Supporting Information

Electrochemical oxidative dearomatization of 2-arylthiophenes

Zhaojiang Shi,†[a] Hao-Kuan Lu,†[a] Nan Li, Yaofeng Yuan,*[a] Zhen Li[b] and Ke-Yin Ye*[a,c]

[a] Institute of Pharmaceutical Science and Technology,
College of Chemistry, Fuzhou University, Fuzhou 350108, China.
E-mail: yaofeng_yuan@fzu.edu.cn (Y.Y.); kyye@fzu.edu.cn (K.Y.)

[b] Institute of Molecular Aggregation Science, Tianjin University, Tianjin 300072, China.

[c] State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China.

† These authors contributed equally to this work.

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1. General Information

All reactions were performed under an atmosphere of argon using standard Schlenk techniques, unless otherwise indicated. All commercial reagents were used without further purification, unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) analysis. TLC plates were viewed under UV light and stained with potassium permanganate. Yields refer to products isolated after purification by column chromatography, unless otherwise stated. Proton nuclear magnetic resonance (^{1}H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra and fluorine nuclear magnetic resonance (^{19}F NMR) were recorded on Bruker AV-400 (400 MHz), JEOL-500 (500 MHz) spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances IR spectra were obtained from Thermo Scientific NICOLET 380 FT-IR (KCl card). HRMS were obtained on an Exactive Plus LC-MS (ESI) mass spectrometer with the use of quadrupole analyzer. Cyclic voltammetry data were measured with a CHI 760E potentiostat (Chinstruments). All chemcials were purchased from *Innochem or Energy Chemical* and used as received.

Electrolysis experiments were performed using MESTEK DC power supply. Electrode clips (PT-1 or PT-3) and platinum plate (99.99%, 15*15*0.3 mm or 30*30*0.1 mm) was purchased from Gaoss Union. The carbon cloth (CeTech WOS1002) was cut into 15 x 15 x 0.1 mm pieces before use, and was clamped between electrode clips.

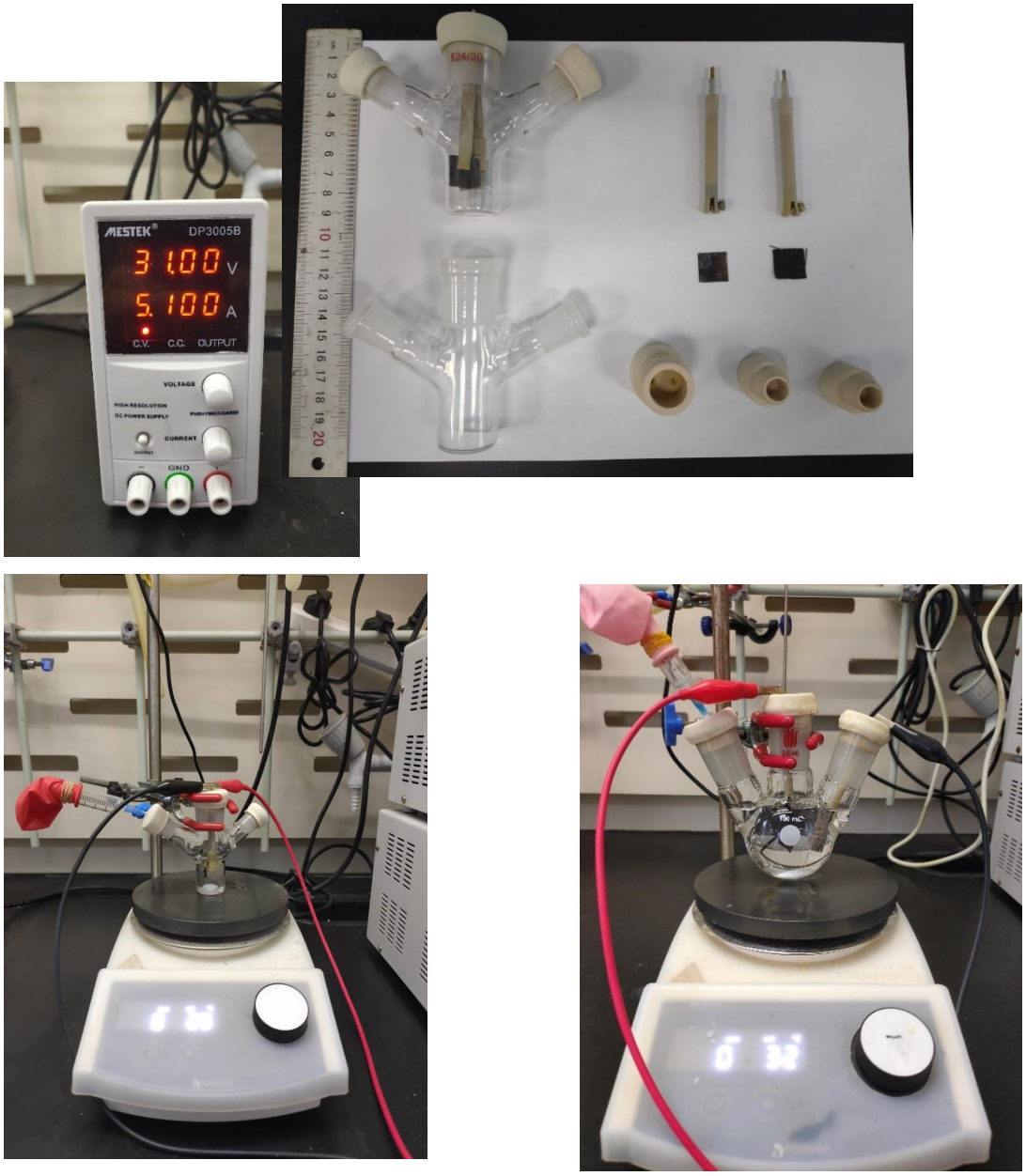
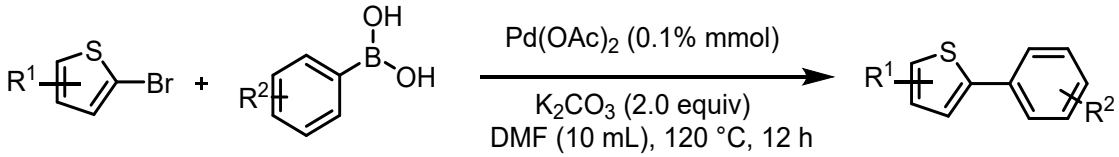


Figure S1 Setup of electrochemical synthesis

2. General Procedures

Method A: General procedure for the preparation of 2-phenylthiophene compounds[1, 2]

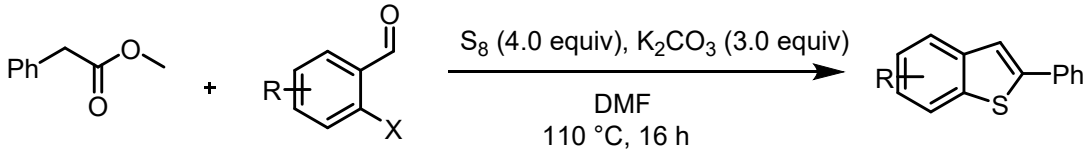


Arylboronic acid (6.0 mmol, 1.2 equiv.) and K_2CO_3 (1.38 g, 10.0 mmol, 2.0 equiv.) were placed in a 100 mL duplex flask, which was filled with nitrogen. 2-Bromothiophene (5.0 mmol, 1.0 equiv.), $Pd(OAc)_2$ (0.24 mg, 0.1 mmol%), and DMF (10.0 mL) were consequently added to the reaction flask. The reaction mixture was stirred at 120 ℃ for 12 h. The resulting mixture was quenched with water. Then the suspension solution was extracted by ethyl acetate (3×25 mL), the organic layers were combined, dried over sodium sulfate, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel (petroleum/ ethyl acetate = 200:1).

The following chemicals can be purchased commercially.

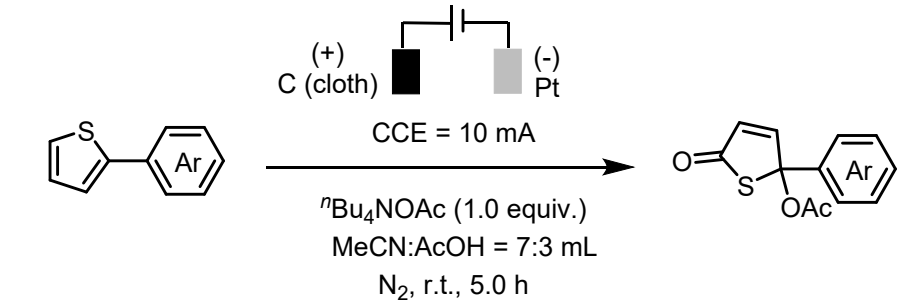
2-phenylthiophene; 2-(4-fluorophenyl)thiophene; 2-(4-bromophenyl)thiophene; 5-phenylthiophene-2-carbaldehyde; 5-phenylthiophene-2-carboxylic acid; 2-bromo-5-phenylthiophene; 2-(benzo[b]thiophen-2-yl)pyridine; 2,5-diphenylthiophene; 6-methoxy-2-(4-methoxyphenyl)benzo[b]thiophene.

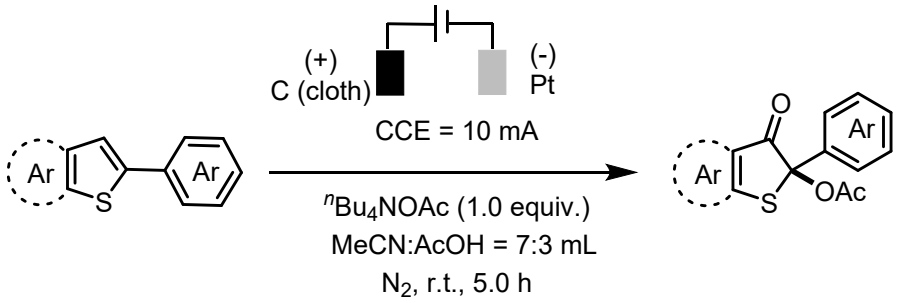
Method B: General procedure for the preparation of 2-phenylthiophene compounds[3]



A 100 mL oven-dried reaction vessel was charged with S_8 (512 mg, 16 mmol, 4 equiv.), K_2CO_3 (1.656 g, 12 mmol, 3.0 equiv.), methyl 2-phenylacetate (900 mg, 6.0 mmol, 1.5 equiv.), substituted benzaldehyde (4.0 mmol, 1.0 equiv.). The reaction vessel was added DMF (20 mL) by syringe. The sealed vessel was stirred at 110 ℃ for 16 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography on silica gel (petroleum/ ethyl acetate = 100:1) to give the desired product.

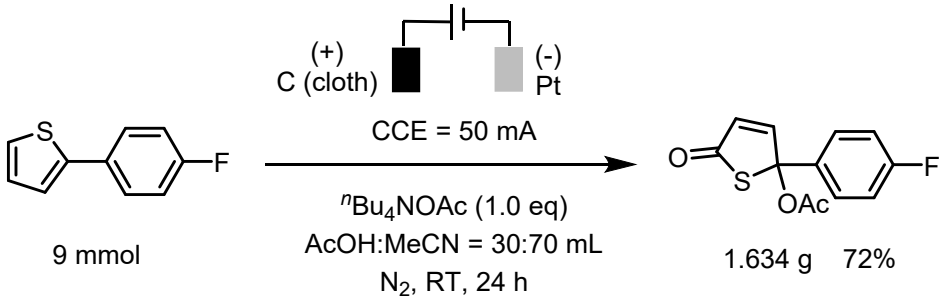
Method C: General procedure for the electrochemically induced thiophene dearomatization





In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, 2-phenylthiophene (0.3 mmol, 1.0 equiv.) and ^{n}Bu$_4$NOAc (0.3 mmol, 1.0 equiv.) were added. The glassware was equipped with carbon cloth (15 mm × 15 mm × 0.1 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N_2, CH_3CO_2H (3 mL) and MeCN (7 mL) were injected into the glassware *via* syringes. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA at an ambient temperature for 5 h. The reaction mixture was concentrated *in vacuo* and the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

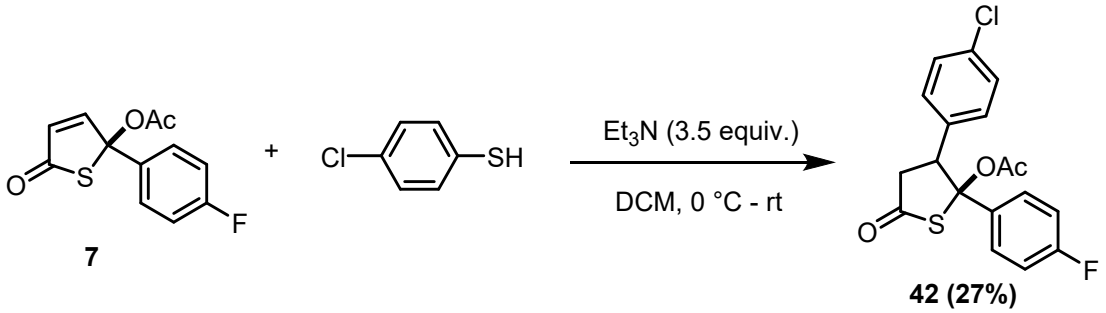
Method D: Scale-up synthesis of compound



In an oven-dried undivided three-necked glassware (100 mL) equipped with a stirring bar, 2-(4-fluorophenyl)thiophene (1.60 g, 9 mmol, 1.0 equiv.) and ^{n}Bu$_4$NOAc (2.72 g, 9 mmol, 1.0 equiv.) were added. The glassware was equipped with carbon cloth (30 mm × 30 mm × 0.1 mm) as the anode and platinum plate (30 mm × 30 mm × 0.1

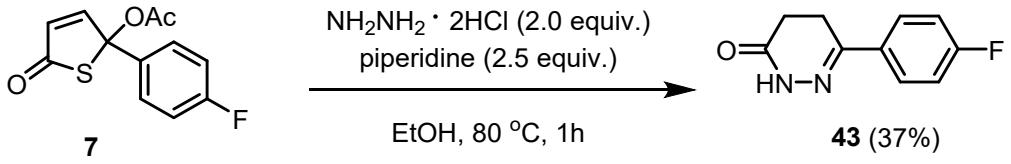
mm) as the cathode. Under the protection of N_2, CH_3CO_2H (30 mL) and MeCN (70 mL) were injected into the glassware *via* syringes. The reaction mixture was stirred and electrolyzed at a constant current of 50 mA at an ambient temperature for 24 h. The reaction mixture was concentrated *in vacuo* and the crude residue was subjected to flash column chromatography on silica gel to give the desired product (1.634 g, 72 % yield).

Method E: Synthesis of compound 42[4]



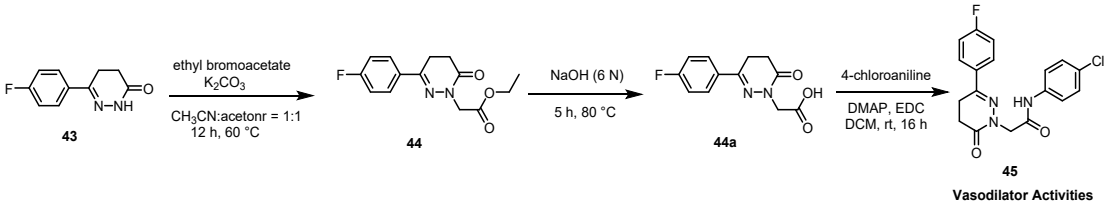
Triethylamine (8 μL, 0.057mmol, 1.0 equiv.) was added to the CH_2Cl_2 (5 mL) solution of the **7** (50.4 mg, 0.2 mmol, 3.5 equiv.) and 4-chlorobenzenethiol (28.8 mg, 0.2 mmol, 3.5 equiv.) at 0 °C. After 15 min, the reaction was allowed to warm to rt overnight. The solvent was removed and the product was purified by flash column chromatography (ethyl acetate/hexanes = 10:1) giving **42** (21.1 mg, 27%) as a white solid.

Method F: Synthesis of compound 43



To a solution of 2-(4-fluorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate **7** (50.4 mg, 0.2 mmol, 1.0 equiv.) and piperidine (50.0 μL, 0.5 mmol, 2.5 equiv.) in EtOH (5 mL) and N_2H_4•HCl (27.4 mg, 0.4 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 1 h. Then the solvent was removed and the product was purified by flash column chromatography (ethyl acetate/hexanes = 1:1) giving 14.2 mg (37%) of **43** as a white solid.

Method G: Synthesis of compound 45[5-7]



General Procedure for 44

A mixture of compound **43** (28.0 mg, 0.146 mmol 1.0 equiv.), K_2CO_3 (60.3 mg, 0.437 mmol, 3.0 equiv.), and ethyl bromoacetate (73.0 mg, 0.437 mmol, 3.0 equiv.) in CH_3CN and acetone (1:1 = 20 mL) was refluxed and stirring for 12 h. The mixture was then concentrated in *vacuo*, diluted with cold water, and extracted with CH_2Cl_2. The solvent was evaporated in *vacuo* and then purified by flash column chromatography (cyclohexane/ethyl acetate = 1:1) giving 22.7 mg (56%) of **44** as a white solid.

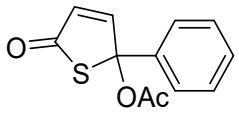
General Procedure for the hydrolysis of 44a

A suspension of compound **44** (22.7 mg, 0.08 mmol, 1.0 equiv.) in 6 N NaOH (2 mL) was stirred at 80 °C for 5 h. The mixture was diluted with ice-cold water and then acidified with 6 N HCl. The solvent was evaporated in *vacuo* to give compound **44a**, which was used directly in the next step without further purification.

General Procedure for 45

An oven-dried round-bottom flask was charged with crude product **44a** (20.0 mg, 0.08 mmol, 1.0 equiv.), 4-chloroaniline (10.2 mg, 0.08 mmol,1.0 equiv.), DMAP (14.7 mg, 0.12 mmol, 1.5 equiv.) and DCM (5 mL). EDC (18.4 mg, 0.12 mmol, 1.5 equiv.) in DCM was added dropwise to the above solution under a nitrogen atmosphere. The reaction mixture was kept stirring at room temperature for 16 h. The reaction was then quenched by HCl (1 M) and extracted with DCM. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by flash column chromatography (DCM/petroleum = 1:1) giving 22.6 mg (79%) of **45** as a white solid.

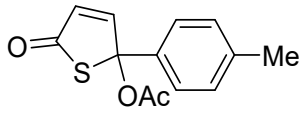
3. Characterization of Products



2: 5-oxo-2-phenyl-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 54.5 mg (78% yield) of **2** as a white solid.

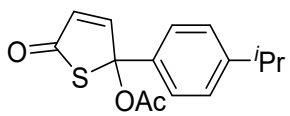
IR (neat, cm^{-1}): 3066 (w), 1756 (m), 1693 (s), 1492 (w), 1447 (w), 1370 (w), 1327 (w), 1218 (s), 1168 (w), 1066 (m), 1013 (w), 968 (w), 797 (w), 761 (m), 710 (w), 527 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.58 – 7.54 (m, 2H), 7.42 (d, *J* = 6.1 Hz, 1H), 7.40 – 7.33 (m, 3H), 6.19 (d, *J* = 6.1 Hz, 1H), 2.18 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 197.2, 169.1, 156.3, 137.4, 129.5, 129.3, 129.2, 125.6, 96.6, 21.4.
HRMS (ESI) calculated for $C_{12}H_{10}NaO_3S$ [M+Na^+]: 257.0243; found: 257.0236.



3: 5-oxo-2-(p-tolyl)-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 49.3 mg (66% yield) of **3** as a white solid.

IR (neat, cm^{-1}): 2923 (w), 2853 (w), 1753 (m), 1695 (s), 1611 (w), 1369 (w), 1216 (s), 1185 (w), 1067 (m), 1012 (m), 961 (w), 816 (w), 810 (w), 623 (w), 520 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 6.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.17 (d, *J* = 6.1 Hz, 1H), 2.34 (s, 3H), 2.17 (s, 3H); ^{13}C NMR **(126 MHz, Chloroform-*d*)** δ 197.3, 169.2, 156.4, 139.4, 134.4, 129.8, 129.3, 125.6, 96.7, 21.5, 21.2.
HRMS (ESI) calculated for $C_{13}H_{12}NaO_3S$ [M+Na^+]: 271.0399; found: 271.0392.



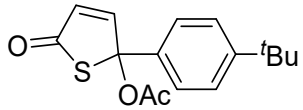
4: 2-(4-isopropylphenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C** (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 46.3 mg (56% yield)

of **4** as a white solid.

IR (neat, cm^{-1}): 2960 (w), 2923 (w), 2852 (w), 1754 (s), 1698 (s), 1463 (w), 1369 (w), 1218 (s), 1170 (w), 1068 (m), 1012 (w), 896 (w), 832 (w), 796 (w), 623 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.49 – 7.45 (m, 2H), 7.41 (d, *J* = 6.1 Hz, 1H), 7.25 – 7.22 (m, 2H), 6.17 (d, *J* = 6.1 Hz, 1H), 2.90 (hept, *J* = 7.0 Hz, 1H), 2.17 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 197.4, 169.2, 156.4, 150.2, 134.6, 129.3, 127.3, 125.7, 96.7, 33.9, 23.9, 21.5.

HRMS (ESI) calculated for $C_{15}H_{16}NaO_3S$ [M+Na$^+$]: 299.0712; found: 299.0717.

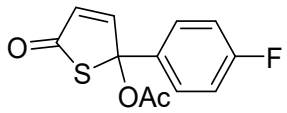


5: 2-(4-(tert-butyl)phenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C** (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 44.4 mg (51% yield) of **5** as a white solid.

IR (neat, cm^{-1}): 2960 (w) 2926 (w), 2868 (w), 1754 (m), 1694 (s), 1506 (w), 1367 (m), 1269 (w), 1218 (s), 1066 (m), 1010 (m), 965 (w), 918 (w), 896 (w), 833 (w), 795 (w), 622 (m), 566 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.48 – 7.45 (m, 2H), 7.41 (d, *J* = 6.1 Hz, 2H), 7.40 – 7.37 (m, 2H), 6.17 (d, *J* = 6.1 Hz, 1H), 2.18 (s, 3H), 1.30 (s, 9H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 197.4, 169.2, 156.4, 152.5, 134.2, 129.3, 126.1, 125.4, 96.6, 34.8, 31.3, 21.5.

HRMS (ESI) calculated for $C_{16}H_{18}NaO_3S$ [M+Na$^+$]: 313.0869; found: 313.0875.



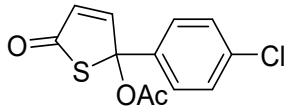
7: 2-(4-fluorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C** (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 61.2 mg (81% yield) of **7** as a white solid.

IR (neat, cm^{-1}): 2955 (w), 2921 (w), 2850 (w), 1754 (m), 1698 (s), 1600 (w), 1507 (w), 1370 (w), 1218 (s), 1162 (m), 1067 (m), 912 (w), 896 (w), 837 (w), 795 (w), 607 (w), 549 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.58 – 7.52 (m, 2H), 7.40 (d, *J* = 6.1 Hz, 1H), 7.11 – 7.02 (m, 2H), 6.20 (d, *J* = 6.1 Hz, 1H), 2.17 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 196.7, 169.1, 163.1 (d, *J* = 249.4 Hz), 156.1, 133.4 (d, *J* = 3.4

Hz), 129.6, 127.7 (d, *J* = 8.5 Hz), 116.1 (d, *J* = 22.1 Hz), 96.0, 21.4; **^{19}F NMR (471 MHz, Chloroform-d)** δ -112.0.

HRMS (ESI) calculated for $C_{12}H_9FNaO_3S$ [M+ Na^+]: 275.0149; found: 275.0145.

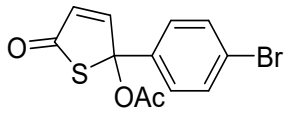


8: 2-(4-chlorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 60.1 mg (75% yield) of **8** as a white solid.

IR (neat, cm^{-1}): 2924 (w), 1746 (m), 1691 (s), 1594 (w), 1491 (m), 1368 (m), 1212 (s), 1094 (m), 1065 (s), 1010 (s), 913 (m), 896 (m), 827 (m), 795 (m), 619 (s), 532 (m), 466 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.51 – 7.48 (m, 2H), 7.38 (d, *J* = 6.1 Hz, 1H), 7.36 – 7.33 (m, 2H), 6.21 (d, *J* = 6.1 Hz, 1H), 2.17 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 196.6, 169.1, 155.9, 136.2, 135.4, 129.8, 129.4, 127.1, 96.0, 21.4.

HRMS (ESI) calculated for $C_{12}H_9ClNaO_3S$ [M+Na^+]: 290.9853; found: 290.9855.

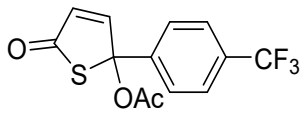


9: 2-(4-bromophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C** (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 60.7 mg (65% yield) of **9** as a white solid.

IR (neat, cm^{-1}): 3073 (w), 2960 (w), 1755 (m), 1691 (s), 1586 (w), 1486 (m), 1369 (m), 1212 (s), 1183 (m), 1066 (s), 1008 (s), 968 (w), 822 (w), 795 (w), 734 (w), 632 (w), 619 (m), 529 (w); **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.53 – 7.49 (m, 2H), 7.45 – 7.42 (m, 2H), 7.38 (d, *J* = 6.1 Hz, 1H), 6.21 (d, *J* = 6.1 Hz, 1H), 2.18 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 196.6, 169.1, 155.8, 136.7, 132.3, 129.9, 127.4, 123.6, 96.0, 21.4.

HRMS (ESI) calculated for $C_{12}H_9BrNaO_3S$ [M+Na^+]: 334.9348; found: 334.9357.

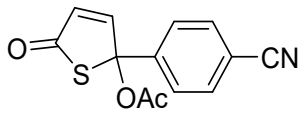


10: 5-oxo-2-(4-(trifluoromethyl)phenyl)-2,5-dihydrothiophen-2-yl acetate

Followed **Method C** (current = 15 mA), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 47.1 mg (52% yield) of **10** as a white solid.

IR (neat, cm^{-1}): 3076 (w), 2929 (w), 1757 (m), 1695 (s), 1409 (w), 1371 (w), 1323 (s), 1215 (m), 1166 (m), 1065 (s), 917 (w), 896 (w), 840 (m), 796 (w), 679 (w), 634 (w), 620 (w), 526 (w), 447 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.70 – 7.63 (m, 4H), 7.40 (d, *J* = 6.1 Hz, 1H), 6.25 (d, *J* = 6.1 Hz, 1H), 2.20 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 196.3, 169.6, 155.6, 141.6, 131.3 (q, *J* = 33.8 Hz), 130.2, 126.2 (q, *J* = 4.2 Hz), 126.1, 123.8 (q, *J* = 279.4 Hz), 95.8, 21.2; **^{19}F NMR (471 MHz, Chloroform-d)** δ -62.7 (s).

HRMS (ESI) calculated for $C_{13}H_9F_3NaO_3S$ [M+Na$^+$]: 325.0117; found: 325.0137.

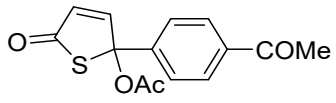


11: 2-(4-cyanophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 39.6 mg (51% yield) of **11** as a white solid.

IR (neat, cm^{-1}): 3047 (w), 2924 (w), 2231 (m), 1754 (s), 1709 (s), 1696 (s), 1370 (m), 1217 (s), 1068 (s), 909 (m), 838 (w), 798 (w), 731 (w), 584 (w), 559 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.68 (d, *J* = 1.2 Hz, 4H), 7.37 (d, *J* = 6.1 Hz, 1H), 6.27 (d, *J* = 6.1 Hz, 1H), 2.21 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 195.8, 169.1, 155.1, 142.8, 133.0, 130.7, 126.4, 118.1, 113.3, 95.6, 21.3.

HRMS (ESI) calculated for $C_{13}H_9KNO_3S$ [M+K$^+$]: 297.9935; found: 297.9943.



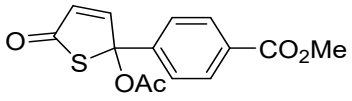
12: 2-(4-acetylphenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 62.7 mg (76% yield) of **12** as a white solid.

IR (neat, cm^{-1}): 2924 (w), 1754 (m), 1682 (s), 1603 (m), 1367 (m), 1266 (s), 1212 (s), 1066 (s), 1011 (m), 896 (w), 797 (w), 756 (w), 622 (m), 594 (w), 526 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.97 – 7.94 (m, 2H), 7.66 – 7.63 (m, 2H), 7.41 (d, *J* = 6.1 Hz, 1H), 6.24 (d, *J* = 6.1 Hz, 1H), 2.58 (s, 3H), 2.19 (s, 3H); **^{13}C NMR (126 MHz,**

Chloroform-*d*) δ 197.2, 196.4, 169.2, 155.6, 142.4, 137.7, 130.2, 129.2, 125.9, 96.0, 26.8, 21.3.

HRMS (ESI) calculated for $C_{14}H_{12}NaO_4S$ [M+Na$^+$]: 299.0349; found: 299.0348.

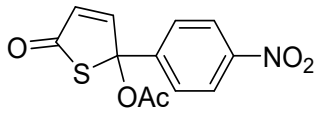


13: methyl 4-(2-acetoxy-5-oxo-2,5-dihydrothiophen-2-yl)benzoate

Followed **Method C** (current = 15 mA), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 63.2 mg (72% yield) of **13** as a white solid.

IR (neat, cm^{-1}): 3071 (w), 2953 (w), 2925 (w), 1756 (m), 1708 (s), 1694 (s), 1608 (w), 1575 (w), 1435 (m), 1406 (w), 1370 (w), 1278 (s), 1212 (s), 1111 (s), 916 (w), 896 (w), 797 (w), 770 (m), 735 (w), 620 (m), 568 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.06 – 8.01 (m, 2H), 7.64 – 7.60 (m, 2H), 7.40 (d, *J* = 6.1 Hz, 1H), 6.23 (d, *J* = 6.1 Hz, 1H), 3.91 (s, 3H), 2.19 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 196.5, 169.1, 166.3, 155.6, 142.3, 131.0, 130.4, 130.2, 125.6, 96.1, 52.4, 21.3.

HRMS (ESI) calculated for $C_{14}H_{13}O_5S$ [M+H$^+$]: 293.0478; found: 293.0480.

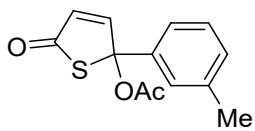


14: 2-(4-nitrophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 21.7 mg (26% yield) of **14** as a white solid.

IR (neat, cm^{-1}): 3079 (w), 2925 (w), 1754 (m), 1693 (s), 1606 (w), 1520 (s), 1491 (w), 1606 (w), 1520 (s), 1491 (w), 1347 (s), 1211 (s), 1169 (m), 1066 (s), 1010 (m), 971 (w), 850 (s), 796 (m), 735 (w), 618 (m), 532 (w), 454 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.25 – 8.22 (m, 2H), 7.76 – 7.72 (m, 2H), 7.41 (d, *J* = 6.1 Hz, 1H), 6.29 (d, *J* = 6.1 Hz, 1H), 2.22 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 195.7, 169.2, 155.0, 148.3, 144.7, 131.4, 126.8, 124.4, 95.5, 21.3.

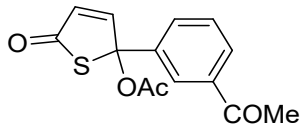
HRMS (ESI) calculated for $C_{12}H_9NNaO_5S$ [M+Na$^+$]: 302.0094; found: 302.0102



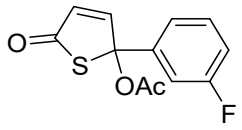
15: 5-oxo-2-(m-tolyl)-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 55.0 mg (74% yield) of **15** as a white solid.

IR (neat, cm^{-1}): 2924 (w), 1750 (m), 1690 (s), 1605 (w), 1485 (w), 1430 (w), 1369 (w), 1325 (w), 1215 (s), 1171 (w), 1159 (w), 1067 (m), 1015 (m), 970 (w), 895 (w), 830 (w), 817 (w), 784 (m), 718 (w), 621 (s), 499 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.40 (d, *J* = 6.1 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.16 (d, *J* = 6.1 Hz, 1H), 2.35 (s, 3H), 2.17 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 197.2, 169.1, 156.4, 138.9, 137.2, 130.1, 129.3, 129.0, 126.2, 122.5, 96.6, 21.6, 21.4.
HRMS (ESI) calculated for $C_{13}H_{12}NaO_3S$ [M+Na$^+$]: 271.0399; found: 271.0399.



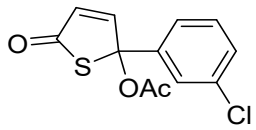
16: 2-(3-acetylphenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate
Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 50.2 mg (61% yield) of **16** as a white solid.
IR (neat, cm^{-1}): 2925 (w), 1754 (m), 1683 (s), 1598 (w), 1430 (m), 1359 (m), 1268 (m), 1214 (s), 1170 (m), 1067 (m), 1014 (m), 960 (w), 894 (w), 797 (w), 735 (w), 712 (w), 620 (m), 590 (w), 526 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.13 (t, *J* = 1.7 Hz, 1H), 7.93 – 7.90 (m, 1H), 7.78 (ddd, *J* = 7.9, 2.1, 1.0 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.43 (d, *J* = 6.1 Hz, 1H), 6.23 (d, *J* = 6.1 Hz, 1H), 2.60 (s, 3H), 2.19 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 197.3, 196.5, 169.2, 155.8, 138.5, 137.9, 130.2, 130.0, 129.6, 129.4, 125.1, 96.1, 26.8, 21.4.
HRMS (ESI) calculated for $C_{14}H_{12}NaO_4S$ [M+Na$^+$]: 299.0349; found: 299.0348.



17: 2-(3-fluorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate
Followed **Method C** (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 50.6 mg (67% yield) of **17** as a white solid.

IR (neat, cm^{-1}): 3075 (w), 2923 (w), 2852 (w), 1752 (m), 1692 (s), 1611 (w), 1600 (m), 1487 (w), 1273 (w), 1211 (s), 1170 (w), 1066 (m), 1014 (m), 940 (w), 894 (w), 844 (m), 828 (m), 785 (m), 719 (w), 691 (m), 508 (w); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.42 (d, *J* = 6.1 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.29 (dd, *J* = 9.8, 2.3 Hz, 1H), 7.10 – 7.04 (m, 1H), 6.24 (d, *J* = 6.2 Hz, 1H), 2.22 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 196.5, 169.1, 163.1 (d, *J* = 249.0 Hz), 155.8, 140.2 (d, *J* = 7.1 Hz), 130.9 (d, *J* = 8.3 Hz), 129.9, 121.3 (d, *J* = 3.2 Hz), 116.3 (d, *J* = 21.4 Hz), 113.1 (d, *J* = 24.3 Hz), 95.8 (d, *J* = 2.3 Hz), 21.4; **^{19}F NMR (471 MHz, Chloroform-d)** δ -110.9.

HRMS (ESI) calculated for $C_{12}H_9FNaO_3S$ [M+Na$^+$]: 275.0149; found: 275.0158.

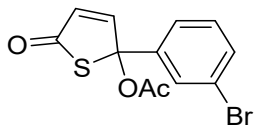


18: 2-(3-chlorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 53.7 mg (67% yield) of **18** as a white solid.

IR (neat, cm^{-1}): 3072 (w), 2927 (w), 1750 (m), 1689 (s), 1593 (w), 1574 (w), 1475 (w), 1213 (s), 1065 (s), 1012 (s), 895 (m), 786 (s), 766 (m), 688 (m), 619 (s), 507 (w), 499 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.54 - 7.53 (m, 1H), 7.46 – 7.44 (m, 1H), 7.38 (d, *J* = 6.1 Hz, 1H), 7.33 – 7.31 (m, 2H), 6.22 (d, *J* = 6.1 Hz, 1H), 2.19 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 196.5, 169.1, 155.8, 139.7, 135.2, 130.5, 130.0, 129.5, 125.9, 123.8, 95.7, 21.4.

HRMS (ESI) calculated for $C_{12}H_9ClNaO_3S$ [M+Na$^+$]: 290.9853; found: 290.9859.



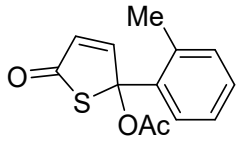
19: 2-(3-bromophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 41.1 mg (44% yield) of **19** as a white solid.

IR (neat, cm^{-1}): 3069 (w), 2926 (w), 1749 (w), 1693 (s), 1588 (w), 1566 (w), 1472 (w), 1214 (s), 1170 (w), 1065 (m), 1013 (m), 970 (w), 896 (w), 785 (m), 748 (w), 652 (w), 620 (s), 573 (w), 505 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.68 (t, *J* = 1.9 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.37 (d, *J* = 6.1 Hz, 1H), 7.25 – 7.22 (m, 1H), 6.21 (d, *J* = 6.1 Hz, 1H), 2.18 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 196.5, 169.1, 155.8,

139.9, 132.5, 130.7, 130.0, 128.7, 124.3, 123.3, 95.6, 21.4.

HRMS (ESI) calculated for $C_{12}H_9BrNaO_3S$ [M+Na$^+$]: 334.9348; found: 334.9356.

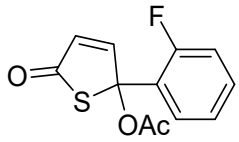


20: 5-oxo-2-(o-tolyl)-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 40.8 mg (55% yield) of **20** as a white solid.

IR (neat, cm^{-1}): 3069 (w), 2928 (w), 1750 (m), 1689 (s), 1602 (w), 1456 (w), 1367 (m), 1206 (s), 1166 (m), 1055 (w), 1009 (w), 957 (w), 795 (w), 757 (s), 724 (w), 622 (s), 607 (s), 459 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.98 (d, *J* = 6.3 Hz, 1H), 7.47 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.23 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.20 – 7.16 (m, 1H), 6.37 (d, *J* = 6.3 Hz, 1H), 2.52 (s, 3H), 2.12 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 195.9, 168.8, 154.2, 135.9, 135.5, 132.9, 131.7, 129.4, 126.2, 125.7, 98.0, 21.3, 21.2.

HRMS (ESI) calculated for $C_{13}H_{12}NaO_3S$ [M+ Na$^+$]: 271.0399; found: 271.0394.

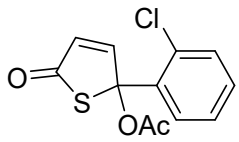


21: 2-(2-fluorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 33.2 mg (44% yield) of **21** as a white solid.

IR (neat, cm^{-1}): 3081 (w), 1749 (m), 1691 (s), 1610 (w), 1484 (m), 1369 (m), 1276 (w), 1212 (s), 1169 (w), 1067 (s), 1011 (m), 960 (m), 807 (w), 793 (w), 756 (s), 656 (w), 620 (s), 501 (w), 479 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.80 (dd, *J* = 6.2, 1.4 Hz, 1H), 7.74 (td, *J* = 8.0, 1.7 Hz, 1H), 7.38 - 7.34 (m, 1H), 7.14 (td, *J* = 7.7, 1.3 Hz, 1H), 7.09 (ddd, *J* = 12.0, 8.2, 1.2 Hz, 1H), 6.25 (d, *J* = 6.2 Hz, 1H), 2.11 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 196.0, 169.4, 159.8 (d, *J* = 250.8 Hz), 154.0 (d, *J* = 4.2 Hz), 131.7 (d, *J* = 8.6 Hz), 130.8, 129.5 (d, *J* = 2.3 Hz), 124.4 (d, *J* = 3.6 Hz), 124.3 (d, *J* = 9.7 Hz), 116.9 (d, *J* = 22.3 Hz), 94.8 (d, *J* = 3.0 Hz), 21.1; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -112.2 (m).

HRMS (ESI) calculated for $C_{12}H_9FNaO_3S$ [M+Na$^+$]: 275.0149; found: 275.0154.

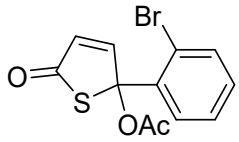


22: 2-(2-chlorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 42.5 mg (53% yield) of **22** as a white solid.

