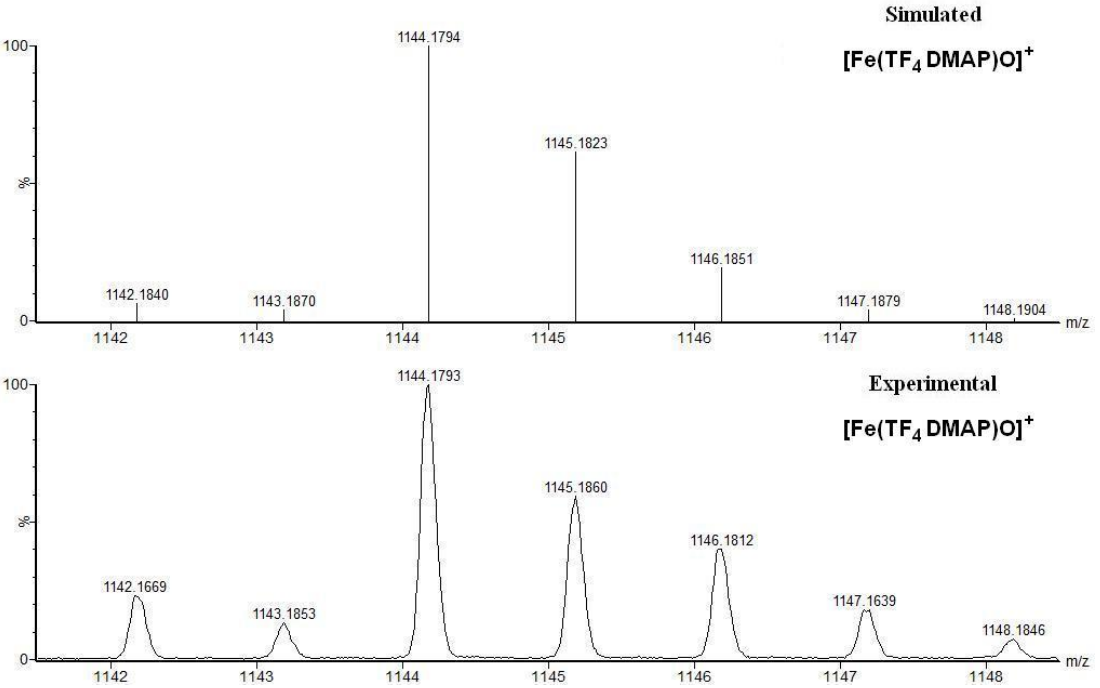


Fig. S2 ESI-MS spectrum of [Fe(TF_4DMAP)(O)]$^+$: simulated isotopic pattern (top), experimentally observed (bottom)

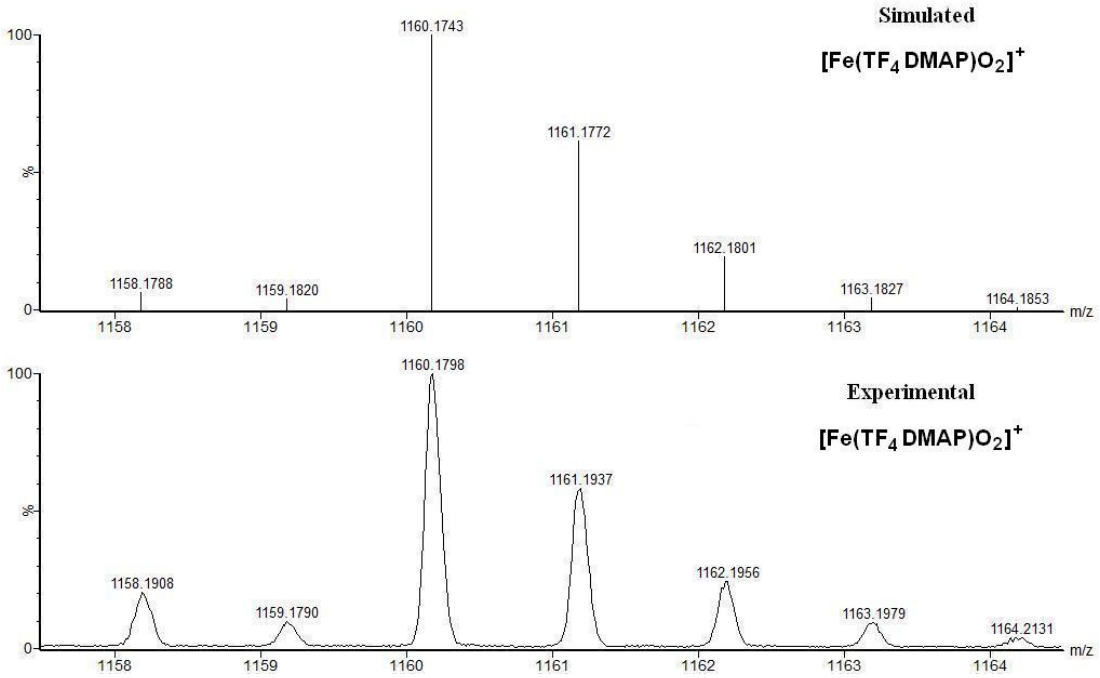


Fig. S3 ESI-MS spectrum of $[Fe(TF_4DMAP)O_2]^+$: simulated isotopic pattern (top), experimentally observed (bottom)

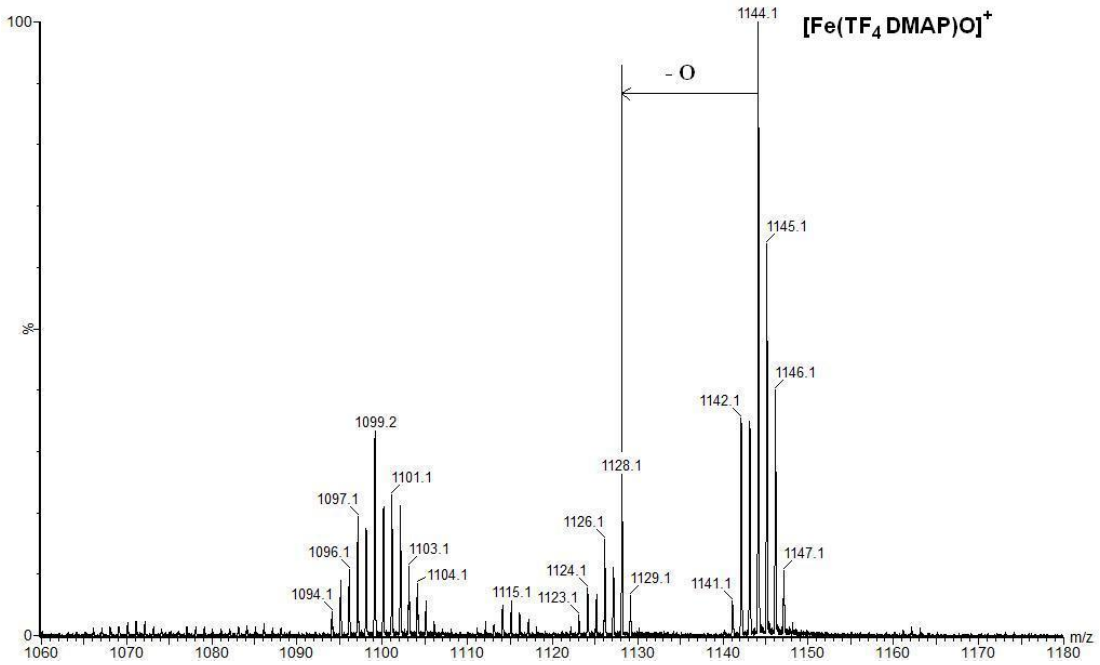


Fig. S4 Collision-induced dissociation spectrum of $[Fe(TF_4DMAP)O]^+$

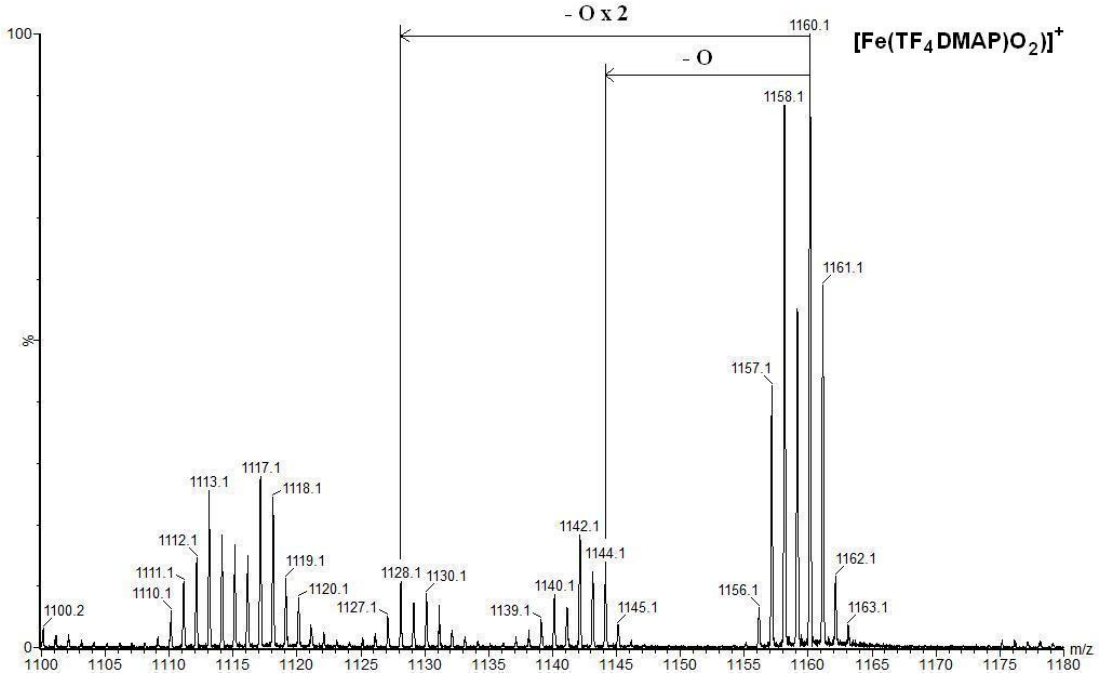


Fig. S5 Collision-induced dissociation spectrum of $[Fe(TF_4DMAP)O_2]^+$

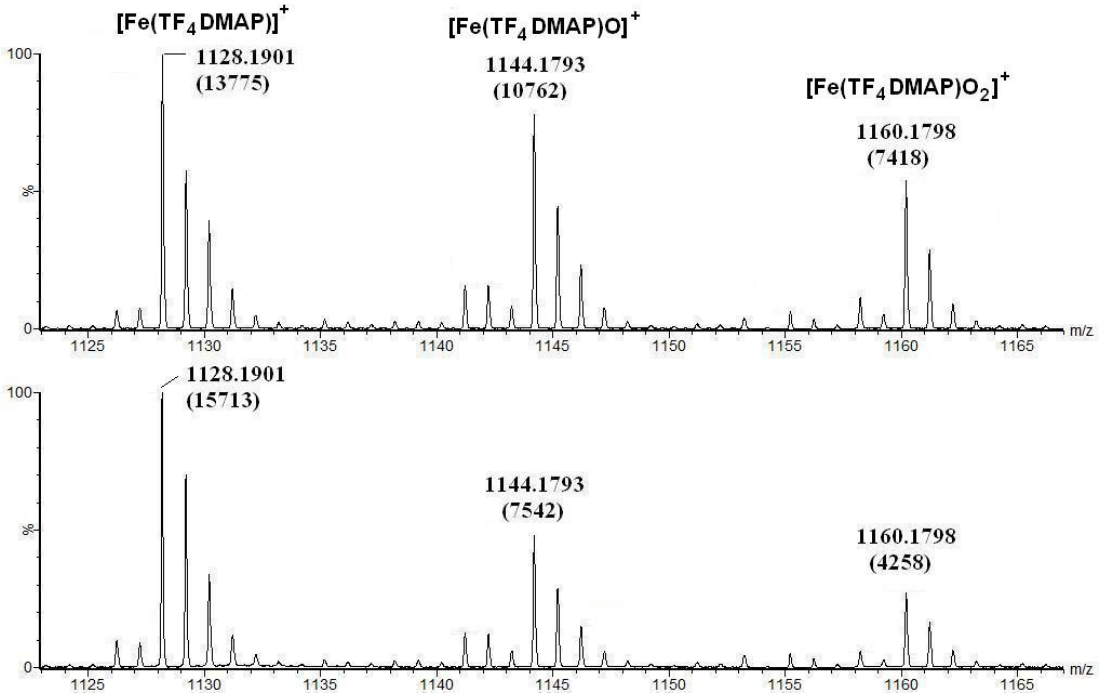


Fig. S6 ESI-MS spectrum of the reaction mixture of $[Fe^{III}(TF_4DMAP)(OTf)]$ (5×10^{-4} M in acetonitrile) with H_2O_2 (5 equiv., top) and in presence of styrene (50 equiv., bottom). Numbers in the brackets represent the signal intensity.

