Supporting Information

Manganese-Mediated Reductive Transamidation of Tertiary Amides with Nitroarenes

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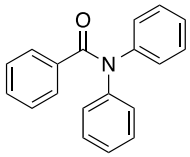
General Considerations

(A) General Analytical Information.

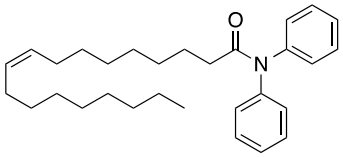
Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 MHz and 600 MHz instruments at ambient temperature. All ^{1}H NMR spectra were measured in part per million (ppm) relative to the signal of tetramethylsilane (TMS) added into the deuterated chloroform ($CDCl_3$, 0.00 ppm), the signal of residual dichloromethane in deuterated dichloromethane (CD_2Cl_2, 5.32 ppm), or the signal of residual dimethyl sufloxide in dimethyl-d_6 sufloxide (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, br = broad), coupling constants, and integration. All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.16 ppm), CD_2Cl_2 (53.84 ppm), or DMSO-d_6 (39.52 ppm)[1] and were obtained with complete ^{1}H decoupling. All ^{19}F NMR spectra were reported in ppm relative to hexafluorobenzene as an internal standard (-164.9 ppm, with reference to $CFCl_3$ at 0 ppm) or relative to $CFCl_3$ (0 ppm) as an external standard, and were obtained with complete ^{1}H decoupling. All gas chromatography (GC) analyses were performed on a Perkin-Elmer Clarus 400 GC system with a FID detector. All gas chromatography-mass spectrometry (GC-MS) analyses were performed on an Agilent Technologies 7890A GC system equipped with a 5975C MS detector. High-resolution mass spectra (HRMS) by electrospray ionization (ESI) method were performed at the EPFL ISIC Mass Spectroscopy Service with a Micro Mass QTOF Ultima spectrometer. Melting points (Mp) of solid compounds were performed using SGW X-4 micro-melting point apparatus. Infra-red (IR) spectroscopies were performed using Bruker Vertex 70 spectrometer.

(B) General Reagent Information.

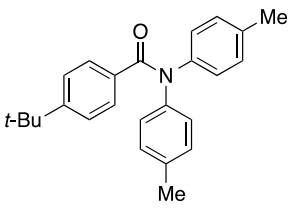
Unless otherwise noted, all chemicals were used as received without further purifications. *N*-Methylpyrrolidone (NMP) was dried using 3Å molecular sieve beads. Manganese powder was in 99.9% purities. Iodotrimethylsilane was stabilized using copper strips and was kept at refrigerator prior to use. The following known starting materials (tertiary amides and nitroarenes) were prepared according to the literature procedures:[2-29]



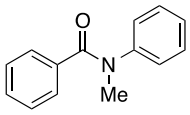
N,*N*-diphenylbenzamide[2]



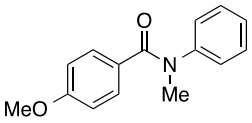
N,*N*-diphenyloleamide[3]



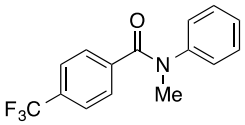
4-(*tert*-butyl)-*N*,*N*-di-*p*-tolylbenzamide[4]



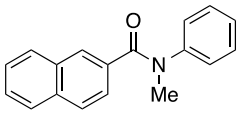
N-methyl-*N*-phenylbenzamide[5]



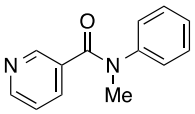
4-methoxy-*N*-methyl-*N*-phenylbenzamide[6]



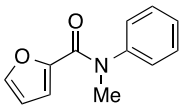
N-methyl-*N*-phenyl-4-(trifluoromethyl)benzamide[7]



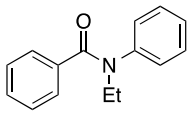
N-methyl-*N*-phenyl-2-naphthamide[8]



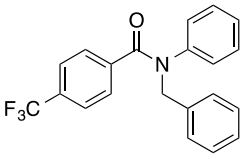
N-methyl-*N*-phenylnicotinamide[9]



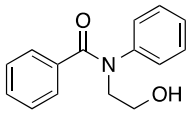
N-methyl-*N*-phenylfuran-2-carboxamide[10]



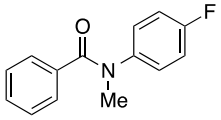
N-ethyl-*N*-phenylbenzamide[11]



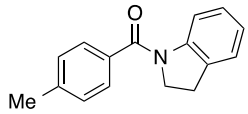
N-benzyl-*N*-phenyl-4-(trifluoromethyl)benzamide[12]



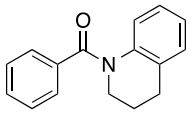
N-(2-hydroxyethyl)-*N*-phenylbenzamide[13]



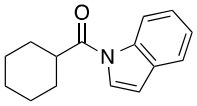
N-(4-fluorophenyl)-*N*-methylbenzamide[14]



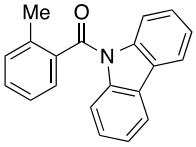
indolin-1-yl(*p*-tolyl)methanone[15]



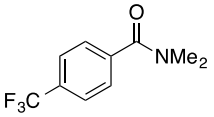
(3,4-dihydroquinolin-1(2*H*)-yl)(phenyl)methanone[16]



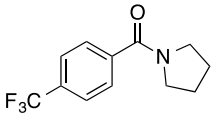
cyclohexyl(1*H*-indol-1-yl)methanone[17]



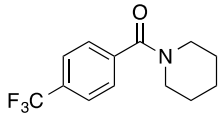
(9*H*-carbazol-9-yl)(*o*-tolyl)methanone[18]



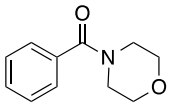
N,*N*-dimethyl-4-(trifluoromethyl)benzamide[19]



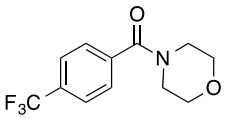
pyrrolidin-1-yl(4-(trifluoromethyl)phenyl)methanone[20]



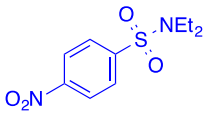
piperidin-1-yl(4-(trifluoromethyl)phenyl)methanone[21]



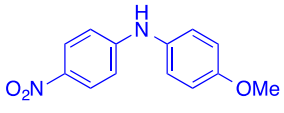
morpholino(phenyl)methanone[22]



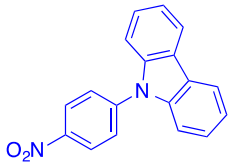
morpholino(4-(trifluoromethyl)phenyl)methanone[23]



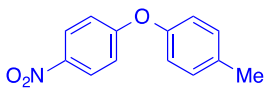
N,*N*-diethyl-4-nitrobenzenesulfonamide[24]



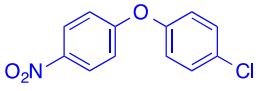
4-methoxy-*N*-(4-nitrophenyl)aniline[25]



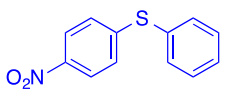
9-(4-nitrophenyl)-9*H*-carbazole[26]



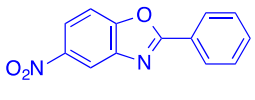
1-methyl-4-(4-nitrophenoxy)benzene[27]



1-chloro-4-(4-nitrophenoxy)benzene[27]



(4-nitrophenyl)(phenyl)sulfane[28]



5-nitro-2-phenylbenzo[*d*]oxazole[29]

(C) General Manipulation Considerations.

All manipulations for the Mn-mediated reductive transamidation of tertiary amides with nitroarenes were set up in either two ways (1) in a 25 mL Schlenk tube under an inert argon (Ar) atmosphere; (2) in a 30 mL Teflon-screw capped test tubes under an inert nitrogen (N_2) atmosphere using glove-box techniques. Flash column chromatography was performed using 200-300 mesh silica gel. Preparative thin-layer chromatography (preparative TLC) was performed using preparative TLC plate (Merck Millipore, TLC Silica gel 60 F_{254}, 20 x 20 cm, catalogue number: 1.05715.0001) in a developing tank. Notably, the TLC plates used for the purification of amide products were washed with hexanes/triethylamine solution (volume ratio ~20:1) prior to use in order to minimize the product loss. The eluents for column chromatography and preparative TLC were presented as ratios of solvent volumes. Yields reported in the publication are of isolated materials unless otherwise noted. All new starting materials and amide products were characterized by ^{1}H and ^{13}C NMR spectroscopies, high-resolution mass spectrometry (HRMS), thin-layer chromatography (TLC, R_f value), and melting point analysis (Mp, for solid compounds), and most of them were further characterized by infra-red spectrosmetry (IR). All known starting materials and amide products were characterized by ^{1}H and ^{13}C NMR spectroscopies and the spectra were compared with the reported data when provided.

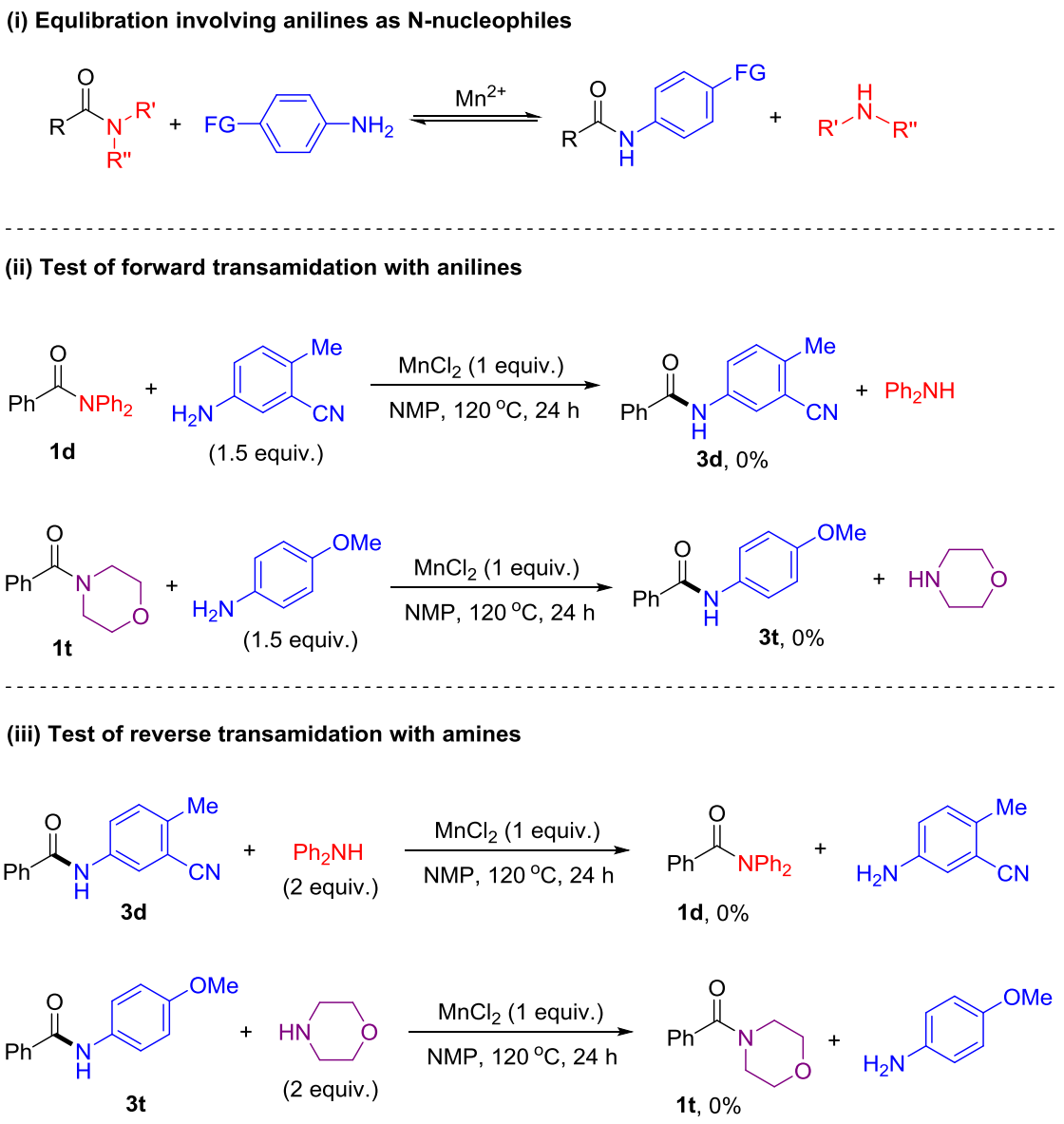
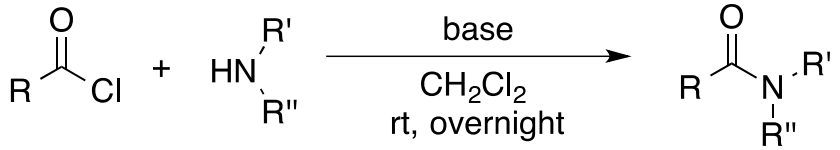


Figure S1. Study of possibility of transamidation of tertiary amides with anilines.

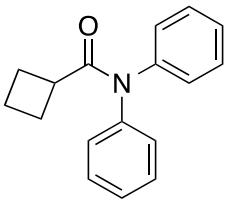
Experimental Section

Synthesis of Starting Materials:

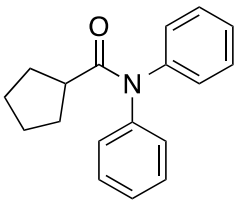
General Procedures for the Synthesis of Tertiary Amides (General Procedures A).



An oven-dried 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar was sequentially charged with dichloromethane solvent (CH_2Cl_2), amide, and base (triethylamine (Et_3N) or pyridine). The reaction mixture was stirred at room temperature, and acyl chloride was slowly added for ~1 minute into the reaction mixture. The resulting mixture was stirred at room temperature overnight. After the reaction, the organic fraction was washed with HCl solution (~1 M (aq), ~100 mL), followed by NaOH solution (~1 M (aq), ~100 mL) and finally saturated NaCl solution (~50 mL). The organic fraction was dried with anhydrous $MgSO_4$ and then concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography using a mixture of hexanes/EtOAc as an eluent to afford the tertiary amide.

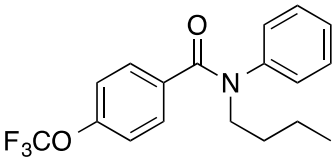


***N,N*-Diphenylcyclobutanecarboxamide (S1).** Following the general procedure A, the title compound was prepared using cyclobutanecarbonyl chloride (2 equiv, 10 mmol, 1.14 mL), diphenylamine (1 equiv, 5 mmol, 845 mg), pyridine (4 equiv, 3.9 mmol, 1.6 mL), and CH_2Cl_2 (100 mL) using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (917 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (br s, 4 H), 7.27-7.10 (m, 6 H), 3.17 (quint, *J* = 8.1 Hz, 1 H), 2.46-2.34 (m, 2 H), 1.89-1.75 (m, 4 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.9, 142.9, 129.2 (br), 126.4 (br), 39.1, 26.0, 17.9 (7 carbon signals were observed out of expected 8 carbon signals). **HRMS** (ESI): Calcd for $C_{17}H_{18}NO$ [M+H]: 252.1388; Found: 252.1418. **Mp:** 76-78 °C. **R_f** = 0.72 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 2987, 2359, 1489, 1260, 1066.

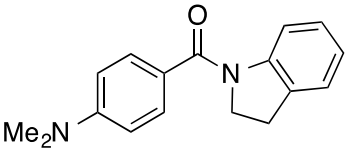


***N,N*-Diphenylcyclopentanecarboxamide (S2).** Following the general procedure A, the title compound

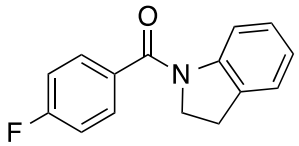
was prepared using cyclopentanecarbonyl chloride (2 equiv, 10 mmol, 1.22 mL), diphenylamine (1 equiv, 5 mmol, 845 mg), pyridine (4 equiv, 3.9 mmol, 1.6 mL), and CH_2Cl_2 (100 mL) using hexanes/EtOAc (10:1) as an eluent to afford the title compound as a white amorphous solid (863 mg, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (br s, 4 H), 7.29-7.14 (m, 6 H), 2.76 (quint, *J* = 7.8 Hz, 1 H), 1.96-1.86 (m, 2 H), 1.80-1.66 (m, 4 H), 1.49-1.39 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.2, 143.3, 129.3 (br), 126.9 (br), 43.0, 31.4, 26.5 (7 carbon signals were observed out of expected 8 carbon signals). **HRMS** (ESI): Calcd for $C_{18}H_{20}NO$ [M+H]: 266.1545; Found: 266.1554. **Mp:** 78-80 °C. **R_f** = 0.75 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 2955, 2362, 1672, 1488, 1364, 1248. 1069.



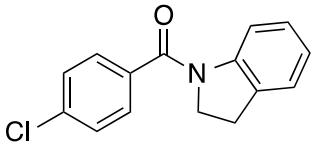
***N*-Butyl-*N*-phenyl-4-(trifluoromethoxy)benzamide (S3).** Following the general procedure A, the title compound was prepared using 4-(trifluoromethoxy)benzoyl chloride (1 equiv, 5.0 mmol, 0.79 mL), *N*-*n*-butylaniline (1.05 equiv, 5.25 mmol, 783 mg), Et_3N (1.5 equiv, 7.5 mmol, 1.0 mL), and CH_2Cl_2 (100 mL) using hexanes/EtOAc (5:1) as an eluent to afford the title compound as a brown oil (1.12 g, 72%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.39 (d, *J* = 8.0 Hz, 2 H), 7.25 (t, *J* = 7.2 Hz, 2 H), 7.16 (t, *J* = 7.1 Hz, 1 H), 7.08 (d, *J* = 7.4 Hz, 2 H), 7.03 (d, *J* = 7.9 Hz, 2 H), 3.95 (t, *J* = 7.1 Hz, 2 H), 1.64 (quint, *J* = 7.1 Hz, 2 H), 1.39 (hex, *J* = 7.3 Hz, 2 H), 0.93 (t, *J* = 7.1 Hz, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 169.0, 150.0, 143.8, 136.0, 130.9, 129.6, 128.4, 127.2, 120.9 (q, $^1J_{CF}$ = 255.8 Hz), 120.3, 50.7, 30.3, 20.7, 14.1. **HRMS** (ESI): Calcd for $C_{18}H_{19}F_3NO_2$ [M+H]: 338.1368; Found: 338.1374. **^{19}F NMR** (376 MHz, $CDCl_3$, C_6F_6 as internal standard): δ -61.0. **R_f** = 0.61 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 1643, 1586, 1494, 1390, 1254, 1210, 1180, 857.



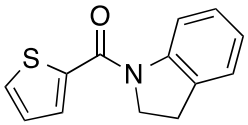
(4-(Dimethylamino)phenyl)(indolin-1-yl)methanone (S4). Following the general procedure A, the title compound was prepared using 4-(*N*,*N*-dimethylamino)benzoyl chloride (1 equiv, 2.6 mmol, 477 mg), indoline (1.2 equiv, 3.12 mmol, 0.35 mL), Et_3N (1.5 equiv, 3.9 mmol, 0.53 mL), and CH_2Cl_2 (60 mL) using hexanes/EtOAc (3:1) as an eluent to afford the title compound as a pale-brown amorphous solid (623 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57-7.36 (m, 3 H), 7.19 (d, *J* = 6.9 Hz, 1 H), 7.10 (t, *J* = 6.8 Hz, 1 H), 6.97 (t, *J* = 7.0 Hz, 1 H), 6.68 (d, *J* = 8.3 Hz, 2 H), 4.15 (t, *J* = 8.0 Hz, 2 H), 3.09 (t, *J* = 8.0 Hz, 2 H), 3.03 (s, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.6, 152.1, 143.6, 132.5, 129.7, 127.2, 124.9, 123.6, 123.3, 117.0, 111.2, 51.0, 40.3, 28.4. **HRMS** (ESI): Calcd for $C_{17}H_{19}N_2O$ [M+H]: 267.1497; Found: 267.1498. **Mp:** 144-146 °C. **R_f** = 0.44 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 2362, 1629, 1608, 1478, 1392, 1367, 1343, 1192, 1157, 817.



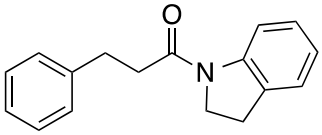
(4-Fluorophenyl)(indolin-1-yl)methanone (S5).[30] Following the general procedure A, the title compound was prepared using 4-fluorobenzoyl chloride (1 equiv, 3 mmol, 0.36 mL), indoline (1.3 equiv, 3.9 mmol, 0.44 mg), Et_3N (1.5 equiv, 4.5 mmol, 0.6 mL), and CH_2Cl_2 (60 mL) using hexanes/EtOAc (5:1) as an eluent to afford the title compound as a white amorphous solid (510 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13 (br s, 1 H), 7.57 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HF}$ = 5.4 Hz, 2 H), 7.21 (d, *J* = 7.1 Hz, 1 H), 7.20-7.06 (m, 3 H), 7.02 (t, *J* = 7.5 Hz, 1 H), 4.07 (t, *J* = 8.0 Hz, 2 H), 3.12 (t, *J* = 8.3 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.0, 163.9 ($^1J_{CF}$ = 249.2 Hz), 142.6, 133.1, 132.5, 129.7 ($^3J_{CF}$ = 8.1 Hz), 127.3, 125.1, 124.1, 117.0, 115.8 ($^2J_{CF}$ = 21.7 Hz), 50.8, 28.2. **HRMS** (ESI): Calcd for $C_{15}H_{13}FNO$ [M+H]: 242.0981; Found: 242.0981.



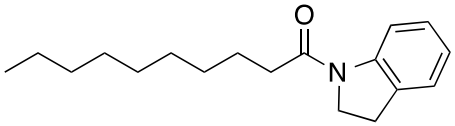
(4-Chlorophenyl)(indolin-1-yl)methanone (S6).[30] Following the general procedure A, the title compound was prepared using 4-chlorobenzoyl chloride (1 equiv, 3 mmol, 0.38 mL), indoline (1.3 equiv, 3.9 mmol, 0.44 mL), Et_3N (1.5 equiv, 4.5 mmol, 0.6 mL), and CH_2Cl_2 (60 mL) using hexanes/EtOAc (5:1) as an eluent to afford the title compound as a white amorphous solid (550 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.14 (br s, 1 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 7.42 (d, *J* = 8.5 Hz, 2 H), 7.26-7.13 (m, 2 H), 7.03 (t, *J* = 7.4 Hz, 1 H), 4.06 (br s, 2 H), 3.12 (t, *J* = 8.2 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.9, 142.5, 136.5, 135.3, 132.4, 129.0, 128.9, 127.4, 125.1, 124.3, 117.2, 50.8, 28.2. **HRMS** (ESI): Calcd for $C_{15}H_{13}ClNO$ [M+H]: 258.0686; Found: 258.0685.



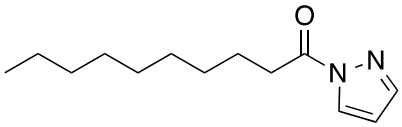
Indolin-1-yl(thiophen-2-yl)methanone (S7).[31] Following the general procedure A, the title compound was prepared using thiophene-2-carbonyl chloride (1 equiv, 10 mmol, 1.1 mL), indoline (1.3 equiv, 13 mmol, 1.5 mL), Et_3N (1.5 equiv, 15 mmol, 2.1 mL), and CH_2Cl_2 (150 mL) using hexanes/EtOAc (3:1) as an eluent to afford the title compound as an off-white amorphous solid (2.09 g, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (br s, 1 H), 7.53 (dd, *J* = 3.8 Hz, *J* = 1.0 Hz, 1 H), 7.49 (dd, *J* = 5.0 Hz, *J* = 1.1 Hz, 1 H), 7.20-7.17 (m, 2 H), 7.07 (dd, *J* = 5.0 Hz, *J* = 3.8 Hz, 1 H), 7.02 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 1 H), 4.30 (t, *J* = 8.3 Hz, 2 H), 3.15 (t, *J* = 8.1 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.4, 143.0, 139.5, 131.9, 130.2, 129.7, 127.4, 127.2, 124.7, 124.2, 117.7, 50.6, 28.6.



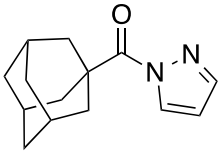
1-(Indolin-1-yl)-3-phenylpropan-1-one (S8).[32] Following the general procedure A, the title compound was prepared using 3-phenylpropanoyl chloride (1 equiv, 3 mmol, 5.1 mL), indoline (1.1 equiv, 3.3 mmol, 0.37 mL), Et_3N (1.5 equiv, 4.5 mmol, 0.6 mL), and CH_2Cl_2 (60 mL) using hexanes/EtOAc (3:1) as an eluent to afford the title compound as a white amorphous solid (511 mg, 2.03 mmol, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.0 Hz, 1 H), 7.31-7.23 (m, 4 H), 7.3-7.13 (m, 3 H), 6.99 (t, *J* = 7.4 Hz, 1 H), 3.92 (t, *J* = 8.4 Hz, 2 H), 3.11 (t, *J* = 8.4 Hz, 2 H), 3.06 (t, *J* = 8.0 Hz, 2 H), 2.70 (t, *J* = Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.4, 143.1, 141.3, 131.1, 128.6, 128.5, 127.6, 126.3, 124.6, 123.6, 117.1, 48.0, 38.0, 30.8, 28.1. **HRMS** (ESI): Calcd for $C_{17}H_{18}NO$ [M+H]: 252.1388; Found: 252.1386.



1-(Indolin-1-yl)decan-1-one (S9). Following the general procedure A, the title compound was prepared using decanoyl chloride (1 equiv, 10 mmol, 1.91 g), indoline (1.3 equiv, 13 mmol, 1.46 mL), Et_3N (1.5 equiv, 15 mmol, 2.1 mL), and CH_2Cl_2 (150 mL) using hexanes/EtOAc (5:1) as an eluent to afford the title compound as a white amorphous solid (2.27 g, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.0 Hz, 1 H), 7.19-7.14 (m, 2 H), 6.99 (d, *J* = 7.4 Hz, 1 H), 4.02 (d, *J* = 8.5 Hz, 2 H), 3.17 (d, *J* = 8.4 Hz, 2 H), 2.39 (d, *J* = 7.5 Hz, 2 H), 1.72 (quint, *J* = 7.3 Hz, 2 H), 1.40-1.24 (m, 12 H), 0.88 (t, *J* = 6.7 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.6, 143.2, 131.1, 127.6, 124.5, 123.5, 117.1, 48.0, 36.1, 32.0, 29.61, 29.59, 29.52, 29.4, 28.1, 24.7, 22.8, 14.2. **GCMS:** $[M]^+$ = 273 was detected, which corresponds to $C_{18}H_{27}NO$ ($[M]^+$ could not be detected by HRMS). **Mp:** 45-47 °C. **R_f** = 0.70 (EtOAc : petroleum ether = 1:2).**IR** (neat, cm^{-1}): 2922, 1655, 1482, 1461, 1409, 1261.

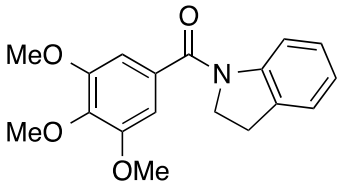


1-(1*H*-Pyrazol-1-yl)decan-1-one (S10). Following the general procedure A, the title compound was prepared using decanoyl chloride (1 equiv, 10 mmol, 1.91 g), pyrazole (1.5 equiv, 15 mmol, 1.02 g), Et_3N (1.5 equiv, 15 mmol, 2.1 mL), and CH_2Cl_2 (150 mL) using hexanes/EtOAc (5:1) as an eluent to afford the title compound as a colorless oil (1.73 g, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 2.8 Hz, 1 H), 7.69 (s, 1 H), 6.42 (dd, *J* = 2.0 Hz, *J* = 1.3 Hz, 1 H), 3.13 (t, *J* = 7.5 Hz, 2 H), 1.78 (quint, *J* = 7.5 Hz, 2 H), 1.43-1.27 (ovlp, 12 H), 0.88 (t, *J* = 6.2 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.3, 143.8, 128.2, 109.4, 34.0, 31.9, 29.5, 29.4, 29.3, 29.2, 24.4, 22.7, 14.1. **HRMS** (ESI): Calcd for $C_{13}H_{22}N_2ONa$ [M+Na]: 245.1630; Found: 245.1630. **R_f** = 0.76 (EtOAc : petroleum ether = 1:2).**IR** (neat, cm^{-1}): 2923, 2854, 1736, 1413, 1382, 1343, 1247, 1199, 1088, 1037, 915.



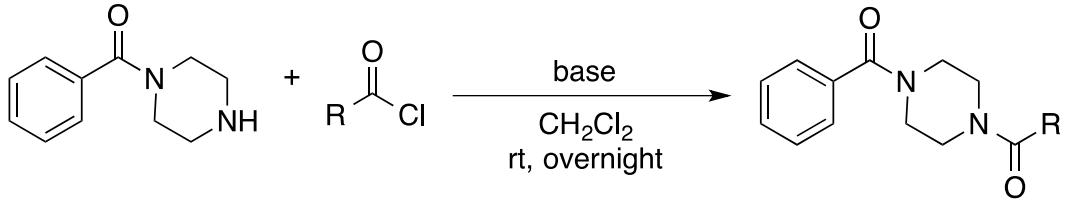
(Adamantan-1-yl)(1*H*-pyrazol-1-yl)methanone (S11). Following the general procedure A, the title

compound was prepared using 1-adamantanecarbonyl chloride (1 equiv, 6 mmol, 1.19 mL), pyrazole (2 equiv, 12 mmol, 817 mg), Et_3N (1.5 equiv, 9.0 mmol, 1.25 mL), and CH_2Cl_2 (100 mL) using hexanes/EtOAc (5:1) as an eluent to afford the title compound as a white amorphous solid (1.11 g, 80%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.23 (d, *J* = 2.6 Hz, 1 H), 7.68 (s, 1 H), 6.35 (dd, *J* = 2.4 Hz, *J* = 1.4 Hz, 1 H), 2.33-2.28 (m 6 H), 2.09-2.05 (m, 3 H), 1.94-1.75 (m, 6 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 175.9, 143.2, 130.3, 108.1, 44.2, 38.9, 37.0, 28.8. **HRMS** (ESI): Calcd for $C_{14}H_{18}N_2ONa$ [M+Na]: 253.1317; Found: 253.1321. **Mp:** 98-100 °C. **R_f** = 0.94 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 2908, 1745, 1541, 1374, 1333, 1311, 1205, 911.

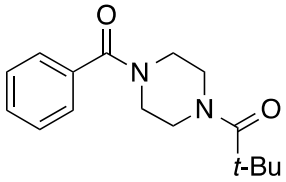


Indolin-1-yl(3,4,5-trimethoxyphenyl)methanone (S12).[33] Following the general procedure A, the title compound was prepared using 3,4,5-trimethoxybenzoyl chloride (1 equiv, 10 mmol, 2.31 g), indoline (1.2 equiv, 12 mmol, 1.4 mL), Et_3N (1.5 equiv, 15 mmol, 2.1 mL), and CH_2Cl_2 (150 mL) using hexanes/EtOAc (1:3) as an eluent to afford the title compound as an off-white amorphous solid (2.66 g, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (br s, 1 H), 7.07 (d, *J* = 7.0 Hz, 1 H), 6.99 (br s, 1 H), 6.88 (t, *J* = 7.1 Hz, 1 H), 6.68 (s, 2 H), 3.97 (t, *J* = 8.2 Hz, 2 H), 3.77 (s, 3 H), 3.73 (s, 6 H), 2.97 (d, *J* = 7.9 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.2, 153.1, 142.3, 139.5, 132.2, 132.0, 126.9, 124.7, 123.7, 116.5, 104.3, 60.6, 56.0, 50.3, 27.8. **HRMS** (ESI): Calcd for $C_{18}H_{20}NO_4$ [M+H]: 314.1392; Found: 314.1397.

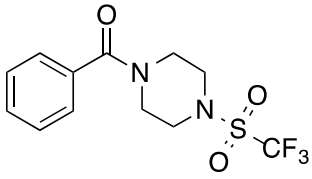
General Procedures for the Synthesis of Tertiary Amides (General Procedures B).



An oven-dried 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar was sequentially charged with dichloromethane solvent (CH_2Cl_2), NH-free tertiary amide, and triethylamine (Et_3N). The reaction mixture was stirred at room temperature, and acyl chloride (or triflic anhydride) was slowly added for ~1 minute into the reaction mixture. The resulting mixture was stirred at room temperature overnight. After the reaction, the organic fraction was washed with dilute HCl solution (~1 M (aq), ~100 mL), followed by dilute NaOH solution (~1 M (aq), ~50 mL), and finally saturated NaCl solution (~50 mL). The organic fraction was dried with anhydrous $MgSO_4$ powder and then concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash chromatography using a mixture of hexanes/EtOAc as an eluent to afford the *N*-protected tertiary amide.

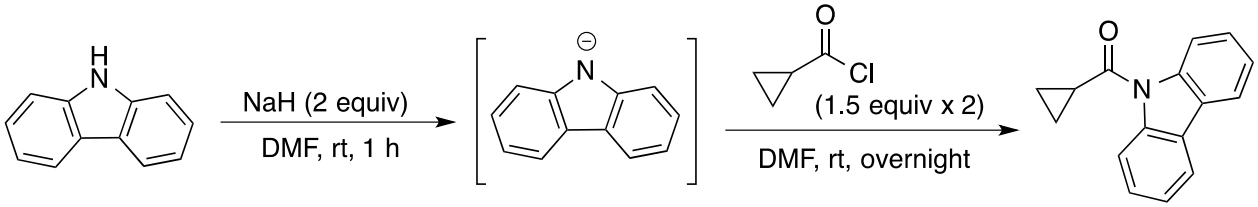


1-(4-Benzoylpiperazin-1-yl)-2,2-dimethylpropan-1-one (S13). Following the general procedure B, the title compound was prepared using phenyl(piperazin-1-yl)methanone (1 equiv, 5.5 mmol, 1.05 g), pivaloyl chloride (2 equiv, 11 mmol, 1.36 mL), Et_3N (1.5 equiv, 8.25 mmol, 1.14 mL), and CH_2Cl_2 (100 mL) using hexanes/EtOAc (1:10) as an eluent to afford the title compound as a white amorphous solid (1.43 g, 95%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.46-7.38 (m, 5 H), 4.21-3.10 (br m, 8 H), 1.26 (s, 9 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 176.6, 170.5, 136.1, 130.1, 128.8, 127.4, 47.9 (br), 45.4, 42.5 (br), 38.9, 28.5 (11 carbon signals were observed out of expected 12 carbon signals). **HRMS** (ESI): Calcd for $C_{16}H_{23}N_2O_2$ [M+H]: 275.1760; Found: 275.1658. **Mp:** 125-127 °C. **R_f** = 0.16 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 1612, 1427, 1281, 1253, 1185, 1006.



Phenyl(4-((trifluoromethyl)sulfonyl)piperazin-1-yl)methanone (S14). Following the general procedure B, the title compound was prepared using phenyl(piperazin-1-yl)methanone (1 equiv, 4.0 mmol, 761 mg), triflic anhydride (2 equiv, 8.0 mmol, 1.35 mL), Et_3N (1.5 equiv, 6.0 mmol, 0.83 mL), and CH_2Cl_2 (100 mL) using hexanes/EtOAc (1:8) as an eluent to afford the title compound as a an off-white amorphous solid (1.04 g, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46-7.35 (m, 5 H), 4.55-3.17 (br m, 8 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.3, 134.4, 130.1, 128.5, 126.9, 118.3 (q, $^1J_{CF}$ = 321.3 Hz), 46.8 (br), 46.3, 42.0 (br) (9 carbon signals were observed out of expected 10 carbon signals). **HRMS** (ESI): Calcd for $C_{12}H_{14}F_3N_2O_3S$ [M+H]: 323.0677; Found: 323.0681. **^{19}F NMR** (376 MHz, $CDCl_3$, C_6F_6 as internal standard): δ -75.3. **Mp:** 74-76 °C. **R_f** = 0.41 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 1790, 1635, 1432, 1384, 1227, 1188, 1153, 1104, 954.

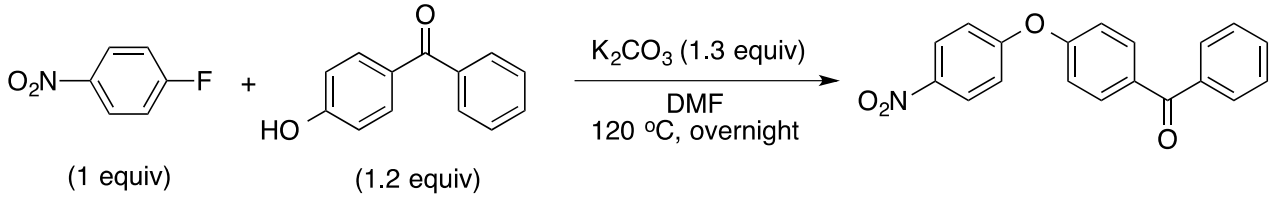
Synthesis of (9*H*-Carbazol-9-yl)(cyclopropyl)methanone (S15).



An oven-dried 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar was sequentially charged with anhydrous dimethylformamide solvent (DMF, 100 mL) and carbazole (1 equiv, 10 mmol, 1.67 g). The reaction mixture was stirred at room temperature, and NaH (~60% in mineral oil, 2 equiv, 20 mmol, ~780 mg) in a few portions was slowly added for ~1 minute
. The reaction mixture was stirred at room temperature for 1 h, after which time cyclopropanecarbonyl

chloride (1.5 equiv, 15 mmol, 1.36 mL) was slowly added for ~1 minute and the resulting mixture was stirred at room temperature for 2 h. After that, another portion of cyclopropanecarbonyl chloride (1.5 equiv, 15 mmol, 1.36 mL) was added and the resulting mixture was stirred at room temperature overnight. After the reaction, the reaction was quenched with water (~20 mL), and the reaction mixture was washed with water (~500 mL) and ethyl acetate (EtOAc, ~100 mL). The organic fraction was further washed with dilute NaOH solution (~1 M (aq), ~50 mL) followed by saturated NaCl solution (~50 mL). The organic fraction was dried with anhydrous $MgSO_4$ and then concentrated *in vacuo* with the aid of a rotary evaporator. The residue was recrystallized using CH_2Cl_2 and hexanes as solvent to afford the title compound as a white amorphous solid (1.53 g, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.3 Hz, 2 H), 7.97 (dd, *J* = 7.6 Hz, *J* = 0.6 Hz, 2 H), 7.44 (td, *J* = 7.4 Hz, *J* = 1.3 Hz, 2 H), 7.35 (td, *J* = 7.6 Hz, *J* = 0.8 Hz, 2 H), 2.55-2.49 (m, 1 H), 1.49-1.45 (m, 2 H), 1.21-1.16 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.9, 138.8, 127.1, 126.1, 123.3, 120.0, 115.6, 17.7, 10.3. **HRMS** (ESI): Calcd for $C_{16}H_{14}NO$ [M+H]: 236.1075; Found: 236.1079. **Mp:** 72-74 °C. **R_f** = 0.88 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 2974, 1670, 1442, 1396, 1286, 1160, 1067, 914.

Synthesis of (4-(4-Nitrophenoxy)phenyl)(phenyl)methanone (S16).



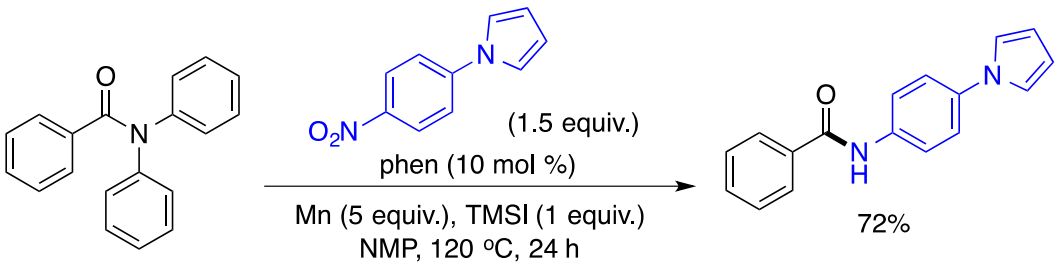
An oven-dried 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with 1-fluoro-4-nitrobenzene (1 equiv, 8 mmol, 1.13 g), 4-hydroxybenzophenone (1.2 equiv, 9.6 mmol, 1.90 g), K_2CO_3 (1.3 equiv, 10.4 mmol, 1.44 g), and anhydrous dimethylformamide solvent (DMF, 150 mL). The reaction mixture was stirred at 120 °C in a preheated oil bath overnight. After the reaction, the reaction was washed with water (~500 mL) and ethyl acetate (EtOAc, ~100 mL). The organic fraction was further washed with dilute NaOH solution (~1 M (aq), ~50 mL) followed by saturated NaCl solution (~50 mL). The organic fraction was dried with anhydrous $MgSO_4$ and then concentrated *in vacuo* with the aid of a rotary evaporator. The residue was recrystallized using CH_2Cl_2 and hexanes as solvents to afford the title compound as a white amorphous solid (1.86 g, 5.83 mmol, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 9.2 Hz, 2 H), 7.91 (d, *J* = 8.7 Hz, 2 H), 7.81 (d, *J* = 7.7 Hz, 2 H), 7.62 (d, *J* = 7.4 Hz, 1 H), 7.50 (d, *J* = 7.3 Hz, 2 H), 7.17 (d, *J* = 8.7 Hz, 2 H), 7.14 (d, *J* = 9.2 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.3, 161.9, 158.7, 143.5, 137.5, 134.2, 132.7, 132.6, 130.0, 128.5, 126.2, 119.5, 118.5. **HRMS** (ESI): Calcd for $C_{19}H_{14}NO_4$ [M+H]: 320.0923; Found: 320.0922. **Mp:** 121-123 °C. **R_f** = 0.66 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 1646, 1586, 1510, 1350, 1283, 1252, 1166, 843.

Amide Synthesis via Mn-Mediated Reductive Transamidation of Tertiary Amides.

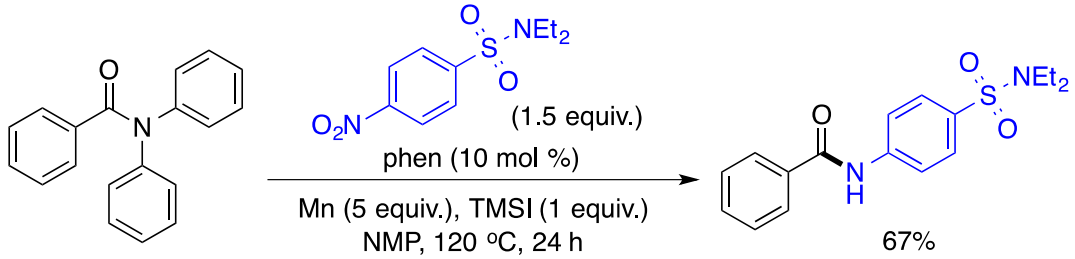
Manganese-Mediated Reductive Transamidation of Tertiary Amide with Nitroarene (General Procedure C). An oven-dried 20 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with manganese powder (Mn, 5 equiv., 2.5 mmol, 138 mg), tertiary amide (1 equiv., 0.50 mmol), nitroarene (1.5 equiv., 0.75 mmol), and 1,10-phenanthroline (phen, 10 mol %, 9.0 mg). The tube was degassed *in vacuo* and then backfilled with argon gas for three times. *N*-Methylpyrrolidone solvent (NMP, 1.0 mL) followed by iodotrimethylsilane (TMSI, 1 equiv., 0.50 mmol, 71 μL) were then transferred into the reaction mixture under the argon atmosphere. The resulting mixture was stirred at 120 ^{o}C in a preheated oil bath for 24 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 KOH solution (~1 M (aq), ~30 mL), washed with saturated NaCl solution, dried with anhydrous $MgSO_4$, and then concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography using a solvent mixture (hexanes, EtOAc, Et_3N) as an eluent to afford the purified amide product.

Manganese-Mediated Reductive Transamidation of Tertiary Amide with Nitroarene (General Procedure D). In a nitrogen-filled glove box, an oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with manganese powder (Mn, 5 equiv., 1.75 mmol, 96 mg), tertiary amide (1 equiv., 0.35 mmol), nitroarene (1.5 equiv., 0.525 mmol), 1,10-phenanthroline (phen, 10 mol %, 6.3 mg), *N*-methylpyrrolidone solvent (NMP, 0.7 mL), and iodotrimethylsilane (TMSI, 1 equiv., 50 μL). The resulting mixture was stirred at 120 ^{o}C in a preheated oil bath for 24 h. After the reaction, the reaction mixture was cooled down to room temperature. The reaction mixture was acidified with saturated NH_4Cl solution (~5 mL) and then neutralized with saturated $NaHCO_3$ solution (~10 mL). The crude product in the aqueous fraction was extracted with ethyl acetate (EtOAc, ~20 mL). The aqueous fraction was further washed with EtOAc (3 x ~10 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by preparative thin-layer chromatography (TLC) using a solvent mixture (hexanes, EtOAc, CH_2Cl_2) as an eluent to afford the purified amide product.

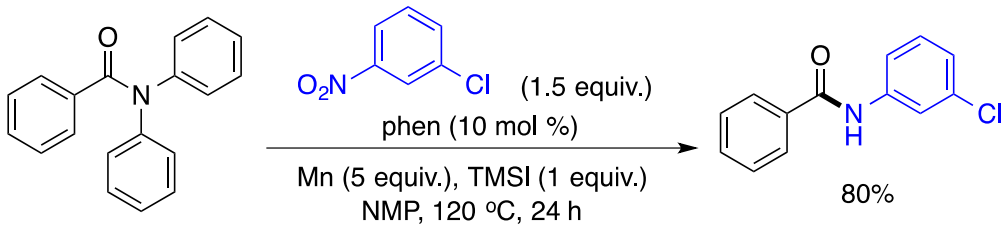
Note: The main difference of procedures **C** and **D** is the conditions for inert atmosphere. Procedure **C** useed argon as the protective gas for reactions in Schlenk tubes, while procedure **D** used glovebox filled with N_2.



***N*-(4-(1*H*-Pyrrol-1-yl)phenyl)benzamide (3a).**[34] Following the general procedure C, the title compound was prepared using *N*,*N*-diphenylbenzamide (1 equiv, 0.50 mmol, 137 mg) and 1-(4-nitrophenyl)-1*H*-pyrrole (1.5 equiv, 0.75 mmol, 141 mg) using hexanes/EtOAc/NEt_3 (90:10:1) and then hexanes/EtOAc/NEt_3 (80:20:1) as an eluent to afford the title compound as a brown amorphous solid (94 mg, 72%). **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.34 (s, 1 H), 7.98 (d, *J* = 6.7 Hz, 2 H), 7.88 (d, *J* = 8.0 Hz, 2 H), 7.62-7.51 (m, 5 H), 7.34 (s, 2 H), 6.26 (s, 2 H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 165.4, 136.5, 135.7, 134.8, 131.6, 128.4, 127.6, 121.3, 119.5, 118.8, 110.2. **HRMS** (ESI): Calcd for $C_{17}H_{15}N_2O$ [M+H]: 263.1184; Found: 263.1190.

