The α-Diimine-based Conjugated Microporous Polymers as Heterogeneous Ligand for highly Efficient Palladium-Catalyzed Direct C-H Arylation

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List of Contents

1. General Information

(1) Materials: All reagents were purchased from commercial sources and used as received without further purification. All the substrates were purchased from Energy Chemical (Shanghai, China) and used as received. DMF was dried by calcium hydride and used after distillation. [$Pd(PPh_3)_2Cl_2$] and 1,3,5-tri(4-ethynylphenyl)benzene were prepared and purified according to the literature procedures. All anhydrous reactions were carried out under dry nitrogen by using Schlenk tube techniques. All catalytic reactions were performed in a 10 mL glass tube.

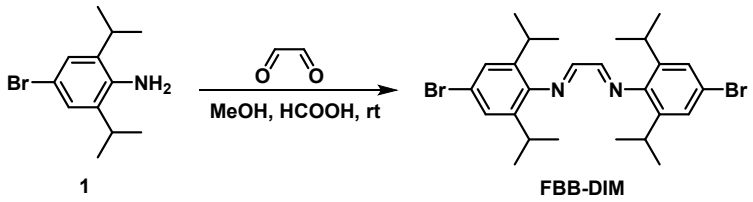
(2) Methods: Chemicals and solvents were purchased from commercial suppliers. All equipment was thoroughly oven-dried. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light. Flash column chromatography (FCC) was carried out with silica gel (200–300 mesh). ^{1}H and ^{13}C liquid NMR spectra were recorded on a Bruker Avance III 500 MHz NMR spectrometer. N_2 adsorption and desorption isotherms were measured at 77 K using a Quantachrome autosorb IQ-2. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDPT) method. Solid-state NMR experiments were performed on a Bruker Avance II WB 400 MHz NMR spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with the contact time of 3 ms (ramp 100) and the recycle delay of 2 s on a 2.5 mm double resonance probe. FT-IR spectra were collected on a Nicolet 6700 instrument. Thermal properties of the synthesized materials were evaluated on a STA PT1600 Linseis thermogravimetric analysis (TGA) instrument in the temperature range of 25 to 800 °C under nitrogen atmosphere with a heating rate of 10 °C/min. Surface morphologies and microstructures of the synthesized materials were examined with a ZEISS Gemini-500 scanning electron microscope (SEM). The Pd contents in polymer frameworks were determined by Perkin-Elmer ICP-OES Optima 8300 spectroscopy. Powder X-ray diffraction (PXRD) data were collected with a Rigaku D/MAX-2400 X-ray diffractometer operated at 40 kV and 100 mA with Cu Kα radiation at a scan rate of 15°/min. X-ray photoelectron spectroscopy (XPS) date were obtained with an Thermo ESCALAB 250XI Scientific electron spectrometer using 150W Al Kα radiation.

(3) General procedure for the direct arylation promoted by DIM-Pd-CMP: Unless otherwise noted, the direct arylation reaction was carried out under aerobic conditions. All solvents were used as received, and no further purification was needed. A parallel reactor containing a stir bar was

charged with DIM-Pd-CMP (0.5 mol%), aryl bromide (0.2 mmol), heteroarene (0.3 mmol), K_2CO_3 (0.3 mmol), PivOH (0.06 mmol), and 0.5 mL of DMAc. The reaction mixture was carried out at 130 ^oC for 12 h. After the reaction was completed (monitored by TLC), the reaction mixture was cooled to room temperature, and then the mixture was centrifugated and the solid was washed with MeOH/H_2O (5 mL) and EtOAc (3 x 5 mL). The combined organic phase was diluted with dichloromethane, followed by extraction three times with dichloromethane. The organic layer was dried with anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The crude products were purified by silica-gel column chromatography using petroleum ether-dichloromethane (10/1) as eluent, the isolated yield was then calculated based on the feeding of aryl halides. The isolated corresponding products were characterized by ^1H NMR and ^{13}C NMR spectra.

2. Synthetic Procedures

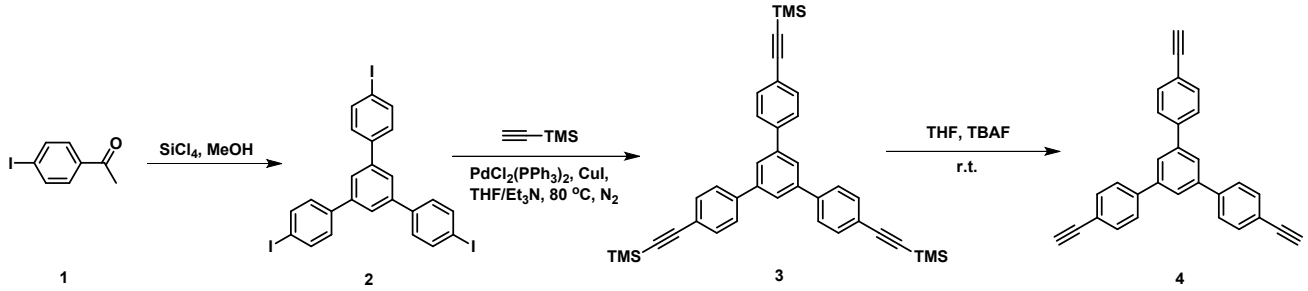
(1) Synthesis of 1,3-bis(2,6-diisopropyl-4-bromophenyl)imidazolium chloride[1]



Scheme S1. Synthesis of FBB-DIM

A 100 mL round-bottom flask was charged with 1.02 g (4.0 mmol, 2.0 eq) of 4-bromo-2,6-diisopropylaniline, 290 mg (2.0 mmol, 40% in water) of glyoxal and 10 ml of methanol. A few drops of formic acid were added as catalyst. The color of the reaction mixture turned from colorless to yellow immediately, and a yellow precipitate appeared after a few hours. The reaction mixture was stirred for 24 h and the yellow solid was collected by filtration and washed with cold methanol to afford the analytically pure **FBB-DIM**. Yield: 748 mg (70 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.28 (s, 4H), 2.88 (dt, J = 13.7, 6.9 Hz, 4H), 1.19 (s, 12H), 1.18 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.25, 146.89, 139.12, 126.49, 118.80, 28.19, 23.16.

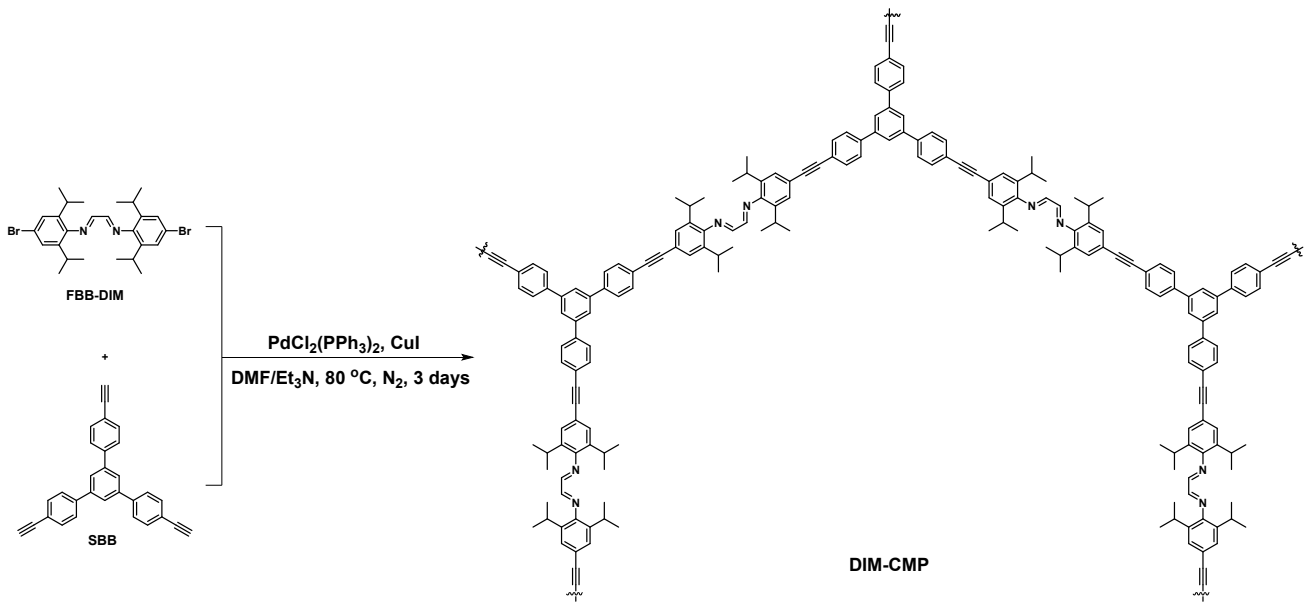
(2) Synthesis of 1,3,5-tri(4-ethynylphenyl)benzene (SBB)[2]



Scheme S2. Synthesis of 1,3,5-tri(4-ethynylphenyl)benzene (SBB)

4-iodooacetophenone (500 mg, 2.03 mmol) was dissolved in ethanol (5 mL) andsilicon tetrachloride (575 mg, 3.39 mmol) was quickly added at 0 °C (a tube is needed to release hydrogen chloride into the fume hood) and the resulting orange solution was stirred at room temperature for 3 d. The mixture was quenched with water (5 mL) and the solution was concentrated to 6 mL. CH_2Cl_2 (5 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on aluminum oxide (hexane/ethyl acetate = 10:1) to give 1,3,5-tris(4-iodophenyl)benzene (396 mg, 85%) as a yellow solid. A mixture of 1,3,5-tris(4-iodophenyl)benzene (350 mg, 512 μmol), ethynyltrimethylsilane (201 mg, 2.05 mmol), $PdCl_2(PPh_3)_2$ (60 mg), and CuI (10 mg) in THF (2.5 mL) and triethylamine (2.5 mL) was heated to 80 °C for 16 h under N_2 atmosphere. The volatile components were removed under reduced pressure and the residue was diluted with CH_2Cl_2 (10 mL). Satd. aq. NH_4Cl solution (10 mL) was added, the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to give **3** (211 mg, 70%) as a pale brownish solid. A solution of **3** (200 mg, 336 μmol) and TBAF (1.2 ml, 1.18 mmol, 1 M in THF) in THF (2 mL) was stirred at room temperature for 30 min. The mixture was quenched with satd. aq. NH_4Cl solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 10:1) to give 1,3,5-tri(4-ethynylphenyl)benzene (102 mg, 80%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.77 (s, 3H); 7.67-7.61 (m, 12H); 3.17 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$): δ (ppm) 141.68, 141.09, 132.69, 127.21, 125.28, 121.52, 83.40, 78.12.

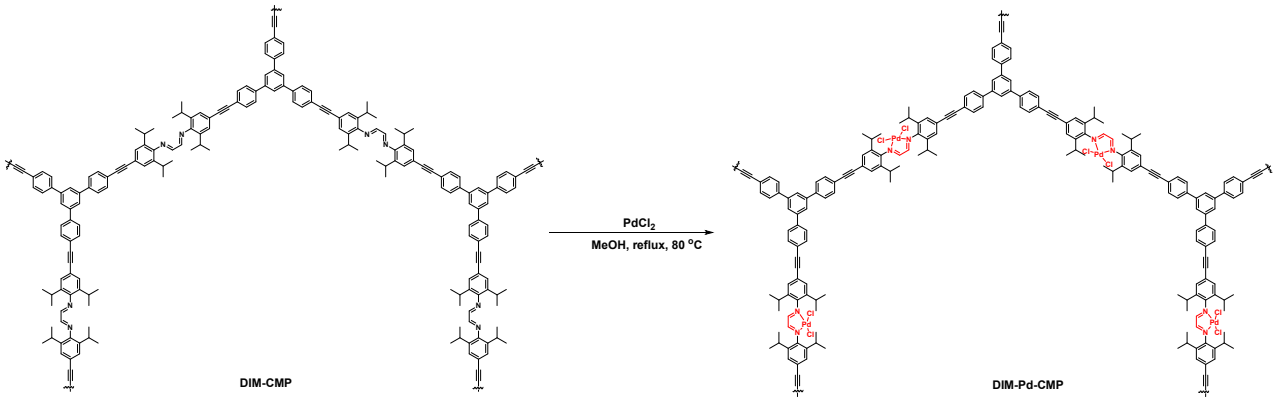
(3) Synthesis of DIM-CMP[3]



Scheme S3. Synthesis of DIM-CMP

FBB-DIM (320 mg, 0.60 mmol), 1,3,5-tri(4-ethynylphenyl)benzene (151 mg, 0.4 mmol), bis-(triphenylphosphine)palladium(II) dichloride (50 mg) , and copper (I) iodide (25 mg) were added into a dried round-bottom flask under nitrogen atmosphere. Anhydrous DMF (6.0 mL) and Et_3N (6.0 mL) were added to the mixture via a syringe. The resulting mixture was heated to 80 °C and stirred for 72 h under nitrogen atmosphere. After cooling to room temperature, the precipitate network polymer was filtered and washed four times (once each) with chloroform, water, methanol and acetone to remove any unreacted monomer or catalyst residues. Further purification of the polymer was carried out by soxhlet extraction with methanol for 48 h. The product was dried at 70 °C under vacuum for 6 h to give a yellow powder. Yield: 302 mg (95%). Elemental combustion analysis (%) Calcd for $C_{46}H_{44}N_2$: C 88.33, N 4.48, H 7.04; The elemental analysis result of **DIM-CMP** found: C 80.85, N 3.79, H 6.69.

(4) Synthesis of DIM-Pd-CMP[4]



DIM-CMP (100 mg, 1.35 mmol/g), $PdCl_2$ (35.0 mg, 1.5 eq) and methanol (10 mL) were added into a two-neck flask, the mixture was heated to 80 °C and refluxed for 12 h under N_2. After the reaction was complete, the obtained polymer was filtered and washed thoroughly with dichloromethane (10 mL × 3), distilled water (10 mL × 3) and acetone (10 mL × 3). Further purification of the polymer was carried out by soxhlet extraction with methanol for 48 h. The solid was dried at 70 °C under vacuum for 6 h to give a brown powder. The Pd content in DIM-Pd-CMP frameworks was 8.51% as determined by ICP-OES.

3. Characterization of DIM-CMP and DIM-Pd-CMP

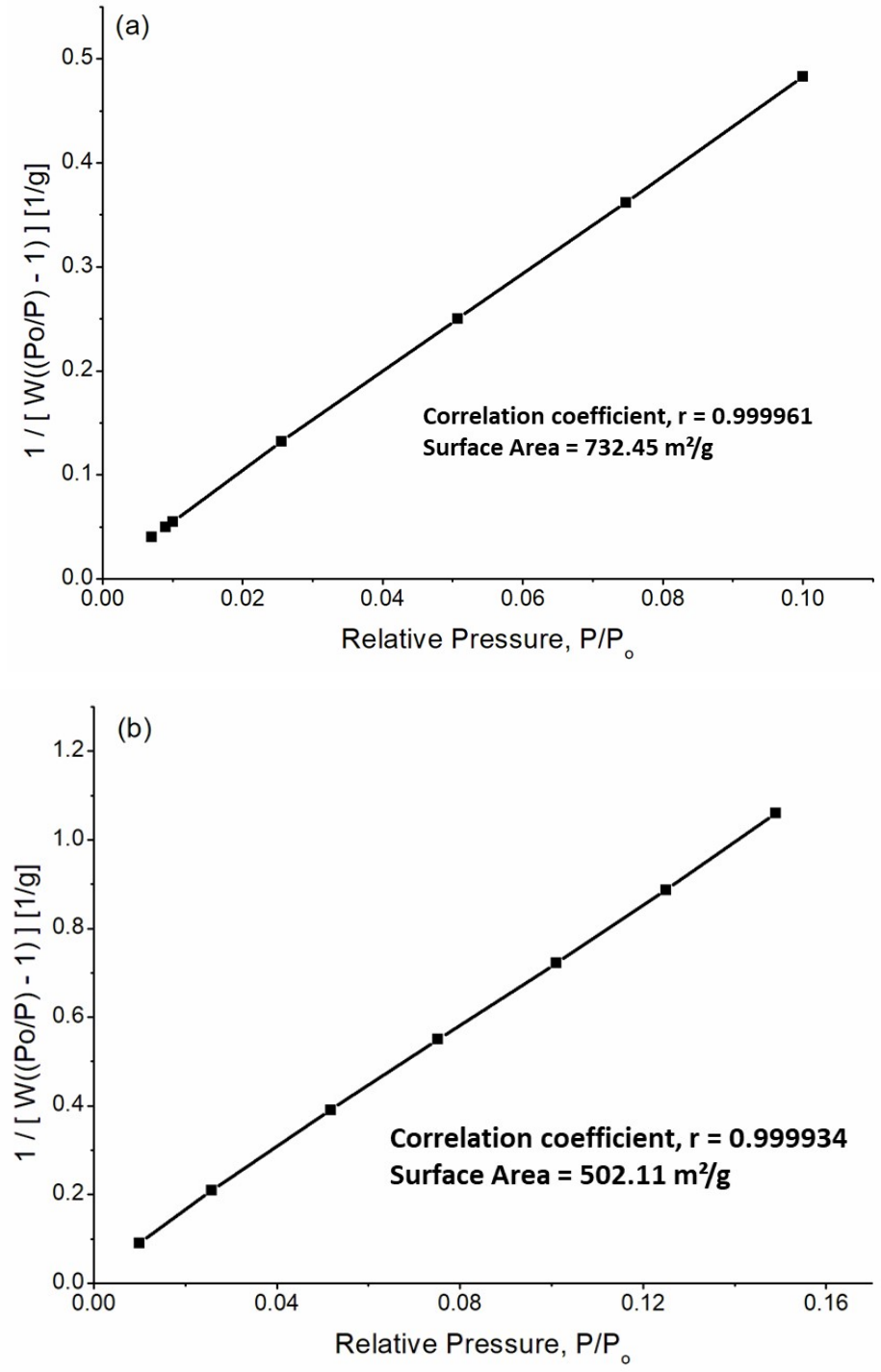


Figure S1. BET surface area plots of DIM-CMP (a) and DIM-Pd-CMP (b)

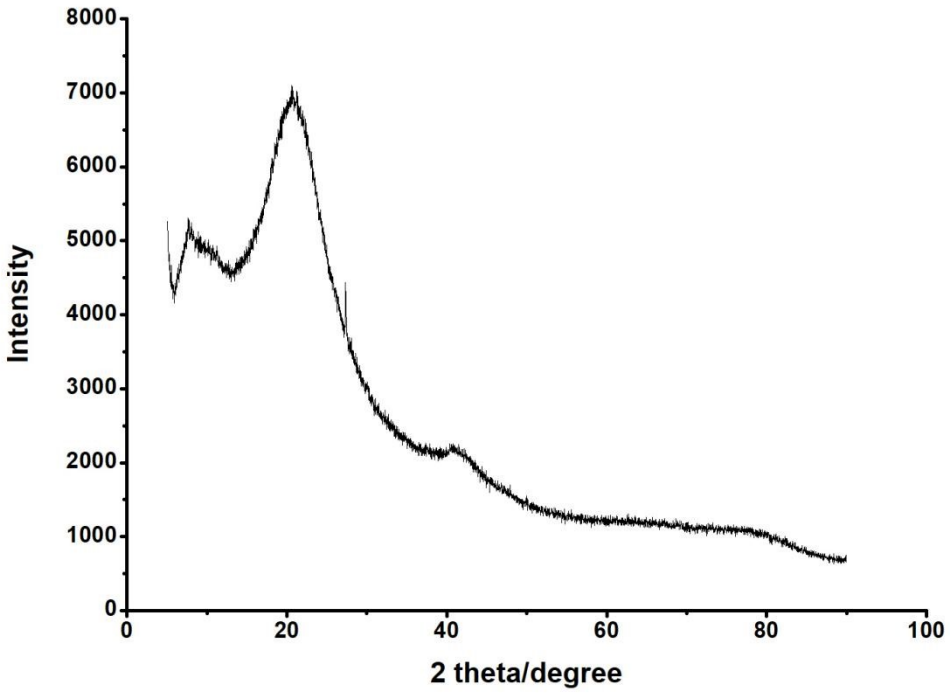
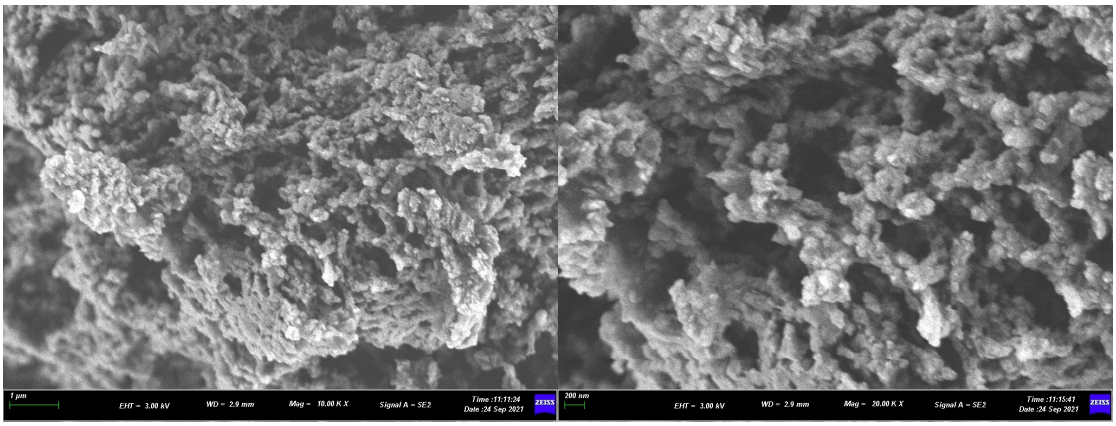
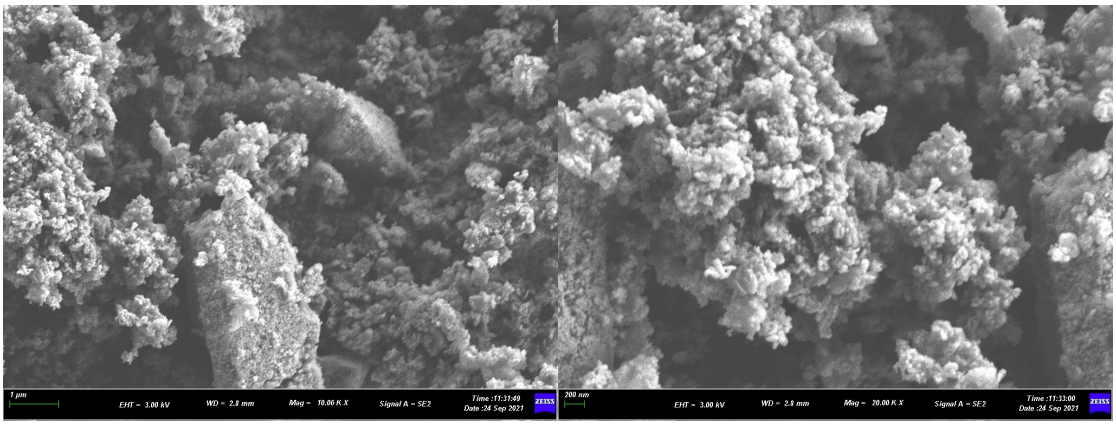


Figure S2. Powder X-ray diffraction pattern of DIM-CMP. No intensive diffraction peaks were observable.



(a) DIM-CMP

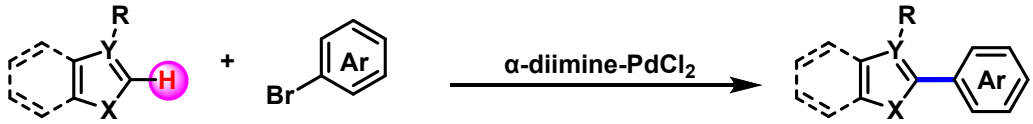


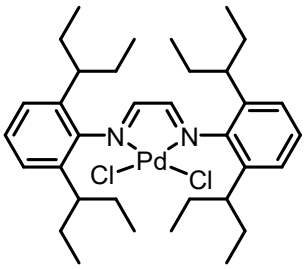
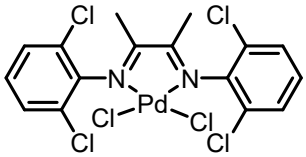
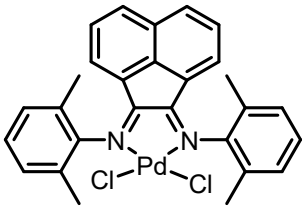
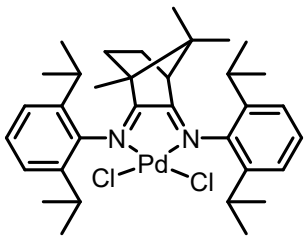
(b) DIM-Pd-CMP

Figure S3. SEM images of DIM-CMP and DIM-Pd-CMP

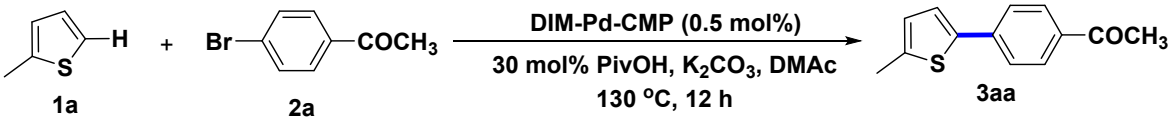
4.The comparable catalytic performance of other α-diimine palladium

Table S1. The comparable catalytic performance of other α–diimine palladium homogeneous catalysts

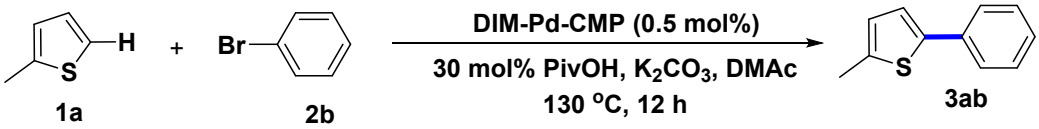


Run	Precatalyst	Pd loading	Yield (%)	Ref
1		1 mol%	13-99%	*ACS Catal.* 2017, **7**, 3336−3343 *Chem. Sci.* 2021, **12**, 363–373
2		5 mol%	27-72%	*ACS Catal.* 2011, **1**, 170–174
3		7 mol%	42-92%	*J. Org. Chem.* 2011, **76**, 3498–3501
4		0.2 mol%	58-95%	*Org. Biomol. Chem.* 2017, **15**, 5731–5736

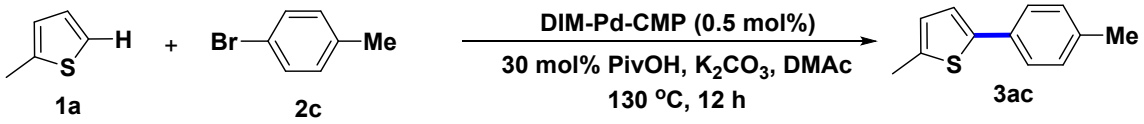
5. Direct C-H Arylation Reaction of 2-Methylthiophene with Aryl bromides[5]



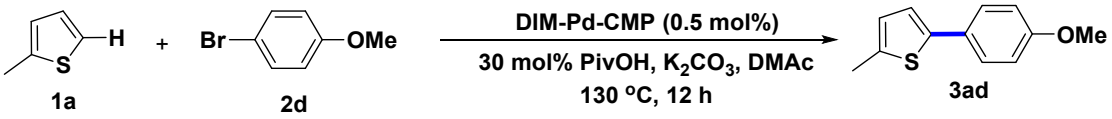
According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 1-(4-bromophenyl)ethan-1-one (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 94% yield (40.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 3.5 Hz, 1H), 6.78 (d, J = 3.1 Hz, 1H), 2.61 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.27, 141.52, 140.51, 139.13, 135.36, 129.08, 126.66, 125.12, 124.61, 26.49, 15.52.



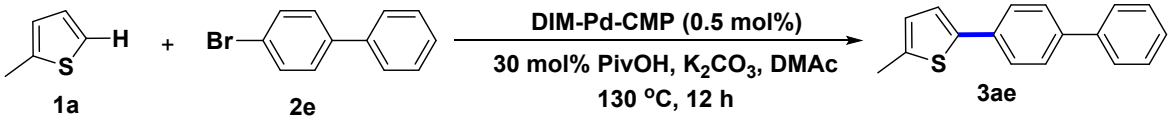
According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), bromobenzene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 90% yield (31.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.5 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.10 (d, J = 3.4 Hz, 1H), 6.72 (d, J = 2.4 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.02, 139.50, 134.76, 128.80, 126.99, 126.18, 125.76, 125.52, 122.90, 15.43.



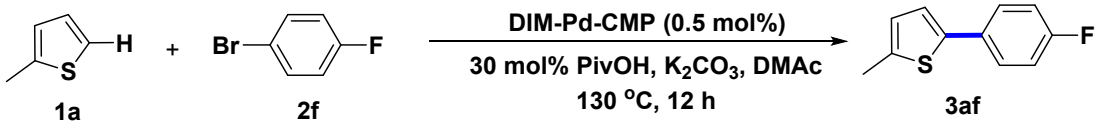
According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 1-bromo-4-methylbenzene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 95% yield (35.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 3.5 Hz, 1H), 6.72 (d, J = 2.3 Hz, 1H), 2.51 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.16, 138.93, 136.79, 131.99, 129.45, 126.06, 125.46, 122.39, 21.26, 15.70.



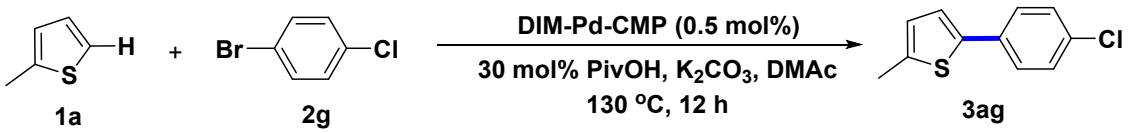
According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 1-bromo-4-methoxybenzene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 88% yield (35.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 6.99 (d, J = 3.5 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.72 – 6.67 (m, 1H), 3.83 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.89, 141.94, 138.45, 137.29, 130.57, 126.78, 126.02, 121.83, 114.23, 55.30, 15.48.



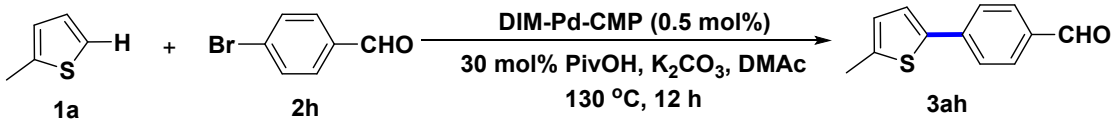
According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 4-bromo-1,1'-biphenyl (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 92% yield (46.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dt, J = 12.4, 7.3 Hz, 6H), 7.45 (d, J = 7.5 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.15 (d, J = 3.5 Hz, 1H), 6.74 (d, J = 2.7 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.61, 140.63, 139.75, 139.63, 133.76, 128.80, 127.46, 127.29, 126.87, 126.28, 125.82, 122.96, 15.47.



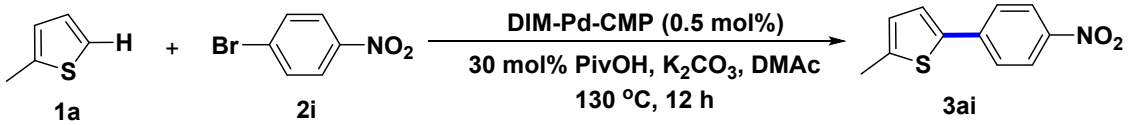
According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 1-bromo-4-fluorobenzene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 96% yield (36.7 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 3H), 7.12 (t, J = 8.6 Hz, 1H), 7.04 (dd, J = 13.7, 5.7 Hz, 2H), 6.72 (d, J = 2.5 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.03, 161.07, 140.89, 139.50, 128.60, 128.54, 127.14, 127.08, 126.20, 122.87, 115.78, 115.76, 115.61, 115.59, 15.38. ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.43.



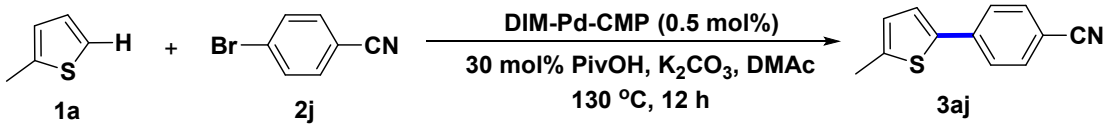
According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 1-bromo-4-chlorobenzene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 92% yield (38.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 3.5 Hz, 1H), 6.72 (d, J = 2.6 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.64, 139.99, 133.26, 132.67, 128.93, 126.64, 126.32, 123.28, 15.49.



According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 4-bromobenzaldehyde (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 90% yield (36.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.85 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.29 – 7.24 (m, 1H), 6.82 – 6.74 (m, 1H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.40, 142.07, 140.46, 140.29, 134.73, 130.44, 126.80, 125.48, 125.09, 15.56.

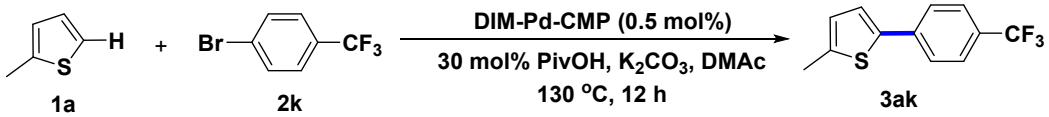


According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 1-bromo-4-nitrobenzene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 88% yield (38.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 3.6 Hz, 1H), 6.80 (d, J = 3.0 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.94, 140.90, 139.17, 128.69, 127.03, 126.06, 125.76, 125.40, 124.39, 15.48.

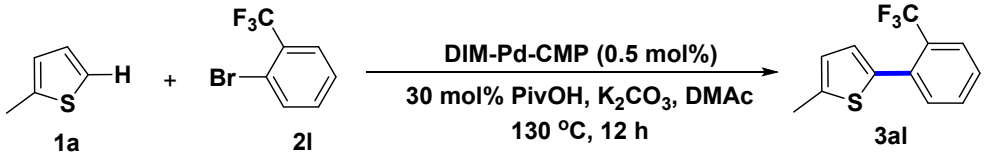


According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 4-

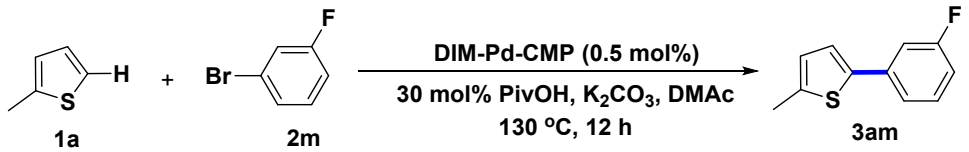
bromobenzonitrile (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 85% yield (33.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 4H), 7.22 (d, J = 3.6 Hz, 1H), 6.78 (dd, J = 3.5, 0.9 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.21, 139.62, 138.96, 132.66, 126.82, 125.54, 125.12, 118.94, 109.98, 15.53.



According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 1-bromo-4-(trifluoromethyl)benzene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 90% yield (43.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 3.5 Hz, 1H), 6.78 (d, J = 3.2 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.18, 140.15, 138.06, 128.84, 128.58, 126.55, 125.85, 125.82, 125.79, 125.76, 125.40, 124.37, 123.15, 15.45. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.48.

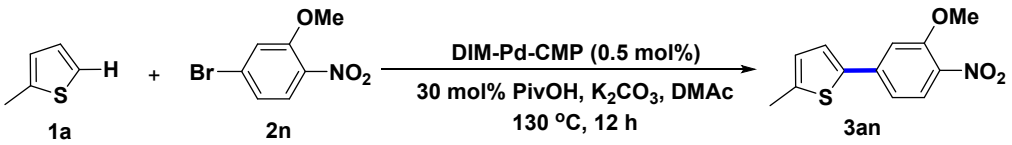


According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 1-bromo-2-(trifluoromethyl)benzene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 86% yield (41.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.9 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.49 (d, J = 7.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 3.1 Hz, 1H), 6.74 (d, J = 3.2 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.83, 137.21, 134.11, 133.13, 131.28, 127.74, 127.72, 127.65, 126.39, 126.35, 125.33, 122.94, 15.16. ^{19}F NMR (471 MHz, $CDCl_3$) δ -57.65.

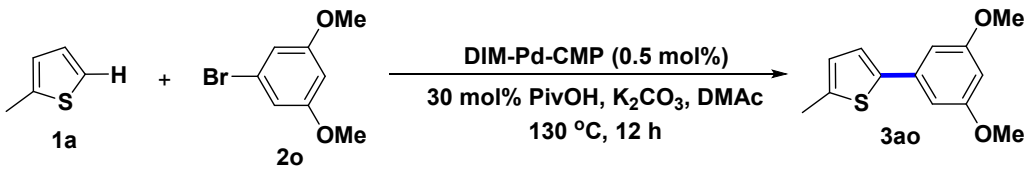


According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 1-bromo-3-fluorobenzene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-

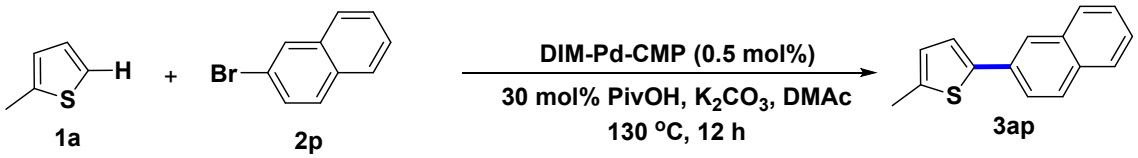
CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 92% yield (35.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (ddd, *J* = 9.2, 7.3, 5.0 Hz, 3H), 7.24 (dd, *J* = 7.9, 7.0 Hz, 1H), 7.11 (d, *J* = 3.4 Hz, 1H), 6.74 – 6.70 (m, 1H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.18, 162.30, 140.30, 130.41, 130.34, 130.30, 130.23, 126.30, 125.75, 123.67, 122.89, 122.74, 122.72, 121.13, 121.11, 114.74, 114.57, 114.14, 113.96, 113.75, 113.58, 112.32, 112.13, 15.43. ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.12.



According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 4-bromo-2-methoxy-1-nitrobenzene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 82% yield (40.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.82 (d, *J* = 1.9 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.50 (d, *J* = 3.6 Hz, 1H), 6.82 (d, *J* = 3.2 Hz, 1H), 4.04 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.15, 143.03, 134.82, 130.27, 128.04, 127.46, 125.82, 116.41, 106.71, 56.05, 15.28.



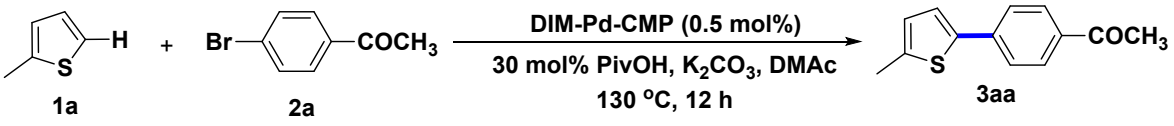
According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 1-bromo-3,5-dimethoxybenzene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 87% yield (40.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 3.4 Hz, 1H), 6.71 (d, *J* = 2.0 Hz, 3H), 6.38 (s, 1H), 3.83 (s, 6H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.06, 139.56, 136.28, 131.35, 126.06, 123.26, 103.96, 99.20, 55.39, 15.69.



According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 1-bromo-3,5-dichlorobenzene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-

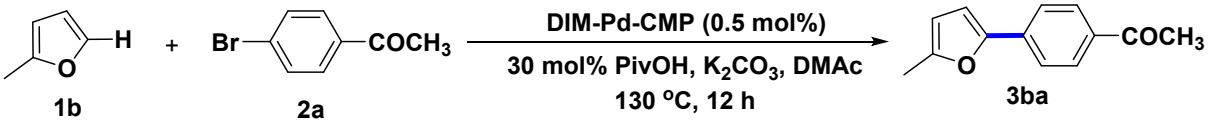
Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 92% yield (41.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.81 (t, *J* = 7.5 Hz, 3H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.37 (m, 2H), 7.24 (dd, *J* = 11.8, 2.4 Hz, 1H), 6.77 (s, 1H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.05, 139.81, 133.71, 132.53, 132.14, 128.41, 127.92, 127.68, 126.45, 126.33, 125.70, 124.15, 123.58, 123.33, 15.49.

