Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Chromium-catalyzed couplings of C(aryl)–SMe bonds in accessing arylated and alkylated benzaldehyde derivatives

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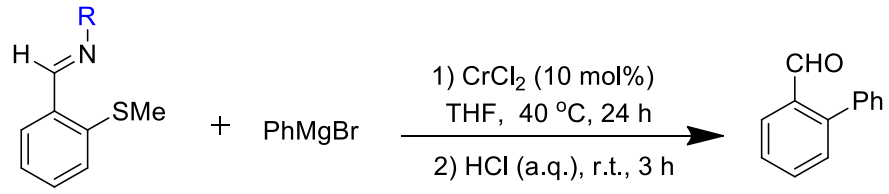
1. General Information

General. All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin–layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still. NMR spectra were measured on a Bruker AV-400 spectrometer and reported in parts per million. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source. Melting points were determined with a Hanon MP-300.

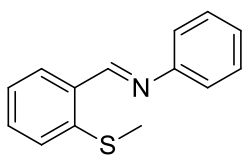
Materials. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, and other commercial suppliers and used as received. Solvents were dried over sodium (for THF and ether) by refluxing for overnight and freshly distilled prior to use. $CrCl_3$ (99.99%), $CoCl_2$ (99.9%), and $FeCl_2$ (>98%) were purchased from Aldrich Inc. and used as received. $Cr(acac)_3$ (97%), $CrCl_2$ (97%), $Cr(CO)_6$ (97%), $PdCl_2$ (97%), $NiCl_2$ were purchased from Alfa Aesar and used as received. Grignard reagents were purchased or were prepared from the corresponding halides and magnesium turnings in anhydrous THF, and titrated prior to use.

2. Optimization of Reaction Parameters

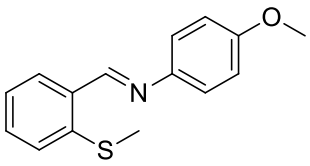
Table S1. **Studying the Effect of *N*-Substituents of Imino Auxiliary on the Cr-Catalyzed Arylation of C(aryl)–SMe Bonds**[a, b]



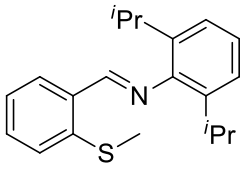
1 **2a** **3a**



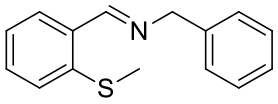
3a (19%)



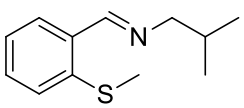
3a (25%)



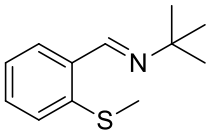
3a (53%)



3a (28%)



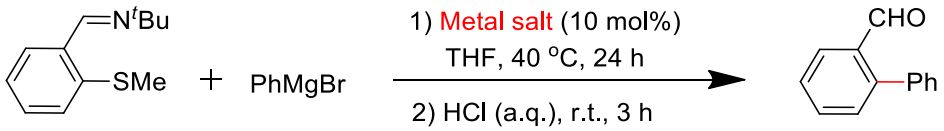
3a (64%)



3a (87%)

[a]Conditions: **1** (0.4 mmol), PhMgBr (1.2 mmol), $CrCl_2$ (10 mol%), THF (2 mL), 40 °C, 12 h. [b]Isolated yield were given.

Table S2. **Studying the Effect of Metal Salts on the Catalytic Arylation of C(aryl)–SMe Bonds**[a]



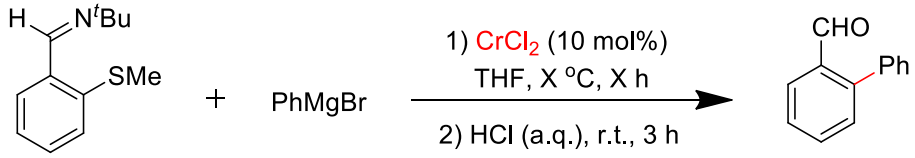
1a **2a** **3a**

entry	Metal salt	Yield (3a)[b]
1	$CrCl_2$	87%
2	$CrCl_3$	75%
3	$Cr(acac)_3$	33%
4	$Cr(CO)_6$	nd[c]
5	$NiCl_2$	11%

6	$CoCl_2$	18%
7	$Ni(COD)_2$	nd[c]
8	$FeCl_2$	nd[c]
9	$PdCl_2$	nd[c]

[a]Conditions: **1a** (0.4 mmol), PhMgBr (1.2 mmol), metal salt (10 mol%), THF (2 mL), 40 °C, 24 h. [b]Isolated yield. [c]Not detected.

Table S3. **Studying the Effect of the Amounts of Phenyl Grignard, Temperature and Reaction Times on the Cr-Catalyzed Arylation of C(aryl)–SMe Bonds[a]**

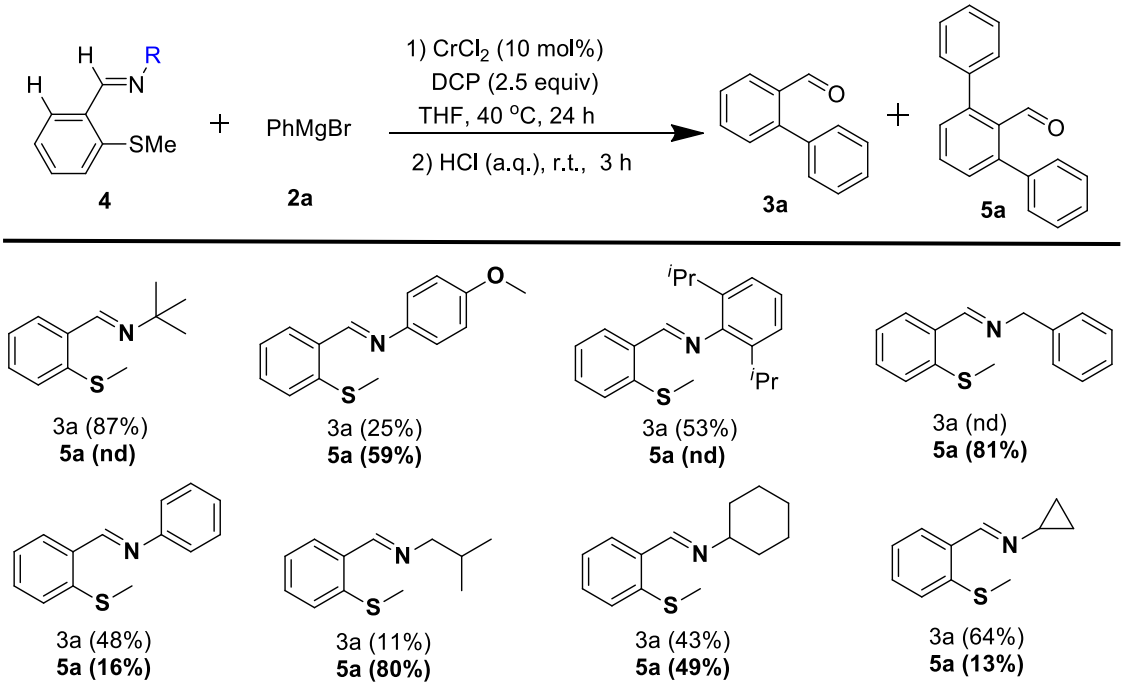


1a **2a** **3a**

Entry	T (°C)	Time (h)	PhMgBr (equiv)	Yield (%)
1	rt	24	3	81
2	40	24	3	87
3	60	24	3	67
4	40	12	3	78
5	40	24	1	trace
6	40	24	2	58
7	40	24	4	81
8[b]	40	24	3	69

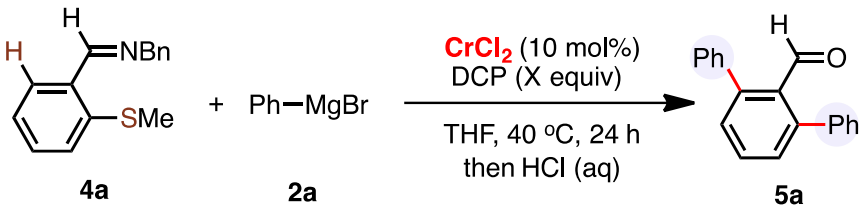
[a]Conditions: **1a** (0.4 mmol), PhMgBr, $CrCl_2$ (10 mol %), THF (2 mL), and isolated yields are given. [b]$CrCl_2$ (5 mol%).

Table S4. **Studying the Effect of *N*-Substituents of Imino Auxiliary on the Cr-Catalyzed Diarylation of C(aryl)–SMe and C(aryl)–H Bonds[a, b]**



[a]Conditions: **4** (0.4 mmol), PhMgBr (1.6 mmol), $CrCl_2$ (10 mol%), DCP (1 mmol), 40 °C, 24 h. Isolated yields are given. [b]The yield of **5a** in parenthesis.

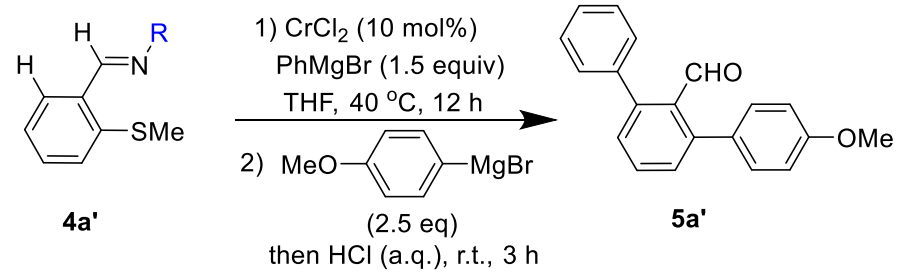
Table S5. **Studying the Effect of the Amounts of DCP on the Cr-Catalyzed Diarylation of C(aryl)–SMe and C(aryl)–H Bonds**[a]

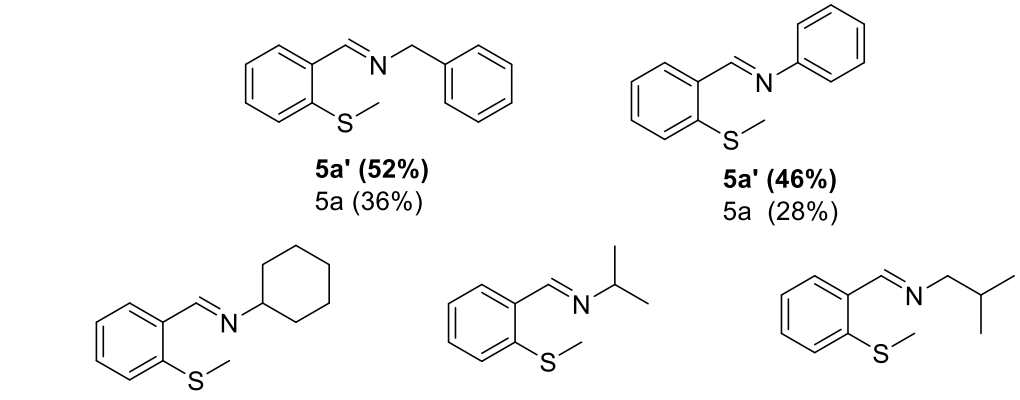


Entry	X (equiv)	Yield (%)
1	0	28
2	1	47
3	2	76
4	2.5	81
5	3	82

[a]Conditions: **4a** (0.4 mmol), PhMgBr (1.6 mmol), $CrCl_2$ (10 mol%), DCP (1.0 mmol), 40 °C, 24 h. Isolated yields are given.

Table S6. **Studying the Effect of *N*-Substituents of Imino Auxiliary on the Cr-Catalyzed Incorporation of Two Different Aryl Groups into Arenes**[a]





[a]Conditions: **4a′** (0.4 mmol), PhMgBr (0.6 mmol), $CrCl_2$ (10 mol%), THF (1 mL), 40 °C, 12 h; ArMgBr (1.0 mmol), DCP (1.0 mmol), 40 °C, 12 h, then quenching with HCl (aq), rt, 3 h. Isolated yields are given.

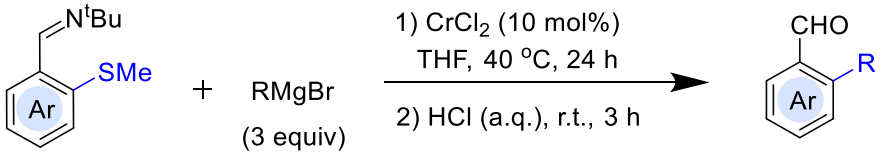
3. Procedure for the Preparation of Substrates

General procedure for the Synthesis of *N-tert*-butyl-substituted *ortho*-methylthio-containing aromatic imines[1]

In a 25 mL screw-capped vial with a stirring bar, the *ortho*-methylthio-substituted aromatic aldehyde (5 mmol) was treated with *tert*-butylamine (25 mmol). The vial was then sealed and the mixture was stirred at 100 °C for overnight. After cooling to room temperature, the excess *tert*-butylamine was evaporated under a reduced pressure. The corresponding imine product was generally obtained in very high purity and employed without further purification.

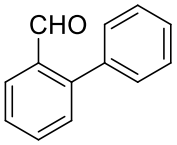
4. General Procedure for Cr-Catalyzed Arylation and Alkylation of C(aryl)–S

Bonds



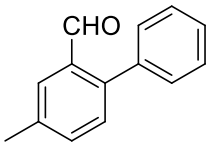
1 **2** **3**

In a dried Schlenk tube were placed an *ortho*-methylthio-containing aromatic aldimine **1** (0.4 mmol) and $CrCl_2$ (5 mg, 0.04 mmol), then THF (2 mL) and Grignard reagent (1.2 mL, 1 M in THF, 1.2 mmol) were dropwise added by a syringe under atmosphere of nitrogen, and the mixture was stirred at 40 °C for 24 h. After quenched by 3 N HCl (1 mL), the resulting mixture was further stirred at room temperature, and then extracted with ethyl acetate (3 x 10 mL). After removal of the volatiles under vacuum, the crude product was purified by silica gel chromatography to afford the desired product **3**.



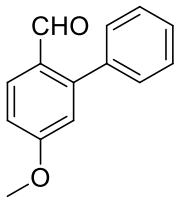
[1,1'-Biphenyl]-2-carbaldehyde (3a, known compound)

The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless oil (63 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.99 (s, 1H), 8.04 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.53–7.43 (m, 5H), 7.38 (dd, J = 7.6, 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.5, 146.0, 137.8, 133.8, 133.6, 130.9, 130.2, 128.5, 128.2, 127.9, 127.6. Spectroscopic data are in accordance with those described in the literature.[2]



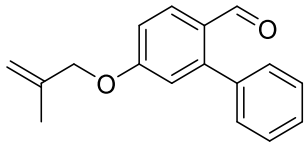
4-Methyl-[1,1'-biphenyl]-2-carbaldehyde (3b, known compound)

The general procedure was applied to *N-tert*-butyl-1-(5-methyl-2-(methylthio)phenyl)methanimine (89 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless oil (65 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1H), 7.84 (s, 1H), 7.48–7.40 (m, 4H), 7.37 (d, J = 1.9 Hz, 1H), 7.36–7.32 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 143.5, 137.9, 137.8, 134.6, 133.6, 130.8, 130.2, 128.5, 128.0, 127.6, 21.1. Spectroscopic data are in accordance with those described in the literature.[2]



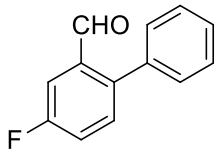
5-Methoxy-[1,1'-biphenyl]-2-carbaldehyde (3c, known compound)

The general procedure was applied to *N-tert*-butyl-1-(4-methoxy-2-(methylthio)phenyl)methanimine (95 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (67 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.84 (s, 1H), 8.03 (d, J = 8.7 Hz, 1H), 7.45 (td, J = 4.9, 2.5 Hz, 3H), 7.41–7.36 (m, 2H), 7.00 (dd, J = 8.7, 2.5 Hz, 1H), 6.88 (d, J = 2.5 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 163.6, 148.6, 137.9, 130.1, 130.0, 128.5, 128.3, 127.5, 115.3, 114.1, 55.7. Spectroscopic data are in accordance with those described in the literature.[2]



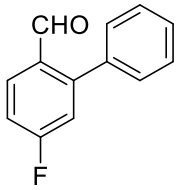
5-((2-Methylallyl)oxy)-[1,1'-biphenyl]-2-carbaldehyde (3d, unknown compound)

The general procedure was applied to *N*-*tert*-butyl-1-(4-((2-methylallyl)oxy)-2-(methylthio)phenyl)methanimine (111 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (72 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.84 (s, 1H), 8.02 (d, J = 8.7 Hz, 1H), 7.49–7.43 (m, 3H), 7.38 (dd, J = 7.5, 2.1 Hz, 2H), 7.02 (dd, J = 8.7, 2.6 Hz, 1H), 6.91 (d, J = 2.5 Hz, 1H), 5.07 (d, J = 32.8 Hz, 2H), 4.54 (s, 2H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 162.8, 148.6, 140.1, 137.9, 130.1, 130.0, 128.5, 128.3, 127.5, 116.2, 114.6, 113.5, 72.1, 19.5. HRMS (ESI$^+$): calcd for $C_{17}H_{16}O_2$ $[M+H]^+$ 253.1223, found 253.1217.



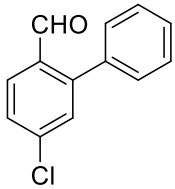
4-Fluoro-[1,1'-biphenyl]-2-carbaldehyde (3e, known compound)

The general procedure was applied to *N*-*tert*-butyl-1-(5-fluoro-2-(methylthio)phenyl)methanimine (90 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless oil (65 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.92 (d, J = 3.3 Hz, 1H), 7.70 (dd, J = 8.9, 2.8 Hz, 1H), 7.51-7.44 (m, 4H), 7.35 (dd, J = 7.6, 2.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3 (d, J = 1.8 Hz), 161.1 (d, J = 247.7 Hz), 142.2 (d, J = 3.0 Hz), 136.9, 135.4 (d, J = 6.4 Hz), 132.9 (d, J = 7.3 Hz), 130.3, 128.7, 128.4, 121.0 (d, J = 21.9 Hz), 113.9 (d, J = 22.3 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ = –113.20. Spectroscopic data are in accordance with those described in the literature.[2]



5-Fluoro-[1,1'-biphenyl]-2-carbaldehyde (3f, known compound)

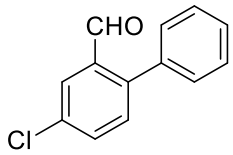
The general procedure was applied to *N*-*tert*-butyl-1-(4-fluoro-2-(methylthio)phenyl)methanimine (90 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless oil (48 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.90 (s, 1H), 8.07 (dd, J = 8.7, 6.0 Hz, 1H), 7.48 (m, 3H), 7.41–7.35 (m, 2H), 7.22–7.10 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 164.3 (d, J = 255.3 Hz), 149.0 (d, J = 9.3 Hz), 136.7, 130.8 (d, J = 9.7 Hz), 130.5 (d, J = 2.8 Hz), 130.0, 128.8, 128.7, 117.4 (d, J = 22.0 Hz), 115.3 (d, J = 21.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ = –103.64. Spectroscopic data are in accordance with those described in the literature.[2]



5-Chloro-[1,1'-biphenyl]-2-carbaldehyde (3g, known compound)

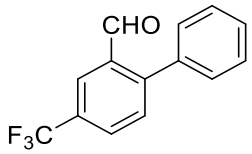
The general procedure was applied to *N*-*tert*-butyl-1-(4-chloro-2-(methylthio)phenyl)methanimine (97 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (62 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.91 (s, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.46 (m, 5H), 7.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 147.5, 139.9, 136.5, 132.2, 130.8, 130.0, 129.3, 128.8, 128.7, 128.3. HRMS (ESI^+): calcd for $C_{13}H_9ClO$ $[M+H]^+$ 217.0415, found

217.0415.



4-Chloro-[1,1'-biphenyl]-2-carbaldehyde (3h, known compound)

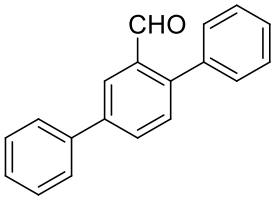
The general procedure was applied to *N-tert*-butyl-1-(5-chloro-2-(methylthio)phenyl)methanimine (97 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (68 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.91 (s, 1H), 7.99 (d, J = 2.4 Hz, 1H), 7.59 (dd, J = 8.2, 2.4 Hz, 1H), 7.50–7.45 (m, 3H), 7.40 (d, J = 8.3 Hz, 1H), 7.39–7.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 144.3, 136.7, 134.8, 134.4, 133.5, 132.3, 130.1, 128.7, 128.6, 127.5. Spectroscopic data are in accordance with those described in the literature.[2]



4-(Trifluoromethyl)-[1,1'-biphenyl]-2-carbaldehyde (3i, known compound)

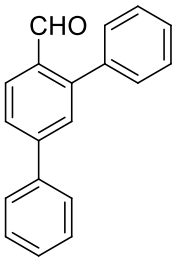
The general procedure was applied to *N-tert*-butyl-1-(2-(methylthio)-5-(trifluoromethyl)phenyl) methanimine (110 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (74 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 1H), 8.30 (d, J = 2.0 Hz, 1H), 7.88 (dd, J = 8.1, 2.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.51 (m, 3H), 7.43–7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 149.0, 136.5, 134.1, 131.7, 130.5 (q, J = 33.4 Hz), 130.1, 129.9 (q, J = 3.3 Hz), 129.1, 128.9, 123.8 (q, J = 272.5 Hz), 123.8 (q, J = 272.5 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ = –62.79. Spectroscopic data are in accordance with those

described in the literature.[3]



[1,1':4',1''-Terphenyl]-2'-carbaldehyde (3j, known compound)

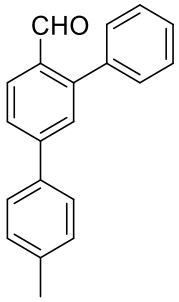
The general procedure was applied to *N-tert*-butyl-1-(4-(methylthio)-[1,1'-biphenyl]-3-yl)methanimine(113 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (85 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.83 (s, 1H), 8.06 (d, J = 9.2 Hz, 1H), 7.67 (dd, J = 7.6, 1.5 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.32–7.25 (m, 3H), 7.23–7.16 (m, 3H), 7.16–7.11 (m, 2H), 7.07 (dd, J = 6.5, 3.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.0, 144.3, 142.6, 140.2, 136.1, 135.6, 134.8, 131.4, 129.9, 128.0, 127.9, 127.7, 126.9, 126.5. Spectroscopic data are in accordance with those described in the literature.[2]



[1,1':3',1''-Terphenyl]-4'-carbaldehyde (3k, known compound)

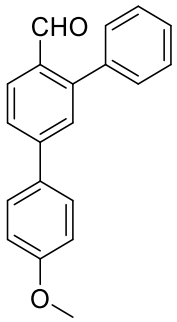
The general procedure was applied to *N-tert*-butyl-1-(3-(methylthio)-[1,1'-biphenyl]-4-yl)methanimine (113 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (85 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.74 (dd, J = 8.4, 1.7 Hz, 1H), 7.68 (m, 3H), 7.46 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.2, 146.6, 146.4, 139.7, 138.0,

132.6, 130.2, 129.5, 129.1, 128.6, 128.4, 128.3, 127.5, 126.6. HRMS (ESI^+): calcd for $C_{19}H_{14}O$ $[M+H]^+$ 259.1117, found 259.1061. Spectroscopic data are in accordance with those described in the literature.[2]



4-Methyl-[1,1':3',1''-terphenyl]-4'-carbaldehyde (3l, unknown compound)

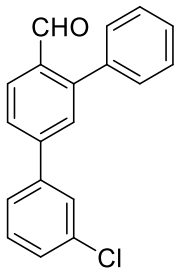
The general procedure was applied to *N-tert*-butyl-1-(4'-methyl-3-(methylthio)-[1,1'-biphenyl]-4-yl)methanimine (119 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (96 mg, 88% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 10.03 (s, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.73 (dd, J = 8.3, 1.7 Hz, 1H), 7.67 (d, J = 1.8 Hz, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.53–7.43 (m, 5H), 7.30 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 146.6, 146.3, 138.6, 138.0, 136.8, 132.4, 130.2, 129.8, 129.2, 128.6, 128.3, 128.3, 127.3, 126.3, 21.3. HRMS (ESI^+): calcd for $C_{20}H_{16}O$ $[M+H]^+$ 273.1274, found 273.1263.



4-Methoxy-[1,1':3',1''-terphenyl]-4'-carbaldehyde (3m, known compound)

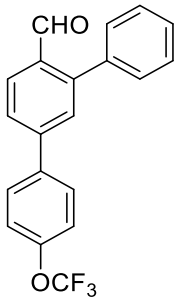
The general procedure was applied to *N-tert*-butyl-1-(4'-methoxy-3-(methylthio)-[1,1'-biphenyl]-4-yl)methanimine (125 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL,

1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (66 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 1H), 8.09 (d, J = 8.1 Hz, 1H), 7.69 (dd, J = 8.2, 1.8 Hz, 1H), 7.65–7.60 (m, 3H), 7.51–7.42 (m, 5H), 7.04–6.98 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 160.2, 146.6, 145.9, 138.1, 132.0, 132.0, 130.2, 128.8, 128.6, 128.5, 128.3, 128.2, 125.9, 114.6, 55.5. Spectroscopic data are in accordance with those described in the literature.[4]



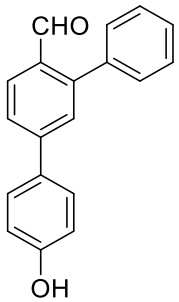
3-Chloro-[1,1':3',1''-terphenyl]-4'-carbaldehyde (3n, unknown compound)

The general procedure was applied to *N-tert*-butyl-1-(4'-chloro-3-(methylthio)-[1,1'-biphenyl]-4-yl)methanimine (127 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (105 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.64 (d, J = 5.2 Hz, 2H), 7.56–7.47 (m, 4H), 7.46–7.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 146.7, 144.7, 141.5, 137.6, 135.1, 133.0, 130.3, 130.2, 129.5, 128.6, 128.6, 128.5, 128.4, 127.6, 126.5, 125.6. HRMS (ESI$^+$): calcd for $C_{19}H_{13}ClO$ $[M+H]^+$ 293.0728, found 293.0725.



4-(Trifluoromethoxy)-[1,1':3',1''-terphenyl]-4'-carbaldehyde (3o, unknown compound)

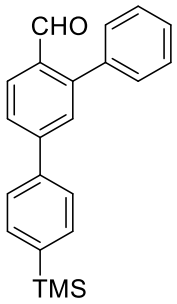
The general procedure was applied to *N*-*tert*-butyl-1-(3-(methylthio)-4'-(trifluoromethoxy)-[1,1'-biphenyl]-4-yl)methanimine (147 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (100 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.69 (dd, J = 9.0, 2.4 Hz, 3H), 7.64 (d, J = 1.9 Hz, 1H), 7.55–7.48 (m, 3H), 7.44 (dd, J = 7.6, 2.0 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 149.6, 146.7, 144.8, 138.4, 137.7, 132.9, 130.2, 129.5, 128.9, 128.7, 128.5, 128.5, 126.5, 121.9, 121.5 (q, J = 256.2). ^{19}F NMR (377 MHz, $CDCl_3$): δ = –57.75. HRMS (ESI^+): calcd for $C_{20}H_{13}OF_3$ $[M+H]^+$ 343.0940, found 343.0935.



4-Hydroxy-[1,1':3',1''-terphenyl]-4'-carbaldehyde (3p, unknown compound)

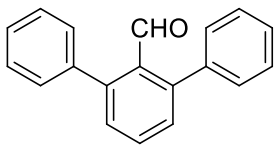
The general procedure was applied to 4'-((*tert*-butylimino)methyl)-3'-(methylthio)-[1,1'-biphenyl]-4-ol (120 mg, 0.4 mmol), phenylmagnesium bromide (1.6 mL, 1.0 M in THF, 1.6 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title

compound as a colorless solid (82 mg, 75% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.89 (s, 1H), 9.65 (s, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.67 (s, 1H), 7.61–7.45 (m, 5H), 7.29 (t, J = 7.8 Hz, 1H), 7.22–7.15 (m, 2H), 6.87 (dd, J = 8.0, 2.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 191.2, 158.0, 145.7, 145.4, 140.0, 137.3, 132.1, 130.1, 128.9, 128.5, 128.2, 126.1, 118.0, 115.7, 114.0. HRMS (ESI$^+$): calcd for $C_{19}H_{14}O_2$ $[M+H]^+$ 275.1061, found 275.1046.



4-(Trimethylsilyl)-[1,1':3',1''-terphenyl]-4'-carbaldehyde (3q, unknown compound)

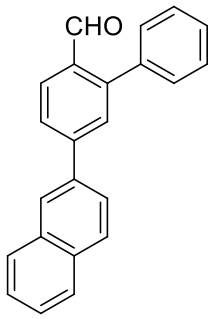
The general procedure was applied to *N-tert*-butyl-1-(3-(methylthio)-4'-(trimethylsilyl)-[1,1'-biphenyl]-4-yl)methanimine (142 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (101 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.04 (s, 1H), 8.14 (d, J = 8.1 Hz, 1H), 7.75 (dd, J = 8.1, 1.8 Hz, 1H), 7.70 (d, J = 1.9 Hz, 1H), 7.67 (s, 4H), 7.54–7.44 (m, 5H), 0.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 146.6, 146.3, 141.1, 140.0, 138.0, 134.1, 132.7, 130.2, 129.5, 128.6, 128.4, 128.3, 126.8, 126.6, –1.0. HRMS (ESI$^+$): calcd for $C_{22}H_{22}SiO$ $[M+H]^+$ 331.1513, found 331.1509.



[1,1':3',1''-Terphenyl]-2'-carbaldehyde (3r, known compound)

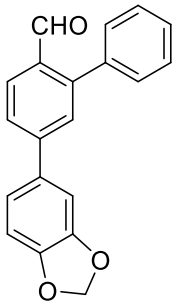
The general procedure was applied to *N-tert*-butyl-1-(3-(methylthio)-[1,1'-biphenyl]-2-

yl)methanimine (113 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (79 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.98 (s, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.47–7.39 (m, 8H), 7.37 (dd, J = 7.7, 1.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.7, 144.4, 139.8, 133.3, 131.7, 130.5, 129.7, 128.3, 127.8. Spectroscopic data are in accordance with those described in the literature.[5]



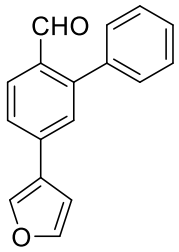
5-(Naphthalen-2-yl)-[1,1'-biphenyl]-2-carbaldehyde (3s, unknown compound)

The general procedure was applied to *N-tert*-butyl-1-(2-(methylthio)-4-(naphthalen–2-yl)phenyl)methanimine (133 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (108 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.07 (s, 1H), 8.18 (d, J = 8.1 Hz, 1H), 8.15 (s, 1H), 7.97–7.83 (m, 4H), 7.82–7.78 (m, 2H), 7.52 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 146.6, 146.1, 137.9, 136.9, 133.6, 133.2, 132.6, 130.2, 129.7, 128.9, 128.6, 128.5, 128.4, 128.3, 127.8, 126.7, 126.7, 125.2. HRMS (ESI$^+$): calcd for $C_{23}H_{16}O$ $[M+H]^+$ 309.1274, found 309.1273.



5-(Benzo[*d*][1,3]dioxol-5-yl)-[1,1'-biphenyl]-2-carbaldehyde (3t, unknown compound)

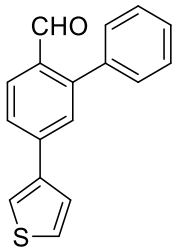
The general procedure was applied to 1-(4-(benzo[*d*][1,3]dioxol-5-yl)-2-(methylthio)phenyl)-*N*–(*tert*-butyl)methanimine (131 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (71 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.99 (s, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.63 (dd, J = 8.2, 1.9 Hz, 1H), 7.57 (d, J = 1.9 Hz, 1H), 7.51–7.40 (m, 5H), 7.19–7.09 (m, 2H), 6.89 (d, J = 8.0 Hz, 1H), 6.00 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 148.5, 148.2, 146.6, 145.9, 137.9, 133.9, 132.2, 130.2, 129.0, 128.5, 128.3, 128.3, 126.1, 121.4, 108.9, 107.7, 101.5. HRMS (ESI$^+$): calcd for $C_{20}H_{14}O_3$ $[M+H]^+$ 303.1016, found 303.1012.



5-(Furan–3-yl)-[1,1'-biphenyl]-2-carbaldehyde (3u, unknown compound)

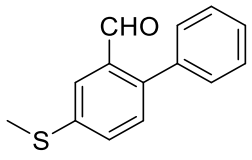
The general procedure was applied to *N-tert*-butyl-1-(4-(furan–3-yl)-2-(methylthio)phenyl)methanimine (109 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (64 mg, 65% yield). ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 9.95 (s, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 0.9 Hz, 1H), 7.61 (dd, J = 8.2, 1.6 Hz, 1H), 7.54 (d, J = 1.8 Hz, 1H), 7.52 (d, J = 1.8 Hz, 1H), 7.50 (s, 1H), 7.49 (s, 2H), 7.42 (dd, J = 7.6, 1.9 Hz, 2H), 6.77 (d, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.8, 146.8, 144.4, 140.2, 137.8, 137.8, 132.4, 130.1, 128.6, 128.5, 128.4, 127.9, 125.6, 125.1, 108.7. HRMS (ESI^+): calcd for $C_{17}H_{12}O_2$ $[M+H]^+$ 249.0910, found 249.0904.



5-(Thiophen–3-yl)-[1,1'-biphenyl]-2-carbaldehyde (3v, unknown compound)

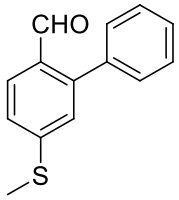
The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)-4-(thiophen-3-yl)phenyl) methanimine (116 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ^{o}C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (72 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.98 (s, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.72 (dd, J = 8.3, 1.6 Hz, 1H), 7.66 (d, J = 1.9 Hz, 1H), 7.62 (dd, J = 2.8, 1.0 Hz, 1H), 7.52–7.46 (m, 4H), 7.45–7.41 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 146.8, 140.9, 140.7, 137.9, 132.4, 130.1, 128.6, 128.5, 128.3, 127.0, 126.3, 125.7, 122.7. HRMS (ESI^+): calcd for $C_{17}H_{12}SO$ $[M+H]^+$ 265.0682, found 265.0678.



4-(Methylthio)-[1,1'-biphenyl]-2-carbaldehyde (3w, unknown compound)

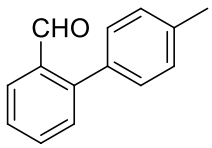
The general procedure was applied to 1-(2,5-bis(methylthio)phenyl)-*N*-(*tert*-butyl)methanimine (101 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in

THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (71 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.87 (s, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.50–7.42 (m, 3H), 7.38 (dd, J = 7.5, 2.1 Hz, 2H), 7.30 (dd, J = 8.3, 1.9 Hz, 1H), 7.20 (d, J = 2.0 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 147.0, 146.5, 137.6, 130.4, 130.1, 128.5, 128.4, 128.0, 126.6, 124.4, 14.8. HRMS (ESI$^+$): calcd for $C_{14}H_{12}SO$ $[M+H]^+$ 229.0682, found 229.0678.



5-(Methylthio)-[1,1'-biphenyl]-2-carbaldehyde (3x, unknown compound)

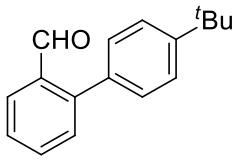
The general procedure was applied to 1-(2,4-bis(methylthio)phenyl)-*N*-(*tert*-butyl)methanimine (101 mg, 0.4 mmol), phenylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (59 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.87 (s, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.50–7.41 (m, 3H), 7.40–7.35 (m, 2H), 7.30 (dd, J = 8.4, 1.9 Hz, 1H), 7.20 (d, J = 2.0 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 146.9, 146.5, 137.6, 130.4, 130.0, 128.5, 128.4, 127.9, 126.4, 124.3, 14.7. HRMS (ESI$^+$): calcd for $C_{14}H_{12}SO$ $[M+H]^+$ 229.0682, found 229.0679.



4'-Methyl-[1,1'-biphenyl]-2-carbaldehyde (3y, known)

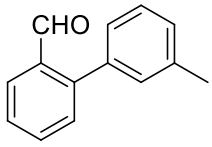
The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), *p*-tolylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to

afford the title compound as a slight yellow oil (72 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 1H), 8.02 (dd, J = 7.7, 1.4 Hz, 1H), 7.63 (td, J = 7.5, 1.5 Hz, 1H), 7.52–7.42 (m, 2H), 7.28 (s, 4H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.7, 146.1, 138.2, 134.9, 133.9, 133.6, 130.9, 130.1, 129.3, 127.7, 127.6, 21.3. Spectroscopic data are in accordance with those described in the literature.[2]



4'-(*Tert*-butyl)-[1,1'-biphenyl]-2-carbaldehyde (3z, known compound)

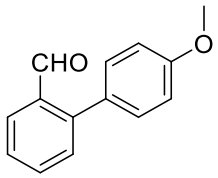
The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), (4-(*tert*-butyl)phenyl)magnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (85 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.54–7.44 (m, 4H), 7.37–7.29 (m, 2H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 151.3, 146.1, 134.8, 133.9, 133.6, 130.9, 130.0, 127.6, 127.6, 125.5, 34.8, 31.5. HRMS (ESI$^+$): calcd for $C_{17}H_{18}O$ $[M+H]^+$ 239.1430, found 239.1430. Spectroscopic data are in accordance with those described in the literature.[10]



3'-Methyl-[1,1'-biphenyl]-2-carbaldehyde (3aa, known compound)

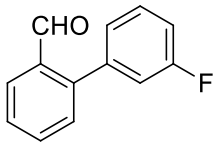
The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), *m*-tolylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (51 mg, 65% yield). ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 9.97 (s, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.51–7.39 (m, 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.27–7.21 (m, 1H), 7.19–7.13 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 146.3, 138.3, 137.8, 133.9, 133.6, 131.0, 130.9, 129.0, 128.4, 127.8, 127.6, 127.4, 21.6. Spectroscopic data are in accordance with those described in the literature.[2]



4'-Methoxy-[1,1'-biphenyl]-2-carbaldehyde (3ab, known compound)

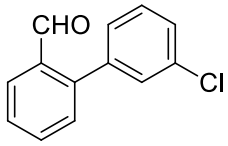
The general procedure was applied to *N-tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), (4-methoxyphenyl)magnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a slight yellow oil (55 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 1H), 8.00 (dd, J = 7.8, 1.4 Hz, 1H), 7.61 (td, J = 7.5, 1.5 Hz, 1H), 7.49–7.40 (m, 2H), 7.33–7.28 (m, 2H), 7.04–6.97 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.7, 159.8, 145.7, 133.8, 133.6, 131.4, 130.9, 130.1, 127.7, 127.5, 114.0, 55.5. Spectroscopic data are in accordance with those described in the literature.[2]



3'-Fluoro-[1,1'-biphenyl]-2-carbaldehyde (3ac, known compound)

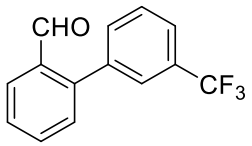
The general procedure was applied to *N-tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), (3-fluorophenyl)magnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (63 mg, 78%

yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.98 (s, 1H), 8.03 (d, J = 7.7 Hz, 1H), 7.69–7.60 (m, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.42 (dd, J = 7.9, 4.0 Hz, 2H), 7.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 164.0 (d, J = 246.2 Hz), 144.6 (d, J = 2.0 Hz), 140.2 (d, J = 7.7 Hz), 133.8, 130.7, 130.1 (d, J = 8.5 Hz), 128.4, 127.9, 126.2 (d, J = 2.9 Hz), 117.2 (d, J = 21.7 Hz), 115.3 (d, J = 20.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ = -112.56. Spectroscopic data are in accordance with those described in the literature.[2]



3'-Chloro-[1,1'-biphenyl]-2-carbaldehyde (3ad, known compound)

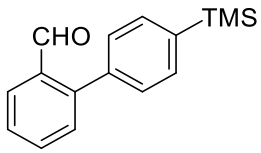
The general procedure was applied to *N-tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), (3-chlorophenyl)magnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (69 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.95 (s, 1H), 8.01 (dd, J = 7.8, 1.4 Hz, 1H), 7.63 (td, J = 7.5, 1.5 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.44-7.38 (m, 4H), 7.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 144.4, 139.7, 134.6, 133.8, 133.8, 130.8, 130.0, 129.7, 128.5, 128.4, 128.4, 128.0. Spectroscopic data are in accordance with those described in the literature.[2]



3'-(Trifluoromethyl)-[1,1'-biphenyl]-2-carbaldehyde (3ae, known compound)

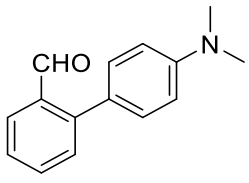
The general procedure was applied to *N-tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), (3- (trifluoromethyl))magnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel

(EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (68 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.95 (s, 1H), 8.06 (dd, J = 7.8, 1.1 Hz, 1H), 7.74–7.65 (m, 3H), 7.64–7.53 (m, 3H), 7.44 (dd, J = 7.7, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 144.3, 138.9, 134.0, 133.8, 131.2 (q, J = 33.0 Hz), 131.0, 129.1, 128.7, 128.3, 126.6 (q, J = 4.0 Hz), 125.4 (q, J = 271.0 Hz), 124.1 (q, J = 4.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ = –62.62. Spectroscopic data are in accordance with those described in the literature.[2]



4'-(Trimethylsilyl)-[1,1'-biphenyl]-2-carbaldehyde (3af, known compound)

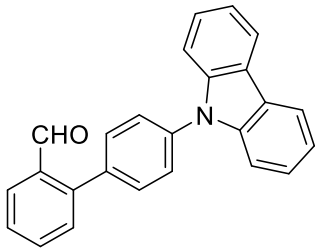
The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), (4-(trimethylsilyl)phenyl)magnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (87 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.01 (s, 1H), 8.04 (dd, J = 7.8, 1.4 Hz, 1H), 7.67–7.62 (m, 3H), 7.53–7.44 (m, 2H), 7.40–7.36 (m, 2H), 0.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6, 146.1, 140.6, 138.2, 133.9, 133.7, 133.5, 130.9, 129.6, 127.9, 127.7, –1.07. Spectroscopic data are in accordance with those described in the literature.[6]



4'-(Dimethylamino)-[1,1'-biphenyl]-2-carbaldehyde (3ag, known compound)

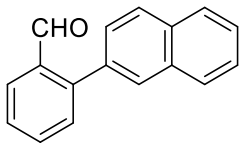
The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), (4-(dimethylamino)phenyl)magnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and

$CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a yellow oil (82 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.94 (s, 1H), 7.89 (dd, J = 7.8, 1.4 Hz, 1H), 7.49 (td, J = 7.5, 1.5 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.20–7.14 (m, 2H), 6.73–6.68 (m, 2H), 2.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.2, 150.4, 146.4, 133.7, 133.5, 131.2, 130.7, 127.6, 126.8, 125.3, 112.2, 40.5. Spectroscopic data are in accordance with those described in the literature.[6]



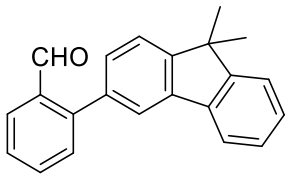
4'-(9*H*-carbazol-9-yl)-[1,1'-biphenyl]-2-carbaldehyde (3ah, known compound)

The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), (4-(9*H*-carbazol-9-yl)phenyl)magnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (124 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.21 (s, 1H), 8.21 (d, J = 7.8 Hz, 2H), 8.14 (d, J = 7.8 Hz, 1H), 7.72 (dd, J = 13.6, 7.4 Hz, 3H), 7.65–7.52 (m, 6H), 7.49 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.4 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.3, 145.0, 140.8, 137.9, 136.9, 133.93, 133.90, 131.7, 130.9, 128.3, 128.1, 127.0, 126.2, 123.7, 120.5, 120.4, 109.9. Spectroscopic data are in accordance with those described in the literature.[6]



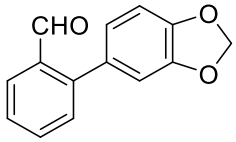
2-(Naphthalen–2-yl)benzaldehyde (3ai, known compound)

The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), naphthalen–2-ylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (72 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.04 (s, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.99–7.87 (m, 3H), 7.83 (s, 1H), 7.68 (t, J = 7.4 Hz, 1H), 7.59–7.51 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6, 146.0, 135.3, 134.1, 133.7, 133.1, 132.9, 131.2, 129.6, 128.3, 128.3, 128.0, 127.9, 127.8, 127.0, 126.8. Spectroscopic data are in accordance with those described in the literature.[2]



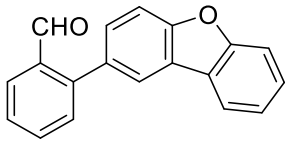
2-(9,9-Dimethyl-9*H*-fluoren–3-yl)benzaldehyde (3aj, known compound)

The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), (9,9-dimethyl-9*H*-fluoren–2-yl)magnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (106 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.09 (s, 1H), 8.09 (d, J = 7.7 Hz, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.82–7.77 (m, 1H), 7.68 (t, J = 7.3 Hz, 1H), 7.58–7.46 (m, 4H), 7.41–7.35 (m, 3H), 1.56 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.7, 154.0, 153.9, 146.5, 139.4, 138.5, 136.7, 134.0, 133.6, 131.0, 129.3, 127.8, 127.7, 127.3, 124.6, 122.8, 120.4, 120.0, 47.1, 27.2. Spectroscopic data are in accordance with those described in the literature.[6]



2-(Benzo[*d*][1,3]dioxol-5-yl)benzaldehyde (3ak, known compound)

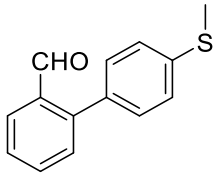
The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), benzo[*d*][1,3]dioxol-5-ylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (77 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 1H), 7.98 (dd, J = 7.8, 1.4 Hz, 1H), 7.60 (td, J = 7.5, 1.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.40 (dd, J = 7.7, 1.2 Hz, 1H), 6.91–6.85 (m, 2H), 6.79 (dd, J = 7.9, 1.8 Hz, 1H), 6.03 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.5, 148.0, 147.9, 145.6, 134.0, 133.6, 131.7, 130.8, 127.7, 127.7, 124.2, 110.4, 108.3, 101.5. HRMS (ESI$^+$): calcd for $C_{14}H_{10}O_3$ $[M+H]^+$ 227.0703, found 227.0704. Spectroscopic data are in accordance with those described in the literature.[11]



2-(Dibenzo[*b,d*]furan–2-yl)benzaldehyde (3al, known compound)

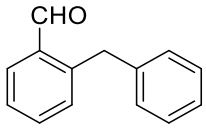
The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), dibenzo[*b,d*]furan–3-ylmagnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (87 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.04 (s, 1H), 8.11–8.04 (m, 1H), 7.99–7.94 (m, 2H), 7.70–7.64 (m, 2H), 7.62 (d, J = 8.2 Hz, 1H), 7.56–7.52 (m, 2H), 7.52–7.45 (m, 2H), 7.38 (t, J = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6, 156.9, 156.1, 146.0, 134.1, 133.7, 132.6, 131.3, 129.3, 127.89, 127.87, 127.8, 124.7, 123.8, 123.2, 122.3, 121.0, 112.0, 111.7. HRMS (ESI$^+$): calcd for $C_{19}H_{12}O_2$ $[M+H]^+$ 273.0910,

found 273.0915. Spectroscopic data are in accordance with those described in the literature.[12]



4'-(Methylthio)-[1,1'-biphenyl]-2-carbaldehyde (3am, known compound)

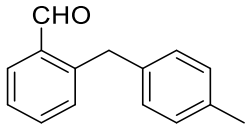
The general procedure was applied to *N-tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), (4-(methylthio)phenyl)magnesium bromide (1.2 mL, 1.0 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a slight yellow oil (81 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.88 (s, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.50–7.43 (m, 3H), 7.39 (d, J = 2.4 Hz, 2H), 7.31 (dd, J = 8.4, 1.9 Hz, 1H), 7.20 (d, J = 1.9 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 147.0, 146.5, 137.6, 130.4, 130.1, 128.6, 128.4, 128.0, 126.6, 124.4, 14.8. HRMS (ESI$^+$): calcd for $C_{14}H_{12}OS$ $[M+H]^+$ 229.0682, found 229.0677. Spectroscopic data are in accordance with those described in the literature.[13]



2-Benzylbenzaldehyde (3an, known compound)

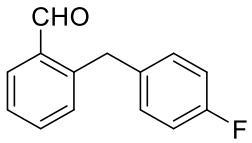
The general procedure was applied to *N-tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), benzylmagnesium bromide (2.4 mL, 0.5 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (54mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.26 (s, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.54 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.4 Hz, 3H), 7.20 (t, J = 7.2 Hz, 1H), 7.15 (d, J = 7.5 Hz,

2H), 4.46 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.5, 143.1, 140.4, 134.1, 134.0, 132.2, 131.8, 128.9, 128.7, 127.1, 126.4, 38.2. Spectroscopic data are in accordance with those described in the literature.[7]



2-(4-Methylbenzyl)benzaldehyde (3ao, known compound)

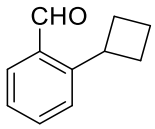
The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), (4-methylbenzyl)magnesium bromide (2.4 mL, 0.5 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (70 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.18 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.00 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 4.33 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.5, 143.5, 137.4, 136.0, 134.0, 131.9, 131.7, 129.4, 128.8, 127.0, 37.7, 21.1. HRMS (ESI$^+$): calcd for $C_{15}H_{14}O$ $[M+H]^+$ 211.1117, found 211.1123. Spectroscopic data are in accordance with those described in the literature.[14]



2-(4-Fluorobenzyl)benzaldehyde (3ap, known compound)

The general procedure was applied to *N*-*tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), (4-fluorobenzyl)magnesium bromide (2.4 mL, 0.5 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow oil (41 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.21 (s, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.54

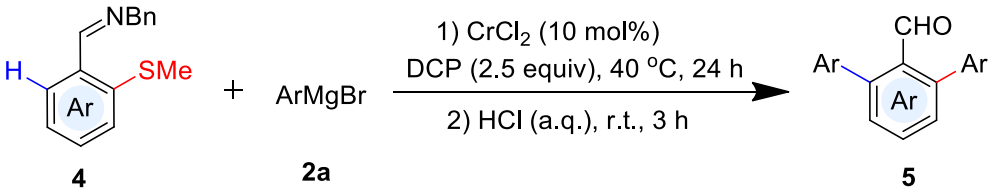
(t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.25 (d, J = 7.7 Hz, 1H), 7.11 (dd, J = 8.3, 5.3 Hz, 2H), 6.96 (t, J = 8.6 Hz, 2H), 4.42 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6, 162.8 (d, J = 243.1 Hz), 142.9, 136.1 (d, J = 3.2 Hz), 134.1, 134.0, 133.0, 131.7, 130.3 (d, J = 7.9 Hz), 127.3, 115.4 (d, J = 21.3 Hz), 37.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -116.97. Spectroscopic data are in accordance with those described in the literature.[7]



2-Cyclobutylbenzaldehyde (3aq, unknown compound)

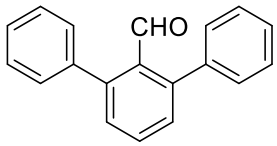
The general procedure was applied to *N-tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), cyclobutylmagnesium bromide (2.4 mL, 0.5 M in THF, 1.2 mmol) and $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/200) to afford the title compound as a slight yellow oil (50 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.28 (s, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 2.45–2.38 (m, 2H), 2.29–2.03 (m, 4H), 1.92–1.84 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4, 148.2, 134.1, 133.6, 130.6, 127.0, 126.3, 37.2, 29.8, 18.7. HRMS (ESI$^+$): calcd for $C_{11}H_{12}O$ $[M+H]^+$ 161.0961, found 161.0966.

5. General Procedure for Cr-Catalyzed Diarylation of C(aryl)–S and C(aryl)–H Bonds



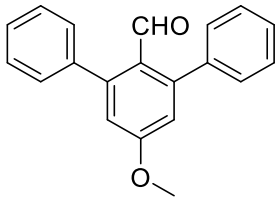
In a dried Schlenk tube were placed an *ortho*-methylthio-containing aromatic aldimine 1 (0.4 mmol) and $CrCl_2$ (5 mg, 0.04 mmol), then 1,2-dichloropropane (98 μL, 1 mmol), aromatic Grignard reagent (1.6 mL, 1 M in THF, 1.6 mmol) and THF (1 mL) was dropwise added by a syringe under atmosphere of nitrogen, and the mixture was stirred

at 40 °C for 24 h. After quenched by 3 N HCl (1 mL), the resulting mixture was further stirred at room temperature, and then extracted with ethyl acetate (3 x 10 mL). After removal of the volatiles under vacuum, the crude product was purified by silica gel chromatography to afford the desired product.



