Supporting Information

for

Synthesis of tetrasubstituted thiophenes via [3 + 2] cascade cyclization reaction of pyridinium 1,4-zwitterionic thiolates and activated allenes

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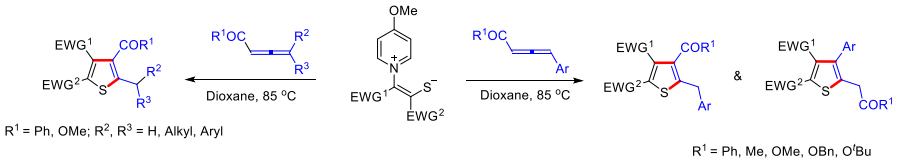
1. General information

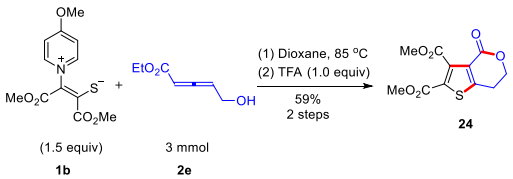
All isolated compounds were characterized on Varian 300, Bruker 400 and JEOL 400 MHz spectrometers in the $CDCl_3$ or $(CD_3)_2CO$. Chemical shifts are reported as δ values relative to internal chloroform (δ 7.26 for ^{1}H NMR and 77.00 for ^{13}C NMR) and acetone (δ 2.05 for ^{1}H NMR and 29.84 for ^{13}C NMR). High resolution mass spectra (HRMS) were obtained on a 4G mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (QTof). All melting points were measured with the samples after column chromatography and uncorrected. Column chromatography was performed on silica gel. Anhydrous THF, PhMe were distilled over sodium benzophenone ketyl under Ar. All other solvents and reagents were used as obtained from commercial sources without further purification.

2. General experimental procedure (for 3-23 and 25)



To a solution of allene (0.3 mmol, 1.0 equiv) in dioxane (3 mL) was added pyridinium 1,4-zwitterionic thiolate (0.45 mmol, 1.5 equiv), then the reaction mixture was stirred at 85 ^{o}C. After completion as monitored by TLC, the mixture was concentrated and the residue was directly subjected to silica gel column chromatography to afford the desired thiophene.

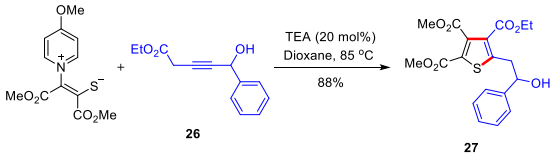
3. Procedures for the synthesis of 24 and 27



To a solution of allene **2e** (426 mg, 3.00 mmol, 1.0 equiv) in 1,4-dioxane (30 mL) was added pyridinium 1,4-zwitterionic thiolate **1b** (4.50 mmol, 1.27 g, 1.5 equiv), then the reaction mixture was stirred at 85 ^{o}C. After completion as monitored by TLC, dilute hydrochloric acid (2 M) was added to adjust the pH value less than 7. The mixture was concentrated to remove 1,4-dioxane and

the aqueous phase was extracted with DCM. The organic phases were combined and concentrated to afford a crude product of **16**, which could be used directly for the next step.

To a solution of crude **16** above-mentioned in PhMe (30 mL) was added TFA (0.22 mL, 1.0 equiv), then the mixture was heated at 85 ^{o}C. After completion as monitored by TLC, the mixture was concentrated and the residue was directly subjected to silica gel column chromatography to afford the desired thiophene product **24** (483 mg, 59% yield).



To a solution of alkyne **26** (46 mg, 0.21 mmol, 1.0 equiv) in 1,4-dioxane (2 mL) were added pyridinium 1,4-zwitterionic thiolate **1b** (90 mg, 0.32 mmol, 1.5 equiv) and TEA (6 μL,0.2 equiv), then the reaction mixture was stirred at 85 ^{o}C. After completion as monitored by TLC, the mixture was concentrated and the residue was directly subjected to silica gel column chromatography to afford the desired product **27** (72 mg, 88% yield).

4. Tables of substrates

All allenoates and allenones were prepared according to the literature.[1] **16s**, **17s** and **26** was prepared according to the literature.[2]

1. (a) Rout, L.; Harned, A. M. *Chem. Eur. J*. **2009**, *15*, 12926.2. (b) Pashikanti, S.; Calderone, J. A.; Nguyen, M. K.; Sibley, C. D.; Santos, W. L. *Org. Lett.* **2016**, *18* 2443. (c) Yao, C.; Bao, Y.; Lu, T.; Zhou, Q. *Org. Lett.* **2018**, *20*, 2152.

2. Hu, J.; Dong, W.; Wu, Xin-Y.; Tong, X. *Org. Lett.* **2012**, *14*, 5530.

Pyridinium 1,4-zwitterionic thiolates were prepared according to the literature.[3] **1a** was known compound, **1b**−**1e** were new compounds as shown below.

3. Moafi, L.; Ahadi, S.; Khavasi, H. R.; Bazgir, A. *Synthesis* **2011**, 1399.

Table S1. Substrates listed below are ***new compounds***.

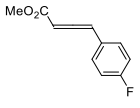
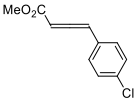
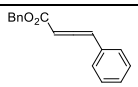
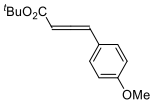
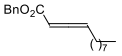
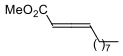
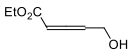
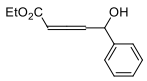
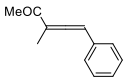
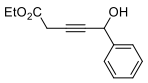
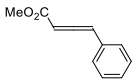
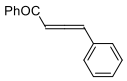
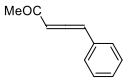
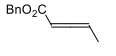
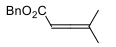
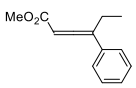
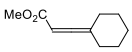
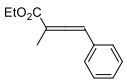
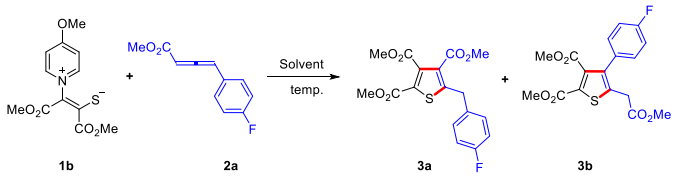
			
3s	**4s**	**6s**	**7s**
			
11s	**12s**	**13s** (i.e., **2e**)	**14s**
			
2c	**26**		

Table S2. Substrates listed below are ***known compounds***, ^{1}H NMR data correspond to the reported values.

Substrate	Data Refs
 **5s**	*Org. Lett.* **2012**, *14*, 1398
 **8s**	*Angew. Chem.* **1980**, *92*, 555
 **9s**	*Org. Lett.* **2011**, *13*, 5024
 **10s**	*Chem. Eur. J.* **2009**, *15*, 12926
 **15s**	*Org. Lett.* **2012**, *14*, 2034
 **16s**	*Synlett* **2015**, *26*, 2135
	*Org. Lett.* **2012**, *14*, 1398

17s	
 **18s**	*Chem. Eur. J.* **2009**, *15*, 12926
 **19s**	*J. Am. Chem. Soc.* **2009**, *131*, 6105
 **20s**	*Org. Lett.* **2011**, *13*, 5024
 **2f**	*J. Chem. Soc., Perkin Trans. 2* **1988**, *0*, 1377
 **2b**	*Org. Lett.* **2011**, *13*, 2388
 **2d**	*Tetrahedron* **1989**, *45*, 1605

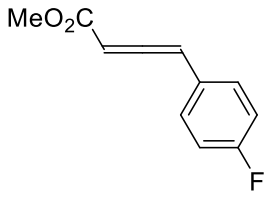
5. Optimization of the reaction conditions



entry	solvent	yield[a]	ratio (**3b**: **3a**)[b]
1	TFE	ND	
2	HFIP	ND	
3	DCM: CH_3OH = 7:1	60%	1:2.9
4	DCM: CH_3OH = 4:1	60%	1:3.2
5	DCM: CH_3OH = 1:1	49%	-[c]
6	Dioxane: CH_3OH = 1:1	41%	1:2.8
7	PhMe: CH_3OH = 1:1	41%	1:6.6
8	PhCl: CH_3OH = 1:1	41%	1:4.1
9	Dioxane: H_2O = 1:1	30%	-[c]

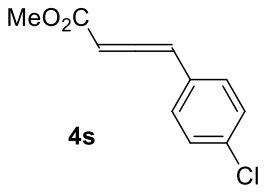
[a] Reaction conditions: **1b** (0.15 mmol, 1.5 equiv), **2a** (0.1 mmol), solvent (1 mL), under air. Isolated yield. ND = not detected. [b]The ratio was determined by the integrals of ^{19}F-NMR. [c] Not determined.

6. Characterization data of substrates



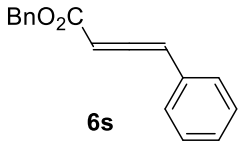
3s

3s: yellow oil, R_f = 0.54 (PE:EA=6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.24 (m, 2H), 7.05–7.00 (m, 2H), 6.60 (d, J = 6.4 Hz, 2H), 6.02 (d, J = 6.4 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.4, 165.3, 162.5 (d, J = 246.5 Hz), 129.1 (d, J = 8.1 Hz), 127.0 (d, J = 3.3 Hz), 116.8 (d, J = 21.9 Hz), 97.7, 91.7, 52.2; ESI-HRMS m/z Calcd. for $C_{11}H_9FO_2$ + Na^+ 215.0479, found 215.0488.



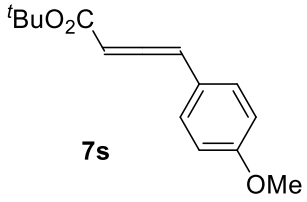
4s

4s: yellow oil, R_f = 0.58 (PE:EA=6:1), ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.41–7.35 (m, 4H), 6.84 (d, J = 6.4 Hz, 1H), 6.11 (d, J = 6.4 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 215.3, 165.4, 134.1, 131.2, 129.8, 129.7, 98.1, 92.3, 52.3; ESI-HRMS m/z Calcd. for $C_{11}H_9ClO_2$ + H^+ 209.0364, found 209.0366.



6s

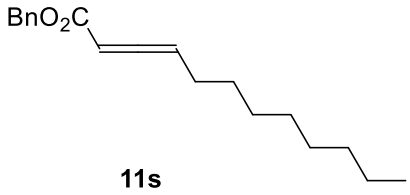
6s: yellow oil, R_f = 0.7 (PE:EA = 6:1), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.22 (m, 10H), 6.63 (d, J = 6.3 Hz, 1H), 6.05 (d, J = 6.3 Hz, 1H), 5.20 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.0, 164.8, 135.8, 130.9, 128.8, 128.5, 128.1 (2C), 128.0, 127.5, 98.8, 91.7, 66.6; ESI-HRMS m/z Calcd. for $C_{17}H_{14}O_2$ + H^+ 251.1067, found 251.1069.



7s

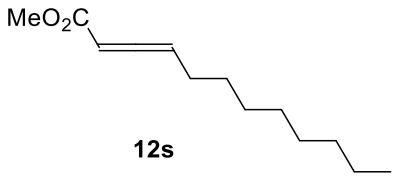
7s: yellow oil, R_f = 0.67 (PE:EA = 6:1), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 5.7 Hz, 2H), 6.87 (d, J = 5.7 Hz, 2H), 6.55 (d, J = 6.3 Hz, 1H), 5.90 (d, J = 6.3 Hz, 1H), 3.80 (s, 3H), 1.48 (s,

9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.0, 164.5, 159.4, 128.6, 123.5, 114.2, 97.9, 93.3, 81.1, 55.3, 28.0; ESI–HRMS m/z Calcd. for $C_{15}H_{18}O_3$ + Na^+ 269.1148, found 269.1151.



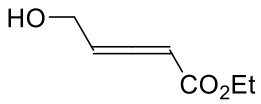
11s

11s: colorless liquid, R_f = 0.8 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.22 (m, 5H), 5.62–5.58 (m, 2H), 5.18 (d, *J* = 12.8 Hz, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 2.14–2.07 (m, 2H), 1.48–1.40 (m, 2H), 1.34–1.25 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.5, 165.8, 136.0, 128.3, 127.9 (2C), 95.4, 87.9, 66.2, 31.7, 29.2, 29.1, 28.8, 28.6, 27.3, 22.5, 14.0; ESI-HRMS m/z Calcd. for $C_{19}H_{26}O_2$ + H^+ 287.2006, found 287.2005.



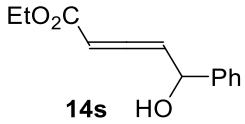
12s

12s: yellow liquid, R_f = 0.75 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70–5.53 (m, 2H), 3.73 (s, 3H), 2.18–2.10 (m, 2H), 1.50–1.42 (m, 2H), 1.36–1.24 (m, 10H), 0.88 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.3, 166.6, 95.4, 87.8, 51.8, 31.8, 29.2 (2C), 28.9, 28.6, 27.4, 22.6, 14.0; ESI-HRMS m/z Calcd. for $C_{13}H_{22}O_2$ + H^+ 211.1693, found 211.1695.



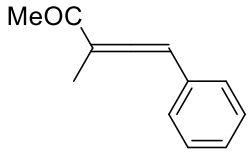
13s

13s (i.e., **2e**): colorless liquid, R_f = 0.25 (PE:EA = 4:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86–5.80 (m, 1H), 5.74–5.71 (m, 1H), 4.30–4.16 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.57 (br s, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.6, 166.1, 96.4, 89.8, 61.1, 58.9, 14.0; ESI-HRMS m/z Calcd. for $C_7H_{10}O_3$ + H^+ 143.0703, found 143.0703.



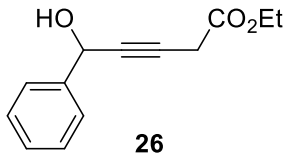
14s

14s: colorless liquid, R_f = 0.3 (PE:EA = 4:1), The ratio of isomers is 1:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.41 (m, 2H), 7.37–7.31 (m, 2H), 5.88–5.83 (m, 1H), 5.74–5.71 (m, 1H), 5.41–5.32 (m, 1H), 4.22–4.11 (m, 2H), 4.05 (d, J = 4.1 Hz, 0.5H), 3.95 (d, J = 4.6 Hz, 0.5H), 1.26 (q, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4 (2C), 166.0, 165.7, 141.7, 141.6, 128.4, 128.3, 127.9, 127.7, 126.2, 126.0, 100.3, 100.1, 90.4, 90.3, 71.2 (2C), 61.1, 61.0, 14.0; ESI-HRMS m/z Calcd. for $C_{13}H_{14}O_3$ + Na^+ 241.0835, found 241.0835.



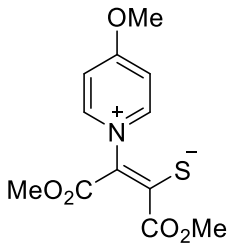
2c

2c: yellow liquid, R_f = 0.6 (PE:EA = 4:1), ^{1}H NMR (400 MHz, $CDCl_3$); δ 7.39–7.22 (m, 5H), 6.53 (q, J = 2.8 Hz, 1H), 2.30 (s, 3H), 1.91 (d, J = 2.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.8, 198.2, 132.0, 128.8, 127.7, 127.0, 107.8, 97.4, 26.7, 13.1; ESI-HRMS m/z Calcd. for $C_{12}H_{12}O$ + H^+ 173.0961, found 173.0962.

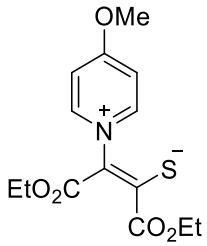


26

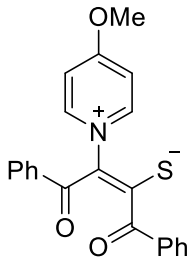
26: colorless liquid, R_f = 0.25 (PE:EA = 4:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.6 Hz, 2H), 7.39–7.29 (m, 3H), 5.48 (d, J = 5.6 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.35 (d, J = 2.0 Hz, 2H), 3.07 (d, J = 4.6 Hz, 1H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 140.6, 128.4, 128.2, 126.6, 83.4, 78.5, 64.4, 61.7, 26.1, 14.0; ESI-HRMS m/z Calcd. for $C_{13}H_{14}O_3$ + Na^+ 241.0835, found 241.0834.



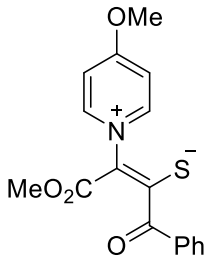
Compound **1b**: yellow solid, mp 161−162 °C. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.62 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 7.6 Hz, 2H), 4.12 (s, 3H), 3.70 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 178.1, 170.8, 169.3, 160.7, 150.0, 123.6, 113.1, 58.1, 52.0, 51.5; ESI-HRMS m/z calcd for $C_{12}H_{13}NO_5S + H^+$ 284.0587, found 284.0584.



Compound **1c**: yellow solid, mp 144−145 °C. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.62 (d, J = 6.8 Hz, 2H), 7.56 (d, J = 7.2 Hz, 2H), 4.16 (q, J = 7.2 Hz, 2H), 4.12 (s, 3H), 4.03 (q, J = 7.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H), 1.10 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 177.9, 170.6, 168.7, 160.3, 150.1, 123.8, 113.0 , 60.6, 60.0, 58.1, 14.3, 14.0; ESI-HRMS m/z calcd for $C_{14}H_{17}NO_5S + H^+$ 312.0900, found 312.0897.

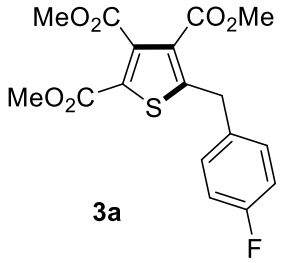


Compound **1d**: yellow solid, mp 175−176 °C. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.92 (d, J = 7.2 Hz, 2H), 7.98–7.86 (m, 2H), 7.59–7.50 (m, 3H), 7.44 (t, J = 7.2 Hz, 2H), 7.31–7.25 (m, 1H), 7.25–7.20 (m, 2H), 7.20–7.12 (m, 2H), 4.07 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 191.2, 191.1, 181.6, 170.6, 150.2, 139.1, 135.8, 135.4, 132.0, 130.1, 129.1, 128.0, 128.0, 127.2, 112.9, 58.1; ESI-HRMS m/z calcd for $C_{22}H_{17}NO_3S + H^+$ 376.1002, found 376.1000.



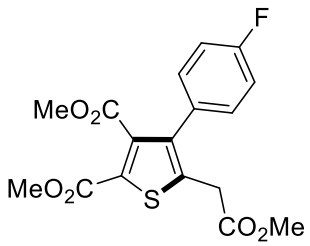
Compound **1e**: yellow solid, mp 169−170 °C. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.83 (d, J = 3.6 Hz, 2H), 8.00–7.92 (m, 2H), 7.66–7.60 (m, 2H), 7.58–7.52 (m, 1H), 7.50–7.44 (m, 2H), 4.14 (s, 3H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 191.0, 185.9, 170.7, 160.8, 150.1, 135.6, 132.2, 129.2, 128.2, 123.9, 113.0, 58.1, 51.10; ESI-HRMS m/z calcd for $C_{17}H_{15}NO_4S + H^+$ 330.0795, found 330.0791.

7. Characterization data of products



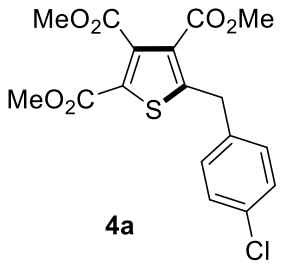
3a

3a: Y = 68%, yellow oil, R_f = 0.25 (PE:EA = 4:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.21 (m, 2H), 7.00–7.05 (m, 2H), 4.47 (s, 2H), 3.97 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 161.9 (d, J = 244.5 Hz), 161.9, 160.4, 160.1, 140.7, 133.6 (d, J = 3.3 Hz), 130.5 (d, J = 8.1 Hz), 127.2, 126.5, 115.6 (d, J = 21.4 Hz), 52.8, 52.5, 52.1, 35.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.0; ESI-HRMS m/z Calcd. for $C_{17}H_{15}FO_6S + H^+$ 367.0646, found 367.0646.



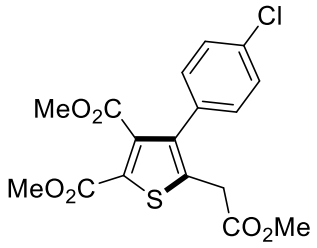
3b

3b: Y = 28%, yellow oil, R_f = 0.3 (PE:EA = 4:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.23 (m, 2H), 7.13–7.06 (m, 2H), 3.88 (s, 3H), 3.72 (s, 3H), 3.71 (s, 3H), 3.70 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 165.7, 162.6 (d, J = 246.7 Hz), 161.1, 139.6, 139.3, 138.2, 131.1 (d, J = 8.2 Hz), 128.9 (d, J = 2.3 Hz), 115.6 (d, J = 21.5 Hz), 52.7, 52.5 (2C), 33.8, (1C missing); ^{19}F NMR (376 MHz, $CDCl_3$) δ –112.97; ESI-HRMS m/z Calcd. for $C_{17}H_{15}FO_6S + H^+$ 367.0646, found 367.0645.



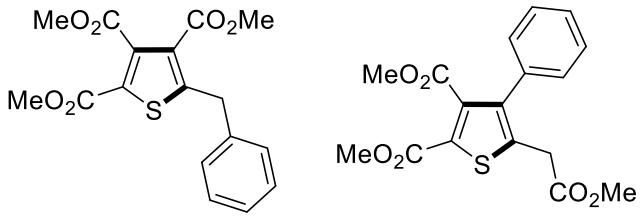
4a

4a: Y = 64%, colorless oil, R_f = 0.15 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 4.46 (s, 2H), 3.96 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 161.8, 160.3, 159.3, 140.7, 136.3, 133.1, 130.2, 128.8, 127.2, 126.6, 52.8, 52.5, 52.1, 35.2; ESI-HRMS m/z Calcd. for $C_{17}H_{15}ClO_6S + H^+$ 383.0351, found 383.0352.



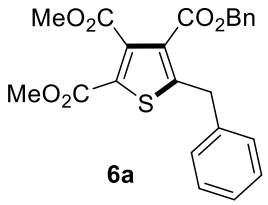
4b

4b: Y = 35%, brown oil, R_f = 0.25 (PE:EA = 6:1), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 3.88 (s, 3H), 3.73 (s, 3H), 3.71 (s, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 165.6, 161.0, 139.3, 139.0, 138.2, 134.5, 131.4, 130.6, 129.0, 128.8, 52.7, 52.5, 33.8, (1C missing); ESI-HRMS m/z Calcd. for $C_{17}H_{15}ClO_6S + H^+$ 383.0351, found 383.0353.



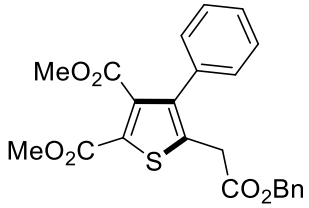
5a, **5b**

5a/5b: Y = 95%, brown oil, R_f = 0.2 (PE:EA = 6:1). The ratio of **5a**:**5b** = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.22 (m, 7.3H), 4.49 (s, 2H), 3.96 (s, 3H), 3.86 (s, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.72 (s, 0.7H), 3.70 (s, 1H), 3.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 165.6, 165.3, 161.9, 161.0, 160.4, 160.3, 140.6, 140.2, 139.5, 137.9, 137.8, 132.8, 129.0, 128.8, 128.6 (2C), 128.4, 128.2, 127.2, 127.0, 126.4, 52.8, 52.4 (2C), 52.3 (2C), 52.0, 36.0, 33.7; ESI-HRMS m/z Calcd. for $C_{17}H_{16}O_6S + H^+$ 349.0740, found 349.0740.



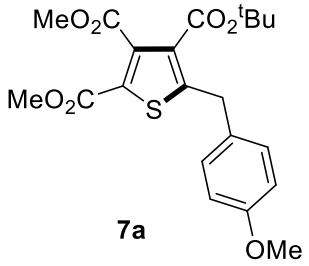
6a

6a: Y = 68%, yellow oil, R_f = 0.26 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.24 (m, 8H), 7.24–7.19 (m, 2H), 5.26 (s, 2H), 4.50 (s, 2H), 3.78 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 161.4, 160.9, 160.5, 140.7, 137.9, 134.8, 129.0, 128.8, 128.6, 128.5, 127.3, 127.1, 126.3, 67.3, 52.6, 52.5, 36.1, (1C missing); ESI-HRMS m/z Calcd. for $C_{23}H_{20}O_6S + H^+$ 425.1053, found 425.1057.



6b

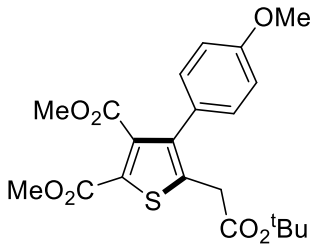
6b: Y = 22%, yellow solid, 119.3–120.1 ^{o}C, R_f = 0.23 (PE:EA = 6:1), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.33 (m, 6H), 7.33–7.29 (m, 2H), 7.25–7.19 (m, 2H), 5.13 (s, 2H), 3.88 (s, 3H), 3.76 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 165.8, 161.2, 140.5, 139.6, 137.8, 135.2, 133.0, 129.2, 128.8, 128.6, 128.5 (2C), 128.4, 128.3, 67.3, 52.6, 52.5, 34.2; ESI-HRMS m/z Calcd. for $C_{23}H_{20}O_6S + H^+$ 425.1053, found 425.1053.



7a

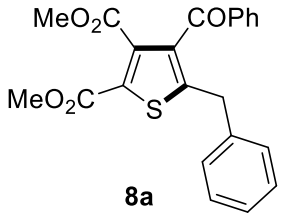
7a: Y = 55%, yellow oil, R_f = 0.29 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.41 (s, 2H), 3.96 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 1.54 (s,

9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 161.0, 160.9, 160.7, 158.8, 140.7, 130.2 (2C), 128.1, 126.7, 114.2, 82.6, 55.2, 52.8, 52.5, 35.4, 28.1; ESI-HRMS m/z Calcd. for $C_{21}H_{24}O_7S + Na^+$ 443.1135, found 443.1135.



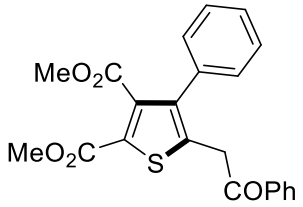
7b

7b: Y = 14%, yellow oil, R_f = 0.24 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 3.74 (s, 3H), 3.61 (s, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 166.2, 161.4, 159.4, 139.8, 138.8, 130.5, 128.2, 125.3, 113.9, 82.1, 55.2, 52.7, 52.4, 35.6, 27.9, (1C missing); ESI-HRMS m/z Calcd. for $C_{21}H_{24}O_7S + H^+$ 421.1316, found 421.1317.



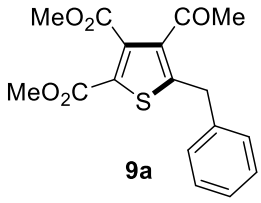
8a

8a: Y = 19%, brownish red oil, mp:132.5–133.2 ^{o}C, R_f = 0.25 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.70 (m, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.30–7.20 (m, 3H), 7.18–7.11 (m, 2H), 4.12 (s, 2H), 3.83 (s, 3H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 163.7, 160.7, 153.6, 138.2, 138.1, 137.5, 133.5, 130.0, 129.2, 128.8, 128.6, 127.2, 52.6, 52.4, 35.1, (2C missing); ESI-HRMS m/z Calcd. for $C_{22}H_{18}O_5S + H^+$ 395.0948, found 395.0947.



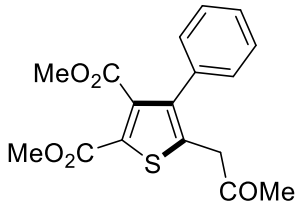
8b

8b: Y = 25%, brownish red solid, mp:132.5–133.2 ^{o}C, R_f = 0.15 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.80 (m, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.45–7.34 (m, 5H), 7.28–7.24 (m, 2H), 4.38 (s, 2H), 3.87 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 166.0, 161.2, 140.2, 139.5, 138.7, 135.6, 133.7, 133.3, 129.2, 129.0, 128.7, 128.6, 128.3, 52.6, 52.4, 38.0, (1C missing); ESI-HRMS m/z Calcd. for $C_{22}H_{18}O_5S + H^+$ 395.0948, found 395.0947.



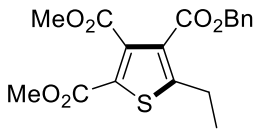
9a

9a: Y = 29%, brownish red oil, R_f = 0.3 (PE:EA = 4:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.29 (m, 3H), 7.27–7.19 (m, 2H), 4.40 (s, 2H), 3.97 (s, 3H), 3.82 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 165.9, 160.7, 157.8, 139.6, 137.7, 136.5, 129.0, 128.9, 127.8, 127.5, 53.2, 52.6, 36.4, 30.1; ESI-HRMS m/z Calcd. for $C_{17}H_{16}O_5S + H^+$ 333.0791, found 333.0790.



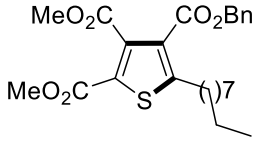
9b

9b: Y = 20%, brownish red oil, R_f = 0.2 (PE:EA = 4:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.36 (m, 3H), 7.25–7.16 (m, 2H), 3.88 (s, 3H), 3.82 (s, 2H), 3.70 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 165.9, 161.2, 140.2, 139.6, 138.1, 133.2, 129.1, 128.9, 128.6, 128.3, 52.6, 52.5, 42.7, 29.6; ESI-HRMS m/z Calcd. for $C_{17}H_{16}O_5S + H^+$ 333.0791, found 333.0789.



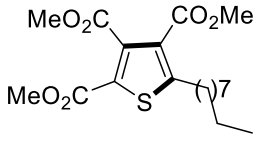
10

10: Y = 87%, brown oil, R_f = 0.25 (PE:EA = 4:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.28 (m, 5H), 5.25 (s, 2H), 3.84 (s, 3H), 3.62 (s, 3H), 3.21 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 163.4, 161.3, 160.6, 140.9, 134.9, 128.7, 128.5, 128.4, 126.1, 126.0, 67.2, 52.5, 23.8, 15.1, (1C missing); ESI-HRMS m/z Calcd. for $C_{18}H_{18}O_6S + H^+$ 363.0897, found 363.0898.



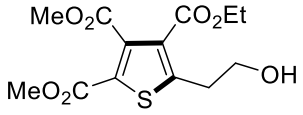
11

11: Y = 85%, brown oil, R_f = 0.4 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.31 (m, 5H), 5.25 (s, 2H), 3.84 (s, 3H), 3.63 (s, 3H), 3.14 (t, J = 8.0 Hz, 2H), 1.71–1.62 (m, 2H), 1.34–1.22 (m, 12H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 161.8, 161.4, 160.6, 140.8, 134.9, 128.8, 128.5 (2C), 126.2 (2C), 67.2, 52.6, 52.5, 31.8, 31.1, 30.2, 29.4, 29.2, 22.6, 14.0 , (2C missing); ESI-HRMS m/z Calcd. for $C_{25}H_{32}O_6S + H^+$ 461.1992, found 461.1991.



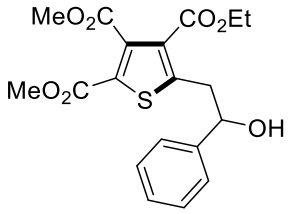
12

12: Y = 89%, yellow oil, R_f = 0.25 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.16 (t, J = 7.6 Hz, 2H), 1.73–1.65 (m, 2H), 1.41–1.26 (m, 12H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 162.1, 161.4, 160.7, 140.9, 126.5, 126.2, 52.9, 52.6, 52.0, 31.8, 31.0, 30.1, 29.4, 29.2, 22.6, 14.0, (2C missing); ESI-HRMS m/z Calcd. for $C_{19}H_{28}O_6S + H^+$ 385.1679, found 385.1682.



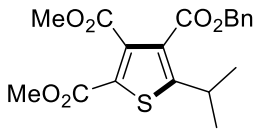
13

13: Y = 73%, brownish red oil, R_f = 0.25 (PE:EA = 2:1), ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.30 (q, J = 8.4 Hz, 2H), 3.95 (s, 3H), 3.91 (t, J = 6.2 Hz, 2H), 3.87 (s, 3H), 3.42 (t, J = 6.0 Hz, 2H), 2.47 (s, 1H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 161.8, 160.6, 156.4, 140.4, 127.4, 127.2, 62.3, 61.4, 52.8, 52.6, 33.0, 13.9; ESI-HRMS m/z Calcd. for $C_{13}H_{16}O_7S + H^+$ 317.0690, found 317.0688.



14

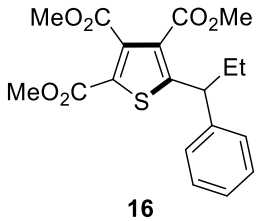
14: Y = 85%, brownish red oil, R_f = 0.5 (PE:EA = 2:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.24 (m, 5H), 4.96 (d, J = 8.0 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 3.93 (s, 3H), 3.83 (s, 3H), 3.68 (dd, J = 14.4, 4.0 Hz, 1H), 3.38 (dd, J = 14.4, 8.4 Hz, 1H), 3.05 (s, 1H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 162.0, 160.6, 155.6, 143.1, 140.1, 128.4, 127.8, 127.6, 125.5, 73.8, 61.4, 52.8, 52.6, 39.3, 13.9. (1C missing); ESI-HRMS m/z Calcd. for $C_{19}H_{20}O_7S + H^+$ 393.1003, found 393.0998.



15

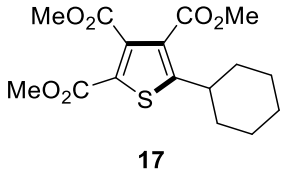
15: Y = 72%, colorless oil, R_f = 0.3 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.30 (m, 5H), 5.25 (s, 2H), 4.17–4.02 (m, 1H), 3.84 (s, 3H), 3.59 (s, 3H), 1.33 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 165.5, 161.3, 160.7, 140.7, 134.9, 128.8, 128.6, 128.5, 126.0,

125.5, 67.3, 52.5 (2C), 29.7, 24.5; ESI-HRMS m/z Calcd. for $C_{19}H_{20}O_6S + Na^+$ 399.0873, found 399.0870.



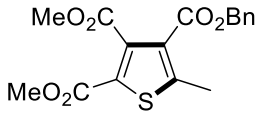
16

16: Y = 52%, yellow oil, R_f = 0.25 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.28 (m, 4H), 7.27–7.20 (m, 1H), 5.05 (t, J = 7.6 Hz, 1H), 3.94 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 2.13–2.04 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 165.3, 162.0, 160.6, 141.9, 140.6, 128.6, 127.9, 127.1, 126.6, 52.9, 52.6, 52.0, 46.9, 30.8, 12.6, (1C missing); ESI-HRMS m/z Calcd. for $C_{19}H_{20}O_6S + Na^+$ 399.0873, found 399.0870.



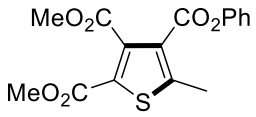
17

17: 49%, yellow oil, R_f = 0.4 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.74–3.61 (m, 1H), 2.05 (d, J = 11.2 Hz, 2H), 1.89–1.73 (m, 3H), 1.51–1.32 (m, 4H), 1.30–1.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 165.9, 162.1, 160.8, 140.6, 126.2, 125.6, 52.9, 52.6, 52.1, 39.4, 35.3, 26.4, 25.7; ESI-HRMS m/z Calcd. for $C_{16}H_{20}O_6S + H^+$ 341.1053, found 341.1050.