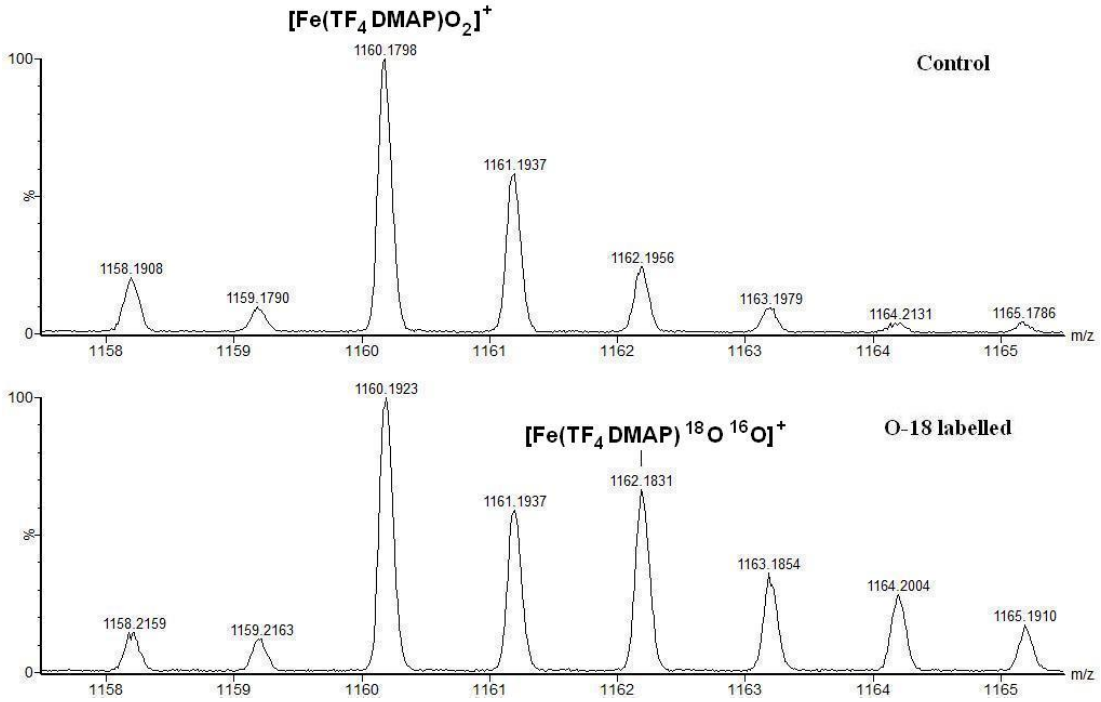


Fig. S7 ESI-MS spectrum of $[Fe(TF_4DMAP)O_2]^+$ in the absence (top) and presence of ^{18}O-H_2O (500 equiv., bottom).

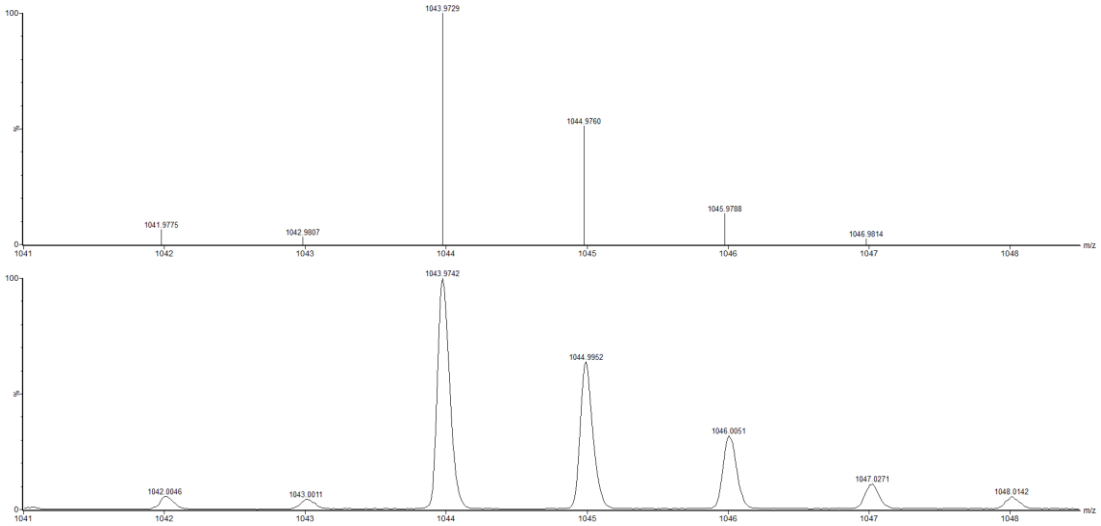


Fig. S8 ESI-MS spectrum of $[Fe(F_{20}TPP)(O)]^+$: simulated isotopic pattern (top), experimentally observed (bottom)

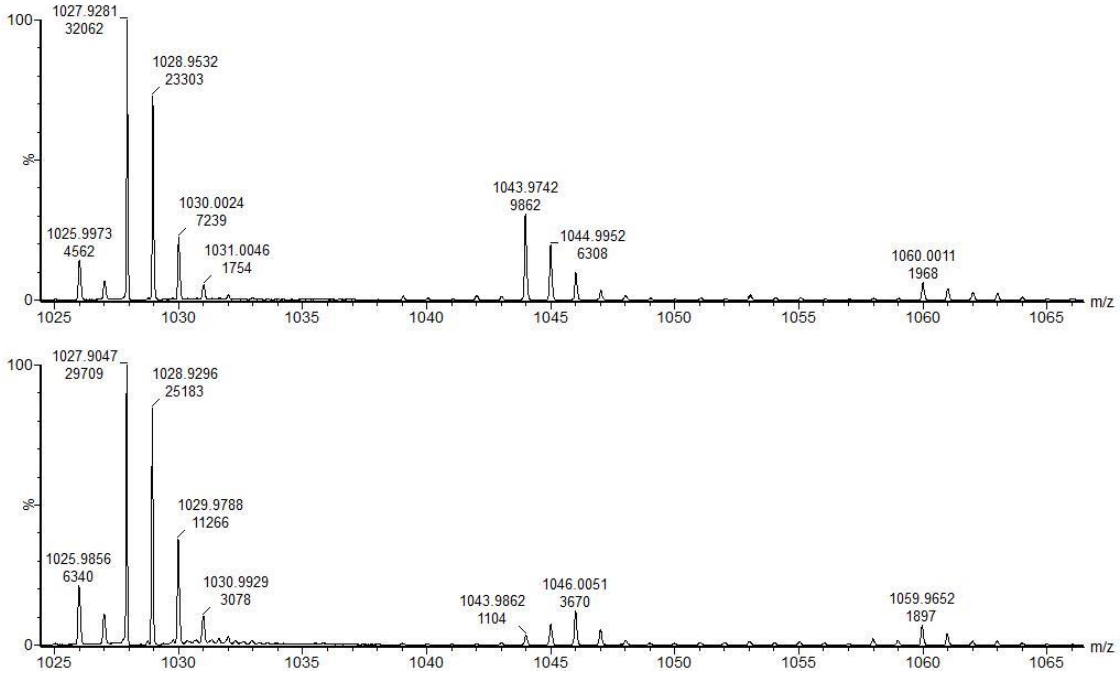


Fig. S9 ESI-MS spectrum of the reaction mixture of Fe(F_{20}TPP)(OTf) (5×10^{-4} M in acetonitrile) with H_2O_2 (5 equiv. top) and in presence of styrene (50 equiv. bottom). Numbers below m/z values represent the signal intensity.

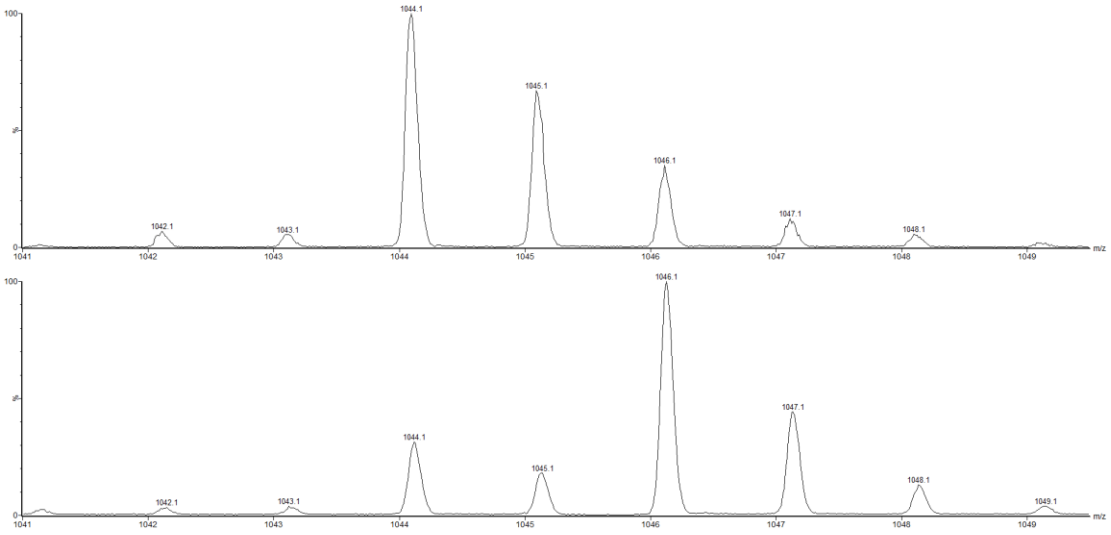


Fig. S10 ESI-MS spectrum of $[Fe(F_{20}TPP)(O)]^+$ in the absence (top) and presence of ^{18}O-H_2O (500 equiv., bottom).

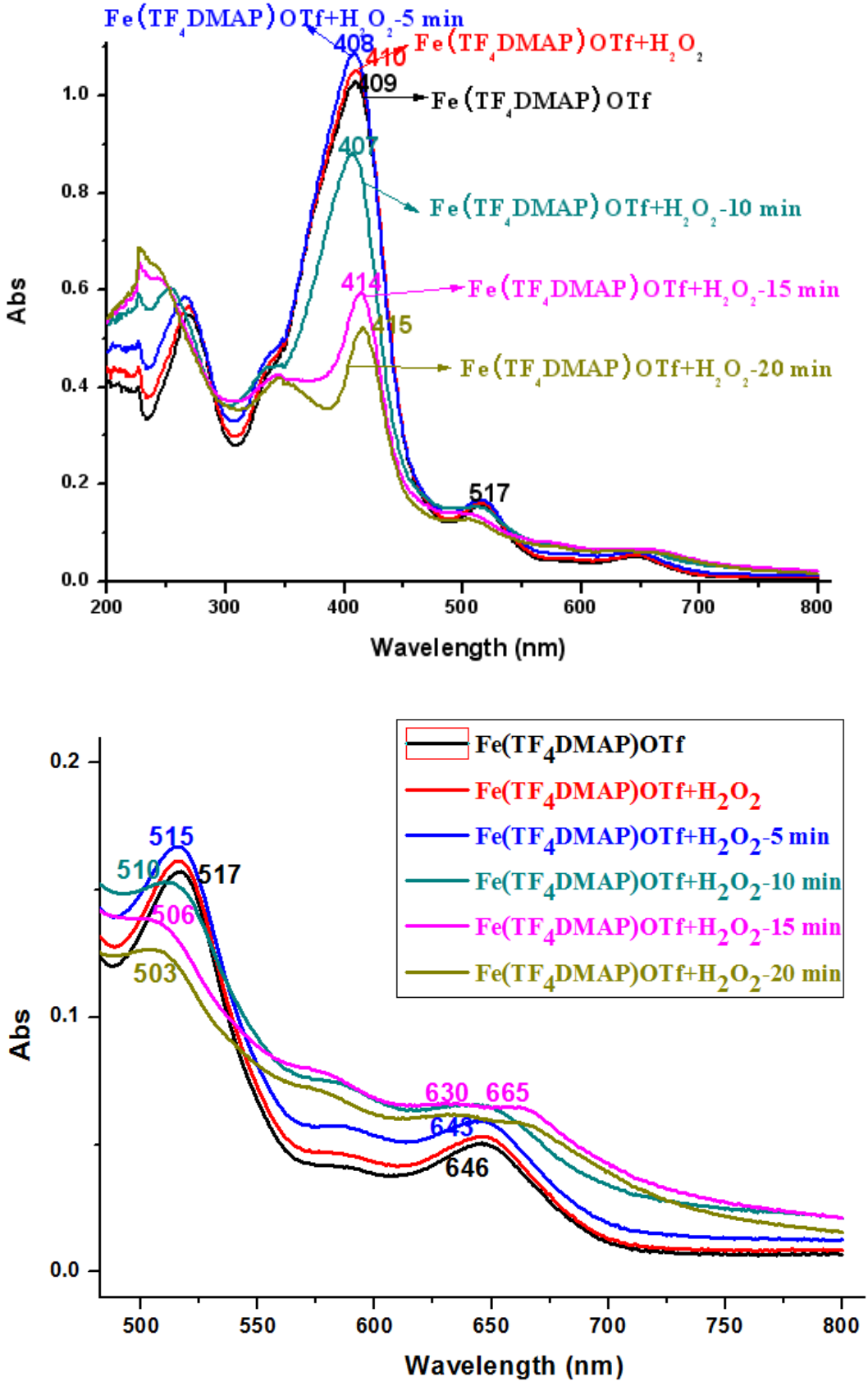
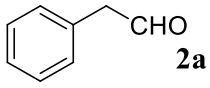


Fig. S11 UV-visible absorption spectra of [Fe(TF4DMAP)OTf] with excess H_2O_2 in dichloromethane at room temperature

<u>Typical procedure</u> for [Fe(TF$_4$DMAP)OTf]-catalysed oxidation of aryl alkenes to aldehydes:

To a solution of [Fe(TF$_4$DMAP)OTf] (1.3 mg, 1 μmol) and styrene (20.8 mg, 0.2 mmol) in dioxane (1.5 mL) was added H_2O_2 (30% aqueous solution, 45.4 mg, 0.4 mmol, diluted in 0.5 mL of dioxane) via syringe pump for 5 h. After stirring for additional 3 ~ 5 h at room temperature, the reaction mixture was filtered through a short column of silica (2 ~ 3 cm) and washed with EtOAc (50 mL). The product yields were determined by ^{1}H NMR with PhTMS as internal standard.

