Electronic Supplementary Information

Direct Amide Synthesis via Ni-mediated Aminocarbonylation of Arylboronic Acids with CO and Nitroarenes

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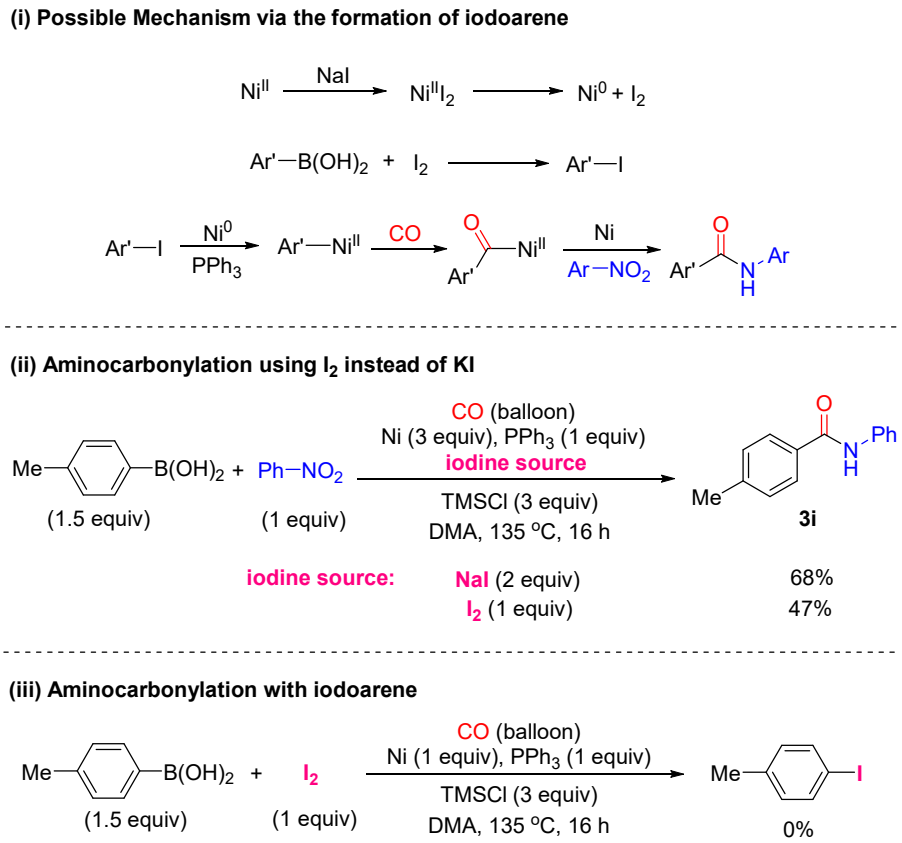
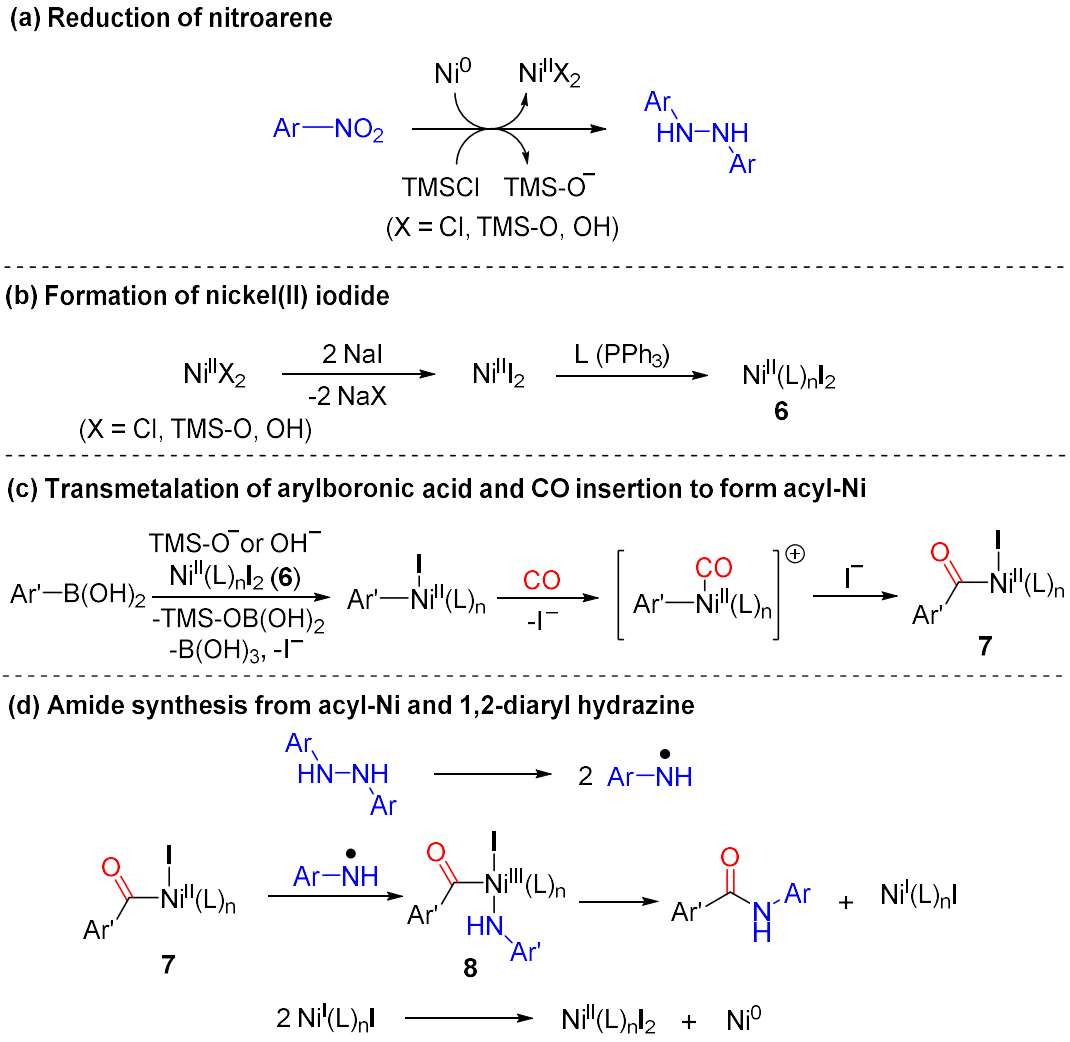
Scheme S1. Possible conversion of iodide to iodine and iodoarene for aminocarbonylation.



The addition of NaI was found to promote the efficiency of aminocarbonylation and significantly enhance the yield of amide (Table 1, entries 7 and 8). A possible role of NaI is to generate I_2, which can also induce the formation of iodoarene, such that both I_2 and iodoarene may promote the aminocarbonylation [Scheme S1, (i)]. Iodide could coordinate to Ni(II) species to form $Ni^{II}I_2$, which can liberate I_2 under high temperature. Arylboronic acid then reacts with I_2 to form iodoarene, which further reacts with Ni metal and nitroarene to give amide. However, when I_2 was used instead of KI, the reaction was less efficient, giving the amide product in much less yield [Scheme S1, (ii)]. Moreover, no iodoarene was formed in the $Ni^{II}Cl_2$-mediated reaction between arylboronic acid and I_2 [Scheme S1, (iii)]. These results suggested that the in-situ formation of iodine or iodoarene does not take place to trigger aminocarbonylation.

Scheme S2. Proposed mechanism of aminocarbonylation.



Based on the experimental results, we proposed a plausible mechanism of this aminocarbonylation reaction (Scheme S2). Ni metal (Ni(0)) reduces nitroarene successively to 1,2-diaryl hydrazine in the presence of TMSCl as a deoxygenating additive [Scheme S2(a)]. Meanwhile, Ni(0) is oxidized to Ni(II) salts, in which the counter anion could be chloride or O-centered ligands [trimethylsilanolate ($TMS\text{-}O^-$), hydroxide (OH^-)]] originated from the reduction process of nitroarene. Ni(II) salts then undergo ligand substitution with NaI to form $Ni^{II}I_2$, which further reacts with PPh_3 to form ligated $Ni^{II}I_2$ complexes **6** [Scheme S2(b)]. We speculated that the formation of complex **6** could prevent Ni precipitation with O-centered ligands. The good leaving group ability of iodide also enables rapid iodide dissociation from **6**,

providing vacant site to effect transmetalation of arylboronic acid via the activation with TMS-O^- or OH^-, as well as the subsequent CO insertion to form acyl-Ni^{II} intermediate **7** [Scheme S2(c)]. 1,2-Diaryl hydrazine bears a weak N-N bond (bond dissociation energy ~ 39 kcal mol^{-1}) and likely splits readily into amino radicals, which then react with **7** to give Ni^{III}(acyl)(amino) complex **8** [Scheme S2(d)]. Finally, **7** undergoes reductive elimination to afford the amide product, while the co-product Ni(I) species could disproportionate to regenerate $Ni^{II}I_2$ and Ni(0). The detailed reaction mechanism will be subjected to the dedicated study in the future.

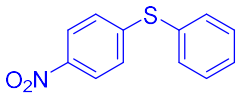
General Considerations

(A) General Analytical Information

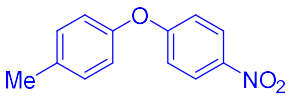
Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz at ambient temperature. All ^{1}H NMR spectra were measured in part per million (ppm) relative to the signal of tetramethylsilane (TMS, 0.00 ppm), the signal of residual chloroform in deuterated chloroform ($CDCl_3$, 7.26 ppm), or the signal of residual dimethyl sulfoxide in dimethyl-d_6 sulfoxide (DMSO-d_6, 2.50 ppm).[1] Data for ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, m = multiplet), coupling constant (*J*, in Hz), and integration. All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm)[1] and were obtained with complete ^{1}H decoupling. High-resolution mass spectrometry (HRMS) images were obtained on a microTOF-QII or Waters Micromass GCT Premier Instrument.

(B) General Reagent Information

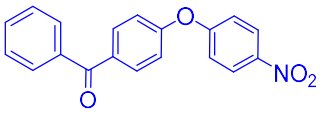
Unless otherwise noted, all chemicals were used as received without further purifications. *N*,*N*-Dimethylacetamide (DMA, 99.8% purity) were dried with 4 Å molecular sieve beads prior to use. Carbon monoxide (CO), nickel powder (Ni), triphenylphosphine (PPh_3), and sodium iodide (NaI) were in 99.9%, 99.9%, 98%, and 99% purities, respectively. Chlorotrimethylsilane (TMSCl, 98% purity) was stored in the refrigerator prior to use. The following known starting materials (nitroarenes) were prepared according to the literature procedures.[2-6]



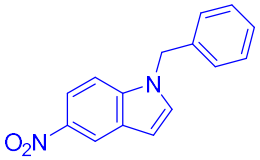
(4-nitrophenyl)(phenyl)sulfane [2]



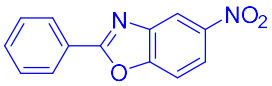
1-methyl-4-(4-nitrophenoxy)benzene [3]



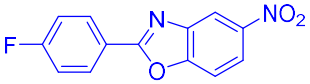
(4-(4-nitrophenoxy)phenyl)(phenyl)methanone [4]



1-benzyl-5-nitro-1H-indole [5]



5-nitro-2-phenylbenzo[d]oxazole [6]



2-(4-fluorophenyl)-5-nitrobenzo[d]oxazole [6]

(C) General Manipulation Considerations

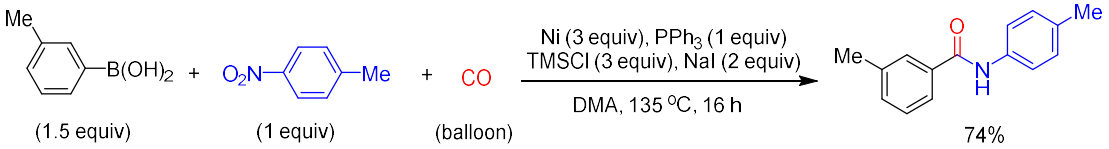
All manipulations for direct reductive aminocarbonylation of nitroarenes with arylboronic acids were set up in a 20 mL rubber septum-capped Schlenk tube. Flash column chromatography was performed using silica gel (200-300 mesh). The eluents used for column chromatography were presented as ratios of solvent volumes. Yields reported in the publication are isolated yields unless otherwise noted. All new amide products were characterized by ^{1}H and ^{13}C NMR spectroscopies amd high-resolution mass spectrometry (HRMS). All known amide products were characterized by ^{1}H and ^{13}C NMR spectroscopies, which were further compared with the reported data when provided.

Experimental Section

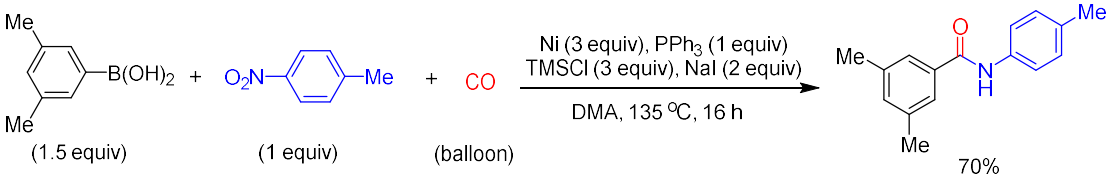
Nickel Metal-mediated Aminocarbonylation of Arylboronic Acids with Nitroarenes (General Procedure). An oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with nickel powder (Ni, 3 equiv, 1.5 mmol, 87 mg), arylboronic acid (1.5 equiv, 0.75 mmol), nitroarene (1 equiv, 0.50 mmol), triphenylphosphine (PPh_3, 1 equiv, 0.5 mmol, 131 mg), and sodium iodide (NaI, 2 equiv, 1.0 mmol, 150 mg). The tube was capped with an airtight rubber septum, and the tube was degassed *in vacuo* and then backfilled with carbon monoxide (CO) for three times via a CO-filled balloon. After being degassed and equipped with a CO-filled balloon, *N*,*N*-dimethylacetamide solvent (DMA, 1.5 mL) followed by chlorotrimethylsilane (TMSCl, 3 equiv, 1.50 mmol, 190 μL) were then transferred into the reaction mixture via a syringe. The reaction mixture was stirred at 135 °C in a preheated oil bath for 16 h. After the reaction, the reaction mixture was cooled down to room temperature. The reaction mixture was diluted with ethyl acetate (EtOAc, ~50 mL), and the organic fraction was further acidified with HCl solution (~1 M (aq), ~10 mL), neutralized with NaOH solution (~1 M (aq), ~30 mL), washed with saturated NaCl solution, dried with anhydrous Na_2SO_4, and then concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography using a mixture of petroleum ether (PE) and ethyl acetate (EtOAc) as eluents to afford the amide product.

4-Methyl-*N*-*p*-tolylbenzamide (3a).[7] Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 101 mg) and 1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 69 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (95 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.73 (d, J = 7.7 Hz, 2H), 7.51 (d, J

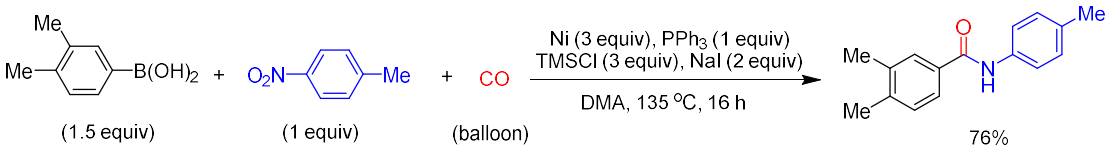
= 7.9 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.77, 142.14, 135.55, 134.01, 132.18, 129.51, 129.33, 127.09, 120.40, 21.51, 20.94.



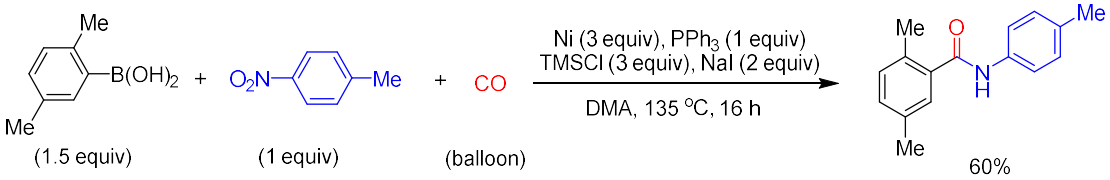
3-Methyl-*N*-*p*-tolylbenzamide (3b).[8] Following the general procedure, the title compound was prepared using 3-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 101 mg) and 1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 69 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (83 mg, 74%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.69 – 7.57 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.34-7.29 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.98, 138.58, 135.49, 135.06, 134.10, 132.43, 129.53, 128.55, 127.83, 124.01, 120.38, 21.39, 20.94.



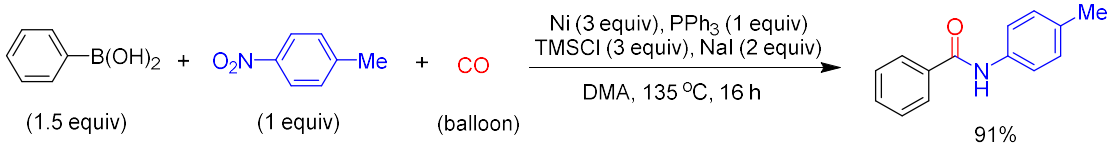
3,5-Dimethyl-*N*-*p*-tolylbenzamide (3c).[9] Following the general procedure, the title compound was prepared using 3,5-dimethylphenylboronic acid (1.5 equiv, 0.75 mmol, 113 mg) and 1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 69 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (84 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.47-7.45 (m, 2H), 7.20 – 7.12 (m, 3H), 2.39 (s, 6H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.93, 138.50, 135.48, 135.14, 134.07, 133.33, 129.56, 124.73, 120.17, 21.29, 20.91.



3,4-Dimethyl-*N*-*p*-tolylbenzamide (3d).[10] Following the general procedure, the title compound was prepared using 3,4-dimethylphenylboronic acid (1.5 equiv, 0.75 mmol, 113 mg) and 1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 69 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (91 mg, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.61 (s, 1H), 7.56-7.50 (m, 3H), 7.16-7.11 (m, 3H), 2.31 (s, 3H), 2.28 (s, 3 H), 2.26 (s, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.06, 140.74, 137.01, 135.69, 133.87, 132.55, 129.77, 129.45, 128.44, 124.47, 120.48, 20.94, 19.85, 19.76.

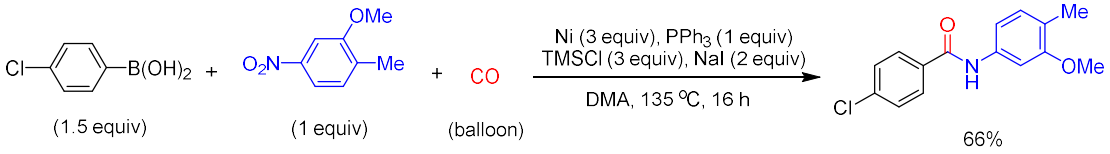


2,5-Dimethyl-*N*-*p*-tolylbenzamide (3e).[11] Following the general procedure, the title compound was prepared using 2,5-dimethylphenylboronic acid (1.5 equiv, 0.75 mmol, 113 mg) and 1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 69 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (71 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.9 Hz, 2H), 7.44 (s, 1H), 7.28 (s, 1H), 7.18 – 7.12 (m, 4H), 2.44 (s, 3H), 2.34 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.14, 136.43, 135.48, 134.12, 133.14, 131.14, 130.86, 129.56, 127.25, 119.93, 20.92, 20.87, 19.35 (13 carbon signals were observed out of expected 14 carbon signals).

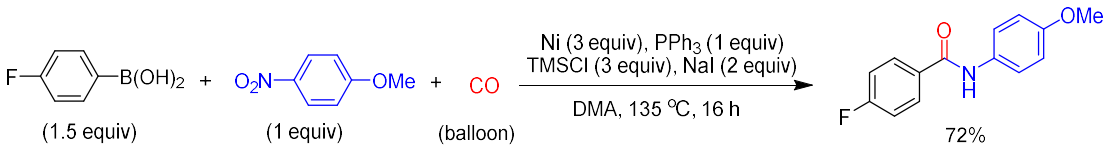


***N*-*p*-Tolylbenzamide (3f).**[12] Following the general procedure, the title compound was prepared using phenylboronic acid (1.5 equiv, 0.75 mmol, 92 mg) and

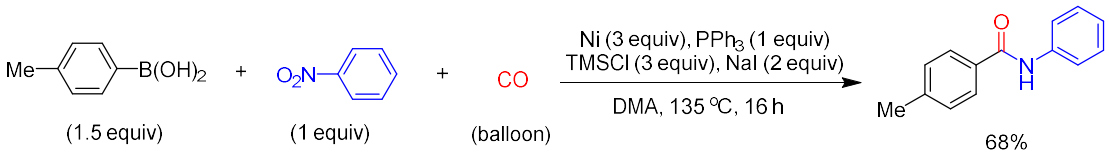
1-methyl-4-nitrobenzene (1 equiv, 0.50 mmol, 69 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (96 mg, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.82 (m, 3H), 7.56-7.50 (m, 3H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.74, 135.39, 135.08, 134.22, 131.71, 129.57, 128.73, 127.03, 120.36, 20.94.



4-Chloro-*N*-(3-methoxy-4-methylphenyl)benzamide (3g).[13] Following the general procedure, the title compound was prepared using 4-chlorophenylboronic acid (1.5 equiv, 0.75 mmol, 117 mg) and 2-methoxy-1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 84 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (91 mg, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 3H), 7.48 – 7.41 (m, 3H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 3.84 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.59, 157.99, 138.07, 136.60, 133.37, 130.49, 129.04, 128.41, 123.18, 111.59, 103.04, 55.39, 15.88.

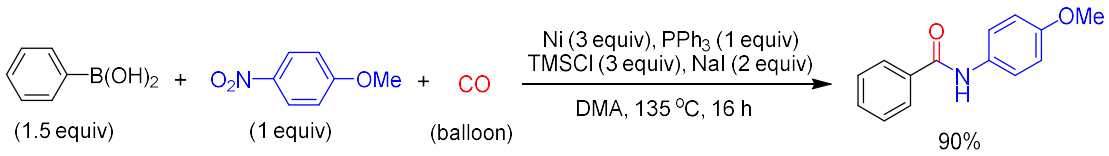


4-Fluoro-*N*-(4-methoxyphenyl)benzamide (3h).[14] Following the general procedure, the title compound was prepared using 4-fluorophenylboronic acid (1.5 equiv, 0.75 mmol, 106 mg) and 1-methoxy-4-nitrobenzene (1.0 equiv, 0.50 mmol, 76 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (88.23 mg, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.85 (m, 2H), 7.70 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.16 (t, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 163.97, 163.94 (d, $J_{C\text{-}F}$ = 247.1 Hz), 155.58, 132.09, 131.44 (d, $J_{C\text{-}F}$ = 2.1 Hz), 130.24 (d, $J_{C\text{-}F}$ = 9.0 Hz), 122.01, 115.28 (d, $J_{C\text{-}F}$ = 21.5 Hz), 113.74, 55.18.



4-Methyl-*N*-phenylbenzamide (3i).[15] Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 101 mg) and nitrobenzene (1.0 equiv, 0.50 mmol, 62 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (72 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.75 (d, J = 7.7 Hz, 2H), 7.64 (d, J = 7.9 Hz, 2H), 7.33 (t, J = 7.7 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 7.5 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.86, 142.31, 138.10, 132.10, 129.39, 129.04, 127.11, 124.41, 120.30, 21.52.

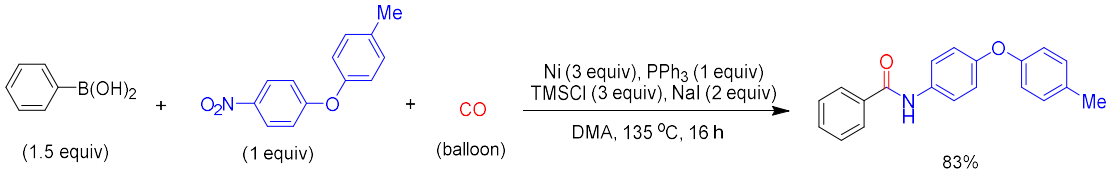
***N*-(4-Methoxyphenyl)-4-methylbenzamide (3j).**[16] Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 101 mg) and 1-methoxy-4-nitrobenzene (1.0 equiv, 0.50 mmol, 77 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (96 mg, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.75 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.24 (s, 2H), 6.88 (d, J = 8.4 Hz, 2H), 3.80 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.63, 156.49, 142.19, 132.10, 131.11, 129.39, 127.02, 122.11, 114.18, 55.51, 21.53.



***N*-(4-Methoxyphenyl)benzamide (3k).**[17] Following the general procedure, the title compound was prepared using phenylboronic acid (1.5 equiv, 0.75 mmol, 92 mg) and

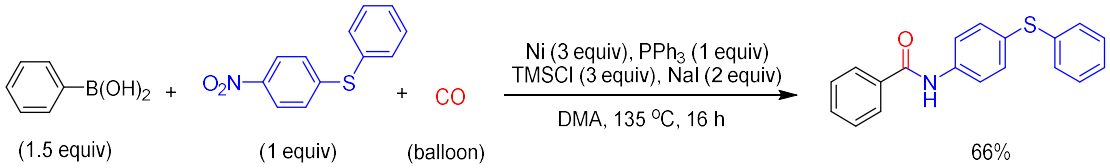
1-methoxy-4-nitrobenzene (1.0 equiv, 0.50 mmol, 77 mg) using PE/EtOAc (6:1) as an eluent to afford the title compound as a white amorphous solid (102 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.76 (s, 1H), 7.60 – 7.52 (m, 3H), 7.48 (t, *J* = 7.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.61, 156.62, 135.03, 131.73, 130.98, 128.77, 126.98, 122.08, 114.24, 55.53.

***N*-(4-(*p*-Tolyloxy)phenyl)-4-methylbenzamide (3l).** Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 102 mg) and 1-(4-nitrophenoxy)-4-methylbenzene (1.0 equiv, 0.50 mmol, 114 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (87 mg, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.77 (m, 3H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.56, 155.05, 154.25, 142.38, 133.14, 132.78, 132.02, 130.23, 129.46, 126.99, 121.90, 119.15, 118.71, 21.51, 20.69. **HRMS** (ESI): Calcd for $C_{21}H_{19}NO_2$ [M+H]: 318.1489; Found: 318.1488.

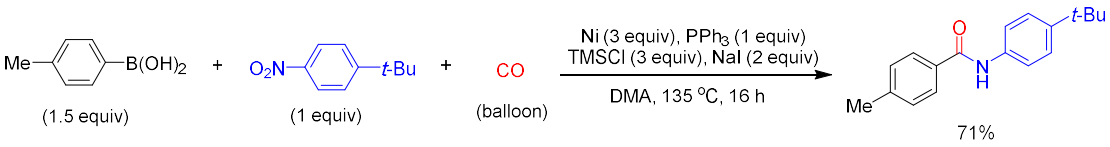


***N*-(4-(*p*-Tolyloxy)phenyl)benzamide (3m).** Following the general procedure, the title compound was prepared using phenylboronic acid (1.5 equiv, 0.75 mmol, 92 mg) and 1-(4-nitrophenoxy)-4-methylbenzene (1.0 equiv, 0.50 mmol, 115 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (126 mg, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.79 (s, 1H),

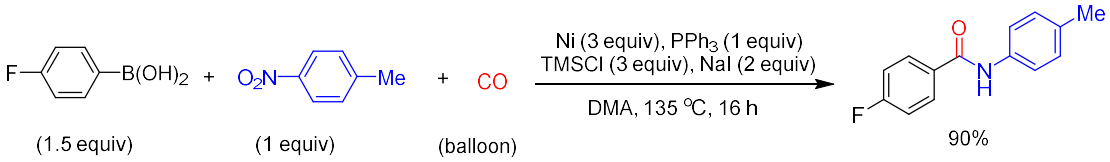
7.61=7.54 (m, 3H), 7.50 (t, J = 7.3 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.66, 154.97, 154.37, 134.89, 132.97, 132.86, 131.88, 130.26, 128.84, 126.99, 121.95, 119.14, 118.75, 20.73. **HRMS** (ESI): Calcd for $C_{20}H_{17}NO_2$ [M+H]: 304.1332; Found: 304.1331.



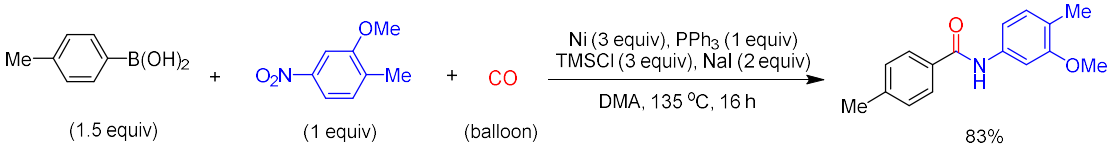
***N*-(4-(Phenylthio)phenyl)benzamide (3n).**[18] Following the general procedure, the title compound was prepared using phenylboronic acid (1.5 equiv, 0.75 mmol, 92 mg) and (4-nitrophenyl)(phenyl)sulfane (1.0 equiv, 0.50 mmol, 116 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (101 mg, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 3H), 7.62 (d, J = 8.8 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.3 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.31-7.27 (m, 4H), 7.24-1.19 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.71, 137.47, 136.74, 134.75, 133.03, 132.02, 130.41, 129.98, 129.14, 128.86, 127.02, 126.66, 120.90.



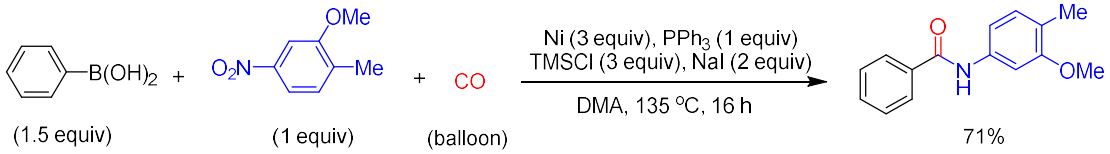
***N*-(4-*tert*-Butylphenyl)-4-methylbenzamide (3o).**[19] Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 102 mg) and 1-*tert*-butyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 87 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (96 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.75 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.7 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.69, 147.39, 142.19, 135.44, 132.21, 129.38, 127.06, 125.87, 120.04, 34.42, 31.40, 21.51.



4-Fluoro-*N*-*p*-tolylbenzamide (3p).[20] Following the general procedure, the title compound was prepared using 4-fluorophenylboronic acid (1.5 equiv, 0.75 mmol, 105 mg) and 1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 68 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (102 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 2H), 7.75 (s, 1H), 7.50 (d, J = 7.9 Hz, 2H), 7.23 – 7.07 (m, 4H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.98 (d, $J_{C\text{-}F}$ = 250.8 Hz), 164.72, 135.33, 134.56, 131.38 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.76, 129.51 (d, $J_{C\text{-}F}$ = 8.9 Hz), 120.50, 115.96 (d, $J_{C\text{-}F}$ = 21.9 Hz), 21.06.

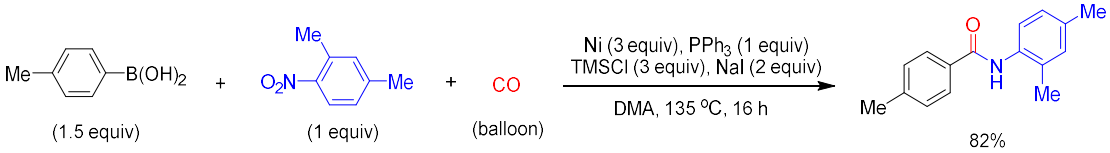


***N*-(3-Methoxy-4-methylphenyl)-4-methylbenzamide (3q).** Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 103 mg) and 2-methoxy-1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 84 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (106 mg, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.76 (d, J = 7.8 Hz, 2H), 7.51 (s, 1H), 7.26 (d, J = 8.6 Hz, 2H), 7.07 (d, J = 7.9 Hz, 1H), 6.88 (d, J = 7.9 Hz, 1H), 3.84 (s, 3H), 2.41 (s, 3H), 2.19 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.67, 157.94, 142.26, 137.06, 132.14, 130.40, 129.40, 127.00, 122.68, 111.53, 103.05, 55.35, 21.50, 15.85. **HRMS** (ESI): Calcd for $C_{16}H_{17}NO_2$ [M+H]: 256.1332; Found: 256.1334.

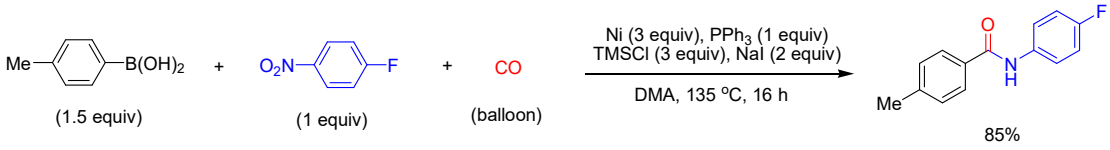


***N*-(3-Methoxy-4-methylphenyl)benzamide (3r).**[21] Following the general procedure,

the title compound was prepared using phenylboronic acid (1.5 equiv, 0.75 mmol, 92 mg) and 2-methoxy-1-methyl-4-nitrobenzene (1.0 equiv, 0.50 mmol, 84 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (86 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.85 (d, J = 7.6 Hz, 2H), 7.56 – 7.40 (m, 4H), 7.07 (d, J = 7.9 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 3.82 (s, 3H), 2.19 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.84, 157.93, 136.96, 135.01, 131.74, 130.43, 128.72, 127.03, 122.85, 111.73, 103.16, 55.33, 15.86.

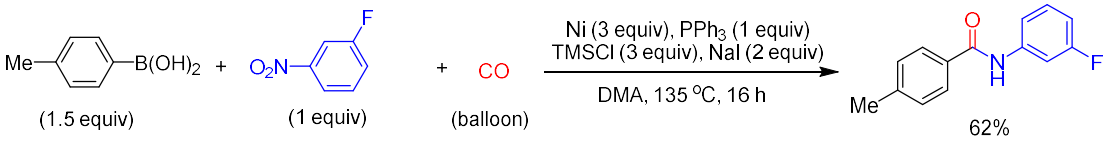


4-Methyl-*N*-(2,4-dimethylphenyl)benzamide (3s).[22] Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 102 mg) and 2,4-dimethyl-1-nitrobenzene (1.0 equiv, 0.50 mmol, 76 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (98 mg, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.71 (m, 3H), 7.60 (s, 1H), 7.28 (d, J = 7.7 Hz, 2H), 7.08-7.02 (m, 2H), 2.42 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.62, 142.23, 135.01, 133.24, 132.22, 131.20, 129.54, 129.43, 127.39, 127.06, 123.41, 21.51, 20.92, 17.80.

