Supporting Information

Zeolite Y Nanosheets Assembled Palladium Catalyst with High Catalytic Activity and Selectivity in the Vinylation of Thiophenes

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1. Material synthesis

1.1 Synthesis of NS-Y

Zeolite Y Nanosheets (NS-Y) was synthesized from self-assembly of zeolite Y seed solution with TPOAB, where the TPOAB is a silane of N,N-dimethyl-N-octadecyl-N-(3-triethoxysilylpropyl) ammonium bromide ($[(C_2H_5O)_3SiC_3H_6N(CH_3)_2C_{18}H_{37}]Br$). The molar ratio of compositions was $1.0Al_2O_3/4.5Na_2O/9.0SiO_2/0.64TPOAB/160.0H_2O$. Typically, 29.0 mL water glass and 3.4 mL of zeolite Y seed solution (zeolite Y seed solution was prepared by mixing 1.409 g $NaAlO_2$, 12.7 mL H_2O, 5.116 g NaOH, and 22.4 mL water glass, followed by aging at room temperature for 40-48 h) were mixed. After stirring at room temperature for 30 min, 6.0 mL of TPOAB was slowly added dropwise. After further stirring for 180 min, 5.7 mL of 0.9 mol/L $Al_2(SO_4)_3$ aqueous solution, and 5.9 mL aqueous solution of 2.9 mol/L $NaAlO_2$ and 2.5 mol/L NaOH were added. After stirring at room temperature for 120 min, the obtained aluminosilicate gel was transferred into Teflon-coated stainless-steel autoclave for static crystallization at 100 °C for 4 days. The resultant product was filtered, washed, dried at 120 °C overnight and calcined in air at 550 °C for 5 h. The conventional zeolite Y (Na-form) was synthesized according to our previous work. The H-form zeolite nanosheets (NS-HY) was prepared as followed, the NS-Y sample was ion-exchanged with a NH_4NO_3 solution (1 M) at 80 °C for 4 h, followed by dried at 100 °C for 12 h and calcined 500 °C for 4 h.

1.2. Catalyst preparation

The NS-Y, NS-HY and Y supported Pd catalysts were prepared by ion-exchange method. In a typical preparation, palladium nitride (200 mg) was dissolved in 200 mL deionized water, and then 2 g calcined zeolite powder was added. The suspension was stirred at room temperature for 48 h. After filtration and washing, the obtained solid sample was dried at 50 °C for 48 h in vacuum oven, which was designated as Pd/NS-Y, Pd/NS-HY and Pd/Y. The alumina (γ-Al_2O_3) supported Pd catalyst was prepared by incipient wetness impregnation of the support using palladium nitrate solution. After impregnation, the sample was exposed under ambient condition for 20 h, and further dried at 50 °C for 48 h in vacuum oven, designated as Pd/γ-Al_2O_3. The palladium content determined by the inductively coupled plasma method (ICP, Perkin-Elmer 3300 DV) is 2.5, 2.1, 2.3 and 2.6 wt.% for the Pd/NS-Y, Pd/NS-HY, Pd/Y and Pd/γ-Al_2O_3 samples, respectively.

2. Characterization

X-ray powder diffraction (XRD) analysis was conducted on a RIGAKU UltimalV diffractometer, using Cu *Kα* radiation. Nitrogen adsorption-desorption isotherm was obtained on a Micromeritics ASAP2020M apparatus at the temperature of liquid nitrogen (-196 °C). Specific surface area was calculated from the adsorption data, using the Brunauer-Emmett-Teller (BET) equation. The pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) model. Scanning electron microscopy (SEM) images were obtained on a field-emission scanning electron microscope (SUPRA55) operating at an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) images of the sample were obtained on a JEM-2100F microscope with a limited line resolution capacity of 1.4 Å, under a voltage of 200 kV. Before characterization by the TEM technique, the sample was cut into thin slices and dropped onto a Cu-grid coated with carbon membrane. X-ray photoelectron spectroscopic (XPS) experiments were performed on an ESCALAB MK II system. The acidity of the NS-Y and NS-HY samples was measured using temperature-programmed desorption of ammonia (NH_3-TPD) on a Micromeritics ASAP2920 instrument. 200 mg of sample was placed in a quartz tube and pretreated in a helium stream at 450 °C for 2 h. After the sample was cooled to 120 °C, NH_3-He mixed gas (10 vol% NH_3) was passed over the sample for 30 min. After removal of the physically adsorbed NH_3 by flowing He stream for 2 h at 120 °C, the sample was heated to 800 °C with a heating rate of 10 °C/min.

3. Activity assessment

All reagents unless otherwise noted were obtained from commercial sources (purity > 99%) and used without further purification. The typical experimental procedure for the cross-coupling reaction was as followed: 50 mg catalyst, 0.5 mmol thiophenes, 0.25 mmol alkenes, 0.5 mmol benzoquinone (BQ), and 2 mL of Co-solvent (1 mL DMSO, 1 mL HOAc) were placed into a 10 mL glass vessel. The reaction was proceeded at setting temperature for desired time. After the reaction finished, the catalyst was separated by centrifugation and filtered to obtain the liquid phase. The liquid products were analyzed by an Agilent 7890B gas chromatograph equipped with a flame ionization detector. The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (60-90 °C) and ethyl acetate as eluents. Compounds described in the

literature were characterized by comparing their **^{1}H** and **^{13}C NMR** spectra and MS data to the reported data. The **^{1}H NMR** (500 MHz) and **^{13}C NMR** (125 MHz) were recorded with spectrometers at 20 °C using $CDCl_3$ as the solvent. Chemical shifts were given in parts per million relative to TMS as the internal standard at room temperature.

The scale-up experiment was carried out in an autoclave (Parr 5500, 300 mL). The reaction mixture was as follows: 5 g Pd/NS-Y catalyst, 50 mmol 2-methyl thiophene, 25 mmol n-butyl acrylate, 50 mmol benzoquinone (BQ), and 150 mL of Co-solvent (75 mL DMSO, 75 mL HOAc) were placed into an autoclave. The reaction temperature is 60 °C, reaction time is 8 h, and stirring rate is 600 rpm.

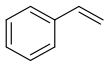
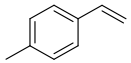
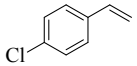
4. Tables

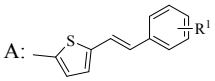
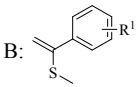
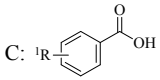
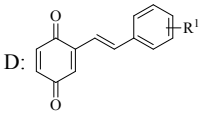
Table S1 Texture parameters of all the samples

Samples	S_{BET} (m^2/g) [a]	V_{mic} (cm^3/g) [b]	S_{ext} (m^2/g) [c]	V_{meso} (cm^3/g) [d]
NS-Y	817	0.27	138	0.20
NS-HY	797	0.26	127	0.16
Y	883	0.32	57	0.06
γ-Al_2O_3	322	-	322	0.45

[a] BET surface area. [b] Microporous pore volume. [c] External surface area. [d] Mesoporous pore volume.

Table S2 The product selectivities of the Pd/NS-Y and $Pd(OAc)_2$ catalysts in the vinylation of thiophenes

Catalyst	Thiohene	Alkene	Conversion (%)	Selectivity (%)				
				S_A (%)	S_B (%)	S_C (%)	S_D (%)	Other (%)
$Pd(OAc)_2$			95	57	16	15	10	2
Pd/NS-Y			96	85	5	4	1	5
$Pd(OAc)_2$			98	79	4	8	5	4
Pd/NS-Y			97	88	2	1	3	6
$Pd(OAc)_2$			96	74	7	9	6	4
Pd/NS-Y			98	93	2	2	1	2

A: 
B: 
C: 
D: 

5. Figures

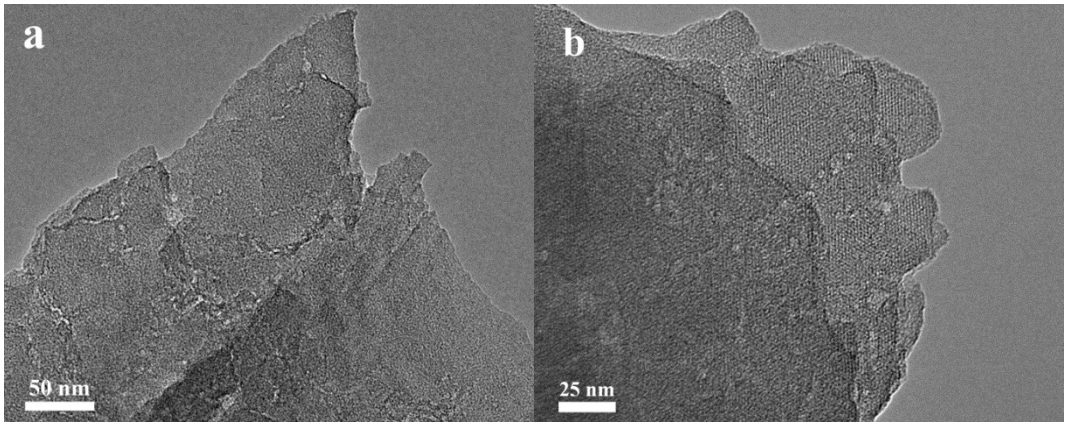


Fig. S1. (a) Low and (b) high resolution TEM images of the thin-sectioned NS-Y sample (the light dots in the images are the mesoporous with pore size of 3-8 nm).

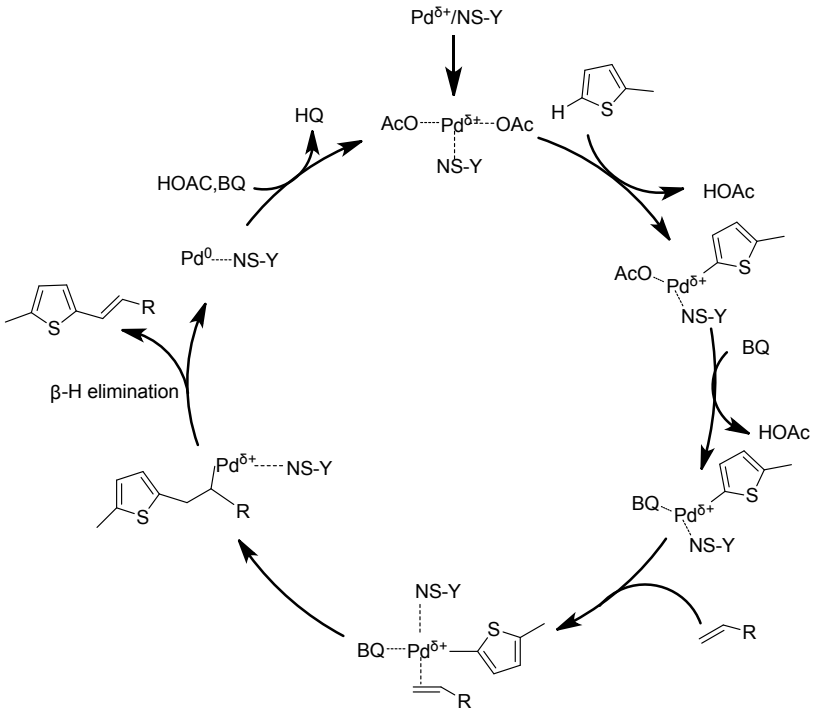


Fig. S2. The proposed reaction mechanism by the facilitation of the $Pd^{\delta+}$ ($\delta<2$) species in the cross-coupling of 2-methyl thiophene with alkenes.

