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Oxidative cross dehydrogenative coupling between iodoarenes and anilides for C–N bond formation under metal-free conditions

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Supplementary Information

Contents

Experimental section **S2**
Instrumentation and chemicals **S2**
Experimental procedures **S2**
Characterization Data **S2−S8**
X-ray crystallography data **S9−S10**
Copies of ^{1}H and ^{13}C NMR spectra **S11−S47**

Experimental Section

Instrumentation and chemicals.

^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard, operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Melting points were measured by SGW X-4A microscopic apparatus. The X-ray crystallography was measured on Bruker D8 Venture Photon instrument. HRMS was measured by Q Exactive Hybrid Quadrupole-Orbitrap LC/MS spectrometer.

Ethyl acetate and petroleum ether were used for column chromatography without further purification. Other chemicals were obtained from commercial sources and used as received unless otherwise noted.

Experimental procedures

General procedure for the oxidative cross dehydrogenative coupling between iodoarenes and anilides. A mixture of iodoarenes (**1**, 0.3 mmol), anilides (**2**, 0.2 mmol), *m*-CPBA (0.3 mmol) were added into a vial containing a stirring bar and sealed with a Teflon–lined cap. Then HFIP (1 mL) was introduced. The resulting mixture was stirred at 60 ℃ for 8 h. After reaction, the mixture was added into H_2O (25 mL) and extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After removal of the solvent *in vacuo*, column chromatography (ethyl acetate/petroleum ether = 1:6) of the residue afforded the pure product.

Procedure for the hydrolysis of 3aa to 4. A mixture of **3aa** (0.2 mmol), saturated KOH aqueous solution (1 mL) and were ethanol (1 mL) added into a vial containing a stirring bar. The resulting mixture was stirred at 70 ℃ for 8 h. After reaction, the mixture was added into H_2O (25 mL) and extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After removal of the solvent *in vacuo*, column chromatography (ethyl acetate/petroleum ether=1:10) of the residue afforded the pure product.

Procedure for the synthesis of 5 from 3aa. A mixture of **3aa** (0.2 mmol), styrene (0.4 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), Na_2CO_3 (0.3 mmol) were added into a vial containing a stirring bar and sealed with a Teflon–lined cap. Then DMF (2 mL) was introduced. The resulting mixture was stirred at 100 ℃ for 4 h. After reaction, the mixture was added into H_2O (25 mL) and extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After removal of the solvent *in vacuo*, column chromatography (ethyl acetate/petroleum ether=1:6) of the residue afforded the pure product.

Procedure for the synthesis of 6 from 3aa. A mixture of **3aa** (0.2 mmol), phenylboronic acid (0.4 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), K_3PO_4 (0.5 mmol) were added into a vial containing a stirring bar and sealed with a Teflon–lined cap. Then toluene (2 mL) was introduced. The resulting mixture was stirred at 80 ℃ for 2 h. After reaction, the mixture was added into H_2O (25 mL) and extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After removal of the solvent *in vacuo*, column chromatography (ethyl acetate/petroleum ether=1:6) of the residue afforded the pure product

Procedure for the synthesis of 7 from 3aa. A mixture of **3aa** (0.2 mmol), phenylacetylene (0.3 mmol), $PdCl_2$ (5 mol%), pyrrolidine (1.0 mmol) were added into a vial containing a stirring bar and sealed with a Teflon–lined cap. Then H_2O (2 mL) was introduced. The resulting mixture was stirred at room temperature for 24 h. After reaction, the

mixture was added into H_2O (25 mL) and extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After removal of the solvent *in vacuo*, column chromatography (ethyl acetate/petroleum ether=1:6) of the residue afforded the pure product.

Characterization Data

***N*-(4-iodophenyl)-*N*-phenylacetamide (3aa)[1]**

yellow solid, 56.6 mg, 84%, mp 88–90 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 3H), 7.00–7.03. (m, 2H), 7.24 (d, J = 7.42 Hz, 2H), 7.39 (s, 3H), 7.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.9, 90.7, 126.7, 128.2, 129.8, 137.7, 138.1, 142.6, 142.8, 170.4. HRMS–ESI(m/z): calcd for $C_{14}H_{13}INO^+$ ($M+H^+$): 338.0036, found 338.0042.

***N*-(4-iodo-3-methylphenyl)-*N*-phenylacetamide (3ba)**

yellow solid, 65.3 mg, 93%, mp 90–92 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 3H), 2.38 (s, 3H), 6.79 (d, J = 7.96 Hz, 1H), 7.16 (s, 1H), 7.24 (d, J = 8.20 Hz, 3H), 7.38 (s, 2H), 7.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3, 28.2, 98.2, 125.7, 127.9, 129.6, 139.5, 139.8, 142.1, 142.5, 142.8, 143.1, 170.3. HRMS–ESI(m/z): calcd for $C_{15}H_{15}INO^+$ ($M+H^+$): 352.0193, found 352.0201.

***N*-(3-ethyl-4-iodophenyl)-*N*-phenylacetamide (3ca)**

yellow oil, 64.3 mg, 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (t, J = 7.32 Hz, 3H), 2.06 (s, 3H), 2.67–2.69 (m, 2H), 6.80 (dd, J_1 = 2.48 Hz, J_2= 8.36 Hz, 1H), 7.14 (d, J = 2.28 Hz, 1H), 7.25 (d, J = 7.72 Hz, 3H), 7.38 (s, 2H), 7.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 23.9, 34.2, 97.2, 125.7, 126.4, 127.4, 128.4, 129.3, 129.8, 139.6, 143.2, 147.2, 170.4. HRMS–ESI(m/z): calcd for $C_{16}H_{17}INO^+$ ($M+H^+$): 366.0349, found 366.0451.

***N*-(4-iodo-3-isopropylphenyl)-*N*-phenylacetamide (3da)**

yellow oil, 60.7 mg, 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (d, J = 6.24 Hz, 6H),2.05 (s, 3H), 3.13–3.16 (m, 1H), 6.79 (dd, J_1= 2.60 Hz, J_2 = 8.41 Hz, 1H), 7.16 (d, J = 2.52 Hz 1H), 7.24–7.26 (m, 2H), 7.38 (s, 3H), 7.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.0, 23.9, 38.1, 97.5, 124.0, 125.6, 126.4, 127.6, 128.4, 129.5, 139.8, 140.6, 142.8, 170.4. HRMS–ESI(m/z): calcd for $C_{17}H_{19}INO^+$ ($M+H^+$): 380.0506, found 380.0501.

***N*-(6-iodo-[1,1'–biphenyl]-3-yl)-*N*-phenylacetamide (3ea)**

yellow oil, 33.1 mg, 40%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3H), 6.99 (dd, J = 2.52 Hz J = 8.44 Hz, 1H), 7.20 (d, J = 2.36 Hz, 1H), 7.25–7.31 (m, 5H), 7.38–7.40 (m, 5H), 7.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.9, 95.3, 126.7, 126.9, 127.4, 127.9, 128.0, 128.4, 128.9, 129.2, 129.8, 139.8, 140.1, 142.9, 143.4, 170.4. HRMS–ESI(m/z): calcd for $C_{20}H_{17}INO^+$ ($M+H^+$): 414.0349, found 414.0352.

***N*-(3-(bromomethyl)-4-iodophenyl)-*N*-phenylacetamide (3fa)**

yellow oil, 38.6 mg, 45%; ^{1}H NMR (400 MHz, $CDCl_3$):δ 2.06 (s, 3H), 4.52 (s, 2H), 6.89 (dd, J = 2.55 Hz J = 8.49 Hz, 1H), 7.25 (d, J = 8.98 Hz, 2H), 7.37–7.46 (m, 4H), 7.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.0, 38.3, 96.1, 127.9, 128.3, 128.9, 129.9, 131.0, 132.8, 140.4, 142.5, 143.5, 170.4. HRMS–ESI(m/z): calcd for $C_{15}H_{14}BrINO^+$ ($M+H^+$): 429.9298, found 429.9295.

***N*-(4-iodo-3-(methoxymethyl)phenyl)-*N*-phenylacetamide (3ga)**

yellow oil, 48 mg, 63%; ^{1}H NMR (400 MHz, $CDCl_3$):*δ* 2.06 (s, 3H), 3.44 (s, 3H), 4.38 (s, 2H), 6.91 (dd, J_1= 2.51 Hz, J_2 = 8.35 Hz 1H), 7.25 (d, *J* = 8.03 Hz, 2H), 7.36–7.37 (m, 4H), 7.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 23.9, 58.7,78.0, 93.8, 126.6, 127.0, 128.1, 128.5, 128.9, 129.4, 139.6, 141.3, 142.9, 170.4. HRMS–ESI(m/z): calcd for $C_{16}H_{17}INO_2^+$ ($M+H^+$): 382.0298, found 382.0296.

2-iodo-5-(*N*-phenylacetamido)benzyl acetate (3ha)

yellow oil, 49.9 mg , 61%; ^{1}H NMR (400 MHz, $CDCl_3$):*δ* 2.07 (s, 3H), 2.11 (s, 3H), 5.05 (s, 2H), 6.95 (dd, J_1= 2.62 Hz, J_2 = 8.43 Hz, 1H), 7.21–7.26 (m, 2H), 7.30–7.41 (m, 4H), 7.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 20.9, 24.0, 69.9, 94.5,119.8, 124.1, 127.5, 128.4, 128.9, 139.9, 142.6, 143.2, 144.8, 170.5. HRMS–ESI(m/z): calcd for $C_{17}H_{17}INO_3^+$ ($M+H^+$): 410.0248, found 410.0251.

***N*-(4-iodo-3, 5-dimethylphenyl)-*N*-phenylacetamide (3ia)**

yellow oil, 46 mg, 63%; ^{1}H NMR (400 MHz, $CDCl_3$):*δ* 2.05 (s, 3H), 2.43 (s, 6H), 6.98 (s, 2H), 7.25–7.27 (m, 3H),7.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 23.8, 29.7, 125.1, 126.6, 127.5, 128.6, 129.7, 138.9, 142.9, 170.4. HRMS–ESI(m/z): calcd for $C_{16}H_{17}INO^+$ ($M+H^+$): 366.0349, found 366.0345.

***N*-(3-ethyl-4-iodo-5-methylphenyl)-*N*-phenylacetamide (3ja)**

yellow oil, 45.5 mg, 60%; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 1.18 (t, *J* = 7.2 Hz, 3H), 2.06 (s, 3H), 2.44 (s, 3H), 2.75–2.88 (m, 2H), 6.95–6.99 (m, 2H), 7.25–7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 14.4, 23.8, 30.0, 35.3, 123.8, 125.3, 126.2, 126.7, 127.9, 128.6, 129.7, 142.9, 147.7, 170.5. HRMS–ESI(m/z): calcd for $C_{17}H_{19}INO^+$ ($M+H^+$): 380.0506, found 380.0510.

***N*-(4-fluorophenyl)-N-(4-iodo-2-methylphenyl)acetamide (3kb)**

yellow oil, 58.8 mg, 80%; ^{1}H NMR (400 MHz, $CDCl_3$):*δ* 1.96 (s, 3H), 2.16 (s, 3H), 6.97–7.08 (m, 3H), 7.20–7.23 (m, 2H), 7.63–7.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 17.6, 23.7, 94.2, 115.5 (d, *J* = 22.77 Hz), 126.8 (d, *J* = 8.12 Hz) , 129.1, 131.3, 136.7, 138.5, 140.9, 141.4, 160.1 (d, *J* = 244.69 Hz), 170.1. HRMS–ESI(m/z): calcd for $C_{15}H_{14}FINO^+$ ($M+H^+$): 370.0099, found 370.0102.

***N*-(4-fluorophenyl)-N-(4-iodo-2, 6-dimethylphenyl)acetamide (3lb)[2]**

yellow oil, 62.8 mg, 82%; ^{1}H NMR (400 MHz, $CDCl_3$):*δ* 1.90 (s, 3H), 2.16 (s, 6H), 6.94–6.99 (m, 2H), 7.21–7.24 (m, 2H), 7.55 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 17.7, 23.6, 94.4, 115.3 (d, *J* = 22.50 Hz), 124.9 (d, *J* = 8.07 Hz), 136.1 (d, *J* = 2.96 Hz) , 138.3, 138.8, 140.2, 159.5 (d, *J* = 245.23 Hz), 170.0. HRMS–ESI(m/z): calcd for $C_{16}H_{16}FINO^+$ ($M+H^+$): 384.0255, found 384.0251.

***N*-(4-fluorophenyl)-N-(4-iodo-2, 3-dimethylphenyl)acetamide (3mb)**

yellow oil, 65.1 mg, 85%; ^{1}H NMR (400 MHz, $CDCl_3$):*δ* 1.95 (s, 3H), 2.26 (s, 3H), 2.48 (s, 3H), 6.85 (d, *J* = 8.26 Hz, 1H), 6.96–7.09 (m, 2H), 7.21–7.25 (m, 2H), 7.79 (d, *J* = 8.27 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 16.3, 23.9, 26.2, 102.4, 115.5 (d, *J* = 22.55 Hz), 126.7 (d, *J* = 8.15 Hz) , 128.4, 135.9, 137.9, 141.9, 142.2, 160.0 (d, *J* = 245.74

Hz), 170.4. HRMS–ESI(m/z): calcd for $C_{16}H_{16}FINO^+$ ($M+H^+$): 384.0255, found 384.0253.

_N_-(4-fluorophenyl)-_N_-(4-iodo-3-methylphenyl)acetamide (3bb)

yellow oil, 66.4 mg, 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 3H), 2.40 (s, 3H), 6.78 (d, J = 7.48 Hz, 1H), 7.07 (s, 2H) , 7.13 (d, J = 2.04 Hz, 1H), 7.21–7.24 (m, 2H) , 7.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.6, 28.2, 99.9, 116.1, 116.8, 125.4, 127.6, 128.2, 129.4, 130.1, 139.6, 142.9, 170.4. HRMS–ESI(m/z): calcd for $C_{15}H_{14}FINO^+$ ($M+H^+$): 370.0099, found 370.0104.

_N_-(4-chlorophenyl)-_N_-(4-iodo-3-methylphenyl)acetamide (3bc)

yellow oil, 75.5 mg, 98%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05(s, 3H), 2.40 (s, 3H), 6.78 (d, J = 7.44 Hz, 1H), 7.12 (d, J = 2.12 Hz, 1H), 7.18 (d, J = 8.56 Hz, 2H), 7.33 (s, 2H), 7.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8, 28.2, 97.7, 125.5, 127.4, 127.7, 128.9, 129.4, 139.6, 139.9, 141.0, 142.8, 170.2. HRMS–ESI(m/z): calcd for $C_{15}H_{14}ClINO^+$ ($M+H^+$): 385.9803, found 385.9805.

_N_-(4-bromophenyl)-_N_-(4-iodo-3-methylphenyl)acetamide (3bd)

yellow oil, 81.5 mg, 95%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05(s, 3H), 2.40 (s, 3H), 6.77 (d, J = 7.44 Hz, 1H), 7.11–7.13 (m, 3H), 7.48 (s, 2H), 7.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8, 28.2, 98.7, 120.0, 125.6, 128.0, 132.4, 140.0, 140.0, 141.7, 142.8, 170.1. HRMS–ESI(m/z): calcd for $C_{15}H_{14}BrINO^+$ ($M+H^+$): 429.9298, found 429.9302.

methyl 4-(_N_-(4-iodo-3-methylphenyl)acetamido)benzoate (3be)

yellow oil, 50.7 mg, 62%; ^{1}H NMR (400 MHz, $CDCl_3$):δ 2.08 (s, 3H), 2.41 (s, 3H), 3.91 (s, 3H), 6.79 (dd, J_1 = 2.25 Hz, J_2 = 8.29 Hz, 1H), 7.13 (d, J = 2.38 Hz, 1H), 7.29–7.33 (m, 2H), 7.83 (d, J = 8.02 Hz, 1H), 8.02 (d, J = 8.15 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.1, 28.2, 52.3, 99.9,126.9, 128.0, 128.9, 129.1, 130.7, 140.0, 142.7, 146.6, 166.3, 170.1. HRMS–ESI(m/z): calcd for $C_{17}H_{17}INO_3^+$ ($M+H^+$): 410.0248, found 410.0253.

_N_-(2-chlorophenyl)-_N_-(4-iodo-3-methylphenyl)acetamide (3bf)

yellow oil, 71.6 mg, 93% ; ^{1}H NMR (400 MHz, $CDCl_3$):δ 2.00 (s, 3H), 2.38 (s, 3H), 6.86 (s, 1H), 7.24 (d, J = 2.33 Hz, 2H), 7.34 (s, 2H) , 7.51 (s, 1H) , 7.72–7.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.0, 23.9, 38.1, 97.5, 124.0, 125.6, 126.4, 127.6, 128.4, 129.5, 139.8, 140.6, 142.8, 170.4. HRMS–ESI(m/z): calcd for $C_{15}H_{14}ClINO^+$ ($M+H^+$): 385.9803, found 385.9808.

_N_-(2-bromophenyl)-_N_-(4-iodo-3-methylphenyl)acetamide (3bg)

yellow oil, 78.1 mg, 91%; ^{1}H NMR (400 MHz, $CDCl_3$):δ 2.00 (s, 3H), 2.37 (s, 3H), 6.87 (s, 1H), 7.26–7.40 (m, 4H), 7.69–7.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8, 28.3, 97.8, 124.3,124.8, 127.0, 129.2, 130.2, 131.1, 134.4, 139.0, 141.4, 141.7, 141.9, 170.1. HRMS–ESI(m/z): calcd for $C_{15}H_{14}BrINO^+$ ($M+H^+$): 429.9298, found 429.9295.

_N_-(3-chlorophenyl)-_N_-(4-iodo-3-methylphenyl)acetamide (3bh)

yellow oil, 54.6 mg, 71%; ^{1}H NMR (400 MHz, $CDCl_3$):δ 2.07 (s, 3H), 2.41 (s, 3H), 6.78 (d, J = 7.39 Hz, 1H), 7.12–7.16 (m, 2H), 7.24–7.29 (m, 3H), 7.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8, 28.2, 100.0, 124.6, 125.4, 126.7, 128.4, 129.3, 130.2, 134.9, 138.8, 140.0,142.8, 143.8, 170.2. HRMS–ESI(m/z): calcd for $C_{15}H_{14}ClINO^+$ ($M+H^+$):

385.9803, found 385.9808.

N-(3-chloro-4-methylphenyl)-N-(4-iodo-3-methylphenyl)acetamide (3bi)

yellow oil, 65.4 mg, 82%; ^{1}H NMR (400 MHz, $CDCl_3$):δ 2.06 (s, 3H), 2.38 (d, J = 15.66 Hz, 6H), 6.78 (d, J = 7.14 Hz, 1H), 7.05–7.07 (m, 1H), 7.13 (d, J = 2.12 Hz, 1H), 7.24 (d, J = 1.88 Hz, 2H), 7.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7, 23.8, 28.2, 98.1, 124.8, 125.5, 127.1, 128.9, 131.8, 134.4, 136.1, 139.4, 140.0, 141.4, 142.8, 170.2. HRMS–ESI(m/z): calcd for $C_{16}H_{16}ClINO^+$ ($M+H^+$): 399.9960, found 399.9954.

N-(3-cyano-4-methylphenyl)-N-(4-iodo-3-methylphenyl)acetamide (3bj)

yellow oil, 54.6 mg, 70%; ^{1}H NMR (400 MHz, $CDCl_3$):δ 2.06 (s, 3H), 2.43 (s, 3H), 2.52 (s, 3H), 6.79 (d, J = 7.16 Hz, 1H), 7.12 (d, J = 2.38 Hz, 1H), 7.30 (s, 1H), 7.41 (dd, J_1 = 2.31 Hz, J_2 = 8.27 Hz, 1H), 7.46 (s, 1H), 7.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.1, 23.8, 28.3, 100.7,113.4, 117.4, 127.3, 128.1, 129.6, 130.5, 131.0, 139.7, 140.2, 140.4, 142.5, 143.8, 170.2. HRMS–ESI(m/z): calcd for $C_{17}H_{16}IN_2O^+$ ($M+H^+$): 391.0302, found 391.0305.

***N*-(4-iodo-3-methylphenyl)-*N*-phenylpropionamide (3bk)**

yellow solid, 64.2 mg, 88%, mp 95–96 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (t, J = 7.42 Hz, 3H), 2.27 (q, J = 7.40 Hz, 2H), 2.38 (s, 3H), 6.78 (dd, J_1 = 8.29 Hz, J_2 = 1.96 Hz, 1H), 7.16 (d, J = 2.16 Hz, 1H) 7.25–7.26 (m, 2H), 7.35–7.38 (m, 3H), 7.75 (d, J = 6.96 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.7, 28.2, 28.8, 97.8, 126.0, 127.5, 128.2, 128.9, 129.6, 139.4, 139.5, 142.6, 143.1, 173.9. HRMS–ESI(m/z): calcd for $C_{16}H_{17}INO^+$ ($M+H^+$): 366.0349, found 366.0351.

***N*-(4-iodo-3-methylphenyl)-*N*-phenylbutyramide (3bl)**

yellow oil, 70.5 mg, 93%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J = 7.40 Hz, 3H), 1.63–1.72 (m, 2H), 2.22 (t, J = 7.41 Hz, 2H), 2.38 (s, 3H), 6.76–6.79 (m, 1H), 7.15 (d, J = 2.08 Hz, 1H), 7.22–7.24 (m, 2H), 7.38 (s, 3H), 7.75 (d, J = 4.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 19.0, 28.2, 37.2, 97.8, 126.6, 127.4, 127.7, 129.5, 139.4, 139.5, 141.7, 142.6, 143.2, 173.1. HRMS–ESI(m/z): calcd for $C_{17}H_{19}INO^+$ ($M+H^+$): 380.0506, found 380.0511.

***N*-(4-iodo-3-methylphenyl)-*N*-phenylisobutyramide (3bm)**

yellow oil, 38.2 mg, 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, J = 6.72 Hz, 6H), 2.31 (s, 3H), 2.56–2.66 (m, 1H), 6.68 (d, J = 7.16 Hz, 1H), 7.06 (d, J = 2.48 Hz, 1H), 7.14–7.18 (m, 3H), 7.30 (s, 2H), 7.68 (d, J = 5.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.6, 27.1, 31.0, 97.7, 124.9, 126.2, 127.2, 128.5, 138.4, 138.5, 140.4, 141.6, 142.2, 176.5. HRMS–ESI(m/z): calcd for $C_{17}H_{19}INO^+$ ($M+H^+$): 380.0506, found 380.0502.

***N*-(4-iodo-3-methylphenyl)-*N*-phenylcyclopropanecarboxamide (3bn)**

yellow oil, 66.4 mg, 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.72–0.76 (m, 2H), 1.11–1.14 (m, 2H), 1.49–1.55 (m, 1H), 2.38 (s, 3H), 6.80 (s, 1H), 7.17 (s, 1H), 7.25–7.28 (m, 3H), 7.35–7.38 (m, 2H), 7.76 (d, J = 7.32 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.5, 13.9, 28.2, 97.9, 125.9, 127.1, 128.2, 129.4, 139.4, 139.5, 141.6, 142.7, 143.3, 173.7. HRMS–ESI(m/z): calcd for $C_{17}H_{17}INO^+$ ($M+H^+$): 378.0349, found 378.0351.

***N*-(4-iodo-3-methylphenyl)-*N*-phenylcyclohexanecarboxamide (3bo)**

yellow solid, 72.1 mg, 86%, mp 140–145 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98–1.07 (m, 2H), 1.16–1.29 (m, 2H), 1.55–1.65 (m, 3H), 1.69–1.80 (m, 4H), 2.37 (s, 3H), 6.74 (d, J = 7.2 Hz, 1H), 7.11 (d, J = 2.44 Hz, 1H), 7.21 (d, J = 7.52 Hz, 3H), 7.37 (s, 2H), 7.76 (d, J = 3.72 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.5, 25.6, 28.2, 29.5, 42.3, 97.7, 126.0,126.9, 128.0, 129.6, 139.4, 141.5, 142.7, 143.3, 176.6. HRMS–ESI(m/z): calcd for $C_{20}H_{23}INO^+$ ($M+H^+$): 420.0819, found 420.0814.

N-(4-iodo-3-methylphenyl)-N-phenylbenzamide (3bp)

yellow oil, 50.4 mg, 61%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 6.68 (dd, J = 8.37 Hz, J = 2.44 Hz, 1H), 7.06–7.10 (m, 3H), 7.15–7.31 (m, 6H), 7.43–7.45 (m, 2H), 7.40 (d, J = 8.44 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.2, 98.1, 126.4, 126.6, 127.6, 128.0, 128.4, 129.2, 129.3, 130.4, 135.8, 139.4, 142.5, 143.6, 144.1, 170.6. HRMS–ESI(m/z): calcd for $C_{20}H_{17}INO^+$ ($M+H^+$): 414.0349, found 414.0352.

***N*-(4-iodo-3-methylphenyl)-*N*-phenylacrylamide (3bq)**

yellow solid, 60.3 mg, 83%, mp 90–92 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 5.57 (dd, J = 10.27 Hz, J = 1.88 Hz, 1H), 6.10 (dd, J = 16.76 Hz, J = 10.24 Hz, 1H), 6.39 (dd, J = 16.77 Hz, J = 1.92 Hz, 1H), 6.68 (dd, J = 8.38 Hz, J = 2.56 Hz, 1H), 7.06 (s, 1H), 7.12–7.14 (m, 2H), 7.18–7.23 (m, 1H), 7.28–7.32 (m, 2H), 7.69 (d, J = 8.32 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.1, 97.7, 125.6, 126.3,126.4, 127.7, 128.2, 128.3, 128.4, 138.5, 141.0, 141.5, 141.7, 164.5. HRMS–ESI(m/z): calcd for $C_{16}H_{15}INO^+$ ($M+H^+$): 364.0193, found 364.0190.

***N*-(4-iodo-3-methylphenyl)-*N*-phenylbut-3-enamide (3br)**

yellow solid, 66.4 mg, 88%, mp 92–95 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 3.06 (d, J = 6.68 Hz, 2H), 5.01 (dd, J = 17.18 Hz, J = 1.24 Hz, 1H), 5.12 (dd, J = 10.19 Hz, J = 1.40 Hz, 1H), 5.91–6.01 (m, 1H), 6.78 (d, J = 7.48 Hz, 1H), 7.17 (d, J = 2.2 Hz, 1H), 7.23–7.25 (m, 3H), 7.36–7.38 (m, 2H), 7.72–7.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.2, 40.3, 97.8, 118.1, 123.6, 125.6, 128.1, 129.4, 129.5, 131.6, 139.6, 141.1, 142.3, 142.9, 170.1. HRMS–ESI(m/z): calcd for $C_{17}H_{17}INO^+$ ($M+H^+$): 378.0349, found 378.0345.

