Supporting Information

The Chapman Rearrangement in a Continuous-Flow Microreactor

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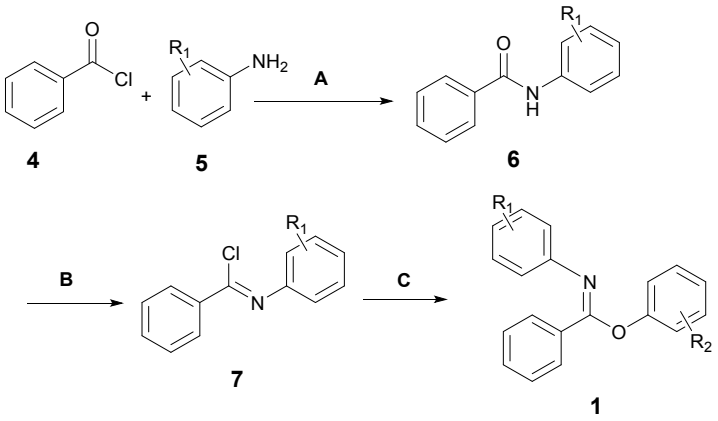
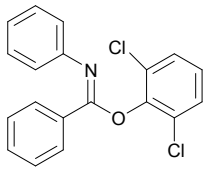
Detailed procedures for preparing the reactants:

The reactants for the Chapman rearrangement used in this work were not commercially available, they were in-house prepared according to Scheme S1. The reagents and solvents involved were purchased from commercial sources and used as received.



Scheme S1. General procedure for preparing the Chapman rearrangement reactants.

2, 6-Dichloro-phenyl-*N*-phenyl benzimidate (1a)



Step A: To a solution of aniline (1.96 g, 21 mmol) in 40 mL dichloromethane was added sodium bicarbonate (1.85 g, 22 mol) and the mixture was cooled down to 0 °C. The benzoyl chloride (2.81 g, 20 mmol) was added dropwise with stirring. After the mixture was warmed to room temperature (r.t.) and it was stirred for 2 hours. Then the reaction was quenched by rapidly adding water (300 mL), and the resulted organic phase were subsequently extracted three times with dichloromethane (30 mL × 3). The combined extracts were washed with brine, and dried over anhydrous Na_2SO_4. Distillation of the product under reduced pressure gave a white solid (6).

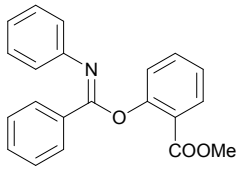
Step B: The compound (6) in thionyl chloride (20 mL) was heated under reflux for 3

hours. The reaction mixture was subject to distillation under reduced pressure. The obtained crude product was dissolved in toluene, and then further distilled under reduced pressure. A slight yellow oil (7) was obtained after repeating this procedure twice.

Step C: To a solution of 2, 6-dichlorophenol (3.26 g, 20 mmol) in 40 mL methanol was added sodium methoxide (1.08 g, 20 mmol). The oil (7) from **Step B** was added dropwise into the mixture. The reaction mixture was stirred for 8 hours at room temperature. Then it was quenched by rapidly adding water (300 mL), and the resulted organic phase was extracted three times with dichloromethane (30 mL x 3). The extract was washed with brine, and dried over anhydrous Na_2SO_4. Distillation of the product under reduced pressure gave a white solid (1a). After recrystallization by methanol, the final while solid product was obtained.

Analytical data: white solid (5.48 g, 16 mmol, isolated yield 80%, purity > 99%); m.p. 72-73 ℃; **1H NMR** (400 MHz, d_6-DMSO) δ 7.72 – 7.45 (m, 5H), 7.45 - 7.38 (m, 2H), 7.37 - 7.25(m, 1H), 7.24 - 7.08 (m, 2H), 7.01 - 6.90 (m, 1H), 6.65 (d, J = 7.7 Hz, 2H); **13C NMR** (100 MHz, d_6-DMSO) δ 145.29, 131.24, 129.10, 129.02, 128.54, 128.31, 127.54, 123.29, 120.49; **HRMS (ESI$^+$)** calcd for $C_{19}H_{14}Cl_2NO$ $[M+H]^+$ = 342.0447, found: 342.0437.

2-Carbomethoxy-phenyl *N*-phenyl benzimidate (1b)



Step A: To a solution of aniline (1.96 g, 21 mmol) in 40 mL dichloromethane was added Sodium bicarbonate (1.85 g, 22 mol) and the mixture was cooled down to 0 °C. The benzoyl chloride (2.81 g, 20 mmol) was added dropwise with stirring. After the mixture was warmed to room temperature (r.t.) and it was stirred for 2 hours. Then the reaction was quenched by rapidly adding water (300 mL), and the resulted organic

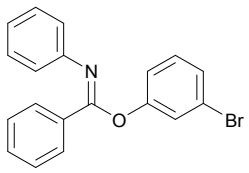
phase were subsequently extracted three times with dichloromethane (30 mL × 3). The combined extracts were washed with brine, and dried over anhydrous Na_2SO_4. Distillation of the product under reduced pressure gave a white solid (6).

Step B: The compound (6) in thionyl chloride (20 mL) was heated under reflux for 3 hours. A slight yellow oil (7) was obtained after the solvent was removed by distillation under reduced pressure.

Step C: To a solution of *o*-carbomethoxyphenol (3.04 g, 20 mmol) in 40 mL methanol was added sodium methoxide (1.08 g, 20 mmol). The oil (7) from **Step B** was added dropwise into the mixture. The reaction mixture was stirred for 8 hours at room temperature. Then it was quenched by rapidly adding water (300 mL), and the resulted organic phase was extracted three times with dichloromethane (30 mL x 3). The extract was washed with brine, and dried over anhydrous Na_2SO_4. Distillation of the product under reduced pressure gave a white solid (1). After recrystallization by methanol, the final while solid product was obtained.

Analytical data: white solid (5.04 g, 15.2 mmol, isolated yield 76%, purity > 99%); **m.p.** 98-99 ℃; **1H NMR** (400 MHz, d_6-DMSO) δ 8.10 - 7.82 (s, 1H), 7.80 - 7.23 (m, 8H), 7.22 - 7.09 (m,2H), 7.01 - 6.86 (m, 1H), 6.59 (s, 2H), 3.83 (s, 3H); **13C NMR** (100 MHz d_6-DMSO) δ δ 165.06(C=O), 134.06, 131.02, 130.73, 129.33, 128.89, 128.25, 128.04, 122.99, 121.80, 120.74, 52.16(OCH_3).; **HRMS (ESI$^+$)** calcd for $C_{21}H_{19}NO_3$ $[M+H]^+ = 332.1281$, found: 332.1282.

3-Bromo-phenyl *N*-phenyl benzimidate (1c)



Step A: To a solution of aniline (1.96 g, 21 mmol) in 40 mL dichloromethane was added Sodium bicarbonate (1.85 g, 22 mol) and the mixture was cooled down to 0 °C. The benzoyl chloride (2.81 g, 20 mmol) was added dropwise with stirring. After the

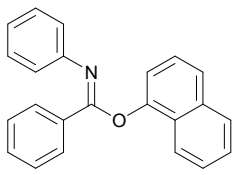
mixture was warmed to room temperature (r.t.) and it was stirred for 2 hours. Then the reaction was quenched by rapidly adding water (300 mL), and the resulted organic phase were subsequently extracted three times with dichloromethane (30 mL × 3). The combined extracts were washed with brine, and dried over anhydrous Na_2SO_4. Distillation of the product under reduced pressure gave a white solid (6).

Step B: The compound (6) in thionyl chloride (20 mL) was heated under reflux for 3 hours. A slight yellow oil (7) was obtained after the solvent was removed by distillation under reduced pressure.

Step C: To a solution of *m*-bromophenol (3.46 g, 20 mmol) in 40 mL methanol was added sodium methoxide (1.08 g, 20 mmol). The oil (7) from **Step B** was added dropwise into the mixture. The reaction mixture was stirred for 8 hours at room temperature. Then it was quenched by rapidly adding water (300 mL), and the resulted organic phase was extracted three times with dichloromethane (30 mL x 3). The extract was washed with brine, and dried over anhydrous Na_2SO_4. Distillation of the product under reduced pressure gave a white solid (1). After recrystallization by methanol, the final while solid product was obtained.

Analytical data: white solid (4.44g, 12.6mmol, isolated yield 63%, purity > 99%); **m.p.** 90.5-91.5 ℃; **1H NMR** (400 MHz, d_6-DMSO) δ 8.32 - 6.31 (m, 14H); **13C NMR** (100 MHz, d_6-DMSO) δ 131.22, 129.13, 128.80, 128.50, 120.96; **HRMS (ESI$^+$)** calcd for $C_{19}H_{15}BrNO$ $[M+H]^+$ = 352.0332, found: 352.0326.

Naphthalen-1-yl-*N*-phenyl benzimidate (1d)



Step A: To a solution of aniline (1.96 g, 21 mmol) in 40 mL dichloromethane was added Sodium bicarbonate (1.85 g, 22 mol) and the mixture was cooled down to 0 °C. The benzoyl chloride (2.81 g, 20 mmol) was added dropwise with stirring. After the

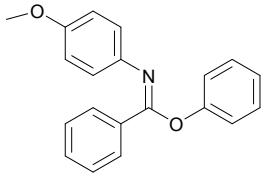
mixture was warmed to room temperature (r.t.) and it was stirred for 2 hours. Then the reaction was quenched by rapidly adding water (300 mL), and the resulted organic phase were subsequently extracted three times with dichloromethane (30 mL × 3). The combined extracts were washed with brine, and dried over anhydrous Na_2SO_4. Distillation of the product under reduced pressure gave a slight yellow solid (6).

Step B: The compound (6) in thionyl chloride (20 mL) was heated under reflux for 3 hours. A slight yellow oil (7) was obtained after the solvent was removed by distillation under reduced pressure.

Step C: To a solution of 1-Naphthol (2.88 g, 20 mmol) in 40 mL methanol was added sodium methoxide (1.08 g, 20 mmol). The oil (7) from **Step B** was added dropwise into the mixture. The reaction mixture was stirred for 8 hours at room temperature. Then it was quenched by rapidly adding water (300 mL), and the resulted organic phase was extracted three times with dichloromethane (30 mL x 3). The extract was washed with brine, and dried over anhydrous Na_2SO_4. Distillation of the product under reduced pressure gave a white solid (1). After recrystallization by methanol, the final while solid product was obtained.

Analytical data: slight yellow solid (3.95g, 12.1 mmol, isolated yield 61%, purity > 99%); **m.p.**82-84 ℃; **1H NMR** (400 MHz, d_6-DMSO) δ 8.70 - 5.78 (m, 17H); **13C NMR** (100 MHz, d_6-DMSO) δ 134.34, 131.32, 128.83, 128.65, 127.99, 126.72, 126.58, 125.86, 121.32, 121.02; **HRMS (ESI$^+$)** calcd for $C_{23}H_{18}NO$ $[M+H]^+$ = 324.1383, found: 324.1372.

