Supporting Information

Ligand-free copper-catalyzed coupling of nitroarenes with arylboronic acids

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1. General experimental details

Chemicals were either purchased or purified by standard techniques without special instructions. ^{1}H NMR and ^{13}C NMR spectra were measured on a 300 MHz or 500 MHz Bruker spectrometer, using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants *J* are given in Hz. All reactions were conducted under air atmosphere. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). All products are known compounds and identified by comparison with authentic samples. Analytical data and spectra (^{1}H and ^{13}C NMR) of all compounds are supplied in the Supporting Information.

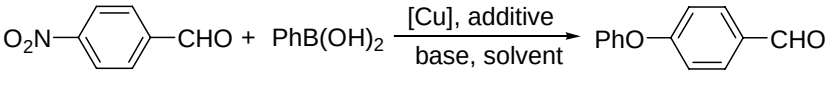
2. General procedure

2.1 Typical Experimental Procedure for the ligand-free copper-catalyzed coupling of nitroarenes with arylboronic acids:

Under air atmosphere, a Schlenk tube was charged with nitroarenes (0.6 mmol), arylboronic acids (0.3 mmol), nano CuO (5 mol%) or $Cu(OAc)_2$ (5 mol%), Oxone (1 equvi) and Cs_2CO_3 (0.9 mmol) in 3 mL of DMF at room temperature. After that, the mixture was stirred constantly at 100 ^{o}C (oil bath temperature) for 48 h. After the completion of the reaction, as monitored by TLC and GC-MS analysis, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum, and the resulting residue was purified by silica gel column chromatography to afford the desired product **3**.

2.2 Screening Optimal Conditions

Table S1 *Screening the optimal conditions*[a]



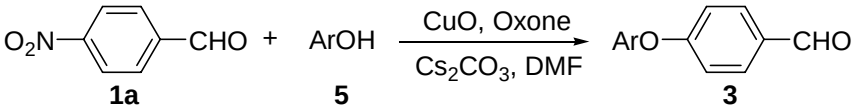
1a **2a** **3a**

Entry	Cu sources	Base	Solvent	Additive	Yield (%)[b]
1	$Cu(OAc)_2$	Na_2CO_3	DMF	-	27
2	$Cu(OAc)_2$	K_2CO_3	DMF	-	46
3	$Cu(OAc)_2$	CsOAc	DMF	-	34
4	$Cu(OAc)_2$	CsF	DMF	-	29
5	$Cu(OAc)_2$	LiF	DMF	-	28
6	$Cu(OAc)_2$	NaOH	DMF	-	14
7	$Cu(OAc)_2$	K_3PO_4	DMF	-	trace
8	$Cu(OAc)_2$	DABCO	DMF	-	trace
9	$Cu(OAc)_2$	Cs_2CO_3	CH_2Cl_2	-	trace
10	$Cu(OAc)_2$	Cs_2CO_3	THF	-	trace
11	$Cu(OAc)_2$	Cs_2CO_3	toluene	-	trace
12	$Cu(OAc)_2$	Cs_2CO_3	xylene	-	trace
13	$Cu(OAc)_2$	Cs_2CO_3	PhCl	-	trace
14	$Cu(OAc)_2$	Cs_2CO_3	CH_3CN	-	trace

[a]Reaction conditions: *p*-nitrobenzaldehyde (0.6 mmol), phenylboronic acid (0.3 mmol), Cu source (5 mol%), base (3 equiv), additive (1 equiv) and solvent (3 ml), air, 100 °C, 48 h. [b]Isolated yield.

2.3 Reaction of 4-nitrobenzaldehyde with phenols

Table S2 *Reaction of 4-nitrobenzaldehyde with phenols*[a]



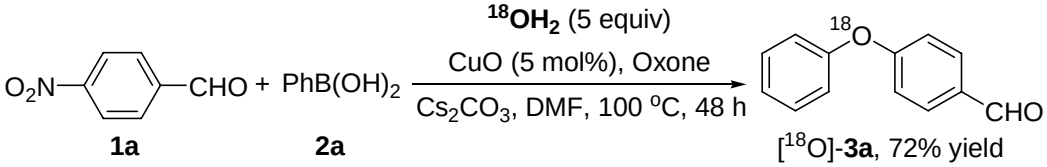
1a **5** **3**

Entry	ArOH (**5**)	Product	Yield (%)[b]
1	PhOH	**3a**	86
2	*p*-(Me)C_6H_4OH	**3b**	88
3	*o*-(Me)C_6H_4OH	**3d**	85
4	*p*-(OMe)C_6H_4OH	**3e**	89
5	*p*-(F)C_6H_4OH	**3g**	71
6	*p*-(Cl)C_6H_4OH	**3h**	84

[a]Reaction conditions: **1a** (0.6 mmol), **5** (0.3 mmol), nano CuO (5 mol%), Cs_2CO_3 (3 equiv), oxone (1 equiv) and DMF (3 ml), air, 100 °C, 48 h. [b]Isolated yield.

3. The ^{18}O-labeled Experiments Determined by GC-MS and HRMS Analysis

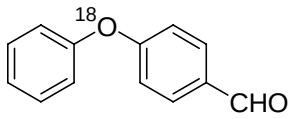
3.1 The reaction of 1a with 2a in the presence of $^{18}OH_2$



1a **2a** [^{18}O]-**3a**, 72% yield

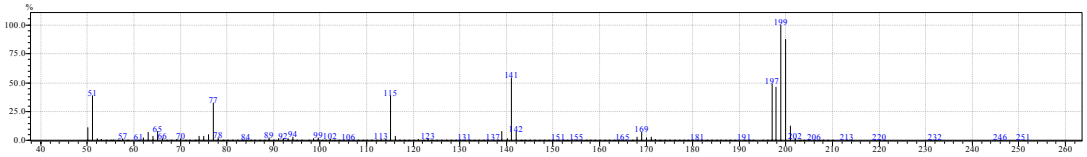
When the reaction was carried out in dry DMF using 5 equiv of $^{18}OH_2$, the mass spectroscopy (both EI and ESI) revealed that isolated **3a** includes one ^{18}O atom ([^{18}O]-**3a**) in 72% yield (Eq. 1). The ^{18}O-labeled experiments determined by GC-MS (**Figure S1)** and ESI analysis (**Figure S3**).

Figure S1. The ^{18}O-labeled Experiments Determined by GC-MS Analysis.



Chemical Formula: $C_{13}H_{10}O^{18}O$

Molecular Weigth: 200



[MS Spectrum]
# of Peaks 324
Raw Spectrum 11.883 (scan : 947)
Background No
Background Spectrum
Base Peak m/z 198.95 (Inten : 1,261,048)

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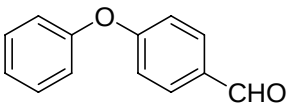
53.05	8692	0.69
54.05	919	0.07
55.05	8021	0.64
55.60	705	0.06
56.65	1226	0.10
57.55	19228	1.52
58.55	652	0.05
61.05	6053	0.48
62.05	26348	2.09
63.05	95091	7.54
64.05	50811	4.03
65.05	96535	7.66
66.05	24729	1.96
67.05	2197	0.17
68.05	3456	0.27
69.15	10111	0.80
70.05	18814	1.49
71.05	7893	0.63
72.00	11190	0.09
73.05	4910	0.39
74.05	49237	3.90
75.05	45816	3.63
76.05	63906	5.07
77.05	415044	32.91
78.05	30159	2.39
79.05	4019	0.32
80.10	353	0.03
81.10	351	0.03
82.10	150	0.01
83.15	599	0.05
84.10	7729	0.61
85.05	4228	0.34
86.00	4708	0.37
87.00	6870	0.54
88.05	6191	0.49

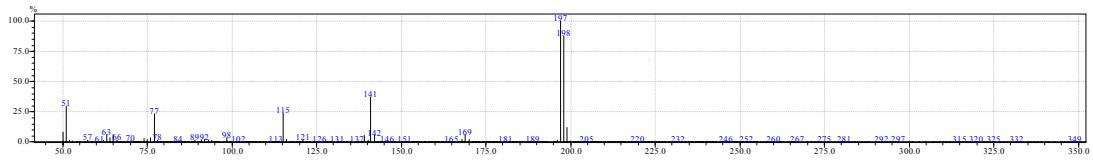
89.05	28742	2.28	133.00	246	0.02	178.00	82	0.01
90.05	4030	0.32	134.00	201	0.02	179.00	146	0.01
91.05	22317	1.77	135.00	209	0.02	180.00	89	0.01
92.05	23734	1.88	136.00	154	0.01	180.95	11810	0.09
93.05	21168	1.68	137.05	1835	0.15	181.90	332	0.03
94.05	40694	3.23	138.15	3584	0.28	182.95	596	0.05
95.05	3329	0.26	139.05	96814	7.68	184.00	326	0.03
96.05	960	0.08	140.15	25242	2.00	185.00	188	0.01
97.55	1577	0.13	141.10	679991	53.92	186.00	50	0.00
98.55	18967	1.50	142.10	103487	8.21	187.00	49	0.00
99.50	33708	2.67	143.10	7119	0.56	188.00	34	0.00
100.45	2868	0.23	144.00	1054	0.08	189.00	22	0.00
101.05	2728	0.22	145.00	450	0.04	191.00	57	0.00
102.05	9404	0.75	146.00	244	0.02	192.00	14	0.00
103.05	3436	0.27	147.00	191	0.02	193.00	42	0.00
104.05	3146	0.25	148.00	105	0.01	194.90	1794	0.14
105.05	2668	0.21	149.00	302	0.02	195.95	2587	0.21
106.05	4827	0.38	150.00	1452	0.12	196.95	621113	49.25
107.05	2049	0.16	151.05	7354	0.58	197.95	584765	46.37
108.10	343	0.03	152.05	4625	0.37	198.95	1261048	100.00
109.10	412	0.03	153.00	2140	0.17	199.95	1104162	87.56
110.00	863	0.07	154.00	738	0.06	200.95	156321	12.40
111.05	1049	0.08	155.00	1001	0.08	201.95	22697	1.80
112.10	599	0.05	156.00	247	0.02	202.95	2146	0.17
113.05	11991	0.95	157.00	418	0.03	203.90	220	0.02
114.15	14260	1.13	158.00	188	0.01	204.95	483	0.04
115.05	485712	38.52	159.00	119	0.01	206.00	71	0.01
116.10	50103	3.97	160.00	76	0.01	207.00	58	0.00
117.05	2451	0.19	161.00	127	0.01	208.00	34	0.00
118.05	740	0.06	162.00	82	0.01	209.00	44	0.00
119.05	552	0.04	163.00	90	0.01	210.00	14	0.00
120.00	2895	0.23	164.00	98	0.01	213.00	24	0.00
121.00	11108	0.88	165.00	145	0.01	214.00	6	0.00
122.05	6347	0.50	167.00	4719	0.37	219.00	44	0.00
123.05	20482	1.62	168.00	4121	3.27	220.00	110	0.01
124.05	1945	0.15	169.00	8732	1 6.92	221.00	26	0.00
125.05	855	0.07	170.00	3274	5 2.60	231.00	3	0.00
126.05	3493	0.28	171.00	3569	5 2.83	232.00	16	0.00
127.05	2705	0.21	172.00	9700	0.77	246.00	13	0.00
128.05	2565	0.20	172.95	1111	0.09	251.00	16	0.00
129.05	1312	0.10	174.00	118	0.01	272.00	5	0.00
130.00	351	0.03	175.00	58	0.00	278.00	31	0.00
131.05	1259	0.10	176.00	54	0.00	281.00	29	0.00
132.00	242	0.02	177.00	108	0.01	294.00	5	0.00

Figure S2. GC-MS Analysis of **3a**.



Chemical Formula: $C_{13}H_{10}O_2$

Molecular Weigth: 198

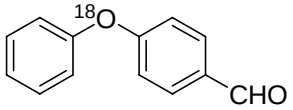


[MS Spectrum]
# of Peaks 414
Raw Spectrum 11.892 (scan : 948)
Background No
Background Spectrum
Base Peak m/z 196.95 (Inten : 2,094,067)

m/z	Absolute Intensity	Relative Intensity
50.00	171740	8.20
51.00	624054	29.80
52.00	34278	1.64
52.95	14193	0.68
54.00	1319	0.06
55.00	10135	0.48
56.55	1772	0.08
57.50	35302	1.69
58.45	1881	0.09
60.05	469	0.02
61.00	8542	0.41
62.00	37338	1.78
63.00	130276	6.22
64.00	69449	3.32
65.00	125636	6.00
66.00	32266	1.54
67.00	2737	0.13
68.00	3092	0.15
69.05	13038	0.62
70.00	25449	1.22
70.95	11319	0.54
71.95	1398	0.07
73.00	5815	0.28
74.00	55969	2.67
75.00	52209	2.49
76.00	74318	3.55
77.00	489415	23.37
78.00	35586	1.70
79.00	4610	0.22
80.00	271	0.01
81.00	86	0.00
82.00	90	0.00
83.15	1070	0.05
84.05	12681	0.61
85.05	5327	0.25
85.95	5607	0.27
87.00	8241	0.39
88.05	8051	0.38
89.00	36674	1.75
90.05	5261	0.25
91.05	29773	1.42
92.00	44686	2.13
93.00	27866	1.33
94.00	39686	1.90
95.05	2628	0.13
96.00	177	0.01
97.55	8023	0.38
98.50	71798	3.43
99.45	5420	0.26
101.05	3082	0.15
102.00	11028	0.53
103.05	4454	0.21
104.00	8628	0.41
105.05	4098	0.20
106.00	498	0.02
107.00	110	0.01
108.00	98	0.00
109.05	348	0.02
109.95	838	0.04
111.00	1010	0.05
112.05	667	0.03
113.05	12537	0.60
114.05	14898	0.71
115.05	507509	24.24
116.05	52538	2.51
117.05	2663	0.13
118.05	832	0.04
119.05	1502	0.07
120.00	9953	0.48
121.00	39142	1.87
122.00	3686	0.18
123.00	433	0.02
124.00	52	0.00
125.00	572	0.03
126.00	3946	0.19
127.05	3299	0.16
128.05	3047	0.15
129.05	19110.09	
130.00	476	0.02
131.00	1074	0.05
132.00	151	0.01
133.00	166	0.01
134.00	106	0.01
135.00	175	0.01
137.05	2137	0.10

138.05	4474	0.21	184.90	89	0.00	229.90	60	0.00
139.00	115342	5.51	185.90	58	0.00	230.90	71	0.00
140.15	36446	1.74	186.90	42	0.00	231.90	81	0.00
141.05	770650	36.80	187.90	29	0.00	232.90	74	0.00
142.05	117808	5.63	188.90	60	0.00	233.90	68	0.00
143.05	8655	0.41	189.90	18	0.00	234.90	47	0.00
144.00	1017	0.05	190.90	55	0.00	235.90	39	0.00
145.00	210	0.01	191.90	39	0.00	236.90	39	0.00
146.00	76	0.00	192.90	46	0.00	237.90	39	0.00
147.00	47	0.00	194.95	5490	0.26	238.90	13	0.00
148.00	30	0.00	196.05	33463	1.60	239.90	34	0.00
150.00	1340	0.06	196.95	2094067	100.00	240.90	19	0.00
151.00	7766	0.37	197.95	1835381	87.65	241.90	26	0.00
152.00	5071	0.24	198.95	255263	12.19	242.90	38	0.00
153.05	2150	0.10	199.95	24271	1.16	243.90	30	0.00
154.00	641	0.03	200.95	1741	0.08	244.90	52	0.00
155.00	1262	0.06	201.90	170	0.01	245.90	66	0.00
156.00	303	0.01	202.90	71	0.00	246.90	63	0.00
157.00	106	0.01	203.90	90	0.00	247.90	49	0.00
158.00	44	0.00	204.90	343	0.02	248.90	34	0.00
159.00	63	0.00	205.90	63	0.00	249.90	62	0.00
160.00	29	0.00	206.90	89	0.00	250.90	70	0.00
161.00	31	0.00	207.90	42	0.00	251.90	76	0.00
162.00	65	0.00	208.90	62	0.00	252.90	76	0.00
163.00	18	0.00	209.90	38	0.00	253.90	11	0.00
164.00	46	0.00	210.90	50	0.00	254.90	26	0.00
165.00	111	0.01	211.90	33	0.00	255.90	10	0.00
167.05	5447	0.26	212.90	38	0.00	256.90	16	0.00
168.00	48766	2.33	213.90	26	0.00	257.90	31	0.00
169.00	127695	6.10	214.90	55	0.00	258.90	29	0.00
170.00	45022	2.15	215.90	33	0.00	259.90	34	0.00
171.00	5386	0.26	216.90	60	0.00	260.90	27	0.00
172.00	417	0.02	217.90	46	0.00	261.90	26	0.00
173.00	81	0.00	218.90	42	0.00	262.90	38	0.00
174.00	62	0.00	219.90	103	0.00	263.90	26	0.00
175.00	41	0.00	220.90	65	0.00	264.90	54	0.00
176.00	29	0.00	221.90	58	0.00	265.90	81	0.00
177.00	118	0.01	222.90	31	0.00	266.90	97	0.00
178.00	121	0.01	223.90	49	0.00	269.90	47	0.00
179.00	146	0.01	224.90	34	0.00	270.90	30	0.00
180.95	1933	0.09	225.90	31	0.00	271.90	39	0.00
181.95	560	0.03	226.90	65	0.00	272.90	36	0.00
182.90	313	0.01	227.90	41	0.00	273.90	47	0.00
183.90	214	0.01	228.90	68	0.00	274.90	52	0.00

