Supporting Information

Visible-Light-Catalyzed C-H Arylation of (Hetero)Arenes *via* Aryl Selenonium Salt

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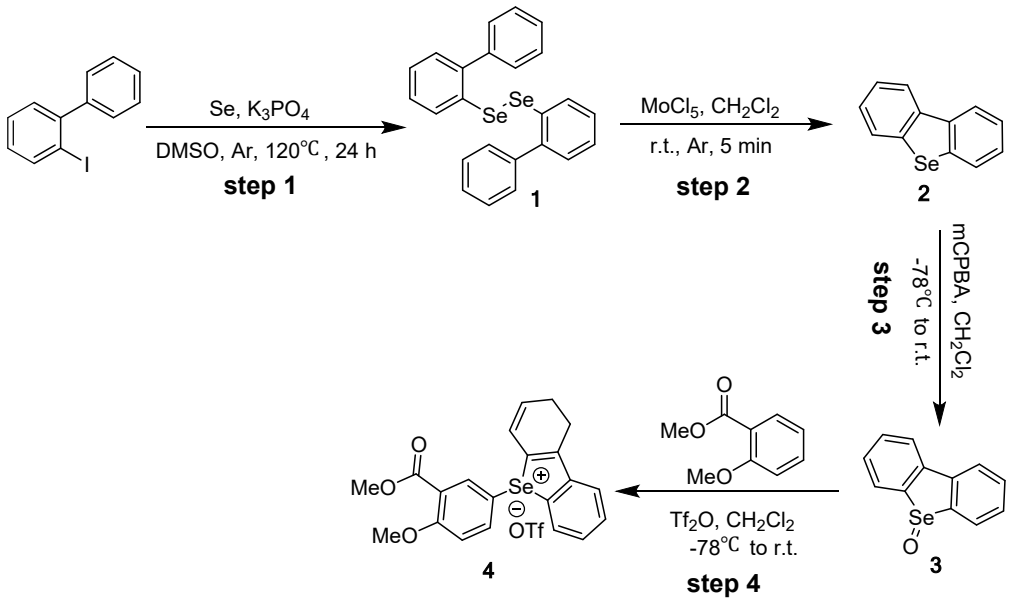
Contents

1 General Experimental Information

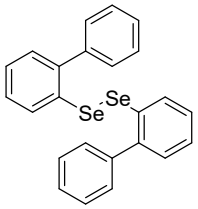
All reagents unless otherwise noted were obtained from commercial sources and used without further purification. Photoredox reactions were subjected to irradiation from a blue LED with an input power of 34 W and a maximum wavelength of 450 nm. The reaction tube is placed about 5 cm away from the bulb. Reactions were monitored by thin-layer chromatography (TLC) on silica gel plates and visualization of the plates was performed under UV light (254 nm and 365nm). Further flash column chromatography was performed on silica gel (200-300 mesh). NMR spectra (^{1}H and ^{13}C) were obtained using Bruker 600 MHz instruments, using TMS (Me_4Si) as an internal standard. Chemical shifts (δ) and coupling constants (J) are reported in units of ppm and Hz, respectively. The following abbreviations are used to set multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet and dt = double triplet. Low-resolution and high-resolution mass spectra were obtained using either positive and/or negative electrospray ionization (ES), or atmospheric-pressure chemical ionization (APCI) techniques.

2 Experiment Section

2.1 General Procedure for the Synthesis of arylselenonium salts (4)

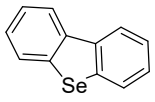


Step 1: Preparation of 2-Biphenylyl diselenide (1) [1]



A flame-dried test tube containing a magnetic stirring bar was charged with CuI (0.1 eq., 0.5 mmol, 0.1 g), K_3PO_4 (3.0 eq., 15 mmol, 3.2 g), Se (3.0 eq., 15 mmol, 1.2 g), 2-iodobiphenyl (1.0 eq., 5 mmol, 1.4 g), and DMSO (10 mL) under N_2. The mixture was heated at the indicated temperature for 18 h and allowed to cool to room temperature. The resulting mixture was extracted with ethyl acetate (30 mL×3). The combined organic layers were dried with Na_2SO_4 and then concentrated under vacuum. The residue was purified by column chromatography on silica gel with an eluent consisting of petroleum ether and ethyl acetate to give an orange solid (0.966 g, 83%). All the physical data for known compounds were consistent with those reported in the literature.

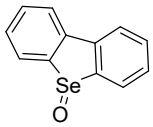
Step 2: Preparation of dibenzoselenophene (2) [2]



Bis-(biphenyl-2-yl)diselenide **1** (1.0 eq., 0.43 mmol, 200 mg) was

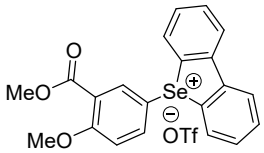
treated with $MoCl_5$ (2.0 eq., 0.86 mmol, 235 mg) in CH_2Cl_2 (10 mL) and stirred for 5 minutes. The crude product was purified by flash column chromatography (cyclohexane:ethyl acetate, 99:1) to yield compound **2** as a colorless solid (190 mg, 88.4%).

Step 3: Preparation of dibenzoselenophene oxide (3) [3]



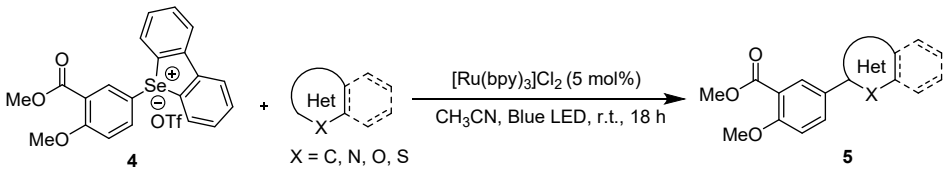
mCPBA (234 mg, 1.04 mmol, dissolved in 10 mL CH_2Cl_2) was added dropwise a solution of dibenzoselenophene **2** (200 mg, 0.87 mmol) in CH_2Cl_2 (50 mL) at -78˚C. The mixture was stirred while it was allowed to slowly warm to 0˚C. An aqueous solution of saturated aqueous $NaHCO_3$ (10 mL) was added into the reaction mixture The combined organic layers were washed with saturated brine and dried over Na_2SO_4 and then concentrated under reduced pressure. The crystals were purified by recrystallizations from CH_2Cl_2 to produce 0.190 g of white crystal **3** (84% yield).

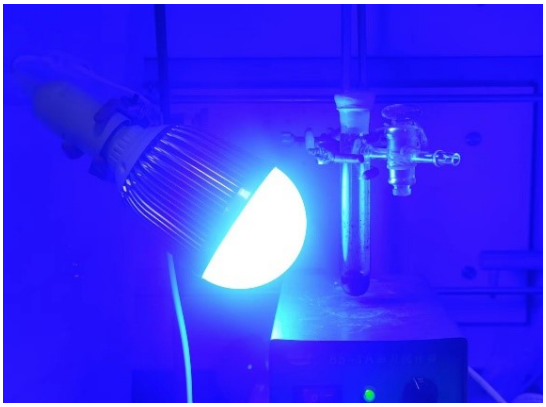
Step 4: Preparation of 5-(4-Methoxy-3-(methoxycarbonyl) phenyl)-5H-dibenzo [b, d] thiophen-5-ium trifluoromethanesulfonate (4)



Tf_2O (1.2 eq., 0.24 mmol, 40 µL) was added dropwise a solution of methyl 2-methoxybenzoate (1.0 eq., 0.2 mmol, 29 µL) and dibenzoselenophene oxide **3** (1.1 eq, 0.22 mmol, 55 mg) in CH_2Cl_2 (0.1 M) at -78°C under N_2. The resulting solution was stirred at this temperature for 15 minutes before warming to room temperature. After stirring for 1 h, TLC showed the arene starting material was consumed completely, at which point the solvent was removed in vacuo. The crude product was purified by recrystallization from CH_2Cl_2/Et_2O to produce 88 mg of off-white solid **4** (81% yield).

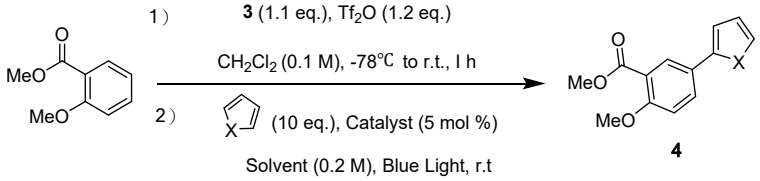
2.2 General method for photo-induced arylation with arylselenonium salts.





To a solution of selenonium salt (1.0 eq., 0.1 mmol, 55 mg), coupling reagent (10 eq., 1.0 mmol), $[Ru(bpy)_3]Cl_2$ (5 mol%) were added to anhydrous acetonitrile (0.2 M) under N_2. The reaction solution was reacted under a blue LED irradiation for 18 h. Then it was quenched with saturated $NaHCO_3$ solution and the reaction solution was diluted with ethyl acetate. The separated organic layer was washed with saturated brine, dried over Na_2SO_4 and evaporated to dryness, the crude product was purified by silica gel column chromatography.

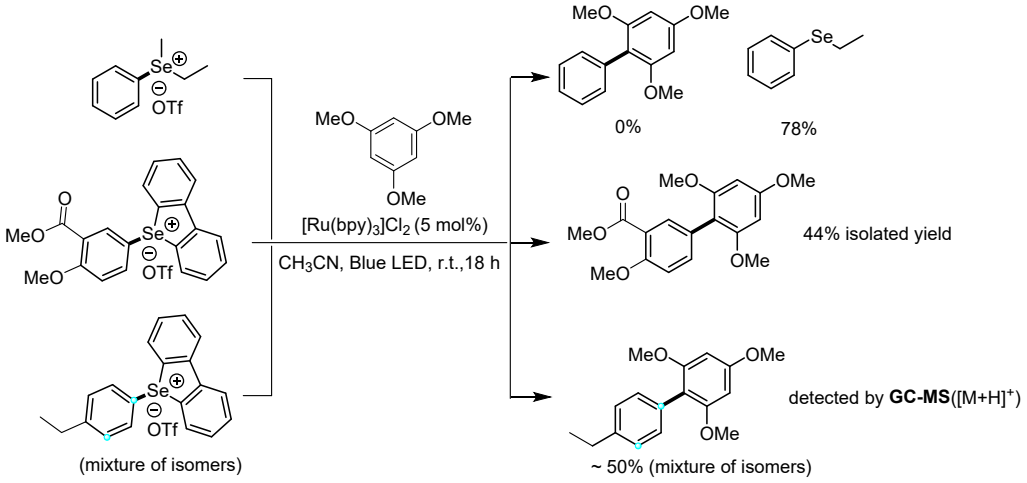
2.3 One-pot preparation of arylselenonium salts and photo-induced arylation of arylselenonium salts.



Tf_2O (1.2 eq., 0.24 mmol, 40 μL) was added dropwise into a solution of methyl 2-methoxybenzoate (1.0 eq., 0.2 mmol, 29 μL) and dibenzoselenophene oxide **3** (1.1 eq., 0.22 mmol, 55 mg) in CH_2Cl_2 (0.1 M) at -78°C under N_2. The resulting solution was stirred at this temperature for 15 minutes before warming to room temperature. After

stirring for 1 h, TLC analysis showed complete consumption of the arene starting material, at which point the solvent was removed in vacuo. $[Ru(bpy)_3]Cl_2$ (5 mol%) was then added to the reaction vial, followed by evacuation and refilling with nitrogen (3 cycles). anhydrous acetonitrile (0.2 M) was then added followed by *N*-methyl pyrrole (10 eq., 2 mmol, 0.18 mL). The reaction mixture was then irradiated with a blue LED for 18 h before quenching with aqueous saturated $NaHCO_3$ and dilution with EtOAc. The separated organic layer was washed with saturated brine, dried over Na_2SO_4 and evaporated to dryness, to give the crude product, which was purified by column chromatography on silica gel.

2.4 Discussion on the construction of selenonium salts

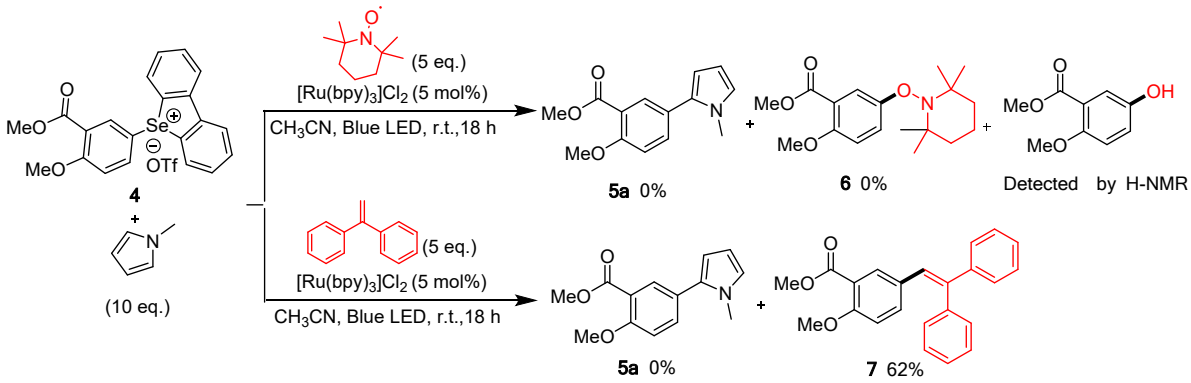


Actually, three kinds of arylselenonium salts were prepared. Firstly, we prepared (methyl)(ethyl)(aryl)selenonium salt. In the subsequent photocatalyzed arylation with 1,3,5-trimethoxybenzene, a large amount of (ethyl)(phenyl)selenide was obtained instead of the arylation product, the selective breaking of the C-Se bond is crucial. Next, the ring-closed 4-methoxy-3-(methoxycarbonyl) aryl dibenzoselenophene salt **4** was prepared with high regioselectivity. Furthermore, the photocatalyzed arylation of **4** took place only at the C_{Aryl}-Se bond selectively and **5a** was successfully obtained. Lastly, we prepared 4-ethylphenyl dibenzoselenophene salt, 2-ethylphenyl dibenzoselenophene salt isomer was produced at the same time. It is difficult to

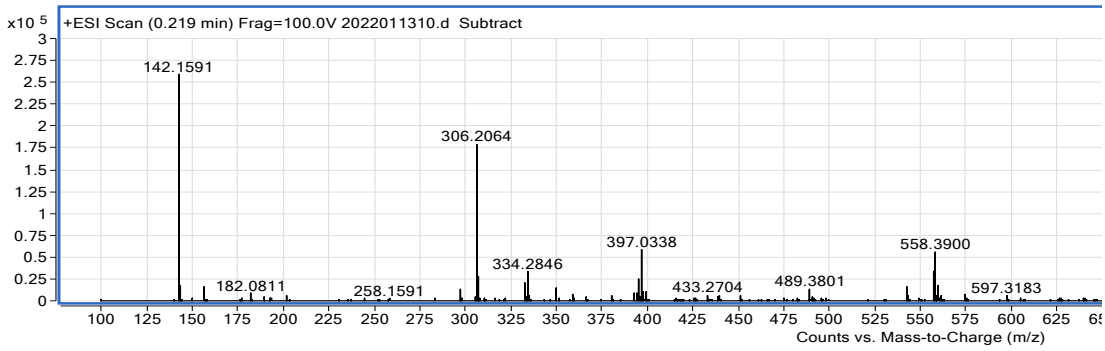
separate two isomers. The mixture yield of photocatalyzed arylation with 1,3,5,-trimethoxybenzene was about 50%, the GC-MS of this compound was added to SI. Therefore we selected 4-methoxy-3-(methoxycarbonyl) aryl dibenzoselenophene salt **4** as aryl source.

