Synthesis of *α*-Allenic Aldehydes/Ketones from Homopropargylic Alcohols by a Visible-Light Irradiation System

Dong-Fang Jiang,*[a,b]† Xing-Xing Zeng,[a]† Si-Miaomiao Wen[b] and Ming-Hua Hu*[a]

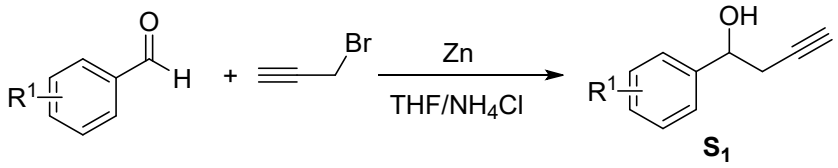
Supporting Information

1 General remark

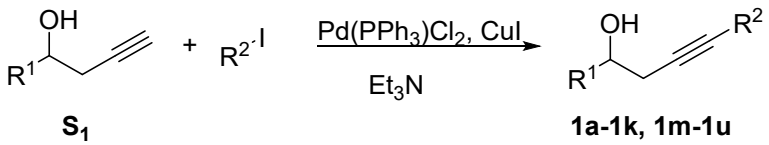
^{1}H NMR and ^{13}C NMR spectra were recorded on 400MHz and 100MHz in $CDCl_3$ (BRUKER 400M or JNM-ECS 400M). All chemical shifts were given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. Unless otherwise noted, commercially available reagents and solvents were used without further purification.

2 Experimental Section

2.1 General procedure for the synthesis of homopropargylic alcohols[1-2]:



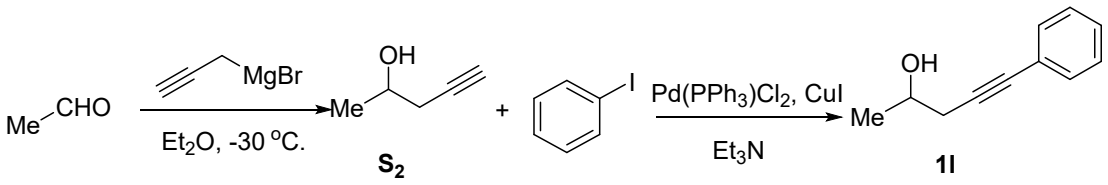
Aldehyde (5 mmol, 1.0 equiv) was dissolved in anhydrous THF. A sample was taken out for analysis and propargyl bromide (2.0 equiv) was added. Another sample was taken out for analysis and saturated aqueous NH_4Cl was added. Portions of activated zinc dust (2.0 equiv) were added slowly on at 0°C and the resulting suspension was stirred overnight at this temperature. The THF layer was separated from the aqueous layer, which was extracted with diethyl ether for 3 times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was directly used in the next step without further purification; the residue was purified by column chromatography (silica gel, appropriate mixture of *n*-hexane/ethyl acetate) to obtain **S1** in 90% yield.



To a dried schlenk flask was added $Pd(PPh_3)_2Cl_2$ (0.5 mmol), CuI (0.5 mmol), iodoarene (5.5 mmol), **S1** (5.0 mmol) and freshly distilled Et_3N under argon. The resulting mixture was stirred for 16 h at rt in 50 mL of EtOAc were added and the mixture filtered. After removal of solvent using

rotary evaporator, the crude compound was purified by SiO_2 chromatography to give **1a-1k, 1m-1u**.

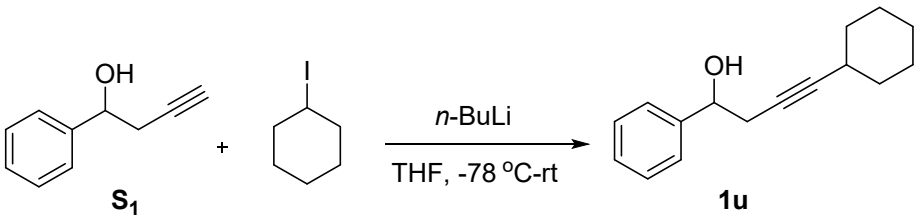
2.2 1l was prepared in the method[3]



Under an argon atmosphere, magnesium turnings (0.67 g, 27.5 mmol) and mercury chloride (0.34 g, 1.3 mmol) were mixed in dry diethyl ether (40 mL) in a 250 mL round-bottom flask. To the solution, propargyl bromide (2.0 mL, 25 mmol) was then added dropwise at 60 °C over about 1 h. The reaction was kept at the same temperature until the yellow solution turned cloudy. This solution was cooled to -30 °C and a solution of acetaldehyde (6 mmol) in Et_2O (12 ml) was added dropwise. After addition the reaction was moved to room temperature for further 30 min then quenched with sat. NH_4Cl (aq). The aqueous layer was extracted with ether and the extracts were combined with the above organic layer. The combined solution was dried over Na_2SO_4. After evaporation of the solvent the residue was purified by column chromatography (silica gel, appropriate mixture of *n*-hexane/ethyl acetate) to afford $\mathbf{S_2}$.

To a dried schlenk flask was added $\mathbf{S_2}$ (10.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.2 mmol), CuI (0.4 mmol), iodoarene (11.0 mmol) and freshly distilled Et_3N (50 ml) under argon. The resulting mixture was stirred for 16 h at rt The reaction mixture was quenched with sat. NH_4Cl (aq) and 50 mL of ethyl acetate were added and the mixture filtered. After removal of solvent using rotary evaporator, the crude compound was purified by column chromatography on silica gel to give **1l**.

2.3 1u was prepared in the method[4]

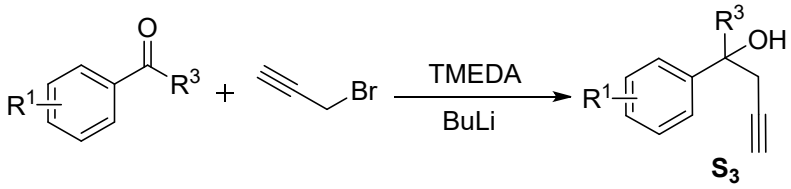


n-BuLi (2.5 M in hexanes, 6 mL, 15 mmol) was slowly added to a stirred solution of the

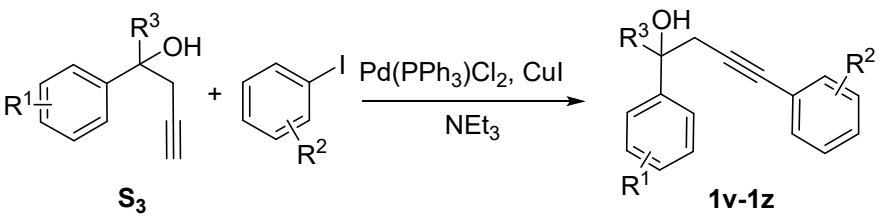
propargyl alcohol (876 mg, 6 mmol) prepared in dry THF (20 mL) at -78 °C under Ar. After being stirred at -78 °C for 1 h, the reaction mixture was treated with iodocyclohexane (3.6 mL, 18 mmol) and then allowed to warm to rt overnight. The reaction mixture was then cooled to -78 °C again, quenched with sat NH_4Cl (aq) (10 mL) and extracted with Et_2O (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give **1u** as yellow oil.

2.4 1v-1z were prepared in the method[5]

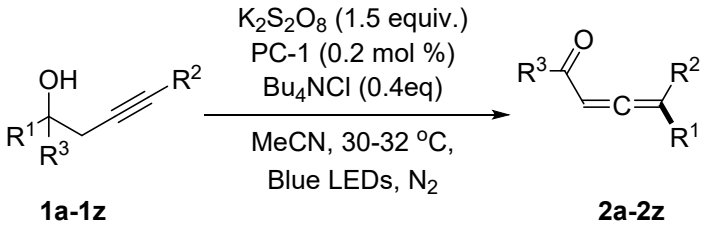
A solution of dry diethyl ether (12.4 mL), dry hexane(7.0 mL) and *n*-BuLi (5.4 mL, 16.4 mmol) was cooled to −78°C and TMEDA added (0.62 mL, 4.1 mmol), followed by dropwise addition of propargyl bromide (0.78 mL, 8.2 mmol) (CAUTION: highly toxic) and the resulting mixture stirred for 20 minutes at this temperature. After this time a white precipitate formed. A solution of ketone (3.90 mmol) in diethyl ether (5 mL) was added dropwise over 5 min and the reaction mixture were allowed to warm to room temperature over 2 h. The resulting suspension was extracted with ether and the organic extracts dried (Na_2SO_4). After evaporation of solvent in vacuo, the residue was purified by column chromatography (silica gel) using ether:hexanes mixtures to afford the **S_3**.



To a dried schlenk flask was added $Pd(PPh_3)_2Cl_2$ (0.06 mmol), CuI (0.06 mmol), iodoarene (3.3 mmol), **S_3** (3.0 mmol) and freshly distilled Et_3N under argon. The resulting mixture was stirred for 16 h at 50 °C. 50 mL of EtOAc were added and the mixture filtered. After removal of solvent using rotary evaporator, the crude compound was purified by SiO_2 chromatography to give **1v-1z.**

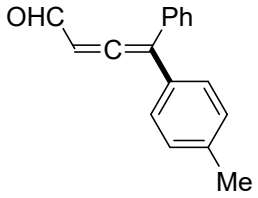


3 General procedure for synthesis of *α*-Allenic Aldehydes/Ketones from Homopropargylic Alcohols



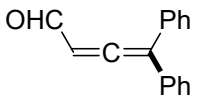
In a sealed tube, $K_2S_2O_8$ (121.5 mg, 0.45 mmol), PC-1 (2 mg, 0.2 mol%) and Bu_4NCl (33.4 mg, 0.12 mmol) were successively added to a solution of **1** (0.3 mmol) in MeCN (3.0 mL). The reactor was flushed with argon. The reaction mixture was stirring at blue LEDs for 12 hour and then the reaction mixture was cooled to room temperature. The solvent was evaporated in vacuo and the crude product was purified by column chromatography, eluting with petroleum ether/EtOAc (10:1) to afford the desired *α*-allenic aldehydes/ketones **2**.

4 The data of products



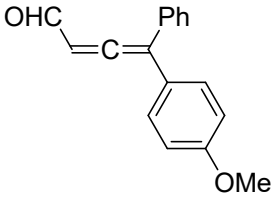
4-Phenyl-4-(*p*-tolyl)buta-2,3-dienal (2a)

Yellow oil (61.3 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.69-9.67 (d, J = 8.0 Hz, 1 H), 7.39-7.35 (m, 5 H), 7.24-7.20 (m, 4 H), 6.33-6.31 (d, J = 8.0 Hz, 1 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 220.9, 191.2, 138.8, 133.5, 130.3, 129.5, 128.8, 128.7, 128.6, 128.6, 115.4, 100.8, 21.2; HRMS calcd for $C_{17}H_{15}O$ $[M+H]^+$ 235.1118; found: 235.1115.



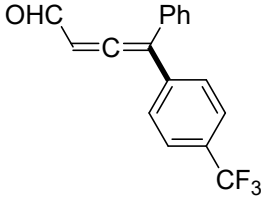
4,4-Diphenylbuta-2,3-dienal (2b)

Yellow oil (54.1 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.71-9.69 (d, J =8.0 Hz, 1 H), 7.43-7.35 (m, 10 H), 6.35-6.33 (d, J =8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 220.8, 191.1, 133.4, 130.1, 128.8, 128.7, 115.6, 100.9; HRMS calcd for $C_{16}H_{13}O$ $[M+H]^+$ 221.0961; found: 221.0956.



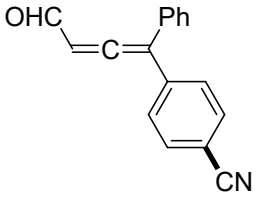
4-(4-Methoxyphenyl)-4-phenylbuta-2,3-dienal (2c)

Yellow solid (48.8 mg, 65% yield). melting point: 89-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.69-9.67 (d, J = 8.0 Hz, 1 H), 7.40-7.36 (m, 5 H), 7.29-7.25 (m, 2 H), 6.94-6.92 (m, 2 H), 6.32-6.31 (d, J = 4.0 Hz, 1 H), 3.84 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 221.0, 191.2, 160.0, 133.7, 130.0, 129.8, 128.7, 125.3, 115.2, 114.4, 114.3, 100.7, 55.4; HRMS calcd for $C_{17}H_{15}O_2$ $[M+H]^+$ 251.1067; found: 251.1066.



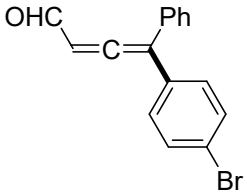
4-Phenyl-4-(4-(trifluoromethyl)phenyl)buta-2,3-dienal (2d)

Yellow oil (51.8 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.72-9.71 (d, J = 6.8 Hz, 1 H), 7.67-7.65 (d, J = 8.4 Hz, 2 H), 7.50-7.48 (d, J = 8.0 Hz, 2 H), 7.44-7.40 (m, 3 H), 7.35-7.33 (m, 2 H), 6.39-6.38 (d, J = 6.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 220.6, 190.5, 137.4, 132.7, 129.1, 129.0, 128.6, 125.8, 125.8, 122.5, 114.7, 101.1; HRMS calcd for $C_{17}H_{12}F_3O$ $[M+H]^+$ 289.0835; found: 289.0832.



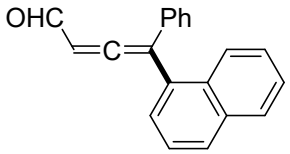
4-(4-Oxo-1-phenylbuta-1,2-dien-1-yl)benzonitrile (2e)

Yellow oil (61.7 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.72-9.71 (d, J = 6.4 Hz, 1 H), 7.71-7.69 (d, J = 8.0 Hz, 2 H), 7.49-7.47 (d, J = 8.0 Hz, 2 H), 7.45-7.43 (m, 3 H), 7.34-7.32 (m, 2 H), 6.41-6.39 (d, J = 6.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 220.5, 190.2, 138.5, 132.6, 132.2, 129.2, 129.1, 128.6, 118.4, 114.6, 112.3, 101.2; HRMS calcd for $C_{17}H_{12}NO$ $[M+H]^+$ 246.0914; found: 246.0913.



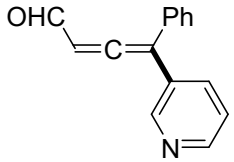
4-(4-Bromophenyl)-4-phenylbuta-2,3-dienal (2f)

Yellow oil (81.4 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.70-9.68 (d, J = 6.8 Hz, 1 H), 7.54-7.52 (m, 2 H), 7.42-7.39 (m, 3 H), 7.35-7.32 (m, 2 H), 7.24-7.20 (m, 2 H), 6.34-6.32 (d, J = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 220.4, 190.7, 132.9, 132.4, 132.0, 130.2, 129.0, 128.9, 128.6, 122.9, 114.8, 101.0; HRMS calcd for $C_{16}H_{12}BrO$ $[M+H]^+$ 299.0066; found: 299.0066.



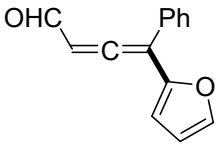
4-(Naphthalen-1-yl)-4-phenylbuta-2,3-dienal (2g)

Yellow oil (53.5 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.76-9.74 (d, J = 8.0 Hz, 1 H), 7.93-7.86 (m, 3 H), 7.56-7.51 (m, 4 H), 7.42-7.23 (m, 5 H), 6.32-6.30 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 219.8, 191.0, 133.9, 133.5, 131.6, 130.6, 129.4, 128.9, 128.5, 128.1, 127.2, 126.7, 126.2, 125.6, 125.5, 114.6, 113.0, 100.3; HRMS calcd for $C_{20}H_{15}O$ $[M+H]^+$ 271.1118; found: 271.1119.



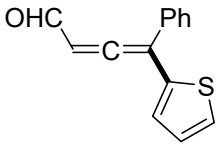
4-Phenyl-4-(pyridin-3-yl)buta-2,3-dienal (2h)

Yellow oil (27.8 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.67-9.65 (d, J = 6.3 Hz, 1H), 8.66 (d, J = 1.2 Hz, 1H), 8.43-8.41 (dd, J = 5.0, 1.3 Hz, 1H), 7.76-7.74 (m 1H), 7.33-7.28 (m, 3H), 7.12-7.08 (dd, J = 8.0, 5.0 Hz, 1H), 7.06-7.02 (m, 2H), 6.21-6.19 (d, J = 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 218.7, 190.7, 151.1, 149.8, 137.4, 134.6, 132.2, 128.7, 128.3, 128.3, 123.2, 110.7, 100.8; HRMS calcd for $C_{15}H_{12}NO$ $[M+H]^+$ 222.0913; found: 222.0911.



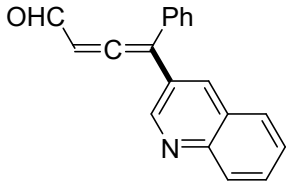
4-(Furan-2-yl)-4-phenylbuta-2,3-dienal (2i)

Yellow oil (53.6 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.68-7.66 (d, J = 6.2 Hz, 1H), 7.33-7.27 (m, 3H), 7.15-7.13 (dd, J = 7.5, 1.5 Hz, 1H), 7.05-7.02 (m, 2H), 6.39-6.37 (dd, J = 7.5, 1.6 Hz, 1H), 6.17-6.08 (t, J = 7.5 Hz, 1H), 6.10-6.08 (d, J = 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 218.9, 190.7, 156.3, 144.6, 137.2, 128.7, 128.3, 128.3, 112.7, 111.9, 101.1, 99.7; HRMS calcd for $C_{14}H_{11}O_2$ $[M+H]^+$ 211.0754; found: 211.0752.



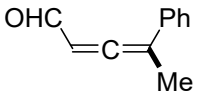
4-Phenyl-4-(thiophen-2-yl)buta-2,3-dienal (2j)

Yellow oil (54.9 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.70-9.68 (d, J = 7.2 Hz, 1 H), 7.52-7.49 (dd, J = 7.3, 1.8 Hz, 1H), 7.42-7.37 (m, 4H), 7.34-7.30 (m, 1H), 7.16-7.09 (m, 2H), 6.33-6.29 (d, J = 6.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 219.9, 190.7, 138.1, 138.0, 129.1, 128.8, 128.7, 128.3, 127.4, 126.9, 106.3, 100.9; HRMS calcd for $C_{14}H_{11}OS$ $[M+H]^+$ 227.0525; found: 227.0524.



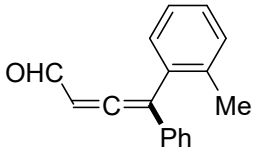
4-Phenyl-4-(quinolin-3-yl)buta-2,3-dienal (2k)

Yellow oil (53.8 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.69-8.67 (d, J = 6.2 Hz, 1H), 8.81 (d, J = 1.6 Hz, 1H), 8.21-8.19 (m, 1H), 8.10 -8.08 (m, 1H), 7.89 (m, 1H), 7.65-7.62 (m, 2H), 7.33-7.27 (m, 3H), 7.05-7.02 (m, 2H), 6.25-6.23 (d, J = 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 218.7, 190.7, 148.7, 145.7, 143.2, 137.4, 129.1, 129.0, 128.7, 128.3, 128.2, 128.1, 126.9, 112.4, 100.9; HRMS calcd for $C_{19}H_{14}NO$ $[M+H]^+$ 272.1070; found: 272.1071.



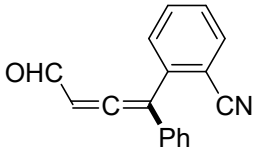
4-Phenylpenta-2,3-dienal (2l)

Yellow oil (6.1 mg, 13% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.58-7.56 (d, J = 7.2 Hz, 1 H), 7.42-7.37 (m, 4 H), 7.34-7.32 (m, 1 H), 6.15-6.12 (m, 1 H), 2.28-2.27 (d, J = 2.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 220.5, 191.7, 133.3, 128.8, 128.3, 126.1, 106.6, 100.2, 16.4; HRMS calcd for $C_{11}H_{11}O$ $[M+H]^+$ 159.0805; found: 159.0804.



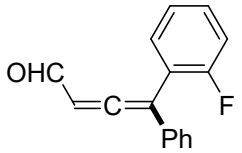
4-Phenyl-4-(*o*-tolyl)buta-2,3-dienal (2m)

Yellow oil (42.8 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.70-9.68 (d, J = 8.0 Hz, 1 H), 7.34-7.28 (m, 7 H), 7.23-7.20 (m, 2 H), 6.26-6.24 (d, J = 8.0 Hz, 1 H), 2.24 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 219.2, 190.9, 136.8, 133.2, 132.6, 130.7, 130.2, 128.8, 128.8, 128.4, 127.1, 126.3, 113.5, 100.3, 20.1; HRMS calcd for $C_{17}H_{15}O$ $[M+H]^+$ 235.1118; found: 235.1119.



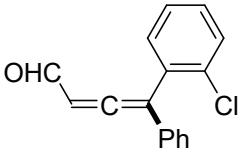
2-(4-Oxo-1-phenylbuta-1,2-dien-1-yl)benzonitrile (2n)

Yellow oil (55.1 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.73-9.71 (d, J = 6.8 Hz, 1 H), 7.67-7.62 (m, 3 H), 7.56-7.52 (m, 1 H), 7.45-7.44 (m, 3 H), 7.34-7.31 (m, 2 H), 6.42-6.40 (d, J = 6.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 220.2, 190.3, 135.1, 132.8, 132.2, 132.1, 131.9, 129.7, 129.2, 129.2, 128.5, 118.2, 114.1, 113.1, 101.3; HRMS calcd for $C_{17}H_{12}NO$ $[M+H]^+$ 246.0914; found: 246.0909.



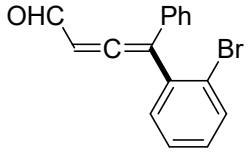
4-(2-Fluorophenyl)-4-phenylbuta-2,3-dienal (2o)

Yellow oil (55.0 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.72-9.70 (d, J = 7.6 Hz, 1 H), 7.39-7.36 (m, 4 H), 7.32-7.29 (m, 3 H), 7.21-7.17 (m, 2 H), 6.29-6.28 (d, J = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 220.7, 191.1, 160.2 (d, J = 249.0 Hz, 1 C), 132.9, 131.3 (d, J = 12.0 Hz, 1 C), 130.6 (d, J = 8.0 Hz, 1 C), 128.9, 128.7, 127.6, 124.4 (d, J = 4.0 Hz, 1 C), 121.2 (d, J = 14.0 Hz, 1 C), 116.3 (d, J = 21.0 Hz, 1 C), 108.9, 100.2; HRMS calcd for $C_{16}H_{12}FO$ $[M+H]^+$ 239.0867; found: 239.0863.



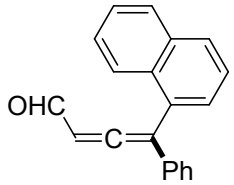
4-(2-Chlorophenyl)-4-phenylbuta-2,3-dienal (2p)

Yellow oil (56.4 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ .70-9.68 (d, J = 8.0 Hz, 1 H), 7.43-7.36 (m, 4 H), 7.35-7.33 (m, 3 H), 7.31-7.28 (m, 2 H), 6.35-6.33 (d, J = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 220.5, 190.7, 134.7, 133.0, 131.9, 130.3, 129.8, 129.5, 129.0, 128.6, 128.2, 114.7, 101.2; HRMS calcd for $C_{16}H_{12}ClO$ $[M+H]^+$ 255.0571; found: 255.0573.



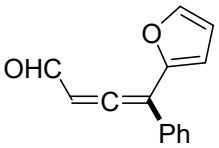
4-(2-Bromophenyl)-4-phenylbuta-2,3-dienal (2q)

Yellow oil (64.4 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.78-9.77 (d, J = 7.2 Hz, 1 H), 7.71-7.68 (d, J = 8.0 Hz, 1 H), 7.41-7.29 (m, 6 H), 7.22-7.20 (m, 2 H), 6.30-6.28 (d, J = 6.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 219.4, 190.7, 134.3, 133.5, 132.6, 131.7, 130.2, 128.9, 128.5, 127.8, 127.1, 124.1, 113.8, 101.0; HRMS calcd for $C_{16}H_{12}BrO$ $[M+H]^+$ 299.0066; found: 299.0063.



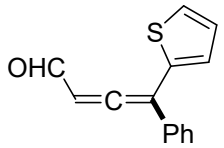
4-(Naphthalen-1-yl)-4-phenylbuta-2,3-dienal (2r)

Yellow oil (55.1 mg, 68% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 9.76-9.74 d, J = 6.6 Hz, 1 H), 7.93-7.86 (m, 3 H), 7.56-7.42 (m, 4 H), 7.30-7.23 (m, 5 H), 6.32-6.30 (d, J = 6.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 219.8, 191.0, 133.9, 133.5, 131.6, 130.6, 129.4, 128.9, 128.5, 128.1, 127.2, 126.7, 126.2, 125.6, 125.5, 114.6, 113.0, 100.3; HRMS calcd for $C_{20}H_{15}O$ $[M+H]^+$ 271.1118; found: 271.1119.