Phenyl-*N*-(4-methoxyphenyl)-benzimidate (1e)



Step A: To a solution of *p*-anisidine (2.59 g, 21 mmol) in 40 mL dichloromethane was added Sodium bicarbonate (1.85 g, 22 mol) and the mixture was cooled down to 0 °C.

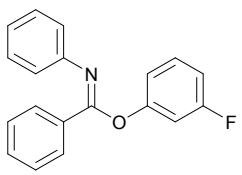
The benzoyl chloride (2.81 g, 20 mmol) was added dropwise with stirring. After the mixture was warmed to room temperature (r.t.) and it was stirred for 2 hours. Then the reaction was quenched by rapidly adding water (300 mL), and the resulted organic phase were subsequently extracted three times with dichloromethane (30 mL × 3). The combined extracts were washed with brine, and dried over anhydrous Na_2SO_4. Distillation of the product under reduced pressure gave a white solid (6).

Step B: The compound (6) in thionyl chloride (20 mL) was heated under reflux for 3 hours. A slight yellow oil (7) was obtained after the solvent was removed by distillation under reduced pressure.

Step C: To a solution of phenol (1.88 g, 20 mmol) in 40 mL methanol was added sodium methoxide (1.08 g, 20 mmol). The oil (7) from **Step B** was added dropwise into the mixture. The reaction mixture was stirred for 8 hours at room temperature. Then it was quenched by rapidly adding water (300 mL), and the resulted organic phase was extracted three times with dichloromethane (30 mL x 3). The extract was washed with brine, and dried over anhydrous Na_2SO_4. Distillation of the product under reduced pressure gave a white solid (1). After recrystallization by methanol, the final while solid product was obtained.

Analytical data: white solid (4.97g, 16.4mmol, isolated yield 82%, purity > 99%); **m.p.** 93.7-95 ℃; **1H NMR** (400 MHz, d_6-DMSO) δ 7.88 (s, 1H), 7.72 - 6.34 (m, 13H), 3.70 (s, 3H); **13C NMR** (100 MHz, d_6-DMSO) δ 131.32, 129.98, 128.83, 128.68, 123.88, 122.98, 122.22, 116.76, 114.09, 109.57, 55.15(OCH_3); **HRMS (ESI$^+$)** calcd for $C_{20}H_{18}NO$ $[M+H]^+$ = 304.1332, found: 304.1332.

3-Fluorophenyl-*N*-phenyl-benzimidate (1f)



Step A: To a solution of aniline (1.96 g, 21 mmol) in 40 mL dichloromethane was

added Sodium bicarbonate (1.85 g, 22 mol) and the mixture was cooled down to 0 °C. The benzoyl chloride (2.81 g, 20 mmol) was added dropwise with stirring. After the mixture was warmed to room temperature (r.t.) and it was stirred for 2 hours. Then the reaction was quenched by rapidly adding water (300 mL), and the resulted organic phase were subsequently extracted three times with dichloromethane (30 mL × 3). The combined extracts were washed with brine, and dried over anhydrous Na_2SO_4. Distillation of the product under reduced pressure gave a white solid (6).

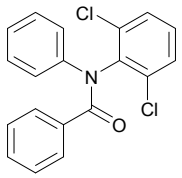
Step B: The compound (6) in thionyl chloride (20 mL) was heated under reflux for 3 hours. A slight yellow oil (7) was obtained after the solvent was removed by distillation under reduced pressure.

Step C: To a solution of *m*-fluorophenol (2.24 g, 20 mmol) in 40 mL methanol was added sodium methoxide (1.08 g, 20 mmol). The oil (7) from **Step B** was added dropwise into the mixture. The reaction mixture was stirred for 8 hours at room temperature. Then it was quenched by rapidly adding water (300 mL), and the resulted organic phase was extracted three times with dichloromethane (30 mL x 3). The extract was washed with brine, and dried over anhydrous Na_2SO_4. Distillation of the product under reduced pressure gave a white solid (1). After recrystallization by methanol, the final white solid product was obtained.

Analytical data: white solid (2.80 g, 9.6 mmol, isolated yield 48%, purity > 99%); **m.p.** 62-63 ℃; **1H NMR** (400 MHz d_6-DMSO) δ 8.38 - 6.24 (m, 14H); **13C NMR** (100 MHz, d_6-DMSO) δ 130.88, 129.20, 128.88, 128.61, 121.14; **HRMS (ESI$^+$)** calcd for $C_{19}H_{15}FNO$ $[M+H]^+$ =292.1132, found: 292.1132.

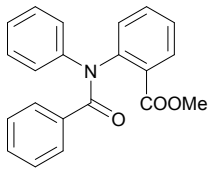
Analytical data of the Chapman rearrangement products:

***N*-(2, 6-dichlorophenyl)-*N*-phenylbenzamide (2a)**



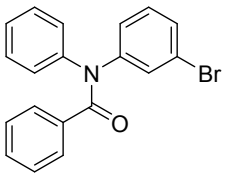
Analytical data: white solid (83mg, 0.243mmol, isolated yield 81%); ***m.p.***131-132 ℃; **1H NMR** (400 MHz, d_6-DMSO) δ 7.68 (d, J = 8.0 Hz, 1H), 7.60 - 7.08 (m,11H), 7.01 (d, J = 7.6 Hz, 1H); **13C NMR** (100 MHz, d_6-DMSO) δ 169.70 (C=O), 168.87, 141.26, 140.24, 137.88, 135.83, 134.58, 134.46, 130.97, 130.87, 130.74, 129.70, 129.51, 128.94, 128.88, 128.24, 127.92, 127.09, 126.26, 126.16, 126.06, 125.15. **HRMS** (**ESI$^+$**) calcd for $C_{19}H_{14}Cl_2NO$ $[M+H]^+$ = 342.0447, found: 342.0438.

***N*-(2-carbomethoxy-phenyl)-*N*-phenylbenzamide (2b)**



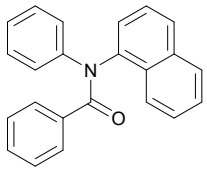
Analytical data: white solid (82 mg, 0.247 mmol, isolated yield 82.8%); ***m.p.***131 - 132 ℃; **1H NMR** (400 MHz, d_6-DMSO) δ 7.84 (s, 1H), 7.65 - 7.52 (m, 1H), 7.48 - 7.05 (m, 12H), 3.71 (s, 3H, OCH_3); **13C NMR** (100 MHz, d_6-DMSO) δ 169.46(C=O), 165.91(C=O), 143.49, 142.79, 136.07, 133.32, 130.68, 130.02, 129.03, 128.52, 127.83, 127.19, 126.41, 52.33 (OCH_3). **HRMS** (**ESI$^+$**) calcd for $C_{21}H_{19}NO_3$ $[M+H]^+$= 332.1281, found: 332.1277

***N*-(3-bromophenyl)-*N*-phenylbenzamide (2c)**



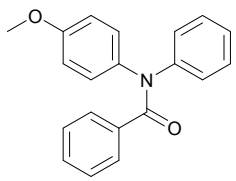
Analytical data: white solid (78 mg, 0.221 mmol, isolated yield 73.8%); ***m.p.*** 150-151°C; **1H NMR** (400 MHz, d_6-DMSO) δ 6.90-7.70 (m, 14H); **13C NMR** (100 MHz, d_6-DMSO) δ 169.76, (C=O) 145.16, 143.22, 135.99, 130.91, 130.28, 130.08, 129.31, 128.59, 128.10, 127.91, 126.90, 126.69, 121.45; **HRMS** (**ESI**$^+$) calcd for $C_{19}H_{15}BrNO$ $[M+H]^+$ = 352.0332, found: 352.0341.

***N*-(1-naphthalen)-*N*-phenylbenzamide (2d)**



Analytical data: white solid (65.3 mg, 0.202 mmol, isolated yield 67.4%); ***m.p.*** 149-150 °C; **1H NMR** (400 MHz, d_6-DMSO) δ 8.14 (d, J = 8.2 Hz, 1H), 7.94 (dd, J = 33.9, 7.5 Hz, 2H), 7.70 - 7.38 (m, 6H), 7.38-7.04 (m, 8H); **13C NMR** (100 MHz, d_6-DMSO) δ 134.13, 130.05, 129.81, 128.91, 128.44, 128.09, 128.02, 127.79, 127.25, 126.37, 125.98, 125.80, 122.87, 109.49; **HRMS** (**ESI**$^+$) calcd for $C_{23}H_{18}NO$ $[M^+H]^+$ = 324.1383, found: 324.1380.

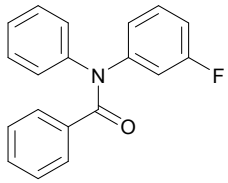
***N*-(4-methoxyphenyl)-*N*-phenylbenzamide (2e)**



Analytical data: white solid (60mg, 19.77mmol, isolated yield 65.9%); ***m.p.*** 119-120 °C; **1H NMR** (400 MHz d_6-DMSO) δ 7.46-7.38 (m, 2H), 7.35 - 7.12 (m,10H), 6.87 (d, J = 8.8 Hz, 2H), 3.71 (s, 3H, OCH_3); **13C NMR** (100 MHz, d_6-DMSO) δ 169.77 (C=O),

157.62, 144.00, 136.61, 136.52, 129.76, 129.18, 129.06, 128.52, 127.87, 127.42, 126.25, 114.40, 55.32 (OCH_3). **HRMS** (**ESI**$^+$) calcd for $C_{20}H_{18}NO$ $[M+H]^+$ = 304.1332, found: 304.1331.

***N*-(3-fluorophenyl)-*N*-phenylbenzamide (2f)**



Analytical data: white solid (47mg, 0.161mmol, isolated yield 53.8%); ***m.p.*** 124-125 °C; **1H NMR** (400 MHz, d_6-DMSO) δ 7.42-7.50 (d, *J* = 3.2Hz, 2H), 7.14 - 7.42 (m, 10H), 7.13 - 7.00 (m, 2H); **13C NMR** (100 MHz, d_6-DMSO) δ 169.74(C=O), 163.26, 160.83, 145.34, 145.24, 143.28, 136.10, 130.64, 130.55, 130.09, 129.28, 128.58, 127.99, 127.91, 126.85, 123.74, 114.96, 114.73, 113.47, 113.27; **HRMS** (**ESI**$^+$) calcd for $C_{19}H_{15}FNO$ $[M+H]^+$ =292.1132, found: 292.1129.

Numerical details for CFD simulations:

The length-to-diameter ratios (i.e., aspect ratios) of the microreactors MR1 and MR2 are 1547.62 and 943.02, respectively. To avoid excessive amounts of elements nodes, the models were scaled by a factor of 200 for both MR1 and MR2.

Initial Conditions & Boundary Conditions

(1) **Initial conditions**

The velocity field, reactant concentration and temperature were assumed as uniformly distributed in the microreactor at t=0 minute with $\boldsymbol{u}$=0 m·s^{-1}, C_r=0 mol·L^{-1} and T =298.15 K.