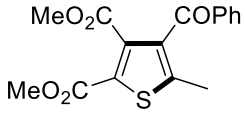
18

18: Y = 74%, yellow oil, R_f = 0.4 (PE:EA = 5:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.31 (m, 5H), 5.26 (s, 2H), 3.84 (s, 3H), 3.63 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 161.5, 160.6, 155.7, 140.8, 135.0, 128.7, 128.6, 128.5, 126.8, 126.1, 67.2, 52.6 (2C), 16.4; ESI-HRMS m/z Calcd. for $C_{17}H_{16}O_6S + H^+$ 349.0746; found : 349.0740.



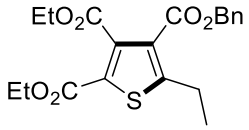
19

19: Y = 67%, yellow oil, R_f = 0.4 (PE:EA = 5:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, J = 7.6 Hz, 2H), 7.30–7.24 (m, 1H), 7.17 (d, J = 7.6 Hz, 2H), 3.92 (s, 3H), 3.89 (s, 3H), 2.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 160.6, 160.1, 156.7, 150.1, 141.0, 129.5, 126.4, 126.2, 121.5, 53.1, 52.7, 16.5, (1C missing); ESI-HRMS m/z Calcd. for $C_{16}H_{14}O_6S + H^+$ 335.0589; found : 335.4584.



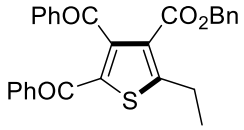
20

20:, Y = 31%, brownish red oil, R_f = 0.2 (PE:EA = 2:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.47(t, J = 7.8 Hz, 2H), 3.88 (s, 3H), 3.55 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 164.0, 160.7, 148.7, 138.7, 137.7, 137.4, 133.4, 129.2, 128.9, 128.6, 52.7, 52.5, 15.0; ESI-HRMS m/z Calcd. for $C_{16}H_{14}O_5S + H^+$ 271.0276, found 271.0271.



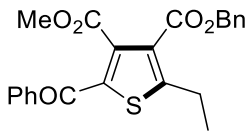
21

21: Y = 89%, colorless oil, R_f = 0.55 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.31 (m, 5H), 5.26 (s, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.20 (q, *J* = 7.2 Hz, 2H), 1.38-1.28 (m, 6H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.2, 161.4, 160.2, 140.7, 135.0, 128.6, 128.5, 128.4, 126.6, 125.9, 67.0, 61.7, 61.6, 23.8, 15.1, 14.0, 13.7; ESI-HRMS m/z Calcd. for $C_{20}H_{22}O_6S + H^+$ 391.1210, found 391.1212.



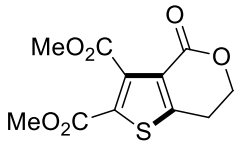
22

22: Y = 36%, yellow oil, R_f = 0.4 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 1.2, 8.0 Hz, 2H), 7.66 (dd, *J* = 1.2, 8.0 Hz, 2H), 7.53–7.44 (m, 2H), 7.40–7.27 (m, 4H), 7.27–7.17 (m, 3H) , 7.01 (dd , *J* = 1.2, 8.0 Hz, 2H), 5.02 (s, 2H), 3.28 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 186.4, 163.4, 161.8, 148.1, 137.7, 137.2, 134.6, 134.4, 132.8, 132.7, 129.0, 128.6, 128.3 (3C), 128.2, 128.1, 67.0, 23.8, 15.3, (1C missing); ESI-HRMS m/z Calcd. for $C_{28}H_{22}O_4S + Na^+$ 477.1131, found 477.1132.



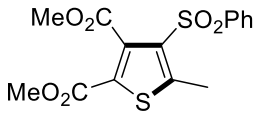
23

23: Y = 34%, yellow oil, R_f = 0.4 (PE:EA = 6:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.75 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.40–7.32 (m, 5H), 5.27 (s, 2H), 3.39 (s, 3H), 3.20 (q, *J* = 7.6 Hz, 2H), 1.34 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 165.1, 162.0 (2C), 139.6, 137.7, 135.6, 135.0, 132.8, 128.9, 128.7, 128.6, 128.5, 128.4, 127.2, 67.3, 52.3, 23.6, 15.4; ESI-HRMS m/z Calcd. for $C_{23}H_{20}O_5S + Na^+$ 431.0924, found 431.0922.



24

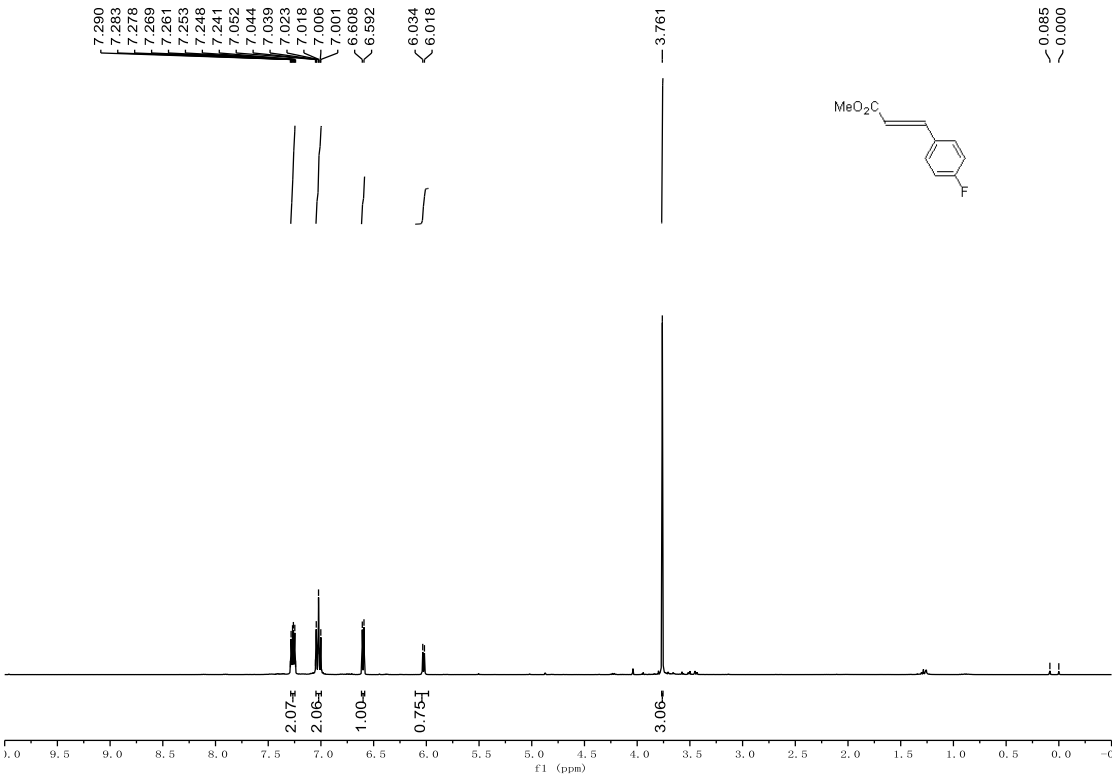
24: Y = 59% for two steps, colorless oil, R_f = 0.2 (PE:EA = 2:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (t, J = 6.0 Hz, 2H), 3.98 (s, 3H), 3.90 (s, 3H), 3.22 (t, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 160.2, 158.8, 154.1, 138.4, 128.9, 126.2, 67.3, 53.1, 52.7, 24.6; ESI-HRMS m/z Calcd. for $C_{11}H_{10}O_6S + H^+$ 271.0271, found 271.0269.



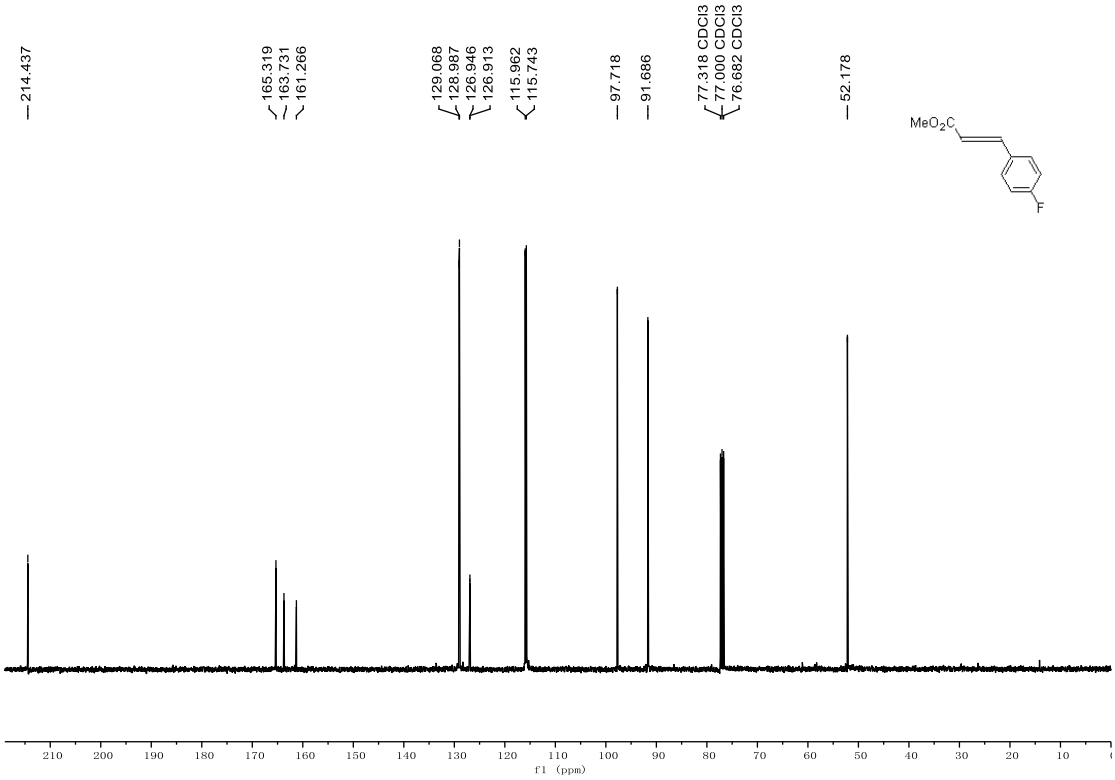
25

25: Y = 83%, colorless oil, R_f = 0.4 (PE:EA = 2:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.54 (t, J = 7.4 Hz, 2H), 4.04 (s, 3H), 3.86 (s, 3H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164. 6, 160.0, 153.0, 140.8, 139.2, 135.3, 133.6, 129.2, 127.4, 126.9, 53.3, 52.8, 15.1; ESI-HRMS m/z Calcd. for $C_{15}H_{14}O_6S_2 + H^+$ 355.0305, found 355.0306.