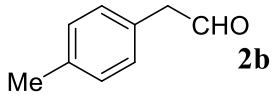
2-phenylacetaldehyde



2a

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.75 (t, *J* = 2.4 Hz, 1H), 7.41-7.21 (m, 5H), 3.69 (d, *J* = 2.4 Hz, 2H); EI-MS *m/z* (relative intensity): 120(M^+, 70), 91 (100), 44 (54), 107 (40), 77 (39), 79 (31), 105 (31), 45 (25).

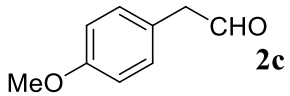
2-p-tolylacetaldehyde



2b

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.73 (t, *J* = 2.1 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 3.65 (d, *J* = 2.1 Hz, 2H), 2.35 (s, 3H); EI-MS *m/z* (relative intensity): 134 (M^+, 25), 105 (100), 77 (22), 79 (21), 103 (13), 91 (11).

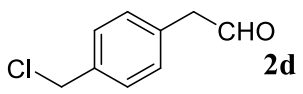
2-(4-methoxyphenyl)acetaldehyde



2c

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.72 (t, *J* = 2.4 Hz, 1H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.63 (d, *J* = 2.4 Hz, 2H); EI-MS *m/z* (relative intensity): 150 (M^+, 13), 121 (100), 77 (18), 78 (14).

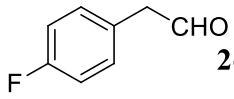
2-(4-(chloromethyl)phenyl)acetaldehyde



2d

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.72 (t, *J* = 2.4 Hz, 1H), 7.32-7.36 (m, 2H), 7.28-7.30 (m, 2H), 4.62 (s, 2H),3.65 (d, *J* = 2.4 Hz, 2H); EI-MS *m/z* (relative intensity): 168 (M^+, 28), 170 (^{37}Cl M^+, 9), 139 (100), 103 (70), 104 (60), 77 (43), 105 (32), 141 (32), 78 (24), 91 (24)

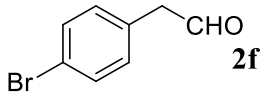
2-(4-fluorophenyl)acetaldehyde



2e

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.75 (t, *J* = 1.5 Hz, 1H), 7.21-7.16 (m, 2H), 7.09-7.04 (m, 2H), 3.69 (d, *J* = 1.5 Hz, 2H); EI-MS *m/z* (relative intensity): 138 (M^+, 19), 109(100), 83 (24), 110 (11).

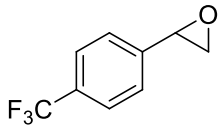
2-(4-bromophenyl)acetaldehyde



2f

^{1}H NMR (300 MHz, $CDCl_3$): δδ 9.70 (t, *J* = 1.9 Hz,1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 3.66 (d, *J* = 1.9 Hz, 2H); EI-MS *m/z* (relative intensity): 198 (M^+, 27), 200 ($^{81}BrM^+$, 28), 169 (100), 171 (93), 90 (93), 89 (78), 91 (54), 63 (49).

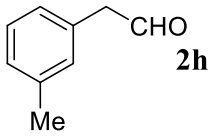
2-(4-(trifluoromethyl)phenyl)oxirane



2g

^{1}H NMR (300 MHz, $CDCl_3$): δ7.60 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 3.92 (dd, *J* = 4.0, 2.6 Hz, 1H), 3.19 (dd, ^1J = 5.6 Hz, ^2J = 4.0 Hz, 1H), 2.77 (dd, ^1J = 5.6 Hz, ^2J = 2.6 Hz, 1H), EI-MS *m/z* (relative intensity): 188 (M^+, 6), 119 (100), 91 (42), 89 (28), 158 (24), 63 (21), 159 (19), 109 (18), 108 (13), 107 (11), 187 (9), 169 (5)

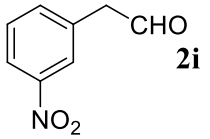
2-*m*-tolylacetaldehyde



2h

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.74 (t, *J* = 2.4 Hz, 1H), 7.26 (m, 1H), 7.12 (m, 1H), 7.02 (m, 2H), 3.64 (d, *J* = 2.4 Hz, 2H), 2.36 (s, 3H). EI-MS *m/z* (relative intensity): 134 (M^+, 32), 105 (100), 106 (33), 91 (31), 77 (27), 79 (25), 103 (16).

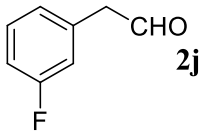
2-(3-nitrophenyl)acetaldehyde



2i

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.84 (t, *J* = 2.4 Hz, 1H), 8.25-8.27 (m, 1H), 8.15-8.18 (m, 1H),7.71-7.73 (m, 1H), 7.62-7.64 (m, 1H), 3.67 (d, *J* = 2.4 Hz, 2H); EI-MS *m/z* (relative intensity): 165 (M^+, 22), 90 (100), 91 (80), 89 (80), 65 (56), 137 (50), 136 (50), 120 (27).

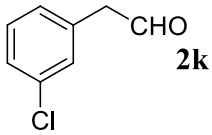
2-(3-fluorophenyl)acetaldehyde



2j

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.77 (t, *J* = 3.0 Hz, 1H), 7.33 (m, 1H), 6.98 (m, 3H), 3.69 (d, *J* = 3.0 Hz, 2H). EI-MS *m/z* (relative intensity):138(M^+,29),109 (100), 110 (43), 83 (33), 57(10).

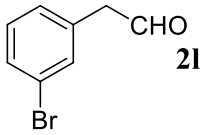
2-(3-chlorophenyl)acetaldehyde



2k

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.75 (t, *J* = 1.8 Hz, 1H), 7.34-7.28 (m, 2H), 7.23 (s, 1H), 7.12-7.10 (m, 1H), 3.69 (d, *J* = 1.8 Hz, 2H); EI-MS *m/z* (relative intensity): 154(M^+, 29), 156 ($^{37}ClM^+$, 9), 125 (100), 91 (92), 89 (51), 126 (36), 127(35).

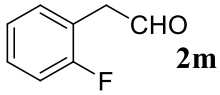
2-(3-bromophenyl)acetaldehyde



2l

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.78 (t, *J* = 2.1 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.42 (s, 1H), 7.26-7.23 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 3.71 (d, *J* = 2.1 Hz, 2H); EI-MS *m/z* (relative intensity): 198(M^+, 15), 200 ($^{81}BrM^+$, 14), 91(100), 90 (59), 89 (55), 63 (38), 169 (31), 171 (30), 170 (14), 172 (13)

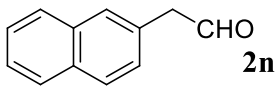
2-(2-fluorophenyl)acetaldehyde



2m

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.76 (s, 1H), 7.34-7.07 (m, 4H), 3.73 (m, 2H); EI-MS *m/z* (relative intensity): 138 (M^+, 25), 109 (100), 83 (25), 110 (21).

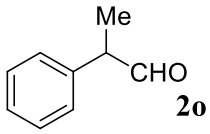
2-(naphthalen-2-yl)acetaldehyde



2n

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.75 (t, *J* = 2.1 Hz, 1H), 7.86-7.79 (m, 3H), 7.69 (s, 1H), 7.50-7.47 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 1H), 3.76 (d, *J* = 2.1 Hz, 2H); EI-MS *m/z* (relative intensity): 170(M^+, 24), 141(100), 115 (39), 142 (21), 139 (12).

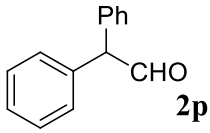
2-phenylpropanal



2o

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.69 (s, 1H), 7.42-7.21 (m, 5H), 3.64 (q, *J* = 7.2 Hz, 1H), 1.45 (d, *J* = 7.2 Hz, 3H); EI-MS *m/z* (relative intensity): 134(M^+, 12), 105 (100), 79 (24), 77 (23), 103 (14), 106 (11), 91 (10).

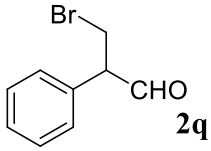
2,2-diphenylacetaldehyde



2p

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.94 (d, *J* = 2.4 Hz, 1H), 7.21-7.40 (m, 10H), 4.88 (d, *J* = 2.4 Hz, 1H); EI-MS *m/z* (relative intensity): 196 (M^+, 3), 167 (100), 165 (47), 152 (30).

3-bromo-2-phenylpropanal

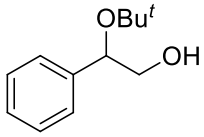


2q

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.67 (d, *J* = 2.4 Hz, 1H), 7.33-7.45 (m, 5H), 4.39 (d, *J* = 4.5 Hz, 2H), 3.67 (m, 1H).

EI-MS *m/z* (relative intensity): 212 (M^+, 1), 214 (^{81}Br-M^+, 1), 103 (100), 77 (27), 104 (16), 51 (15), 133 (12), 102 (12), 91 (7).

2-*tert*-butoxy-2-phenylethanol

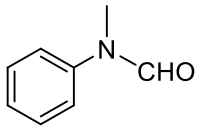


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23–7.36 (m, 5H), 4.62 (dd, ^1J = 4.4 Hz, ^2J =8.2 Hz, 1H), 3.43–3.57 (m, 2H), 2.27 (br, OH), 1.17 (s, 9H).

EI-MS *m/z* (relative intensity): 163 (22), 107 (100), 57 (60), 79 (24), 77 (16), 108 (9), 91 (9), 103 (8).

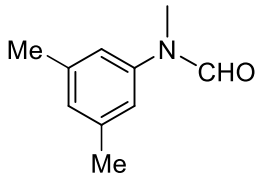
<u>Typical procedure</u> for [Fe(TF$_4$DMAP)OTf]-catalysed oxidation of methyl aryl tertiary amines to formamides:

To a solution of [Fe(TF$_4$DMAP)OTf] (3.9 mg, 3 μmol) and *N*,*N*-dimethyl aniline (121.2 mg, 1.0 mmol) and acetic acid (60.0 mg, 1.0 mmol) in dioxane (1.2 mL) was added H_2O_2 (30% aqueous solution, 283.5 mg, 2.5 mmol) via syringe pump for 1 h. After stirring for additional 1 h at room temperature, the reaction mixture was filtered through a short column of silica (2 ~ 3 cm) and washed with EtOAc (50 mL). The product yields were determined by GC and purified by column chromatography with PE/EA (10:1 ~ 2:1).



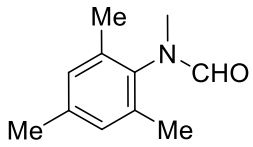
4a

^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.47 (s, 1H), 7.39-7.44 (m, 2H), 7.25-7.30 (m, 1H), 7.17 (d, 2H, *J* = 7.5 Hz), 3.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.2, 142.0, 129.4, 126.2, 122.1, 31.8.



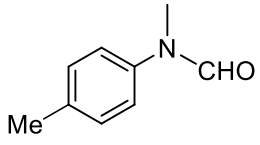
4b

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.43 (s, 1H), 6.91 (s, 1H), 6.78 (s, 2H), 3.28 (s, 3H), 2.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.2, 142.0, 139.2, 127.9, 120.0, 31.9, 21.1.



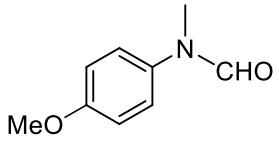
4c

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.98 (s, 1H), 6.93 (s, 2H), 3.09 (s, 3H), 2.28 (s, 3H), 2.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.4, 138.2, 136.6, 136.2, 129.2, 31.7, 20.8, 17.5.



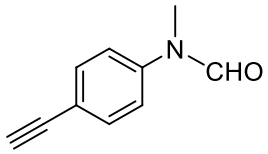
4d

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.35 (s, 1H), 7.15 (d, 2H, *J* = 8.2 Hz), 7.00 (d, 2H, *J* = 8.2 Hz), 3.23 (s, 3H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.1, 139.4, 136.0, 129.9, 122.2, 31.9, 20.6.



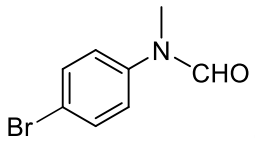
4e

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.30 (s, 1H), 7.05 (d, 2H, *J* = 9.0 Hz), 6.89 (d, 2H, *J* = 9.0 Hz), 3.78 (s, 3H), 3.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.4, 158.1, 134.8, 124.5, 114.6, 55.4, 32.5.



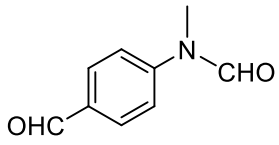
4f

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.50 (s, 1H), 7.50 (d, 2H, *J* = 7.6 Hz), 7.10 (d, 2H, *J* = 7.6 Hz), 3.29 (s, 3H), 3.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.8, 142.2, 133.3, 121.3, 119.8, 82.4, 78.0, 31.5.