(2) **Boundary conditions**

(2.1) at the inlet:

The uniform and constant distributions of $\boldsymbol{u}$, T and C_r were imposed at the inlet.

(2.2) at the outlet:

Ambient pressure was used as the velocity field outlet conditions. Zero normal gradients were specified for all other variables at the outlet boundary.

(2.3) at the wall:

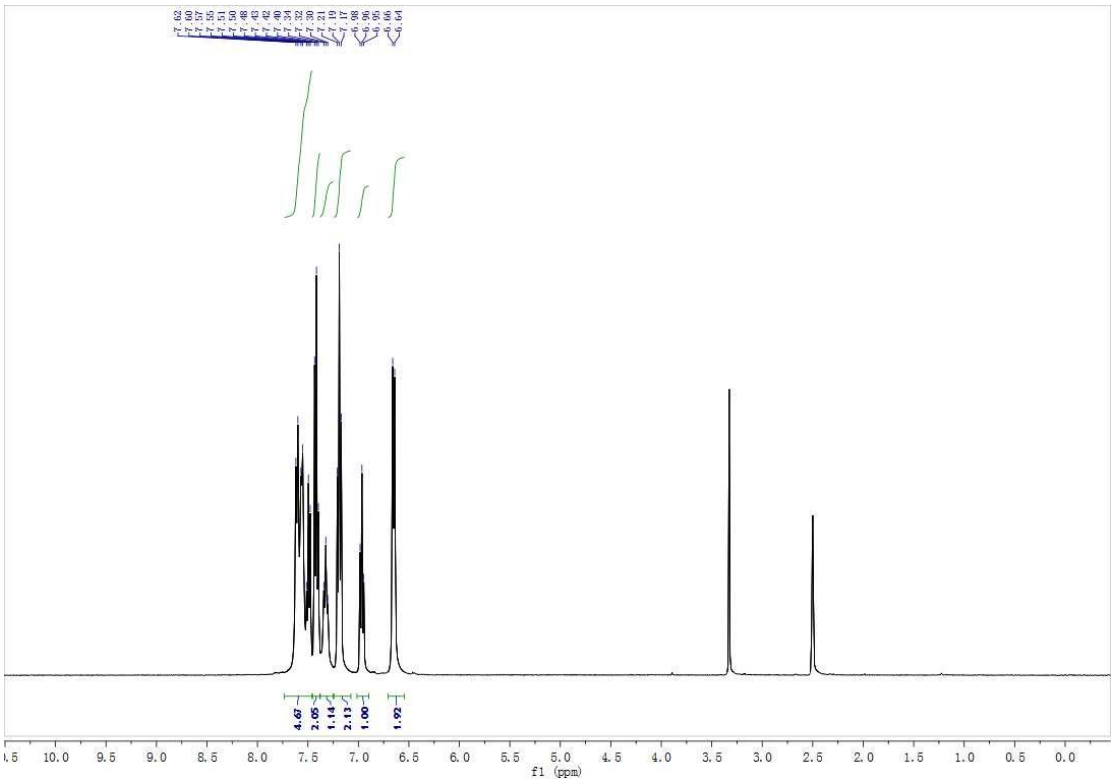
The no-slip condition was imposed for the flow field calculation at the wall. Zero flux was used for the concentration transport equation. Fixed temperature was used for the energy transport equation.

The finite element based solver COMSOL Multiphysics was applied to solve the equation systems. The geometry was discretized using structured elements. The mesh was refined near the inlet, outlet and the wall. Mesh-independency check has been carried out and the used total number of mesh elements was 13123 (after scale of the length of the geometry by a factor of 200).

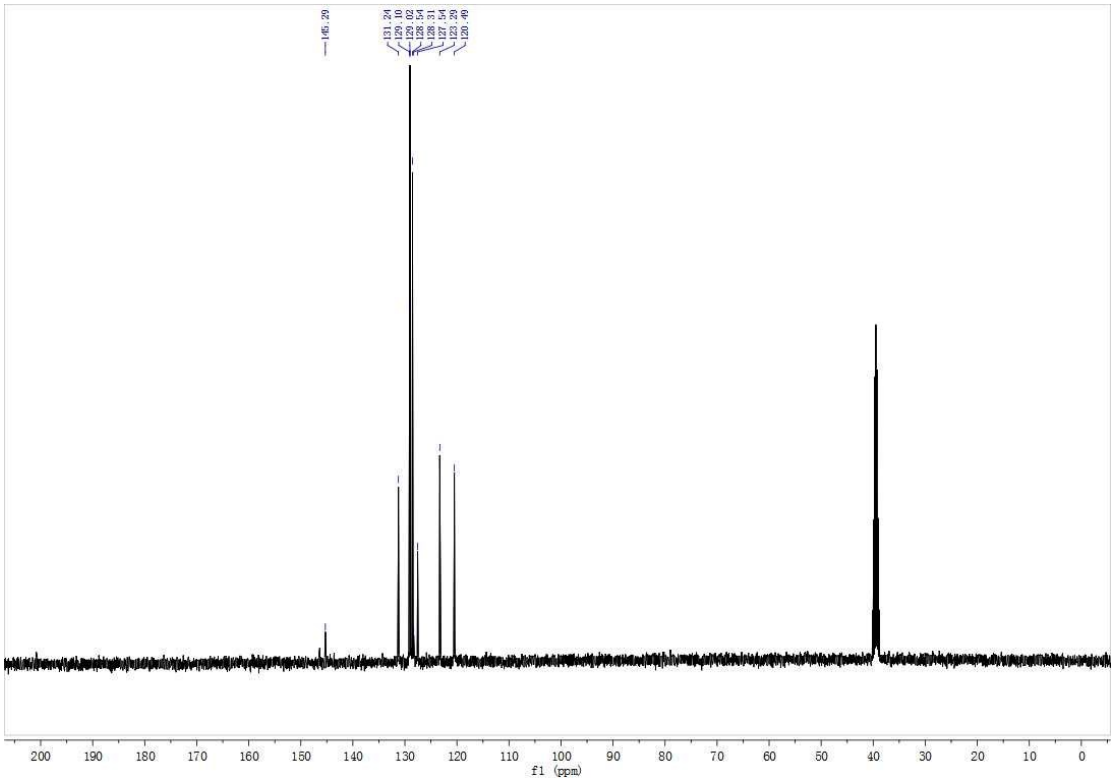
1H and 13C spectra of the synthesized compounds:

2, 6-Dichloro-phenyl-*N*-phenyl benzimidate (1a)

1H NMR

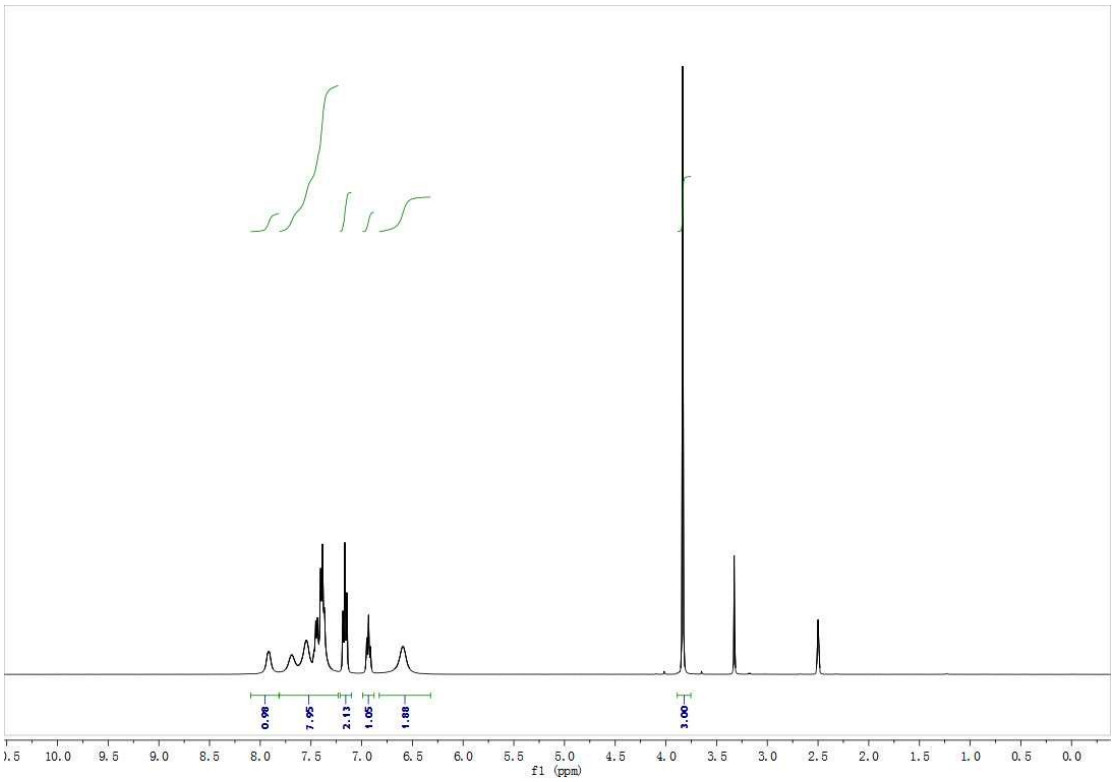


13C NMR

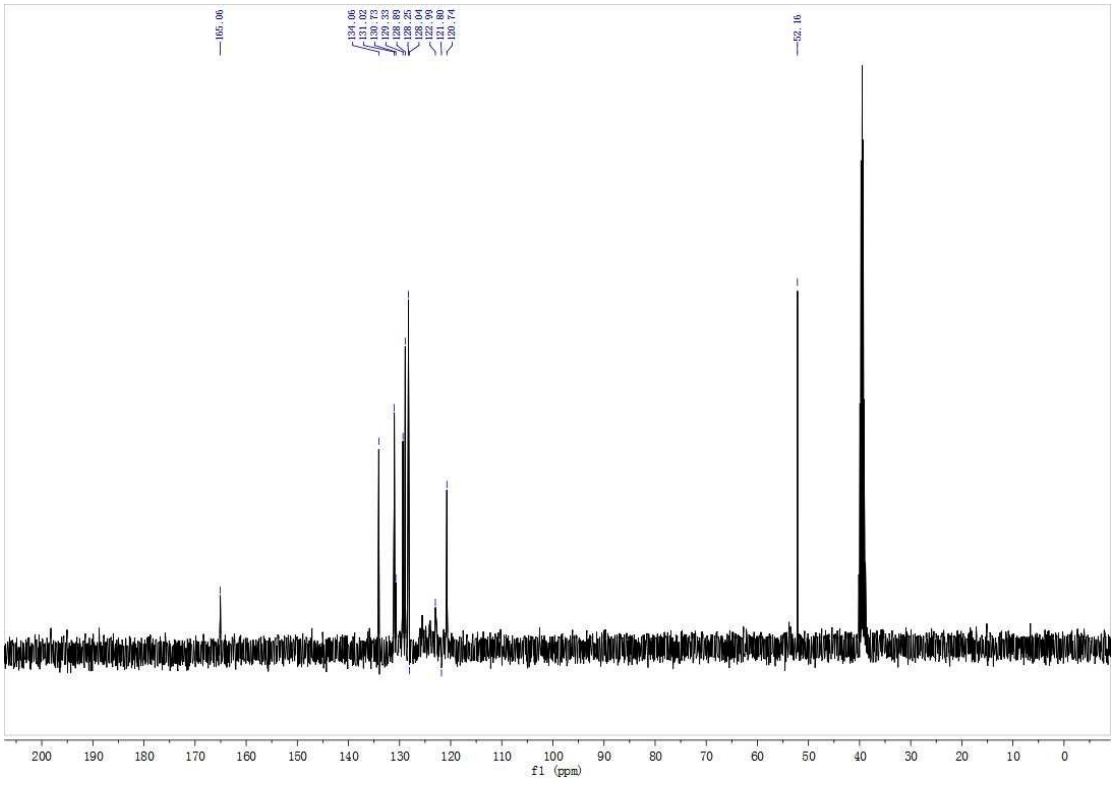


2-Carbomethoxy-phenyl *N*-phenyl benzimidate (1b)