***N*-(4-iodo-3-methylphenyl)-*N*-phenylcinnamamide (3bs)**

yellow solid, 58.8 mg, 67%, mp 150–152 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 6.46 (d, J = 15.48 Hz, 1H), 6.80 (dd, J = 8.35 Hz, J = 2.32 Hz, 1H), 7.17 (s, 1H), 7.24–7.76 (m, 2H), 7.31–7.41 (m, 8H), 7.75–7.79 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.3, 98.6, 119.3, 119.4,126.9, 128.1, 128.3, 128.5,128.8,128.9,129.5, 129.8,129.9, 134.9, 139.5, 142.4, 143.0, 143.1, 166.1.HRMS–ESI(m/z): calcd for $C_{22}H_{19}INO^+$ ($M+H^+$): 440.0506, found 440.0509.

4-iodo-*N*-phenylaniline (4)[3]

white solid, 56.1 mg, 95%, mp 100–102 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.67 (s, 1H), 6.80–6.83 (m, 2H) , 6.95–6.99 (m, 1H) , 7.04–7.06 (m, 2H) , 7.24–7.30 (m, 2H) , 7.49–7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.1, 118.5, 119.3, 121.8, 129.5, 138.1, 142.2, 143.1. HRMS–ESI(m/z): calcd for $C_{12}H_{11}IN^+$ ($M+H^+$): 295.9931, found 295.9926.

(*E*)-*N*-phenyl-*N*-(4-styrylphenyl)acetamide (5)

white solid, 50.7 mg, 81%, mp 120–122 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 3H), 7.07 (s, 2H), 7.24–7.28 (m,

6H), 7.35 (t, J = 7.28 Hz, 4H), 7.50 (d, J = 7.32 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.0, 126.6, 127.0, 127.3, 127.8, 128.6, 128.8, 129.1, 129.9, 135.1, 137.1, 142.1, 142.5, 143.3, 170.6. HRMS–ESI(m/z): calcd for $C_{22}H_{20}NO^+$ ($M+H^+$): 314.1539, found 314.1535.

***N*-([1,1'-biphenyl]-4-yl)-*N*-phenylacetamide (6)[4]**

white solid, 47.7 mg, 83%, mp 120–122 ℃;^{1}H NMR (400 MHz, $CDCl_3$): δ 2.10 (s, 3H), 7.25 (s, 1H), 7.30–7.35 (m, 6H), 7.40–7.43 (m, 3H), 7.55 (d, J = 6.72 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.0, 126.6, 127.1, 127.4, 127.7, 127.8, 128.6, 128.9, 129.8, 140.4, 140.8, 141.9, 142.6, 170.6. HRMS–ESI(m/z): calcd for $C_{20}H_{18}NO^+$ ($M+H^+$): 288.1383, found 288.1385.

***N*-phenyl-*N*-(4-(phenylethynyl)phenyl)acetamide (7)**

yellow oil, 56.6 mg, 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3H), 7.20–7.26 (m, 4H), 7.33–7.41 (m, 6H), 7.50–7.53 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.1, 88.7, 123.0, 126.0, 126.5, 128.4, 128.5, 128.6, 129.7, 129.9, 131.6, 131.7, 132.2, 142.8, 170.5. HRMS–ESI(m/z): calcd for $C_{22}H_{18}NO^+$ ($M+H^+$): 312.1383, found 312.1386.

References

1. (a) N. Itoh, T. Sakamoto, E. Miyazawa and Y. Kikugawa, *J. Org. Chem.*, 2002, **67**, 7424. (b) C. He, C. Chen, J. Cheng, C. Liu, W. Liu, Q. Li and A. Lei, *Angew. Chem. Int. Ed.*, 2008, **47**, 6414.
2. A. P. Antonchick, R. Samanta, K. Kulikov and J. Lategahn, *Angew. Chem. Int. Ed.*, 2011, **50**, 8605.
3. Q. Yang, Xi. Lei, Z. Yin, Z. Deng and Y. Peng, *Synthesis*, 2019, **51**, 538.
4. P. E. Maligres, S. W. Krska and P. G. Dormer, *J. Org. Chem.*, 2012, **77**, 7646.

X-ray crystallography data

Crystals of **3aa** were obtained by recrystallization from CH_2Cl_2/hexane (1:8). The X-ray crystallography was measured on Bruker D8 Venture Photon instrument.

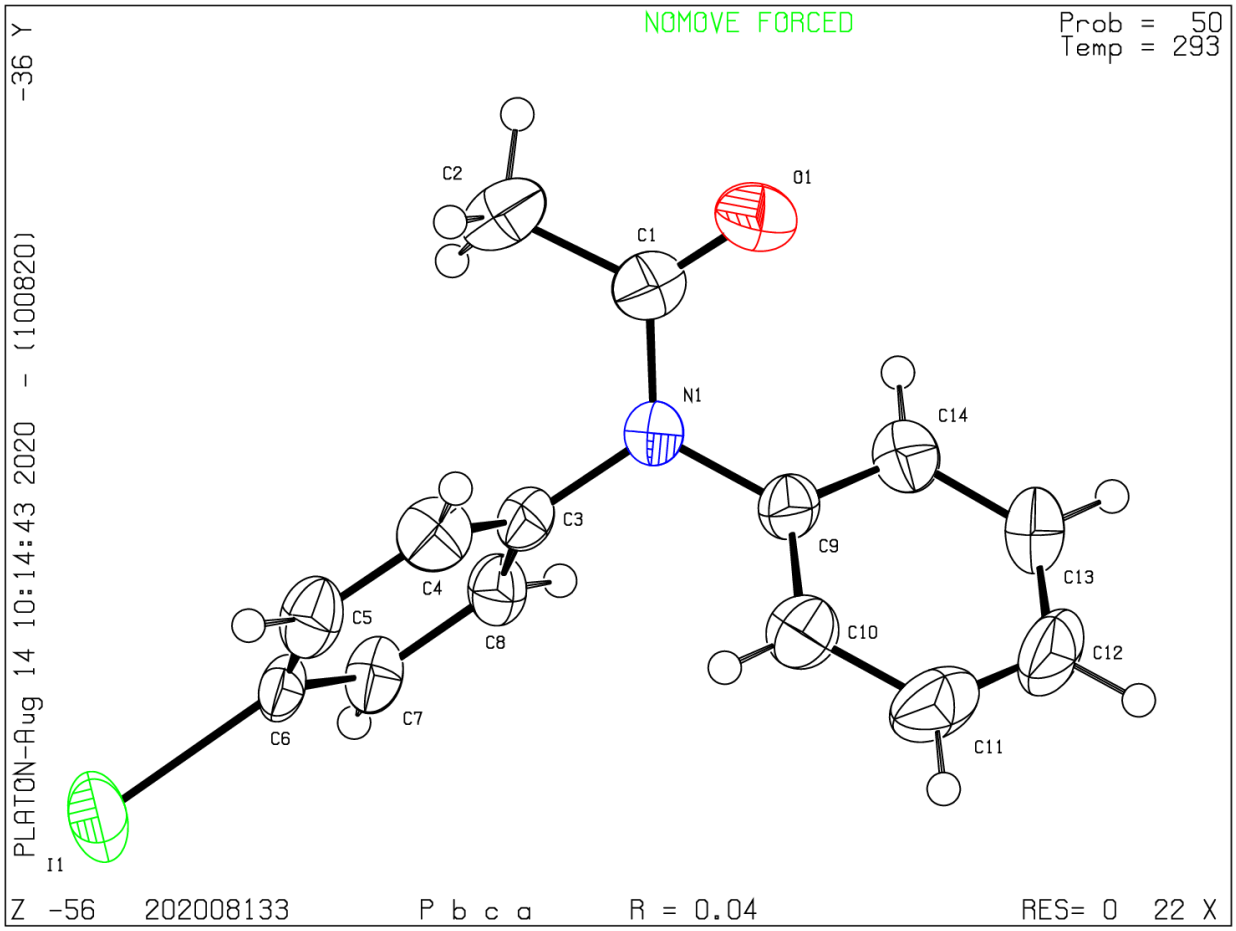


Figure 1. X-ray crystallography of **3aa**.Thermal ellipsoids are drawn at the 50% probability level.

Bond precision: C-C = 0.0078 A Wavelength=1.54184

Cell: a=13.8944(4) b=8.9694(2) c=20.9762(6)
alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	2614.15(12)	2614.14(12)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C14 H12 I N O	C14 H12 I N O
Sum formula	C14 H12 I N O	C14 H12 I N O
Mr	337.15	337.15
Dx,g cm-3	1.713	1.713
Z	8	8
Mu (mm-1)	19.109	19.109
F000	1312.0	1312.0
F000'	1313.13	
h,k,lmax	16,10,25	16,10,25
Nref	2326	2327
Tmin,Tmax	0.096,0.148	0.433,1.000
Tmin'	0.020	

Correction method= # Reported T Limits: Tmin=0.433 Tmax=1.000
AbsCorr = MULTI-SCAN

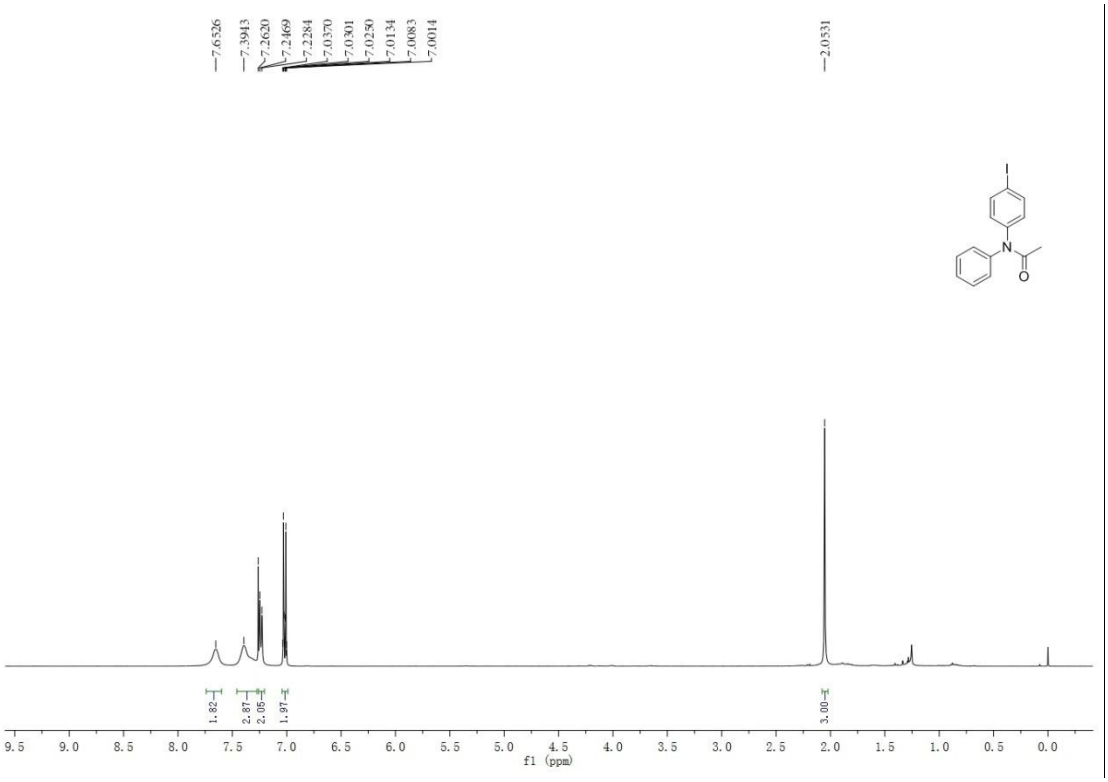
Data completeness= 1.000 Theta(max)= 67.065

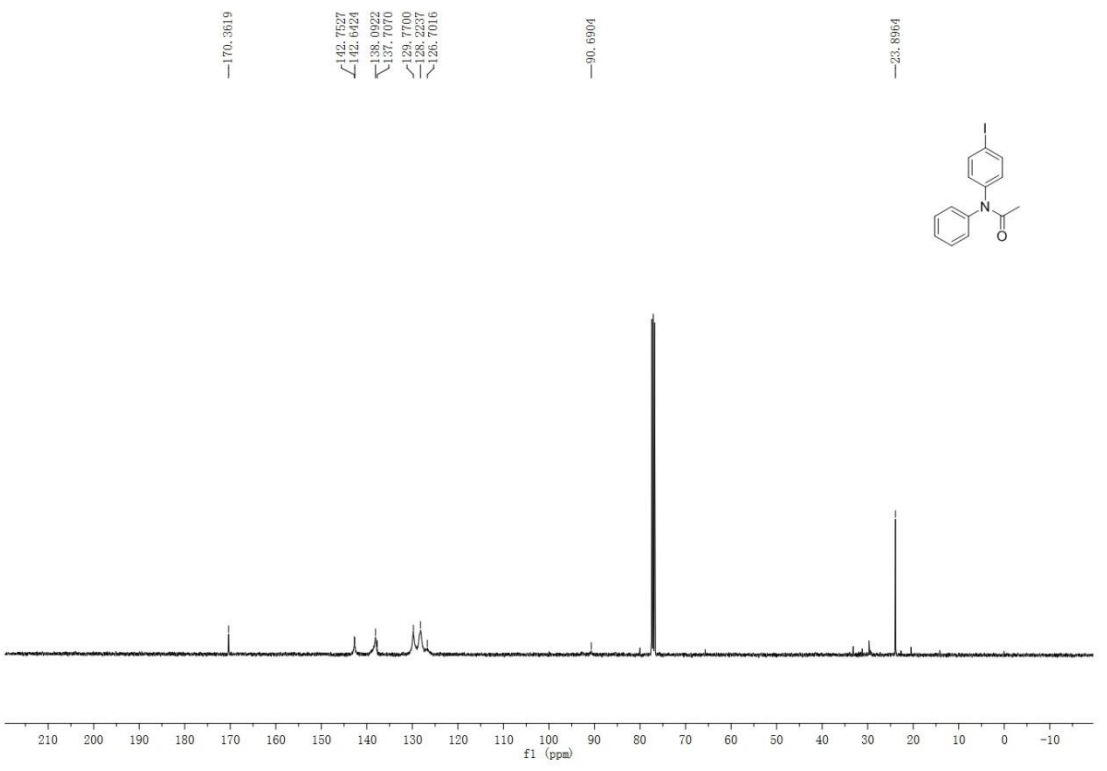
R(reflections)= 0.0428(1761) wR2(reflections)= 0.1311(2327)

S = 1.028 Npar= 155

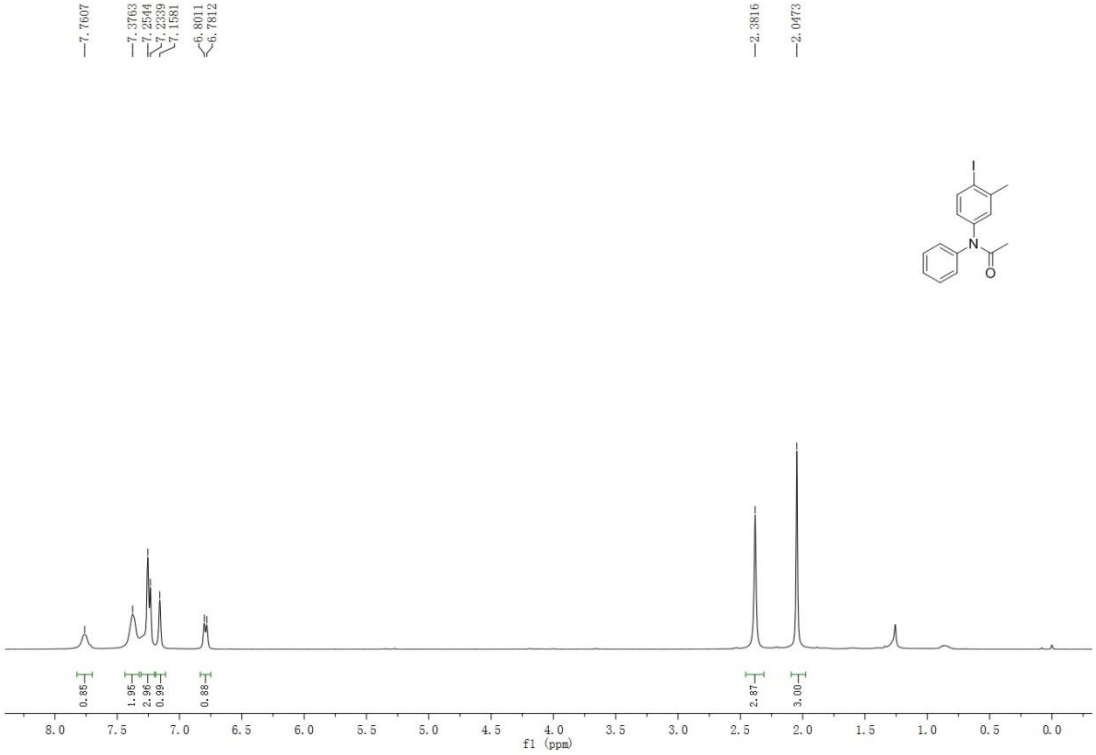
Copies of ^{1}H and ^{13}C NMR spectra

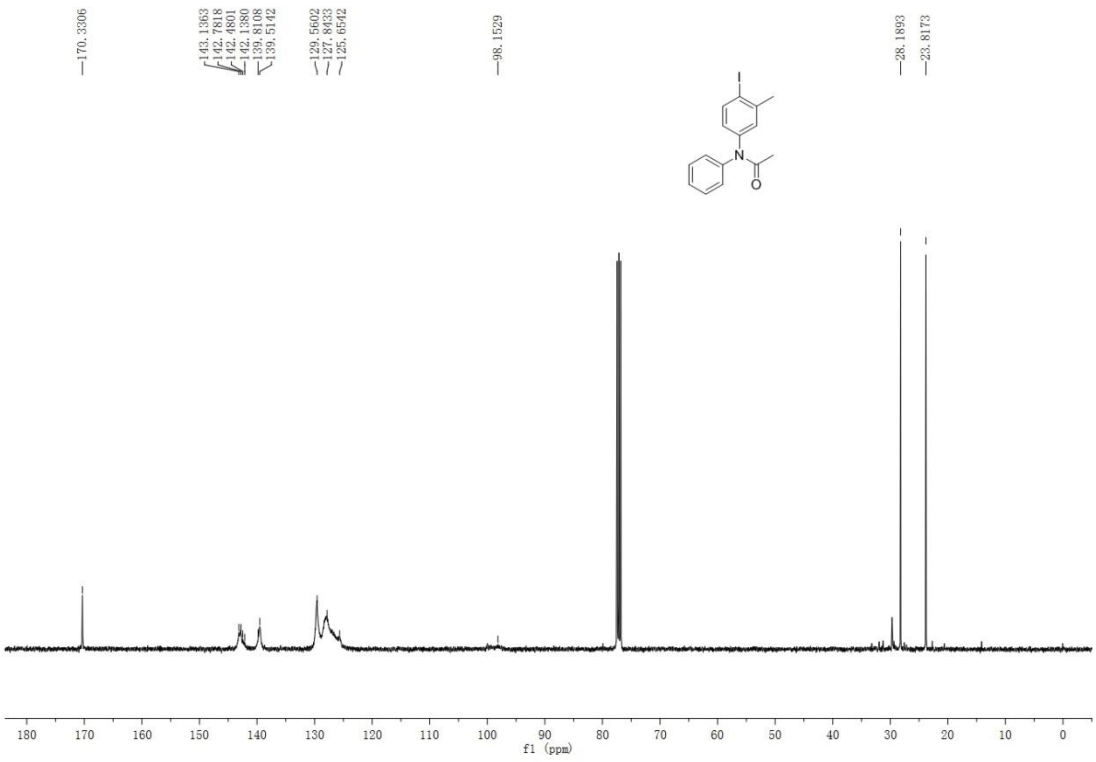
N-(4-iodophenyl)-N-phenylacetamide(3aa)



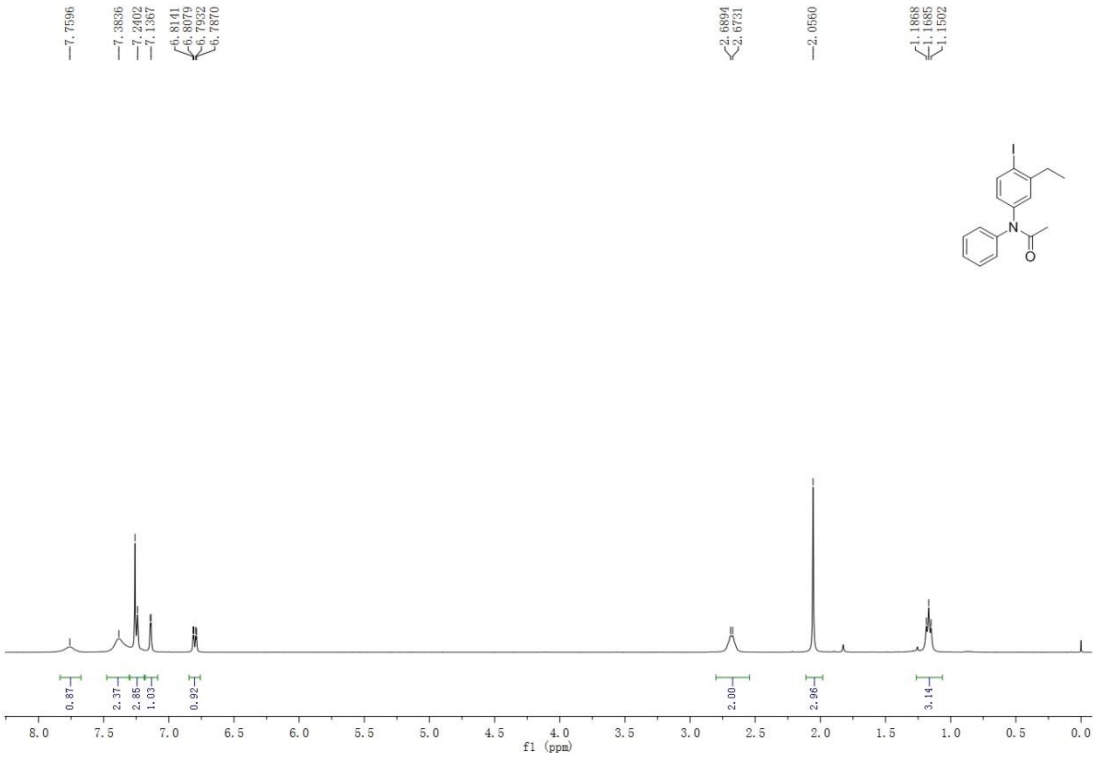


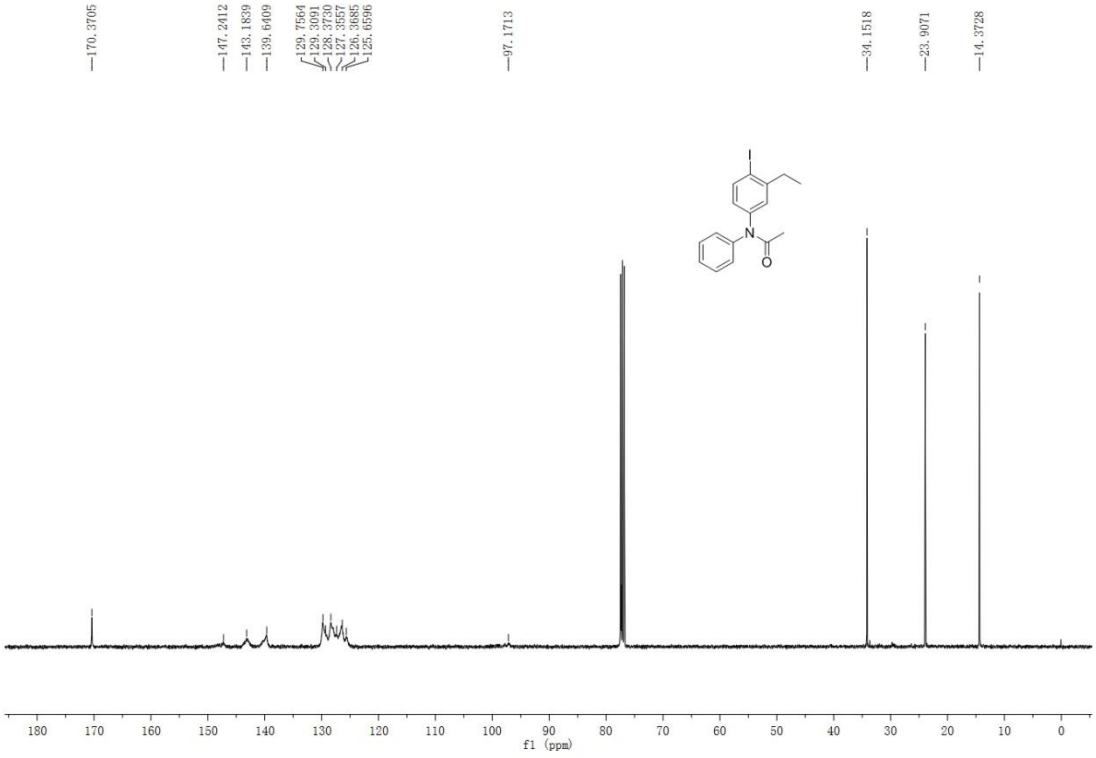
N-(4-iodo-3-methylphenyl)-N-phenylacetamide(3ba)