[1,1':3',1''-Terphenyl]-2'-carbaldehyde (5a, known compound)

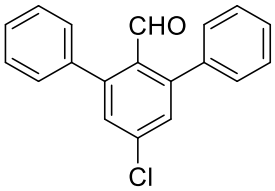
The general procedure was applied to *N*–benzyl-1-(2-(methylthio)phenyl)methanimine (97 mg, 0.4 mmol), phenylmagnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (72 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.98 (s, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.47–7.39 (m, 8H), 7.37 (dd, J = 7.7, 1.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 144.3, 139.7, 133.2, 131.6, 130.4, 129.6, 128.2, 127.7. Spectroscopic data are in accordance with those described in the literature.[5]



5'-Methoxy-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5b, known compound)

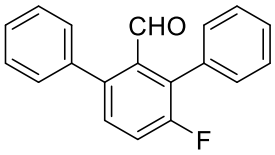
The general procedure was applied to *N*-benzyl-1-(4-methoxy-2-(methylthio)phenyl)methanimine (109 mg, 0.4 mmol), phenylmagnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a slight yellow solid (84 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.83 (s, 1H), 7.45 (d, J = 5.7 Hz, 2H), 7.44–7.40 (m, 4H), 7.37 (dd, J = 7.5, 1.9 Hz, 4H), 6.88 (s, 2H), 3.91 (s, 3H). ^{13}C NMR (100

MHz, $CDCl_3$): δ = 191.8, 161.6, 147.7, 140.1, 129.5, 128.2, 127.8, 126.1, 116.0, 55.8. Spectroscopic data are in accordance with those described in the literature.[2]



5'-Chloro-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5c, known compound)

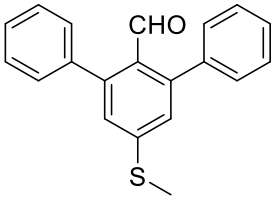
The general procedure was applied to *N*-benzyl-1-(4-chloro-2-(methylthio)phenyl)methanimine (111 mg, 0.4 mmol), phenylmagnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 ^{o}C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (72 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.89 (s, 1H), 7.45 (m, 6H), 7.40 (s, 2H), 7.37–7.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4, 146.2, 138.5, 137.6, 131.6, 130.4, 129.5, 128.5, 128.3. Spectroscopic data are in accordance with those described in the literature.[8]



4'-Fluoro-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5d, known compound)

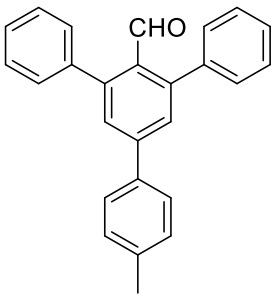
The general procedure was applied to *N*-benzyl-1-(3-fluoro-2-(methylthio)phenyl)methanimine (104 mg, 0.4 mmol), phenylmagnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 ^{o}C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (65 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.84 (s, 1H), 7.45 (m, 6H), 7.41–7.37 (m, 2H), 7.34 (d, J = 7.3 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6 (d, J = 2.9 Hz), 159.2 (d, J = 247.4 Hz), 140.4 (d, J = 3.7 Hz), 138.7, 135.0 (d, J = 2.0 Hz), 132.3, 131.9 (d, J = 7.9 Hz), 131.0, 130.8, 130.3, 129.8, 128.4, 128.3, 128.0, 119.3 (d, J = 23.4 Hz). ^{19}F

NMR (377 MHz, $CDCl_3$): δ = –115.90. Spectroscopic data are in accordance with those described in the literature.[5]



5'-(Methylthio)-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5e, unknown compound)

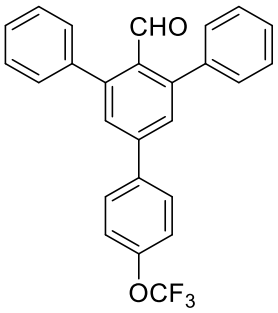
The general procedure was applied to *N*-benzyl-1-(2,4-bis(methylthio)phenyl)methanimine (115 mg, 0.4 mmol), phenylmagnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a slight yellow solid (81 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.88 (s, 1H), 7.48–7.42 (m, 6H), 7.38 (d, J = 2.3 Hz, 2H), 7.36 (d, J = 1.8 Hz, 2H), 7.19 (s, 2H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.3, 145.3, 144.7, 139.6, 129.5, 129.2, 128.3, 127.9, 126.7, 14.8. HRMS (ESI^+): calcd for $C_{20}H_{16}SO$ $[M+H]^+$ 305.0995, found 305.0963.



5'-(*p*-Tolyl)-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5f, unknown compound)

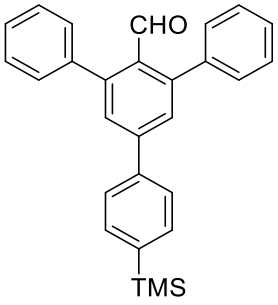
The general procedure was applied to *N*–benzyl-1-(4'-methyl-3-(methylthio)-[1,1'-biphenyl]-4-yl)methanimine (133 mg, 0.4 mmol), phenylmagnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (127 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.05 (s, 1H), 7.68 (s, 2H), 7.64 (d, J = 7.9 Hz,

2H), 7.52 (d, J = 7.1 Hz, 2H), 7.49 (t, J = 5.7 Hz, 8H), 7.33 (d, J = 7.8 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.1, 145.3, 144.2, 140.0, 138.60, 136.45, 131.43, 129.82, 129.65, 128.85, 128.28, 127.78, 127.28, 21.26. HRMS (ESI^+): calcd for $C_{26}H_{20}O$ $[M+H]^+$ 349.1587, found 349.1585.



5'-(4-(Trifluoromethoxy)phenyl)-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5g, unknown compound)

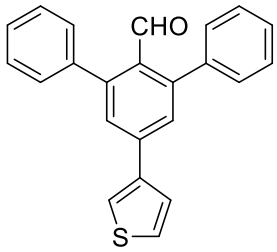
The general procedure was applied to *N*-benzyl-1-(3-(methylthio)-4'-(trifluoromethoxy)-[1,1'-biphenyl]-4-yl)methanimine (161 mg, 0.4 mmol), phenylmagnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (113.4 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 1H), 7.74–7.70 (m, 2H), 7.62 (s, 2H), 7.52–7.42 (m, 10H), 7.34 (d, J = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.1, 149.6, 145.4, 142.8, 139.6, 138.2, 132.1, 129.7, 129.1, 128.9, 128.4, 128.0, 121.9, 121.5 (q, J = 255.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ = –57.71. HRMS (ESI^+): calcd for $C_{26}H_{17}FO_3$ $[M+H]^+$ 419.1253, found 419.1248.



5'-(4-(Trimethylsilyl)phenyl)-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5h,

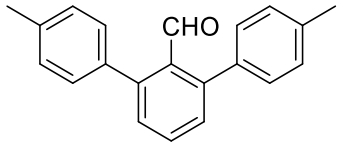
unknown compound)

The general procedure was applied to *N*–benzyl-1-(3-(methylthio)-4'-(trimethylsilyl)-[1,1'-biphenyl]-4-yl)methanimine (157 mg, 0.4 mmol), phenylmagnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 ^oC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (124 mg, 76% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.99 (s, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 7.6 Hz, 4H), 7.48–7.44 (m, 5H), 7.44–7.40 (m, 5H), 0.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 145.3, 144.4, 141.2, 139.9, 139.8, 134.2, 131.8, 129.7, 129.2, 128.4, 126.8, –1.0. HRMS (ESI^+): calcd for $C_{28}H_{26}SiO$ $[M+H]^+$ 407.1826, found 407.1821.



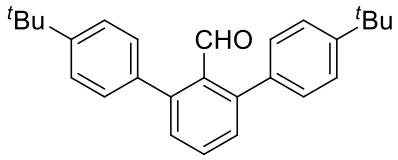
5'-(Thiophen–3-yl)-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5i, unknown compound)

The general procedure was applied to *N*-benzyl-1-(2-(methylthio)-4-(thiophen–3-yl)phenyl)methanimine (130 mg, 0.4 mmol), phenylmagnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 ^oC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (93 mg, 68% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.98 (s, 1H), 7.64 (s, 3H), 7.50 (d, J = 6.1 Hz, 2H), 7.47 (d, J = 3.9 Hz, 4H), 7.44 (t, J = 2.4 Hz, 4H), 7.42 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 145.5, 140.7, 139.9, 138.7, 131.5, 129.6, 128.33, 128.31, 127.9, 127.0, 126.3, 122.7. HRMS (ESI^+): calcd for $C_{23}H_{16}SO$ $[M+H]^+$ 341.0995, found 341.0992.



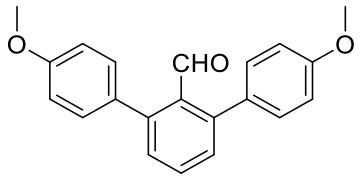
4,4''-Dimethyl-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5j, known compound)

The general procedure was applied to *N*-benzyl-1-(2-(methylthio)phenyl)methanimine (97 mg, 0.4 mmol), *p*-tolylmagnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (98 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 7.7 Hz, 2H), 7.24 (s, 8H), 2.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 144.4, 137.5, 136.8, 133.4, 131.6, 130.3, 129.6, 129.0, 21.3. Spectroscopic data are in accordance with those described in the literature.[9]



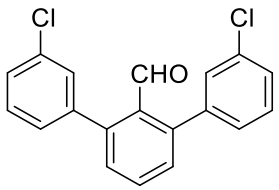
4,4''-Di-*tert*-butyl-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5k, known compound)

The general procedure was applied to *N*-benzyl-1-(2-(methylthio)phenyl)methanimine (97 mg, 0.4 mmol), (4-(*tert*-butyl)phenyl)magnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (110 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.99 (s, 1H), 7.60–7.54 (m, 1H), 7.49–7.43 (m, 4H), 7.39 (d, J = 7.6 Hz, 2H), 7.33–7.28 (m, 4H), 1.39 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.2, 150.7, 144.3, 136.8, 133.5, 131.5, 130.4, 129.5, 125.3, 34.8, 31.5. Spectroscopic data are in accordance with those described in the literature.[5]



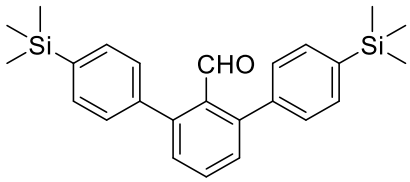
4,4''-Dimethoxy-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5l, known compound)

The general procedure was applied to *N*-benzyl-1-(2-(methylthio)phenyl)methanimine (97 mg, 0.4 mmol), (4-methoxyphenyl)magnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/20) to afford the title compound as a slight yellow solid (102 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1H), 7.59–7.53 (m, 1H), 7.36 (d, J = 7.7 Hz, 2H), 7.30 (d, J = 2.1 Hz, 2H), 7.29 (d, J = 2.1 Hz, 2H), 6.99 (d, J = 2.2 Hz, 2H), 6.97 (d, J = 2.1 Hz, 2H). 3.87 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1, 159.4, 144.0, 133.4, 132.0, 131.6, 131.0, 130.2, 113.7, 55.4. Spectroscopic data are in accordance with those described in the literature.[5]



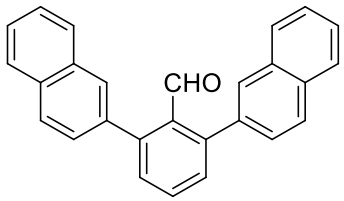
3,3''-Dichloro-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5m, unknown compound)

The general procedure was applied to *N*-benzyl-1-(2-(methylthio)phenyl)methanimine (97 mg, 0.4 mmol), (3-chlorophenyl)magnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a slight yellow solid (106 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.94 (s, 1H), 7.65–7.59 (m, 1H), 7.42–7.34 (m, 8H), 7.22 (d, J = 2.3 Hz, 1H), 7.21 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.7, 143.1, 141.4, 134.3, 132.9, 132.0, 130.9, 129.6, 129.5, 128.1, 128.0. HRMS (ESI$^+$): calcd for $C_{19}H_{12}Cl_2O$ $[M+H]^+$ 327.0338, found 327.0339.



4,4''-Bis(trimethylsilyl)-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5n, known compound)

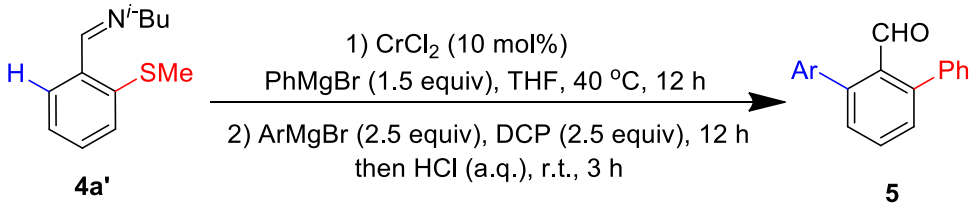
The general procedure was applied to *N*-benzyl-1-(2-(methylthio)phenyl)methanimine (97 mg, 0.4 mmol), (4-(trimethylsilyl)phenyl)magnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/200) to afford the title compound as a slight yellow solid (111 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.97 (s, 1H), 7.58 (dd, J = 7.9, 3.0 Hz, 5H), 7.39 (d, J = 7.7 Hz, 2H), 7.34 (d, J = 8.0 Hz, 4H), 0.31 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 144.4, 140.1, 139.9, 133.34, 133.27, 131.7, 130.5, 129.0, –0.9. Spectroscopic data are in accordance with those described in the literature.[5]



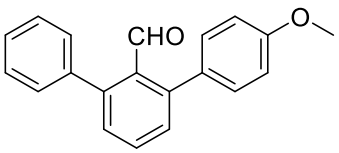
2,6-Di(naphthalen–2-yl)benzaldehyde (5o, known compound)

The general procedure was applied to *N*-benzyl-1-(2-(methylthio)phenyl)methanimine (97 mg, 0.4 mmol), naphthalen–2-ylmagnesium bromide (1.6 mL, 1 M in THF, 1.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) and DCP (98 μL, 1 mmol) at 40 °C for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (102 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.10 (s, 1H), 7.93 (dd, *J* = 18.5, 7.1 Hz, 8H), 7.71–7.66 (m, 1H), 7.61–7.53 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 144.5, 137.3, 133.4, 133.2, 132.7, 131.8, 130.9, 128.6, 128.2, 127.88, 127.87, 127.8, 126.6, 126.4. Spectroscopic data are in accordance with those described in the literature.[5]

6. General Procedure for Cr-Catalyzed Incorporation of Two Different Aryl Scaffolds into Benzaldehydes



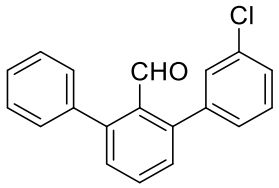
In a dried Schlenk tube were placed an *ortho*-methylthio-containing aromatic aldimine **4a'** (83 mg, 0.4 mmol) and $CrCl_2$ (5 mg, 0.04 mmol), then phenyl Grignard reagent (0.6 mL, 1 M in THF, 0.6 mmol) and THF (1 mL) was drop wise added by a syringe under atmosphere of nitrogen, and the mixture was stirred at 40 °C for 12 h. Then the aromatic Grignard reagent (1.0 mL, 1.0 M in THF, 1.0 mmol) and DCP (98 μL, 1.0 mmol) was drop wise added by a syringe under atmosphere of nitrogen, and the mixture was stirred at 40 °C for 12 h. After quenched by 3 N HCl (1 mL), the resulting mixture was further stirred at room temperature, and then extracted with ethyl acetate (3 x 10 mL). After removal of the volatiles under vacuum, the crude product was purified by silica gel chromatography to afford the desired product **5**.



4-Methoxy-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5p, known compound)

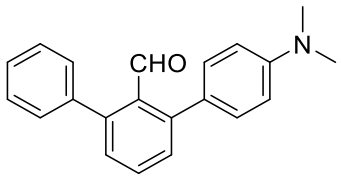
The general procedure was applied to *N*-isobutyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), phenylmagnesium bromide (0.6 mL, 1 M in THF, 0.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 12 h. Then (4-methoxyphenyl)magnesium bromide (1 mL, 1.0 M in THF, 1 mmol) and DCP (98 μL, 1 mmol) at 40 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the title compound as a colorless solid (78 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.98 (s, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.47–7.34 (m, 7H), 7.32 (d, J = 2.1 Hz, 1H), 7.30 (d, J = 2.2 Hz, 1H), 7.00 (d, J = 2.2 Hz, 1H), 6.98 (d, J = 2.1 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9,

159.4, 144.3, 144.1, 139.9, 133.3, 131.8, 131.6, 131.0, 130.5, 130.2, 129.7, 128.2, 127.7, 113.8, 55.4. HRMS (ESI$^+$): calcd for $C_{20}H_{13}O_2$ $[M+H]^+$ 289.1228, found 289.1225. Spectroscopic data are in accordance with those described in the literature.[5]



3-Chloro-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5q, unknown compound)

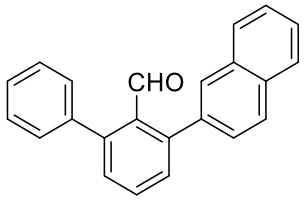
The general procedure was applied to *N*-isobutyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), phenylmagnesium bromide (0.6 mL, 1 M in THF, 0.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 12 h. Then (3-chlorophenyl)magnesium bromide (1 mL, 1.0 M in THF, 1 mmol) and DCP (98 μL, 1 mmol) at 40 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/200) to afford the title compound as a yellow colorless solid (74 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.95 (s, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.48–7.42 (m, 4H), 7.36 (m, 6H), 7.21 (d, J = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 145.2, 142.5, 142.0, 139.2, 134.2, 133.1, 131.9, 130.9, 130.5, 129.9, 129.5, 129.4, 128.5, 128.8, 127.9, 127.8. HRMS (ESI$^+$): calcd for $C_{19}H_{13}OCl$ $[M+H]^+$ 293.0728, found 293.0726.



4-(Dimethylamino)-[1,1':3',1''-terphenyl]-2'-carbaldehyde (5r, unknown compound)

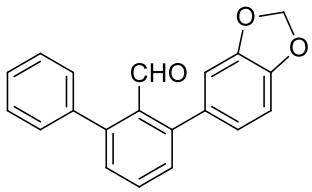
The general procedure was applied to *N*-isobutyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), phenylmagnesium bromide (0.6 mL, 1 M in THF, 0.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) at 40 ºC for 12 h. Then (4-(dimethylamino)phenyl)magnesium bromide (1 mL, 1.0 M in THF, 1 mmol) and DCP

(98 μL, 1 mmol) at 40 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/200) to afford the title compound as a yellow solid (60 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.99 (s, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.46–7.38 (m, 4H), 7.37–7.33 (m, 2H), 7.31 (d, J = 7.5 Hz, 1H), 7.28 (d, J = 2.0 Hz, 1H), 7.26 (d, J = 1.0 Hz, 1H), 6.80 (d, J = 8.8 Hz, 2H), 3.03 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.2, 150.2, 145.2, 143.8, 140.5, 133.2, 131.5, 130.9, 130.3, 129.7, 129.6, 128.1, 127.4, 126.7, 112.1, 40.5. HRMS (ESI^+): calcd for $C_{21}H_{19}NO$ $[M+H]^+$ 302.1539, found 302.1518.



3-(Naphthalen–2-yl)-[1,1'-biphenyl]-2-carbaldehyde (5s, known compound)

The general procedure was applied to *N*-isobutyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), phenylmagnesium bromide (0.6 mL, 1 M in THF, 0.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 12 h. Then naphthalen-2-ylmagnesium bromide (1 mL, 1.0 M in THF, 1 mmol) and DCP (98 μL, 1 mmol) at 40 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/200) to afford the title compound as a colorless solid (76 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 1H), 7.94–7.85 (m, 3H), 7.83 (s, 1H), 7.64 (d, J = 15.3 Hz, 1H), 7.57–7.52 (m, 2H), 7.51 (s, 1H), 7.49 (s, 1H), 7.48–7.42 (m, 4H), 7.42–7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.62, 144.67, 144.34, 139.72, 137.43, 133.37, 133.24, 132.75, 131.76, 130.84, 130.60, 129.76, 128.58, 128.33, 128.26, 127.89, 127.84, 127.79, 126.59, 126.44. HRMS (ESI^+): calcd for $C_{23}H_{16}O$ $[M+H]^+$ 309.1274, found 309.1273. Spectroscopic data are in accordance with those described in the literature.[15]

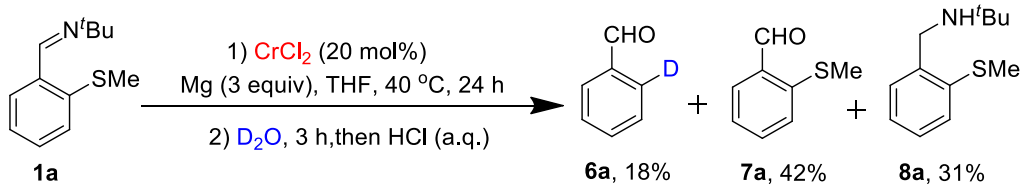


3-(Benzo[*d*][1,3]dioxol-5-yl)-[1,1'-biphenyl]-2-carbaldehyde (5t, known compound)

The general procedure was applied to *N*-isobutyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol), phenylmagnesium bromide (0.6 mL, 1 M in THF, 0.6 mmol), $CrCl_2$ (5 mg, 0.04 mmol) at 40 °C for 12 h. Then benzo[*d*][1,3]dioxol-5-ylmagnesium bromide (1 mL, 1.0 M in THF, 1 mmol) and DCP (98 μL, 1 mmol) at 40 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/200) to afford the title compound as a colorless solid (63 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.97 (s, 1H), 7.62–7.53 (m, 1H), 7.46–7.43 (m, 1H), 7.43–7.40 (m, 2H), 7.39 (s, 1H), 7.37–7.35 (m, 2H), 7.35–7.33 (m, 1H), 6.90–6.85 (m, 2H), 6.79 (dd, J = 7.9, 1.8 Hz, 1H), 6.02 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.7, 147.7, 147.5, 144.3, 144.0, 139.8, 133.5, 133.4, 131.6, 130.4, 130.4, 129.7, 128.3, 127.7, 123.5, 110.2, 108.2, 101.4. HRMS (ESI$^+$): calcd for $C_{20}H_{14}O_3$ $[M+H]^+$ 303.1016, found 303.1017. Spectroscopic data are in accordance with those described in the literature.[5]

7. Mechanistic Studies

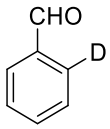
1) Deuterium experiment:



1a **6a**, 18% **7a**, 42% **8a**, 31%

In a dried Schlenk tube were placed magnesium (29 mg, 1.2 mmol) and $CrCl_2$ (10 mg, 0.08 mmol). The tube was heated to around 400 °C under vacuum for 10 min using a heat gun. After cooling to room temperature, *N-tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol) and dry THF (2 mL) was added under nitrogen atmosphere and the resulting mixture was stirred at 40 °C for 24 h. After

treatment of the reaction with D_2O (1 mL) at room temperature for 3 h, HCl (aq) was added for 3 h, and then neutralized with saturated aqueous solution of K_2CO_3, the aqueous phase was extracted with EtOAc for three times. The reaction mixture was detected by GC-MS analysis using tridecane as internal standard. Compound **6a** and **8a** was isolated for NMR spectrum.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 1H), 7.92–7.86 (m, 1H), 7.64 (td, *J* = 7.4, 1.4 Hz, 1H), 7.52 (s, 1H).

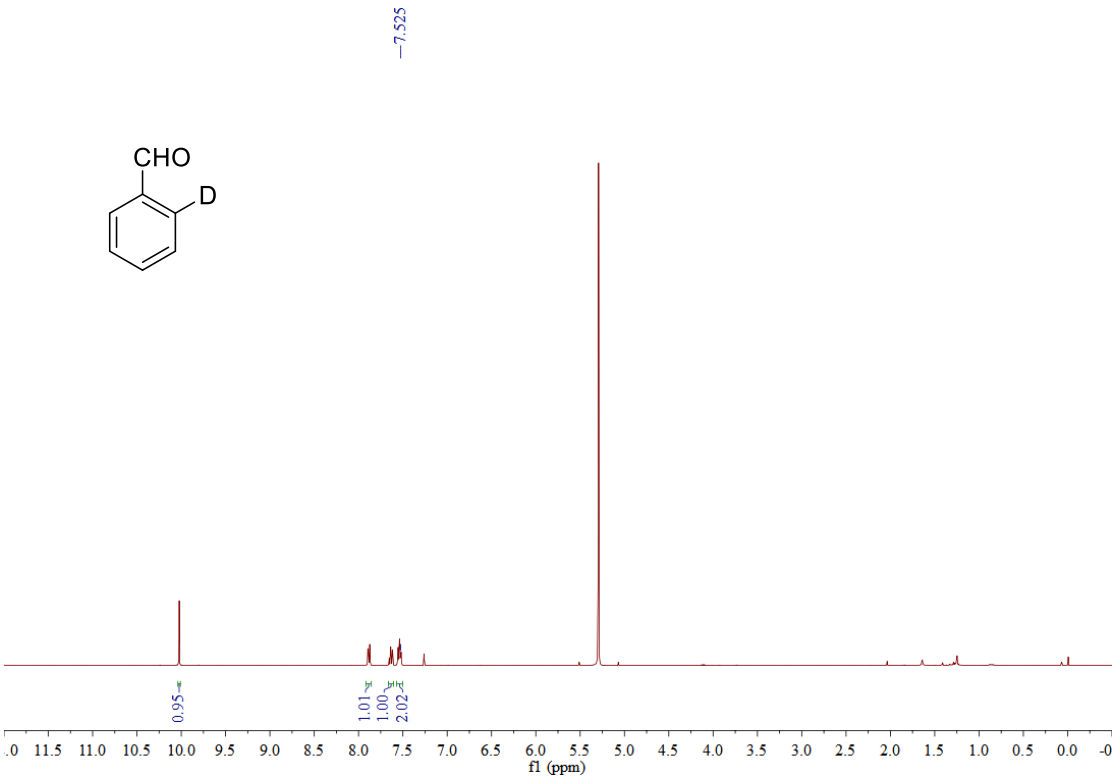
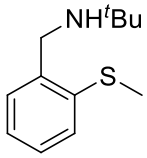


Figure S1. ^{1}H NMR Spectra for compound **6a**



2-Methyl-*N*–(2-(methylthio)benzyl)propan–2-amine

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 7.4 Hz, 1H), 7.26–7.18 (m, 2H), 7.12 (td, *J* = 7.3, 1.7 Hz, 1H), 3.80 (s, 2H), 2.47 (s, 3H), 1.50 (s, 1H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.92, 137.42, 129.35, 127.69, 125.61, 125.24, 51.06, 45.27, 29.17, 15.80. HRMS (ESI+): calcd for $C_{13}H_{21}NS$ [M+H]+ 224.1467, found 224.1461.

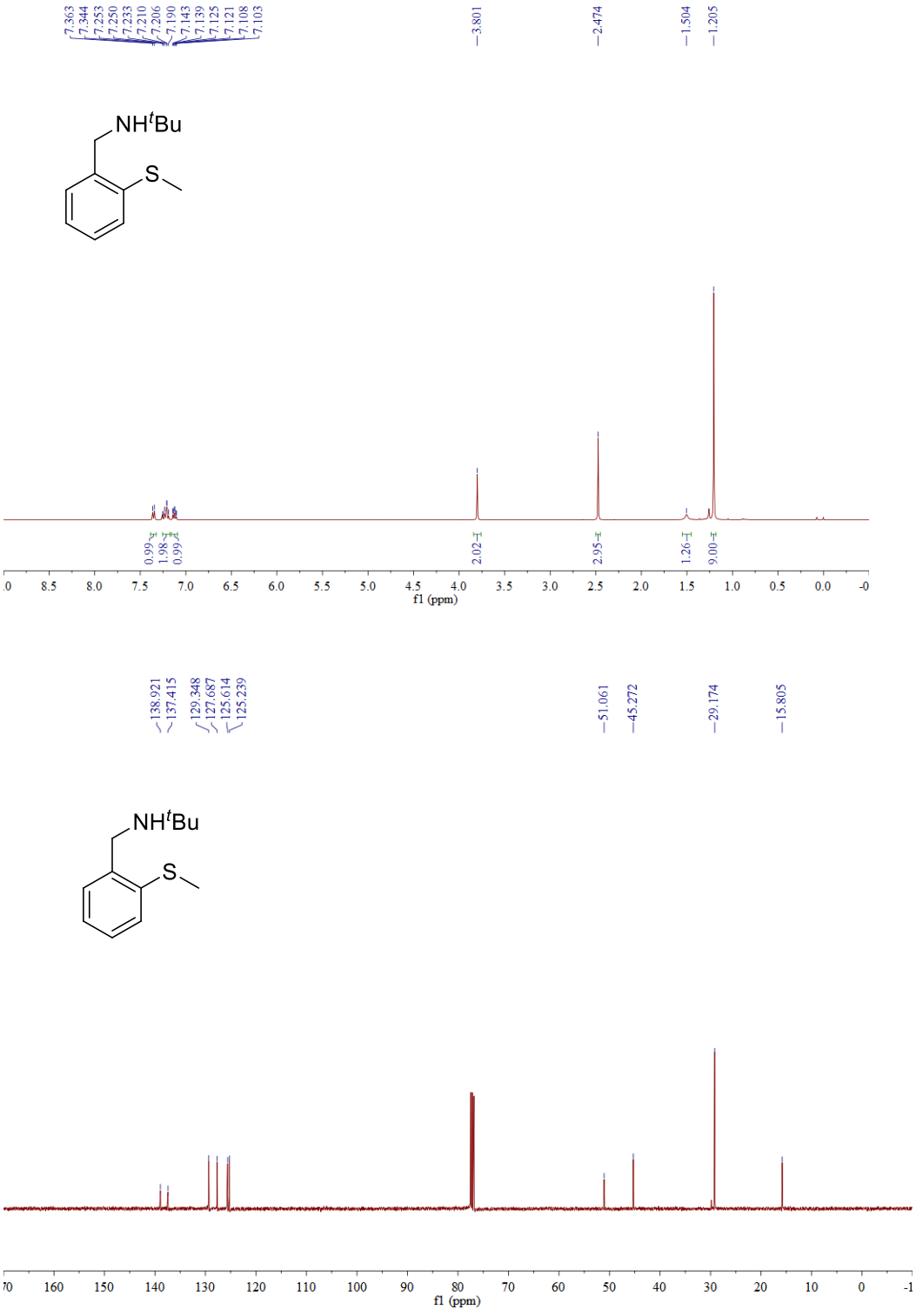
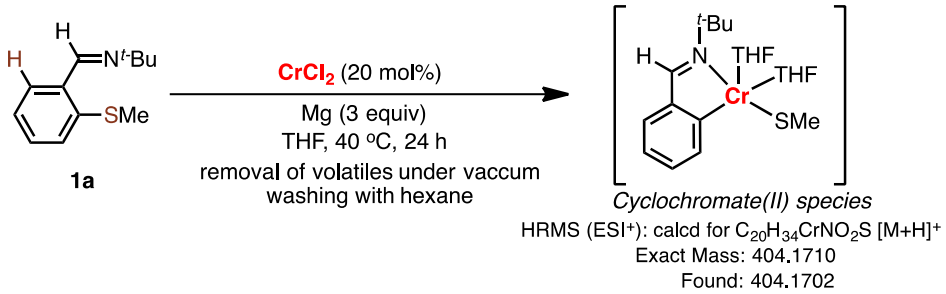


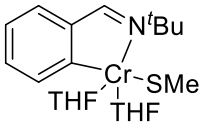
Figure S2. ^{1}H and ^{13}C NMR Spectra for compound **8a**

2) Characterization for the Cr-catalyzed cleavage of C-S bonds to form cyclic chromium intermediates.



HRMS (ESI$^+$): calcd for $C_{20}H_{34}CrNO_2S$ $[M+H]^+$
Exact Mass: 404.1710
Found: 404.1702

In a dried Schlenk tube were placed magnesium (29 mg, 1.2 mmol) and $CrCl_2$ (10 mg, 0.08 mmol). The tube was heated to around 400 °C under vacuum for 10 min using a heat gun. After cooling to room temperature, *N-tert*-butyl-1-(2-(methylthio)phenyl)methanimine (83 mg, 0.4 mmol) and dry THF (2 mL) was added under nitrogen atmosphere and the resulting mixture was stirred at 40 °C for 24 h. After the reaction was completed, high-resolution mass spectrometry samples were directly prepared under nitrogen protection and tested immediately.



HRMS (ESI$^+$): calcd for $C_{20}H_{34}CrNO_2S$ $[M+H]^+$ 404.1710, found 404.1702.

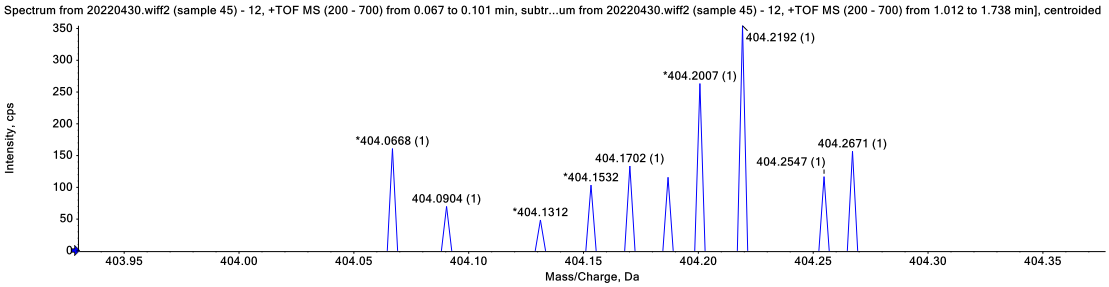
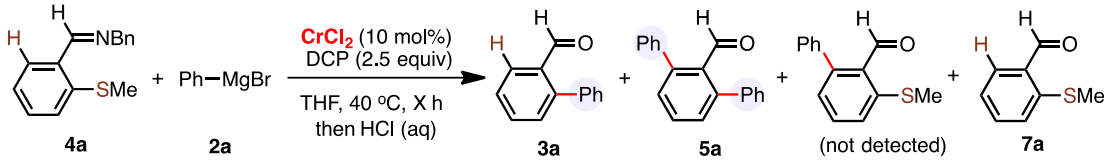


Figure S3. Cyclochromate intermediates characterized by high resolution mass spectrometry.

3) Reaction profile for the Cr-catalyzed arylation of C(aryl)–SMe and C(aryl)–H bonds

In a dried Schlenk tube were placed an *ortho*-methylthio-containing aromatic aldimine **4a** (0.4 mmol) and $CrCl_2$ (5 mg, 0.04 mmol), then 1,2-dichloropropane (98 μL, 1 mmol), PhMgBr (1.6 mL, 1 M in THF, 1.6 mmol) and THF (1 mL) was dropwise added by a syringe under atmosphere of nitrogen, and the mixture was stirred at 40 °C. After reacted for X minutes or hours, then quenched by 3 N HCl (1 mL), the resulting mixture was further stirred at room temperature, and then extracted with ethyl acetate (3 x 10 mL). The crude product was purified by silica gel chromatography to give the motifs of **3a, 5a** and **7a** in different time.

Table S7. **Time course for the Cr-catalyzed C(aryl)–S and C-H bonds.**



Time	**3a** (%)	**5a** (%)	**7a** (%)
1 min	57	2	31
3 min	65	3	21
5 min	69	5	13
10 min	72	12	2
0.5 h	60	24	0
1.0 h	43	40	0
1.5 h	26	55	0
2.0 h	18	61	0
3.0 h	8	74	0
4.0 h	2	79	0
6.0 h	0	81	0

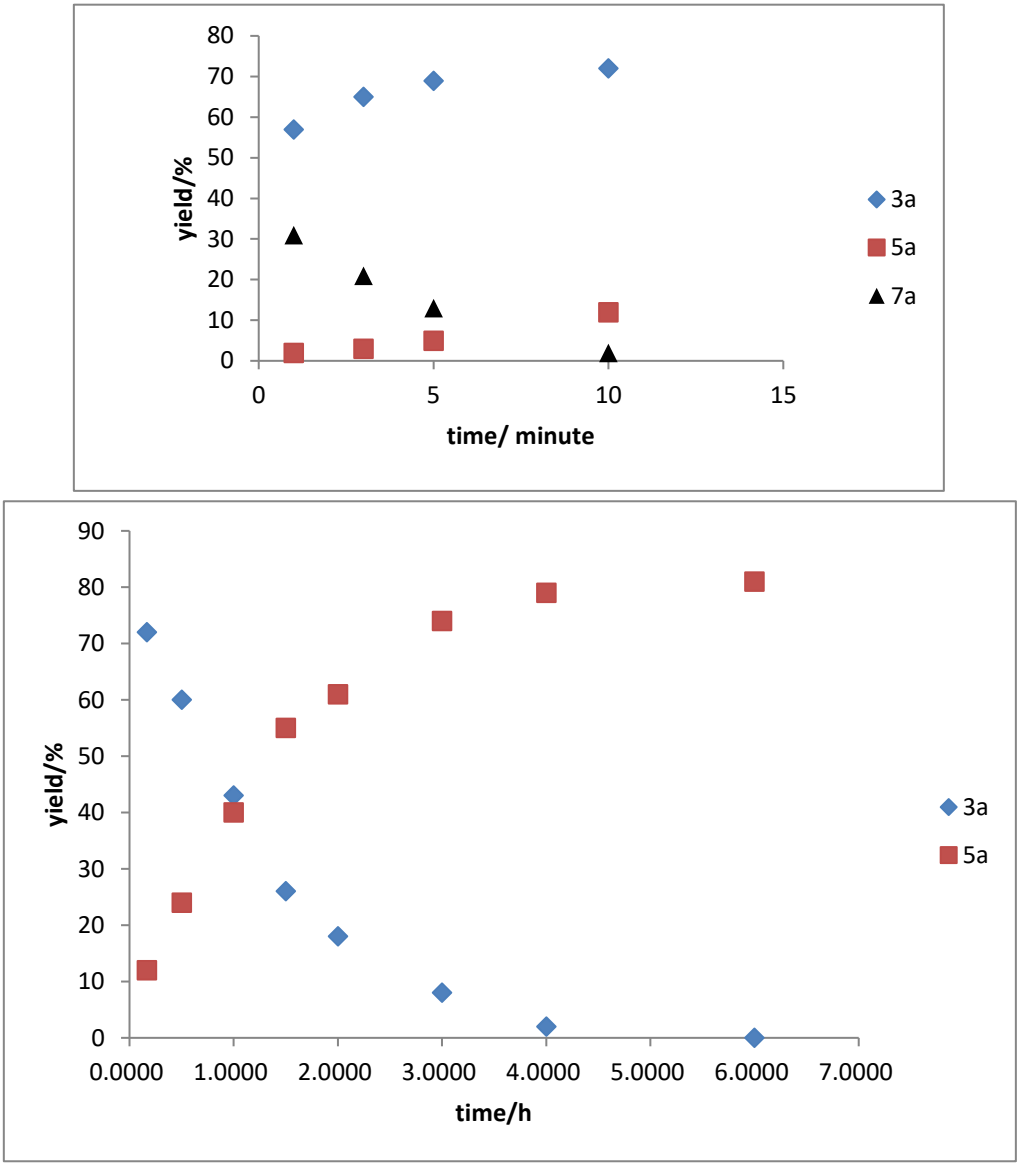


Figure S4. Reaction profile of the Cr-catalyzed difunctionalization of *ortho*-C(aryl)–SMe and *ortho'*-C(aryl)–H bonds.

4) Theoretical Studies for Chromium-Catalyzed Cleavage of C(aryl)–S Bonds

Computational Details. All molecular geometries were optimized in gas phase, employing PBE0 density functional with def2-SVP basis set[16] for all atoms. Optimized minima and transition states (TS) was verified by harmonic vibrational analysis to have no and one proper imaginary frequency, respectively. To refine the calculated energy, single point calculation with larger basis set were then done based on these optimized structures, by using PBE0 functional with def2-TZVP basis set. Solvent effect was modeled in these single point calculations by employing continuum solvation model of SMD[17], with THF as the solvent. The free energies reported in this work were calculated

based on the single point energy at the PBE0/def2-TZVP level, including the Gibbs free energy thermal correction obtained from vibrational analysis at the geometry optimization level (PBE0/def2-SVP) in gas phase at the reaction temperature, as well as Grimme's DFT empirical dispersion correction DFT-D3 with Grimme's[18] original short range damping. All geometry optimizatons and single point calculations were performed with Gaussian 09 program.[19]

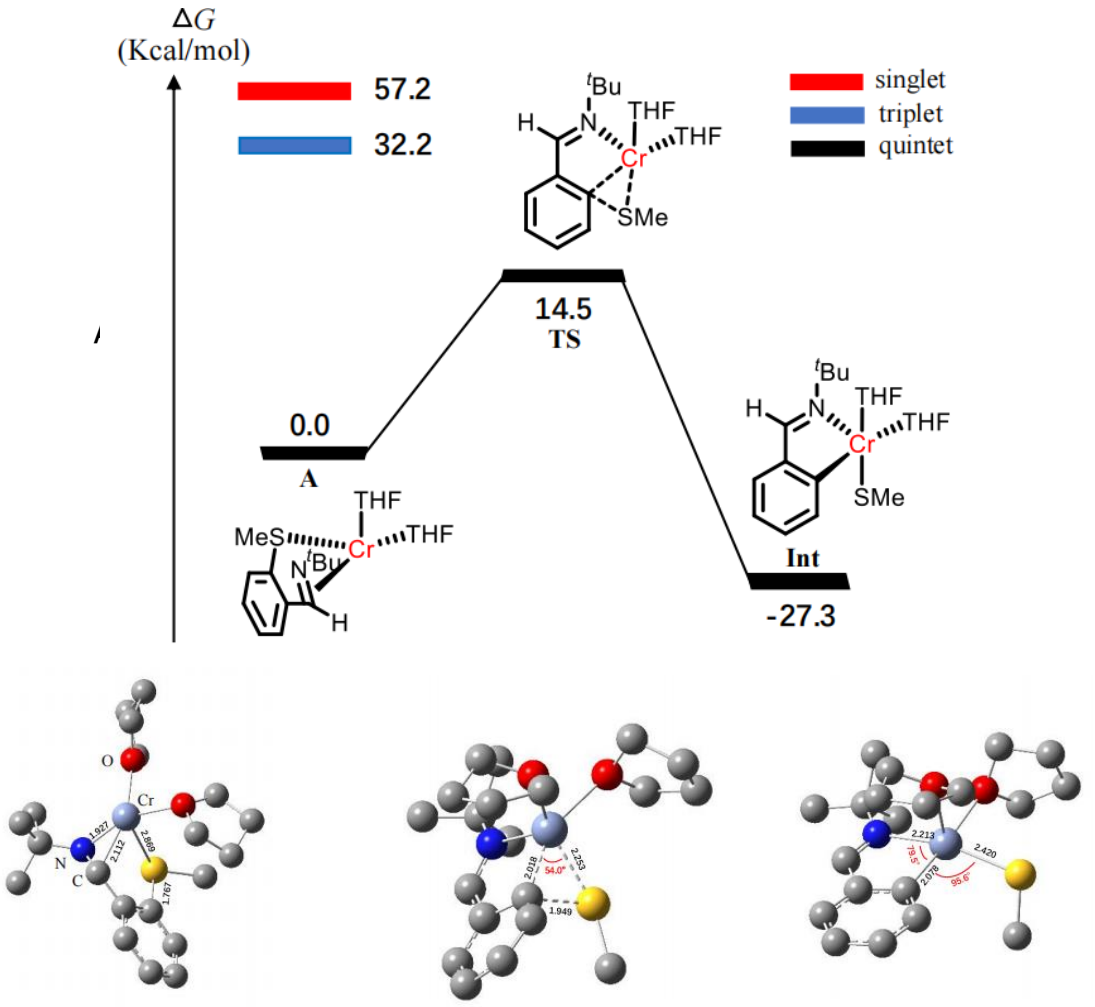


Figure S5. Reaction energy profiles for the cleavage of the C(aryl)–S bond by reactive Cr(0) species, Optimized structures of complex A, TS and intermediate Int for C(aryl)−S bond cleavage (the H atoms are not shown for clarity, and key bond distances are labeled in Å).

Table *S8.* Cartesian Coordinates of Intermediates and Transition States from DFT Calculations

A

Cr	-0.62733100	0.11805300	-0.68244600
C	-0.69500700	-2.93640000	-0.38590500
O	-0.41441200	-1.91446900	-1.36214600
C	0.79261500	-2.23945400	-2.07217900
C	1.56810600	-3.11035900	-1.10994700
C	0.44744400	-3.93919300	-0.49018100
H	-1.68157200	-3.37611500	-0.59859500
H	-0.72985800	-2.45424800	0.60356400
H	1.29021400	-1.29658800	-2.33656600
H	0.52986500	-2.78324500	-2.99715200
H	2.05965200	-2.47881300	-0.35216700
H	2.33682100	-3.71571300	-1.61015200
H	0.70751000	-4.36773700	0.48805700
H	0.17385500	-4.76888600	-1.16078000
C	4.70876000	-0.23002700	0.66393600
C	4.66972700	0.39321200	-0.58553000
C	3.47750300	0.92926900	-1.05593500
C	2.26472900	0.86240800	-0.32939700
C	2.31931400	0.17441200	0.92121500
C	3.52936500	-0.32932800	1.40547800
H	5.64025200	-0.64090700	1.06103000
H	5.57877600	0.47777500	-1.18846100
H	3.45941700	1.43724800	-2.02581200
H	3.56071800	-0.83060000	2.37468200
C	1.03810700	1.39911800	-0.89523900
H	1.20645800	1.90805300	-1.86320500

N	-0.01941100	1.84170900	-0.07100000
C	-0.55172100	3.18309100	-0.22264000
C	-3.00324000	-0.38050000	1.36097300
O	-2.59981200	-0.39597600	-0.01565400
C	-3.70253300	-0.72028800	-0.87289800
C	-4.79004900	-1.21538000	0.06144600
C	-4.51889200	-0.39710300	1.31945700
H	-2.57426600	0.51094600	1.83958700
H	-2.59858900	-1.27851400	1.85980800
H	-3.36603200	-1.46787200	-1.60668200
H	-4.00942600	0.19123800	-1.41436500
H	-4.65895100	-2.29020600	0.26679200
H	-5.79661000	-1.06547900	-0.35340500
H	-4.95695700	-0.83032000	2.22952600
H	-4.90880400	0.62698400	1.20336600
C	-1.03205000	3.47714900	-1.65426300
H	-0.20506500	3.41060400	-2.37883300
H	-1.46574400	4.48742100	-1.74291000
H	-1.80317200	2.74646100	-1.95331600
C	-1.74814500	3.29550900	0.72282800
H	-1.43461000	3.08867800	1.75826900
H	-2.51625200	2.55433600	0.44758500
H	-2.20755400	4.29679600	0.68892100
C	0.50810000	4.21718000	0.17429200
H	0.11936100	5.24821900	0.12732600
H	1.38159600	4.15262200	-0.49415500
H	0.85994000	4.02199300	1.19989200
S	0.79127300	-0.11806200	1.79999000
C	1.20071000	-1.61442100	2.74184300
H	0.24558100	-1.97366600	3.15371200

H	1.63628700	-2.39678300	2.10222100
H	1.87536000	-1.40974300	3.58634500

TS

Cr	0.41173000	-0.09231300	0.05625700
C	0.00770800	-0.57196000	2.99740200
O	0.53163500	-1.31918300	1.88981500
C	-0.06896100	-2.62364500	1.92098600
C	-1.39268300	-2.47654400	2.69115900
C	-1.45098800	-0.98448000	3.04448600
H	0.55478000	-0.84651100	3.91837200
H	0.15349600	0.49559100	2.78720700
H	-0.19851200	-2.94893200	0.87909400
H	0.62448800	-3.32072600	2.42131900
H	-2.25546500	-2.77567000	2.08177700
H	-1.37991900	-3.10289300	3.59518800
H	-2.00794900	-0.42868400	2.27470300
H	-1.91583100	-0.78726100	4.02086300
C	3.32819300	-1.35100900	0.50739300
O	2.59481400	-0.26539100	-0.06260500
C	3.24530000	0.06201400	-1.29755600
C	3.81439400	-1.26470100	-1.83179700
C	3.58615600	-2.26117700	-0.67868000
H	4.26760600	-0.96213600	0.94198600
H	2.71794500	-1.78771600	1.30766500
H	2.49484400	0.51486000	-1.95872500
H	4.03918900	0.80003600	-1.09310300
H	3.29576000	-1.58535400	-2.74524300
H	4.88082100	-1.15551400	-2.07592100
H	2.69137000	-2.87431700	-0.86825400

H	4.43406800	-2.94063200	-0.51299400
C	-3.64296700	-1.57505800	-0.79556800
C	-4.33259400	-0.33301000	-0.96903600
C	-3.62476800	0.84297500	-0.85468800
C	-2.23075200	0.83237000	-0.58136200
C	-1.46253000	-0.42482600	-0.61224800
C	-2.28264000	-1.62301700	-0.62239900
H	-4.21964000	-2.50671500	-0.79100200
H	-5.41047600	-0.32565400	-1.14941400
H	-4.14495400	1.80653700	-0.92015300
H	-1.79365300	-2.60053300	-0.52994700
C	-1.52062300	1.98098500	-0.19277400
H	-2.01908600	2.95996000	-0.24987600
N	-0.26455300	1.88649600	0.22735000
C	0.49991000	3.11360600	0.50340200
C	1.73373100	2.72260500	1.32033200
H	1.45415600	2.34095300	2.31382400
H	2.30658900	1.93416300	0.80984000
H	2.39517100	3.59032000	1.47102300
C	-0.30808600	4.14334500	1.30448200
H	-1.12823400	4.58499400	0.71920200
H	-0.73955300	3.68028700	2.20616500
H	0.34455200	4.97135100	1.62217800
C	0.94916000	3.73466900	-0.82655300
H	1.56032800	4.63768800	-0.66556700
H	1.54433400	3.01383100	-1.40780400
H	0.07536400	4.01396100	-1.43616100
S	-0.18093600	-0.49993000	-2.07831700
C	-1.24635000	-1.11237300	-3.40141100
H	-0.62155400	-1.35686500	-4.26193000

H	-1.79059100	-2.00211700	-3.07971000
H	-1.95934900	-0.33541700	-3.68424100

Int

Cr	0.32013300	-0.14315200	-0.46838000
C	-0.89957200	0.03838800	2.67856700
O	-0.02045000	-0.70003800	1.84532200
C	-0.22398200	-2.08162100	2.13482100
C	-1.68908400	-2.22089500	2.57173400
C	-2.18572600	-0.77214300	2.70093500
H	-0.46110300	0.12837500	3.69140300
H	-1.00808700	1.04506900	2.25361900
H	0.02256000	-2.64399800	1.22179100
H	0.46654400	-2.38592200	2.94222800
H	-2.27751700	-2.77583100	1.82787500
H	-1.75896900	-2.76481800	3.52502100
H	-2.81123100	-0.50129700	1.83823400
H	-2.76940200	-0.59581200	3.61578700
C	3.02412800	-0.19592500	1.28614100
O	2.43596400	0.20421300	0.04813000
C	3.43157200	-0.00818400	-0.95859300
C	4.25777100	-1.21223100	-0.49366300
C	3.77111700	-1.47019800	0.94060100
H	3.71311500	0.59884800	1.62729500
H	2.21534200	-0.31611600	2.01649300
H	2.90694600	-0.18246000	-1.90704900
H	4.04680900	0.90485500	-1.03761100
H	4.06053200	-2.08261700	-1.13317100
H	5.33285300	-0.98316400	-0.52958500
H	3.07317400	-2.32060800	0.95721600

H	4.58694900	-1.67714600	1.64770900
C	-3.88578300	-1.49877000	-1.06342100
C	-4.56419300	-0.28003500	-0.95456600
C	-3.83260700	0.89114800	-0.77878900
C	-2.43178300	0.82407500	-0.70929500
C	-1.71255300	-0.39062100	-0.82239300
C	-2.48905300	-1.54563700	-0.99962500
H	-4.45717600	-2.42252600	-1.20067200
H	-5.65569100	-0.24848800	-1.00703700
H	-4.34402100	1.85501900	-0.68608400
H	-1.98422400	-2.51496700	-1.08189000
C	-1.64527200	2.02702600	-0.47757500
H	-2.17252200	2.99124900	-0.45069900
N	-0.37391300	1.95207800	-0.30494200
C	0.43666600	3.16506600	-0.09644600
C	1.12430300	3.02694300	1.26263600
H	0.38314300	3.02836300	2.07669700
H	1.69824700	2.09354600	1.31323000
H	1.81535200	3.86761800	1.42773300
C	-0.36340800	4.46477500	-0.12134700
H	-0.86944700	4.62156300	-1.08651500
H	-1.11796100	4.50315300	0.67973100
H	0.32406500	5.30921300	0.03313300
C	1.47581500	3.19461100	-1.21858800
H	2.15386000	4.05261400	-1.09333500
H	2.07714500	2.27633500	-1.21410800
H	0.98273400	3.28277200	-2.19917700
S	0.97304000	-2.31579200	-1.31132400
C	0.30046700	-2.33793400	-3.00350800
H	-0.78770200	-2.16682600	-3.01645200