3 Mechanism Study

competitive experiment:

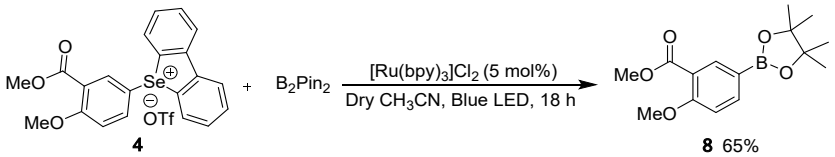


To a solution of selenonium salt **4** (1.0 eq., 0.1 mmol, 55 mg), coupling reagent (10 eq., 1.0 mmol), TEMPO/1,1-diphenylethylene (1.0 eq., 0.5 mmol), $[Ru(bpy)_3]Cl_2$ (5 mol%) were added to anhydrous acetonitrile (0.2 M) under N_2. The reaction solution was reacted under a blue LED irradiation for 18 h. Then it was quenched with saturated $NaHCO_3$ solution and the reaction solution was diluted with ethyl acetate. The separated organic layer was washed with saturated brine, dried over Na_2SO_4 and evaporated to dryness, the crude product was purified by silica gel column chromatography.

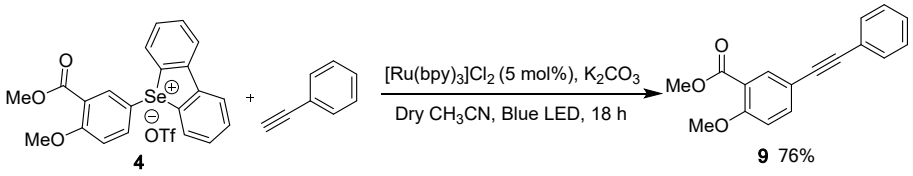


Mass spectrum of product of TEMPO capturing radical experiment

4 Post - functionalization



To a solution of selenonium salt **4** (1.0 eq., 0.1 mmol, 55 mg), B_2Pin_2 (10 eq., 1.0 mmol, 0.254 g), $[Ru(bpy)_3]Cl_2$ (5 mol%) were added to anhydrous acetonitrile (0.2 M) under N_2. The reaction solution was reacted under a blue LED irradiation for 18 h. Then it was quenched with saturated $NaHCO_3$ solution and the reaction solution was diluted with ethyl acetate. The separated organic layer was washed with saturated brine, dried over Na_2SO_4 and evaporated to dryness, the crude product was purified by silica gel column chromatography using a mixture of EtOAc and PE as eluent to provide the substrates **8**.

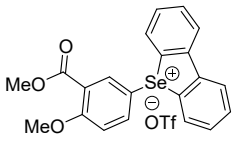


To a solution of selenonium salt **4** (1.0 eq., 0.1 mmol, 55 mg), Phenylacetylene (10 eq., 1.0 mmol, 0.102 g), $[Ru(bpy)_3]Cl_2$ (5 mol%), K_2CO_3 (3 eq., 0.3 mmol, 0.415 g) were added to anhydrous acetonitrile (0.2 M) under N_2. The reaction solution was reacted under a blue LED irradiation for 18 h. Then it was quenched with saturated $NaHCO_3$ solution and the reaction solution was diluted with ethyl acetate. The

separated organic layer was washed with saturated brine, dried over Na_2SO_4 and evaporated to dryness, the crude product was purified by silica gel column chromatography using a mixture of EtOAc and PE as eluent to provide the substrates **9**.

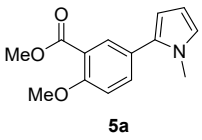
5 Characterization data of products.

5-(4-Methoxy-3-(methoxycarbonyl) phenyl)-5H-dibenzo [b, d] thiophen-5-ium trifluoromethanesulfonate (4)



off-white solid, 88 mg, 81%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, J = 7.5 Hz, 2H), 8.10 (d, J = 7.7 Hz, 3H), 7.82 (t, J = 7.5 Hz, 2H), 7.63 (t, J = 10.7 Hz, 3H), 6.94 (s, 1H), 3.90 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.58, 162.57, 140.96, 137.04, 135.03, 133.73, 132.85, 131.83, 130.96, 124.57, 122.98, 119.33, 114.66, 65.87, 56.66, 52.65; HRMS(ESI) m/z $C_{21}H_{17}O_3Se^+$ [M] $^+$ calcd for 397.0337, found 397.0340.

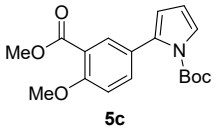
methyl 2-methoxy-5-(1-methyl-1H-pyrrol-2-yl)benzoate (5a)



5a

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 35 mg, 72%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, J = 2.4 Hz, 1H), 7.49 (dd, J = 8.6, 2.4 Hz, 1H), 7.11 - 5.98 (m, 4H), 4.12 - 3.40 (m, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.56, 158.08, 133.72, 133.20, 131.95, 125.67, 123.43, 119.99, 112.15, 108.52, 107.74, 56.18, 52.11, 34.91; MS(ESI) calculated *m/z* for $C_{14}H_{15}NO_3$ [M + H]$^+$: 246.11, found 246.12.

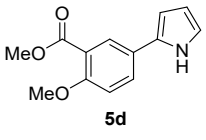
tert-butyl 2-(4-methoxy-3-(methoxycarbonyl)phenyl)-1H-pyrrole-1-carboxylate (5c)



5c

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 49 mg, 74%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.4 Hz, 1H), 7.47 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.35 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 1H), 6.22 (t, *J* = 3.3 Hz, 1H), 6.17 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.40, 158.49, 149.34, 134.24, 133.57, 132.78, 126.56, 122.58, 119.06, 114.55, 111.26, 110.59, 83.78, 56.17, 52.01, 27.68; HRMS(ESI) calculated *m/z* for $C_{18}H_{21}NO_5$ [M + Na]$^+$: 354.1318, found 354.1315.

methyl 2-methoxy-5-(1H-pyrrol-2-yl)benzoate (5d)

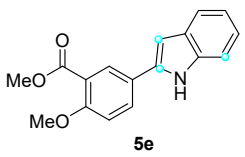


5d

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 31 mg, 68%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.90 (d, J = 2.5 Hz, 1H), 7.59 (dd, J = 8.5, 2.4 Hz, 1H), 6.99 (d, J = 8.7 Hz, 1H), 6.88 - 6.80 (m, 1H), 6.45 (d, J = 2.2 Hz, 1H), 6.29 (d, J = 3.0 Hz,

1H), 3.91 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.66, 157.64, 131.01, 129.19, 127.08, 125.58, 120.23, 118.71, 112.75, 110.10, 105.54, 56.20, 52.17; MS(ESI) calculated *m/z* for $C_{13}H_{13}NO_3$ $[M + H]^+$: 323.09, found 323.10.

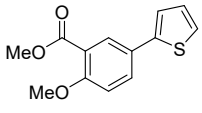
methyl 5-(1H-indol-2-yl)-2-methoxybenzoate (5e)



5e

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 38 mg, 68%. C-2: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.02 (d, *J* = 2.3 Hz, 1H), 7.71 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.12 (s, 1H), 7.10 (s, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 6.70 (d, *J* = 2.2 Hz, 1H), 3.85-3.94 (d, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.40, 157.70, 135.79, 132.56, 132.23, 130.83, 130.16, 129.31, 127.29, 123.51, 121.28, 119.52, 119.32, 111.77, 98.51, 55.23, 51.24. C-3: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.09 (d, *J* = 2.4 Hz, 1H), 7.74 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.32 (s, 1H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.13 (s, 1H), 7.05 (d, *J* = 3.3 Hz, 1H), 6.62 (d, *J* = 3.0 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.56, 157.24, 135.74, 132.23, 128.28, 123.86, 123.46, 121.34, 120.80, 119.30, 119.07, 118.49, 111.86, 102.18, 100.92, 55.18, 51.06. C-7: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.01 (s, 1H), 7.66 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.33 (s, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 7.13 (d, *J* = 6.9 Hz, 1H), 7.09 (s,1H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.56 (t, *J* = 2.7 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.77, 157.43, 135.24, 132.69, 131.99, 130.28, 127.34, 125.02, 123.19, 119.56, 119.40, 119.03, 111.19, 109.18, 102.18, 55.20, 51.19; HRMS(ESI) calculated *m/z* for $C_{17}H_{15}NO_3$ $[M + Na]^+$: 304.0950, found 304.0952.

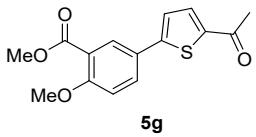
methyl 2-methoxy-5-(thiophen-2-yl)benzoate (5f)



5f

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 31 mg, 62%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.3 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.25 (s, 2H), 7.07 (d, *J* = 4.4 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 3.93 (d, *J* = 7.8 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.42, 158.52, 143.08, 130.87, 129.21, 128.06, 126.99, 124.48, 122.80, 120.41, 112.55, 56.23, 52.19; MS(APCI) calculated *m/z* for $C_{13}H_{12}O_3S$ $[M + H]^+$: 249.14, found 249.15.

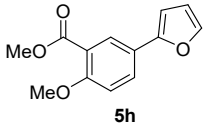
methyl 5-(5-acetylthiophen-2-yl)-2-methoxybenzoate (5g)



5g

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 38 mg, 66%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.5 Hz, 1H), 7.68 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.58 (d, *J* = 4.0 Hz, 1H), 7.21 (s, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.49, 166.04, 159.64, 151.50, 142.82, 133.54, 131.20, 129.60, 125.76, 123.47, 120.65, 112.69, 56.29, 52.30, 26.54; HRMS(ESI) calculated *m/z* for $C_{15}H_{14}O_4S$ $[M + Na]^+$: 313.3228, found 313.3230.

methyl 5-(furan-2-yl)-2-methoxybenzoate (5h)

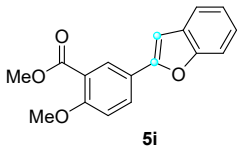


5h

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 30 mg,

65%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.4 Hz, 1H), 7.77 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.58 (d, *J* = 3.3 Hz, 1H), 6.46 (dd, *J* = 3.3, 1.8 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.44, 158.34, 152.91, 141.84, 128.79, 127.31, 123.63, 120.21, 112.34, 111.68, 104.24, 56.18, 52.18; MS(APCI) calculated *m/z* for $C_{13}H_{12}O_4$ $[M + H]^+$: 233.15, found 233.17.

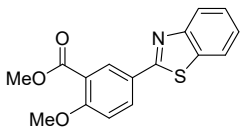
methyl 5-(benzofuran-2-yl)-2-methoxybenzoate (5i)



5i

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 38 mg, 68%. C-2: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.3 Hz, 1H), 7.96 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.58 - 7.55 (m, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 1.4 Hz, 1H), 7.24 - 7.22 (m, 1H), 7.07 (d, *J* = 8.7 Hz, 1H), 6.96 (s, 1H), 3.97 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.32, 159.26, 154.87, 154.81, 129.90, 129.29, 128.49, 124.16, 123.04, 123.01, 120.81, 120.45, 112.44, 111.10, 100.57, 56.24, 52.26. C-3: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.4 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 11.0 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.12 - 7.10 (m, 1H), 6.92 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.22, 145.34, 136.64, 133.27, 131.60, 130.75, 125.28, 124.53, 123.36, 122.12, 119.43, 117.73, 110.40, 105.85, 56.24, 52.26; MS(APCI) calculated *m/z* for $C_{17}H_{14}O_4$ $[M + H]^+$: 283.17, found 283.19.

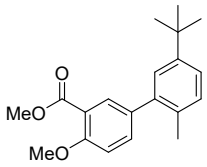
methyl 5-(benzo[d]thiazol-2-yl)-2-methoxybenzoate (5j)



5j

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 36 mg, 61%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, *J* = 2.4 Hz, 1H), 8.24 (dd, *J* = 8.7, 2.4 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.50 (td, *J* = 7.5, 1.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 1H), 4.00 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.71, 165.87, 161.14, 154.10, 134.93, 132.46, 131.10, 126.43, 126.00, 125.15, 123.03, 121.63, 120.64, 112.45, 56.35, 52.29; MS(ESI) calculated *m/z* for $C_{16}H_{13}NO_3S$ $[M + H]^+$: 300.06, found 300.07.

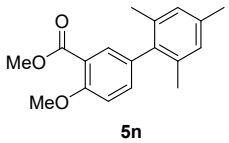
methyl 5'-(tert-butyl)-4-methoxy-2'-methyl-[1,1'-biphenyl]-3-carboxylate (5m)



5m

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 37 mg, 63%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.2 Hz, 1H), 7.44 (d, *J* = 8.5, 2.2 Hz, 1H), 7.29 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.22 - 7.19 (m, 2H), 7.04 (d, *J* = 8.5 Hz, 1H), 3.96 (d, *J* = 1.6 Hz, 3H), 3.90 (d, *J* = 1.6 Hz, 3H), 2.22 (s, 3H), 1.33 (d, *J* = 1.7 Hz, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.75, 158.02, 148.81, 140.03, 134.48, 134.20, 132.46, 132.35, 130.10, 126.81, 124.41, 119.67, 111.78, 56.18, 52.08, 34.40, 31.43, 19.90; HRMS(ESI) calculated *m/z* for $C_{20}H_{24}O_3$ $[M + Na]^+$: 335.1623, found 335.1621.

methyl 4-methoxy-2',4',6'-trimethyl-[1,1'-biphenyl]-3-carboxylate (5n)

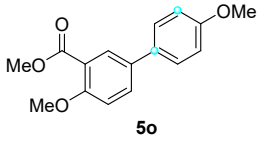


5n

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 34 mg, 60%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.3 Hz, 1H),

7.24 (d, *J* = 2.2 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.93 (s, 2H), 3.95 (s, 3H), 3.87 (s, 3H), 2.32 (s, 3H), 2.00 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.70, 157.92, 137.51, 136.85, 136.32, 134.44, 132.88, 132.58, 128.14, 119.91, 112.12, 56.08, 52.00, 21.02, 20.80; HRMS(ESI) calculated *m/z* for $C_{18}H_{20}O_3$ [M + Na]$^+$: 307.1305, found 307.1308.

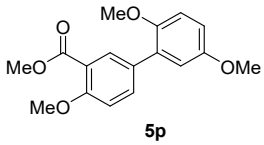
methyl 4,4'-dimethoxy-[1,1'-biphenyl]-3-carboxylate (5o)



5o

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 34 mg, 62%. C-p: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.3 Hz, 1H), 7.67 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.02 (dd, *J* = 8.1, 4.3 Hz, 2H), 6.97 (d, *J* = 2.7 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.76, 158.21, 156.45, 134.63, 132.75, 130.62, 130.54, 128.67, 120.91, 111.68, 111.26, 56.15, 55.60, 52.02. C-o: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.5 Hz, 1H), 7.71 - 7.68 (m, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 1H), 7.16 - 7.14 (m, 2H), 7.09 (t, *J* = 2.2 Hz, 1H), 6.88 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.95 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.03, 159.05, 158.14, 131.97, 130.34, 129.86, 129.26, 127.78, 119.61, 119.27, 114.28, 112.58, 112.47, 56.21, 55.37, 52.14; HRMS(ESI) calculated *m/z* for $C_{16}H_{16}O_4$ [M + Na]$^+$: 295.0947, found 295.0945.

