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Support Information

Catalyst-free highly regioselective hydrated ring-opening and formylation of quinazolinones

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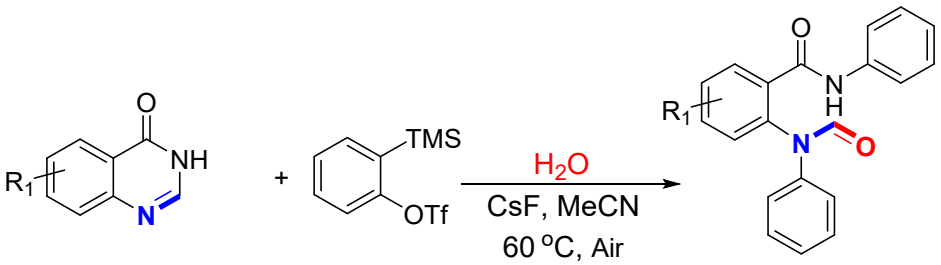
1. General information

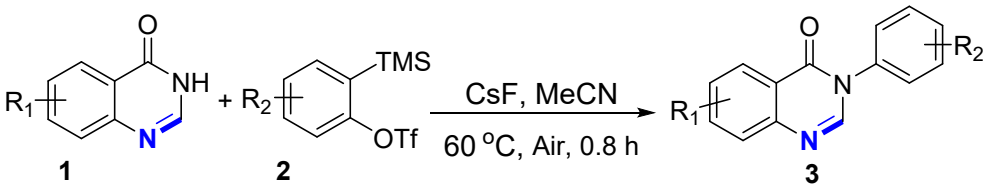
All chemicals and reagents were used of commercial grade and were used without further purification. The reactions were monitored by thin-layer chromatography (TLC) using silica gel GF254. Column chromatography was performed with 200–300 mesh silica gel. All yields refer to isolated products after purification. The intermediates and the products synthesized were fully characterized by spectroscopic data. The NMR spectra were recorded on Bruker DRX-600 (^{1}H: 600 MHz, ^{13}C: 151 MHz) using $CDCl_3$ as solvents. The following abbreviation were used to explain the multiplicities: (s) = singlet, (d) = doublet, (t) = triplet, (q) = quartet, (sept) = septuplet, (dd) = double doublet, (dt) = double triplet, (dq) = double quartet, (ddd) = double-double doublet, (m) = multiplet; Chemical shifts (δ) are expressed in parts per million (ppm) and J values are given in hertz (Hz). IR spectra were recorded on an FT-IR Thermo Nicolet Avatar 360 using a KBr pellet. HRMS was performed on an Agilent LC/MSD TOF instrument. The melting points were measured by the XT-4A melting point apparatus without correction.

2. General Procedure for preparing compounds **3, 4,** or **5**

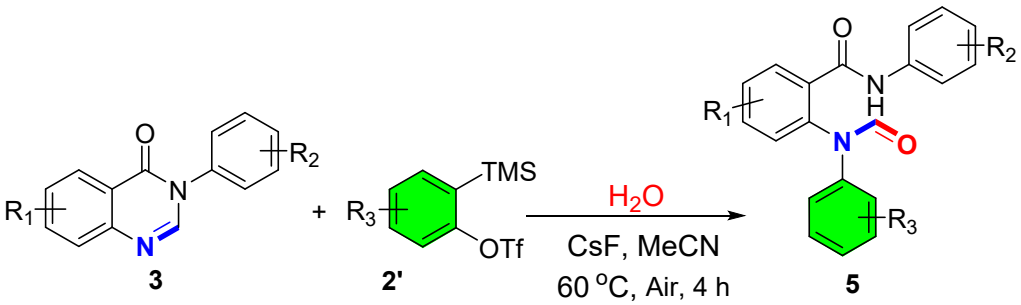


Under air atmosphere, quinazolinone **1** (1 mmol), Kobayashi benzyne precursor **2a** (2 mmol, 596 mg), CsF (2 mmol, 604 mg), H_2O (100 μL), MeCN (10 ml) were added to 25 mL reaction tube. The mixture was stirred at 60 °C in oil bath for 4 h. After cooling to room temperature, the reaction was quenched with saturated NaCl solution and extracted with 60 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the products **4a-4l**.

The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS.

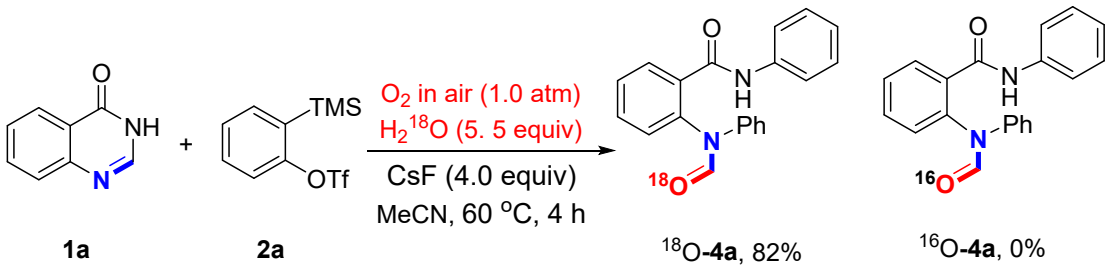


Under air atmosphere, quinazolinone **1** (1 mmol), Kobayashi benzyne precursor **2** (1 mmol), CsF (2 mmol, 302 mg), MeCN (10 ml) were added to 25 mL reaction tube. The mixture was stirred at 60 °C in oil bath for 0.8 h. After cooling to room temperature, the reaction was quenched with saturated NaCl solution and extracted with 60 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the products **3a-3f**. The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS.

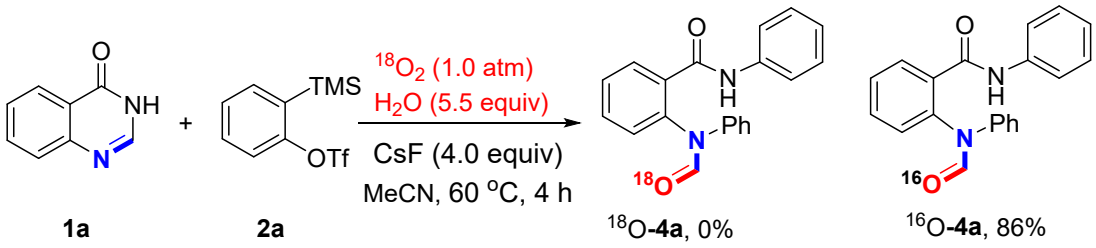


Under air atmosphere, 3-phenylquinazolinone **3** (0.5 mmol), Kobayashi benzyne precursor **2'** (0.5 mmol), CsF (1 mmol, 151 mg), H_2O (50 μL), MeCN (10 ml) were added to 25 mL reaction tube. The mixture was stirred at 60 °C in oil bath for 4 h. After cooling to room temperature, the reaction was quenched with saturated NaCl solution and extracted with 60 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the products **5a-5g**. The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS.

3. General Procedure for ^{18}O labeling experiment



Under air atmosphere, quinazolinone **1a** (0.2 mmol, 29 mg), Kobayashi benzyne precursor **2a** (0.4 mmol, 119 mg), CsF (0.4 mmol, 121 mg), $H_2{}^{18}O$ (20 μL), MeCN (2 ml) were added to 10 mL dry reaction tube. The mixture was stirred at 60 °C in oil bath for 4 h. After cooling to room temperature, the reaction was quenched with saturated NaCl solution and extracted with 10 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the products **4a**. The products were further identified by HRMS.

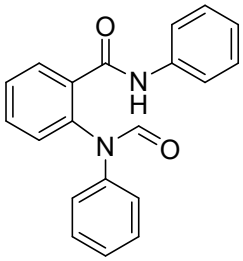


Under $^{18}O_2$ atmosphere, quinazolinone **1a** (0.2 mmol, 29 mg), Kobayashi benzyne precursor **2a** (0.4 mmol, 119 mg), CsF (0.4 mmol, 121 mg), H_2O (20 μL), MeCN (2 ml) were added to 10 mL dry schlenk tube. The mixture was stirred at 60 °C in oil bath for 4 h. After cooling to room temperature, the reaction was quenched with saturated NaCl solution and extracted with 10 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced

pressure. The residues were purified by flash column chromatography on silica gel to provide the products **4a**. The products were further identified by HRMS.

4. Spectroscopic Data of **4**-**5** & ^{18}O-**4a**

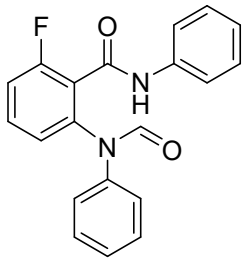
4.1 Spectroscopic Data of **4a**



N-phenyl-2-(*N*-phenylformamido)benzamide(**4a**)**.**

Synthesized according to General Procedure 1. Crude **4a** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 85% yield (269 mg, 0.85 mmol) as a white solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 207.2-207.7 °C; **IR** (KBr): 3264, 3202, 3138, 3083, 2886, 1672, 1603, 1553, 1497, 1445, 1399, 1324, 1261, 754, 708, 696; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.65 (s, 1H, CHO), 8.22 (s, 1H, NH), 7.70 (dd, *J* = 7.6, 1.7 Hz, 1H, ArH), 7.58 (d, *J* = 8.0 Hz, 2H, ArH), 7.51 (td, *J* = 7.7, 1.7 Hz, 1H, ArH), 7.47 (t, *J* = 7.5 Hz, 1H, ArH), 7.33 (dt, *J* = 9.9, 7.6 Hz, 4H, ArH), 7.30 – 7.22 (m, 3H, ArH), 7.19 (dd, *J* = 8.2, 3.6 Hz, 3H, ArH), 7.12 (t, *J* = 7.4 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 165.65, 163.17, 141.15, 137.82, 136.88, 135.97, 131.55, 129.76, 129.20 – 128.74 (m), 127.19, 124.57, 124.15, 119.95. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{20}H_{16}O_2N_2$ [M+H] $^+$, 317.1285; found, 317.1284.

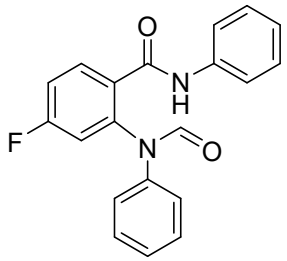
4.2 Spectroscopic Data of **4b**



2-fluoro-*N*-phenyl-6-(*N*-phenylformamido)benzamide(**4b**).

Synthesized according to General Procedure 1. Crude **4b** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 76% yield (254 mg, 0.76 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 210.7-211.4 °C; **IR** (KBr): 3270, 3208, 3145, 3096, 2882, 1676, 1610, 1556, 1496, 1450, 1403, 1322, 1276, 1239, 1150, 1052, 901, 858, 754, 691; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.60 (s, 1H, CHO), 8.08 (s, 1H, NH), 7.58 (d, *J* = 7.9 Hz, 2H, ArH), 7.48 – 7.42 (m, 1H, ArH), 7.35 (dt, *J* = 19.4, 7.7 Hz, 4H, ArH), 7.30 – 7.18 (m, 6H, ArH), 7.15 – 7.11 (m, 1H, ArH), 6.98 (d, *J* = 8.0 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 162.72, 160.64 (d, *J* = 39.5 Hz), 158.85, 140.85, 137.83, 137.39, 131.81, 131.74, 129.80, 129.04, 127.41, 125.61 (d, *J* = 39.3 Hz), 124.86, 124.57, 124.55, 124.38, 120.16, 116.21 (d, *J* = 22.1 Hz); **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -113.32. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{20}H_{15}FO_2N_2$ [M+H] $^+$, 335.1190; found, 335.1192.

4.3 Spectroscopic Data of **4c**

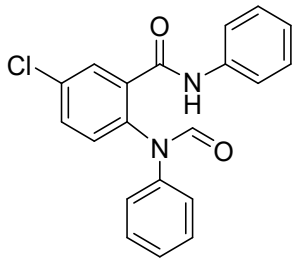


4-fluoro-*N*-phenyl-2-(*N*-phenylformamido)benzamide(**4c**).

Synthesized according to General Procedure 1. Crude **4c** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 79% yield (264 mg, 0.79 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 138.5-139.3 °C; **IR** (KBr): 3319, 3207, 3140, 3072, 1676, 1602, 1547, 1498, 1437, 1329, 1281, 1210,

1128, 914, 843, 758, 727, 691; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.61 (s, 1H, CHO), 8.17 (s, 1H, NH), 7.70 (dd, *J* = 8.6, 6.0 Hz, 1H, ArH), 7.55 (d, *J* = 8.0 Hz, 2H, ArH), 7.37 (t, *J* = 7.7 Hz, 2H, ArH), 7.31 (dt, J = 19.0, 7.6 Hz, 4H, ArH), 7.20 (d, *J* = 7.8 Hz, 2H, ArH), 7.16 (td, *J* = 8.2, 2.7 Hz, 2H, ArH), 7.13 (t, J = 7.4 Hz, 1H, ArH), 6.91 (dd, *J* = 8.8, 2.5 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.85, 164.66 (d, *J* = 2.1 Hz), 162.95, 140.65, 137.68, 133.06, 130.77, 130.71, 129.91, 129.07, 127.57, 124.71, 124.37, 120.01, 116.35 (d, *J* = 23.0 Hz), 116.02 (d, *J* = 22.2 Hz); **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -107.27. **HRMS** (TOF-ESI^{+}): *m/z* calcd for $C_{20}H_{15}FO_2N_2$ [M+H] $^{+}$, 335.1190; found, 335.1188.

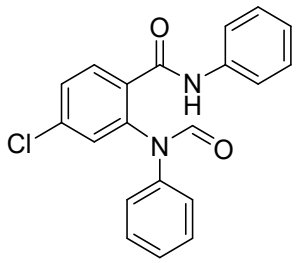
4.4 Spectroscopic Data of **4d**



5-chloro-*N*-phenyl-2-(*N*-phenylformamido)benzamide(**4d**).

Synthesized according to General Procedure 1. Crude **4d** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 81% yield (300 mg, 0.81 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 98.4-98.8 °C; **IR** (KBr): 3329, 3207, 3143, 3061, 1671, 1599, 1545, 1491, 1440, 1400, 1324, 1279, 1255, 1109, 753, 690; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.60 (s, 1H, CHO), 7.64 (d, *J* = 2.6 Hz, 1H, NH), 7.55 (d, *J* = 8.0 Hz, 2H, ArH), 7.44 – 7.39 (m, 1H, ArH), 7.36 (t, *J* = 7.7 Hz, 2H, ArH), 7.28 (dq, *J* = 7.4, 3.3, 2.8 Hz, 4H, ArH), 7.20 (dd, *J* = 7.5, 1.6 Hz, 2H, ArH), 7.13 – 7.06 (m, 2H, ArH); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.30, 162.90, 140.88, 137.79, 137.62, 134.66, 134.40, 131.52, 130.17, 129.86, 129.01, 127.45, 124.74, 124.38, 120.06. **HRMS** (TOF-ESI^{+}): *m/z* calcd for $C_{20}H_{15}ClO_2N_2$ [M+Na] $^{+}$, 373.0714; found, 373.0716.

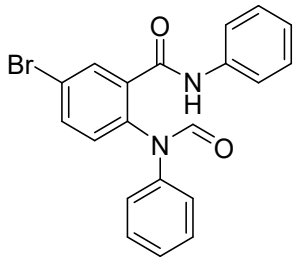
4.5 Spectroscopic Data of **4e**



4-chloro-*N*-phenyl-2-(*N*-phenylformamido)benzamide(**4e**).

Synthesized according to General Procedure 1. Crude **4e** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 82% yield (305 mg, 0.81 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 172.2-172.9 °C; **IR** (KBr): 3321, 3084, 3024, 2928, 2876, 1675, 1597, 1538, 1494, 1442, 1405, 1325, 1283, 1163, 1104, 773, 751, 692; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.59 (s, 1H, CHO), 8.26 (d, *J* = 6.6 Hz, 1H, NH), 7.62 (d, *J* = 8.3 Hz, 1H, ArH), 7.54 (d, *J* = 8.0 Hz, 2H, ArH), 7.41 (dd, *J* = 8.2, 2.1 Hz, 1H, ArH), 7.37 (t, *J* = 7.8 Hz, 2H, ArH), 7.30 (dt, *J* = 12.4, 7.7 Hz, 4H, ArH), 7.20 (d, *J* = 7.8 Hz, 2H, ArH), 7.16 (d, *J* = 2.1 Hz, 1H, ArH), 7.12 (t, *J* = 7.4 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.79, 162.97, 140.66, 137.65, 137.32, 137.01, 135.11, 130.05, 129.91, 129.13, 129.06, 128.96, 127.57, 124.75, 124.41, 120.07. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{20}H_{15}ClO_2N_2$ $[M+H]^+$, 351.0895; found, 351.0892.

4.6 Spectroscopic Data of **4f**

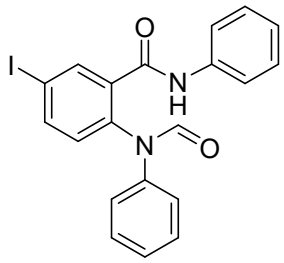


5-bromo-*N*-phenyl-2-(*N*-phenylformamido)benzamide(**4f**).

Synthesized according to General Procedure 1. Crude **4f** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 83% yield (327 mg, 0.83 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 116.6-117.6 °C; **IR** (KBr): 3331, 3206, 3141, 3066, 1682, 1598, 1548, 1483, 1443, 1394, 1326, 1288,

1257, 1097, 902, 763, 694; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.58 (s, 1H, CHO), 8.55 (s, 1H, NH), 7.75 (s, 1H, ArH), 7.56 – 7.49 (m, 3H, ArH), 7.36 (t, *J* = 7.7 Hz, 2H, ArH), 7.31 – 7.20 (m, 6H, ArH), 7.07 (t, *J* = 7.4 Hz, 1H, ArH), 6.99 (d, *J* = 8.5 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.20, 162.66, 140.91, 137.82, 137.73, 135.33, 134.42, 131.85, 130.26, 129.83, 128.94, 127.46, 124.64, 124.54, 122.03, 120.07. **HRMS** (TOF-ESI^{+}): *m/z* calcd for $C_{20}H_{15}BrO_2N_2$ [M+H] $^{+}$, 395.0390; found, 395.0390.

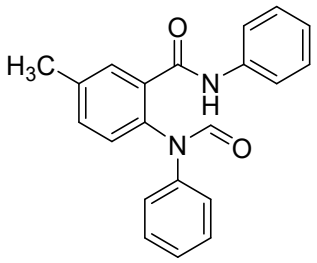
4.7 Spectroscopic Data of **4g**



5-iodo-*N*-phenyl-2-(*N*-phenylformamido)benzamide(**4g**).

Synthesized according to General Procedure 1. Crude **4g** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 82% yield (362 mg, 0.82 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 118.1-119.0 °C; **IR** (KBr): 3326, 3135, 3063, 2924, 1677, 1600, 1543, 1496, 1442, 1389, 1324, 1265, 1160, 1085, 897, 831, 756, 691; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.60 (s, 1H, CHO), 8.31 (s, 1H, NH), 7.98 (dd, J = 4.7, 2.2 Hz, 1H, ArH), 7.78 (ddd, *J* = 8.3, 6.0, 2.2 Hz, 1H, ArH), 7.55 (d, *J* = 7.9 Hz, 2H, ArH), 7.36 (d, *J* = 7.1 Hz, 2H, ArH), 7.32 – 7.27 (m, 4H, ArH), 7.26 (d, *J* = 1.7 Hz, 1H, ArH), 7.21 (d, *J* = 7.8 Hz, 2H, ArH), 7.11 (td, *J* = 7.5, 3.4 Hz, 1H, ArH), 6.90 (dd, *J* = 8.4, 3.0 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.02, 162.79, 140.80, 140.49, 138.24, 137.72, 137.61, 135.91, 130.53, 129.85, 129.02, 127.46, 124.73, 124.42, 120.02, 93.64. **HRMS** (TOF-ESI^{+}): *m/z* calcd for $C_{20}H_{15}IO_2N_2$ [M+H] $^{+}$, 443.0251; found, 443.0251.

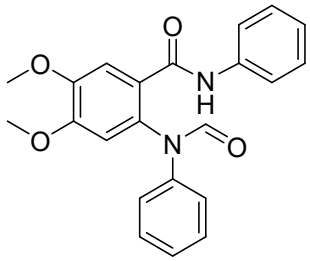
4.8 Spectroscopic Data of **4h**



5-methyl-*N*-phenyl-2-(*N*-phenylformamido)benzamide(**4h**).

Synthesized according to General Procedure 1. Crude **4h** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 90% yield (297 mg, 0.90 mmol) as a white solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 74.8-75.5 °C; **IR** (KBr): 3304, 3200, 3137, 3063, 1676, 1600, 1539, 1497, 1442, 1405, 1325, 1260, 1206, 1154, 1079, 831, 755, 696; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.65 (s, 1H, CHO), 8.26 (s, 1H, NH), 7.57 (d, *J* = 8.0 Hz, 2H, ArH), 7.51 (s, 1H, ArH), 7.32 (q, *J* = 7.3 Hz, 5H, ArH), 7.26 – 7.21 (m, 2H, ArH), 7.17 (d, *J* = 7.9 Hz, 2H, ArH), 7.11 (t, *J* = 7.4 Hz, 2H, ArH), 7.07 (d, *J* = 8.1 Hz, 1H, ArH), 2.41 (s, 3H, ArH); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 165.77, 163.32, 141.27, 139.24, 137.88, 136.61, 133.24, 132.24, 129.71, 129.62, 129.03, 128.83, 127.06, 124.49, 123.97, 119.90, 21.04. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{21}H_{18}FO_2N_2$ [M+H] $^+$, 331.1441; found, 331.1442.

4.9 Spectroscopic Data of **4i**

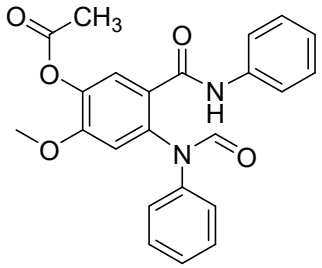


4,5-dimethoxy-*N*-phenyl-2-(*N*-phenylformamido)benzamide(**4i**).