IR (neat, cm^{-1}): 3076 (w), 1748 (m), 1694 (s), 1568 (w), 1465 (w), 1435 (w), 1368 (m), 1213(s), 1169 (w), 1073 (m), 1010 (w), 965 (w), 797 (w), 758 (m), 718 (w), 621 (m), 606 (w), 464 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.08 (d, *J* = 6.3 Hz, 1H), 7.74 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.43 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.31 (td, *J* = 7.6, 1.8 Hz, 1H), 7.26 (td, *J* = 7.7, 1.5 Hz, 1H), 6.34 (d, *J* = 6.2 Hz, 1H), 2.13 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 195.9, 169.3, 153.2, 134.8, 132.1, 132.0, 131.7, 130.8, 128.7, 127.2, 96.6, 21.0.

HRMS (ESI) calculated for $C_{12}H_{10}ClO_3S$ [M+H$^+$]: 269.0034; found: 269.0038.

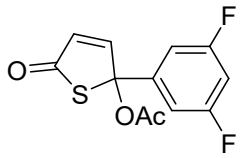


23: 2-(2-bromophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 53.3 mg (57% yield) of **23** as a white solid.

IR (neat, cm^{-1}): 3075 (w), 2925 (w), 1749 (m), 1697 (s), 1468 (w), 1432 (w), 1368 (w), 1213 (s), 1169 (w), 1073 (w), 1026 (w), 964 (w), 932 (w), 797 (w), 757 (m), 739 (w), 713 (w), 644 (w), 620 (w), 535 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.13 (d, *J* = 6.3 Hz, 1H), 7.67 (ddd, *J* = 16.4, 7.9, 1.5 Hz, 2H), 7.31 (td, *J* = 7.7, 1.4 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.36 (d, *J* = 6.3 Hz, 1H), 2.14 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 196.0, 169.3, 153.3, 136.6, 135.7, 132.1, 130.9, 128.7, 127.7, 121.0, 97.1, 21.2.

HRMS (ESI) calculated for $C_{12}H_9BrNaO_3S$ [M+Na$^+$]: 334.9348; found: 334.9344.

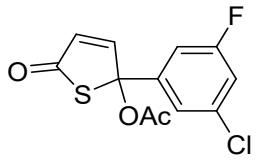


24: 2-(3,5-difluorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 55.0 mg (68% yield) of **24** as a white solid.

IR (neat, cm^{-1}): 3088 (w), 2925 (w), 1751 (m), 1693 (s), 1622 (m), 1579 (m), 1437 (m), 1370 (m), 1314 (m), 1208 (s), 1121 (s), 1071 (s), 896 (w), 858 (m), 811 (s), 789 (w), 526 (w), 511 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.36 (d, *J* = 6.0 Hz, 1H), 7.12 – 7.07 (m, 2H), 6.81 – 6.71 (m, 1H), 6.24 (d, *J* = 6.1 Hz, 1H), 2.20 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 196.0, 169.1, 163.4 (d, *J* = 250.6 Hz), 163.3 (d, *J* = 250.4 Hz), 155.2, 141.9 (t, *J* = 9.2 Hz), 130.3, 109.06 (d, *J* = 28.2 Hz), 109.06 (d, *J* = 13.7 Hz), 104.8 (t, *J* = 25.2 Hz), 95.2, 21.3; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -107.1 (m).

HRMS (ESI) calculated for $C_{12}H_8F_2NaO_3S$ [M+Na$^+$]: 293.0054; found: 293.0057.

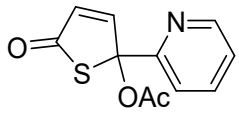


25: 2-(3-chloro-5-fluorophenyl)-5-oxo-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 48.9 mg (57% yield) of **25** as a white solid.

IR (neat, cm^{-1}): 3084 (w), 1751 (m), 1695 (s), 1605 (m), 1588 (m), 1434 (m), 1369 (m), 1263 (m), 1211 (s), 1171 (w), 1071 (m), 1020 (m), 956 (w), 888 (m), 860 (m), 800 (m), 769 (w), 703 (w), 622 (m), 526 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.38 – 7.32 (m, 2H), 7.18 (dq, *J* = 9.3, 1.5 Hz, 1H), 7.08 (dt, *J* = 8.1, 2.0 Hz, 1H), 6.24 (dd, *J* = 6.1, 1.0 Hz, 1H), 2.20 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 195.9, 169.1, 162.9 (d, *J* = 252.0 Hz), 155.2, 141.7 (d, *J* = 8.2 Hz), 136.1 (d, *J* = 10.6 Hz), 130.4, 121.8 (d, *J* = 3.3 Hz), 117.2 (d, *J* = 24.4 Hz), 111.7 (d, *J* = 23.7 Hz), 95.1 (d, *J* = 2.0 Hz), 21.3; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -108.5 (m).

HRMS (ESI) calculated for $C_{12}H_8ClFNaO_3S$ [M+Na$^+$]: 308.9759; found: 308.9766.

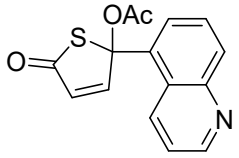


26: 5-oxo-2-(pyridin-2-yl)-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 2:1) to give 49.3 mg (70% yield) of **26** as a white solid.

IR (neat, cm^{-1}): 3070 (w), 2926 (w), 1746 (m), 1691 (s), 1586 (m), 1464 (w), 1432 (m), 1370 (m), 1221 (s), 1102 (w), 1070 (m), 1017 (m), 801 (w), 781 (m), 747 (m), 623 (m), 528 (m); **^{1}H NMR (500 MHz, Chloroform-d)** δ 8.60 – 8.58 (m, 1H), 7.76 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.66 (d, *J* = 6.1 Hz, 1H), 7.28 – 7.24 (m, 1H), 6.29 (d, *J* = 6.1 Hz, 1H), 2.19 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 196.9, 169.7, 155.8, 155.7, 149.8, 137.5, 130.9, 123.8, 121.7, 96.2, 21.2.

HRMS (ESI) calculated for $C_{11}H_9NNaO_3S$ [M+Na$^+$]: 258.0195; found: 258.0192.

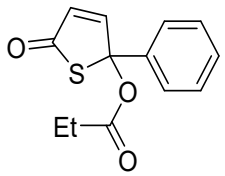


27: 5-oxo-2-(quinolin-5-yl)-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 2:1) to give 33.3 mg (39% yield) of **27** as a white solid.

IR (neat, cm^{-1}): 3077 (w), 2926 (w), 1751 (m), 1697 (s), 1595 (w), 1500 (m), 1368 (m), 1319 (w), 1205 (s), 1067 (w), 1017 (w), 954 (m), 828 (w), 803 (s), 735 (w), 621 (m), 543 (w), 495 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.98 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.73 (ddd, *J* = 8.8, 1.6, 0.8 Hz, 1H), 8.21 (d, *J* = 6.3 Hz, 1H), 8.15 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.82 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.67 - 7.64 (m, 1H), 7.51 (dd, *J* = 8.8, 4.1 Hz, 1H), 6.45 (d, *J* = 6.3 Hz, 1H), 2.05 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 195.0, 168.9, 153.5, 150.5, 149.4, 134.1, 132.6, 132.4, 132.2, 128.5, 125.4, 124.5, 121.6, 97.7, 21.3.

HRMS (ESI) calculated for $C_{15}H_{12}NO_3S$ [M+H$^+$]: 286.0532; found: 286.0533.

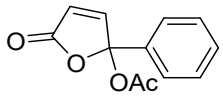


28: 5-oxo-3-phenyl-2,5-dihydrothiophen-2-yl propionate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 39.4 mg (53% yield) of **28** as a white solid.

IR (neat, cm^{-1}): 3066 (w), 2924 (w), 1748 (m), 1492 (w), 1447 (w), 1354 (w), 1152 (m), 1064 (m), 992 (w), 799 (w), 761 (m), 697 (m), 556 (w); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 6.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 3H), 6.19 (d, *J* = 6.4 Hz, 1H), 2.47 (q, *J* = 7.7 Hz, 2H), 1.16 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 197.3, 172.6, 156.4, 137.5, 129.5, 129.3, 129.2, 125.6, 96.5, 28.0, 8.8.

HRMS (ESI) calculated for $C_{13}H_{12}NaO_3S$ [M+Na^+]:271.0399; found: 271.0397.

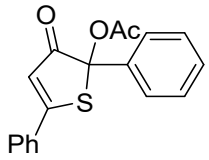


29: 5-oxo-2-phenyl-2,5-dihydrofuran-2-yl acetate

Following **Method C** (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 33.0 mg (50% yield) of **29** as a yellow oil.

IR (neat, cm^{-1}): 2985 (w), 1733 (s), 1373 (m), 1266 (m), 1240 (s), 1097 (w), 1045 (m), 911 (w), 847 (w), 734 (s), 704 (m), 608 (w), 461 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.74 (d, *J* = 5.6 Hz, 1H), 7.51 – 7.49 (m, 2H), 7.43 – 7.40 (m, 3H), 6.25 (d, *J* = 5.6 Hz, 1H), 2.11 (s, 3H)； **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 169.7, 168.3, 153.4, 135.2, 130.1, 129.0, 125.5, 122.2, 106.5, 21.7.

HRMS (ESI) calculated for $C_{12}H_1O_4$ [M+H^+]: 219.0652; found: 219.0650.



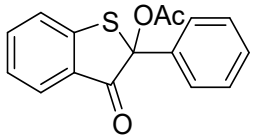
30: 3-oxo-2,5-diphenyl-2,3-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 39.8 mg (43% yield) of **30** as a white solid.

IR (neat, cm^{-1}): 3062 (w), 1761 (m), 1692 (s), 1581 (w), 1552 (m), 1490 (m), 1249 (w), 1223 (m), 1195 (w), 1044 (m), 1000 (w), 926 (w), 767 (m), 755 (m), 703 (m), 489 (w); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 6.9 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 3H),

6.49 (s, 1H), 2.26 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.1, 173.8, 168.9, 135.9, 132.8, 132.3, 129.3, 128.9, 126.9, 126.8, 125.8, 113.7, 91.8, 21.1.

HRMS (ESI) calculated for $C_{18}H_{14}NaO_3S$ [M+ Na^+]: 333.0556; found: 333.0545.

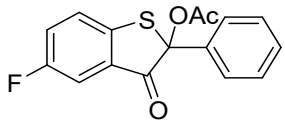


31: 3-oxo-2-phenyl-2,3-dihydrobenzo[b]thiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 52.8 mg (62% yield) of **31** as a white solid.

IR (neat, cm^{-1}): 3063 (m), 2925 (w), 1758 (m), 1589 (m), 1574 (w), 1447 (m), 1368 (w), 1308 (w), 1280 (m), 1222 (s), 1196 (m), 1057 (m), 990 (m), 908 (m), 753 (m), 738 (m), 695 (m), 616 (w), 478 (m); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.77 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.60 (m, 1H), 7.40 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.35 (m, 3H), 7.27 – 7.23 (m, 1H), 2.24 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 195.9, 169.0, 149.5, 136.5, 135.9, 129.4, 128.9, 127.9, 127.7, 126.0, 125.7, 123.8, 92.3, 21.0.

HRMS (ESI) calculated for $C_{16}H_{12}NaO_3S$ [M+Na^+]: 307.0399; found: 307.0400.

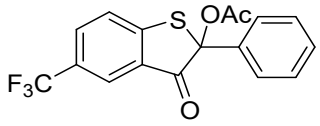


32: 5-fluoro-3-oxo-2-phenyl-2,3-dihydrobenzo[b]thiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 60.7 mg (67% yield) of **32** as a white solid.

IR (neat, cm^{-1}): 3065 (w), 1756(m), 1719 (s), 1601 (w), 1464 (s), 1447 (w), 1427 (w), 1370 (w), 1304 (w), 1264 (s), 1221 (s), 1196 (m), 1053 (m), 1002 (m), 888 (w), 867 (w), 821 (s), 795 (w), 734 (s), 694 (s), 502 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.66 – 7.63 (m, 2H), 7.47 – 7.43 (m, 1H), 7.38 – 7.33 (m, 5H), 2.24 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 195.2 (d, *J* = 3.2 Hz) 169.0, 161.1 (d, *J* = 248.2 Hz), 144.3 (d, *J* = 2.6 Hz), 135.5, 129.6, 129.2 (d, *J* = 7.2 Hz), 129.0, 126.0, 124.6 (d, *J* = 7.9 Hz), 124.2 (d, *J* = 24.0 Hz), 113.8 (d, *J* = 23.7 Hz), 93.2, 20.9; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -116.2.

HRMS (ESI) calculated for $C_{16}H_{11}FKO_3S$ [M+ K^+]: 341.0045; found: 341.0040.

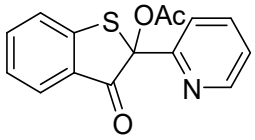


33: 3-oxo-2-phenyl-5-(trifluoromethyl)-2,3-dihydrobenzo[b]thiophen-2-yl acetate

Followed **Method C** (current = 15 mA), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 57.8 mg (55% yield) of **33** as a white solid.

IR (neat, cm^{-1}): 3062 (w), 2926 (w), 1760 (m), 1722 (s), 1613 (s), 1492 (w), 1329 (s), 1255 (s), 1195 (s), 1092 (s), 1080 (w), 1049 (w), 737 (m), 720 (w), 707 (m), 541 (w), 523 (m), 450 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.01 (dt, *J* = 1.7, 0.8 Hz, 1H), 7.82 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.40 – 7.36 (m, 3H), 2.25 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 194.8, 169.1, 153.4, 135.1, 132.7 (q, *J* = 3.7 Hz), 129.8, 129.1, 128.7 (q, *J* = 33.58 Hz), 128.2, 126.0, 124.8 (q, *J* = 4.3 Hz), 123.7 (q, *J* = 271.0 Hz), 124.3, 92.7, 20.9; **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -62.5.

HRMS (ESI) calculated for $C_{17}H_{11}F_3NaO_3S$ [M+ Na^+]: 375.0273; found: 375.0264.

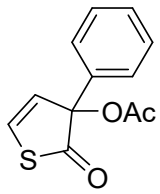


34: 3-oxo-2-(pyridin-2-yl)-2,3-dihydrobenzo[b]thiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 37.6 mg (44% yield) of **34** as a white solid.

IR (neat, cm^{-1}):2924 (w), 2854 (w), 1764 (m), 1587 (m), 1370 (w), 1282 (m), 1210 (s), 1108 (w), 1064 (w), 1006 (w), 767 (w), 740 (w), 699 (w), 531 (w); **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.52 – 8.51 (m, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.73 (td, *J* = 7.7, 1.8 Hz, 1H), 7.68 (dt, *J* = 8.1, 1.2 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.21 (m, 2H), 2.26 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 197.1, 168.0, 156.5, 149.93, 149.88, 137.2, 136.3, 128.4, 127.4, 125.6, 123.83, 123.81, 120.8, 91.5, 21.0.

HRMS (ESI) calculated for $C_{15}H_{12}NO_3S$ [M+H^+]: 286.0532; found: 286.0534.

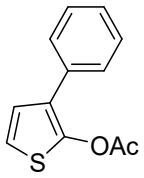


36 :2-oxo-3-phenyl-2,3-dihydrothiophen-3-yl acetate

Following **Method C** (reaction time = 4 h), the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 20.9 mg (30% yield) of **36** as a white solid and 9.0 mg (14% yield) of **37** as a white solid.

IR (neat, cm^{-1}): 3060 (w), 2933 (w), 1749 (m), 1702 (m), 1492 (w), 1216 (s), 1054 (w), 908 (s), 836 (w), 728 (s), 652 (w), 487 (w); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 – 7.59 (m, 2H), 7.44 – 7.41 (m, 4H), 6.84 (d, *J* = 3.1 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.3, 170.4, 145.6, 144.9, 130.0, 129.9, 128.8, 128.3, 76.5, 20.8.

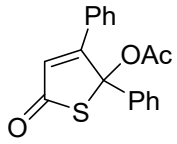
HRMS (ESI) calculated for $C_{12}H_{11}O_3S$ [M+ H^+]: 235.0423; found: 235.0419.



37: 3-phenylthiophen-2-yl acetate

IR (neat, cm^{-1}): 3055 (w), 2928 (w), 1760 (w), 1265 (w), 1204 (w), 907 (m), 728 (s), 652 (m), 508 (w); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.52 (m, 2H), 7.44 – 7.39 (m, 2H), 7.33 – 7.29 (m, 1H), 7.04 (d, *J* = 5.9 Hz, 1H), 6.97 (d, *J* = 5.9 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.9, 146.1, 134.2, 128.7, 128.1, 127.6, 127.3, 125.2, 117.8, 21.0.

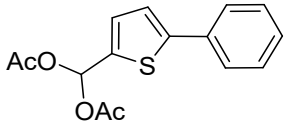
HRMS (ESI) calculated for $C_{12}H_{11}O_2S$ [M+ H^+]: 219.0474; found: 219.0487.



39: 5-oxo-2,3-diphenyl-2,5-dihydrothiophen-2-yl acetate

Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 52.7 mg (56% yield) of **39** as a white solid.

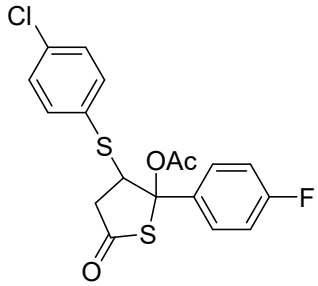
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 6.9, 1.5 Hz, 2H), 7.36 – 7.24 (m, 8H), 6.58 (s, 1H), 2.19 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 194.8, 168.2, 167.1, 137.9, 131.5, 130.5, 129.0, 128.9, 128.7, 128.6, 128.3, 125.2, 96.7, 21.7.
HRMS (ESI) calculated for $C_{18}H_{14}NaO_3S$ [M+Na$^+$]: 333.0556; found:333.0560.



41: (5-phenylthiophen-2-yl)methylene diacetate

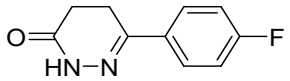
Followed **Method C**, the desired product was purified using silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give 29.9 mg (34% yield) of **41** as a white solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.61 – 7.57 (m, 2H), 7.41 – 7.37 (m, 2H), 7.33 – 7.29 (m, 1H), 7.22 – 7.17 (m, 2H), 2.15 (s, 6H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 168.7, 146.4, 137.1, 133.9, 129.1, 128.4, 128.2, 126.1, 122.7, 86.7, 21.0.
HRMS (ESI) calculated for $C_{15}H_{14}NaO_4S$ [M+Na$^+$]: 313.0505; found:313.0495.



42: 3-((4-chlorophenyl)thio)-2-(4-fluorophenyl)-5-oxotetrahydrothiophen-2-yl acetate

Following **Method E**, the desired product was purified using silica gel chromatography (ethyl acetate/hexanes = 10:1) to give 21.1 mg (27% yield) of **42** as a white solid.
IR (neat, cm^{-1}): 2924 (w), 2853 (w), 1757 (s), 1712 (s), 1601 (w), 1508 (s), 1476 (s), 1213 (s), 1162 (m), 1093 (m), 1012 (s), 907 (m), 833 (m), 772 (w), 738 (w), 503 (w);
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 – 7.51 (m, 2H), 7.16 – 7.12 (m, 2H), 7.10 – 7.05 (m, 2H), 6.93 – 6.90 (m, 2H), 3.65 (dd, *J* = 12.3, 6.7 Hz, 1H), 3.23 (dd, *J* = 16.9, 12.3 Hz, 1H), 3.08 (dd, *J* = 16.8, 6.7 Hz, 1H), 2.24 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 200.7, 168.5, 162.9 (d, *J* = 246.6 Hz), 134.7, 134.1, 133.4 (d, *J* = 3.5 Hz), 132.1, 129.4, 128.2 (d, *J* = 8.4 Hz), 115.6 (d, *J* = 21.9 Hz), 99.0, 61.4, 47.7, 21.7;
^{19}F NMR (471 MHz, Chloroform-d) δ -112.6 (m).
HRMS (ESI) calculated for $C_{18}H_{14}ClFO_3S_2Na$ [M+Na$^+$]: 418.9949; found: 418.9946

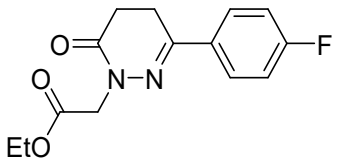


43: 6-(4-fluorophenyl)-4,5-dihydropyridazin-3(2H)-one[5]

Following **Method F**, the desired product was purified using silica gel chromatography (ethyl acetate/hexanes = 1:1) to give 14.2 mg (37% yield) of **43** as a white solid.

IR (neat, cm^{-1}): 3233 (w), 3103 (w), 2922 (w), 2851 (w), 1684 (s), 1617 (w), 1599 (w), 1512 (m), 1347 (m), 1217 (w), 1158 (w), 840 (m), 817 (w), 770 (w), 520 (w); **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.91 (br s, 1H), 7.74 – 7.69 (m, 2H), 7.12 – 7.06 (m, 2H), 2.97 (dd, *J* = 8.9, 7.6 Hz, 2H), 2.61 (dd, *J* = 8.9, 7.5 Hz, 2H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 167.3, 163.9 (d, *J* = 252.0 Hz), 149.7, 131.8 (d, *J* = 3.46 Hz), 127.9 (d, *J* = 8.45 Hz), 115.8 (d, *J* = 22.1 Hz), 26.4, 22.7; **^{19}F NMR (471 MHz, Chloroform-d)** δ -110.6 (m).

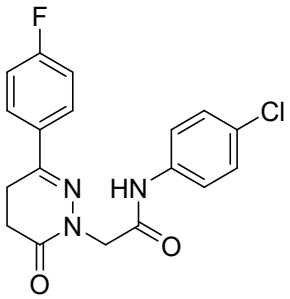
HRMS (ESI) calculated for $C_{10}H_{10}FN_2O$ [M+ H^+]: 193.0772; found: 193.0771.



44: ethyl 2-(3-(4-fluorophenyl)-6-oxo-5,6-dihydropyridazin-1(4H)-yl)acetate[5]

Following **Method G**, the desired product was purified using silica gel chromatography (cyclohexane/ethyl acetate 1:1) to give 22.7 mg (56% yield) of **44** as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.67 (m, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 4.58 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.00 (t, *J* = 8.1 Hz, 2H), 2.66 (t, *J* = 8.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H).



45: N-(4-chlorophenyl)-2-(3-(4-fluorophenyl)-6-oxo-5,6-dihydropyridazin-1(4H)-yl)acetamide[6]

Following **Method F**, the desired product was purified using silica gel chromatography (DCM/petroleum = 1:1) to give 22.6 mg (79% yield) of **45** as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (br s, 1H), 7.76 – 7.70 (m, 2H), 7.46 – 7.41 (m, 2H), 7.24 – 7.19 (m, 2H), 7.12 – 7.05 (m, 2H), 4.64 (s, 2H), 3.01 (dd, *J* = 9.0, 7.4 Hz, 2H), 2.69 (dd, *J* = 9.0, 7.4 Hz, 2H).

4. Cyclic Voltammetry Studies

General information: Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter), a platinum wire auxiliary electrode and SCE reference electrode. Current was reported in A, while all potentials were reported in V against the Fc^{+}/Fc redox couple. The scan rate was 0.1 V/s.

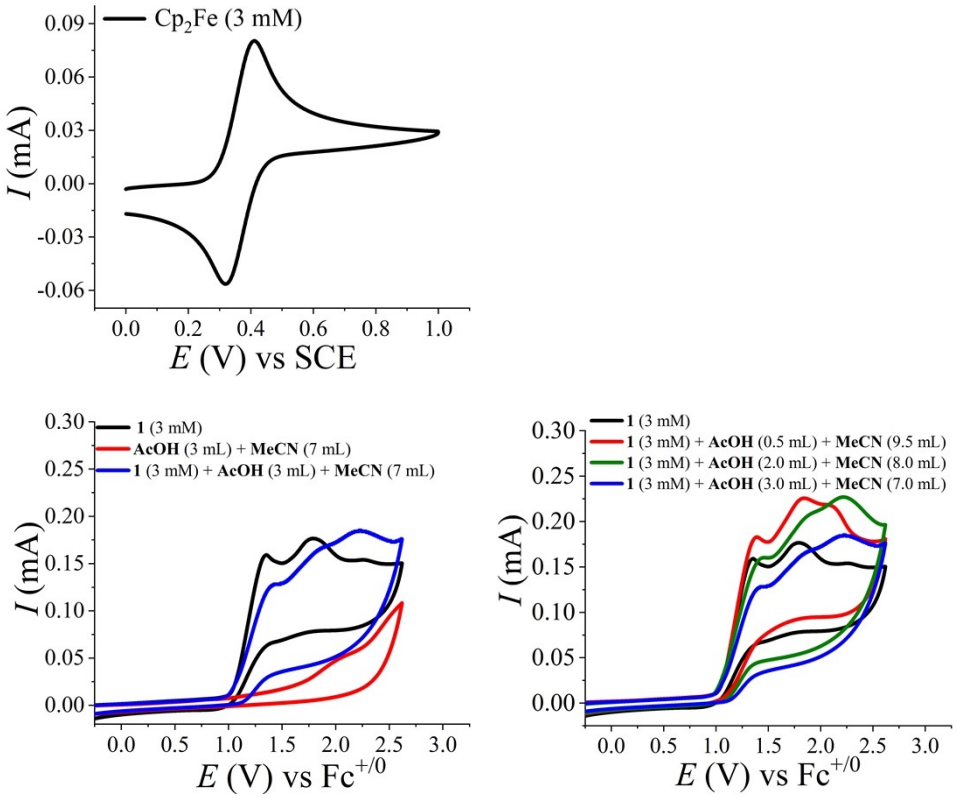


Figure S2-1. Cyclic voltammograms.

Left: Cyclic voltammograms of **1** (3 mM), AcOH (3 mL), **1** (3 mM) and AcOH (3 mL) in acetonitrile (MeCN) containing 10 mM $^{n}Bu_4NPF_6$ as the electrolyte.

Right: Cyclic voltammograms of **1** (3 mM) and **1** (3 mM) with varying concentrations of AcOH in acetonitrile (MeCN) containing 10 mM $^{n}Bu_4NPF_6$ as the electrolyte.

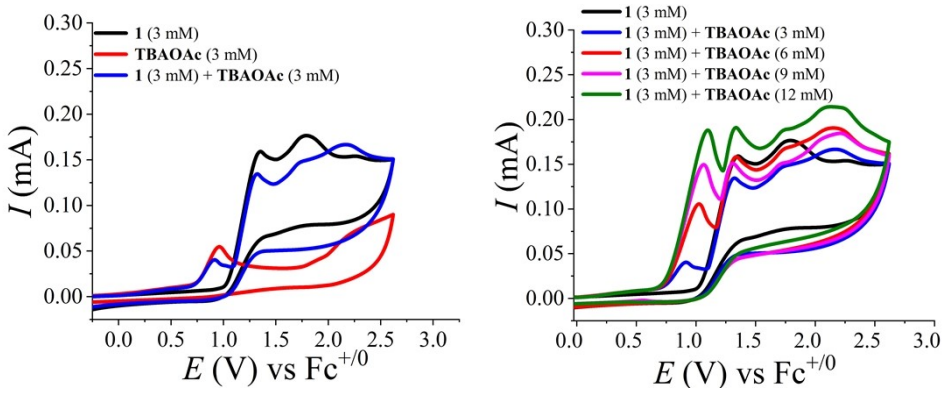


Figure S2-2. Cyclic voltammograms.

Left: Cyclic voltammograms of **1** (3 mM), $^{n}Bu_4NOAc$ (3 mM), an equivalent mixture of **1** and $^{n}Bu_4NOAc$ in acetonitrile (MeCN) containing 10 mM $^{n}Bu_4NPF_6$ as the electrolyte.

Right: Cyclic voltammograms of **1** (3 mM) and **1** (3 mM) with varying concentrations of $^{n}Bu_4NOAc$ in acetonitrile (MeCN) containing 10 mM $^{n}Bu_4NPF_6$ as the electrolyte.

5. References

1. N. Kuhl, M. N. Hopkinson and F. Glorius, Selective rhodium(III)-catalyzed cross-dehydrogenative coupling of furan and thiophene derivatives, *Angew. Chem. Int. Ed.* , 2012, **51**, 8230-8234.
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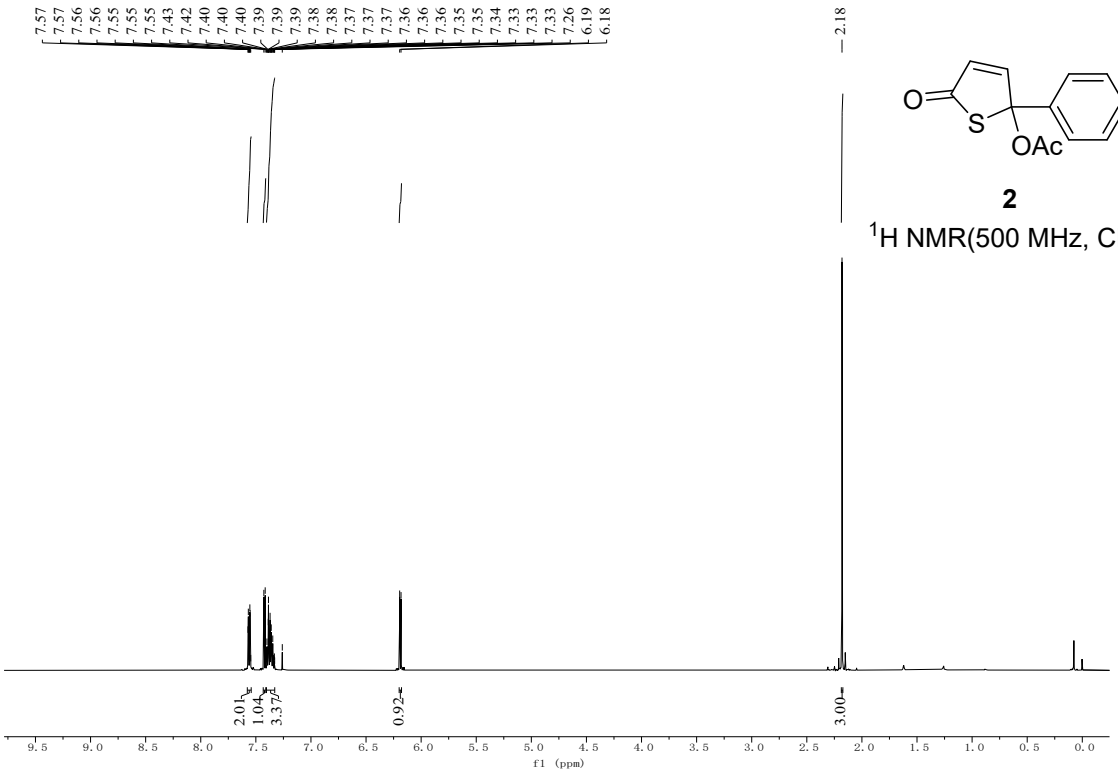
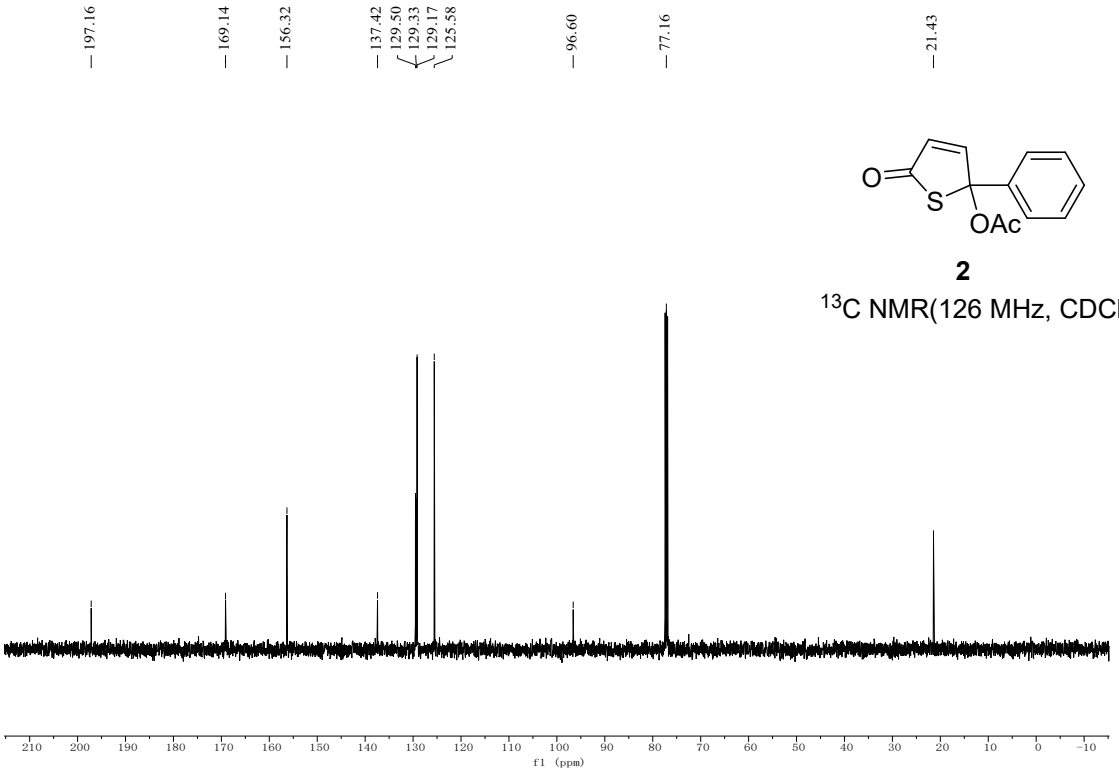
6. Spectral Data (^{1}H, ^{13}C, ^{19}F)



2

^{1}H NMR(500 MHz, $CDCl_3$)



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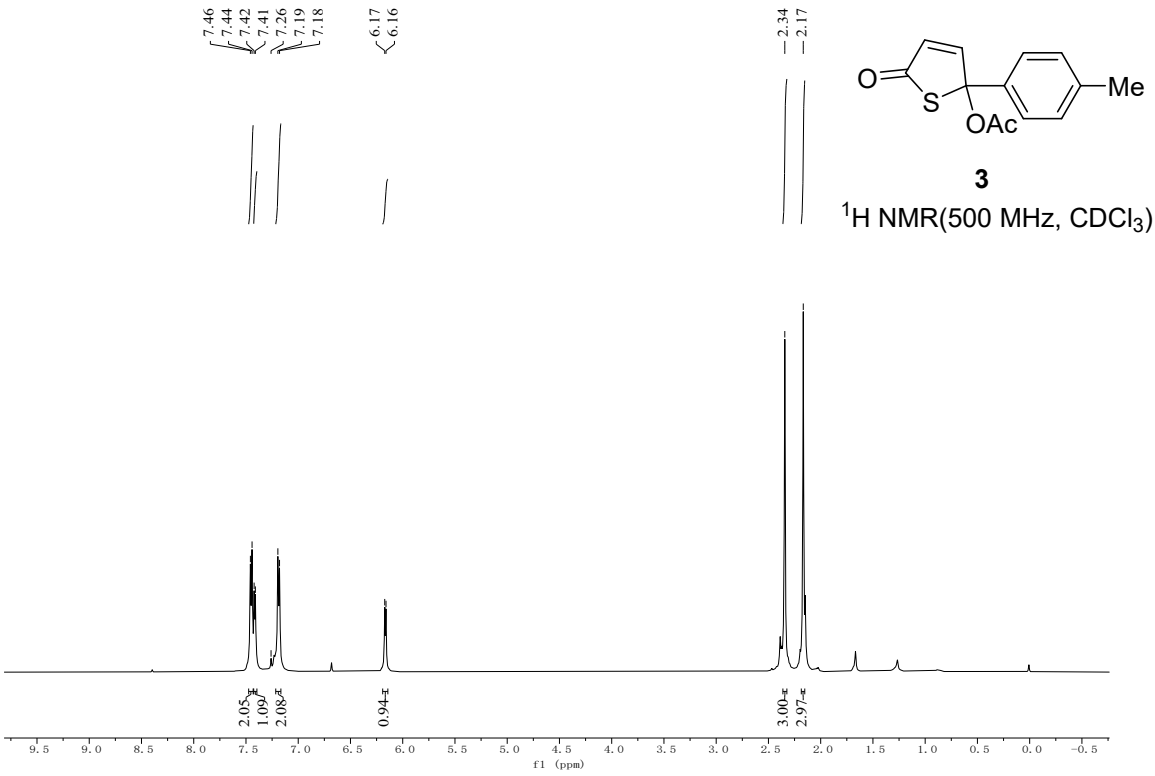
^{13}C NMR(126 MHz, $CDCl_3$)



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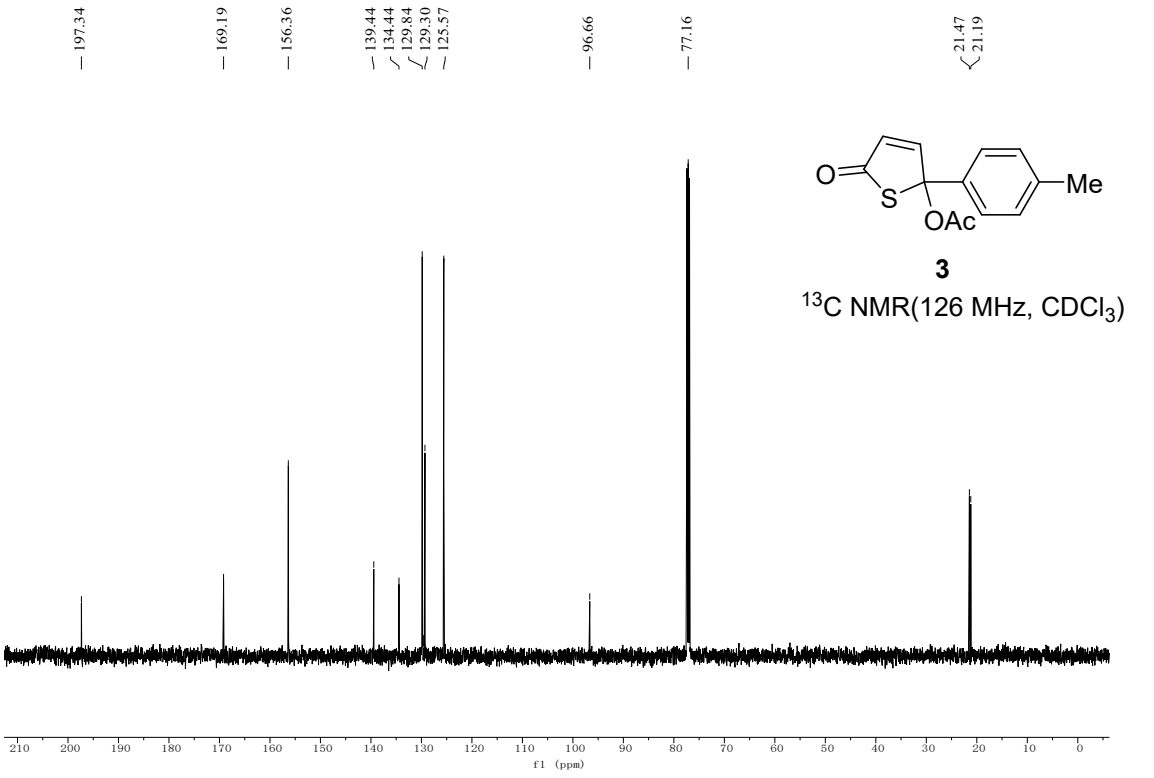
^{1}H NMR(500 MHz, $CDCl_3$)