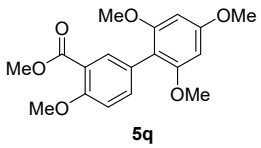
methyl 2',4,5'-trimethoxy-[1,1'-biphenyl]-3-carboxylate (5p)



5p

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 35 mg, 58%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.8 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 6.93 - 6.87 (m, 2H), 6.84 (dd, *J* = 8.6, 2.9 Hz, 1H), 3.94 (s, 3H), 3.89 (s, 1H), 3.80 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.71, 158.33, 153.83, 150.78, 134.58, 132.66, 130.37, 130.25, 119.64, 116.53, 113.06, 112.72, 111.71, 56.37, 56.16, 55.85, 52.04; HRMS(ESI) calculated *m/z* for $C_{17}H_{18}O_5$ [M + Na]$^+$: 325.1046, found 325.1048.

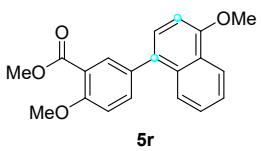
methyl 2',4,4',6'-tetramethoxy-[1,1'-biphenyl]-3-carboxylate (5q)



5q

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 42 mg, 64%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.4 Hz, 1H), 7.46 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 6.24 (s, 2H), 3.95 (s, 3H), 3.89 (d, *J* = 4.7 Hz, 6H), 3.74 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.86, 160.61, 158.44, 157.86, 136.41, 134.67, 125.98, 119.25, 111.46, 111.03, 90.91, 56.04, 55.91, 55.41, 51.88; MS(ESI) calculated *m/z* for $C_{18}H_{20}O_6$ [M + H]$^+$: 333.13, found 333.14.

methyl 2-methoxy-5-(4-methoxynaphthalen-1-yl)benzoate (5r)

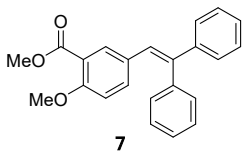


5r

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (5:1), 44 mg, 68%. C-*α*: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, *J* = 2.0 Hz, 1H), 8.19 (d, *J* = 2.4 Hz, 1H), 7.86 (dd, *J* = 8.6, 2.7 Hz, 2H), 7.73 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.45 (d, *J* = 3.8 Hz, 1H),

7.43 (d, *J* = 1.4 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 4.04 (s, 3H), 3.97 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.82, 158.53, 155.64, 137.44, 135.84, 133.73, 132.26, 130.53, 128.16, 125.99, 125.59, 121.29, 119.97, 119.50, 112.52, 104.26, 56.25, 55.55, 52.18. C-*β*: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.48 - 7.45 (m, 1H), 7.40 (d, *J* = 4.7 Hz, 1H), 7.39 (d, *J* = 4.7 Hz, 1H), 7.25 (d, *J* = 1.3 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 3.98 (s, 3H), 3.87 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.93, 157.60, 156.61, 136.42, 133.55, 133.49, 132.03, 129.30, 127.86, 126.06, 125.82, 125.45, 120.37, 118.14, 110.36, 106.17, 56.25, 55.55, 52.18; HRMS(ESI) calculated *m/z* for $C_{20}H_{18}O_4$ $[M + Na]^+$: 345.1103, found 345.1103.

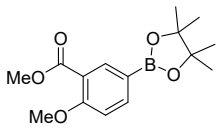
methyl 5-(2,2-diphenylvinyl)-2-methoxybenzoate (7)



7

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (6:1), 43 mg, 62%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 2.4 Hz, 1H), 7.32 - 7.25 (m, 4H), 7.25 - 7.22 (m, 4H), 7.17 - 7.11 (m, 2H), 6.96 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.84 (s, 1H), 6.63 (d, *J* = 8.8 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.41, 157.83, 143.12, 141.90, 140.23, 134.14, 133.29, 130.31, 129.64, 128.85, 128.25, 127.42, 126.47, 119.44, 111.56, 56.00, 51.90; HRMS(ESI) calculated *m/z* for $C_{23}H_{20}O_3$ $[M + Na]^+$: 267.1310, found 267.1309.

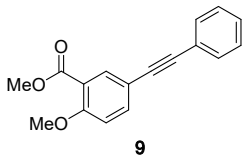
methyl 2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (8)



8

Pale yellow solid, Eluent: petroleum ether/ethyl acetate (6:1), 38 mg, 65%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.8 Hz, 1H), 7.83 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 1.27 (s, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.60, 162.55, 161.46, 140.25, 138.38, 119.63, 111.19, 83.89, 55.94, 51.94, 24.87; HRMS(ESI) calculated *m/z* for $C_{15}H_{21}BO_5$ $[M + Na]^+$: 315,1380, found 315.1381.

methyl 2-methoxy-5-(phenylethynyl)benzoate (9)

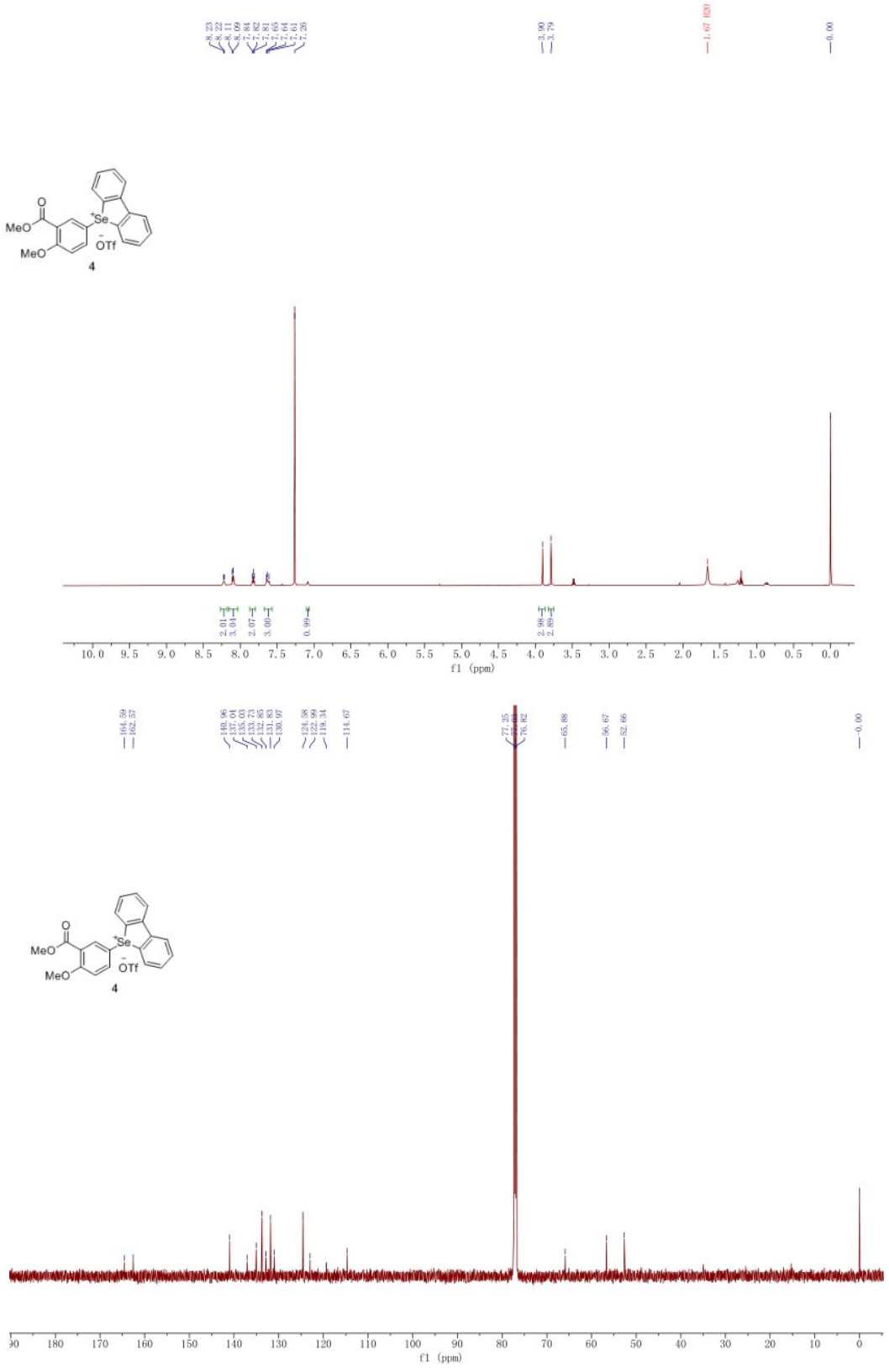


9

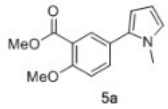
Pale yellow solid, Eluent: petroleum ether/ethyl acetate (7:1), 40 mg, 76%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.3 Hz, 1H), 8.06 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.91 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.59 (d, *J* = 7.1 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 1H), 3.93 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.04, 192.23, 165.31, 163.92, 135.49, 134.95, 134.09, 132.98, 130.04, 129.05, 125.45, 120.84, 112.19, 56.54, 52.37; HRMS(ESI) calculated *m/z* for $C_{17}H_{14}O_3$ $[M + H]^+$: 267.1023, found 267.0659.

6 NMR spectra

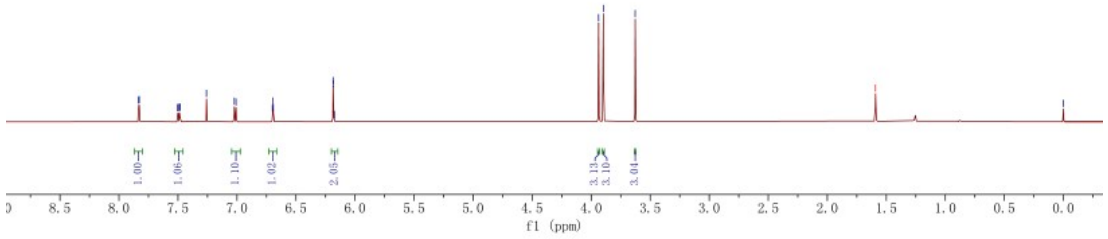
5-(4-Methoxy-3-(methoxycarbonyl) phenyl)-5H-dibenzo [b, d] thiophen-5-ium trifluoromethanesulfonate (4)

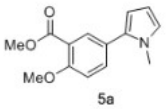


methyl 2-methoxy-5-(1-methyl-1H-pyrrol-2-yl)benzoate (5a)

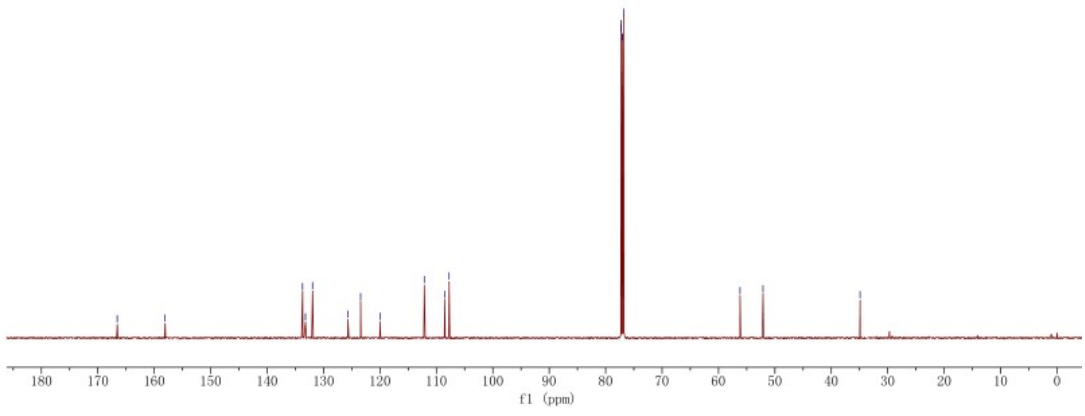


5a

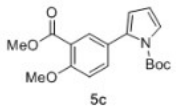




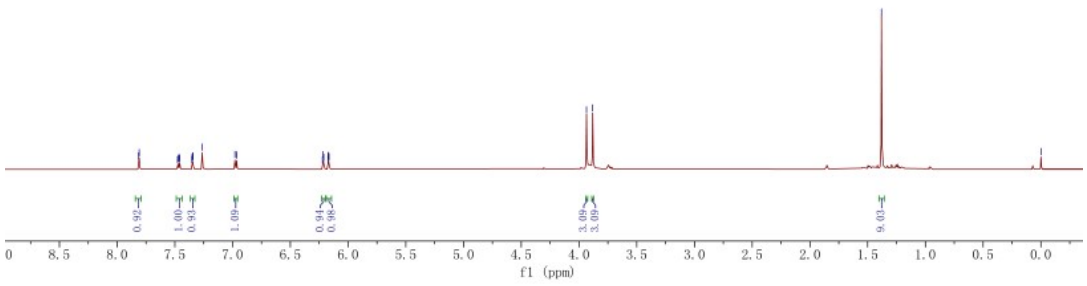
5a

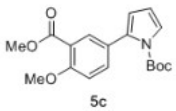


tert-butyl 2-(4-methoxy-3-(methoxycarbonyl)phenyl)-1H-pyrrole-1-carboxylate (5c)