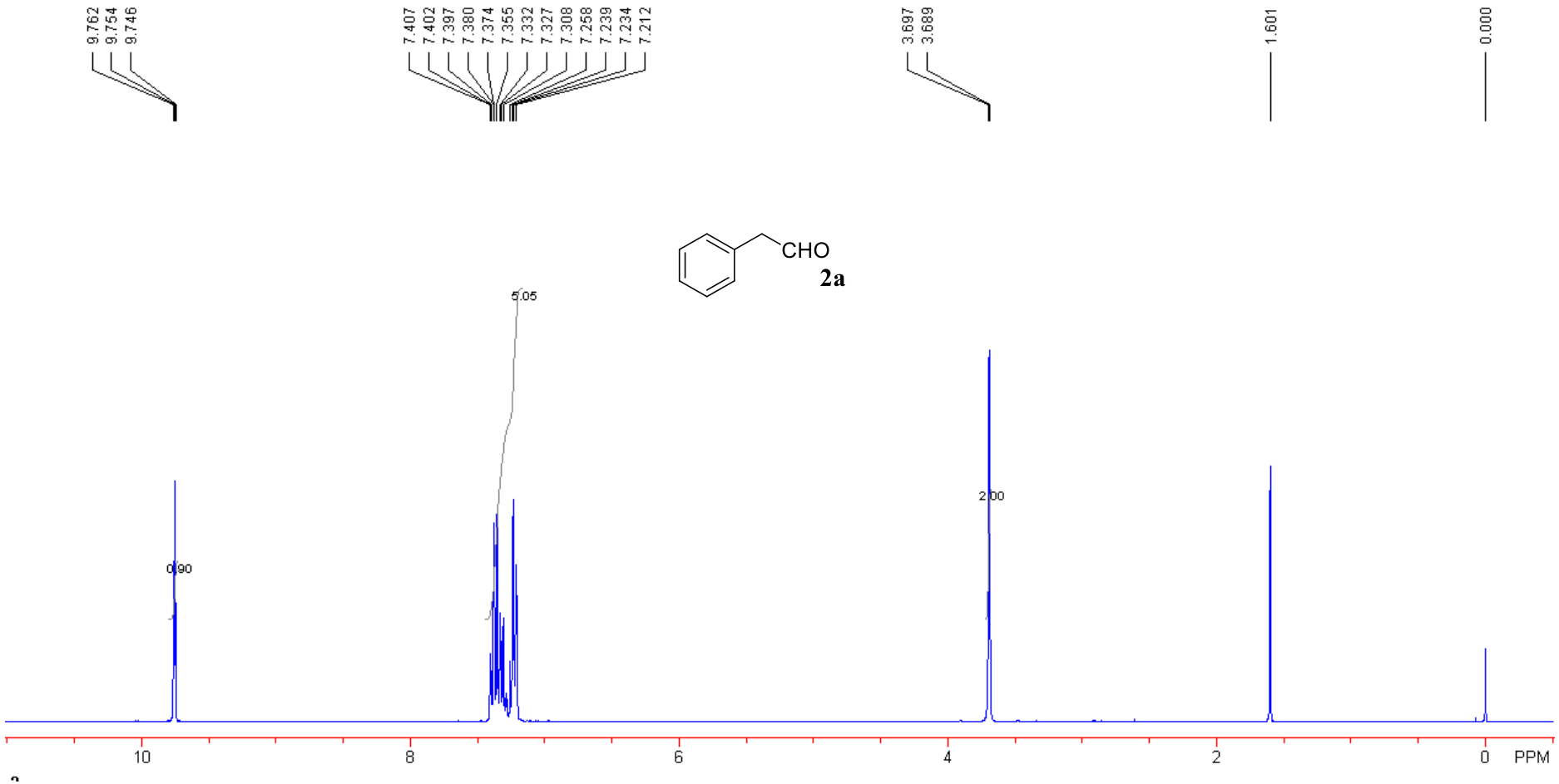
4g

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.42 (s, 1H), 7.48 (d, *J* = 8.4 Hz), 7.02 (d, *J* = 8.4 Hz), 3.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.7, 141.0, 132.5, 123.5, 119.4, 31.7.