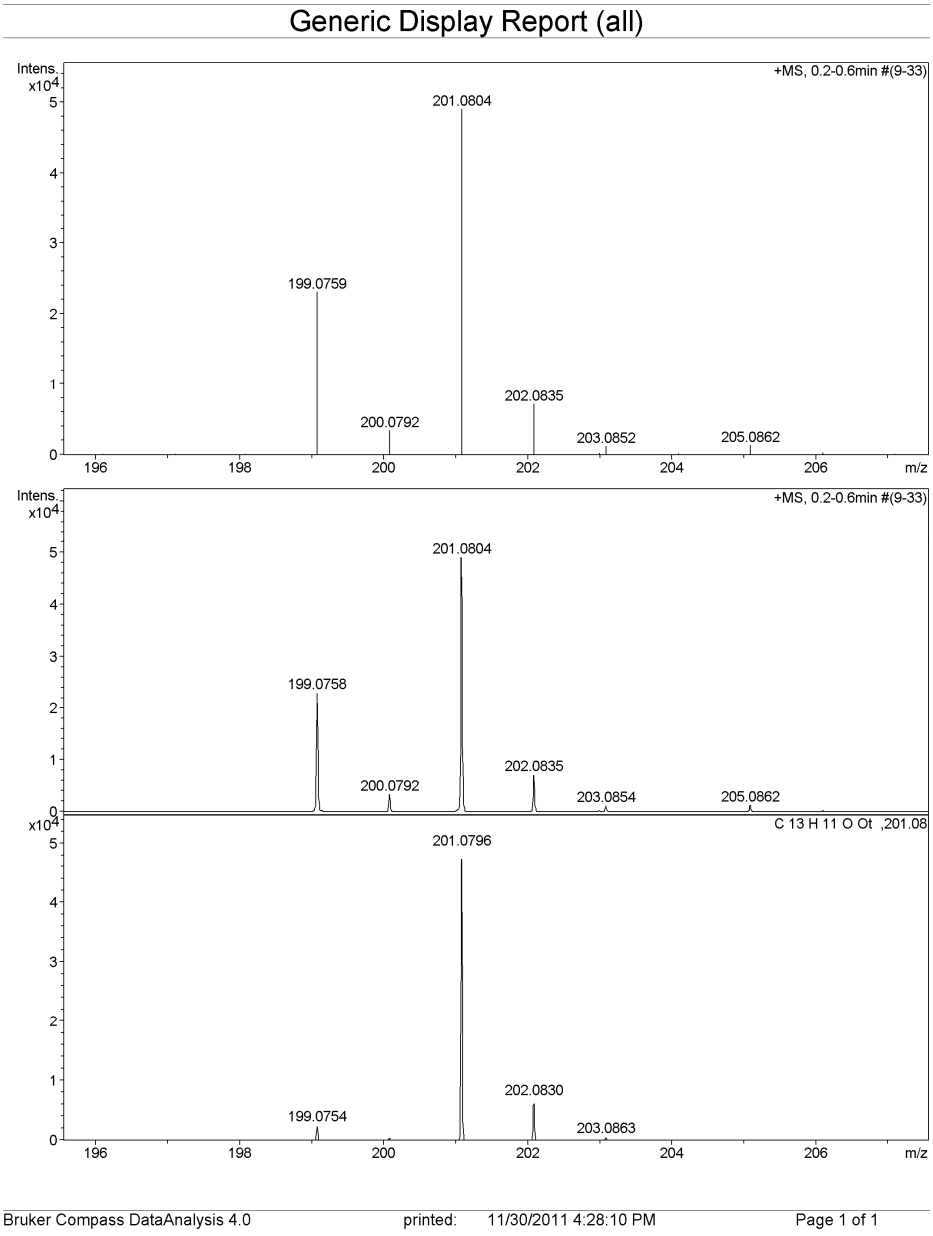
Figure S3. The ^{18}O-labeled Experiments Determined by HRMS (ESI) Analysis.



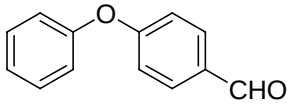
Chemical Formula: $C_{13}H_{10}O^{18}O$

Calcd. for $C_{13}H_{10}O^{18}O$ $[M+H]^+$ 201.0796

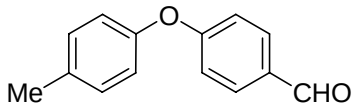
Found: m/z 201.0804



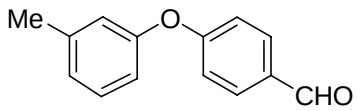
4. Analytical data for products



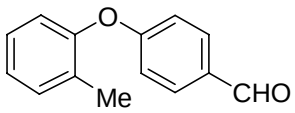
4-Phenoxybenzaldehyde (**3a**)[1]: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.05-7.11 (m, 4H), 7.23-7.25 (m, 1H), 7.39-7.45 (m, 2H), 7.83-7.86 (m, 2H), 9.92 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 117.6, 120.4, 124.9, 130.1, 131.3, 131.9, 155.1, 163.2, 190.7.



4-(*p*-Tolyloxy)benzaldehyde (**3b**)[2]: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.37 (s, 3H), 6.97-7.05 (m, 4H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.81-7.84 (m, 2H), 9.91 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.8, 117.2, 120.4, 130.6, 131.0, 131.9, 134.7, 152.7, 163.7, 190.7.



4-(*m*-Tolyloxy)benzaldehyde (**3c**)[3]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.36 (s, 3H), 6.87-7.05 (m, 5H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.82-7.85 (m, 2H), 9.91 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 117.3, 117.5, 121.0, 125.7, 129.8, 131.1, 131.9, 140.4, 155.0, 163.3, 190.7.



4-(*o*-Tolyloxy)benzaldehyde (**3d**)[4]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.18 (s, 3H), 6.95-7.02 (m, 2H), 7.18 (d, *J* = 7.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 9.90 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 16.0, 116.4, 121.1, 125.5, 127.5, 130.6, 130.9, 131.9, 132.0, 152.7, 163.4, 190.7.

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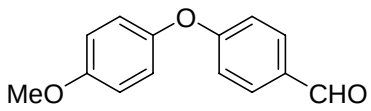
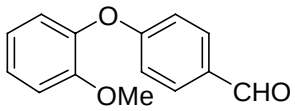
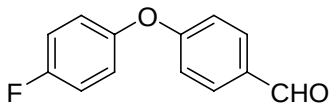
[1] Liu, Y. H.; Li, G.; Yang, L. M. *Tetrahedron. Lett.* **2009**, 50, 343.
[2] Koyama, H.; Julia K.; Boueres, J. K. *Bioorg. Med. Chem. Lett.* **2003**, 13, 1801.
[3] Shimizu, K.; Kizawa, K.; Yoshimoto, T.; Imamura, J. *Sekiyu Gakkaishi* **1982**, 25, 7.
[4] Hu, T. J.; Schulz, T.; Torborg, C.; Chen, X. R.; Wang, J.; Beller, M.; Huang, J. *Chem. Commun.* **2009**, *47*, 7330.



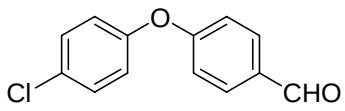
4-(4-Methoxyphenoxy)benzaldehyde (**3e**)[5]: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.82 (s 3H), 6.91-7.04 (m, 6H), 7.81 (d, *J* = 8.6 Hz, 2H). 9.89 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.6, 115.1, 116.7, 121.8, 130.8, 131.9, 148.1, 156.8, 164.1, 190.7.



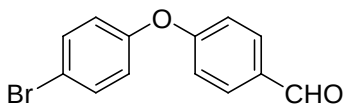
4-(2-Methoxyphenoxy)benzaldehyde (**3f**)[6]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.78 (s, 3H), 6.97-7.05 (m, 4H), 7.09-7.10 (m, 1H), 7.22-7.25 (m, 1H), 7.80-7.82 (m, 2H), 9.89 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.8, 113.0, 116.2, 121.3, 122.5, 126.4, 130.8, 131.8, 142.8, 151.7, 163.5, 190.7.



4-(4-Fluorophenoxy)benzaldehyde (**3g**)[5]: ^{1}H NM R($CDCl_3$, 300 MHz) δ 7.01-7.14 (m, 6H), 7.84 (d, *J* = 8.7 Hz, 2H), 9.92 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 116.8 (d, $^{2}J_{C\text{-}F}$ = 23.4 Hz, 1C), 117.12, 122.0 (d, $^{3}J_{C\text{-}F}$ = 8.8Hz, 1C), 131.2, 132, 150.7 (d, $^{4}J_{C\text{-}F}$ = 3.8 Hz, 1C), 159.7 (d, $^{1}J_{C\text{-}F}$ = 242.5 Hz, 1C), 163.3, 190.8.

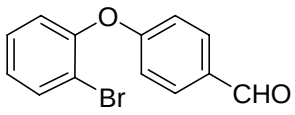


4-(4-Chlorophenoxy)benzaldehyde (**3h**)[5]: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.01-7.07(m, 4H), 7.36-7.39 (m, 2H), 7.86 (d, *J*=8.7 Hz, 2H), 9.93 (s, 1H). ^{13}C NMR (125 MHz) δ 117.7, 121.6, 130.1, 130.2, 131.6, 132.0, 153.8, 162.7, 190.6.

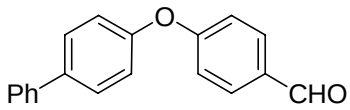


[5] Zheng, X.; Ding, J.; Chen, J.; Gao, W.; Liu, M.; Wu, H. *Org. Lett.* **2011**, 13, 1726.
[6] Ungnade, H. E. *J. Am. Chem. Soc.***1941**, 63, 2091.

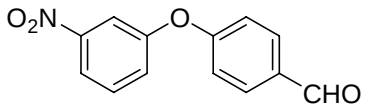
4-(4-Bromophenoxy)benzaldehyde (**3i**)[7]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.95-7.07 (m, 4H), 7.49-7.52 (m, 2H), 7.83-7.86 (m, 2H), 9.92 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 117.6, 117.7, 122.0, 131.6, 132.0, 133.1, 154.3, 162.6, 190.7.



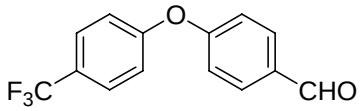
4-(2-Bromophenoxy)benzaldehyde (**3j**)[8]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.99-7.15 (m, 4H), 7.34-7.38 (m, 1H), 7.66-7.68 (m, 1H), 7.85 (d, *J*=8.7 Hz, 2H), 9.92 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 116.1, 116.9, 122.6, 126.7, 129.1, 131.5, 131.9, 134.2, 151.7, 162.4, 190.6.



4-(Biphenyl-4-yloxy)benzaldehyde (**3k**)[9]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.12-7.18 (m, 4H), 7.37 (t, *J*=7.4 Hz, 1H), 7.45-7.48 (m, 2H), 7.59-7.65 (m, 4H), 7.86-7.89 (m, 2H), 9.94 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 117.7, 120.6, 126.9, 127.3, 128.7, 128.8, 131.4, 131.9, 138.0, 140.1, 154.6, 163.1, 190.7.



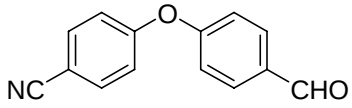
4-(3-Nitrophenoxy)benzaldehyde (**3l**)[10]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.12-7.14 (m, 2H), 7.40-7.42 (m, 1H), 7.58 (t, *J*=8.2 Hz, 1H), 7.89-8.06 (m, 4H), 9.97 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 114.7, 118.7, 119.3, 125.7, 130.8, 132.1, 132.5, 149.4, 156.4, 161.3, 190.5.



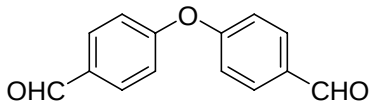
4-(4-(Trifluoromethyl)phenoxy)benzaldehyde[5] (**3m**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ

[7] Tu, N.; Link, J. T.; Sorensen, B. K. *Bioorg. Med. Chem. Lett.* **2004**, 14, 4179.
[8] Ames, D. E.; Opalko, A. *Tetrahedron* **1984**, 40, 1919.
[9] Igarashi, S.; Kimura, T.; Naito, R.; Hara, H.; Fujii, M.; Koutoku, H.; Oritani, H.; Mase, T. *Chem. Pharm. Bull.* **1999**, 47, 1073.
[10] Marin, L. Cozan, V.; Bruma, M. *Revue Roumaine de Chimie* **2005**, 50, 649.

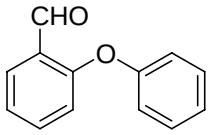
7.12-7.17 (m, 4H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.89-7.91 (m, 2H). 9.96 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 118.6, 119.7, 122.8, 125.0, 126.5, 127.4, 127.5, 127.5, 127.5, 1302.0, 132.1, 158.3, 161.6, 190.7.



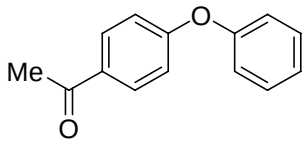
4-(4-Formylphenoxy)benzonitrile (**3n**)[11]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.11-7.16 (m, 4H), 7.67 (d, *J*=8.2 Hz, 2H), 7.92 (d, *J*=8.1 Hz, 2H), 9.97 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 107.7, 118.3, 119.4, 119.6, 132.0, 132.8, 134.4, 159.6, 160.6, 190.4.



4,4'-Oxydibenzaldehyde (**3o**)[12]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.17 (d, *J*=8.5 Hz, 4H), 7.92 (d, *J*=8.7 Hz, 4H), 9.97 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 119.3, 132.0, 132.6, 161.0, 190.6.



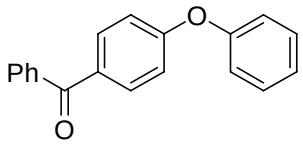
2-Phenoxybenzaldehyde (**3p**)[13]: ^{1}H NMR($CDCl_3$, 500 MHz) δ 6.90 (d, *J* = 8.3 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 2H), 7.17-7.52 (m, 5H), 7.93-7.95 (m, 1H), 10.52 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 118.4, 119.4, 123.3, 124.3, 126.9, 128.4, 130.1, 135.7, 156.4, 160.0, 189.4.



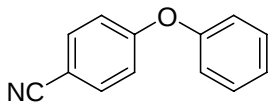
1-(4-Phenoxyphenyl)ethanone (**3q**)[5]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.57 (s, 3H), 7.00 (d, *J* = 8.5Hz, 2H), 7.07 (d, *J* = 8.5Hz, 2H), 7.20-7.22 (m, 1H), 7.38-7.41(m, 2H),

[11] Lazo, J. S.; Nunes, R.; Skoko, J. J.; Queiroz de Oliveira, P. E.; Vogt, A.; Wipf, P. *Bioorg. Med. Chem.* **2006**, 14, 5643.
[12] Sugimura, R.; Qiao, K.; Tomida, D.; Yokoyama, C. *Catal. Commun.* **2007**, 8, 770.
[13] Fish, P. V.; Ryckmans, T.; Stobie, A.; Wakenhut, F. *Bioorg. Med. Chem. Lett.* **2008**, 18, 1795.