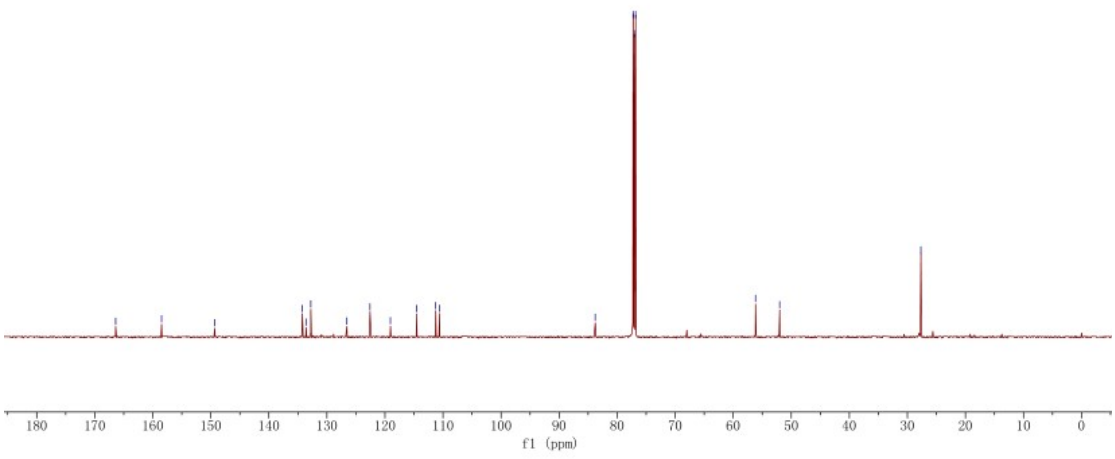


5c

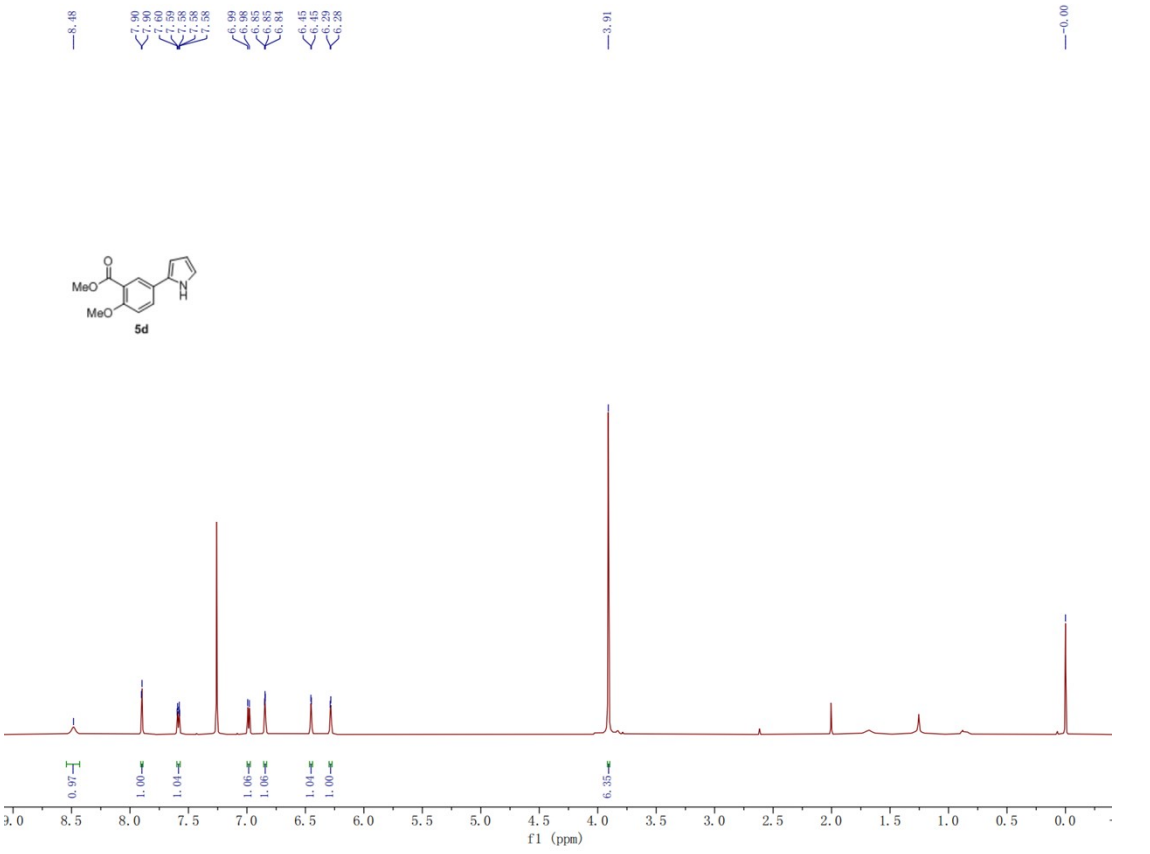


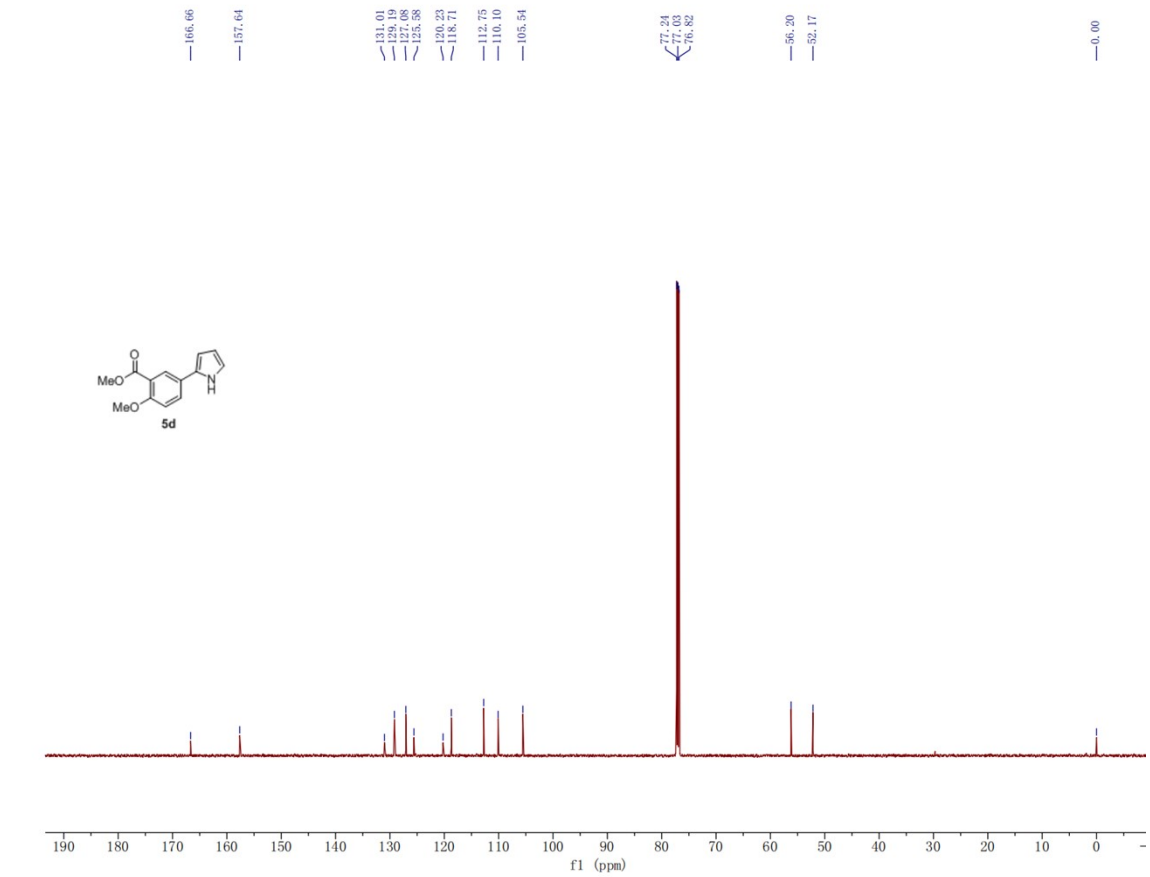


5c

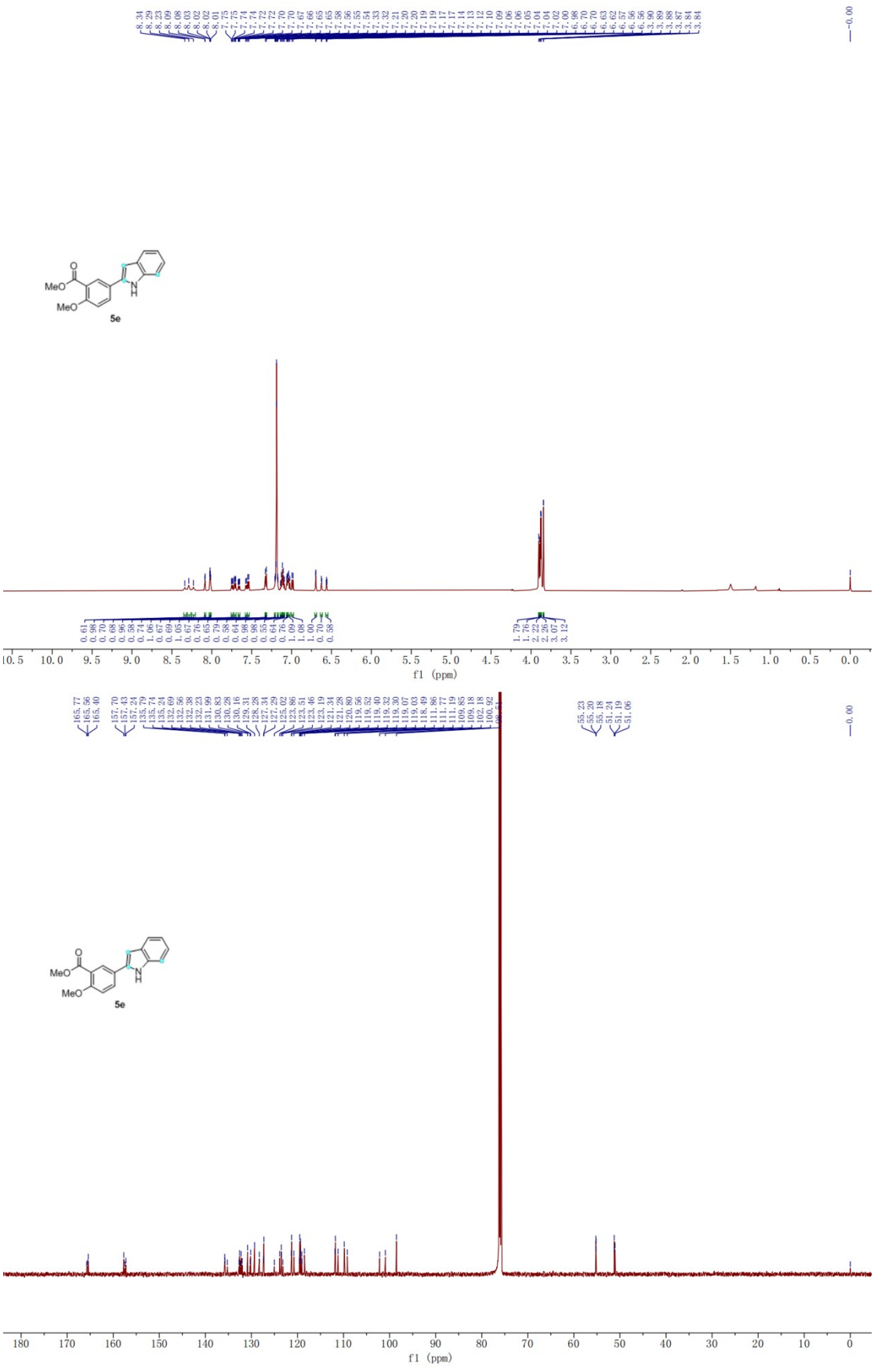


methyl 2-methoxy-5-(1H-pyrrol-2-yl)benzoate (5d)

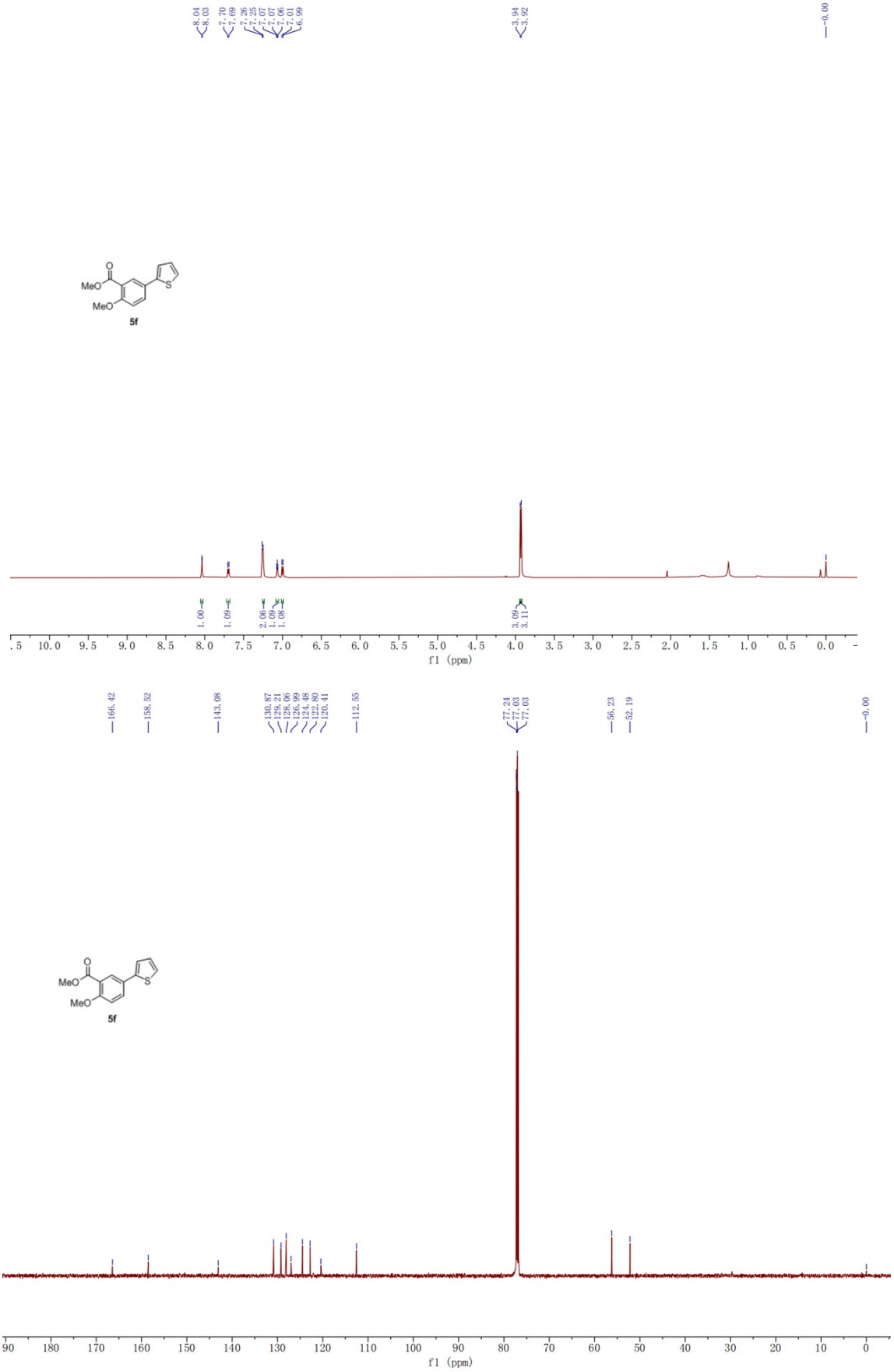




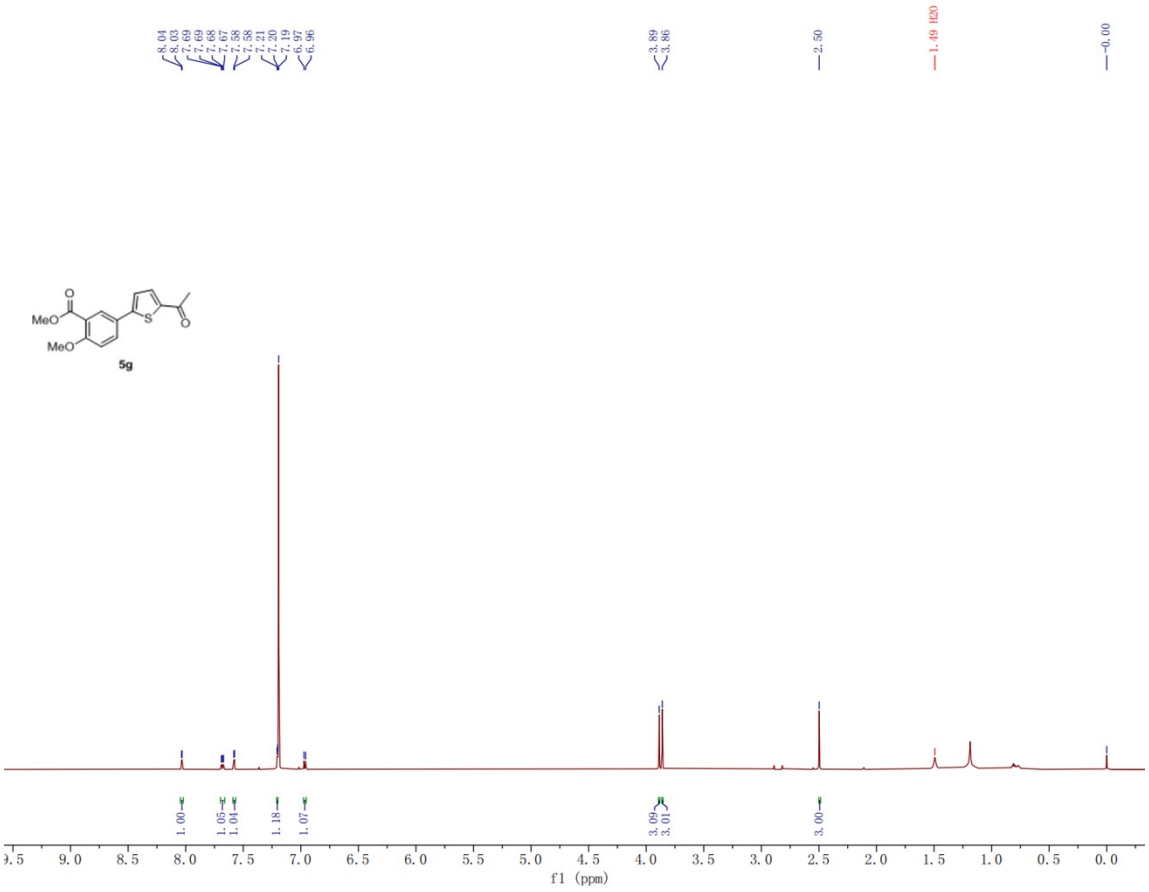
methyl 5-(1H-indol-2-yl)-2-methoxybenzoate (5e) (isomer mixtures, C-2:C-3:C-7=1:0.7:0.6)