4h

^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.00 (s, 1H), 8.72 (s, 1H), 7.96 (d, 2H, *J* = 8.2 Hz), 7.37 (d, 2H, *J* = 8.2 Hz), 3.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 190.6, 161.6, 147.0, 133.4, 131.1, 120.6, 31.1.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10
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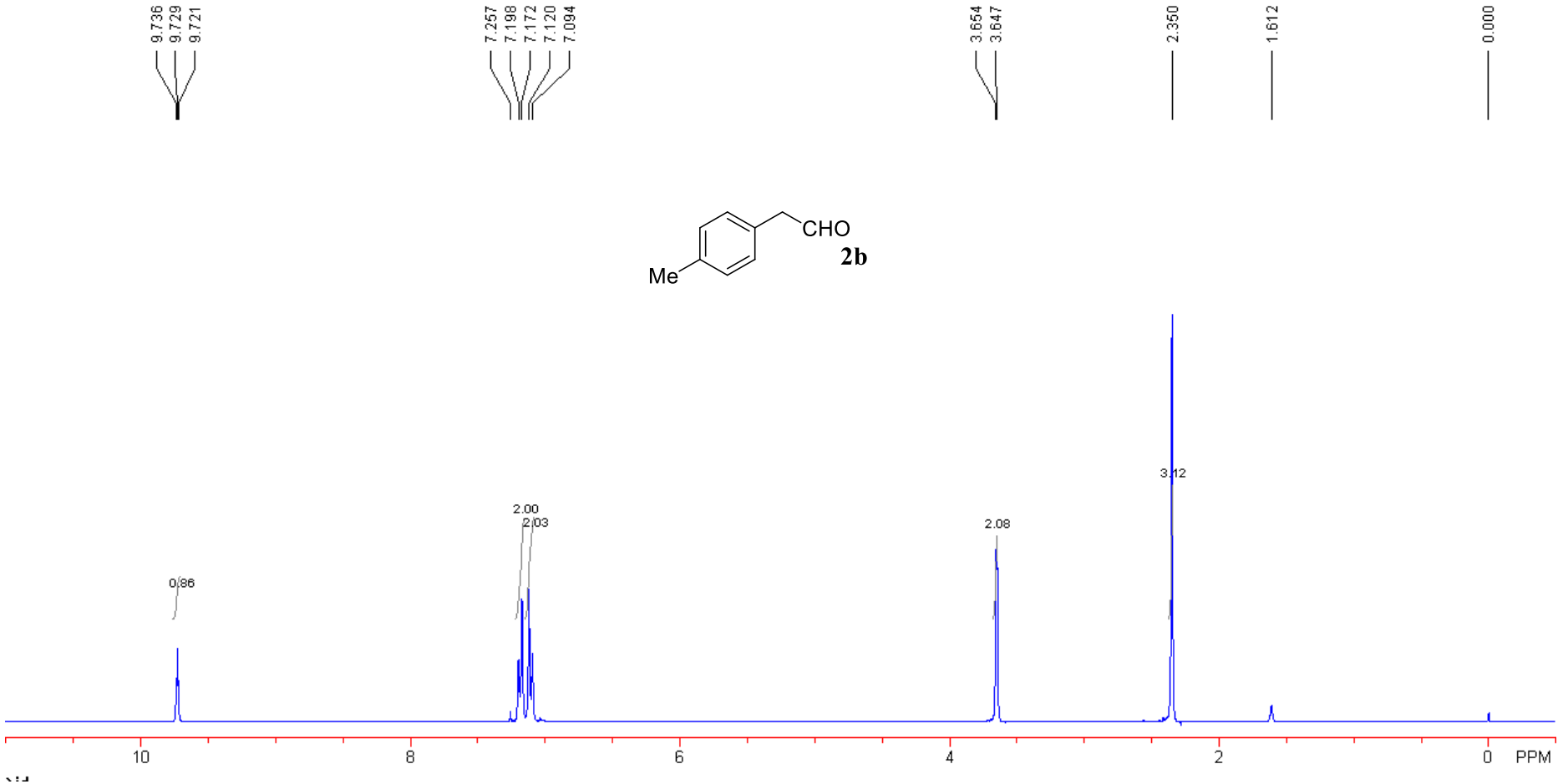
PPM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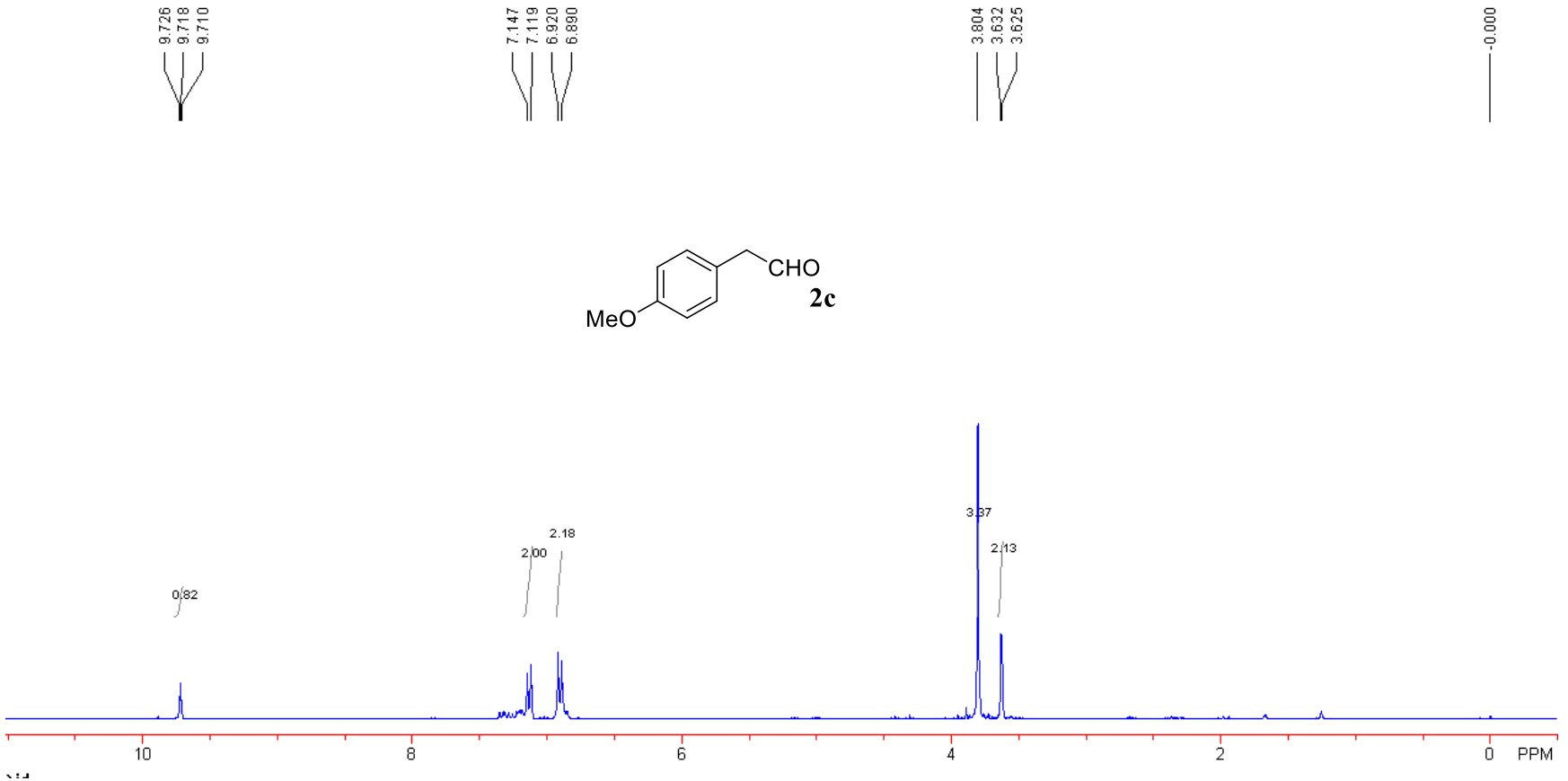