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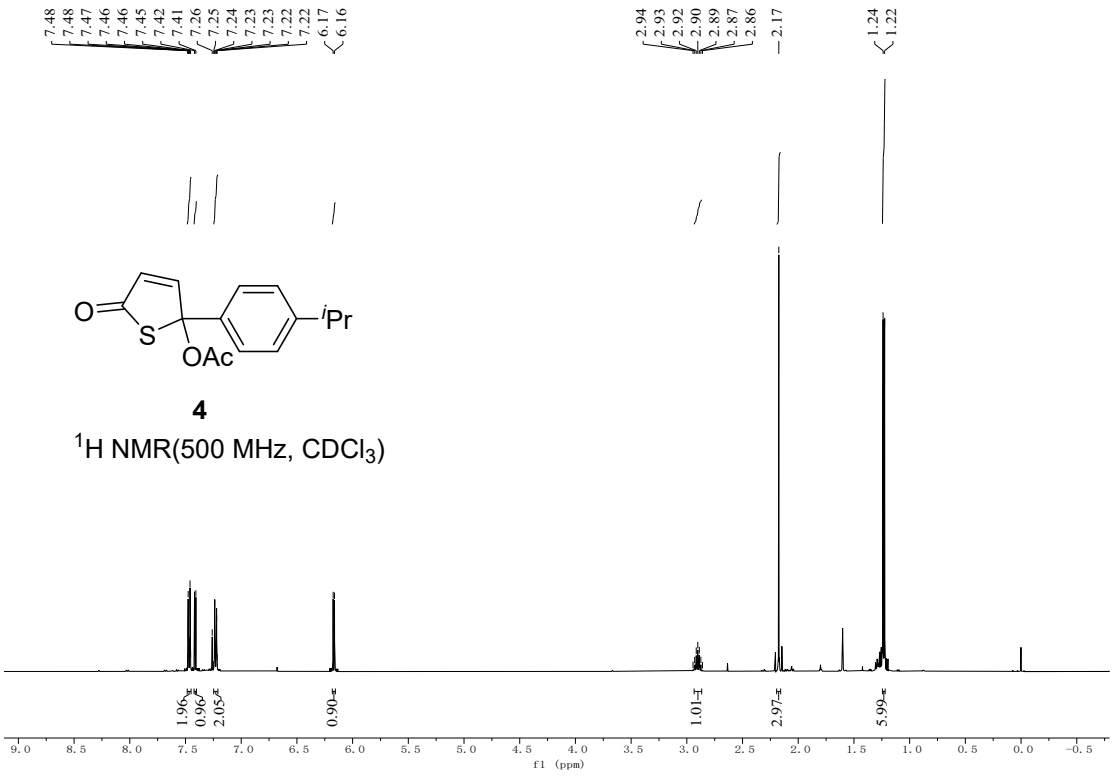
^{13}C NMR(126 MHz, $CDCl_3$)



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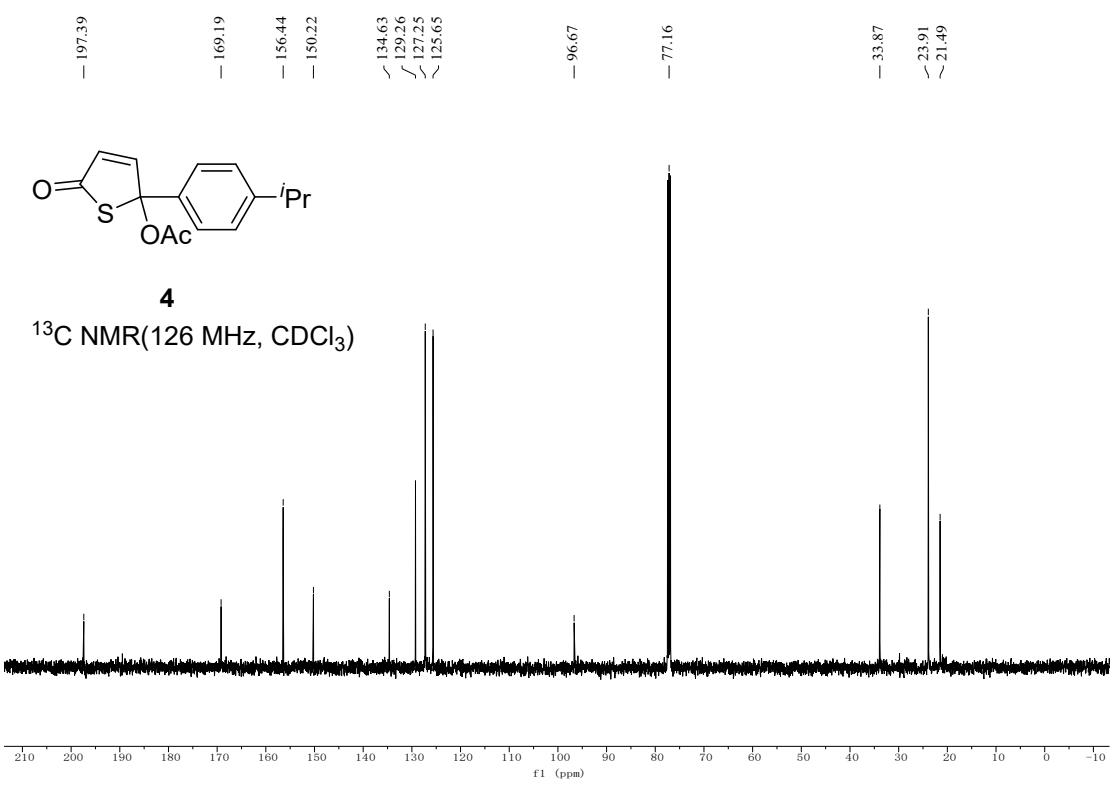

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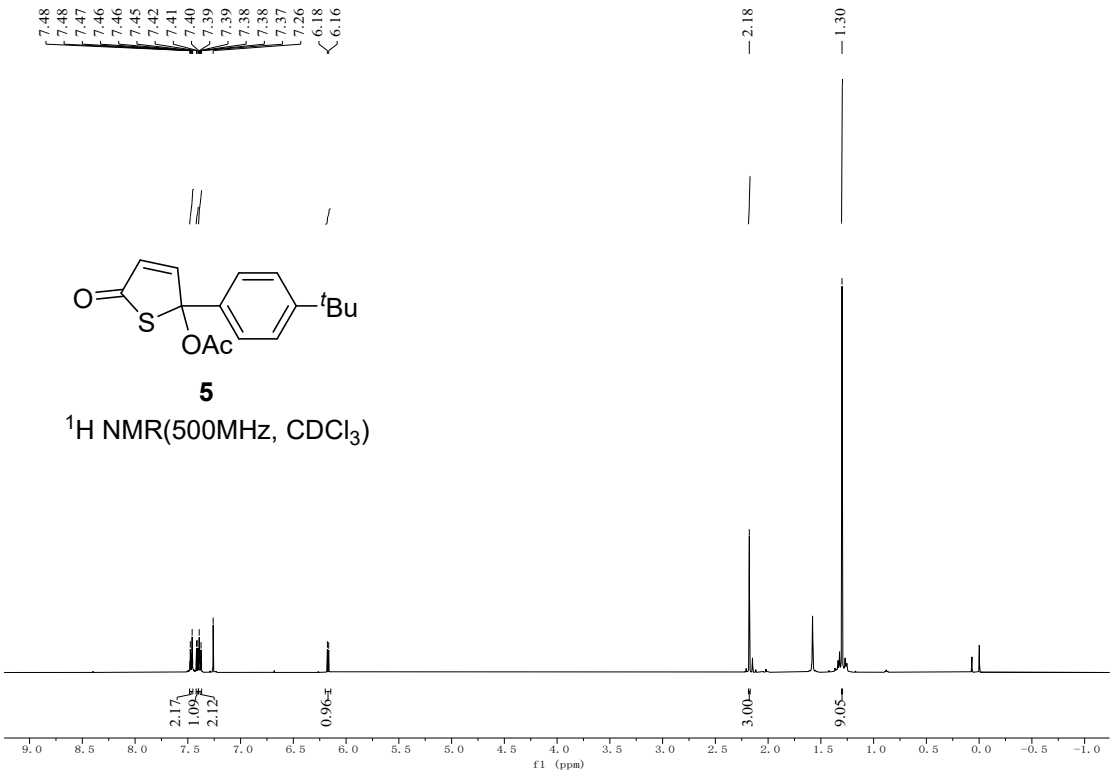

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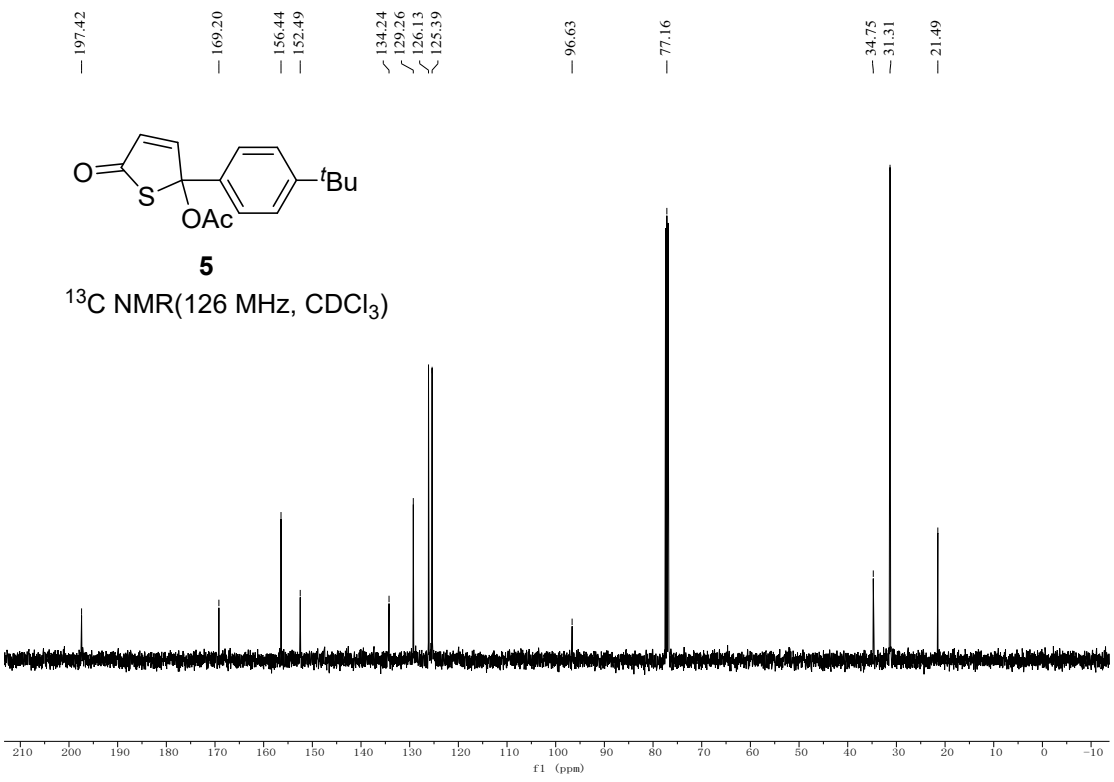

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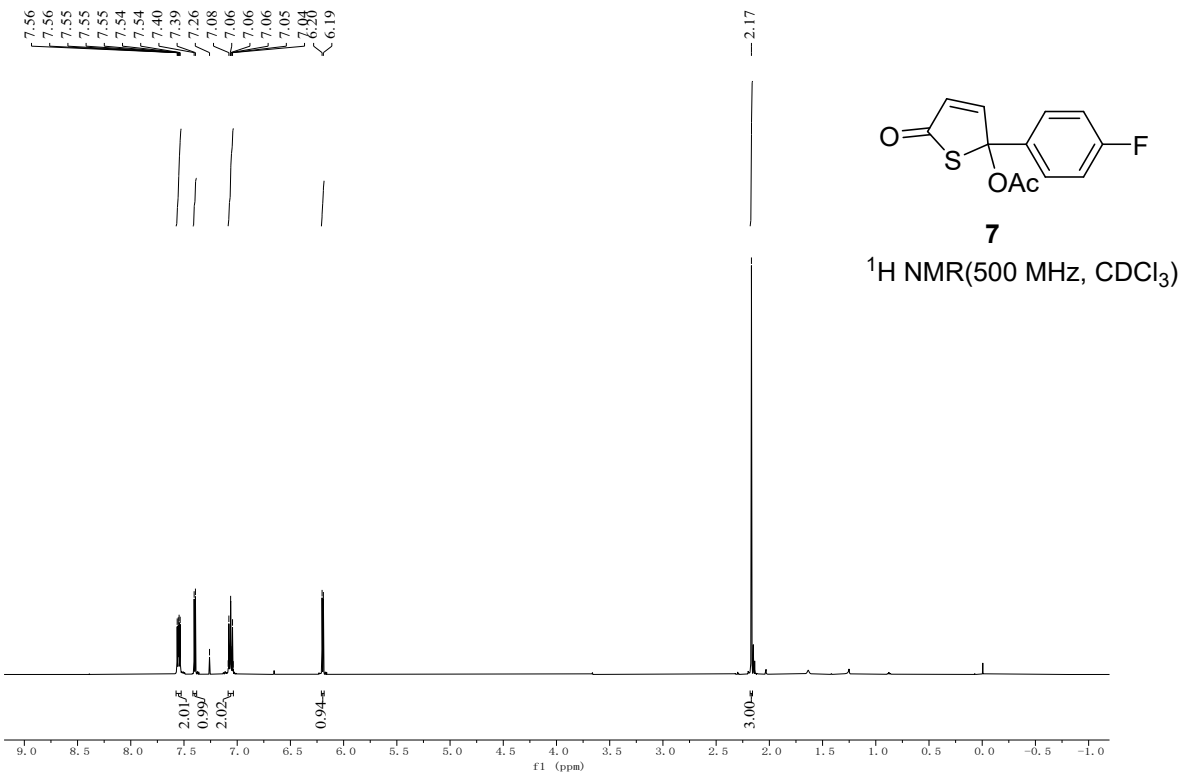

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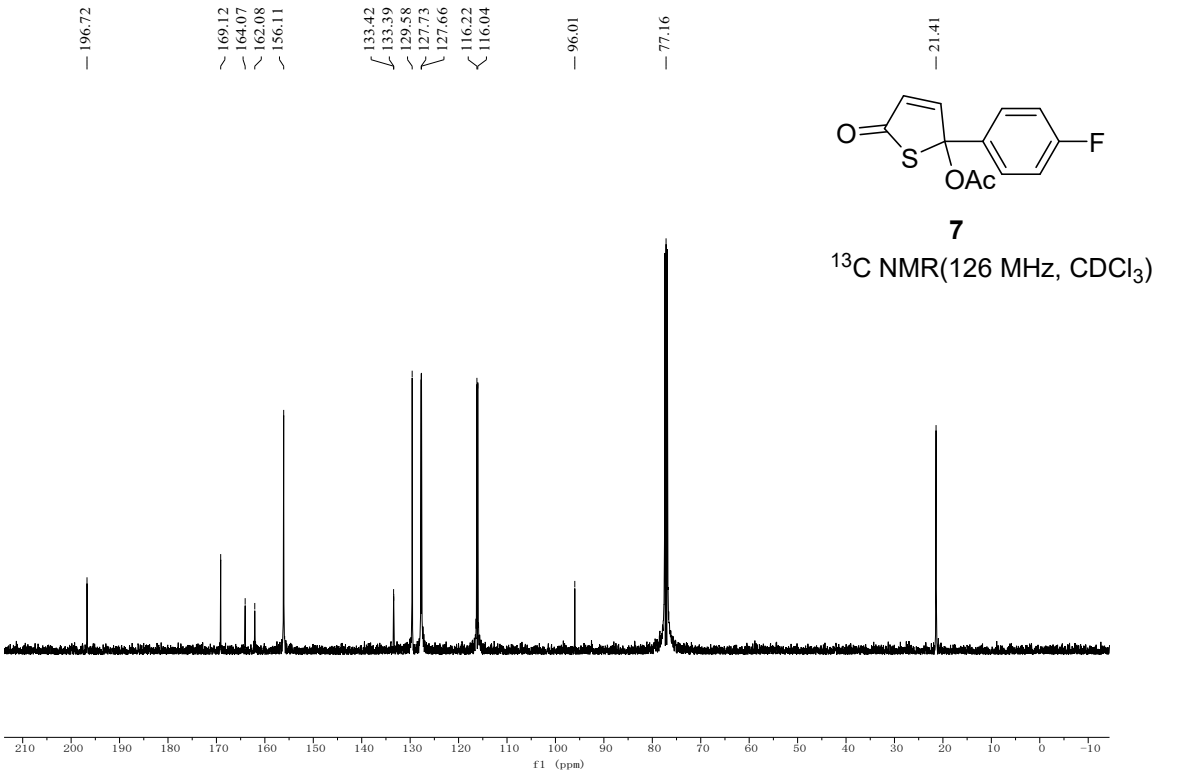
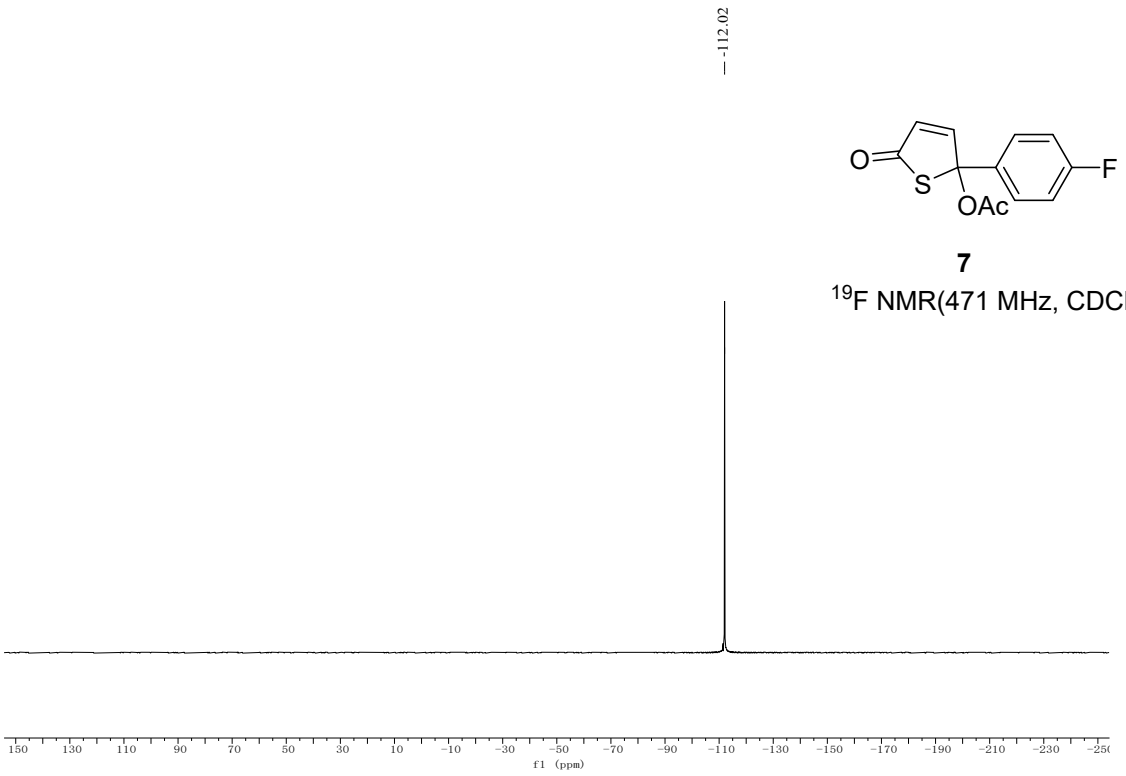


7

^{13}C NMR(126 MHz, $CDCl_3$)



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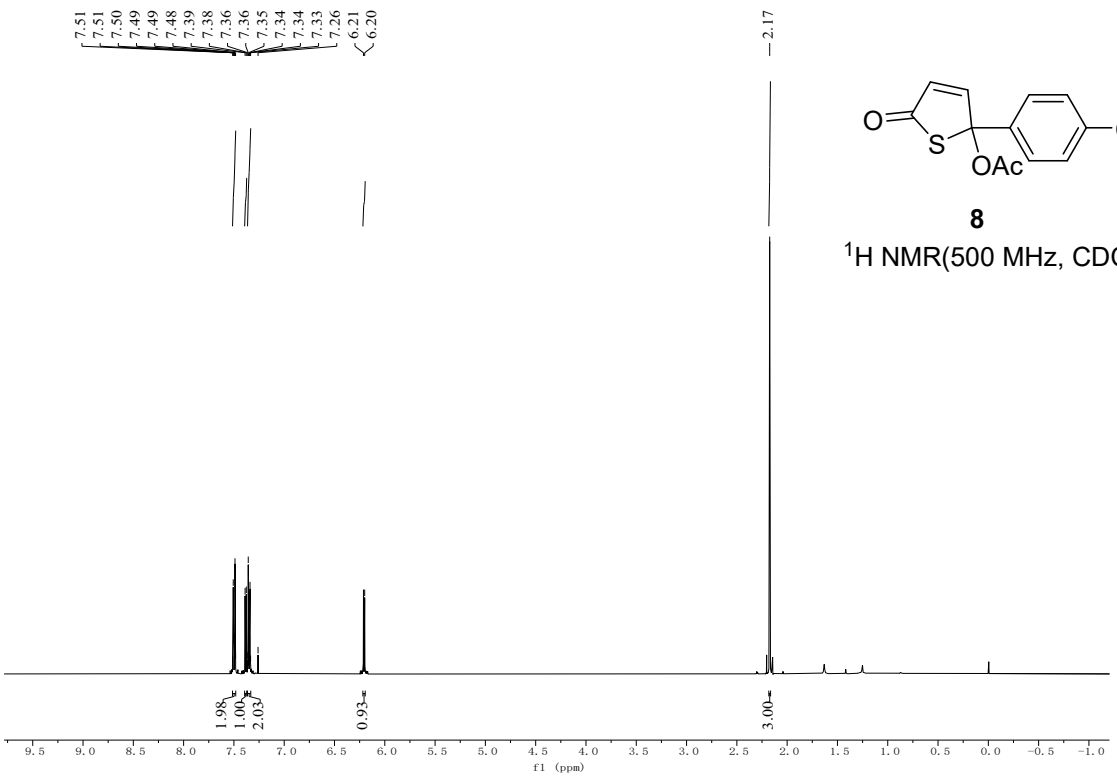
^{19}F NMR(471 MHz, $CDCl_3$)



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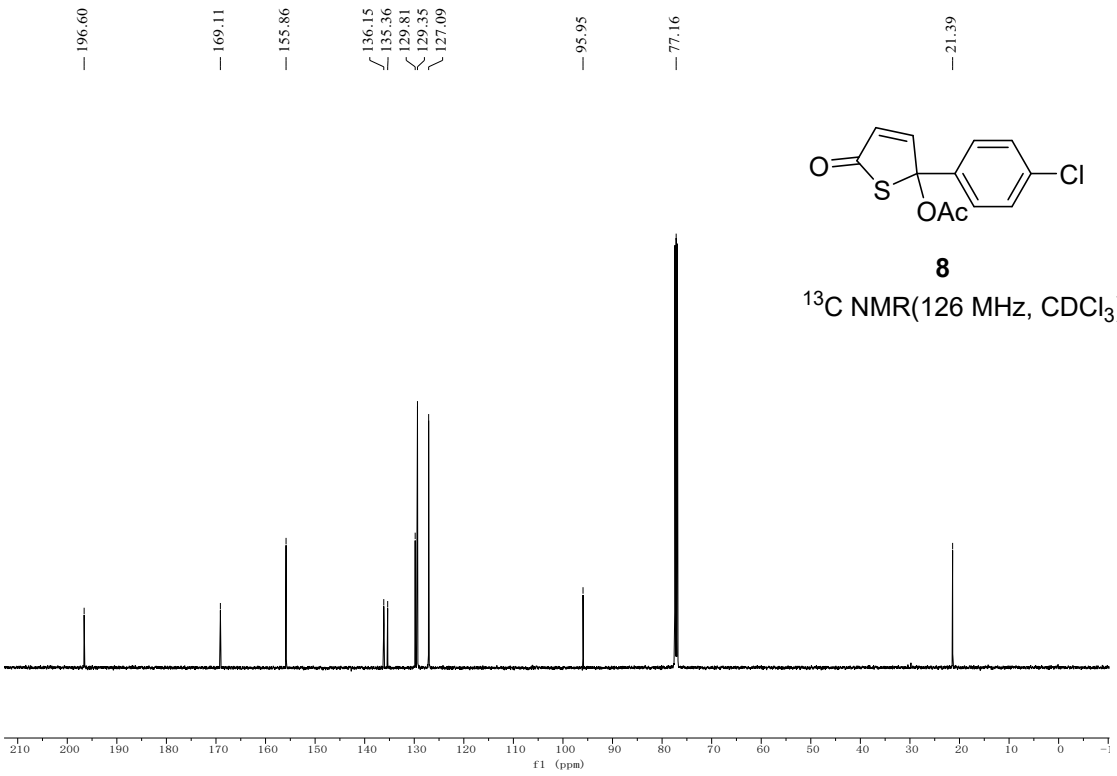

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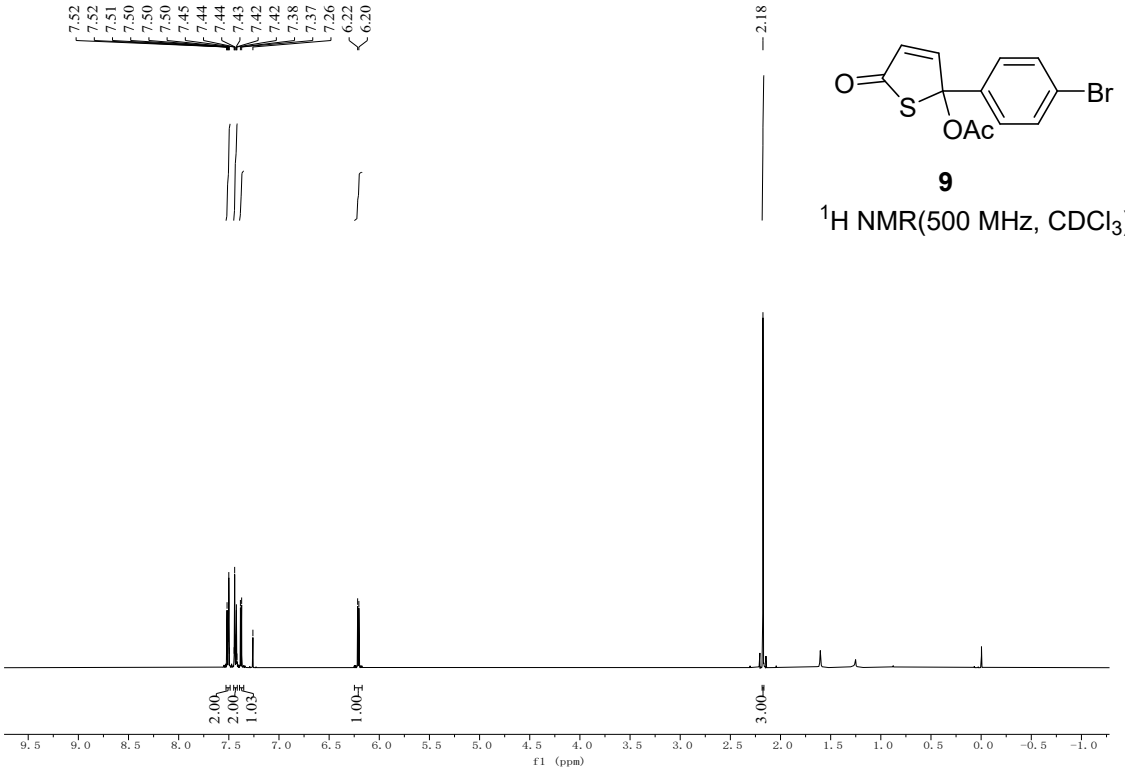

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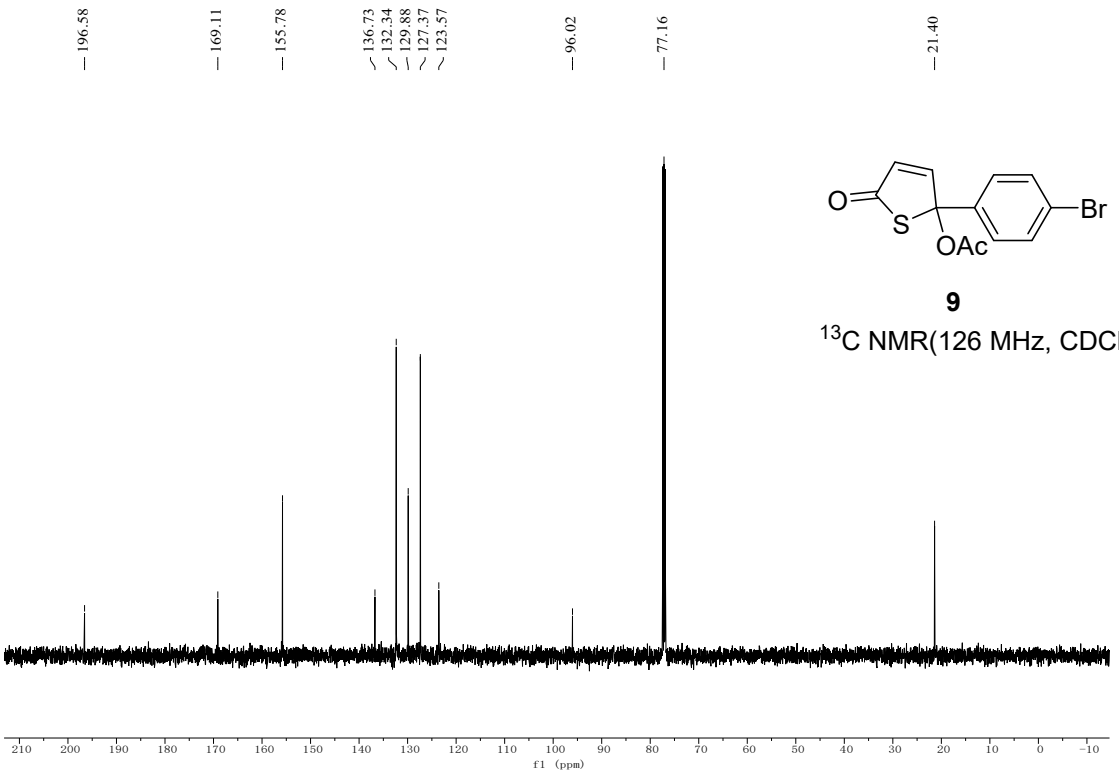

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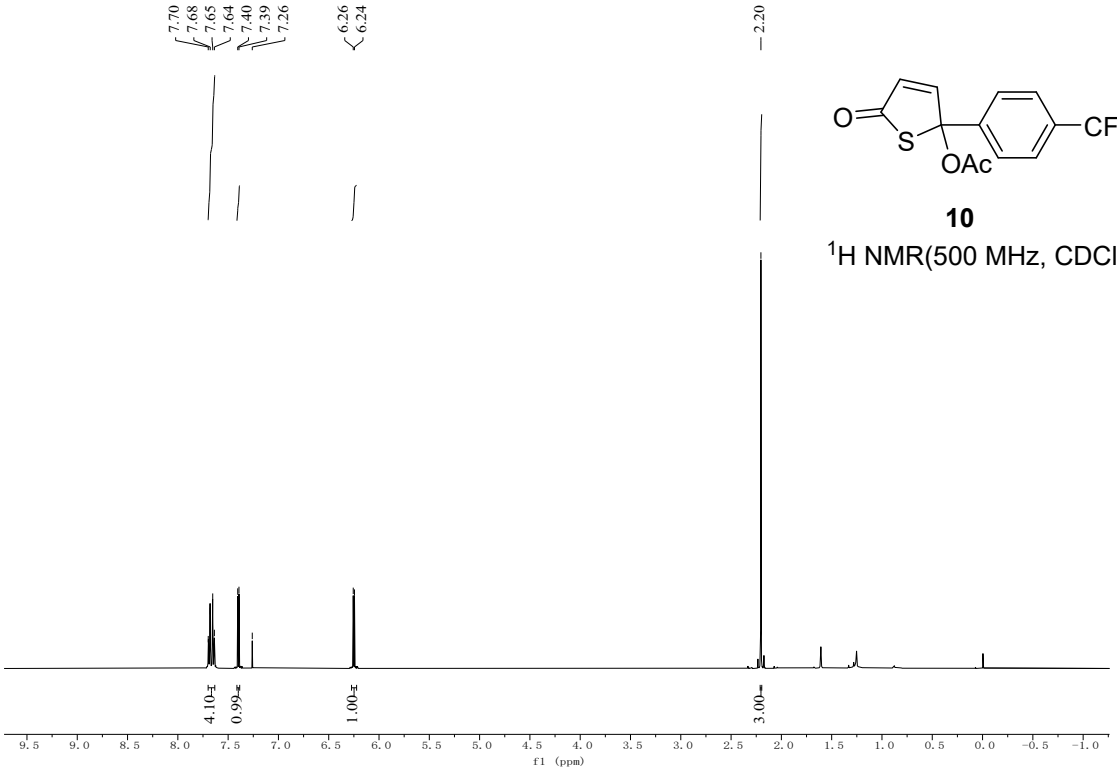
^{13}C NMR(126 MHz, $CDCl_3$)



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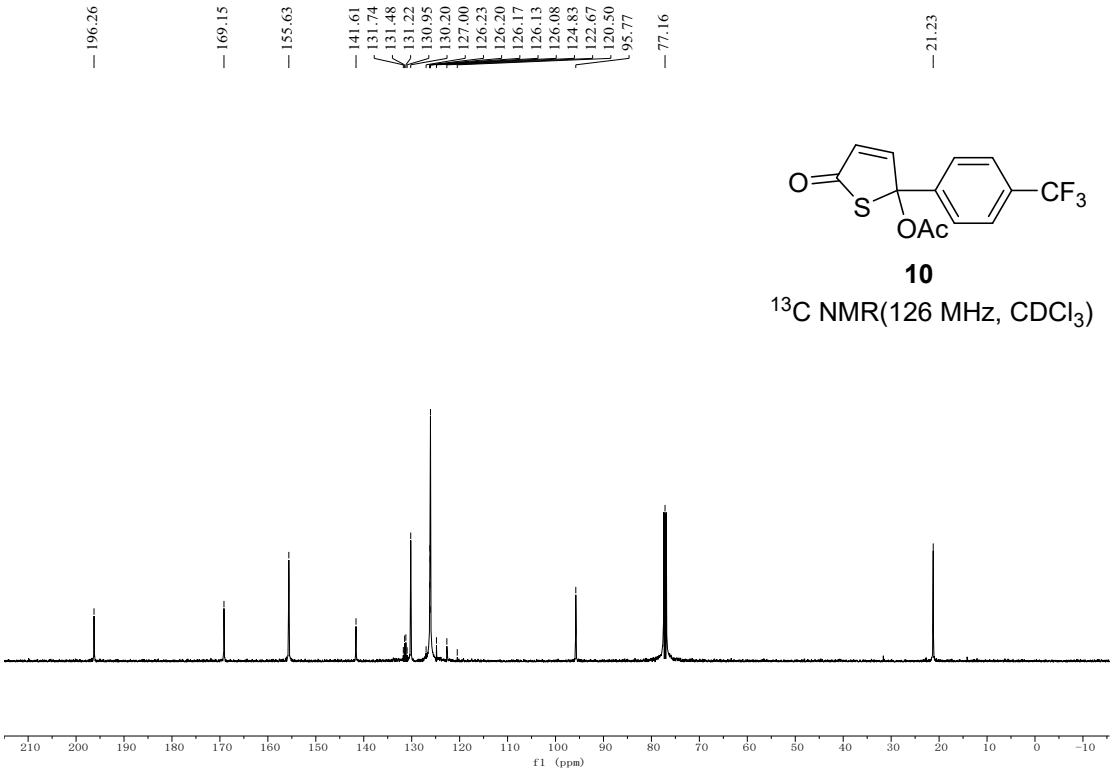

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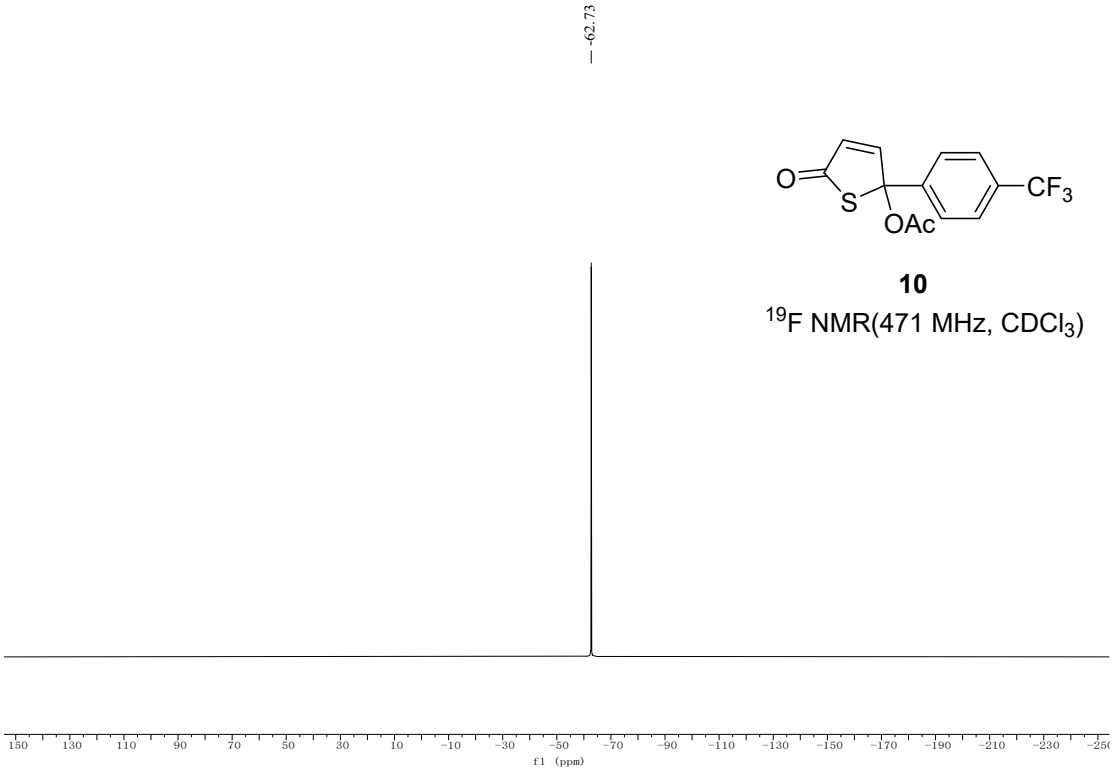

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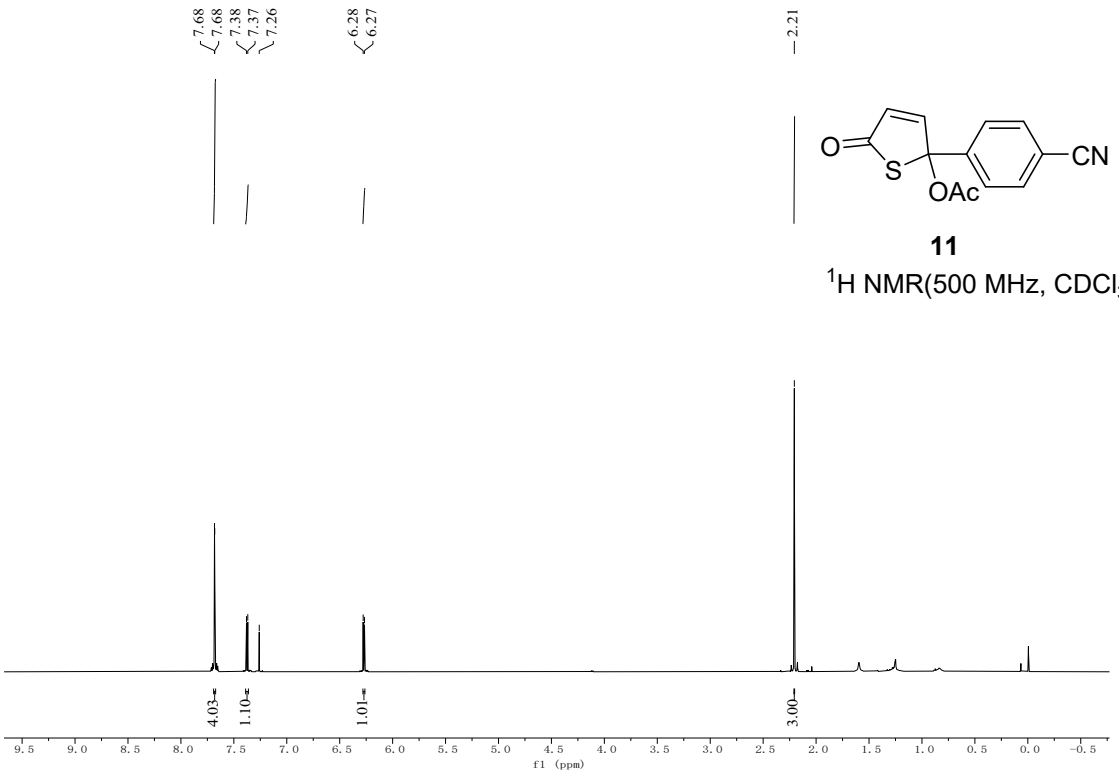

