Supporting Information

Regiodivergent CDC Reactions of Aromatic Aldehydes with Unactivated Arenes Controlled by Transient Directing Strategy

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Contents

1. Chemicals

All Palladium catalysts, aldehydes, acetohydrazide, TDGs, arenes and solvents were purchased from Shanghai Aladdin Industrial Corporation. Silica gel GF254 were

purchased from Sinopharm Chemical Reagent Beijing Limited Corporation. All the chemicals were commercial grade materials without further purification.

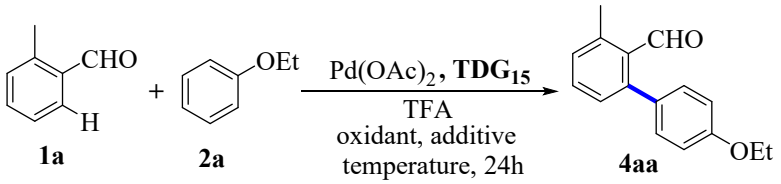
2. Experimental details

Characterization techniques. Thin layer chromatography (TLC) was performed on pre-coated silica gel GF254 plates. The ^{1}H NMR and ^{13}C NMR spectra were measured on a 600 MHz Bruker Avance III nuclear magnetic resonance spectrometer, using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) were expressed in ppm. The structures of known compounds were further corroborated by comparing their ^{1}H NMR data with those of literatures.

General procedure for the C(sp^3)-C(sp^2) cross-coupling reaction of aldehydes with arenes. In a typical reaction, a 25 mL oven-dried reaction tube was charged with catalyst (10 mol% $Pd(OAc)_2$), *o*-methylbenzaldehydes **1** (0.1 mmol), arenes **2** (1 mL), acetohydrazide (40 mol%), $K_2S_2O_8$ (0.2 mmol), MCM-48(12 mg, 0.2 mmol), H_2O (9.0 μL, 0.5 mmol) and trifluoroacetic acid (67 μL, 0.9 mmol). The reaction tube was placed in an oil bath at 110 °C and the reaction mixture was stirred for 24 h. After being cooled to room temperature, the mixture was filtered, and the filtrate was evaporated in vacuo. The residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether =1:20 to 1:50 as an eluent) to afford the desired 2-benzylbenzaldehydes **3**.

Reaction Conditions Screening for the C(sp^2)-C(sp^2) cross-coupling reaction. According to the experiment results of Table 2, we began our experimental efforts by selecting *o*-methyl benzaldehyde (**1a**) and phenetole (**2a**) as the model substrates and **TDG$_{15}$** as TDG to screen the optimal conditions for the C(sp^2)-H bonds arylation reaction. At first, four kinds of [F^+] oxidants instead of $K_2S_2O_8$ have been examined successively and *N*-Fluoro-*N*′-(chloromethyl)triethylenediamine bis(tetrafluoroborate) **O$_1$** showed the best activity (entries 2-5). Unlike C(sp^3)-H bonds arylation, a better yield of desired product was obtained without MCM-48 and H_2O (entries 6-8). We next turned our attention to the optimization of temperature after many fruitless attempts (entries 9-14). To our great delight, the product **4aa** was afforded in 75% yield after decreasing the temperature to 60℃.

Table S1. Reaction Conditions Screening for the C(sp^2)-C(sp^2) cross-coupling reaction[a]

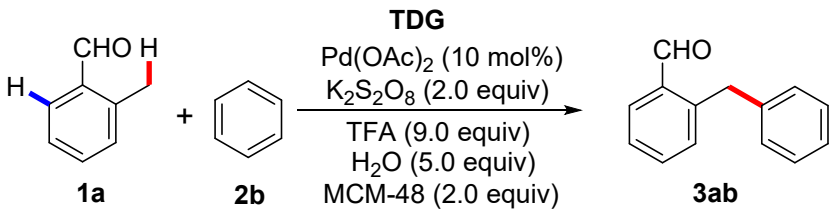


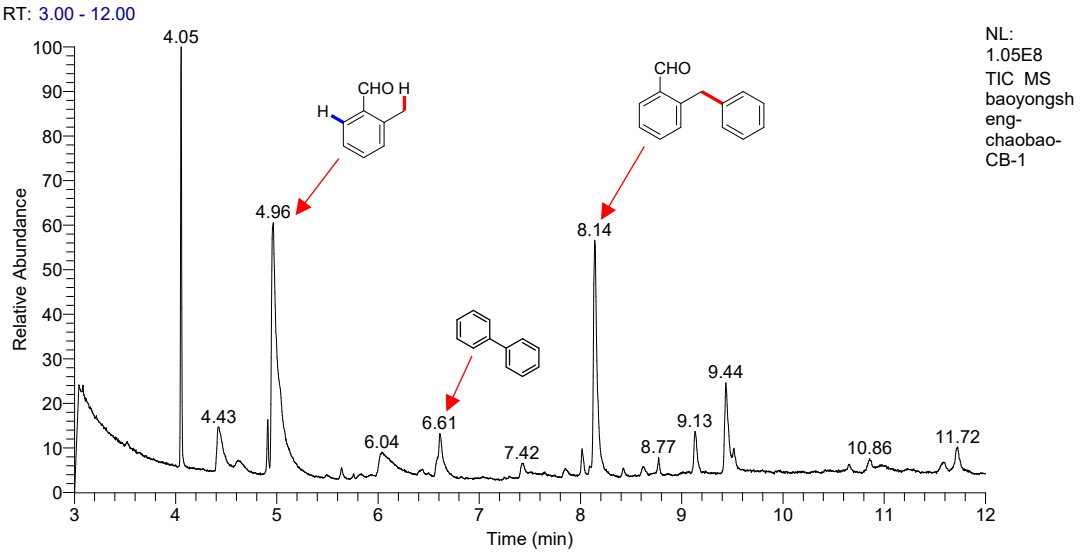
Entry	Oxidant	Additive	T (°C)	Yield (%)[b]
1	$K_2S_2O_8$	H_2O, MCM-48	70	33
2	**O_1**	H_2O, MCM-48	70	46
3	**O_2**	H_2O, MCM-48	70	7
4	**O_3**	H_2O, MCM-48	70	29
5	**O_4**	H_2O, MCM-48	70	15
6	**O_1**	H_2O	70	13
7	**O_1**	MCM-48	70	15
8	**O_1**	-	70	57
9	**O_1**	-	50	45
10	**O_1**	-	60	75
11	**O_1**	-	80	54
12	**O_1**	-	90	44
13	**O_1**	-	100	43
14	**O_1**	-	110	43

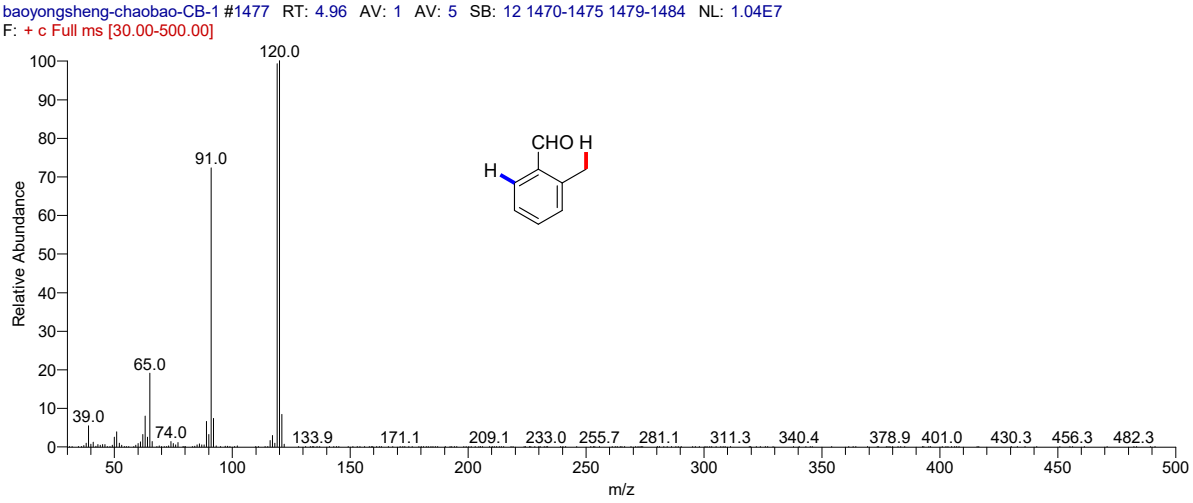
[a]Reaction conditions: **1a** (0.1mmol), **2a** (1mL), Pd catalyst (10 mol%), **TDG_{15}** (40 mol%), TFA (9.0 equiv), Oxidant (2.0 equiv), Additives, 24h. [b] isolated yield.

General procedure for the C(sp²)-C(sp²) cross-coupling reaction of aldehydes with arenes. In a typical reaction, a 25 mL oven-dried reaction tube was charged with catalyst (10 mol% $Pd(OAc)_2$), 2-Amino-4-chlorobenzonic Acid (40 mol%), *o*-methyl benzaldehydes **1** (0.1 mmol), *N*-Fluoro-*N*′-(chloromethyl)triethylenediamine bis(tetrafluoroborate) **O_1** (0.2 mmol), trifluoroacetic acid (67 μL, 0.9 mmol) and arenes **2** (1 mL). The reaction tube was placed in an oil bath at 60 °C and the reaction mixture was stirred for 24 h. After being cooled to room temperature, the mixture was filtered, and the filtrate was evaporated in vacuo. The residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether =1:10-1:30 as an eluent) to afford the desired **4**.

3. GCMS Analysis of C(sp³)-C(sp²) Cross-Coupling of 1a with 2b




RT: 3.00 - 12.00
NL:
1.05E8
TIC MS
baoyongsh
eng-
chaobao-
CB-1
Relative Abundance
Time (min)
4.05
4.96
4.43
6.04
6.61
7.42
8.14
8.77
9.13
9.44
10.86
11.72
CHO H
H
CHO


baoyongsheng-chaobao-CB-1 #1477 RT: 4.96 AV: 1 AV: 5 SB: 12 1470-1475 1479-1484 NL: 1.04E7
F: + c Full ms [30.00-500.00]
Relative Abundance
m/z
120.0
91.0
65.0
39.0
74.0
133.9
171.1
209.1
233.0
255.7
281.1
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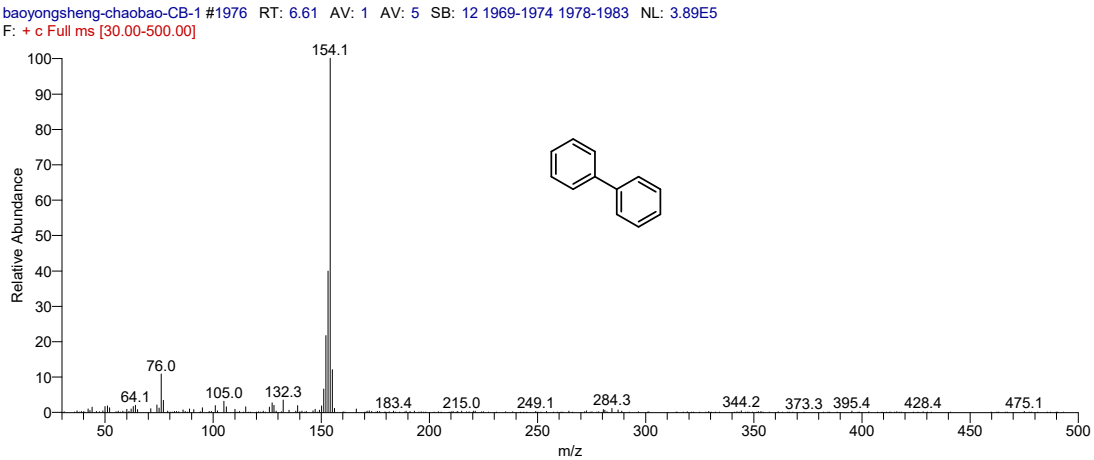
340.4
378.9
401.0
430.3
456.3
482.3
CHO H
H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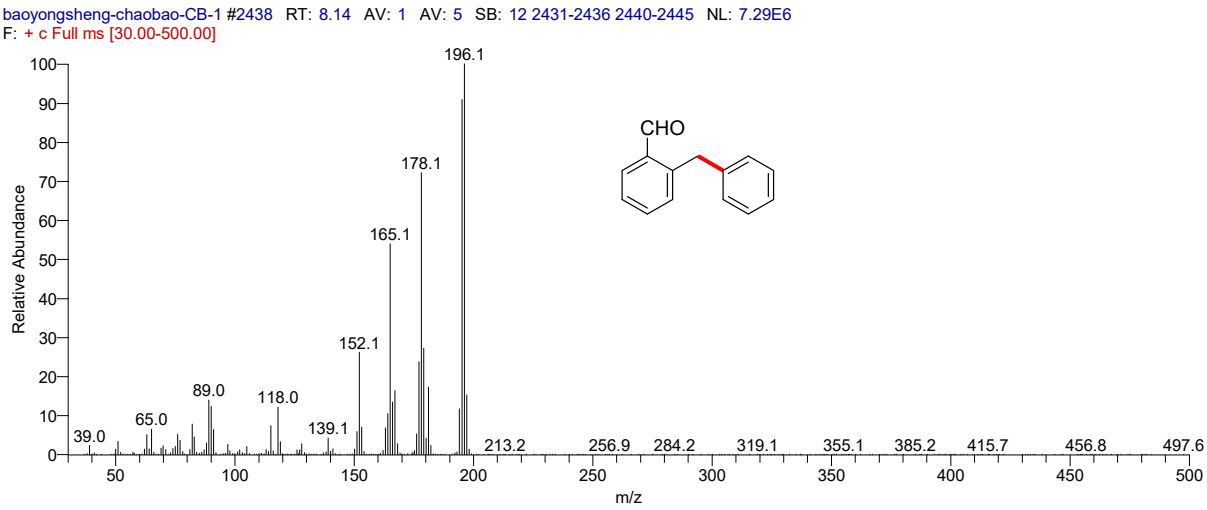
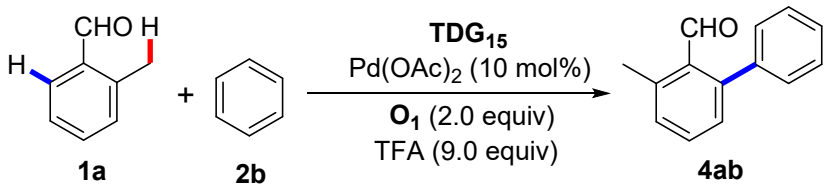
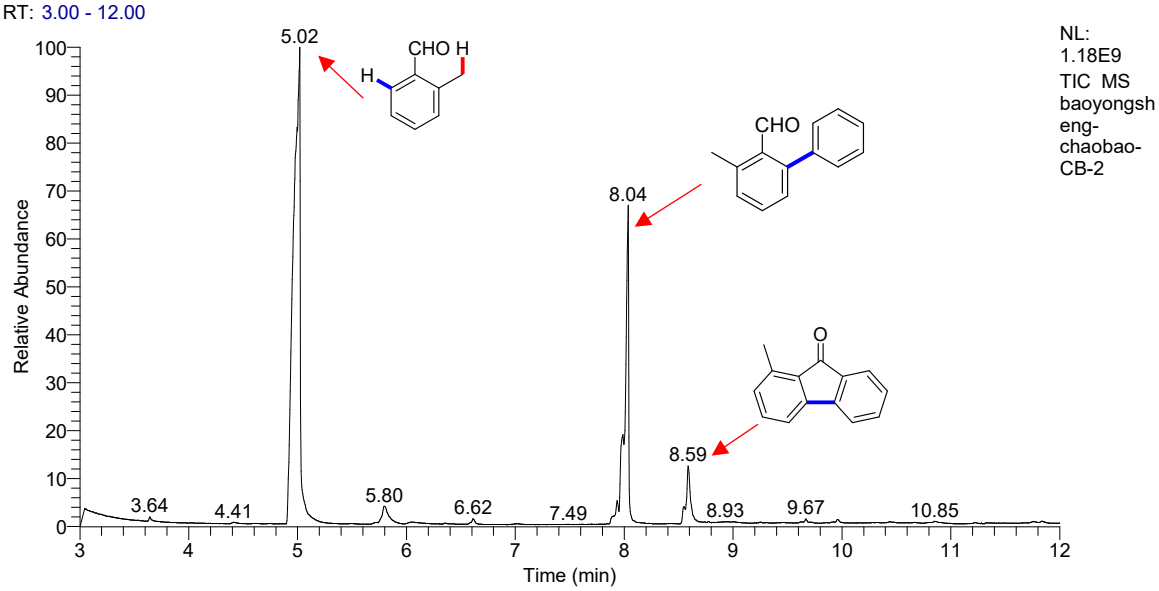
Relative Abundance
m/z
154.1
76.0
64.1
105.0
132.3
183.4
215.0
249.1
284.3
344.2
373.3
395.4
428.4
475.1



4. GCMS Analysis of $C(sp^2)$-$C(sp^2)$ Cross-Coupling of 1a with 2b





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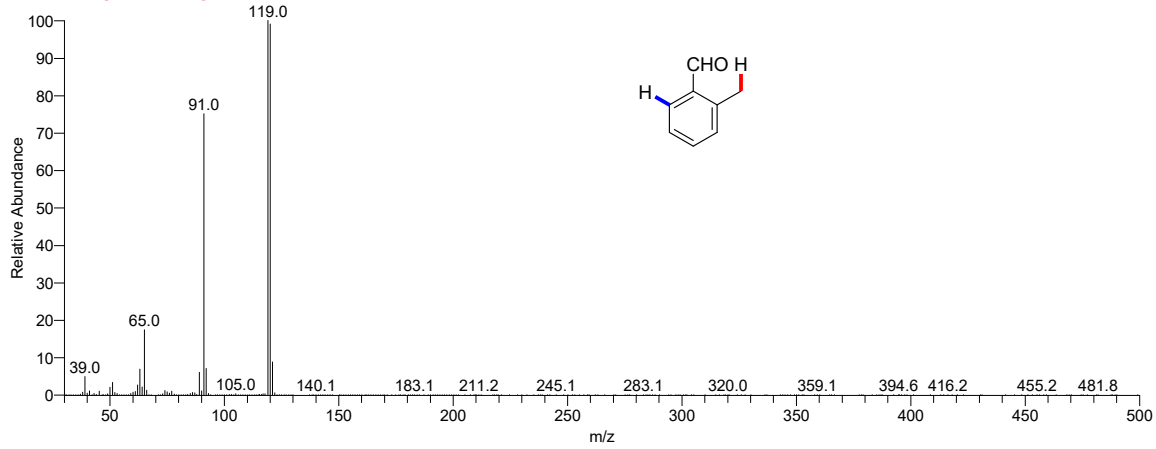

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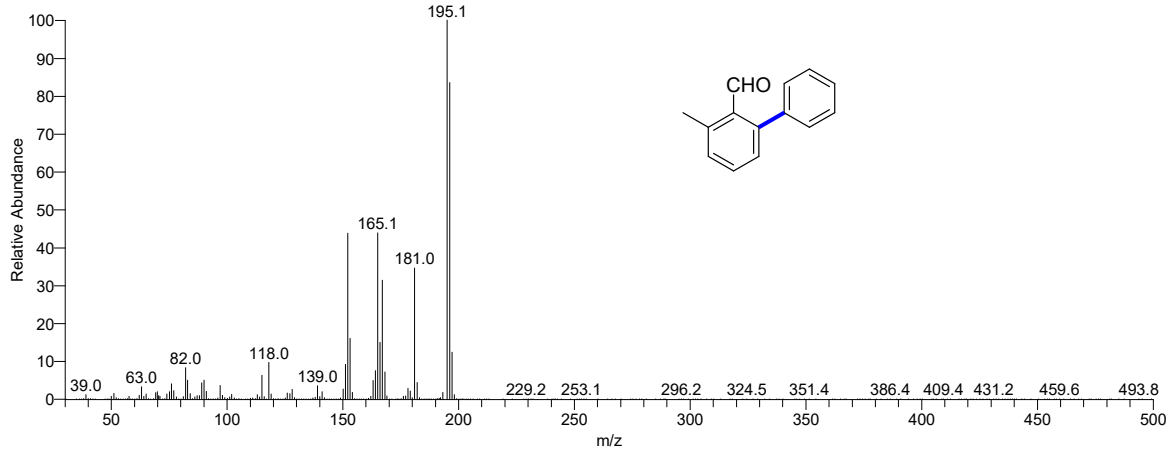
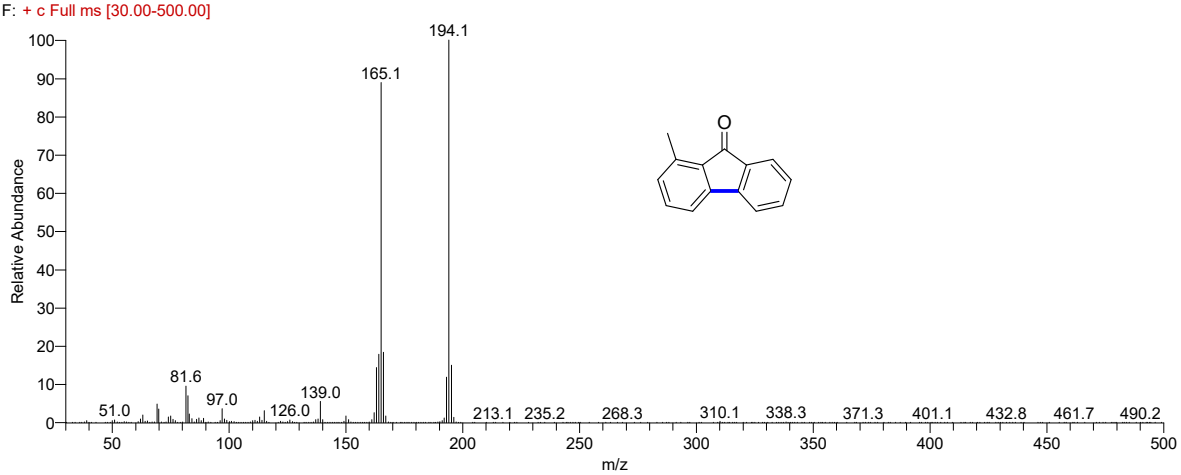
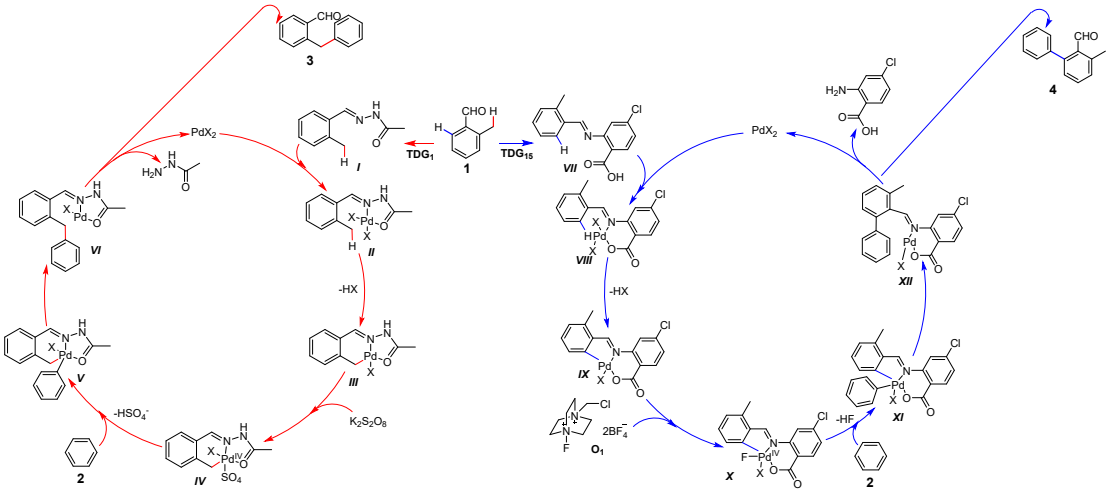


baoyongsheng-chaobao-CB-2 #2565 RT: 8.59 AV: 1 AV: 5 SB: 12 2558-2563 2567-2572 NL: 3.50E7
F: + c Full ms [30.00-500.00]



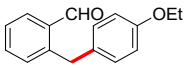
5. Proposed Mechanism

Based on the experiment results, a possible mechanism was outlined in Scheme S1. The first step of C(sp^3)-H arylation reaction is the transient formation of imine **I** from *o*-methyl benzaldehyde **1** and **TDG$_1$**. Following Pd complexation give rise to the five-membered palladacycle **II** and then generate 5,6-fused ring **III** by C(sp^3)-H activation. Oxidative addition with $K_2S_2O_8$ generate the Pd(IV) intermediate **IV**. Next, sulfate anion is displaced by **2** via C-H activation to provide intermediate **V**. The following reductive elimination and hydrolysis results in product **3** and Pd-catalyst regeneration. Similarly, the first step of C(sp^2)-H arylation reaction is the transient formation of imine **VII** from *o*-methyl benzaldehyde **1** and **TDG$_{15}$**. Following Pd complexation give rise to the six-membered palladacycle **VIII** and then generate 6,5-fused ring **IX** by C(sp^2)-H activation. Oxidative addition with **O$_1$** generate the Pd(IV) intermediate **X**. Next, fluoride anion is displaced by **2** via C-H activation to provide intermediate **XI**. The following reductive elimination and hydrolysis results in product **4** and Pd-catalyst regeneration.

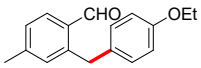


Scheme S1. Proposed Mechanism

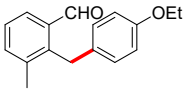
6. Characterization Data for the Products



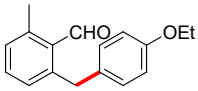
2-(4-ethoxybenzyl)-benzaldehyde **3aa**. Yield:71% (17.0mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.85 (d, *J* = 7.0 Hz, 1H), 7.51 (td, *J* = 7.5, 1.0 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 6.5 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.38 (s, 2H), 3.99 (q, *J* = 7.0 Hz, 2H), 1.38 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 157.5, 143.6, 133.9, 133.9, 132.2, 131.8, 131.5, 129.7, 126.9, 114.6, 63.4, 37.2, 14.9; MS (EI) m/z (%) 240.0(M^+, 60), 223.1(100), 211.0(65), 195.0(75), 164.9(80),117.9(75) ,90.0(75); Anal. Calcd. For $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%. Found: C, 80.01; H, 6.70%.



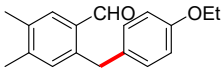
2-(4-ethoxybenzyl)-4-methylbenzaldehyde **3ba**. Yield: 64% (16.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 4.42 (s, 2H), 3.97 (q, *J* = 7.0 Hz, 2H), 2.31 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.8, 157.3, 141.1, 138.7, 136.1, 134.7, 131.4, 129.0, 126.8, 114.6, 63.4, 32.3, 19.6, 14.9. MS (EI) m/z (%) 254.0(M^+), 237.1(5), 209.1(6), 165.0(7), 104.0(8),77.0(12) ,29.0(100); Anal. Calcd. For $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%. Found: C, 80.30; H, 7.11%.



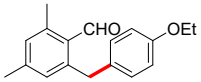
2-(4-ethoxybenzyl)-3-methylbenzaldehyde **3ca**. Yield: 70% (17.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 8.9 Hz, 3H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.34 (s, 2H), 3.99 (q, *J* = 7.0 Hz, 2H), 2.38 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.0, 157.4, 144.9, 143.6, 132.4, 132.3, 132.2, 131.6, 129.7, 127.7, 114.5, 63.4, 37.1, 21.8, 14.9. MS (EI) m/z (%) 254.0(M^+, 38), 237.1(43), 209.0(57), 165.0(58), 131.9(50),104.0(55) ,29.0(100); Anal. Calcd. For $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%. Found: C, 80.26; H, 7.12%.



2-(4-ethoxybenzyl)-6-methylbenzaldehyde **3da.** Yield: 51% (12.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.55 (s, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 4.29 (s, 2H), 3.99 (q, *J* = 7.0 Hz, 2H), 2.60 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.6, 157.4, 143.9, 141.3, 132.9, 132.5, 132.4, 130.4, 129.6, 114.5, 63.4, 37.9, 20.8, 14.9. MS (EI) m/z (%) 254.1(M^+, 2), 237.1(16), 209.1(57), 165.0(12), 131.9(20),104.0(22) ,29.0(100); Anal. Calcd. For $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%. Found: C, 80.31; H, 7.15%.

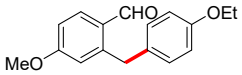


2-(4-ethoxybenzyl)-4,5-dimethylbenzaldehyde **3ea**. Yield: 45% (12.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.61 (s, 1H), 7.05-7.00 (m, 3H), 6.79 (d, *J* = 8.6 Hz, 2H), 4.30 (s, 2H), 3.99 (q, *J* = 7.0 Hz, 2H), 2.29 (d, *J* = 7.2 Hz, 6H), 1.38 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.2, 157.3, 143.7, 141.1, 135.3, 132.9, 132.8, 132.7, 131.8, 129.6, 114.5, 63.4, 36.6, 20.1, 19.2, 14.9. MS (EI) m/z (%) 268.1(M^+), 251.1(5), 223.1(6), 195.1(4), 165.1(6), 118.1(8), 29.0(100); Anal. Calcd. For $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%. Found: C, 80.55; H, 7.52%.

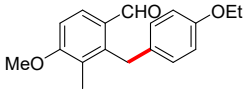


2-(4-ethoxybenzyl)-4,6-dimethylbenzaldehyde **3fa**. Yield: 40% (10.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.95 (s, 1H), 6.91 (s, 1H), 6.79 (d, *J* = 8.6 Hz, 2H), 4.26 (s, 2H), 3.99 (q, *J* = 7.0 Hz, 2H), 2.57 (s, 3H), 2.32 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.1, 193.0, 157.3, 144.2, 143.9, 141.7, 132.6, 131.2, 130.5, 129.8, 129.6, 114.5, 63.4, 37.9, 21.6, 20.9, 14.9. MS (EI) m/z (%) 268.1(M^+, 1), 251.1(5), 223.1(4), 146.0(7),

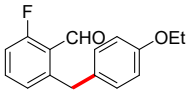
118.1(10),77.0(9) ,29.0(100); Anal. Calcd. For $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%. Found: C, 80.58; H, 7.53%.



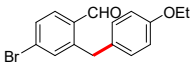
2-(4-ethoxybenzyl)-4-methoxybenzaldehyde **3ga**. Yield: 50% (13.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.87 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 2.3 Hz, 1H), 4.35 (s, 2H), 3.99 (q, *J* = 7.0 Hz, 2H), 3.83 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.9, 163.9, 157.5, 146.3, 134.7, 131.9, 129.8, 127.5, 117.0, 114.6, 111.7, 63.4, 55.5, 37.3, 14.9. MS (EI) m/z (%) 270.0(M^+), 225.1(3), 181.1(5), 148.0(5), 120.0(8),77.0(9) ,29.0(100); Anal. Calcd. For $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%. Found: C, 75.50; H, 6.70%.