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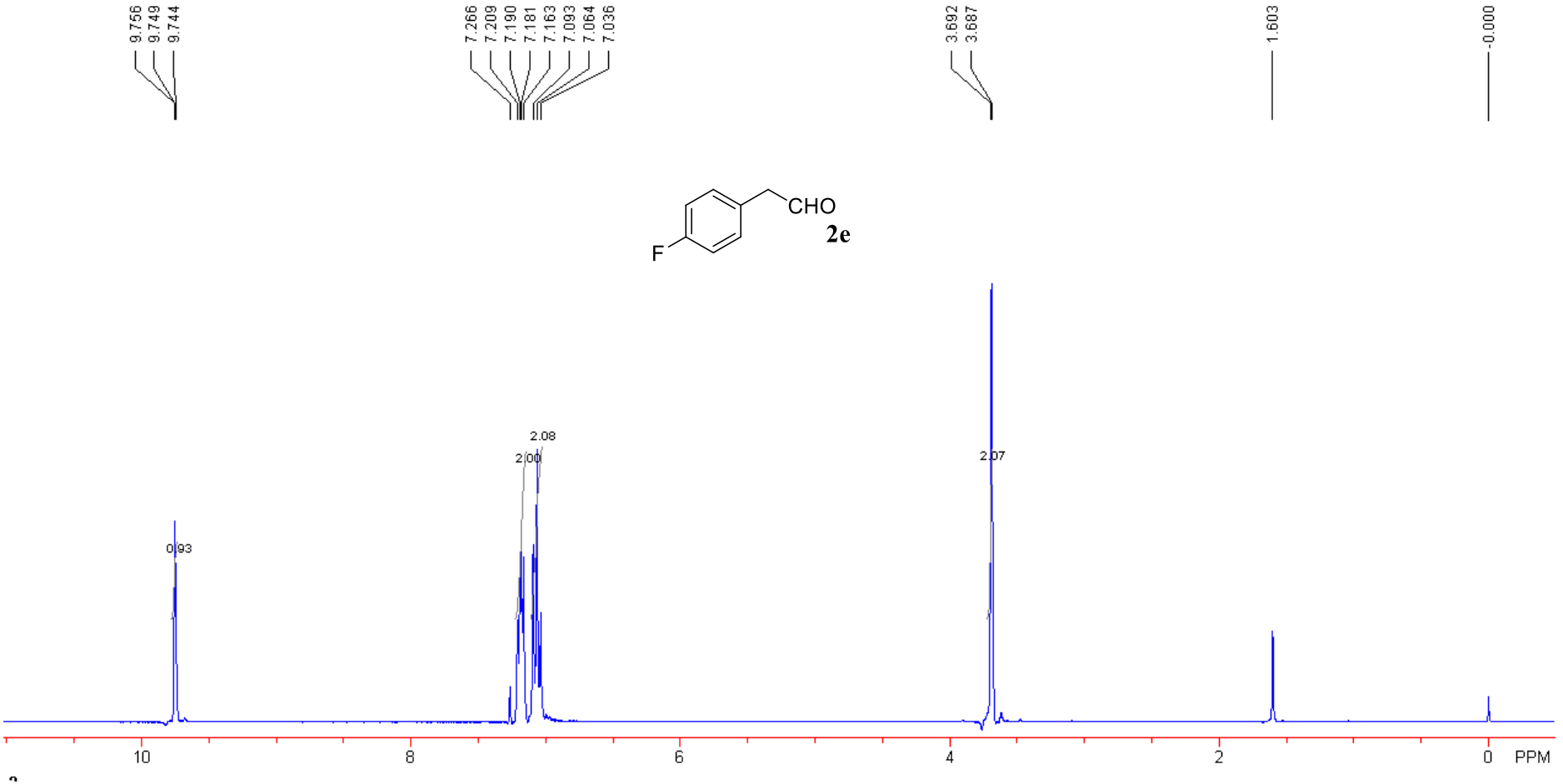
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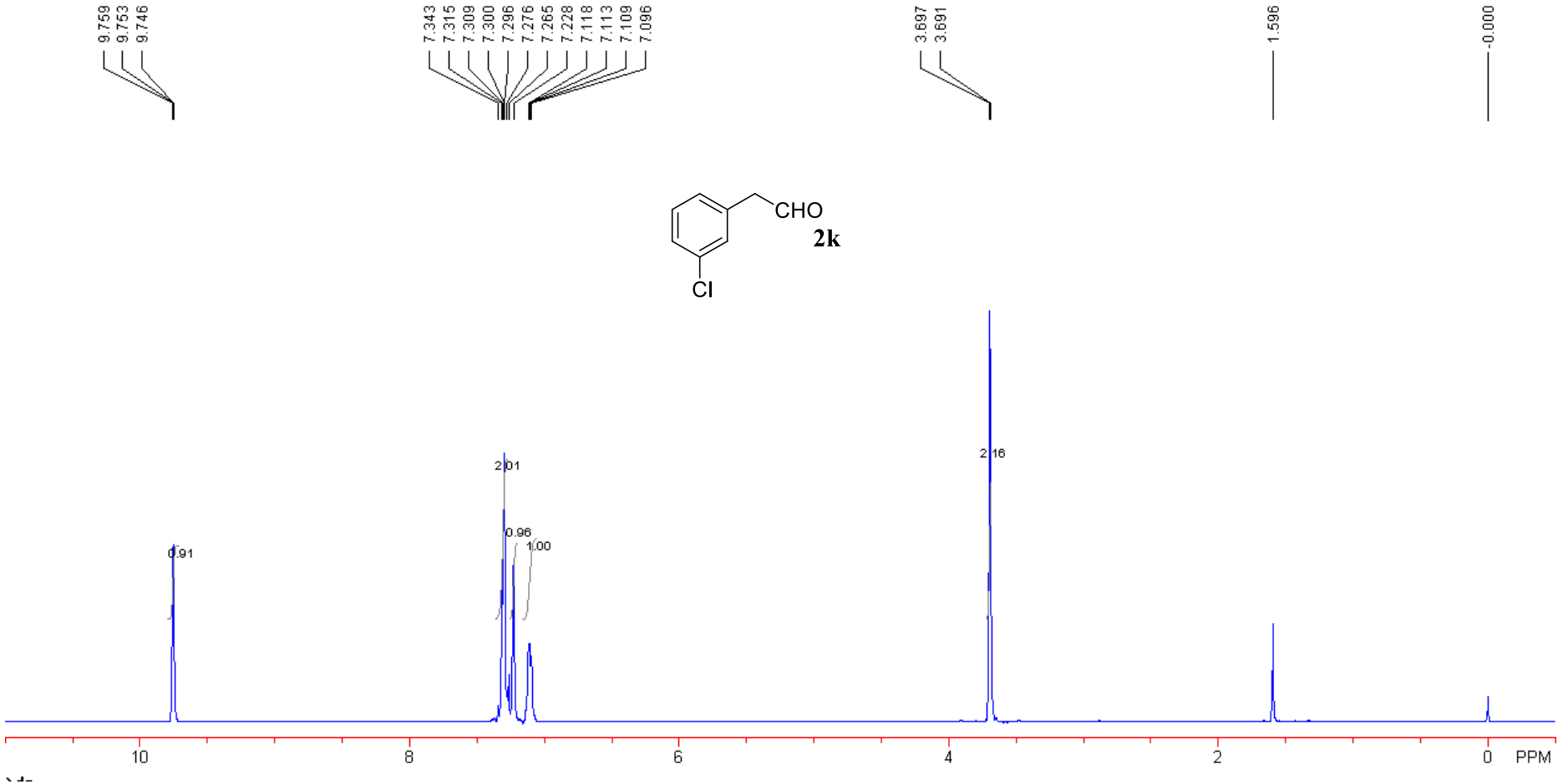
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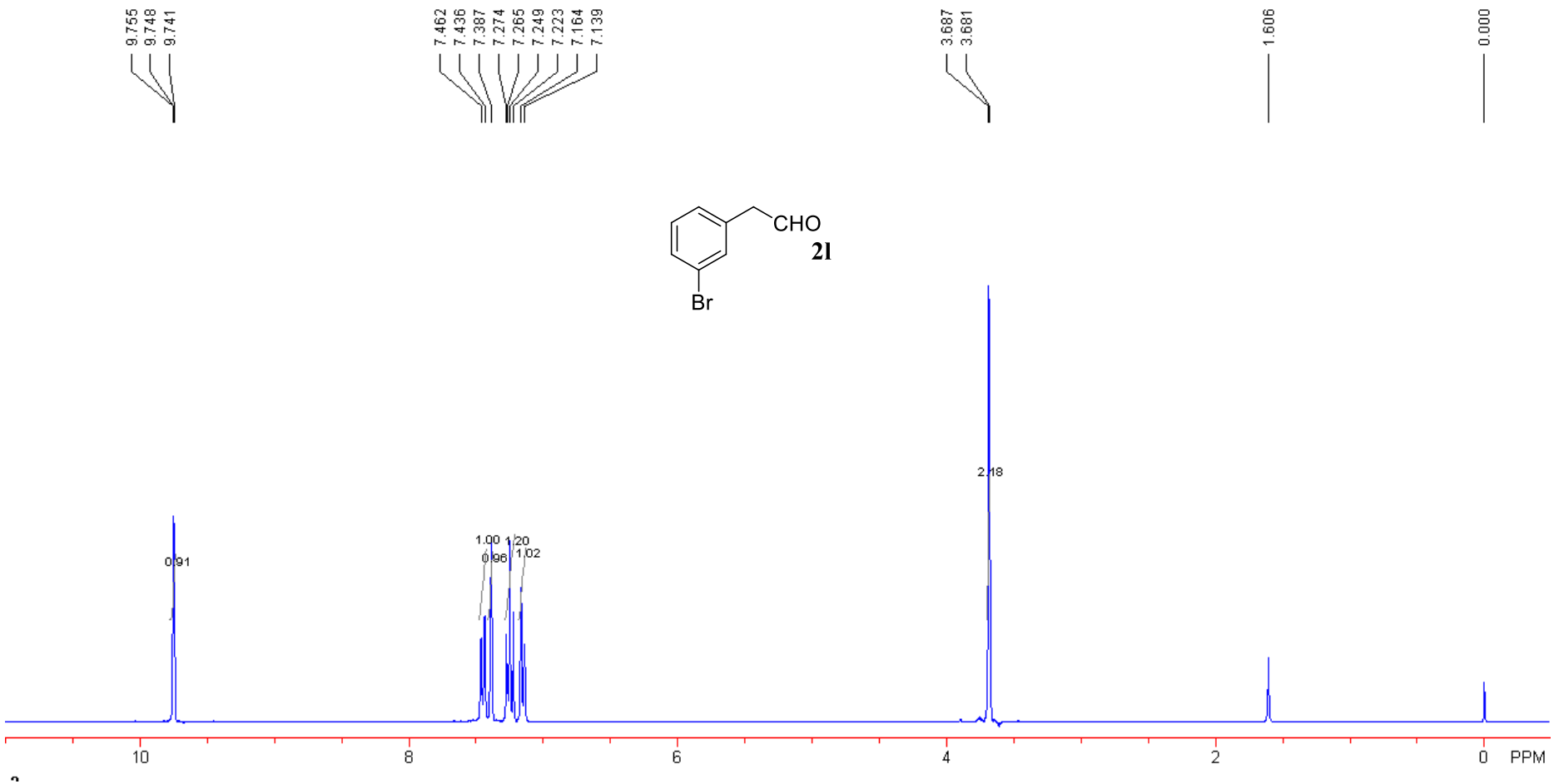
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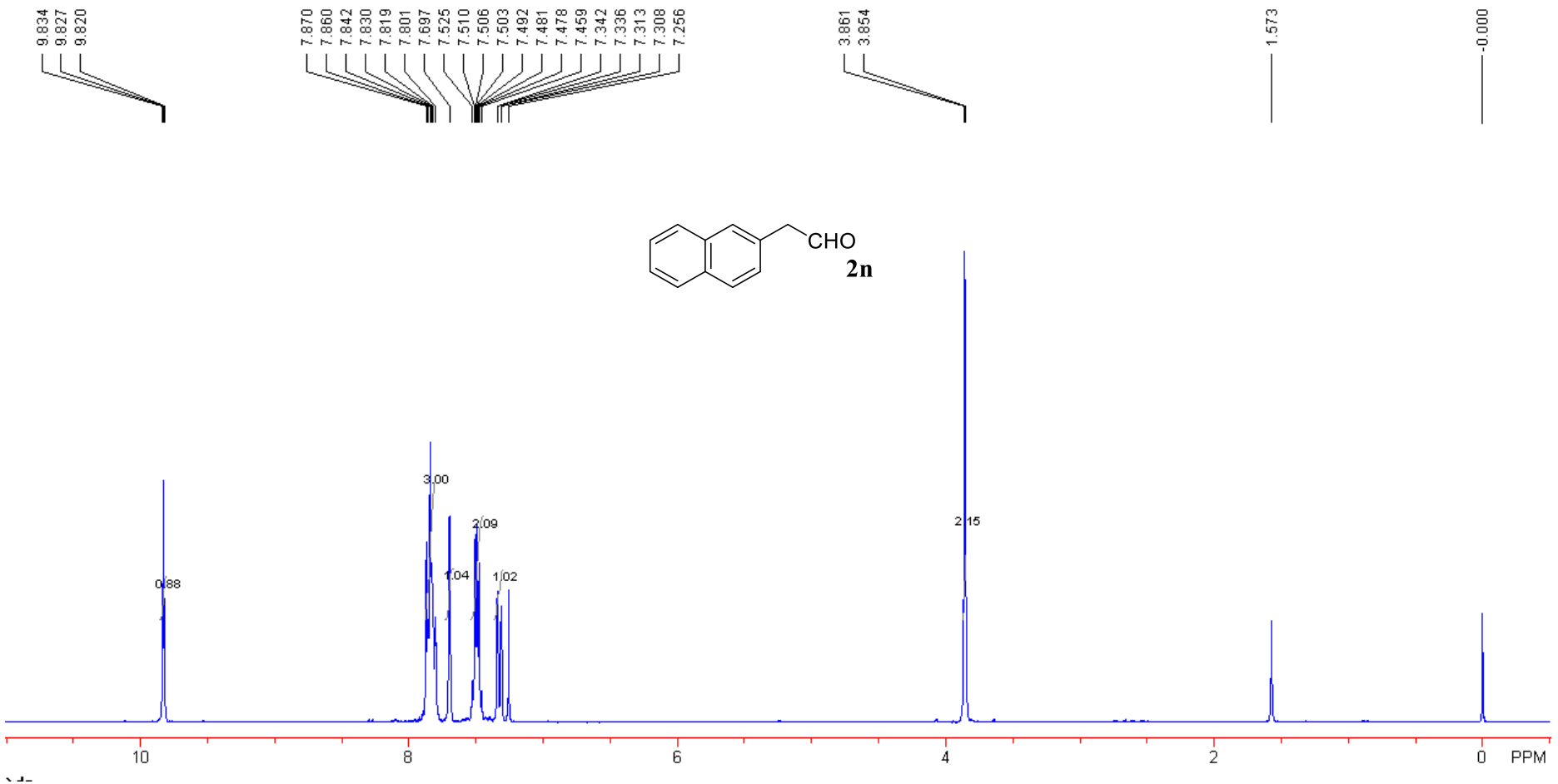
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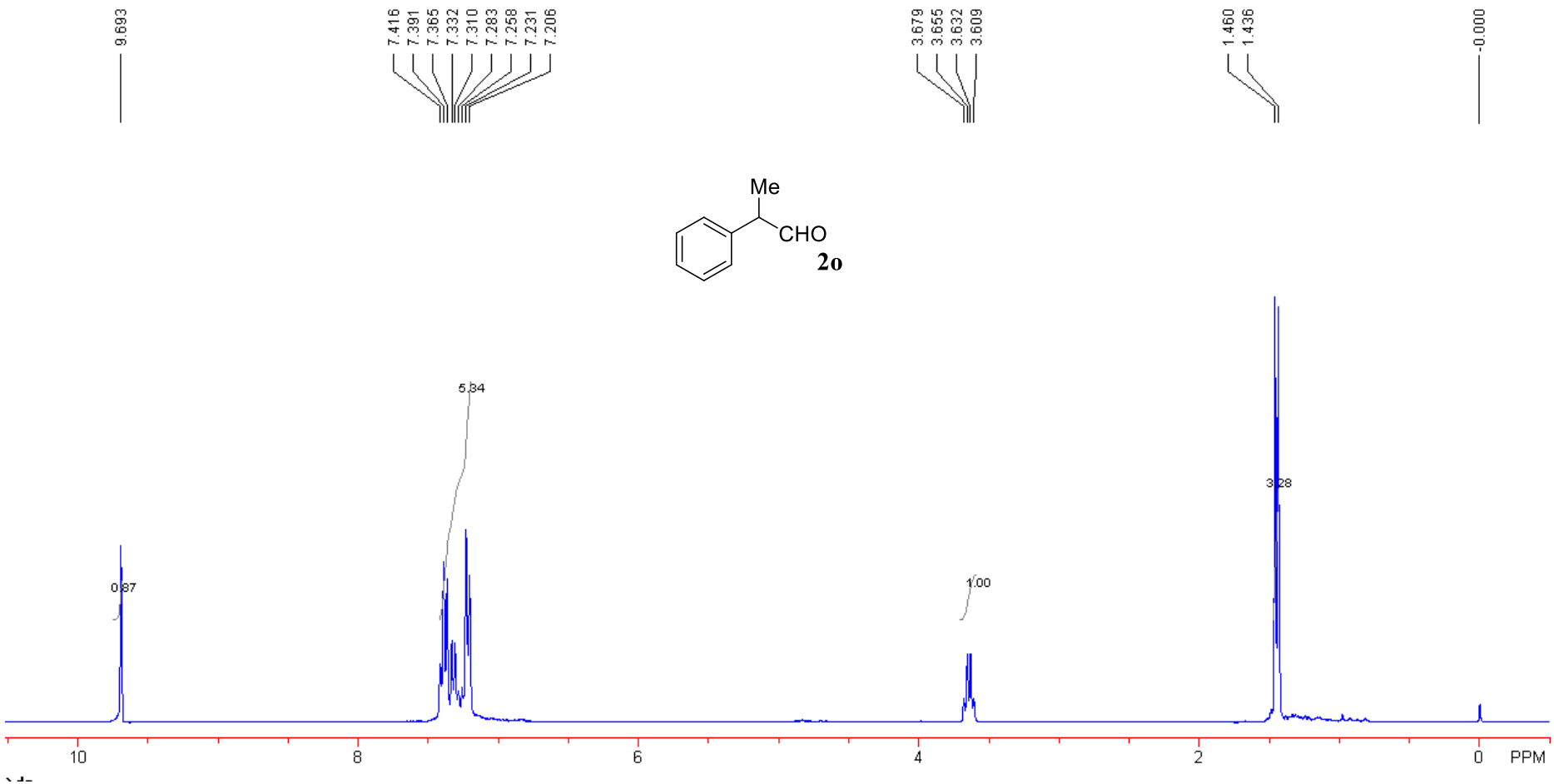