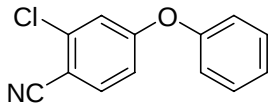
7.94 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 26.4, 117.2, 120.2, 124.6, 130.0, 130.6, 131.9, 155.5, 162.0, 196.7.



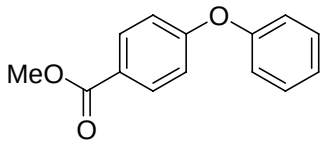
(4-Phenoxyphenyl)(phenyl)methanone (**3r**)[14]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.02-7.05 (m, 2H), 7.10 (d, *J* = 7.7Hz, 2H), 7.20 (t, *J* = 7.5Hz, 1H), 7.39-7.42 (m, 2H), 7.46-7.49 (m, 2H), 7.57 (t, *J* = 7.4Hz, 1H), 7.78-7.84 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 117.1, 120.1, 124.5, 128.2, 129.7, 130.0, 131.9, 132.0, 132.4, 137.9, 155.5, 161.5, 195.3.



4-Phenoxybenzonitrile (**3s**)[5]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.98-7.01 (m, 2H), 7.05-7.07 (m, 2H), 7.23 (t, *J* = 7.5Hz, 1H), 7.39-7.43 (m, 2H), 7.57-7.60 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 105.8, 117.8, 118.7, 120.3, 125.1, 130.1, 134.0, 154.7, 161.6.

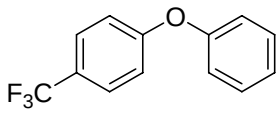


2-Chloro-4-phenoxybenzonitrile (**3t**)[15]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.90-6.92 (m, 1H), 7.03-7.08 (m, 3H), 7.26-7.29 (m, 1H), 7.42-7.46 (m, 2H), 7.58 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 106.7, 116.0, 118.4, 120.5, 125.7, 130.4, 135.2, 138.4, 154.1, 162.2.

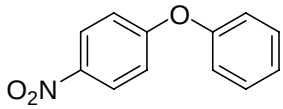


[14] Liu, Y.; Li, G.; Yang, L. *Ttrahedron Lett.* **2009**, 50, 343.
[15] Patel, K. M. *Patent* EP 659047 (**1993**).

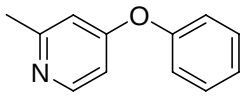
Methyl 4-phenoxybenzoate (**3u**)[16]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.90 (s, 3H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.37-7.41 (m, 2H), 8.00 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 52.0, 117.3, 120.1, 124.5, 130.0, 131.7, 155.6, 161.8, 166.6.



1-Phenoxy-4-(trifluoromethyl)benzene (**3v**)[17]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.04-7.07 (m, 4H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.38-7.41 (m, 2H), 7.57 (d, *J* = 8.5 Hz , 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 117.9, 119.9, 123.1, 124.5, 124.7, 125.0, 125.3, 127.0, 127.1, 127.1, 127.2, 130.1, 155.7, 160.5.



1-Nitro-4-phenoxybenzene (**3w**)[18]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.99-7.10 (m, 4H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.41-7.45 (m, 2H), 8.18-8.21 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 117.1, 120.5, 125.4, 125.9, 130.3, 142.6, 154.7, 163.3.



2-Methyl-4-phenoxypyridine (**3x**)[19]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.48 (s, 3H), 6.63-6.68 (m, 2H), 7.07 (d, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.39-7.42 (m, 2H), 8.32 (d, *J* = 5.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.5, 109.6, 111.3, 120.7, 125.2, 130.1, 150.6, 154.2, 160.4, 165.1.

[16] Hu, T.; Schulz, T.; Torborg, C.; Chen, X.; Wang, J.; Beller, M.; Huang, J. *Chem. Commun.* **2009**, 7330.
[17] Liu, T.; Shen, Q. *Org. Lett.* **2011**, 13, 2342.
[18] Tlili, A.; Monnier, F.; Taillefer, M. *Chem. Eur. J.* **2010**, 16, 12299.
[19] Fujikawa, K.; Kondo, K.; Yokomichi, I.; Kimura, F.; Haga, T.; Nishiyama, R. *Agric. Bio. Chem.* **1970**, 34, 68.

5. Copies of product ^{1}H NMR and ^{13}C NMR

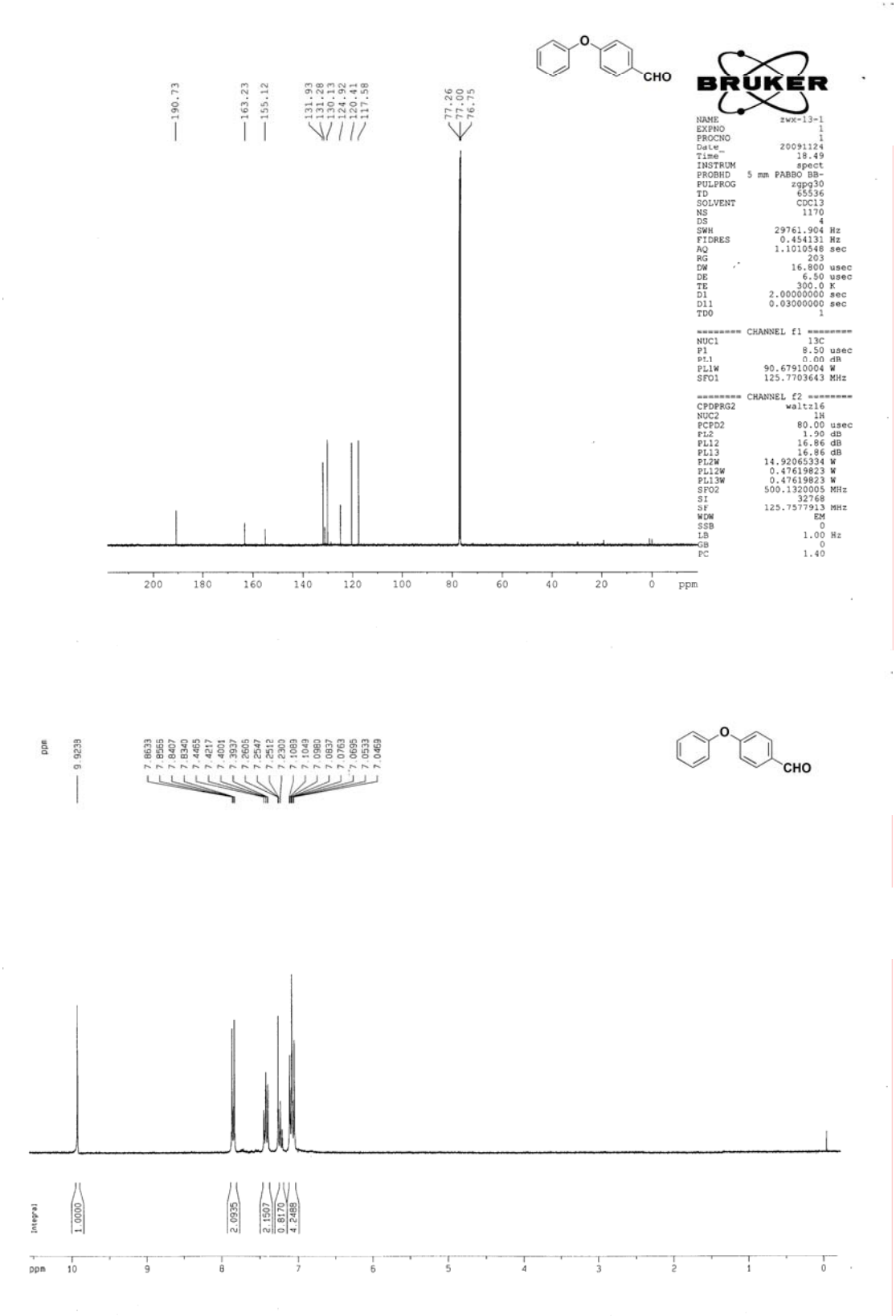


Figure S4. ^{1}H NMR of **3a** (300 MHz, $CDCl_3$) and ^{13}C NMR of **3a** (125 MHz, $CDCl_3$).

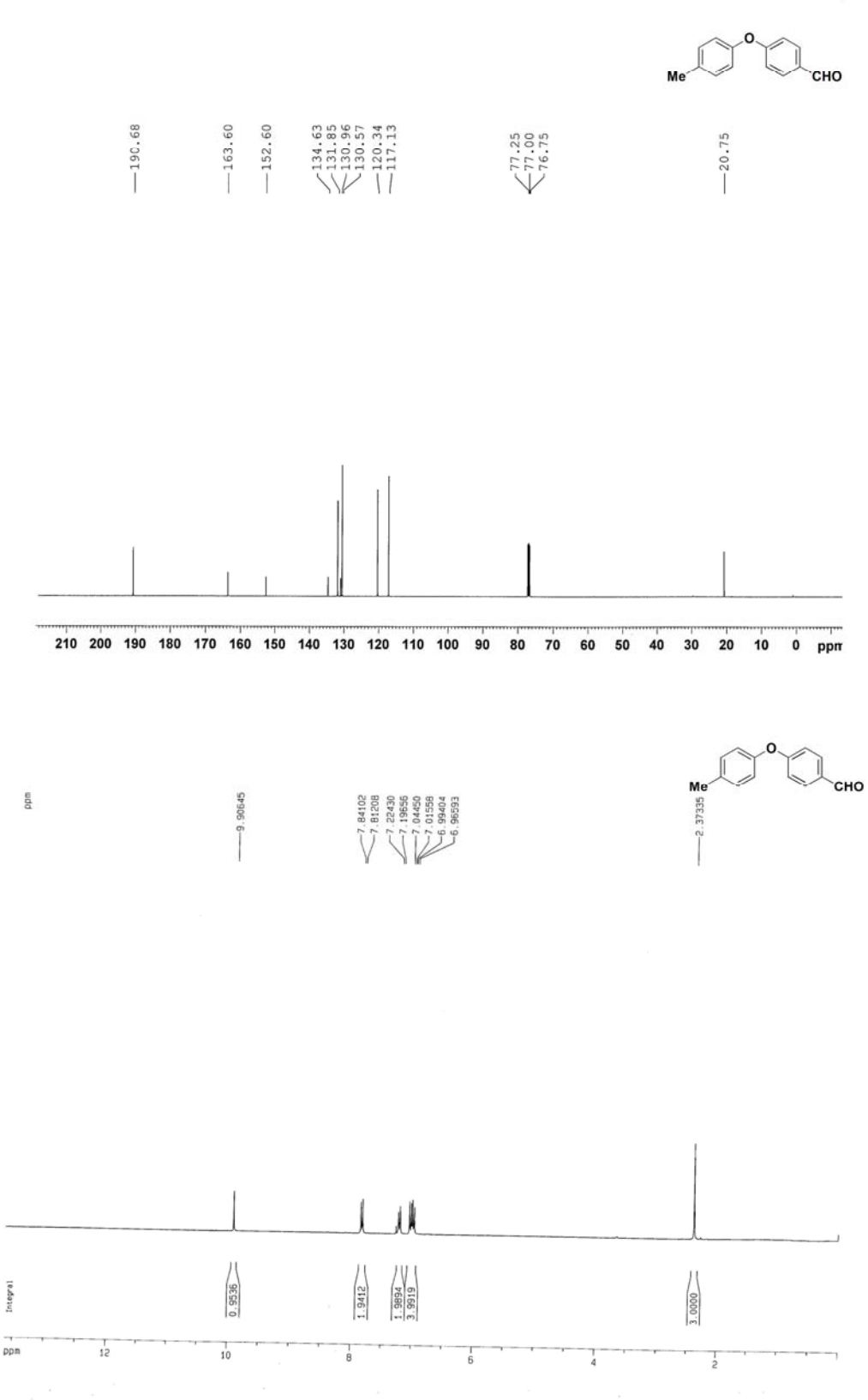


Figure S5. ^{1}H NMR of **3b** (300 MHz, $CDCl_3$) and ^{13}C NMR of **3b** (125 MHz, $CDCl_3$).

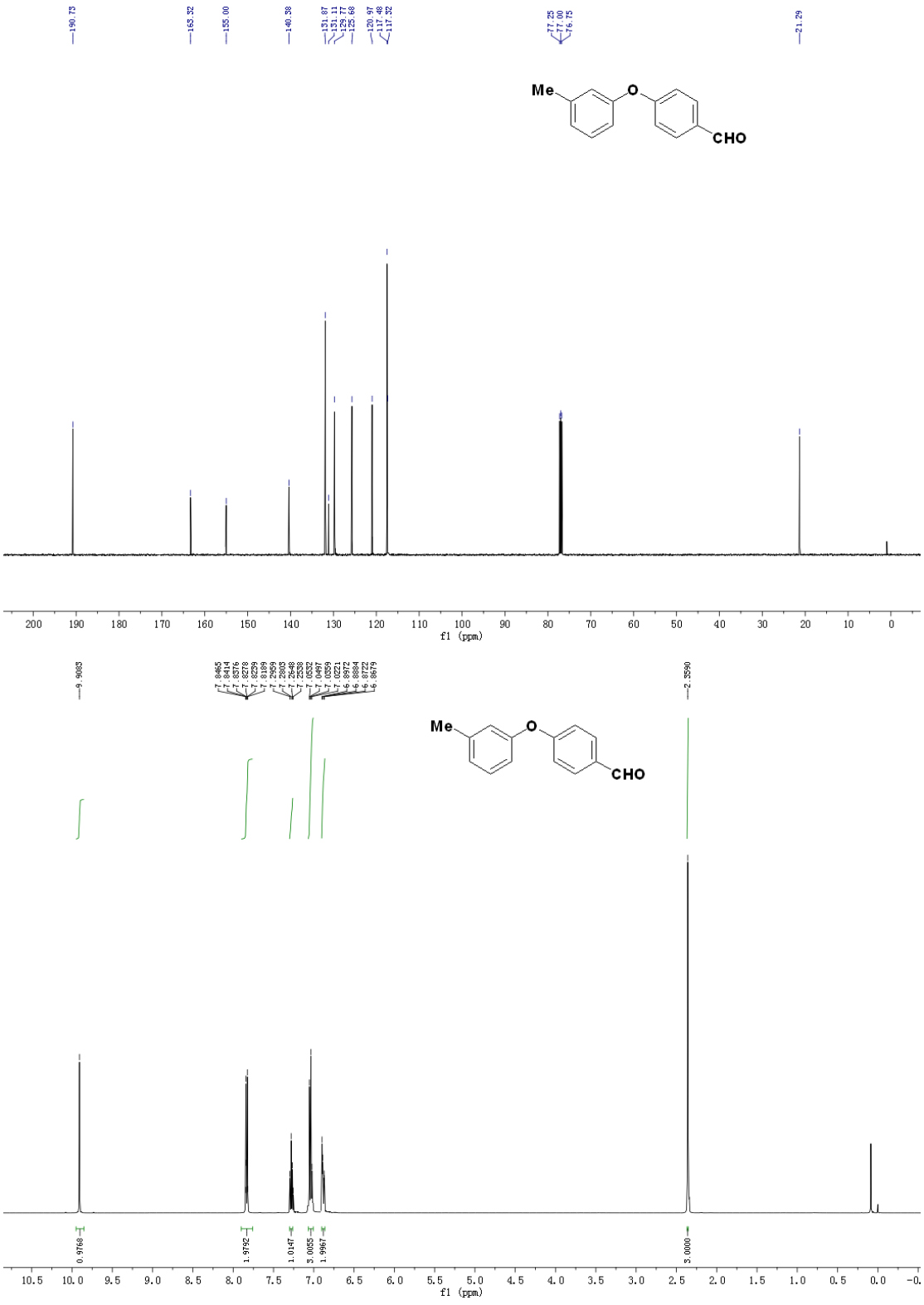


Figure S6. ^{1}H NMR of **3c** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3c** (125 MHz, $CDCl_3$).