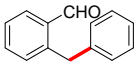
2-(4-ethoxybenzyl)-4-methoxy-3-methylbenzaldehyde **3ha**. Yield: 42% (11.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 6.92 (t, *J* = 9.5 Hz, 3H), 6.76 (d, *J* = 8.6 Hz, 2H), 4.44 (s, 2H), 3.97 (q, *J* = 7.0 Hz, 2H), 3.91 (s, *J* = 7.9 Hz, 3H), 2.15 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.6, 162.3, 157.2, 142.7, 131.8, 131.6, 129.0, 128.1, 127.0, 114.5, 108.3, 63.4, 55.7, 32.4, 14.9, 11.3. MS (EI) m/z (%) 284.0(M^+), 267.2(3), 224.1(4), 195.1(4), 134.1(11),77.0(9) ,29.0(100); Anal. Calcd. For $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%. Found: C, 76.08; H, 7.10%.



2-(4-ethoxybenzyl)-6-fluorobenzaldehyde **3ia**. Yield: 43% (11.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.52 (s, 1H), 7.47-7.43 (m, *J* = 5.9 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 9.3 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.35 (s, 2H), 4.00 (q, *J* = 7.0 Hz, 2H), 1.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.1, 189.0, 157.5, 145.5, 135.1, 135.1, 131.6, 130.0, 127.1, 127.1, 114.5, 63.4, 37.7, 14.9. MS (EI) m/z (%) 258.1(M^+, 5), 240.1(13), 213.0(19), 183.0(18), 136.0(10), 108.0(17), 29.0(100); Anal. Calcd. For $C_{16}H_{15}FO_2$: C, 74.40; H, 5.85%. Found: C, 74.36; H, 5.89%.

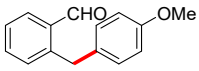


4-bromo-2-(4-ethoxybenzyl)-benzaldehyde **3ja.** Yield: 63% (20.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.97 (d, *J* = 2.2 Hz, 1H), 7.62 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.31 (s, 2H), 3.99 (q, *J* = 7.0 Hz, 2H), 1.39 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.7, 157.6, 142.4, 136.7, 135.3, 133.9, 133.3, 131.5, 129.6, 120.9, 114.7, 63.5, 36.6, 14.8. MS (EI) m/z (%) 320.1(M^+), 210.0(6), 194.0(11), 165.0(7), 88.9(8), 62.9(4) ,29.0(100); Anal. Calcd. For $C_{16}H_{15}BrO_2$: C, 60.21; H, 4.74%. Found: C, 60.28; H, 4.70%.

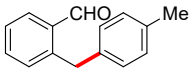


2-benzylbenzaldehyde **3ab**.[1] Yield: 69% (13.5 mg).^{1}H NMR (600 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H),

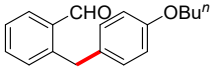
7.20 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 7.5 Hz, 2H), 4.46 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 143.0, 140.3, 133.9, 133.9, 132.1, 131.7, 128.8, 128.6, 127.0, 126.3, 38.0.



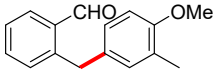
2-(4-methoxybenzyl)-benzaldehyde **3ac**.[2] Yield: 51% (11.5 mg).^{1}H NMR (600 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.85 (dd, J = 7.6, 1.2 Hz, 1H), 7.52 (td, J = 7.5, 1.3 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.25 (d, J = 6.7 Hz, 1H), 7.06 (d, J = 8.5 Hz, 2H), 6.91 – 6.74 (m, 2H), 4.39 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 158.1, 143.5, 133.9, 133.9, 132.4, 131.9, 131.5, 129.7, 126.9, 114.0, 55.3, 37.2.



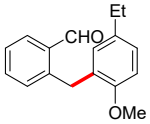
2-(4-methylbenzyl)-benzaldehyde **3ad**.[2] Yield: 56% (11.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 7.7 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 4.41 (s, 2H), 2.30 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 143.4, 137.2, 135.8, 133.9, 131.8, 131.6, 129.3, 128.7, 126.9, 37.6, 20.9.



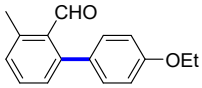
2-(4-butoxybenzyl)-benzaldehyde **3ae**. Yield: 55% (14.7 mg).^{1}H NMR (600 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.25 (s, 1H), 7.04 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 4.38 (s, 2H), 3.92 (t, J = 6.5 Hz, 2H), 1.88 – 1.60 (m, 2H), 1.60 – 1.35 (m, J = 14.6, 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 157.7, 143.6, 133.9, 133.9, 132.1, 131.8, 131.5, 129.7, 126.9, 114.6, 67.7, 37.2, 31.4, 19.3, 13.9. MS (EI) m/z (%) 268.0(M^+), 221.1(8), 195.1(21), 165.0(16), 90.0(12), 57.0(11), 41.0(31), 29.0(100); Anal. Calcd. For $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%. Found: C, 80.60; H, 7.49%.



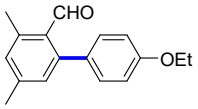
2-(4-methoxy-3-methylbenzyl)-benzaldehyde **3af**. Yield: 53% (12.7 mg).^{1}H NMR (600 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.27 (s, 1H), 6.91 (d, J = 9.0 Hz, 2H), 6.72 (d, J = 8.0 Hz, 1H), 4.35 (s, 2H), 3.79 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 156.3, 143.8, 133.9, 133.9, 131.9, 131.6, 131.5, 131.1, 126.9, 126.8, 126.8, 110.0, 55.3, 37.1, 16.2; MS (EI) m/z (%) 240.1(M^+, 20), 222.1(55), 179.0(45), 165.0(58), 152.0(45),117.9(65) ,90.0(90); Anal. Calcd. For $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%. Found: C, 80.00; H, 6.67%.



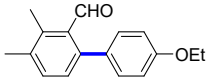
2-(5-ethyl-2-methoxybenzyl)-benzaldehyde **3ag**. Yield: 41% (10.4 mg).^{1}H NMR (600 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.88 (d, J = 7.7 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.03 (d, J = 8.3 Hz, 1H), 6.79 (d, J = 7.0 Hz, 2H), 4.37 (s, 2H), 3.78 (s, 3H), 2.50 (q, 2H), 1.14 (t, J = 7.6 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 192.5, 192.5, 155.1, 143.5, 136.4, 133.8, 131.2, 130.0, 129.8, 128.5, 126.7, 126.6, 110.3, 55.4, 31.9, 27.9, 15.9. MS (EI) m/z (%) 254.1(M^+, 15), 237.1(25), 225.1(45), 194.0(35),165.0(42) ,118.0(90), 91.0(90), 29.0(100); Anal. Calcd. For $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%. Found: C, 80.25; H, 7.15%.



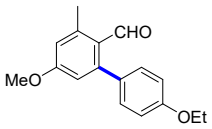
4'-ethoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4aa**.[3] Yield:75% (18.1mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.25-7.24 (m, 2H), 6.96 (d, 3H), 4.09 (q, *J* = 7.0 Hz, 2H), 2.64 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.8, 158.9, 146.8, 139.8, 132.7, 132.1, 131.3, 130.9, 130.6, 128.6, 114.3, 63.6, 21.5, 14.8.



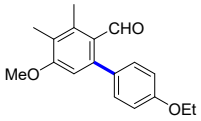
4'-ethoxy-3,5-dimethyl-[1,1'-biphenyl]-2-carbaldehyde **4ba**. Yield:64% (16.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.25 (d, 2H), 7.06 (s, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 2.62 (s, 3H), 2.40 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.5, 158.9, 147.3, 142.9, 140.2, 131.6, 131.2, 131.1, 130.2, 129.3, 114.3, 63.6, 21.6, 21.5, 14.8; MS (EI) m/z (%) 254.2(M^+, 100), 239.1(11), 225.1(54), 197.1(27), 182.1(15), 153.1(17), 132.0(8), 104.1(4); Anal. Calcd. For $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%. Found: C, 80.24; H, 7.16%.



4'-ethoxy-3,4-dimethyl-[1,1'-biphenyl]-2-carbaldehyde **4ca**. Yield:62% (15.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 2.53 (s, 3H), 2.37 (s, 3H), 1.45 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.8, 158.8, 144.1, 137.6, 137.0, 133.6, 133.4, 131.2, 127.9, 114.3, 63.6, 20.3, 16.0, 14.8; MS (EI) m/z (%) 254.2(M^+, 100), 239.1(10), 225.1(46), 197.1(29), 182.1(13), 153.1(16), 115.0(5); Anal. Calcd. For $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%. Found: C, 80.31; H, 7.09%.

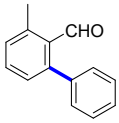


4'-ethoxy-5-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ga**. Yield:41% (11.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.26-7.24 (m, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 2.1 Hz, 1H), 6.72 (d, *J* = 2.5 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 2.66 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.3, 161.9, 159.0, 150.1, 143.2, 131.2, 131.1, 126.3, 116.6, 114.3, 113.4, 63.6, 55.4, 22.2, 14.8; MS (EI) m/z (%) 270.2(M^+, 100), 255.1(7), 241.1(36), 213.1(18), 185.1(8), 148.0(23), 120.0(6); Anal. Calcd. For $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%. Found: C, 75.55; H, 6.73%.

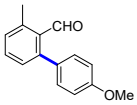


4'-ethoxy-5-methoxy-3,4-dimethyl-[1,1'-biphenyl]-2-carbaldehyde **4ha**. Yield:38% (10.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.25 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.69 (s, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 2.60 (s, 3H), 2.22 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.3, 160.1, 158.8, 147.2, 140.3, 131.7, 131.1, 126.6, 125.6, 114.3, 109.8, 63.6, 55.6, 16.5, 14.8, 11.5; MS (EI) m/z (%) 284.2(M^+, 100), 269.2(12), 255.1(24), 227.1(13), 212.1(8), 162.0(24), 134.0(4); Anal. Calcd. For $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%. Found:

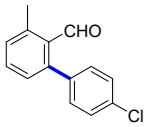
C, 76.05; H, 7.06%.



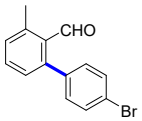
3- methyl-[1,1'-biphenyl]-2-carbaldehyde **4ab**.[4] Yield:53% (10.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.49-7.40 (m, 4H), 7.35 (d, *J* = 6.9 Hz, 2H), 7.30-7.26 (m, 2H), 2.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.6, 147.1, 140.0, 138.9, 132.6, 132.2, 131.1, 130.1, 128.6, 128.3, 127.9, 21.5; MS (EI) m/z (%) 196.1(M^+, 82), 195.1(100), 181.1(33), 165.1(42), 118.0(10), 82.0(9).



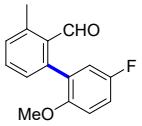
4'-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ac**.[4] Yield:61% (13.8 mg).^{1}H NMR (600 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 6.5 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.8, 159.6, 146.7, 139.9, 132.7, 132.1, 131.3, 131.1, 130.7, 128.6, 113.8, 55.4, 21.5.



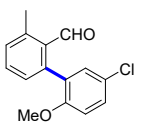
4'-chloro-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ah**.[4] Yield:49% (11.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.28 (t, 3H), 7.23 (d, *J* = 7.6 Hz, 1H), 2.65 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.1, 145.6, 140.4, 137.4, 134.3, 132.5, 132.3, 131.4, 131.2, 128.6, 128.5, 21.4.



4'-bromo-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ai**.[3] Yield:42% (11.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.22 (t, 3H), 2.65 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.04, 145.64, 140.27, 137.88, 132.30, 131.55, 131.51, 131.45, 128.42, 122.42, 21.41.

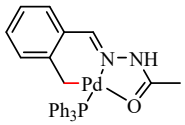


5'-fluoro-2'-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4aj**. Yield:39% (9.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.28 (d, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.10-7.07 (m, *J* = 5.6, 3.3 Hz, 1H), 7.01-6.99 (m, 1H), 6.88-6.85 (m, 1H), 3.71 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.1, 156.7, 155.1, 151.8, 141.0, 138.7, 131.5, 131.3, 130.7, 127.8, 117.0, 116.9, 114.6, 114.4, 110.4, 110.4, 54.9, 28.7, 20.4; MS (EI) m/z (%) 244.1(M^+, 24), 218.1(5), 213.1(100), 183.0(10), 152.1(4), 118.0(3); Anal. Calcd. For $C_{15}H_{13}FO_2$: C, 73.76; H, 5.36%. Found: C, 73.80; H, 5.40%.

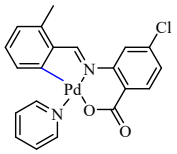


5'-chloro-2'-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ak**. Yield:51% (13.3 mg).^{1}H NMR (600 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.48 (t, 1H), 7.35-7.34 (m, *J* = 6.2 Hz, 1H), 7.29 (d, 1H), 7.24 (d,

J = 2.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.86 (d, 1H), 3.72 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.04, 155.25, 141.80, 139.77, 132.57, 132.22, 131.76, 130.87, 129.61, 129.28, 128.88, 125.78, 111.66, 55.73, 21.45; MS (EI) m/z (%) 260.1(M^+, 28), 229.1(100), 215.0(6), 193.1(12), 165.1(15), 118.0(3), 76.0(6); Anal. Calcd. For $C_{15}H_{13}ClO_2$: C, 69.10; H, 5.03%. Found: C, 69.10; H, 5.04%.



Intermediate **5**. yield:41% (M=543.08, 22.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 9.4 Hz, 1H), 7.65-7.60 (m, 6H), 7.50-7.44 (m, 4H), 7.44-7.39 (m, 6H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 7.4 Hz, 1H), 2.94 (d, *J* = 6.2 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.1 (d, *J* = 4.7 Hz, 1C), 148.5, 143.7, 134.5, 134.5, 134.4, 132.9, 132.5, 132.2, 132.1, 132.1, 132.0, 131.9, 131.1, 130.8, 130.7, 130.7, 130.2, 128.9, 128.7, 128.6, 128.5, 128.5, 124.8, 26.5 (d, *J* = 5.3 Hz, 1C), 19.3; HRMS (ESI): m/z $[M+2H]^+$ calcd for $C_{28}H_{26}N_2OPPd$ 545.0818, found 545.0826.



Intermediate **6**. yield:59% (M=455.99, 26.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84 (d, *J* = 5.0 Hz, 2H), 8.71 (s, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 7.4, 6.6 Hz, 2H), 7.40 (d, *J* = 1.7 Hz, 1H), 7.30 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.28 (d, *J* = 7.6 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 169.3, 160.8, 152.6, 145.5, 144.0, 141.0, 138.6, 136.4, 136.3, 133.0, 131.8, 130. 9, 128.3, 127.0, 125.6, 117.6, 20.2; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{15}ClN_2O_2Pd$ 456.99296, found 456.99094.

References:

[1] Li, Bijin; Lawrence, Brianna; Li, Guigen; Ge, Haibo. *Angewandte Chemie, International Edition* **2020**, *59*, 3078-3082.

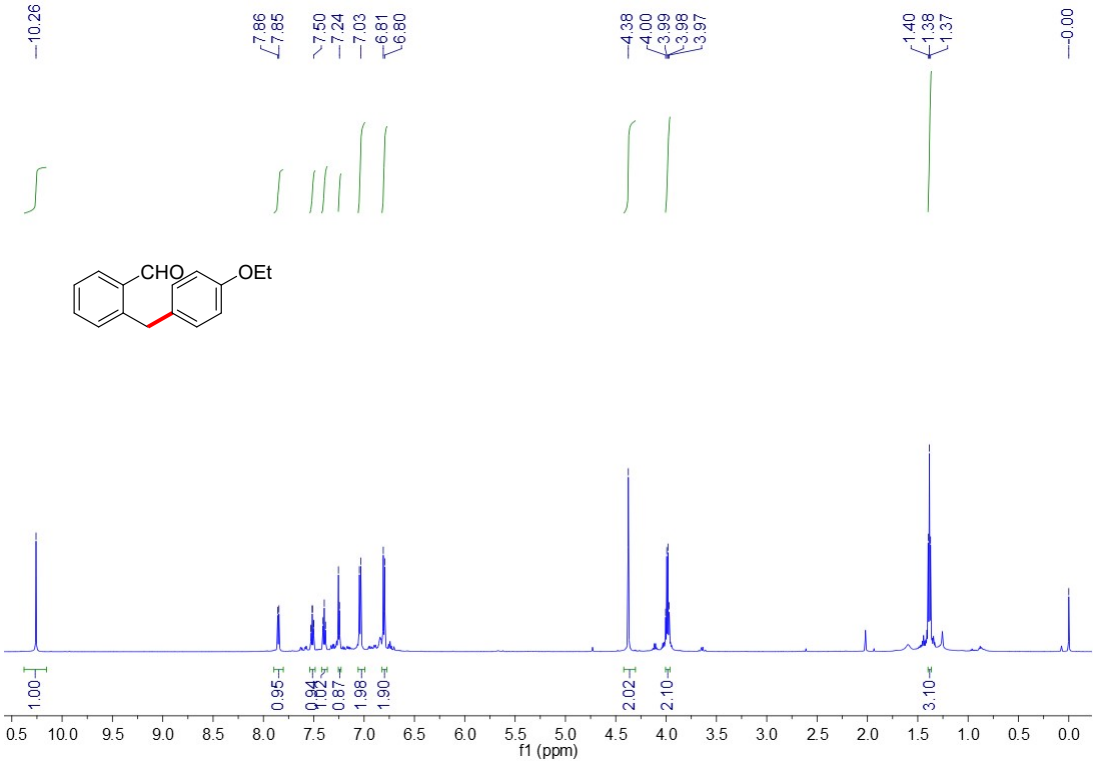
[2] Wen, Fei; Li, Zheng. *Advanced Synthesis & Catalysis* **2020**, *362*, 133-138.

[3] Mu, Delong; He, Gang; Chen, Gong *Chemistry-An Asian Journal* **2018**, *13*, 2423-2426.

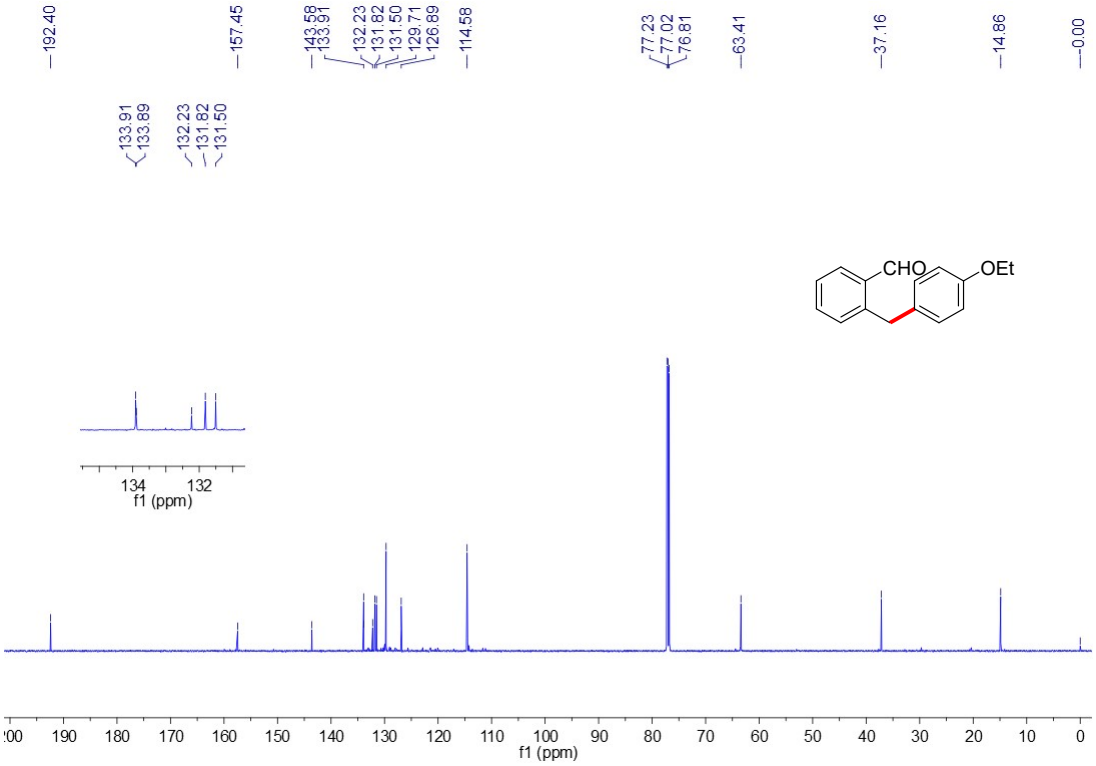
[4] Hu, Feng; Szostak, Michal *Organic Letters* **2016**, *18*, 4186-4189.

7. ^{1}H NMR, ^{13}C NMR and MS Spectra of the Products

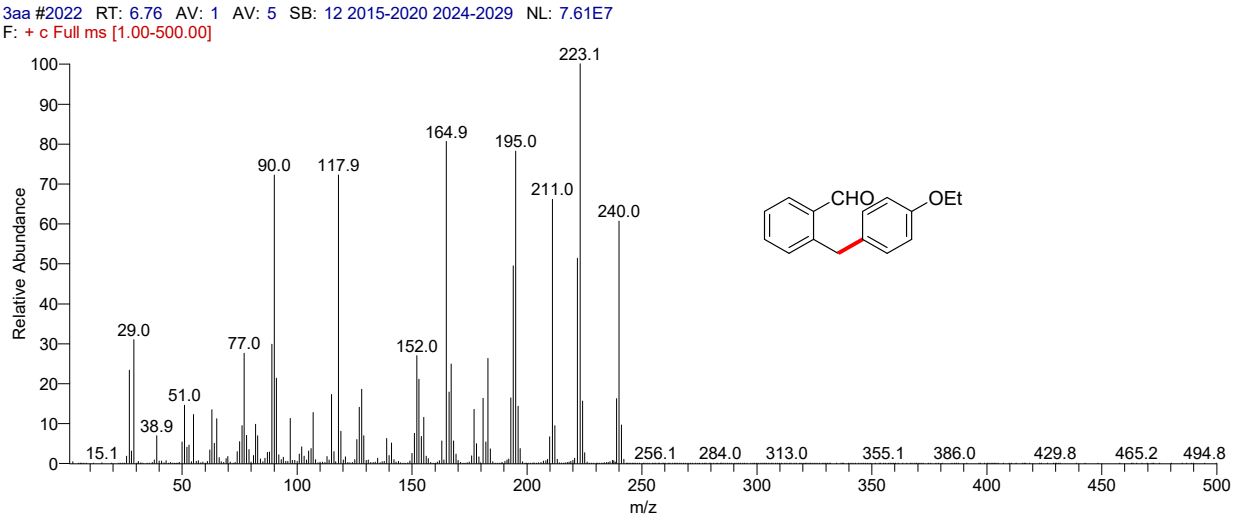
^{1}H NMR of 2-(4-ethoxybenzyl)-benzaldehyde **3aa**



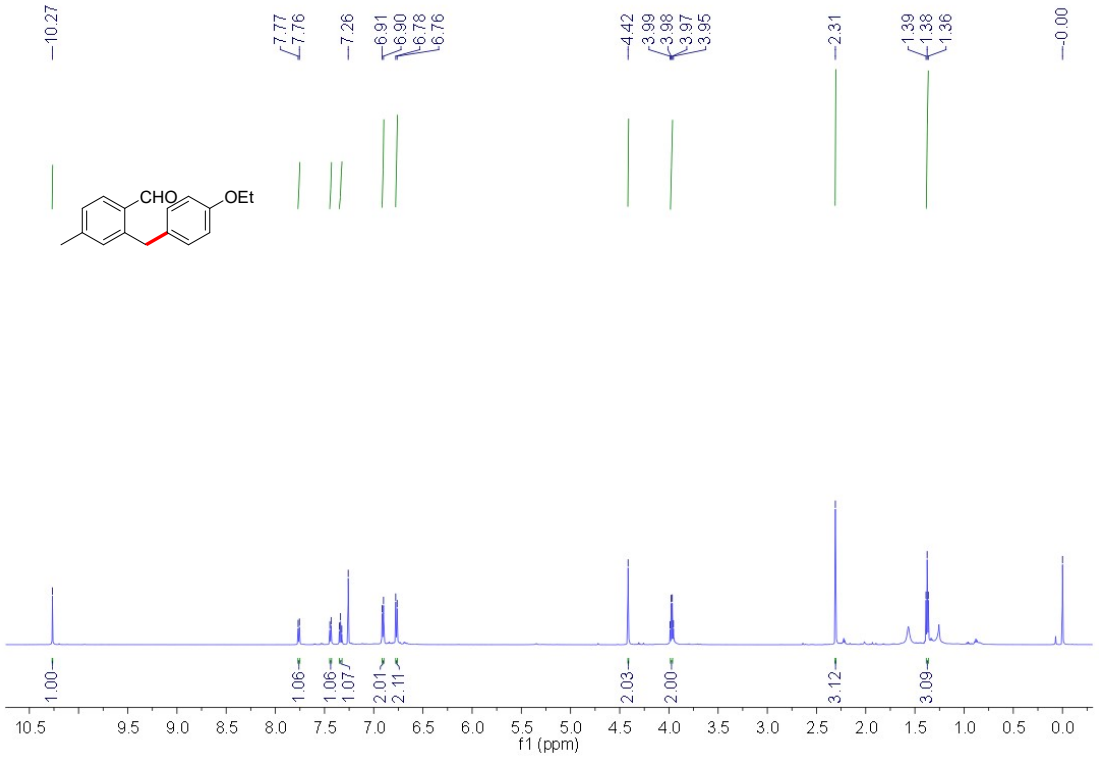
^{13}C NMR of 2-(4-ethoxybenzyl)-benzaldehyde **3aa**



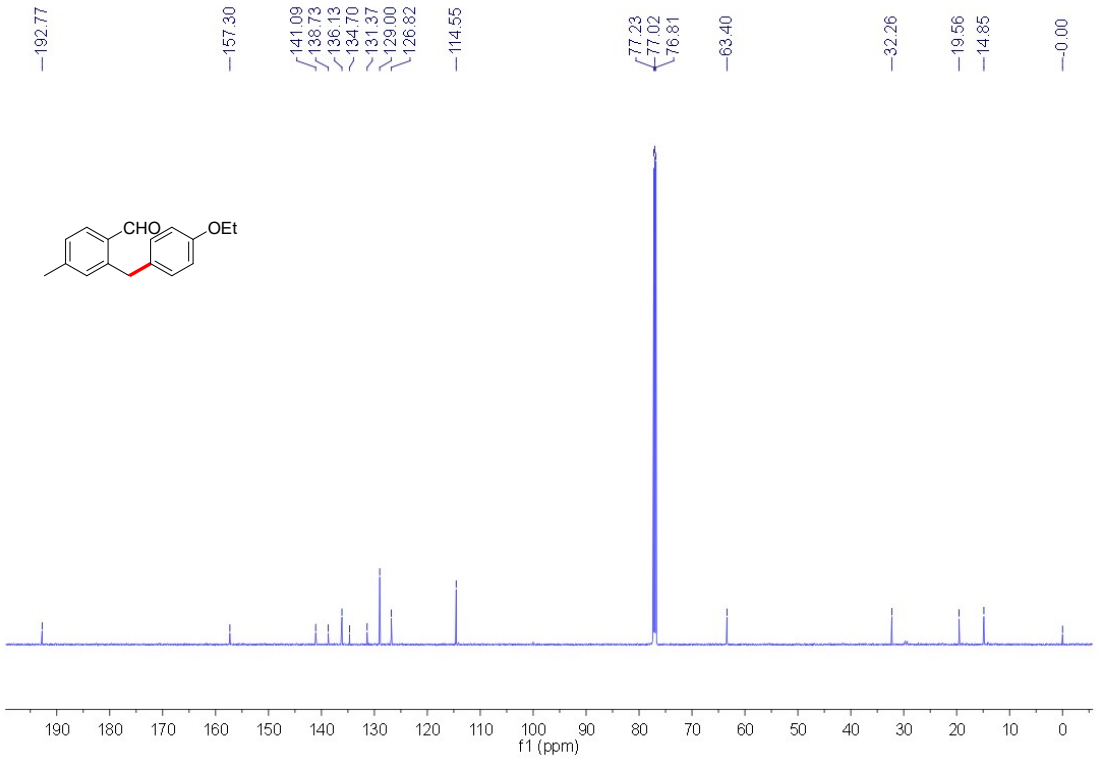
MS(EI) of 2-(4-ethoxybenzyl)-benzaldehyde **3aa**



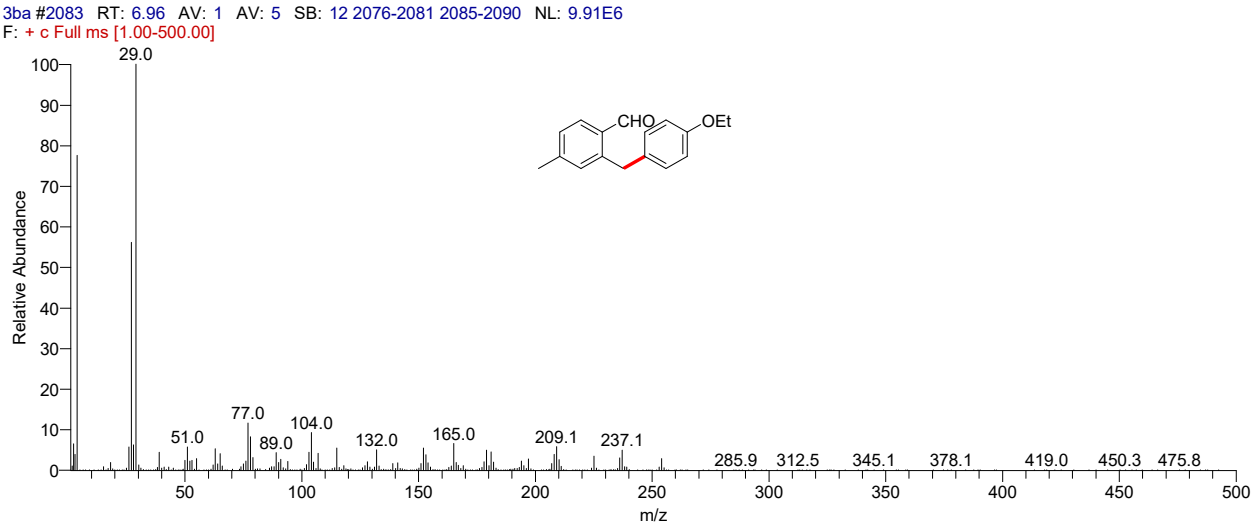
^{1}H NMR of 2-(4-ethoxybenzyl)-4-methylbenzaldehyde **3ba**