Synthesized according to General Procedure 1. Crude **4i** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 89% yield (354 mg, 0.89 mmol) as a white solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 90.8-100.5 °C; **IR** (KBr): 3321, 3065, 2935, 2859, 1675, 1602, 1514, 1444, 1400, 1361, 1317, 1261, 1181, 1140, 1075, 1029, 877, 756, 690; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.62 (s,

1H, CHO), 8.39 (s, 1H, NH), 7.49 (d, *J* = 8.0 Hz, 2H, ArH), 7.26 (t, *J* = 7.8 Hz, 2H, ArH), 7.24 (s, 1H, ArH), 7.20 (dd, *J* = 21.5, 7.6 Hz, 4H, ArH), 7.13 (s, 1H, ArH), 7.08 (d, *J* = 7.9 Hz, 2H, ArH), 7.02 (t, *J* = 7.4 Hz, 1H, ArH), 6.53 (s, 1H, ArH), 3.86 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.25, 162.59, 150.33, 148.22, 140.17, 136.93, 128.79, 128.23, 127.99, 127.56, 126.08, 123.40, 122.49, 118.79, 110.55, 110.35, 55.22, 55.20. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{22}H_{20}O_4N_2$ [M+H] $^+$, 399.1315; found, 399.1312.

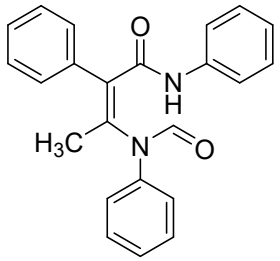
4.10 Spectroscopic Data of **4j**



2-methoxy-5-(phenylcarbamoyl)-4-(*N*-phenylformamido)phenyl acetate(**4j**).

Synthesized according to General Procedure 1. Crude **4j** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 89% yield (347 mg, 0.86 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 143.5-144.3 °C; **IR** (KBr): 3240, 3199, 3140, 3071, 2944, 2892, 1763, 1691, 1648, 1601, 1545, 1502, 1446, 1326, 1253, 1207, 1170, 1065, 1007, 913, 756, 695; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.64 (s, 1H, CHO), 8.24 (s, 1H, NH), 7.53 (d, *J* = 8.0 Hz, 2H, ArH), 7.41 (s, 1H, ArH), 7.36 (t, *J* = 7.7 Hz, 2H, ArH), 7.29 (ddd, *J* = 17.6, 8.7, 4.8 Hz, 3H, ArH), 7.26 (s, 1H, ArH), 7.20 (d, *J* = 7.9 Hz, 2H, ArH), 7.10 (t, *J* = 7.4 Hz, 1H, ArH), 6.71 (s, 1H, ArH), 3.79 (s, 3H, OCH_3), 2.32 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 168.32, 164.44, 163.07, 153.49, 140.98, 139.56, 137.86, 134.73, 129.81, 129.10, 129.00, 127.22, 124.50, 123.97, 123.52, 119.96, 112.80, 56.25, 20.54. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{23}H_{20}O_5N_2$ [M+H] $^+$, 405.1445; found, 405.1450.

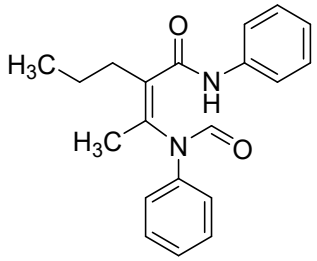
4.11 Spectroscopic Data of **4k**



(*Z*)-*N*,2-diphenyl-3-(*N*-phenylformamido)but-2-enamide(**4k**).

Synthesized according to General Procedure 1. Crude **4k** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 84% yield (299 mg, 0.84 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 161.7-162.5 °C; **IR** (KBr): 3323, 3198, 3062, 2927, 2859, 1684, 1636, 1588, 1540, 1495, 1440, 1383, 1338, 1313, 1277, 1210, 1771, 1079, 1034, 753, 699; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.47 (s, 1H, CHO), 8.16 (s, 1H, NH), 7.58 – 7.50 (m, 4H, ArH), 7.42 (t, *J* = 7.7 Hz, 4H, ArH), 7.41 – 7.34 (m, 4H, ArH), 7.30 (dd, *J* = 28.9, 7.3 Hz, 4H, ArH), 7.06 (t, *J* = 7.4 Hz, 1H, ArH), 1.81 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 165.81, 162.39, 139.17, 138.80, 137.61, 134.83, 133.03, 129.88, 128.93, 128.91, 128.68, 128.55, 127.60, 124.37, 124.18, 119.82, 17.36.**HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{23}H_{20}O_2N_2$ $[M+H]^+$, 357.1598; found, 357.1601.

4.12 Spectroscopic Data of **4l**

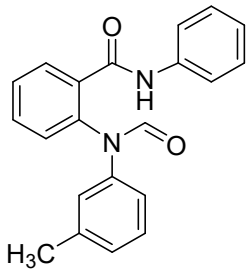


(*Z*)-*N*-phenyl-2-(1-(*N*-phenylformamido)ethylidene)pentanamide(**4l**).

Synthesized according to General Procedure 1. Crude **4l** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 91% yield (313 mg, 0.91 mmol) as a white solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 102.5-102.9 °C; **IR** (KBr): 3334, 3065, 2966, 2933, 2877, 1666, 1600, 1540, 1497, 1441, 1386, 1333, 1274, 1248, 1178, 1112, 1079, 1033, 912, 761, 691; **^{1}H NMR** (600 MHz,

Chloroform-*d*) δ 8.40 (s, 1H, CHO), 8.31 (s, 1H, NH), 7.56 (d, *J* = 7.2 Hz, 2H, ArH), 7.36 (t, *J* = 7.9 Hz, 2H, ArH), 7.31 – 7.21 (m, 6H, ArH), 7.07 (t, *J* = 7.4 Hz, 1H, ArH), 2.51 – 2.20 (m, 2H, $C\underline{H_2}CH_2CH_3$), 1.84 (s, 3H, CH_3), 1.66 (h, *J* = 7.5 Hz, 2H, $CH_2C\underline{H_2}CH_3$), 1.03 (t, *J* = 7.3 Hz, 3H, $CH_2CH_2C\underline{H_3}$); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 167.34, 162.63, 139.07, 138.95, 137.67, 130.53, 129.81, 128.98, 127.48, 124.26, 123.92, 119.68, 32.67, 21.49, 16.32, 13.85. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{20}H_{22}O_2N_2$ [M+H] $^+$, 345.1573; found, 345.1571.

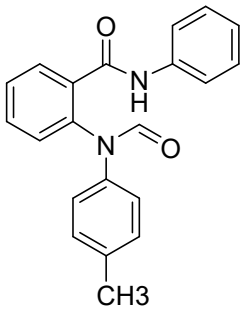
4.13 Spectroscopic Data of **5aa**



N-phenyl-2-(*N*-*m*-tolylformamido)benzamide(**5aa**).

Synthesized according to General Procedure 1. Crude **5aa** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 42% yield (74 mg, 0.21 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 131.0-131.6 °C; **IR** (KBr): 3266, 3202, 3137, 3080, 2928, 2881, 1669, 1604, 1550, 1497, 1446, 1330, 1260, 757, 716, 693; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.63 (s, 1H, CHO), 8.27 (s, 1H, NH), 7.72 – 7.67 (m, 2H, ArH), 7.61 – 7.55 (m, 4H, ArH), 7.54 – 7.42 (m, 4H, ArH), 7.33 (t, *J* = 7.8 Hz, 4H, ArH), 7.24 – 7.17 (m, 3H, ArH), 7.15 – 7.09 (m, 4H, ArH), 7.07 (dd, *J* = 8.1, 6.3 Hz, 3H, ArH), 6.98 (d, *J* = 7.3 Hz, 2H, ArH), 2.29 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 165.70, 163.26, 139.91, 137.87, 136.76, 136.04, 131.50, 130.31, 129.51, 129.05, 129.01, 128.94, 128.81, 128.04, 124.87, 124.54, 124.22, 121.33, 119.95, 21.32. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{21}H_{18}O_2N_2$ [M+Na] $^+$, 353.1260; found, 353.1258.

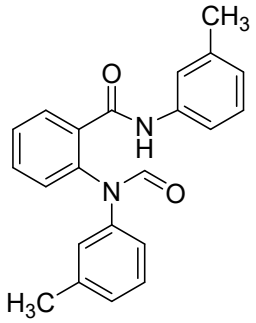
4.14 Spectroscopic Data of **5aa'**



N-phenyl-2-(*N*-*p*-tolylformamido)benzamide(**5aa'**).

Synthesized according to General Procedure 1. Crude **5aa'** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 40% yield (70 mg, 0.20 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 131.0-131.6 °C; **IR** (KBr): 3266, 3202, 3137, 3080, 2928, 2881, 1669, 1604, 1550, 1497, 1446, 1330, 1260, 757, 716, 693; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.60 (s, 1H, CHO), 8.29 (s, 1H, NH), 7.72 – 7.67 (m, 2H, ArH), 7.61 – 7.55 (m, 4H, ArH), 7.54 – 7.42 (m, 5H, ArH), 7.33 (t, *J* = 7.8 Hz, 5H, ArH), 7.24 – 7.17 (m, 4H, ArH), 7.15 – 7.04 (m, 8H, ArH), 6.98 (d, *J* = 7.3 Hz, 3H, ArH), 2.31 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 163.22, 141.06, 138.62, 137.87, 136.76, 136.12, 131.50, 130.31, 129.51, 129.05, 129.01, 128.94, 128.81, 128.04, 124.87, 124.54, 124.22, 121.33, 119.95, 20.89. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{21}H_{18}O_2N_2$ [M+Na] $^+$, 353.1260; found, 353.1258.

4.15 Spectroscopic Data of **5bb**

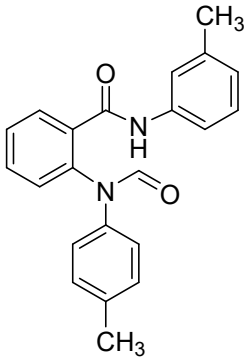


N-(*m*-tolyl)-2-(*N*-*m*-tolylformamido)benzamide(**5bb**).

Synthesized according to General Procedure 1. Crude **5bb** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 35% yield (63 mg, 0.17 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 123.5-124.4

°C; **IR** (KBr): 3273, 3153, 3099, 3038, 2924, 2879, 1669, 1601, 1557, 1491, 1445, 1406, 1341, 1257, 1175, 781, 716, 689; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 6.1 Hz, 1H, CHO), 8.29 (s, 1H, NH), 7.67 (d, *J* = 7.1 Hz, 3H, ArH), 7.45 (ddd, *J* = 26.1, 12.3, 6.0 Hz, 9H, ArH), 7.36 (t, *J* = 7.8 Hz, 2H, ArH), 7.29 – 7.12 (m, 8H, ArH), 7.12 – 7.03 (m, 7H, ArH), 6.95 (dd, *J* = 26.7, 8.8 Hz, 5H, ArH), 2.30 (s, 3H, CH_3), 2.28 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 165.55, 163.21, 141.12, 139.87, 138.68, 136.15, 135.39, 134.13, 131.42, 131.38, 130.30, 130.28, 129.50, 129.04, 128.98, 128.91, 128.85, 128.73, 128.00, 125.34, 124.87, 124.23, 121.35, 120.56, 120.54, 120.04, 120.01, 117.11, 117.09, 21.48, 21.32. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{22}H_{20}O_2N_2$ [M+Na] $^+$, 367.1417; found, 367.1416.

4.16 Spectroscopic Data of **5bb'**

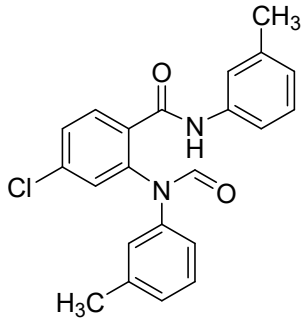


N-(*m*-tolyl)-2-(*N*-*p*-tolylformamido)benzamide(**5bb'**).

Synthesized according to General Procedure 1. Crude **5bb'** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 40% yield (73 mg, 0.20 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 123.5-124.4 °C; **IR** (KBr): 3273, 3153, 3099, 3038, 2924, 2879, 1669, 1601, 1557, 1491, 1445, 1406, 1341, 1257, 1175, 781, 716, 689; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.60 (d, *J* = 6.1 Hz, 1H, CHO), 8.26 (d, *J* = 9.9 Hz, 1H, NH), 7.67 (d, *J* = 7.1 Hz, 2H, ArH), 7.45 (ddd, *J* = 26.1, 12.3, 6.0 Hz, 7H, ArH), 7.36 (t, *J* = 7.8 Hz, 2H, ArH), 7.29 – 7.12 (m, 6H, ArH), 7.12 – 7.03 (m, 6H, ArH), 6.95 (dd, *J* = 26.7, 8.8 Hz, 4H, ArH), 2.32 (s, 3H, CH_3), 2.30 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 165.66, 163.17, 141.12, 138.95, 137.85, 136.79, 136.09, 131.42, 131.38, 130.30, 130.28, 129.50, 129.04, 128.98, 128.91, 128.85, 128.73, 128.00, 125.34, 124.87, 124.23, 121.35,

120.56, 120.54, 120.04, 120.01, 117.11, 117.09, 21.32, 20.89. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{22}H_{20}O_2N_2$ [M+Na] $^+$, 367.1417; found, 367.1416.

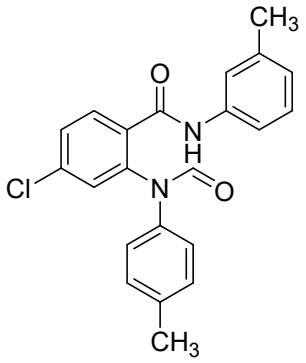
4.17 Spectroscopic Data of **5cc**



4-chloro-*N*-(*m*-tolyl)-2-(*N*-*m*-tolylformamido)benzamide(**5cc**).

Synthesized according to General Procedure 1. Crude **5cc** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 40% yield (75 mg, 0.20 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 84.2-84.8 °C; **IR** (KBr): 3317, 3042, 2925, 1675, 1599, 1519, 1489, 1409, 1327, 1155, 1105, 893, 830, 784, 698, 691; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 6.3 Hz, 1H, CHO), 8.24 (s, 1H, NH), 7.60 (dd, *J* = 8.4, 3.8 Hz, 2H, ArH), 7.45 – 7.31 (m, 6H, ArH), 7.27 – 7.18 (m, 3H, ArH), 7.17 (d, *J* = 8.1 Hz, 4H, ArH), 7.13 – 7.06 (m, 5H, ArH), 6.99 (d, *J* = 7.8 Hz, 2H, ArH), 6.93 (d, *J* = 7.6 Hz, 1H, ArH), 2.32 (s, 3H, CH_3), 2.31 (d, *J* = 2.4 Hz, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.79, 163.00, 139.00, 137.62, 137.37, 136.89, 135.14, 130.46, 130.45, 130.09, 129.65, 129.52, 129.04, 128.99, 128.87, 128.40, 125.54, 125.12, 124.48, 121.58, 120.61, 120.10, 117.16, 21.46, 21.32. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{22}H_{19}ClO_2N_2$ [M+H] $^+$, 379.1208; found, 379.1211.

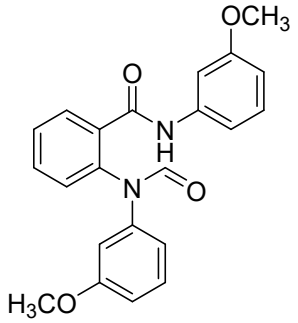
4.18 Spectroscopic Data of **5cc'**



4-chloro-*N*-(*m*-tolyl)-2-(*N*-*p*-tolylformamido)benzamide(**5cc'**).

Synthesized according to General Procedure 1. Crude **5cc'** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 34% yield (64 mg, 0.17 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 84.2-84.8 °C; **IR** (KBr): 3317, 3042, 2925, 1675, 1599, 1519, 1489, 1409, 1327, 1155, 1105, 893, 830, 784, 698, 691; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 6.2 Hz, 1H, CHO), 8.25 (s, 1H, NH), 7.60 (dd, *J* = 8.4, 3.8 Hz, 2H, ArH), 7.45 – 7.31 (m, 7H, ArH), 7.27 – 7.18 (m, 4H, ArH), 7.17 (d, *J* = 8.1 Hz, 5H, ArH), 7.13 – 7.06 (m, 6H, ArH), 6.99 (d, *J* = 7.8 Hz, 3H, ArH), 6.93 (d, *J* = 7.6 Hz, 2H, ArH), 2.32 (s, 3H, CH_3), 2.31 (d, *J* = 2.4 Hz, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.68, 163.05, 140.59, 139.00, 137.69, 135.10, 130.46, 130.45, 130.09, 129.65, 129.52, 129.04, 128.99, 128.87, 128.40, 125.54, 125.12, 124.48, 121.58, 120.61, 120.10, 117.16, 20.92, 20.89. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{22}H_{19}ClO_2N_2$ [M+H] $^+$, 379.1208; found, 379.1211.

4.19 Spectroscopic Data of **5dd**

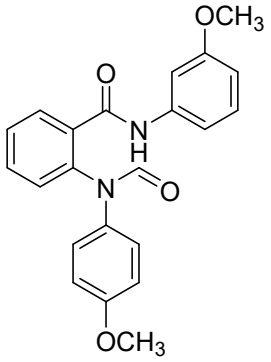


N-(3-methoxyphenyl)-2-(*N*-(3-methoxyphenyl)formamido)benzamide(**5dd**).

Synthesized according to General Procedure 1. Crude **5dd** was purified by FC on

silica gel (Petroleum ether/EtOAc 20:1), affording the product in 40% yield (79 mg, 0.2 mmol) as a white solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 162.9-164.0 °C; **IR** (KBr): 3266, 3207, 3139, 3083, 2962, 2929, 1667, 1605, 1555, 1511, 1462, 1415, 1348, 1245, 1180, 1037, 836; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.66 (s, 1H, CHO), 8.07 (s, 1H, NH), 7.72 – 7.66 (m, 3H, ArH), 7.48 (tdd, *J* = 18.5, 14.1, 7.8 Hz, 8H, ArH), 7.35 (s, 2H, ArH), 7.28 – 7.22 (m, 4H, ArH), 7.20 (dd, *J* = 8.3, 6.0 Hz, 4H, ArH), 7.15 (d, *J* = 8.8 Hz, 3H, ArH), 7.08 (d, *J* = 6.9 Hz, 2H, ArH), 6.86 (dd, *J* = 8.8, 6.5 Hz, 5H, ArH), 6.79 (t, *J* = 8.6 Hz, 3H, ArH), 6.74 (s, 1H, ArH), 6.69 (dd, *J* = 8.3, 2.5 Hz, 1H, ArH), 3.81 (s, 3H, CH_3), 3.79 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 165.44, 163.11, 160.60, 160.25, 158.84, 142.25, 139.06, 136.87, 136.28, 131.49, 131.43, 130.41, 129.76, 129.04, 128.99, 128.88, 128.78, 128.73, 126.17, 121.67, 116.30, 114.95, 114.25, 112.76, 112.14, 110.50, 110.22, 105.59, 55.41, 55.36. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{21}H_{18}O_3N_2$ [M+Na] $^+$, 399.1315; found, 399.1314.

4.20 Spectroscopic Data of **5dd'**

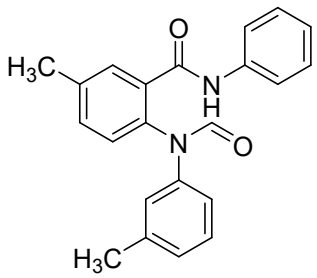


N-(4-methoxyphenyl)-2-(*N*-(4-methoxyphenyl)formamido)benzamide(**5dd'**).

Synthesized according to General Procedure 1. Crude **5dd'** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 40% yield (79 mg, 0.2 mmol) as a white solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 162.9-164.0 °C; **IR** (KBr): 3266, 3207, 3139, 3083, 2962, 2929, 1667, 1605, 1555, 1511, 1462, 1415, 1348, 1245, 1180, 1037, 836; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.55 (s, 1H, CHO), 8.27 (s, 1H, NH), 7.72 – 7.66 (m, 3H, ArH), 7.48 (tdd, *J* = 18.5, 14.1, 7.8 Hz,

8H, ArH), 7.35 (s, 2H, ArH), 7.28 – 7.22 (m, 4H, ArH), 7.20 (dd, *J* = 8.3, 6.0 Hz, 4H, ArH), 7.15 (d, *J* = 8.8 Hz, 3H, ArH), 7.08 (d, *J* = 6.9 Hz, 2H, ArH), 6.86 (dd, *J* = 8.8, 6.5 Hz, 5H, ArH), 6.79 (t, *J* = 8.6 Hz, 3H, ArH), 6.74 (s, 1H, ArH), 6.69 (dd, *J* = 8.3, 2.5 Hz, 1H, ArH), 3.77 (s, 3H, CH_3), 3.73 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 165.76, 163.33, 160.60, 160.25, 158.84, 142.25, 139.06, 136.87, 136.28, 131.49, 131.43, 130.41, 129.76, 129.04, 128.99, 128.88, 128.78, 128.73, 126.17, 121.67, 116.30, 114.95, 114.25, 112.76, 112.14, 110.50, 110.22, 105.59, 55.52. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{21}H_{18}O_3N_2$ [M+Na] $^+$, 399.1315; found, 399.1314.

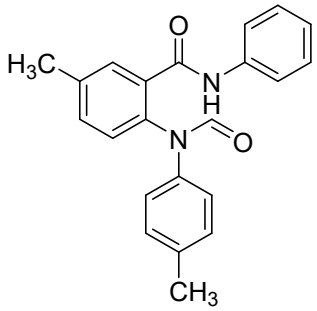
4.21 Spectroscopic Data of **5ee**



5-methyl-*N*-phenyl-2-(*N*-*m*-tolylformamido)benzamide(**5ee**).

Synthesized according to General Procedure 1. Crude **5ee** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 45% yield (84 mg, 0.23 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 68.8-70.2 °C; **IR** (KBr): 3306, 3201, 3039, 2983, 2926, 1675, 1604, 1541, 1499, 1442, 1327, 1258, 1201, 1154, 1082, 1035, 901, 821, 757, 692, 625, 551; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.61 (s, 1H, CHO), 8.32 (s, 1H, NH), 7.58 (t, *J* = 7.1 Hz, 4H, ArH), 7.51 (s, 2H, ArH), 7.32 (q, *J* = 6.0, 4.3 Hz, 7H, ArH), 7.25 (s, 1H, ArH), 7.21 (t, *J* = 8.2 Hz, 2H, ArH), 7.14 – 7.03 (m, 10H, ArH), 6.96 (d, *J* = 6.0 Hz, 3H, ArH), 2.41 (s, 3H, CH_3), 2.30 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 165.79, 163.44, 139.87, 139.17, 137.90, 136.52, 133.27, 132.22, 130.28, 129.66, 129.48, 129.04, 128.80, 128.72, 127.93, 124.68, 124.47, 124.02, 121.12, 119.88, 21.32, 21.05. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{22}H_{20}O_2N_2$ [M+Na] $^+$, 367.1417; found, 367.1415.