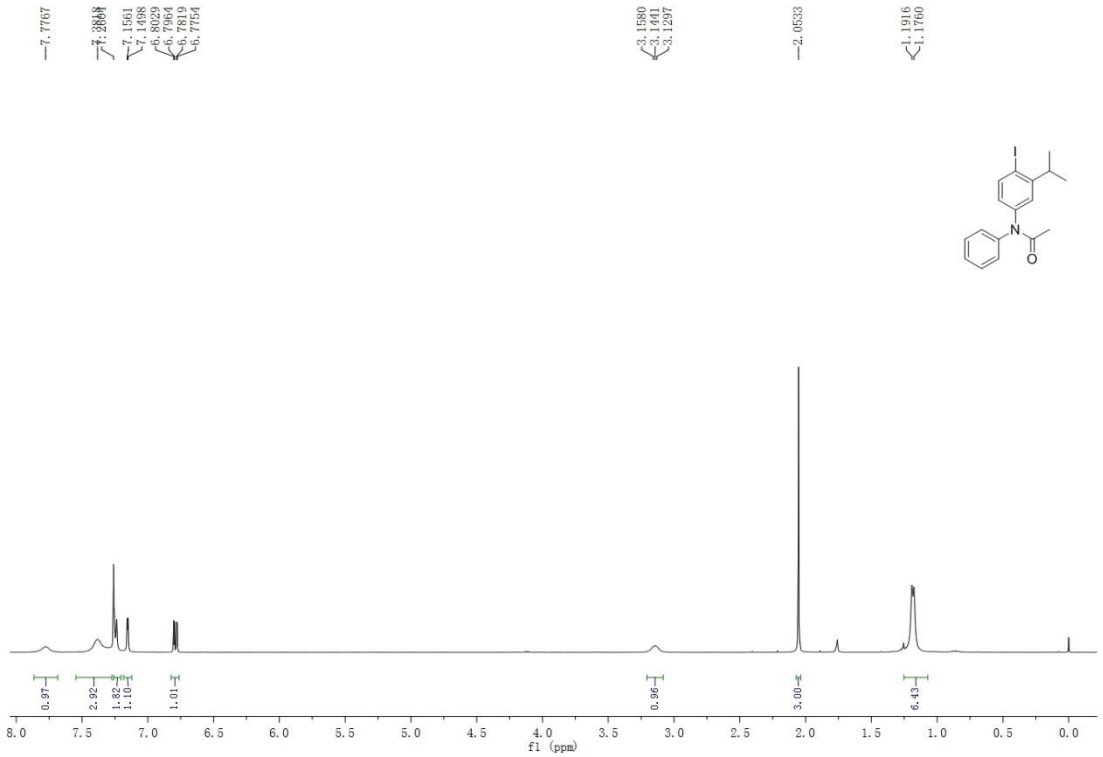


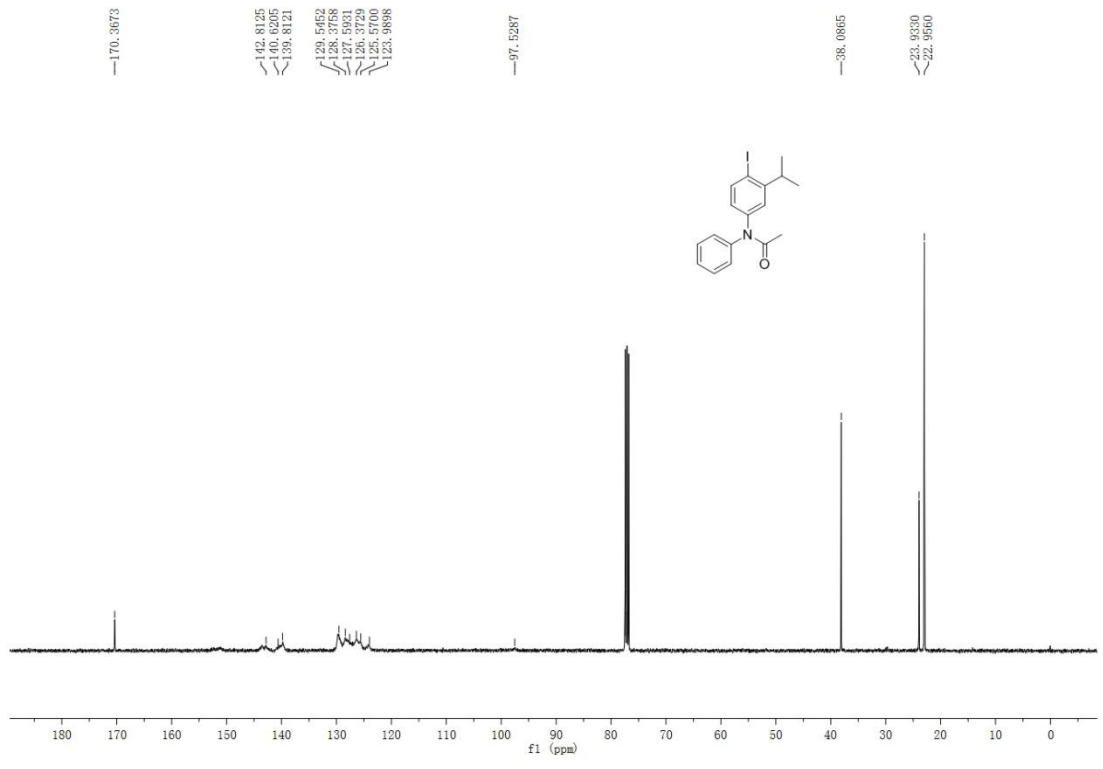
N-(3-ethyl-4-iodophenyl)-N-phenylacetamide(3ca)



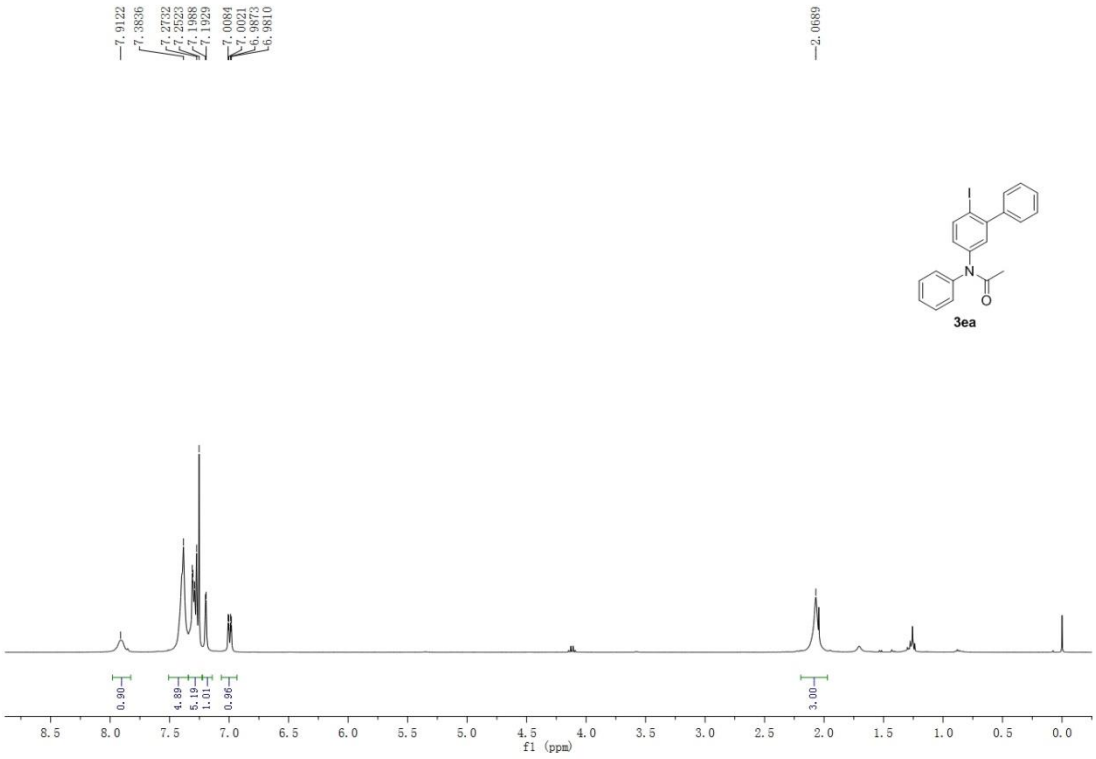


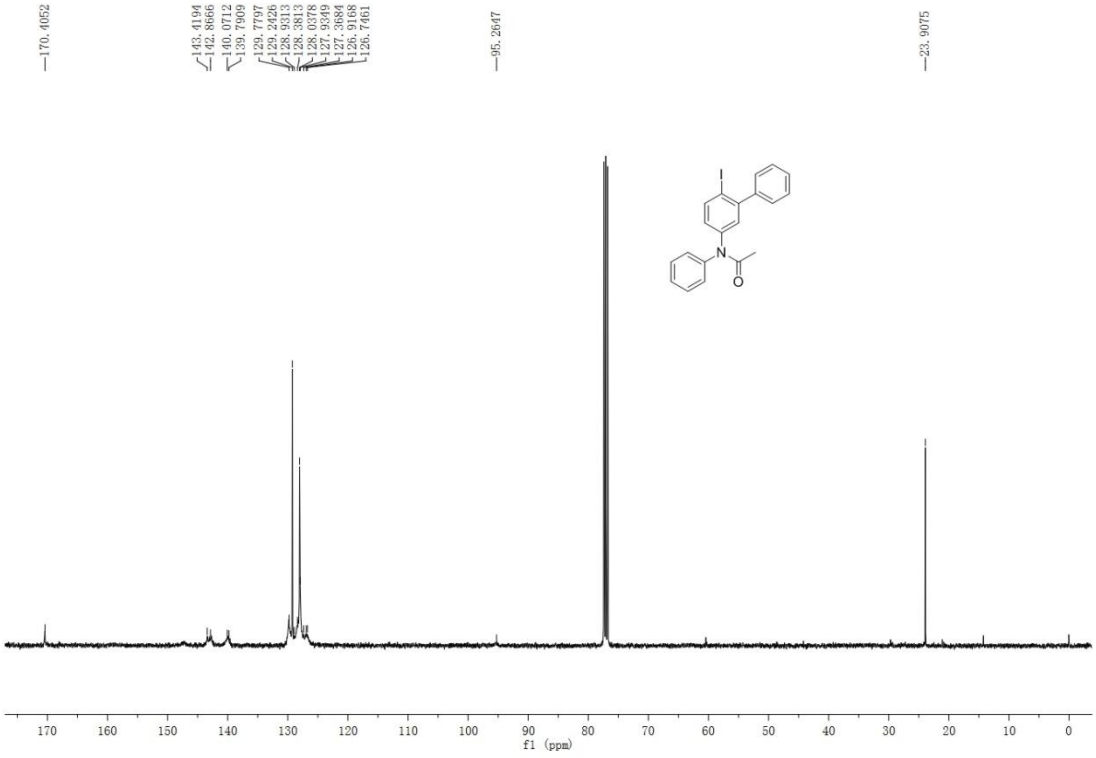
N-(4-iodo-3-isopropylphenyl)-N-phenylacetamide(3da)



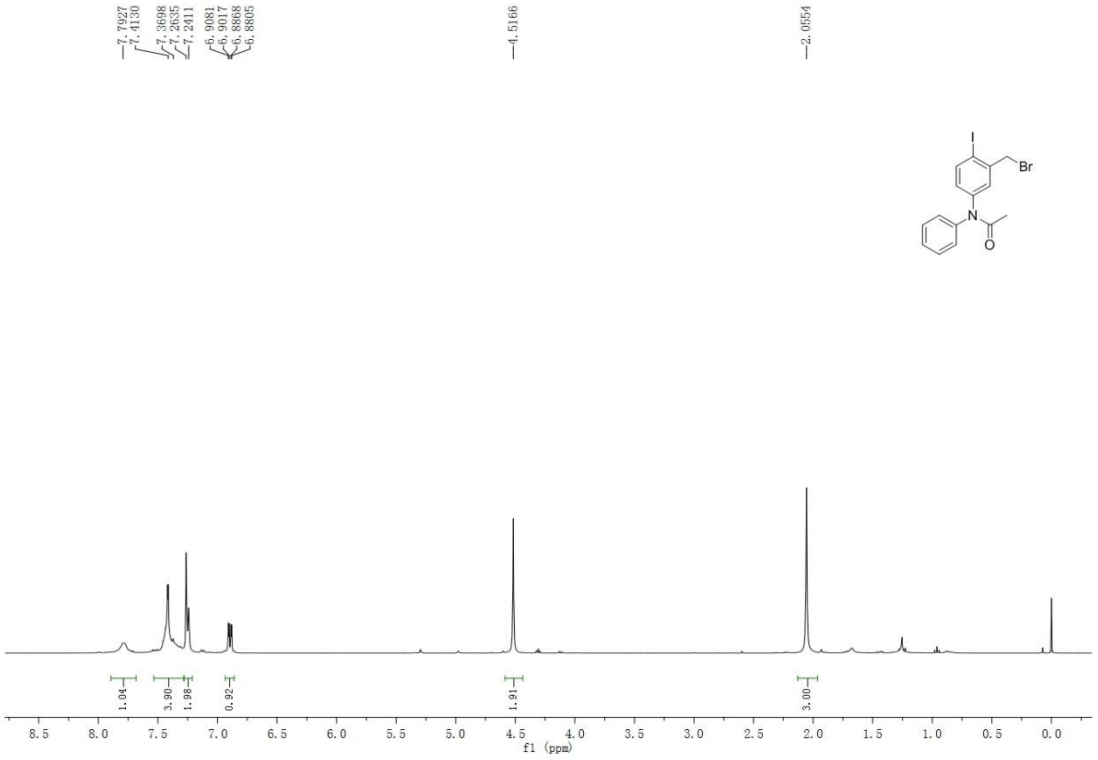


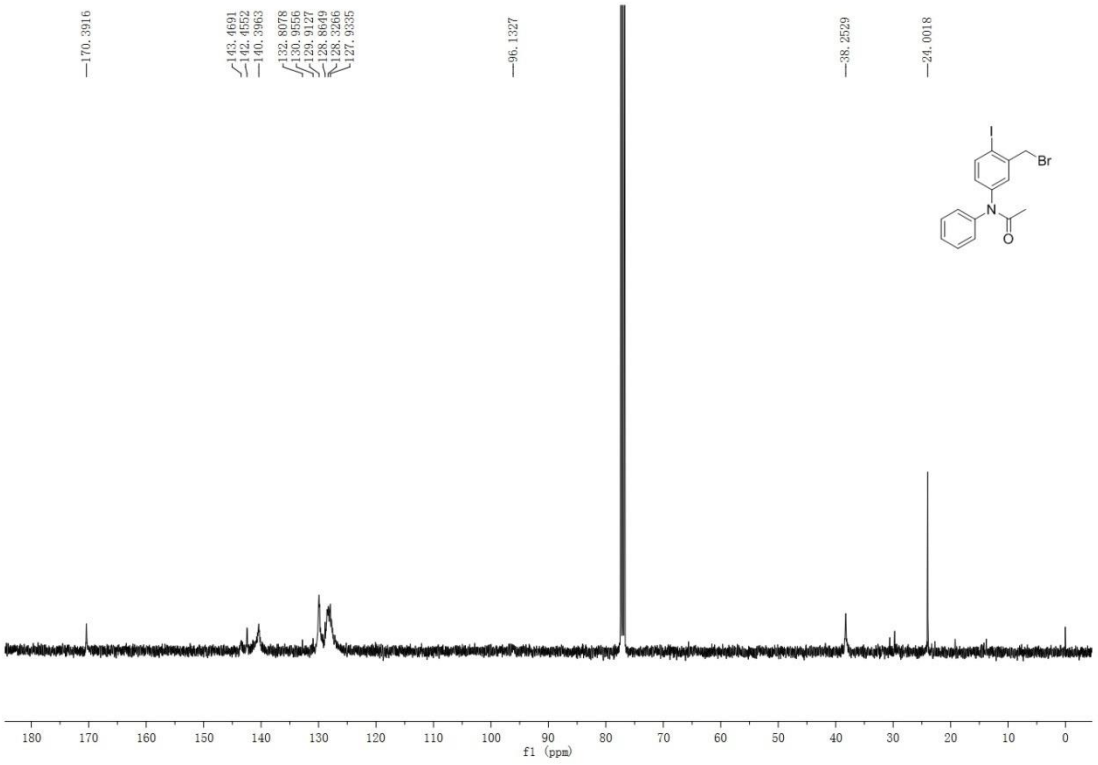
N-(6-iodo-[1,1'-biphenyl]-3-yl)-N-phenylacetamide(3ea)



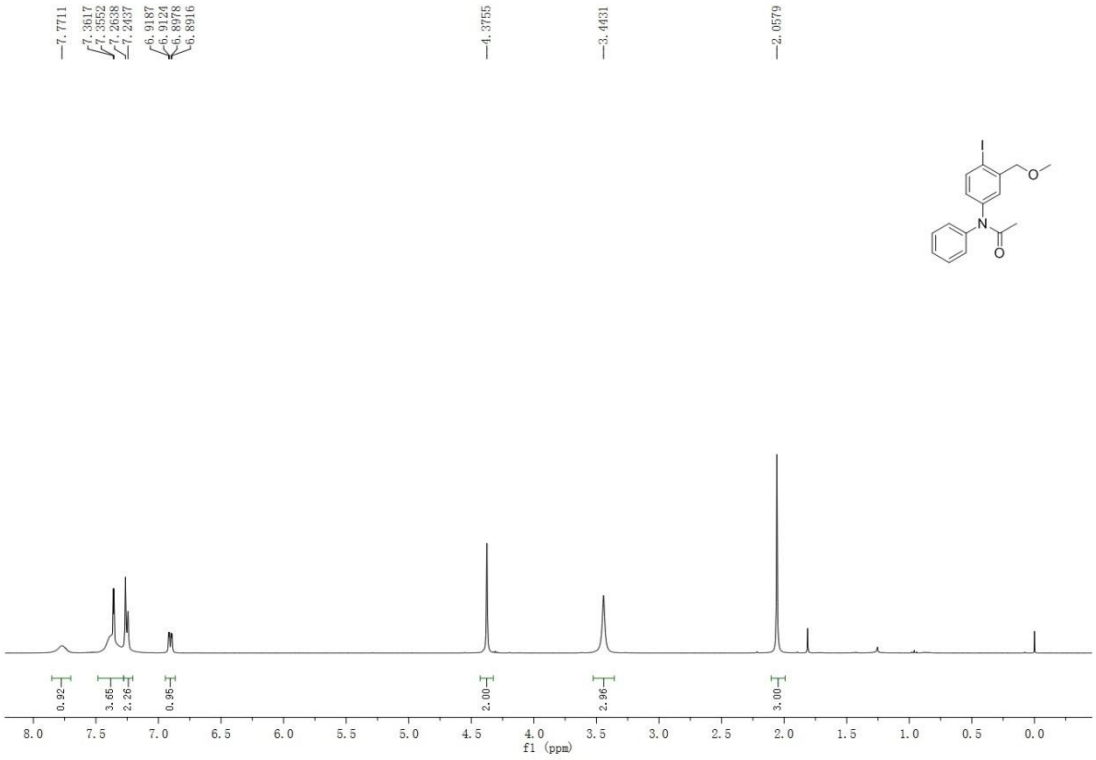


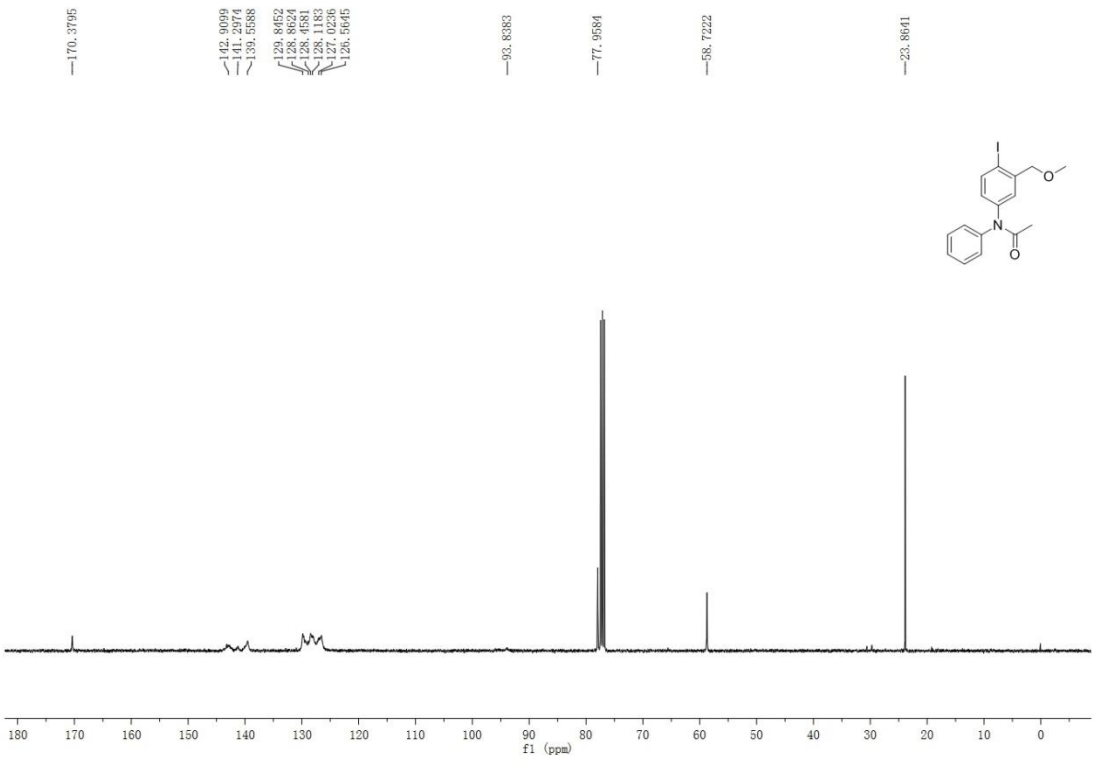
N-(3-(bromomethyl)-4-iodophenyl)-N-phenylacetamide(3fa)



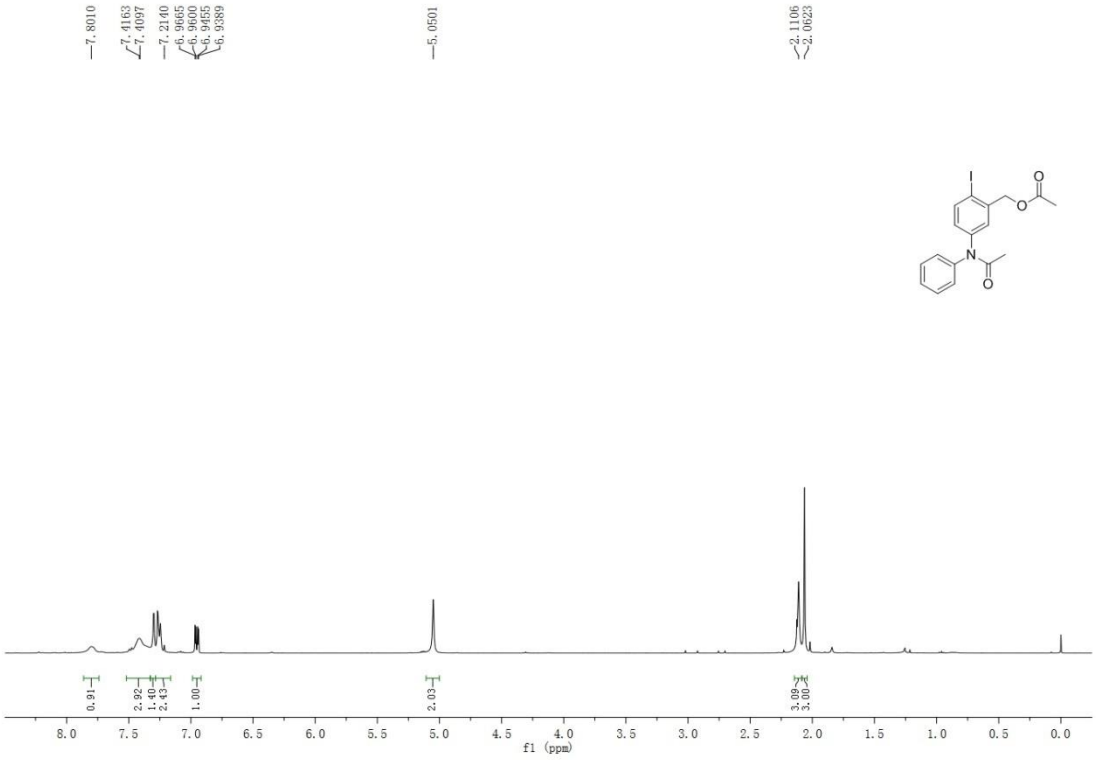


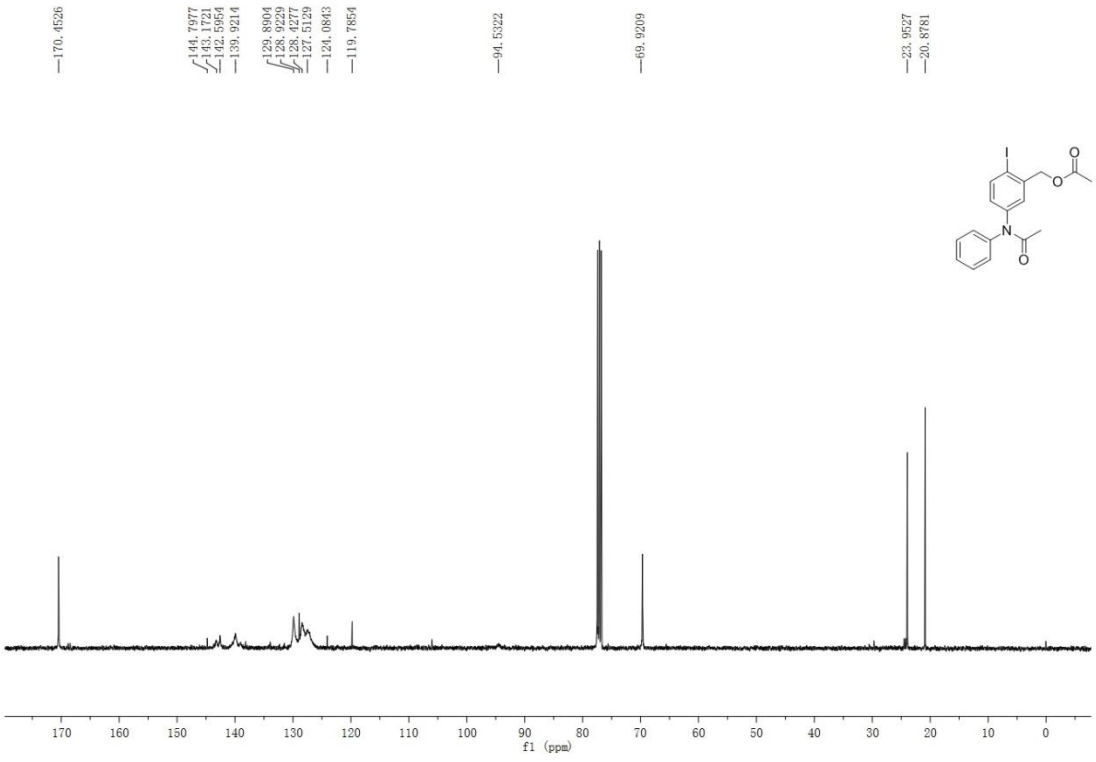
N-(4-iodo-3-(methoxymethyl)phenyl)-N-phenylacetamide (3ga)



