# Supporting Information

*for*

## Palladium-Catalyzed Hydroformylation of Terminal Arylacetylenes with Glyoxylic Acid

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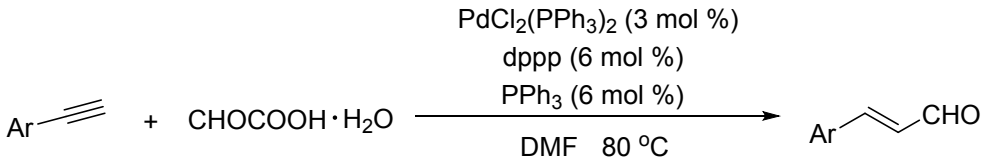
**CONTENTS**

## 1. General Information and Catalytic Experiments

### 1.1. General information.

All reagents and solvents were purchased from commercial sources and used without further purification. Most arylacetylenes were bought by commodity resource, and Compounds (**1h**, **1i**, **1g**, **1r**) was synthesized according to the reported literature (S. S. Ichake, A. Konala, V. Kavala, C. W. Kuo and C. F. Yao, *Org Lett*, 2017, **19**, 54-57).[1] Compound spots were visualized by UV light (254nm). Column chromatography was performed on silica gel FCP 200-300. NMR spectra were recorded by using a Bruker 400 MHz spectrometer. Chemical shifts in $^{1}$H-NMR are reported in parts per million (ppm) relative to residual chloroform (7.26ppm), multiplicites were indicated by using abbreviations (s = singlet; d = doublet; t = triplet; m = multiplet). Coupling constants are expressed in Hertz (Hz). $^{13}$C-NMR chemical shifts are reported in ppm relative to the central peak of chloroform (77.16ppm) as internal standards. Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods.

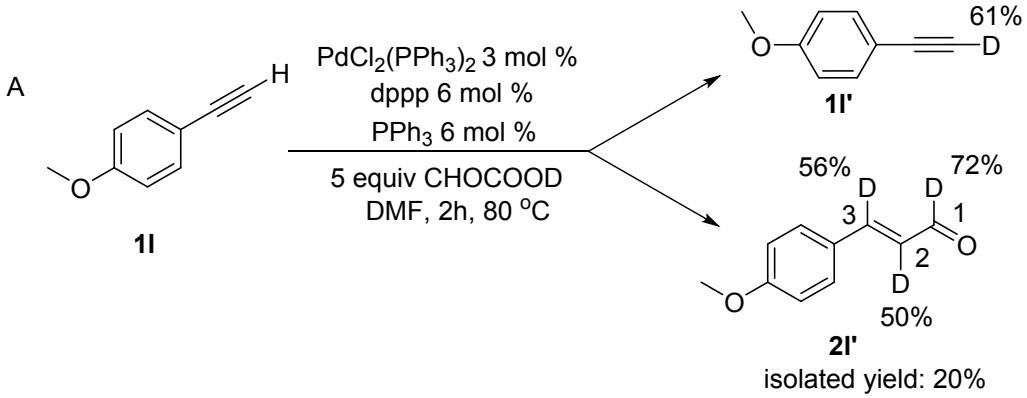
### 1.2. General Procedure for Palladium catalyzed hydroformylation of arylacetylenes.



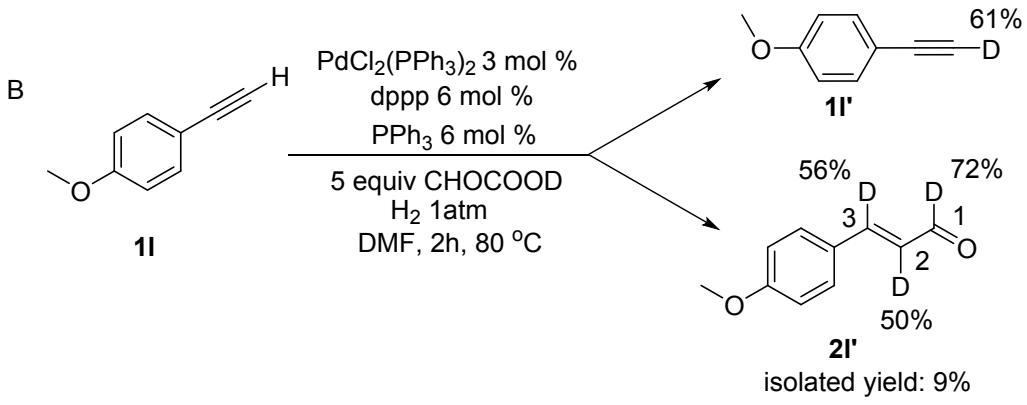

Standard reaction condition: The terminal alkyne (2mmol) was dissolved in DMF (4ml) in a 25ml Schlenk tube. Then $PdCl_2(PPh_3)_2$ (0.042g, 0.06mmol), dppp (0.049g, 0.12mmol), $PPh_3$ (0.031g, 0.12mmol) and glyoxylic acid monohydrate (0.92g, 10mmol) were added in one batch, and the resulting solution was intensively stirred under an argon atmosphere at 80 $^{o}$C for 2-4 hours, and then the mixture was poured into saturated aqueous $NaHCO_3$ solution (25ml) and extracted with $CH_2Cl_2$ (4 x 15ml), The combined organic layers were washed with brine (4 x 20ml), dried over $MgSO_4$, filtered, and concentrated, the residue was purified by flash chromatography on silica gel to obtain the desired product by using light petroleum ether/ethyl acetate (15:1) as the eluent.

**1.3. General Procedure for Deuterium-Labeling experiments.**

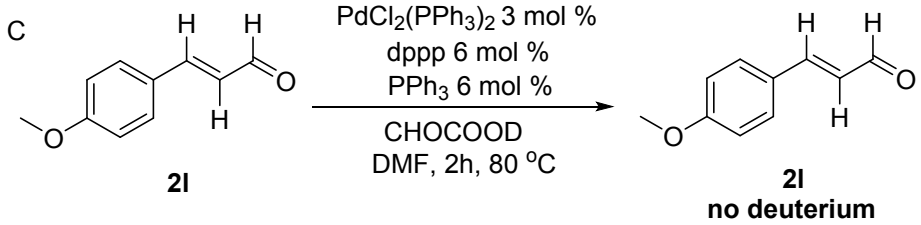
Preparation of CHOCOOD: The $CHOCOOH \cdot H_2O$ (0.45g) was dissolved in 5ml $D_2O$. Then the solution was dried with $P_2O_5$ at 50 °C to 0.45g.




Reaction A: The CHOCOOD (0.9g) was dissolved in DMF (4ml) and was added in a 25ml Schlenk tube. Then 1-ethynyl-4-methoxybenzene (0.264g, 2mmol), $PdCl_2(PPh_3)_2$ (0.042g, 0.06mmol), dppp (0.050g, 0.12mmol), $PPh_3$ (0.030g, 0.12mmol) were added in one batch, and the resulting solution was intensively stirred under an argon atmosphere at 80 °C for 2 hours, and then the mixture was poured into saturated aqueous $NaHCO_3$ solution (25ml) and extracted with $CH_2Cl_2$ (4 x 15ml), The combined organic layers were washed with brine (4 x 20ml), dried over $MgSO_4$, filtered, and concentrated, the residue was purified by flash chromatography on silica gel to obtain the desired product by using light petroleum ether/ethyl acetate (from 100:1 to 15:1) as the eluent. The isolated yield of aldehyde product was 0.062g (20%).



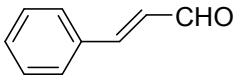
Reaction B: The CHOCOOD (0.9g) was dissolved in DMF (4ml) and was added in a 25ml Schlenk tube. Then 1-ethynyl-4-methoxybenzene (0.264g, 1mmol), $PdCl_2(PPh_3)_2$ (0.042g, 0.06mmol), dppp (0.050g, 0.12mmol), $PPh_3$ (0.030g, 0.12mmol) were added in one batch, and the resulting solution was intensively stirred under an $H_2$ atmosphere (1atm) at 80 $^oC$ for 2 hours, and then the mixture was poured into saturated aqueous $NaHCO_3$ solution (25ml) and extracted with $CH_2Cl_2$ (4 x 15ml), The combined organic layers were washed with brine (4 x 20ml), dried over $MgSO_4$, filtered, and concentrated, the residue was purified by flash chromatography on silica gel to obtain the desired product by using light petroleum ether/ethyl acetate (from 100:1 to 15:1) as the eluent. The isolated yield of aldehyde product was 0.029g (9%).




Reaction C: The CHOCOOD (0.45g) was dissolved in DMF (2ml) and was added in a 25ml Schlenk tube. Then (E)-3-(4-methoxyphenyl)acrylaldehyde (0.162g, 1mmol), $PdCl_2(PPh_3)_2$ (0.021g, 0.03mmol), dppp (0.025g, 0.06mmol), $PPh_3$ (0.015g, 0.06mmol) were added in one batch, and the resulting solution was intensively stirred under an argon atmosphere at 80 $^oC$ for 2 hours, and then the mixture was poured into saturated aqueous $NaHCO_3$ solution (25ml) and extracted with $CH_2Cl_2$ (4 x 15ml), The combined organic layers were washed with brine (4 x 20ml), dried over $MgSO_4$, filtered, and concentrated, the residue was purified by flash chromatography on silica gel to obtain the desired product by using light petroleum ether/ethyl acetate (15:1) as the eluent. The isolated yield of aldehyde product was 99%.

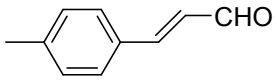
## 2. Characterizations of α,β-unsaturated aldehydes Products

**2a: cinnamaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 72%, light yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.48 (d, *J* = 16.0 Hz, 1H), 7.44 (m, 3H), 6.72 (dd, *J* = 16.0, 7.7 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.82, 152.91, 134.09, 131.39, 129.21, 128.69, 128.60.



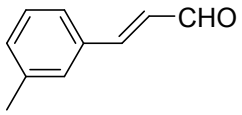

This NMR analysis is consistent with the literature.[2]

**2b: (E)-3-(p-tolyl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 63%, light yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.67 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 15.9 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.67 (dd, *J* = 15.9, 7.7 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.88, 153.04, 142.06, 131.40, 129.93, 128.62, 127.79, 21.67.



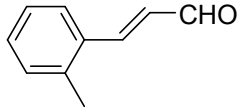

This NMR analysis is consistent with the literature.[3]

**2c: (E)-3-(m-tolyl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA =15:1) and the yield was 56%, light yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 15.9 Hz, 1H), 7.37 (m, 3H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.27 – 7.24 (d, J=7.7Hz, 1H), 6.71 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.86, 153.16, 138.85, 133.96, 132.17, 129.14, 129.00, 128.42, 125.75, 21.32.



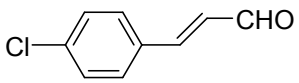

This NMR analysis is consistent with the literature.[3]

**2d: (E)-3-(o-tolyl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 51%, light yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.73 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 15.9 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.33 (m, 1H), 7.25 (m, 2H), 6.67 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.99, 150.40, 138.04, 132.91, 131.18, 131.14, 129.69, 126.93, 126.71, 19.87.




This NMR analysis is consistent with the literature.[3]

**2e: (E)-3-(4-chlorophenyl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 45%, yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* =



7.6 Hz, 1H), 7.40 – 7.46 (m, 2H), 7.43 (d, *J* = 16 Hz, 1H), 7.31 – 7.35 (m, 2H), 6.68 (dd, *J* = 16.0, 7.6 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.49, 151.17, 137.37, 132.59, 129.73, 129.53, 129.04.
This NMR analysis is consistent with the literature.[2]

**2f: (E)-3-(2-chlorophenyl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 64%, yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.75 (d, *J* = 7.7 Hz, 1H), 7.93 (d, *J* = 16.0 Hz, 1H), 7.66 (dd, *J* = 7.8, 2 Hz, 1H), 7.46 (dd, J=7.8, 2Hz, 1H), 7.36 (td, *J* = 7.8, 2.0 Hz, 1H), 7.32 (td, *J* = 7.8, 2 Hz, 1H), 6.70 (dd, *J* = 16.0, 7.7 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.71, 148.11, 135.32, 132.19, 132.12, 130.63, 130.47, 127.96, 127.43.
This NMR analysis is consistent with the literature.[2]

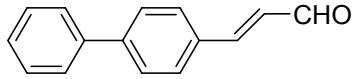
**2g: (E)-3-(4-bromophenyl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 52%, yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.52 (m, 2H), 7.41 (d, *J* = 16 Hz, 1H), 7.37 – 7.44 (m, 2H), 6.68 (dd, *J* = 16.0, 7.6 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.45, 151.19, 132.98, 132.47, 129.87, 129.08, 125.76.
This NMR analysis is consistent with the literature.[2]

**2h: (E)-3-(naphthalen-2-yl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 64%, yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.76 (d, *J* = 7.7 Hz, 1H), 7.98 (s, 1H), 7.87 (m, 3H), 7.72 – 7.50 (m, 4H), 6.83 (dd, *J* = 15.9, 7.7 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.82, 152.91, 134.74, 133.30, 131.65, 130.82, 129.09, 128.88, 128.80, 127.98, 127.94, 127.08, 123.63.
This NMR analysis is consistent with the literature.[4]

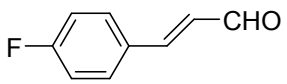
**2i: (E)-3-(naphthalen-1-yl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 72%, yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.85 (d, *J* = 7.7 Hz, 1H), 8.32 (d, *J* = 15.7 Hz, 1H), 8.24 – 8.16 (m, 1H), 8.02 – 7.88 (m,

2H), 7.85 – 7.78 (m, 1H), 7.67 – 7.44 (m, 2H), 6.84 (dd, *J* = 15.7, 7.7 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.84, 149.48, 133.85, 131.75, 131.29, 131.03, 130.97, 129.10, 127.39, 126.54, 125.84, 125.59, 122.88.
This NMR analysis is consistent with the literature.[3]

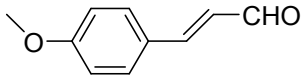
**2j: (E)-3-([1,1'-biphenyl]-4-yl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 62%, yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.73 (d, *J* = 7.7 Hz, 1H), 7.71 – 7.59 (m, 6H), 7.51 (d, *J* = 15.9 Hz, 1H), 7.49 – 7.36 (m, 3H), 6.76 (dd, *J* = 15.9, 7.7 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.76, 152.38, 144.09, 139.92, 133.01, 129.12, 129.06, 128.47, 128.20, 127.78, 127.15.
This NMR analysis is consistent with the literature.[3]



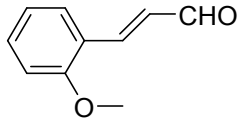

**2k: (E)-3-(4-fluorophenyl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 63%, light yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.44 (d, *J* = 16.0 Hz, 1H), 7.17 – 7.08 (m, 2H), 6.65 (dd, *J* = 16.0, 7.7 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.57, 164.54 (d, *J* = 253.2 Hz), 151.45, 130.61 (d, *J* = 8.7 Hz), 130.41 (d, *J* = 3.4 Hz), 128.47 (d, *J* = 2.3 Hz), 116.48 (d, *J* = 22.0 Hz).
This NMR analysis is consistent with the literature.[2]




**2l: (E)-3-(4-methoxyphenyl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 61%, yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.52 (m, 2H), 7.40 (d, *J* = 15.8 Hz, 1H), 6.90 – 6.94 (m, 2H), 6.59 (dd, *J* = 15.8, 7.7 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.75, 162.25, 152.80, 130.41, 126.81, 126.54, 114.62, 55.51.
This NMR analysis is consistent with the literature.[4]

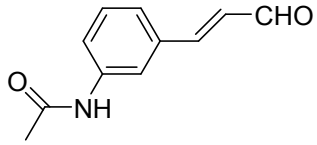



**2m: (E)-3-(2-methoxyphenyl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 82%, yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 16.1 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.41

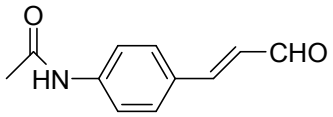


(ddd, *J* = 8.4, 7.4, 1.7 Hz, 1H), 7.00 (ddd, *J* = 7.4, 7.7, 1.1 Hz, 1H), 6.95 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.80 (dd, *J* = 16.1, 7.9 Hz, 1H), 3.92 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 194.76, 158.43, 148.39, 132.83, 129.23, 129.02, 123.11, 121.02, 111.42, 55.71.
This NMR analysis is consistent with the literature.[5]

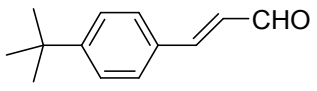
**2n: (E)-N-(3-(3-oxoprop-1-en-1-yl)phenyl)acetamide.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 5:1) and the yield was 73%, white solid, *mp.*178-179 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.67 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.87 (s, 1H), 7.83 (t, *J* = 2.0 Hz, 1H), 7.55 (d, J=7.8 Hz, 1H), 7.43 (d, *J* = 16.0 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.68 (dd, *J* = 16.0, 7.7 Hz, 1H), 2.20 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.96, 169.01, 152.82, 139.00, 134.83, 129.78, 128.97, 124.33, 122.64, 119.72, 24.67. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{11}H_{11}NO_2$: 190.0868; found: 190.0867.




**2o: (E)-N-(4-(3-oxoprop-1-en-1-yl)phenyl)acetamide.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 5:1) and the yield was 63%, white solid, *mp.*167-170 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.45 (s，1H), 7.43 (d, *J* = 15.9 Hz, 1H), 6.65 (dd, *J* = 15.9, 7.7 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.85, 168.56, 152.32, 140.81, 129.90, 129.74, 127.68, 119.81, 24.93. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{11}H_{11}NO_2$: 190.0868; found: 190.0867.

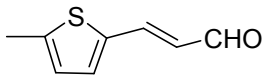



**2p: (E)-3-(4-(tert-butyl)phenyl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 67%, yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.54 (m, 2H), 7.47 (d, *J* = 15.9 Hz, 1H), 7.44 – 7.48 (m, 2H), 6.70 (dd, *J* = 15.9, 7.8 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.98, 155.21, 152.97, 131.41, 128.54, 128.02, 126.24, 35.16, 31.24.
This NMR analysis is consistent with the literature.[4]

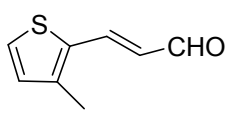



**2q: (E)-3-(5-methylthiophen-2-yl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1)

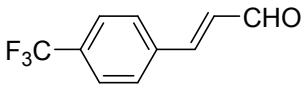
and the yield was 60%, yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.57 (d, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 15.5 Hz, 1H), 7.16 (d, *J* = 3.6 Hz, 1H), 6.77 (d, *J* = 3.6 Hz, 1H), 6.38 (dd, *J* = 15.5, 7.7 Hz, 1H), 2.52 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.07, 146.54, 145.06, 137.44, 133.12, 127.20, 126.27, 16.08. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_8H_8OS$: 153.0374; found: 153.0376.