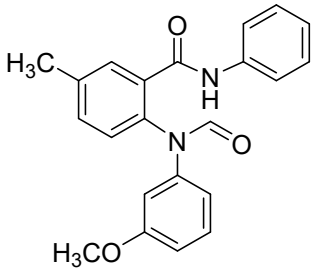
4.22 Spectroscopic Data of **5ee'**



5-methyl-*N*-phenyl-2-(*N*-*p*-tolylformamido)benzamide(**5ee'**).

Synthesized according to General Procedure 1. Crude **5ee'** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 40% yield (73 mg, 0.20 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 68.8-70.2 °C; **IR** (KBr): 3306, 3201, 3039, 2983, 2926, 1675, 1604, 1541, 1499, 1442, 1327, 1258, 1201, 1154, 1082, 1035, 901, 821, 757, 692, 625, 551; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.63 (s, 1H, CHO), 8.29 (s, 1H, NH), 7.58 (t, *J* = 7.1 Hz, 4H, ArH), 7.51 (s, 2H, ArH), 7.32 (q, *J* = 6.0, 4.3 Hz, 7H, ArH), 7.25 (s, 1H, ArH), 7.21 (t, *J* = 8.2 Hz, 2H, ArH), 7.14 – 7.03 (m, 10H, ArH), 6.96 (d, *J* = 6.0 Hz, 3H, ArH), 2.41 (s, 3H, CH_3), 2.28 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 165.82, 163.41, 141.16, 139.17, 138.73, 137.14, 133.35, 132.22, 130.28, 129.66, 129.48, 129.04, 128.80, 128.72, 127.93, 124.68, 124.47, 124.02, 121.12, 119.88, 21.05, 20.88. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{22}H_{20}O_2N_2$ [M+Na] $^+$, 367.1417; found, 367.1415.

4.23 Spectroscopic Data of **5ff**

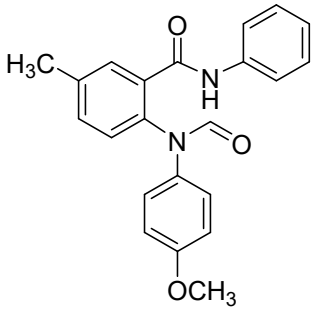


2-(*N*-(3-methoxyphenyl)formamido)-5-methyl-*N*-phenylbenzamide(**5ff**).

Synthesized according to General Procedure 1. Crude **5ff** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 43% yield (84 mg, 0.22

mmol) as a white solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 103.6-104.4 °C; **IR** (KBr): 3320, 3135, 3069, 2931, 1679, 1601, 1538, 1498, 1448, 1327, 1226, 1043, 835, 756, 701, 684; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.67 (s, 1H, CHO), 8.21 (s, 1H, NH), 7.58 (d, *J* = 8.0 Hz, 2H, ArH), 7.51 (s, 1H, ArH), 7.33 (t, *J* = 8.0 Hz, 3H, ArH), 7.27 – 7.20 (m, 2H, ArH), 7.10 (t, *J* = 7.8 Hz, 2H, ArH), 6.77 (ddd, *J* = 16.3, 8.2, 2.3 Hz, 2H, ArH), 6.70 (t, *J* = 2.3 Hz, 1H, ArH), 3.71 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 165.75, 163.35, 160.58, 142.30, 139.33, 137.86, 136.58, 133.11, 132.27, 130.41, 129.63, 129.06, 128.81, 124.50, 119.84, 116.08, 112.70, 109.97, 55.39, 21.06. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{22}H_{20}O_3N_2$ $[M+Na]^+$, 383.1366; found, 383.1366.

4.24 Spectroscopic Data of **5ff'**

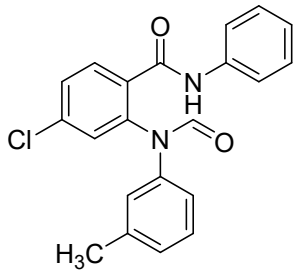


2-(*N*-(4-methoxyphenyl)formamido)-5-methyl-*N*-phenylbenzamide(**5ff'**).

Synthesized according to General Procedure 1. Crude **5ff'** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 35% yield (65 mg, 0.17 mmol) as a white solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 93.7-94.5 °C; **IR** (KBr): 3310, 3136, 3057, 2931, 1680, 1603, 1508, 1443, 1406, 1328, 1250, 1179, 1083, 1035, 958, 833, 757, 697; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.55 (s, 1H, CHO), 8.31 (s, 1H, NH), 7.60 (d, *J* = 7.9 Hz, 2H, ArH), 7.49 (s, 1H, ArH), 7.34 (t, *J* = 7.9 Hz, 2H, ArH), 7.30 (dd, *J* = 8.2, 2.1 Hz, 1H, ArH), 7.26 (s, 1H, ArH), 7.12 (d, *J* = 15.0 Hz, 3H, ArH), 7.08 (d, *J* = 8.1 Hz, 1H, ArH), 6.85 – 6.82 (m, 2H, ArH), 3.76 (s, 3H, OCH_3), 2.41 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 165.91, 163.51, 158.75, 139.09, 137.90, 136.38, 134.20, 133.57, 132.20, 129.59, 129.07, 128.56, 125.99, 124.49, 119.86, 114.90, 55.52, 21.03. **HRMS** (TOF-ESI$^+$): *m/z* calcd for

$C_{22}H_{20}O_3N_2$ [M+Na] $^+$, 383.1366; found, 383.1367.

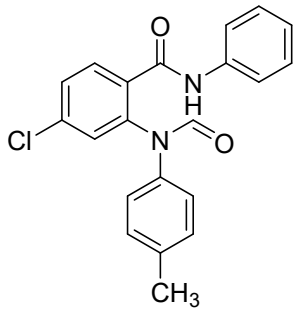
4.25 Spectroscopic Data of **5gg**



4-chloro-*N*-phenyl-2-(*N*-*m*-tolylformamido)benzamide(**5gg**).

Synthesized according to General Procedure 1. Crude **5gg** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 52% yield (94 mg, 0.26 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 164.8-165.5 °C; **IR** (KBr): 3320, 3204, 3140, 3071, 2961, 2945, 1675, 1599, 1544, 1493, 1441, 1412, 1328, 1280, 1156, 1103, 760, 698, 690; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.59 (s, 1H, CHO), 8.22 (s, 1H, NH), 7.63 (dd, *J* = 8.3, 3.9 Hz, 2H, ArH), 7.58 – 7.53 (m, 3H, ArH), 7.45 – 7.35 (m, 3H, ArH), 7.35 – 7.22 (m, 7H, ArH), 7.20 – 7.05 (m, 8H, ArH), 6.99 (d, *J* = 5.9 Hz, 2H, ArH), 2.31 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.80, 163.08, 140.53, 140.15, 137.65, 136.99, 135.10, 130.49, 130.11, 129.68, 129.11, 129.08, 128.97, 128.44, 125.09, 124.74, 124.45, 121.54, 120.00, 21.33. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{21}H_{17}ClO_2N_2$ [M+H] $^+$, 365.1051; found, 365.1051.

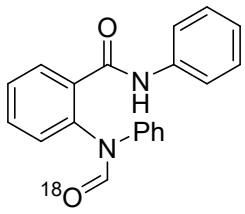
4.26 Spectroscopic Data of **5gg'**



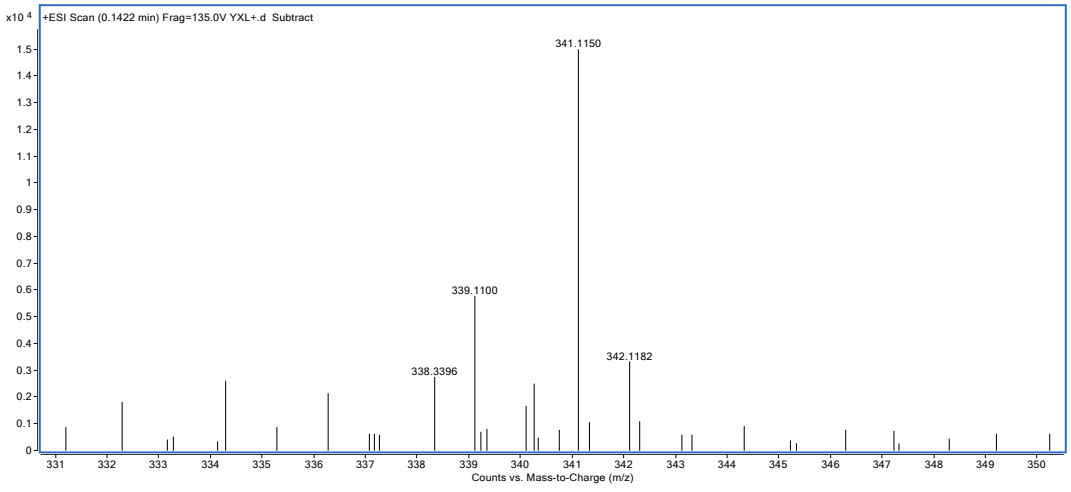
4-chloro-*N*-phenyl-2-(*N*-*p*-tolylformamido)benzamide(**5gg'**).

Synthesized according to General Procedure 1. Crude **5gg'** was purified by FC on silica gel (Petroleum ether/EtOAc 20:1), affording the product in 26% yield (47 mg, 0.13 mmol) as a yellow solid. R_f (Petroleum ether/EtOAc 5:1) 0.4. Mp: 164.8-165.5 °C; **IR** (KBr): 3320, 3204, 3140, 3071, 2961, 2945, 1675, 1599, 1544, 1493, 1441, 1412, 1328, 1280, 1156, 1103, 760, 698, 690; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.56 (s, 1H, CHO), 8.24 (s, 1H, NH), 7.63 (dd, *J* = 8.3, 3.9 Hz, 3H, ArH), 7.58 – 7.53 (m, 6H, ArH), 7.42 (ddd, *J* = 7.4, 5.1, 2.0 Hz, 3H, ArH), 7.40 – 7.22 (m, 15H, ArH), 7.20 – 7.05 (m, 15H, ArH), 6.99 (d, *J* = 5.9 Hz, 4H, ArH), 2.33 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.80, 163.12, 140.53, 138.08, 137.74, 137.38, 135.11, 130.49, 130.11, 129.84, 129.68, 129.11, 129.08, 129.06, 128.97, 128.44, 125.09, 124.74, 124.45, 121.54, 120.00, 20.93. **HRMS** (TOF-ESI$^+$): *m/z* calcd for $C_{21}H_{17}ClO_2N_2$ [M+H] $^+$, 365.1051; found, 365.1051.

4.27 Spectroscopic Data of ^{18}O-**4a**



HRMS (TOF-ESI$^+$): *m/z* calcd for $C_{20}H_{16}O^{18}ON_2$ [M+Na] $^+$, 341.1146; found, 341.1150.



5. X-ray Structure and Data of **4d**

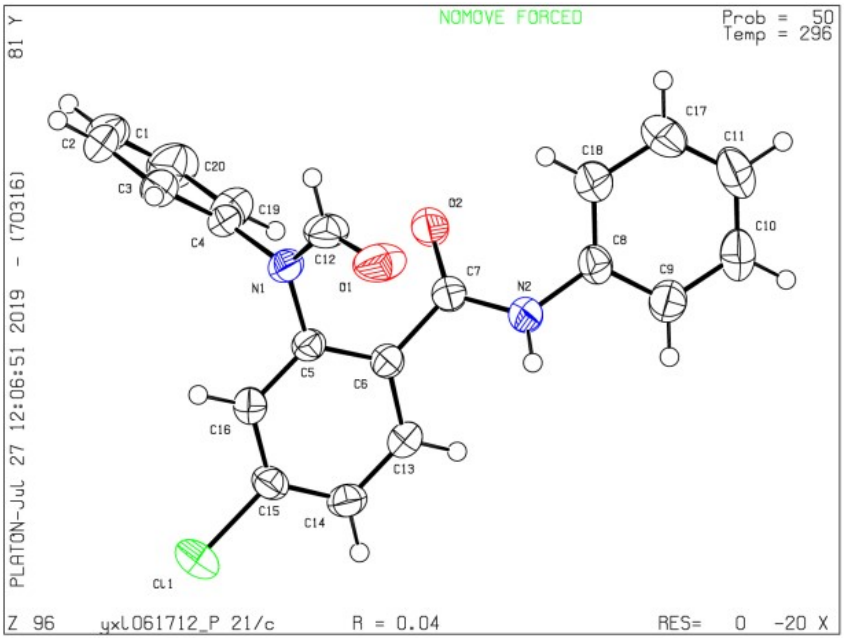


Figure S1. X-Ray crystal structure of **4d**, ellipsoids was drawn at the 50% probability level.

Table S1. Crystal data and structure refinement for **4d**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) yxl061712_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: yxl061712_0m

Bond precision: C-C = 0.0023 A Wavelength=0.71073

Cell: a=7.4409(10) b=12.1832(16) c=19.152(3)
alpha=90 beta=91.399(2) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1735.7(4)	1735.7(4)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C20 H15 Cl N2 O2	?
Sum formula	C20 H15 Cl N2 O2	C20 H15 Cl N2 O2
Mr	350.79	350.79
Dx,g cm-3	1.342	1.342
Z	4	4
Mu (mm-1)	0.235	0.235
F000	728.0	728.0
F000'	728.88	
h,k,lmax	9,15,25	9,15,24
Nref	4052	4011
Tmin,Tmax	0.956,0.972	
Tmin'	0.956	

Correction method= Not given

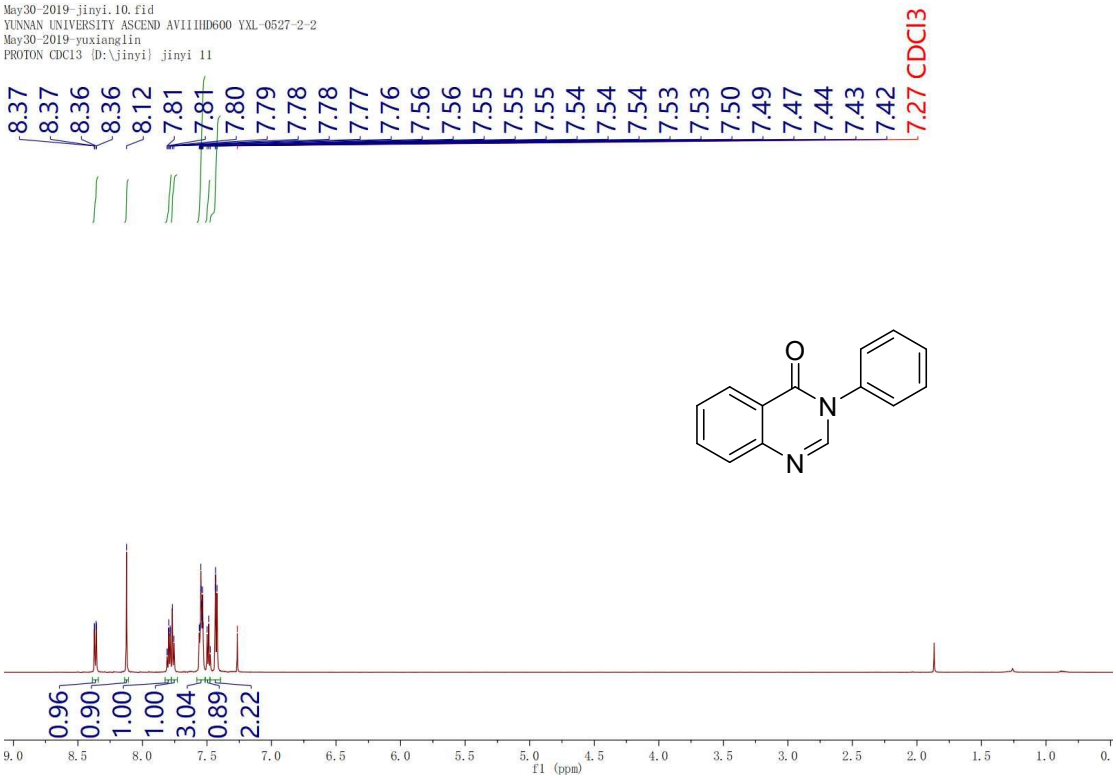
Data completeness= 0.990 Theta(max)= 27.659

R(reflections)= 0.0379(3158) wR2(reflections)= 0.1404(4011)

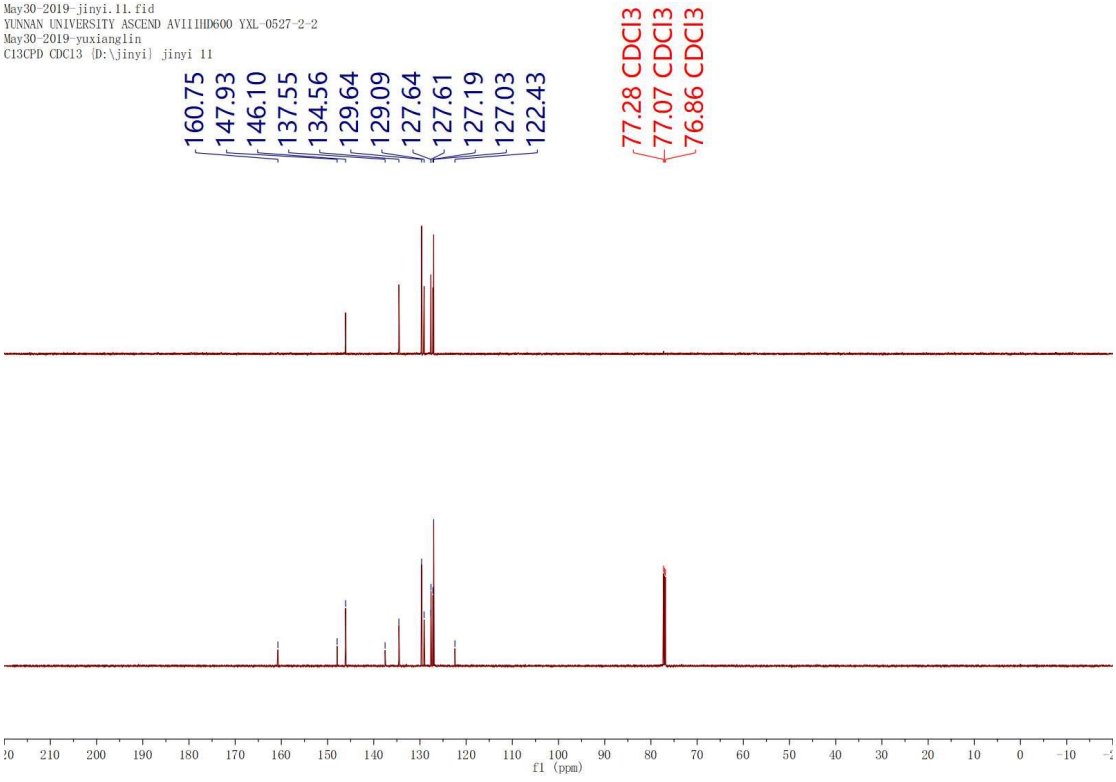
S = 1.004 Npar= 226

Compound **4d** (50mg) was add to a 10mL sample bottle, following to add DCM (2mL), n-hexane (2.5mL) and toluene (0.1mL), then seal the bottle with a parafilm, and poke 15 small holes on the parafilm, place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it for single crystal diffraction test to obtain relevant data. Instrument model：
Intensity data for single crystals of each complex were collected on a BRUKER SMART APEX II CCD detector with graphite-monochromatized Mo Kα radiation (k = 0.071073 nm). The structures were solved by direct method using the program SHELXS-97 and subsequent Fourier difference techniques, and refined anisotropically by full matrix least-squares on F2 using SHELXL-97.