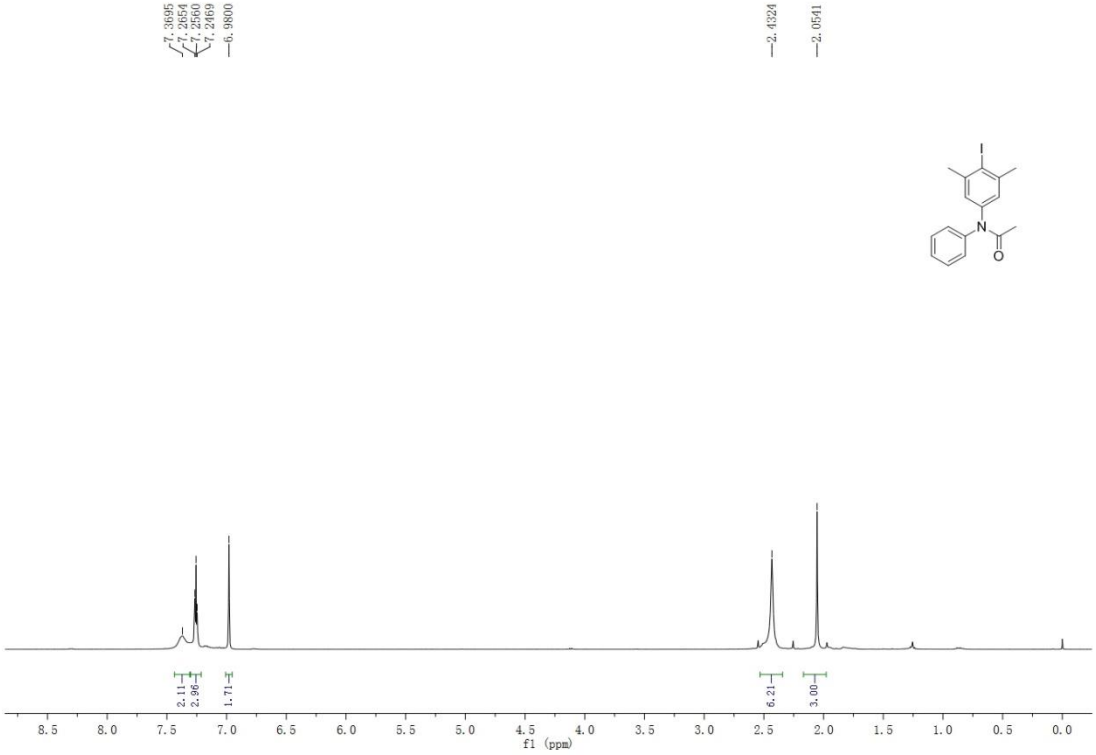


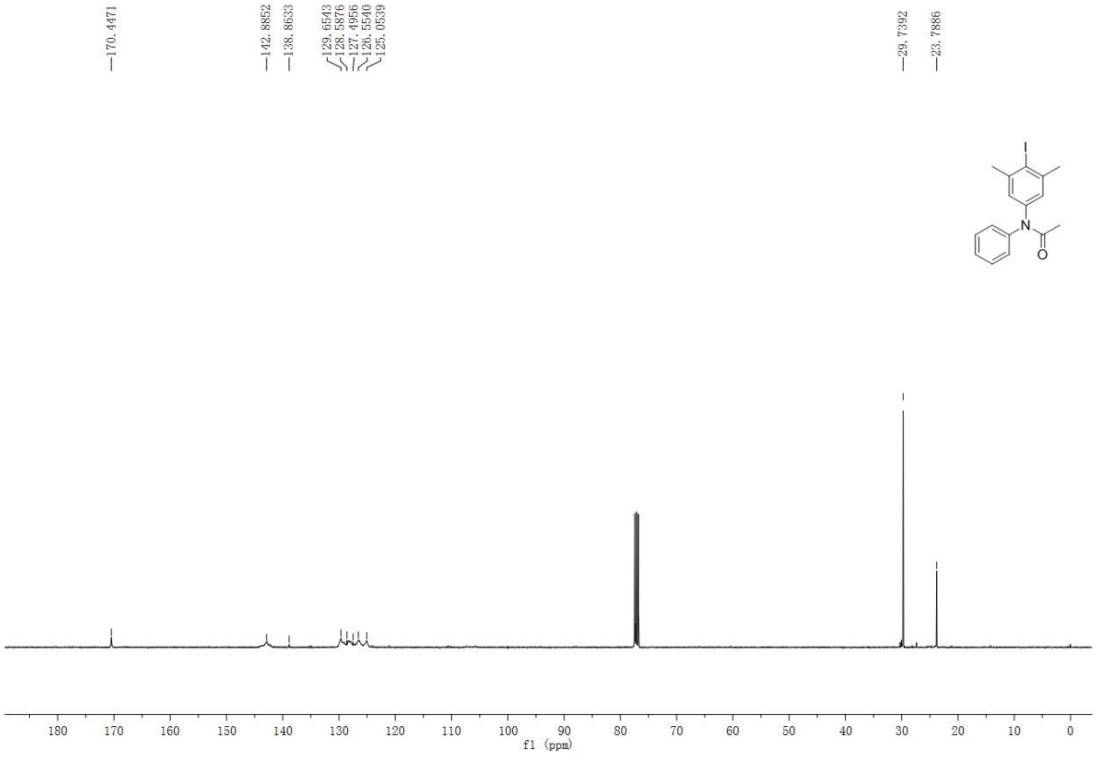
2-iodo-5-(N-phenylacetamido)benzyl acetate (3ha)



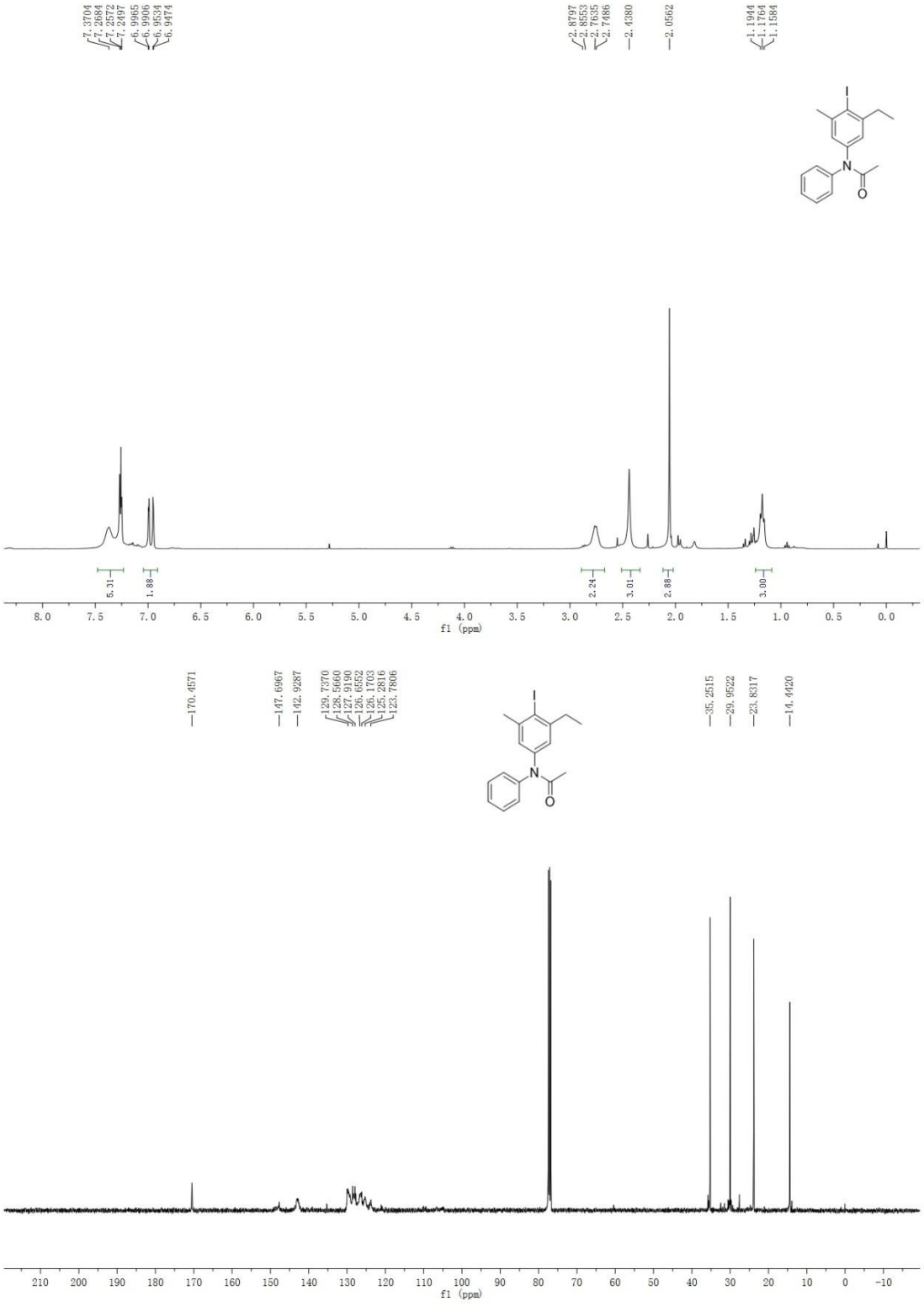


N-(4-iodo-3,5-dimethylphenyl)-N-phenylacetamide(3ia)

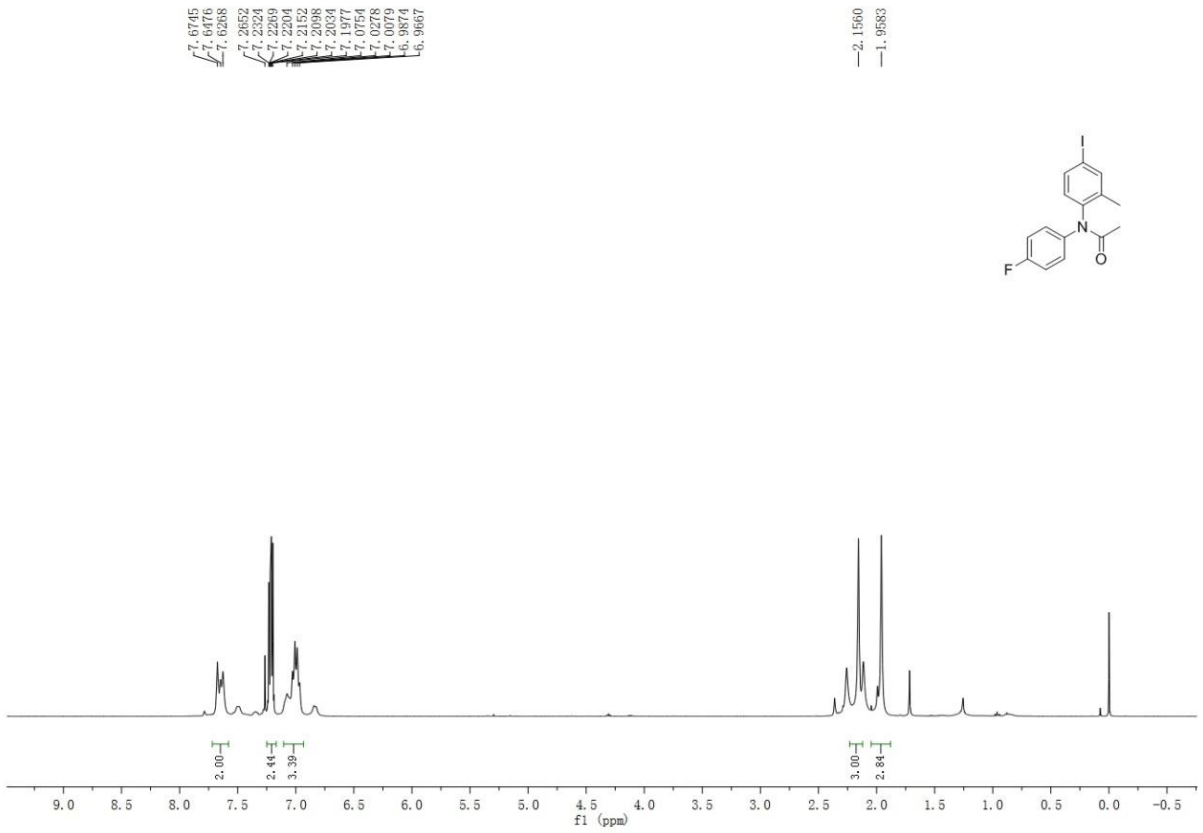


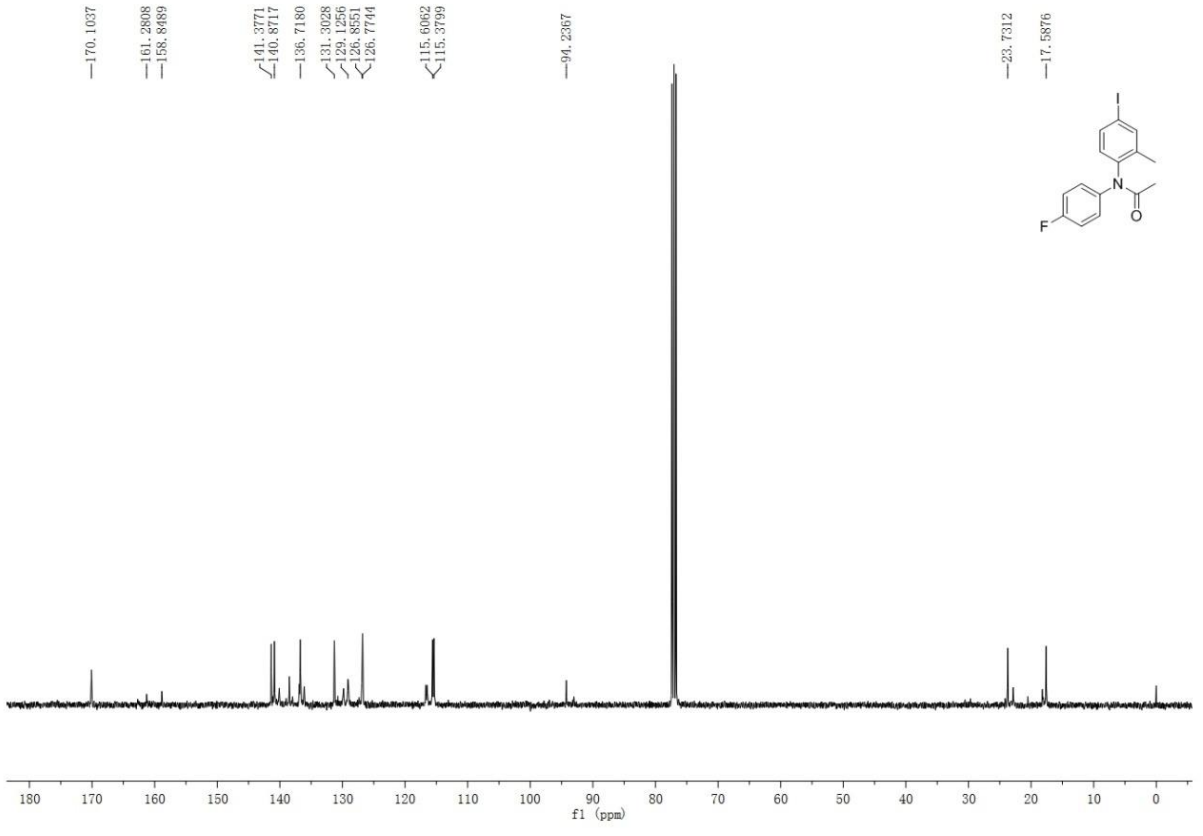


N-(3-ethyl-4-iodo-5-methylphenyl)-N-phenylacetamide(3ja)

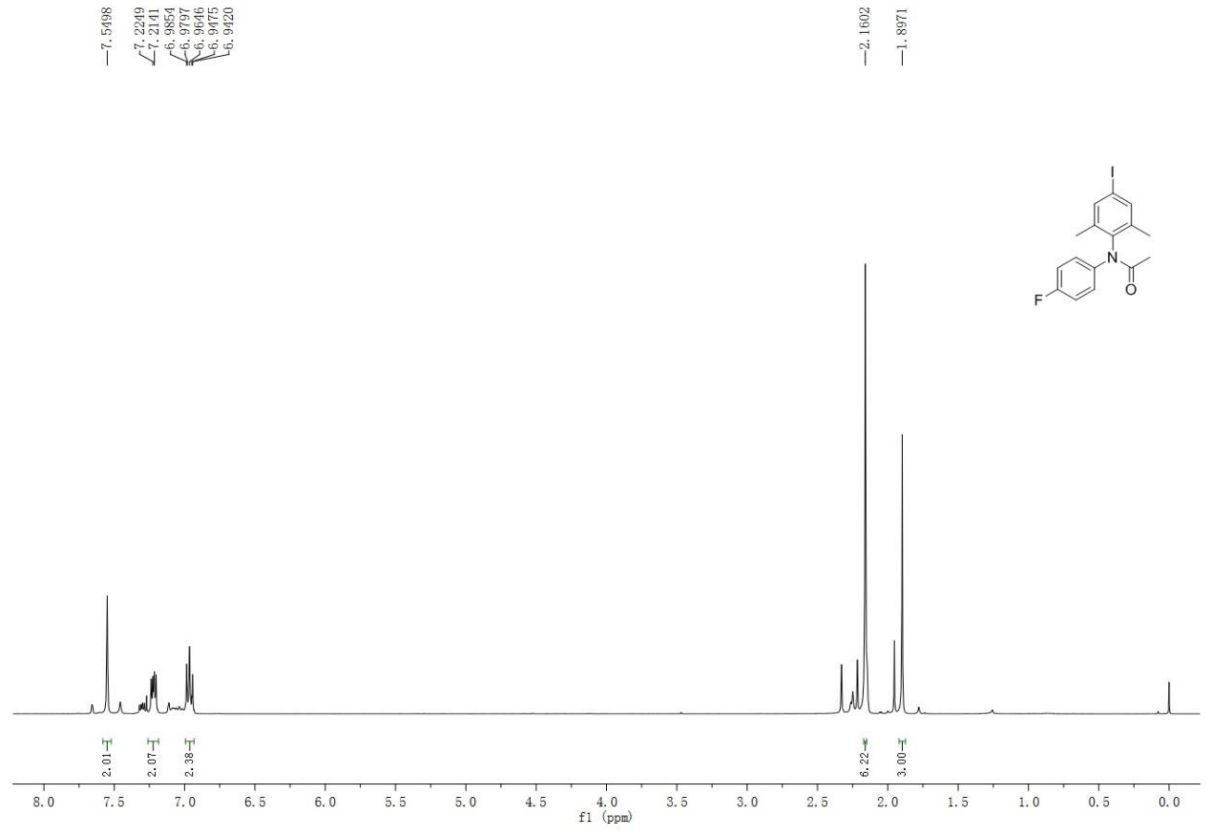


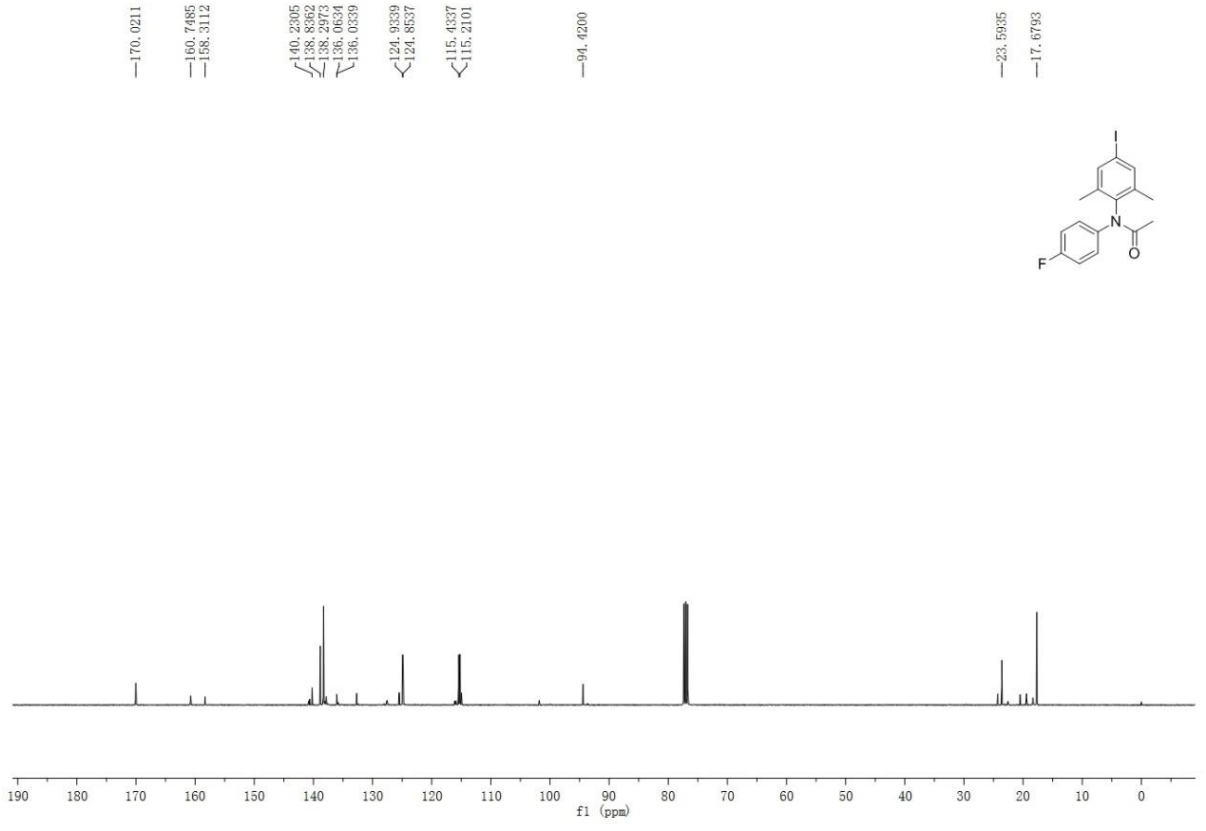
N-(4-fluorophenyl)-N-(4-iodo-2-methylphenyl)acetamide (3kb)



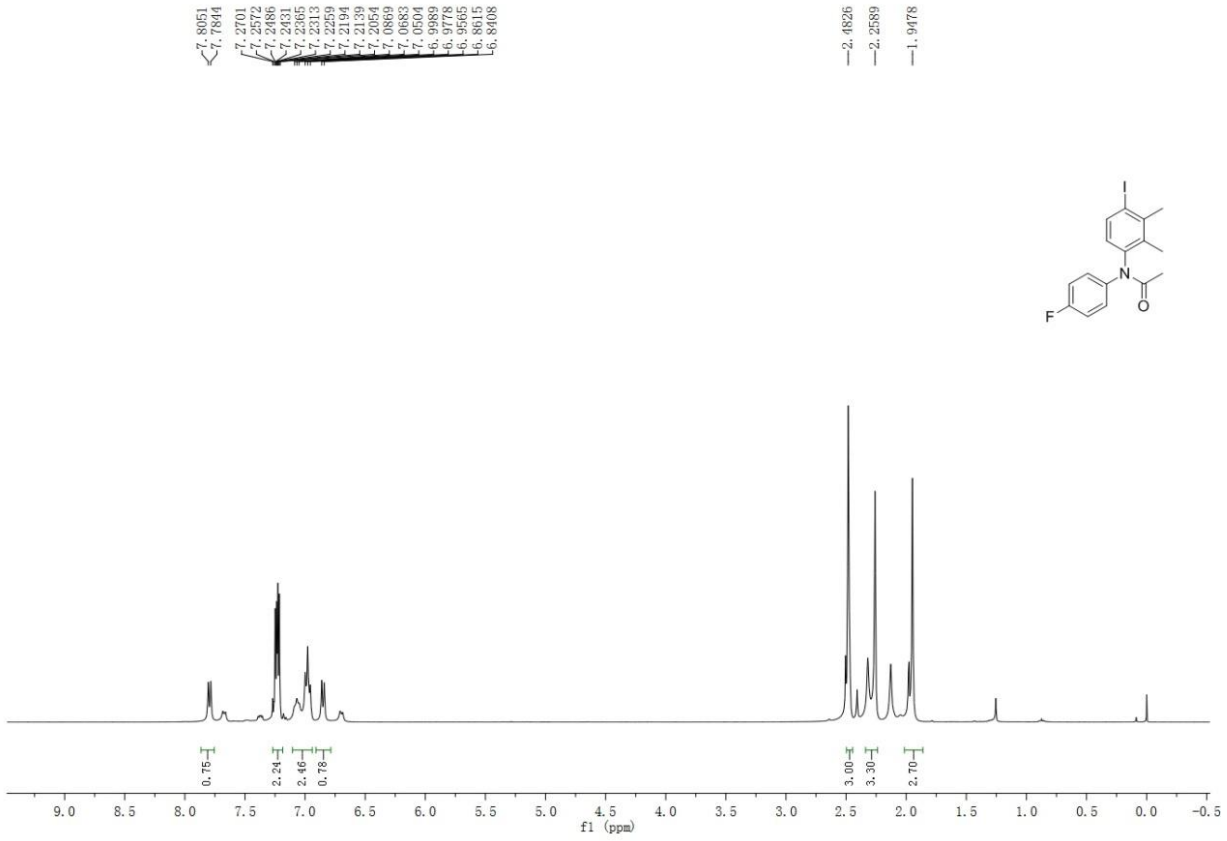


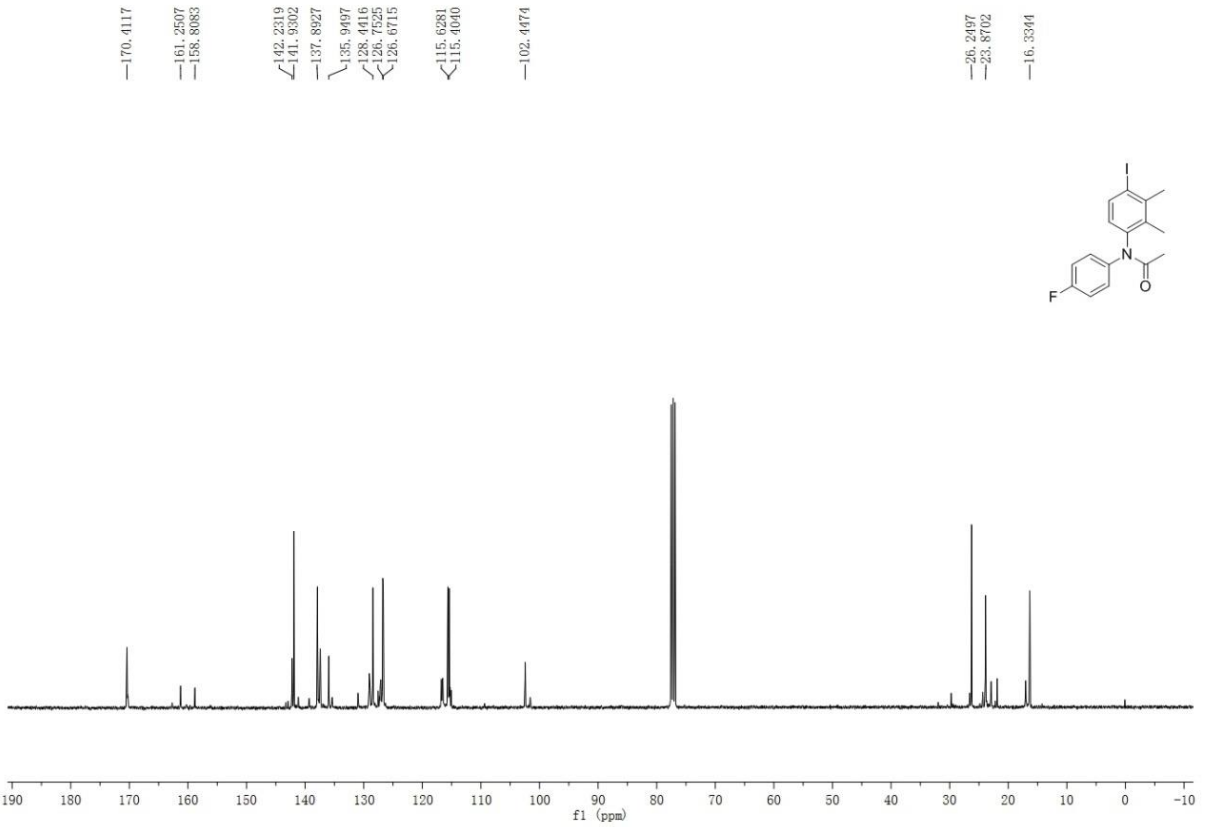
N-(4-fluorophenyl)-N-(4-iodo-2, 6-dimethylphenyl)acetamide (3lb)