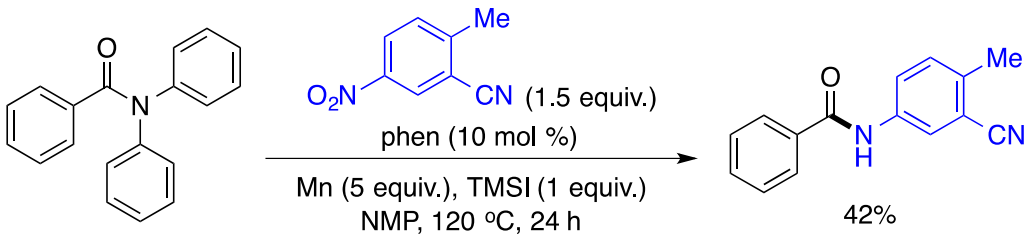


***N*-(4-(*N*,*N*-diethylsulfamoyl)phenyl)benzamide (3b).** Following the general procedure C, the title compound was prepared using *N*,*N*-diphenylbenzamide (1 equiv, 0.50 mmol, 194 mg) and *N*,*N*-diethyl-4-nitrobenzenesulfonamide (1.5 equiv, 0.75 mmol, 141 mg) using hexanes/EtOAc/NEt_3 (90:10:1) and then hexanes/EtOAc/NEt_3 (70:30:1) as an eluent to afford the title compound as an off-white amorphous solid (112 mg, 67%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.84 (s, 1 H), 7.89 (d, *J* = 7.6 Hz, 2 H), 7.83 (d, *J* = 8.5 Hz, 2 H), 7.67 (d, *J* = 8.4 Hz, 2 H), 7.52 (t, *J* = 7.3 Hz, 1 H), 7.41 (d, *J* = 7.6 Hz, 2 H), 3.18 (q, *J* = 7.1 Hz, 4 H), 1.09 (d, *J* = 7.2 Hz, 6 H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 166.5, 142.1, 134.9, 134.2, 132.3, 128.8, 128.0, 127.4, 120.2, 42.1, 14.2. **HRMS** (ESI): Calcd for $C_{17}H_{21}N_2O_3S$ [M+H]: 333.1273; Found: 333.1265. **Mp:** 104-106 °C. **R_f** = 0.33 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 2360, 1666, 1593, 1523, 1399, 1329, 1151, 1021, 938, 832.

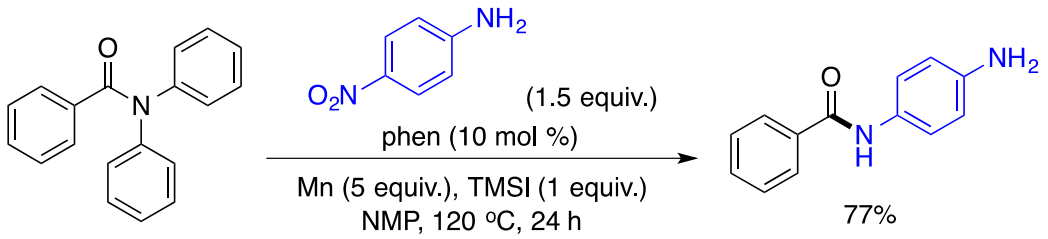


***N*-(3-chlorophenyl)benzamide (3c).**[35] Following the general procedure C, the title compound was prepared using *N*,*N*-diphenylbenzamide (1 equiv, 0.50 mmol, 137 mg) and 3-chloronitrobenzene (1.5

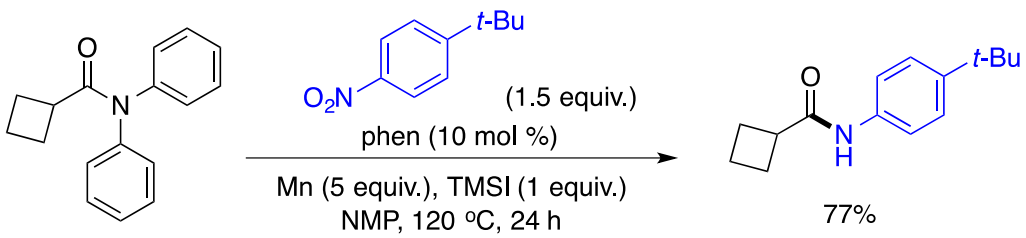
equiv, 0.75 mmol, 118 mg) using hexanes/EtOAc/NEt_3 (90:10:1) and then hexanes/EtOAc/NEt_3 (80:20:1) as an eluent to afford the title compound as an off-white amorphous solid (93 mg, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (s, 1 H), 7.84 (d, *J* = 7.4 Hz, 2 H), 7.77 (s, 1 H), 7.55 (t, *J* = 7.3 Hz, 1 H), 7.49-7.45 (ovrlp, 3 H), 7.27 (t, *J* = 8.1 Hz, 1 H), 7.12 (d, *J* = 7.9 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.4, 139.2, 134.6, 134.5, 132.1, 130.0, 128.8, 127.2, 124.6, 120.7, 118.6.



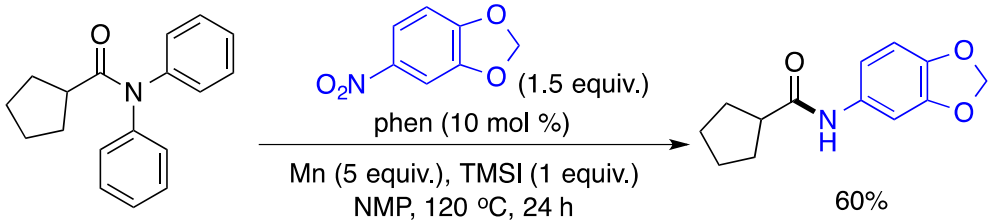
***N*-(3-Cyano-4-methylphenyl)benzamide (3d).** Following the general procedure C, the title compound was prepared using *N*,*N*-diphenylbenzamide (1 equiv, 0.50 mmol, 137 mg) and 2-methyl-5-nitrobenzonitrile (1.5 equiv, 0.75 mmol, 122 mg) using hexanes/EtOAc/NEt_3 (90:10:1) and then hexanes/EtOAc/NEt_3 (30:70:1) as an eluent to afford the title compound as a pale-yellow amorphous solid (50 mg, 42%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.05 (s, 1 H), 8.03 (d, *J* = 2.0 Hz, 1 H), 7.87 (d, *J* = 7.3 Hz, 2 H), 7.71 (dd, *J* = 8.4 Hz, *J* = 2.1 Hz, 1 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.50 (t, *J* = 7.7 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 2.51 (s, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 166.0, 138.1, 136.8, 134.8, 132.5, 131.2, 129.2, 127.4, 124.8, 123.9, 118.1, 113.5, 20.1. **HRMS** (ESI): Calcd for $C_{15}H_{13}N_2O$ [M+H]: 237.1028; Found: 237.1040. **Mp:** 174-176 °C. **R_f** = 0.50 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 3344, 2363, 2223, 1652, 1580, 1527, 1445, 1401, 1311, 1253, 833.



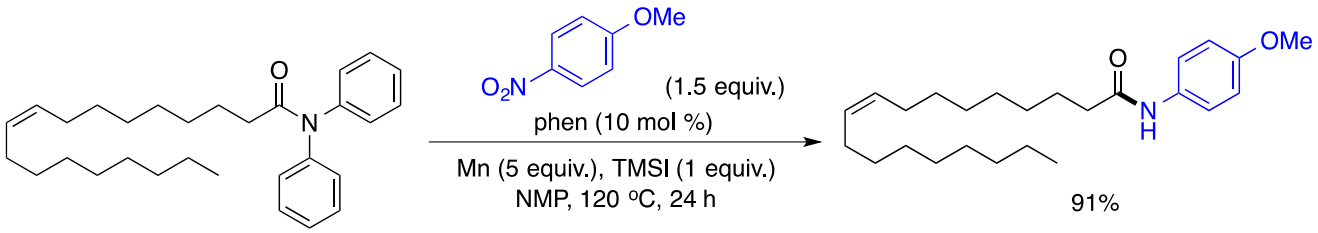
***N*-(4-aminophenyl)benzamide (3e).**[36] Following the general procedure C, the title compound was prepared using *N*,*N*-diphenylbenzamide (1 equiv, 0.50 mmol, 137 mg) and 4-nitroaniline (1.5 equiv, 0.75 mmol, 104 mg) using hexanes/EtOAc/NEt_3 (90:10:1) and then hexanes/EtOAc/NEt_3 (20:80:1) as an eluent to afford the title compound as a brown amorphous solid (81 mg, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 6.8 Hz, 2 H), 7.67 (s, 1 H), 7.55 (t, *J* = 6.8 Hz, 1 H), 7.47 (t, *J* = 7.2 Hz, 2 H), 7.40 (d, *J* = 7.6 Hz, 2 H), 6.69 (d, *J* = 8.0 Hz, 2 H), 3.63 (br s, 2 H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.7, 143.7, 135.3, 131.6, 129.4, 128.8, 127.1, 122.5, 115.6.



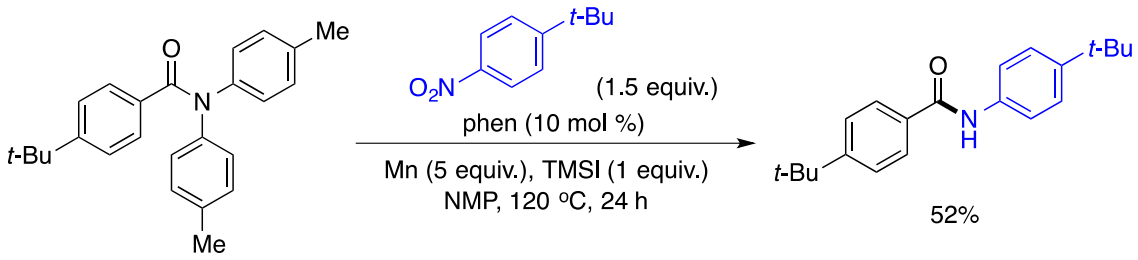
***N*-(4-(*tert*-Butyl)phenyl)cyclobutanecarboxamide (3f).** Following the general procedure C, the title compound was prepared using *N*,*N*-diphenylcyclobutanecarboxamide (1 equiv, 0.50 mmol, 126 mg) and 1-(*tert*-butyl)-4-nitrotoluene (1.5 equiv, 0.75 mmol, 127 μL) using hexanes/EtOAc/NEt_3 (90:10:1) and then hexanes/EtOAc/NEt_3 (80:20:1) as an eluent to afford the title compound as an off-white amorphous solid (89 mg, 77%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.43 (d, *J* = 8.2 Hz, 2 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.16 (s, 1 H), 3.14 (quint, *J* = 8.4 Hz, 1 H), 2.39-2.30 (m, 2 H), 2.23-2.15 (m, 2 H), 2.05-1.96 (m, 1 H), 1.92-1.81 (m, 1 H), 1.30 (s, 9 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 173.4, 147.3, 136.2, 126.1, 119.9, 41.2, 34.6, 31.5, 25.7, 18.4. **HRMS** (ESI): Calcd for $C_{15}H_{22}NO$ [M+H]: 232.1701; Found: 232.1713. **Mp:** 133-135 °C. **R_f** = 0.68 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 2959, 1658, 1597, 1529, 1494, 1312, 1258, 826.



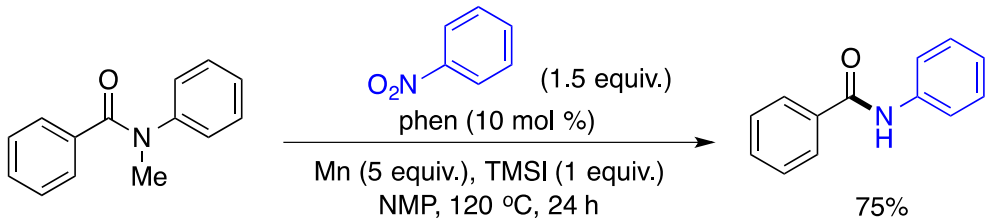
***N*-(Benzo[*d*][1,3]dioxol-5-yl)cyclopentanecarboxamide (3g).** Following the general procedure C, the title compound was prepared using *N*,*N*-diphenylcyclopentanecarboxamide (1 equiv, 0.50 mmol, 133 mg) and 5-nitrobenzo[*d*][1,3]dioxole (1.5 equiv, 0.75 mmol, 125 mg) using hexanes/EtOAc/NEt_3 (90:10:1) and then hexanes/EtOAc/NEt_3 (70:30:1) as an eluent to afford the title compound as a pale brown amorphous solid (70 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26 (s, 1 H), 7.09 (s, 1 H), 6.78 (d, *J* = 7.5 Hz, 1 H), 6.72 (d, *J* = 8.2 Hz, 1 H), 5.93 (s, 2 H), 2.63 (quint, *J* = 7.9 Hz, 1 H), 1.99-1.74 (m, 6 H), 1.63-1.54 (m, 2 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 174.8, 148.1, 144.3, 133.3, 113.2, 108.2, 103.0, 101.8, 47.1, 30.9, 26.4. **HRMS** (ESI): Calcd for $C_{13}H_{16}NO_3$ [M+H]: 234.1130; Found: 234.1136. **Mp:** 150-152 °C. **R_f** = 0.53 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 3266, 2363, 1646, 1534, 1504, 1489, 1446, 1215, 1038, 932.



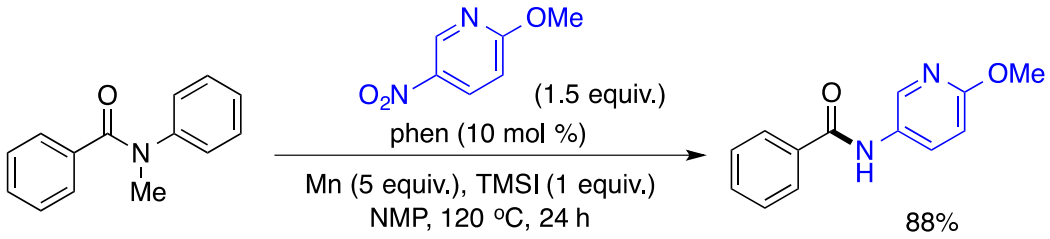
***N*-(4-methoxyphenyl)oleamide (3h).**[37] Following the general procedure C, the title compound was prepared using *N*,*N*-diphenyloleamide (1 equiv, 0.50 mmol, 217 mg) and 4-nitroanisole (1.5 equiv, 0.75 mmol, 115 mg) using hexanes/EtOAc/NEt_3 (90:10:1) and then hexanes/EtOAc/NEt_3 (70:30:1) as an eluent to afford the title compound as a brown amorphous solid (176 mg, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (s, 1 H), 7.40 (d, *J* = 8.6 Hz, 2 H), 6.80 (d, *J* = 8.7 Hz, 2 H), 5.37-5.31 (m, 2 H), 3.76 (s, 3 H), 2.30 (t, *J* = 7.4 Hz, 2 H), 2.08-1.92 (m, 4 H), 1.68 (quint, *J* = 6.0 Hz, 2 H), 1.40-1.20 (m, 20 H), 0.88 (t, *J* = 6.6 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.8, 156.3, 131.3, 130.0, 129.8, 122.0, 114.0, 55.5, 37.5, 32.0, 29.83, 29.80, 29.6, 29.42, 29.39, 29.2, 27.3, 27.2, 25.9, 22.8, 14.2 (21 carbon signals were observed out of expected 23 carbon signals)



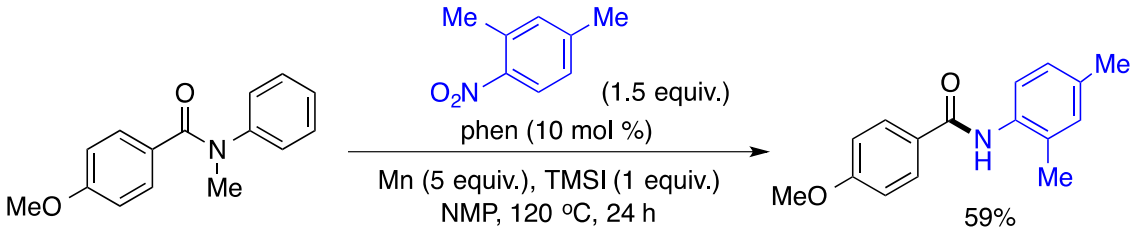
4-(*tert*-Butyl)-*N*-(4-(*tert*-butyl)phenyl)benzamide (3i). Following the general procedure D, the title compound was prepared using 4-(*tert*-butyl)-*N*,*N*-di-*p*-tolylbenzamide (1 equiv, 0.35 mmol, 125 mg) and 1-*tert*-butyl-4-nitrobzenene (1.5 equiv, 0.525 mmol, 94 mg) using hexanes/EtOAc/CH_2Cl_2 (80:15:5) as an eluent to afford the title compound as a brown amorphous solid (57 mg, 52%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (s, 1 H), 7.79 (d, *J* = 8.5 Hz, 2 H), 7.56 (d, *J* = 8.5 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.36 (d, *J* = 8.6 Hz, 2 H), 1.33 (s, 9 H), 1.31 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.8, 155.3, 147.5, 135.6, 132.3, 127.0, 126.0, 125.8, 120.1, 35.1, 34.5, 31.5, 31.3. **HRMS** (ESI): Calcd for $C_{21}H_{28}NO$ [M+H]: 310.2171; Found: 310.2169. **Mp:** 151-153 °C. **R_f** = 0.89 (EtOAc : petroleum ether = 1:2).



***N*-Phenylbenzamide (3j).**[38] Following the general procedure C, the title compound was prepared using *N*-methyl-*N*-phenylbenzamide (1 equiv, 0.50 mmol, 106 mg) and nitrobenzene (1.5 equiv, 0.75 mmol, 92 mg) using hexanes/EtOAc/NEt_3 (90:10:1) as an eluent to afford the title compound as a white amorphous solid (74 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (s, 1 H), 7.85 (d, *J* = 7.4 Hz, 2 H), 7.64 (d, *J* = 7.9 Hz, 2 H), 7.53 (t, *J* = 7.3 Hz, 1 H), 7.45 (d, *J* = 7.6 Hz, 2 H), 7.35 (d, *J* = 7.7 Hz, 2 H), 7.14 (t, *J* = 7.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.0, 138.1, 135.1, 131.9, 129.2, 128.9, 127.2, 124.1, 120.4.

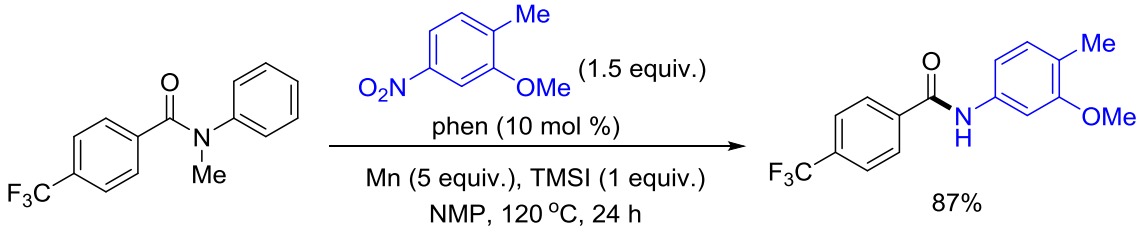


***N*-(6-Methoxypyridin-3-yl)benzamide (3k).**[39] Following the general procedure D, the title compound was prepared using *N*-methyl-*N*-phenylbenzamide (1 equiv, 0.35 mmol, 74 mg) and 2-methoxy-5-nitropridine (1.5 equiv, 0.525 mmol, 81 mg) using hexanes/EtOAc/CH_2Cl_2 (20:75:5) as an eluent to afford the title compound as a brown amorphous solid (70 mg, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.26 (s, 1 H), 8.02 (d, *J* = 8.8 Hz, 1 H), 7.90-7.85 (m, 3 H), 7.56 (d, *J* = 7.3 Hz, 1 H), 7.48 (d, *J* = 7.4 Hz, 2 H), 6.77 (d, *J* = 8.7 Hz, 1 H), 3.93 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): 166.2, 161.4, 139.2, 134.5, 132.9, 132.2, 128.9, 128.7, 127.2, 110.9, 53.8. **HRMS** (ESI): Calcd for $C_{13}H_{13}N_2O_2$ [M+H]: 229.0972; Found: 229.0974.



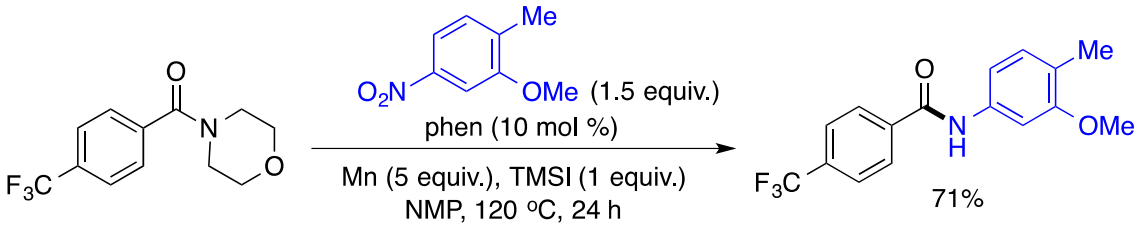
***N*-(2,4-dimethylphenyl)-4-methoxybenzamide (3l).**[34] Following the general procedure C, the title compound was prepared using 4-methoxy-*N*-methyl-*N*-phenylbenzamide (1 equiv, 0.50 mmol, 121 mg) and 2,4-dimethyl-1-nitrobenzene (1.5 equiv, 0.75 mmol, 113 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as an off-white amorphous solid (75 mg, 59%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.84 (d, *J* = 8.8 Hz, 2 H), 7.66-7.60 (m, 2 H), 7.06 (s, 1 H), 7.04 (d, *J* = 8.2 Hz, 1 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H), 2.32 (s, 3 H), 2.27 (s, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 165.4, 162.8, 135.5, 133.9, 131.5, 130.8, 129.3, 127.6, 127.5, 124.1, 114.2, 55.9, 21.0, 18.0. **HRMS** (ESI): Calcd for $C_{16}H_{18}NO_2$ [M+H]: 256.1338; Found: 256.1353.

***N*-(3-methoxy-4-methylphenyl)-4-(trifluoromethyl)benzamide (3m).**[34]

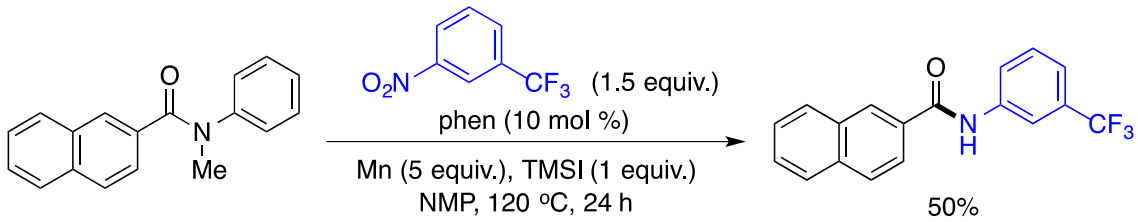


Reaction (1): Following the general procedure C, the title compound was prepared using *N*-methyl-*N*-phenyl-4-(trifluoromethyl)benzamide (1 equiv, 0.50 mmol, 140 mg) and 3-methoxy-4-

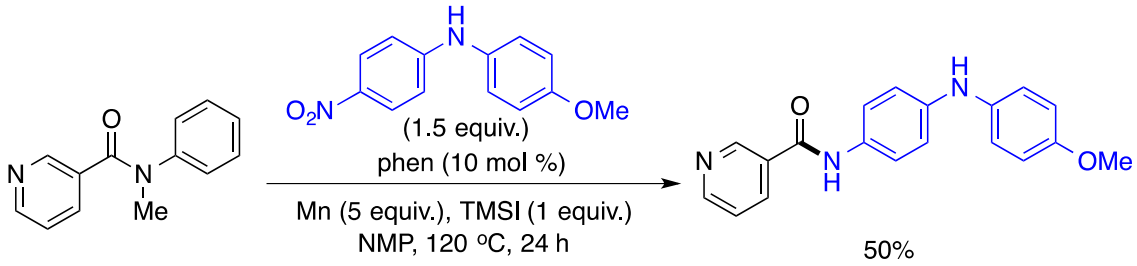
methylnitrobenzene (1.5 equiv, 0.75 mmol, 125 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as a pale-brown amorphous solid (135 mg, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 2 H), 7.87 (s, 1 H), 7.73 (d, *J* = 8.2 Hz, 2 H), 7.45 (s, 1 H), 7.09 (d, *J* = 7.9 Hz, 1 H), 6.91 (dd, *J* = 7.8 Hz, *J* = 1.3 Hz, 1 H), 3.85 (s, 3 H), 2.20 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.6, 158.2, 138.5, 136.6, 133.5 (q, $^2J_{CF}$ = 32.6 Hz), 130.7, 127.6, 125.9 (q, $^3J_{CF}$ = 3.7 Hz), 123.74 (q, $^1J_{CF}$ = 271.2 Hz), 123.67, 112.0, 103.4, 55.5, 15.9.



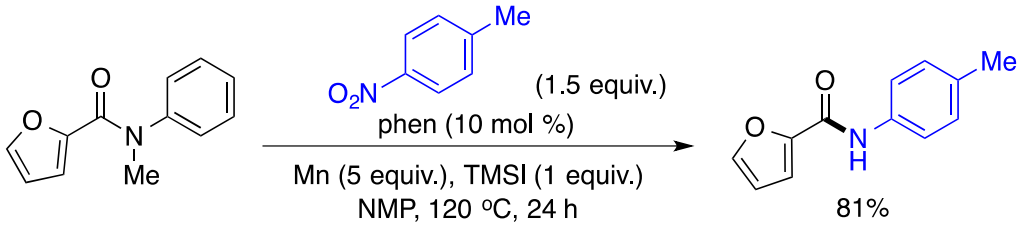
Reaction (2): Following the general procedure C, the title compound was prepared using morpholino(4-(trifluoromethyl)phenyl)methanone (1 equiv, 0.50 mmol, 130 mg) and 3-methoxy-4-methylnitrobenzene (1.5 equiv, 0.75 mmol, 125 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as an off-white amorphous solid (109 mg, 71%). Spectral and analytical data were identical to those reported for the same compound above.



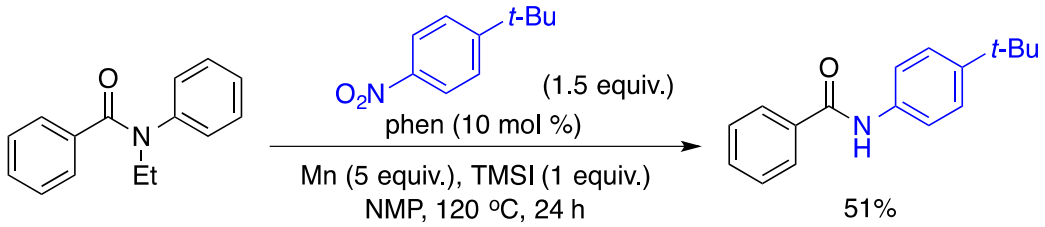
***N*-(3-(trifluoromethyl)phenyl)-2-naphthamide (3n).**[40] Following the general procedure C, the title compound was prepared using *N*-methyl-*N*-phenyl-2-naphthamide (1 equiv, 0.50 mmol, 131 mg) and 3-nitrobenzotrifluoride (1.5 equiv, 0.75 mmol, 143 mg) using hexanes/EtOAc/Et_3N (90:10:1) as an eluent to afford the title compound as a pale-brown amorphous solid (79 mg, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 (s, 1 H), 8.27 (s, 1 H), 7.98 (s, 1 H), 7.93-7.85 (m, 5 H), 7.60-7.52 (m, 2 H), 7.47 (t, *J* = 8.0 Hz, 1 H), 7.40 (d, *J* = 7.8 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 138.7, 135.1, 132.7, 131.7, 131.6 (q, $^2J_{CF}$ = 32.3 Hz), 129.8, 129.1, 129.0, 128.3, 128.1, 128.0, 127.8, 127.2 (q, $^1J_{CF}$ = 270.6 Hz), 123.52, 123.46 (q, $^4J_{CF}$ = 0.8 Hz), 121.2 (q, $^3J_{CF}$ = 3.8 Hz), 117.1 (q, $^3J_{CF}$ = 4.0 Hz).



***N*-(4-((4-methoxyphenyl)amino)phenyl)nicotinamide (3o).[41]** Following the general procedure C, the title compound was prepared using *N*-methyl-*N*-phenylnicotinamide (1 equiv, 0.70 mmol, 147 mg), 4-methoxy-*N*-(4-nitrophenyl)aniline (1.5 equiv, 1.05 mmol, 256 mg), phen (10 mol %, 12.6 mg), Mn (5 equiv, 3.5 mmol, 195 mg), NMP (1.4 mL), and TMSI (1 equiv, 0.70 mmol, 99 μL) using hexanes/EtOAc/Et_3N (60:40:1) and then hexanes/EtOAc (20:80) as an eluent to afford the title compound as an deep-brown amorphous solid (79 mg, 50%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ 10.25 (s, 1 H), 9.10 (s, 1 H), 8.74 (d, *J* = 3.8 Hz, 1 H), 8.28 (d, *J* = 7.9 Hz, 1 H), 7.84 (s, 1 H), 7.59-7.53 (m, 3 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 3.71 (s, 3 H). **^{13}C NMR** (150 MHz, DMSO-d_6): δ 163.3, 153.5, 151.9, 148.7, 141.5, 136.6, 135.3, 130.8, 130.2, 123.5, 122.0, 119.7, 115.2, 114.6, 55.2.

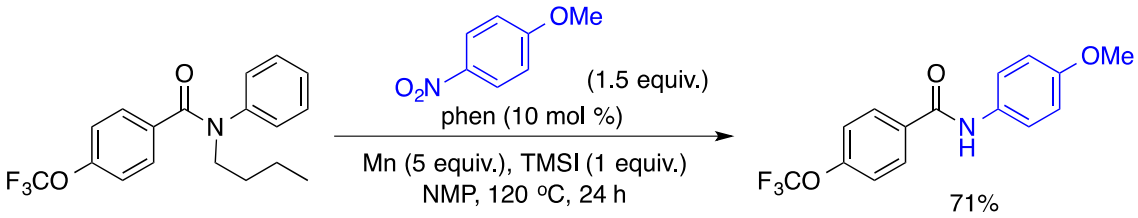


***N*-(*p*-Tolyl)furan-2-carboxamide (3p).[42]** Following the general procedure C, the title compound was prepared using *N*-methyl-*N*-phenylfuran-2-carboxamide (1 equiv, 0.50 mmol, 101 mg) and 4-nitrotoluene (1.5 equiv, 0.75 mmol, 103 mg) using hexanes/EtOAc/Et_3N (90:10:1) as an eluent to afford the title compound as a brown amorphous solid (85 mg, 81%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.07 (s, 1 H), 7.54 (dd, *J* = 1.6 Hz, *J* = 0.7 Hz, 1 H), 7.52 (d, *J* = 8.4 Hz, 2 H), 7.19-7.16 (m, 3 H), 6.57 (dd, *J* = 3.5 Hz, *J* = 1.8 Hz, 1 H), 2.33 (s, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 156.3, 148.5, 144.7, 135.4, 134.6, 129.9, 120.4, 115.1, 112.8, 21.0.



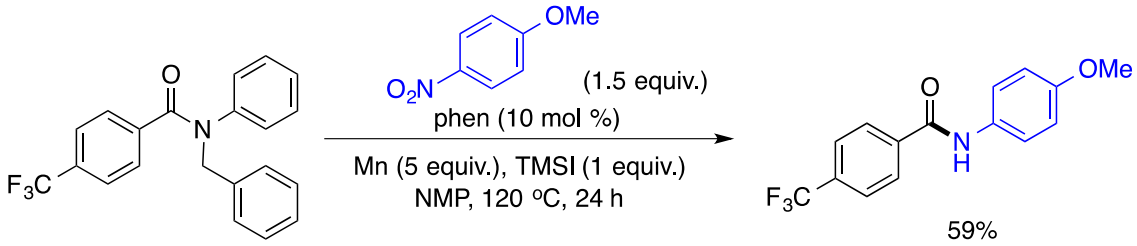
***N*-(4-(*tert*-butyl)phenyl)benzamide (3q).[43]** Following the general procedure C, the title compound was prepared using *N*-ethyl-*N*-phenylbenzamide (1 equiv, 0.50 mmol, 113 mg) and 1-*tert*-butyl-4-nitrobenzene (1.5 equiv, 0.75 mmol, 128 μL) using hexanes/EtOAc/Et_3N (95:5:1) as an eluent to afford the title compound as a brown amorphous solid (65 mg, 51%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.96 (s,

1 H), 7.86 (d, *J* = 7.2 Hz, 2 H), 7.58-7.53 (m, 3 H), 7.49 (t, *J* = 7.1 Hz, 2 H), 7.40 (d, *J* = 8.6 Hz, 2 H), 1.33 (s, 9 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 165.9, 147.9, 135.9, 135.6, 132.1, 129.1, 127.3, 126.2, 120.4, 34.7, 31.5.

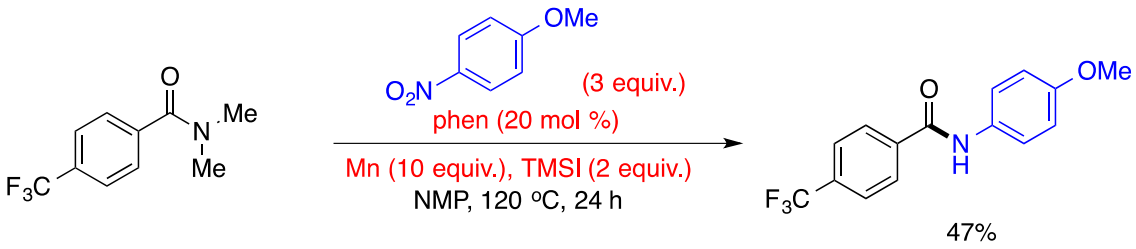


***N*-(4-methoxyphenyl)-4-(trifluoromethoxy)benzamide (3r).** Following the general procedure C, the title compound was prepared using *N*-butyl-*N*-phenyl-4-(trifluoromethoxy)benzamide (1 equiv, 0.50 mmol, 169 mg) and 4-nitroanisole (1.5 equiv, 0.75 mmol, 115 mg) using hexanes/EtOAc/Et_3N (90:10:1) as an eluent to afford the title compound as an off-white amorphous solid (111 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.2 Hz, 2 H), 7.70 (s, 1 H), 7.52 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 6.91 (d, *J* = 8.6 Hz, 2 H), 3.82 (s, 3 H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 163.9, 155.7, 150.4, 134.2, 132.0, 129.9, 122.0, 120.0 (q, $^1J_{CF}$ = 255.5 Hz), 120.7, 113.8, 55.2. **^{19}F NMR** (376 MHz, $CDCl_3$, $CFCl_3$ as external standard): δ -57.7. **HRMS (ESI):** Calcd for $C_{15}H_{13}F_3NO_3$ [M+H]: 312.0848; Found: 312.0859. **Mp:** 197-199 °C. **R_f** = 0.60 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 3440, 2362, 1644, 1515, 1209, 1160, 1104, 1031, 899, 863, 825.

***N*-benzyl-*N*-phenyl-4-(trifluoromethyl)benzamide (3s).[44]**

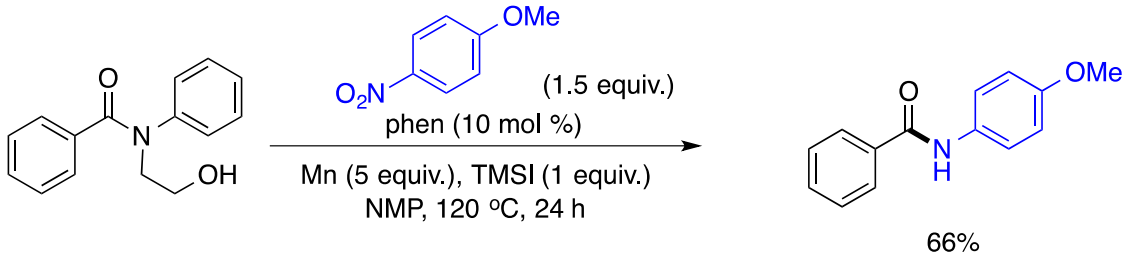


Reaction 1: Following the general procedure C, the title compound was prepared using *N*-benzyl-*N*-phenyl-4-(trifluoromethyl)benzamide (1 equiv, 0.50 mmol, 178 mg) and 4-nitroanisole (1.5 equiv, 0.75 mmol, 115 mg) using hexanes/EtOAc/Et_3N (90:10:1) as an eluent to afford the title compound as an off-white amorphous solid (87 mg, 59%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ 10.3 (s, 1 H), 8.14 (d, *J* = 7.9 Hz, 2 H), 7.90 (d, *J* = 8.0 Hz, 2 H), 7.68 (d, *J* = 8.6 Hz, 2 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 3.75 (s, 3 H). **^{13}C NMR** (150 MHz, DMSO-d_6): δ 163.9, 155.8, 138.8, 131.8, 131.2 (q, $^2J_{CF}$ = 31.6 Hz), 128.4, 125.3 (q, $^3J_{CF}$ = 3.7 Hz), 123.9 (q, $^1J_{CF}$ = 270.9 Hz), 122.0, 113.8, 55.2.

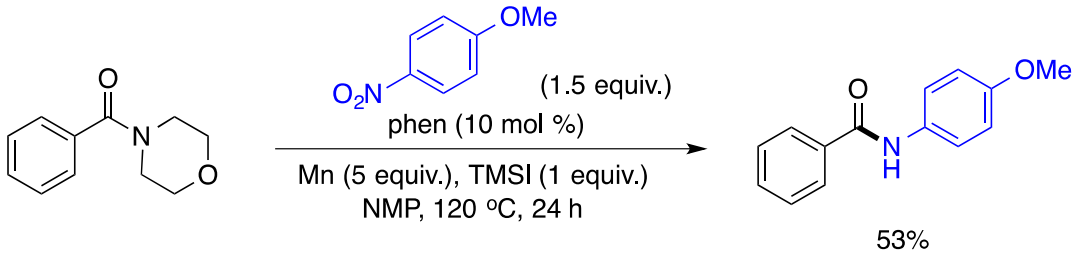


Reaction 2: Following the general procedure C, the title compound was prepared using *N*,*N*-dimethyl-4-(trifluoromethyl)benzamide (1 equiv, 0.50 mmol, 109 mg), 4-nitroanisole (3 equiv, 1.5 mmol, 231 mg), phen (20 mol %, 18 mg), Mn (10 equiv, 276 mg), and TMSI (2 equiv, 143 μL) using hexanes/EtOAc/Et_3N (90:10:1) as an eluent to afford the title compound as a brown amorphous solid (69 mg, 47%). Spectral and analytical data were identical to those reported for the same compound above.

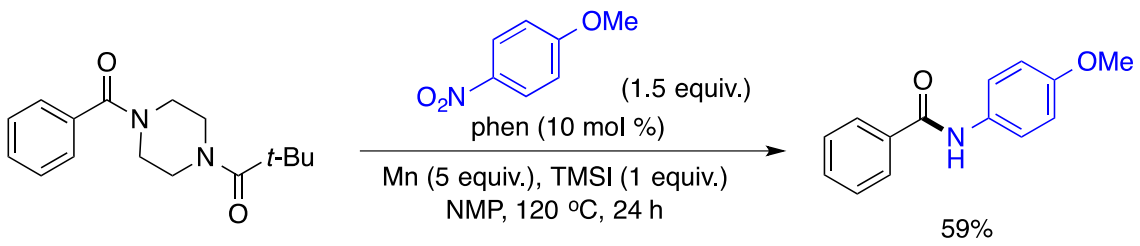
***N*-(4-methoxyphenyl)benzamide (3t).**[45]



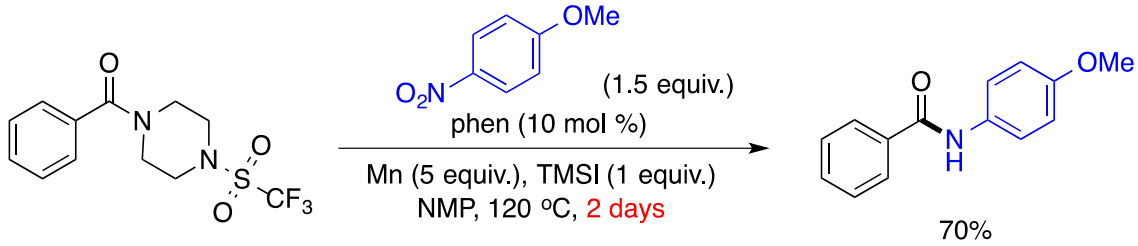
Reaction 1: Following the general procedure C, the title compound was prepared using *N*-(2-hydroxyethyl)-*N*-phenylbenzamide (1 equiv, 0.50 mmol, 121 mg) and 4-nitroanisole (1.5 equiv, 0.75 mmol, 115 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as a pale brown amorphous solid (75 mg, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87-7.83 (m, 3 H), 7.55-7.51 (m, 3 H), 7.46 (t, *J* = 7.5 Hz, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 3.81 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.8, 156.7, 135.1, 131.8, 131.1, 128.9, 127.1, 122.3, 114.3, 55.6.



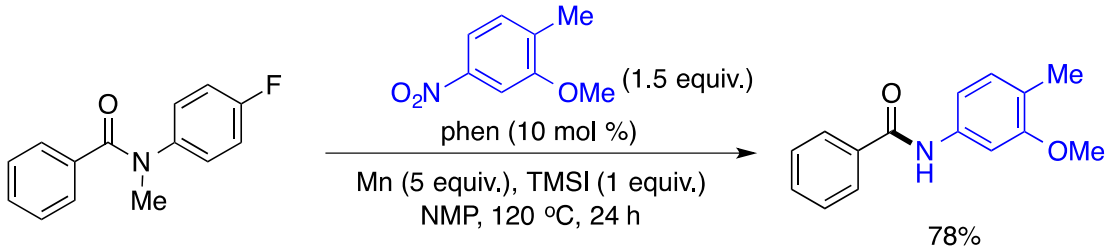
Reaction 2: Following the general procedure C, the title compound was prepared using morpholino(phenyl)methanone (1 equiv, 0.50 mmol, 96 mg) and 4-nitroanisole (1.5 equiv, 0.75 mmol, 115 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as an off-white amorphous solid (61 mg, 53%). Spectral and analytical data were identical to those reported for the same compound above.



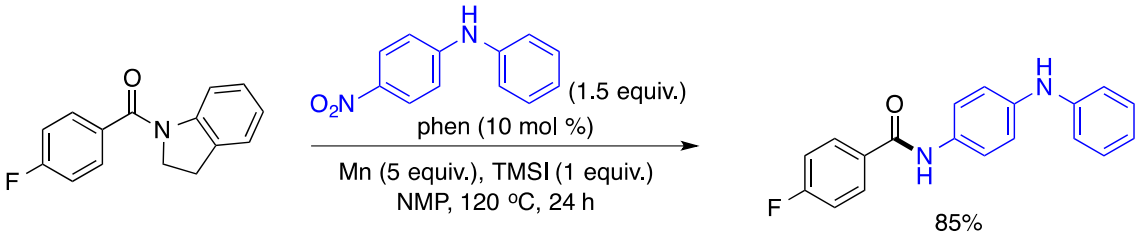
Reaction 3: Following the general procedure C, the title compound was prepared using 1-(4-benzoylpiperazin-1-yl)-2,2-dimethylpropan-1-one (1 equiv, 0.50 mmol, 137 mg), and 4-nitroanisole (1.5 equiv, 0.75 mmol, 115 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as an off-white amorphous solid (61 mg, 59%). Spectral and analytical data were identical to those reported for the same compound above.



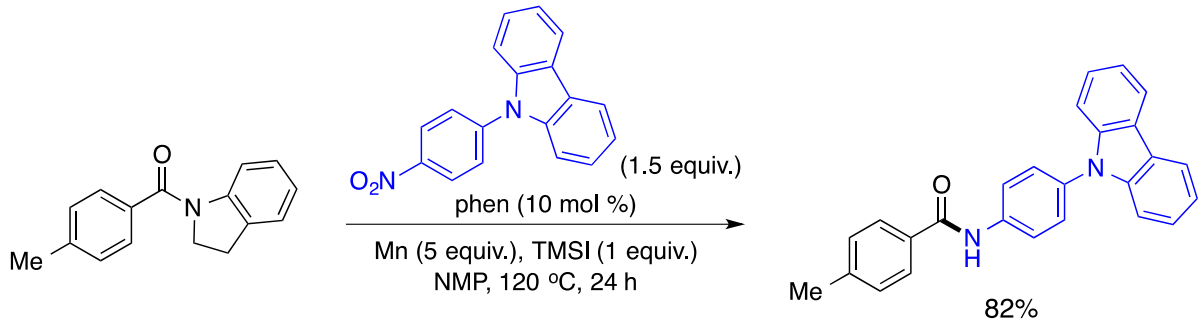
Reaction 4: Following the general procedure C, the title compound was prepared using phenyl(4-((trifluoromethyl)sulfonyl)piperazin-1-yl)methanone (1 equiv, 0.50 mmol, 161 mg) and 4-nitroanisole (1.5 equiv, 0.75 mmol, 115 mg) for 2 days using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as an off-white amorphous solid (80 mg, 70%). Spectral and analytical data were identical to those reported for the same compound above.



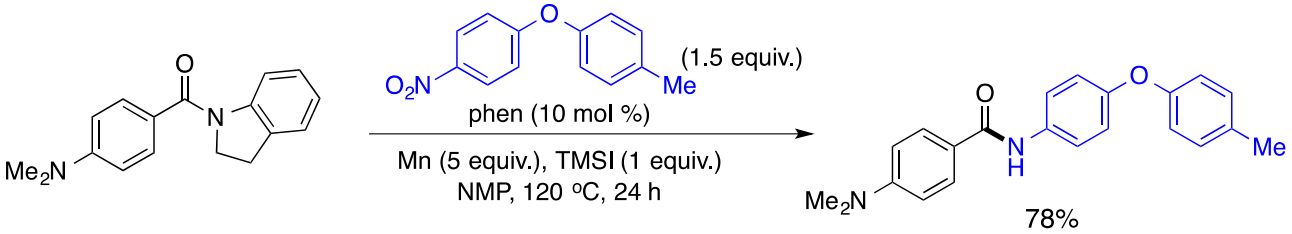
***N*-(3-methoxy-4-methylphenyl)benzamide (3u).**[40] Following the general procedure C, the title compound was prepared using *N*-(4-fluorophenyl)-*N*-methylbenzamide (1 equiv, 0.50 mmol, 115 mg) and 3-methoxy-4-methylnitrobenzene (1.5 equiv, 0.75 mmol, 125 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as a brown amorphous solid (95 mg, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.22 (s, 1 H), 7.83 (d, *J* = 7.6 Hz, 2 H), 7.50-7.44 (m, 2 H), 7.39 (t, *J* = 7.5 Hz, 2 H), 7.03 (d, *J* = 8.0 Hz, 1 H), 6.93 (d, *J* = 7.4 Hz, 1 H), 3.76 (s, 3 H), 2.17 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.0, 158.0, 137.1, 135.1, 131.7, 130.5, 128.7, 127.1, 122.9, 111.9, 103.3, 55.3, 15.9.