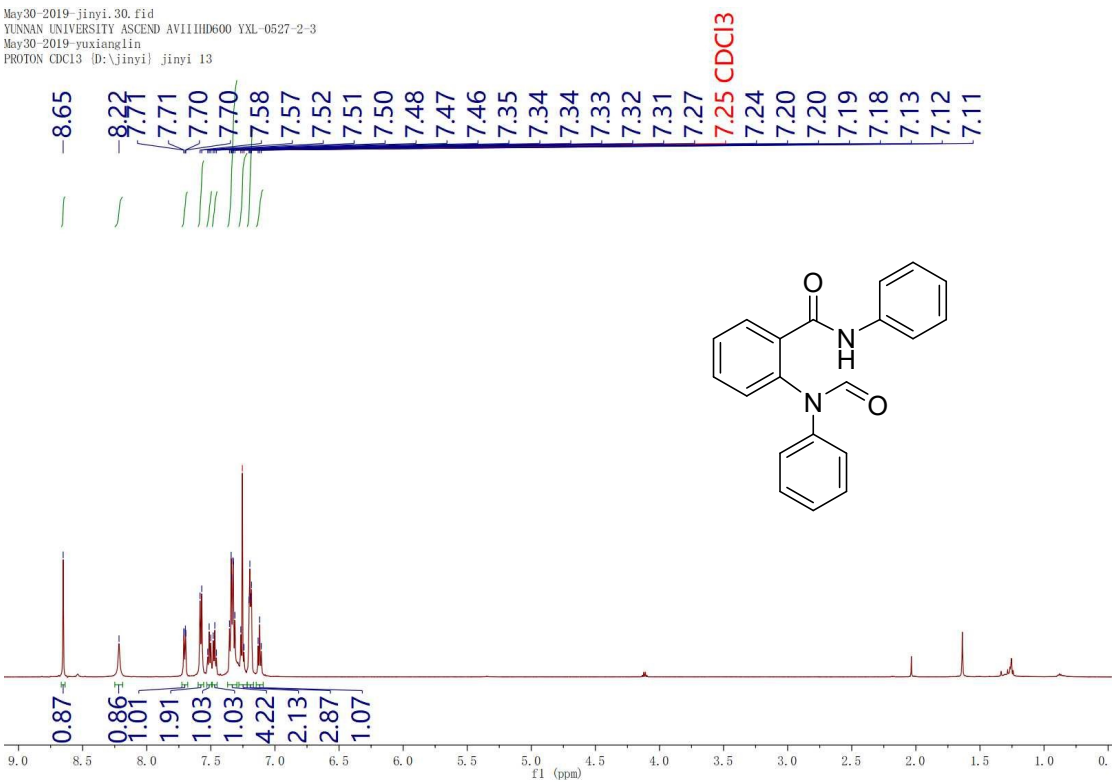
6. ^{1}H NMR and ^{13}C NMR Spectra of These Compounds



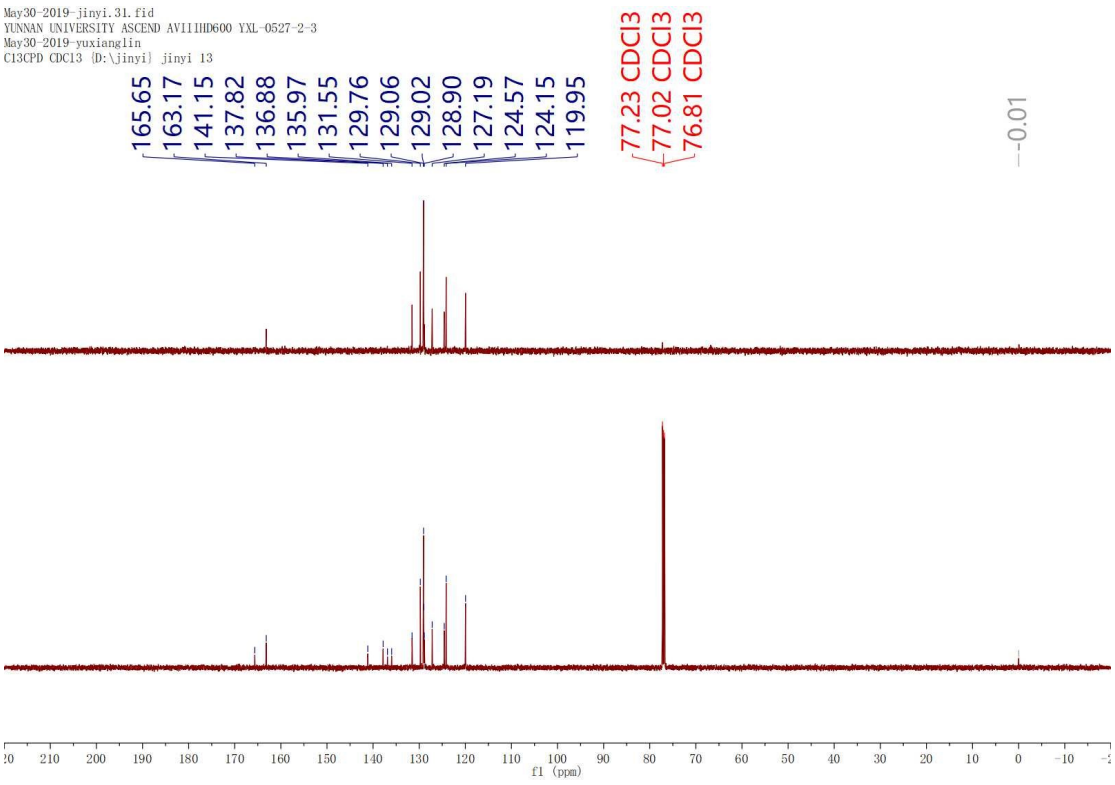
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **3a**



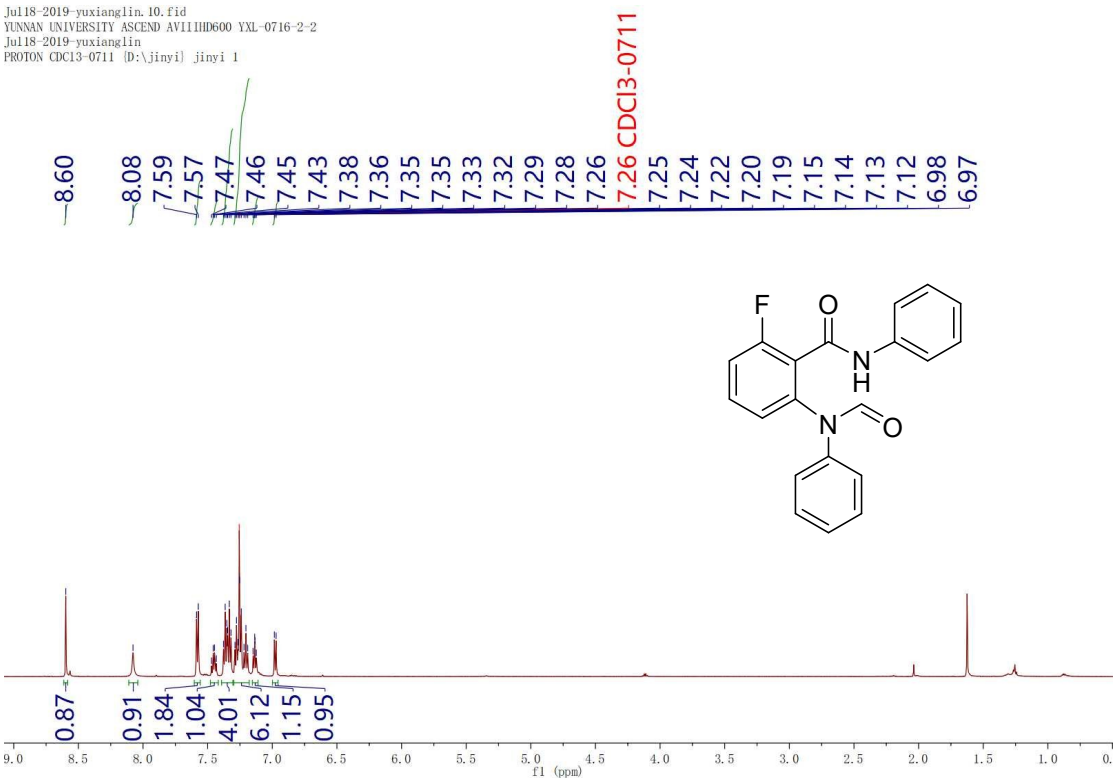
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **3a**



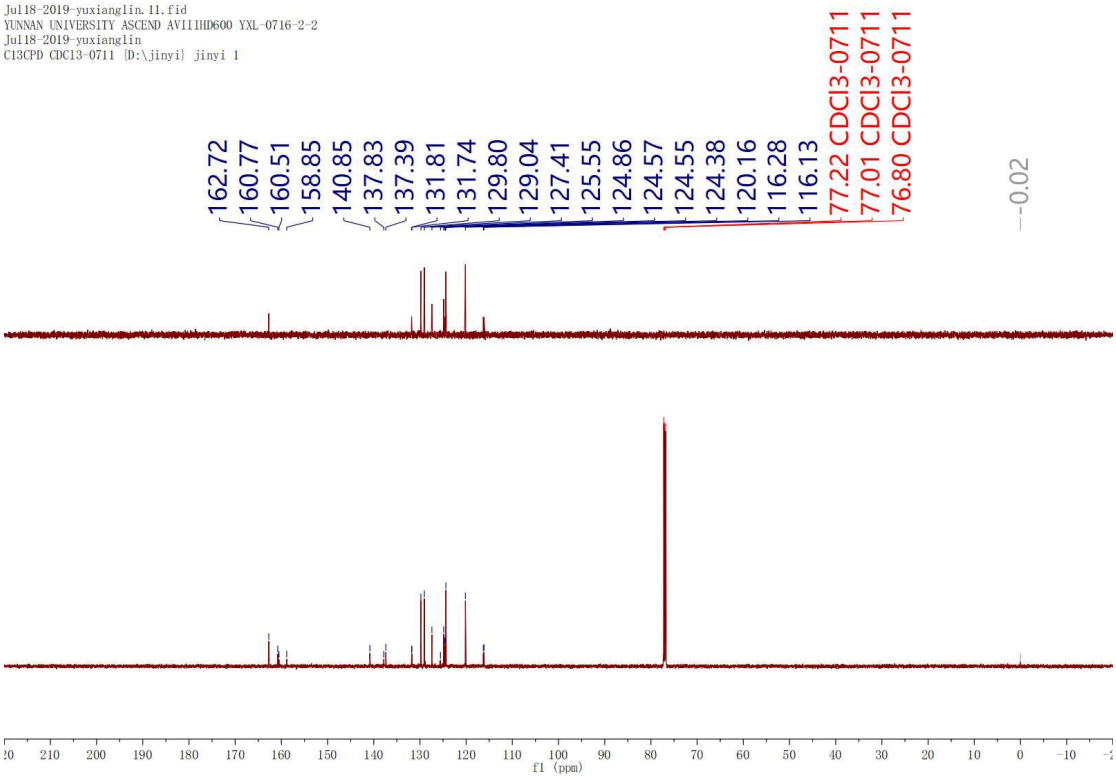
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **4a**



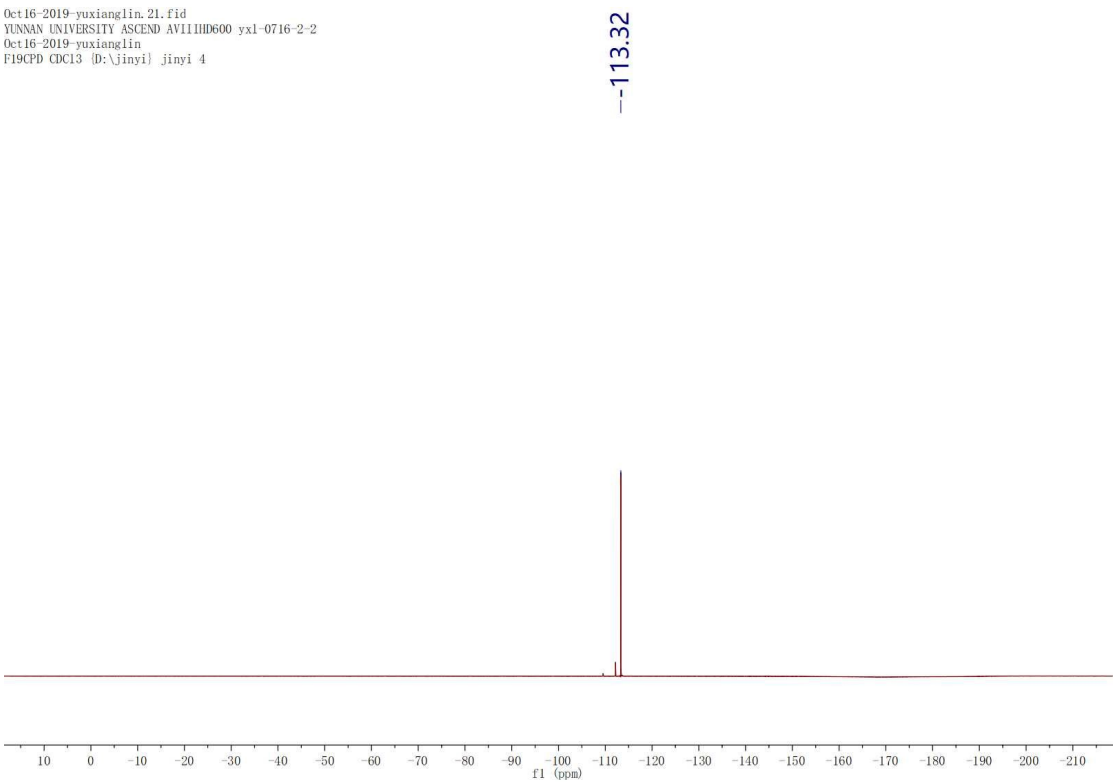
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **4a**



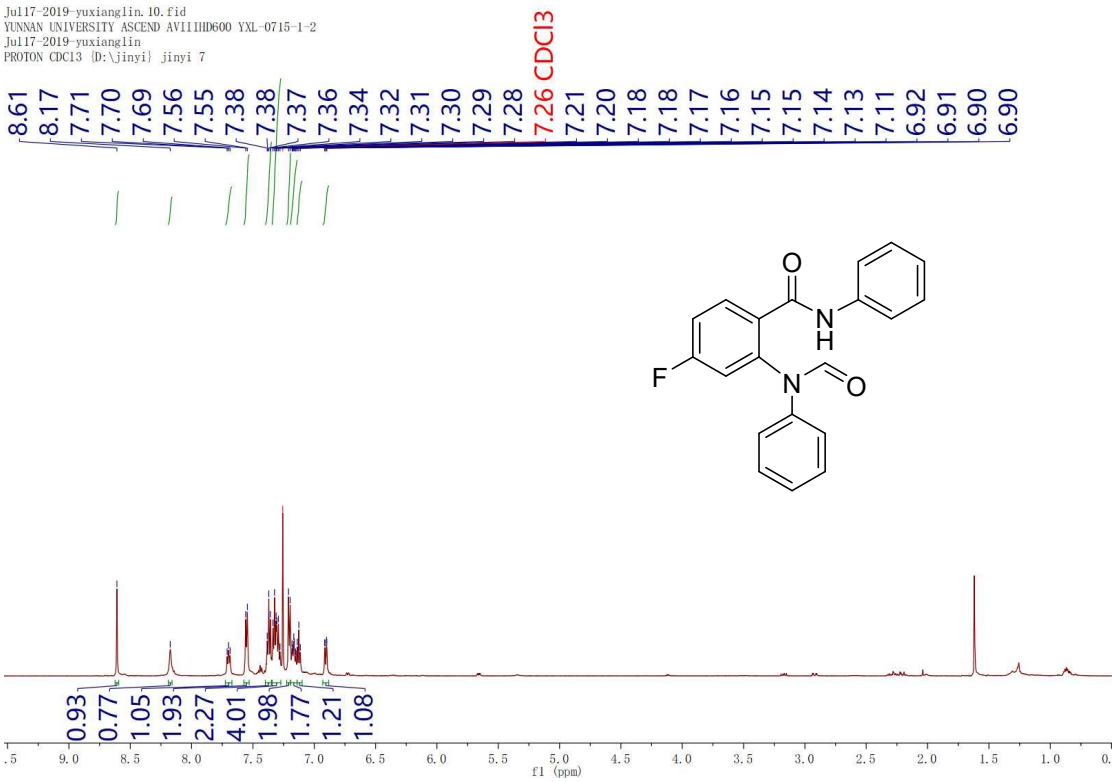
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **4b**



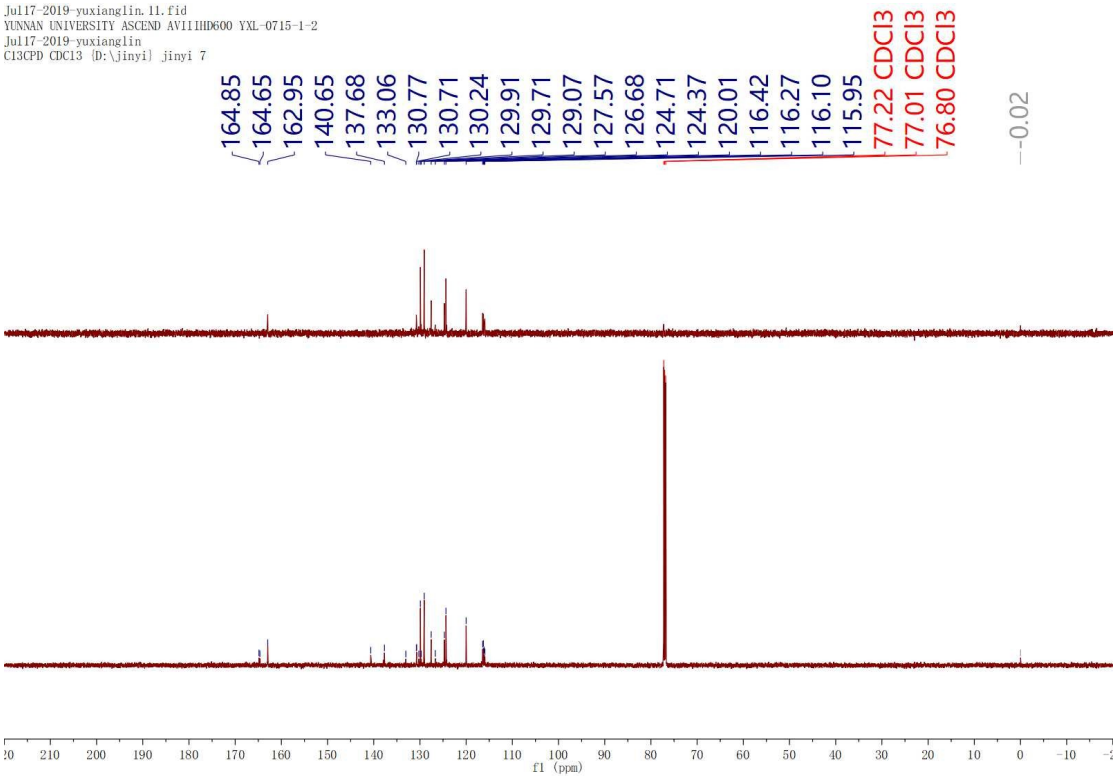
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **4b**



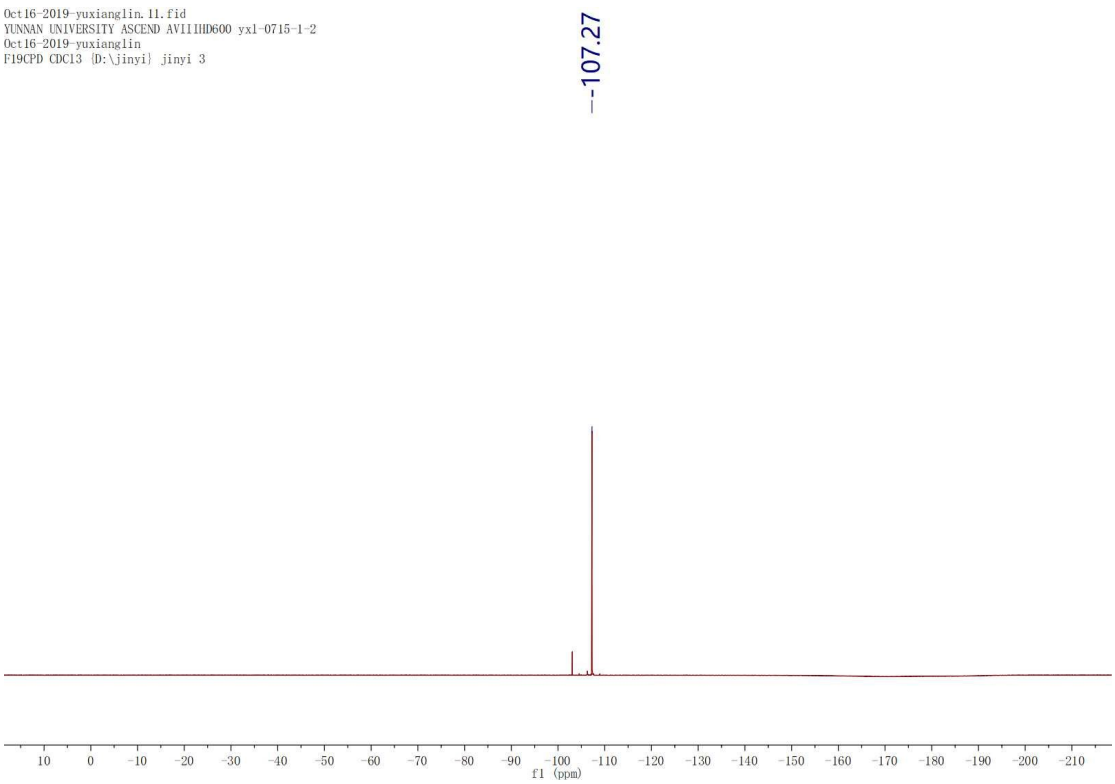
^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of compound **4b**



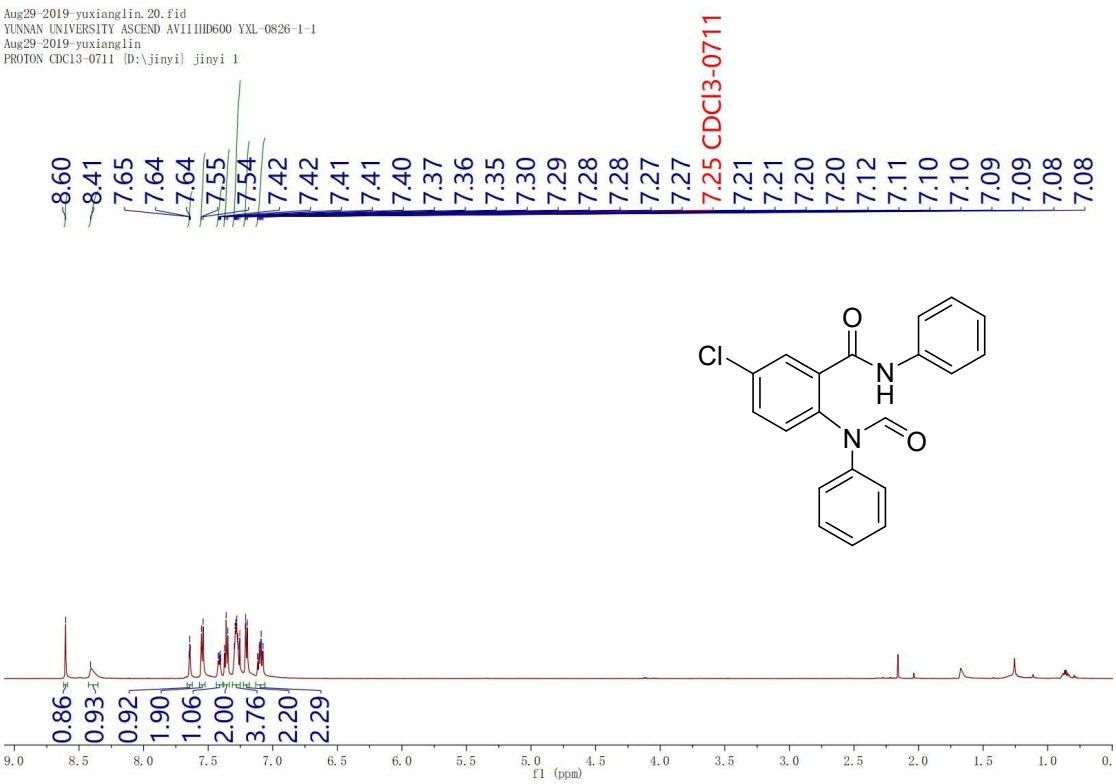
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **4c**