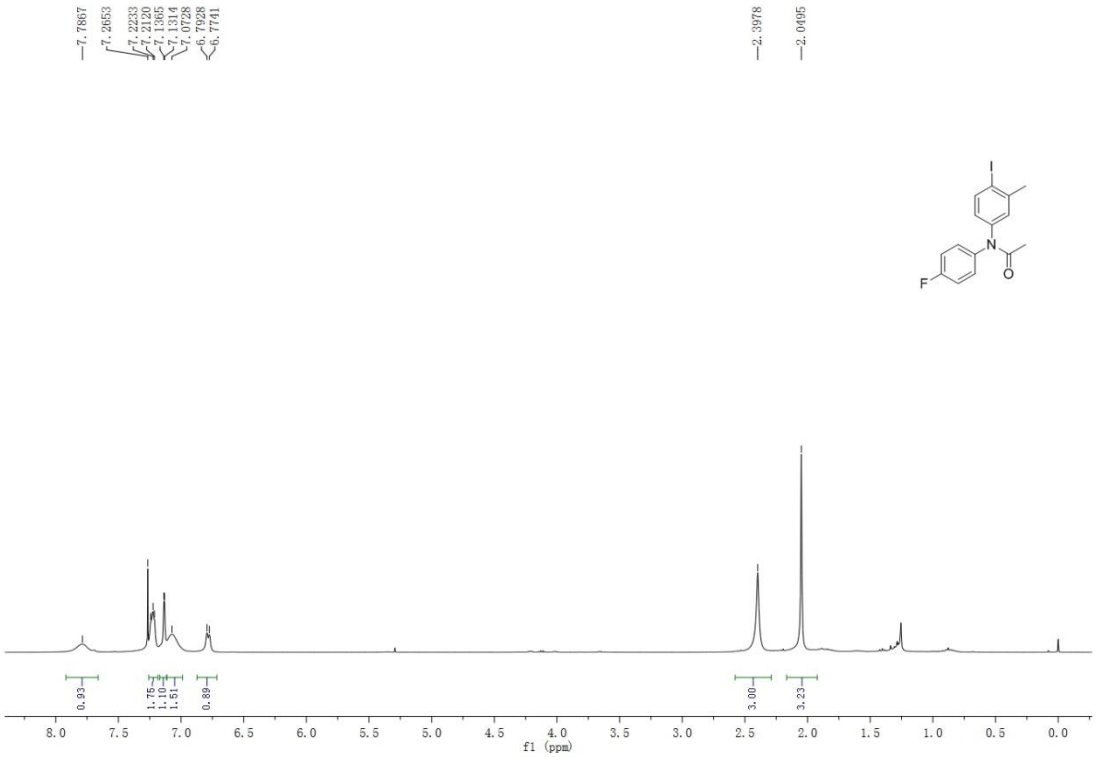


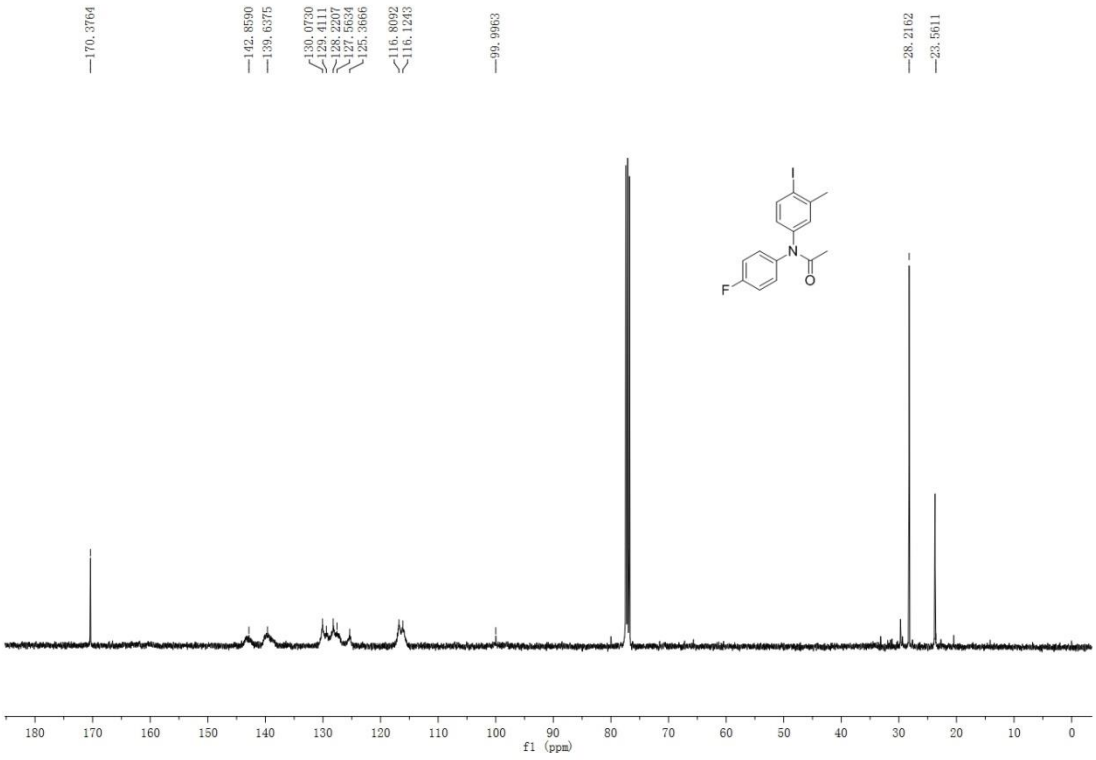
N-(4-fluorophenyl)-N-(4-iodo-2, 3-dimethylphenyl)acetamide (3mb)



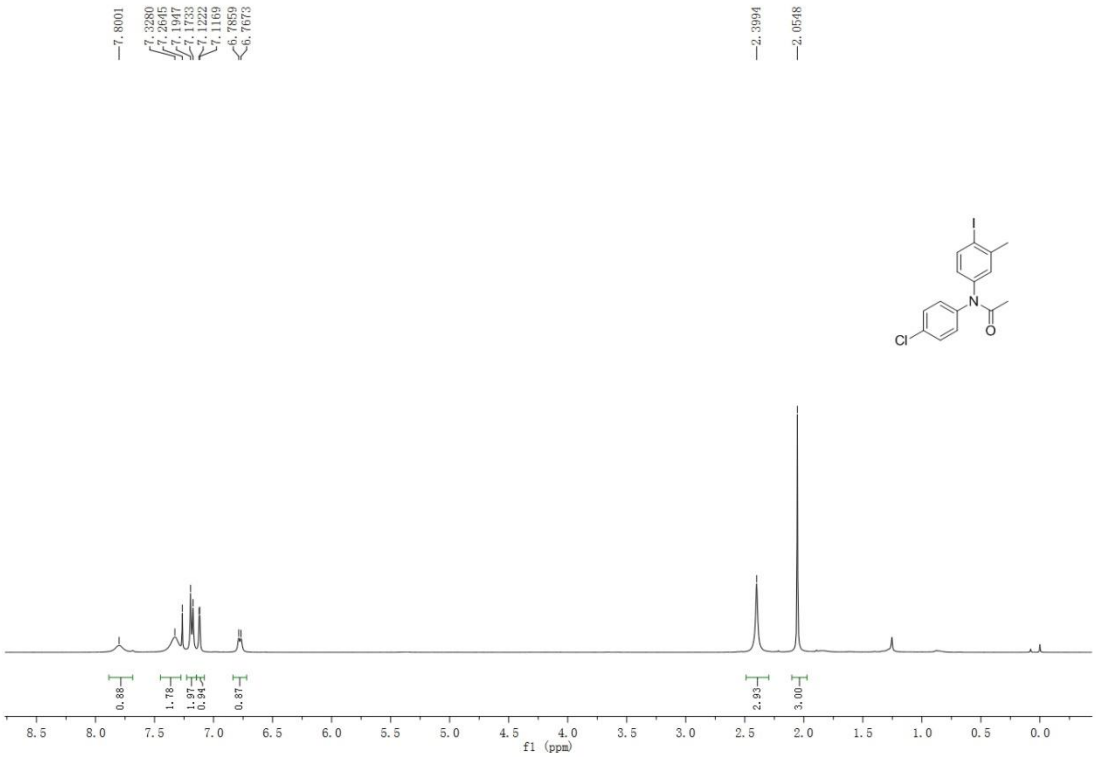


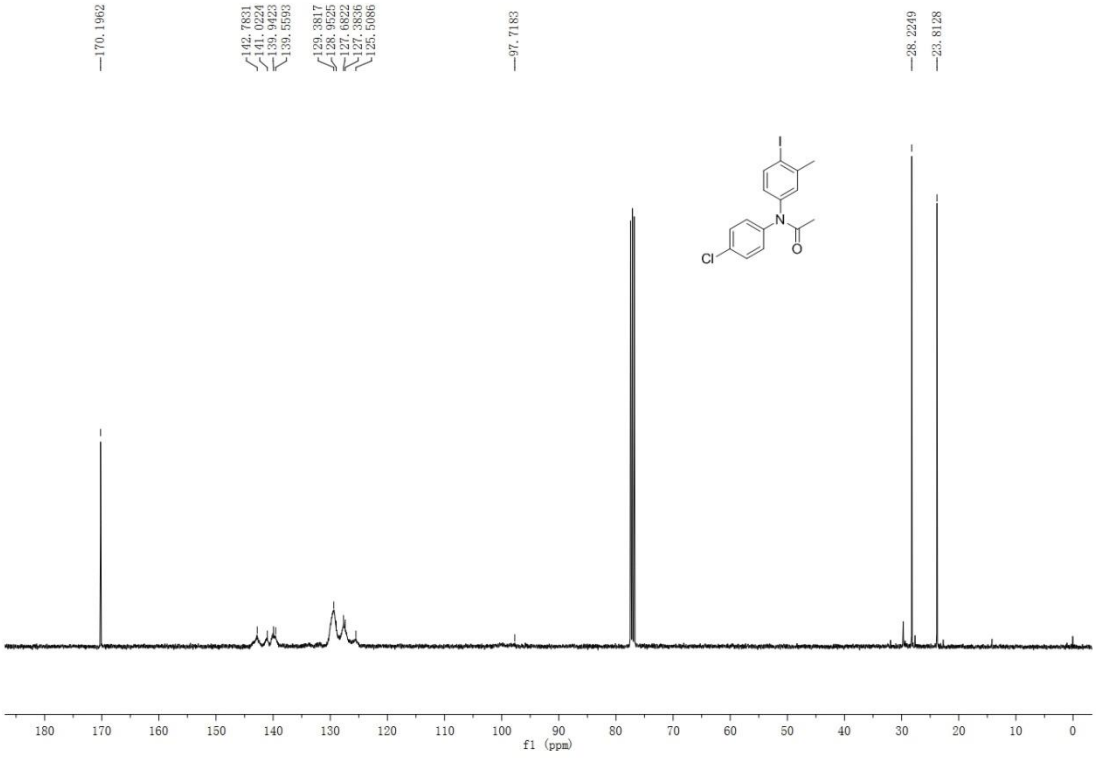
N-(4-fluorophenyl)-N-(4-iodo-3-methylphenyl)acetamide(3bb)



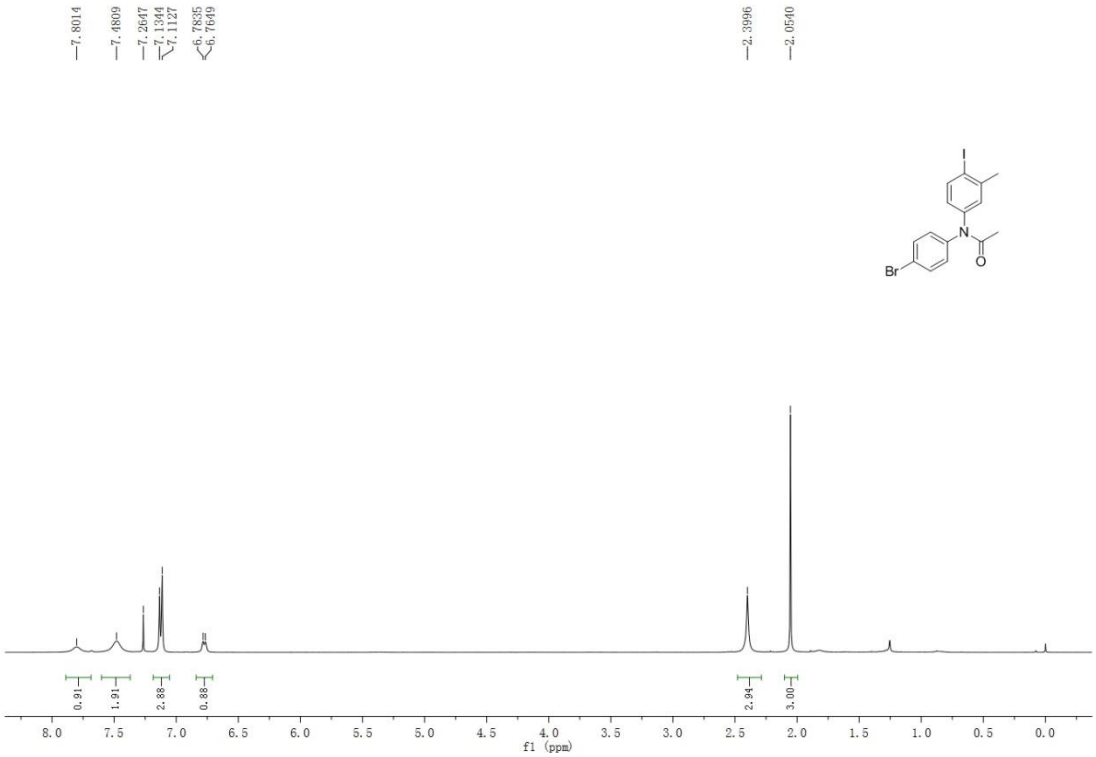


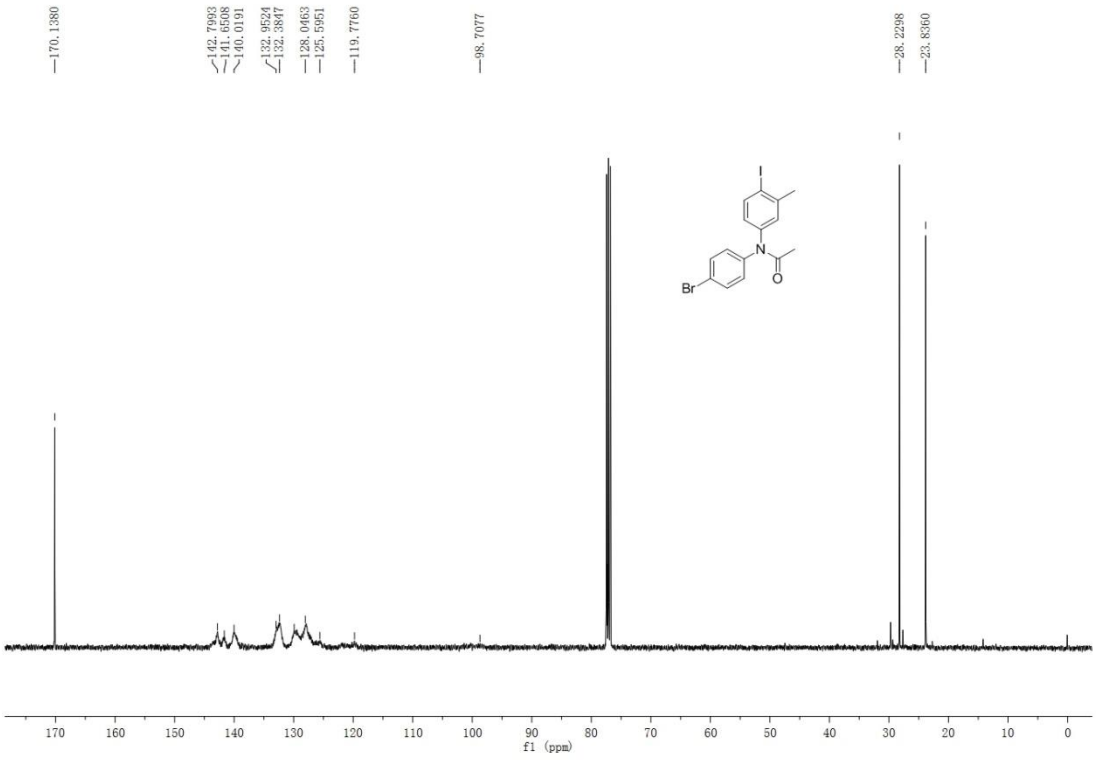
N-(4-chlorophenyl)-N-(4-iodo-3-methylphenyl)acetamide(3bc)



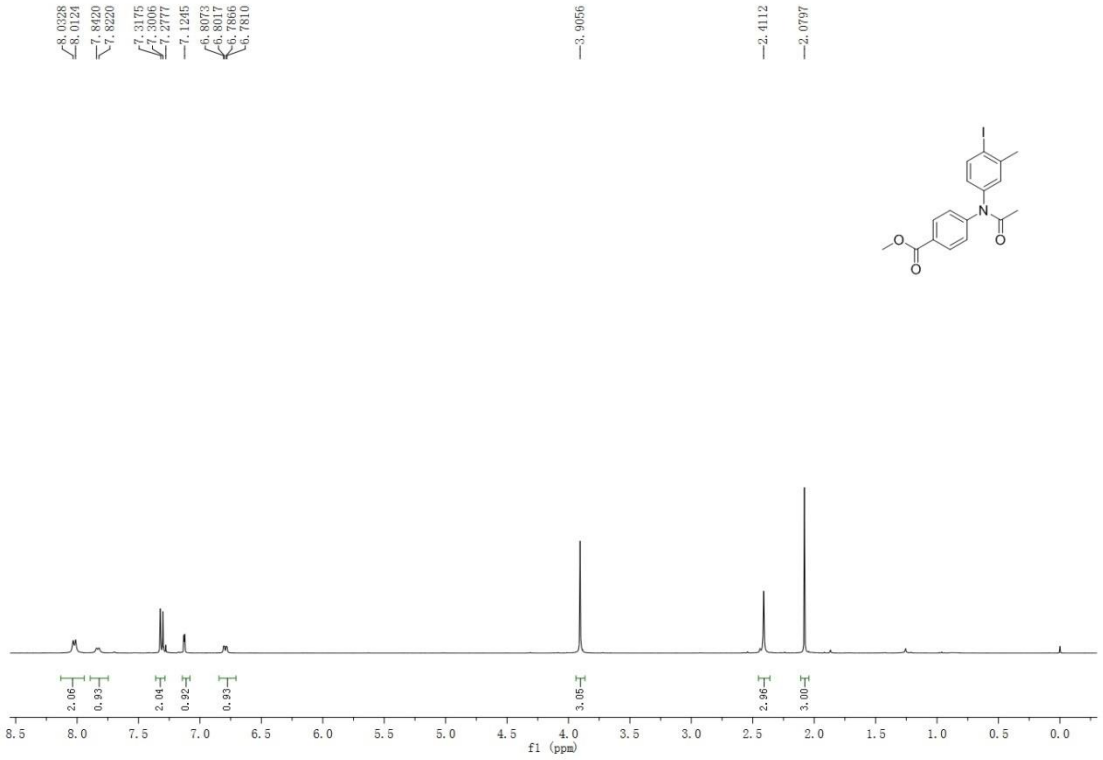


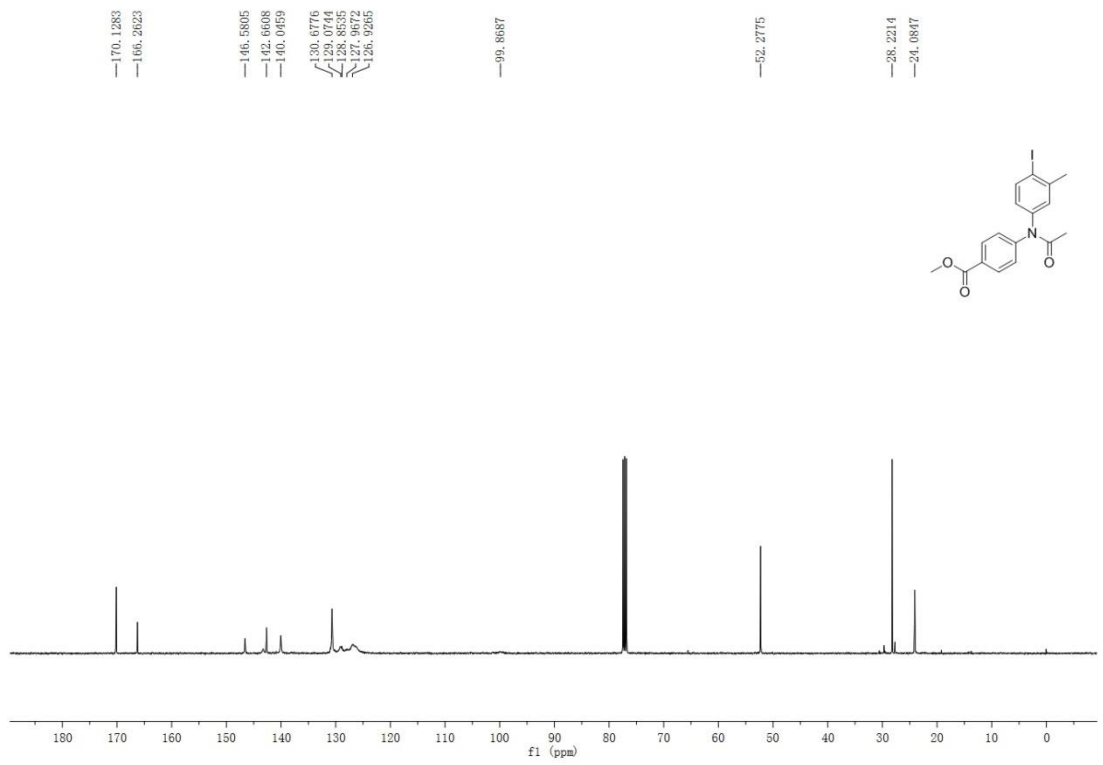
N-(4-bromophenyl)-N-(4-iodo-3-methylphenyl)acetamide(3bd)



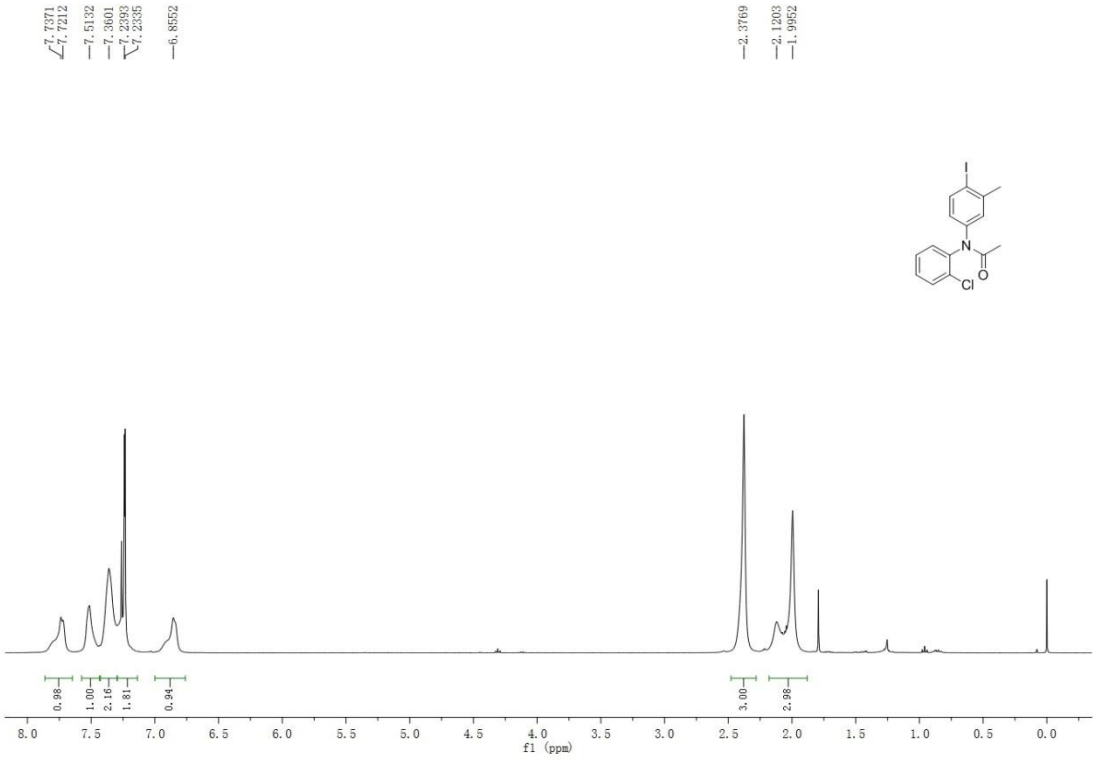


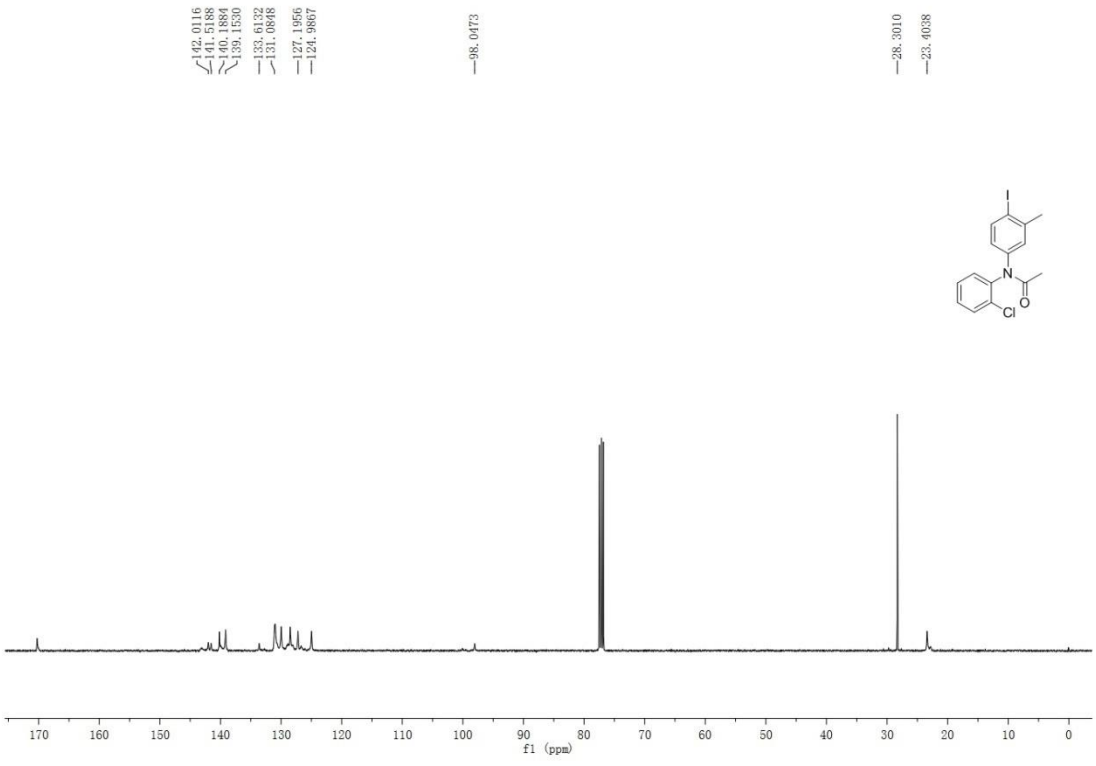
methyl 4-(N-(4-iodo-3-methylphenyl)acetamido)benzoate (3be)