H	0.77074000	-1.57274900	-3.64244700
H	0.49345900	-3.31990200	-3.46584500

A_1

Cr	-0.53633600	0.22803400	0.00680100
C	-1.26913600	-2.31718000	-1.38250800
O	-0.95694600	-0.96013800	-1.73480700
C	-0.05917100	-1.00337700	-2.84404100
C	0.85378500	-2.16487500	-2.52143800
C	-0.12814900	-3.18272400	-1.93513400
H	-2.24394200	-2.58626000	-1.82244300
H	-1.36173000	-2.36131000	-0.28846700
H	0.43729300	-0.02876500	-2.90738800
H	-0.64051800	-1.18568400	-3.76747500
H	1.58644200	-1.84395200	-1.76515000
H	1.39539800	-2.54133800	-3.40059400
H	0.33015700	-3.80609500	-1.15470400
H	-0.50648000	-3.85615700	-2.71847800
C	4.74654900	-0.94780600	1.15954900
C	4.89229800	-0.17085300	0.00657600
C	3.79563500	0.48855700	-0.54450500
C	2.50542100	0.37786200	0.01417900
C	2.38142800	-0.46839400	1.13909800
C	3.47924500	-1.08536300	1.73240500
H	5.60729600	-1.45590000	1.60192900
H	5.87787600	-0.06309900	-0.45621500
H	3.93028400	1.11946800	-1.42927100
H	3.34685800	-1.70958900	2.62050800
C	1.31441900	1.01058100	-0.55748100
H	1.51419100	1.42342800	-1.56192300

N	0.45121200	1.79187400	0.26003200
C	-0.02569100	3.07455800	-0.26828100
C	-2.96955400	-0.64120000	1.80898900
O	-2.50461300	-0.16392600	0.53471900
C	-3.61447700	0.13387000	-0.32834100
C	-4.77759500	-0.62386400	0.27472800
C	-4.48113800	-0.49728700	1.76569300
H	-2.48880800	-0.05170800	2.60283700
H	-2.65728700	-1.69370600	1.91406700
H	-3.33974300	-0.17240400	-1.34684300
H	-3.79318500	1.22342400	-0.31988100
H	-4.74985000	-1.67998800	-0.03932500
H	-5.74993100	-0.20258200	-0.01683800
H	-4.98774600	-1.25368500	2.38133100
H	-4.78226400	0.49781100	2.12978300
C	-0.68354400	2.94626900	-1.65347500
H	0.03197000	2.60829100	-2.41847900
H	-1.09915600	3.90903700	-1.99324000
H	-1.51899400	2.22267200	-1.62632900
C	-1.07456700	3.57873200	0.72275700
H	-0.62599500	3.71060500	1.71992300
H	-1.88580800	2.83763000	0.81966700
H	-1.51547200	4.53789000	0.40584800
C	1.12943300	4.07550900	-0.34334700
H	0.78497900	5.07522300	-0.65636900
H	1.89416900	3.73968200	-1.06133900
H	1.61376600	4.16674700	0.64186300
S	0.68976400	-0.71082700	1.67787300
C	0.66246400	-2.51570900	1.89552700
H	-0.37777100	-2.78627900	2.12929200

H	0.97947200	-3.02171300	0.97224500
H	1.29842700	-2.82570100	2.73703200

A_3

Cr	-0.39674300	0.21200400	-0.31424400
C	-1.66168300	-2.71791700	-0.81766100
O	-0.62936700	-1.77412100	-1.12070200
C	0.54729600	-2.44279900	-1.60758600
C	0.28871400	-3.92077100	-1.38089000
C	-1.22858300	-4.00143300	-1.49921100
H	-2.61992900	-2.32573600	-1.18658600
H	-1.73052600	-2.83999900	0.27717300
H	1.42203300	-2.05325600	-1.06620200
H	0.66623300	-2.20248900	-2.67727600
H	0.60924300	-4.21555600	-0.36886600
H	0.82208700	-4.55224700	-2.10504500
H	-1.66116000	-4.89323700	-1.02402700
H	-1.53372800	-3.99386700	-2.55809300
C	4.79210900	-0.70298700	0.98537100
C	4.91260300	-0.08913800	-0.26548400
C	3.81790300	0.53628700	-0.85497200
C	2.54616500	0.56221000	-0.23947000
C	2.44309500	-0.12508100	0.99965900
C	3.54576200	-0.70955600	1.61774400
H	5.65189700	-1.18360500	1.45887100
H	5.87937100	-0.08176900	-0.77806900
H	3.93561900	1.03782300	-1.82123500
H	3.43203100	-1.20736900	2.58472400
C	1.37179800	1.17102300	-0.85285600
H	1.58757500	1.57665500	-1.85774200

N	0.46813900	1.91148100	-0.02536400
C	-0.09174300	3.13953900	-0.57829700
C	-2.81408200	-0.07785800	1.70811100
O	-2.40735500	0.08264000	0.34095600
C	-3.54050000	0.34767400	-0.49420500
C	-4.73386300	-0.10833900	0.31938000
C	-4.29405900	0.26354000	1.73187300
H	-2.19510800	0.57698400	2.33780500
H	-2.62794700	-1.12506500	2.00159200
H	-3.40230700	-0.19087200	-1.44397000
H	-3.58964800	1.42965200	-0.70926400
H	-4.86599600	-1.19884000	0.22872500
H	-5.66746000	0.37979700	0.00627100
H	-4.83495900	-0.28015400	2.51912500
H	-4.43531500	1.34269100	1.90254300
C	-0.76206700	2.93870400	-1.95152200
H	-0.03676400	2.63190300	-2.72072900
H	-1.25080000	3.86068700	-2.30807000
H	-1.54273300	2.15717500	-1.89238400
C	-1.15641400	3.61052900	0.41368100
H	-0.70411100	3.77191700	1.40474300
H	-1.93389800	2.83735800	0.52707200
H	-1.63979500	4.54717400	0.09079300
C	0.99156400	4.21685500	-0.70227100
H	0.57976800	5.17986200	-1.04835100
H	1.77257100	3.90678000	-1.41451500
H	1.47573100	4.37480000	0.27471300
S	0.77378600	-0.27380200	1.64559500
C	0.75965100	-2.01239800	2.16275100
H	-0.28509400	-2.25111200	2.40976800

H	1.10821700	-2.67300700	1.35658500
H	1.37096500	-2.16734400	3.06291400

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9. ^{1}H, ^{13}C and ^{19}F NMR Spectra

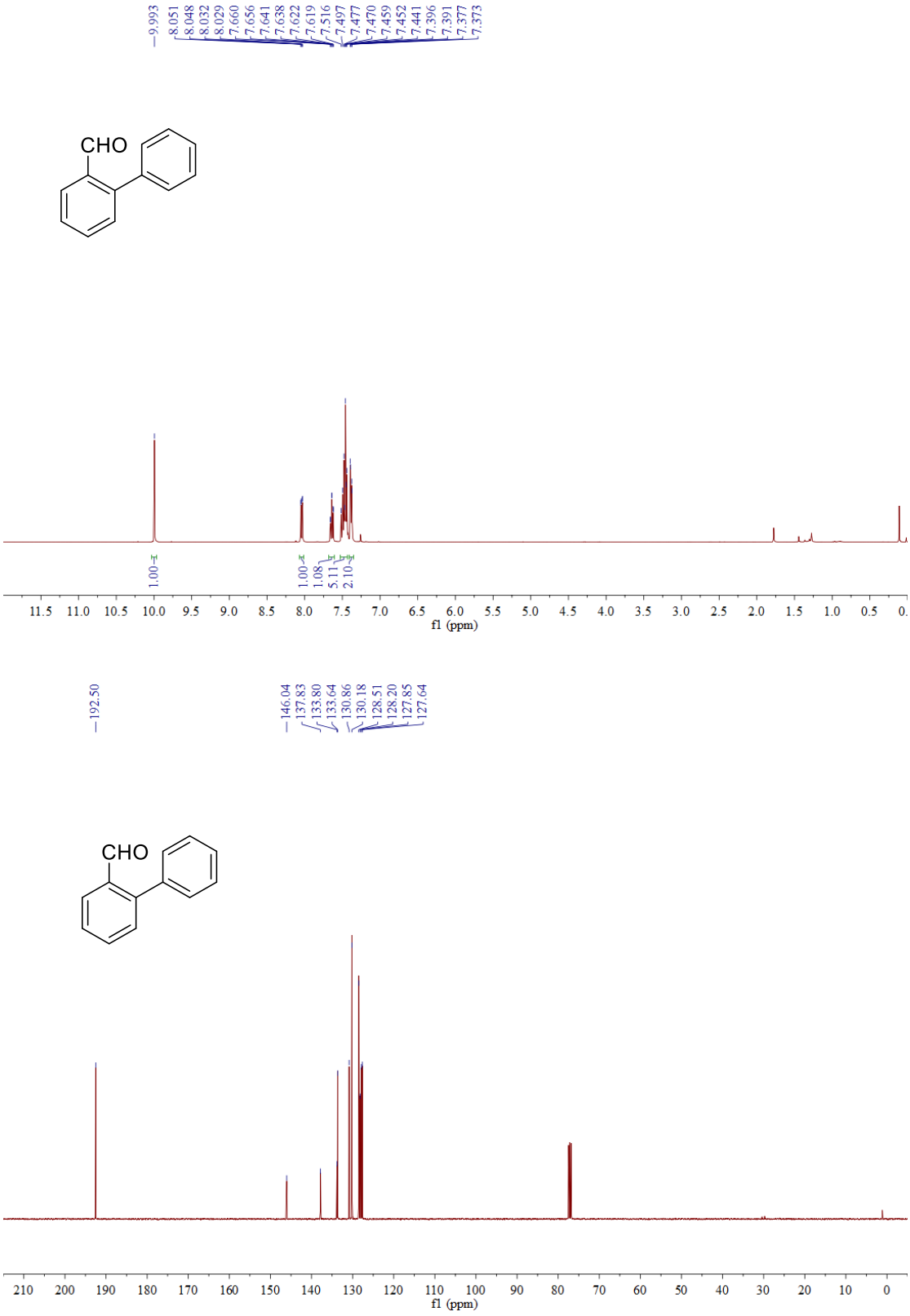


Figure S6. ^{1}H and ^{13}C NMR Spectra for compound **3a**

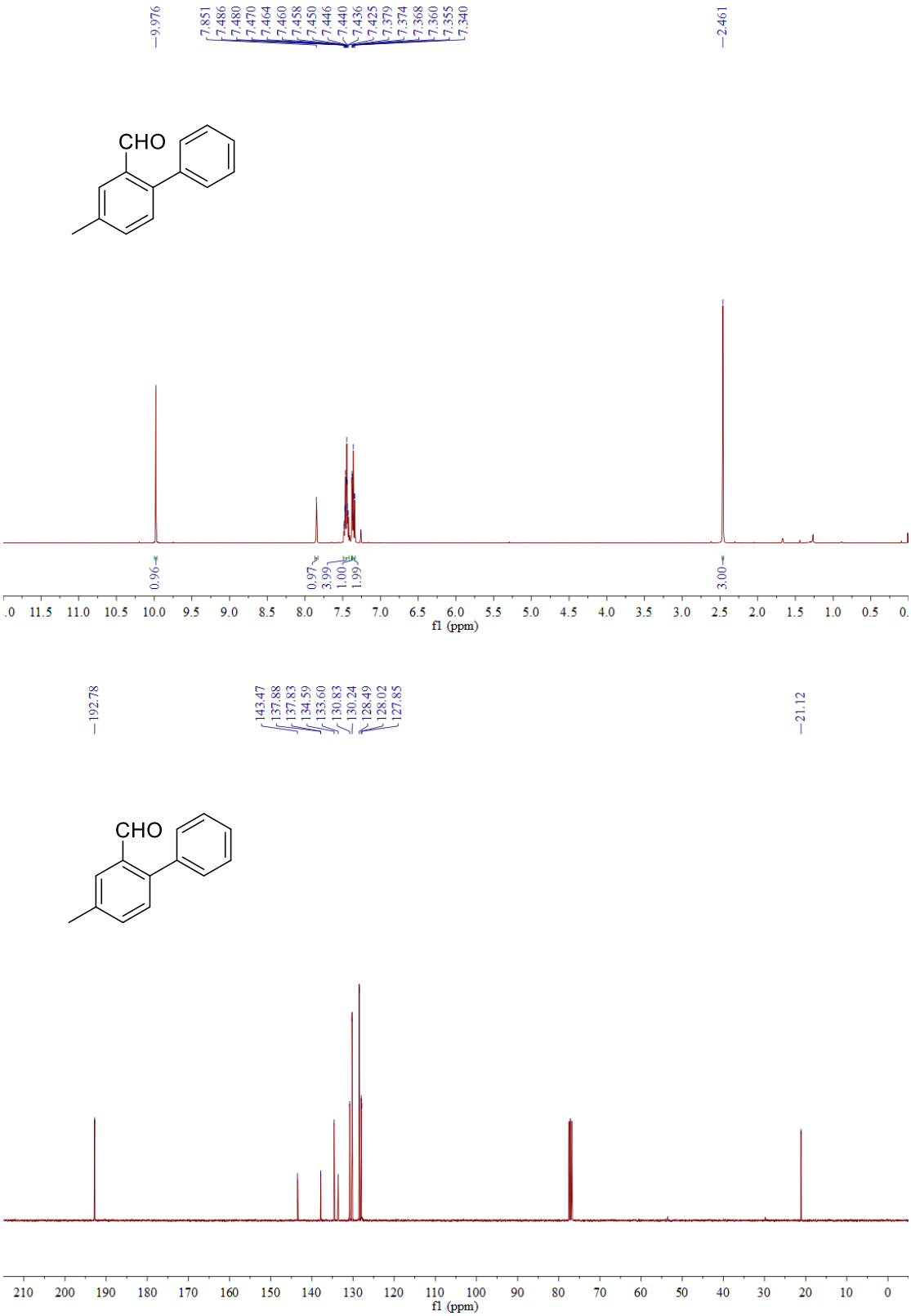


Figure S7. ^{1}H and ^{13}C NMR Spectra for compound **3b**

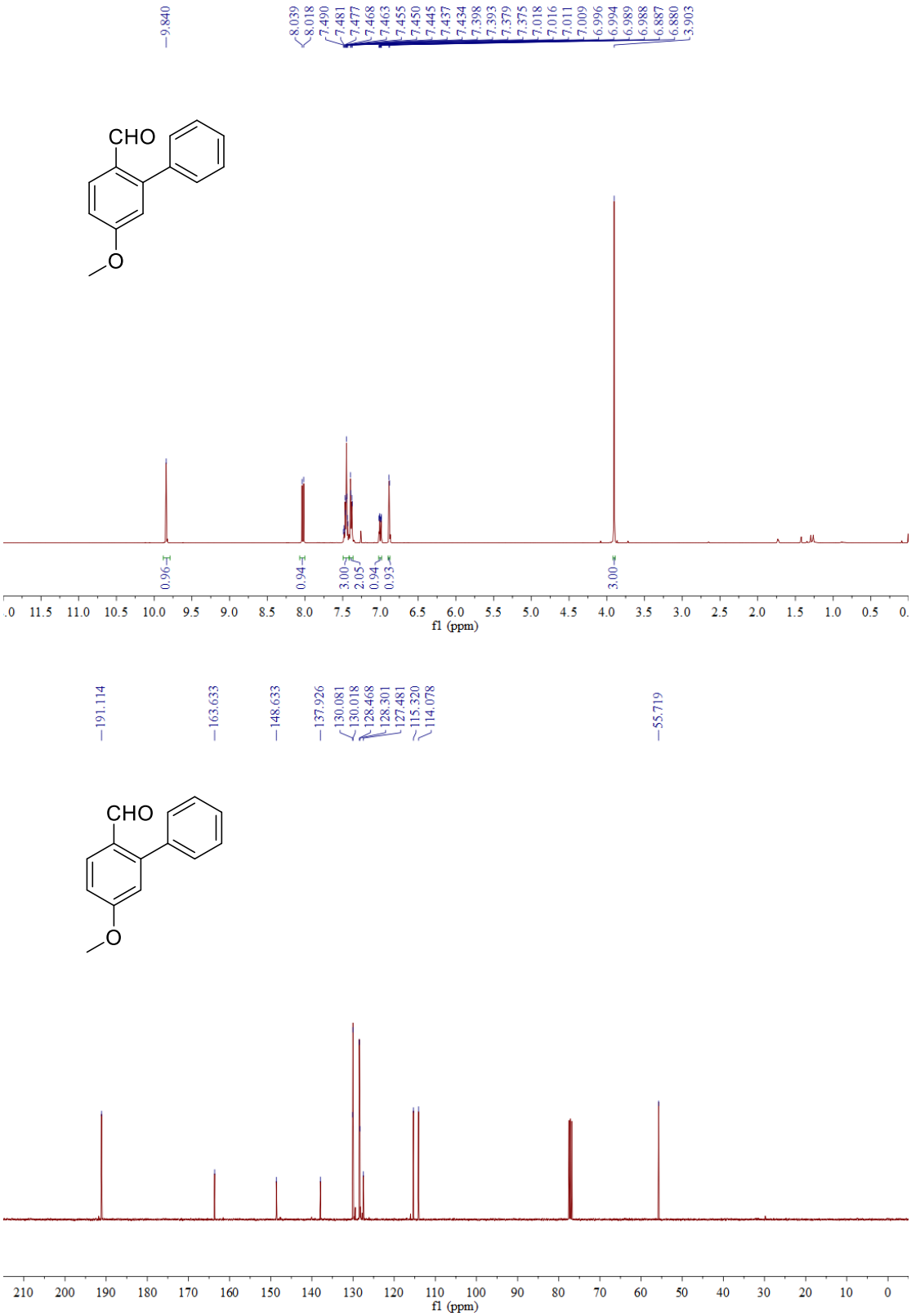


Figure S8. ^{1}H and ^{13}C NMR Spectra for compound **3c**

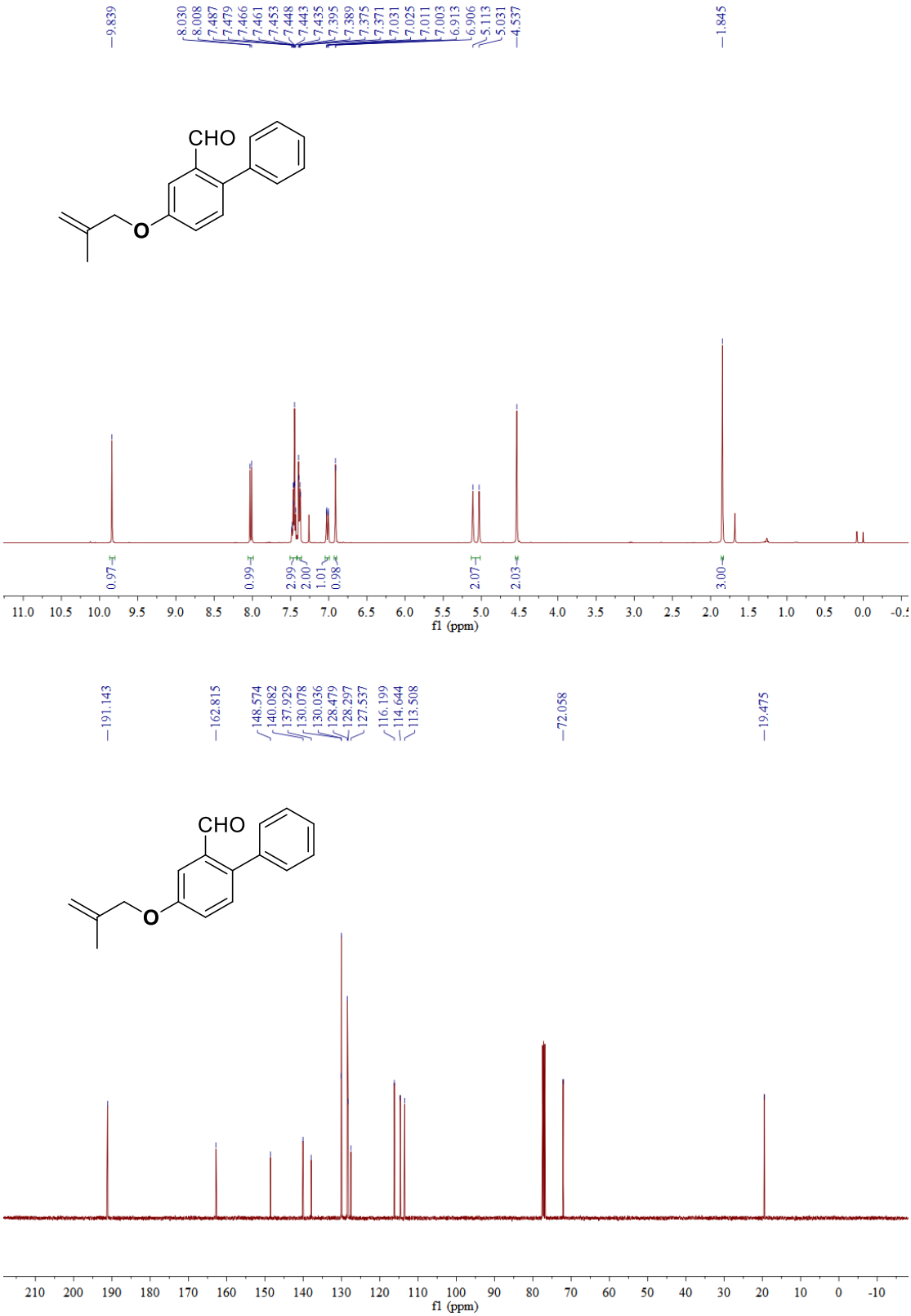
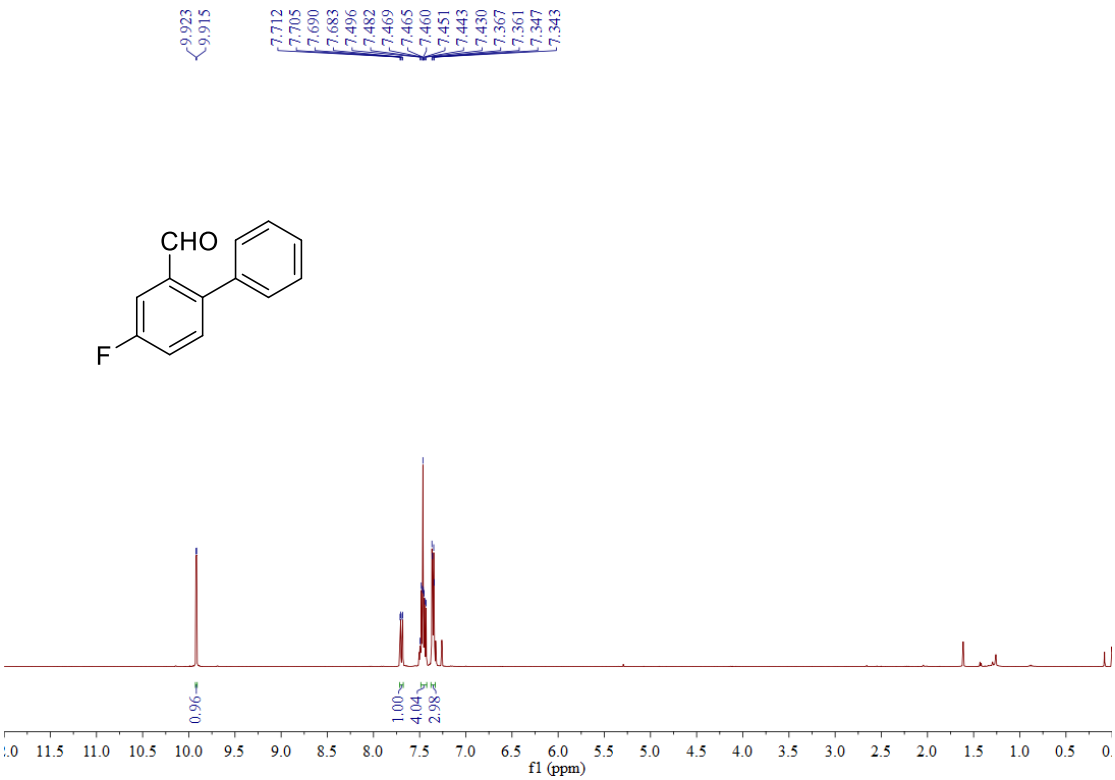


Figure S9. ^{1}H and ^{13}C NMR Spectra for compound **3d**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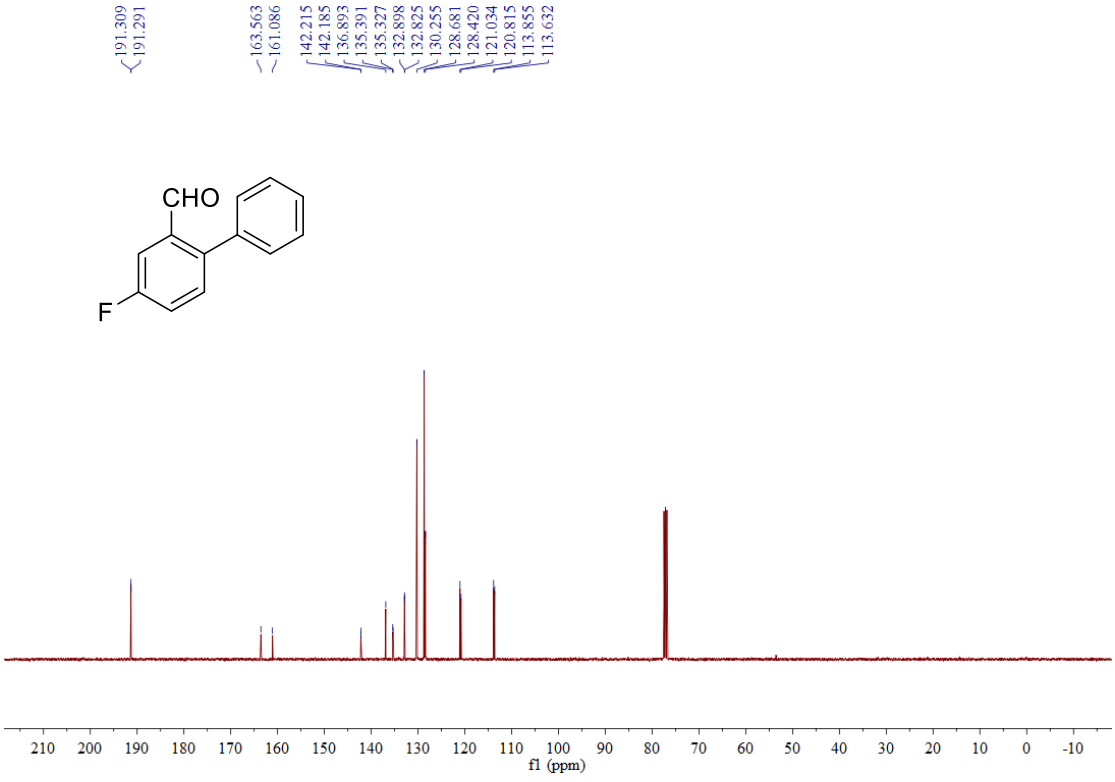
9.915
7.712
7.705
7.690
7.683
7.496
7.482
7.469
7.465
7.460
7.451
7.443
7.430
7.367
7.361
7.347
7.343
CHO
F
0.96
1.00
4.04
2.98
f1 (ppm)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191.291
163.563
161.086
142.215
142.185
136.893
135.391
135.327
132.898
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130.255
128.681
128.420
121.034
120.815
113.855
113.632
CHO
F
f1 (ppm)

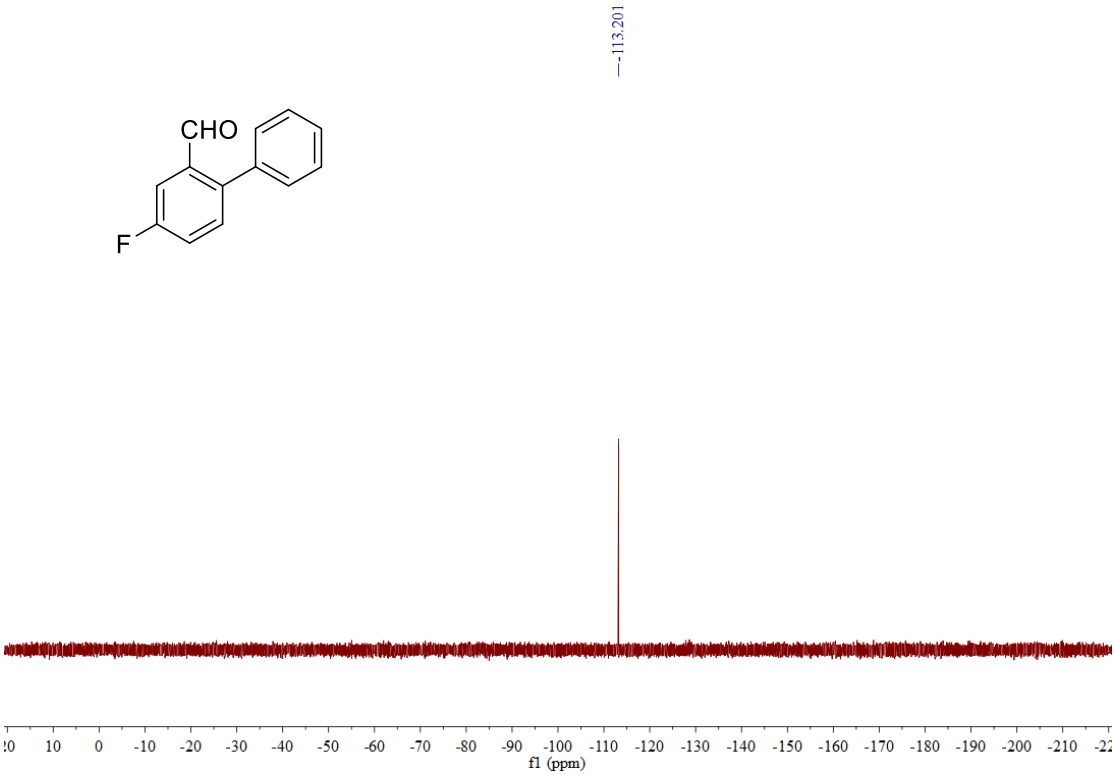
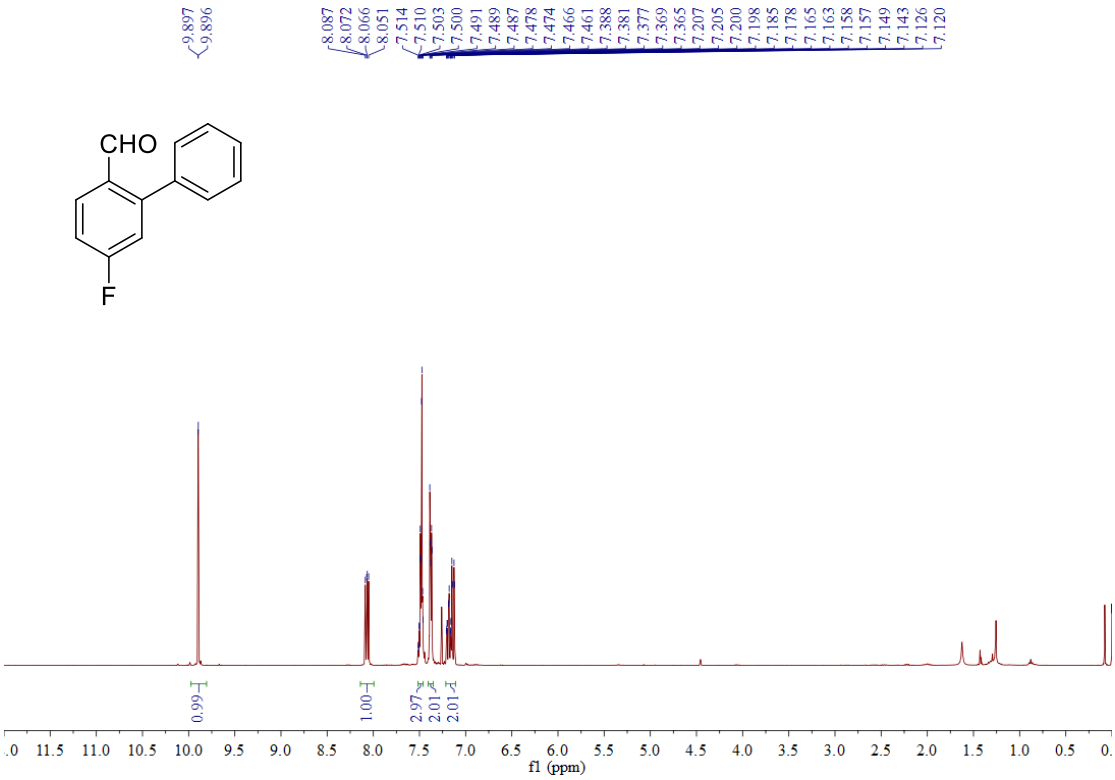


Figure S10. ^{1}H, ^{13}C and ^{19}F NMR Spectra for compound **3e**



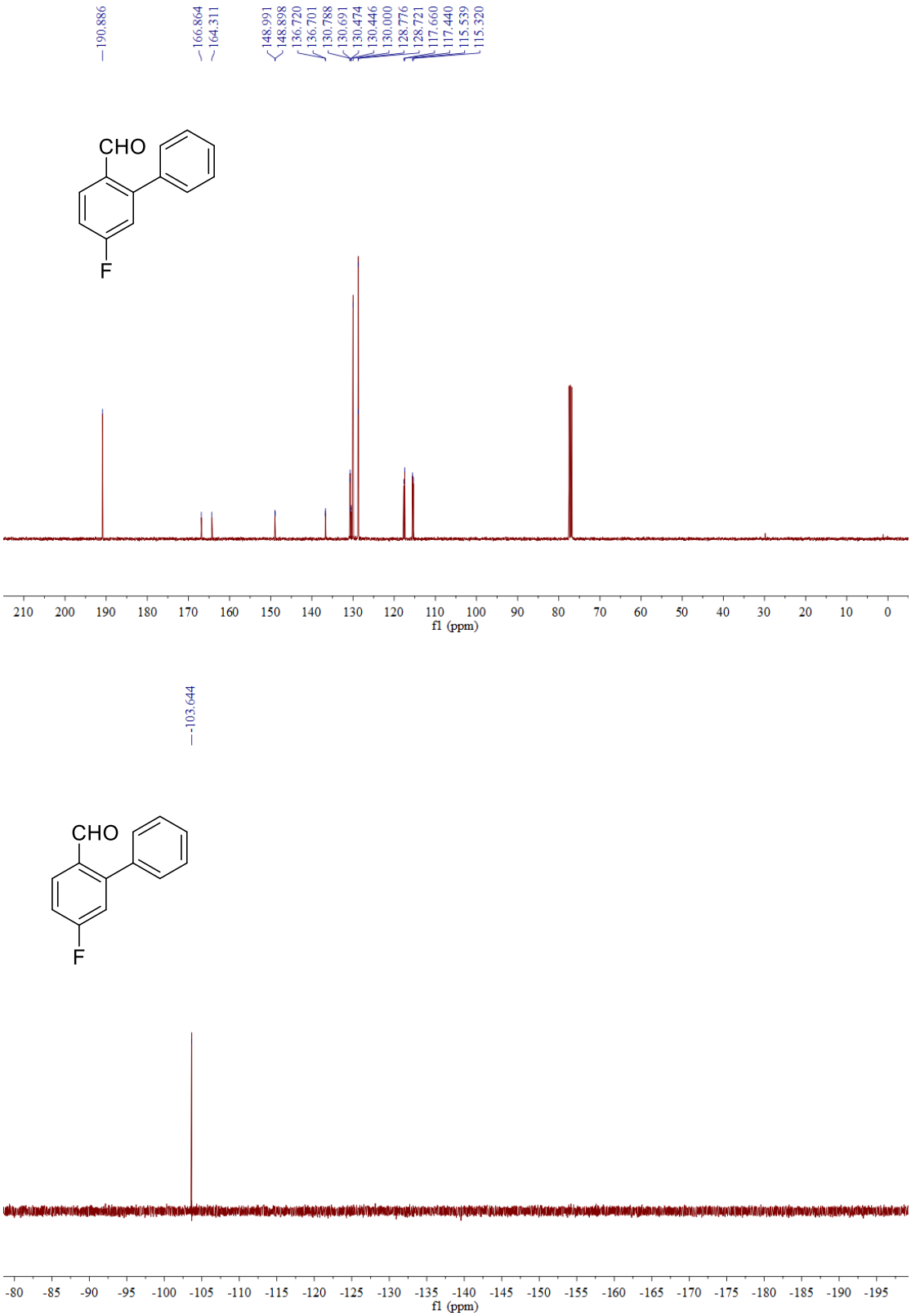


Figure S11. ^{1}H, ^{13}C and ^{19}F NMR Spectra for compound **3f**

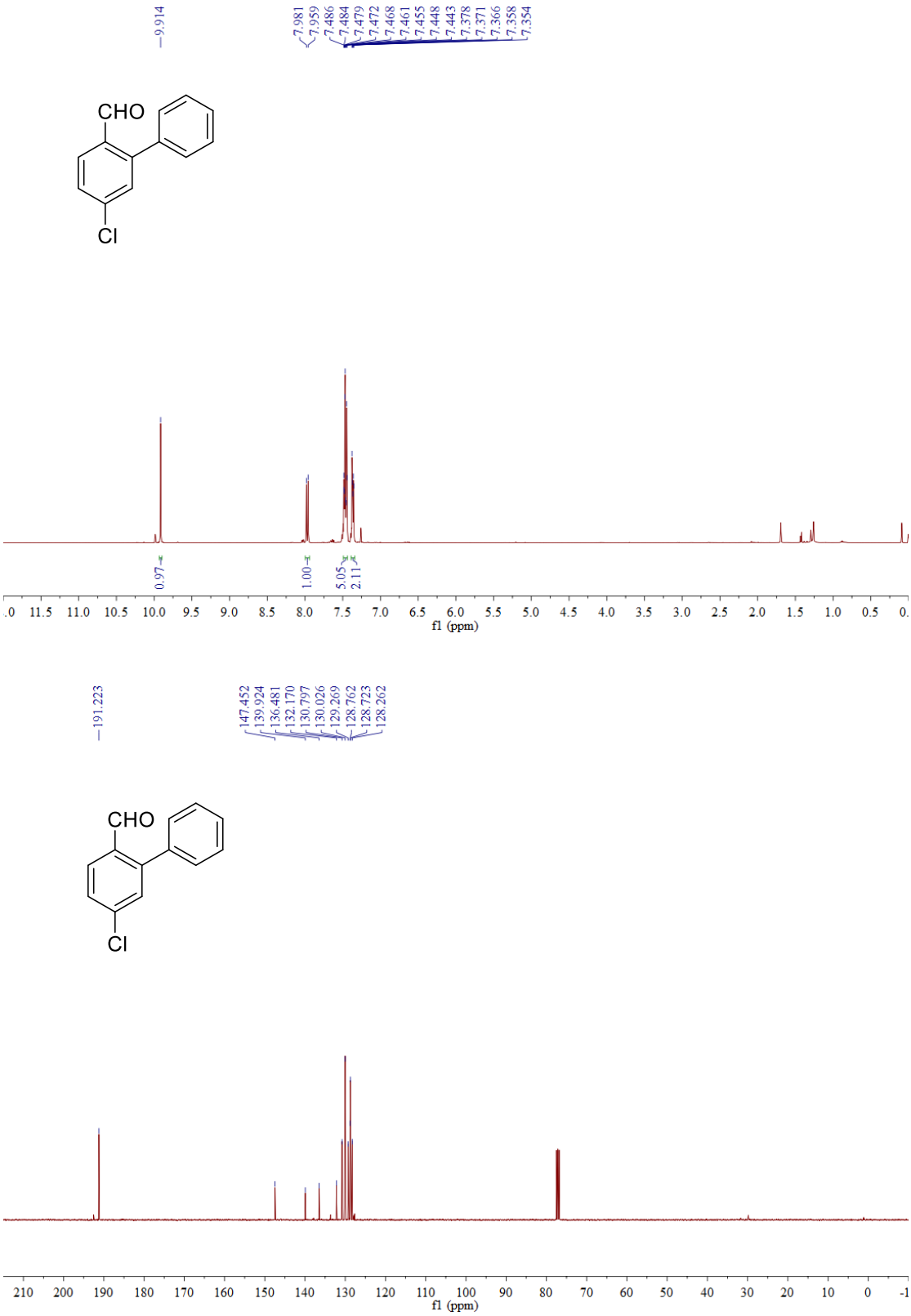


Figure S12. ^{1}H and ^{13}C NMR Spectra for compound **3g**

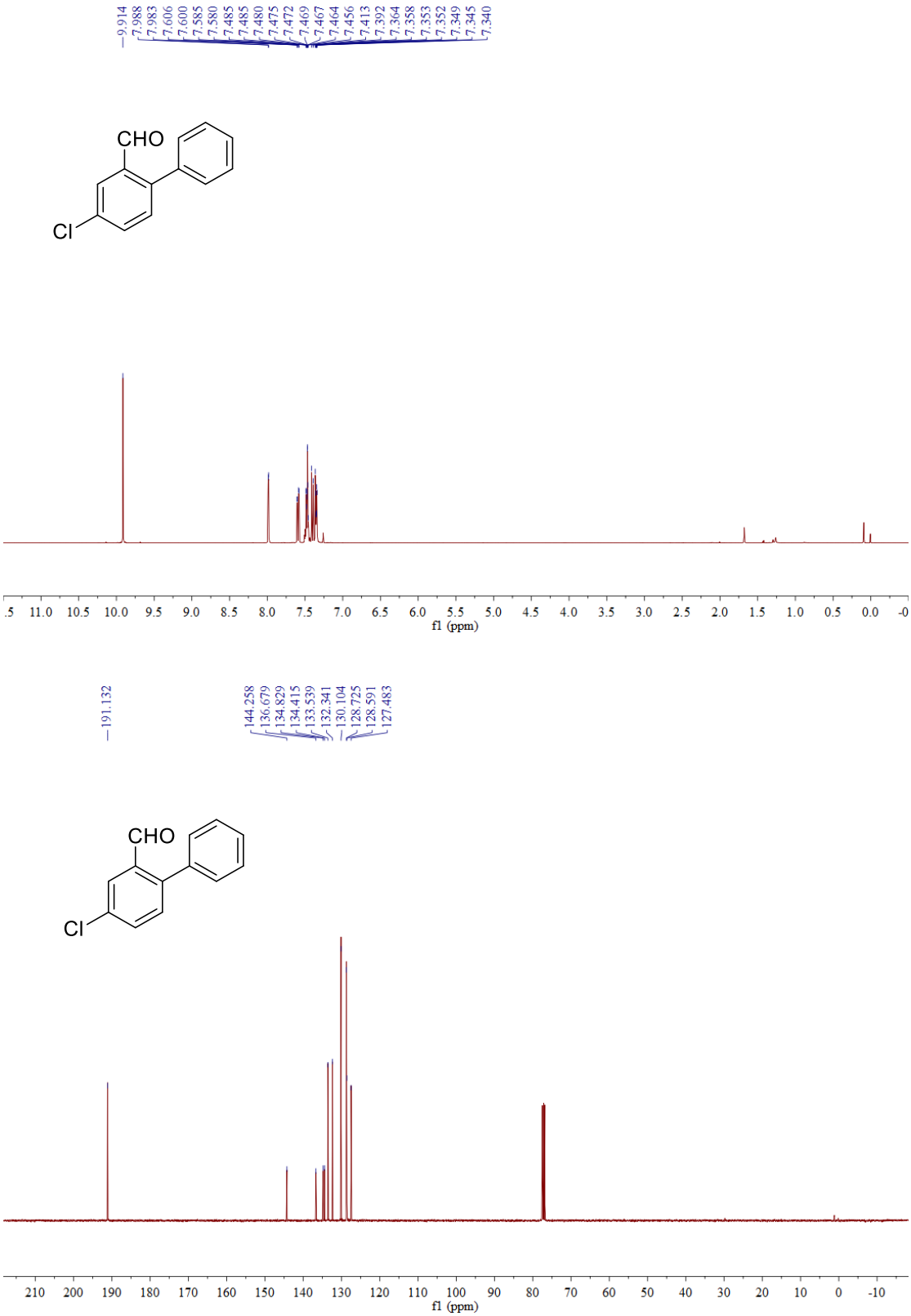
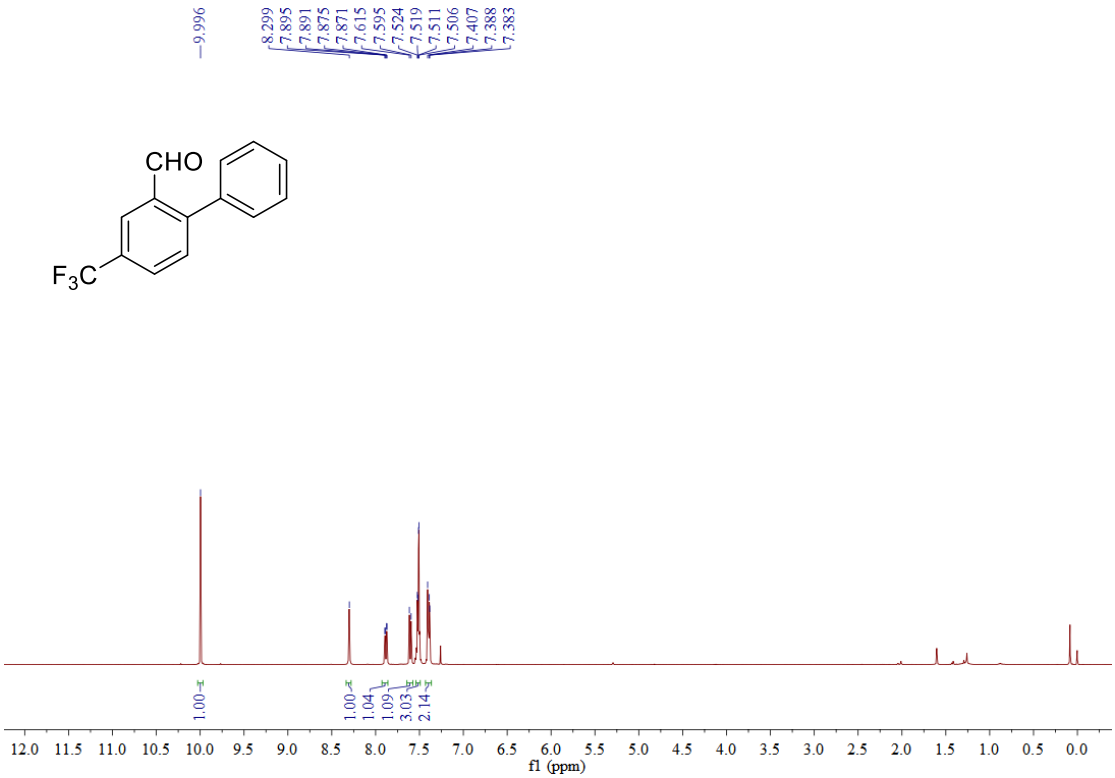


Figure S13. ^{1}H and ^{13}C NMR Spectra for compound **3h**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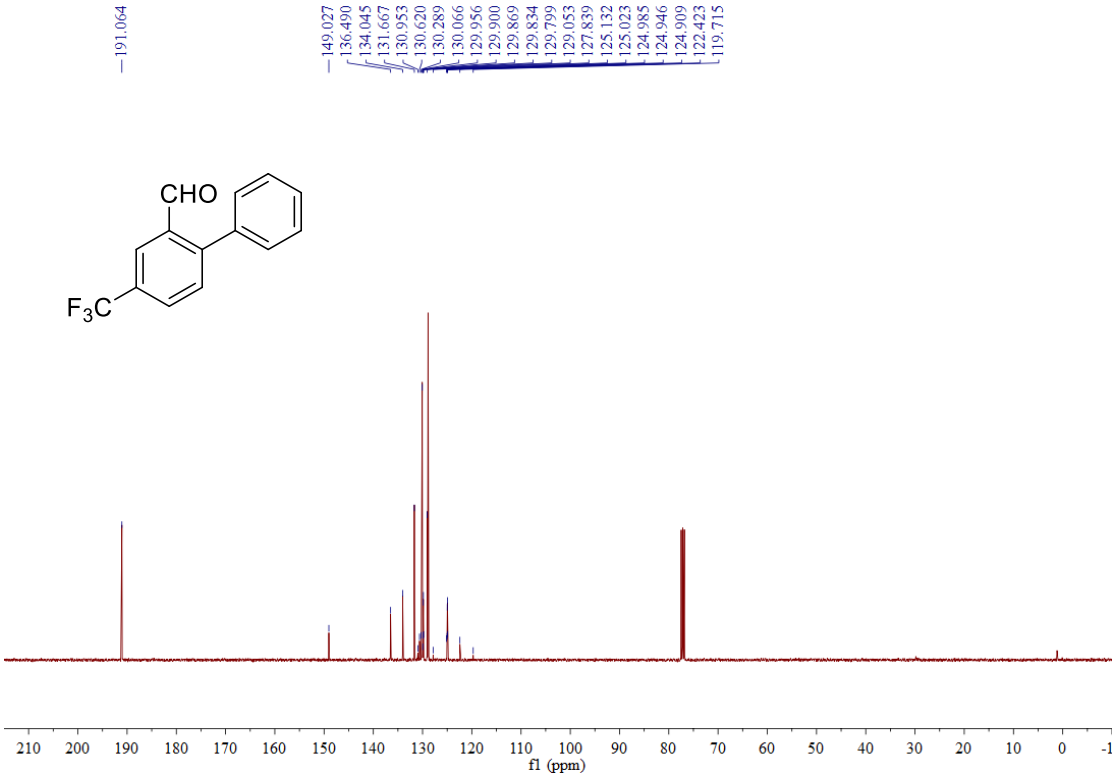
7.875
7.871
7.615
7.595
7.524
7.519
7.511
7.506
7.407
7.388
7.383
CHO
F3C
1.00
1.00
1.04
1.09
3.03
2.14
f1 (ppm)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129.956
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129.834
129.799
129.053
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125.023
124.985
124.946
124.909
122.423
119.715
CHO
F3C
f1 (ppm)