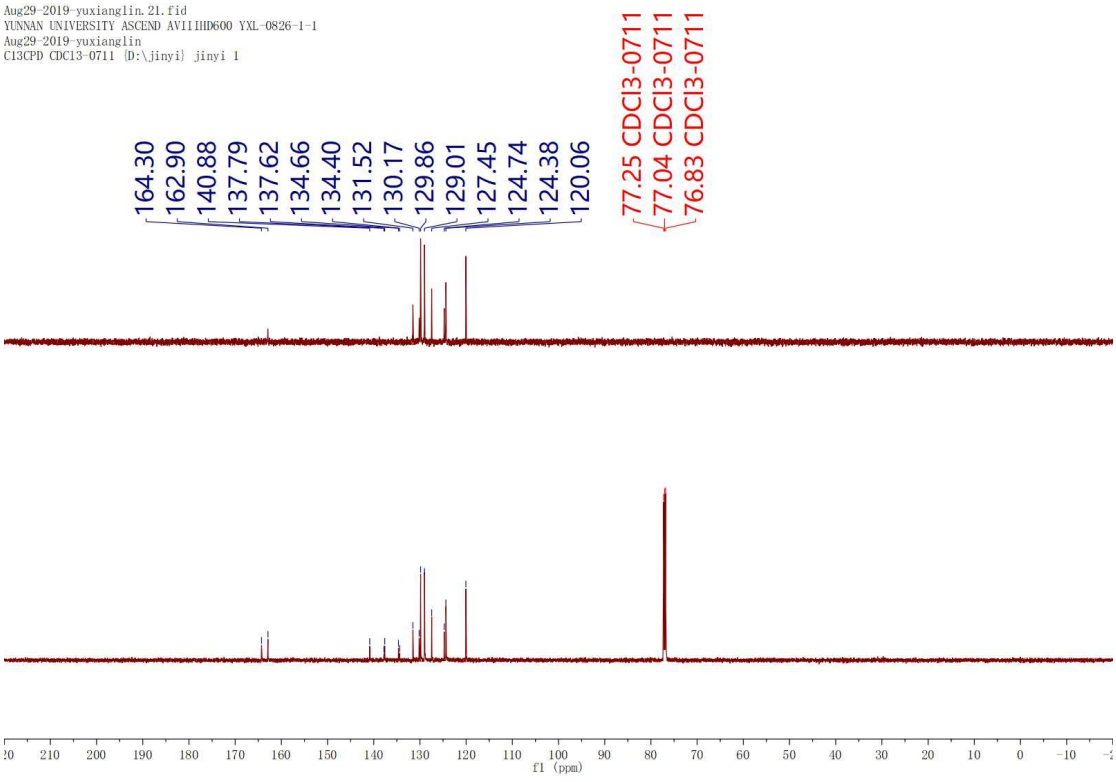
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **4c**



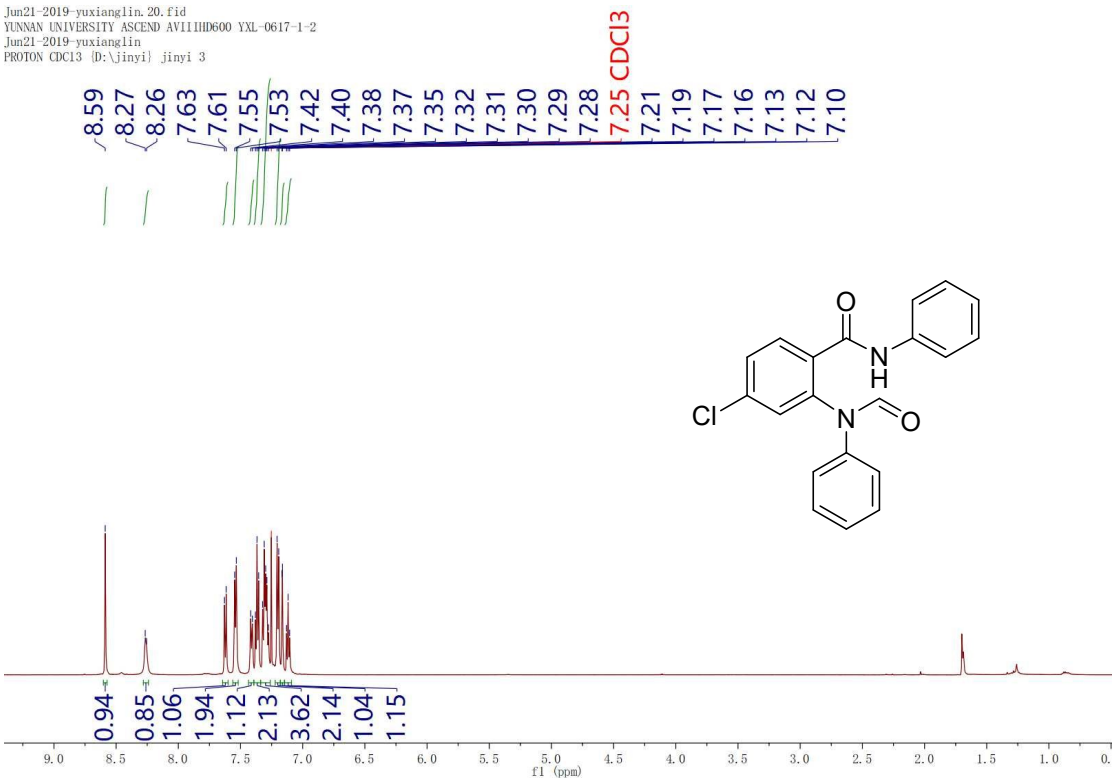
^{19}F-NMR (565 MHz, $CDCl_3$) spectrum of compound **4c**



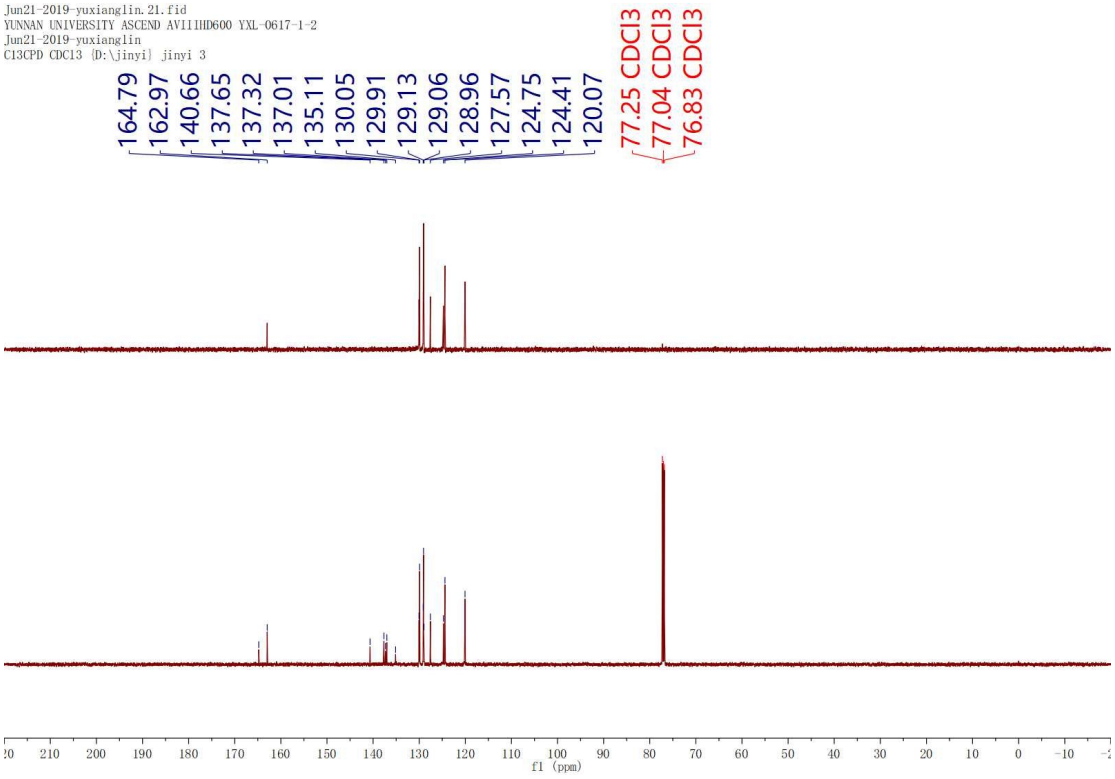
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **4d**



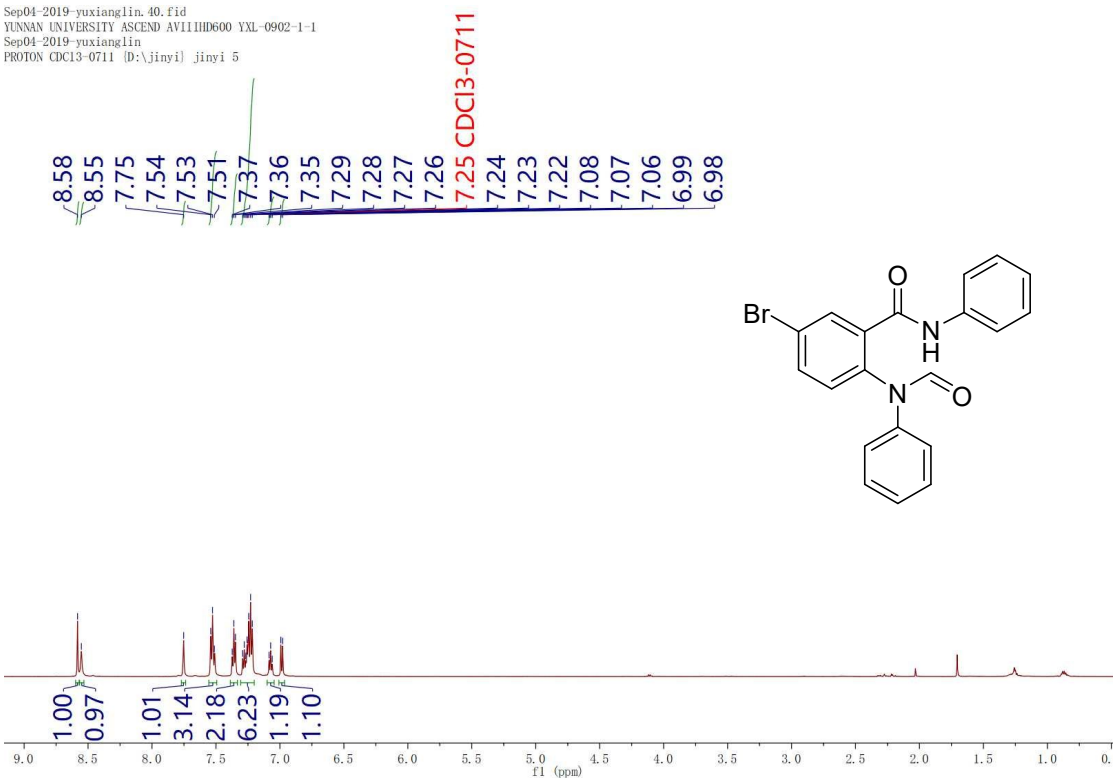
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **4d**



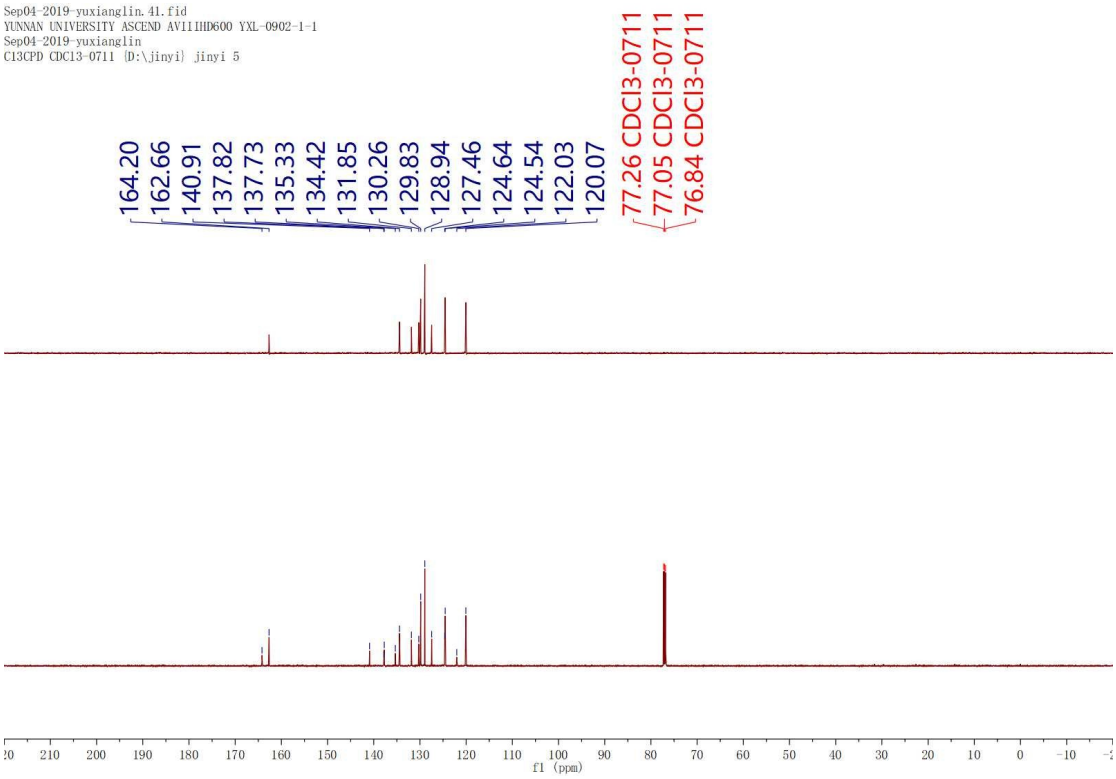
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **4e**



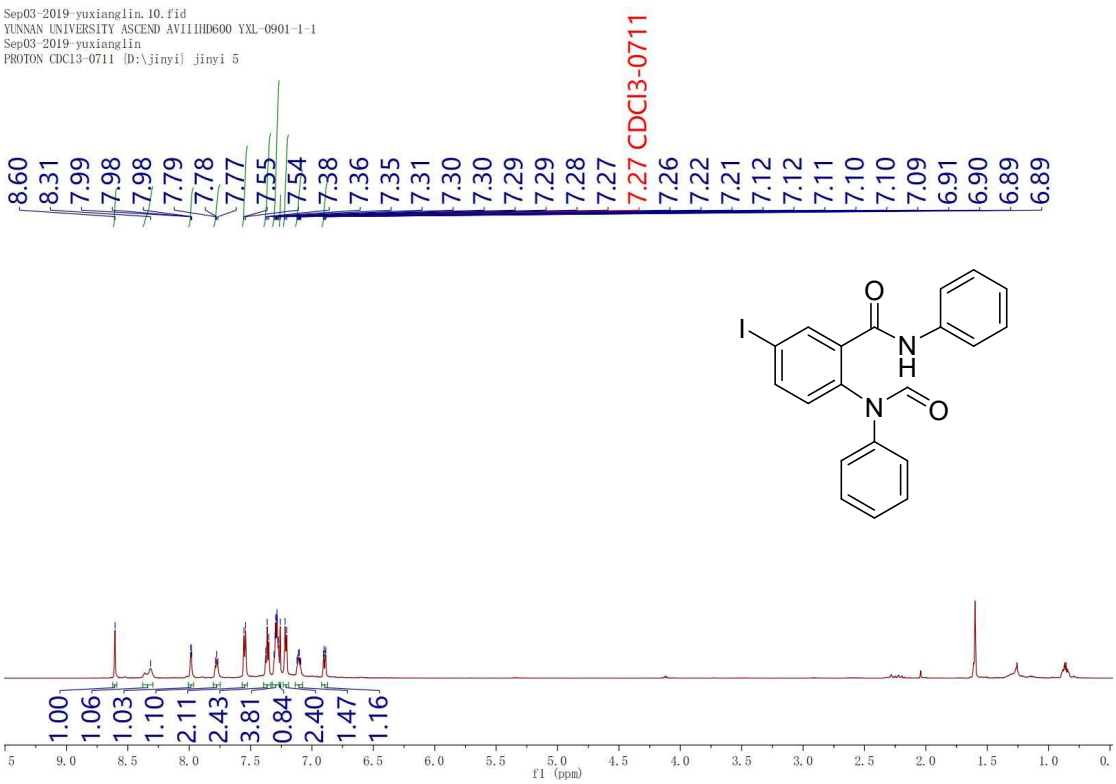
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **4e**



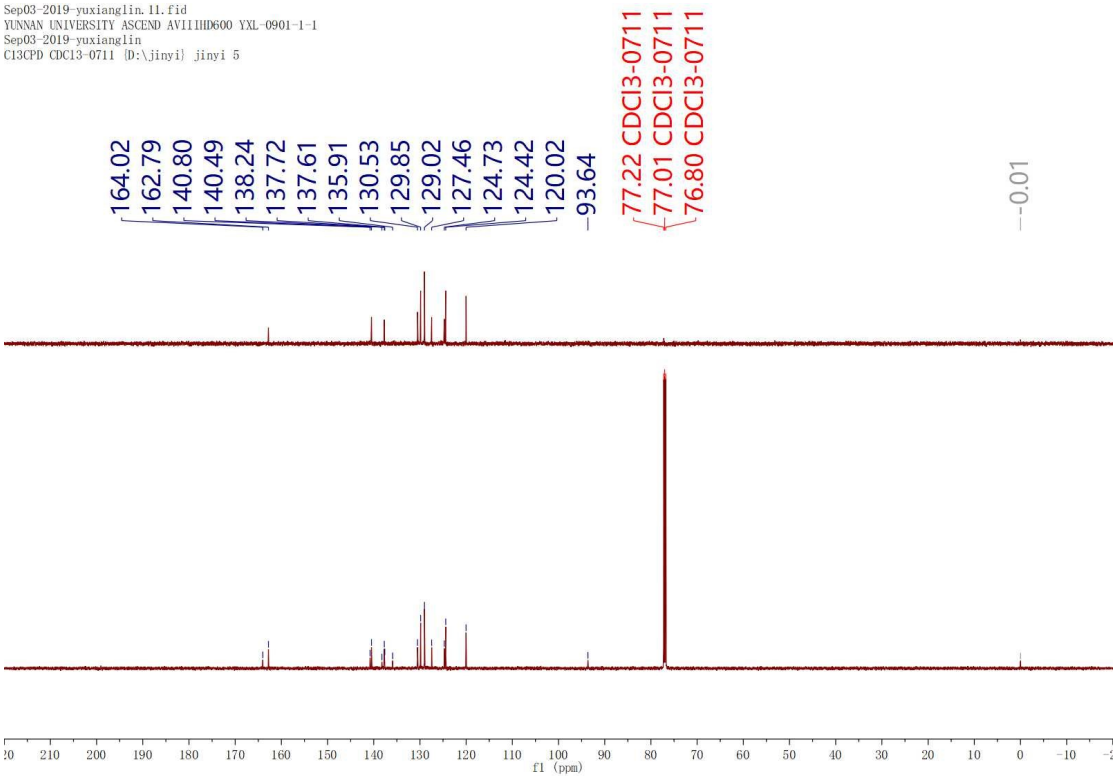
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **4f**



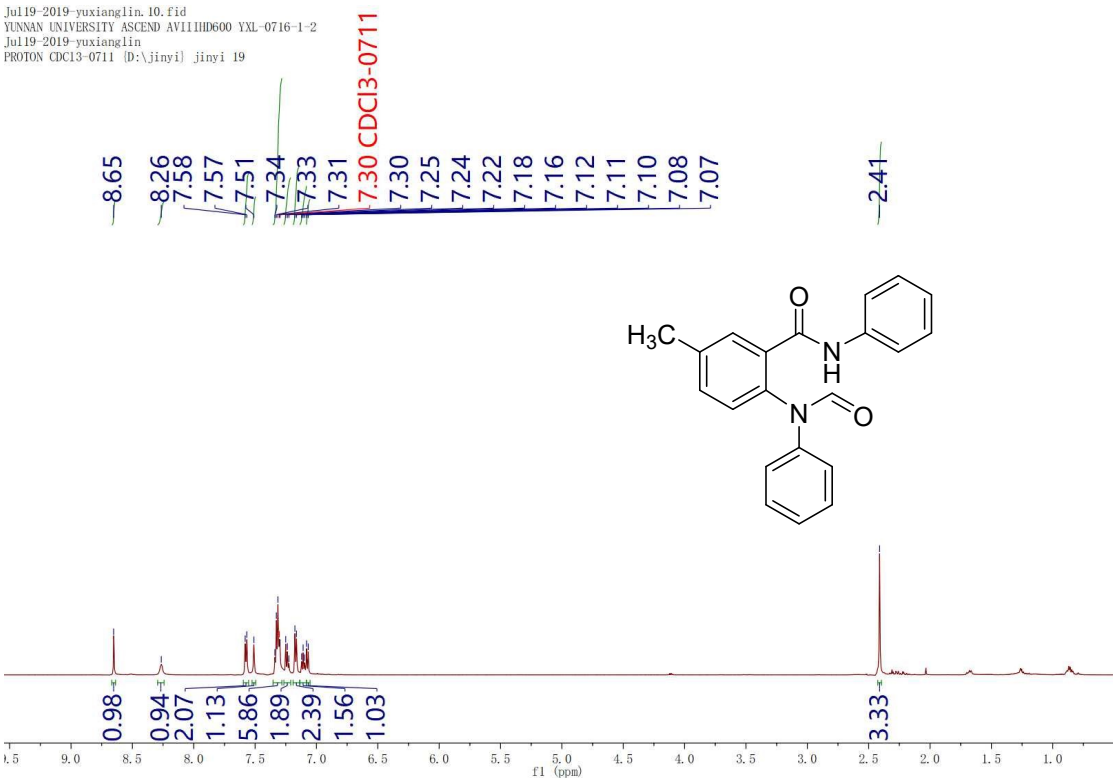
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **4f**