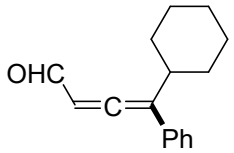
4-(Furan-2-yl)-4-phenylbuta-2,3-dienal (2r)

Yellow oil (51.3 mg, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 9.70-9.68 (d, J = 6.3 Hz, 1H), 7.33-7.27 (m, 3H), 7.15-7.13 (dd, J = 7.5, 1.5 Hz, 1H), 7.05-7.02 (m, 2H), 6.39-6.37 (dd, J = 7.5, 1.5 Hz, 1H), 6.21-6.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 218.7, 190.7, 156.3, 144.6, 137.2, 128.7, 128.3, 128.3, 112.7, 111.9, 102.4, 100.8; HRMS calcd for $C_{14}H_{11}O_2$ $[M+H]^+$ 211.0754; found: 211.0753.



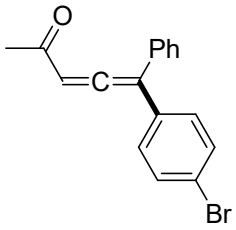
4-Phenyl-4-(thiophen-2-yl)buta-2,3-dienal (2t)

Yellow oil (55.1 mg, 73% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 9.65-9.64 (d, J = 6.2 Hz, 1H), 7.51-7.50 (dd, J = 7.5, 1.5 Hz, 1H), 7.33-7.27 (m, 3H), 7.06-7.00 (m, 3H), 6.80-6.78 (dd, J = 7.5, 1.6 Hz, 1H), 6.28-6.27 (d, J = 6.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 219.8, 190.7, 138.1, 138.0, 129.1, 128.8, 128.7, 128.3, 127.4, 126.9, 106.3, 100.8; HRMS calcd for $C_{14}H_{11}OS$ $[M+H]^+$ 227.0525; found: 227.0524.



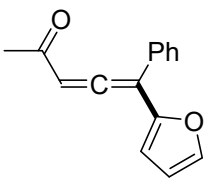
4-Cyclohexyl-4-phenylbuta-2,3-dienal (2u)

Yellow oil (36.6 mg, 54% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 9.61 (s, 1H), 7.34-7.32 (m, 2H), 7.22-7.18 (m, 3H), 6.04 (s, 1H), 1.83-1.78 (m, 1H), 1.67-1.40 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 210.3, 190.7, 136.4, 130.5, 128.1, 126.0, 100.5, 50.2, 40.1, 33.1, 25.4, 22.4; HRMS calcd for $C_{16}H_{19}O$ $[M+H]^+$ 227.1430; found: 227.1432.



5-(4-Bromophenyl)-5-phenylpenta-3,4-dien-2-one (2v)

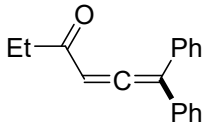
Yellow oil (70.2 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.53-7.51 (m, 2 H), 7.41-7.32 (m, 5 H), 7.24-7.22 (m, 2 H), 6.24 (s, 1 H), 2.32 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 215.0, 197.7, 133.4, 133.0, 132.0, 130.0, 128.9, 128.6, 128.4, 122.5, 113.0, 100.2, 27.2; HRMS calcd for $C_{17}H_{14}BrO$ $[M+H]^+$ 313.0223; found: 313.0221.



5-(Furan-2-yl)-5-phenylpenta-3,4-dien-2-one (2w)

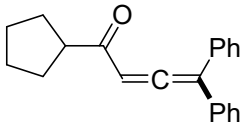
Yellow oil (53.8 mg, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.33-7.27 (m, 3H), 7.15-

7.13 (m, 1H), 7.05-7.02 (m, 2H), 6.46 (s, 1H), 6.39-6.37 (dd, J = 7.5, 1.5 Hz, 1H), 6.26-6.22 (t, J = 7.5 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 214.8, 197.3, 156.3, 144.6, 137.2, 128.7, 128.3, 128.3, 116.0, 115.2, 112.3, 99.7, 26.4; HRMS calcd for $C_{15}H_{13}O_2$ $[M+H]^+$ 225.0910; found: 225.0911.



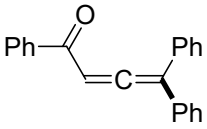
6,6-Diphenylhexa-4,5-dien-3-one (2x)

Yellow oil (43.2 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.42-7.34 (m, 10 H), 6.25 (s, 1 H), 2.76-2.71 (m, 2 H), 1.10-1.07 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 214.5, 201.0, 134.0, 128.8, 128.4, 128.3, 113.7, 99.1, 33.1, 8.2; HRMS calcd for $C_{18}H_{17}O$ $[M+H]^+$ 249.1274; found: 249.1271.



1-Cyclopentyl-4,4-diphenylbuta-2,3-dien-1-one (2y)

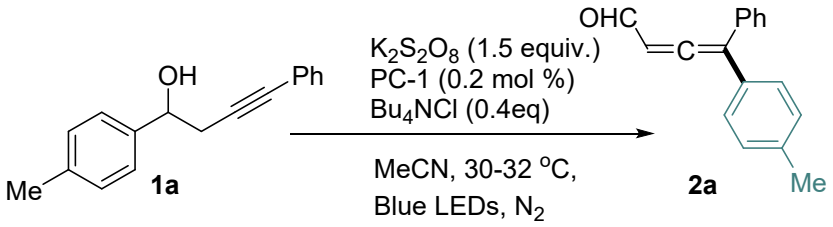
Yellow oil (43.8 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38-7.19 (m, 10H), 6.51 (s, 1H), 3.21-3.16 (m, 1H), 2.13-2.06 (m, 2H), 1.77-1.72 (m, 2H), 1.58-1.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 216.0, 199.7, 137.4, 131.8, 128.3, 125.9, 113.3, 98.1, 48.3, 33.9, 22.4; HRMS calcd for $C_{21}H_{21}O$ $[M+H]^+$ 289.1587; found: 289.1585.



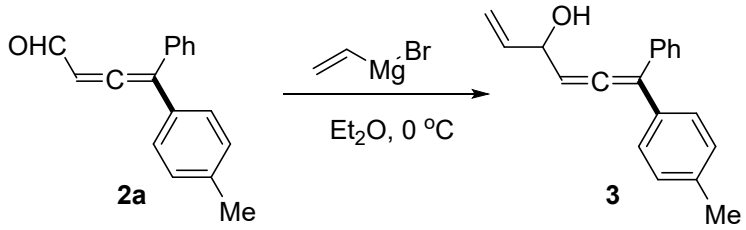
1,4,4-Triphenylbuta-2,3-dien-1-one (2z)

Yellow oil (48.8 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.82-7.80 (m, 2 H), 7.52-7.48 (m, 1 H), 7.39-7.26 (m, 12 H), 6.80 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 216.1, 191.5, 137.4, 134.2, 132.8, 128.7, 128.6, 128.5, 128.3, 113.7, 96.5; HRMS calcd for $C_{22}H_{17}O$ $[M+H]^+$ 297.1274; found: 297.1269.

5 Synthetic transformations of 2a



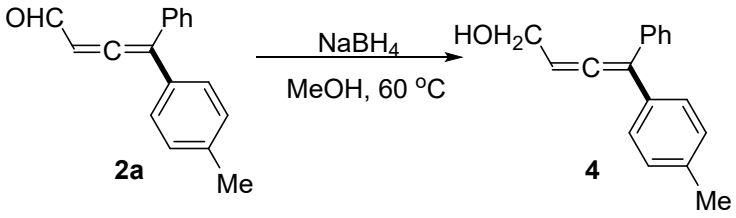
In a sealed tube, $K_2S_2O_8$ (7.5 mmol), PC-1 (0.2 mol%) and Bu_4NCl (2 mmol) were successively added to a solution of **1a** (1.18 g, 5 mmol) in MeCN (3.0 mL). The reactor was flushed with argon. The reaction mixture was stirring at blue LEDs for 18 hour and then the reaction mixture was cooled to room temperature. The solvent was evaporated in vacuo and the crude product was purified by column chromatography, eluting with petroleum ether/EtOAc (10:1) to afford the desired *α*-allenic aldehydes/ketones **2a**.



In an oven dried round bottom flask, a solution of the allene **2a** (1.0 equiv., 0.3 mmol) in dry Et_2O was taken. The resulting solution was cooled to 0 °C and freshly vinylmagnesium bromide solution (1.8 equiv.) was added dropwise. The resulting mixture was stirred at 0 °C for 2 h. Reaction was monitored by TLC and quenched by adding sat. aqueous NH_4Cl solution. Organic phase was separated and the aqueous layer was extracted with EtOAc. The combined organic phase was washed with sat. aqueous NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the crude product was purified by column chromatography, eluting with petroleum ether/EtOAc (5:1) to afford the desired **3** in 72% yield.

6-Phenyl-6-(*p*-tolyl)hexa-1,4,5-trien-3-ol (3)

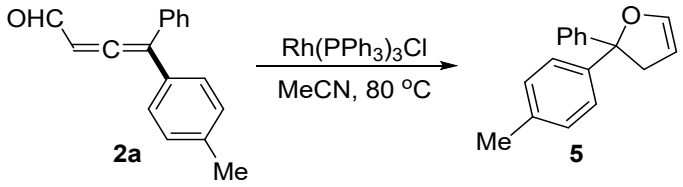
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.36-7.27 (m, 3H), 7.21-7.15 (m, 2H), 7.07-6.98 (m, 4H), 5.98-5.82 (m, 2H), 5.29-5.12 (m, 2H), 4.96 (ddd, *J* = 7.2, 6.1, 5.0 Hz, 1H), 2.41 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): *δ* 184.5, 141.1, 140.1, 138.3, 138.0, 134.3, 129.3, 129.04, 128.9, 120.1, 117.4, 99.7, 79.3, 21.4; HRMS calcd for $C_{19}H_{18}O$ $[M+H]^+$ 262.1358; found: 262.1352.



To a solution of **2a** (1.0 equiv., 0.5 mmol) in 5 mL methanol, $NaBH_4$ (1.2 equiv.) was added and stirred for 12 h at 60 °C. Reaction was monitored by TLC and quenched by adding sat. aqueous NH_4Cl solution. Organic phase was separated and the aqueous layer was extracted with EtOAc. The combined organic phase was washed with sat. aqueous NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the crude product was purified by column chromatography, eluting with petroleum ether/EtOAc (5:1) to afford the desired **4** in 62% yield.

4-Phenyl-4-(*p*-tolyl)buta-2,3-dien-1-ol (4)

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.33-7.24 (m, 3H), 7.22-7.10 (m, 3H), 7.09-6.94 (m, 3H), 5.98 (t, J = 6.9 Hz, 1H), 4.19-4.05 (m, 3H), 2.30 (d, J = 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 205.0, 140.1, 138.8, 136.7, 135.6, 133.1, 130.0, 128.9, 124.5, 108.1, 103.0, 61.6, 21.4; HRMS calcd for $C_{17}H_{16}O$ $[M+H]^+$ 236.1201; found: 236.1205.



In a sealed tube, $Rh(PPh_3)_3Cl$ (5 mol%) was successively added to a solution of **2a** (1.0 equiv., 0.3 mmol) in MeCN (3.0 mL) at 80 °C under argon. The reaction mixture was stirring for 18 hour and then the reaction mixture was cooled to room temperature. The solvent was evaporated in vacuo and the crude product was purified by column chromatography, eluting with petroleum ether/EtOAc (10:1) to afford the desired **5** in 43% yield.

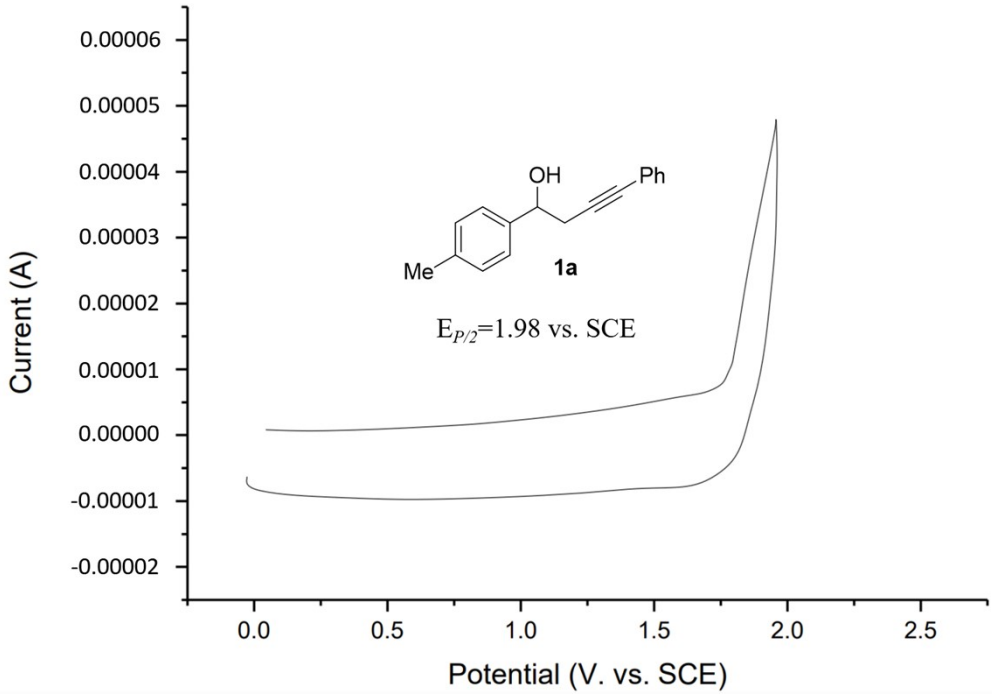
2-Phenyl-2-(*p*-tolyl)-2,3-dihydrofuran (5)

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.61 (dp, J = 6.5, 2.1 Hz, 1H), 7.51-7.47 (m, 2H), 7.45 (dd, J = 4.2, 2.0 Hz, 1H), 7.35-7.28 (m, 3H), 7.06-7.00 (m, 2H), 6.50 (d, J = 10.9 Hz, 1H), 5.25 (dt, J = 11.0, 6.2 Hz, 1H), 3.10-2.94 (m, 2H), 2.21 (d, J = 1.1 Hz, 3H*)*; ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.3, 142.1, 140.4, 136.8, 131.5, 128.7, 127.3, 126.4, 125.9, 102.9, 92.5, 48.5, 21.2; HRMS

calcd for $C_{17}H_{16}O$ $[M+H]^+$ 236.1201; found: 236.1204.

6 Cyclic voltammograms of 1a

All voltammograms were taken at room temperature using a saturated calomel (SCE) reference electrode, a mesh platinum (Pt) counter electrode, and a glassy carbon working electrode. The conditions of the experiments were the following: an acetonitrile solution of 100 mM tetrabutylammonium hexafluorophosphate (NBu_4PF_6) and 1 mM aryl alcohol, a scan rate of 0.1 V/s, and a positive initial scan direction. The reported potentials were averages over segments, and were taken at half-height of the cathodic peaks (Ep/2) of 1a, since all oxidations were nonreversible. To convert the potentials from SCE to Fc/Fc+ reference, 380 mV were subtracted from the measured values. The positive peaks on the return sweep of most substrates were thought to signify an ECE-type mechanism.



7 Refrence

(1) P. Gao, Y. -W. Shen, R. Fang, X.-H. Hao, Z.-H. Qiu, F. Yang, X.-B. Yan, Q. Wang, X.-J. Gong, X.-Y. Liu and Y. -M. Liang, *Angew. Chem., Int. Ed.,* 2014, **53**, 7629.

(2) D.-Q. Chen, P. Gao, P.-X. Zhou, X.-R. Song, Y.-F. Qiu, X.-Y. Liu and Y.-M. Liang, *Chem. Commun.,* 2015, **51**, 6637.

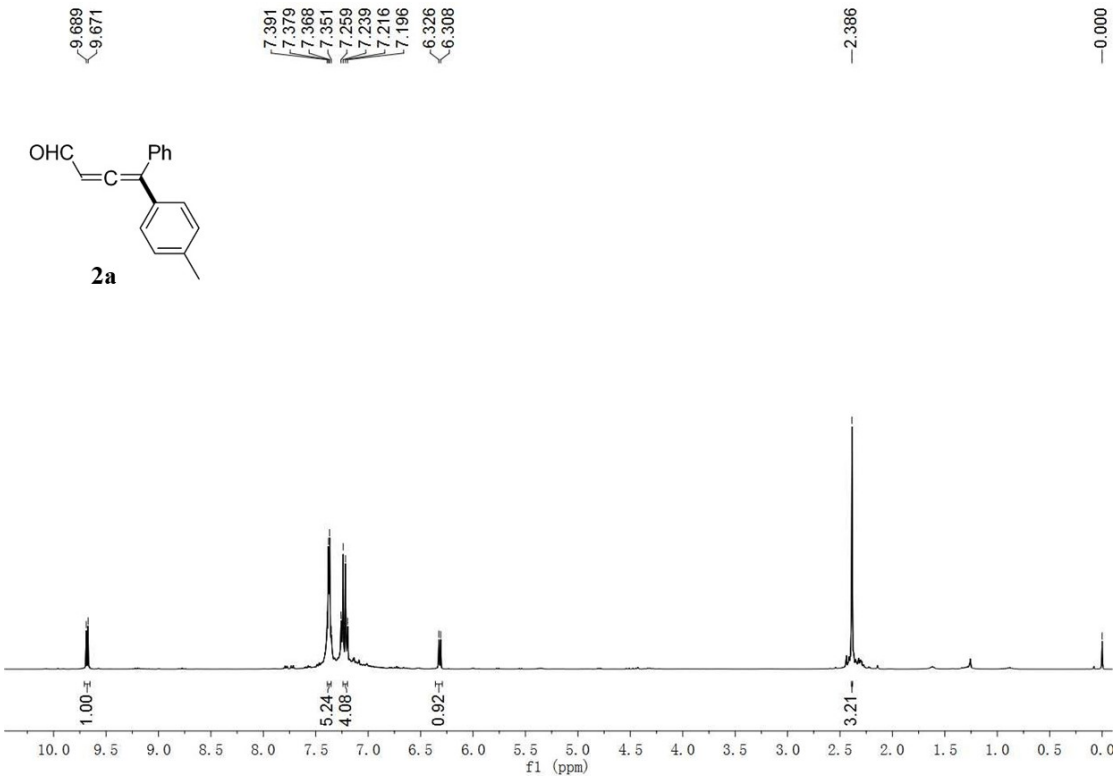
(3) A. Arrault, F. Touzeau, G. Guillaumet, J.-Y. Mérour, *Synthesis.* 1999, **7**, 1241.

(4) Y.-Z. Chen, L.-Z. Wu, M.-L. Peng, D. Zhang, L.-P. Zhang and C.-H. Tung, *Tetrahedron* 2006, **62**, 10688.

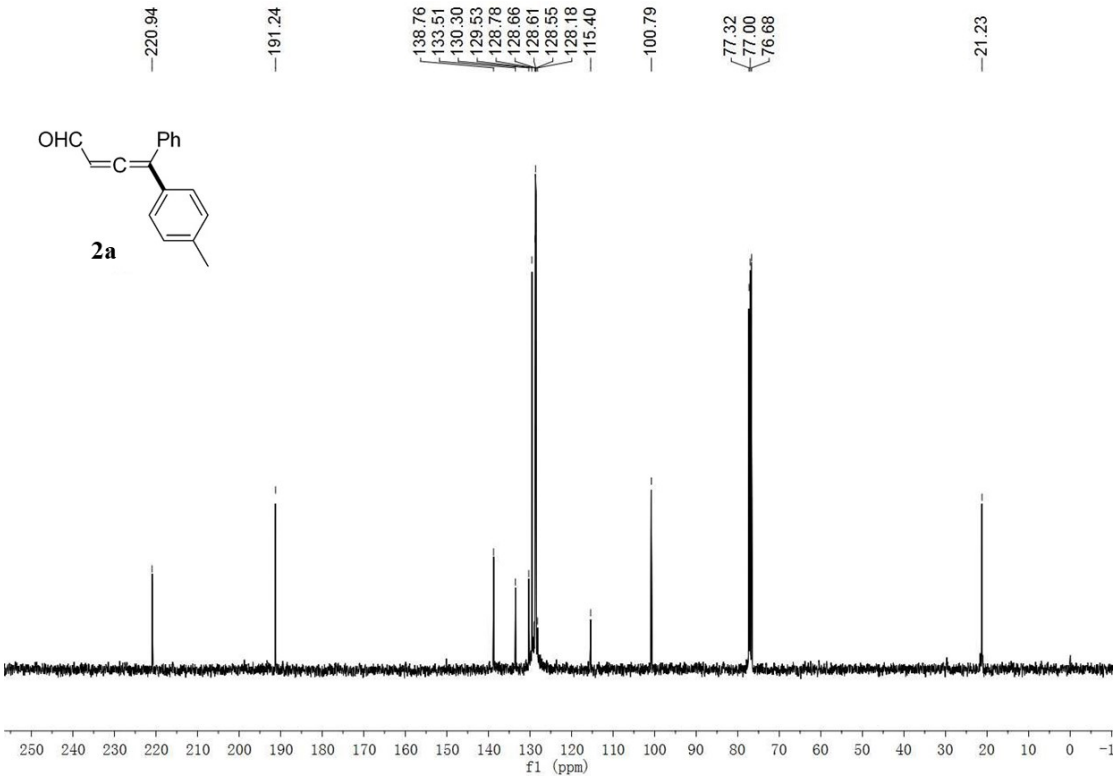
(5) J. A. Cabezas, *Tetrahedron Lett.* 2001, **42**, 6819.