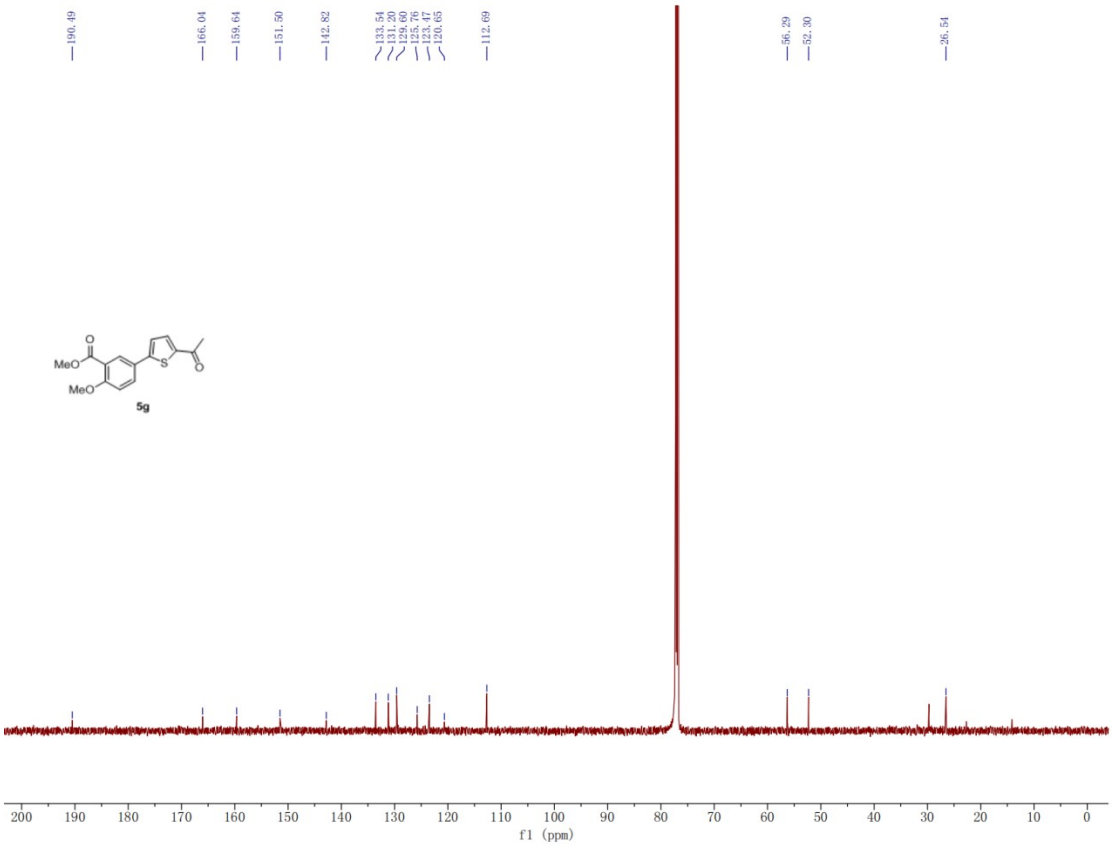


methyl 2-methoxy-5-(thiophen-2-yl)benzoate (5f)

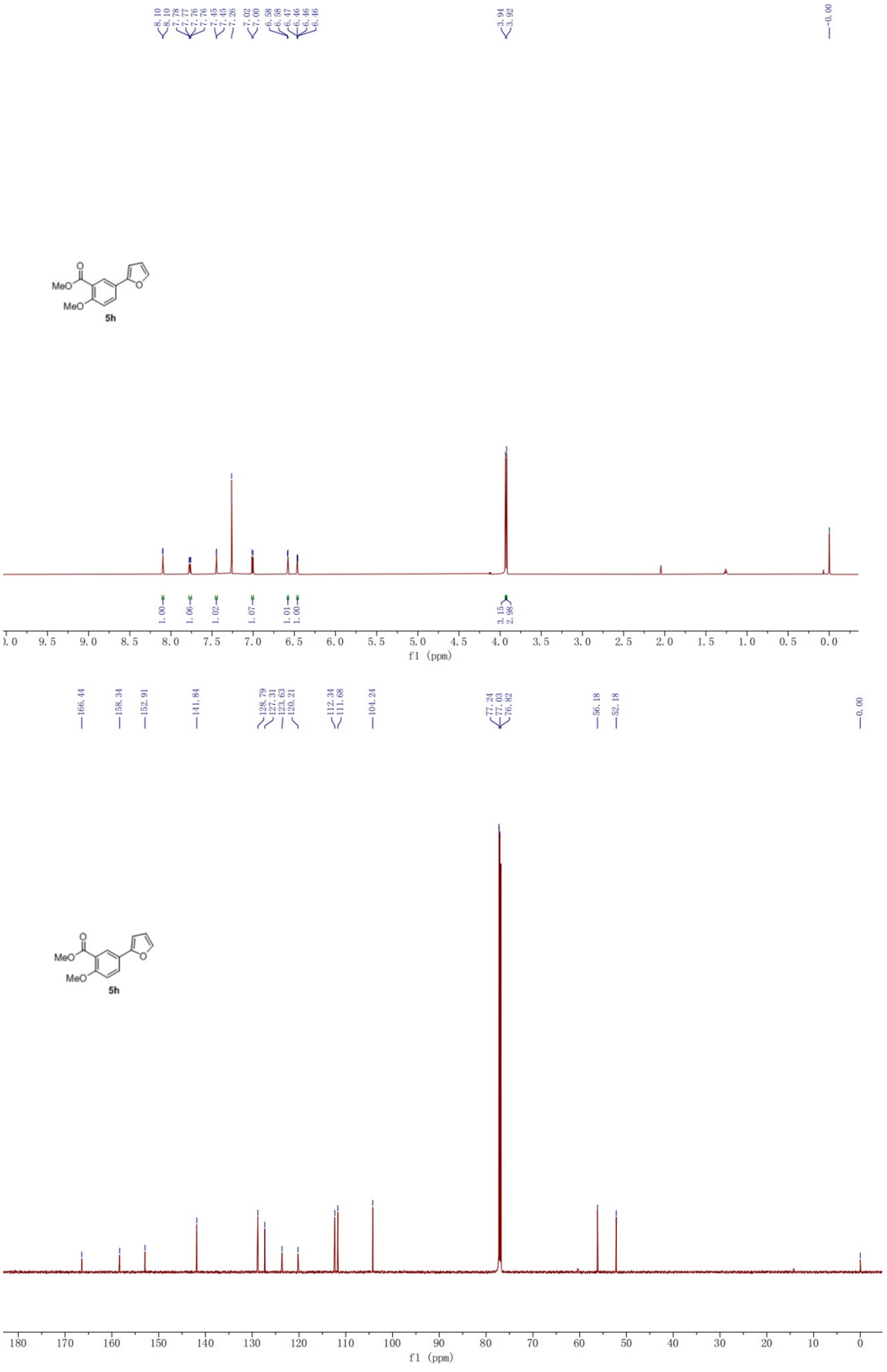


methyl 5-(5-acetylthiophen-2-yl)-2-methoxybenzoate (5g)

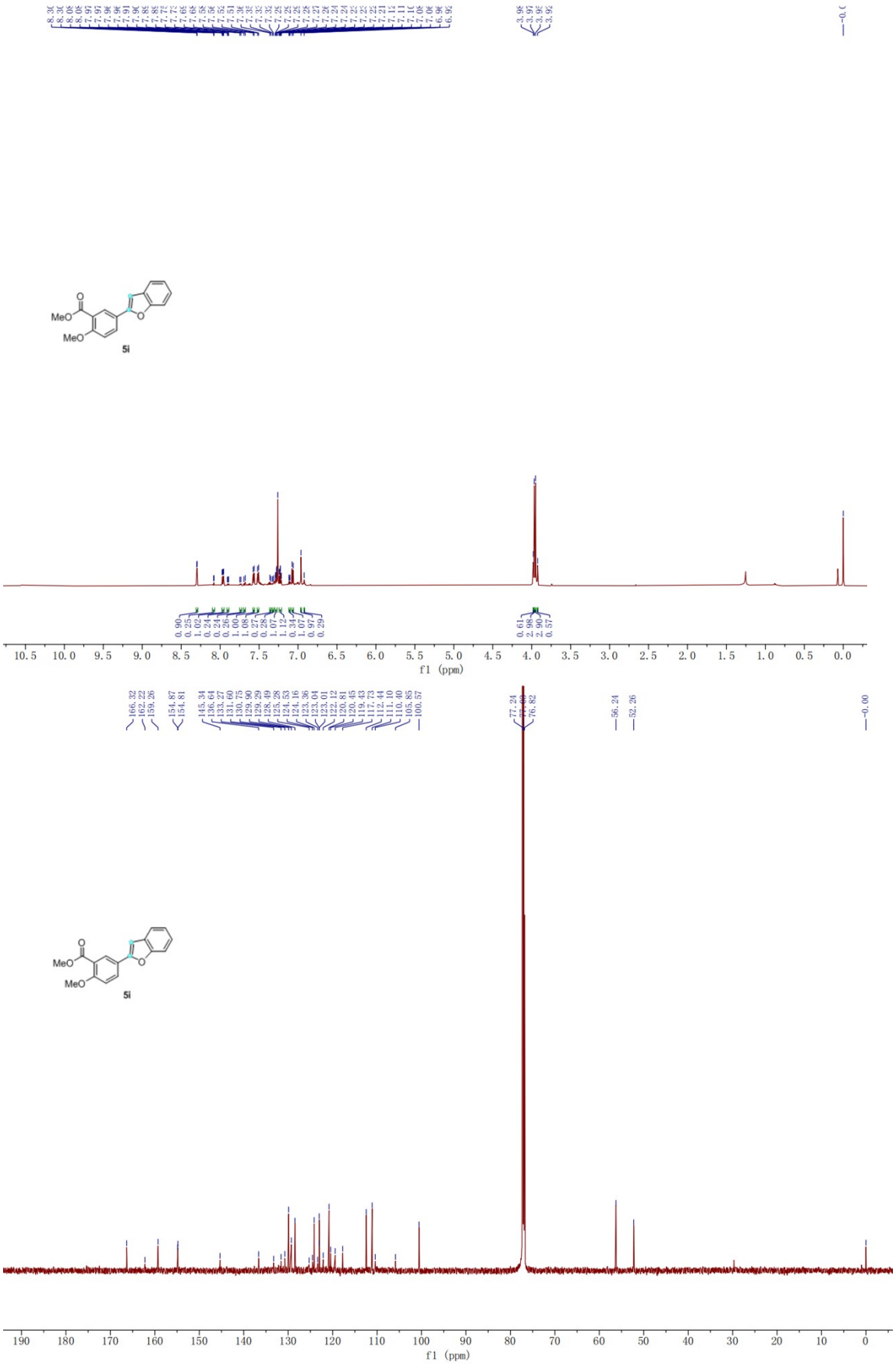




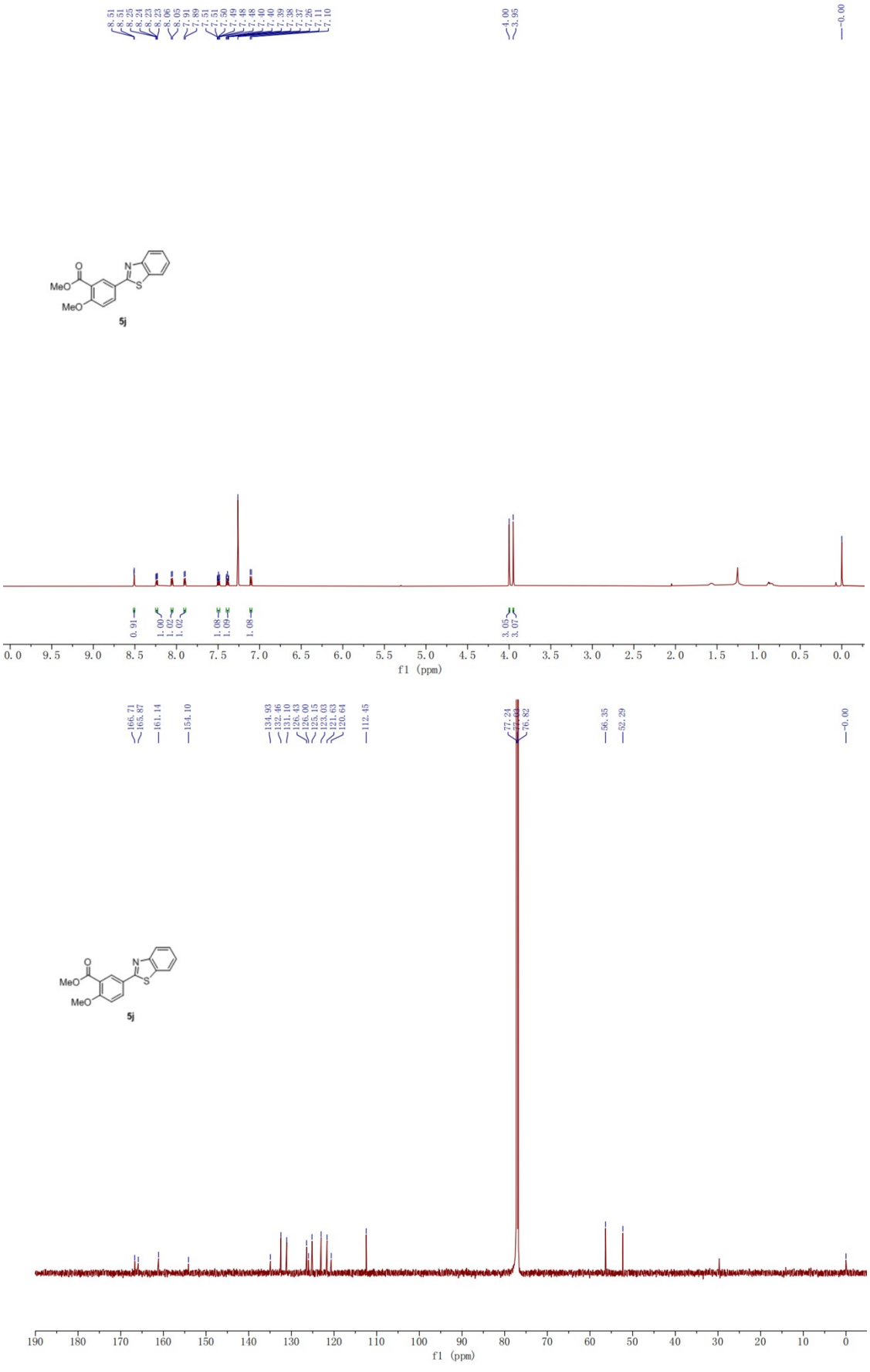
methyl 5-(furan-2-yl)-2-methoxybenzoate (5h)