4-Fluoro-*N*-(4-(phenylamino)phenyl)benzamide (3v).[34] Following the general procedure D, the title compound was prepared using (4-fluorophenyl)(indolin-1-yl)methanone (1 equiv, 0.35 mmol, 84 mg) and 4-nitro-*N*-phenylaniline (1.5 equiv, 0.525 mmol, 112 mg) using hexanes/EtOAc/CH_2Cl_2 (60:35:5) as an eluent to afford the title compound as a brown amorphous solid (93 mg, 85%). **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.12 (s, 1 H), 8.09 (s, 1 H), 8.03 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HF}$ = 5.7 Hz, 2 H), 7.63 (d, J = 8.0 Hz, 2 H), 7.35 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HF}$ = 8.3 Hz, 2 H), 7.21 (t, J = 7.0 Hz, 2 H), 7.09-7.03 (m, 4 H), 6.78 (t, J = 6.7 Hz, 1 H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 163.93 (d, $^1J_{CF}$ = 246.6 Hz), 163.90, 143.9, 139.4, 131.7, 131.5 (d, $^4J_{CF}$ = 2.2 Hz), 130.2 (d, $^3J_{CF}$ = 8.7 Hz), 129.1, 121.8, 119.1, 117.4, 116.0, 115.2 (d, $^2J_{CF}$ = 21.7). **HRMS** (ESI): Calcd for $C_{19}H_{16}FN_2O$ [M+H]: 307.1247; Found: 307.1247.

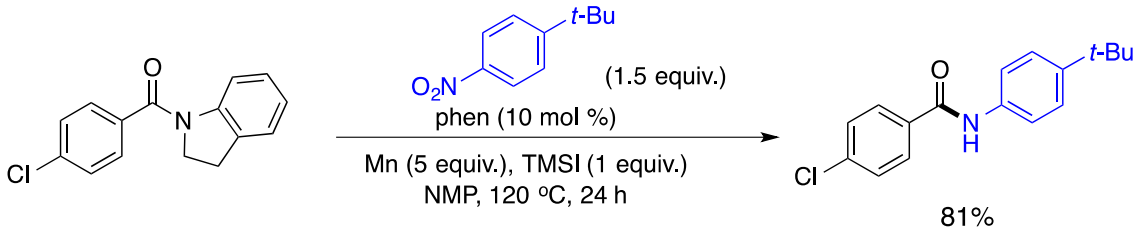


***N*-(4-(9*H*-Carbazol-9-yl)phenyl)-4-methylbenzamide (3w).**[40] Following the general procedure C, the title compound was prepared using indolin-1-yl(*p*-tolyl)methanone (1 equiv, 0.50 mmol, 119 mg) and 9-(4-nitrophenyl)-9*H*-carbazole (1.5 equiv, 0.75 mmol, 216 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (70:30:1) as an eluent to afford the title compound as a pale-brown amorphous solid (154 mg, 82%). **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.45 (s, 1 H), 8.25 (d, J = 7.6 Hz, 2 H), 8.10 (d, J = 8.5 Hz, 2 H), 7.94 (d, J = 7.8 Hz, 2 H), 7.60 (d, J = 8.5 Hz, 2 H), 7.44 (t, J = 7.6 Hz, 2 H), 7.40-7.36 (m, 4 H), 7.29 (t, J = 7.3 Hz, 2 H), 2.41 (s, 3 H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 165.6, 141.7, 140.3, 138.7, 132.0, 131.9, 129.0, 127.8, 127.0, 126.2, 122.6, 121.6, 120.5, 119.9, 109.6, 21.0.

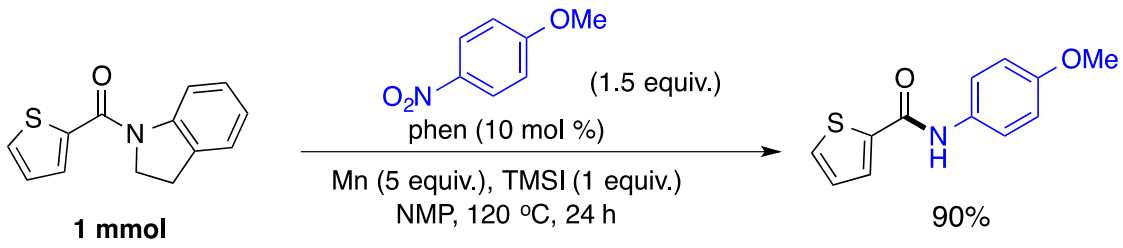


4-(Dimethylamino)-*N*-(4-(*p*-tolyloxy)phenyl)benzamide (3x). Following the general procedure C, the

title compound was prepared using (4-(dimethylamino)phenyl)(indolin-1-yl)methanone (1 equiv, 0.50 mmol, 133 mg) and 1-methyl-4-(4-nitrophenoxy)benzene (1.5 equiv, 0.75 mmol, 172 mg) using hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as a pale-brown amorphous solid (135 mg, 78%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.08 (s, 1 H), 7.79 (d, *J* = 8.1 Hz, 2 H), 7.60 (d, *J* = 8.1 Hz, 2 H), 7.15 (d, *J* = 7.7 Hz, 2 H), 6.95 (d, *J* = 8.2 Hz, 2 H), 6.90 (d, *J* = 7.9 Hz, 2 H), 6.68 (d, *J* = 8.2 Hz, 2 H), 3.02 (s, 6 H), 2.33 (s, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 165.9, 155.6, 154.0, 153.1, 134.5, 133.1, 130.6, 129.0, 122.3, 121.5, 119.3, 118.9, 111.4, 40.3, 20.8. **HRMS** (ESI): Calcd for $C_{22}H_{23}N_2O_2$ [M+H]: 347.1760; Found: 347.1761. **Mp:** 141-143 °C. **R_f** = 0.46 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 3490, 2919, 1728, 1637, 1611, 1501, 1261, 1226, 1193, 821.

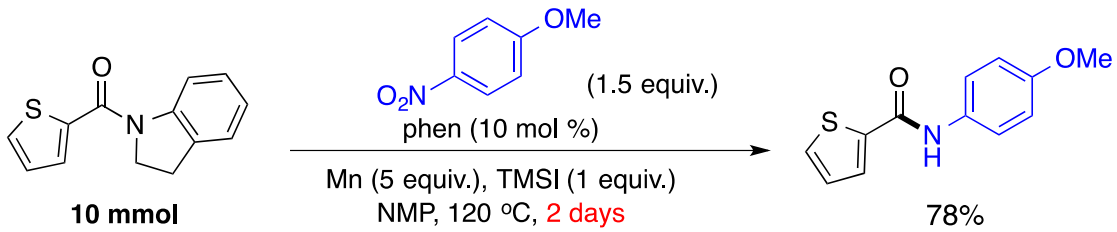


***N*-(4-(*tert*-Butyl)phenyl)-4-chlorobenzamide (3y).**[34] Following the general procedure D, the title compound was prepared using (4-chlorophenyl)(indolin-1-yl)methanone (1 equiv, 0.35 mmol, 90 mg) and 1-*tert*-butyl-4-nitrobenzene (1.5 equiv, 0.525 mmol, 94 mg) using hexanes/EtOAc/CH_2Cl_2 (70:25:5) as an eluent to afford the title compound as a white amorphous solid (81 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88 (s, 1 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 7.53 (d, *J* = 8.5 Hz, 2 H), 7.41 (d, *J* = 8.4 Hz, 2 H), 7.37 (d, *J* = 8.6 Hz, 2 H), 1.32 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.8, 148.0, 138.1, 135.2, 133.6, 129.1, 128.6, 126.1, 120.3, 34.6, 31.5. **HRMS** (ESI): Calcd for $C_{17}H_{19}ClNO$ [M+H]: 288.1155; Found: 288.1154.

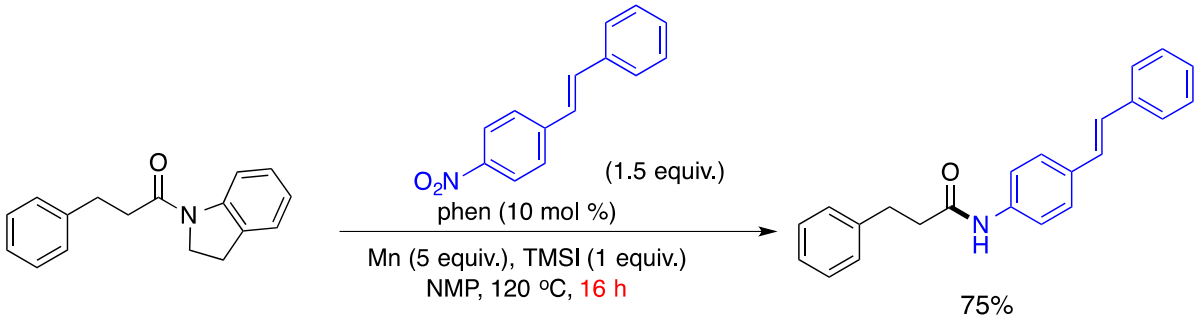


***N*-(4-methoxyphenyl)thiophene-2-carboxamide (3z).**[46]

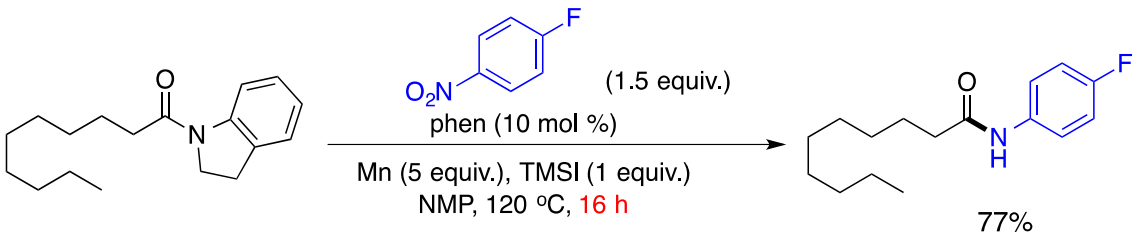
(i) 0.5 mmol: Following the general procedure C, the title compound was prepared using indolin-1-yl(thiophen-2-yl)methanone (1 equiv, 0.50 mmol, 115 mg) and 4-nitroanisole (1.5 equiv, 0.75 mmol, 115 mg) using hexanes/EtOAc/Et_3N (70:30:1) as an eluent to afford the title compound as an off-white amorphous solid (105 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (s, 1 H), 7.62 (d, *J* = 3.3 Hz, 1 H), 7.51-7.48 (m, 3 H), 7.07 (dd, *J* = 4.8 Hz, *J* = 3.8 Hz, 1 H), 6.85 (d, *J* = 9.0 Hz, 2 H), 3.78 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.2, 156.8, 139.5, 130.7, 130.6, 128.5, 127.9, 122.5, 114.3, 55.6.



(ii) 10 mmol: Following the general procedure C, the title compound was prepared using indolin-1-yl(thiophen-2-yl)methanone (1 equiv, 10 mmol, 2.29 g), 4-nitroanisole (1.5 equiv, 15 mmol, 2.30 g), phen (10 mol %, 180 mg), Mn (5 equiv, 50 mmol, 2.75 g), NMP (20 mL), and TMSI (1 equiv, 10 mmol, 1.43 mL) in a 100 mL round-bottom Schlenk flask for reaction time of 2 days using hexanes/EtOAc/Et_3N (70:30:1) as an eluent to afford the title compound as an off-white amorphous solid (1.81 g, 78%). Spectral and analytical data were identical to those reported for the same compound above.

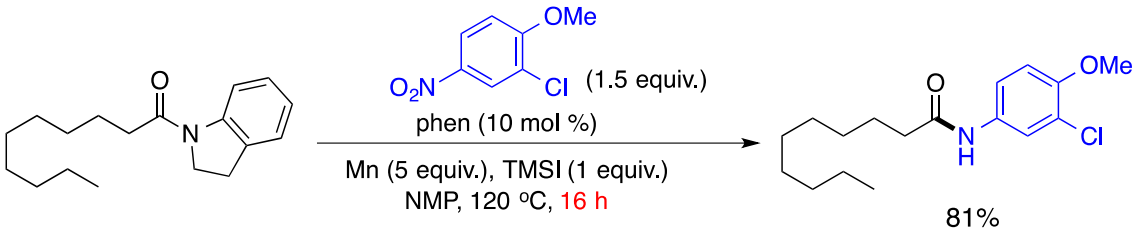


(*E*)-3-Phenyl-*N*-(4-styrylphenyl)propanamide (3aa).[40] Following the general procedure D, the title compound was prepared using 1-(indolin-1-yl)-3-phenylpropan-1-one (1 equiv, 0.35 mmol, 88 mg) and (*E*)-1-nitro-4-styrylbenzene (1.5 equiv, 0.525 mmol, 118 mg) for reaction time of 16 h using hexanes/EtOAc/CH_2Cl_2 (60:35:5) as an eluent to afford the title compound as a pale brown amorphous solid (86 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.1 Hz, 2 H), 7.47-7.41 (m, 4 H), 7.36-7.29 (m, 4 H), 7.27-7.21 (m, 4 H), 7.09 (s, 1 H), 7.05-7.02 (m, 2 H), 3.06 (t, *J* = 7.6 Hz, 2 H), 2.67 (t, *J* = 7.6 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.4, 137.5, 137.3, 133.6, 128.8, 128.6, 128.1, 127.7, 127.2, 126.6, 126.5, 120.1, 39.7, 31.7 (14 carbon signals were observed out of expected 17 carbon signals).

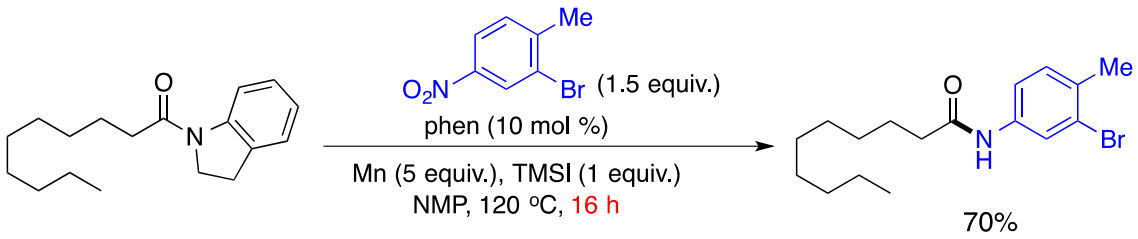


1-(4-Fluorophenyl)undecan-2-one (3ab). Following the general procedure D, the title compound was prepared using 1-(indolin-1-yl)decan-1-one (1 equiv, 0.35 mmol, 96 mg) and 1-fluoro-4-nitrobenzene (1.5 equiv, 0.525 mmol, 74 mg) for reaction time of 16 h using hexanes/EtOAc/CH_2Cl_2 (80:15:5) as an eluent to afford the title compound as a brown amorphous solid (71 mg, 77%). **^{1}H NMR** (400 MHz,

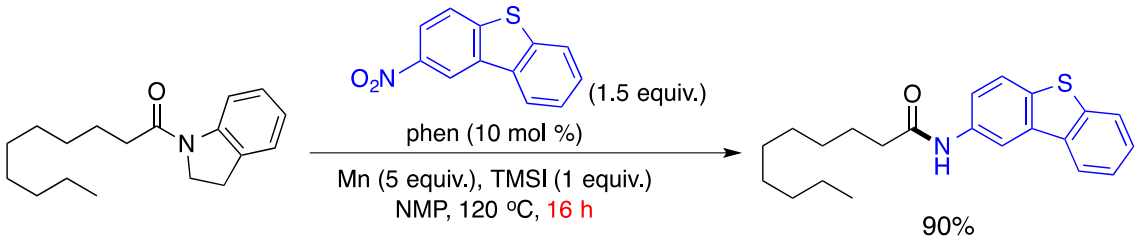
$CDCl_3$): δ 7.47 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HF}$ = 4.6 Hz, 2 H), 7.42 (s, 1 H), 6.99 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HF}$ = 8.0 Hz, 2 H), 2.33 (t, *J* = 7.0 Hz, 2 H), 1.71 (quint, *J* = 7.4 Hz, 2 H), 1.41-1.18 (m, 12 H), 0.88 (t, *J* = 7.2 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.2, 159.4 (d, $^1J_{CF}$ = 241.6 Hz), 134.1 (d, $^4J_{CF}$ = 1.9 Hz), 121.8 (d, $^3J_{CF}$ = 7.7 Hz), 115.7 (d, $^2J_{CF}$ = 22.2 Hz), 37.8, 32.0, 29.6, 29.5, 29.42, 29.40, 25.8, 22.8, 14.2. **HRMS** (ESI): Calcd for $C_{16}H_{25}FNO$ [M+H]: 266.1920; Found: 266.1924. **^{19}F NMR** (376 MHz, $CDCl_3$, $CFCl_3$ as external standard): δ -118.2. **Mp:** 79-81 °C. **R_f** = 0.70 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 2923, 2361, 1665, 1618, 1557, 1508, 1406, 1211, 835.



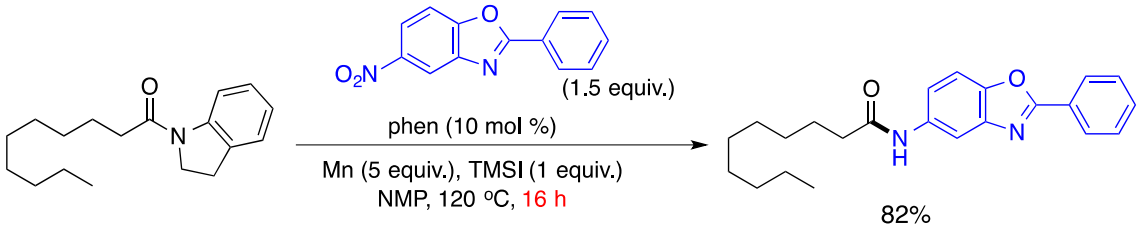
1-(3-Chloro-4-methoxyphenyl)undecan-2-one (3ac). Following the general procedure D, the title compound was prepared using 1-(indolin-1-yl)decan-1-one (1 equiv, 0.35 mmol, 96 mg) and 2-chloro-4-nitroanisole (1.5 equiv, 0.525 mmol, 99 mg) for reaction time of 16 h using hexanes/EtOAc/CH_2Cl_2 (60:35:5) as an eluent to afford the title compound as a brown amorphous solid (89 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 1.7 Hz, 1 H), 7.40-7.37 (ovlp, 2 H), 6.84 (d, *J* = 8.8 Hz, 1 H), 3.86 (s, 3 H), 2.32 (d, *J* = 7.6 Hz, 2 H), 1.70 (d, *J* = 7.2 Hz, 2 H), 1.38-1.22 (m, 12 H), 0.88 (t, *J* = 6.5 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.7, 151.9, 131.7, 122.7, 122.5, 119.8, 112.3, 56.5, 37.7, 32.0, 29.6, 29.5, 29.4, 25.8, 22.8, 14.2 (16 carbon signals were observed out of expected 17 carbon signals). **HRMS** (ESI): Calcd for $C_{17}H_{26}ClNO_2$ [M+H]: 312.1730; Found: 312.1725. **Mp:** 131-133 °C. **R_f** = 0.47 (EtOAc : petroleum ether = 1:2).



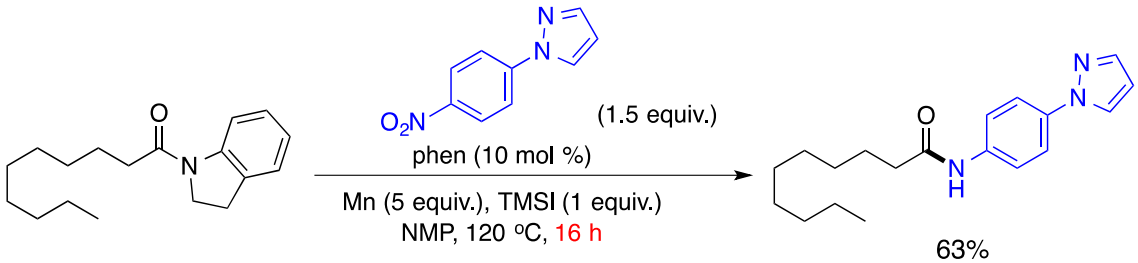
1-(3-Bromo-4-methylphenyl)undecan-2-one (3ad).[40] Following the general procedure D, the title compound was prepared using 1-(indolin-1-yl)decan-1-one (1 equiv, 0.35 mmol, 96 mg) and 2-bromo-4-nitrotoluene (1.5 equiv, 0.525 mmol, 113 mg) for reaction time of 16 h using hexanes/EtOAc/CH_2Cl_2 (80:15:5) as an eluent to afford the title compound as a deep brown amorphous solid (83 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (s, 1 H), 7.45 (s, 1 H), 7.34 (d, *J* = 7.7 Hz, 1 H), 7.13 (d, *J* = 8.2 Hz, 1 H), 2.36-2.29 (m, 5 H), 1.68 (quint, *J* = 7.3 Hz, 2 H), 1.36-1.21 (m, 12 H), 0.87 (t, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.8, 136.9, 133.6, 130.8, 124.8, 123.7, 119.0, 37.8, 32.0, 29.6, 29.5, 29.4, 25.7, 22.8, 22.4, 14.2 (16 carbon signals were observed out of expected 17 carbon signals).



1-(Dibenzo[*b*,*d*]thiophen-3-yl)undecan-2-one (3ae).[47] Following the general procedure D, the title compound was prepared using 1-(indolin-1-yl)decan-1-one (1 equiv, 0.35 mmol, 110 mg) and 3-nitrodibenzo[*b*,*d*]thiophene (1.5 equiv, 0.525 mmol, 94 mg) for reaction time of 16 h using hexanes/EtOAc/CH_2Cl_2 (70:25:5) as an eluent to afford the title compound as an off-white amorphous solid (111 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (s, 1 H), 8.00 (d, *J* = 7.7 Hz, 1 H), 7.81-7.76 (m, 2 H), 7.66 (d, *J* = 8.5 Hz, 1 H), 7.42-7.32 (m, 3 H), 2.37 (t, *J* = 7.7 Hz, 2 H), 1.73 (quint, *J* = 7.0 Hz, 2 H), 1.36-1.19 (m, 12 H), 0.87 (t, *J* = 6.2 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.1, 140.2, 136.2, 135.4, 135.2, 134.9, 126.9, 124.4, 122.95, 122.85, 121.9, 119.8, 113.2, 37.9, 32.0, 29.59, 29.55, 29.5, 29.4, 25.8, 22.8, 14.2.

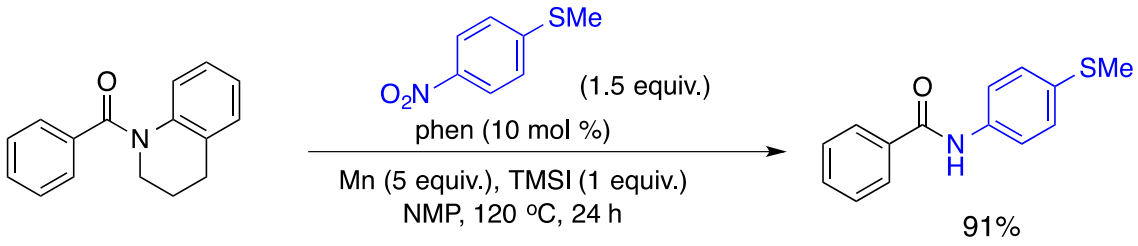


1-(2-Phenylbenzo[*d*]oxazol-5-yl)undecan-2-one (3af).[47] Following the general procedure D, the title compound was prepared using 1-(indolin-1-yl)decan-1-one (1 equiv, 0.35 mmol, 96 mg) and 2-phenyl-5-nitrobenzoxazole (1.5 equiv, 0.525 mmol, 126 mg) for reaction time of 16 h using hexanes/EtOAc/CH_2Cl_2 (70:25:5) as an eluent to afford the title compound as a deep brown amorphous solid (104 mg, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 6.8 Hz, 2 H), 7.90 (s, 1 H), 7.77 (s, 1 H), 7.56-7.45 (m, 5 H), 2.36 (t, *J* = 7.6 Hz, 2 H), 1.72 (quint, *J* = 7.5 Hz, 2 H), 1.36-1.24 (m, 12 H), 0.86 (d, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.9, 163.9, 147.6, 142.5, 135.2, 131.7, 129.0, 127.7, 127.1, 118.5, 111.7, 110.5, 37.8, 32.0, 29.6, 29.53, 29.46, 29.4, 25.8, 22.8, 14.2.

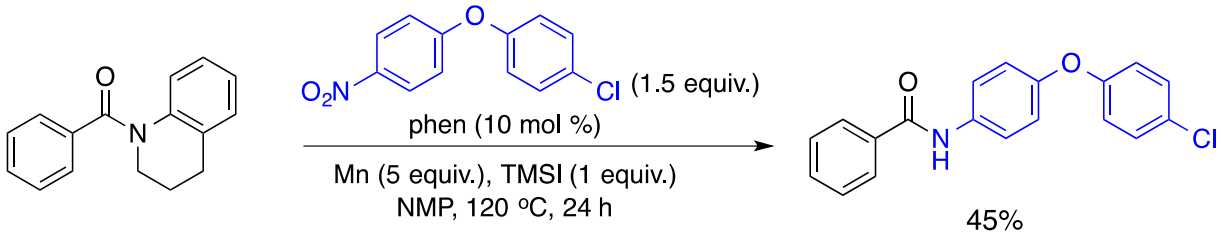


1-(4-(1*H*-Pyrazol-1-yl)phenyl)undecan-2-one (3ag).[47] Following the general procedure D, the title compound was prepared using 1-(indolin-1-yl)decan-1-one (1 equiv, 0.35 mmol, 96 mg) and 1-(4-nitrophenyl)-1*H*-pyrazole (1.5 equiv, 0.525 mmol, 99 mg) for reaction time of 16 h using

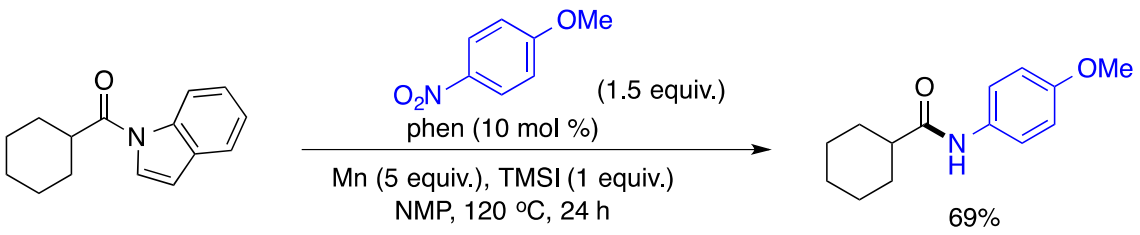
hexanes/EtOAc/CH_2Cl_2 (60:35:5) as an eluent to afford the title compound as a pale brown amorphous amorphous solid (69 mg, 63%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (s, 1 H), 7.70 (s, 1 H), 7.65-7.56 (m, 4 H), 7.47 (s, 1 H), 6.45 (s, 1 H), 2.36 (t, *J* = 7.6 Hz, 2 H), 1.72 (quint, *J* = 7.6 Hz, 2 H), 1.41-1.20 (m, 12 H), 0.88 (t, *J* = 7.0 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.7, 141.0, 136.6, 136.5, 126.9, 120.7, 120.0, 107.6, 37.9, 32.0, 29.6, 29.5, 29.43, 29.41, 25.7, 22.8, 14.2.



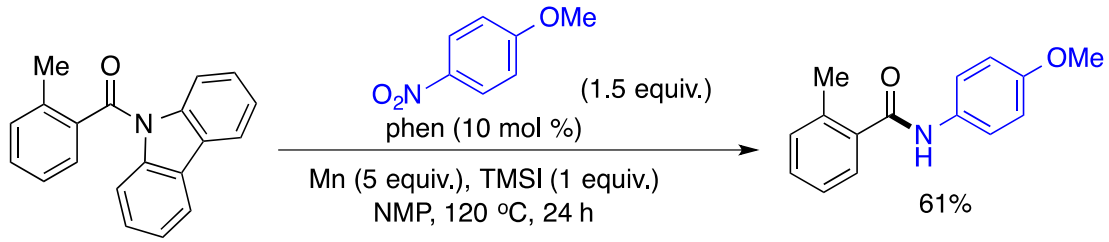
***N*-(4-(Methylthio)phenyl)benzamide (3ah).**[48] Following the general procedure C, the title compound was prepared using (3,4-dihydroquinolin-1(2*H*)-yl)(phenyl)methanone (1 equiv, 0.50 mmol, 119 mg) and 4-nitrothioanisole (1.5 equiv, 0.75 mmol, 127 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as a pale-brown amorphous solid (110 mg, 91%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.90 (s, 1 H), 7.86 (d, *J* = 7.2 Hz, 2 H), 7.61-7.55 (m, 3 H), 7.50 (t, *J* = 7.2 Hz, 2 H), 7.28 (d, *J* = 8.2 Hz, 2 H), 2.49 (s, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 165.8, 136.2, 135.4, 134.4, 132.2, 129.2, 128.2, 127.4, 121.2, 16.8.



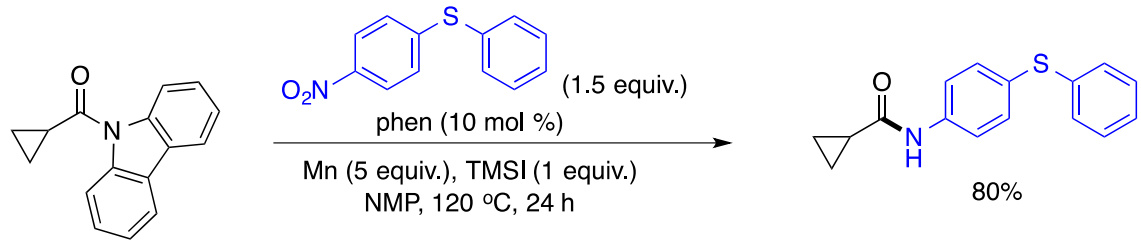
***N*-(4-(4-Chlorophenoxy)phenyl)benzamide (3ai).**[49] Following the general procedure C, the title compound was prepared using (3,4-dihydroquinolin-1(2*H*)-yl)(phenyl)methanone (1 equiv, 0.50 mmol, 119 mg) and 1-chloro-4-(4-nitrophenoxy)benzene (1.5 equiv, 0.75 mmol, 187 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as an off-white amorphous solid (73 mg, 45%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90 (s, 1 H), 7.87 (d, *J* = 7.4 Hz, 2 H), 7.61 (d, *J* = Hz, 2 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.28 (d, *J* = 8.8 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 6.93 (d, *J* = 8.8 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.9, 156.3, 153.4, 134.9, 133.9, 132.1, 129.9, 129.0, 128.2, 127.1, 122.2, 119.9, 119.8.



C**yclohexyl(1*H*-indol-1-yl)methanone (3aj).**[50] Following the general procedure C, the title compound was prepared using cyclohexyl(1*H*-indol-1-yl)methanone (1 equiv, 0.50 mmol, 114 mg) and 4-nitroanisole (1.5 equiv, 0.75 mmol, 115 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as a pale brown amorphous solid (81 mg, 69%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.46-7.35 (m, 3 H), 6.83 (d, *J* = 8.2 Hz, 2 H), 3.77 (s, 3 H), 2.19 (t, *J* = 11.2 Hz, 1 H), 1.95-1.87 (m, 2 H), 1.84-1.76 (m, 2 H), 1.71-1.64 (m, 1 H), 1.54-1.45 (m, 2 H), 1.36-1.19 (m, 3 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 174.6, 156.6, 131.9, 122.1, 114.3, 55.8, 46.6, 30.1, 26.2, 26.1.

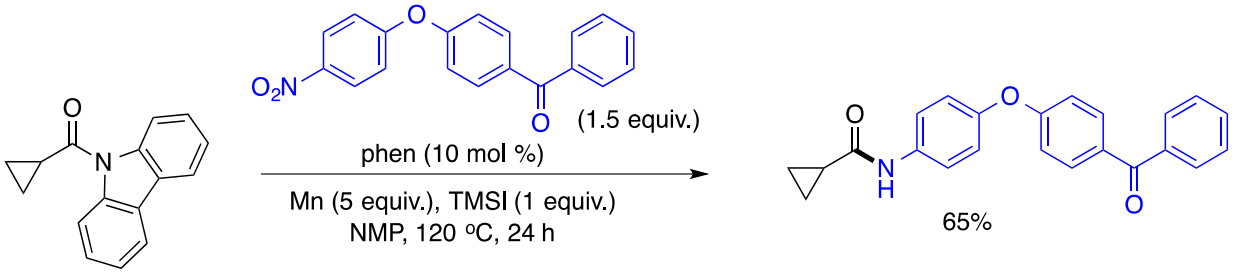


***N*-(4-methoxyphenyl)-2-methylbenzamide (3ak).**[44] Following the general procedure C, the title compound was prepared using (9*H*-carbazol-9-yl)(*o*-tolyl)methanone (1 equiv, 0.33 mmol, 93 mg), 4-nitroanisole (1.5 equiv, 0.495 mmol, 76 mg), phen (10 mol %, 6 mg), Mn (5 equiv, 91 mg), TMSI (1 equiv, 0.33 mmol, 47 μL), and NMP (0.7 mL) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as an off-white amorphous solid (74 mg, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (s, 1 H), 7.49 (d, *J* = 7.3 Hz, 2 H), 7.40 (d, *J* = 6.0 Hz, 1 H), 7.32 (t, *J* = 6.3 Hz, 1 H), 7.25-7.16 (m, 2 H), 6.86 (d, *J* = 7.3 Hz, 2 H), 3.79 (s, 3 H), 2.45 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.1, 156.6, 136.6, 136.4, 131.2, 130.2, 126.7, 125.9, 121.9, 114.3, 55.6, 19.9 (12 carbon signals were observed out of expected 13 carbon signals).

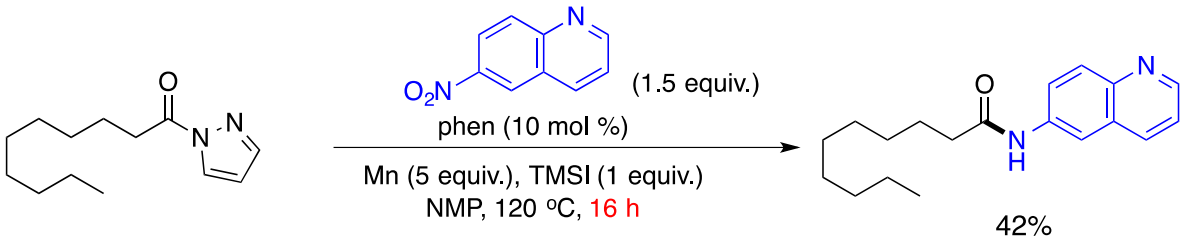


***N*-(4-(Phenylthio)phenyl)cyclopropanecarboxamide (3al).**[51] Following the general procedure C, the title compound was prepared using (9*H*-carbazol-9-yl)(cyclopropyl)methanone (1 equiv, 0.50 mmol, 118 mg) and (4-nitrophenyl)(phenyl)sulfane (1.5 equiv, 0.75 mmol, 173 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (70:30:1) as an eluent to afford the title compound as an off-

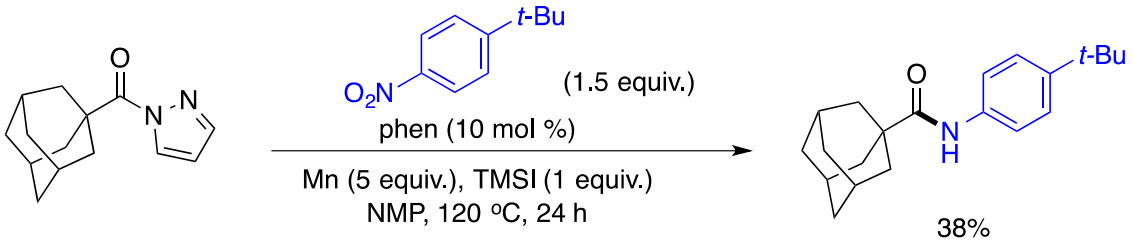
white amorphous solid (108 mg, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.70 (s, 1 H), 7.49 (d, *J* = 7.2 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.27-7.15 (m, 5 H), 1.55-1.45 (m, 1 H), 1.10-1.02 (m, 2 H), 0.89-0.79 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.3, 137.9, 137.1, 133.3, 129.7, 129.5, 129.2, 126.6, 120.6, 15.9, 8.3.



***N*-(4-(4-Benzoylphenoxy)phenyl)cyclopropanecarboxamide (3am).** Following the general procedure C, the title compound was prepared using (9*H*-carbazol-9-yl)(cyclopropyl)methanone (1 equiv, 0.50 mmol, 118 mg) and (4-(4-nitrophenoxy)phenyl)(phenyl)methanone (1.5 equiv, 0.75 mmol, 239 mg) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (60:40:1) as an eluent to afford the title compound as a pale brown amorphous solid (117 mg, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81-7.71 (m, 5 H), 7.60-7.55 (m, 3 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.05 (d, *J* = 8.6 Hz, 2 H), 6.99 (t, *J* = 8.5 Hz, 2 H), 1.59-1.48 (m, 1 H), 1.14-1.03 (m, 2 H), 0.90-0.79 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.8, 172.2, 162.1, 151.4, 138.0, 135.1, 132.6, 132.3, 131.8, 129.9, 128.4, 121.6, 121.0, 116.9, 15.8, 8.2. **HRMS (ESI):** Calcd for $C_{23}H_{20}NO_3$ [M+H]: 358.1443; Found: 358.1431. **Mp:** 175-177 °C. **R_f** = 0.30 (EtOAc : petroleum ether = 1:2). **IR** (neat, cm^{-1}): 3282, 1650, 1598, 1552, 1503, 1249, 939, 835.

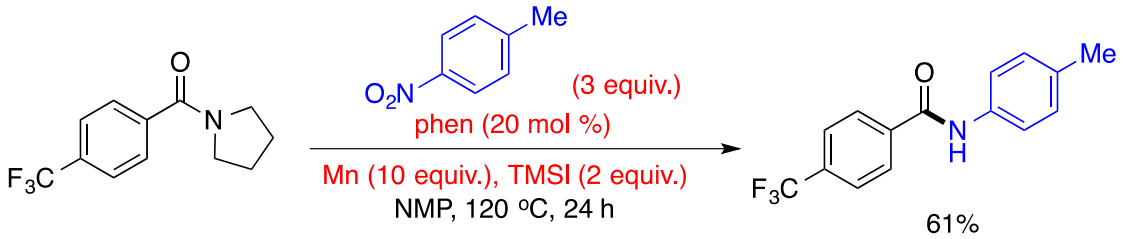


1-(Quinolin-6-yl)undecan-2-one (3an).[40] Following the general procedure D, the title compound was prepared using 1-(1*H*-pyrazol-1-yl)decan-1-one (1 equiv, 0.35 mmol, 78 mg) and 6-nitroquinoline (1.5 equiv, 0.525 mmol, 91 mg) for reaction time of 16 h using hexanes/EtOAc/CH_2Cl_2 (20:75:5) as an eluent to afford the title compound as a pale brown amorphous solid (43 mg, 42%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.81 (s, 1 H), 8.70 (s, 1 H), 8.45 (s, 1 H), 8.05 (d, *J* = 8.4 Hz, 1 H), 7.98 (d, *J* = 9.0 Hz, 1 H), 7.61 (d, *J* = 9.1 Hz, 1 H), 7.34 (dd, *J* = 8.4 Hz, *J* = 4.3 Hz, 1 H), 2.42 (t, *J* = 7.6 Hz, 2 H), 1.74 (quint, *J* = 7.7 Hz, 2 H), 1.36-1.17 (m, 12 H), 0.86 (t, *J* = 7.1 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.5, 149.2 145.4, 136.5, 136.1, 129.8, 129.0, 123.5, 121.7, 116.2, 37.8, 31.9, 29.50, 29.47, 29.39, 29.3, 25.8, 22.7, 14.2.

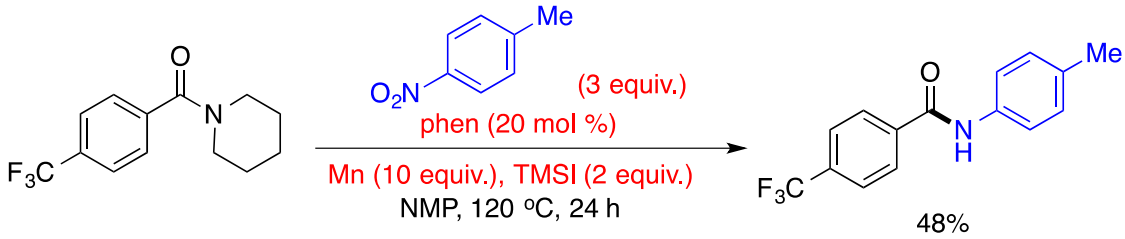


***N*-(4-(*tert*-butyl)phenyl)adamantane-1-carboxamide (3ao).**[40] Following the general procedure C, the title compound was prepared using (adamantan-1-yl)(1*H*-pyrazol-1-yl)methanone (1 equiv, 0.50 mmol, 116 mg) and 1-(*tert*-butyl)-4-nitrobenzene (1.5 equiv, 0.75 mmol, 128 μL) using hexanes/EtOAc/Et_3N (90:10:1) as an eluent to afford the title compound as an off-white amorphous solid (59 mg, 38%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.46 (d, *J* = 8.6 Hz, 2 H), 7.38 (s, 1 H), 7.34 (d, *J* = 8.6 Hz, 2 H), 2.09-2.05 (m, 3 H), 1.96-1.93 (m, 6 H), 1.80-1.72 (m, 6 H), 1.31 (s, 9 H). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 176.2, 147.4, 136.2, 126.0, 120.3, 41.8, 39.7, 36.9, 34.6, 31.5, 28.8.

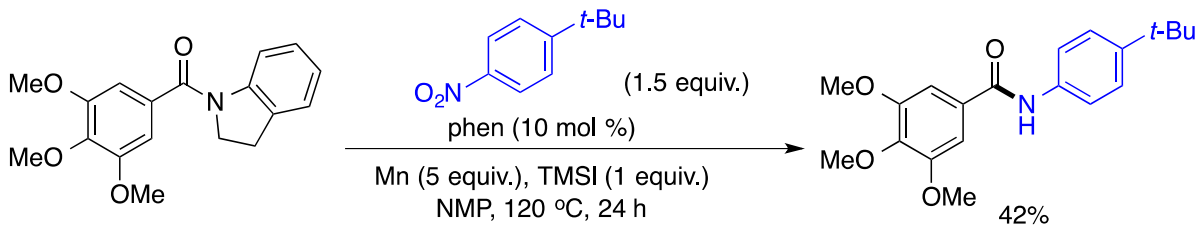
***N*-(*p*-tolyl)-4-(trifluoromethyl)benzamide (3ap).**[52]



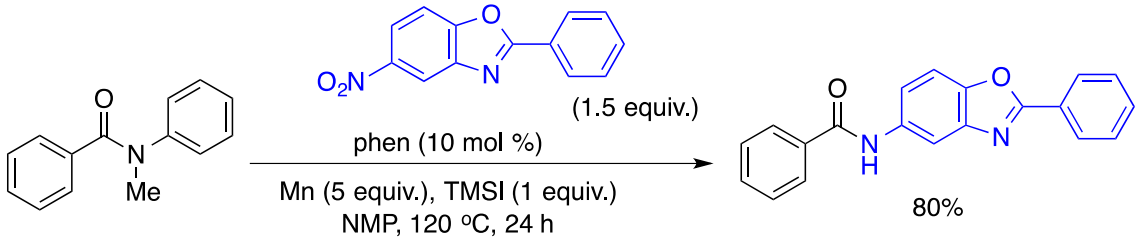
Reaction 1: Following the general procedure C, the title compound was prepared using pyrrolidin-1-yl(4-(trifluoromethyl)phenyl)methanone (1 equiv, 0.50 mmol, 122 mg), 4-nitrotoluene (3 equiv, 1.5 mmol, 206 mg), phen (20 mol %, 18 mg), Mn (10 equiv, 276 mg), and TMSI (2 equiv, 143 μL) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as an off-white amorphous solid (85 mg, 61%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ 10.37 (s, 1 H), 8.14 (d, *J* = 7.9 Hz, 2 H), 7.90 (d, *J* = 8.0 Hz, 2 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 2.29 (s, 3 H). **^{13}C NMR** (150 MHz, DMSO-d_6): 164.1, 138.8, 136.3, 133.0, 131.2 (q, $^2J_{CF}$ = 31.6 Hz), 129.0, 128.5, 125.3 (q, $^2J_{CF}$ = 3.6 Hz), 123.9 (q, $^1J_{CF}$ = 271.1 Hz), 120.4, 20.5.



Reaction 2: Following the general procedure C, the title compound was prepared using piperidin-1-yl(4-(trifluoromethyl)phenyl)methanone (1 equiv, 0.50 mmol, 129 mg), 4-nitrotoluene (3 equiv, 1.5 mmol, 206 mg), phen (20 mol %, 18 mg), Mn (10 equiv, 276 mg), and TMSI (2 equiv, 143 μL) using hexanes/EtOAc/Et_3N (90:10:1) and then hexanes/EtOAc/Et_3N (80:20:1) as an eluent to afford the title compound as an off-white solid (67 mg, 48%). Spectral and analytical data were identical to those reported for the same compound above.



***N*-(4-(*tert*-Butyl)phenyl)-3,4,5-trimethoxybenzamide (4a).** Following the general procedure D, the title compound was prepared using indolin-1-yl(3,4,5-trimethoxyphenyl)methanone (1 equiv, 0.35 mmol, 110 mg) and 1-(*tert*-butyl)-4-nitrobenzene (1.5 equiv, 0.525 mmol, 94 mg) using hexanes/EtOAc/CH_2Cl_2 (40:55:5) as an eluent to afford the title compound as pale brown amorphous solid (50 mg, 42%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.68 (s, 1 H), 7.55 (d, *J* = 5.8 Hz, 2 H), 7.40 (d, *J* = 5.8 Hz, 2 H), 7.07 (s, 2 H), 3.93 (s, 6 H), 3.91 (s, 3 H), 1.33 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.7, 153.3, 147.6, 141.1, 135.5, 130.7, 125.9, 120.3, 104.7, 61.0, 56.4, 34.5, 31.5. **HRMS** (ESI): Calcd for $C_{20}H_{26}NO_4$ [M+H]: 344.1862; Found: 344.1862. **Mp:** 158-160 °C. **R_f** = 0.49 (EtOAc : petroleum ether = 1:2).



***N*-(2-Phenylbenzo[*d*]oxazol-5-yl)benzamide (4b).**[40] Following the general procedure D, the title compound was prepared using *N*-methyl-*N*-phenylbenzamide (1 equiv, 0.35 mmol, 74 mg) and 5-nitro-2-phenylbenzo[*d*]oxazole (1.5 equiv, 0.525 mmol, 126 mg) using hexanes/EtOAc/CH_2Cl_2 (70:25:5) as an eluent to afford the title compound as a brown amorphous solid (88 mg, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 4.6 Hz, 2 H), 8.12 (s, 1 H), 8.03 (s, 1 H), 7.89 (d, *J* = 6.7 Hz, 2 H), 7.65 (d, *J* = 7.7 Hz, 1 H), 7.57-7.44 (m, 7 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 164.1, 148.0, 142.7, 135.01, 134.98, 132.0, 131.8, 129.0, 128.9, 127.8, 127.2, 127.1, 118.9, 112.3, 110.7.