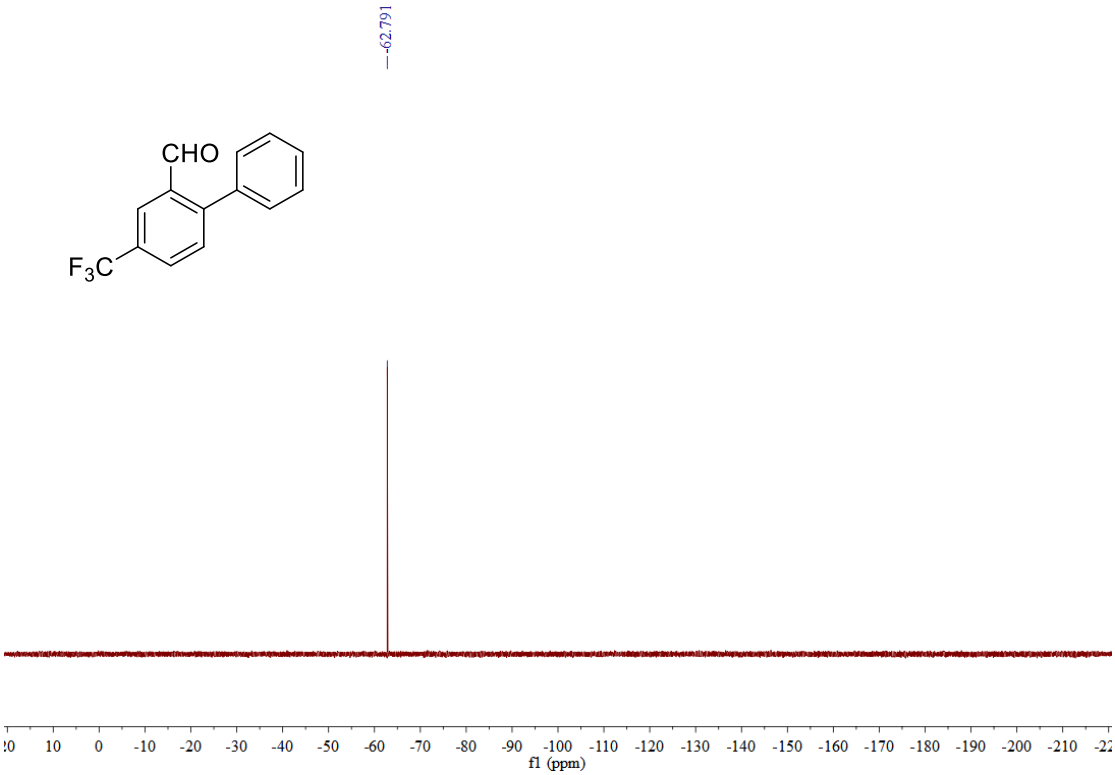
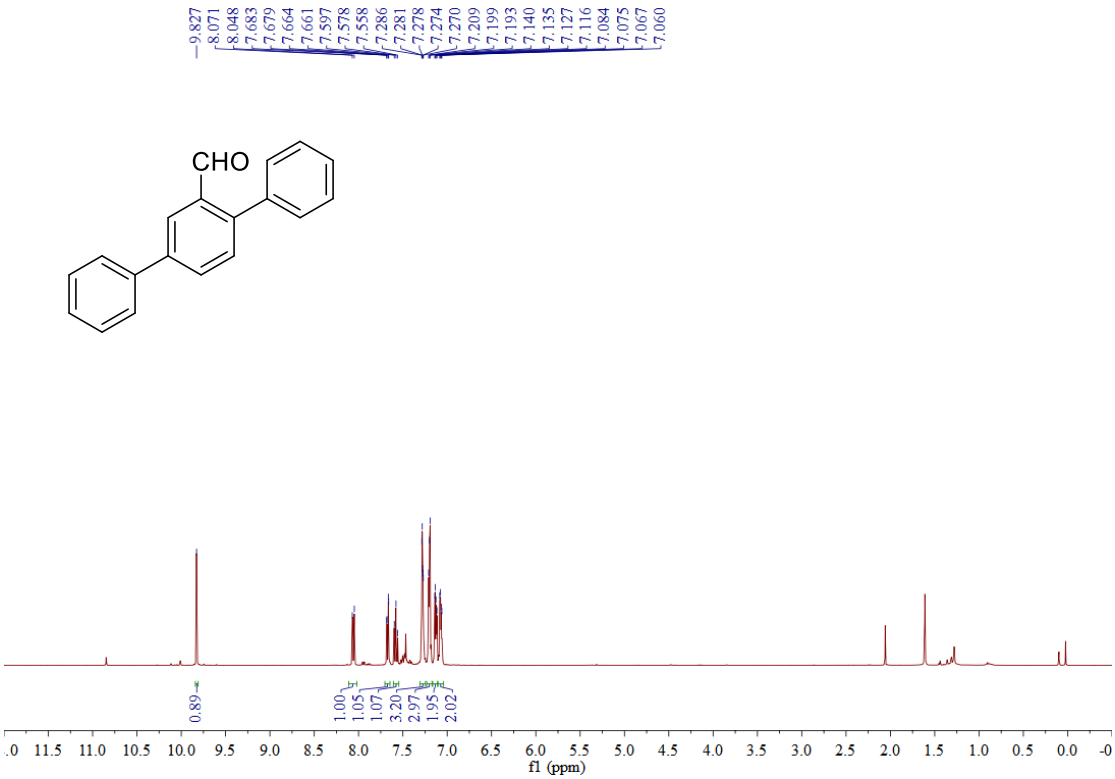


Figure S14. ^{1}H, ^{13}C and ^{19}F NMR Spectra for compound **3i**



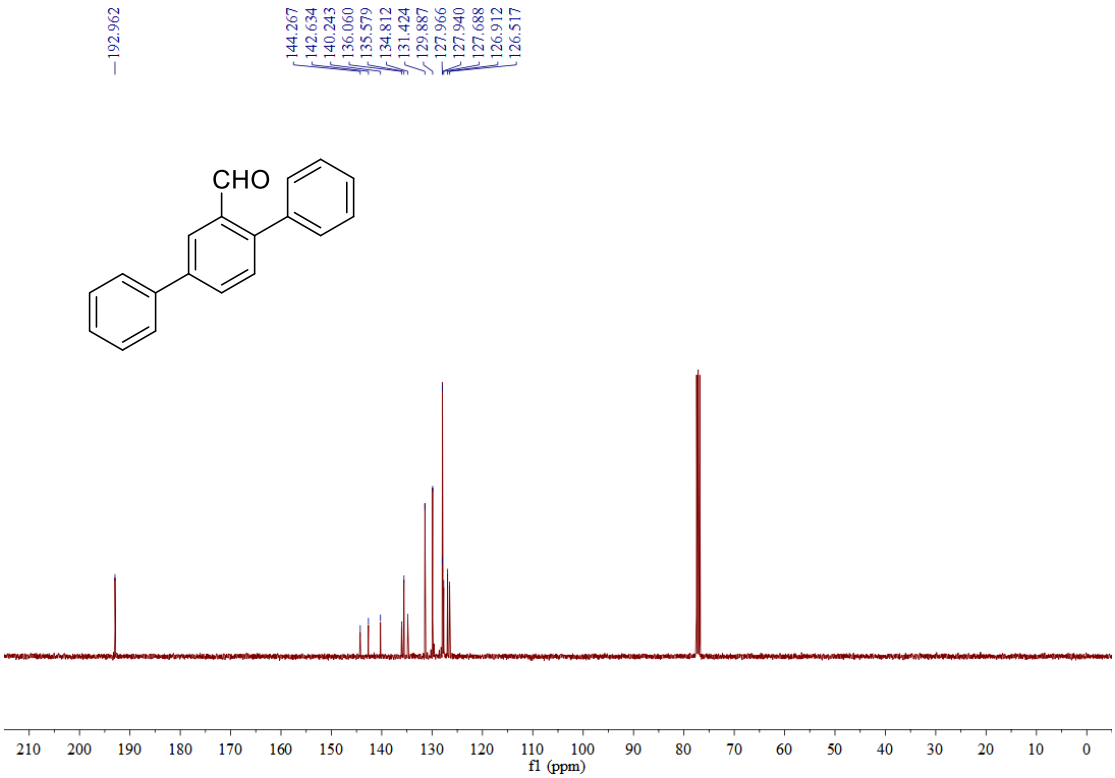
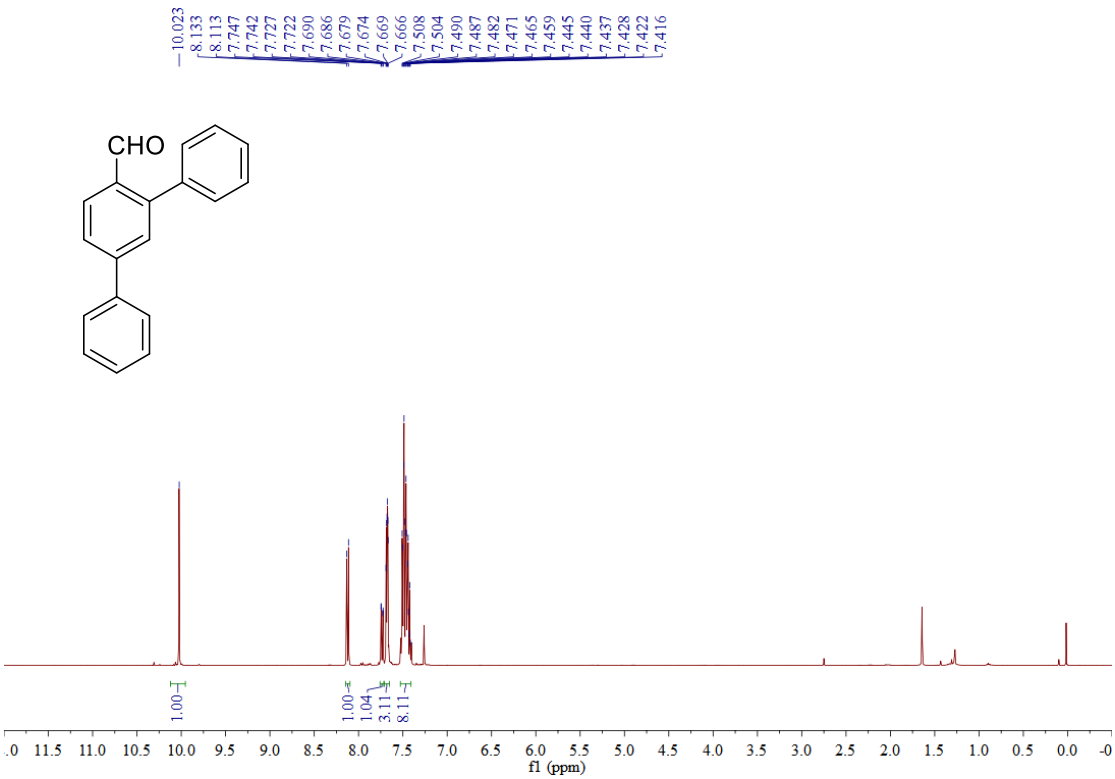


Figure S15. ^{1}H and ^{13}C NMR Spectra for compound **3j**



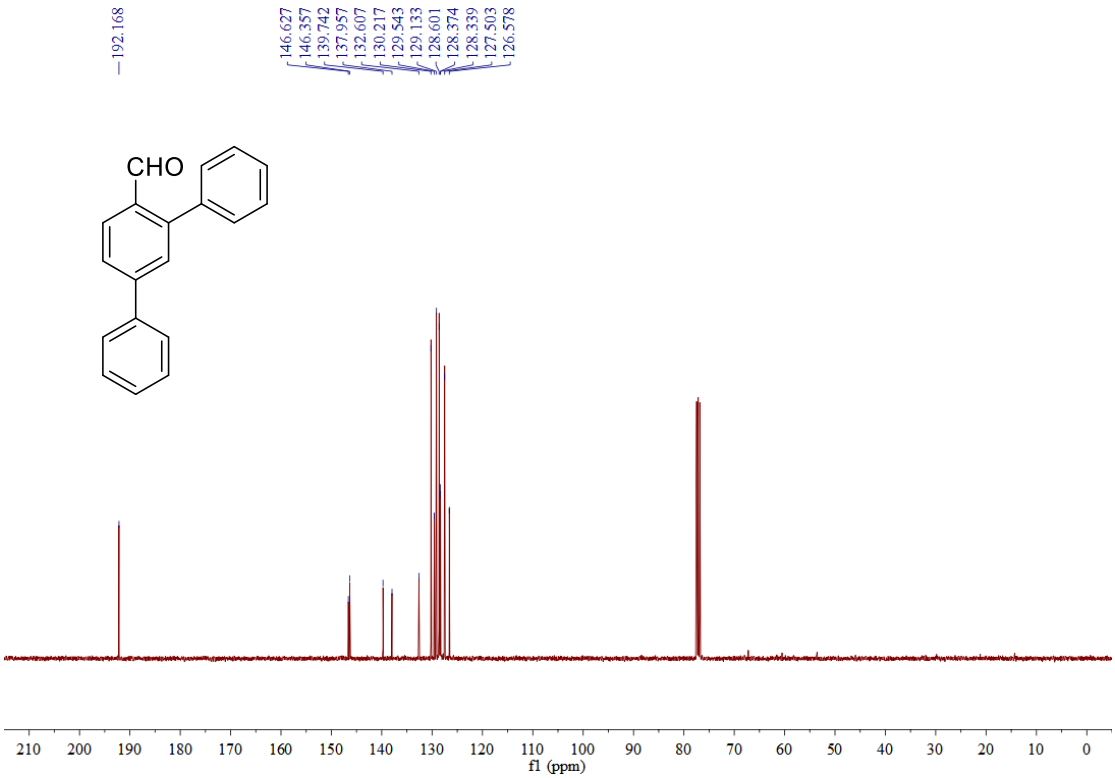
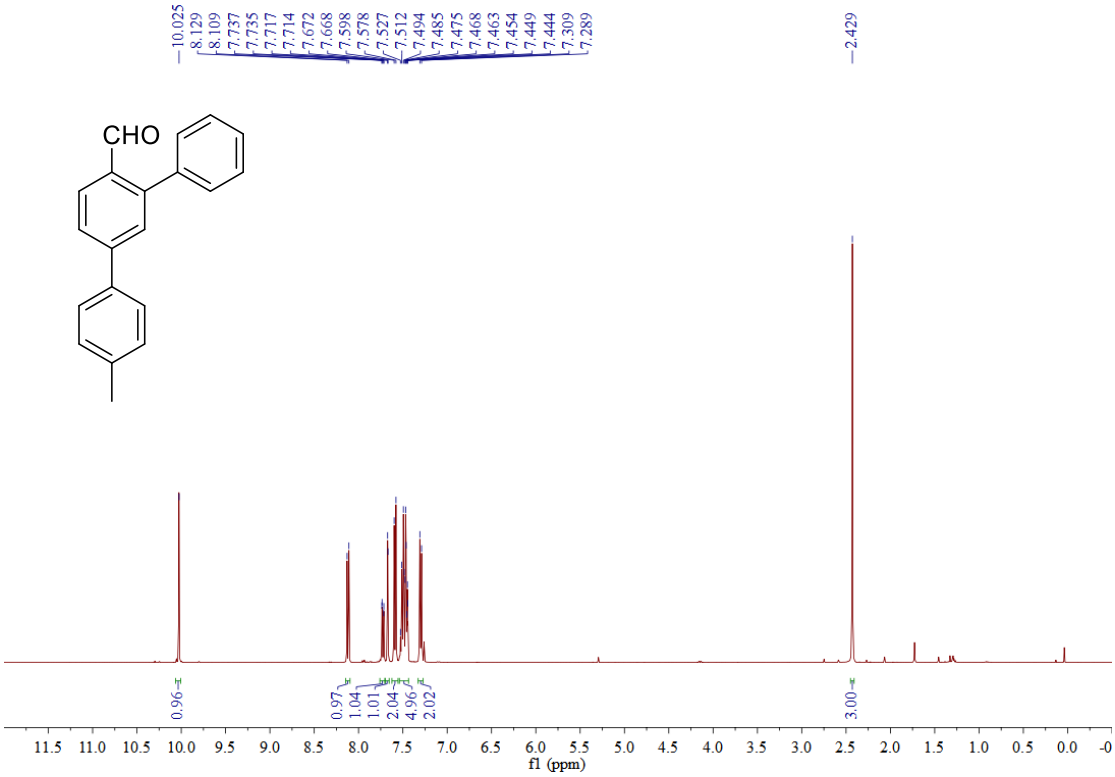


Figure S16. ^{1}H and ^{13}C NMR Spectra for compound **3k**



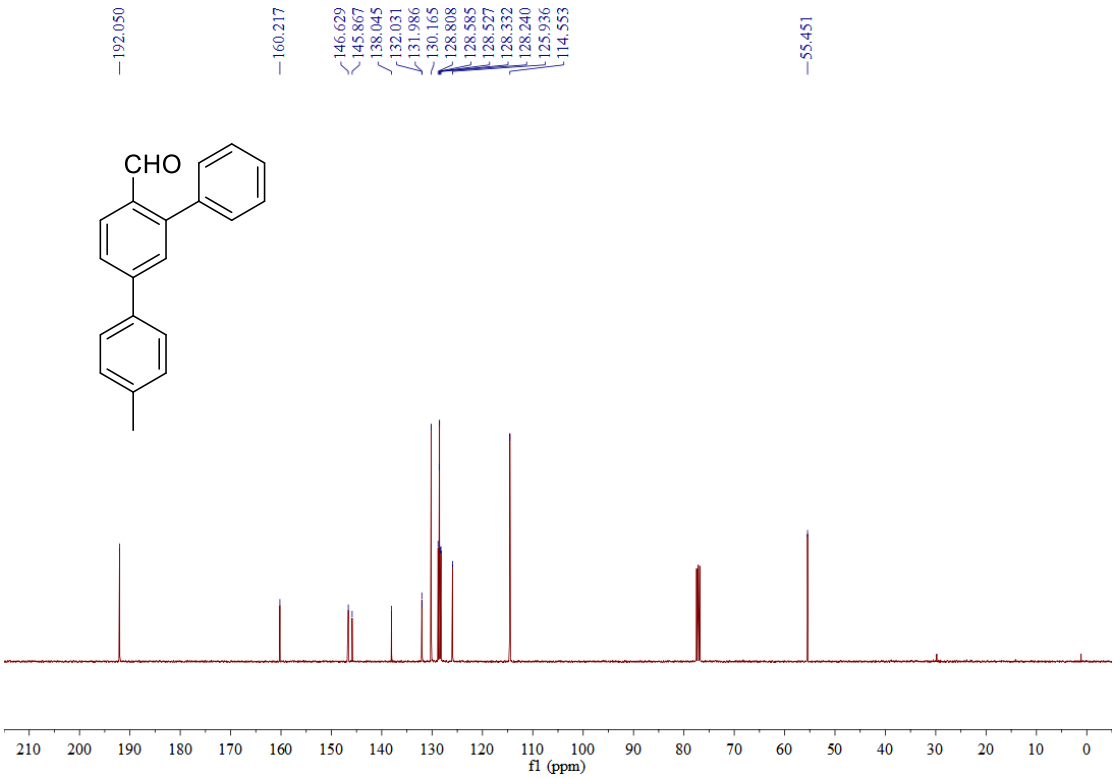
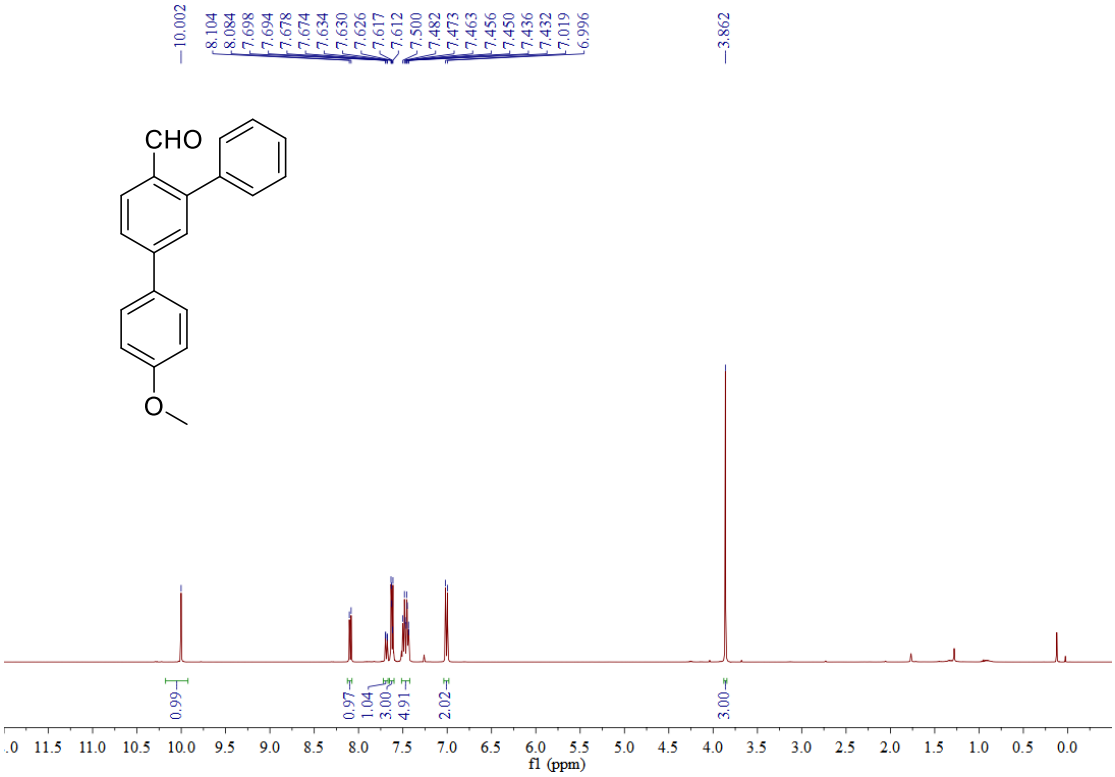


Figure S17. ^{1}H and ^{13}C NMR Spectra for compound **3l**



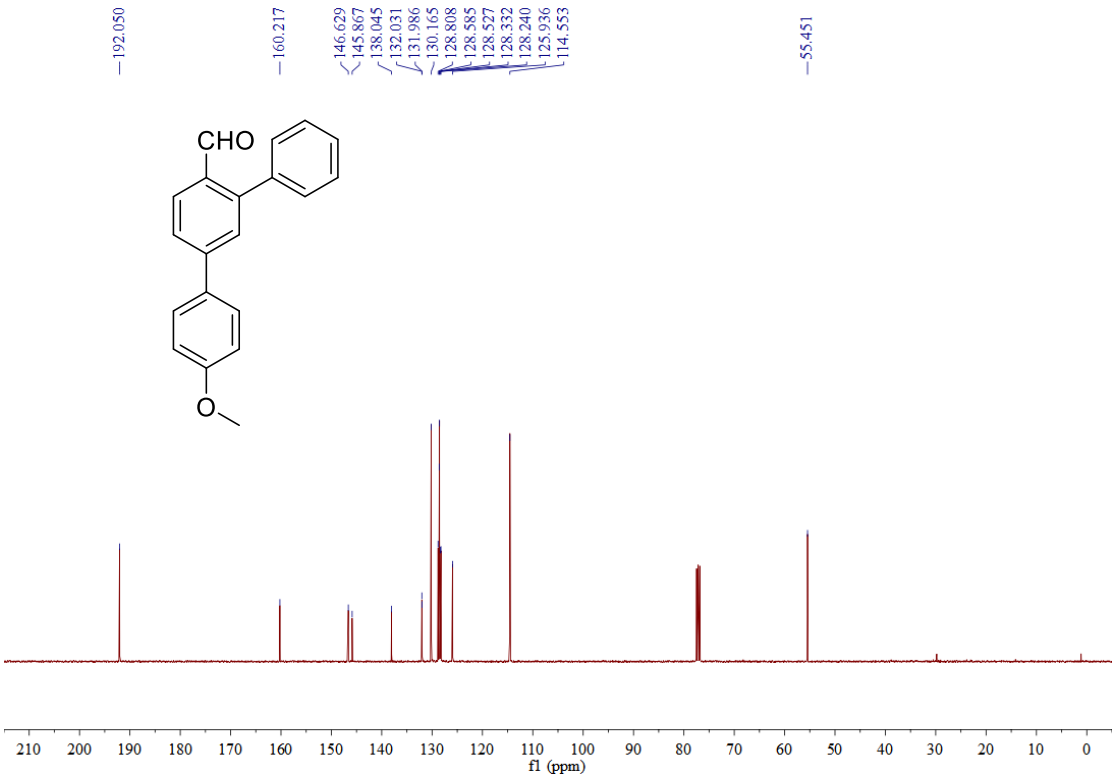
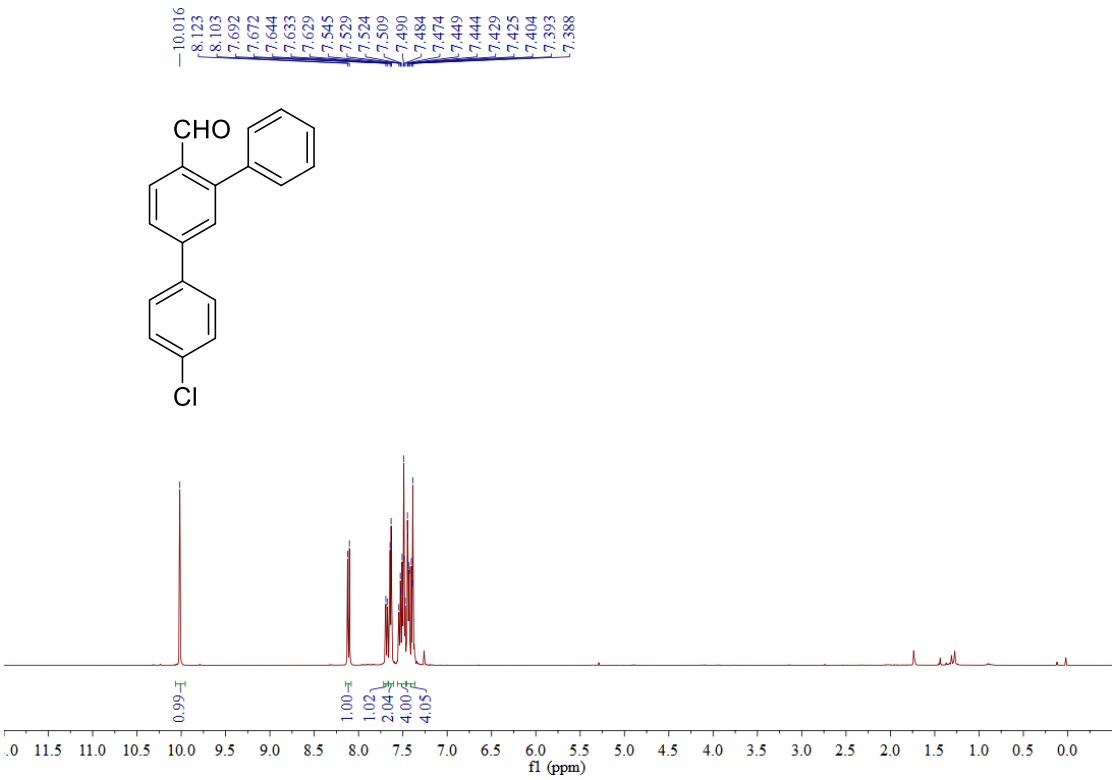


Figure S18. ^{1}H and ^{13}C NMR Spectra for compound **3m**



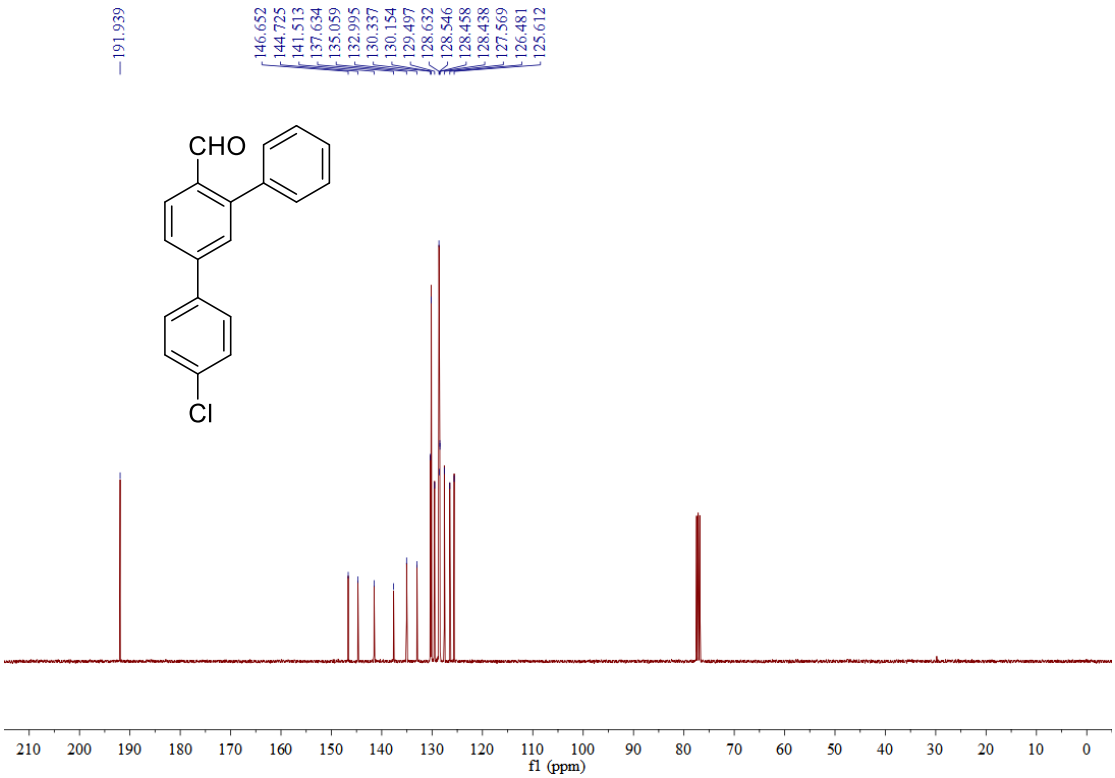
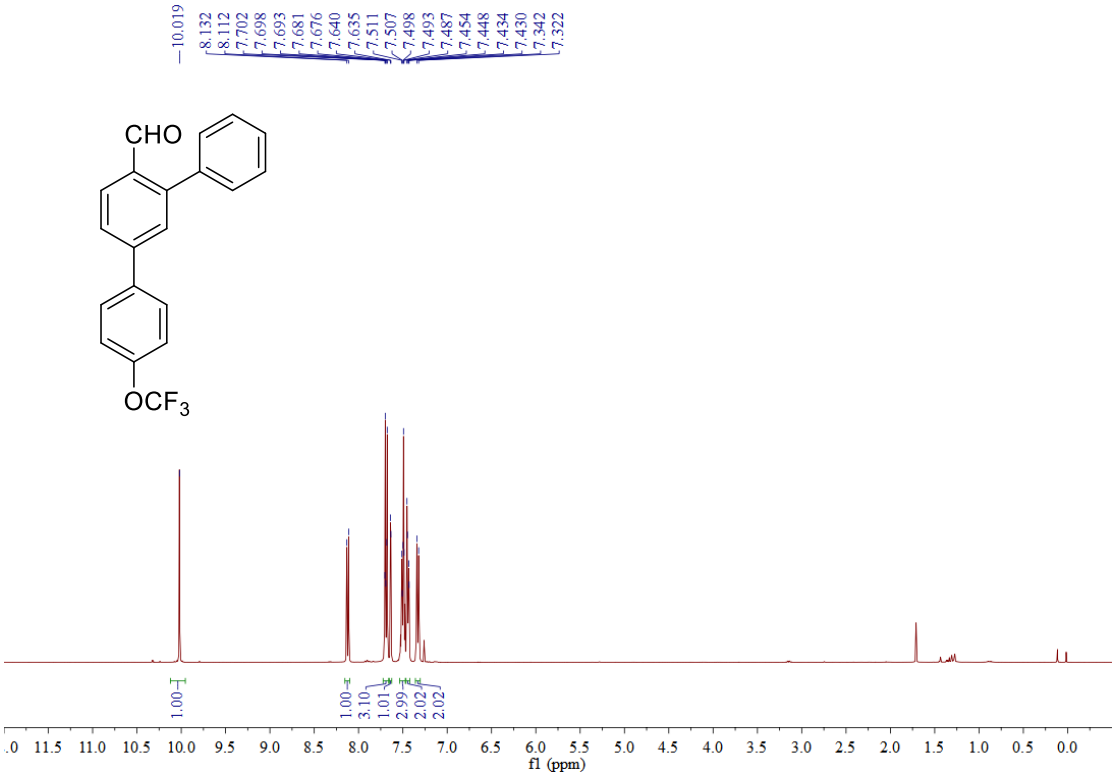