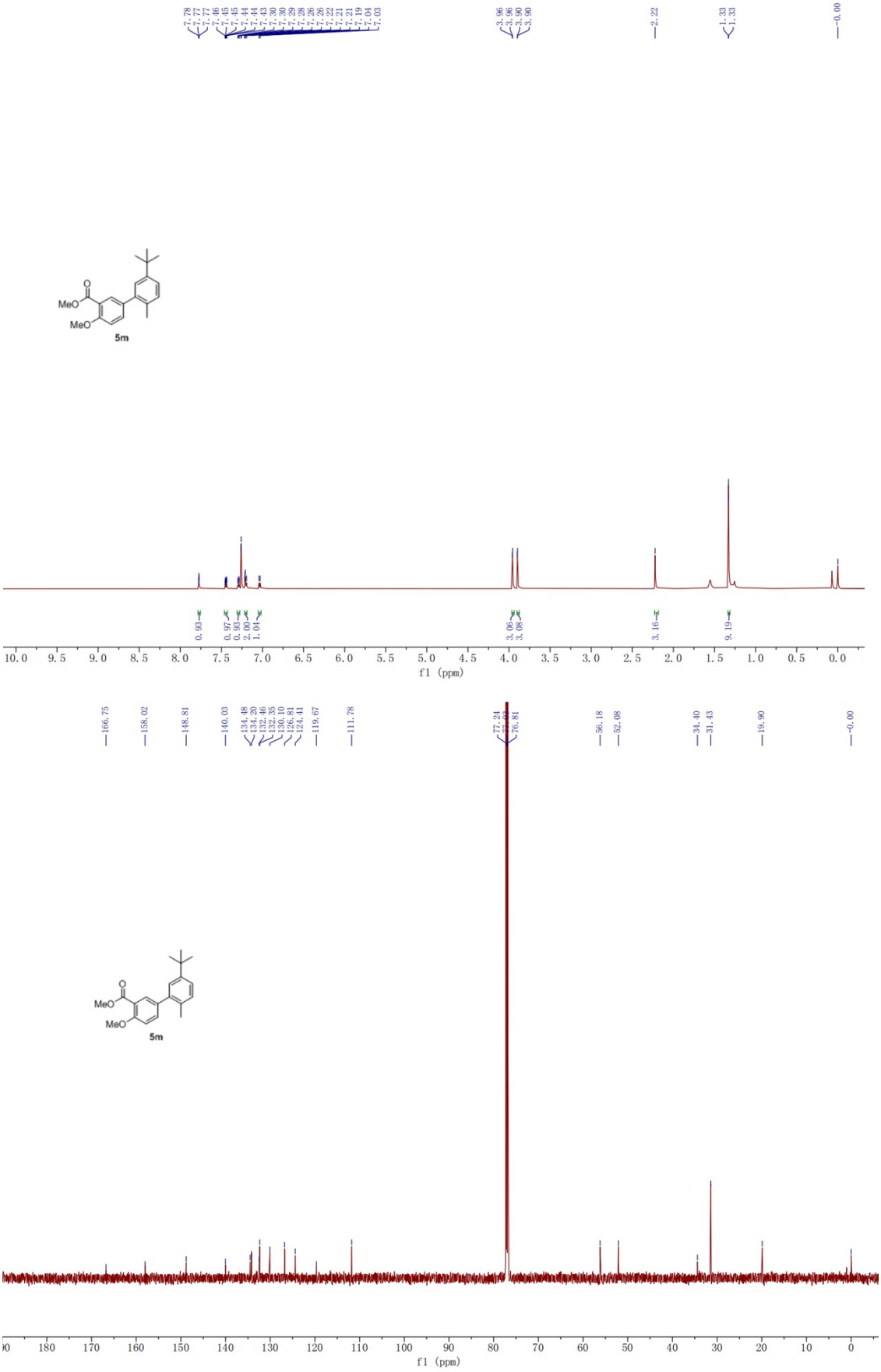
methyl 5-(benzofuran-2-yl)-2-methoxybenzoate (5i) (isomer mixtures, C-2:C-3=5:1)



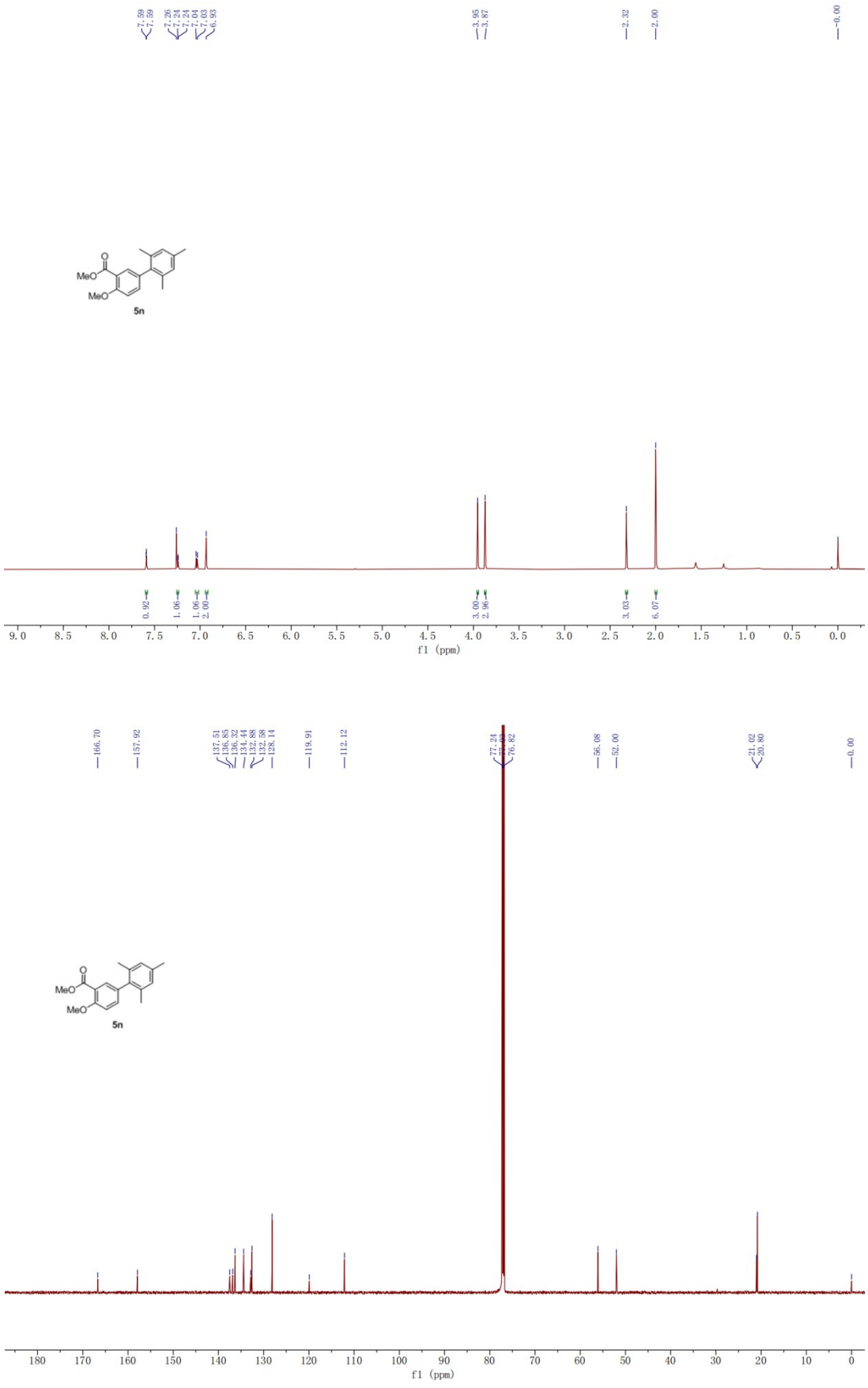
methyl 5-(benzo[d]thiazol-2-yl)-2-methoxybenzoate (5j)



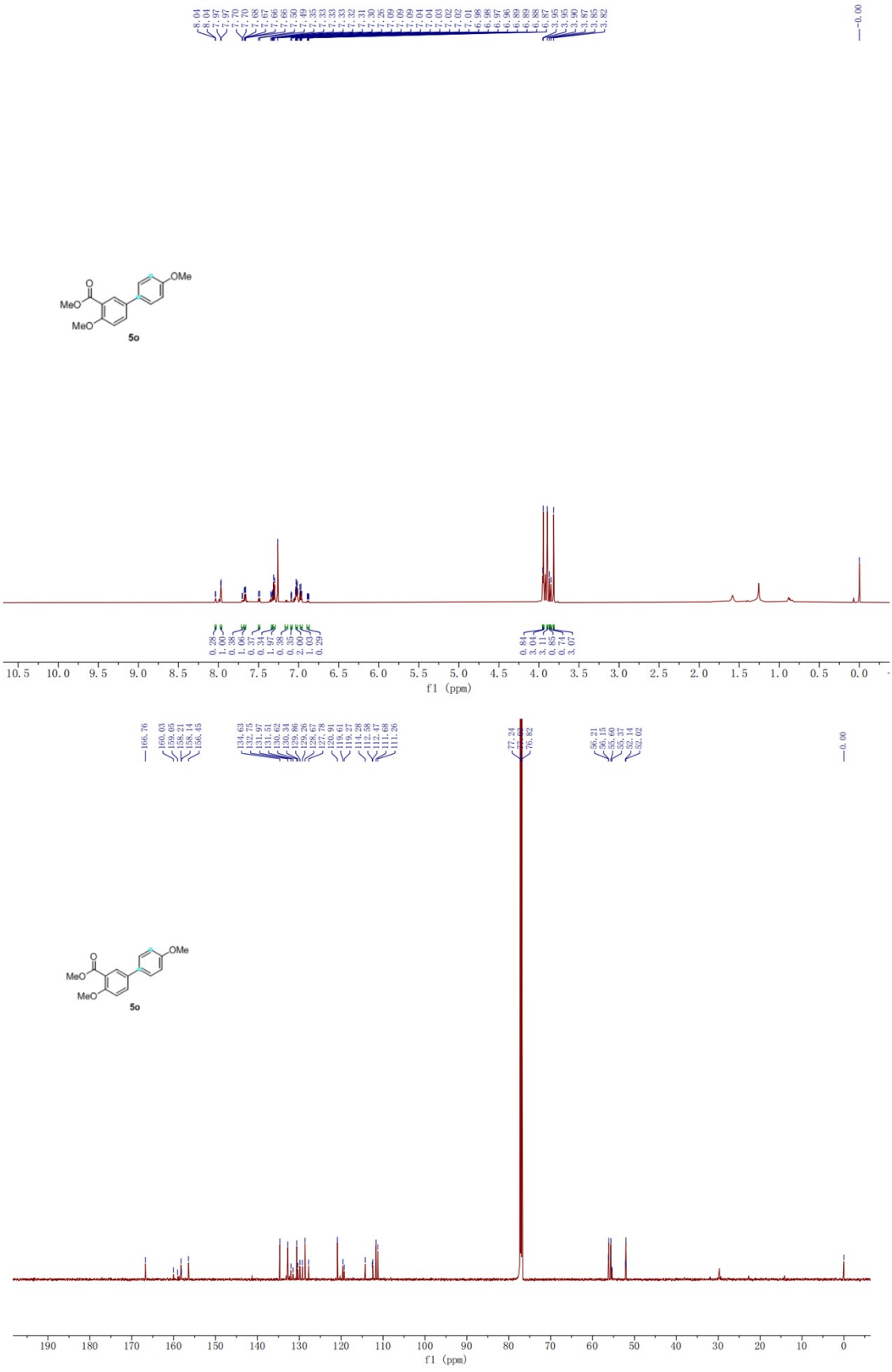
methyl 5'-(tert-butyl)-4-methoxy-2'-methyl-[1,1'-biphenyl]-3-carboxylate (5m)



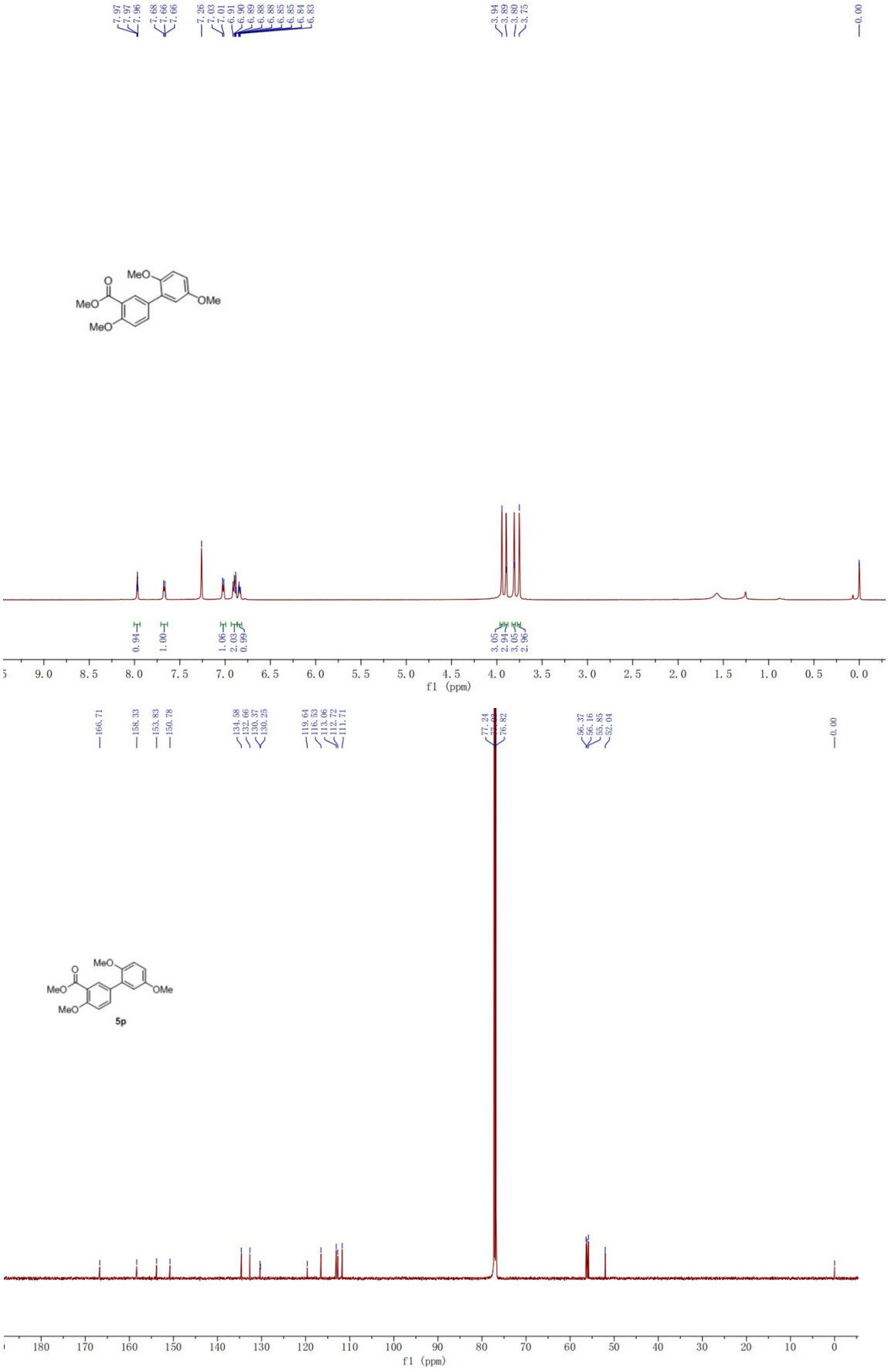
methyl 4-methoxy-2',4',6'-trimethyl-[1,1'-biphenyl]-3-carboxylate (5n)