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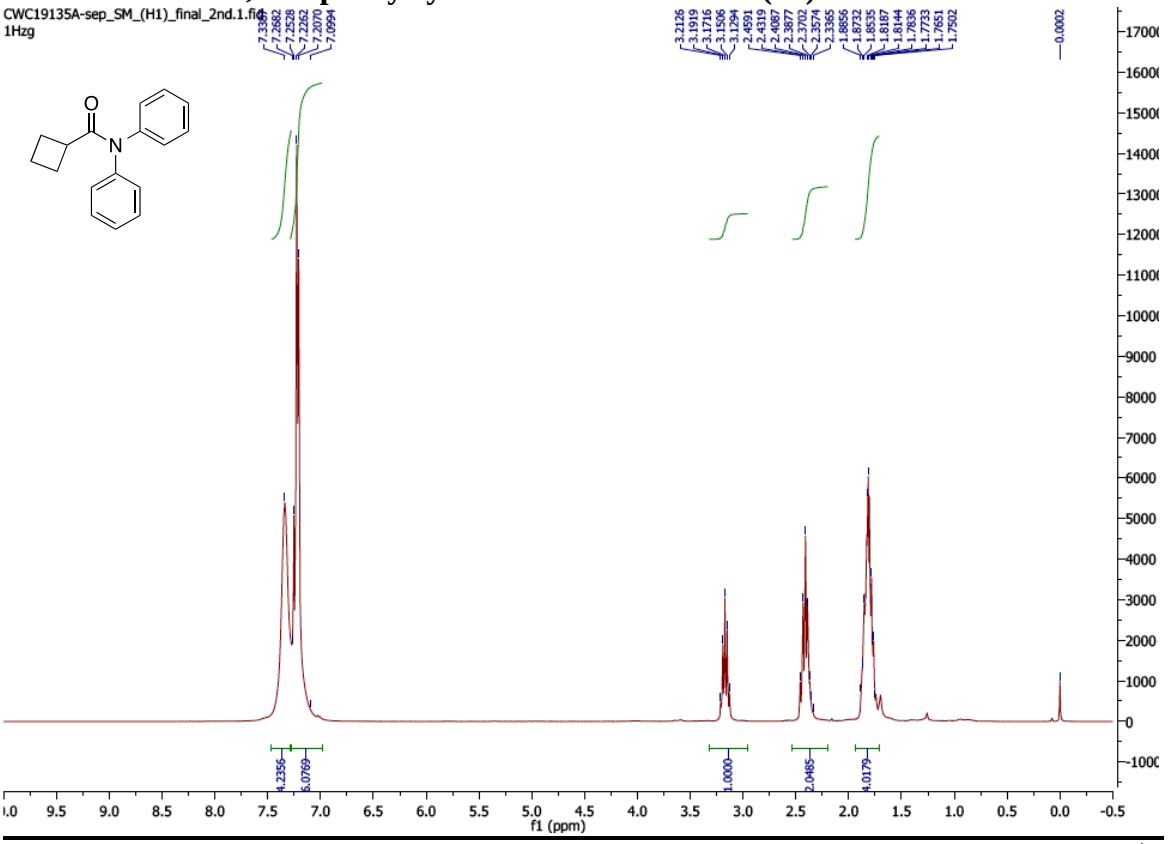
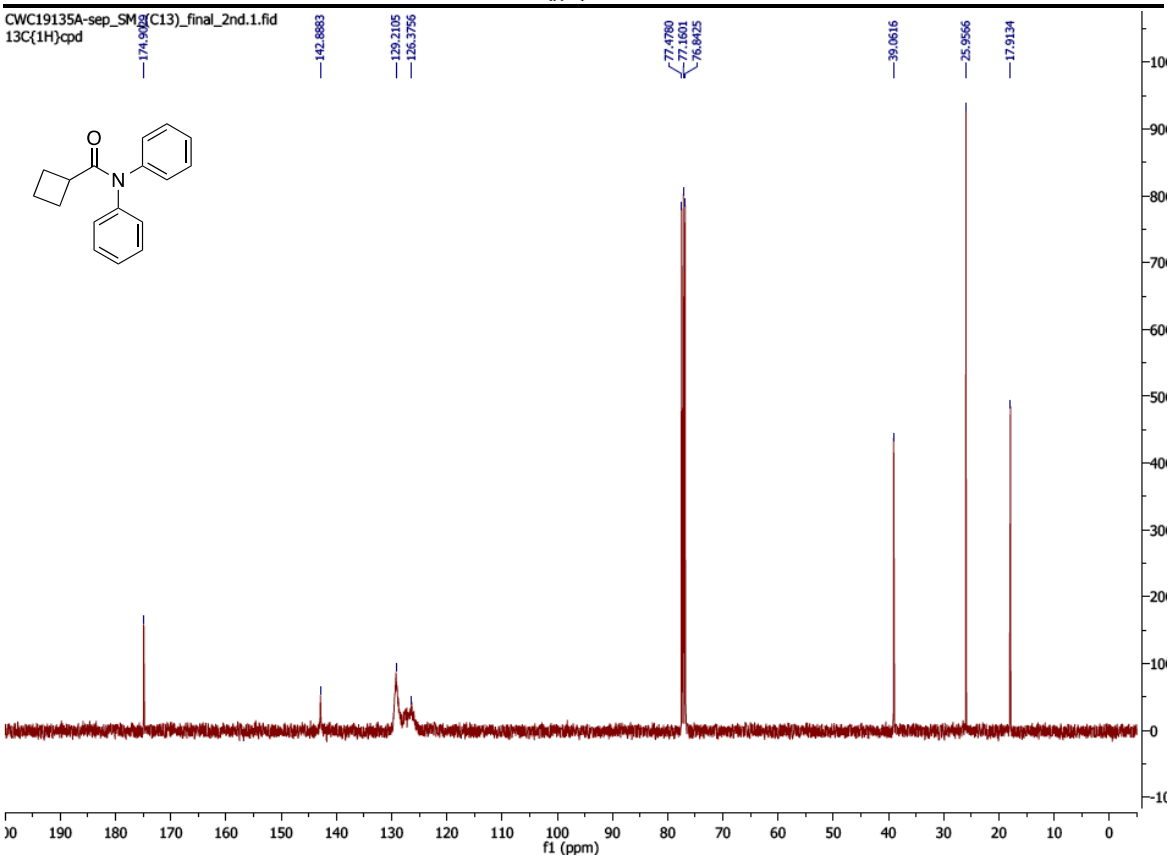
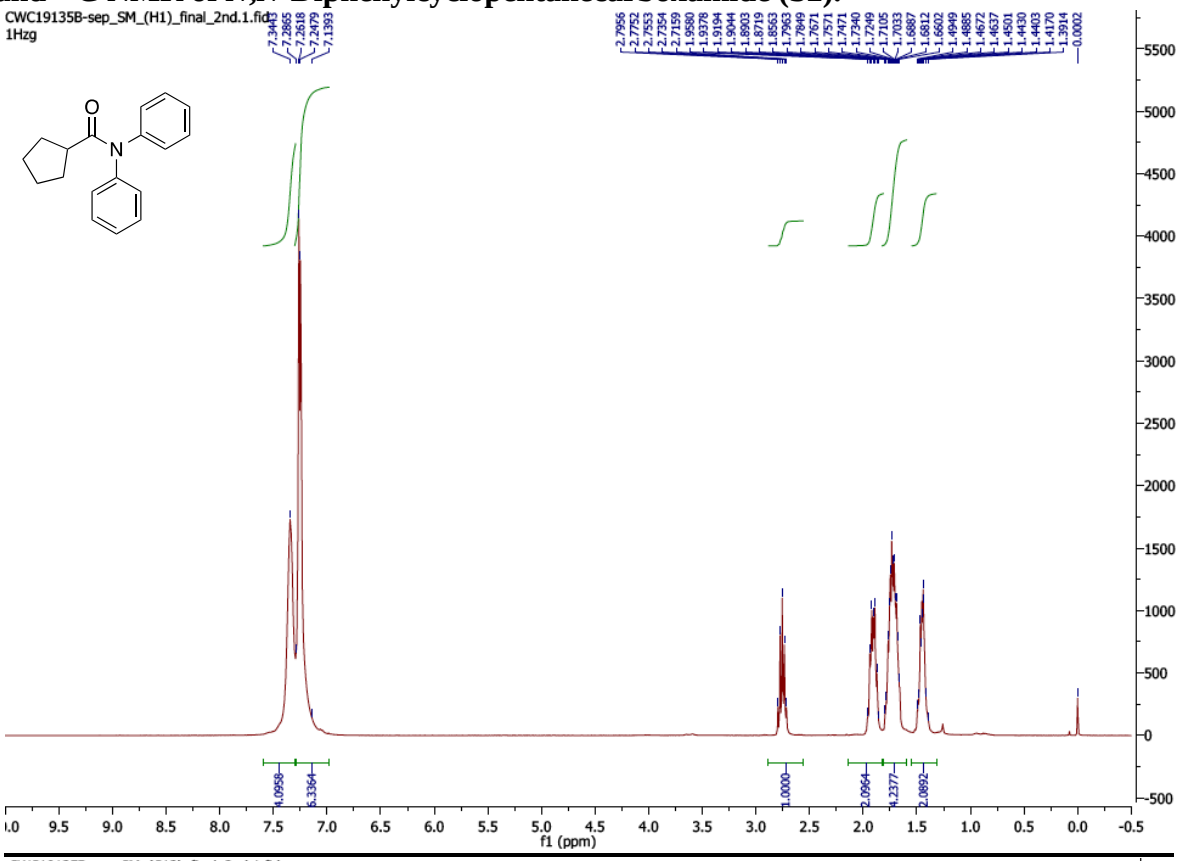
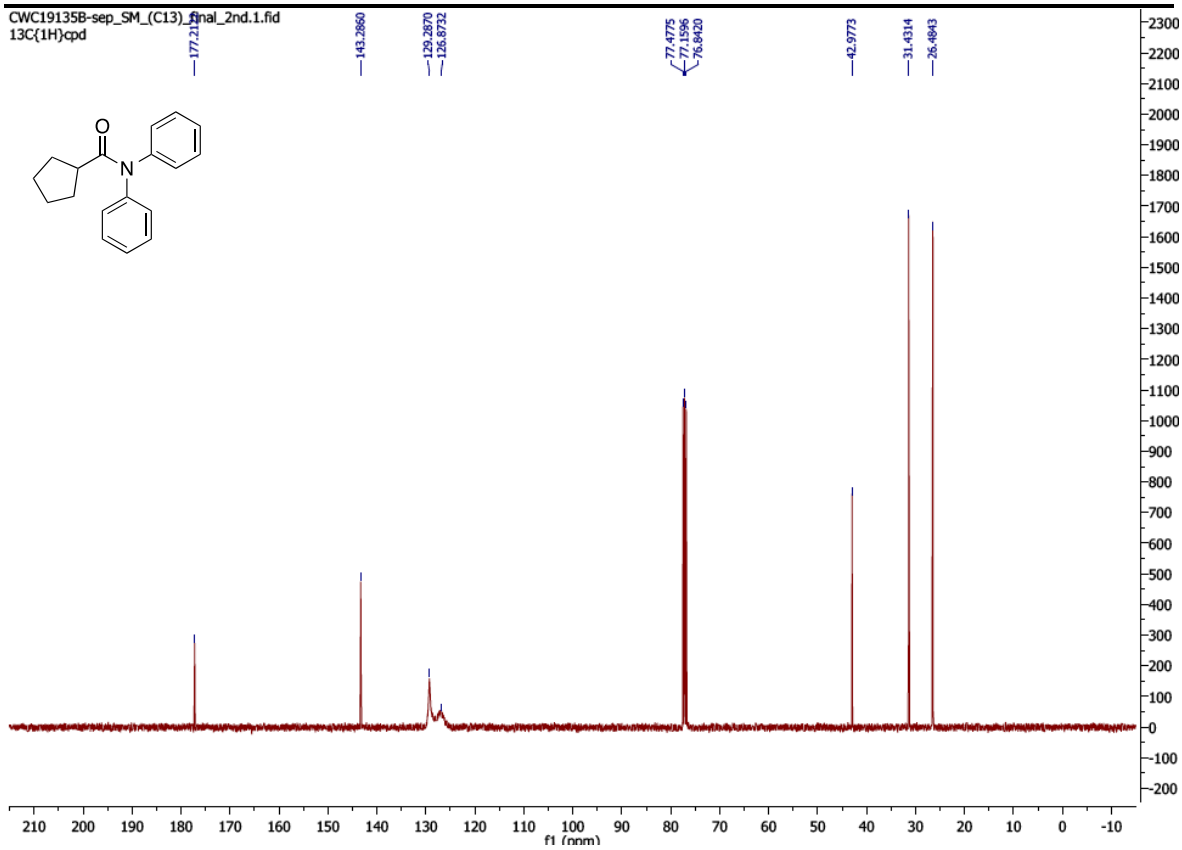
^{1}H and ^{13}C NMR of *N,N*-Diphenylcyclobutanecarboxamide (S1).





^{1}H and ^{13}C NMR of *N,N*-Diphenylcyclopentanecarboxamide (S2).





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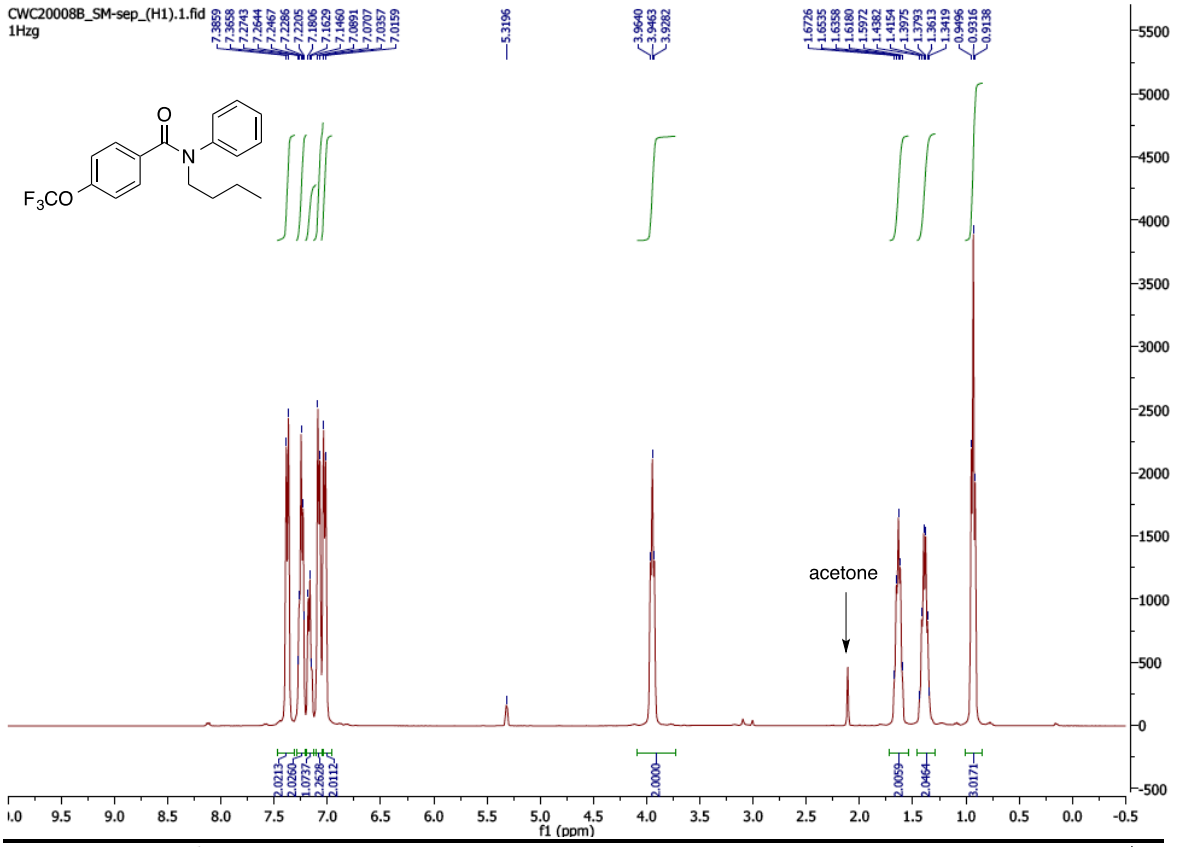
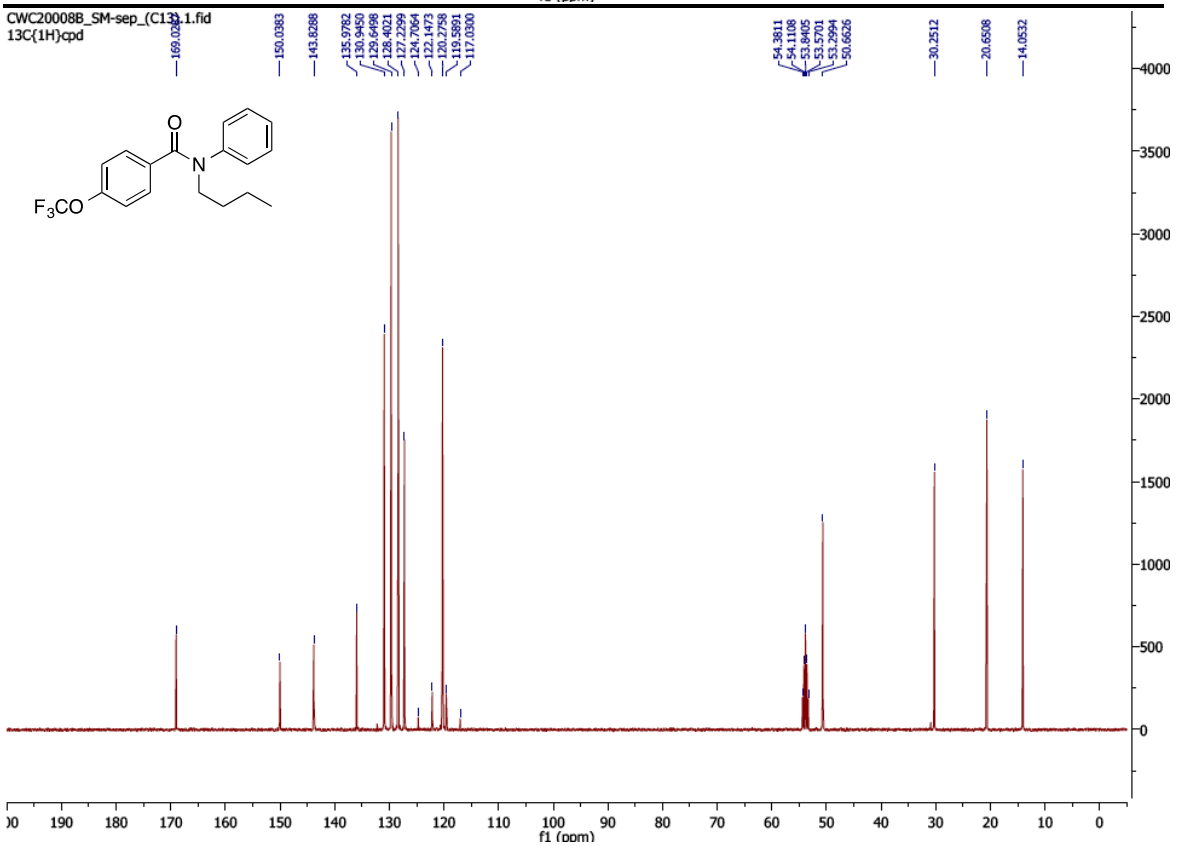
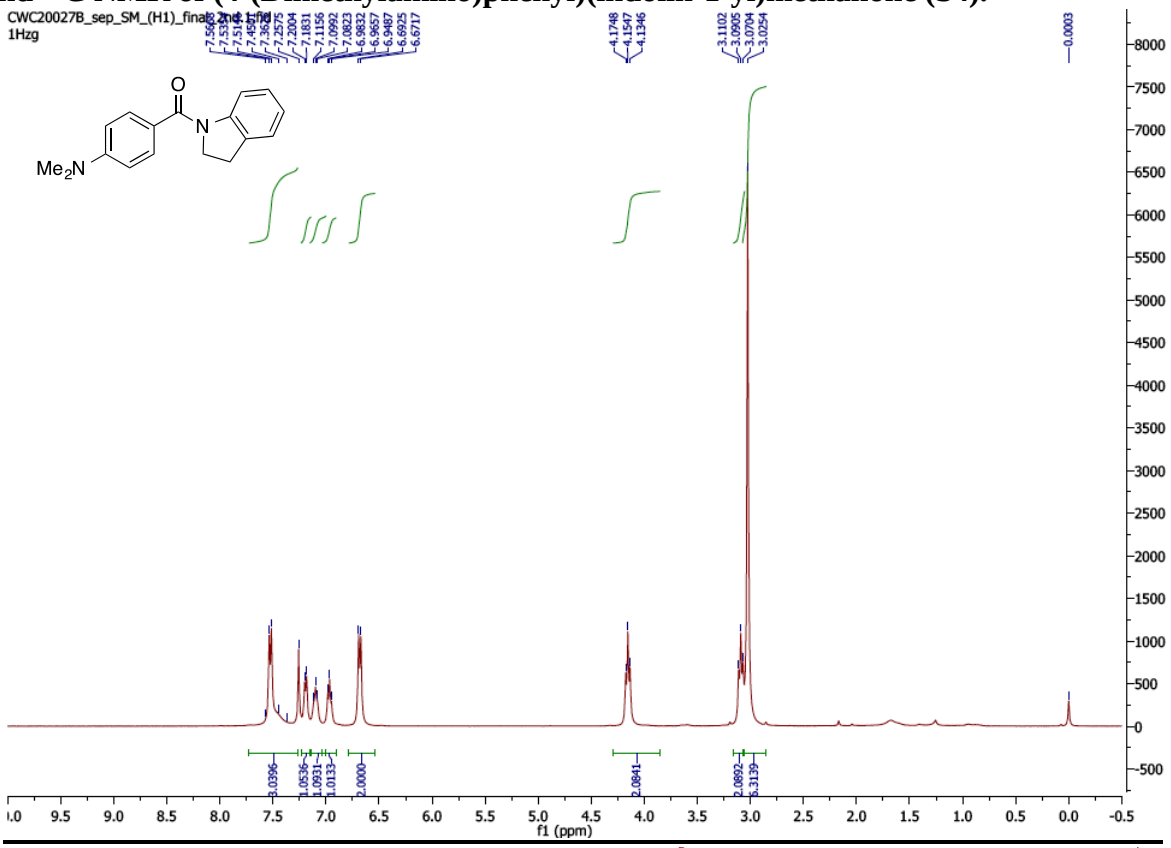
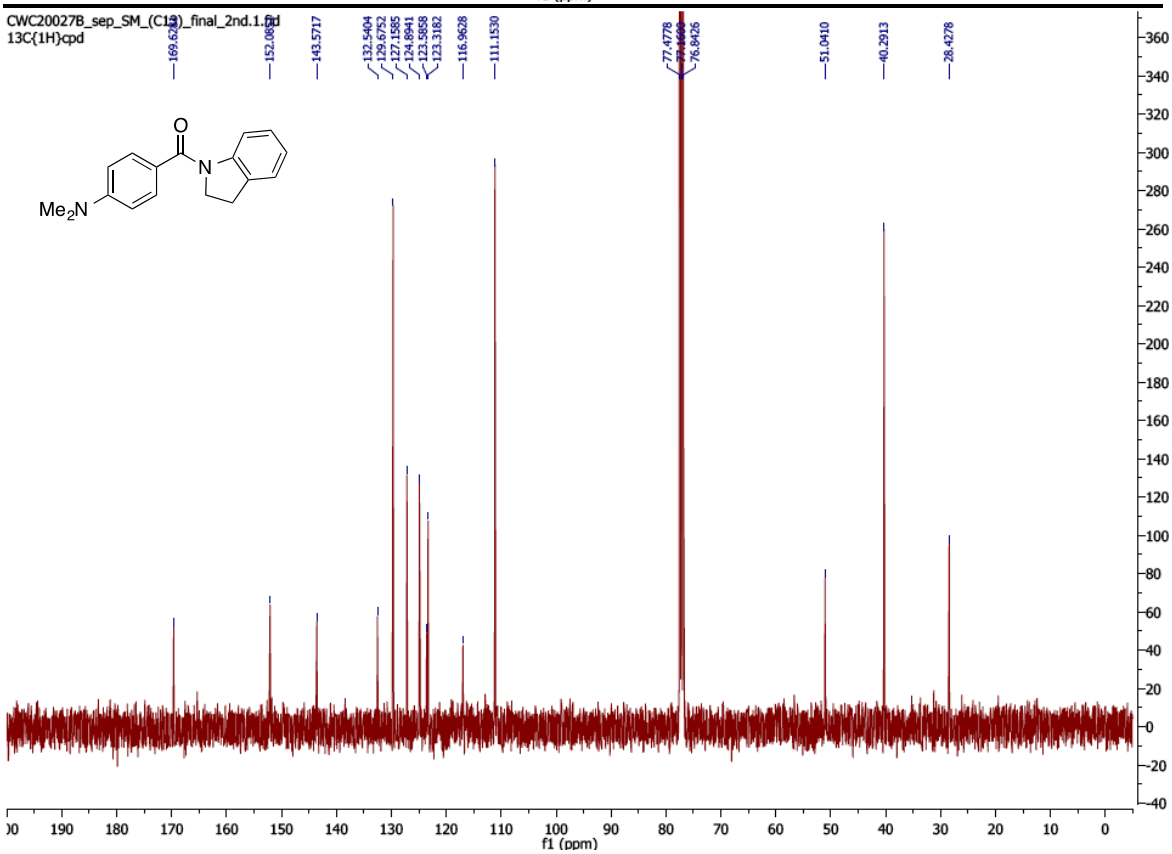


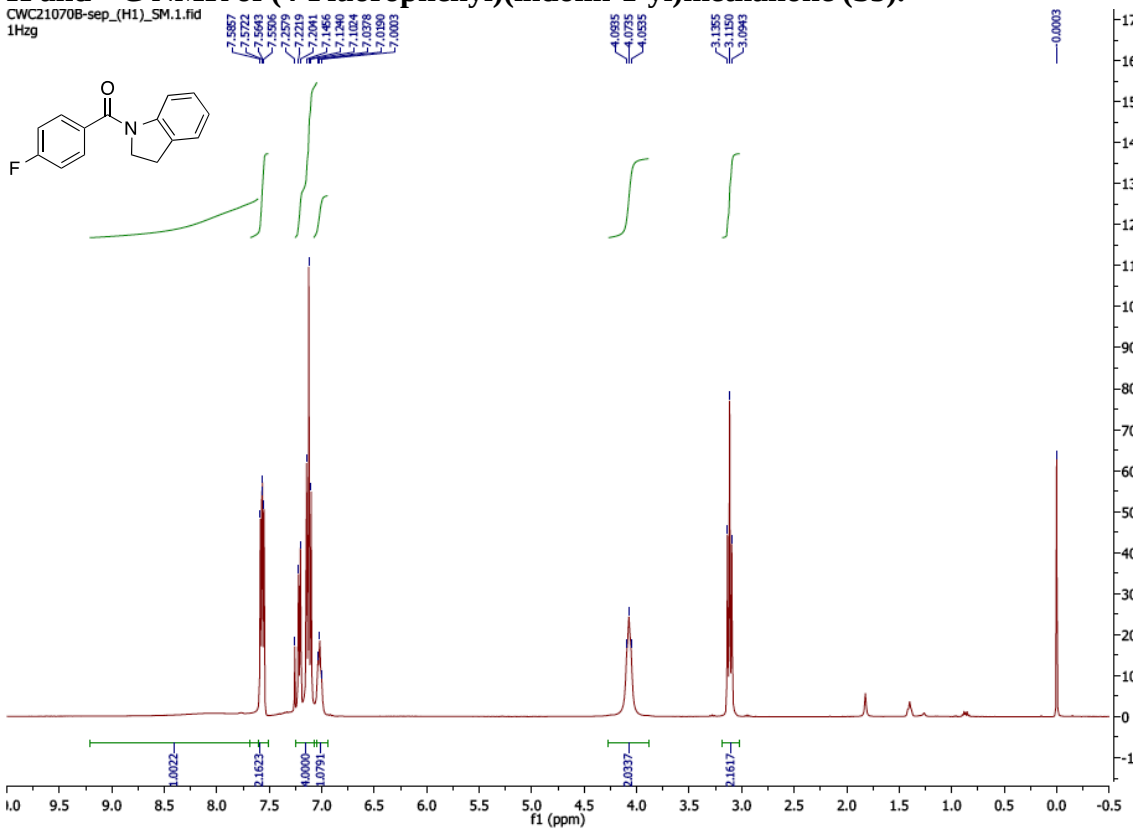


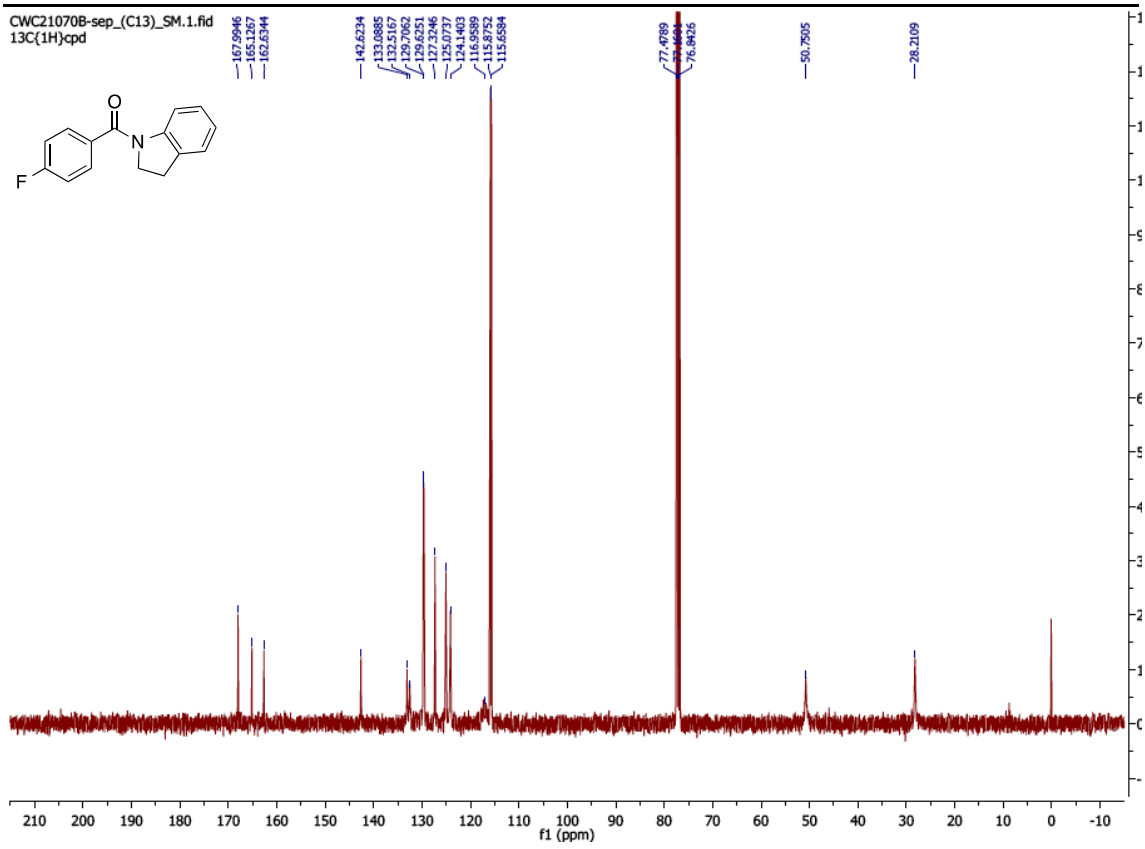
^{1}H and ^{13}C NMR of (4-(Dimethylamino)phenyl)(indolin-1-yl)methanone (S4).



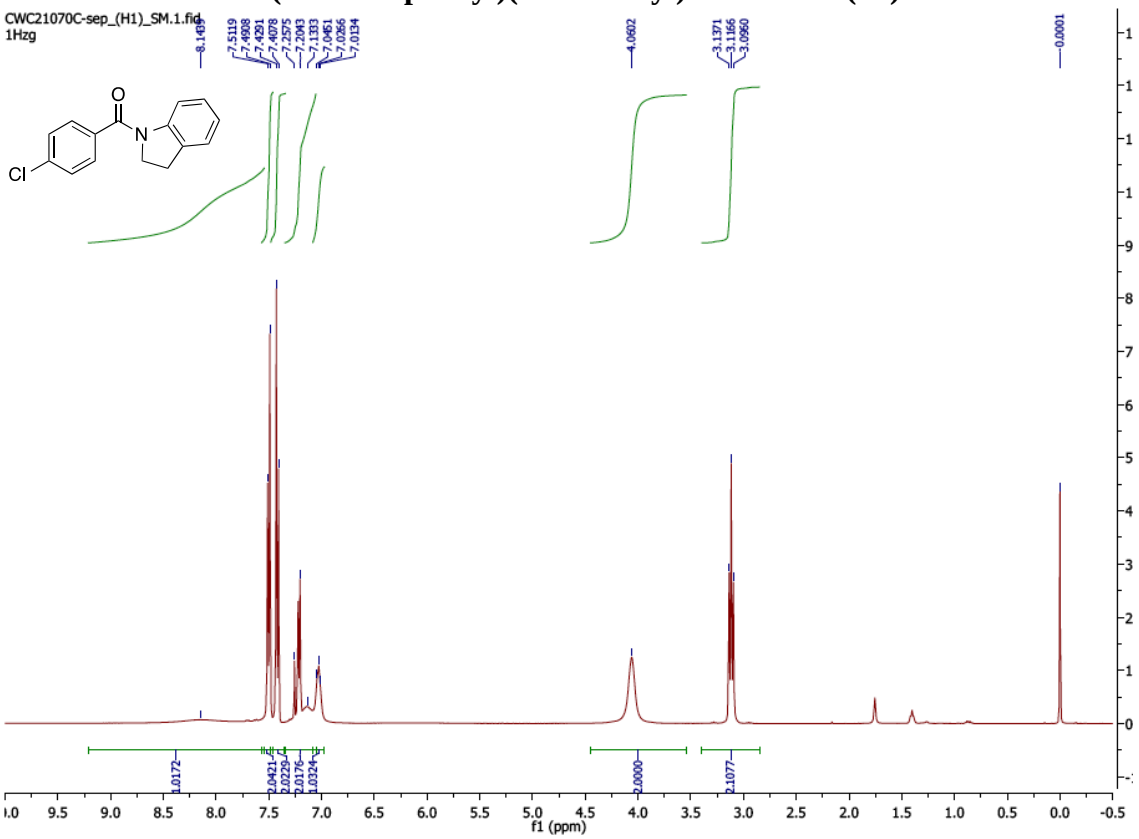


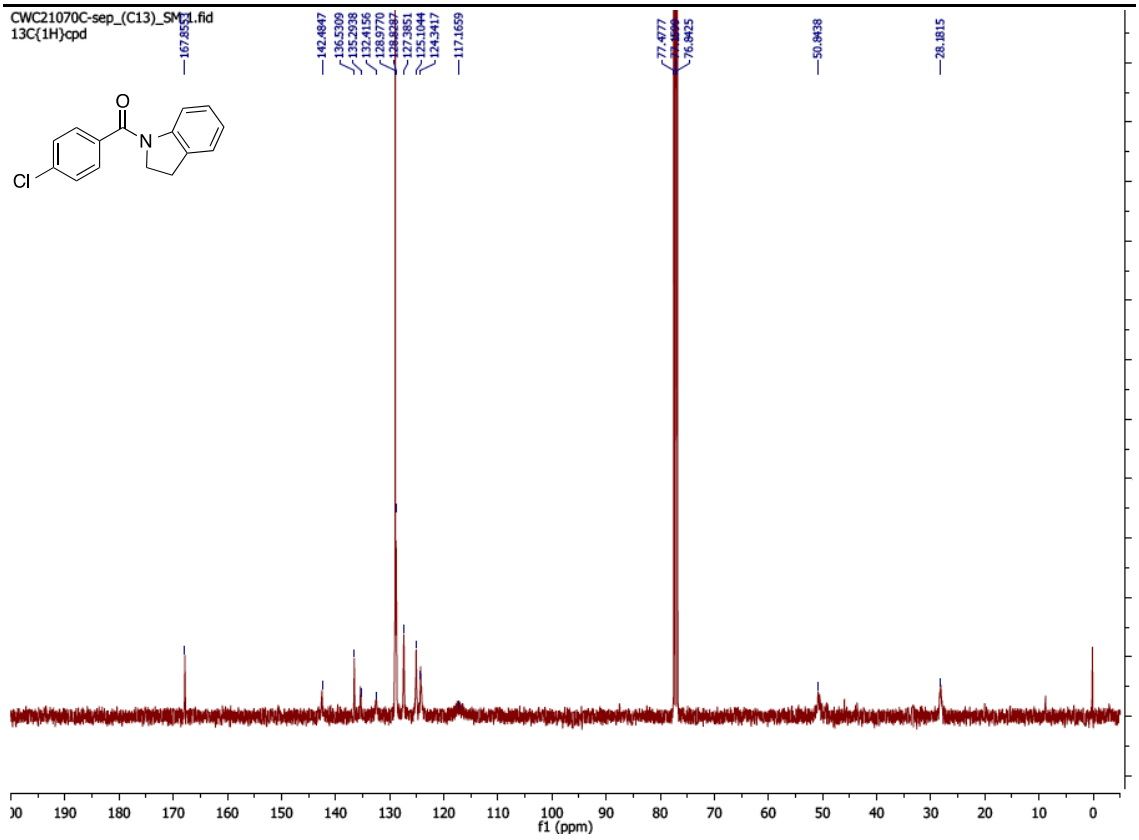
^{1}H and ^{13}C NMR of (4-Fluorophenyl)(indolin-1-yl)methanone (S5).



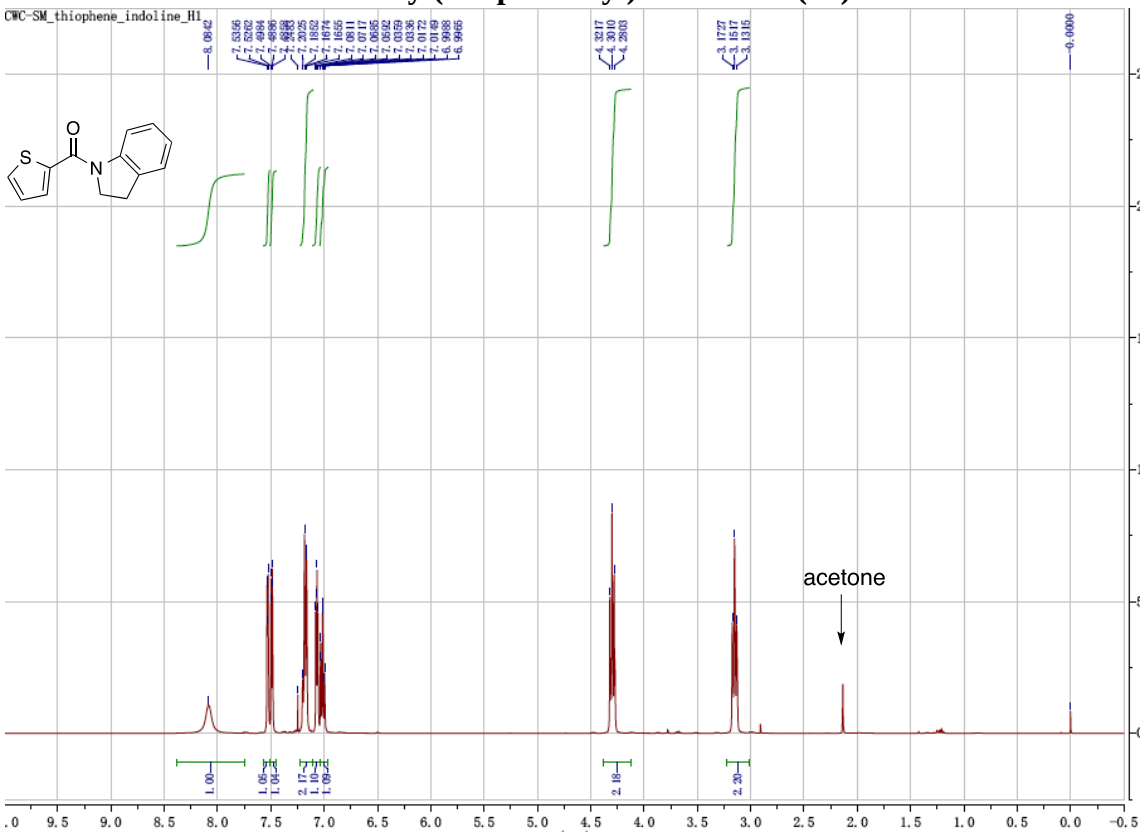


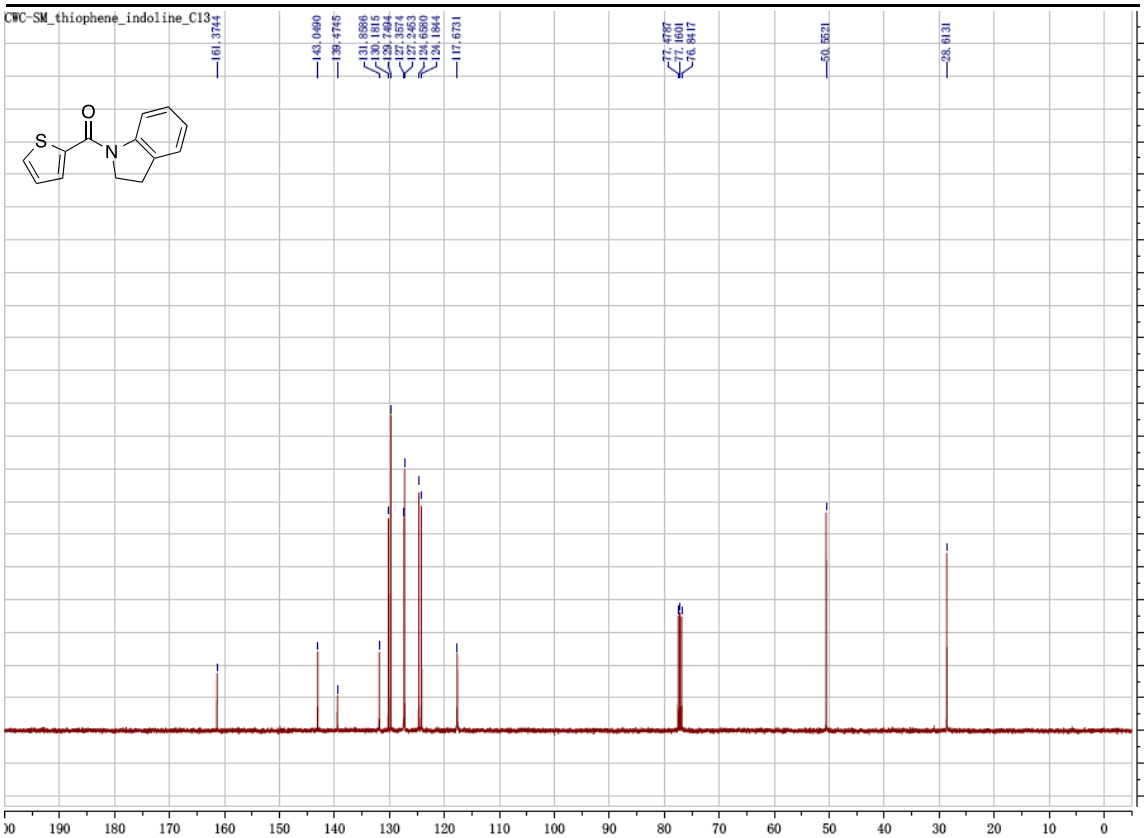
^{1}H and ^{13}C NMR of (4-Chlorophenyl)(indolin-1-yl)methanone (S6).