1H NMR

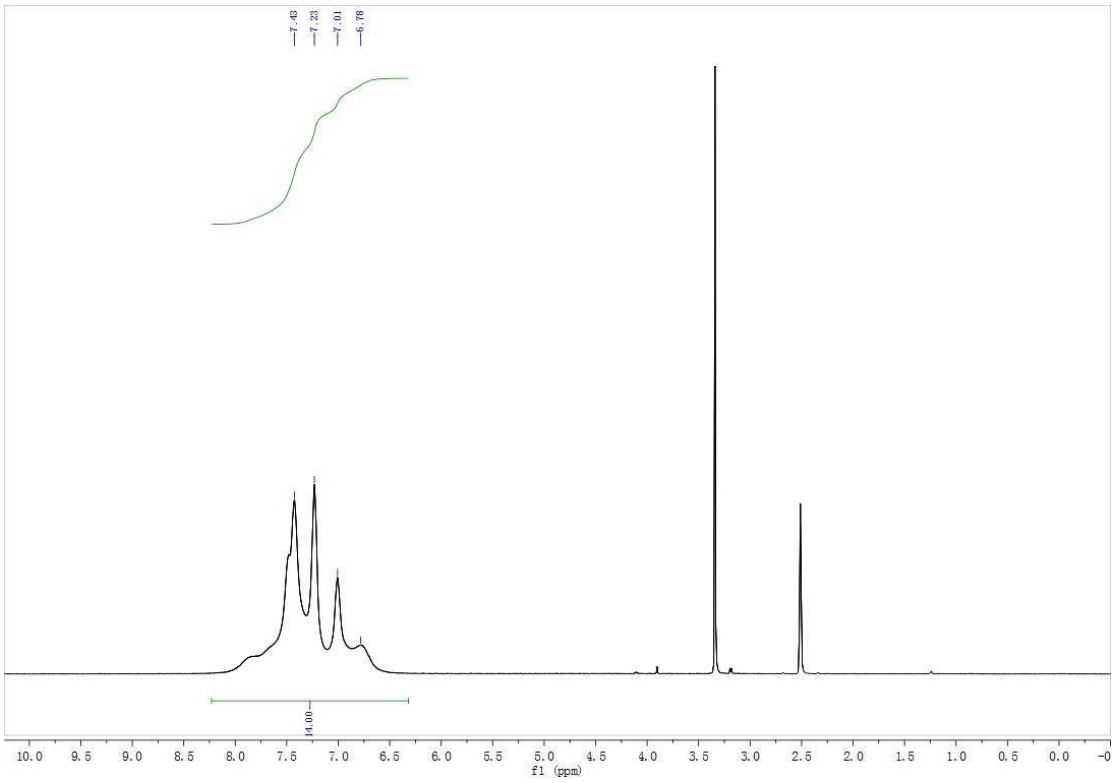


13C NMR

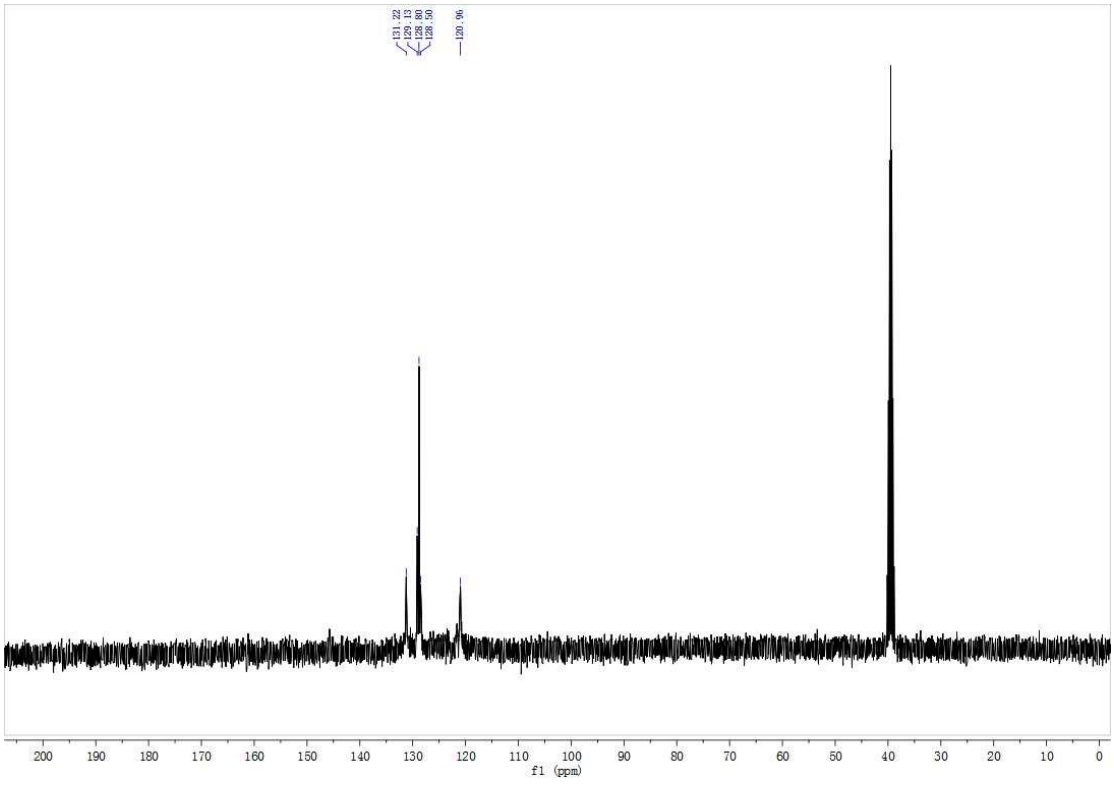


3-Bromo-phenyl *N*-phenyl benzimidate (1c)

1H NMR

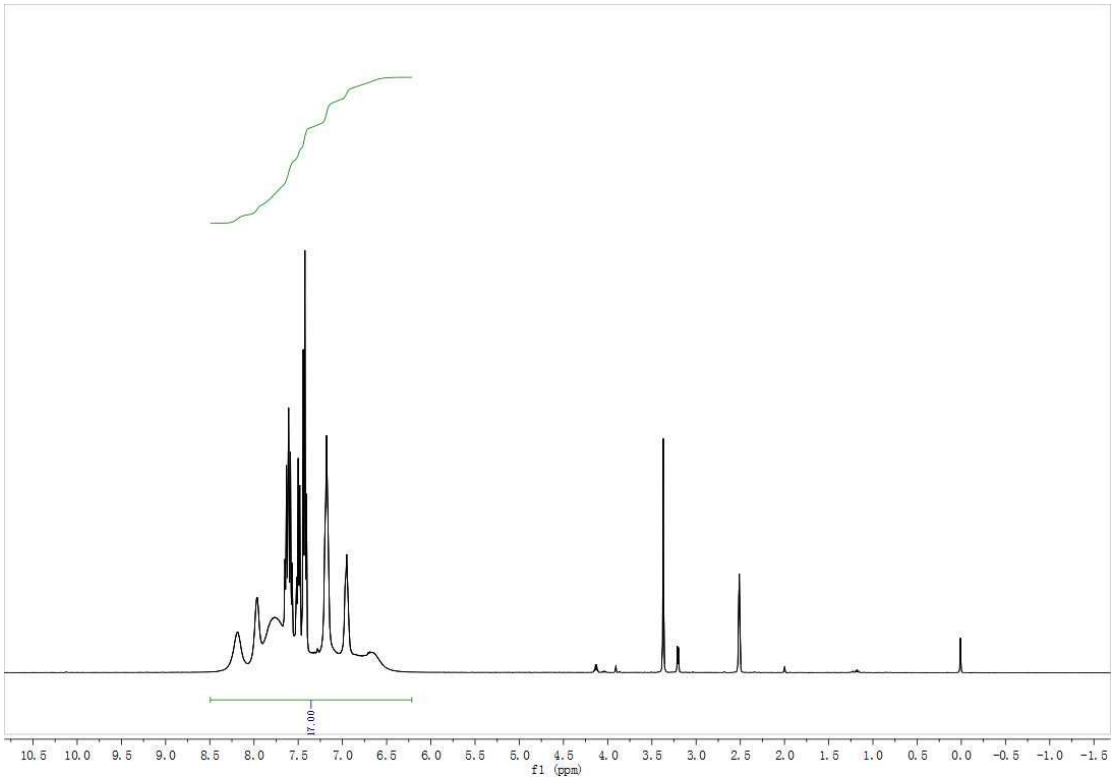


13C NMR

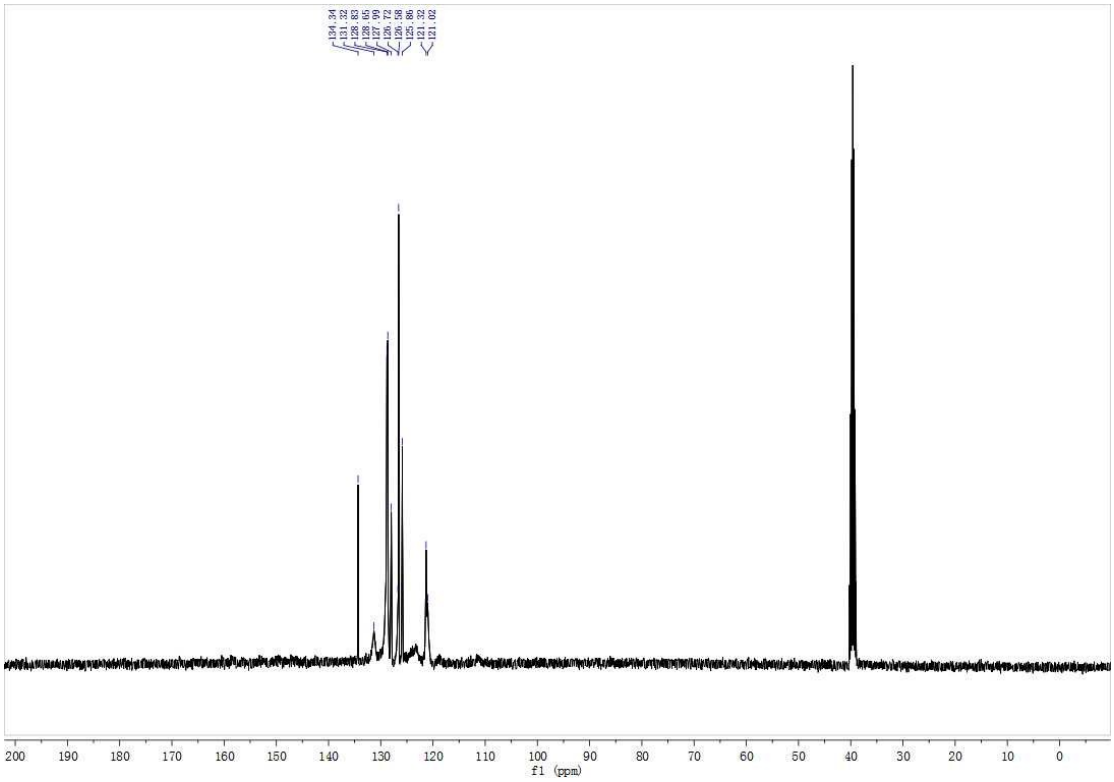


Naphthalen-1-yl-*N*-phenylbenzimidate (1d)