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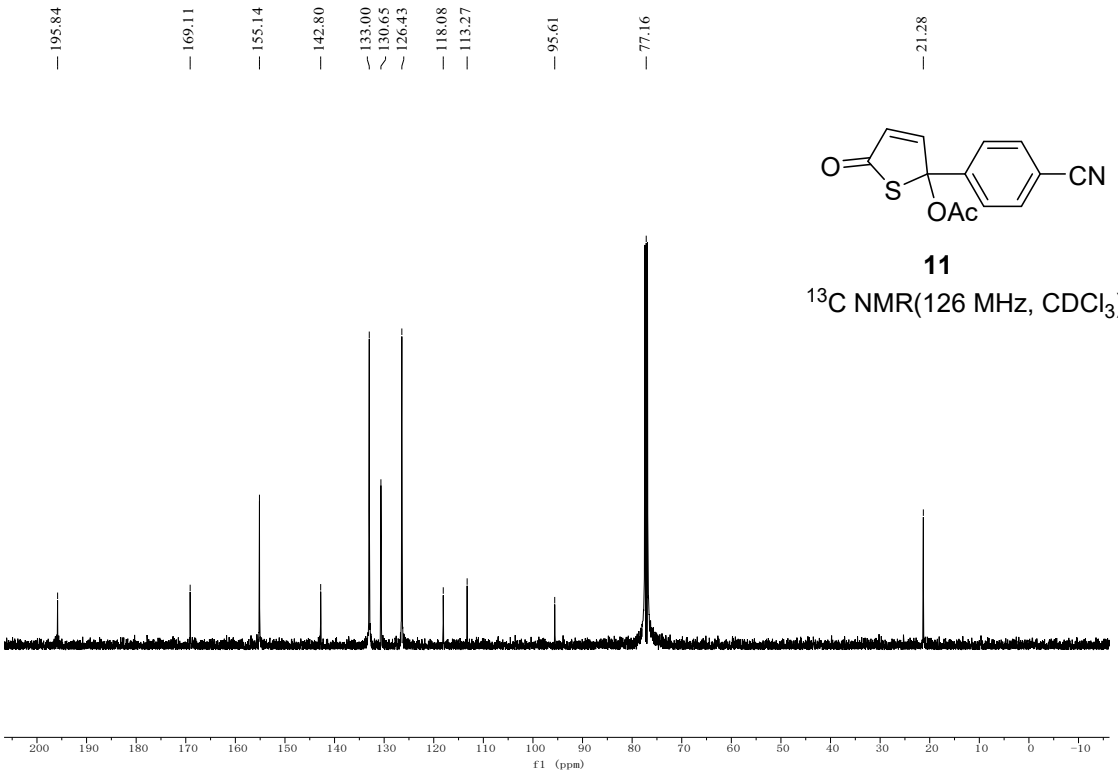

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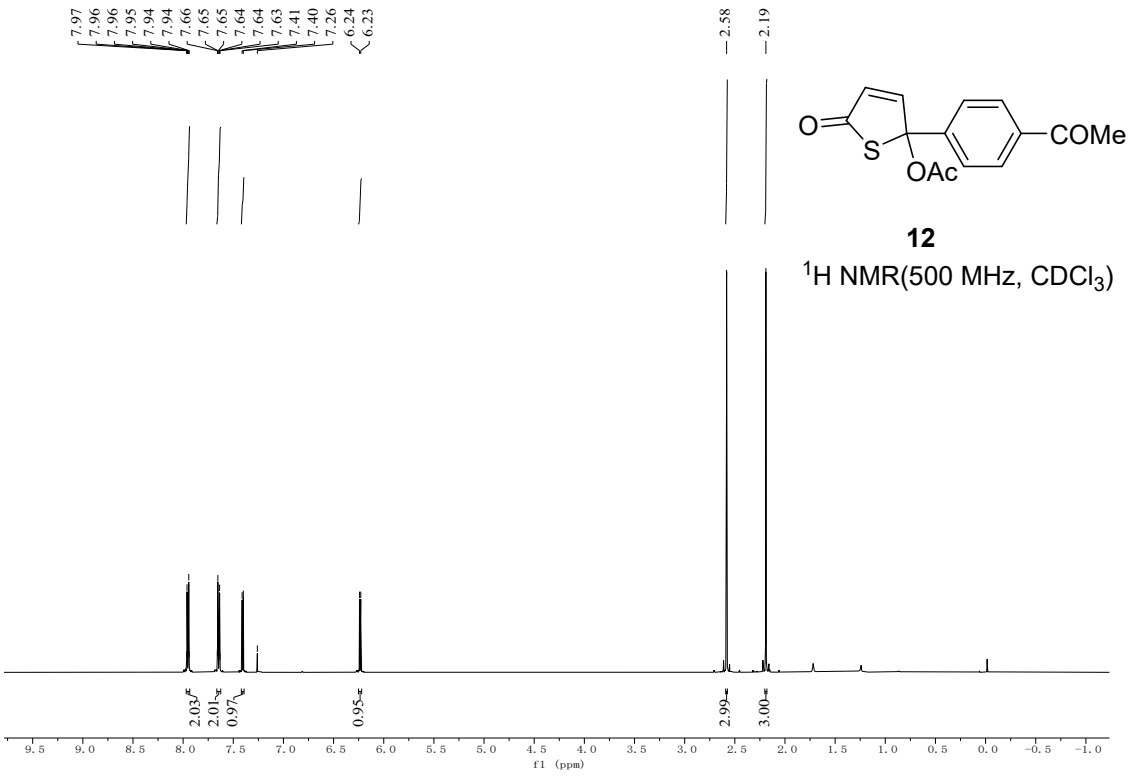

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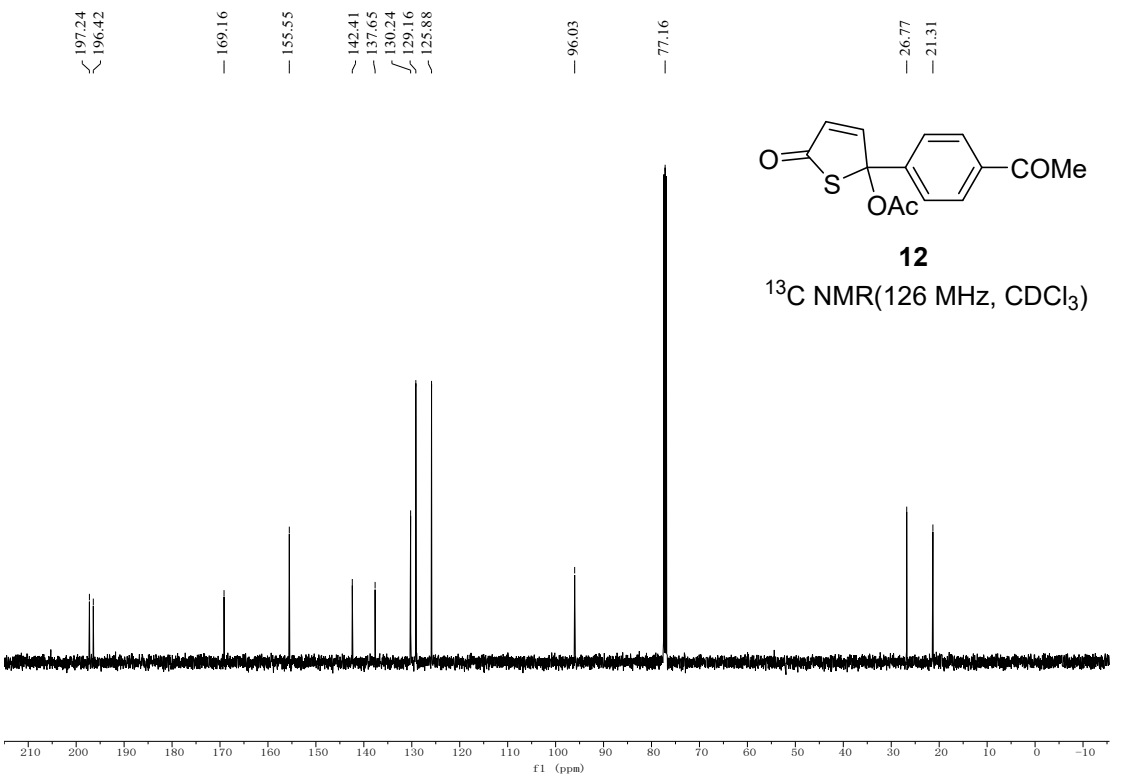

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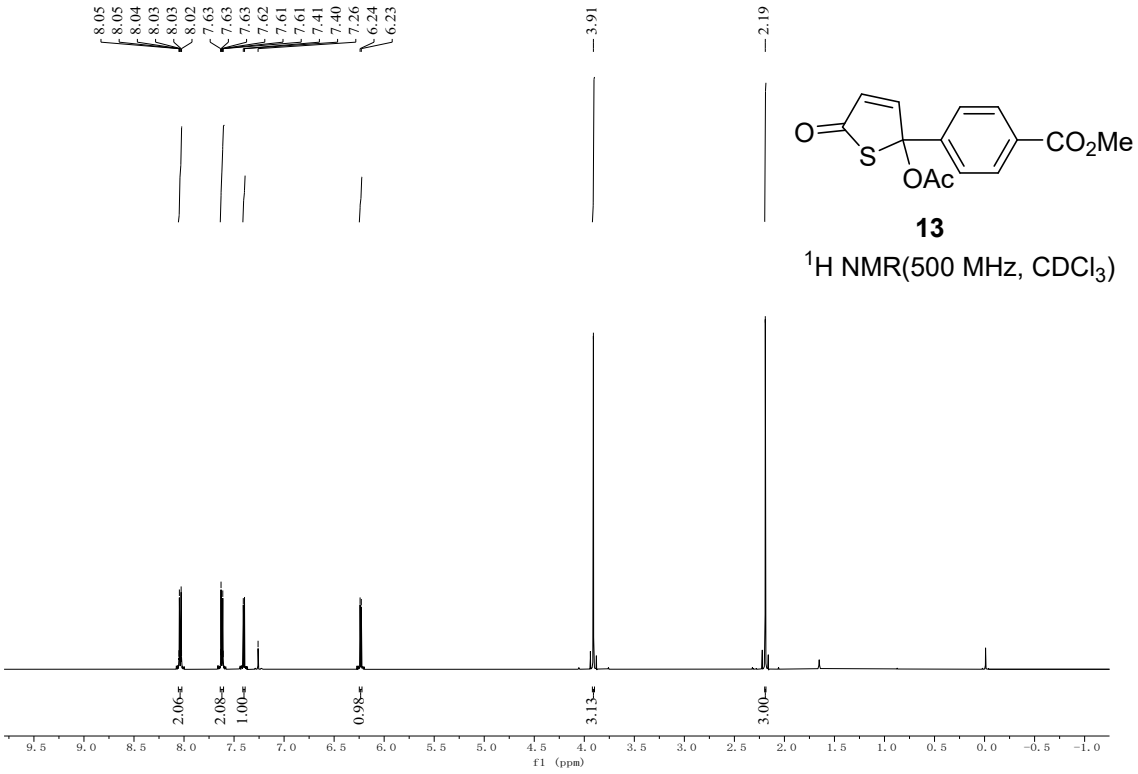

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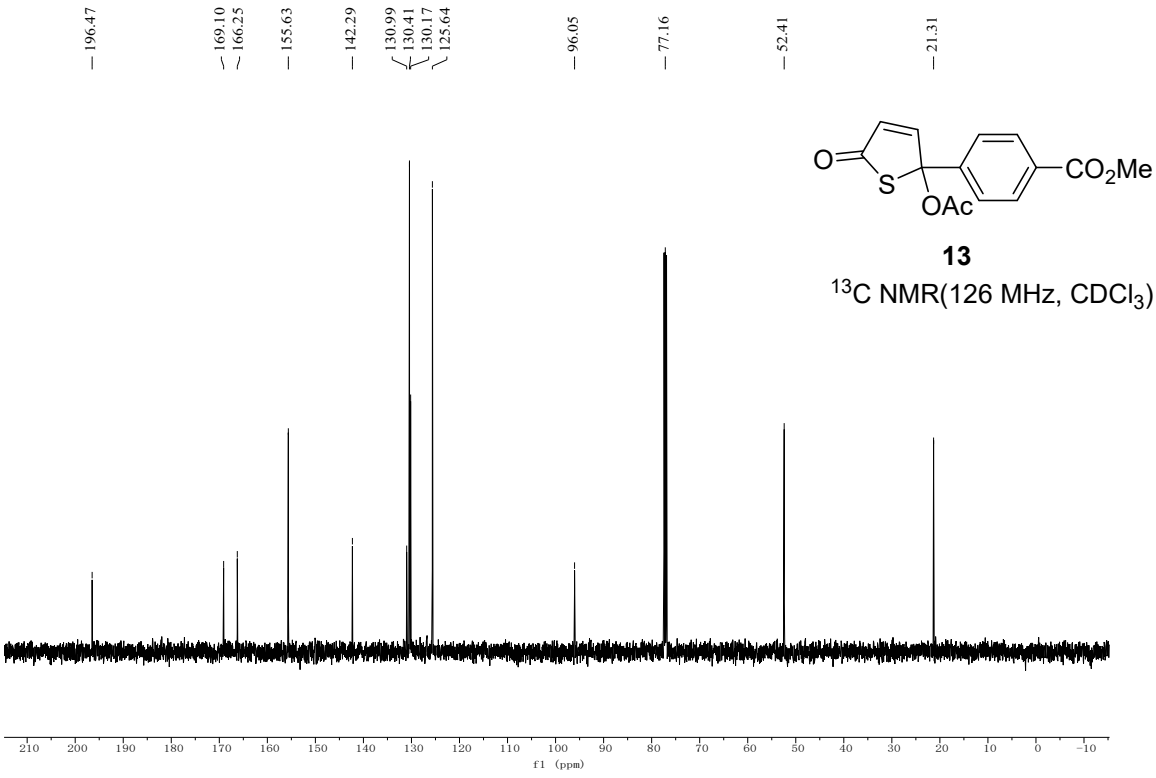

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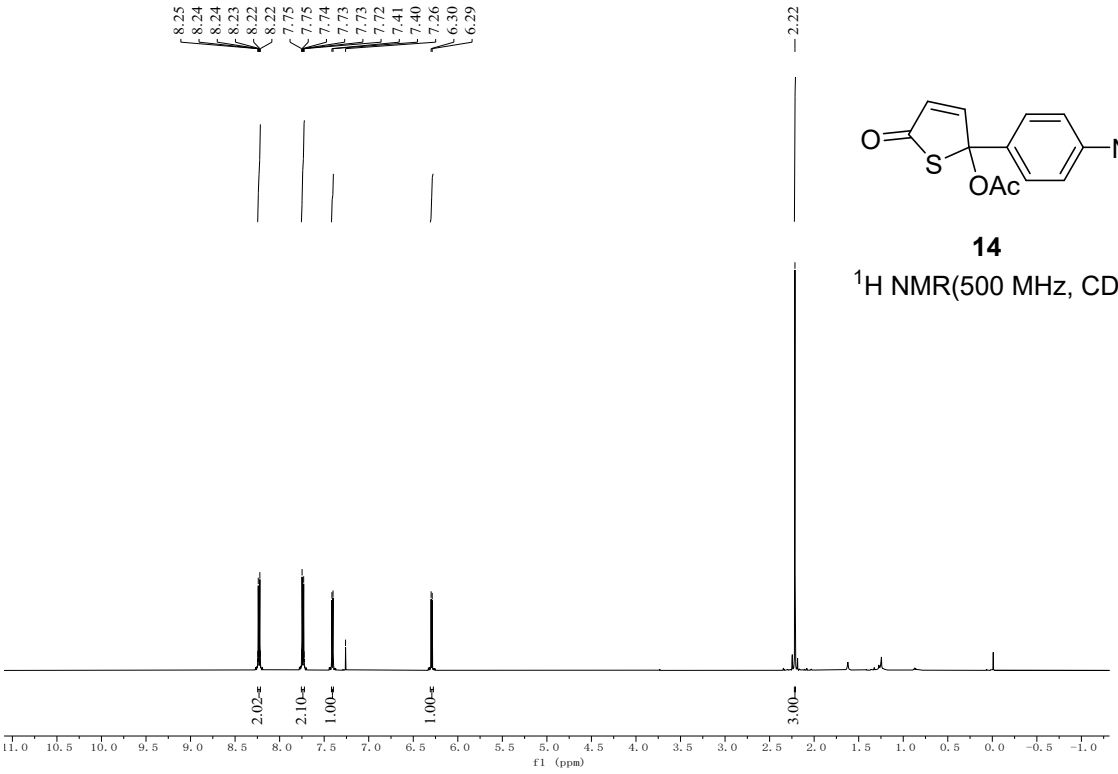

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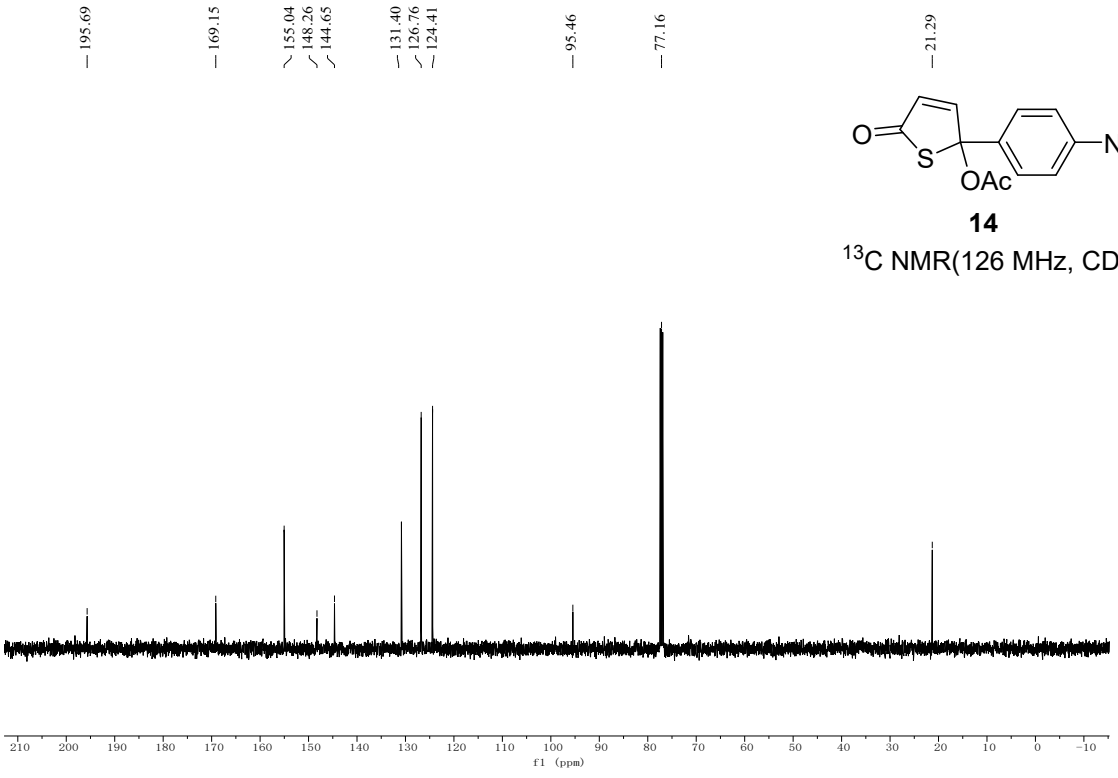

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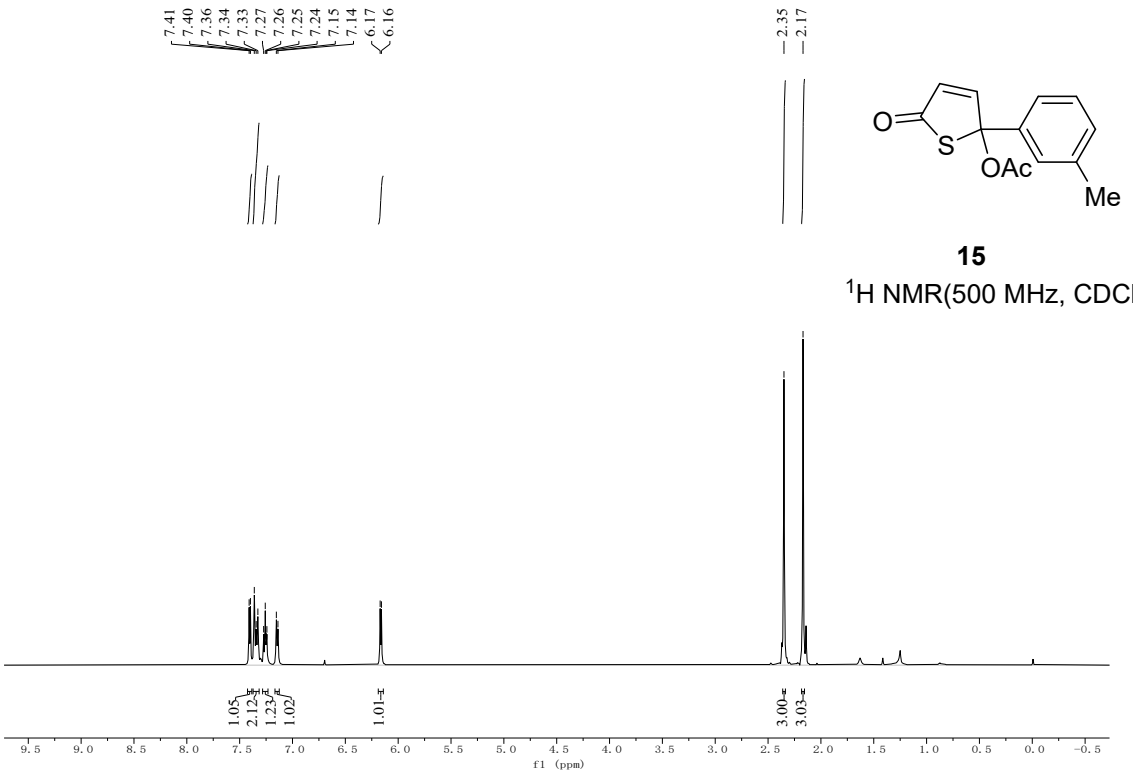

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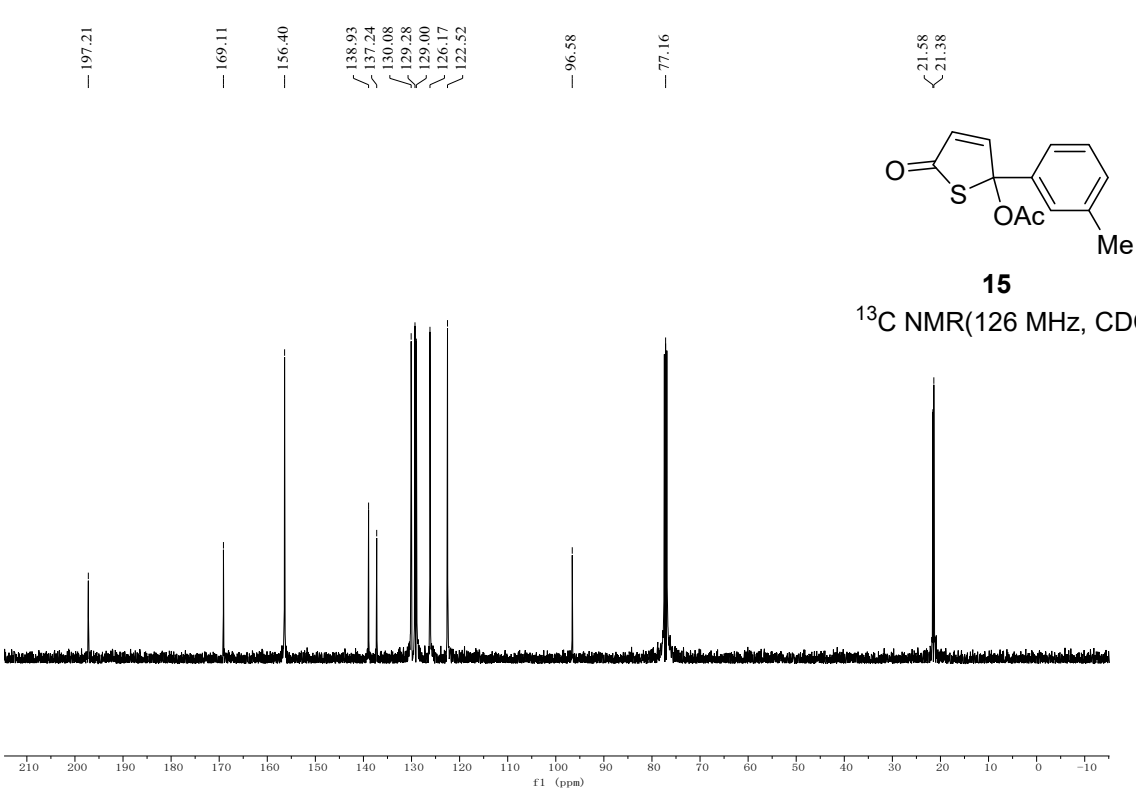

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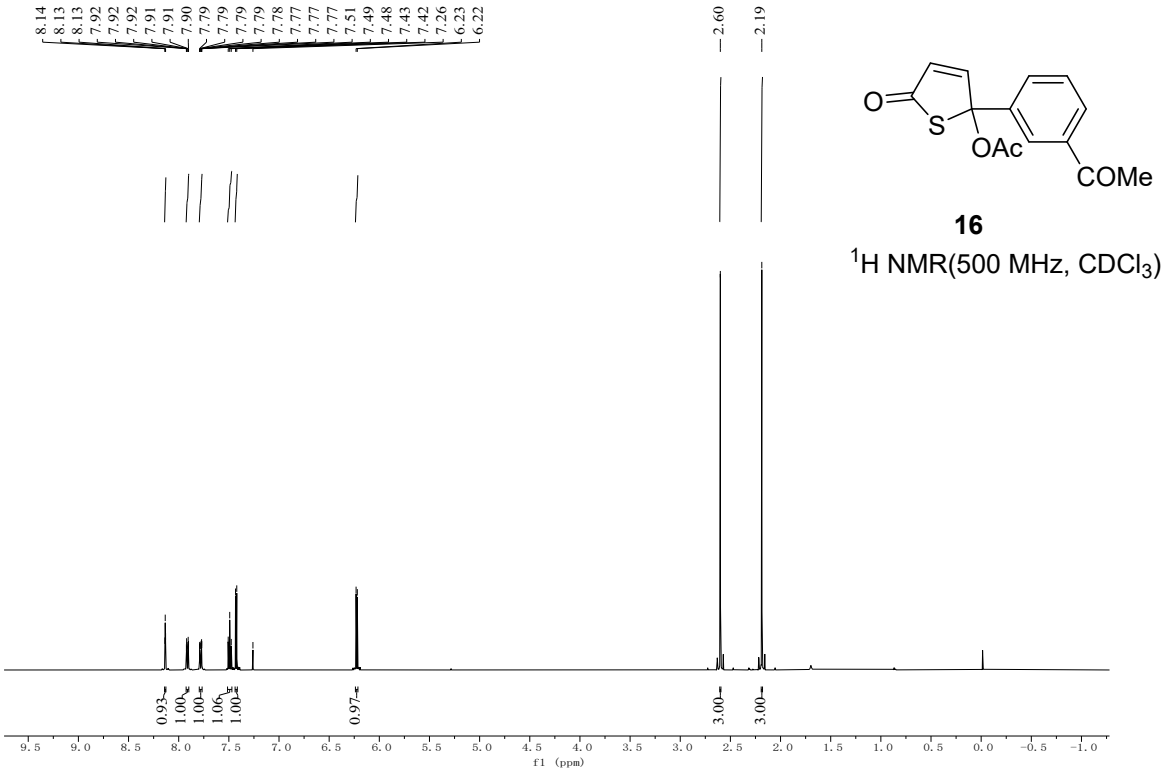

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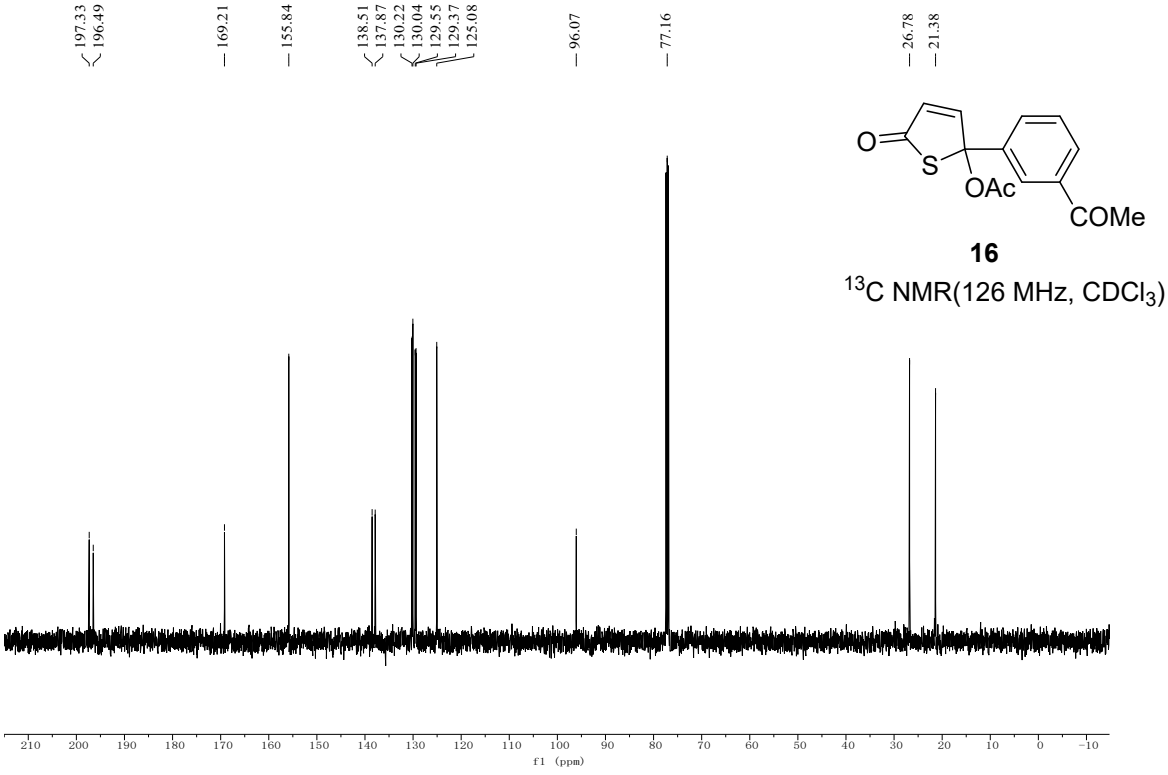

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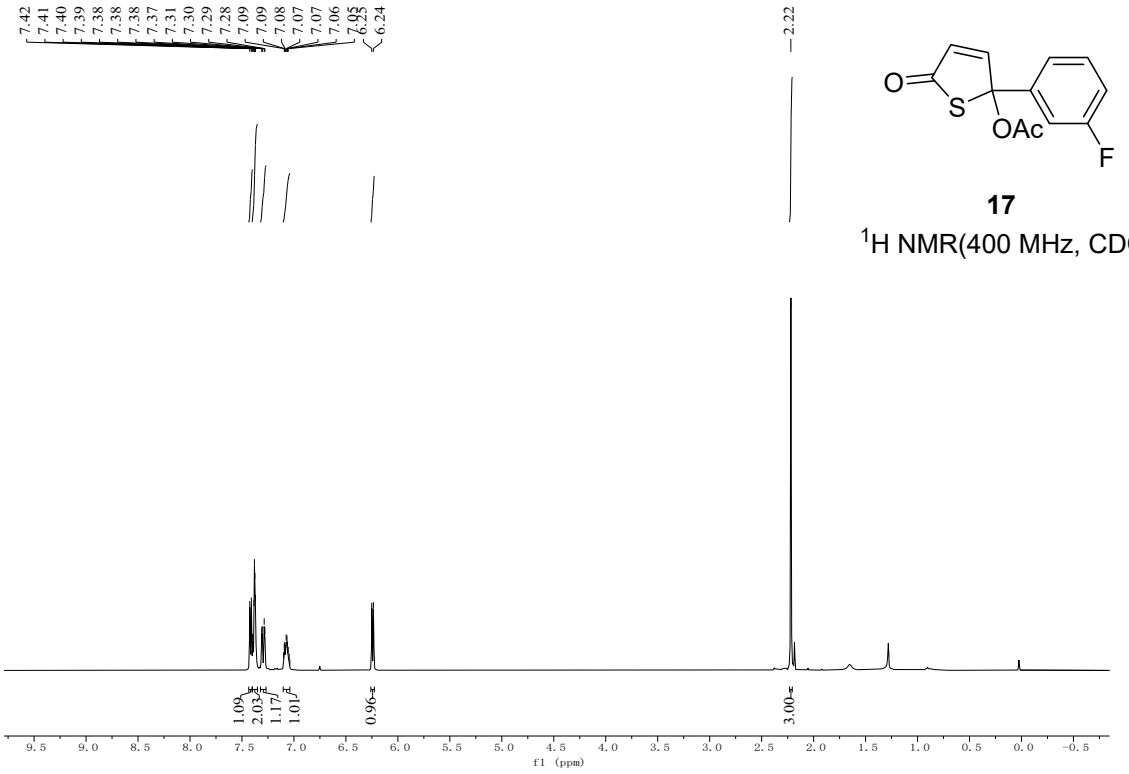

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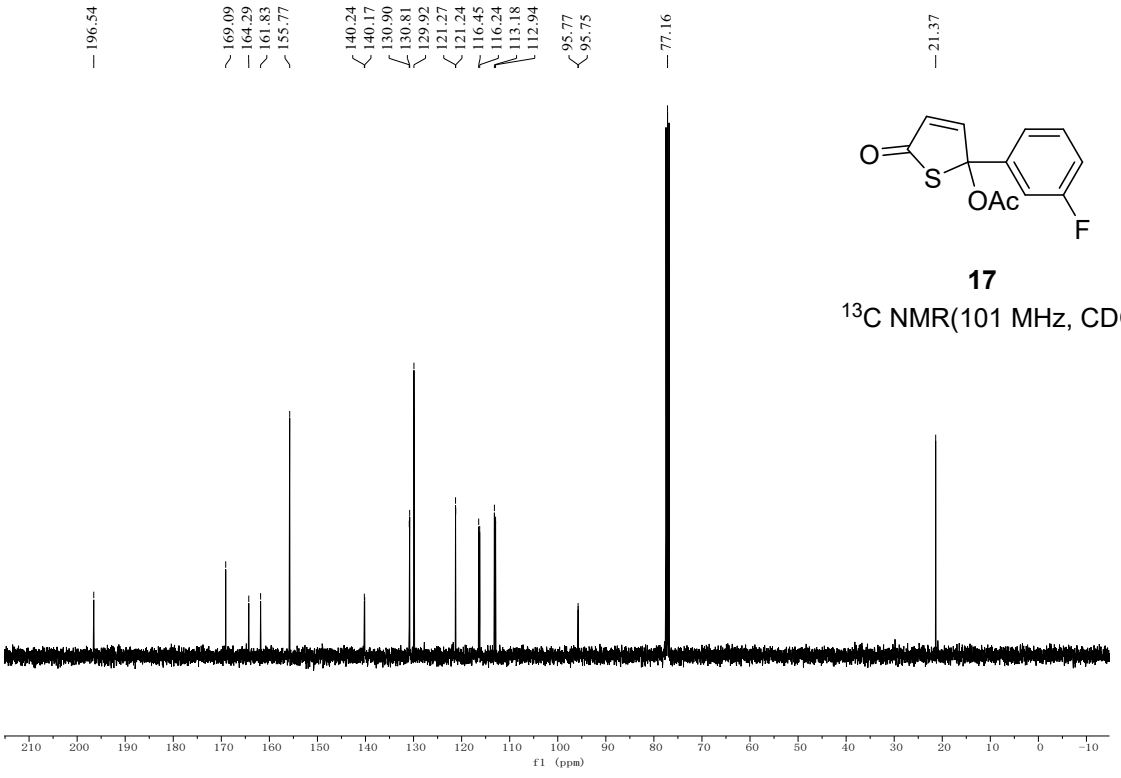

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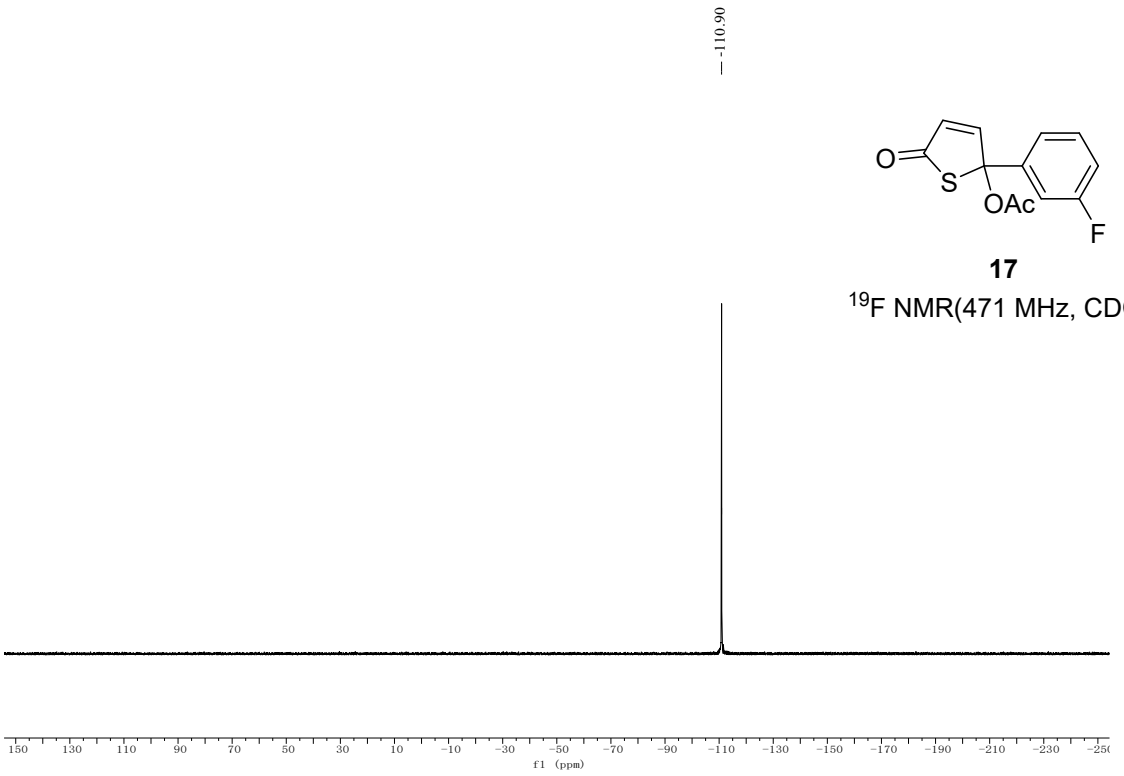