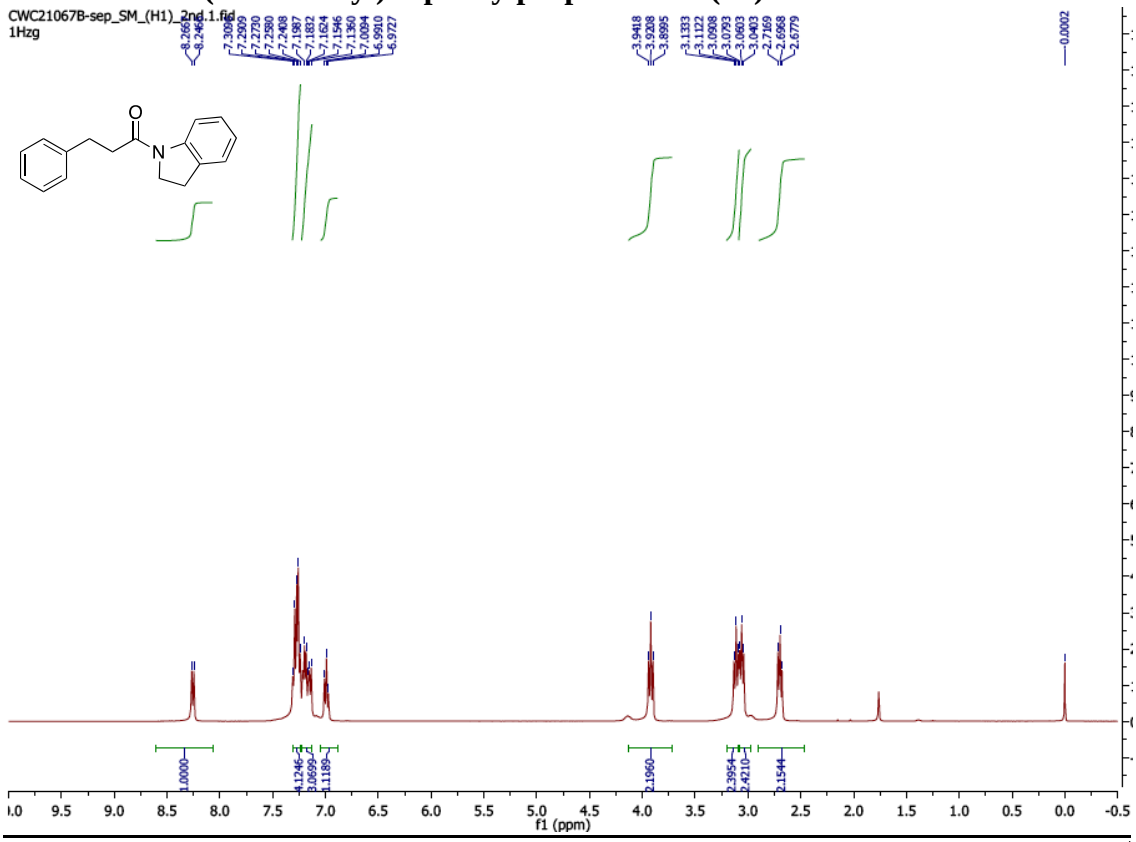


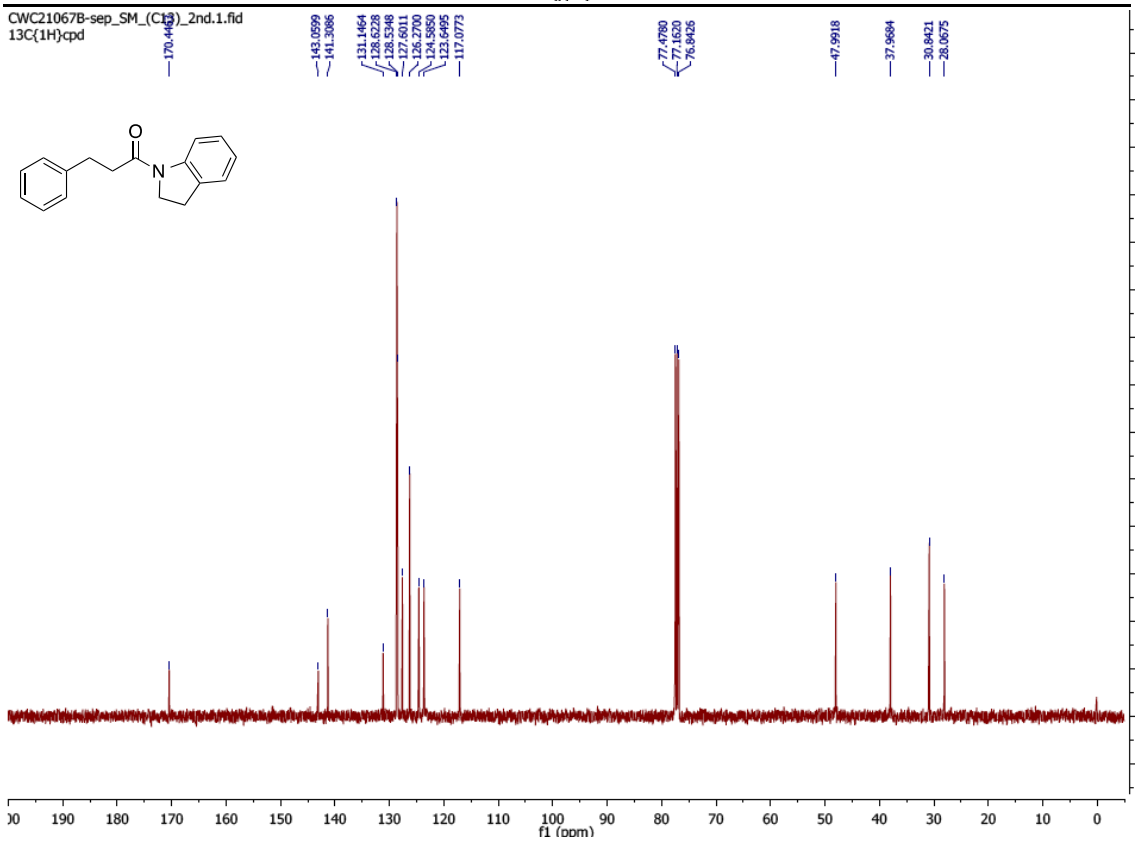
^{1}H and ^{13}C NMR of Indolin-1-yl(thiophen-2-yl)methanone (S7).



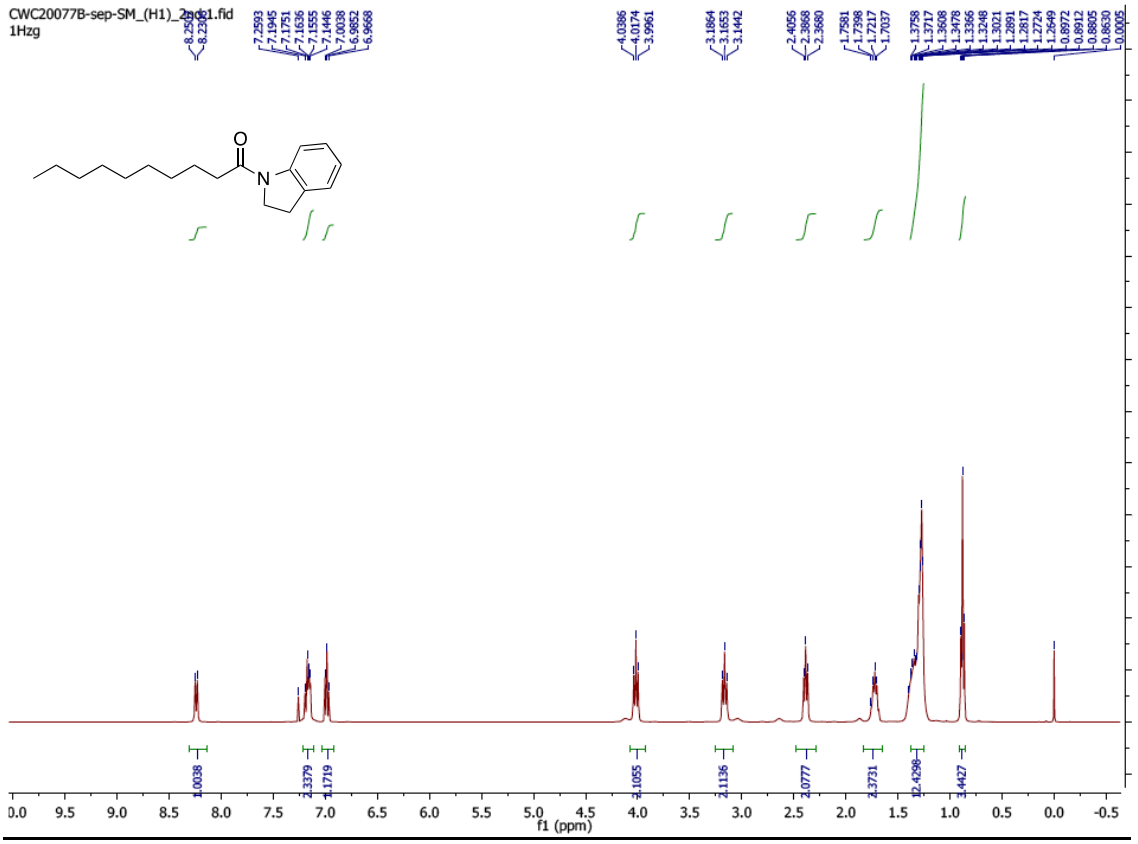


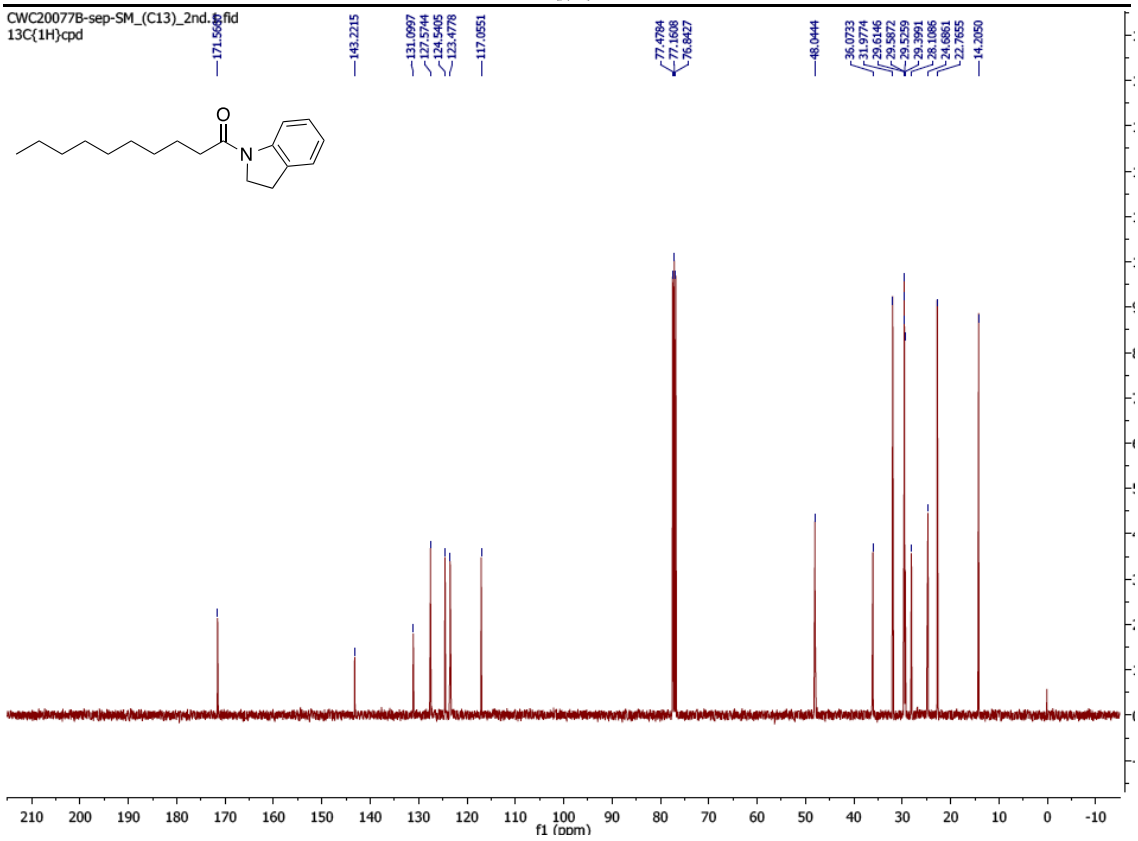
^{1}H and ^{13}C NMR of 1-(Indolin-1-yl)-3-phenylpropan-1-one (S8).



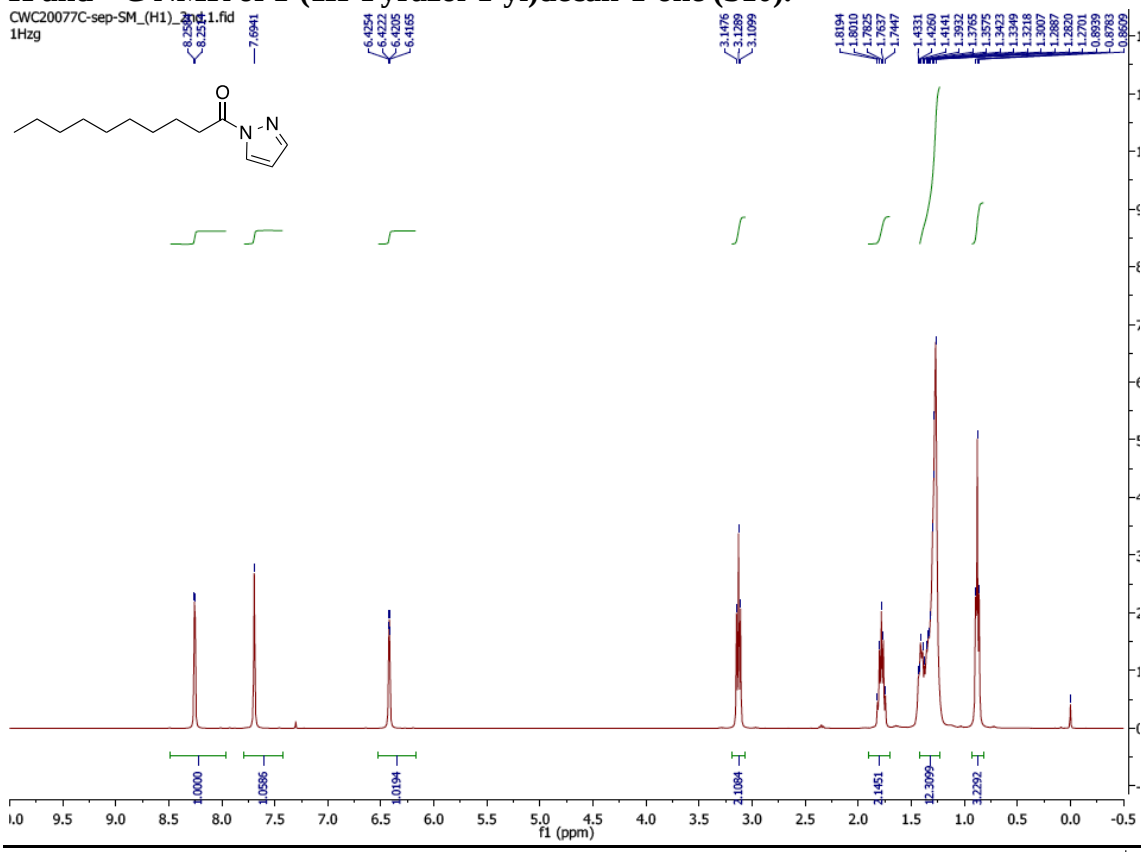


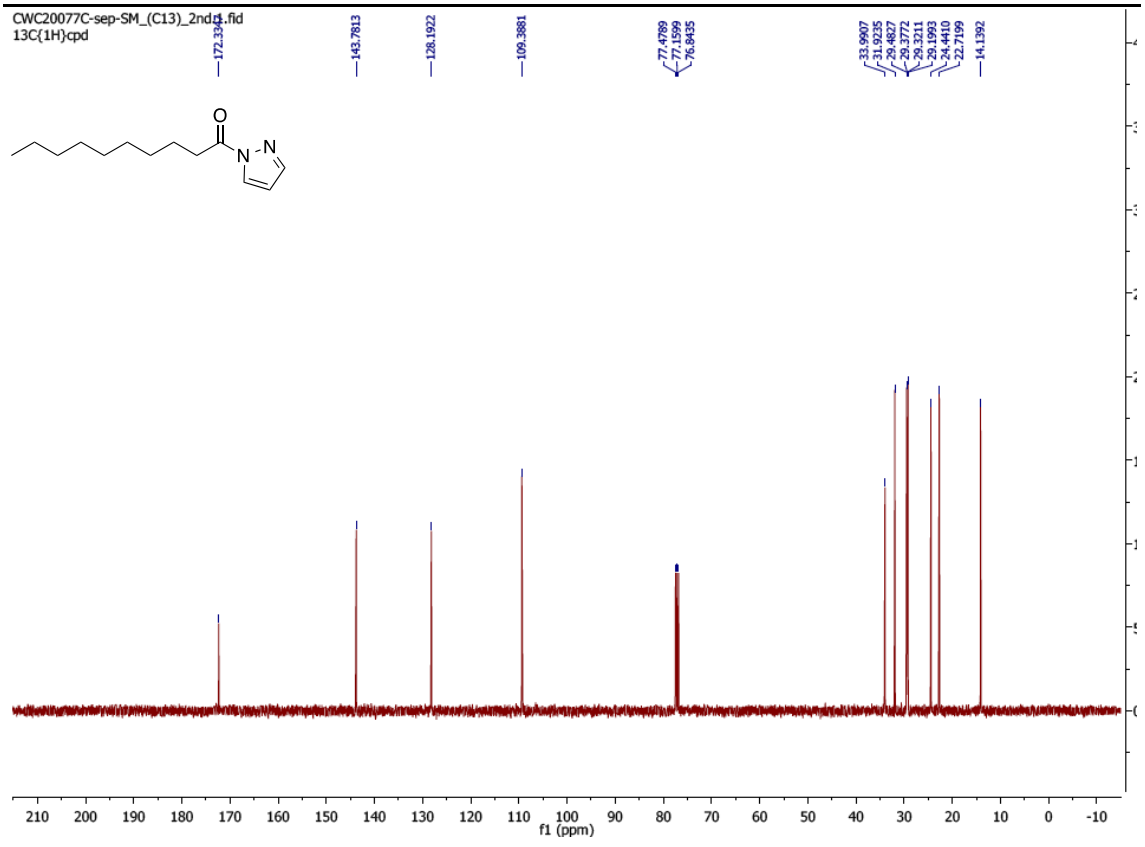
^{1}H and ^{13}C NMR of 1-(Indolin-1-yl)decan-1-one (S9).



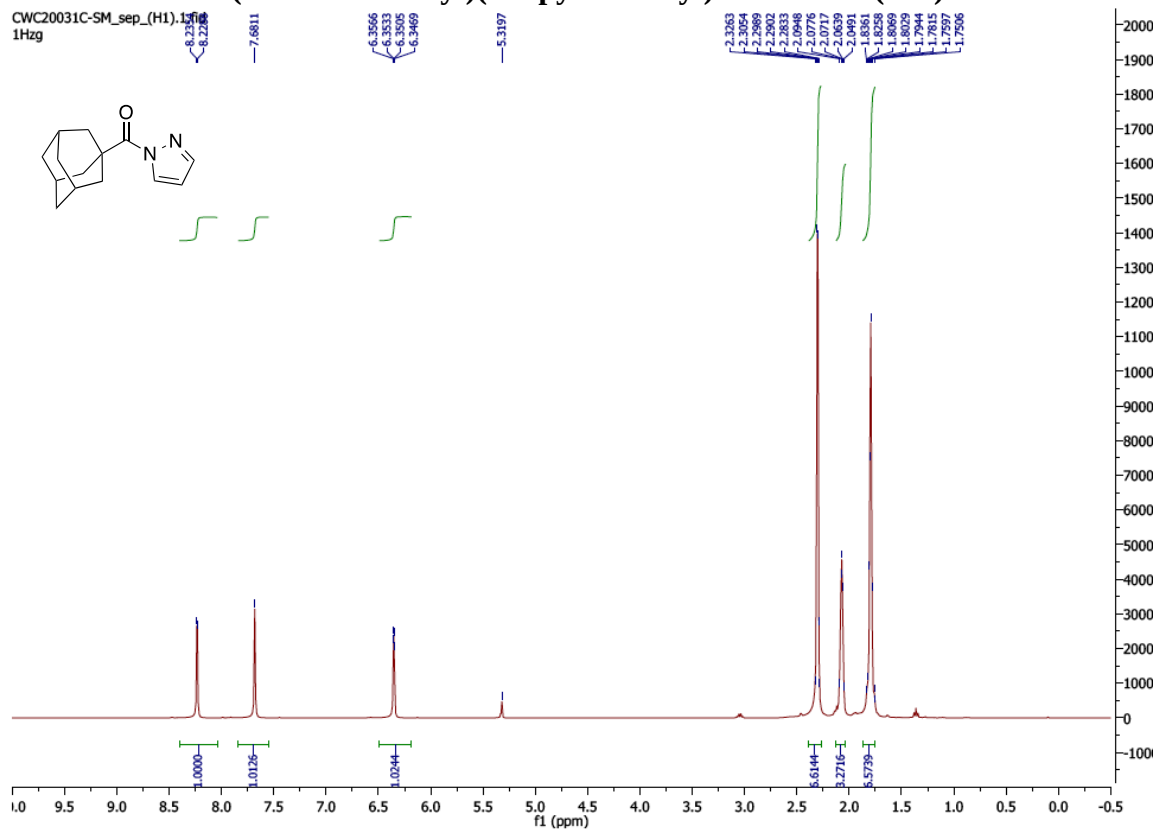


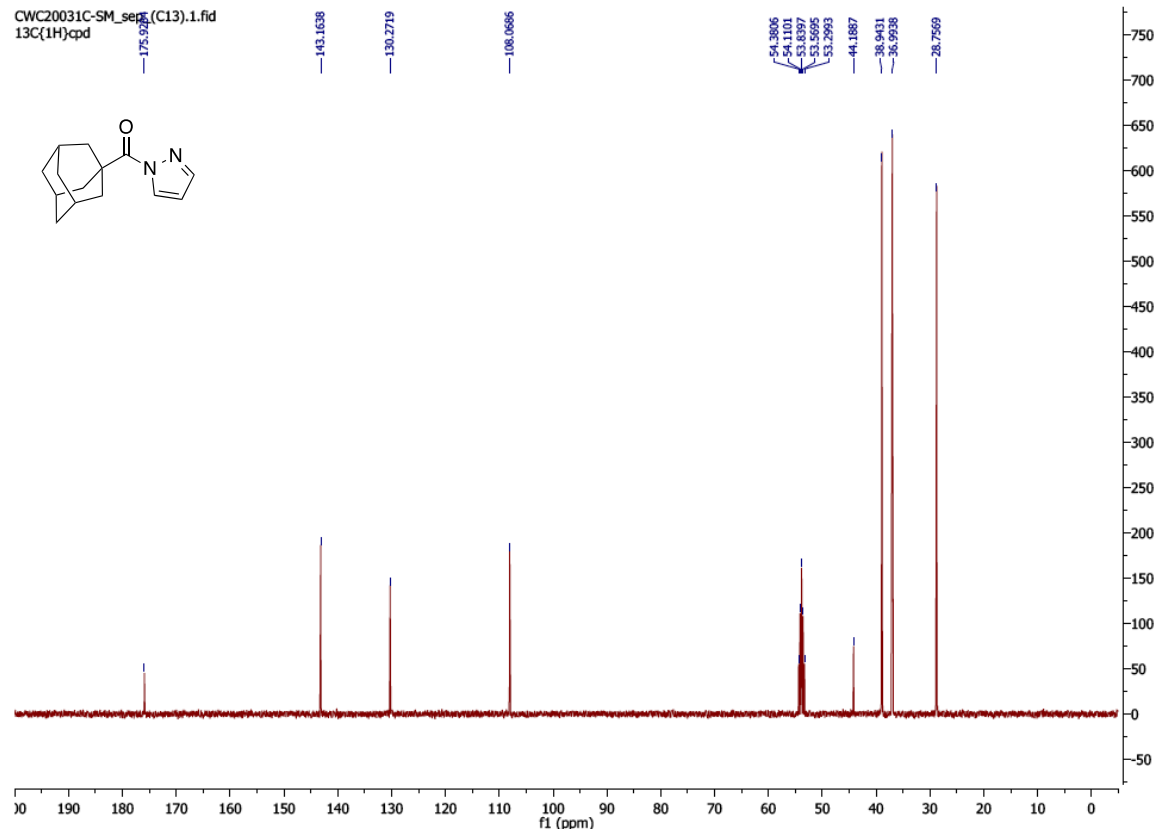
^{1}H and ^{13}C NMR of 1-(1*H*-Pyrazol-1-yl)decan-1-one (S10).



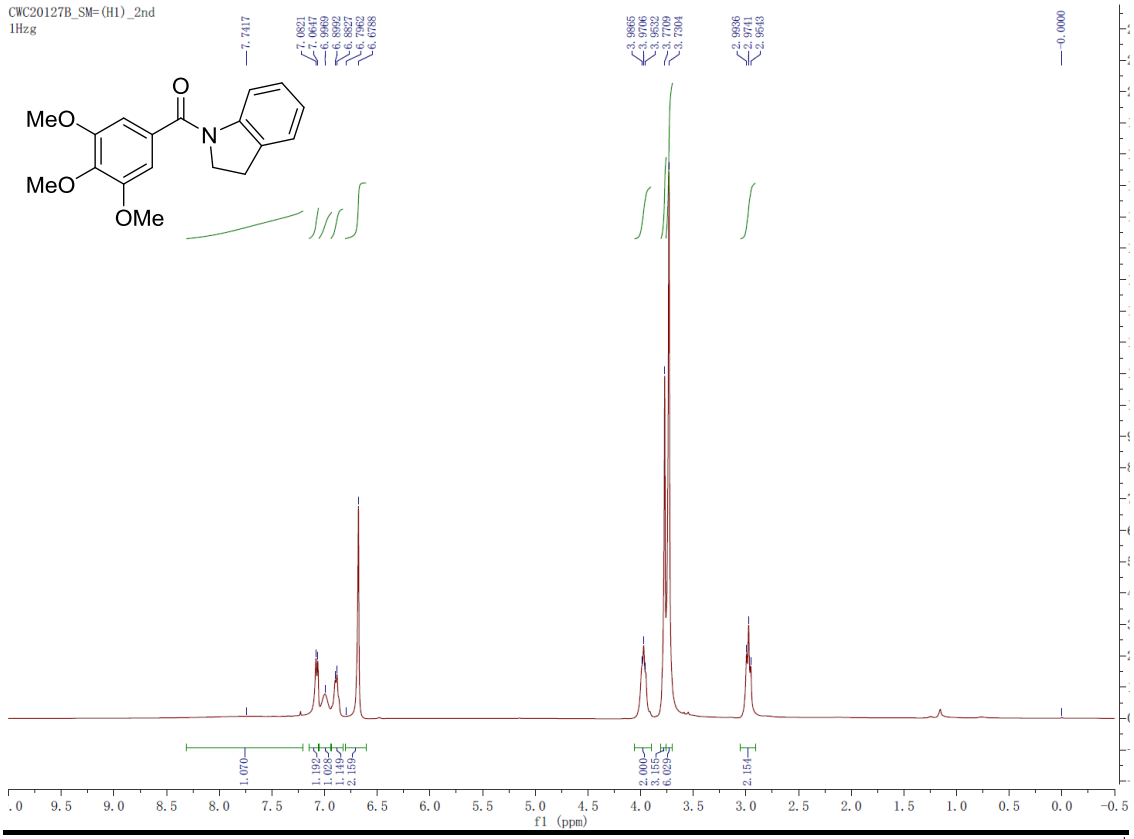


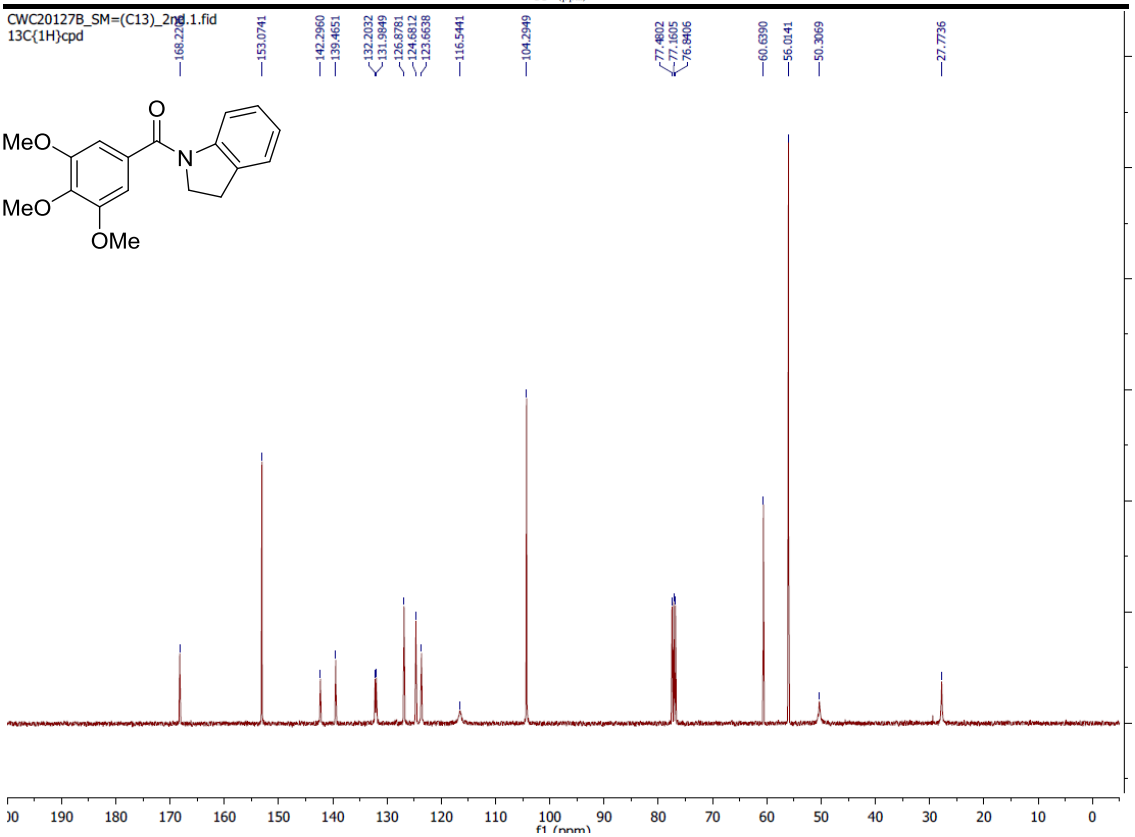
^{1}H and ^{13}C NMR of (Adamantan-1-yl)(1*H*-pyrazol-1-yl)methanone (S11).



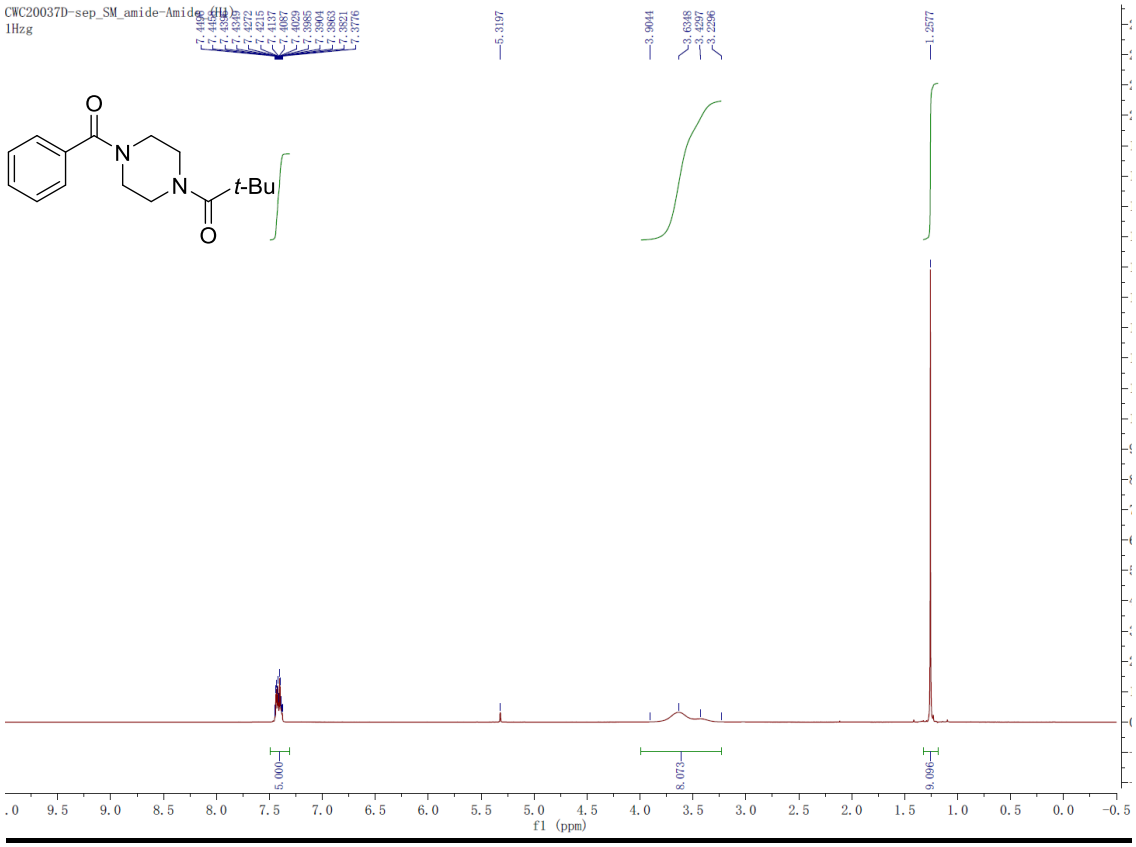


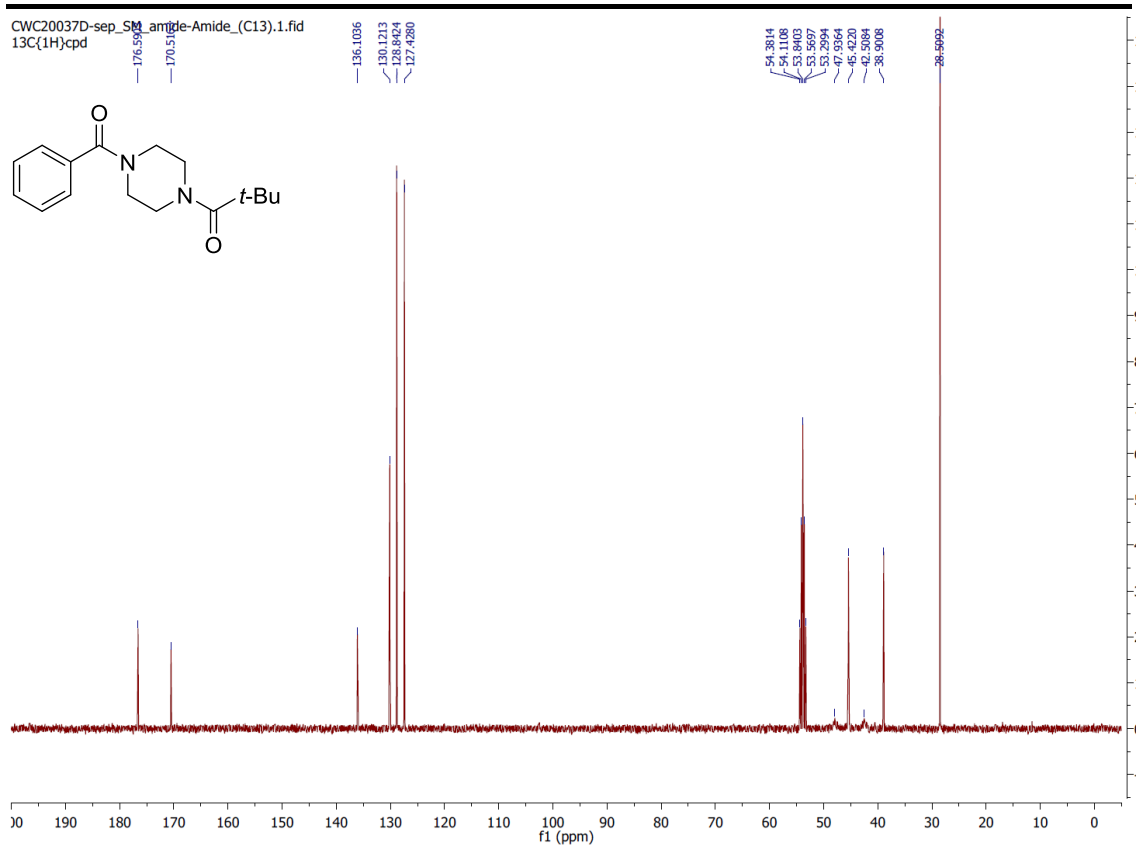
^{1}H and ^{13}C NMR of Indolin-1-yl(3,4,5-trimethoxyphenyl)methanone (S12).



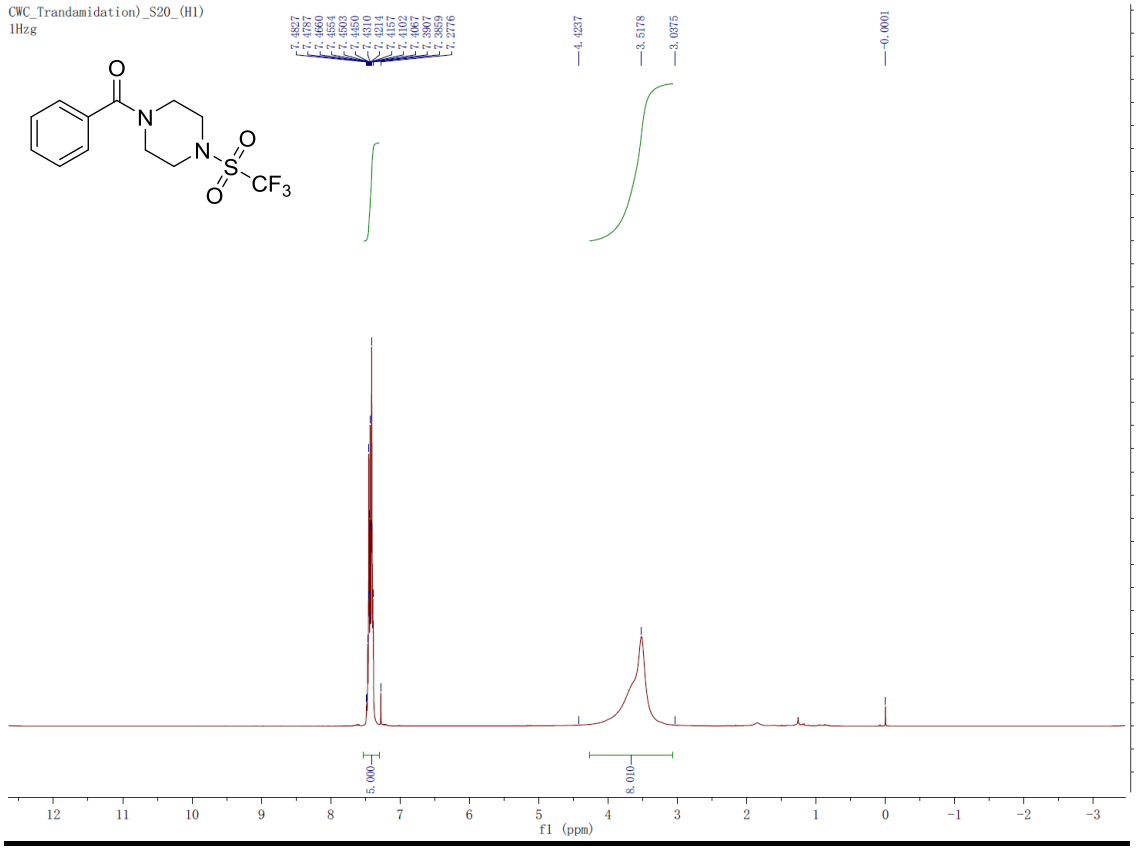


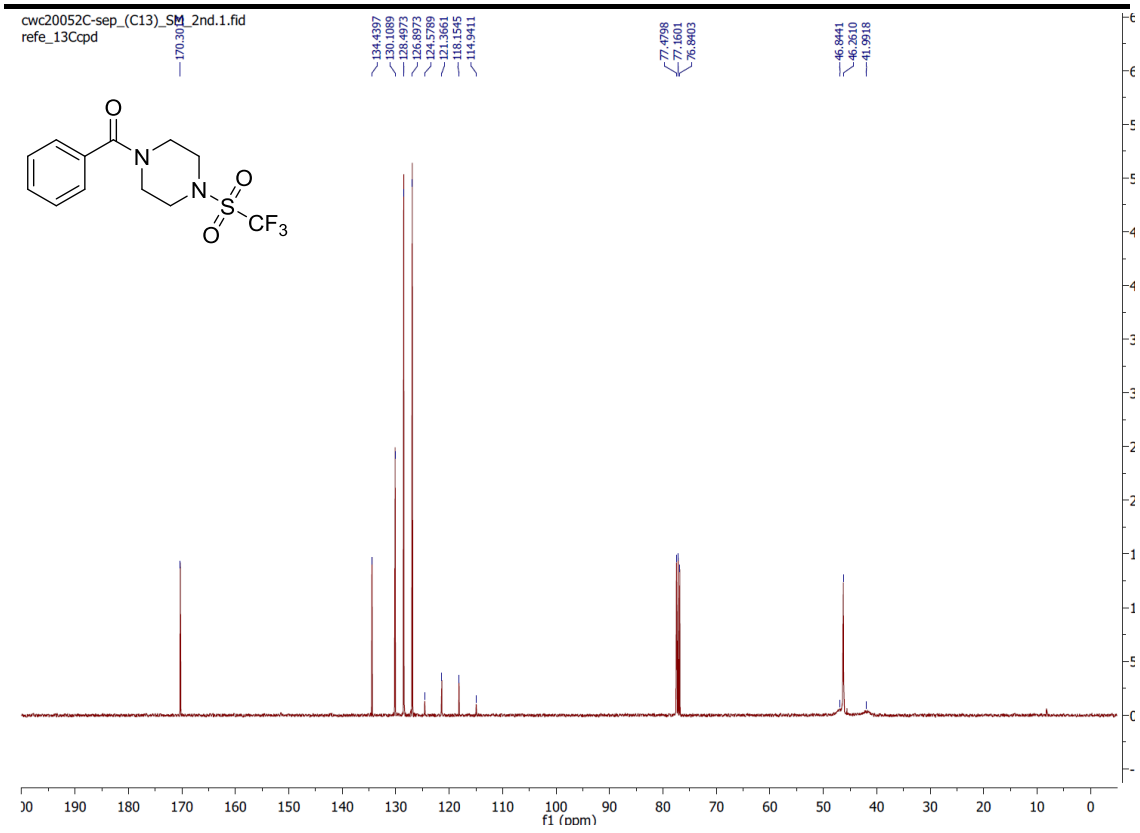
^{1}H and ^{13}C NMR of 1-(4-Benzoylpiperazin-1-yl)-2,2-dimethylpropan-1-one (S13).



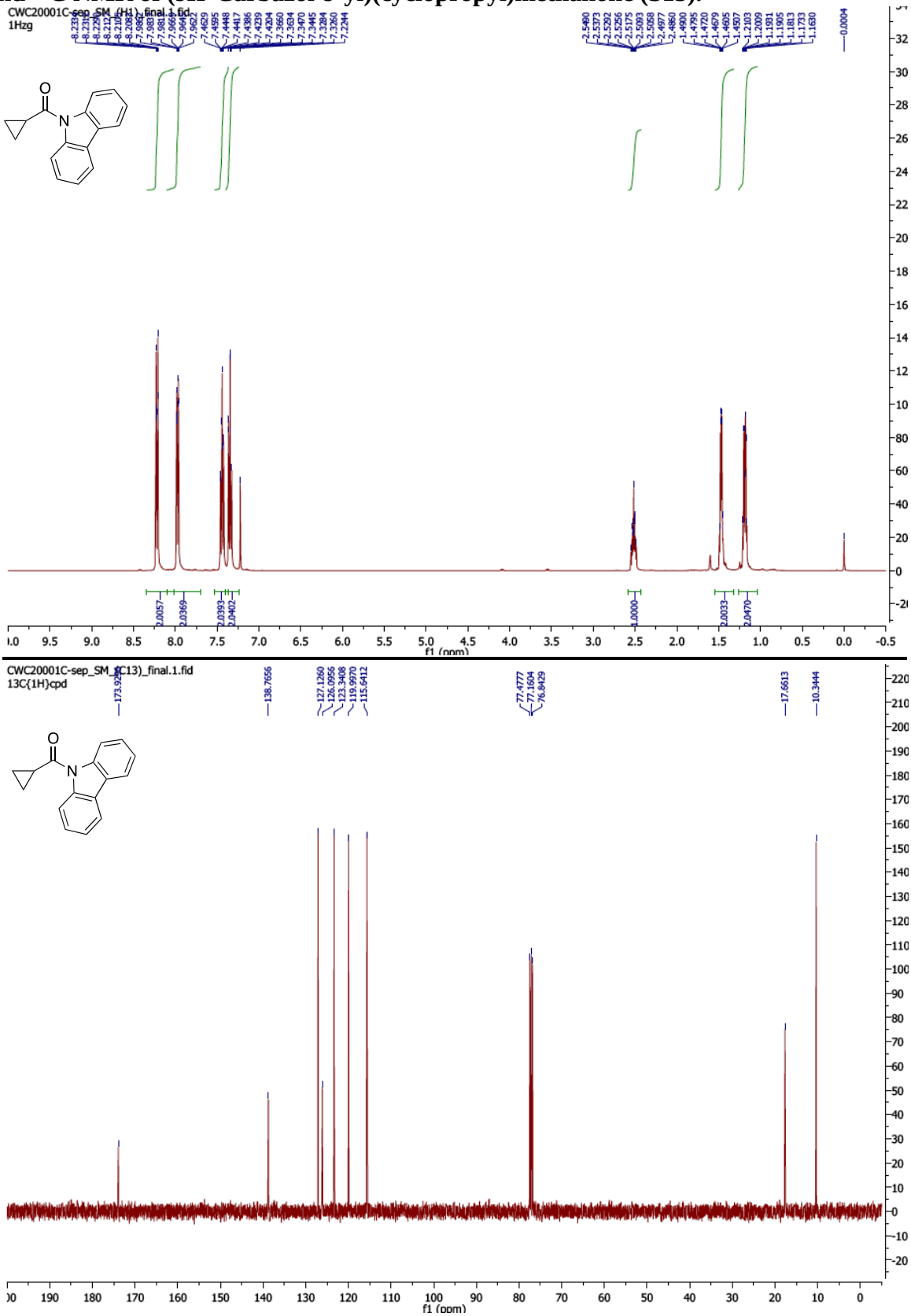


^{1}H and ^{13}C NMR of Phenyl(4-((trifluoromethyl)sulfonyl)piperazin-1-yl)methanone (S14).