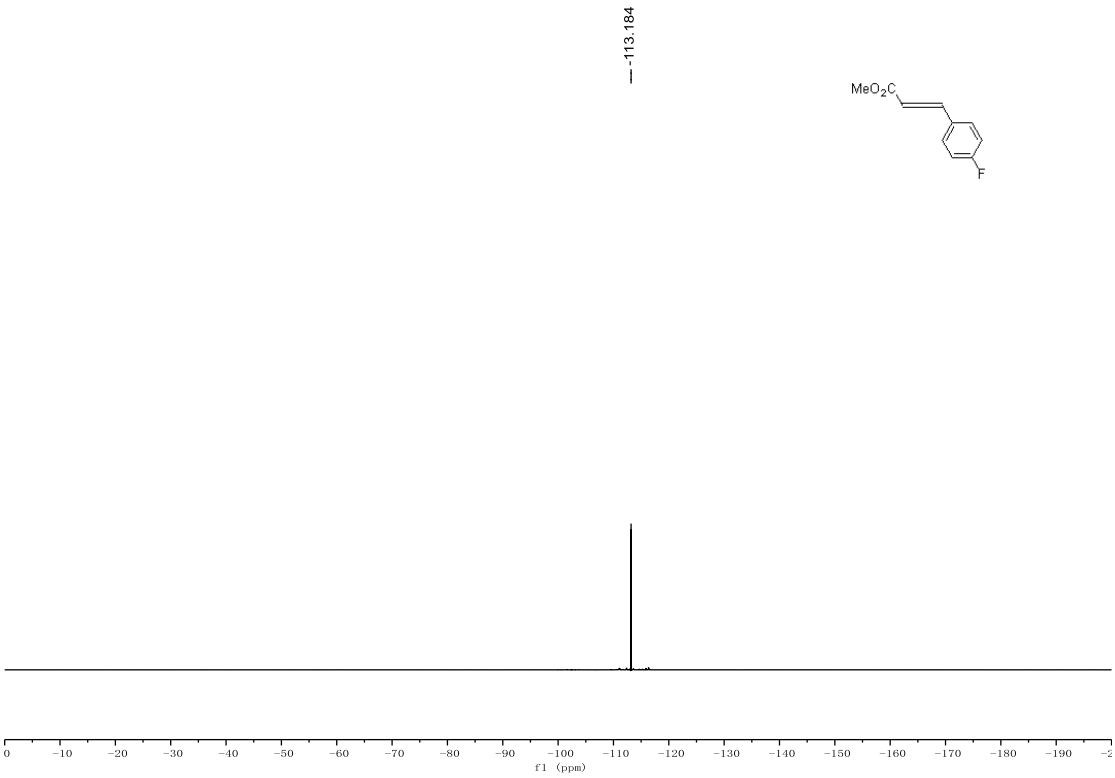
8. Copies of NMR spectra



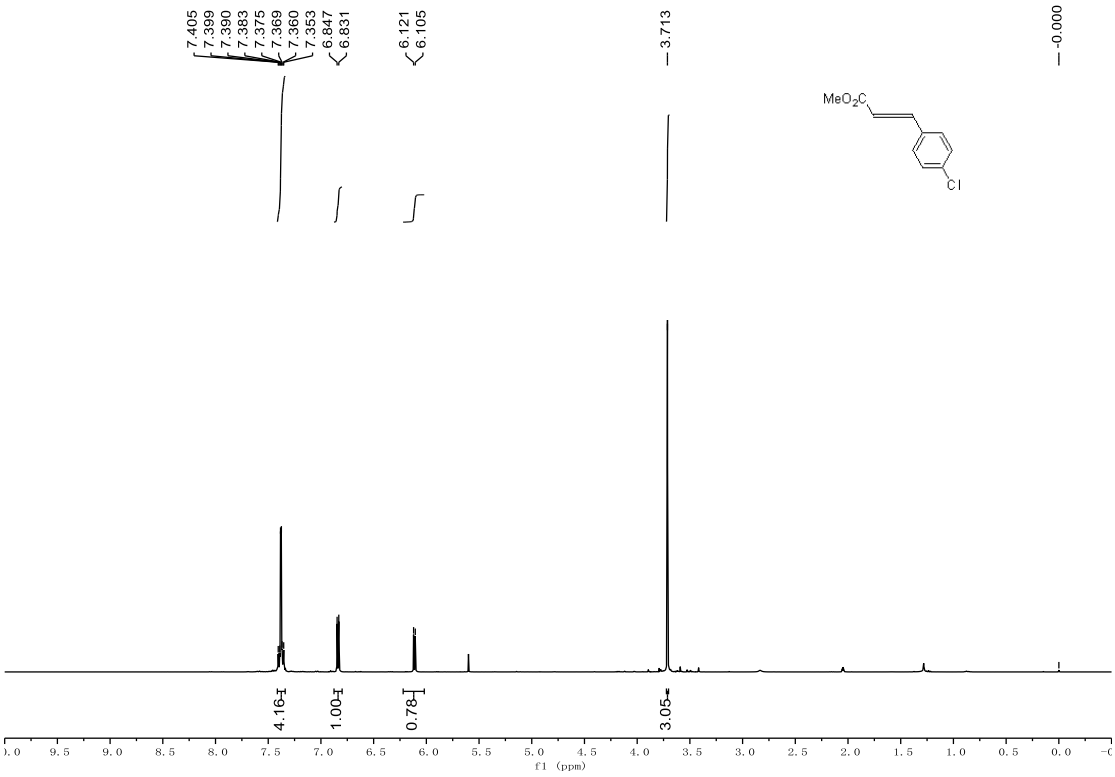
^{1}H NMR of **3s**



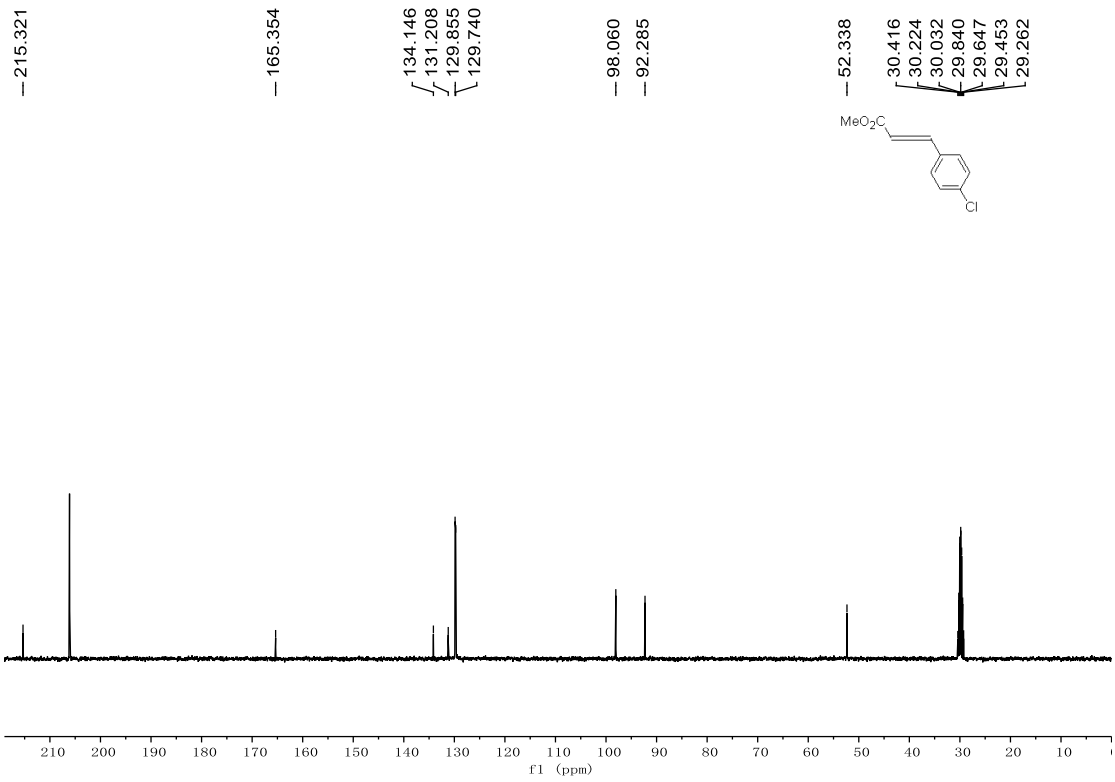
^{13}C NMR of **3s**



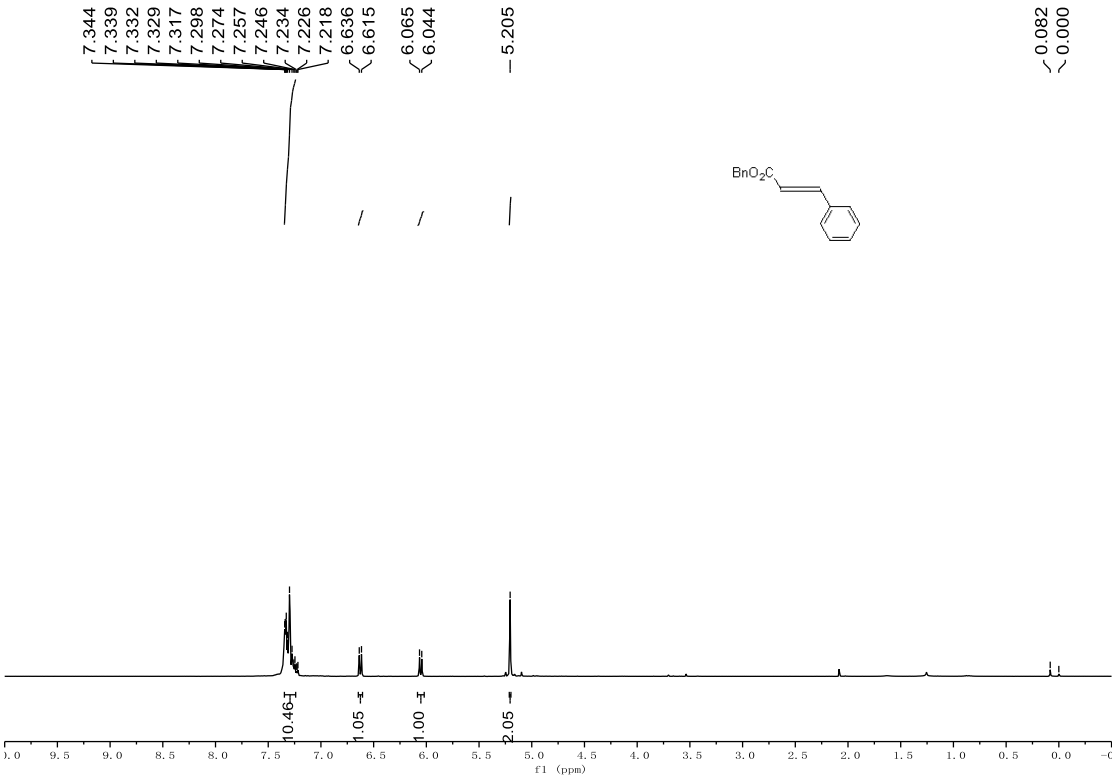
^{19}F NMR of **3s**



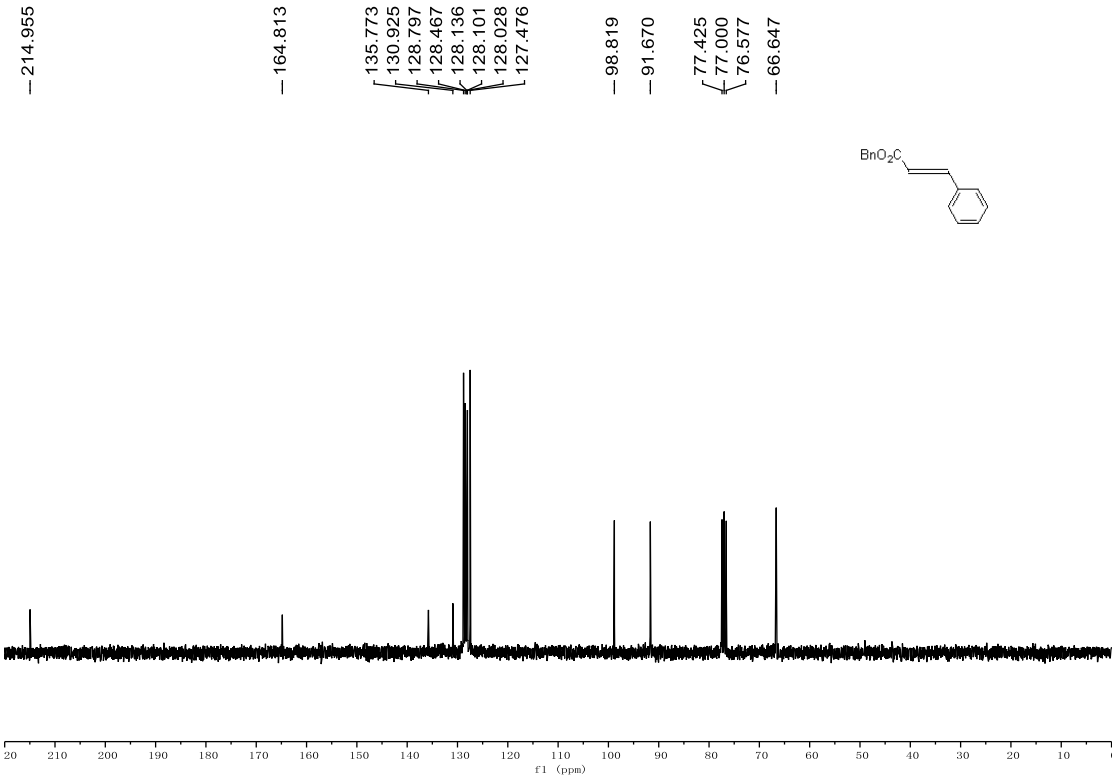
^{1}H NMR of **4s**



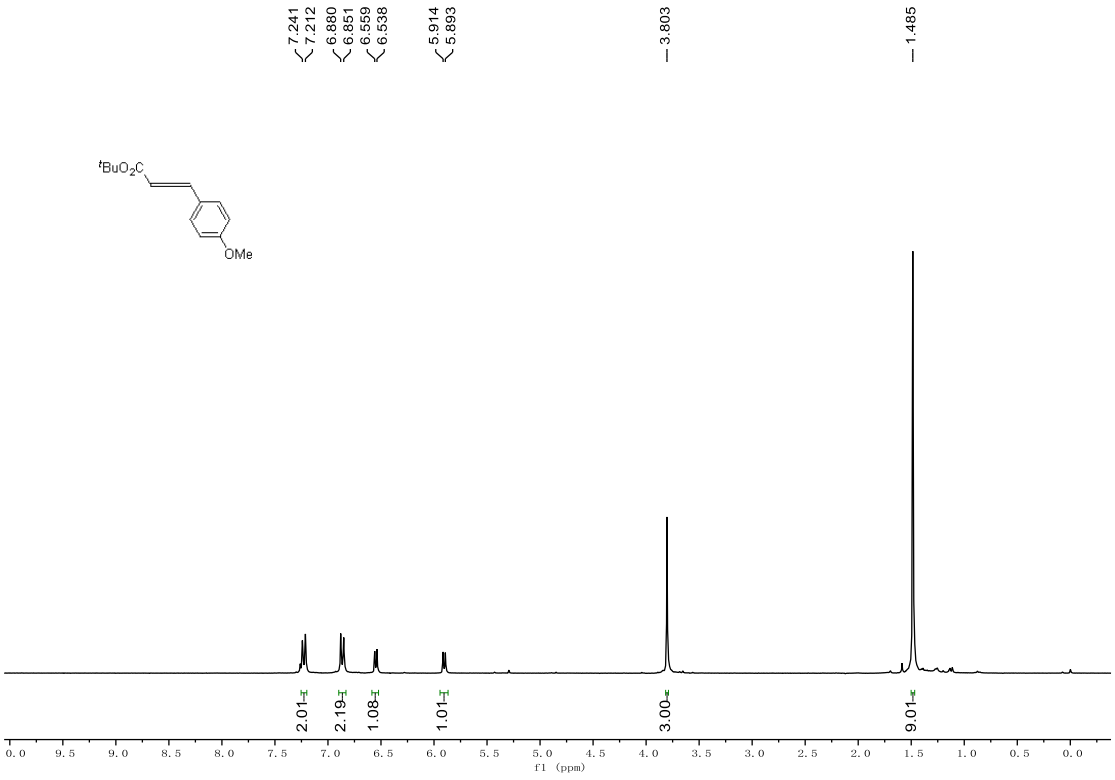
^{13}C NMR of **4s**



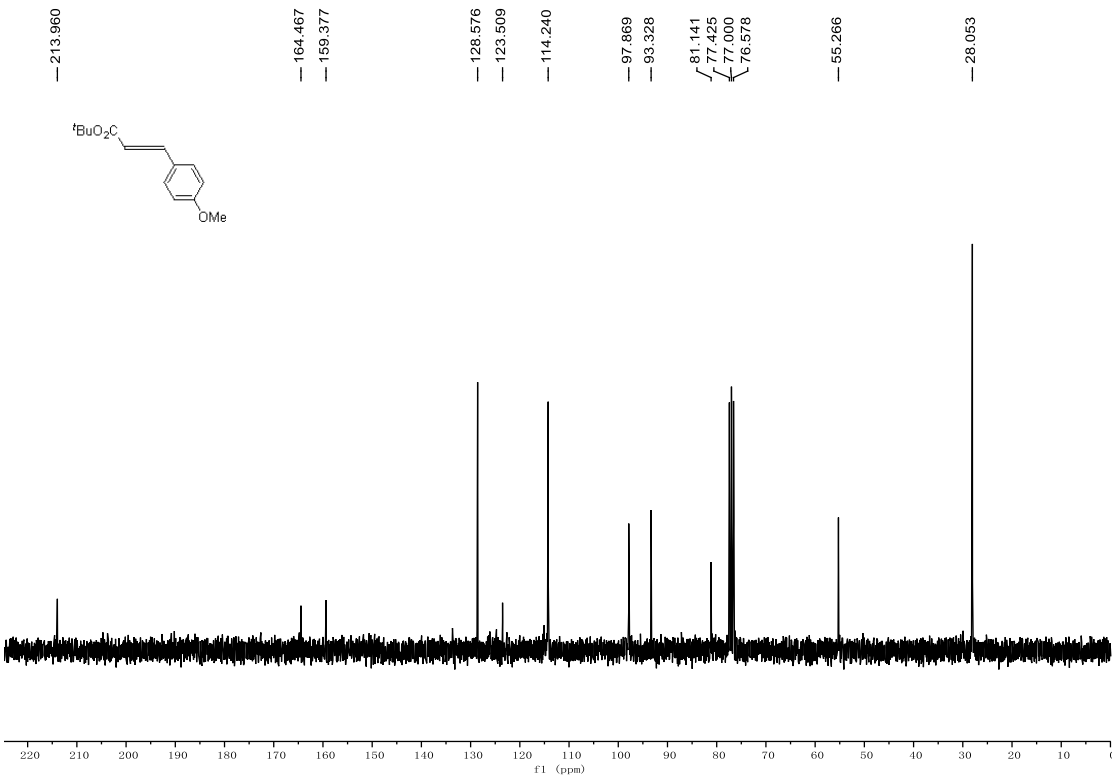
^{1}H NMR of **6s**



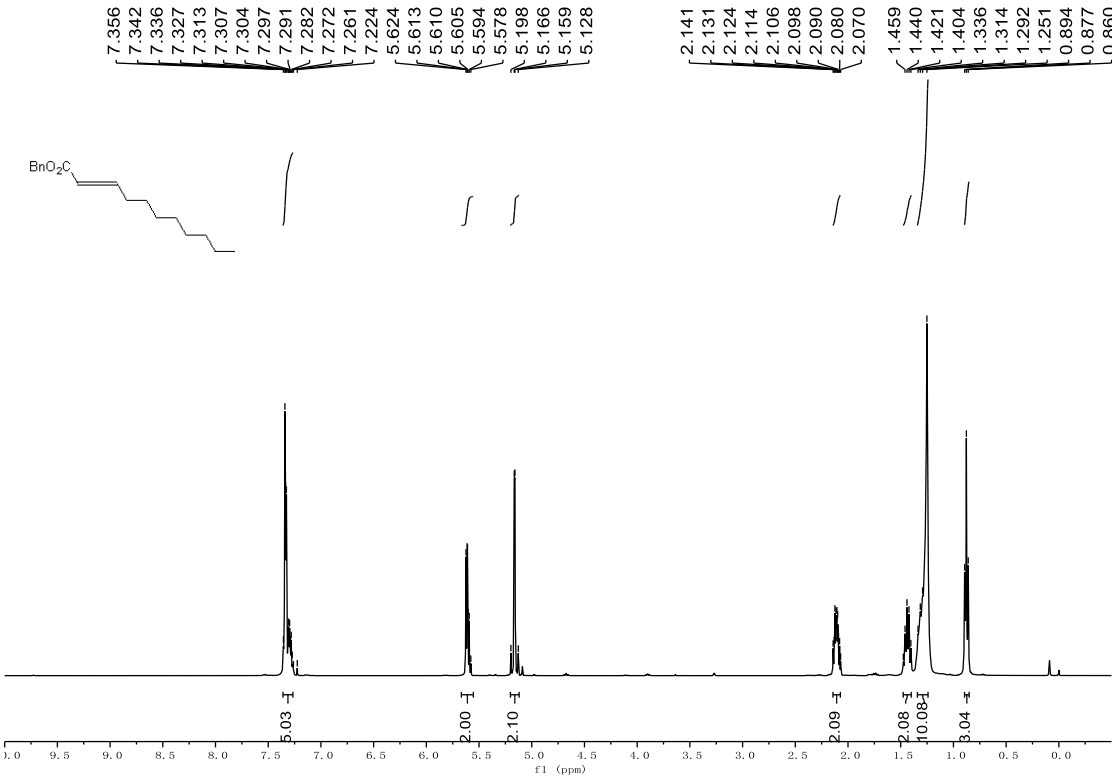
^{13}C NMR of **6s**



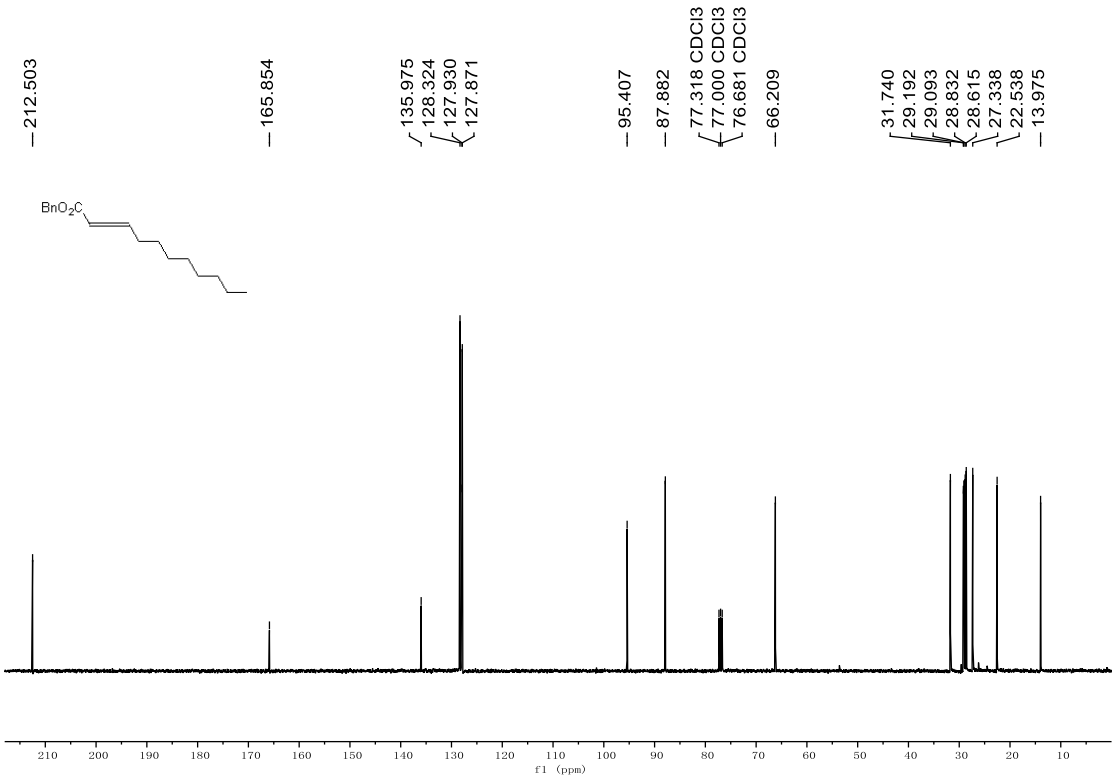
^{1}H NMR of **7s**



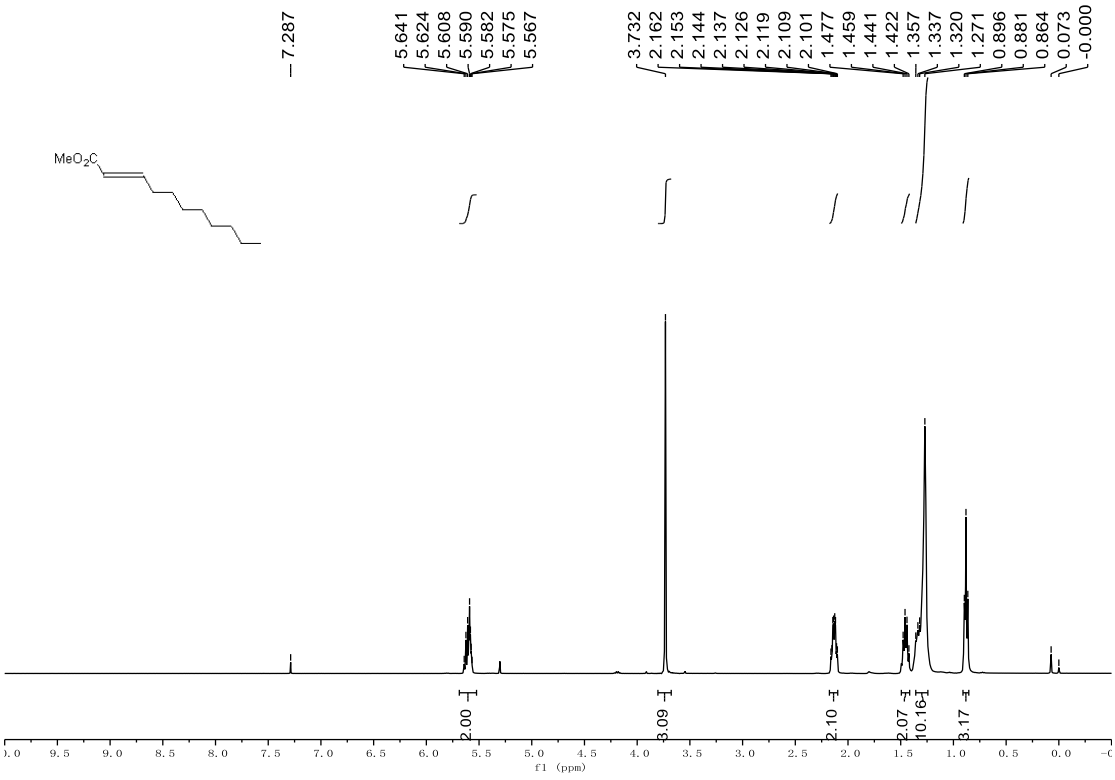
^{13}C NMR of **7s**



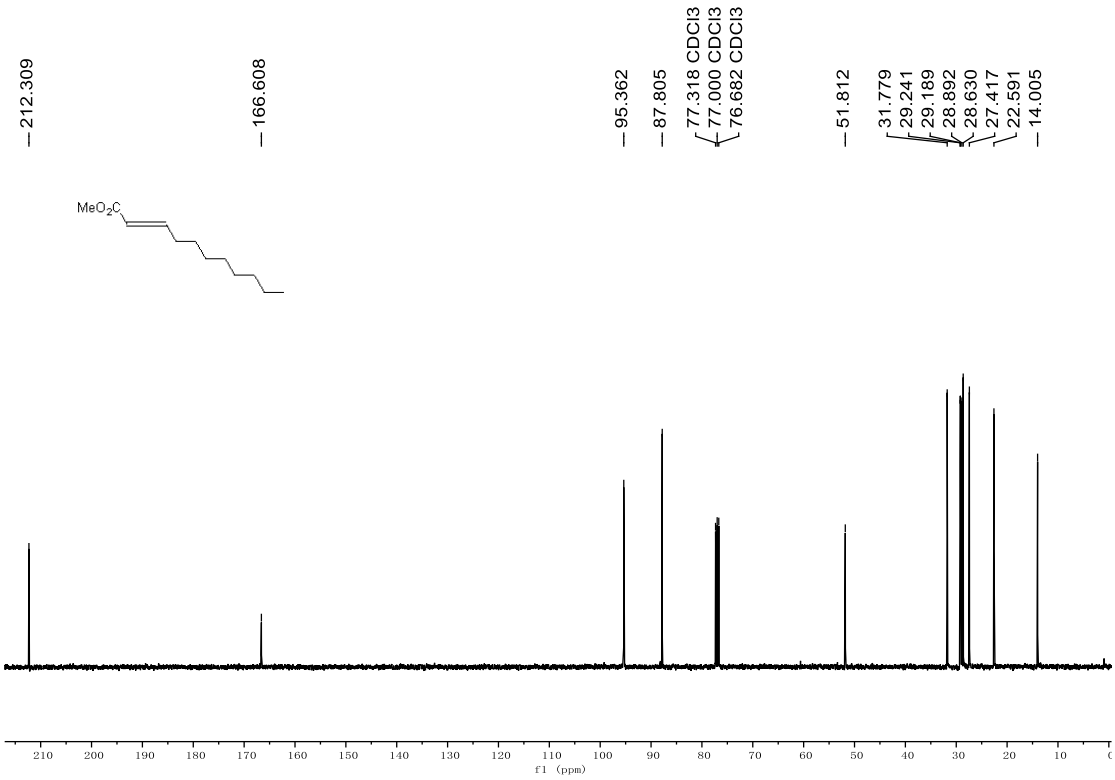
^{1}H NMR of **11s**



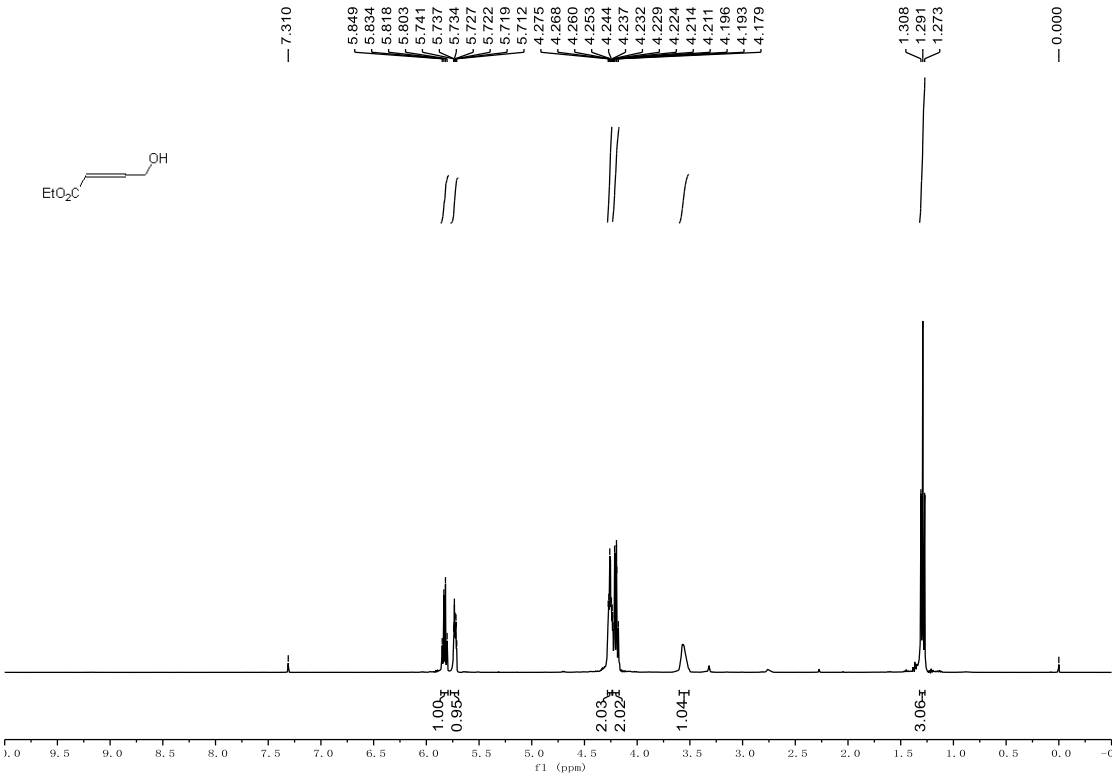
^{13}C NMR of **11s**



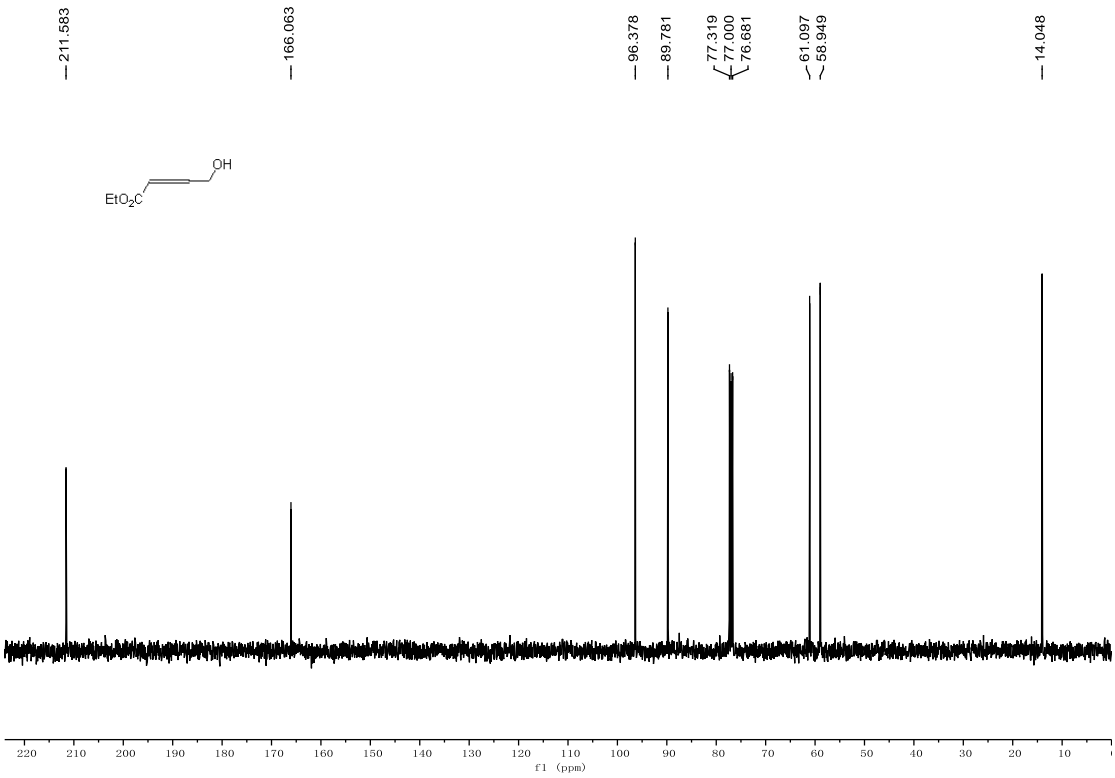
^{1}H NMR of **12s**



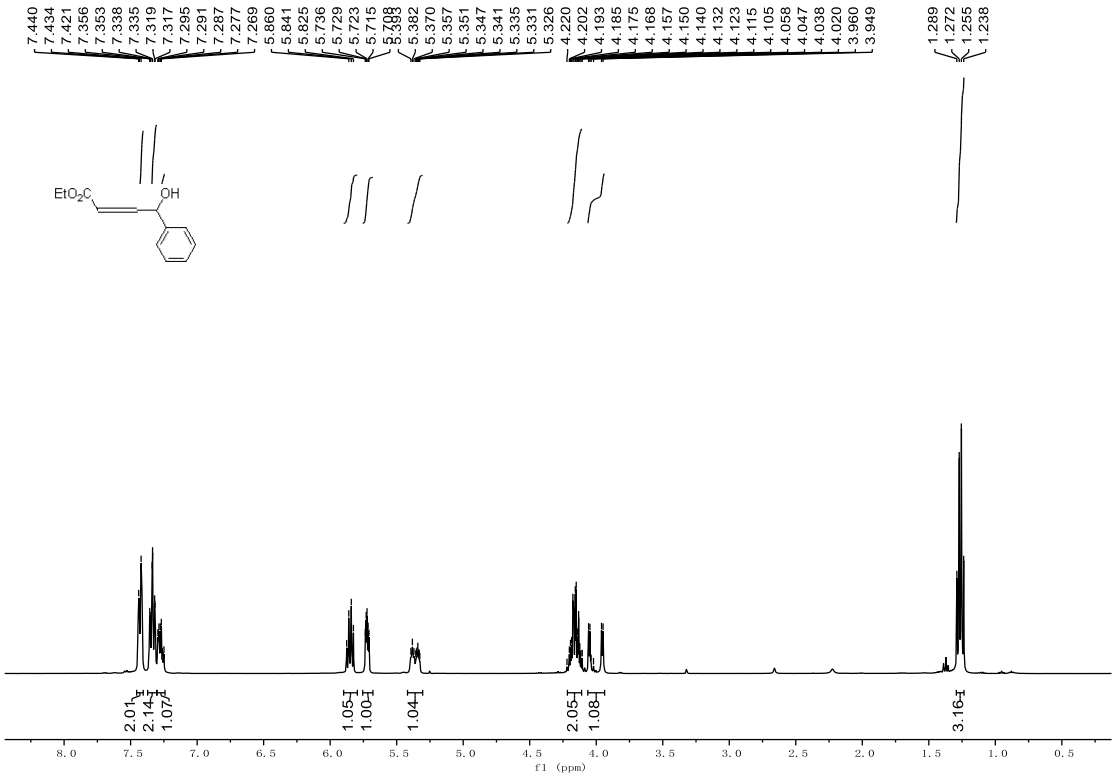
^{13}C NMR of **12s**



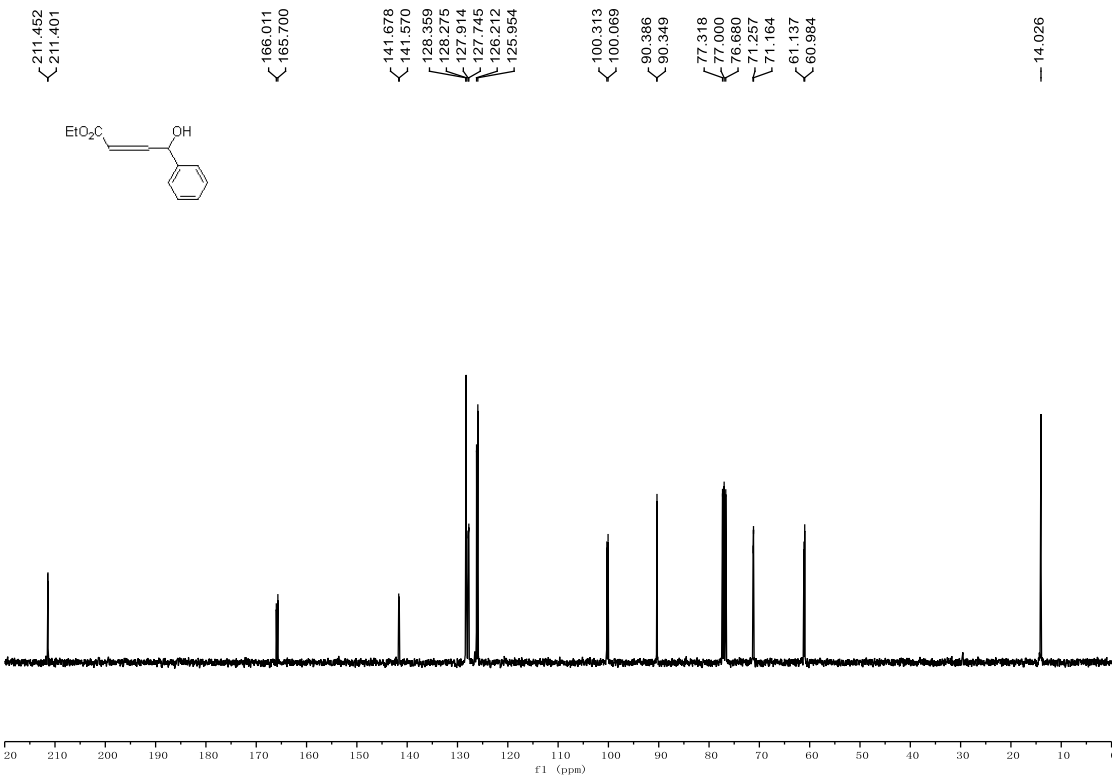
^{1}H NMR of **13s**



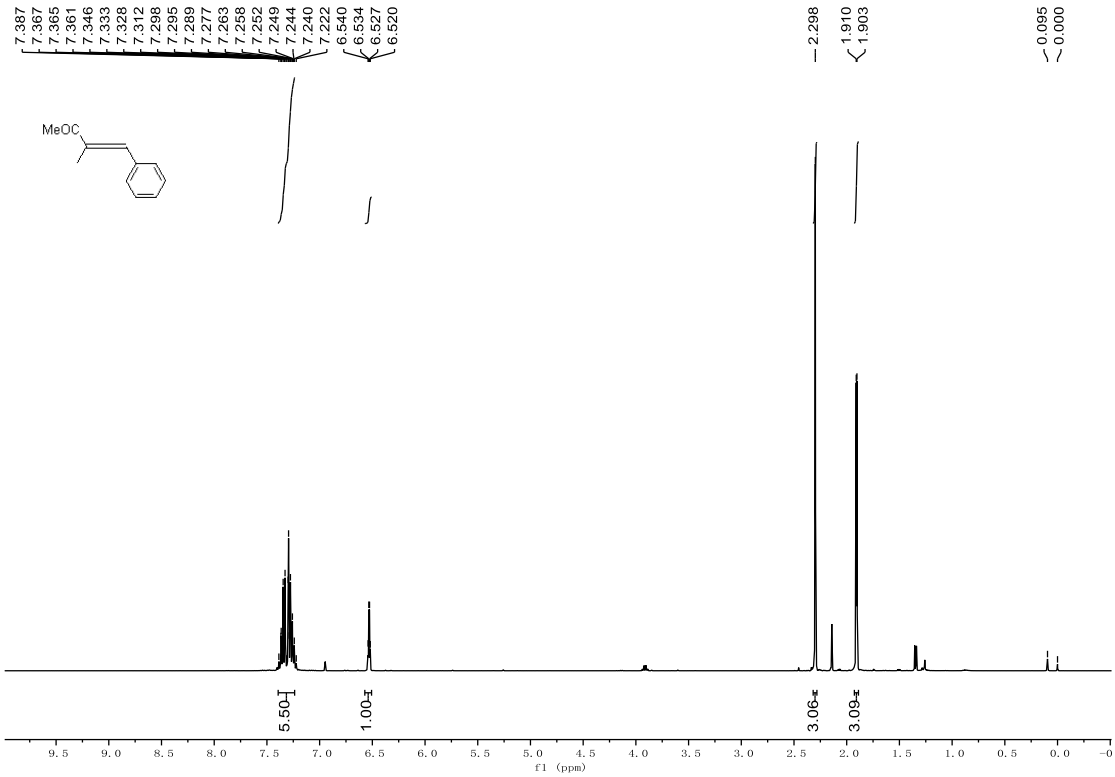