8 Copies of NMR Spectra

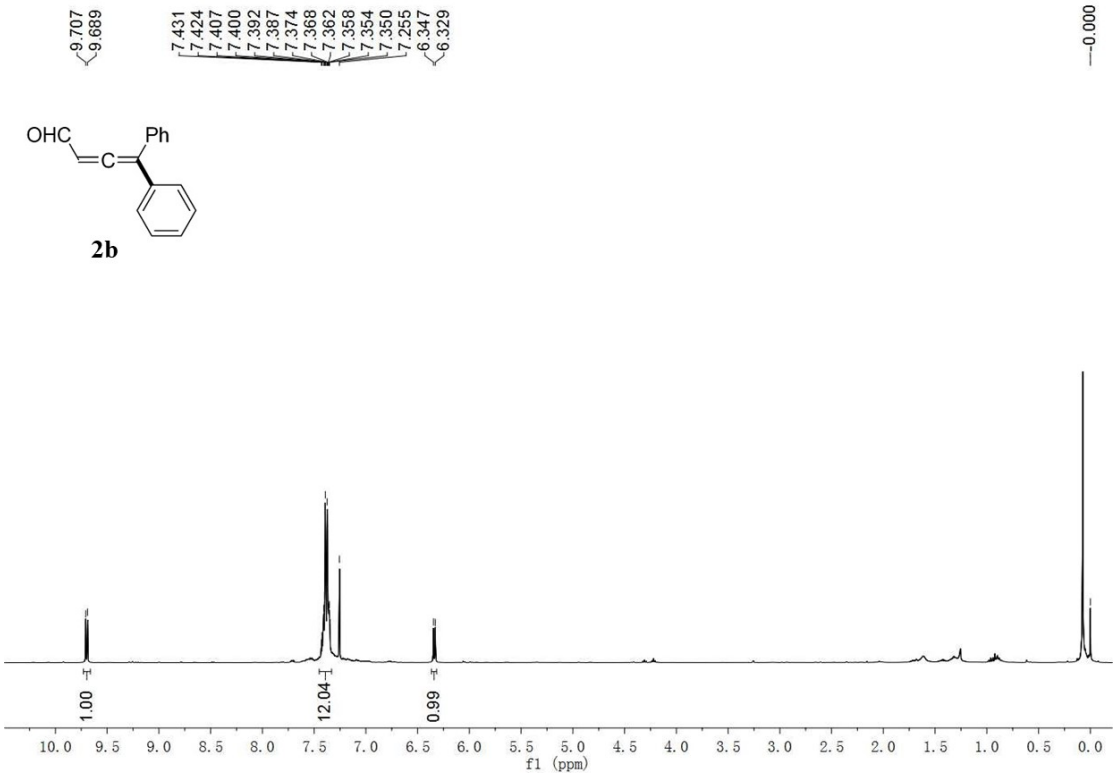
^{1}H NMR of **2a** (400 MHz, $CDCl_3$):



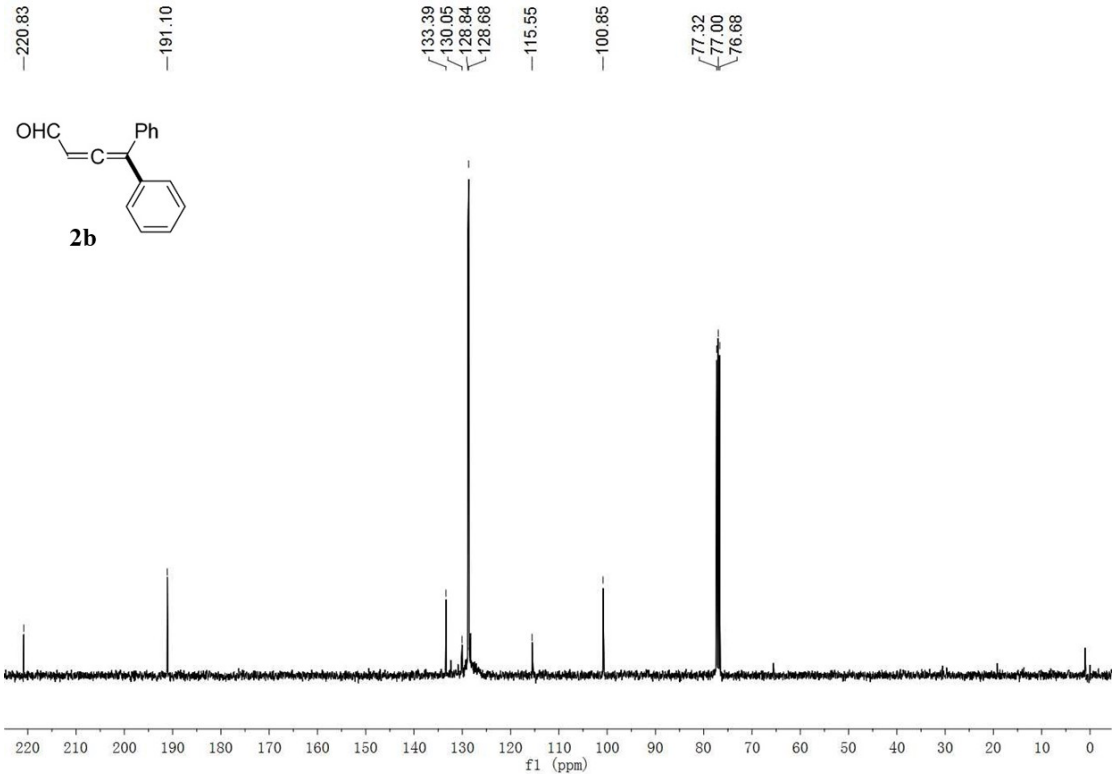
^{13}C NMR of **2a** (100 MHz, $CDCl_3$):



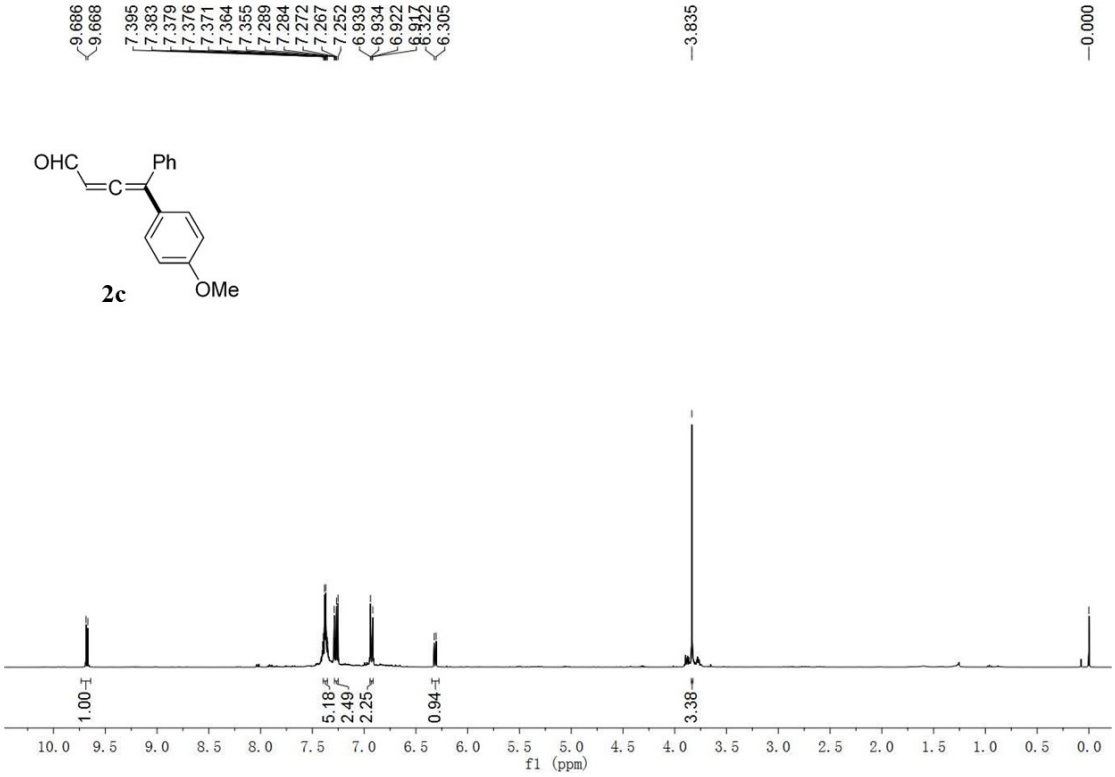
^{1}H NMR of **2b** (400 MHz, $CDCl_3$):



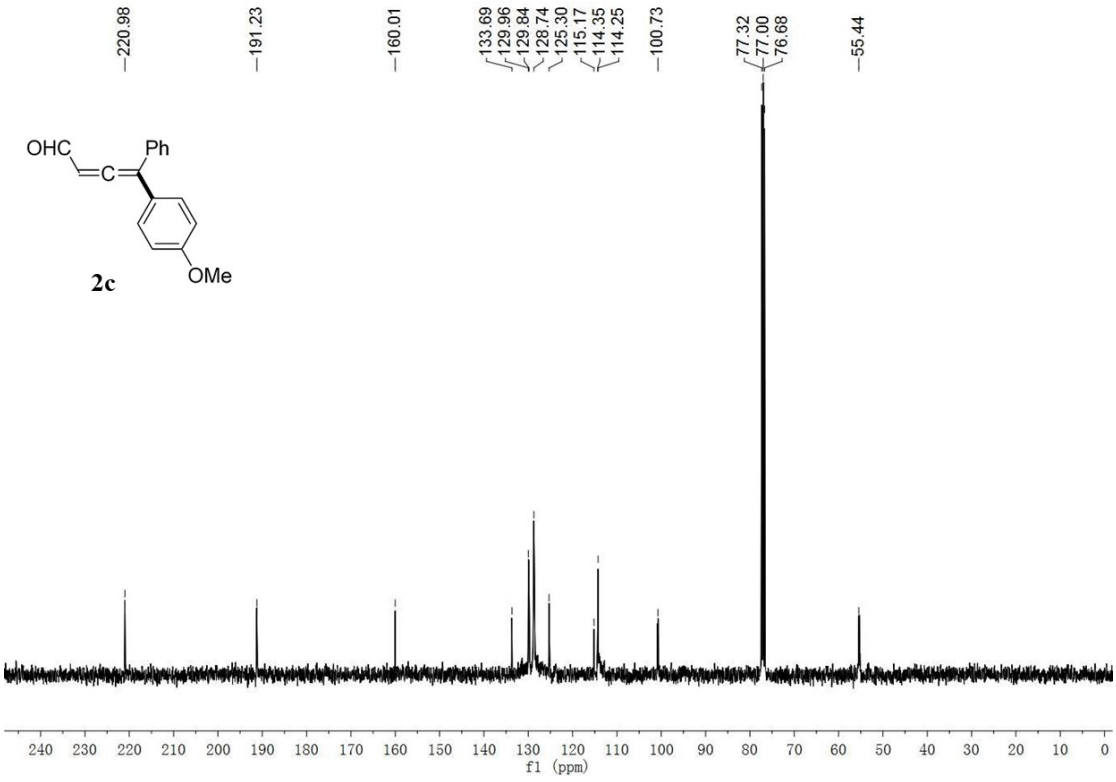
^{13}C NMR of **2b** (100 MHz, $CDCl_3$):



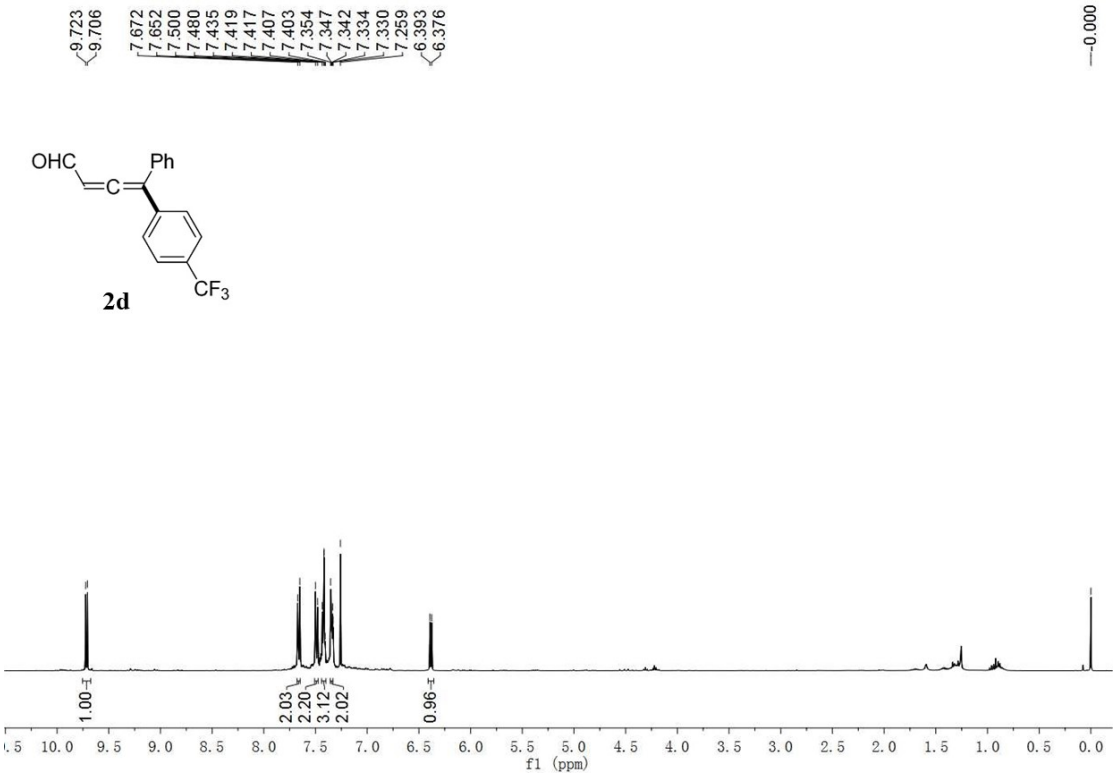
^{1}H NMR of **2c** (400 MHz, $CDCl_3$):



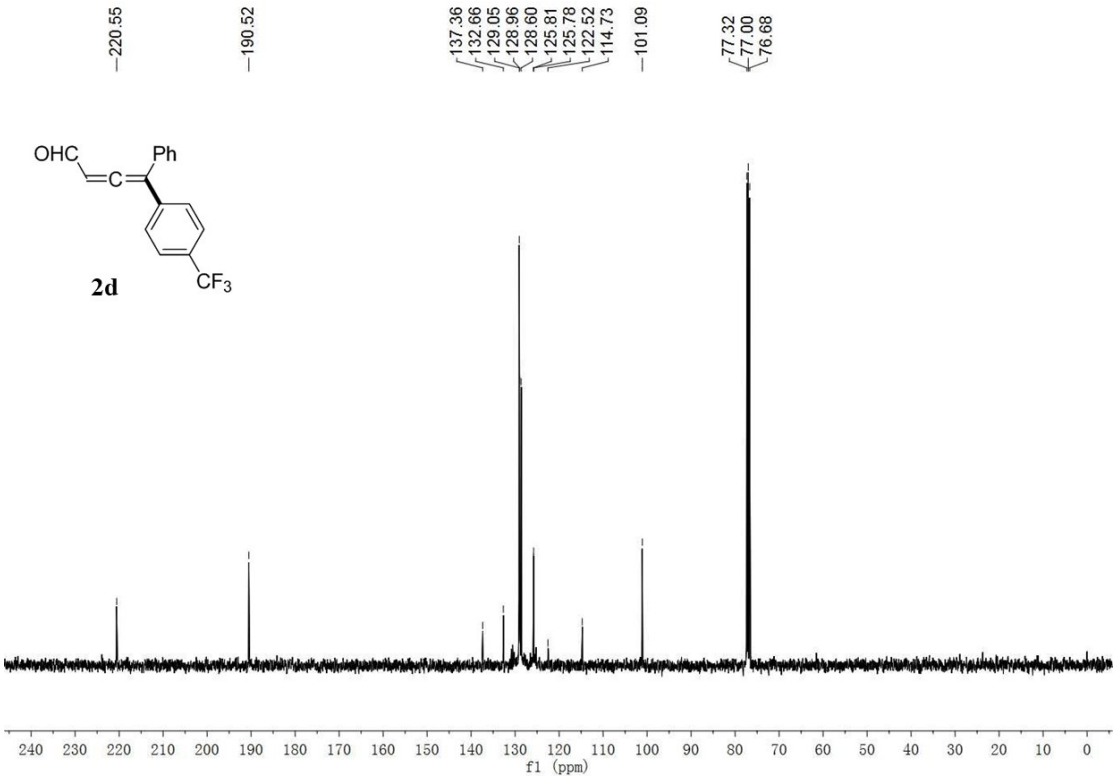
^{13}C NMR of **2c** (100 MHz, $CDCl_3$):



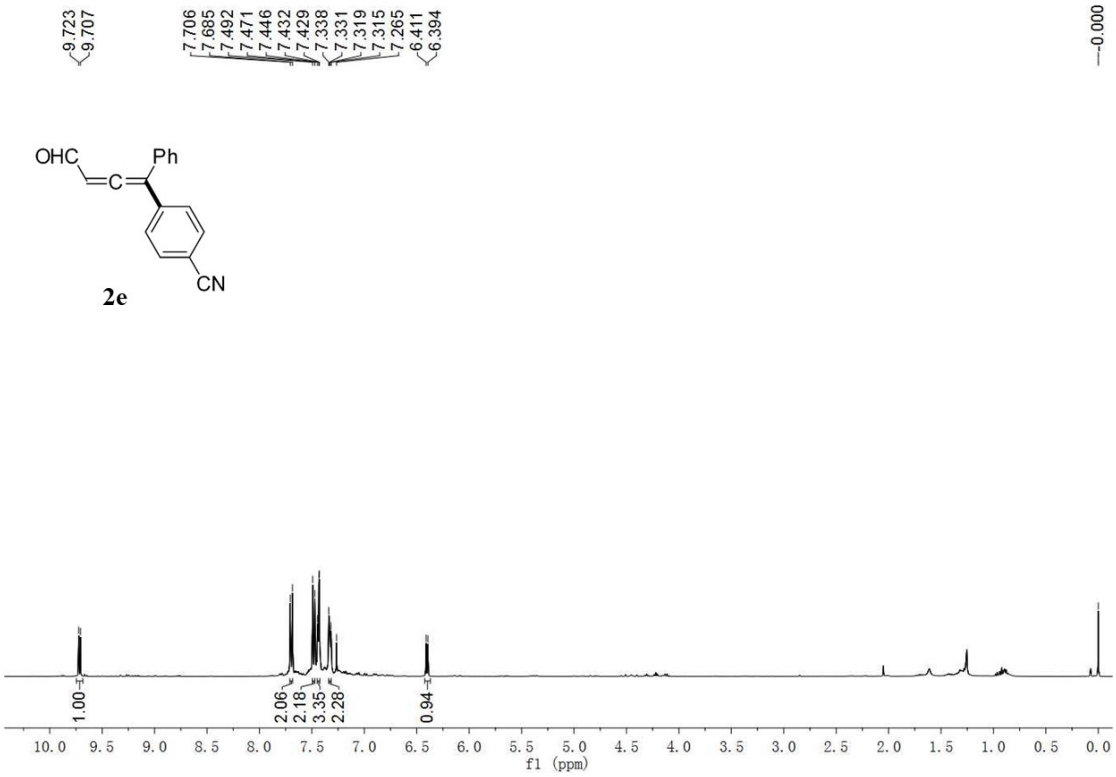
^{1}H NMR of **2d** (400 MHz, $CDCl_3$):



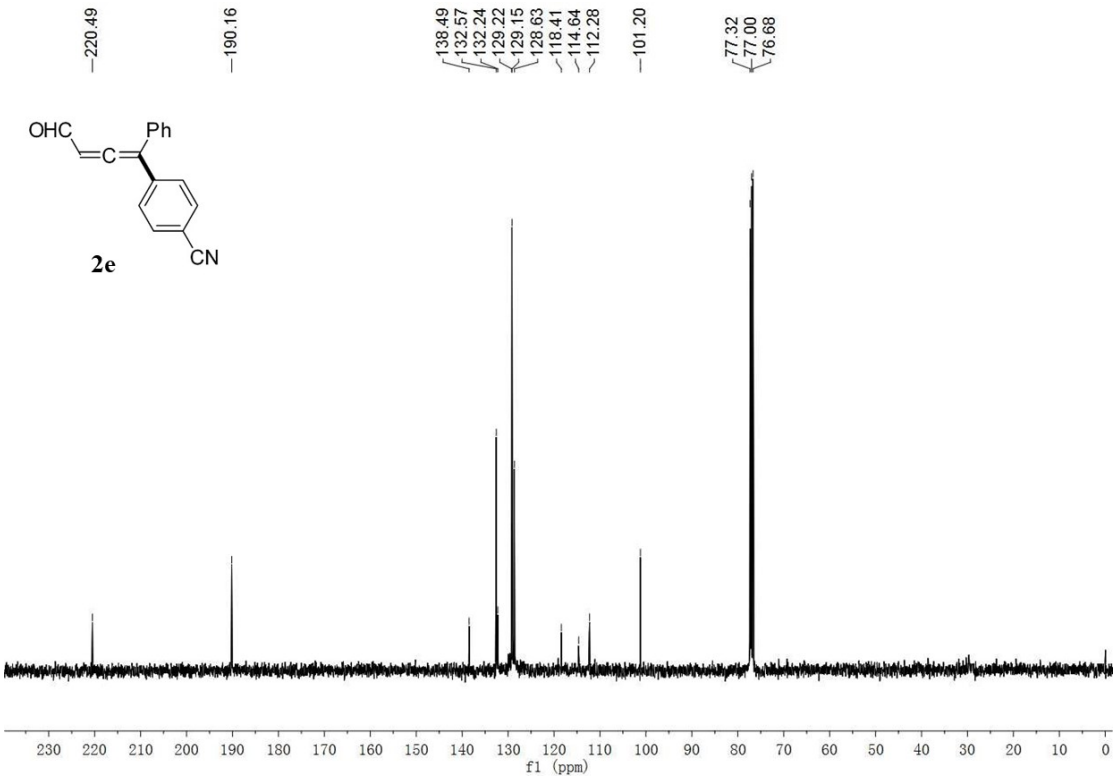
^{13}C NMR of **2d** (100 MHz, $CDCl_3$):



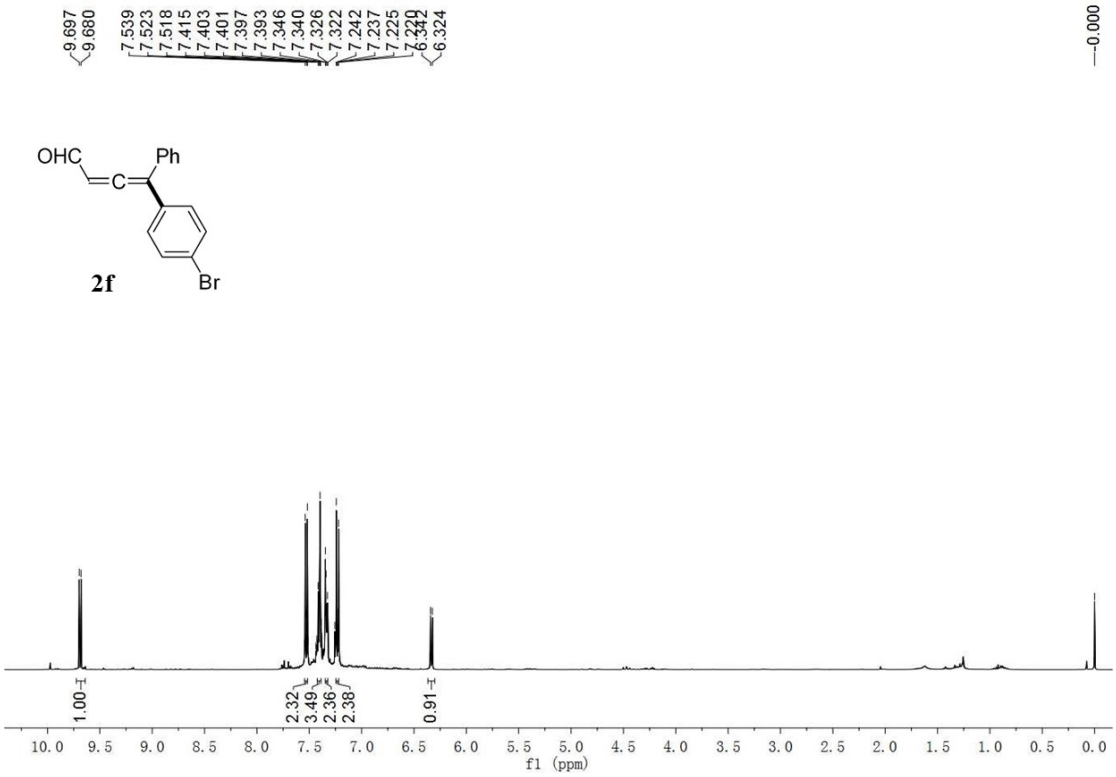
^{1}H NMR of **2e** (400 MHz, $CDCl_3$):



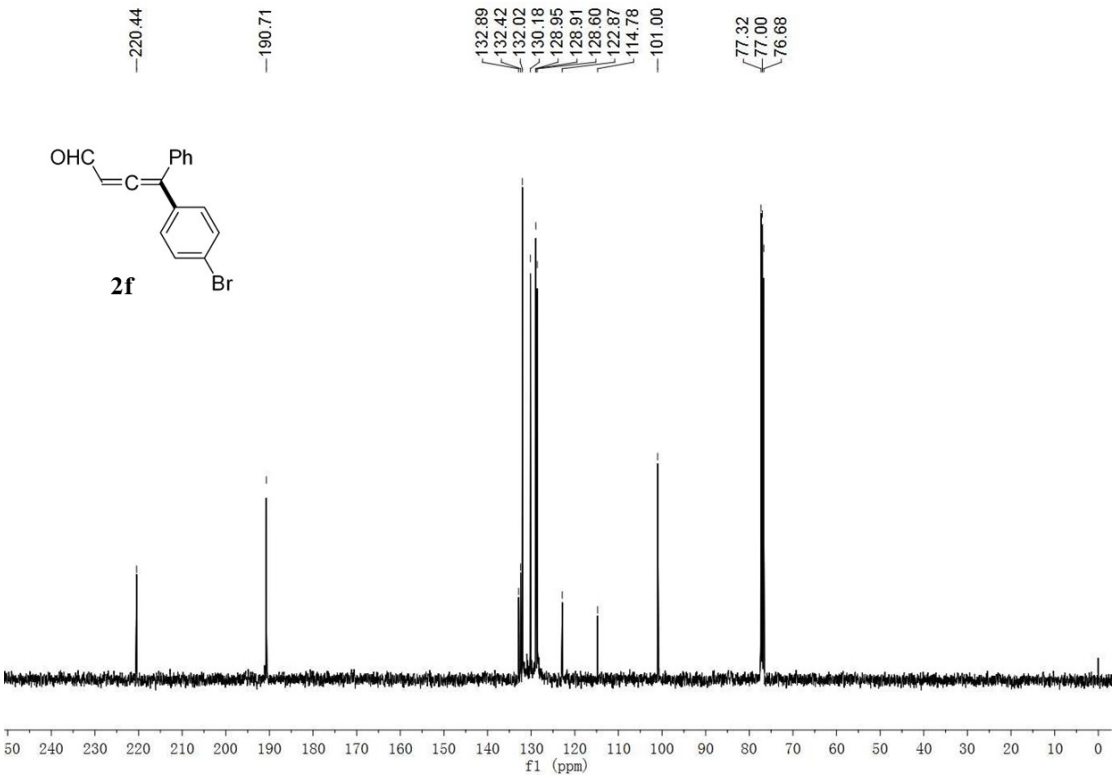
^{13}C NMR of **2e** (100 MHz, $CDCl_3$):