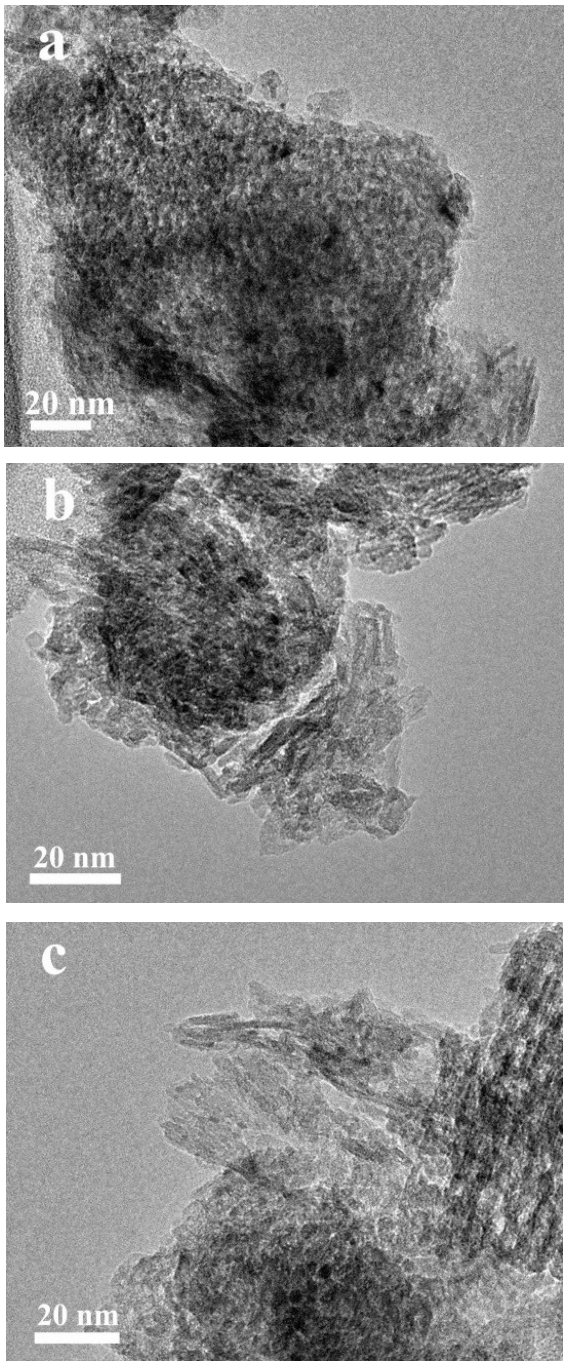


Fig. S3. The TEM images of the (a), (b) and (c) are the selected different zones for the Pd/γ-Al_2O_3 catalyst.

Discussion: The Pd/γ-Al_2O_3 catalyst was prepared by impregnation of the support using palladium nitrate solution, and further dried at 50 °C for 48 h in vacuum oven. Therefore, the dispersion and average size of Pd particles measured by CO chemisorption technique may be inappropriate. The dispersion and average size of Pd particles on the Pd/γ-Al_2O_3 catalyst were investigated by TEM technique. The different zone was selected to observe the Pd particles on the

Pd/γ-Al_2O_3 catalyst, and no distinct Pd particles were observed. This result indicates that the Pd particles are highly dispersed on Pd/γ-Al_2O_3 catalyst relative to the Pd/NS-Y (Fig. 3d in the text) and Pd/NS-HY (Fig. S6) catalysts.

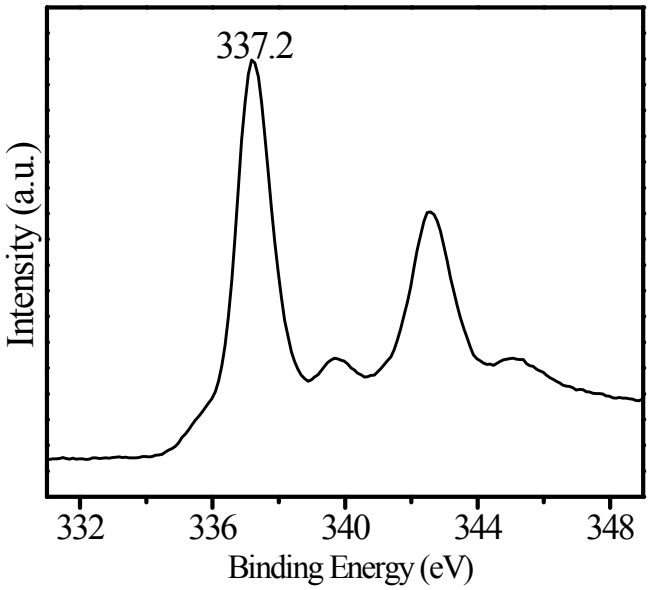


Fig. S4. XPS spectrum of $Pd3d_{5/2}$ in the Pd/γ-Al_2O_3 catalyst.

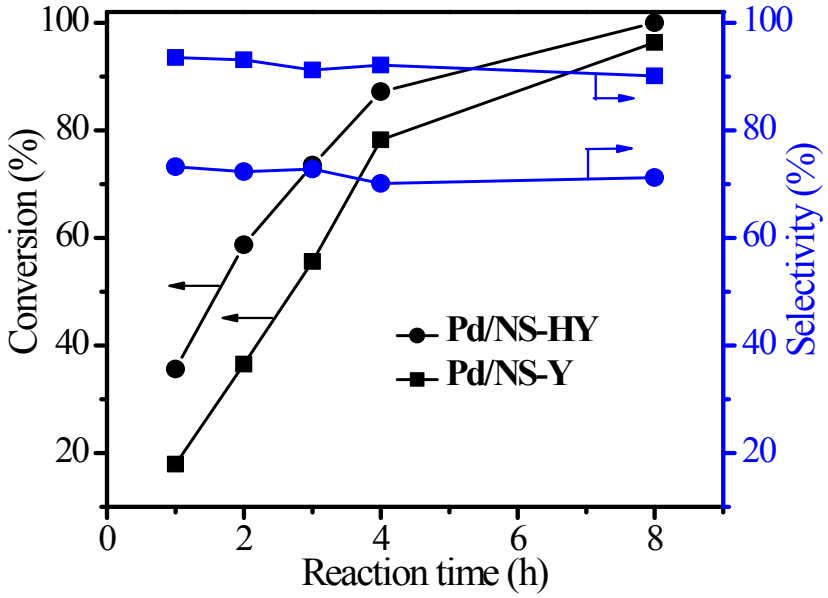


Fig. S5. Dependence of the butyl acrylate conversion and the target product selectivity on reaction time over Pd/NS-HY and Pd/NS-Y catalysts.

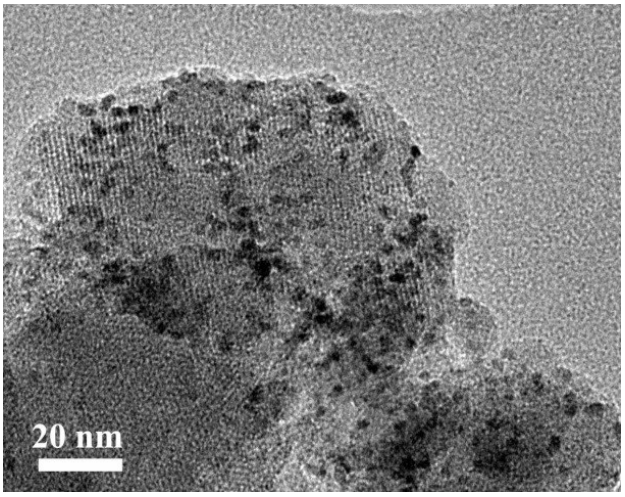


Fig. S6. The TEM image of the Pd/NS-HY catalyst.

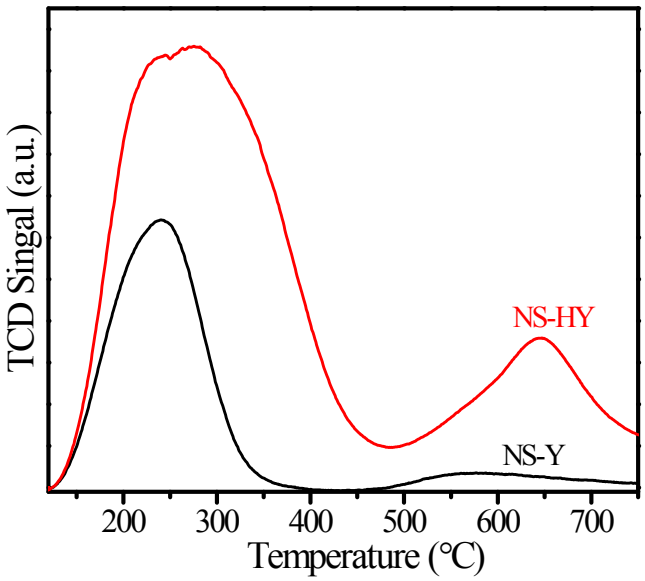
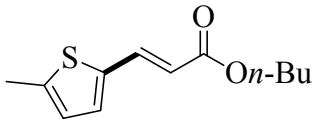


Fig. S7. The NH_3-TPD curves of the NS-HY and NS-Y samples (the number of acidic sites on the NS-HY is larger than NS-Y, and the acidic strength of the NS-HY is stronger than NS-Y).

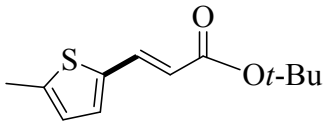
6. Analytical data



(E)-butyl 3-(5-methylthiophen-2-yl)acrylate (3a)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 15.5 Hz, 1H), 6.97 (d, *J* = 3.5 Hz, 1H), 6.63 (dd, *J* = 1.0, 3.5 Hz, 1H), 6.04 (d, *J* = 15.5 Hz, 1H), 4.10 (t, *J* = 6.5 Hz, 2H), 2.42 (s, 3H), 1.64-1.56 (m, 2H), 1.39-1.30 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H);

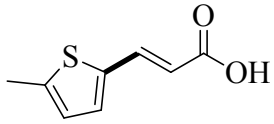
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 143.8, 137.6, 137.3, 131.4, 126.4, 115.6, 64.2, 30.8, 19.1, 15.7, 13.7.



(E)-tert-butyl 3-(5-methylthiophen-2-yl)acrylate (3b)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 15.5 Hz, 1H), 6.93 (d, *J* = 3.5 Hz, 1H), 6.61 (dd, *J* = 1.0, 3.5 Hz, 1H), 5.97 (d, *J* = 15.5 Hz, 1H), 2.40 (s, 3H), 1.43 (s, 9H);

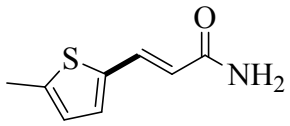
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 143.3, 137.7, 136.4, 131.0, 126.3, 117.5, 80.2, 28.1, 15.7.



(E)-3-(5-methylthiophen-2-yl)acrylic acid (3c)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 15.5 Hz, 1H), 7.10 (d, 3.0 Hz, 1H), 6.73 (d, *J* = 2.5 Hz, 1H), 6.11 (d, *J* = 15.5 Hz, 1H), 2.51 (s, 3H);

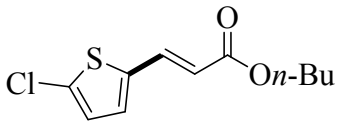
^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 145.0, 139.7, 137.2, 132.4, 126.6, 114.3, 15.8.



(E)-3-(5-methylthiophen-2-yl)acrylamide (3d)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 15.5 Hz, 1H), 6.94 (d, *J* = 3.5 Hz, 1H), 6.61 (dd, *J* = 1.0, 3.5 Hz, 1H), 6.07 (d, *J* = 15.5 Hz, 1H), 5.85 (s, 1H), 5.65 (s, 1H), 2.40 (s, 3H);

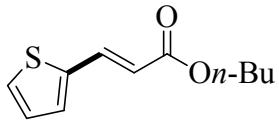
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 143.1, 137.6, 135.4, 131.3, 126.3, 116.9, 15.7.