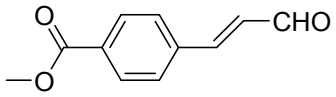

**2r: (E)-3-(3-methylthiophen-2-yl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 15:1) and the yield was 52%, yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 15.5 Hz, 1H), 7.38 (d, *J* = 5.1 Hz, 1H), 6.92 (d, *J* = 5.1 Hz, 1H), 6.45 (dd, *J* = 15.5, 7.6 Hz, 1H), 2.39 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.15, 142.98, 142.92, 133.70, 131.63, 129.13, 126.65, 14.42. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_8H_8OS$: 153.0374; found: 153.0375.



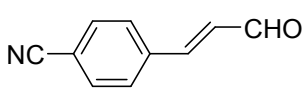

**2s: (E)-3-(4-(trifluoromethyl)phenyl)acrylaldehyde.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 10:1) and the yield was 45%, light yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.75 (d, *J* = 7.5 Hz, 1H), 7.68 (m, 4H), 7.51 (d, *J* = 16.0 Hz, 1H), 6.77 (dd, *J* = 16.0, 7.5 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.33, 150.43, 137.42, 132.70 (q, *J* = 32.8 Hz), 130.62, 128.70, 126.19 (q, *J* = 3.8 Hz), 123.79 (q, *J* = 272.5 Hz).
This NMR analysis is consistent with the literature.[2]




**2t: methyl (E)-4-(3-oxoprop-1-en-1-yl)benzoate.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 5:1) and the yield was 42%, white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.74 (d, *J* = 7.4 Hz, 1H), 8.09 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 16.0 Hz, 1H), 6.78 (dd, *J* = 16.0, 7.4 Hz, 1H), 3.94 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.47, 166.37, 151.02, 138.18, 132.32, 130.48, 130.38, 128.43, 52.54.
This NMR analysis is consistent with the literature.[2]




**2u: (E)-4-(3-oxoprop-1-en-1-yl)benzonitrile.** The title compound was prepared according to the general procedure after silica gel chromatography (PE: EA = 5:1) and the yield was 36%, white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.76 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 16.0 Hz, 1H), 6.77




(dd, $J$ = 16.0, 7.5 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.03, 149.59, 138.27, 132.95, 131.31, 128.86, 118.26, 114.41.

This NMR analysis is consistent with the literature.[3]

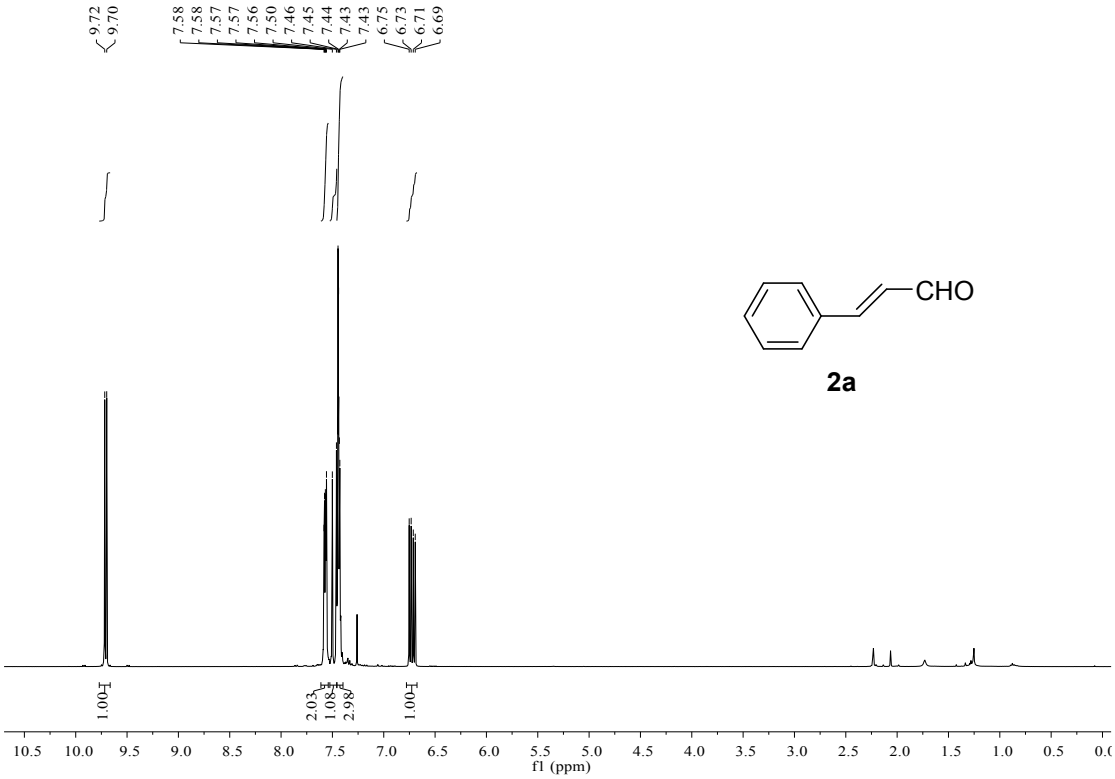
**2l':** $^1$H NMR (400 MHz, $CDCl_3$) δ 9.63 (m, 0.12H), 7.48 – 7.52 (m, 2H), 7.40 (m, 0.23H), 6.90 – 6.94 (m, 2H), 6.59 (m, 0.23H). HRMS (ESI): m/z $[M]^+$ calculated for $C_{10}H_9DO_2$: 163.0744; found: 163.0728. $[M]^+$ calculated for $C_{10}H_8D_2O_2$: 164.0806; found: 164.0805. $[M]^+$ calculated for $C_{10}H_7D_3O_2$: 165.0869; found: 165.0871.

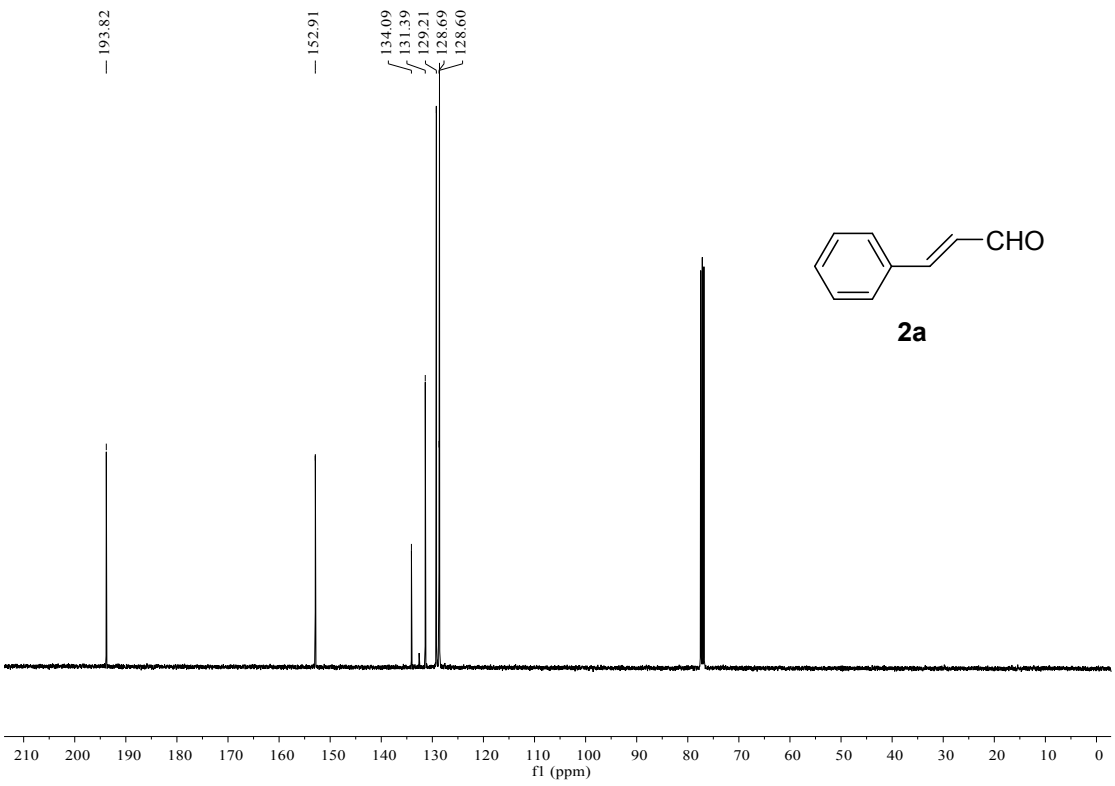
## Reference

1. S. S. Ichake, A. Konala, V. Kavala, C. W. Kuo and C. F. Yao, *Org Lett*, 2017, **19**, 54-57.
2. H. Huang, C. Yu, X. Li, Y. Zhang, Y. Zhang, X. Chen, P. S. Mariano, H. Xie and W. Wang, *Angew.Chem.Int.Ed.*, 2017, **56**, 8201-8205.
3. J. Liu, J. Zhu, H. Jiang, W. Wang and J. Li, Chem. Commun., 2010, 46, 415-417.
4. H. Chen, H. Jiang, C. Cai, J. Dong and W. Fu, *Org. Lett.*, 2011, **13**, 992-994.
5. J.-A. Jiang, J.-L. Du, Z.-G. Wang, Z.-N. Zhang, X. Xu, G.-L. Zheng and Y.-F. Ji, *Tetrahedron Lett.*, 2014, **55**, 1677-1681.

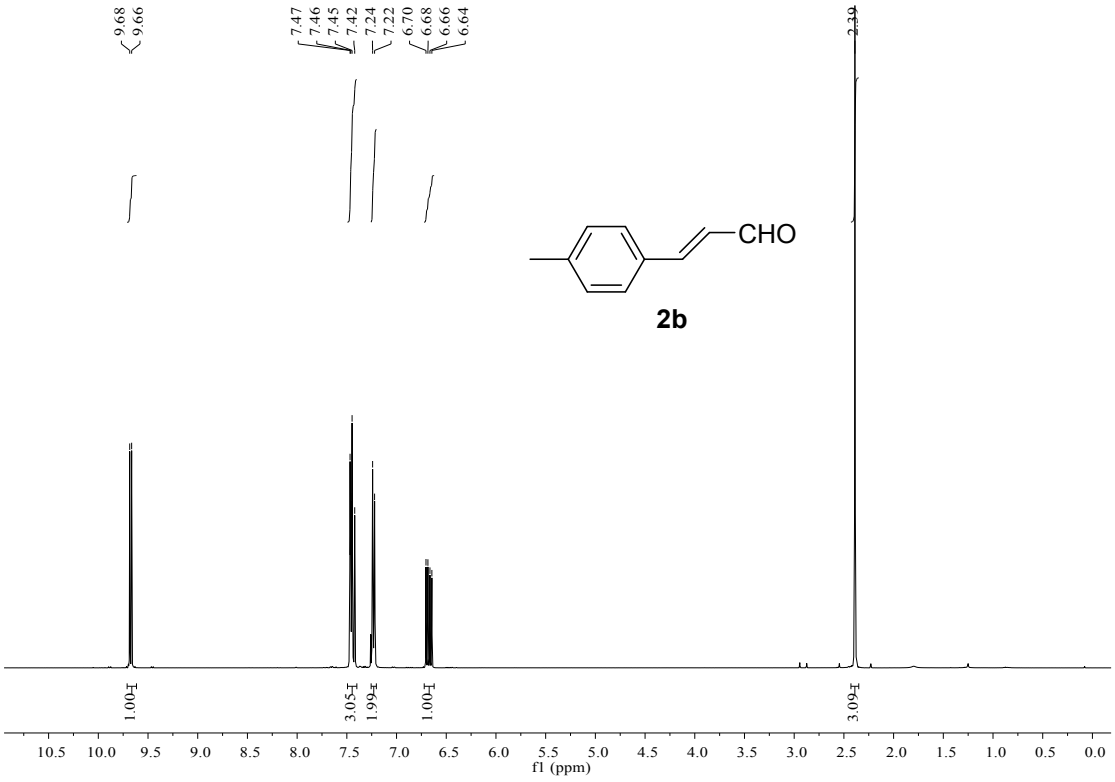
## 3. $^{1}H$ NMR, $^{13}C$ NMR of α,β-unsaturated aldehydes Products