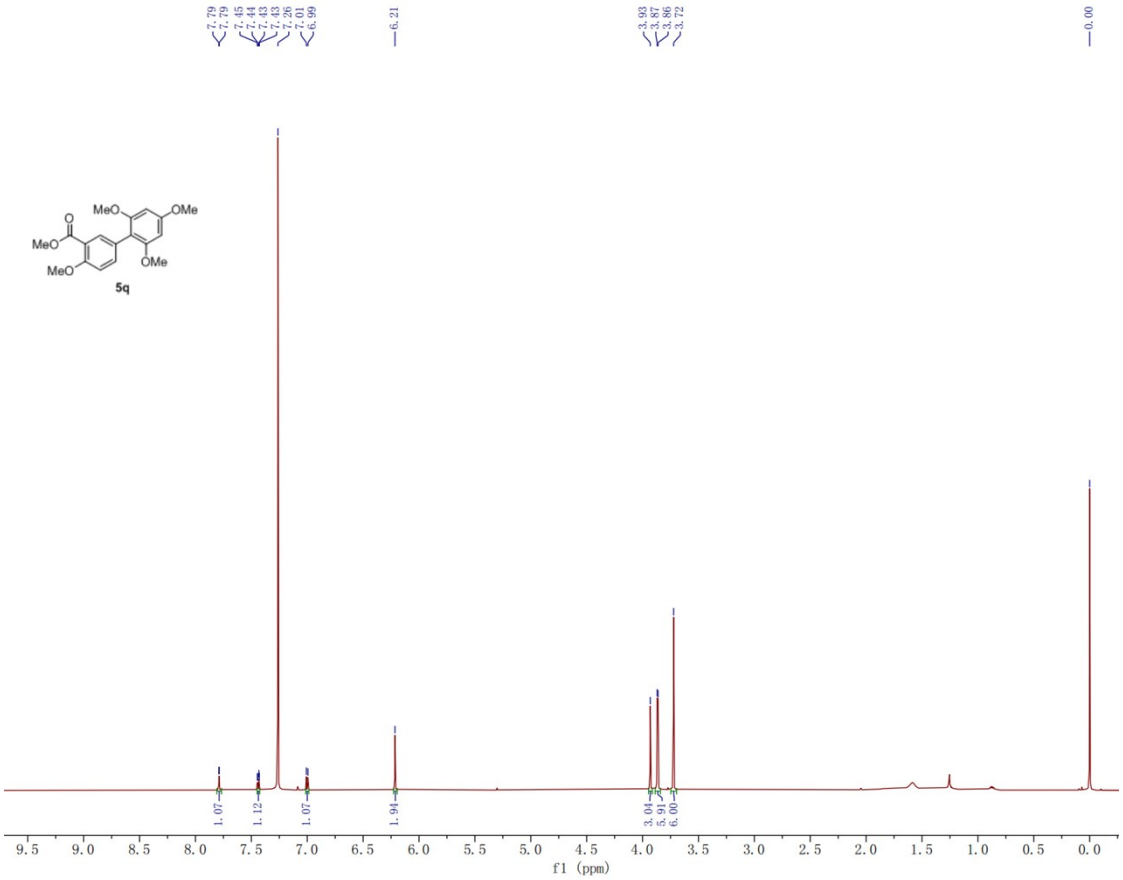
methyl 4,4'-dimethoxy-[1,1'-biphenyl]-3-carboxylate (5o) (isomer mixtures, p:o=3.5:1)

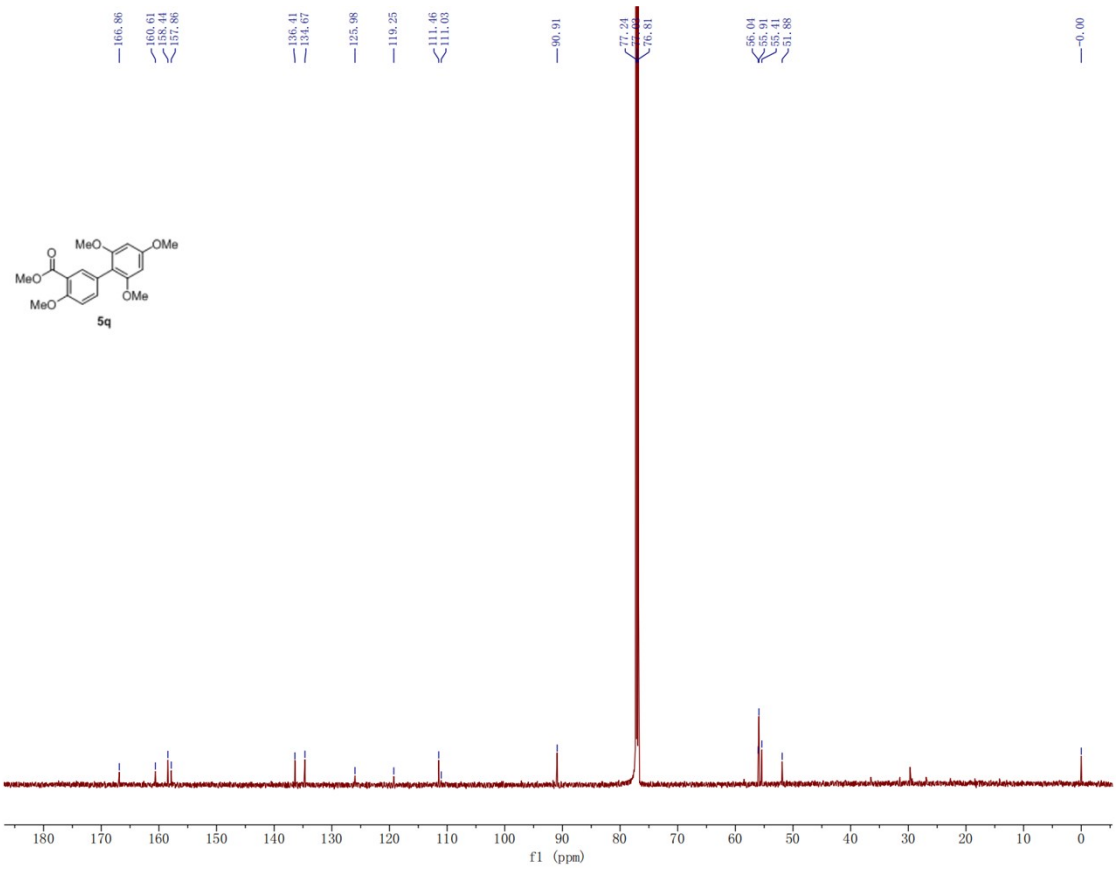


methyl 2',4,5'-trimethoxy-[1,1'-biphenyl]-3-carboxylate (5p)

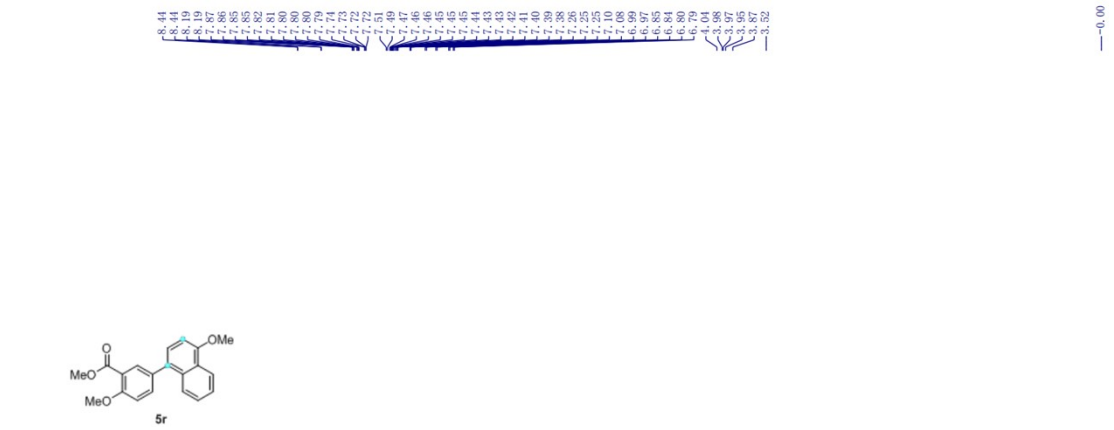


methyl 2',4,4',6'-tetramethoxy-[1,1'-biphenyl]-3-carboxylate (5q)

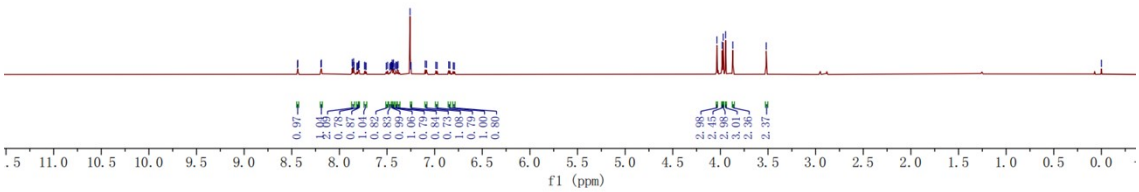


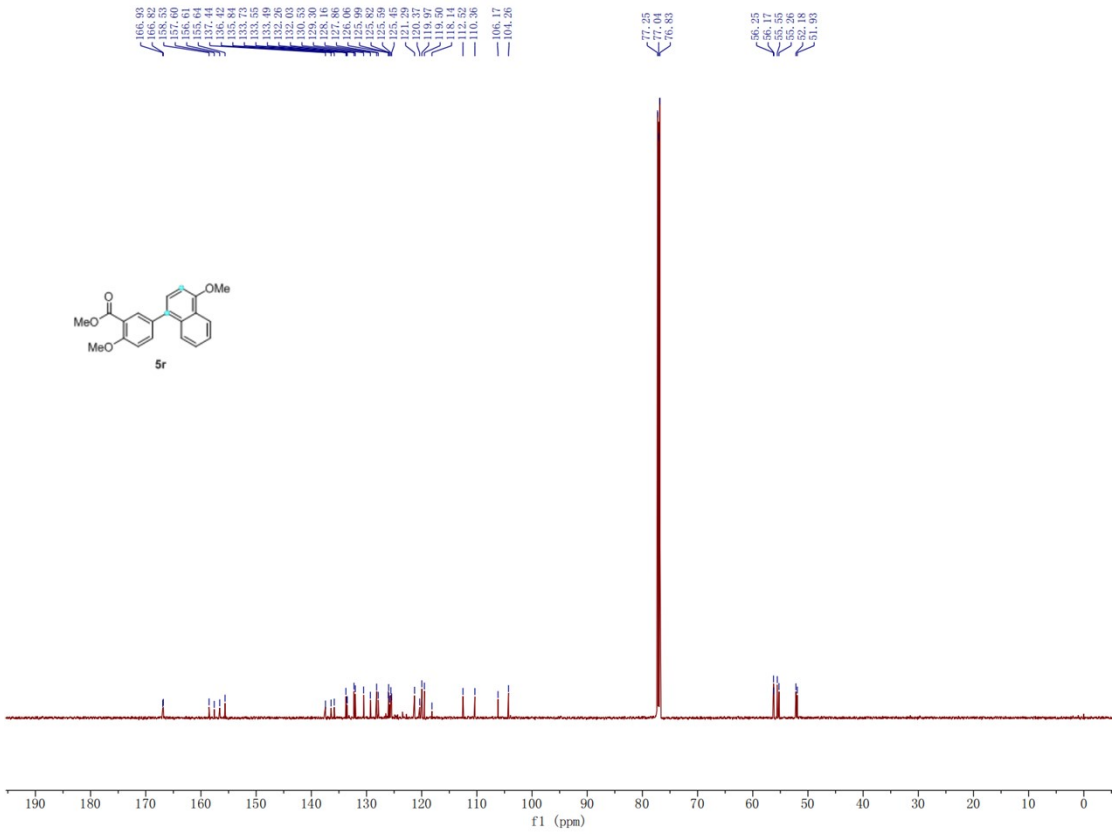


methyl 2-methoxy-5-(4-methoxynaphthalen-1-yl)benzoate (5r) (isomer mixtures, *α*:*β*=1:2)



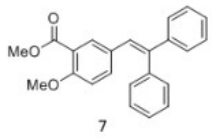
5r

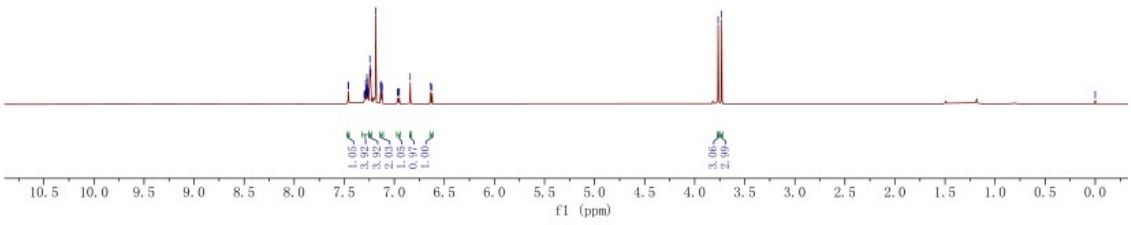


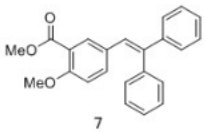


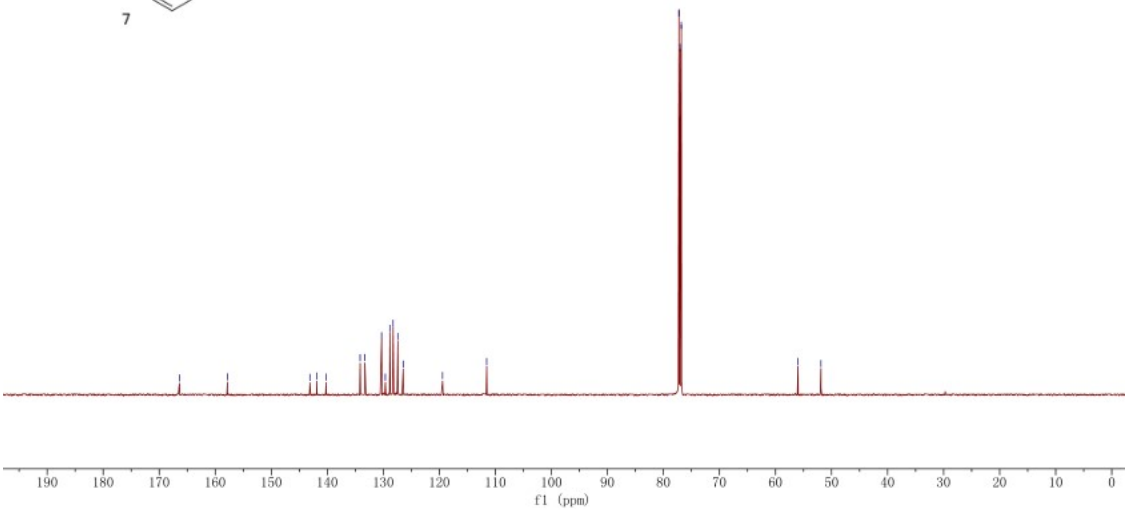
5r

methyl 5-(2,2-diphenylvinyl)-2-methoxybenzoate (7)