(E)-butyl 3-(5-chlorothiophen-2-yl)acrylate (3e)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 15.5 Hz, 1H), 6.95 (d, *J* = 4.0 Hz, 1H), 6.80 (d, *J* = 4.0 Hz, 1H), 6.05 (d, *J* = 16.0 Hz, 1H), 4.11 (t, *J* = 6.5 Hz, 2H), 1.64-1.56 (m, 2H), 1.40-1.30 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 138.3, 136.3, 133.1, 130.3, 127.2, 117.1, 64.5, 30.7, 19.1, 13.6.

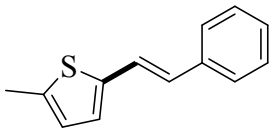


(E)-butyl 3-(thiophen-2-yl)acrylate (3f)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 16.0 Hz, 1H), 7.37 (d, *J* = 5.0 Hz, 1H), 7.25 (d, *J* = 3.5 Hz, 1H), 7.05 (dd, *J* = 3.5, 5.0 Hz, 1H), 6.25 (d, *J* = 15.5 Hz, 1H), 4.19 (t, *J* = 6.5 Hz, 2H), 1.72-

1.64 (m, 2H), 1.48-1.38 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H);

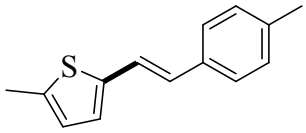
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 139.6, 136.9, 130.7, 128.2, 128.0, 117.0, 64.4, 30.7, 19.1, 13.7.



(E)-2-methyl-5-styrylthiophene (3g)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 9.0 Hz, 2H), 7.33 (t, *J* = 9.0 Hz, 2H), 7.23-7.18 (m, 1H), 7.15 (d, *J* = 20.0 Hz, 1H), 6.84 (d, *J* = 4.5 Hz, 1H), 6.76 (d, *J* = 20.0 Hz, 1H), 6.65-6.61 (m, 1H), 2.46 (s, 3H);

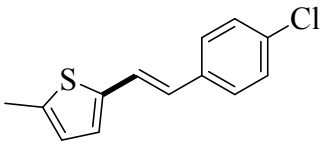
^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 139.2, 137.1, 128.6, 127.2, 127.0, 126.3, 126.1, 125.7, 122.1, 15.6.



(E)-2-methyl-5-(4-methylstyryl)thiophene (3h)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 16.0 Hz, 1H), 6.82 (d, *J* = 3.5 Hz, 1H), 6.78 (d, *J* = 16.0 Hz, 1H), 6.64-6.61 (m, 1H), 2.47 (s, 3H), 2.33 (s, 3H);

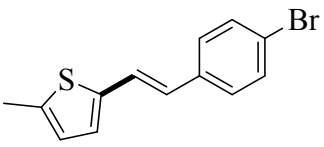
^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 138.9, 137.1, 134.4, 129.3, 127.0, 126.0, 125.9, 125.6, 121.2, 21.2, 15.5.



(E)-2-(4-chlorostyryl)-5-methylthiophene (3i)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.5 Hz, 2H), 7.22-7.16 (d, *J* = 16.0 Hz, 1H), 7.04 (d, *J* = 16.0 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.58-6.54 (m, 1H), 2.40 (s, 3H);

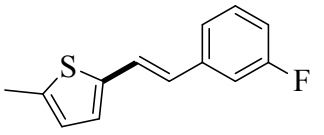
^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 139.6, 135.7, 132.7, 128.7, 127.2, 126.7, 125.8, 125.6, 122.7, 15.6.



(E)-2-(4-bromostyryl)-5-methylthiophene (3j)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 16.0 Hz, 1H), 6.85 (d, *J* = 3.5 Hz, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 6.66-6.62 (m, 1H), 2.47 (s, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 139.7, 136.1, 131.7, 127.5, 126.7, 125.8, 125.6, 122.8, 120.8, 15.6.

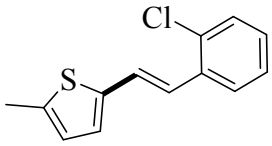


(E)-2-(3-fluorostyryl)-5-methylthiophene (3k)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.25 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.15-7.10 (m, 2H), 6.93-6.88 (m, 1H), 6.86 (d, *J* = 3.5 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.66-6.62 (m, 1H), 2.47 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1 (d, *J* = 243.7 Hz), 140.2, 139.8, 139.6 (d, *J* = 7.8 Hz),130.0 (d,

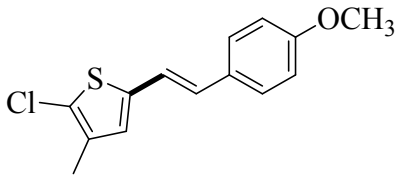
J = 8.5 Hz), 127.0, 125.8, 125.7 (d, J = 2.8 Hz), 123.4, 122.0 (d, J = 2.8 Hz), 114.1 (d, J = 21.5 Hz), 112.4 (d, J = 21.8 Hz), 15.5.



(E)-2-(2-chlorostyryl)-5-methylthiophene (3l)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, J = 1.5, 3.0 Hz, 1H), 7.36 (dd, J = 1.5, 3.0 Hz, 1H), 7.24-7.09 (m, 4H), 6.89 (d, J = 3.5 Hz, 1H), 6.67-6.64 (m, 1H), 2.48 (s, 1H);

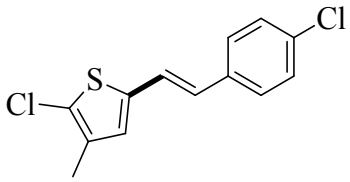
^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 140.1, 135.2, 133.0, 129.8, 128.1, 127.0, 126.8, 126.0, 125.8, 124.5, 122.8, 15.6.



(E)-3-chloro-5-(4-methoxystyryl)-2-methylthiophene (3m)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 9.0 Hz, 2H), 6.85-6.77 (m, 3H), 6.65 (d, J = 16.0 Hz, 1H), 6.60 (s, 1H), 3.74 (s, 3H), 2.06 (s, 3H);

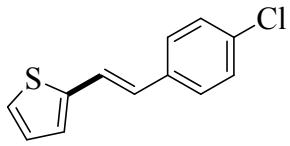
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 139.4, 134.7, 129.4, 127.7, 127.5, 126.9, 122.8, 119.3, 114.1, 55.3, 13.5.



(E)-3-chloro-5-(4-chlorostyryl)-2-methylthiophene (3n)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 16.5 Hz, 1H), 6.73 (s, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 2.15 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 135.1, 134.9, 133.2, 128.8, 128.0, 127.3, 126.6, 124.0, 121.9, 13.4.

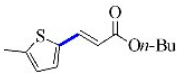


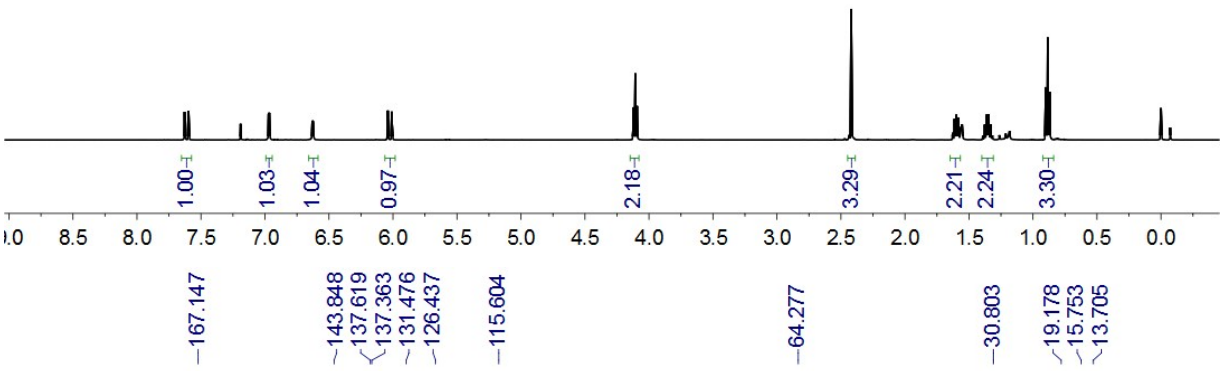
(E)-2-(4-chlorostyryl)thiophene (3o)

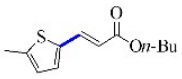
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 10.5 Hz, 2H), 7.31 (d, *J* = 10.5 Hz, 2H), 7.22-7.16 (m, 2H), 7.07 (d, *J* = 3.5 Hz, 1H), 7.00 (dd, *J* = 4.5, 6.5 Hz, 1H), 6.88 (d, *J* = 20.0 Hz, 1H),

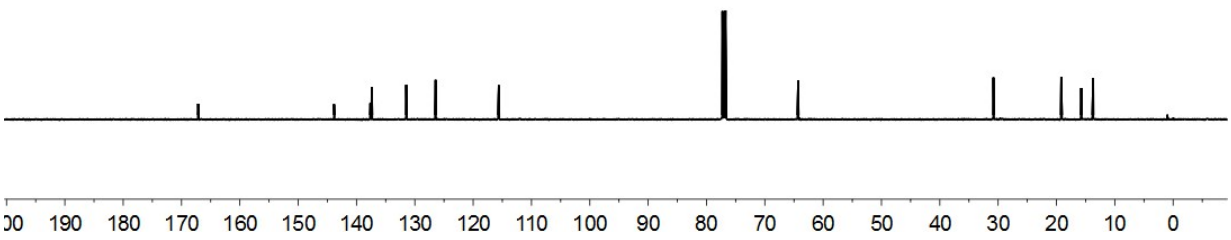
^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 135.4, 133.0, 128.8, 127.6, 127.4, 126.9, 126.4, 124.6, 122.3.