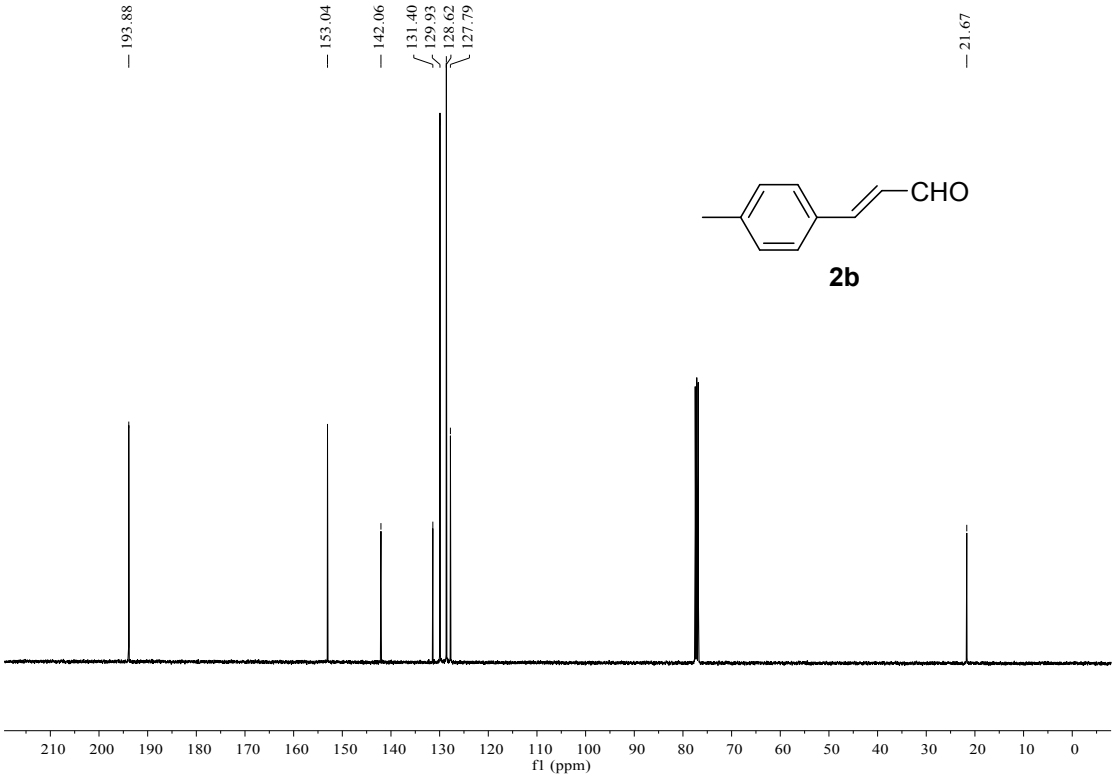
**2a:** cinnamaldehyde**.**



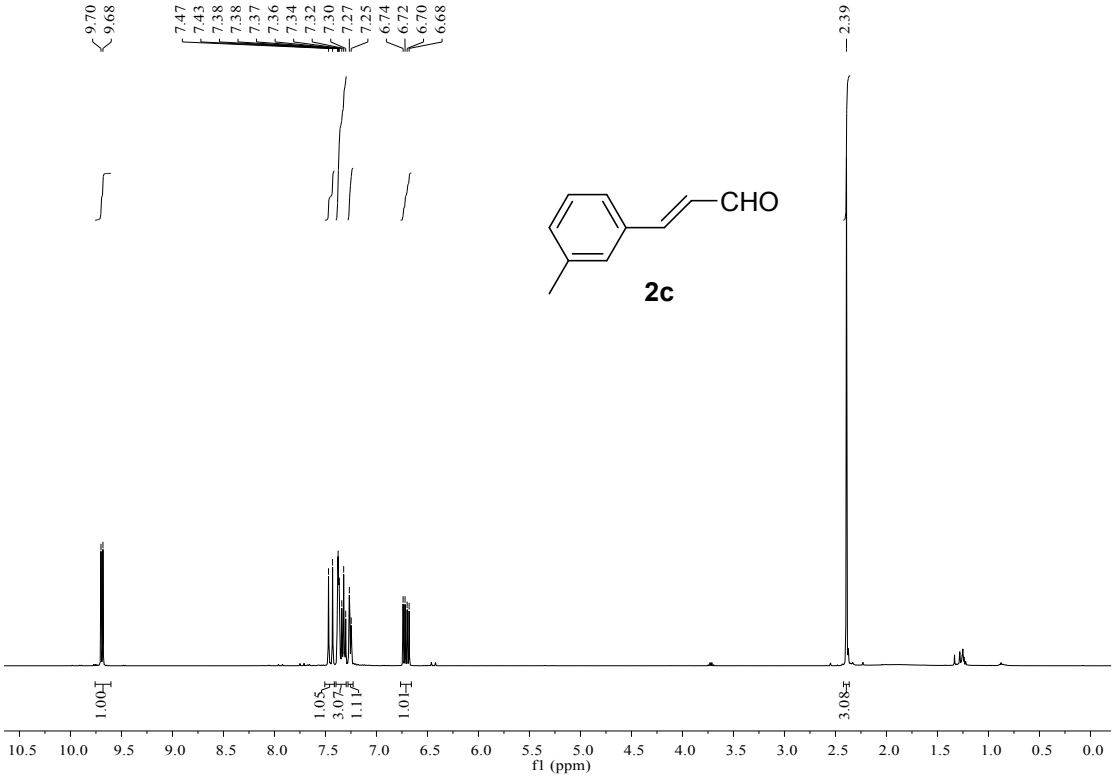



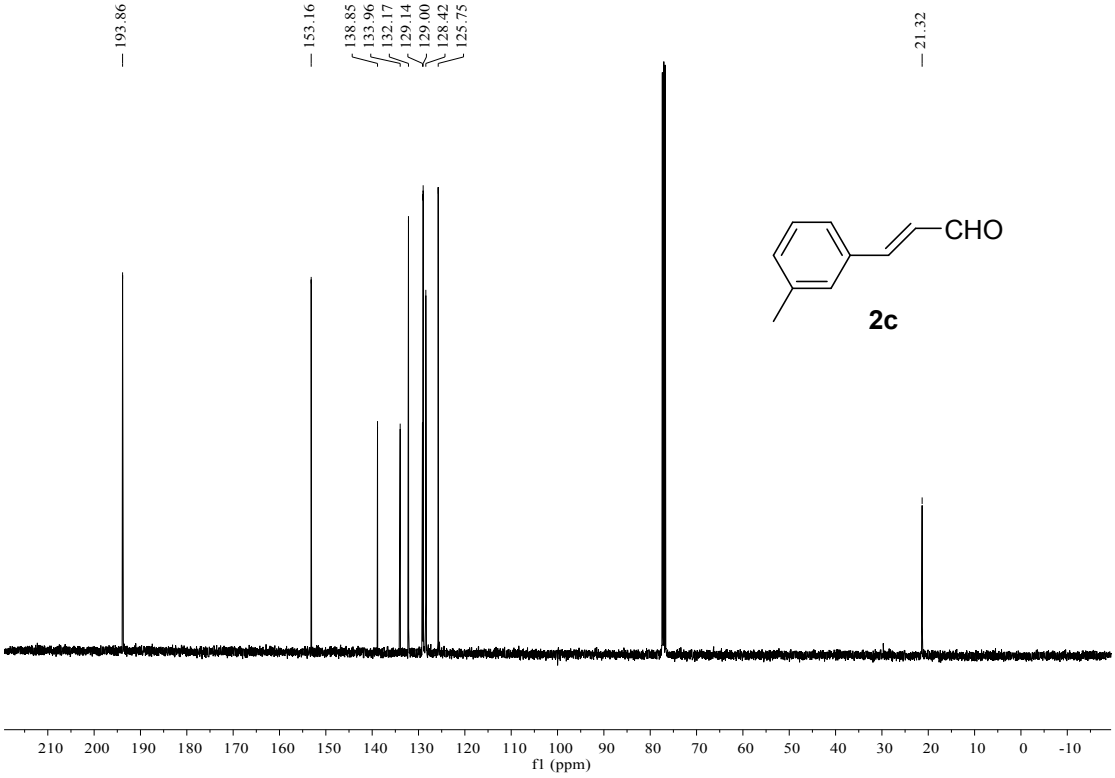
**2b: (E)-3-(p-tolyl)acrylaldehyde.**



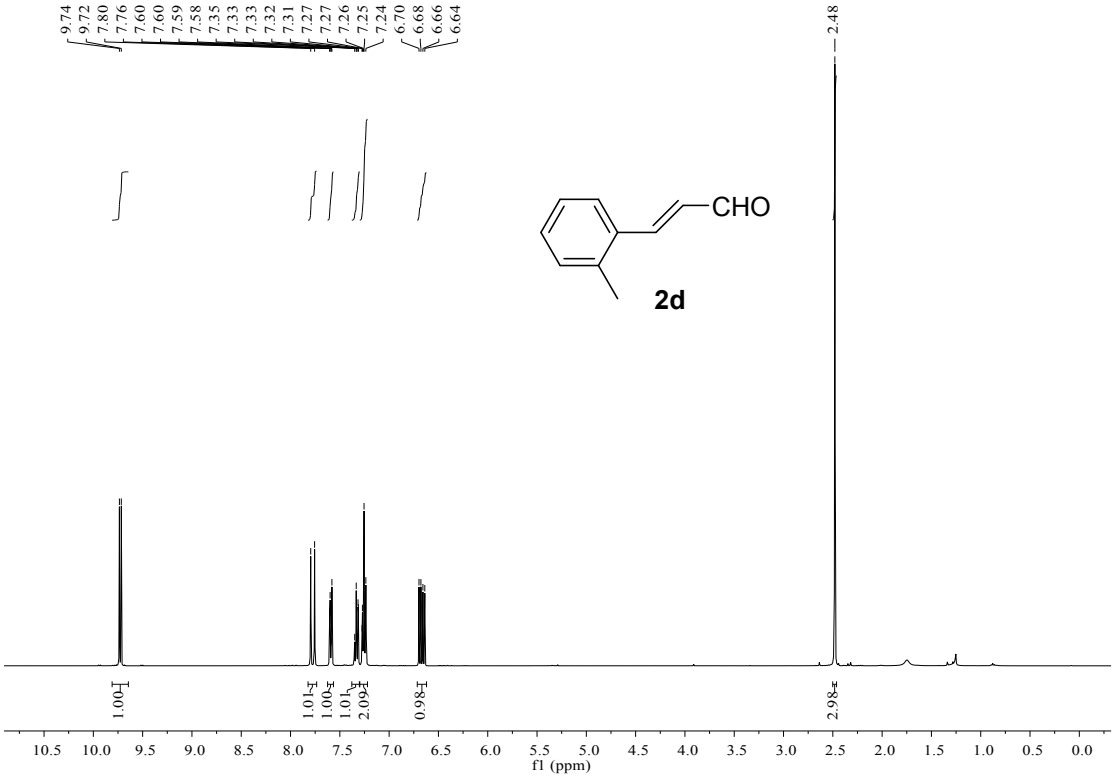



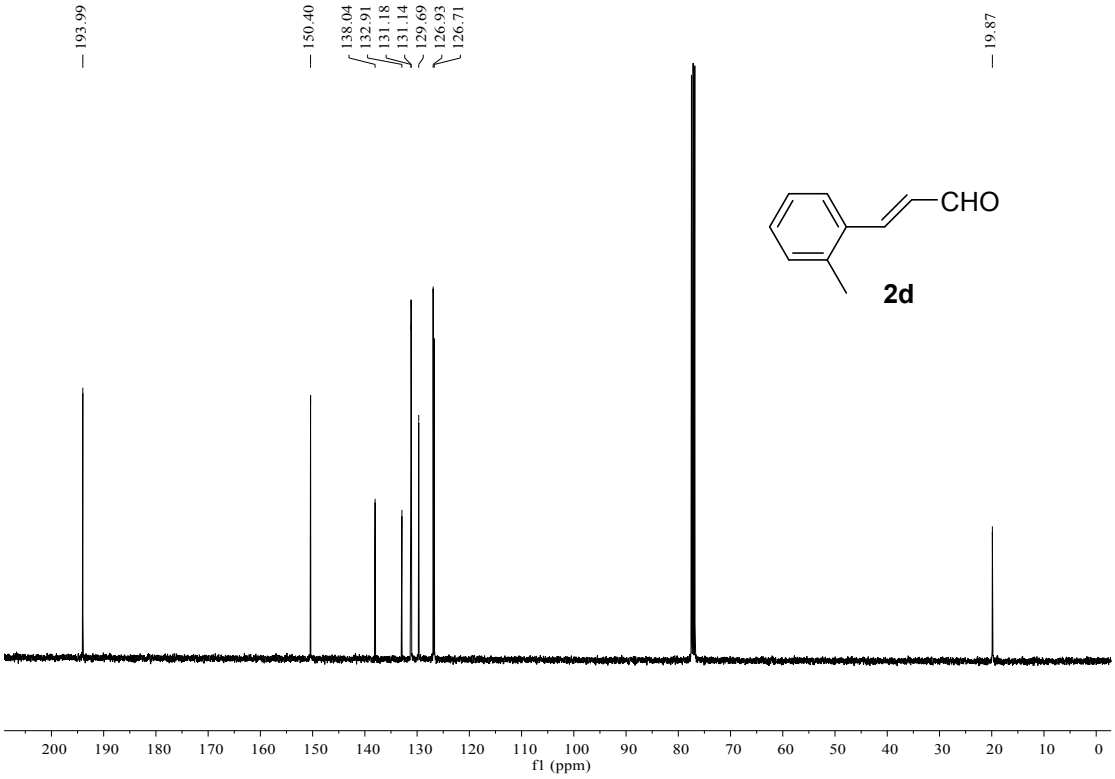
**2c: (E)-3-(m-tolyl)acrylaldehyde.**



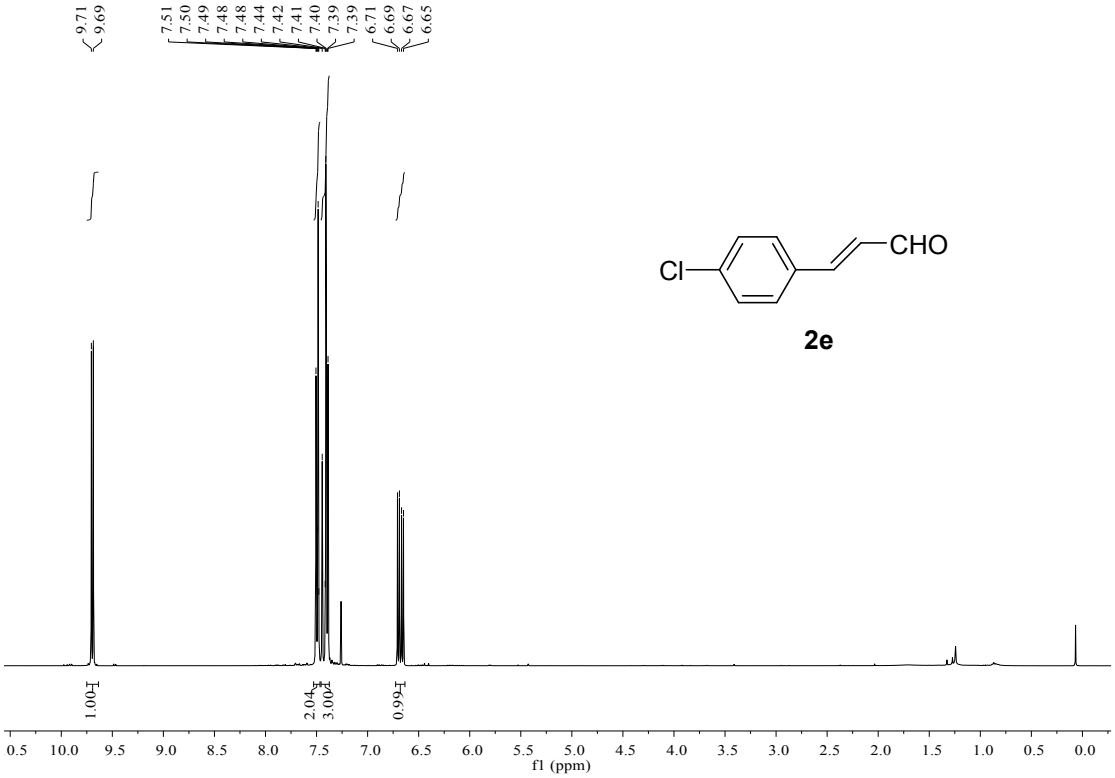



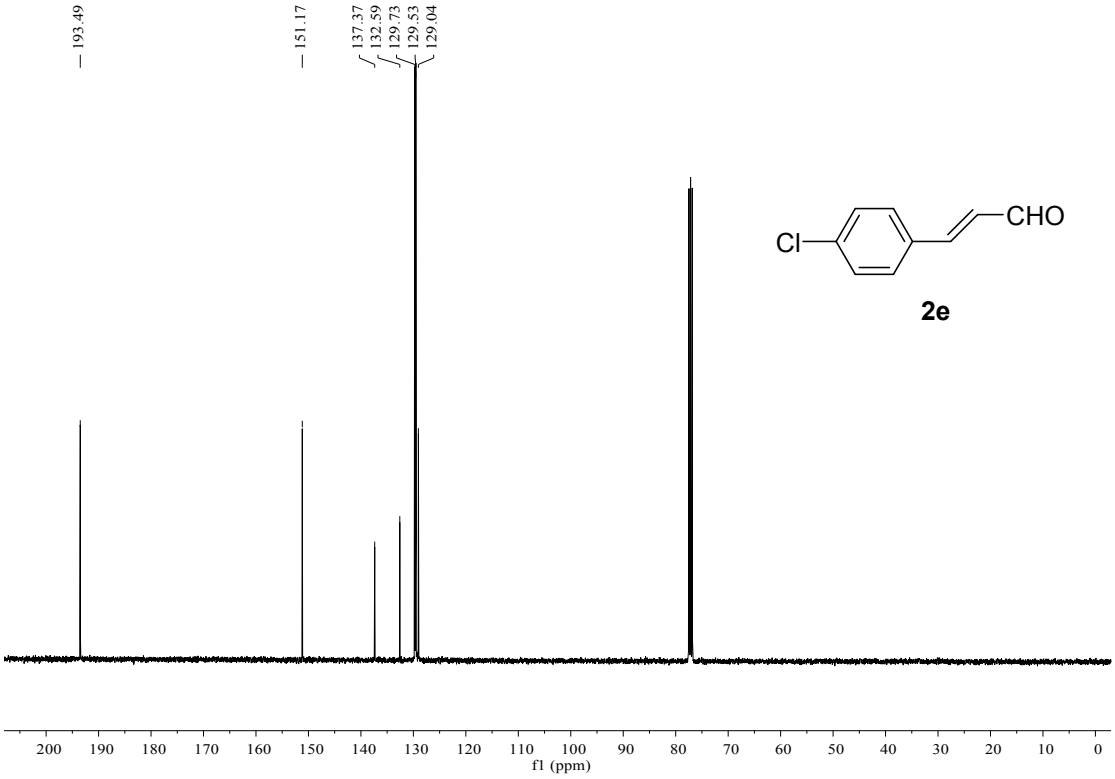
**2d: (E)-3-(o-tolyl)acrylaldehyde.**



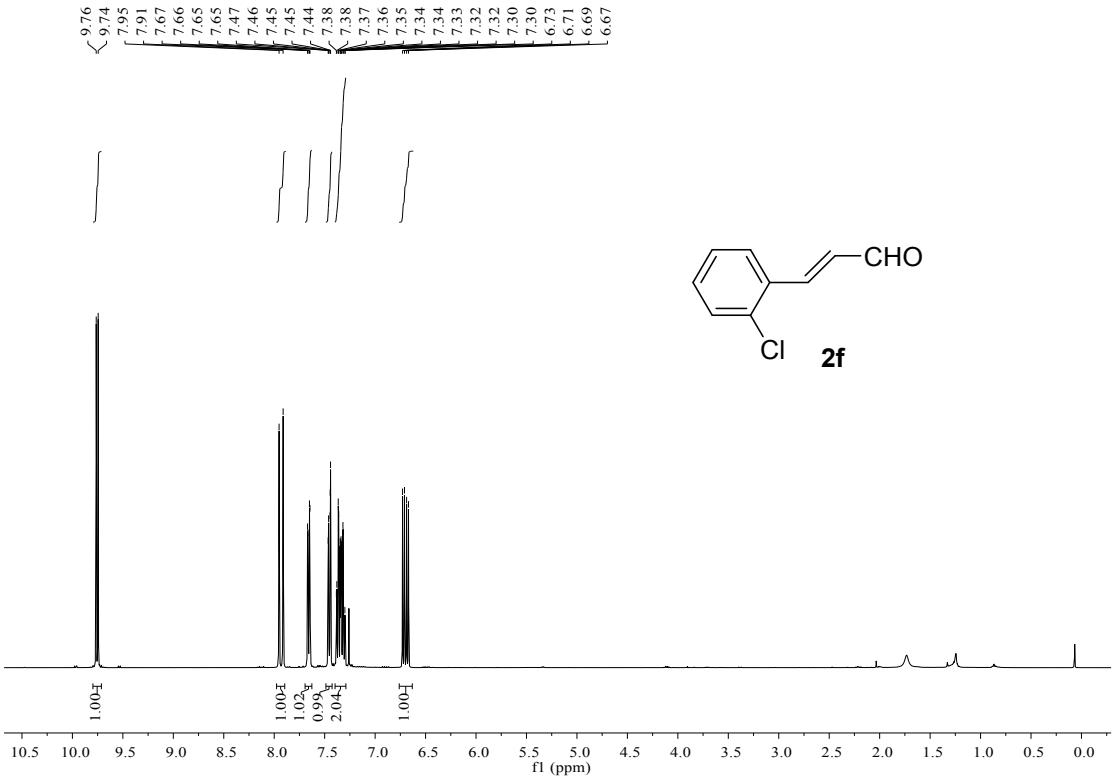



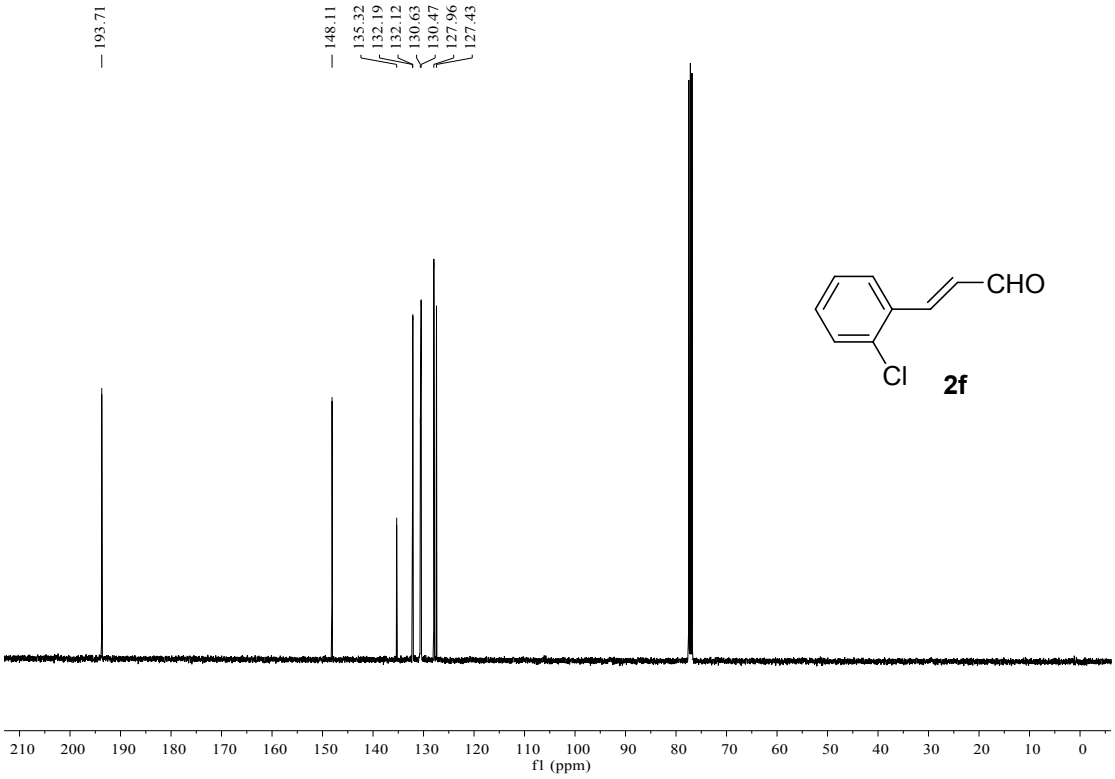
**2e: (E)-3-(4-chlorophenyl)acrylaldehyde.**