6. Direct C-H Arylation Reaction of Heteroarenes with Aryl bromide[5]

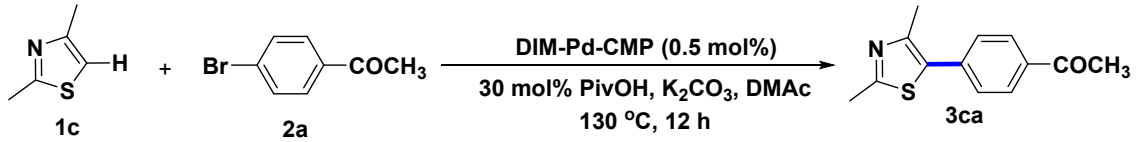


According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 1-(4-

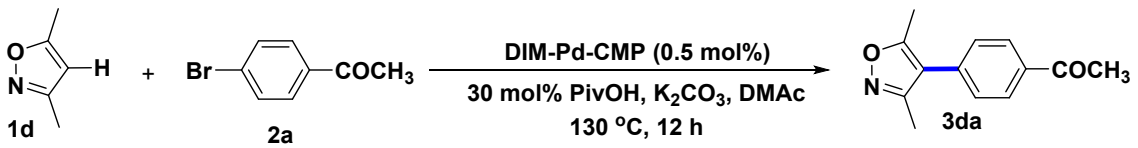
bromophenyl)ethan-1-one (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 94% yield (40.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 3.5 Hz, 1H), 6.78 (d, *J* = 3.1 Hz, 1H), 2.61 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.27, 141.52, 140.51, 139.13, 135.36, 129.08, 126.66, 125.12, 124.61, 26.49, 15.52.



According to the general procedure, the reaction of 2-methylfuran (0.30 mmol, 1.5 equiv), 1-(4-bromophenyl)ethan-1-one (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 96% yield (38.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 3.2 Hz, 1H), 6.12 (d, *J* = 2.6 Hz, 1H), 2.61 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.34, 153.51, 151.21, 135.21, 135.06, 128.95, 122.96, 108.61, 108.32, 29.70, 14.09.

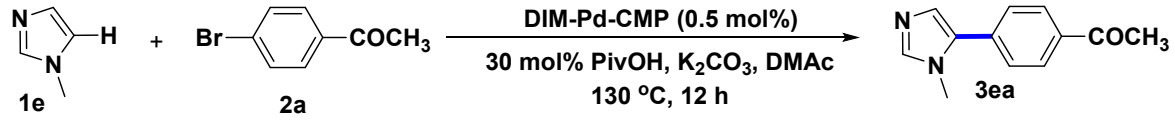


According to the general procedure, the reaction of 2,4-dimethylthiazole (0.30 mmol, 1.5 equiv), 1-(4-bromophenyl)ethan-1-one (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 95% yield (43.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 2.70 (s, 3H), 2.63 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.31, 164.33, 148.30, 137.26, 135.88, 130.30, 129.02, 128.70, 26.56, 19.12, 16.32.

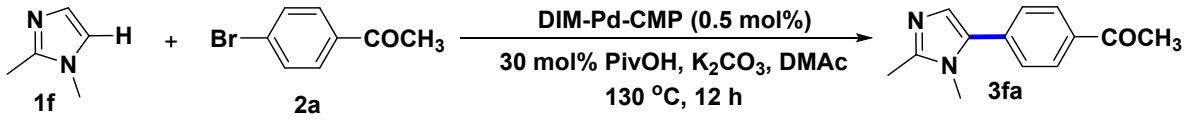


According to the general procedure, the reaction of 3,5-dimethylisoxazole (0.30 mmol, 1.5 equiv), 1-(4-bromophenyl)ethan-1-one (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and

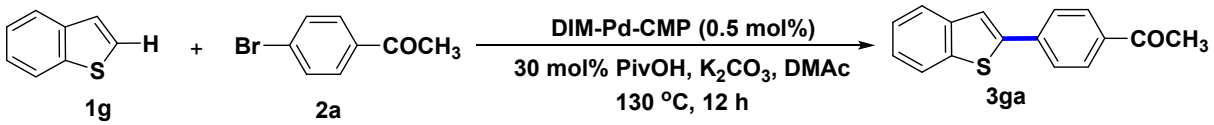
chromatography the product in 88% yield (37.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H), 2.65 (s, 3H), 2.45 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.40, 165.81, 158.34, 136.13, 135.51, 129.11, 128.82, 115.92, 26.57, 11.69, 10.84.



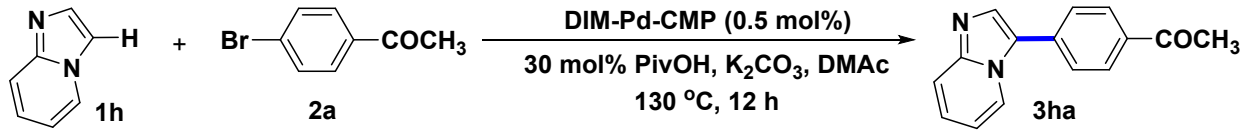
According to the general procedure, the reaction of 1-methyl-1H-imidazole (0.30 mmol, 1.5 equiv), 1-(4-bromophenyl)ethan-1-one (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 92% yield (36.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 2H), 7.57 (s, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.21 (s, 1H), 3.73 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.32, 140.13, 136.14, 134.46, 132.73, 129.38, 128.83, 128.01, 32.84, 26.57.



According to the general procedure, the reaction of 1,2-dimethyl-1H-imidazole (0.30 mmol, 1.5 equiv), 1-(4-bromophenyl)ethan-1-one (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 93% yield (39.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.04 (s, 1H), 3.57 (s, 3H), 2.62 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.40, 170.71, 147.20, 135.86, 135.16, 132.56, 128.81, 128.02, 127.20, 54.73, 52.93, 31.78, 26.62, 13.47.

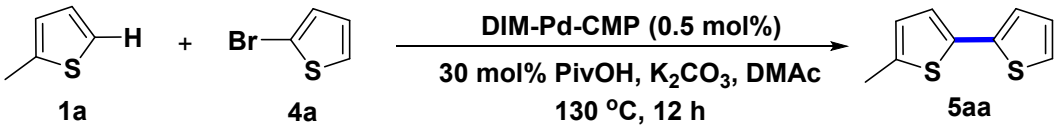


According to the general procedure, the reaction of benzo[b]thiophene (0.30 mmol, 1.5 equiv), 1-(4-bromophenyl)ethan-1-one (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 90% yield (45.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 7.4 Hz, 1H), 7.84 – 7.78 (m, 3H), 7.68 (s, 1H), 7.38 (dq, J = 7.2, 6.0 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.24, 142.66, 140.48, 139.95, 138.74, 136.45, 129.07, 126.38, 125.02, 124.80, 123.99, 122.36, 121.19, 29.70.



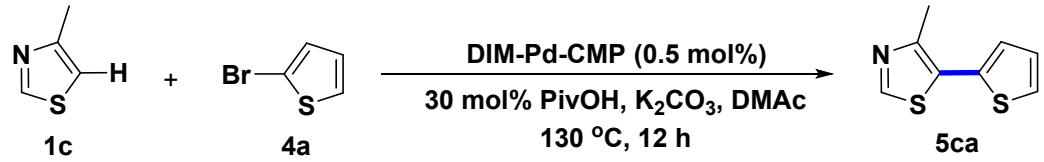
According to the general procedure, the reaction of imidazo[1,2-a]pyridine (0.30 mmol, 1.5 equiv), 1-(4-bromophenyl)ethan-1-one (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 94% yield (44.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, J = 7.0 Hz, 1H), 8.10 (d, J = 8.4 Hz, 2H), 7.80 (s, 1H), 7.70 (t, J = 8.4 Hz, 3H), 7.28 – 7.22 (m, 1H), 6.88 (td, J = 6.9, 0.8 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.16, 146.88, 136.25, 134.02, 133.79, 129.34, 127.34, 124.85, 124.74, 123.37, 118.56, 113.1, 26.58.

7. Direct C-H Arylation Reaction of Heteroarenes with Heteroaryl bromides[5]



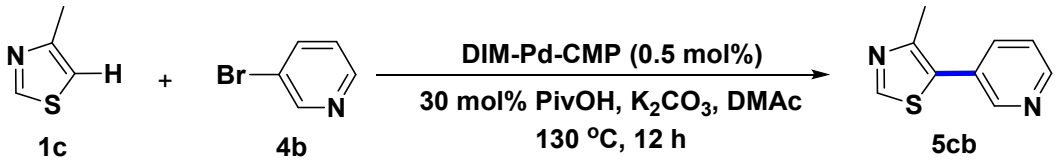
According to the general procedure, the reaction of 2-methylthiophene (0.30 mmol, 1.5 equiv), 2-bromothiophene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5

mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 83% yield (29.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, J = 5.0 Hz, 1H), 7.15 (d, J = 3.3 Hz, 1H), 7.03 – 6.95 (m, 2H), 6.66 (s, 1H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.36, 135.67, 134.41, 127.82, 125.98, 124.28, 123.60, 123.53, 15.34.



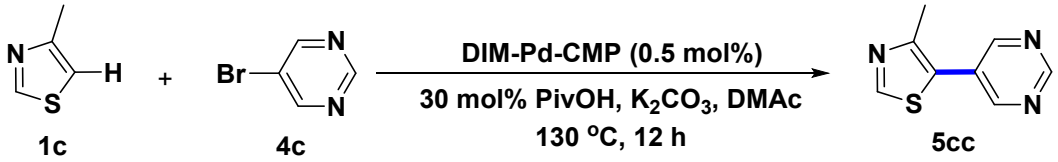
1c 4a 5ca

According to the general procedure, the reaction of 4-methylthiazole (0.30 mmol, 1.5 equiv), 2-bromothiophene (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 90% yield (32.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.37 (d, J = 3.9 Hz, 1H), 7.16 (s, 1H), 7.10 (s, 1H), 2.62 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.90, 149.13, 133.24, 127.62, 127.16, 126.18, 125.53, 16.47.



1c 4b 5cb

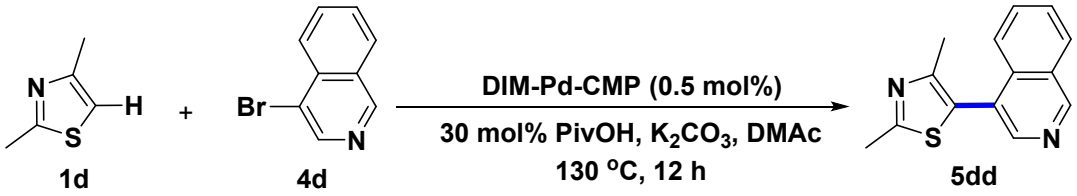
According to the general procedure, the reaction of 4-methylthiazole (0.30 mmol, 1.5 equiv), 3-bromopyridine (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 89% yield (31.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, J = 17.1 Hz, 2H), 8.61 (d, J = 4.5 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.38 (dd, J = 7.6, 4.9 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.19, 149.90, 149.82, 148.98, 136.39, 128.32, 128.07, 123.40, 15.94.



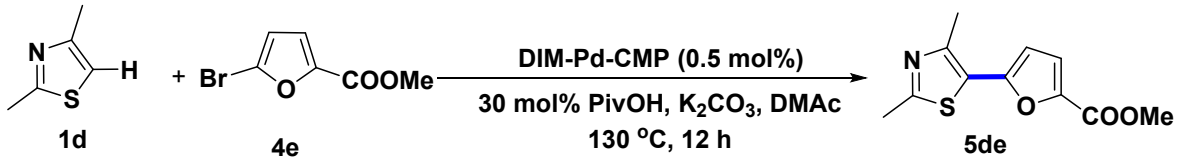
1c 4c 5cc

According to the general procedure, the reaction of 4-methylthiazole (0.30 mmol, 1.5 equiv), 5-bromopyrimidine (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 96% yield (33.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.83 (d, J = 8.9 Hz, 3H),

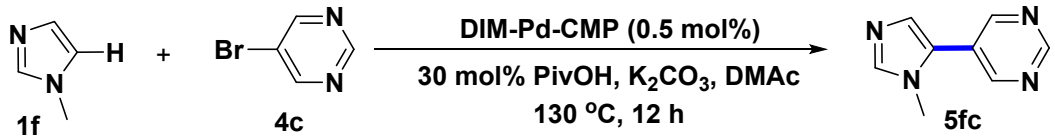
2.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.70, 156.33, 152.13, 151.09, 126.96, 124.27, 15.96.



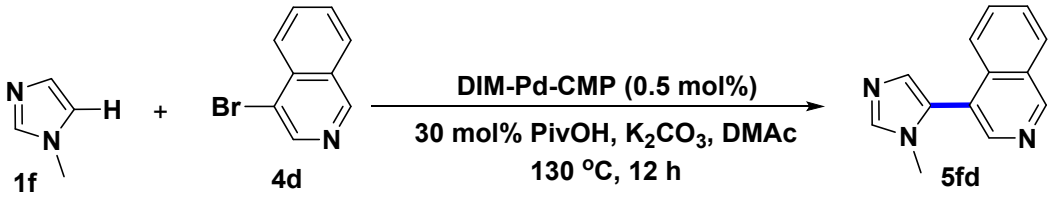
According to the general procedure, the reaction of 2,4-dimethylthiazole (0.30 mmol, 1.5 equiv), 4-bromoisoquinoline (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 92% yield (44.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.51 (s, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 2.77 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.35, 153.05, 150.52, 144.86, 135.12, 131.05, 128.35, 128.02, 127.57, 124.67, 124.60, 123.38, 19.16, 15.74.



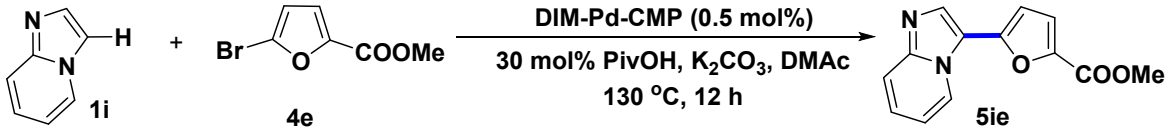
According to the general procedure, the reaction of 2,4-dimethylthiazole (0.30 mmol, 1.5 equiv), methyl 5-bromofuran-2-carboxylate (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 98% yield (46.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 9.2, 7.8 Hz, 1H), 6.50 (d, *J* = 3.4 Hz, 1H), 3.91 (s, 3H), 2.69 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.78, 158.90, 150.88, 150.19, 143.45, 120.67, 119.80, 108.90, 51.88, 19.10, 16.89.



According to the general procedure, the reaction of 1-methyl-1H-imidazole (0.30 mmol, 1.5 equiv), 5-bromopyrimidine (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 88% yield (28.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.80 (s, 2H), 7.61 (s, 1H), 7.24 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.70, 157.72, 155.49, 140.76, 130.10, 124.57, 32.62.



According to the general procedure, the reaction of 1-methyl-1H-imidazole (0.30 mmol, 1.5 equiv), 4-bromoisoquinoline (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 90% yield (37.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.48 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.61 (m, 4H), 7.21 (s, 1H), 3.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.36, 144.52, 139.24, 135.43, 131.28, 130.49, 128.36, 128.06, 127.68, 124.42, 121.12, 32.06.

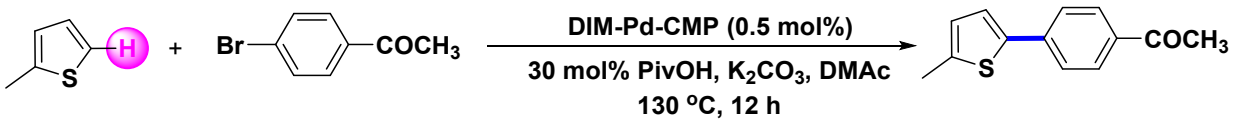


According to the general procedure, the reaction of imidazo[1,2-a]pyridine (0.30 mmol, 1.5 equiv), methyl 5-bromofuran-2-carboxylate (0.2 mol, 1.0 equiv.), PivOH (30 mol%), K_2CO_3 (1.5 equiv), and DIM-Pd-CMP (0.5 mol%) in 0.5 mL DMAc for 12 h at 130 °C, afforded after filtration and chromatography the product in 98% yield (47.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (d, *J* = 6.9 Hz, 1H), 8.01 (s, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.30 (dd, *J* = 10.9, 5.7 Hz, 2H), 6.99 (t, *J* = 6.8 Hz, 1H), 6.71 (d, *J* = 3.5 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.95, 148.92, 146.80, 143.16, 134.44, 125.73, 125.53, 119.71, 118.21, 116.46, 113.81, 107.21, 51.89.

8. Recyclability Tests of DIM-Pd-CMP

The recycling experiments were performed by recovering the **DIM-Pd-CMP** catalyst using the centrifugation method. The recovered **DIM-Pd-CMP** catalyst was washed with EtOAc and MeOH/H_2O to remove the residual product and simply dried before reuse. We chose the direct C-H arylation of 2-methylthiophene and 1-(4-bromophenyl)ethan-1-one to investigate the recyclability of **DIM-Pd-CMP** catalyst, and the results are summarized in **Table S2.**

Table S2. Recycling of **DIM-Pd-CMP** for the direct C-H arylation. [a]



Cycle	Time (h)	Yield (%)[b]
1	12	94
2	12	93
3	12	93
4	12	93
5	12	92
6	12	90

[a] Reaction conditions: 2-methylthiophene (0.3 mmol), 1-(4-bromophenyl)ethan-1-one (0.2 mmol), DIM-Pd-CMP (0.5 mol%), PivOH (30 mol%), K_2CO_3 (0.3 mmol), DMAc (0.5 mL), 130 °C for 12 h in an aerobic environment. [b] Isolated yields by column chromatography.

9. XPS characterization of DIM-Pd-CMP after catalytic runs

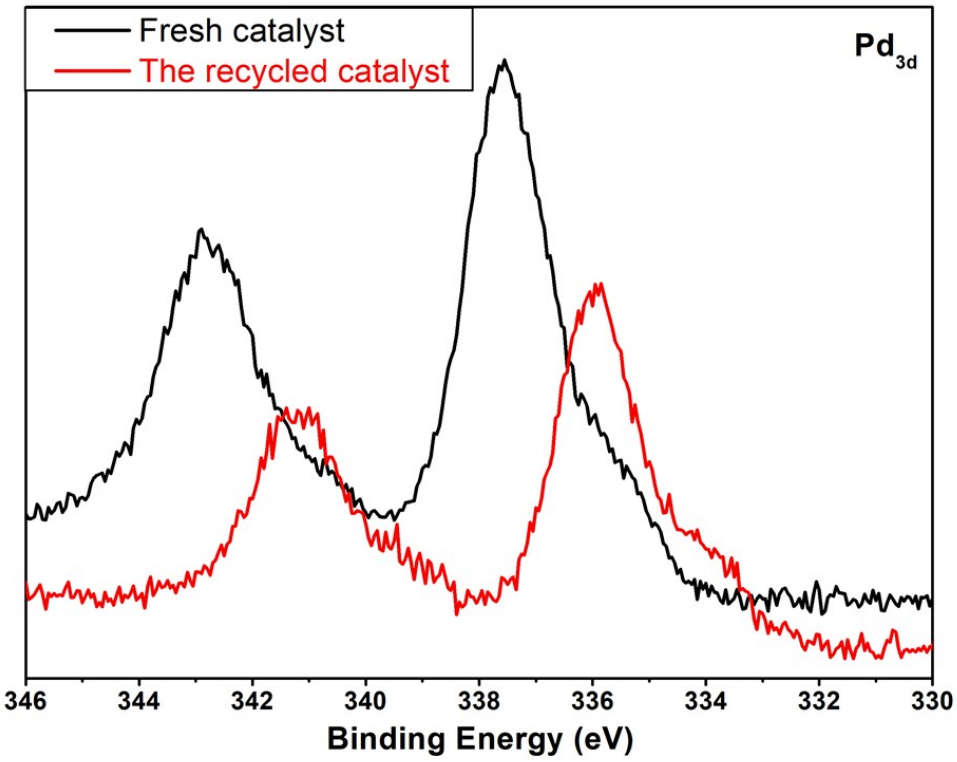


Figure S4. XPS characterization of **DIM-Pd-CMP** (in black) and **the recycled DIM-Pd-CMP catalyst** (run 6 in red).

XPS spectrum of the recycled DIM-Pd-CMP showed that the binding energy (BE) at 335.85 eV, corresponding to the $Pd3d_{5/2}$ orbital, suggested that the Pd species in the recycled DIM-Pd-CMP were in a 0 state.

10. FT-IR spectra of fresh catalyst and the recovered DIM-Pd-CMP

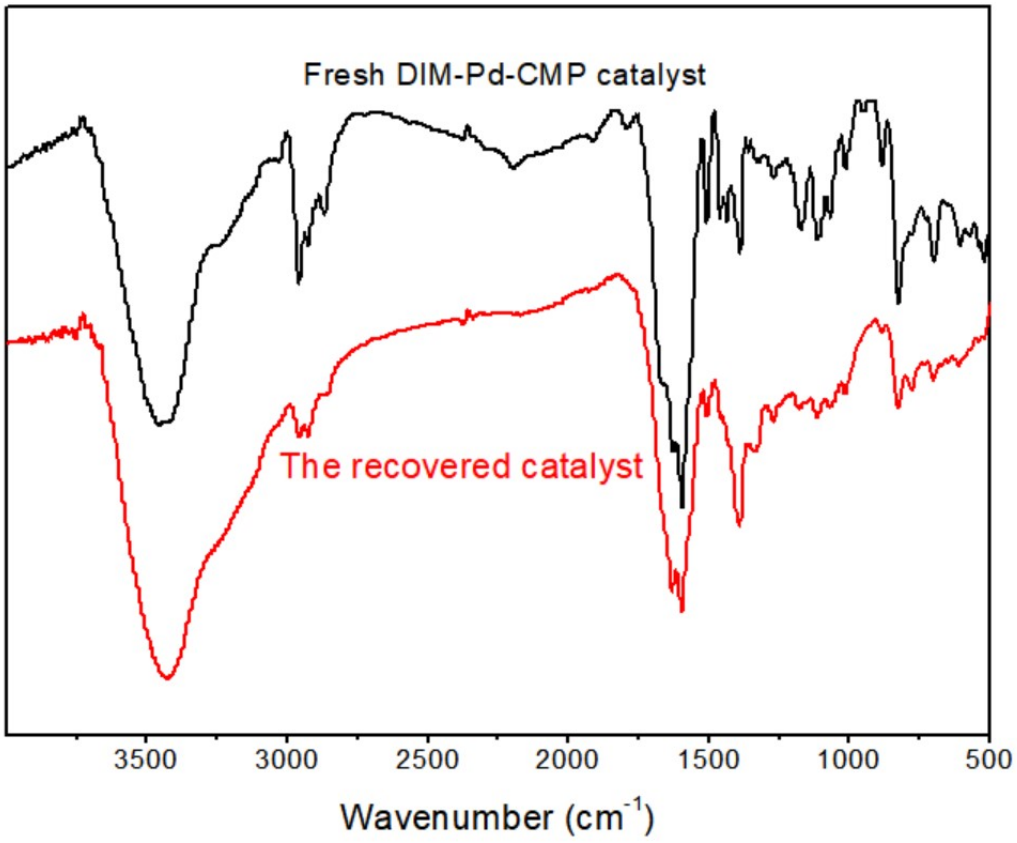
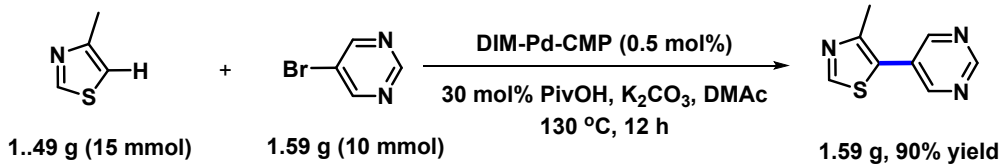


Figure S5. FT-IR spectra of fresh catalyst (black) and the recovered DIM-Pd-CMP (red)

FT-IR spectra of the recovered DIM-Pd-CMP indicated no apparent structural change, which suggested that DIM-Pd-CMP has a satisfactory stability.

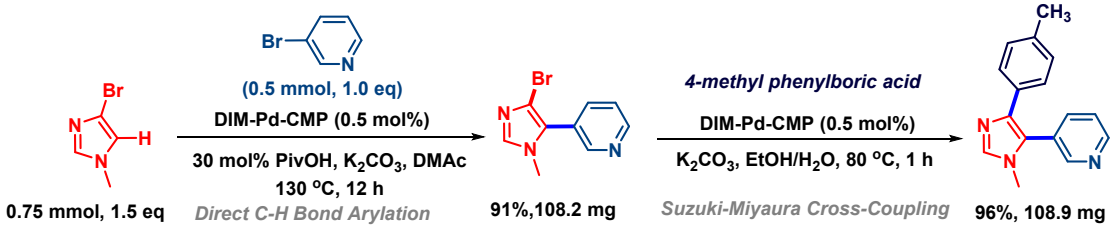
11.The practical application of DIM-Pd-CMP catalyst

a. Gram-Scale Synthesis of the Biheteroarene via Direct C-H Bond Arylation



A 150 mL round-bottom flask containing a stir bar was charged with DIM-Pd-CMP (0.5 mol%), 4-methylthiazole (15.0 mmol, 1.5 equiv), 5-bromopyrimidine (10.0 mmol, 1.0 equiv.), K_2CO_3 (15.0 mmol), PivOH (3.0 mmol) and 50 mL of DMAc. The reaction mixture was carried out at 130 °C for 12 h. After the reaction was completed (monitored by TLC), the mixture was filtered and the solid was washed with dichloromethane (3 x 50 mL). The combined organic phase was washed with water to remove K_2CO_3 and DMAc residue. The organic layer was dried with anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The product was collected as a yellow solid (1.59 g) after silica-gel column chromatography with petroleum ether/EtOAc (6/1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.83 (d, J = 8.9 Hz, 3H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.70, 156.33, 152.13, 151.09, 126.96, 124.27, 15.96.

b. Synthesis of Potentially Bioactive Molecule[6]



A 25 mL round-bottom flask containing a stir bar was charged with DIM-Pd-CMP (0.5 mol%), 4-bromo-1-methyl-1H-imidazole (0.75 mmol, 1.5 equiv), 3-bromopyridine (0.5 mmol, 1.0 equiv), K_2CO_3 (0.75 mmol), PivOH (0.15 mmol) and 2.5 mL of DMAc. After the reaction was completed (monitored by TLC), the mixture was filtered and the solid was washed with dichloromethane (3 x 10 mL). The combined organic phase was washed with water to remove K_2CO_3 and DMAc residue. The organic layer was dried with anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The product 3-(4-bromo-1-methyl-1H-imidazol-5-yl)pyridine was collected as a white solid (108.2 mg) after silica-gel column chromatography with petroleum ether/EtOAc (10/1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 – 8.60 (m, 2H), 7.74 (d, J = 7.9 Hz, 1H), 7.54 (s, 1H), 7.43 (dd, J = 7.6, 5.1 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.09, 139.38, 137.86, 137.14, 124.67, 123.43, 94.26, 38.38.

Then 3-(4-bromo-1-methyl-1H-imidazol-5-yl)pyridine (108.2 mg, 0.45 mmol), 4-methyl phenylboric acid (1.5 equiv), K_2CO_3 (2.0 equiv), and DIM-Pd-CMP (0.5 mol%) were dissolved in in 2.0 mL of EtOH/H_2O under an aerobic atmosphere. The reaction mixture was stirred at 80 °C for 1 h. After the reaction was completed (monitored by TLC), the mixture was filtered and the solid was washed with dichloromethane (3 x 10 mL). The combined organic phase was washed with water to remove K_2CO_3 residue. The organic layer was dried with anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The residue was purified by silica-gel column chromatography to give the product in 96% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 3.7 Hz, 1H), 8.61 (s, 1H), 7.77 (s, 1H), 7.67 (dt, J = 7.8, 1.9 Hz, 1H), 7.40 (dd, J = 7.8, 4.9 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 3.56 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.12, 149.73, 138.24, 138.12, 137.39, 136.84, 130.52, 129.17, 126.87, 126.67, 124.92, 123.80, 32.58, 21.17.

12.References

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(b) Chen, F.-M.; Huang, F.-D.; Yao, X.-Y.; Li, T.; Liu, F.-S. *Org. Chem. Front.* **2017,** *4*, 2336.

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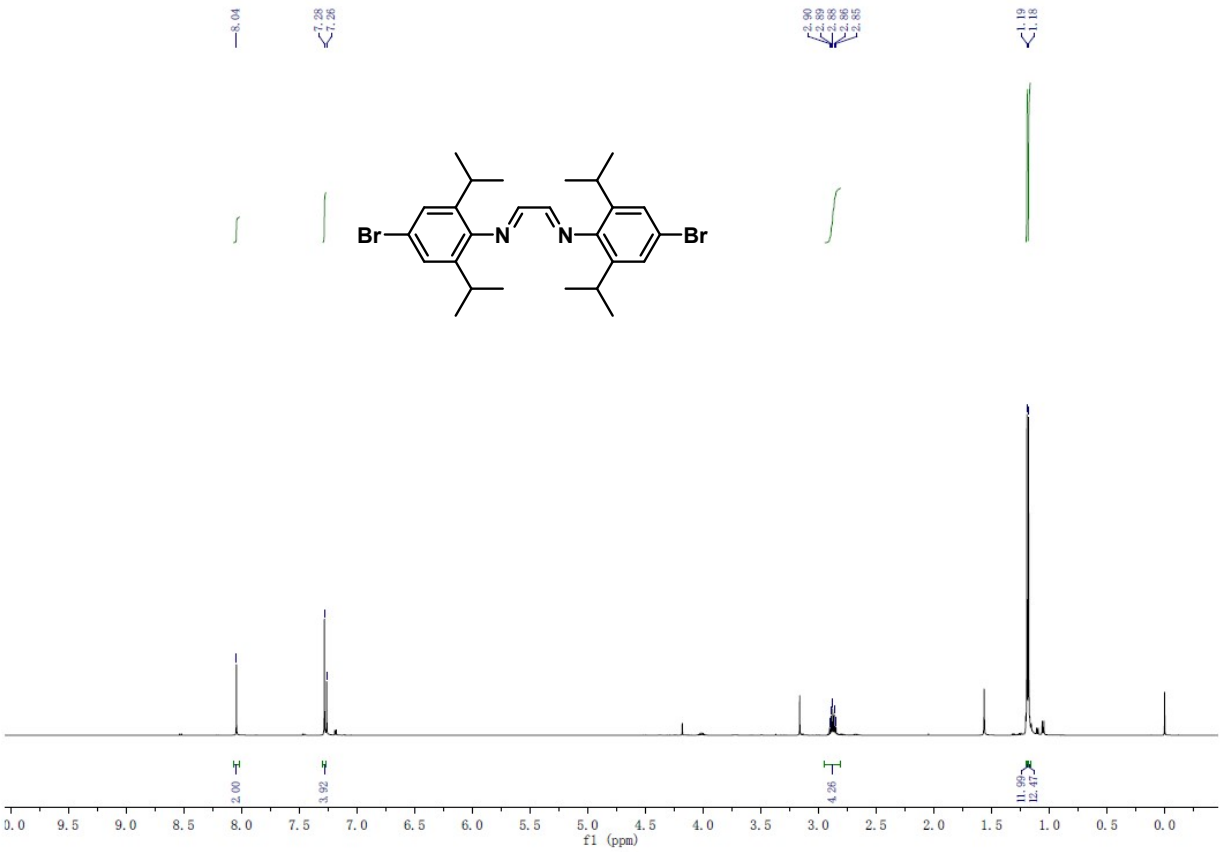
13. ^{1}H NMR and ^{13}C NMR spectra for the products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2.88
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1.18
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Br
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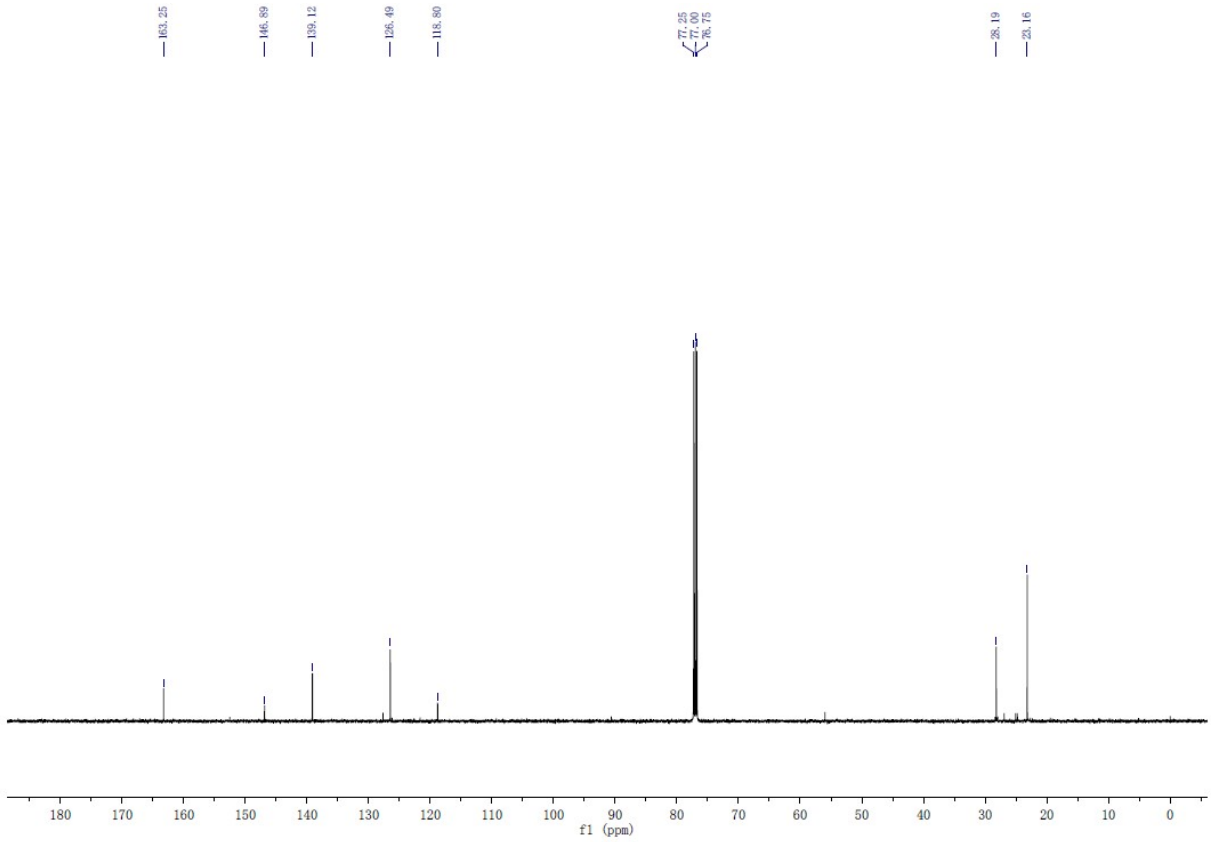
12.47
f1 (ppm)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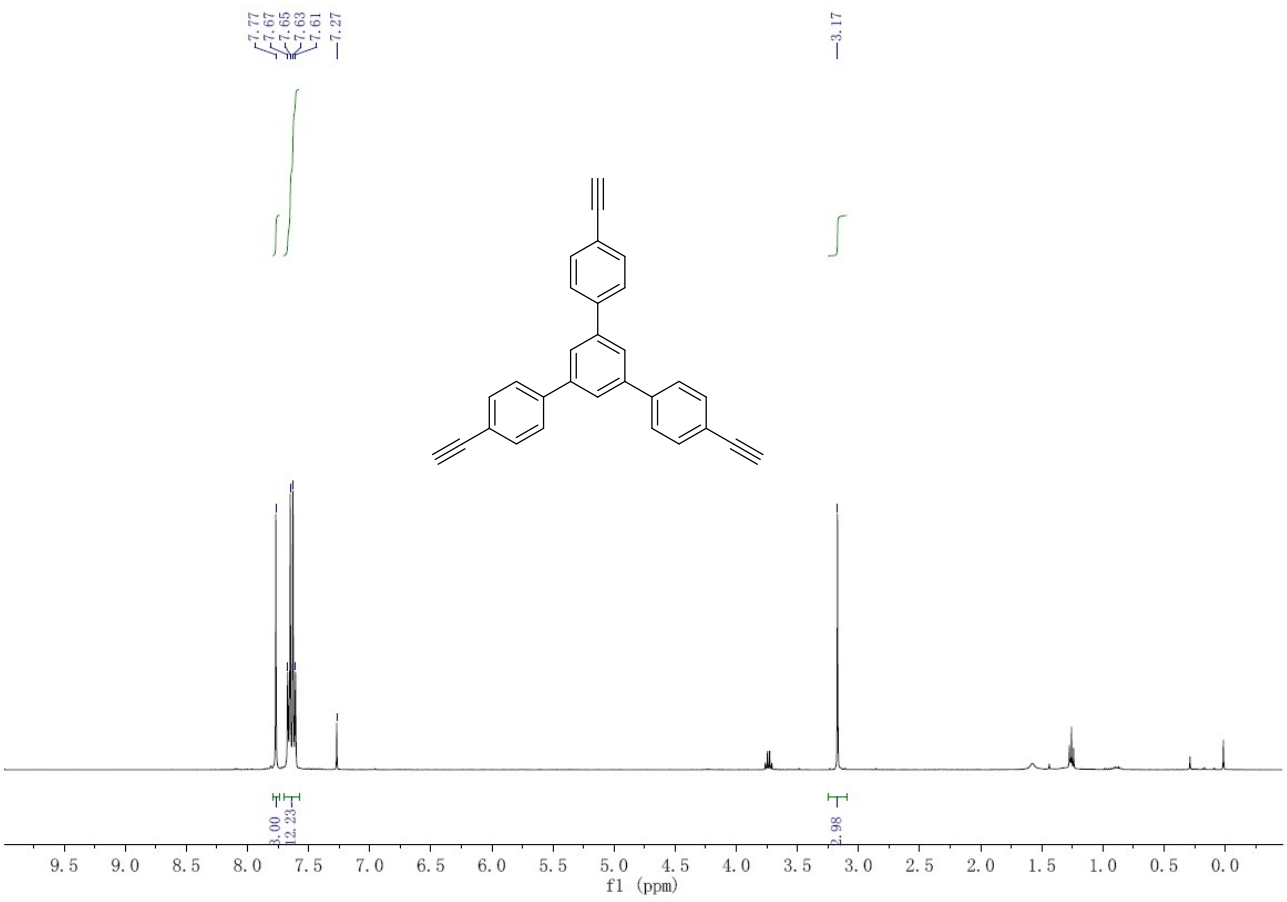
f1 (ppm)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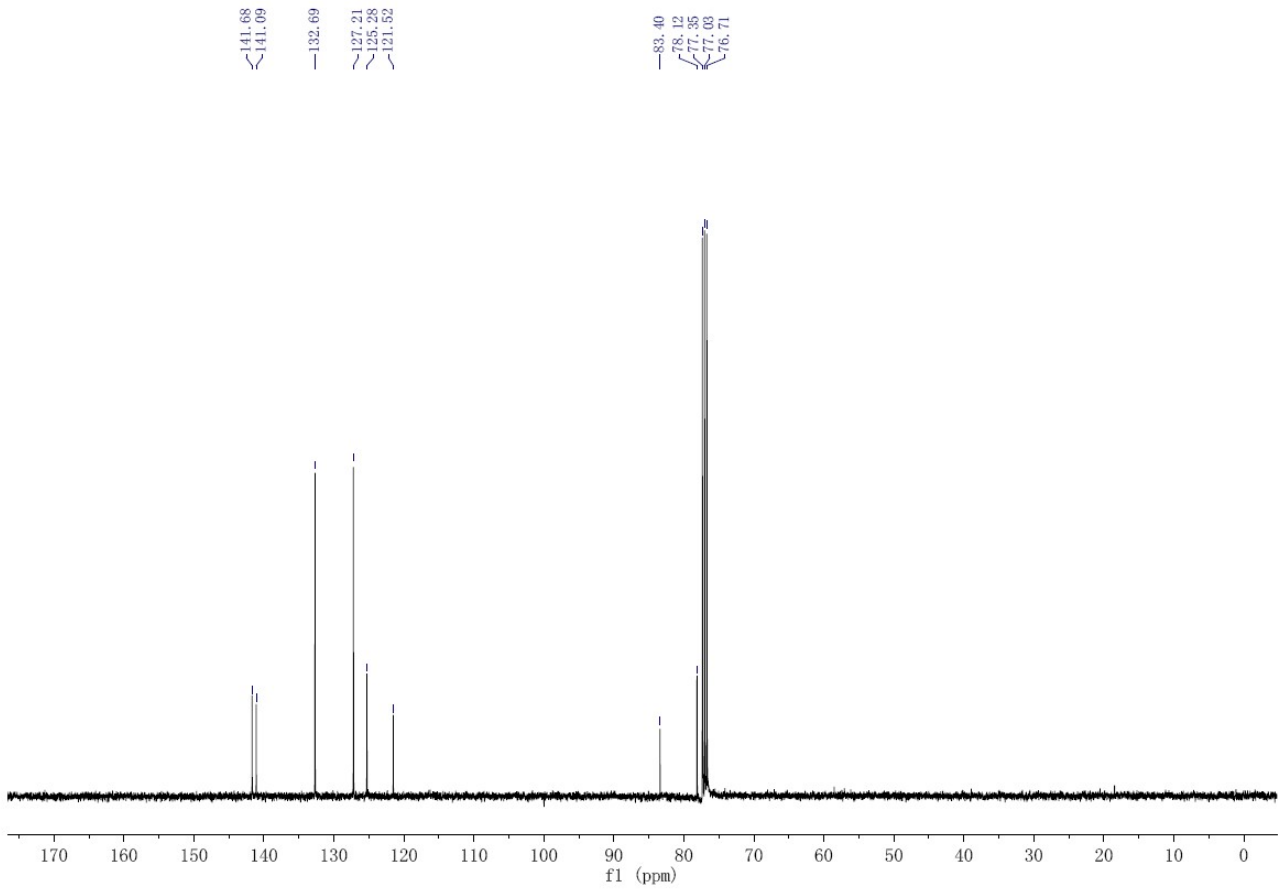
7.63
7.61
7.27
3.17
3.00
12.23
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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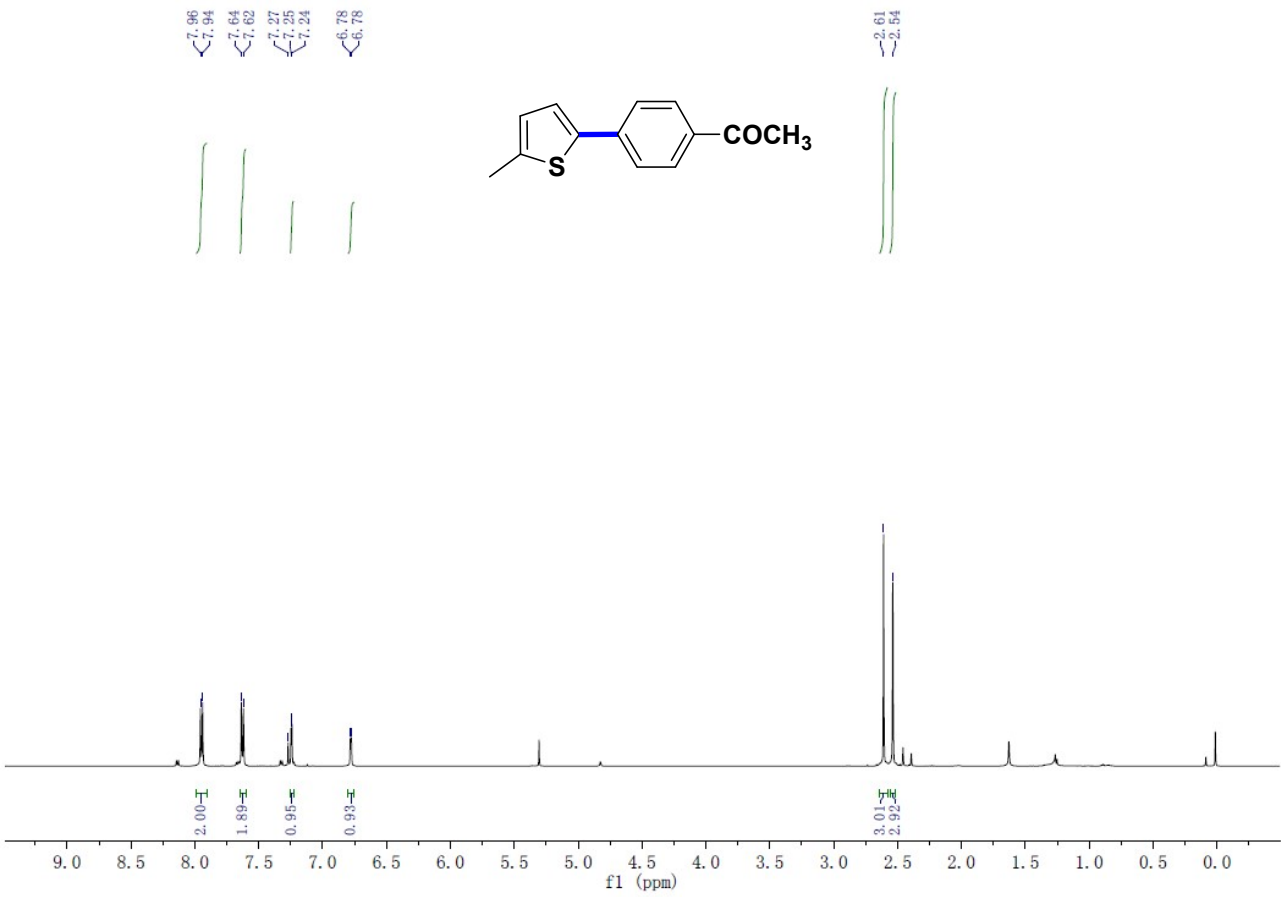
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7.25
7.24
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2.54
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S
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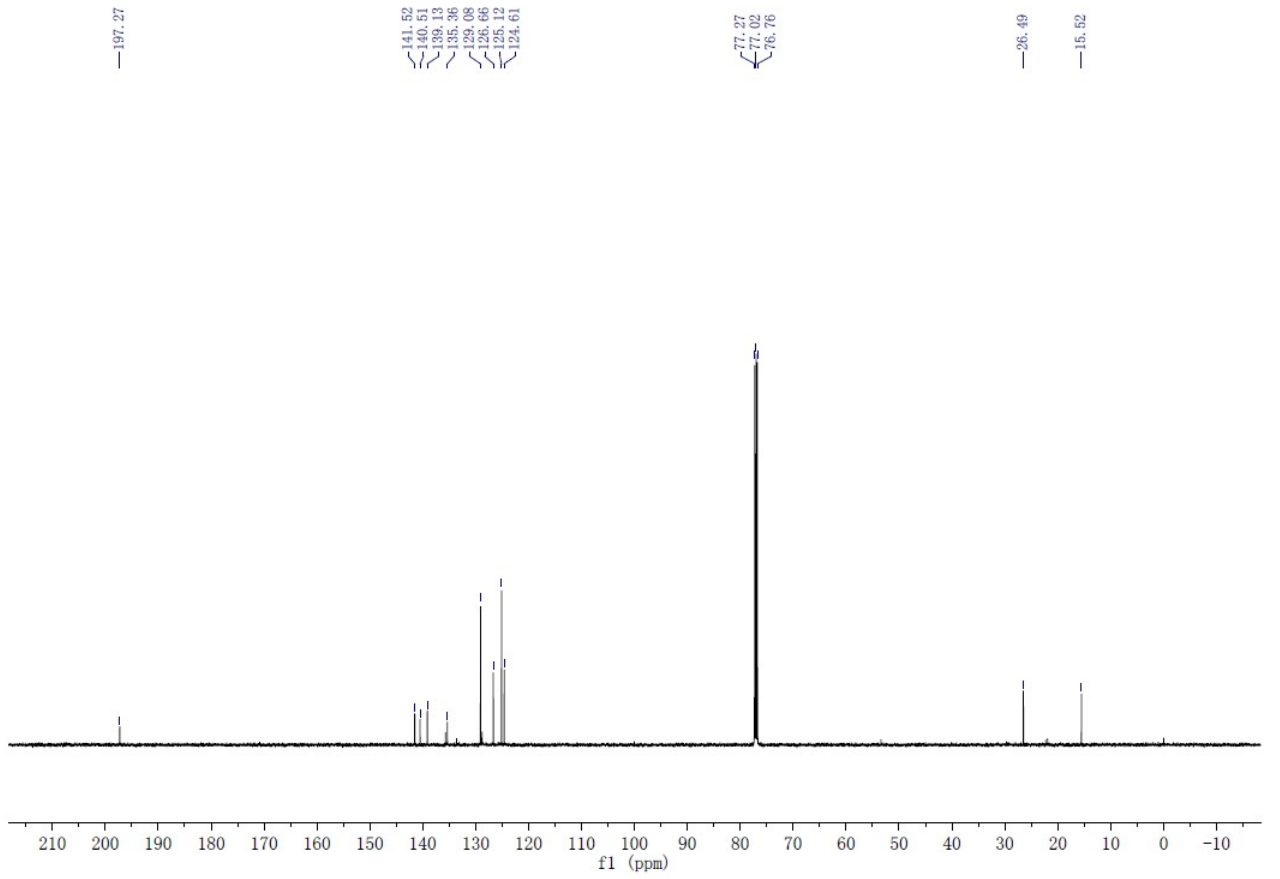
0.93
3.01
2.92
f1 (ppm)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76.76
26.49
15.52
f1 (ppm)