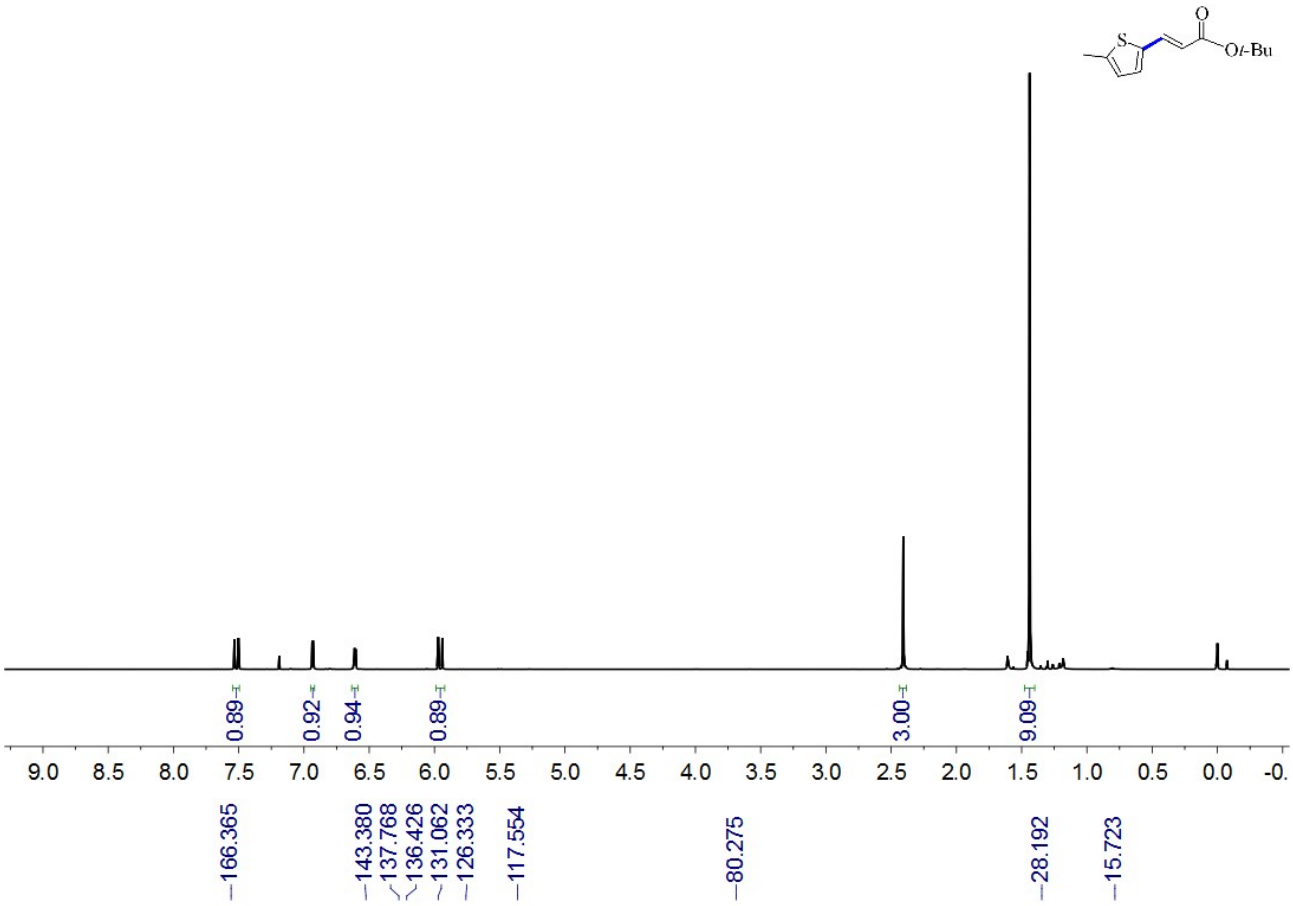
VI. Spectra of these compounds







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9.09
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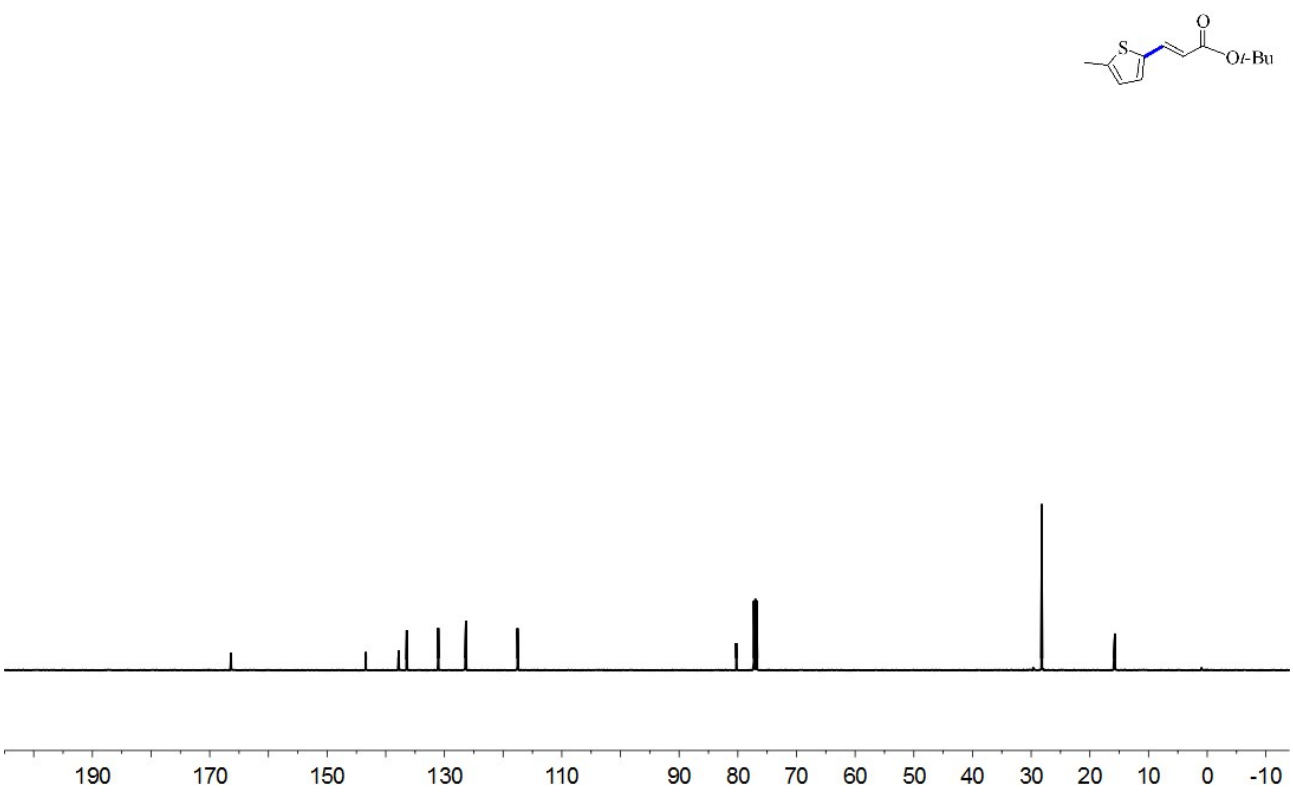
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S
Ot-Bu
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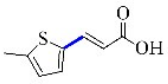
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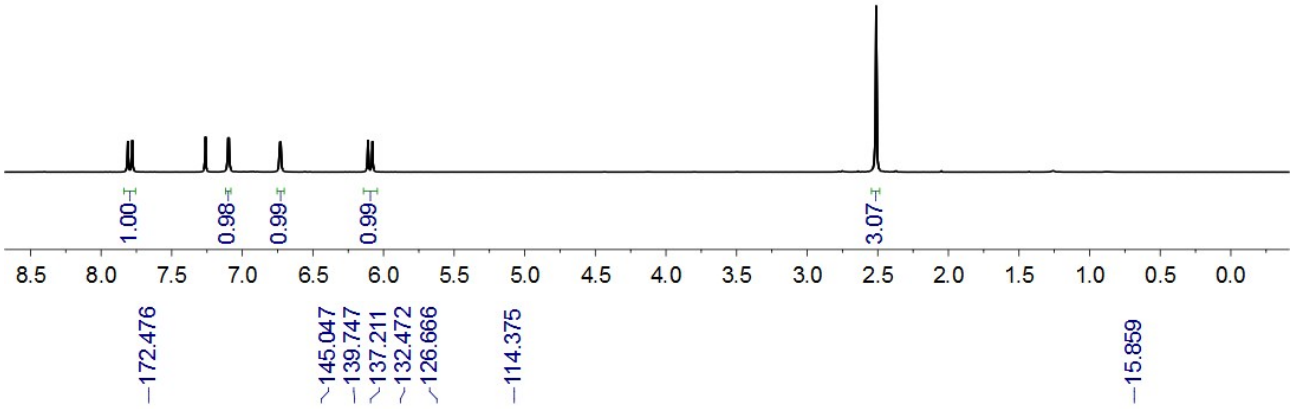
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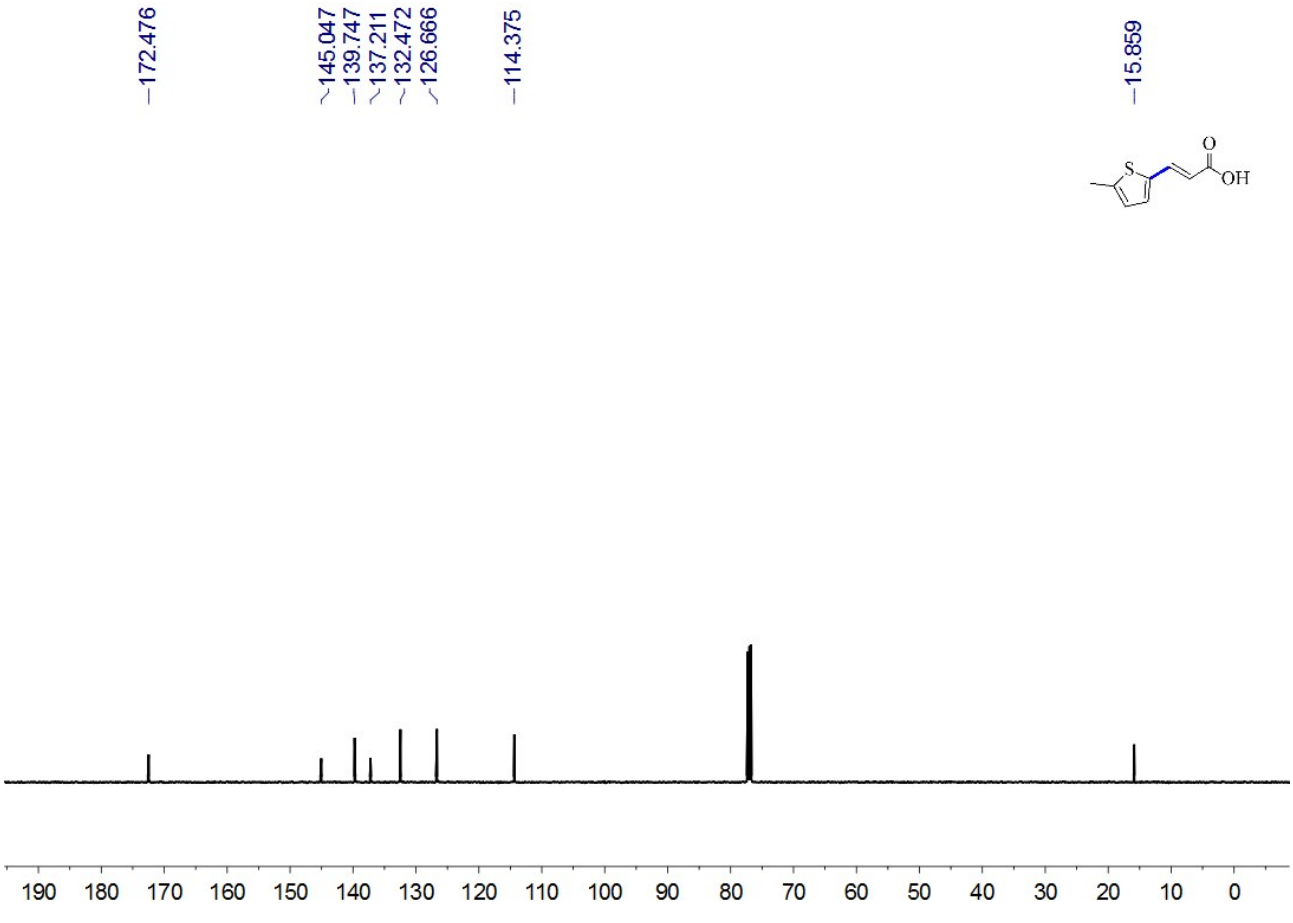
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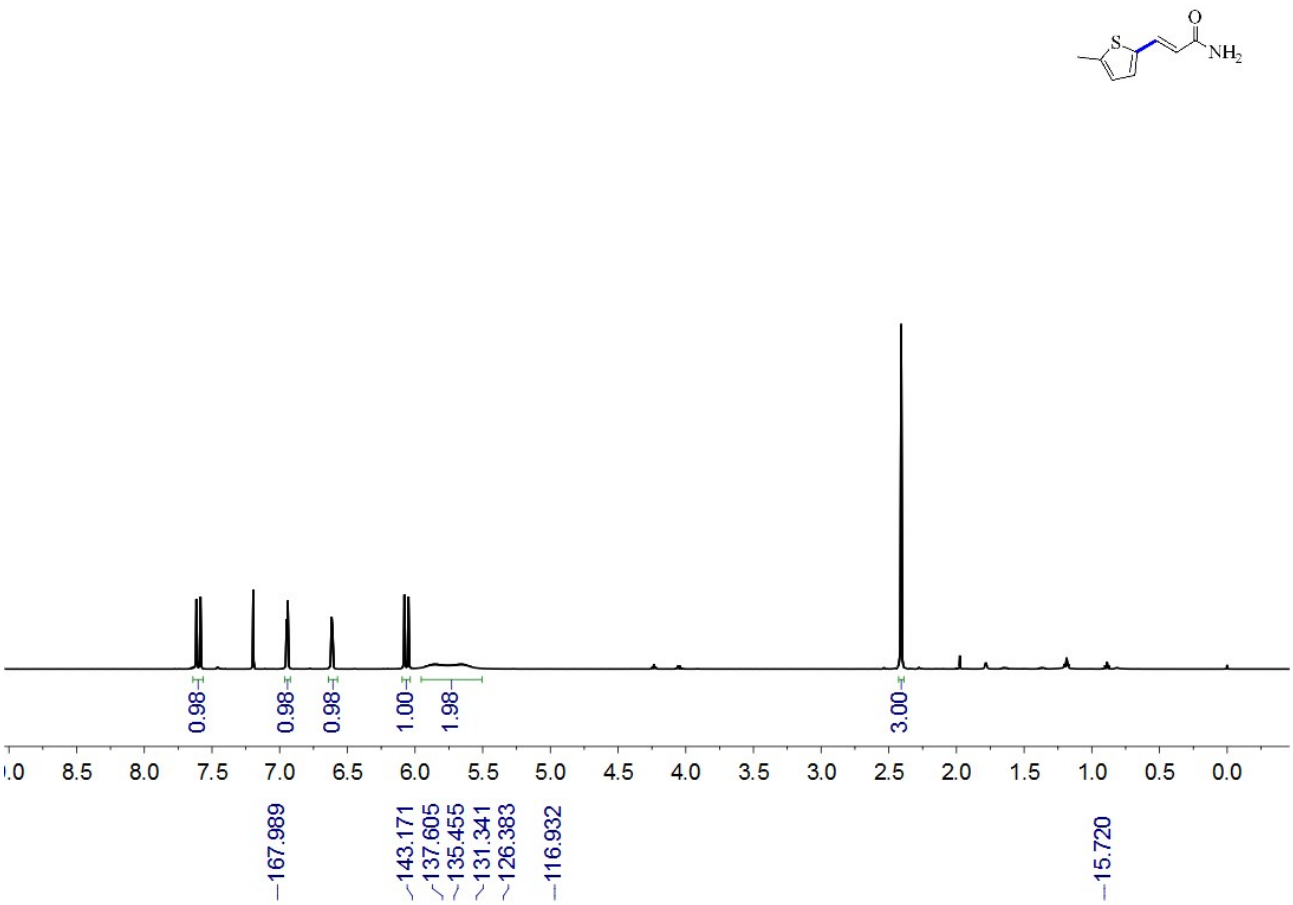
S
O
OH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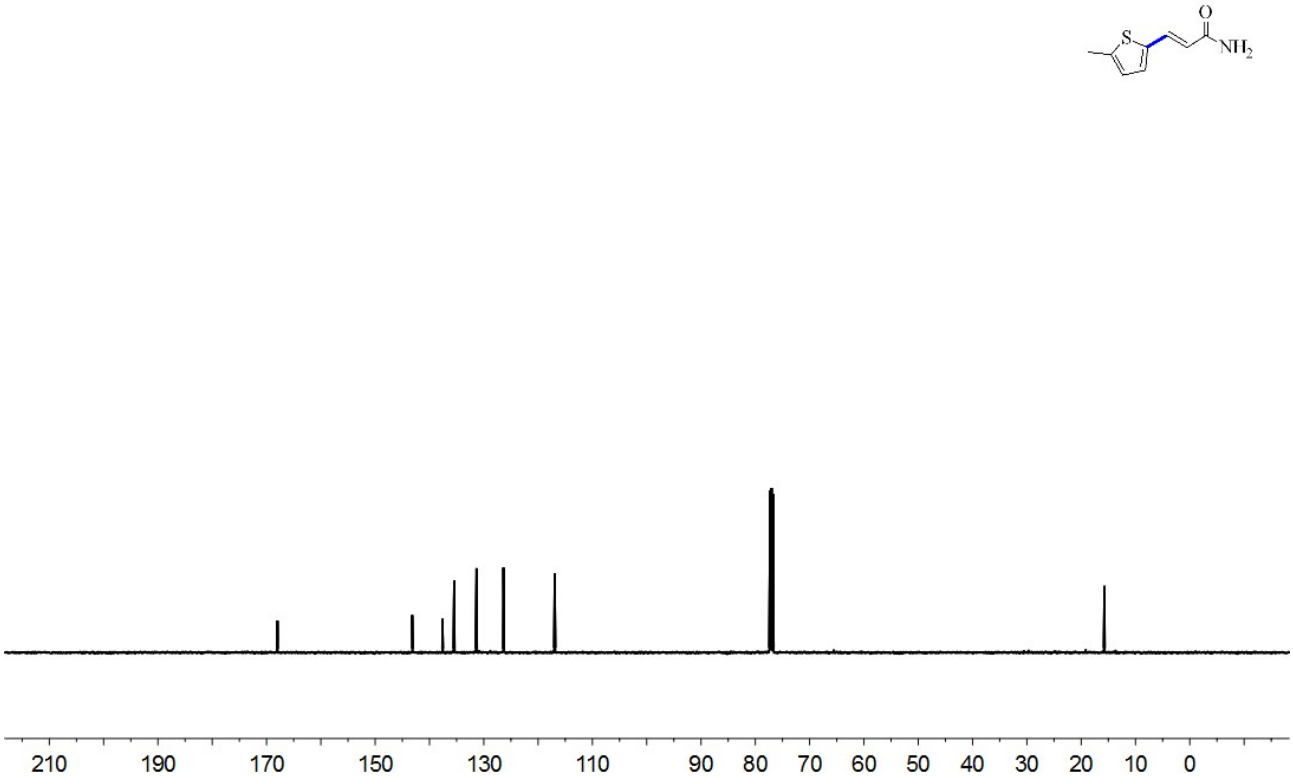