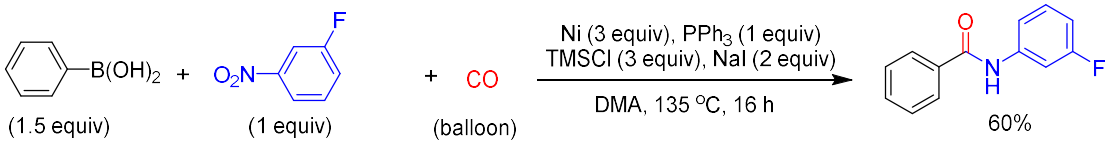


***N*-(4-Fluorophenyl)-4-methylbenzamide (3t).**[23] Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 102 mg) and 1-fluoro-4-nitrobenzene (1.0 equiv, 0.50 mmol, 70 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (97 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (s, 1 H), 7.76 (d, J = 8.6 Hz, 2H), 7.59 (dd, J = 7.7 Hz, J = 5.0 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.10 – 7.01 (m, 2H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.76, 159.58 (d, $J_{C\text{-}F}$ = 242.2 Hz),

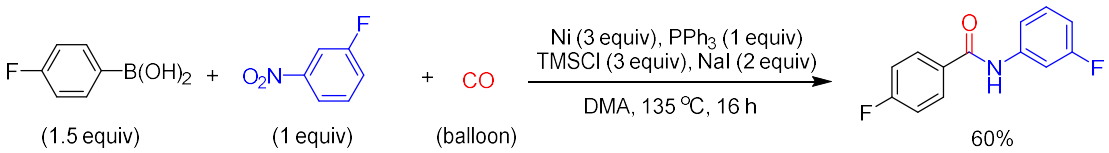
142.66, 134.10 (d, $J_{C\text{-}F}$ = 2.6 Hz), 131.93, 129.62, 127.13, 122.14 (d, $J_{C\text{-}F}$ = 7.9 Hz), 115.87 (d, $J_{C\text{-}F}$ = 22.4 Hz), 21.7.



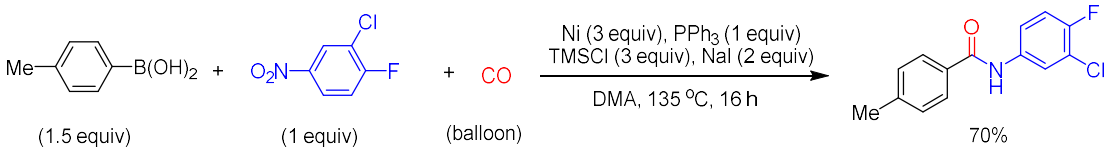
***N*-(3-Fluorophenyl)-4-methylbenzamide (3u).**[24] Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 102 mg) and 1-fluoro-3-nitrobenzene (1.0 equiv, 0.50 mmol, 70 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (71 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.76 (d, J = 7.8 Hz, 2H), 7.64 (d, J = 10.9 Hz, 1H), 7.33-7.25 (m, 4H), 6.84 (t, J = 8.4 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.84, 163.16 (d, $J_{C\text{-}F}$ = 243.2 Hz), 142.81, 139.70 (d, $J_{C\text{-}F}$ = 10.9 Hz), 131.81, 130.22 (d, $J_{C\text{-}F}$ = 9.3 Hz), 129.62, 127.16, 115.42 (d, $J_{C\text{-}F}$ = 2.9 Hz), 111.24 (d, $J_{C\text{-}F}$ = 21.2 Hz), 107.73 (d, $J_{C\text{-}F}$ = 26.2 Hz), 21.7.



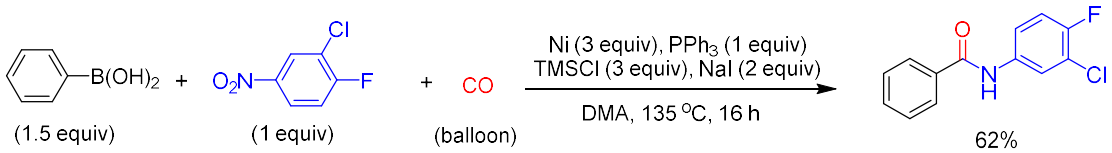
***N*-(3-Fluorophenyl)benzamide (3v).**[25] Following the general procedure, the title compound was prepared using phenylboronic acid (1.5 equiv, 0.75 mmol, 91 mg) and 1-fluoro-3-nitrobenzene (1.0 equiv, 0.50 mmol, 71 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (64.2 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.63 (d, J = 10.7 Hz, 1H), 7.56 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.34-7.24 (m, 2H), 6.85 (t, J = 7.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.92, 163.18 (d, $J_{C\text{-}F}$ = 243.5 Hz), 139.58 (d, $J_{C\text{-}F}$ = 10.8 Hz), 134.7, 132.2, 130.28 (d, $J_{C\text{-}F}$ = 9.2 Hz), 128.99, 127.15, 115.49 (d, $J_{C\text{-}F}$ = 3.4 Hz), 111.41 (d, $J_{C\text{-}F}$ = 21.2 Hz), 107.80 (d, $J_{C\text{-}F}$ = 9.0 Hz).



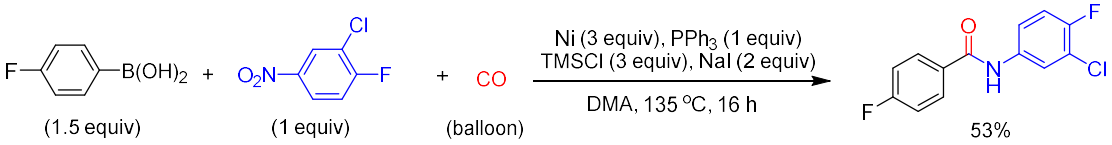
4-Fluoro-*N*-(3-fluorophenyl)benzamide (3w).[26] Following the general procedure, the title compound was prepared using 4-fluorophenylboronic acid (1.5 equiv, 0.75 mmol, 106 mg) and 1-fluoro-3-nitrobenzene (1.0 equiv, 0.50 mmol, 71 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (70 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.84 (m, 3H), 7.61 (d, J = 10.9 Hz, 1H), 7.37-7.24 (m, 2H), 7.17 (t, J = 8.6 Hz, 2H), 6.86 (t, J = 8.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.18 (d, $J_{C\text{-}F}$ = 251.6 Hz), 164.76, 163.19 (d, $J_{C\text{-}F}$ = 243.7 Hz), 139.40 (d, $J_{C\text{-}F}$ = 10.8 Hz), 130.89 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.35 (d, $J_{C\text{-}F}$ = 9.3 Hz), 129.57 (d, $J_{C\text{-}F}$ = 9.0 Hz), 116.14 (d, $J_{C\text{-}F}$ = 21.9 Hz), 115.48 (d, $J_{C\text{-}F}$ = 2.9 Hz), 111.58 (d, $J_{C\text{-}F}$ = 21.2 Hz), 107.84 (d, $J_{C\text{-}F}$ = 26.2 Hz).



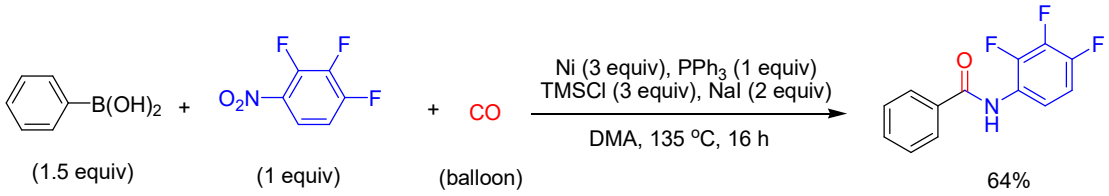
***N*-(3-Chloro-4-fluorophenyl)-4-methylbenzamide (3x).** Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 102 mg) and 2-chloro-1-fluoro-4-nitrobenzene (1.0 equiv, 0.50 mmol, 88.0 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (92 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.81 (d, J = 5.5 Hz, 1H), 7.73 (d, J = 7.8 Hz, 2H), 7.46-7.41 (m, 1 H), 7.25 (d, J = 7.5 Hz, 2H), 7.09 (t, J = 8.8 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.99, 154.94 (d, $J_{C\text{-}F}$ = 244.9 Hz), 142.87, 134.76 (d, $J_{C\text{-}F}$ = 3.5 Hz), 131.49, 129.58, 127.19, 122.74, 121.22 (d, $J_{C\text{-}F}$ = 22.0 Hz), 120.19 (d, $J_{C\text{-}F}$ = 6.8 Hz), 116.69 (d, $J_{C\text{-}F}$ = 22.0 Hz), 21.63. **HRMS** (ESI): Calcd for $C_{14}H_{11}ClFNO$ [M+H]: 264.0586; Found: 264.0589.



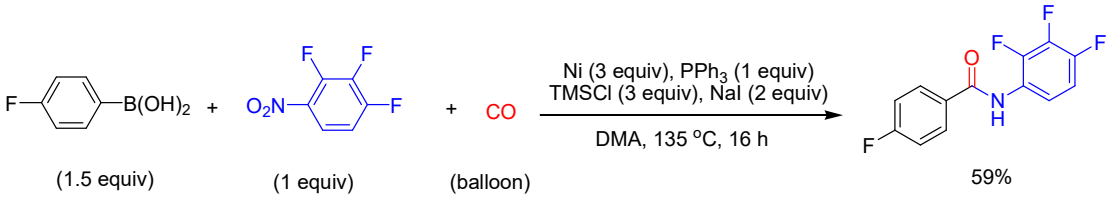
***N*-(3-Chloro-4-fluorophenyl)benzamide (3y).**[27] Following the general procedure, the title compound was prepared using phenylboronic acid (1.5 equiv, 0.75 mmol, 91 mg) and 2-chloro-1-fluoro-4-nitrobenzene (1.0 equiv, 0.50 mmol, 88 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (77.5 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.86-7.81 (m, 3H), 7.56 (t, J = 7.4 Hz, 1H), 7.52 – 7.39 (m, 3H), 7.11 (t, J = 8.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.84, 155.08 (d, $J_{C\text{-}F}$ = 245.2 Hz), 134.62 (d, $J_{C\text{-}F}$ = 3.4 Hz), 134.4, 132.3, 129.05, 127.13, 122.67, 121.4 (d, $J_{C\text{-}F}$ = 18.5 Hz), 120.06 (d, $J_{C\text{-}F}$ = 6.9 Hz), 116.84 (d, $J_{C\text{-}F}$ = 22.0 Hz).



***N*-(3-Chloro-4-fluorophenyl)-4-fluorobenzamide (3z).** Following the general procedure, the title compound was prepared using 4-fluorophenylboronic acid (1.5 equiv, 0.75 mmol, 106 mg) and 2-chloro-1-fluoro-4-nitrobenzene (1.0 equiv, 0.50 mmol, 88 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (72 mg, 53%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.85 (dd, J = 8.4, J = 5.2 Hz, 2H), 7.79 (d, J = 6.5 Hz, 1H), 7.44-7.40 (m, 1H), 7.18 – 7.08 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.20 (d, $J_{C\text{-}F}$ = 251.9 Hz), 164.92, 155.16 (d, $J_{C\text{-}F}$ = 245.4 Hz), 134.44 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.55 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.59 (d, $J_{C\text{-}F}$ = 8.9 Hz), 122.86, 121.41 (d, $J_{C\text{-}F}$ = 18.5 Hz), 120.26 (d, $J_{C\text{-}F}$ = 6.8 Hz), 116.84 (d, $J_{C\text{-}F}$ = 22.0 Hz), 116.11 (d, $J_{C\text{-}F}$ = 21.8 Hz). **HRMS** (ESI): Calcd for $C_{13}H_8ClF_2NO$ [M+Na]: 290.0155; Found: 290.0157.

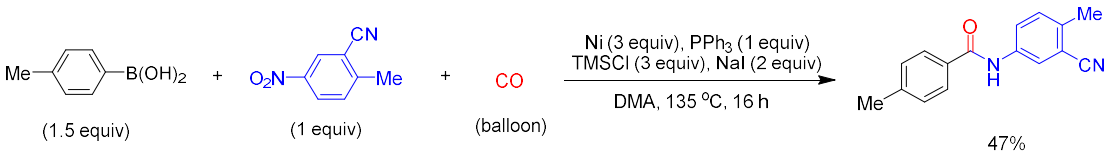


***N*-(2,3,4-Trifluorophenyl)benzamide (3aa).** Following the general procedure, the title compound was prepared using phenylboronic acid (1.5 equiv, 0.75 mmol, 92 mg) and 1,2,3-trifluoro-4-nitrobenzene (1.0 equiv, 0.50 mmol, 89 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (80 mg, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17-8.10 (m, 1H), 7.97 (s, 1H), 7.88 (d, J = 7.7 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.05 – 6.97 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.61, 147.5 (ddd, $J_{C\text{-}F}$ = 246.1 Hz, $J_{C\text{-}F}$ = 9.9 Hz, $J_{C\text{-}F}$ = 2.9 Hz), 142.56 (ddd, $J_{C\text{-}F}$ = 245.4 Hz, $J_{C\text{-}F}$ = 12.0 Hz, $J_{C\text{-}F}$ = 3.3 Hz), 139.79 (ddd, $J_{C\text{-}F}$ = 249.2 Hz, $J_{C\text{-}F}$ = 16.1 Hz, $J_{C\text{-}F}$ = 13.5 Hz), 133.89, 132.47, 128.98, 127.11, 123.86 (dd, $J_{C\text{-}F}$ = 8.0 Hz, $J_{C\text{-}F}$ = 3.6 Hz), 116.04 (dd, $J_{C\text{-}F}$ = 9.9 Hz, $J_{C\text{-}F}$ = 4.4 Hz), 111.76 (dd, $J_{C\text{-}F}$ = 17.8 Hz, $J_{C\text{-}F}$ = 4.0 Hz). **HRMS** (ESI): Calcd for $C_{13}H_8F_3NO$ [M+Na]: 274.0450; Found: 274.0453

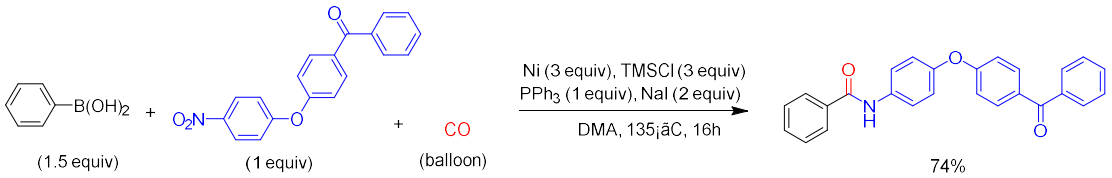


4-Fluoro-*N*-(2,3,4-trifluorophenyl)benzamide (3ab). Following the general procedure, the title compound was prepared using 4-fluorophenylboronic acid (1.5 equiv, 0.75 mmol, 105 mg) and 1,2,3-trifluoro-4-nitrobenzene (1.0 equiv, 0.50 mmol, 89 mg, 57.2µl) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (80 mg, 59%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15-8.08 (m, 1H), 7.92 – 7.85 (m, 3H), 7.20 (t, J = 8.6 Hz, 2H), 7.06 – 6.99 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.39 (d, $J_{C\text{-}F}$ = 252.3 Hz), 164.62, 147.80 (ddd, $J_{C\text{-}F}$ = 246.1 Hz, $J_{C\text{-}F}$ = 9.8 Hz, $J_{C\text{-}F}$ = 2.6 Hz), 142.70 (ddd, $J_{C\text{-}F}$ = 245.3 Hz, $J_{C\text{-}F}$ = 11.9 Hz, $J_{C\text{-}F}$ = 3.1 Hz), 139.98 (ddd, $J_{C\text{-}F}$ = 242.9 Hz, $J_{C\text{-}F}$ = 16.1 Hz, $J_{C\text{-}F}$ = 13.8 Hz), 130.22 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.72 (d, $J_{C\text{-}F}$ = 9.1 Hz), 123.85 (dd, $J_{C\text{-}F}$ = 7.9 Hz, $J_{C\text{-}F}$ = 3.6 Hz), 116.29

(d, $J_{C\text{-}F}$ = 21.9 Hz), 116.17 (dd, $J_{C\text{-}F}$ = 7.5 Hz, $J_{C\text{-}F}$ = 3.3 Hz), 111.98 (dd, $J_{C\text{-}F}$ = 17.7 Hz, $J_{C\text{-}F}$ = 3.9 Hz). **HRMS** (ESI): Calcd for $C_{13}H_8F_3NO$ [M+H]: 270.0537; Found: 270.0541

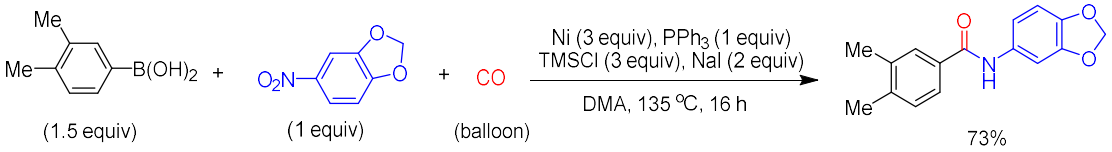


***N*-(3-Cyano-4-methylphenyl)-4-methylbenzamide (3ac).** Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 101 mg) and 2-methyl-5-nitrobenzonitrile (1.0 equiv, 0.50 mmol, 82 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (56 mg, 47%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.95 (s, 1H), 7.79-7.72 (m, 3H), 7.31-7.23 (m, 3H), 2.51 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.88, 142.88, 137.68, 136.40, 131.29, 130.86, 129.51, 127.13, 124.66, 123.70, 117.83, 113.06, 21.55, 19.91. **HRMS** (ESI): Calcd for $C_{16}H_{14}N_2O$ [M+H]: 251.1179; Found: 251.1174.



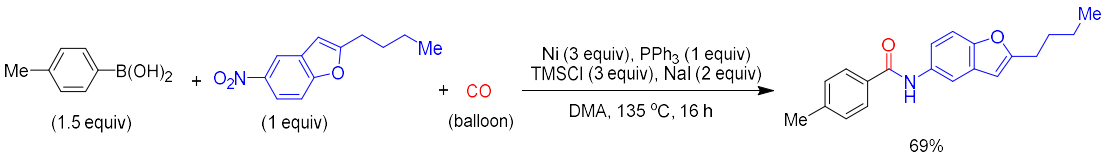
***N*-(4-(4-Benzoylphenoxy)phenyl)benzamide (3ad).** Following the general procedure, the title compound was prepared using phenylboronic acid (1.5 equiv, 0.75 mmol, 92 mg) and (4-(4-nitrophenoxy)phenyl)(phenyl)methanone (1.0 equiv, 0.50 mmol, 159 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (145 mg, 74%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.89 (d, J = 7.7 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.60-7.54 (m, 2H), 7.52-7.46 (m, 4 H), 7.11 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.54, 165.77, 161.81, 151.92, 137.93, 134.76, 134.63, 132.51, 132.17, 131.98, 131.90, 129.82, 128.85, 128.27, 127.04,

122.10, 120.92, 116.89. **HRMS** (ESI): Calcd for $C_{26}H_{19}NO_3$ [M+H]: 394.1438; Found: 394.1439.

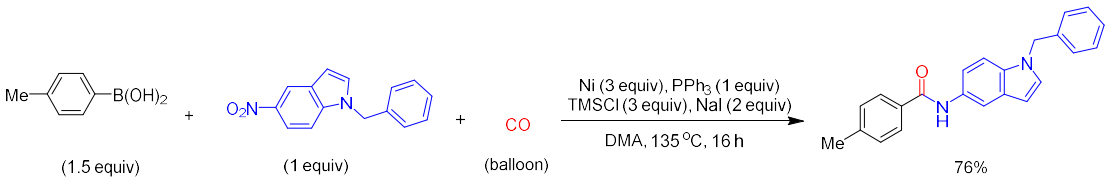


***N*-(Benzo[d][1,3]dioxol-6-yl)-3,4-dimethylbenzamide (3ae).** Following the general procedure, the title compound was prepared using 3,4-dimethylphenylboronic acid (1.5 equiv, 0.75 mmol, 112 mg) and 5-nitrobenzo[d][1,3]dioxole (1.0 equiv, 0.50 mmol, 84 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (95 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.62 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.35 (s, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 5.95 (s, 2H), 2.30 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.87, 147.80, 144.32, 140.92, 137.13, 132.36, 132.32, 129.84, 128.32, 124.34, 113.56, 108.05, 103.22, 101.28, 19.88, 19.81. **HRMS** (ESI): Calcd for $C_{16}H_{15}NO_3$ [M+H]: 270.1125; Found: 270.1129.

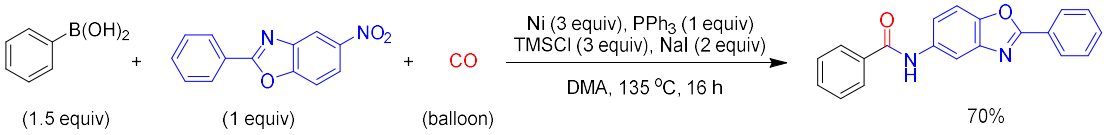
***N*-(Benzo[b]thiophen-5-yl)-4-methylbenzamide (3af).** Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 101 mg) and 5-nitrobenzo[b]thiophene (1.0 equiv, 0.50 mmol, 90 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (112 mg, 84%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.94 (s, 1H), 7.85-7.76 (m, 3H), 7.49-7.43 (m, 2H), 7.33-7.28 (m, 3H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.74, 142.42, 140.27, 135.67, 134.81, 132.10, 129.49, 127.60, 127.03, 124.01, 122.78, 117.84, 114.90, 21.55. **HRMS** (ESI): Calcd for $C_{16}H_{13}NOS$ [M+H]: 268.0791; Found: 268.0790.



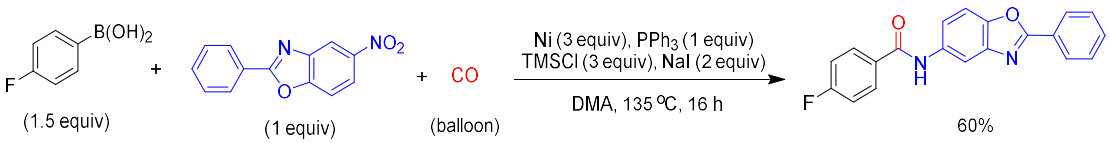
***N*-(2-Butylbenzofuran-5-yl)-4-methylbenzamide (3ag).** Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 101 mg) and 2-butyl-5-nitrobenzofuran (1.0 equiv, 0.50 mmol, 109 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (108 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94-7.86 (m, 2H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.29-7.23 (m, 3H), 6.34 (s, 1H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.72 (quint, *J* = 7.6 Hz, 2H), 1.42 (sex, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.74, 160.80, 151.73, 142.10, 132.83, 132.24, 129.48, 129.34, 127.02, 116.59, 112.54, 110.66, 102.08, 29.69, 28.19, 22.28, 21.48, 13.82. **HRMS** (ESI): Calcd for $C_{20}H_{21}NO_2Na$ [M+Na]: 330.1465 ; Found: 330.1463.



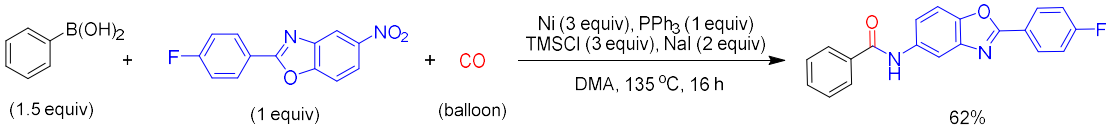
***N*-(1-Benzyl-1H-indol-5-yl)-4-methylbenzamide (3ah).** Following the general procedure, the title compound was prepared using 4-methylphenylboronic acid (1.5 equiv, 0.75 mmol, 102 mg) and 1-benzyl-5-nitro-1H-indole (1.0 equiv, 0.50 mmol, 126 mg) using PE/EtOAc (8:1) as an eluent to afford the title compound as a white amorphous solid (129 mg, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.85-7.73 (m, 3H), 7.35-7.20 (m, 8H), 7.15 (d, *J* = 3.1 Hz, 1H), 7.09 (d, *J* = 7.1 Hz, 2H), 6.54 (d, *J* = 3.1 Hz, 1H), 5.33 (s, 2H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.64, 141.97, 137.42, 133.90, 132.55, 130.43, 129.37, 129.24, 128.91, 128.78, 127.65, 126.99, 126.68, 116.27, 113.19, 109.94, 101.92, 50.25, 21.51. **HRMS** (ESI): Calcd for $C_{23}H_{20}N_2O$ [M+H]: 341.1648; Found: 341.1648.



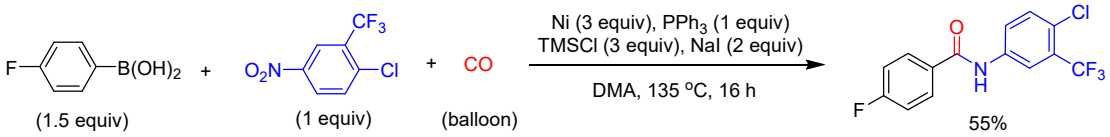
***N*-(2-Phenylbenzo[d]oxazol-5-yl)benzamide (4a).**[28] Following the general procedure, the title compound was prepared using phenylboronic acid (1.5 equiv, 0.75 mmol, 92 mg) and 5-nitro-2-phenylbenzo[d]oxazole (1.0 equiv, 0.50 mmol, 120 mg) using PE/EtOAc (5:1) as an eluent to afford the title compound as a white amorphous solid (101 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, J = 6.8 Hz, 2H), 8.10-8.00 (m, 2H), 7.91 (d, J = 7.5 Hz, 2H), 7.66 (d, J = 8.9 Hz, 1H), 7.60-7.45 (m, 7H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.92, 164.01, 147.85, 142.61, 134.86, 131.92, 131.66, 128.94, 128.82, 127.68, 127.10, 127.01, 118.70, 112.10, 110.60 (15 carbon signals were observed out of expected 16 carbon signals).



4-Fluoro-*N*-(2-phenylbenzo[d]oxazol-5-yl)benzamide (4b).[28] Following the general procedure, the title compound was prepared using 4-fluorophenylboronic acid (1.5 equiv, 0.75 mmol, 105 mg) and 5-nitro-2-phenylbenzo[d]oxazole (1.0 equiv, 0.50 mmol, 120 mg) using PE/EtOAc (5:1) as an eluent to afford the title compound as a white amorphous solid (100 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 – 8.22 (m, 2H), 8.02 (s, 1H), 7.98 – 7.86 (m, 3H), 7.64 (d, J = 8.9 Hz, 1H), 7.60-7.50 (m, 4H), 7.20 (t, J = 8.3 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.54, 164.11 (d, $J_{C\text{-}F}$ = 247.6 Hz), 162.98, 146.70, 141.62, 136.28, 132.02, 131.33 (d, $J_{C\text{-}F}$ = 2.9 Hz), 130.44 (d, $J_{C\text{-}F}$ = 9.0 Hz), 129.37, 127,28, 126.42, 118.88, 115.41 (d, $J_{C\text{-}F}$ = 21.6 Hz), 111.35, 110.67.



***N*-(2-(4-Fluorophenyl)benzo[d]oxazol-5-yl)benzamide (4c).**[29] Following the general procedure, the title compound was prepared using phenylboronic acid (1.5 equiv, 0.75 mmol, 92 mg) and 2-(4-fluorophenyl)-5-nitrobenzo[d]oxazole (1.0 equiv, 0.50 mmol, 129 mg) using PE/EtOAc (5:1) as an eluent to afford the title compound as a white amorphous solid (103 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 8.2, *J* = 5.1 Hz, 2H), 8.05 (s, 1H), 7.96-7.88 (m, 3H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.62 – 7.48 (m, 4H), 7.22 (t, *J* = 8.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.97, 165.02 (d, $J_{C\text{-}F}$ = 251.5 Hz), 163.30, 147.99, 142.76, 135.05, 124.99, 132.12, 130.06 (d, $J_{C\text{-}F}$ = 8.8 Hz), 129.01. 127.20, 123.49 (d, $J_{C\text{-}F}$ = 3.0 Hz), 118.74, 116.38 (d, $J_{C\text{-}F}$ = 22.1 Hz), 112.13, 110.75.



***N*-(4-Chloro-3-(trifluoromethyl)phenyl)-4-fluorobenzamide (4d).**[30] Following the general procedure, the title compound was prepared using 4-fluorophenylboronic acid (1.5 equiv, 0.75 mmol, 105 mg) and 2-chloro-5-nitrobenzotrifluoride (1.0 equiv, 0.50 mmol, 113 mg) using PE/EtOAc (6:1) as an eluent to afford the title compound as a white amorphous solid (87 mg, 55%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.63 (s, 1H), 8.34 (s, 1H), 8.11-8.00 (m, 3H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.39 (t, *J* = 8.4 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.9, 164.3 (d, $J_{C\text{-}F}$ = 248.4 Hz), 138.6, 132.0, 130.63, 130.60 (d, $J_{C\text{-}F}$ = 9.2 Hz), 126.7 (q, $J_{C\text{-}F}$ = 30.6 Hz), 125.0, 124.4 (d, $J_{C\text{-}F}$ = 1.7 Hz), 122.8 (q, $J_{C\text{-}F}$ = 271.4 Hz), 119.0 (q, $J_{C\text{-}F}$ = 5.7 Hz), 115.5 (d, $J_{C\text{-}F}$ = 21.8 Hz).

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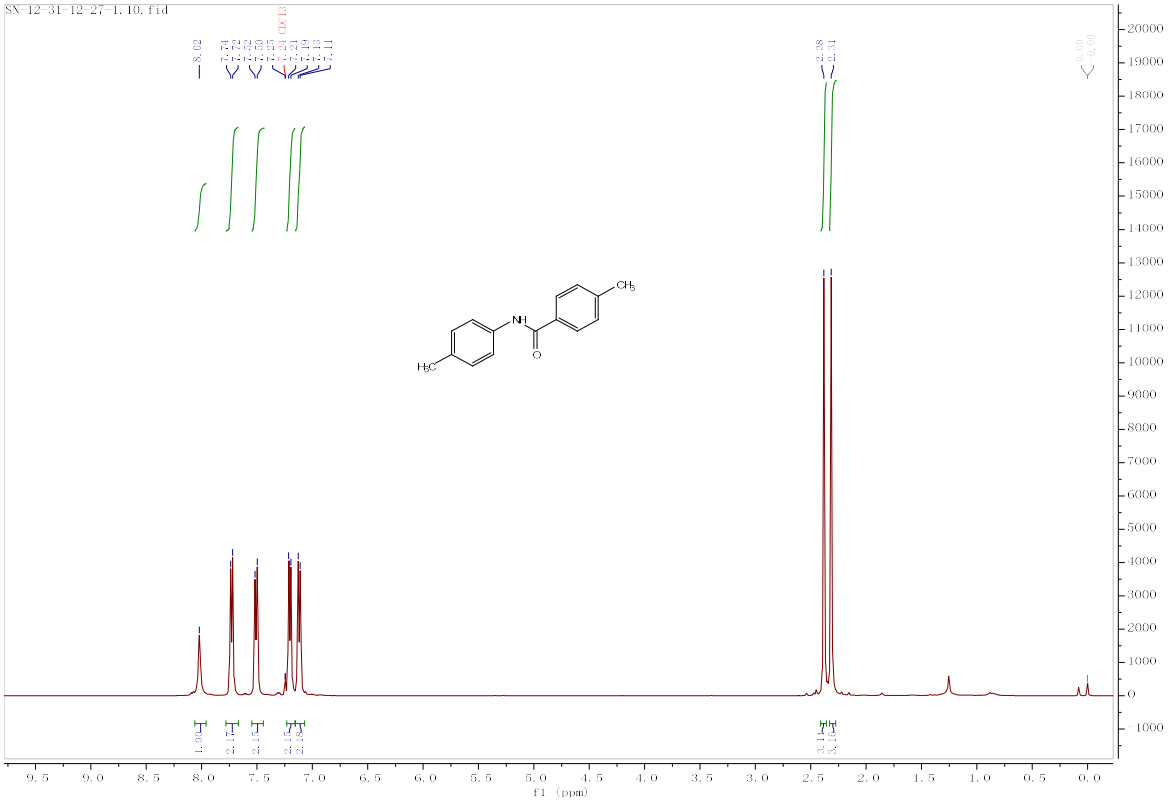
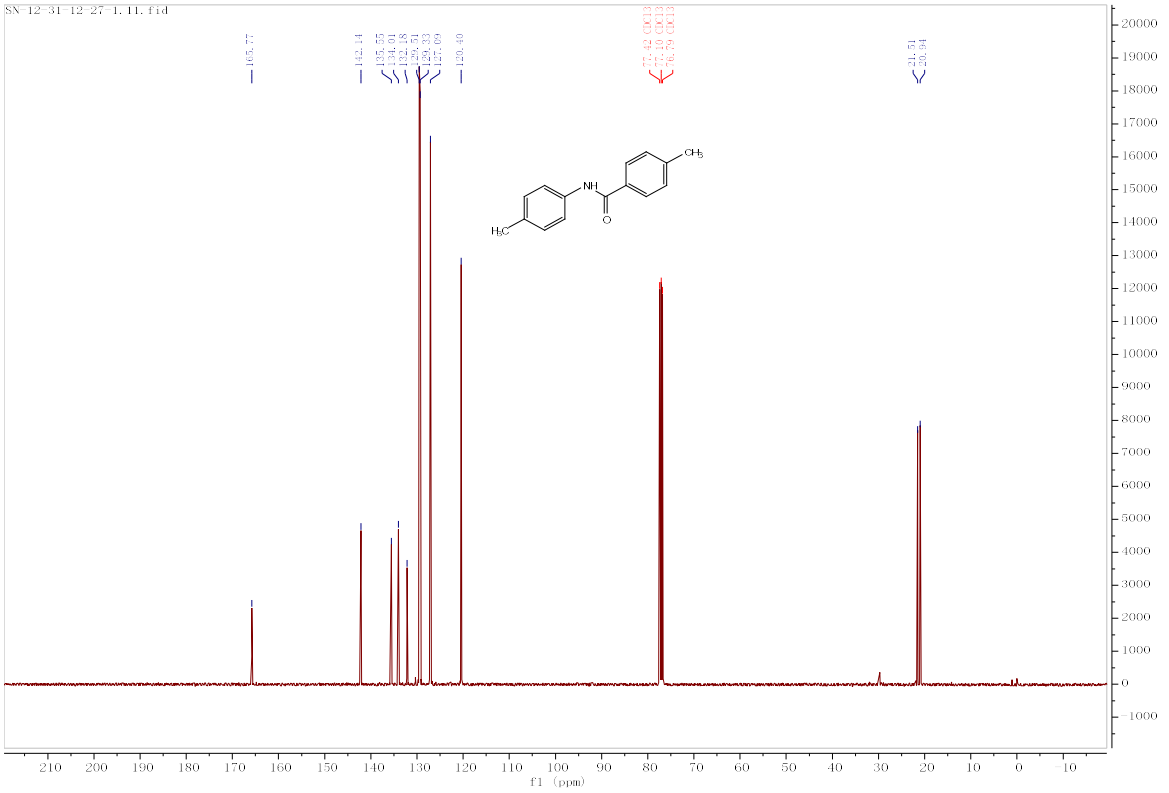
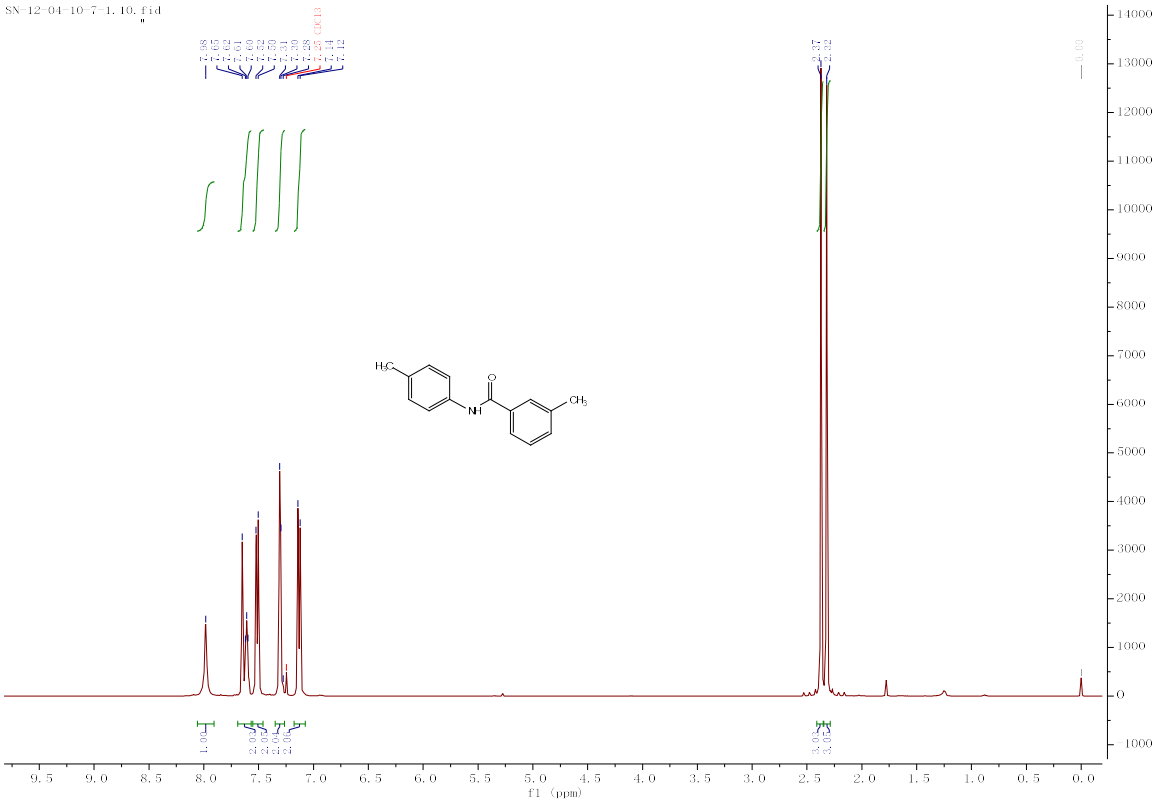
NMR Spectra