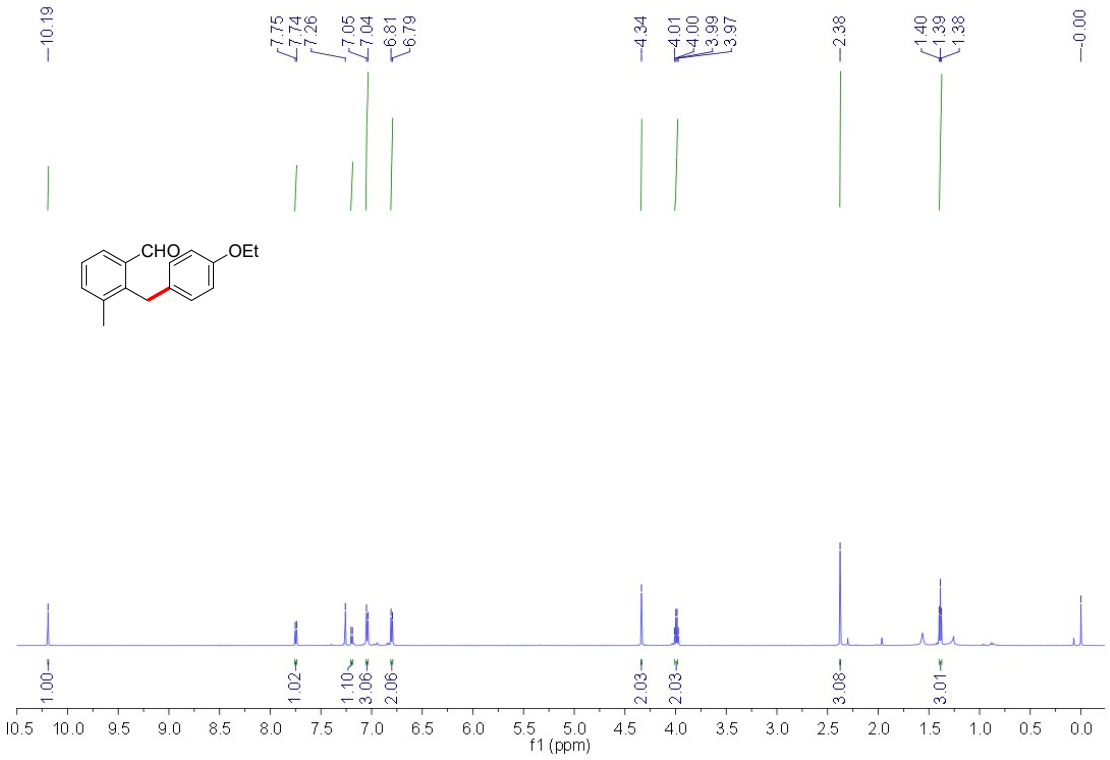
^{13}C NMR of 2-(4-ethoxybenzyl)-4-methylbenzaldehyde **3ba**



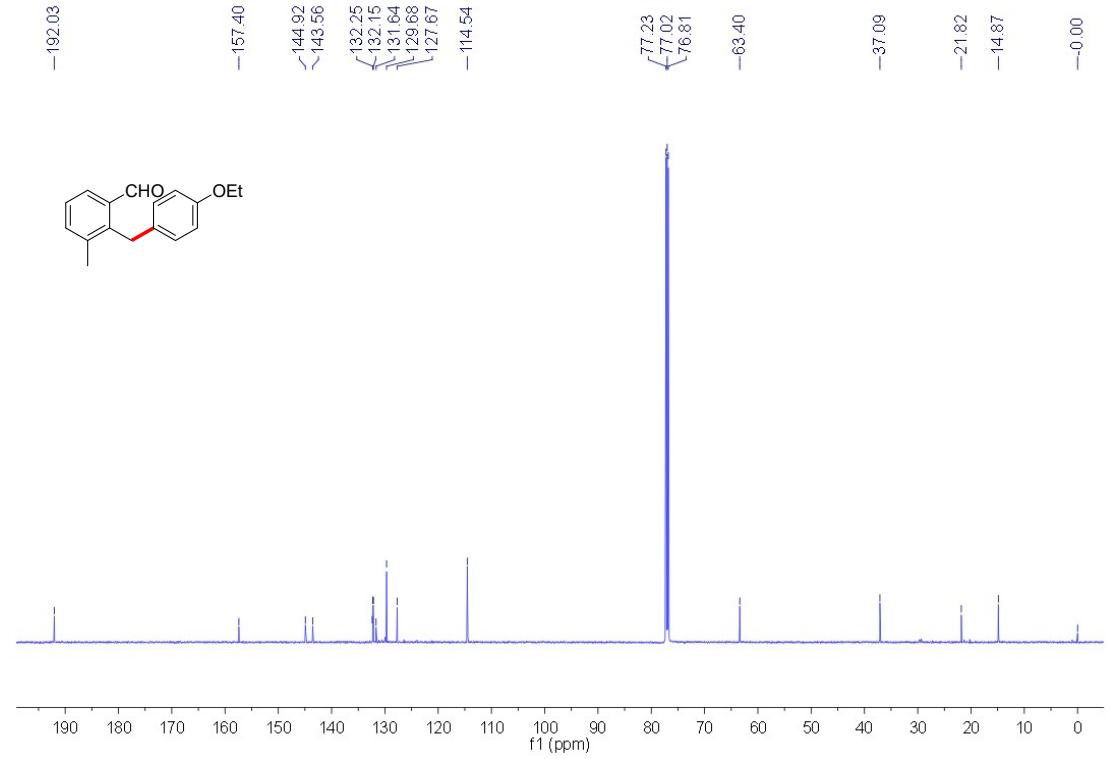
MS(EI) of 2-(4-ethoxybenzyl)-4-methylbenzaldehyde **3ba**



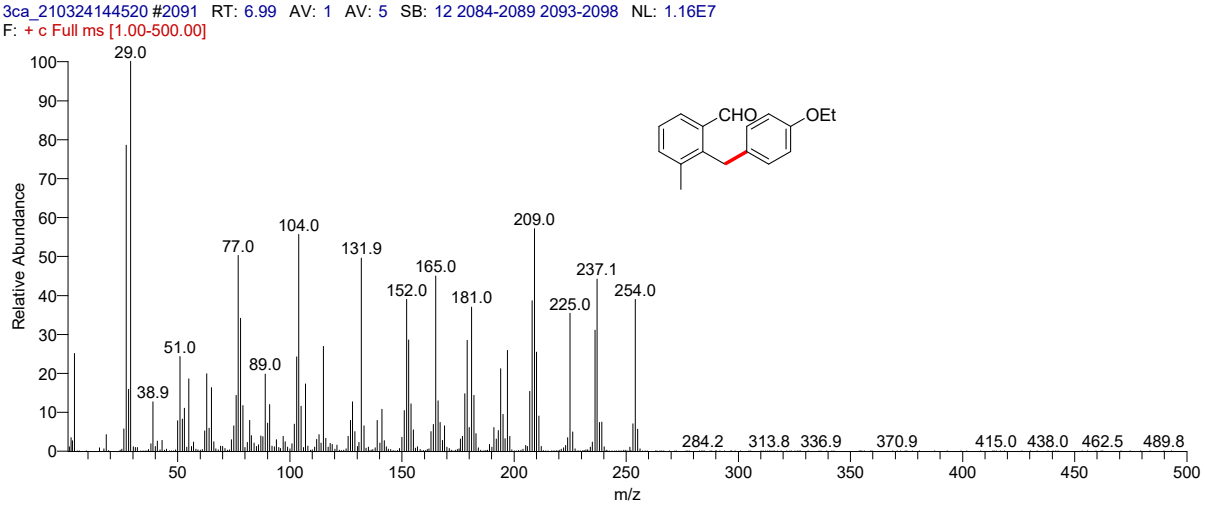
^{1}H NMR of 2-(4-ethoxybenzyl)-3-methylbenzaldehyde **3ca**



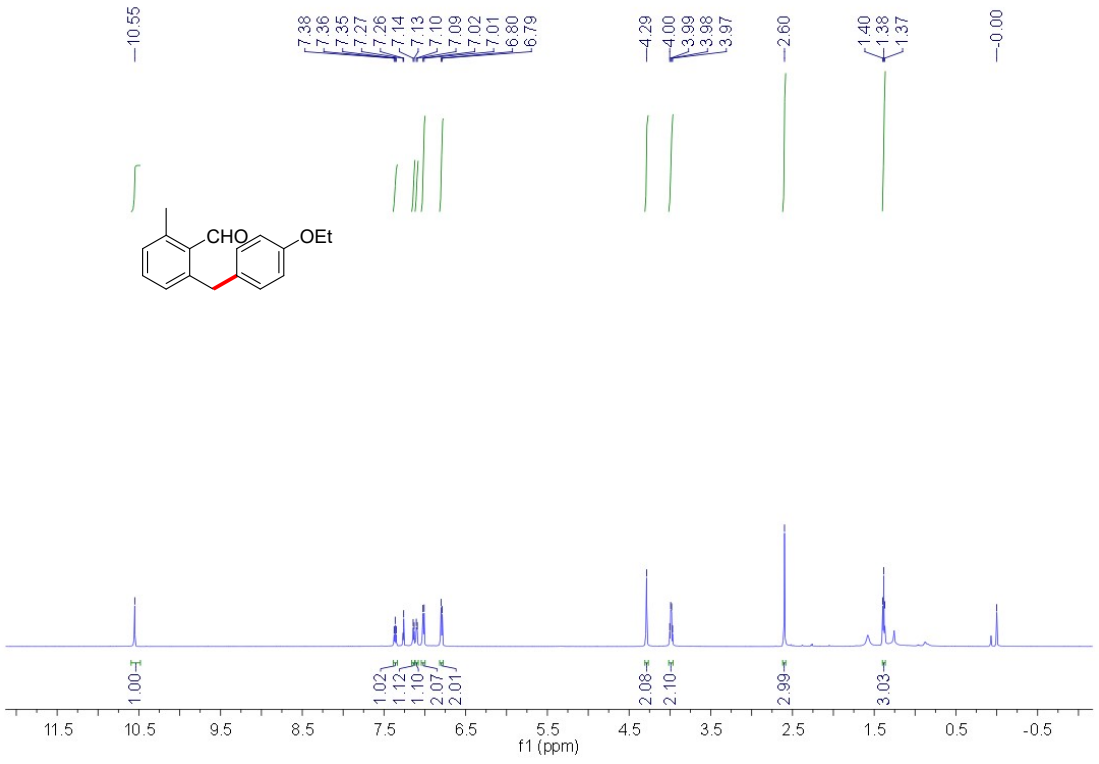
^{13}C NMR of 2-(4-ethoxybenzyl)-3-methylbenzaldehyde **3ca**



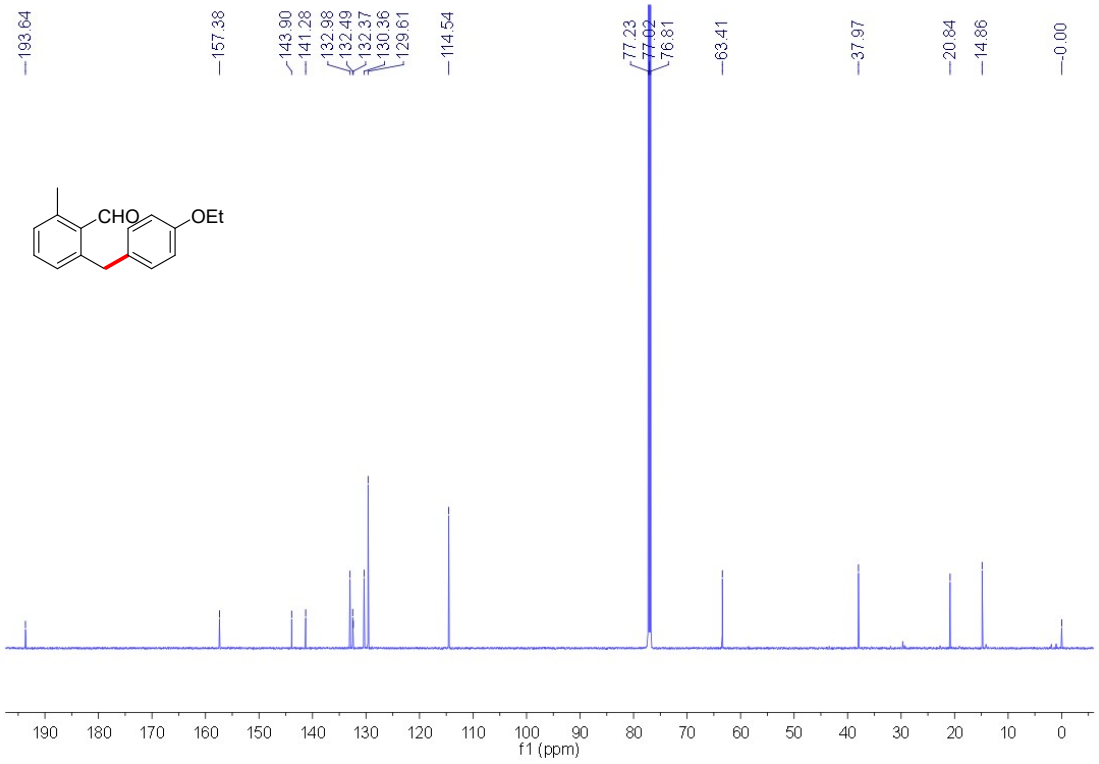
MS(EI) of 2-(4-ethoxybenzyl)-3-methylbenzaldehyde **3ca**



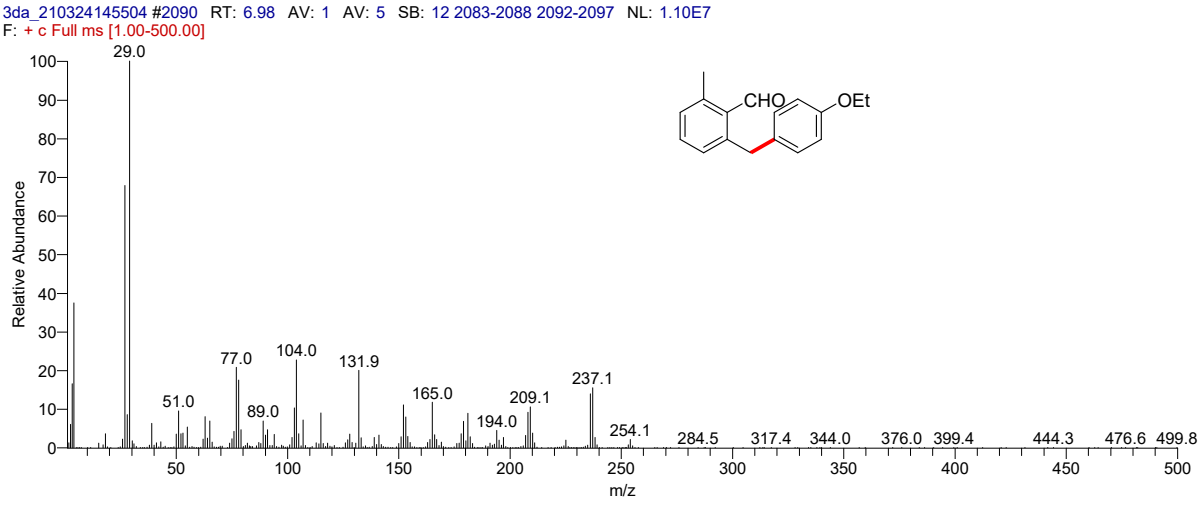
^{1}H NMR of 2-(4-ethoxybenzyl)-6-methylbenzaldehyde **3da**



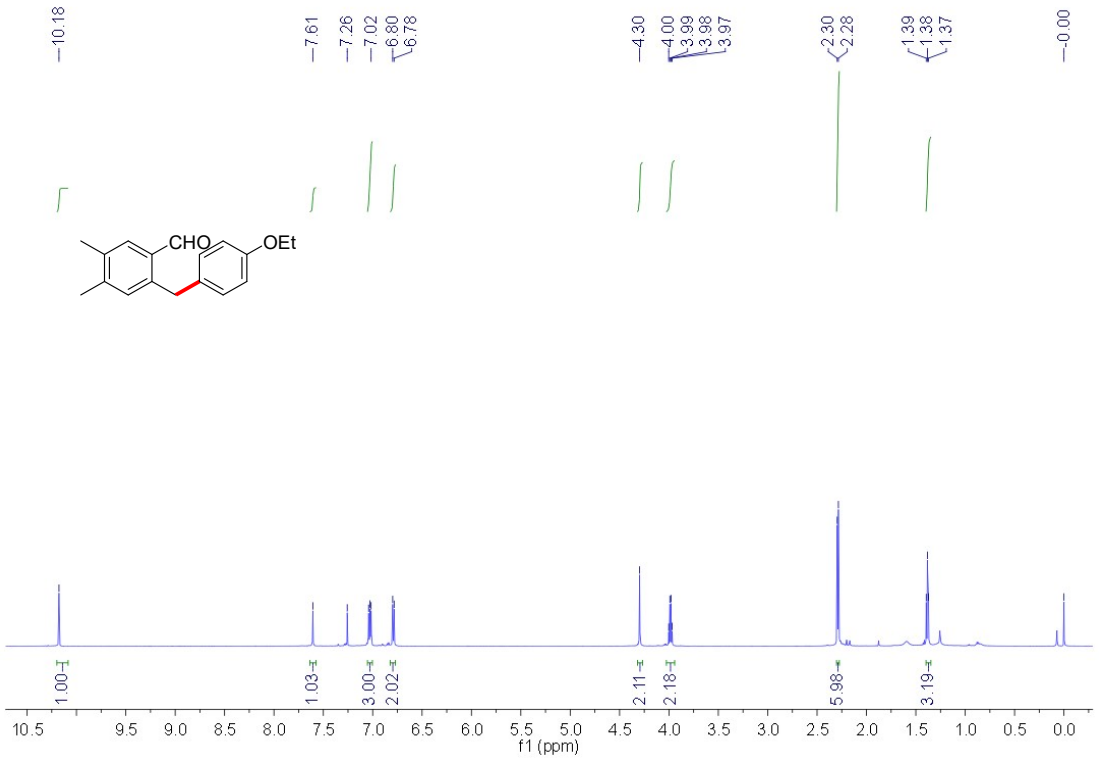
^{13}C NMR of 2-(4-ethoxybenzyl)-6-methylbenzaldehyde **3da**



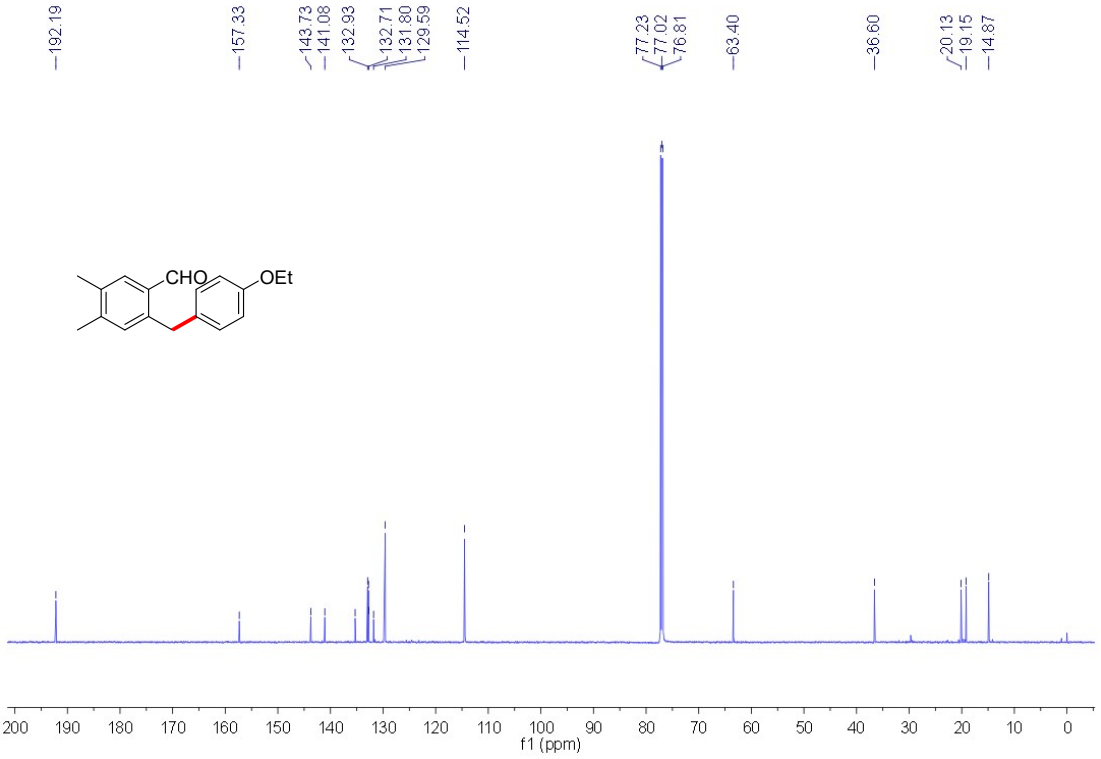
MS(EI) of 2-(4-ethoxybenzyl)-6-methylbenzaldehyde **3da**



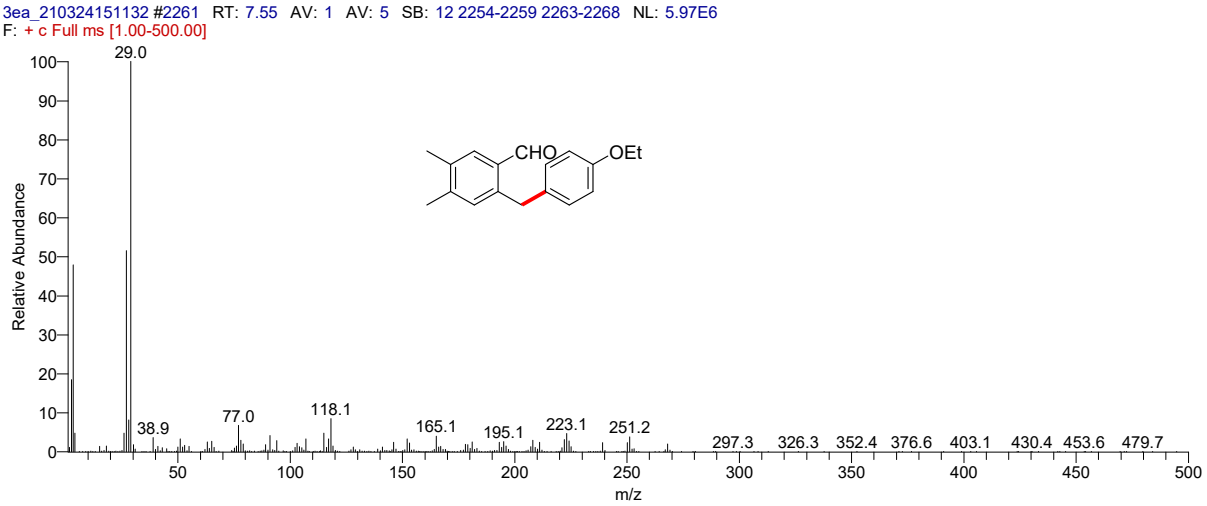
^{1}H NMR of 2-(4-ethoxybenzyl)-4,5-dimethylbenzaldehyde **3ea**



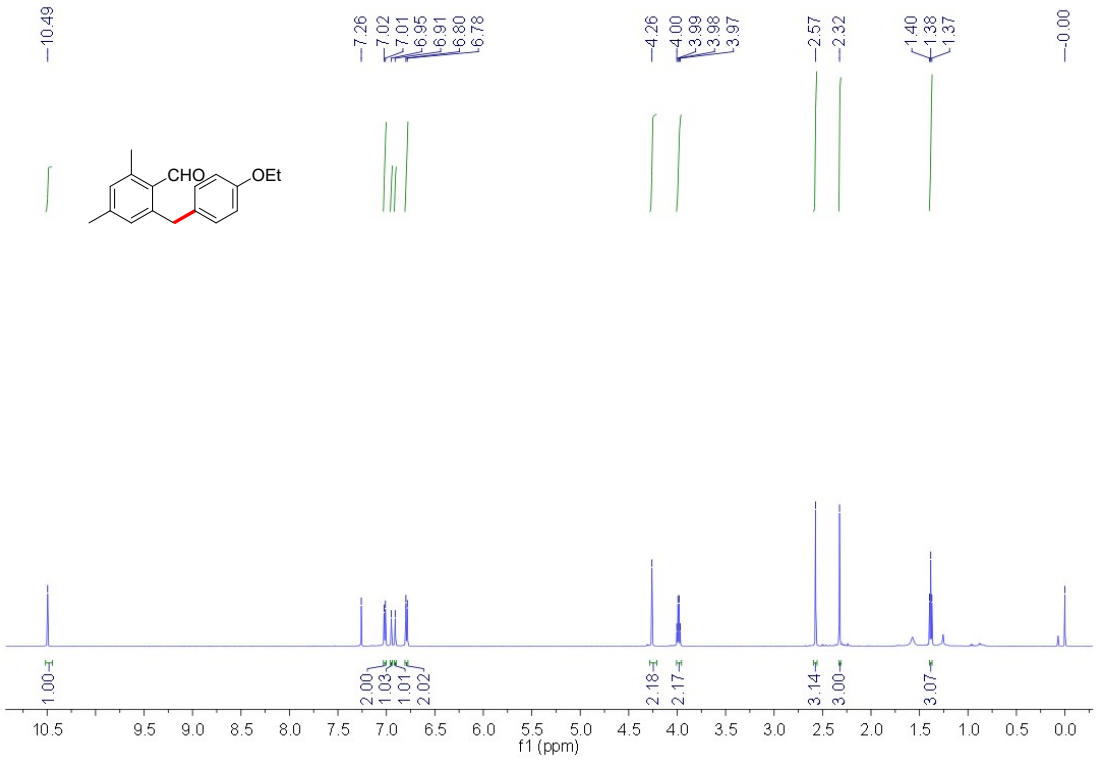
^{13}C NMR of 2-(4-ethoxybenzyl)-4,5-dimethylbenzaldehyde **3ea**



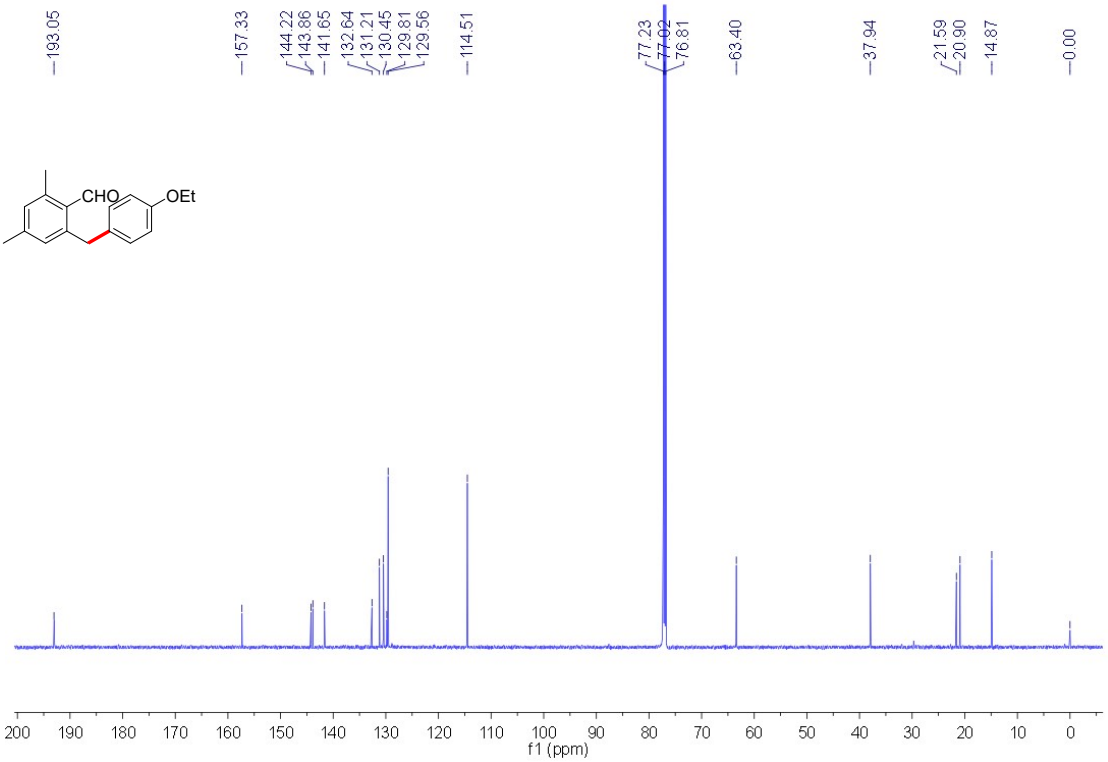
MS(EI) of 2-(4-ethoxybenzyl)-4,5-dimethylbenzaldehyde **3ea**



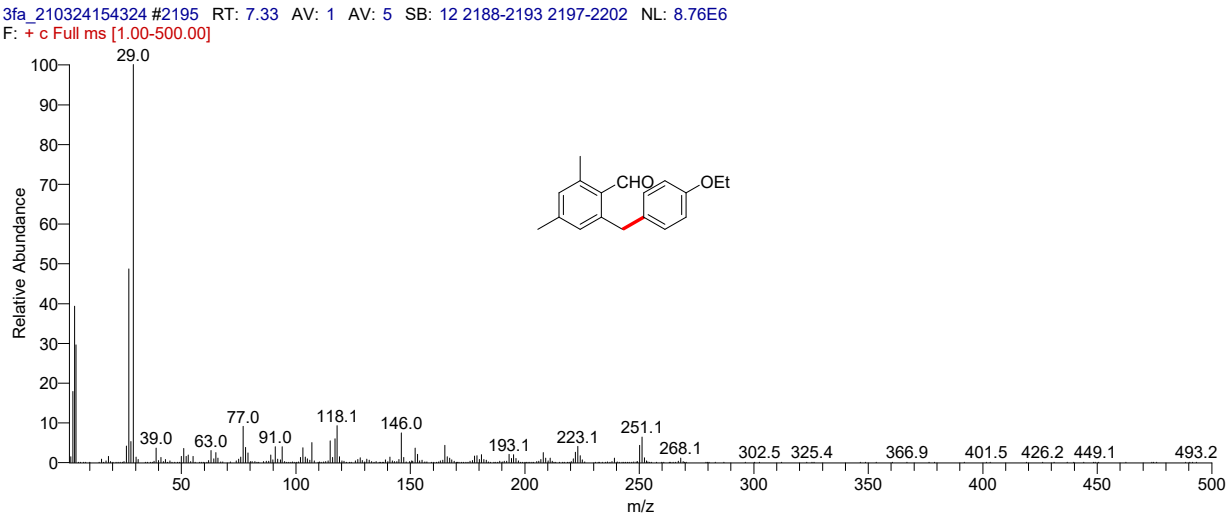
^{1}H NMR of 2-(4-ethoxybenzyl)-4,6-dimethylbenzaldehyde **3fa**



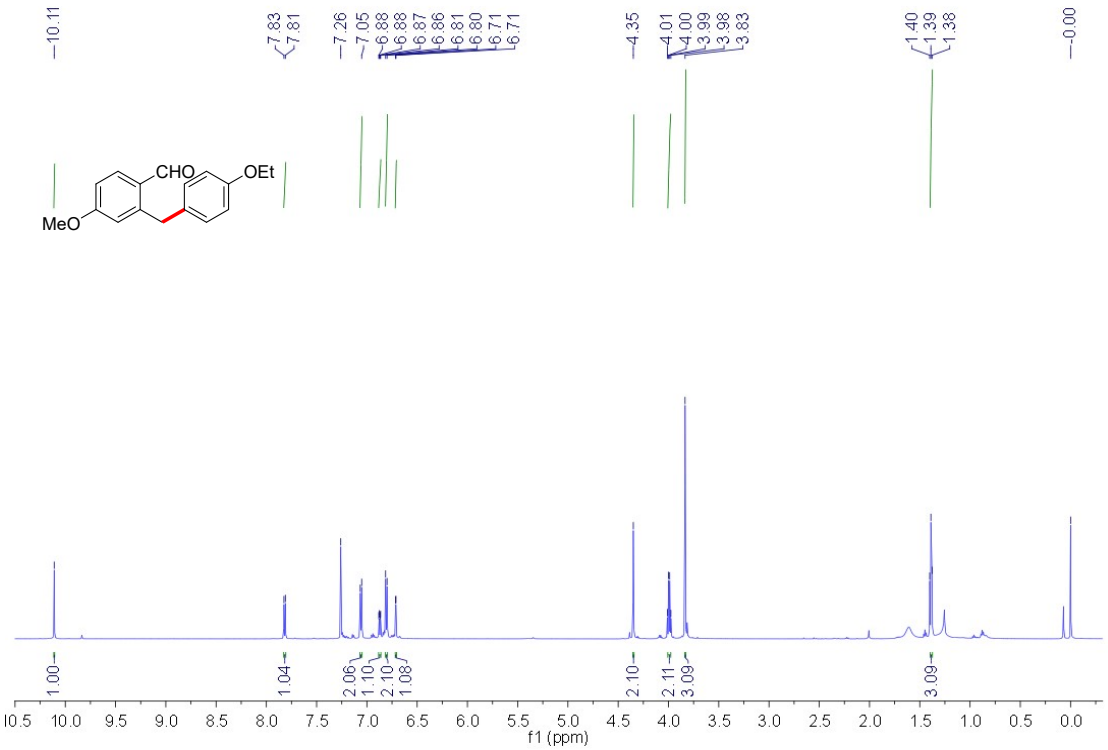
^{13}C NMR of 2-(4-ethoxybenzyl)-4,6-dimethylbenzaldehyde **3fa**