^{13}C NMR of **13s**



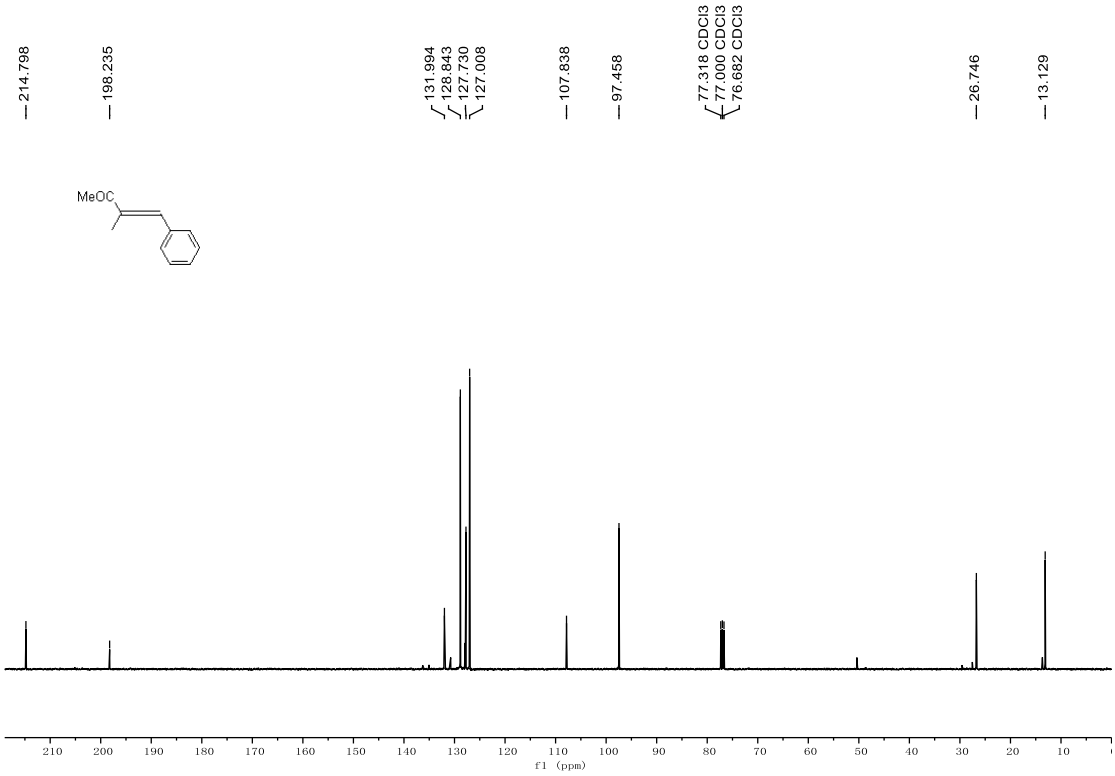
^{1}H NMR of **14s**



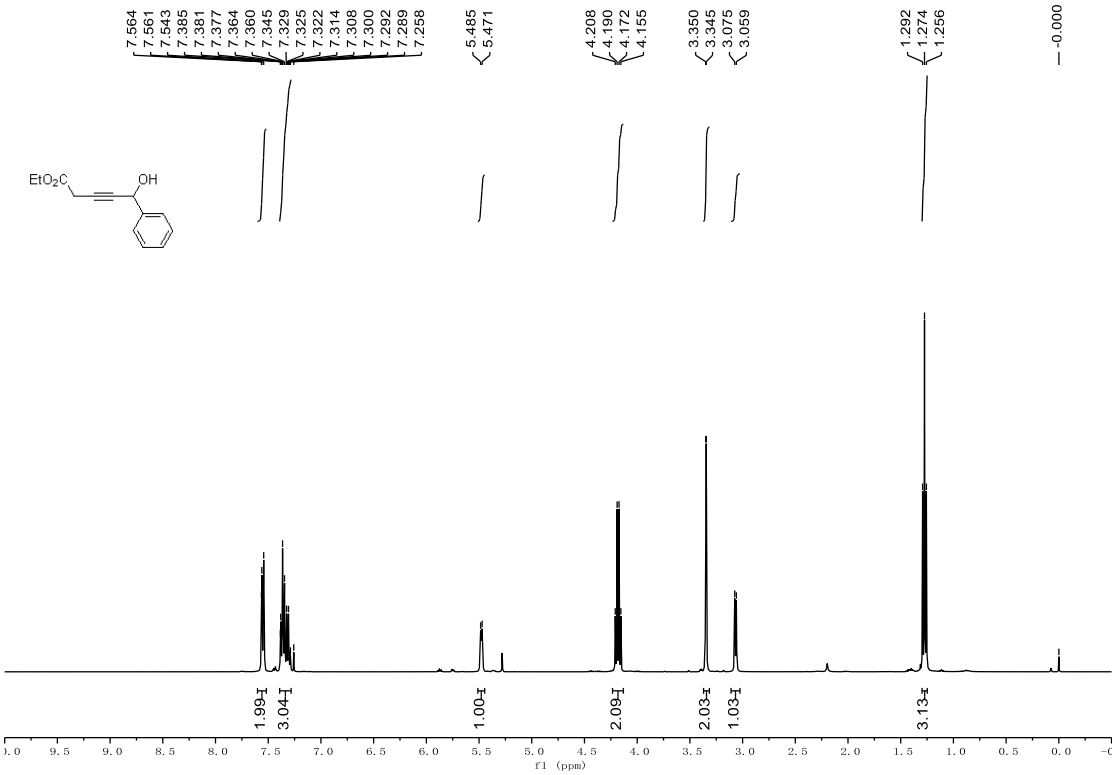
^{13}C NMR of **14s**



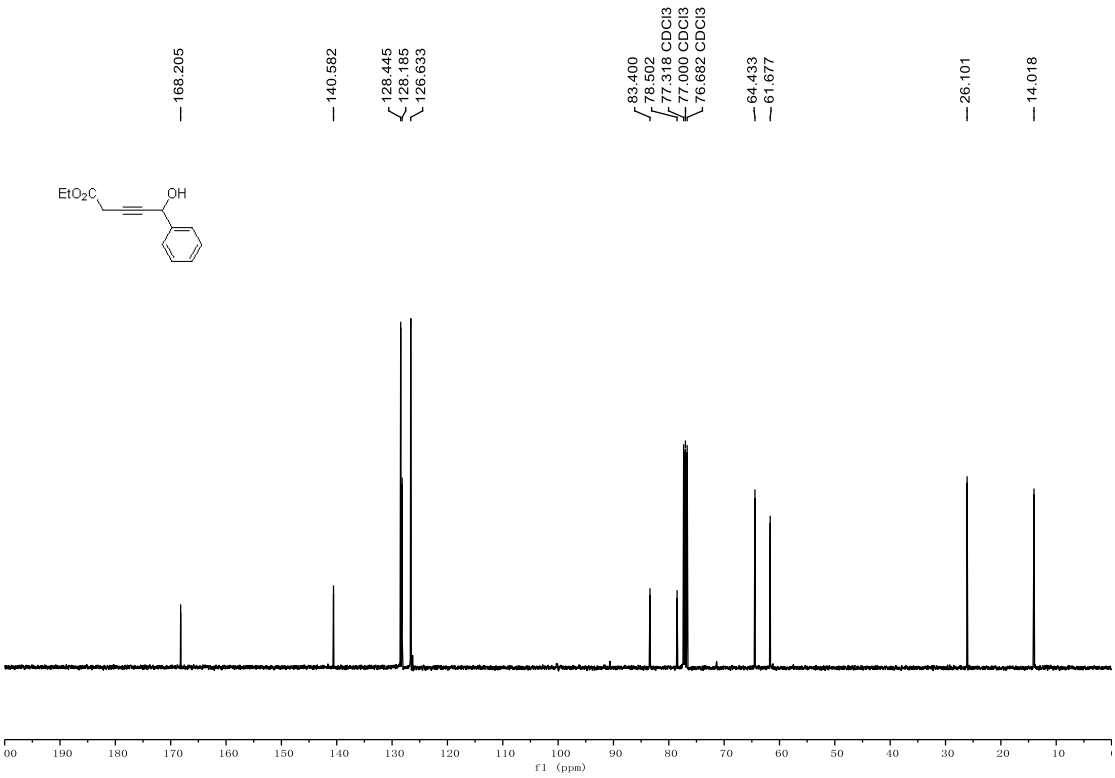
^{1}H NMR of **2c**



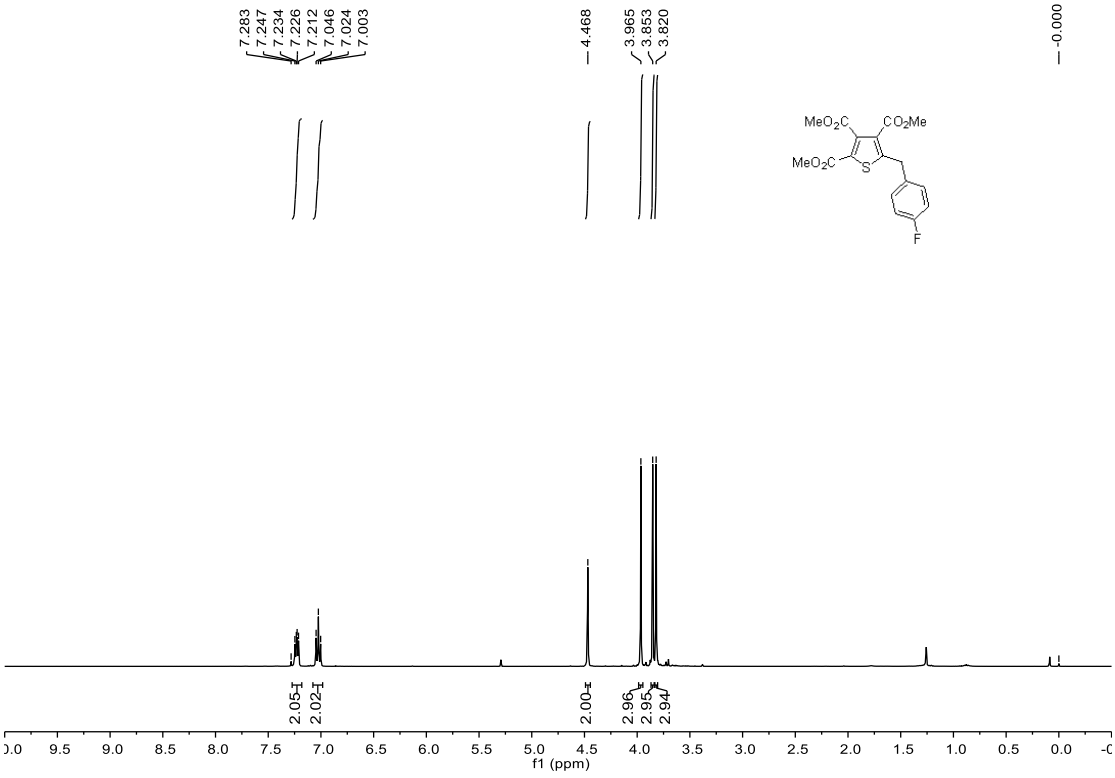
^{13}C NMR of **2c**



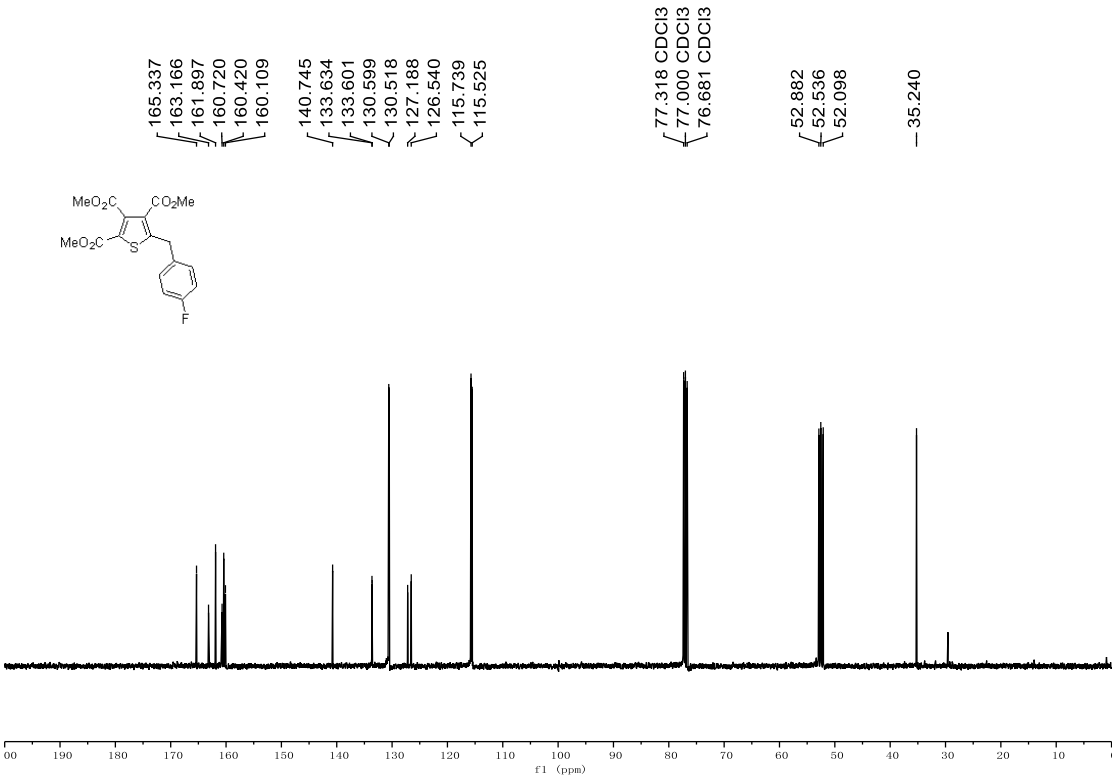
^{1}H NMR of **26**



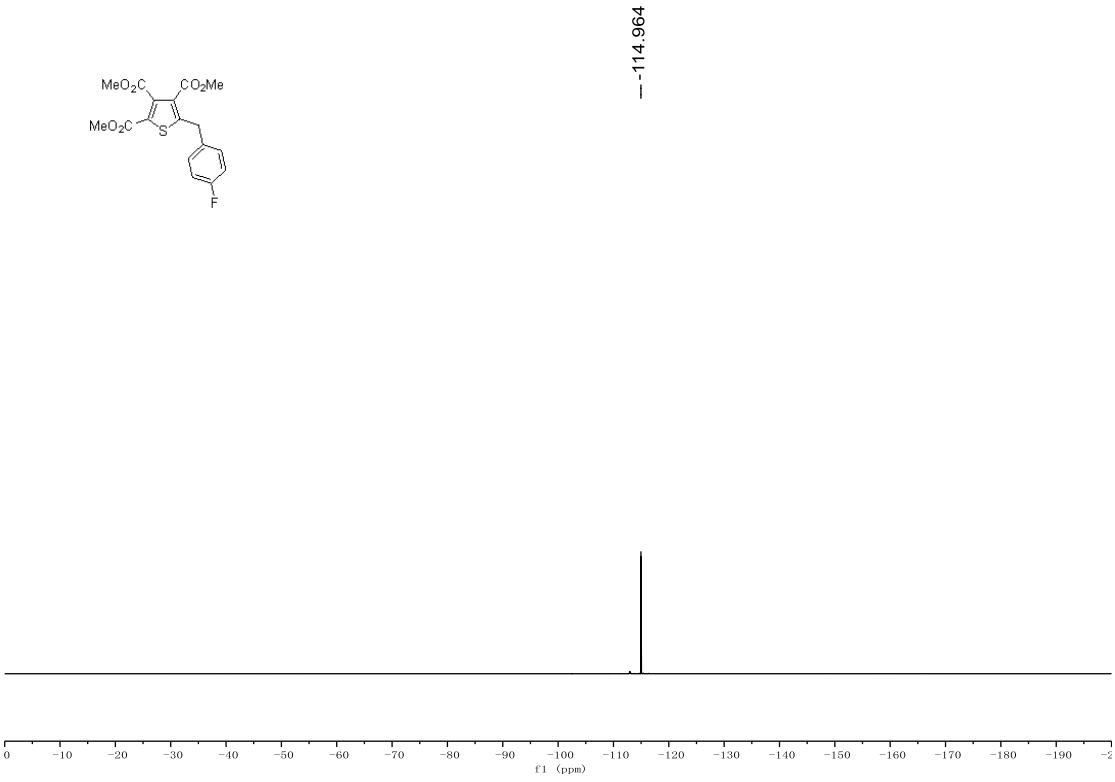
^{13}C NMR of **26**



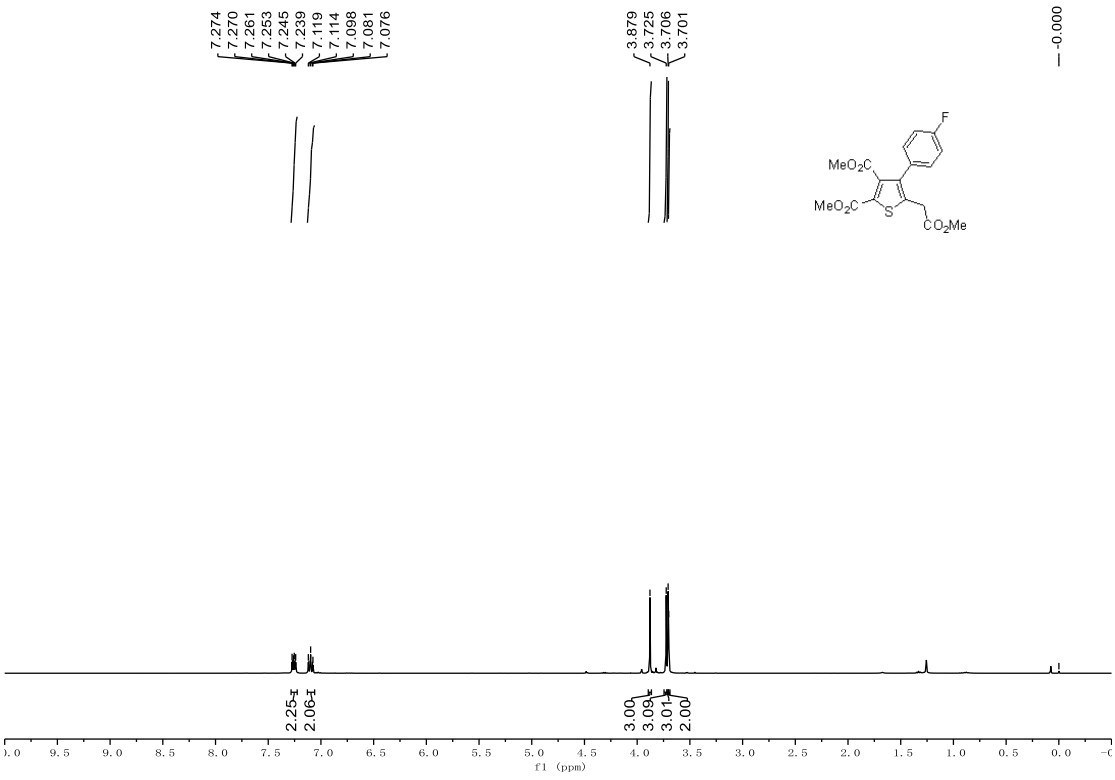
^{1}H NMR of **3a**



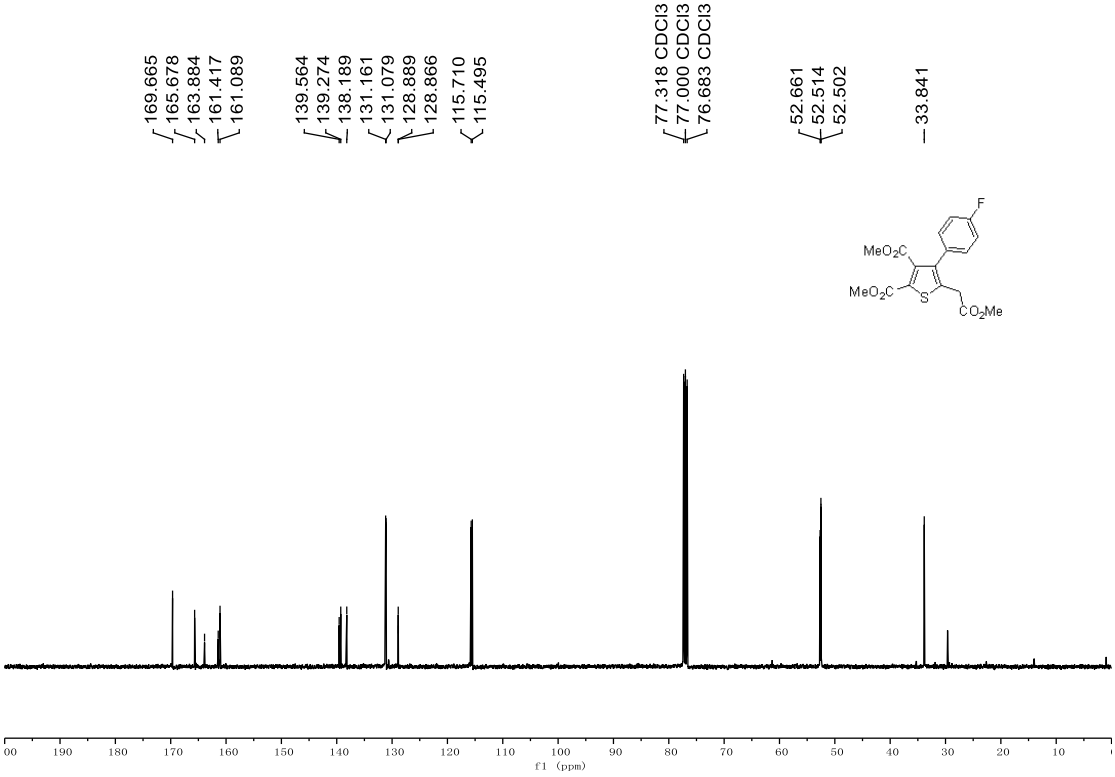
^{13}C NMR of **3a**



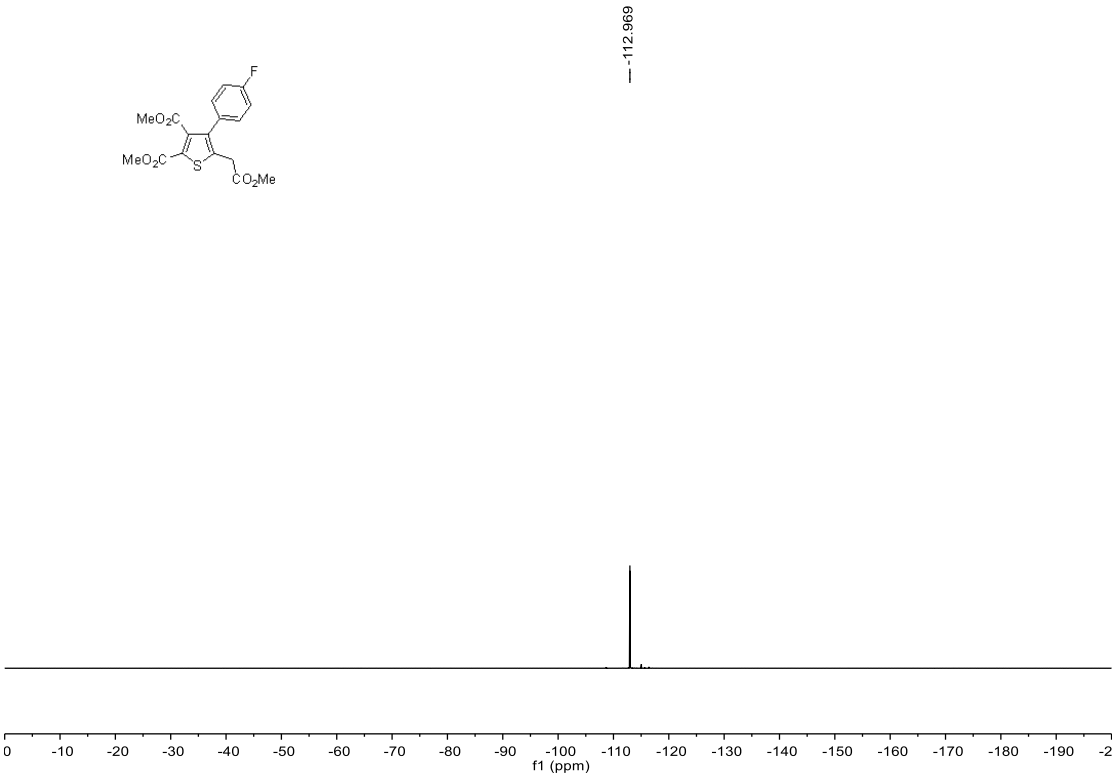
^{19}F NMR of **3a**



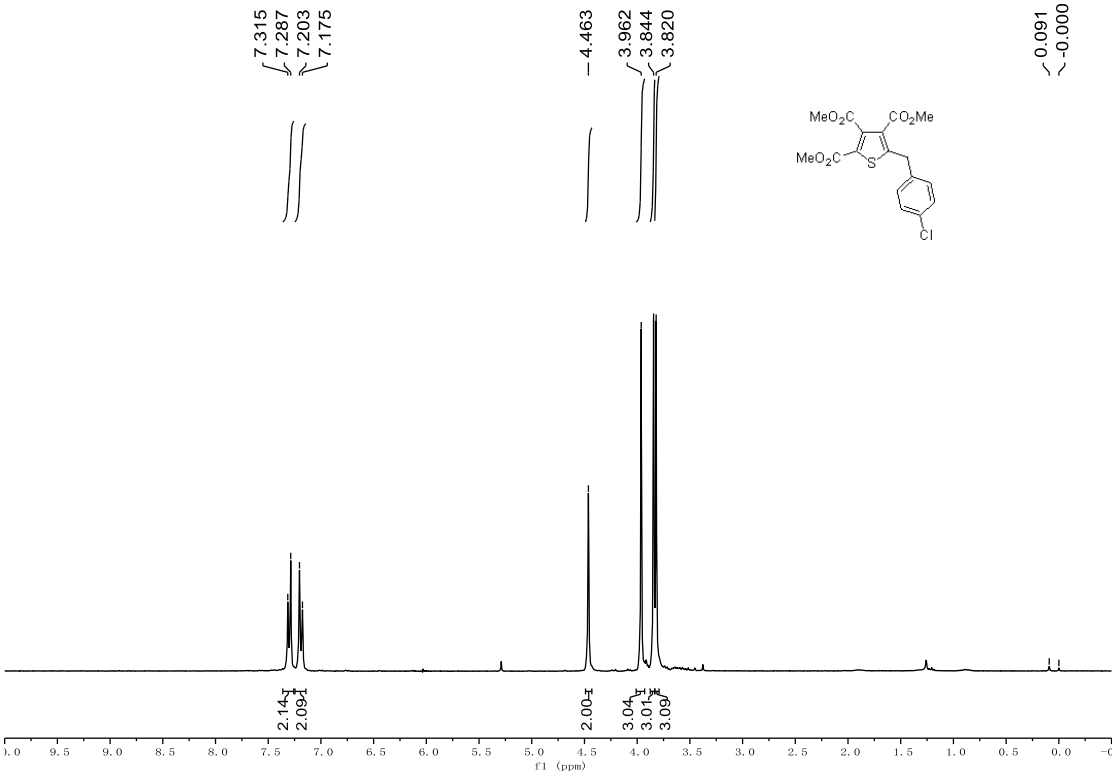
^{1}H NMR of **3b**



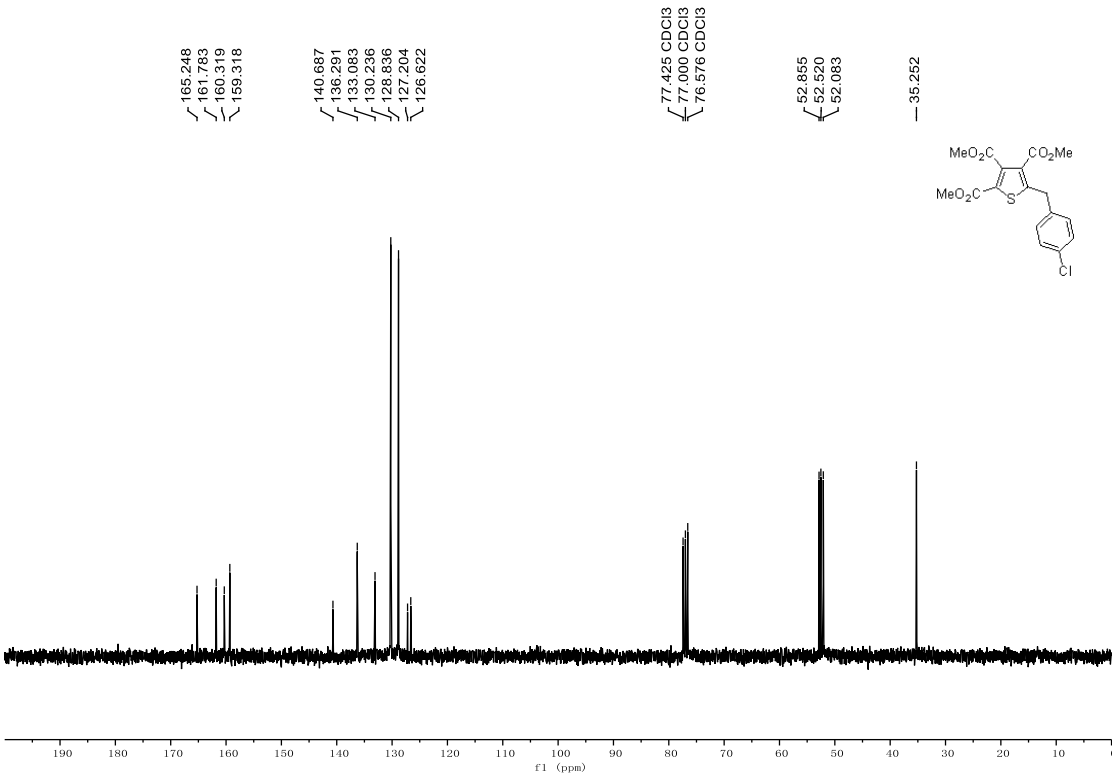
^{13}C NMR of **3b**



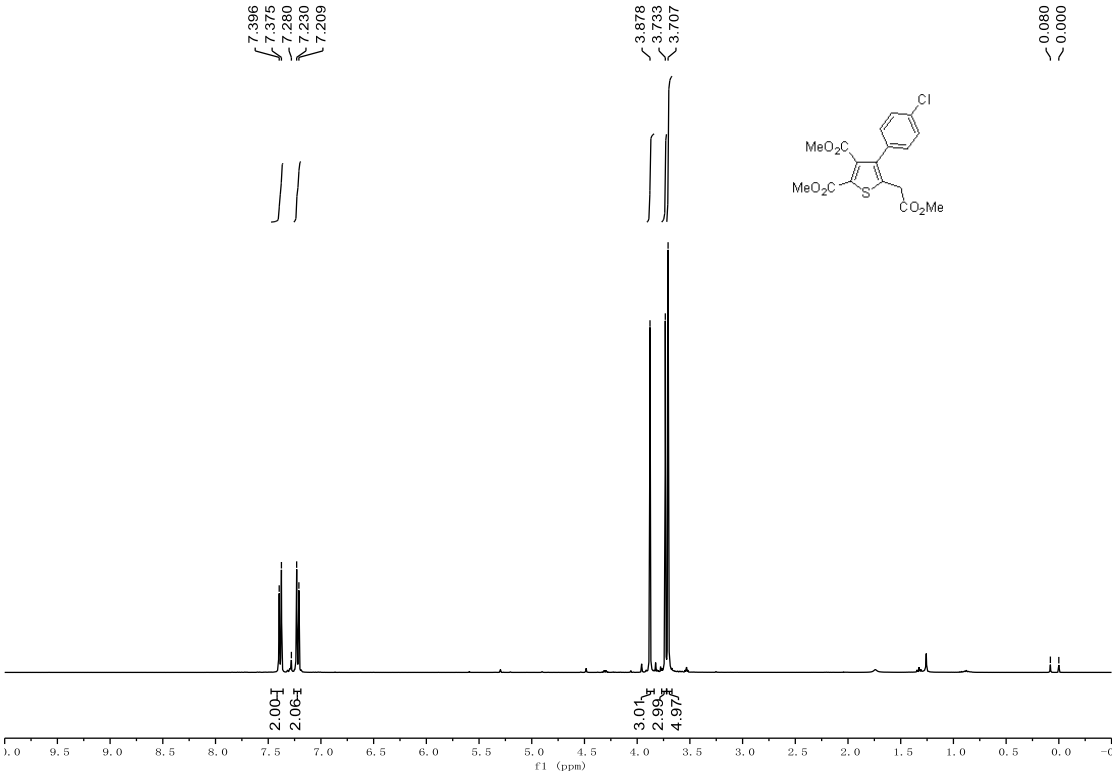
^{19}F NMR of **3b**



^{1}H NMR of **4a**



^{13}C NMR of **4a**



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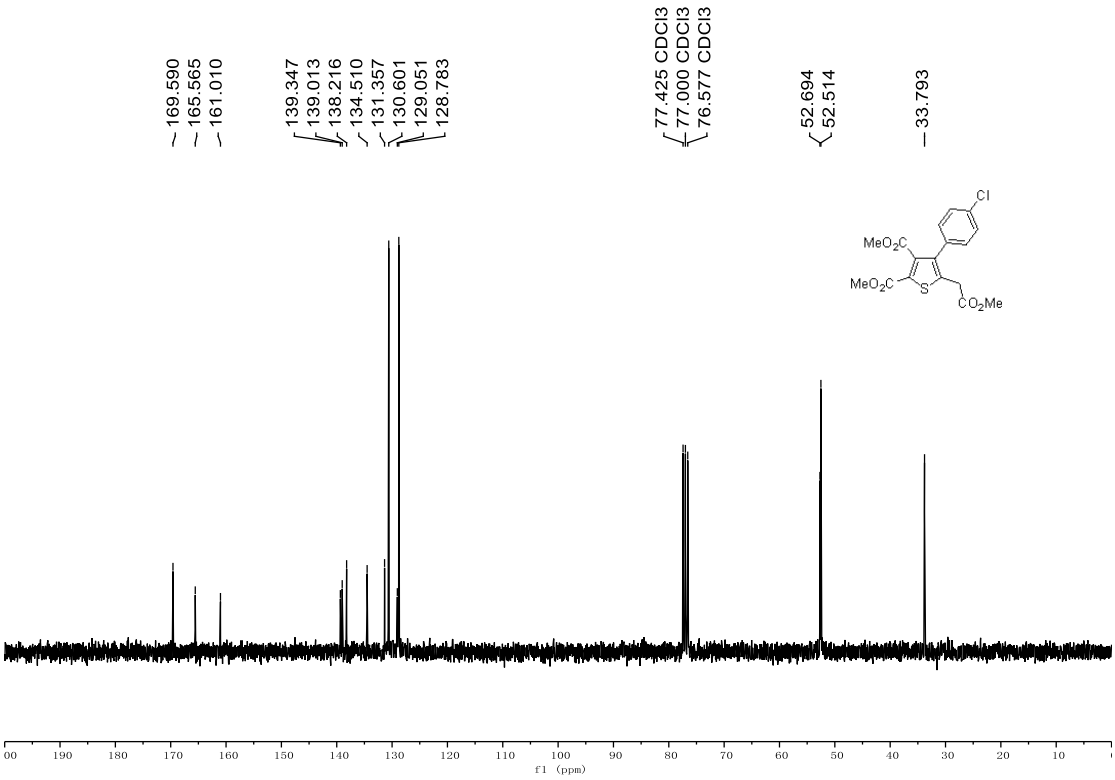
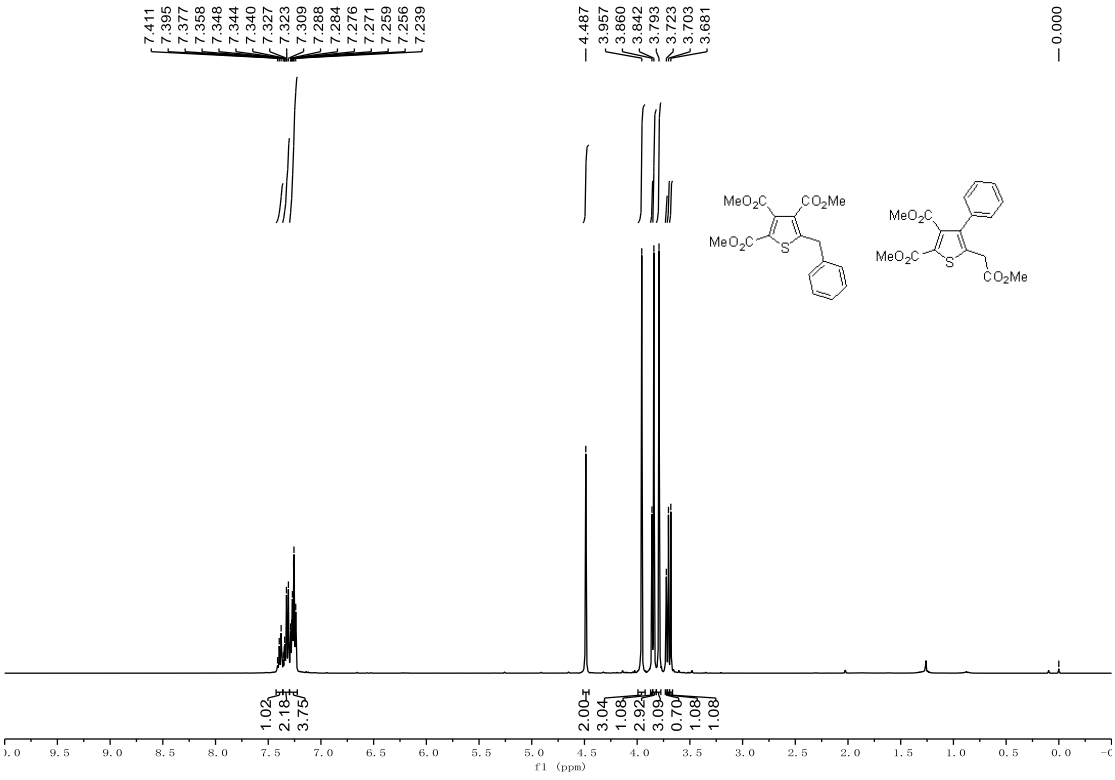
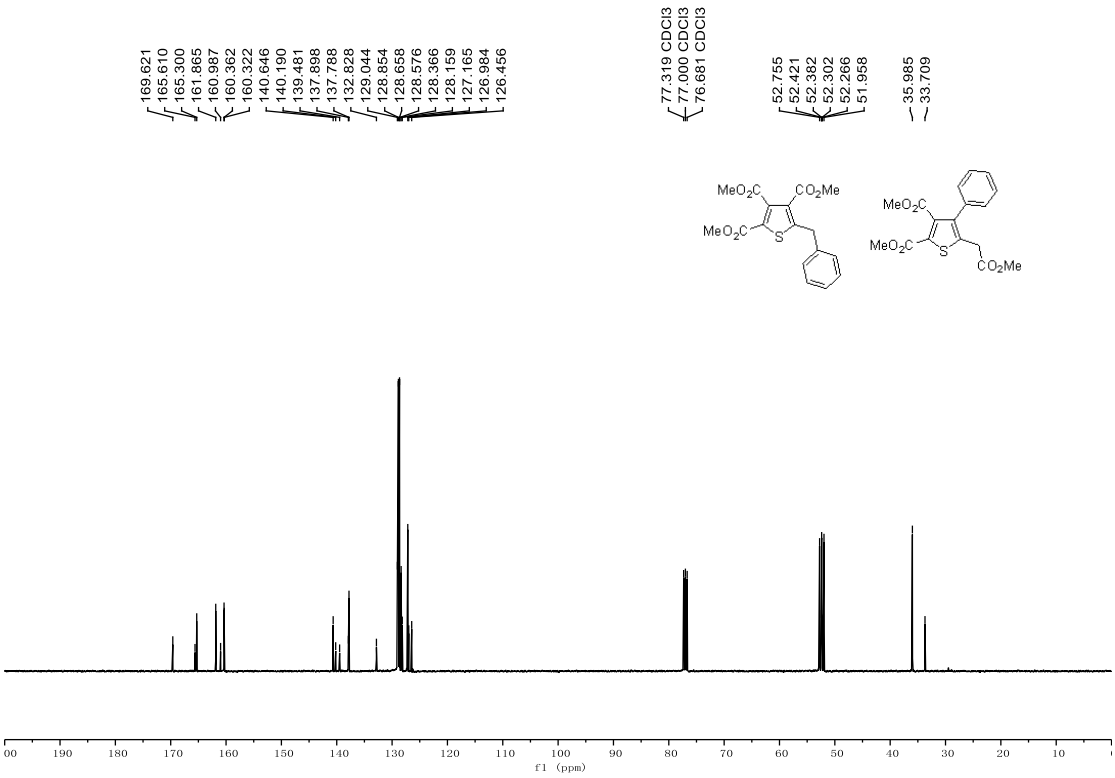