Figure S19. ^{1}H and ^{13}C NMR Spectra for compound **3n**



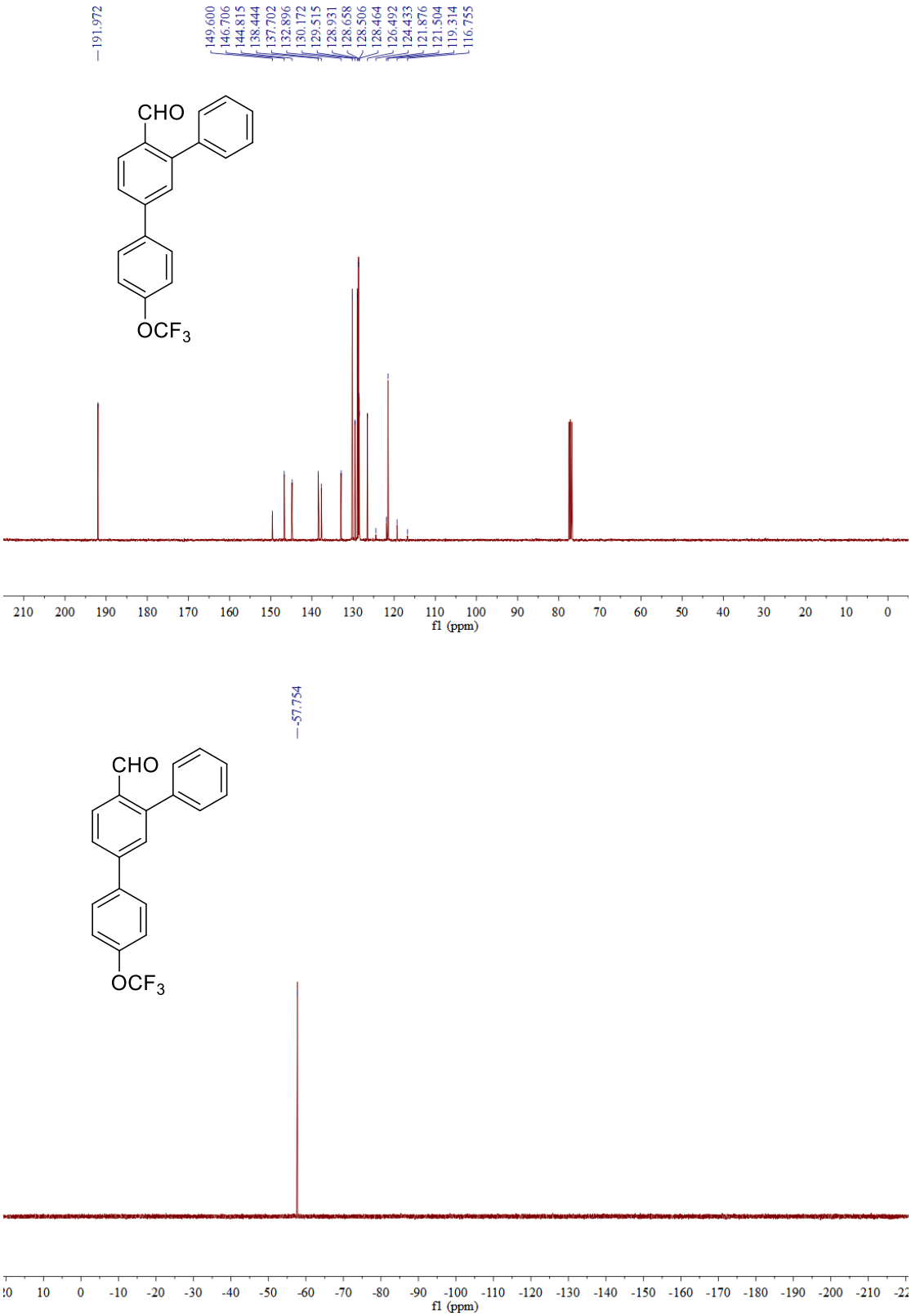


Figure S20. ^{1}H, ^{13}C and ^{19}F NMR Spectra for compound **3o**

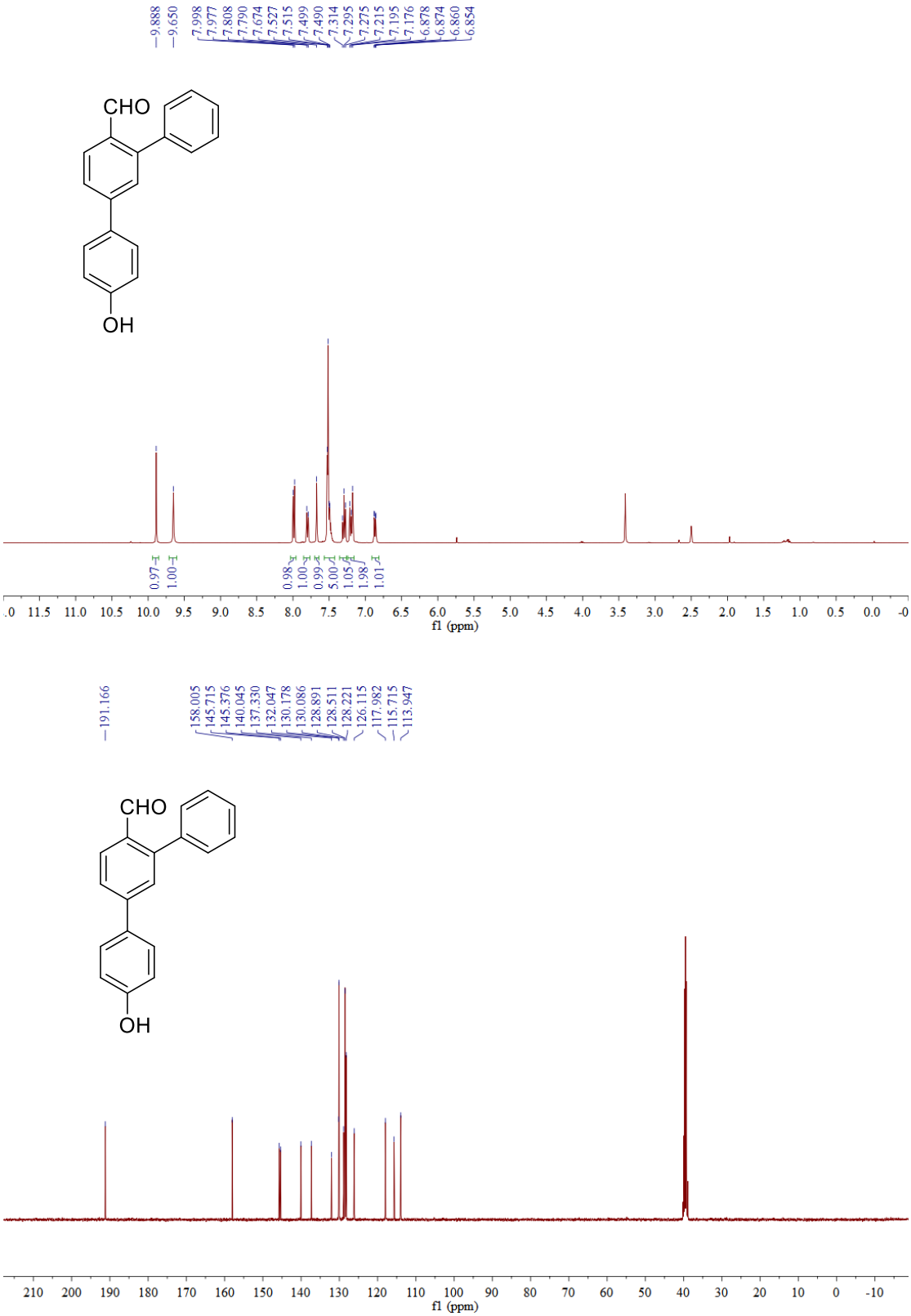


Figure S21. ^{1}H and ^{13}C NMR Spectra for compound **3p**

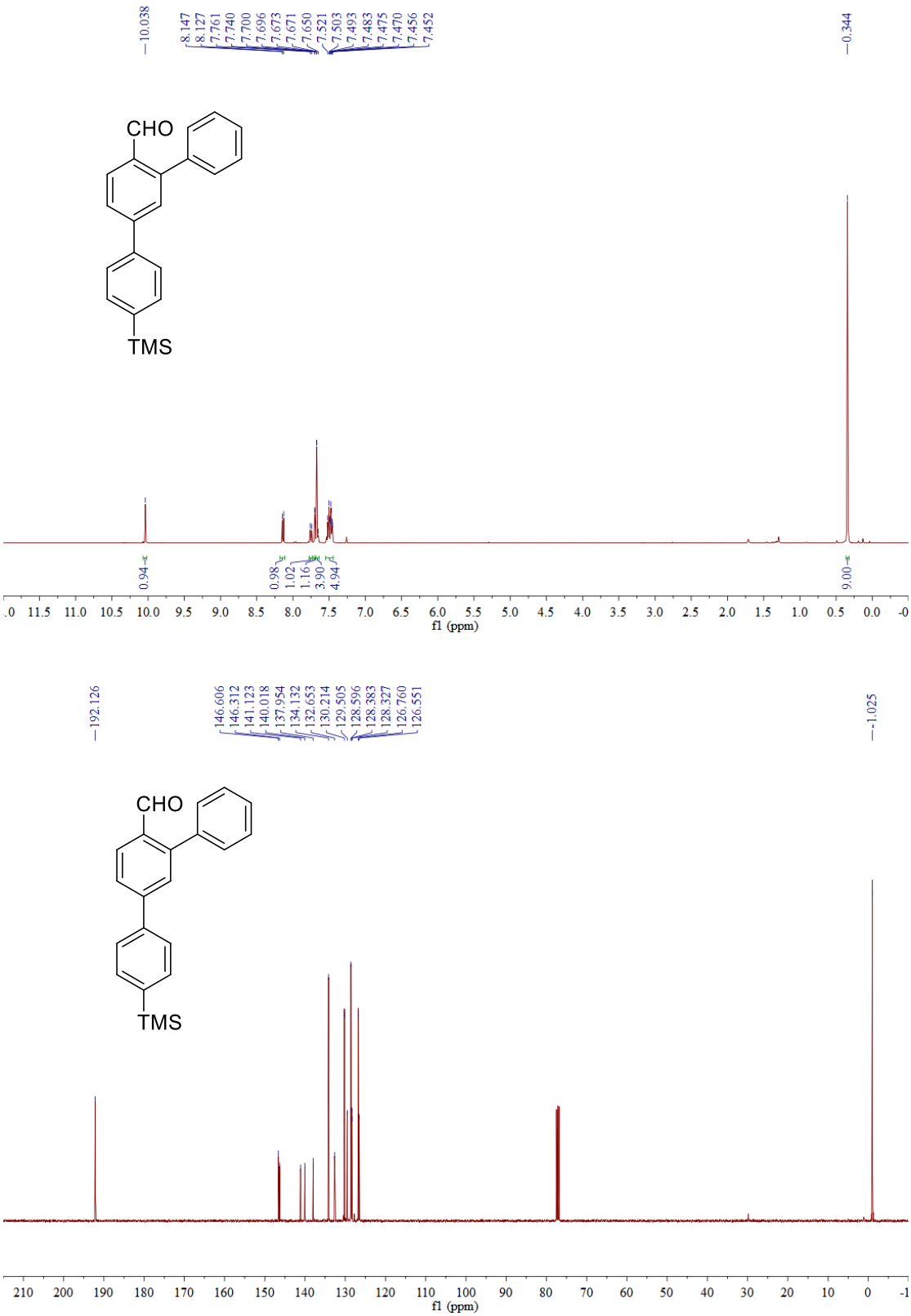


Figure S22. ^{1}H and ^{13}C NMR Spectra for compound **3q**

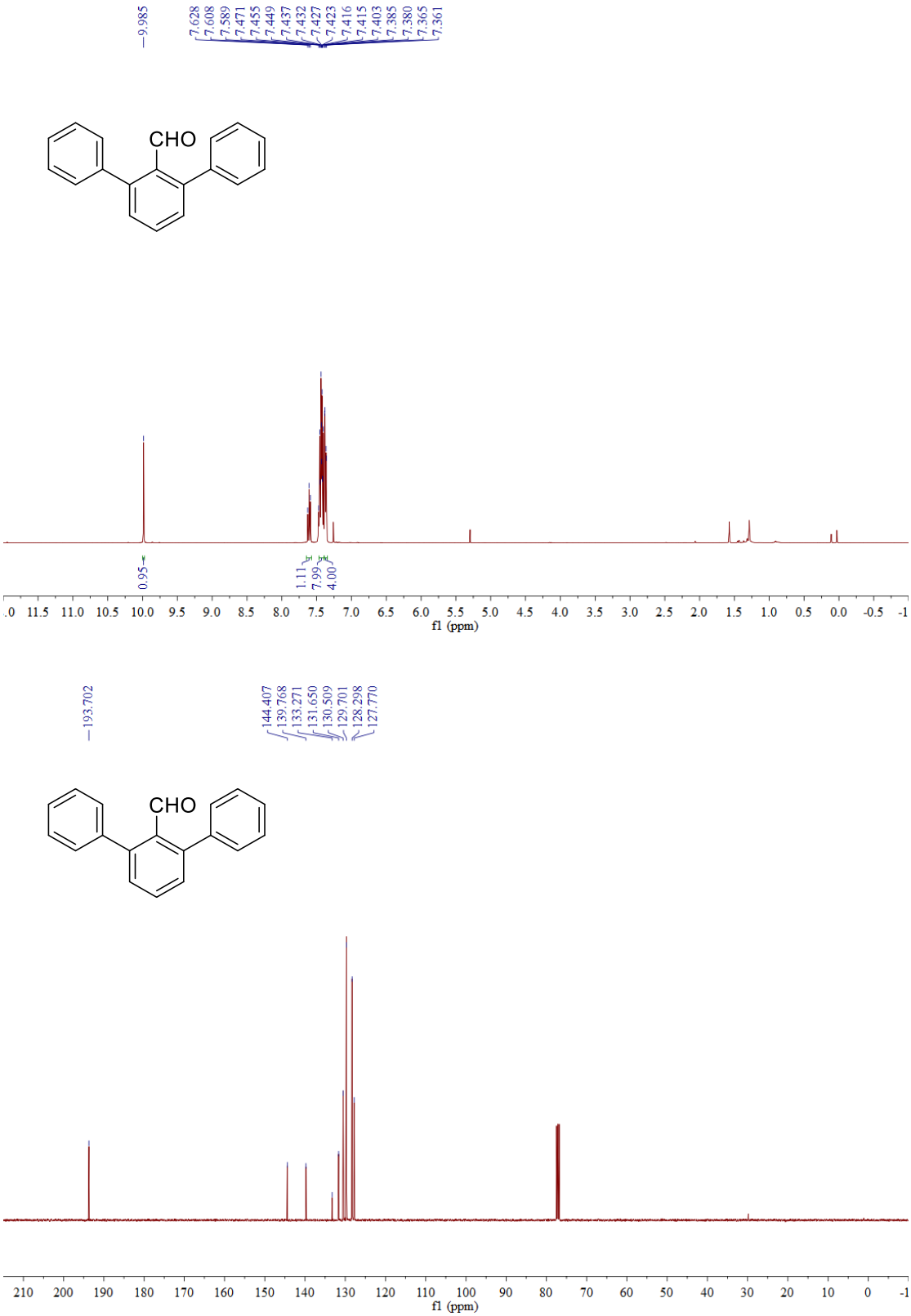


Figure S23. ^{1}H and ^{13}C NMR Spectra for compound **3r**

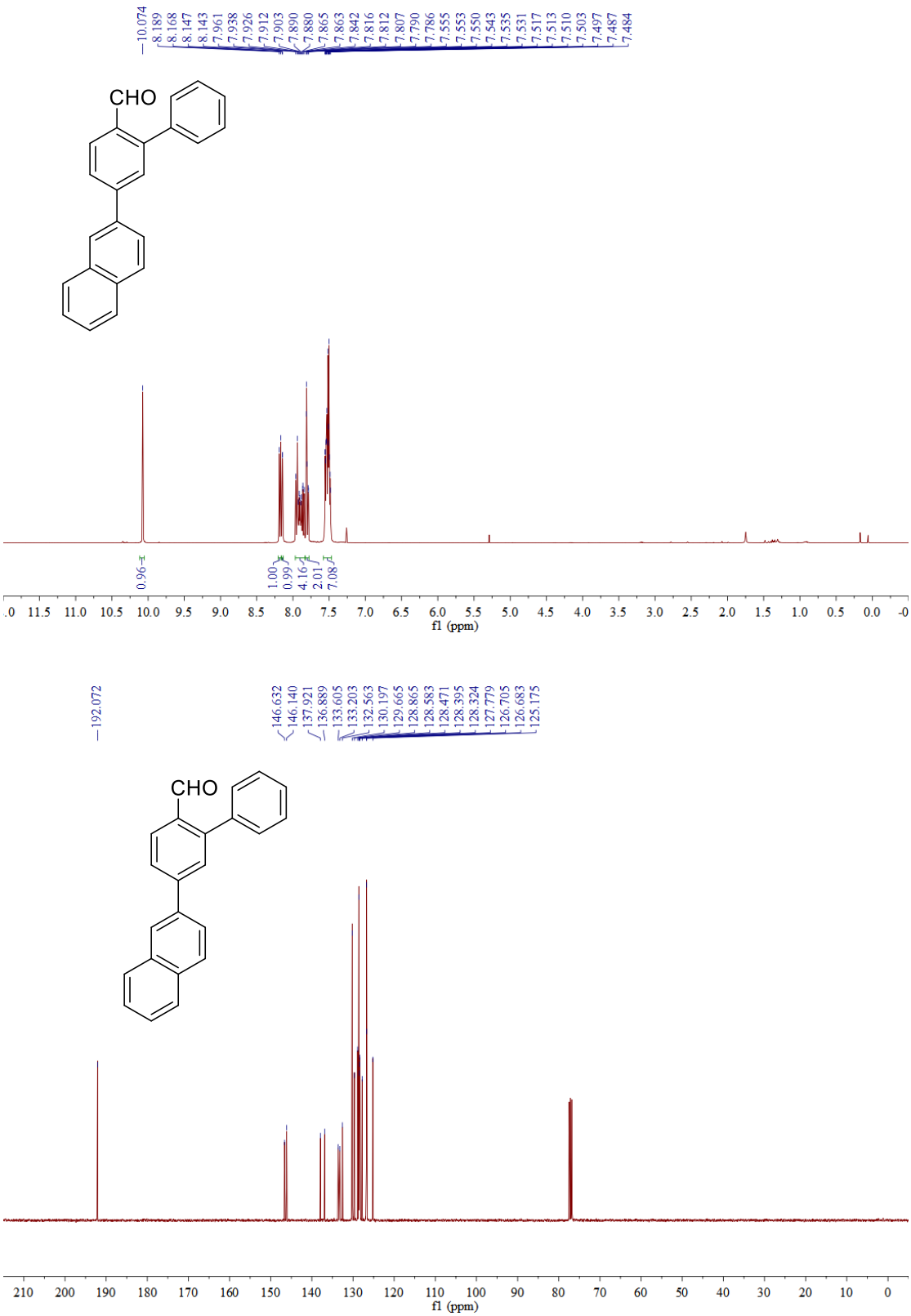


Figure S24. ^{1}H and ^{13}C NMR Spectra for compound **3s**

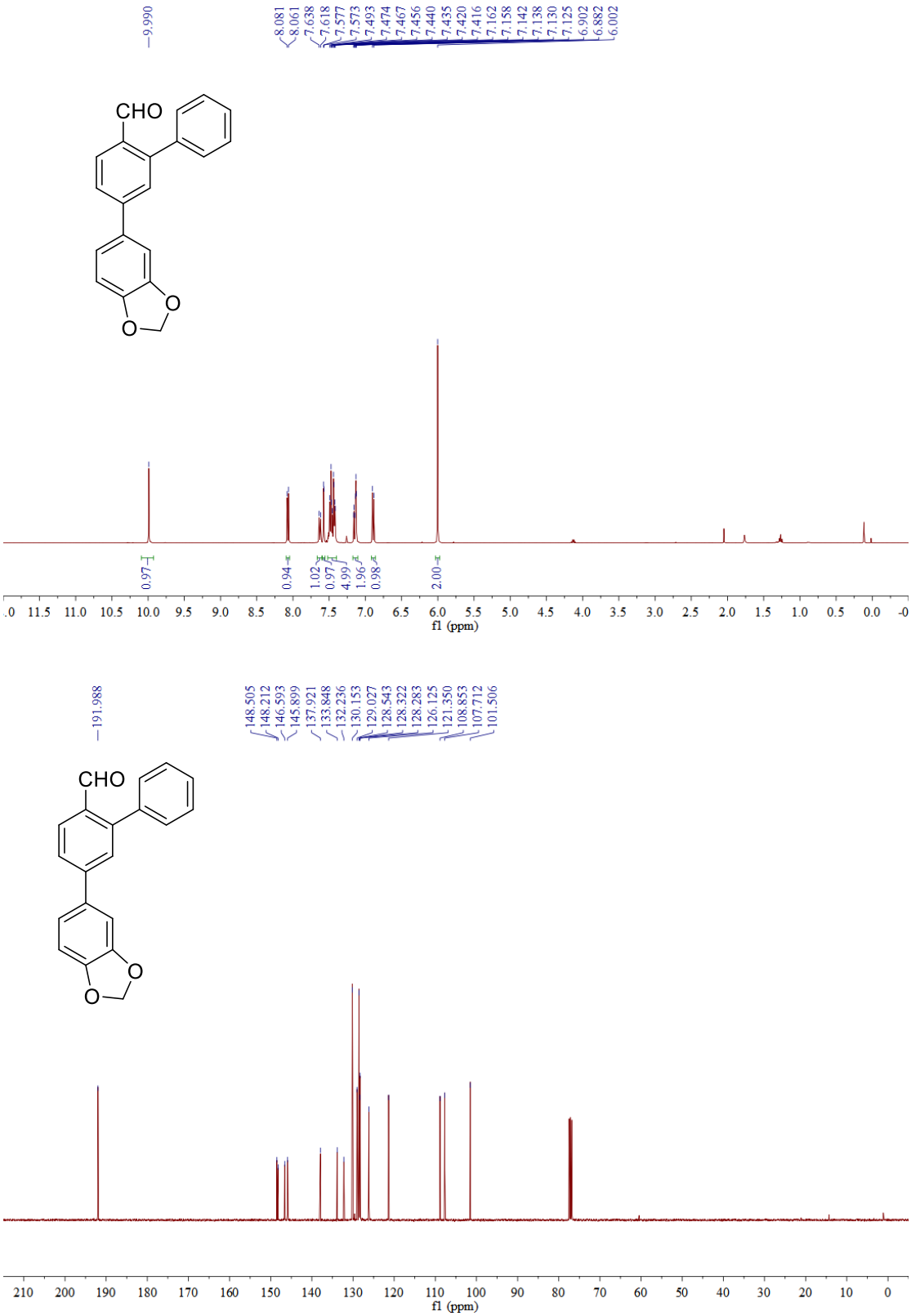


Figure S25. ^{1}H and ^{13}C NMR Spectra for compound **3t**

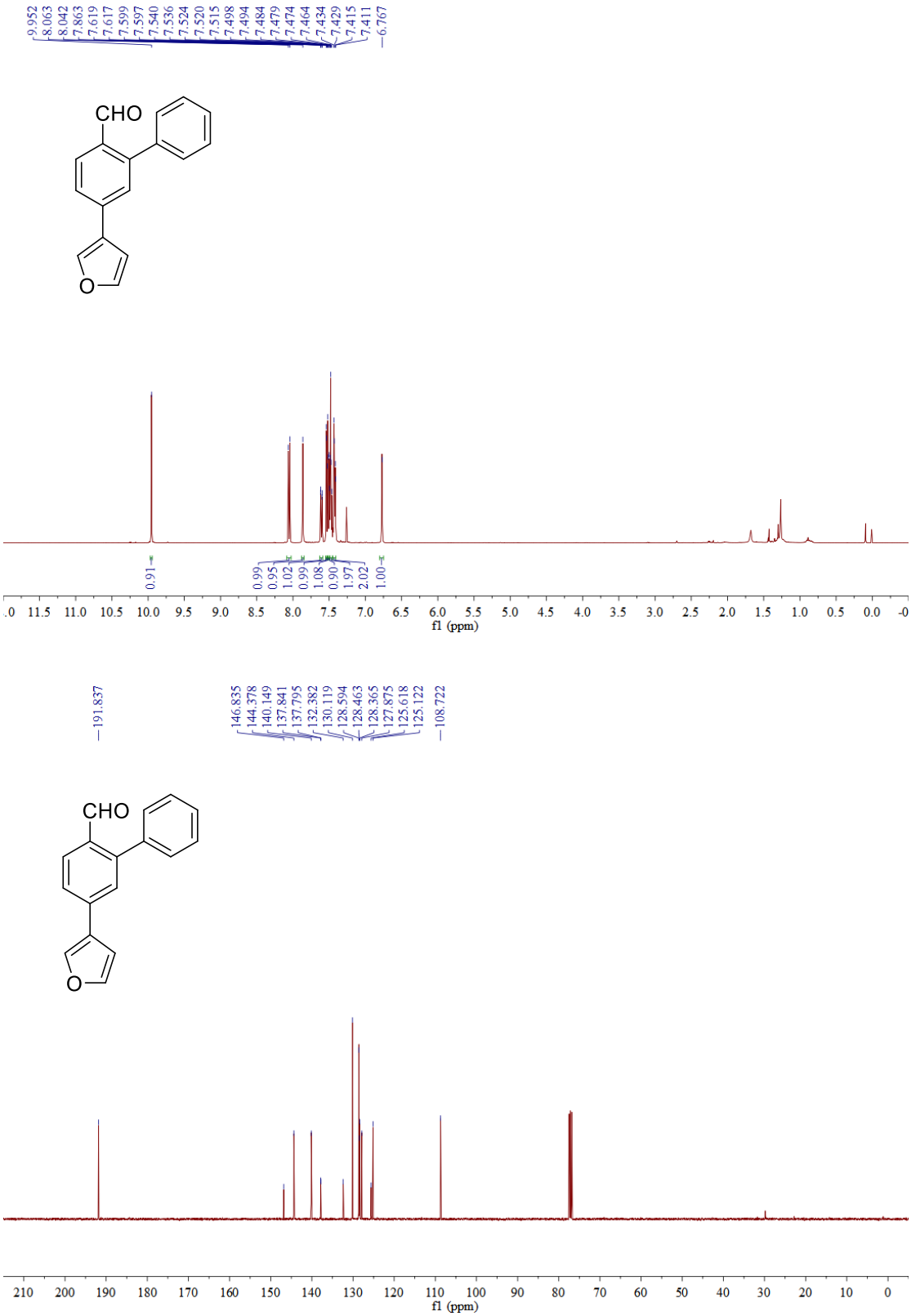


Figure S26. ^{1}H and ^{13}C NMR Spectra for compound **3u**

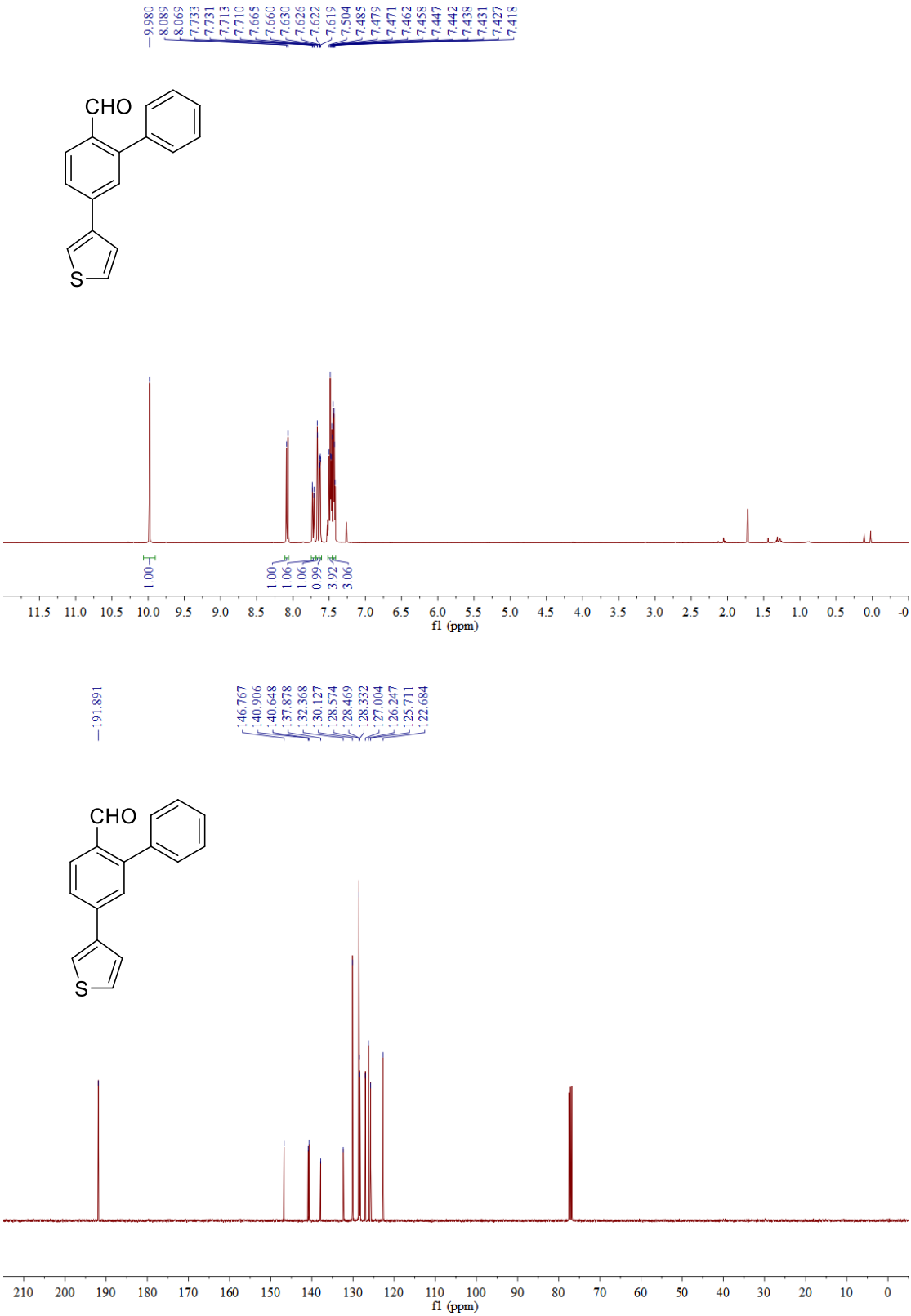


Figure S27. ^{1}H and ^{13}C NMR Spectra for compound **3v**

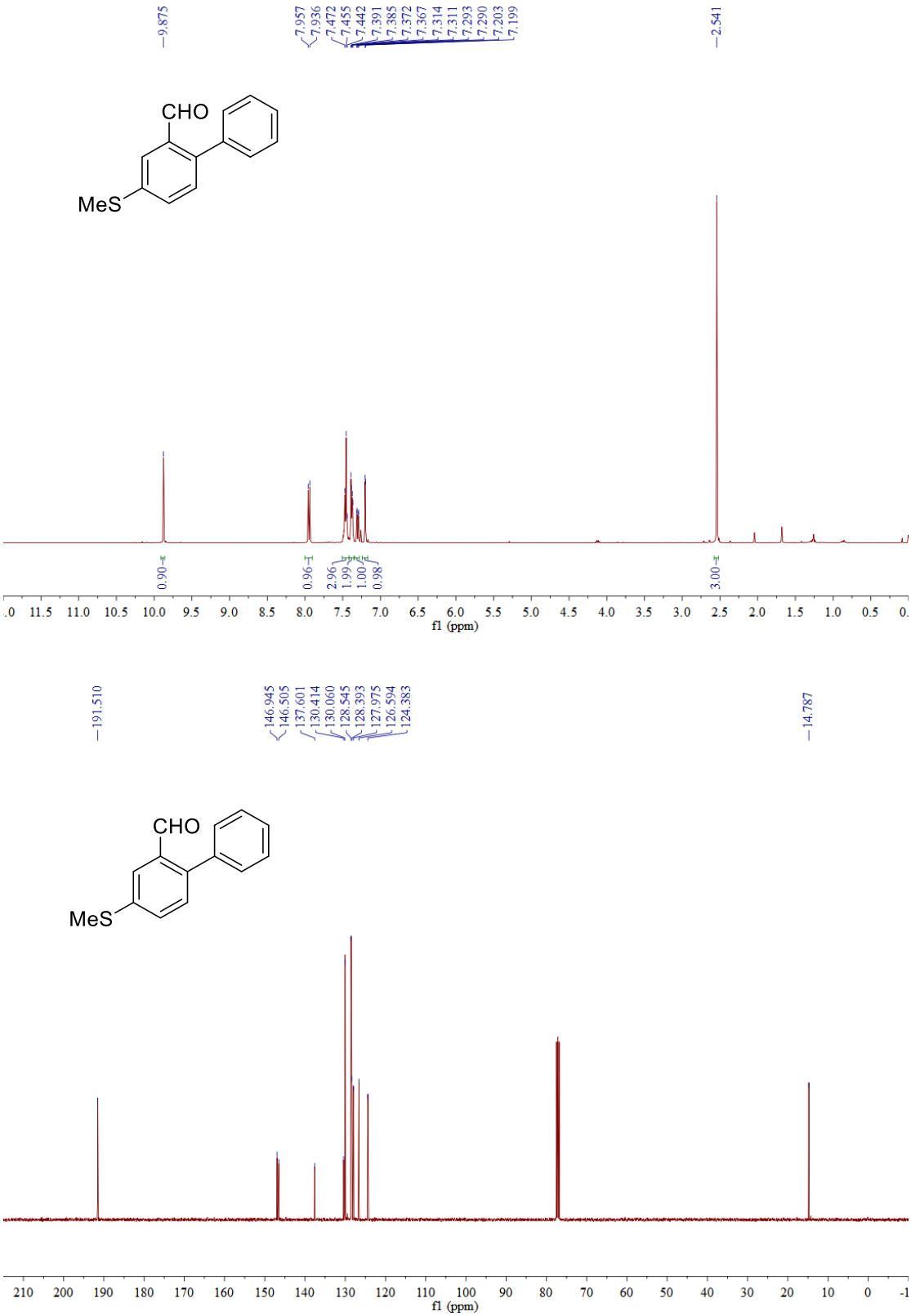


Figure S28. ^{1}H and ^{13}C NMR Spectra for compound **3w**

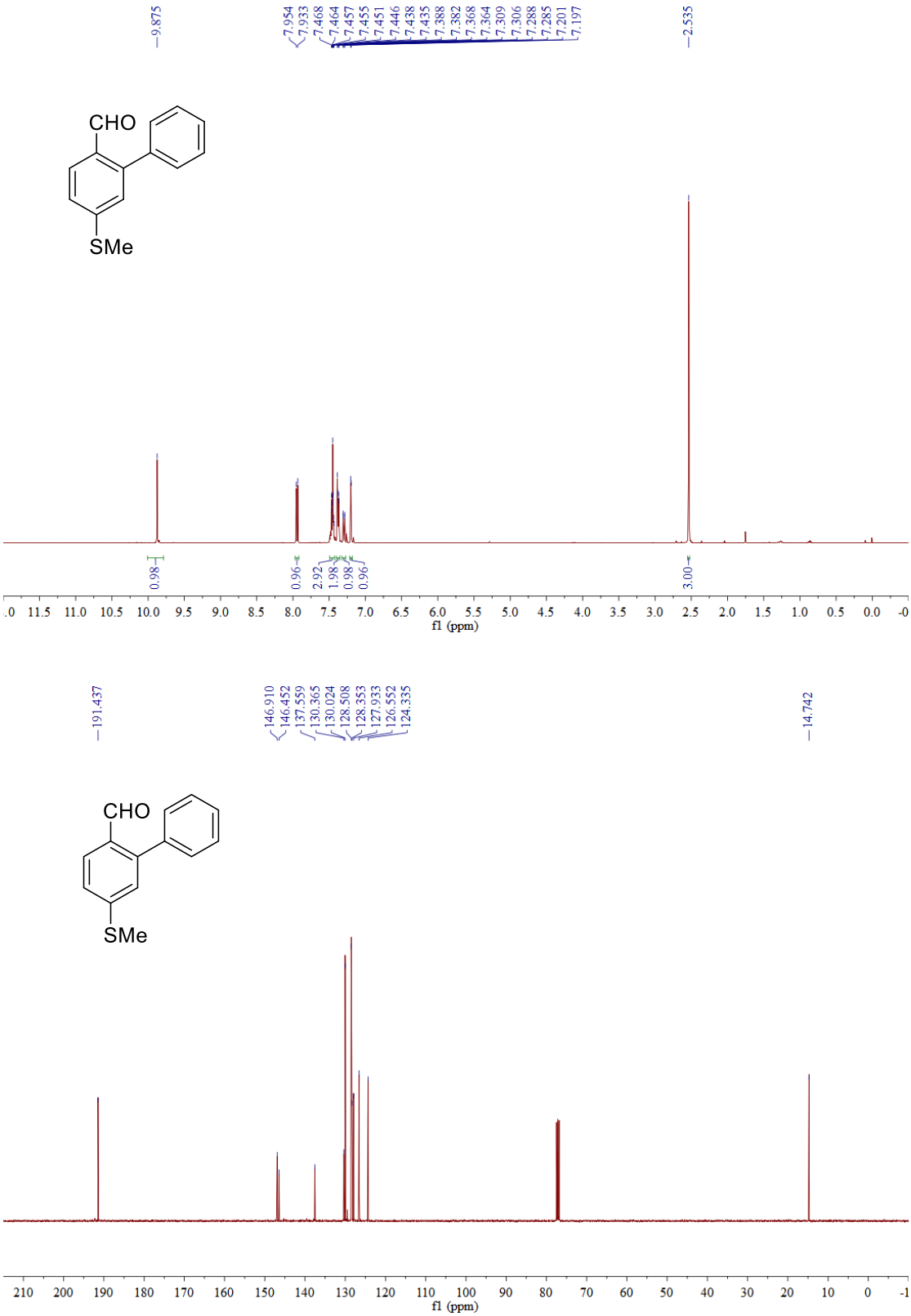


Figure S29. ^{1}H and ^{13}C NMR Spectra for compound **3x**

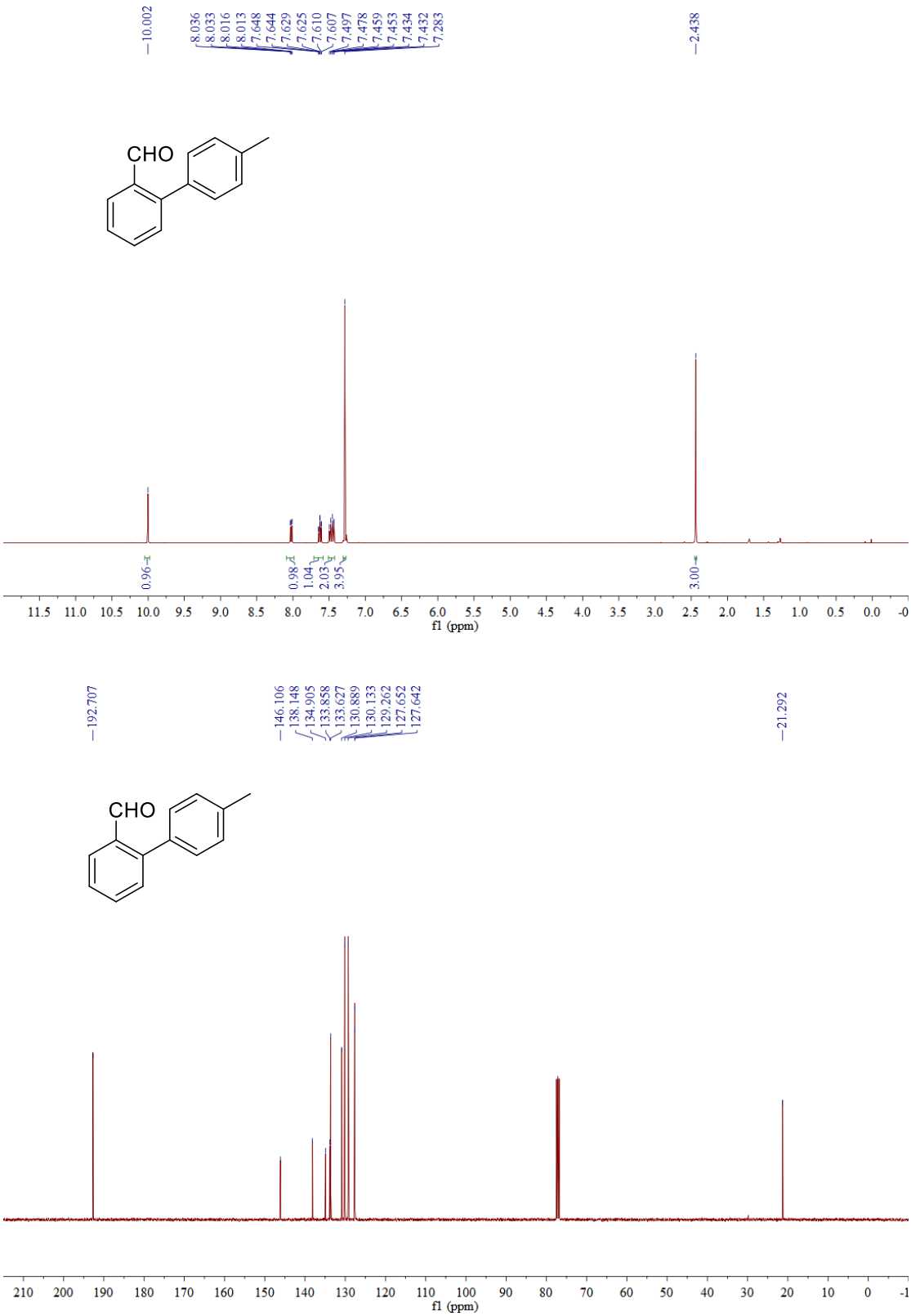


Figure S30. ^{1}H and ^{13}C NMR Spectra for compound **3y**

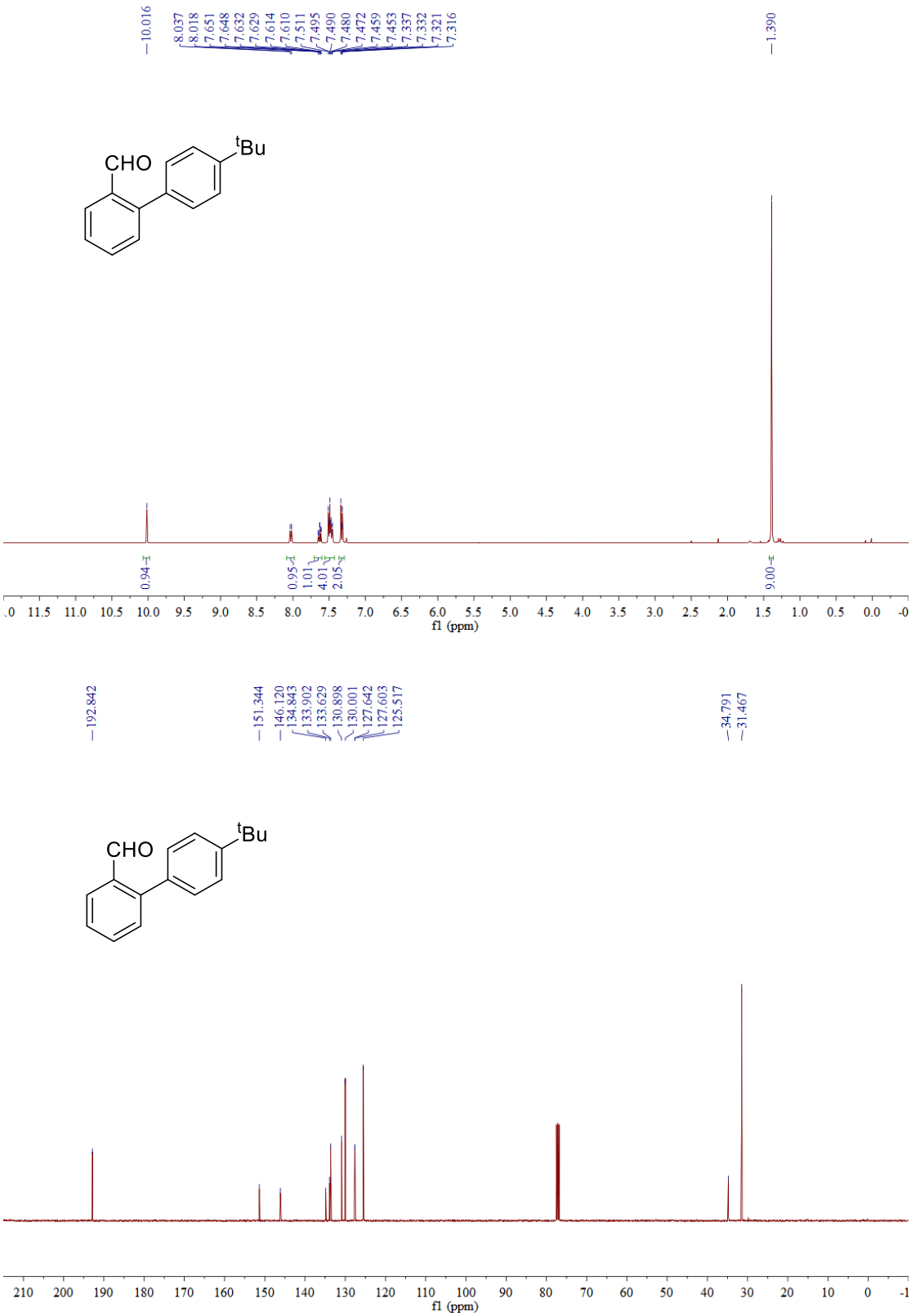


Figure S31. ^{1}H and ^{13}C NMR Spectra for compound **3z**

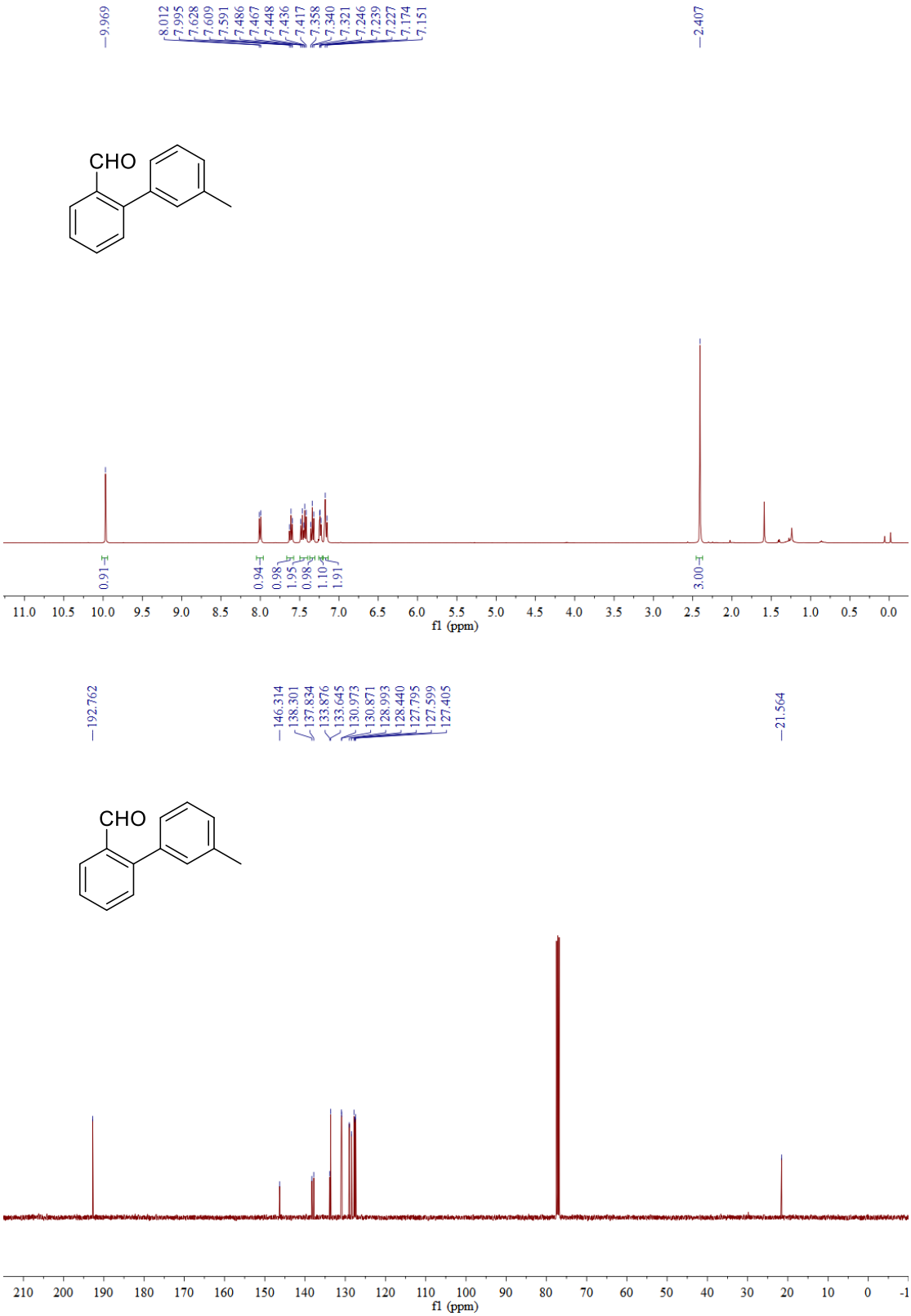


Figure S32. ^{1}H and ^{13}C NMR Spectra for compound **3aa**

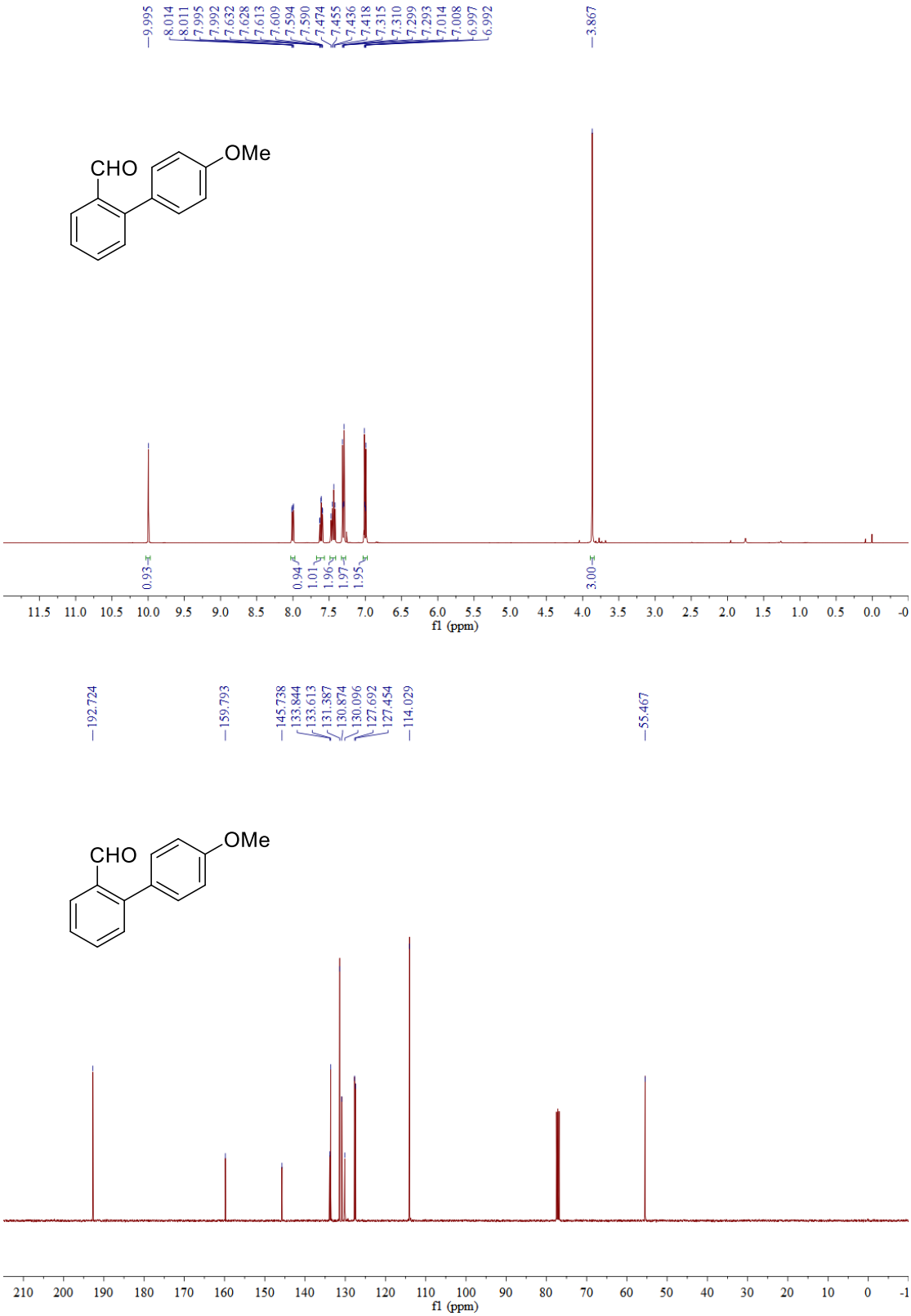
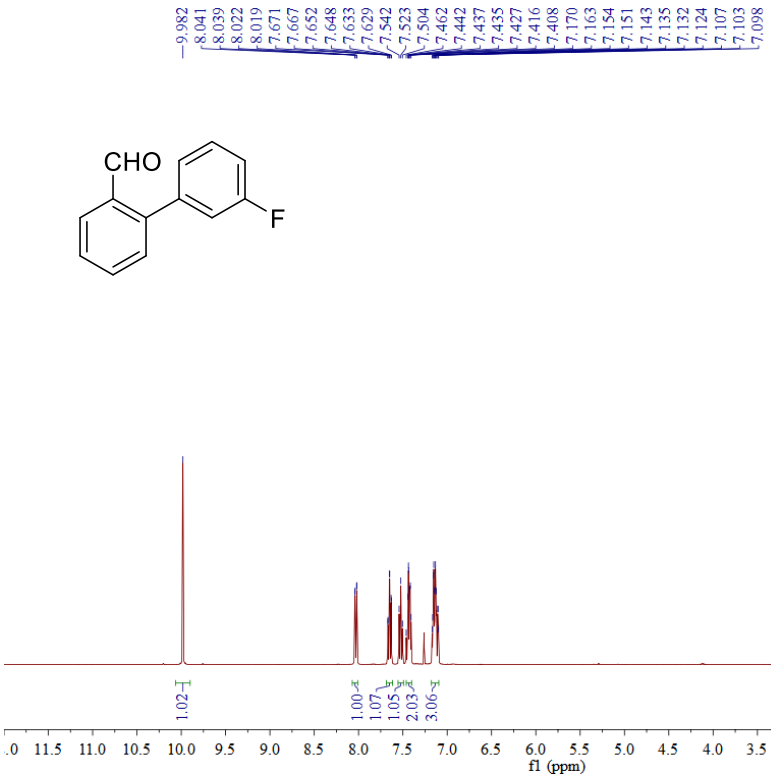


Figure S33. ^{1}H and ^{13}C NMR Spectra for compound **3ab**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7.408
7.170
7.163
7.154
7.151
7.143
7.135
7.132
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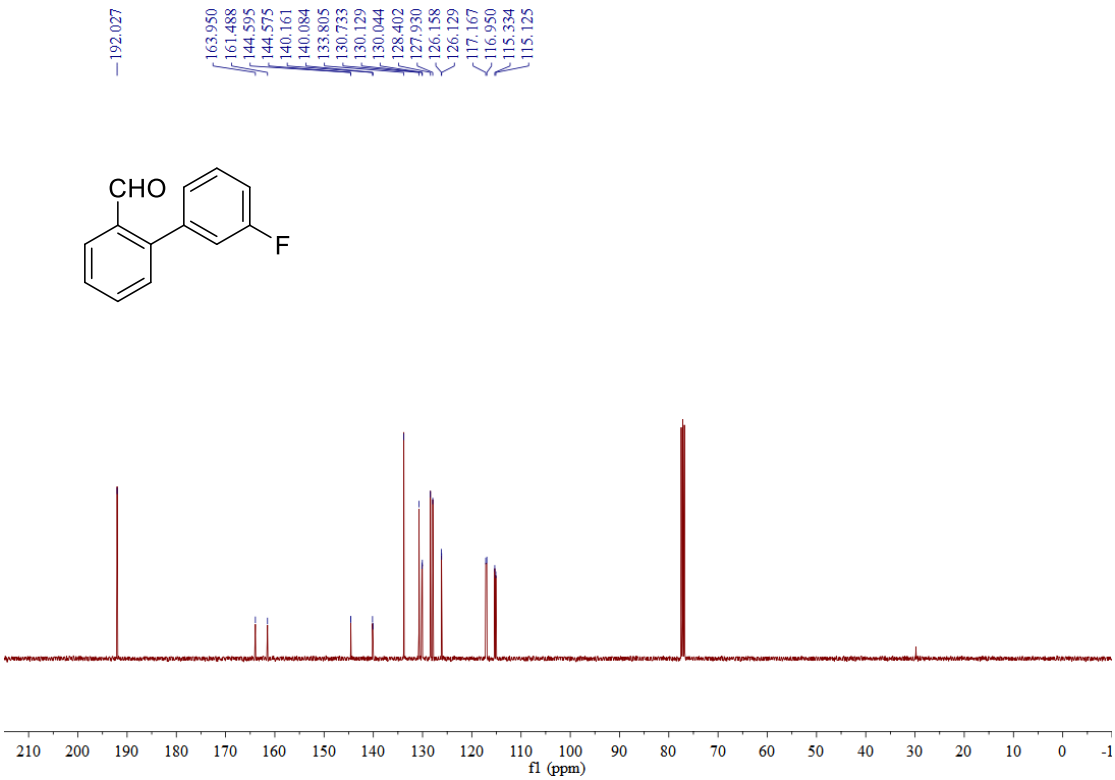
3.06
fl (ppm)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fl (ppm)

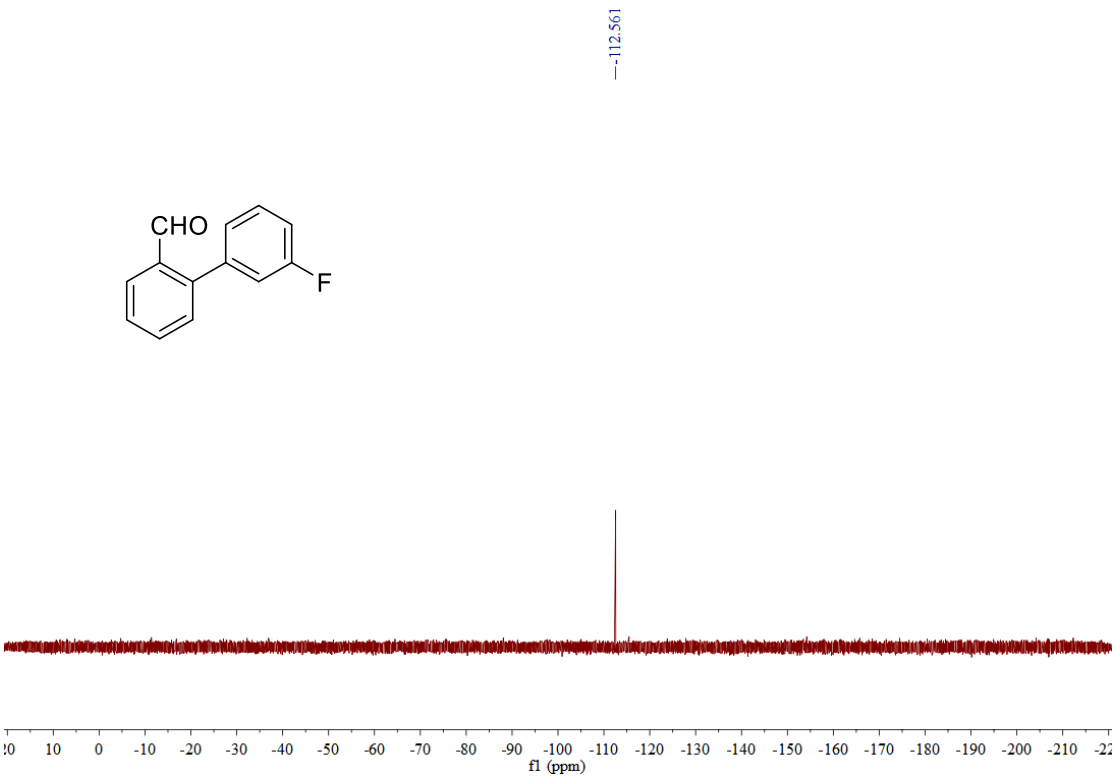
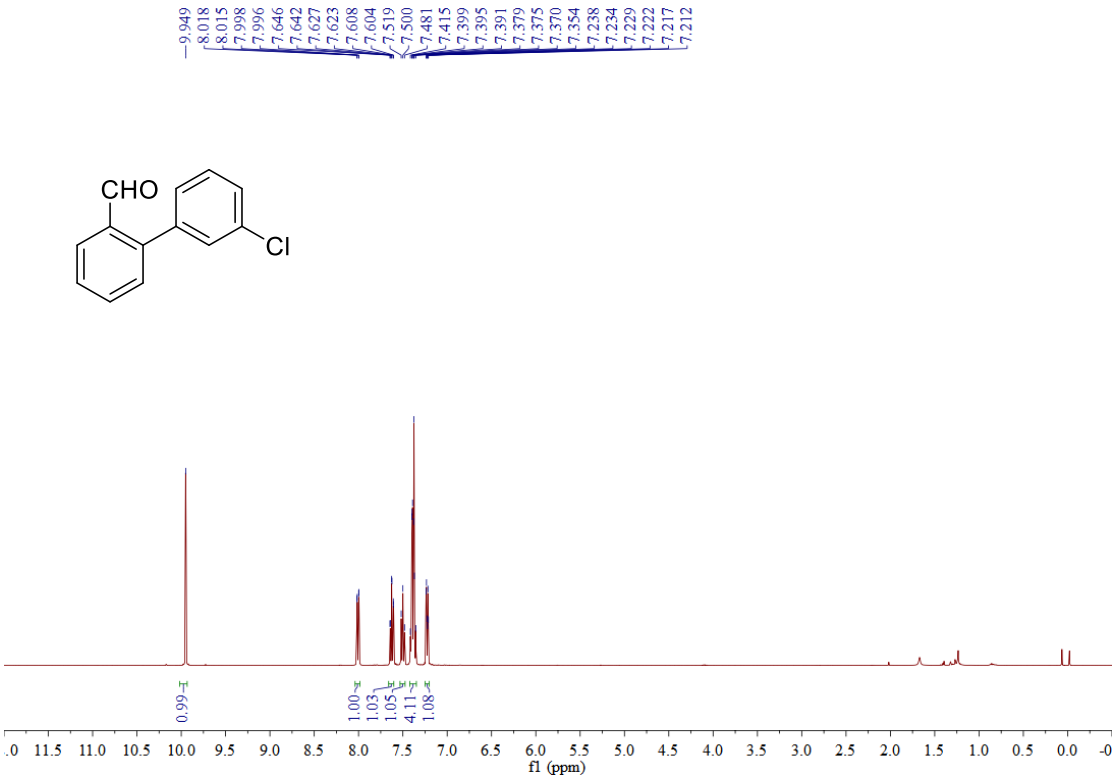


Figure S34. ^{1}H, ^{13}C and ^{19}F NMR Spectra for compound **3ac**



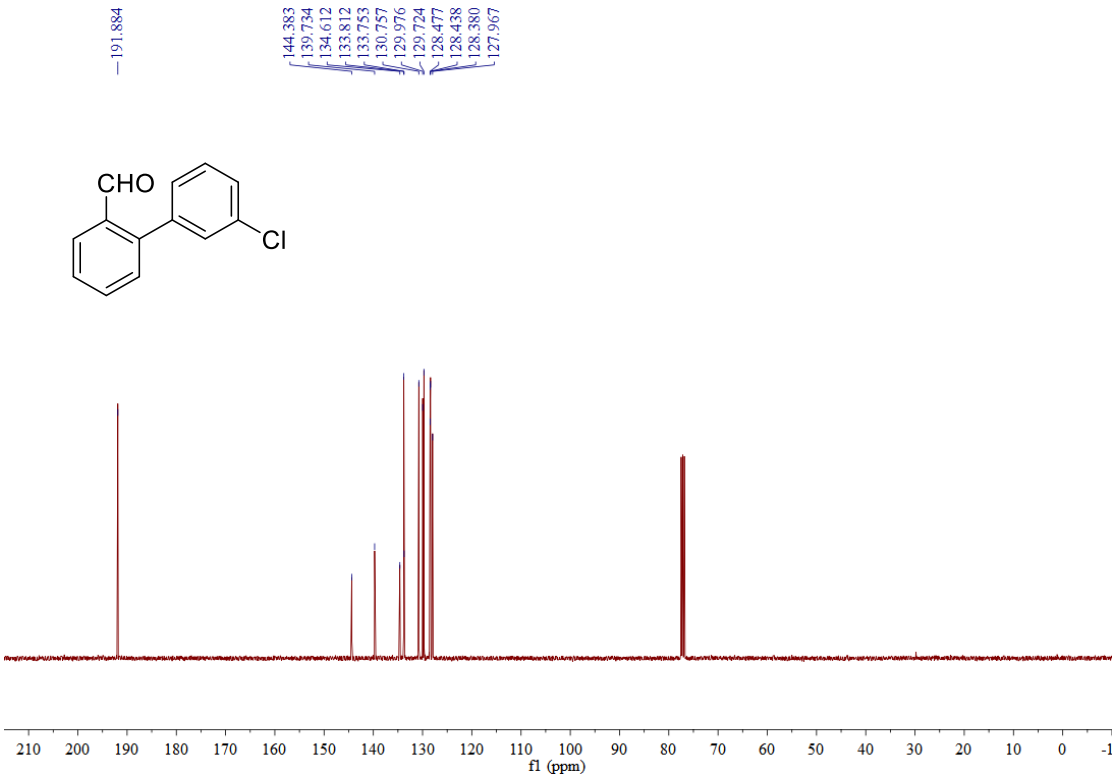
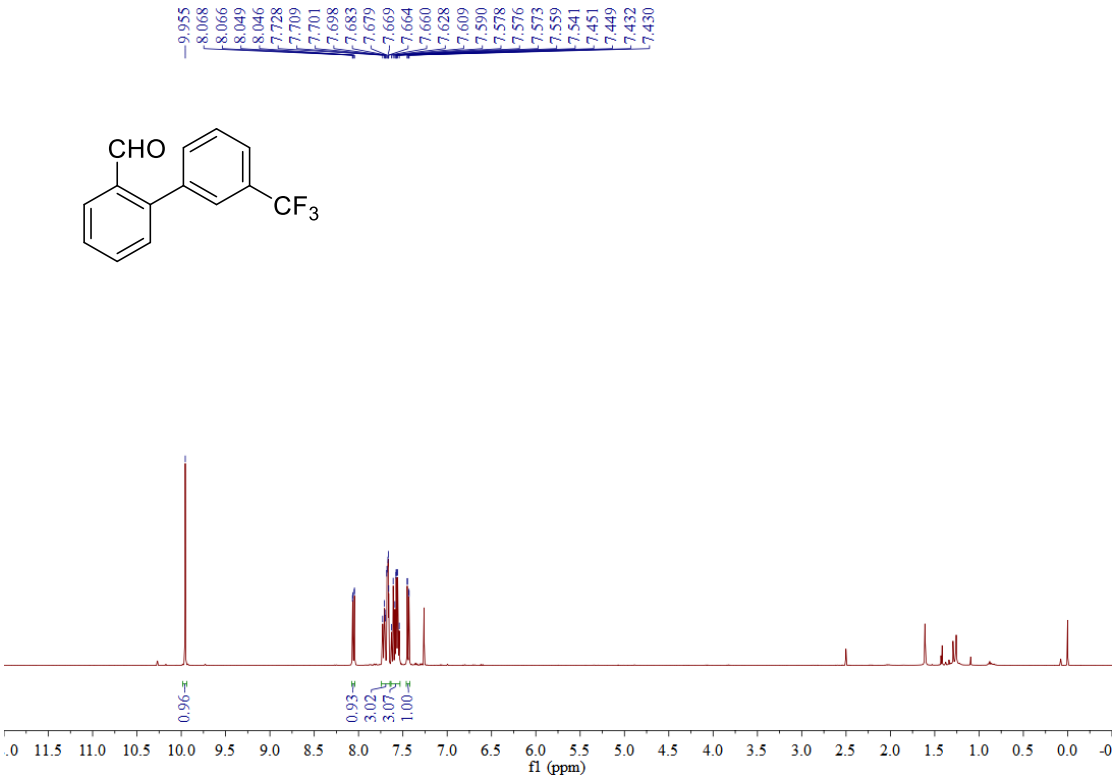