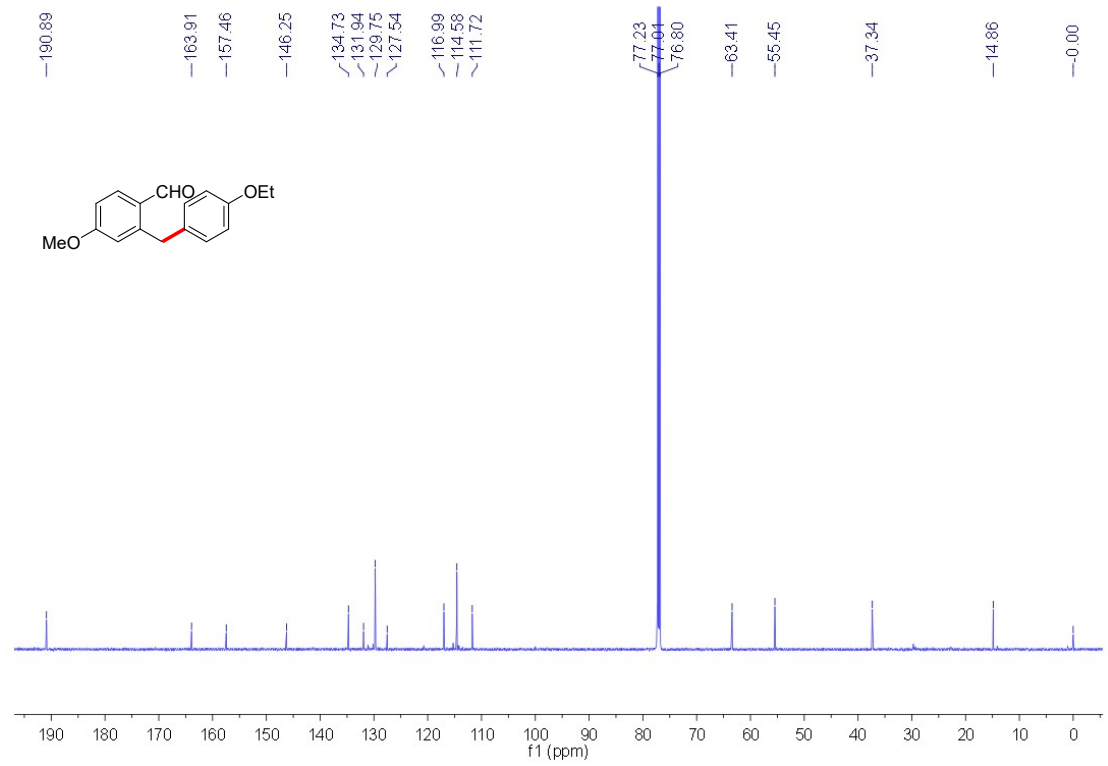
MS(EI) of 2-(4-ethoxybenzyl)-4,6-dimethylbenzaldehyde **3fa**



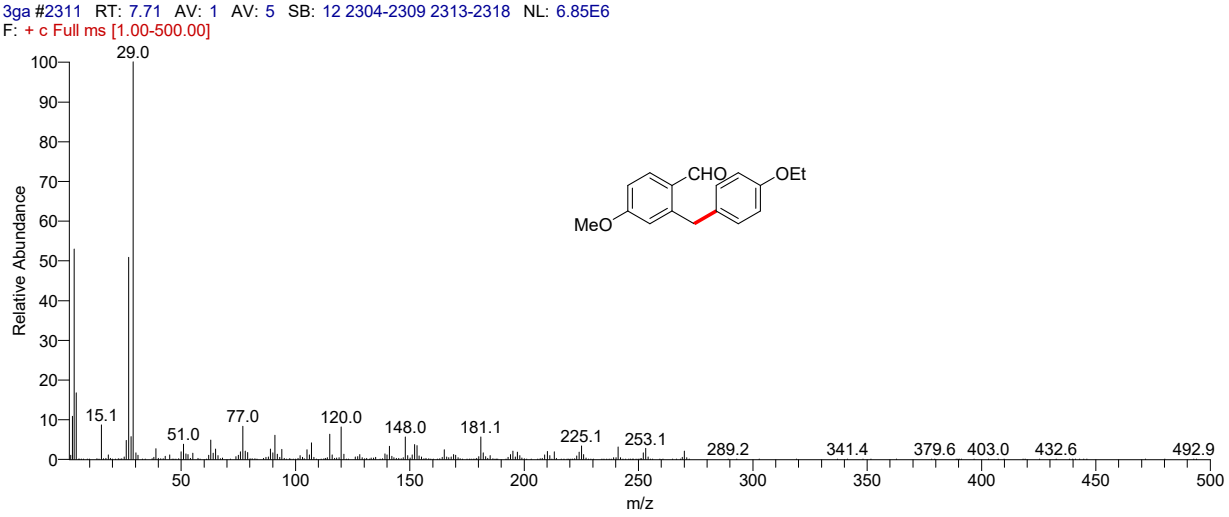
^{1}H NMR of 2-(4-ethoxybenzyl)-4-methoxybenzaldehyde **3ga**



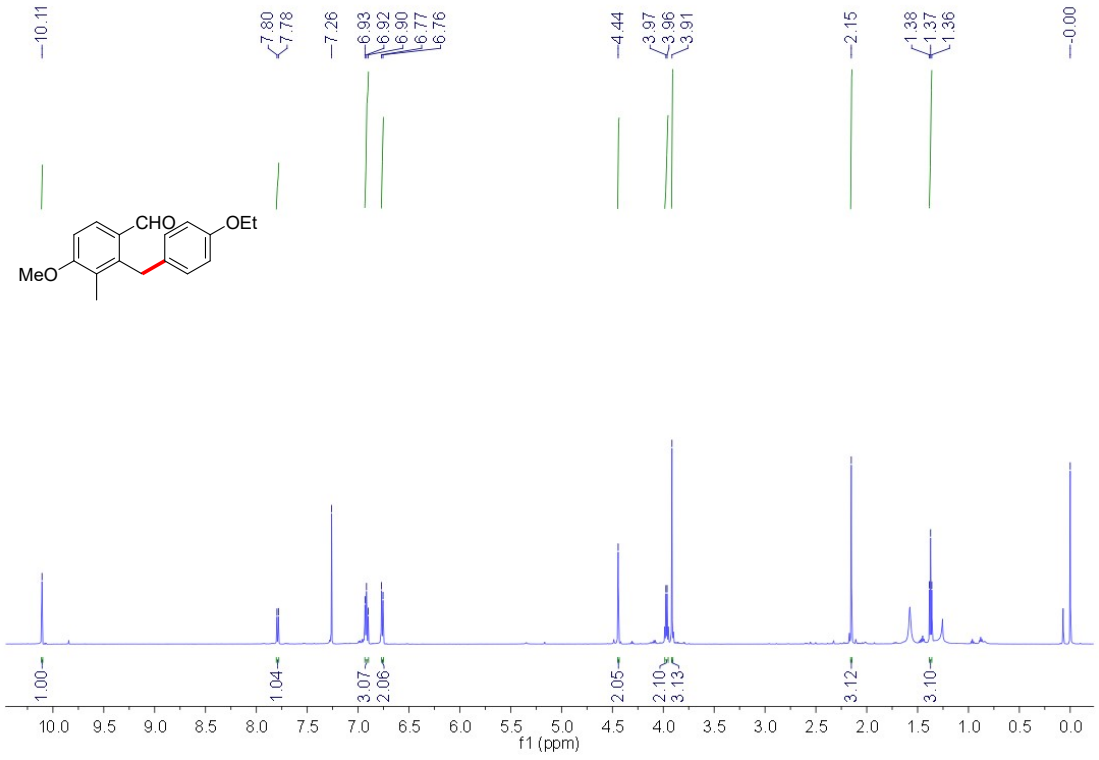
^{13}C NMR of 2-(4-ethoxybenzyl)-4-methoxybenzaldehyde **3ga**



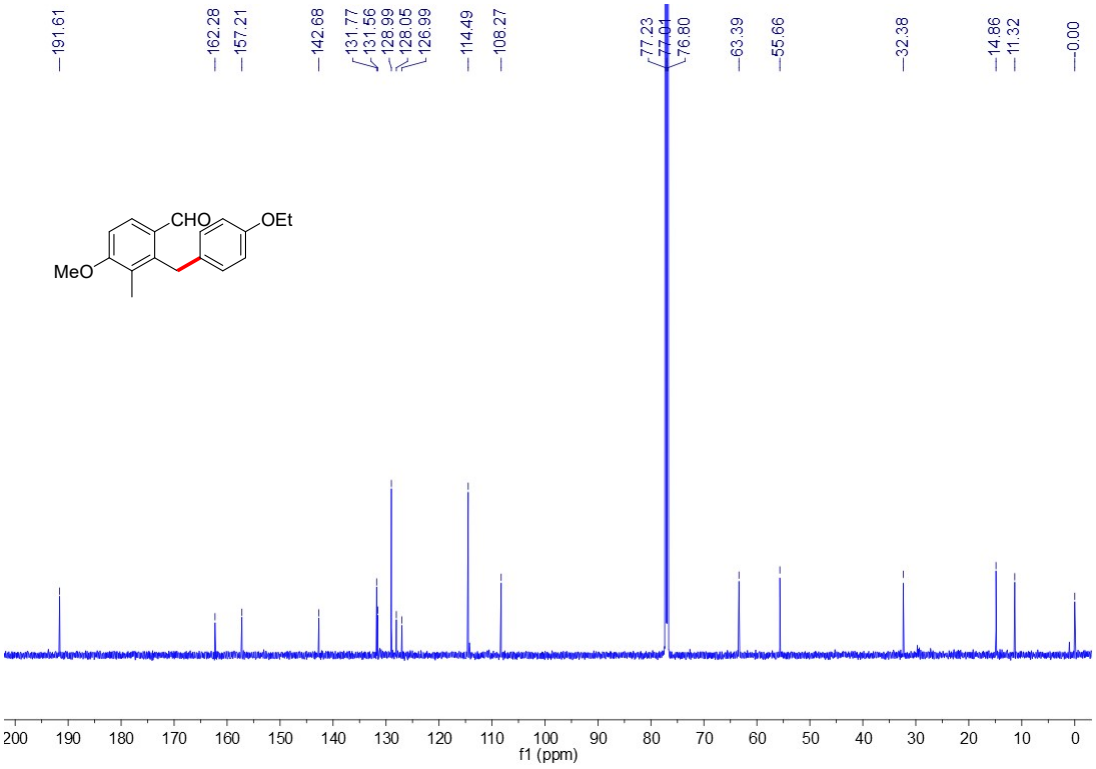
MS(EI) of 2-(4-ethoxybenzyl)-4-methoxybenzaldehyde **3ga**



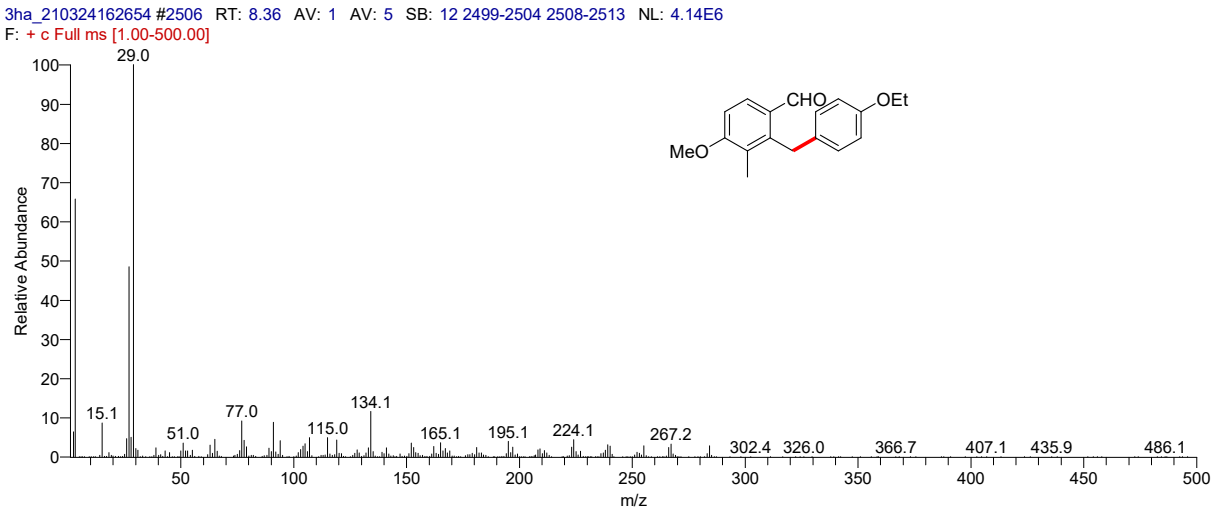
^{1}H NMR of 2-(4-ethoxybenzyl)-4-methoxy-3-methylbenzaldehyde **3ha**



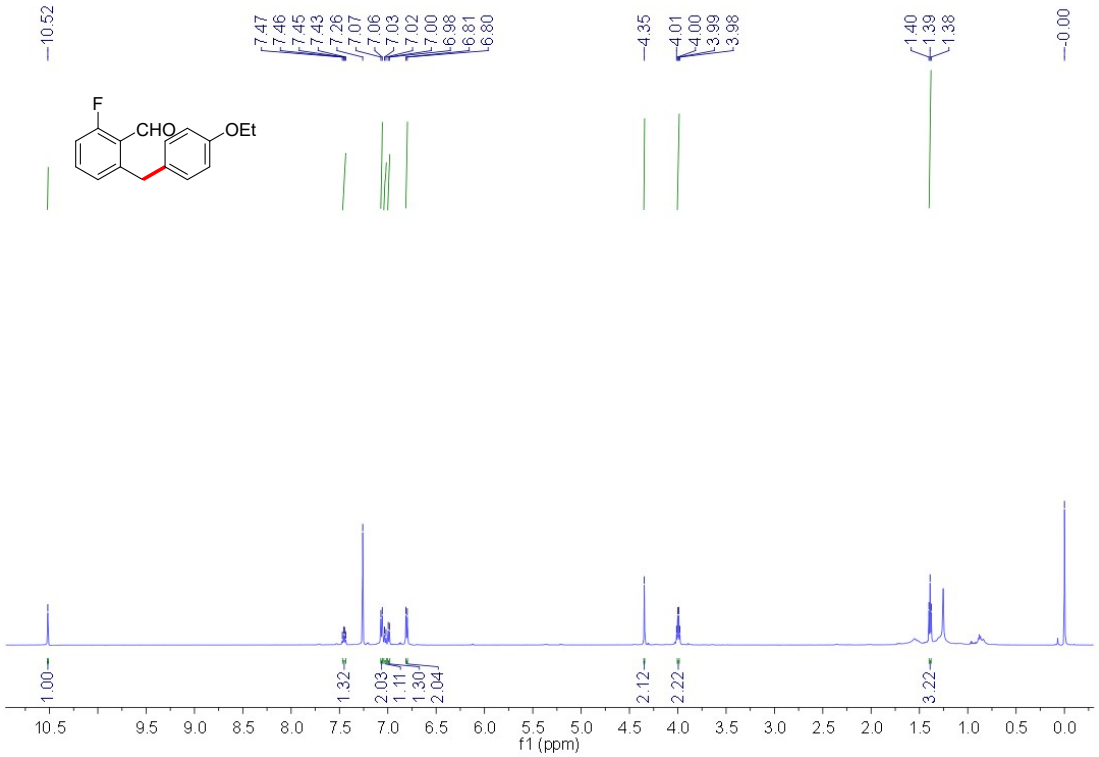
^{13}C NMR of 2-(4-ethoxybenzyl)-4-methoxy-3-methylbenzaldehyde **3ha**



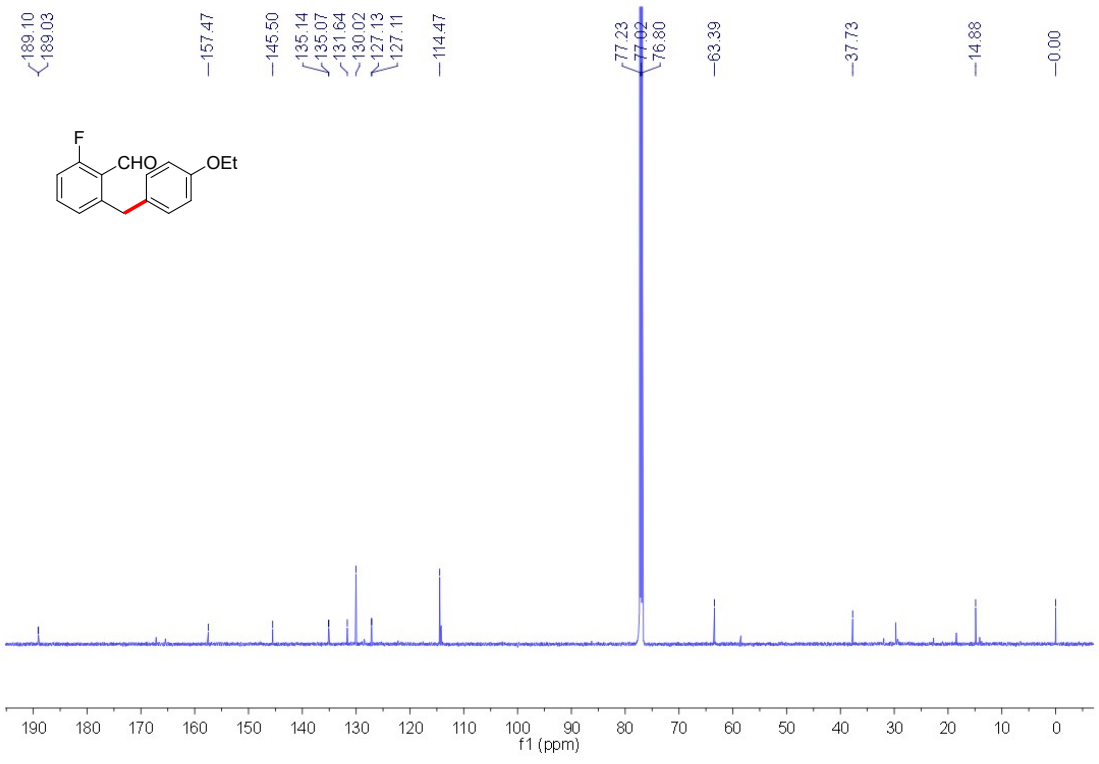
MS(EI) of 2-(4-ethoxybenzyl)-4-methoxy-3-methylbenzaldehyde **3ha**



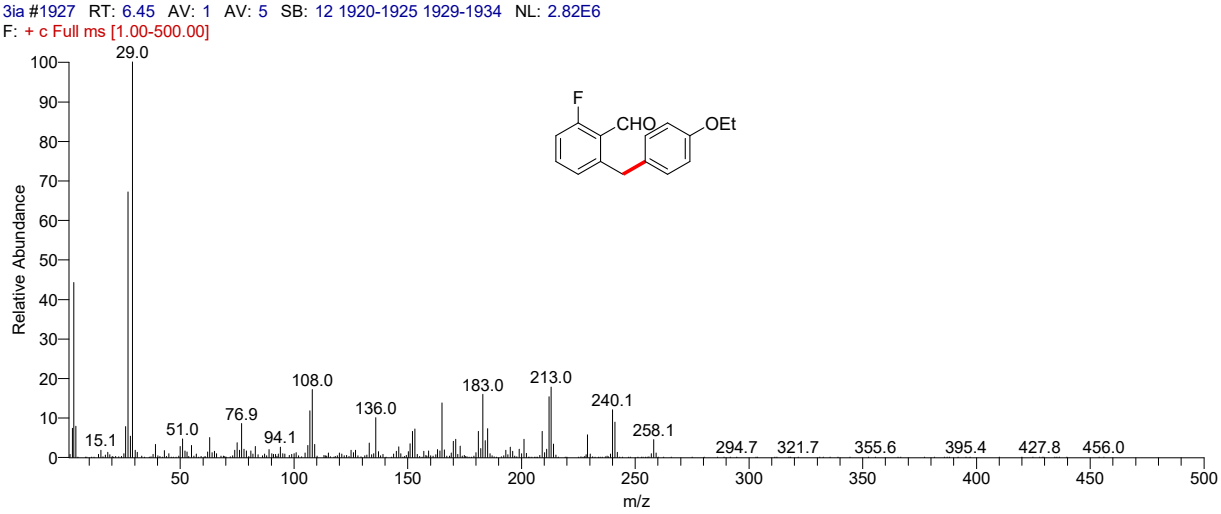
^{1}H NMR of 2-(4-ethoxybenzyl)-6-fluorobenzaldehyde **3ia**



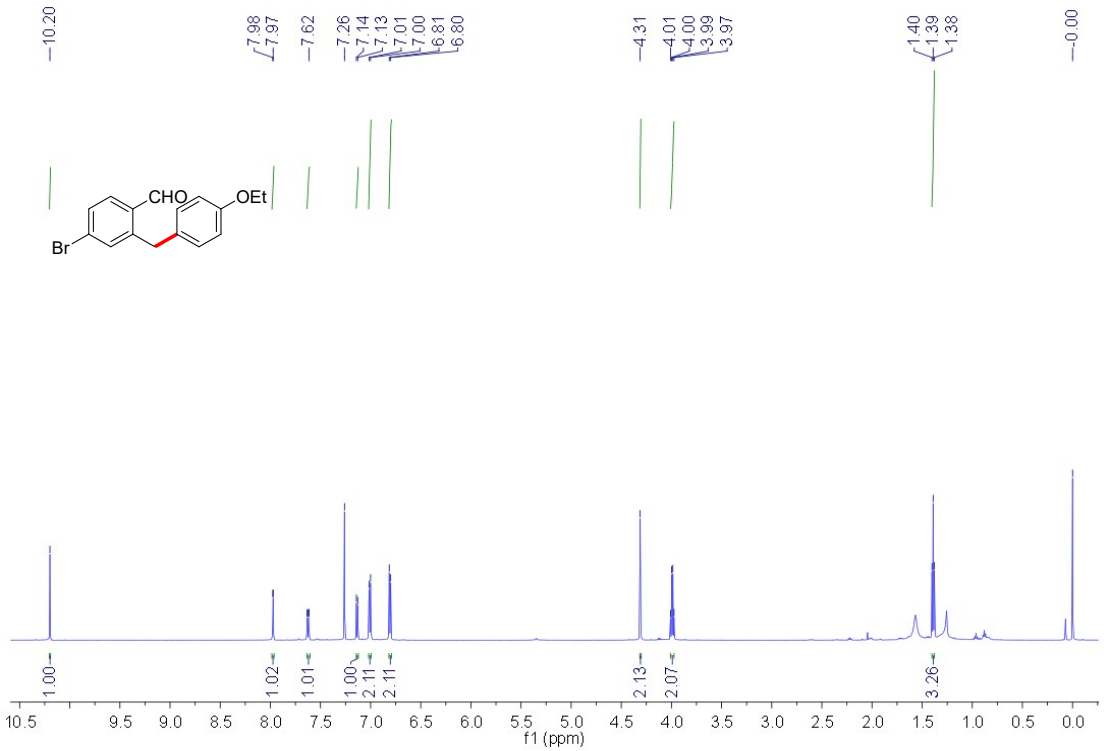
^{13}C NMR of 2-(4-ethoxybenzyl)-6-fluorobenzaldehyde **3ia**



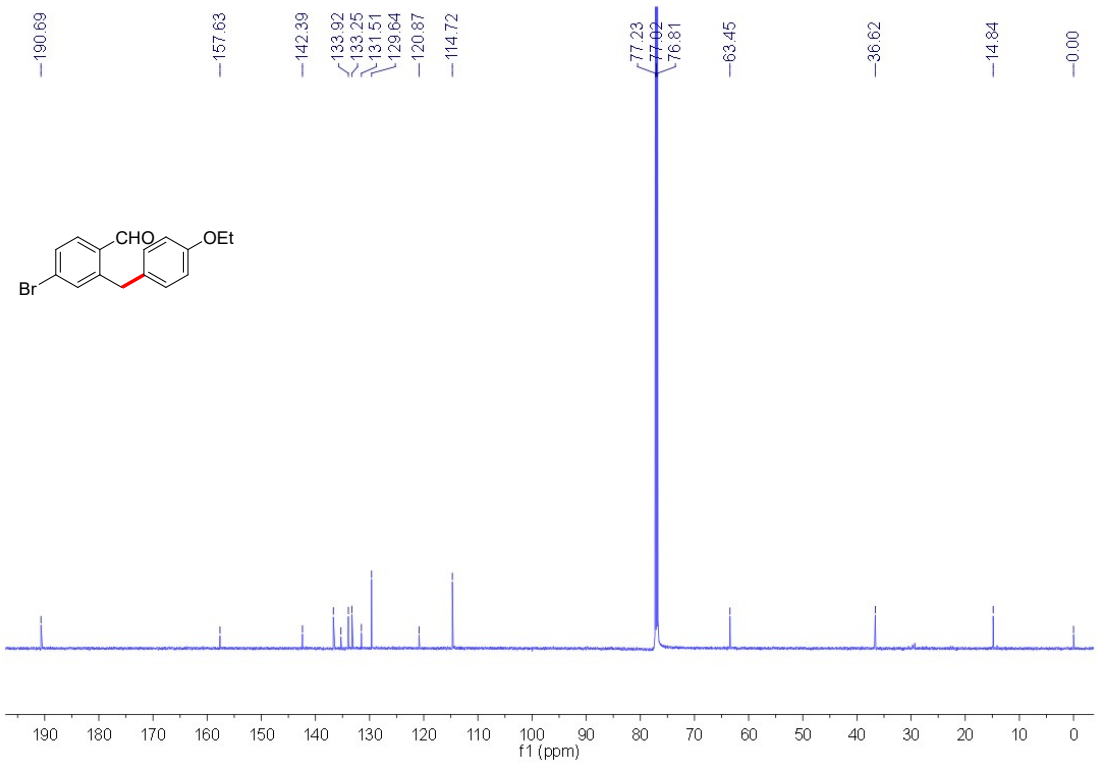
MS(EI) of 2-(4-ethoxybenzyl)-6-fluorobenzaldehyde **3ia**



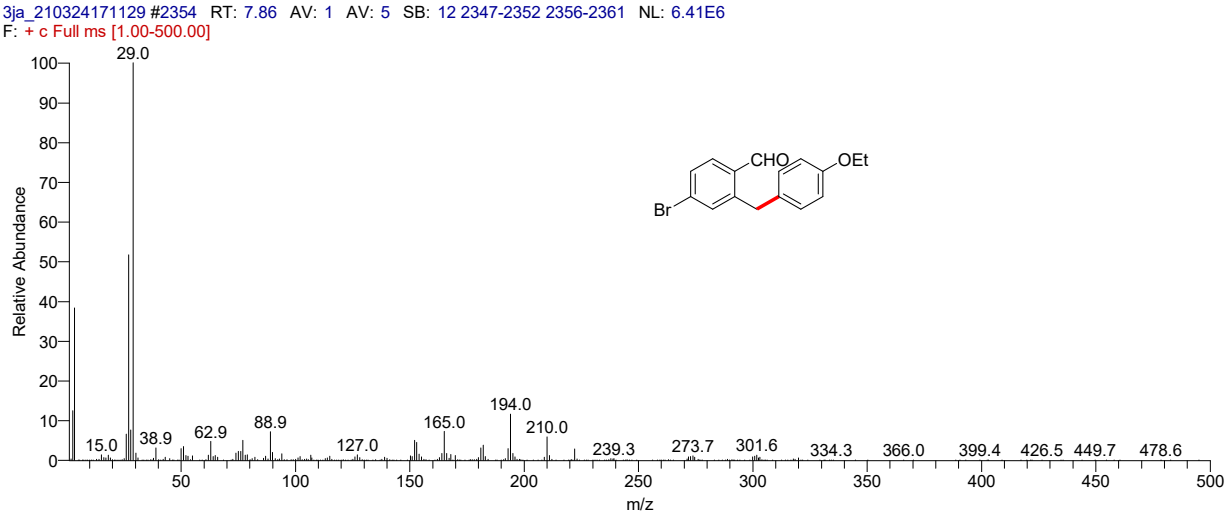
^{1}H NMR of 4-bromo-2-(4-ethoxybenzyl)-benzaldehyde **3ja**



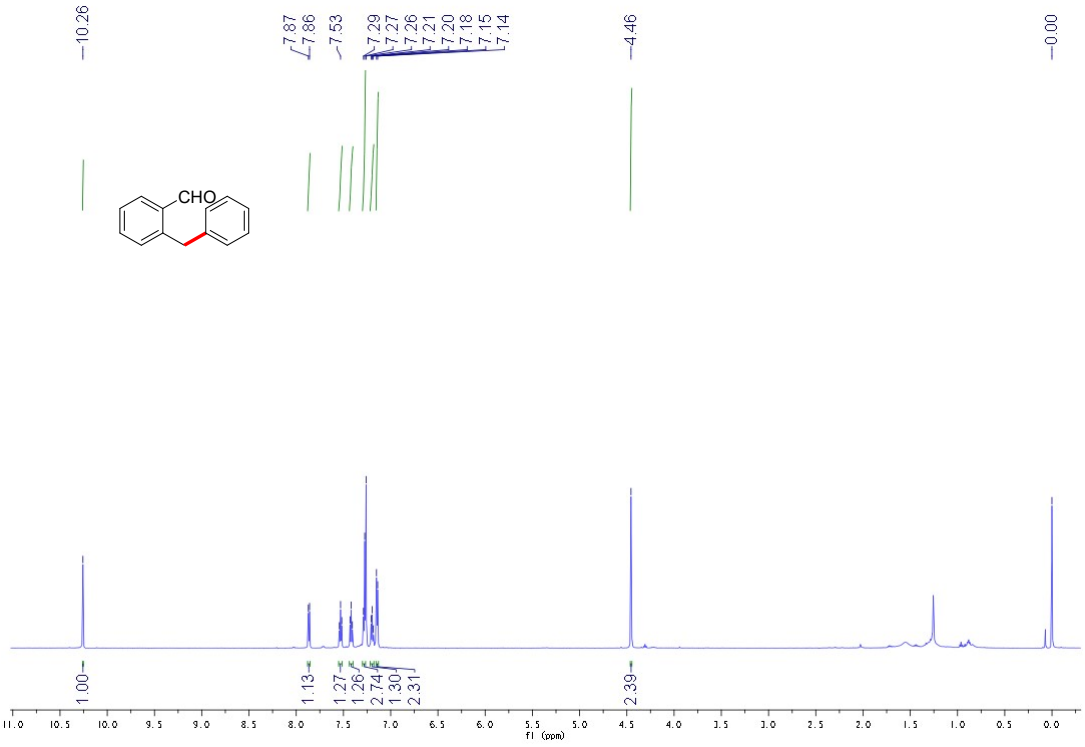
^{13}C NMR of 4-bromo-2-(4-ethoxybenzyl)-benzaldehyde **3ja**