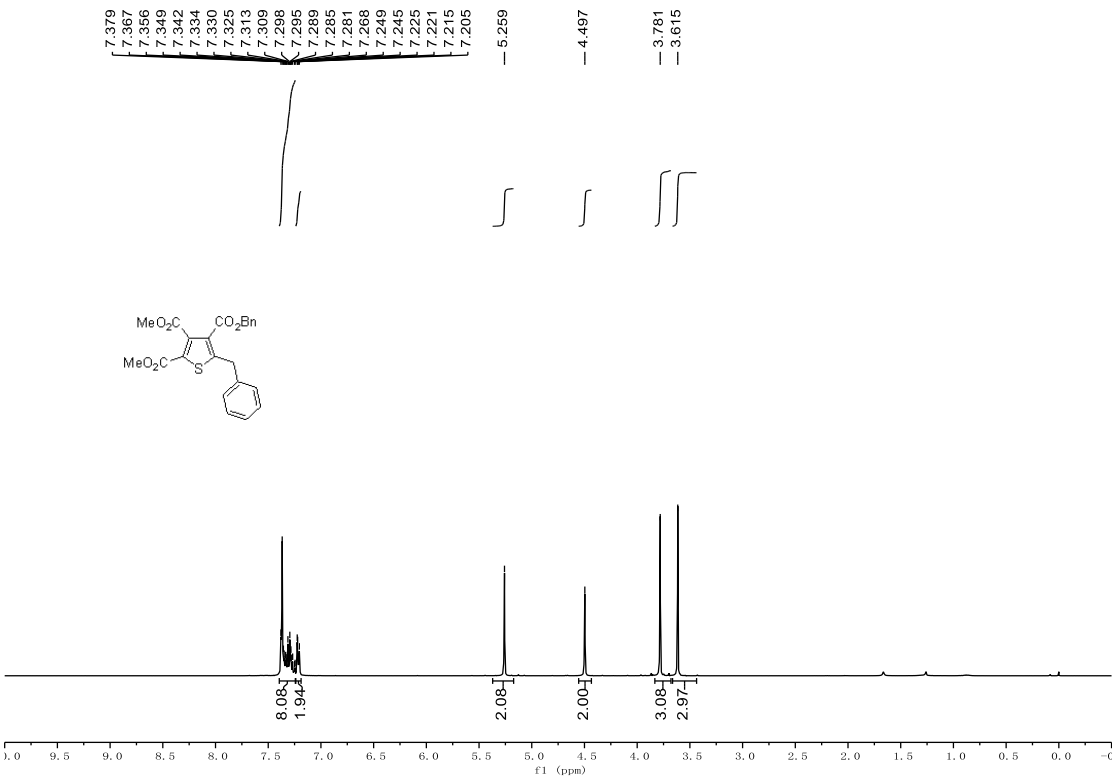
^{13}C NMR of **4b**



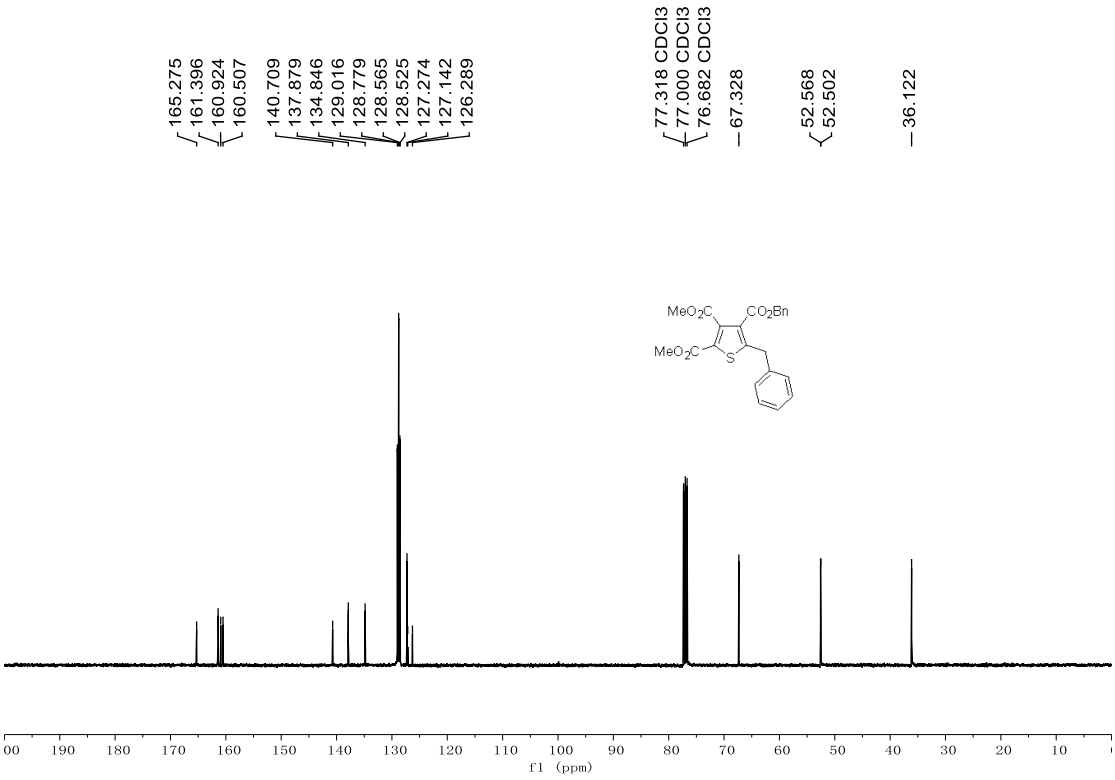
^{1}H NMR of **5a**, **5b**



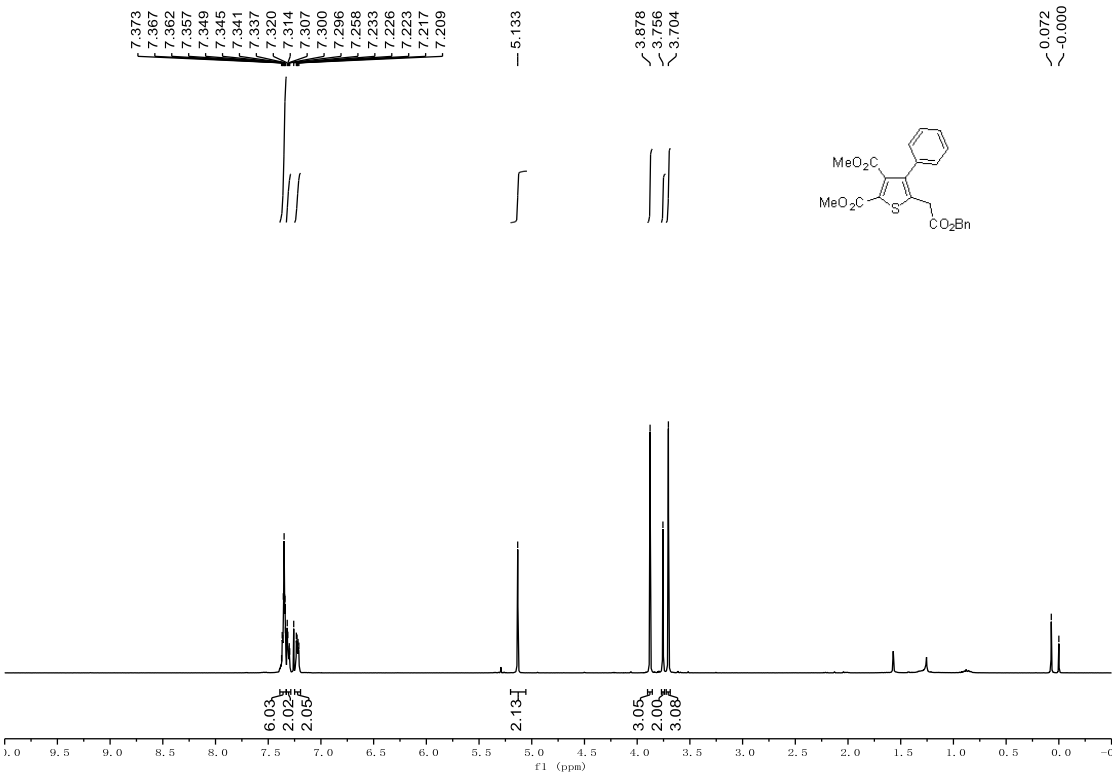
^{13}C NMR of **5a**, **5b**



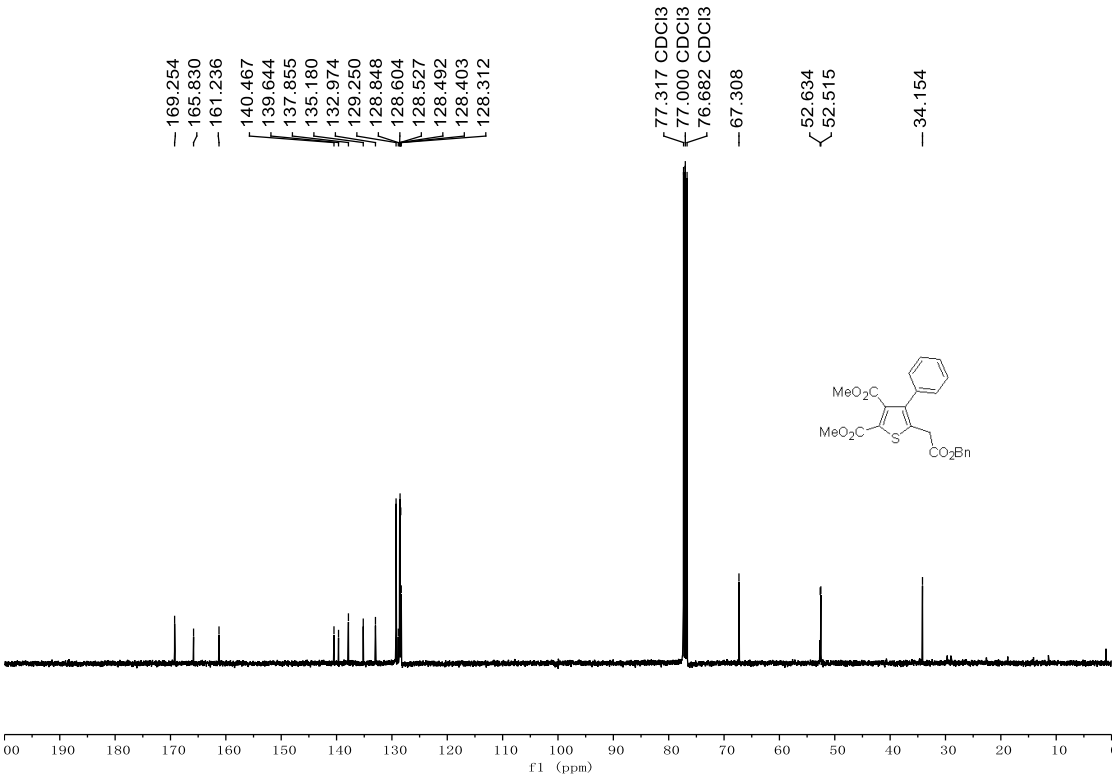
^{1}H NMR of **6a**



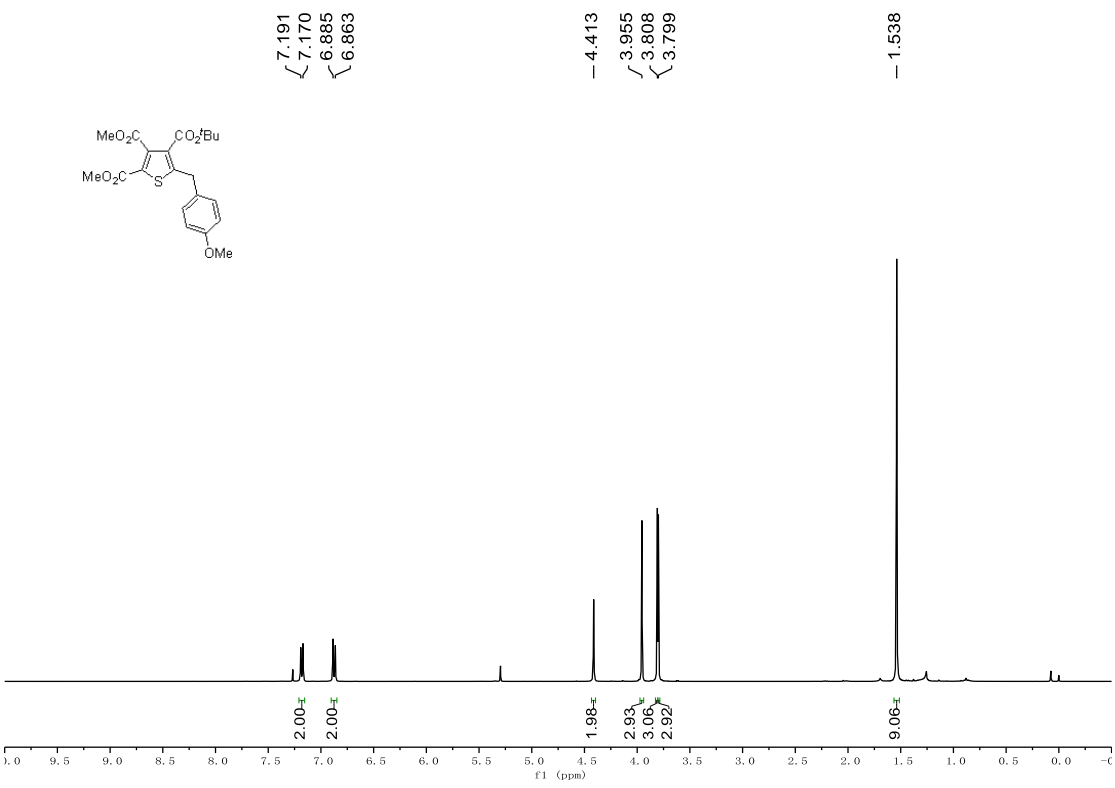
^{13}C NMR of **6a**



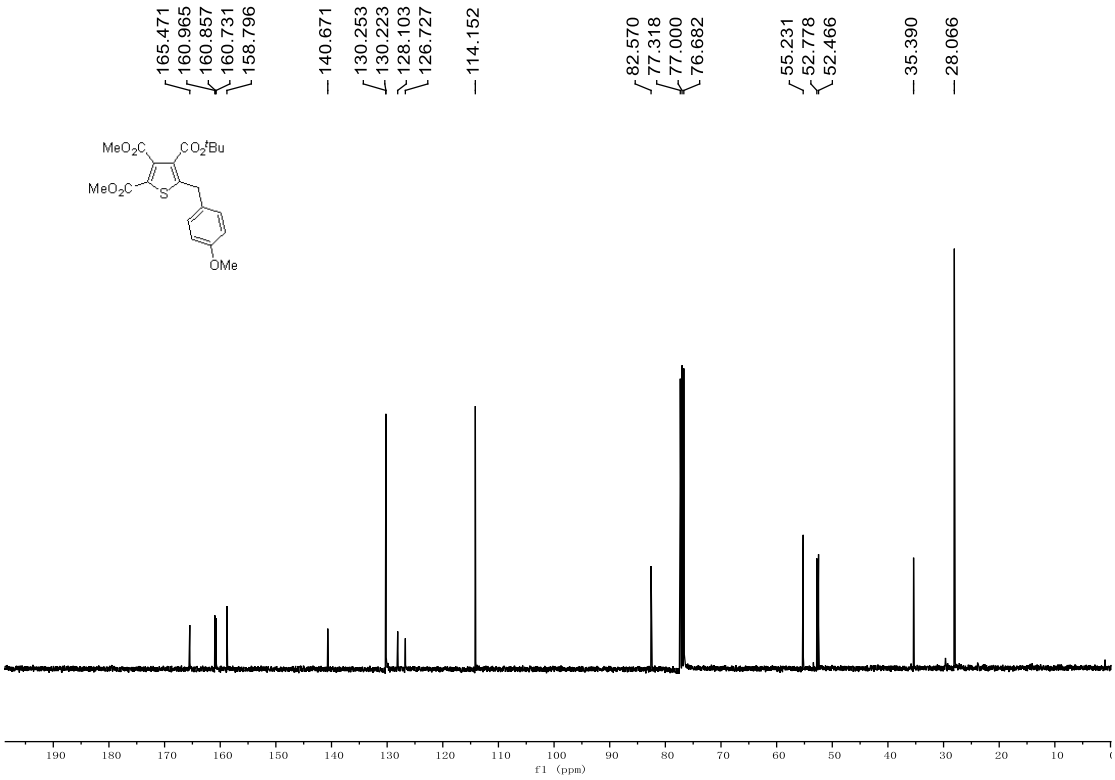
^{1}H NMR of **6b**



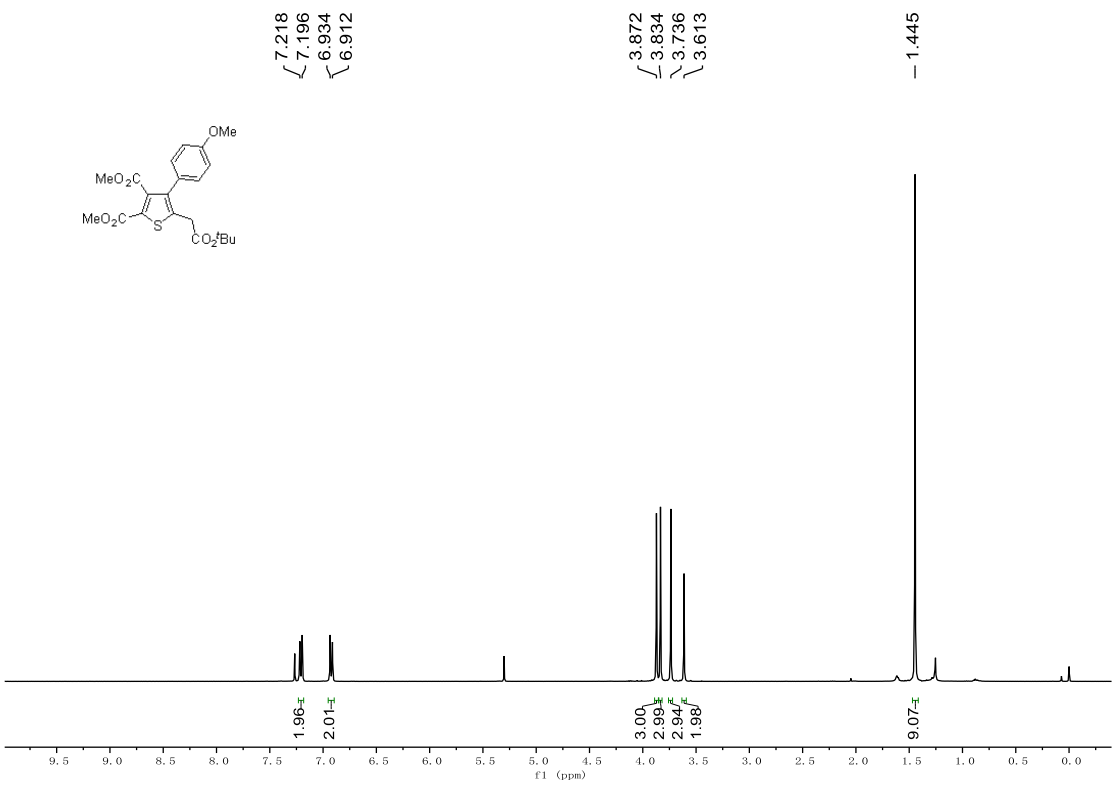
^{13}C NMR of **6b**



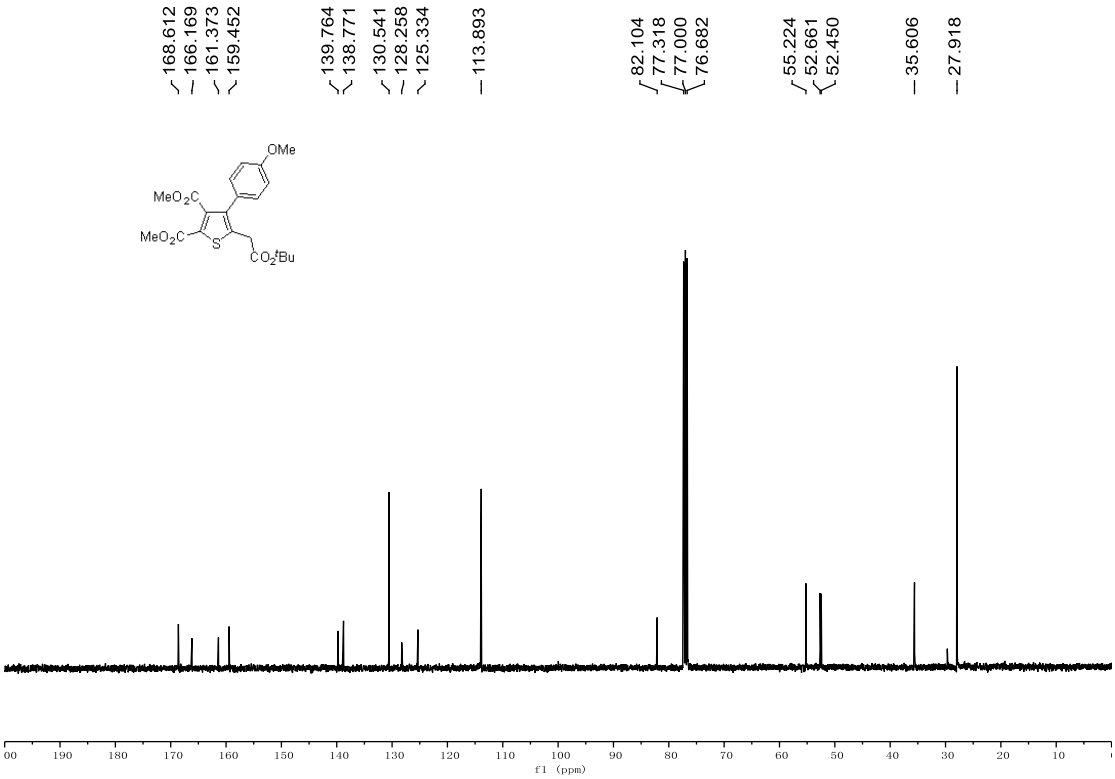
^{1}H NMR of **7a**



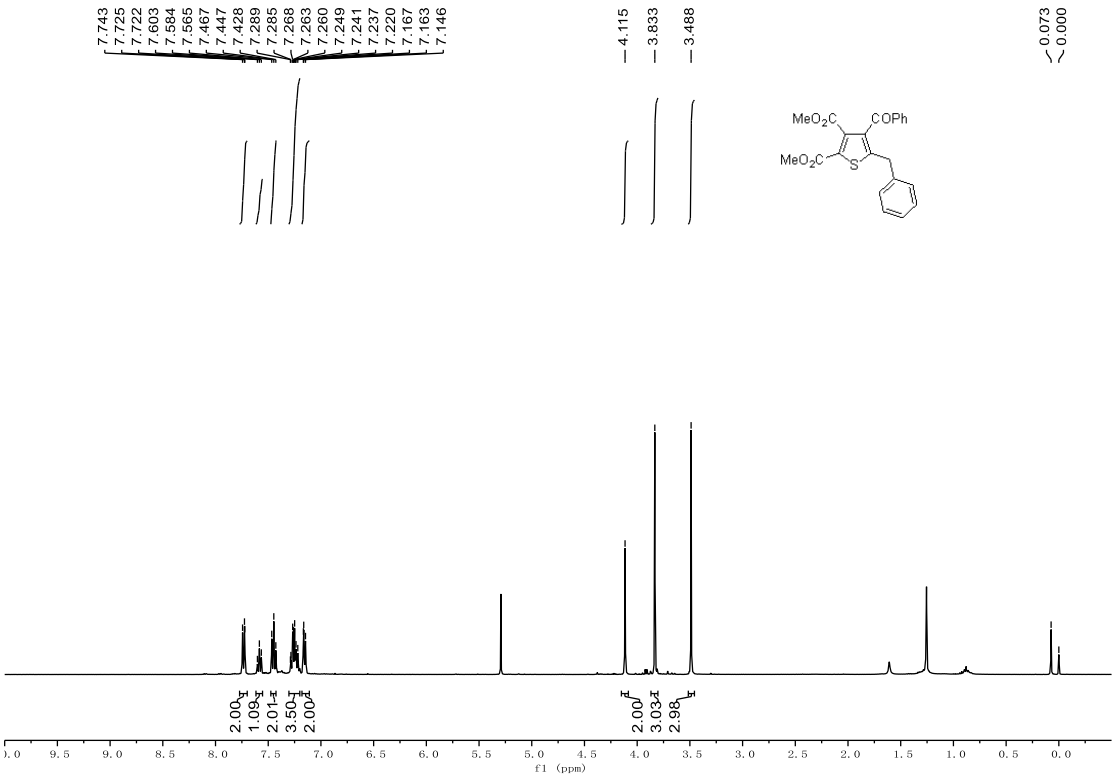
^{13}C NMR of **7a**



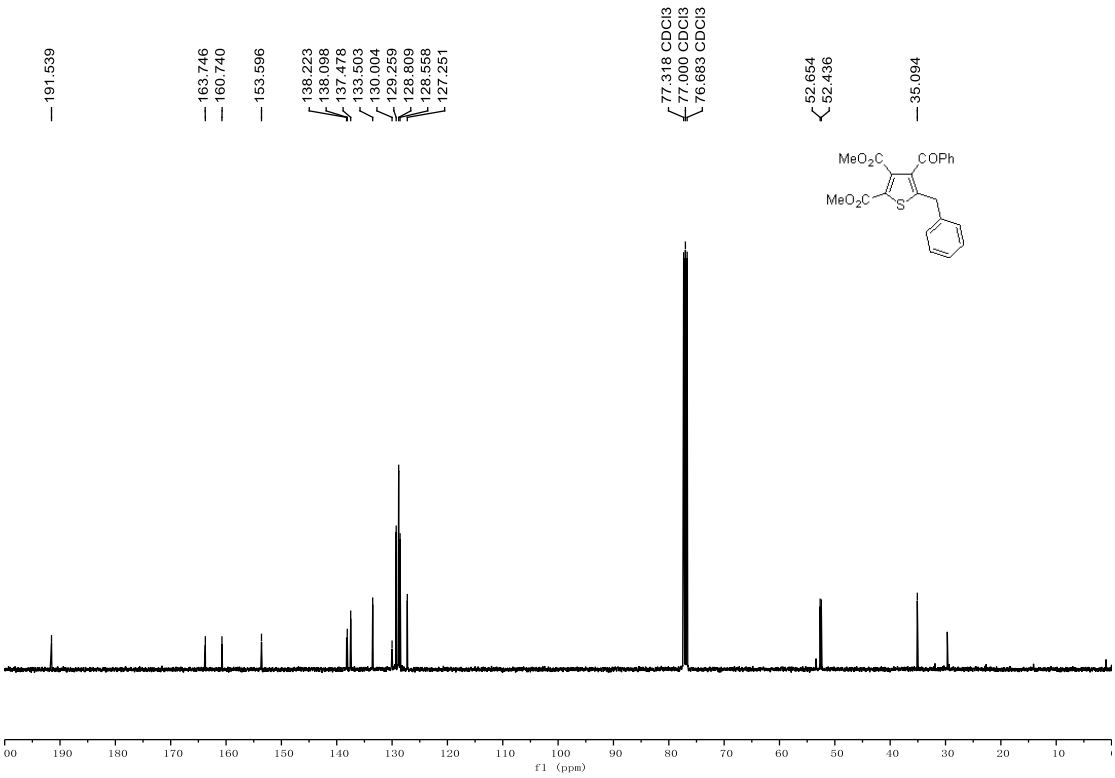
^{1}H NMR of **7b**



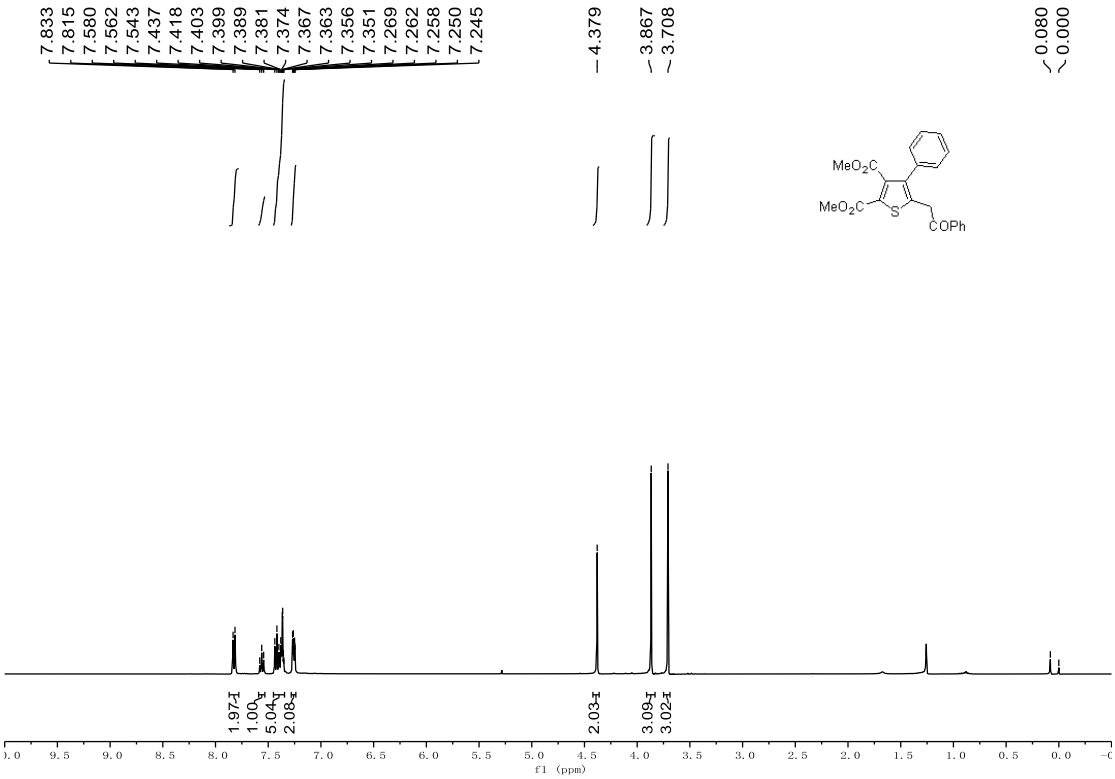
^{13}C NMR of **7b**



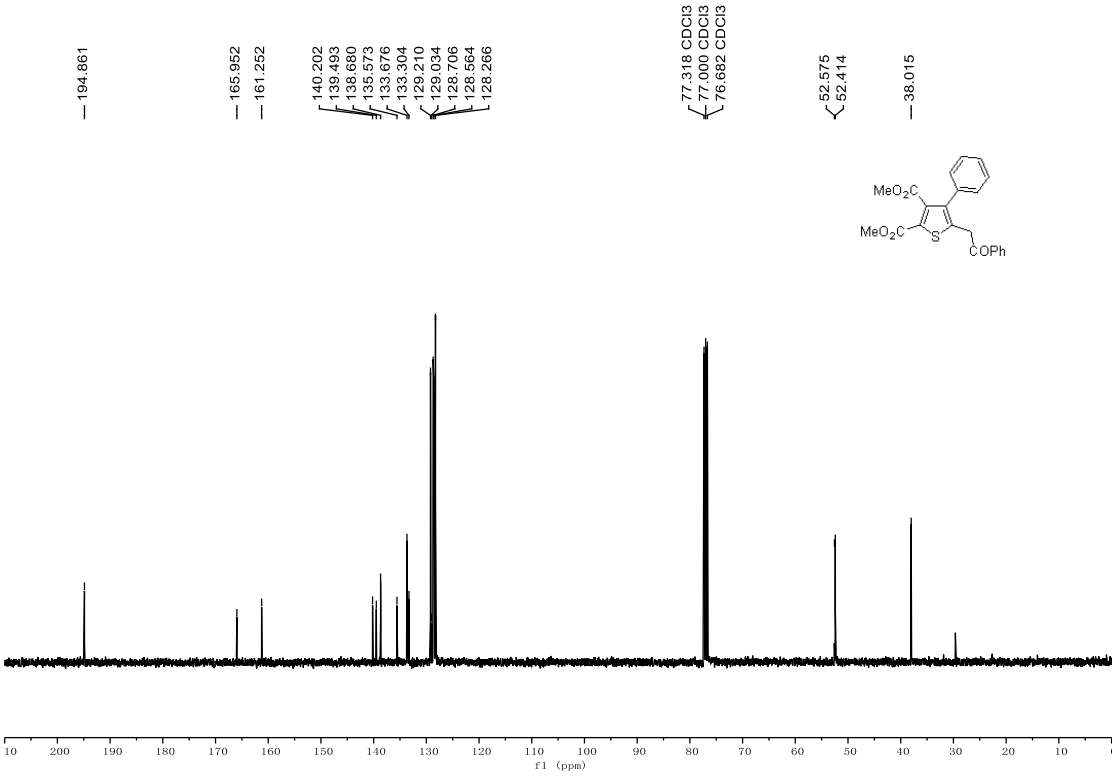
^{1}H NMR of **8a**



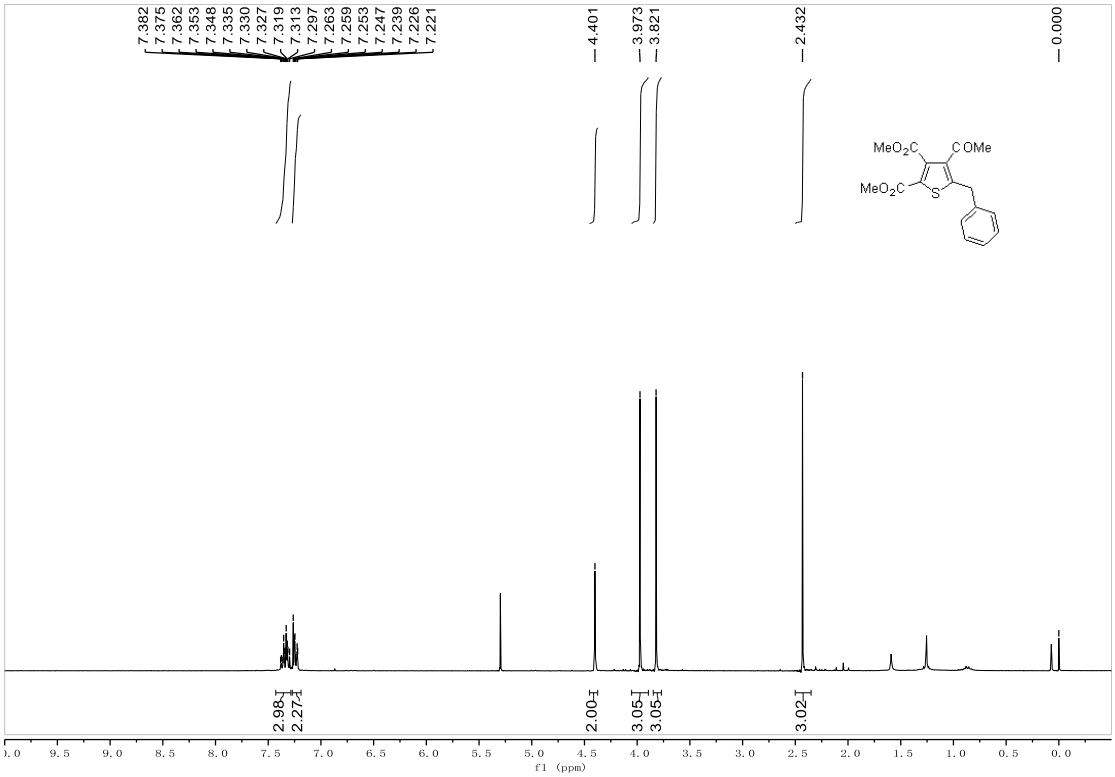
^{13}C NMR of **8a**