7.55
7.53
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7.24
7.24
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7.10
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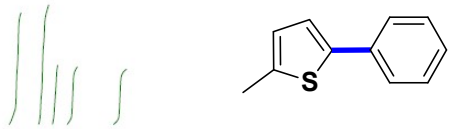
6.71


2.50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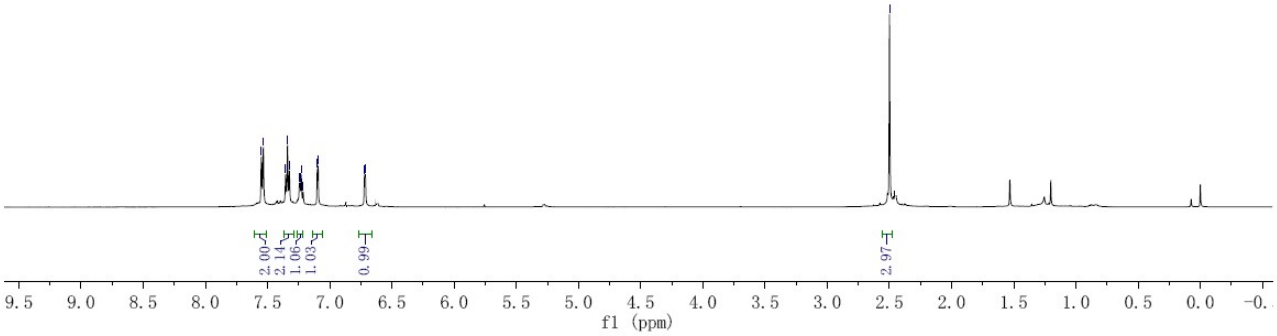
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f1 (ppm)