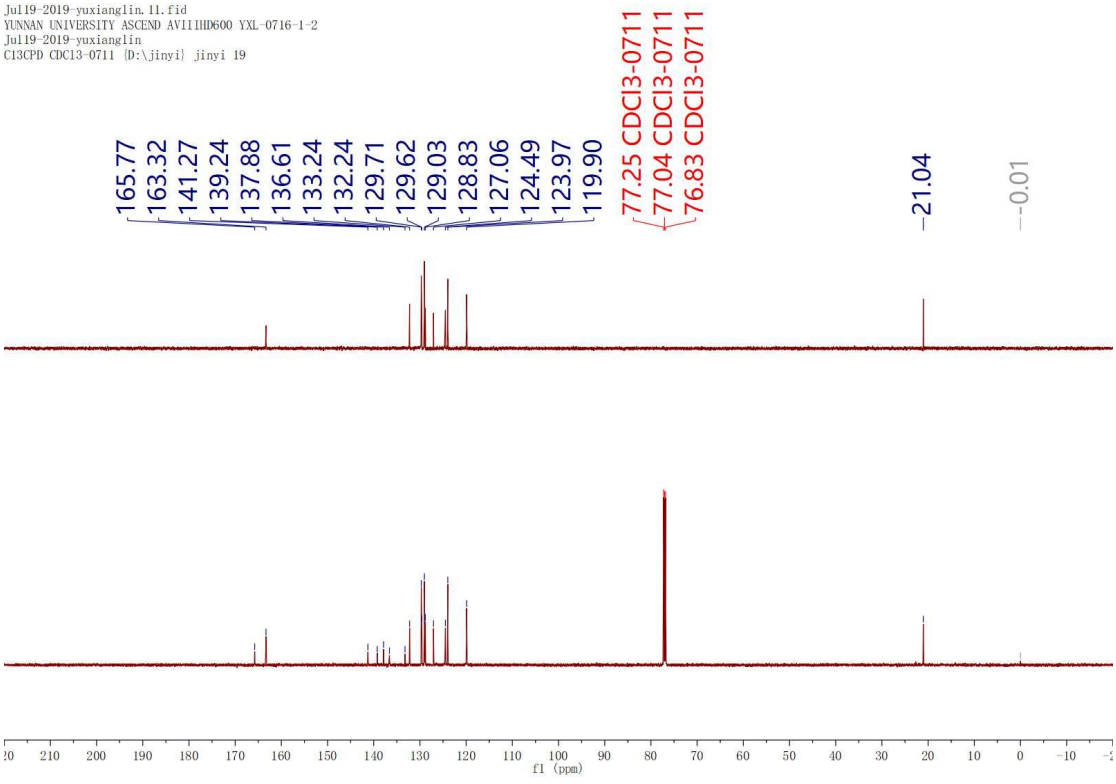
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **4g**



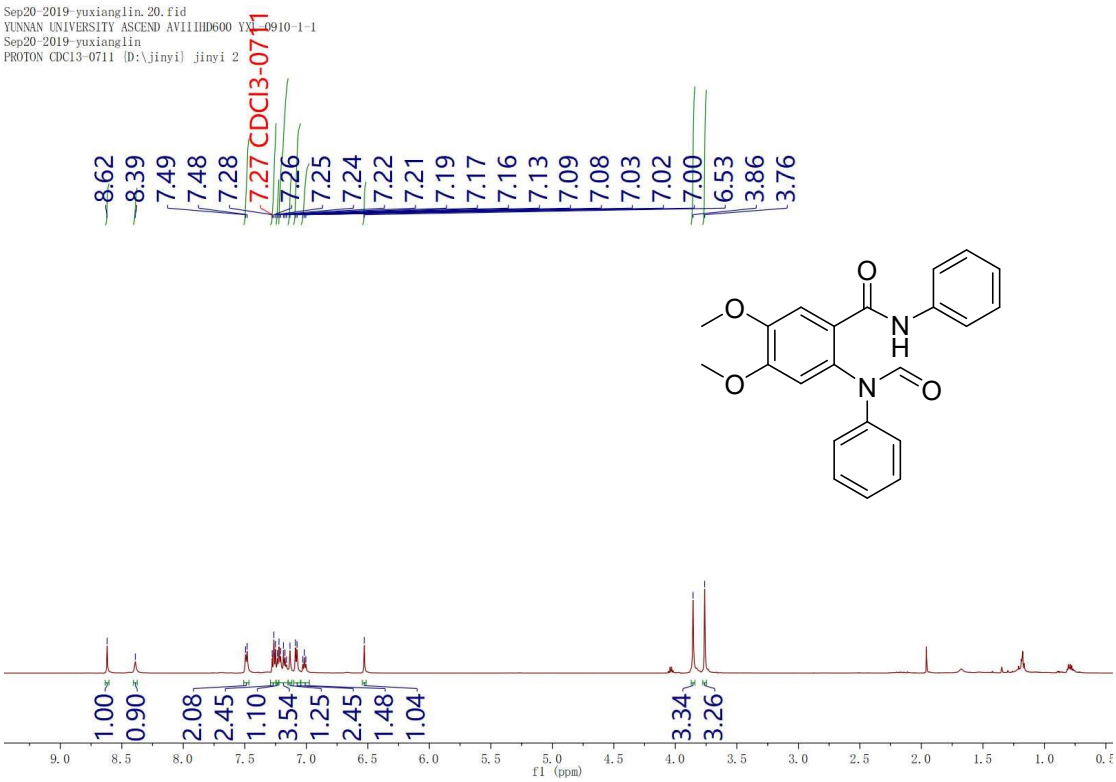
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **4g**



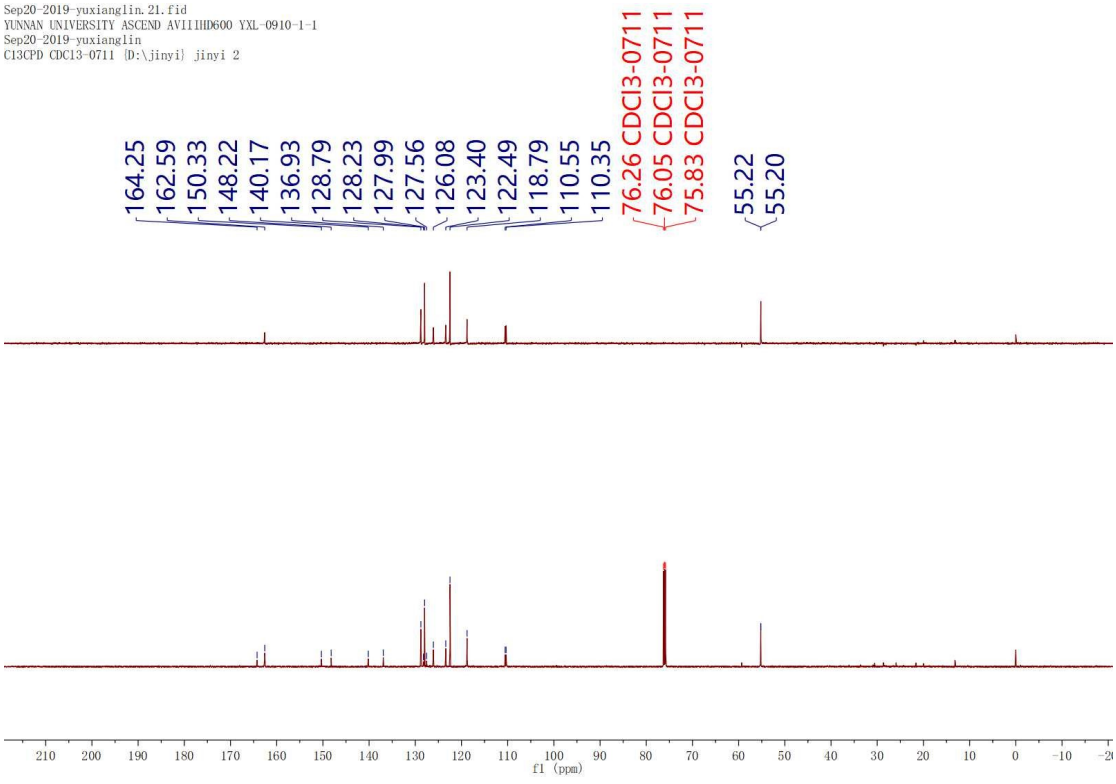
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **4h**



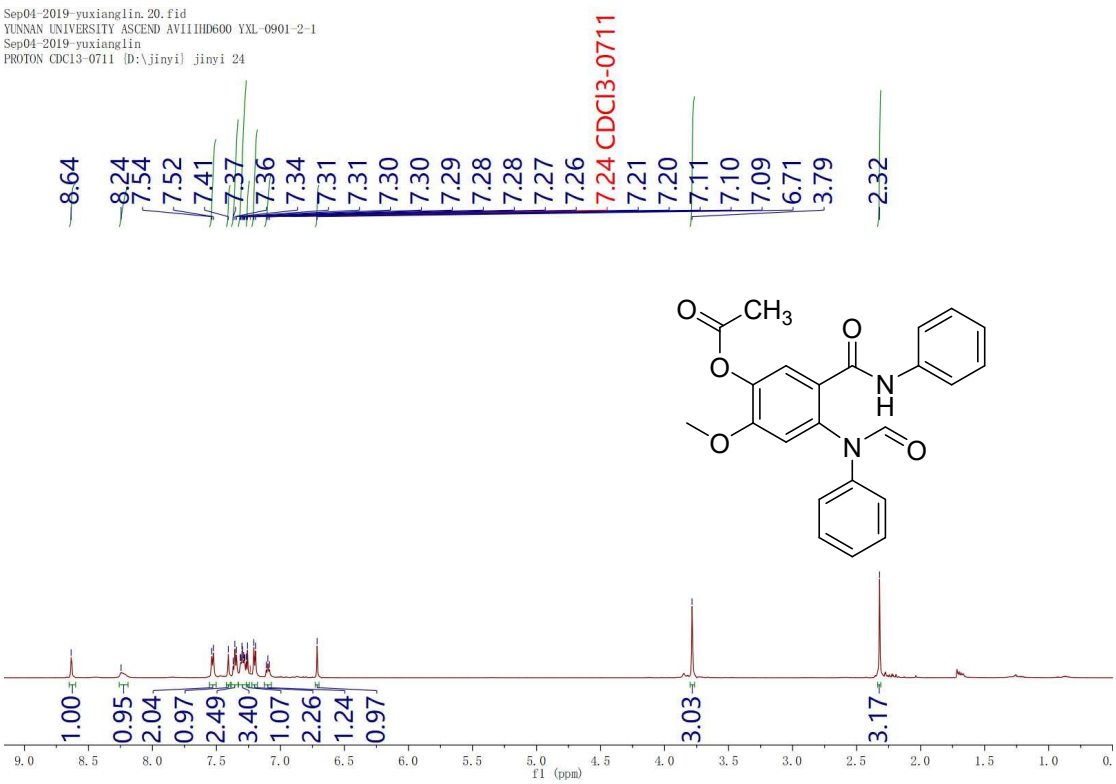
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **4h**



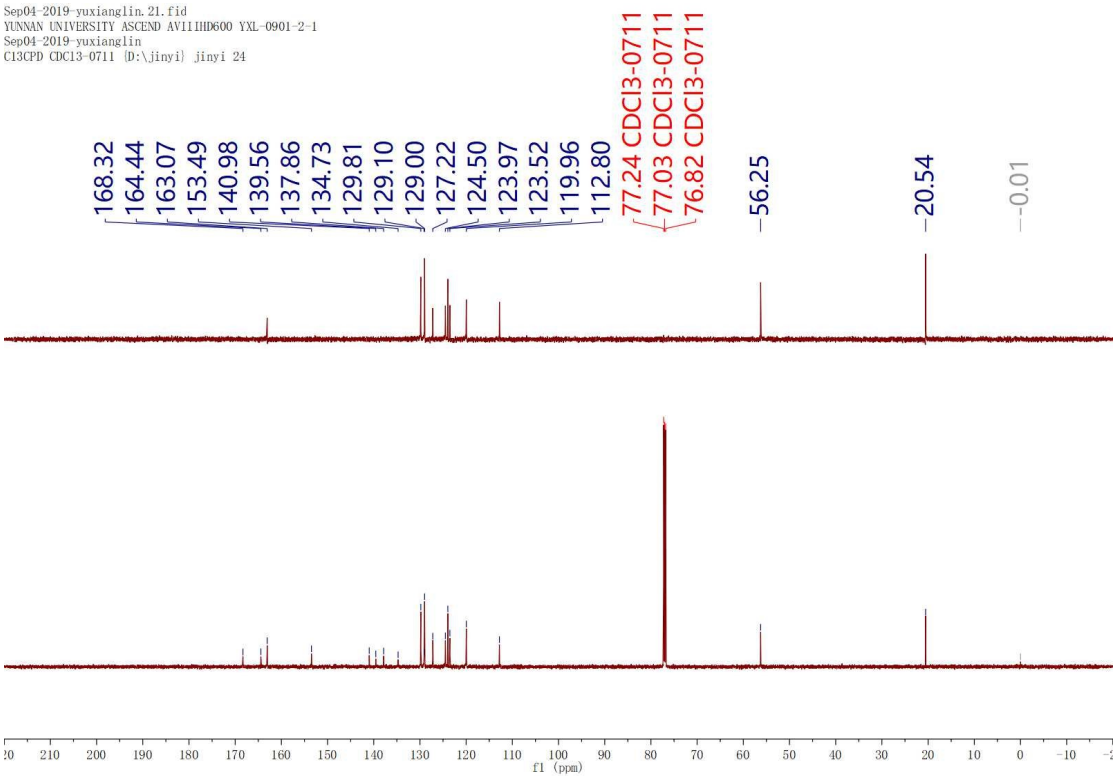
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **4i**



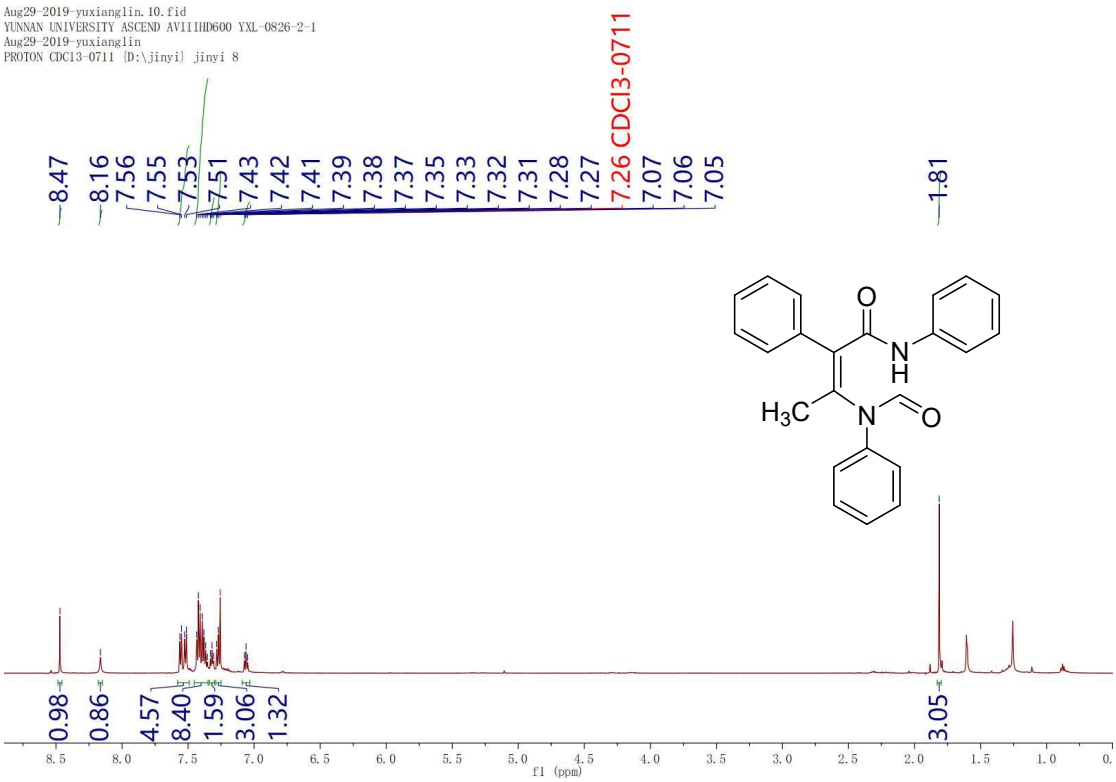
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **4i**



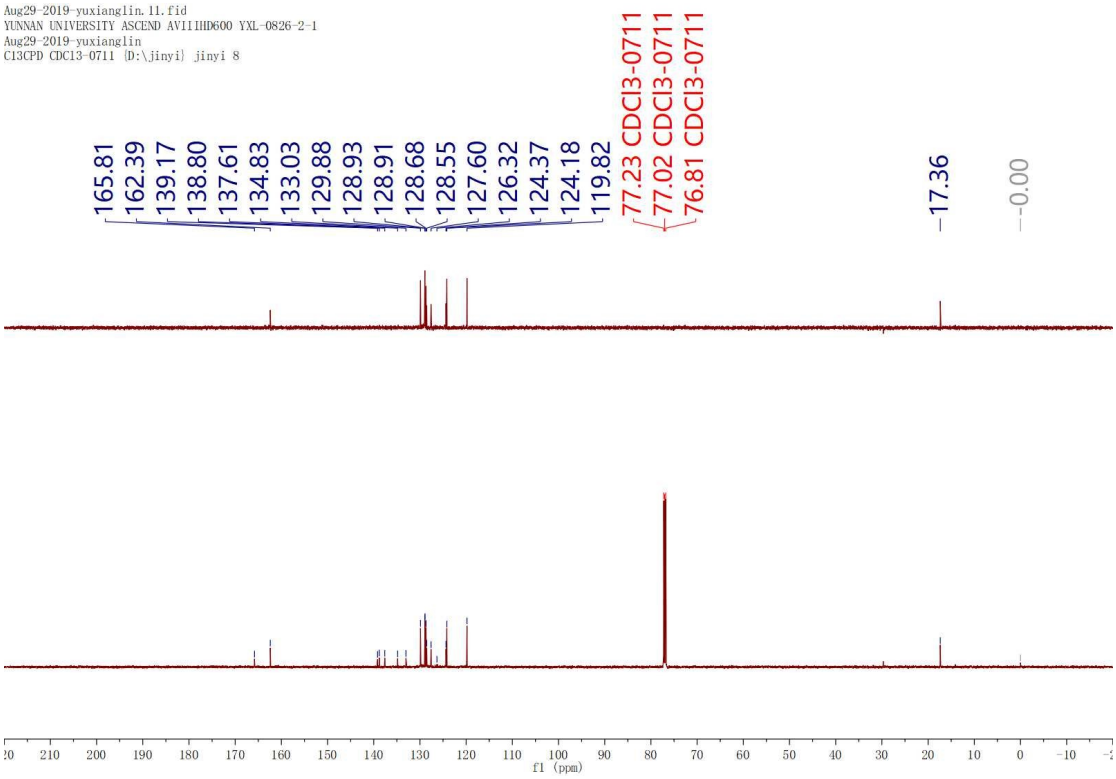
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **4j**



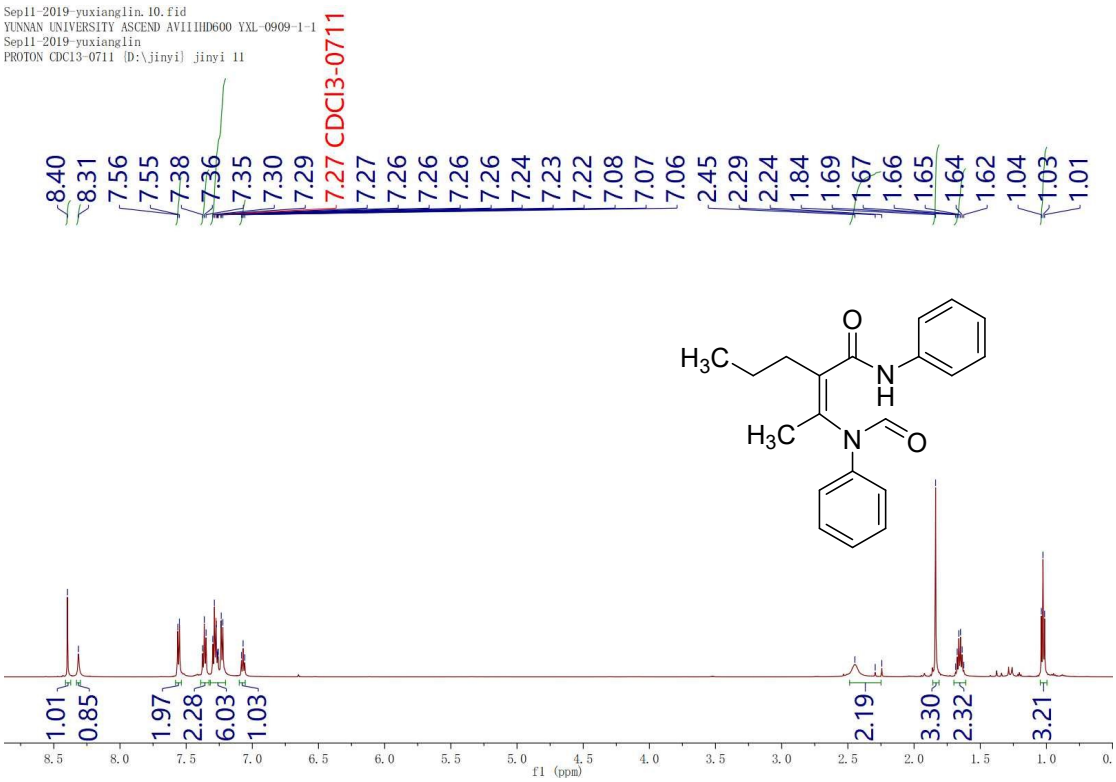
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **4j**



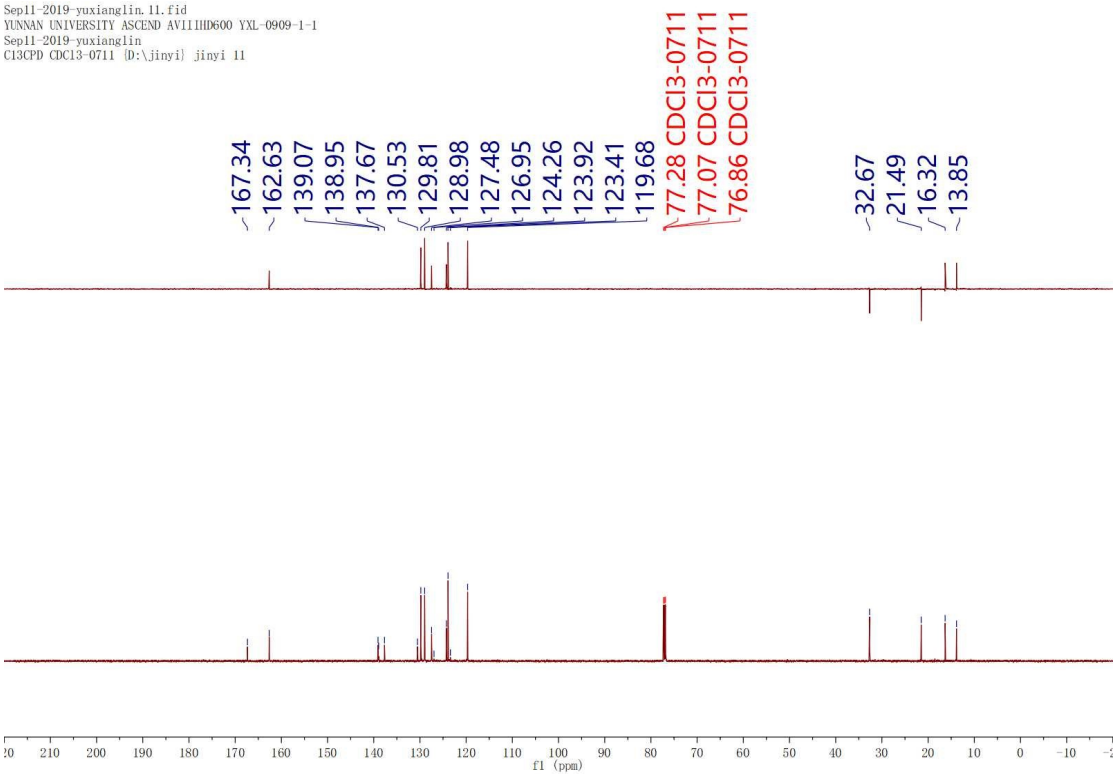
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **4k**