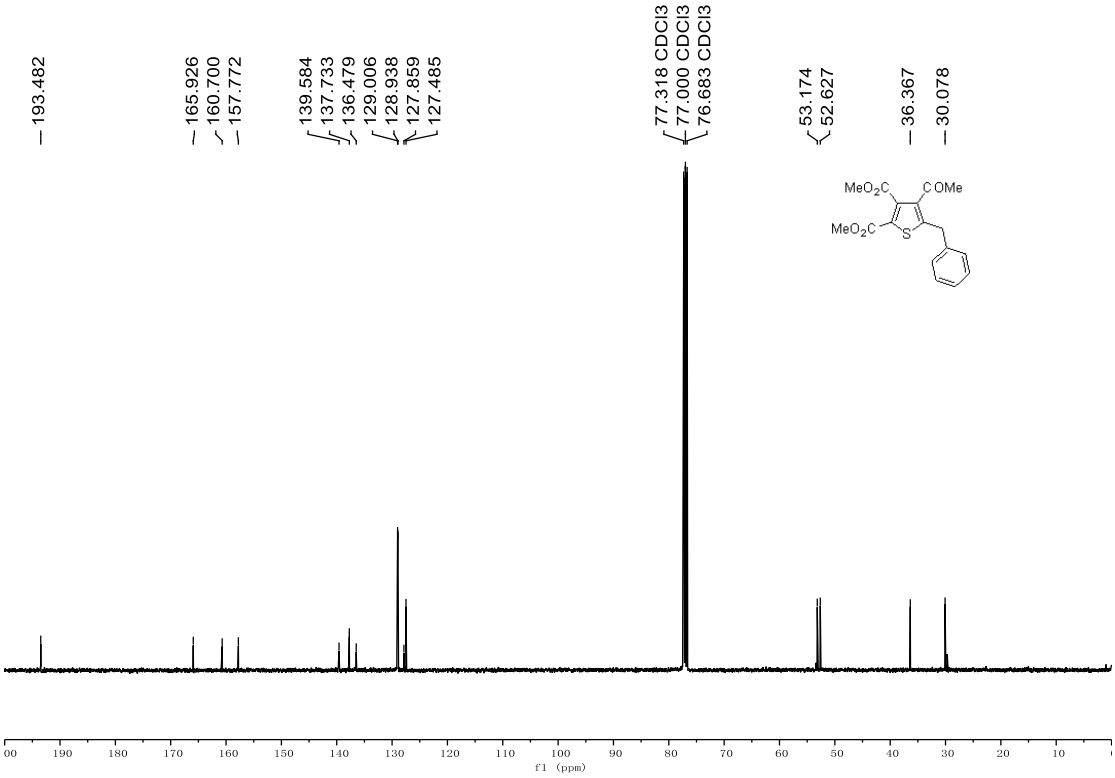
^{1}H NMR of **8b**



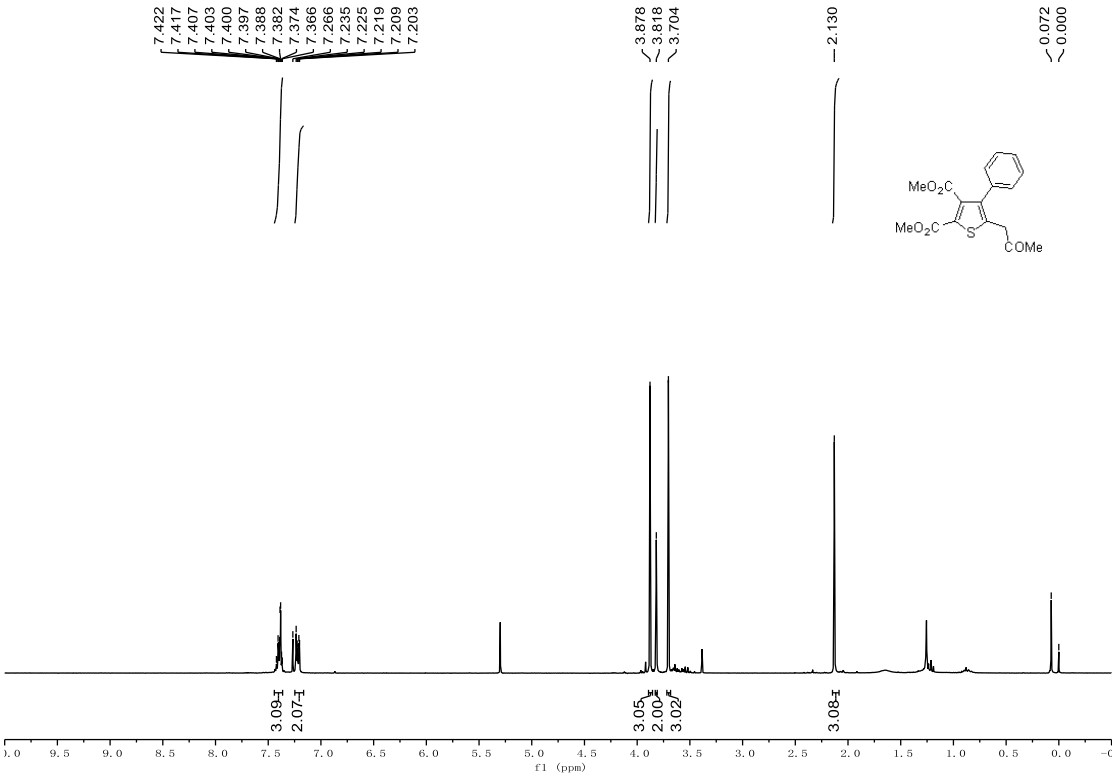
^{13}C NMR of **8b**



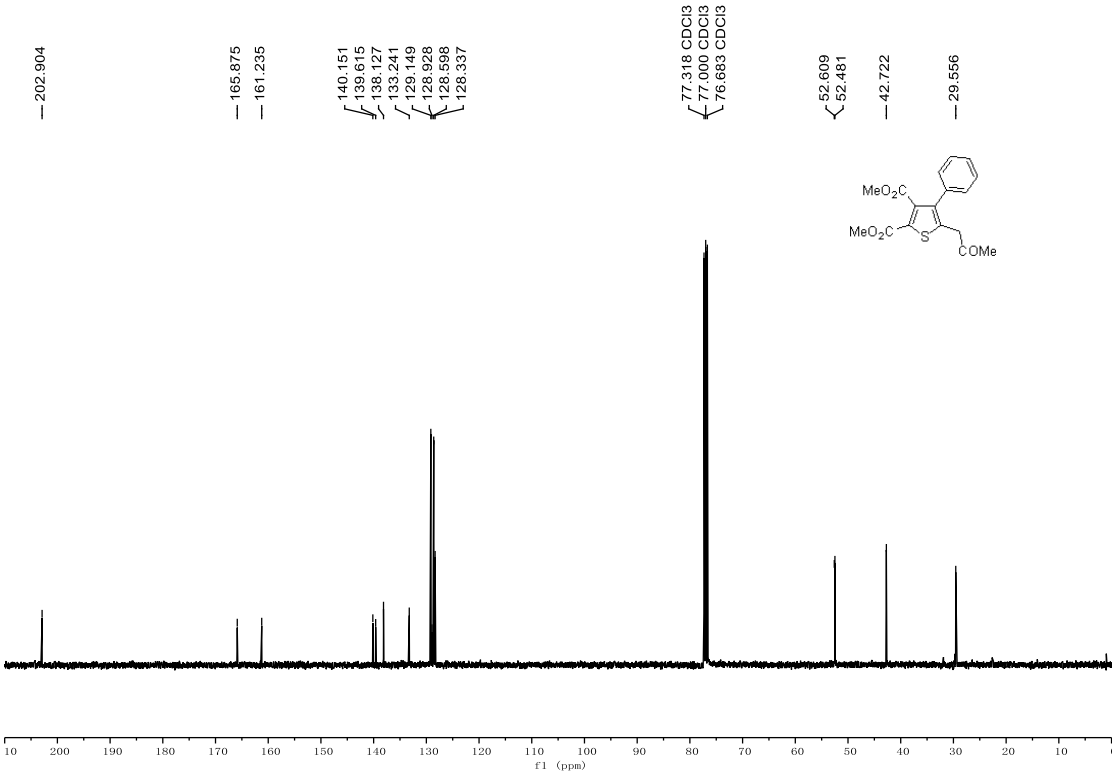
^{1}H NMR of **9a**



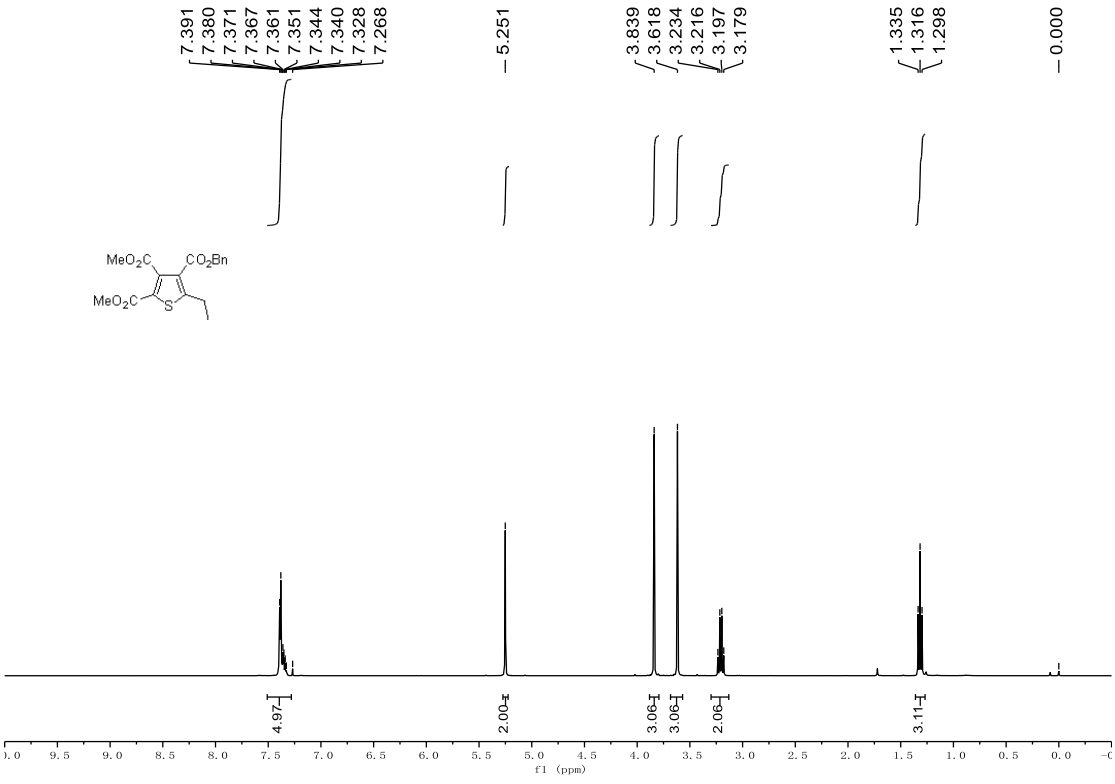
^{13}C NMR of **9a**



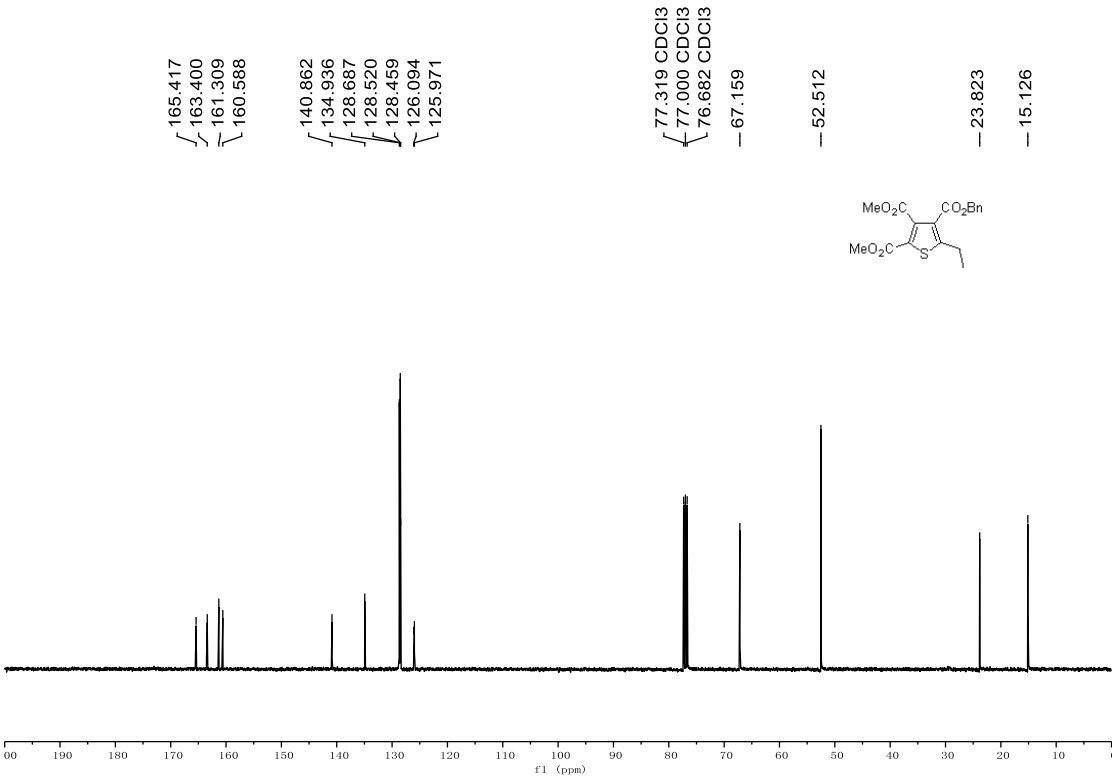
^{1}H NMR of **9b**



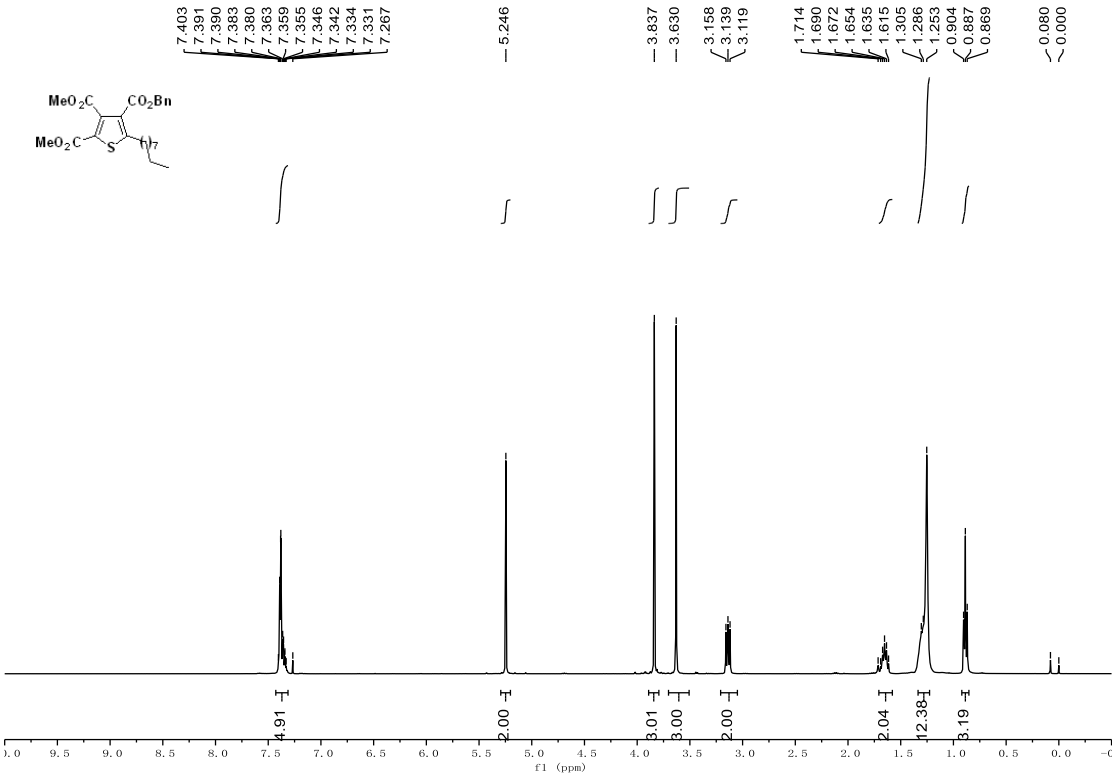
^{13}C NMR of **9b**



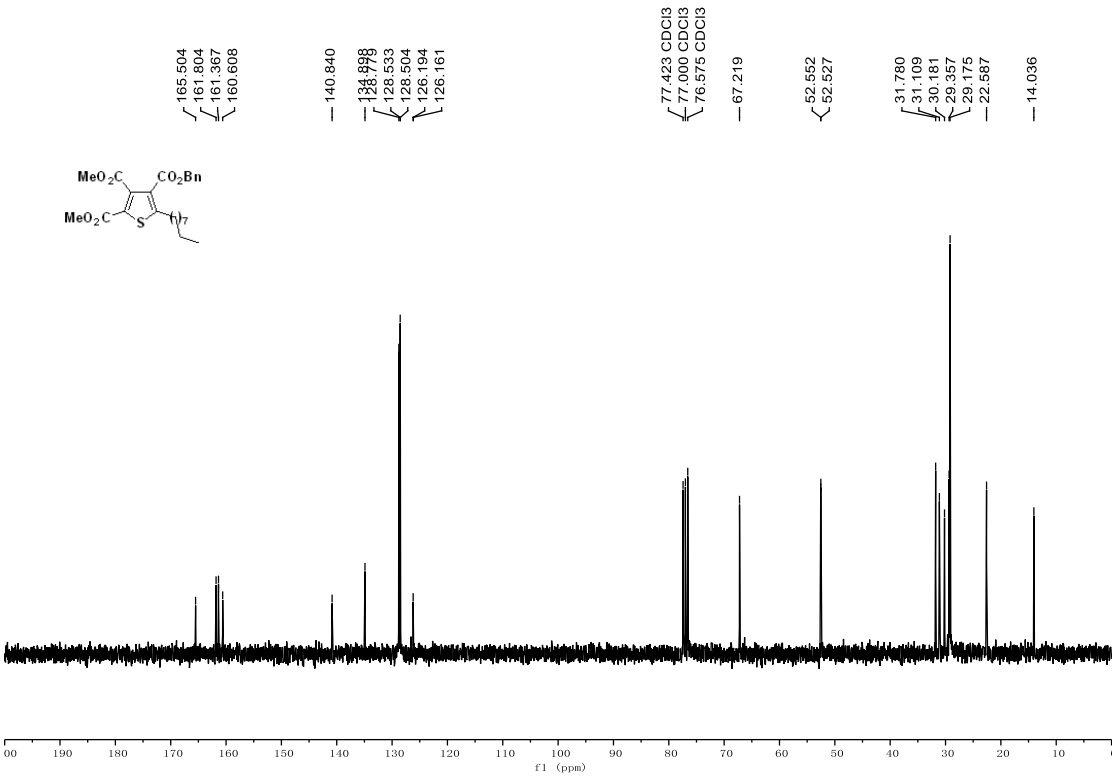
^{1}H NMR of **10**



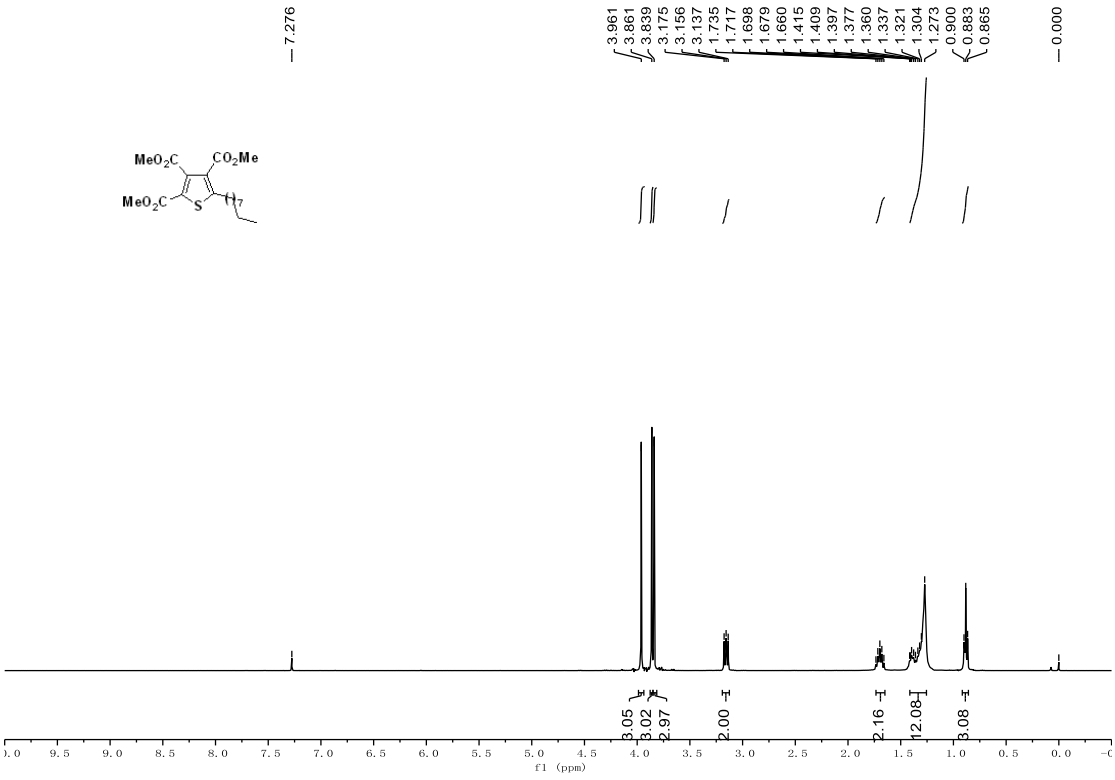
^{13}C NMR of **10**



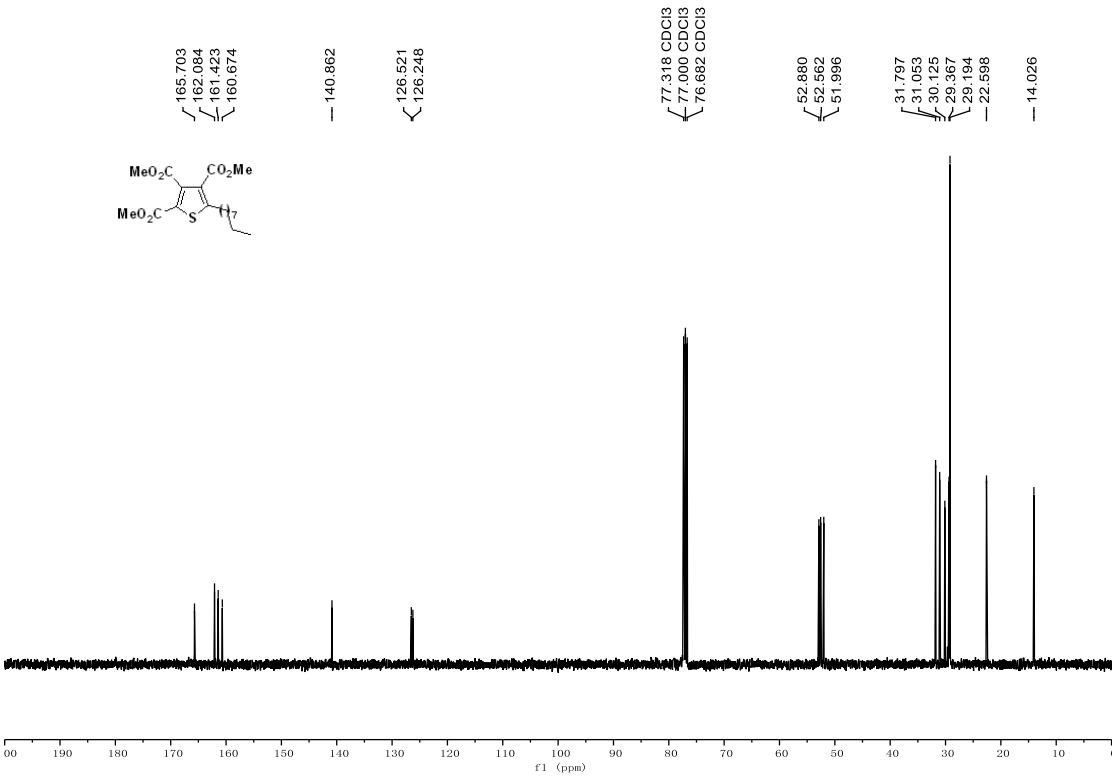
^{1}H NMR of **11**



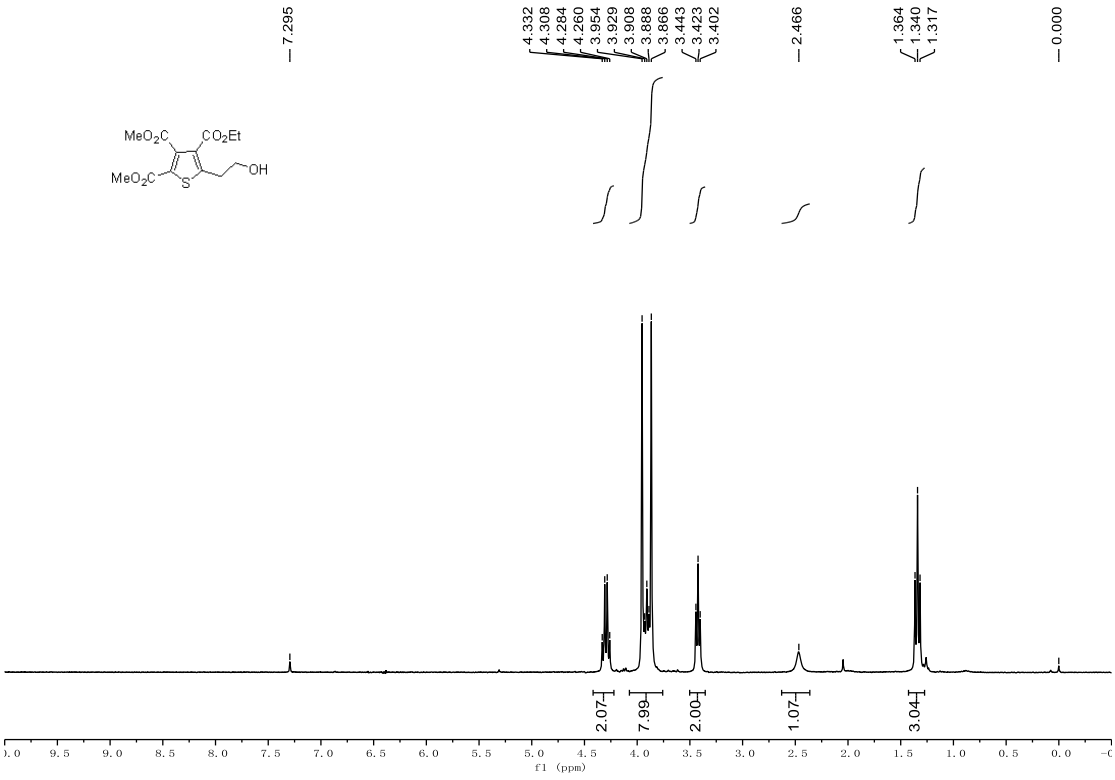
^{13}C NMR of **11**



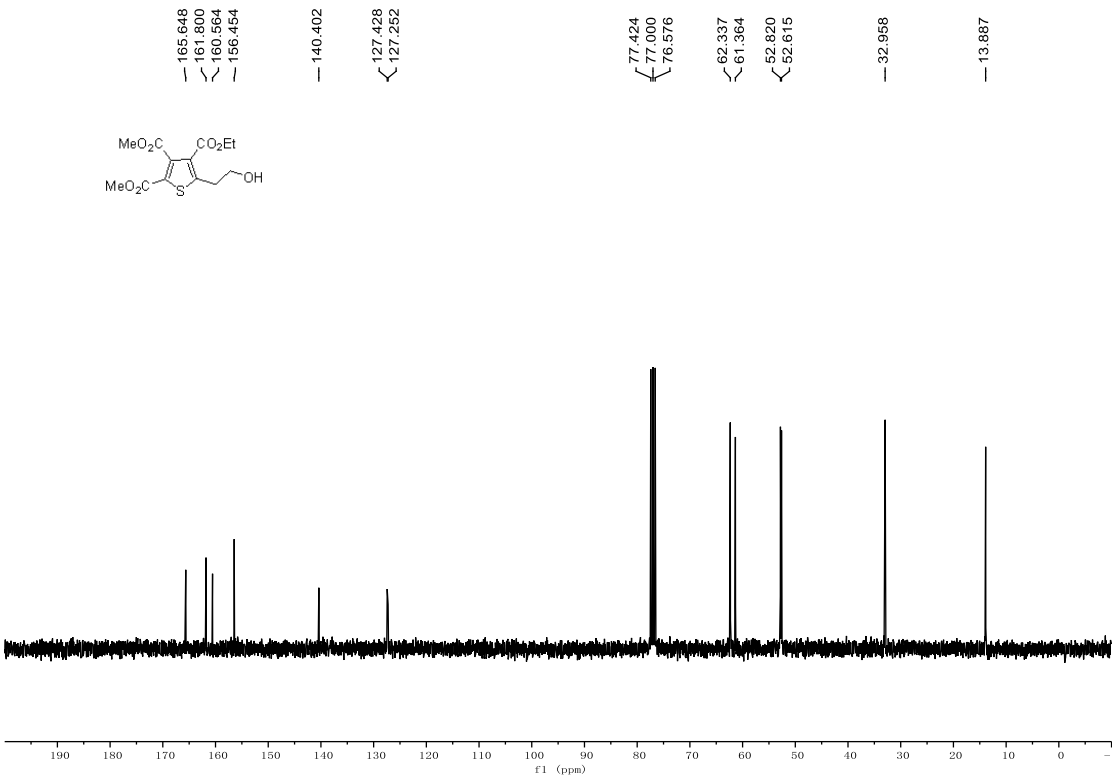
^{1}H NMR of **12**



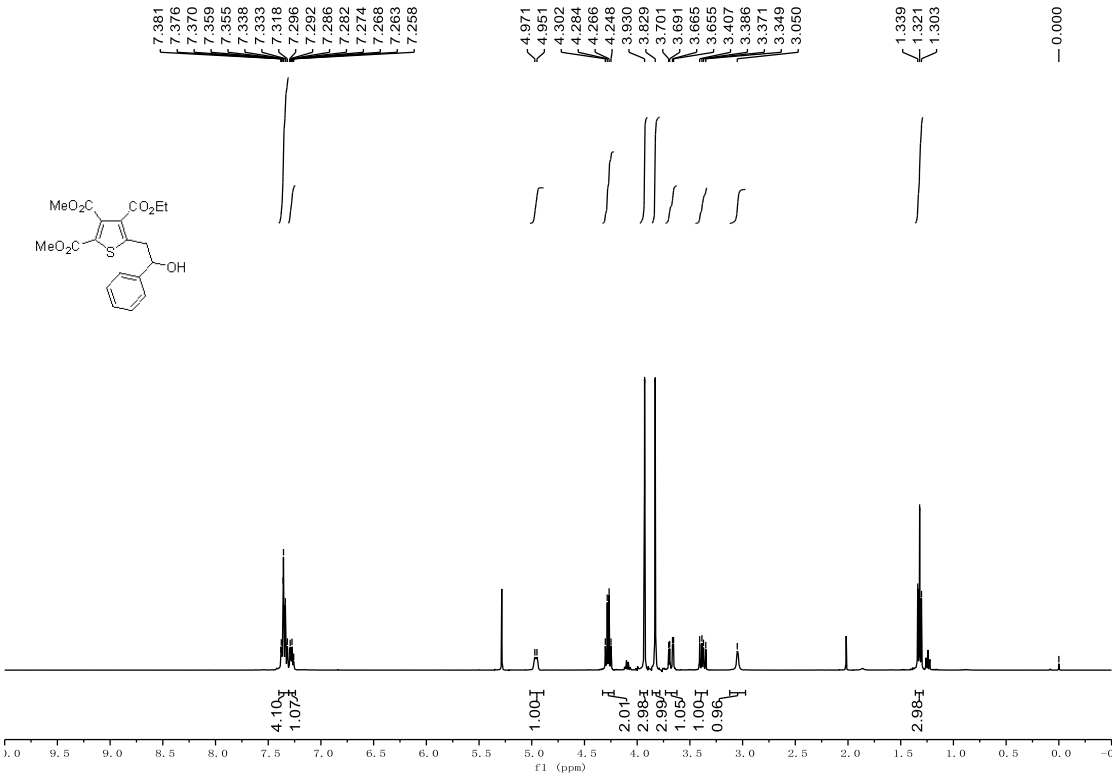
^{13}C NMR of **12**



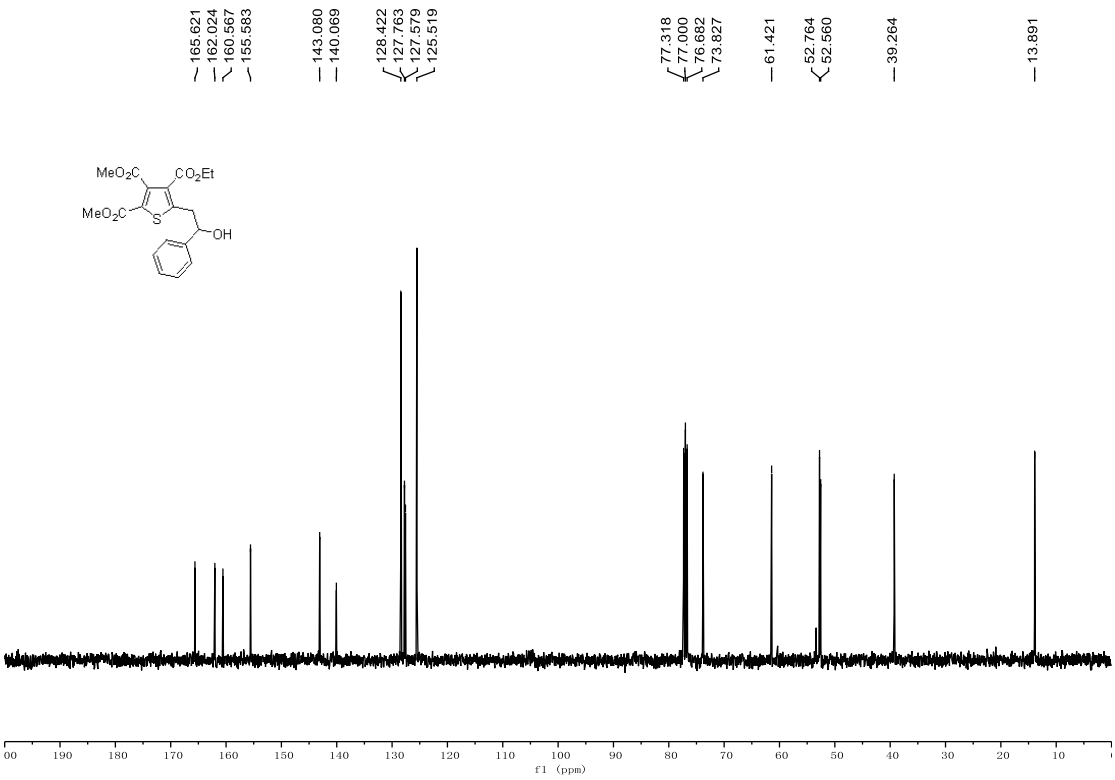
^{1}H NMR of **13**