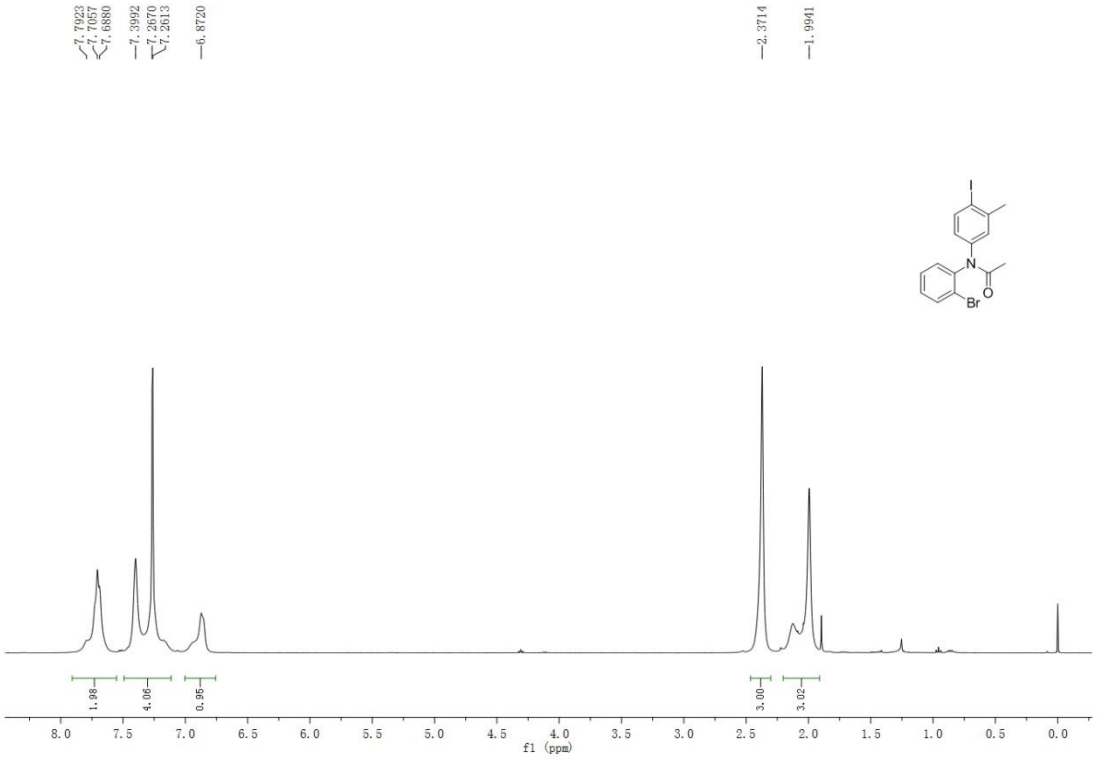


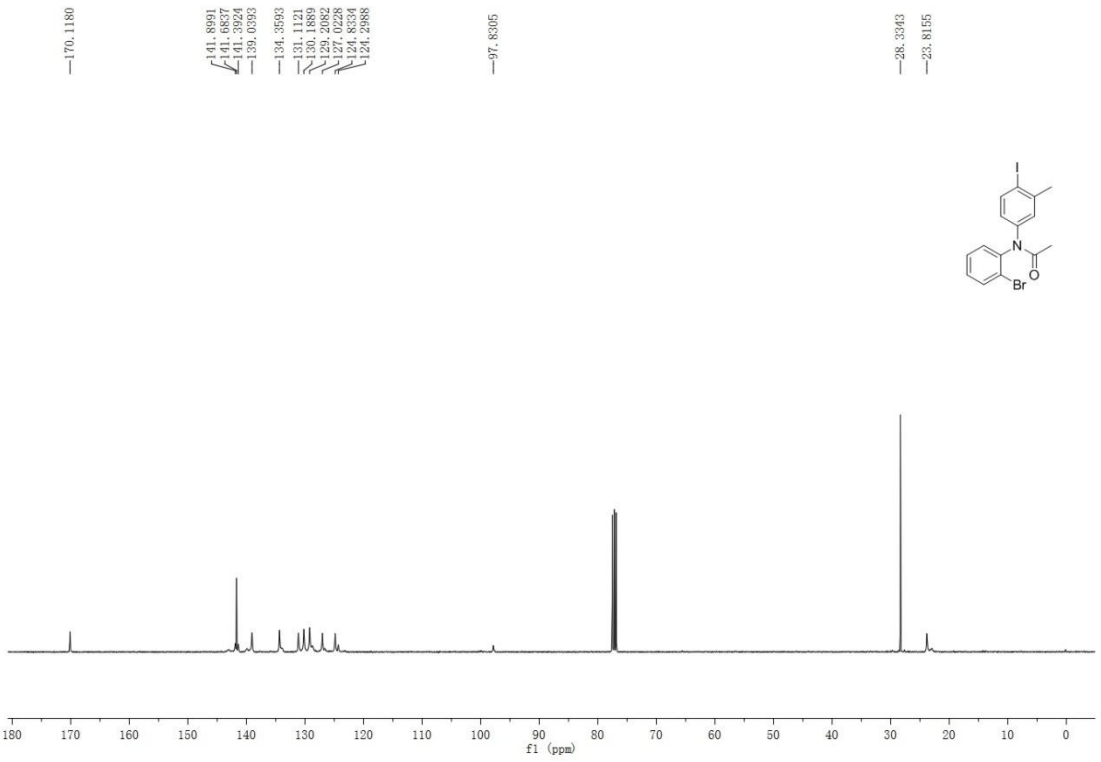
N-(2-chlorophenyl)-N-(4-iodo-3-methylphenyl)acetamide (3bf)



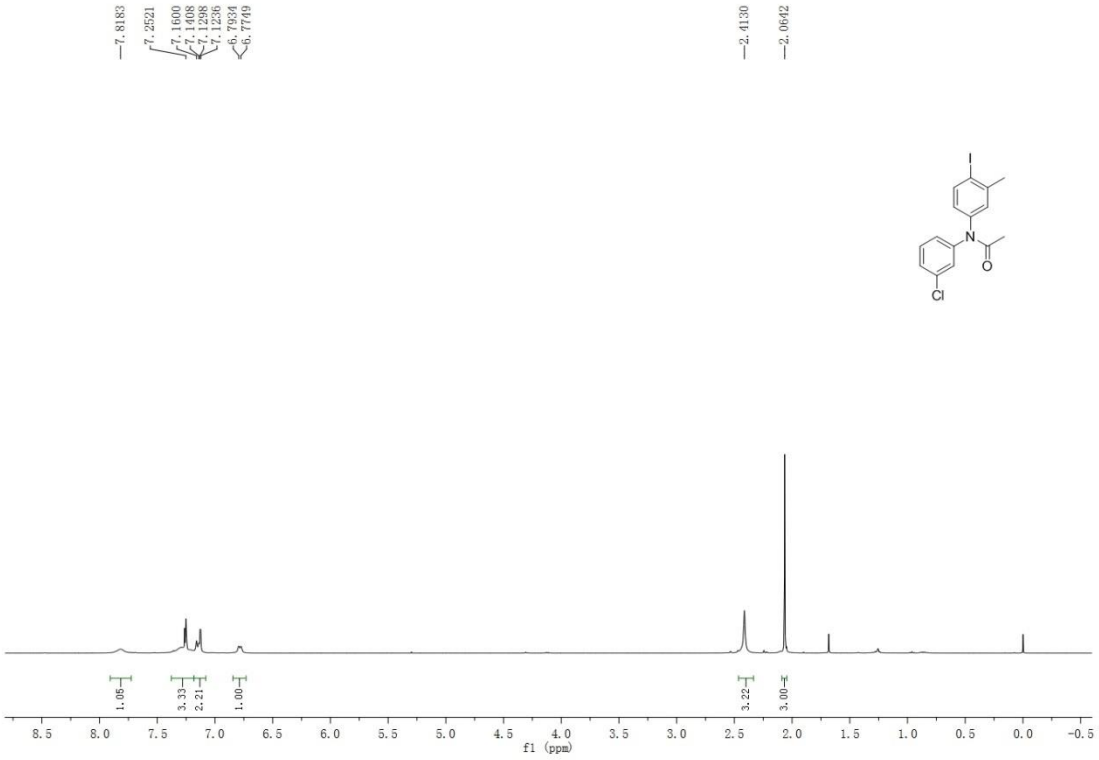


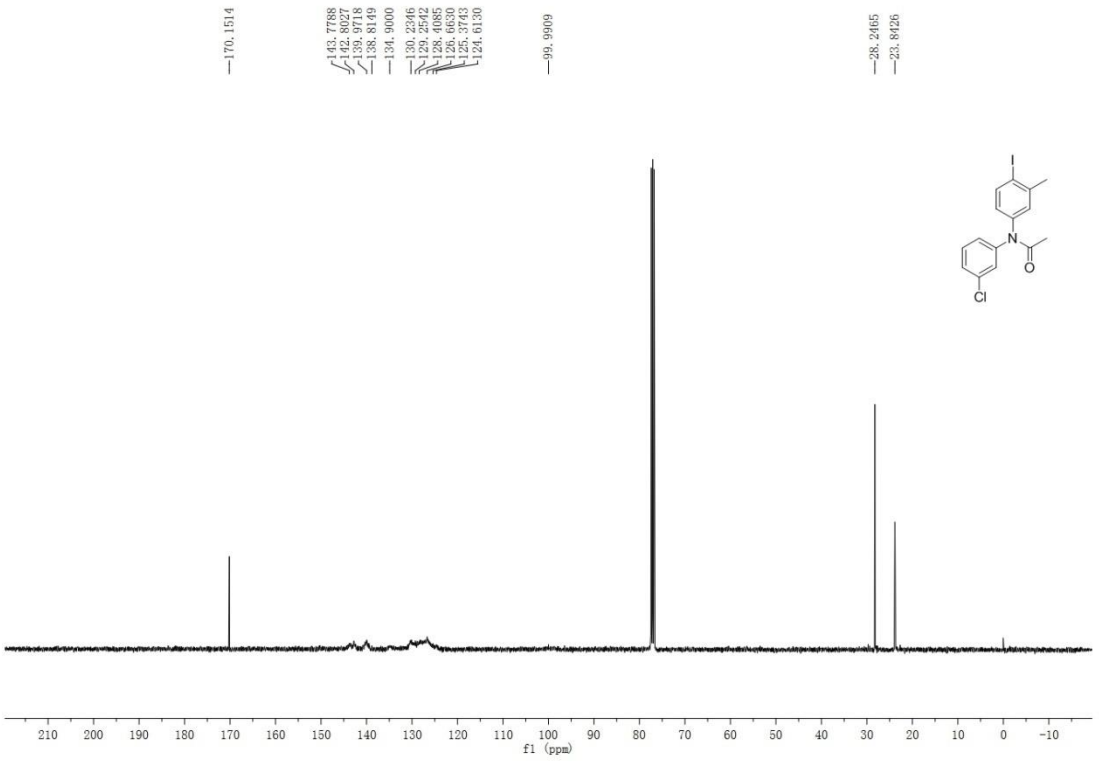
N-(2-bromophenyl)-N-(4-iodo-3-methylphenyl)acetamide(3bg)



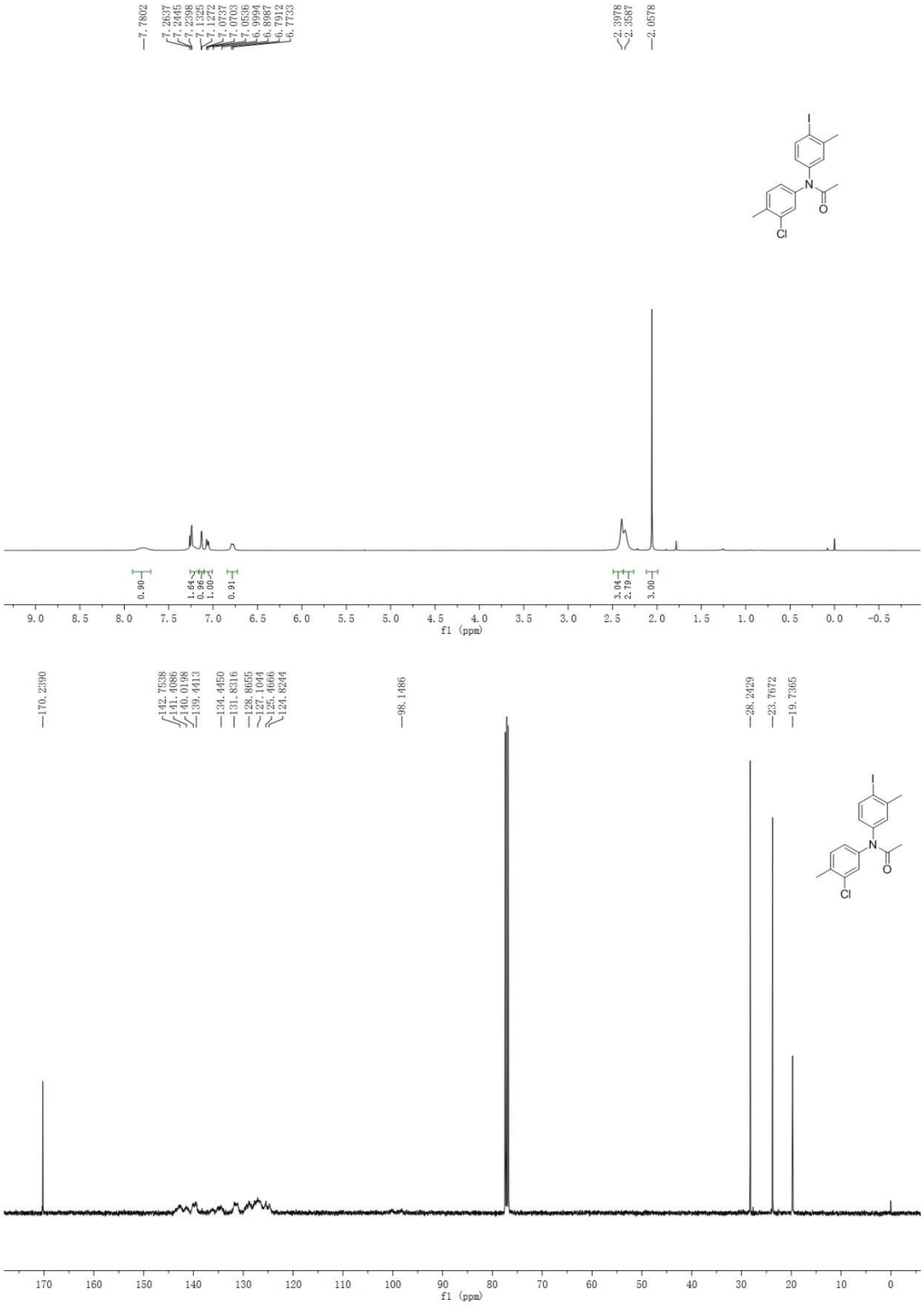


N-(3-chlorophenyl)-N-(4-iodo-3-methylphenyl)acetamide(3bh)

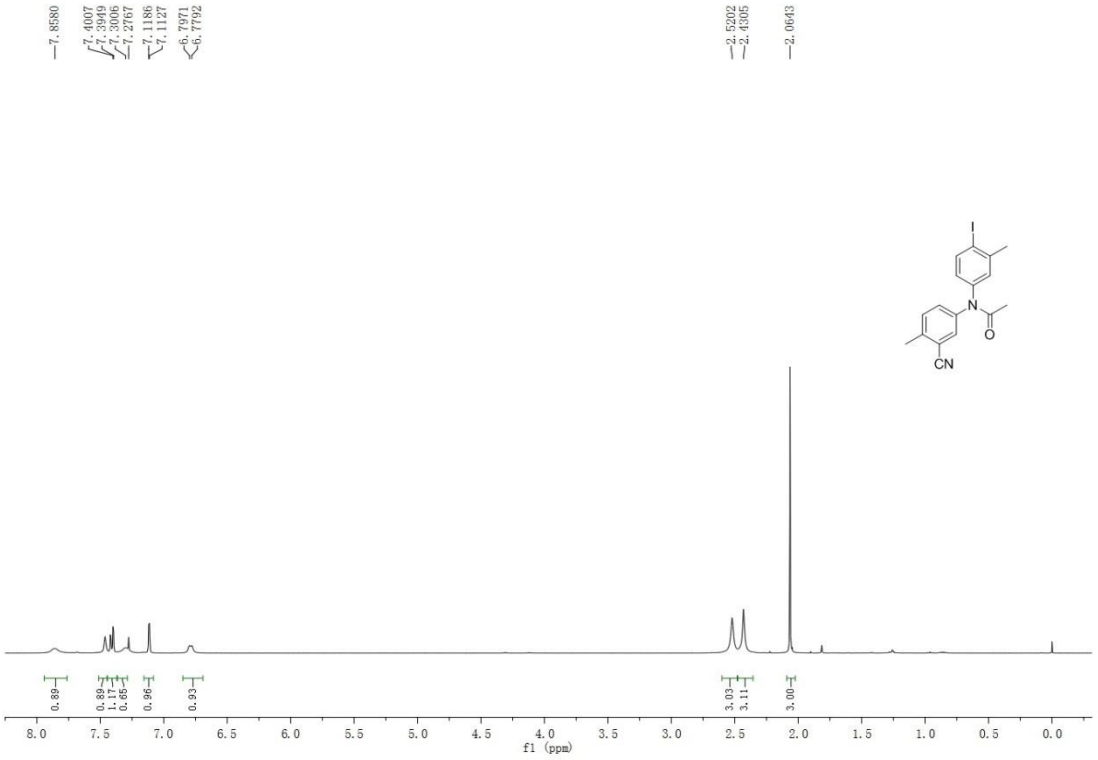


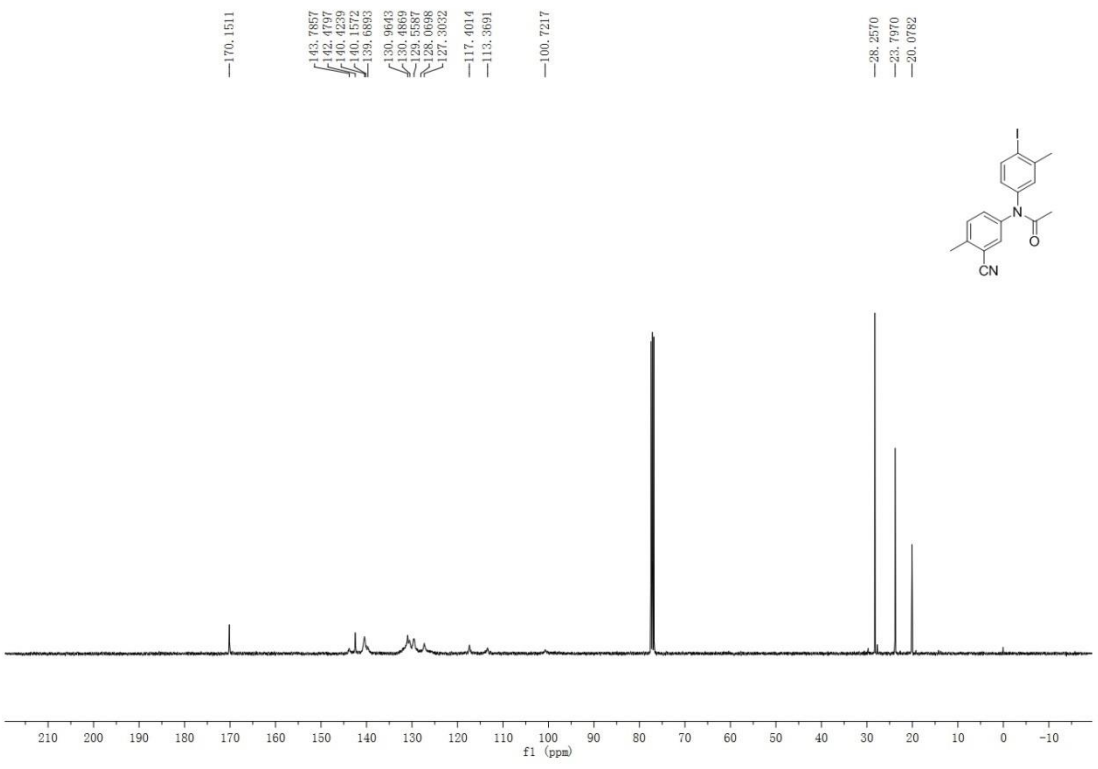


N-(3-chloro-4-methylphenyl)-N-(4-iodo-3-methylphenyl)acetamide (3bi)

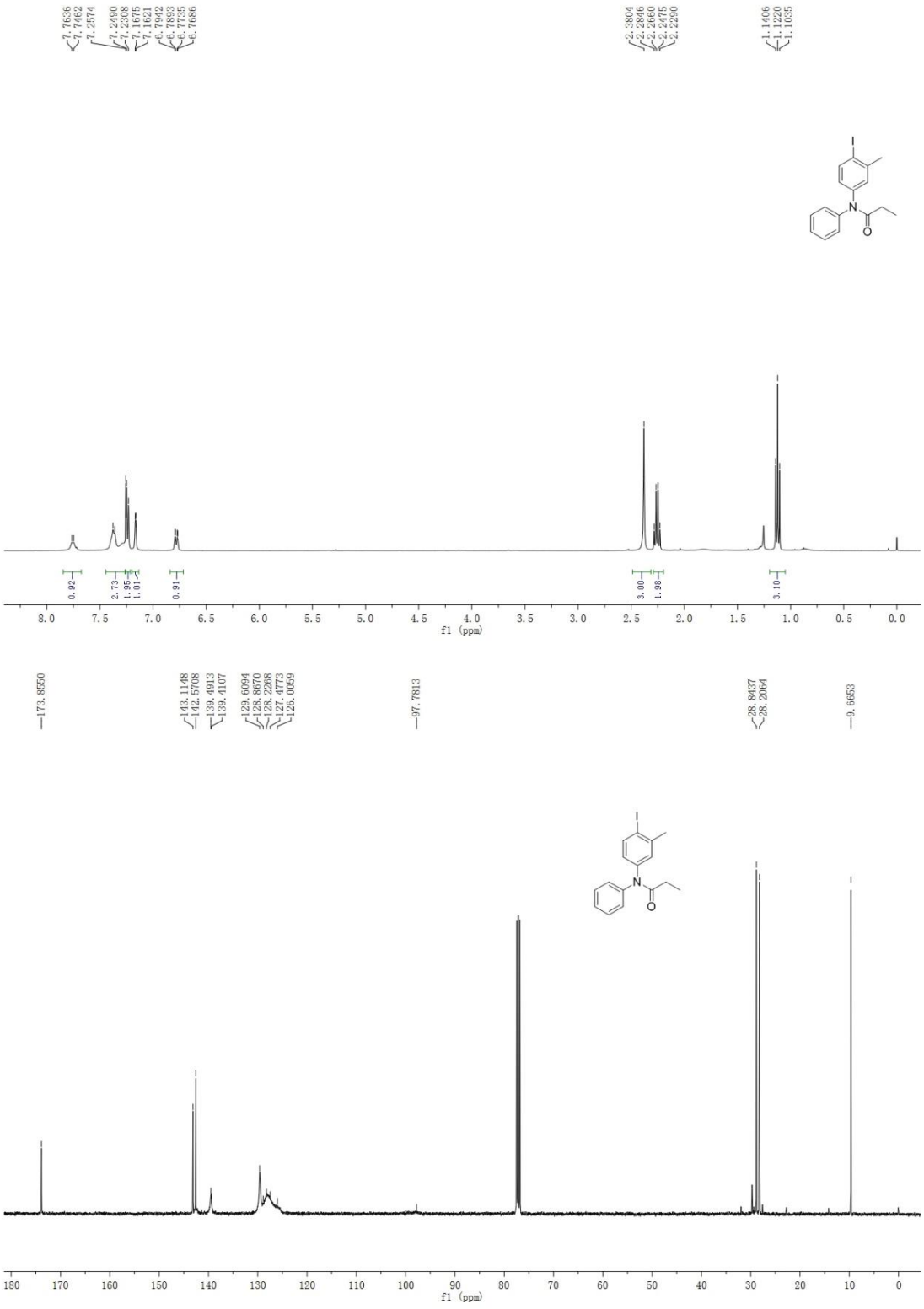


N-(3-cyano-4-methylphenyl)-N-(4-iodo-3-methylphenyl)acetamide (3bj)