1H NMR

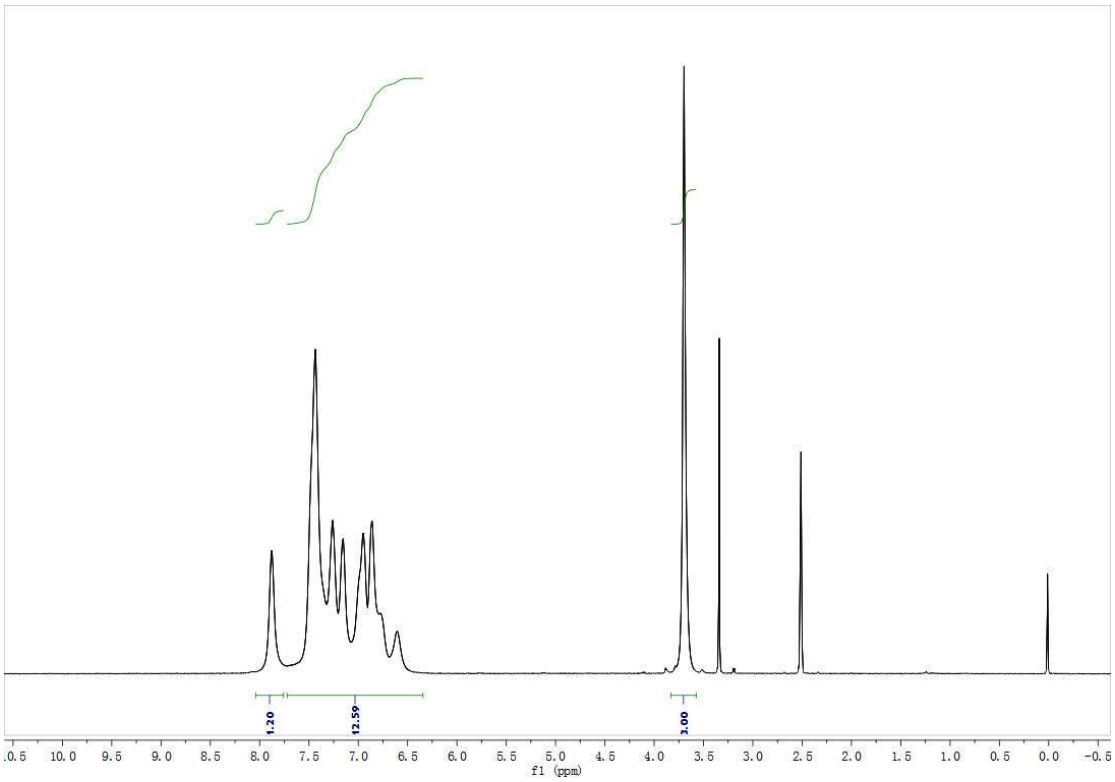


13C NMR

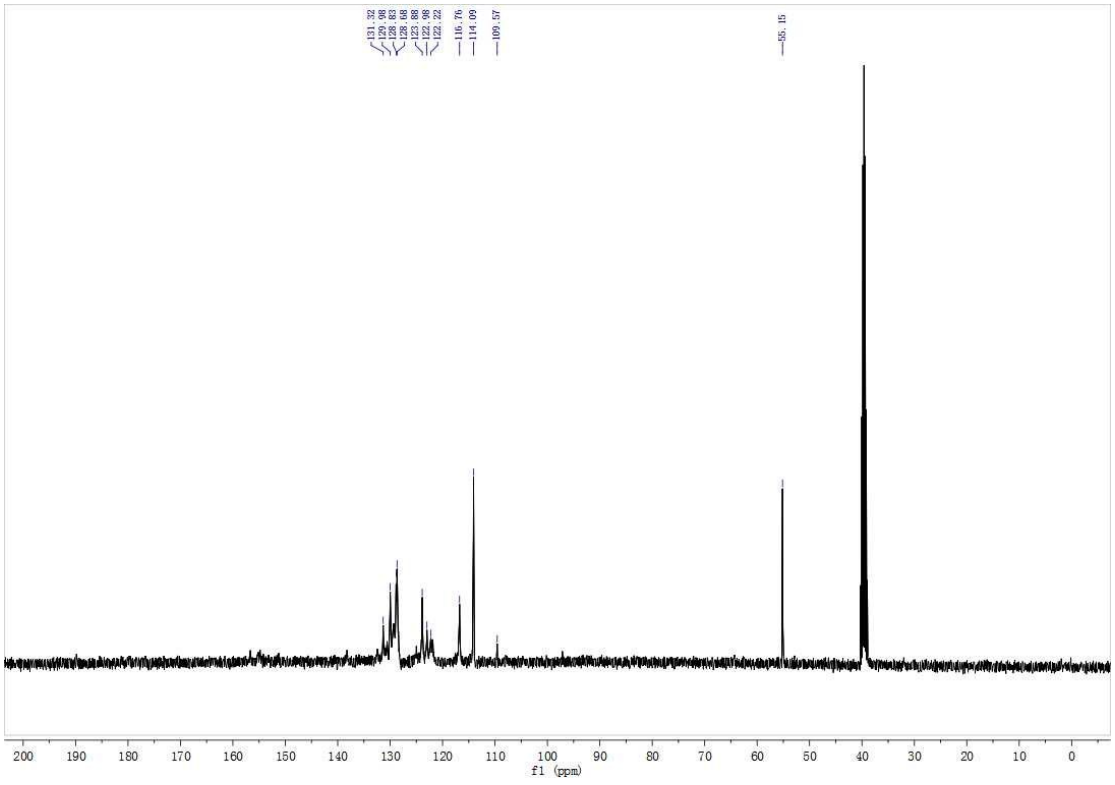


Phenyl-*N*-(4-methoxyphenyl)-benzimidate (1e)