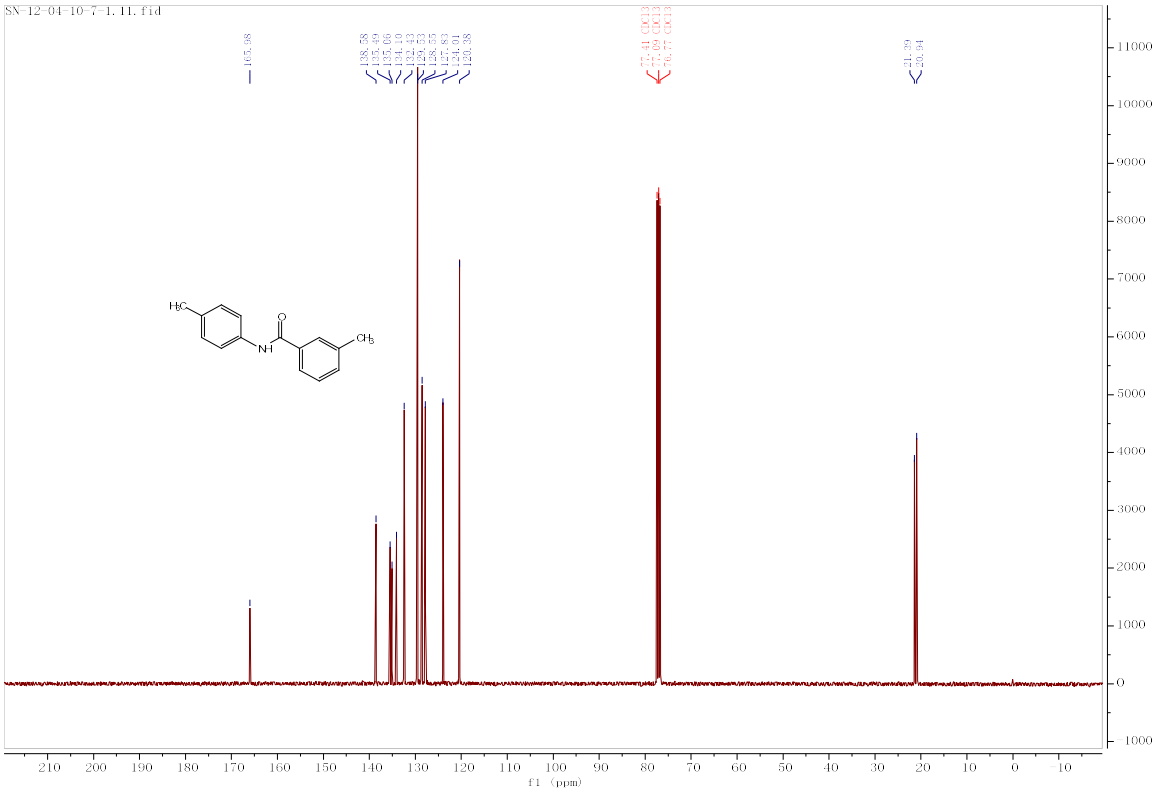
^{1}H and ^{13}C NMR Spectra of 4-Methyl-*N*-*p*-tolylbenzamide (3a)



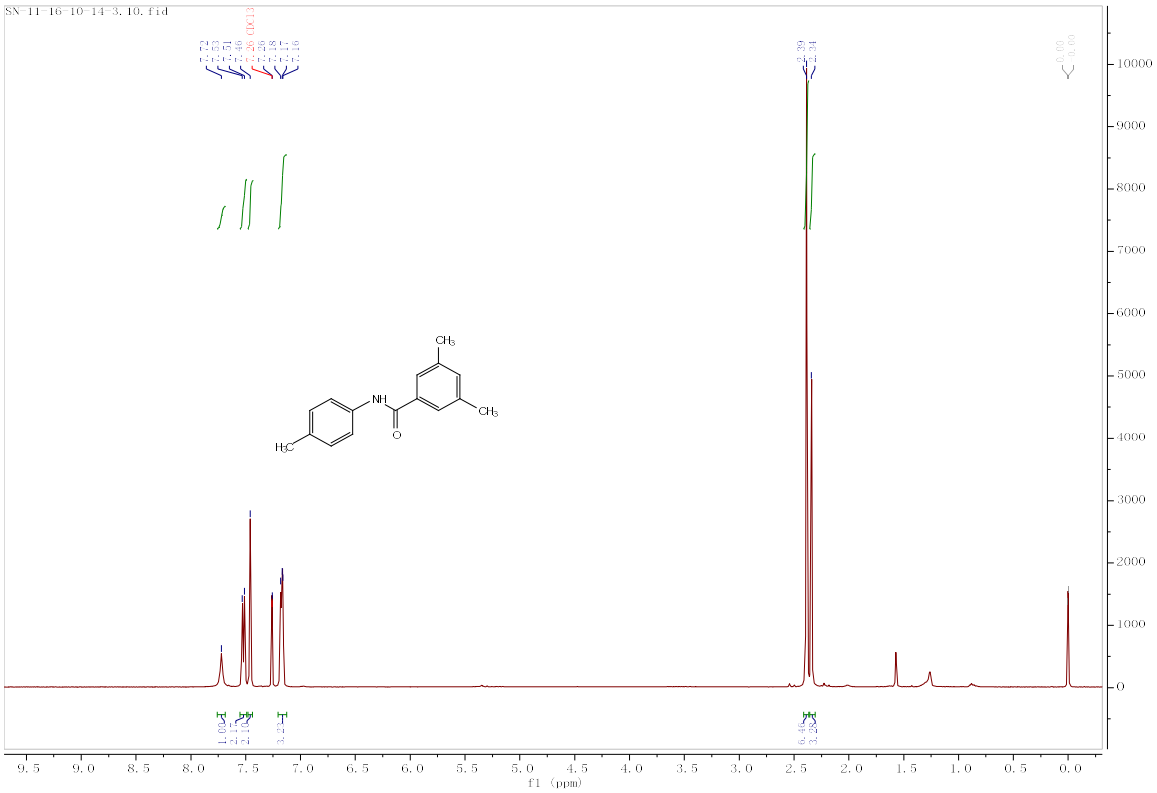


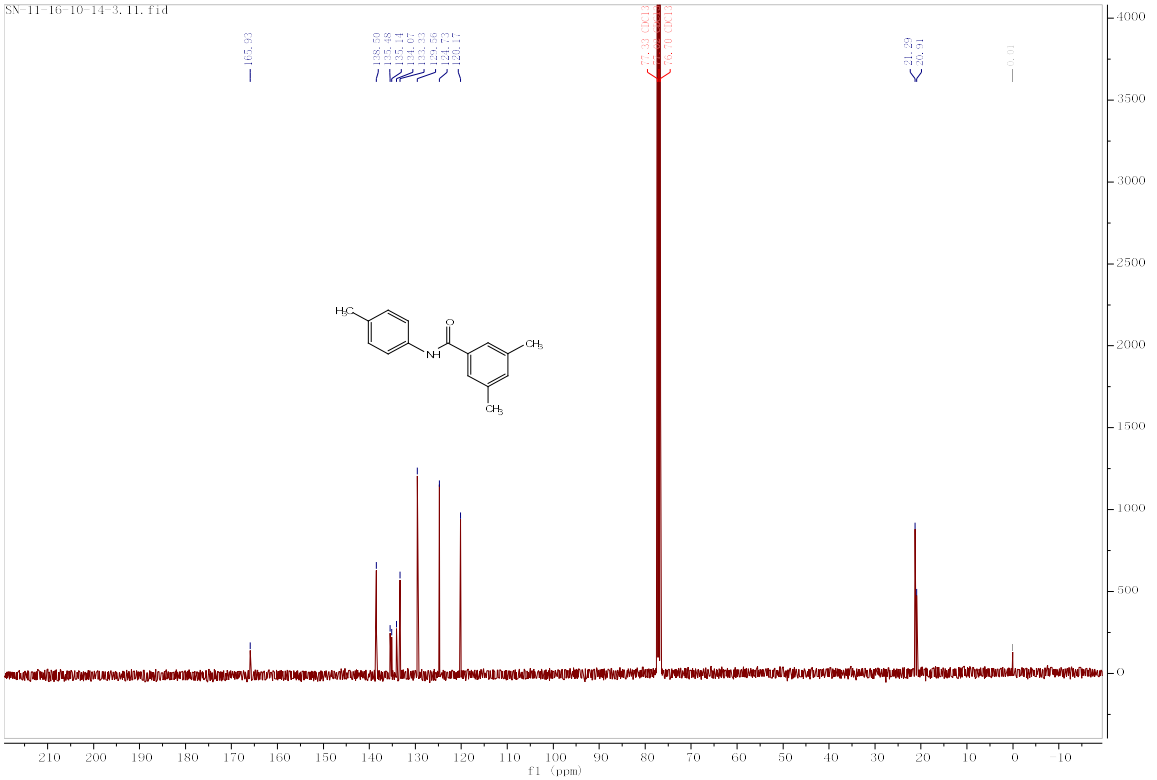
^{1}H and ^{13}C NMR Spectra of 3-Methyl-*N*-*p*-tolylbenzamide (3b)



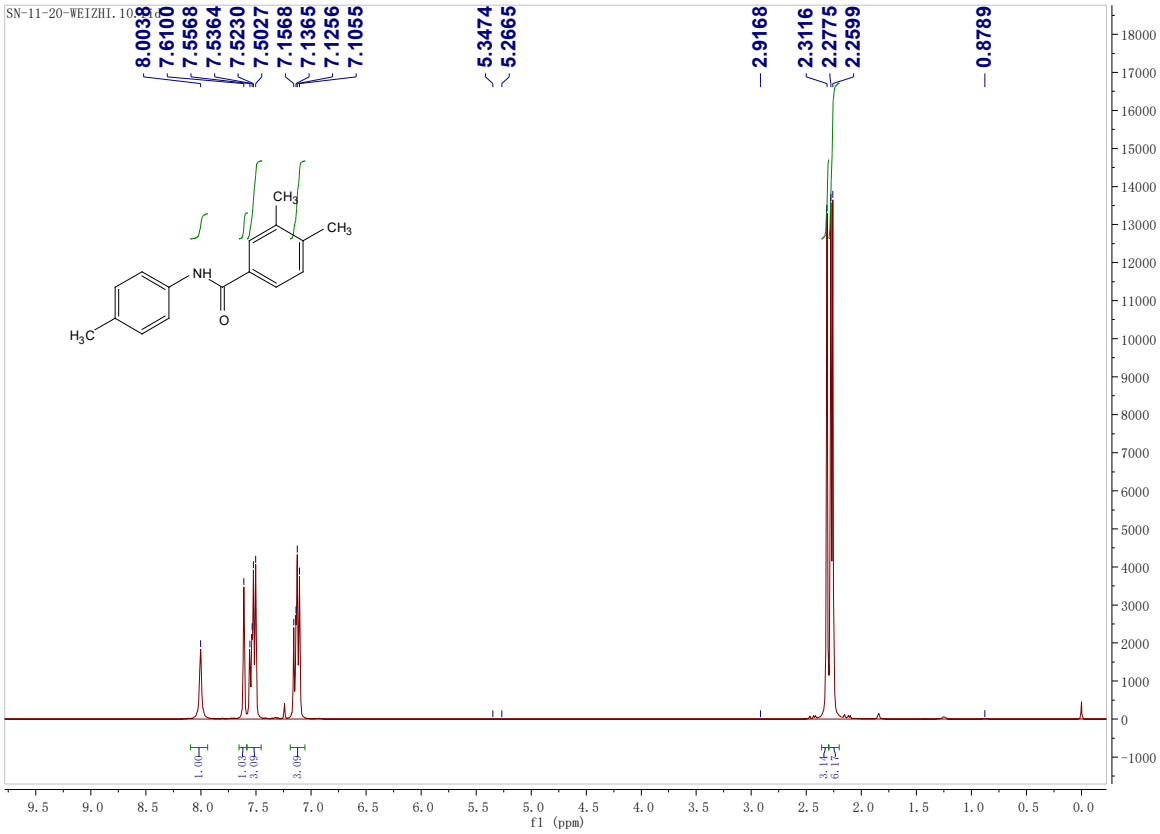


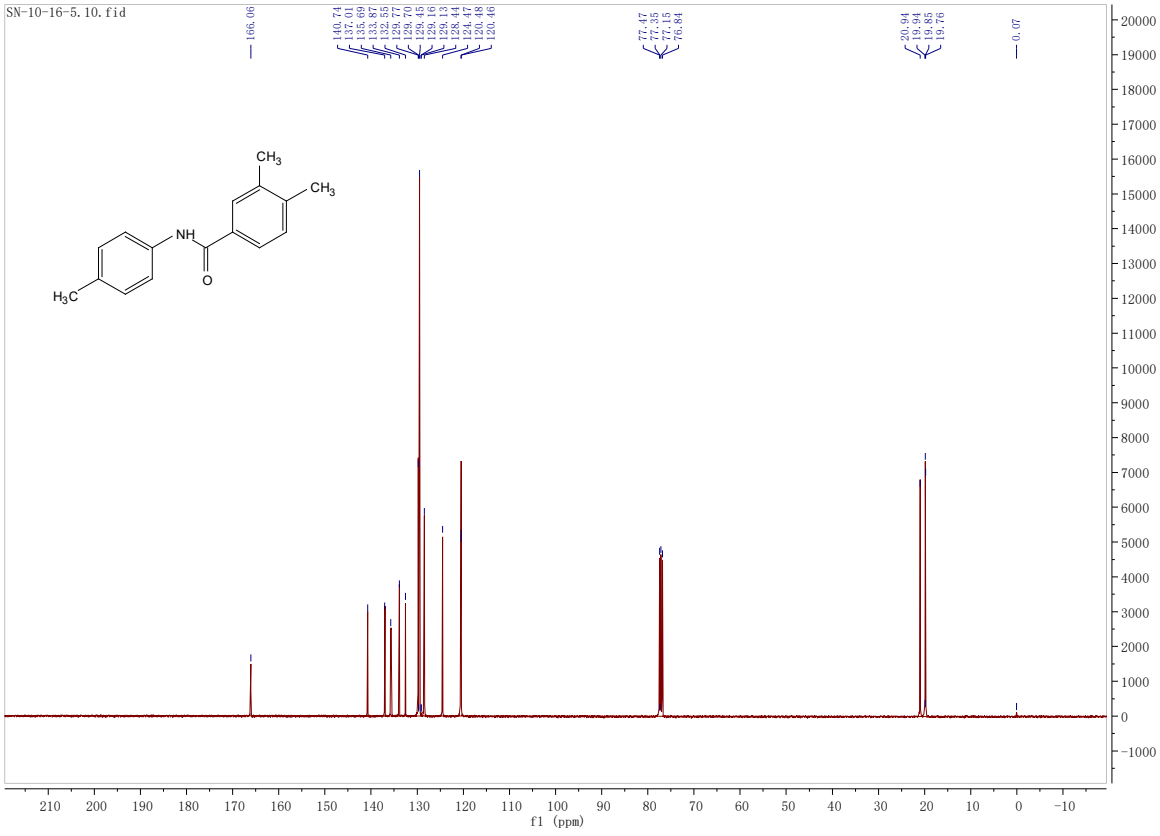
^{1}H and ^{13}C NMR Spectra of 3,5-Dimethyl-*N*-*p*-tolylbenzamide (3c)



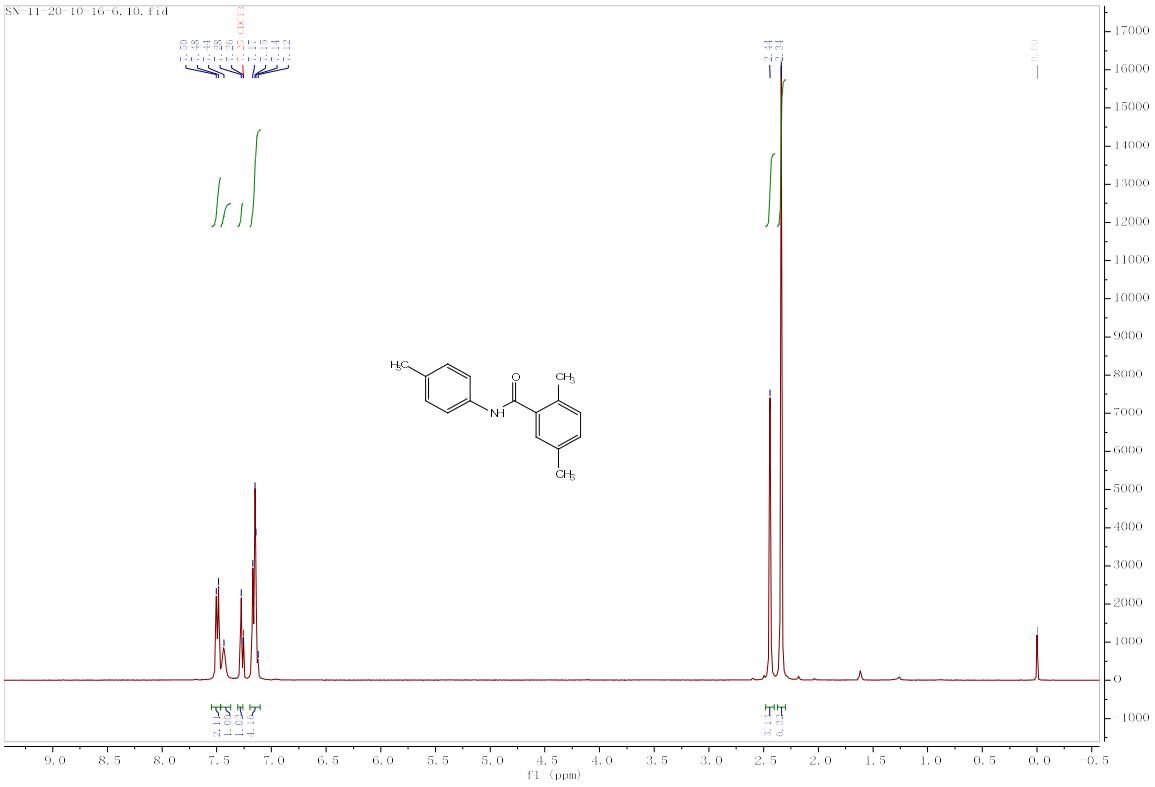


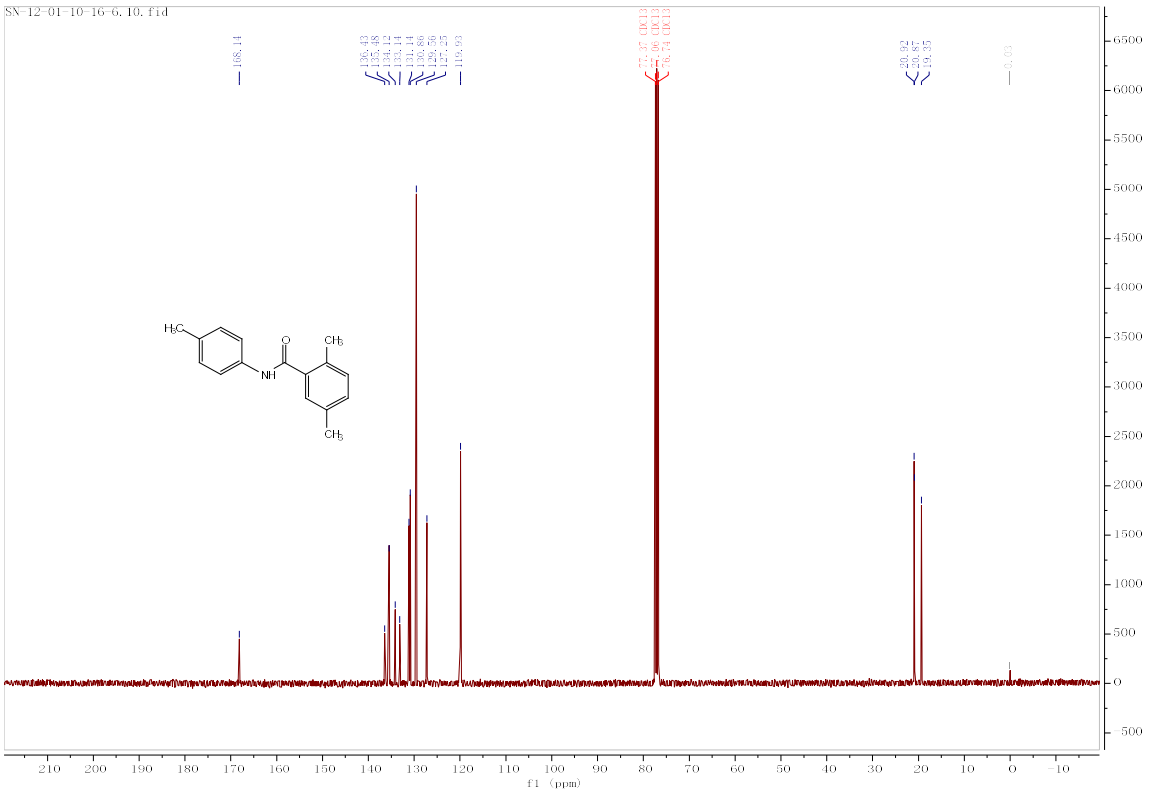
^{1}H and ^{13}C NMR Spectra of 3,4-Dimethyl-*N*-*p*-tolylbenzamide (3d)



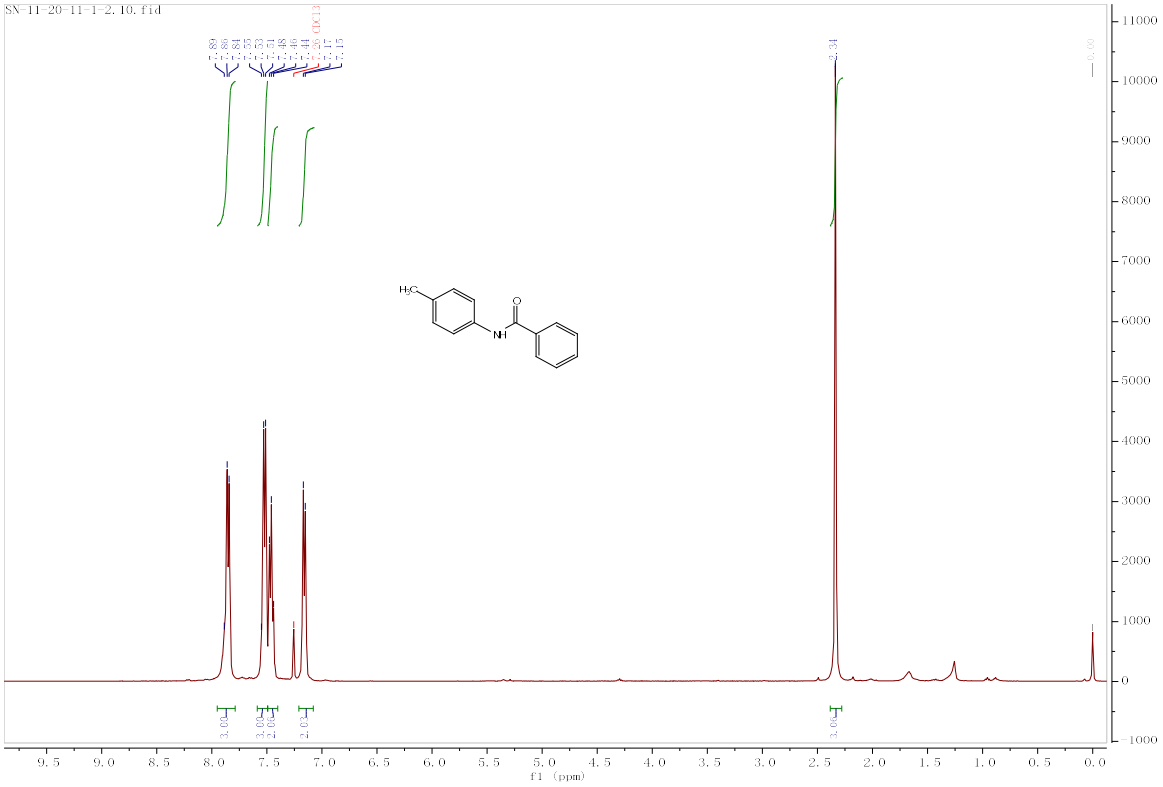


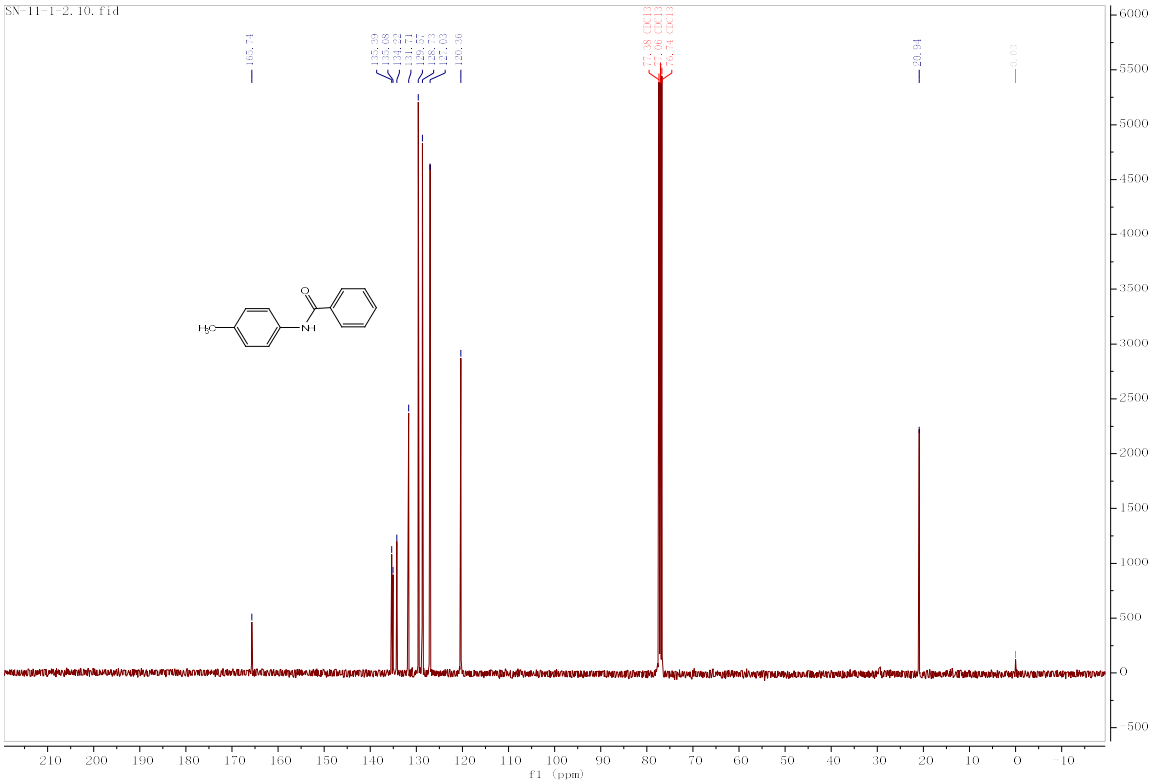
^{1}H and ^{13}C NMR Spectra of 2,5-Dimethyl-*N*-*p*-tolylbenzamide (3e)



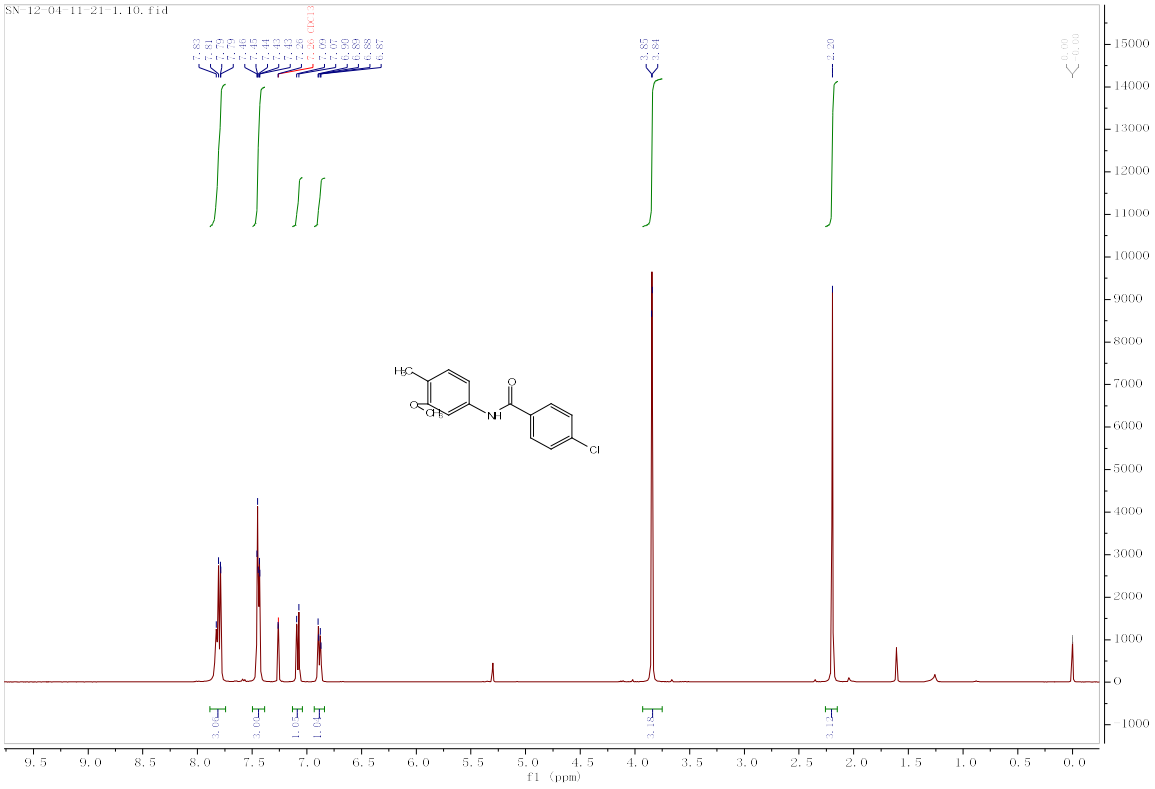


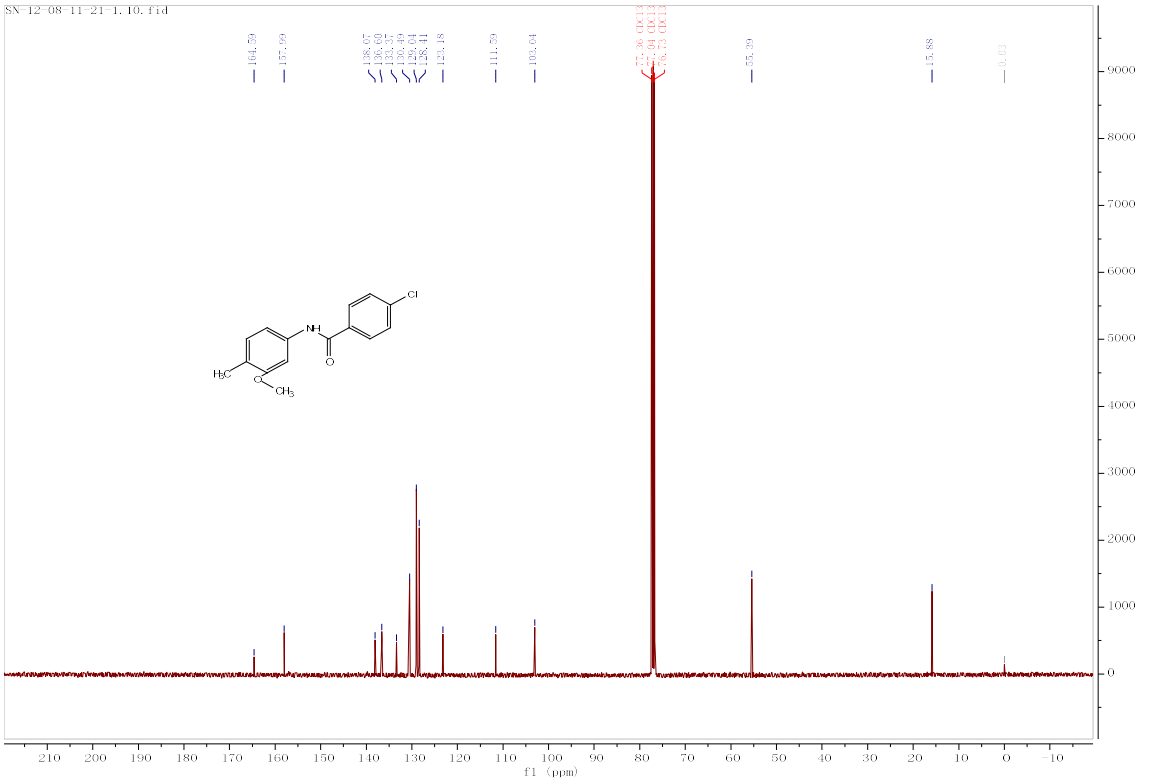
^{1}H and ^{13}C NMR Spectra of *N*-*p*-Tolylbenzamide (3f)