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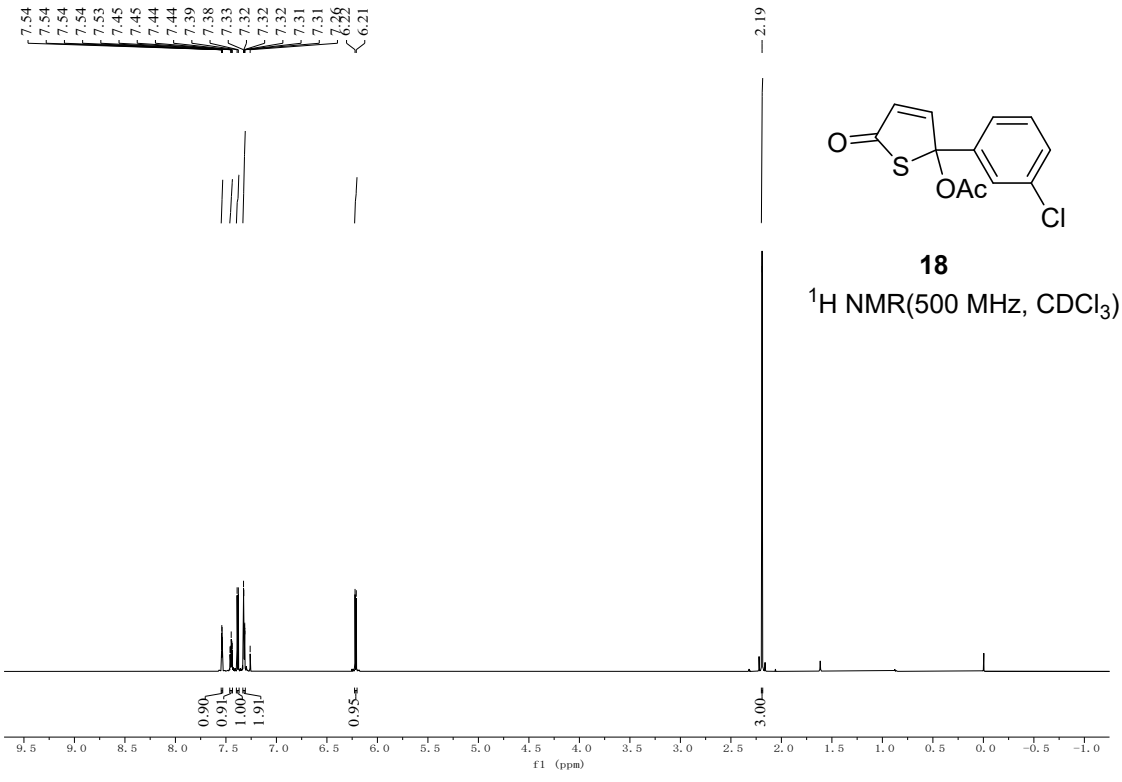

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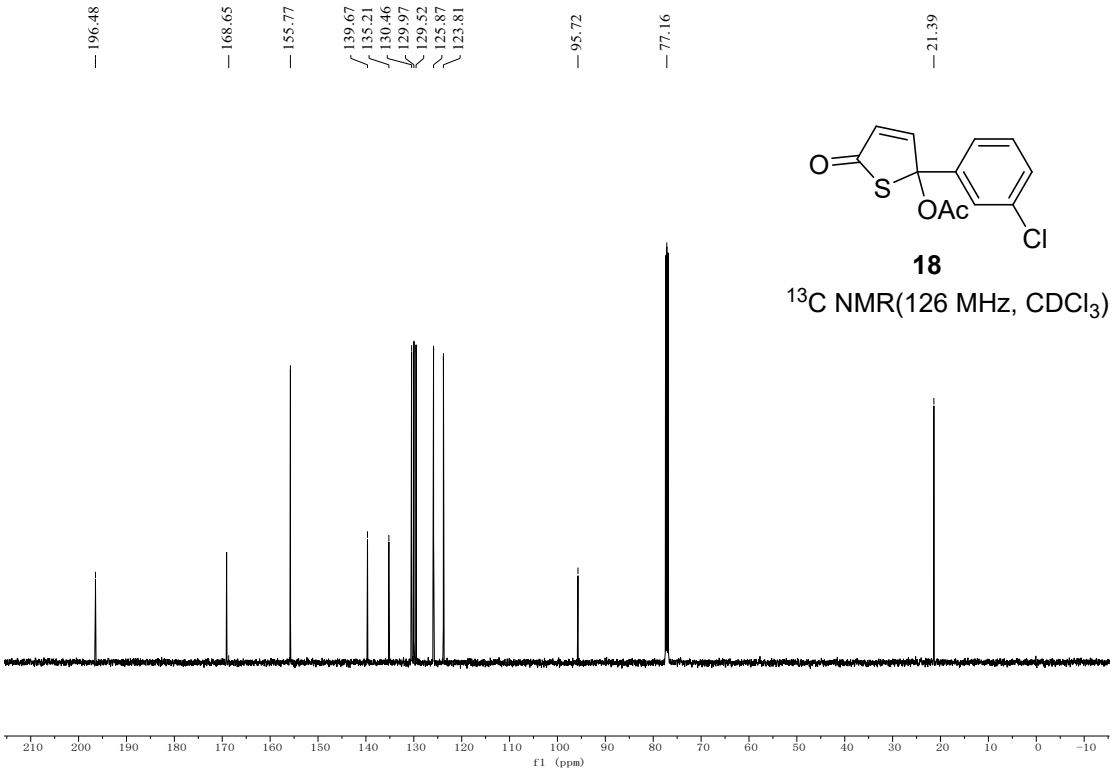

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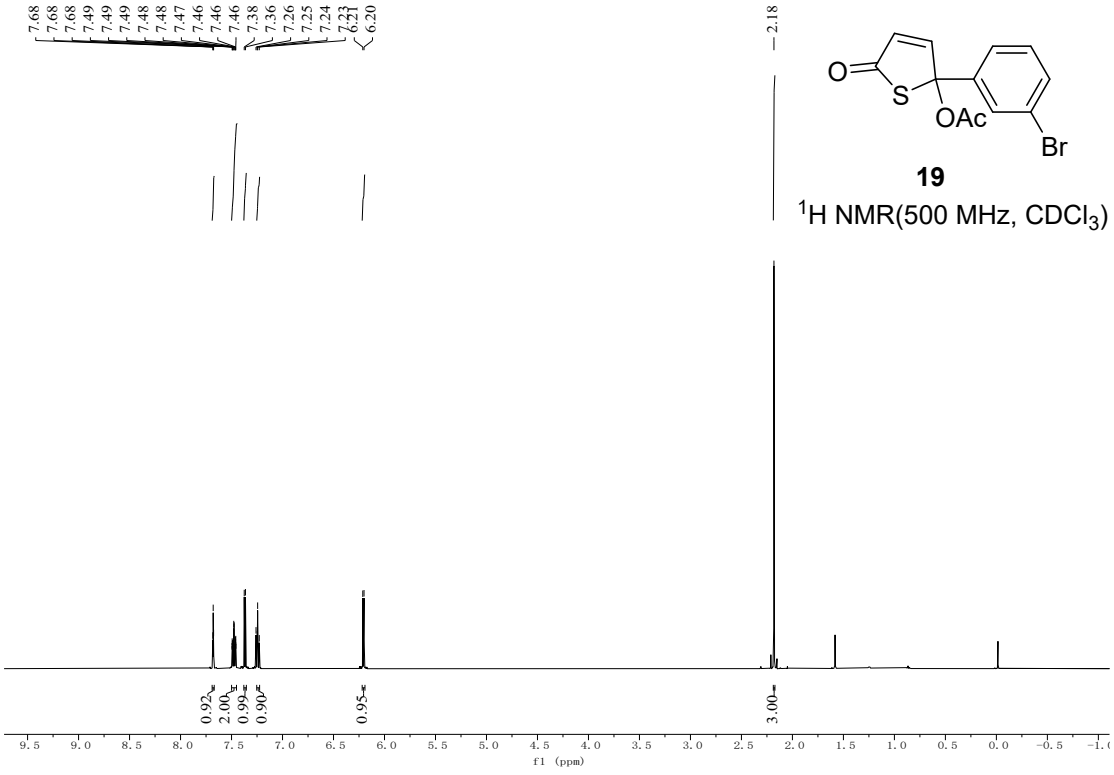

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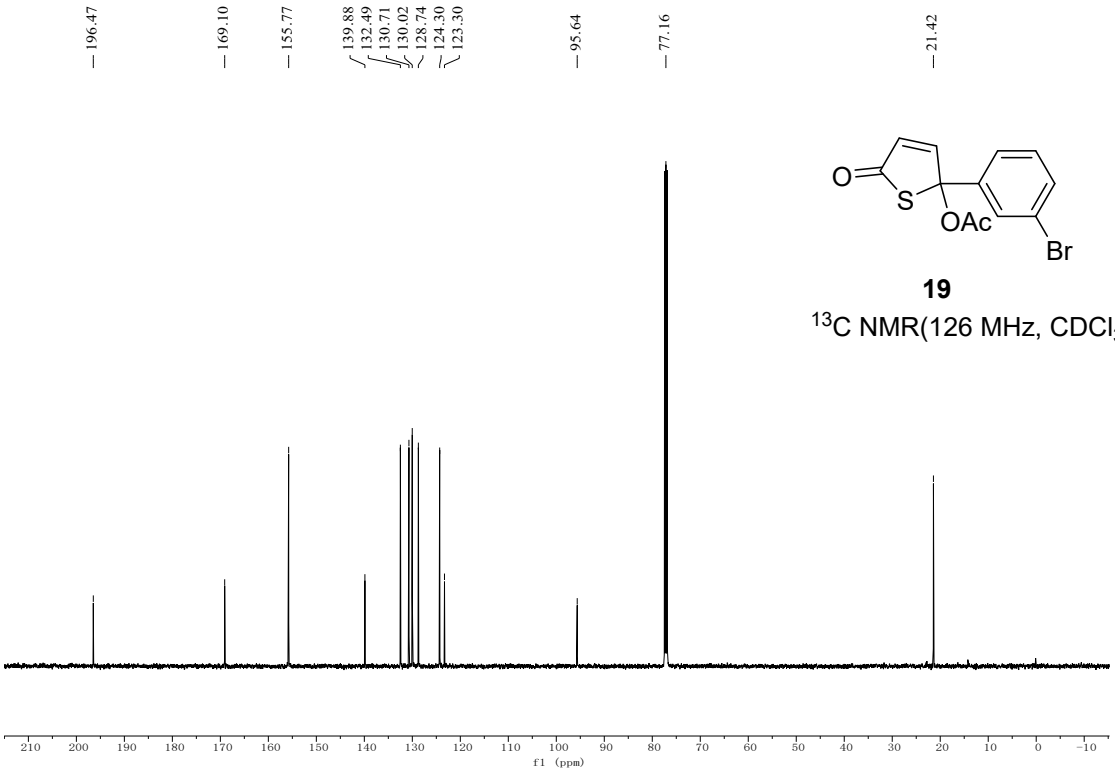

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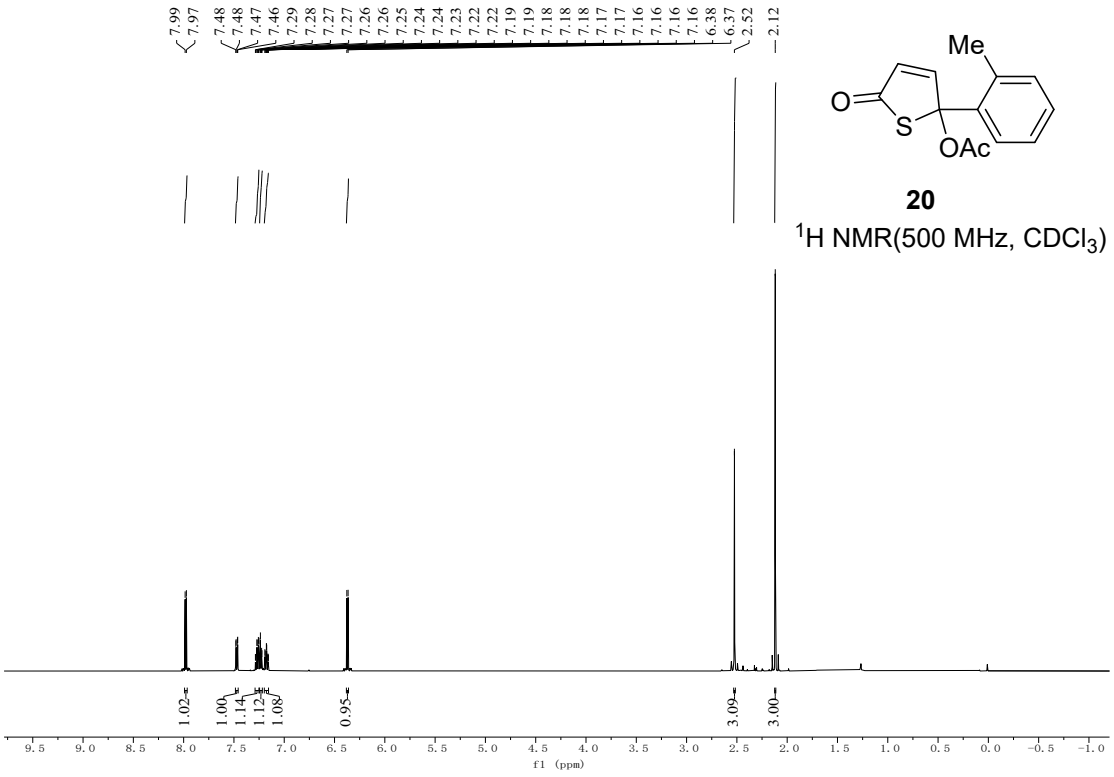
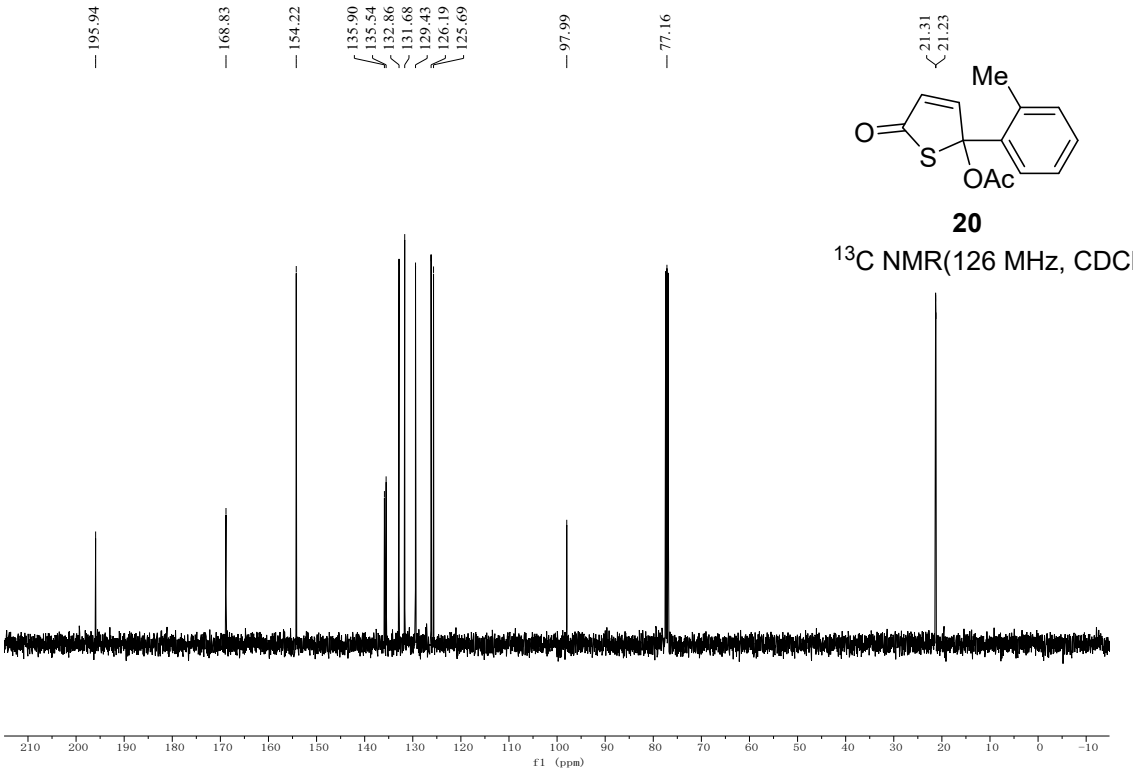


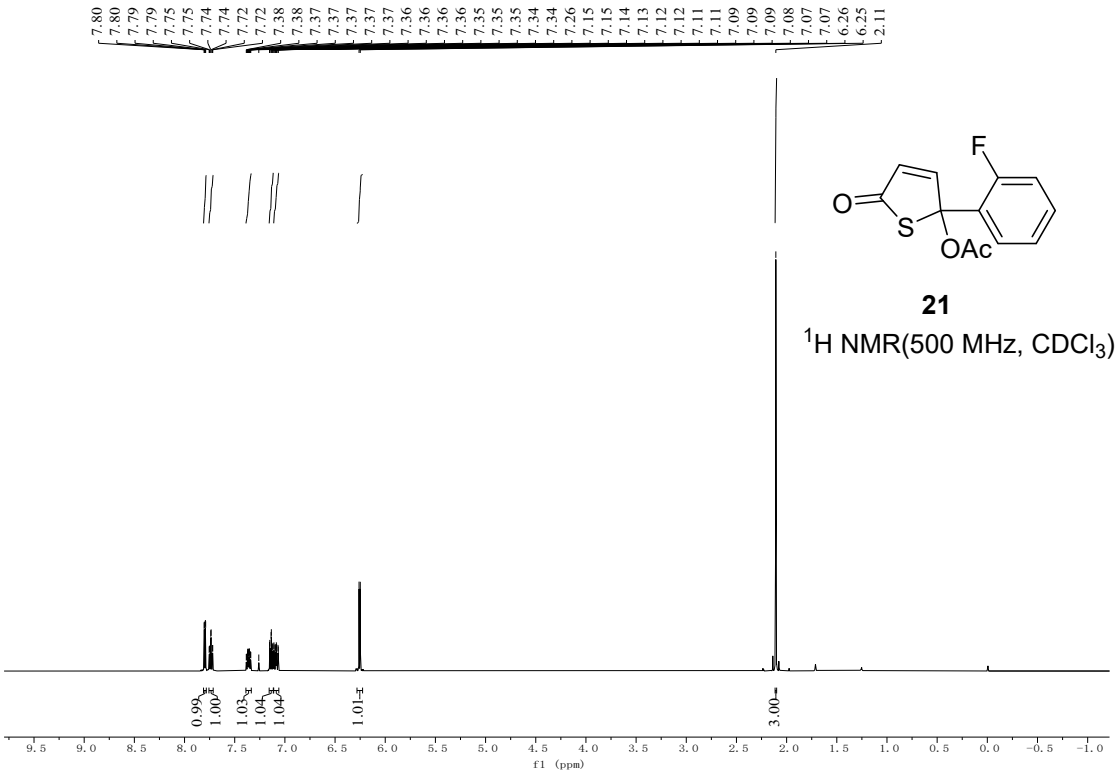
20

^{1}H NMR(500 MHz, $CDCl_3$)



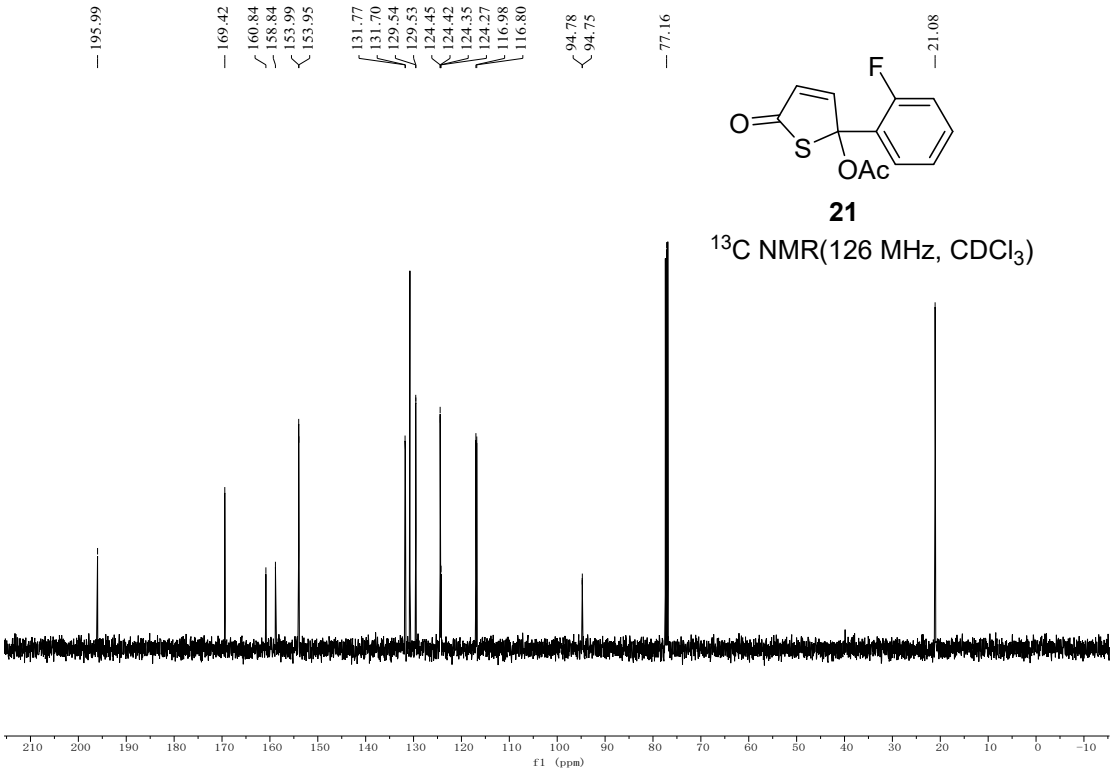
20

^{13}C NMR(126 MHz, $CDCl_3$)



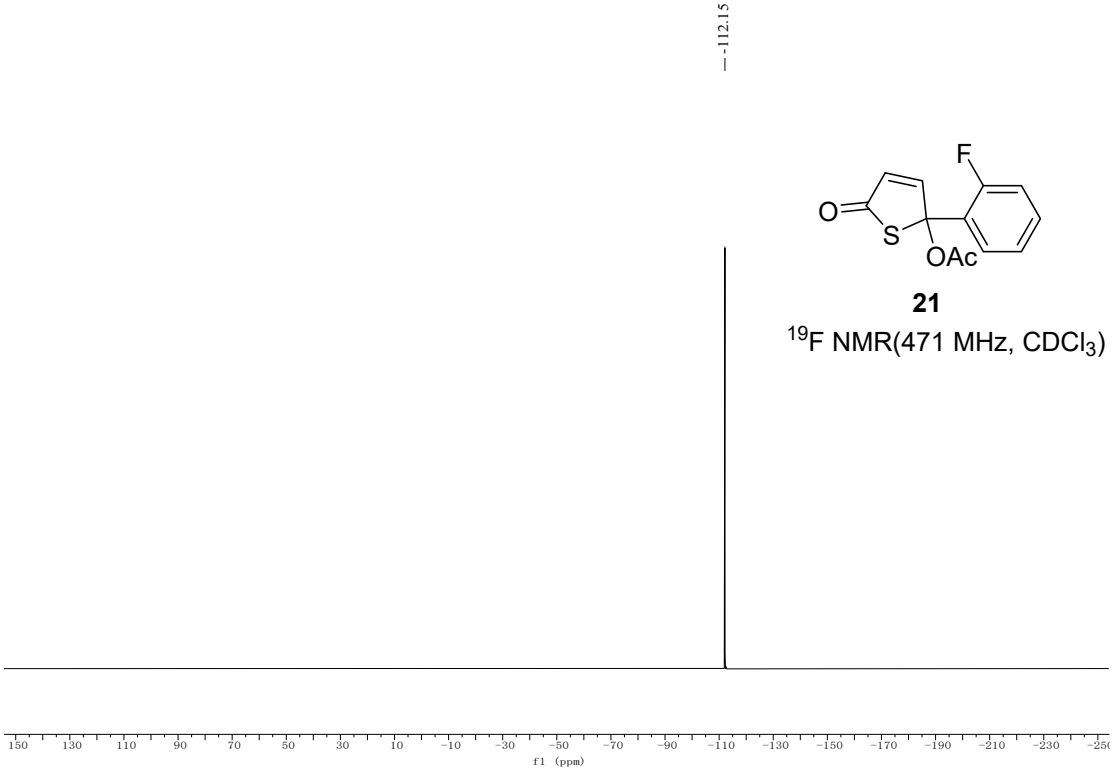
21

^{1}H NMR(500 MHz, $CDCl_3$)



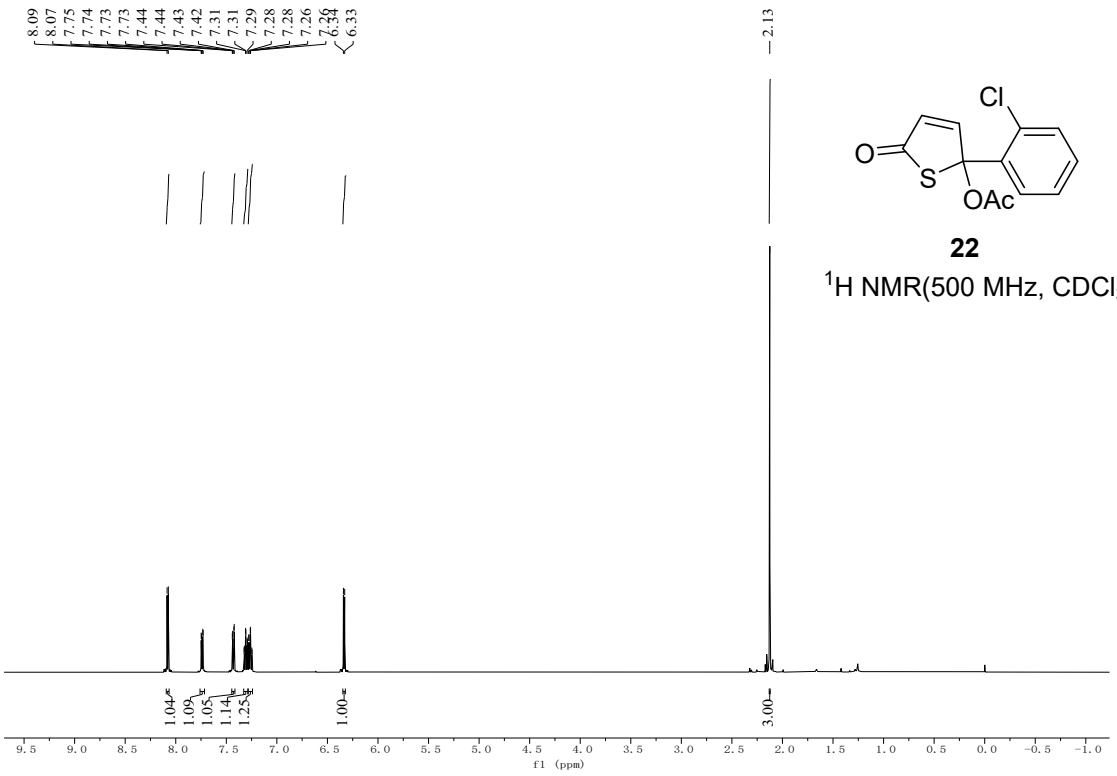
21

^{13}C NMR(126 MHz, $CDCl_3$)



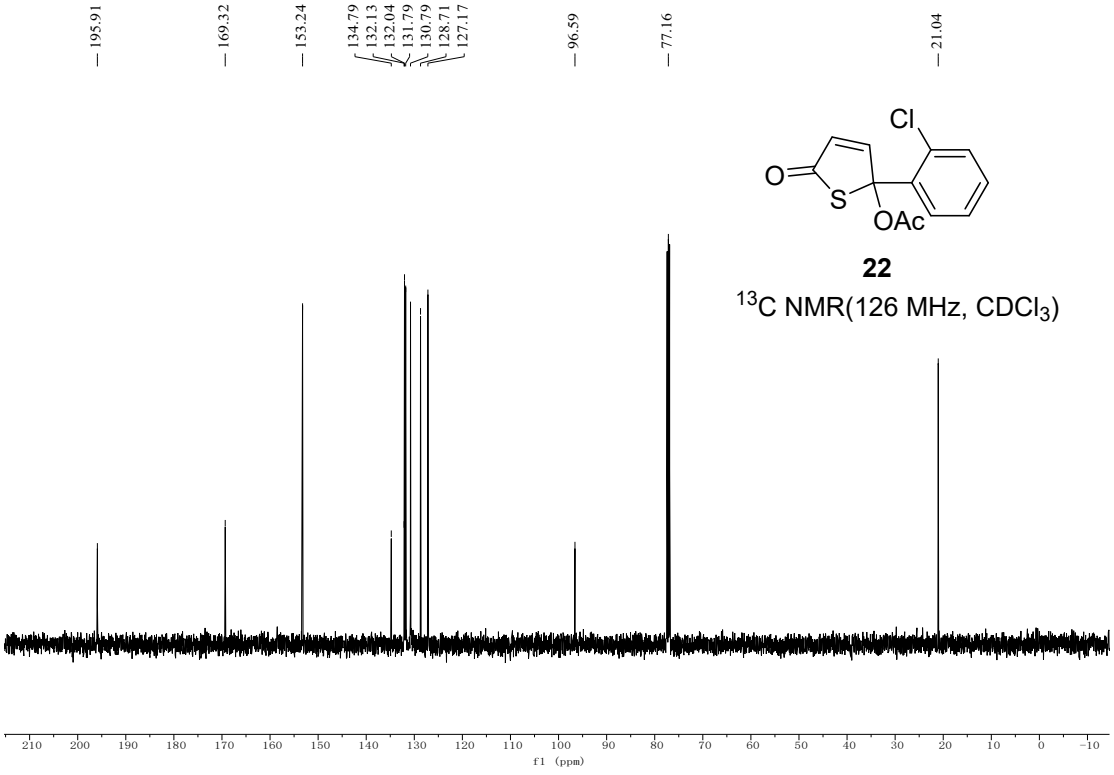
21

^{19}F NMR(471 MHz, $CDCl_3$)



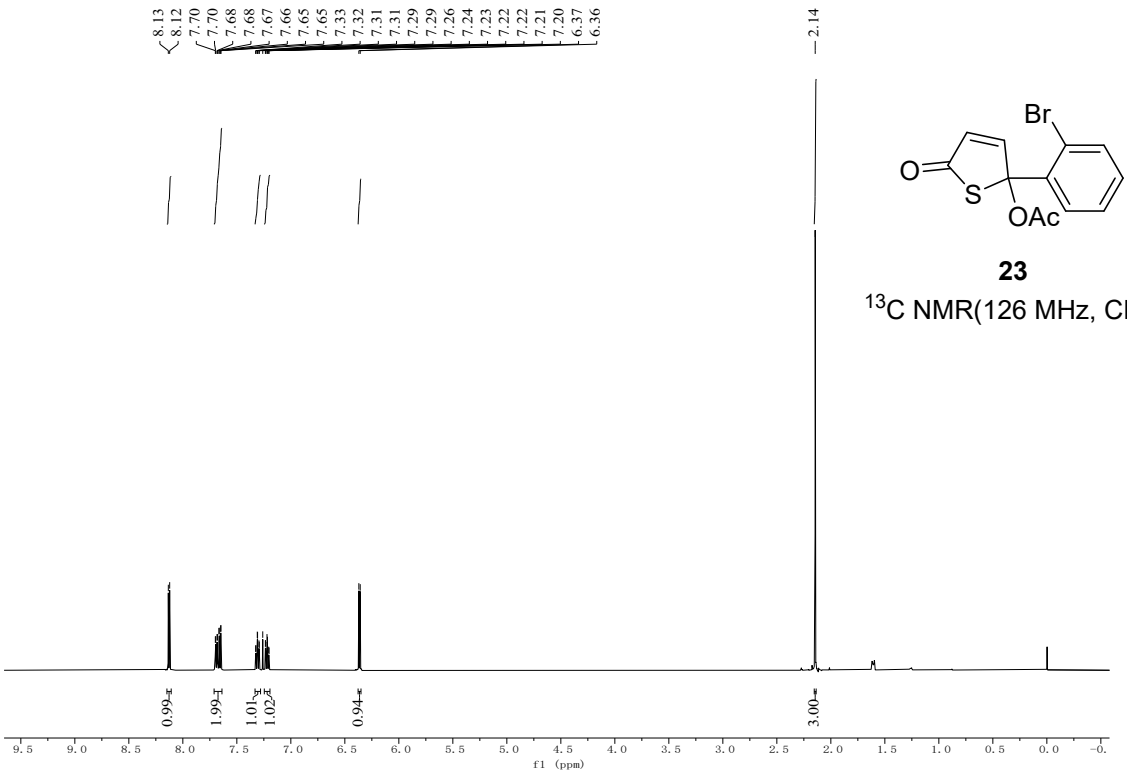
22

^{1}H NMR(500 MHz, $CDCl_3$)



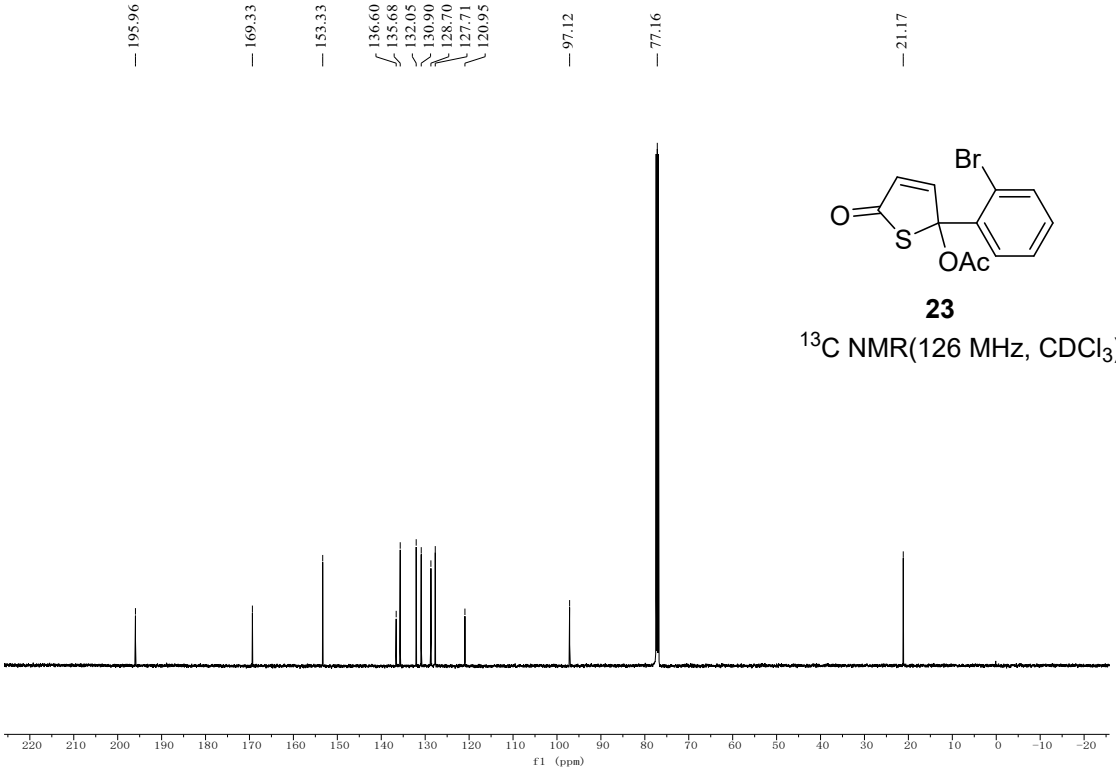
22

^{13}C NMR(126 MHz, $CDCl_3$)



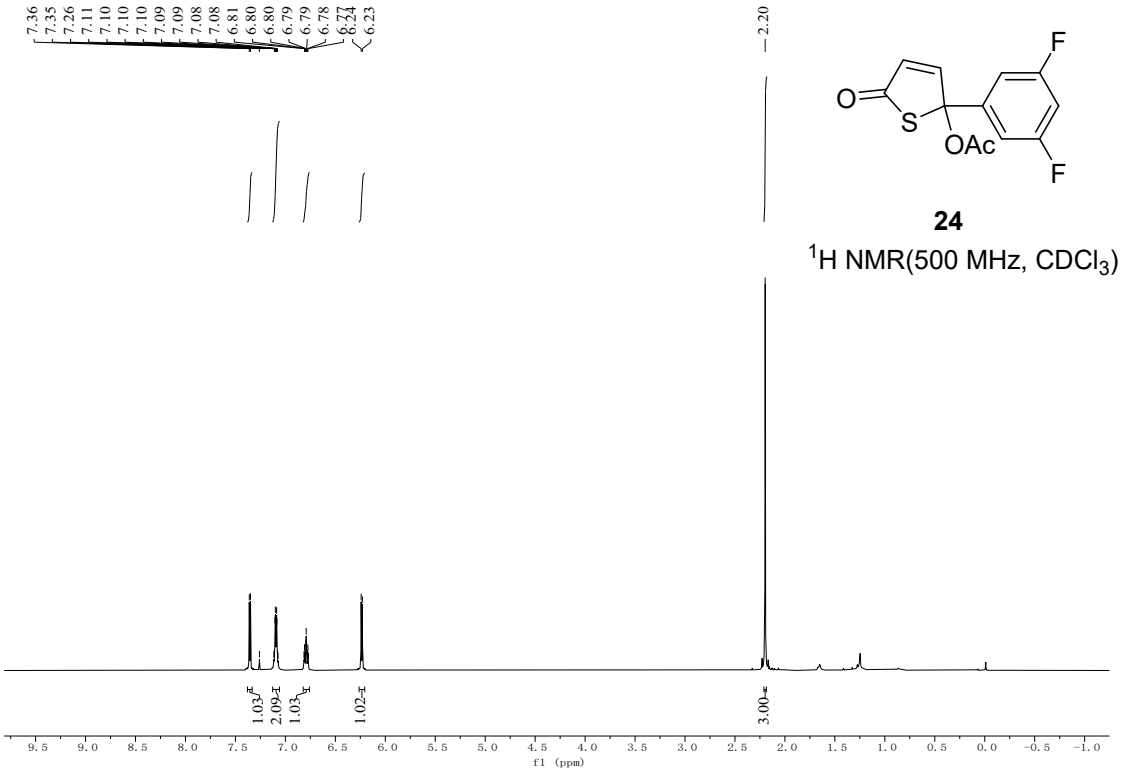
23

^{13}C NMR(126 MHz, $CDCl_3$)



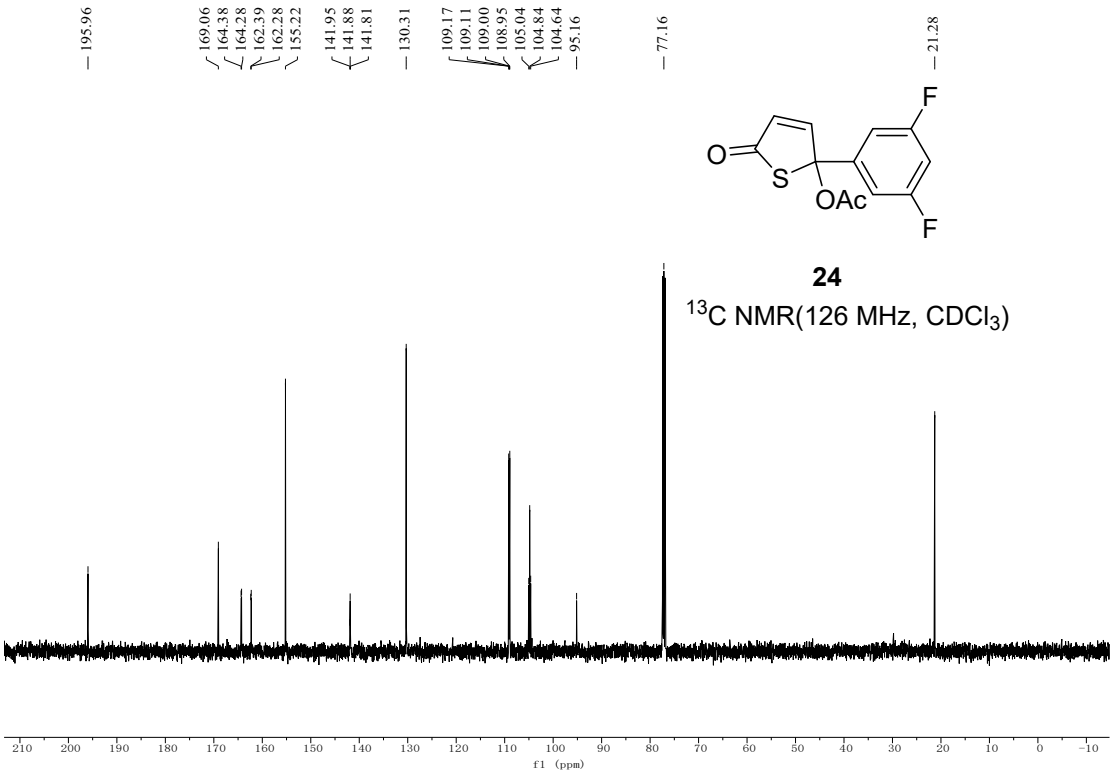
23

^{13}C NMR(126 MHz, $CDCl_3$)