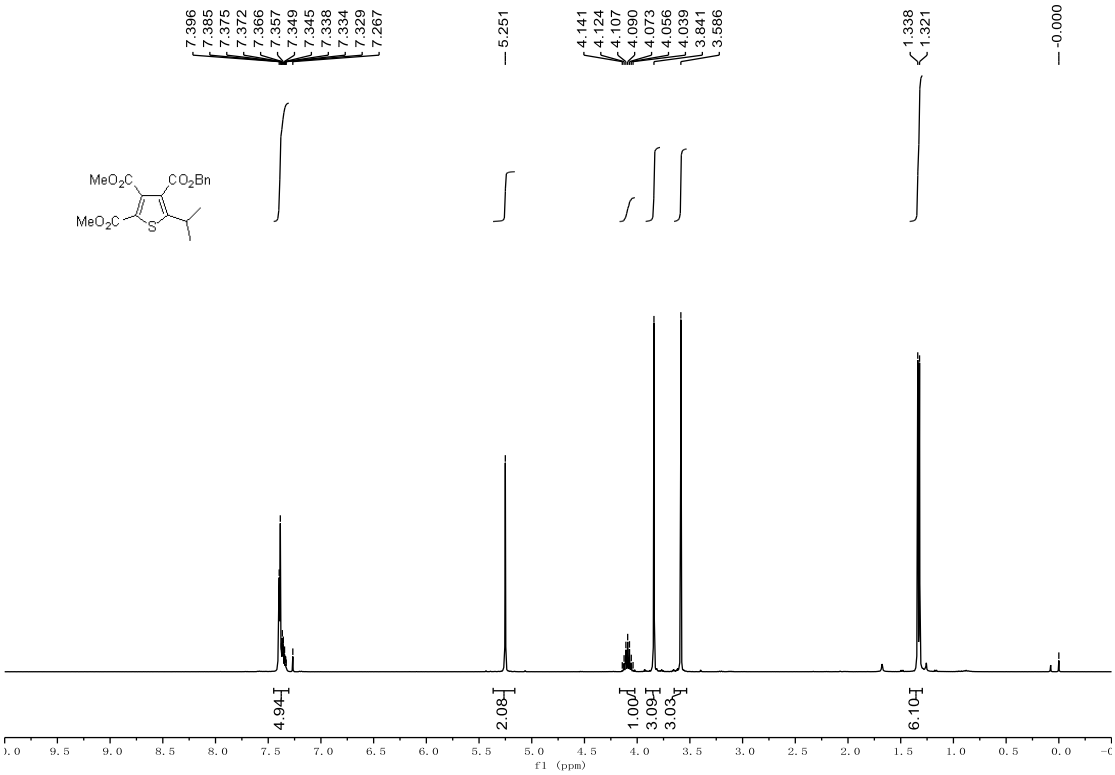
^{13}C NMR of **13**



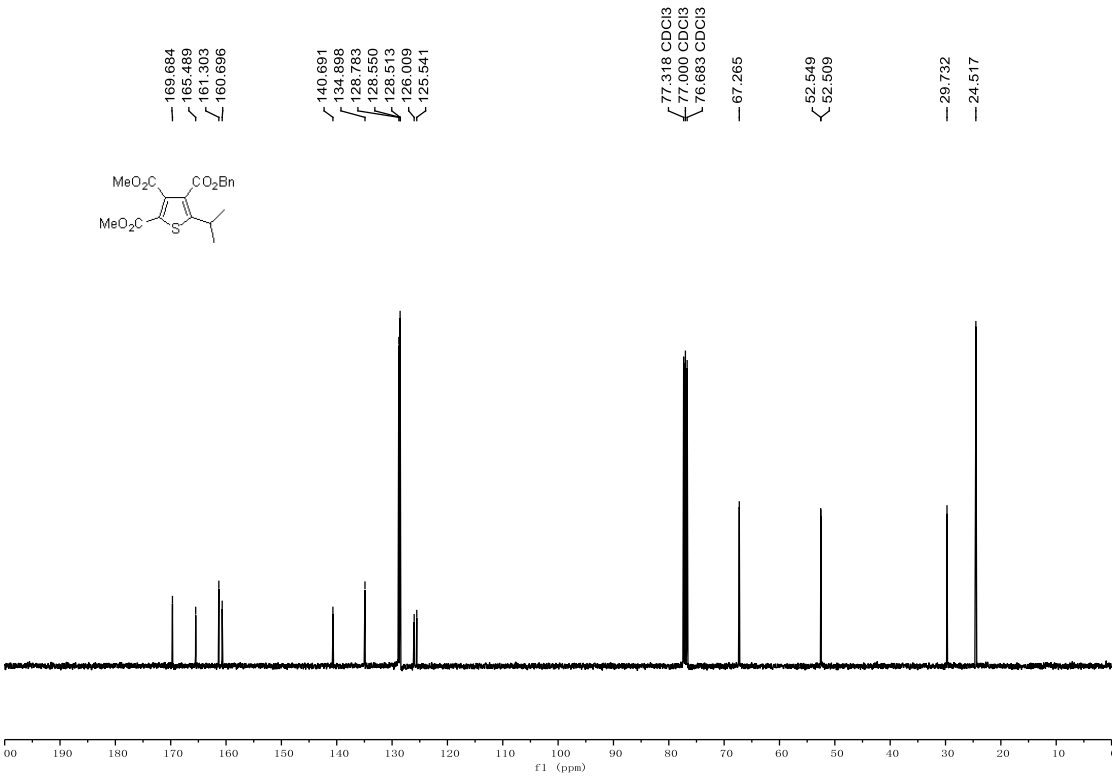
^{1}H NMR of **14**



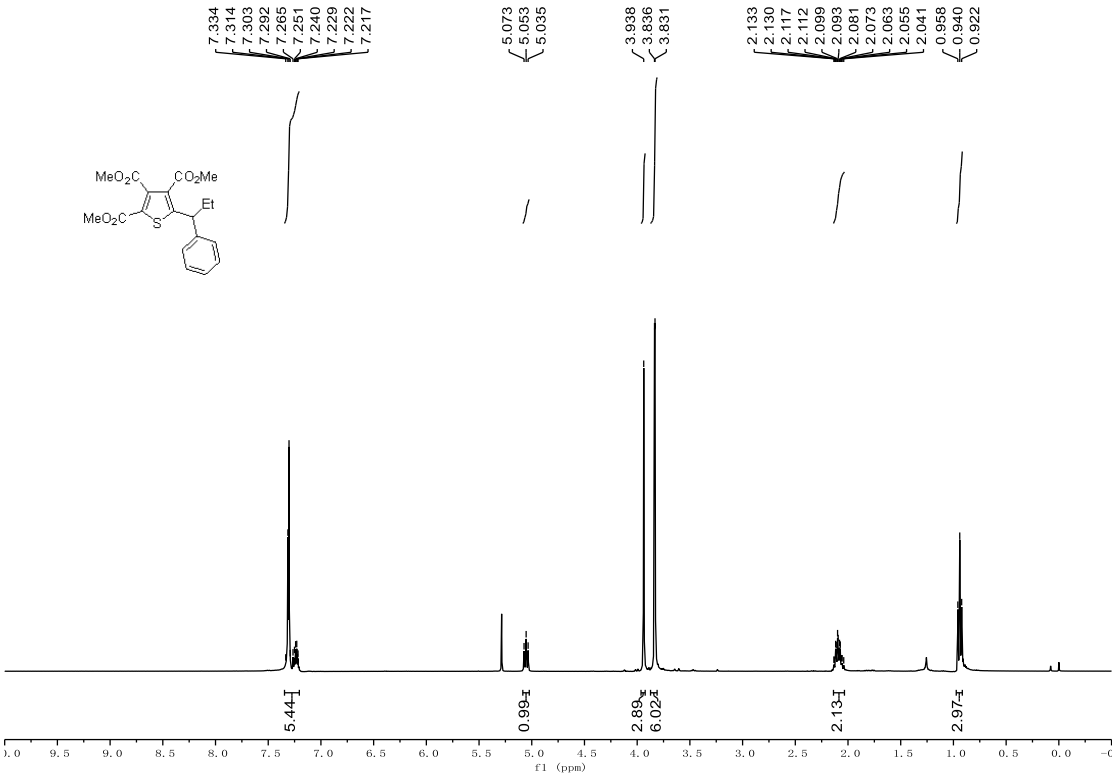
^{13}C NMR of **14**



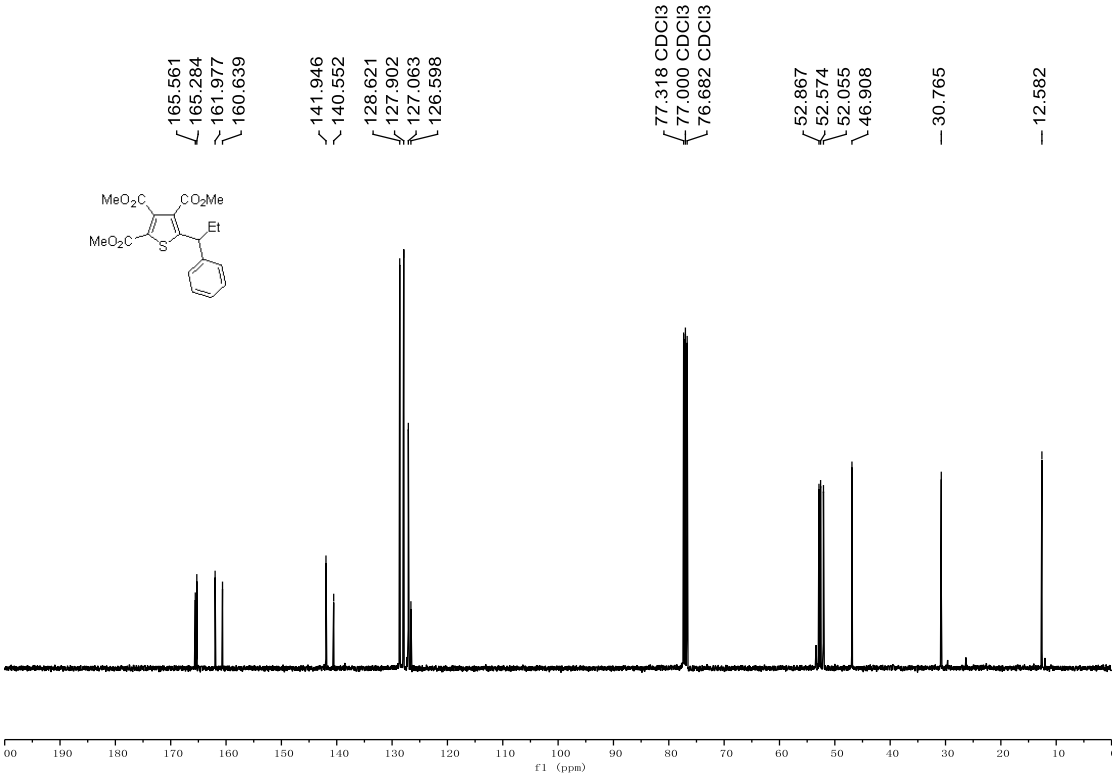
^{1}H NMR of **15**



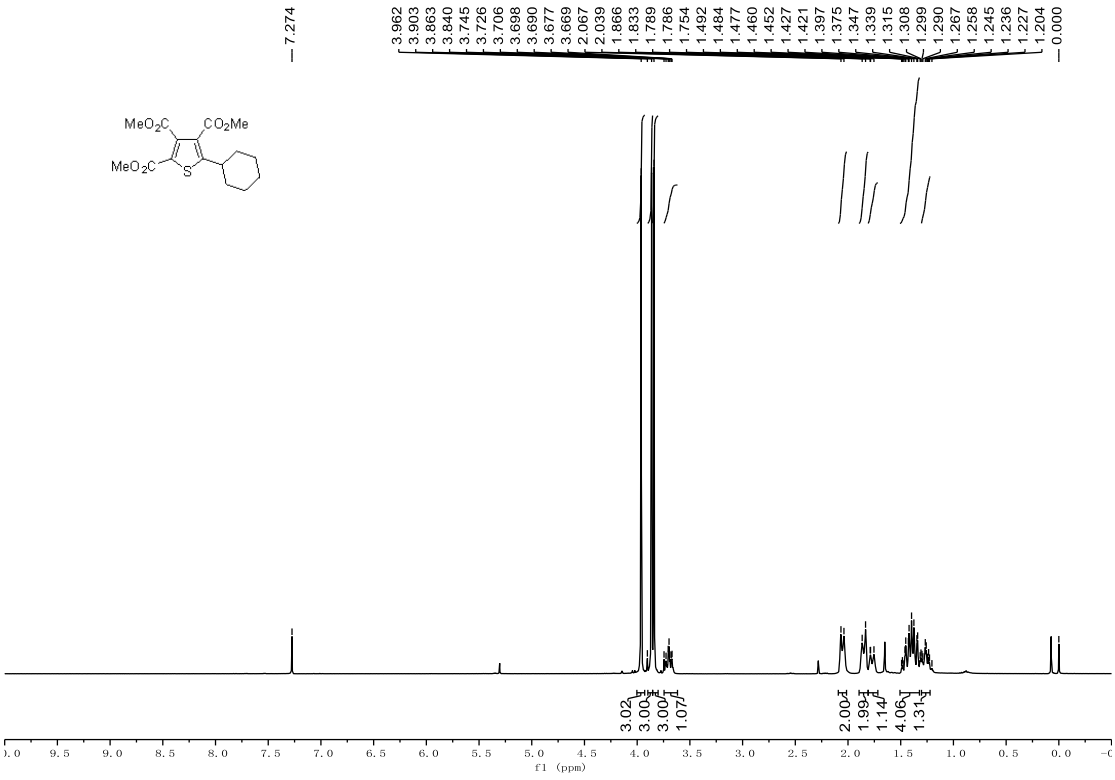
^{13}C NMR of **15**



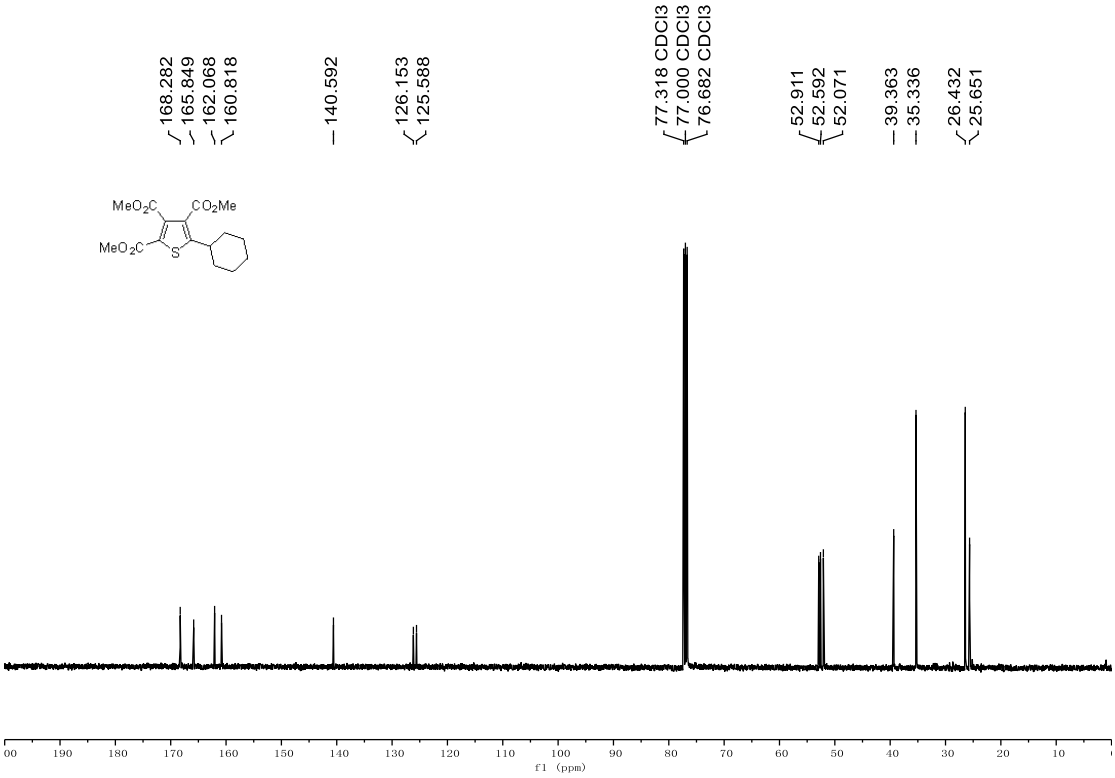
^{1}H NMR of **16**



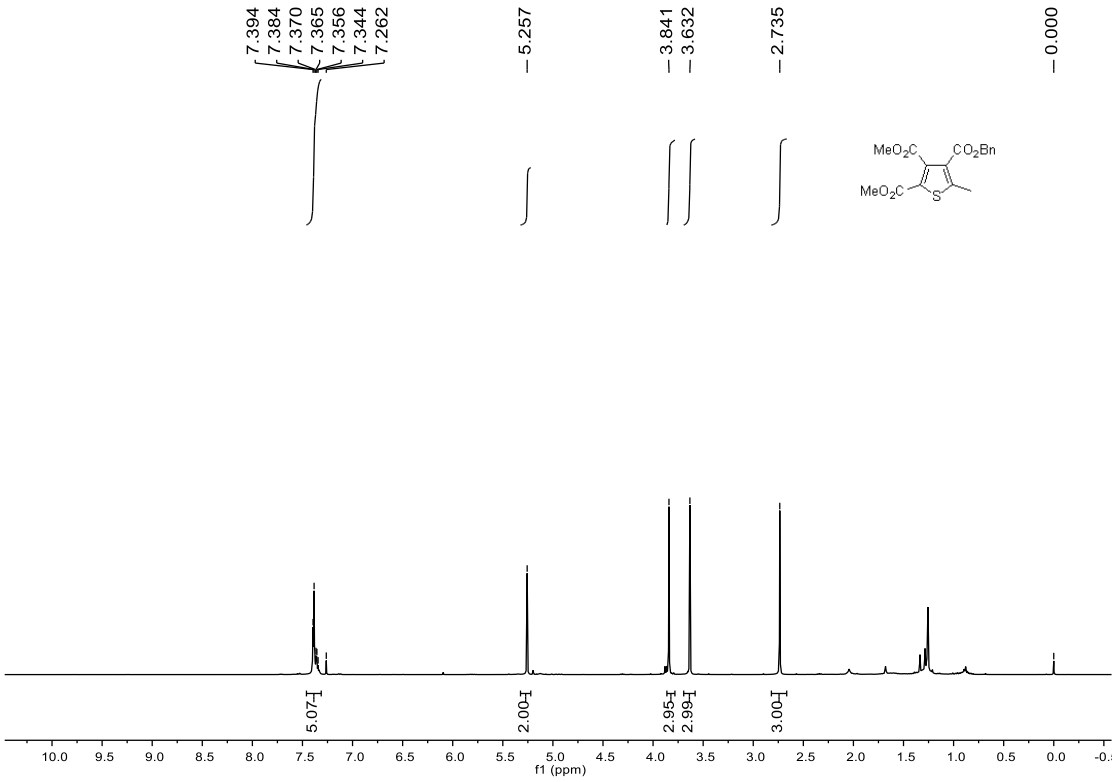
^{13}C NMR of **16**



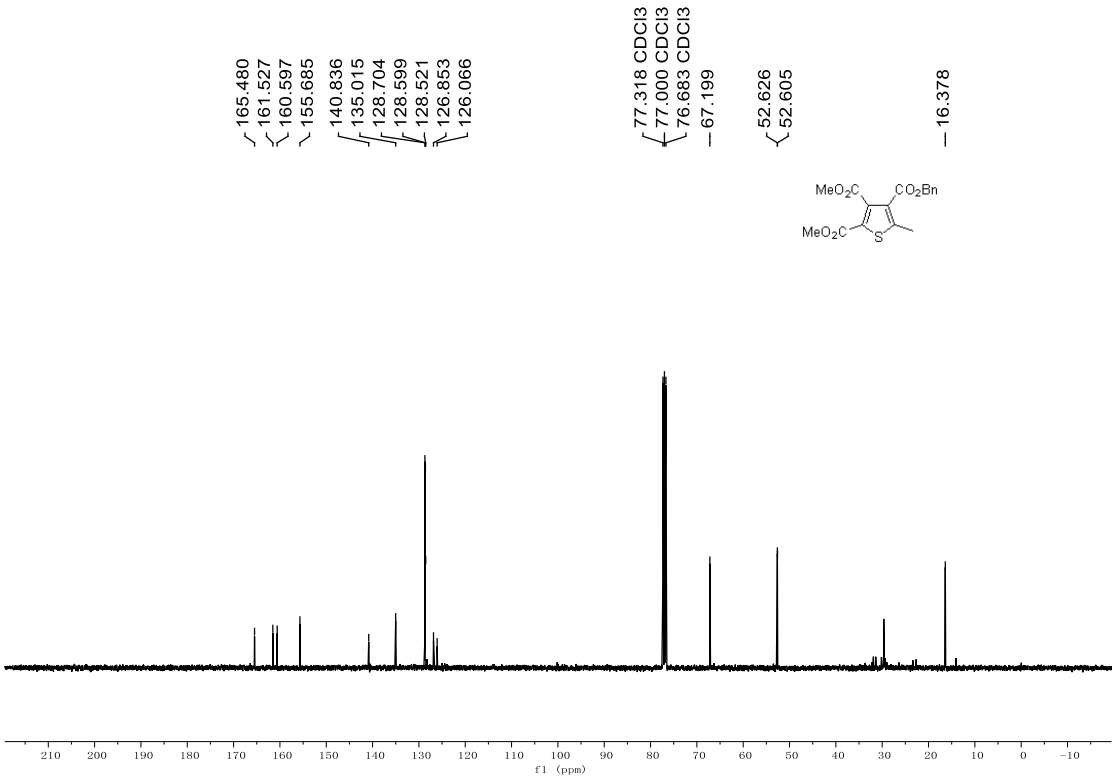
^{1}H NMR of **17**



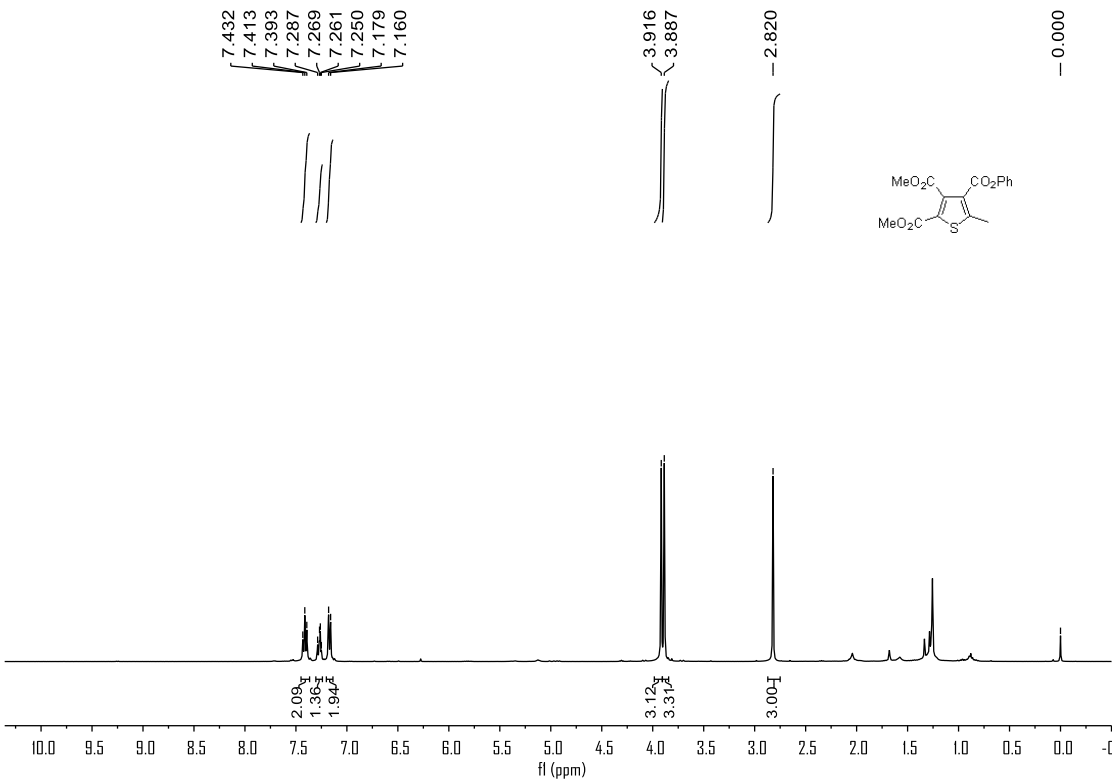
^{13}C NMR of **17**



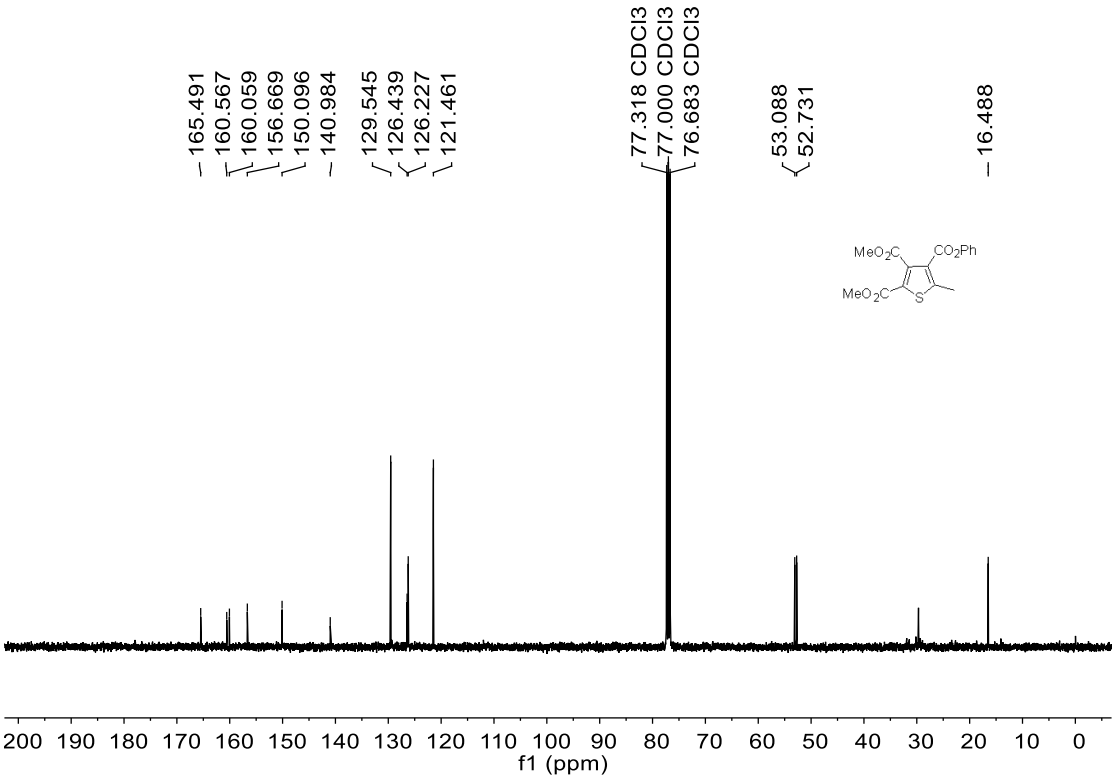
^{1}H NMR of **18**



^{13}C NMR of **18**



^{1}H NMR of **19**



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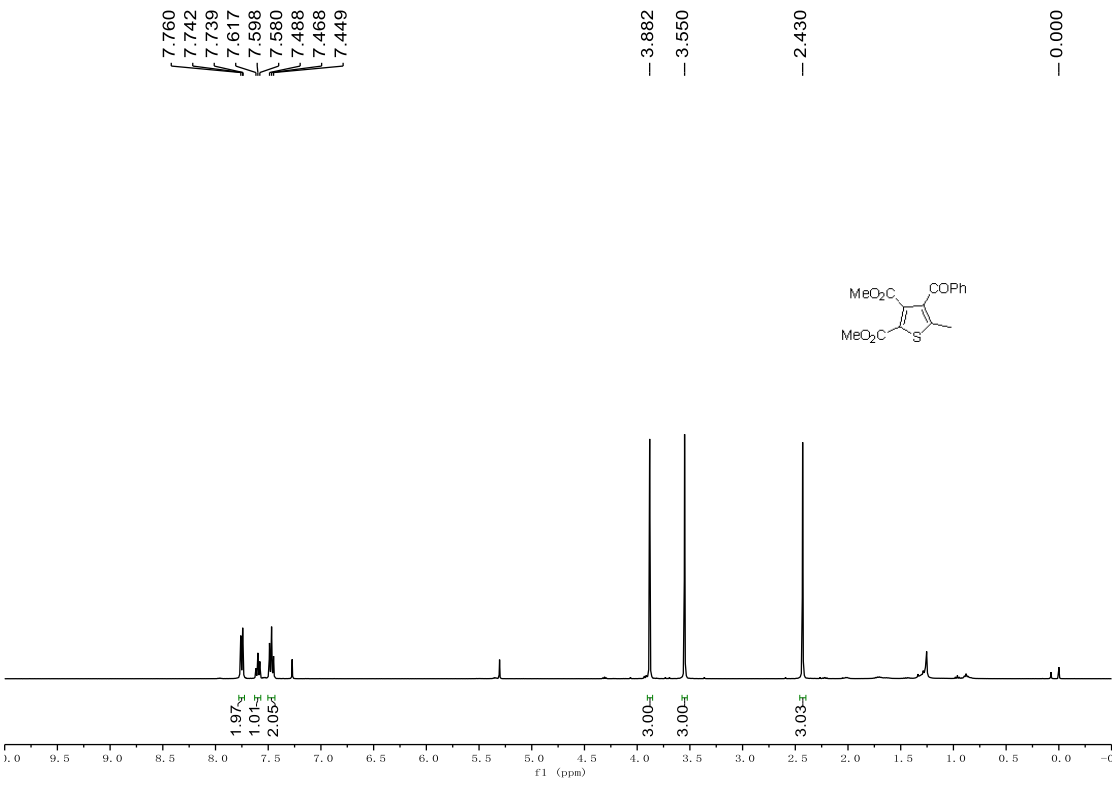
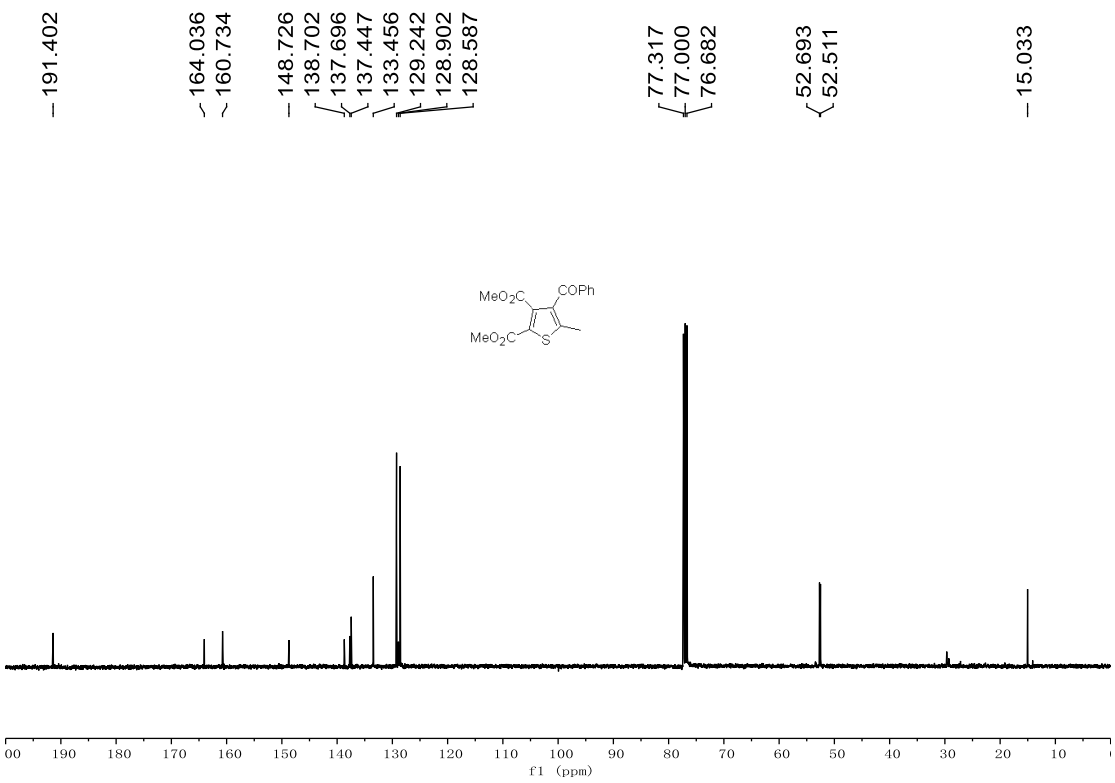
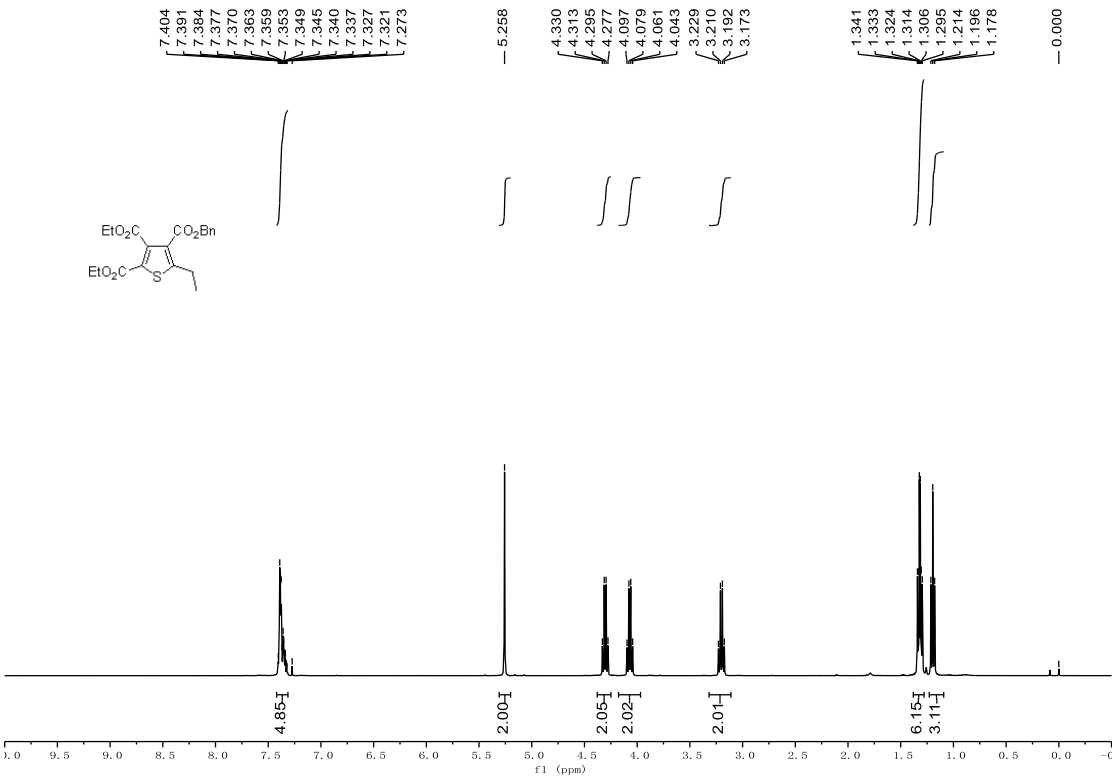