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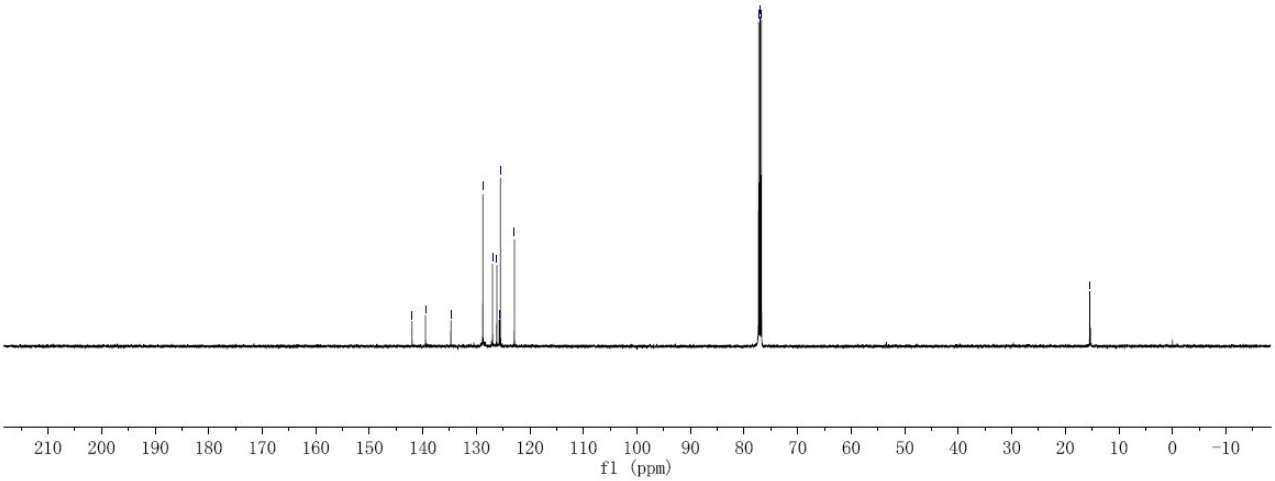
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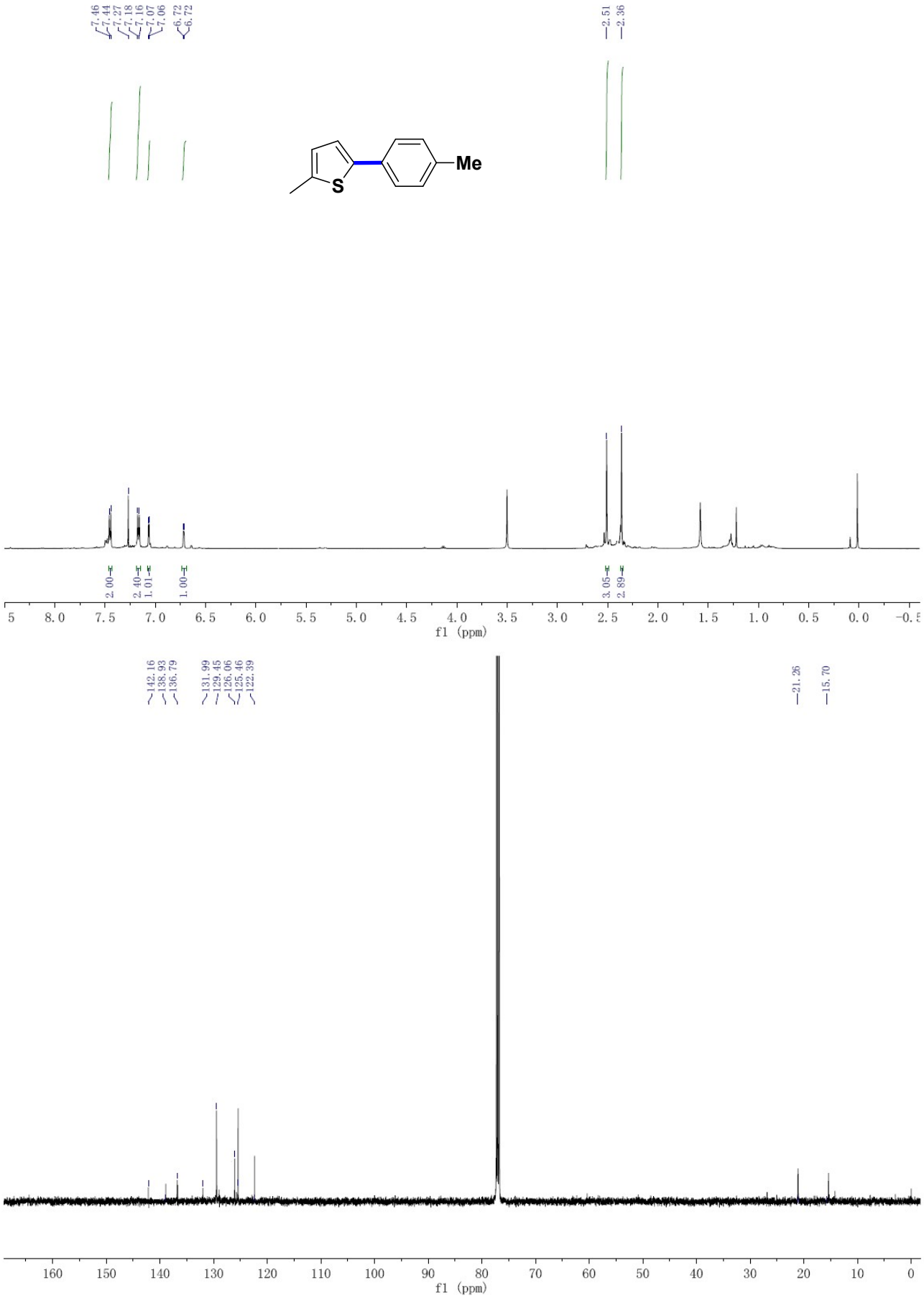
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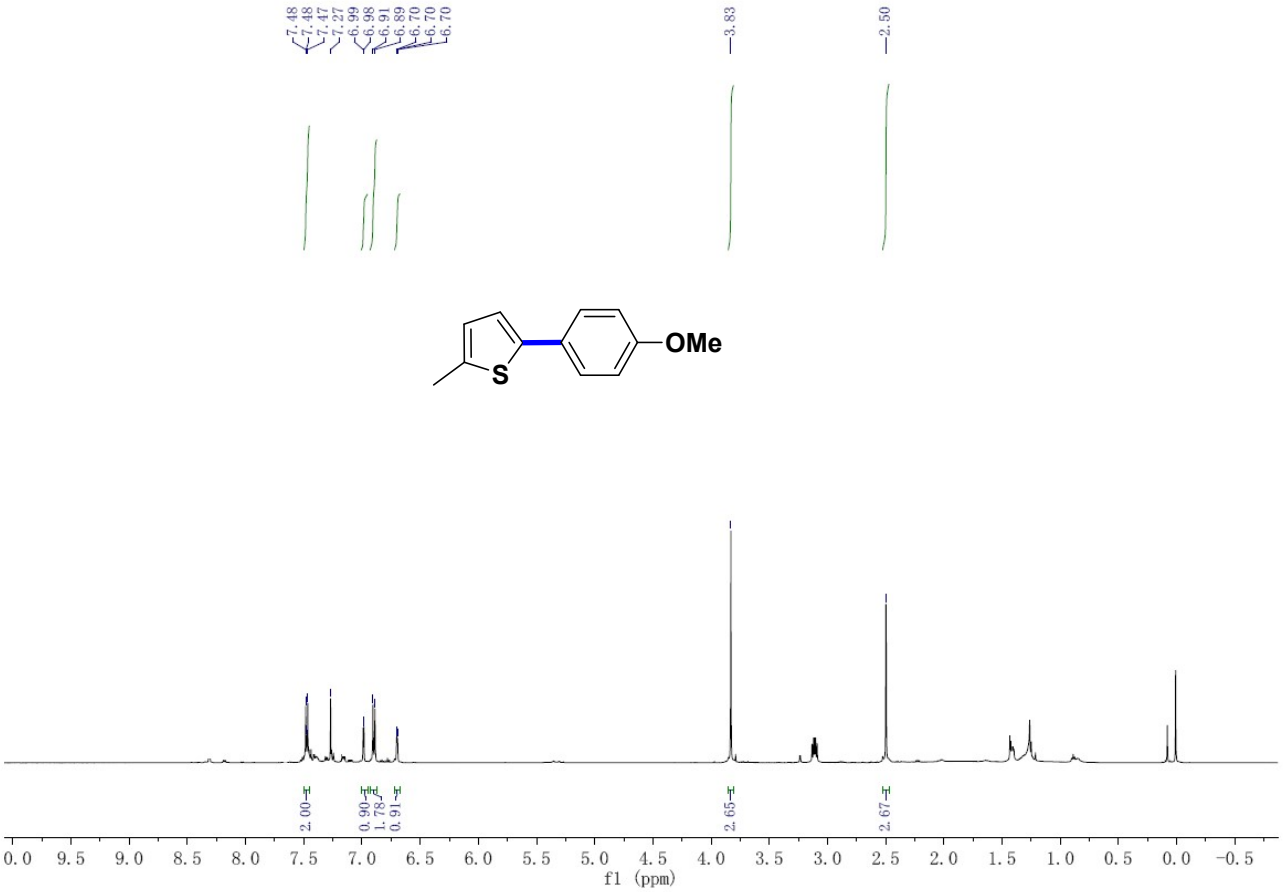
f1 (ppm)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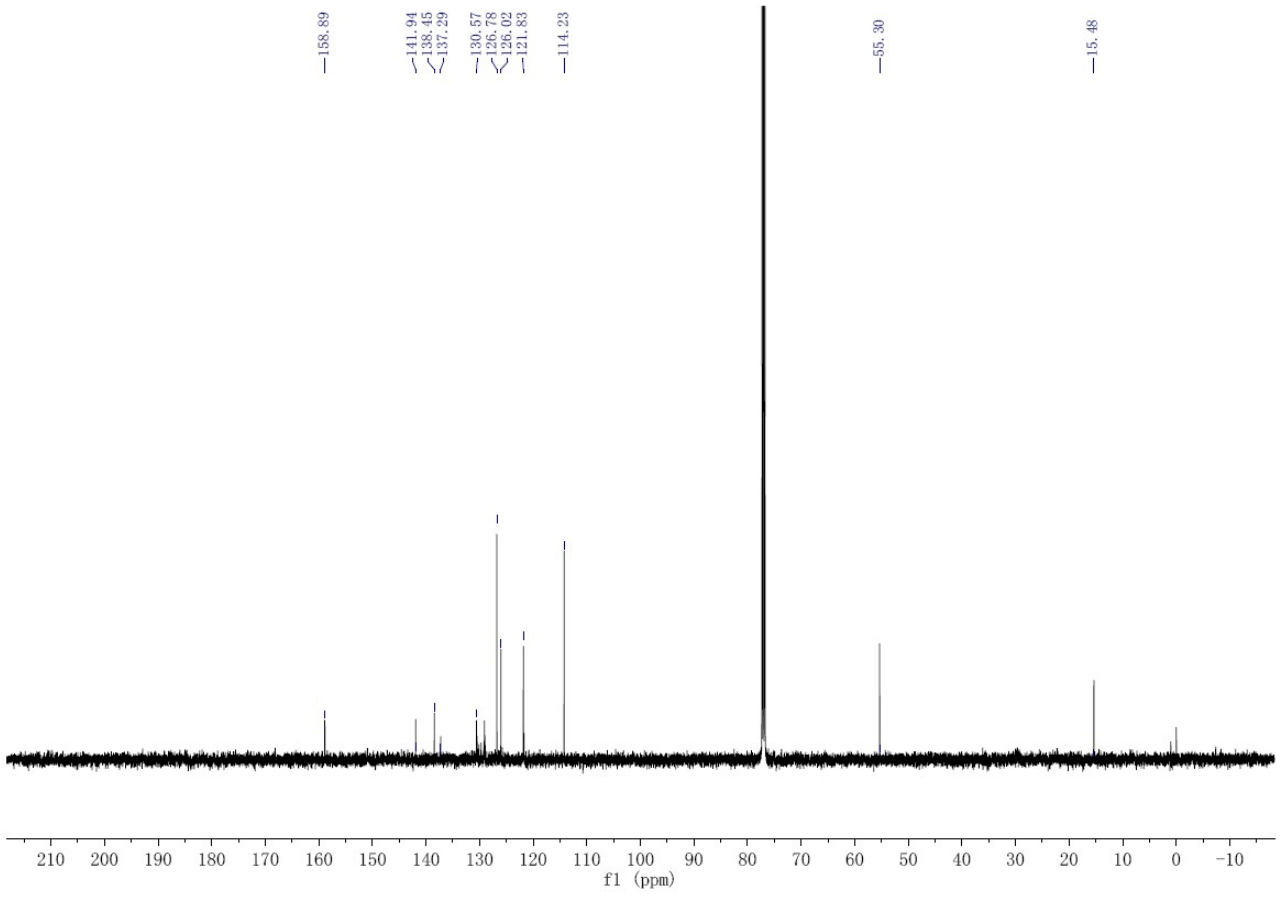
f1 (ppm)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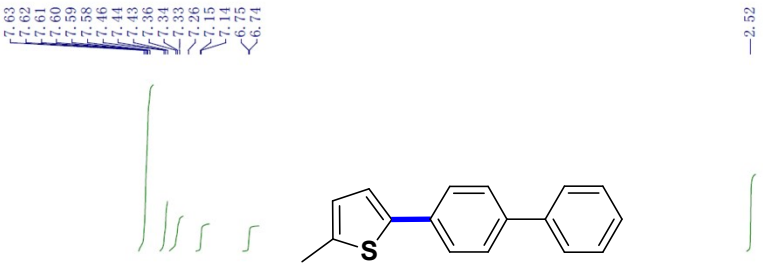
f1 (ppm)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7.58
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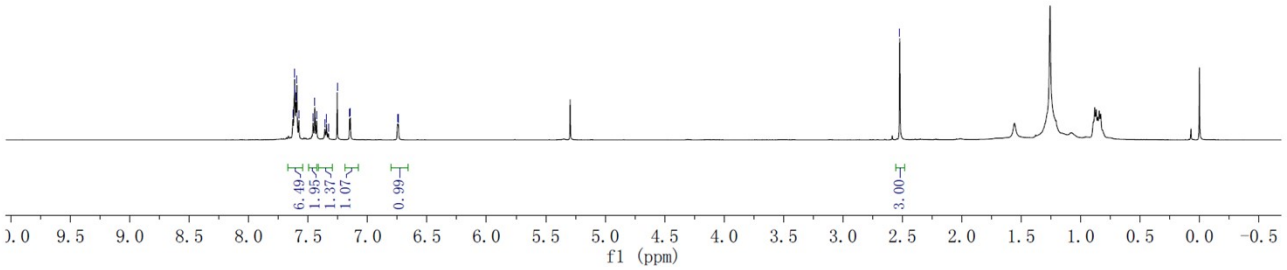
7.26
7.15
7.14
6.75
6.74
2.52
S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1.37
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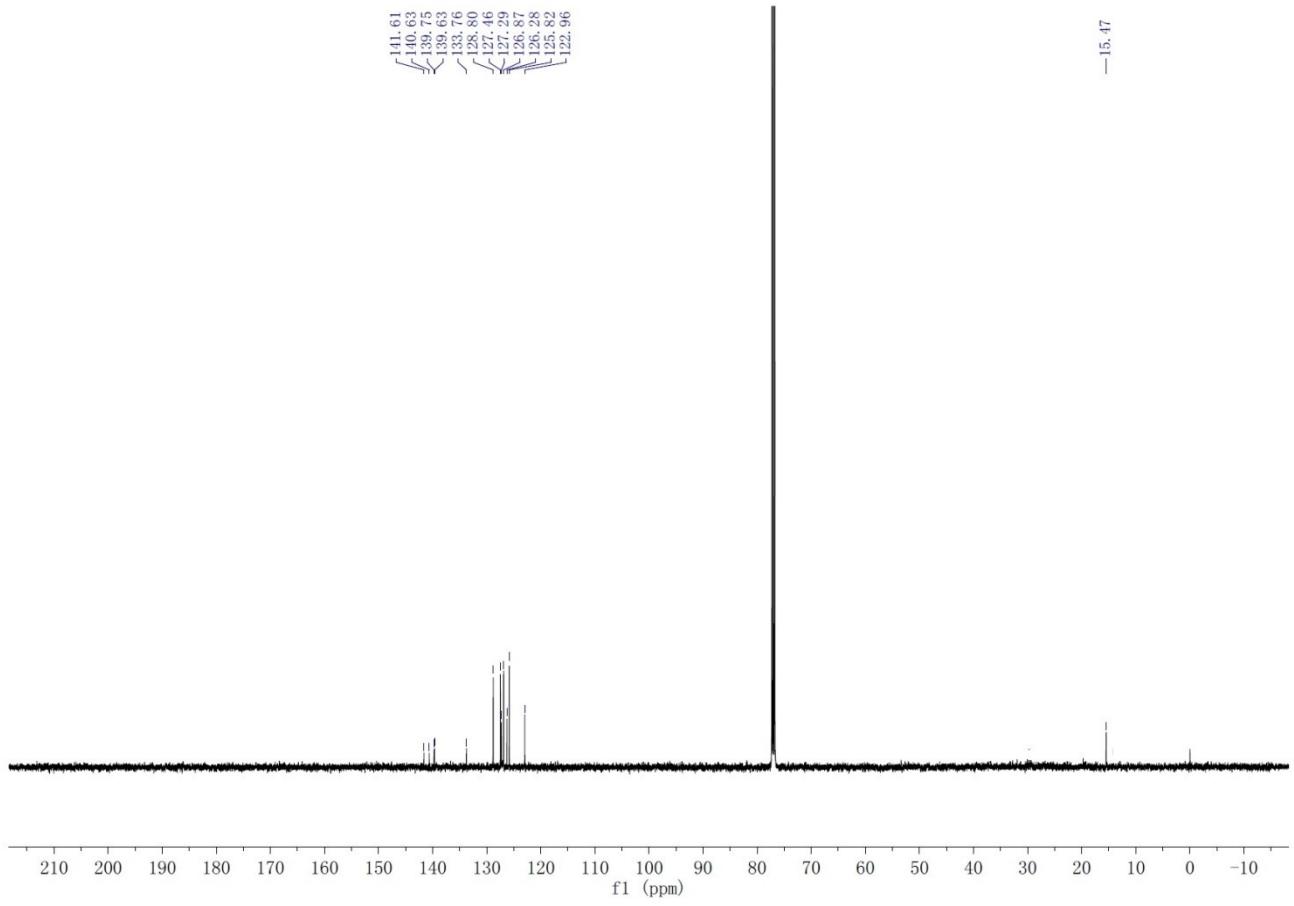
f1 (ppm)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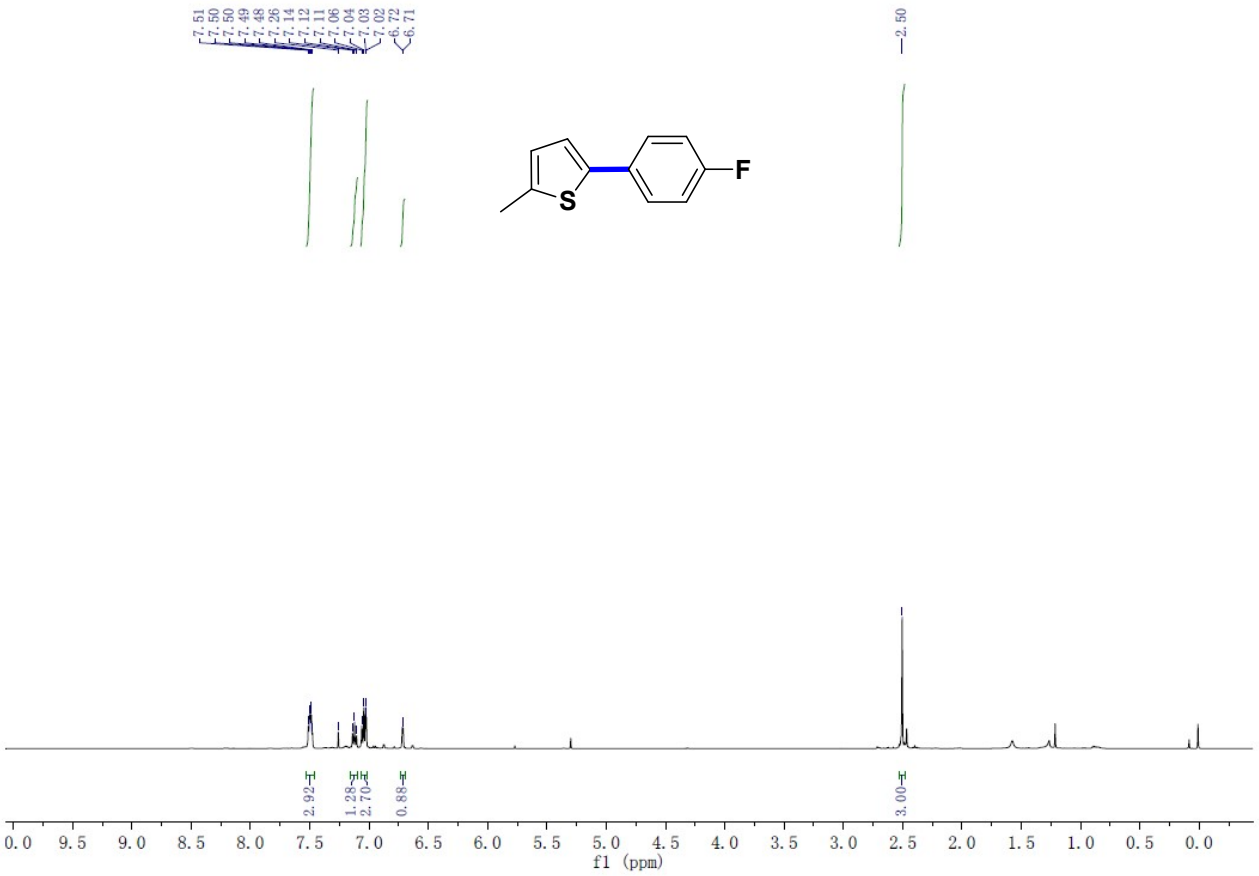
127.29
126.87
126.28
125.82
122.96
15.47
f1 (ppm)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7.26
7.14
7.12
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7.06
7.04
7.03
7.02
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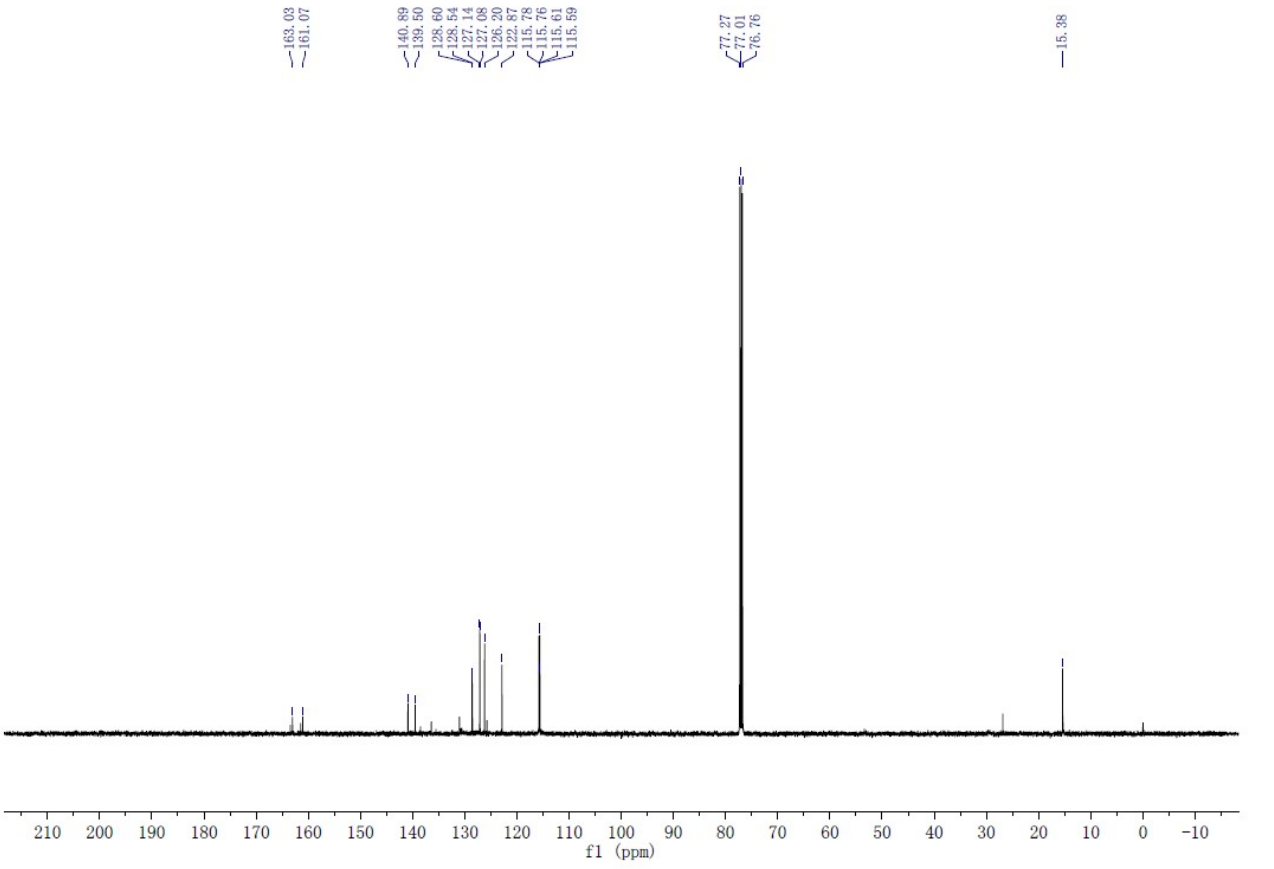
6.71
2.50
S
F
2.92
1.28
2.70
0.88
3.00
f1 (ppm)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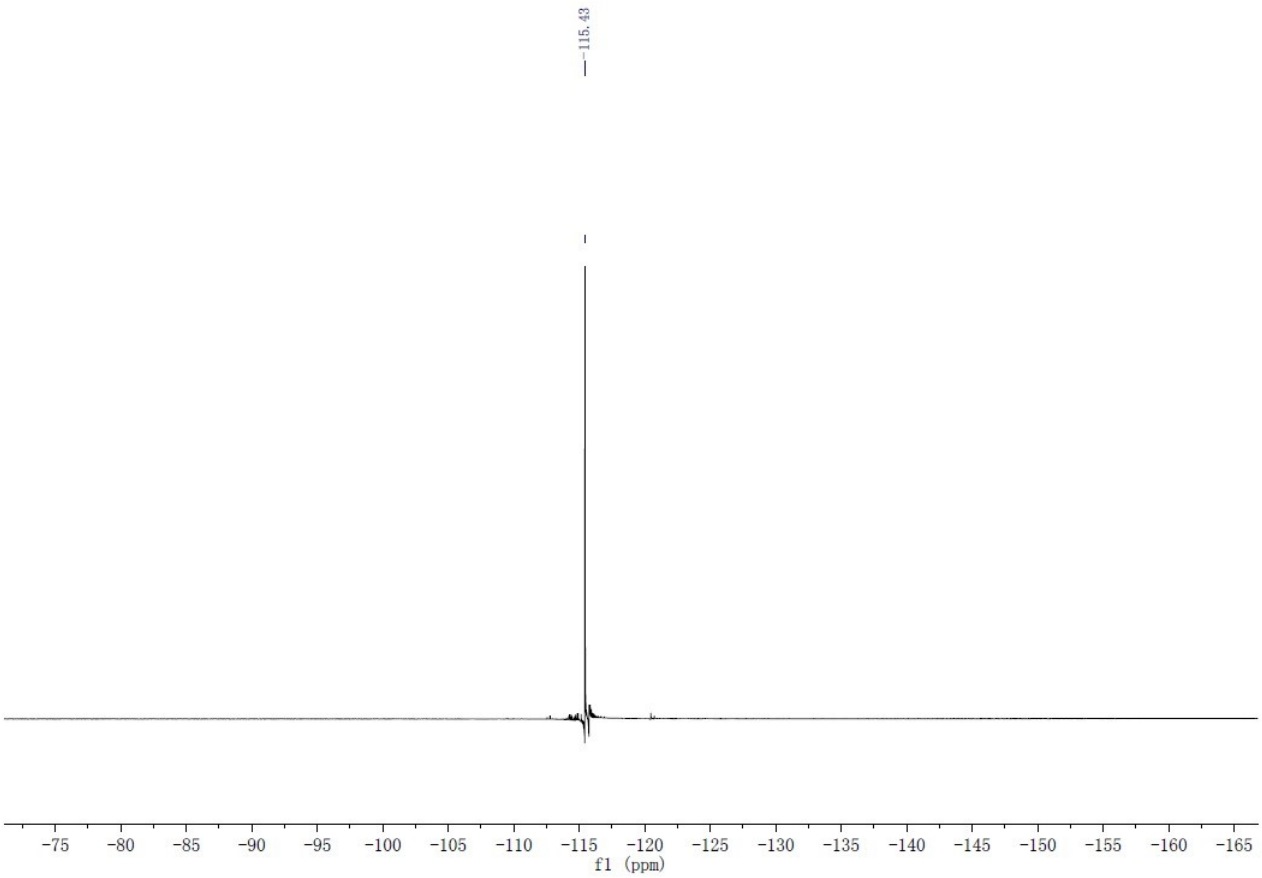
77.27
77.01
76.76
15.38
f1 (ppm)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-95
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-120
-125
-130
-135
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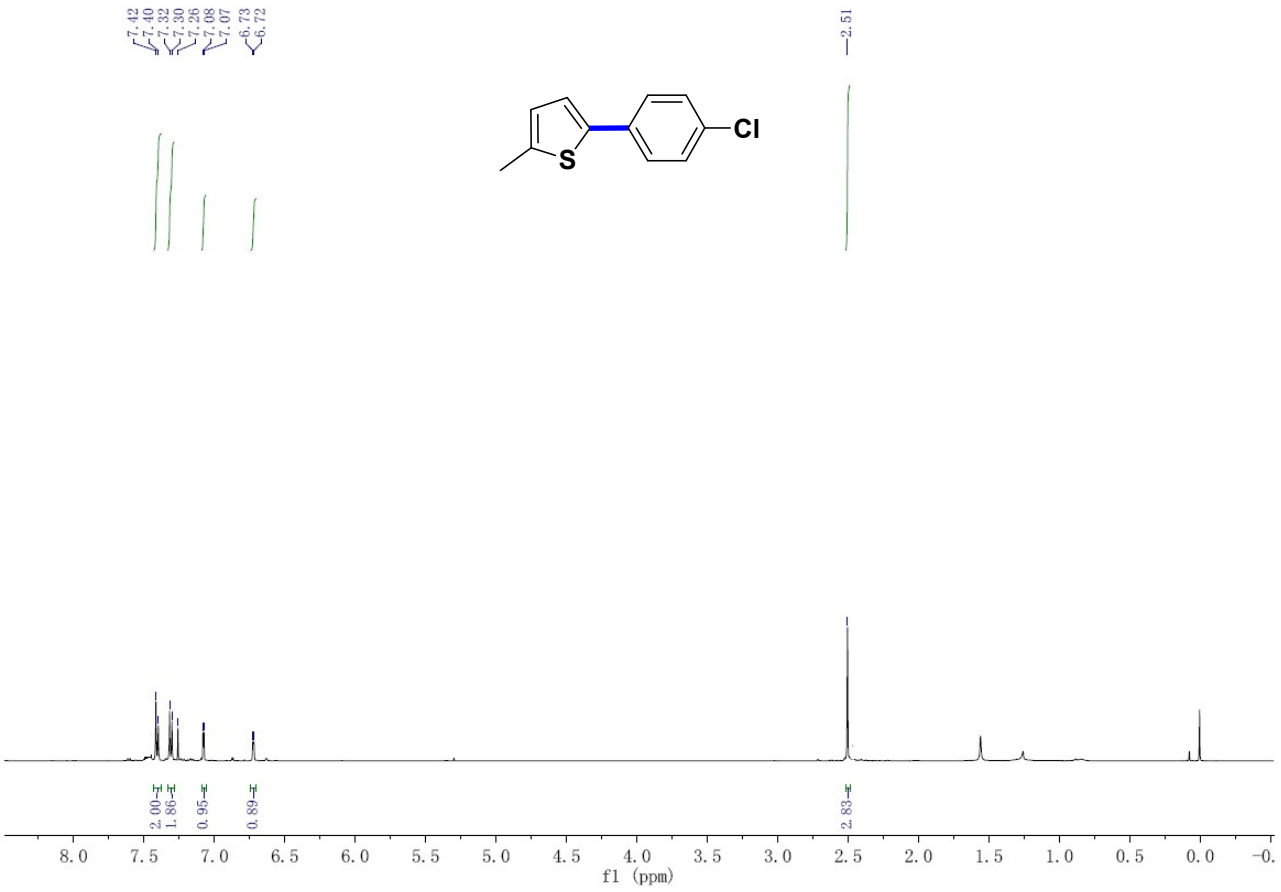
-145
-150
-155
-160
-165
f1 (ppm)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6.72
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Cl
S
2.00
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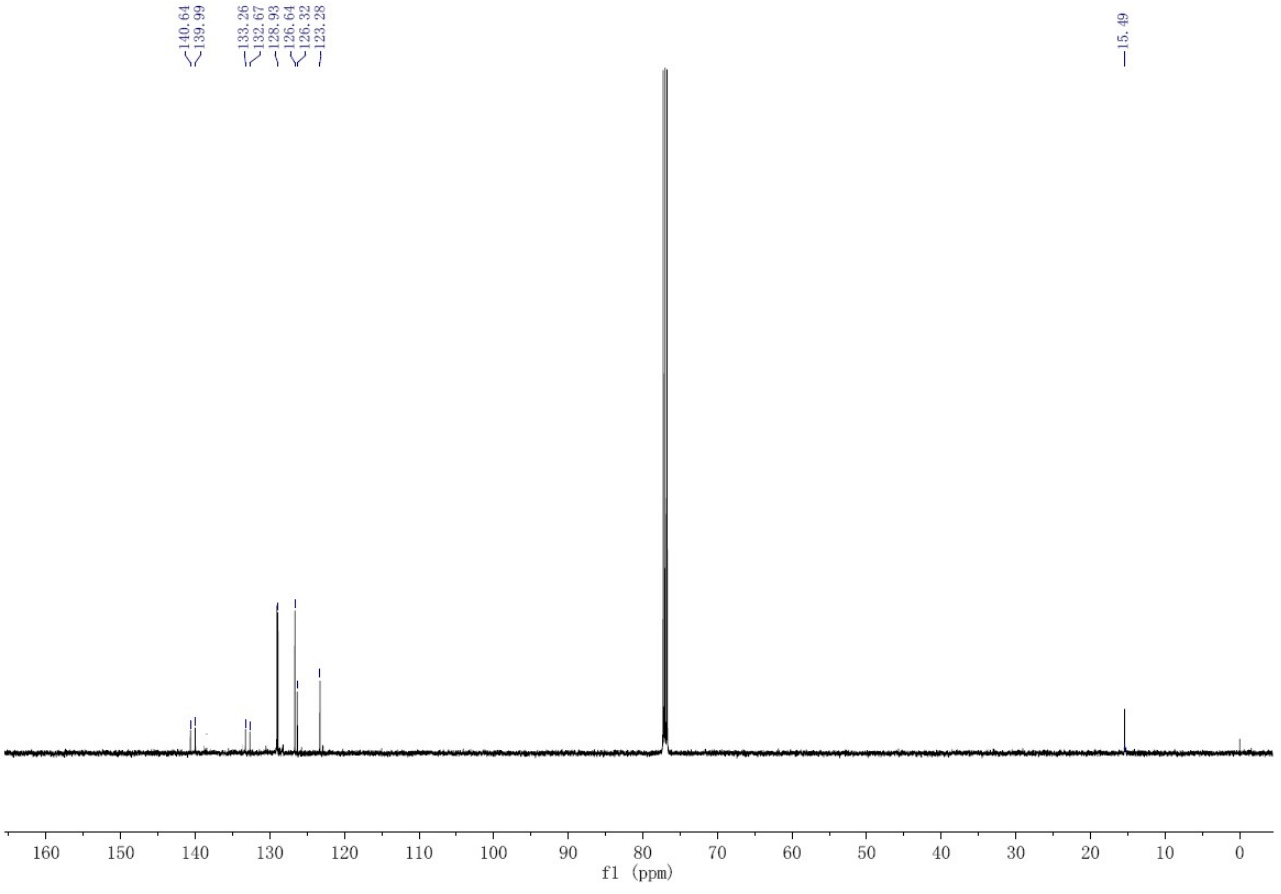
0.95
0.89
2.83
f1 (ppm)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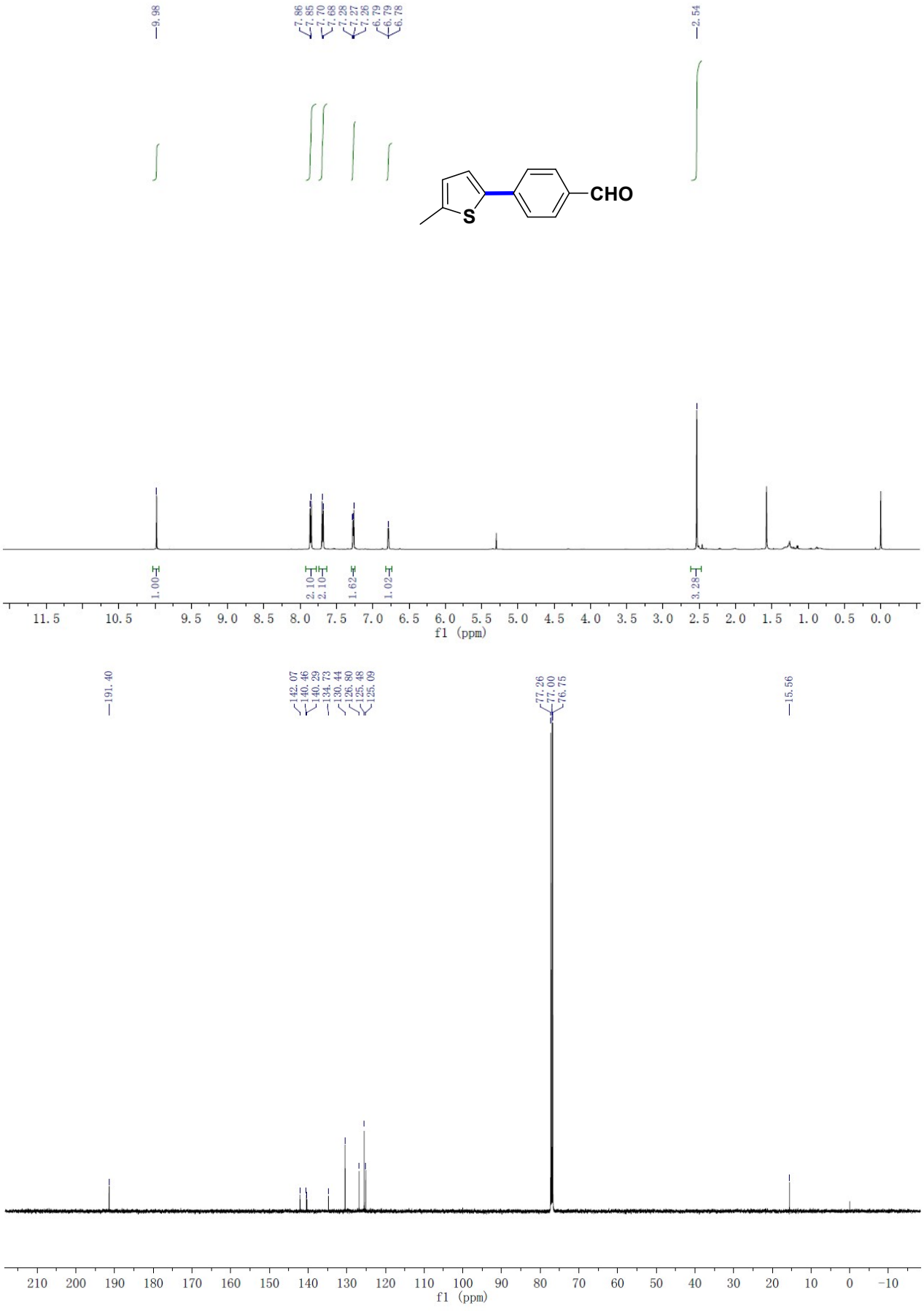
126.64
126.32
123.28
15.49
f1 (ppm)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7.28
7.27
7.26
6.79
6.79
6.78
2.54
CHO
S
1.00
2.10
2.10
1.62
1.02
3.28
f1 (ppm)
191.40
142.07
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140.29
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130.44
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125.09
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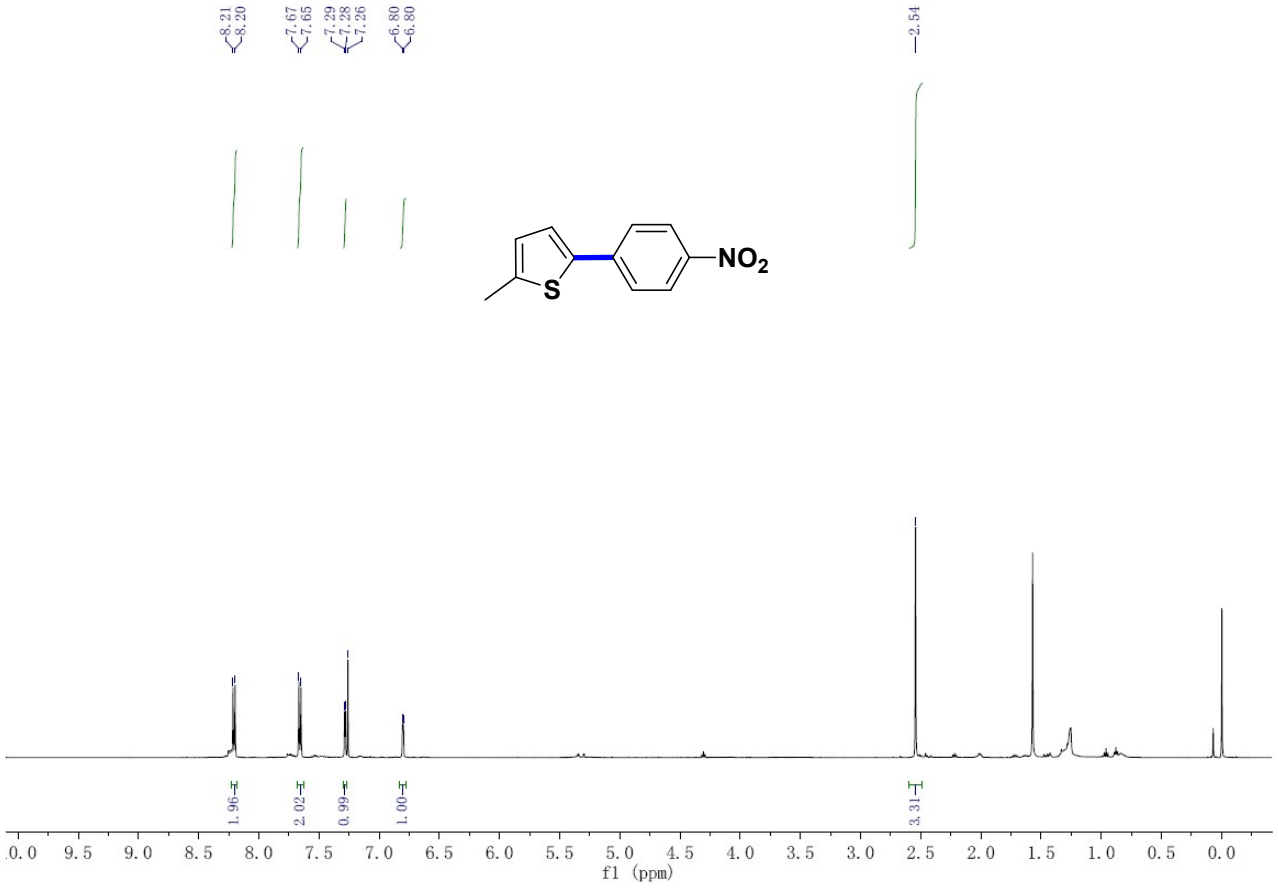
76.75
15.56
f1 (ppm)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7.28
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6.80
2.54
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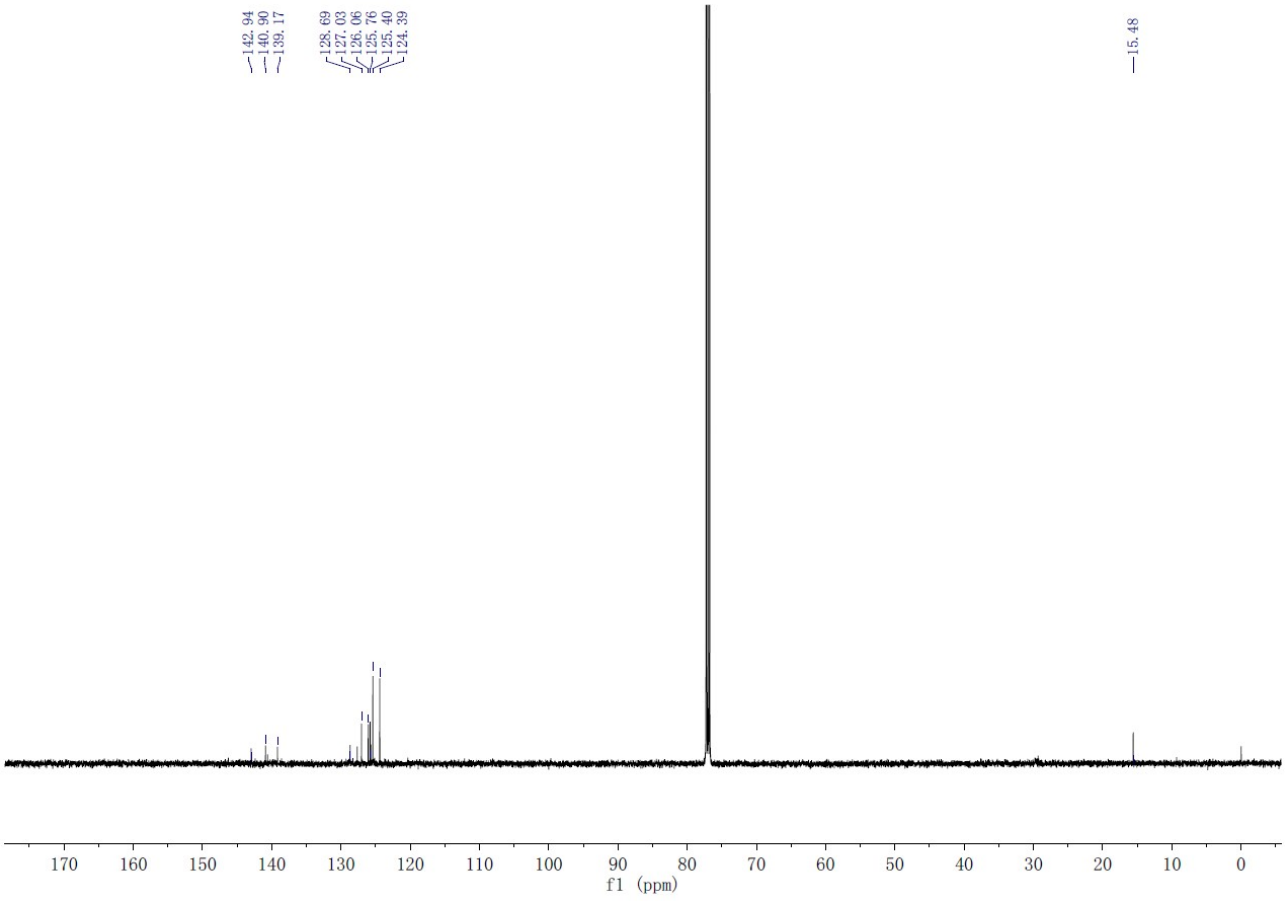
2.02
0.99
1.00
3.31
f1 (ppm)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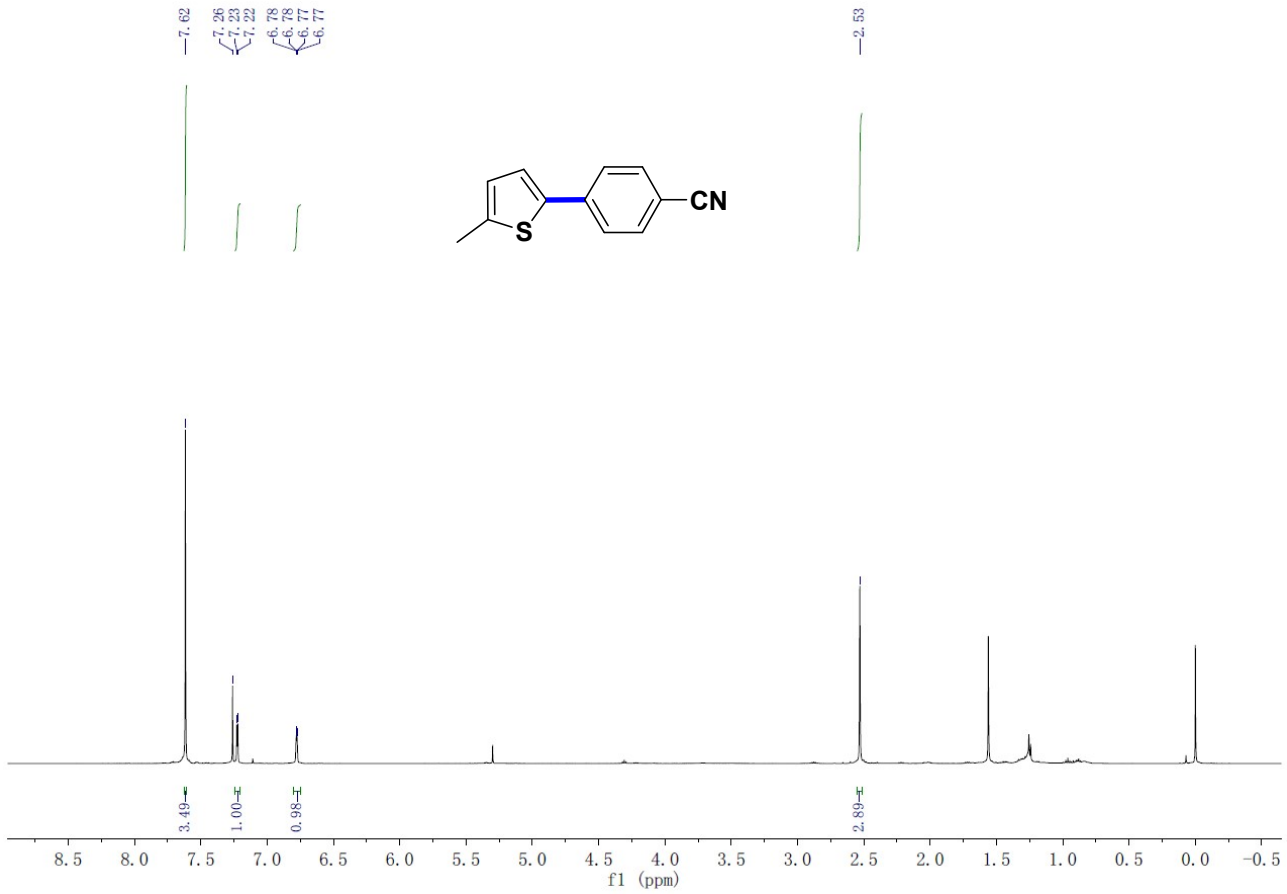
127.03
126.06
125.76
125.40
124.39
15.48
f1 (ppm)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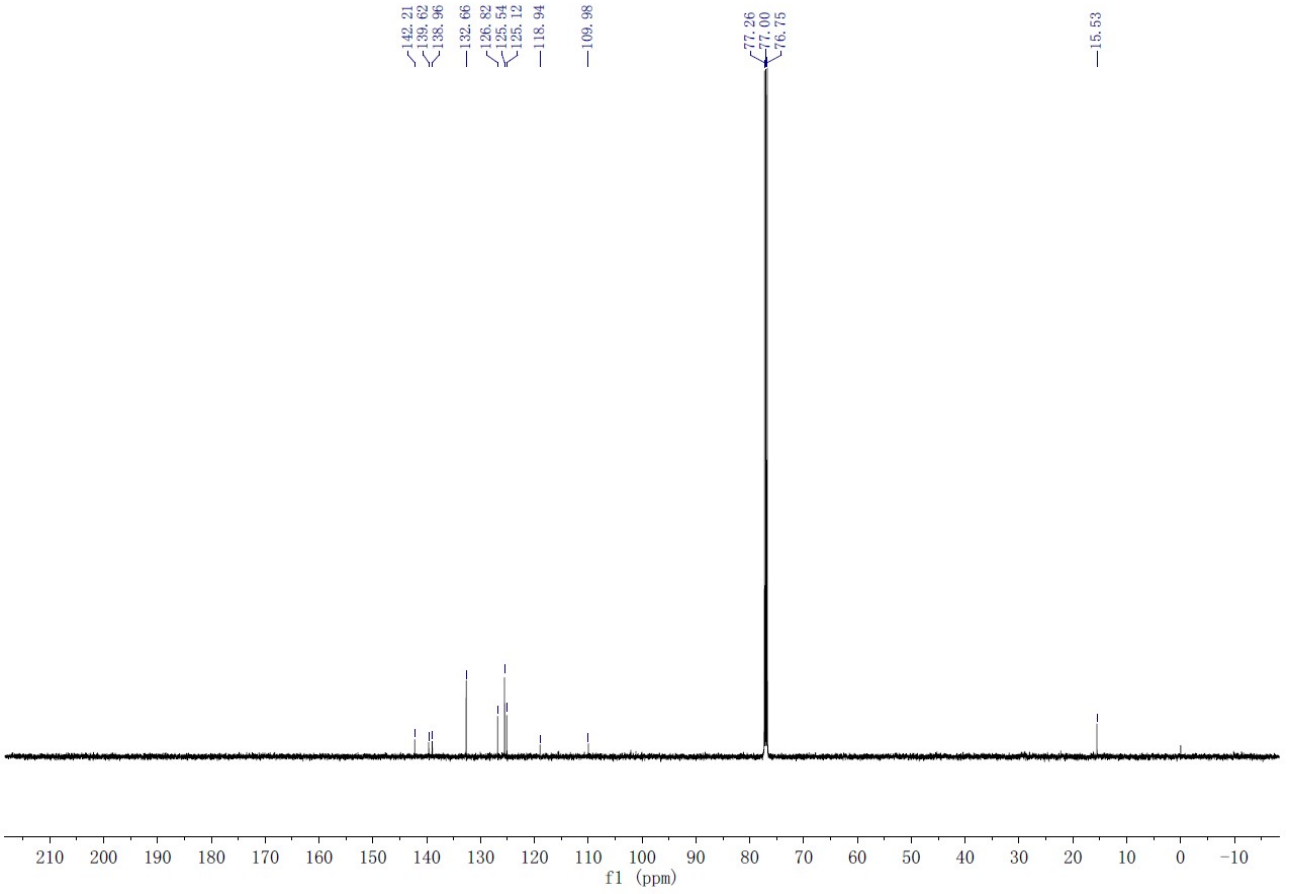
7.26
7.23
7.22
6.78
6.78
6.77
6.77
2.53
CN
S
3.49
1.00
0.98
2.89
f1 (ppm)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139.62
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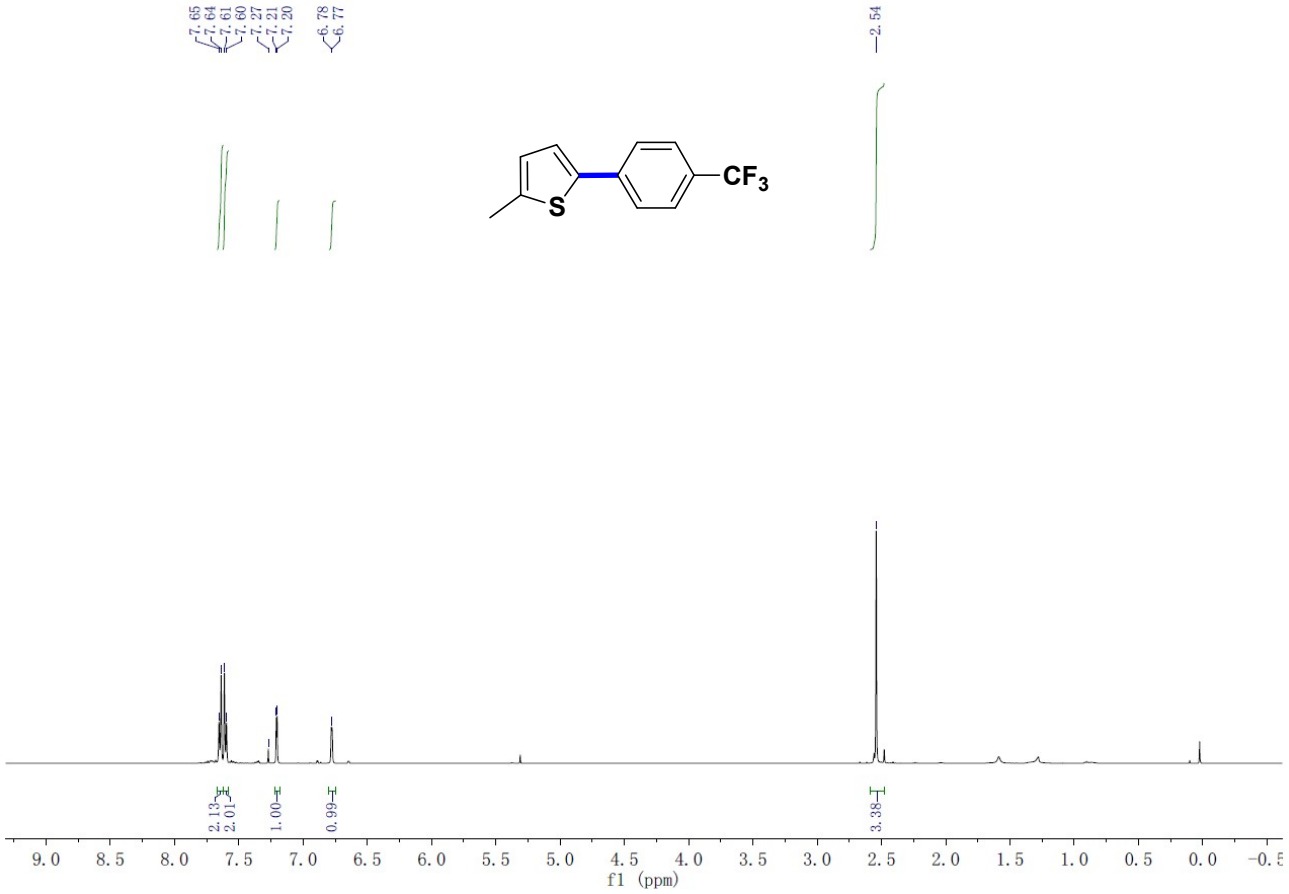
109.98
77.26
77.00
76.75
15.53
f1 (ppm)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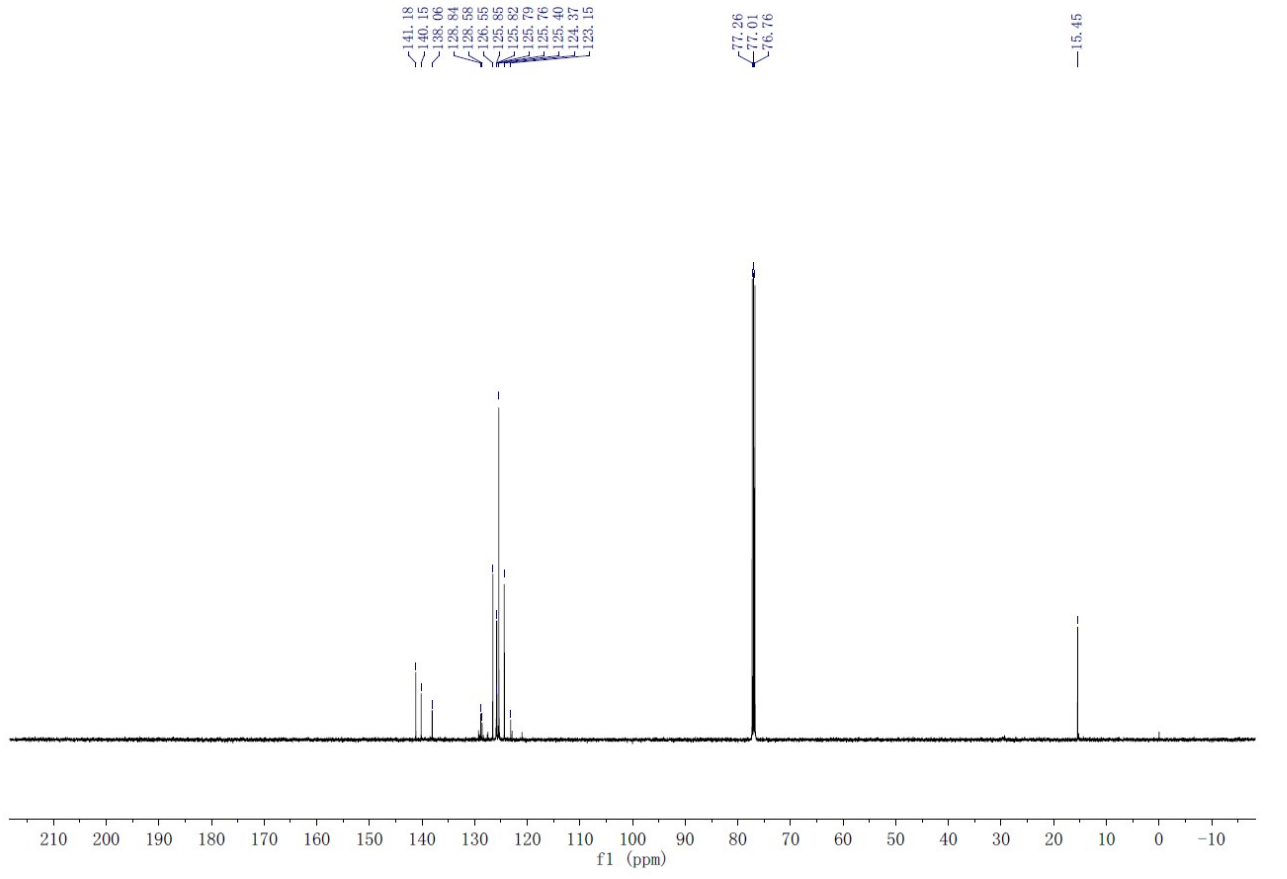
7.64
7.61
7.60
7.27
7.21
7.20
6.78
6.77
2.54
S
CF3
2.13
2.01
1.00
0.99
3.38
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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140.15
138.06
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128.58
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125.85
125.82
125.79
125.76
125.40
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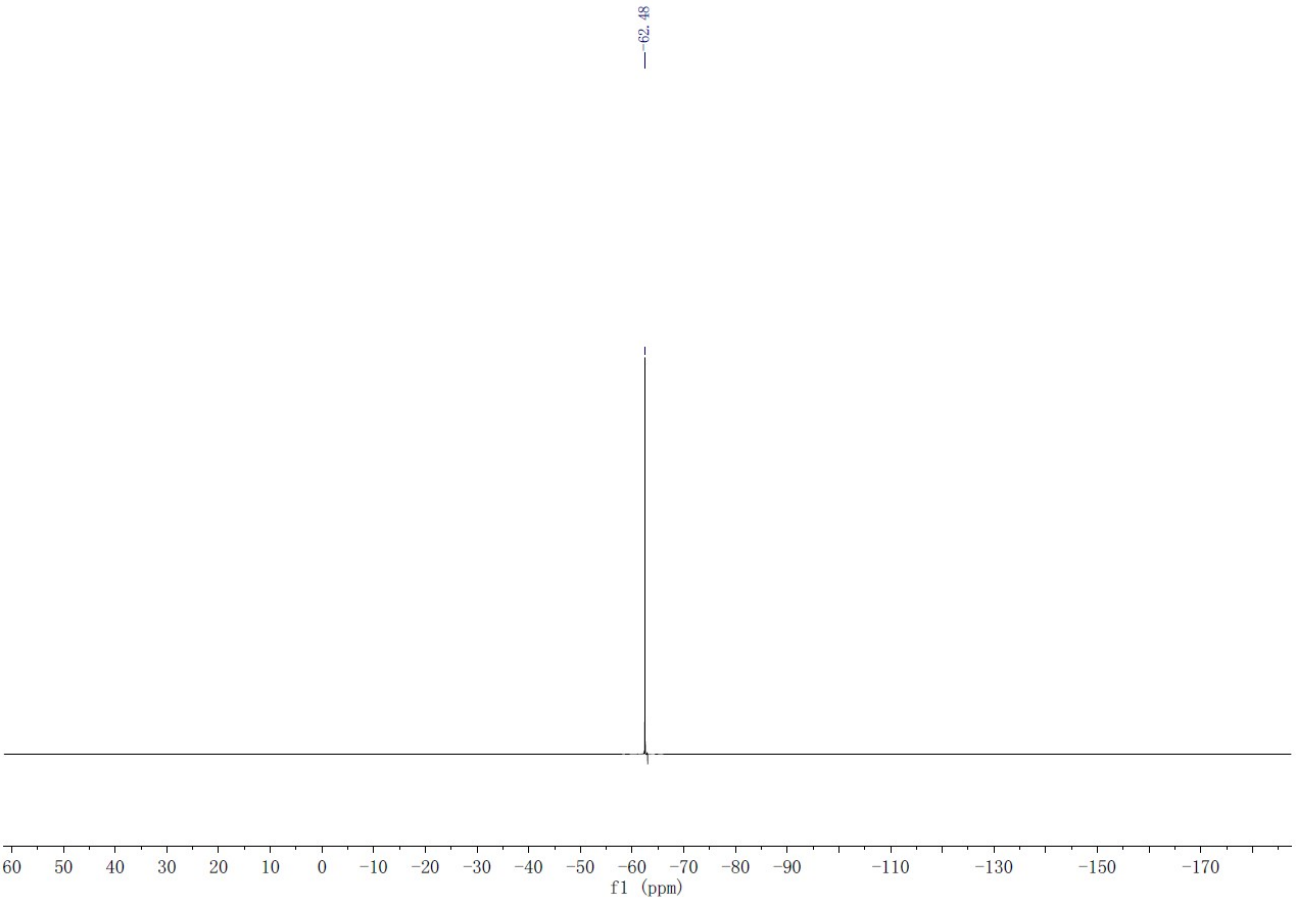
77.01
76.76
15.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