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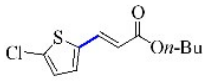
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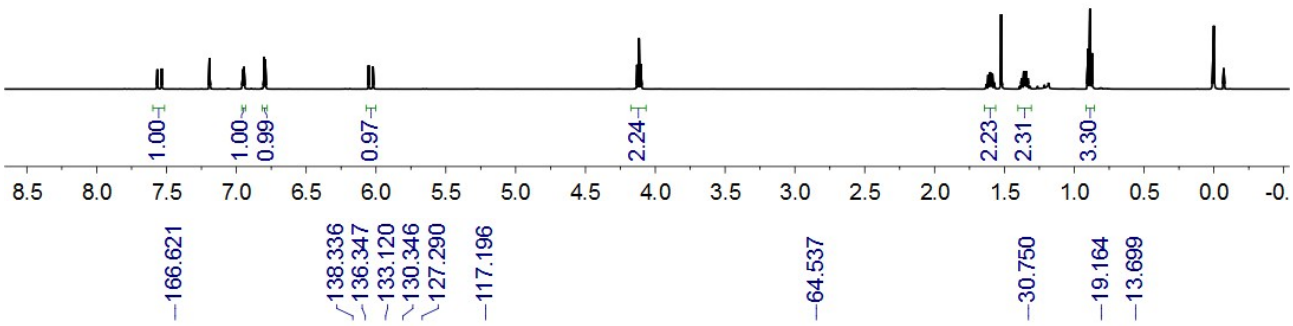
O
O
n-Bu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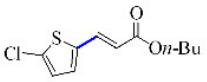
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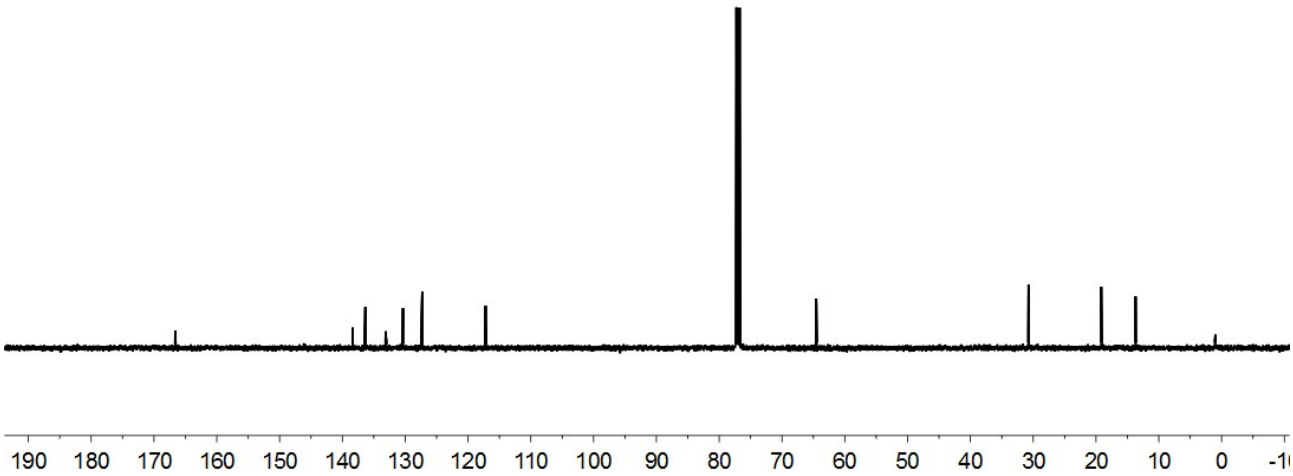
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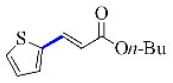
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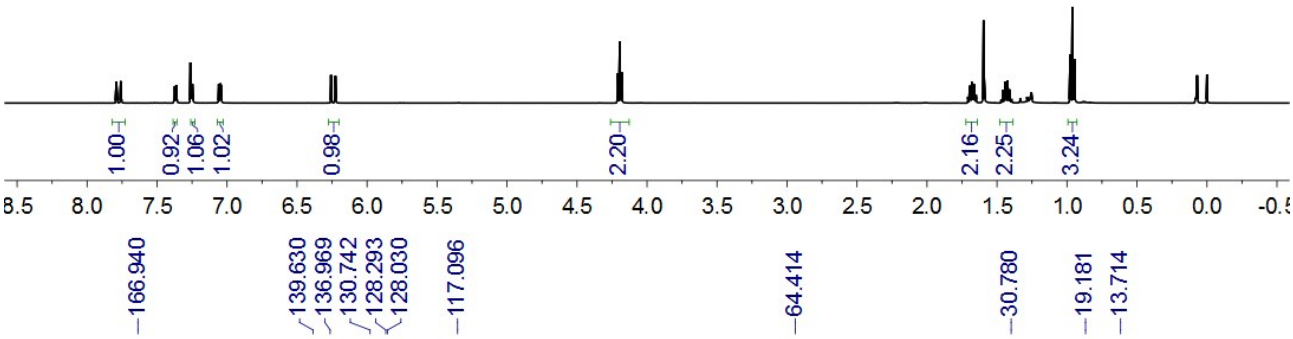
O
n-Bu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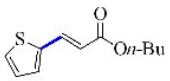
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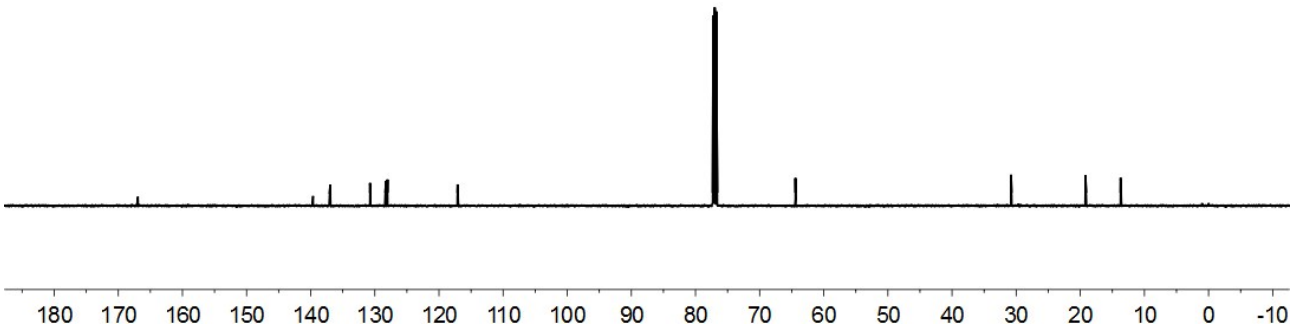
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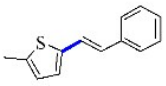