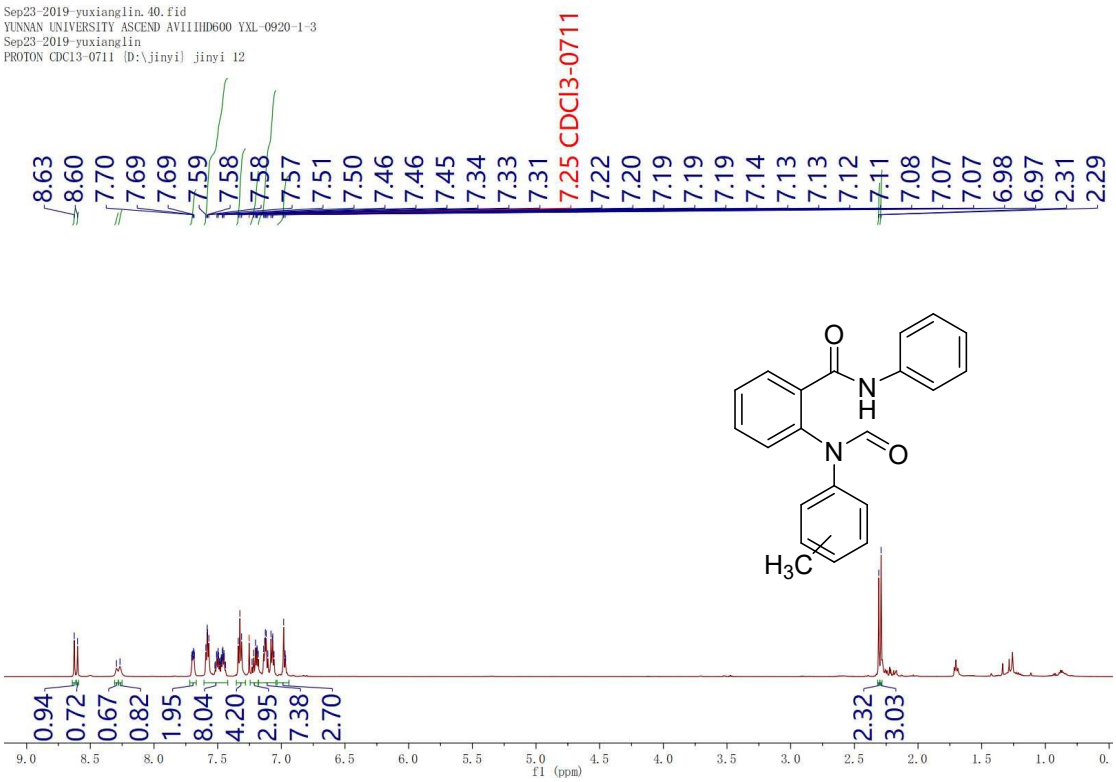
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **4k**



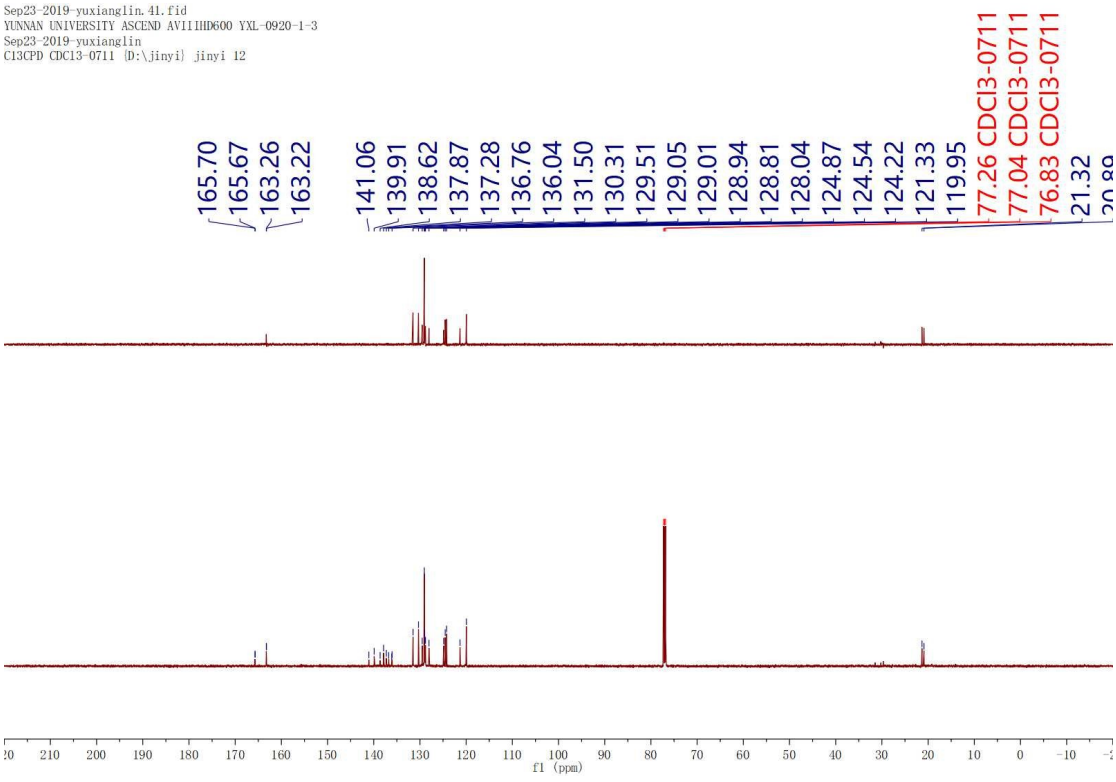
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **4l**



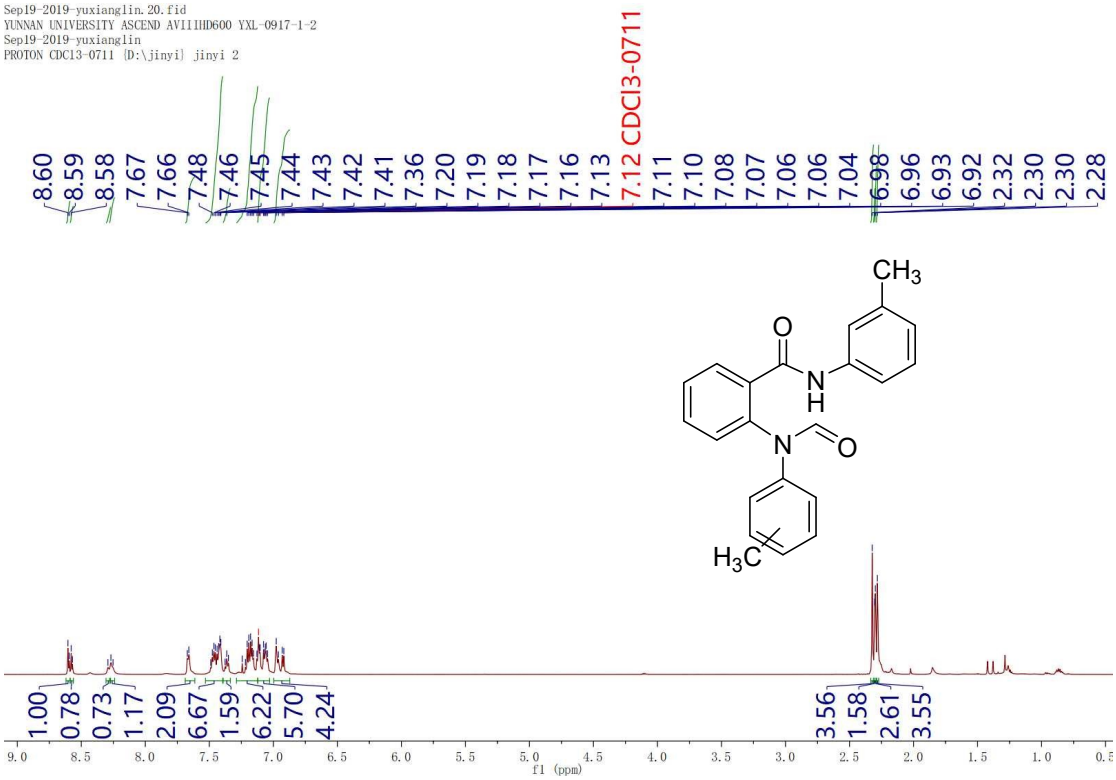
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **4l**



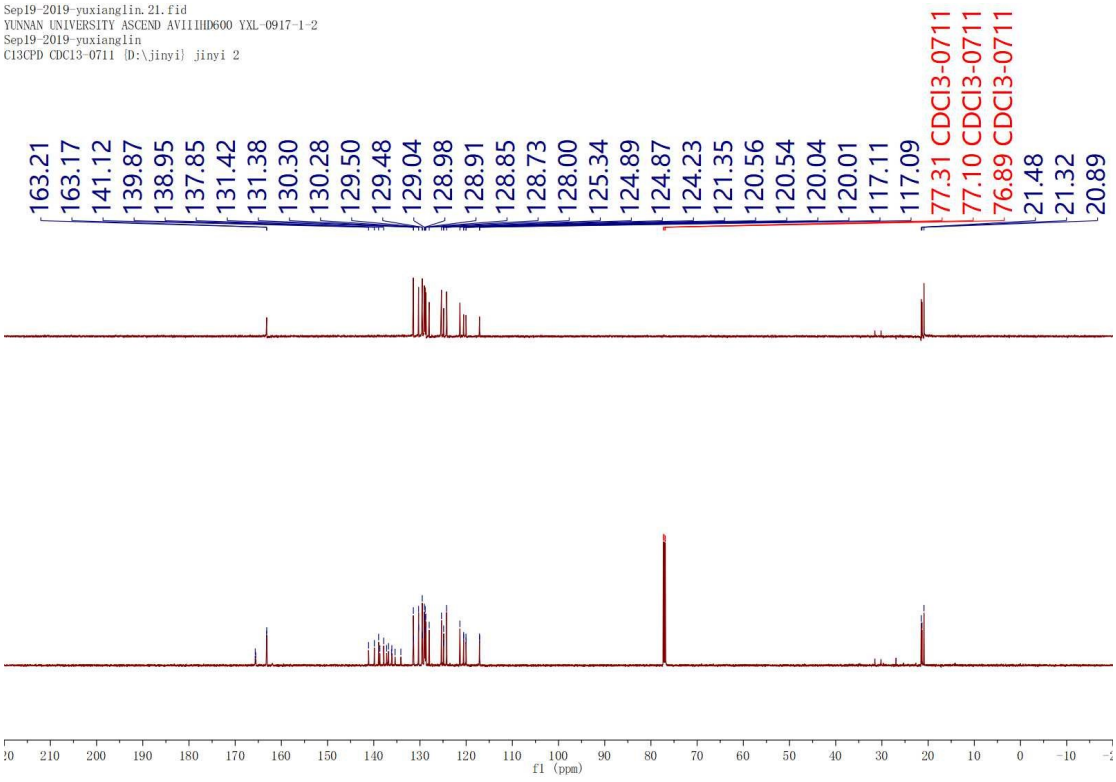
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **5aa** and **5aa'**



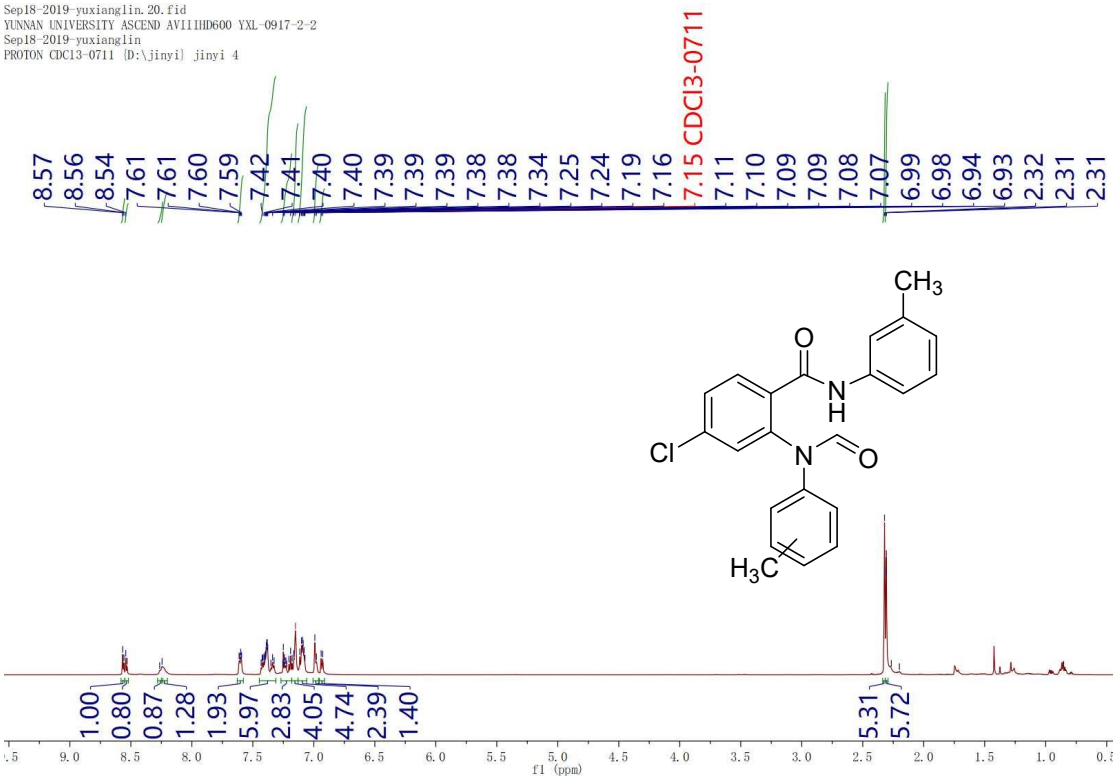
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **5aa** and **5aa'**



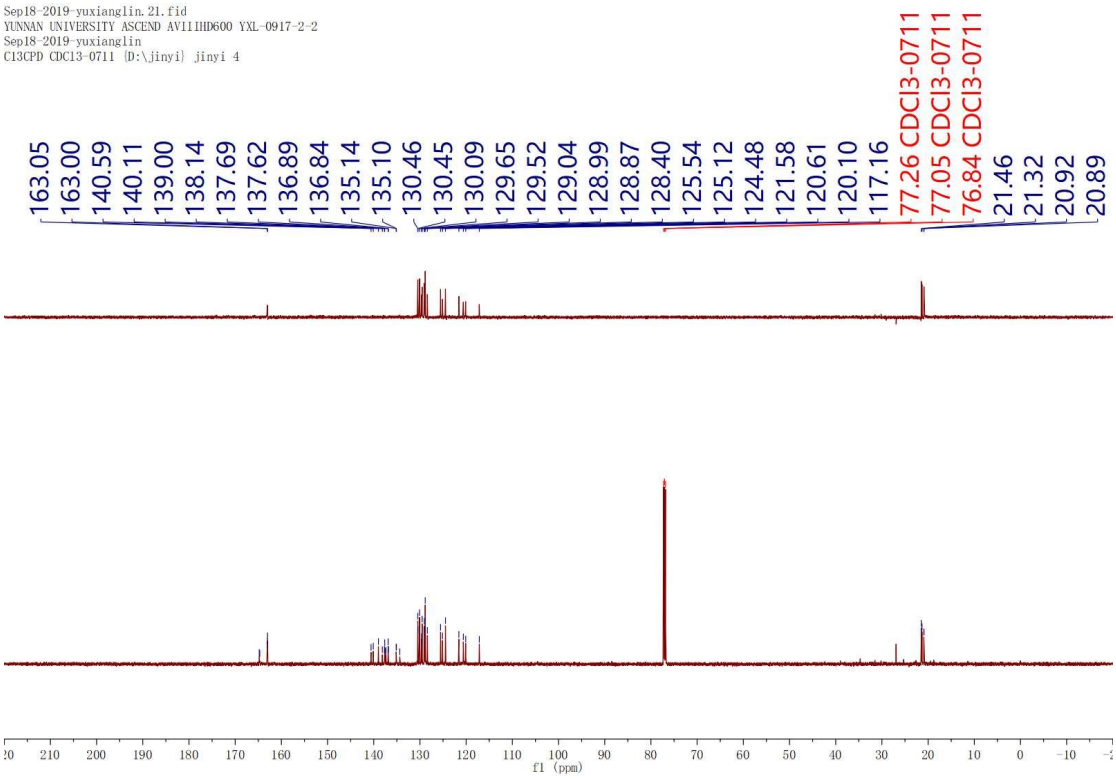
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **5bb** and **5bb'**



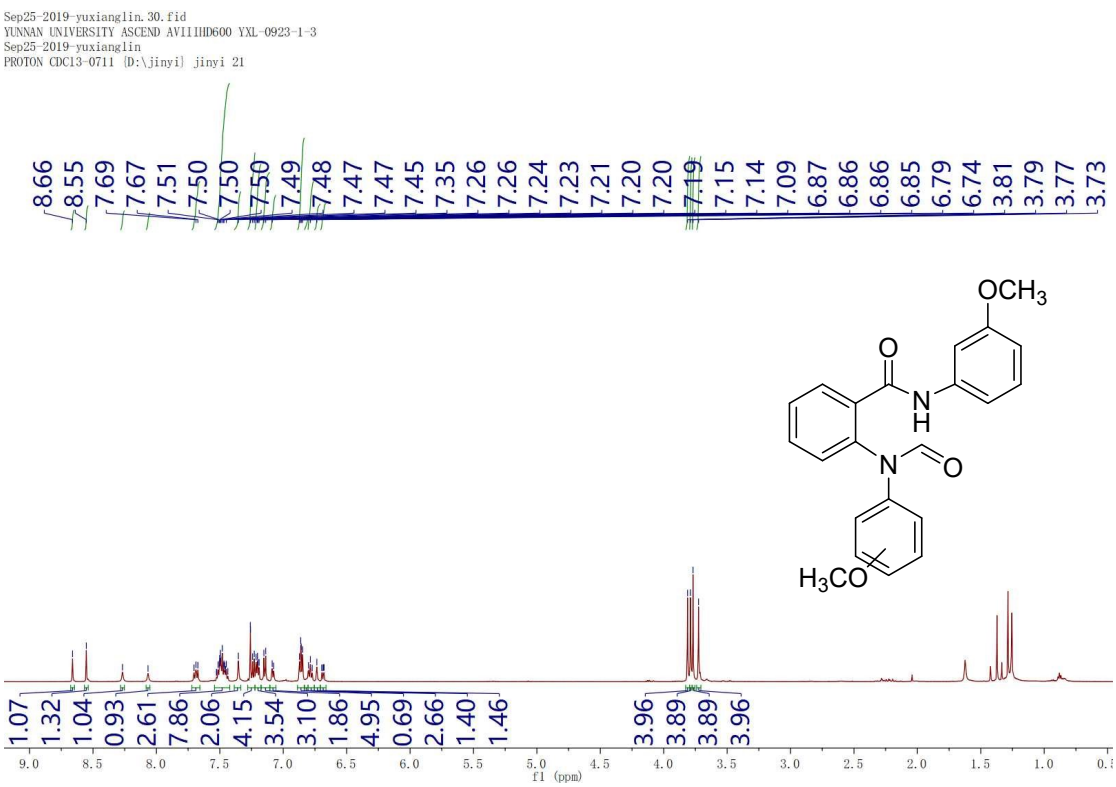
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **5bb** and **5bb'**



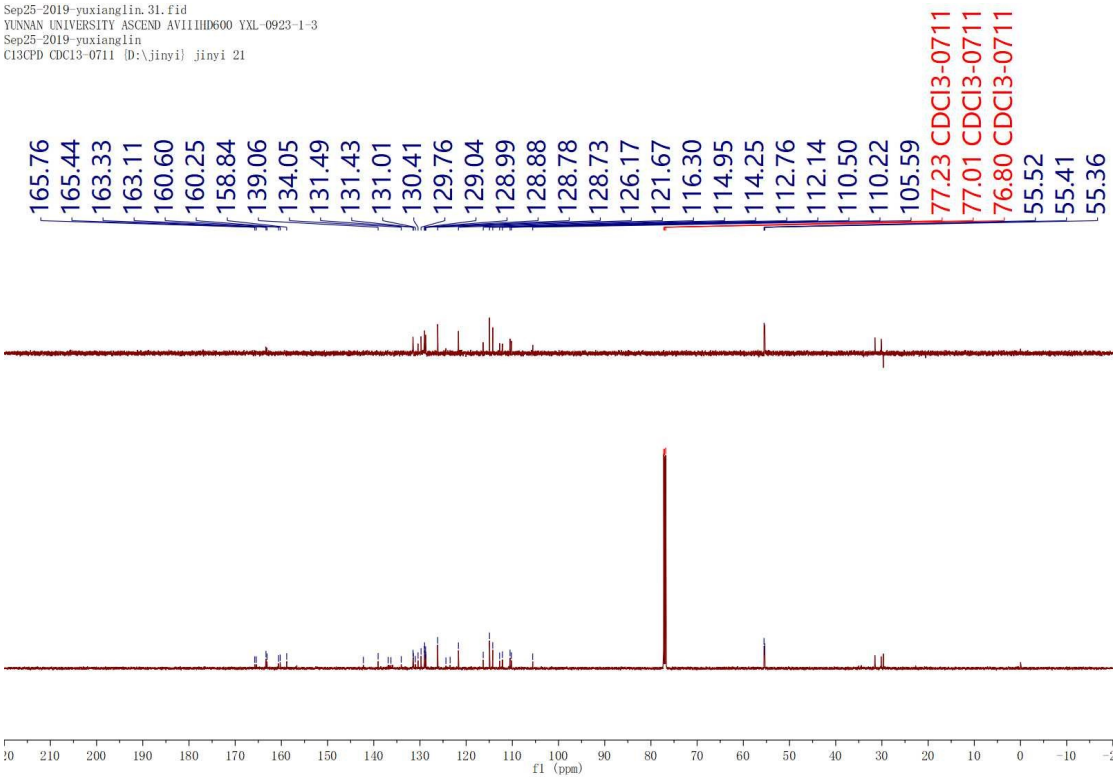
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **5cc** and **5cc'**