PPM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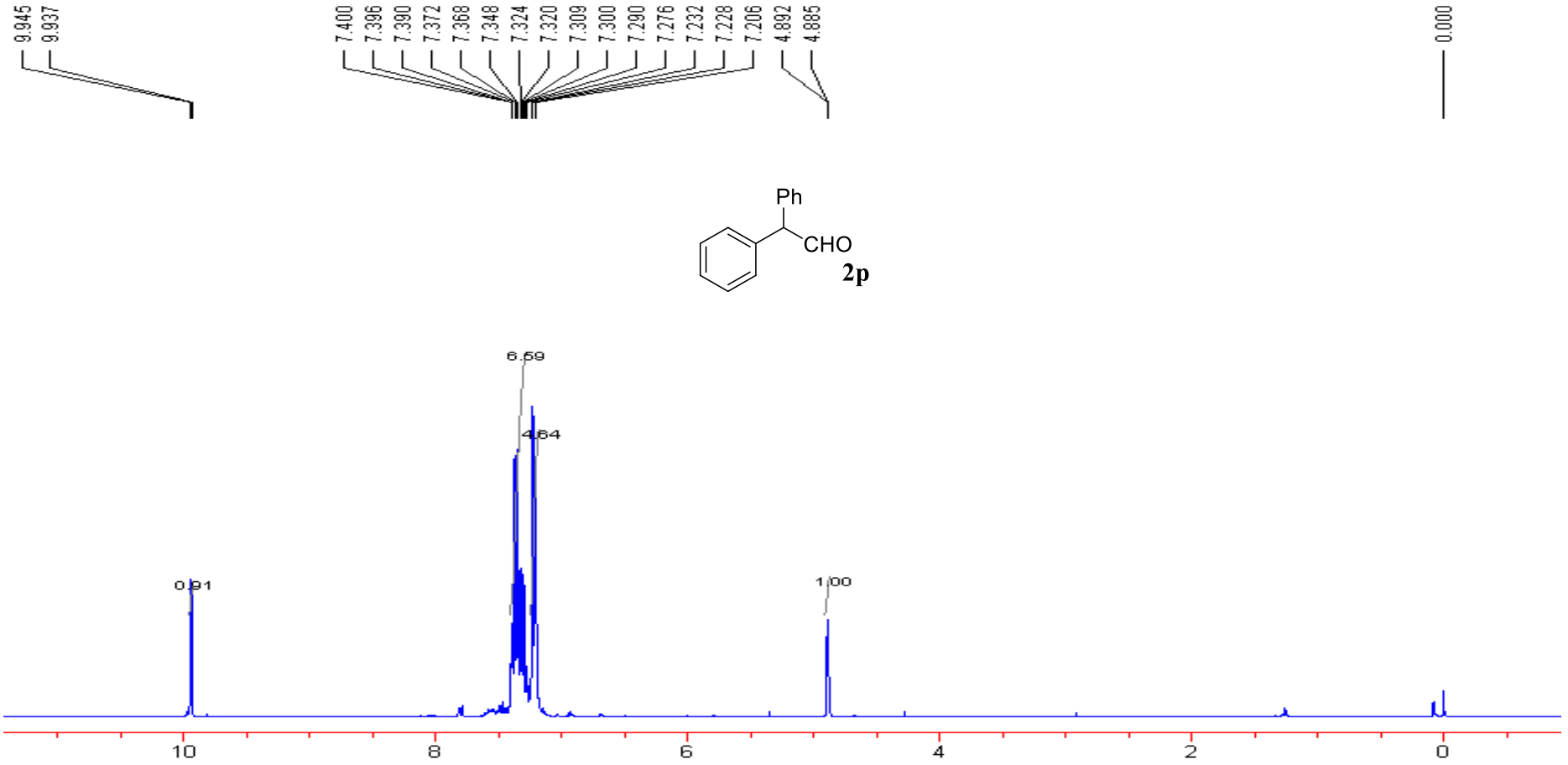
PPM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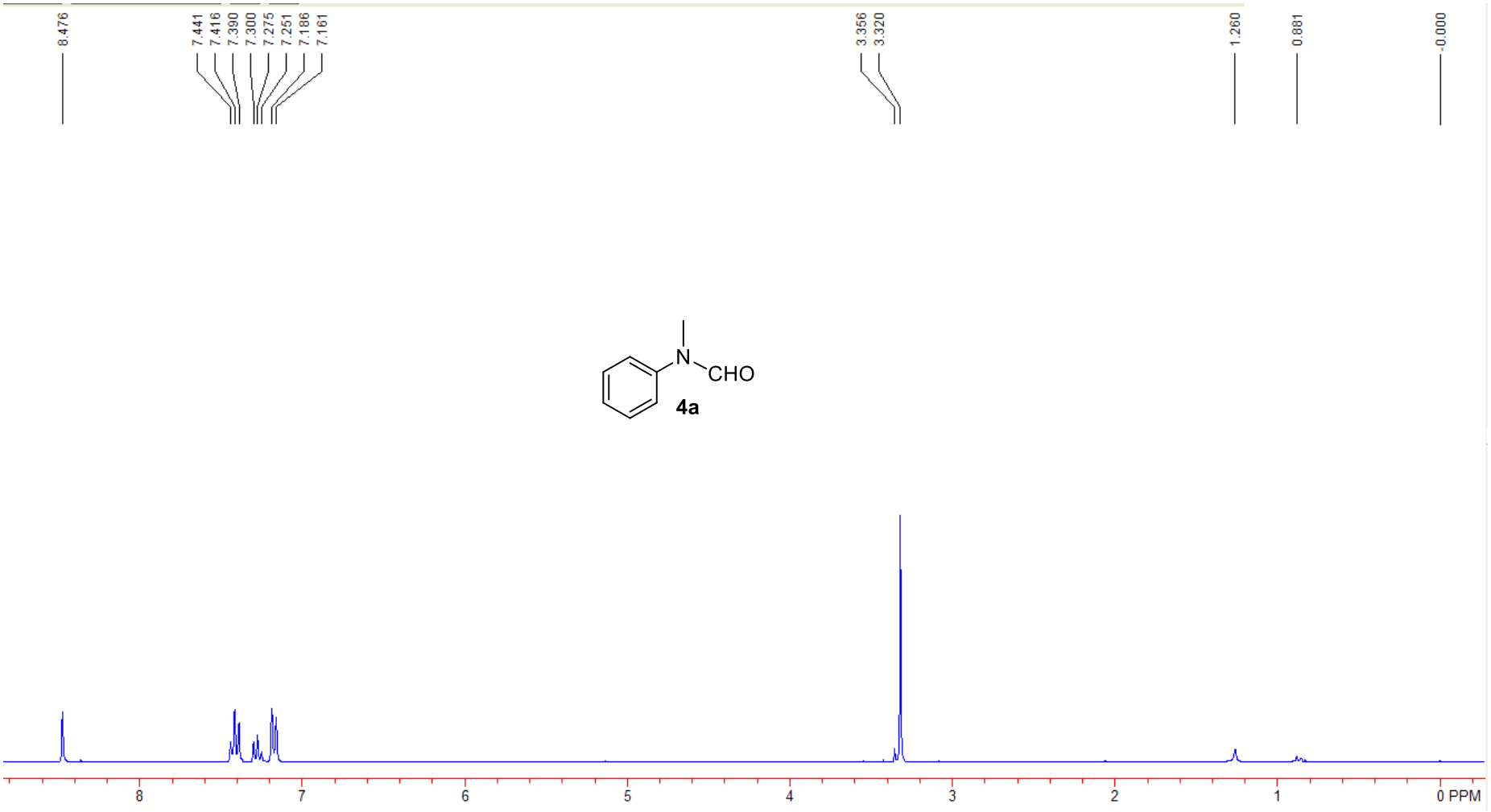
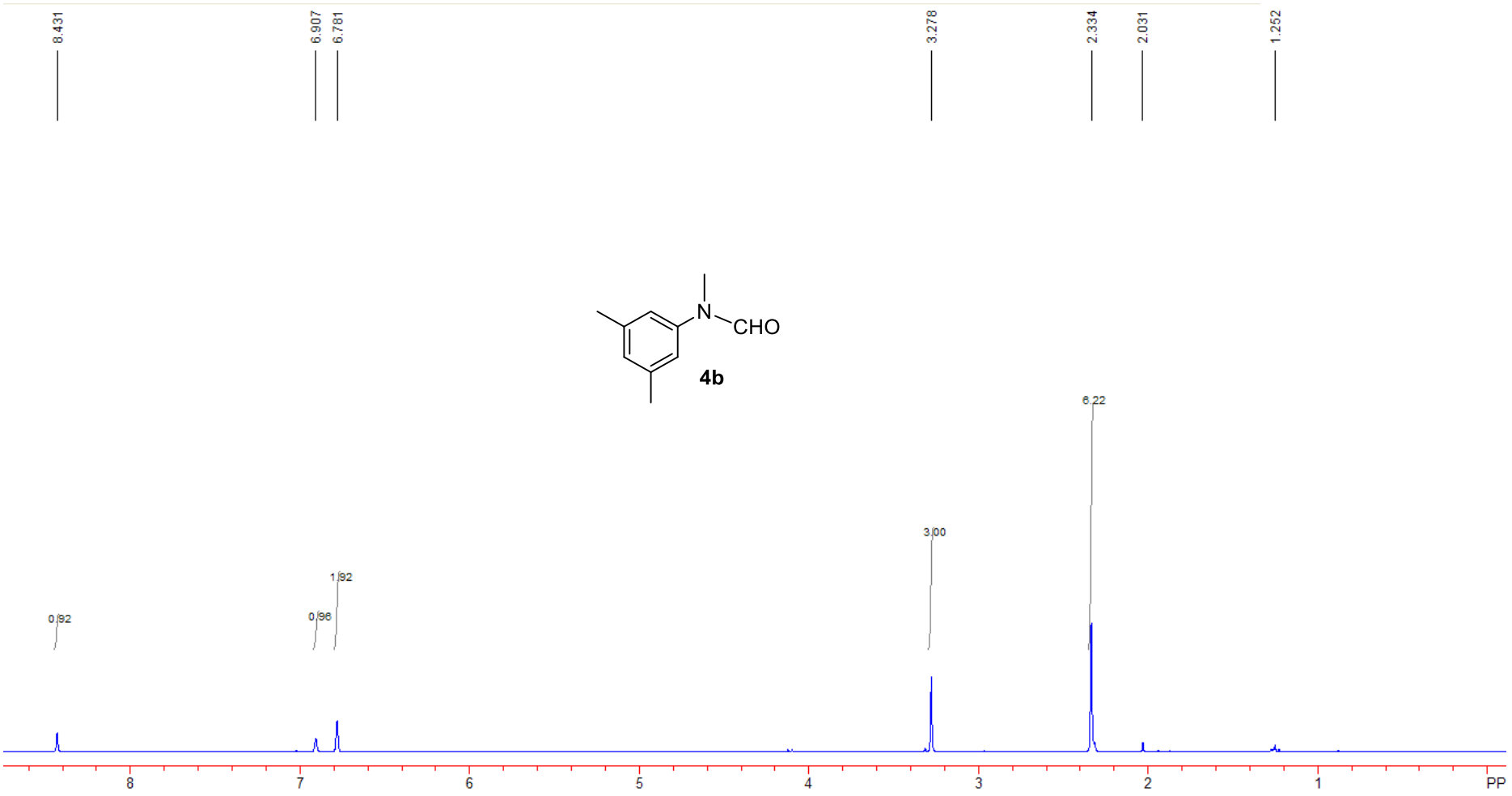
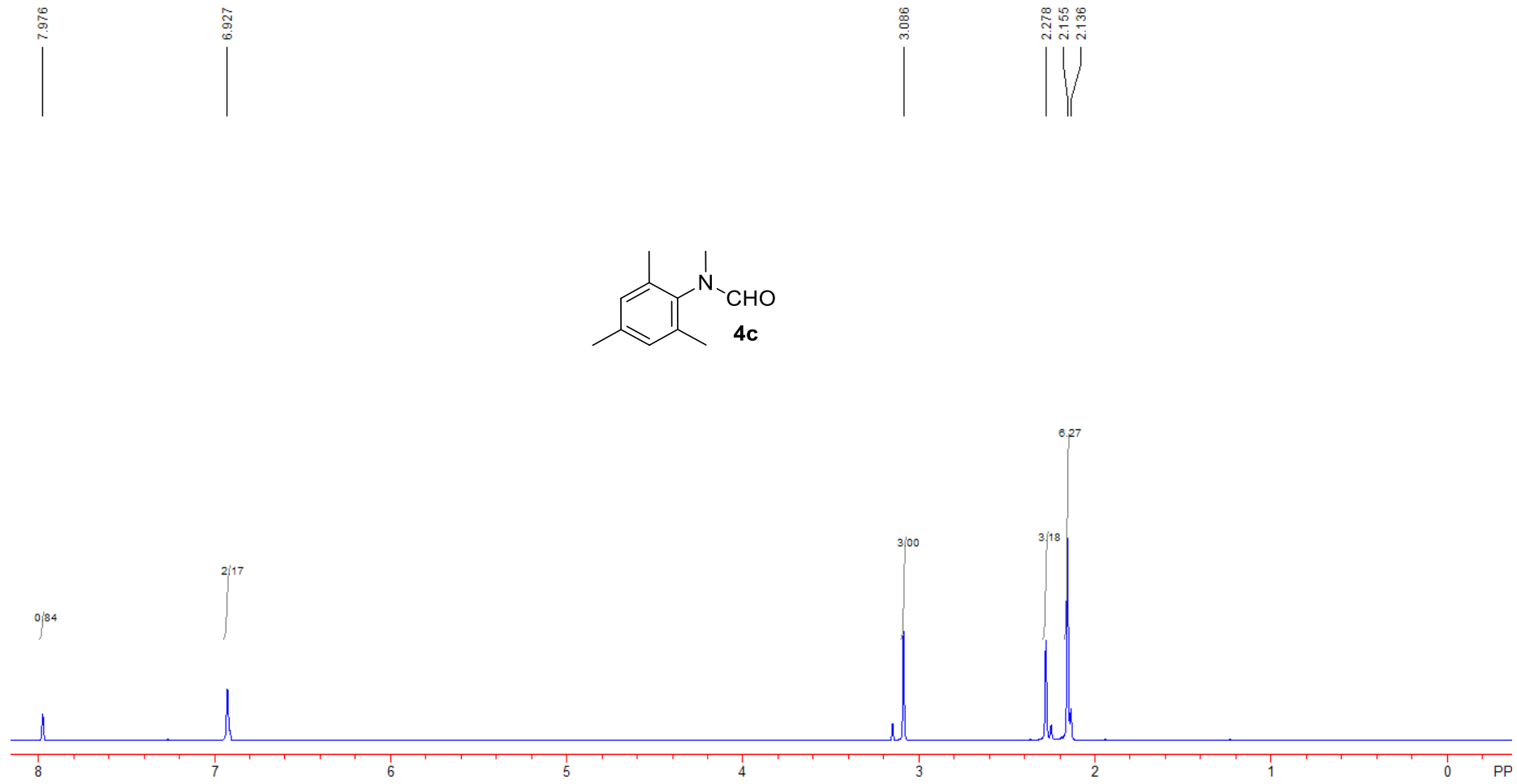
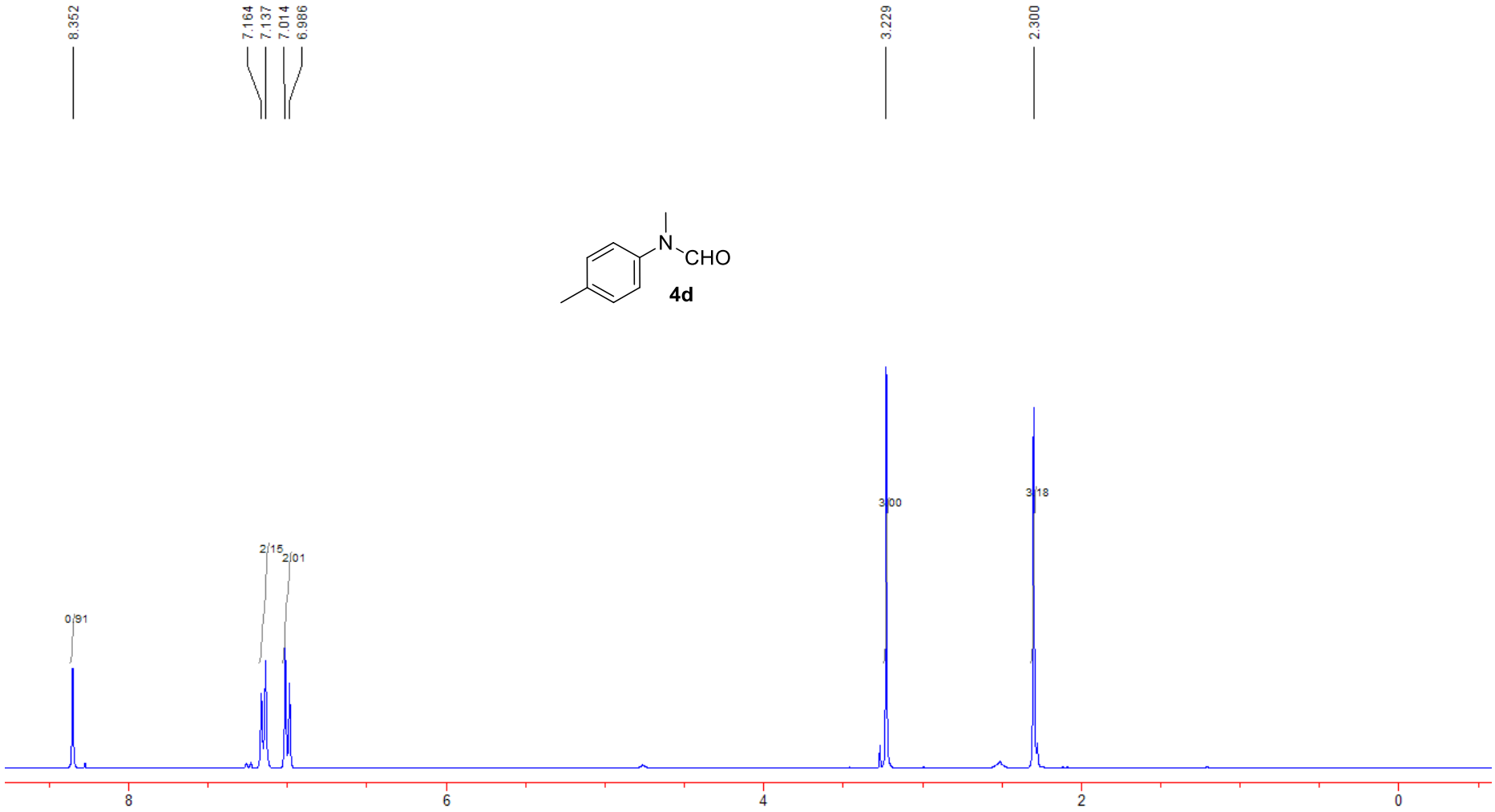
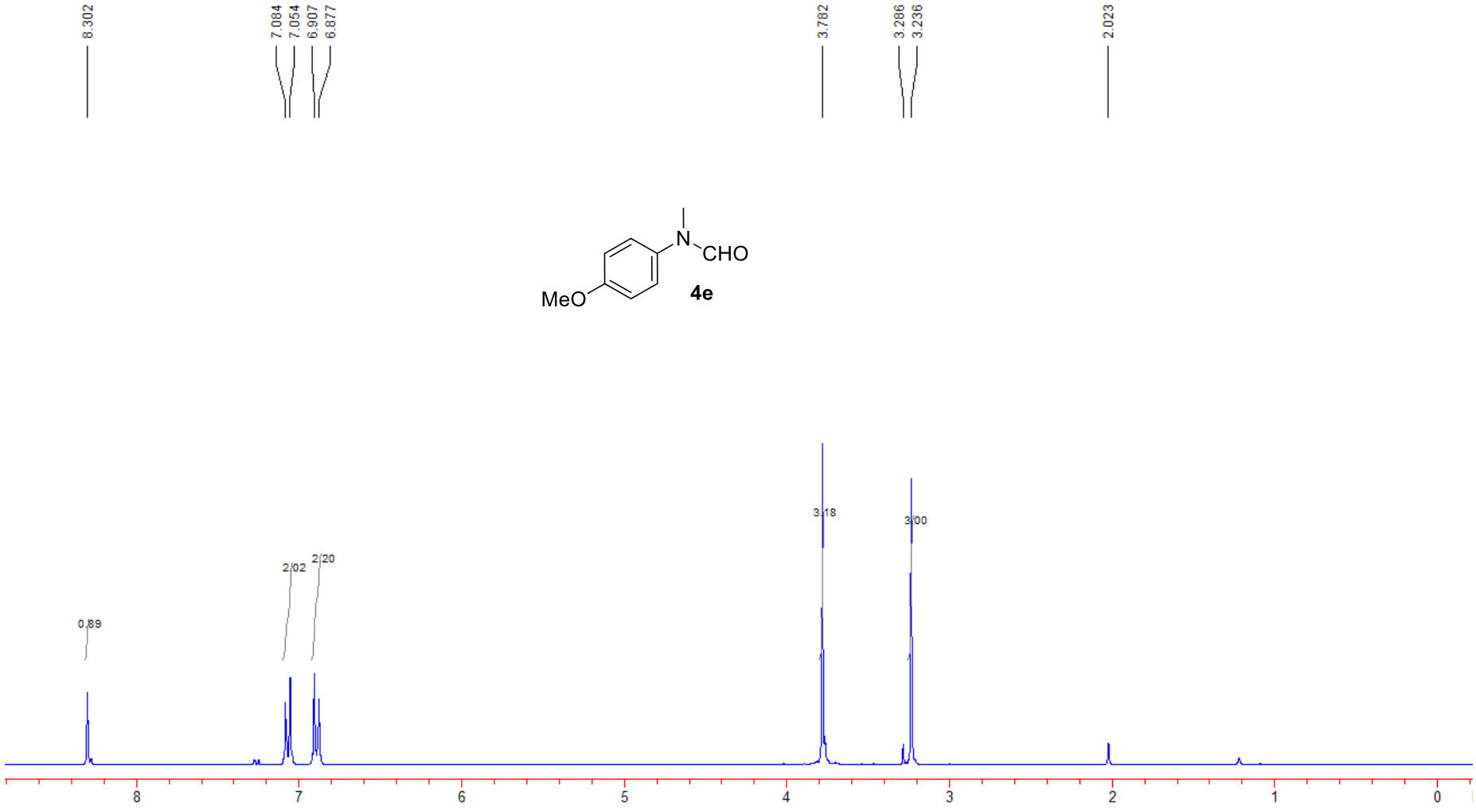
7.290
7.276
7.232
7.228
7.206
4.892
4.885
0.000
Ph
CHO
2p
6.69
4.64
0.91
1.00
10
8
6
4
2
0