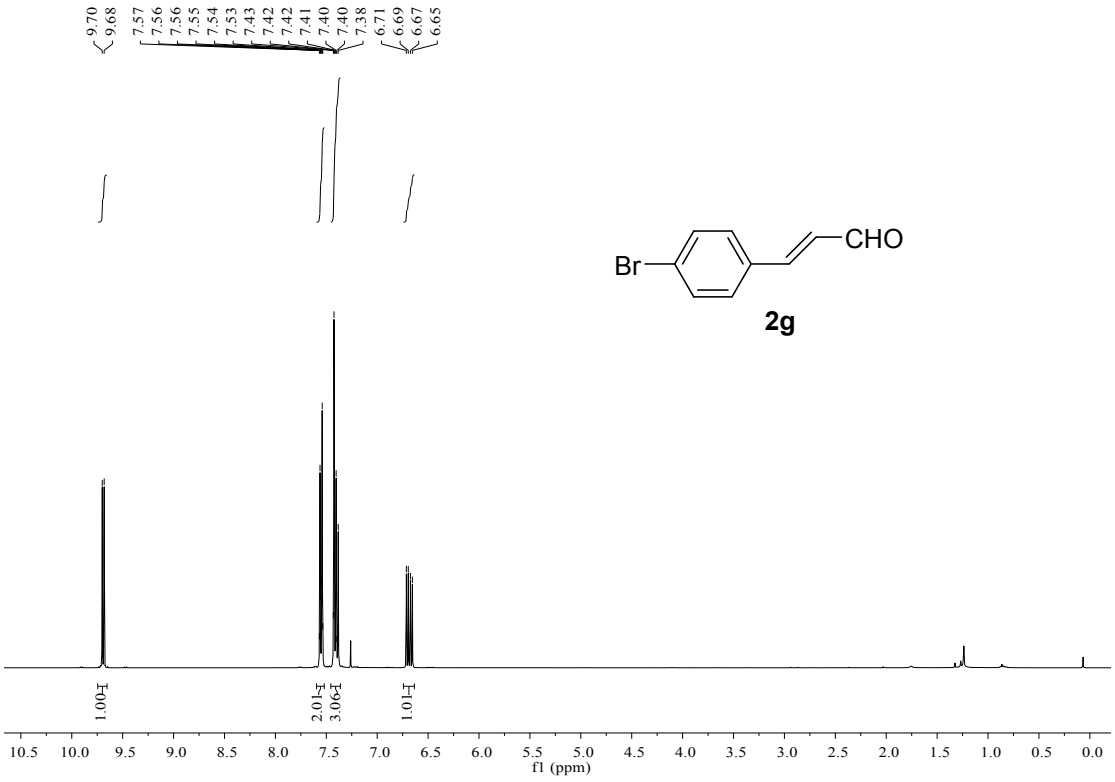



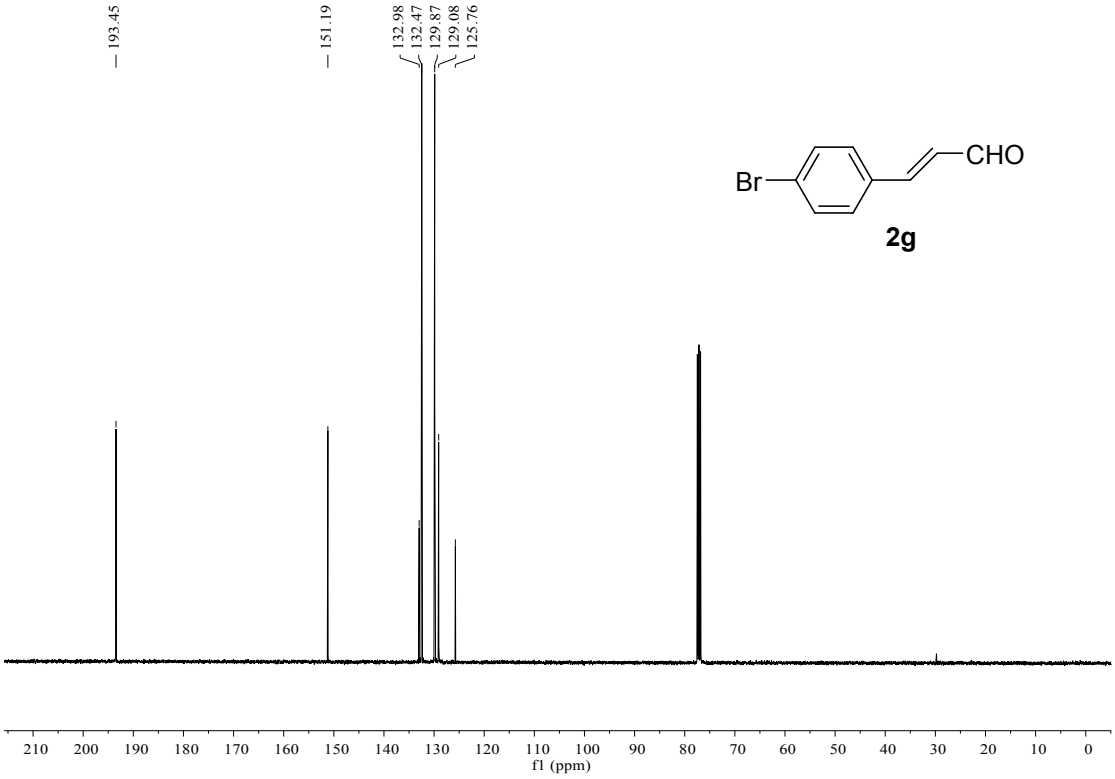
**2f: (E)-3-(2-chlorophenyl)acrylaldehyde.**



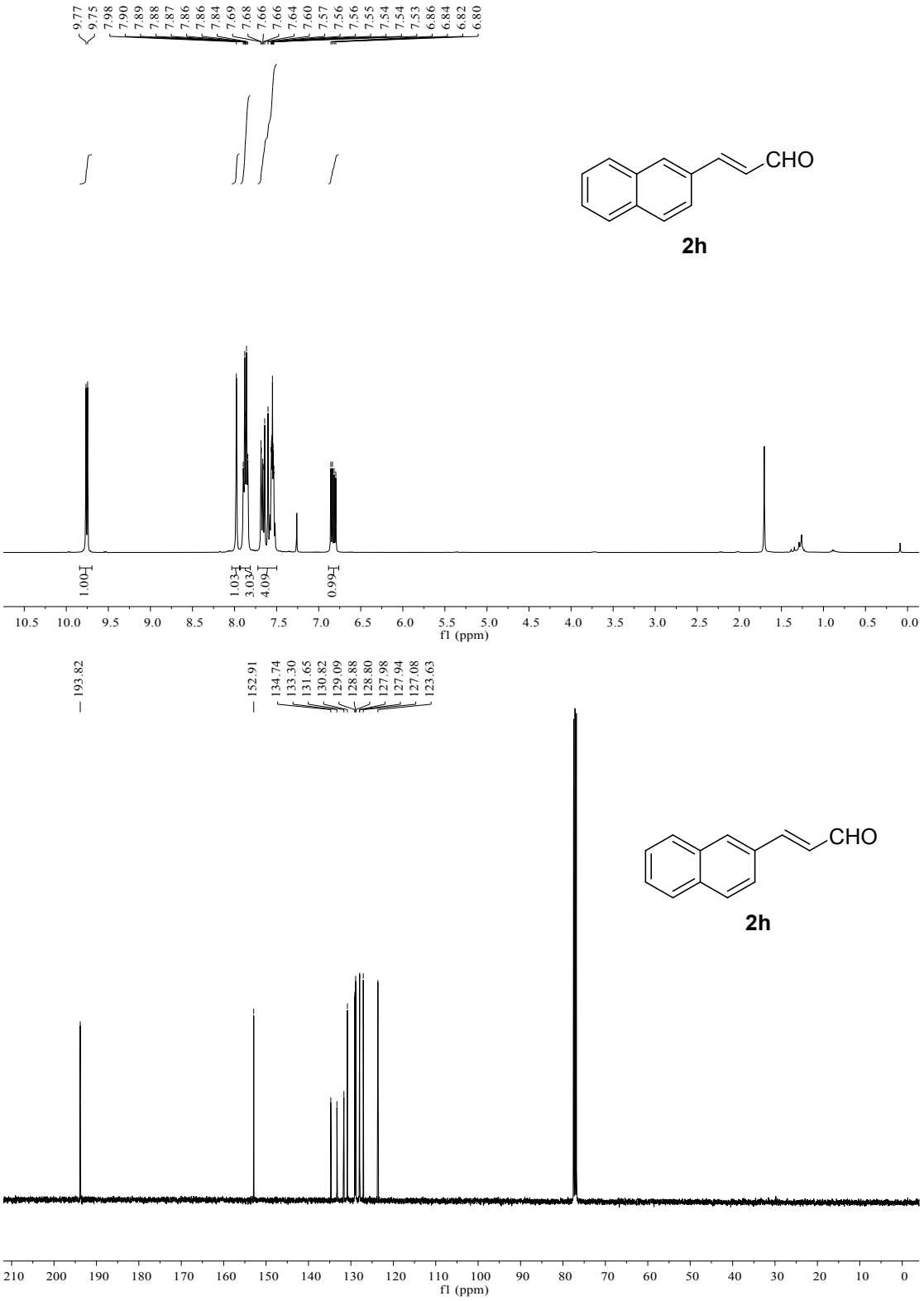



**2g: (E)-3-(4-bromophenyl)acrylaldehyde.**

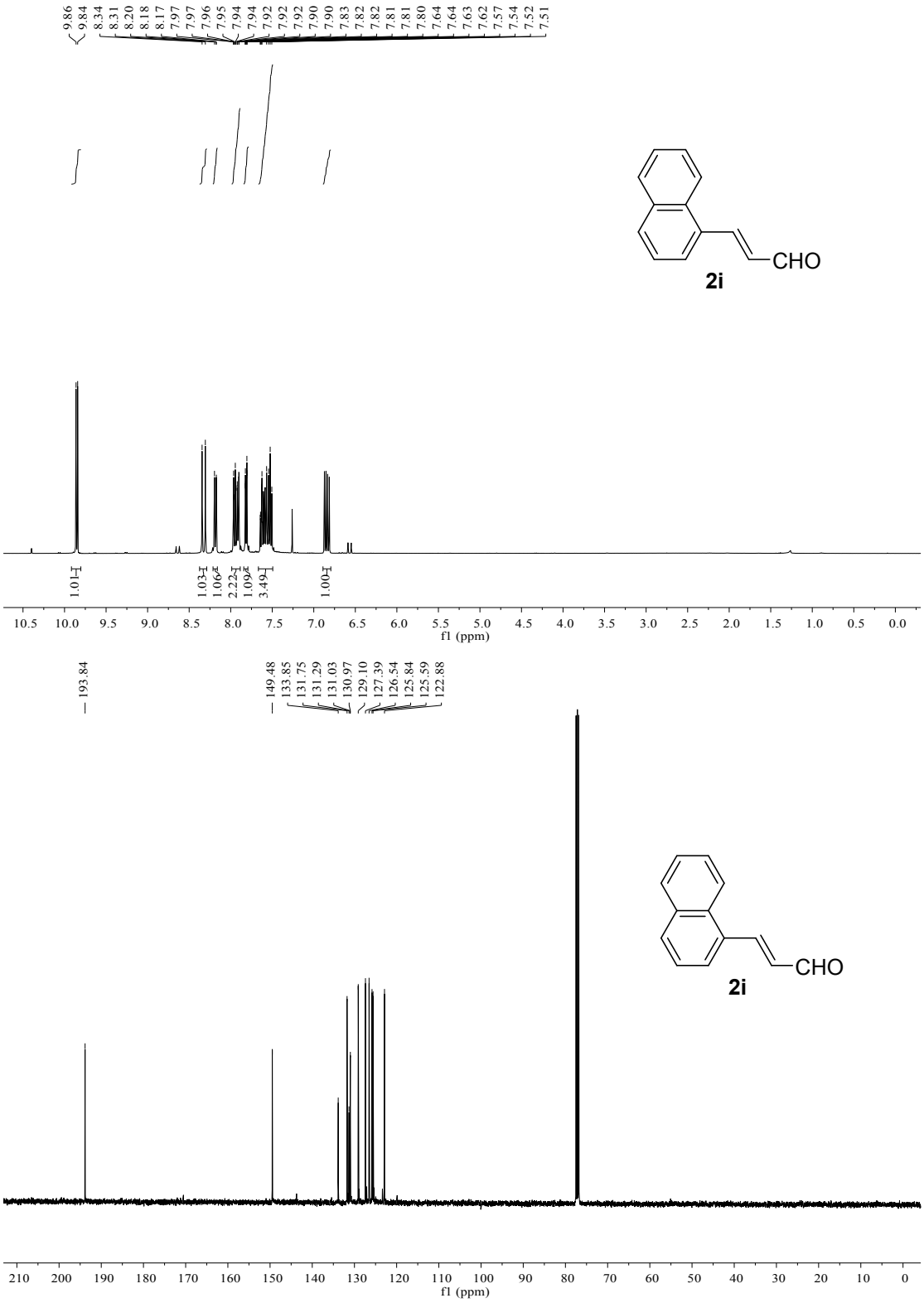


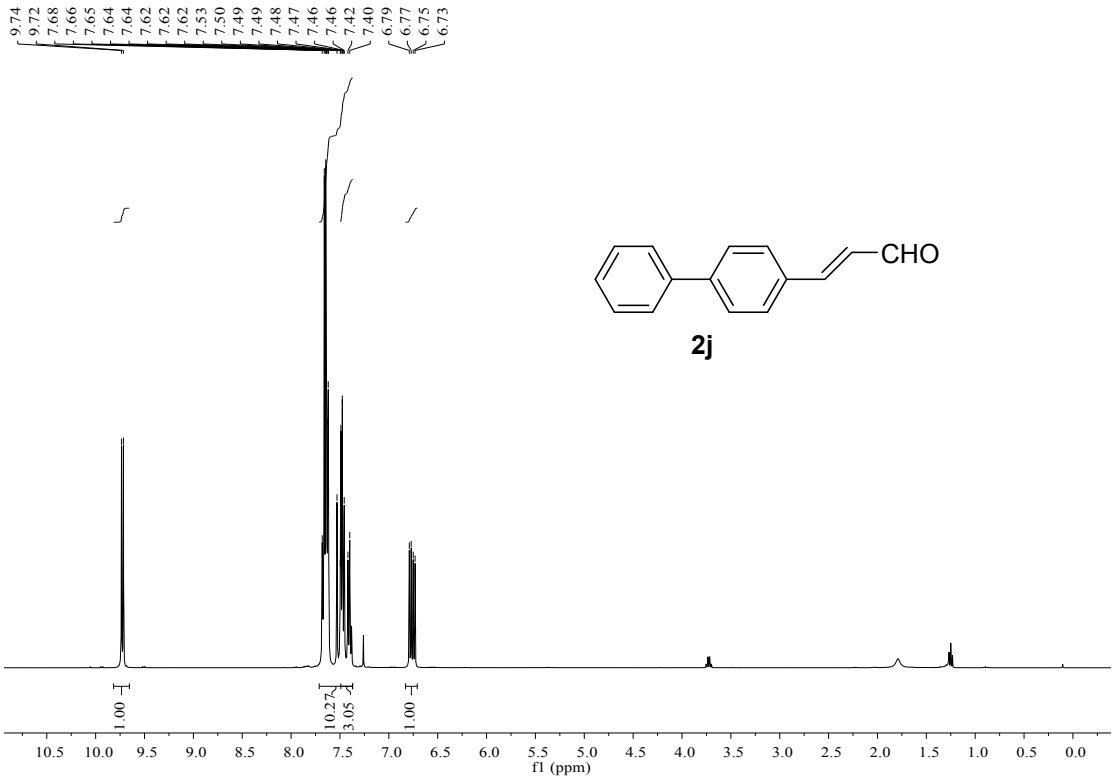
**2h: (E)-3-(naphthalen-2-yl)acrylaldehyde.**