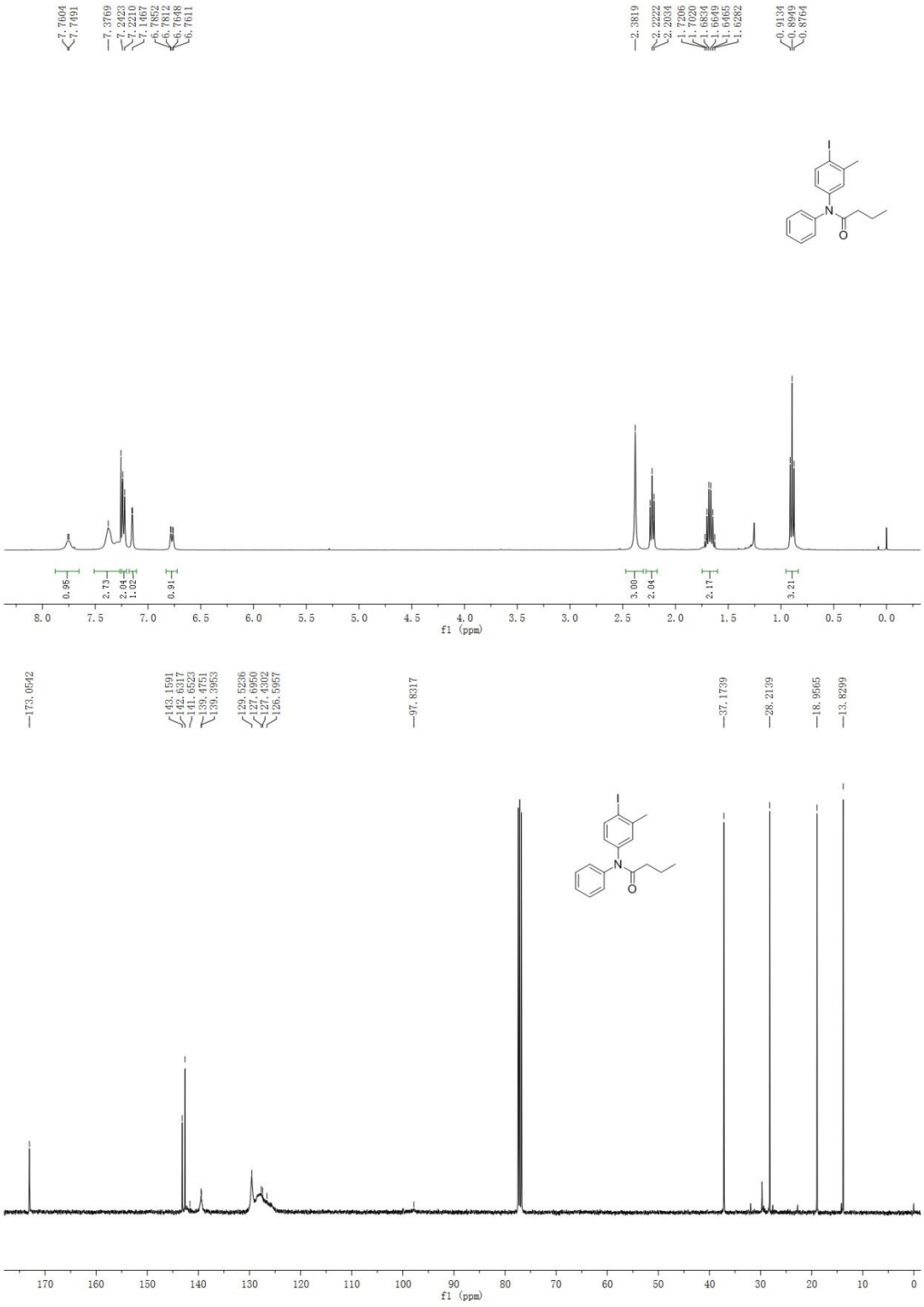




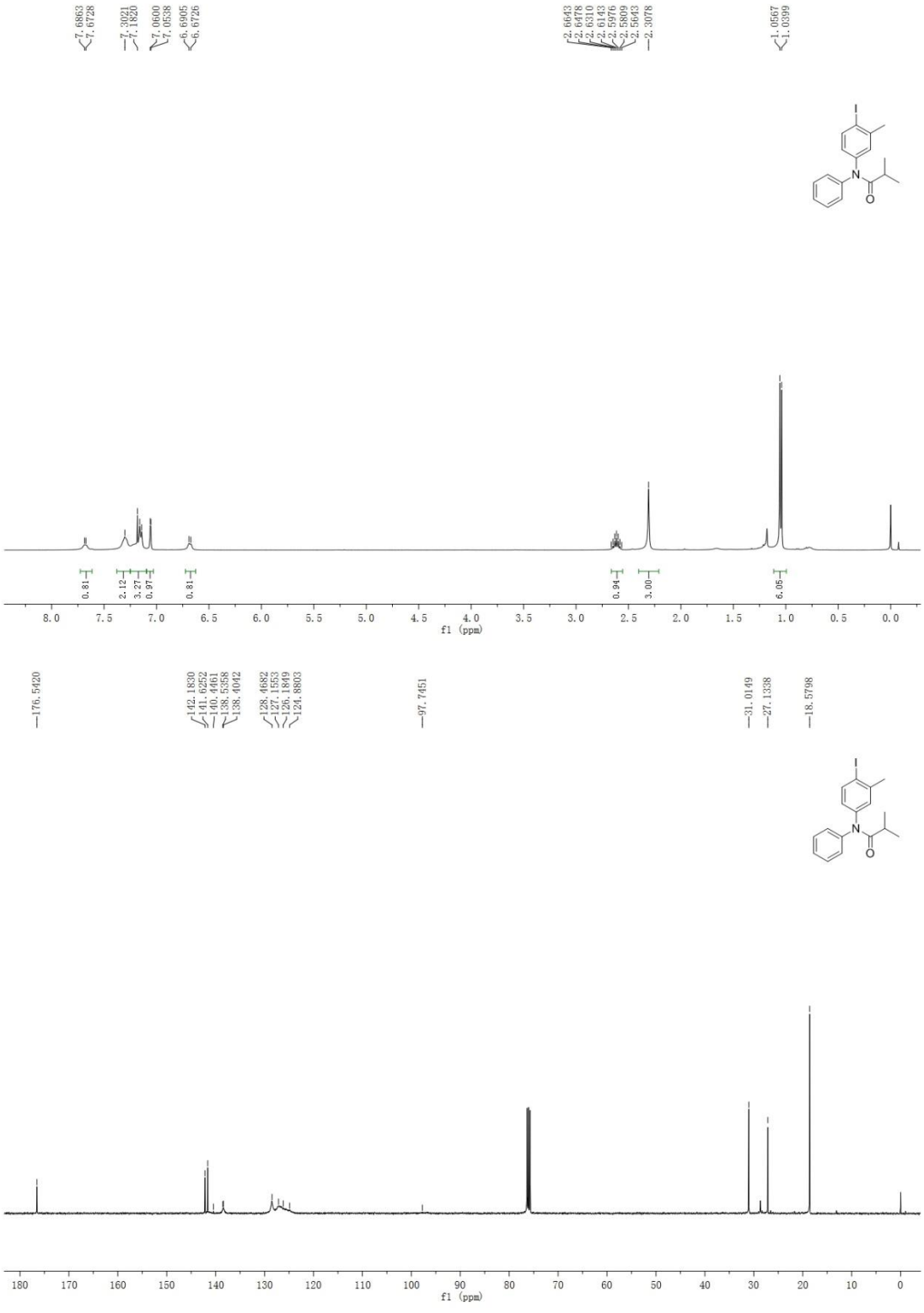
N-(4-iodo-3-methylphenyl)-N-phenylpropionamide(3bk)



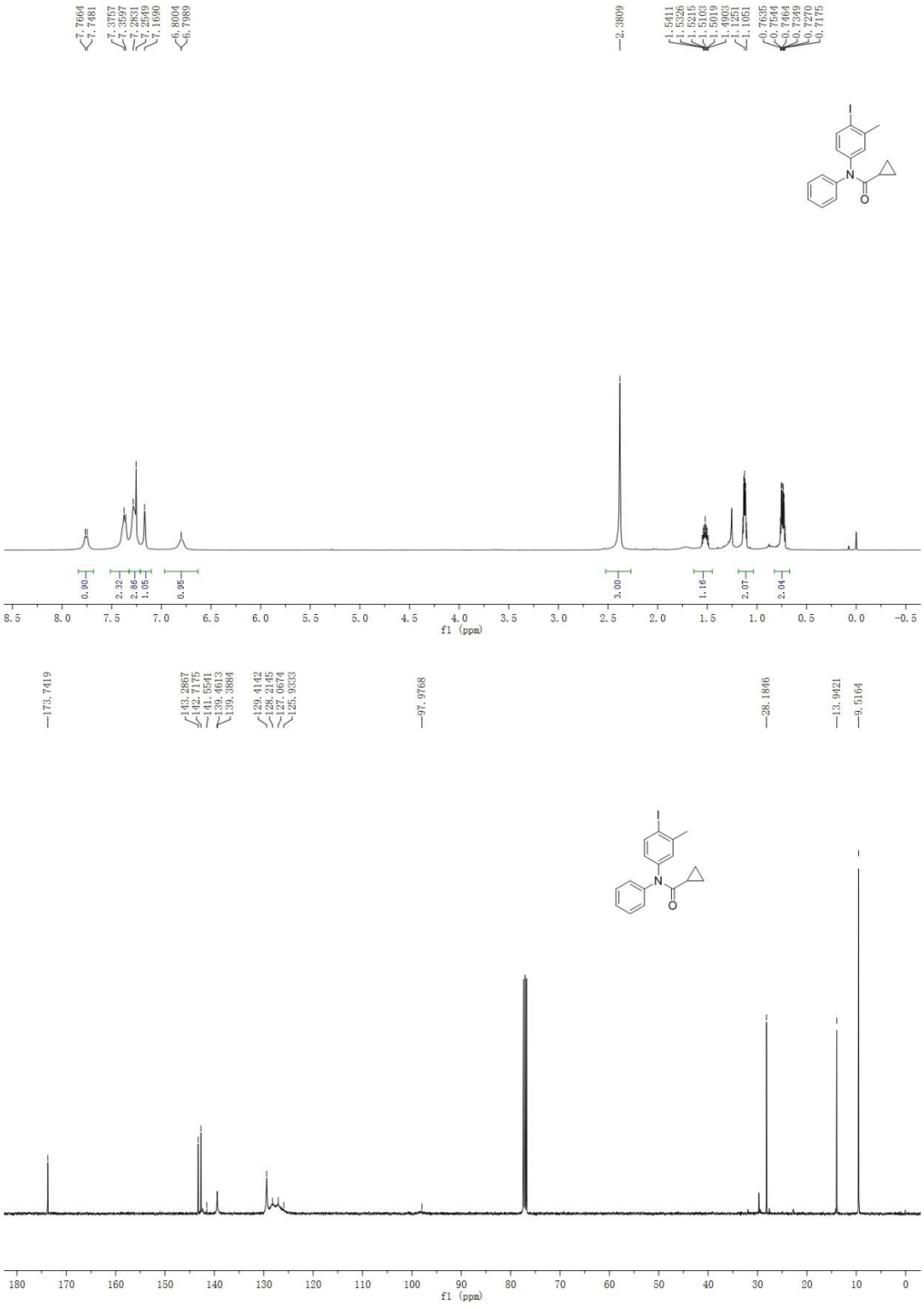
N-(4-iodo-3-methylphenyl)-N-phenylbutyramide(3bl)



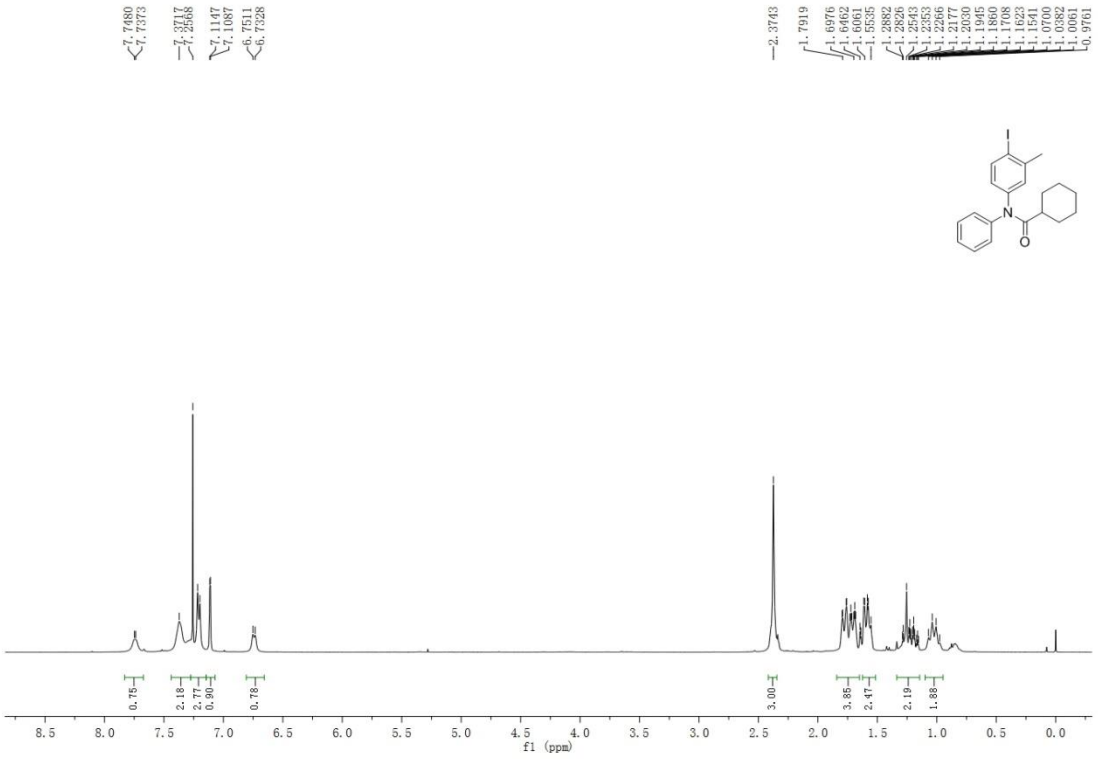
N-(4-iodo-3-methylphenyl)-N-phenylisobutyramide(3bm)

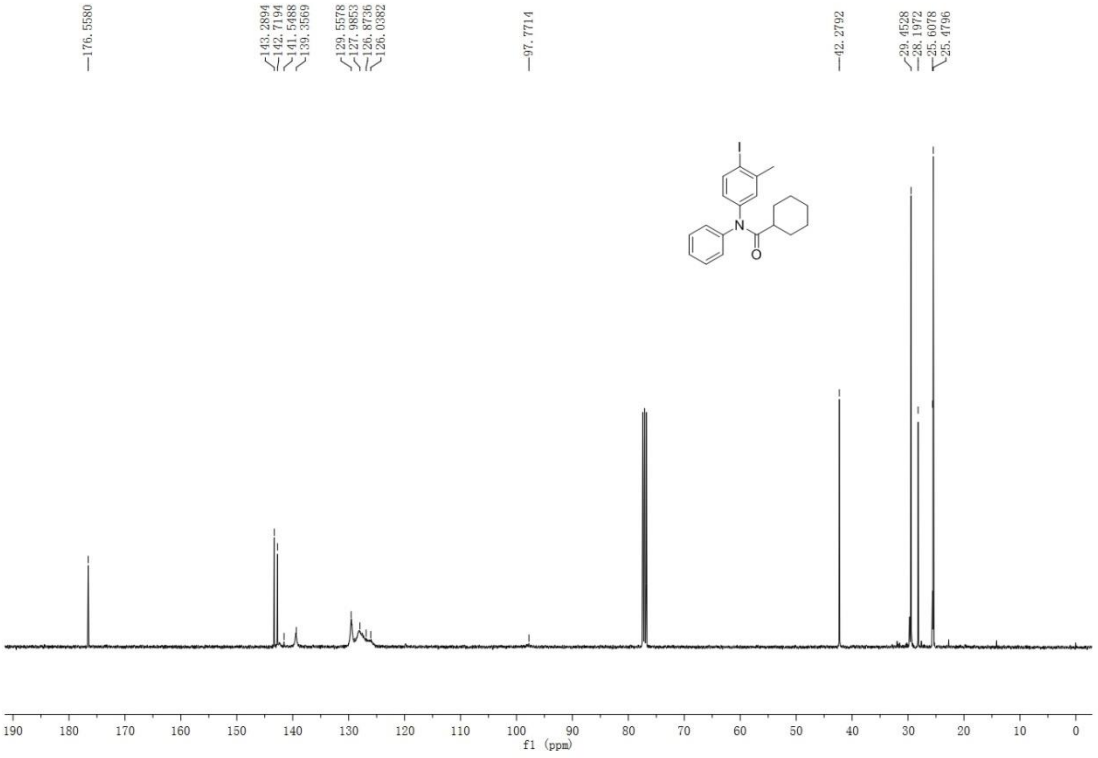


N-(4-iodo-3-methylphenyl)-N-phenylcyclopropanecarboxamide(3bn)

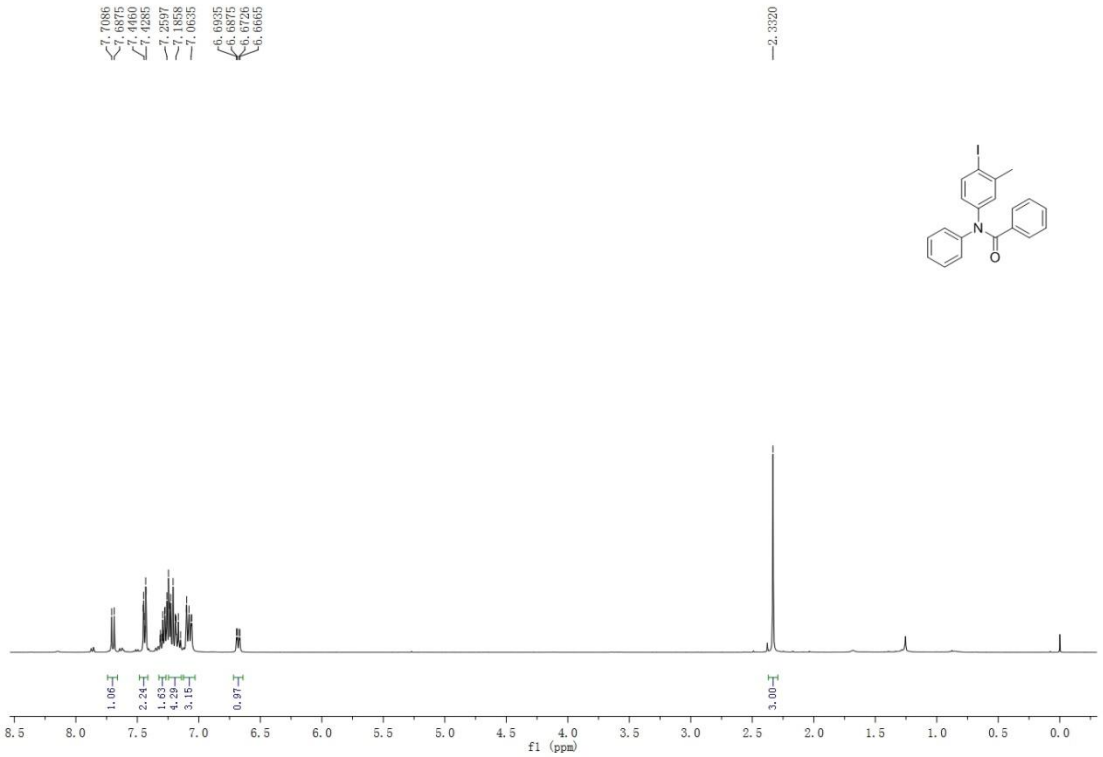


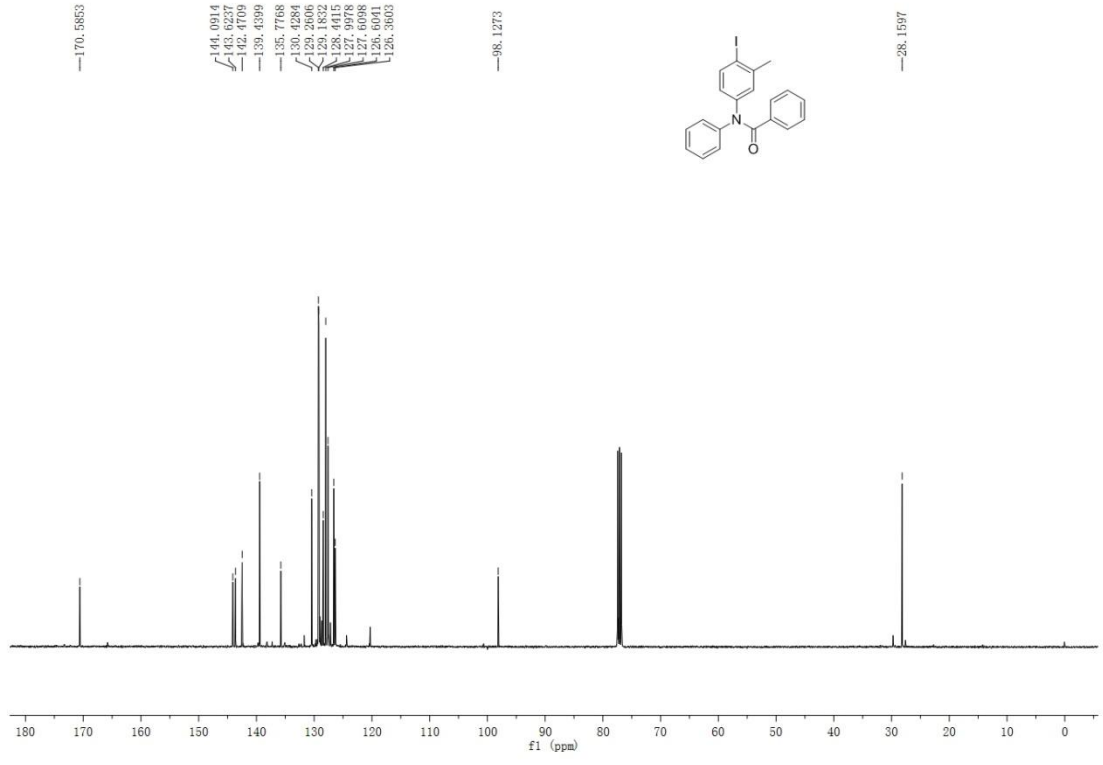
N-(4-iodo-3-methylphenyl)-N-phenylcyclohexanecarboxamide(3bo)



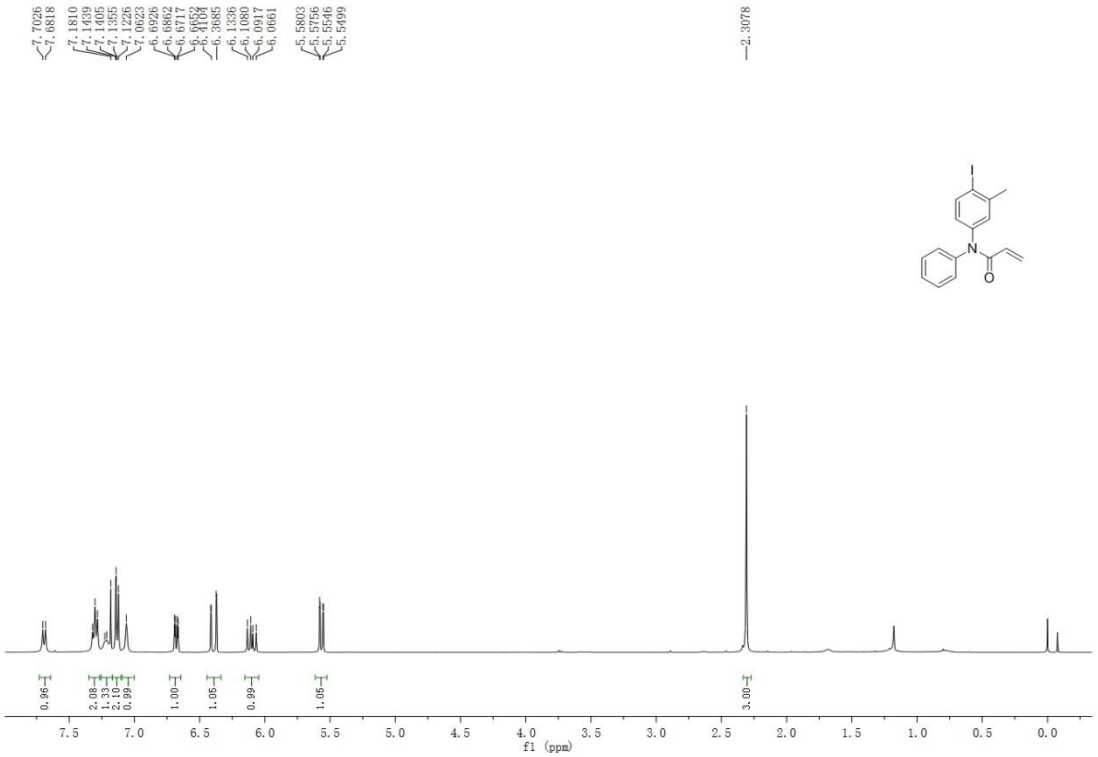


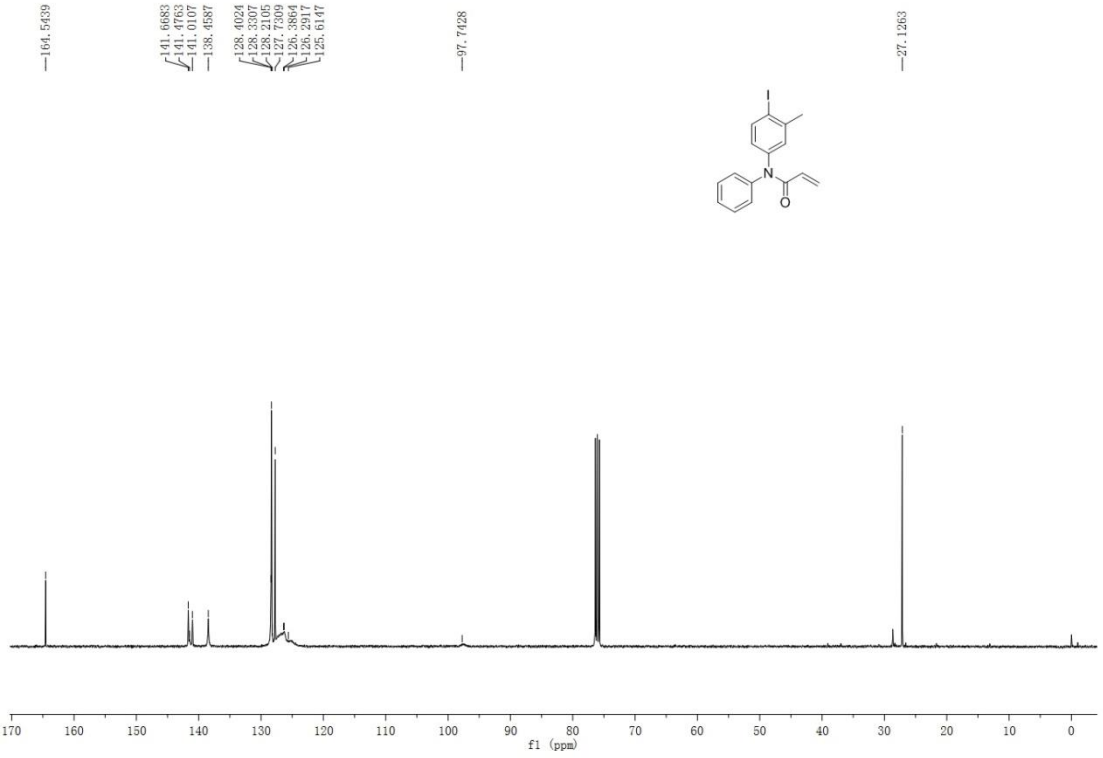
N-(4-iodo-3-methylphenyl)-N-phenylbenzamide(3bp)