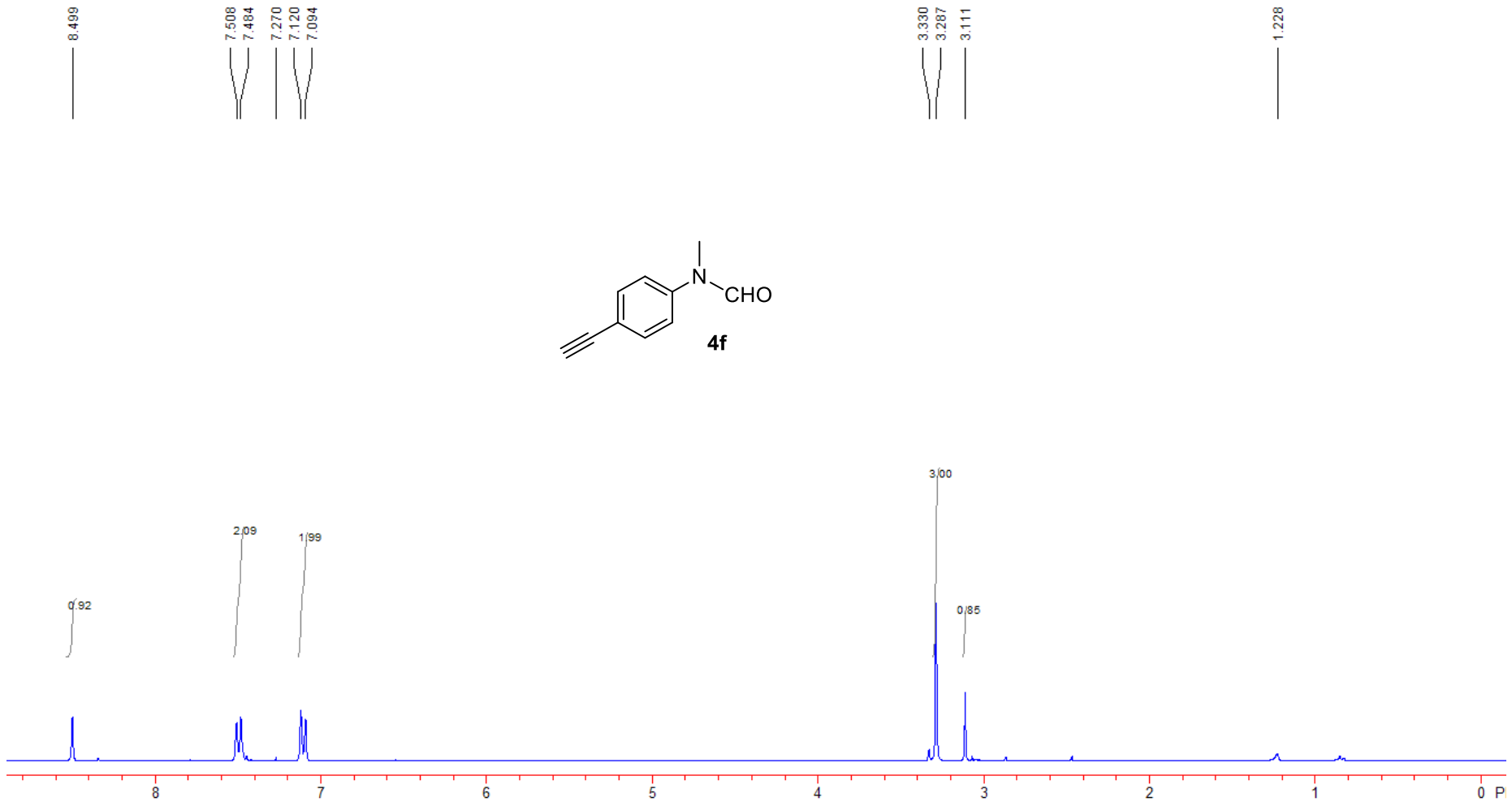

8.476
7.441
7.416
7.390
7.300
7.275
7.251
7.186
7.161
3.356
3.320
1.260
0.881
-0.000
N
CHO
4a
8
7
6
5
4
3
2
1
0 PPM

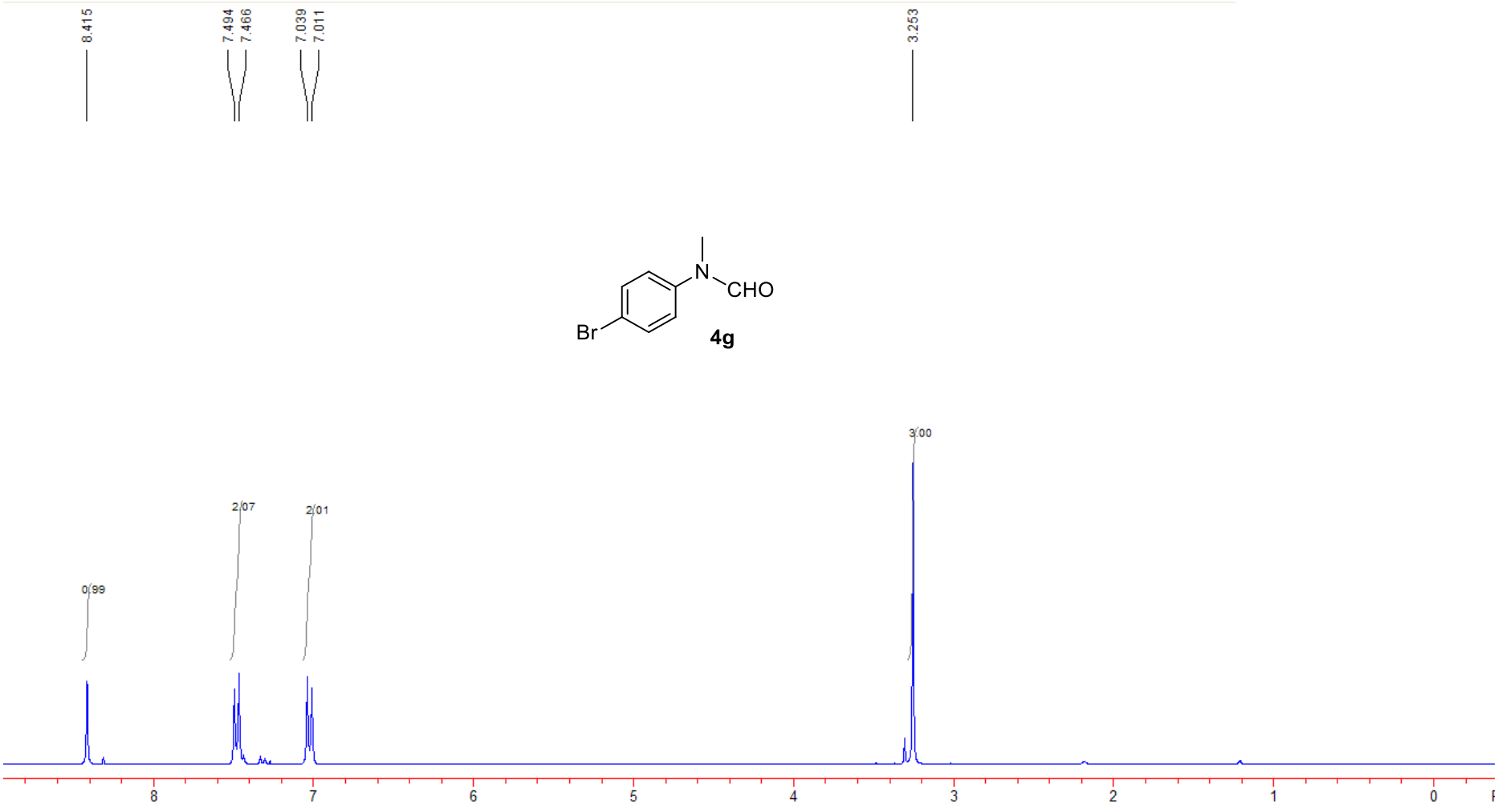

8.431
6.907
6.781
3.278
2.334
2.031
1.252
N
CHO
4b
6.22
3.00
1.92
0.92
0.96
8
7
6
5
4
3
2
1
PP

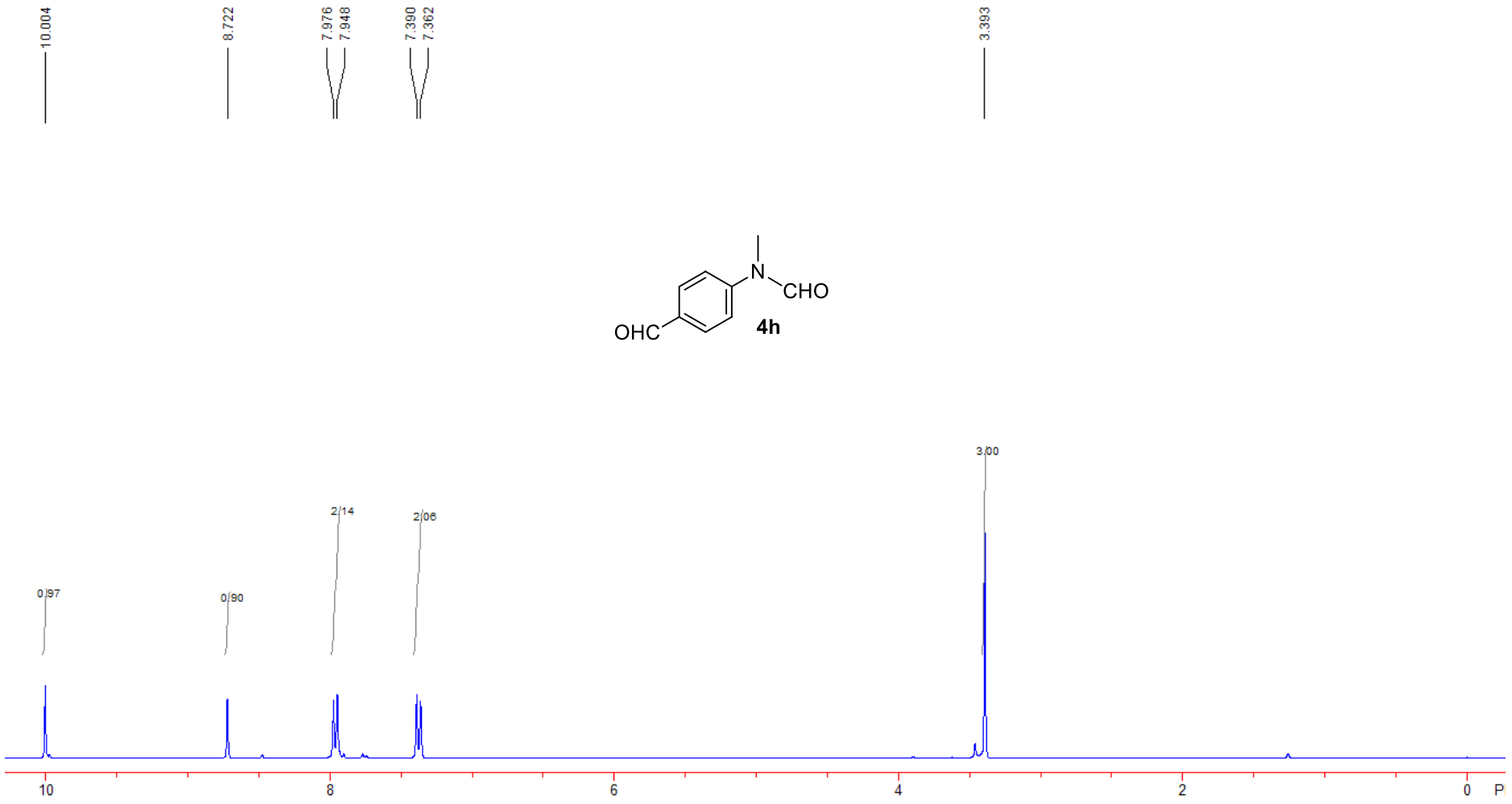

7.976
6.927
3.086
2.278
2.155
2.136
N
CHO
4c
6.27
3.00
3.18
2.17
0.84
8
7
6
5
4
3
2
1
0
PP


8.352
7.164
7.137
7.014
6.986
3.229
2.300
N
CHO
4d
0.91
2.15
2.01
3.00
3.18
8
6
4
2
0


8.302
7.084
7.054
6.907
6.877
3.782
3.286
3.236
2.023
N
CHO
MeO
4e
0.89
2.02
2.20
3.18
3.00
8
7
6
5
4
3
2
1
0


8.499
7.508
7.484
7.270
7.120
7.094
3.330
3.287
3.111
1.228
N
CHO
4f
0.92
2.09
1.99
3.00
0.85
8
7
6
5
4
3
2
1
0 PI


8.415
7.494
7.466
7.039
7.011
3.253
N
CHO
Br
4g
0.99
2.07
2.01
3.00
8
7
6
5
4
3
2
1
0


10.004
8.722
7.976
7.948
7.390
7.362
3.393
N
CHO
OHC
4h
0.97
0.90
2.14
2.06
3.00
10
8
6
4
2
0