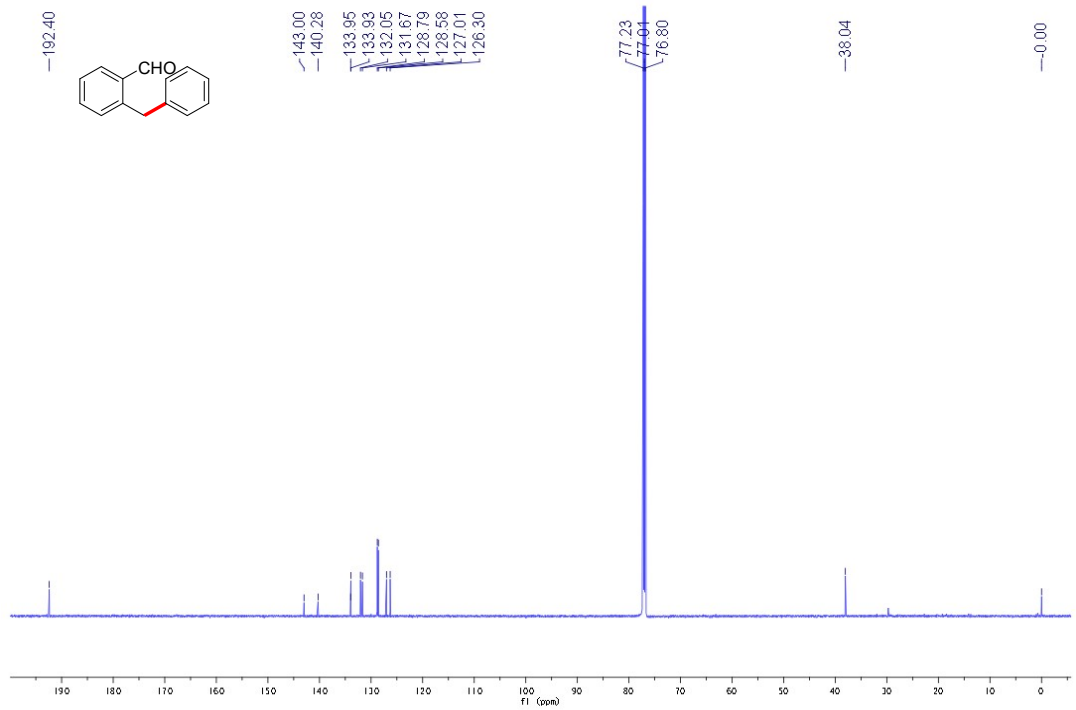
MS(EI) of 4-bromo-2-(4-ethoxybenzyl)-benzaldehyde **3ja**



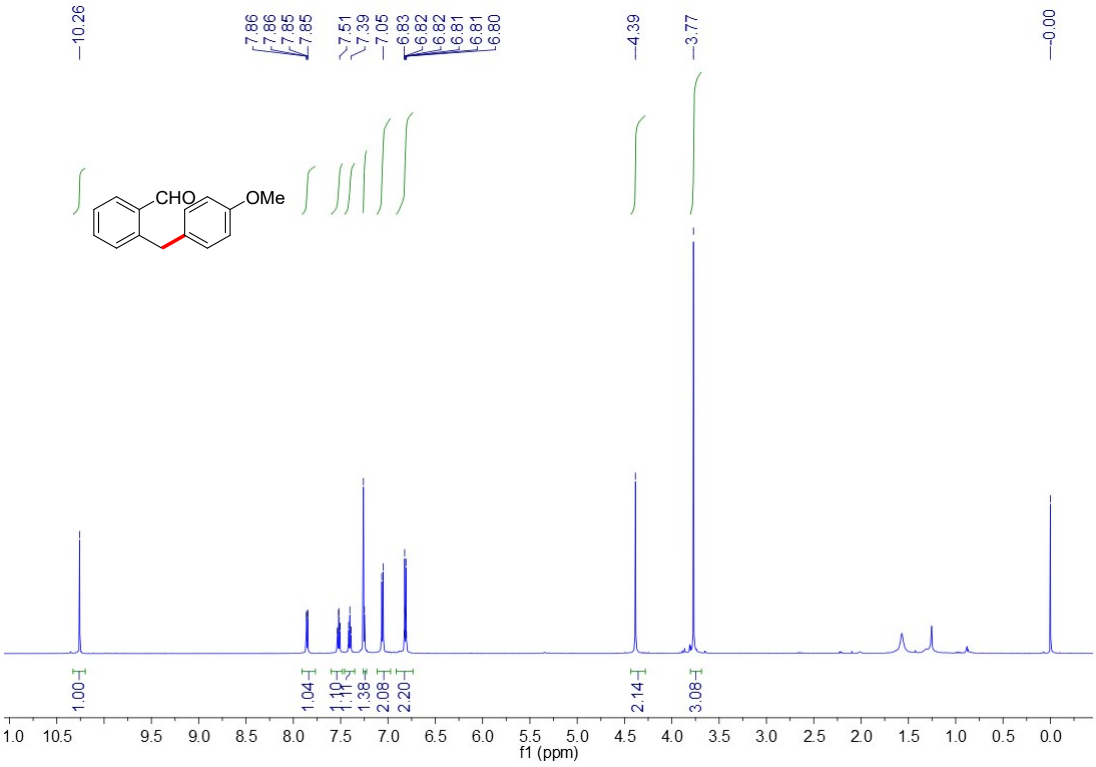
^{1}H NMR of 2-benzylbenzaldehyde **3ab**



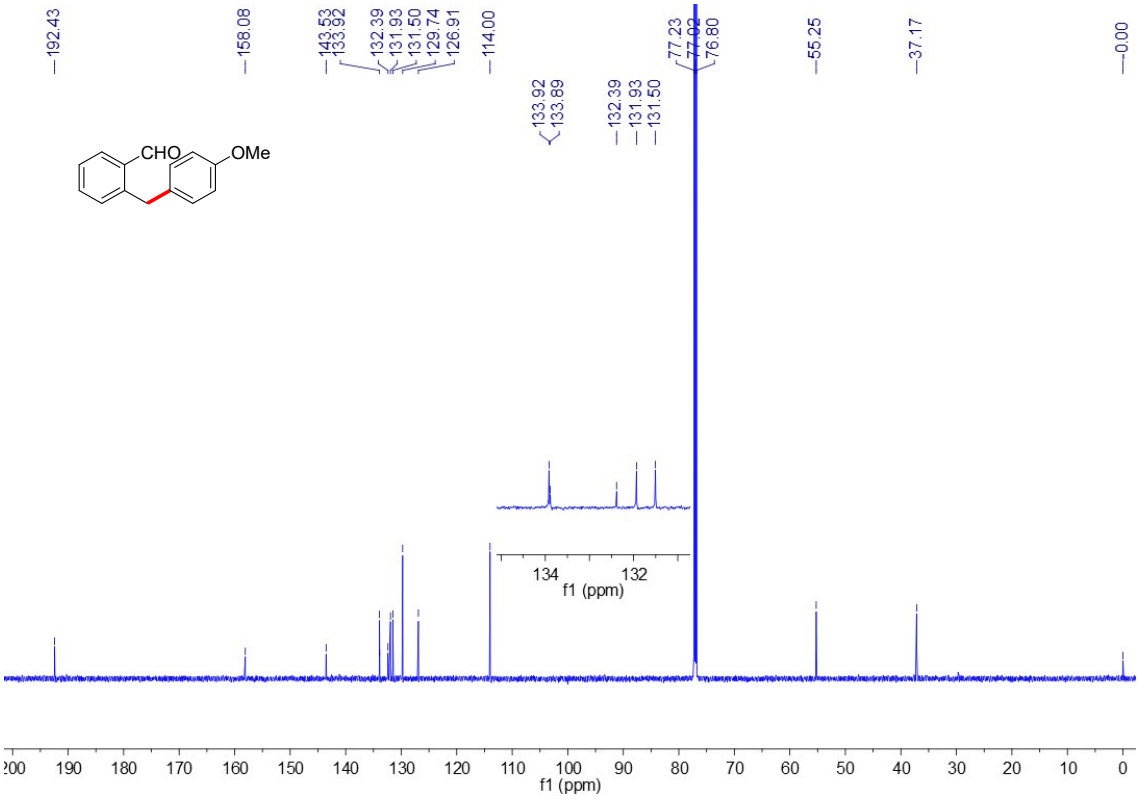
^{13}C NMR of 2-benzylbenzaldehyde **3ab**



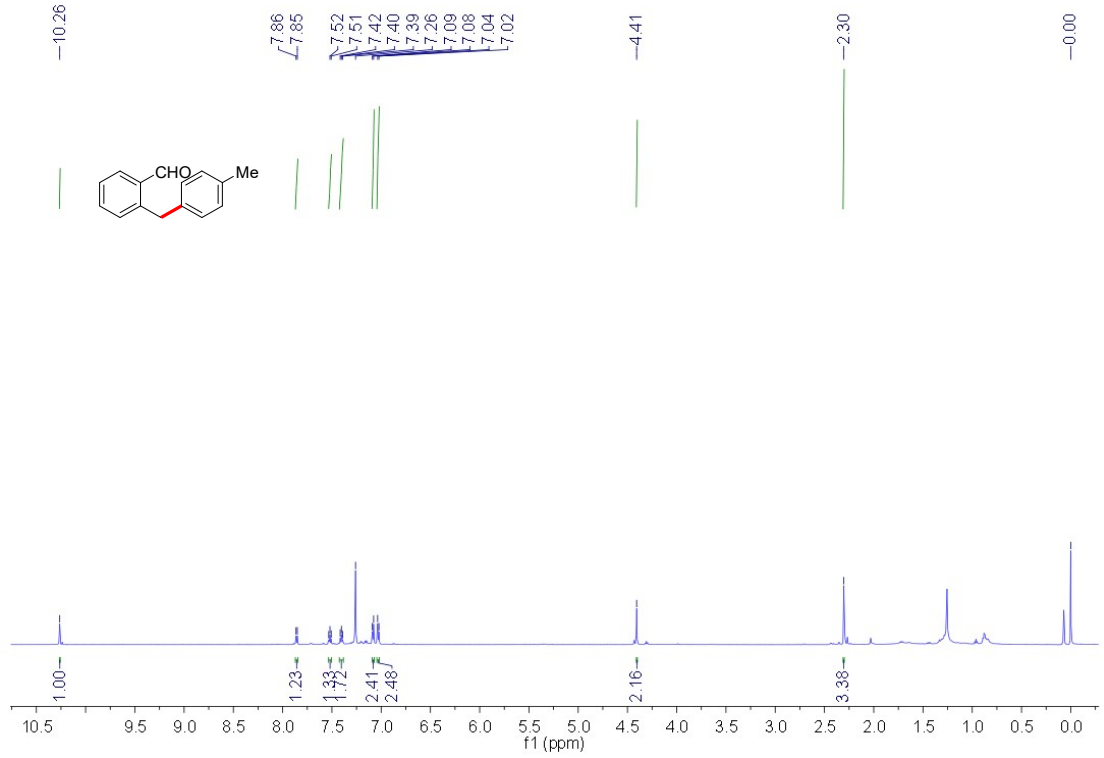
^{1}H NMR of 2-(4-methoxybenzyl)-benzaldehyde **3ac**



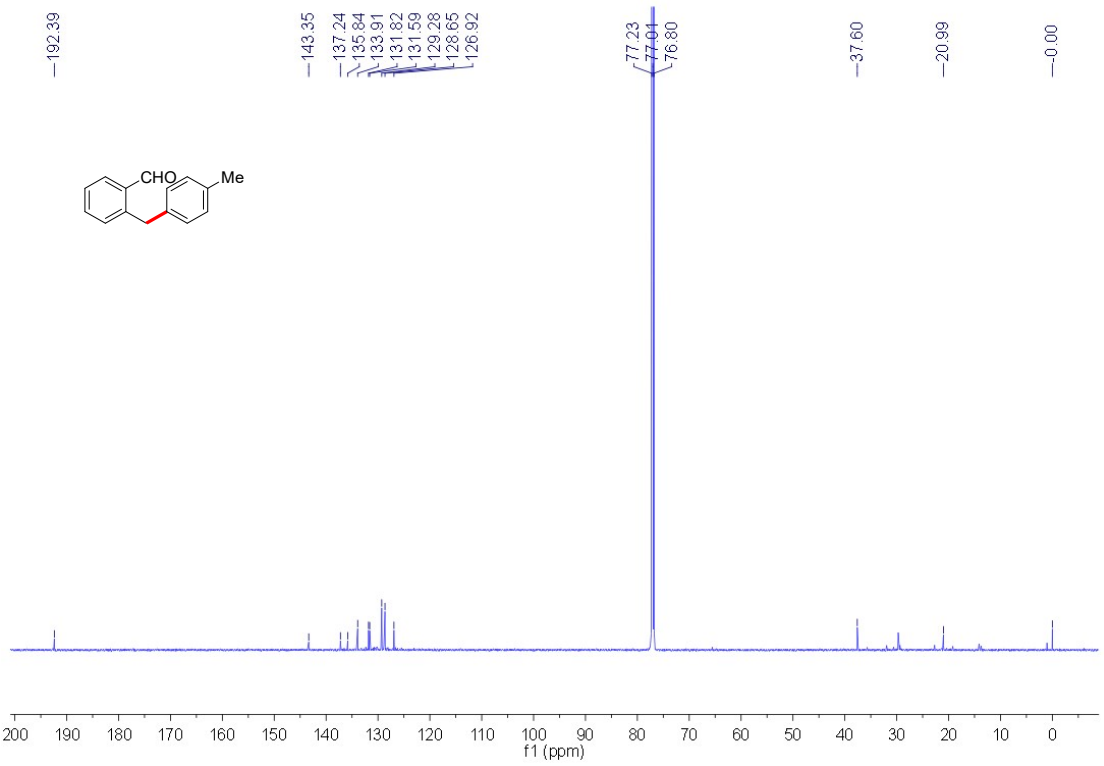
^{13}C NMR of 2-(4-methoxybenzyl)-benzaldehyde **3ac**



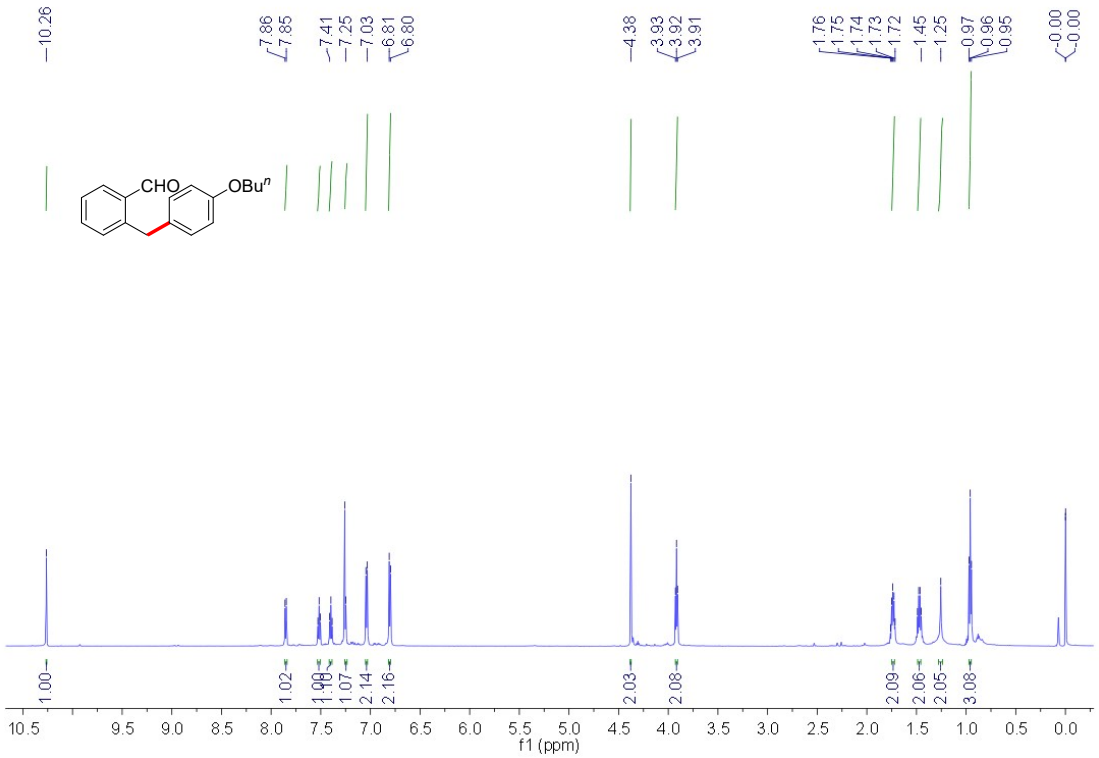
^{1}H NMR of 2-(4-methylbenzyl)-benzaldehyde **3ad**



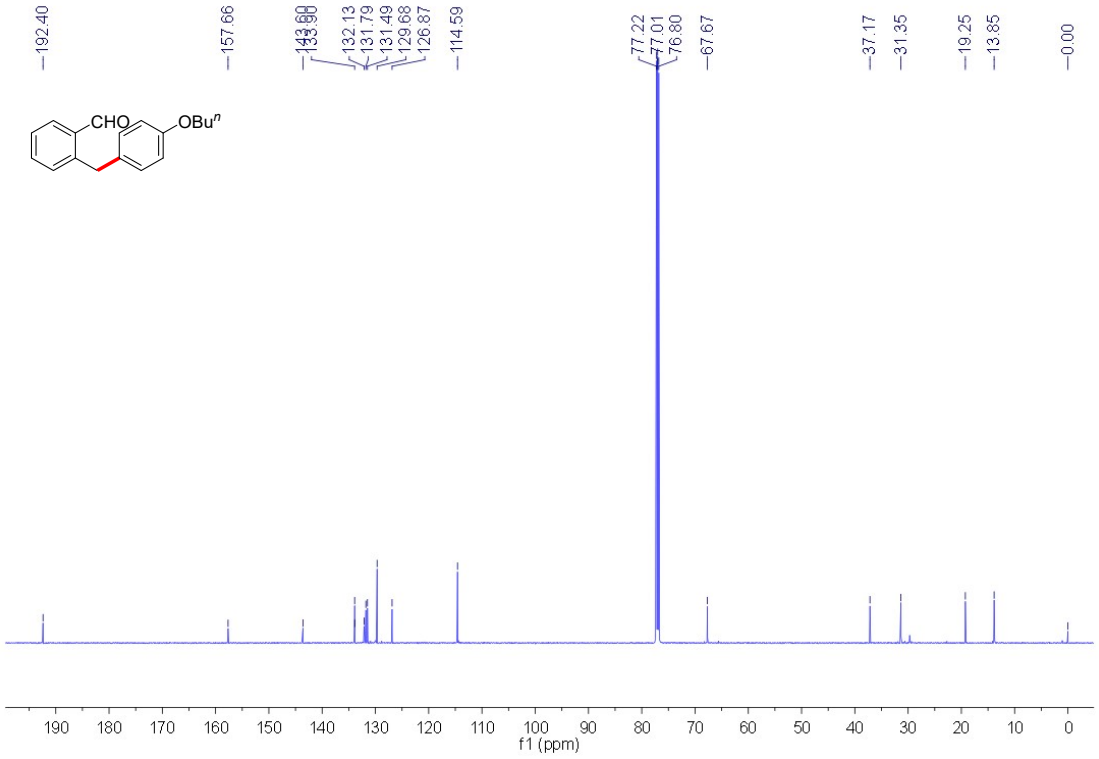
^{13}C NMR of 2-(4-methylbenzyl)-benzaldehyde **3ad**



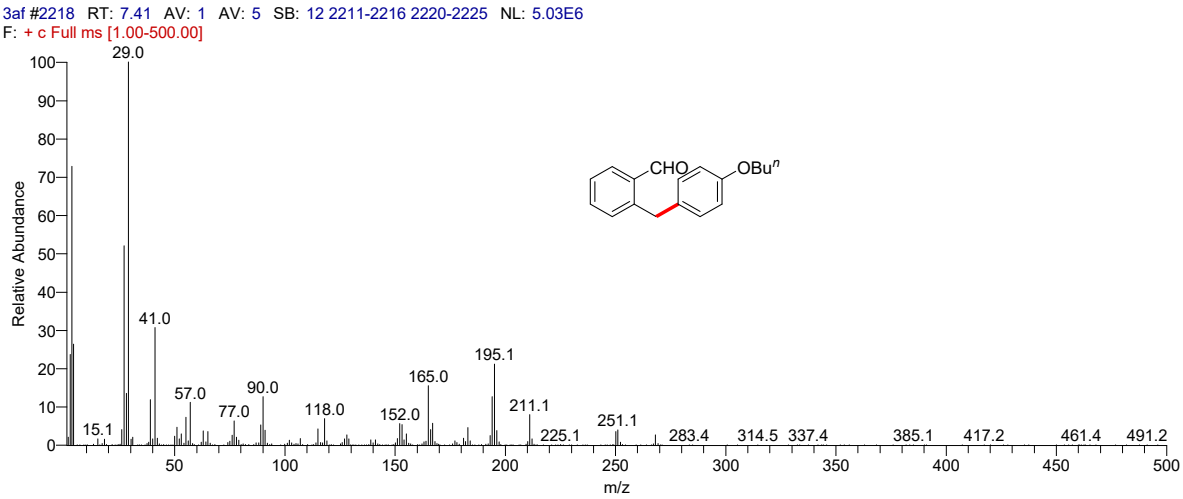
^{1}H NMR of 2-(4-butoxybenzyl)-benzaldehyde **3ae**



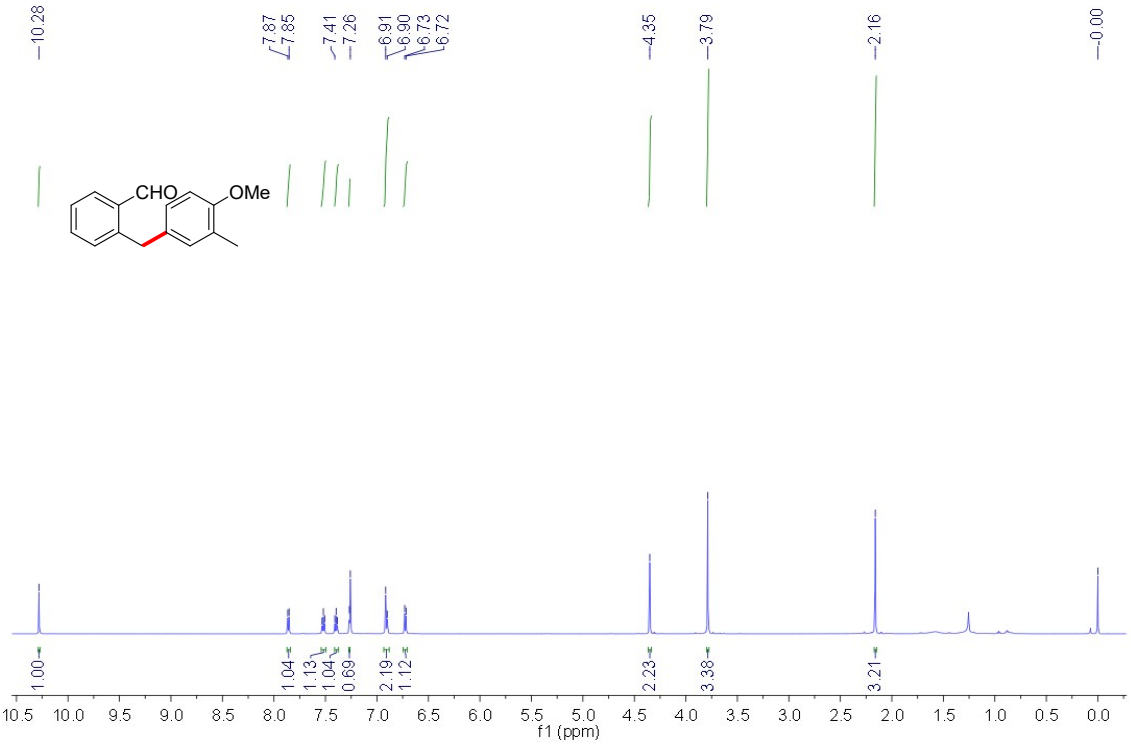
^{13}C NMR of 2-(4-butoxybenzyl)-benzaldehyde **3ae**



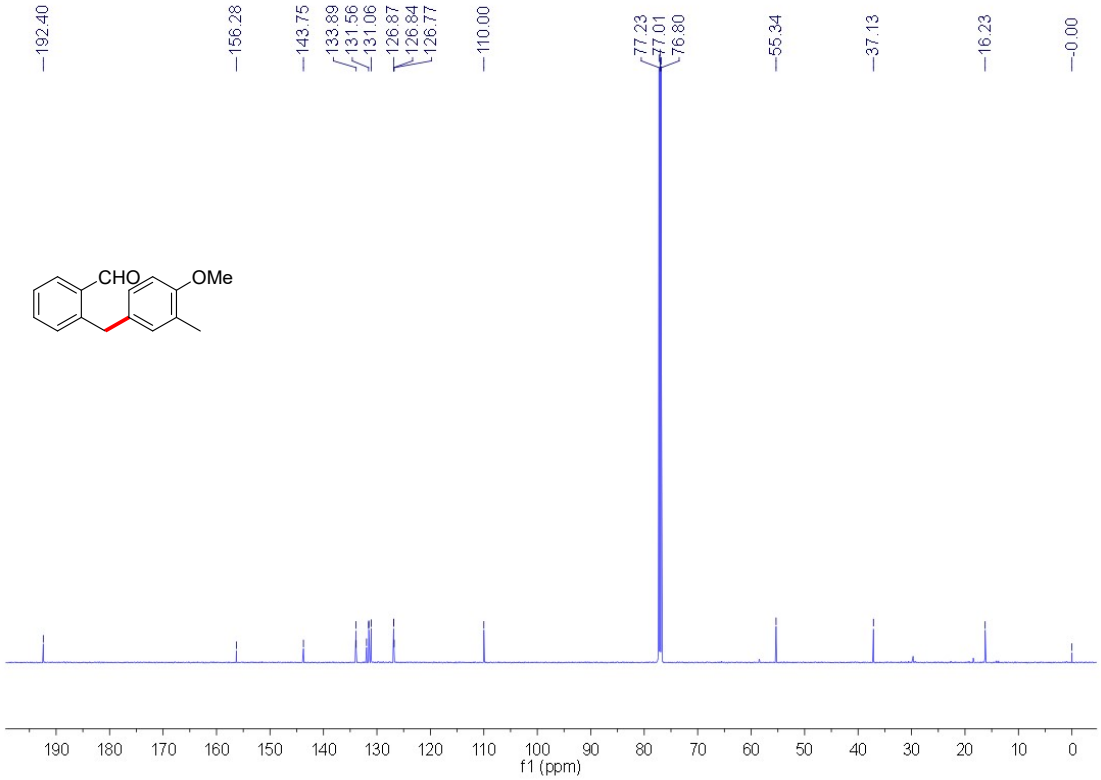
MS(EI) of 2-(4-butoxybenzyl)-benzaldehyde **3ae**



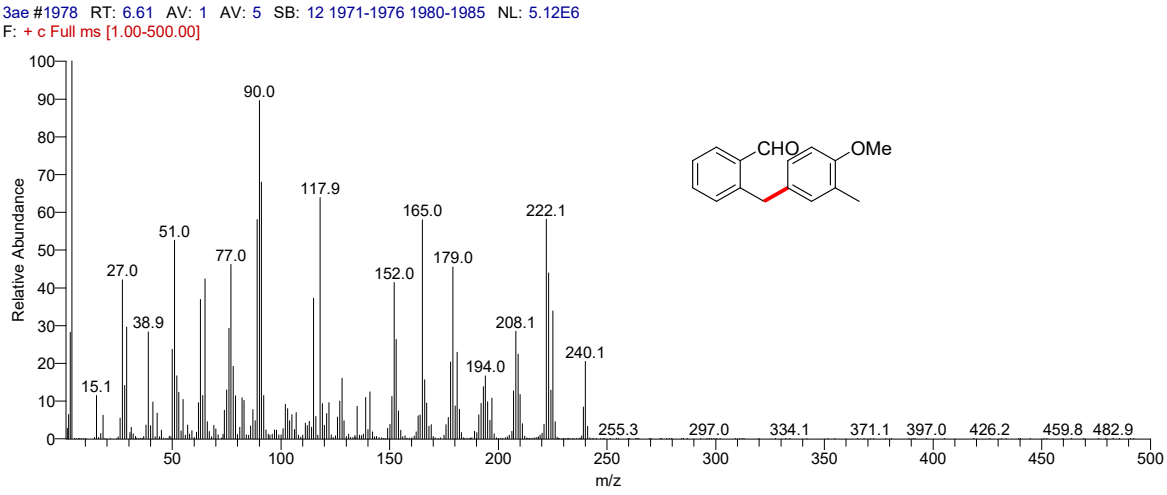
^{1}H NMR of 2-(4-methoxy-3-methylbenzyl)-benzaldehyde **3af**



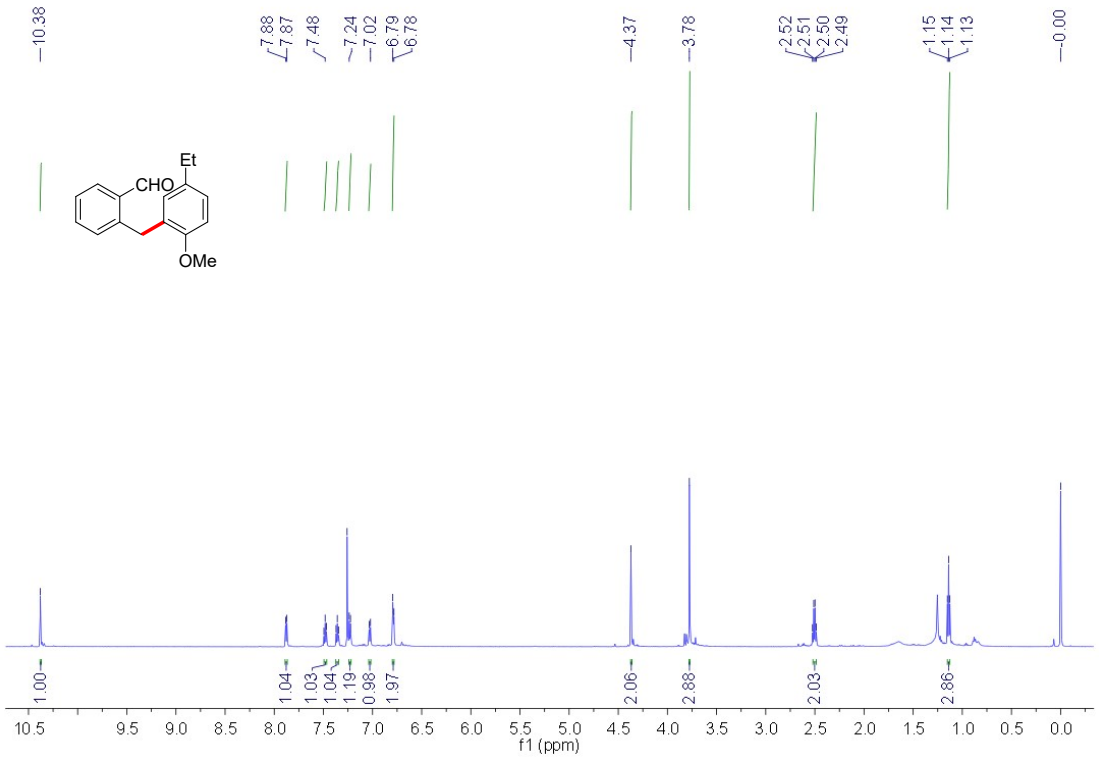
^{13}C NMR of 2-(4-methoxy-3-methylbenzyl)-benzaldehyde **3af**