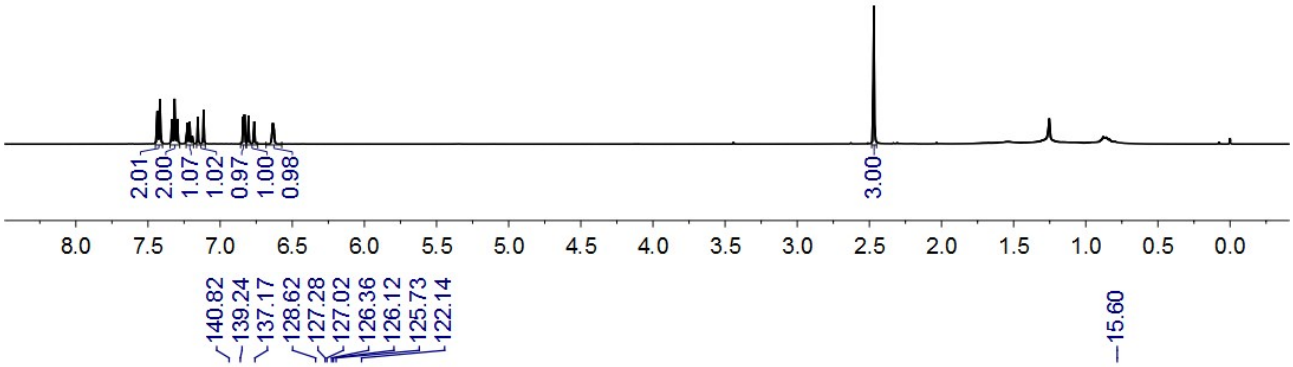
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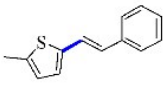

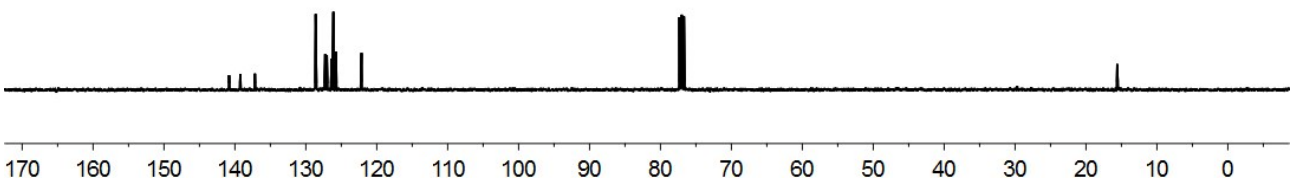
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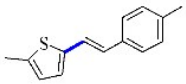

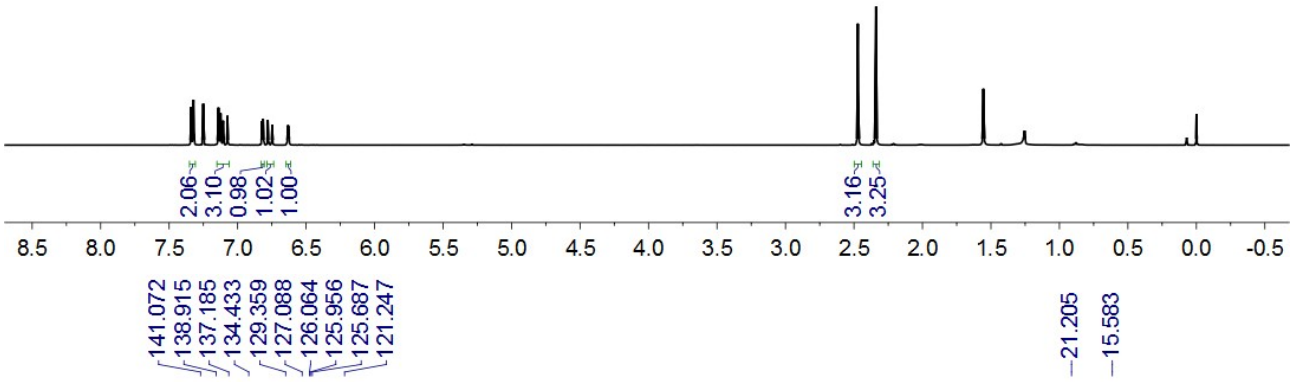
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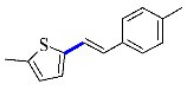