Figure S35. ^{1}H and ^{13}C NMR Spectra for compound **3ad**



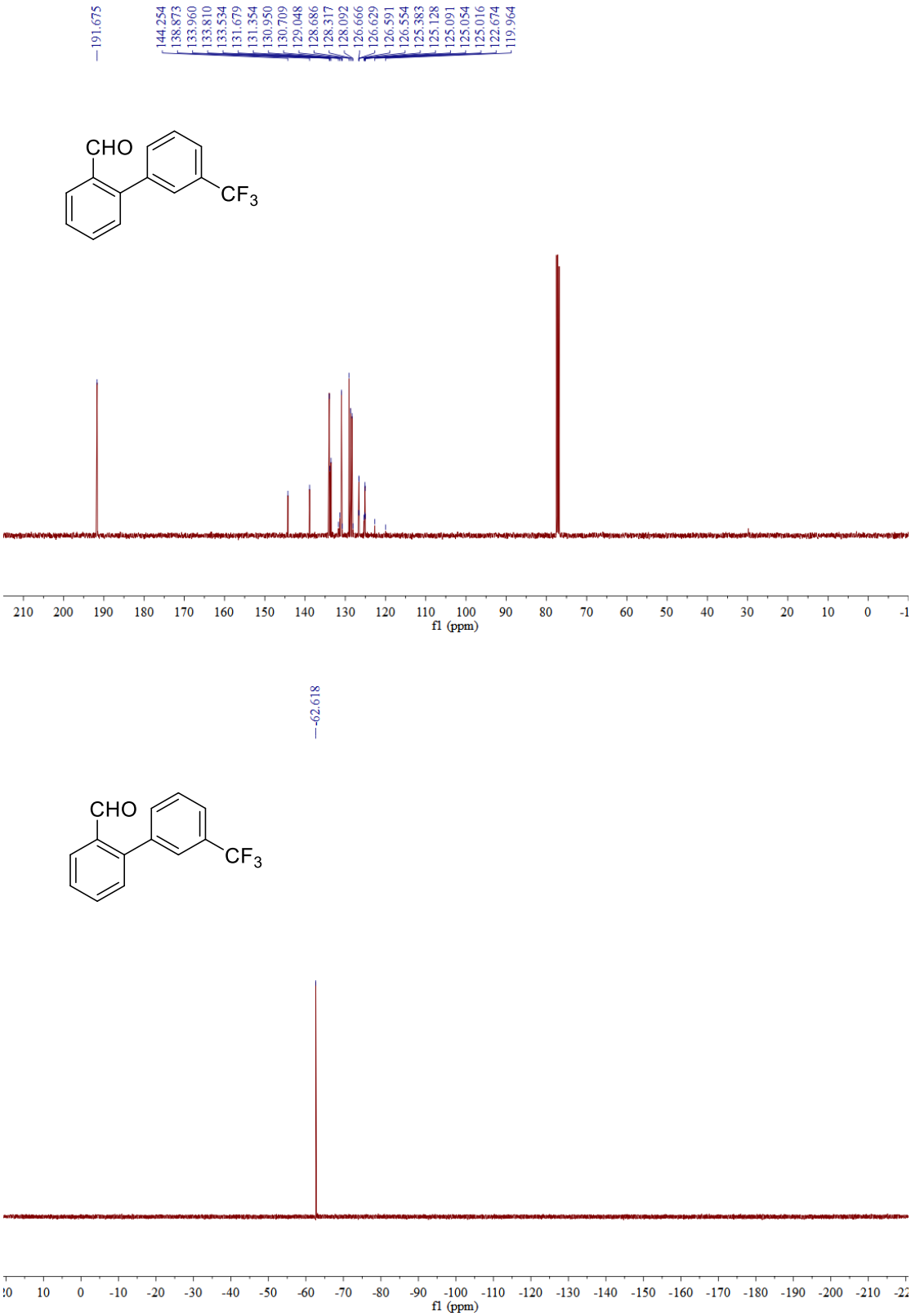


Figure S36. ^{1}H, ^{13}C and ^{19}F NMR Spectra for compound **3ae**

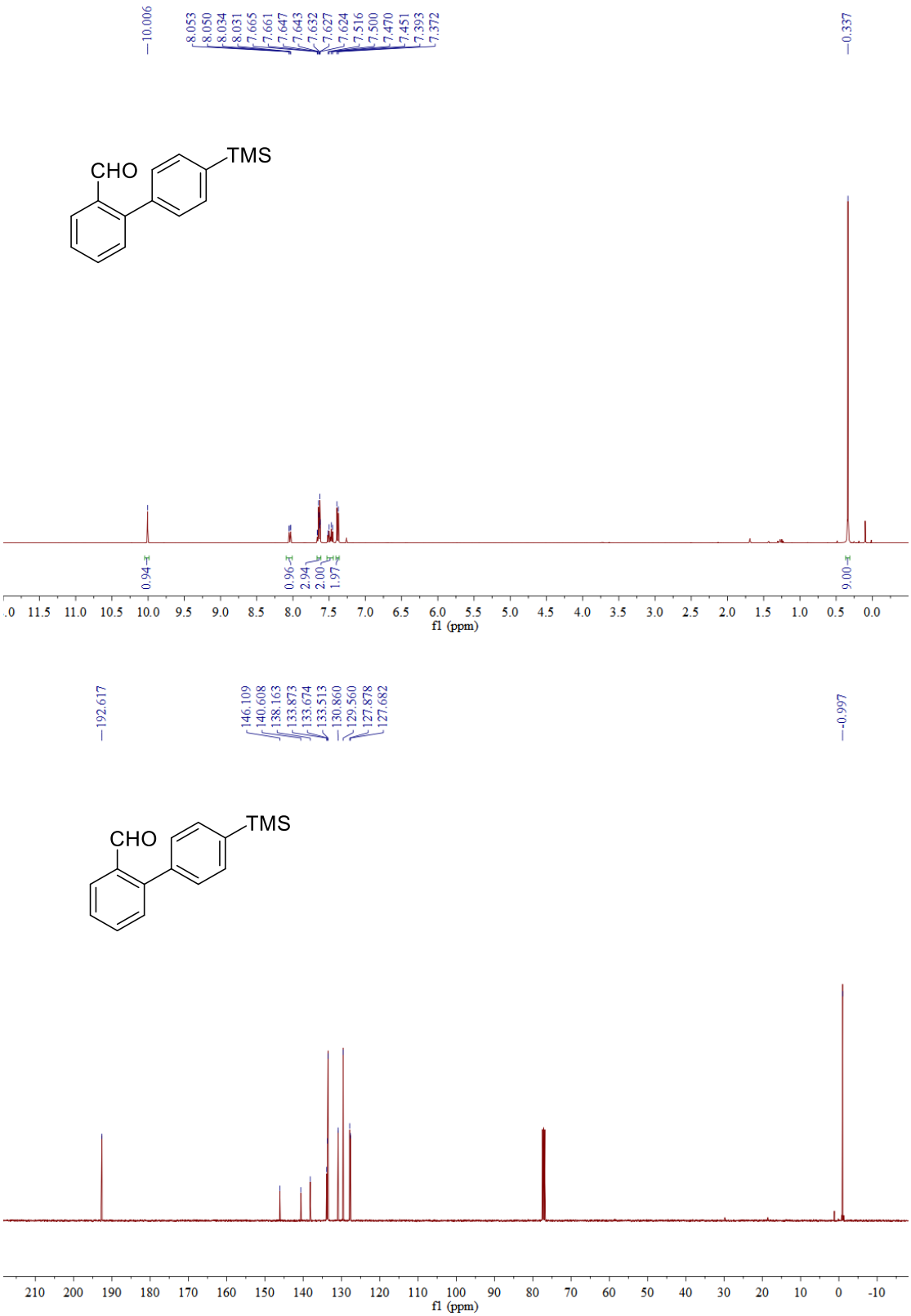


Figure S37. ^{1}H and ^{13}C NMR Spectra for compound **3af**

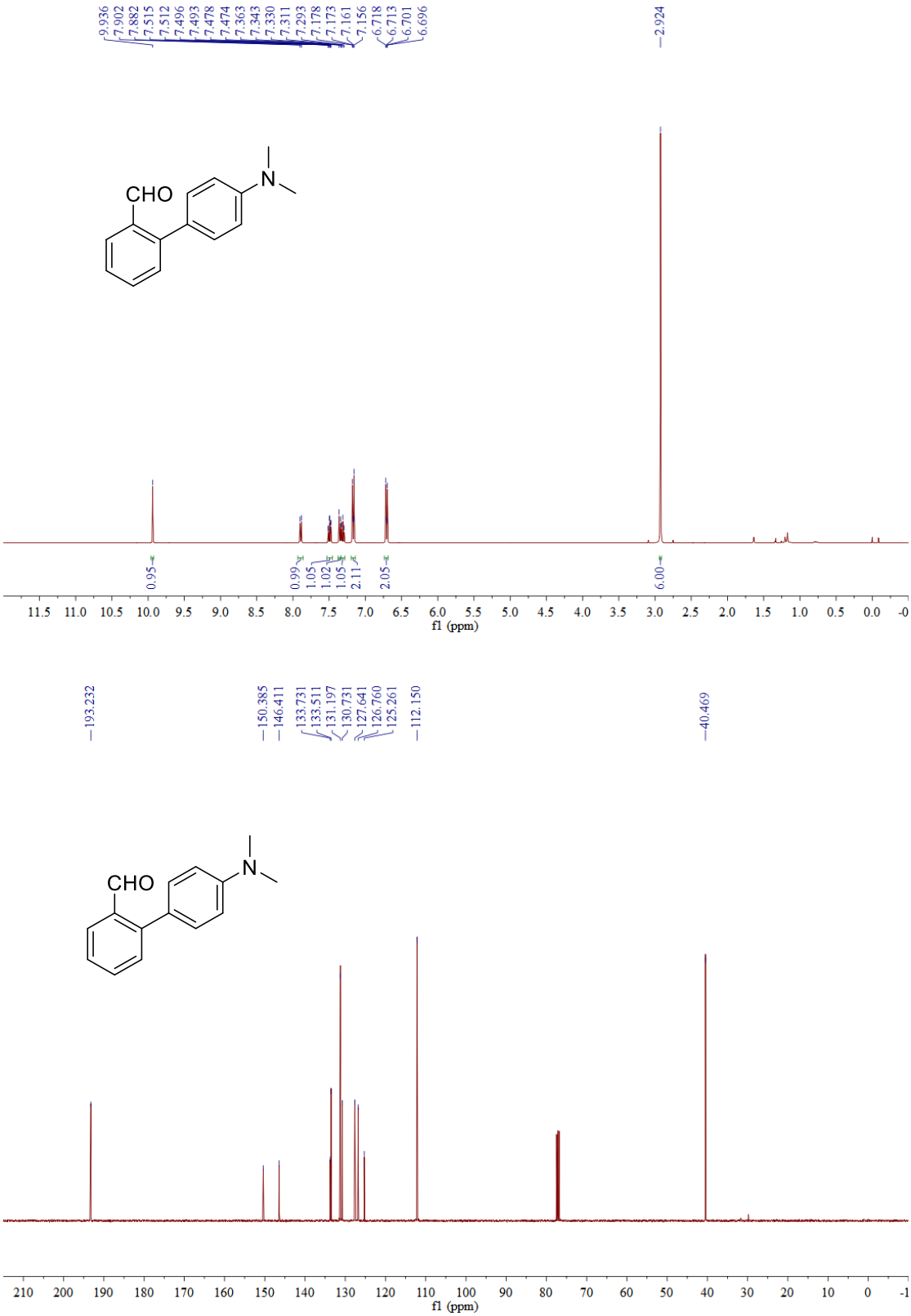


Figure S38. ^{1}H and ^{13}C NMR Spectra for compound **3af**

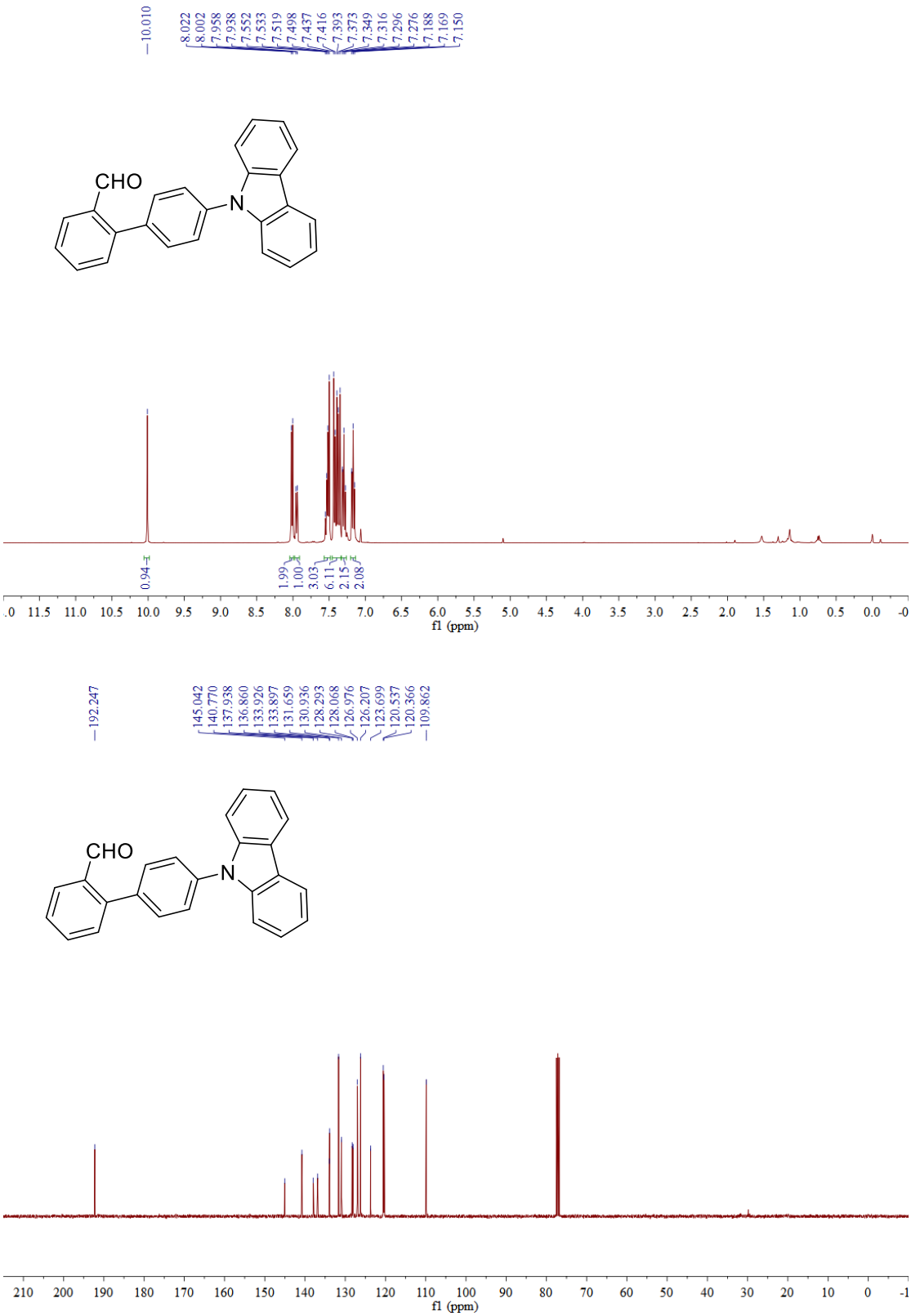


Figure S39. ^{1}H and ^{13}C NMR Spectra for compound **3ah**

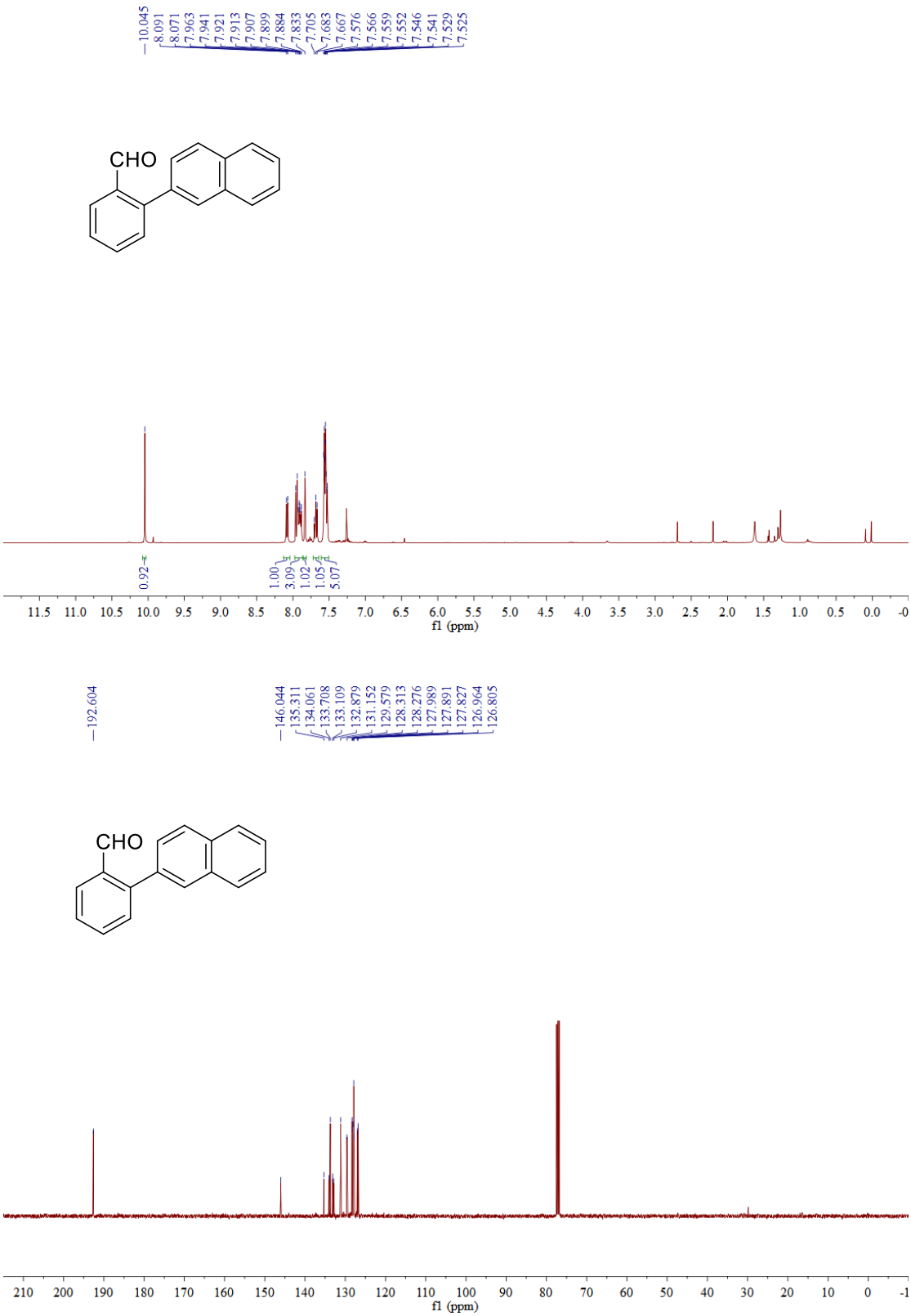


Figure S40. ^{1}H and ^{13}C NMR Spectra for compound **3ai**

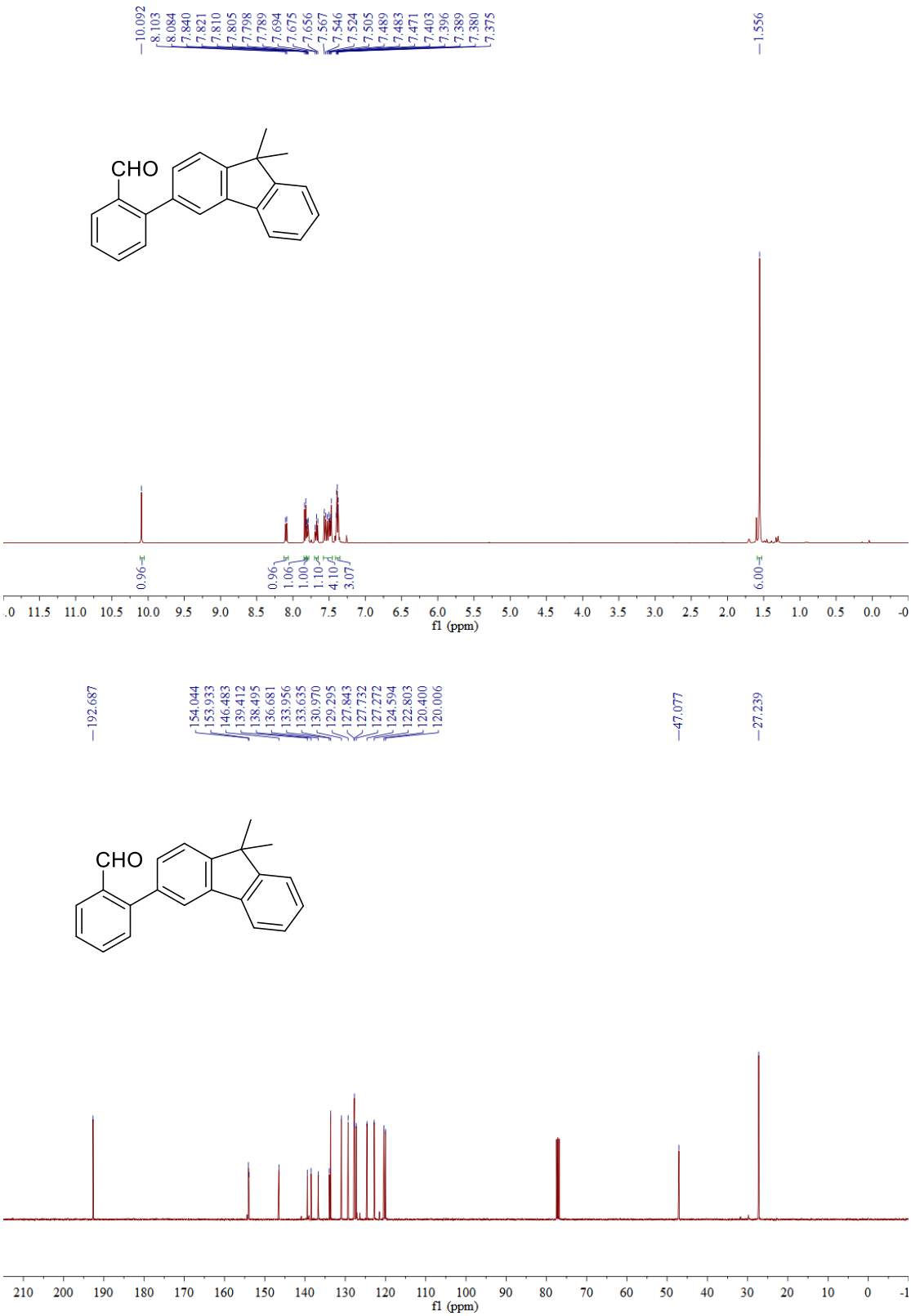


Figure S41. ^{1}H and ^{13}C NMR Spectra for compound **3aj**

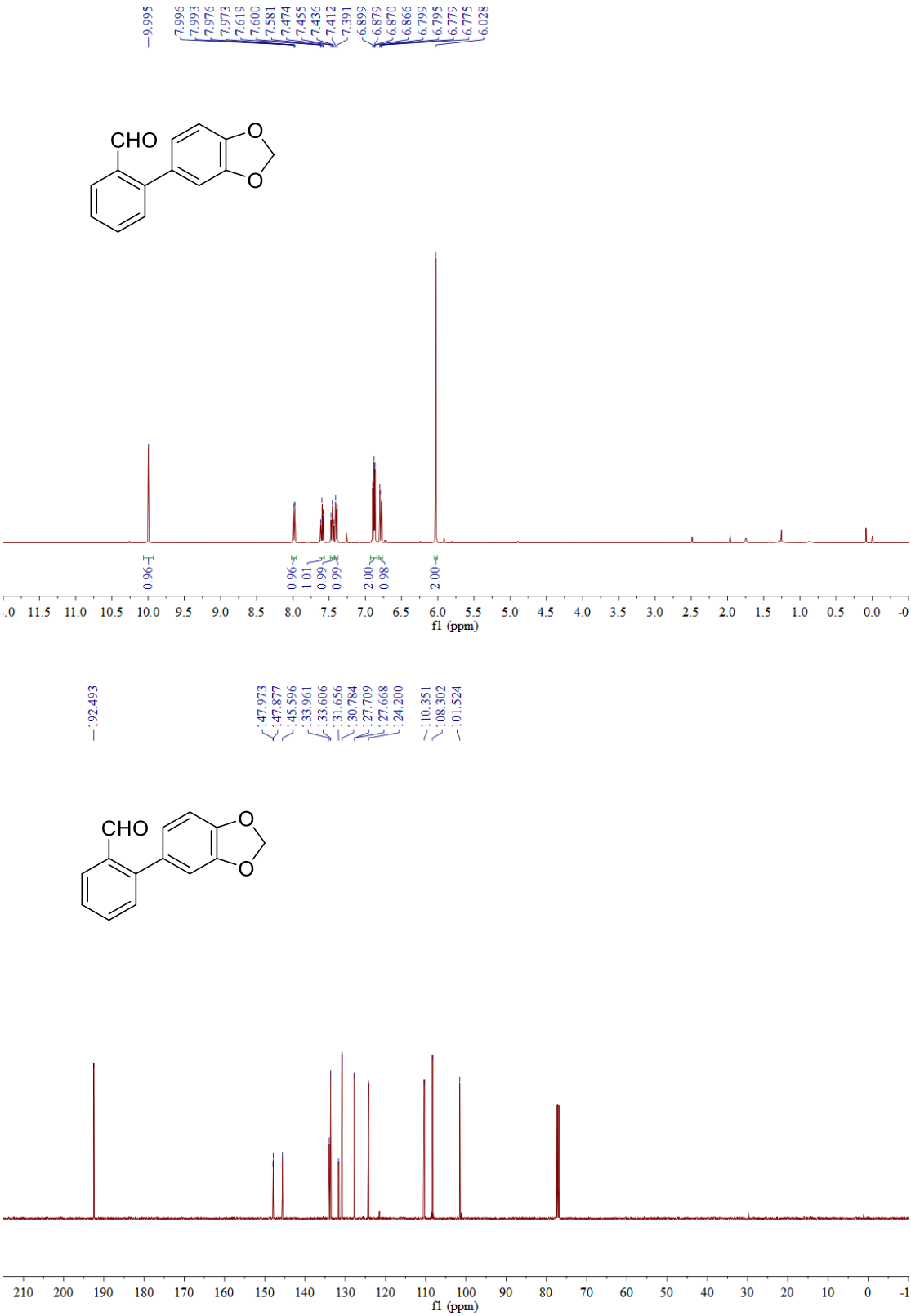


Figure S42. ^{1}H and ^{13}C NMR Spectra for compound **3ak**

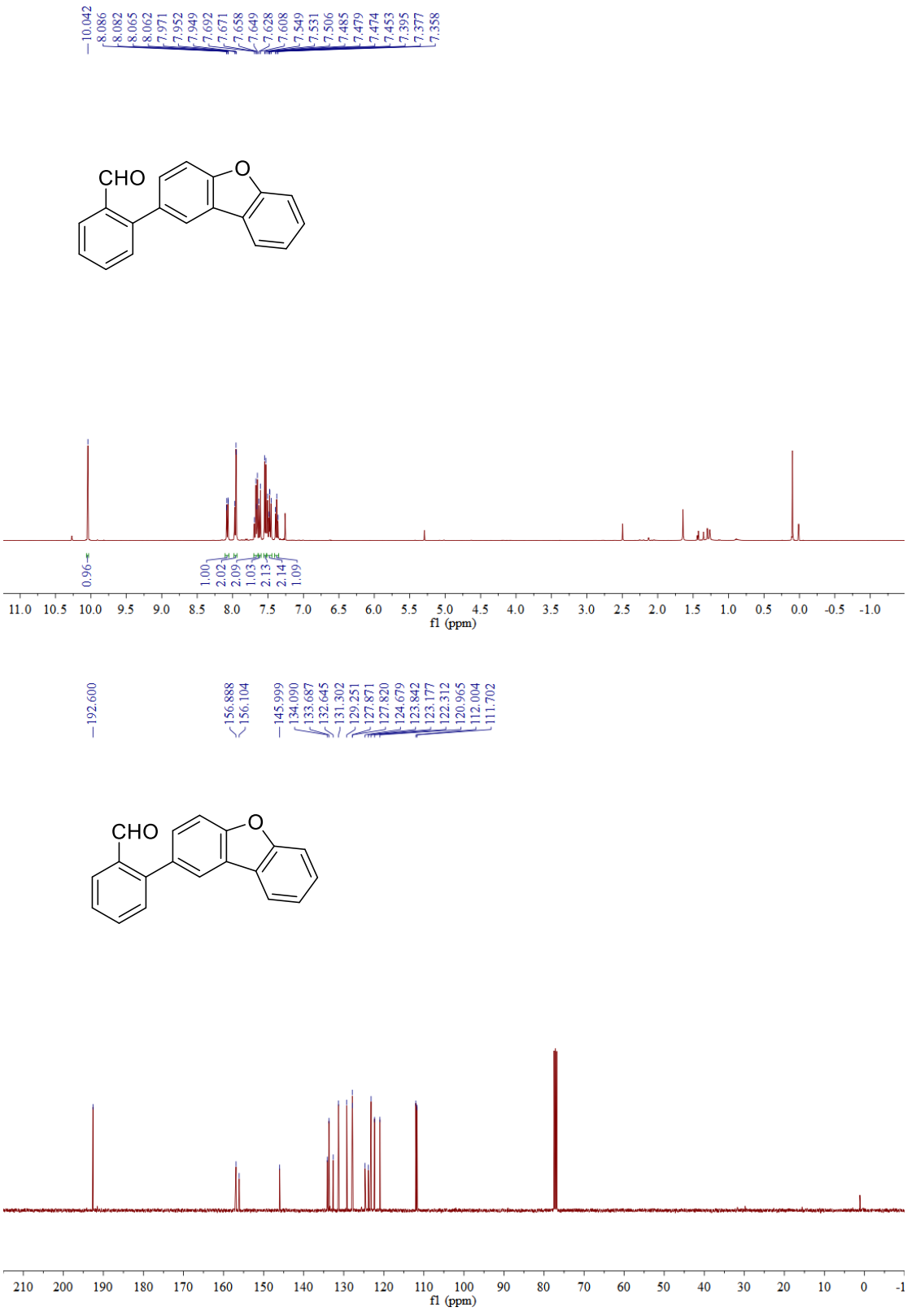


Figure S43. ^{1}H and ^{13}C NMR Spectra for compound **3al**

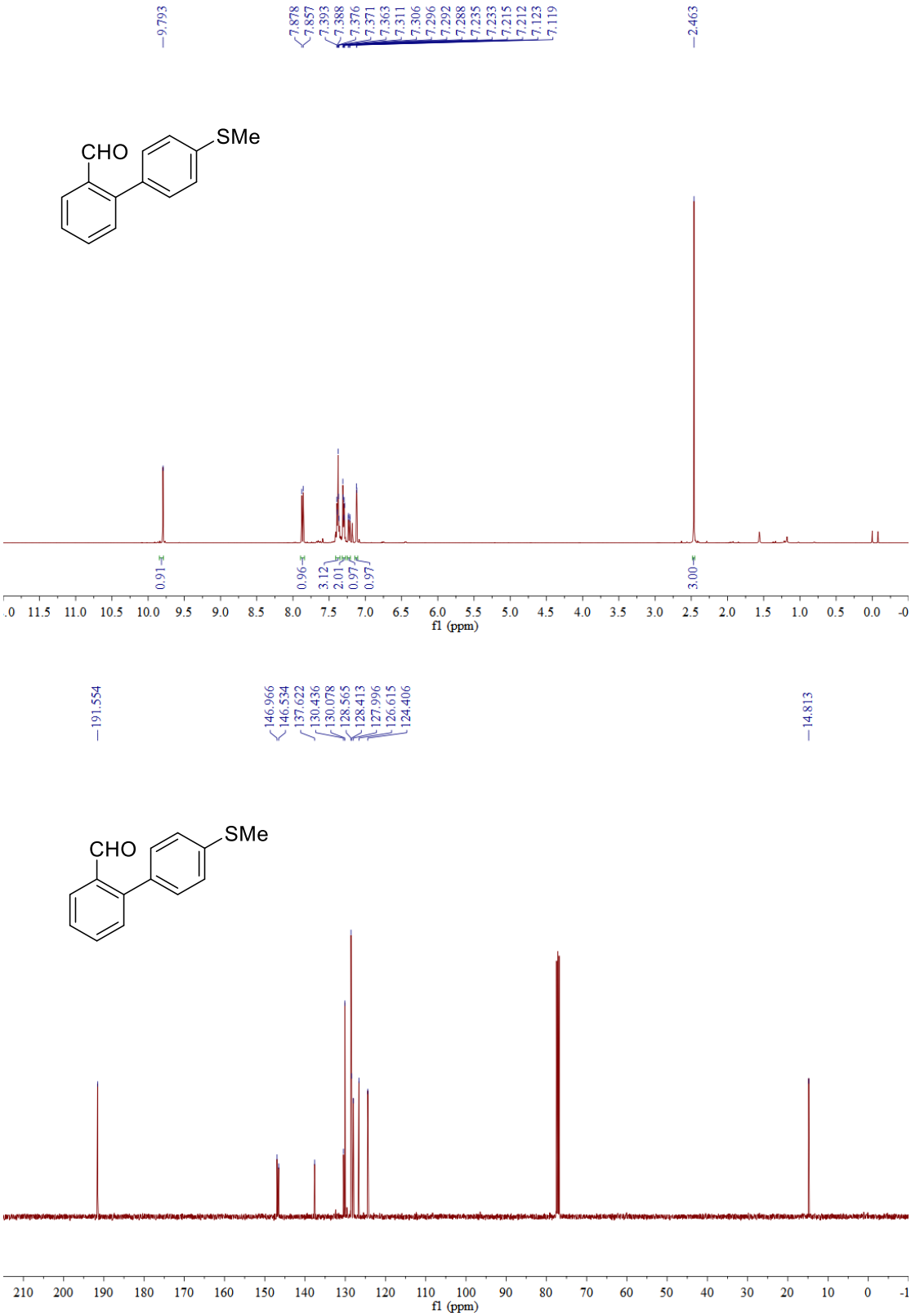


Figure S44. ^{1}H and ^{13}C NMR Spectra for compound **3am**

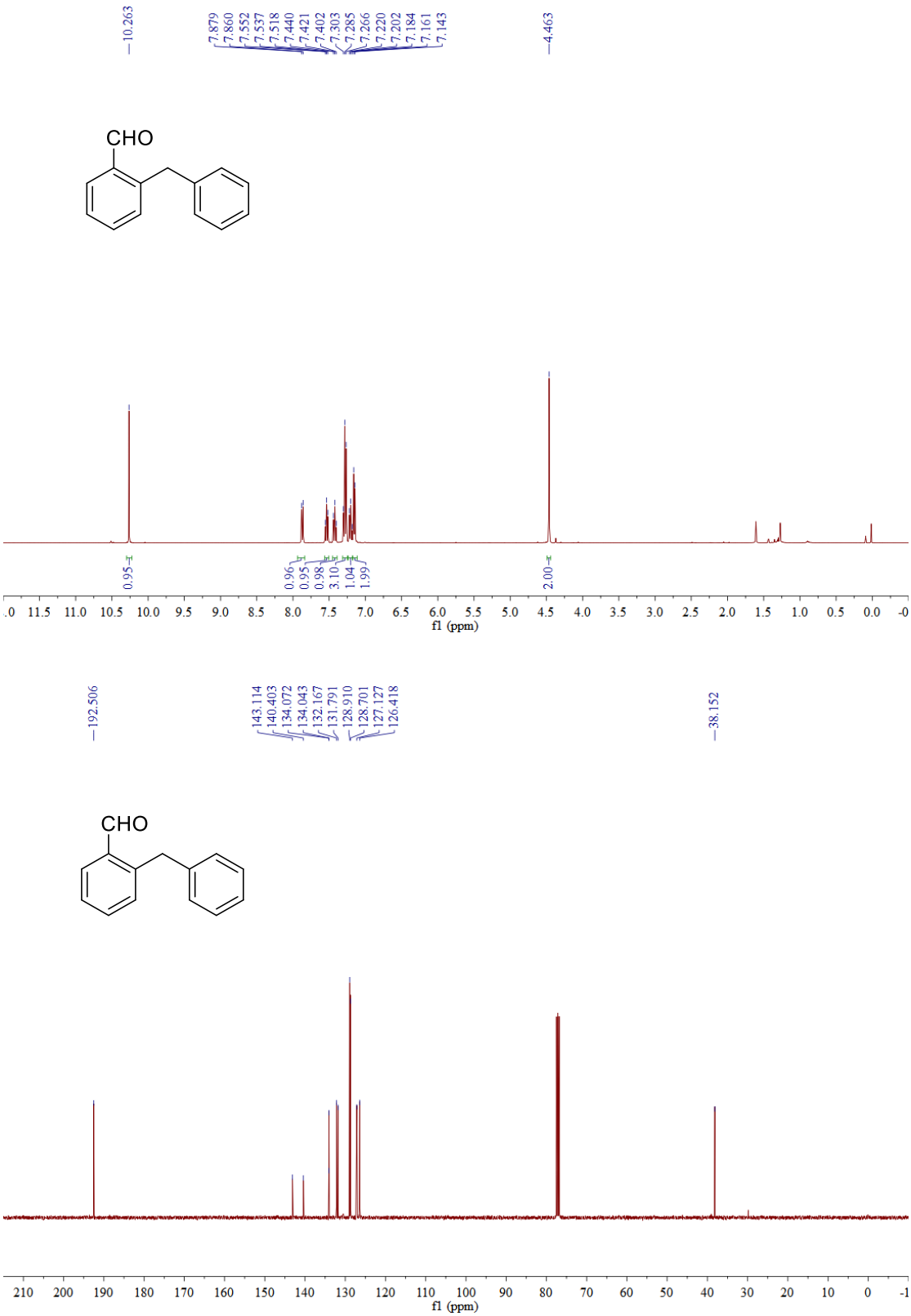


Figure S45. ^{1}H and ^{13}C NMR Spectra for compound **3an**

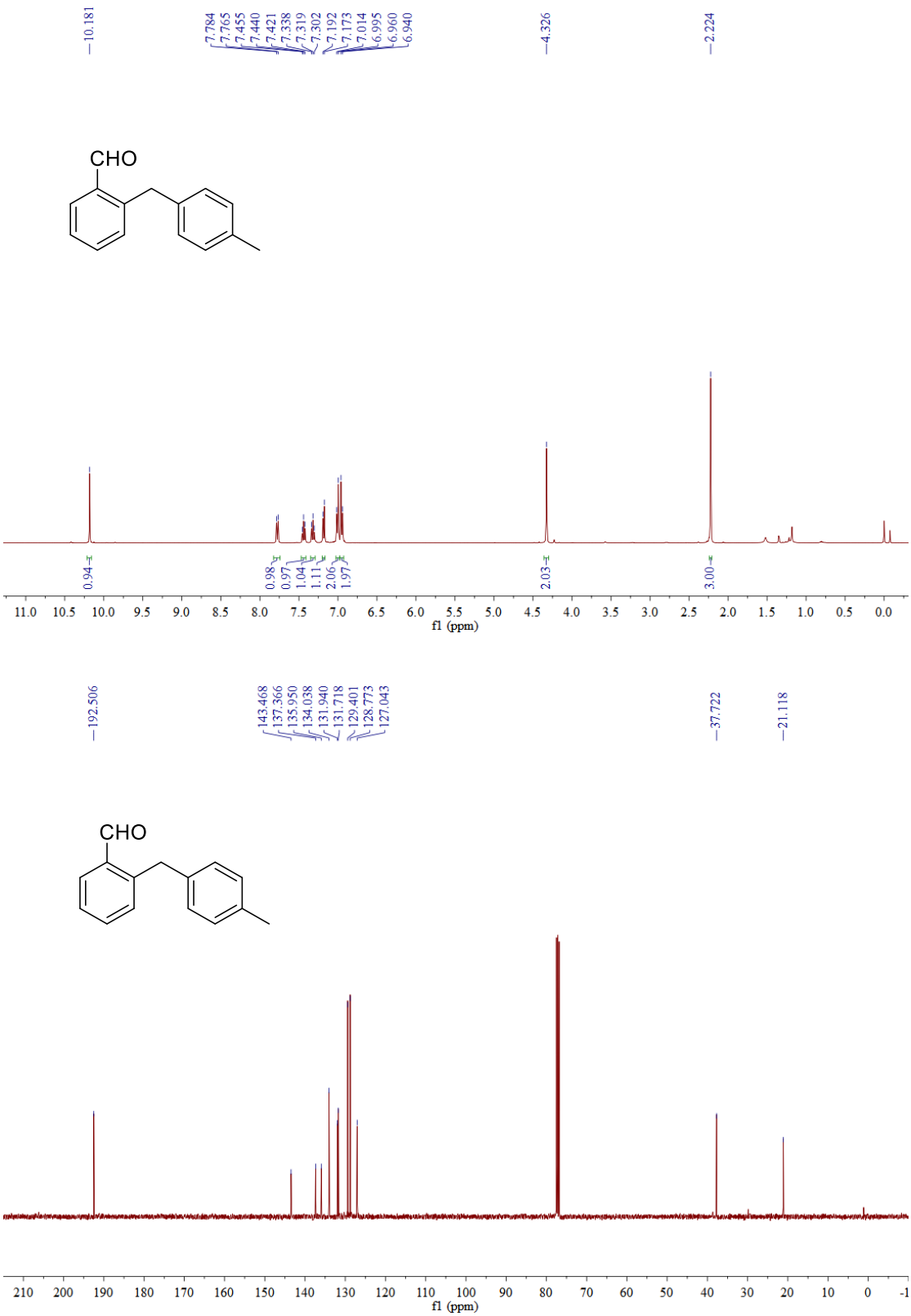
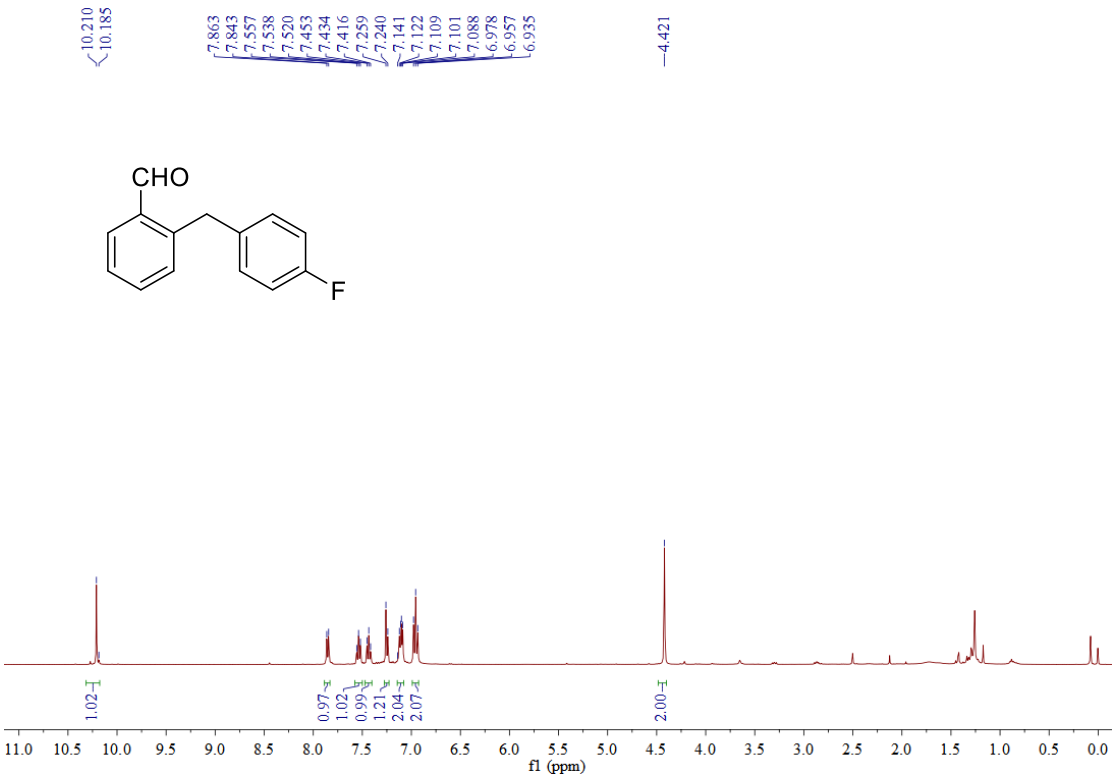
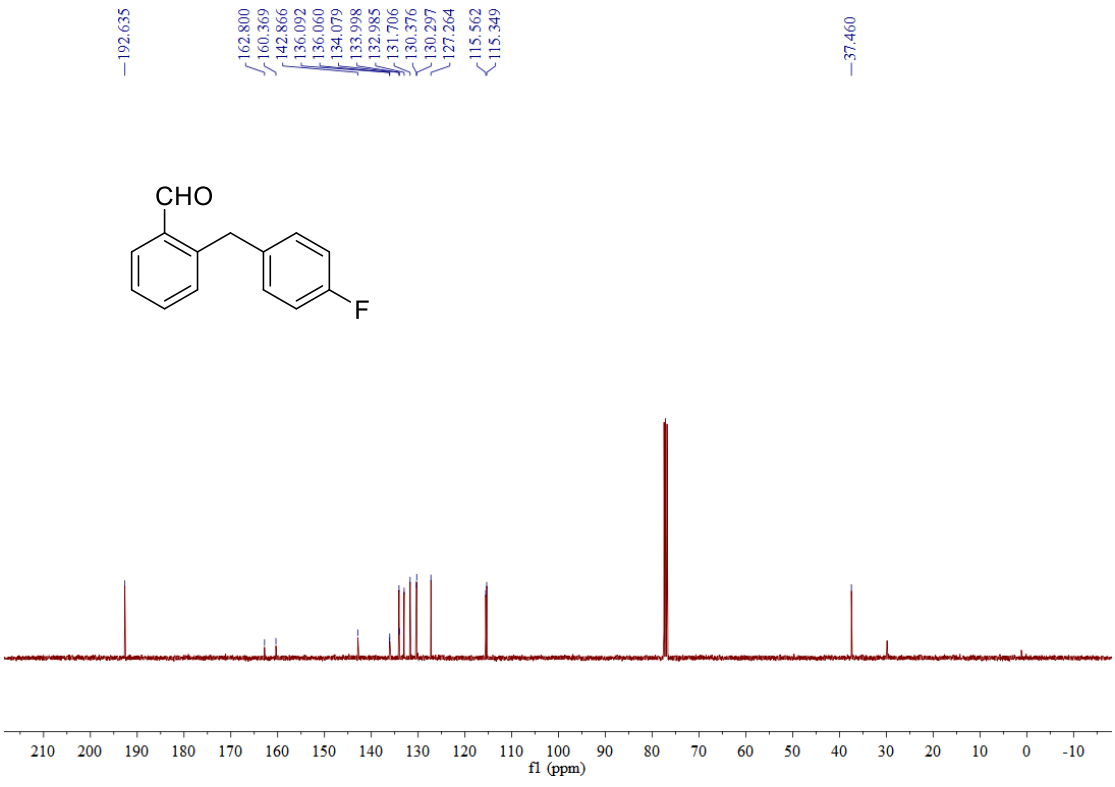


Figure S46. ^{1}H and ^{13}C NMR Spectra for compound **3ao**


10.210
10.185
7.863
7.843
7.557
7.538
7.520
7.453
7.434
7.416
7.259
7.240
7.141
7.122
7.109
7.101
7.088
6.978
6.957
6.935
4.421
CHO
F
1.02
0.97
1.02
0.99
1.21
2.04
2.07
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


192.635
162.800
160.369
142.866
136.092
136.060
134.079
133.998
132.985
131.706
130.376
130.297
127.264
115.562
115.349
37.460
CHO
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

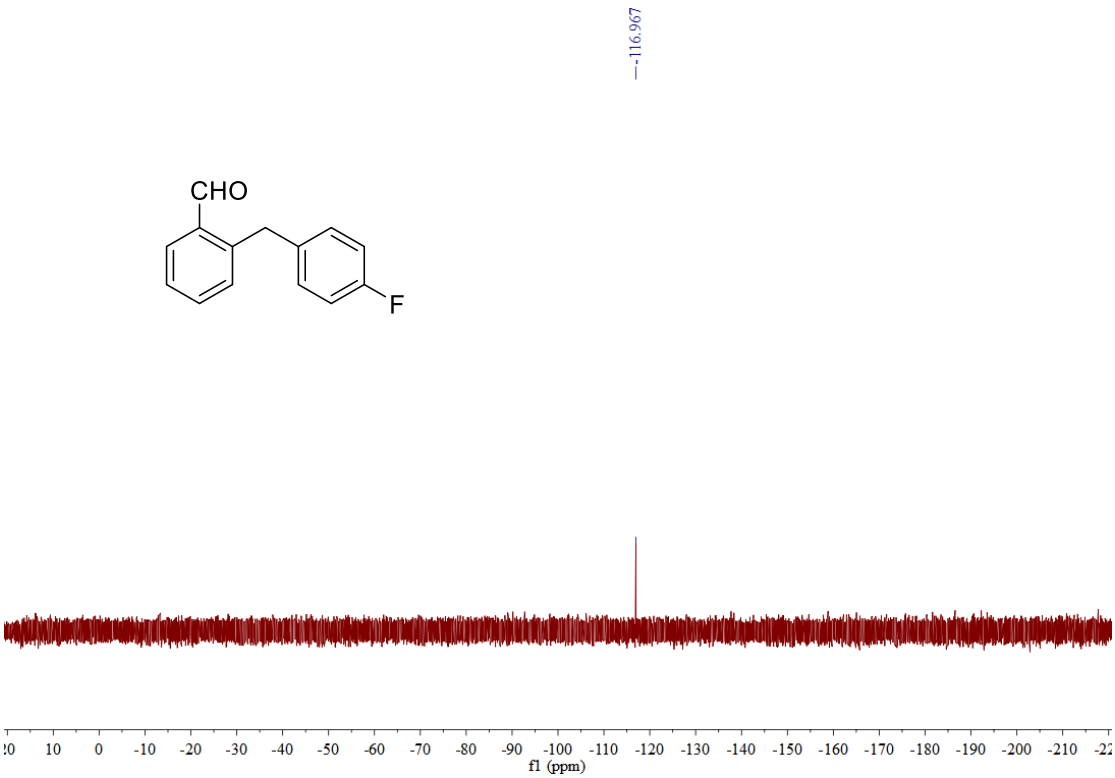
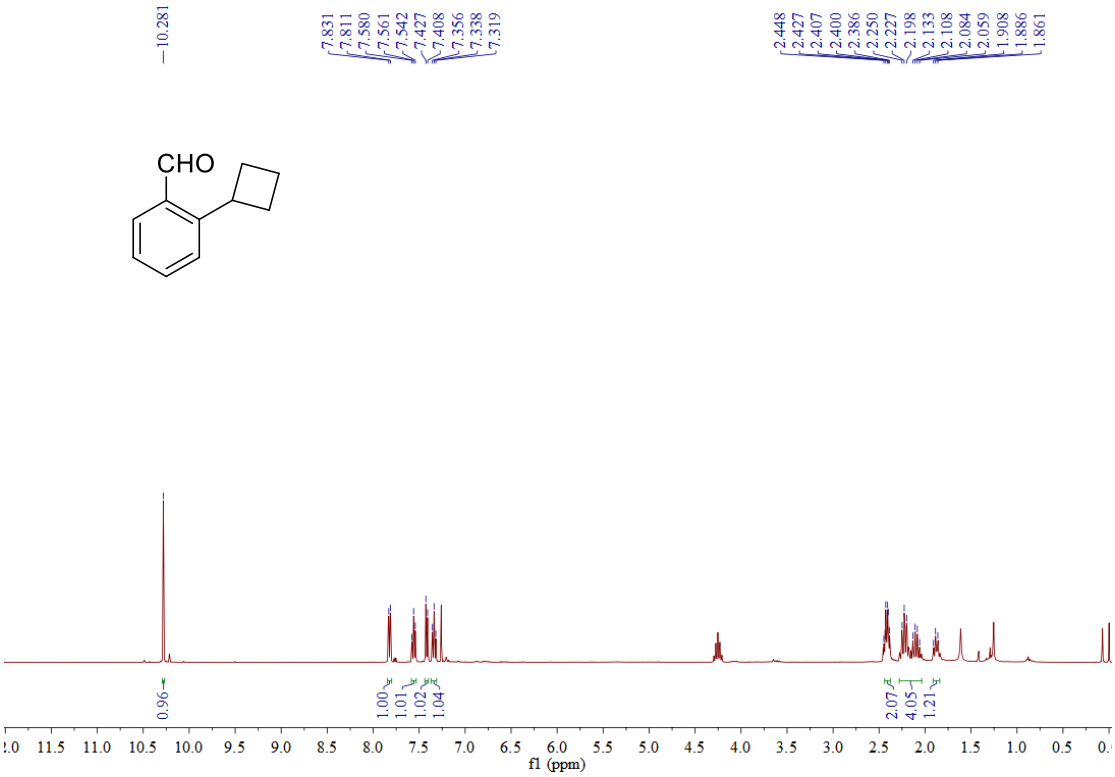


Figure S47. ^{1}H, ^{13}C and ^{19}F NMR Spectra for compound **3ap**



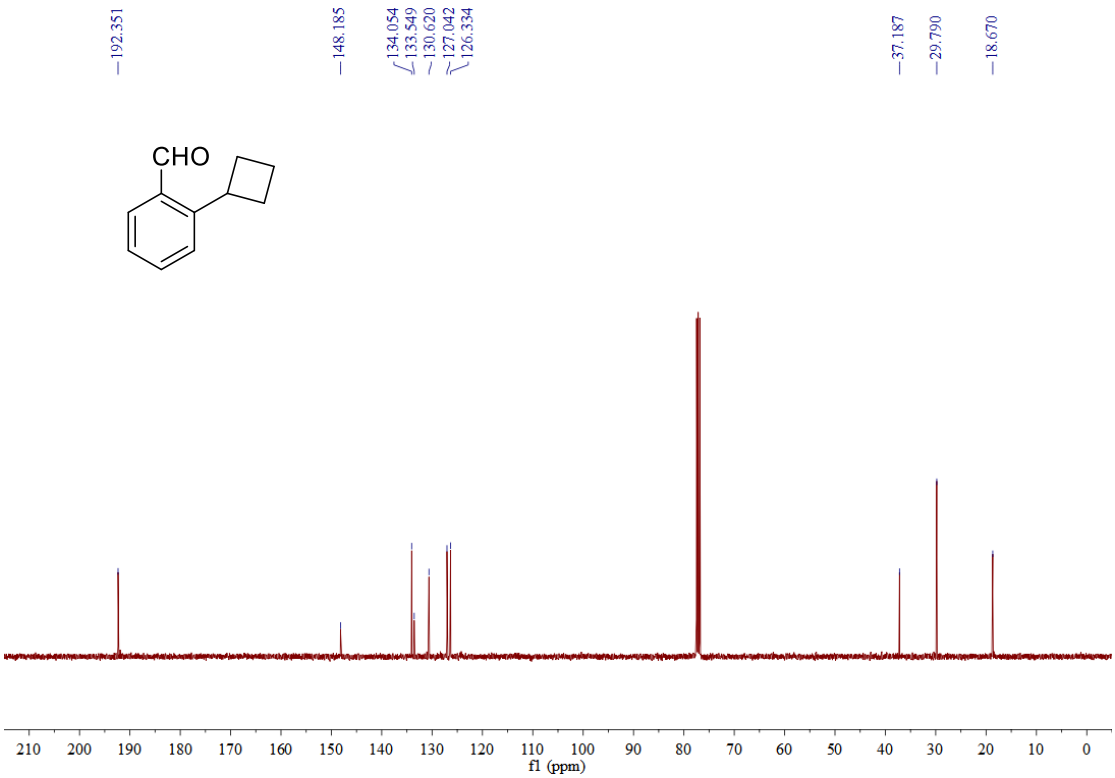
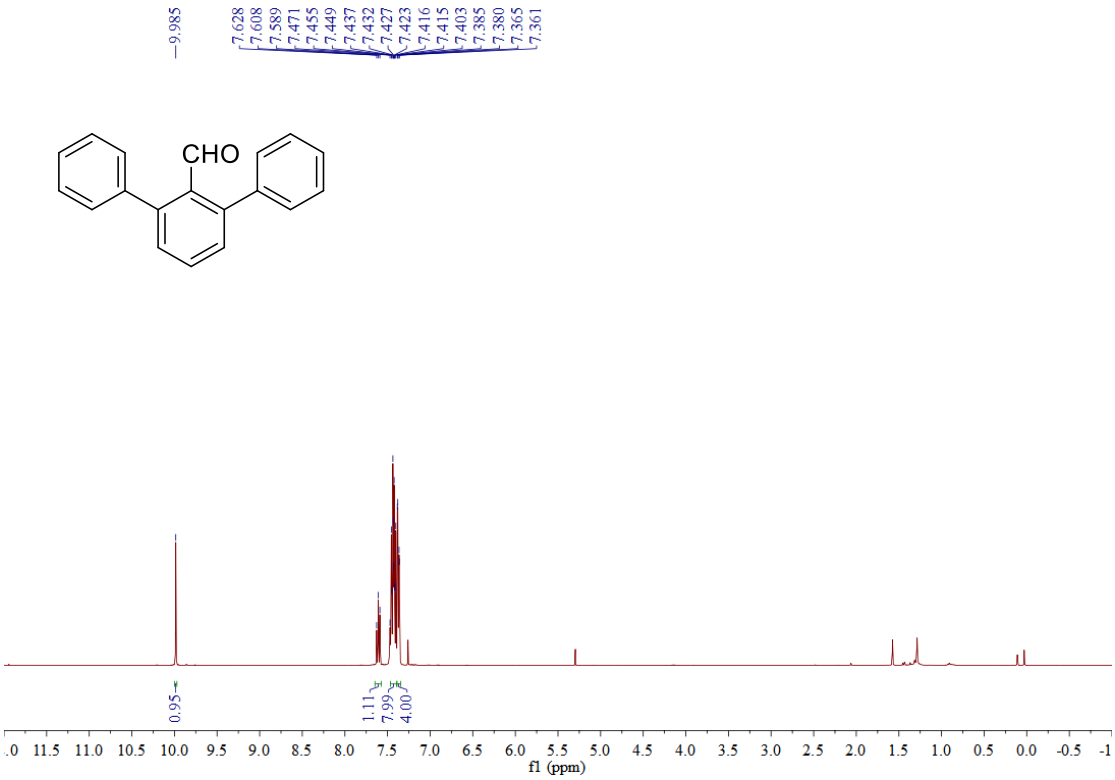