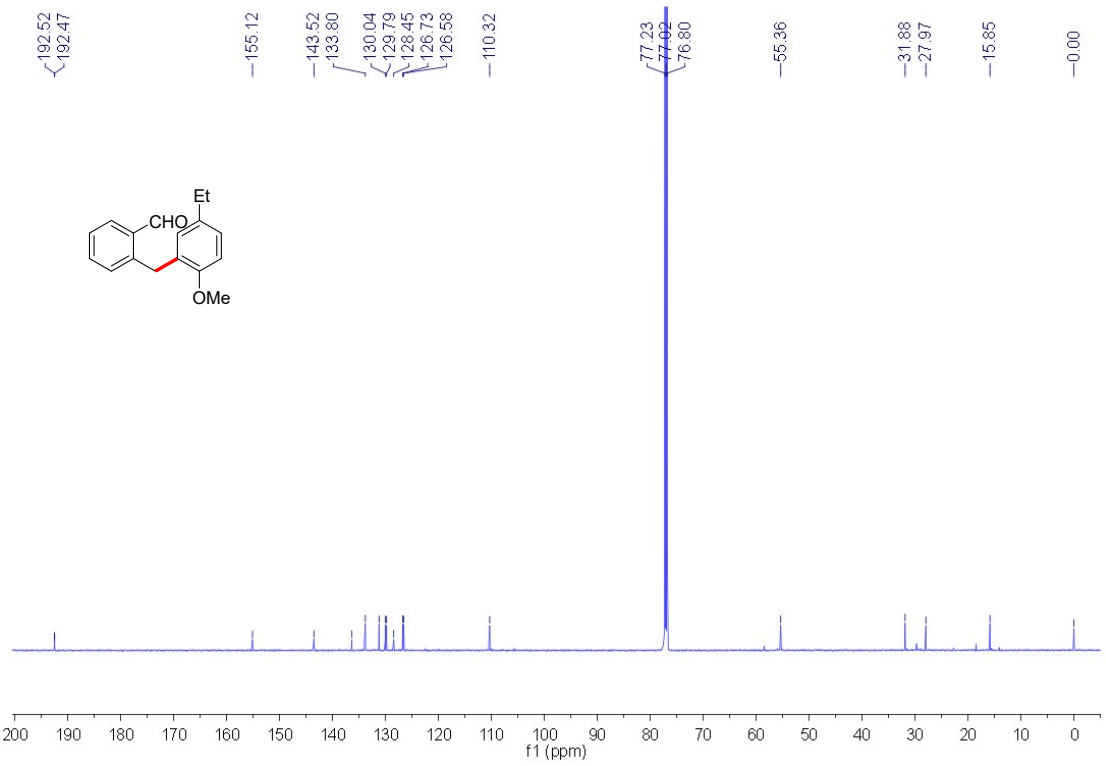
MS(EI) of 2-(4-methoxy-3-methylbenzyl)-benzaldehyde **3af**



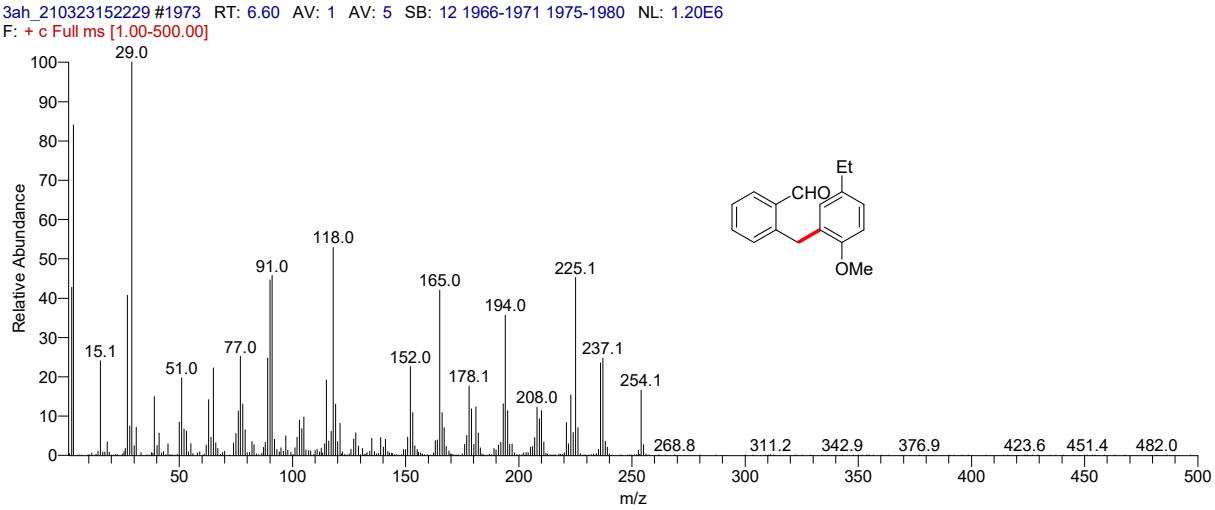
^{1}H NMR of 2-(5-ethyl-2-methoxybenzyl)-benzaldehyde **3ag**



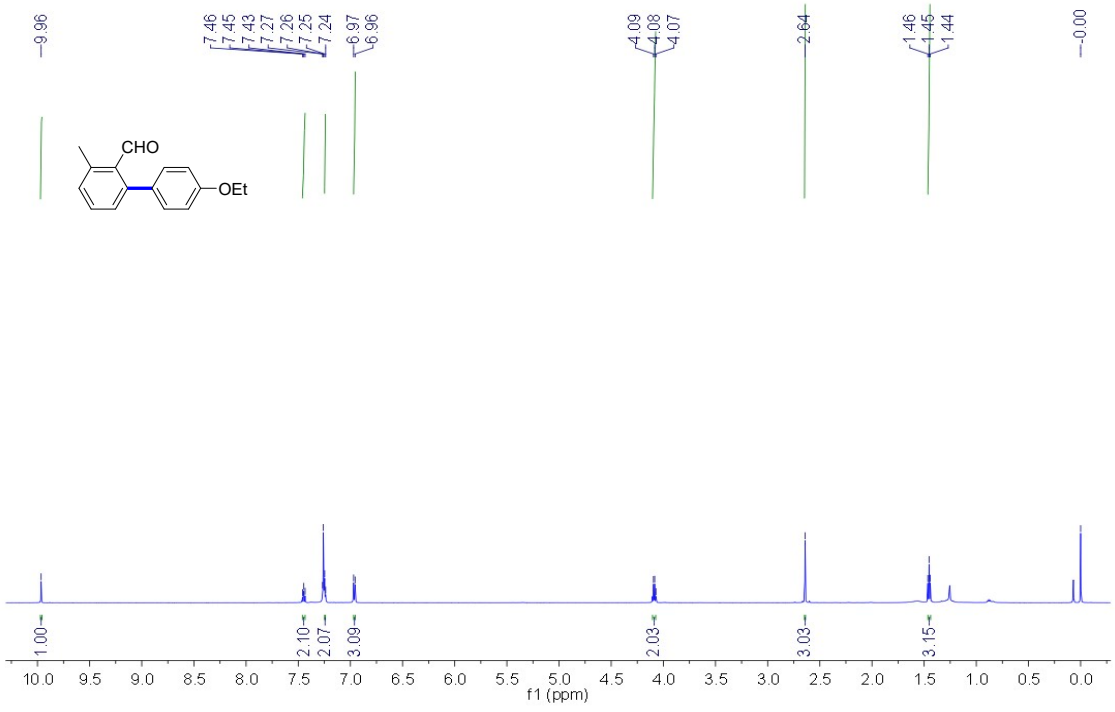
^{13}C NMR of 2-(5-ethyl-2-methoxybenzyl)-benzaldehyde **3ag**



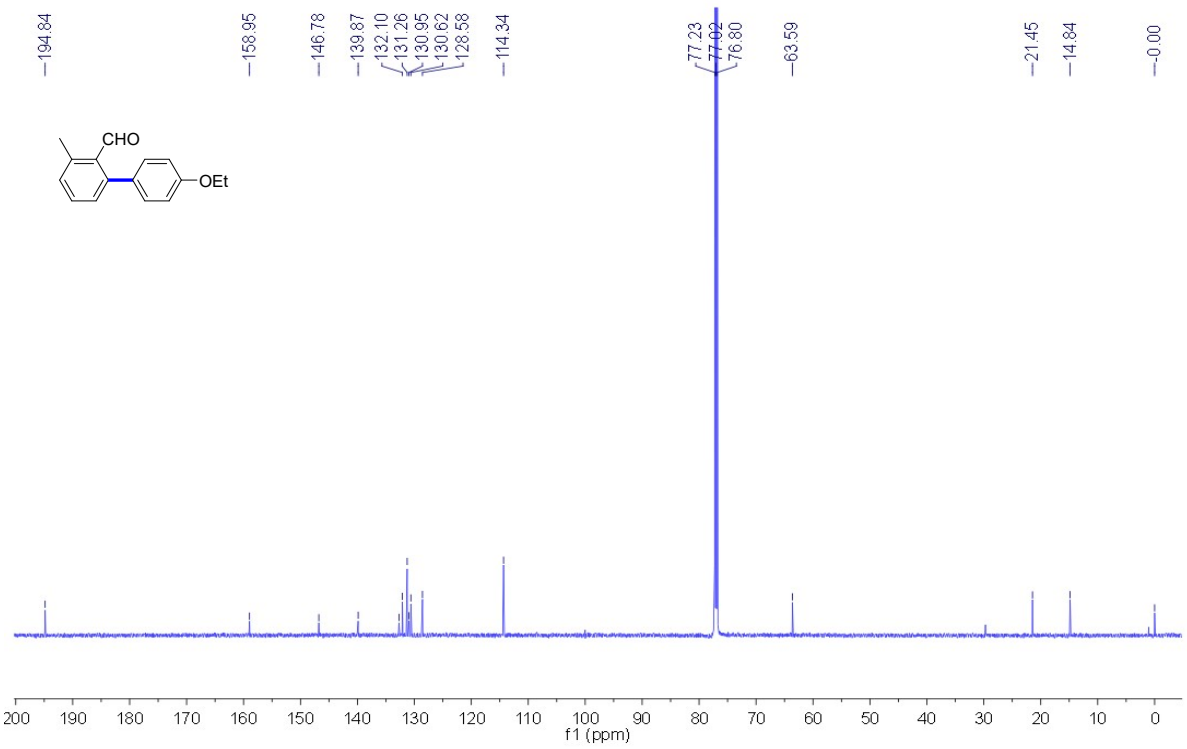
MS(EI) of 2-(5-ethyl-2-methoxybenzyl)-benzaldehyde **3ag**



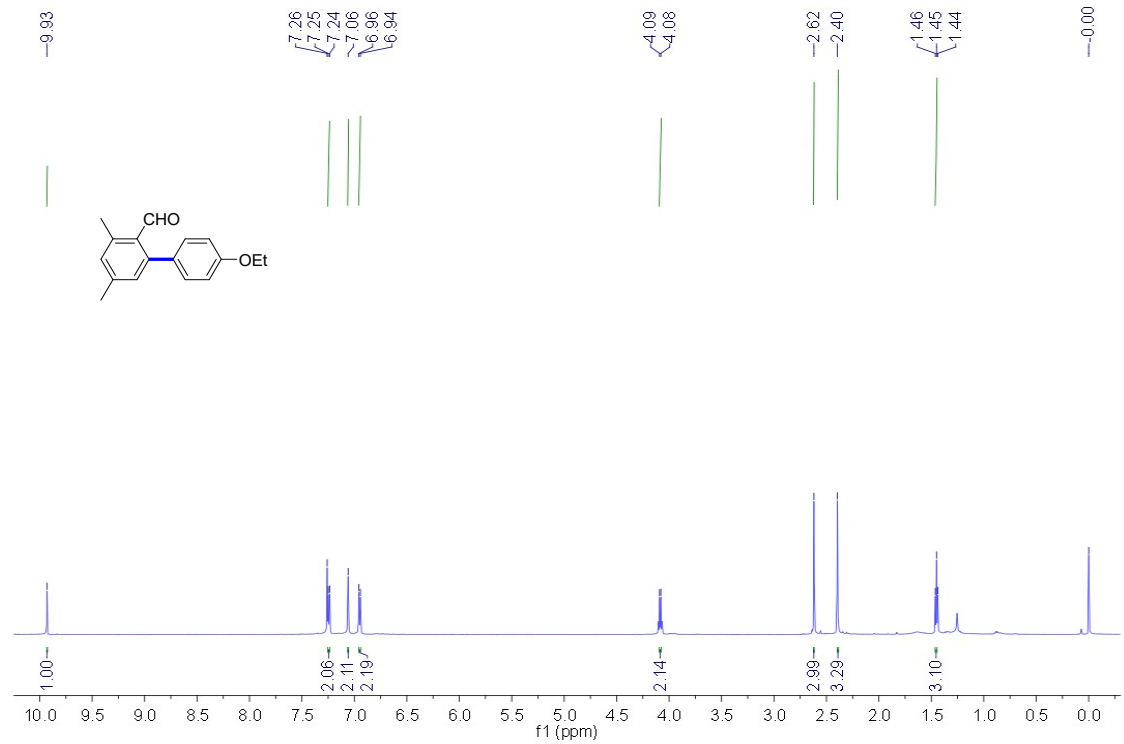
^{1}H NMR of 4'-ethoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4aa**



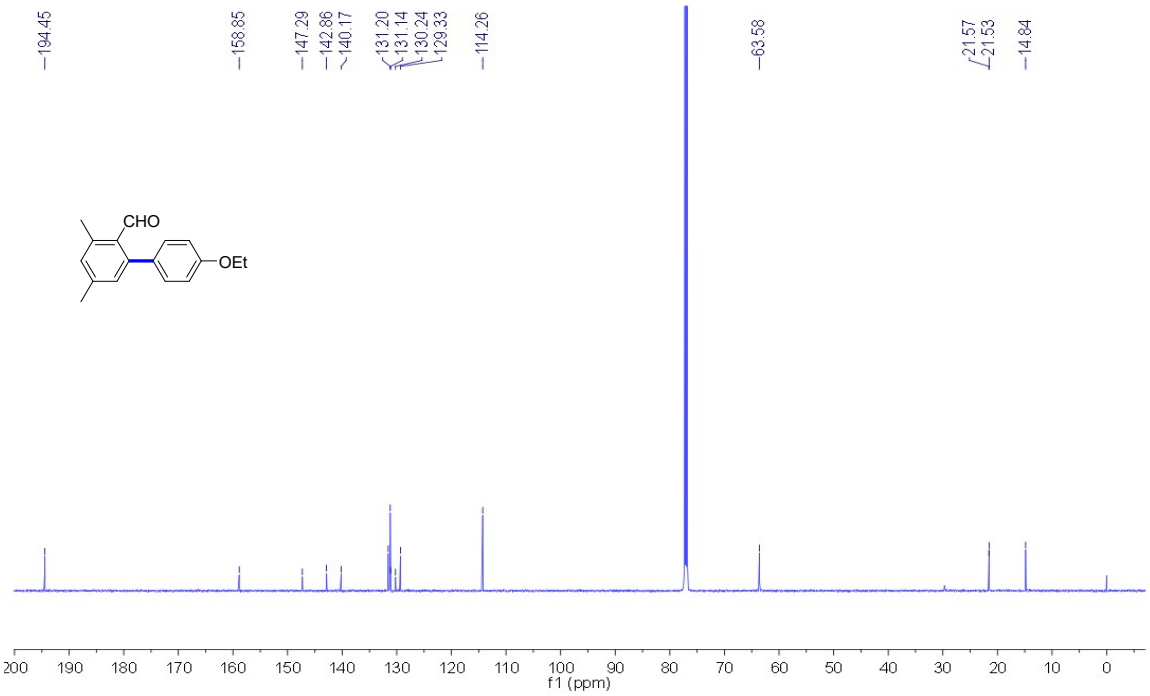
^{13}C NMR of 4'-ethoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4aa**



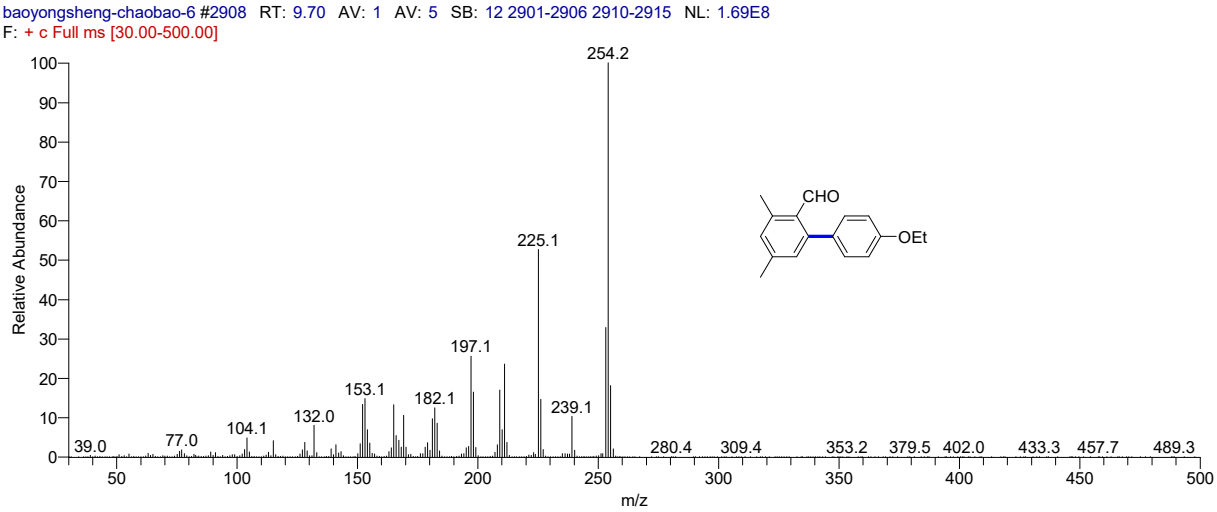
^{1}H NMR of 4'-ethoxy-3,5-dimethyl-[1,1'-biphenyl]-2-carbaldehyde **4ba**



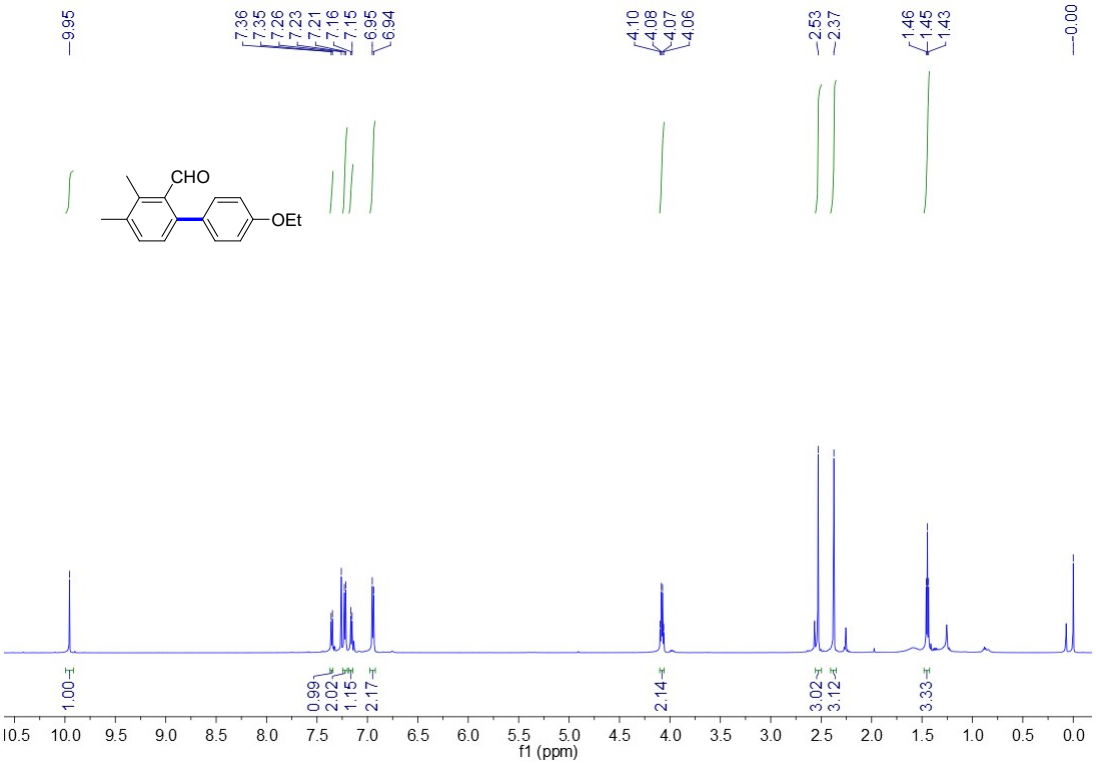
^{13}C NMR of 4'-ethoxy-3,5-dimethyl-[1,1'-biphenyl]-2-carbaldehyde **4ba**



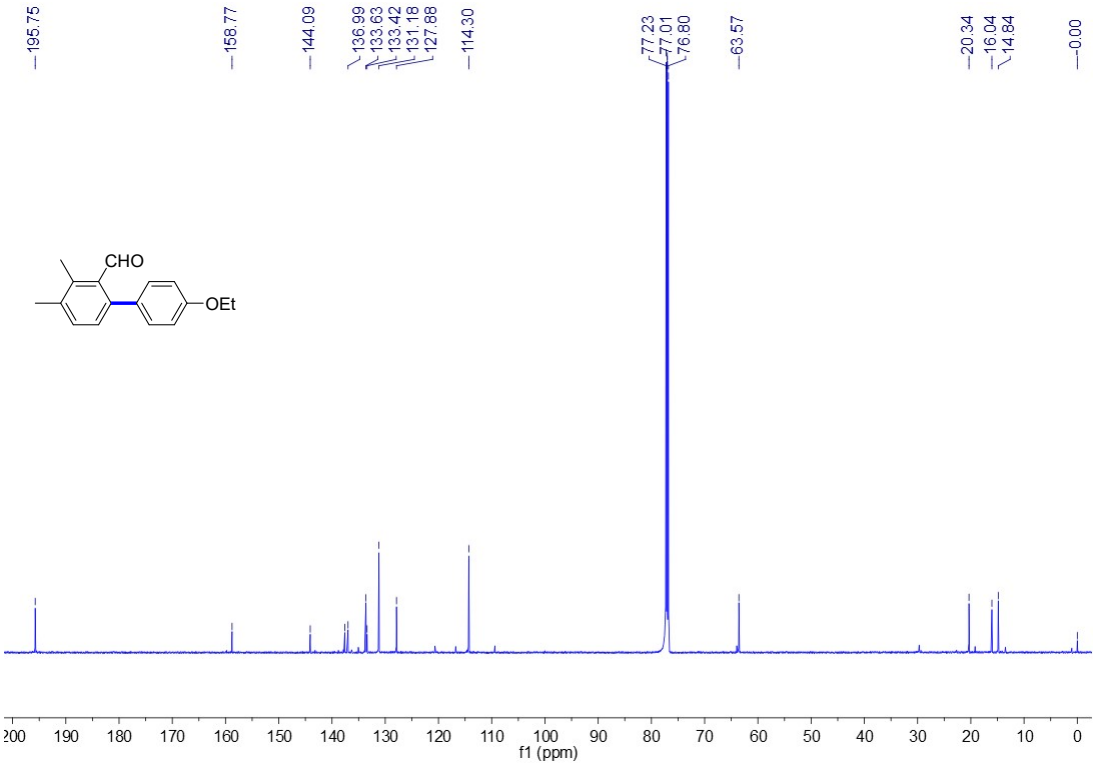
MS(EI) of 4'-ethoxy-3,5-dimethyl-[1,1'-biphenyl]-2-carbaldehyde **4ba**



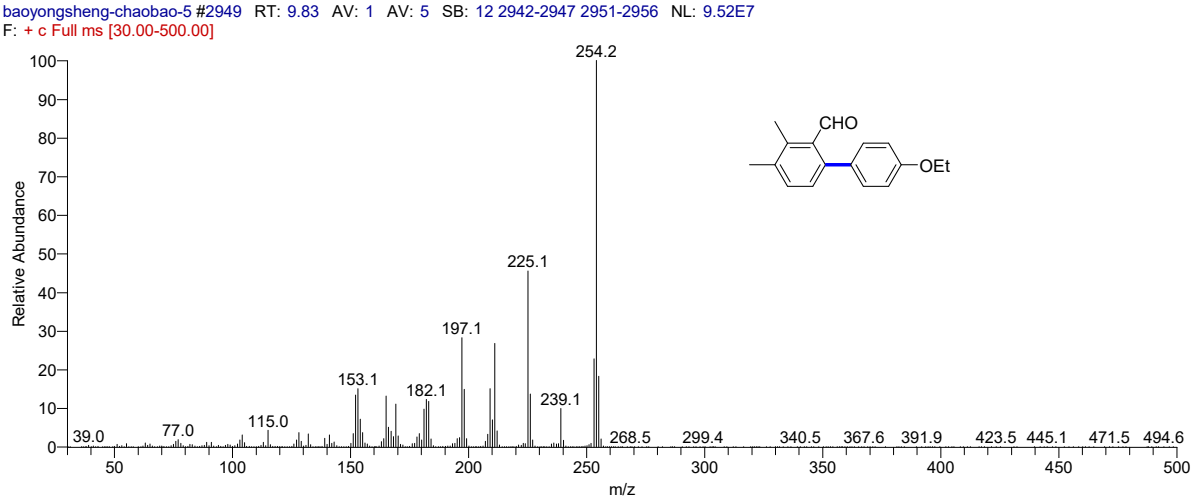
^{1}H NMR of 4'-ethoxy-3,4-dimethyl-[1,1'-biphenyl]-2-carbaldehyde **4ca**



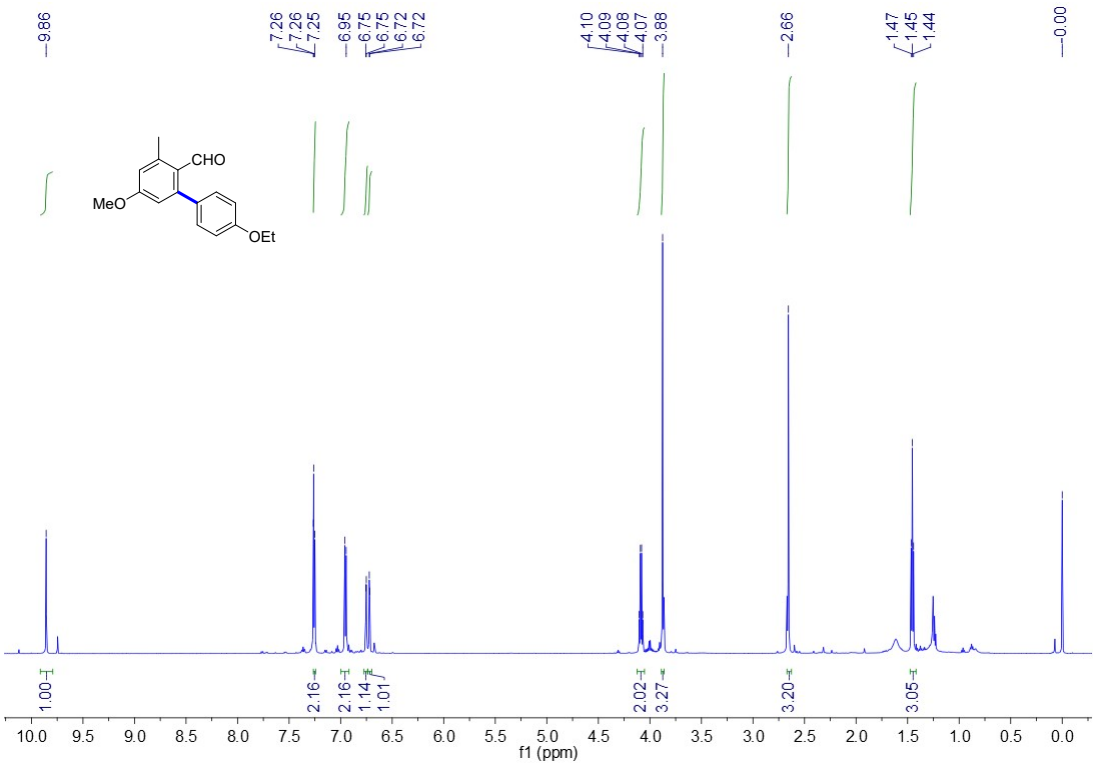
^{13}C NMR of 4'-ethoxy-3,4-dimethyl-[1,1'-biphenyl]-2-carbaldehyde **4ca**