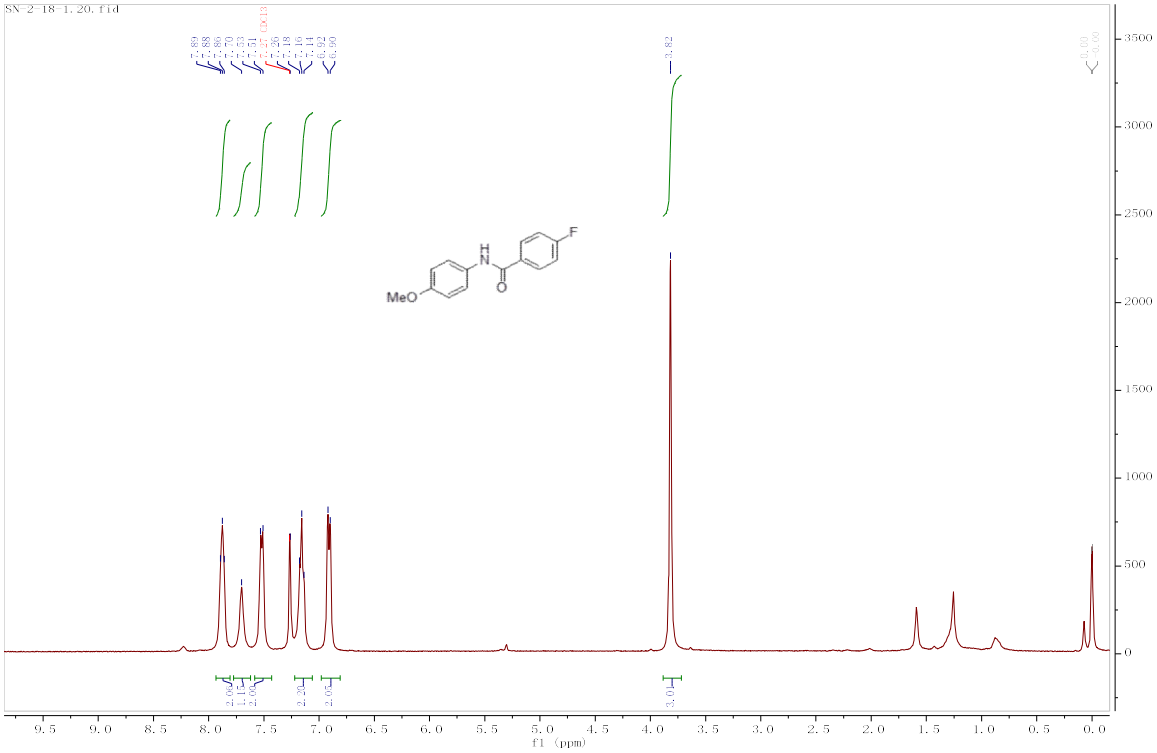


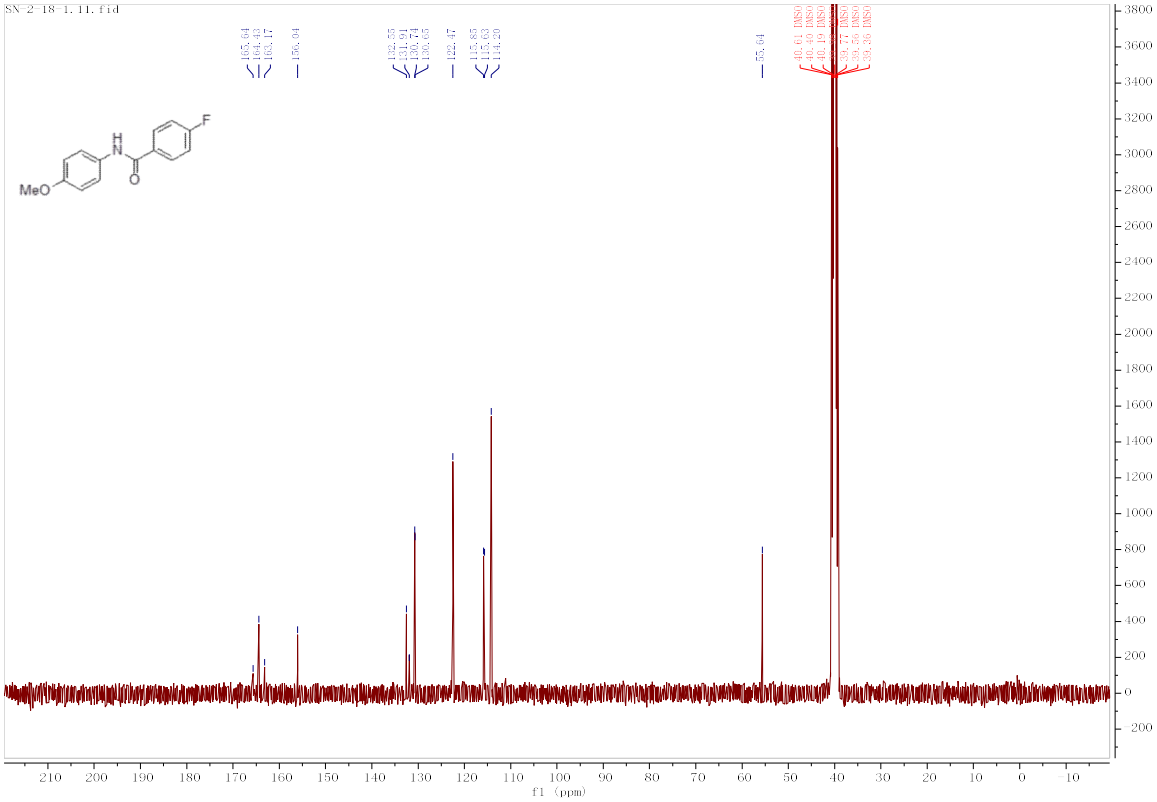
^{1}H and ^{13}C NMR Spectra of 4-Chloro-*N*-(3-methoxy-4-methylphenyl)benzamide (3g)



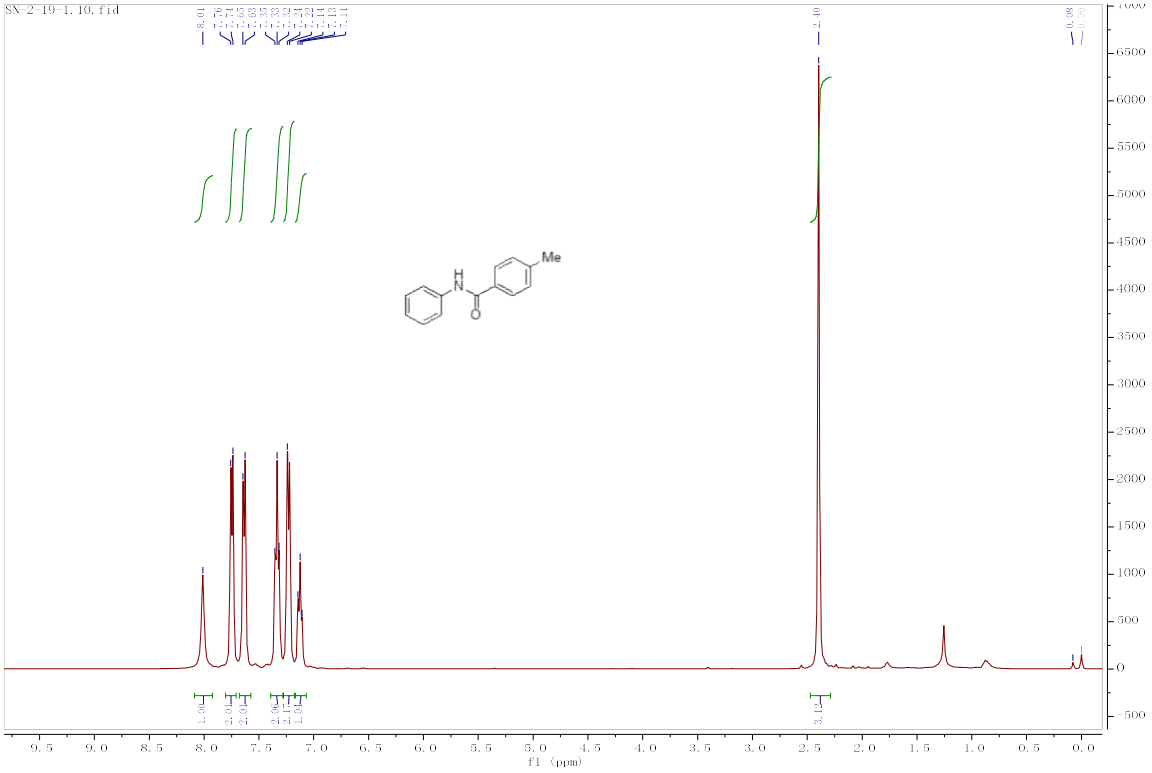


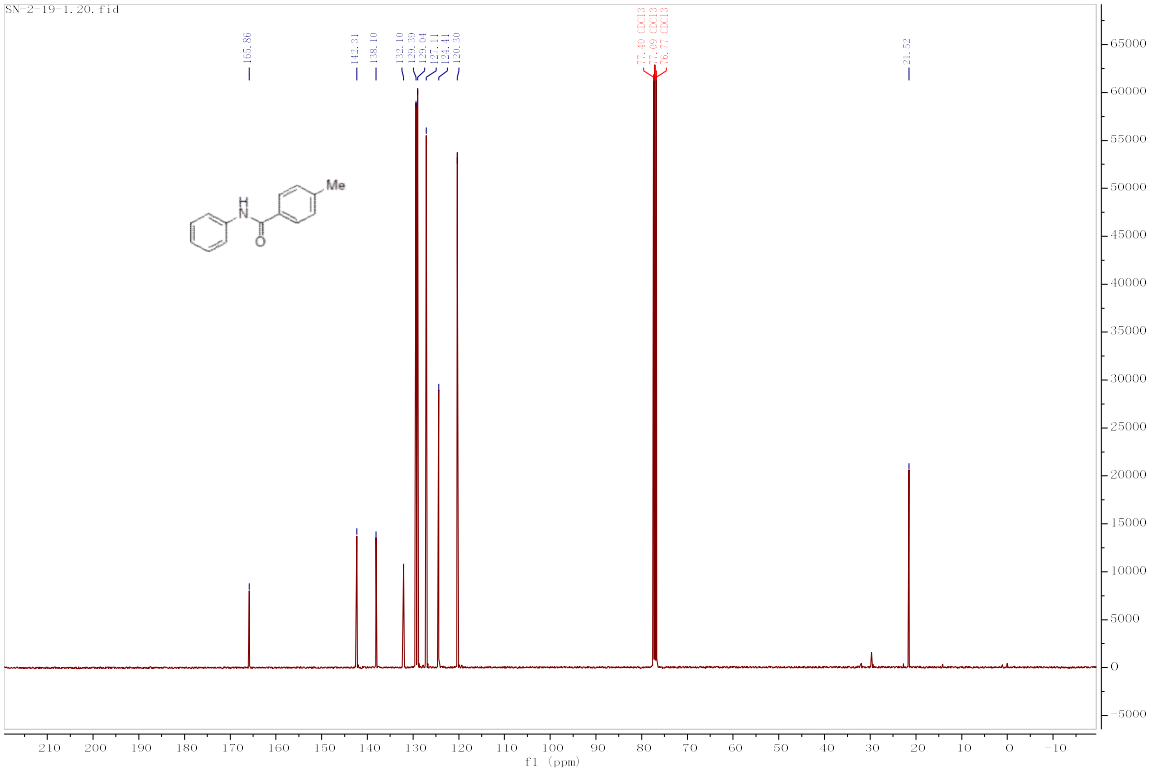
^{1}H and ^{13}C NMR Spectra of 4-Fluoro-*N*-(4-methoxyphenyl)benzamide (3h)



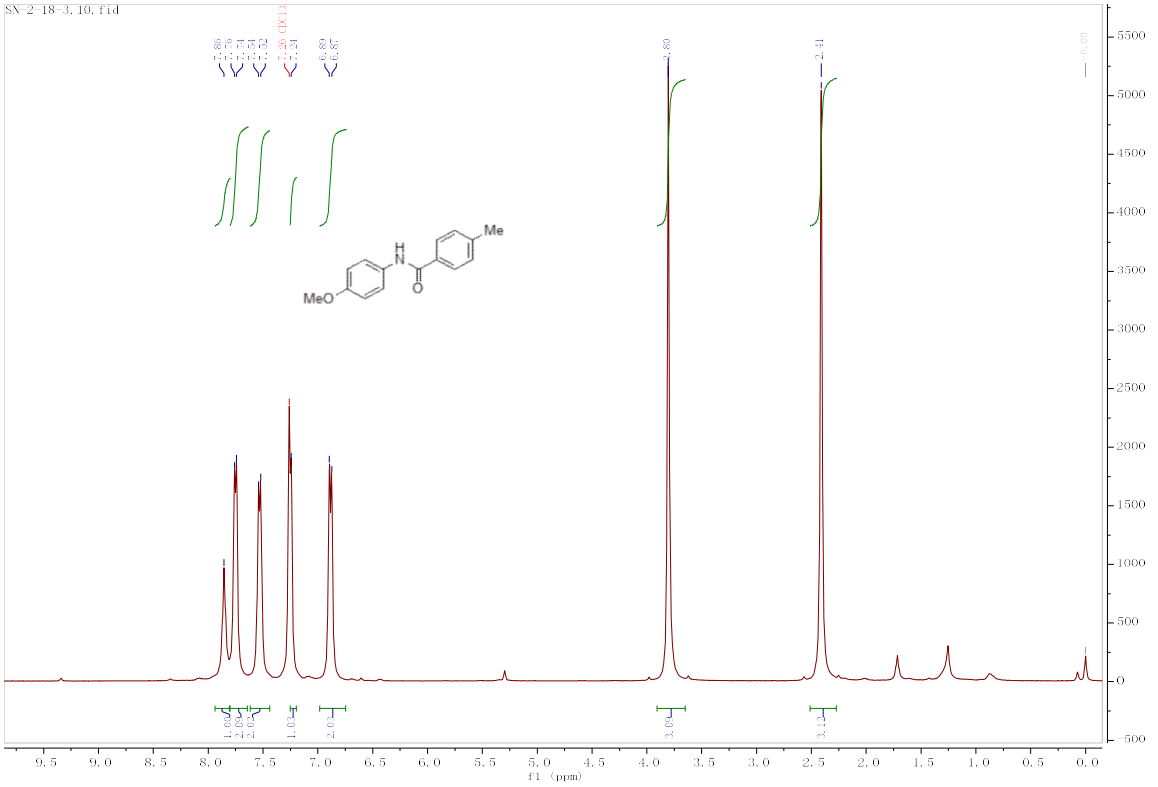


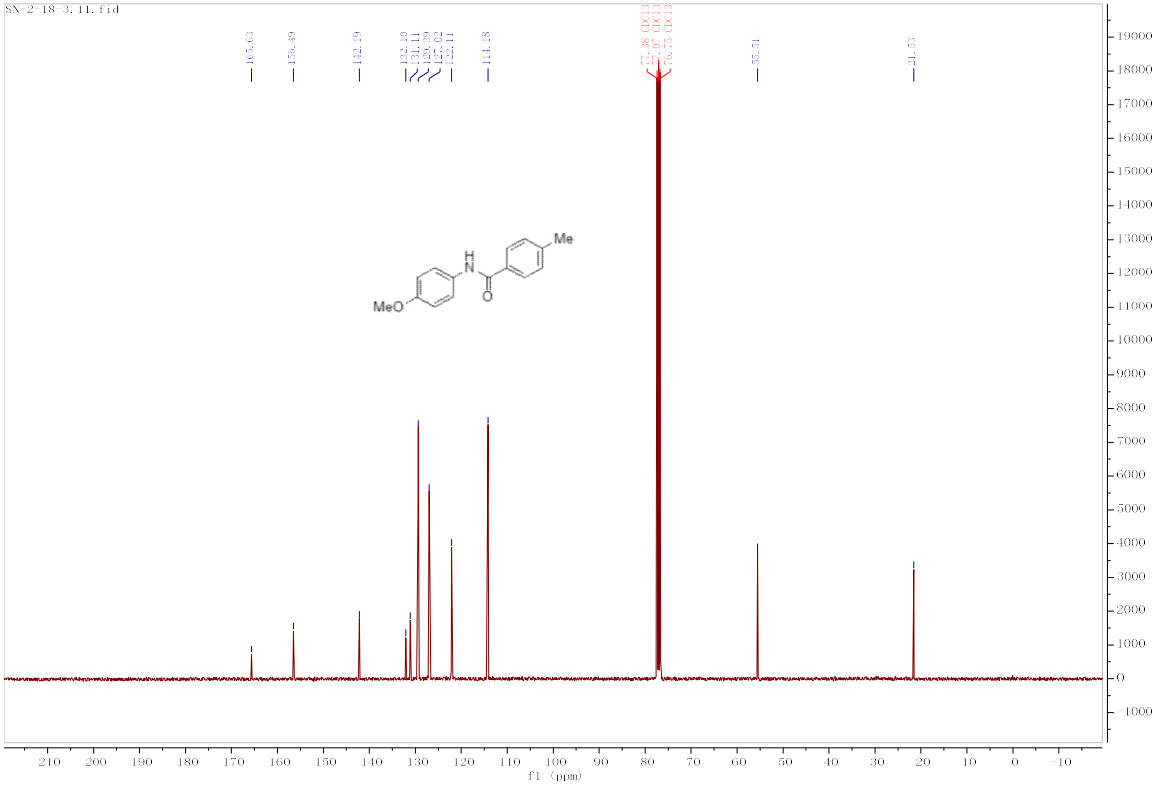
^{1}H and ^{13}C NMR Spectra of 4-Methyl-*N*-phenylbenzamide (3i)



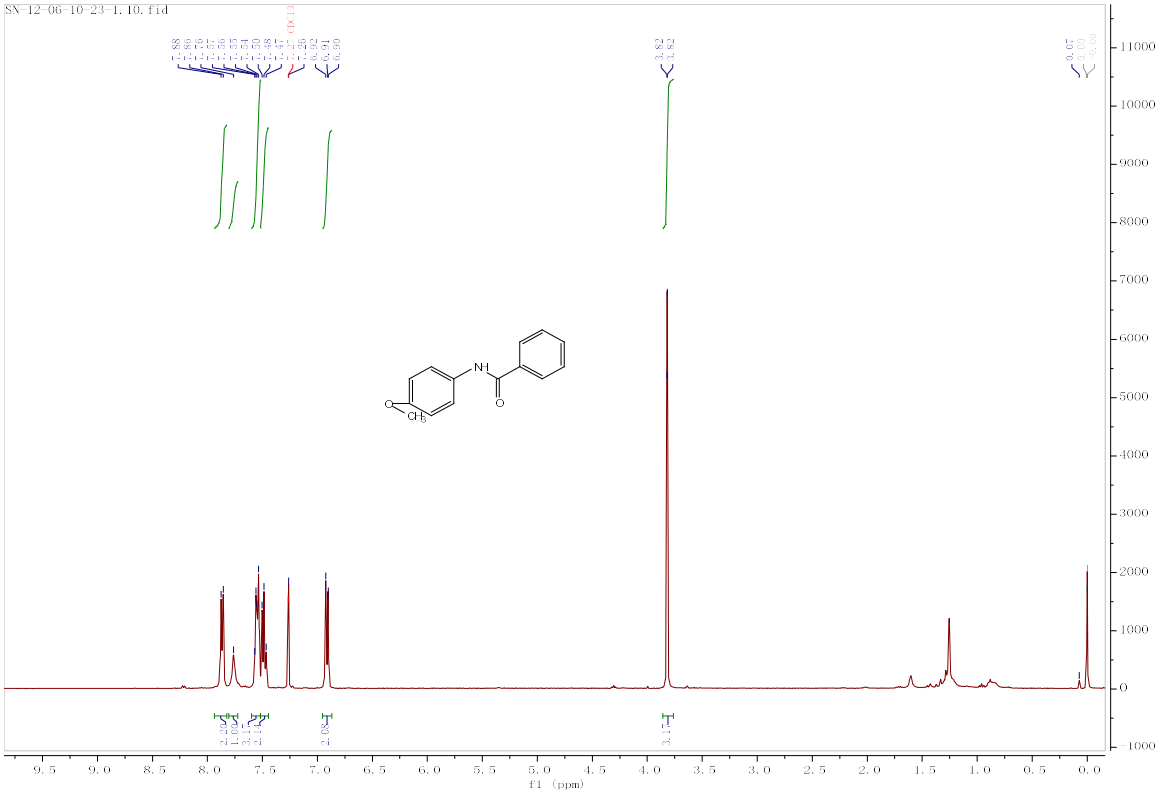


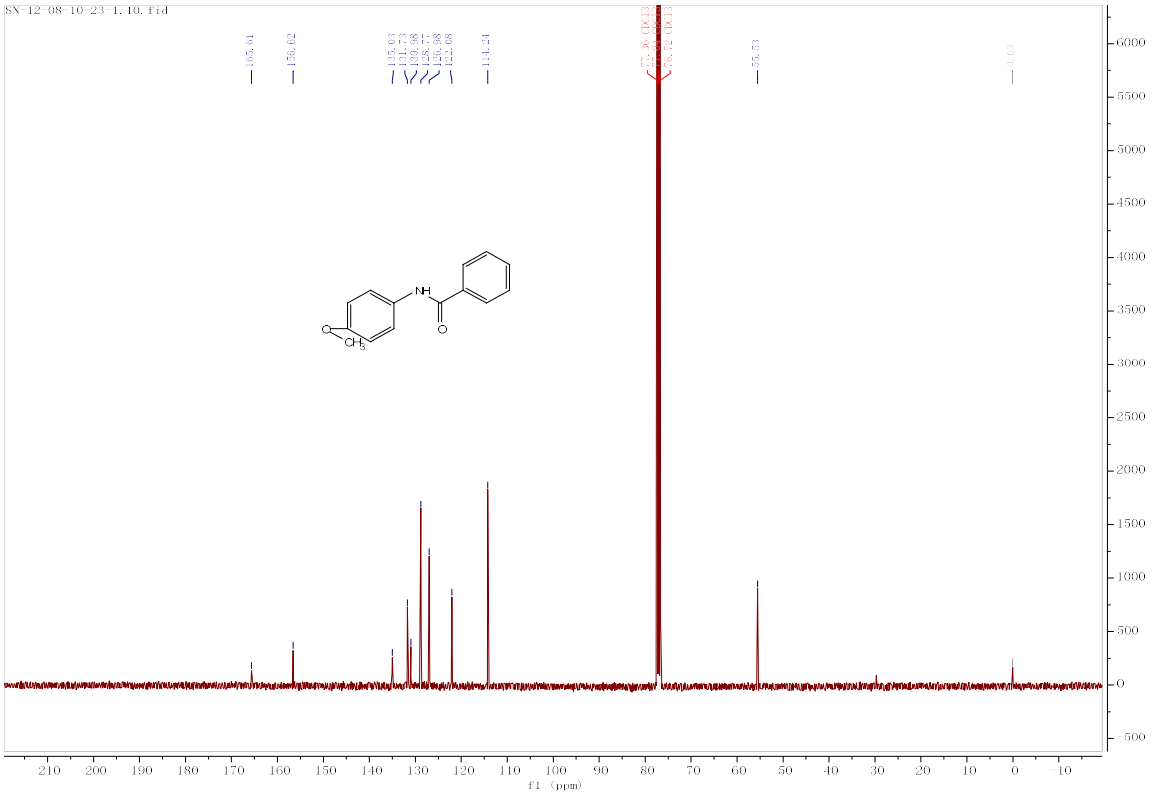
^{1}H and ^{13}C NMR Spectra of *N*-(4-Methoxyphenyl)-4-methylbenzamide (3j)



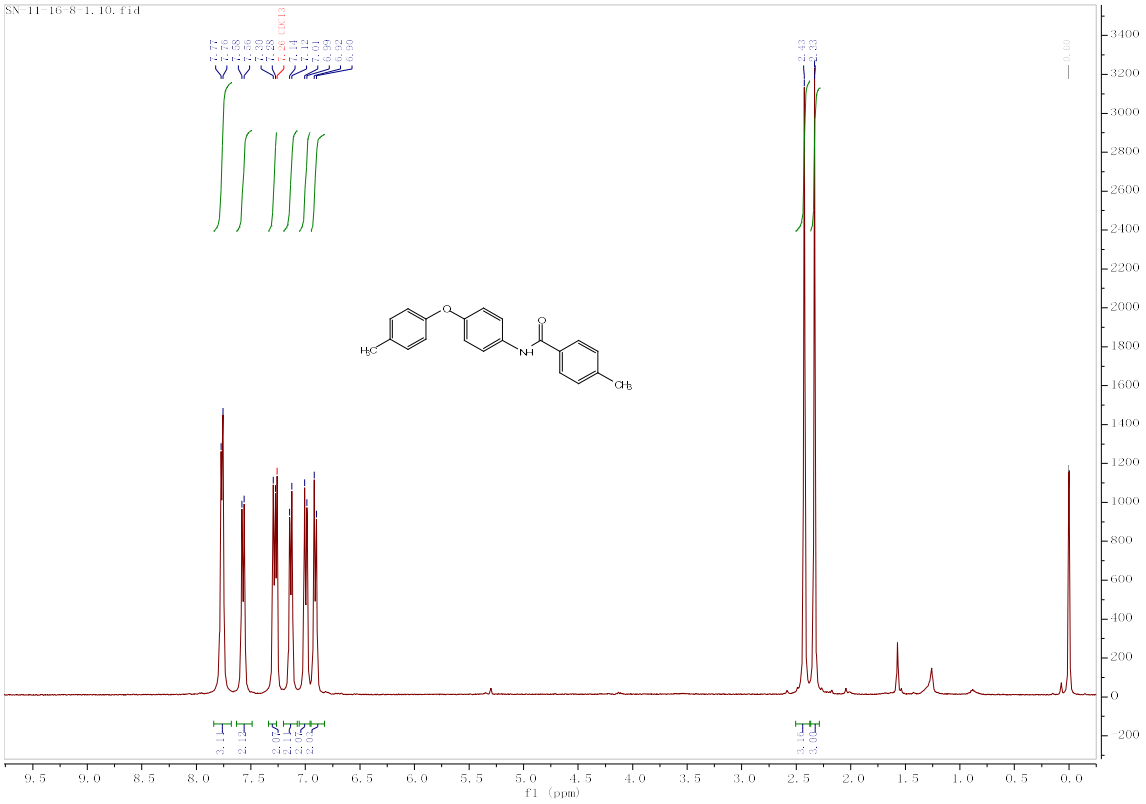


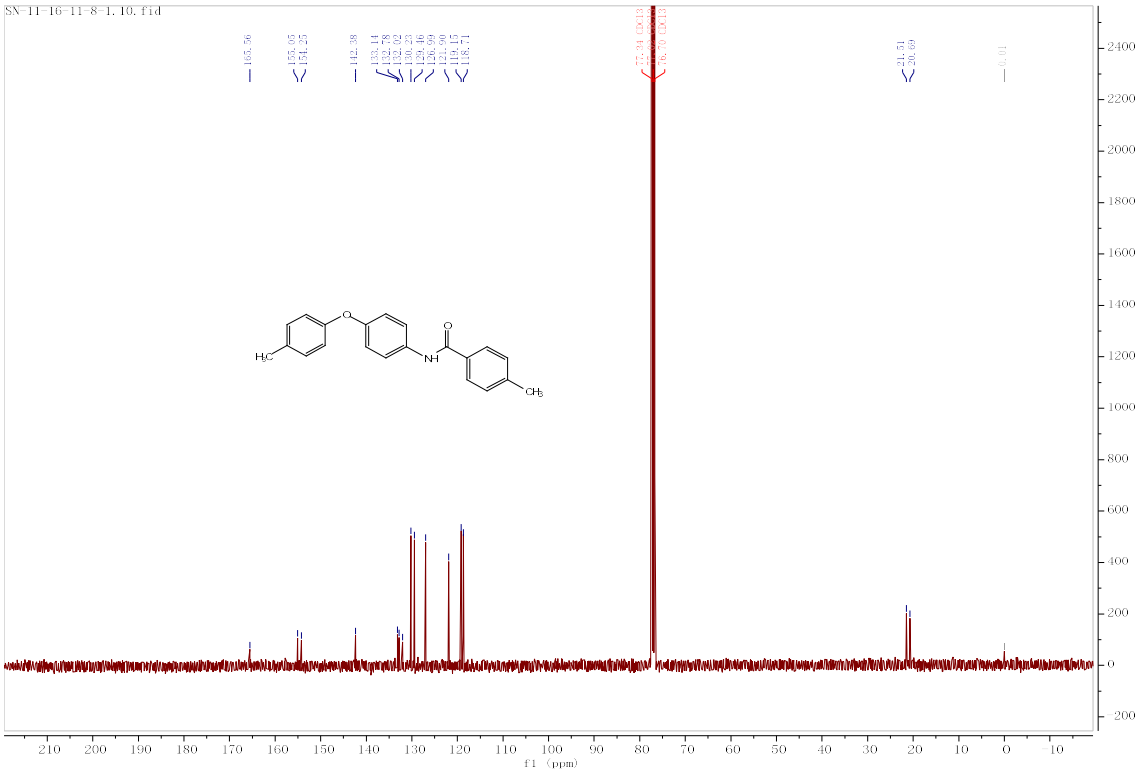
^{1}H and ^{13}C NMR Spectra of *N*-(4-Methoxyphenyl)benzamide (3k)



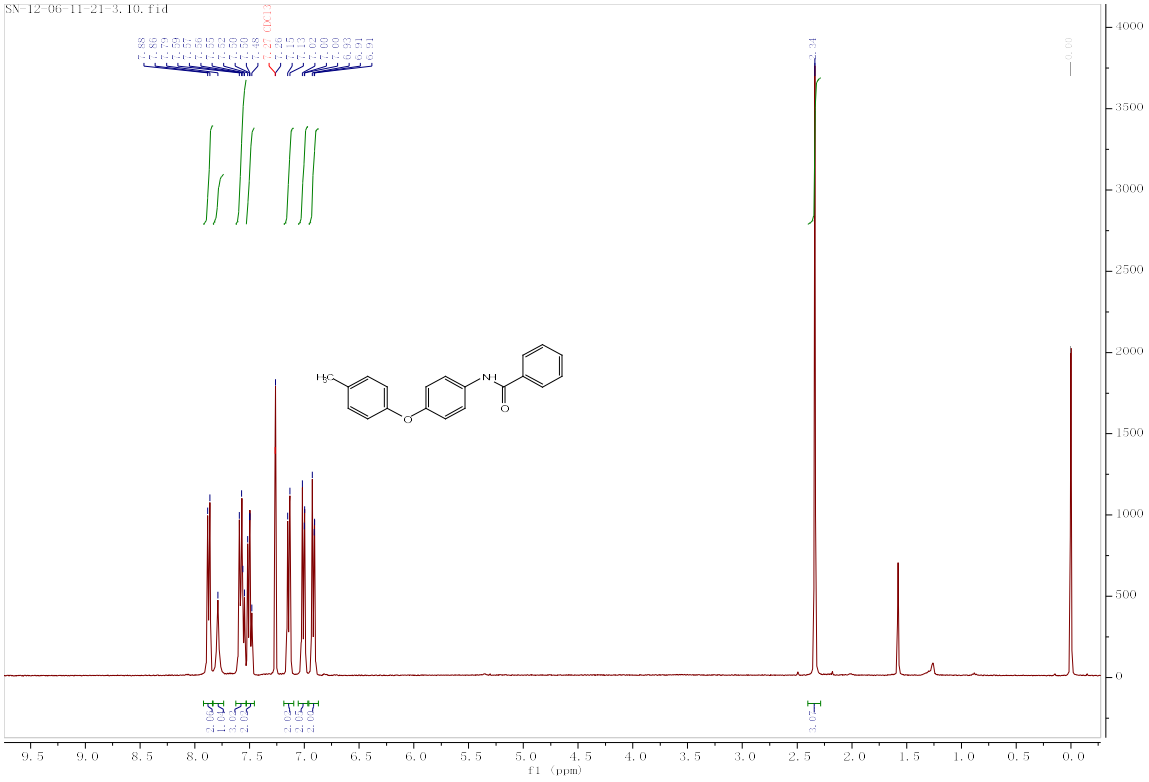


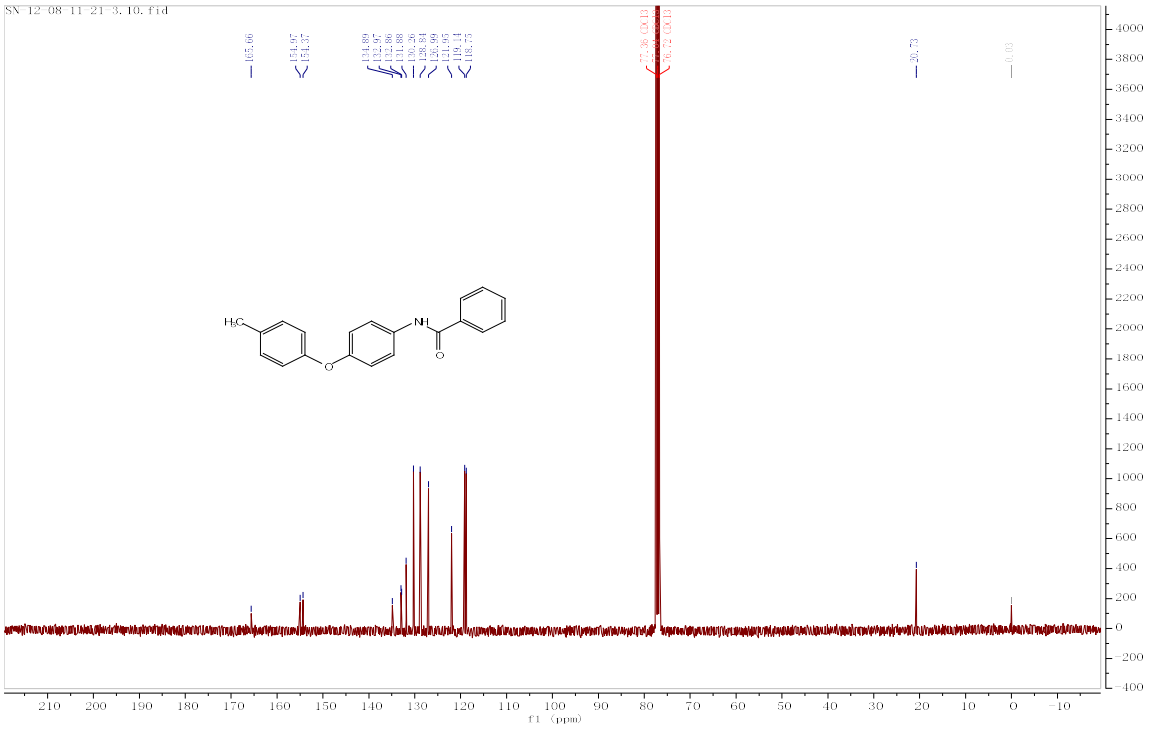
^{1}H and ^{13}C NMR Spectra of *N*-(4-(*p*-Tolyloxy)phenyl)-4-methylbenzamide (3l)