62.48
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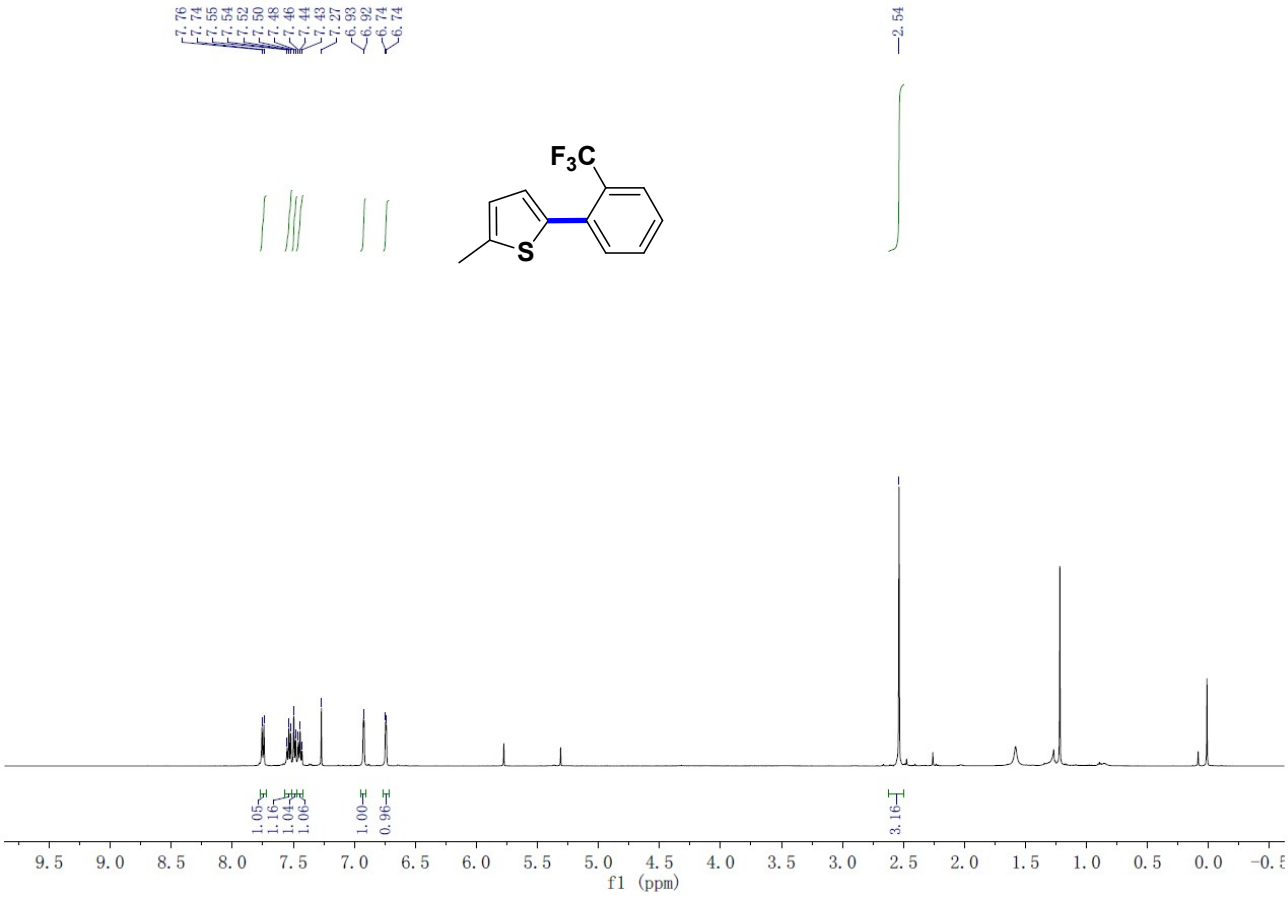
f1 (ppm)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7.50
7.48
7.46
7.44
7.43
7.27
6.93
6.92
6.74
6.74
2.54
F3C
S
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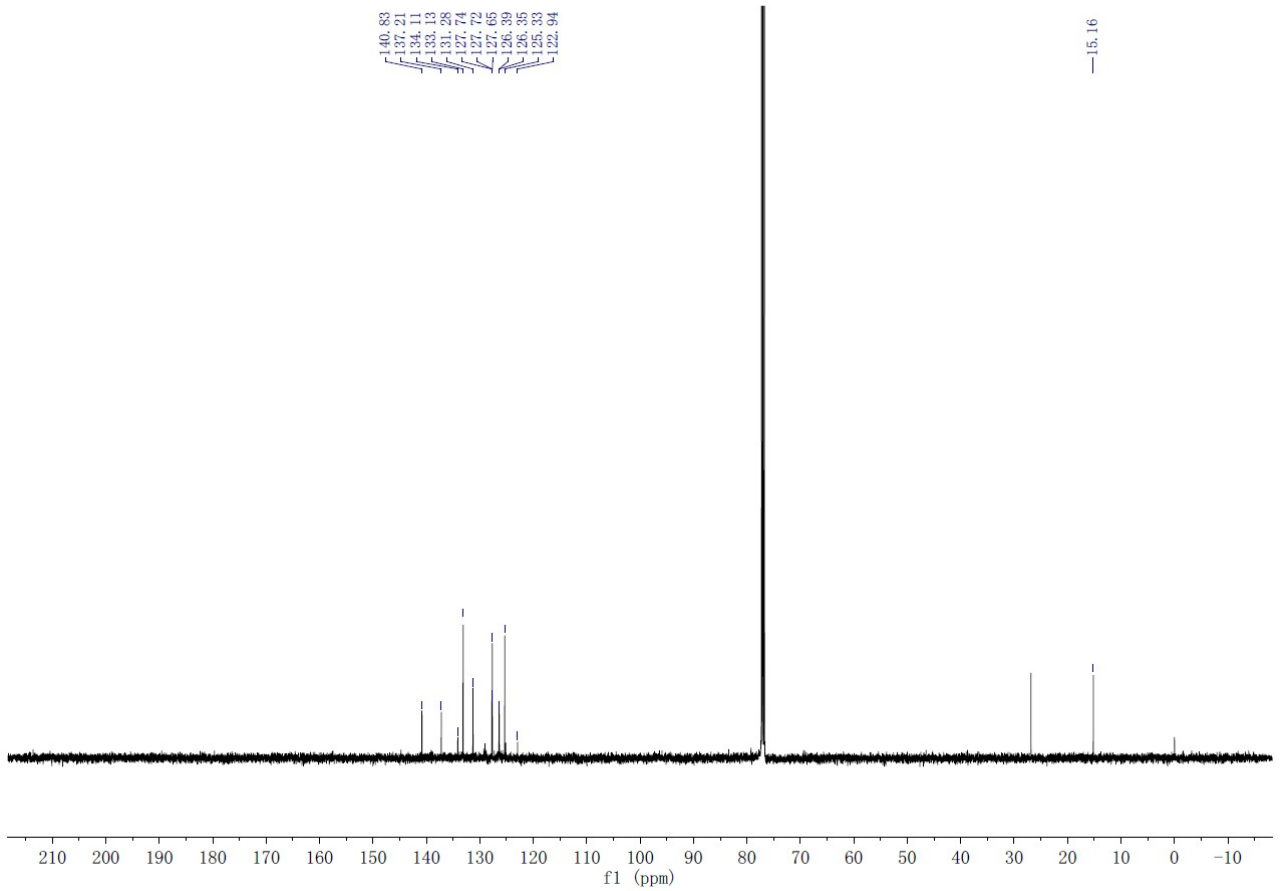
1.16
1.04
1.06
1.00
0.96
3.16
f1 (ppm)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137.21
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127.65
126.39
126.35
125.33
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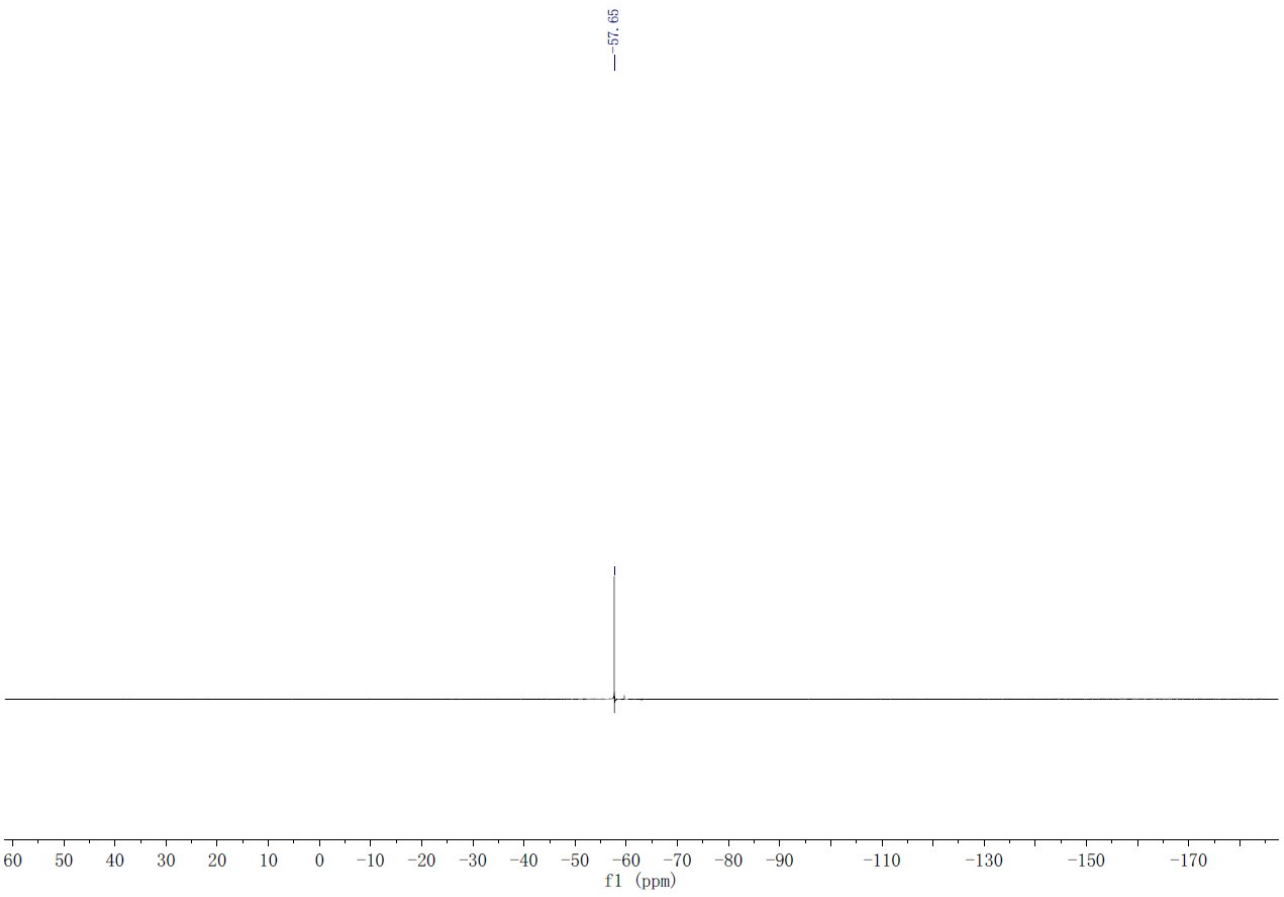
15.16
f1 (ppm)


-57.65
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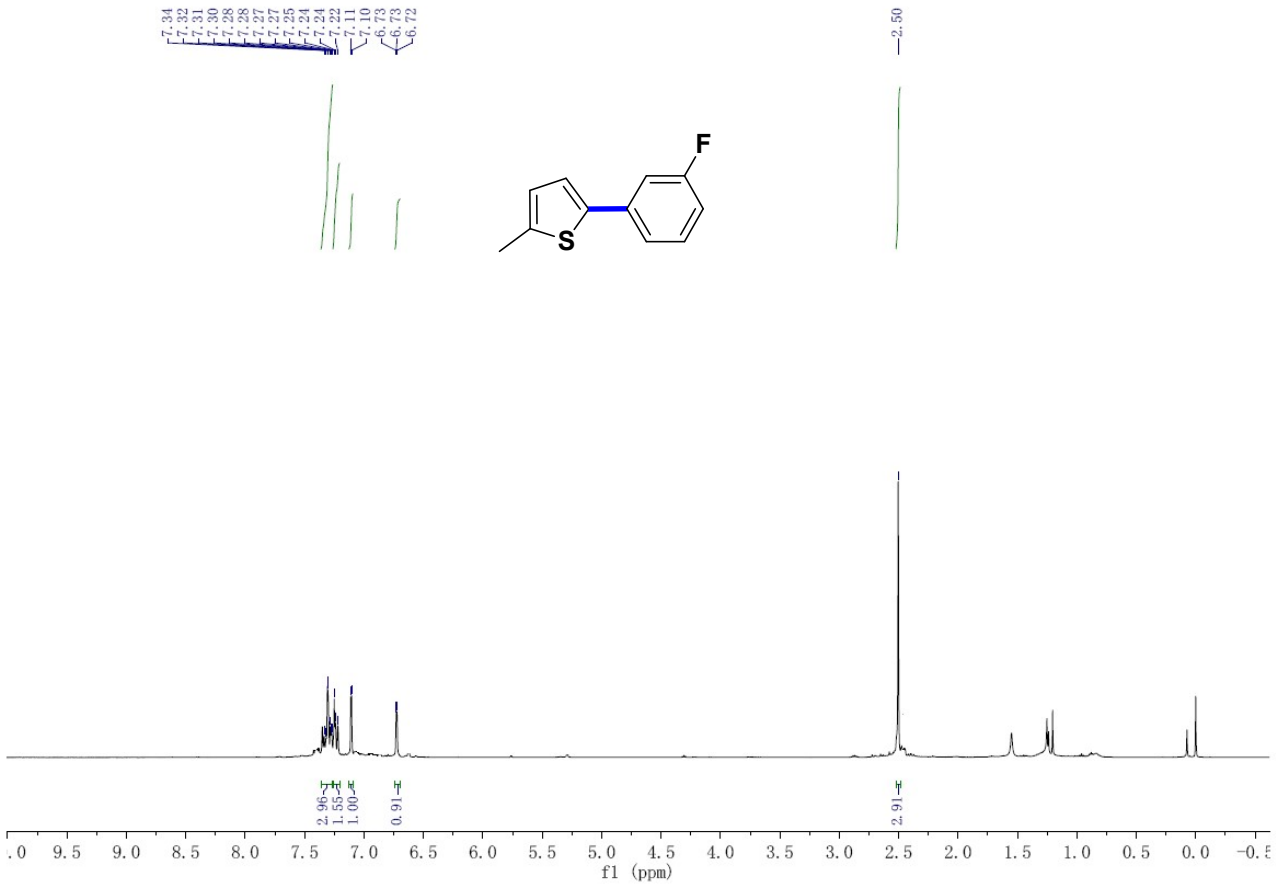
f1 (ppm)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7.28
7.27
7.27
7.25
7.24
7.24
7.22
7.11
7.10
6.73
6.73
6.72
2.50
F
S
2.96
1.55
1.00
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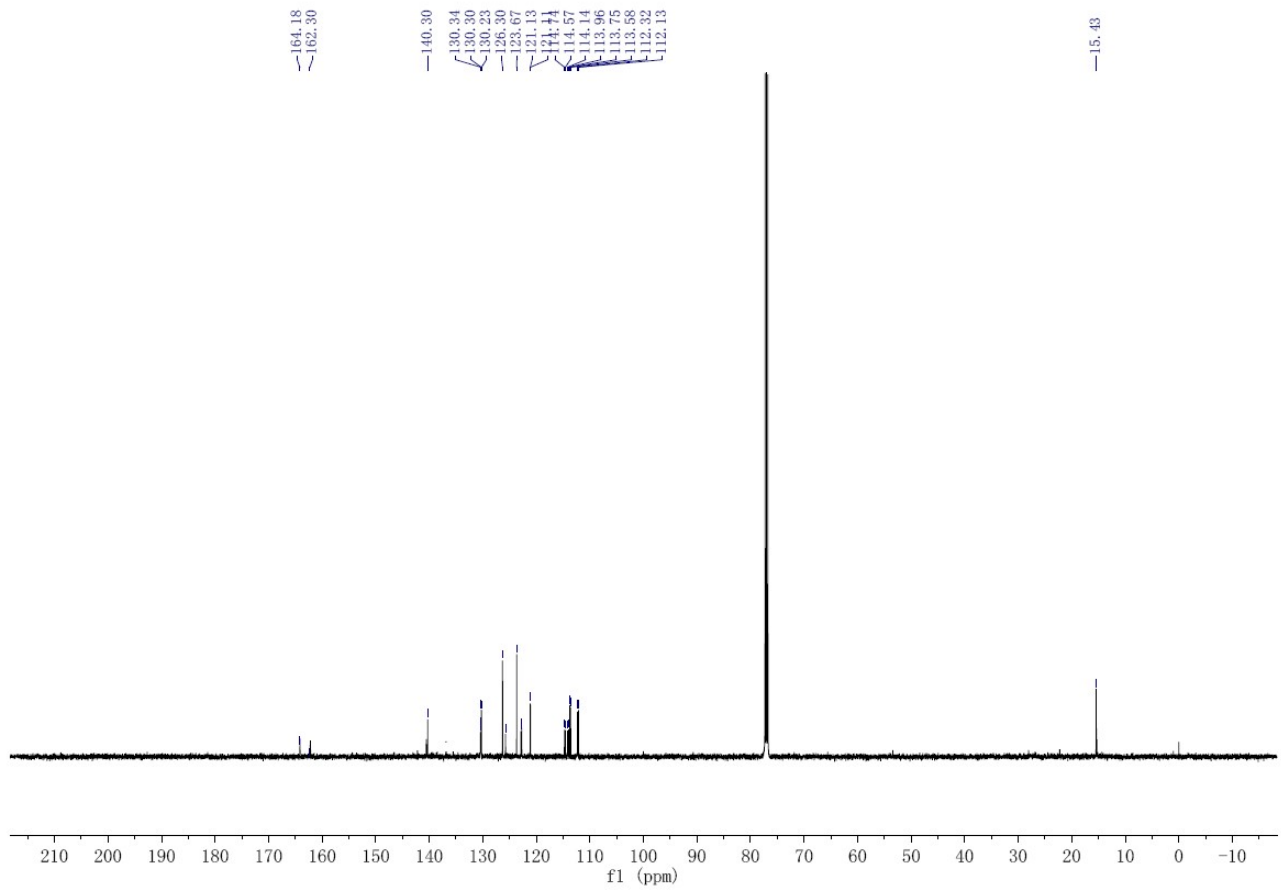
2.91
f1 (ppm)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130.30
130.23
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123.67
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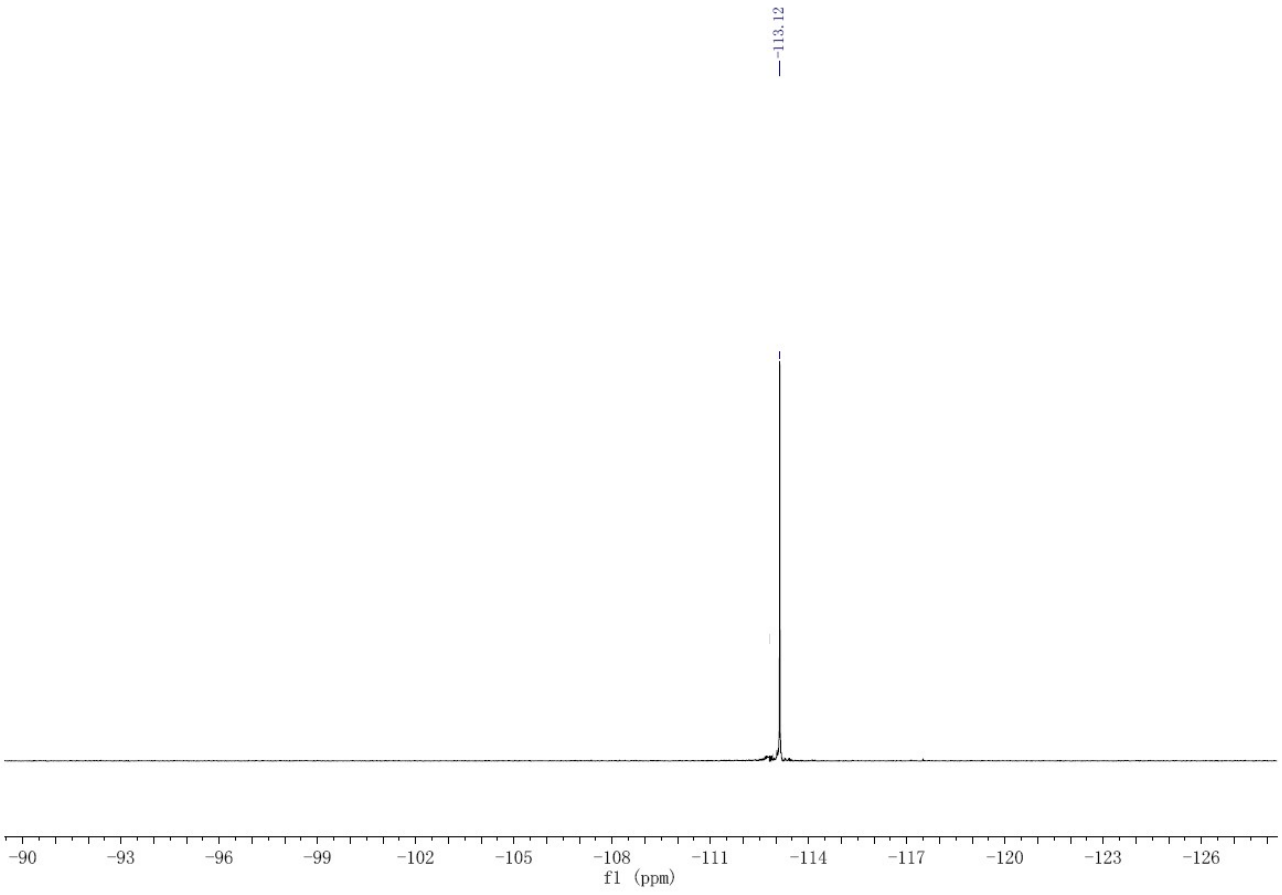
114.57
114.14
113.96
113.75
113.58
112.32
112.13
15.43
f1 (ppm)


-113.12
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-96
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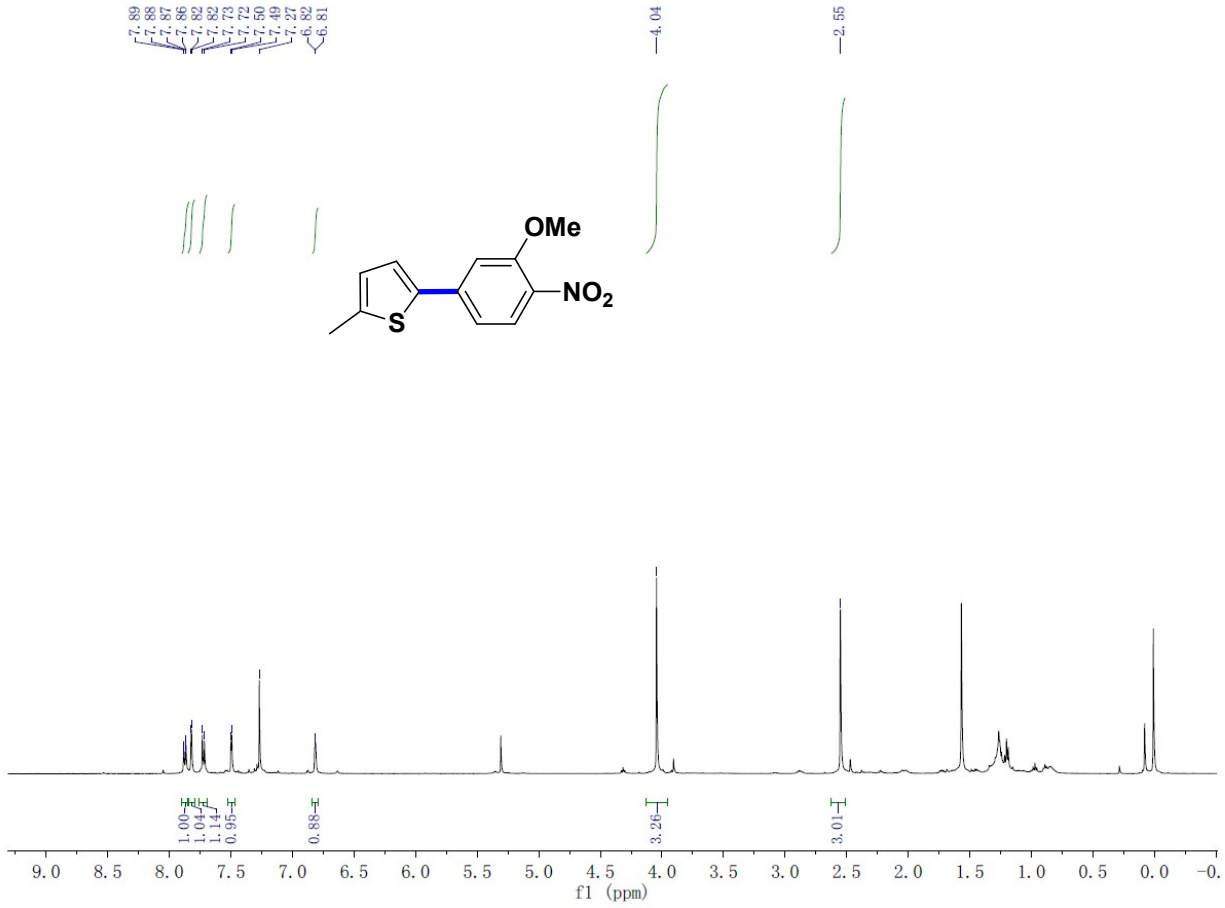
-102
-105
-108
-111
-114
-117
-120
-123
-126
f1 (ppm)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7.87
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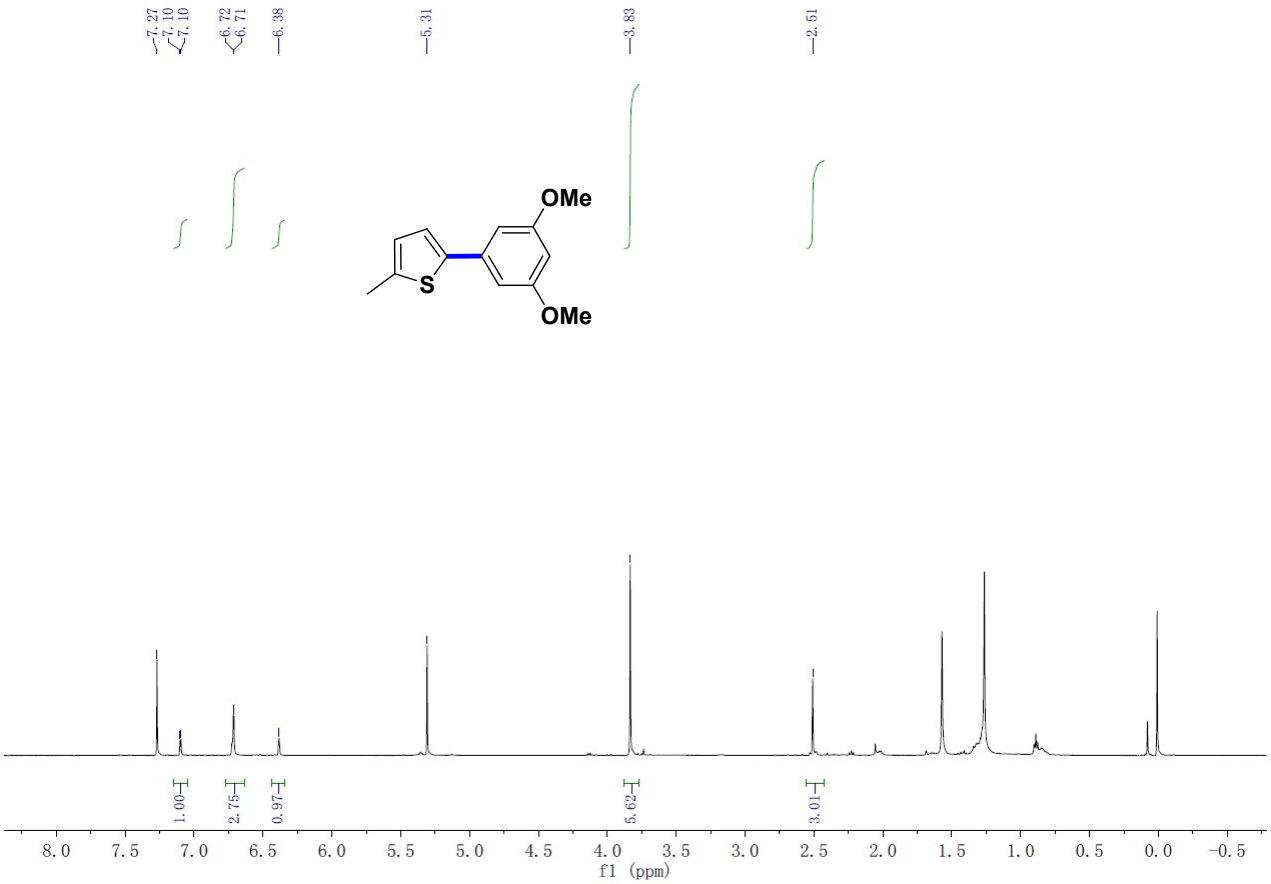
7.82
7.82
7.73
7.72
7.50
7.49
7.27
6.82
6.81
4.04
2.55
OMe
NO2
S
1.00
1.04
1.14
0.95
0.88
3.26
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)
155.15
143.03
134.82
130.27
128.04
127.46
125.82
116.41
106.71
56.05
15.28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.10
7.10
6.72
6.71
6.38
5.31
3.83
2.51
OMe
OMe
S
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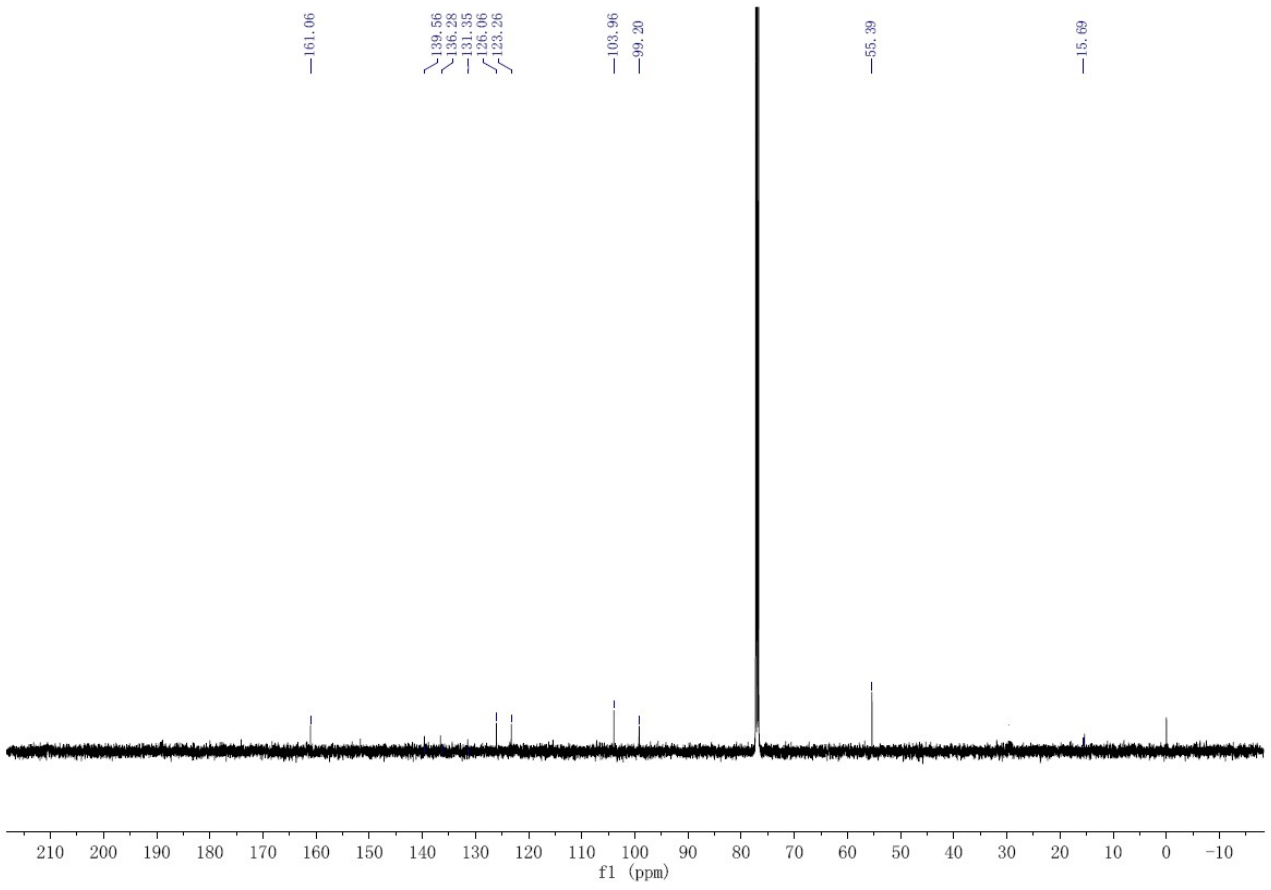
2.75
0.97
5.62
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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139.56
136.28
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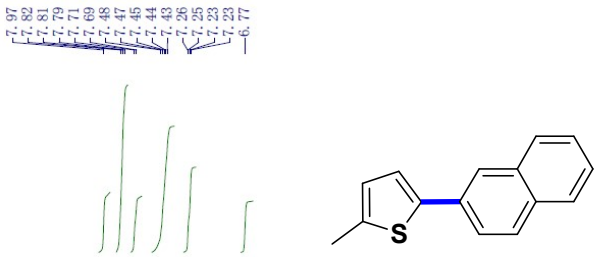
126.06
123.26
103.96
99.20
55.39
15.69
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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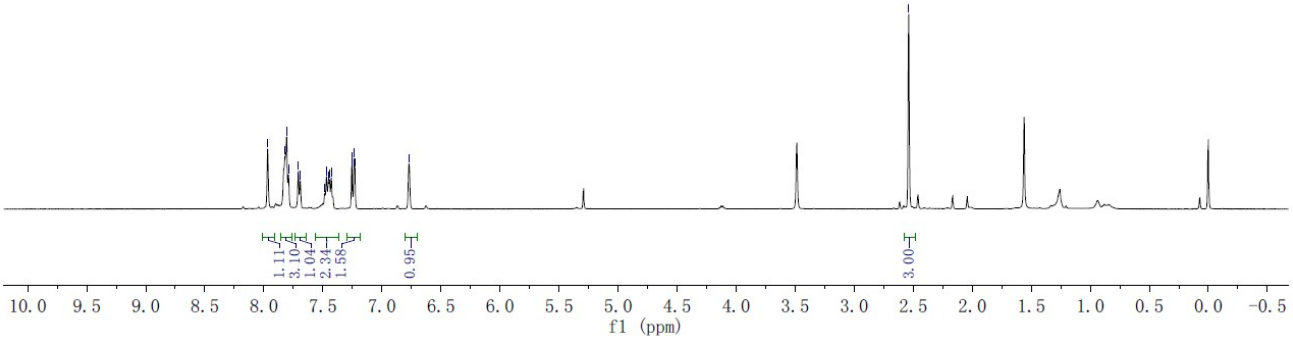
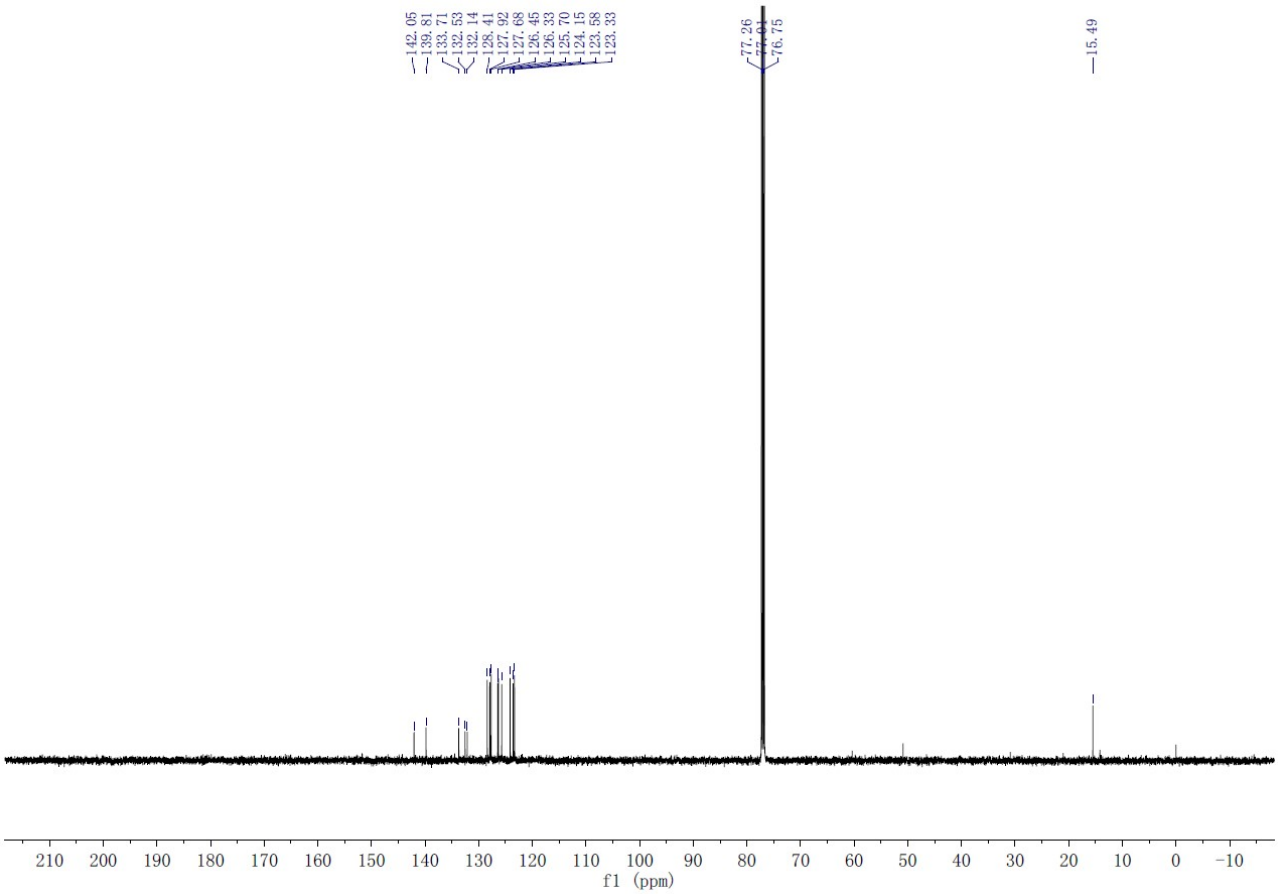
7.25
7.23
7.23
6.77
2.54
S