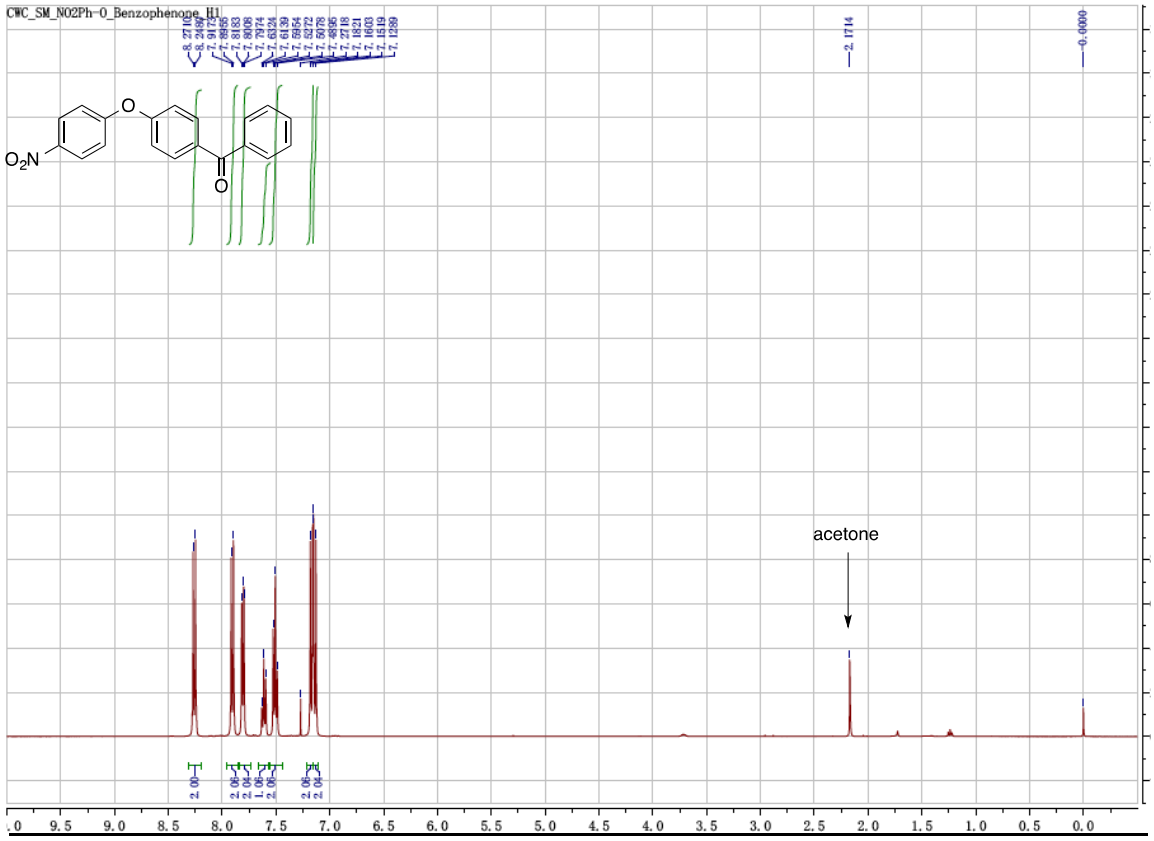


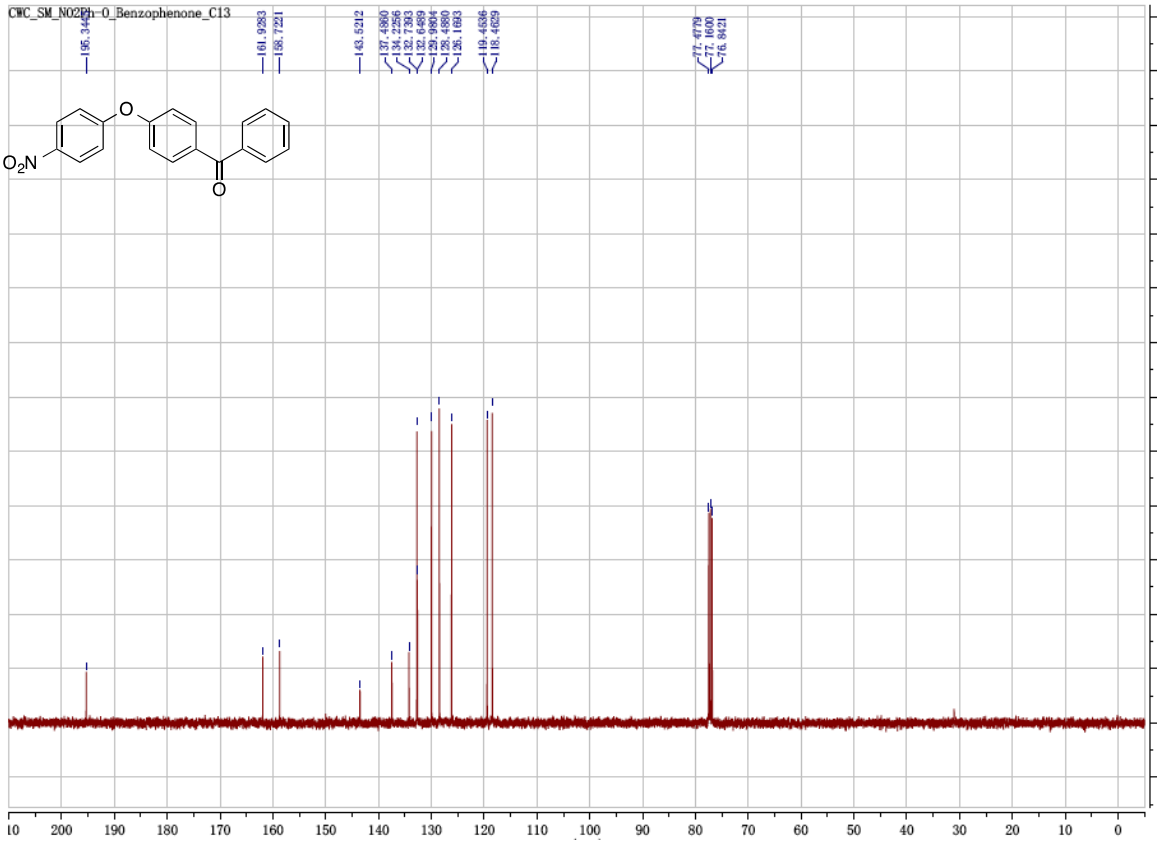


^{1}H and ^{13}C NMR of (9*H*-Carbazol-9-yl)(cyclopropyl)methanone (S15).

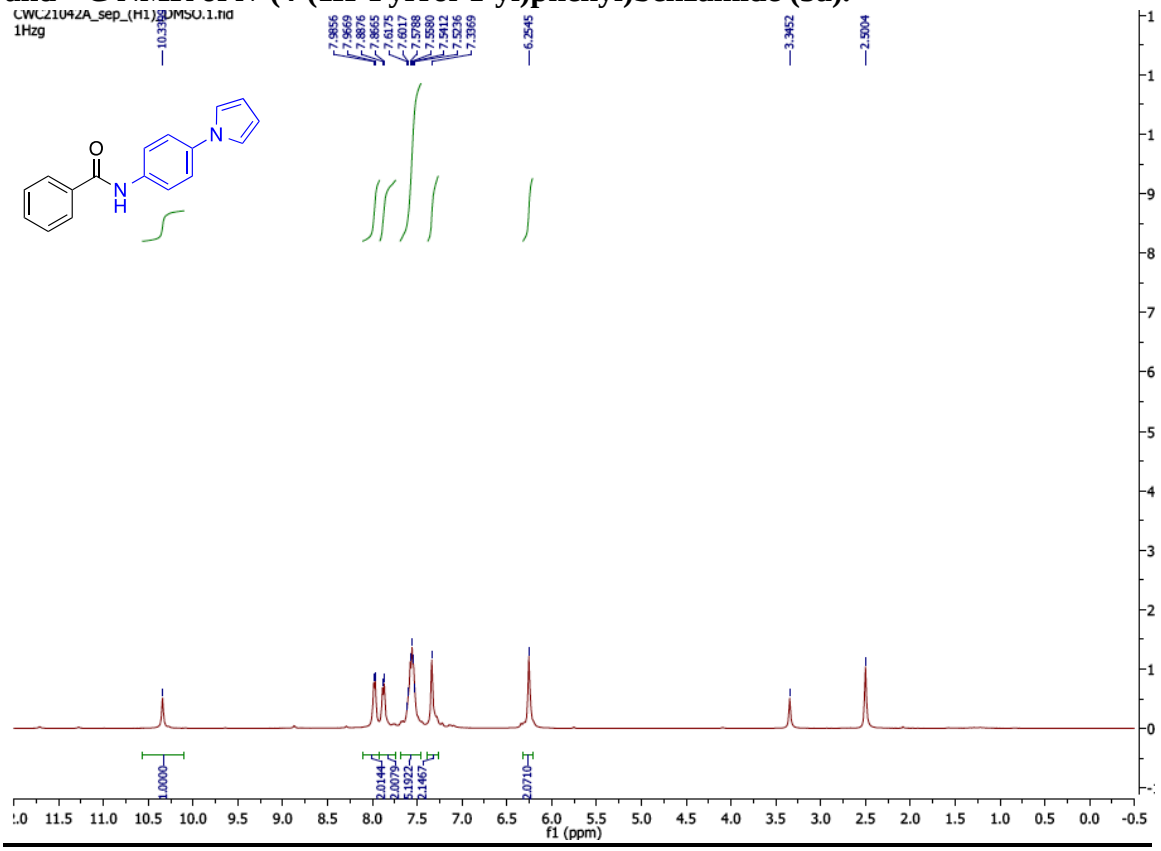


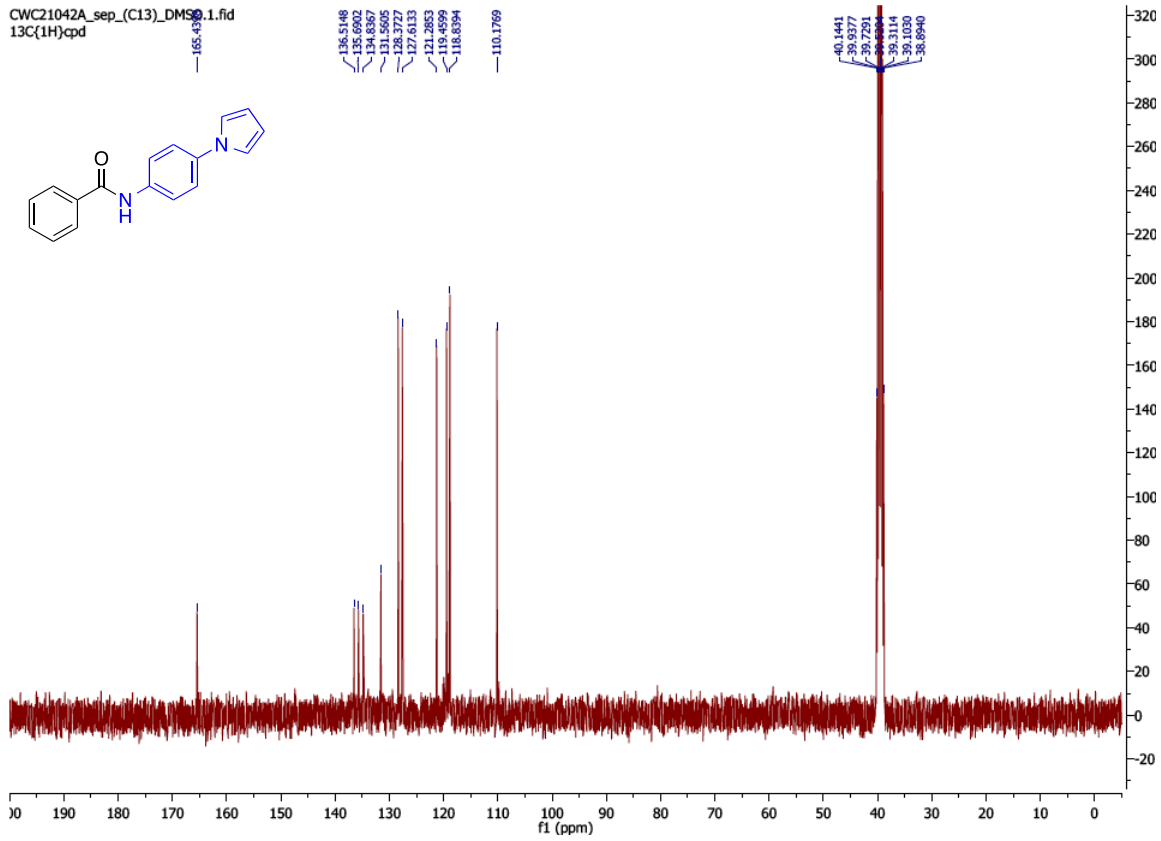
^{1}H and ^{13}C NMR of (4-(4-Nitrophenoxy)phenyl)(phenyl)methanone (S16).



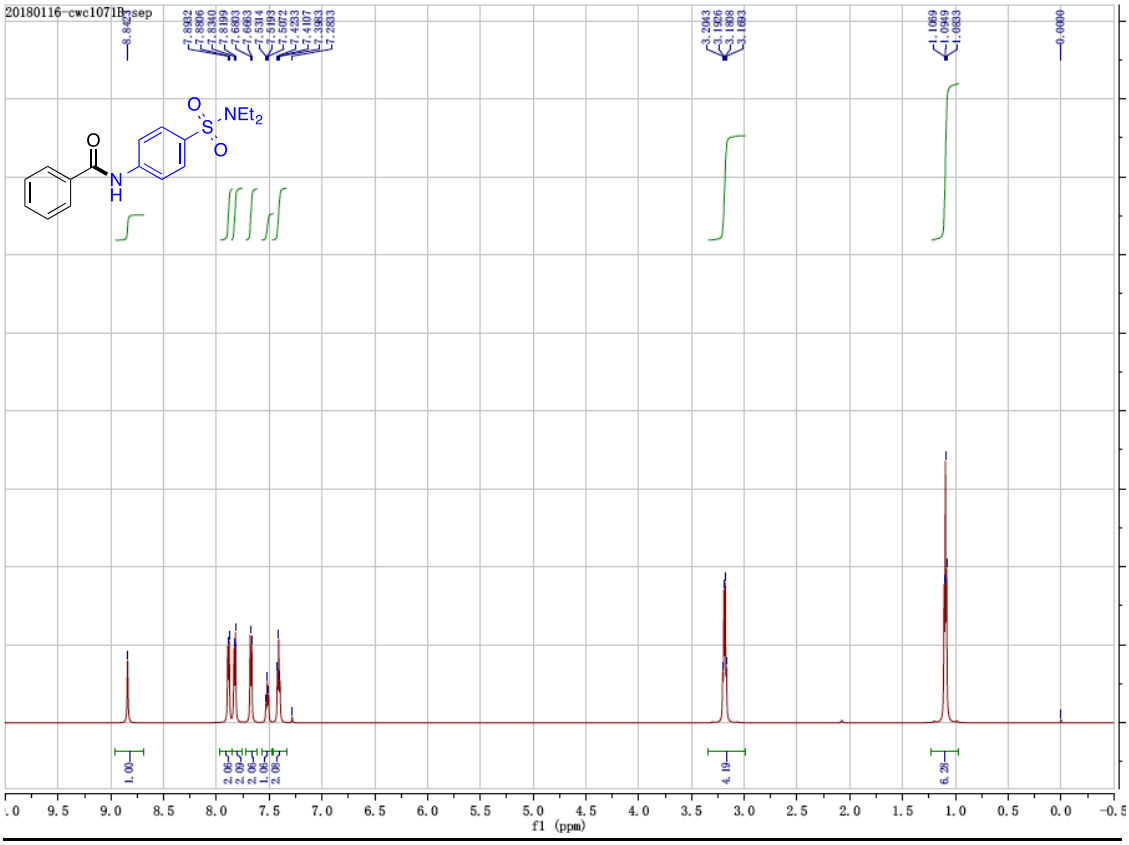


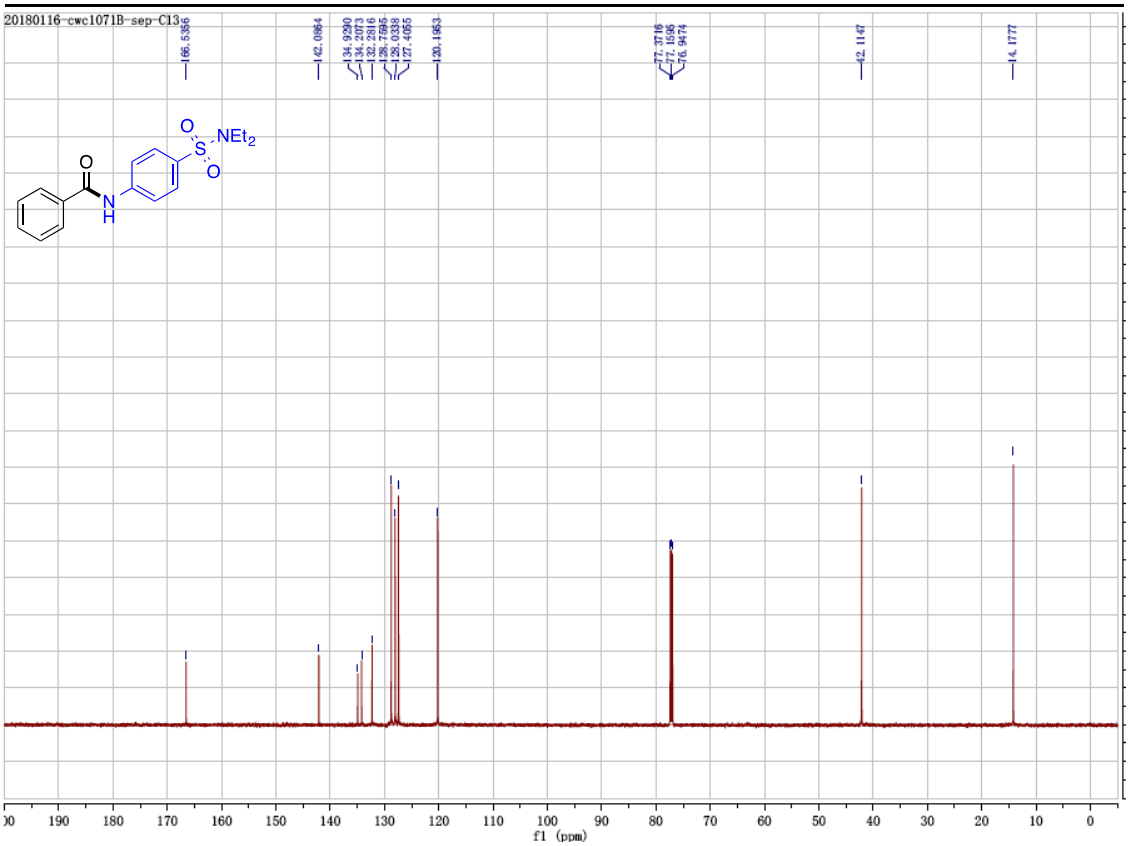
^{1}H and ^{13}C NMR of *N*-(4-(1*H*-Pyrrol-1-yl)phenyl)benzamide (3a).



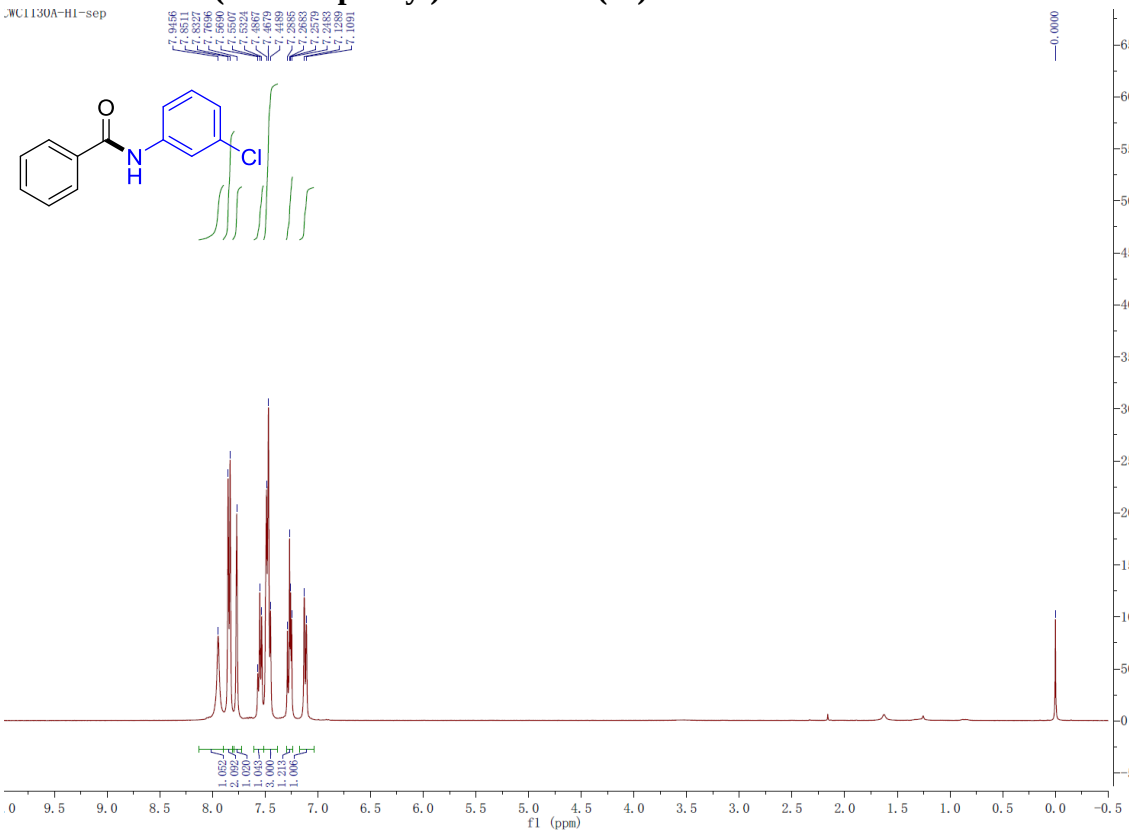


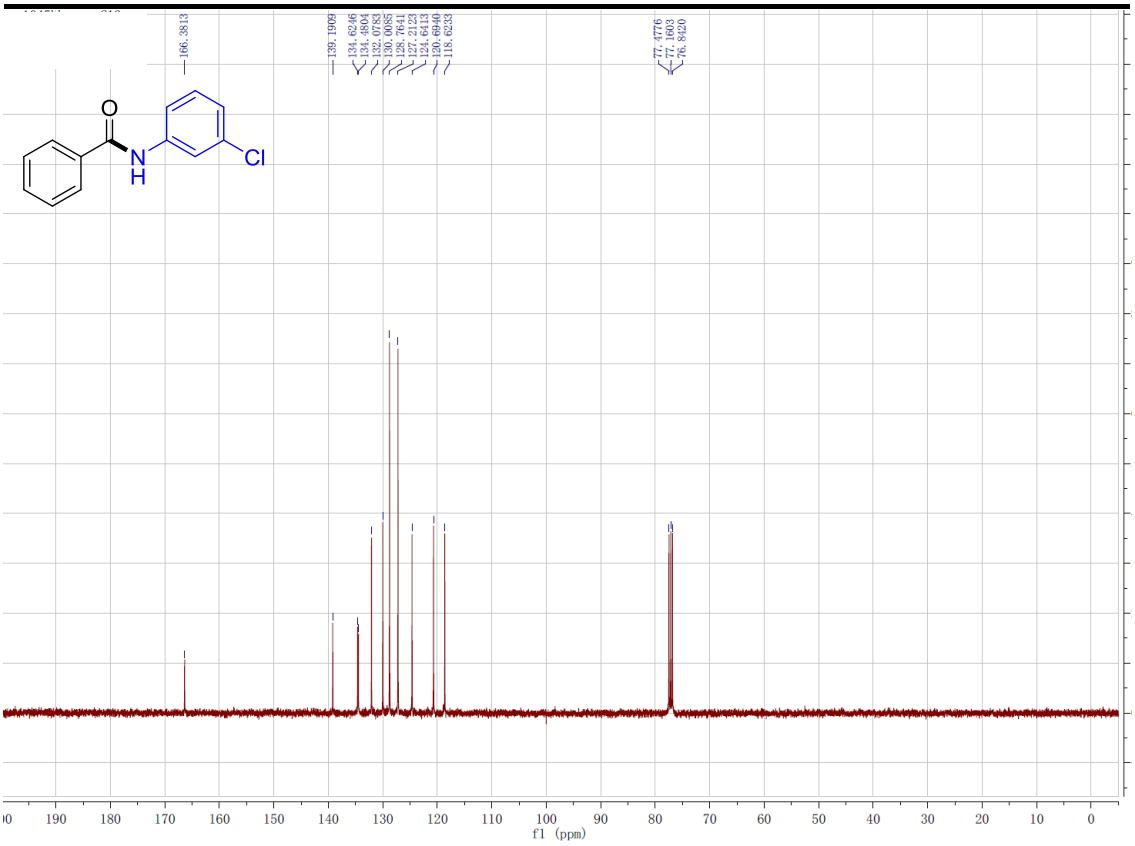
^{1}H and ^{13}C NMR of *N*-(4-(*N*,*N*-diethylsulfamoyl)phenyl)benzamide (3b).



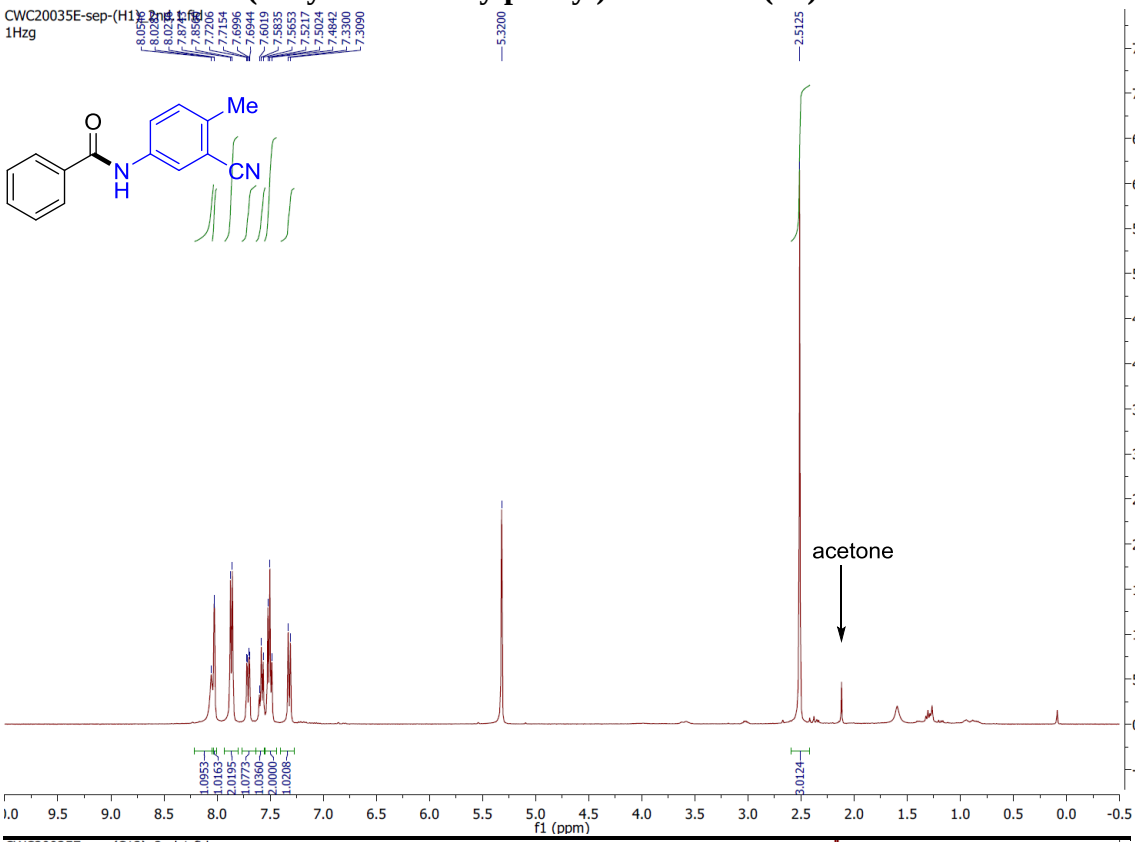


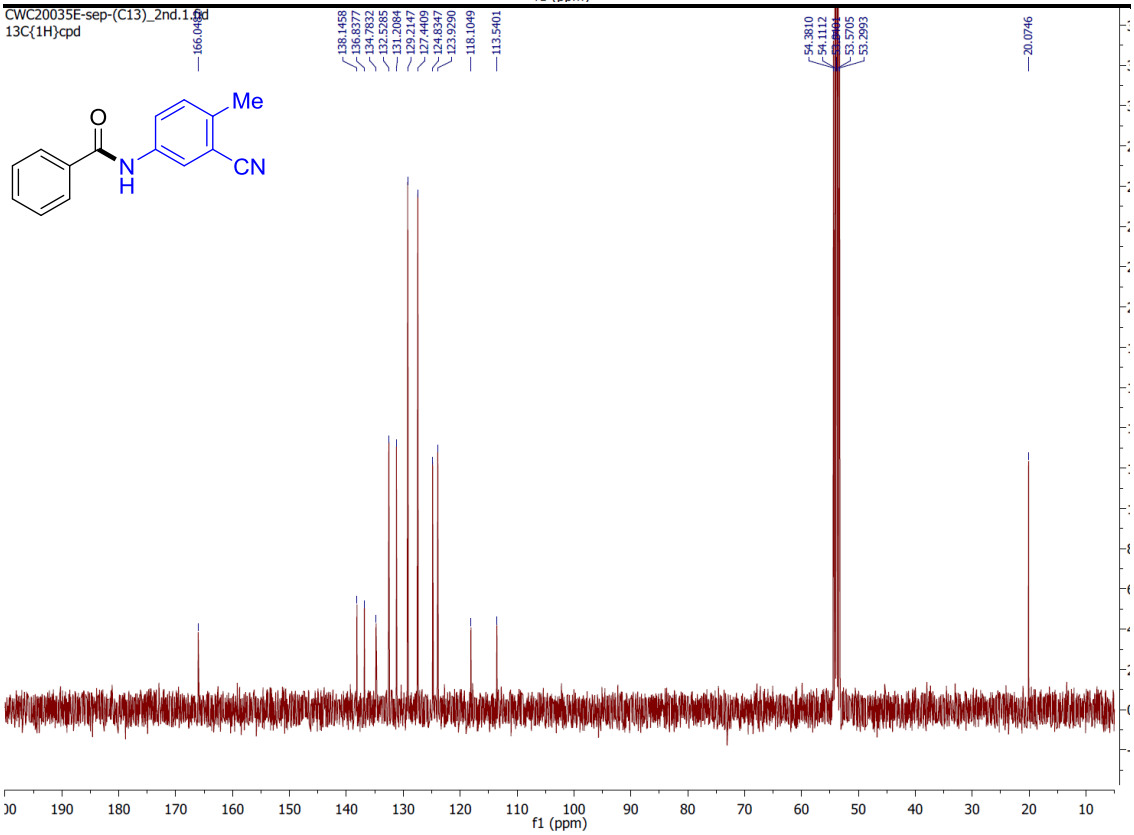
^{1}H and ^{13}C NMR of *N*-(3-chlorophenyl)benzamide (3c).



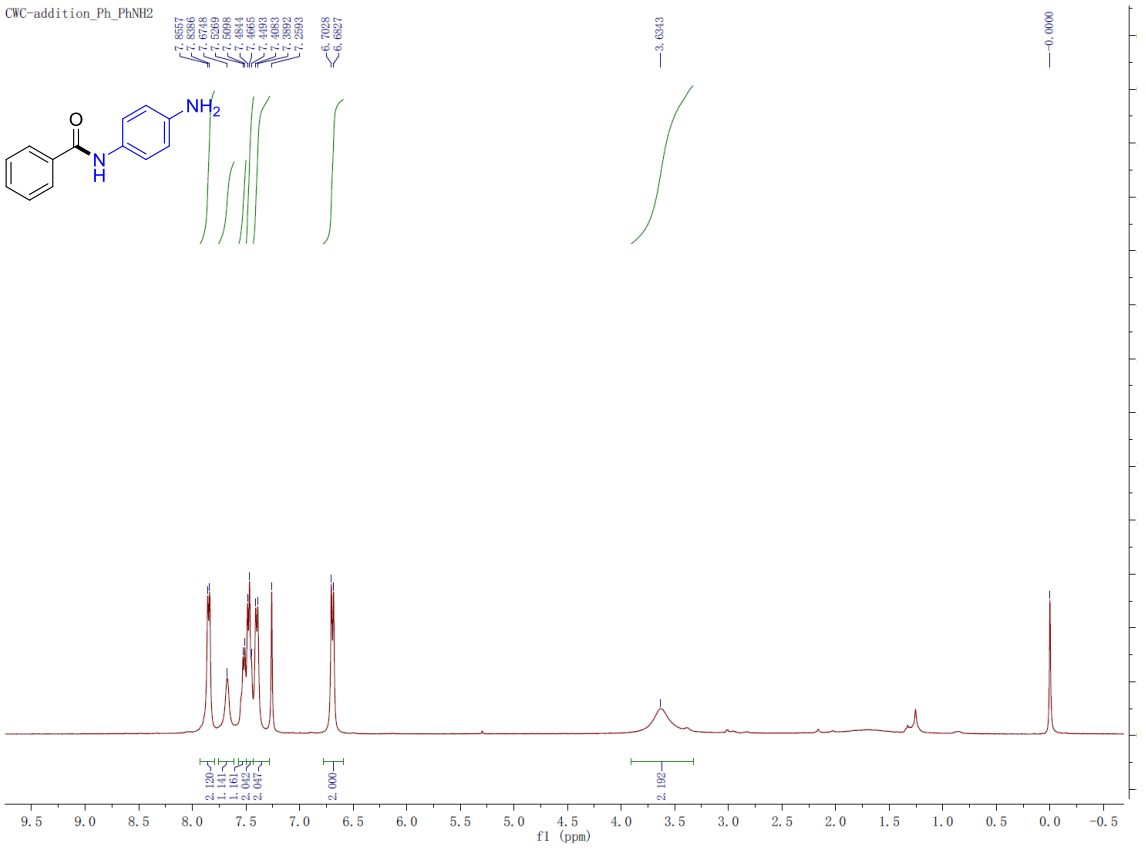


^{1}H and ^{13}C NMR of *N*-(3-Cyano-4-methylphenyl)benzamide (3d).





^{1}H and ^{13}C NMR of *N*-(4-aminophenyl)benzamide (3e).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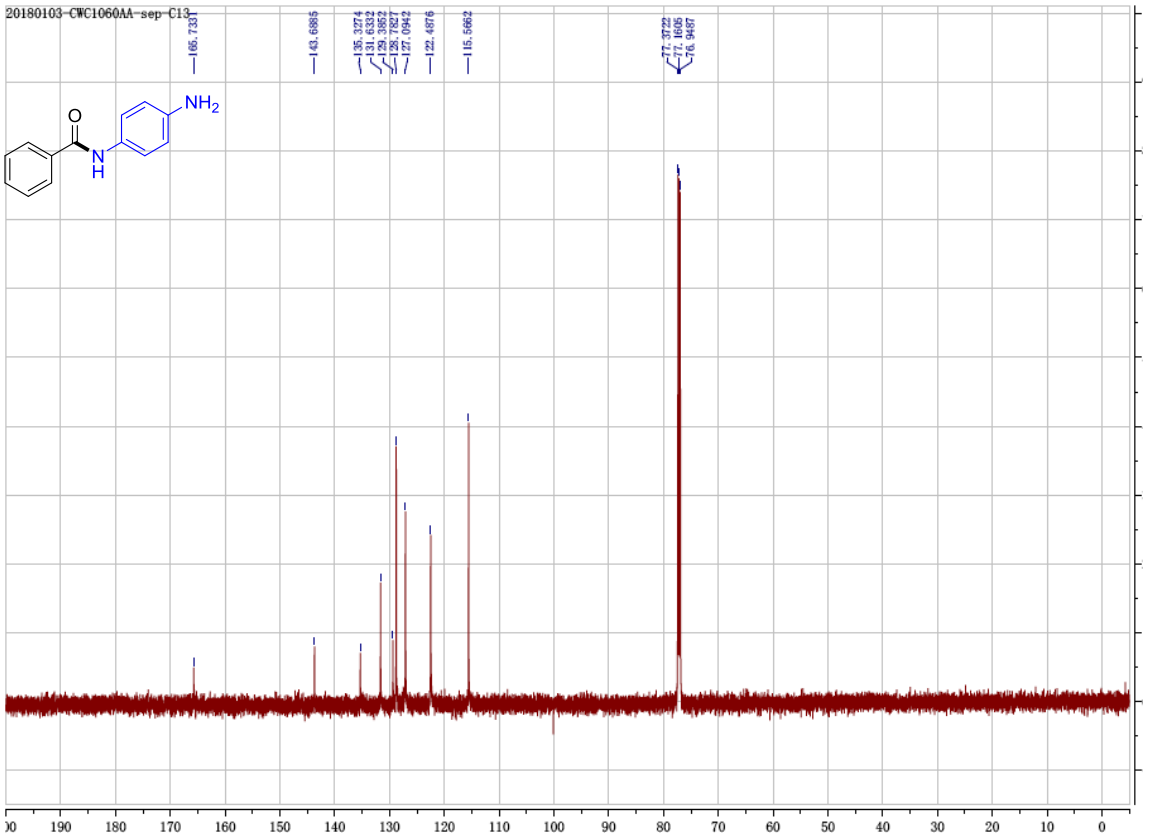
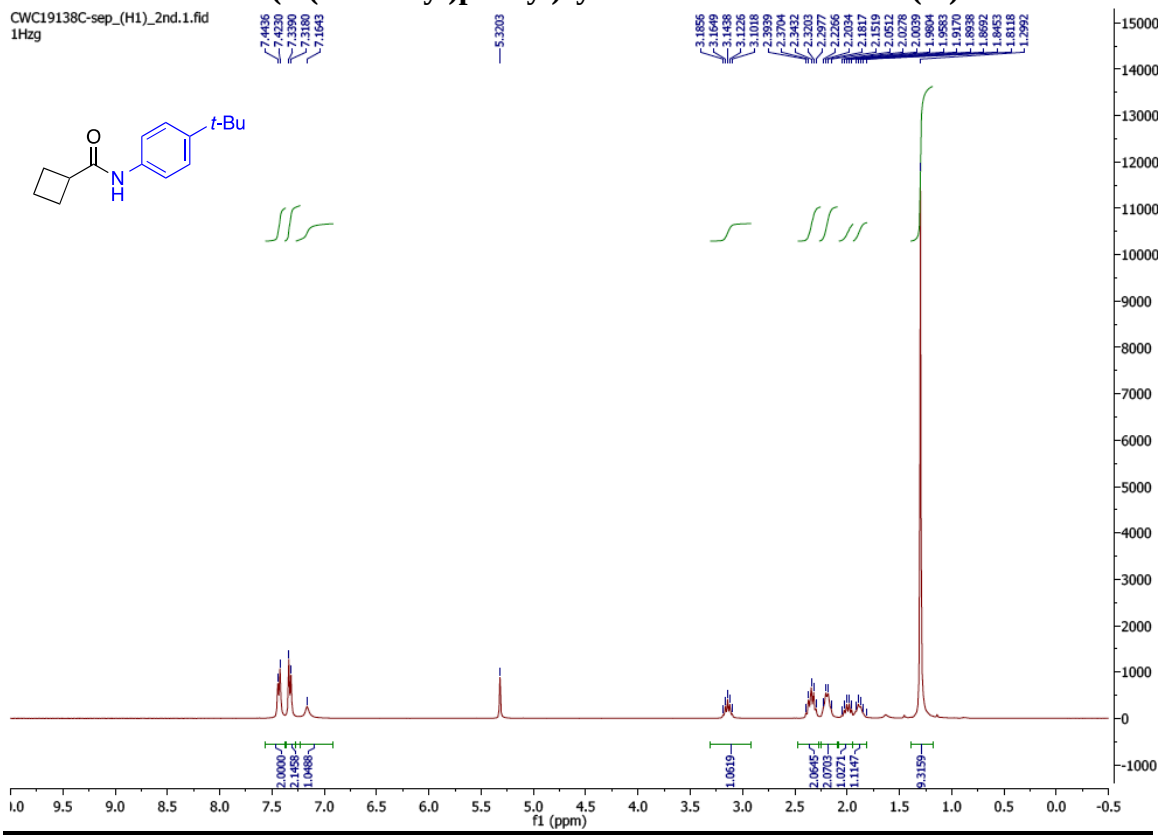
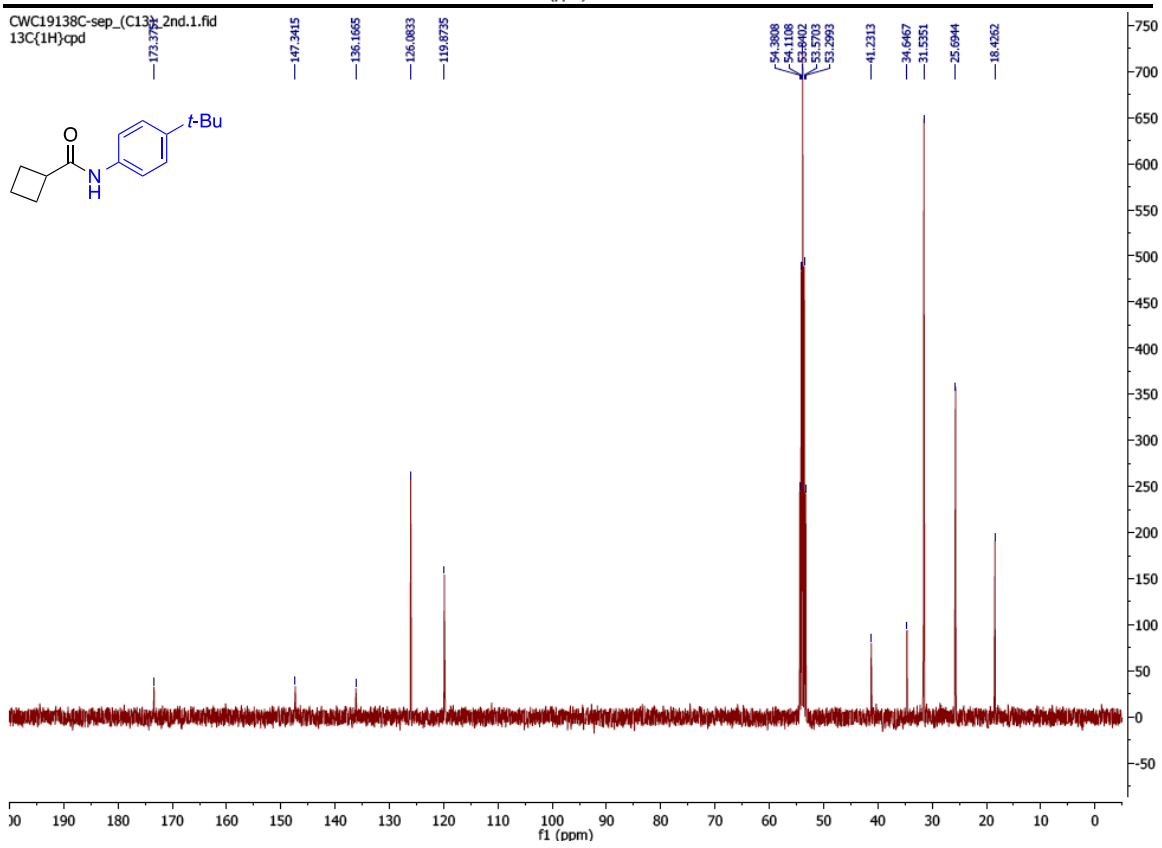
7.8386
7.6748
7.5898
7.5698
7.5008
7.4844
7.4665
7.4493
7.4083
7.3892
7.2593
6.7028
6.6827
3.6343
0.0000
NH2
O
N
H
2.120
1.141
1.161
2.092
2.047
2.000
2.192
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

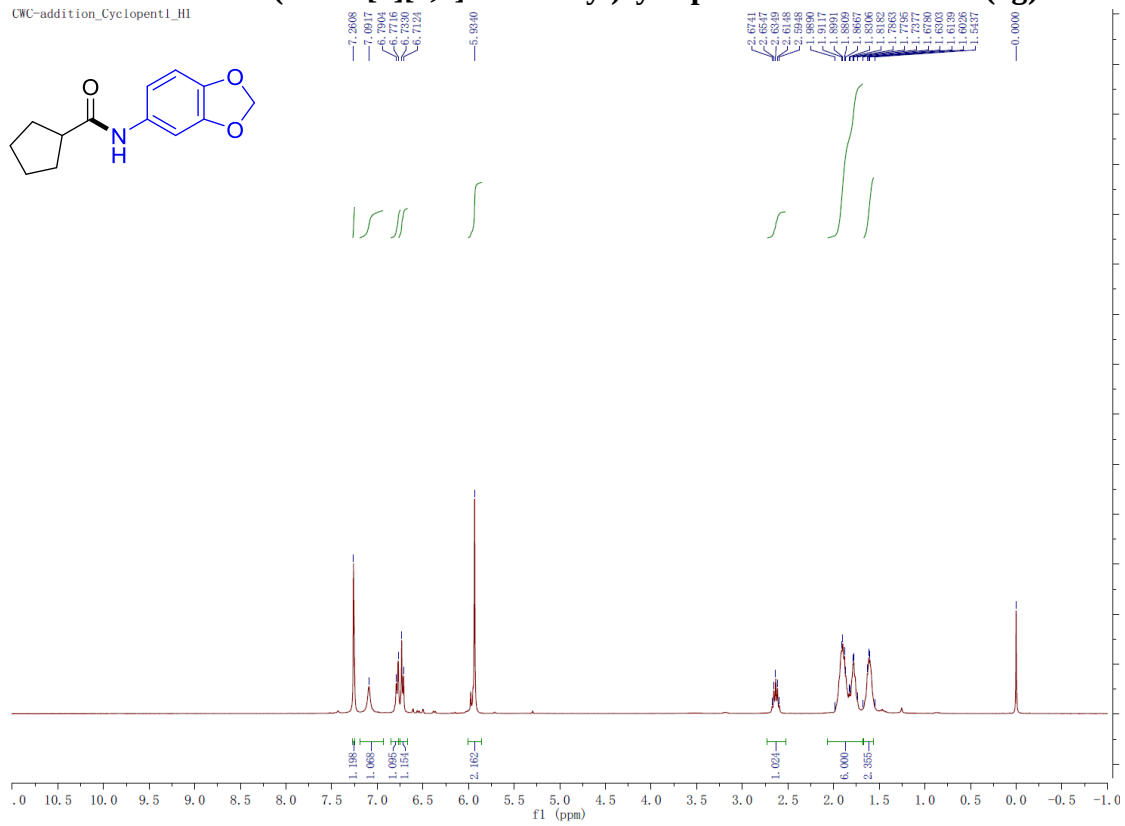

20180103-CWC1060AA-sep-C13
166.7331
143.6885
135.3274
131.6332
129.3365
128.7827
127.0942
122.4576
115.5662
77.3722
77.1695
76.9667
NH2
O
N
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

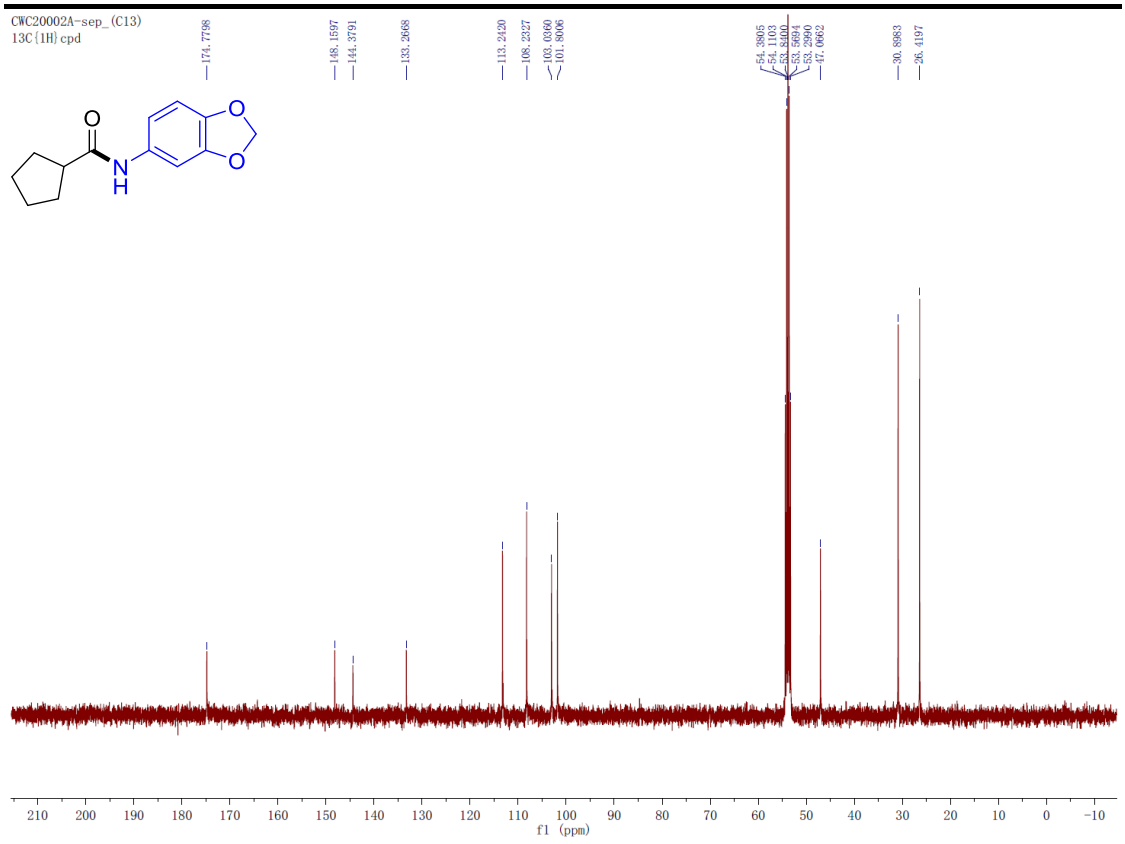
^{1}H and ^{13}C NMR of *N*-(4-(*tert*-Butyl)phenyl)cyclobutanecarboxamide (3f).