Figure S48. ^{1}H and ^{13}C NMR Spectra for compound **3aq**



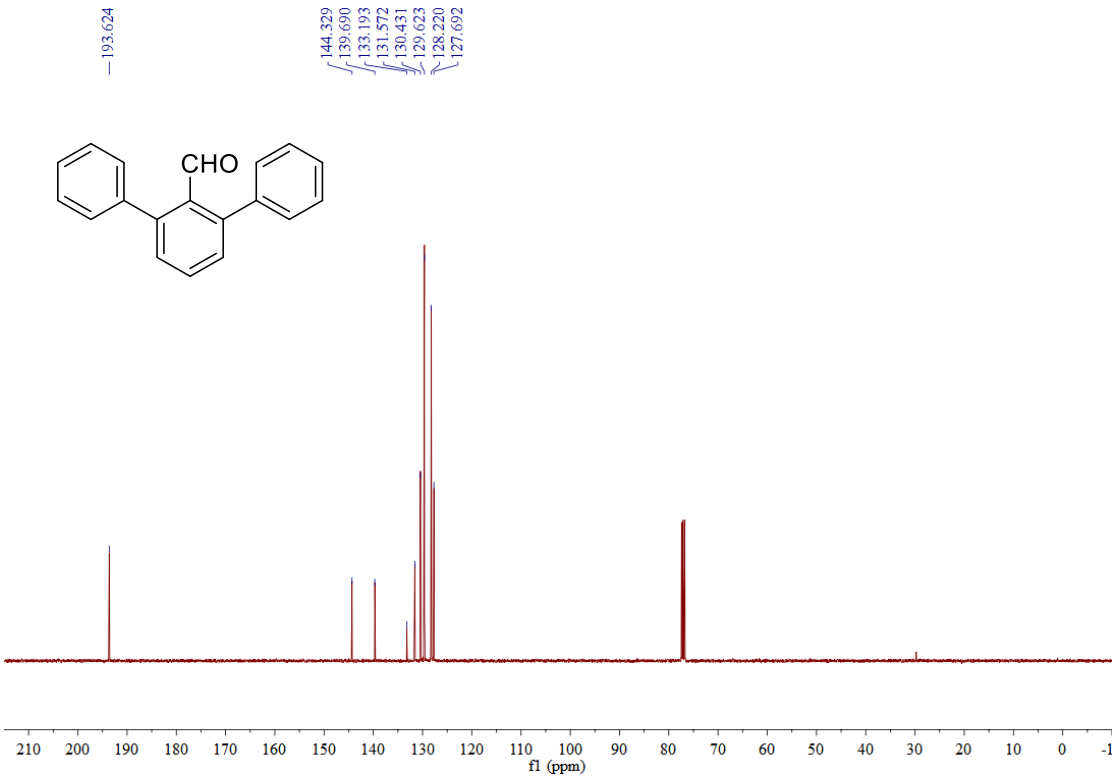
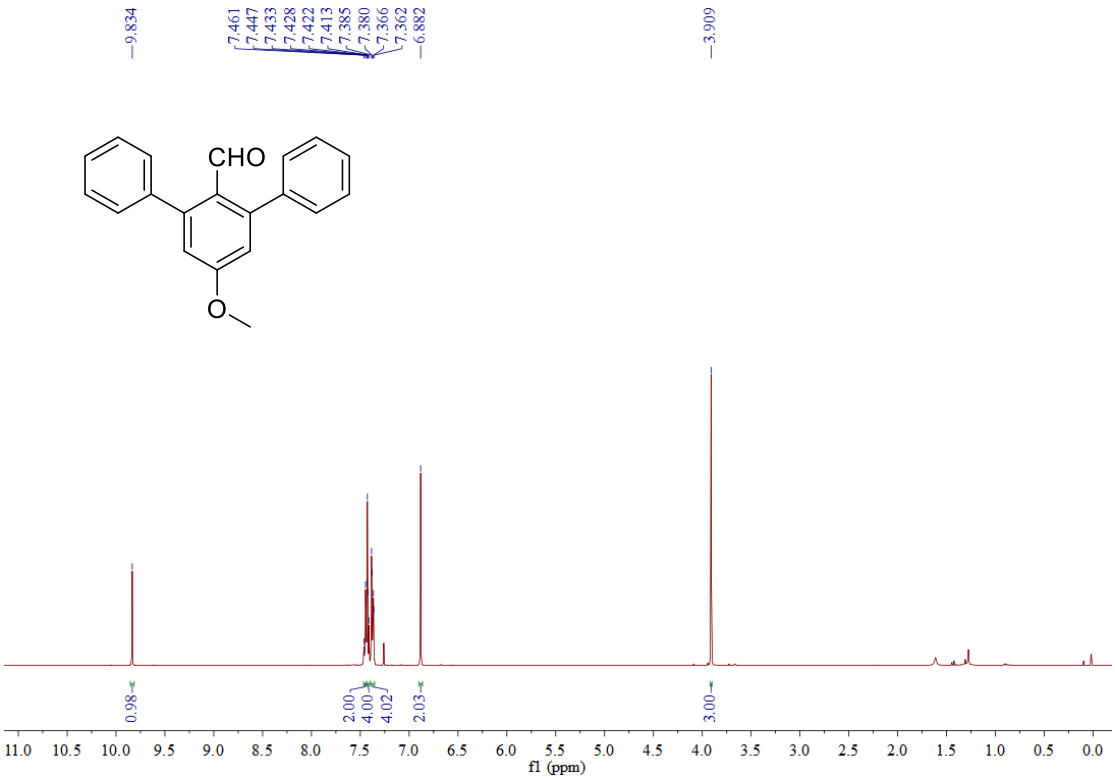


Figure S49. ^{1}H and ^{13}C NMR Spectra for compound **5a**



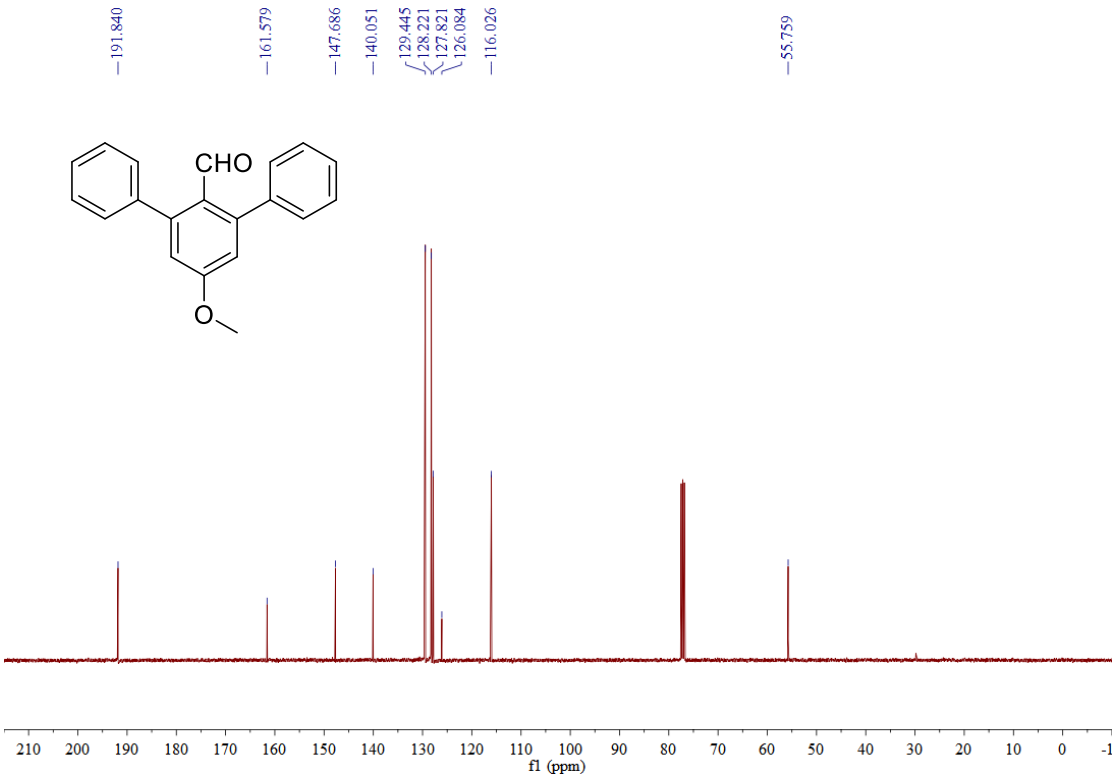
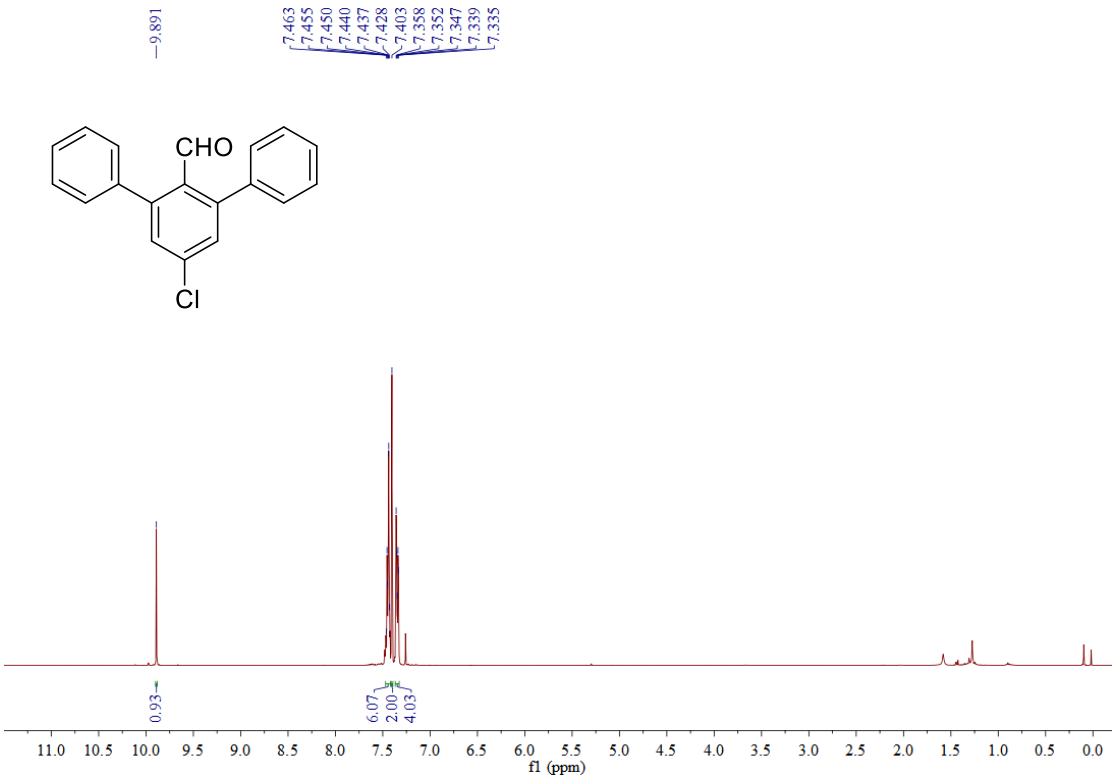


Figure S50. ^{1}H and ^{13}C NMR Spectra for compound **5b**



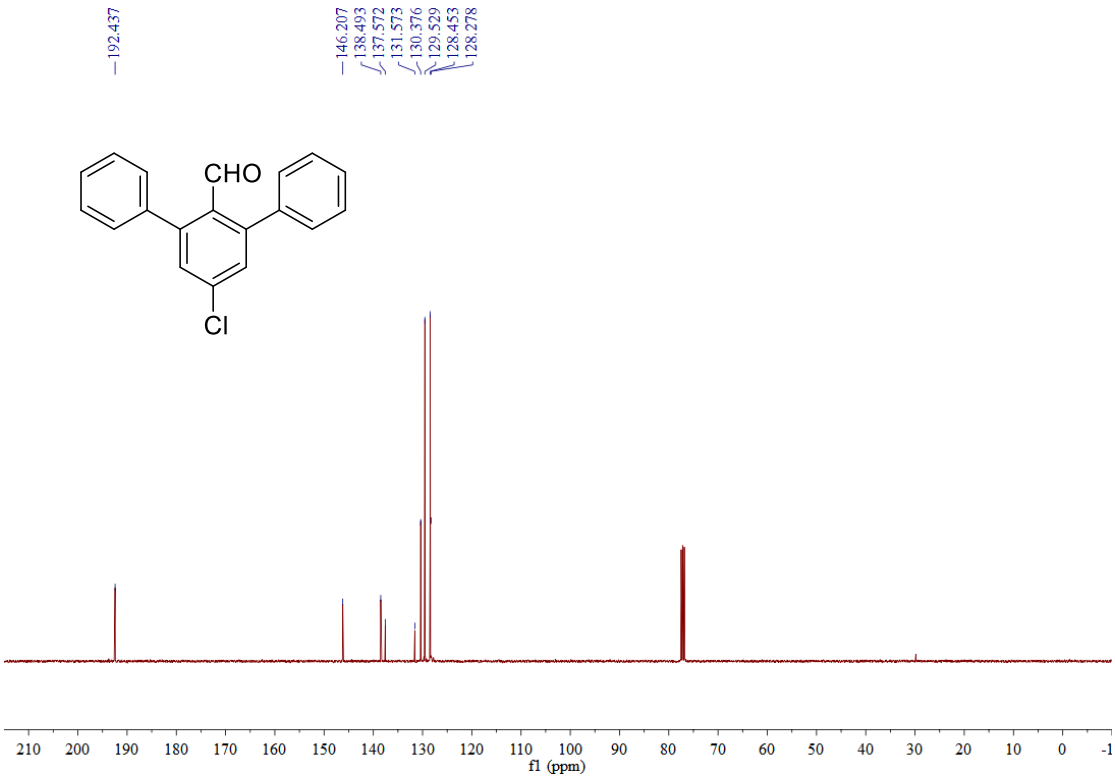
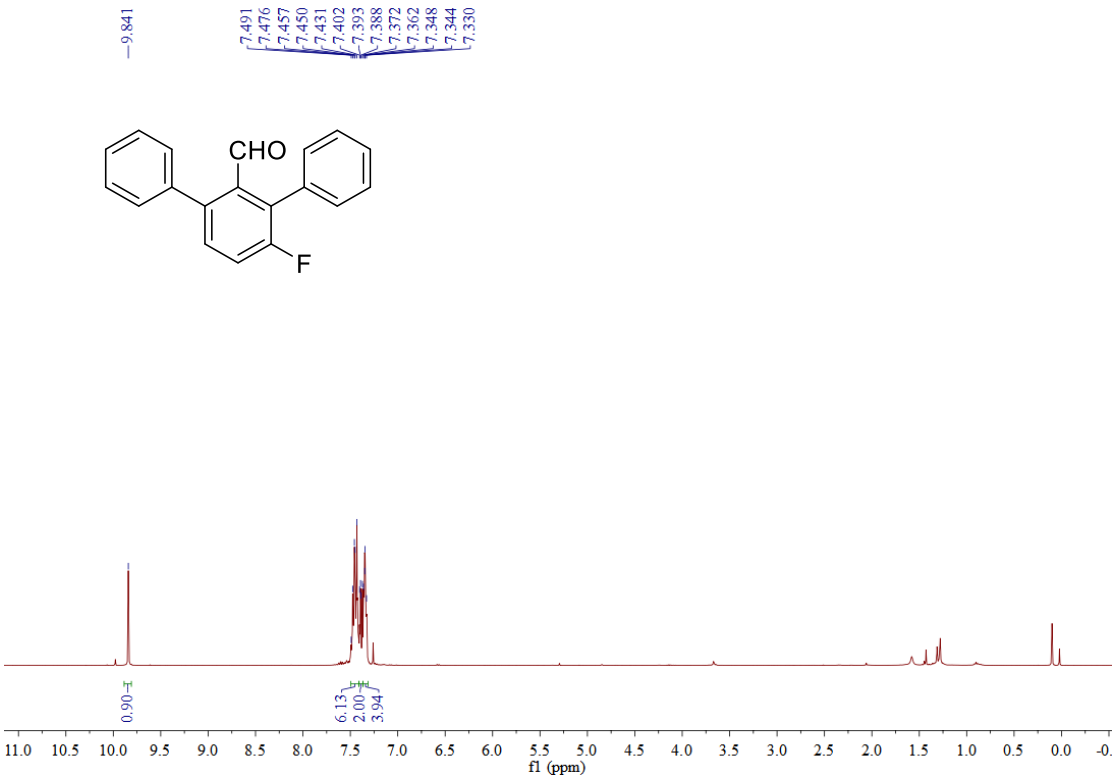


Figure S51. ^{1}H and ^{13}C NMR Spectra for compound **5c**



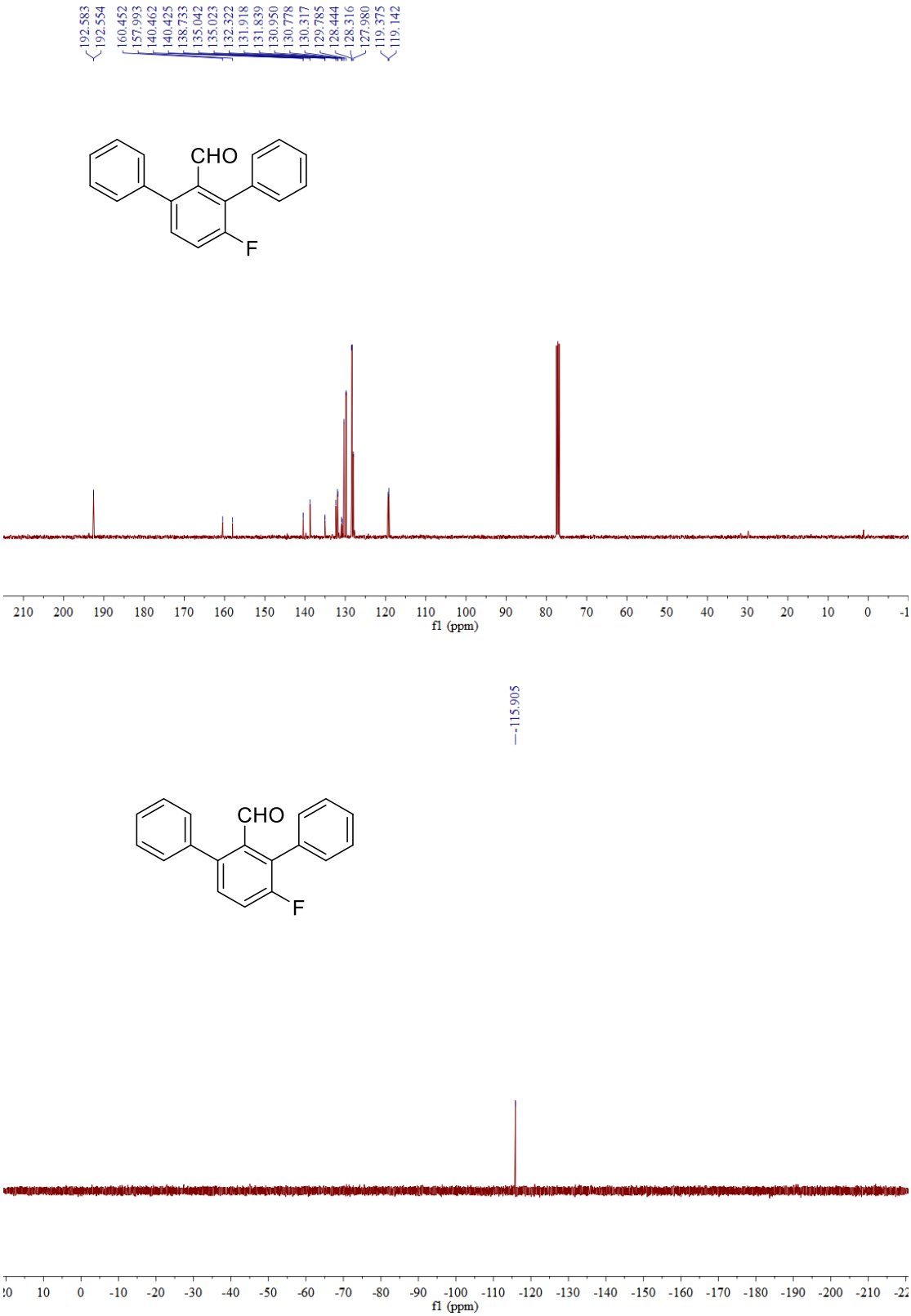


Figure S52. ^{1}H, ^{13}C and ^{19}F NMR Spectra for compound **5d**

Figure S53. ^{1}H and ^{13}C NMR Spectra for compound **5e**

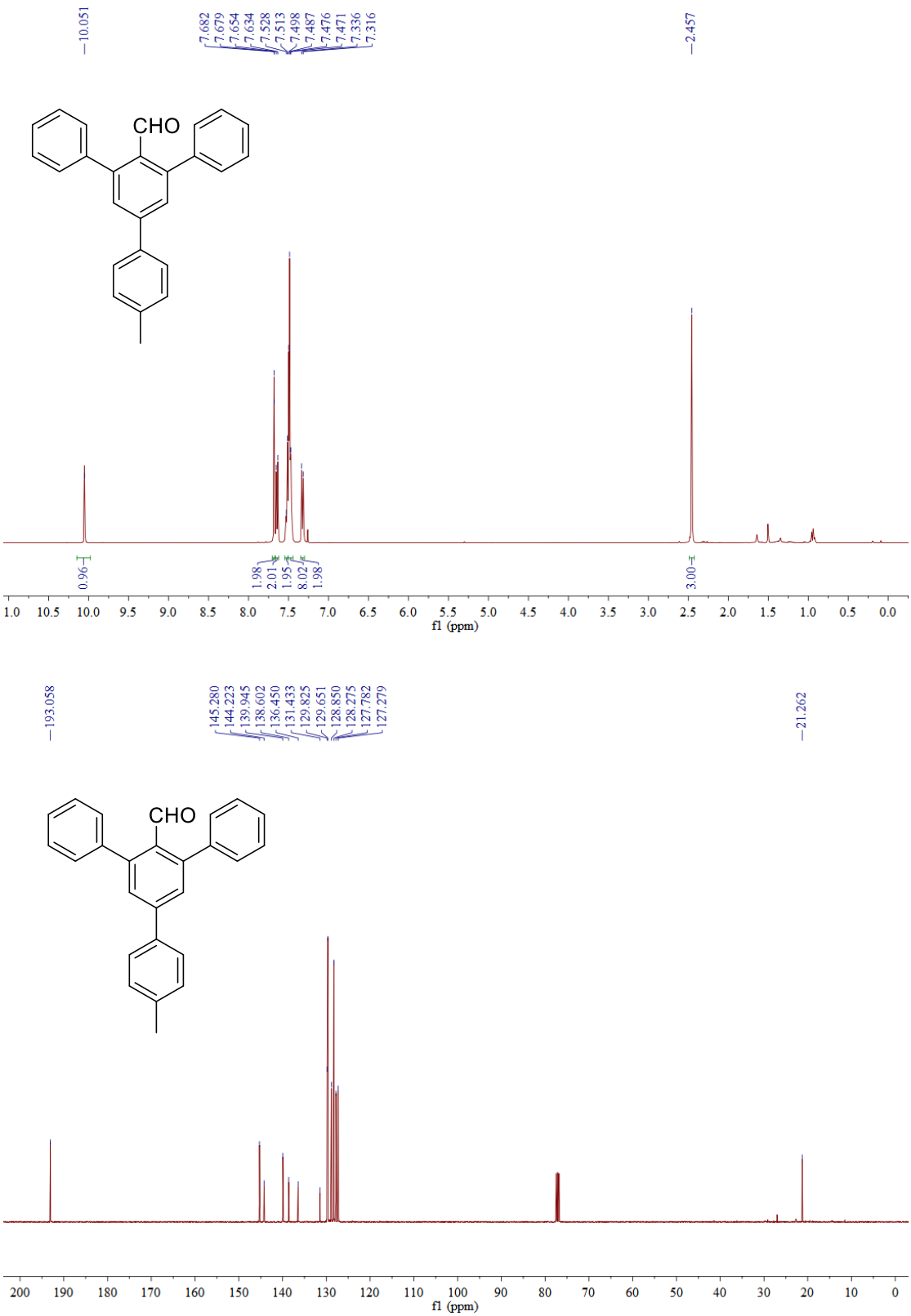
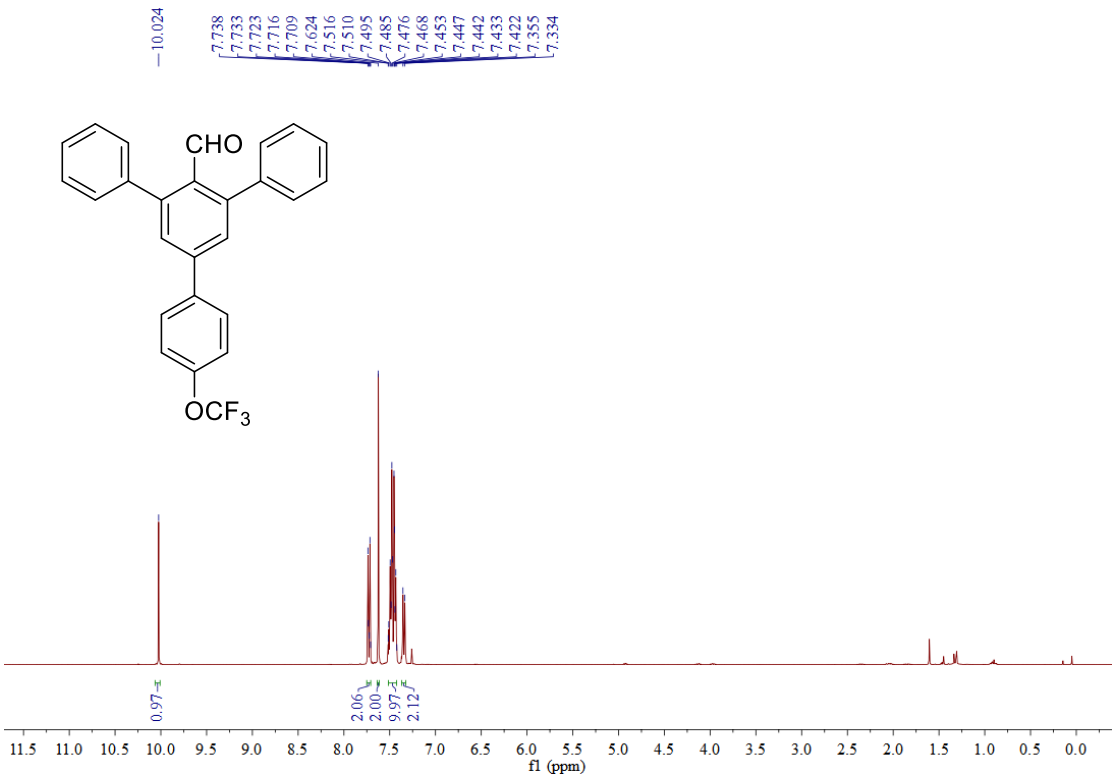
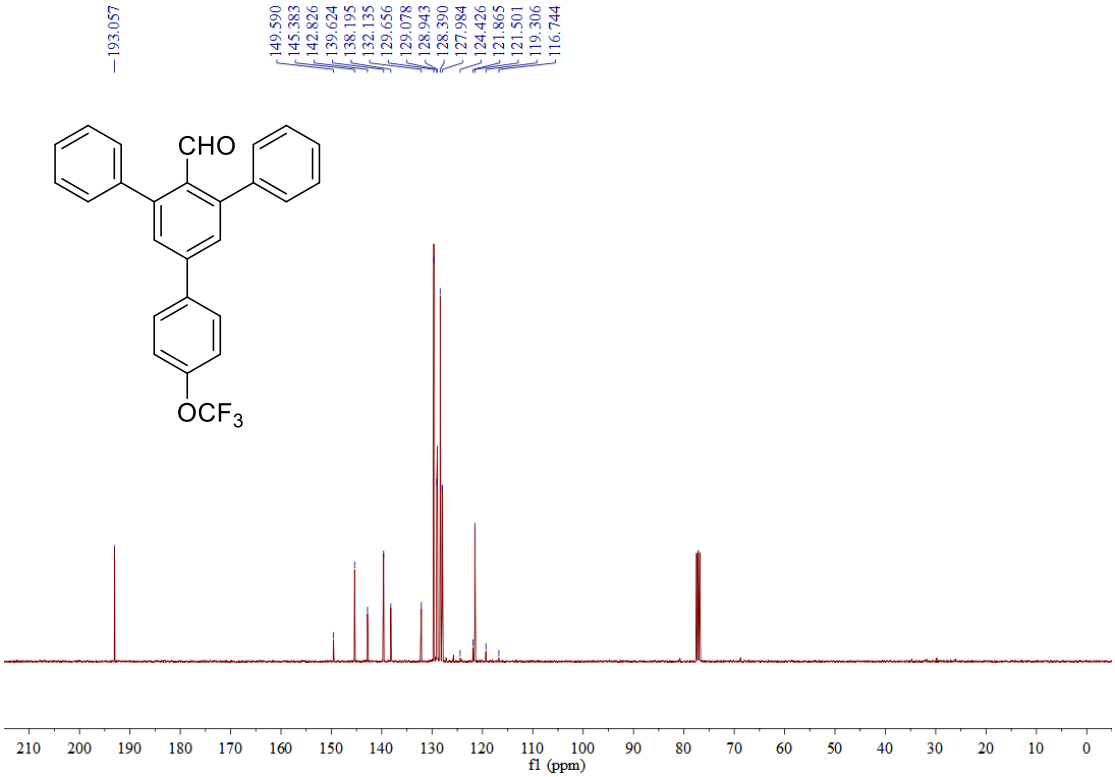


Figure S54. ^{1}H and ^{13}C NMR Spectra for compound **5f**


10.024
7.738
7.733
7.723
7.716
7.709
7.624
7.516
7.510
7.495
7.485
7.476
7.468
7.453
7.447
7.442
7.433
7.422
7.355
7.334
CHO
OCF3
0.97
2.06
2.00
9.97
2.12
fl (ppm)


193.057
149.590
145.383
142.826
139.624
138.195
132.135
129.656
129.078
128.943
128.390
127.984
124.426
121.865
121.501
119.306
116.744
CHO
OCF3
fl (ppm)

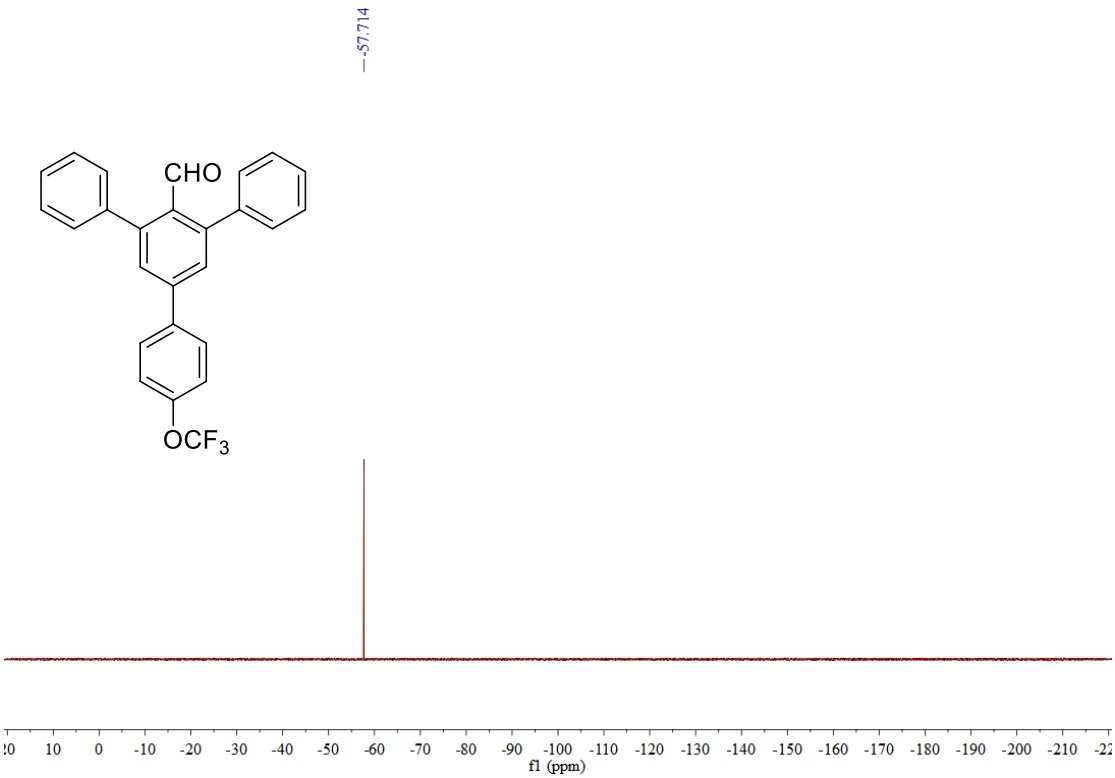
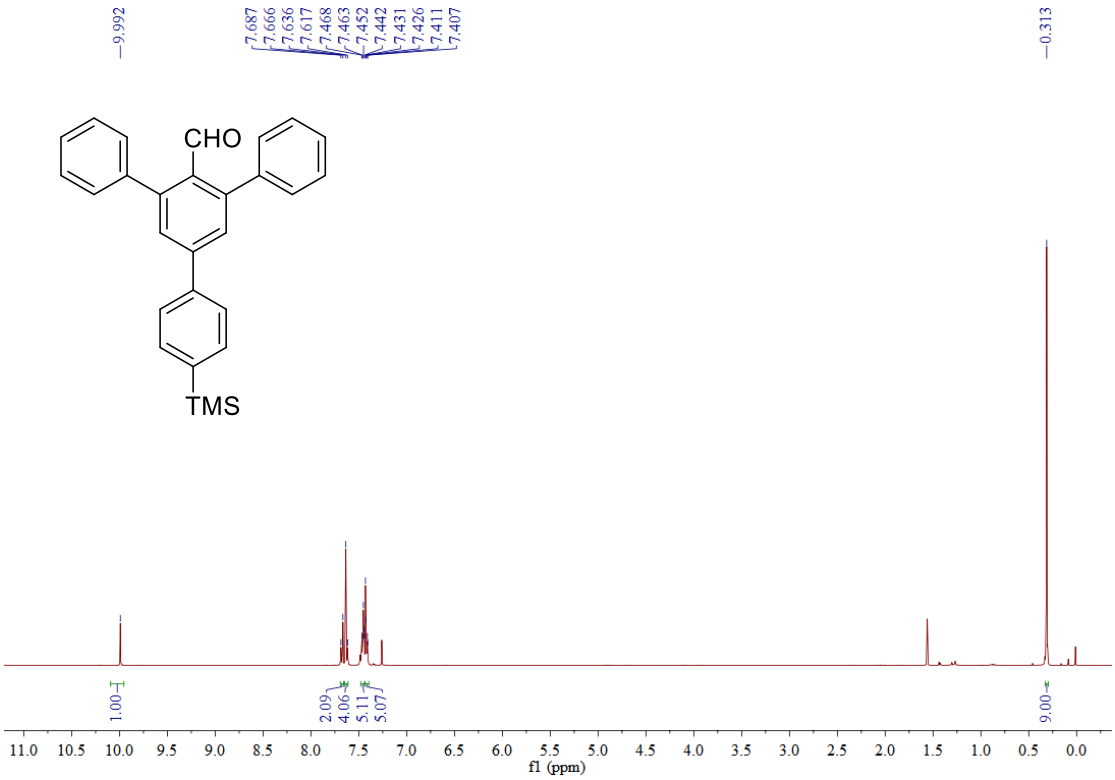


Figure S55. ^{1}H, ^{13}C and ^{19}F NMR Spectra for compound **5g**



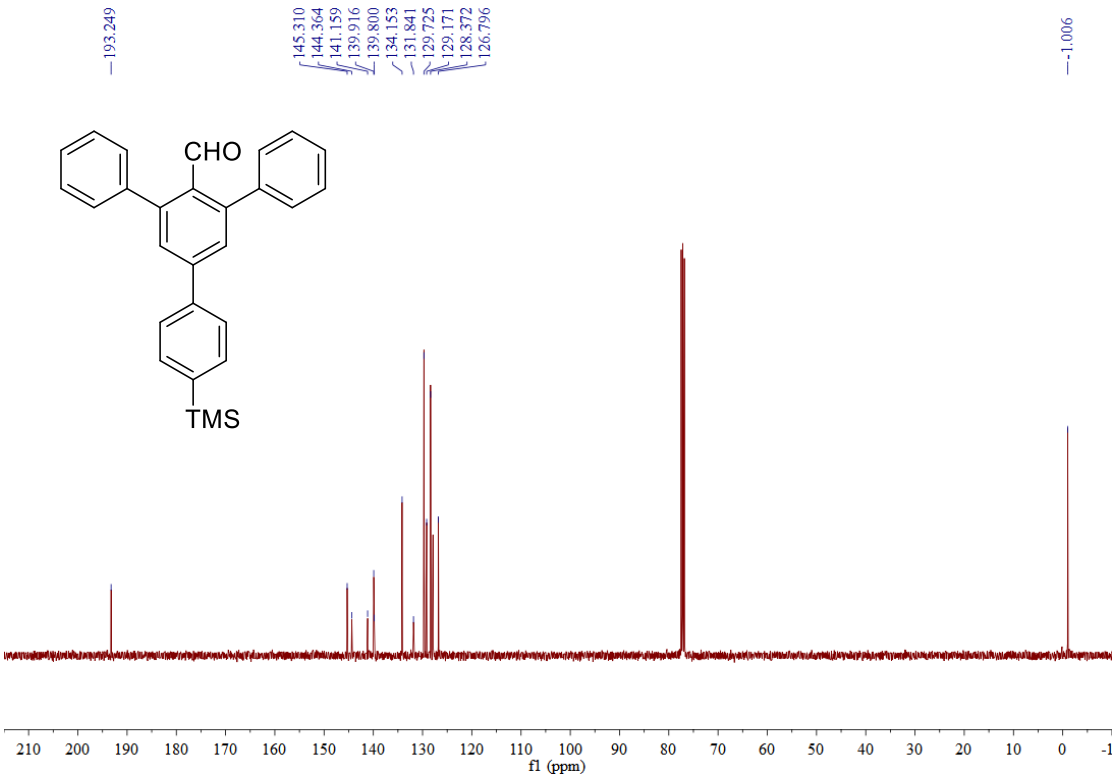
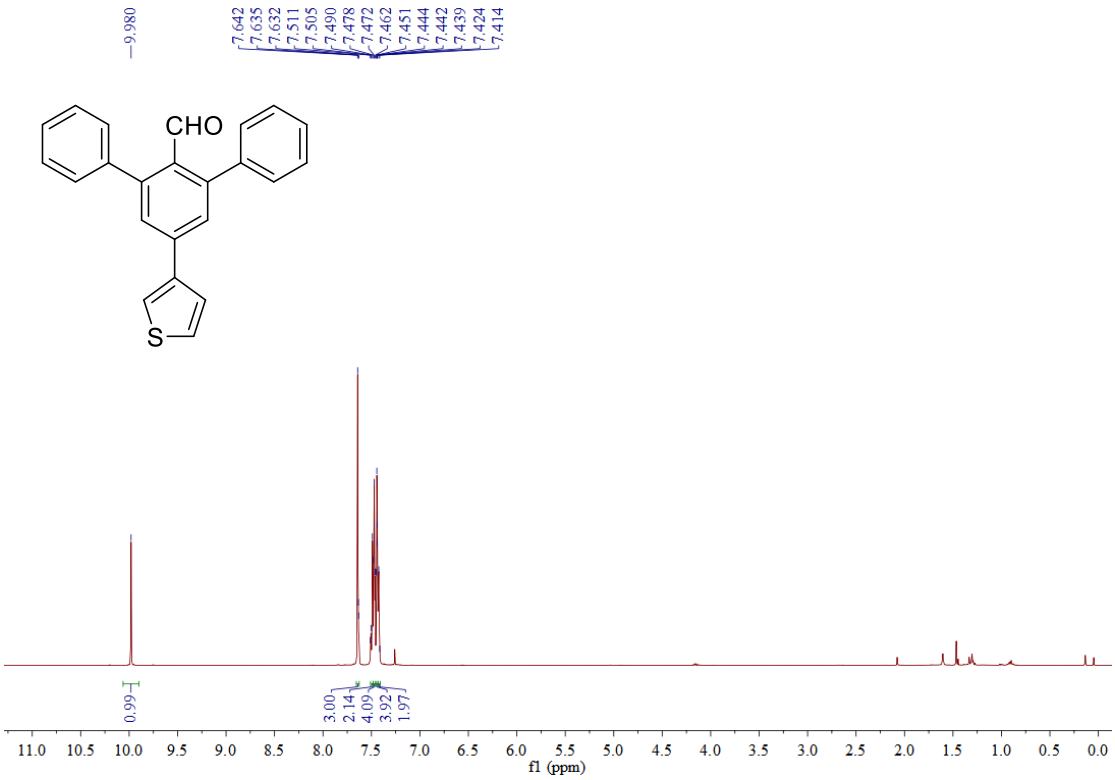


Figure S56. ^{1}H and ^{13}C NMR Spectra for compound **5h**



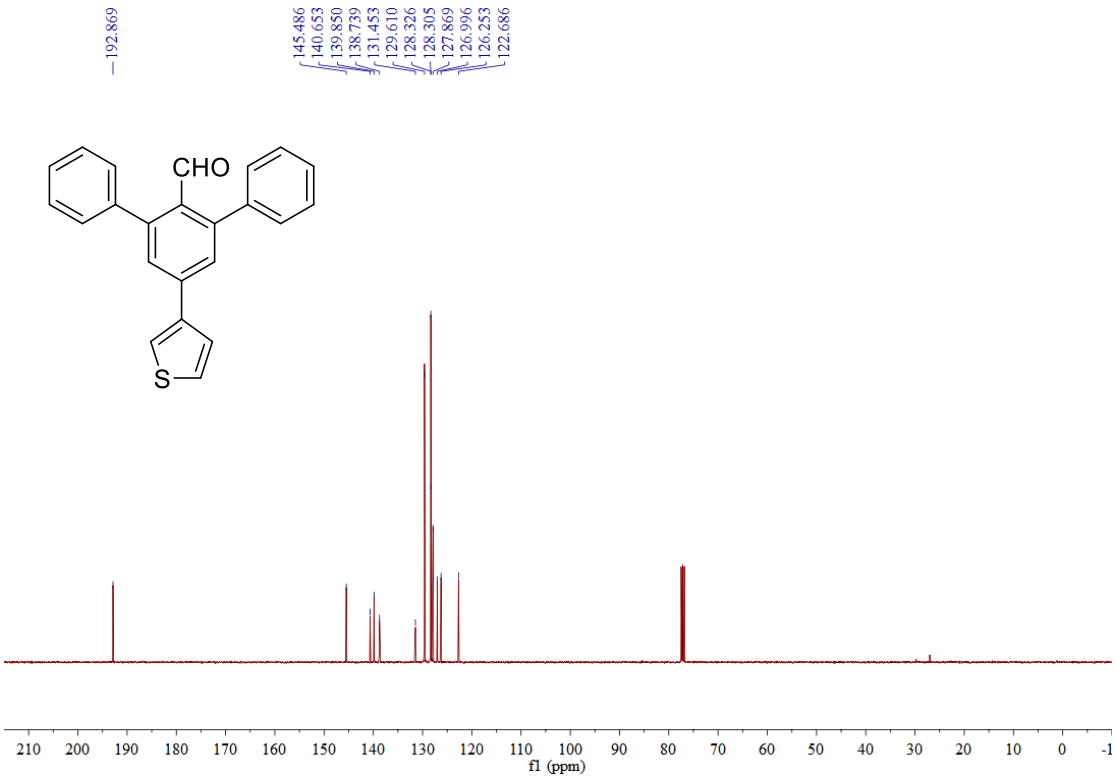
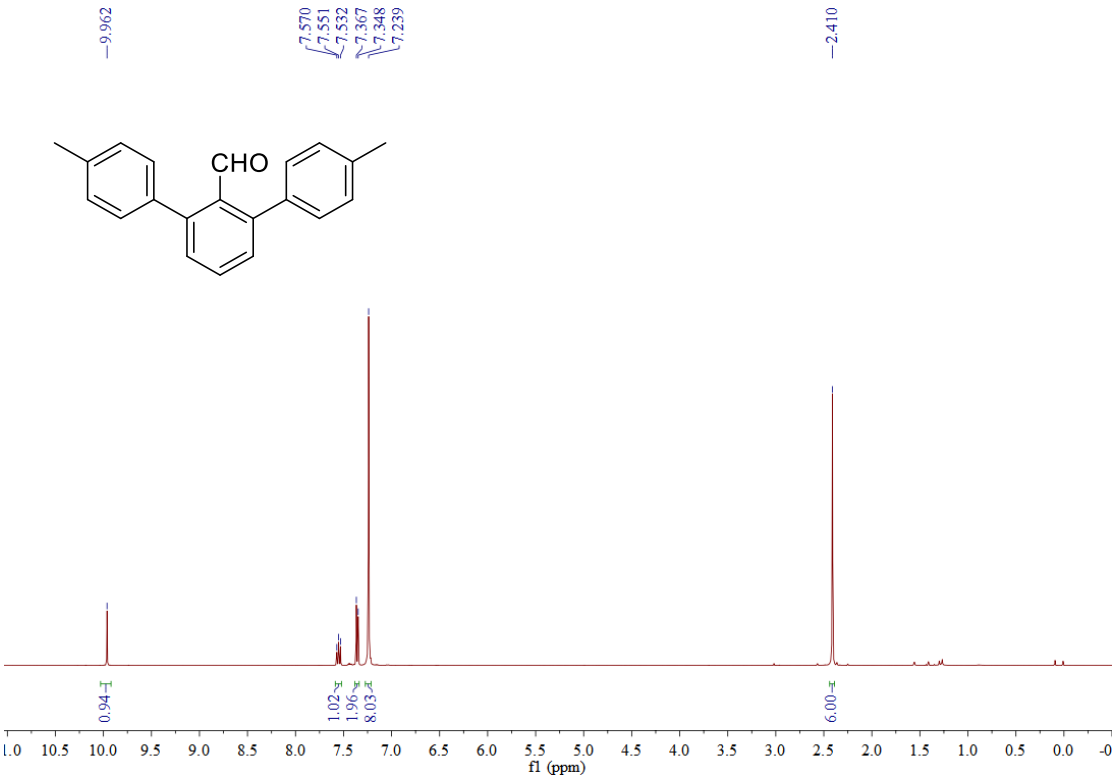


Figure S57. ^{1}H and ^{13}C NMR Spectra for compound **5i**



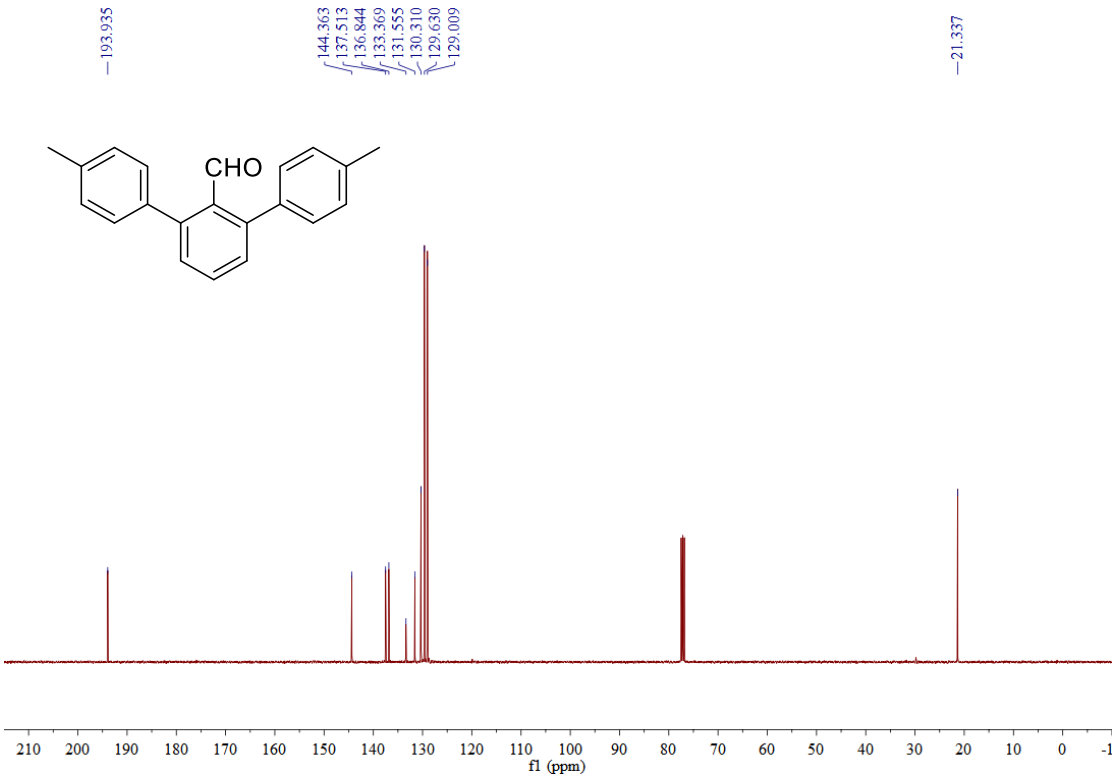
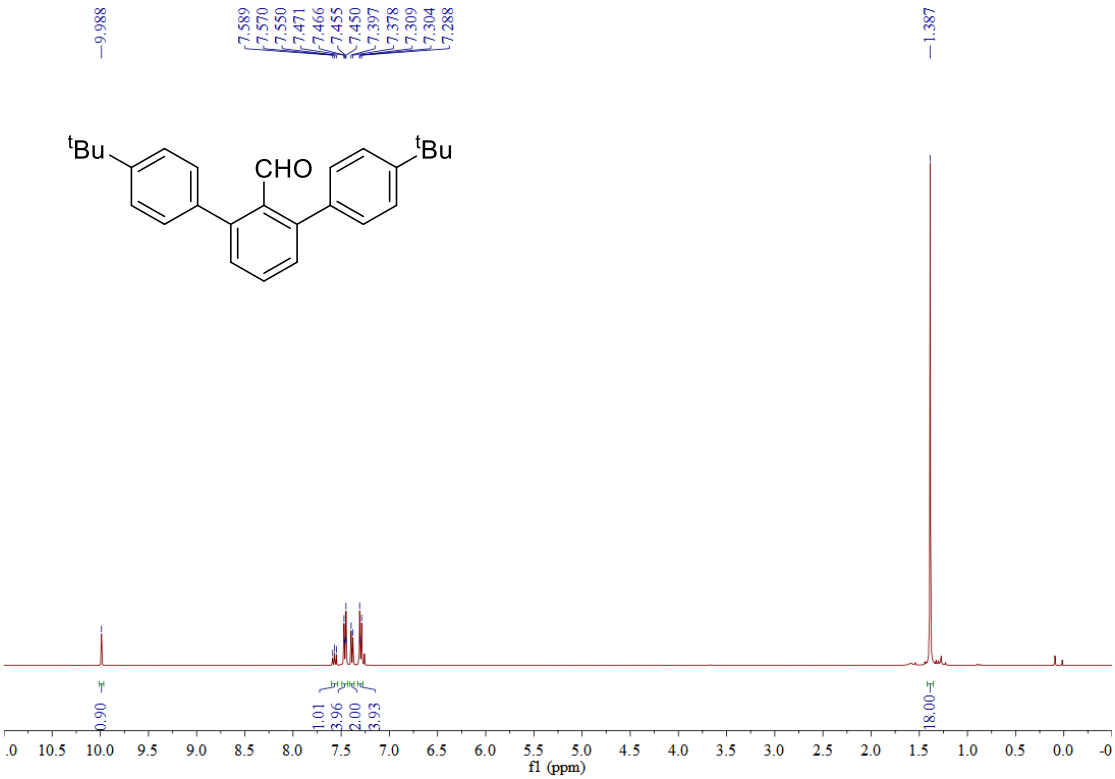