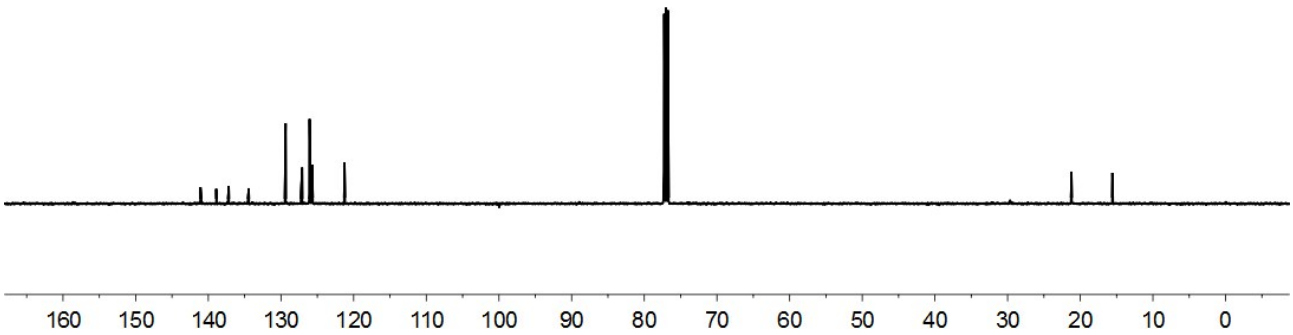
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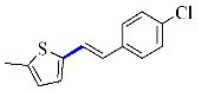
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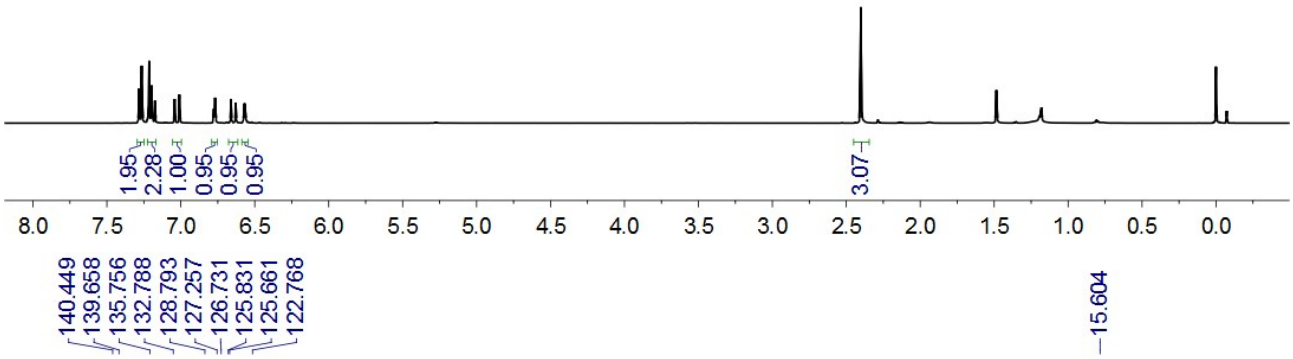
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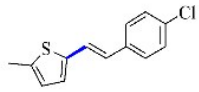
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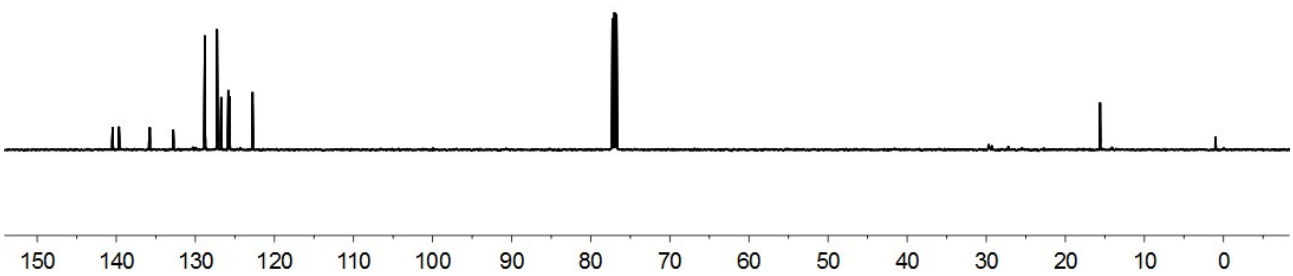
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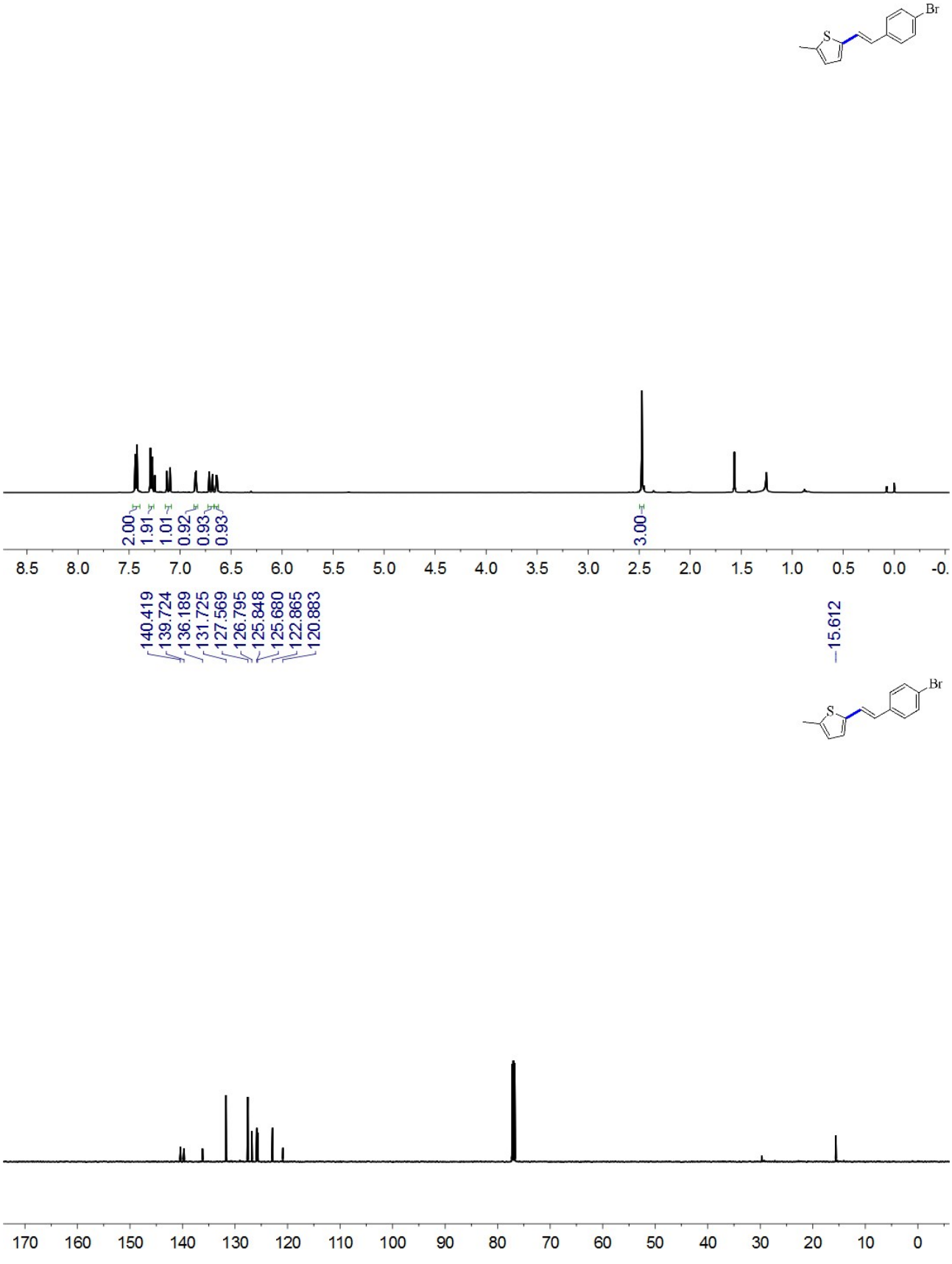
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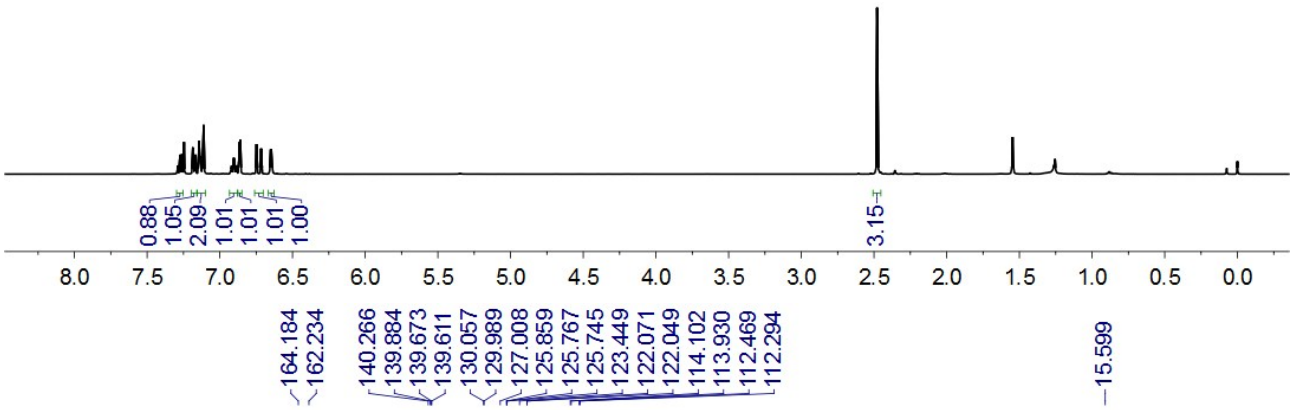
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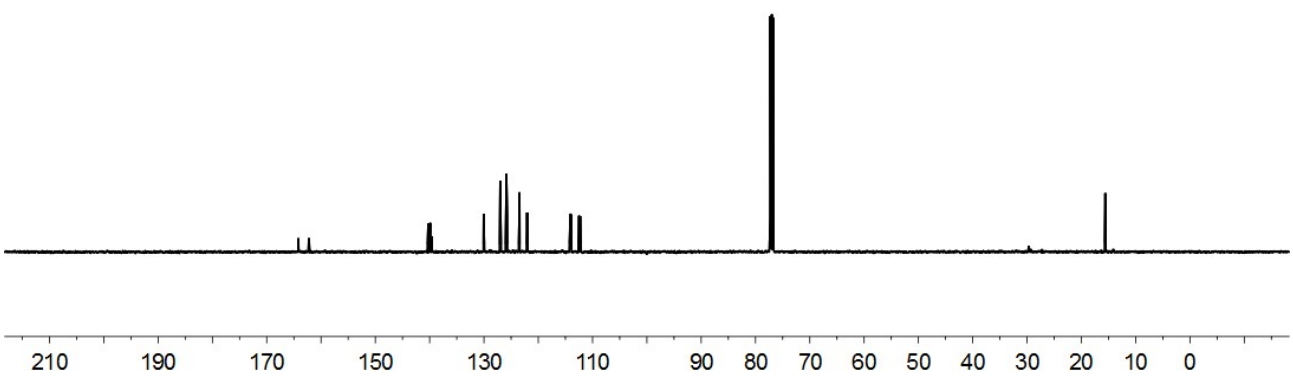
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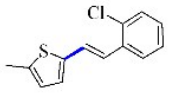
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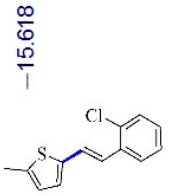