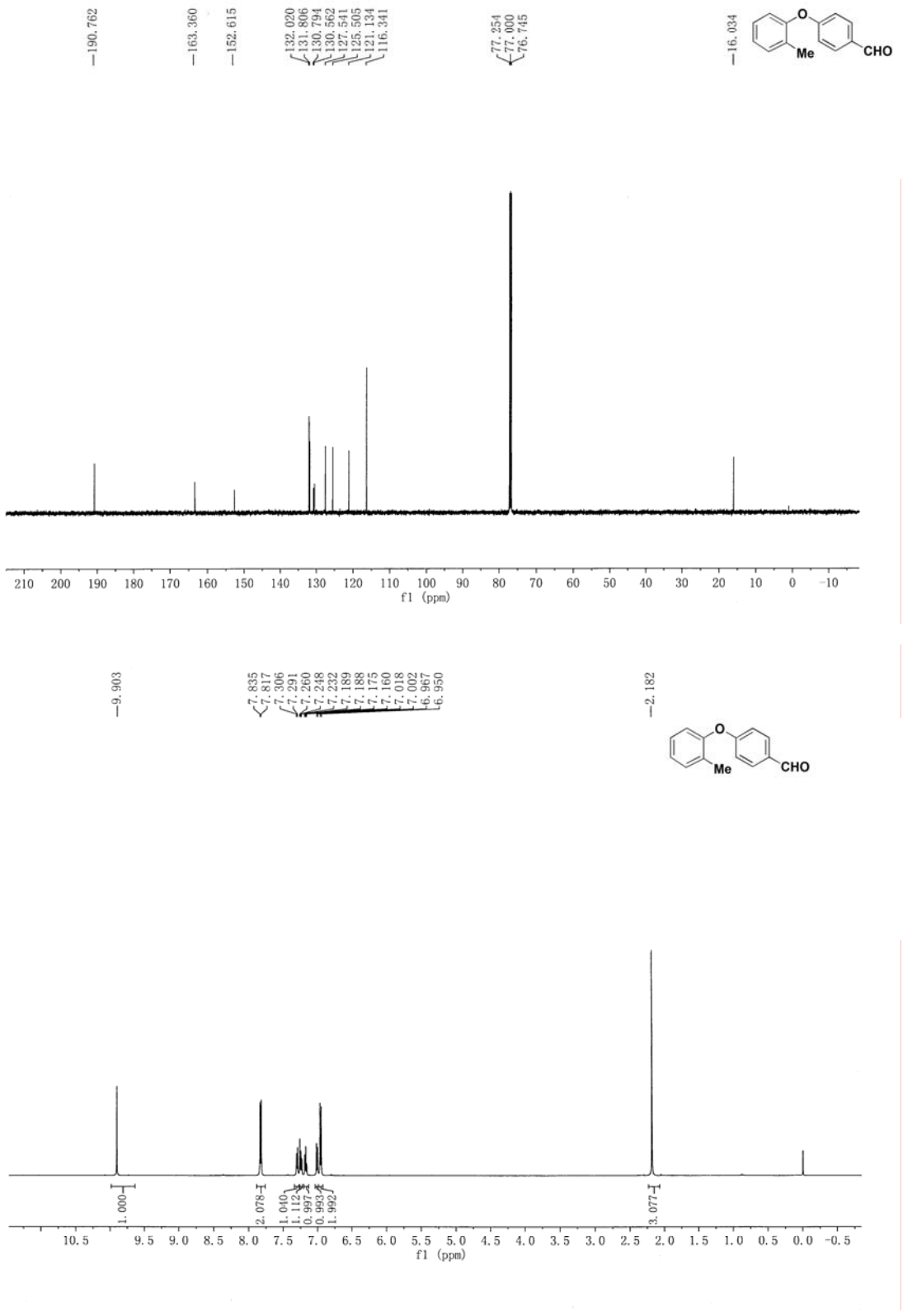


Figure S7. ^{1}H NMR of **3d** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3d** (125 MHz, $CDCl_3$).

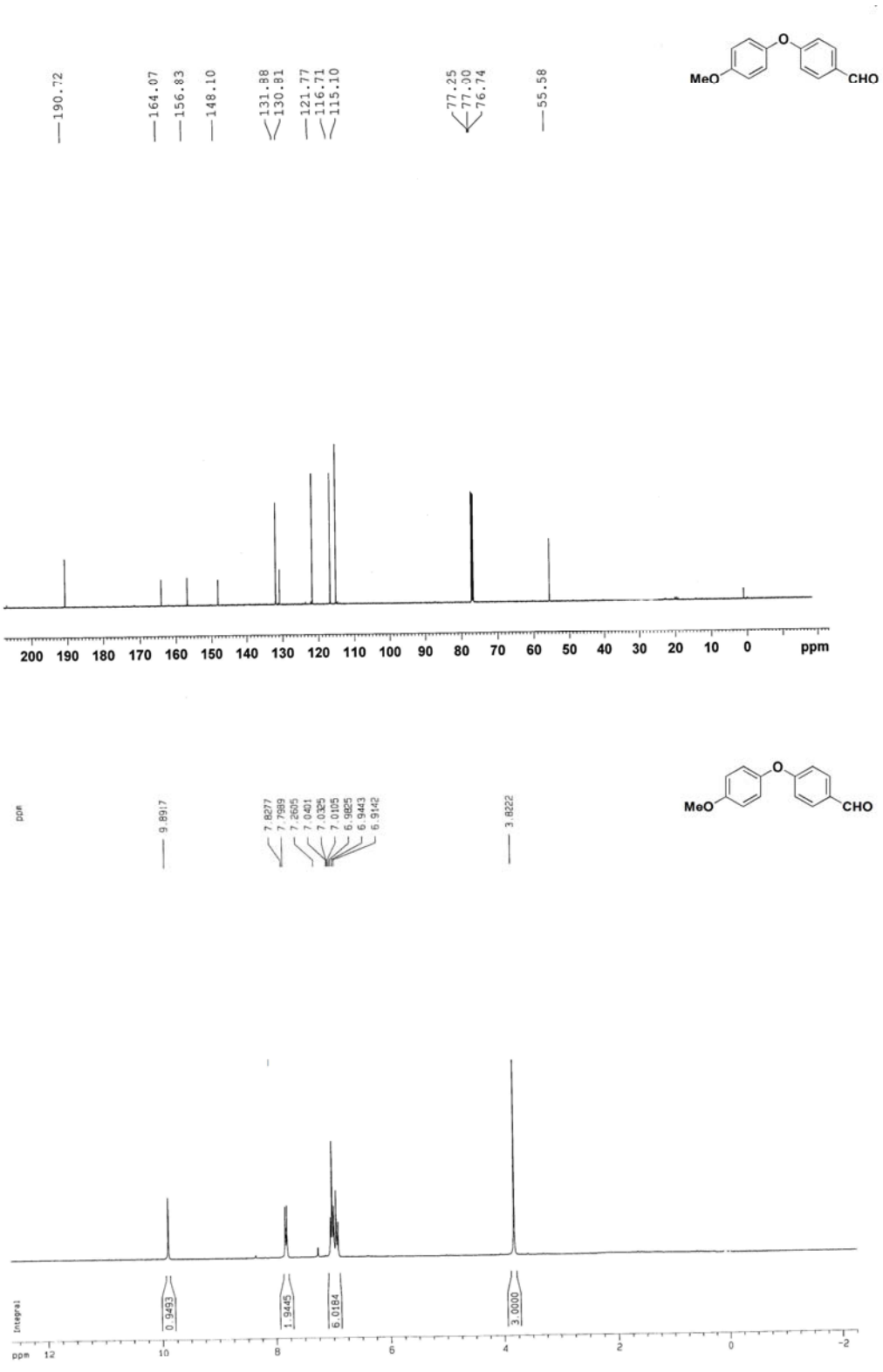


Figure S8. ^{1}H NMR of **3e** (300 MHz, $CDCl_3$) and ^{13}C NMR of **3e** (125 MHz, $CDCl_3$).

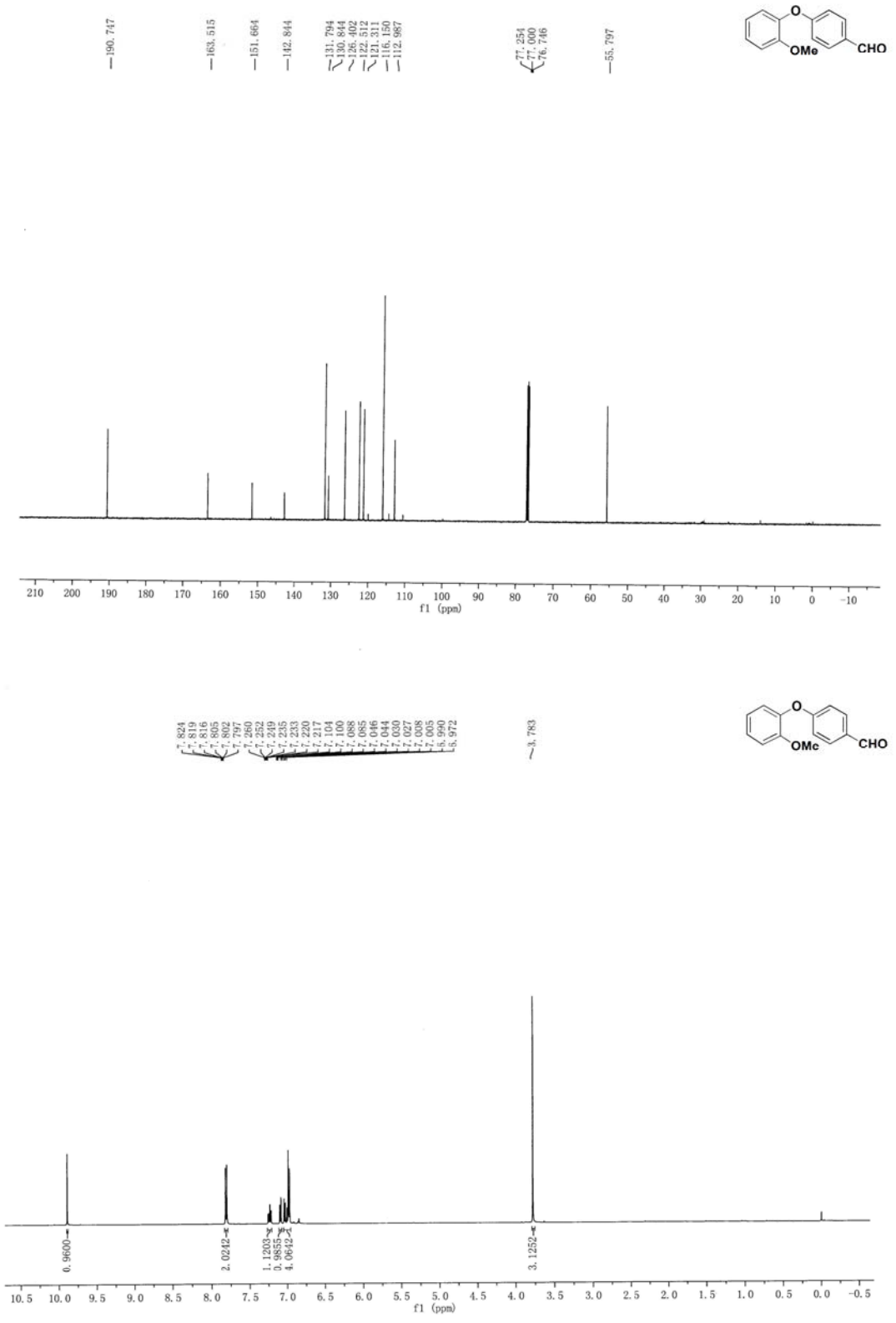


Figure S9. ^{1}H NMR of **3f** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3f** (125 MHz, $CDCl_3$).

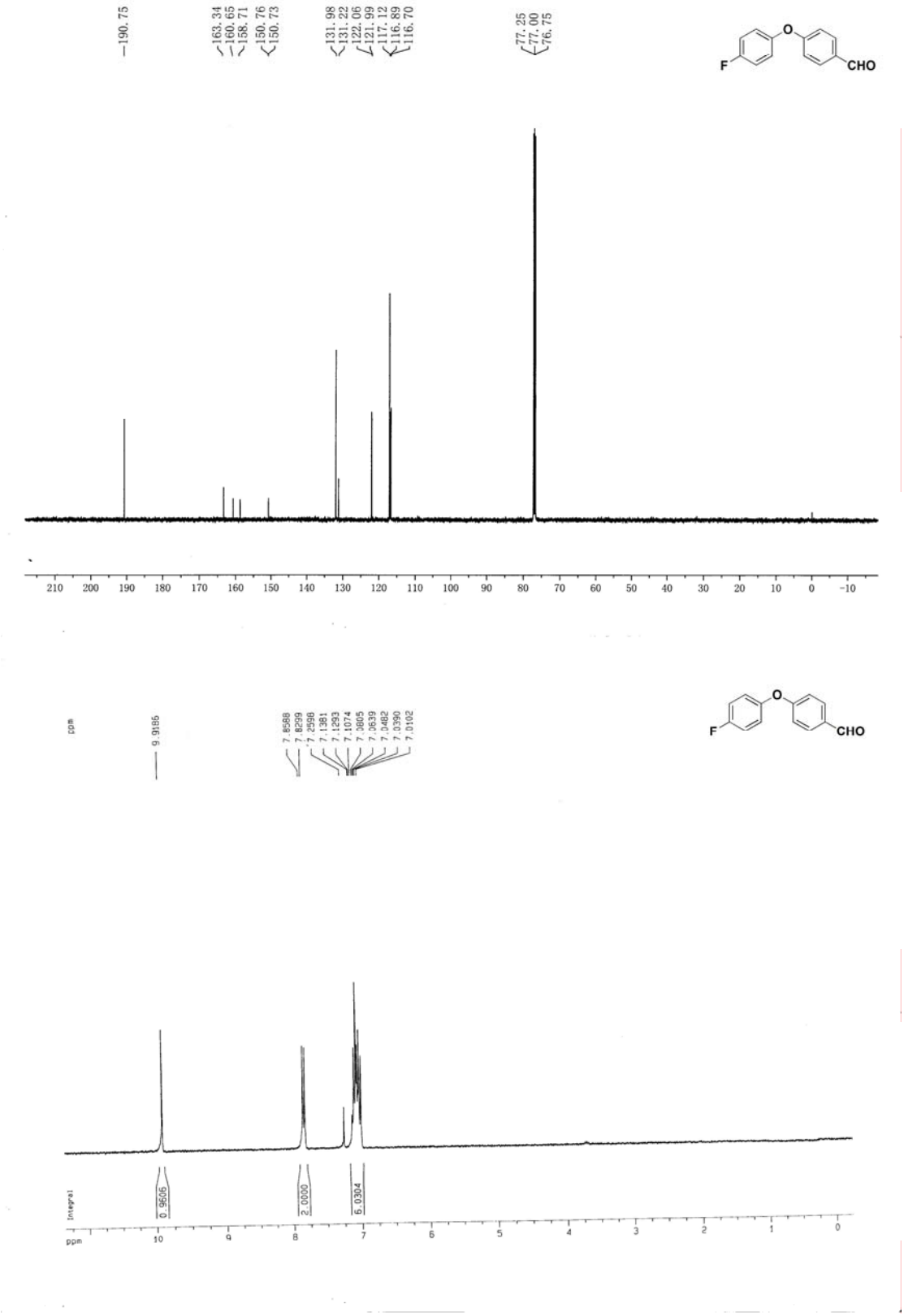


Figure S10. ^{1}H NMR of **3g** (300 MHz, $CDCl_3$) and ^{13}C NMR of **3g** (125 MHz, $CDCl_3$).