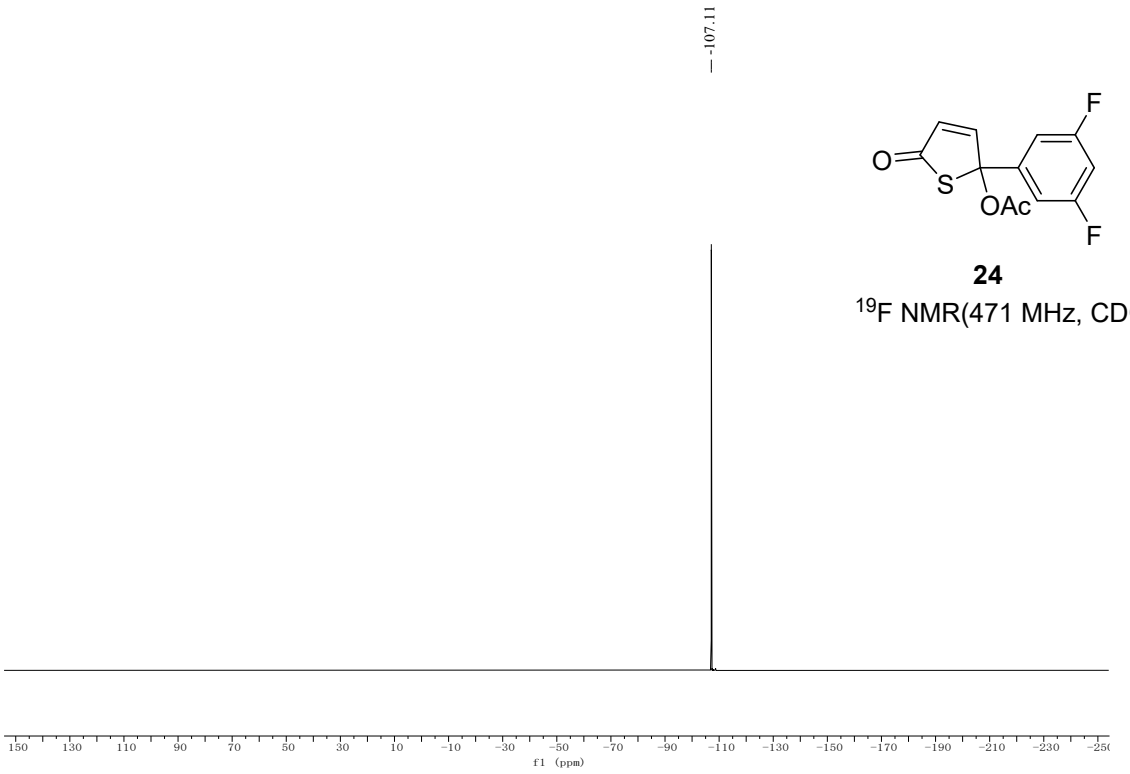
24

^{1}H NMR(500 MHz, $CDCl_3$)



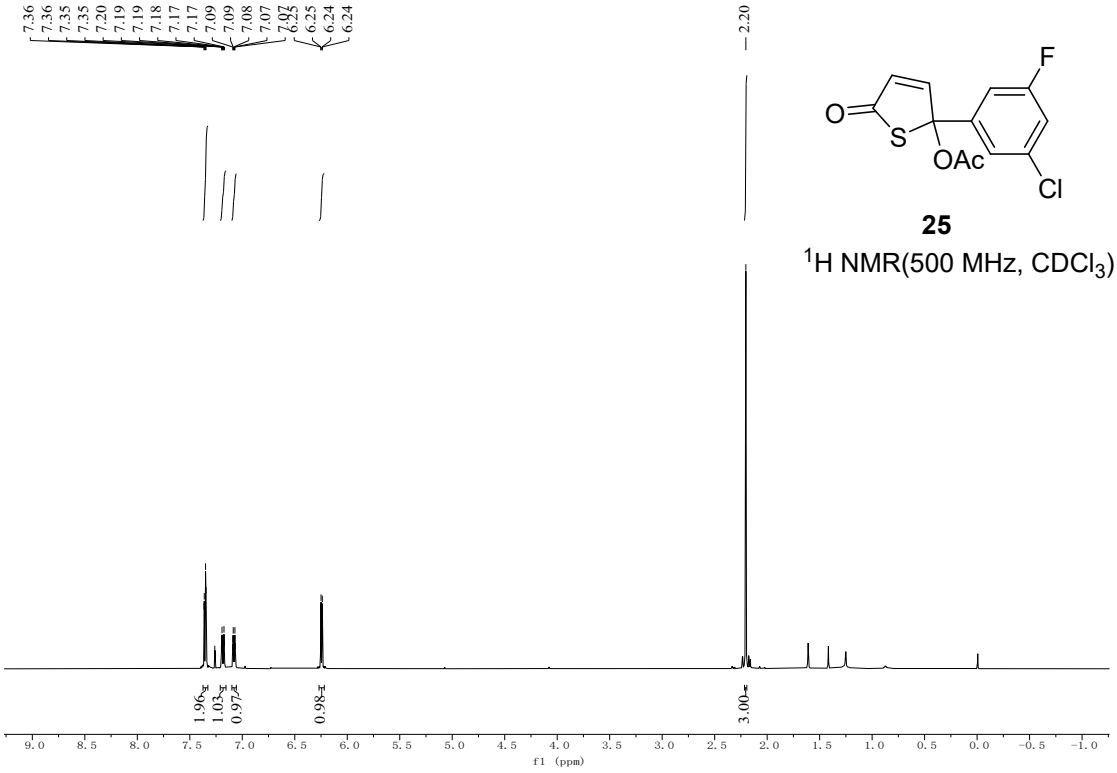
24

^{13}C NMR(126 MHz, $CDCl_3$)



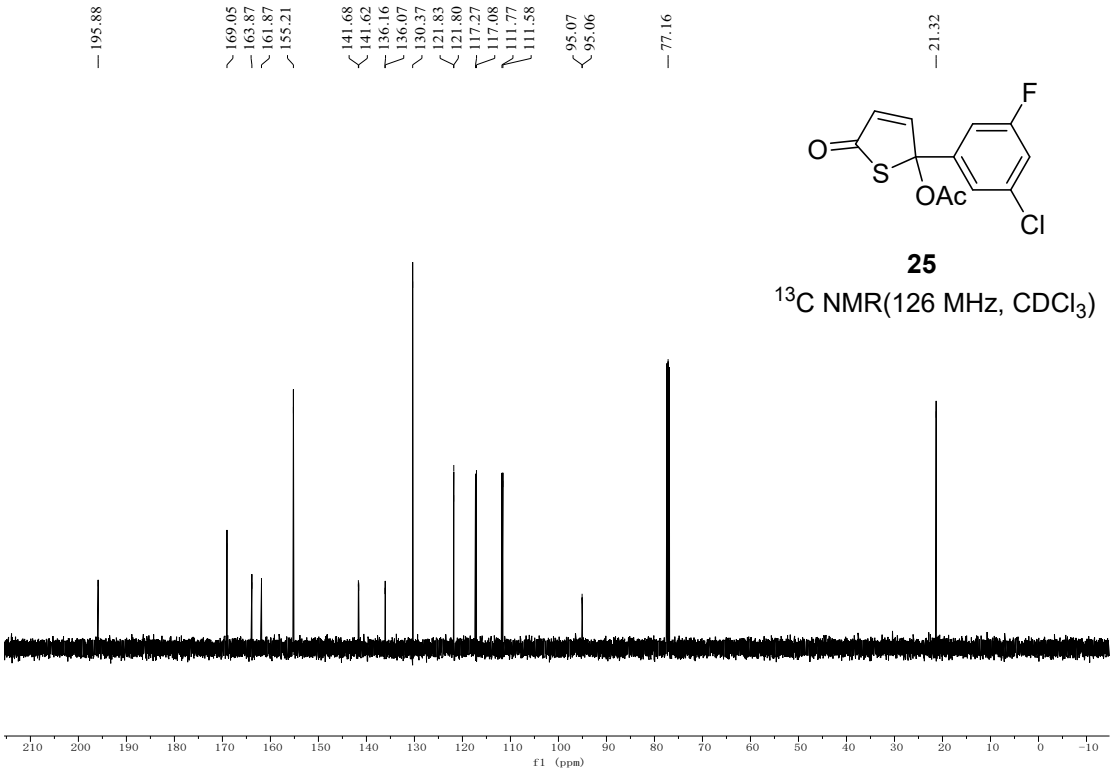
24

^{19}F NMR(471 MHz, $CDCl_3$)



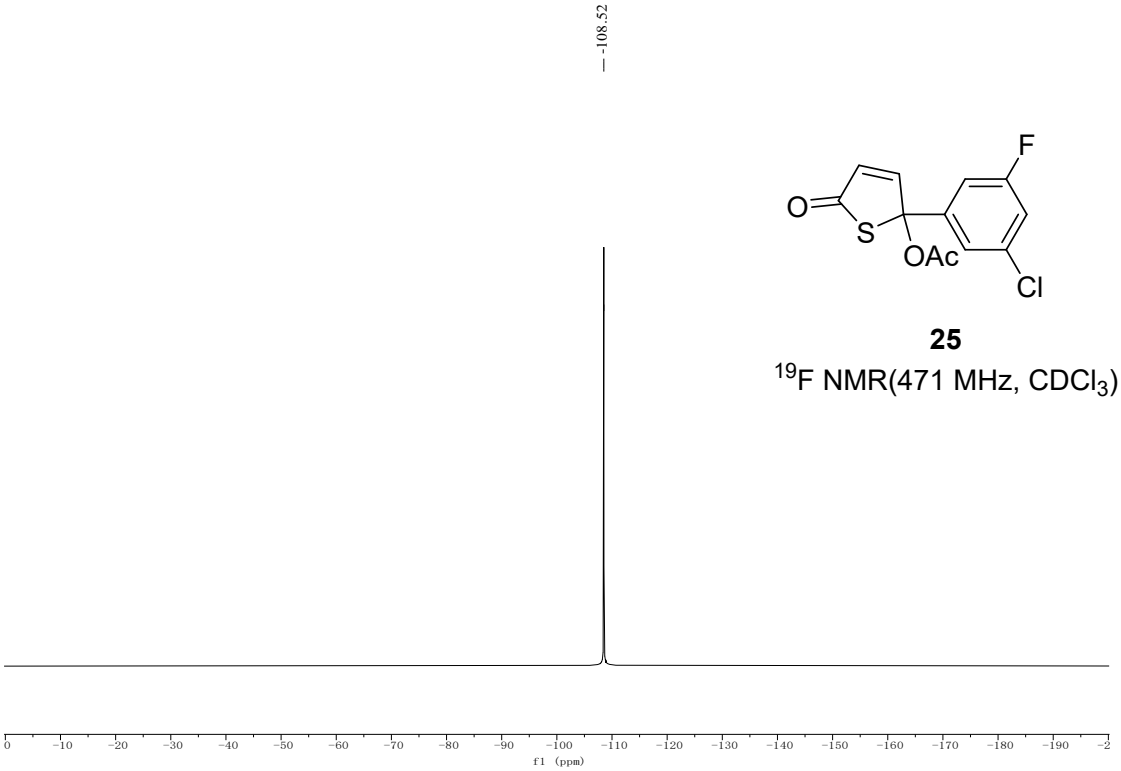
25

^{1}H NMR(500 MHz, $CDCl_3$)



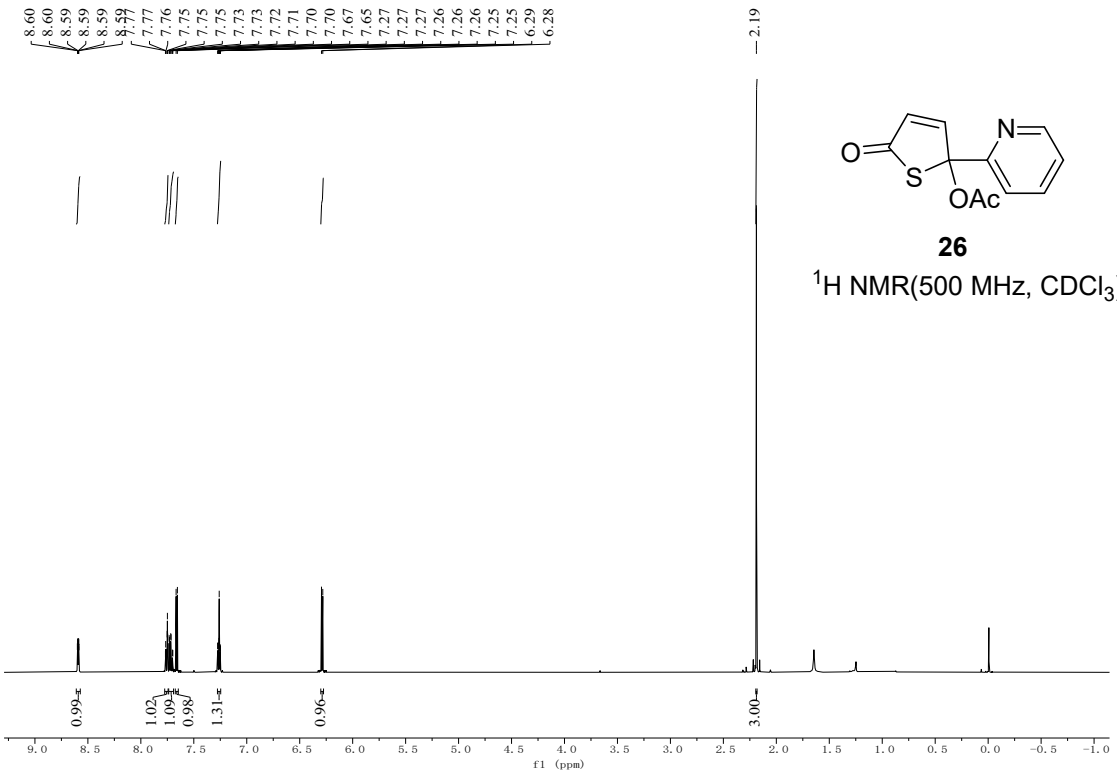
25

^{13}C NMR(126 MHz, $CDCl_3$)



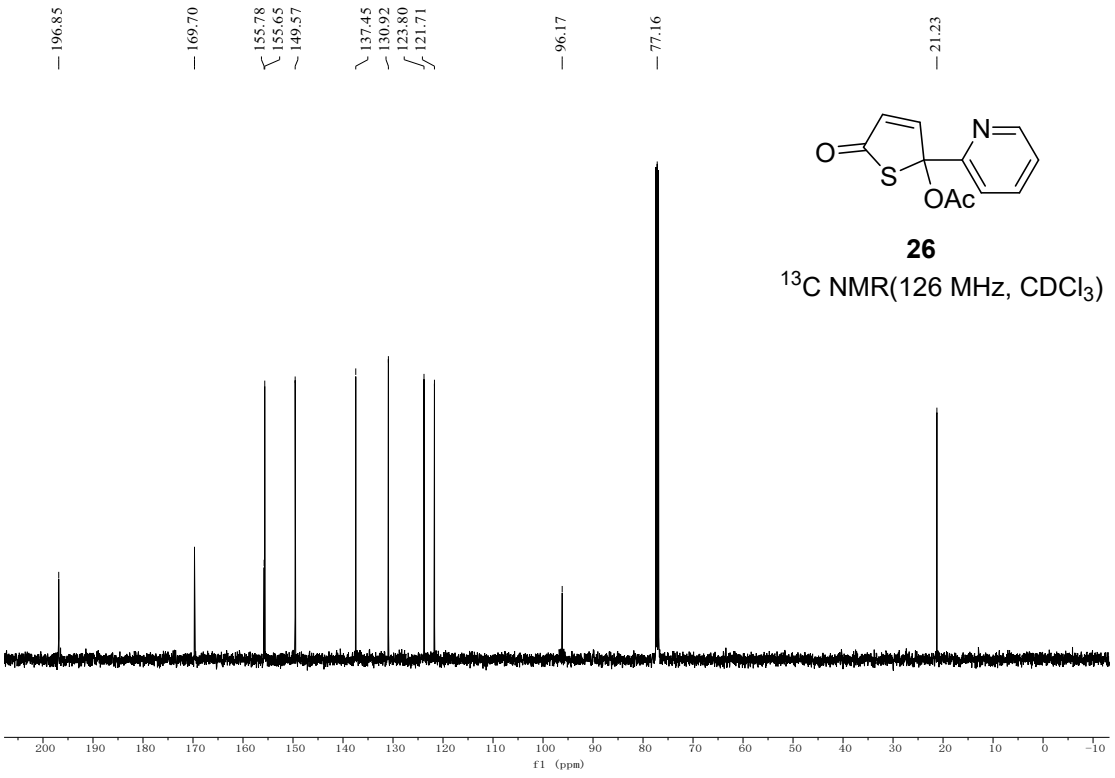
25

^{19}F NMR(471 MHz, $CDCl_3$)



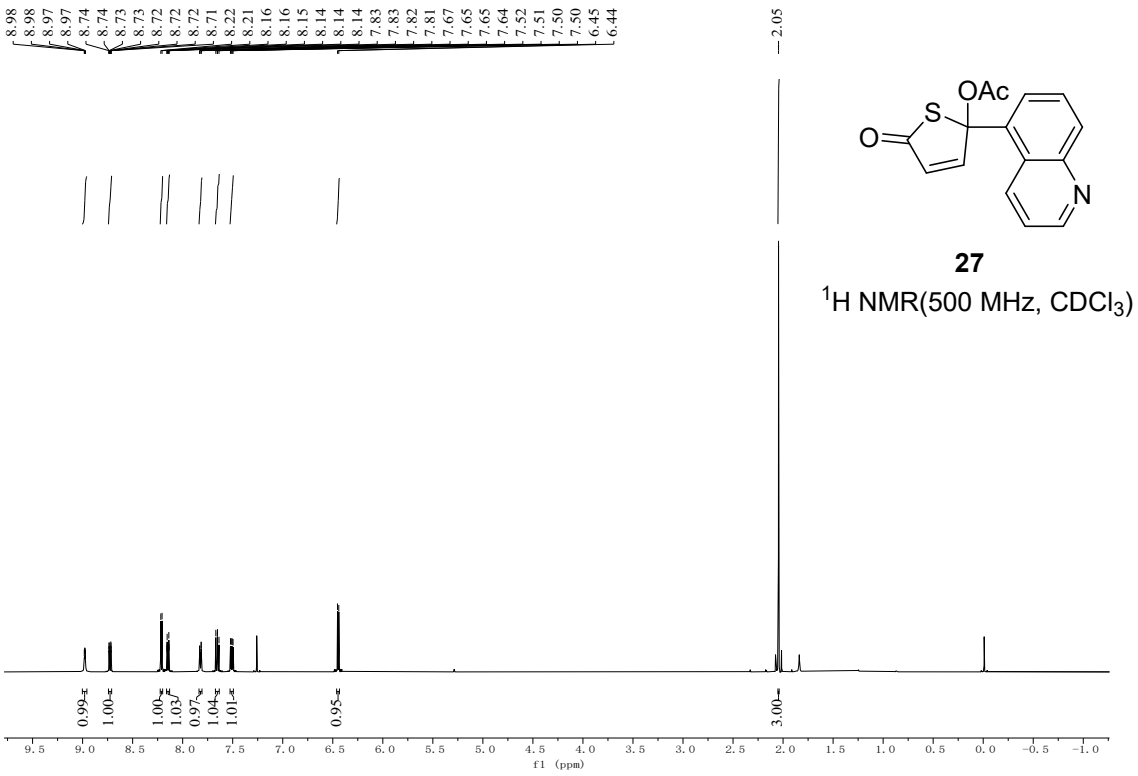
26

^{1}H NMR(500 MHz, $CDCl_3$)



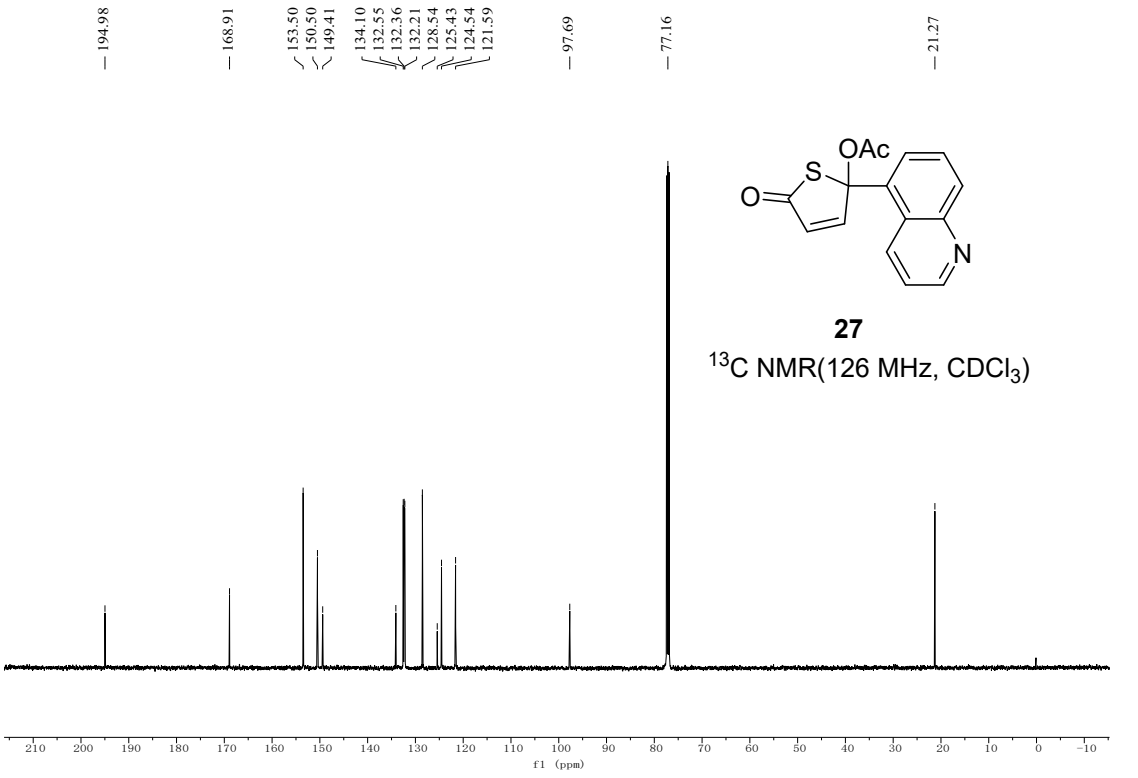
26

^{13}C NMR(126 MHz, $CDCl_3$)



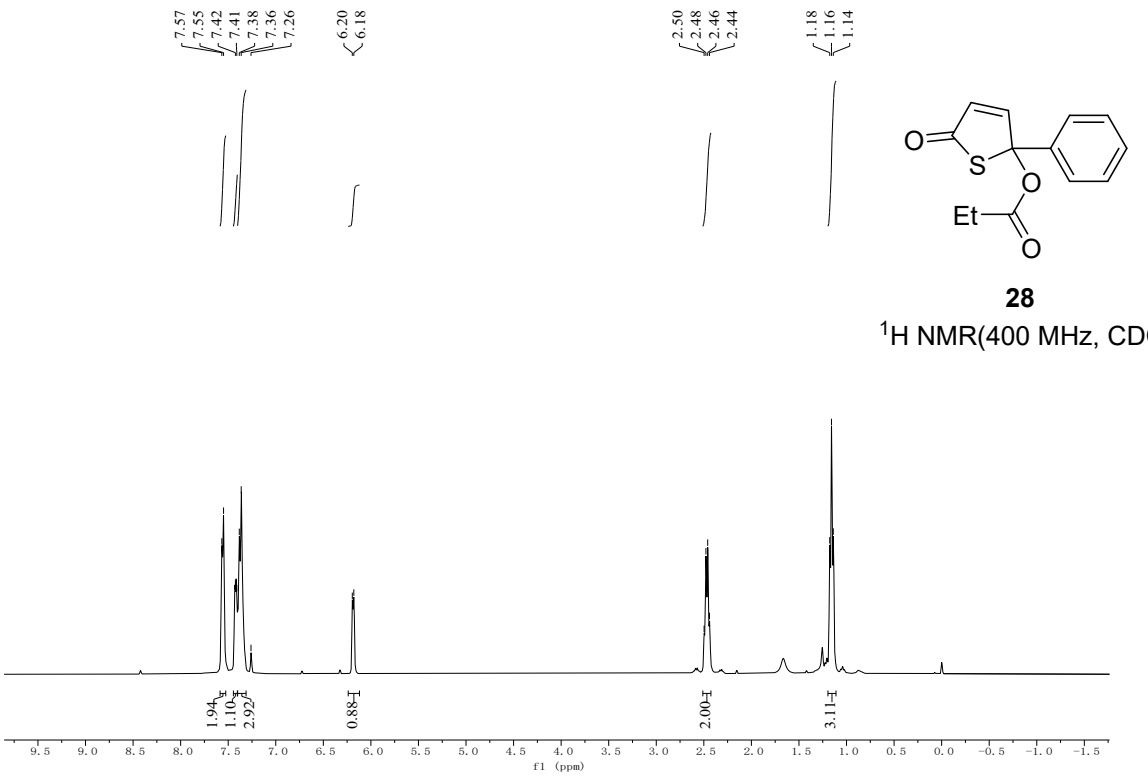
27

^{1}H NMR(500 MHz, $CDCl_3$)



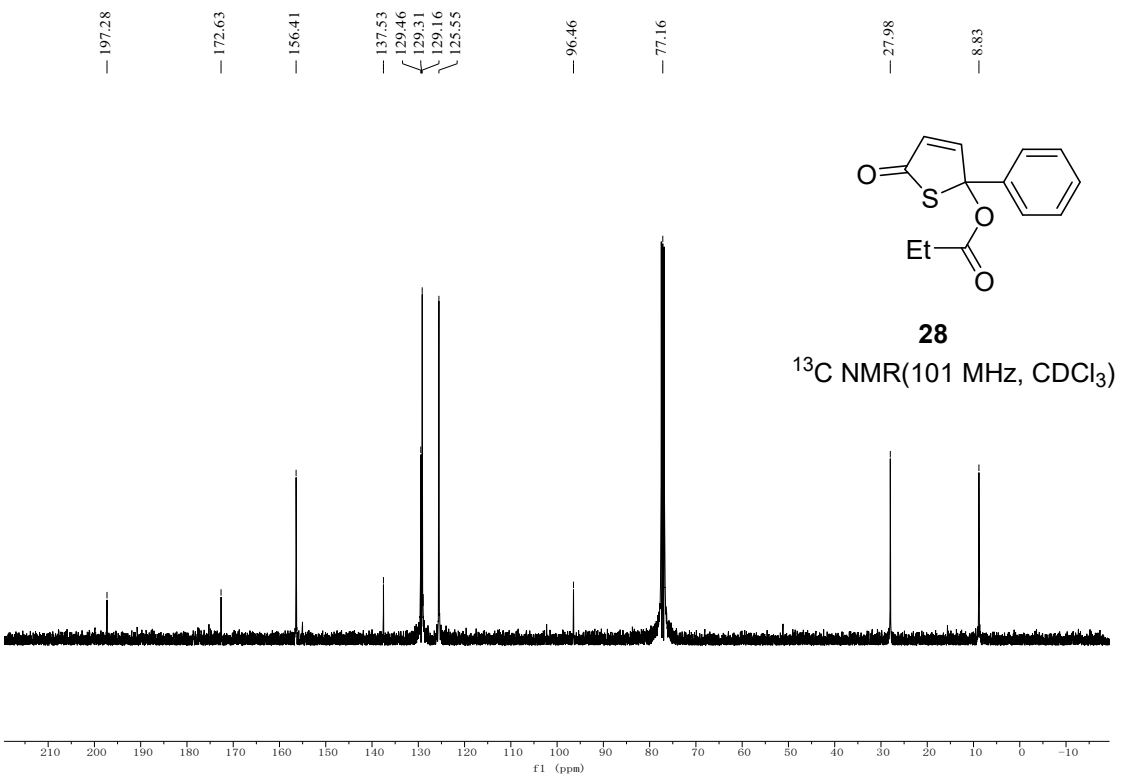
27

^{13}C NMR(126 MHz, $CDCl_3$)



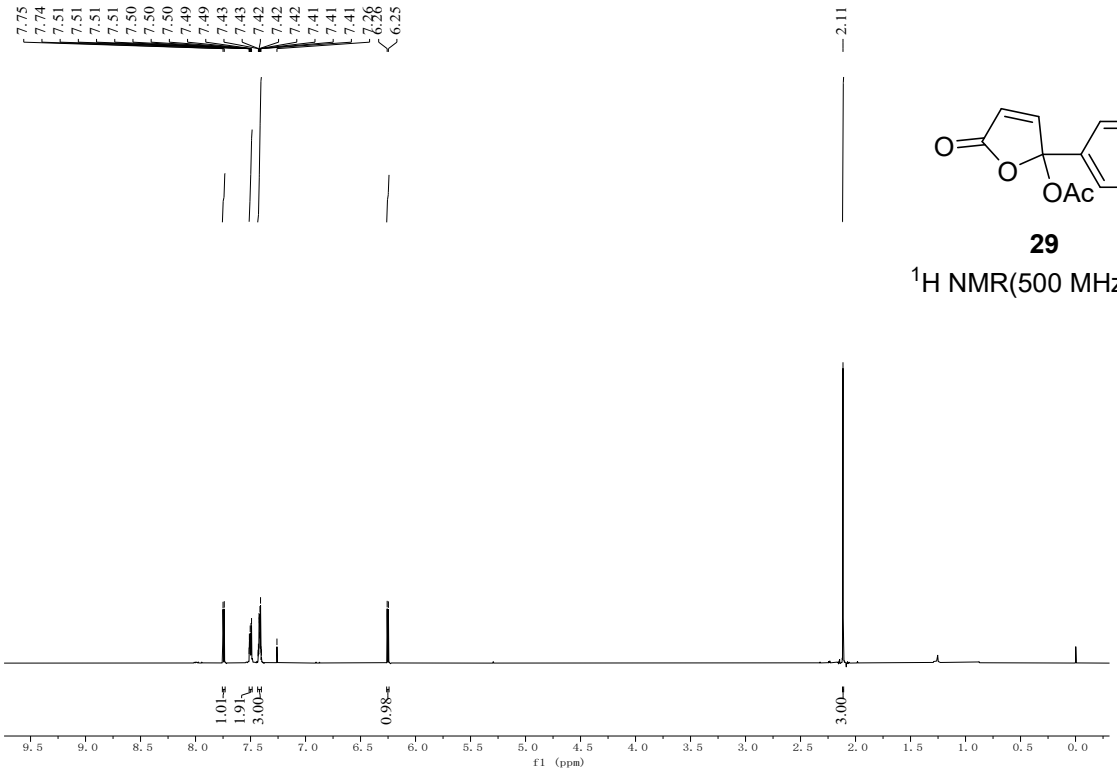
28

^{1}H NMR(400 MHz, $CDCl_3$)



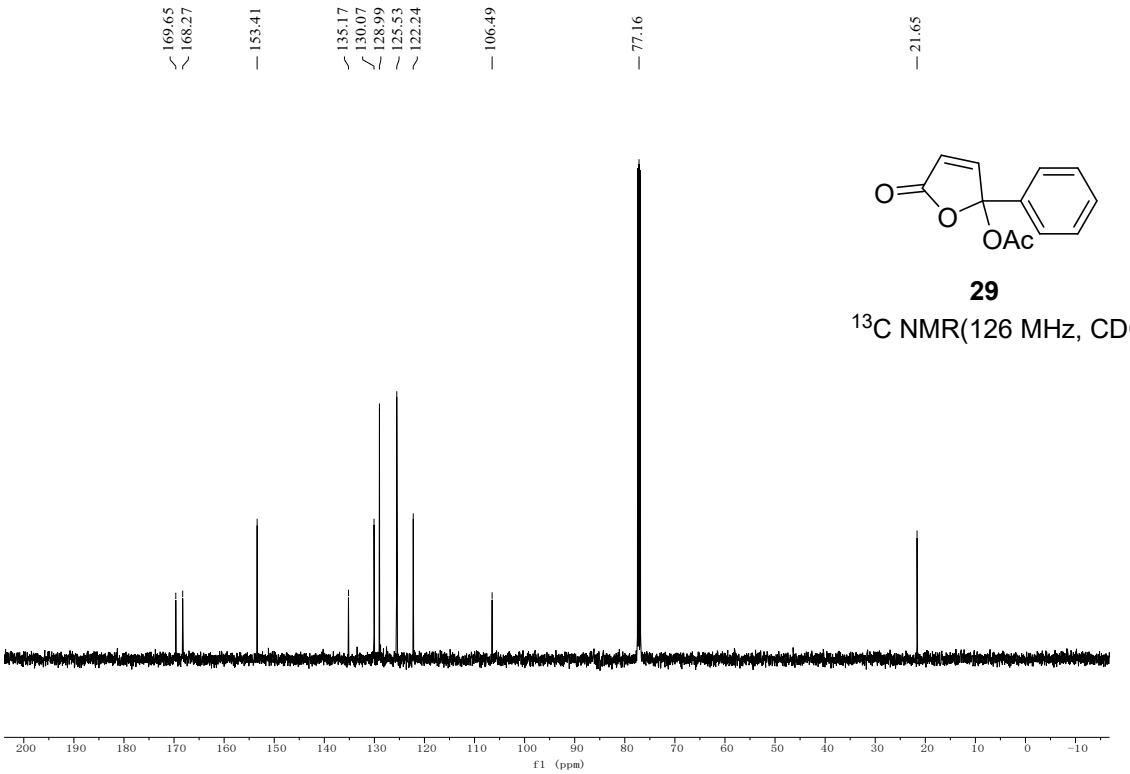
28

^{13}C NMR(101 MHz, $CDCl_3$)



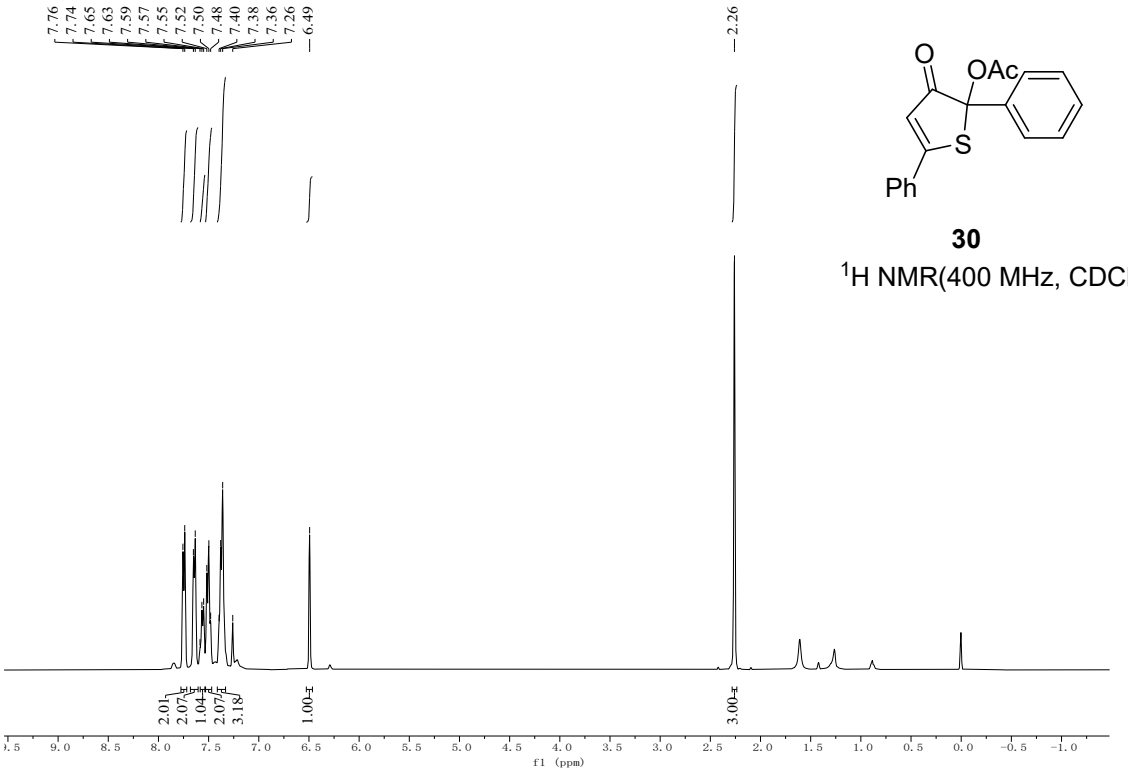
29

^{1}H NMR(500 MHz, $CDCl_3$)



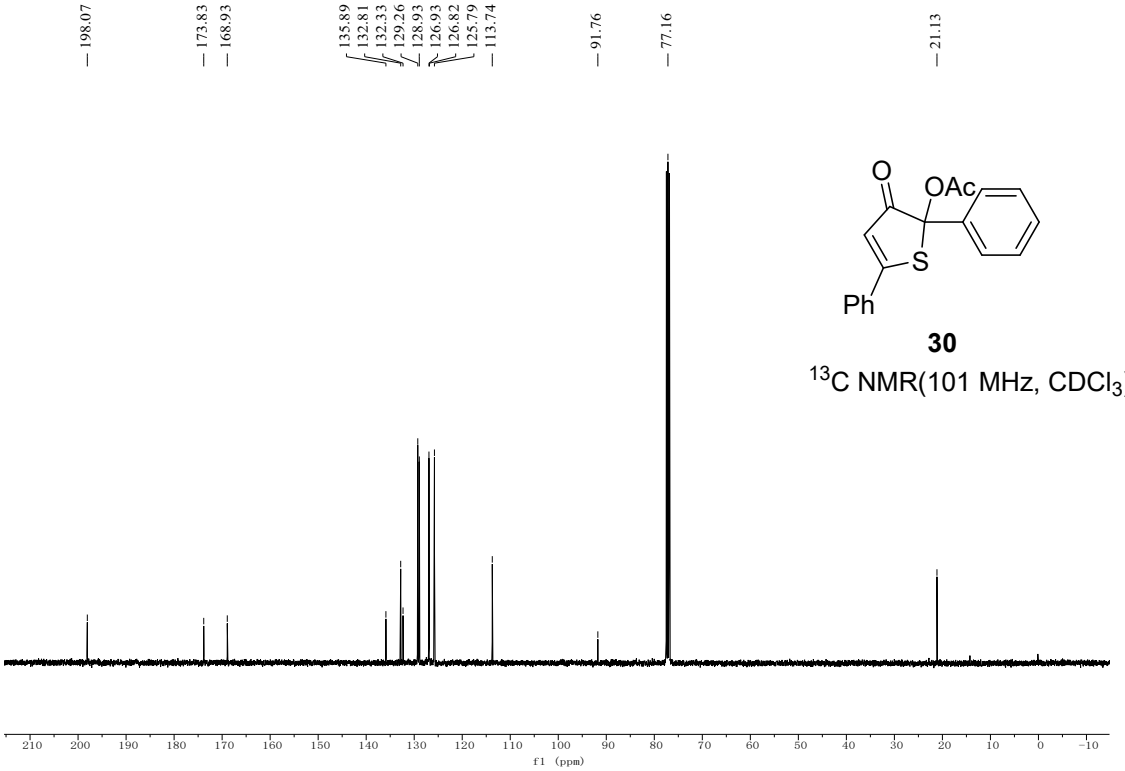
29

^{13}C NMR(126 MHz, $CDCl_3$)