1.11
3.10
1.04
2.34
1.58
0.95
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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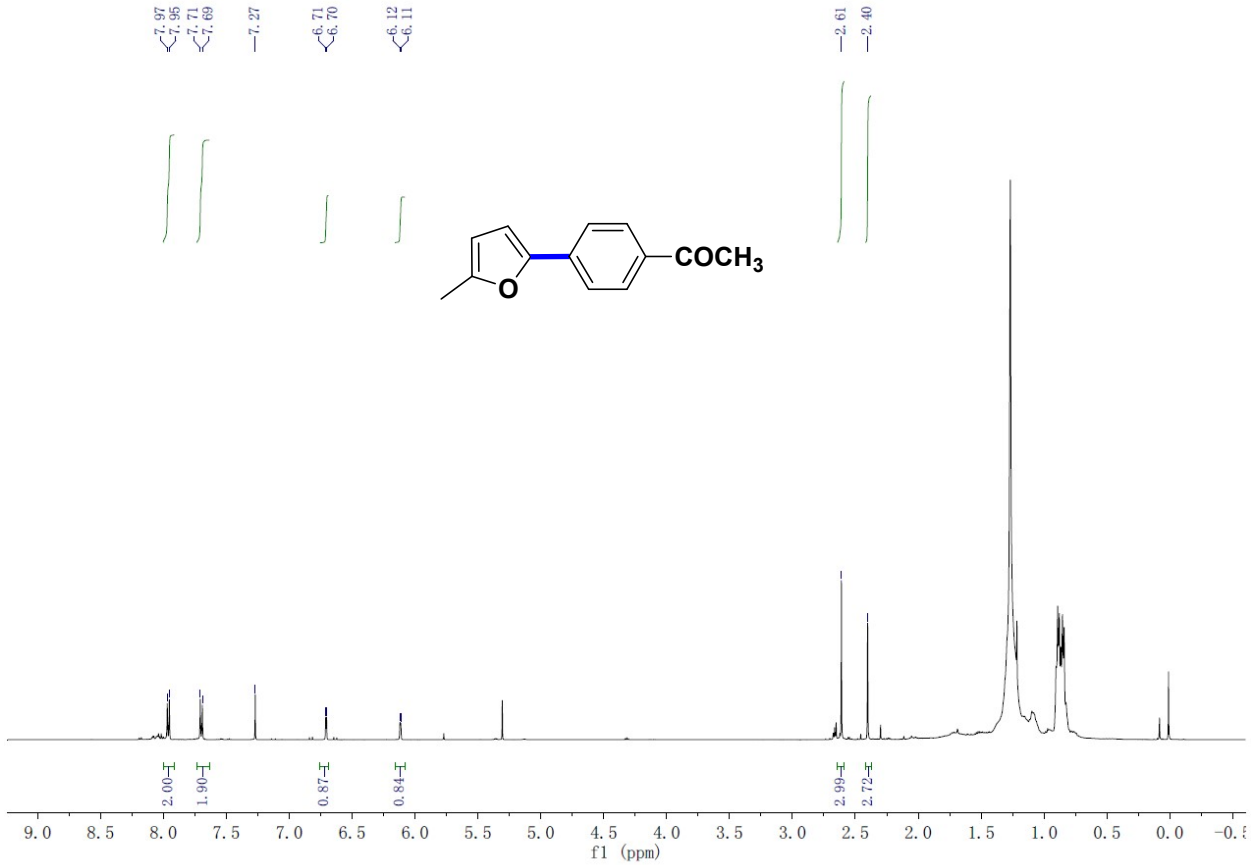
139.81
133.71
132.53
132.14
128.41
127.92
127.68
126.45
126.33
125.70
124.15
123.58
123.33
77.26
77.01
76.75
15.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.96
7.71
7.69
7.27
6.71
6.70
6.12
6.11
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2.40
COCH3
O
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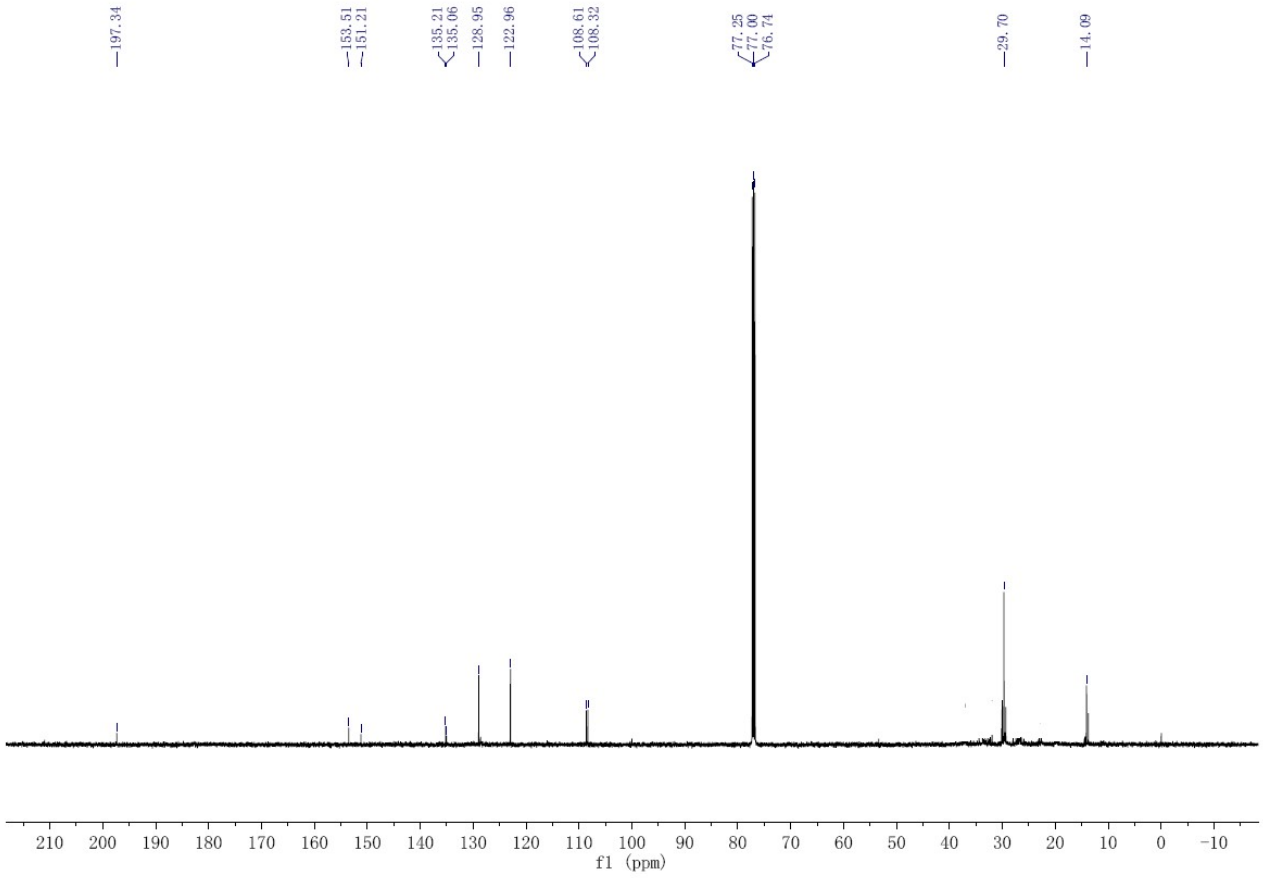
1.90
0.87
0.84
2.99
2.72
f1 (ppm)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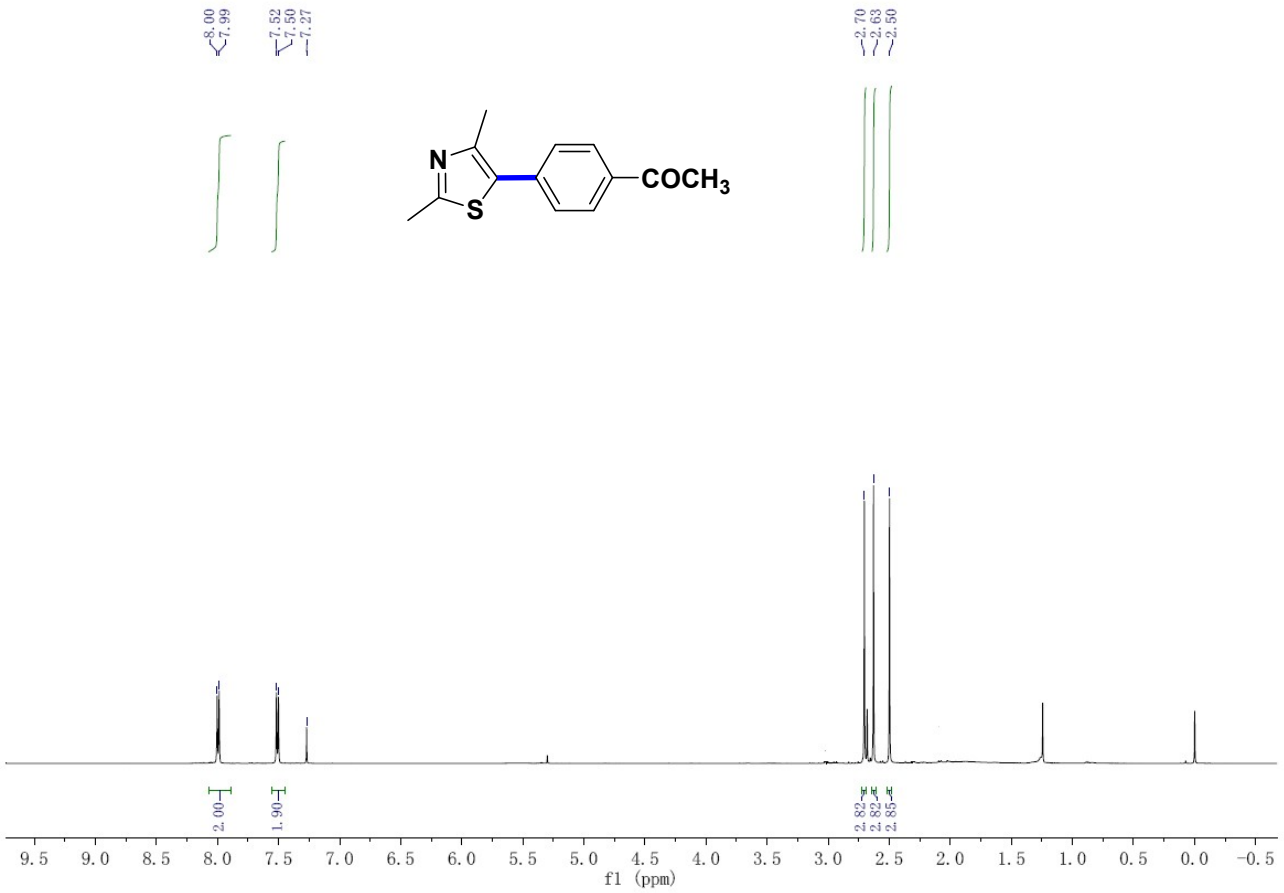
153.51
151.21
135.21
135.06
128.95
122.96
108.61
108.32
77.25
77.00
76.74
29.70
14.09
f1 (ppm)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7.99
7.52
7.50
7.27
2.70
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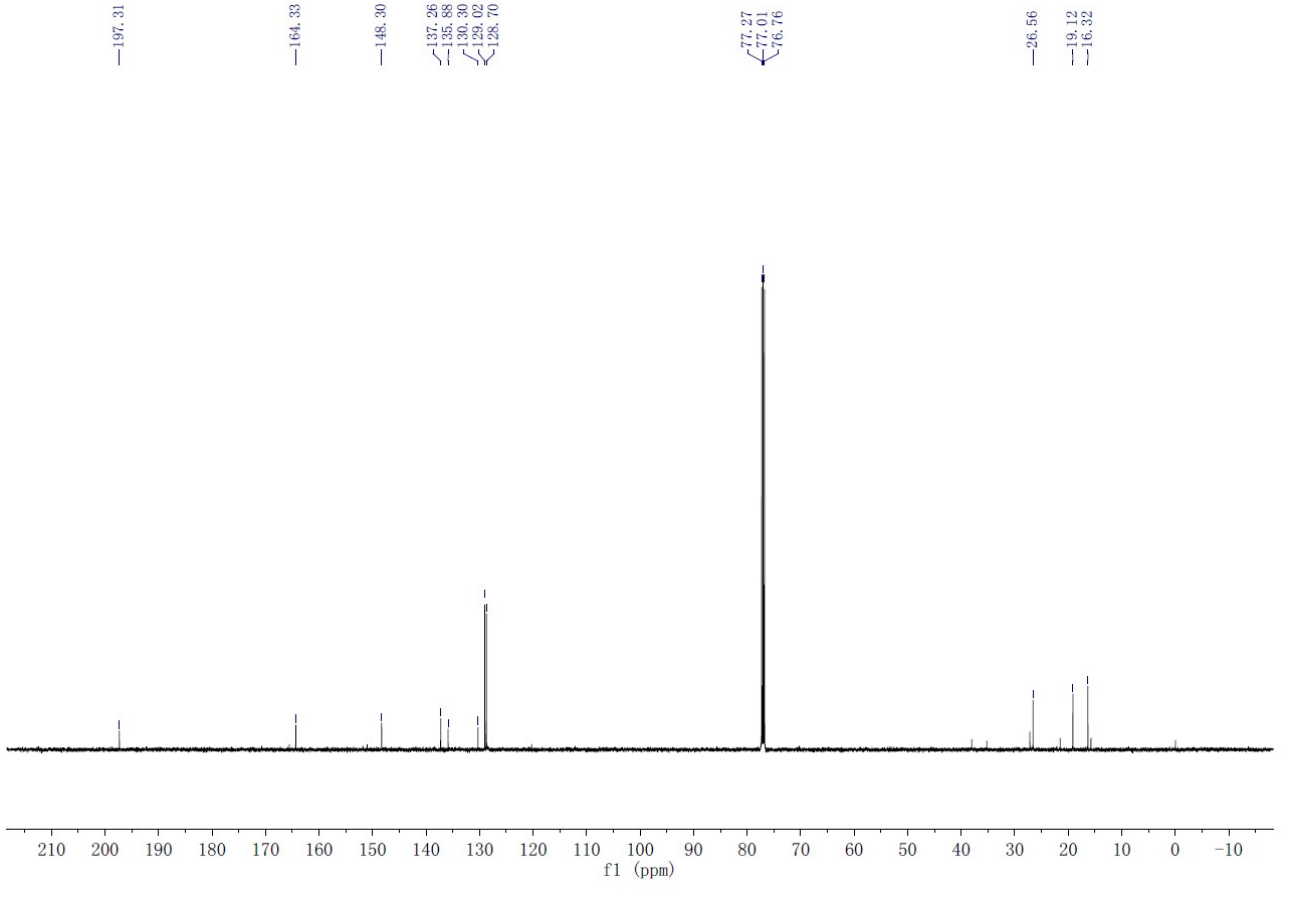
2.50
N
S
COCH3
2.00
1.90
2.82
2.82
2.85
f1 (ppm)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164.33
148.30
137.26
135.88
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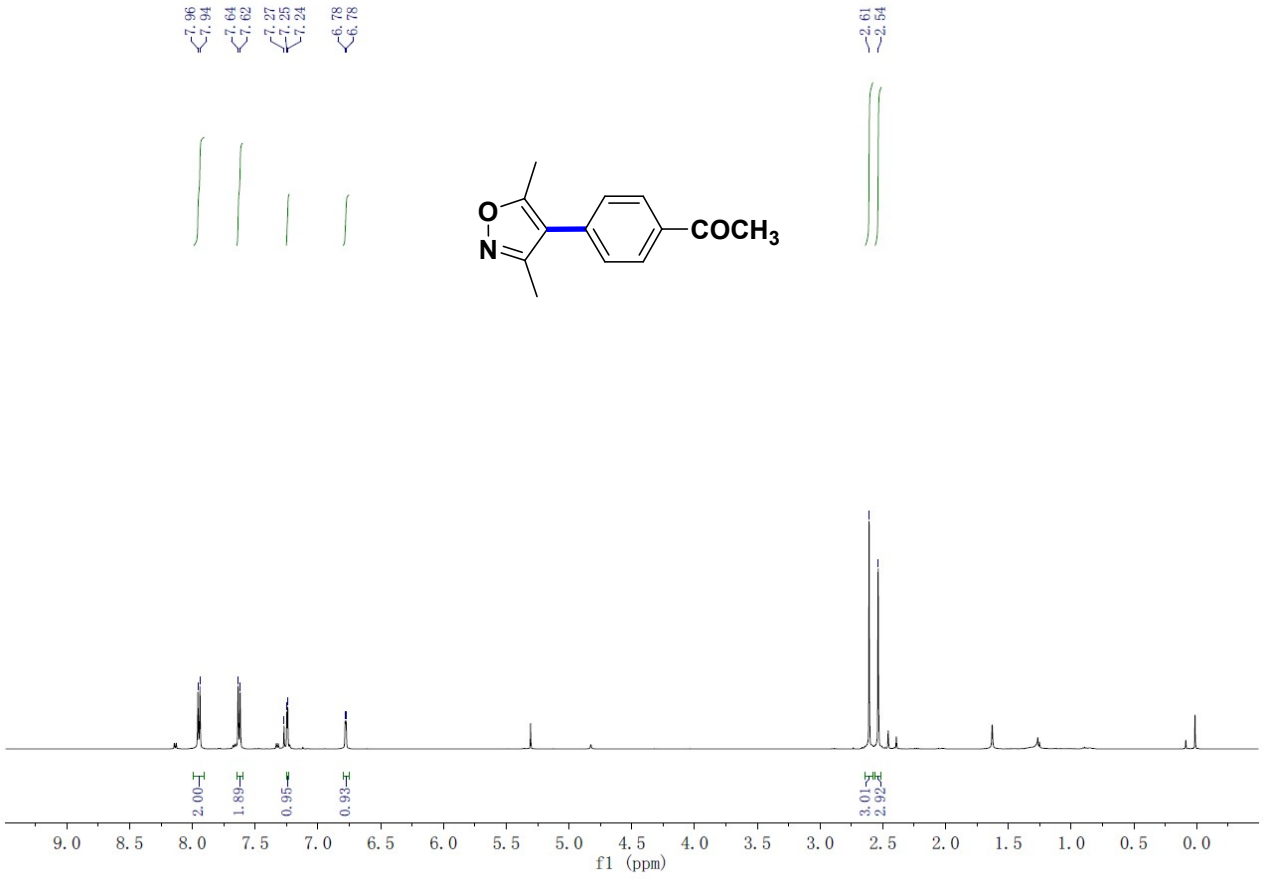
129.02
128.70
77.27
77.01
76.76
26.56
19.12
16.32
f1 (ppm)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7.94
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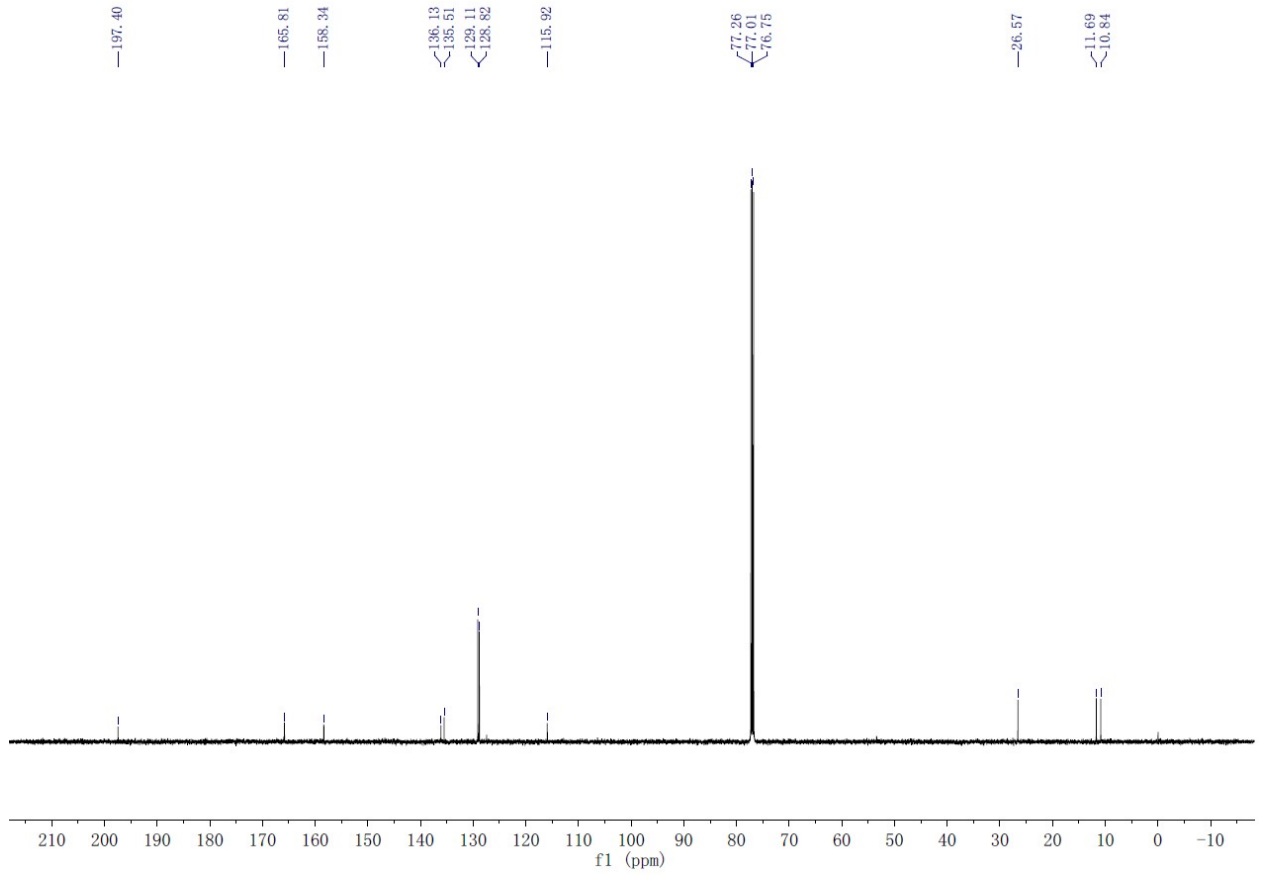
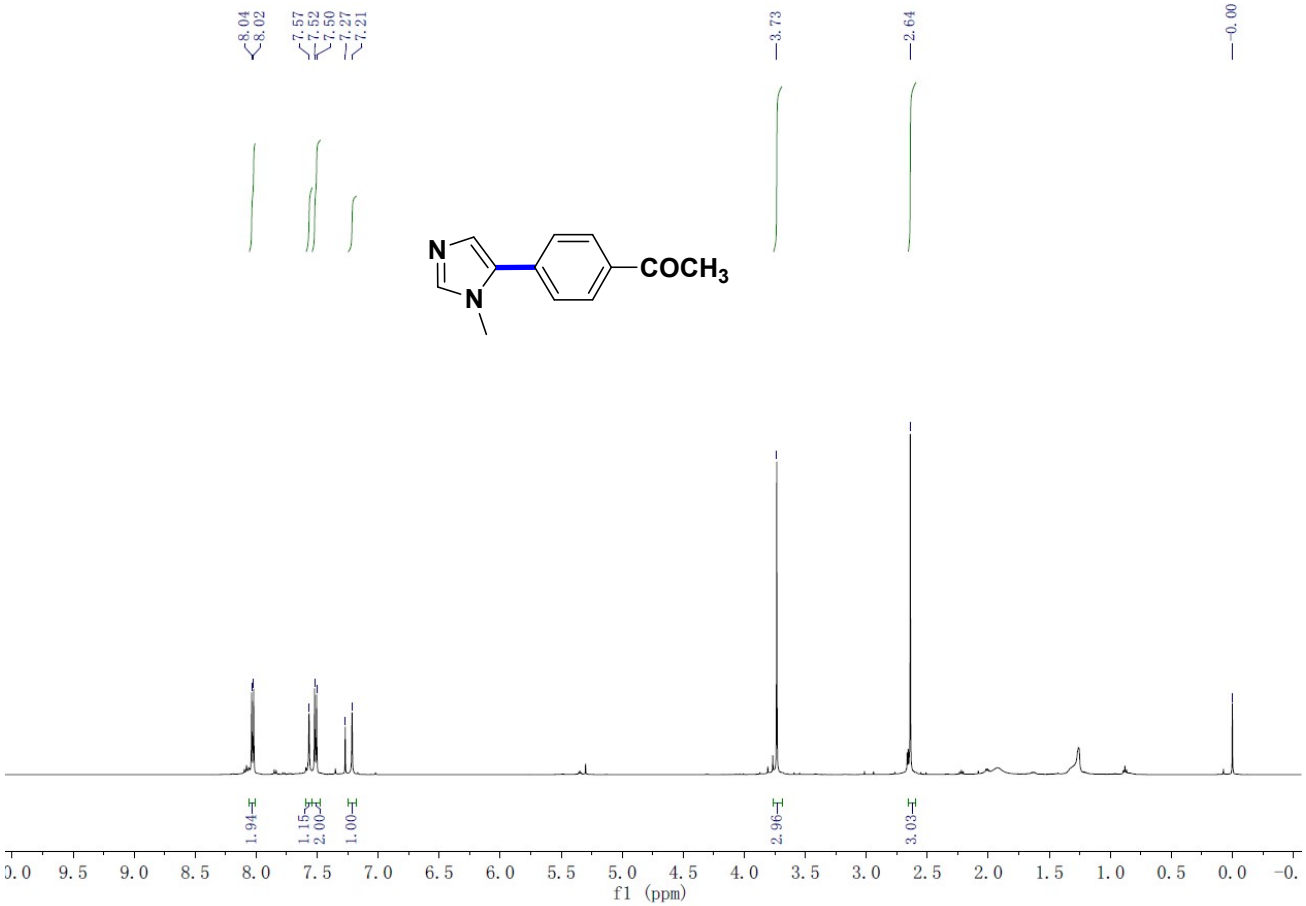
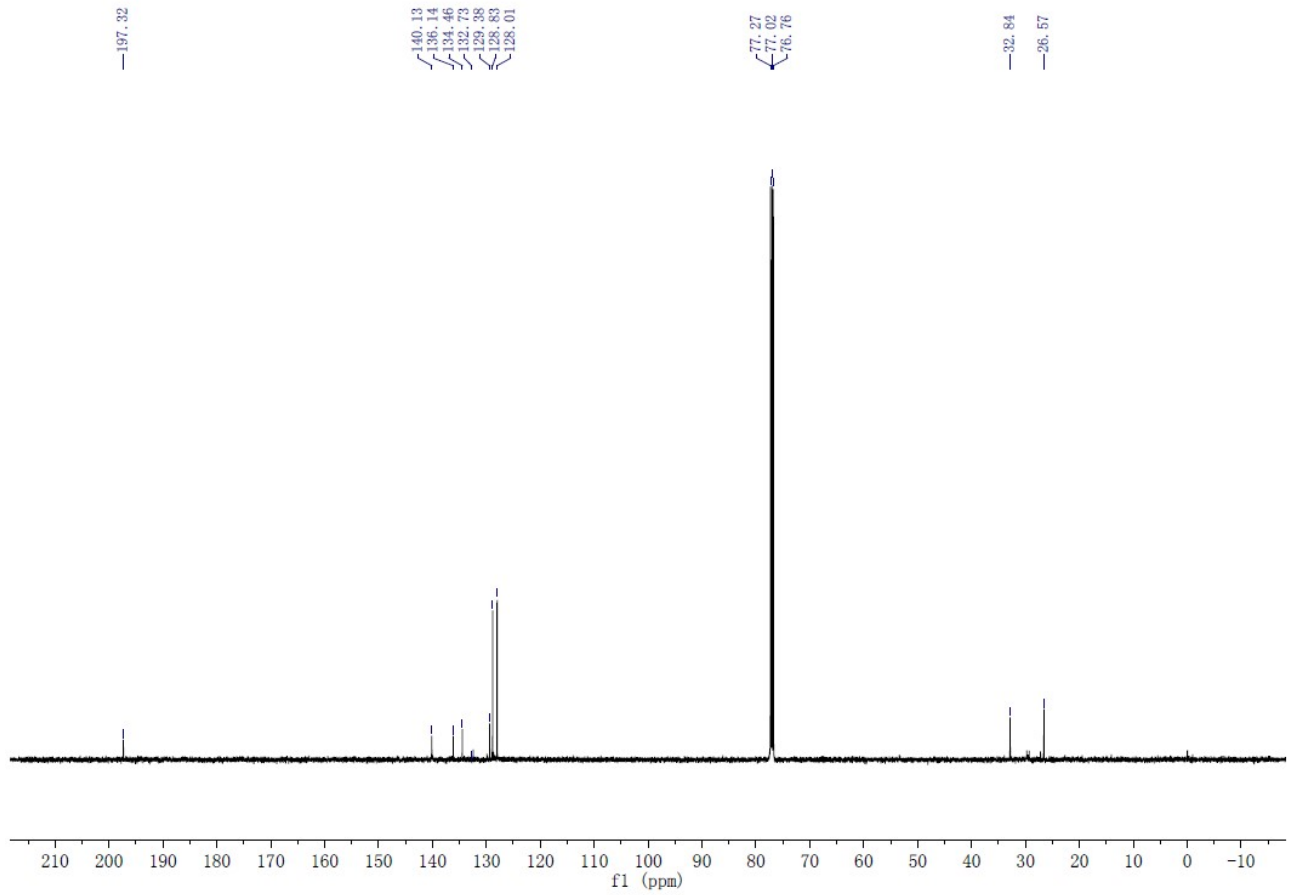
7.27
7.25
7.24
6.78
6.78
2.61
2.54
O
N
COCH3
2.00
1.89
0.95
0.93
3.01
2.92
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


197.40
165.81
158.34
136.13
135.51
129.11
128.82
115.92
77.26
77.01
76.75
26.57
11.69
10.84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.04
8.02
7.57
7.52
7.50
7.27
7.21
3.73
2.64
0.00
N
N
COCH3
1.94
1.15
2.00
1.00
2.96
3.03
f1 (ppm)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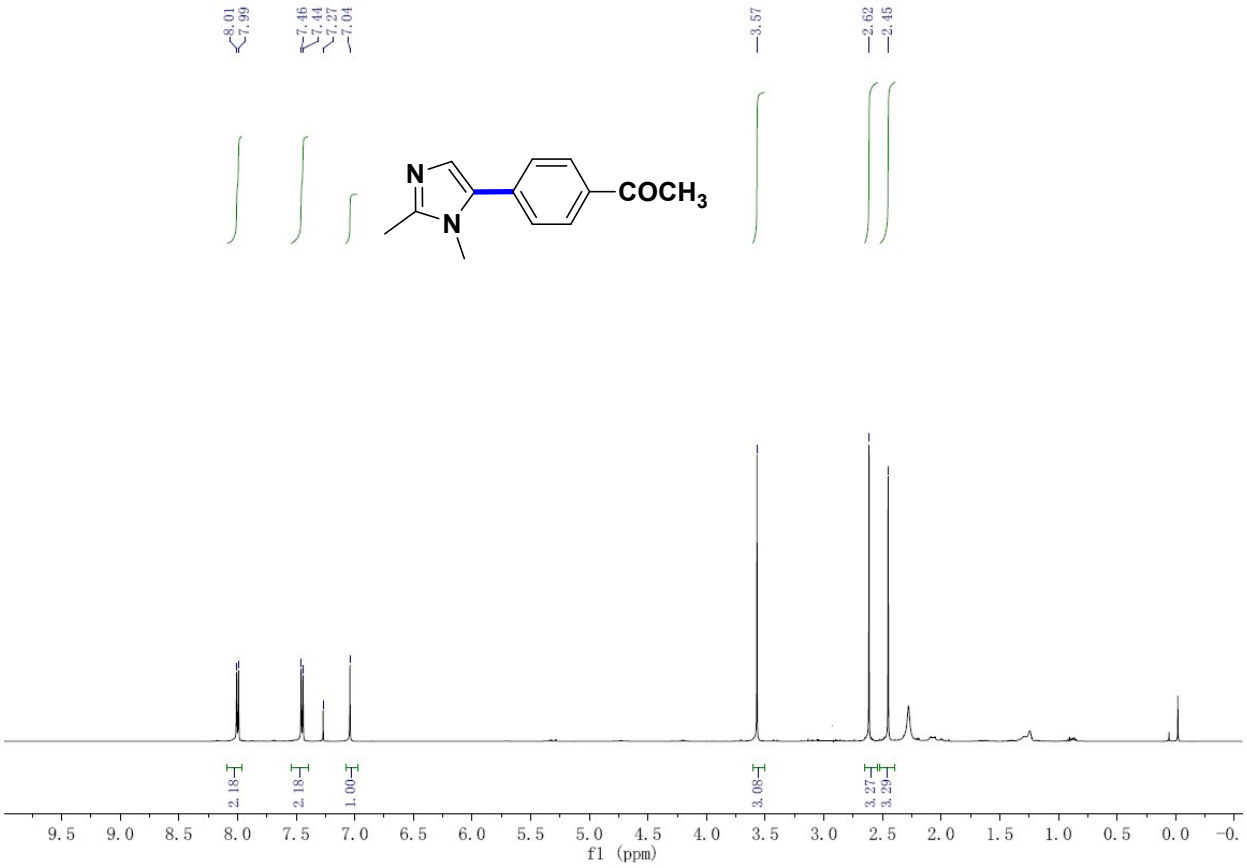
140.13
136.14
134.46
132.73
129.38
128.83
128.01
77.27
77.02
76.76
32.84
26.57
f1 (ppm)


8.01
7.99
7.46
7.44
7.27
7.04
3.57
2.62
2.45
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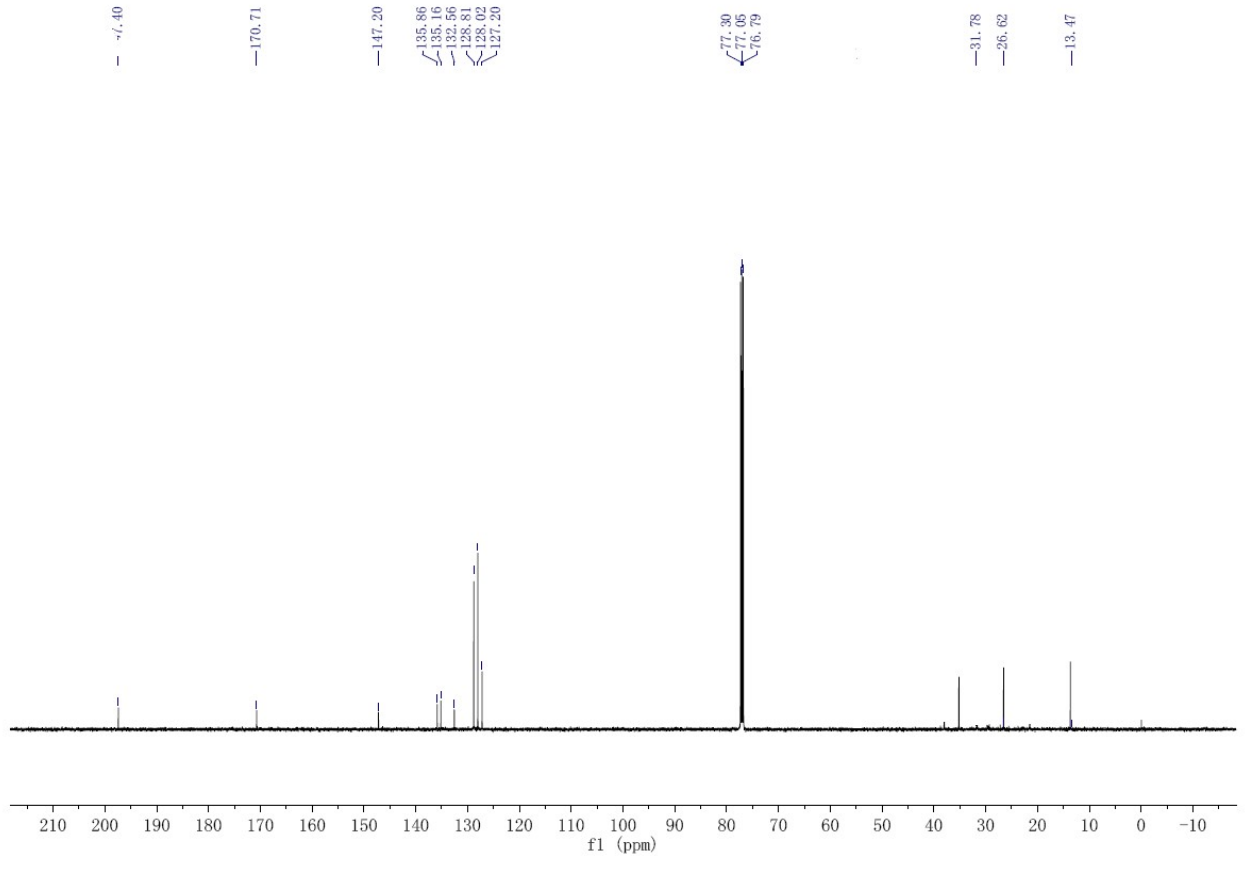
N
COCH3
2.18
2.18
1.00
3.08
3.27
3.29
f1 (ppm)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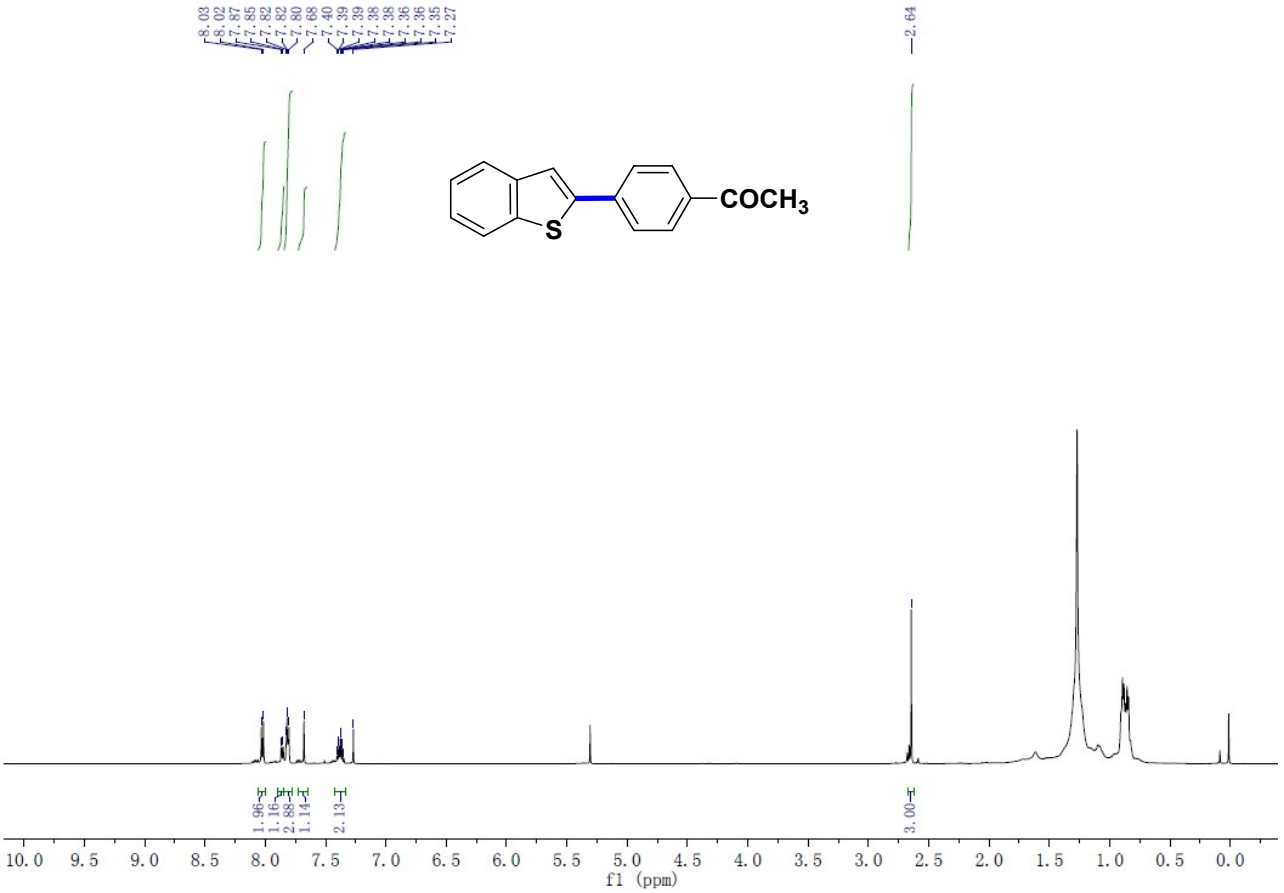
147.20
135.86
135.16
132.56
128.81
128.02
127.20
77.30
77.05
76.79
31.78
26.62
13.47
f1 (ppm)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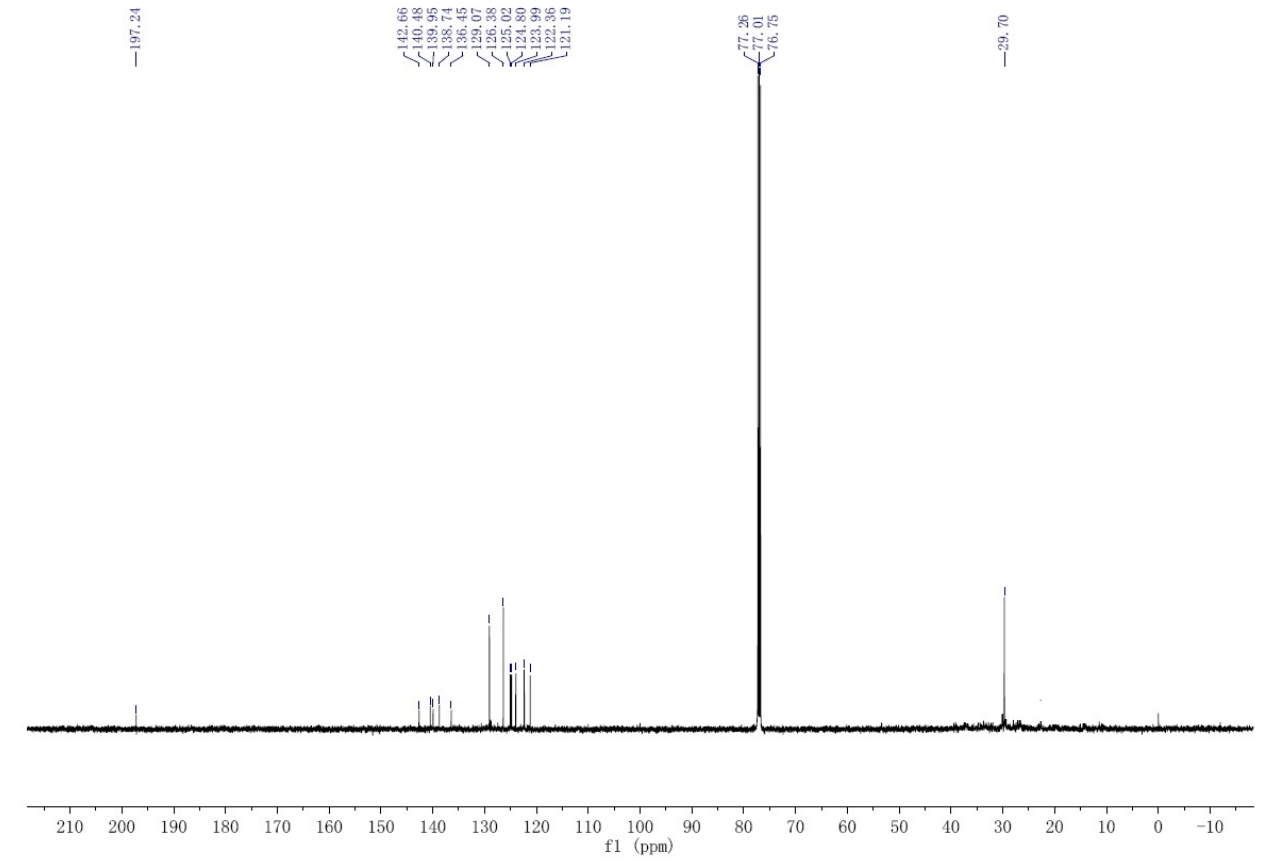
8.02
7.87
7.85
7.82
7.82
7.80
7.68
7.40
7.39
7.39
7.38
7.38
7.36
7.36
7.35
7.27
2.64
COCH3
S
1.96
1.16
2.88
1.14
2.13
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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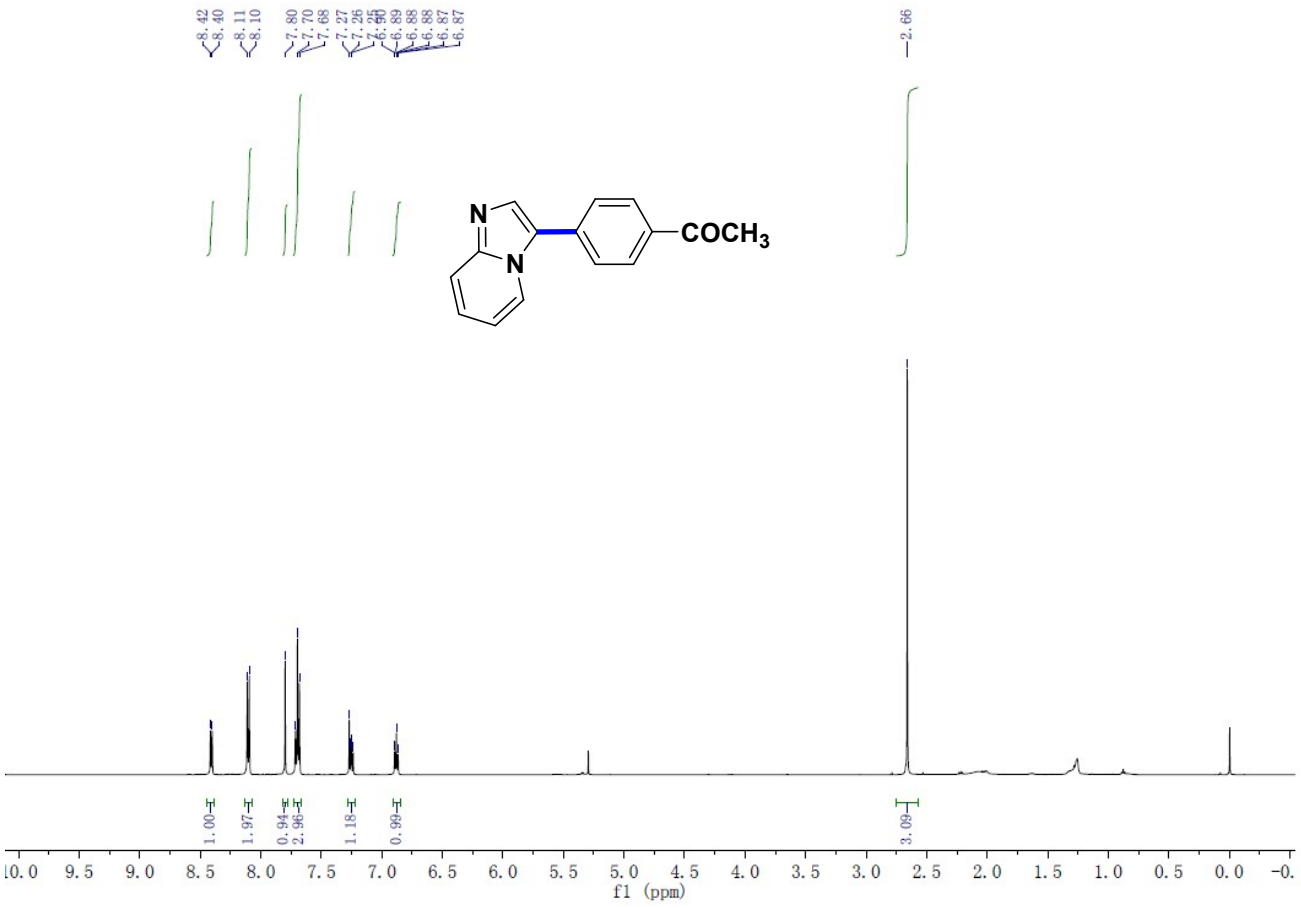
140.48
139.95
138.74
136.45
129.07
126.38
125.02
124.80
123.99
122.36
121.19
77.26
77.01
76.75
29.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.40
8.11
8.10
7.80
7.70
7.68
7.27
7.26
7.25
6.90
6.89
6.88
6.88
6.87
6.87
2.66
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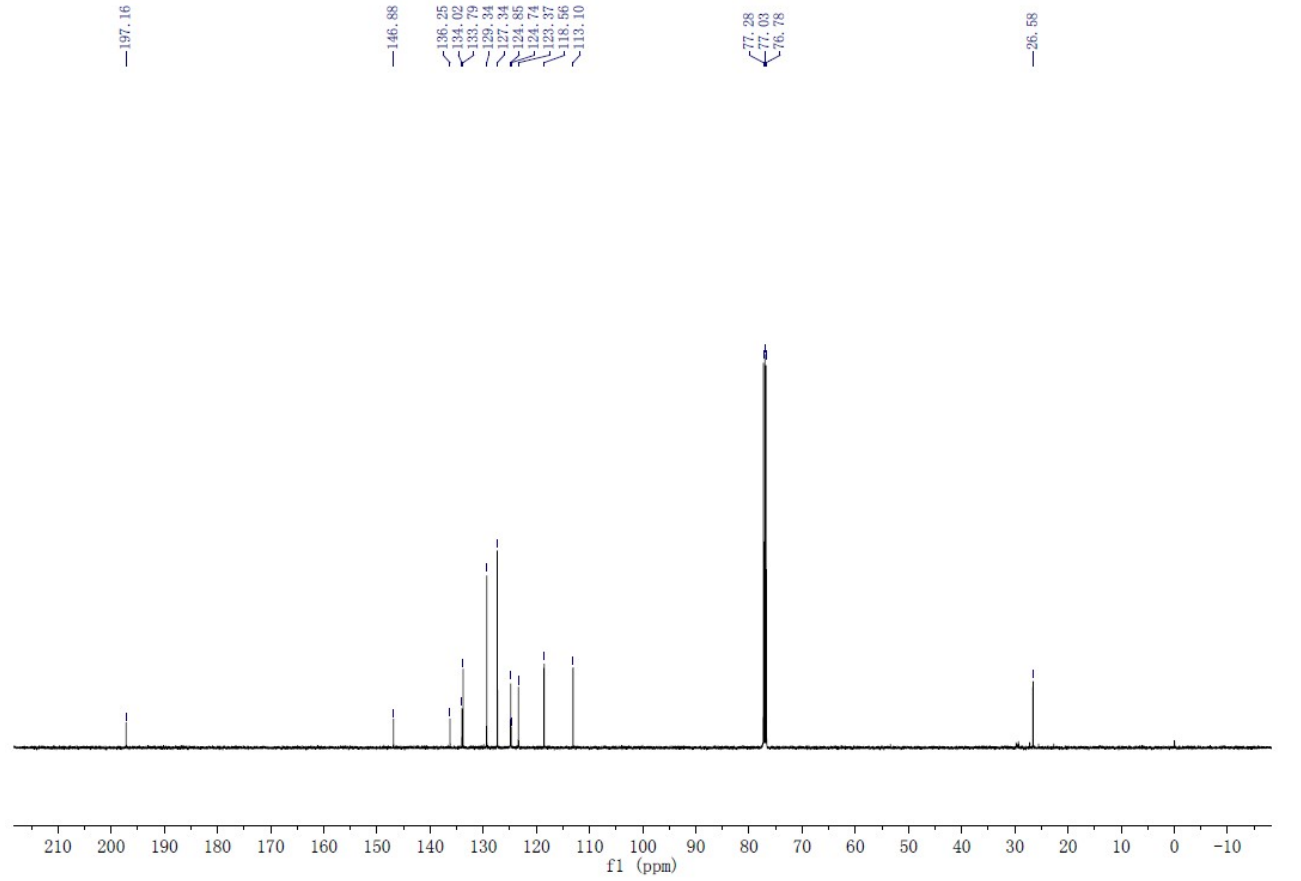
N
COCH3
1.00
1.97
0.94
2.96
1.18
0.99
3.09
f1 (ppm)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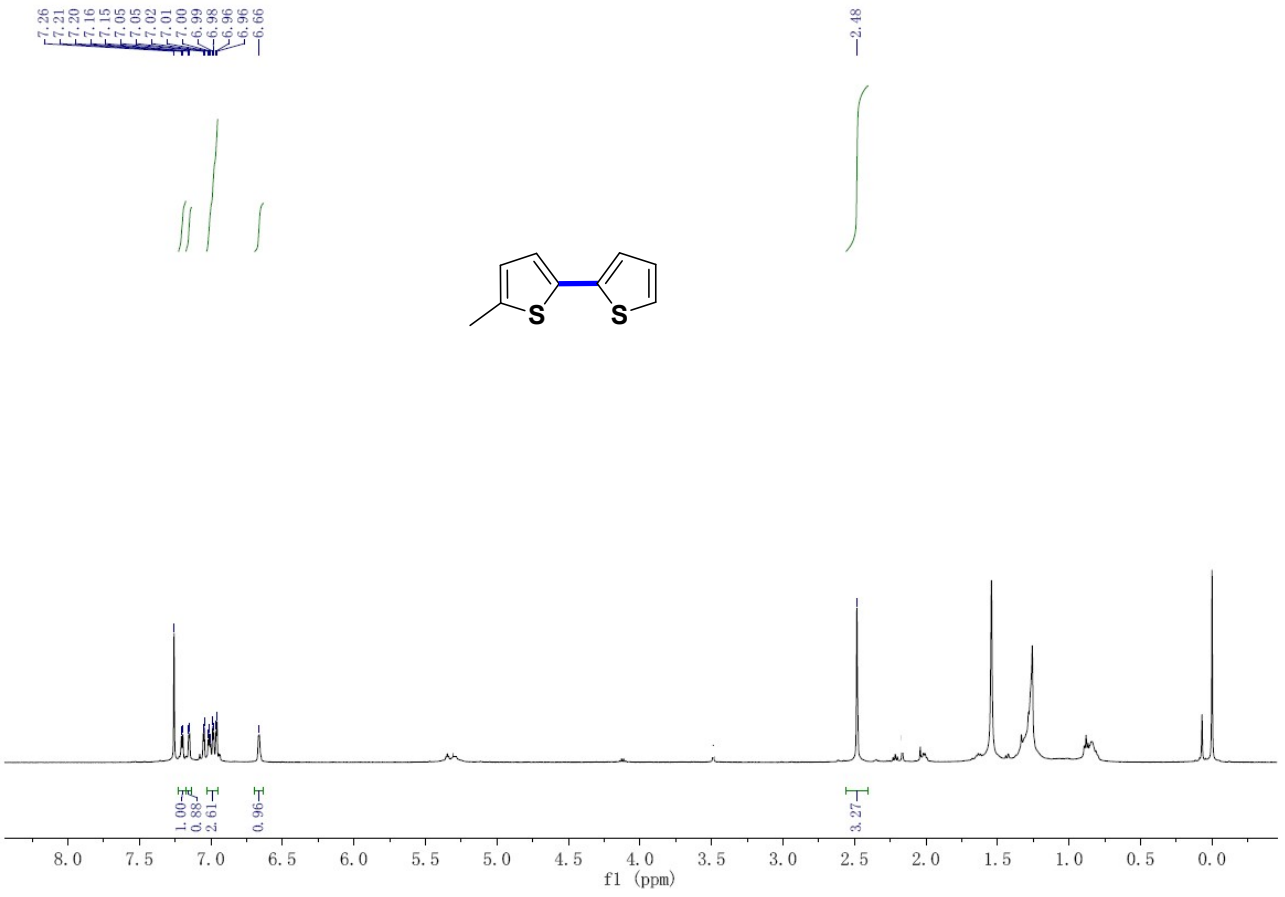
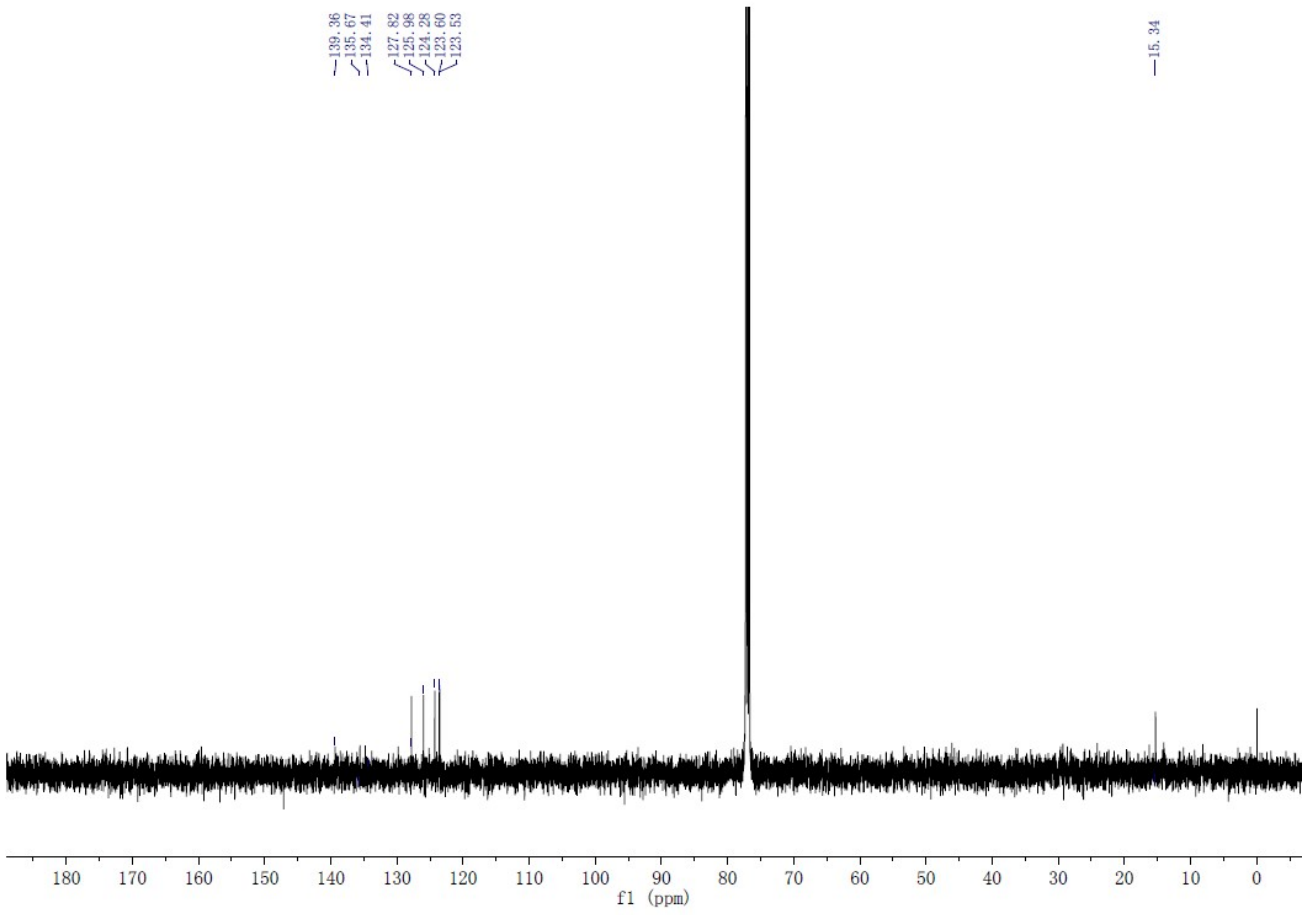
146.88
136.25
134.02
133.79
129.34
127.34
124.85
124.74
123.37
118.56
113.10
77.28
77.03
76.78
26.58
f1 (ppm)