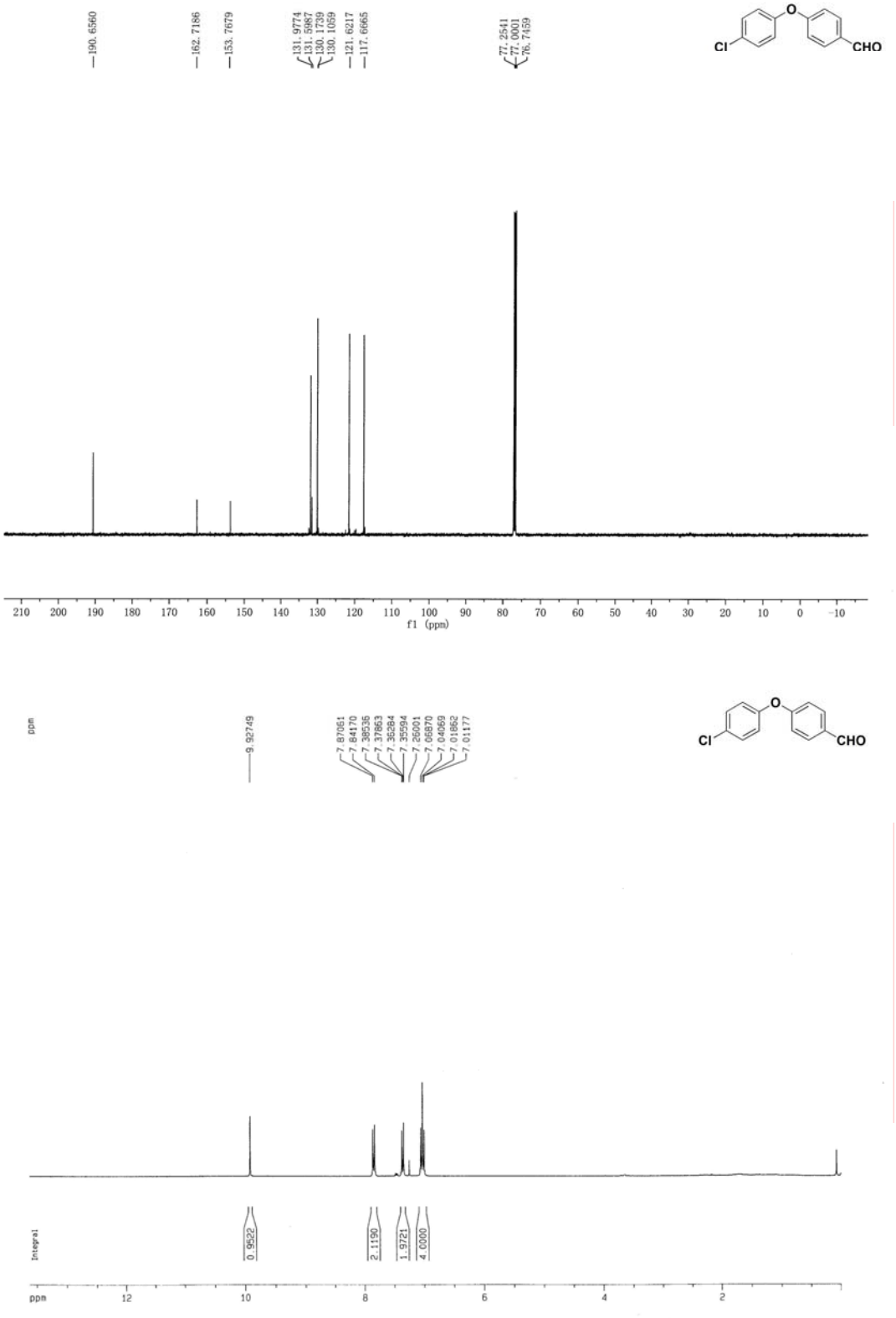


Figure S11. ^{1}H NMR of **3h** (300 MHz, $CDCl_3$) and ^{13}C NMR of **3h** (125 MHz, $CDCl_3$).

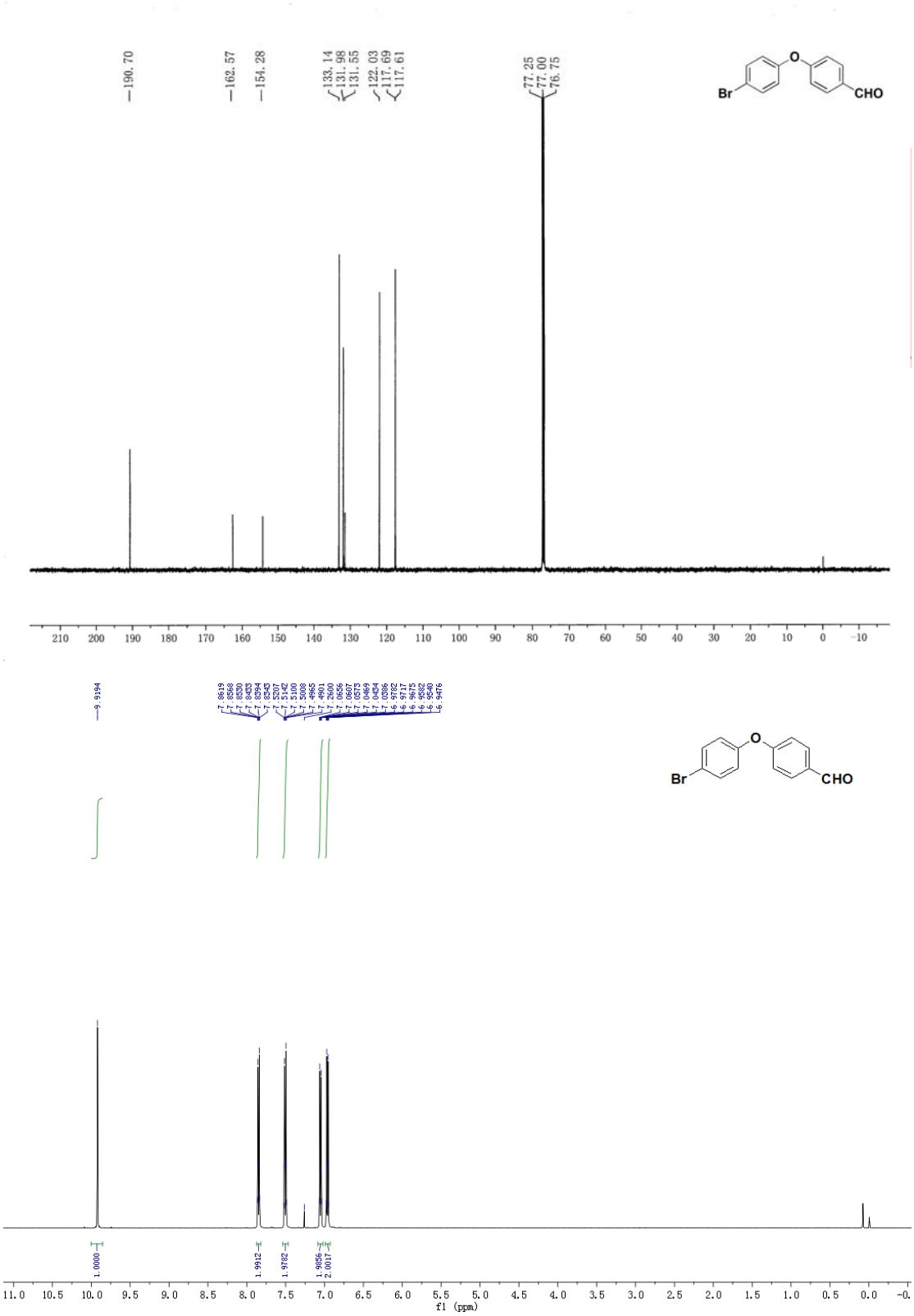


Figure S12. ^{1}H NMR of **3i** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3i** (125 MHz, $CDCl_3$).

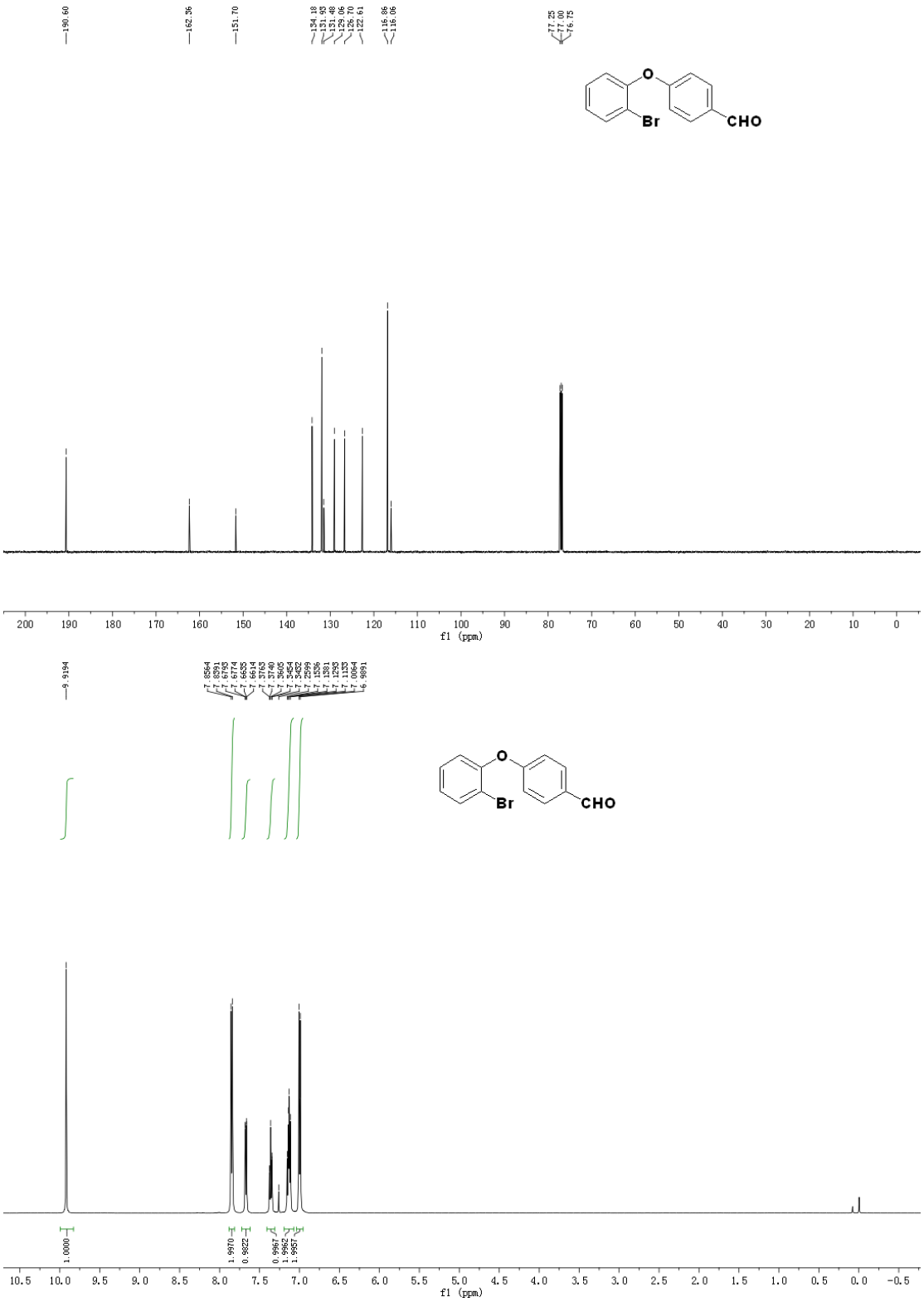


Figure S13. ^{1}H NMR of **3j** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3j** (125 MHz, $CDCl_3$).

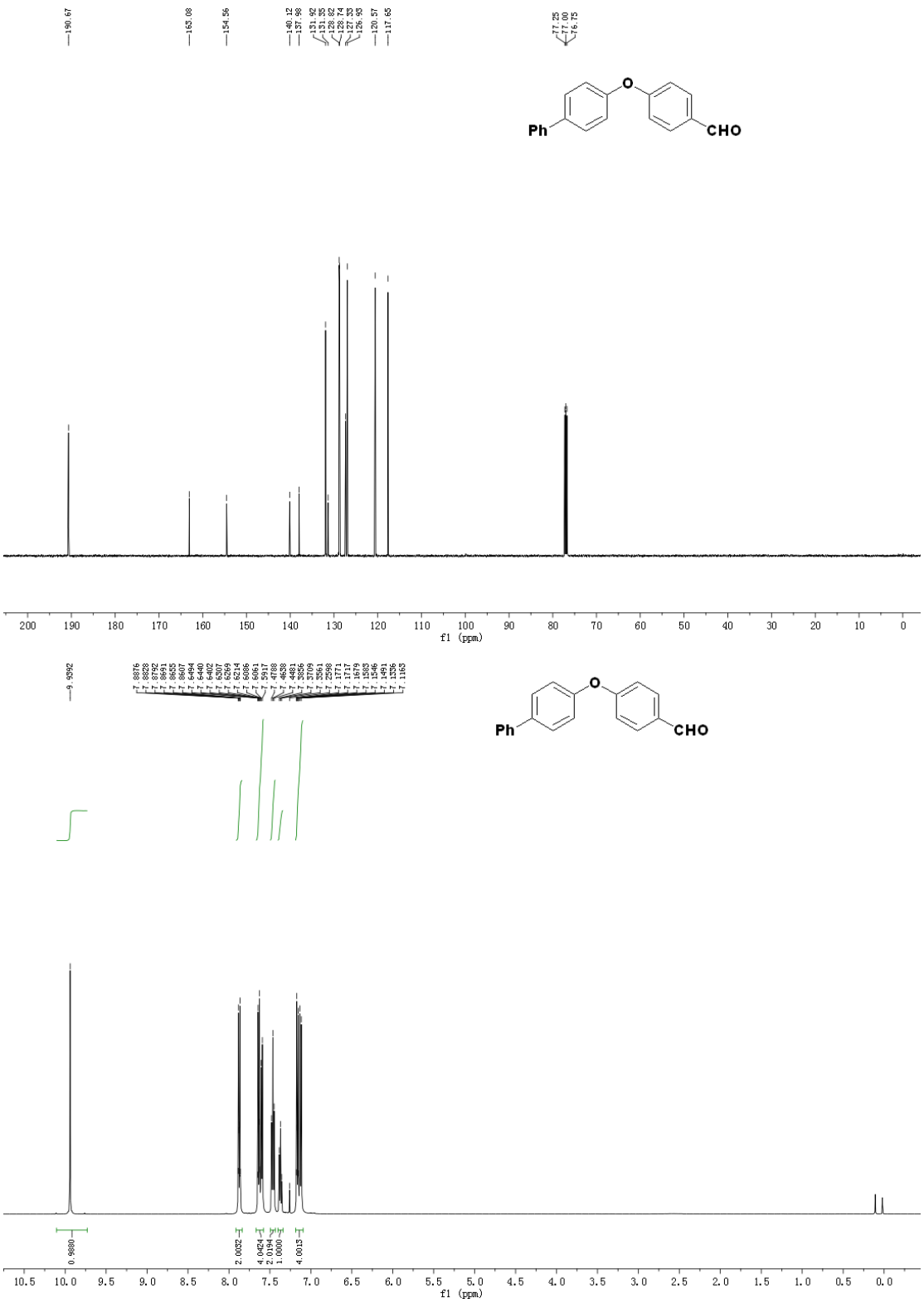


Figure S14. ^{1}H NMR of **3k** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3k** (125 MHz, $CDCl_3$).