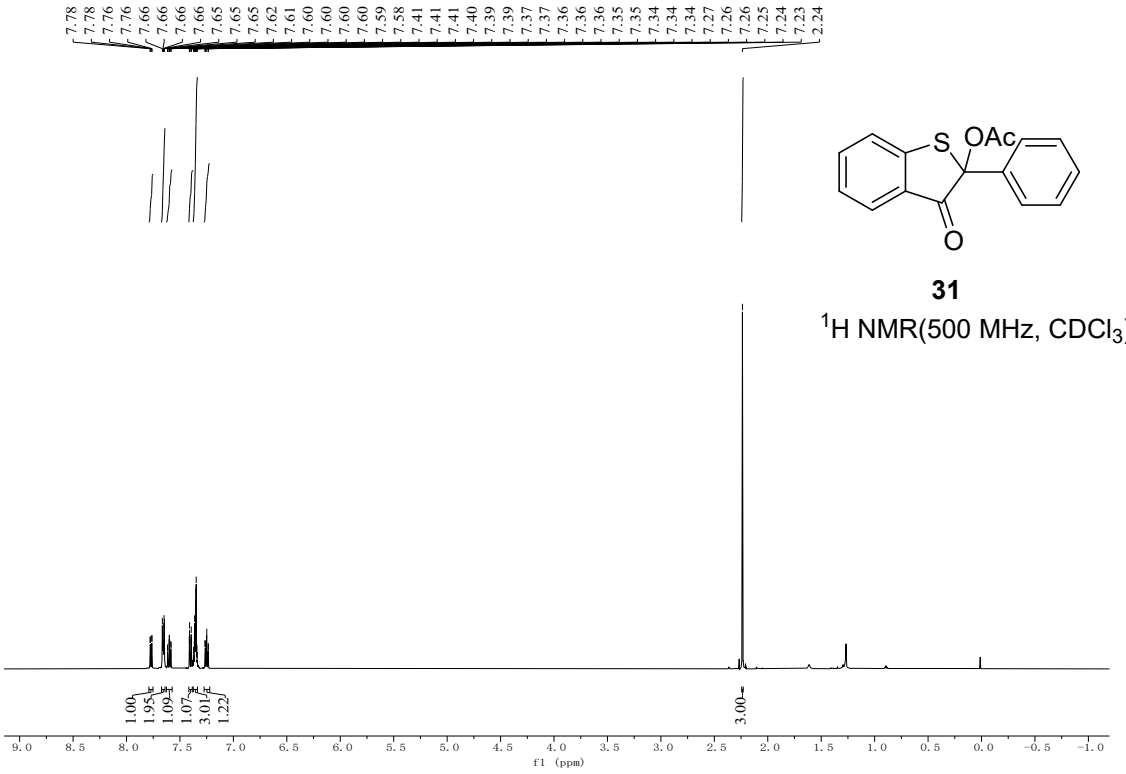
30

^{1}H NMR(400 MHz, $CDCl_3$)



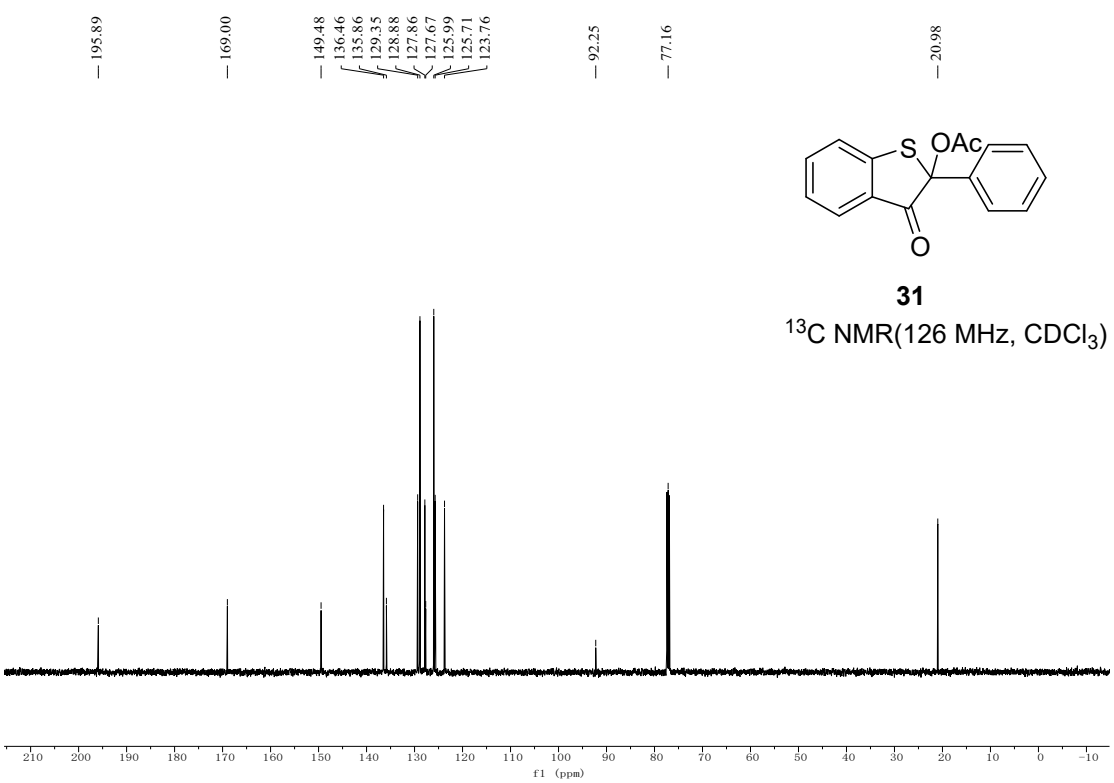
30

^{13}C NMR(101 MHz, $CDCl_3$)



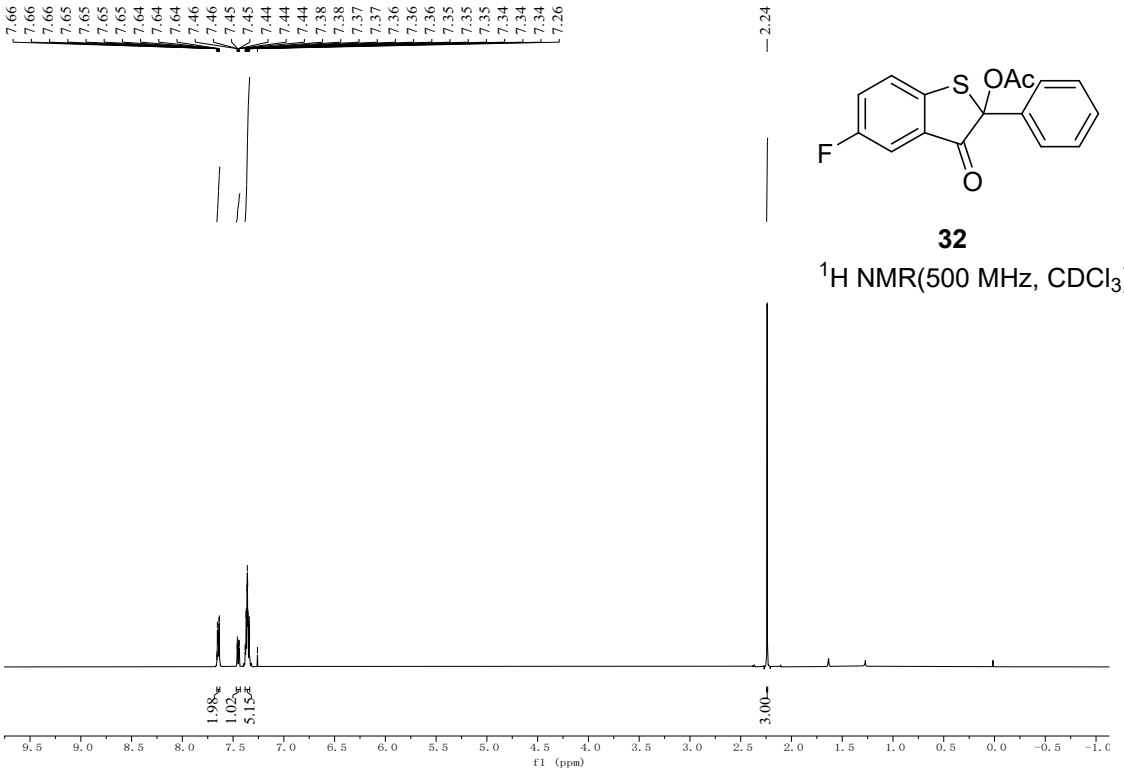
31

^{1}H NMR(500 MHz, $CDCl_3$)



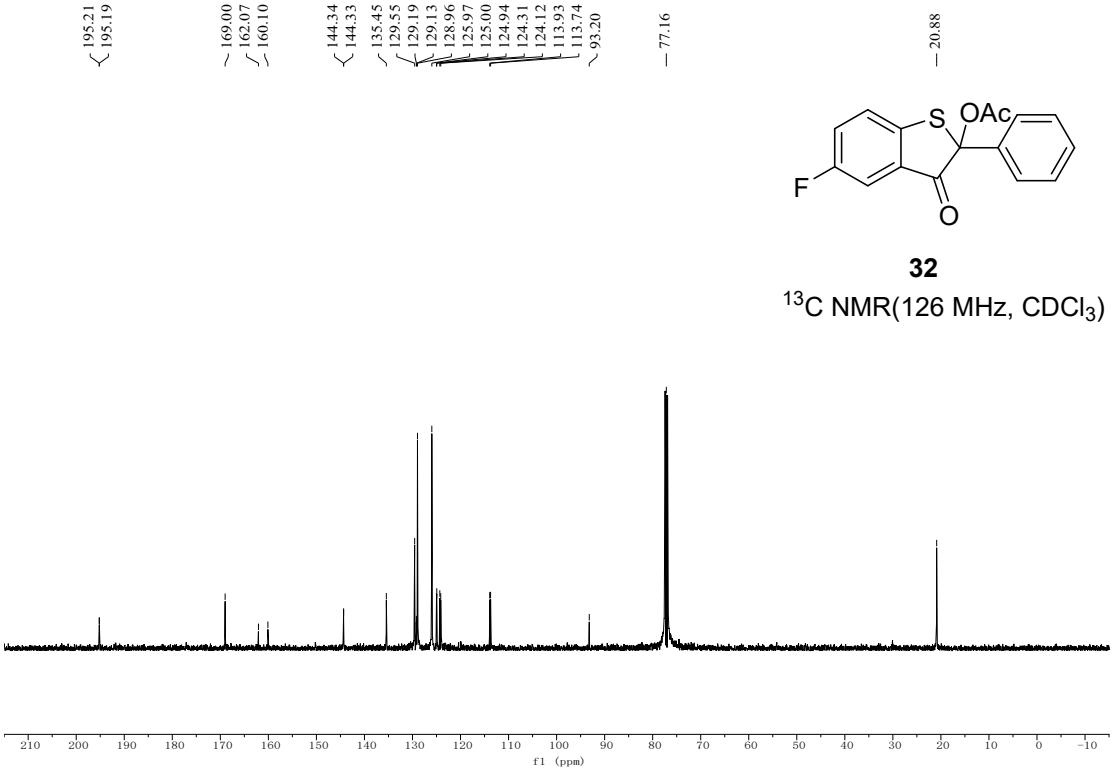
31

^{13}C NMR(126 MHz, $CDCl_3$)



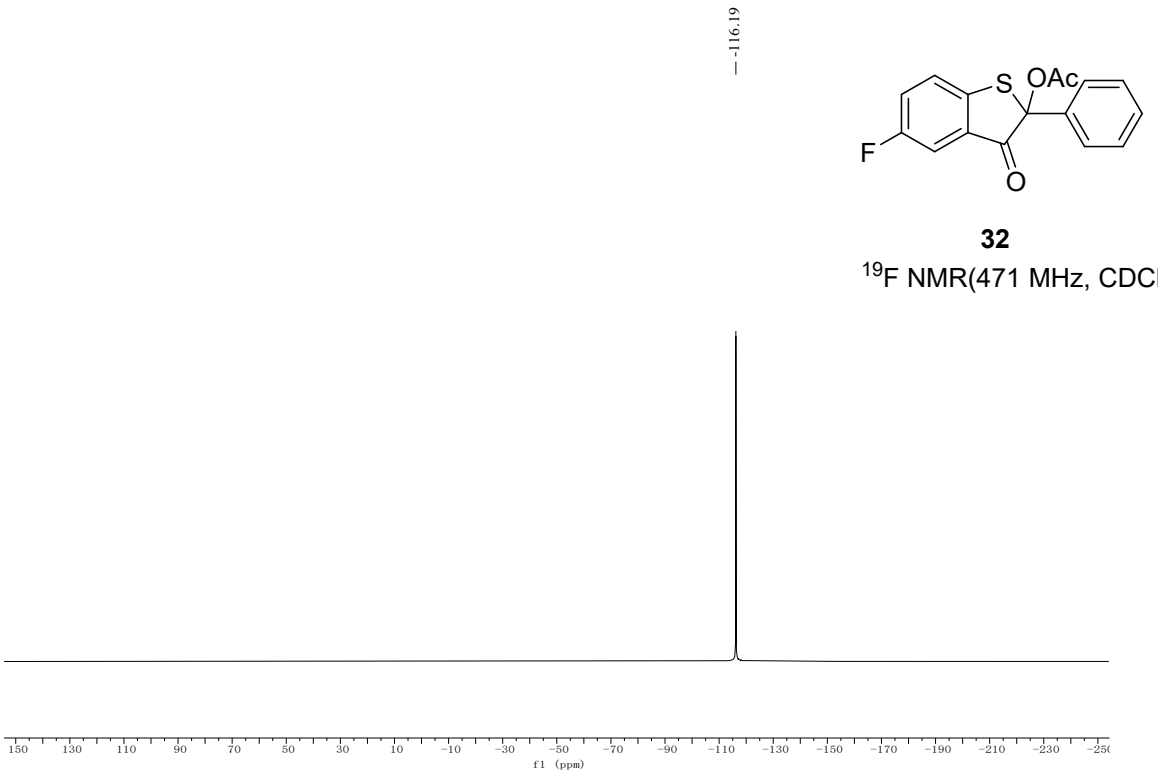
32

^{1}H NMR(500 MHz, $CDCl_3$)



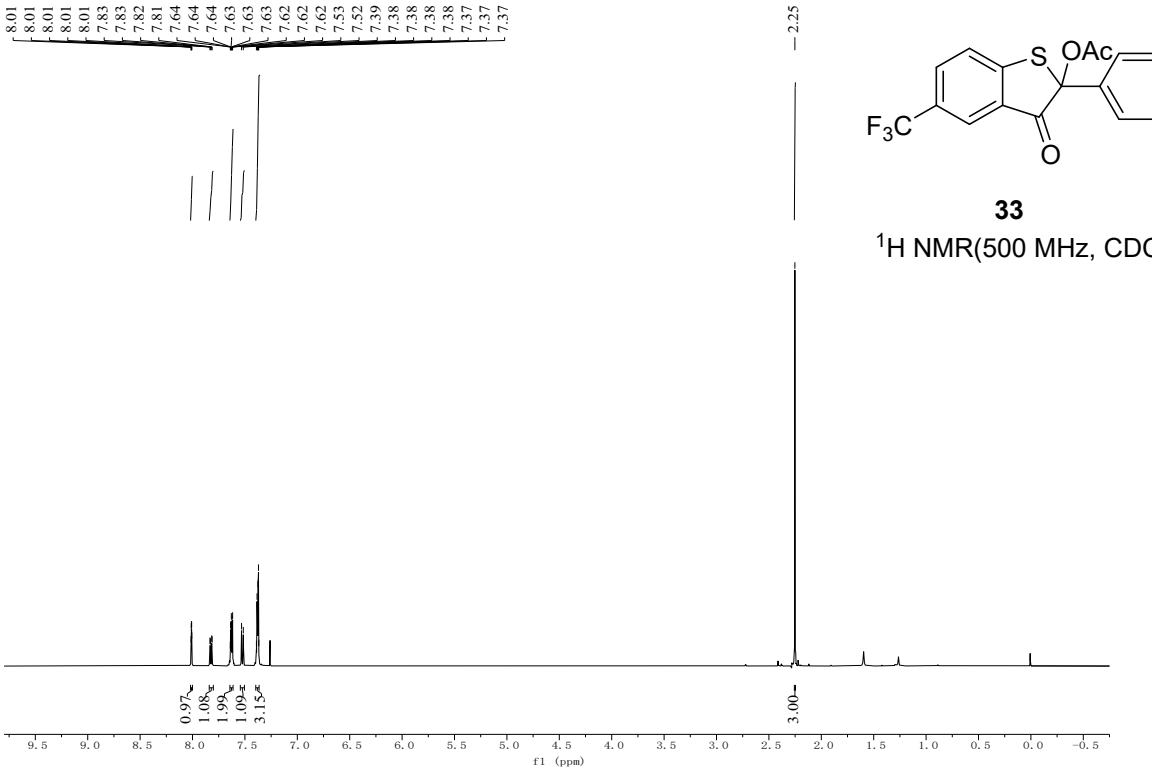
32

^{13}C NMR(126 MHz, $CDCl_3$)



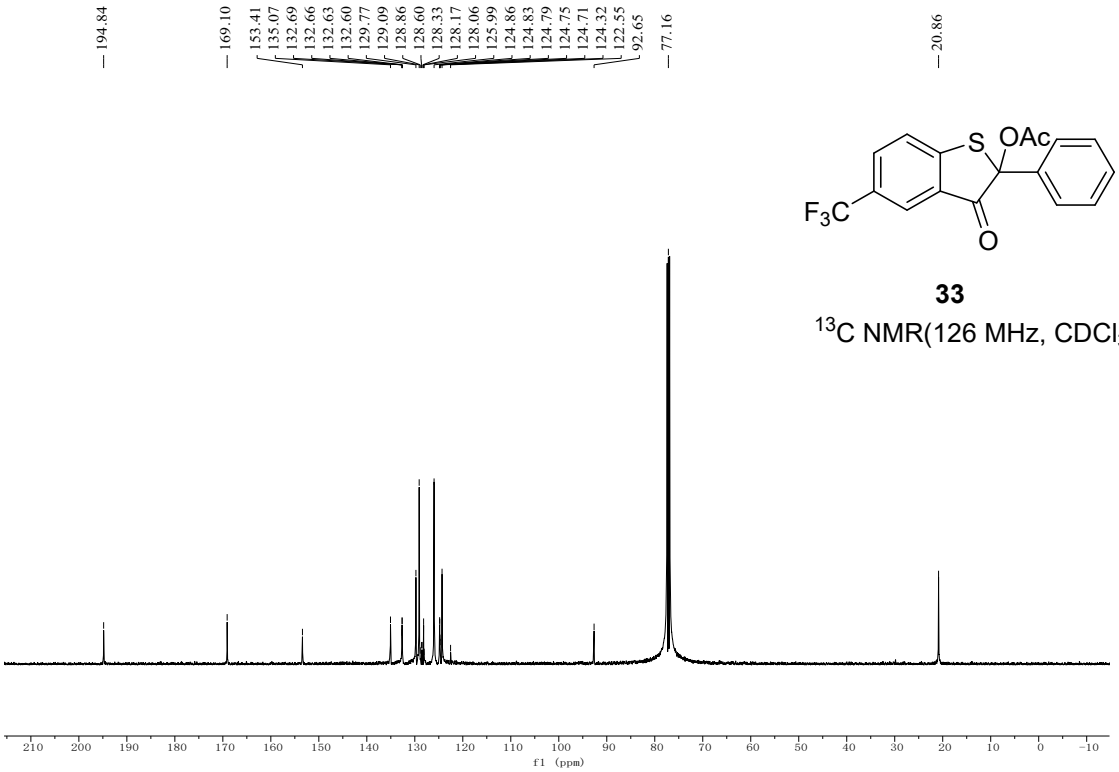
32

^{19}F NMR(471 MHz, $CDCl_3$)



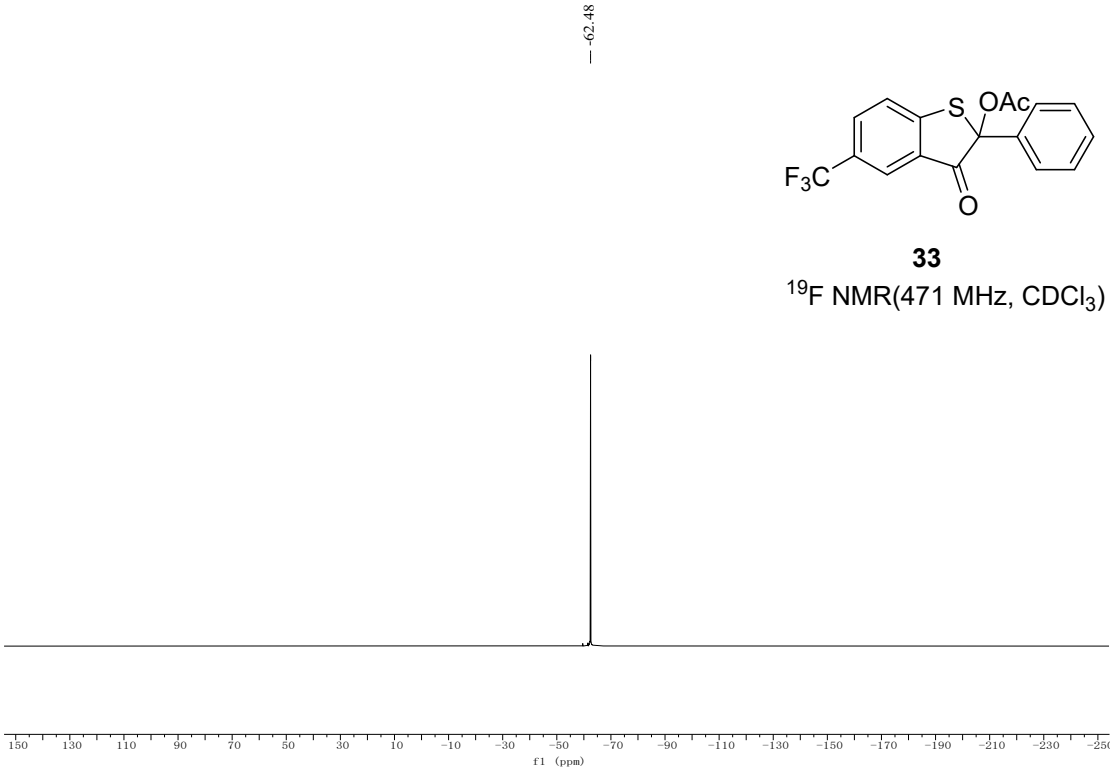
33

^{1}H NMR(500 MHz, $CDCl_3$)



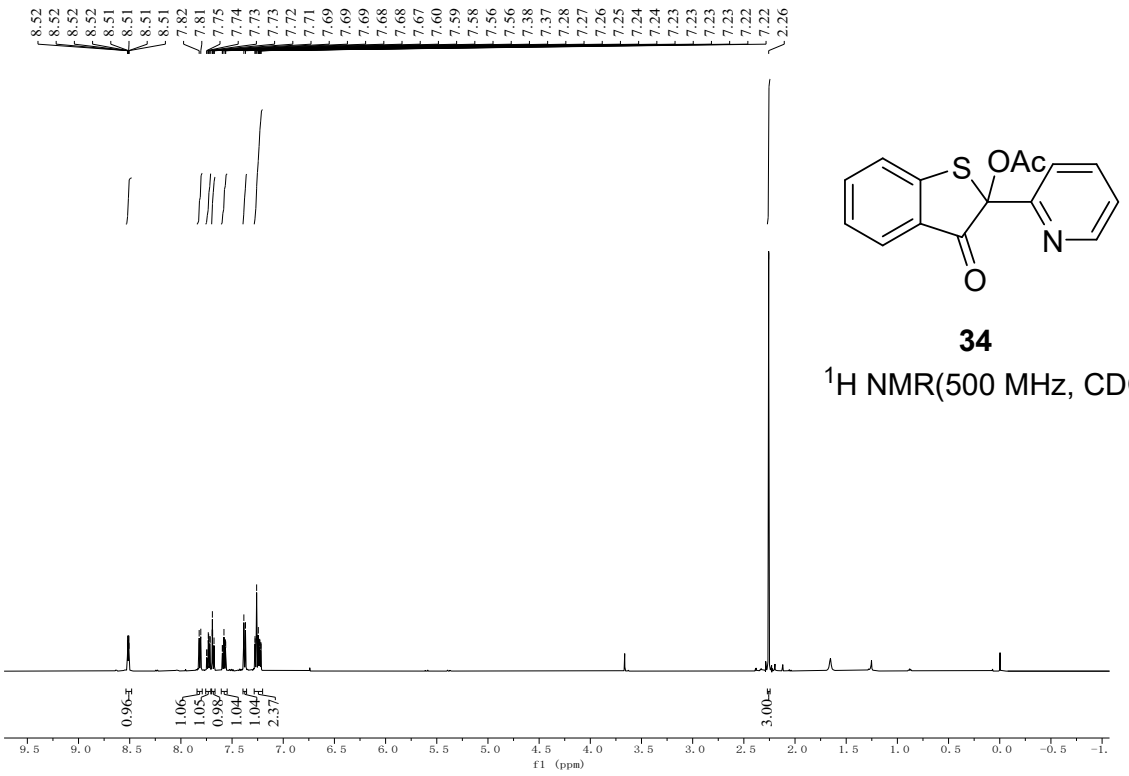
33

^{13}C NMR(126 MHz, $CDCl_3$)



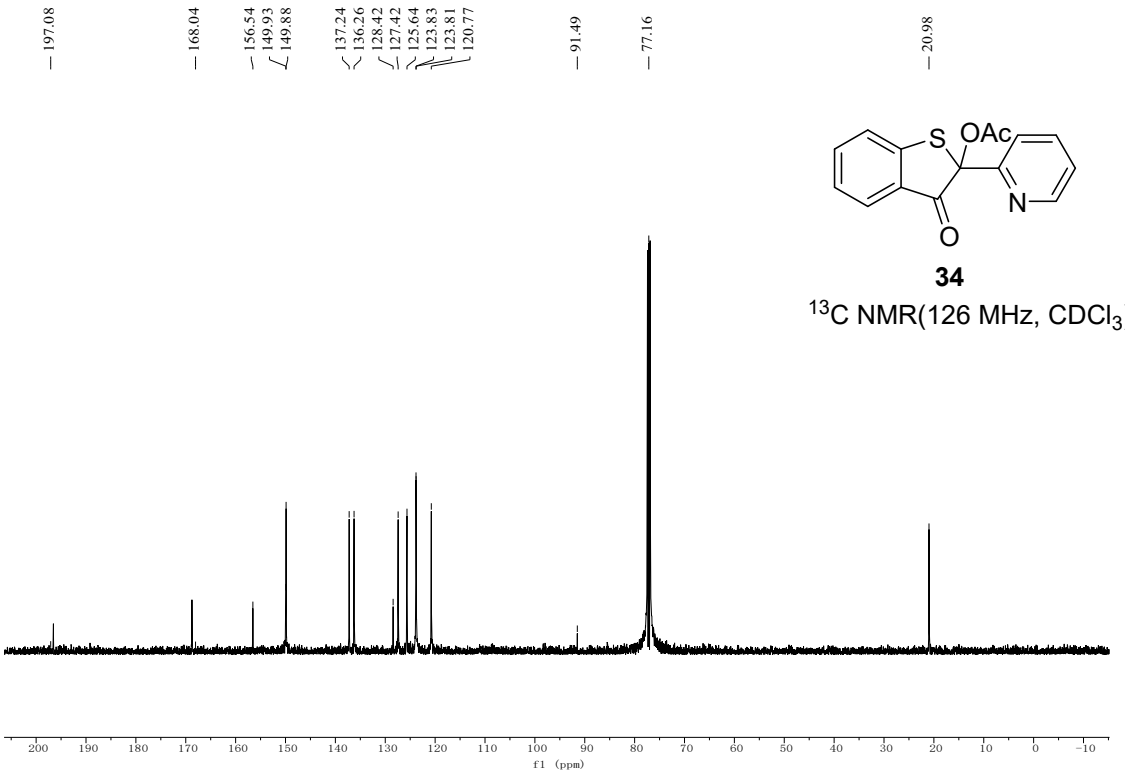
33

^{19}F NMR(471 MHz, $CDCl_3$)



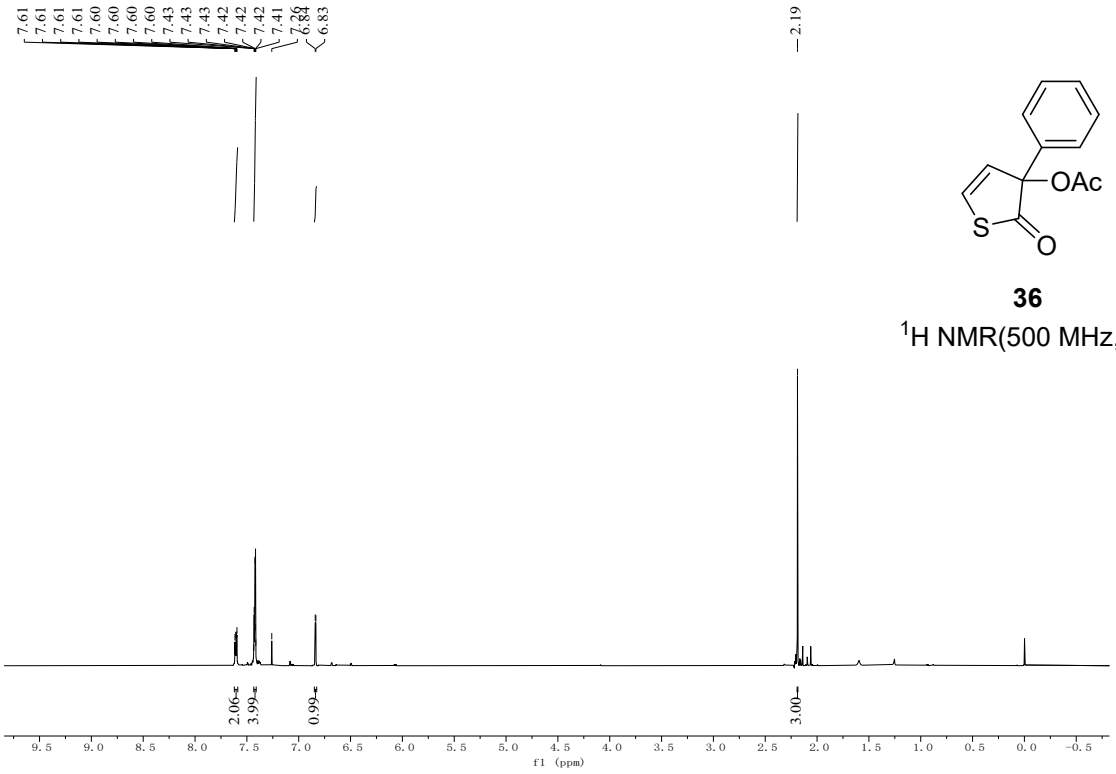
34

^{1}H NMR(500 MHz, $CDCl_3$)



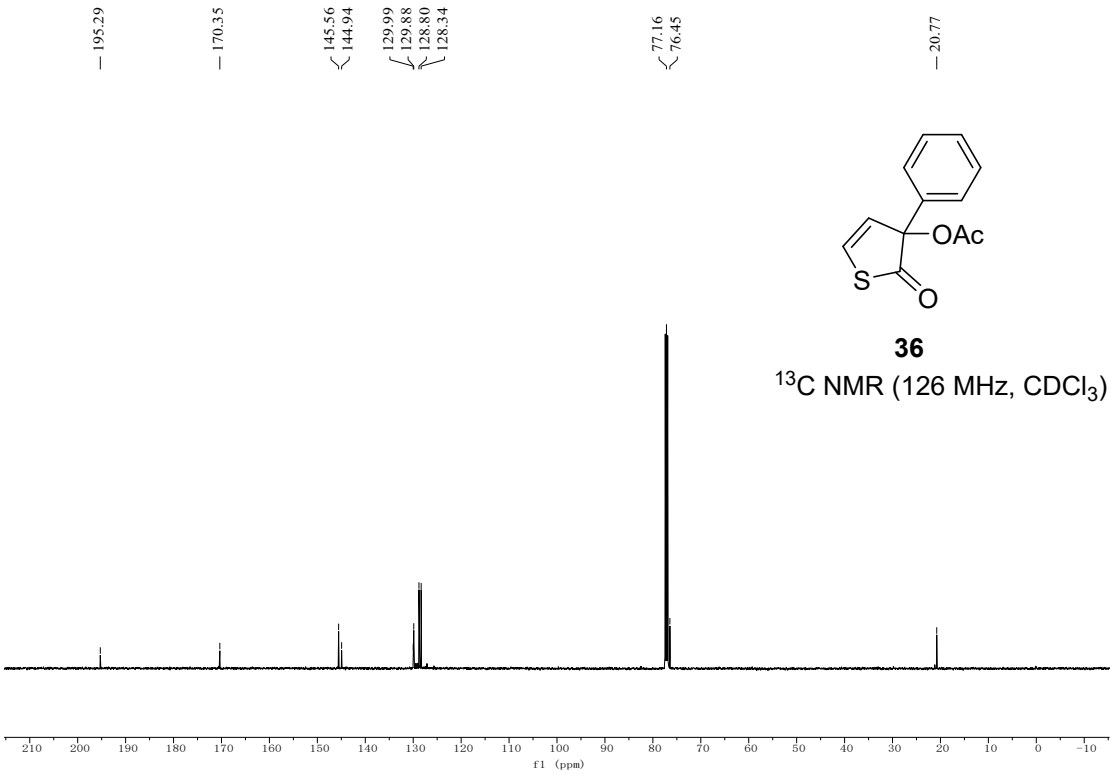
34

^{13}C NMR(126 MHz, $CDCl_3$)



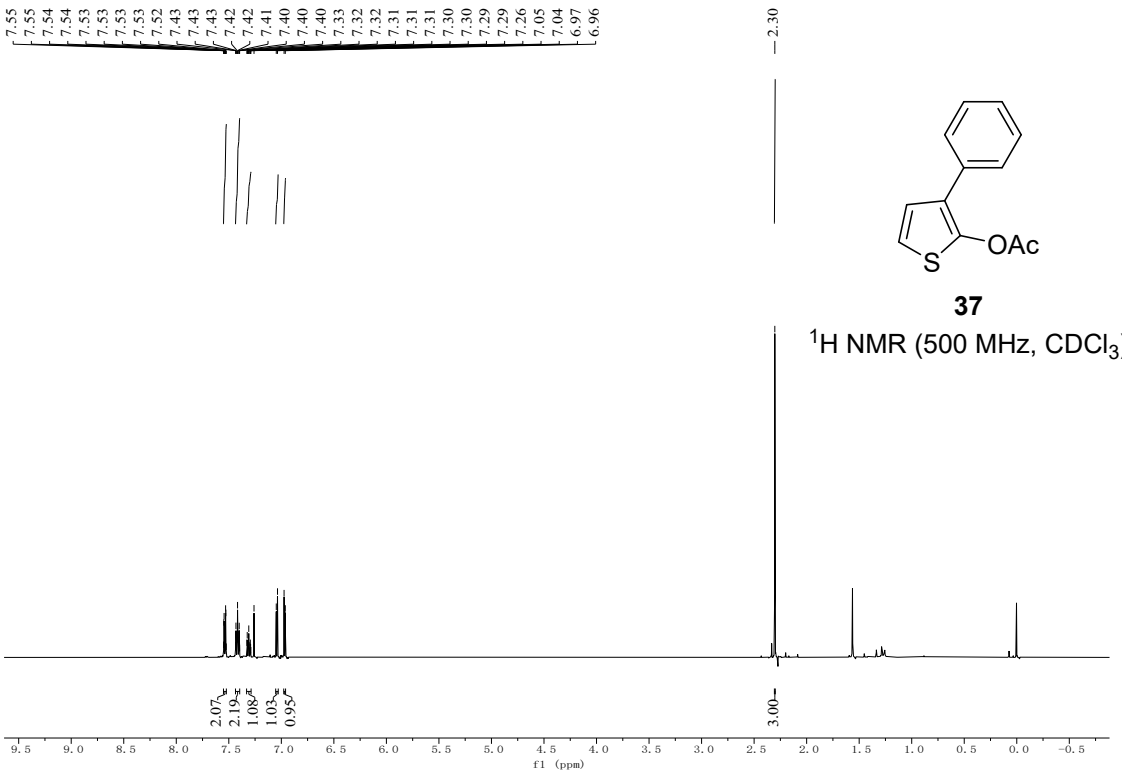
36

^{1}H NMR(500 MHz, $CDCl_3$)



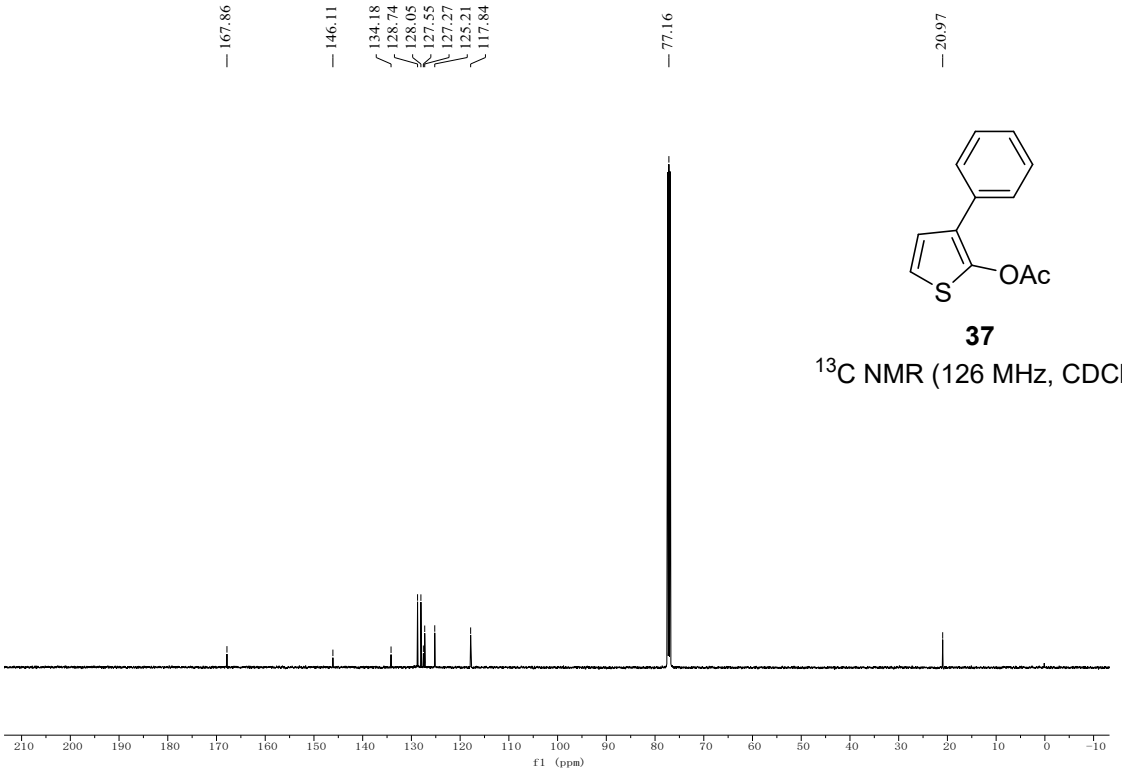
36

^{13}C NMR (126 MHz, $CDCl_3$)