7.26
7.21
7.20
7.16
7.15
7.05
7.05
7.02
7.01
7.00
6.99
6.98
6.96
6.96
6.66
2.48
S
S
1.00
0.88
2.61
0.96
3.27
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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135.67
134.41
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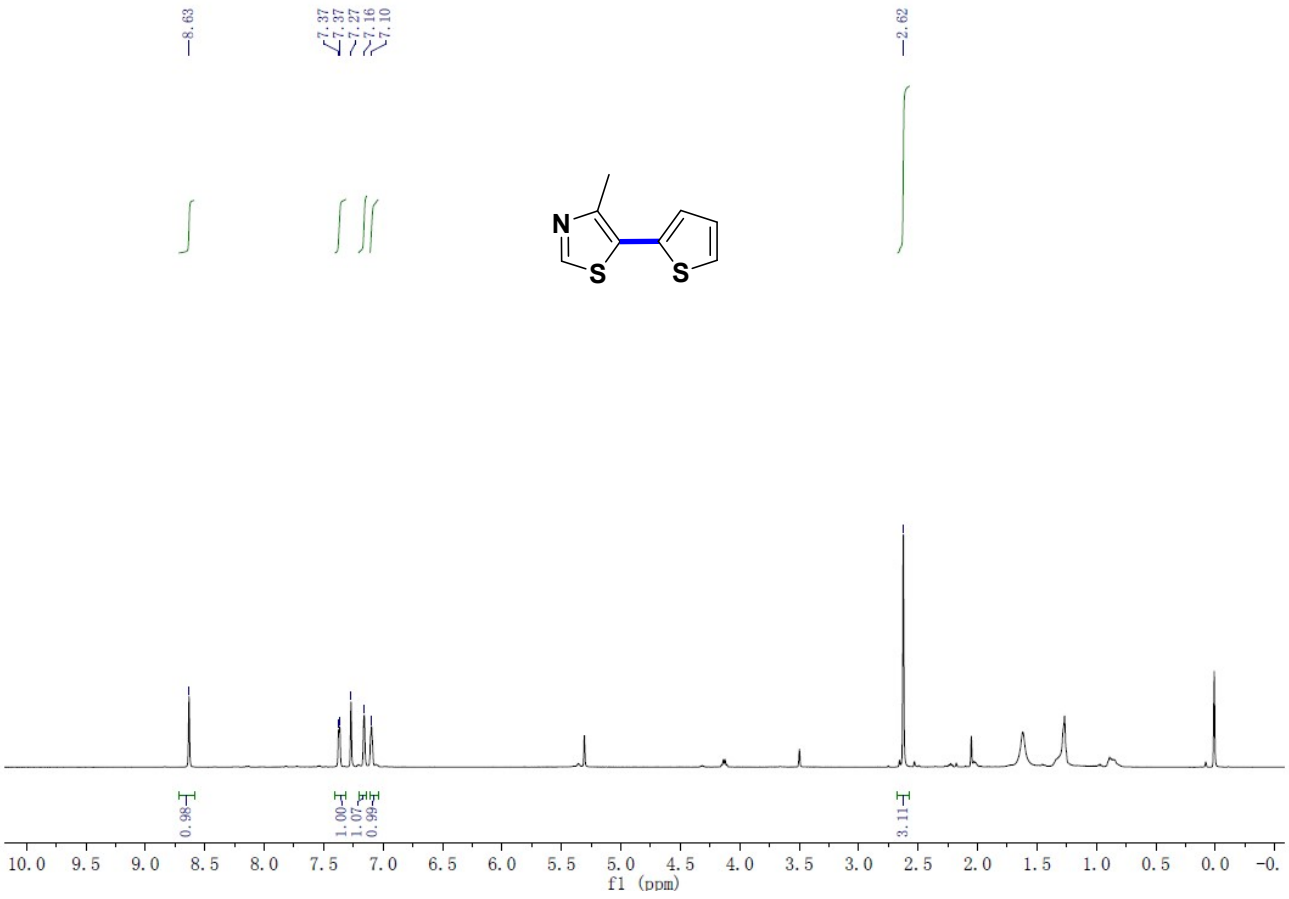
125.98
124.28
123.60
123.53
15.34
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.37
7.37
7.27
7.16
7.10
2.62
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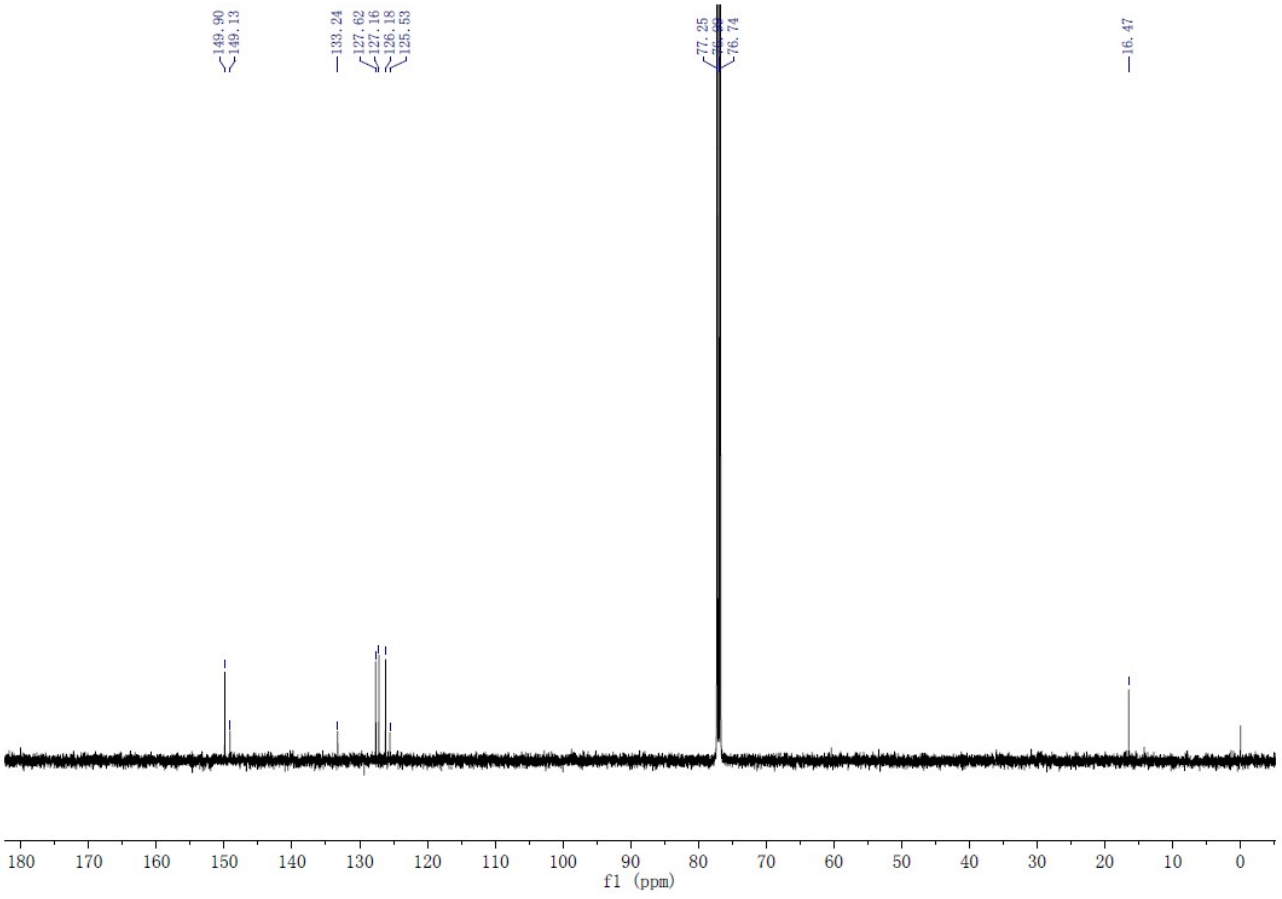
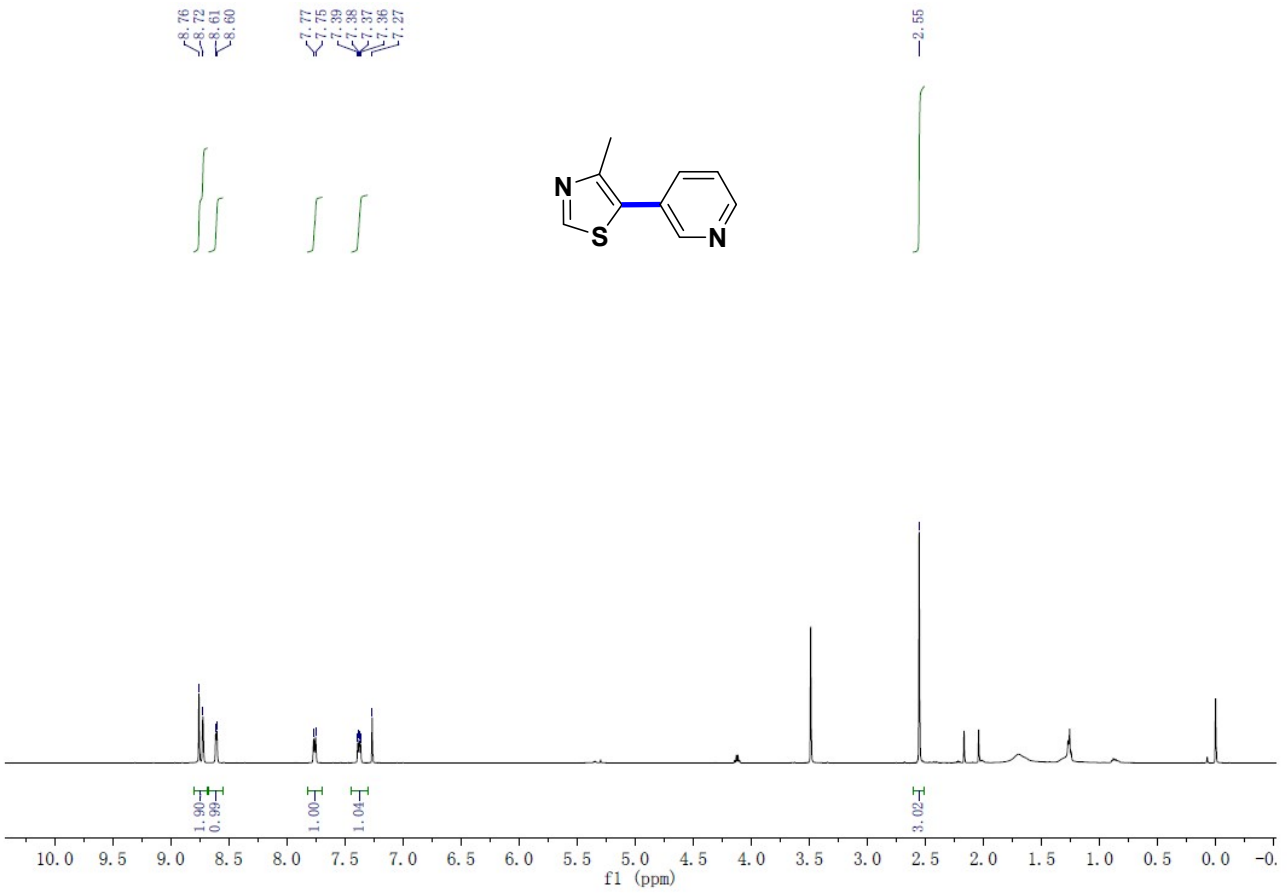
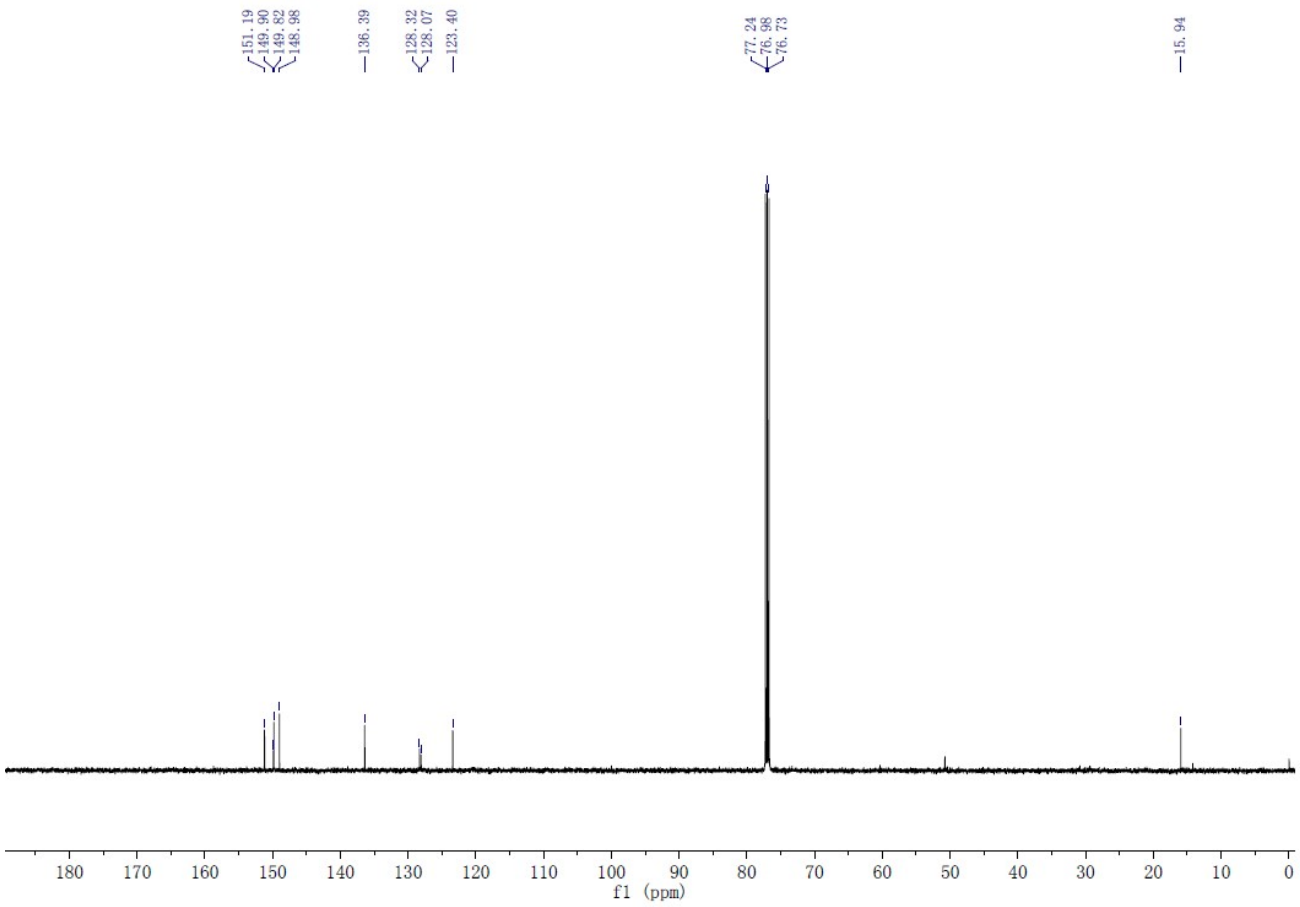
S
S
0.98
1.00
1.07
0.99
3.11
f1 (ppm)


149.90
149.13
133.24
127.62
127.16
126.18
125.53
77.25
76.99
76.74
16.47
f1 (ppm)


8.76
8.72
8.61
8.60
7.77
7.75
7.39
7.38
7.37
7.36
7.27
2.55
N
S
N
1.90
0.99
1.00
1.04
3.02
f1 (ppm)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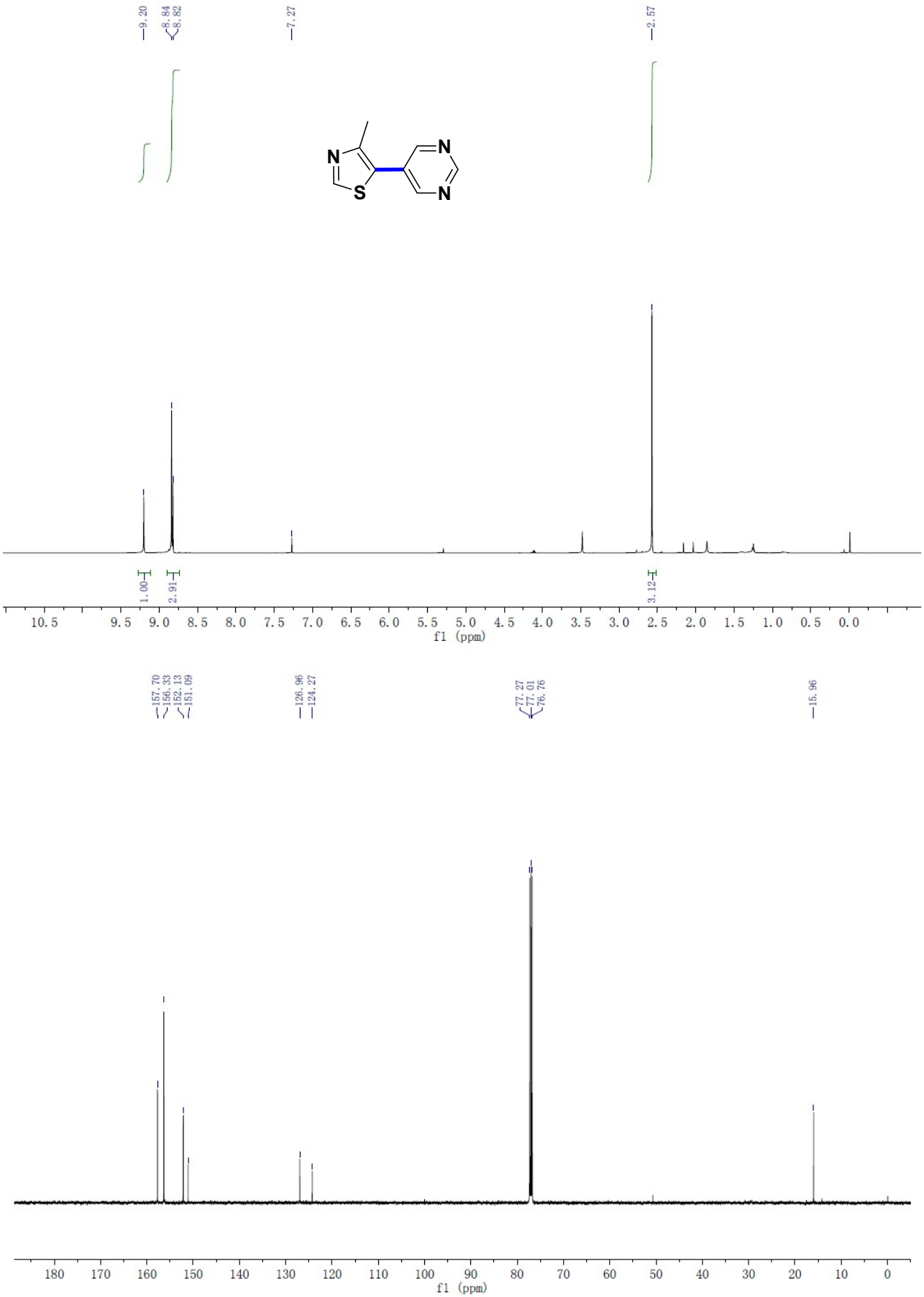
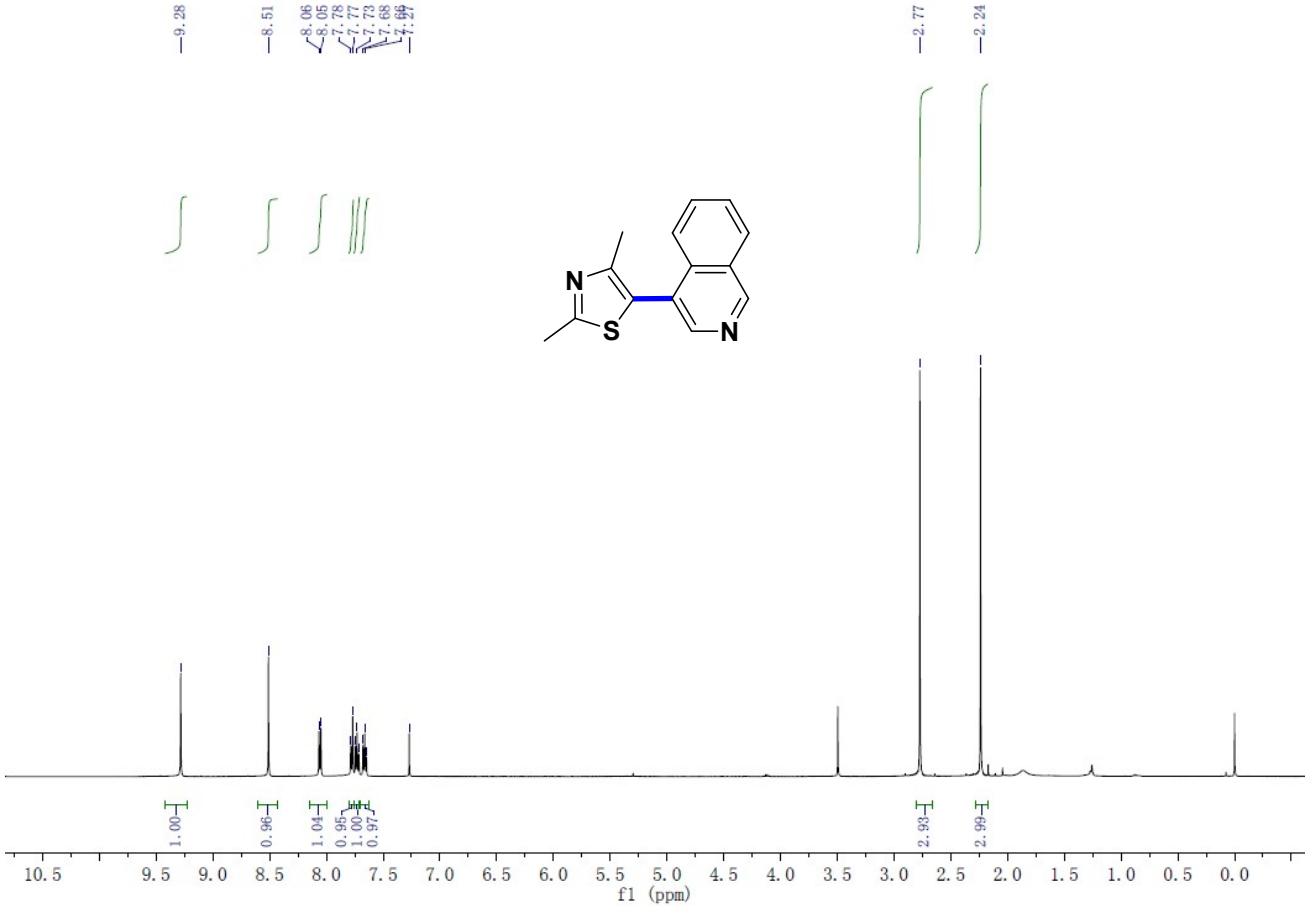
149.90
149.82
148.98
136.39
128.32
128.07
123.40
77.24
76.98
76.73
15.94
f1 (ppm)