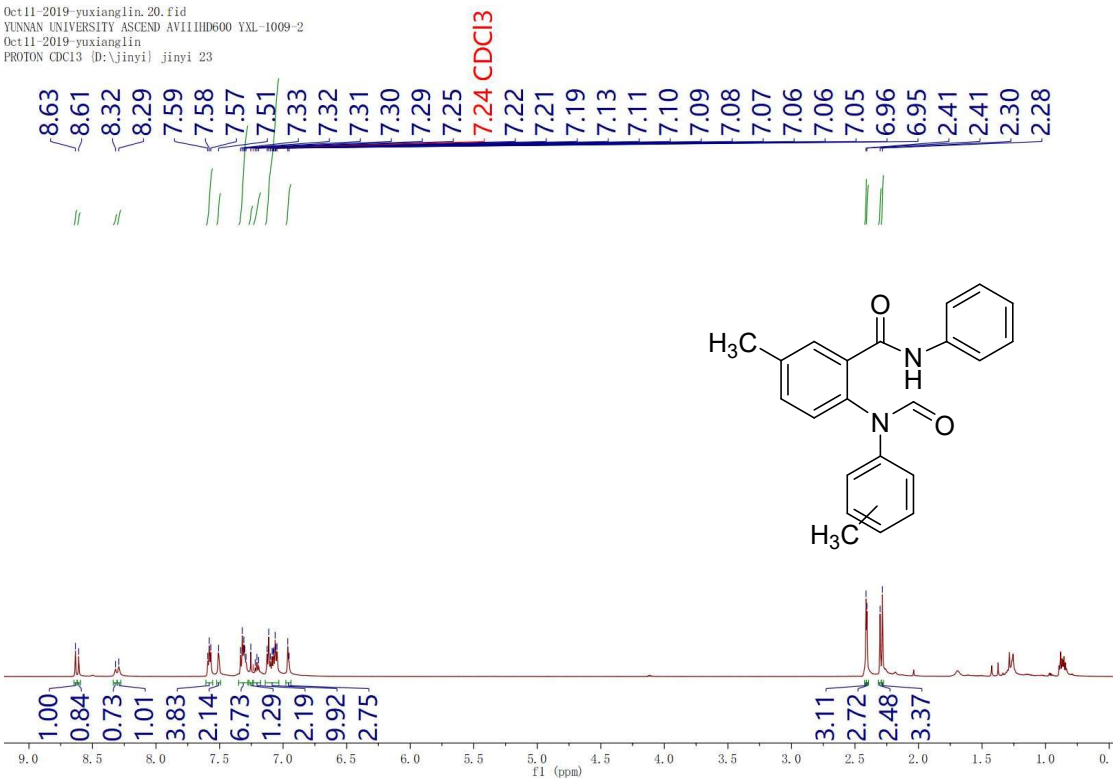
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **5cc** and **5cc'**



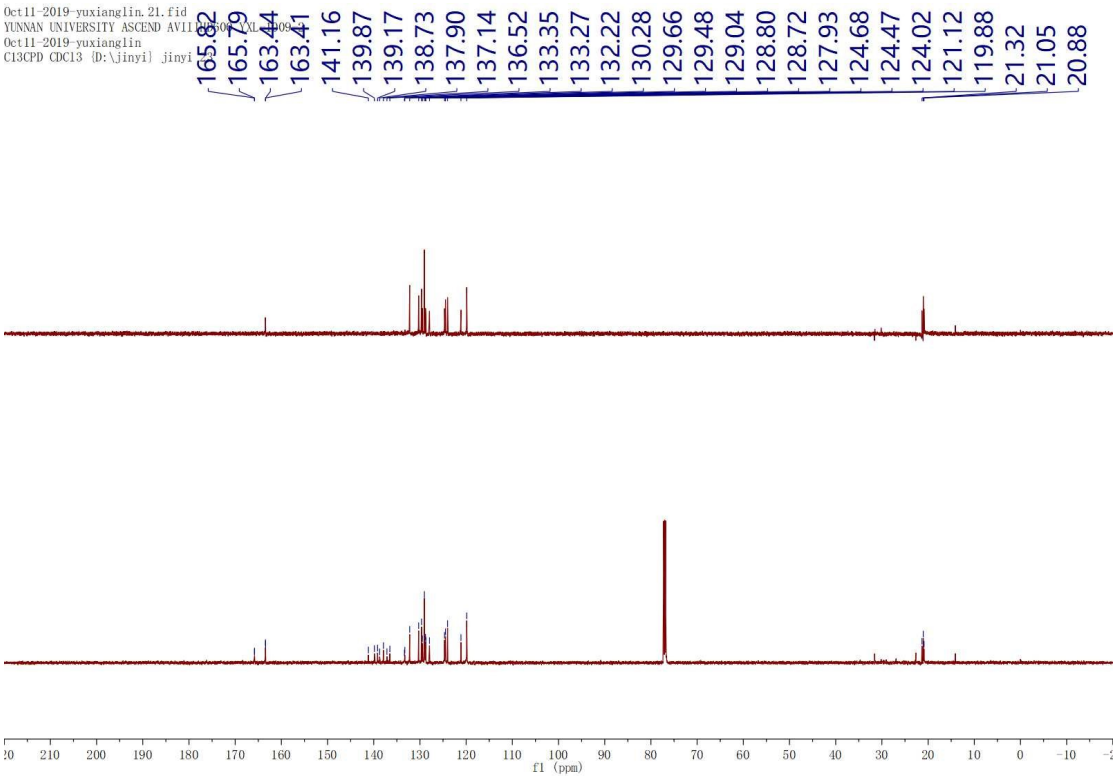
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **5dd** and **5dd'**



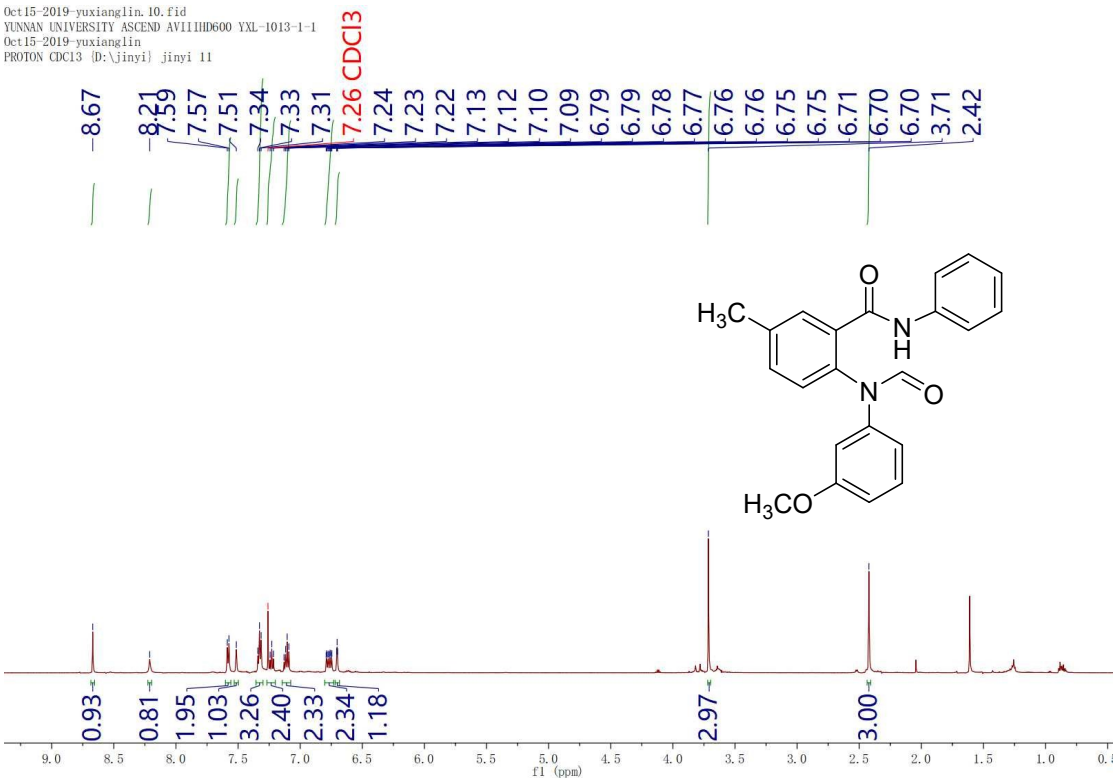
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **5dd** and **5dd'**



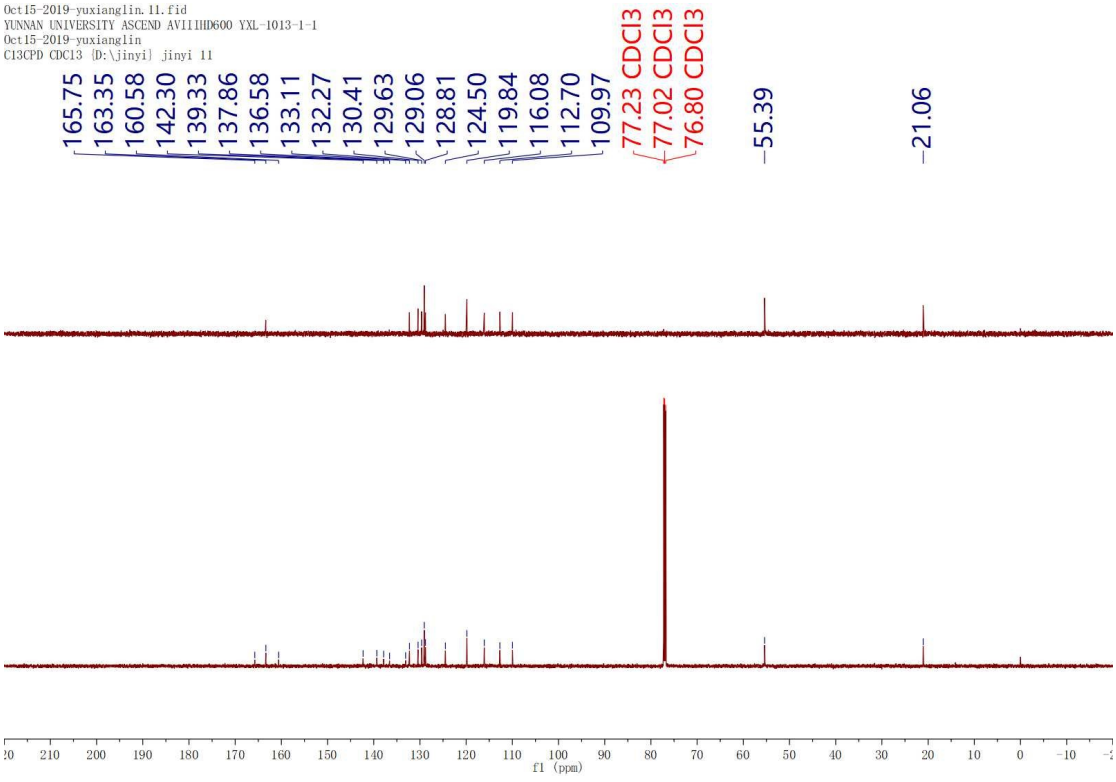
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **5ee** and **5ee'**



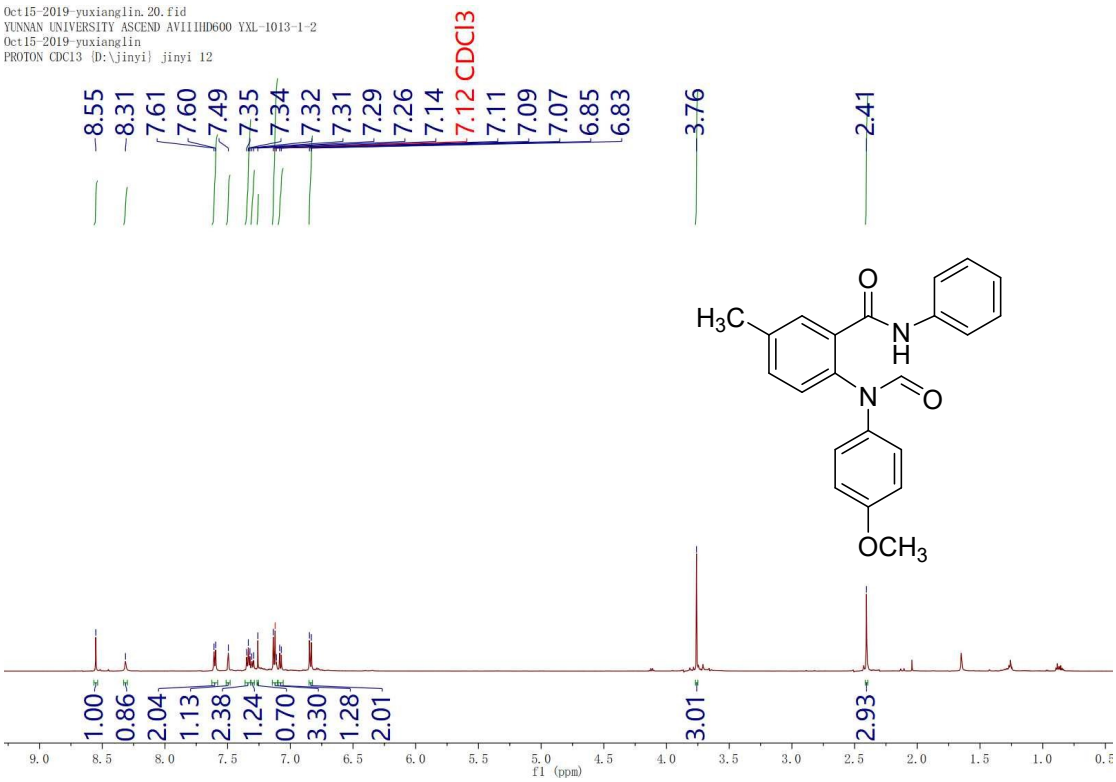
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **5ee** and **5ee'**



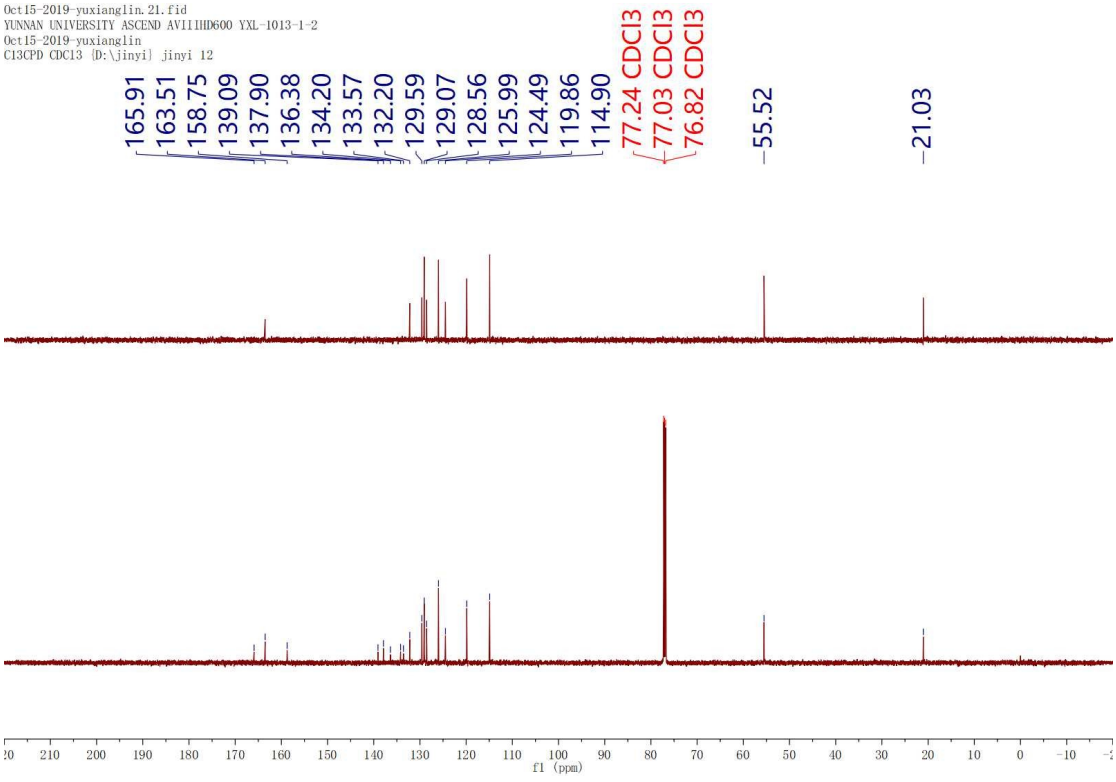
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **5ff**



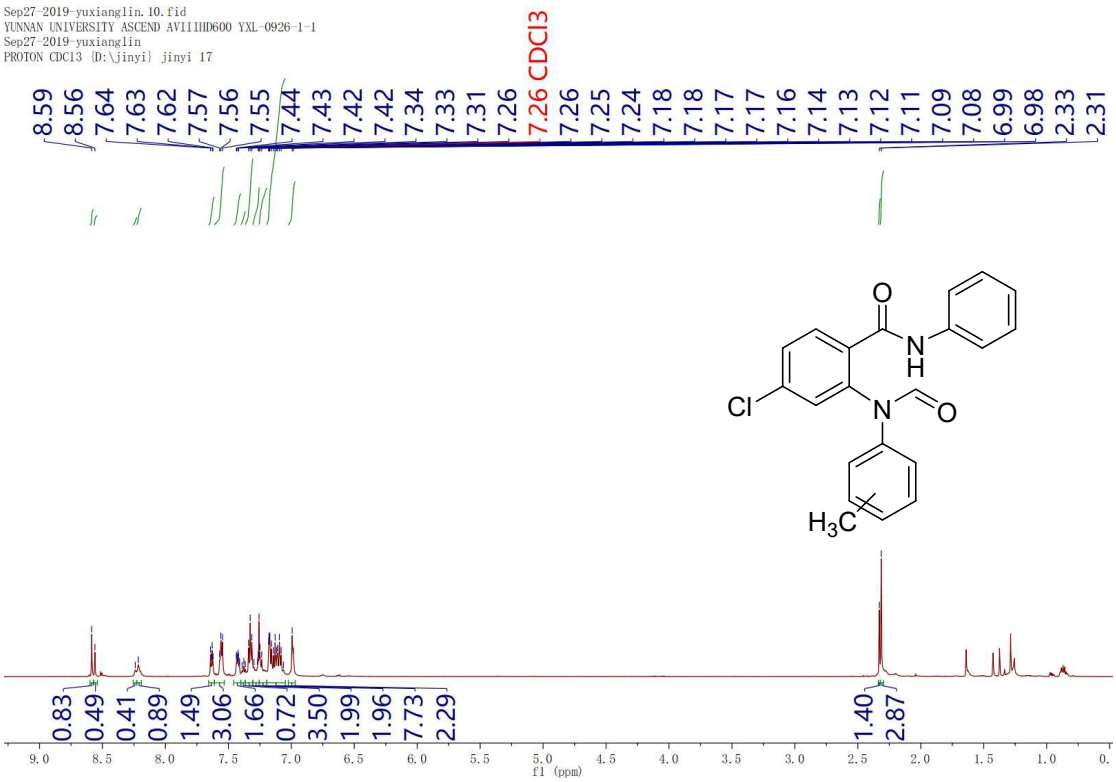
^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **5ff**



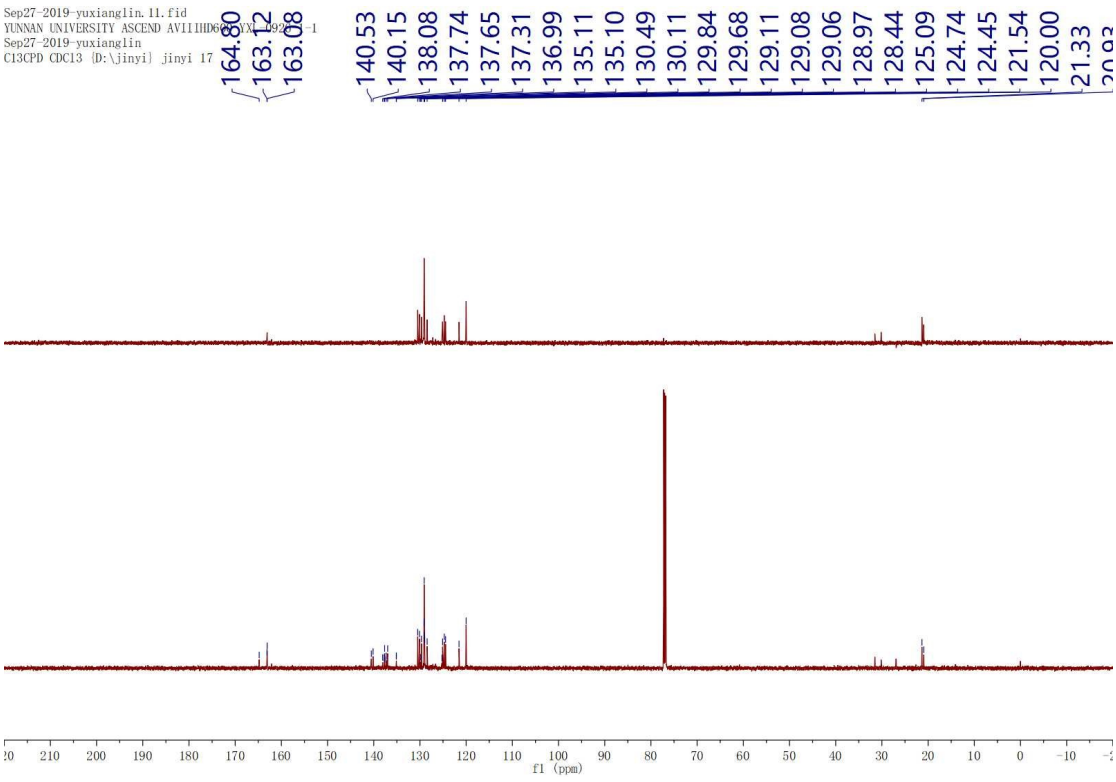
^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **5ff'**



^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **5ff'**



^{1}H-NMR (600 MHz, $CDCl_3$) Spectra of compound **5gg and 5gg'**



^{13}C-NMR (151 MHz, $CDCl_3$) Spectra of compound **5gg** and **5gg'**