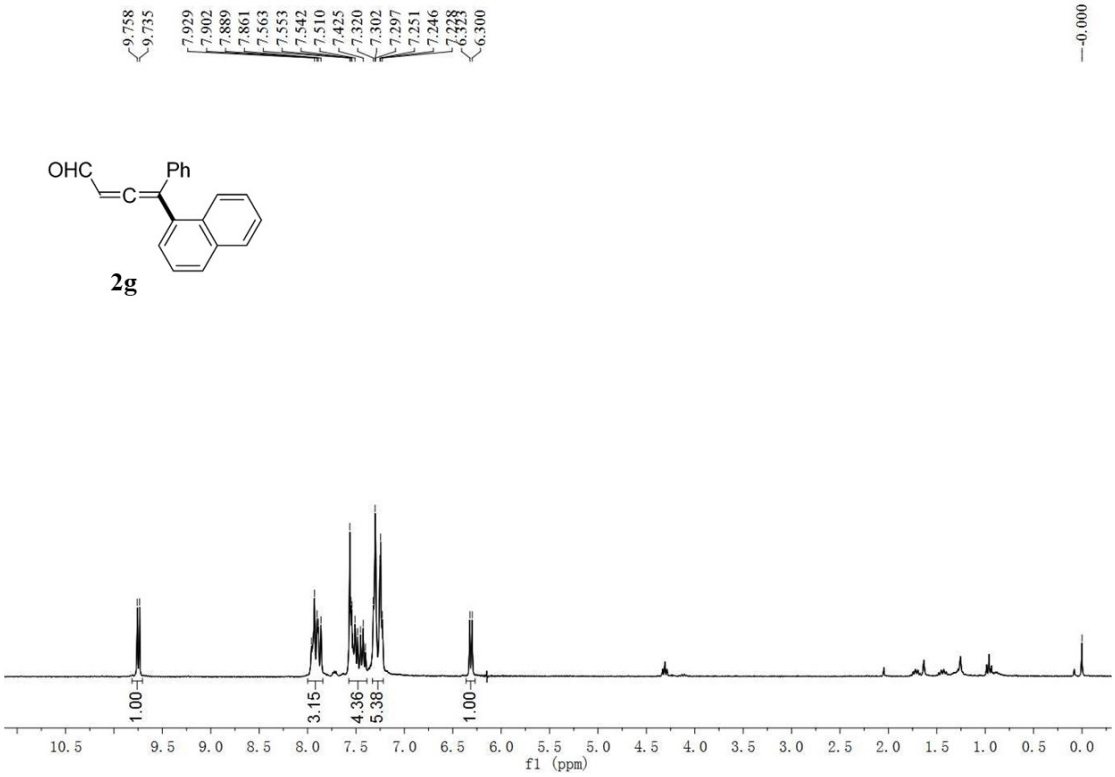
^{1}H NMR of **2f** (400 MHz, $CDCl_3$):



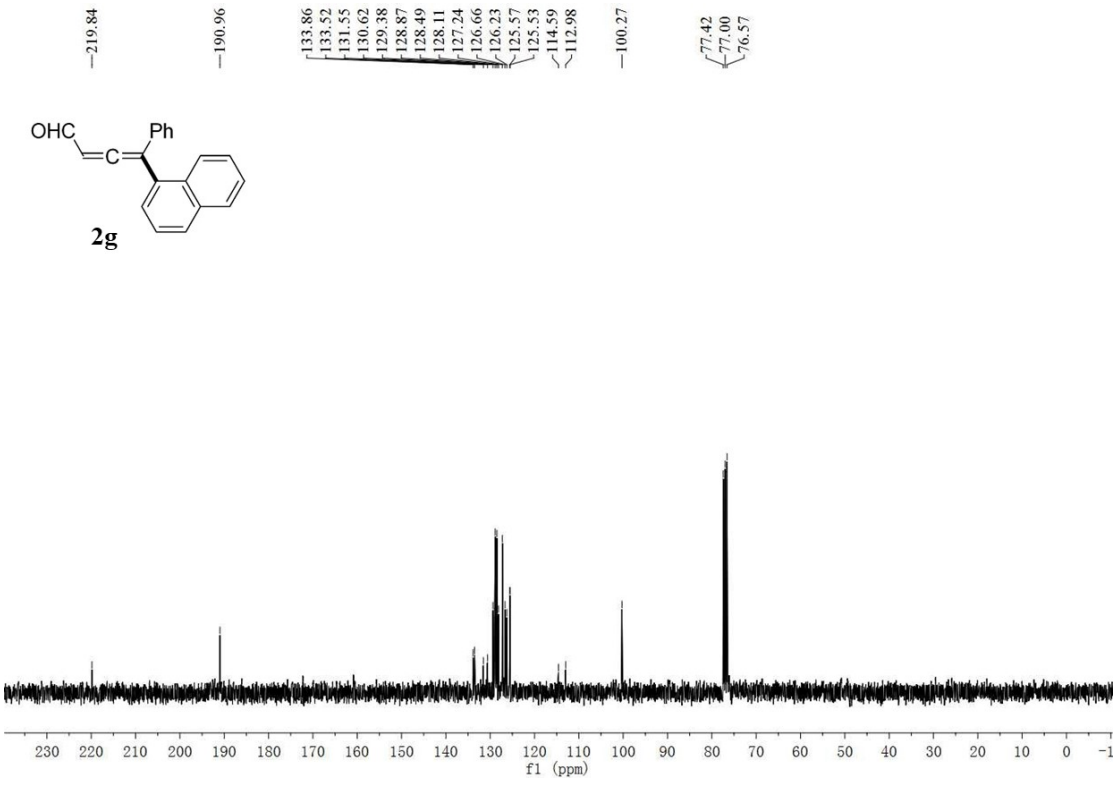
^{13}C NMR of **2f** (100 MHz, $CDCl_3$):



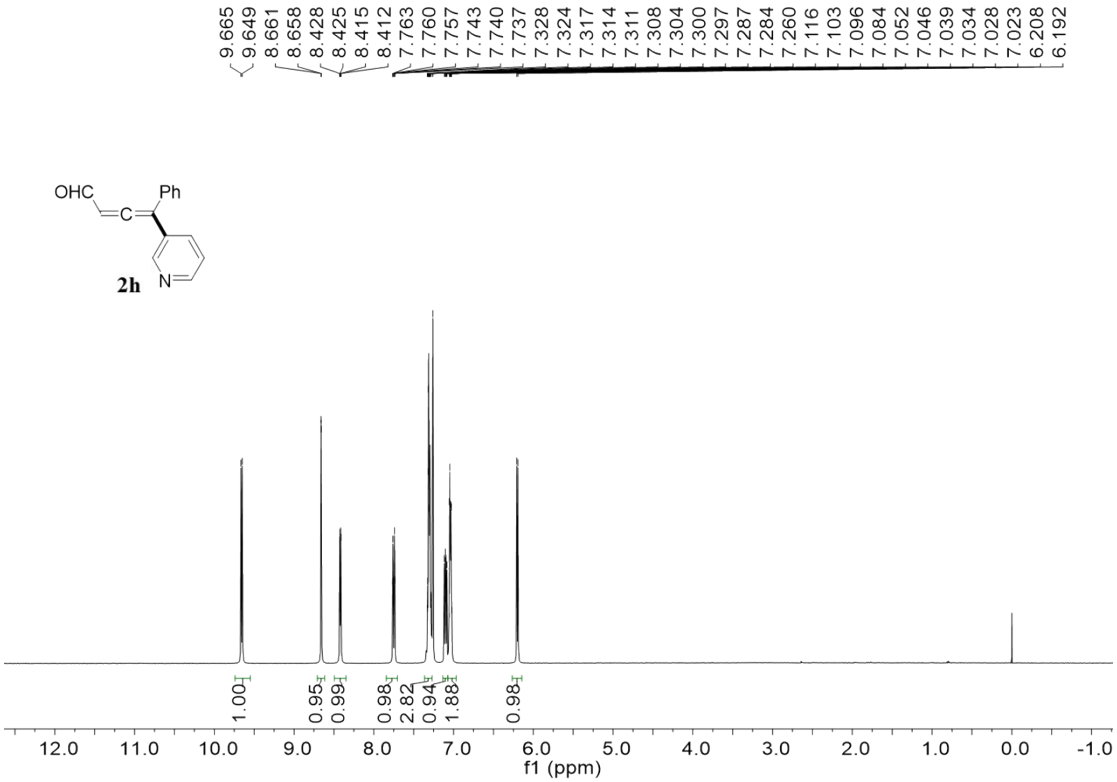
^{1}H NMR of **2g** (400 MHz, $CDCl_3$):



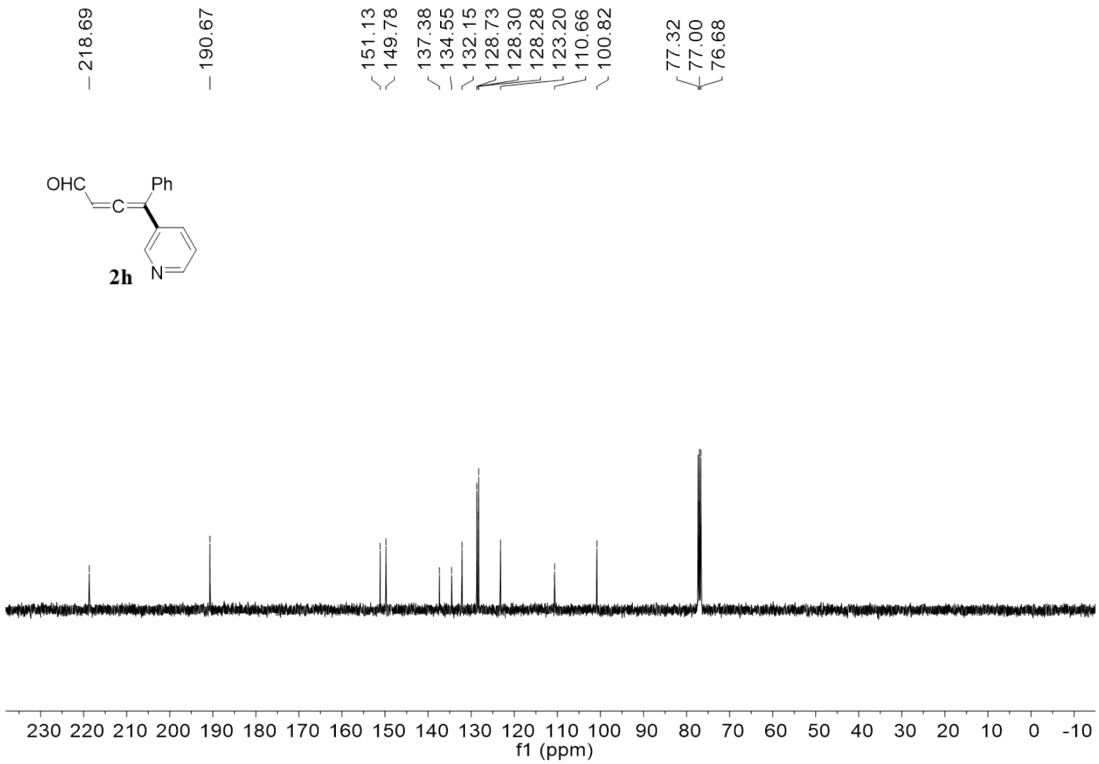
^{13}C NMR of **2g** (100 MHz, $CDCl_3$):



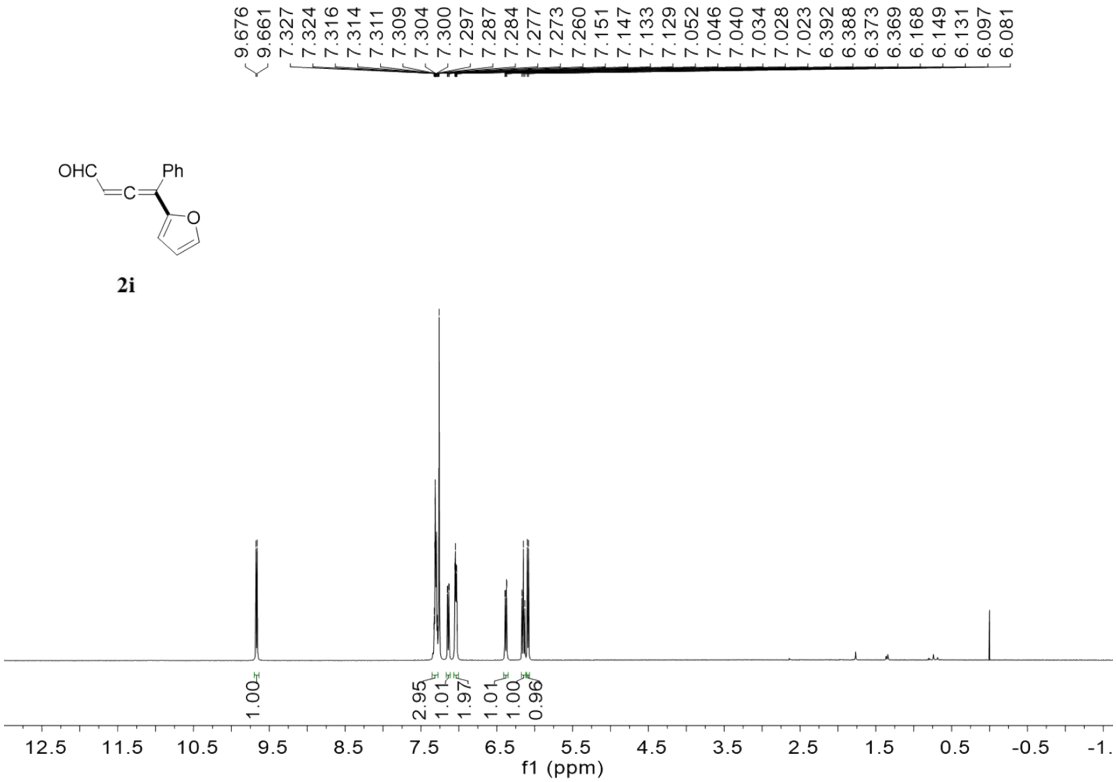
^{1}H NMR of **2h** (400 MHz, $CDCl_3$):



^{13}C NMR of **2h** (100 MHz, $CDCl_3$):

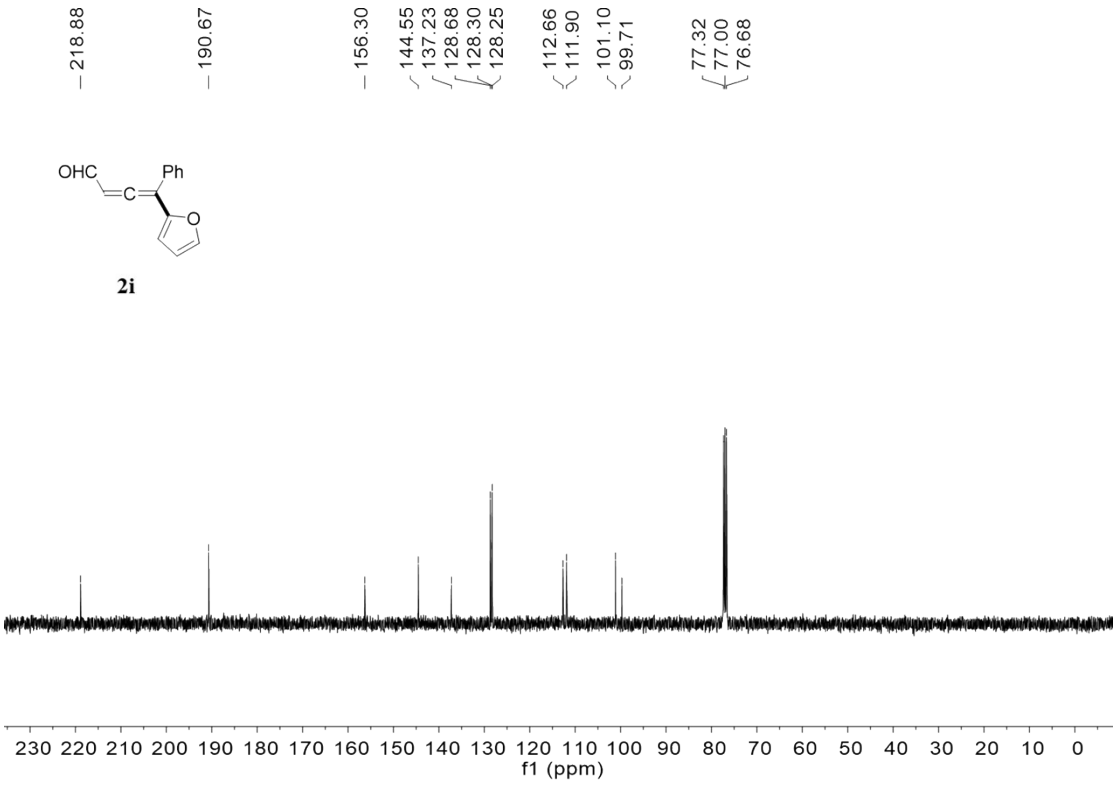


^{1}H NMR of **2i** (400 MHz, $CDCl_3$):



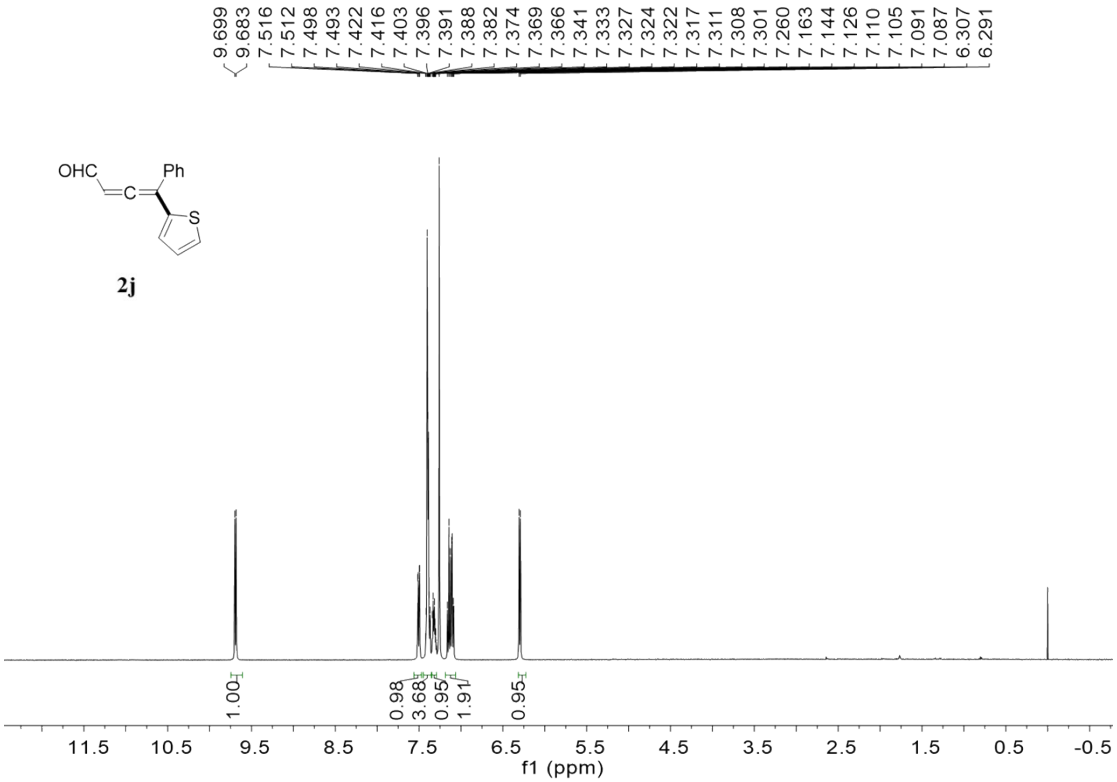
2i

^{13}C NMR of **2i** (100 MHz, $CDCl_3$):

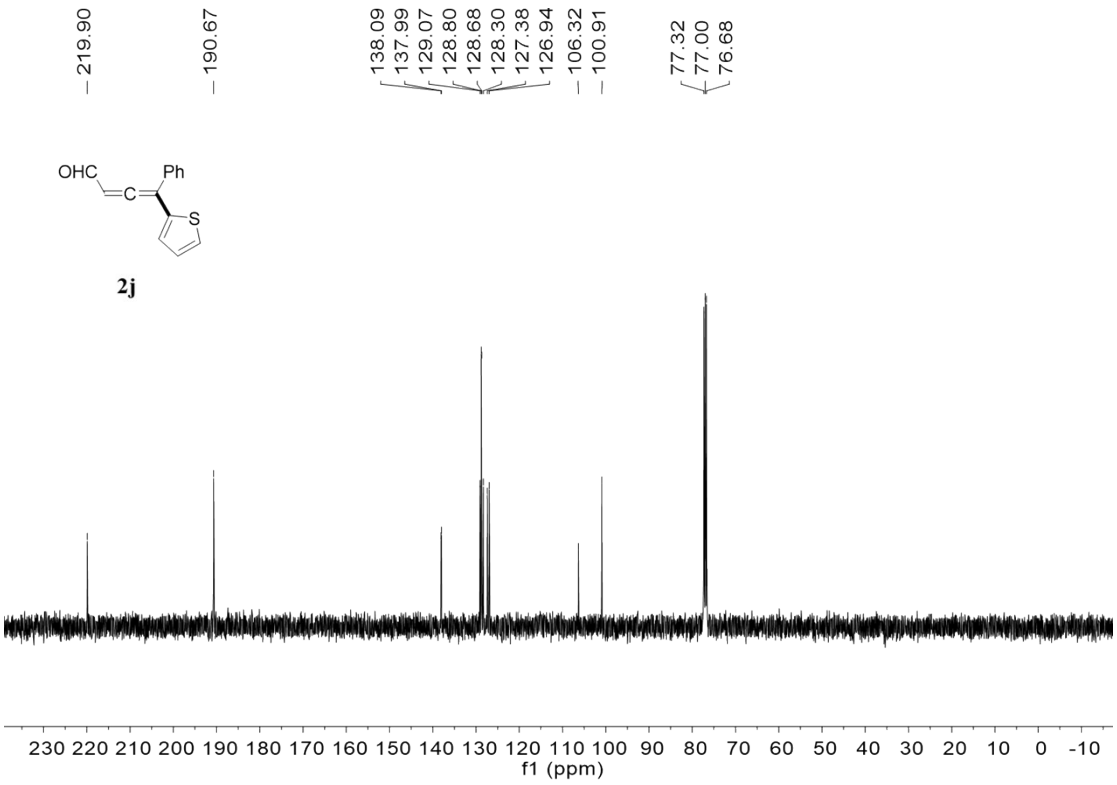


2i

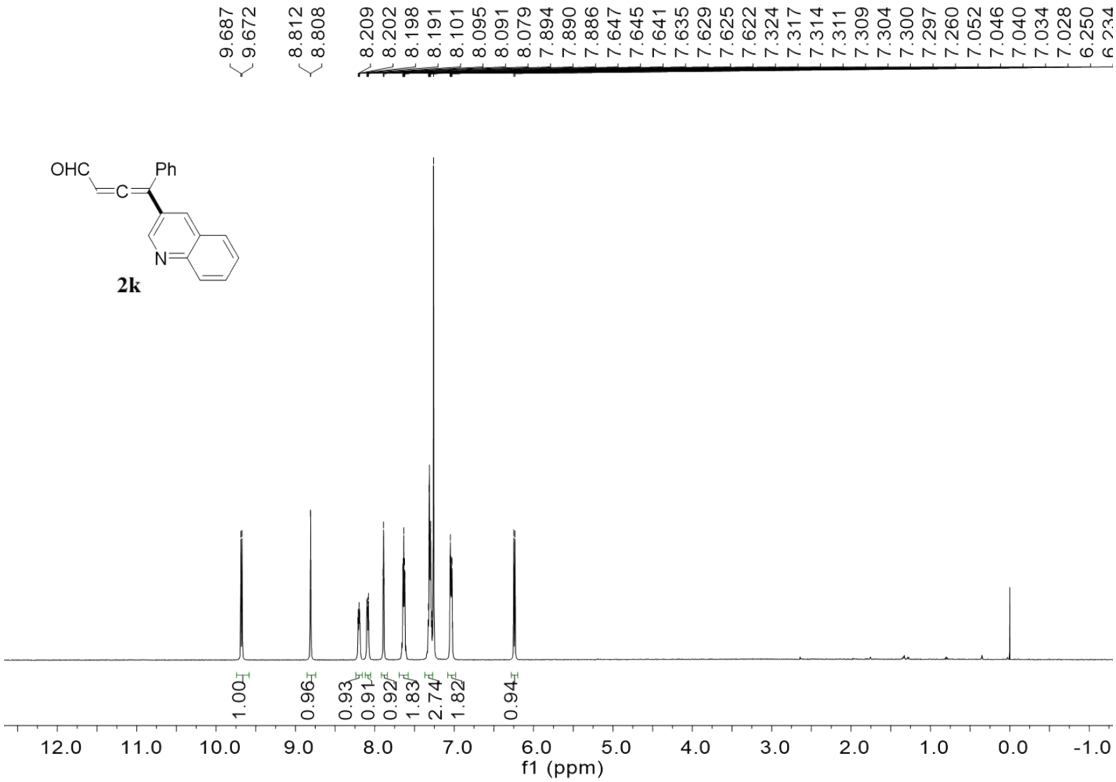
^{1}H NMR of **2j** (400 MHz, $CDCl_3$):