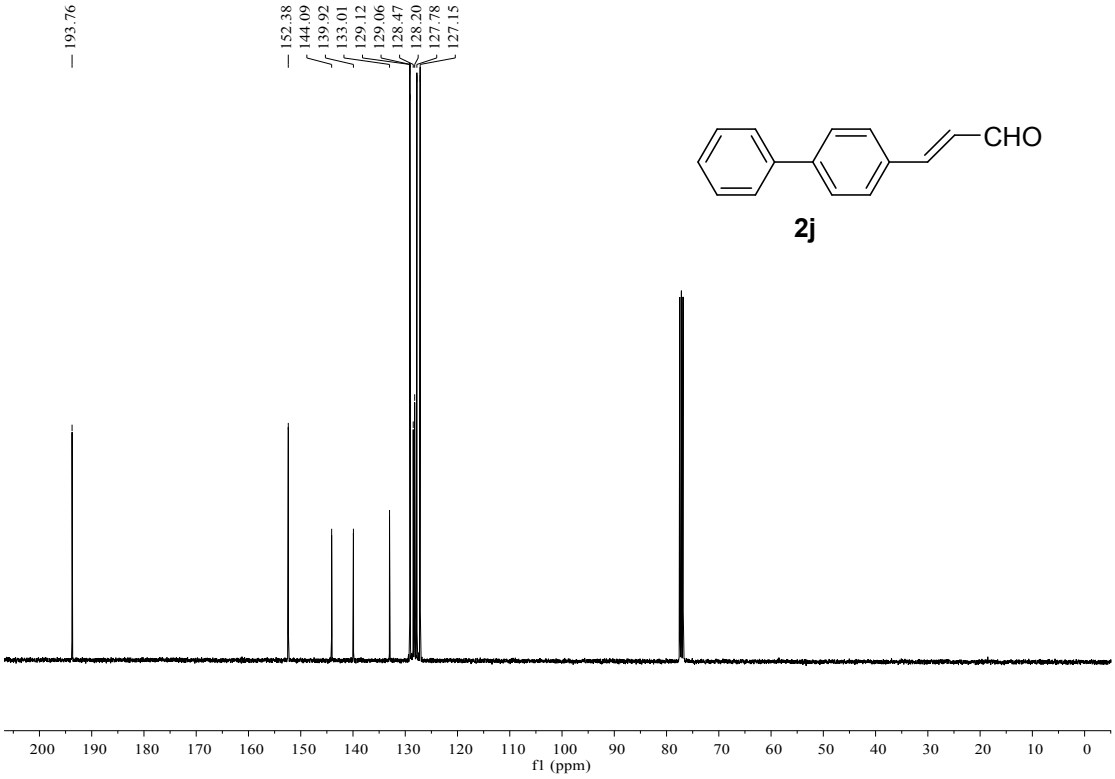


**2i: (E)-3-(naphthalen-1-yl)acrylaldehyde.**

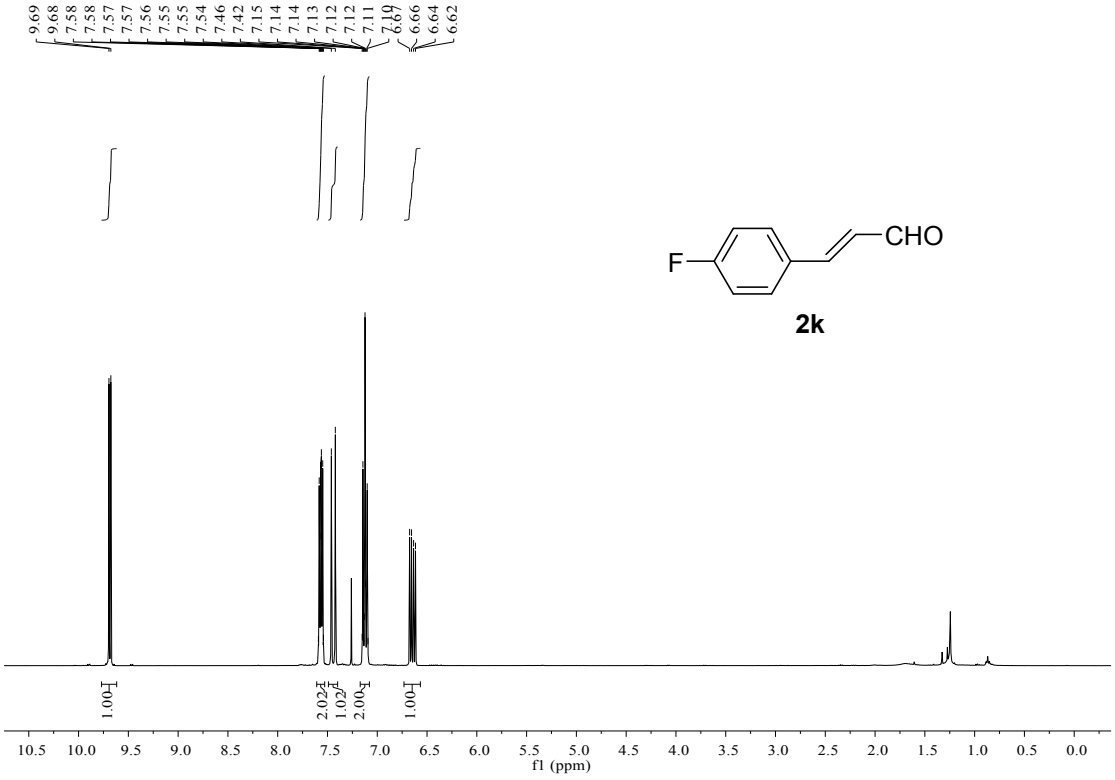


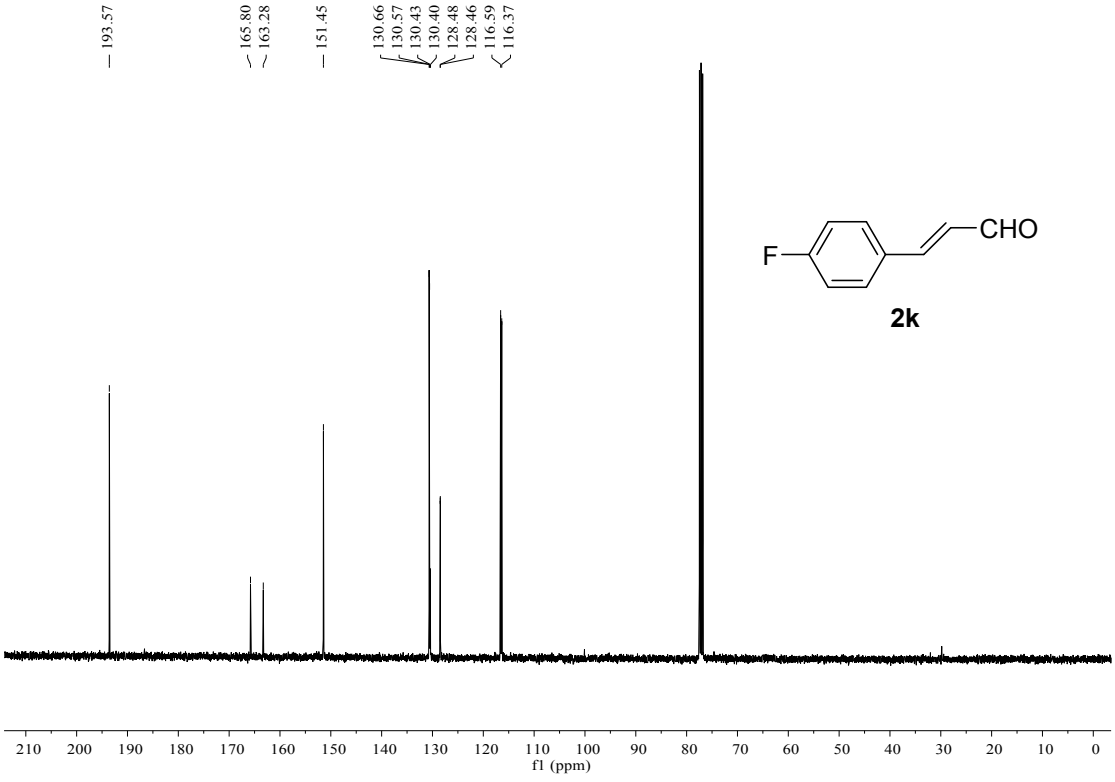
**2j: (E)-3-([1,1'-biphenyl]-4-yl)acrylaldehyde.**



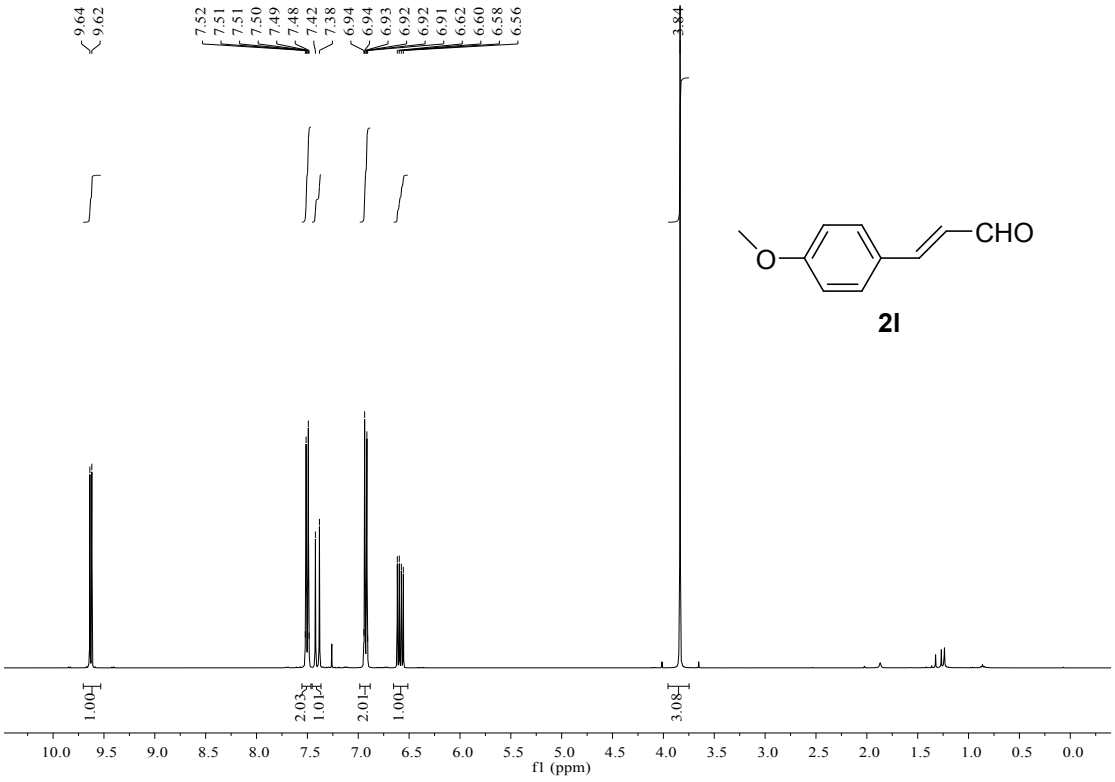



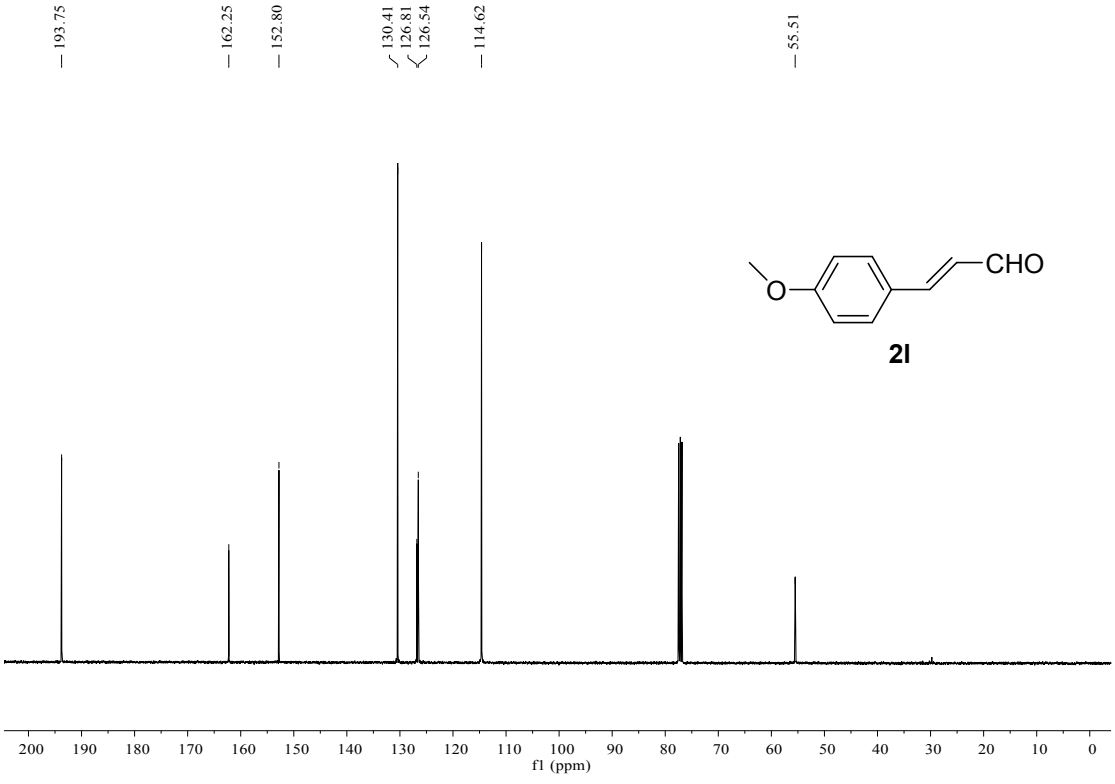
**2k: (E)-3-(4-fluorophenyl)acrylaldehyde.**



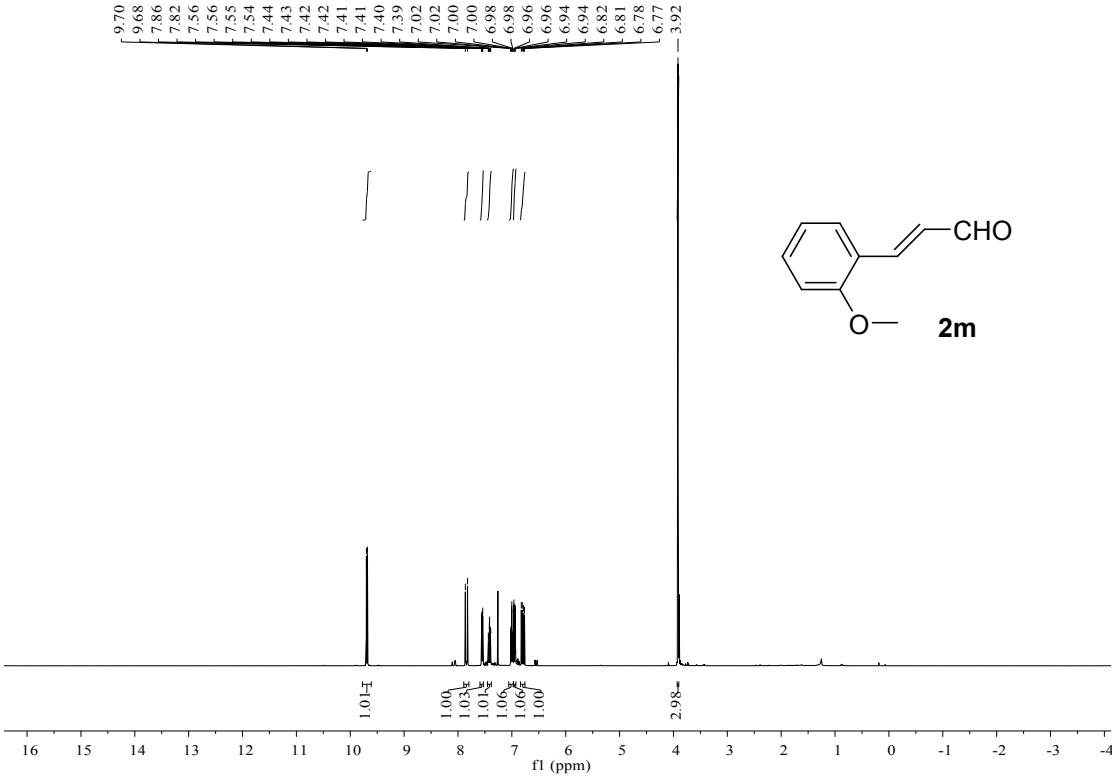



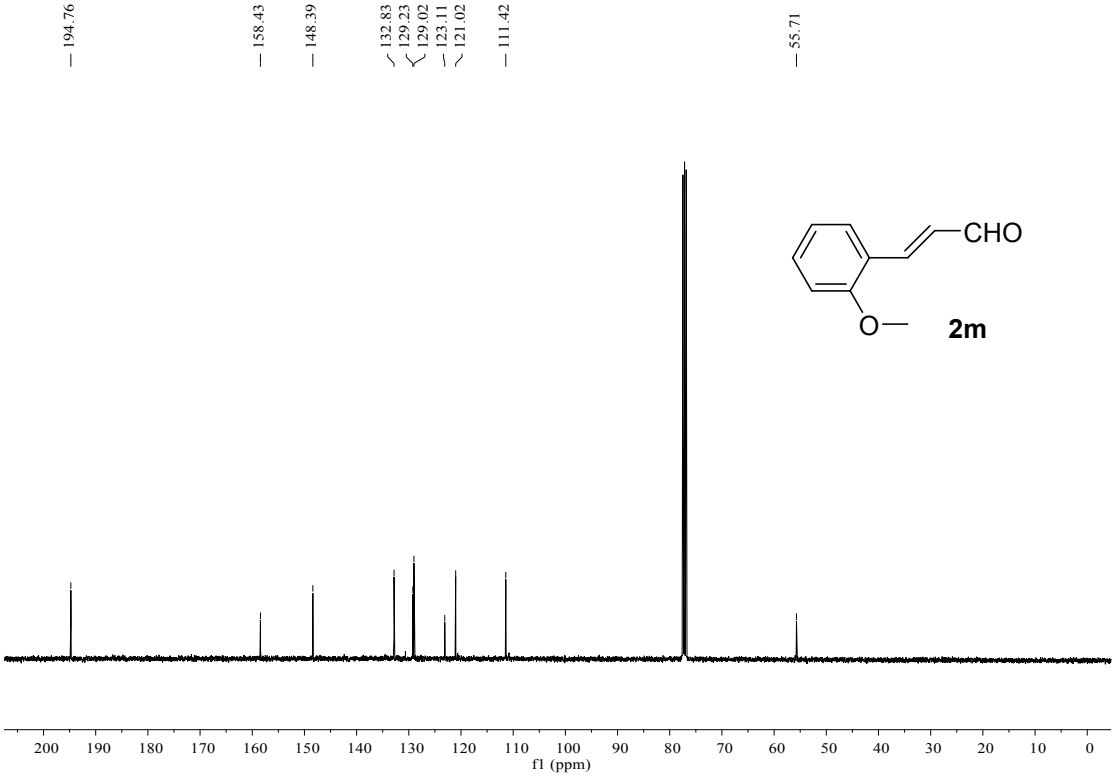
**2l: (E)-3-(4-methoxyphenyl)acrylaldehyde.**