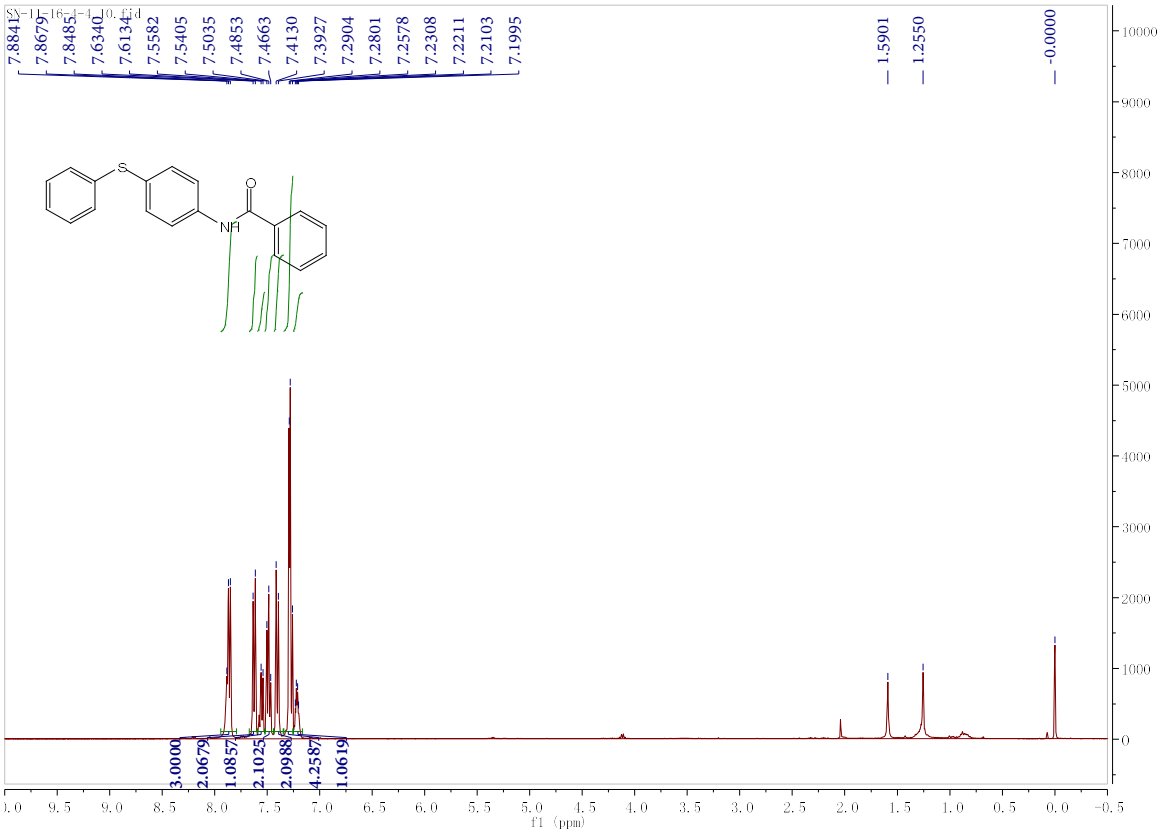


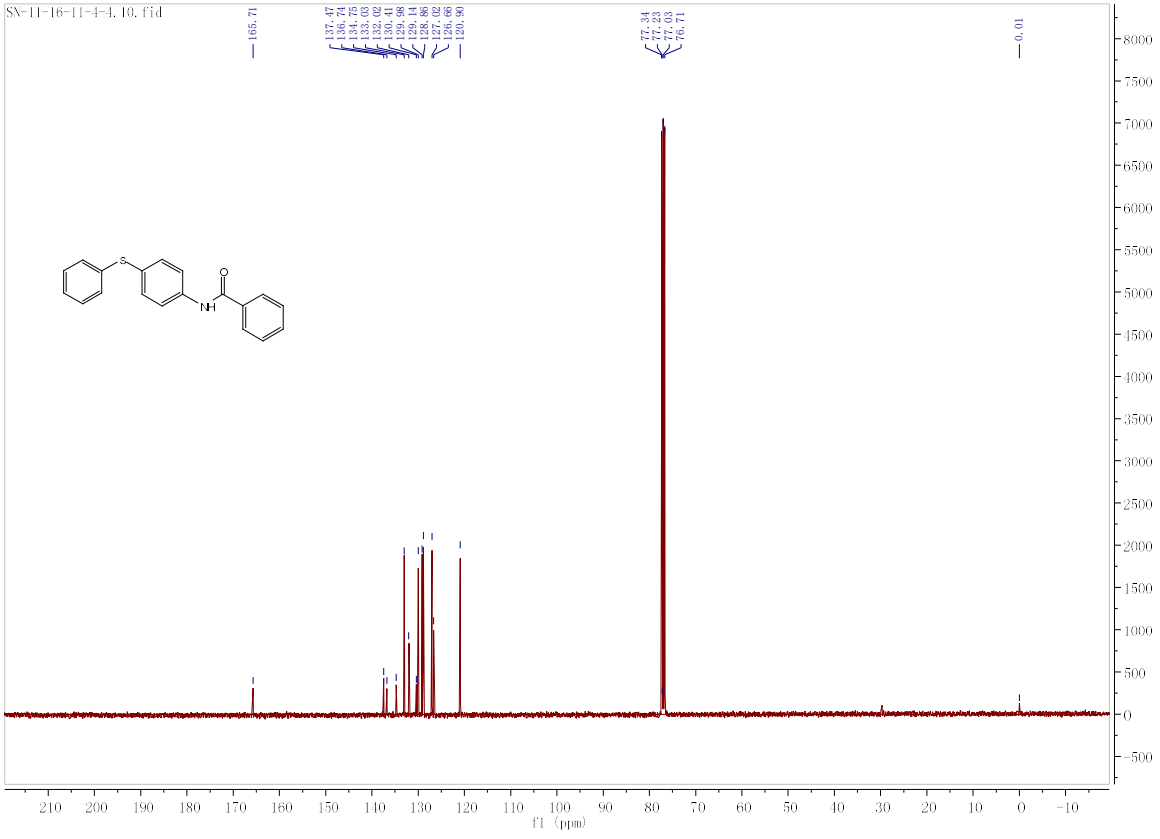
^{1}H and ^{13}C NMR Spectra of *N*-(4-(*p*-Tolyloxy)phenyl)benzamide (3m)



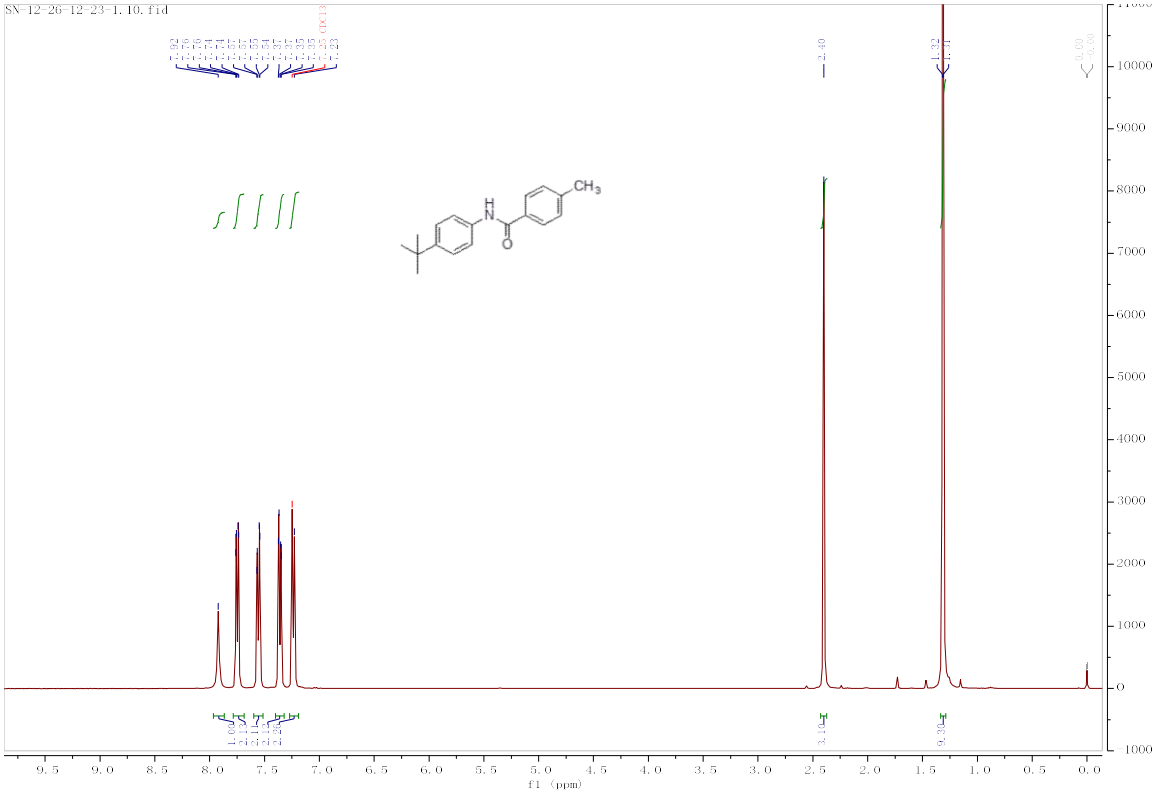


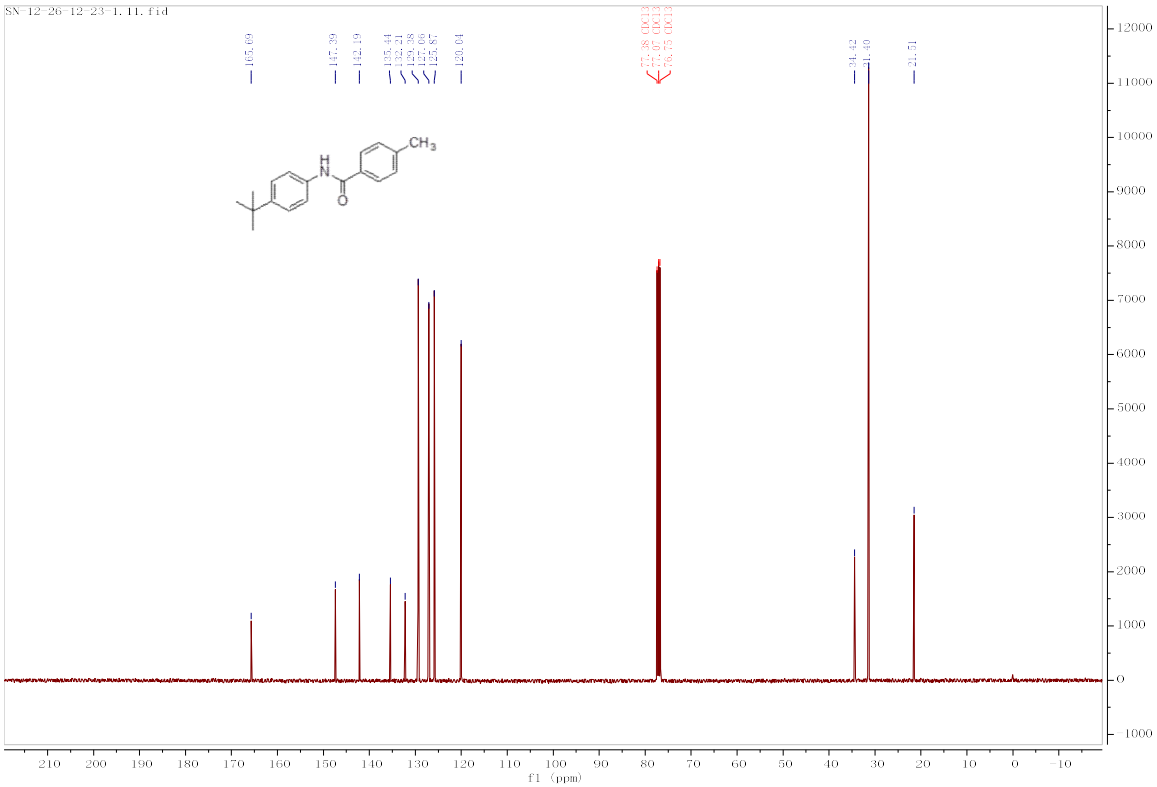
^{1}H and ^{13}C NMR Spectra of *N*-(4-(Phenylthio)phenyl)benzamide (3n)



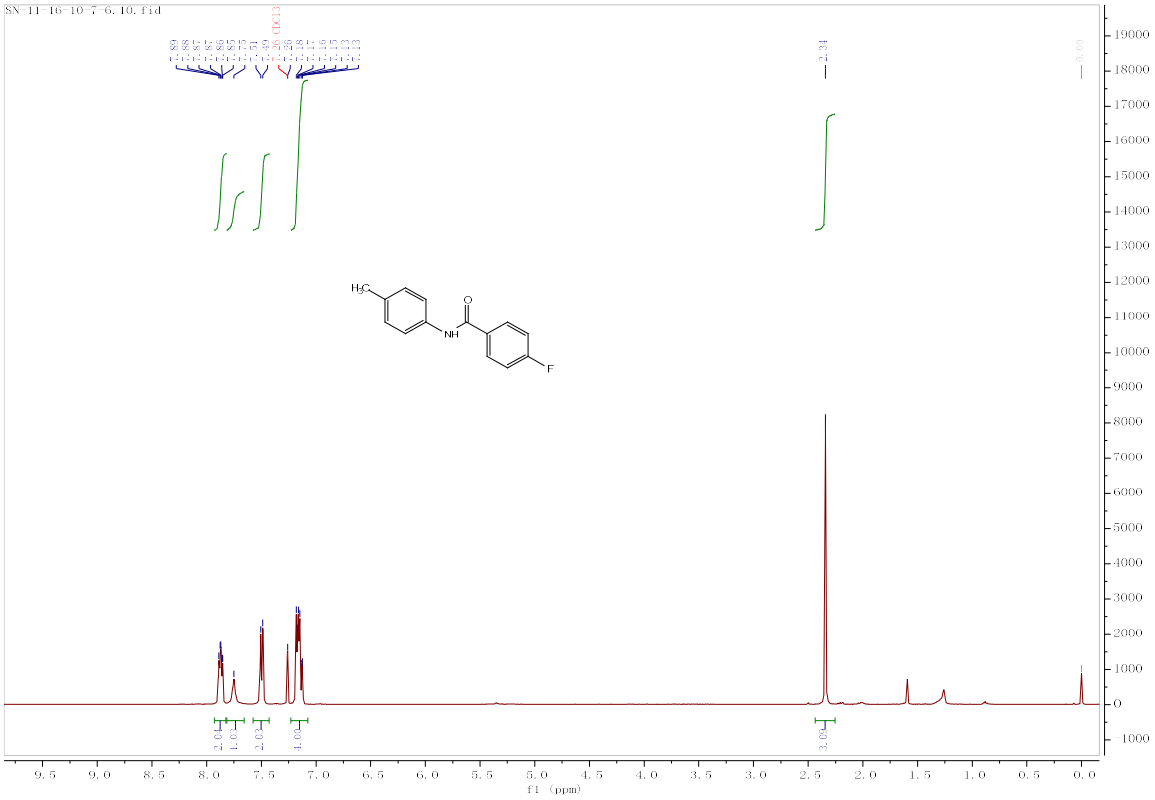


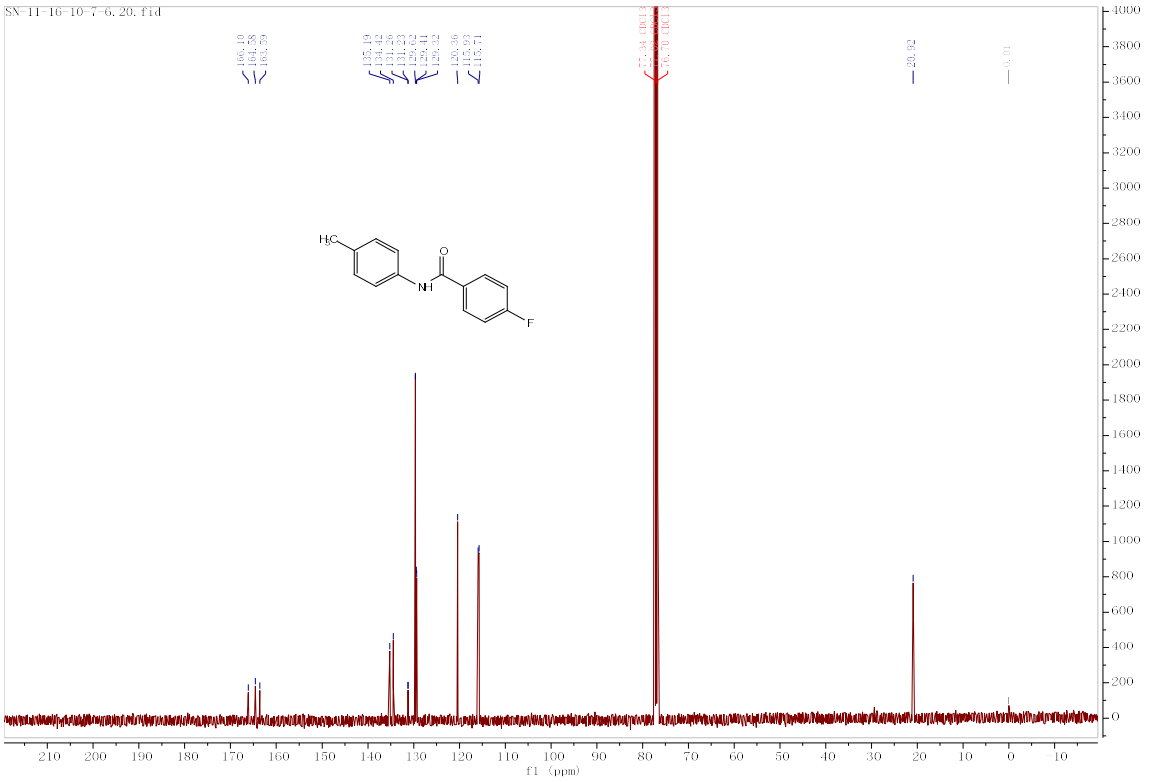
^{1}H and ^{13}C NMR Spectra of *N*-(4-*tert*-Butylphenyl)-4-methylbenzamide (3o)



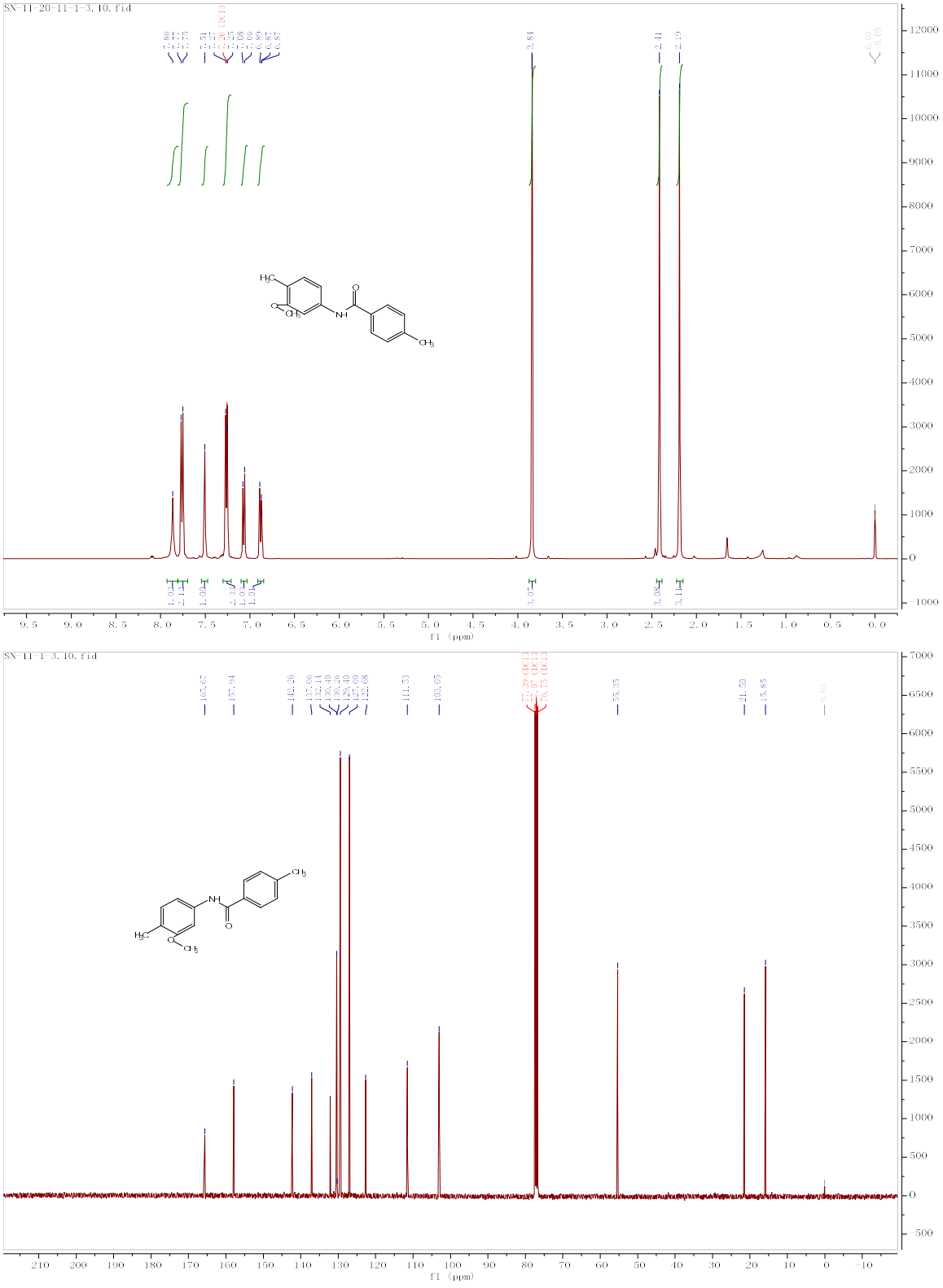


^{1}H and ^{13}C NMR Spectra of 4-Fluoro-*N*-*p*-tolylbenzamide (3p)

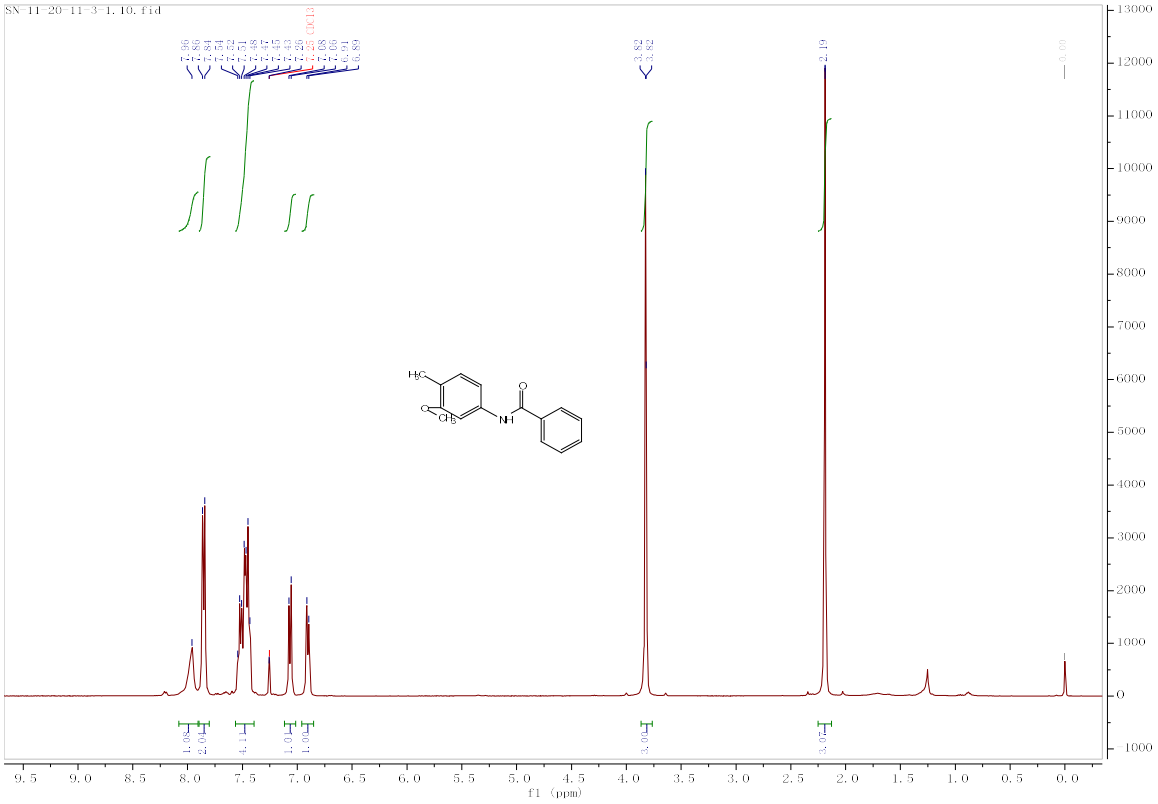


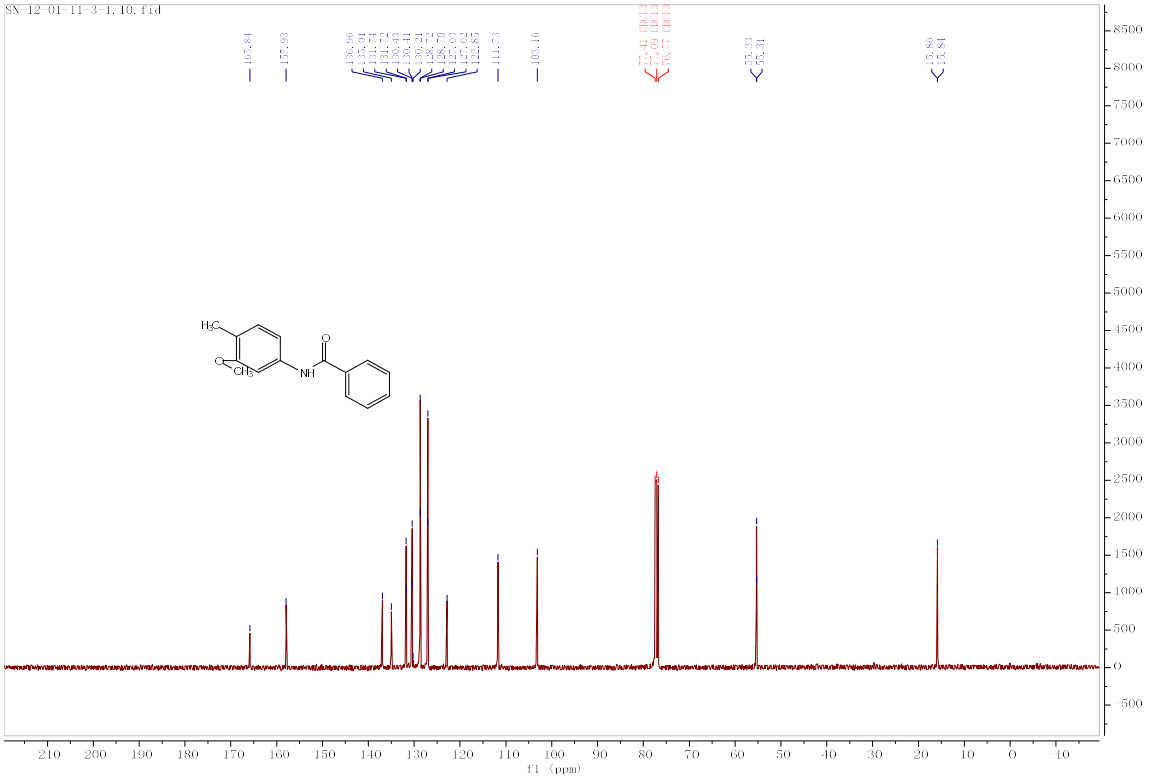


^{1}H and ^{13}C NMR Spectra of *N*-(3-Methoxy-4-methylphenyl)-4-methylbenzamide (3q)

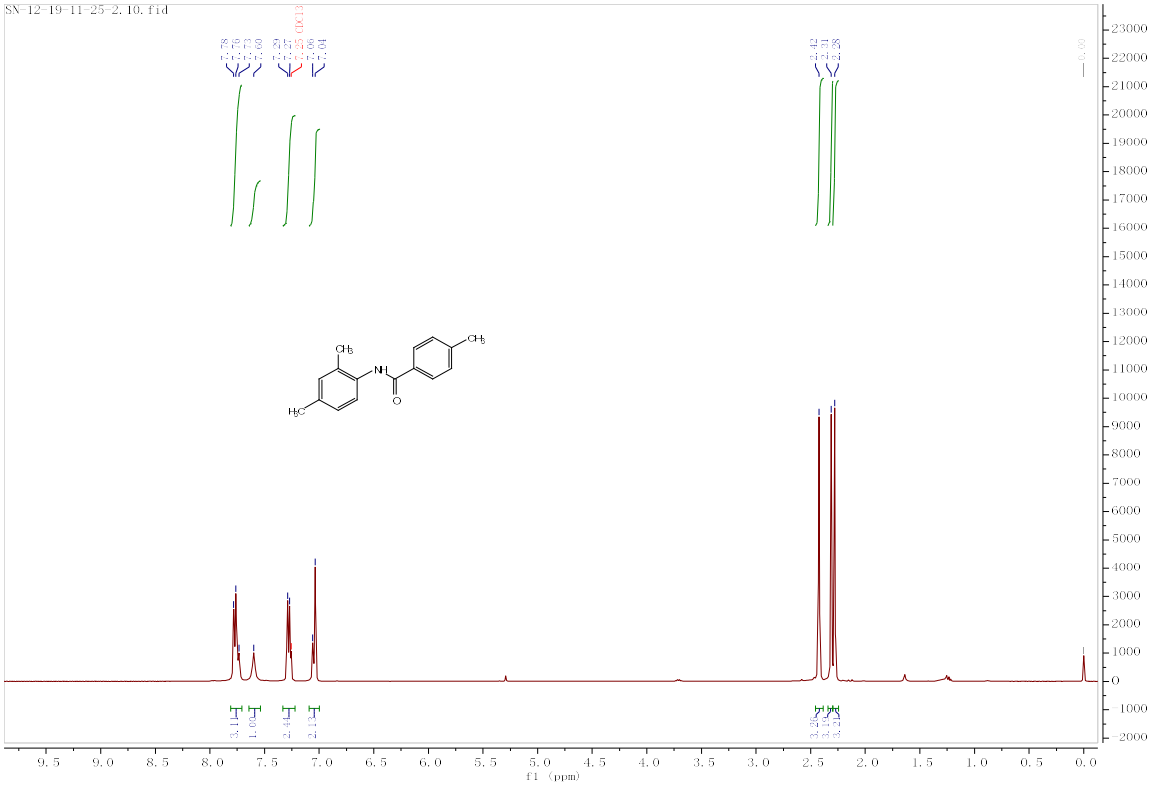


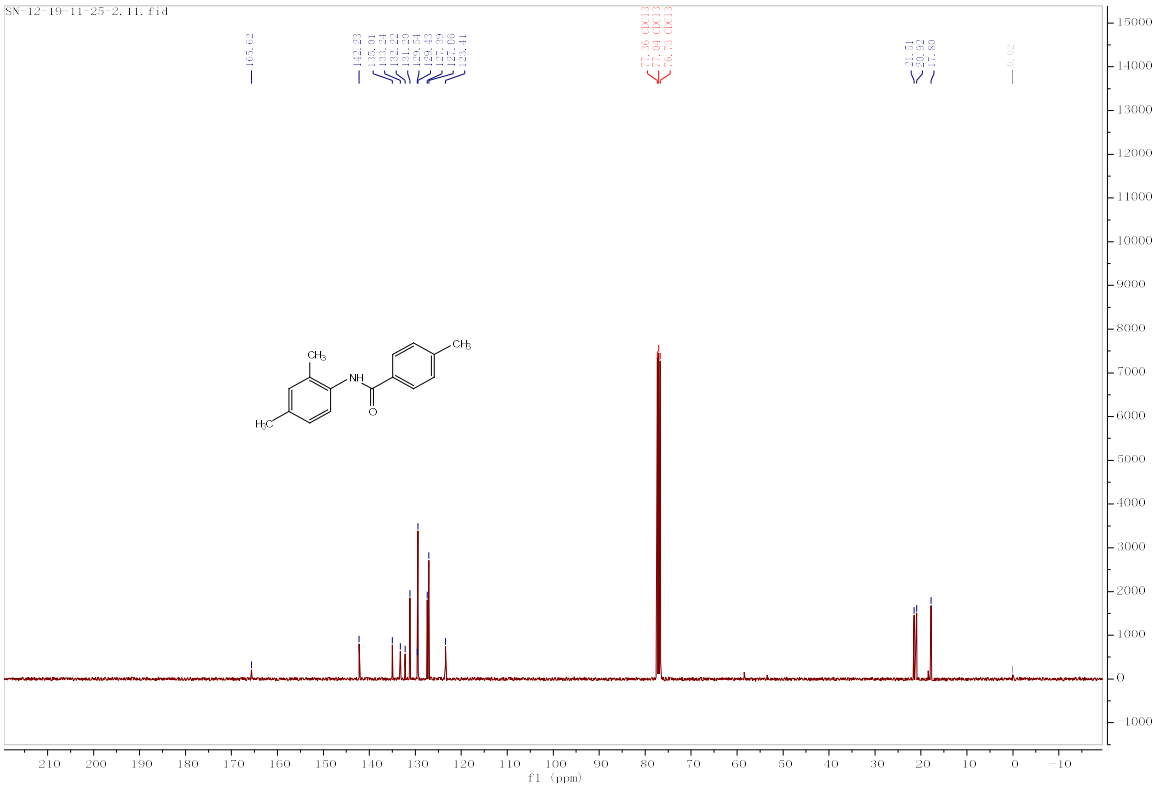
^{1}H and ^{13}C NMR Spectra of *N*-(3-Methoxy-4-methylphenyl)benzamide (3r)