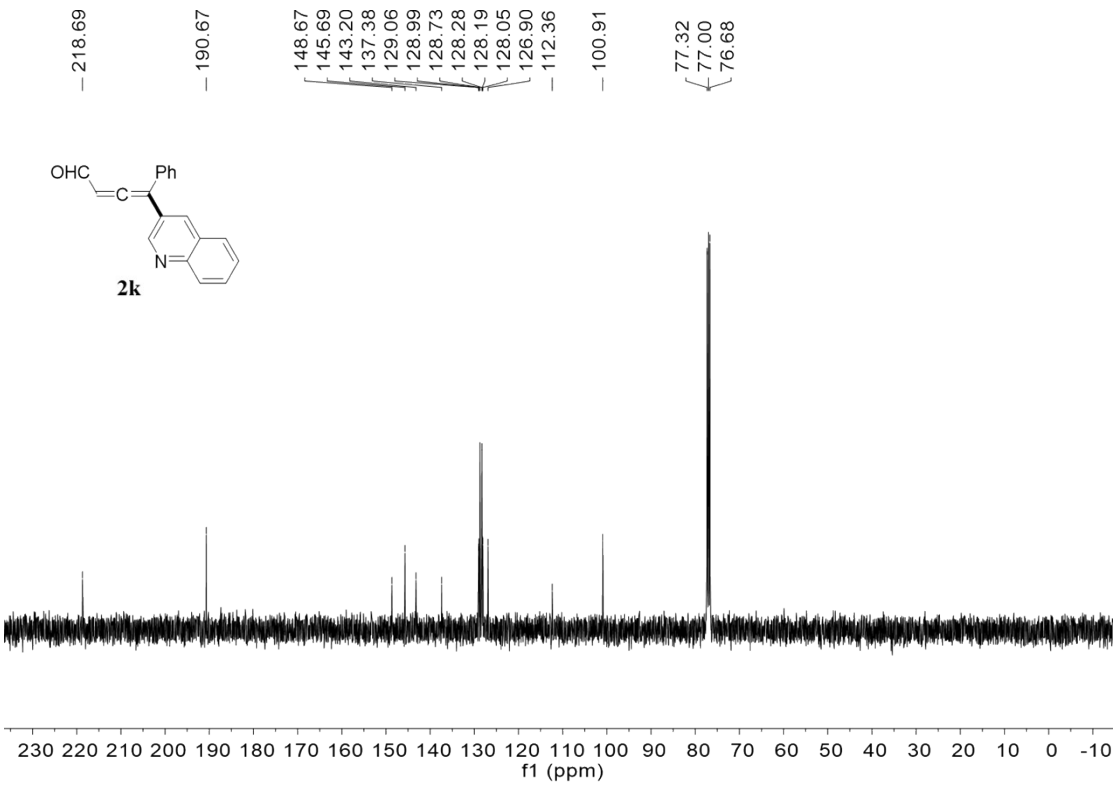
^{13}C NMR of **2j** (100 MHz, $CDCl_3$):



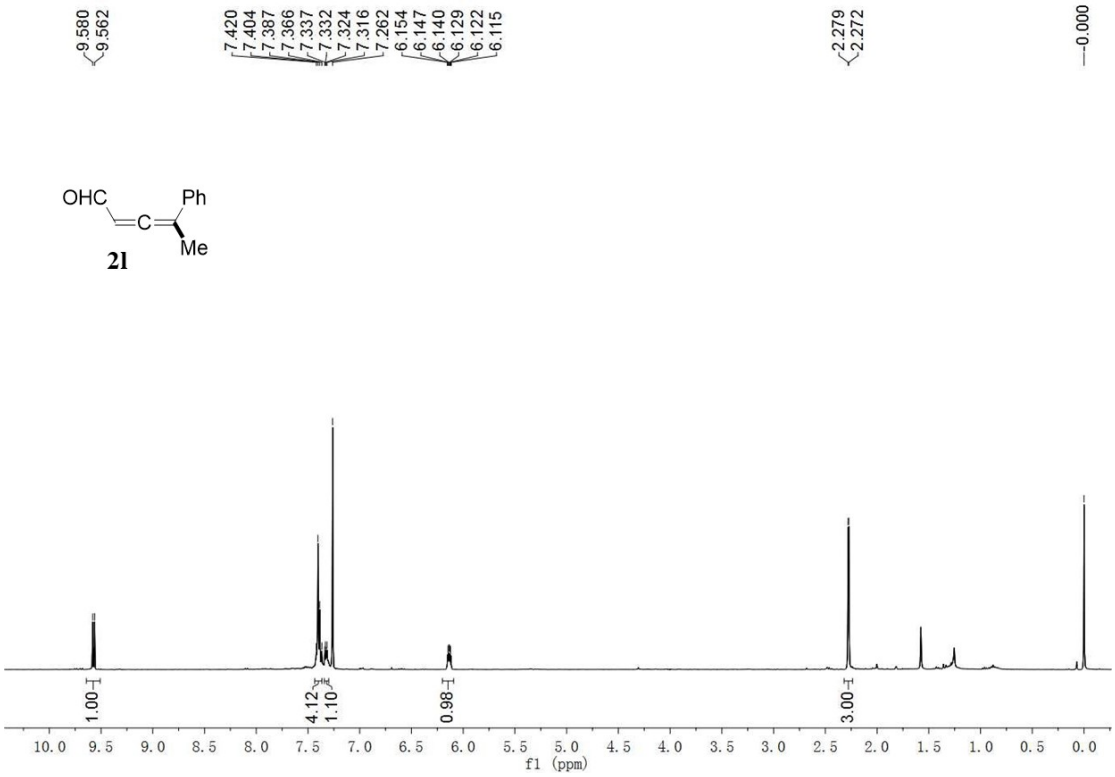
^{1}H NMR of **2k** (400 MHz, $CDCl_3$):



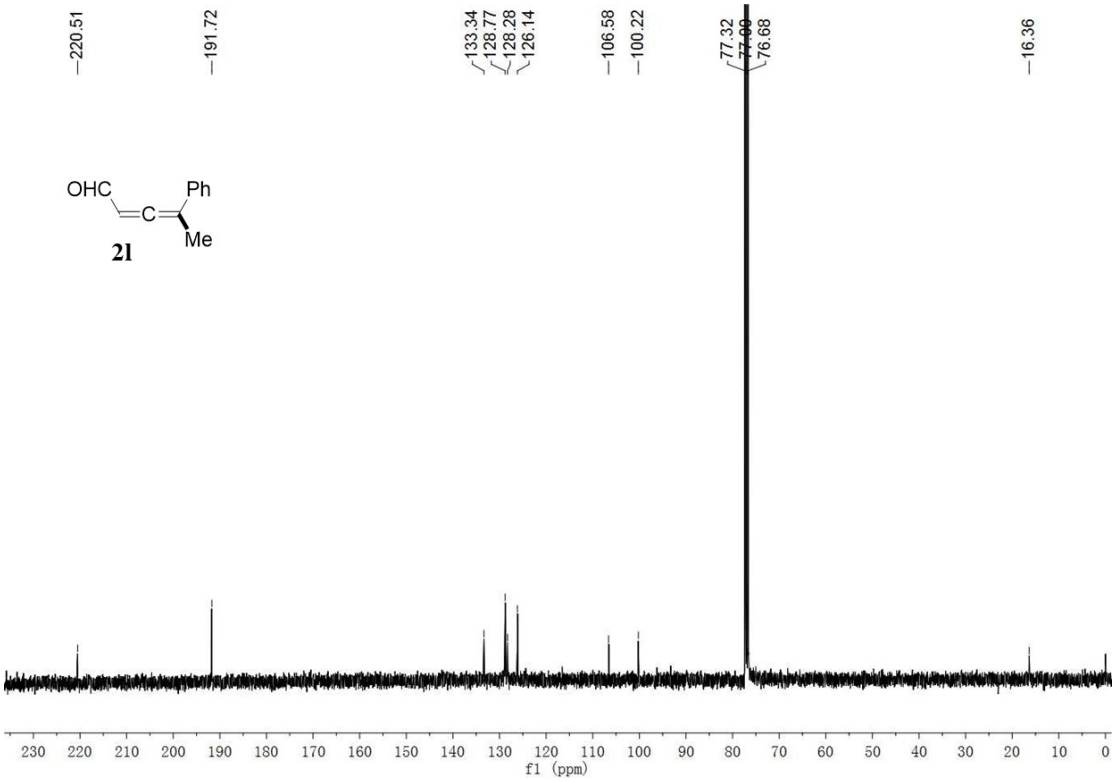
^{13}C NMR of **2k** (100 MHz, $CDCl_3$):



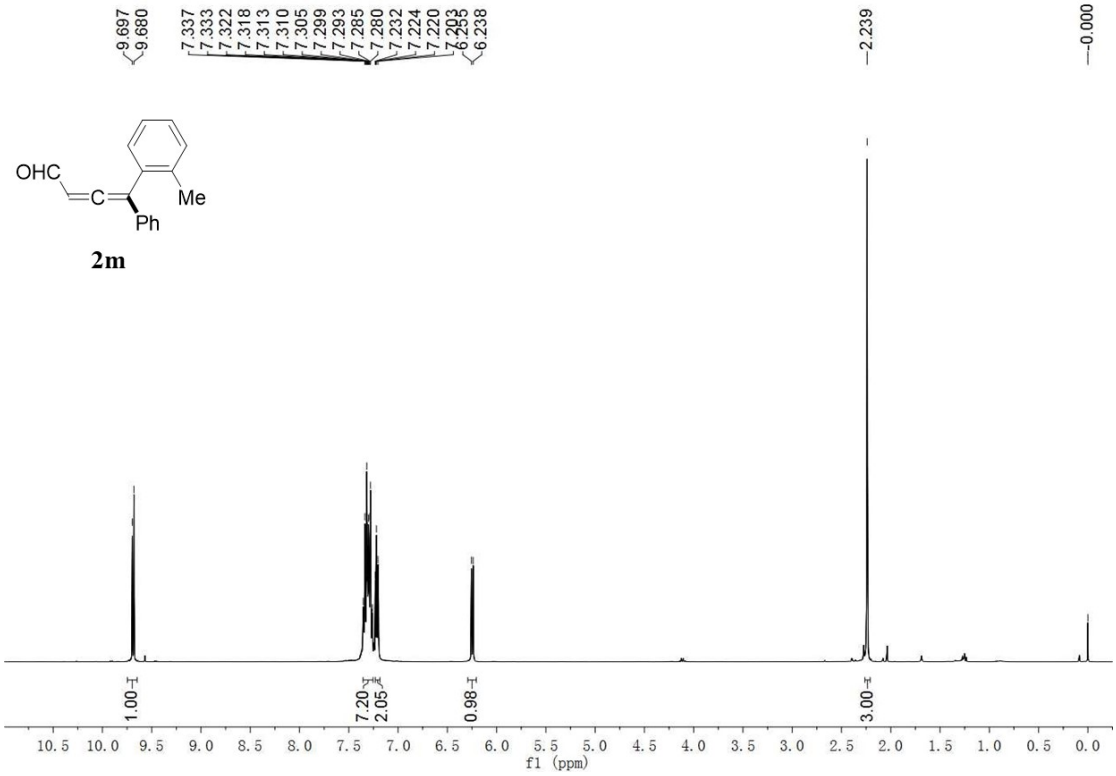
^{1}H NMR of **2l** (400 MHz, $CDCl_3$):



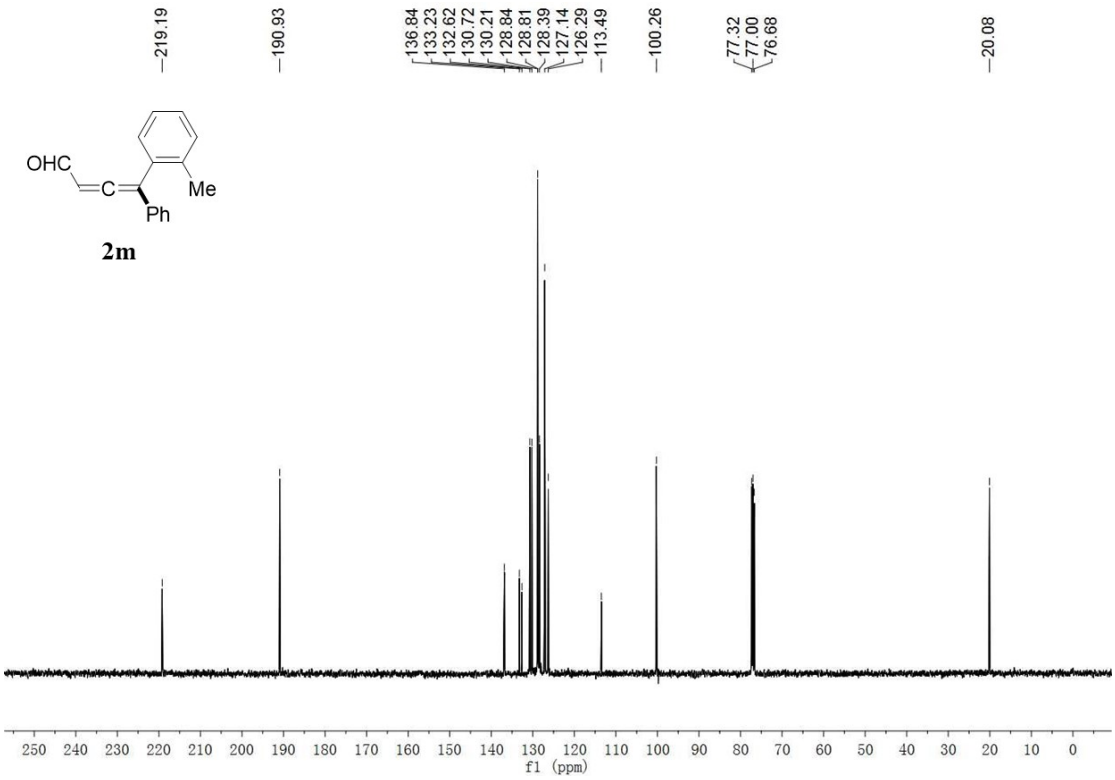
^{13}C NMR of **2l** (100 MHz, $CDCl_3$):



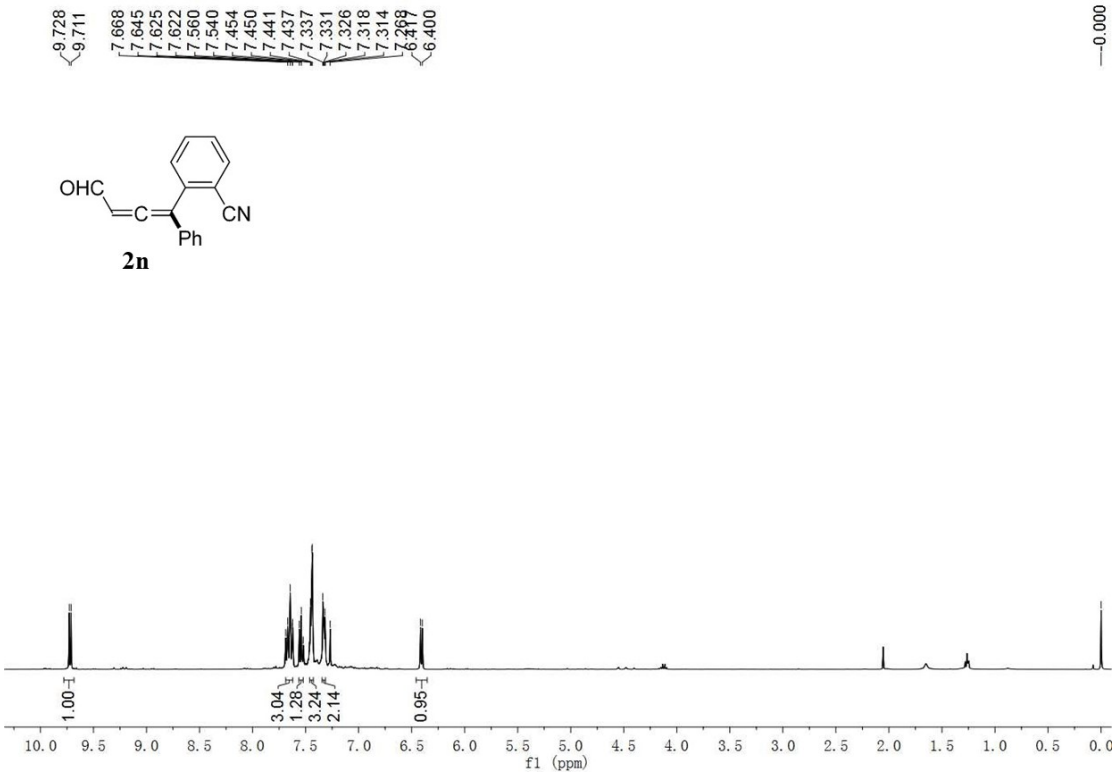
^{1}H NMR of **2m** (400 MHz, $CDCl_3$):



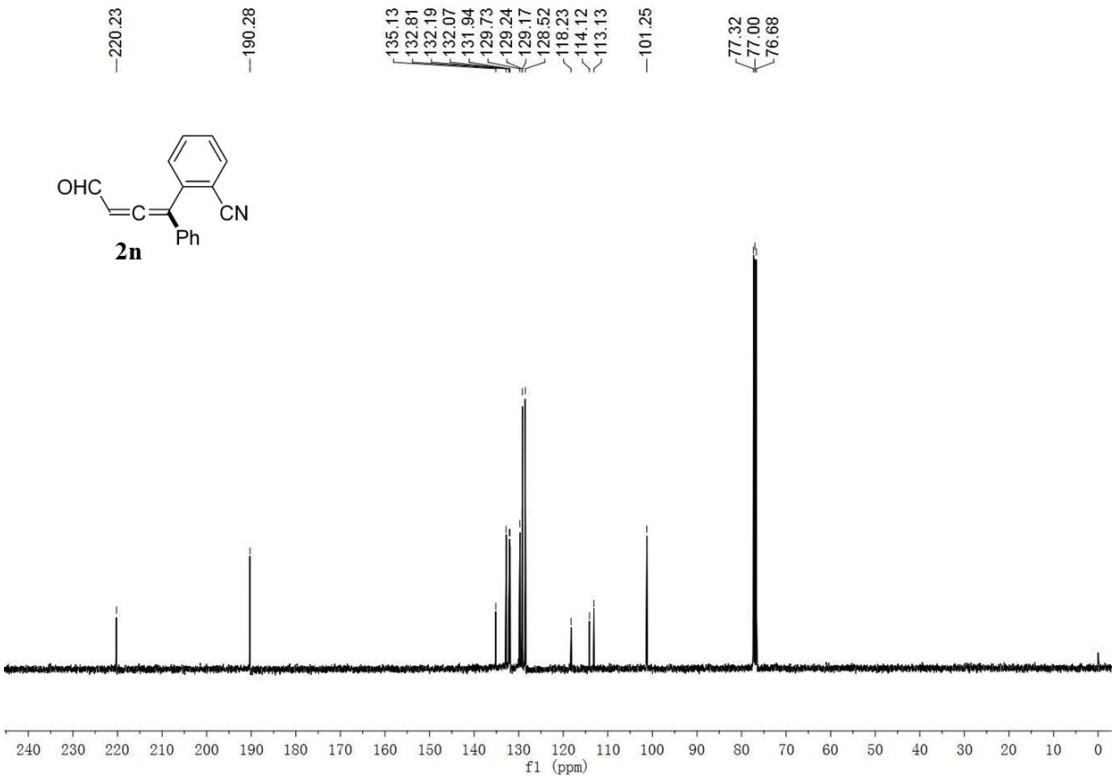
^{13}C NMR of **2m** (100 MHz, $CDCl_3$):



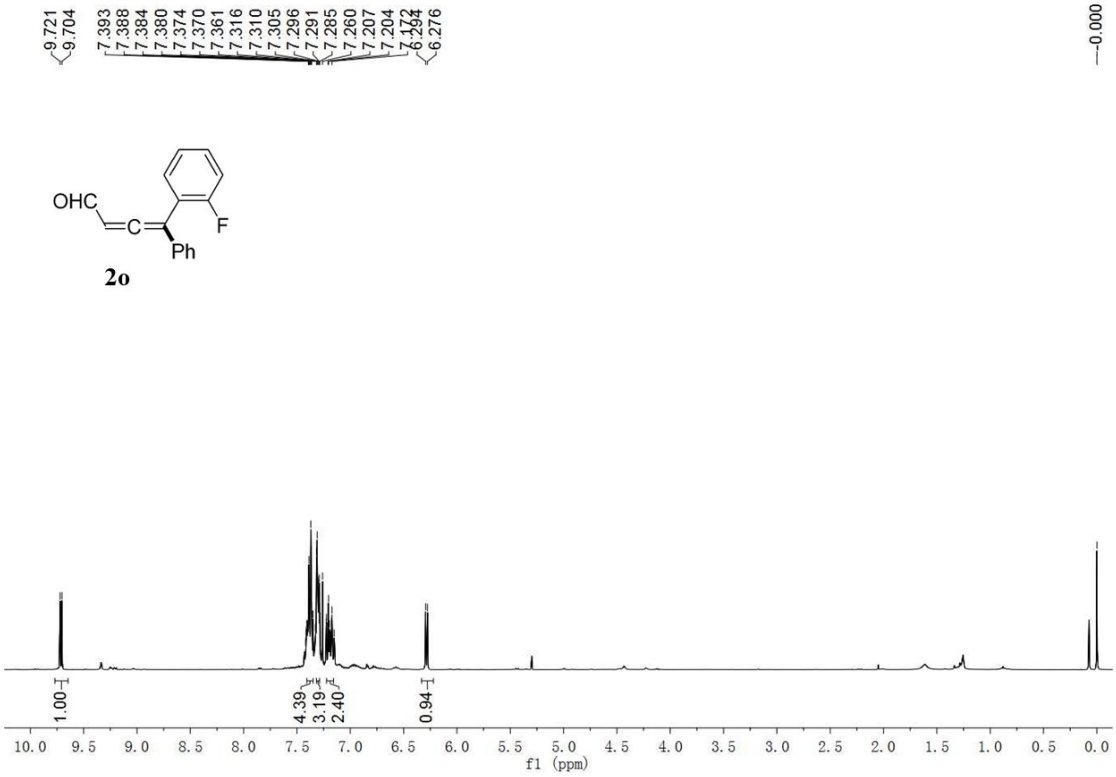
^{1}H NMR of **2n** (400 MHz, $CDCl_3$):



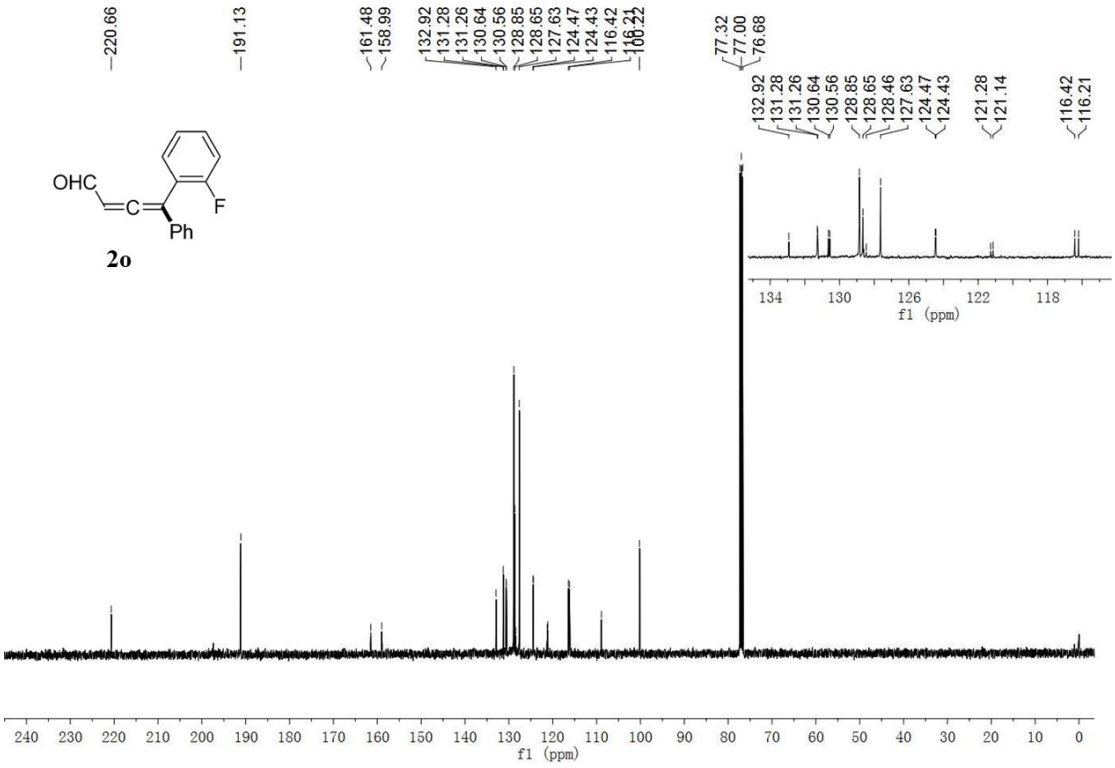
^{13}C NMR of **2n** (100 MHz, $CDCl_3$):