9.20
8.84
8.82
7.27
2.57
N
S
N
N
1.00
2.91
3.12
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
157.70
156.33
152.13
151.09
126.96
124.27
77.27
77.01
76.76
15.96
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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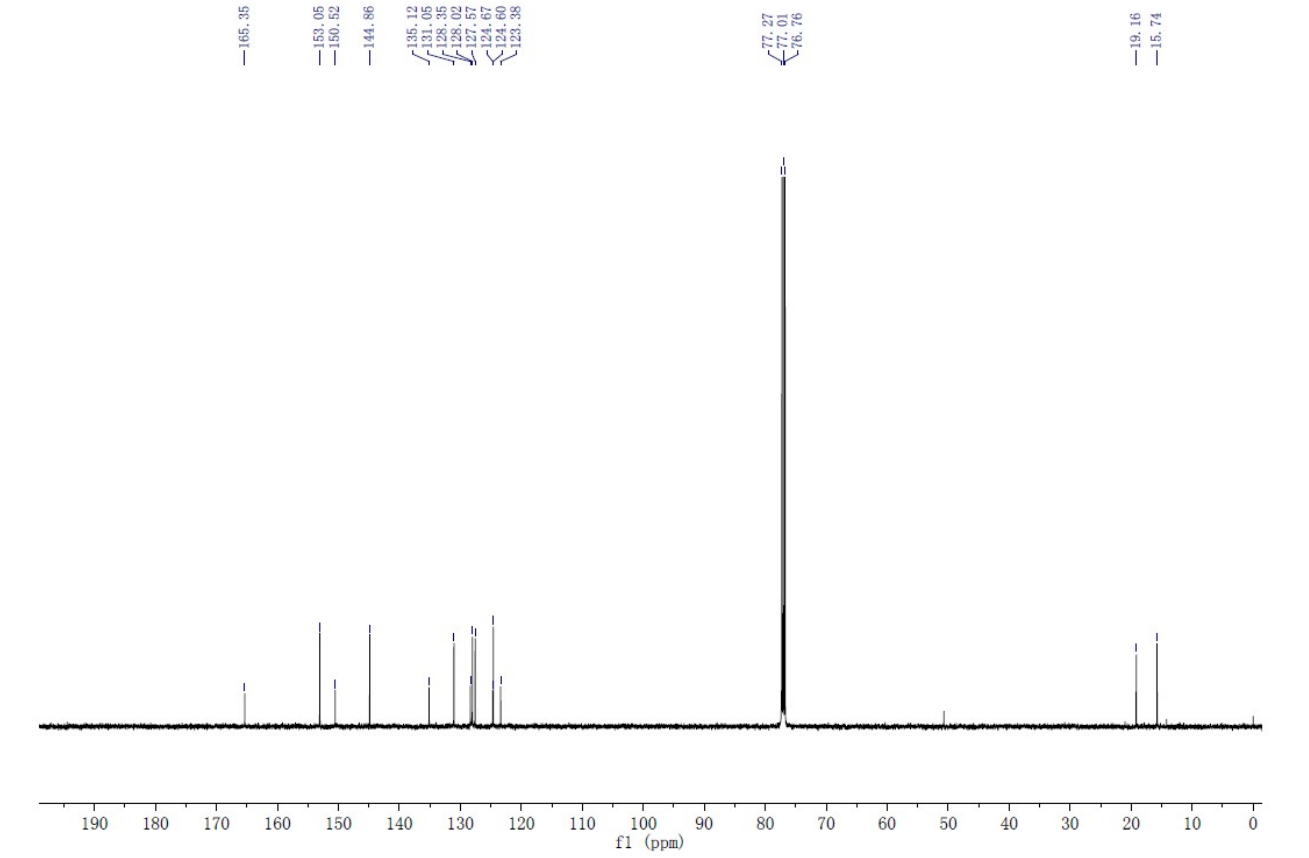
8.51
8.06
8.05
7.78
7.77
7.73
7.68
7.27
2.77
2.24
N
S
N
1.00
0.96
1.04
0.95
1.00
0.97
2.93
2.99
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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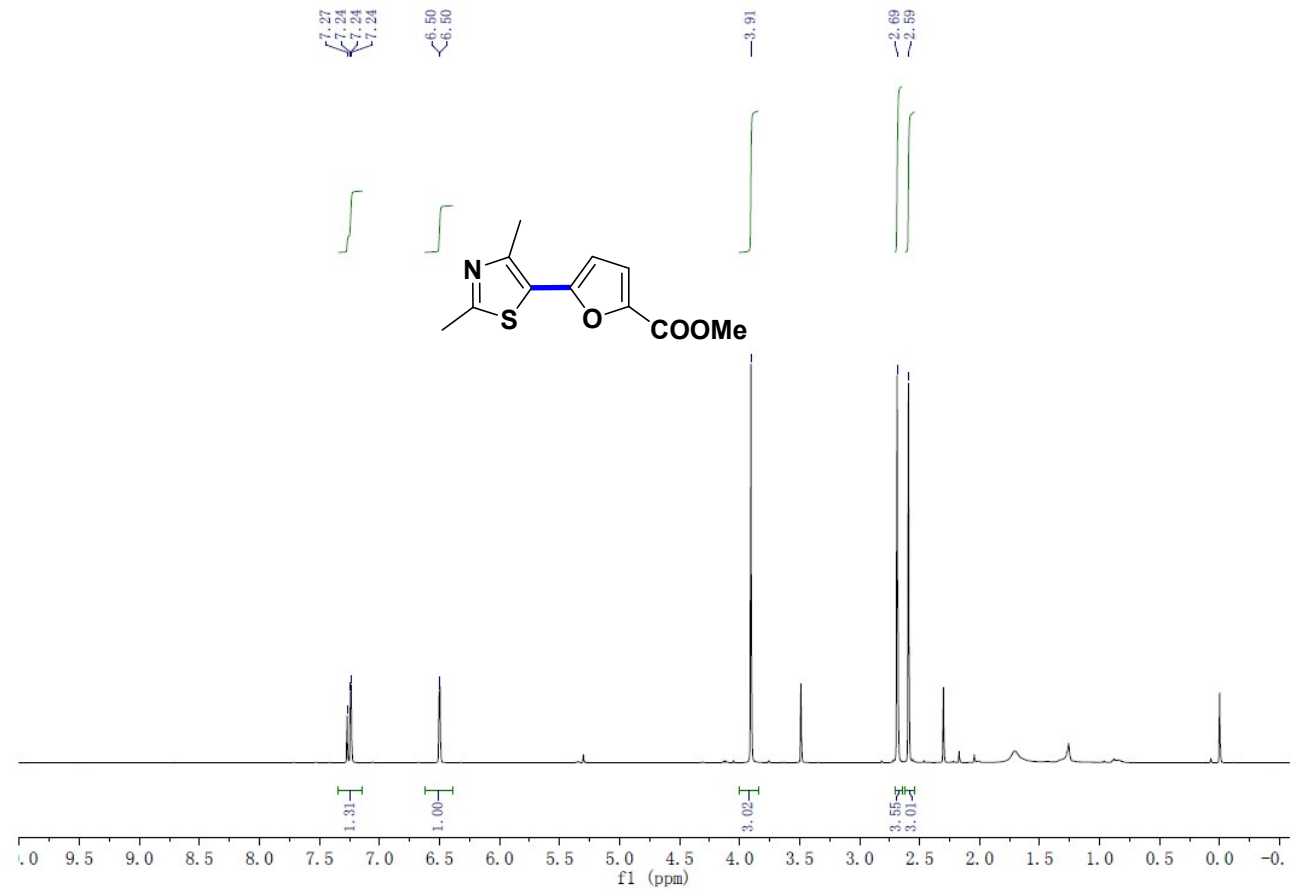
153.05
150.52
144.86
135.12
131.05
128.35
128.02
127.57
124.67
124.60
123.38
77.27
77.01
76.76
19.16
15.74
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.27
7.24
7.24
7.24
6.50
6.50
3.91
2.69
2.59
N
S
O
COOMe
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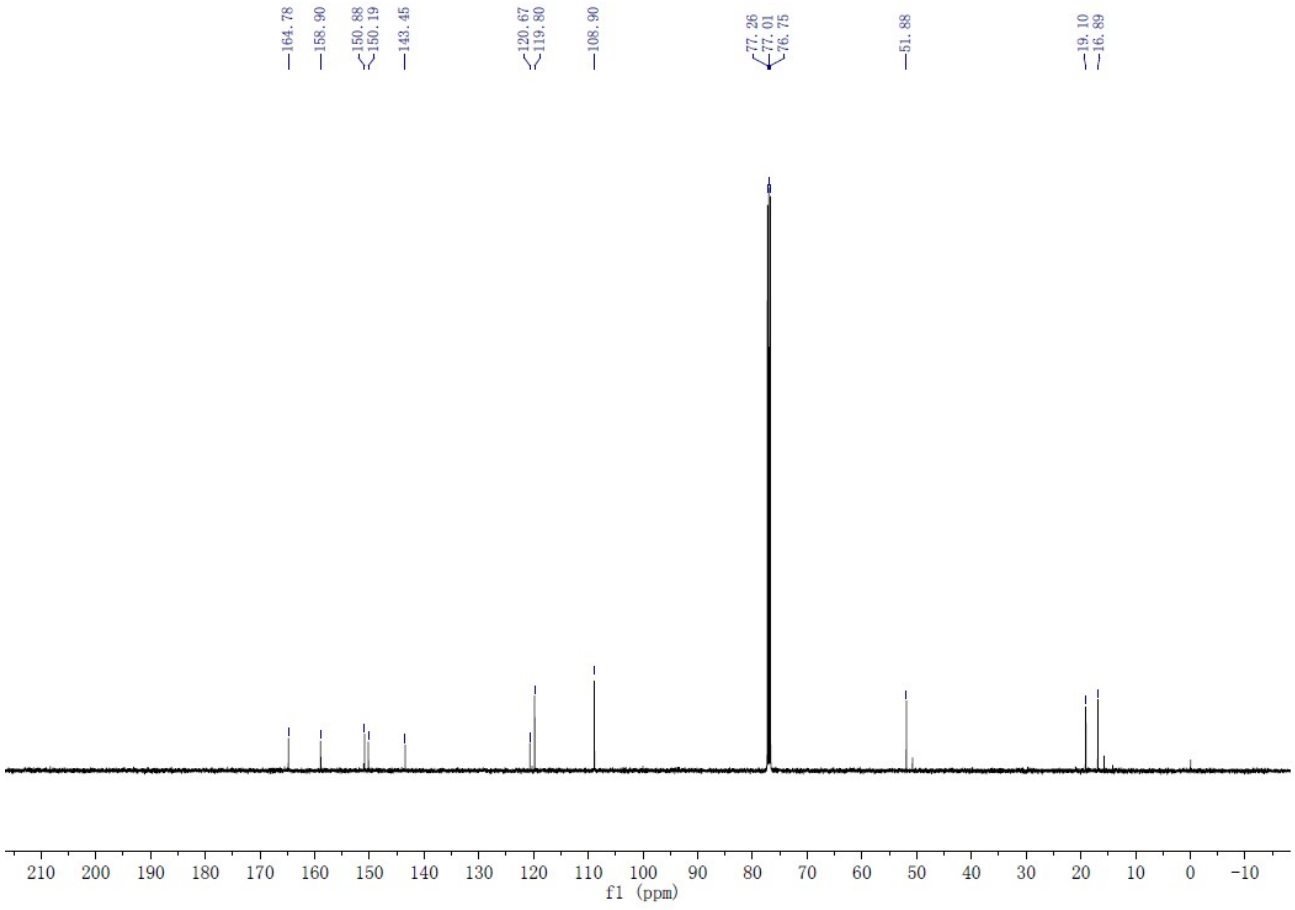
1.00
3.02
3.55
3.01
f1 (ppm)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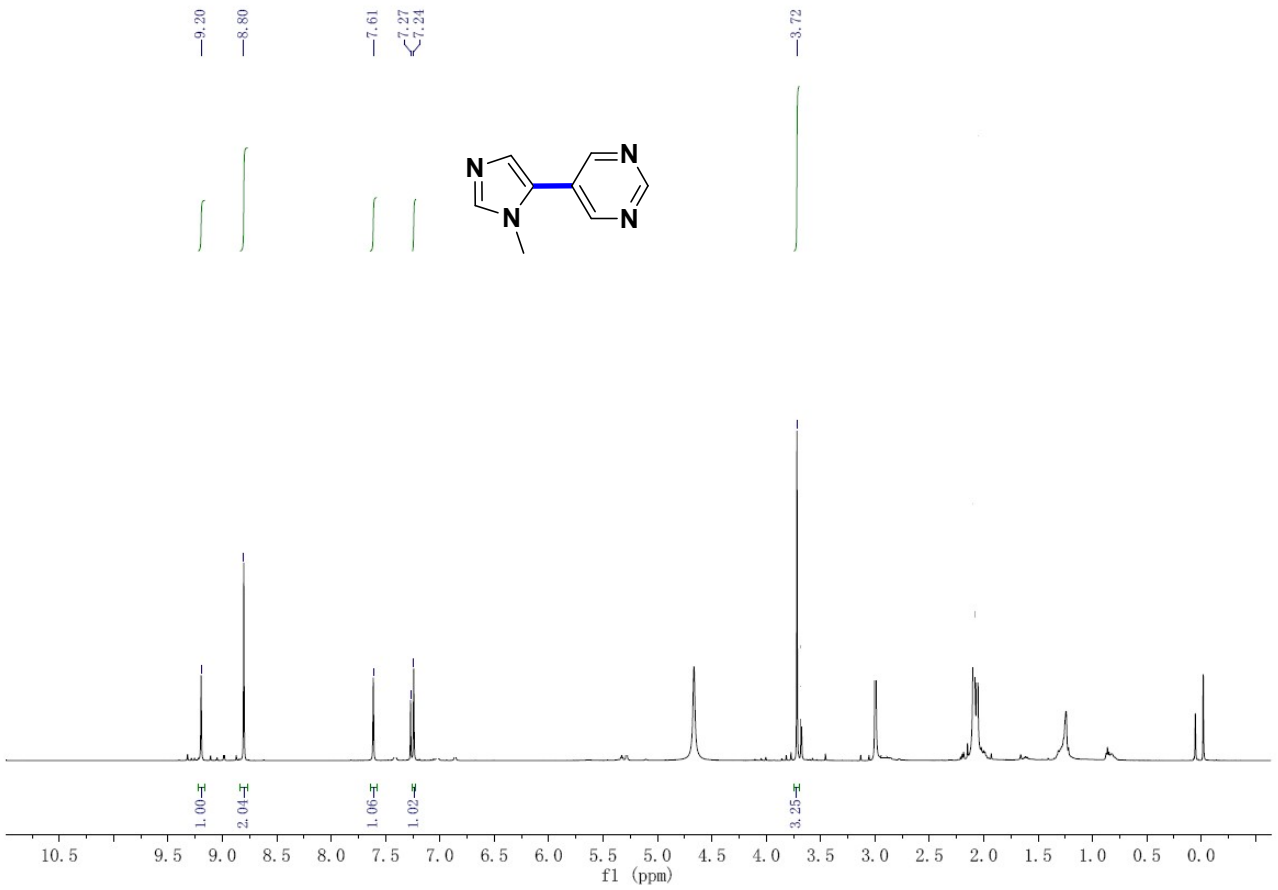
108.90
77.26
77.01
76.75
51.88
19.10
16.89
f1 (ppm)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8.80
7.61
7.27
7.24
3.72
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N
N
N
1.00
2.04
1.06
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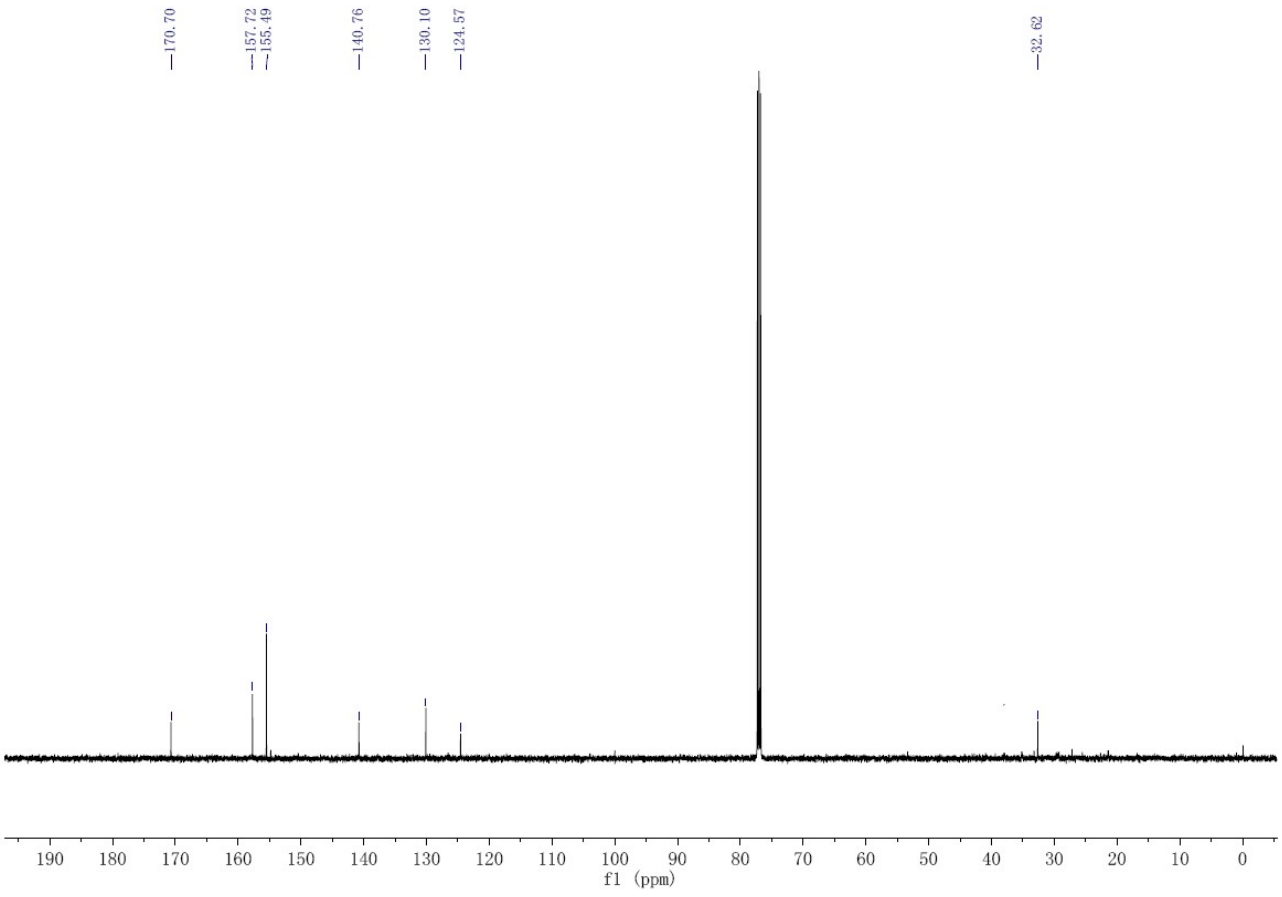
3.25
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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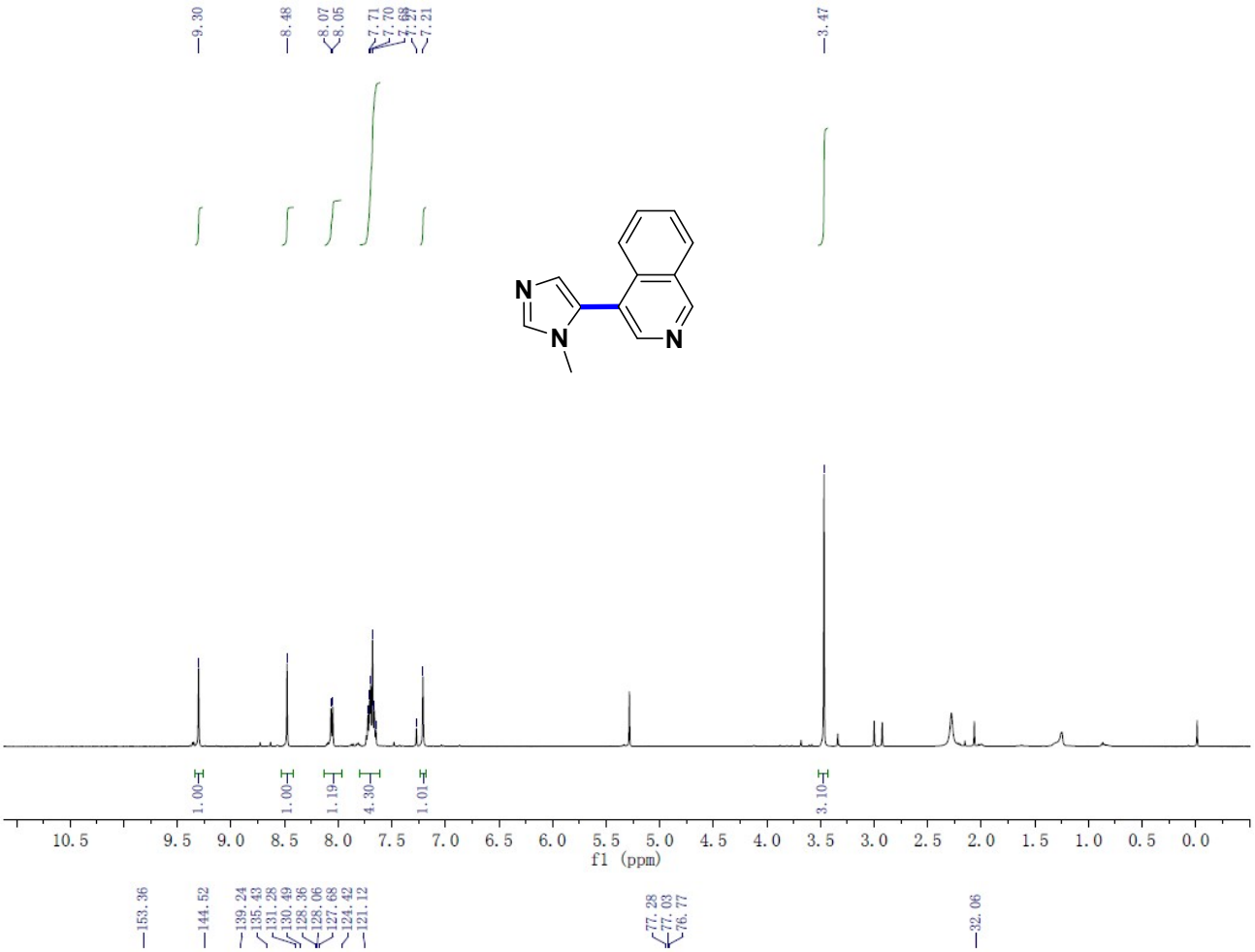
130.10
124.57
32.62
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.05
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7.70
7.68
7.27
7.21
3.47
N
N
N
1.00
1.00
1.19
4.30
1.01
3.10
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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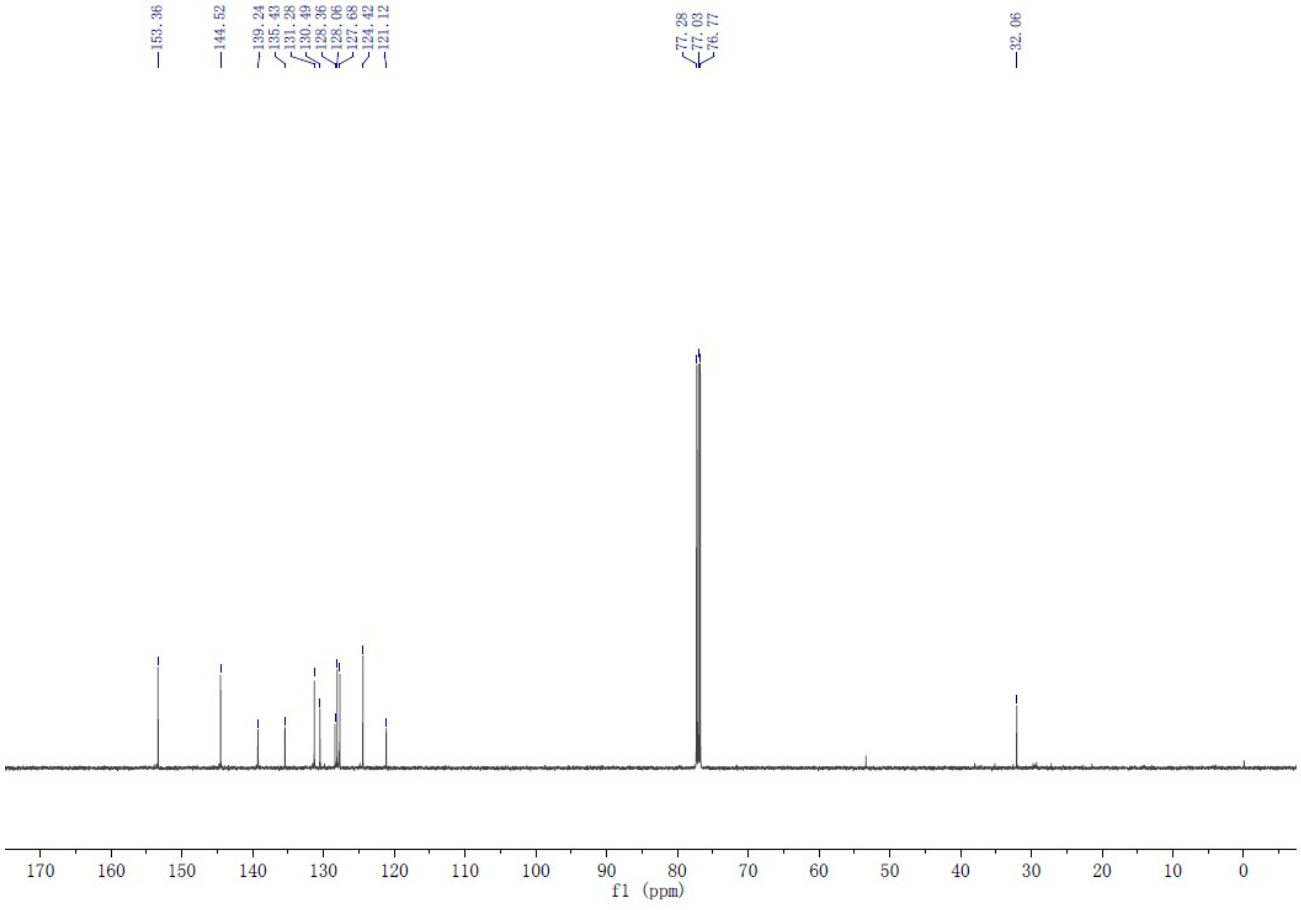
0.0
f1 (ppm)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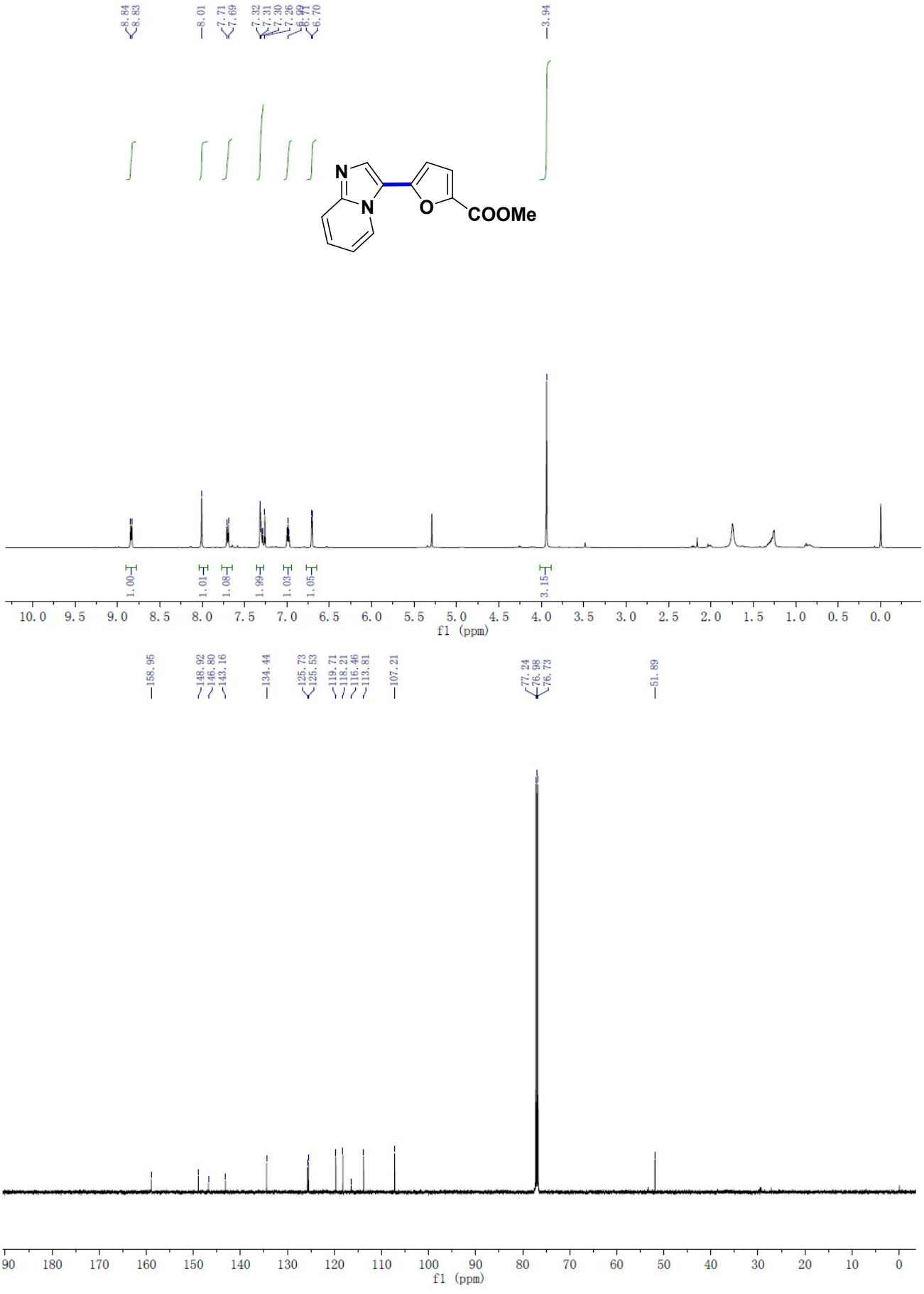
128.36
128.06
127.68
124.42
121.12
77.28
77.03
76.77
32.06
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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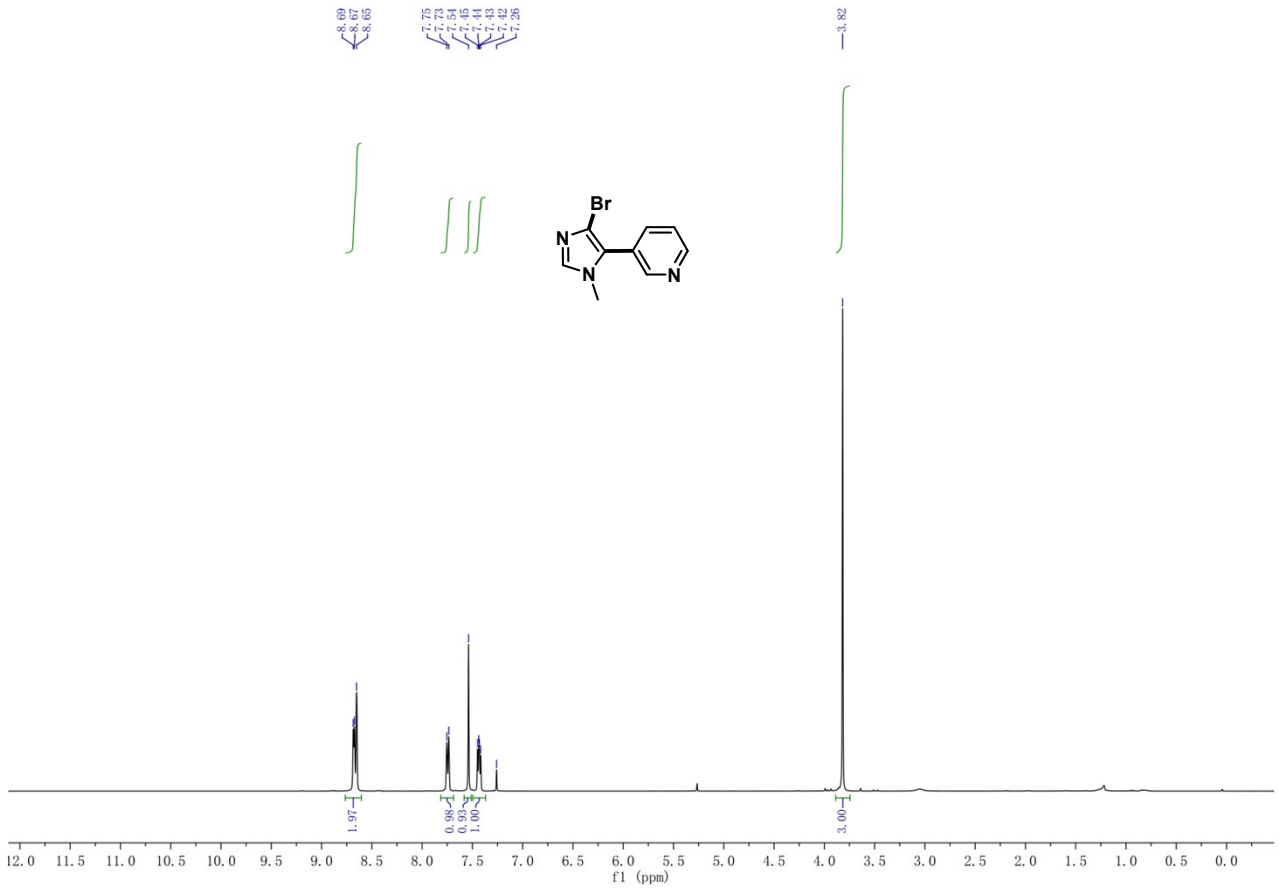
7.71
7.69
7.32
7.31
7.30
7.26
6.71
6.70
3.94
N
N
O
COOMe
1.00
1.01
1.08
1.99
1.03
1.05
3.15
f1 (ppm)
158.95
148.92
146.80
143.16
134.44
125.73
125.53
119.71
118.21
116.46
113.81
107.21
77.24
76.98
76.73
51.89
f1 (ppm)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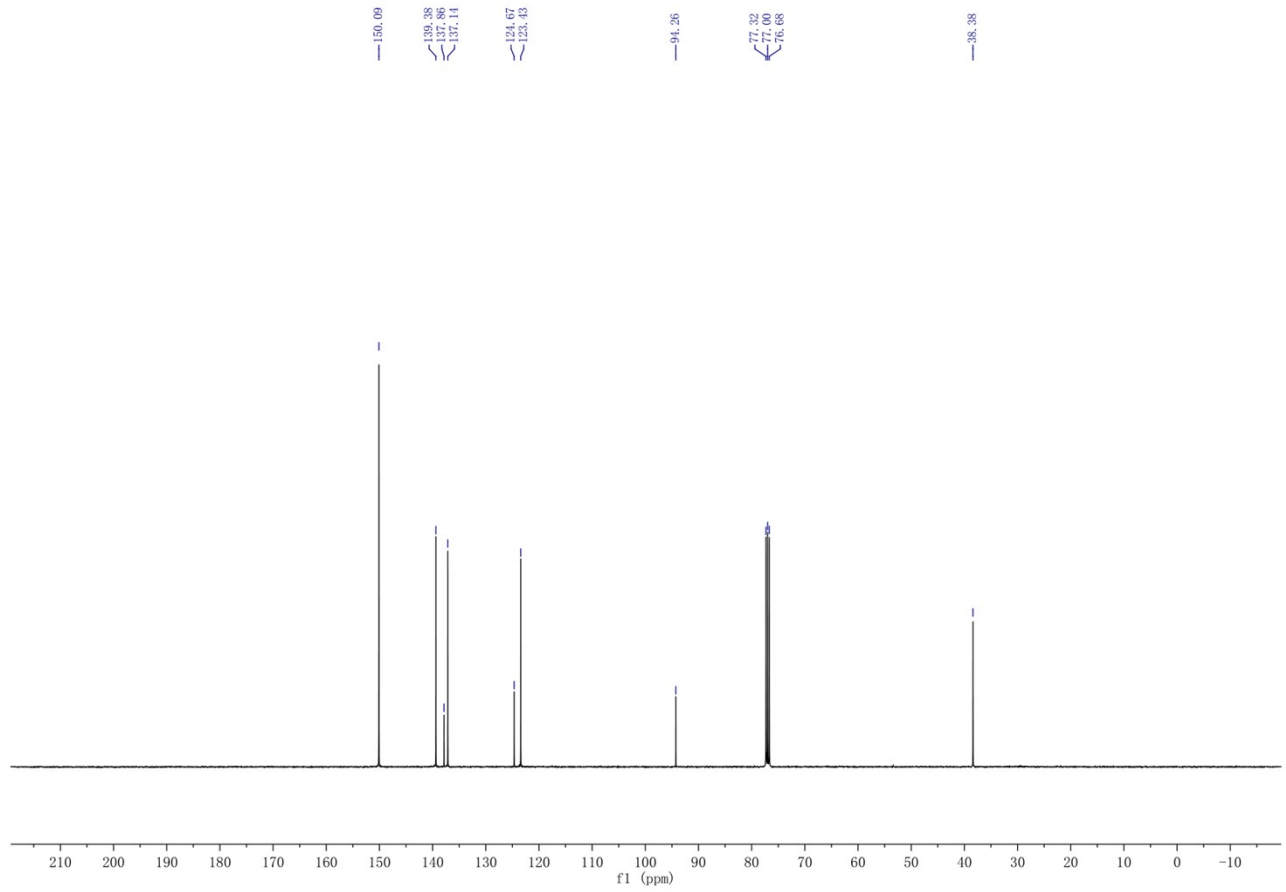
7.43
7.42
7.26
3.82
Br
N
N
N
1.97
0.98
0.93
1.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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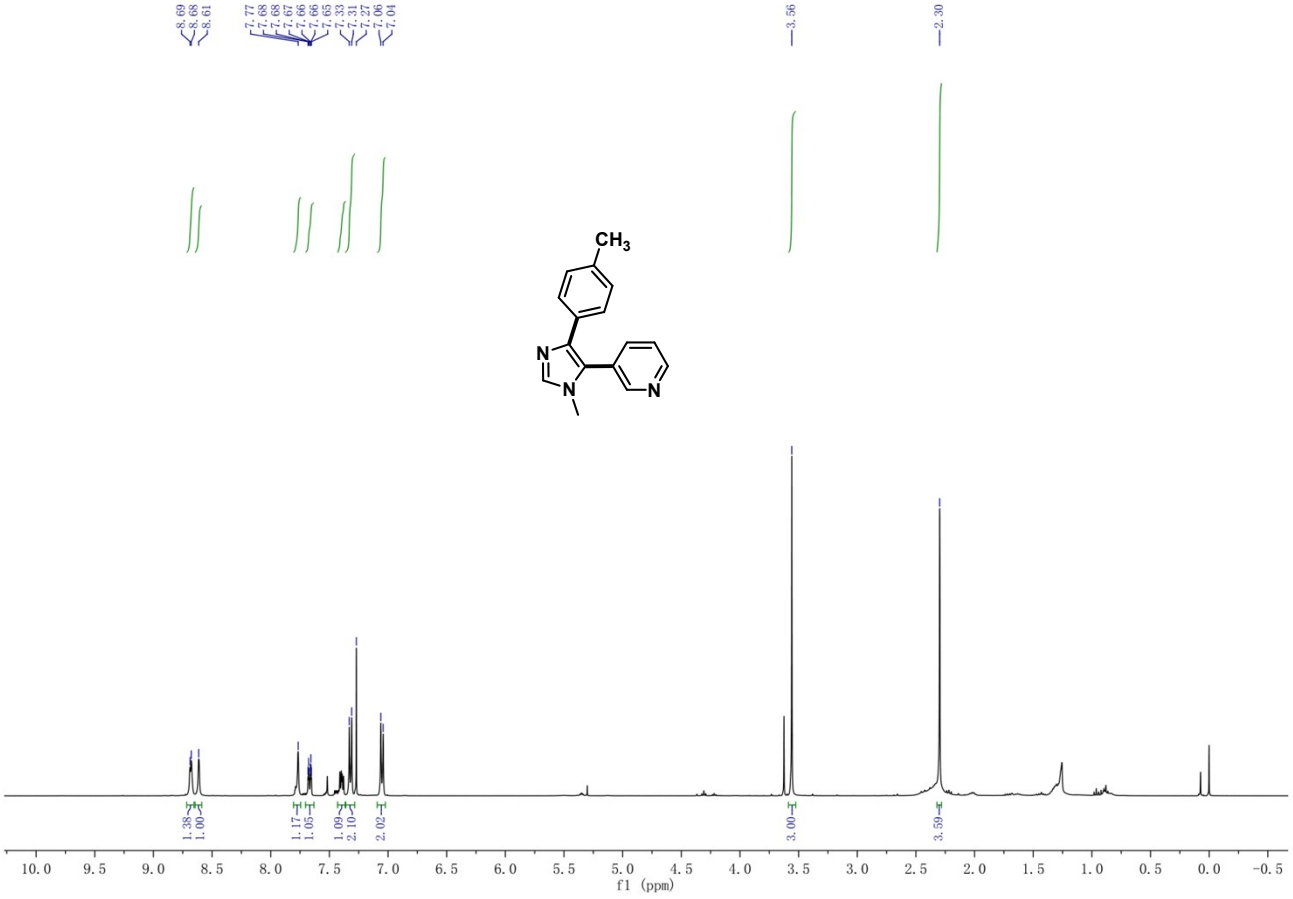
137.86
137.14
124.67
123.43
94.26
77.32
77.00
76.68
38.38
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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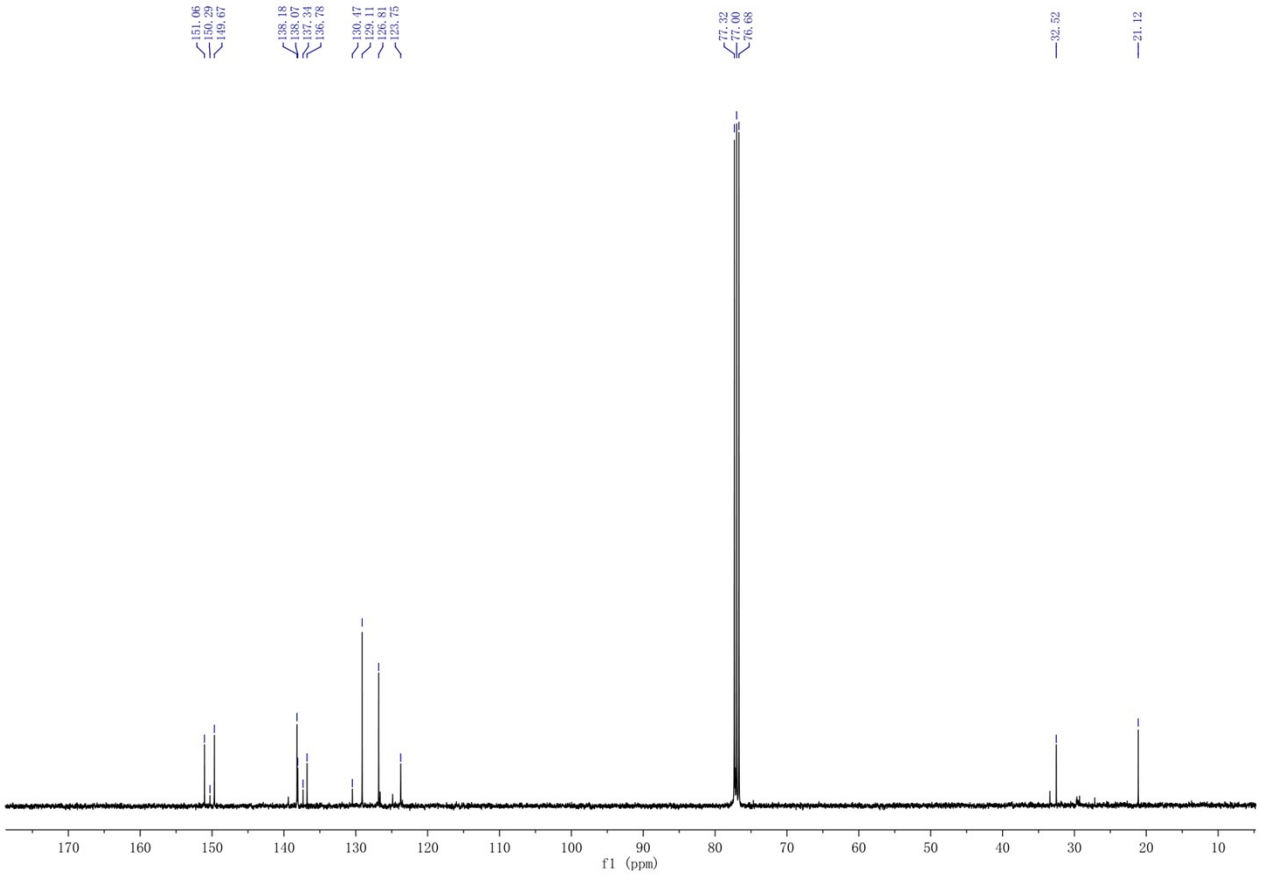
7.68
7.67
7.66
7.66
7.65
7.33
7.31
7.27
7.06
7.04
3.56
2.30
CH3
N
N
N
1.38
1.00
1.17
1.05
1.09
2.10
2.02
3.00
3.59
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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129.11
126.81
123.75
77.32
77.00
76.68
32.52
21.12
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)