Figure S58. ^{1}H and ^{13}C NMR Spectra for compound **5j**



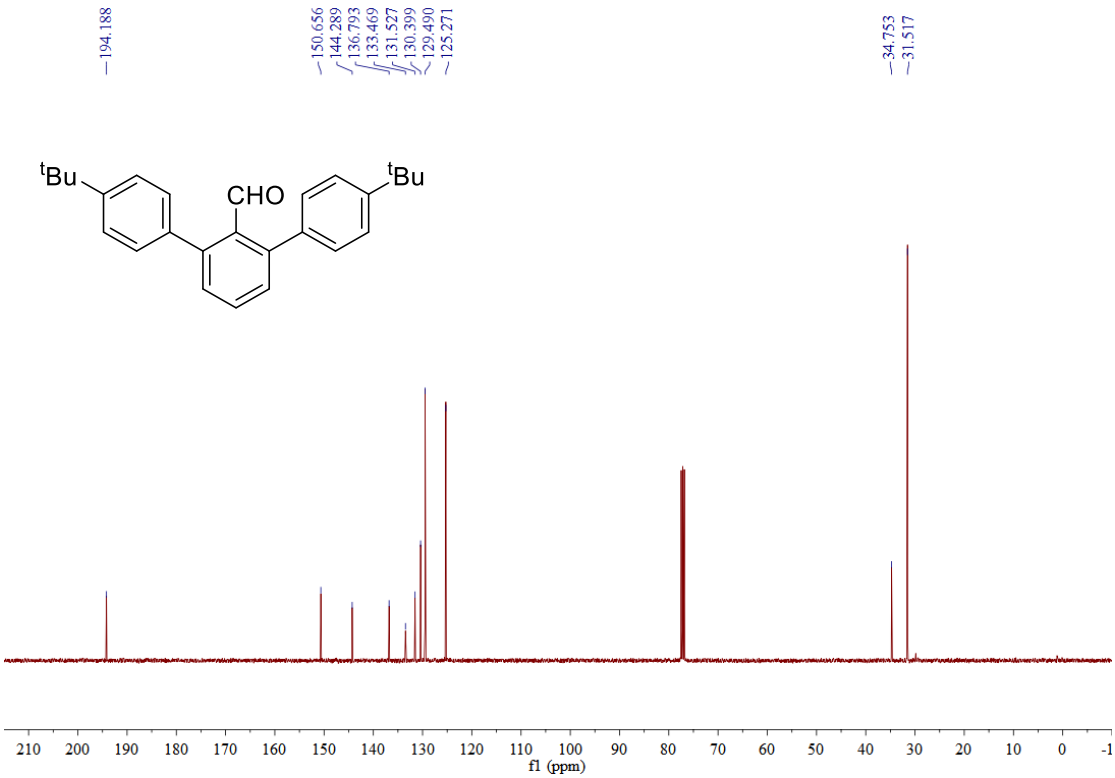
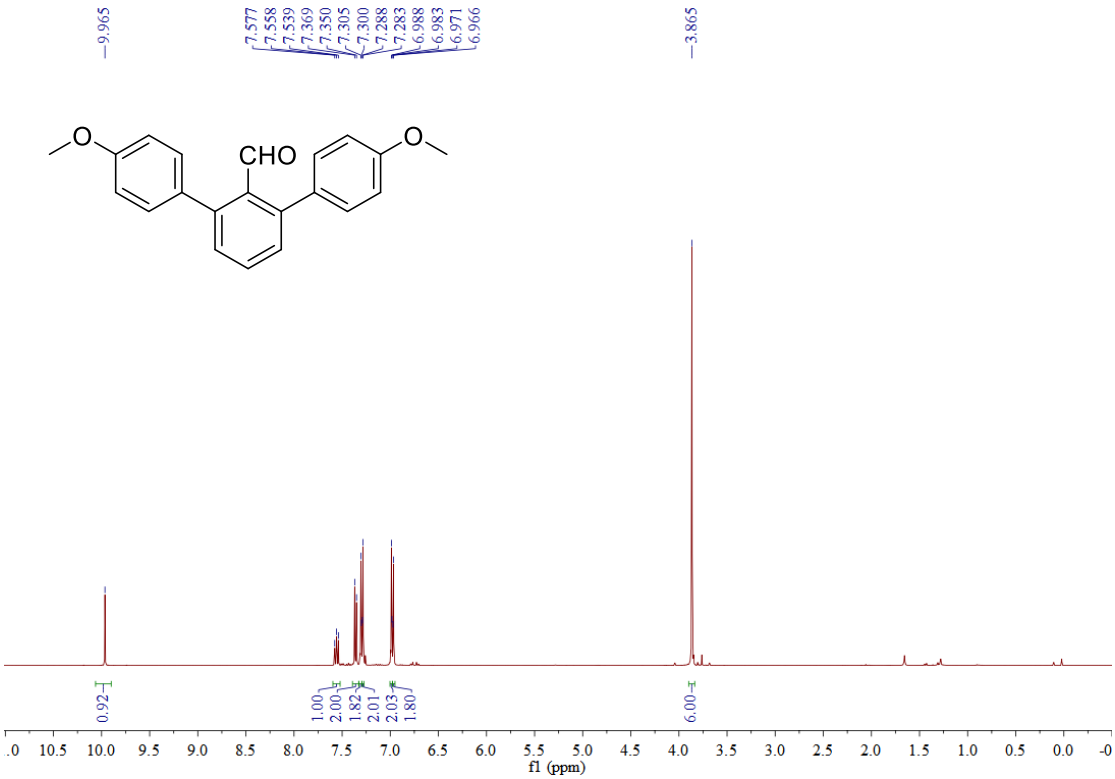


Figure S59. ^{1}H and ^{13}C NMR Spectra for compound **5k**



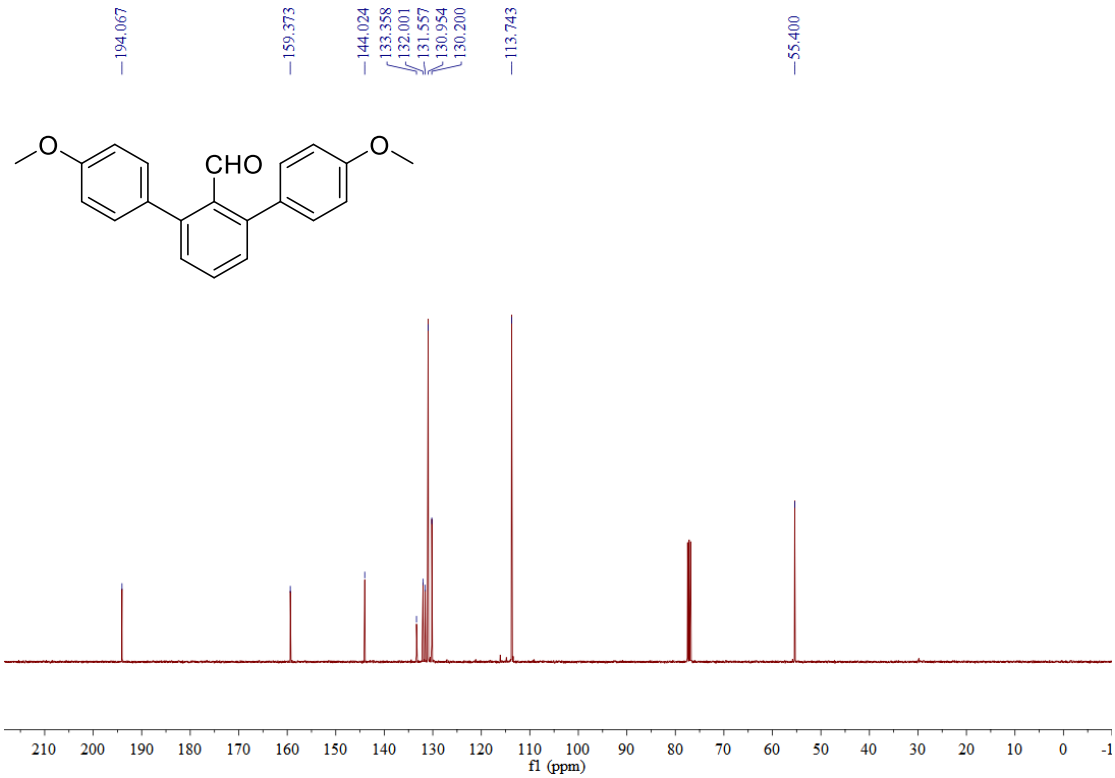
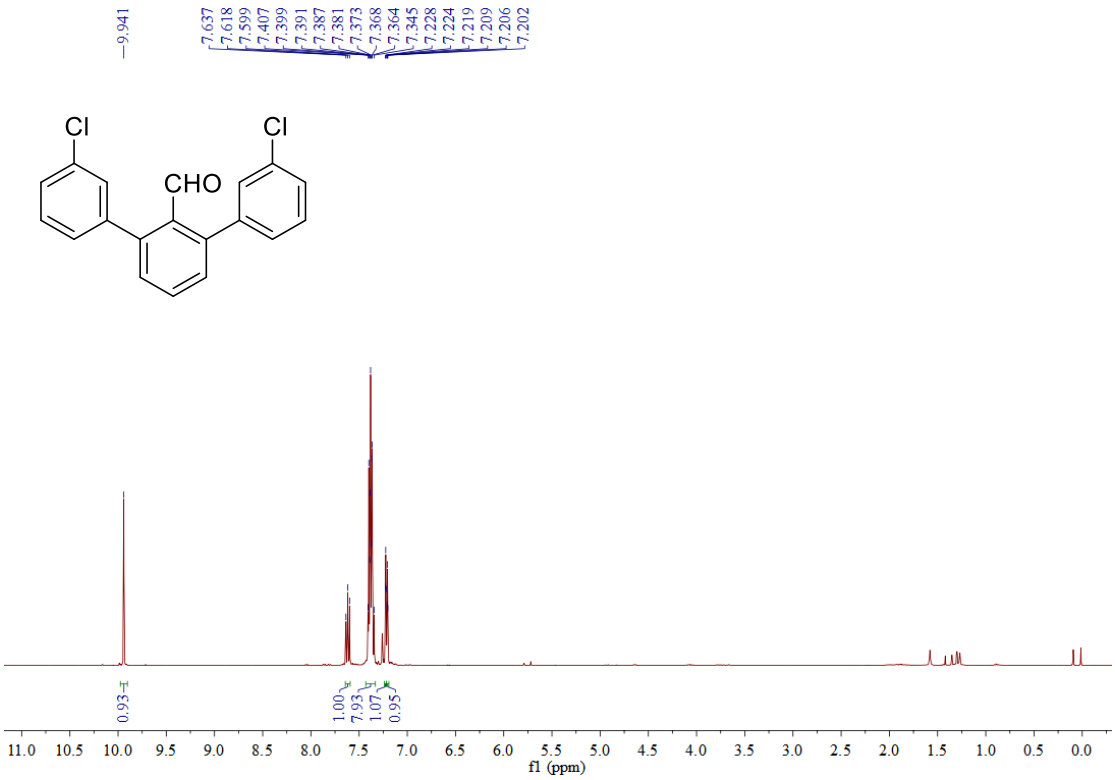


Figure S60. ^{1}H and ^{13}C NMR Spectra for compound **5l**



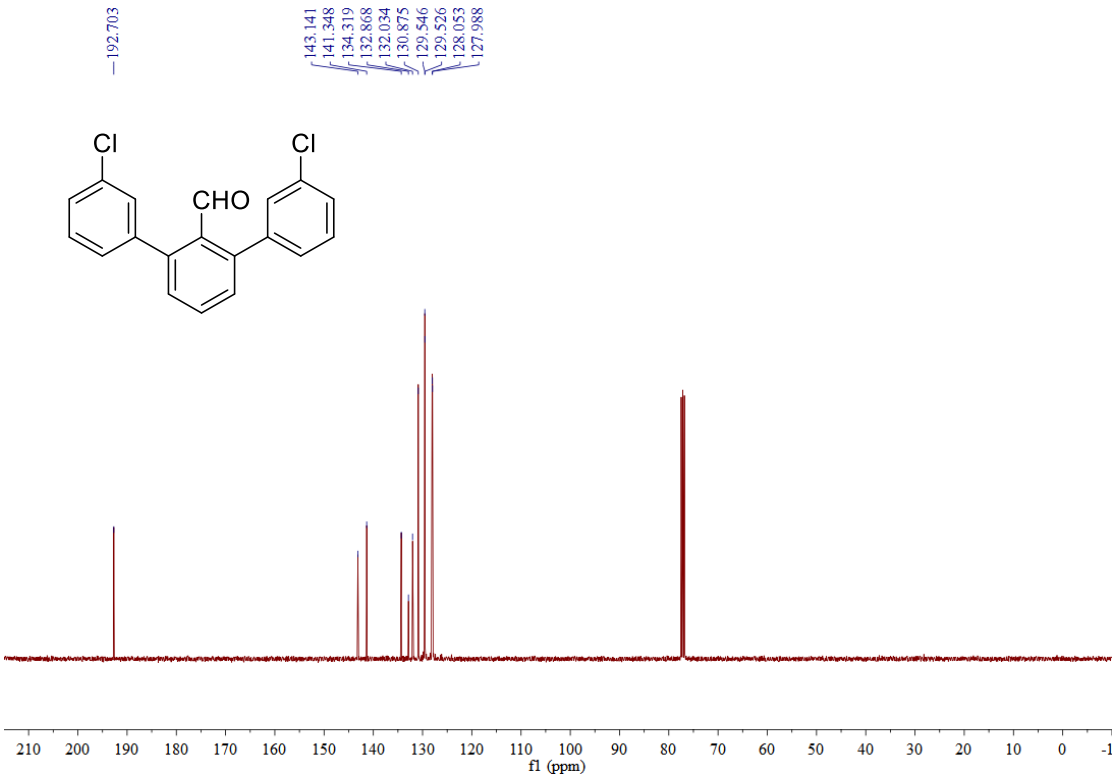
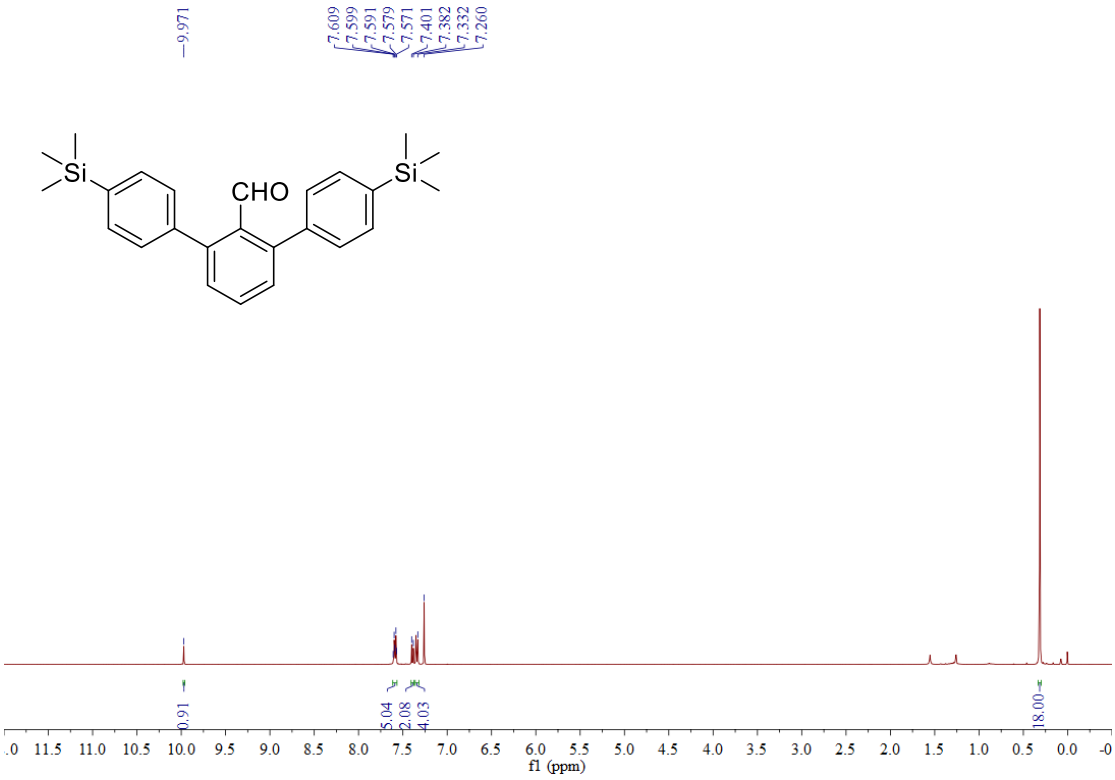


Figure S61. ^{1}H and ^{13}C NMR Spectra for compound **5m**



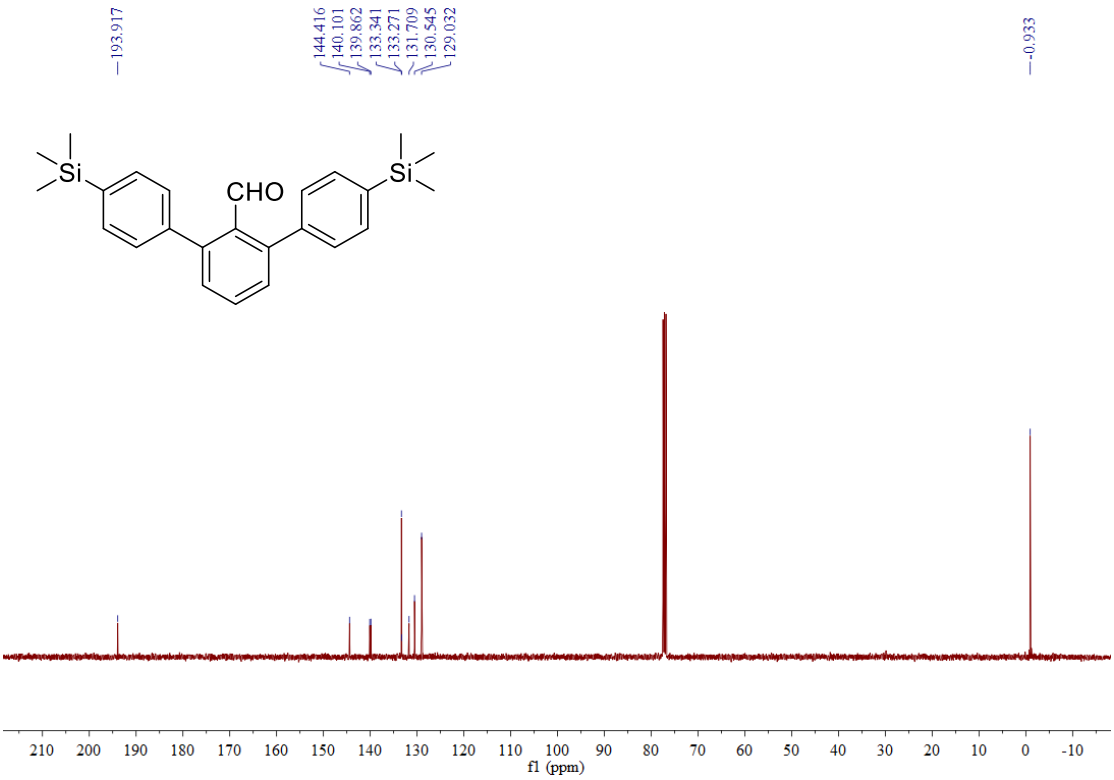
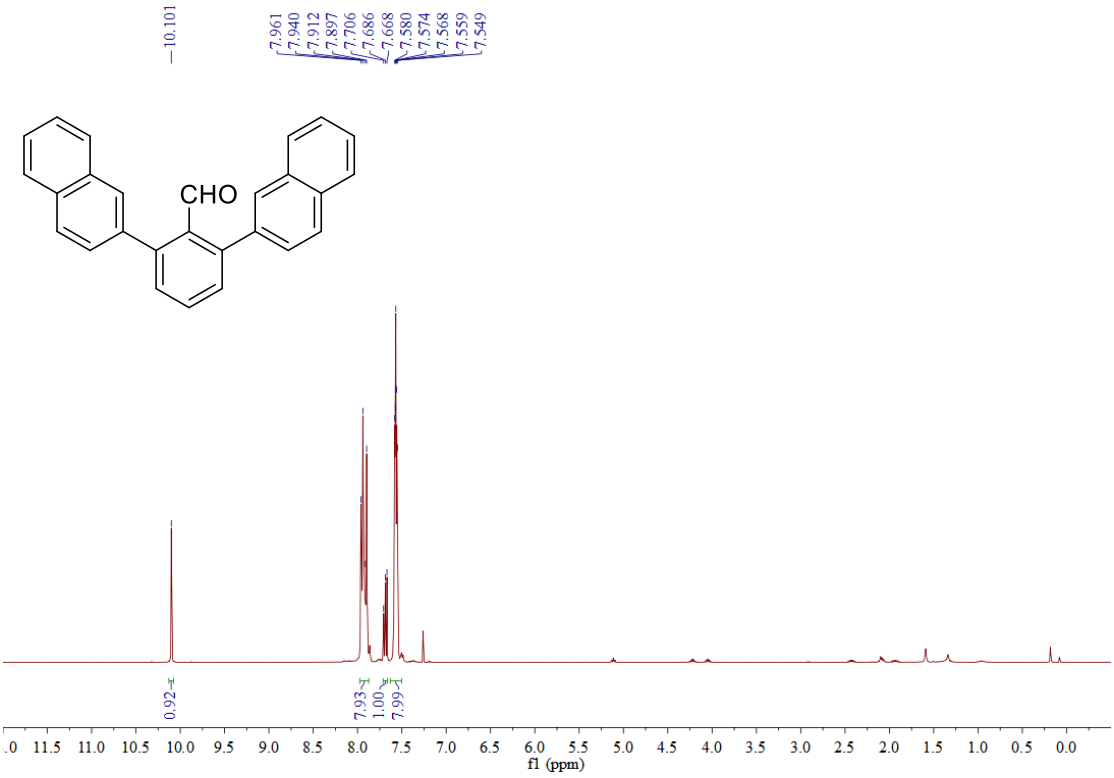


Figure S62. ^{1}H and ^{13}C NMR Spectra for compound **5n**



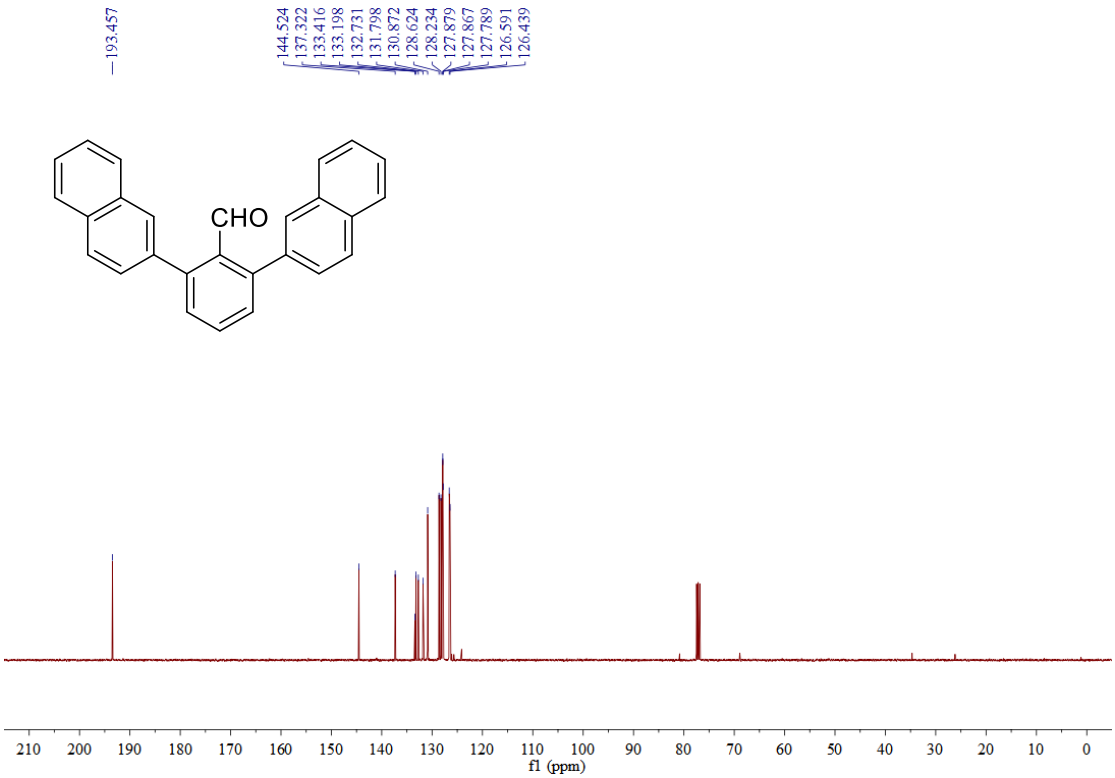
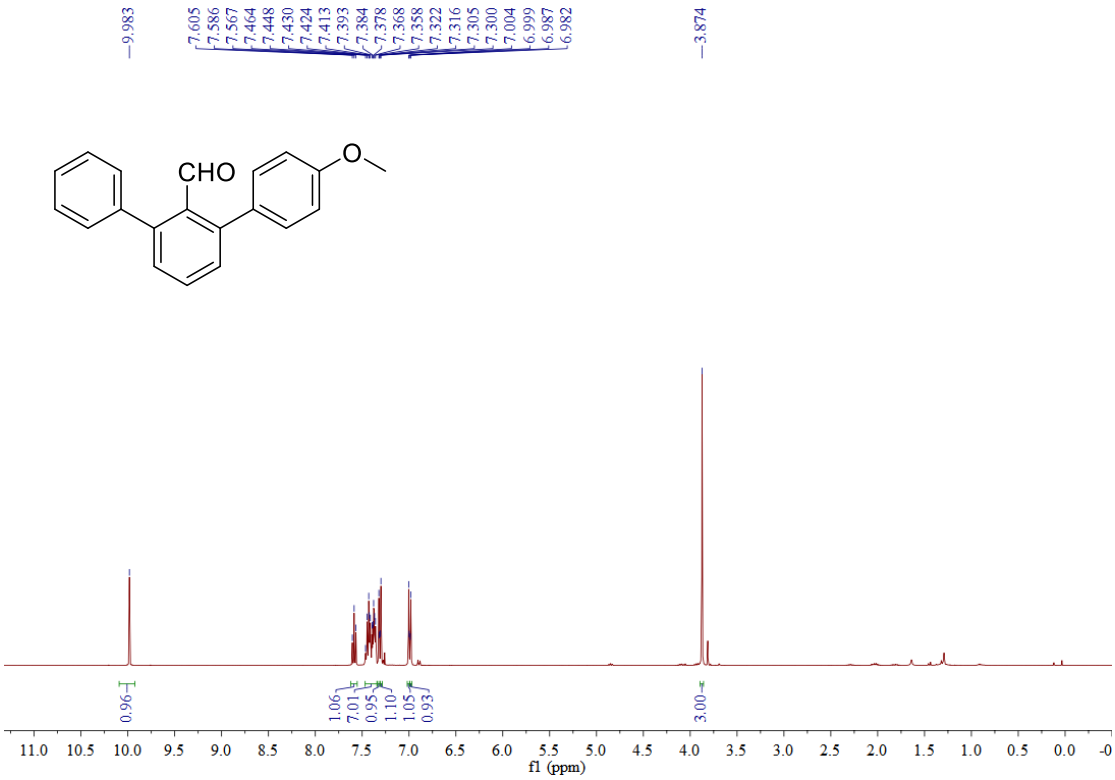


Figure S63. ^{1}H and ^{13}C NMR Spectra for compound **5o**



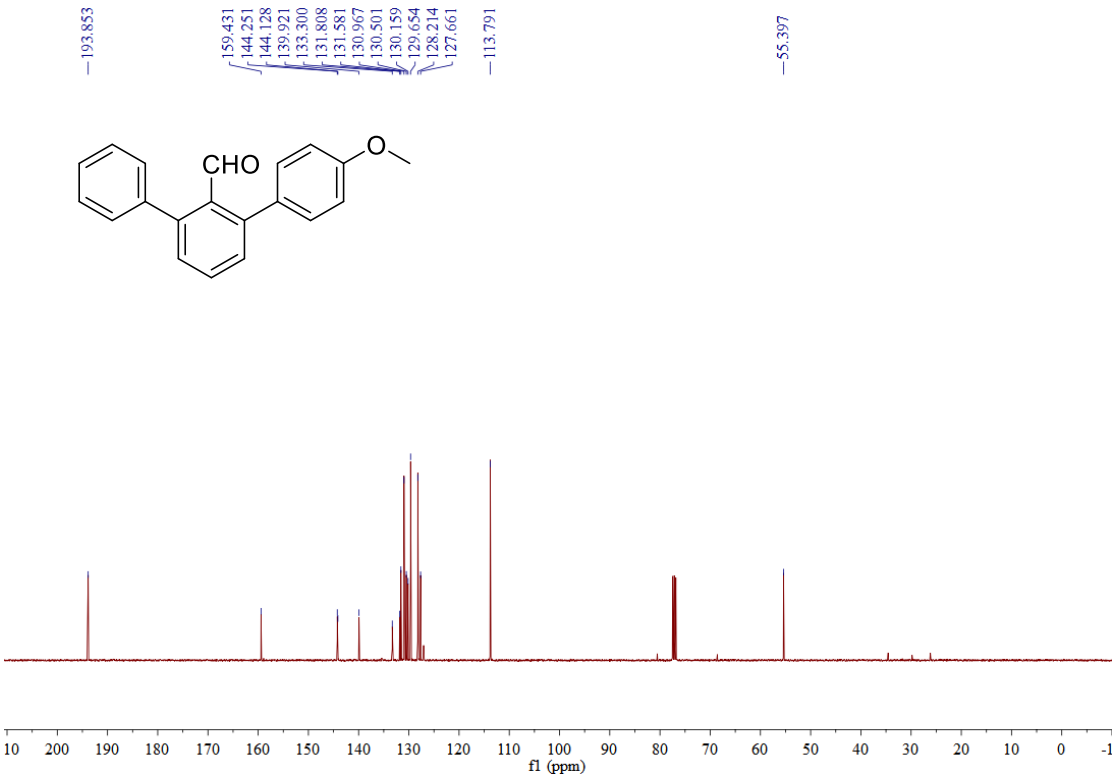
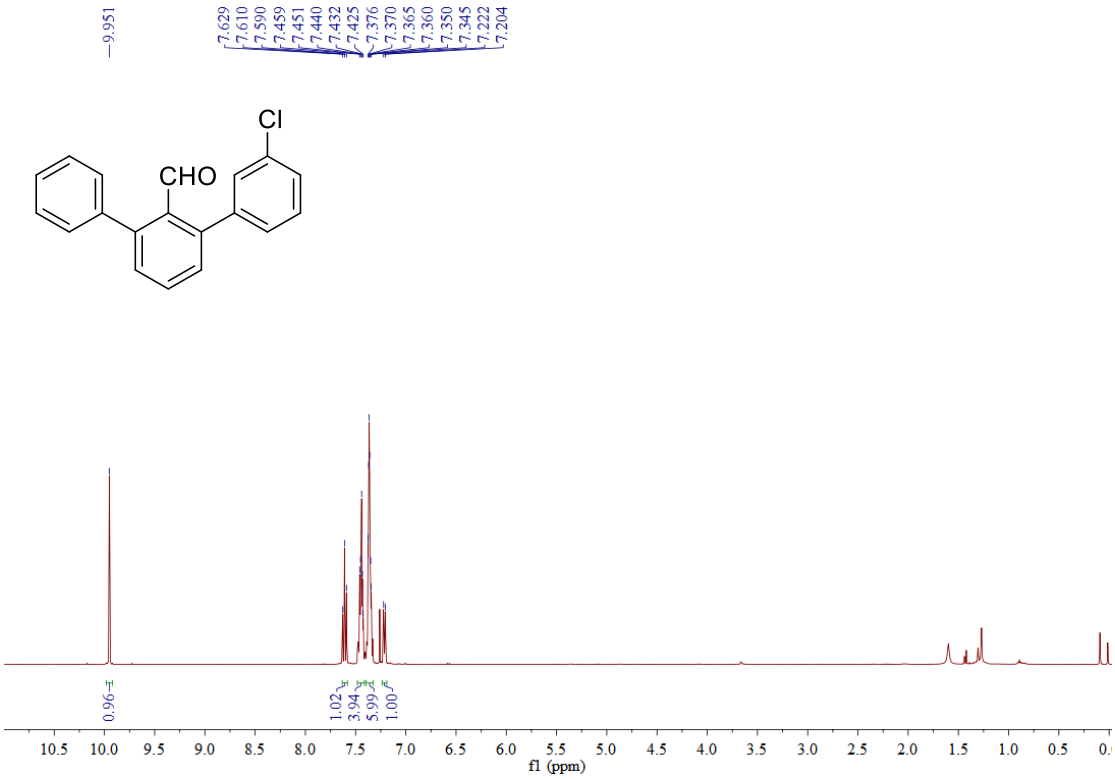


Figure S64. ^{1}H and ^{13}C NMR Spectra for compound **5p**



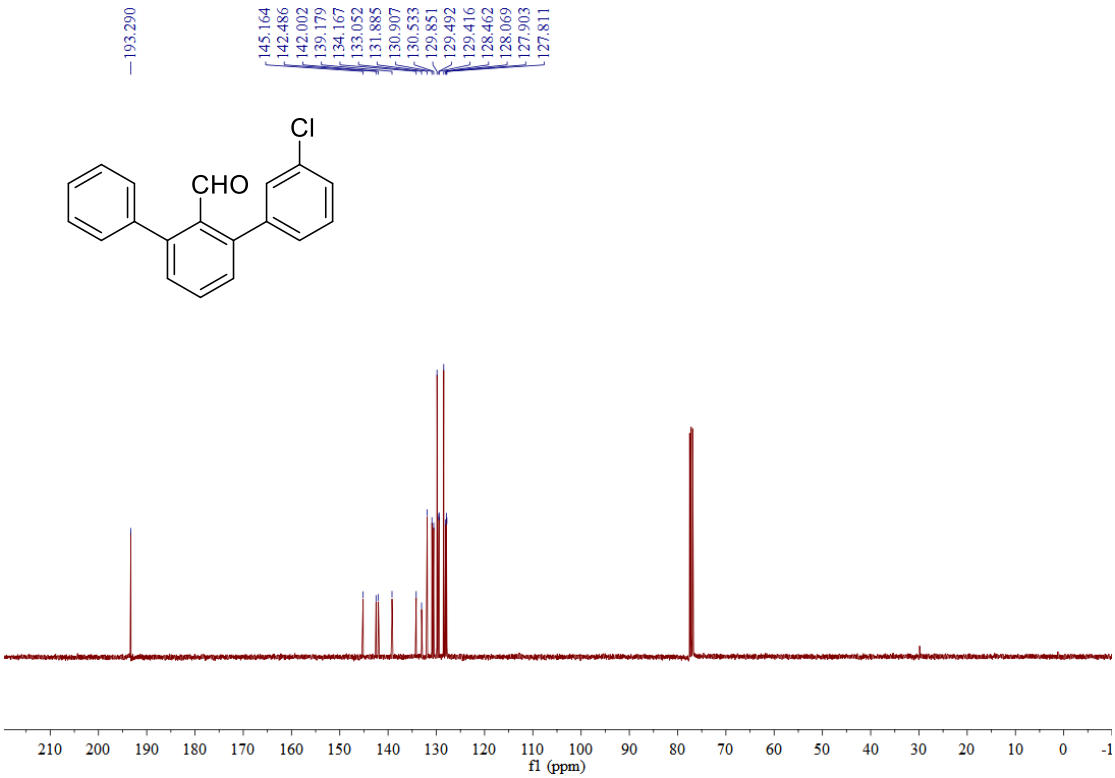
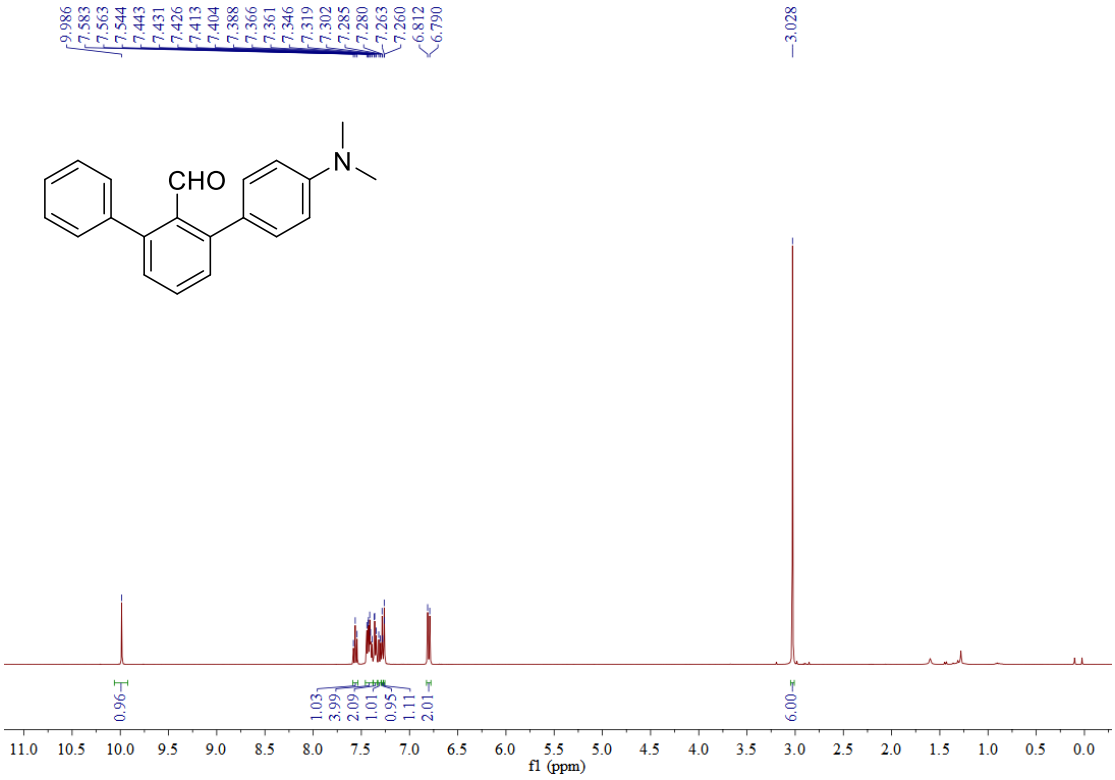


Figure S65. ^{1}H and ^{13}C NMR Spectra for compound **5q**



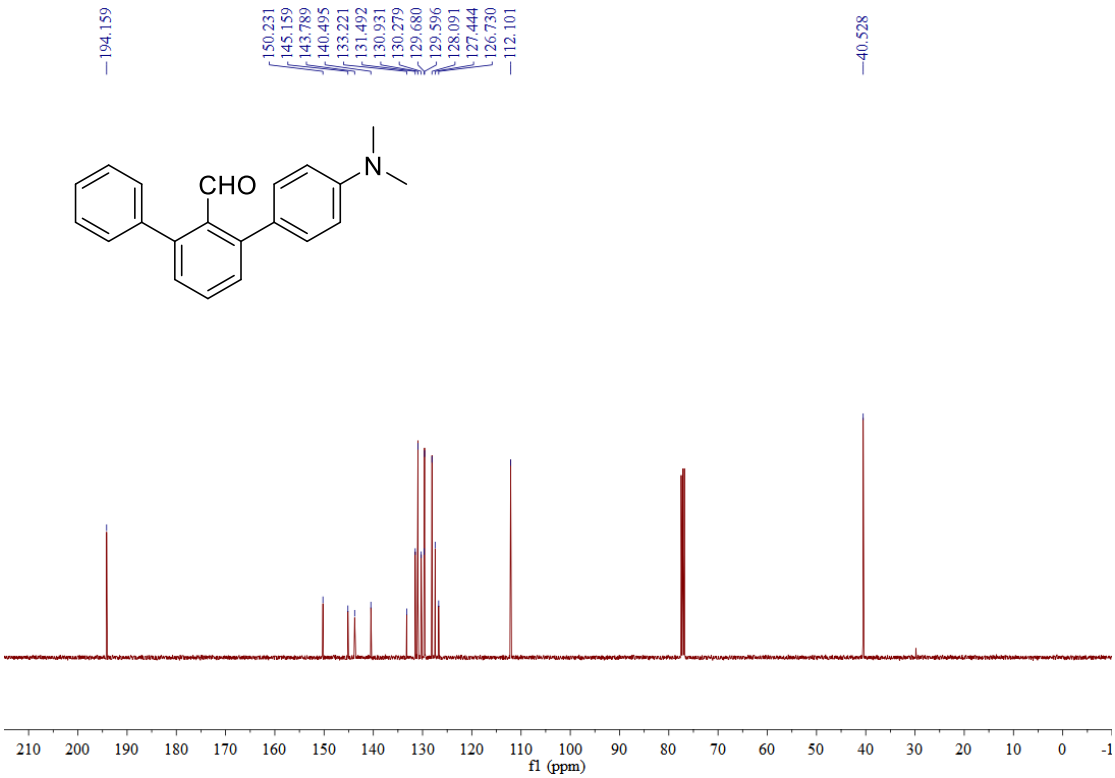
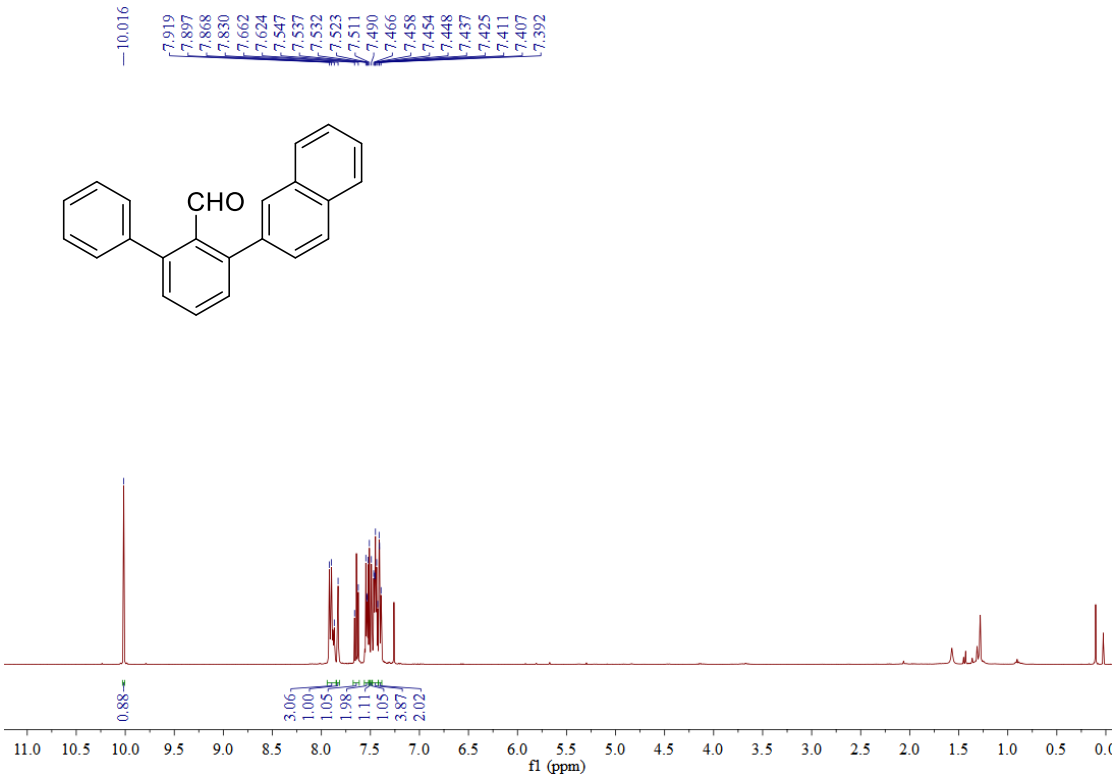


Figure S66. ^{1}H and ^{13}C NMR Spectra for compound **5r**



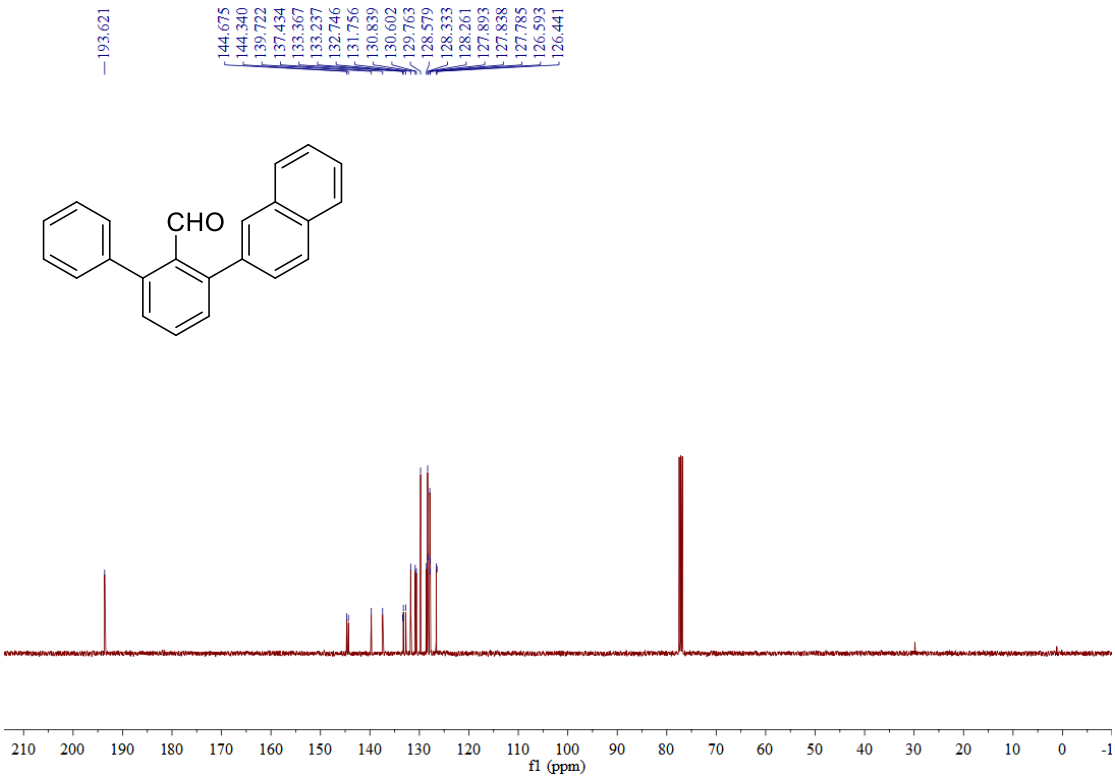
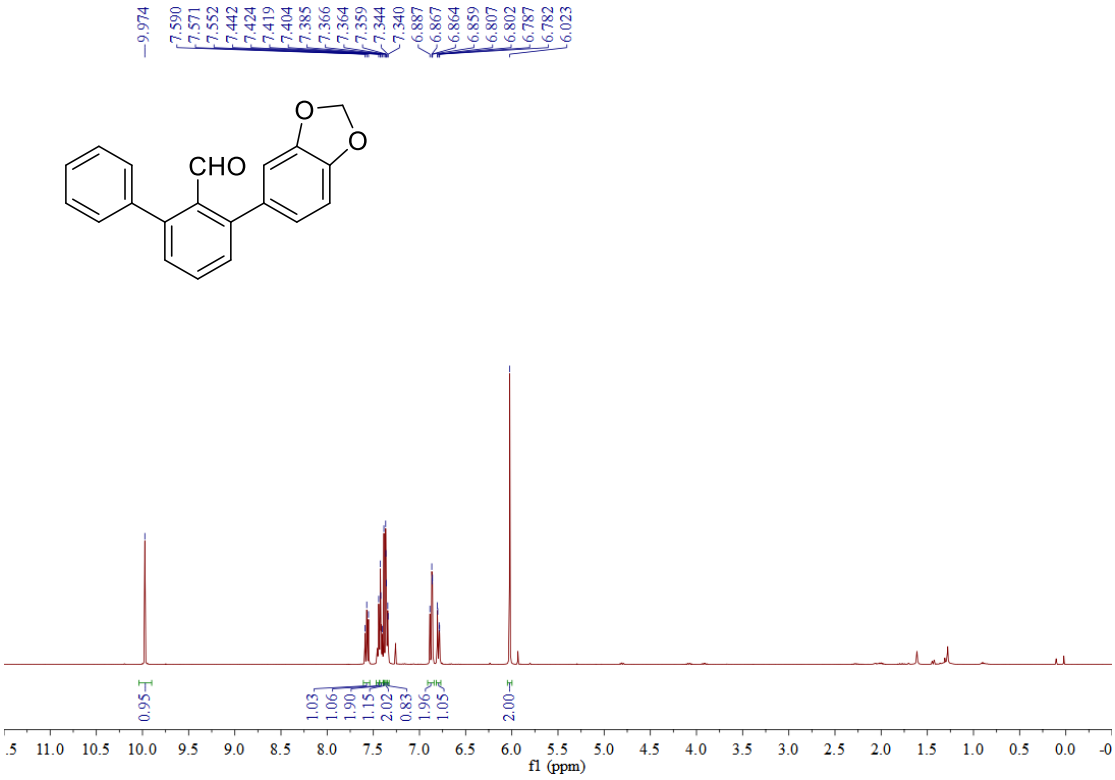


Figure S67. ^{1}H and ^{13}C NMR Spectra for compound **5s**



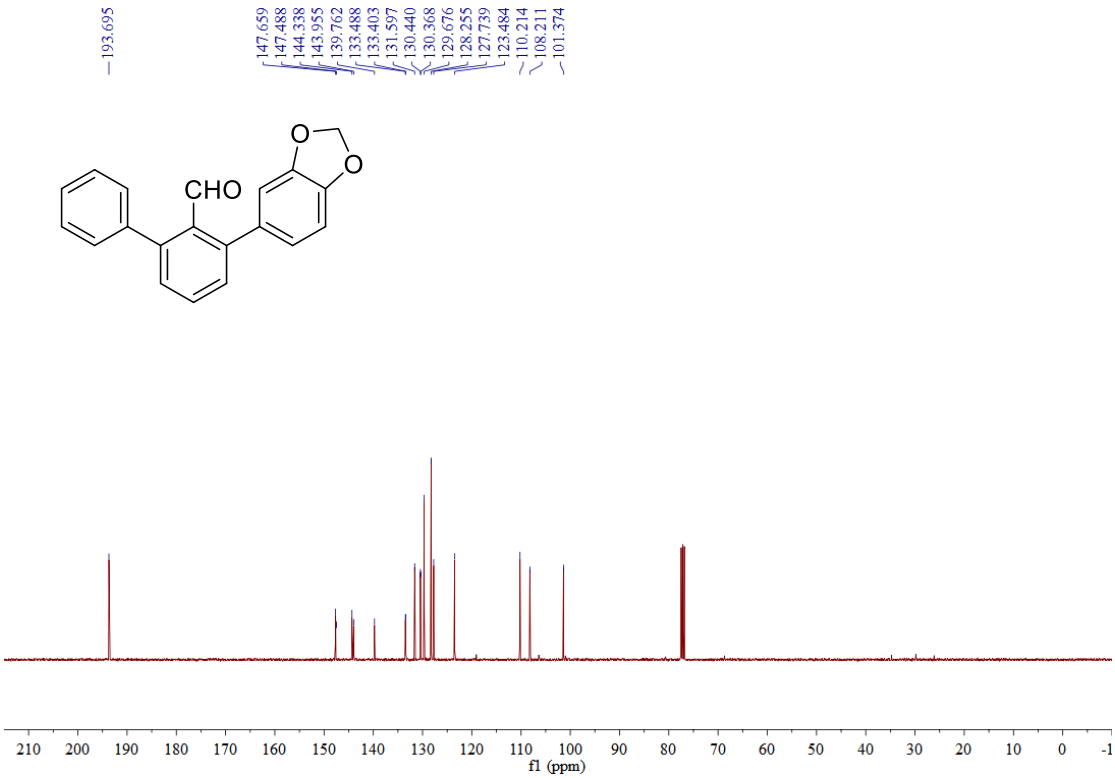


Figure S68. ^{1}H and ^{13}C NMR Spectra for compound **5t**