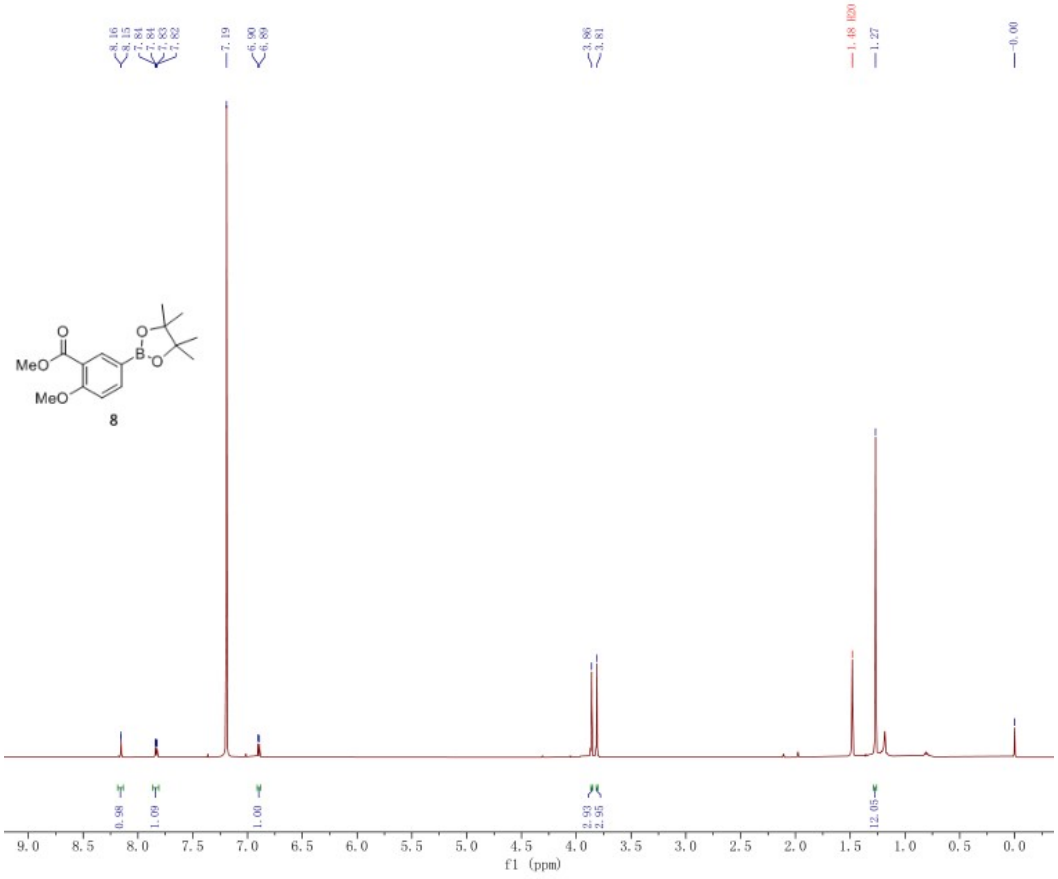


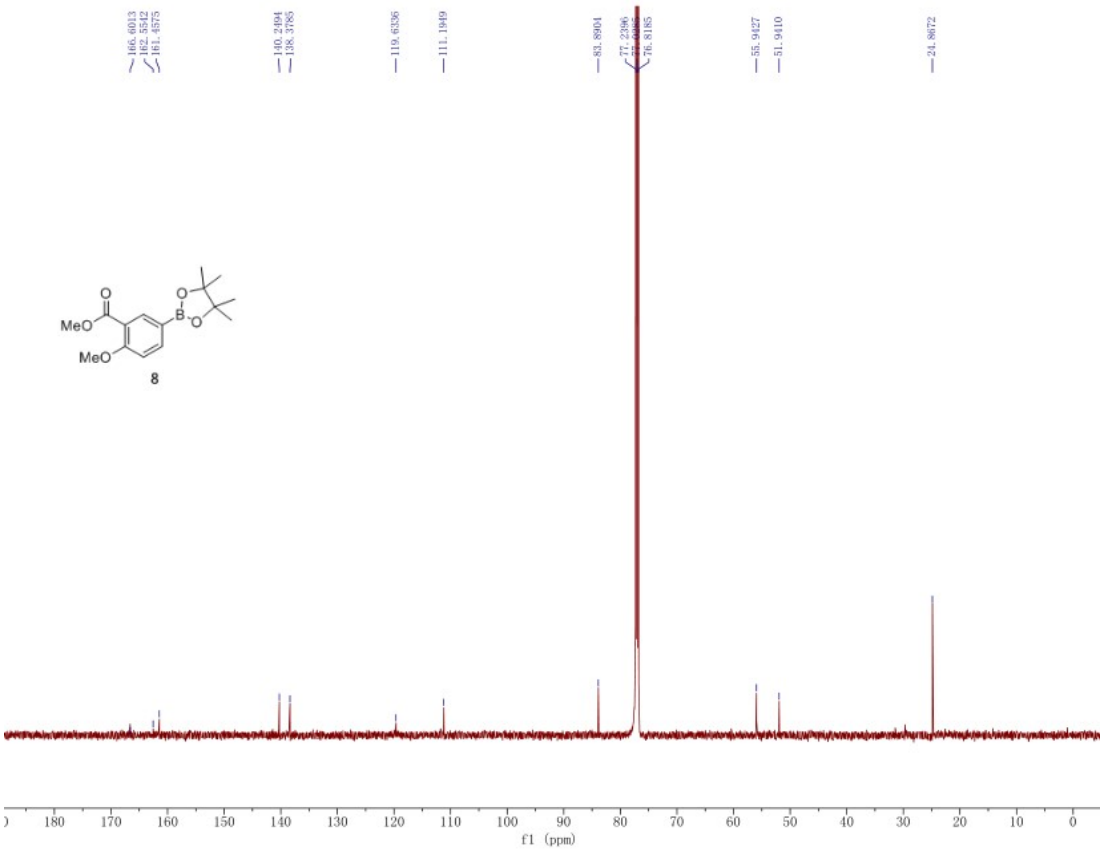




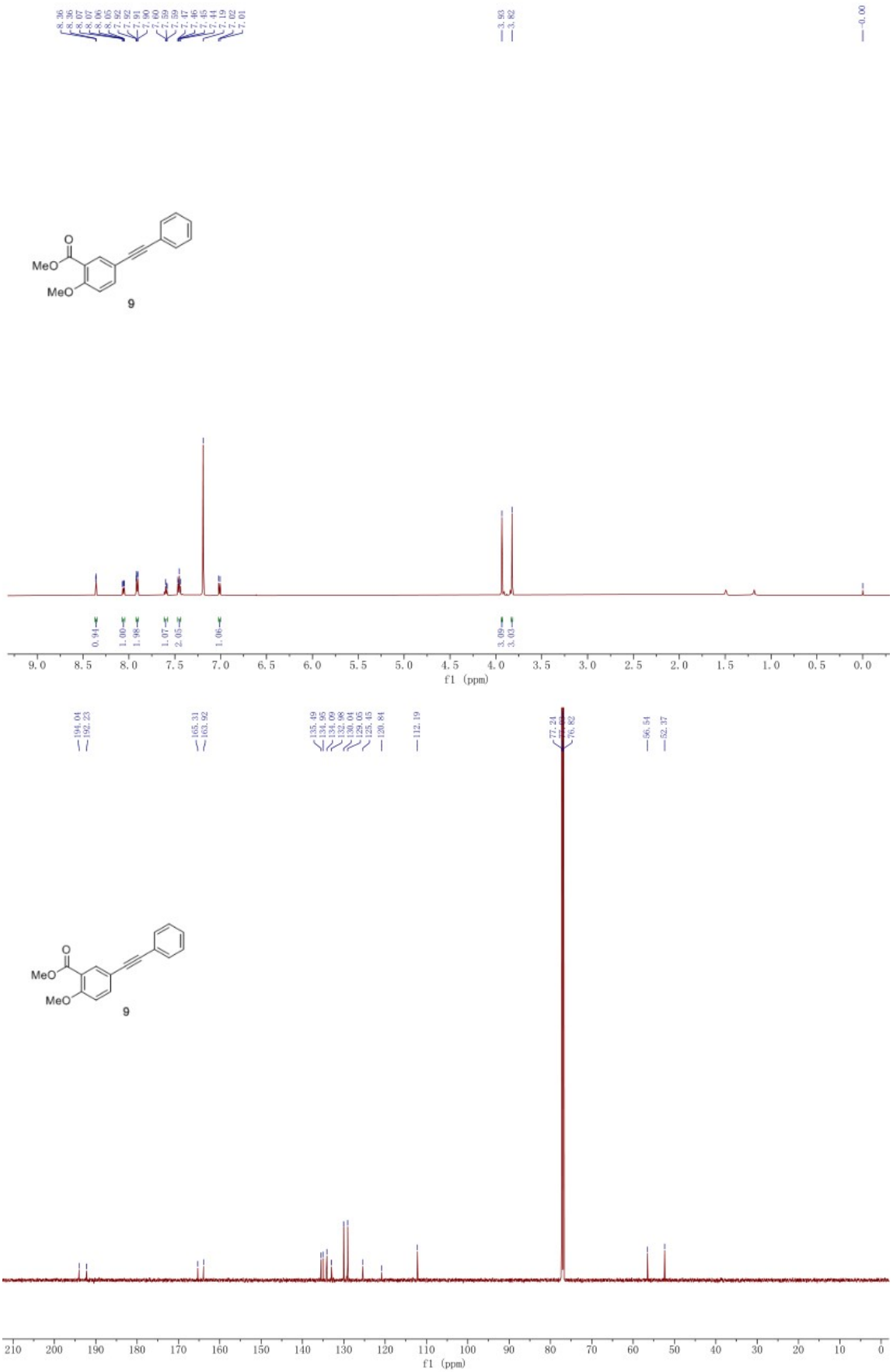


methyl 2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (8)

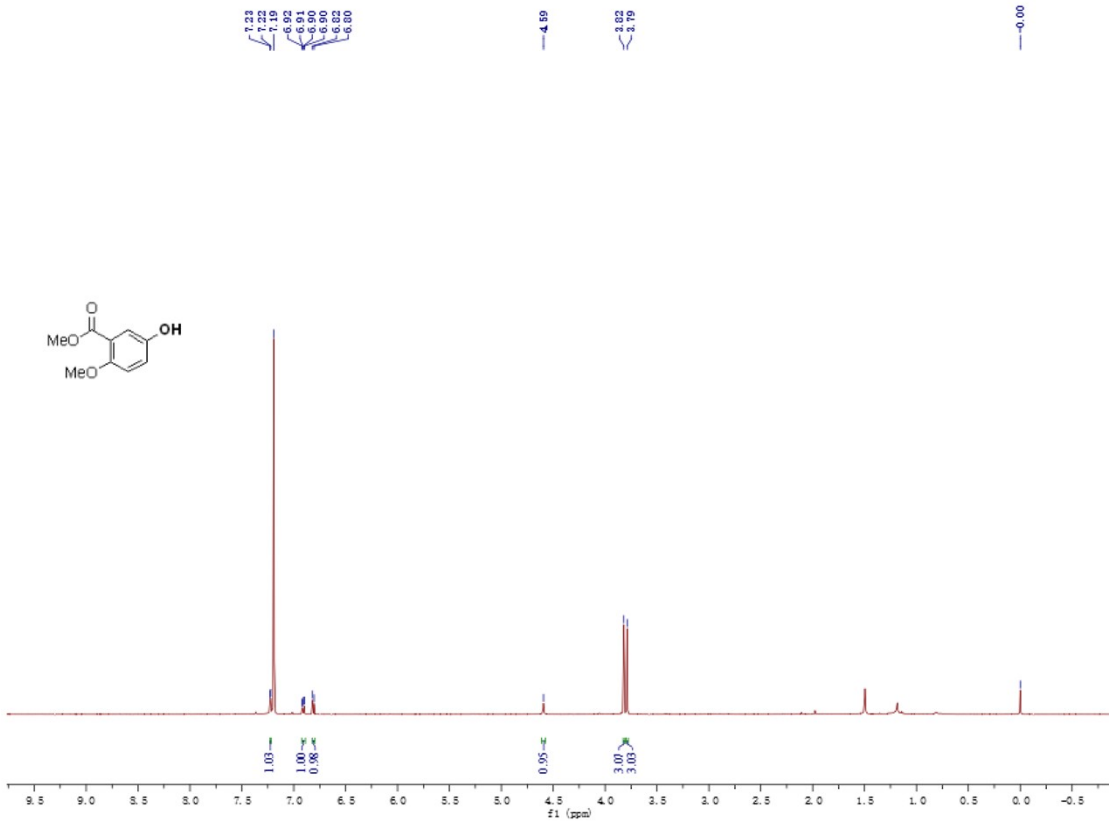




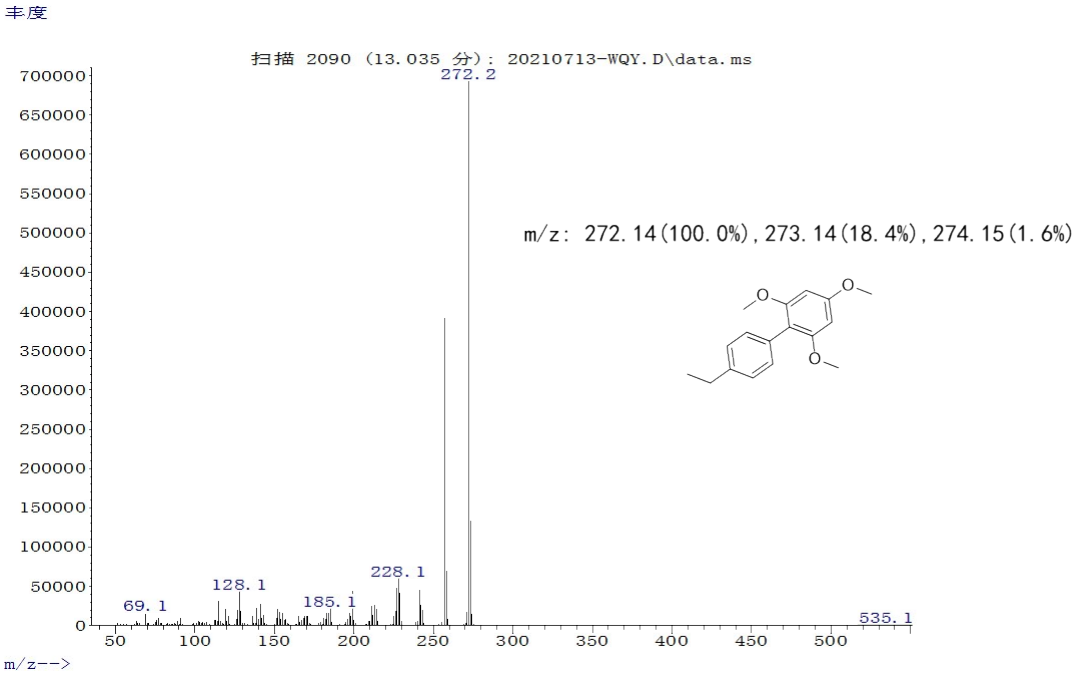
methyl 2-methoxy-5-(phenylethynyl)benzoate (9)



methyl 2-methoxy-5-hydroxybenzoate



GC-MS spectrum of 2-(4-ethylphenyl)-1-methyl-1H-pyrrole



7 Reference

[1] Y. M. Li, C. P. Nie, H. F. Wang, X. Y. Li, F. Verpoort and C. Y. Duan, *Eur. J. Org. Chem.*, 2011, **2011**, 7331-7338.

[2] P. Franzmann, S. B. Beil, D. Schollmeyer and S. R. Waldvogel, *Chem.-Eur. J.*, 2019, **25**, 1936-1940.

[3] R. D. Mcculla and W. S. Jenks, *J. Am. Chem. Soc.*, 2004, **126**, 16058-16065.