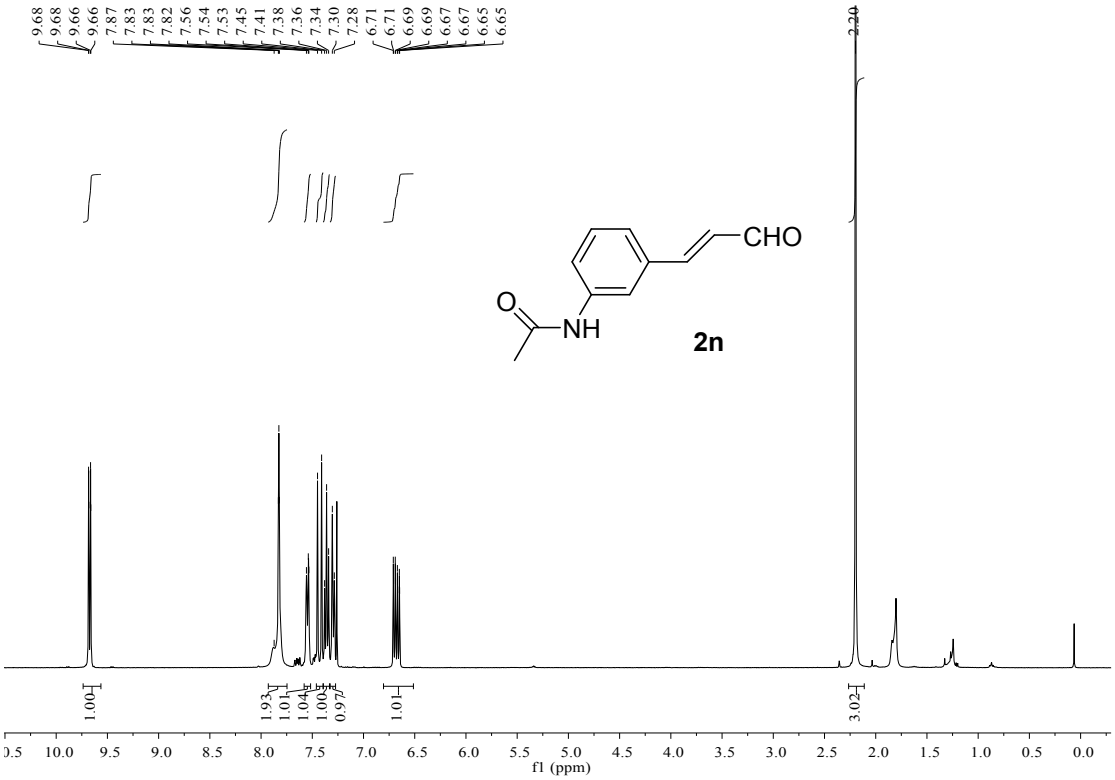



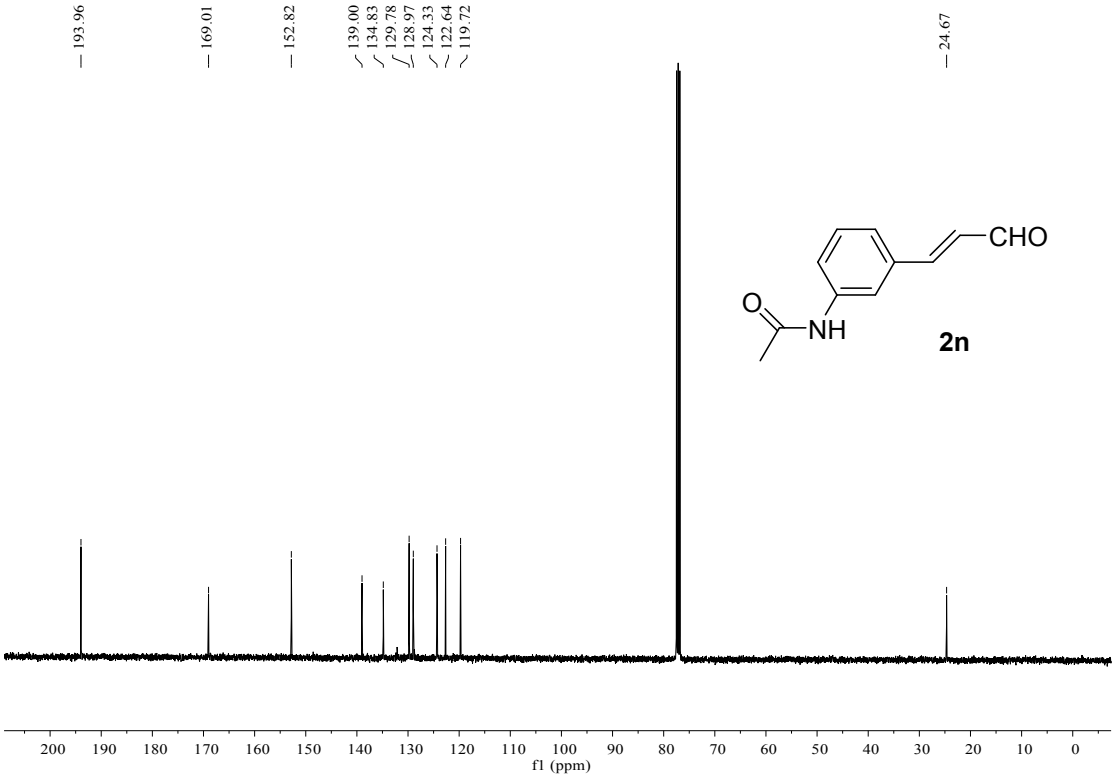
**2m: (E)-3-(2-methoxyphenyl)acrylaldehyde.**



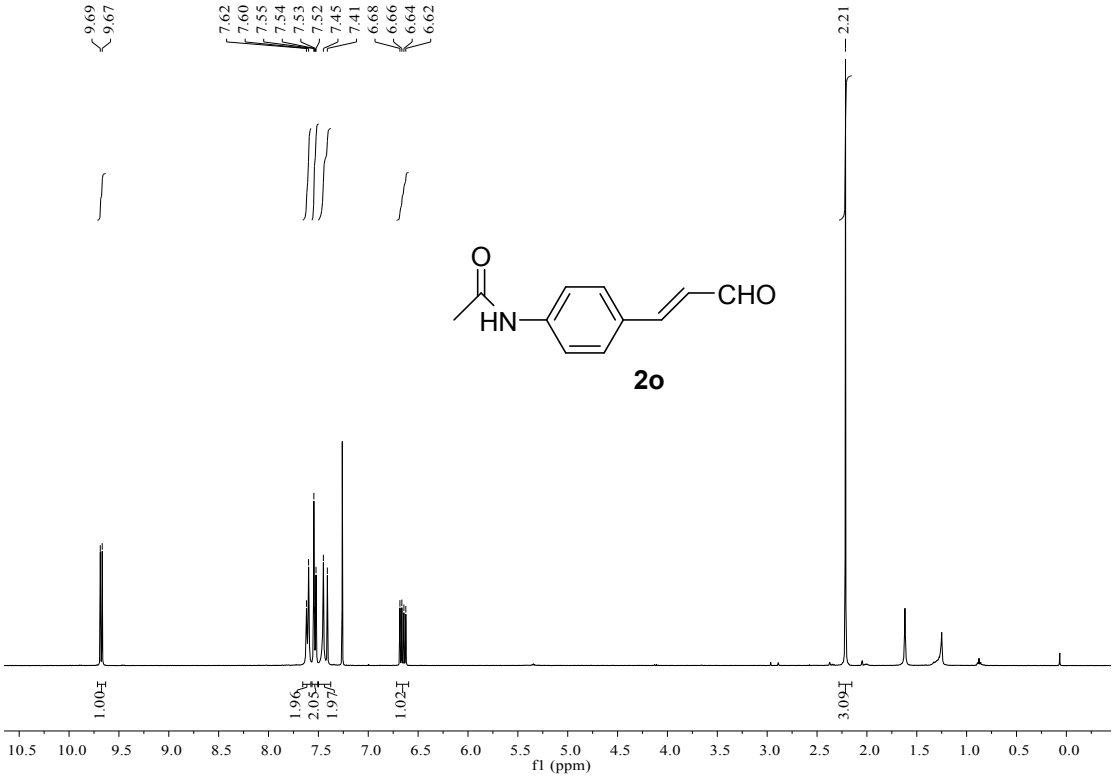



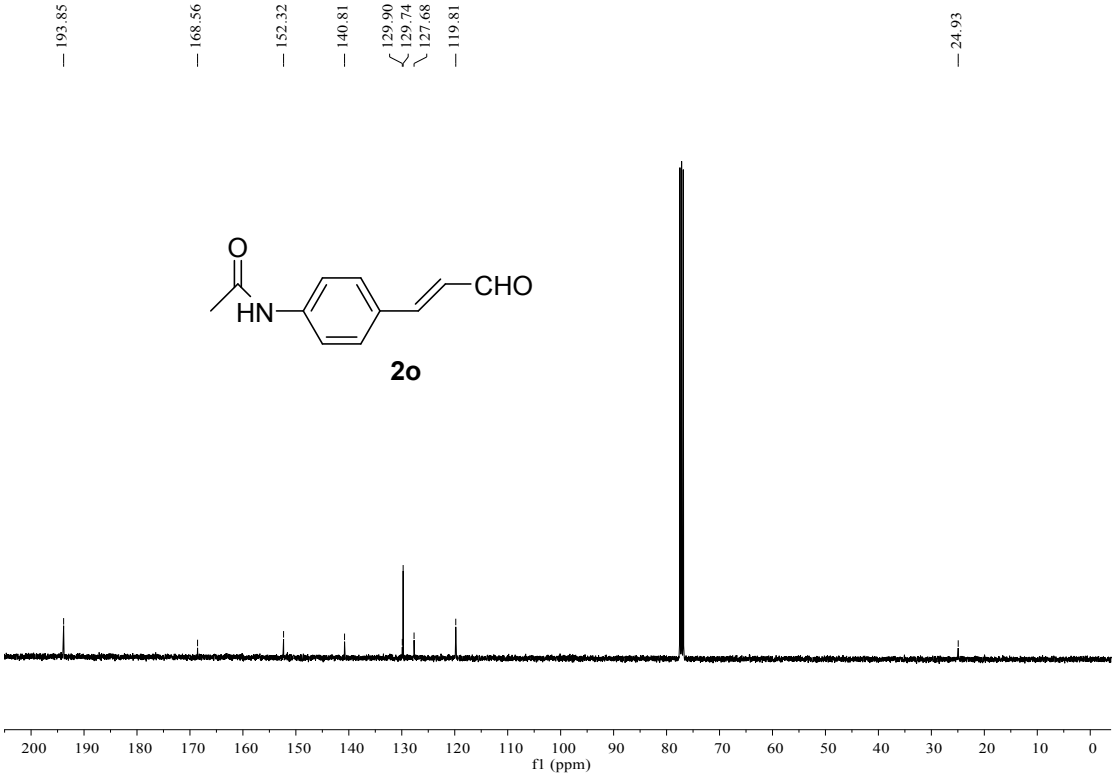
**2n: (E)-N-(3-(3-oxoprop-1-en-1-yl)phenyl)acetamide.**



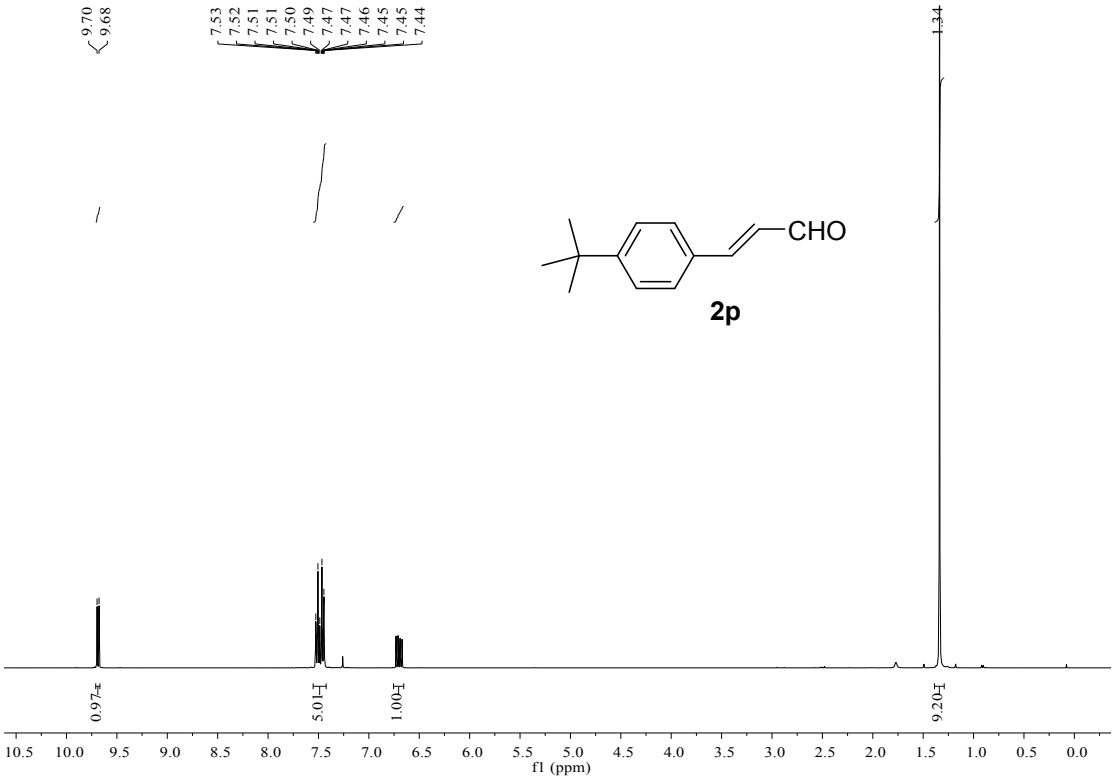



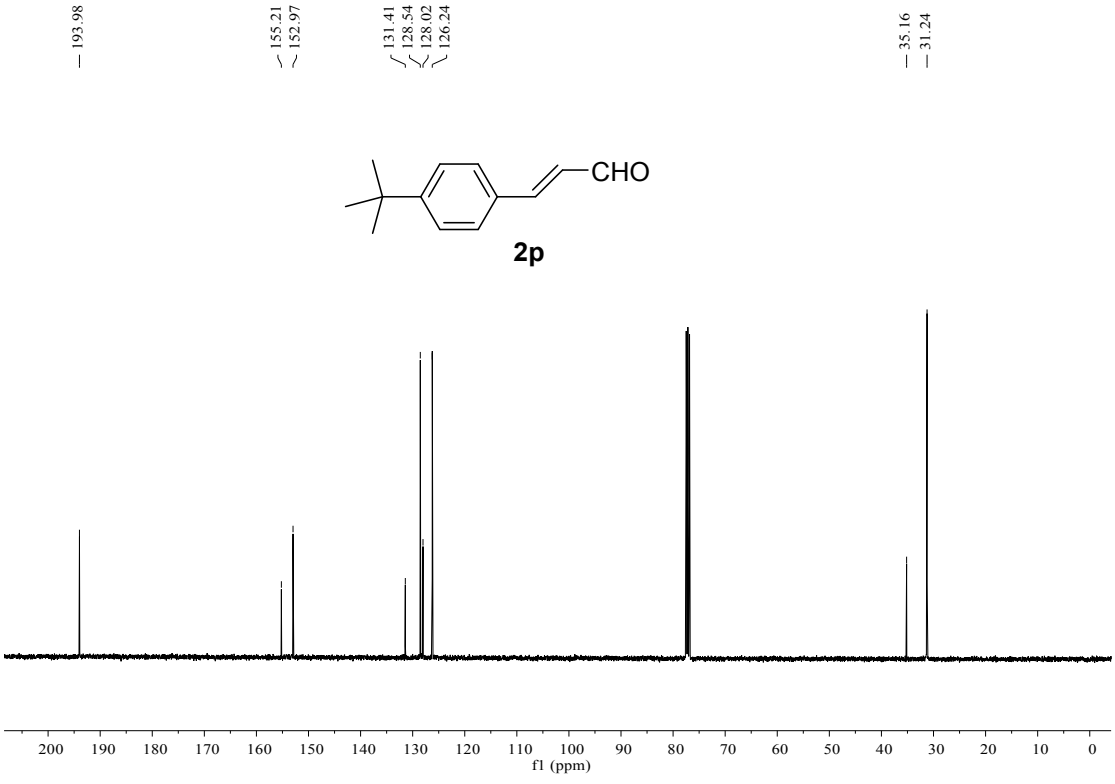
**2o: (E)-N-(4-(3-oxoprop-1-en-1-yl)phenyl)acetamide.**



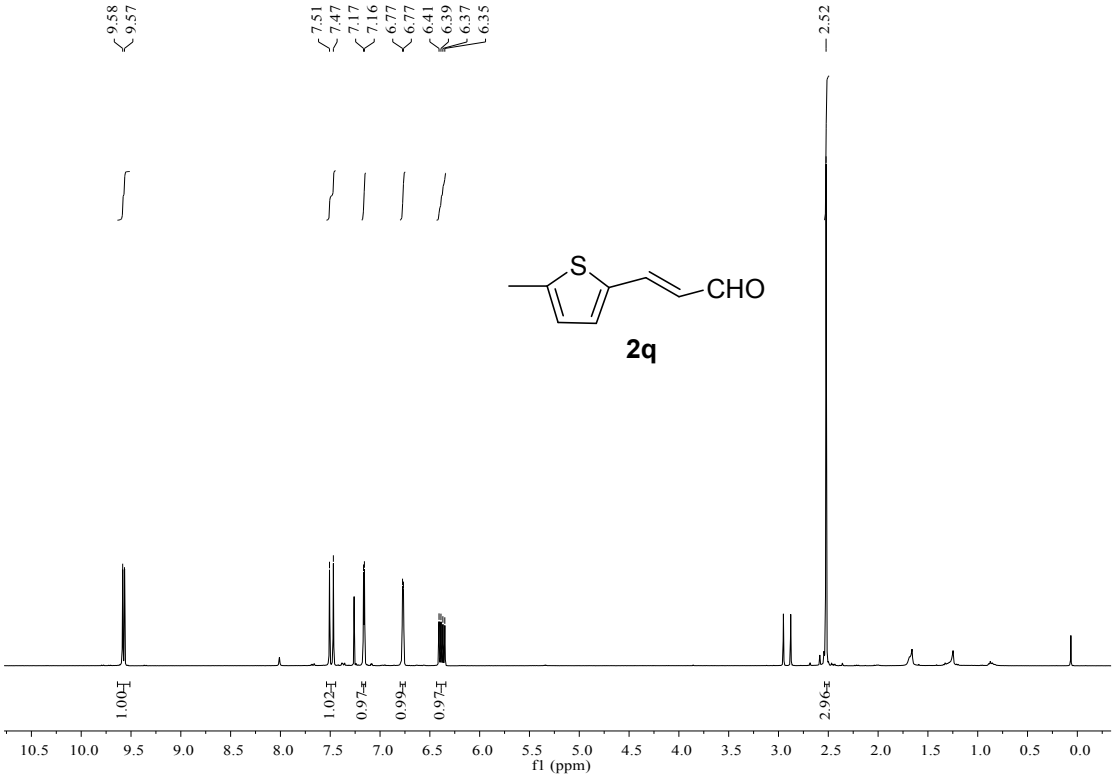



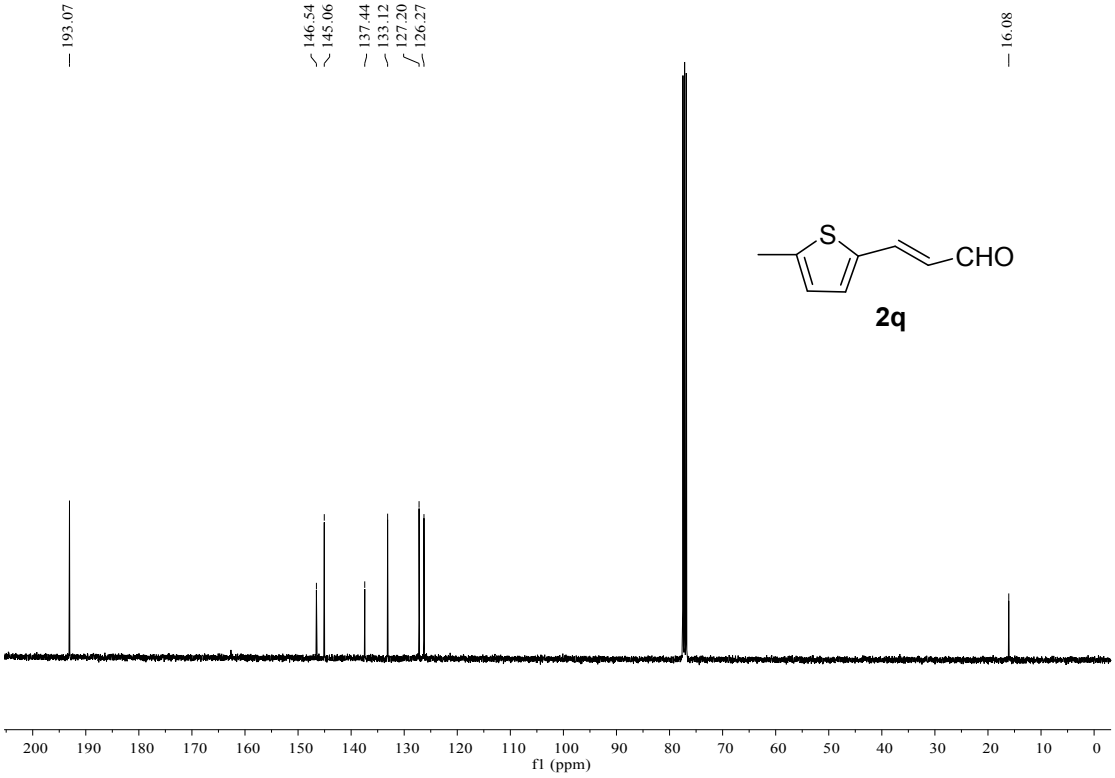
**2p: (E)-3-(4-(tert-butyl)phenyl)acrylaldehyde.**