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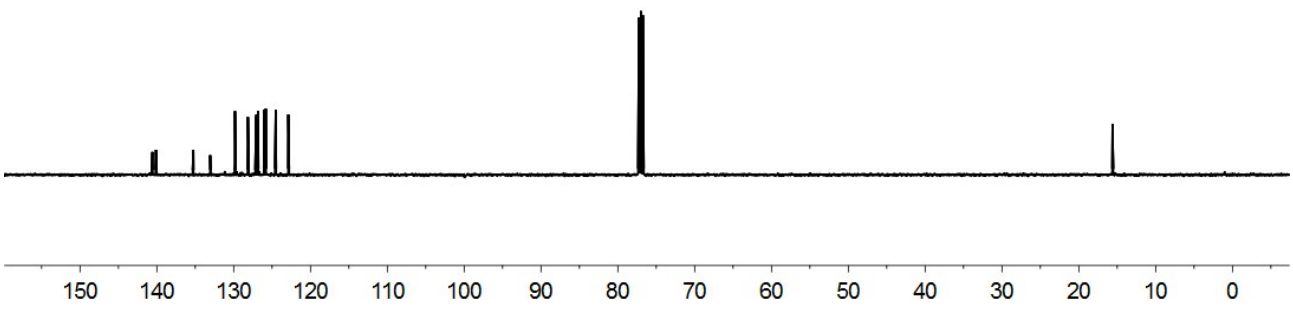
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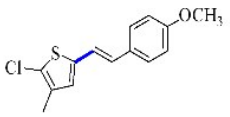
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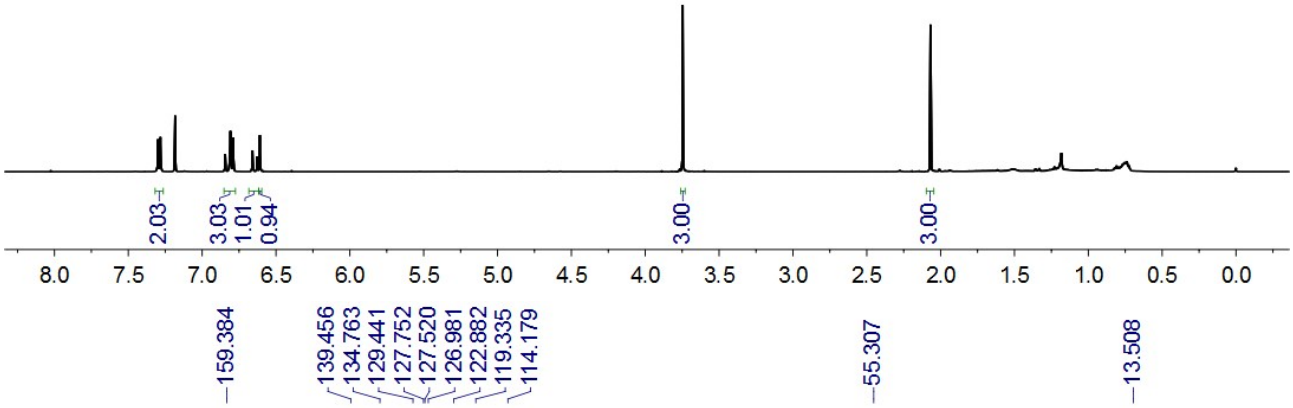
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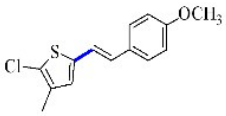
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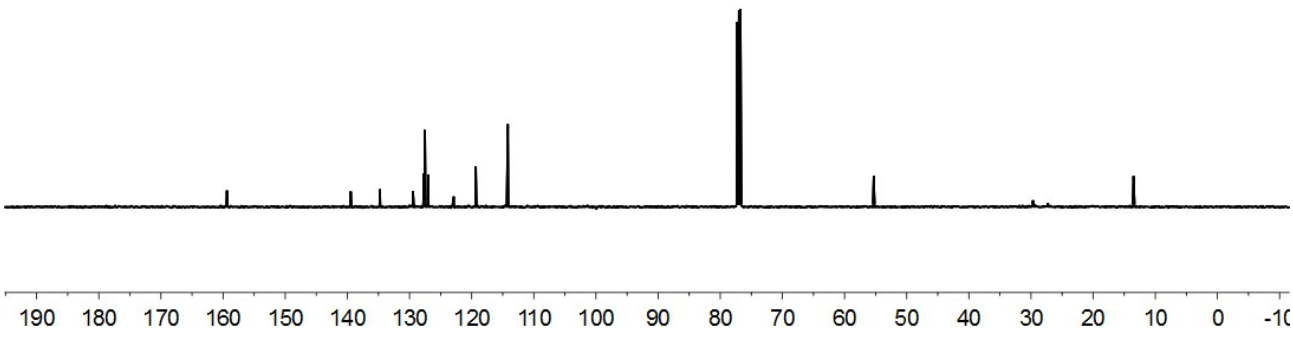
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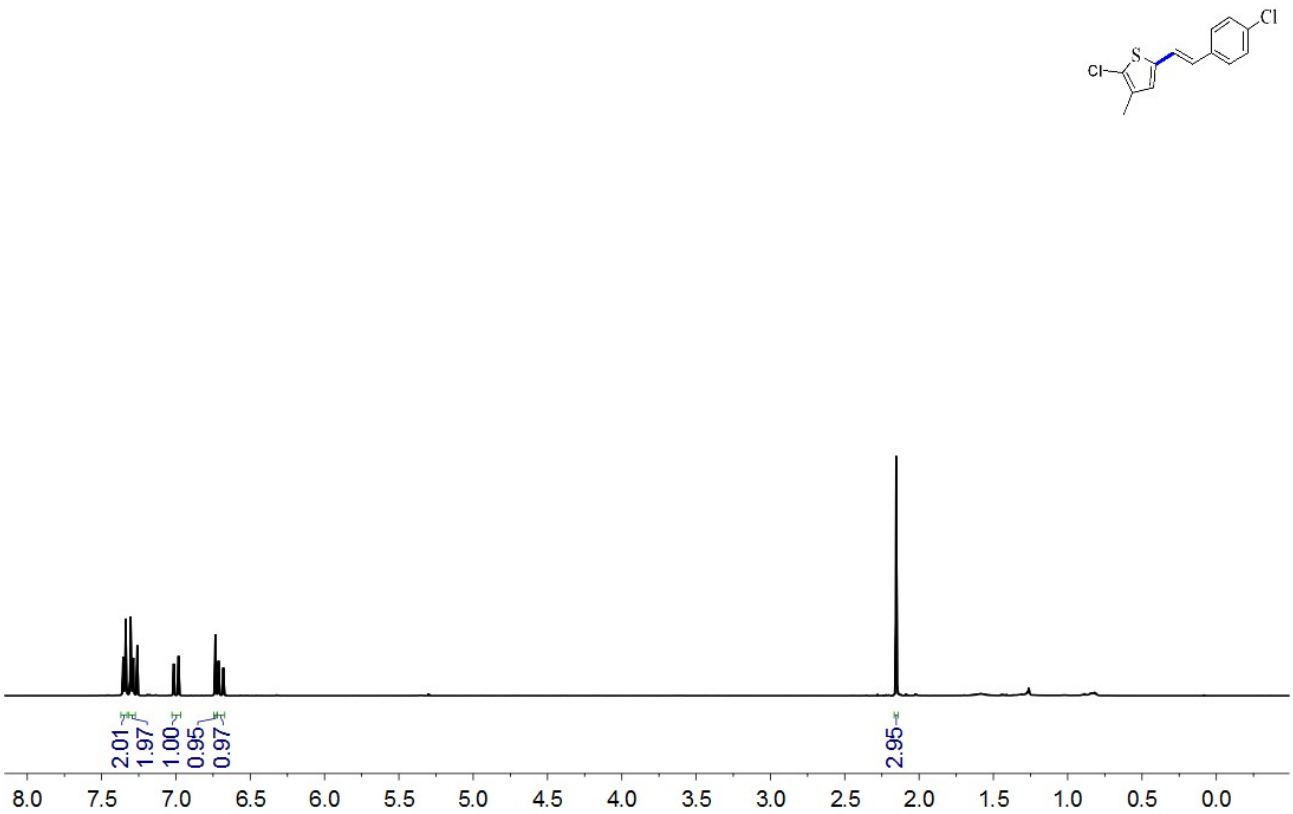
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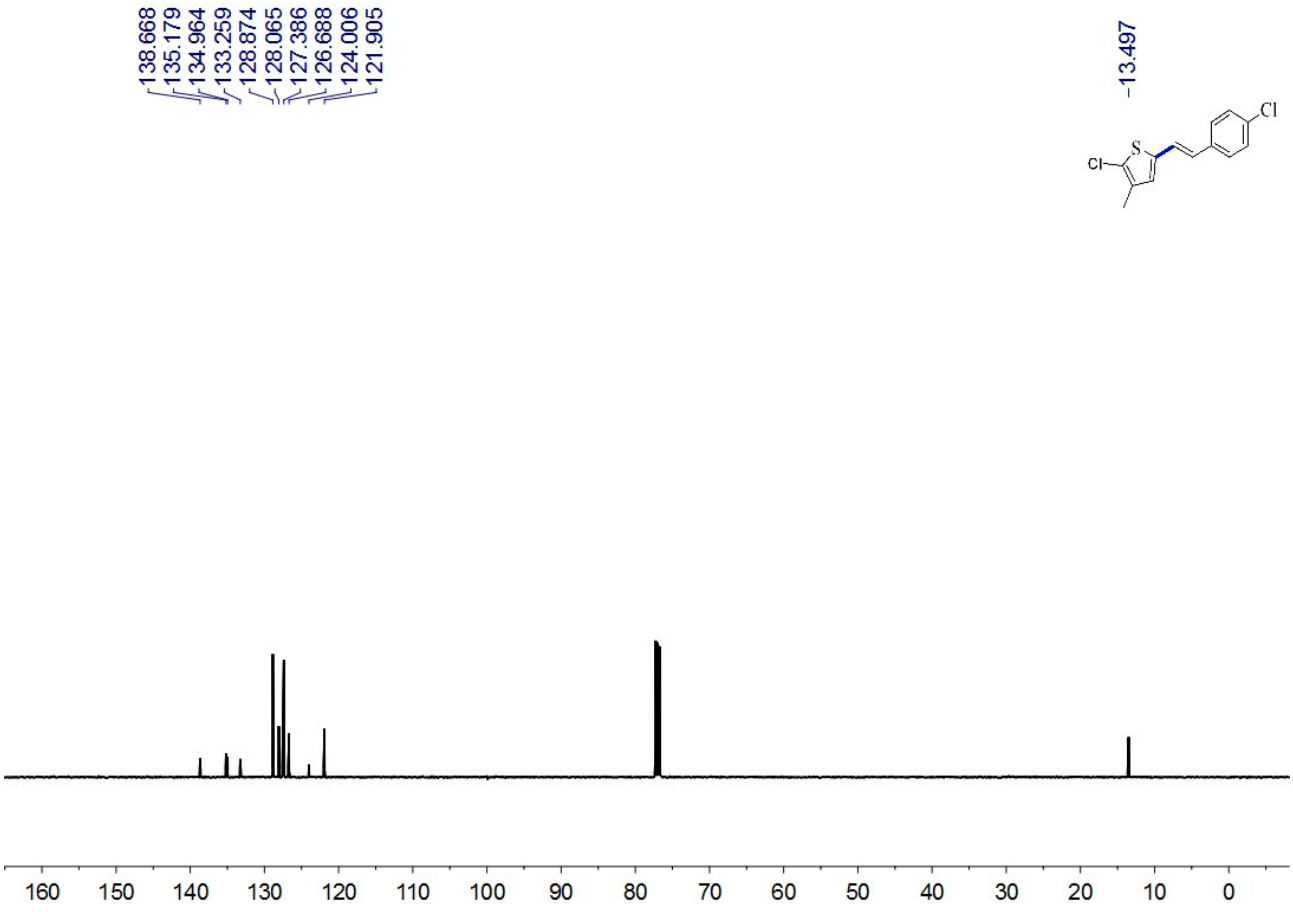
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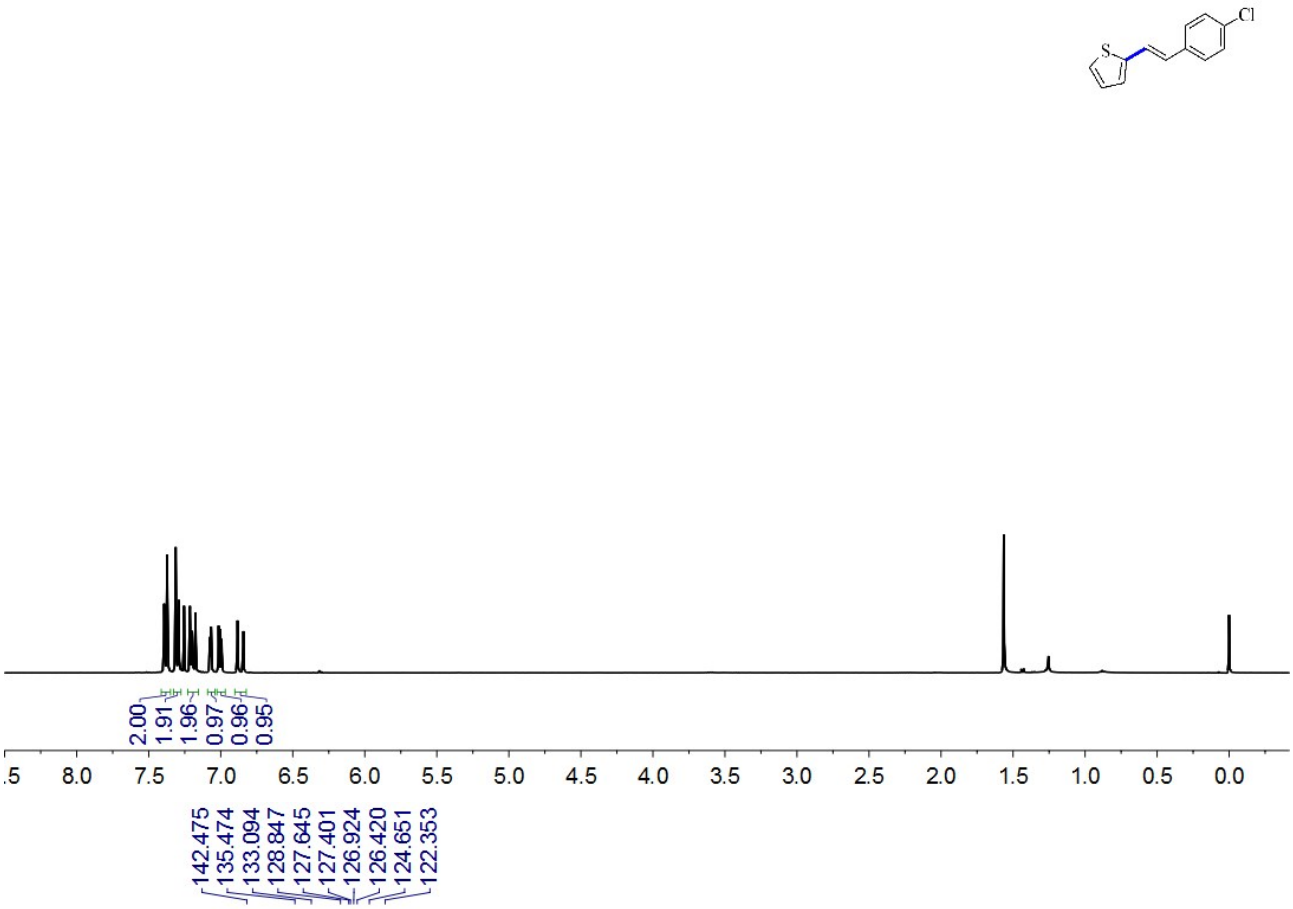
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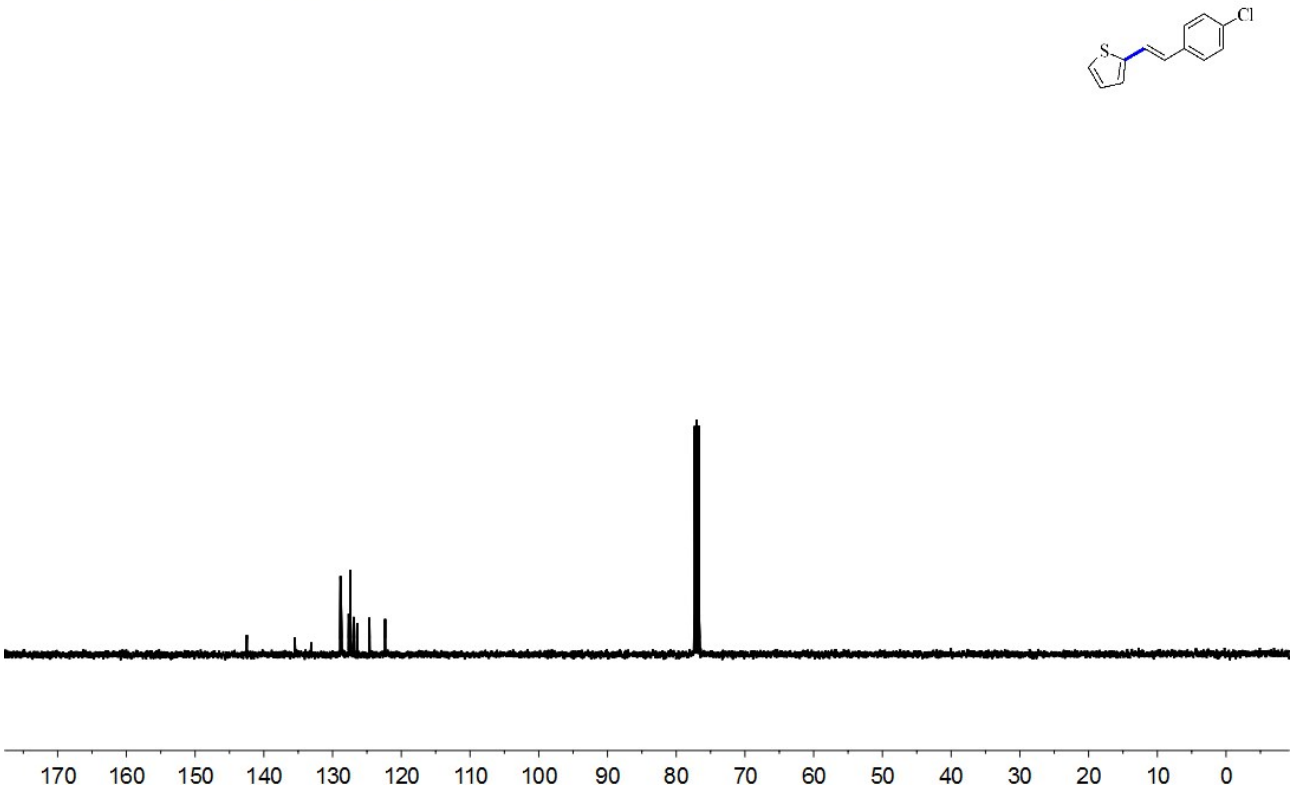
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