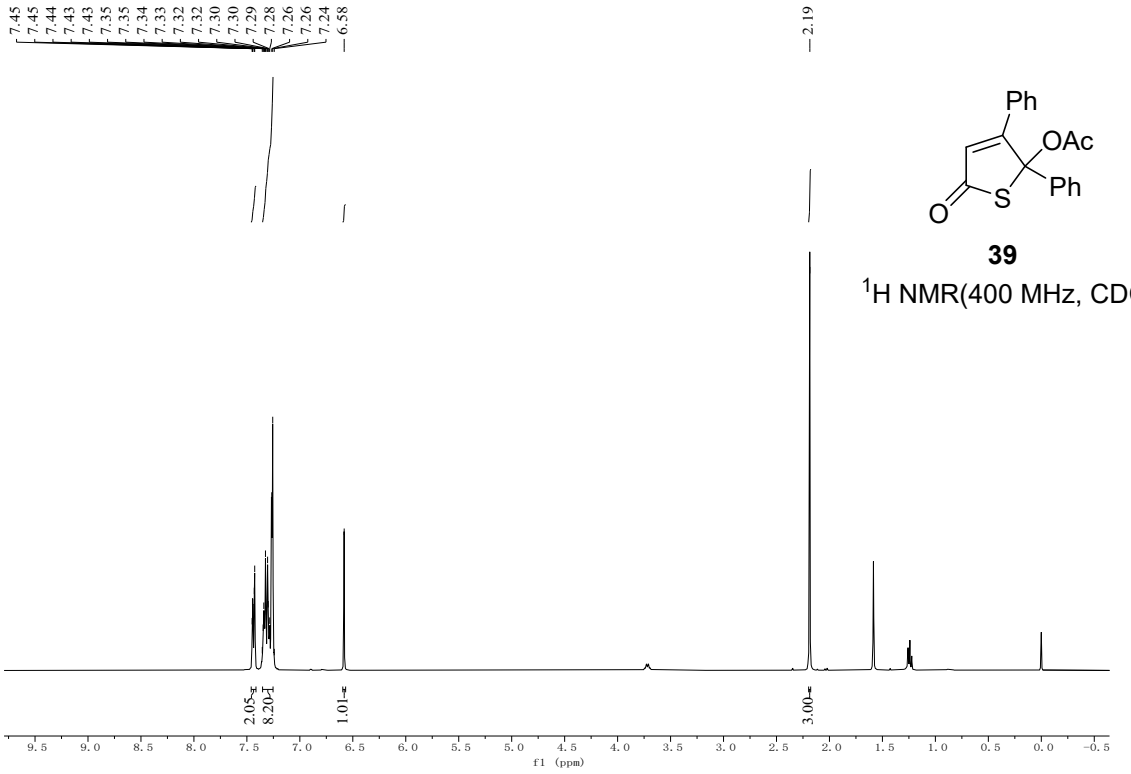
37

^{1}H NMR (500 MHz, $CDCl_3$)



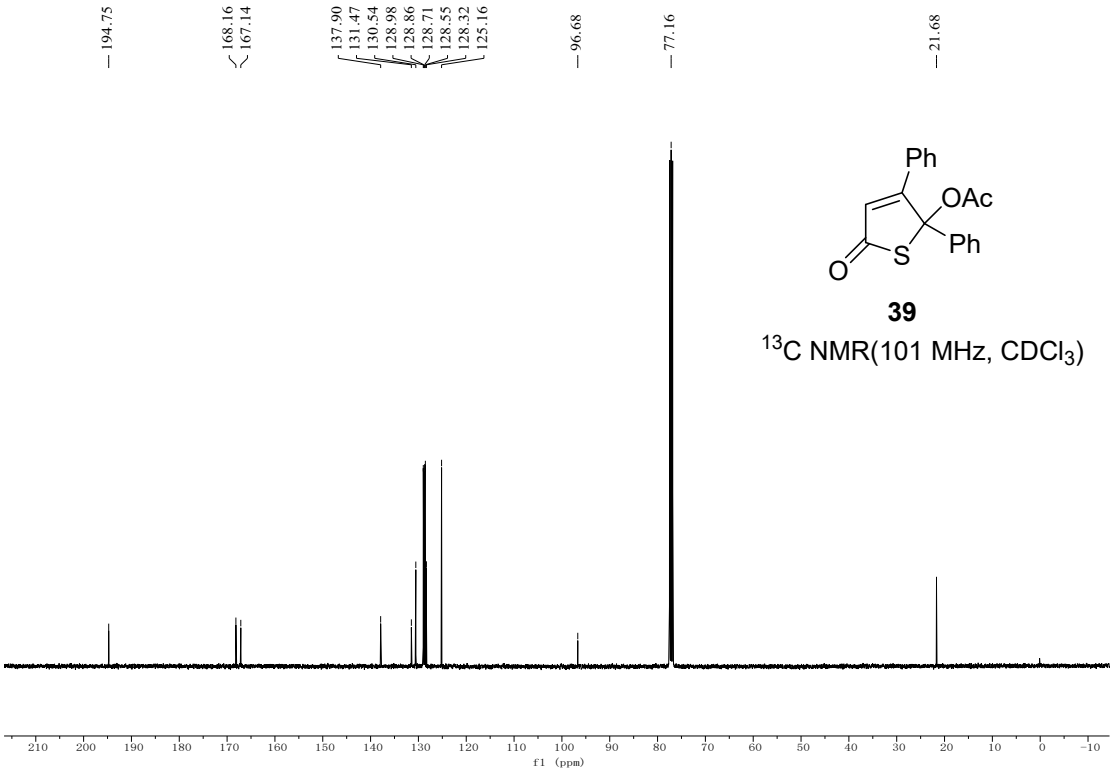
37

^{13}C NMR (126 MHz, $CDCl_3$)



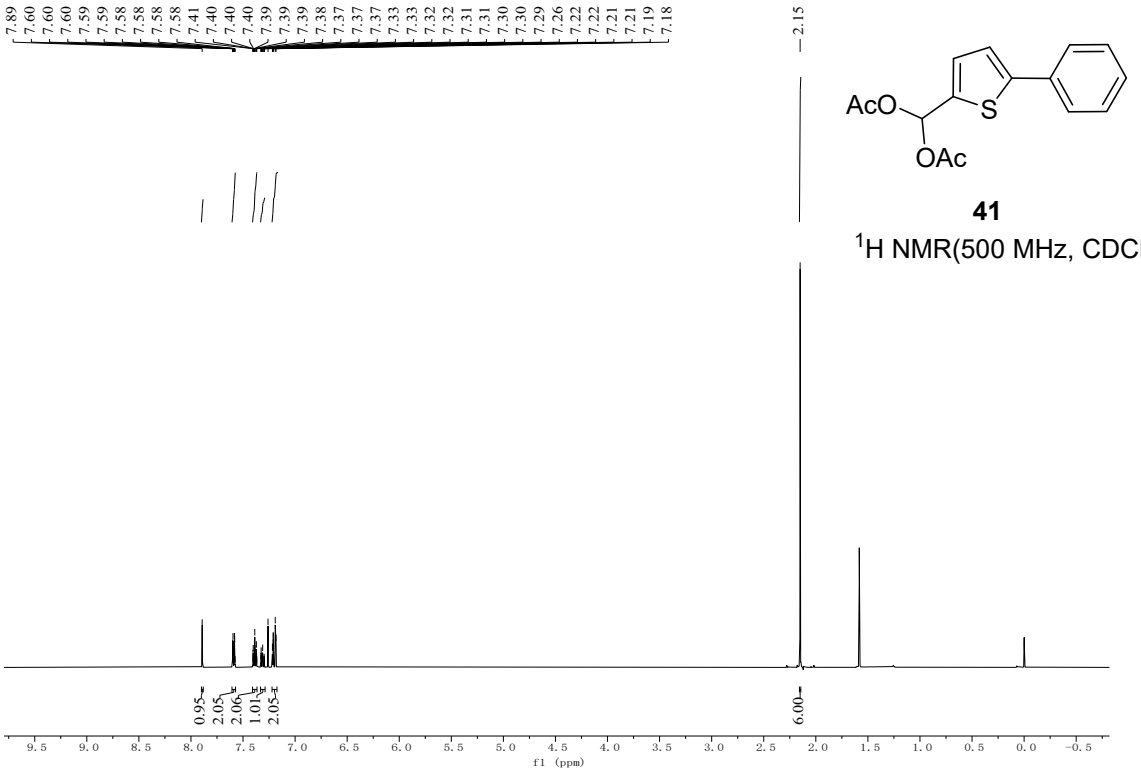
39

^{1}H NMR(400 MHz, $CDCl_3$)



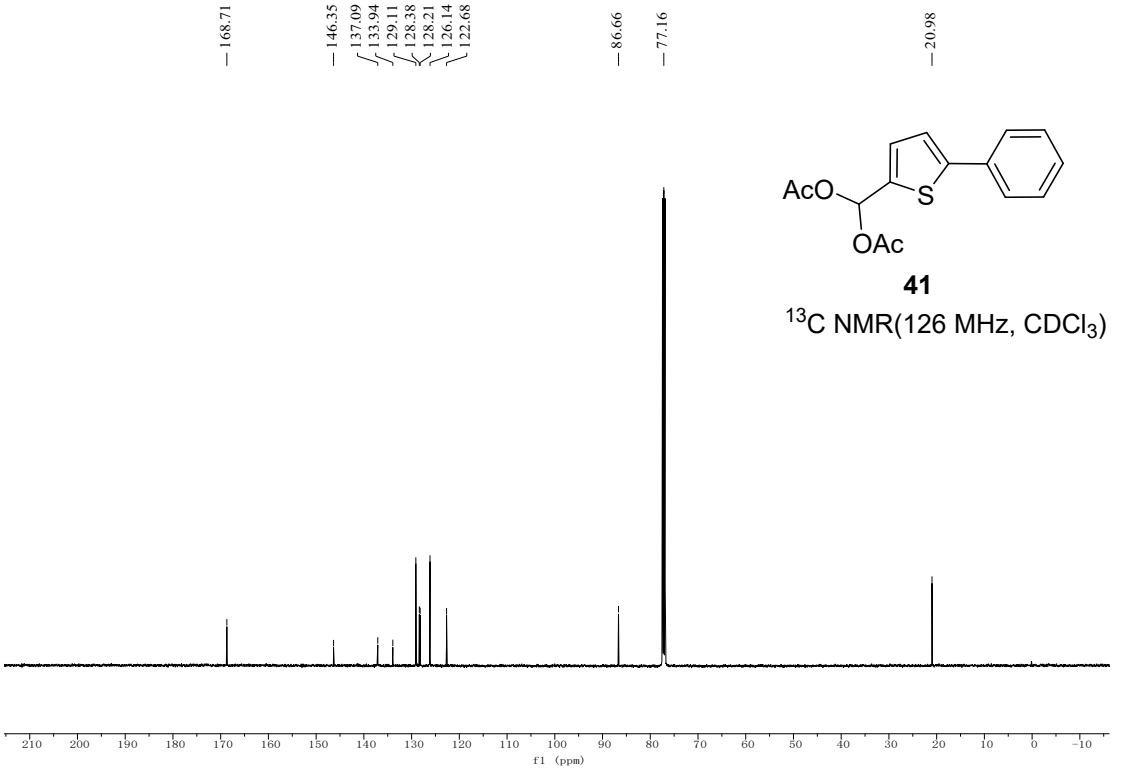
39

^{13}C NMR(101 MHz, $CDCl_3$)



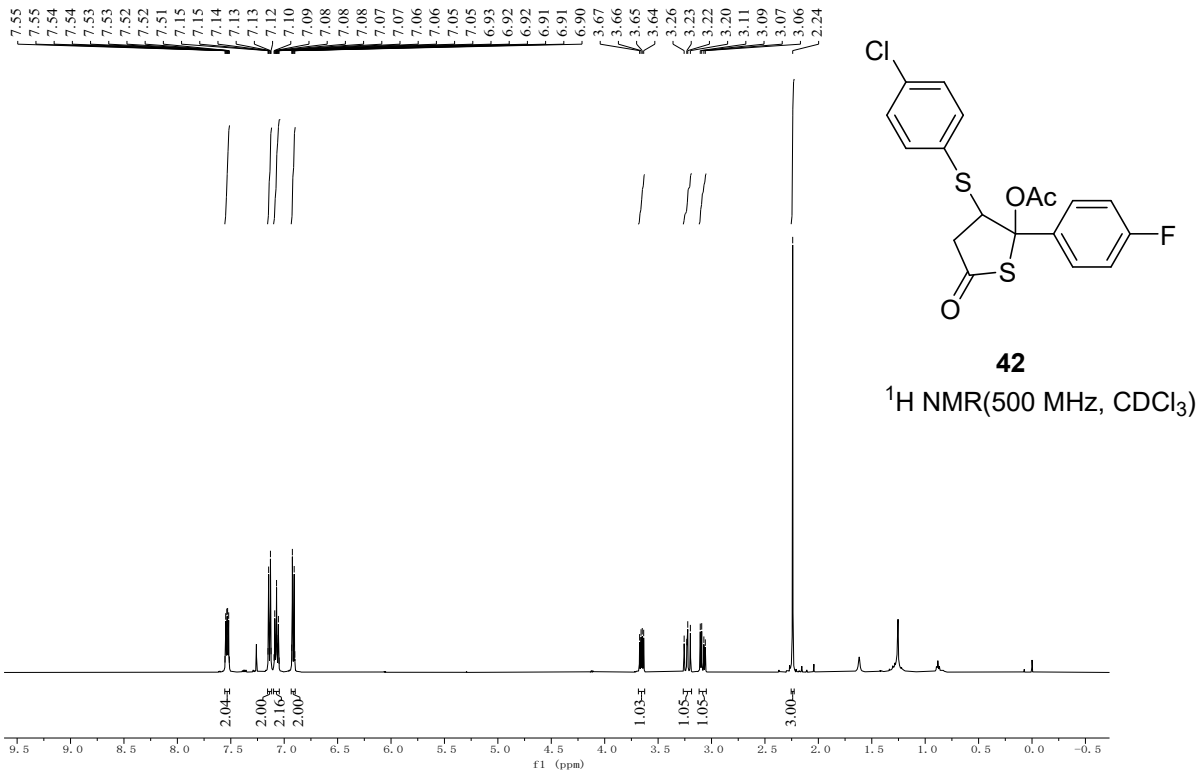
41

^{1}H NMR(500 MHz, $CDCl_3$)



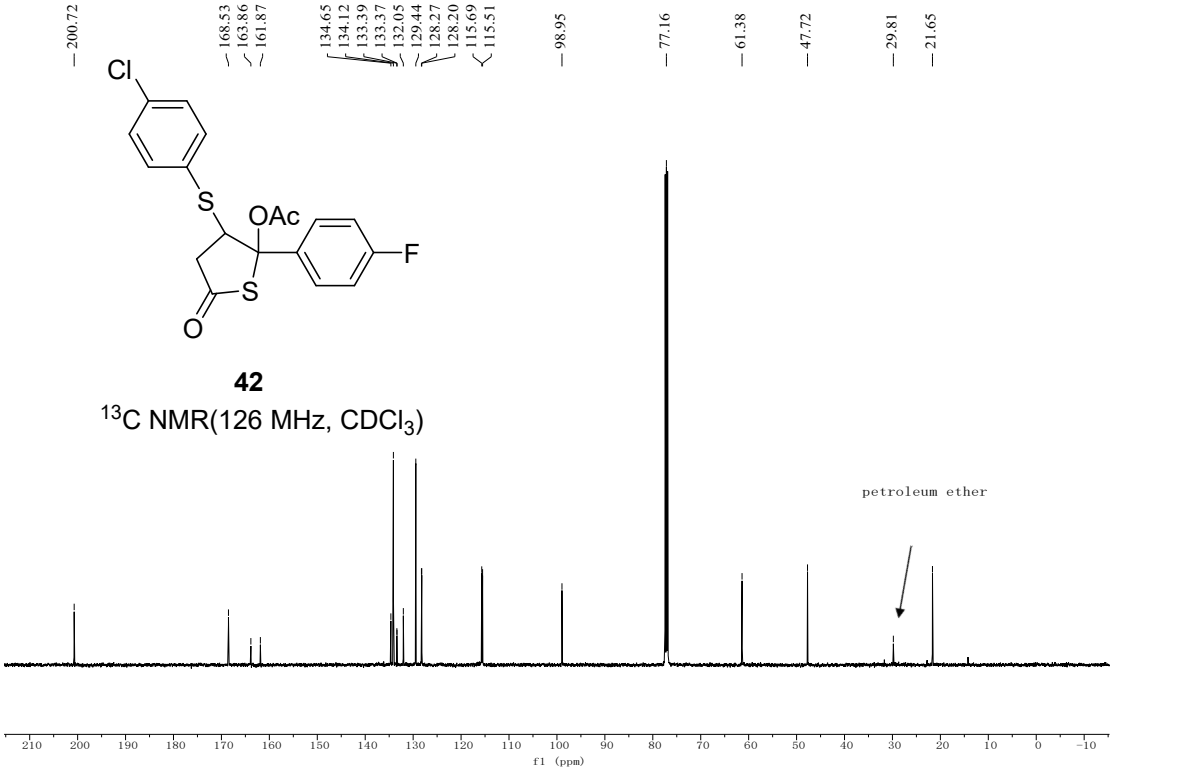
41

^{13}C NMR(126 MHz, $CDCl_3$)



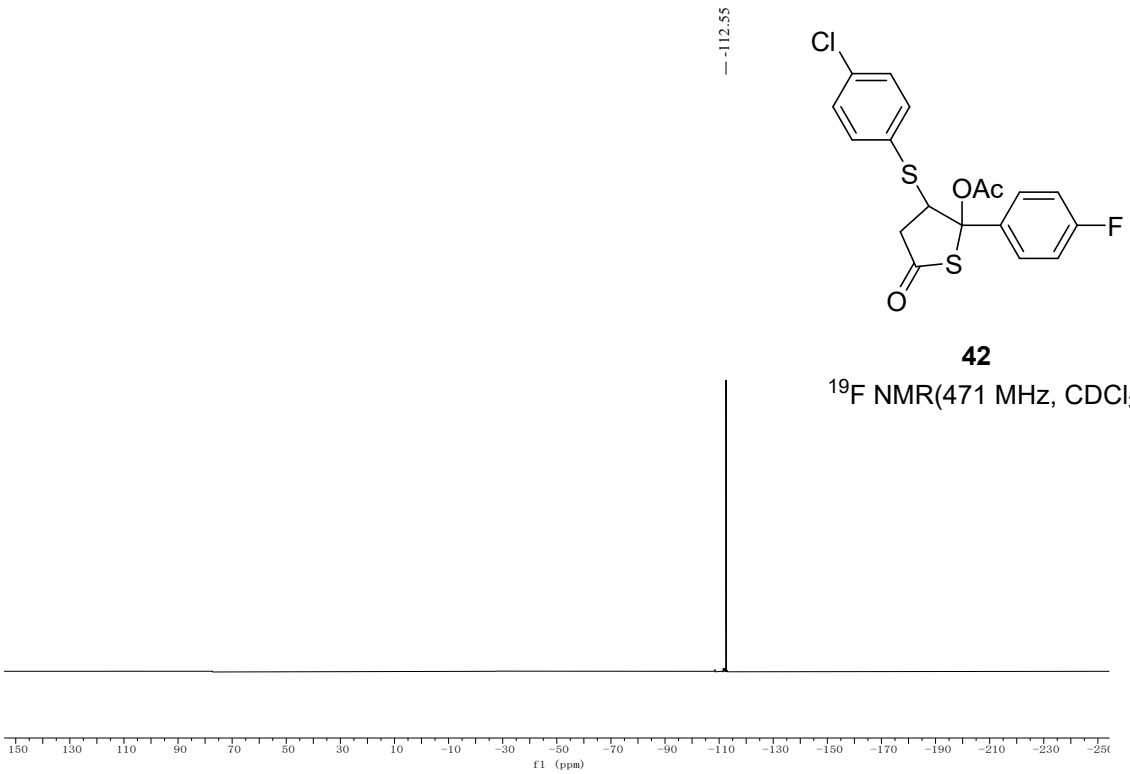
42

^{1}H NMR(500 MHz, $CDCl_3$)



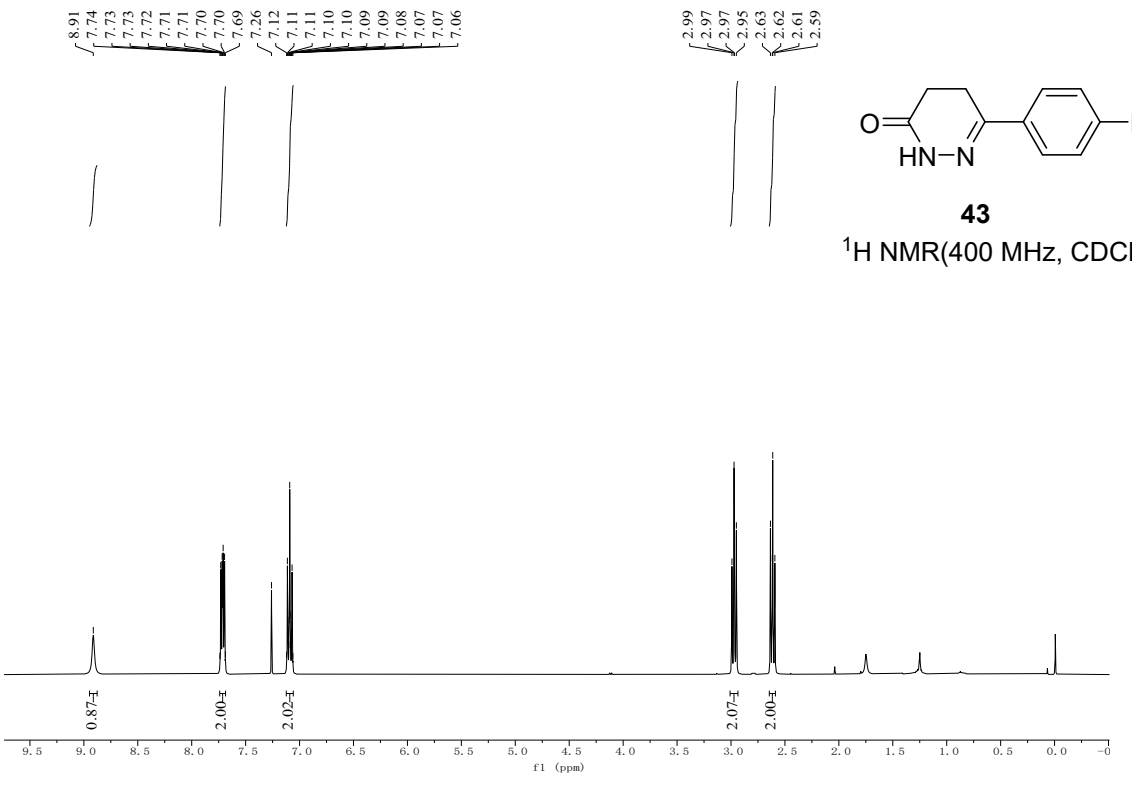
42

^{13}C NMR(126 MHz, $CDCl_3$)



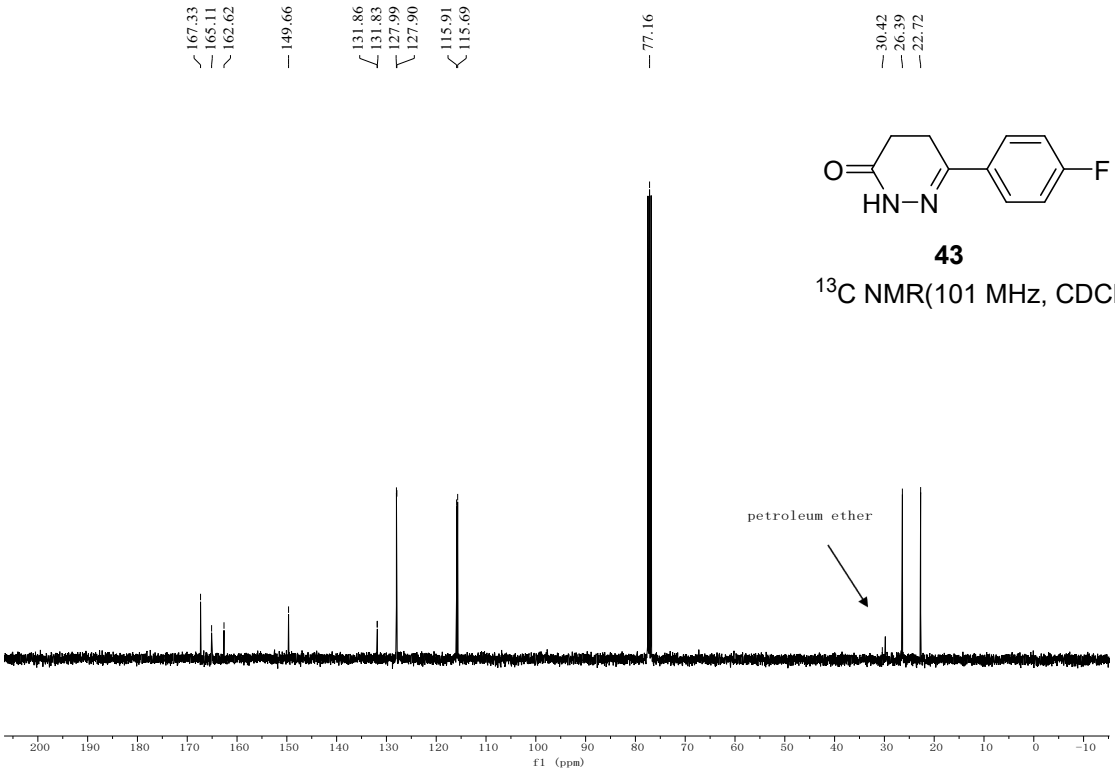
42

^{19}F NMR(471 MHz, $CDCl_3$)



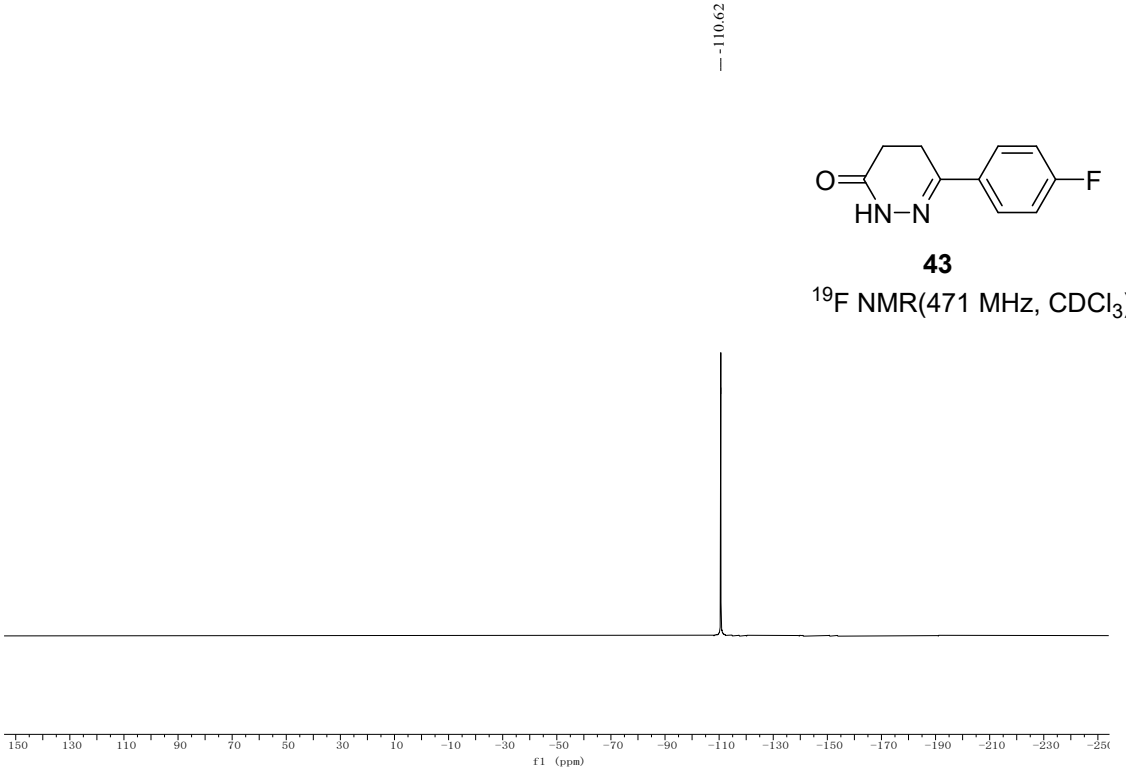
43

^{1}H NMR(400 MHz, $CDCl_3$)



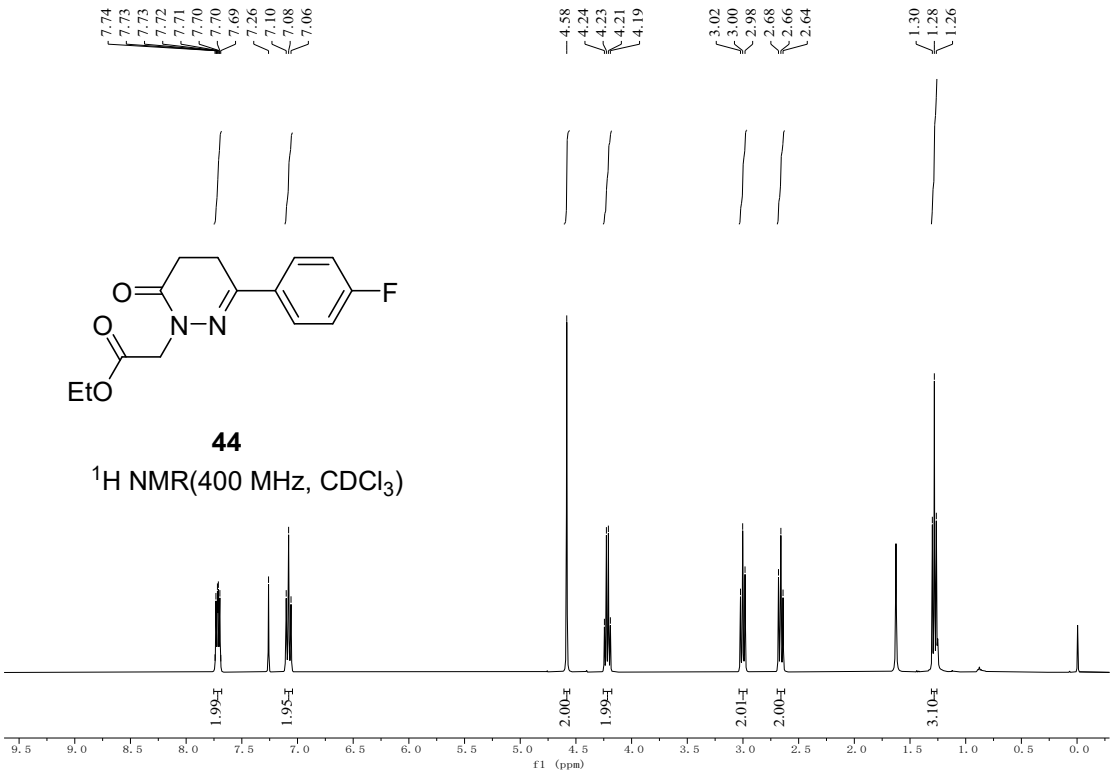
43

^{13}C NMR(101 MHz, $CDCl_3$)



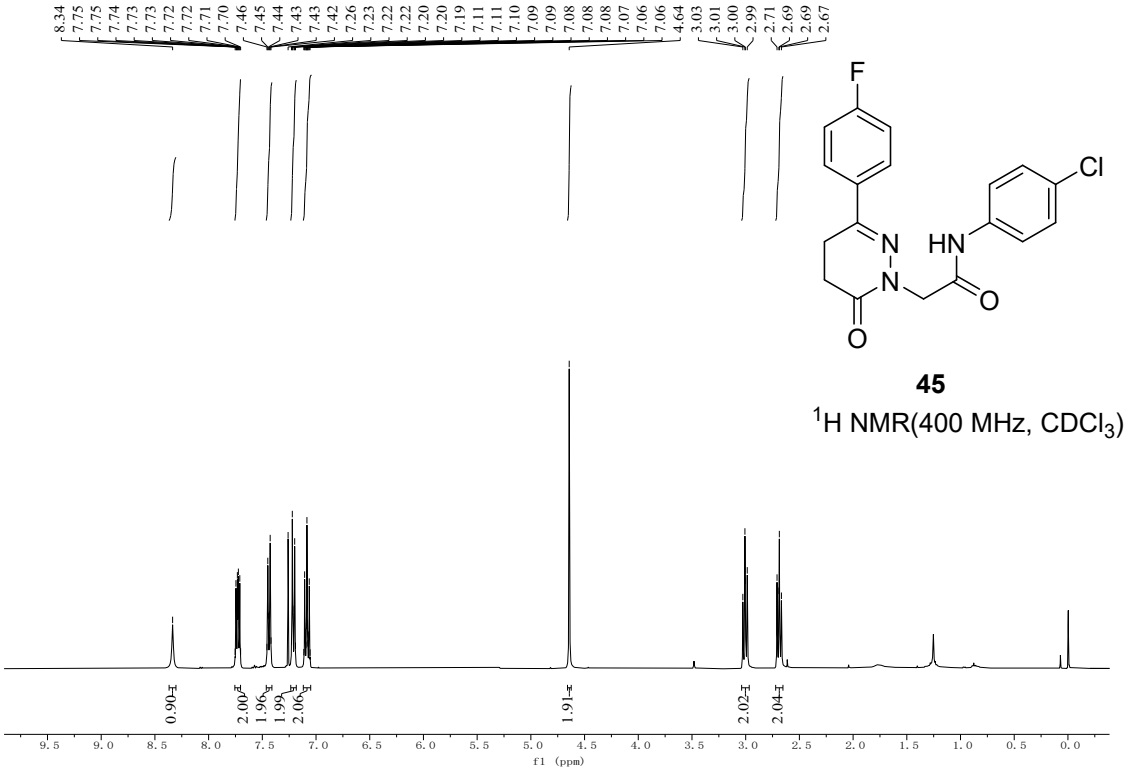
43

^{19}F NMR(471 MHz, $CDCl_3$)



44

^{1}H NMR(400 MHz, $CDCl_3$)



45

^{1}H NMR(400 MHz, $CDCl_3$)

7. X-ray Crystallographic Data

7.1 The structure of **16** was determined by the X-ray diffraction. Recrystallized from DCM and PE. Further information can be found in the CIF file (Deposition number: CCDC 2106081)

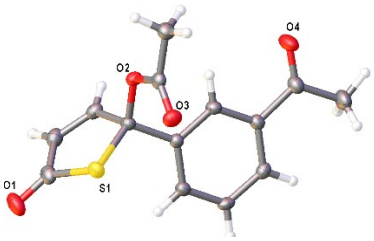


Figure S3. X-ray structure of 16

```
Bond precision:   C-C = 0.0020 A          Wavelength=0.71073

Cell:          a=6.6773(4)        b=8.2045(4)      c=12.3368(8)
               alpha=103.440(2)   beta=98.505(2)   gamma=98.528(2)
Temperature:   296 K

                Calculated                Reported
Volume          638.29(6)                 638.29(6)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C14 H12 O4 S              C14 H12 O4 S
Sum formula     C14 H12 O4 S              C14 H12 O4 S
Mr              276.30                    276.30
Dx,g cm-3       1.438                     1.438
Z               2                         2
Mu (mm-1)       0.260                     0.260
F000            288.0                     288.0
F000'           288.40
h,k,lmax        10,12,18                  10,12,18
Nref            4730                      4662
Tmin,Tmax       0.856,0.878               0.713,0.747
Tmin'           0.771

Correction method= # Reported T Limits: Tmin=0.713 Tmax=0.747
AbsCorr = NONE

Data completeness= 0.986          Theta(max)= 32.774

R(reflections)= 0.0450( 2993)                wR2(reflections)=
                                             0.1040( 4662)
S = 1.032                 Npar= 174
```

7.2 The structure of **27** was determined by the X-ray diffraction. Recrystallized from DCM and PE. Further information can be found in the CIF file (Deposition number: CCDC 2106079)

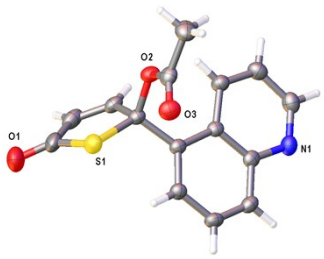


Figure S4. X-ray structure of 27

```
Bond precision:   C-C = 0.0040 A          Wavelength=0.71073

Cell:             a=11.5157(9)     b=7.2349(5)        c=15.7485(12)
                  alpha=90         beta=95.933(3)     gamma=90
Temperature:      296 K

                  Calculated                Reported
Volume            1305.06(17)               1305.06(17)
Space group       P 21/c                    P 1 21/c 1
Hall group        -P 2ybc                   -P 2ybc
Moiety formula    C15 H11 N O3 S            C15 H11 N O3 S
Sum formula       C15 H11 N O3 S            C15 H11 N O3 S
Mr                285.31                    285.31
Dx,g cm-3         1.452                     1.452
Z                 4                         4
Mu (mm-1)         0.254                     0.254
F000              592.0                     592.0
F000'             592.77
h,k,lmax          13,8,18                   13,8,18
Nref              2307                      2304
Tmin,Tmax         0.968,0.975               0.601,0.746
Tmin'             0.968

Correction method= # Reported T Limits: Tmin=0.601 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 25.022

R(reflections)= 0.0476( 1491)                wR2(reflections)=
                                             0.1247( 2304)
S = 1.037                 Npar= 182
```

7.3 The structure of **30** was determined by the X-ray diffraction. Recrystallized from DCM and PE. Further information can be found in the CIF file (Deposition number: CCDC 2106084)

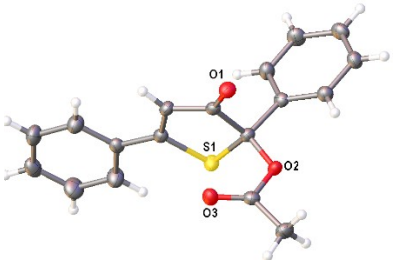


Figure S4. X-ray structure of 30

Bond precision: C-C = 0.0025 A Wavelength=0.71073

Cell: a=9.346(5) b=11.033(5) c=15.429(6)
alpha=77.727(15) beta=82.415(19) gamma=80.856(18)
Temperature: 296 K

	Calculated	Reported
Volume	1526.9(12)	1526.9(12)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C18 H14 O3 S	C18 H14 O3 S
Sum formula	C18 H14 O3 S	C18 H14 O3 S
Mr	310.35	310.35
Dx,g cm-3	1.350	1.350
Z	4	4
Mu (mm-1)	0.221	0.221
F000	648.0	648.0
F000'	648.80	
h,k,lmax	13,15,21	13,15,21
Nref	9089	9037
Tmin,Tmax	0.895,0.895	0.489,0.746
Tmin'	0.895	

Correction method= # Reported T Limits: Tmin=0.489 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.994 Theta(max)= 30.245

R(reflections)= 0.0480(6312) wR2(reflections)= 0.1235(9037)

S = 1.038 Npar= 399

7.4 The structure of **31** was determined by the X-ray diffraction. Recrystallized from DCM and PE. Further information can be found in the CIF file (Deposition number: CCDC 2106078)

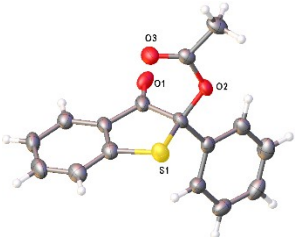


Figure S5. X-ray structure of 31

Bond precision: C-C = 0.0040 A Wavelength=0.71073

Cell: a=10.5967(12) b=8.9452(8) c=14.5399(15)
alpha=90 beta=92.211(4) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1377.2(2)	1377.2(2)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C16 H12 O3 S	C16 H12 O3 S
Sum formula	C16 H12 O3 S	C16 H12 O3 S
Mr	284.32	284.32
Dx,g cm-3	1.371	1.371
Z	4	4
Mu (mm-1)	0.238	0.238
F000	592.0	592.0
F000'	592.78	
h,k,lmax	14,12,20	14,12,20
Nref	3940	3876
Tmin,Tmax	0.888,0.954	0.565,0.746
Tmin'	0.888	

Correction method= # Reported T Limits: Tmin=0.565 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.984 Theta(max)= 29.761

R(reflections)= 0.0716(2583) wR2(reflections)= 0.1913(3876)

S = 1.039 Npar= 182