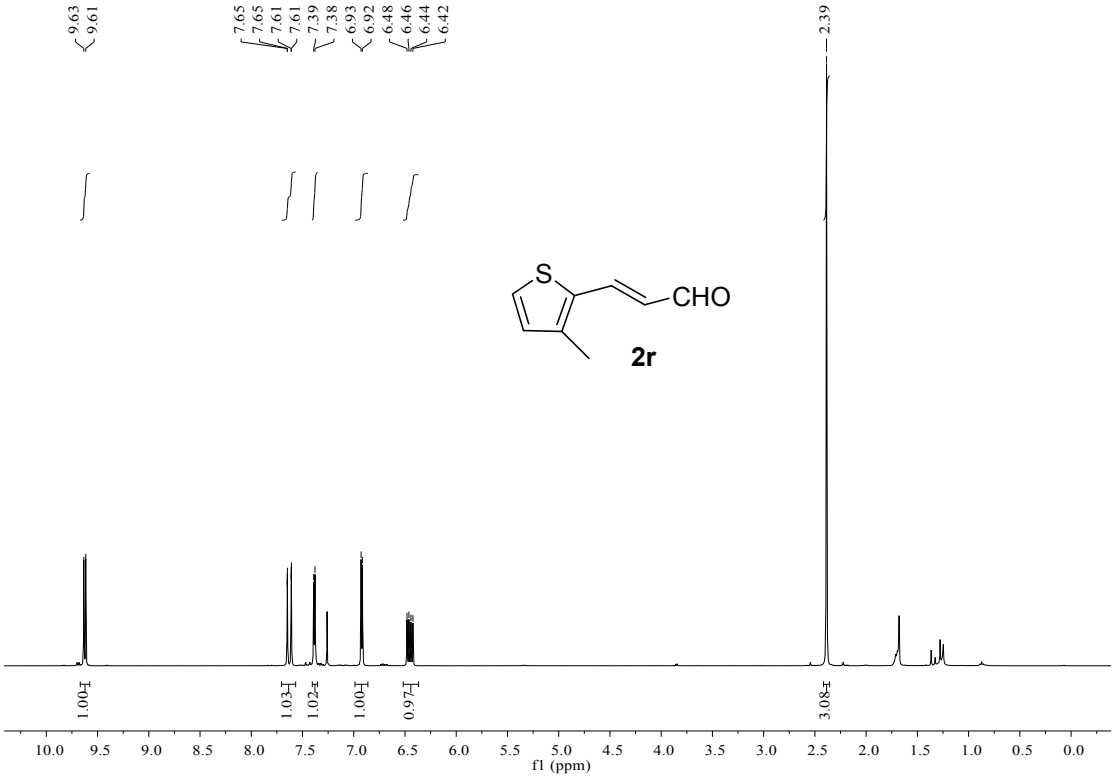



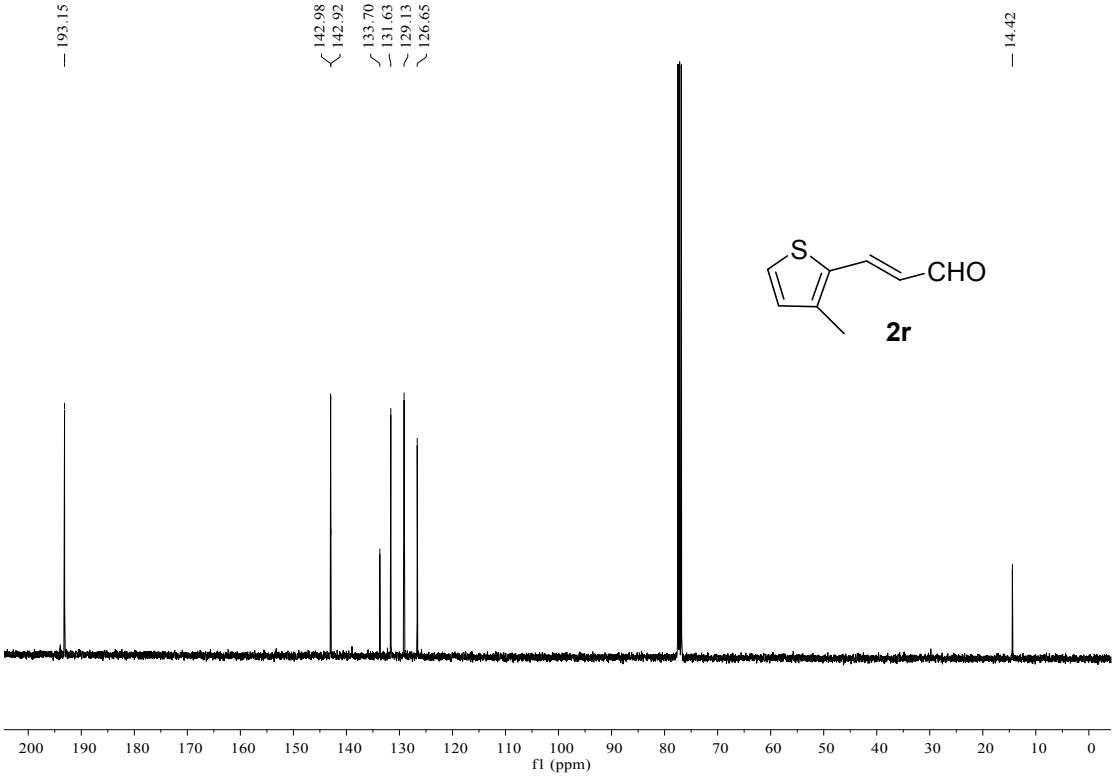
**2q: (E)-3-(5-methylthiophen-2-yl)acrylaldehyde.**



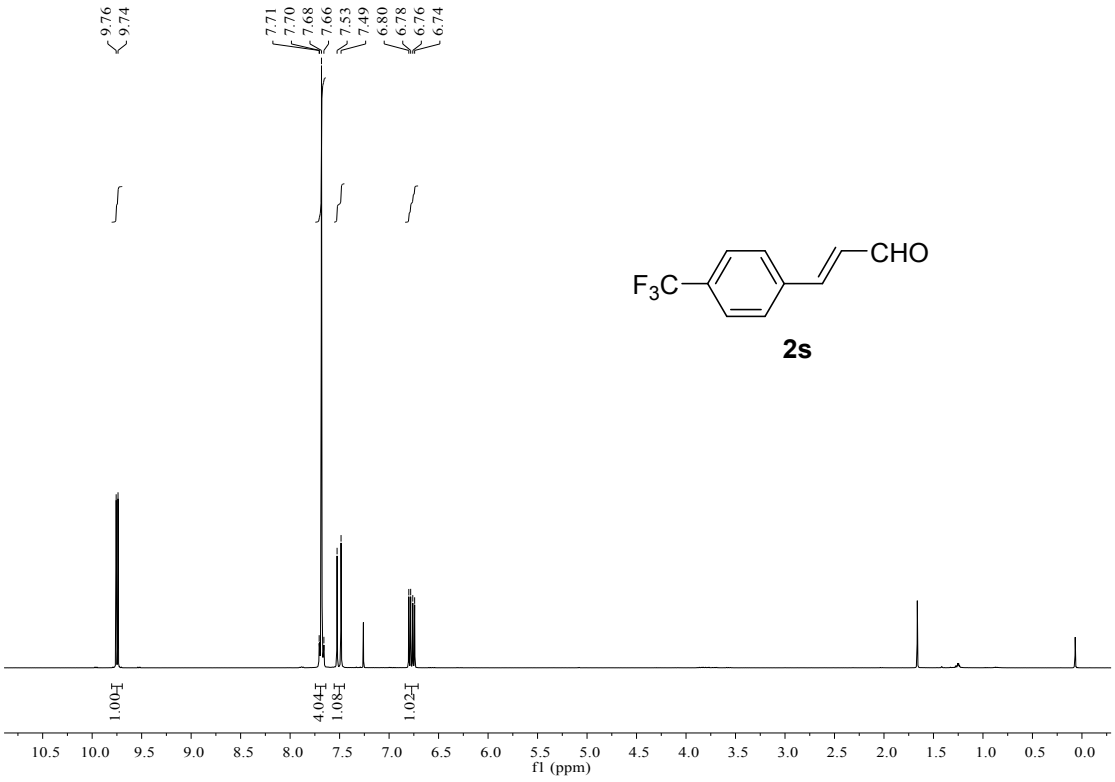



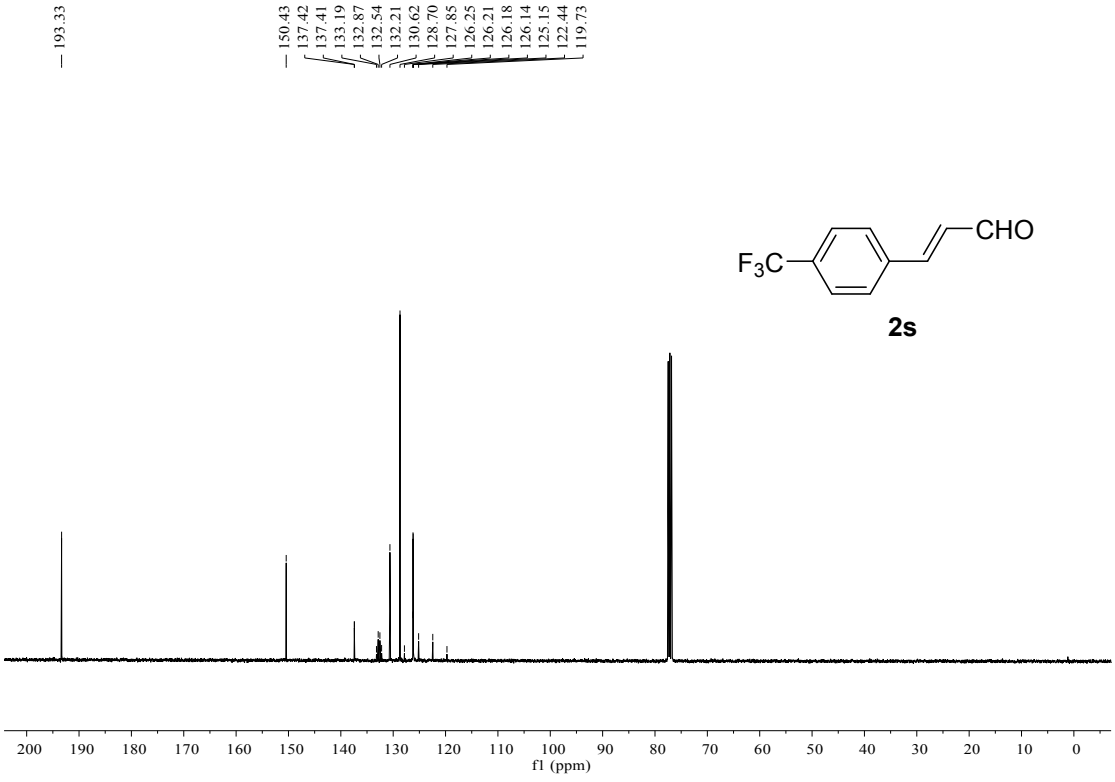
**2r: (E)-3-(3-methylthiophen-2-yl)acrylaldehyde.**



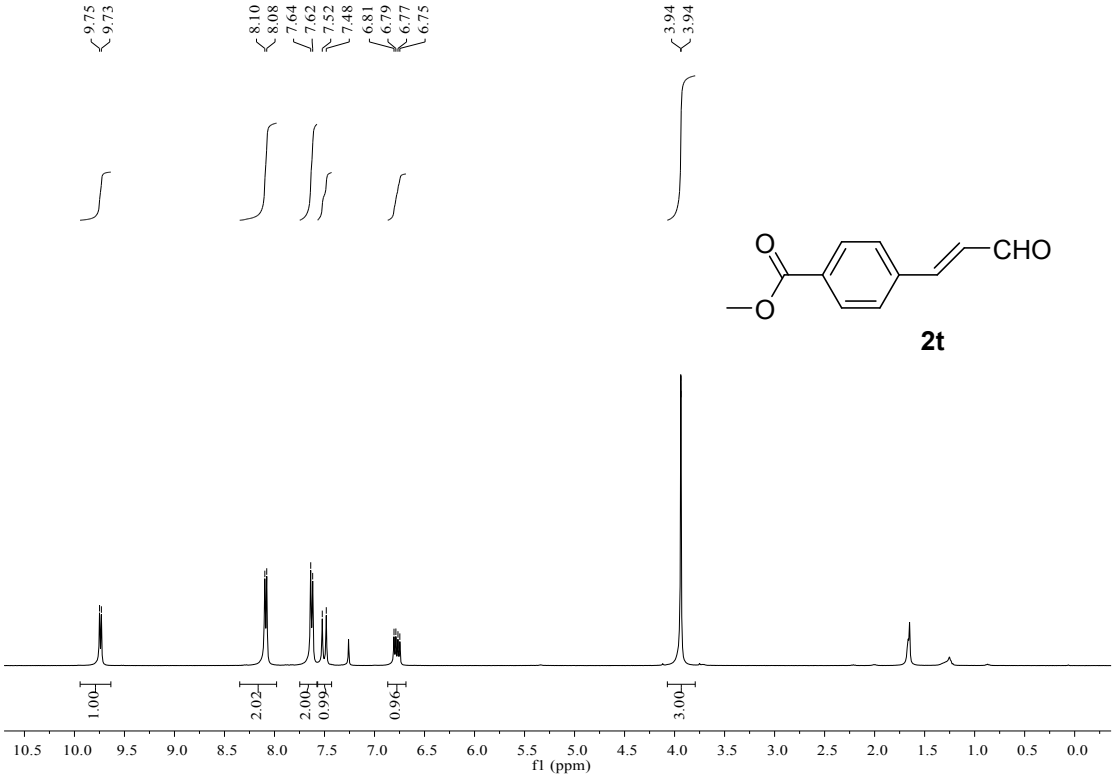



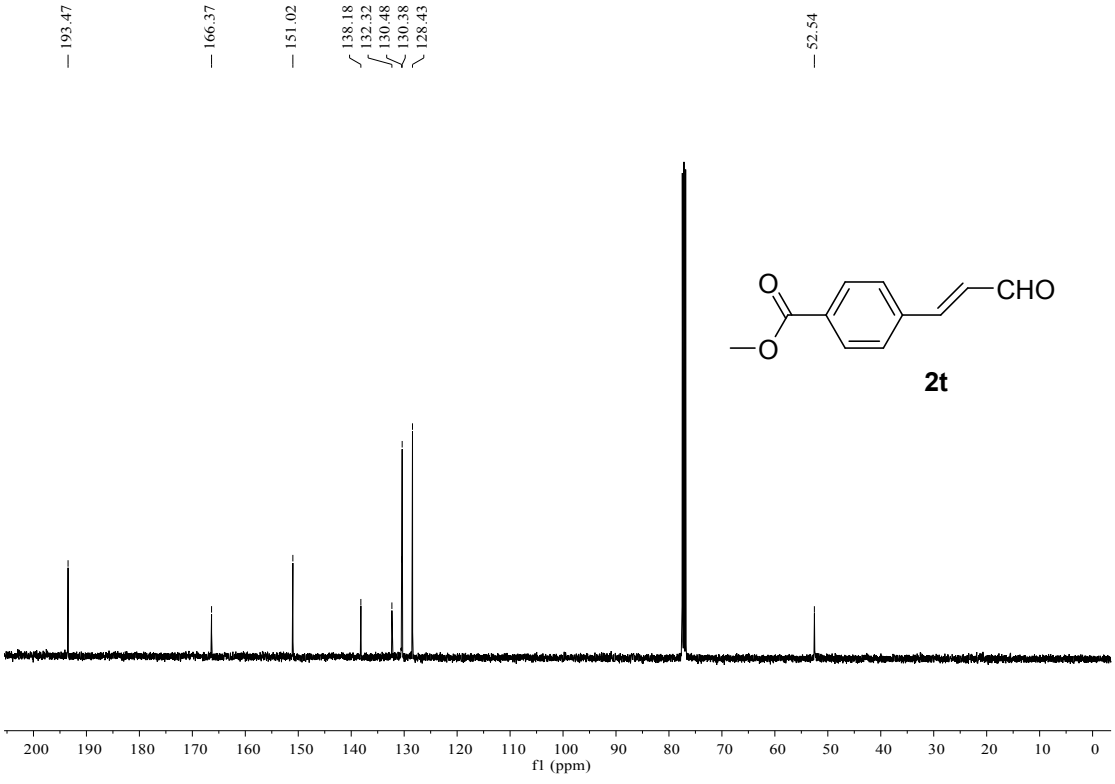
**2s: (E)-3-(4-(trifluoromethyl)phenyl)acrylaldehyde.**