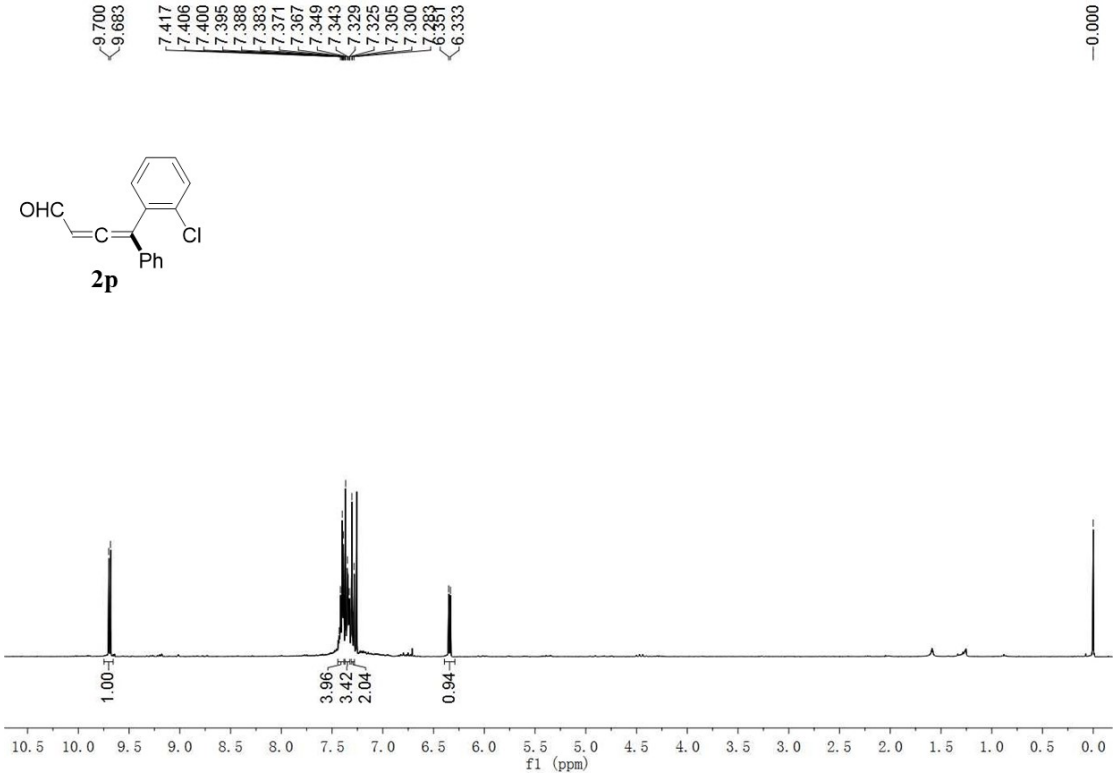
^{1}H NMR of **2o** (400 MHz, $CDCl_3$):



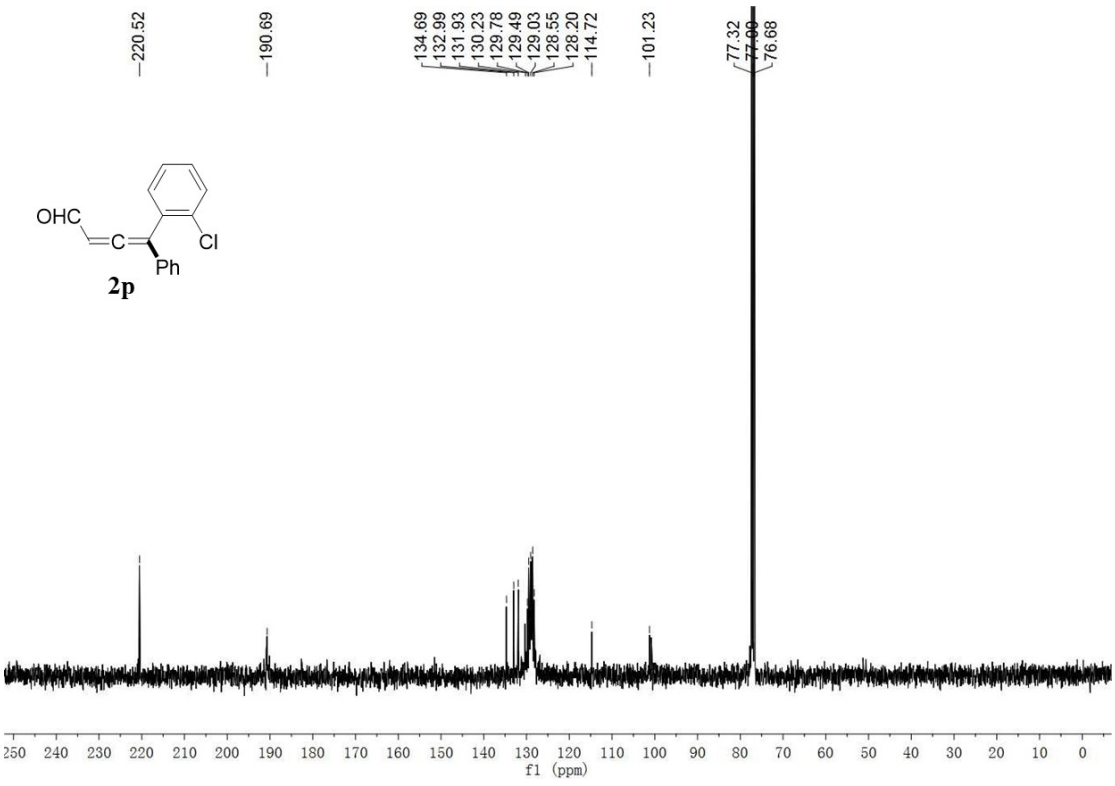
^{13}C NMR of **2o** (100 MHz, $CDCl_3$):



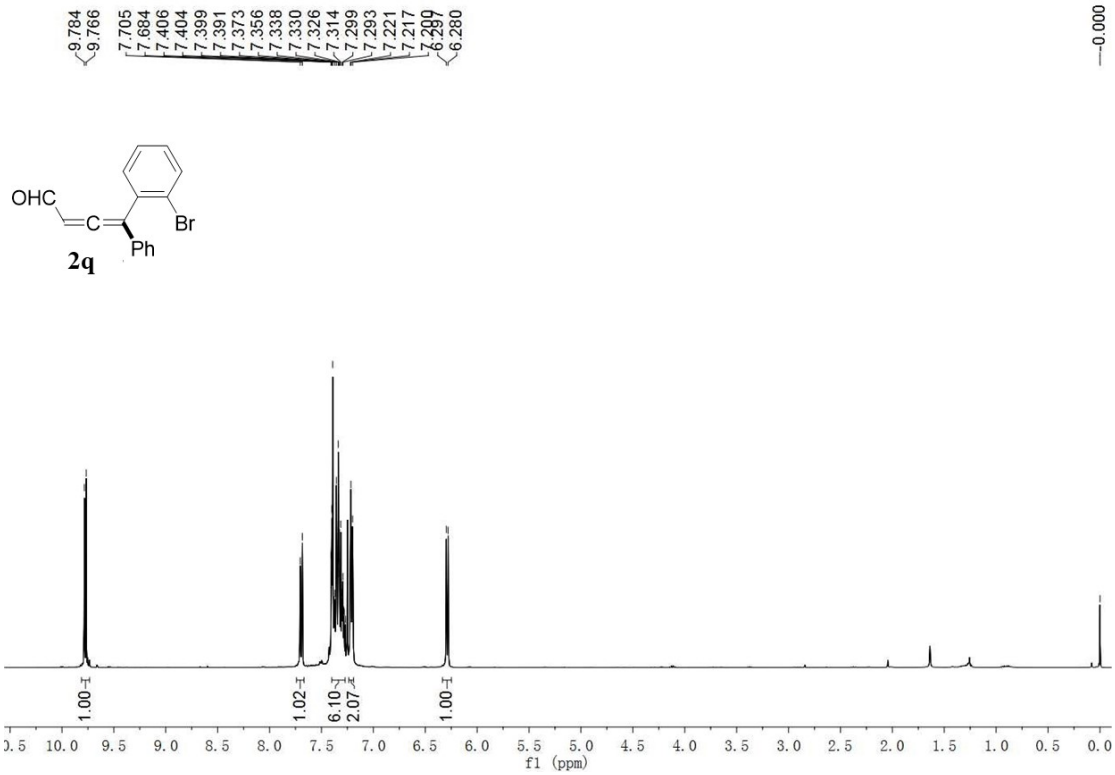
^{1}H NMR of **2p** (400 MHz, $CDCl_3$):



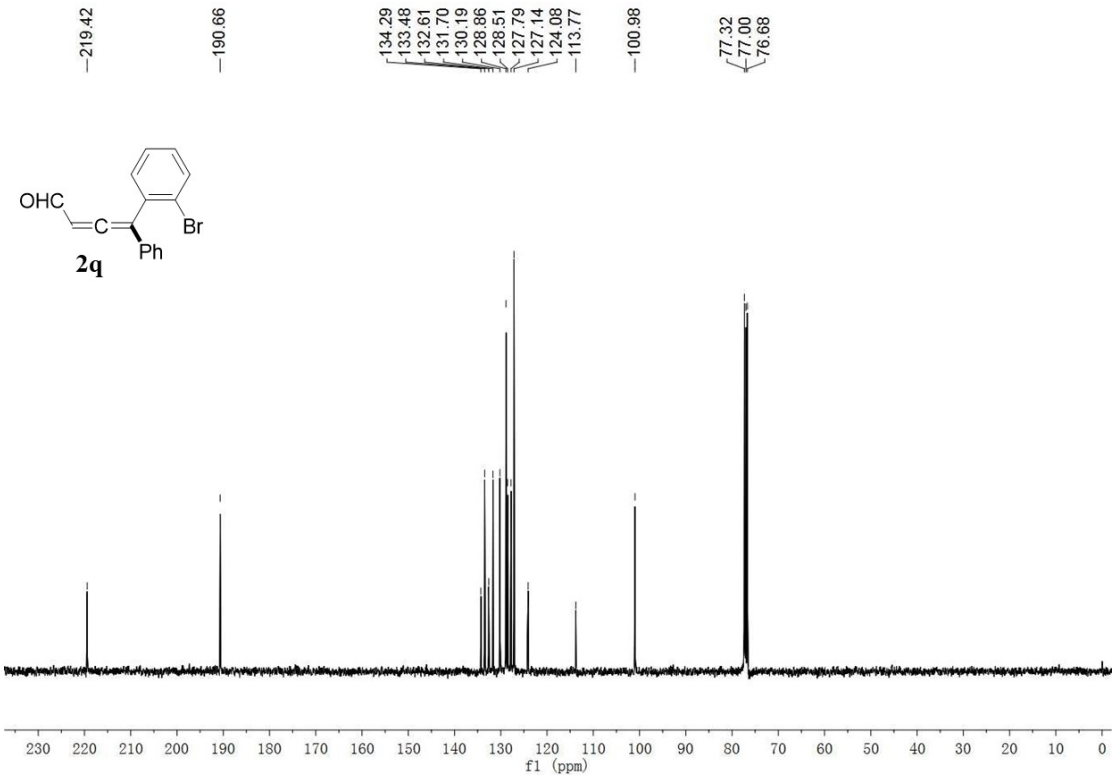
^{13}C NMR of **2p** (100 MHz, $CDCl_3$):



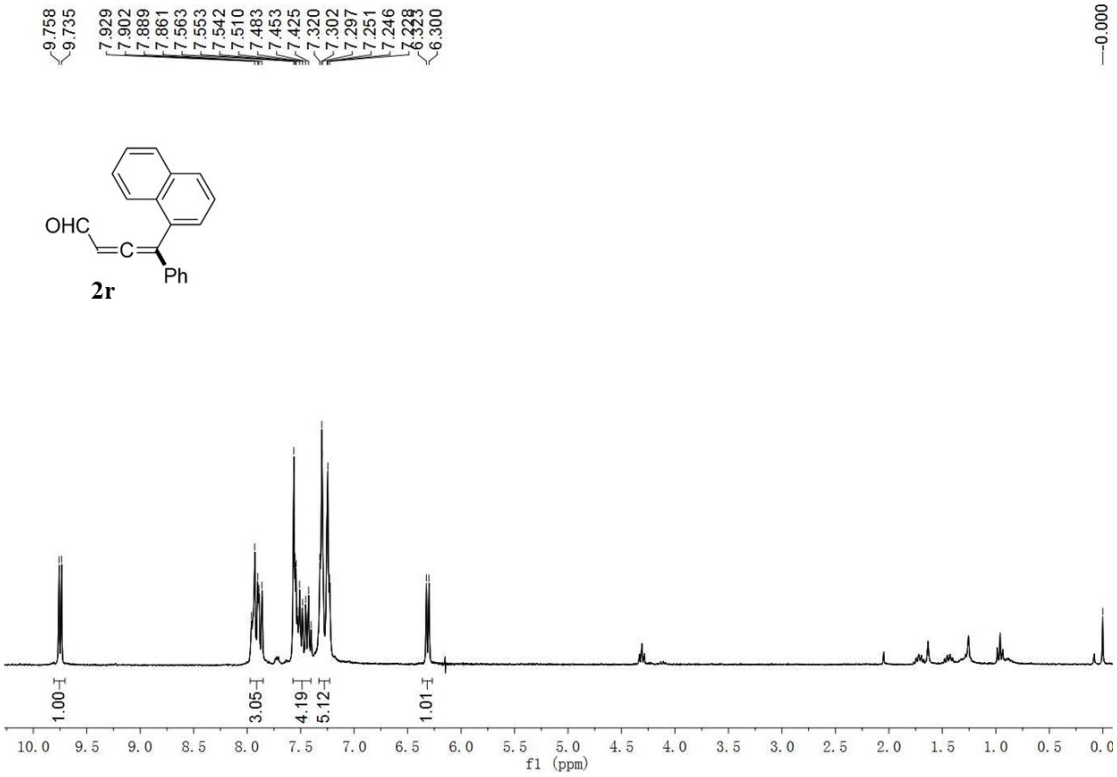
^{1}H NMR of **2q** (400 MHz, $CDCl_3$):



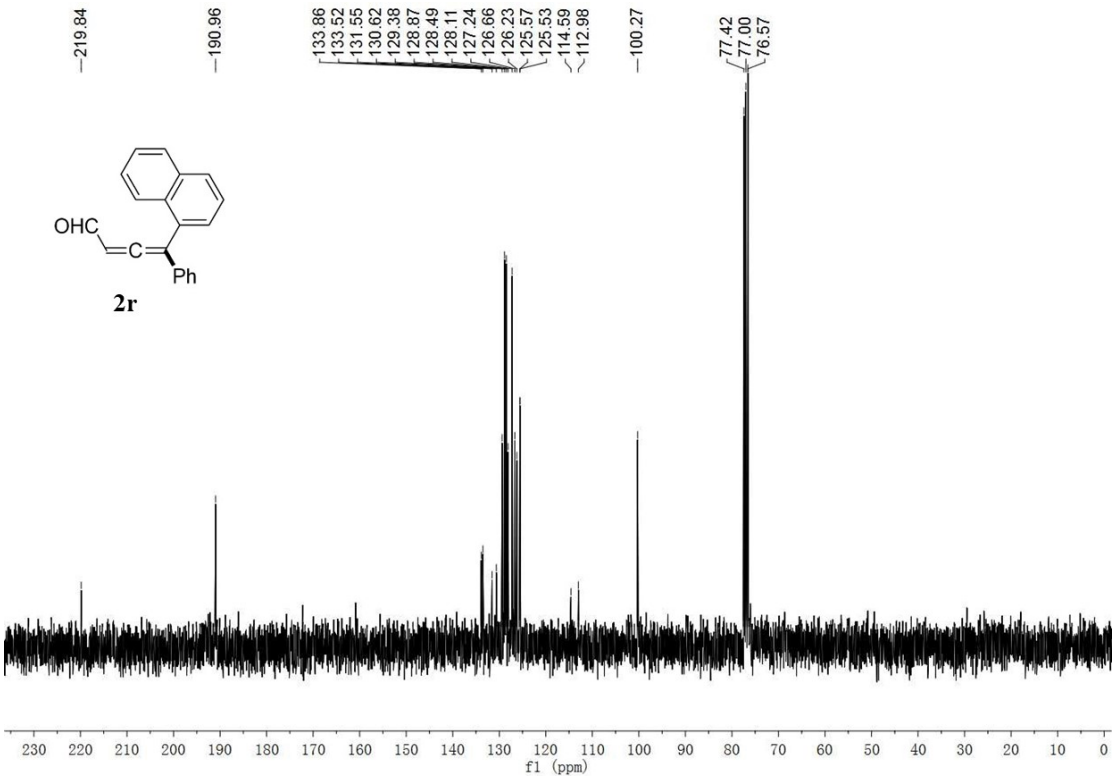
^{13}C NMR of **2q** (100 MHz, $CDCl_3$):



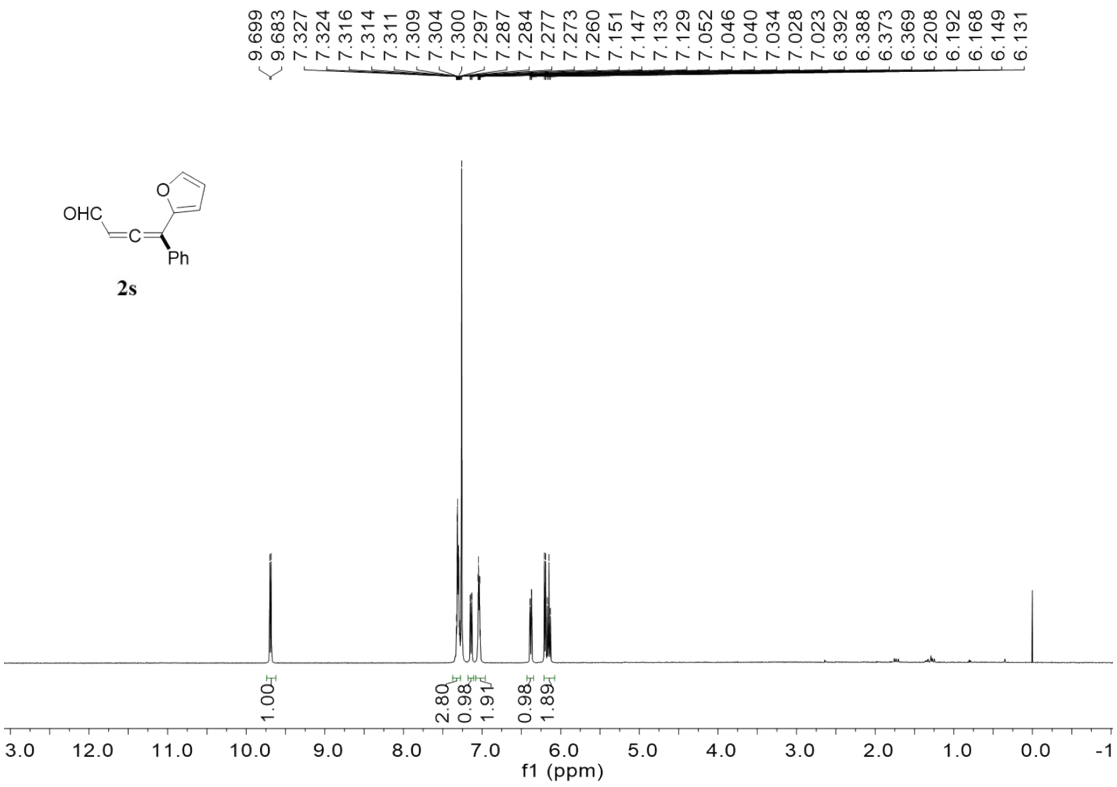
^{1}H NMR of **2r** (400 MHz, $CDCl_3$):



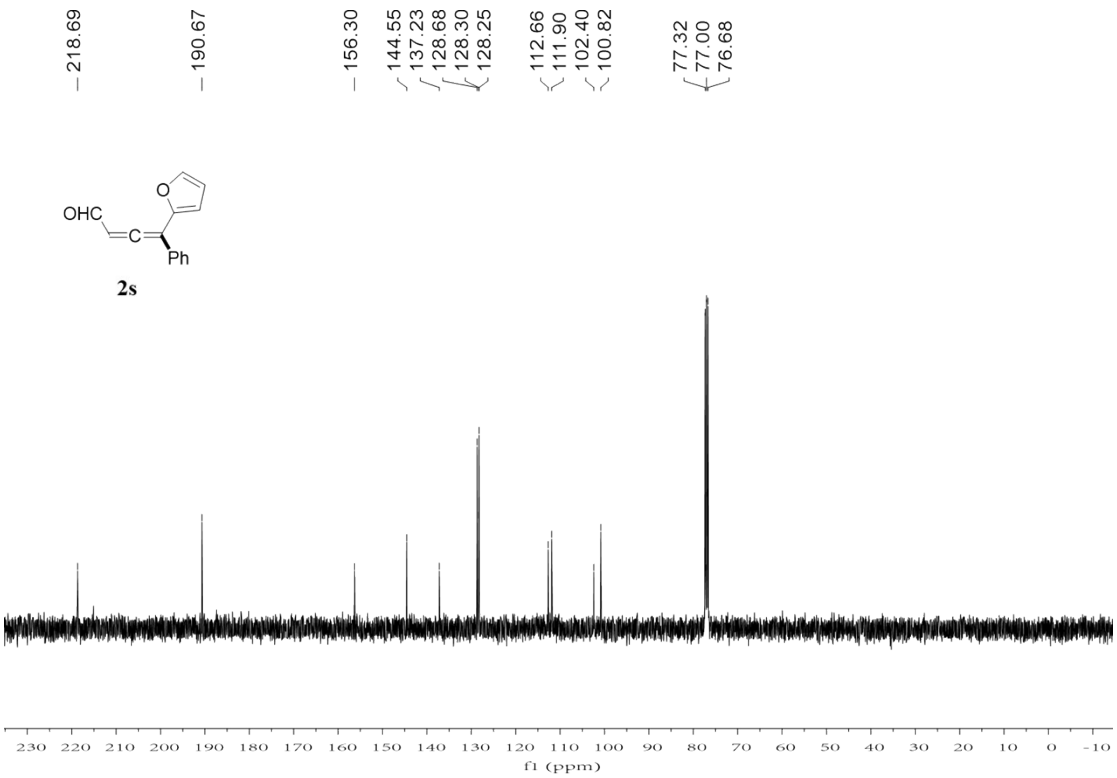
^{13}C NMR of **2r** (100 MHz, $CDCl_3$):



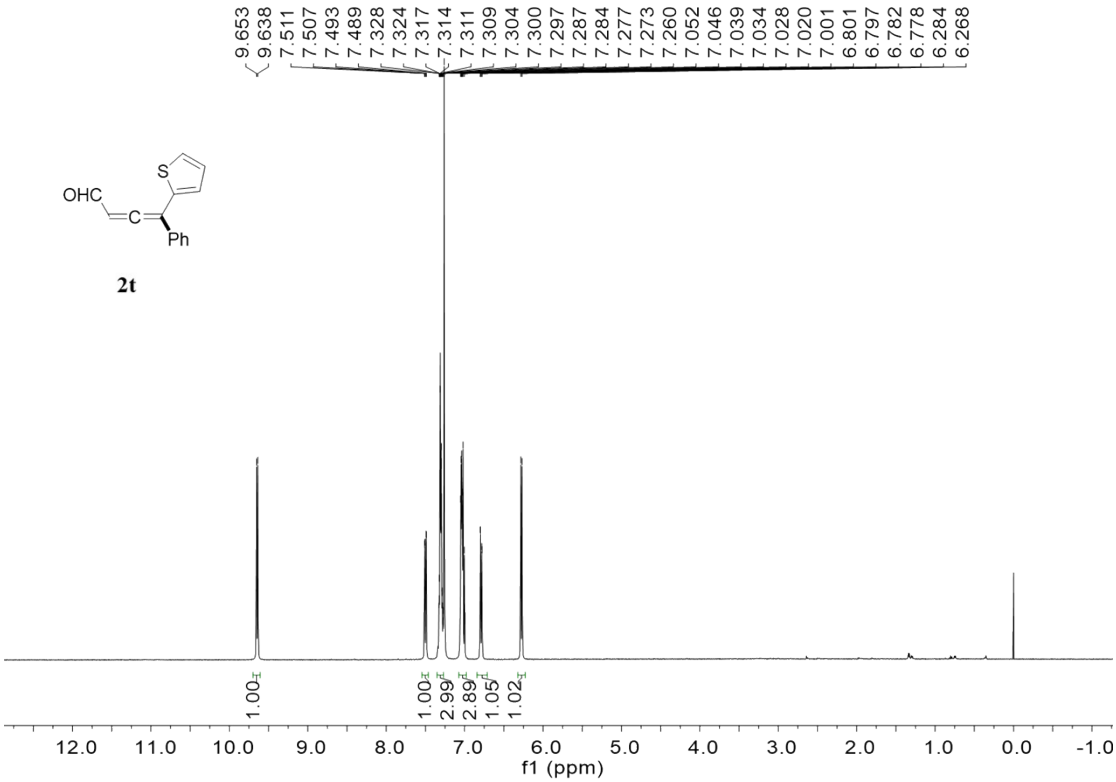
^{1}H NMR of **2s** (400 MHz, $CDCl_3$):