1H NMR

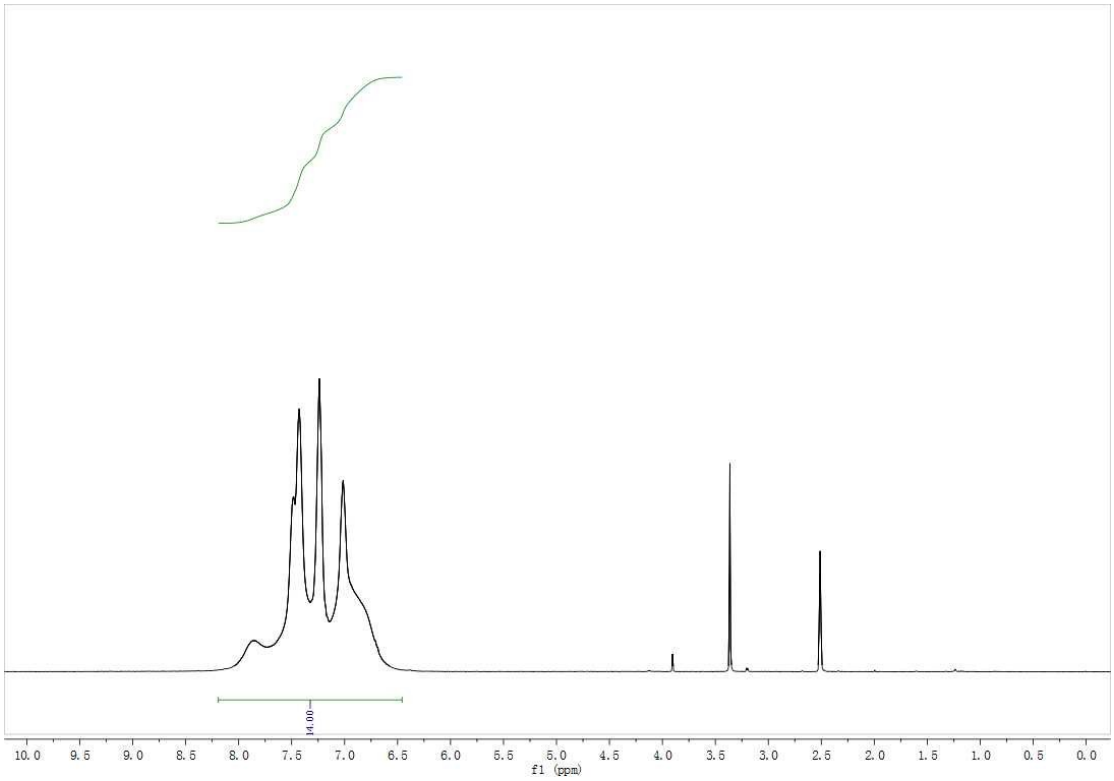


13C NMR

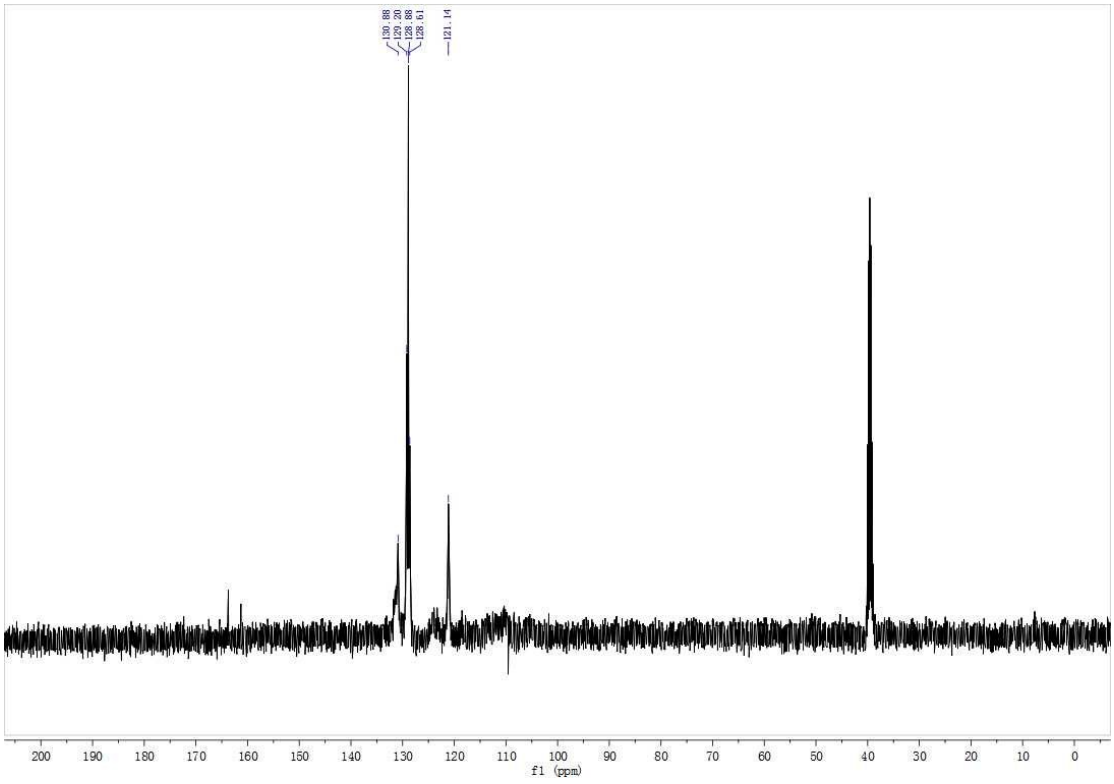


3-Fluorophenyl-*N*-phenyl-benzimidate (1f)

1H NMR

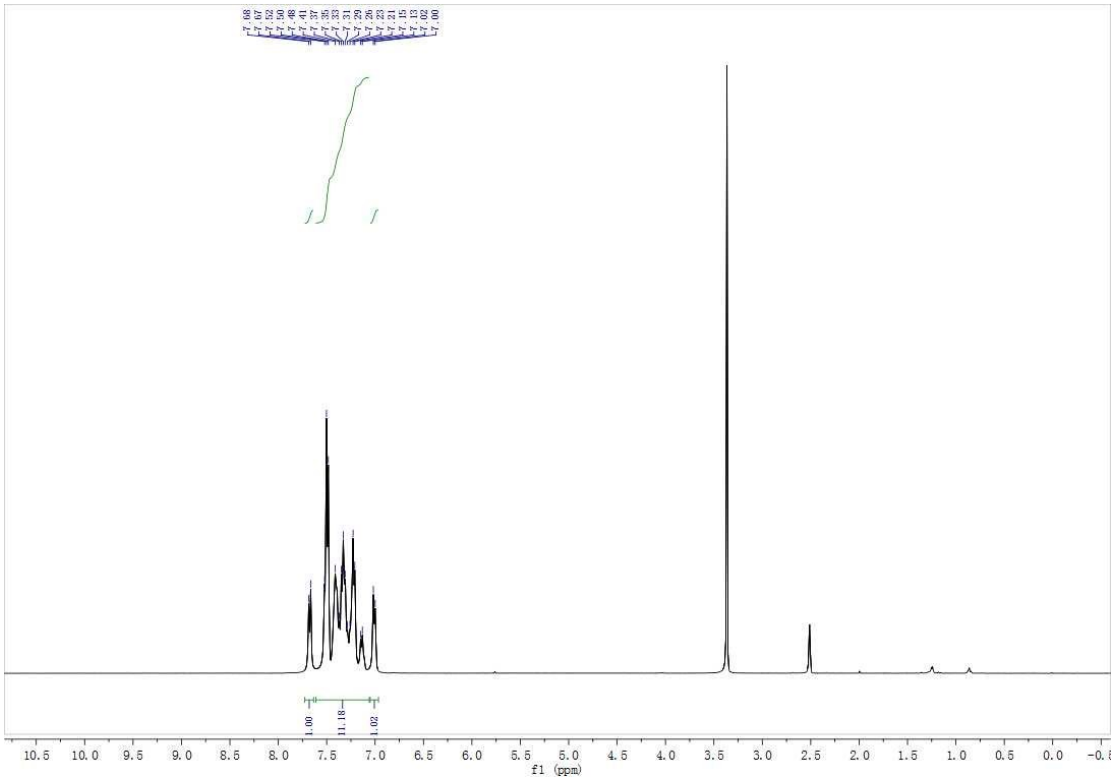


13C NMR

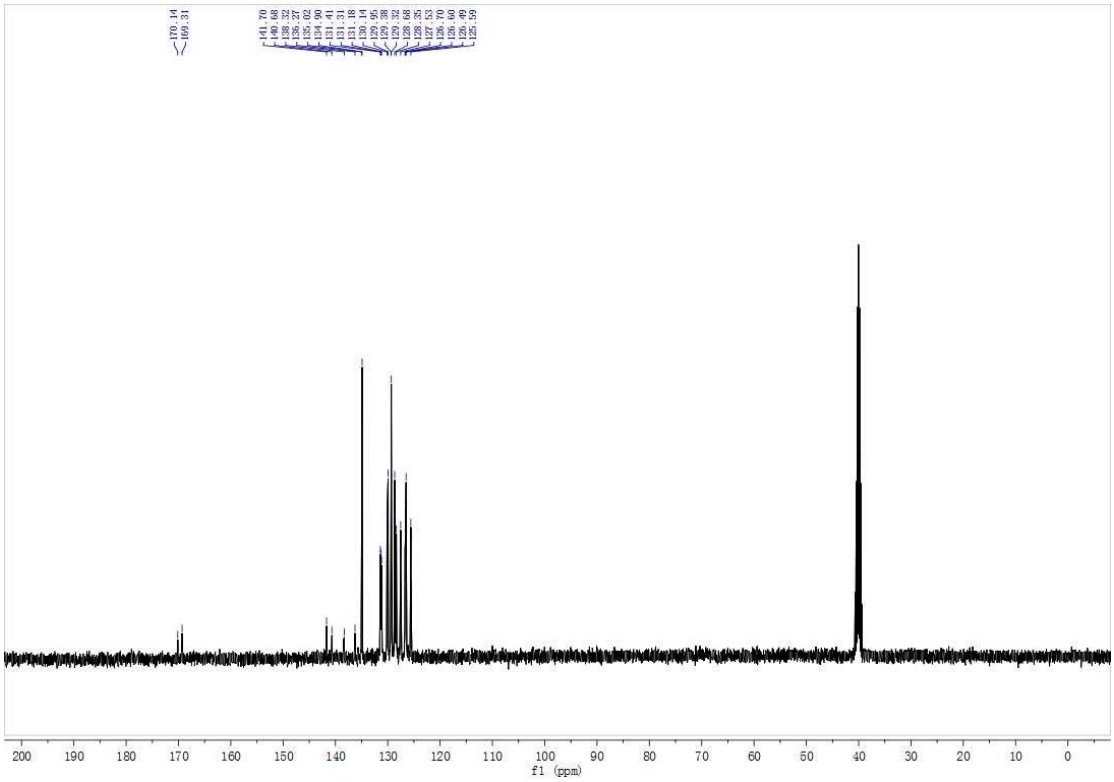


N-(2, 6-dichlorophenyl)-*N*-phenylbenzamide (2a)