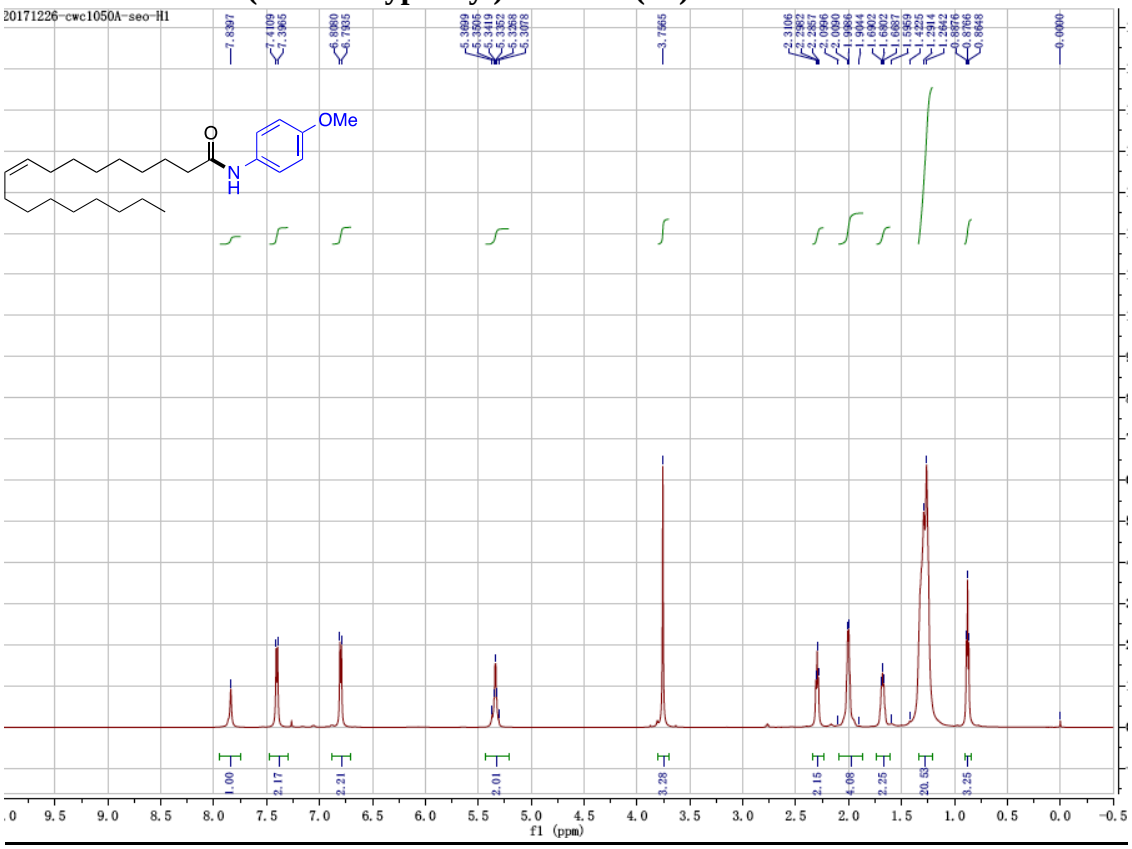


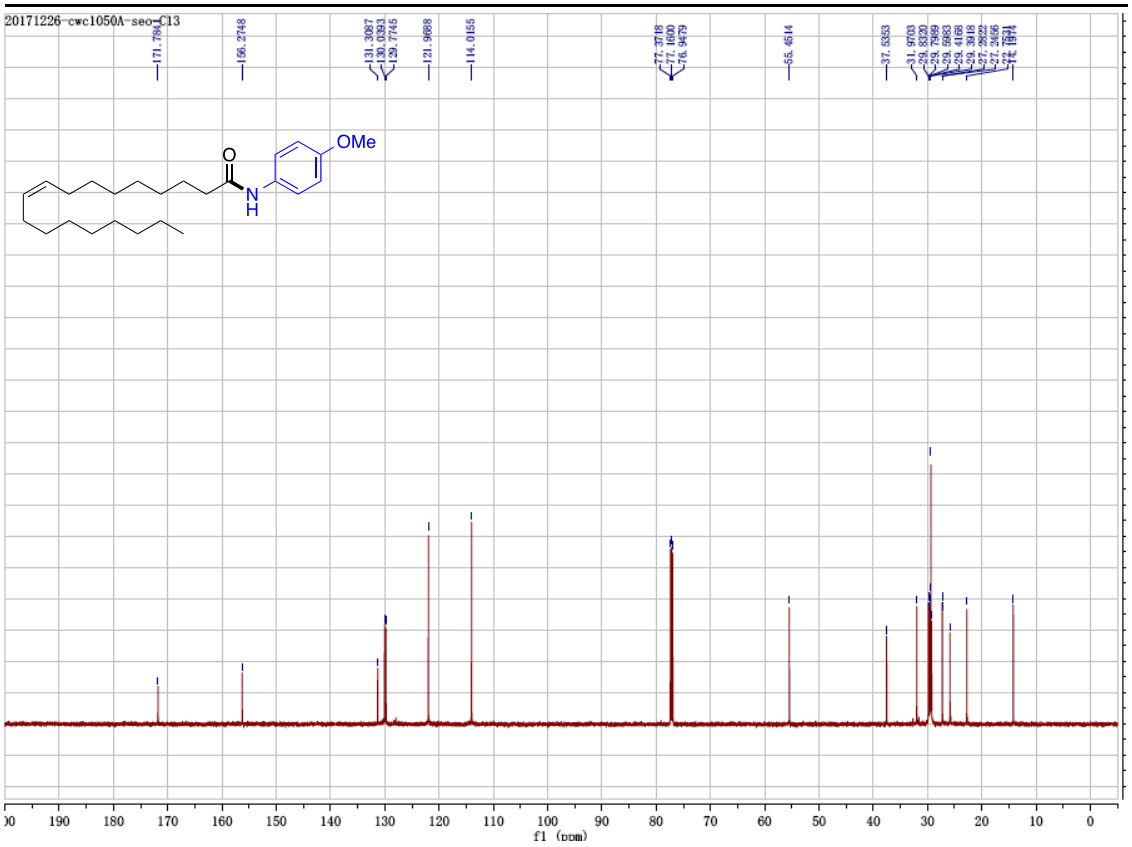
^{1}H and ^{13}C NMR of *N*-(Benzo[*d*][1,3]dioxol-5-yl)cyclopentanecarboxamide (3g).



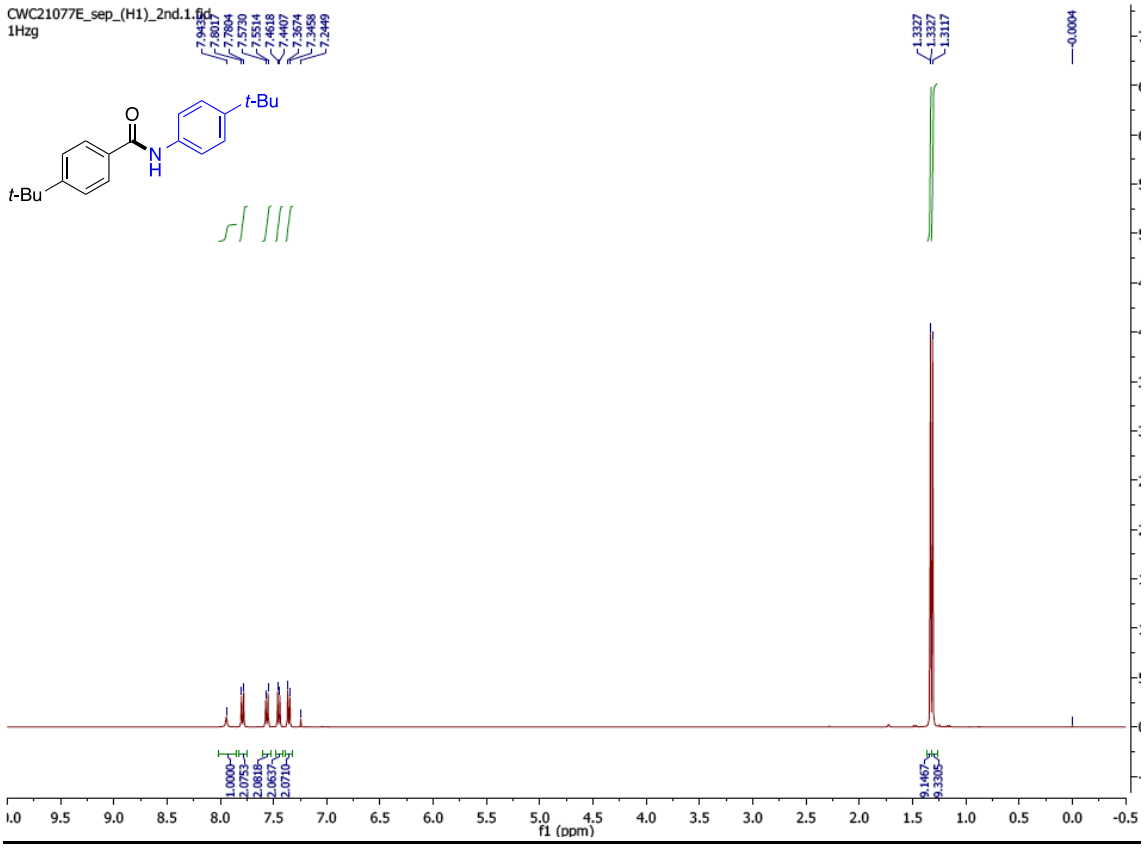


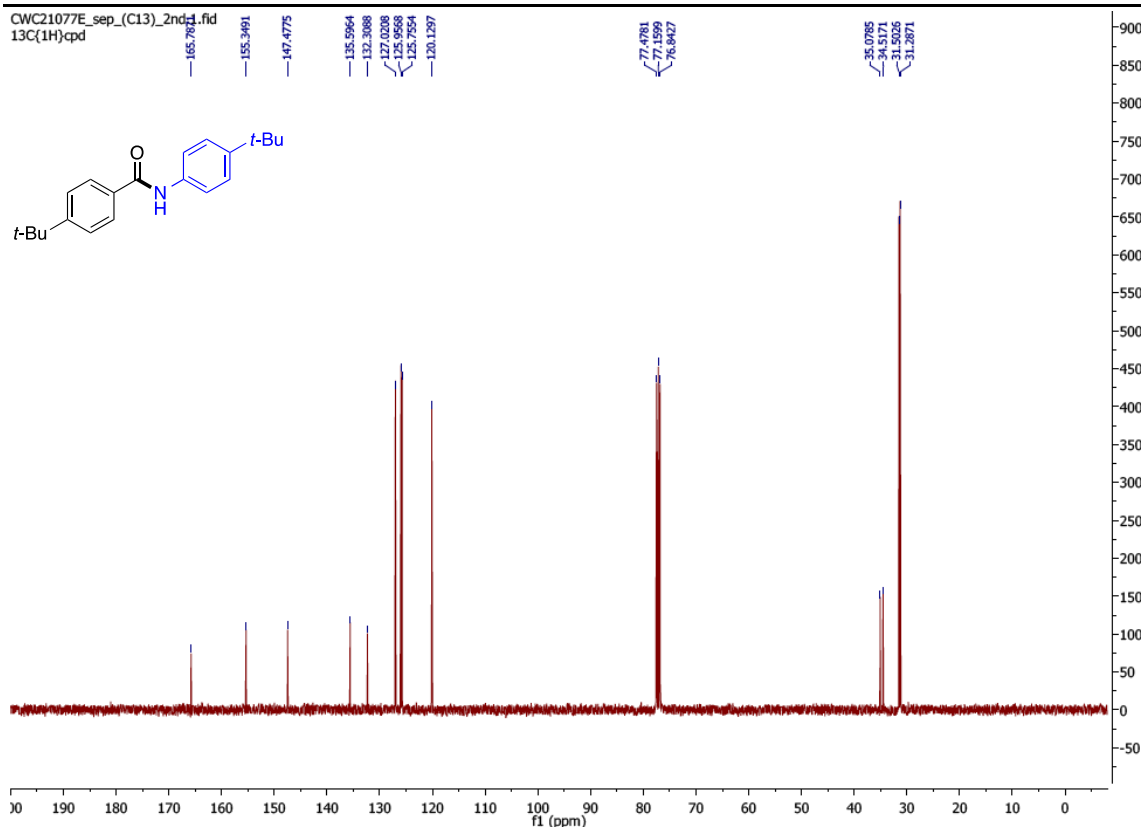
^{1}H and ^{13}C NMR of *N*-(4-methoxyphenyl)oleamide (3h).



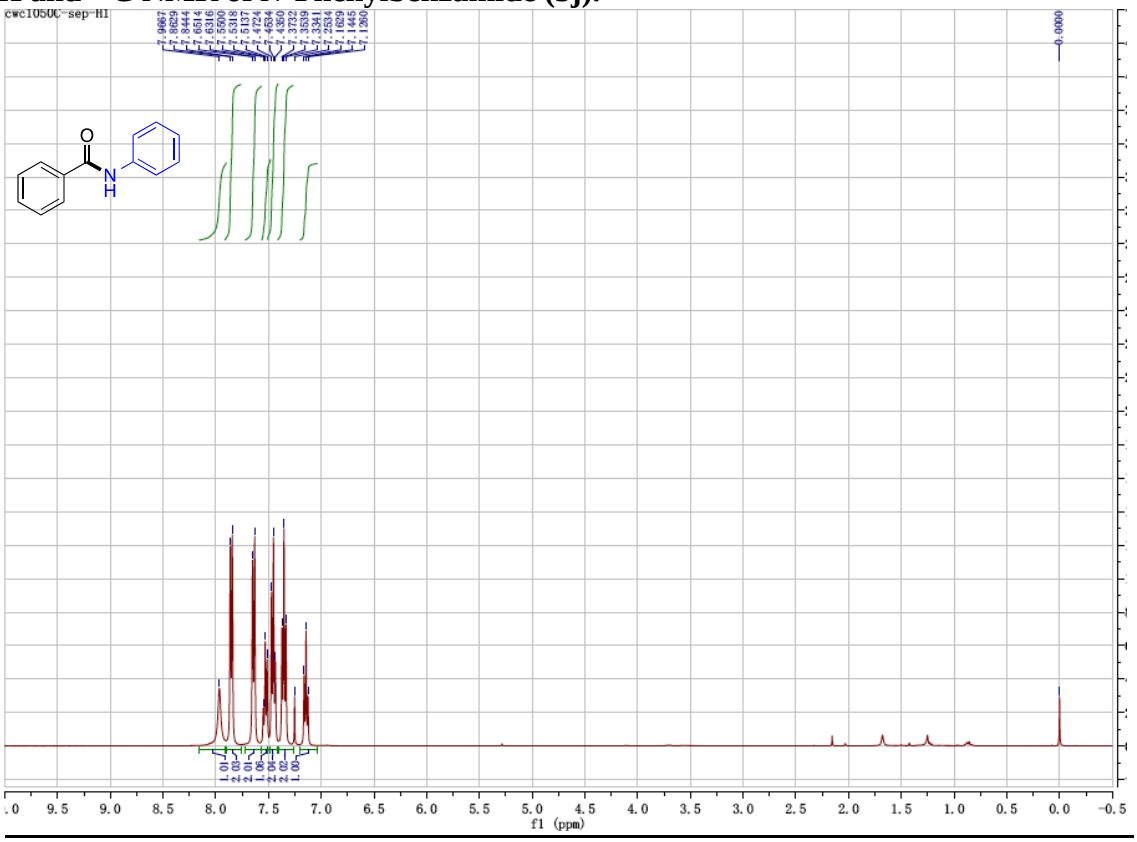


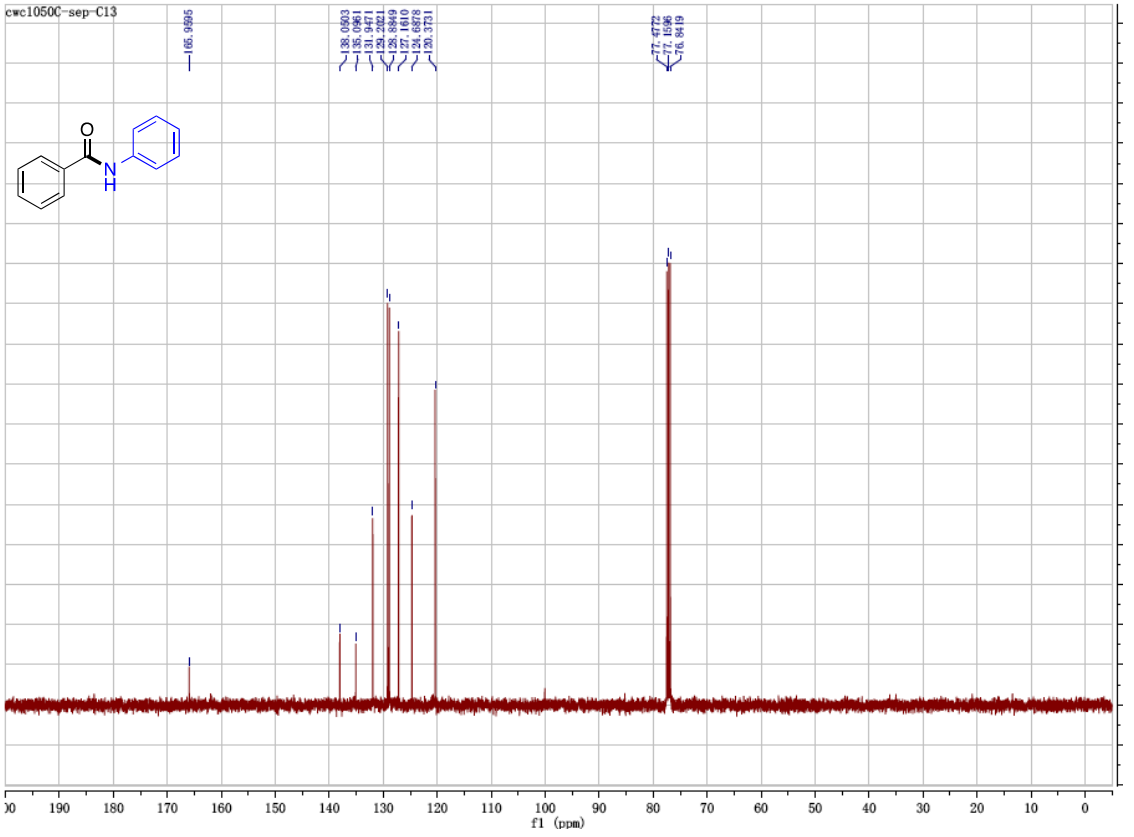
^{1}H and ^{13}C NMR of 4-(*tert*-Butyl)-*N*-(4-(*tert*-butyl)phenyl)benzamide (3i).



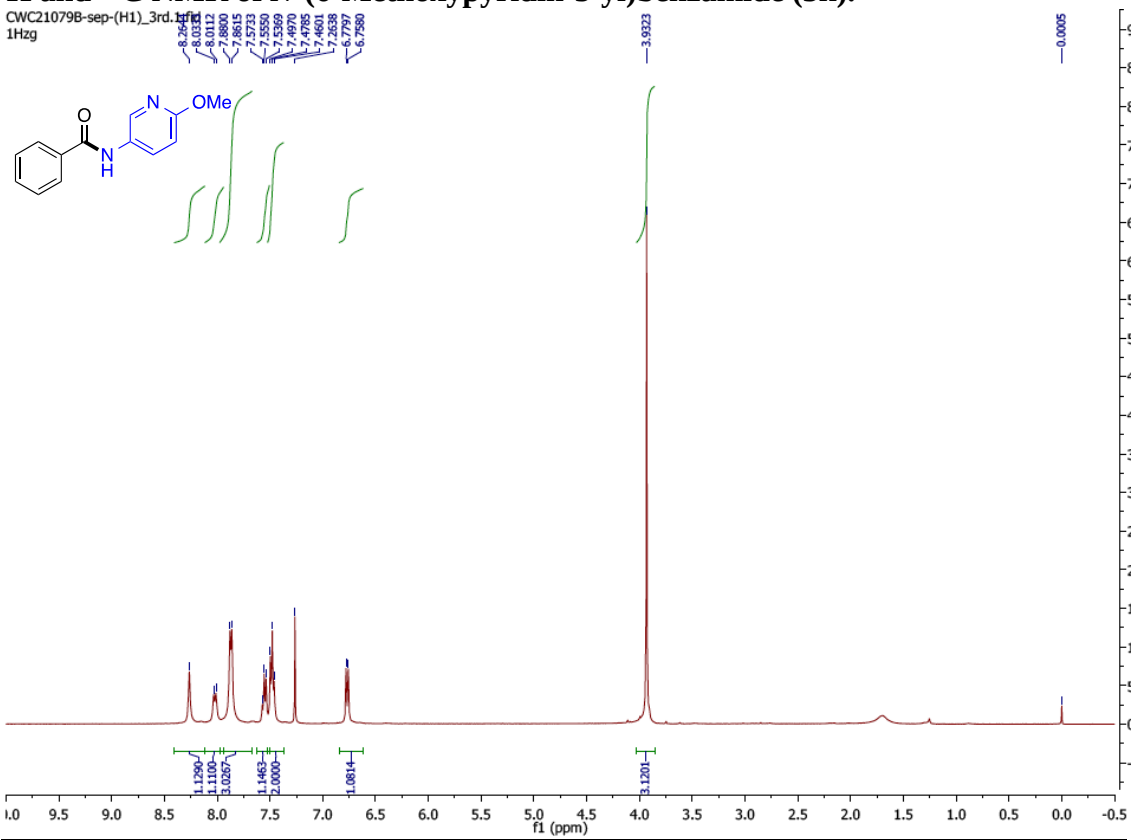


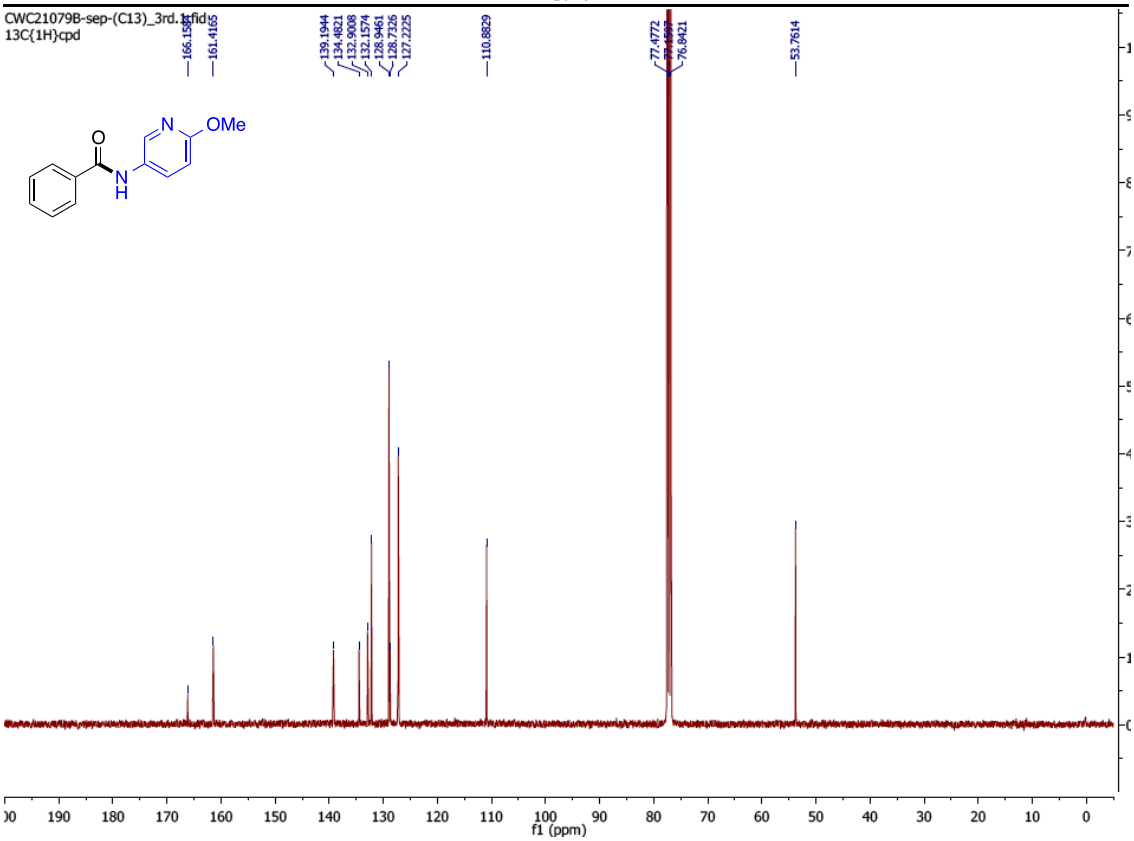
^{1}H and ^{13}C NMR of *N*-Phenylbenzamide (3j).



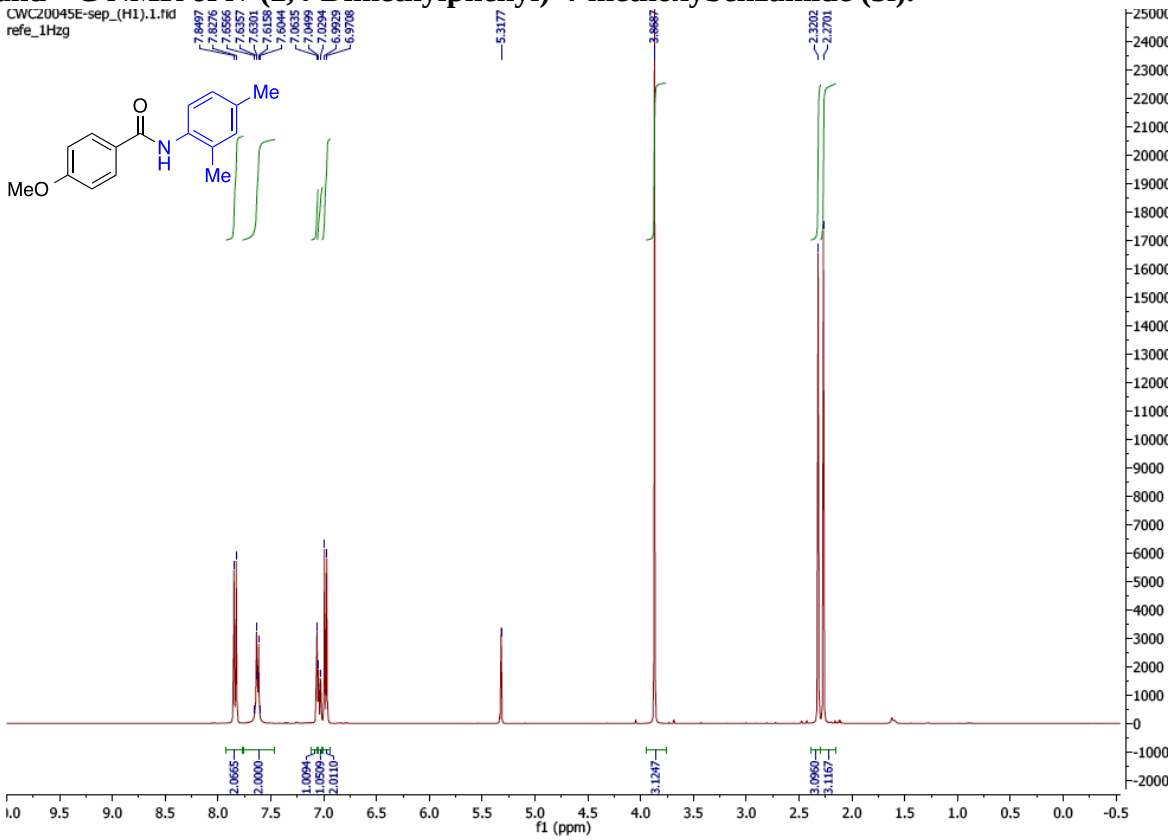


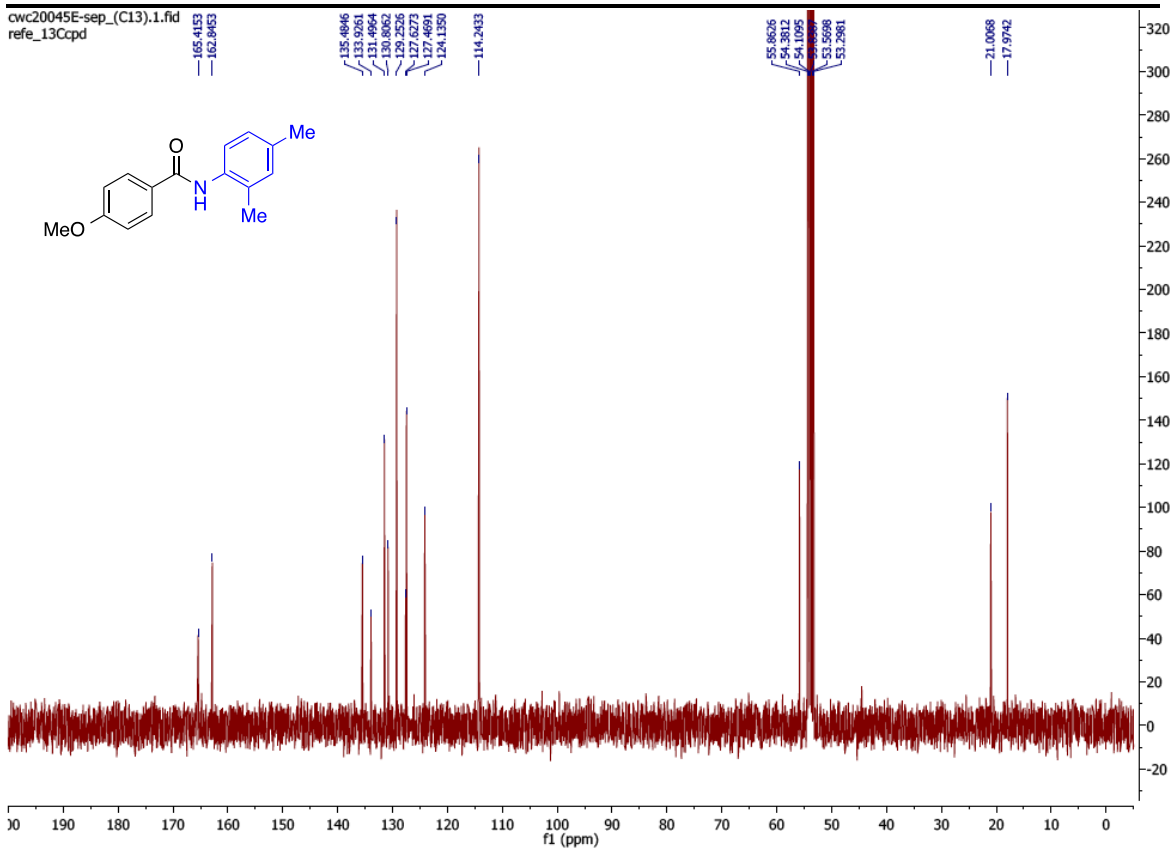
^{1}H and ^{13}C NMR of *N*-(6-Methoxypyridin-3-yl)benzamide (3k).



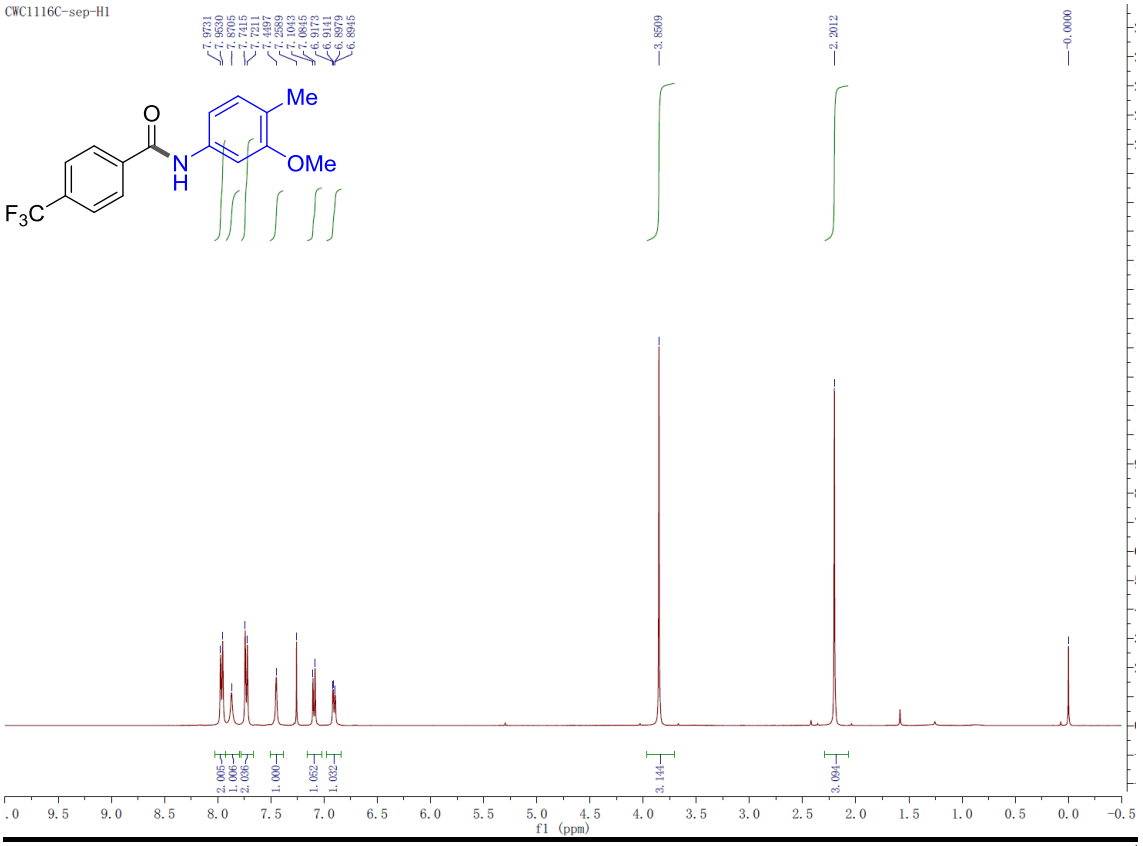


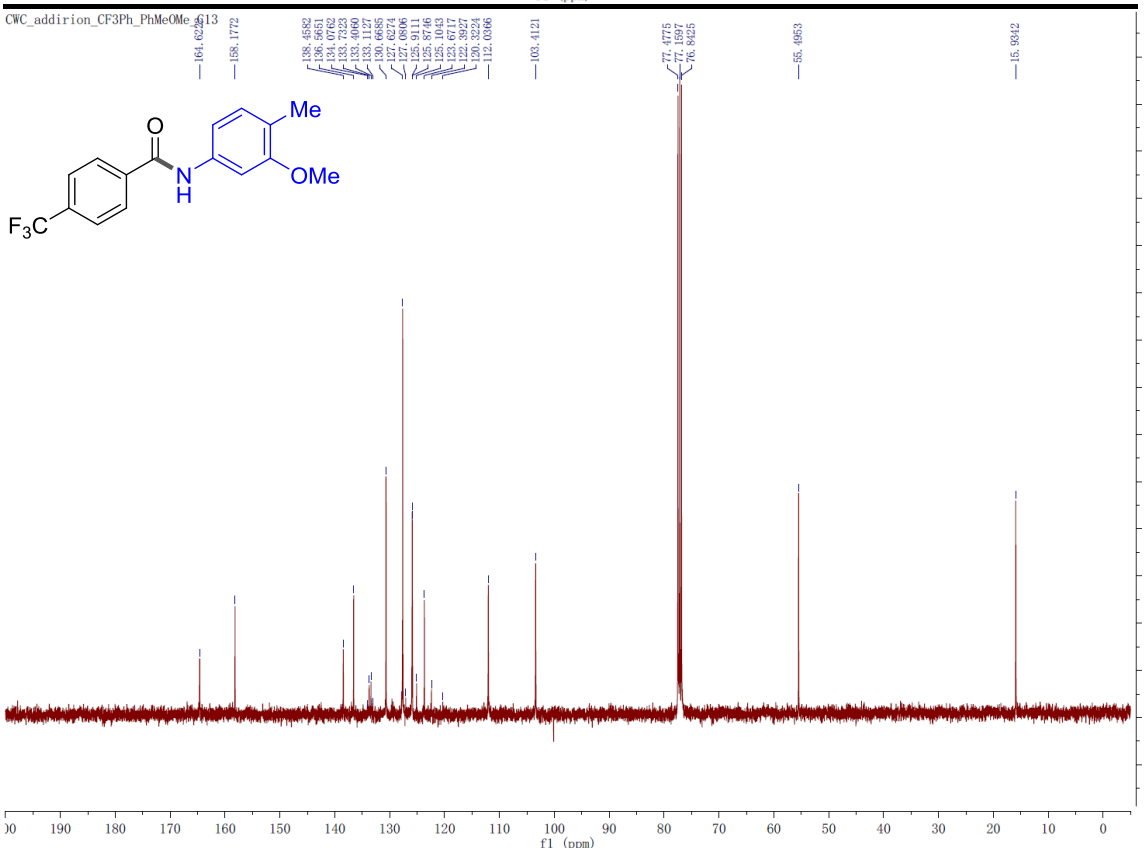
^{1}H and ^{13}C NMR of *N*-(2,4-Dimethylphenyl)-4-methoxybenzamide (3l).



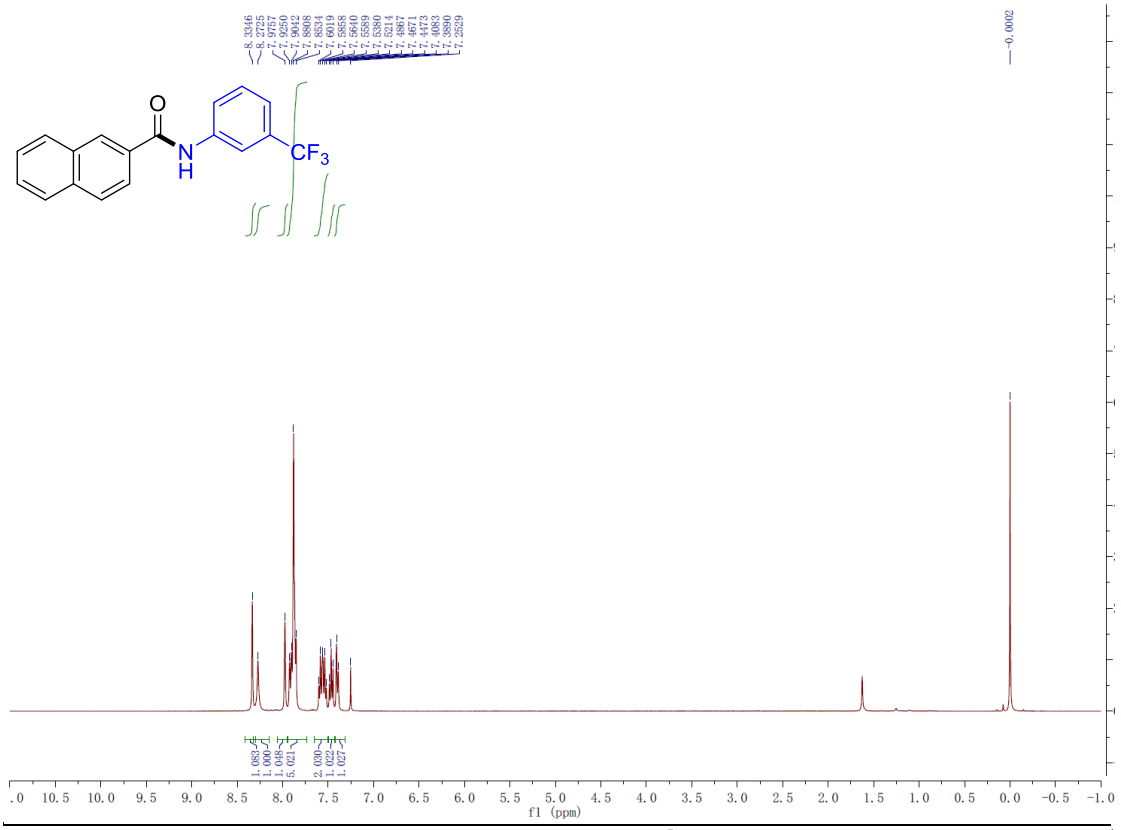


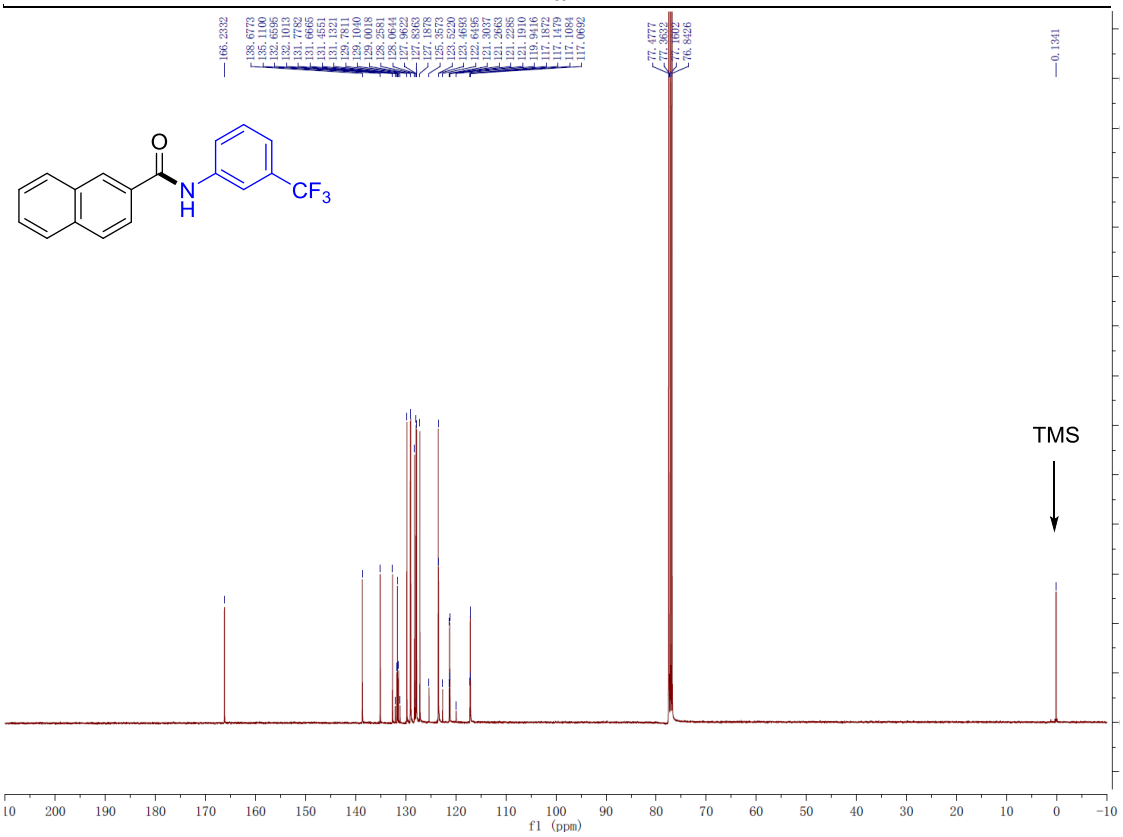
^{1}H and ^{13}C NMR of *N*-(3-Methoxy-4-methylphenyl)-4-(trifluoromethyl)benzamide (3m).



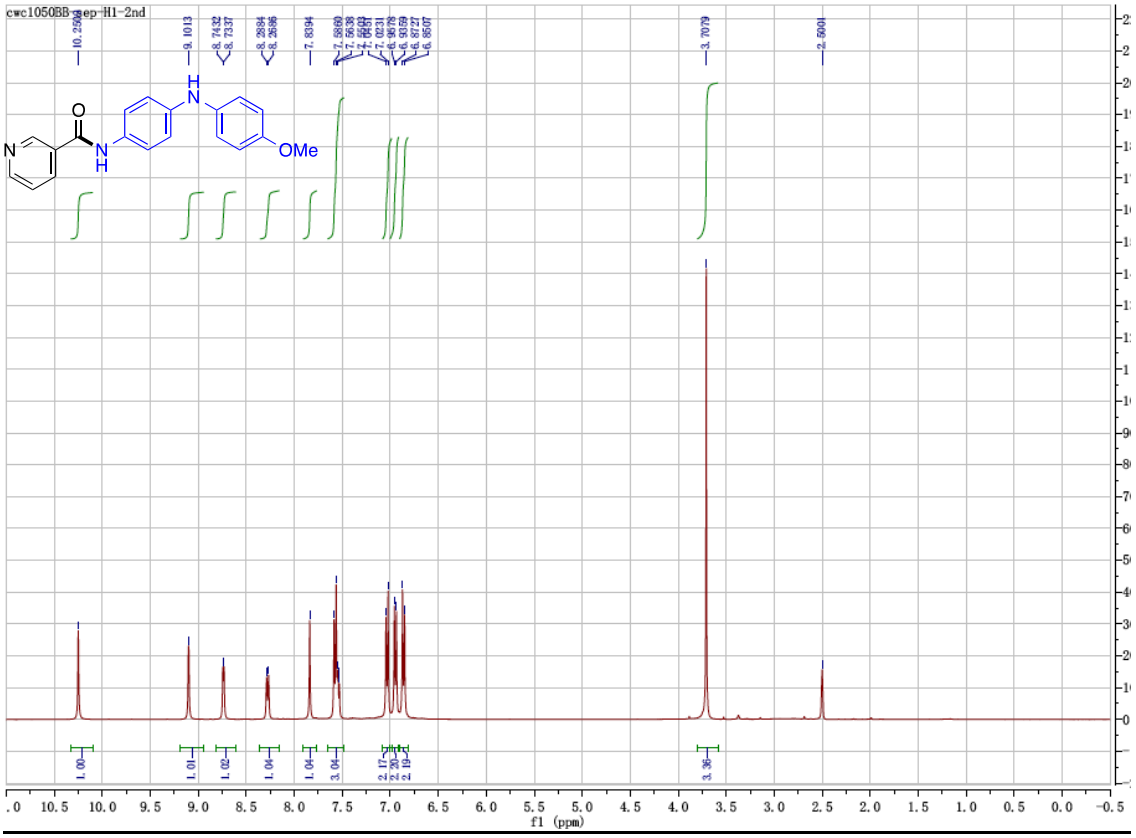


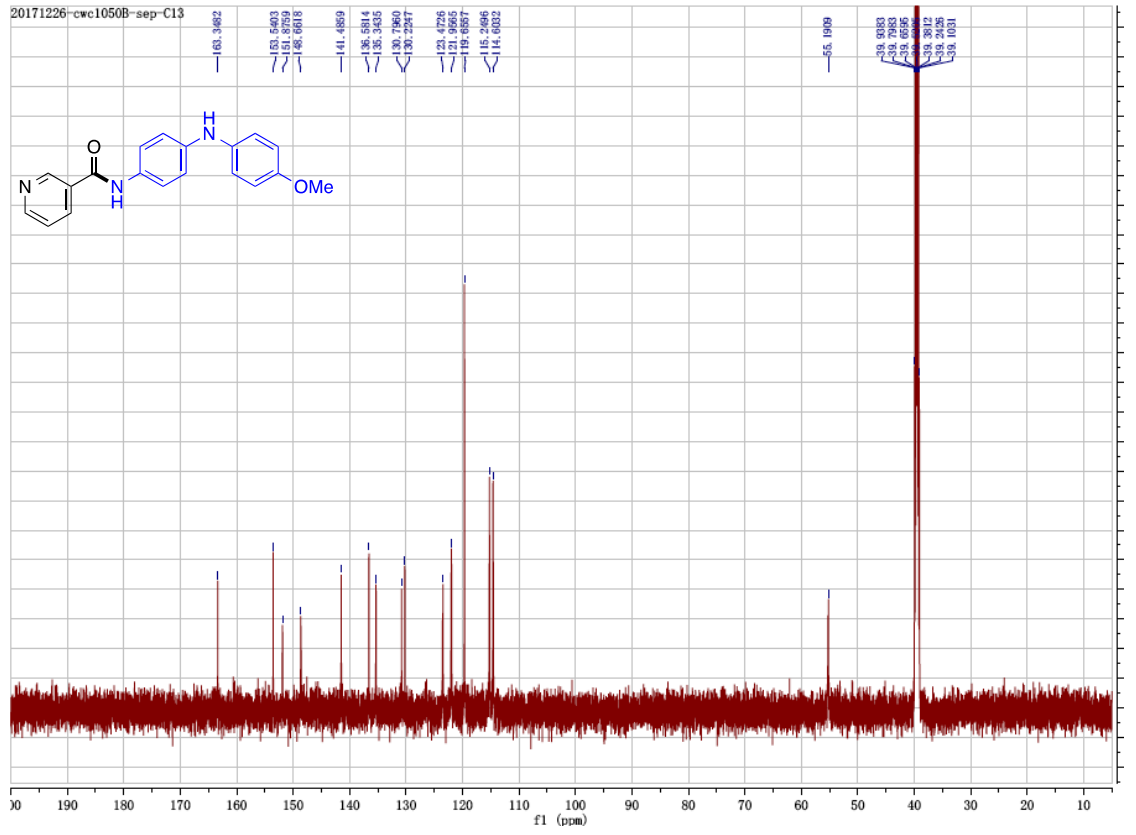
^{1}H and ^{13}C NMR of *N*-(3-(Trifluoromethyl)phenyl)-2-naphthamide (3n).