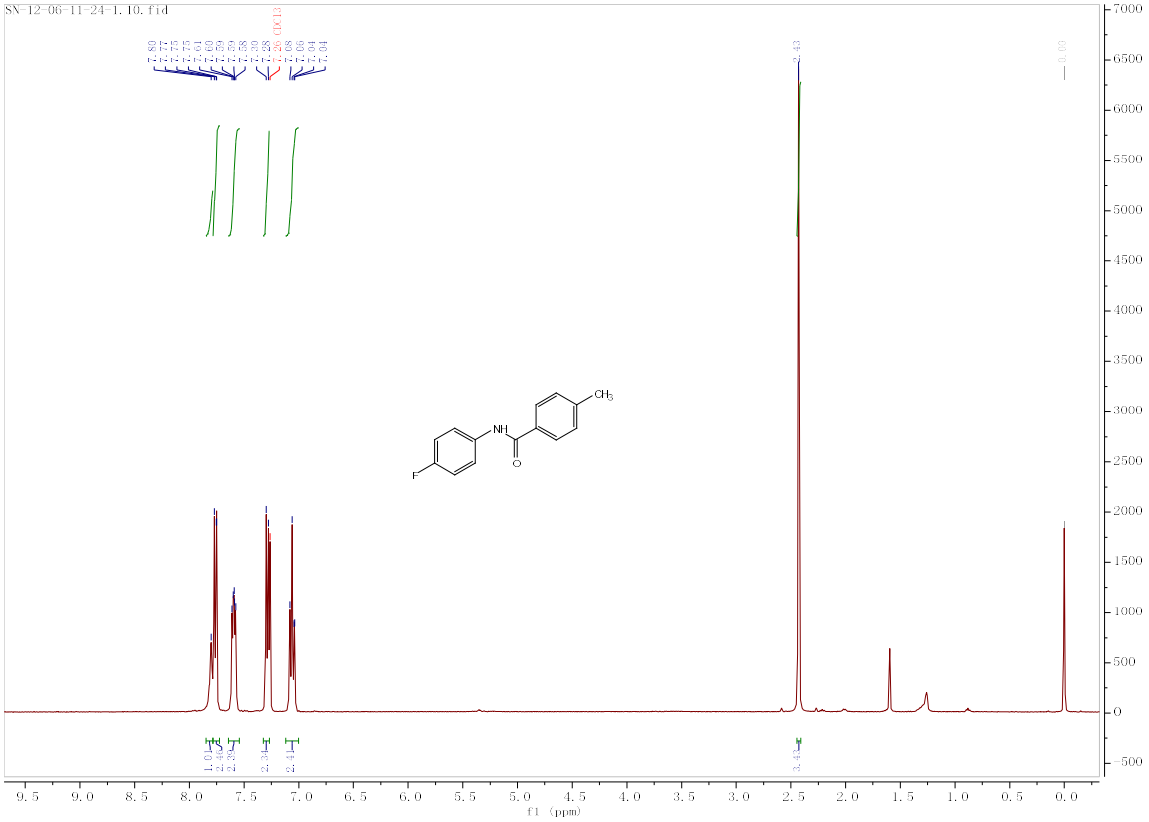


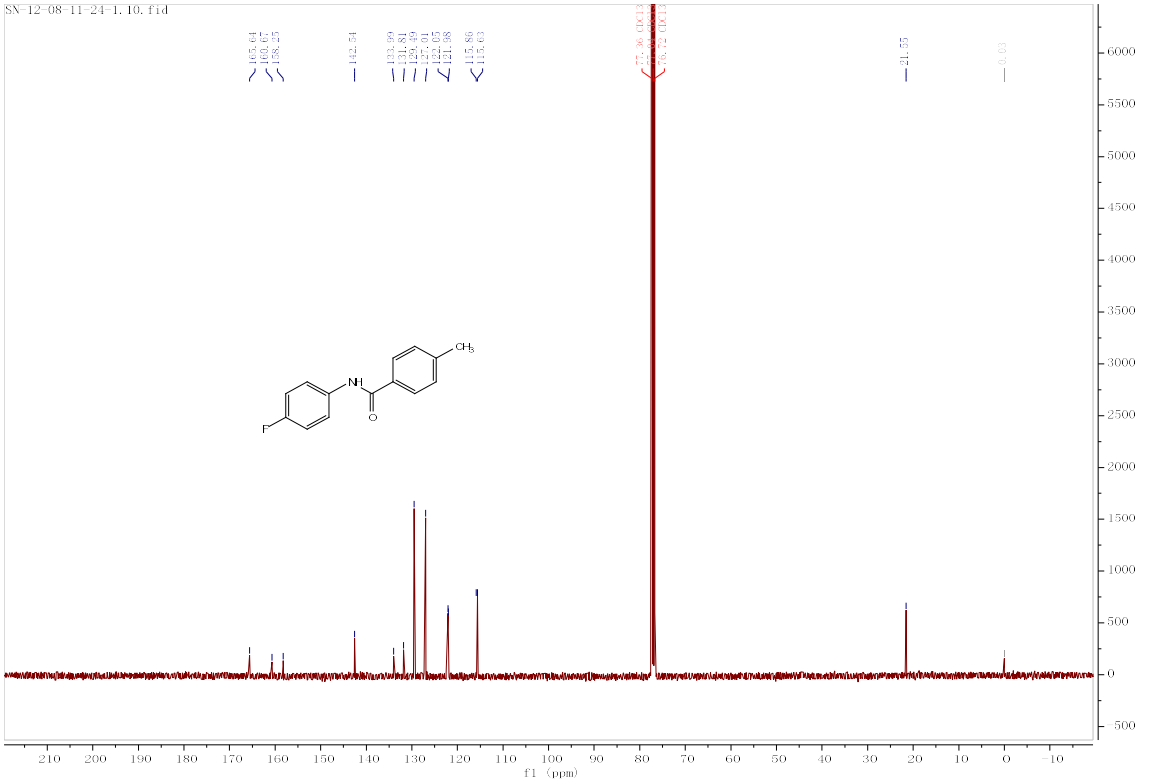
^{1}H and ^{13}C NMR Spectra of 4-Methyl-*N*-(2,4-dimethylphenyl)benzamide (3s)



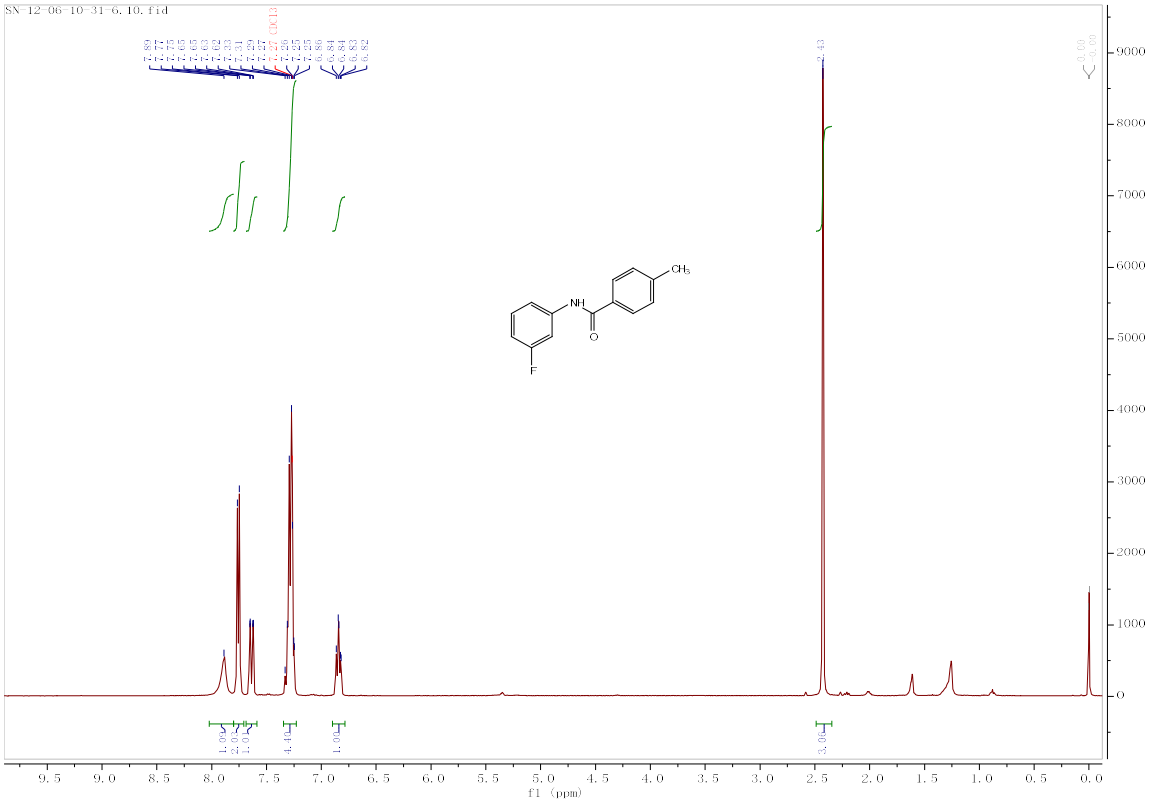


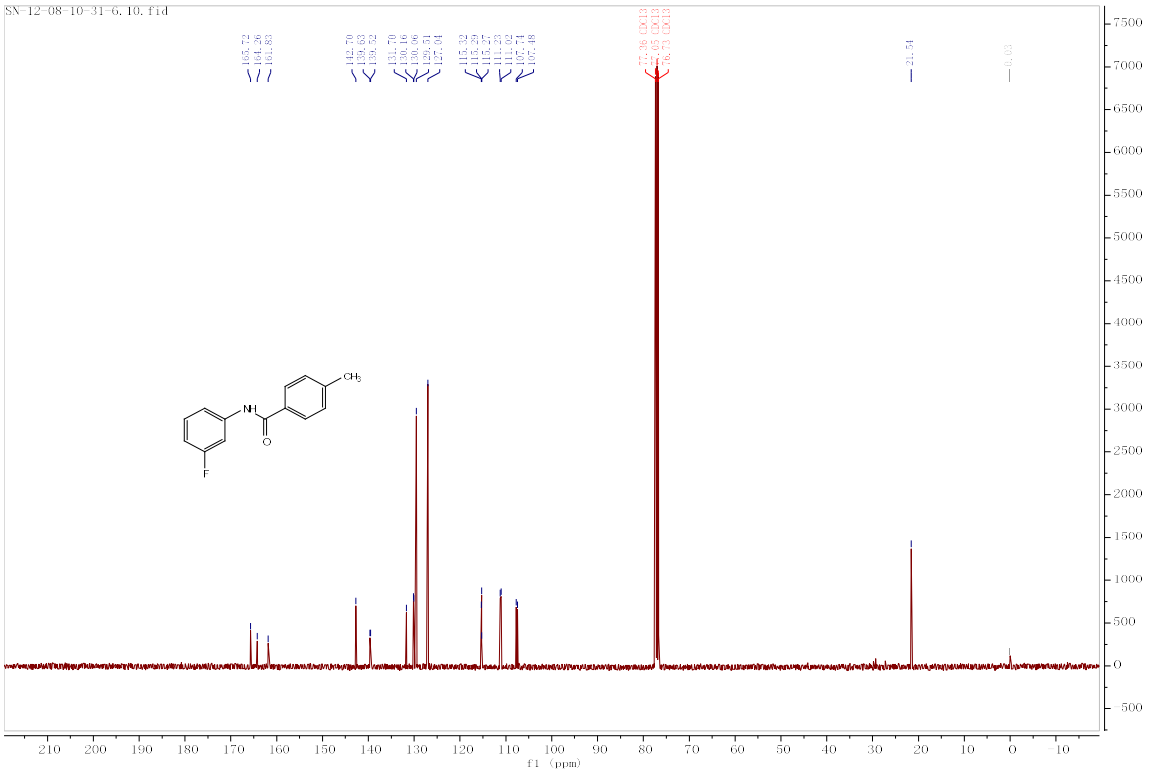
^{1}H and ^{13}C NMR Spectra of *N*-(4-Fluorophenyl)-4-methylbenzamide (3t)



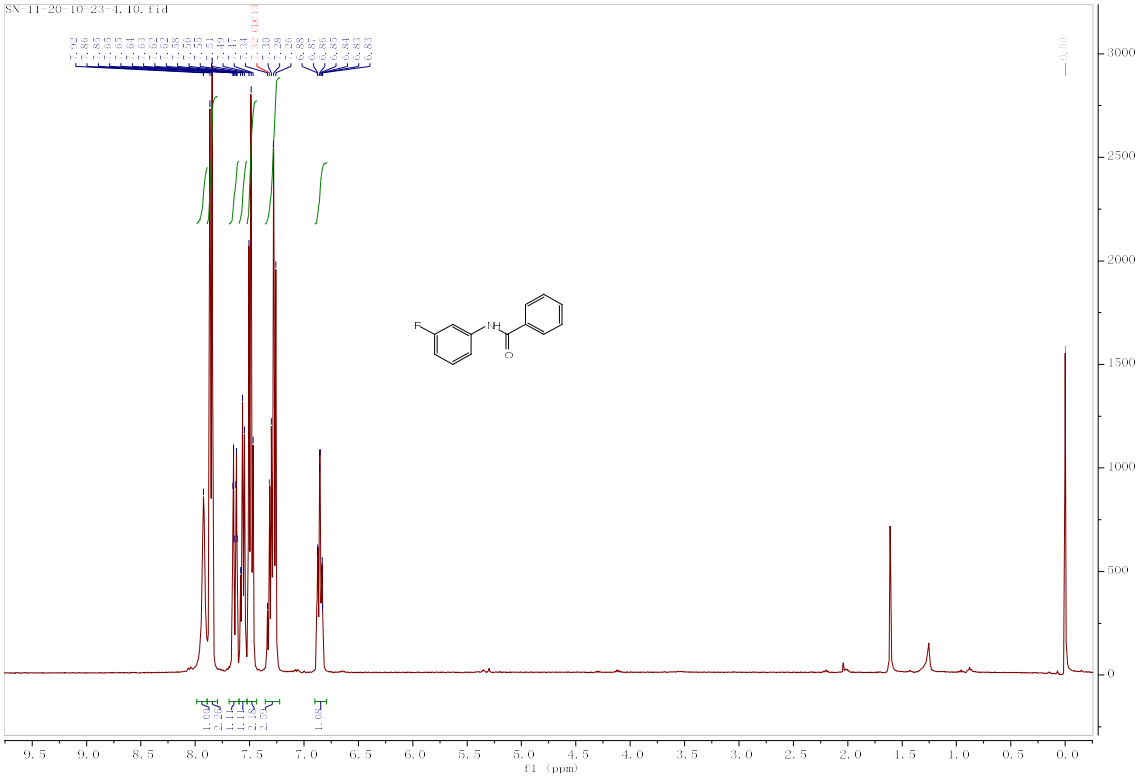


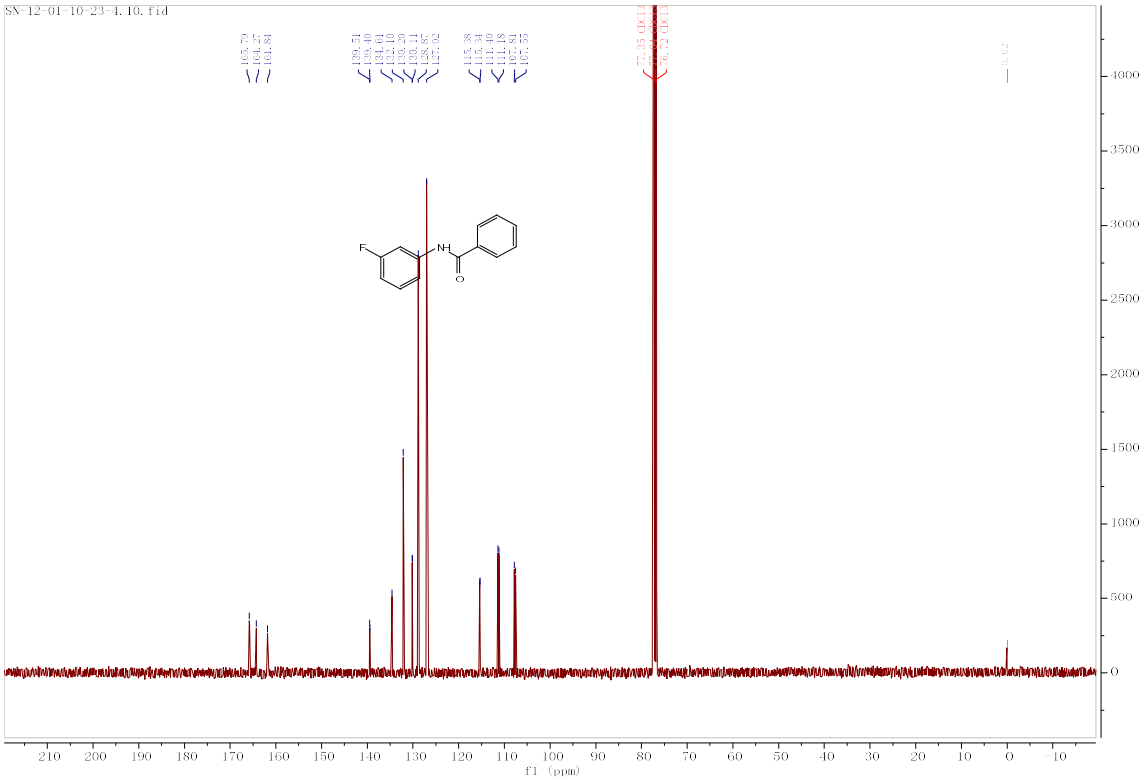
^{1}H and ^{13}C NMR Spectra of *N*-(3-Fluorophenyl)-4-methylbenzamide (3u)



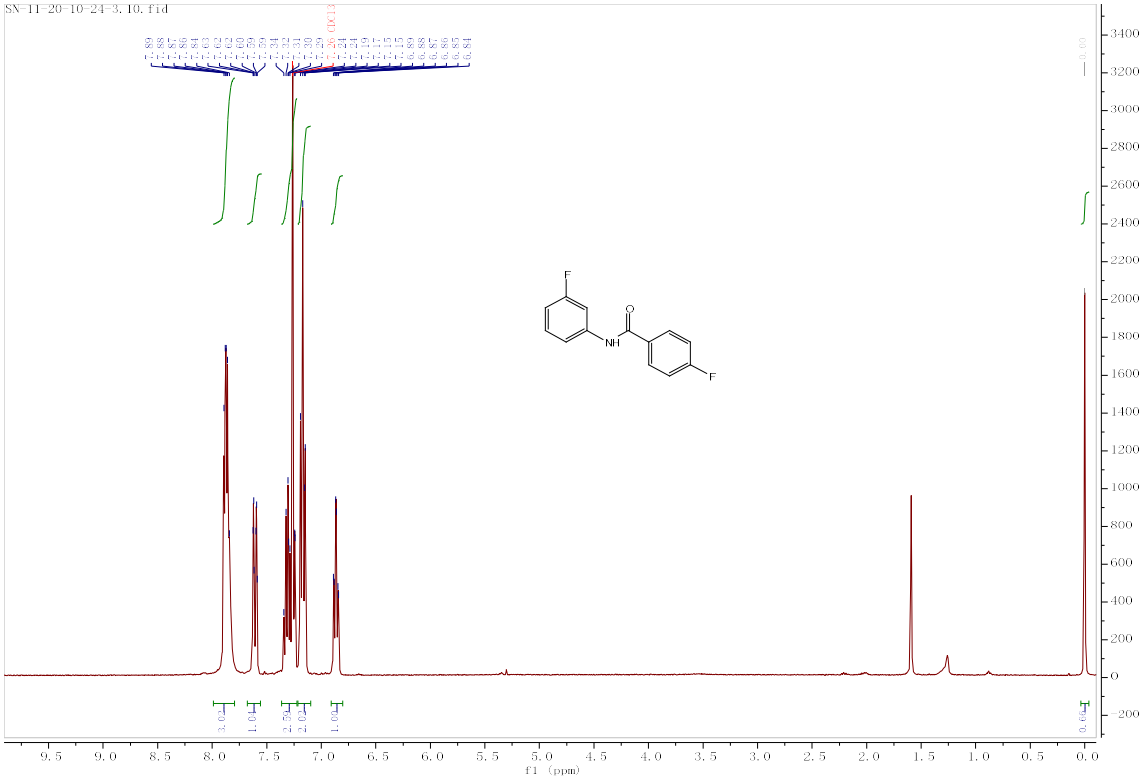


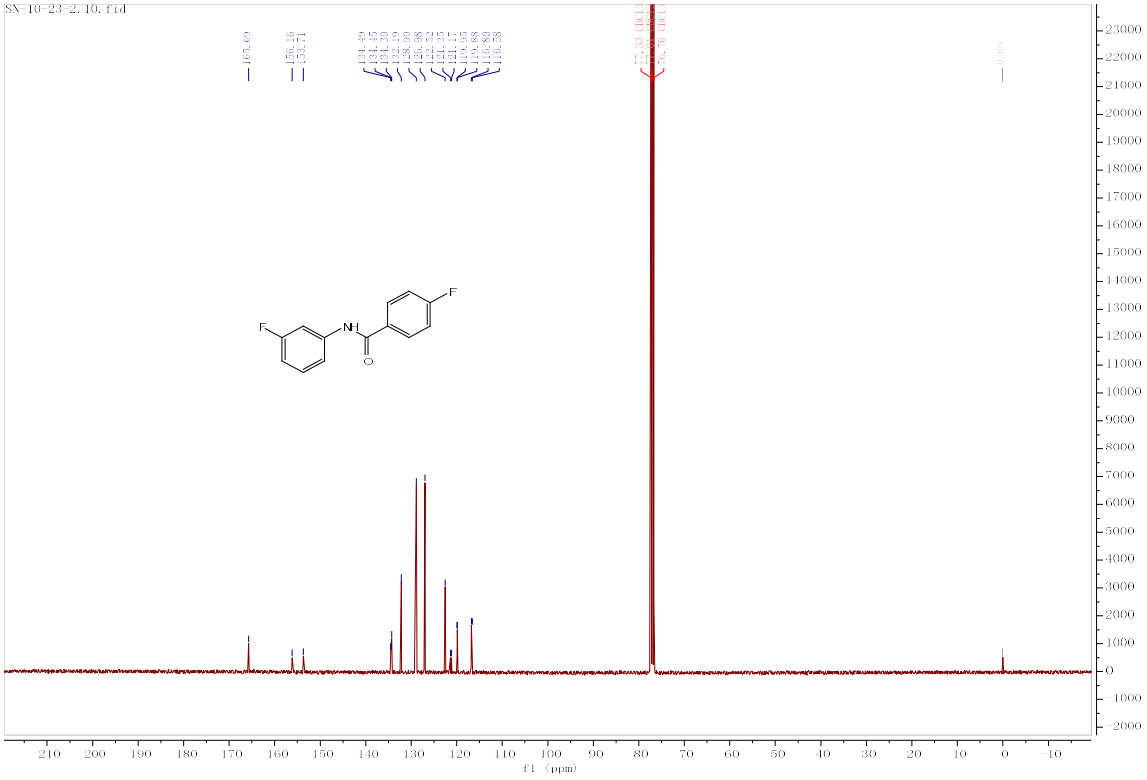
^{1}H and ^{13}C NMR Spectra of *N*-(3-Fluorophenyl)benzamide (3v)



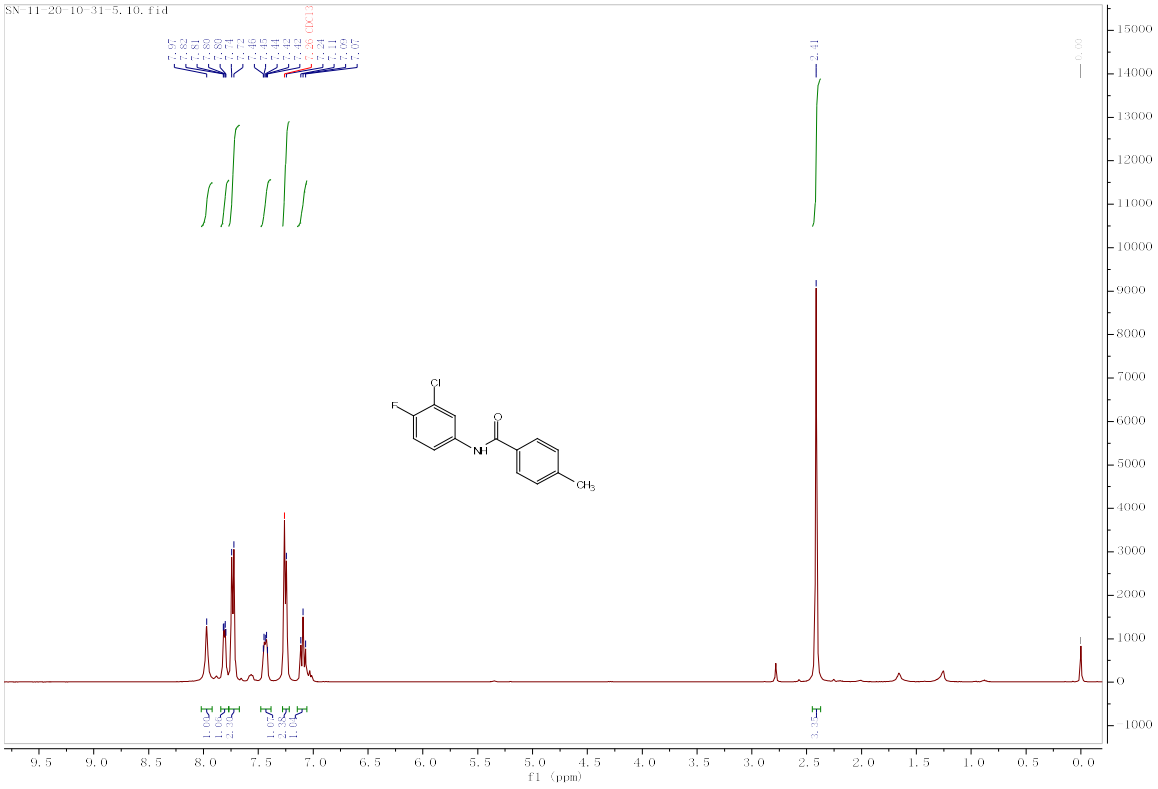


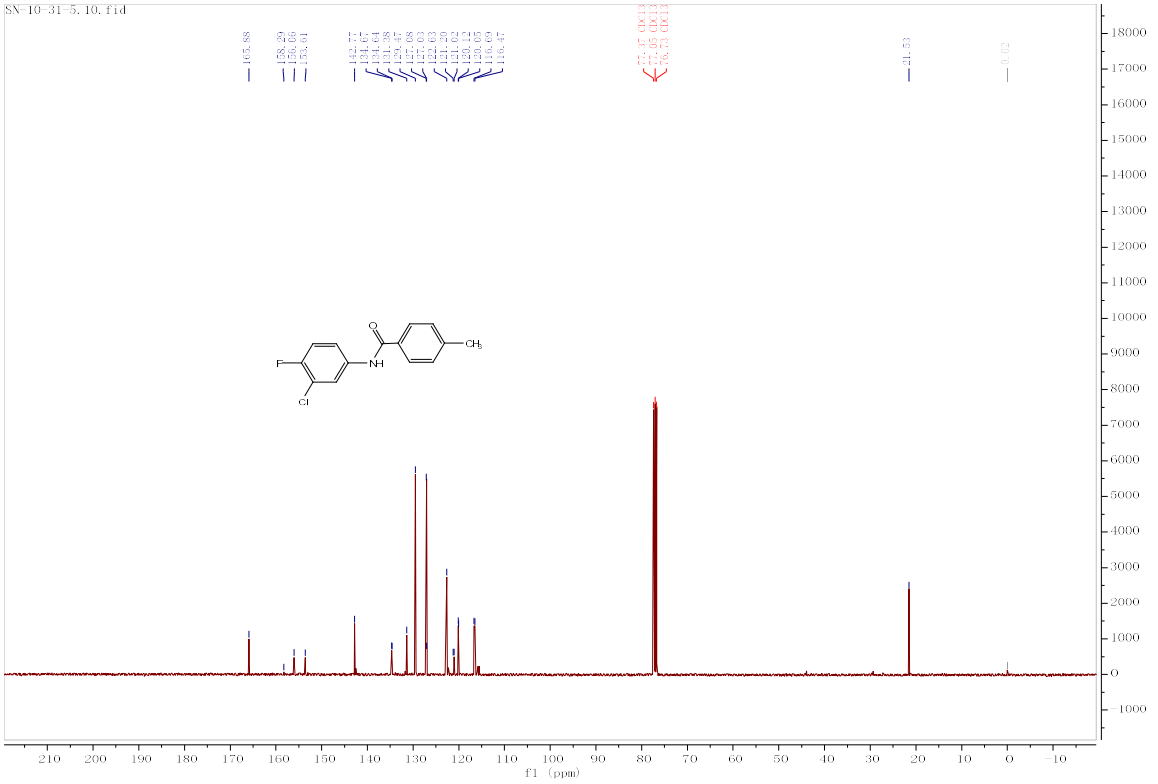
^{1}H and ^{13}C NMR Spectra of 4-Fluoro-*N*-(3-fluorophenyl)benzamide (3w)



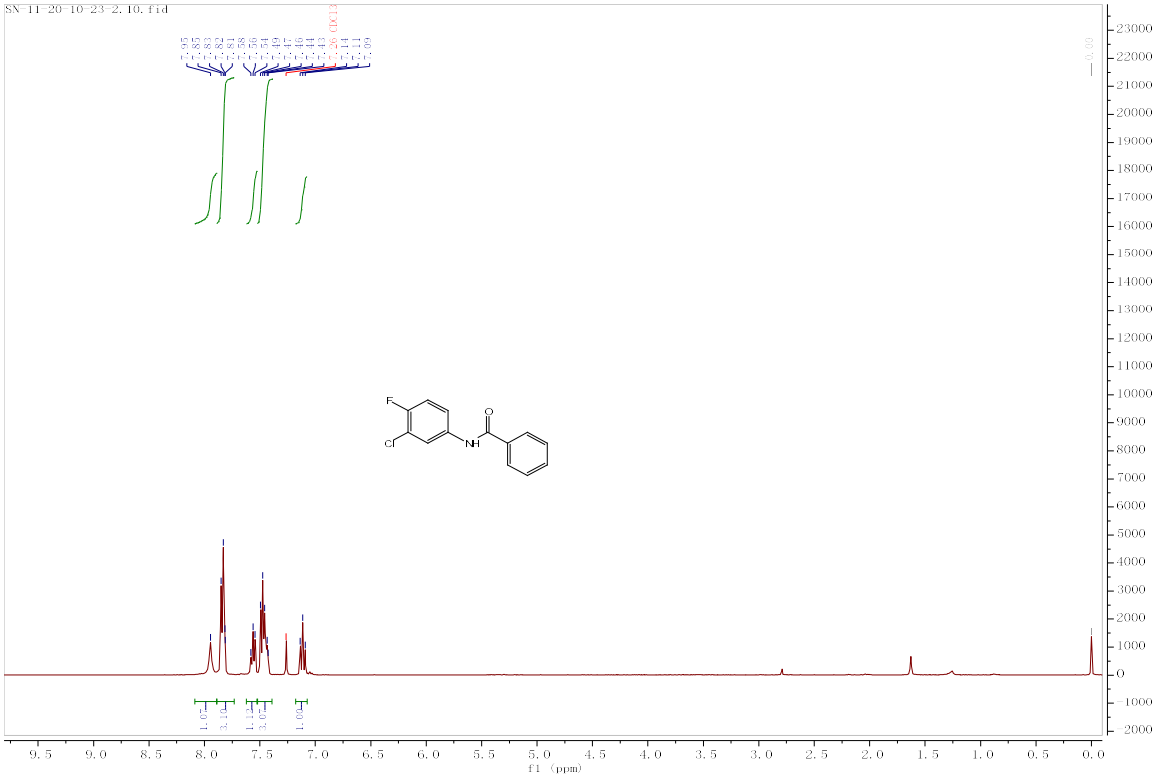


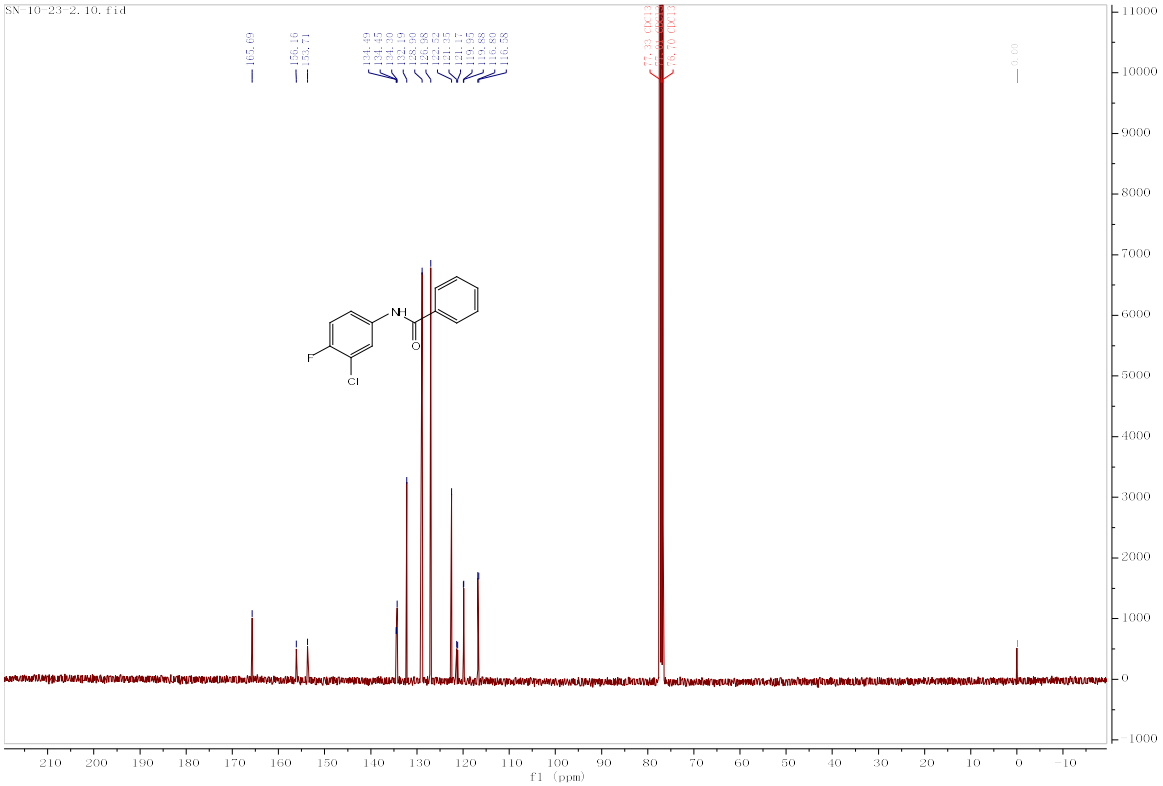
^{1}H and ^{13}C NMR Spectra of *N*-(3-Chloro-4-fluorophenyl)-4-methylbenzamide (3x)