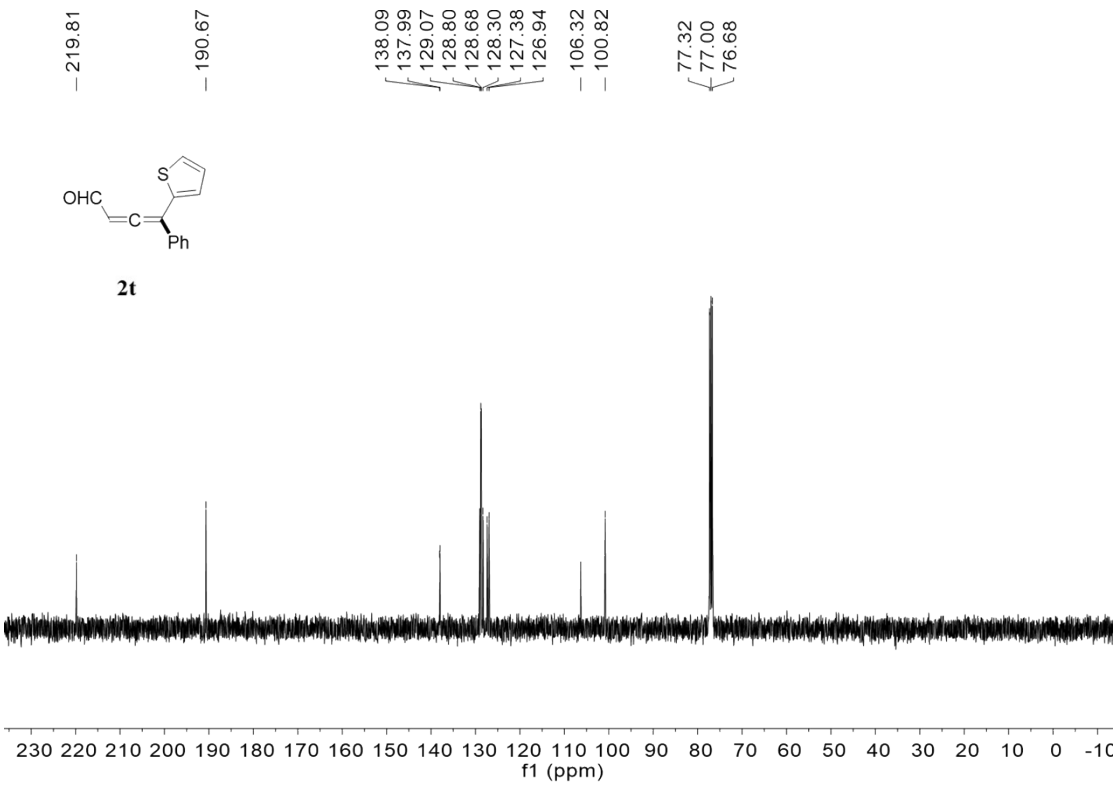
^{13}C NMR of **2s** (100 MHz, $CDCl_3$):



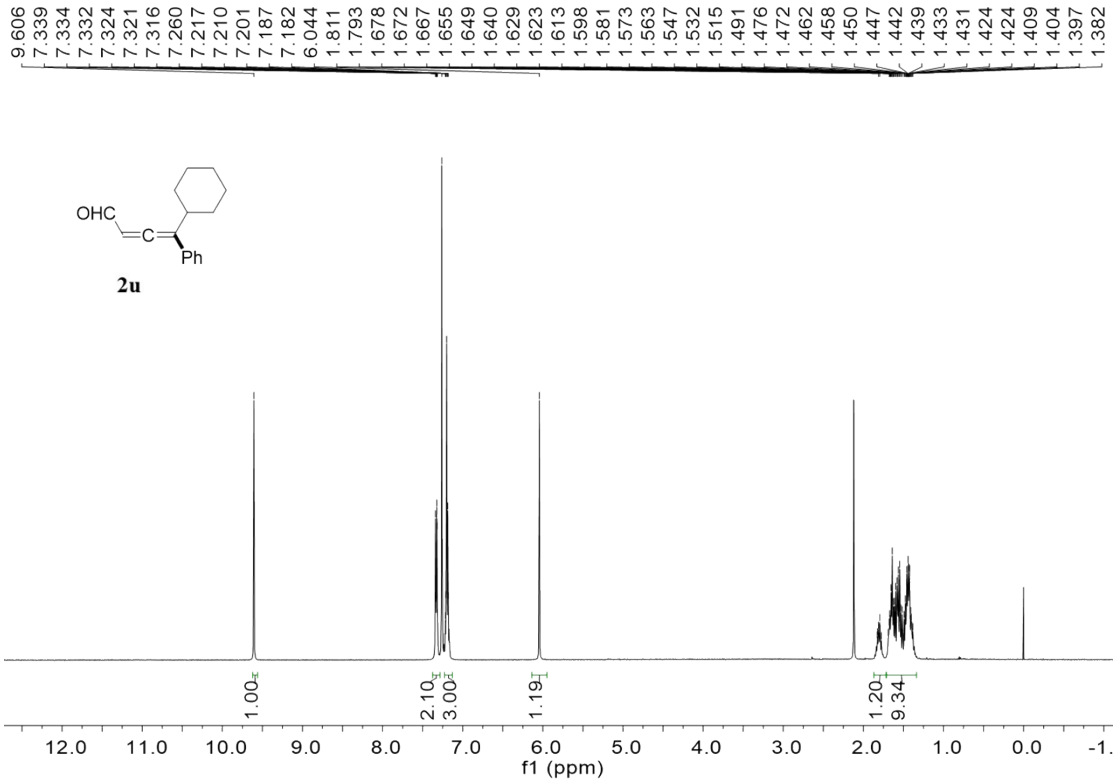
^{1}H NMR of **2t** (400 MHz, $CDCl_3$):



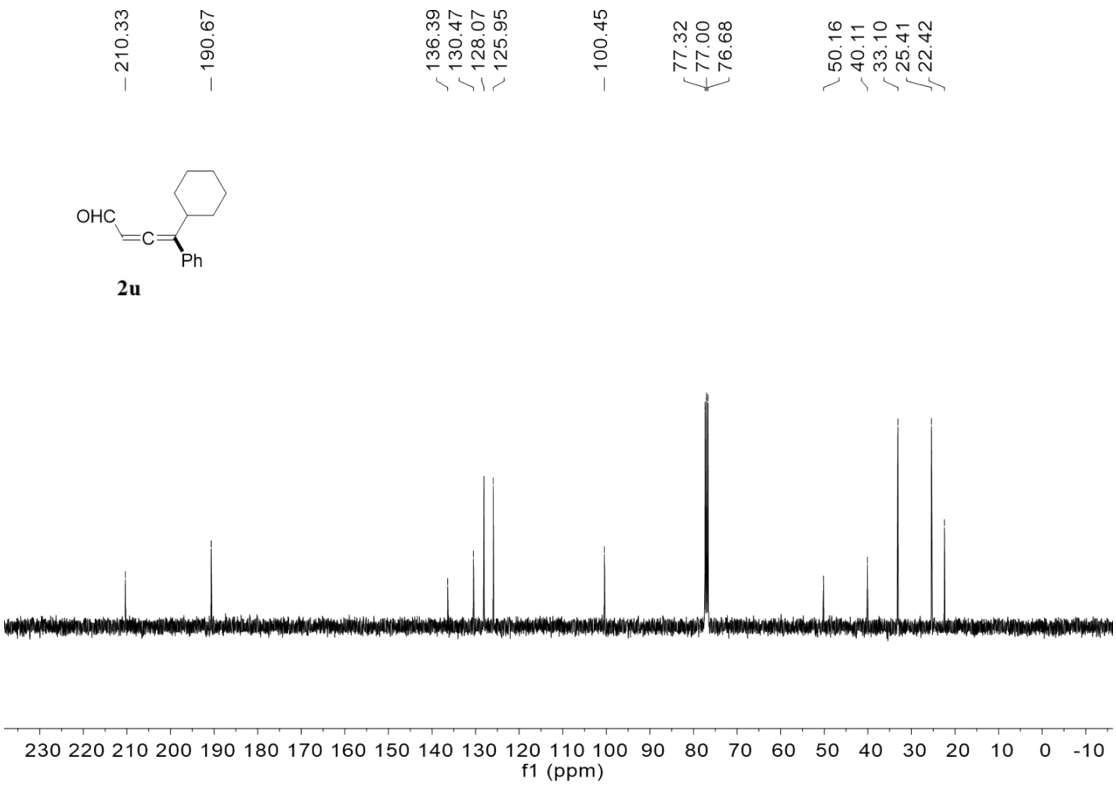
^{13}C NMR of **2t** (100 MHz, $CDCl_3$):



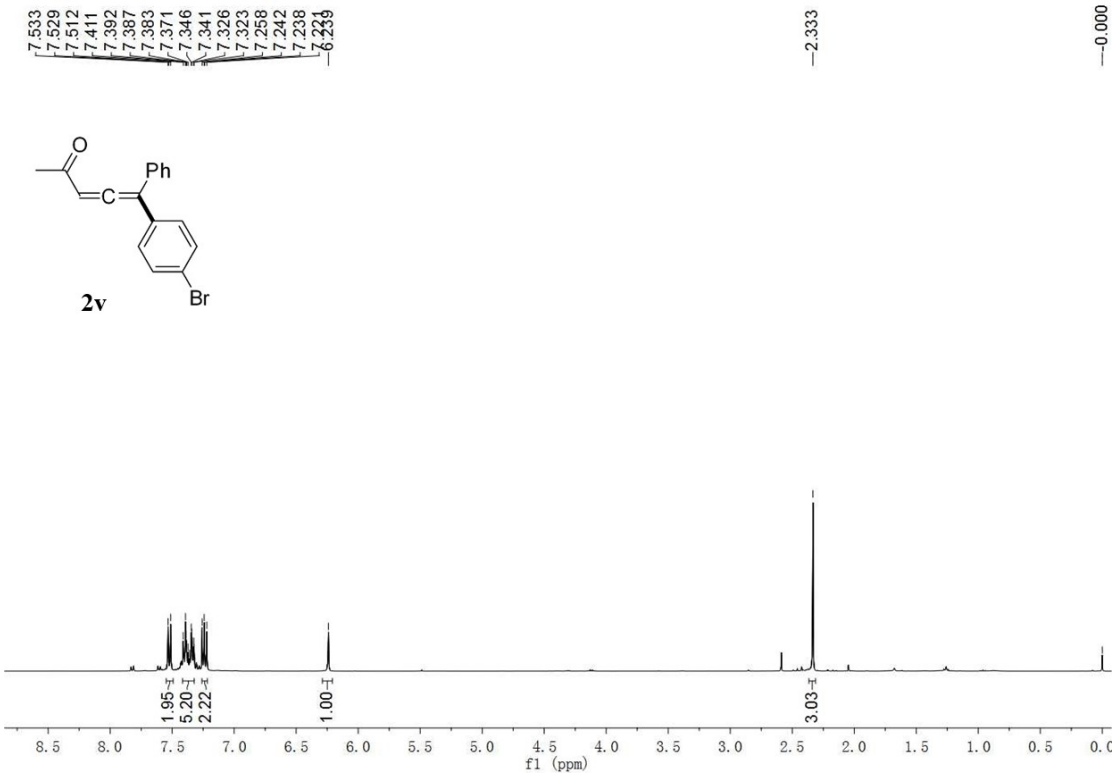
^{1}H NMR of **2u** (400 MHz, $CDCl_3$):



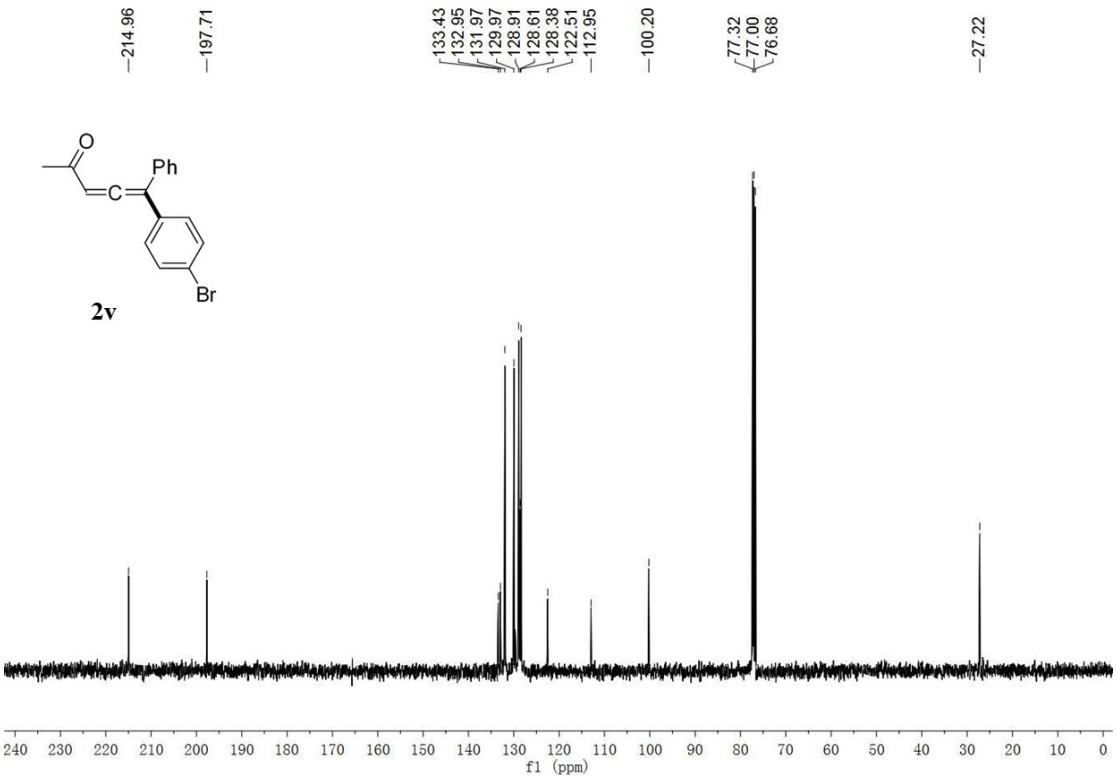
^{13}C NMR of **2u** (100 MHz, $CDCl_3$):



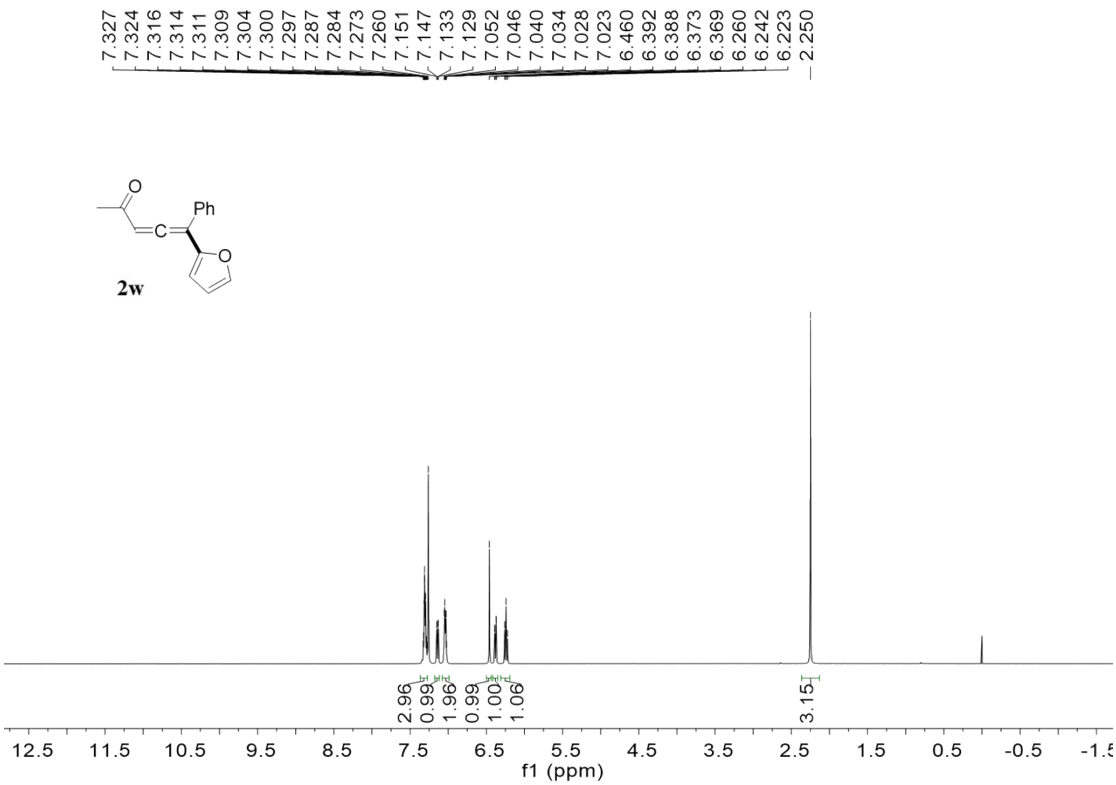
^{1}H NMR of **2v** (400 MHz, $CDCl_3$):



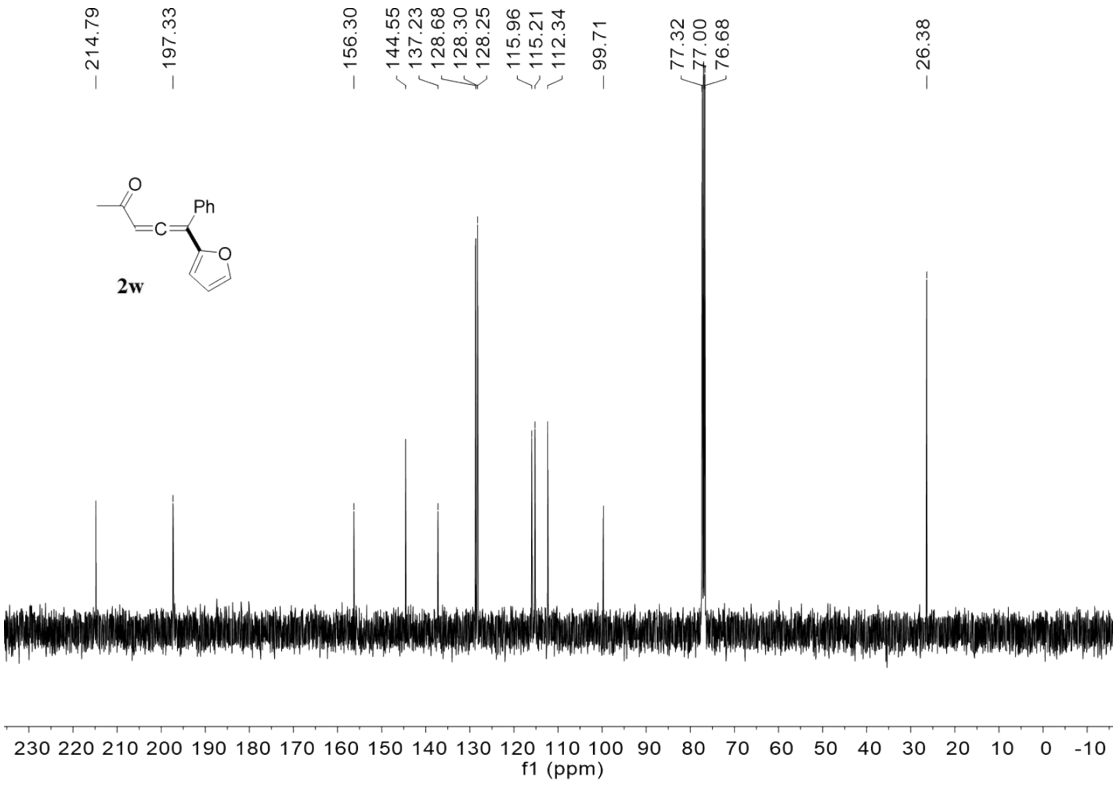
^{13}C NMR of **2v** (100 MHz, $CDCl_3$):



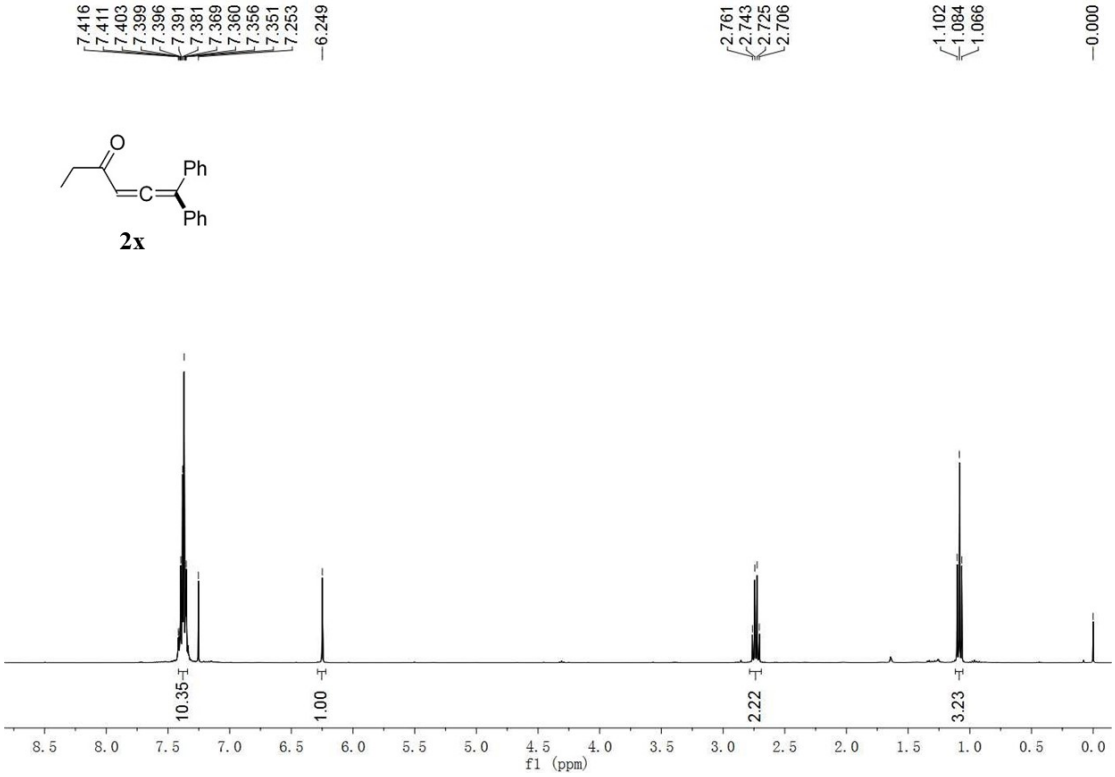
^{1}H NMR of **2w** (400 MHz, $CDCl_3$):



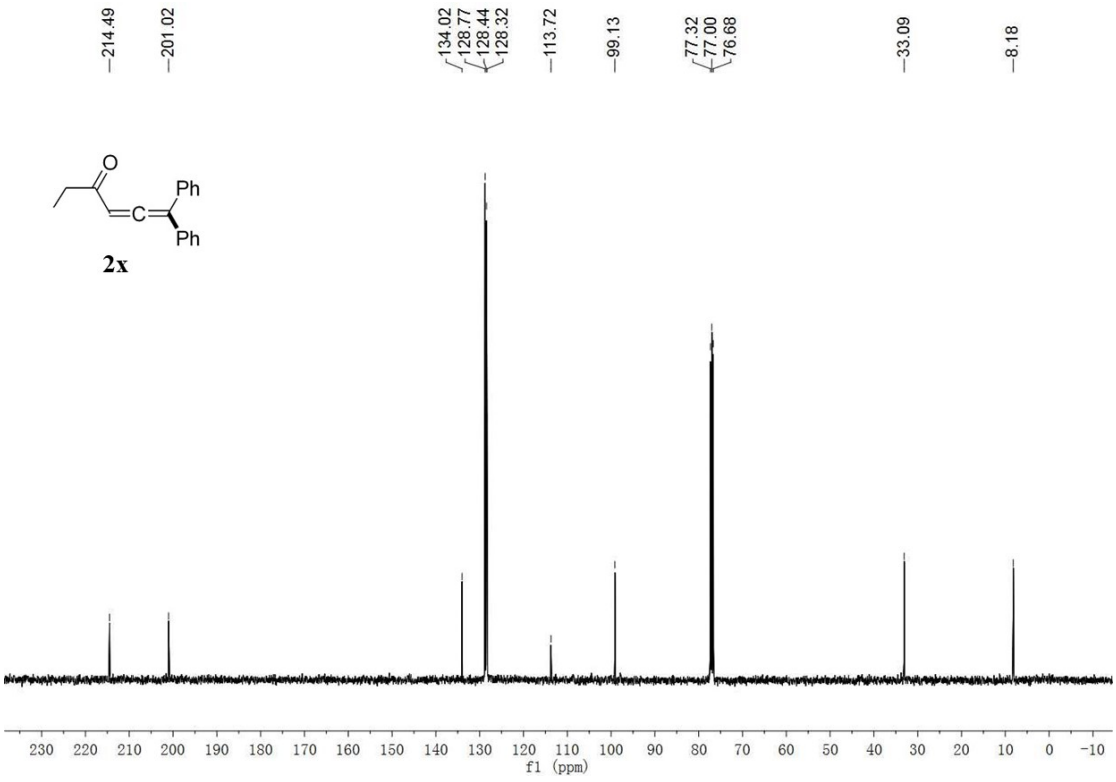
^{13}C NMR of **2w** (100 MHz, $CDCl_3$):