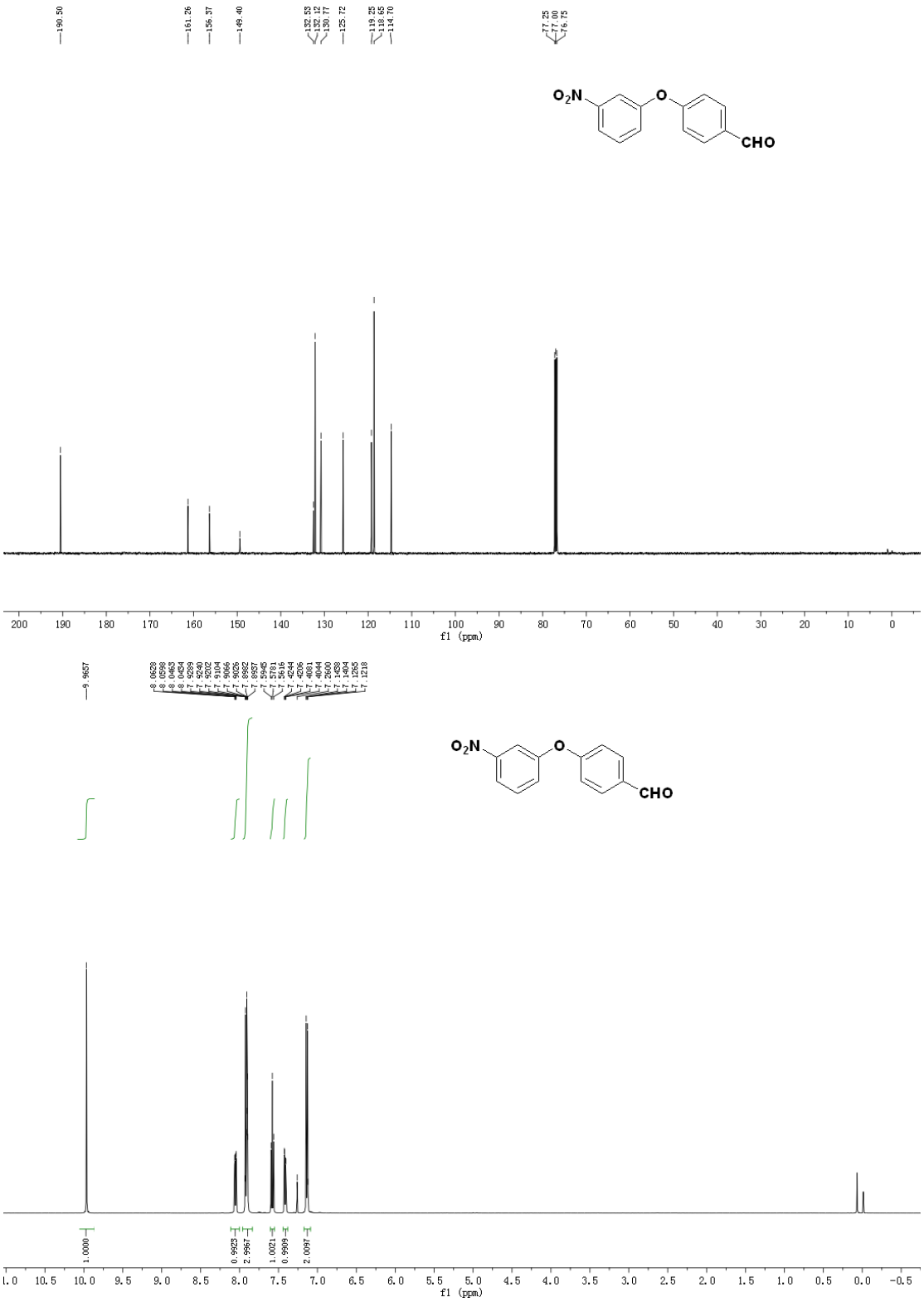


Figure S15. ^{1}H NMR of **3l** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3l** (125 MHz, $CDCl_3$).

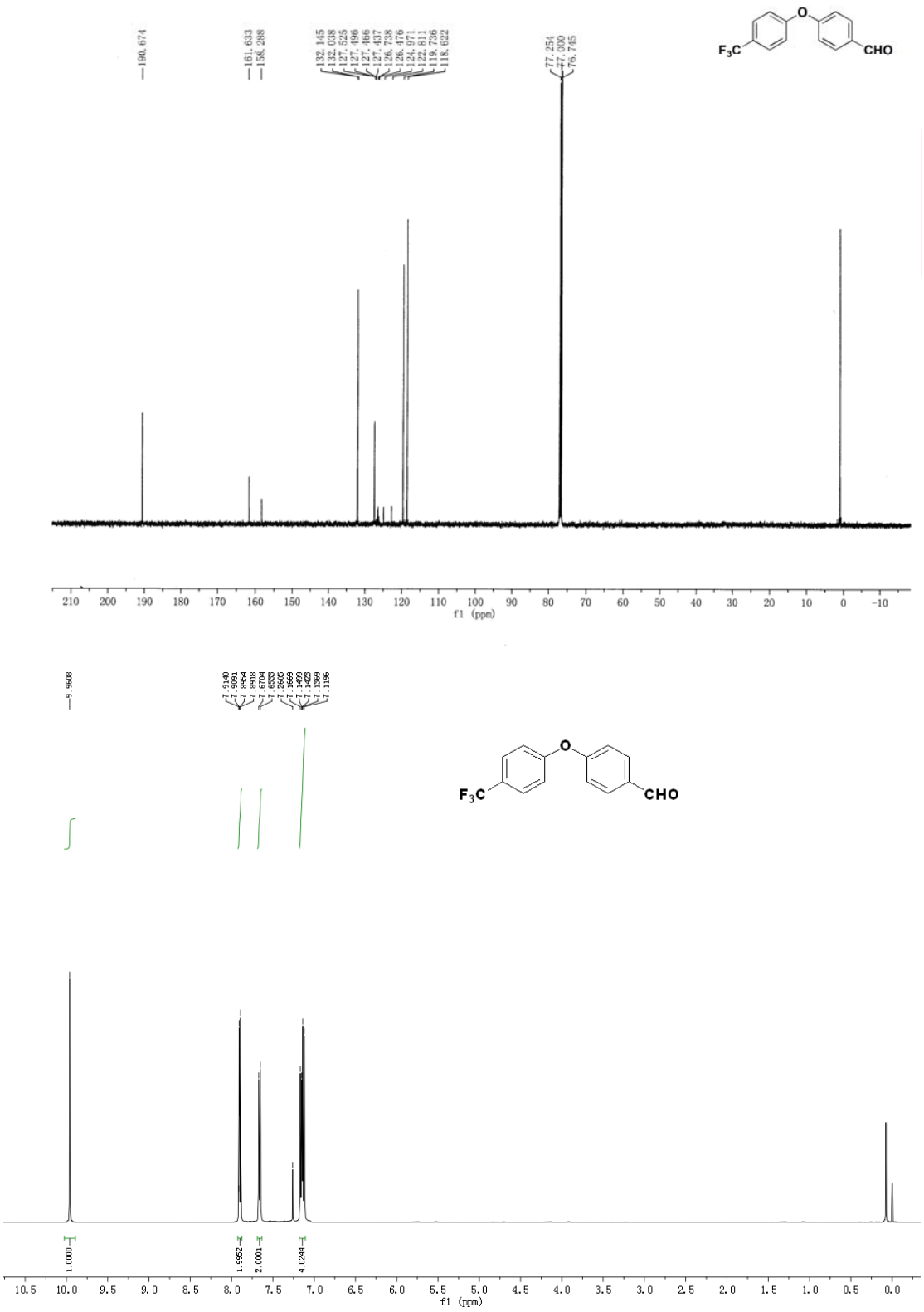


Figure S16. ^{1}H NMR of **3m** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3m** (125 MHz, $CDCl_3$).

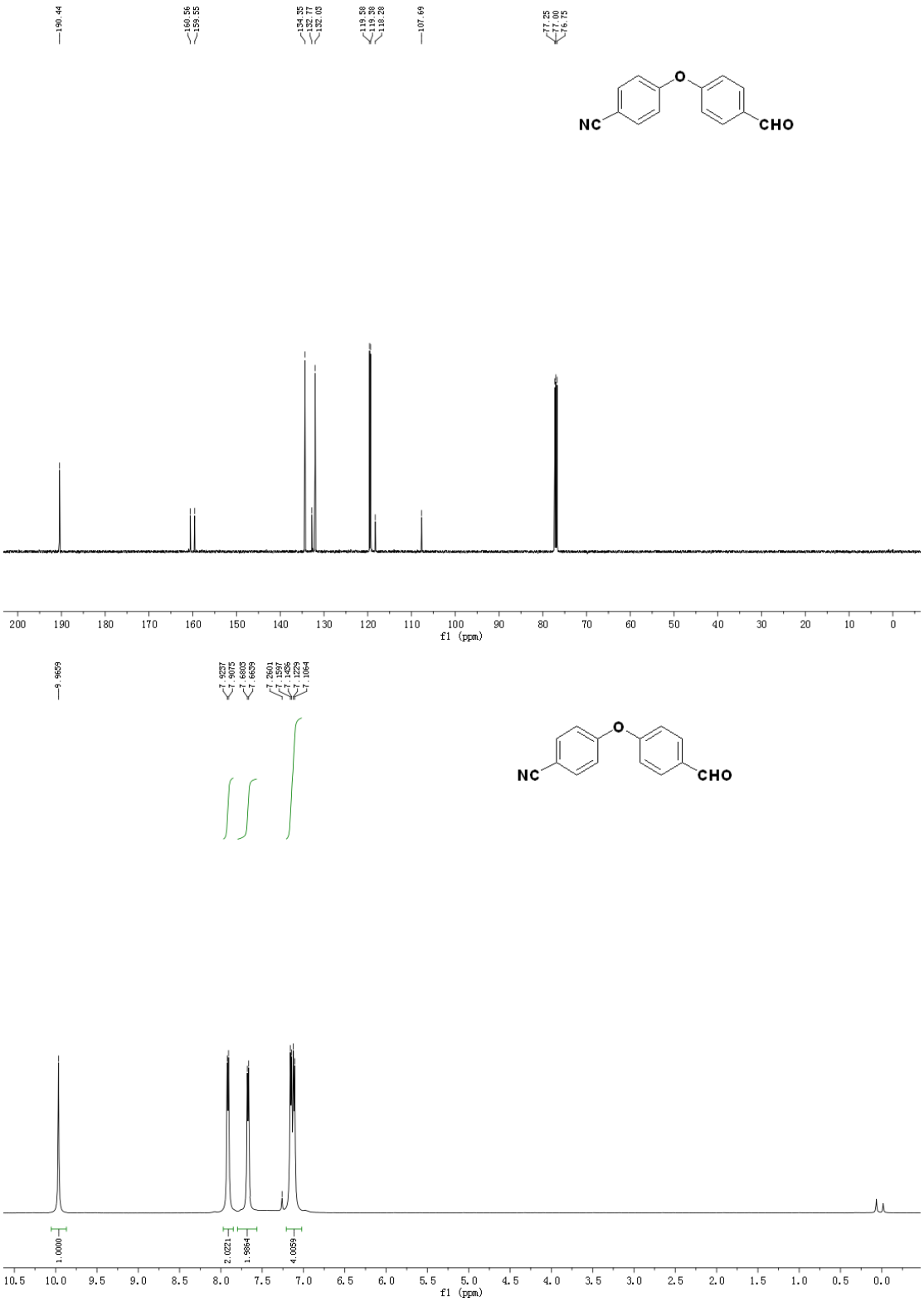


Figure S17. ^{1}H NMR of **3n** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3n** (125 MHz, $CDCl_3$).

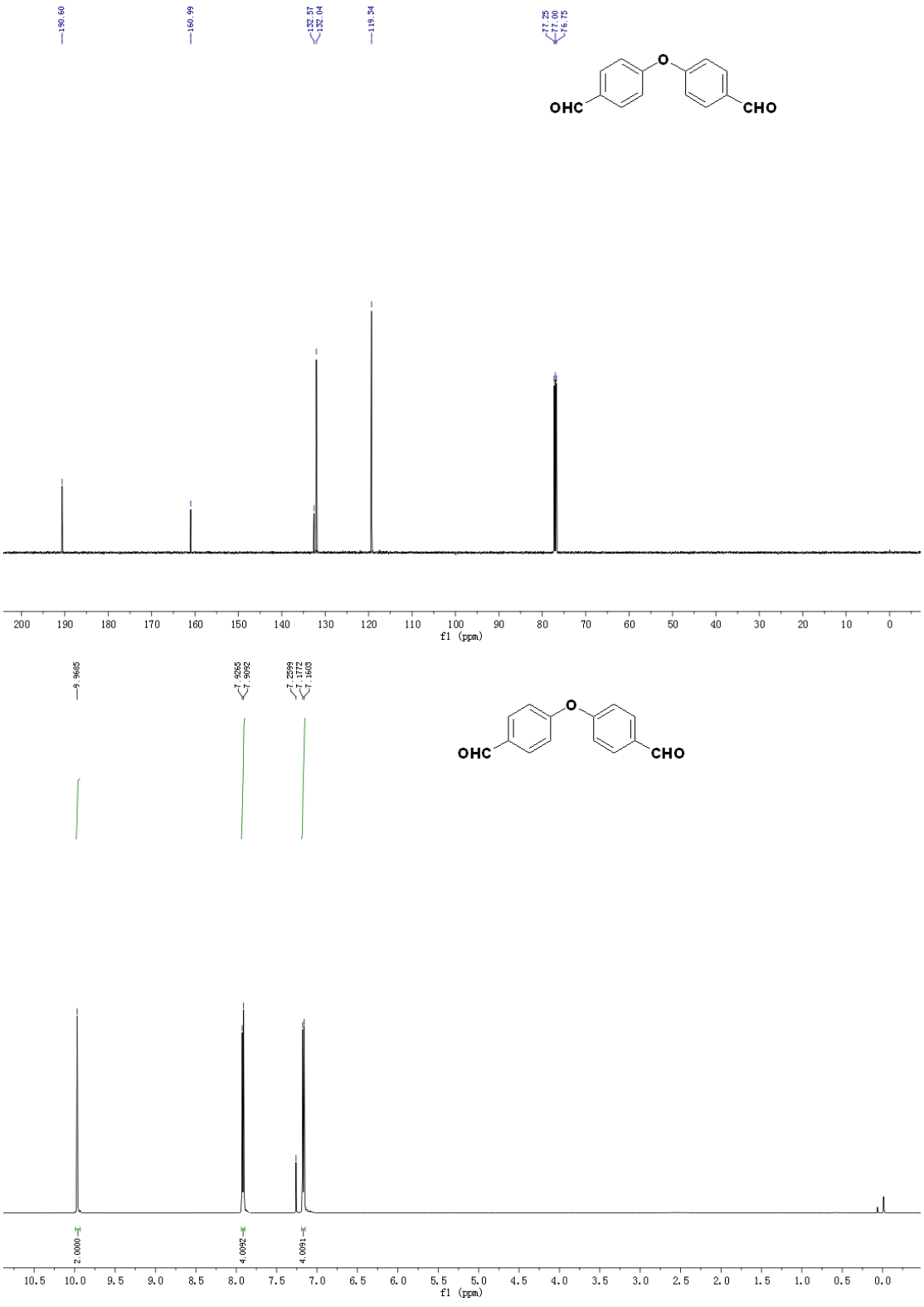


Figure S18. ^{1}H NMR of **3o** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3o** (125 MHz, $CDCl_3$).

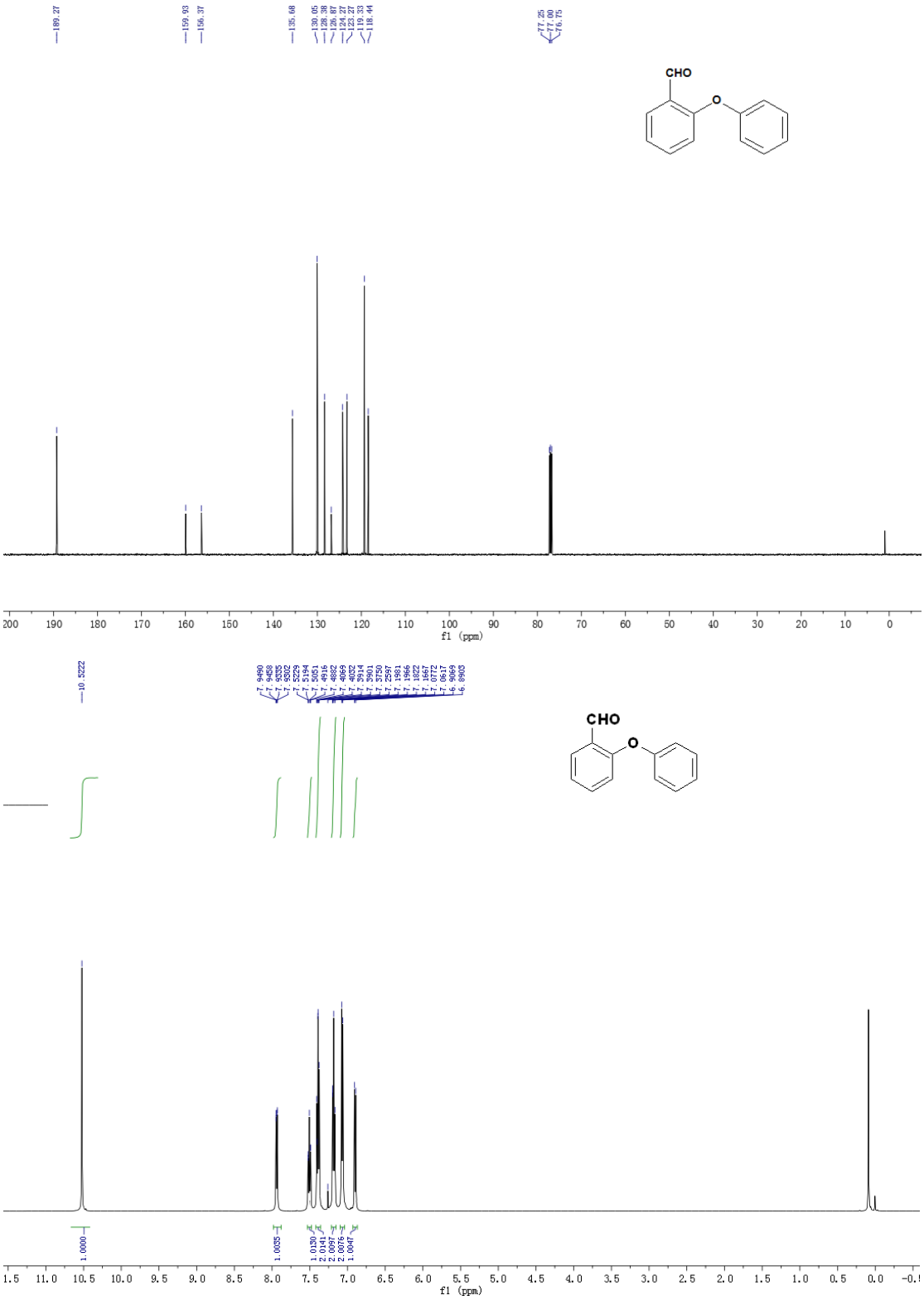


Figure S19. ^{1}H NMR of **3p** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3p** (125 MHz, $CDCl_3$).