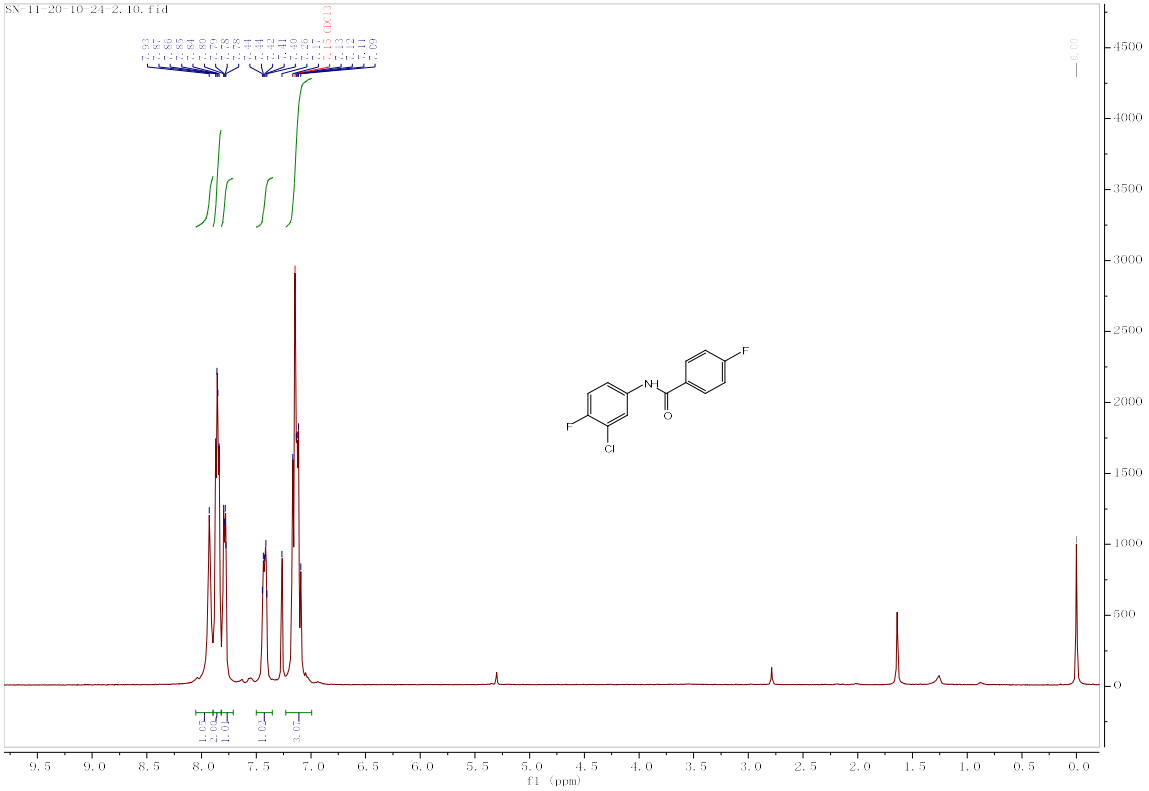


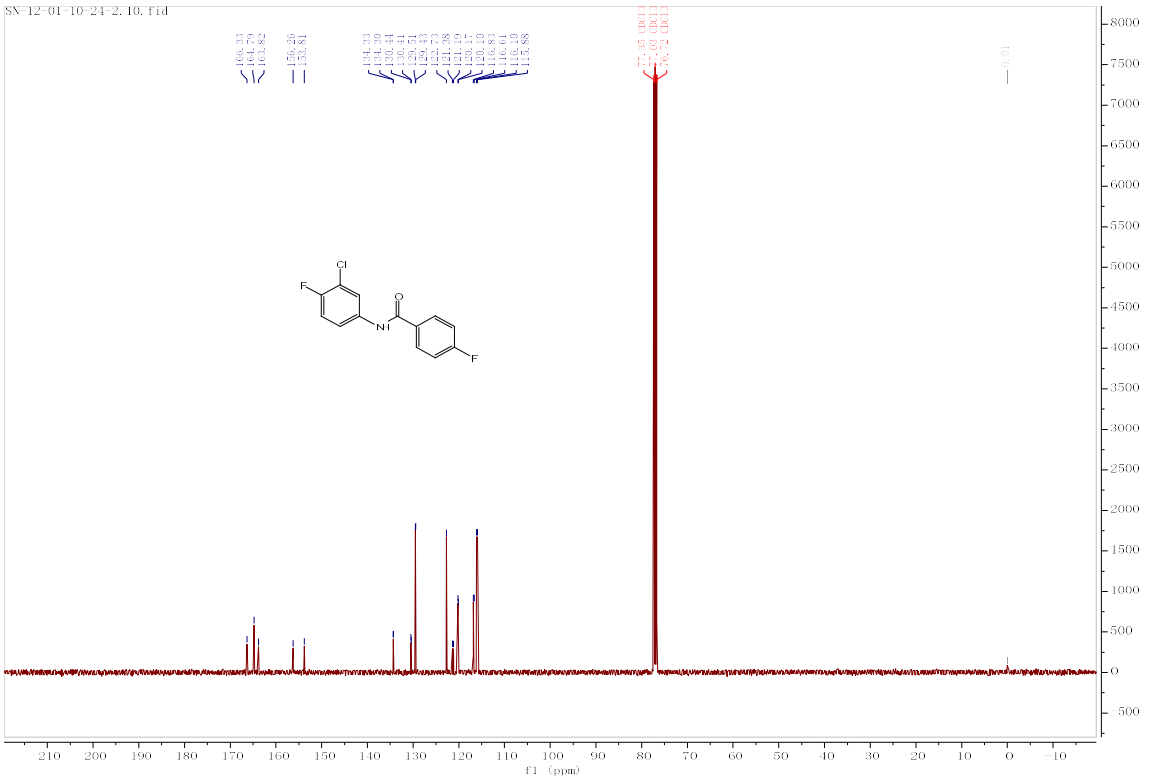
^{1}H and ^{13}C NMR Spectra of *N*-(3-Chloro-4-fluorophenyl)benzamide (3y)



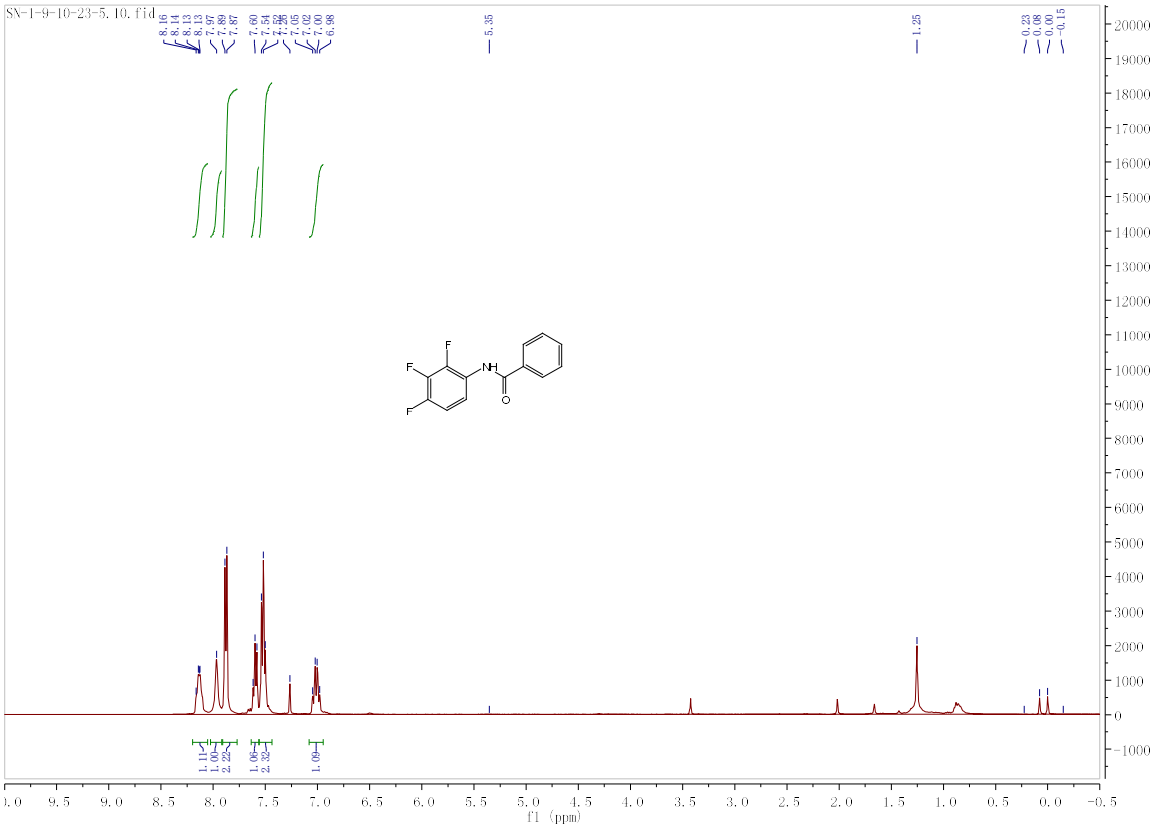


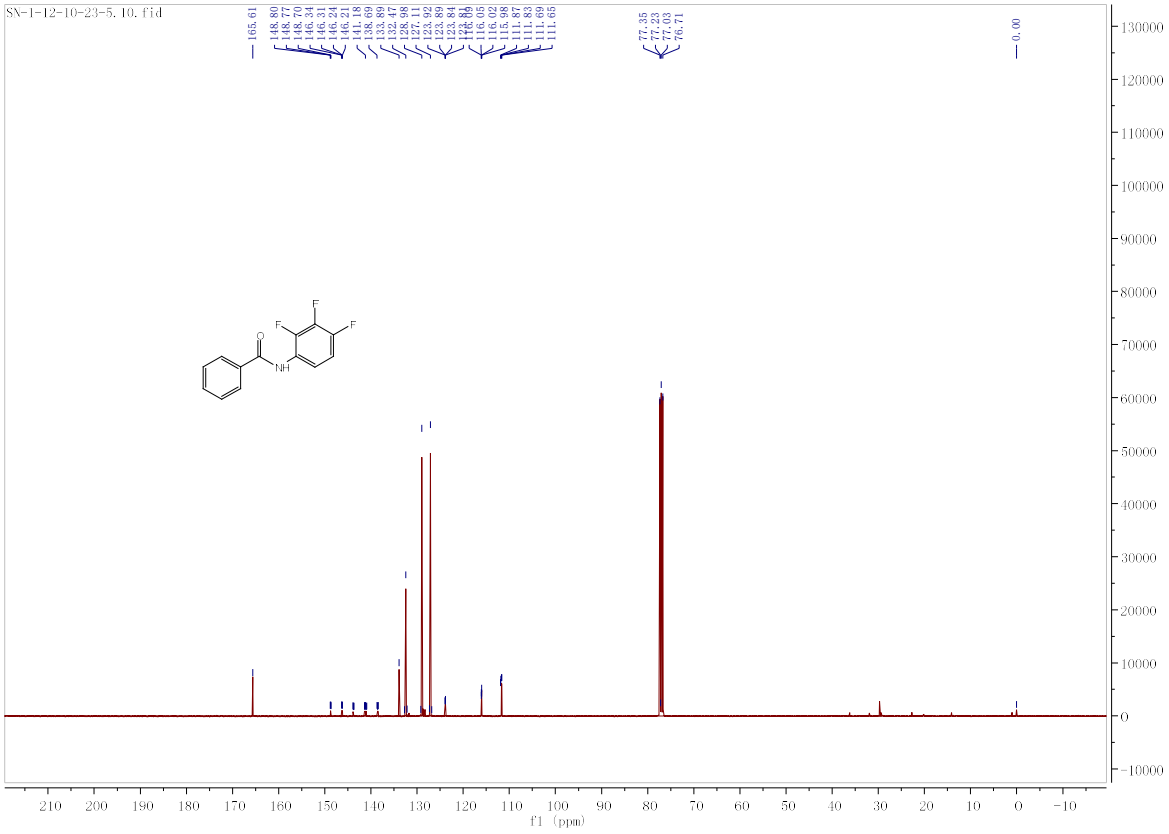
^{1}H and ^{13}C NMR Spectra of *N*-(3-Chloro-4-fluorophenyl)-4-fluorobenzamide (3z)



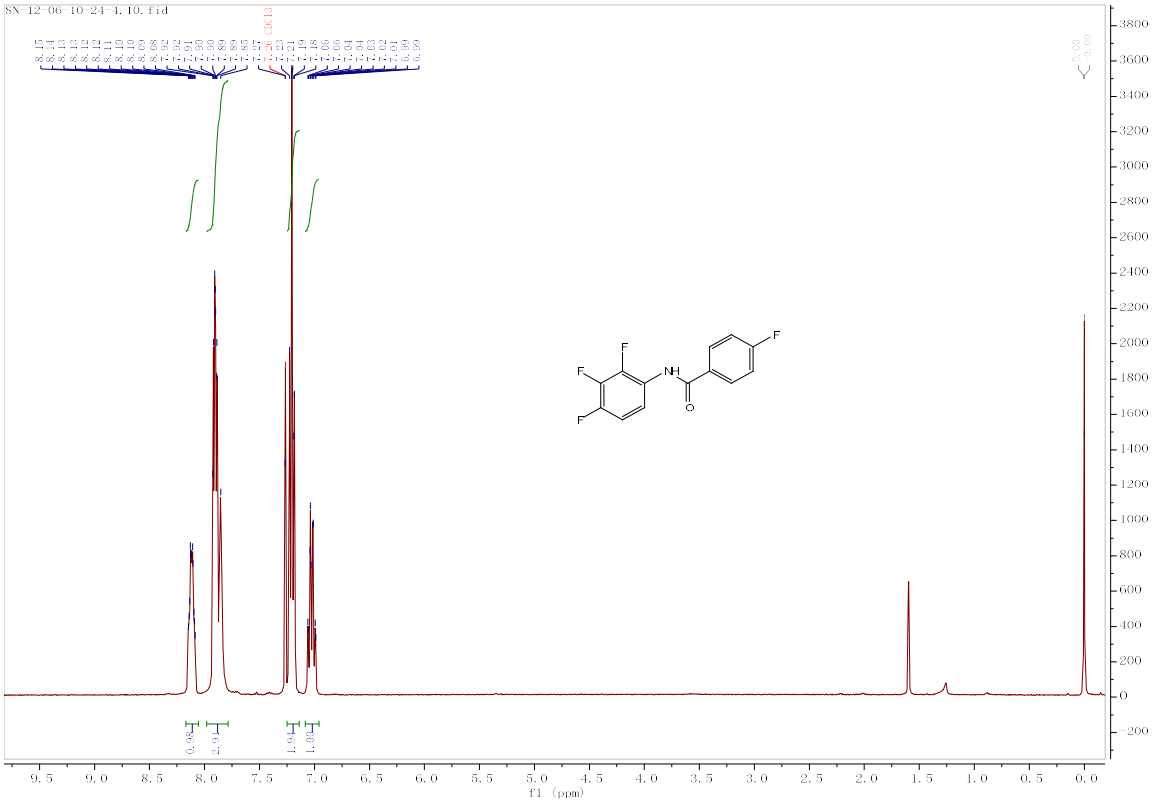


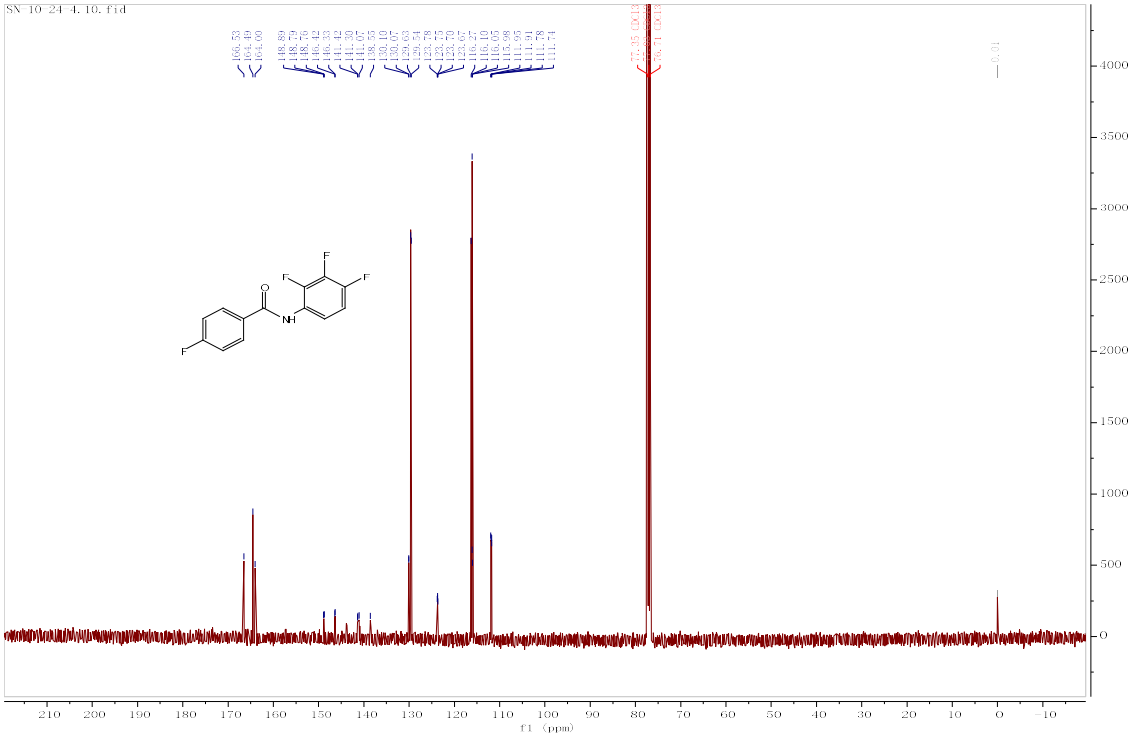
^{1}H and ^{13}C NMR Spectra of *N*-(2,3,4-Trifluorophenyl)benzamide (3aa)



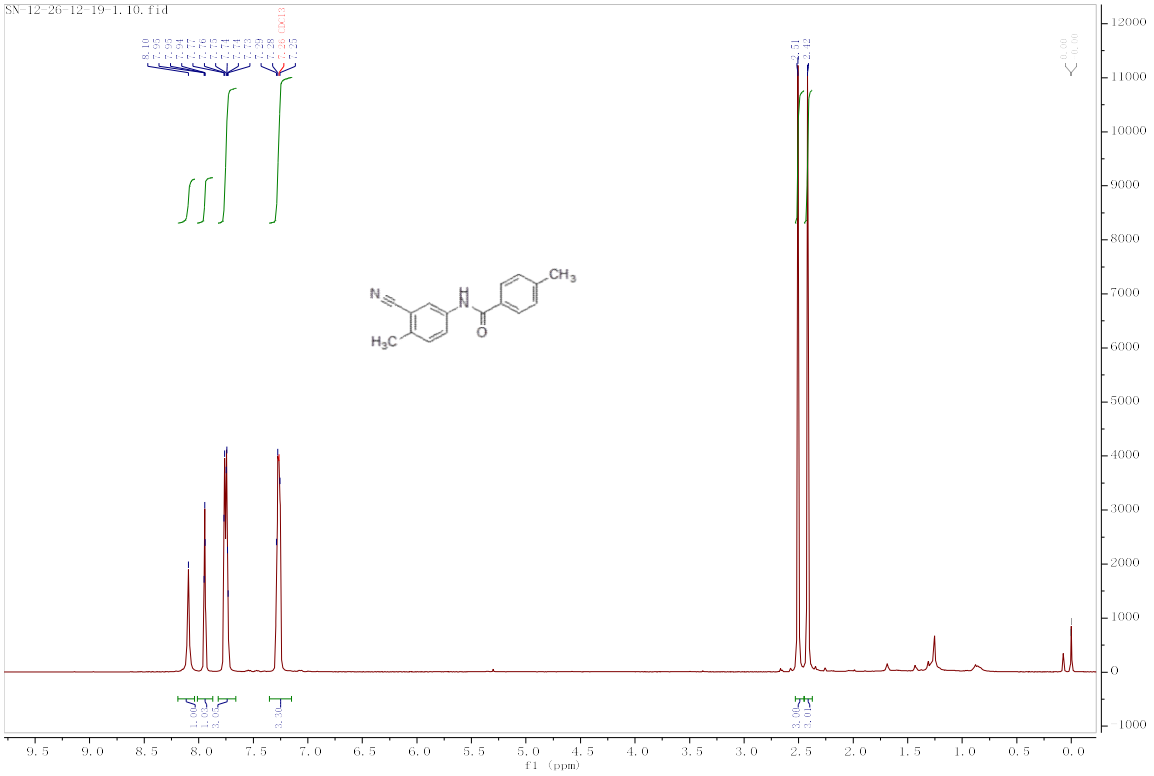


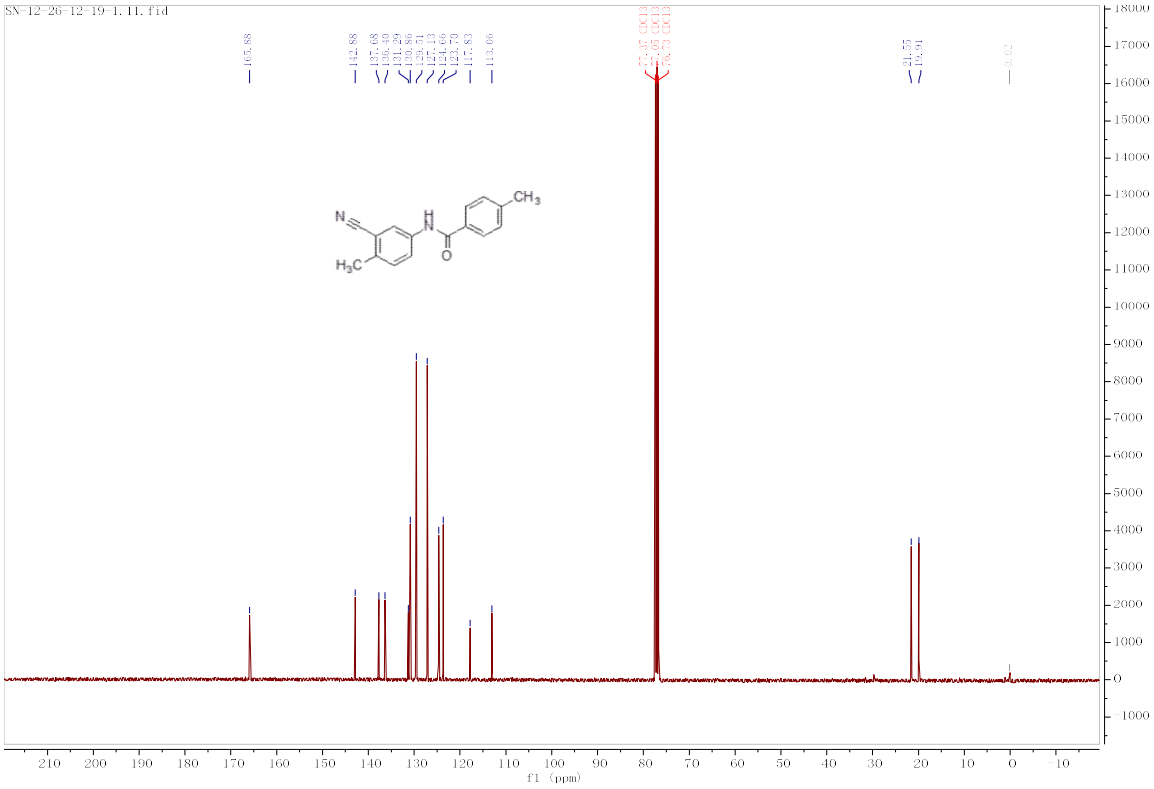
^{1}H and ^{13}C NMR Spectra of 4-Fluoro-*N*-(2,3,4-trifluorophenyl)benzamide (3ab)



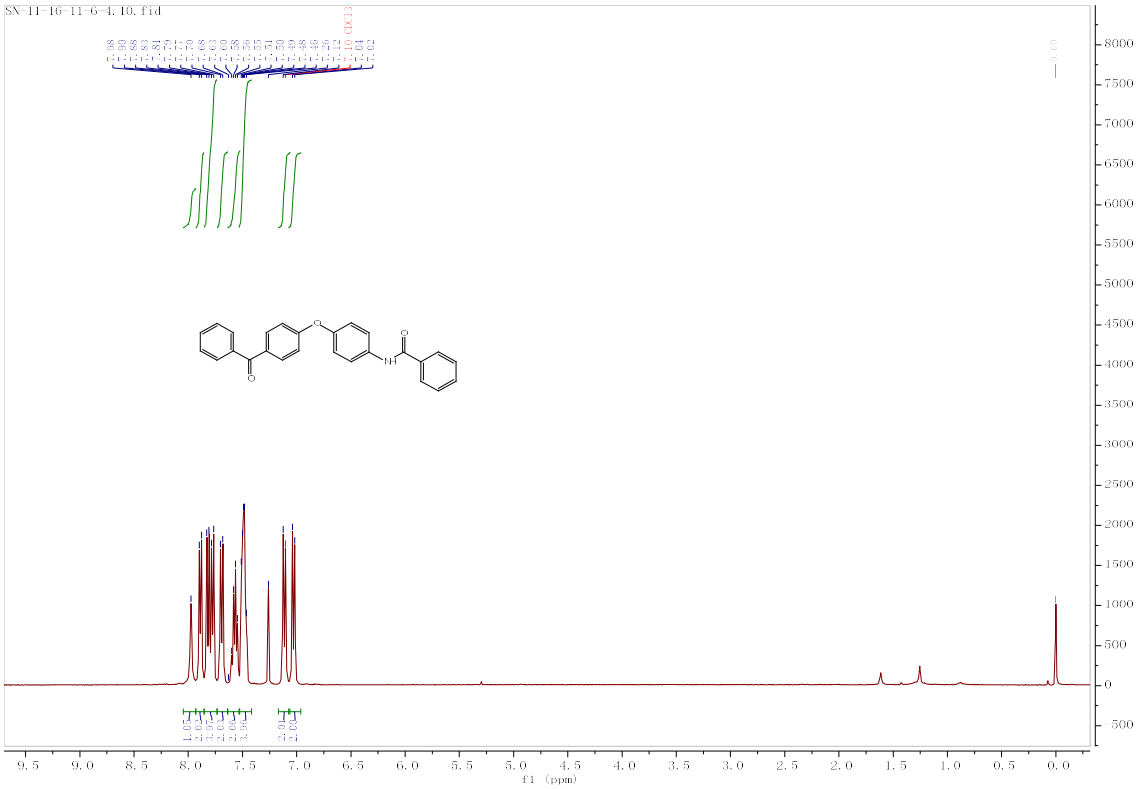


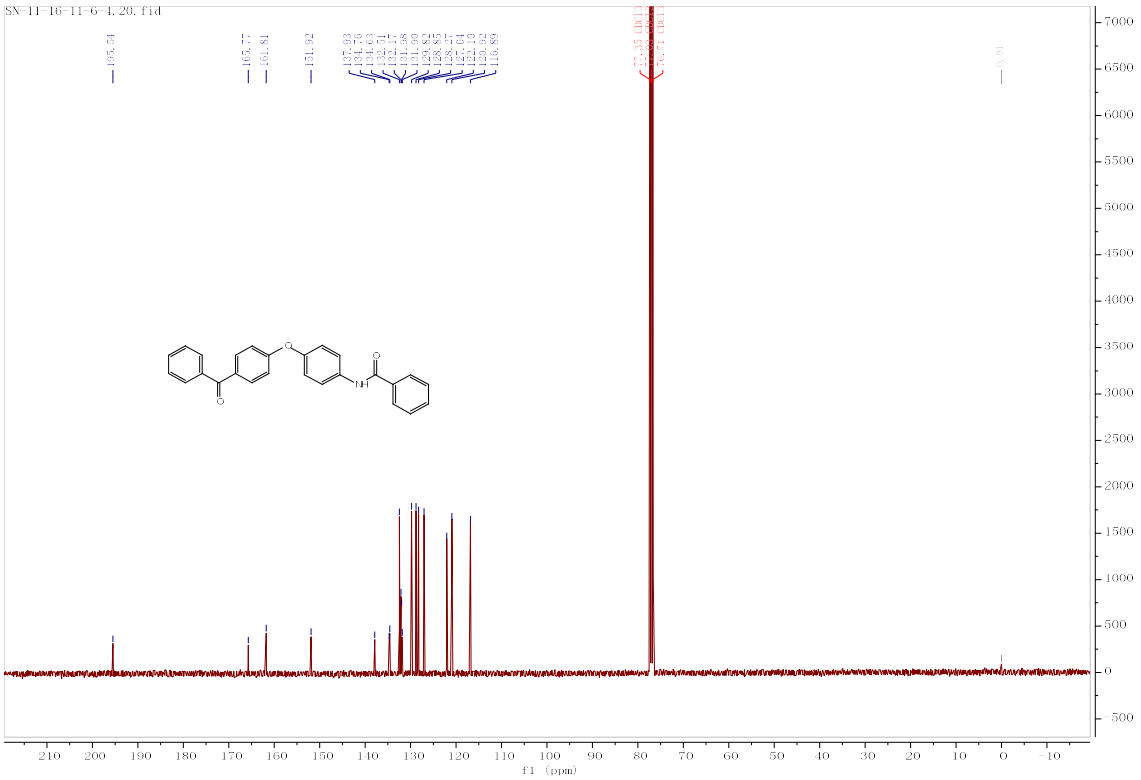
^{1}H and ^{13}C NMR Spectra of *N*-(3-Cyano-4-methylphenyl)-4-methylbenzamide (3ac)



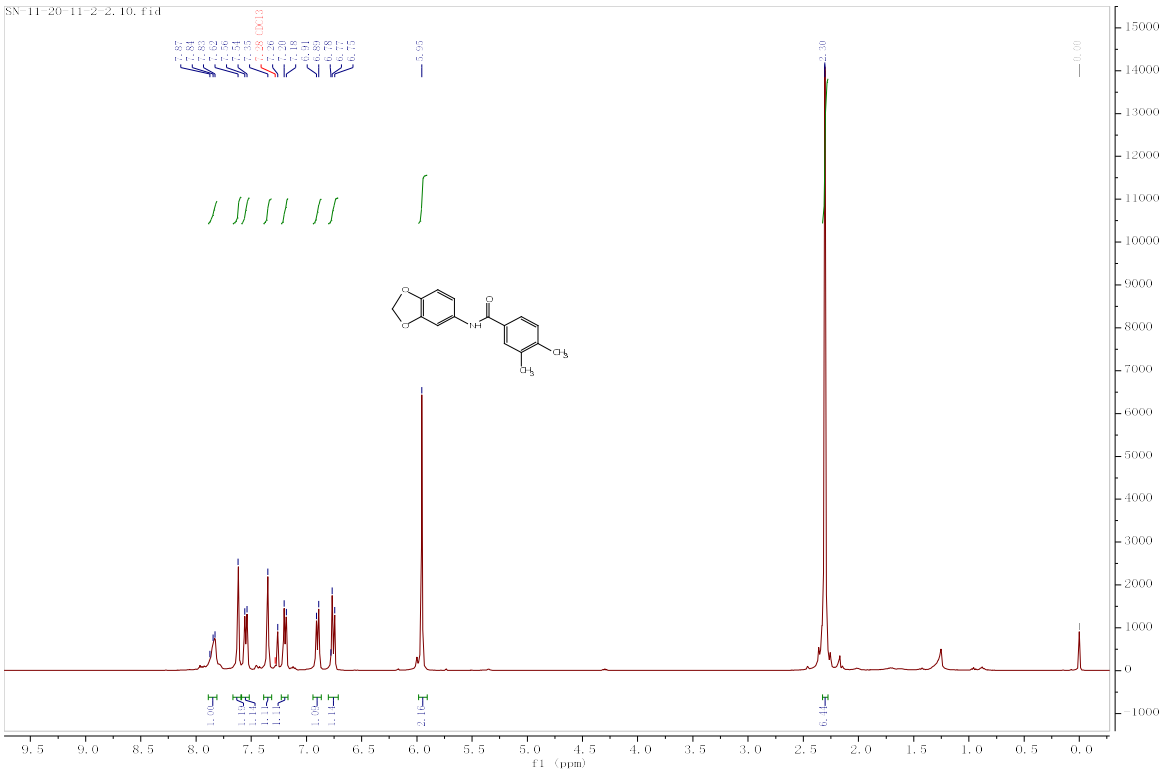


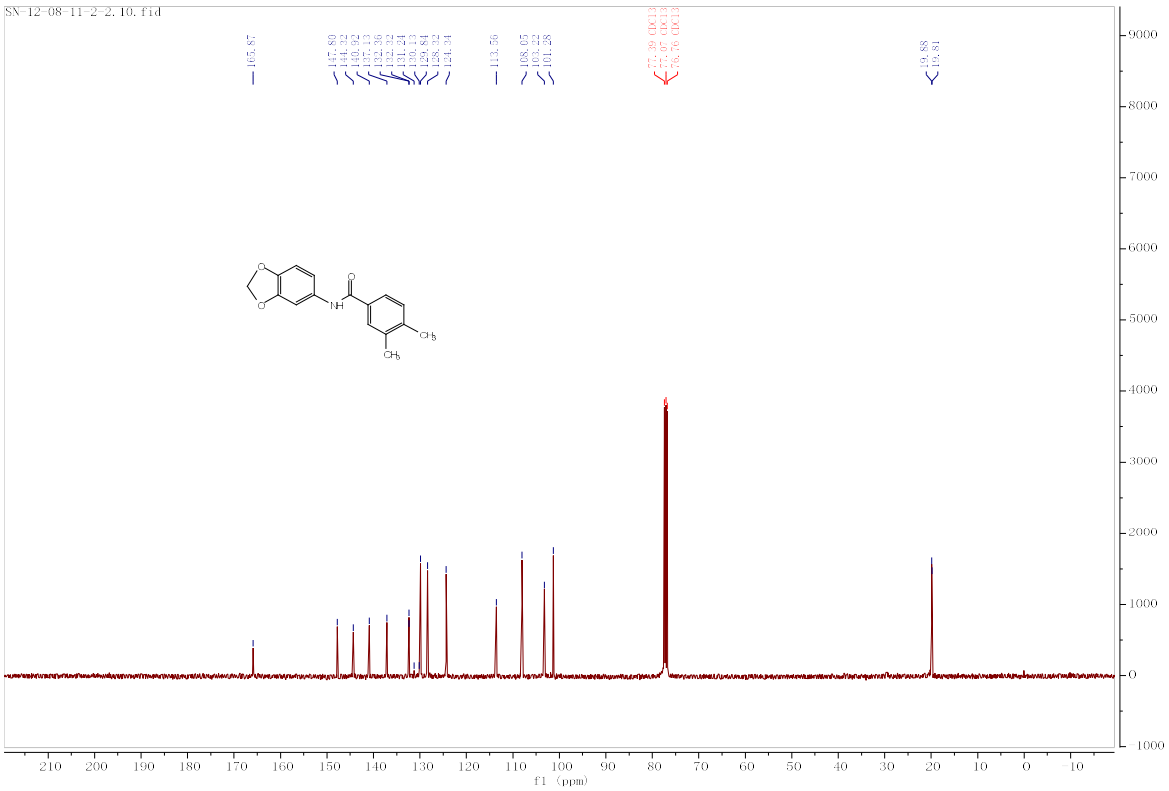
^{1}H and ^{13}C NMR Spectra of *N*-(4-(4-Benzoylphenoxy)phenyl)benzamide (3ad)