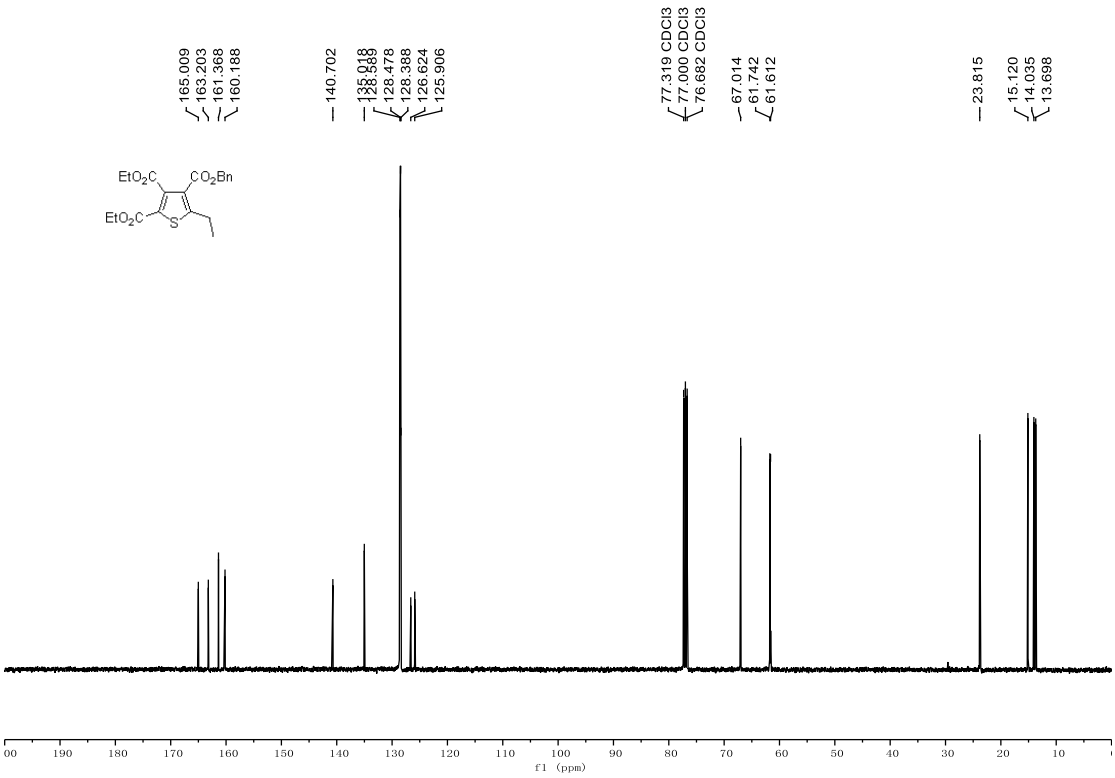
^{1}H NMR of **20**



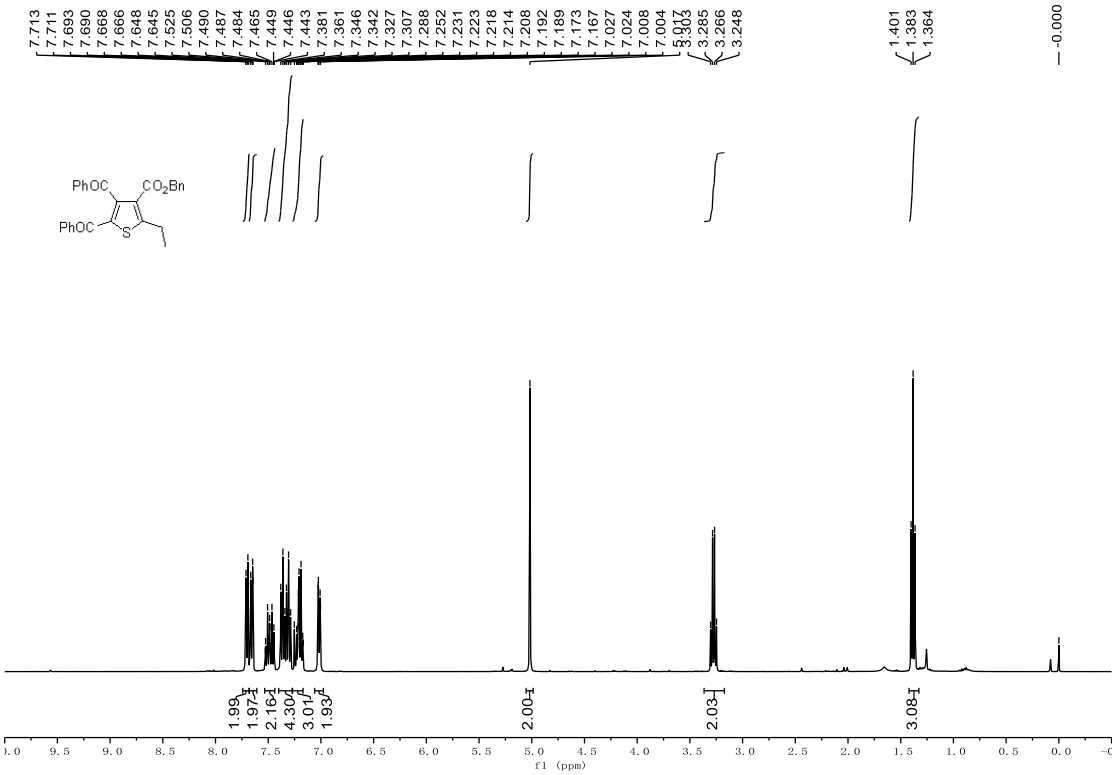
^{13}C NMR of **20**



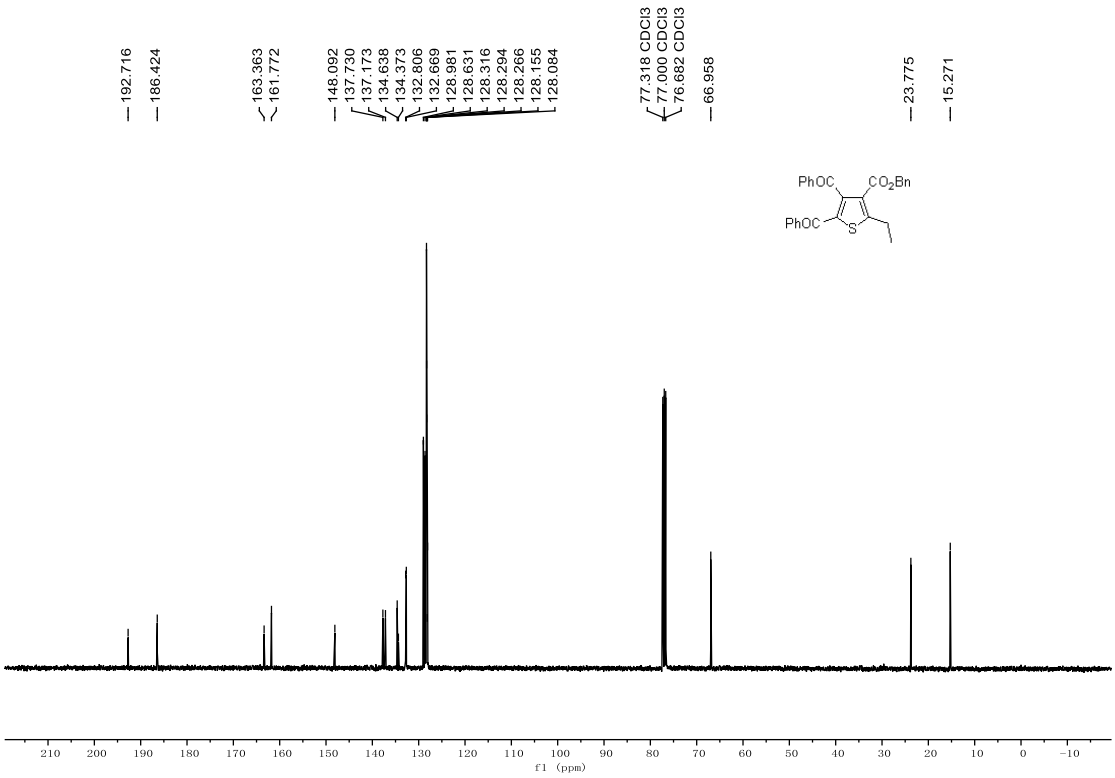
^{1}H NMR of **21**



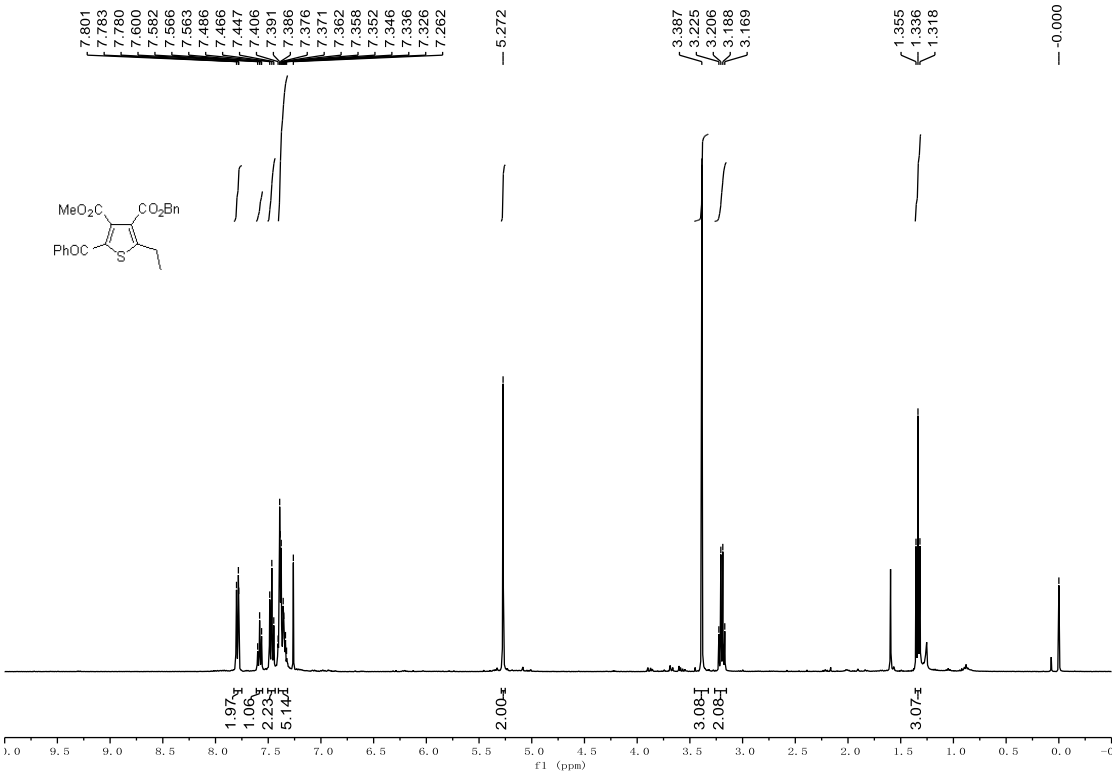
^{13}C NMR of **21**



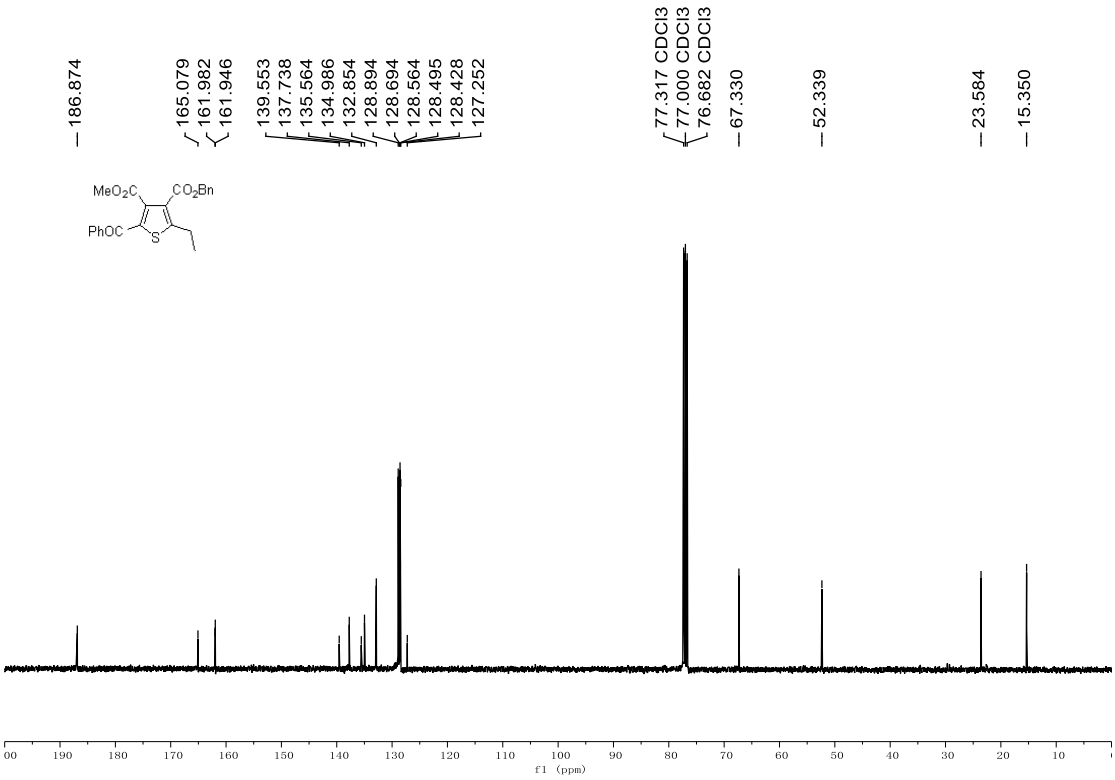
^{1}H NMR of **22**



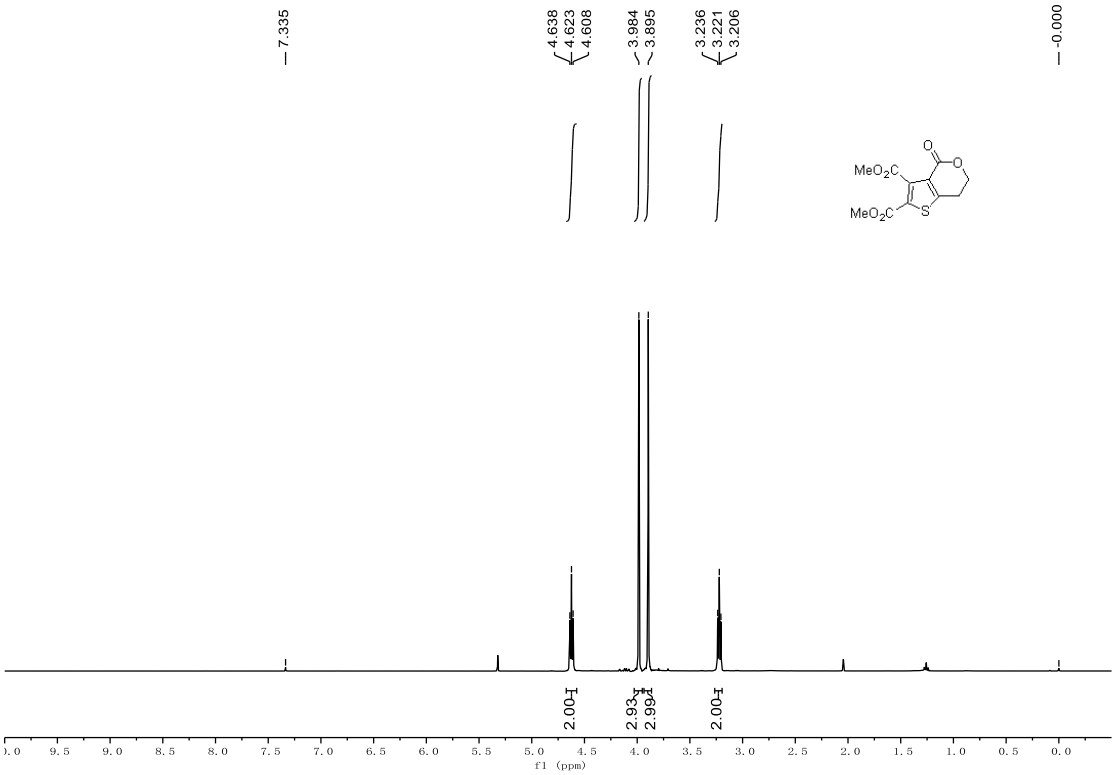
^{13}C NMR of **22**



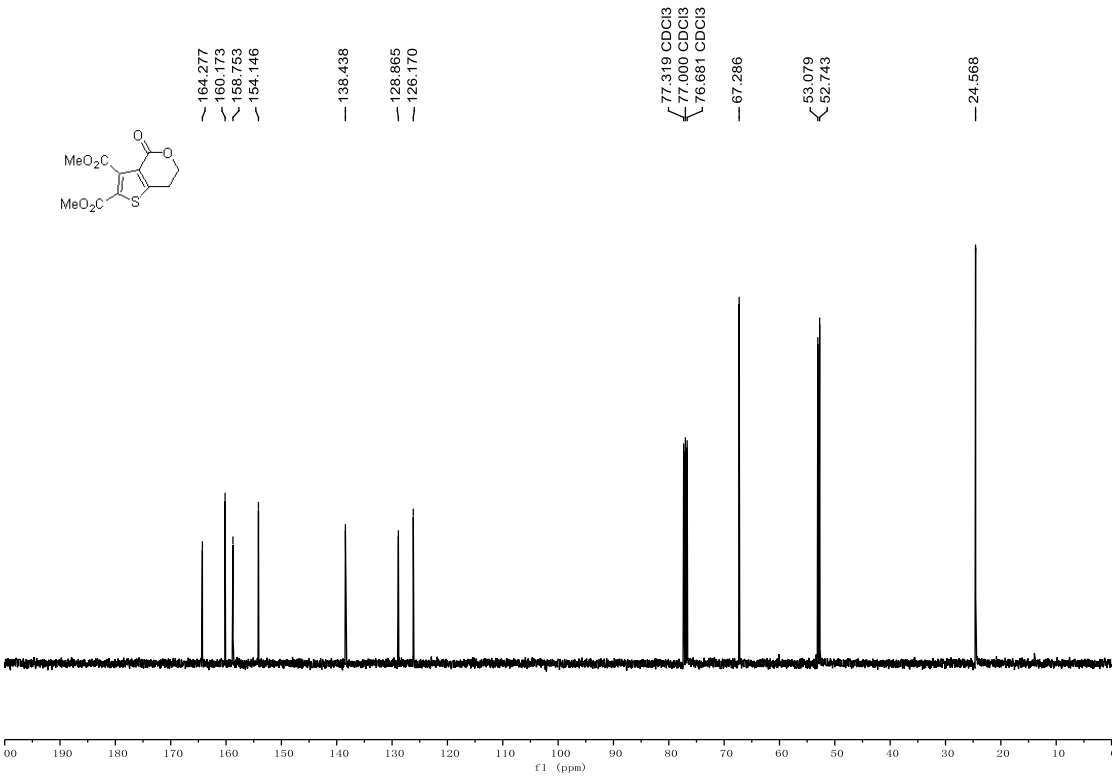
^{1}H NMR of **23**



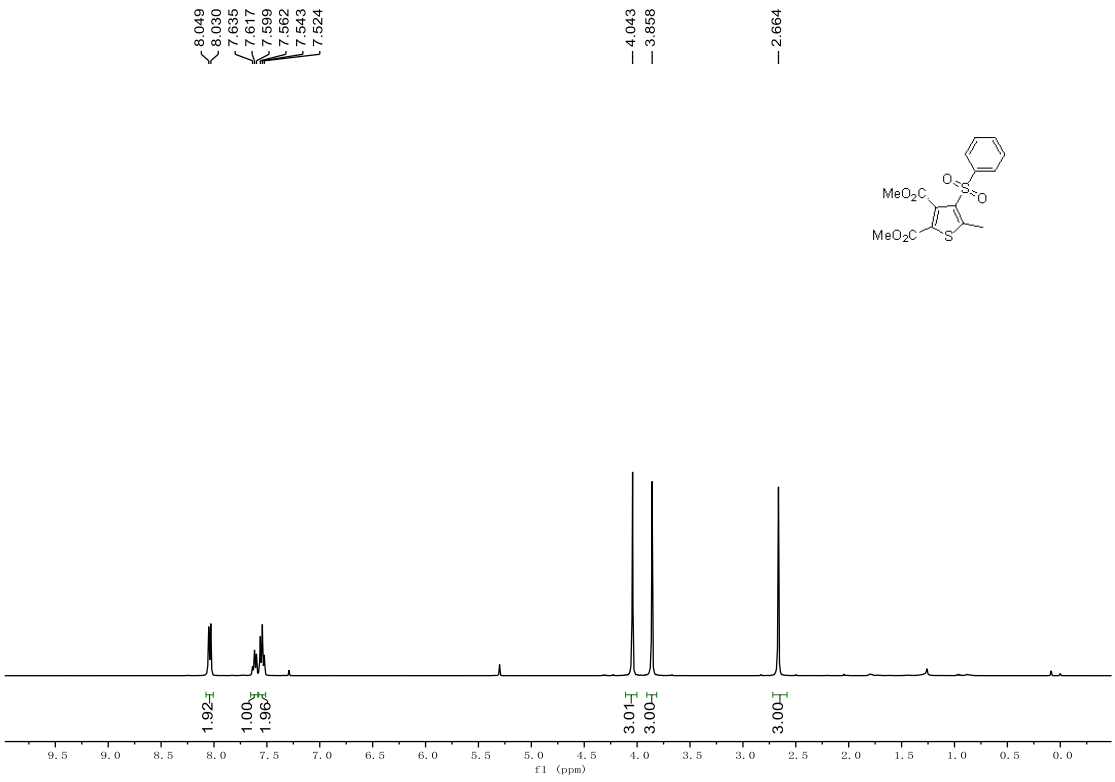
^{13}C NMR of **23**



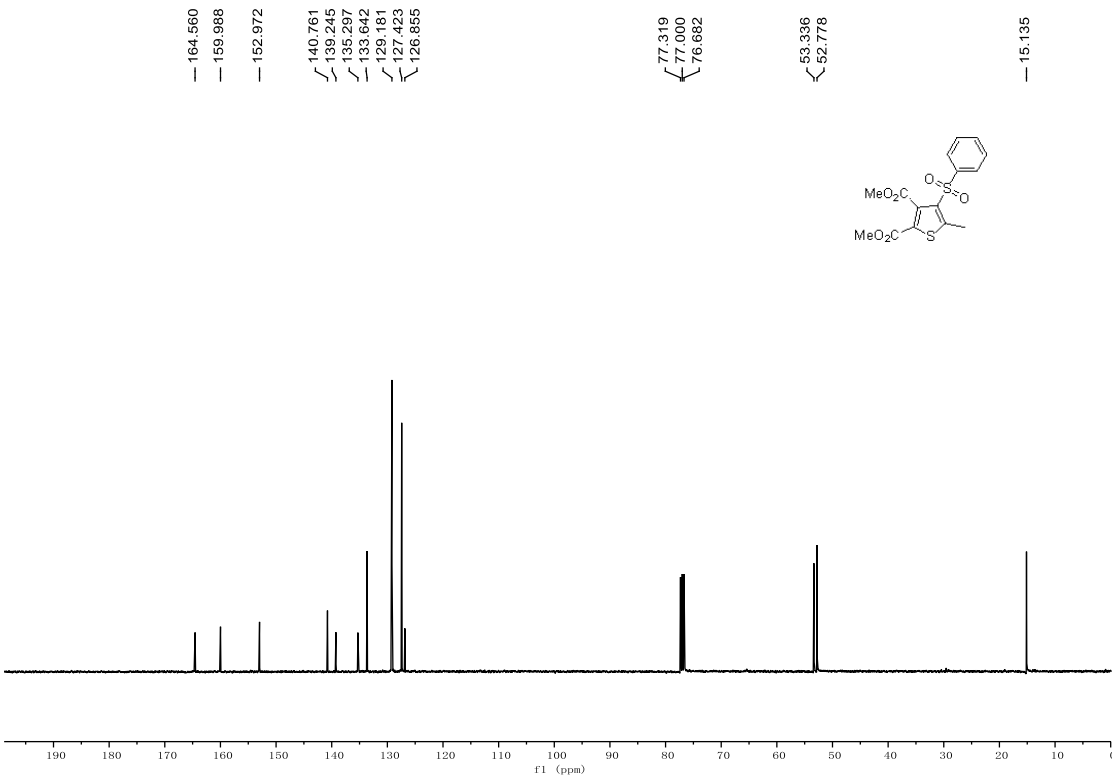
^{1}H NMR of **24**



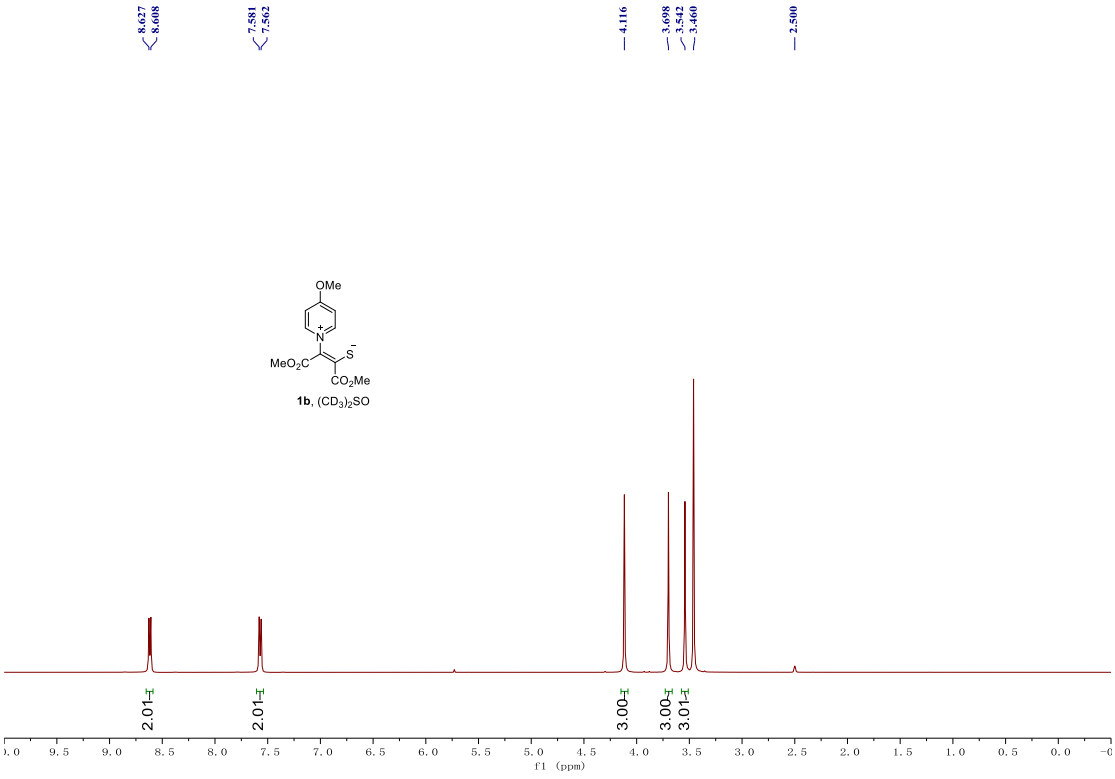
^{13}C NMR of **24**



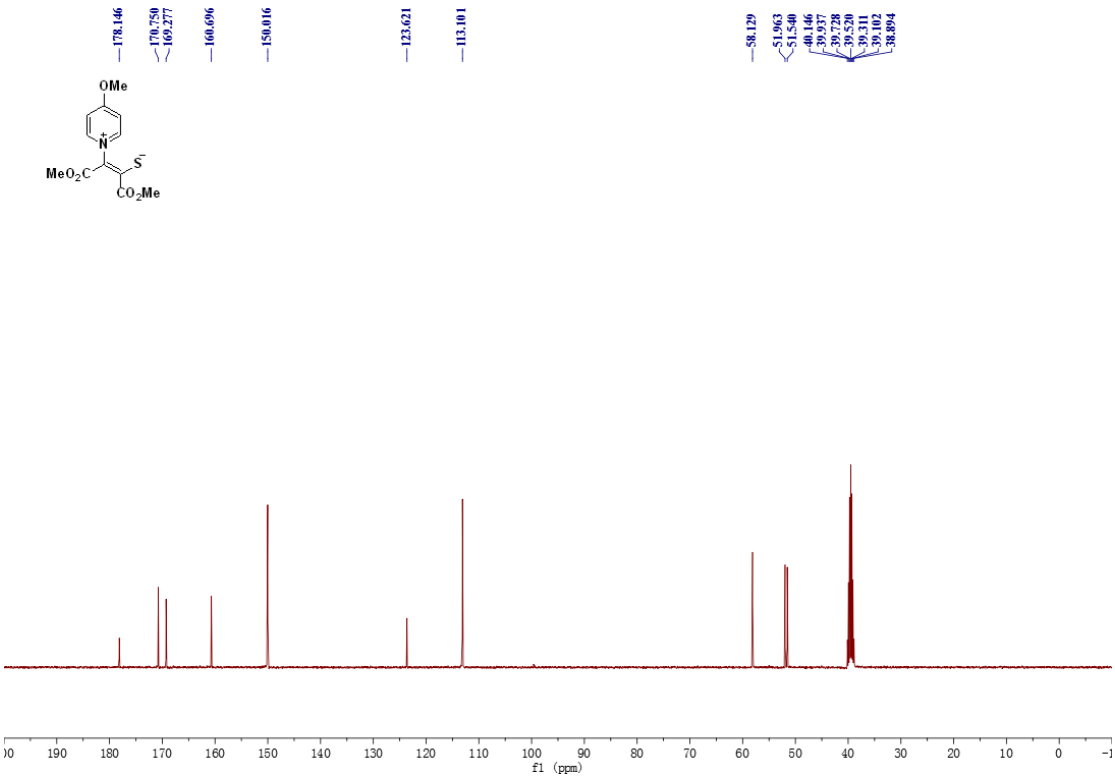
^{1}H NMR of **25**



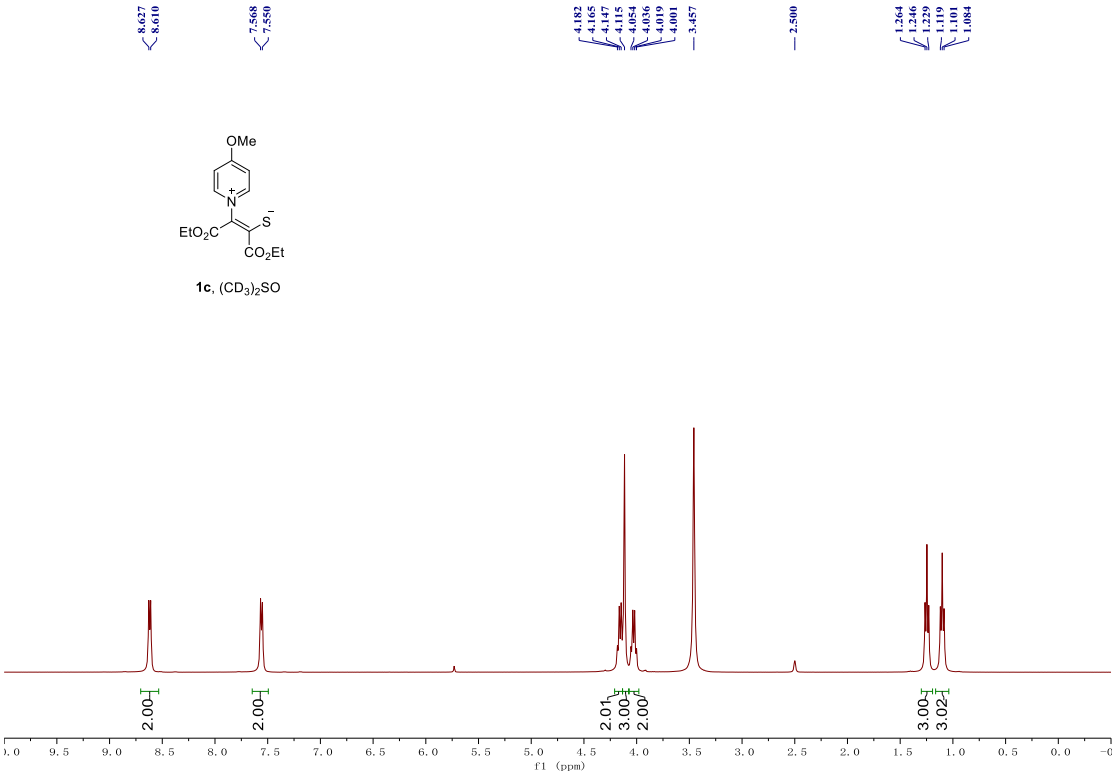
^{13}C NMR of **25**



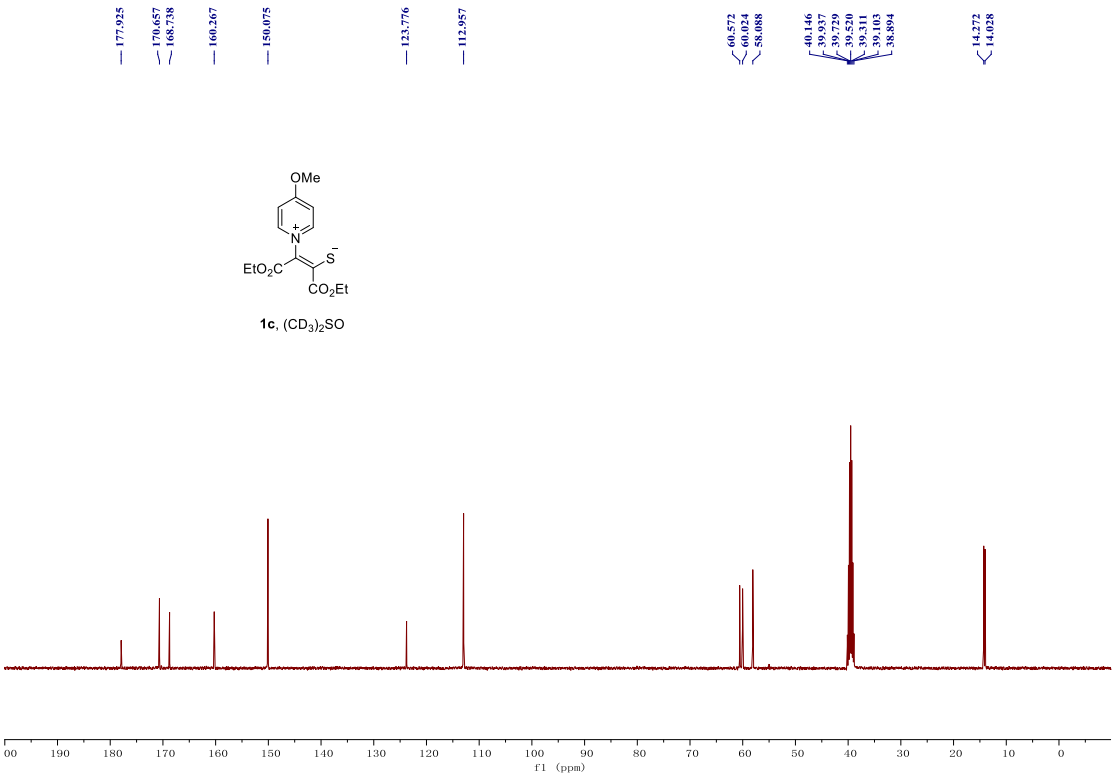
^{1}H NMR of **1b**



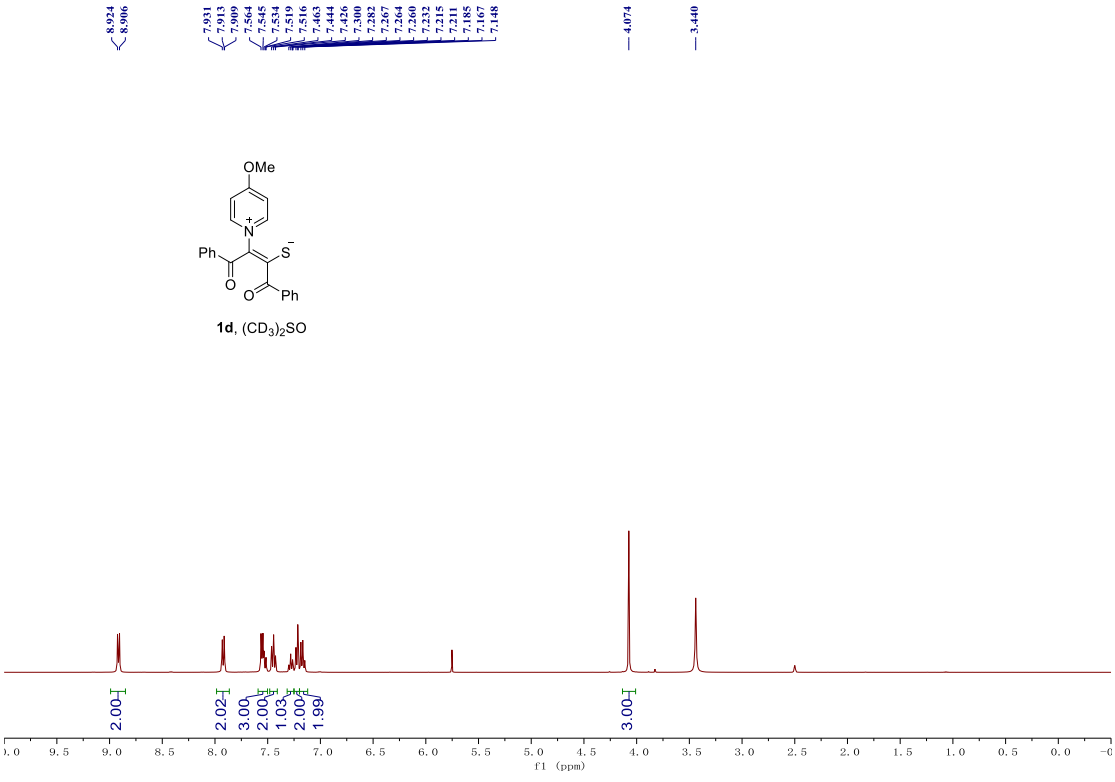
^{13}C NMR of **1b**



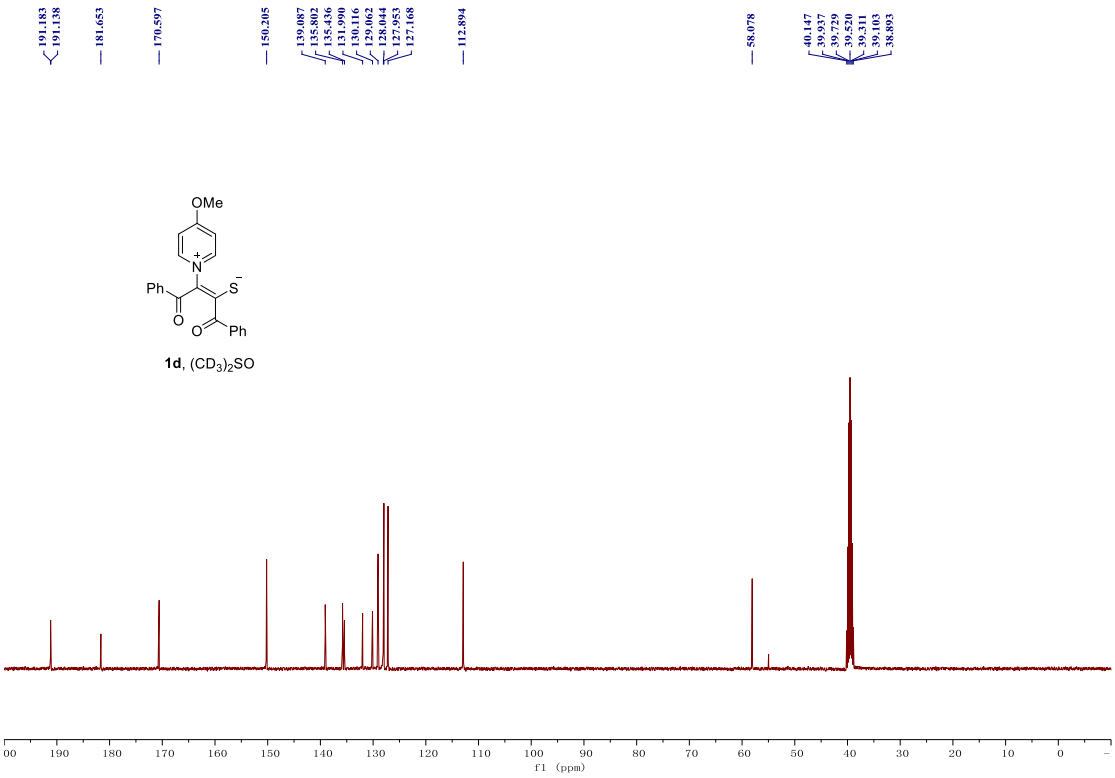
^{1}H NMR of **1c**



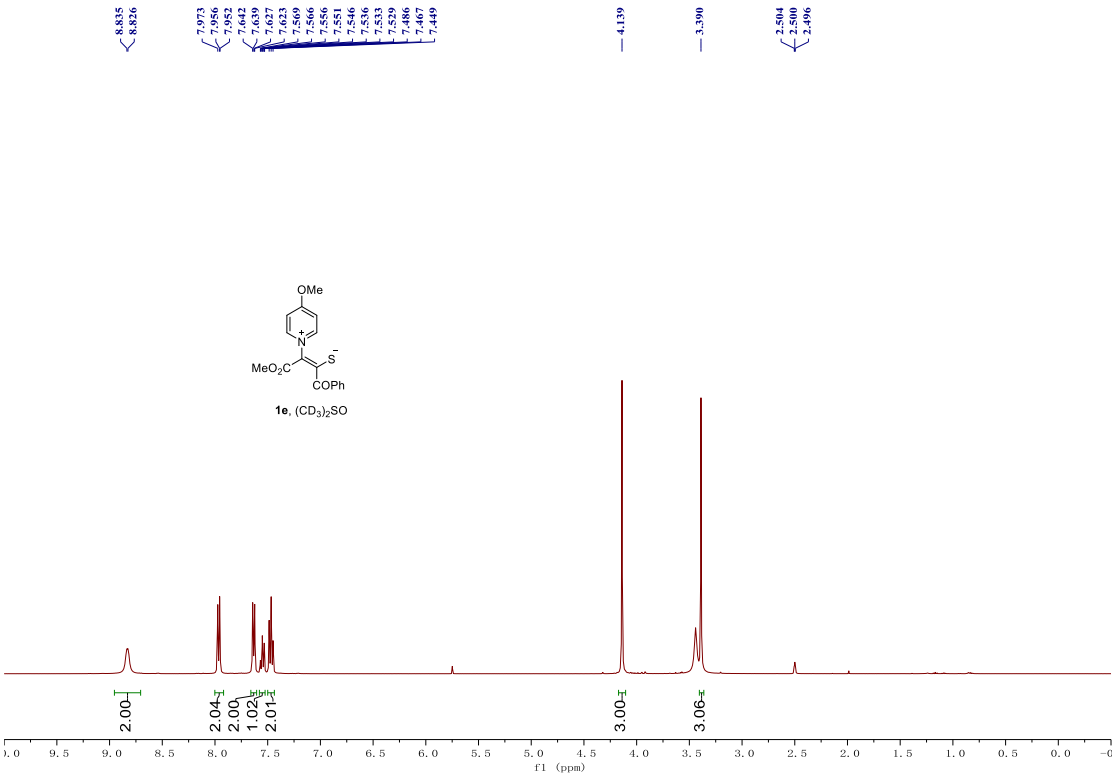
^{13}C NMR of **1c**



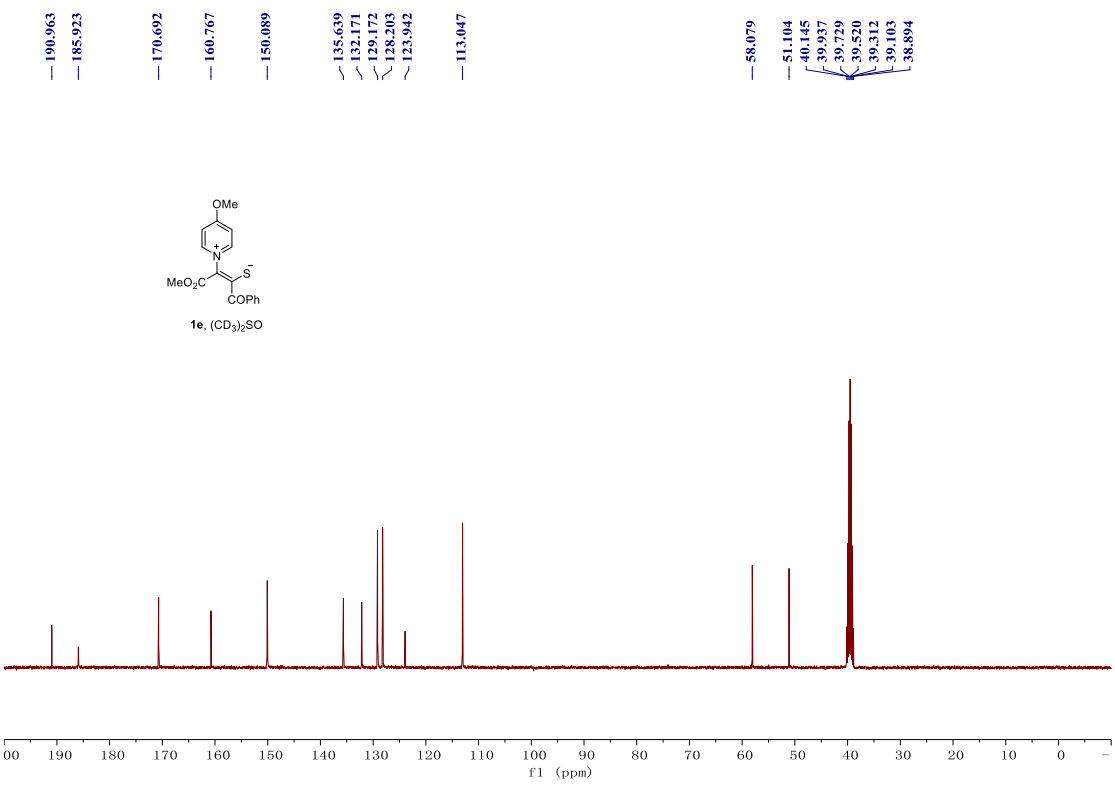
^{1}H NMR of **1d**



^{13}C NMR of **1d**



^{1}H NMR of **1e**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170.692
160.767
150.089
135.639
132.171
129.172
128.203
123.942
113.047
58.079
51.104
40.145
39.937
39.729
39.520
39.312
39.103
38.894
OMe
N+
MeO2C
S−
COPh
1e, (CD3)2SO
f1 (ppm)

^{13}C NMR of **1e**