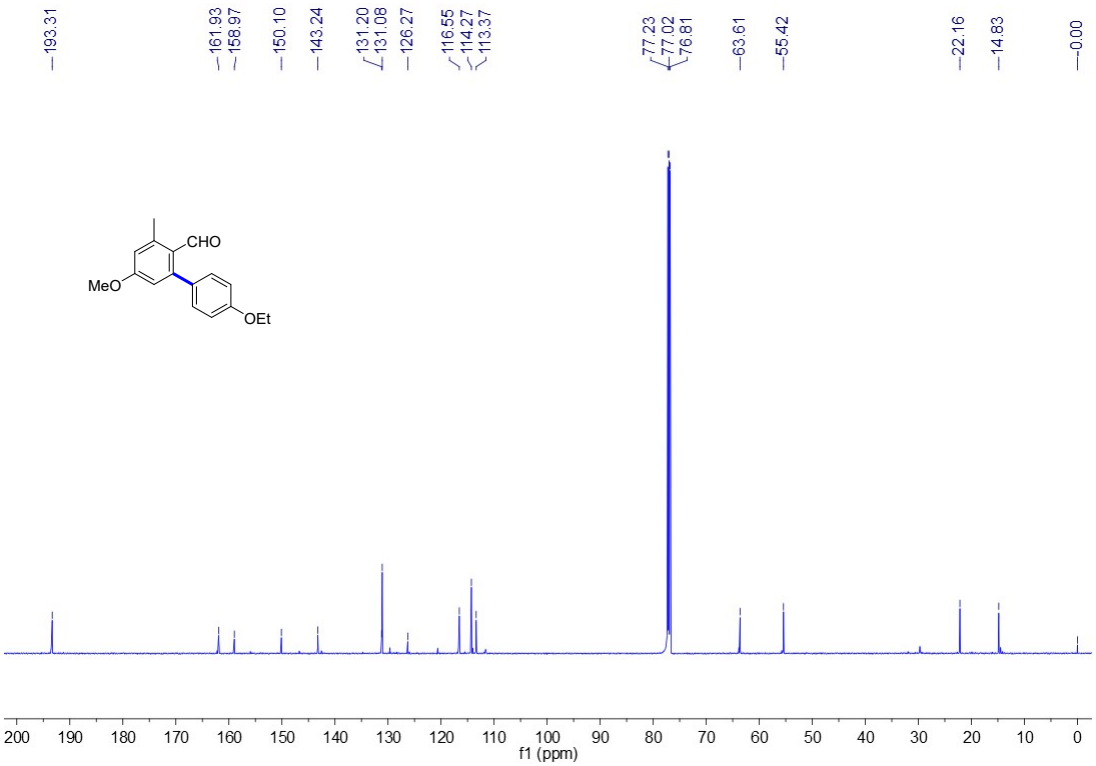
MS(EI) of 4'-ethoxy-3,4-dimethyl-[1,1'-biphenyl]-2-carbaldehyde **4ca**



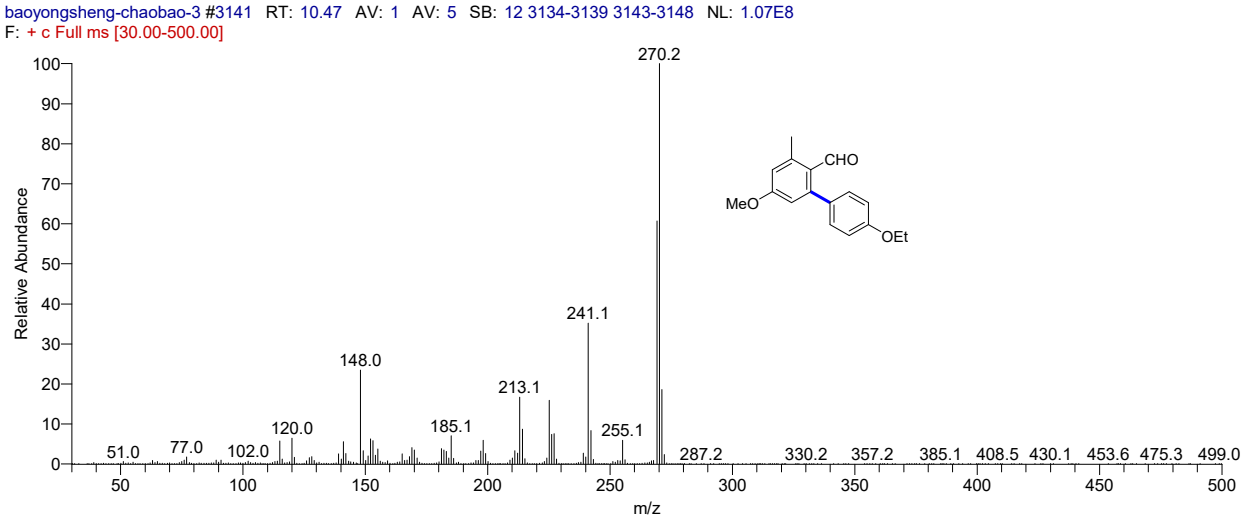
^{1}H NMR of 4'-ethoxy-5-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ga**



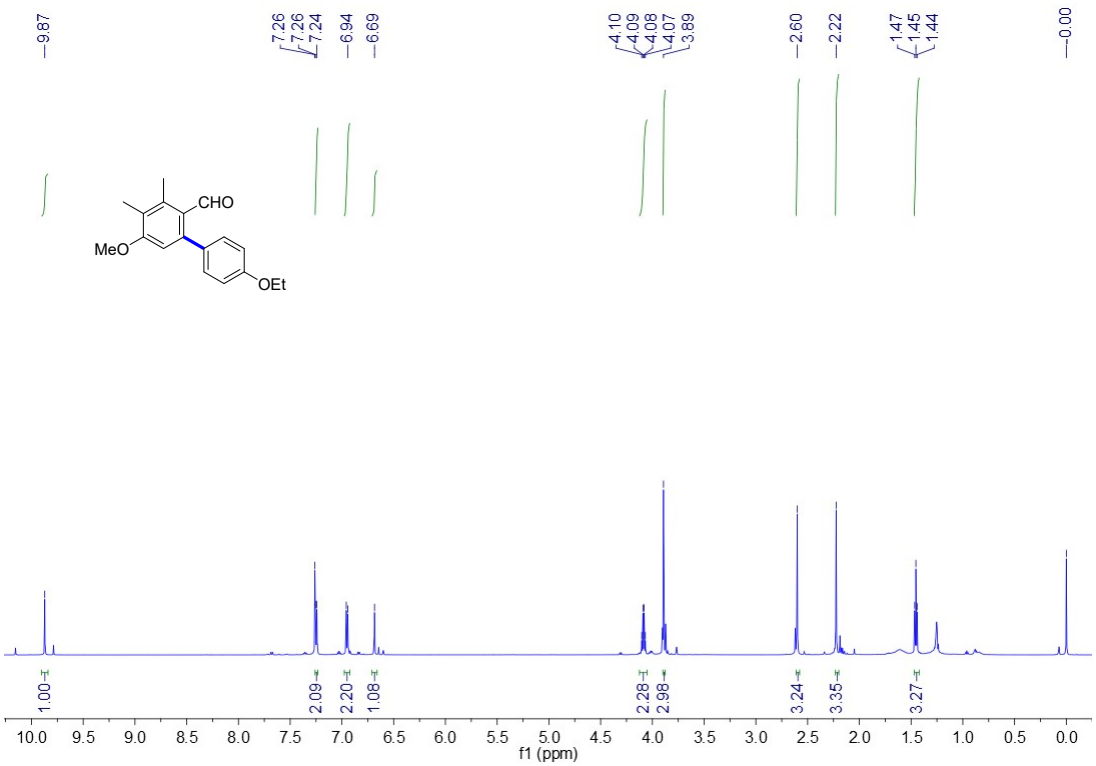
^{13}C NMR of 4'-ethoxy-5-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ga**



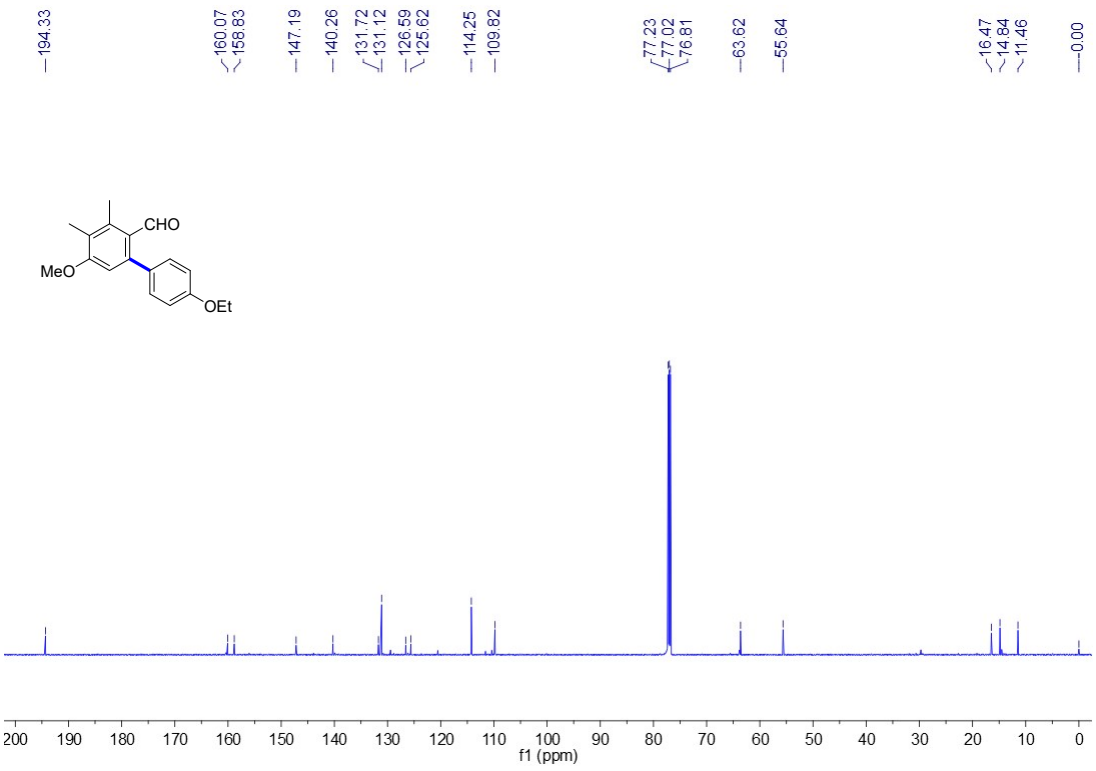
MS(EI) of 4'-ethoxy-5-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ga**



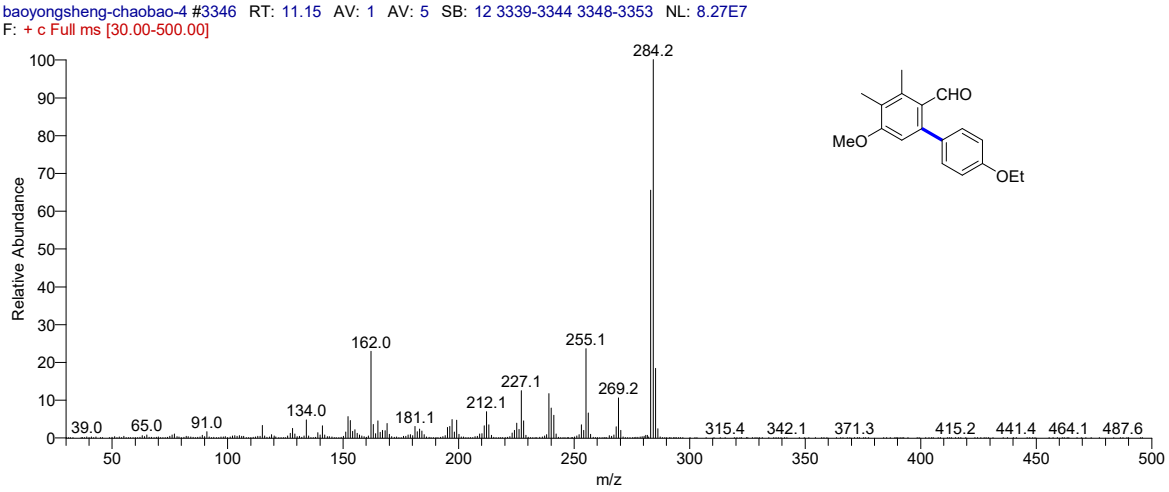
^{1}H NMR of 4'-ethoxy-5-methoxy-3,4-dimethyl-[1,1'-biphenyl]-2-carbaldehyde **4ha**



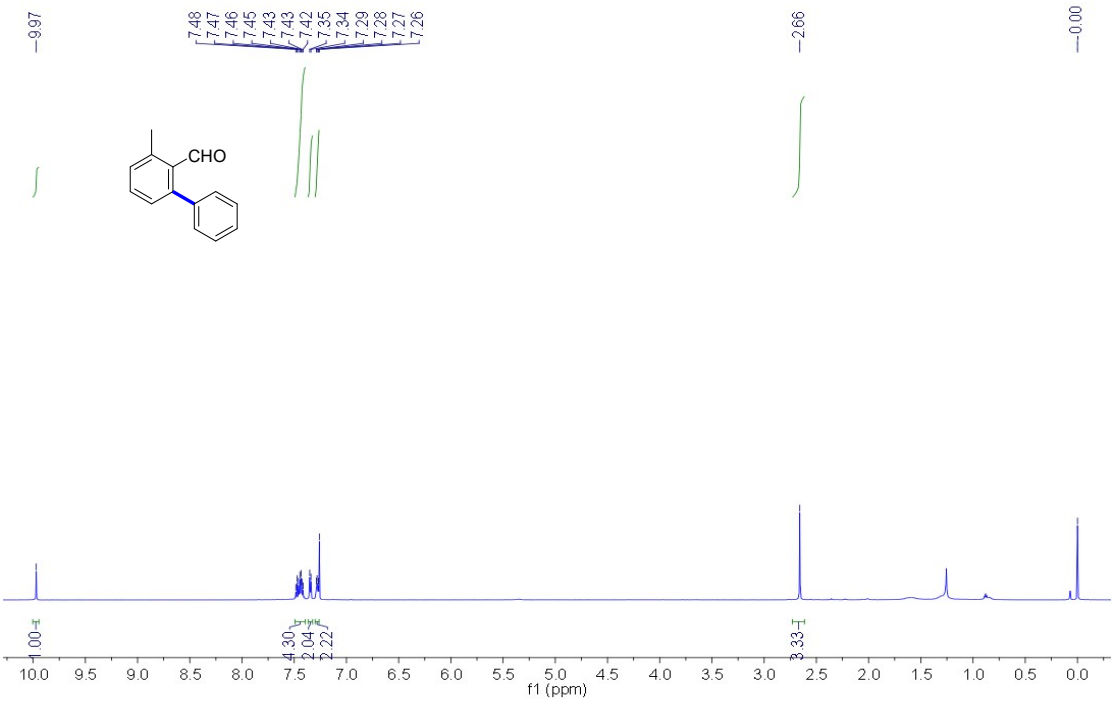
^{13}C NMR of 4'-ethoxy-5-methoxy-3,4-dimethyl-[1,1'-biphenyl]-2-carbaldehyde **4ha**



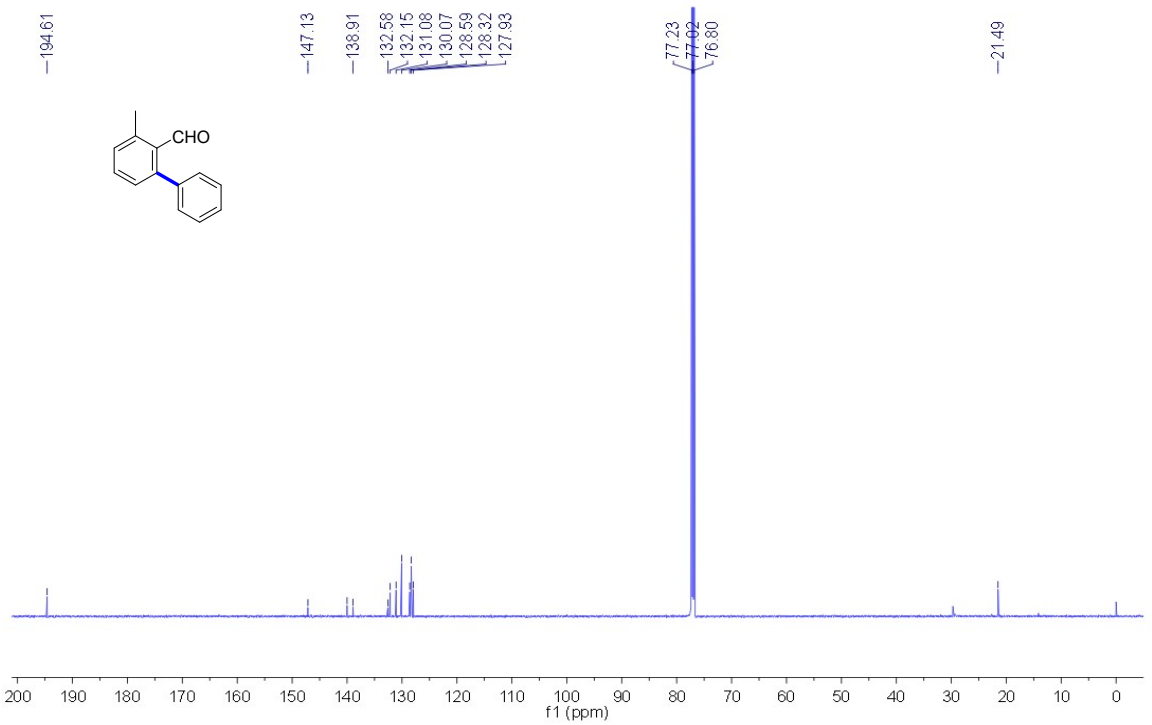
MS(EI) of 4'-ethoxy-5-methoxy-3,4-dimethyl-[1,1'-biphenyl]-2-carbaldehyde **4ha**



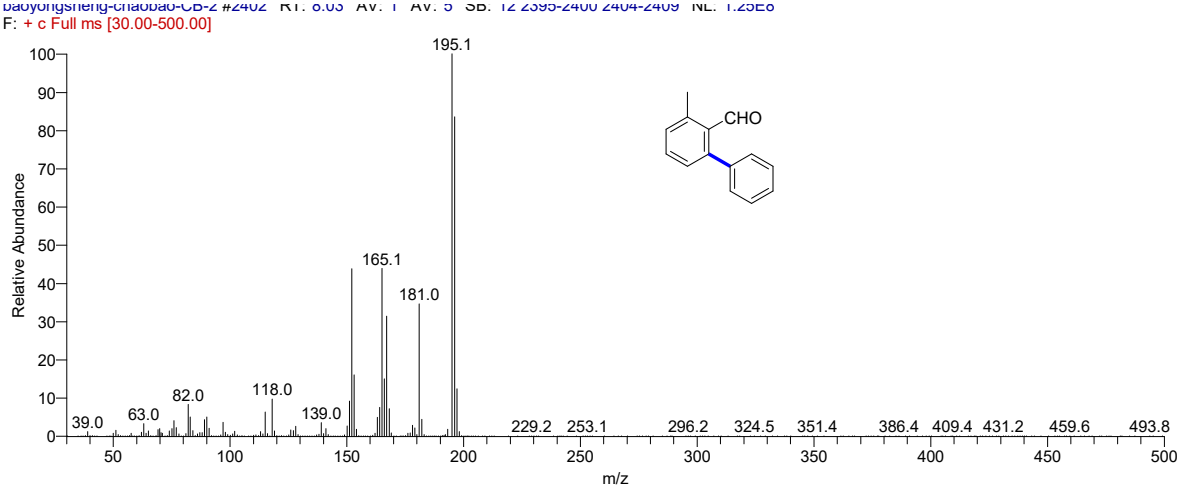
^{1}H NMR of 3- methyl-[1,1'-biphenyl]-2-carbaldehyde **4ab**



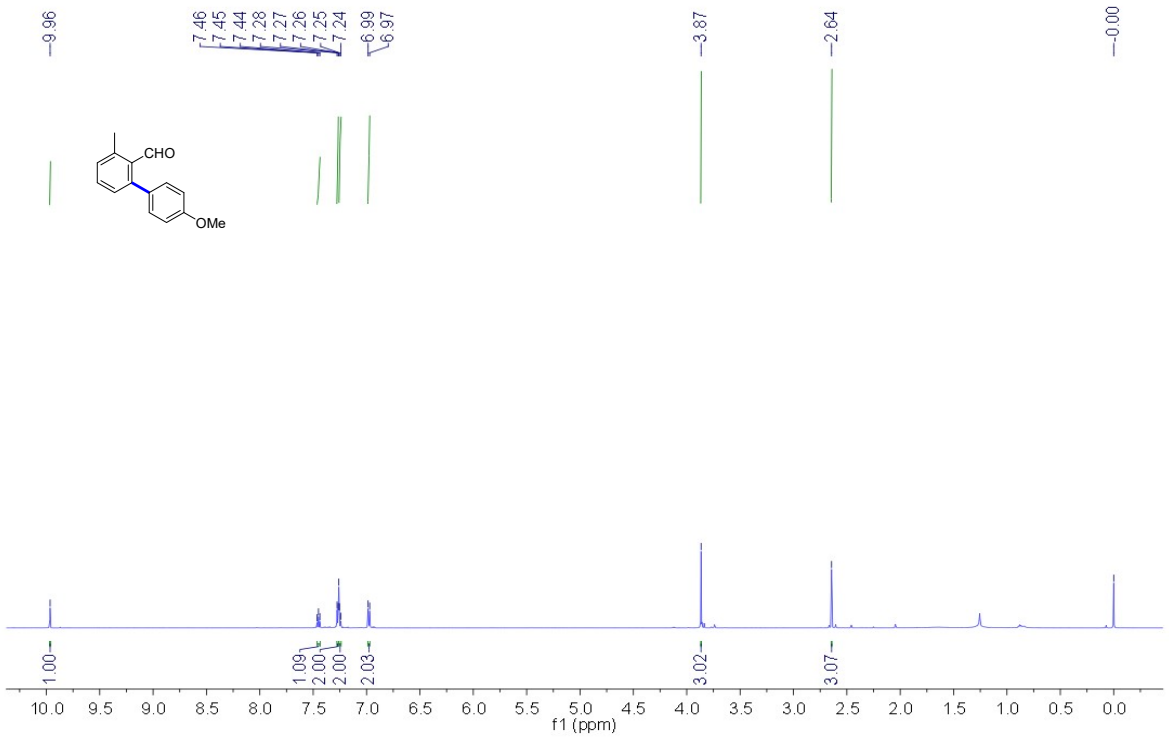
^{13}C NMR of 3- methyl-[1,1'-biphenyl]-2-carbaldehyde **4ab**



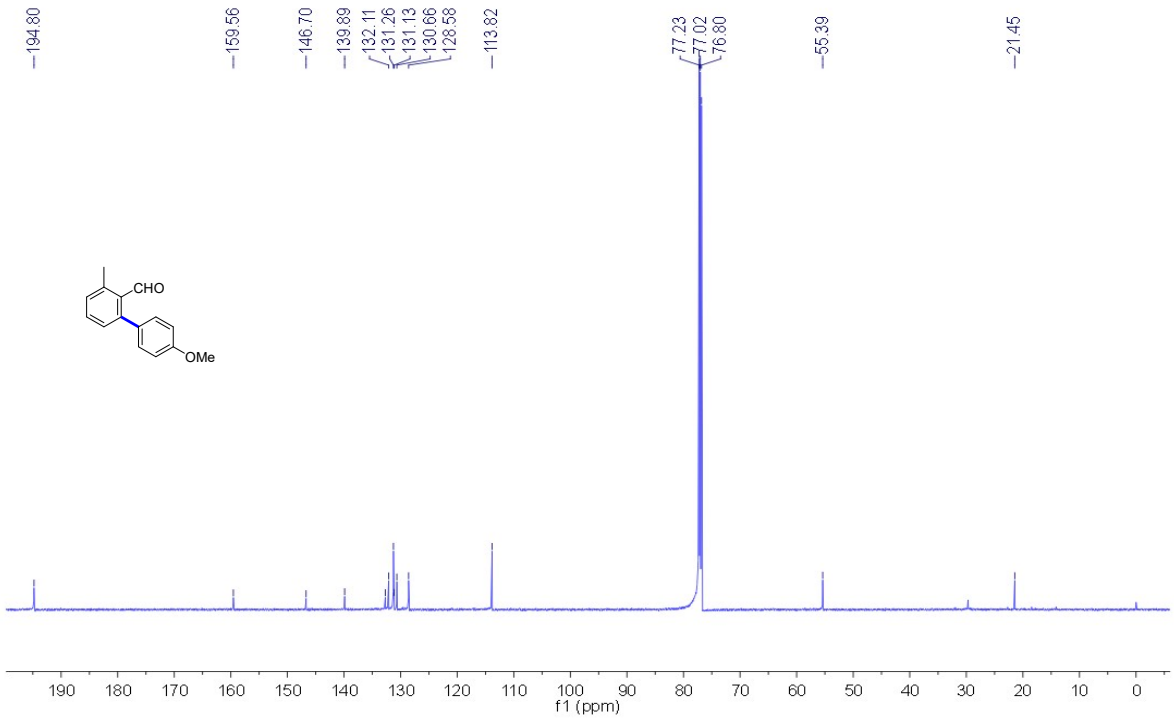
MS(EI) of 3- methyl-[1,1'-biphenyl]-2-carbaldehyde **4ab**



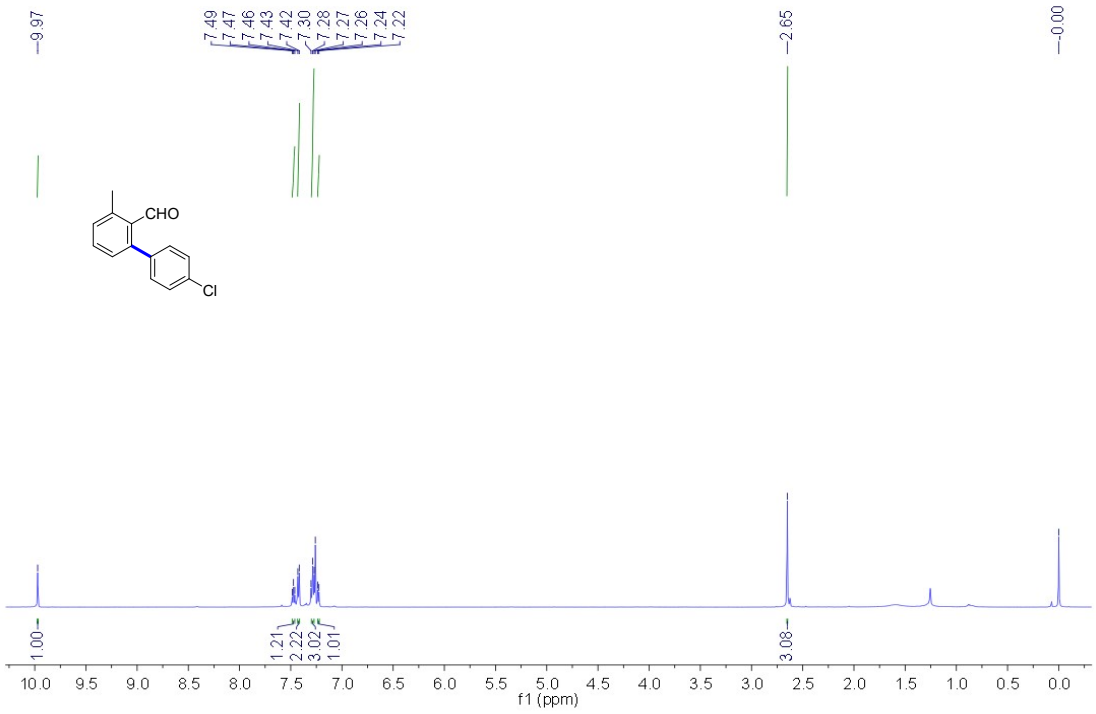
^{1}H NMR of 4'-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ac**



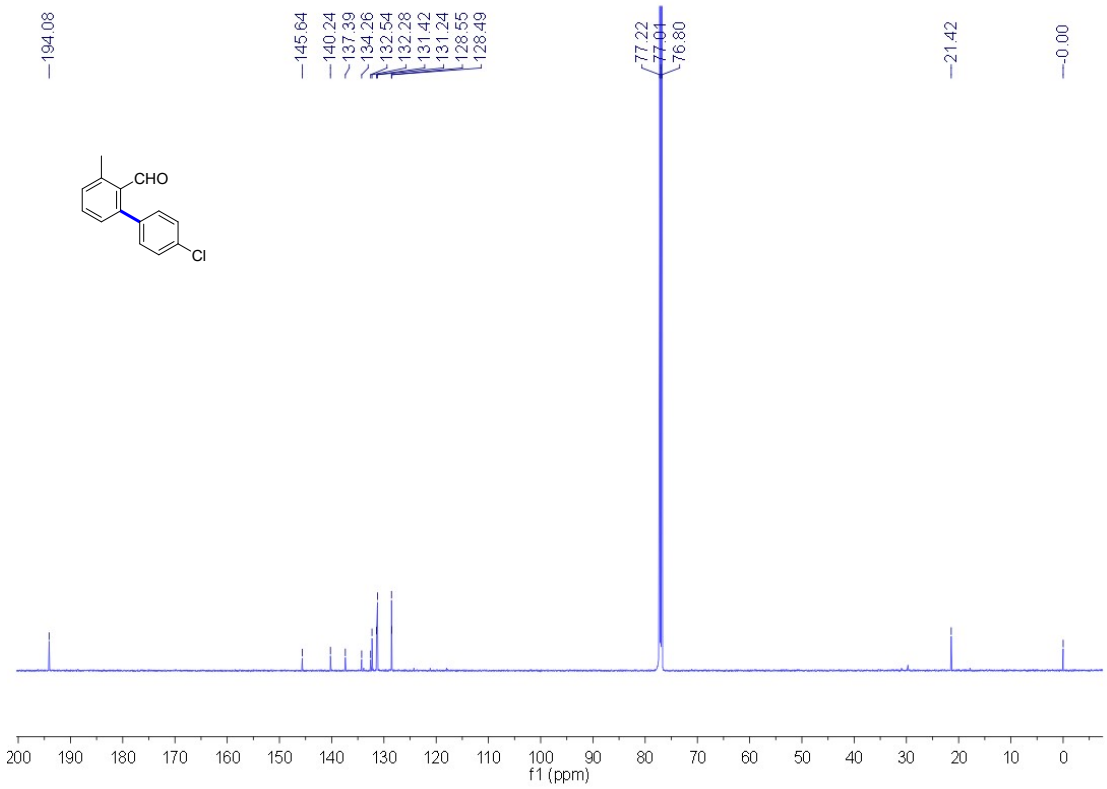
^{13}C NMR of 4'-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ac**



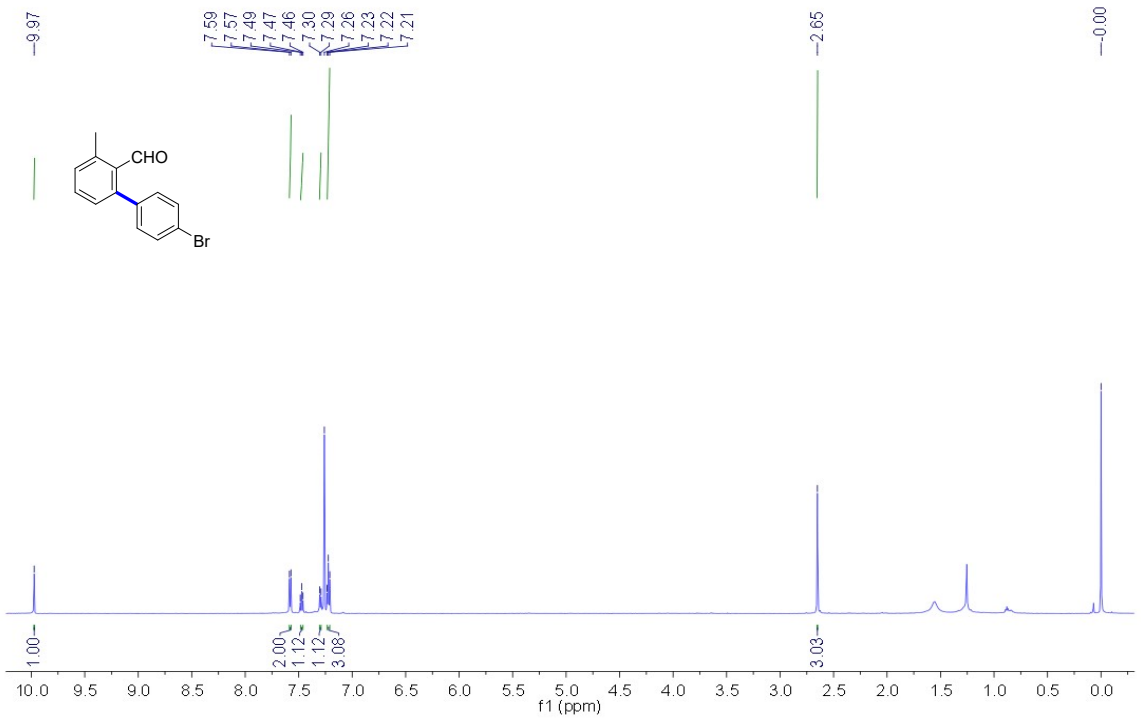
^{1}H NMR of 4'-chloro-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ah**