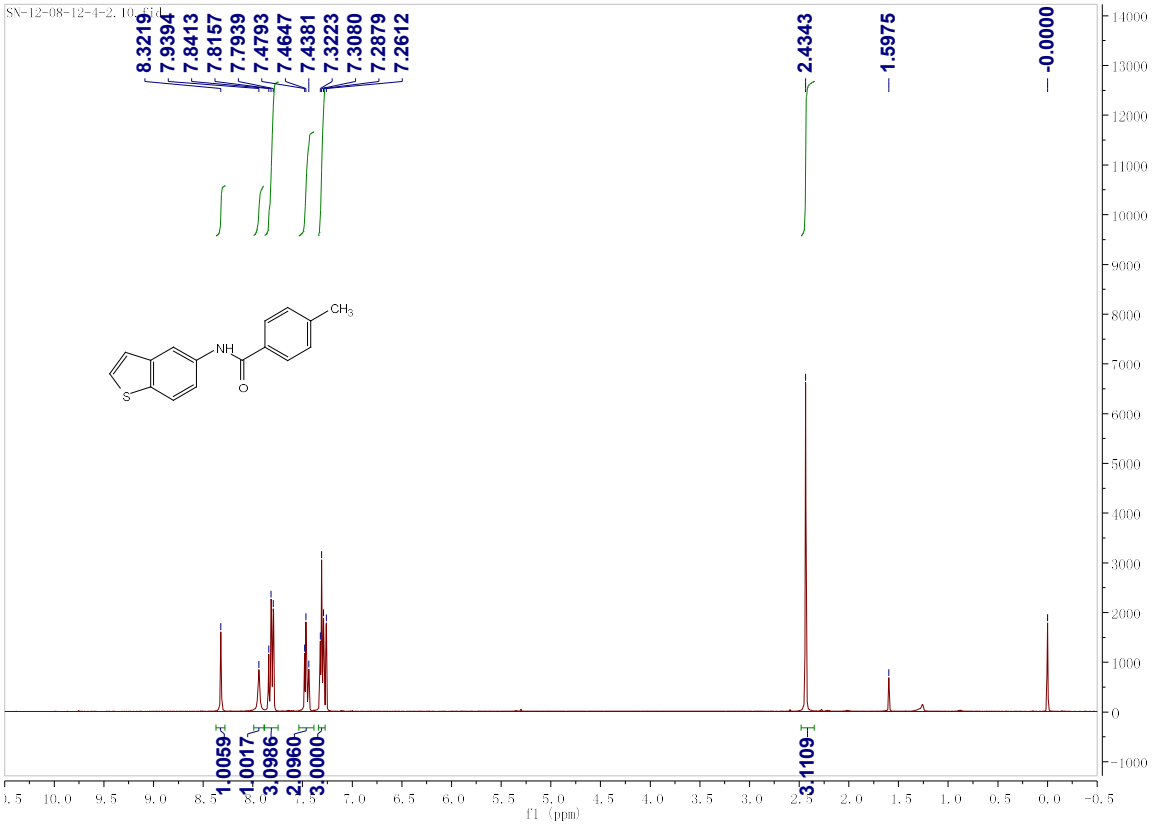


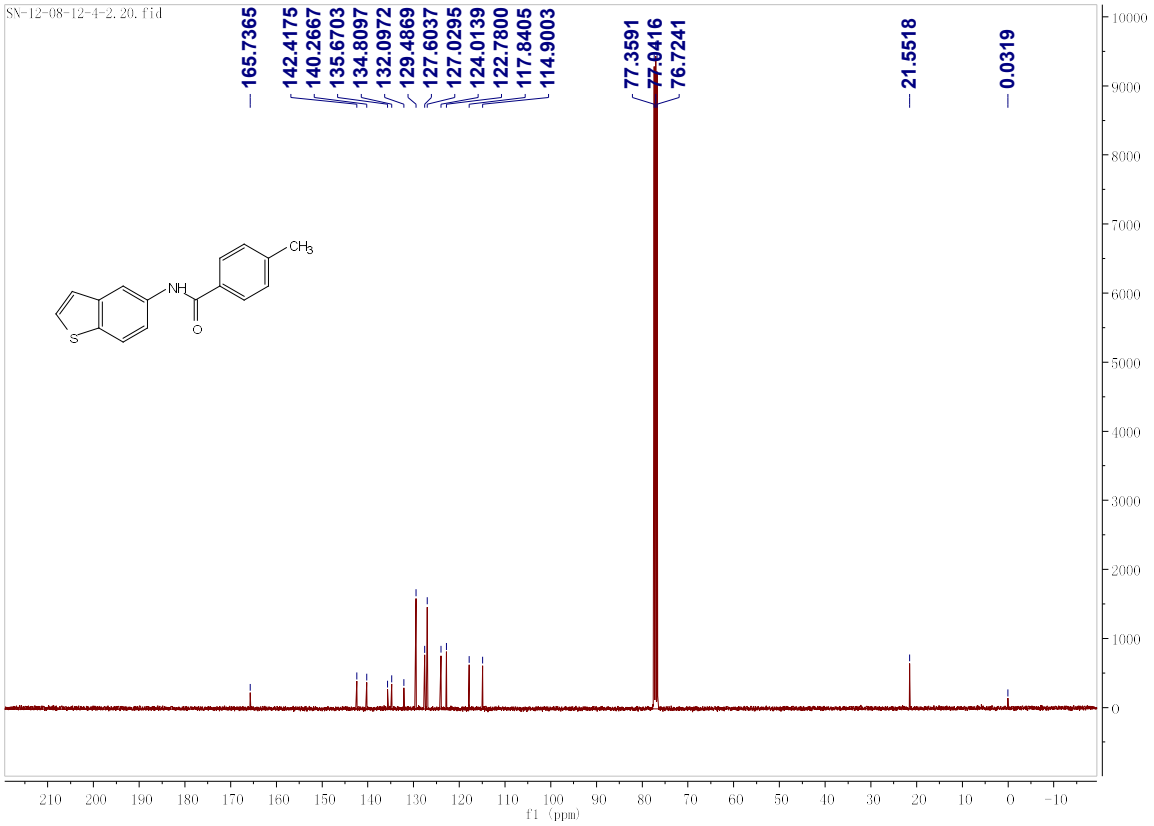
^{1}H and ^{13}C NMR Spectra of *N*-(Benzo[d][1,3]dioxol-6-yl)-3,4-dimethylbenzamide (3ae)



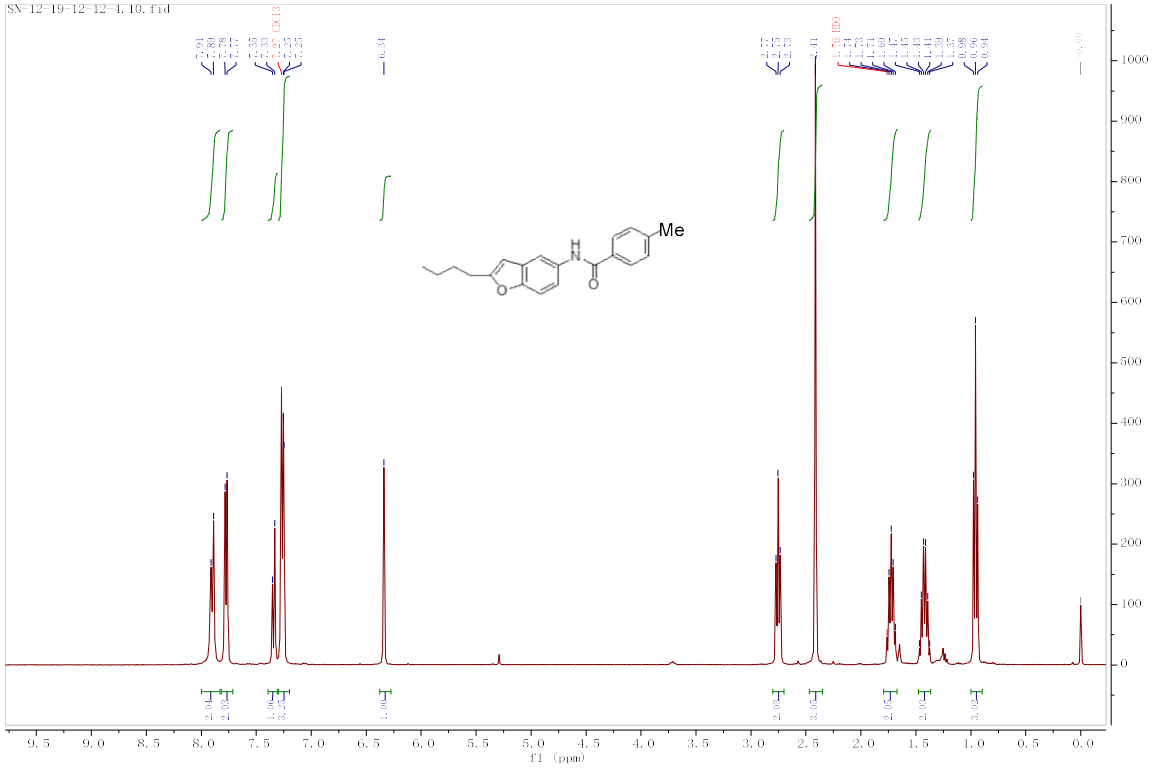


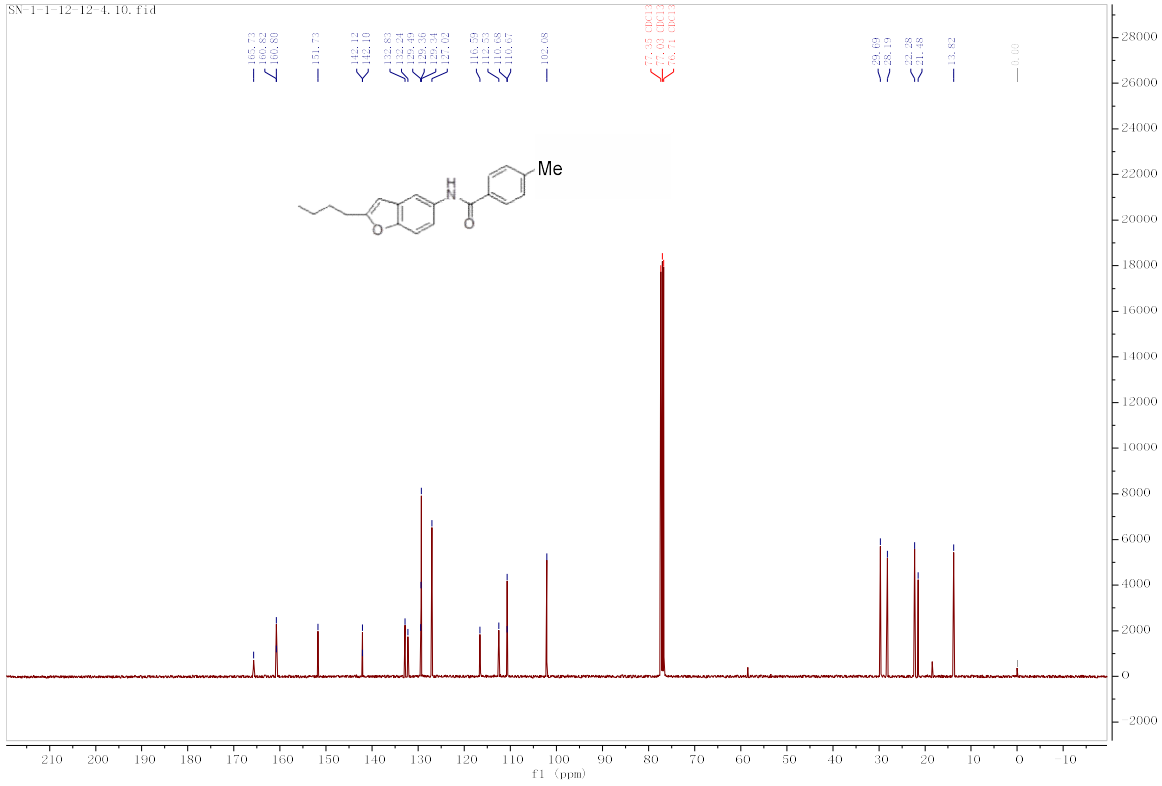
^{1}H and ^{13}C NMR Spectra of *N*-(Benzo[b]thiophen-5-yl)-4-methylbenzamide (3af)



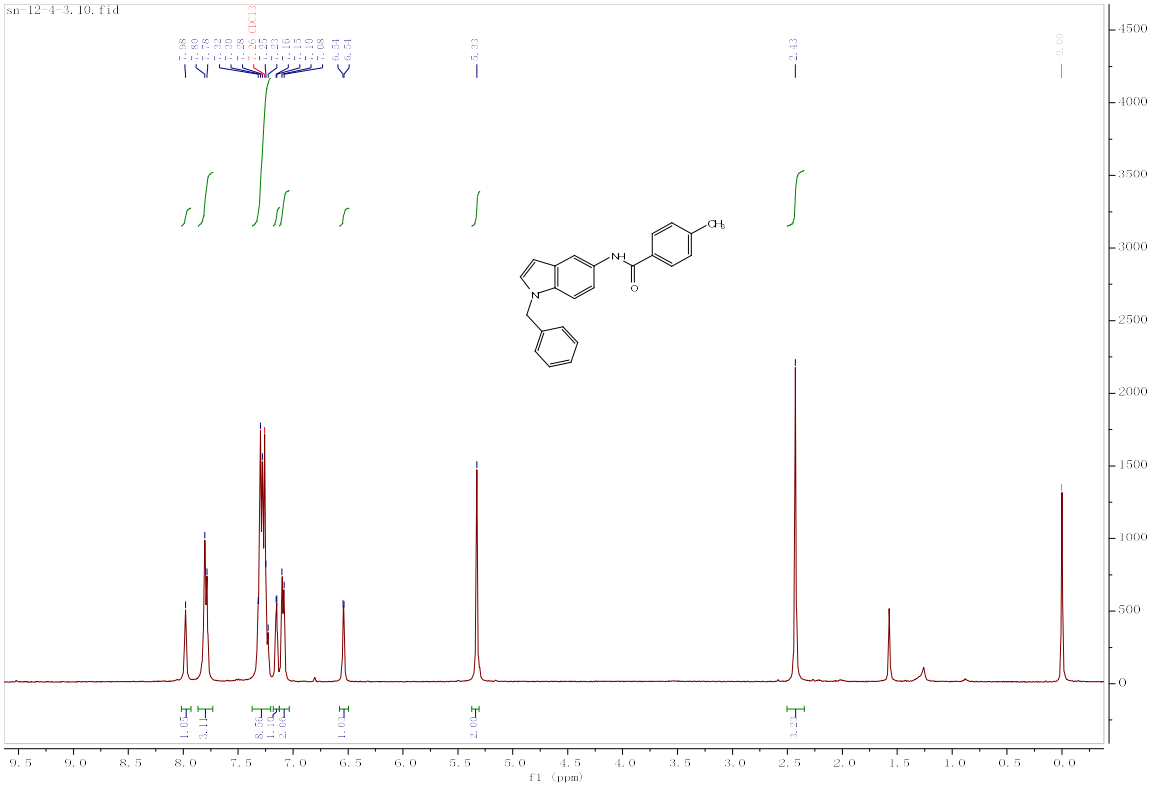


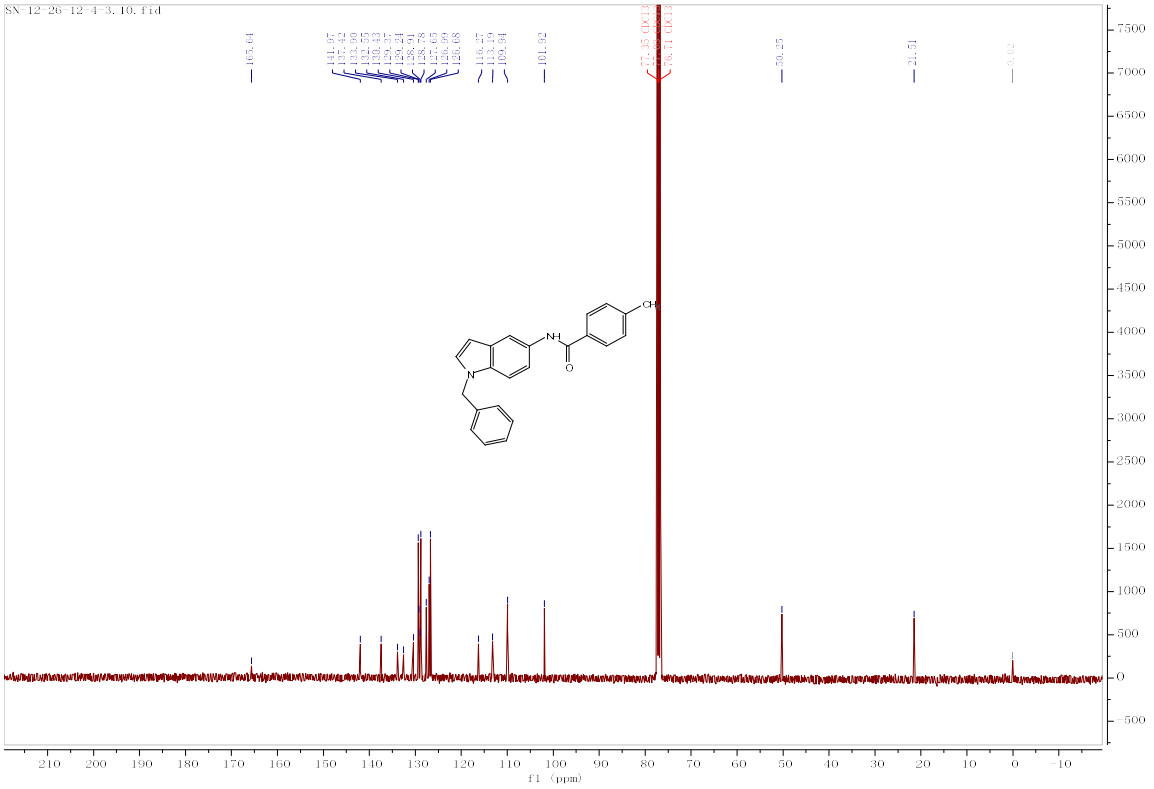
^{1}H and ^{13}C NMR Spectra of *N*-(2-Butylbenzofuran-5-yl)-4-methylbenzamide (3ag)



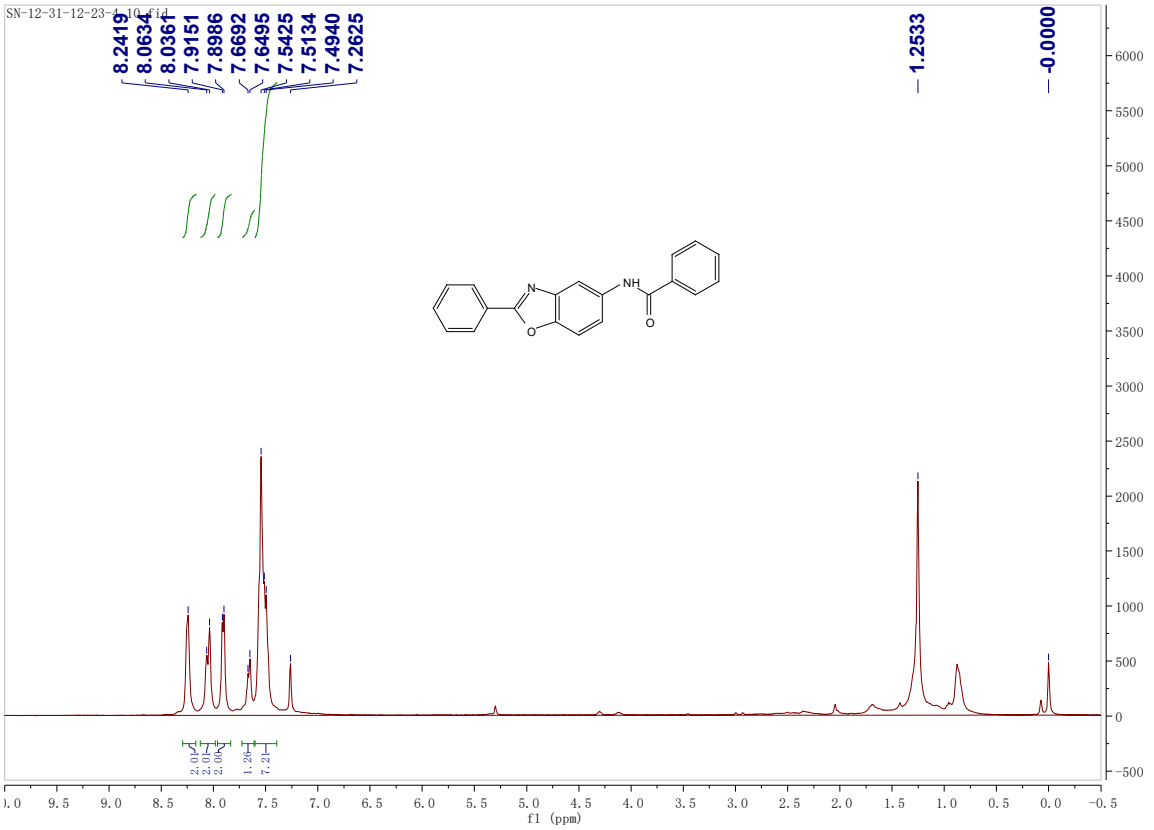


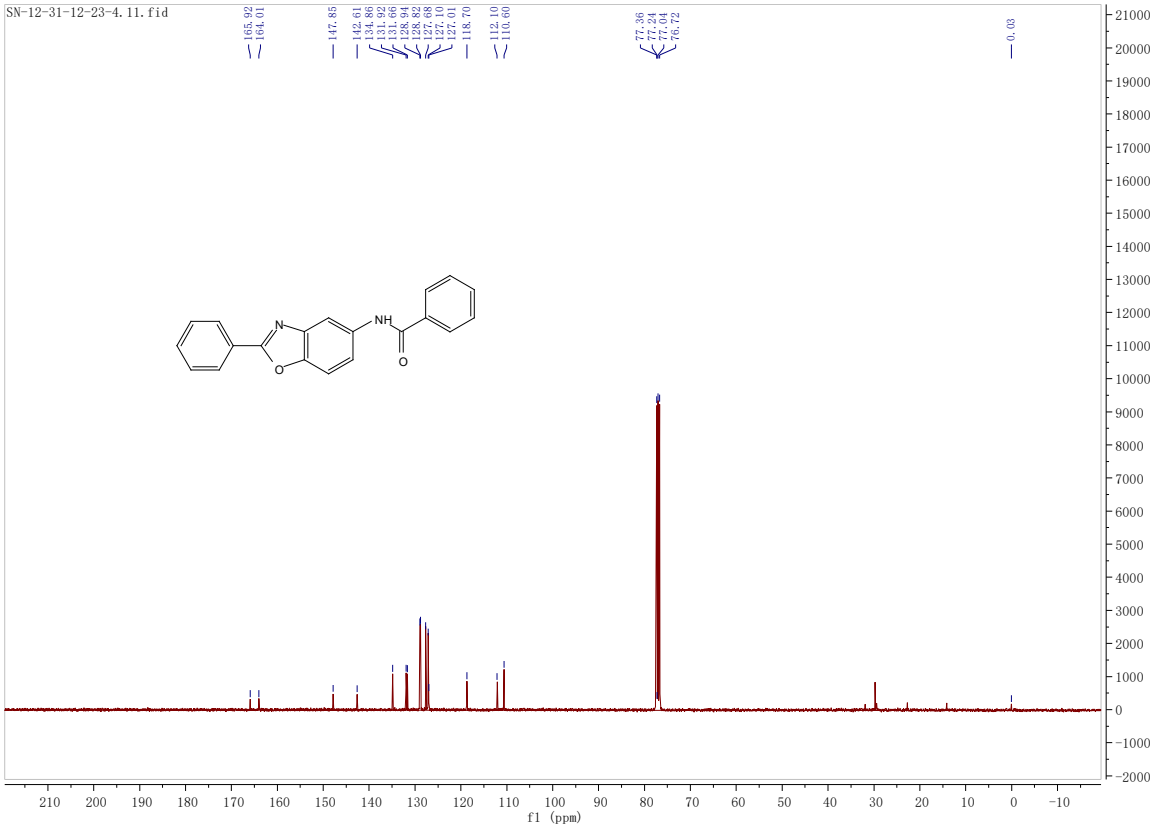
^{1}H and ^{13}C NMR Spectra of *N*-(1-Benzyl-1H-indol-5-yl)-4-methylbenzamide (3ah)



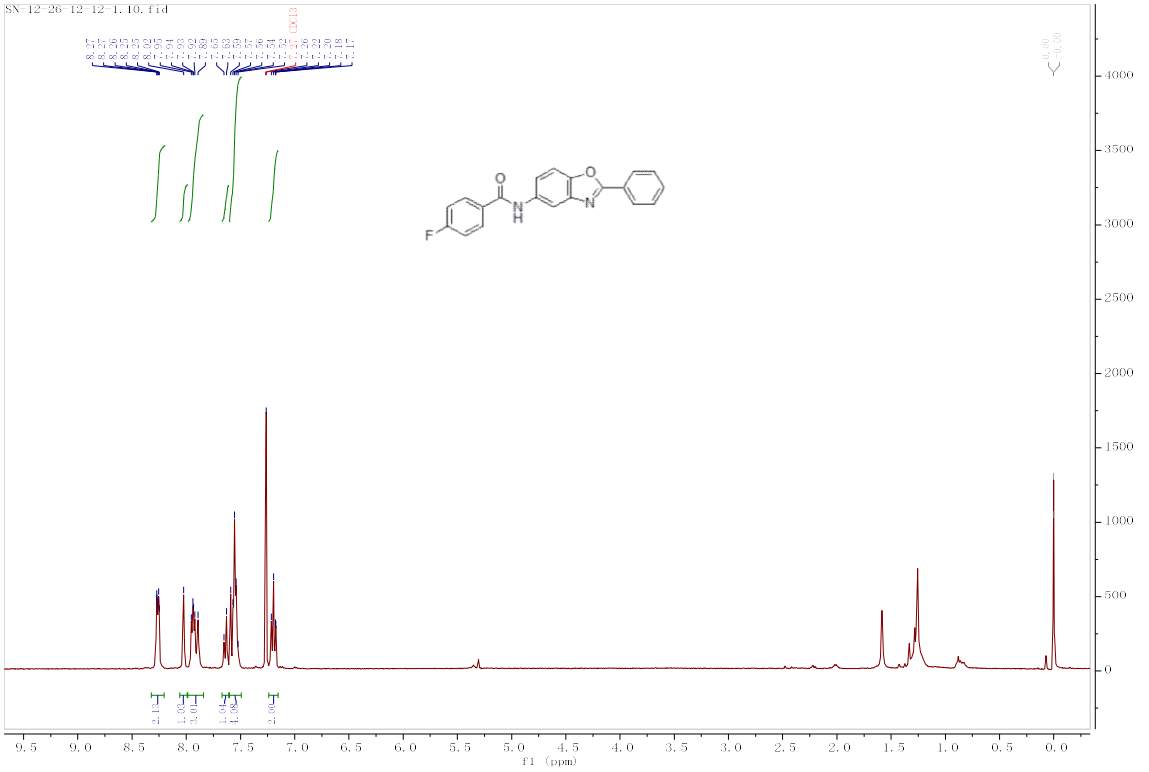


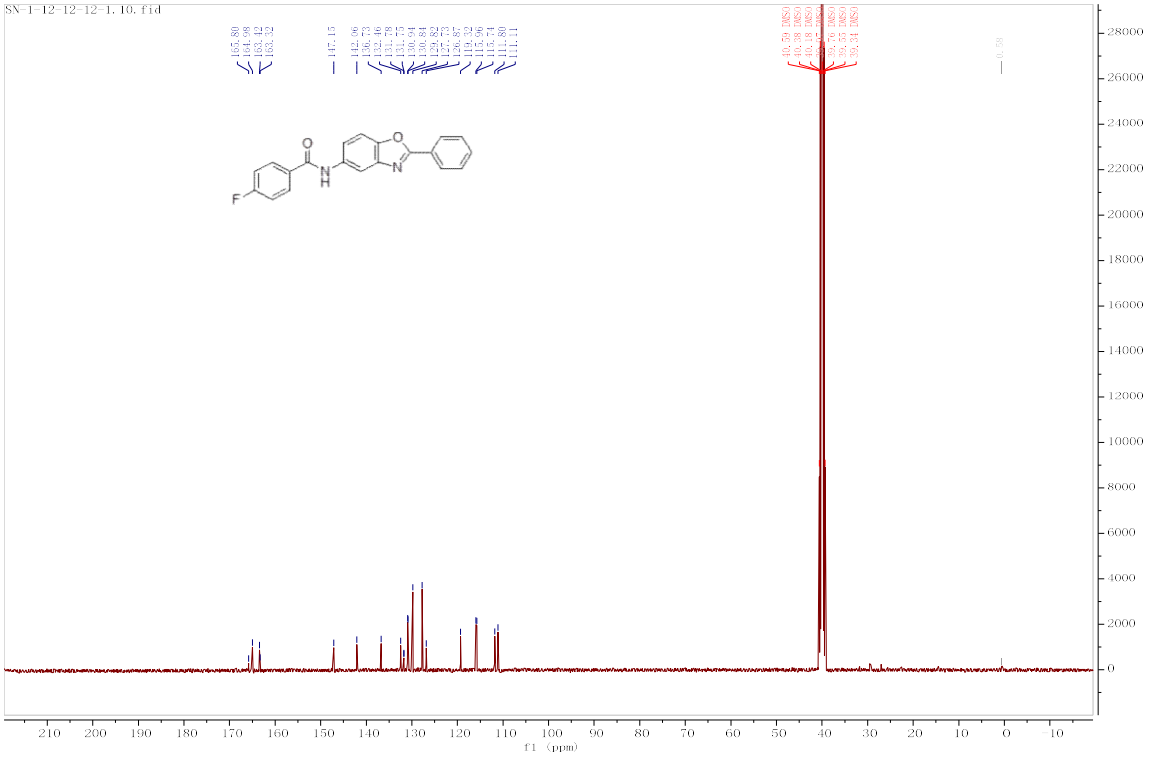
^{1}H and ^{13}C NMR Spectra of *N*-(2-Phenylbenzo[d]oxazol-5-yl)benzamide (4a)



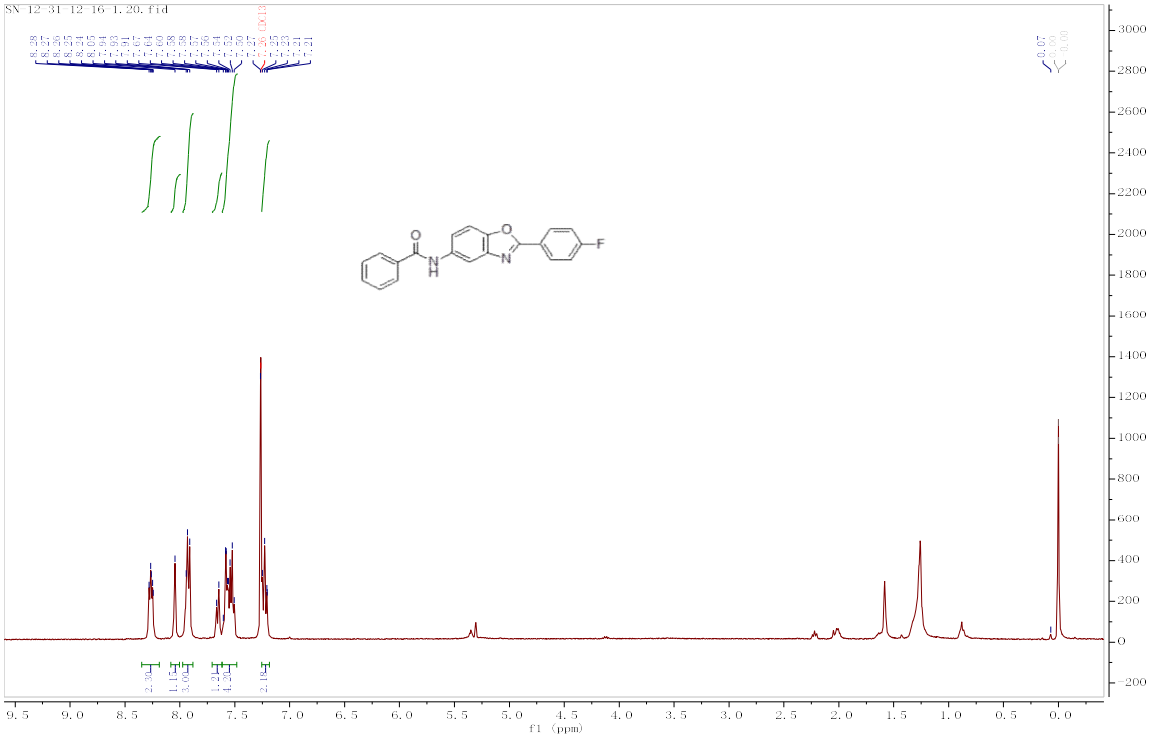


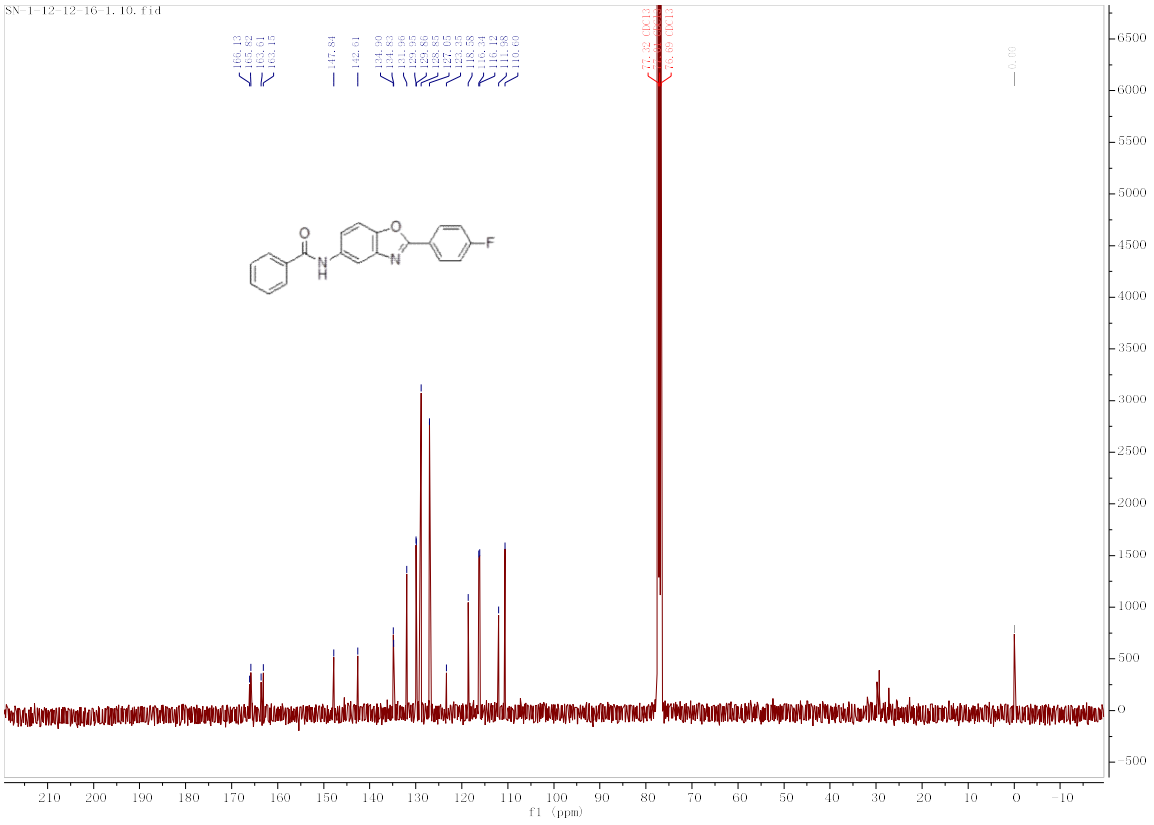
^{1}H and ^{13}C NMR Spectra of 4-Fluoro-*N*-(2-phenylbenzo[d]oxazol-5-yl)benzamide (4b)





^{1}H and ^{13}C NMR Spectra of
***N*-(2-(4-Fluorophenyl)benzo[d]oxazol-5-yl)benzamide (4c)**





^{1}H and ^{13}C NMR Spectra of
***N*-(4-Chloro-3-(trifluoromethyl)phenyl)-4-fluorobenzamide (4d)**