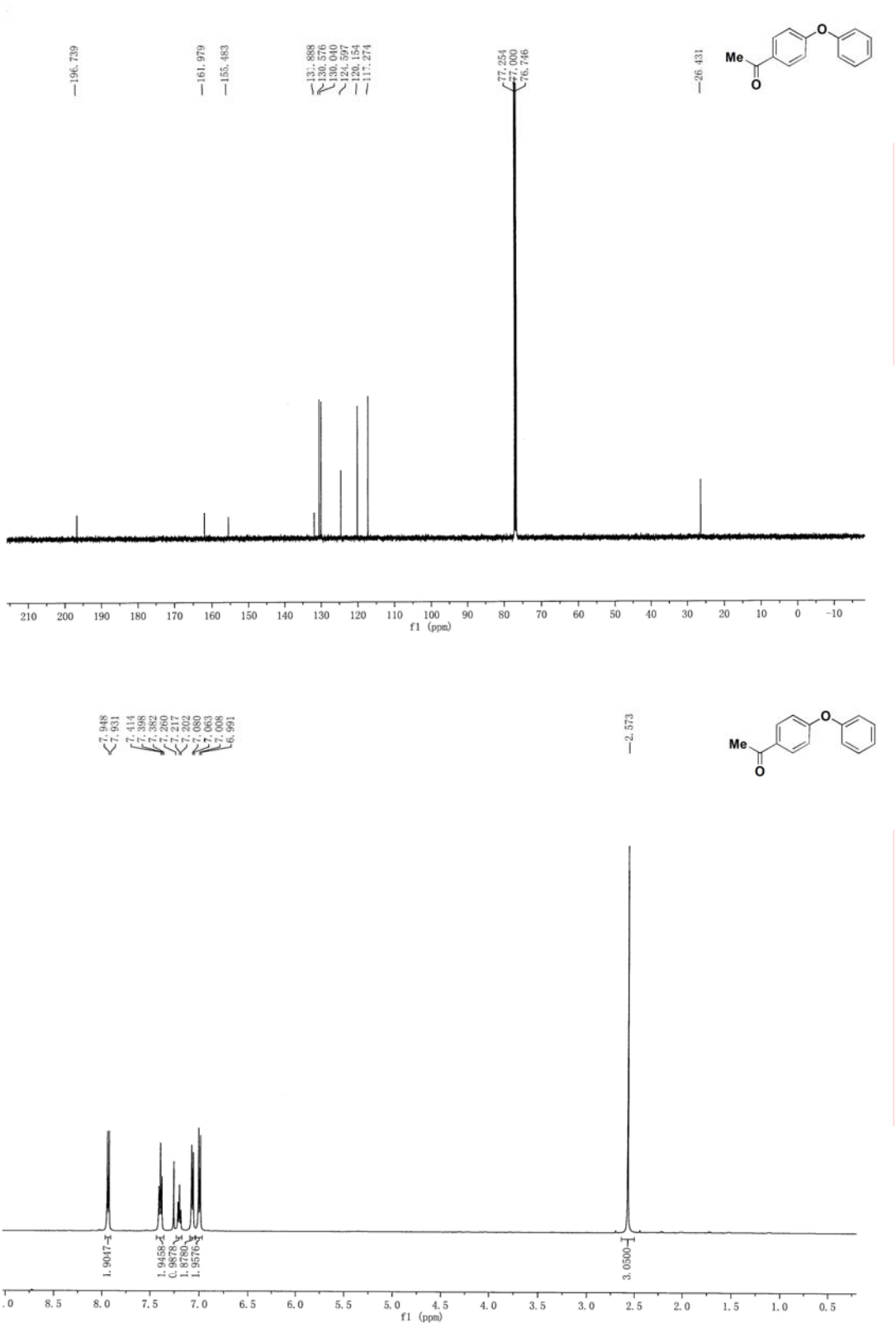


Figure 20. ^{1}H NMR of **3q** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3q** (125 MHz, $CDCl_3$).

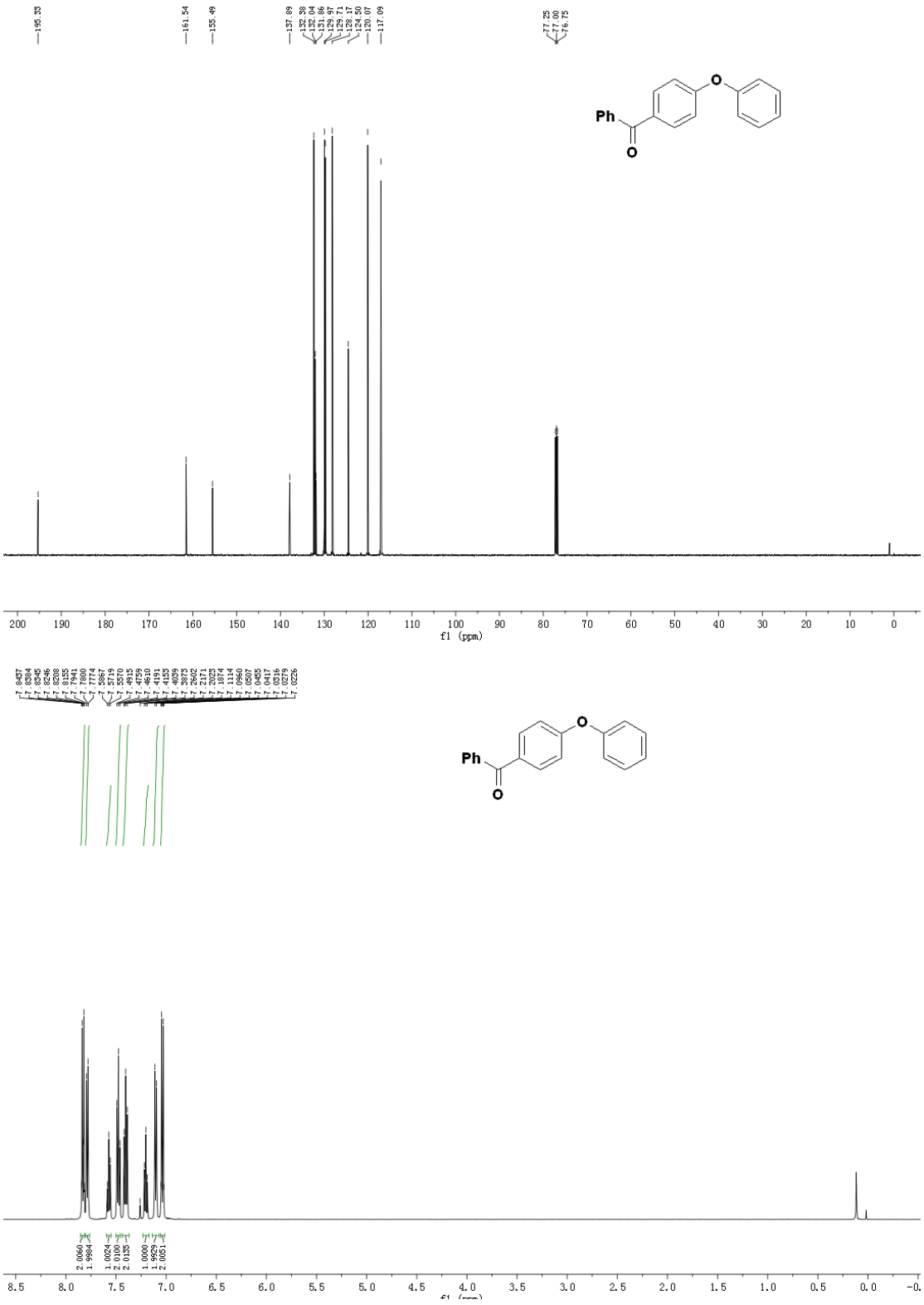


Figure S21. ^{1}H NMR of **3r** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3r** (125 MHz, $CDCl_3$).

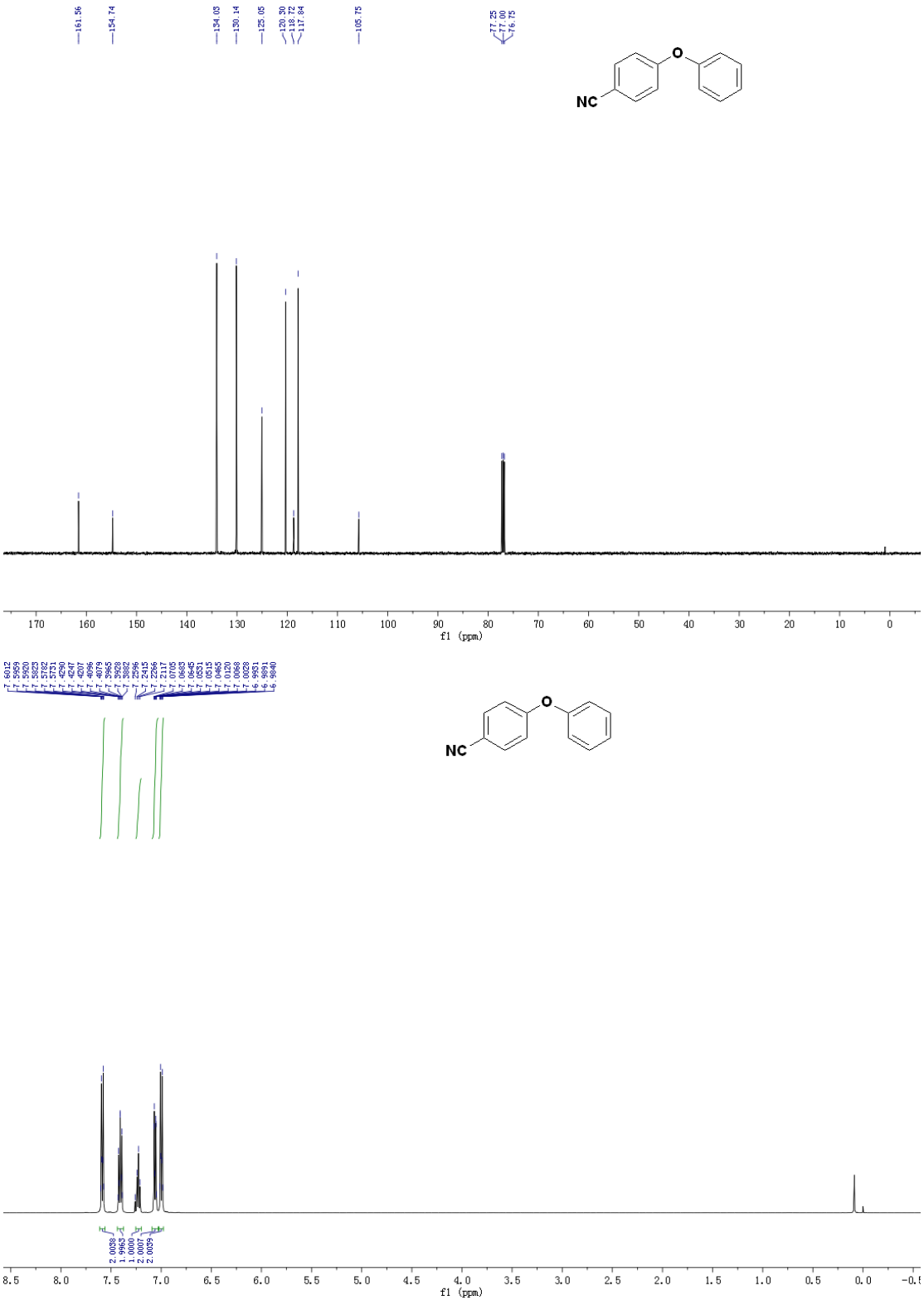


Figure S22. ^{1}H NMR of **3s** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3s** (125 MHz, $CDCl_3$).

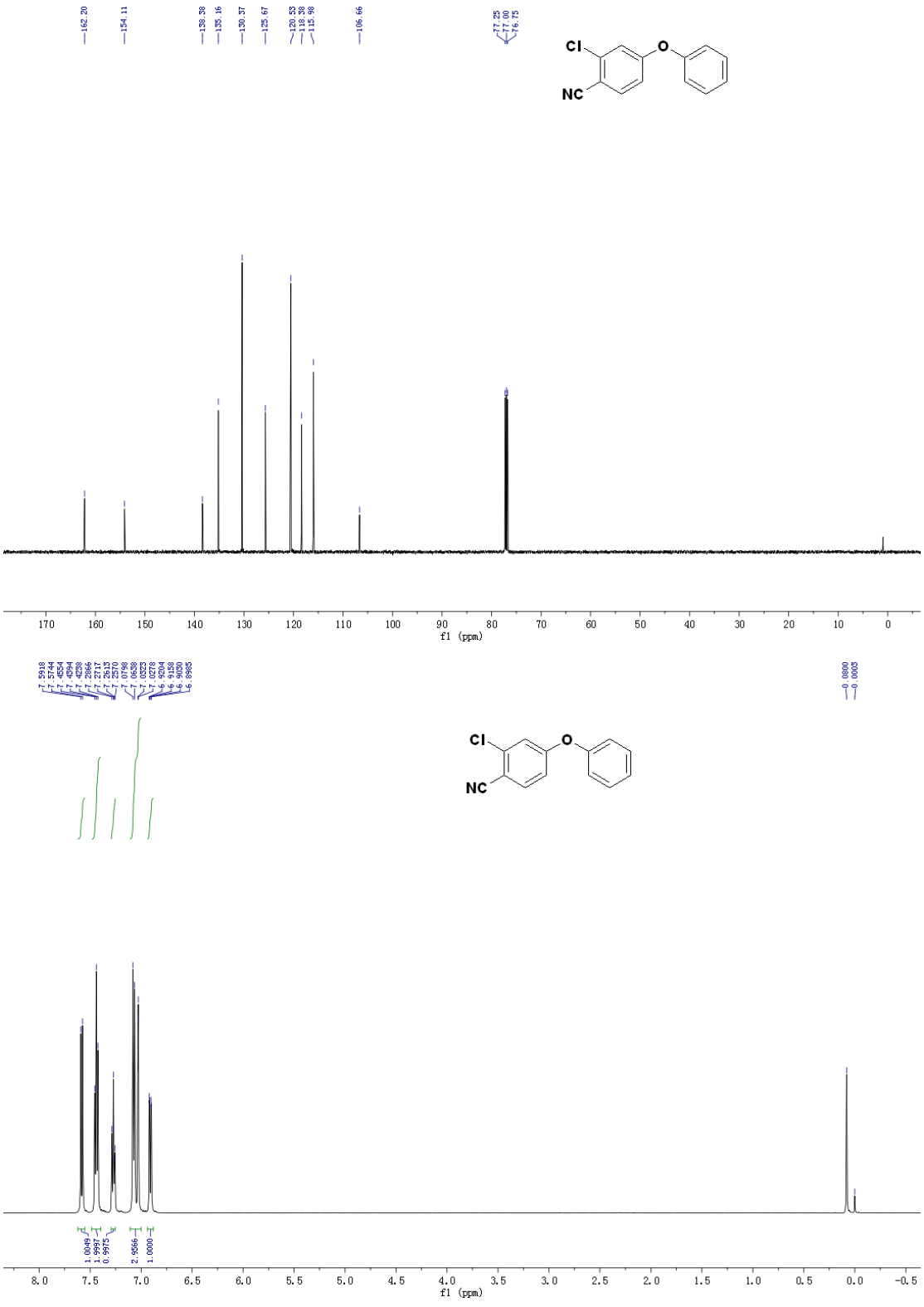


Figure S23. ^{1}H NMR of **3t** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3t** (125 MHz, $CDCl_3$).