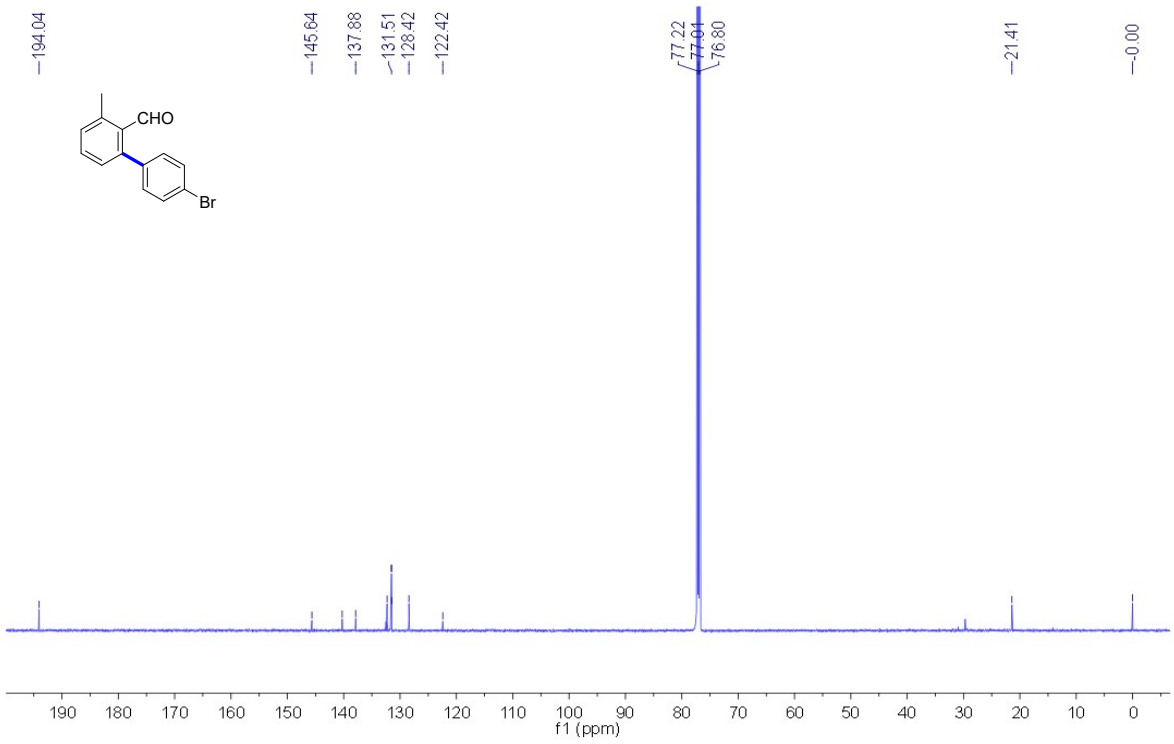
^{13}C NMR of 4'-chloro-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ah**



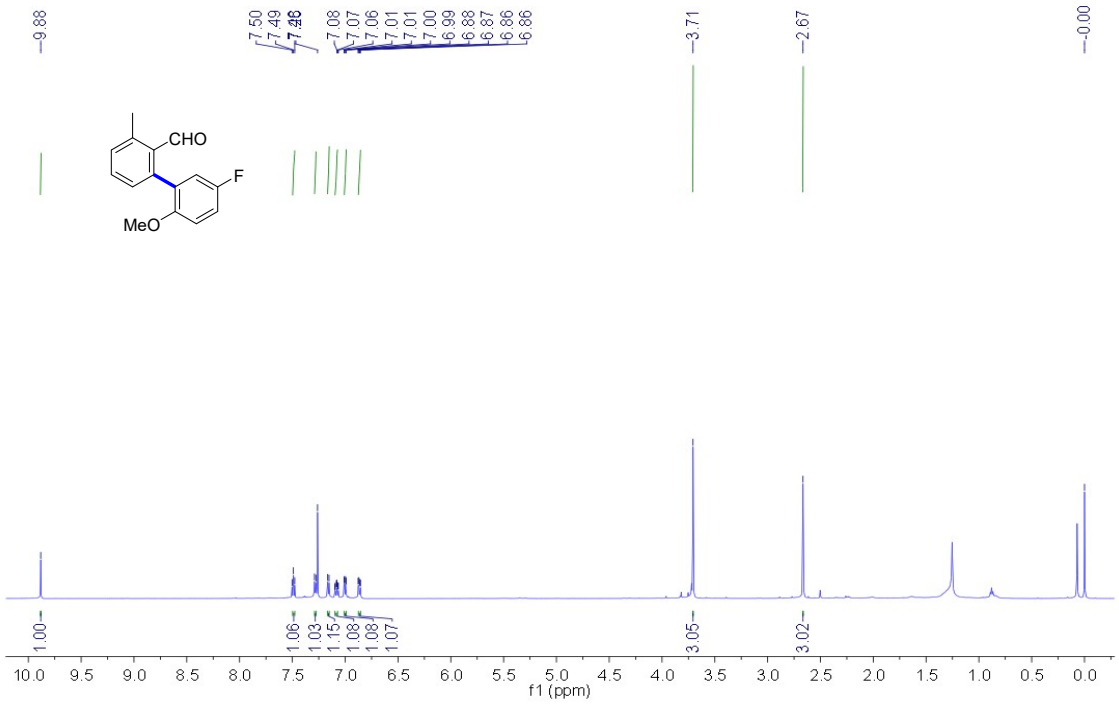
^{1}H NMR of 4'-bromo-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ai**



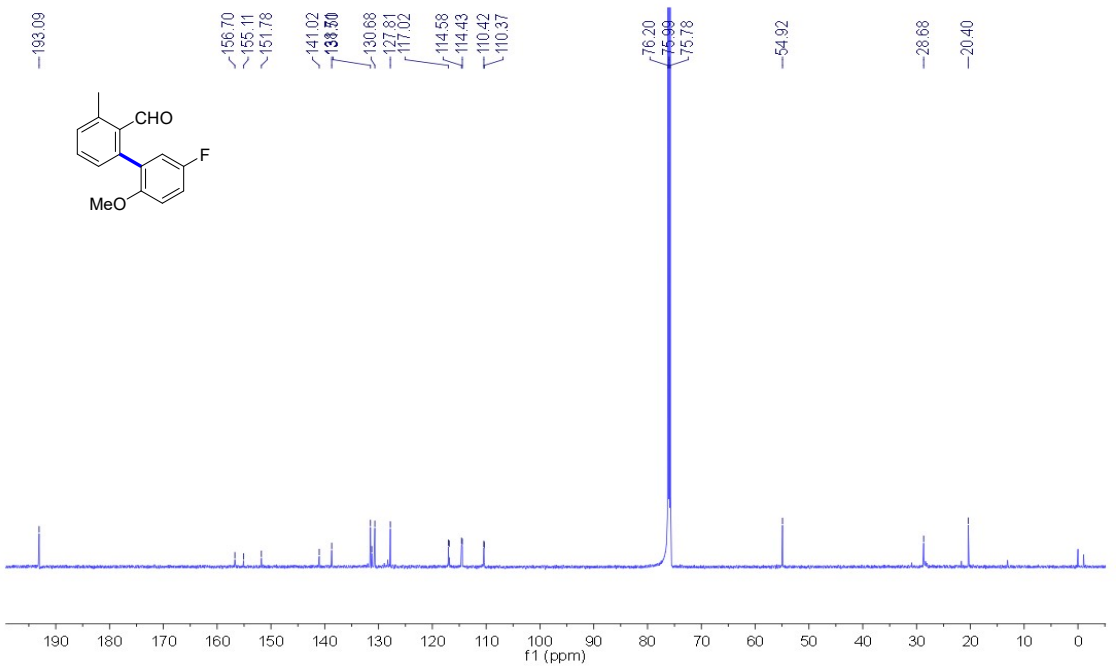
^{13}C NMR of 4'-bromo-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ai**



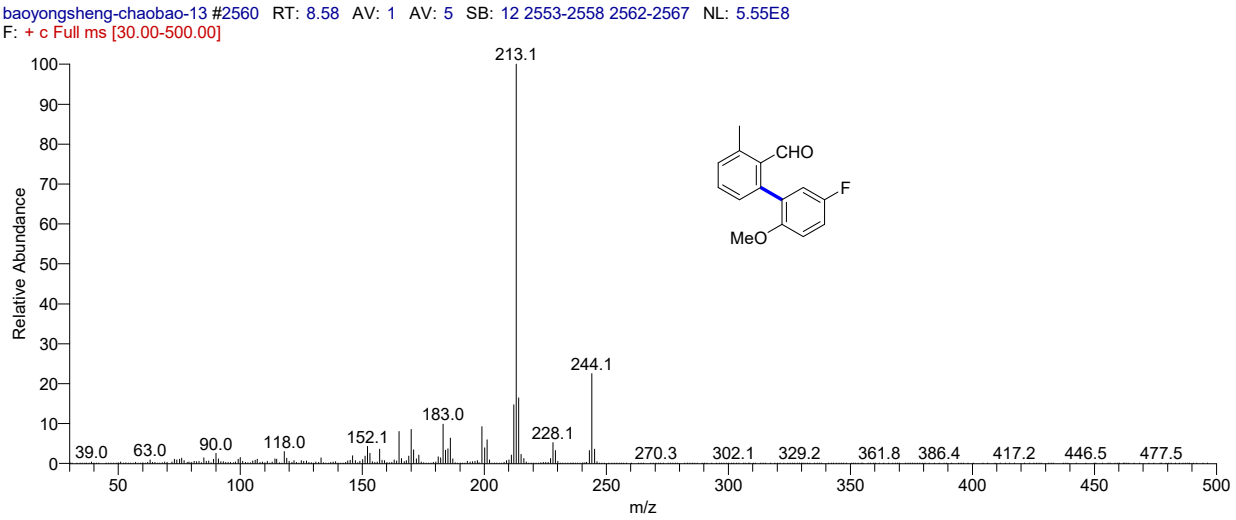
^{1}H NMR of 5'-fluoro-2'-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4aj**



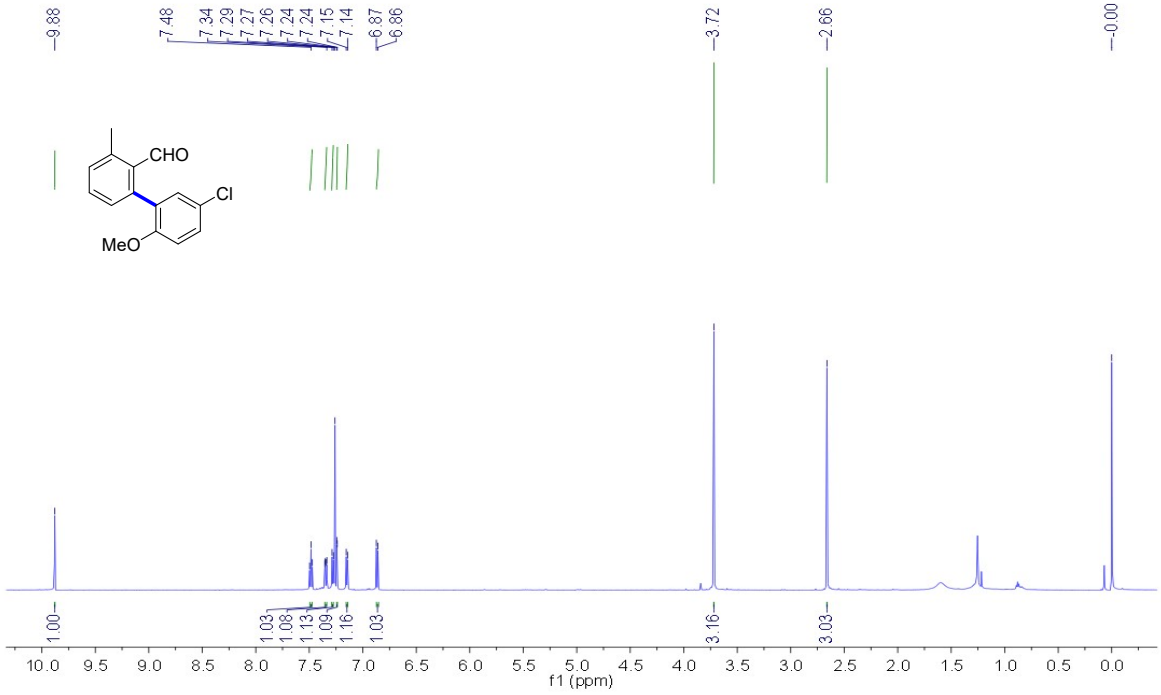
^{13}C NMR of 5'-fluoro-2'-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4aj**



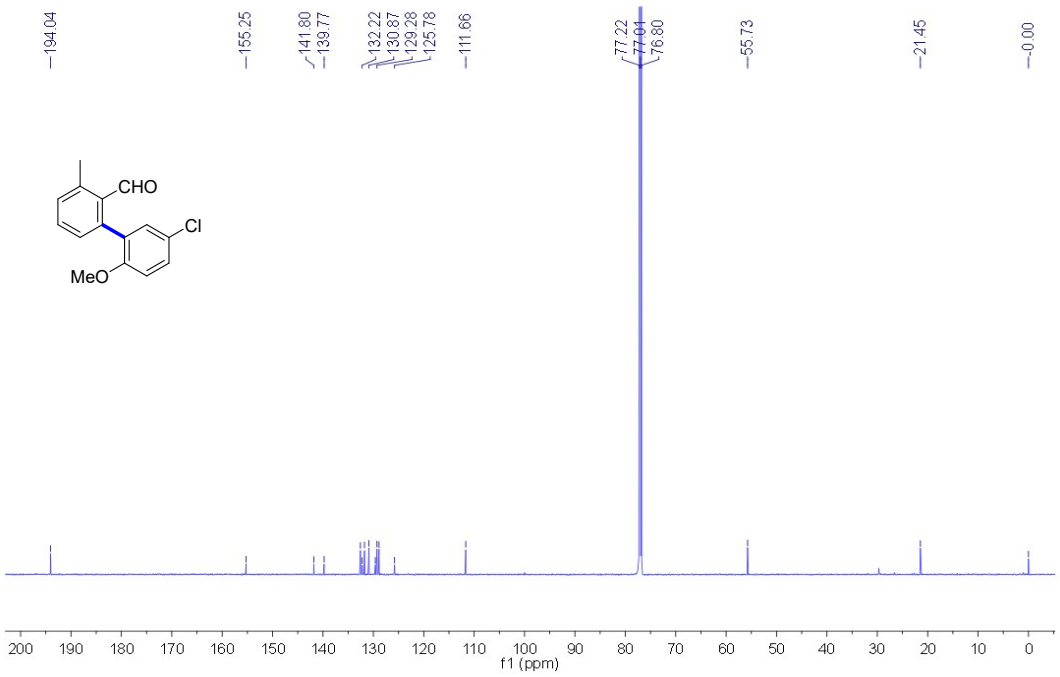
MS(EI) of 5'-fluoro-2'-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4aj**



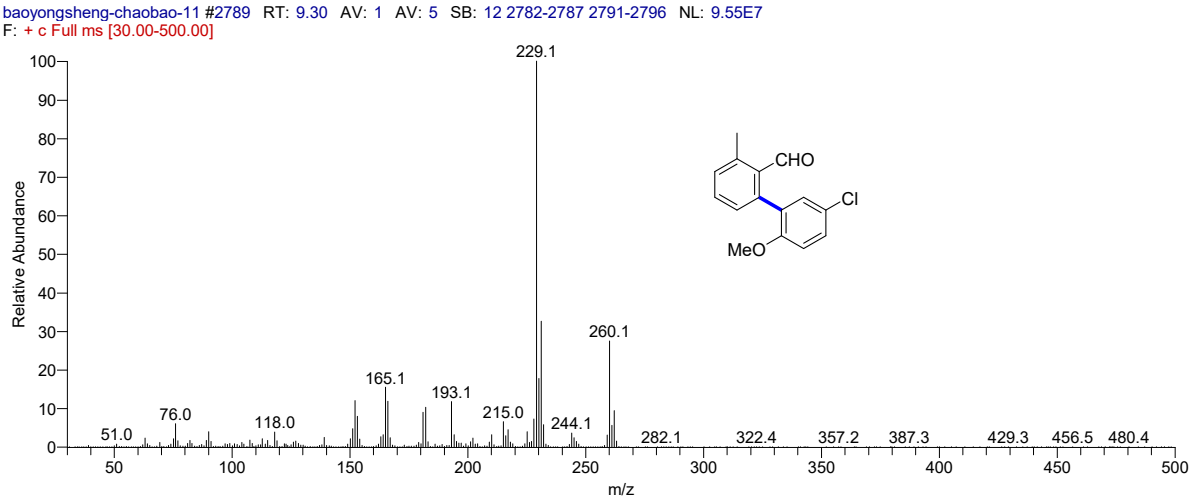
^{1}H NMR of 5'-chloro-2'-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ak**



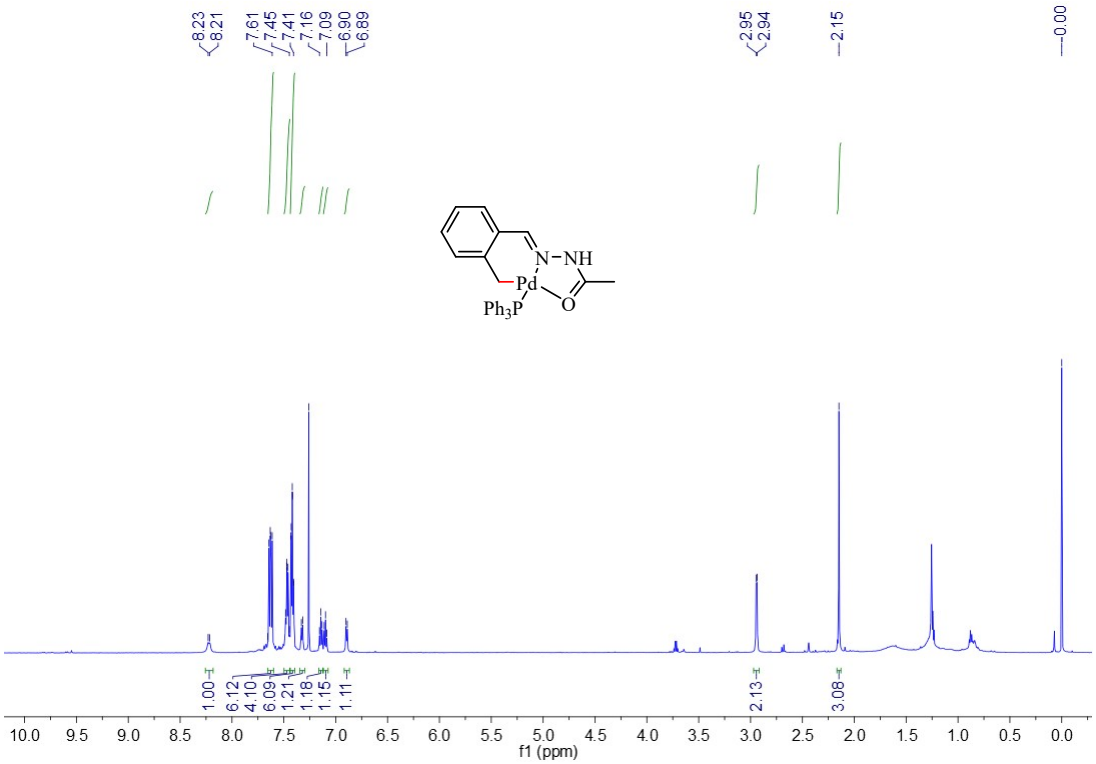
^{13}C NMR of 5'-chloro-2'-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ak**



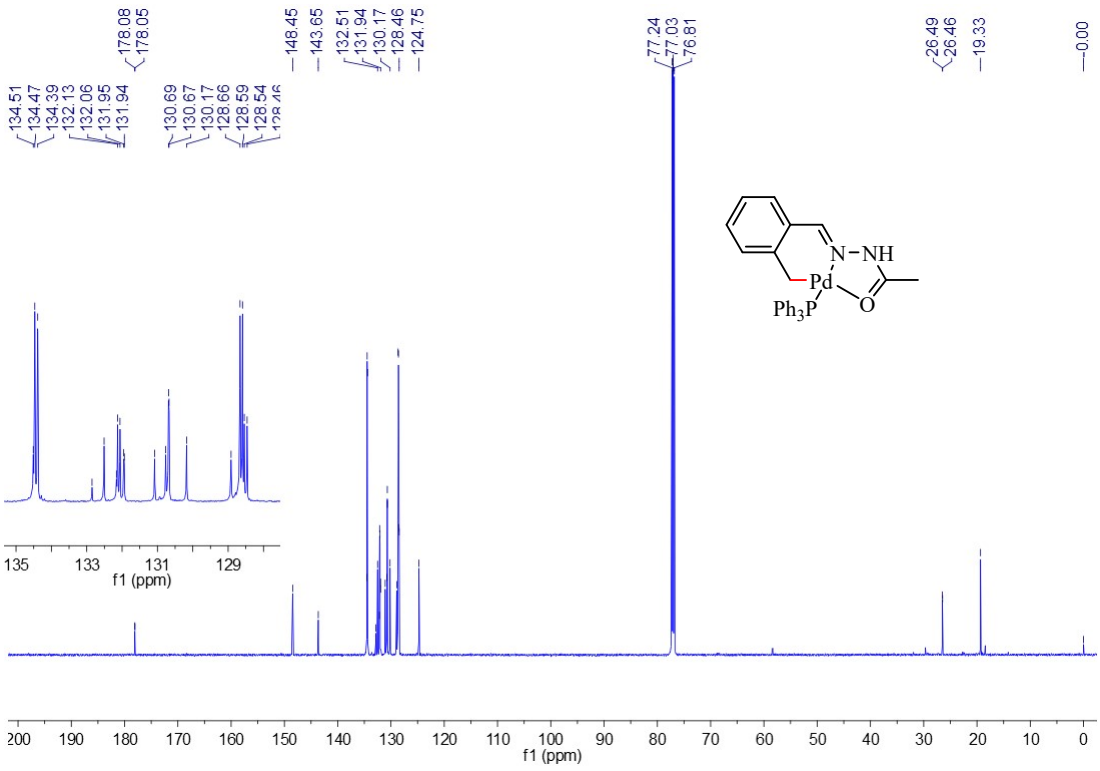
MS(EI) of 5'-chloro-2'-methoxy-3-methyl-[1,1'-biphenyl]-2-carbaldehyde **4ak**



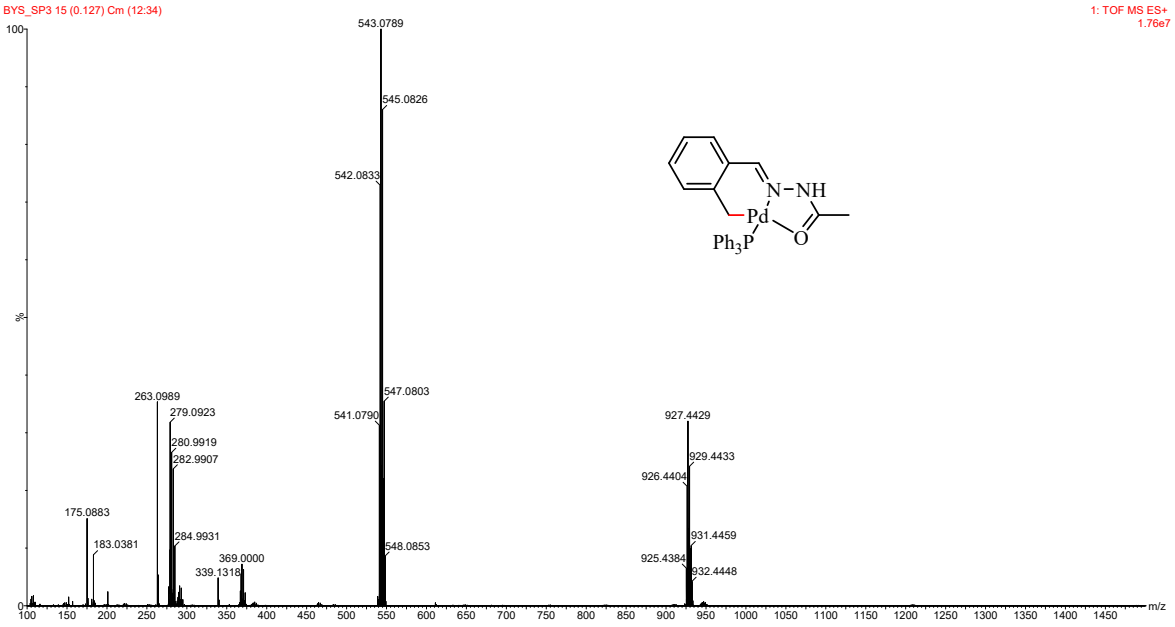
^{1}H NMR of Intermediate **5**



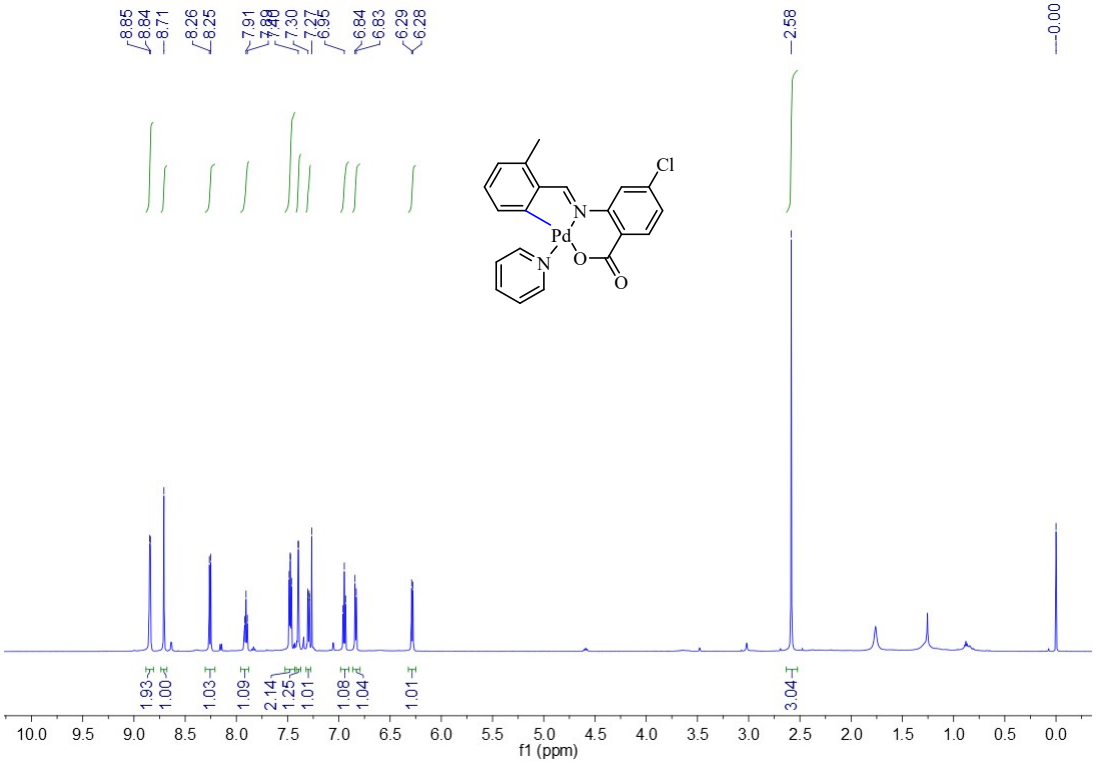
^{13}C NMR of Intermediate **5**



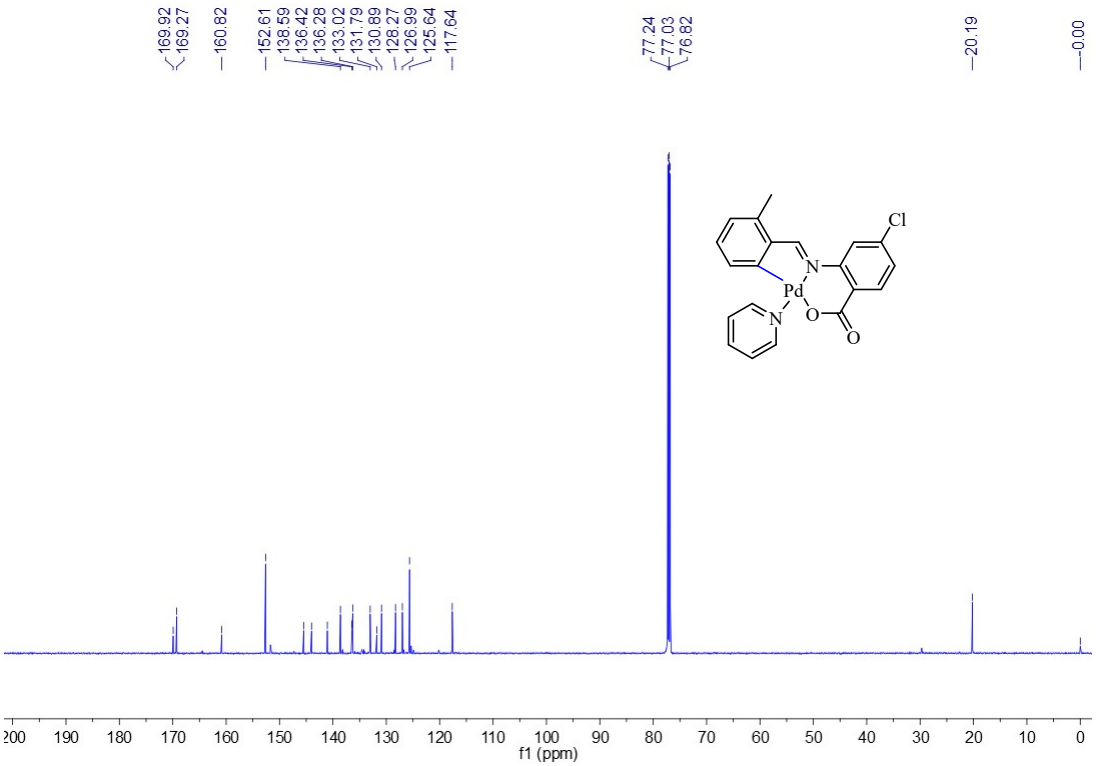
HRMS(ESI) of Intermediate **5**



^{1}H NMR of Intermediate **6**



^{13}C NMR of Intermediate **6**



MS(ESI) of Intermediate **6**