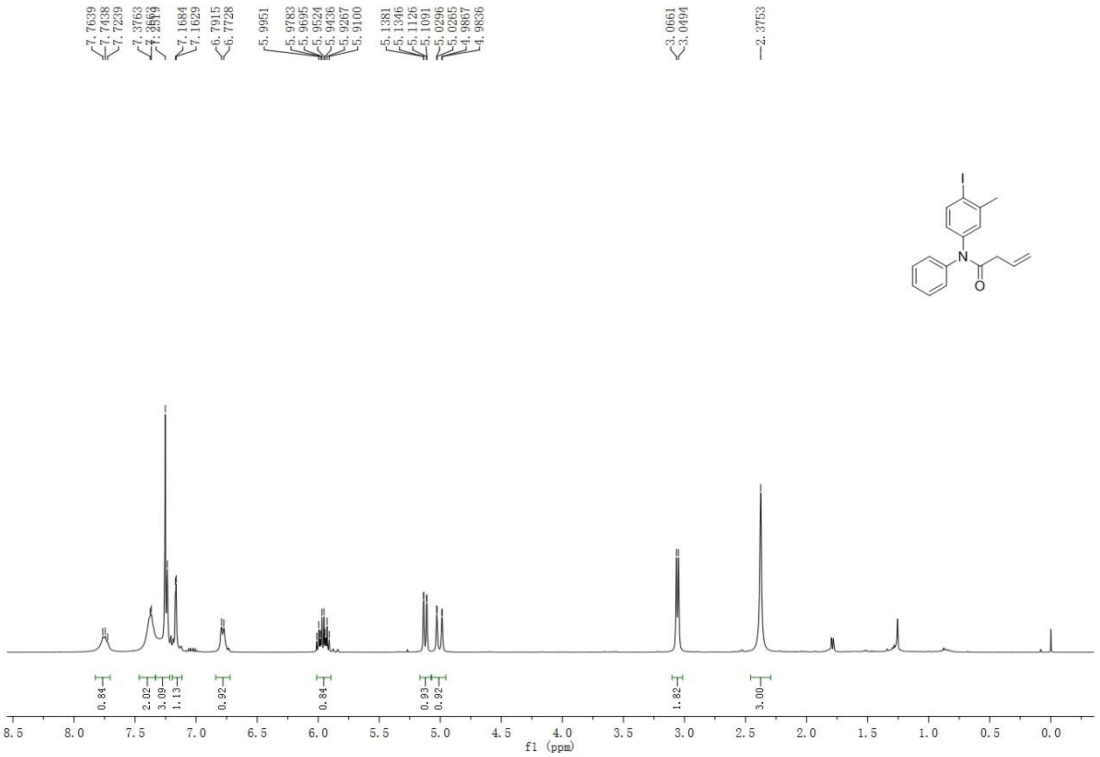


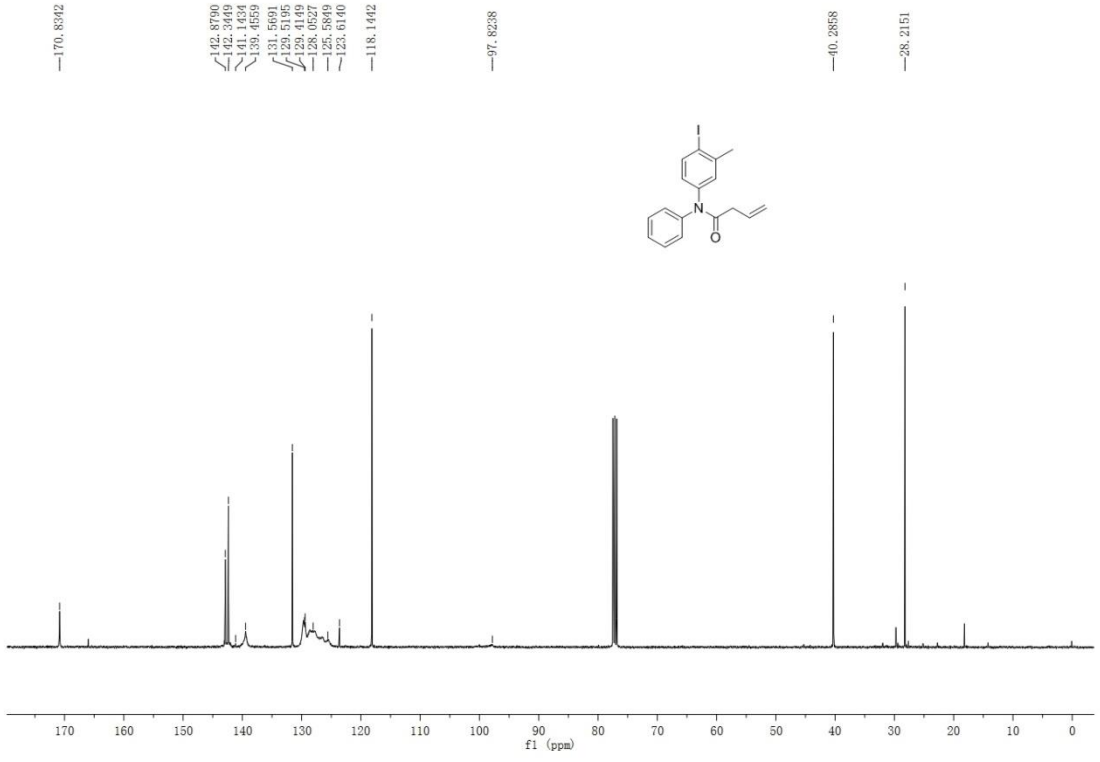
N-(4-iodo-3-methylphenyl)-N-phenylacrylamide(3bq)



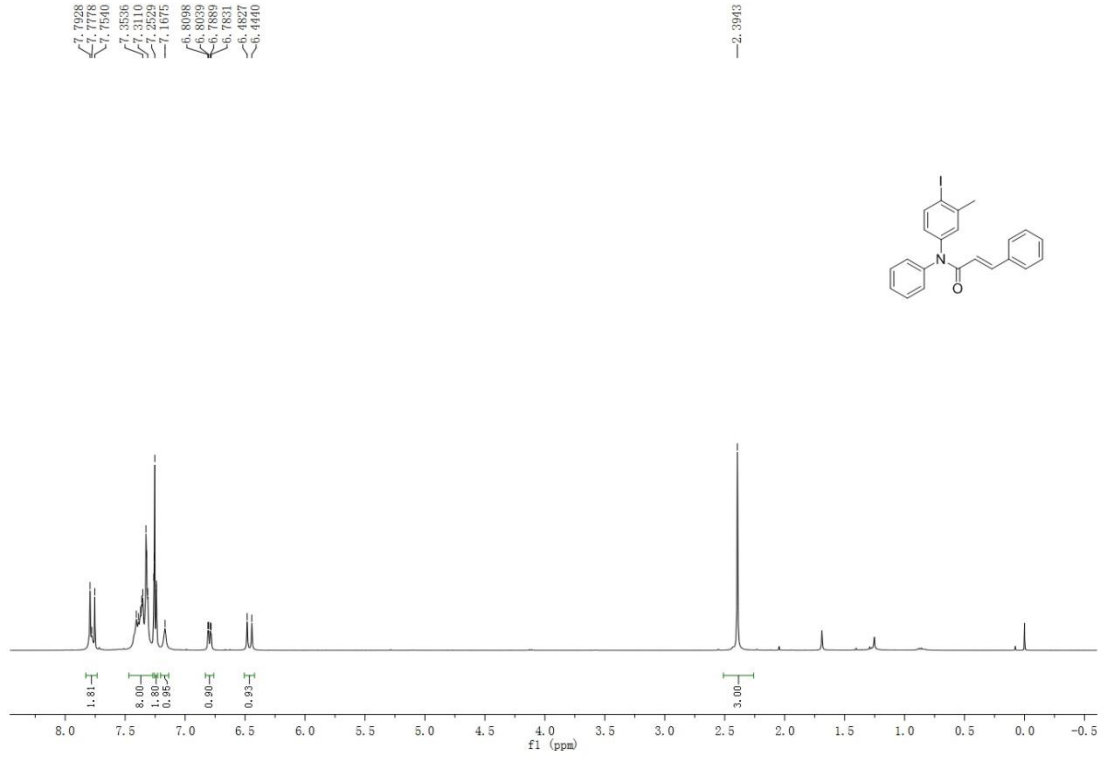


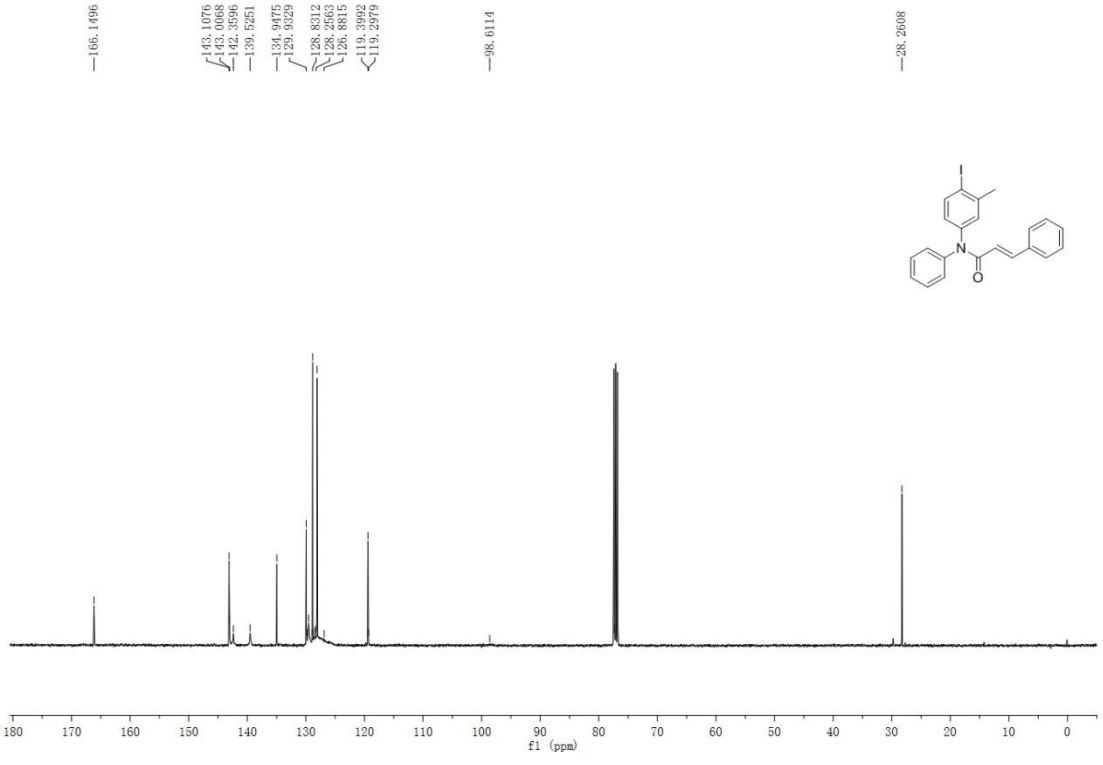
N-(4-iodo-3-methylphenyl)-N-phenylbut-3-enamide(3br)



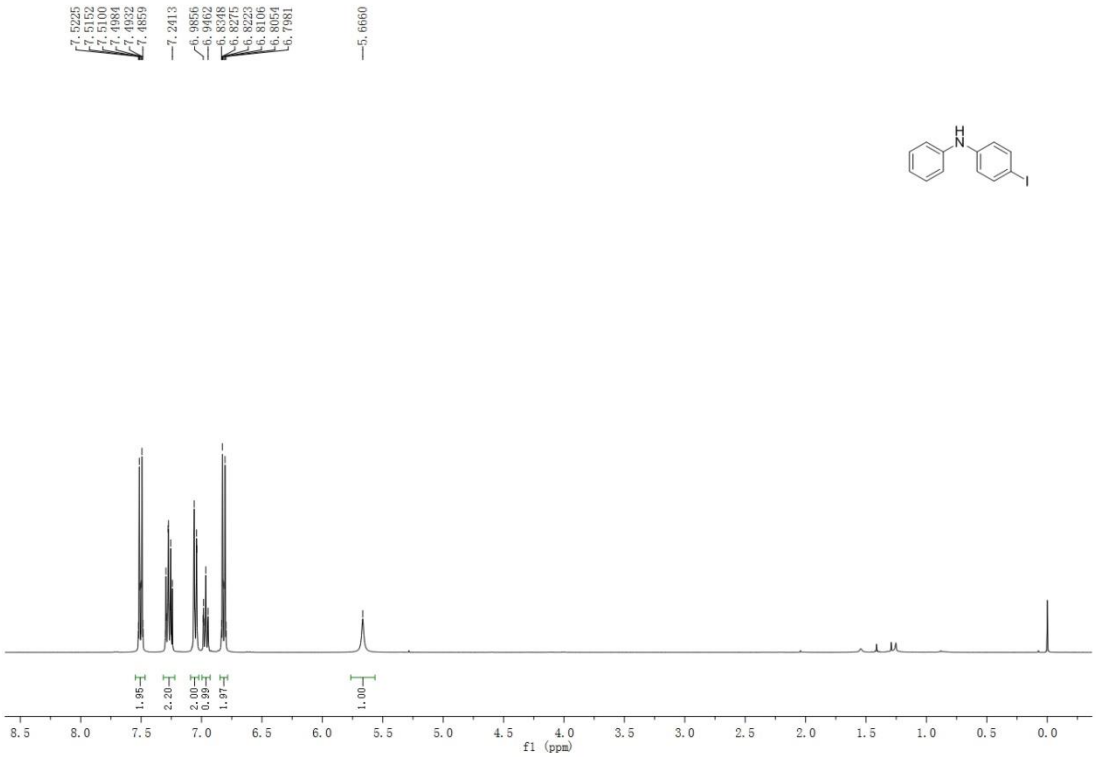


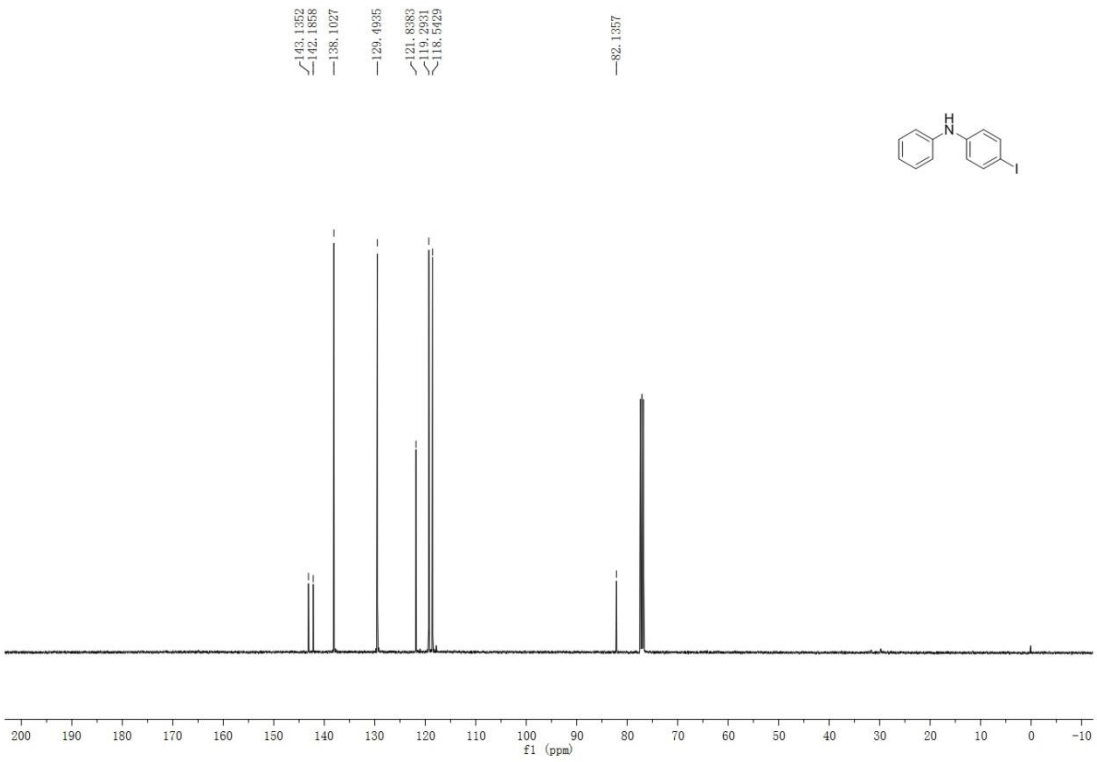
N-(4-iodo-3-methylphenyl)-N-phenylcinnamamide(3bs)



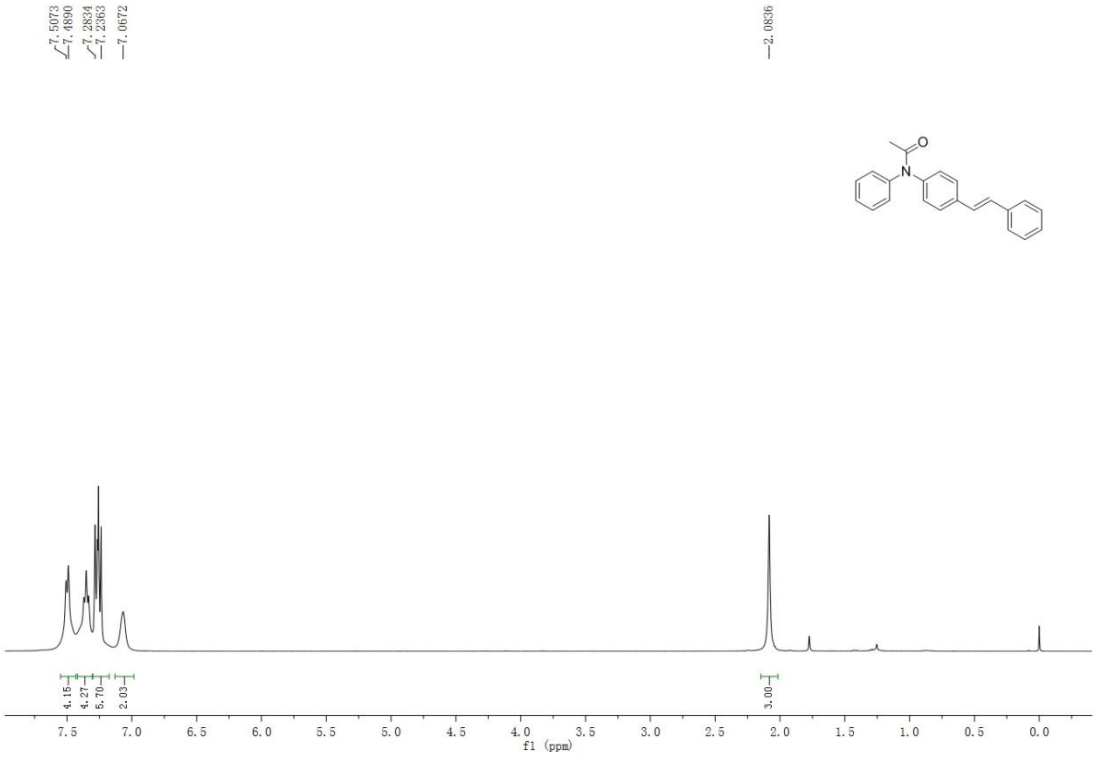


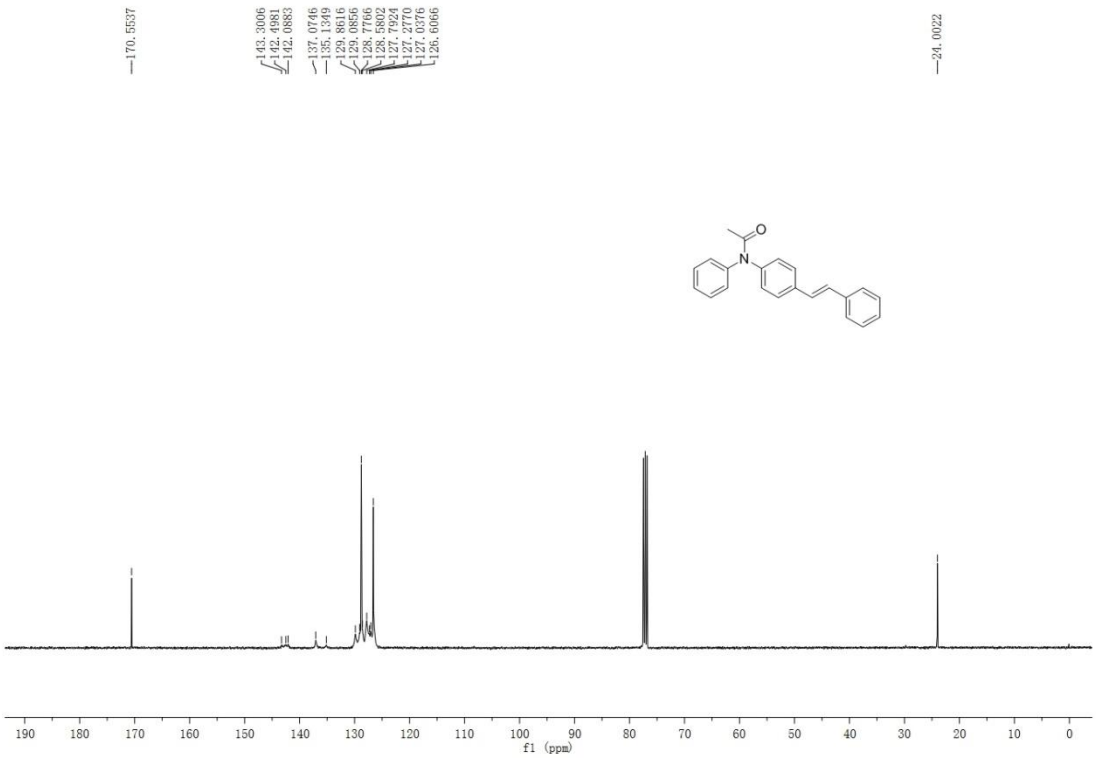
4-iodo-N-phenylaniline(4)



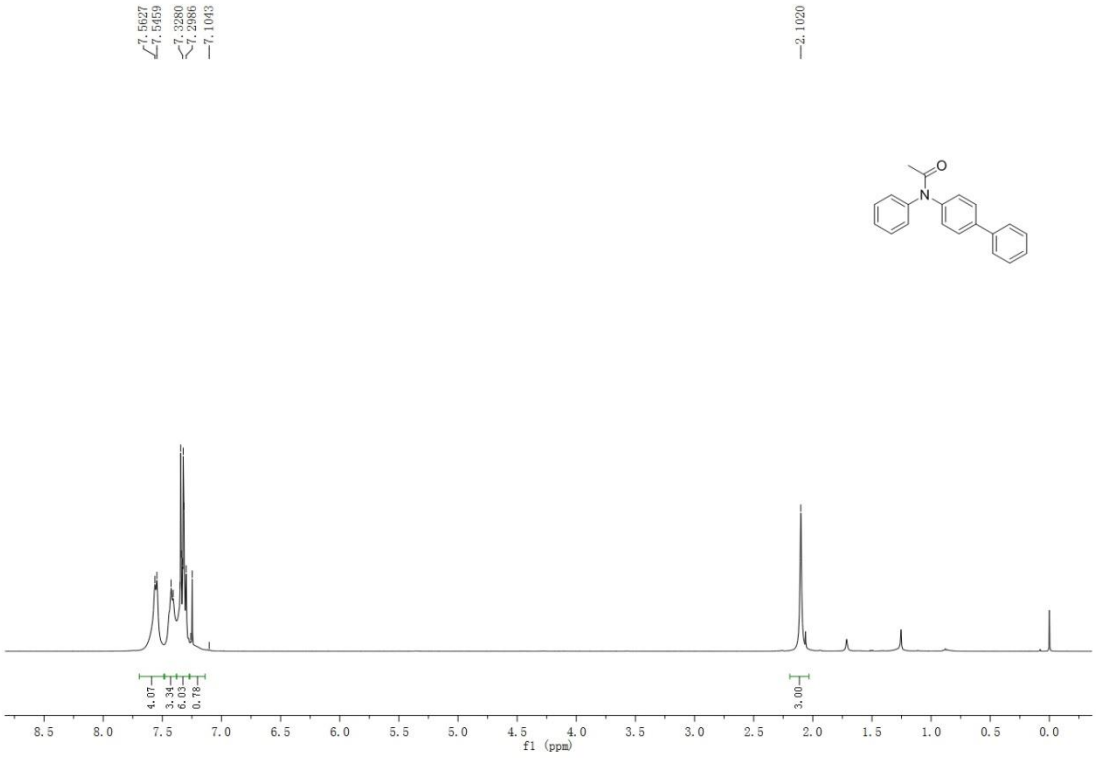


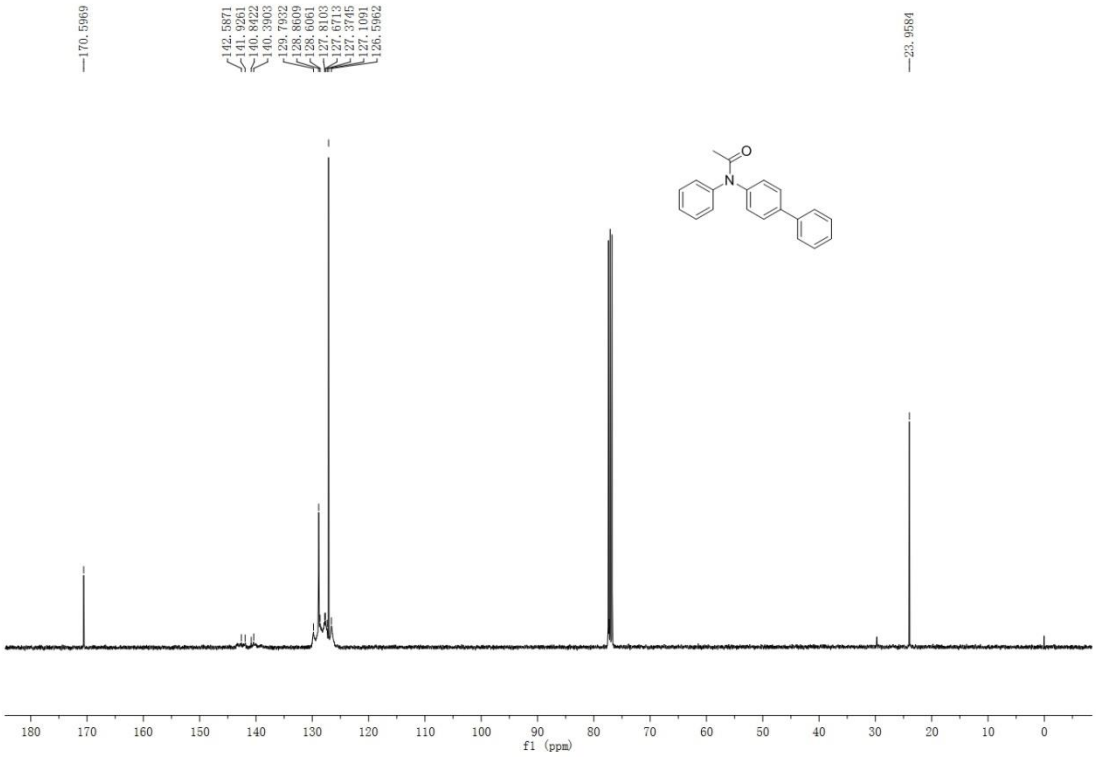
(E)-N-phenyl-N-(4-styrylphenyl)acetamide(5)





N-([1,1'-biphenyl]-4-yl)-N-phenylacetamide(6)





N-phenyl-N-(4-(phenylethynyl)phenyl)acetamide(7)