1H NMR

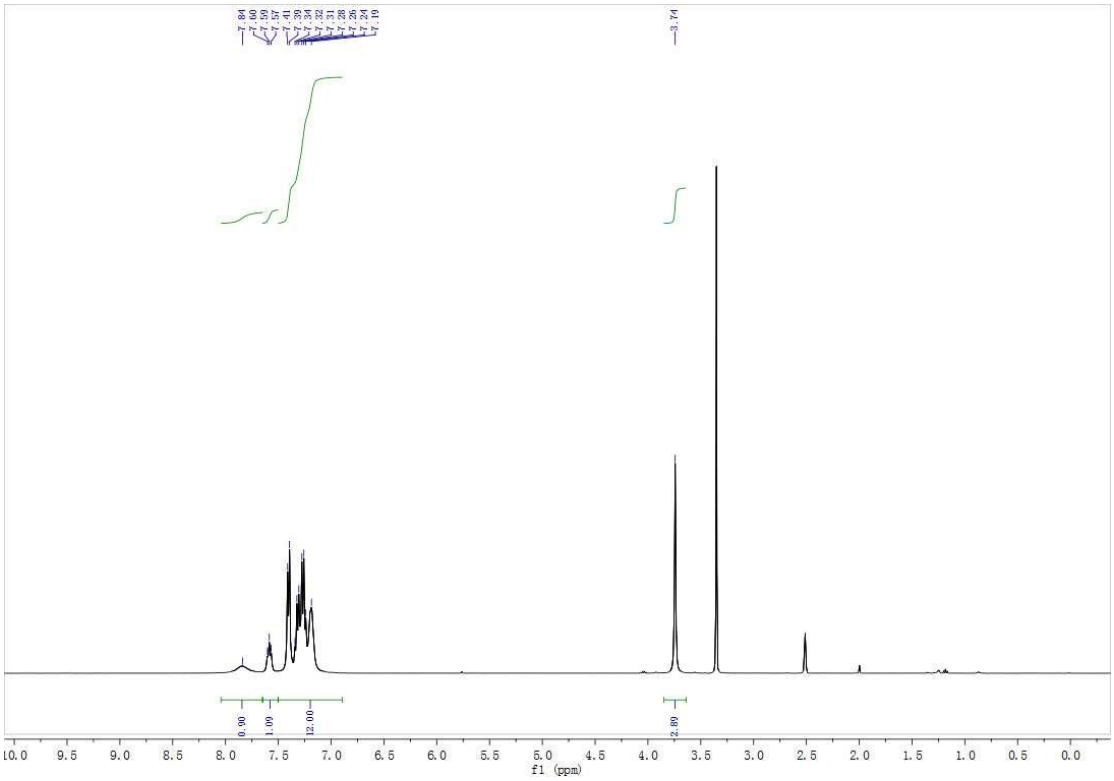


13C NMR

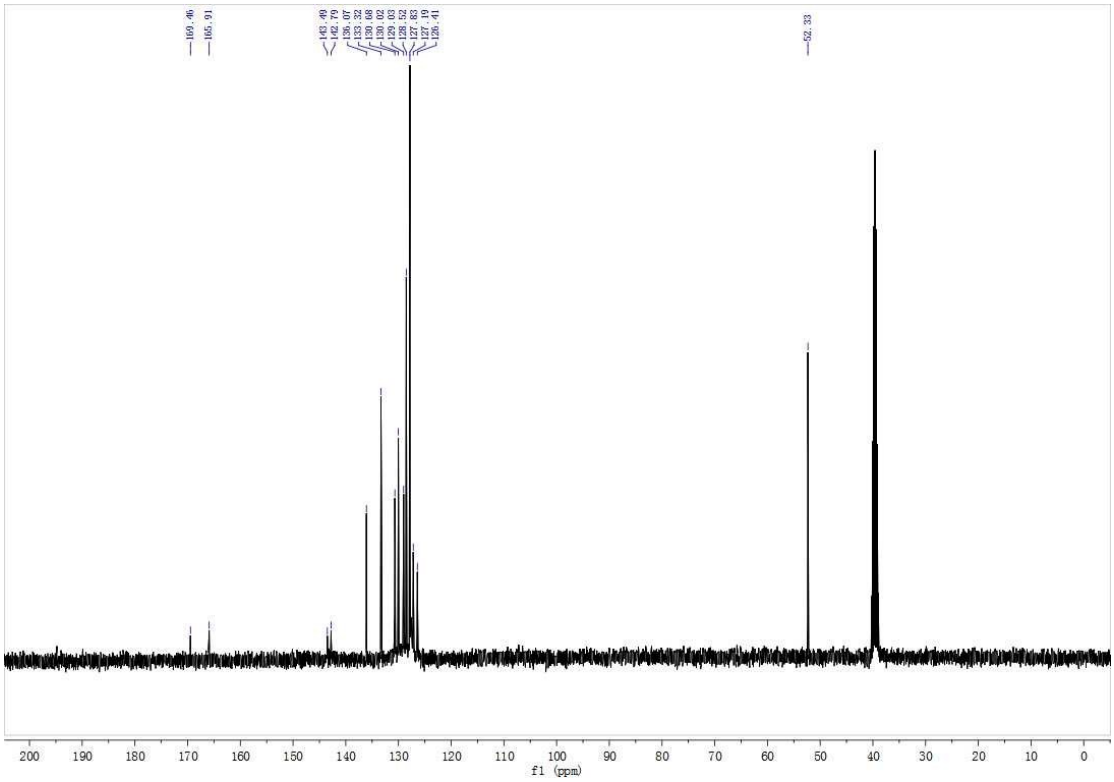


N-(2-carbomethoxy-phenyl)-*N*-phenylbenzamide (2b)

1H NMR

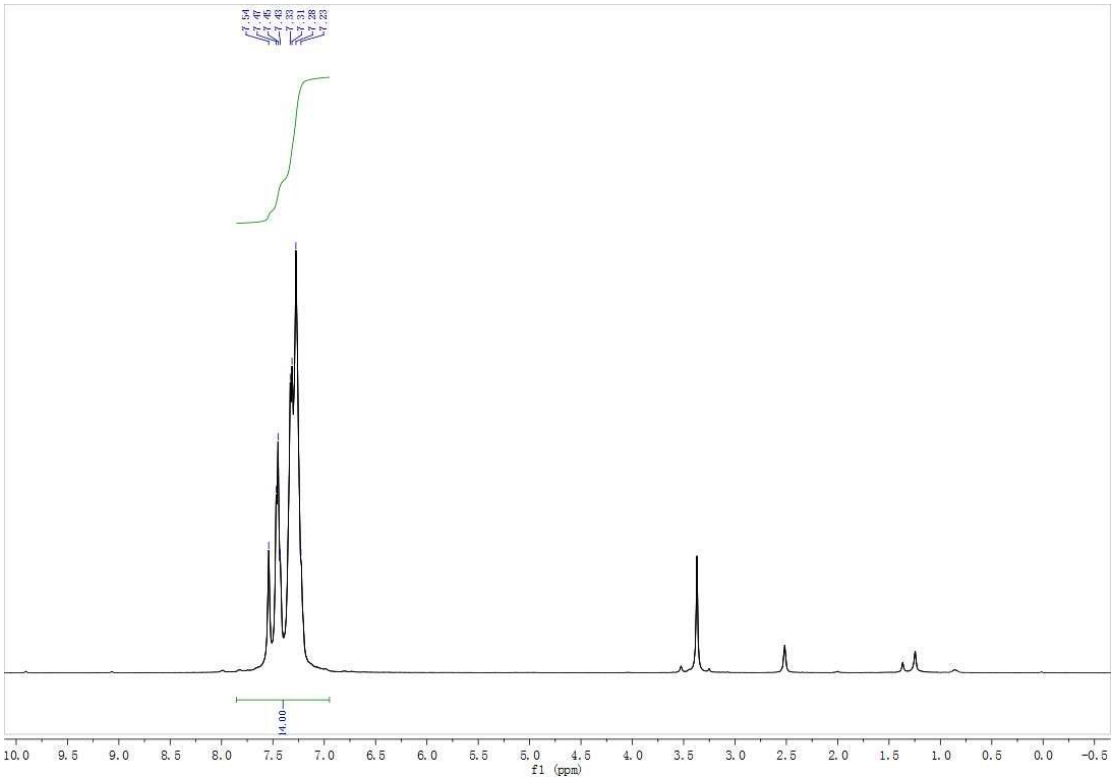


13C NMR

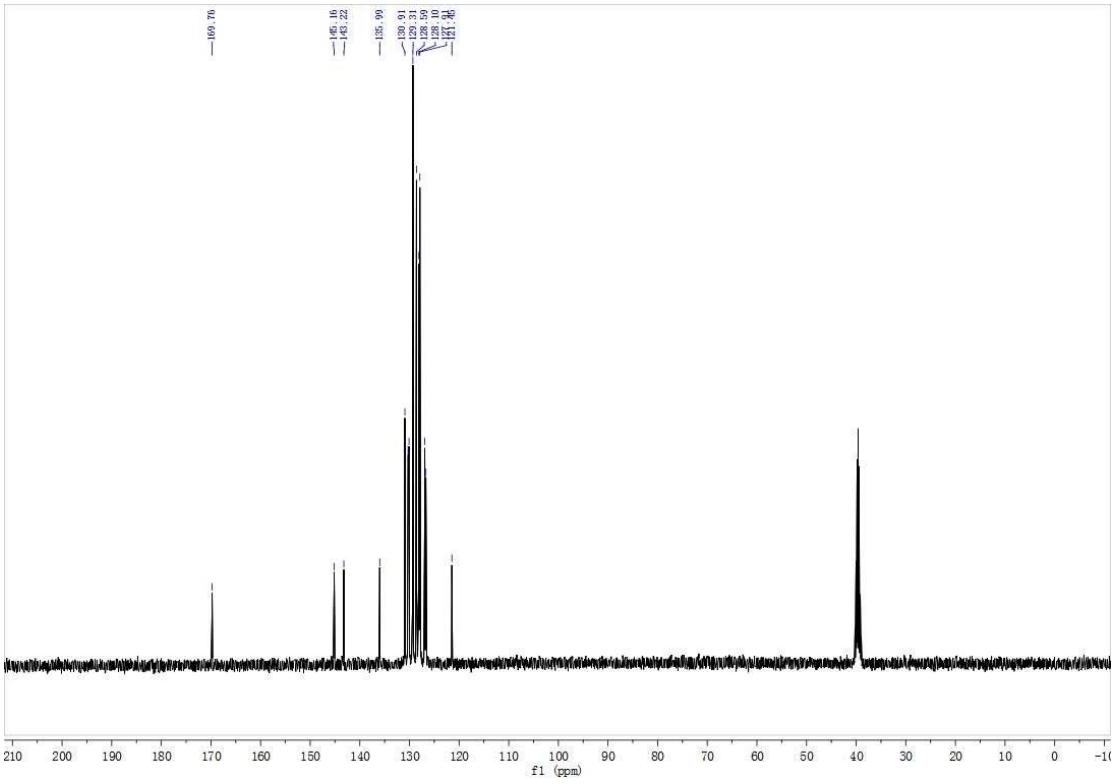


N-(3-bromophenyl)-*N*-phenylbenzamide (2c)