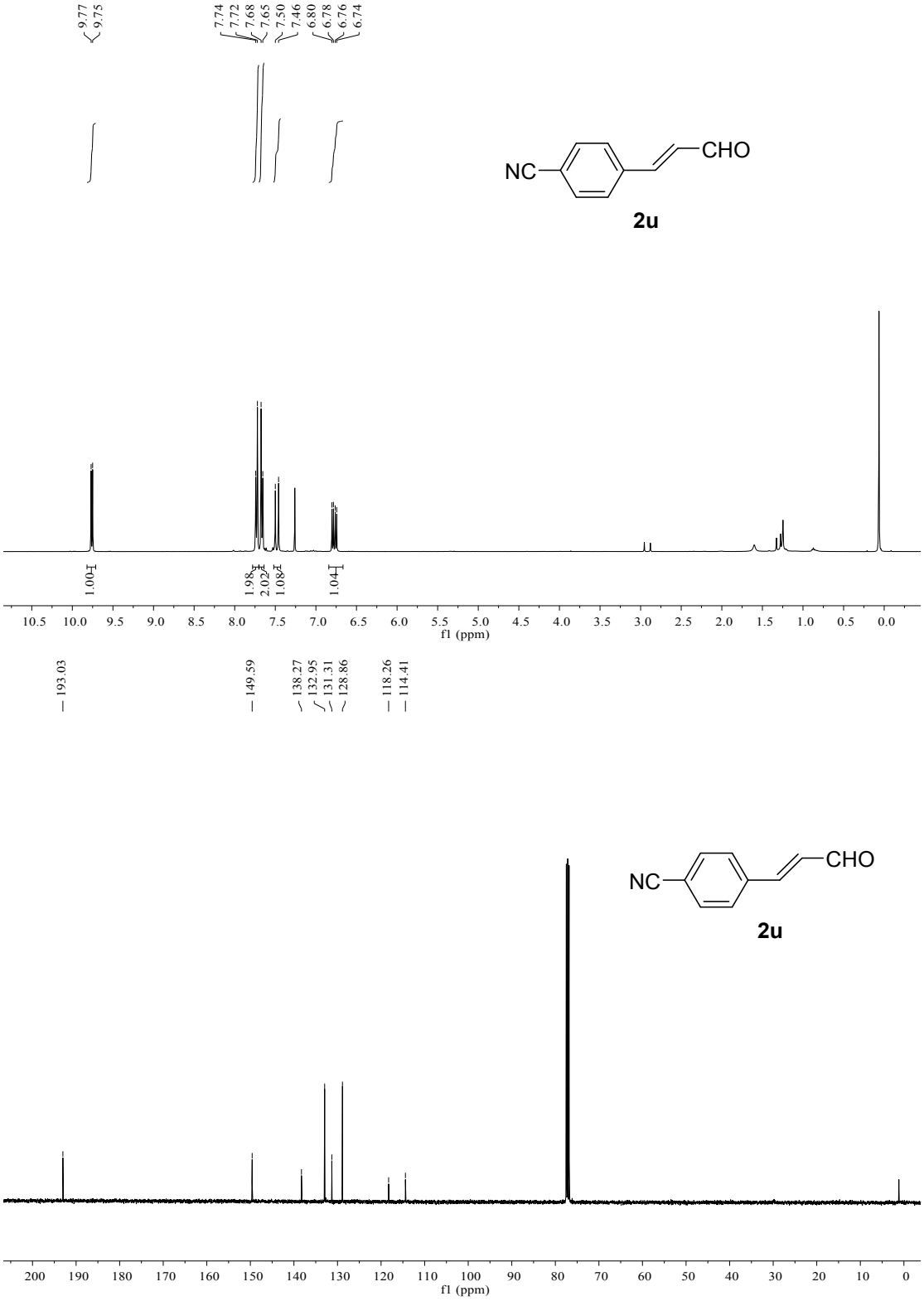



**2t: methyl (E)-4-(3-oxoprop-1-en-1-yl)benzoate.**



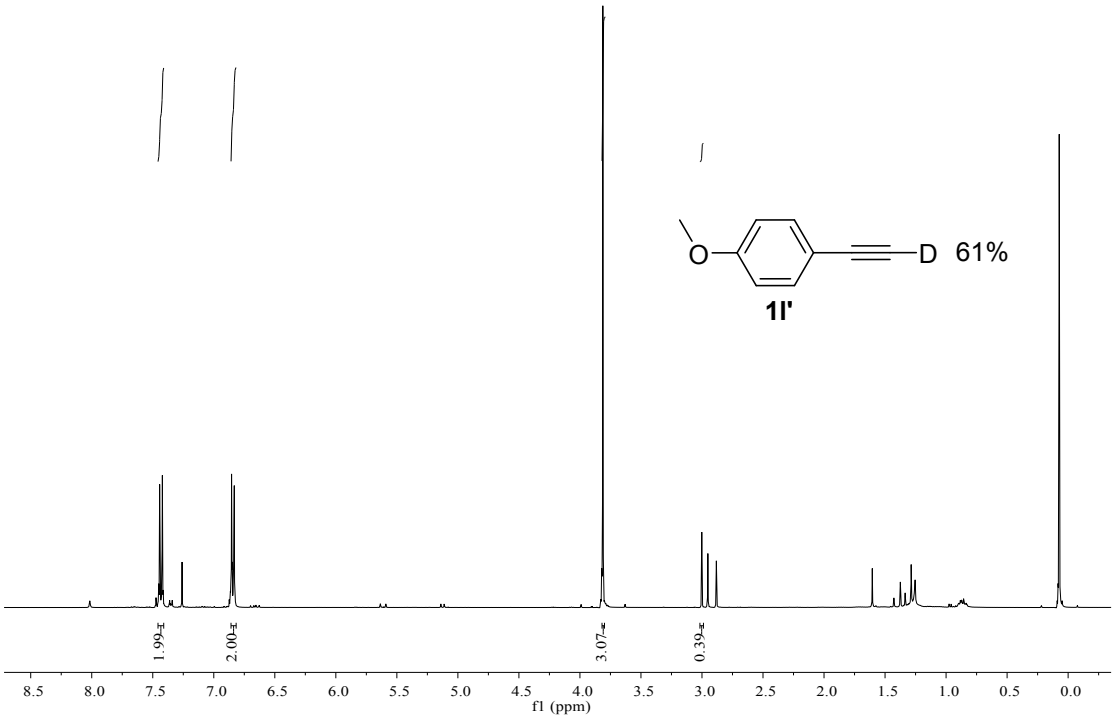



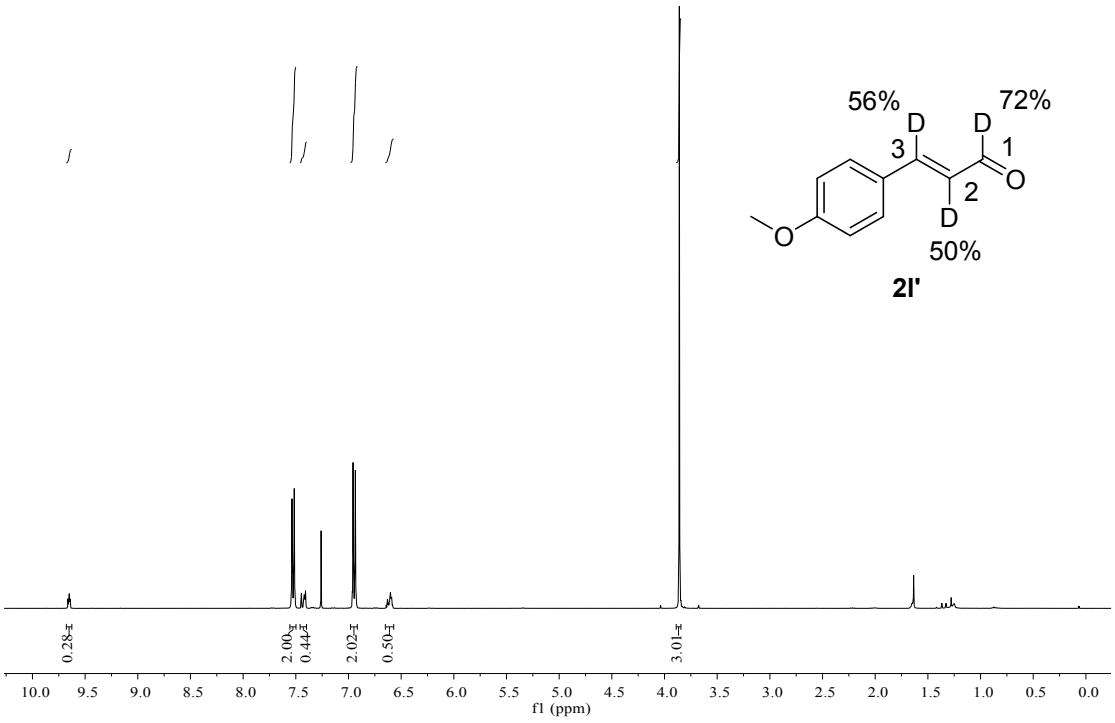
**2u: (E)-4-(3-oxoprop-1-en-1-yl)benzonitrile.**



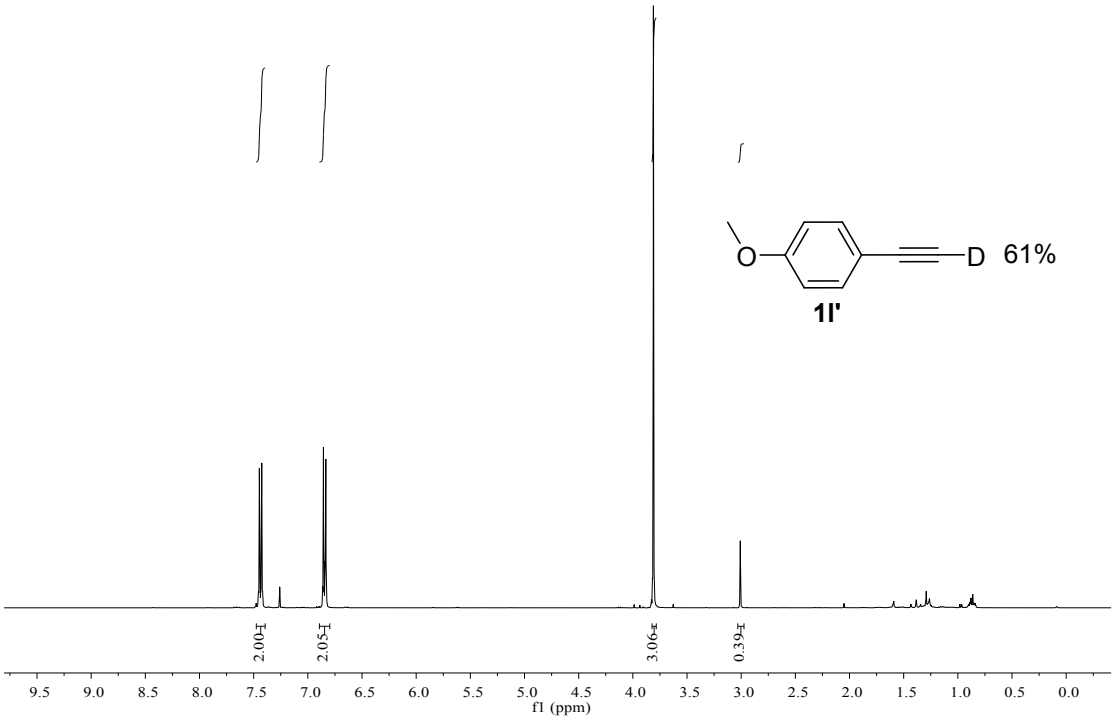
## 4. $^{1}$H NMR of Deuterium-Labeling experiments

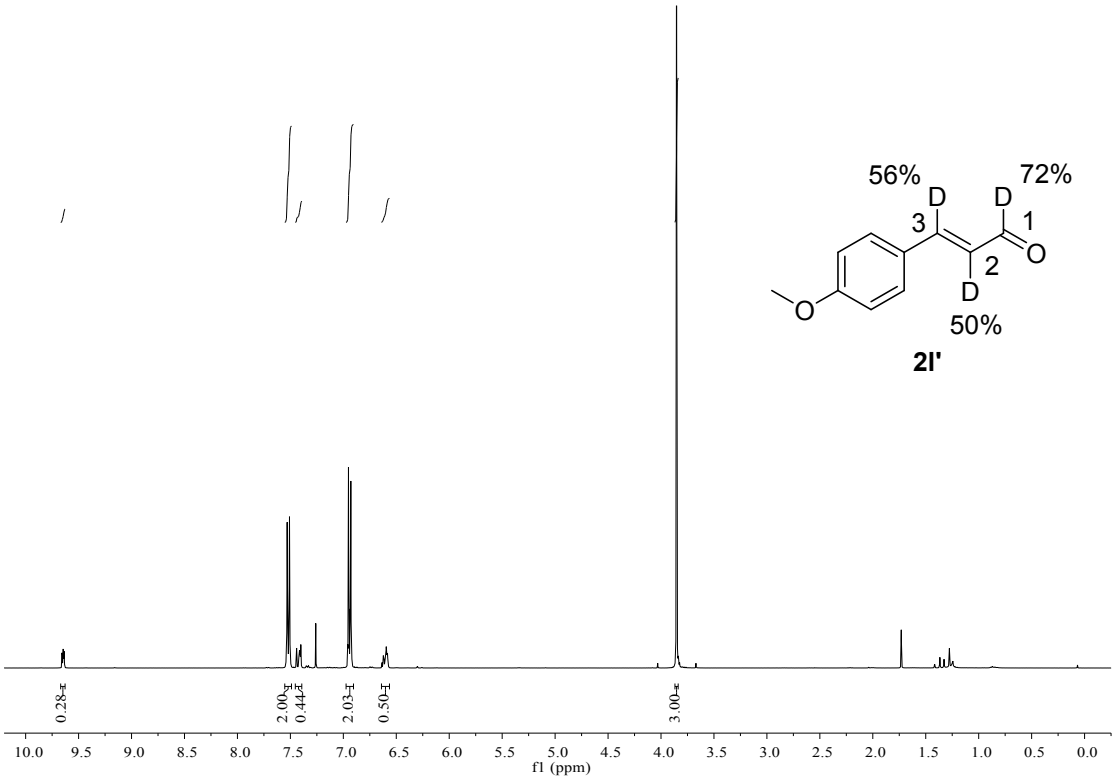
### Reaction A:



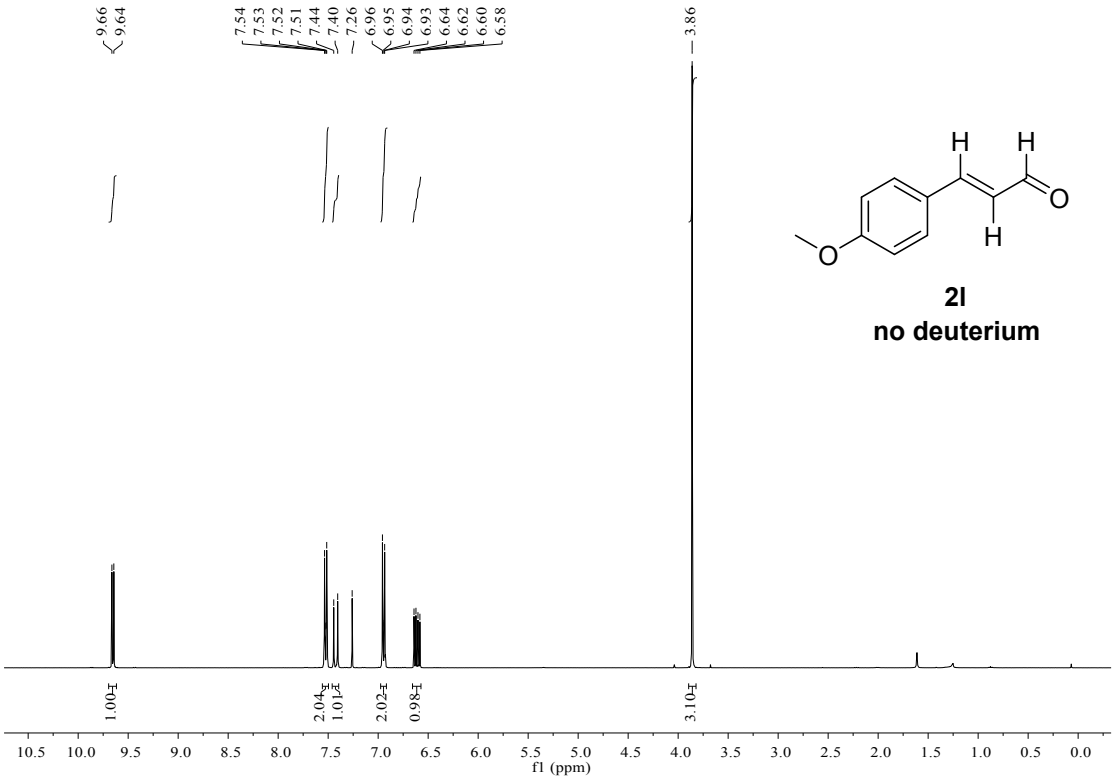



**Reaction B:**


O
D 61%
1l'
2.00
2.05
3.06
0.39
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)


56%
D
3
D
72%
1
O
2
D
50%
O
2l'
0.28
2.00
0.44
2.03
0.50
3.00
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)

**Reaction C:**


9.66
9.64
7.54
7.53
7.52
7.51
7.44
7.40
7.26
6.96
6.95
6.94
6.93
6.64
6.62
6.60
6.58
3.86
H
H
O
H
O
2l
no deuterium
1.00
2.04
1.01
2.02
0.98
3.10
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)