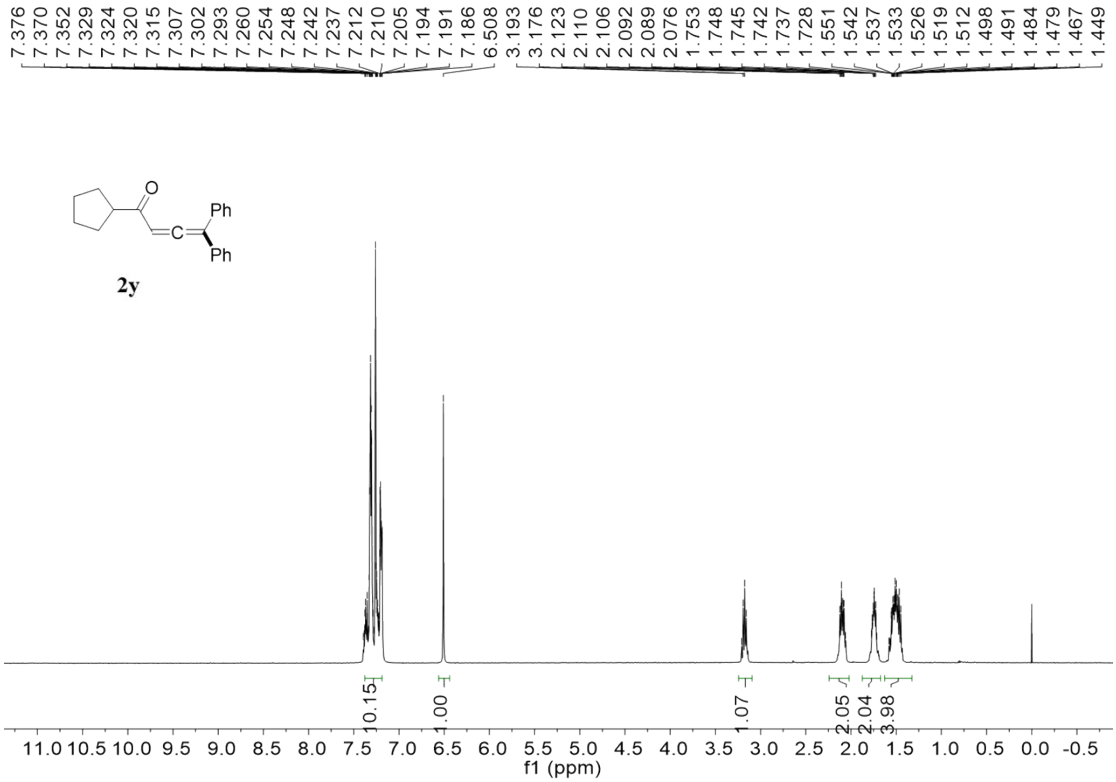
^{1}H NMR of **2x** (400 MHz, $CDCl_3$):



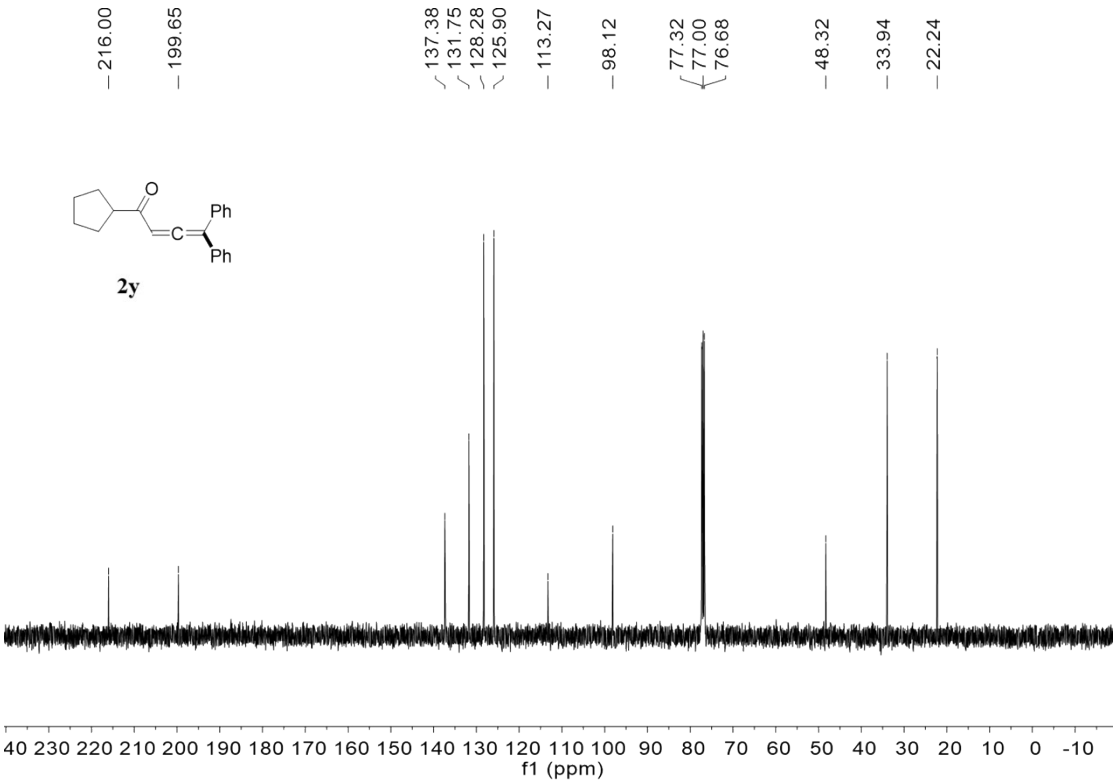
^{13}C NMR of **2x** (100 MHz, $CDCl_3$):



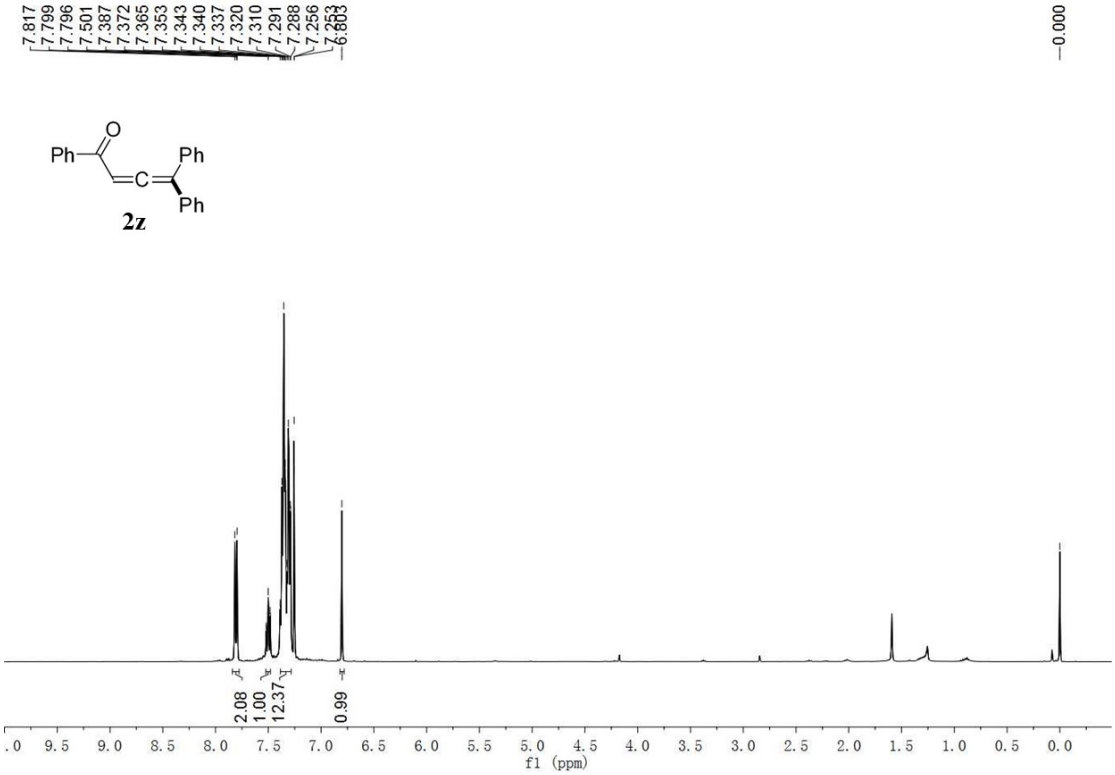
^{1}H NMR of **2y** (400 MHz, $CDCl_3$):



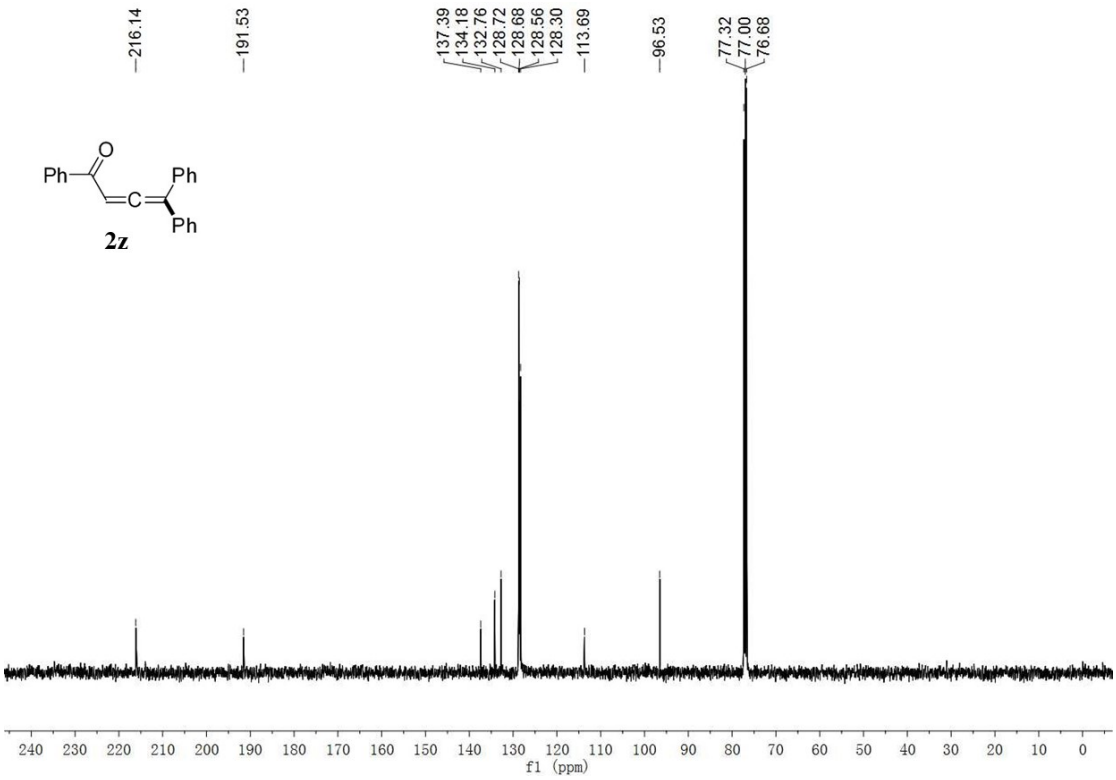
^{13}C NMR of **2y** (100 MHz, $CDCl_3$):



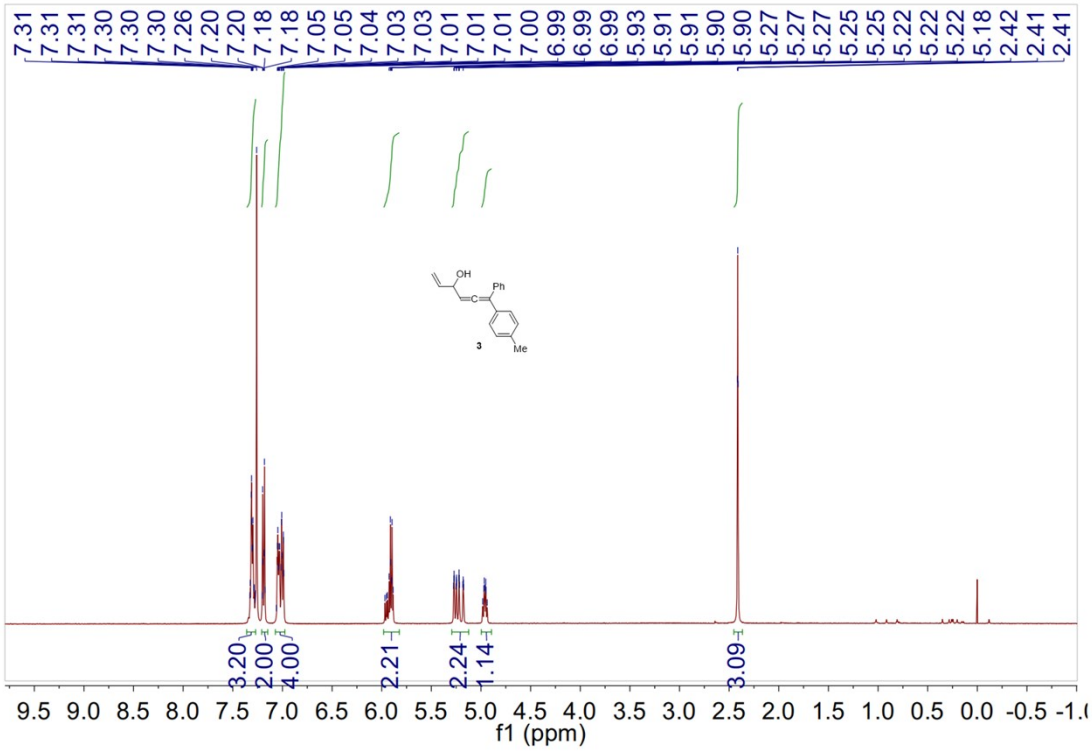
^{1}H NMR of **2z** (400 MHz, $CDCl_3$):



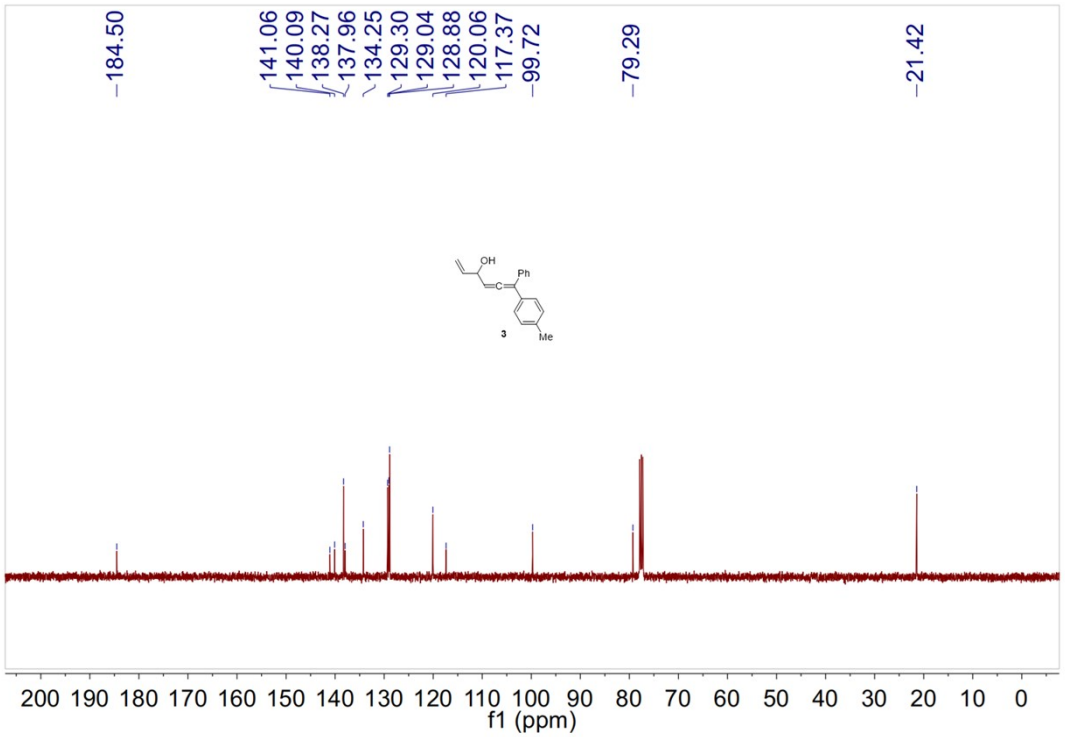
^{13}C NMR of **2z** (100 MHz, $CDCl_3$):



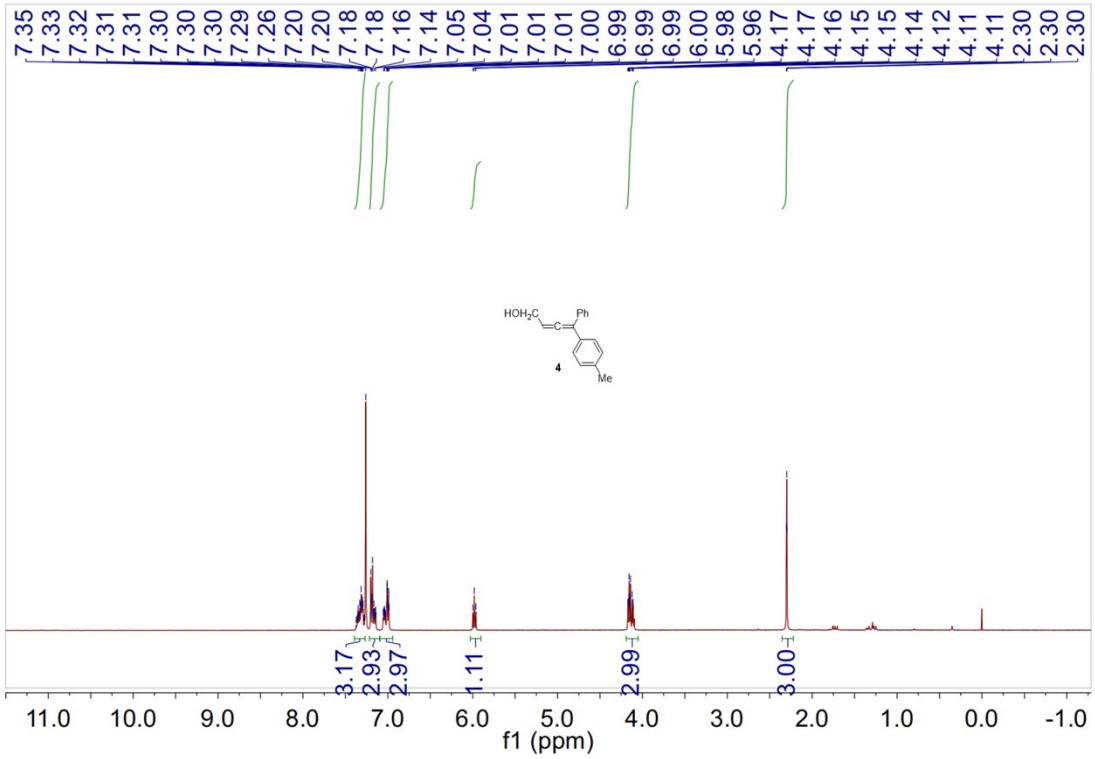
^{1}H NMR of **3** (400 MHz, $CDCl_3$):



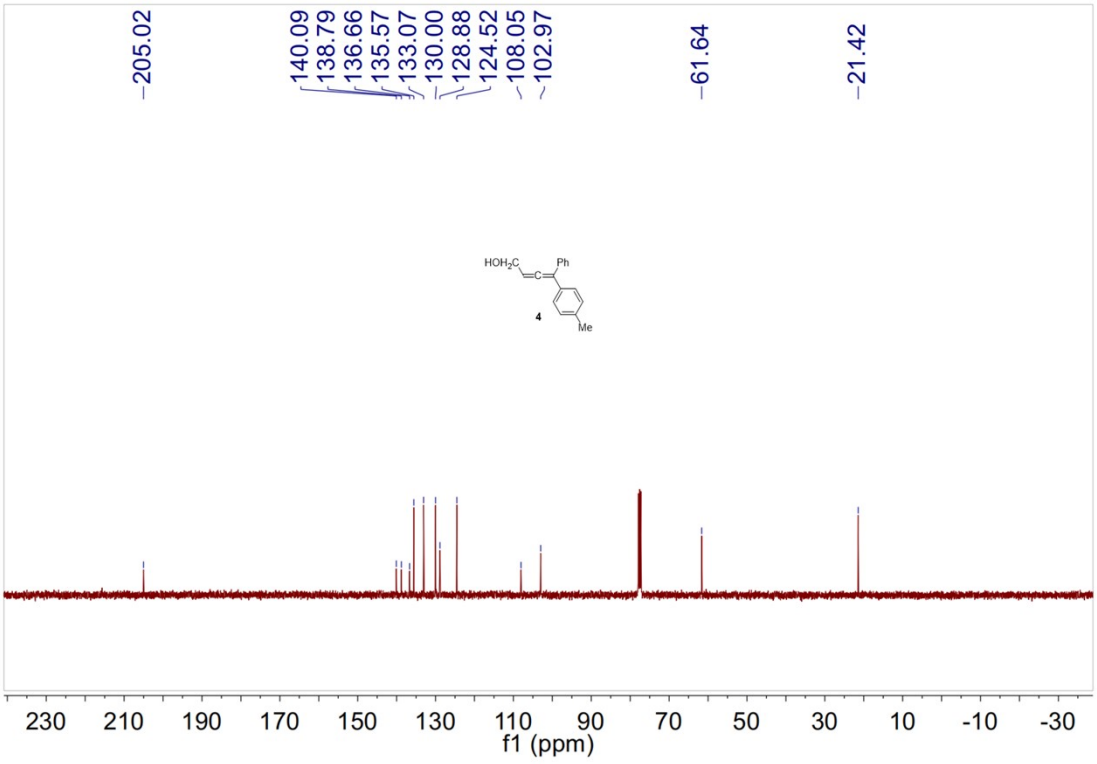
^{13}C NMR of **3** (100 MHz, $CDCl_3$):



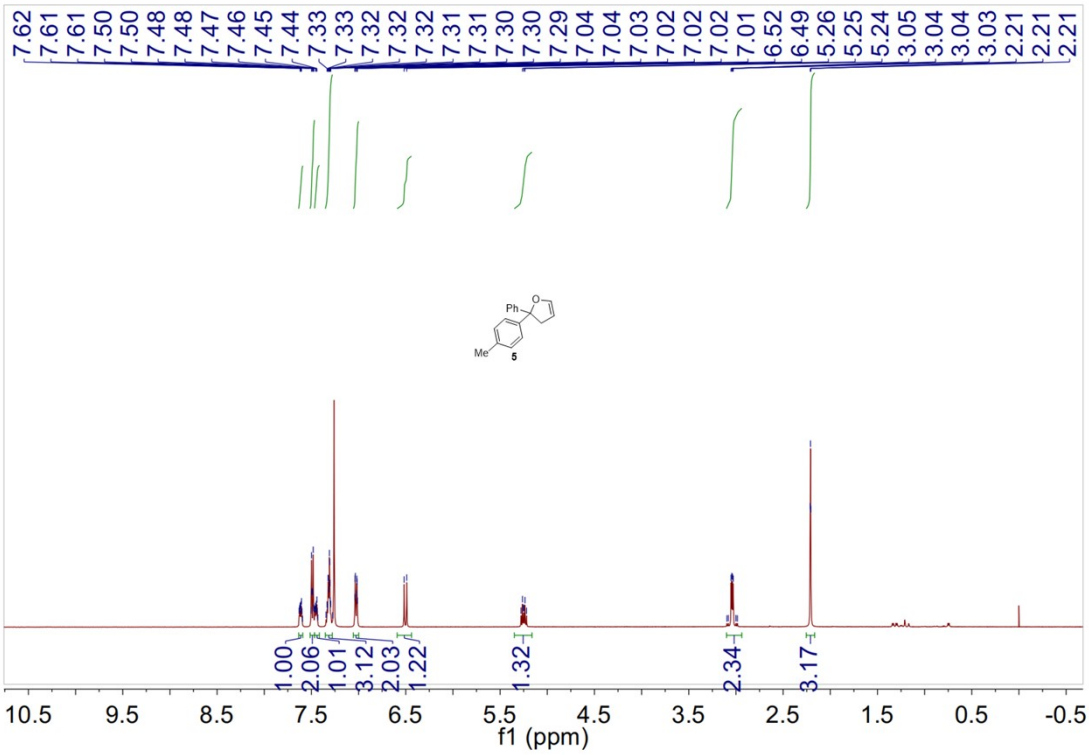
^{1}H NMR of **4** (400 MHz, $CDCl_3$):



^{13}C NMR of **4** (100 MHz, $CDCl_3$):



^{1}H NMR of **5** (400 MHz, $CDCl_3$):



^{13}C NMR of **5** (100 MHz, $CDCl_3$):