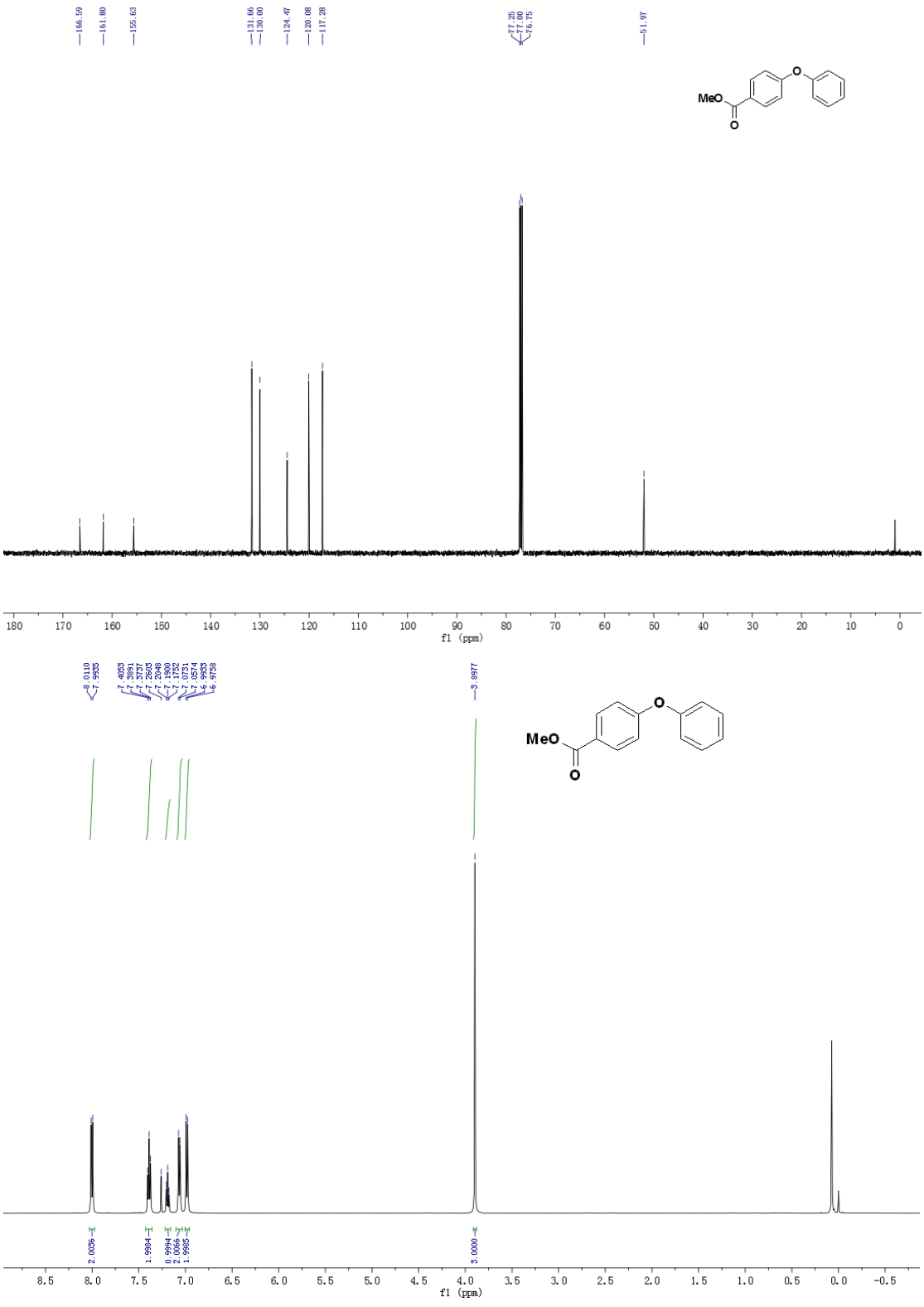


Figure S24. ^{1}H NMR of **3u** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3u** (125 MHz, $CDCl_3$).

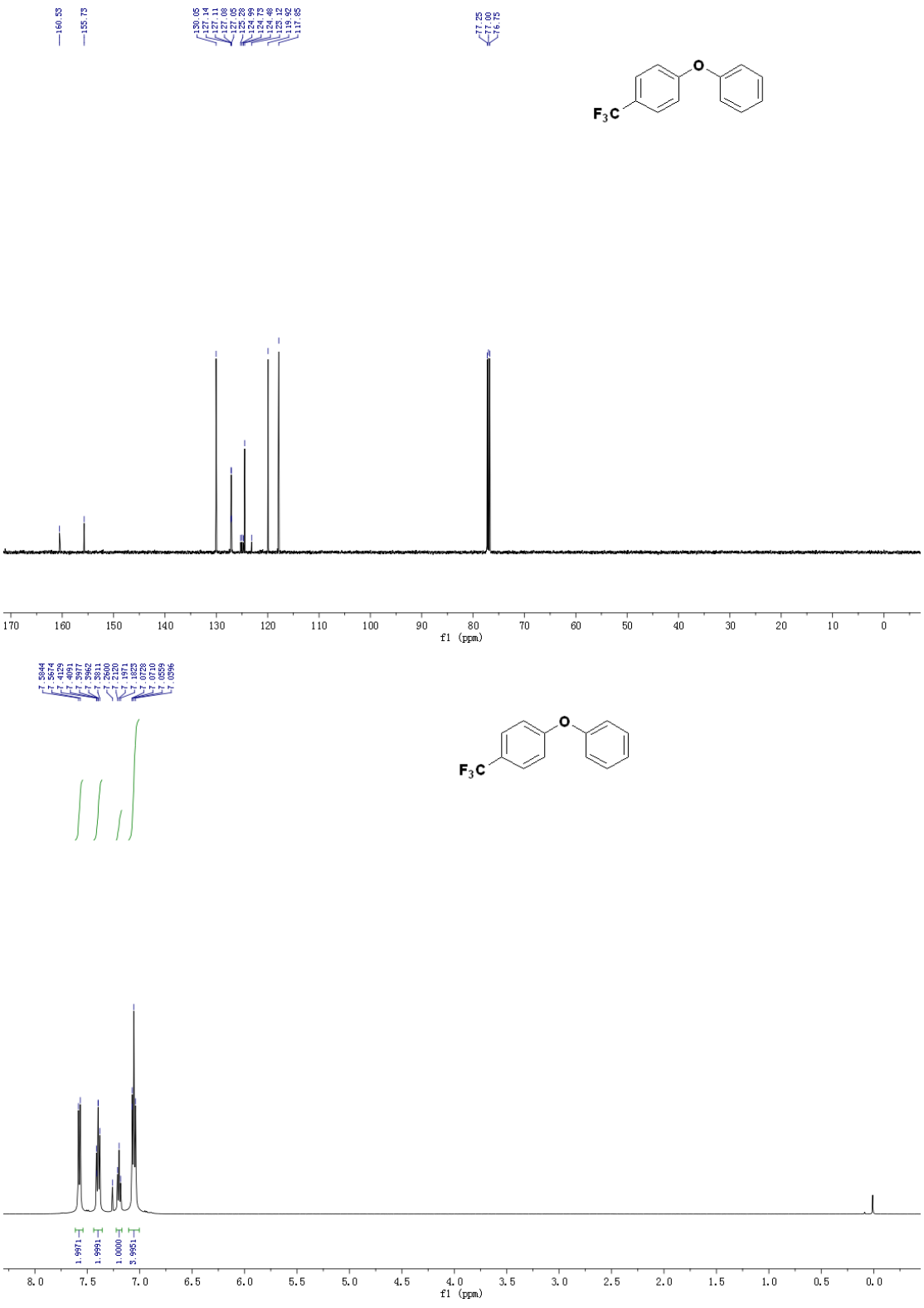


Figure S25. ^{1}H NMR of **3v** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3v** (125 MHz, $CDCl_3$).

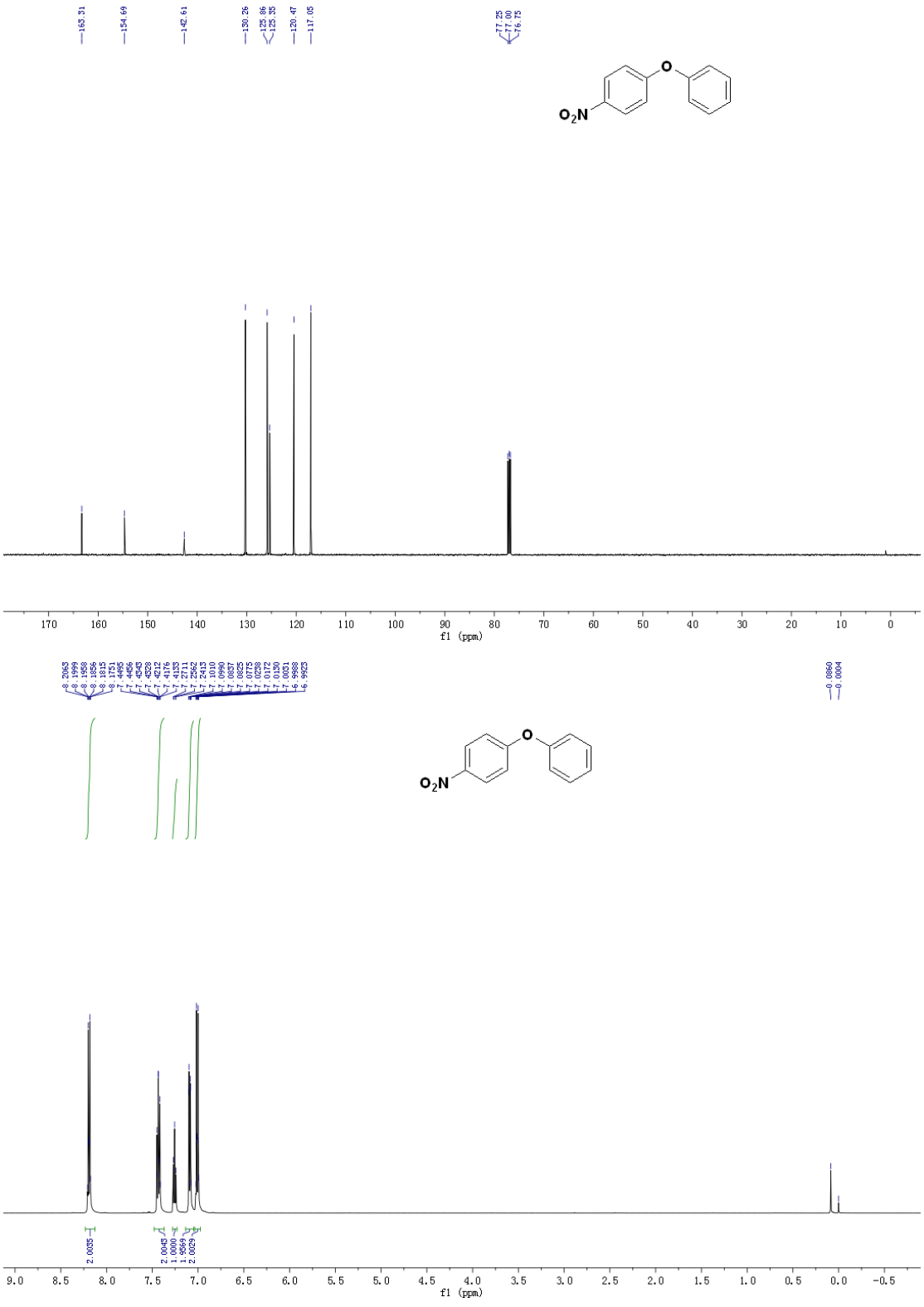


Figure S26. ^{1}H NMR of **3w** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3w** (125 MHz, $CDCl_3$).

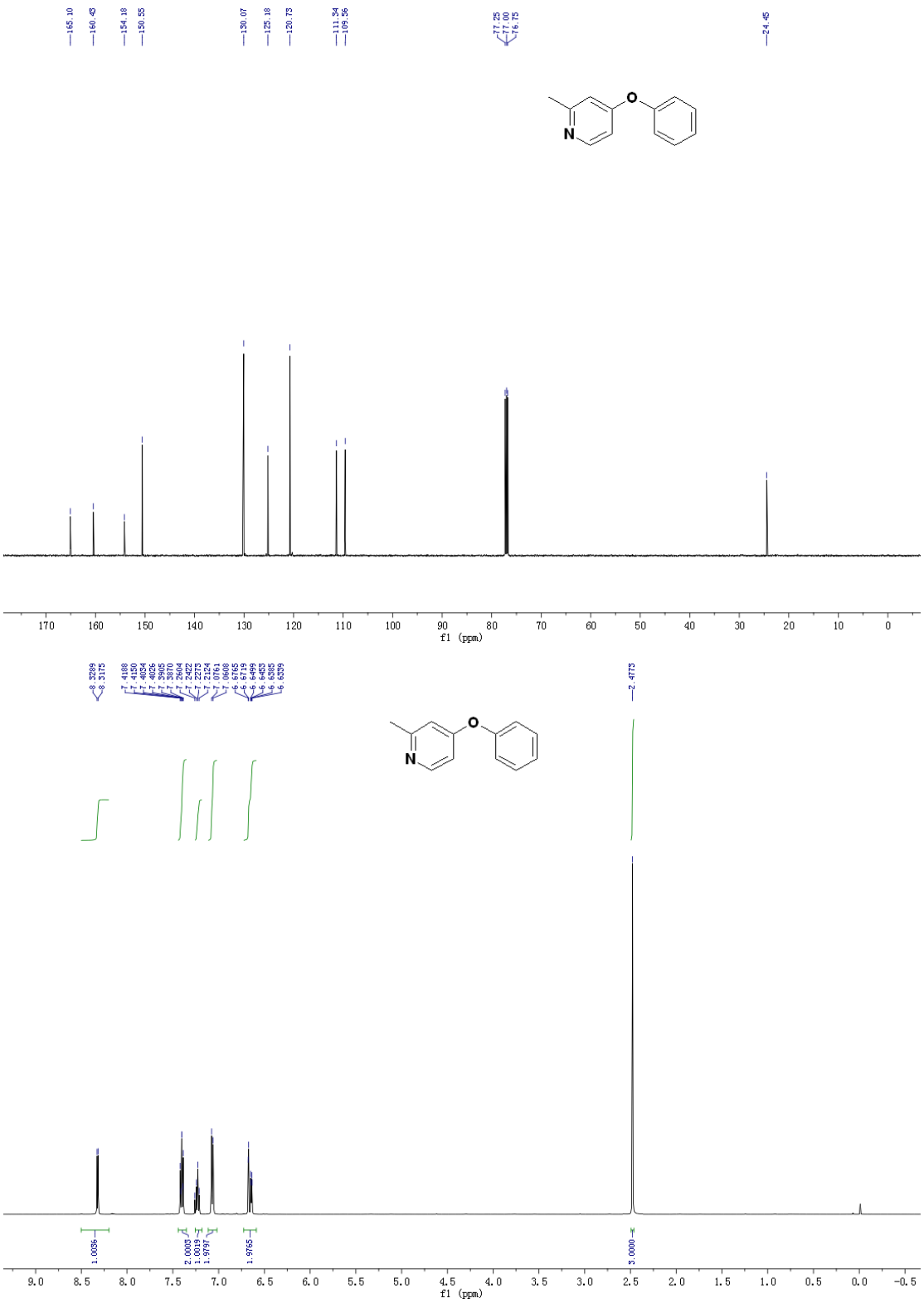


Figure S27. ^{1}H NMR of **3x** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3x** (125 MHz, $CDCl_3$).