1H NMR

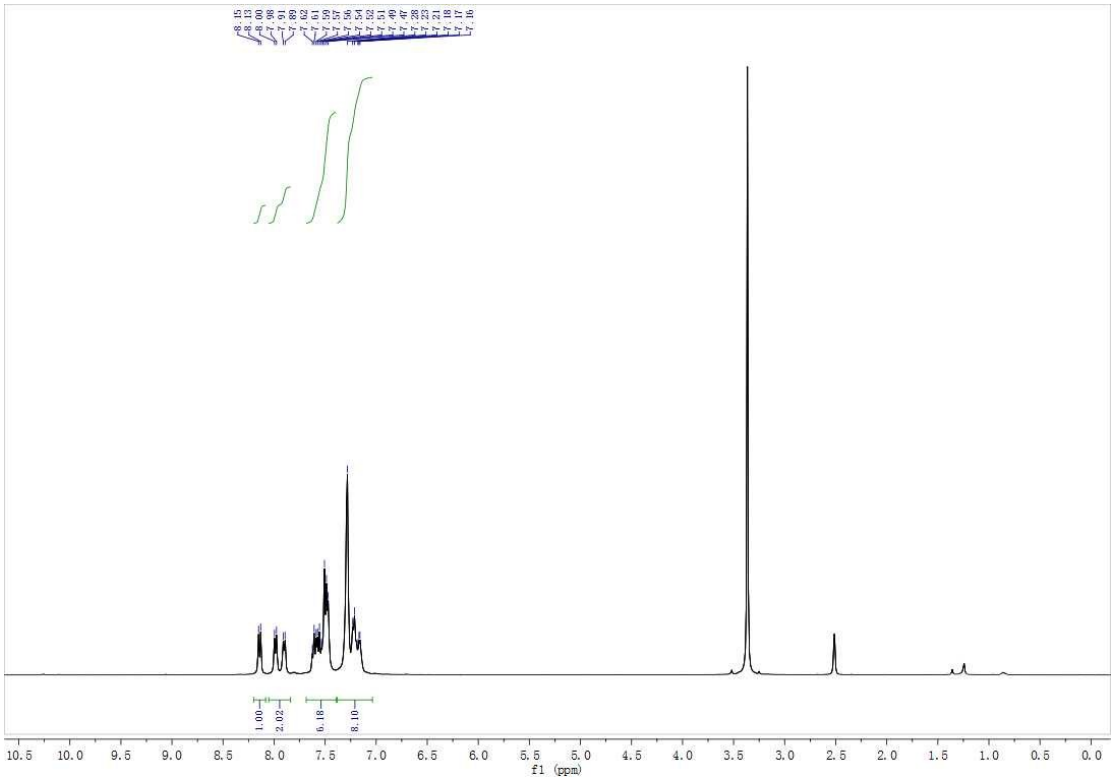


13C NMR

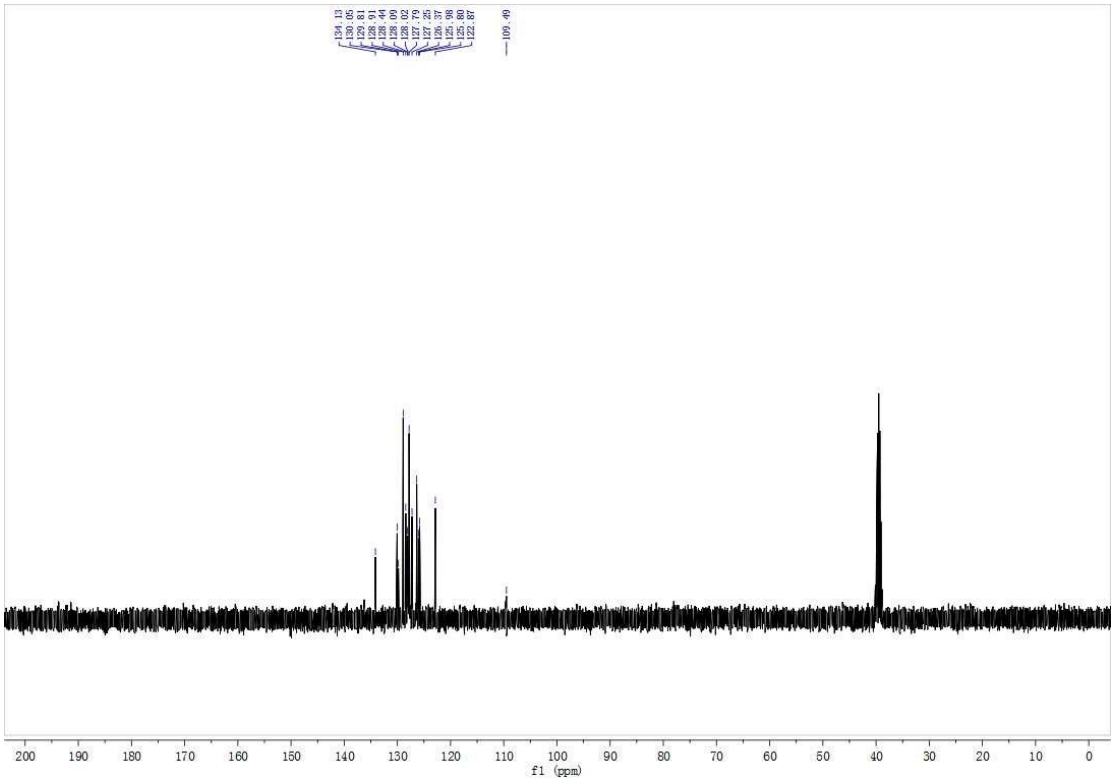


N-(1-naphthalen)-*N*-phenylbenzamide (2d)

1H NMR

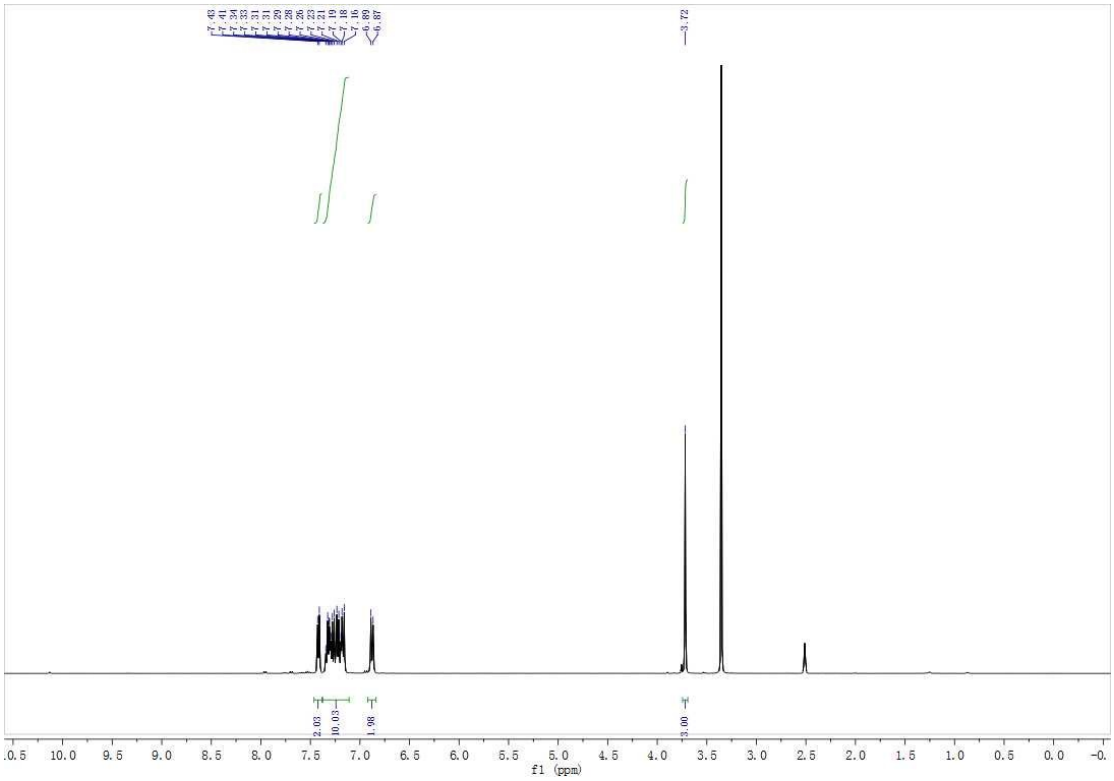


13C NMR

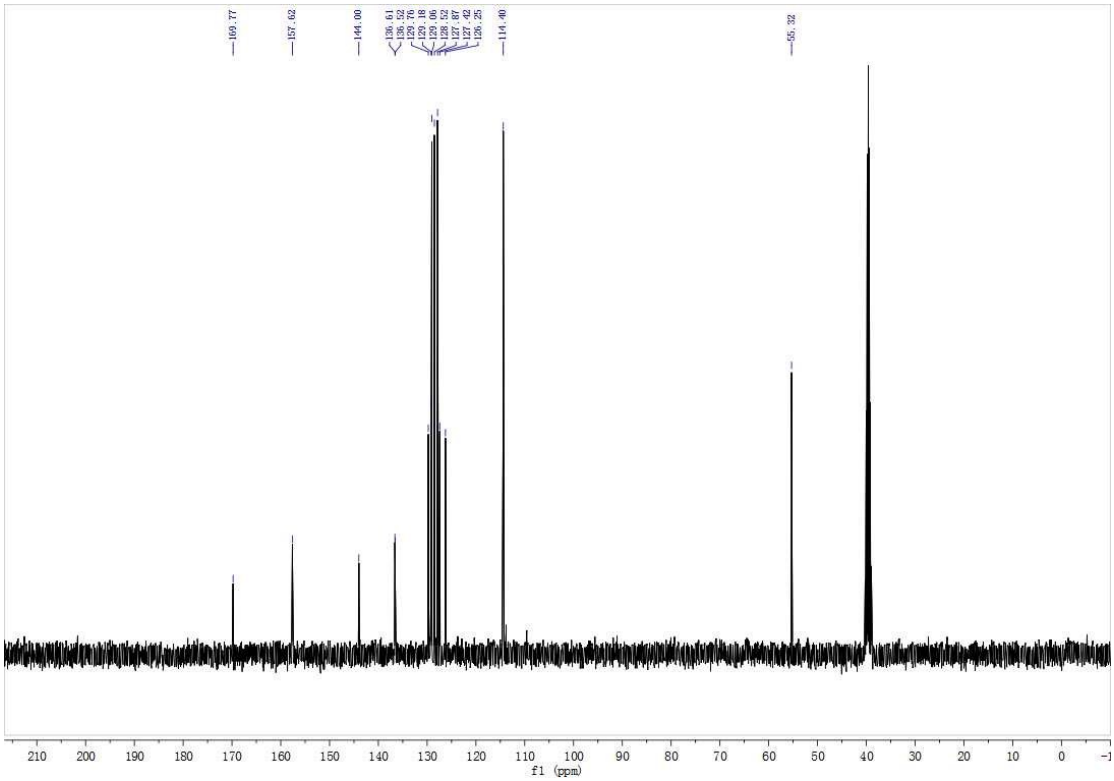


N-(4-methoxyphenyl)-*N*-phenylbenzamide (2e)

1H NMR

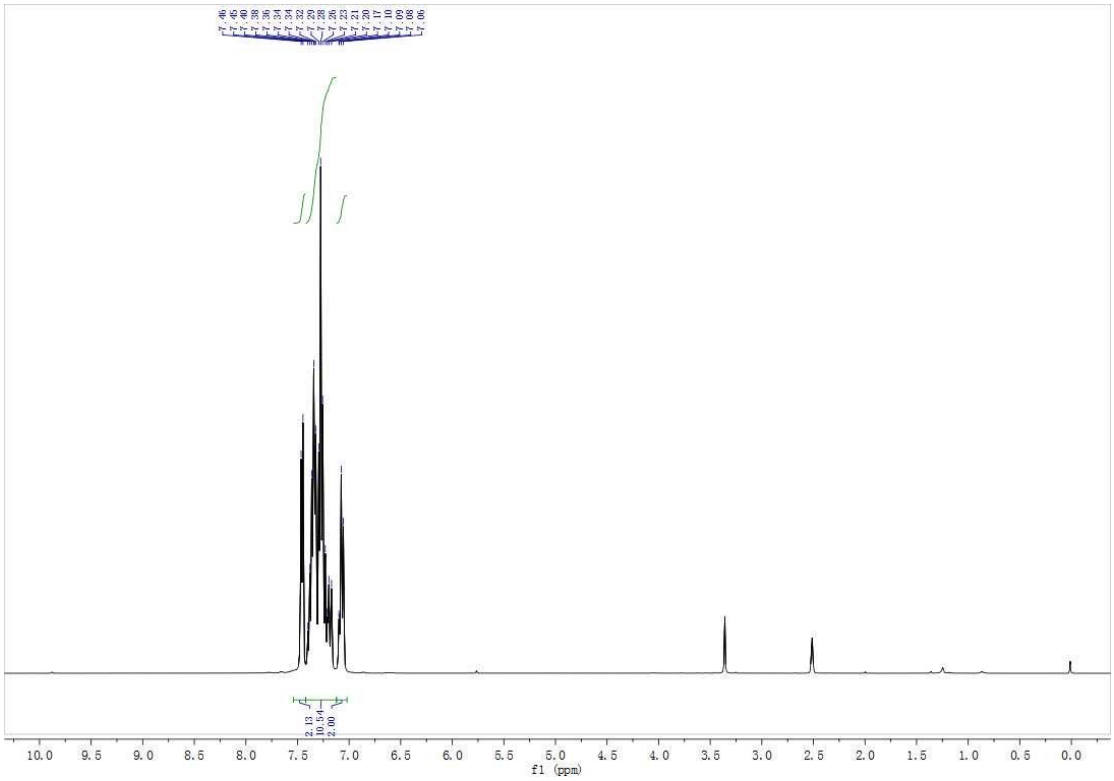


13C NMR



N-(3-fluorophenyl)-*N*-phenylbenzamide (2f)

1H NMR



13C NMR