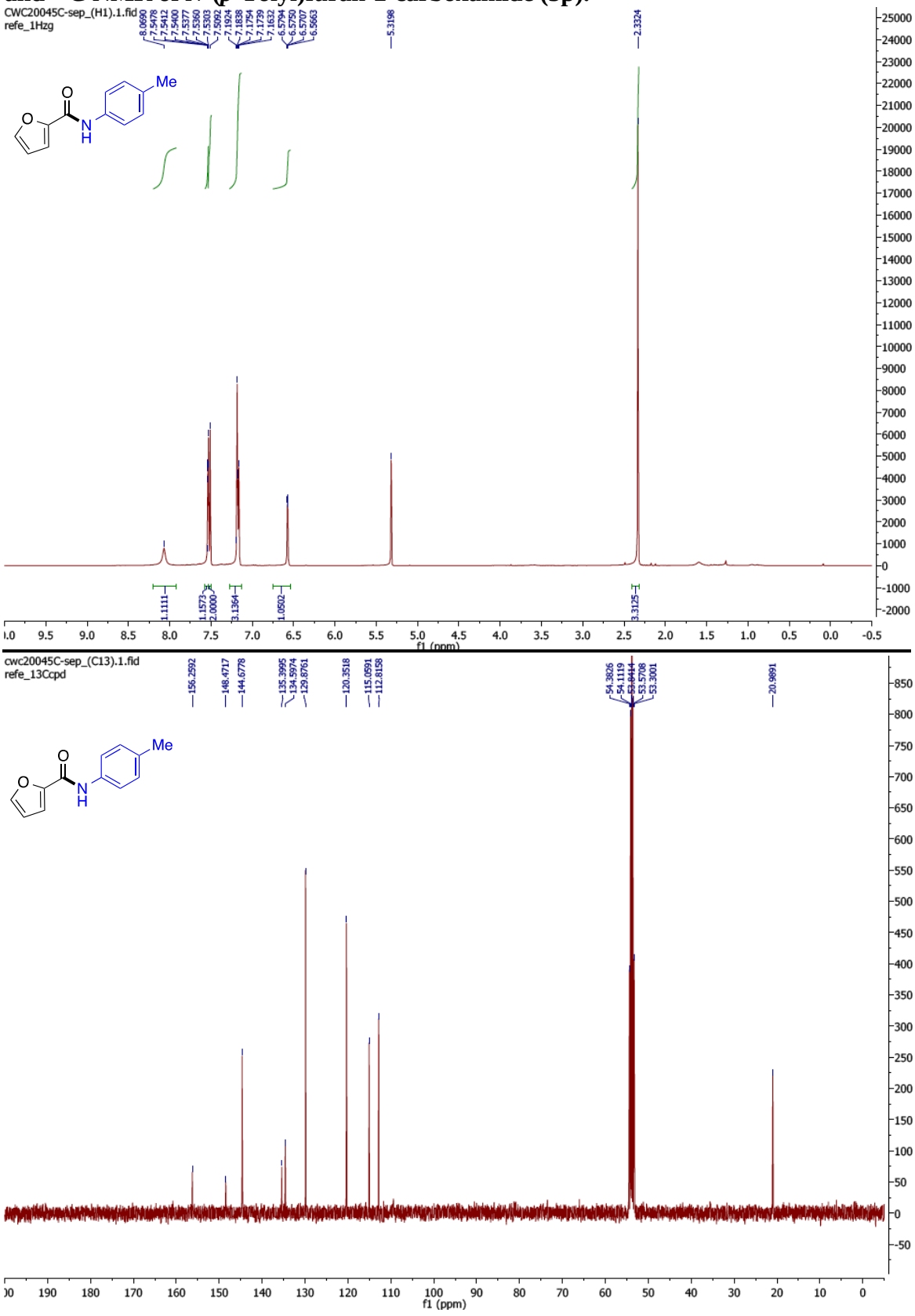


^{1}H and ^{13}C NMR of *N*-(4-((4-methoxyphenyl)amino)phenyl)nicotinamide (3o).

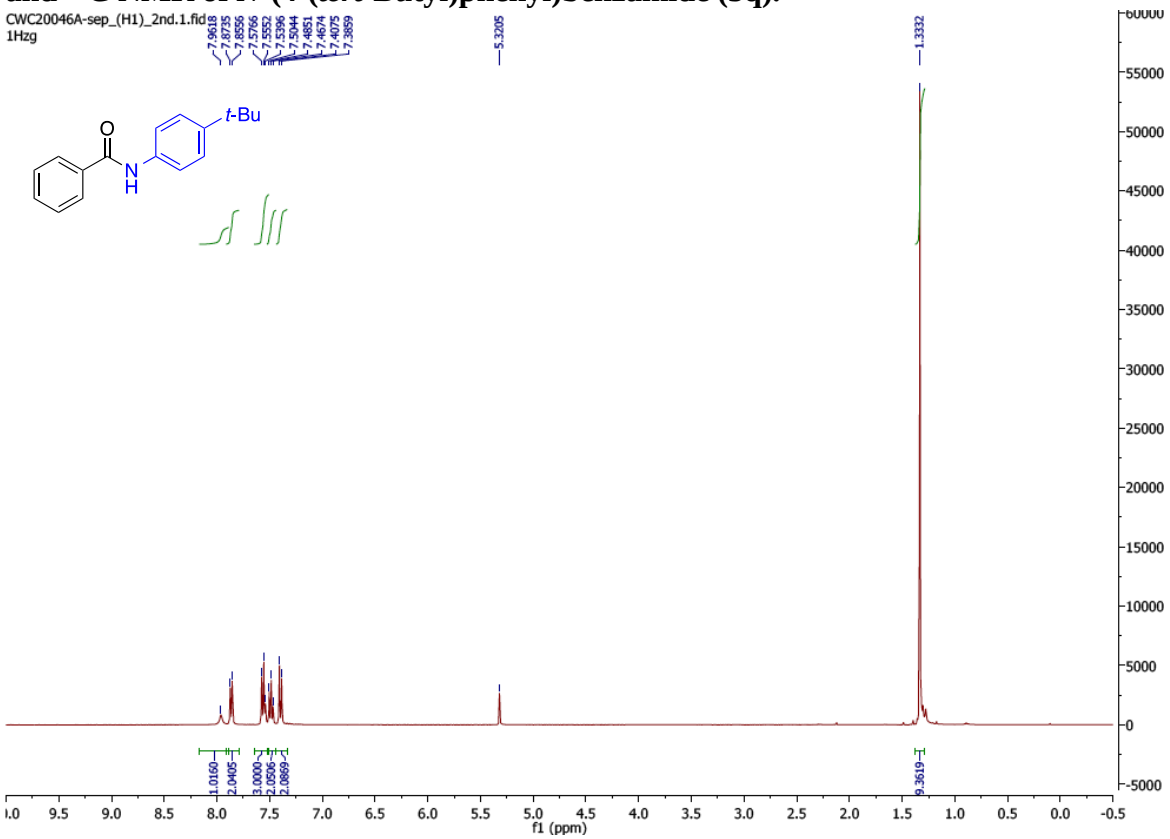


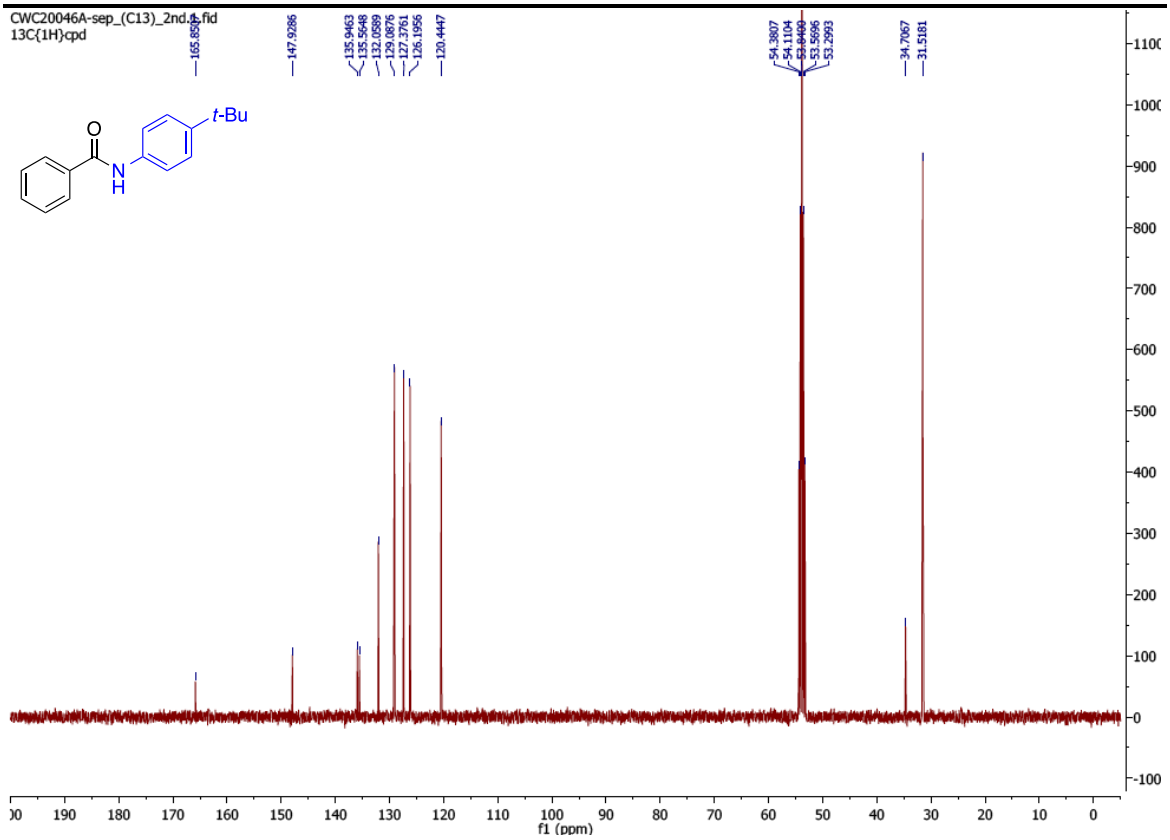


^{1}H and ^{13}C NMR of *N*-(*p*-Tolyl)furan-2-carboxamide (3p).

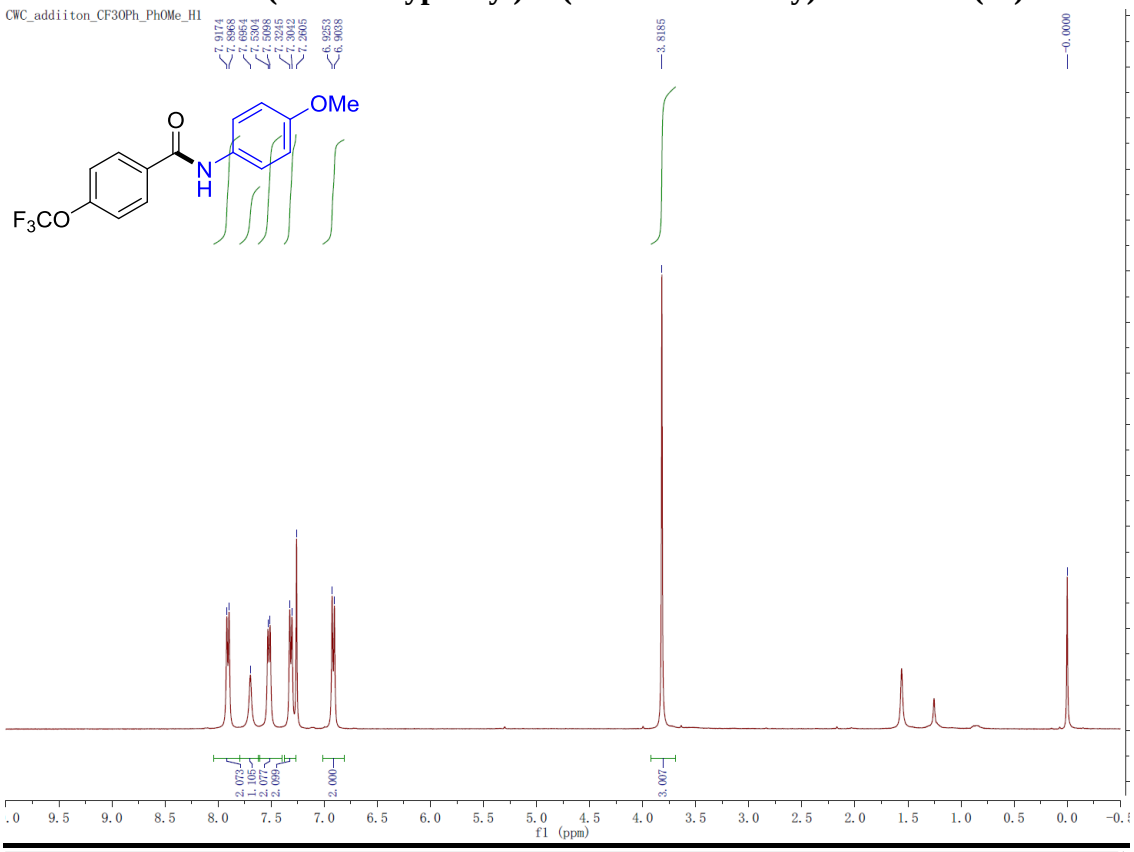


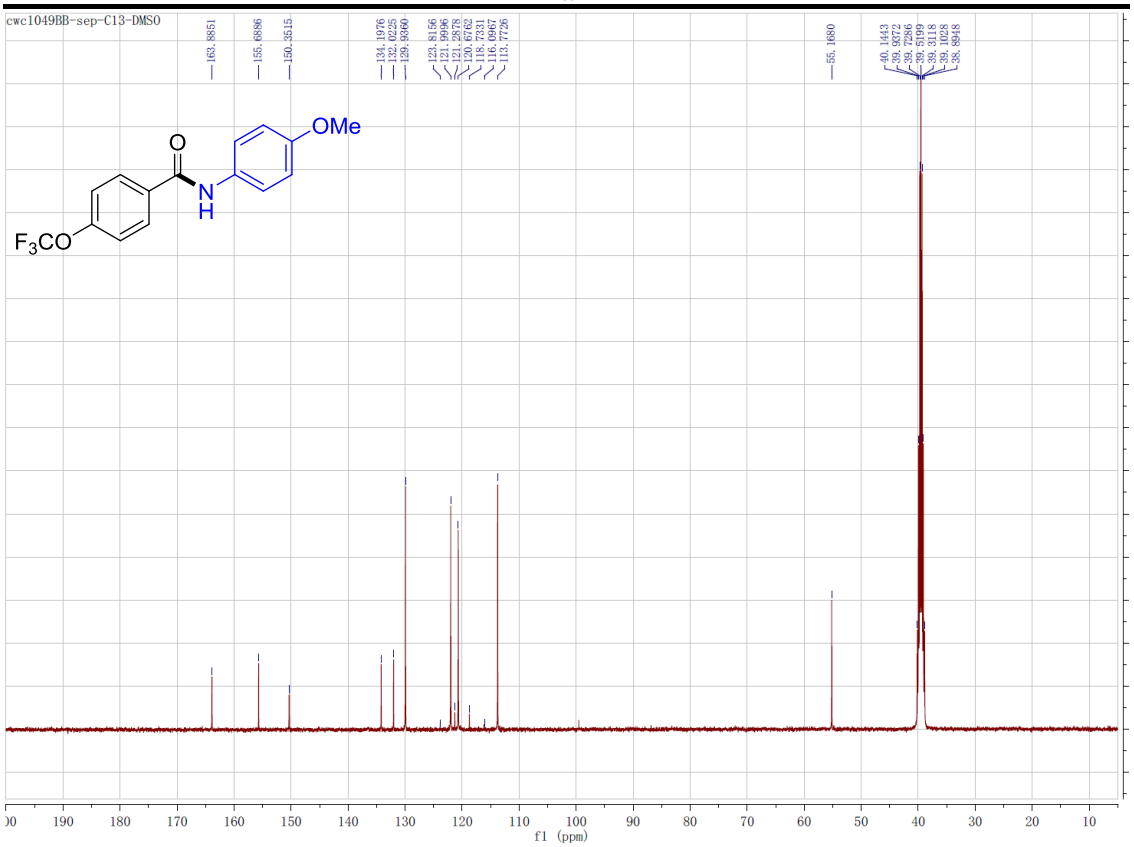
^{1}H and ^{13}C NMR of *N*-(4-(*tert*-Butyl)phenyl)benzamide (3q).



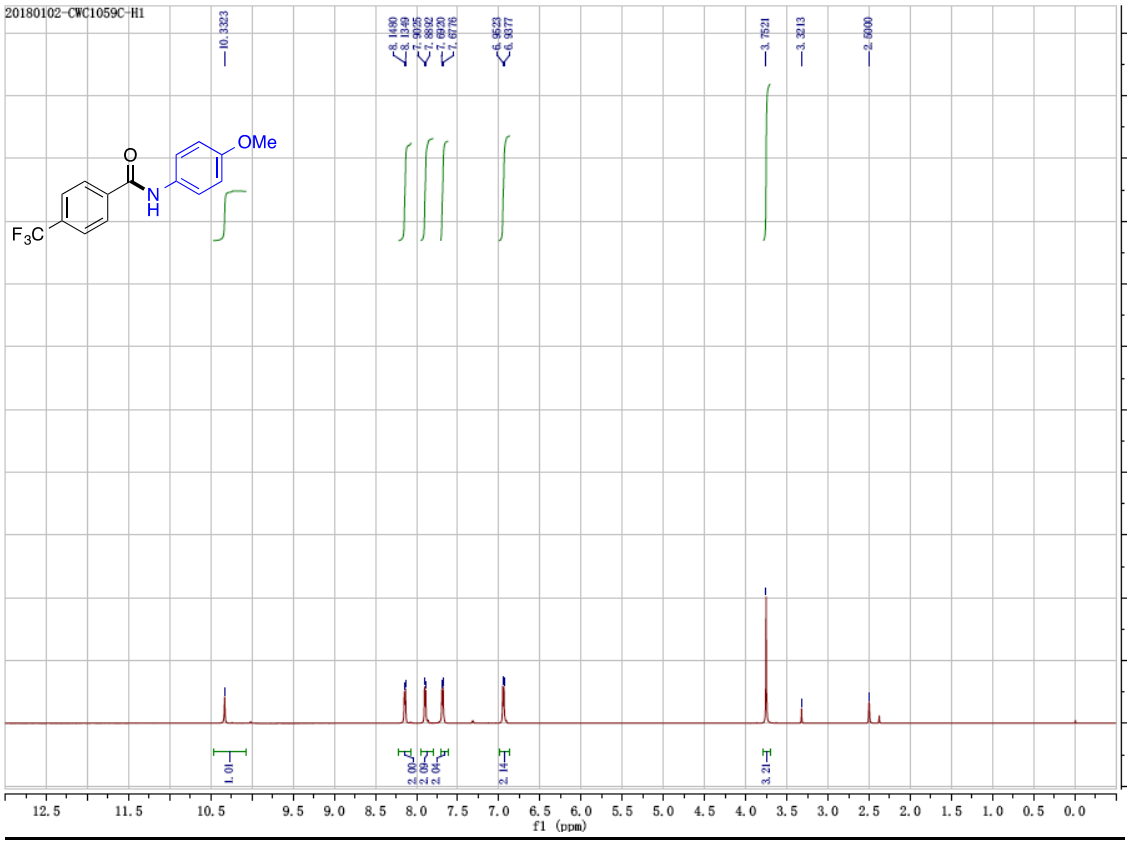


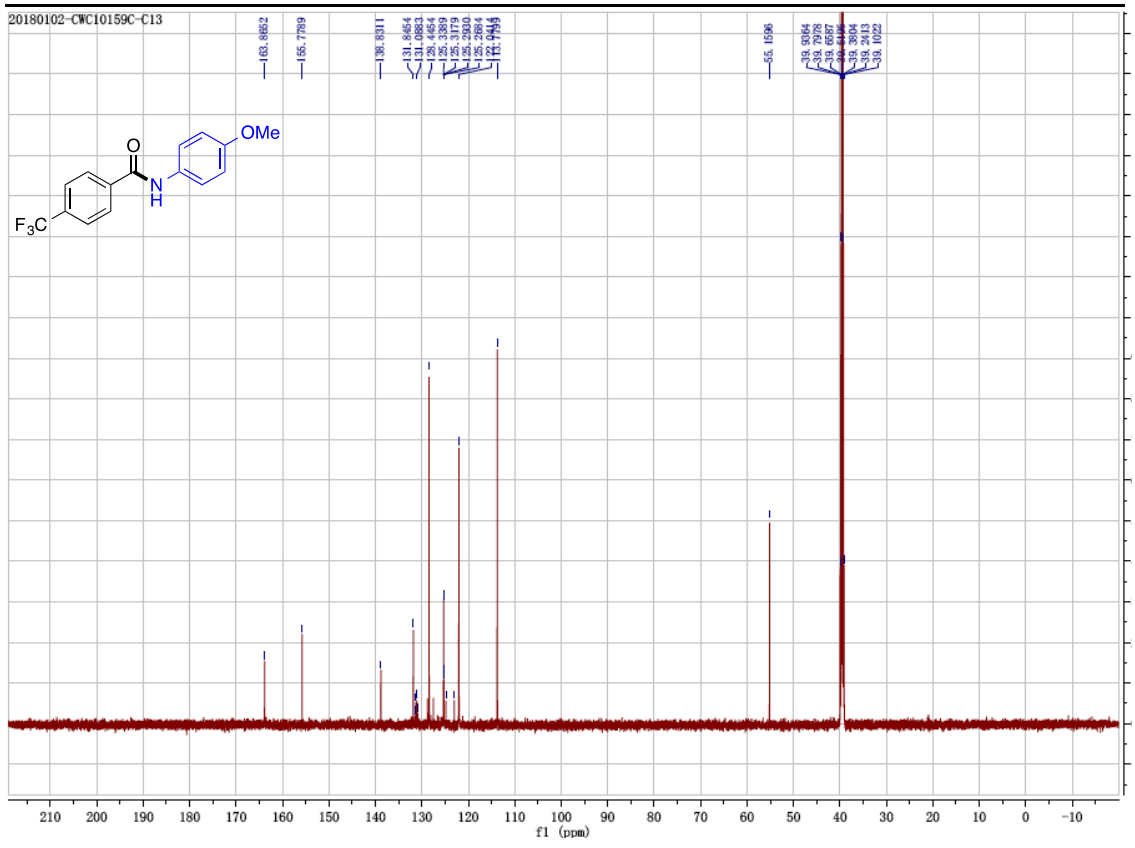
^{1}H and ^{13}C NMR of *N*-(4-methoxyphenyl)-4-(trifluoromethoxy)benzamide (3r).



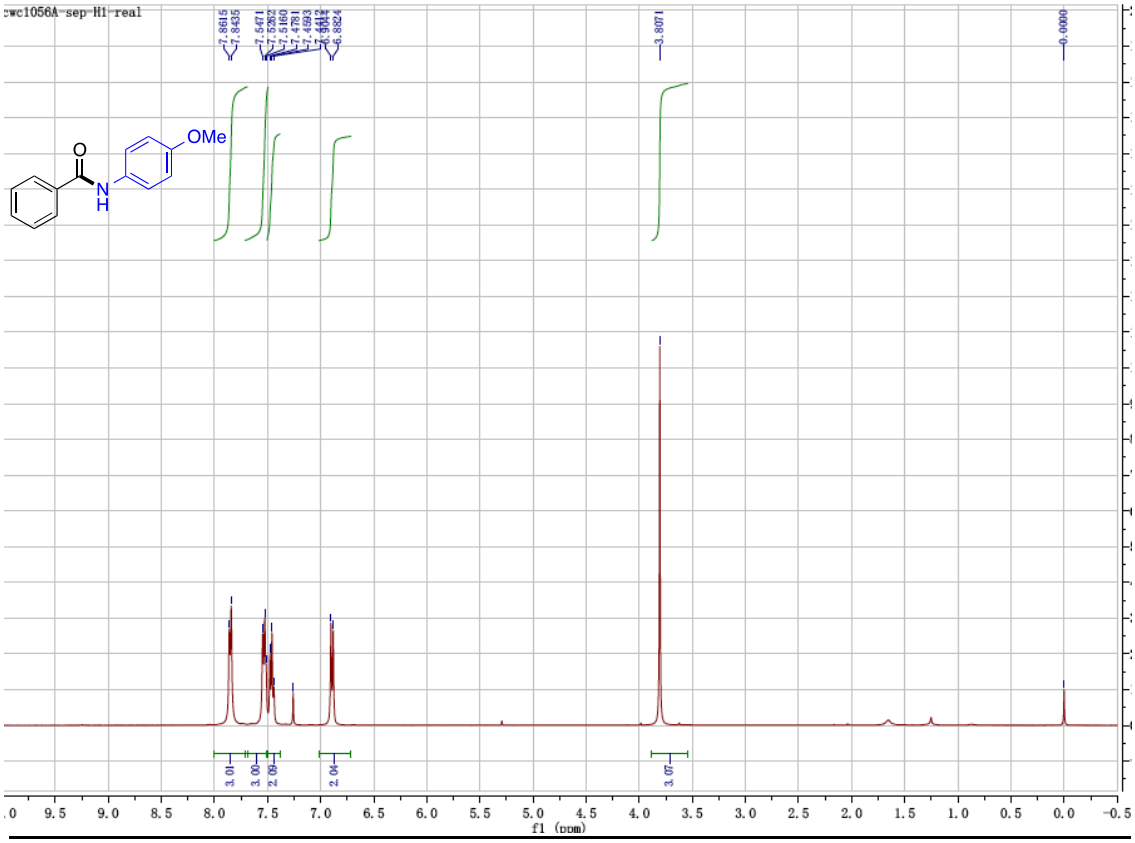


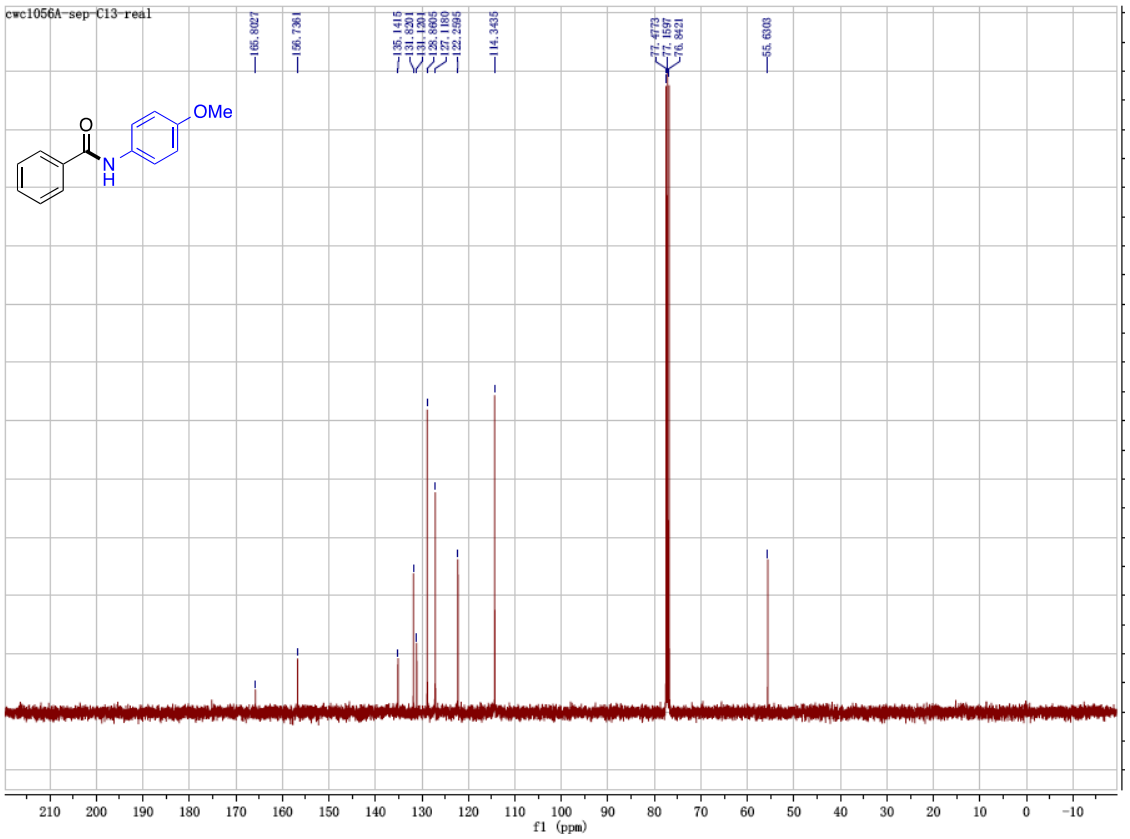
^{1}H and ^{13}C NMR of *N*-benzyl-*N*-phenyl-4-(trifluoromethyl)benzamide (3s).



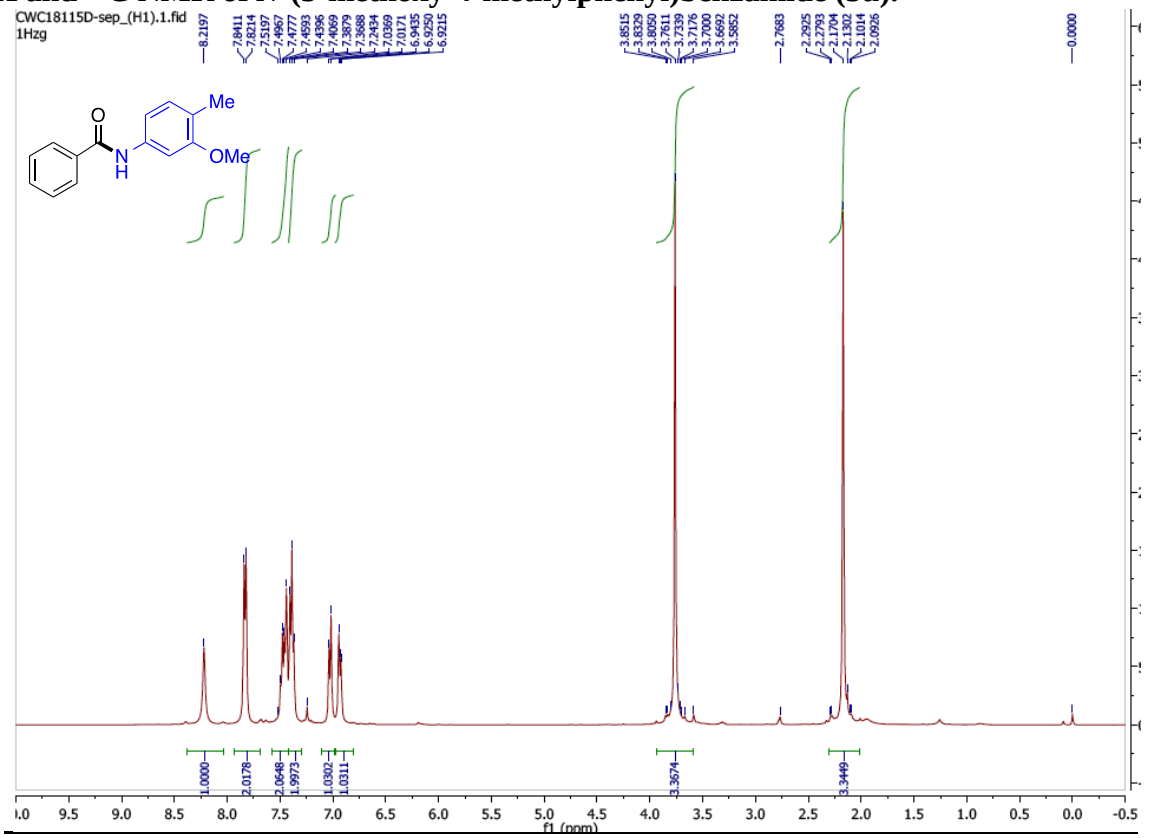


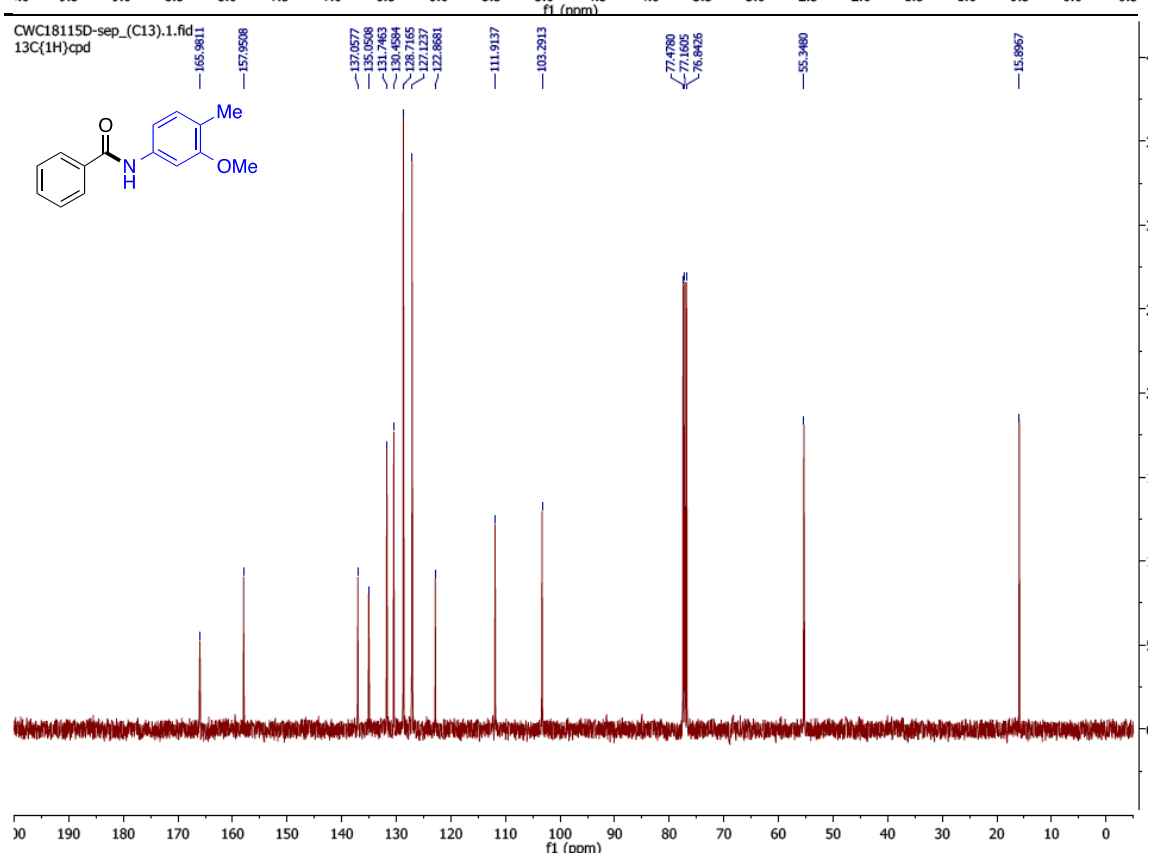
^{1}H and ^{13}C NMR of *N*-(4-methoxyphenyl)benzamide (3t).



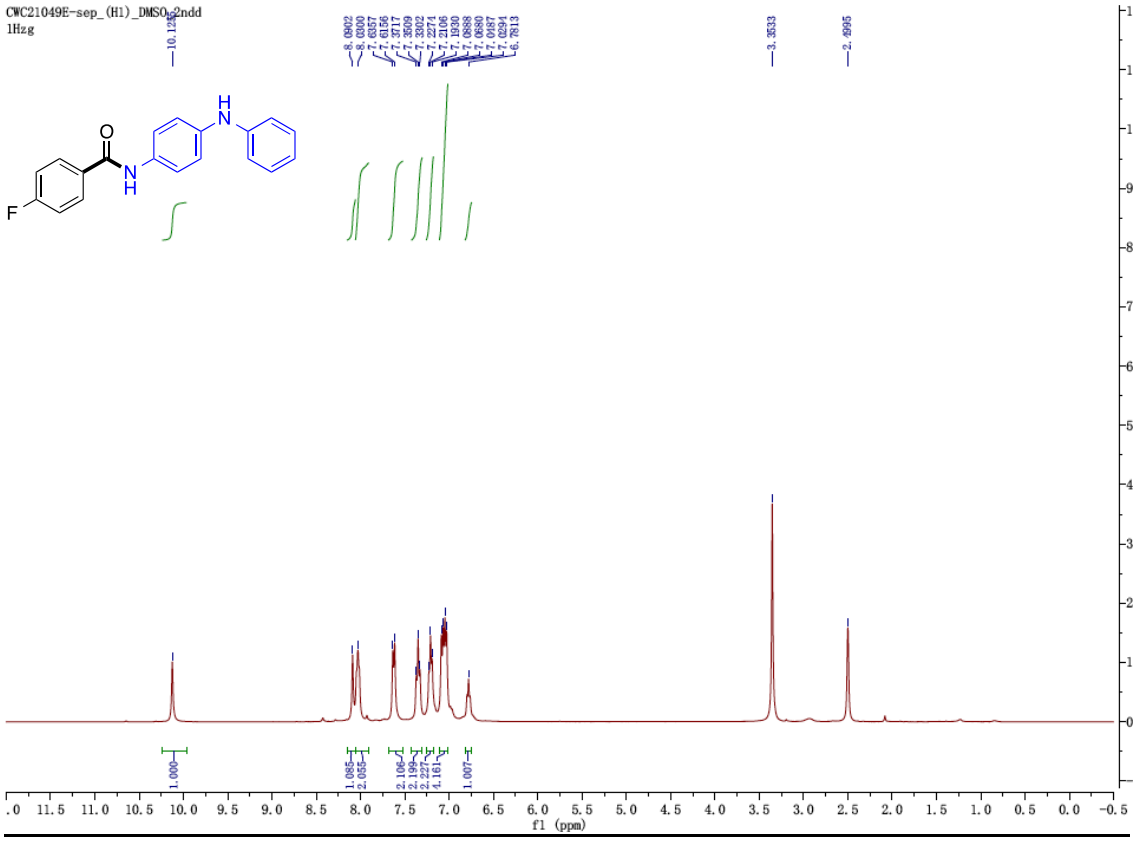


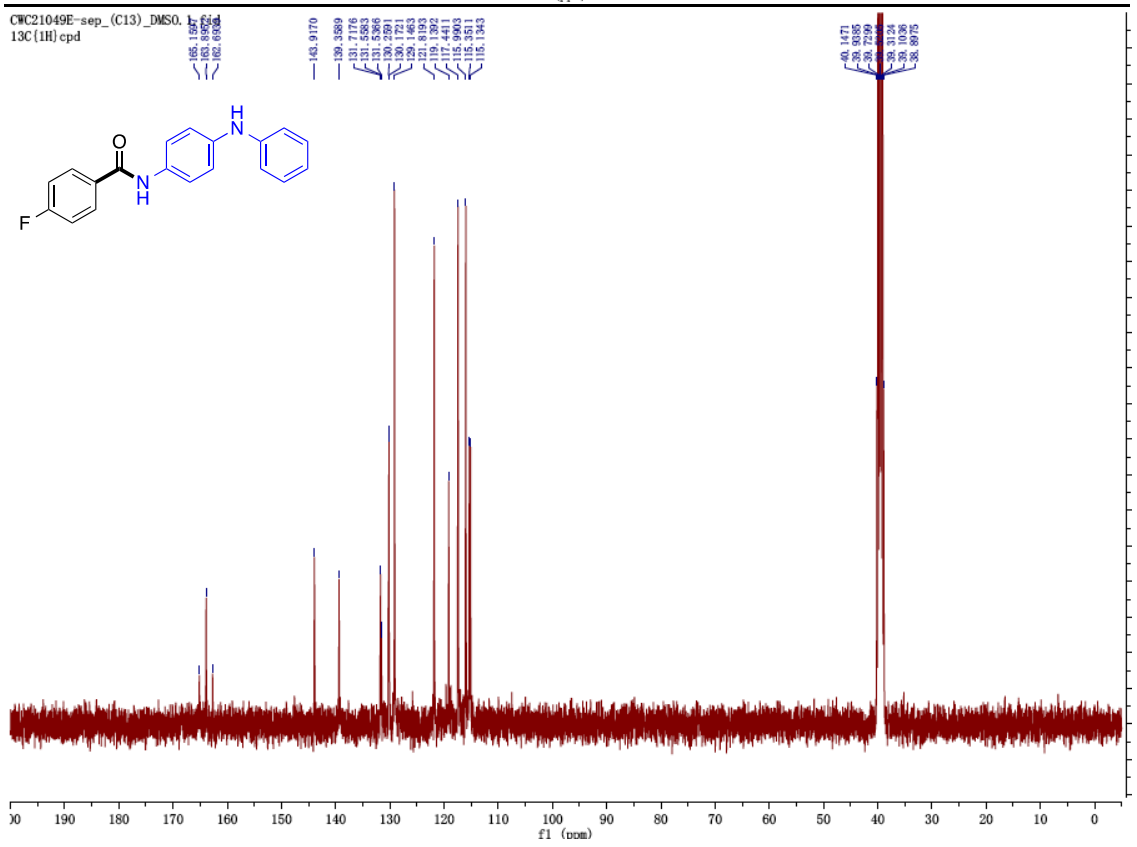
^{1}H and ^{13}C NMR of *N*-(3-methoxy-4-methylphenyl)benzamide (3u).



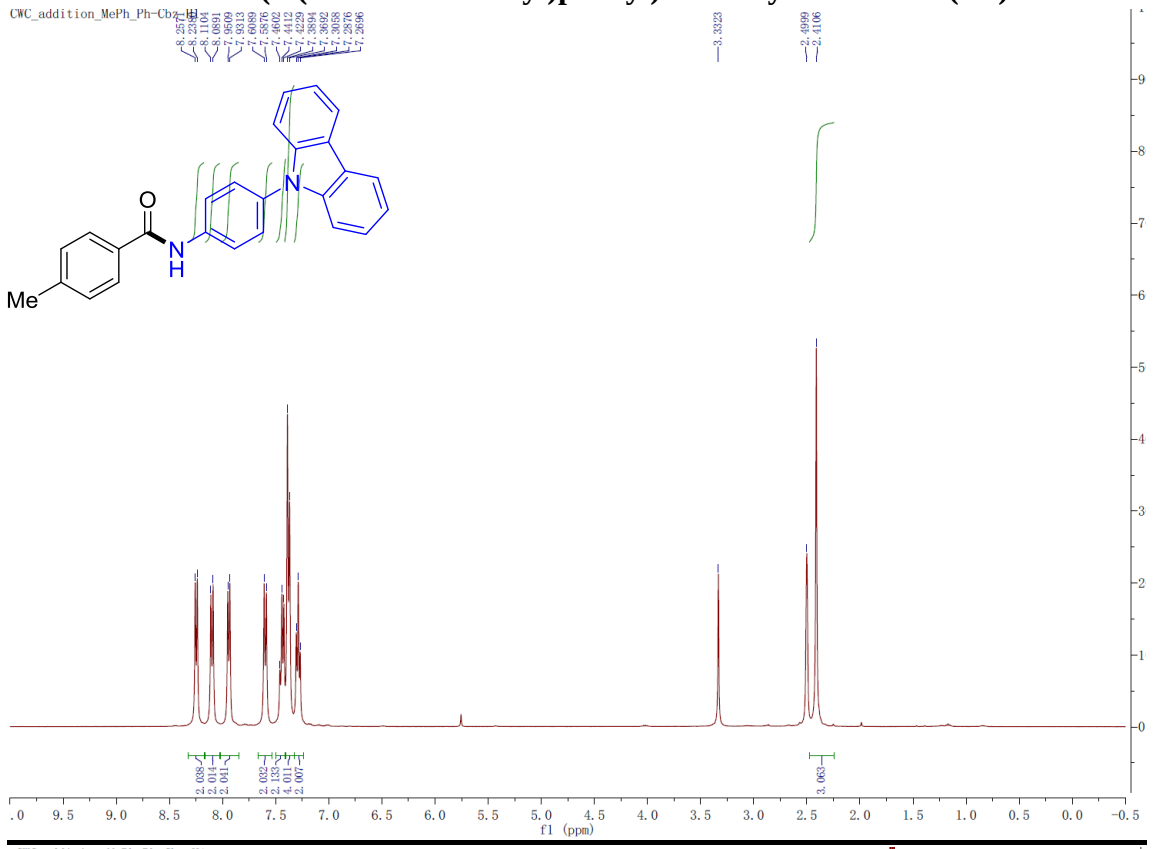


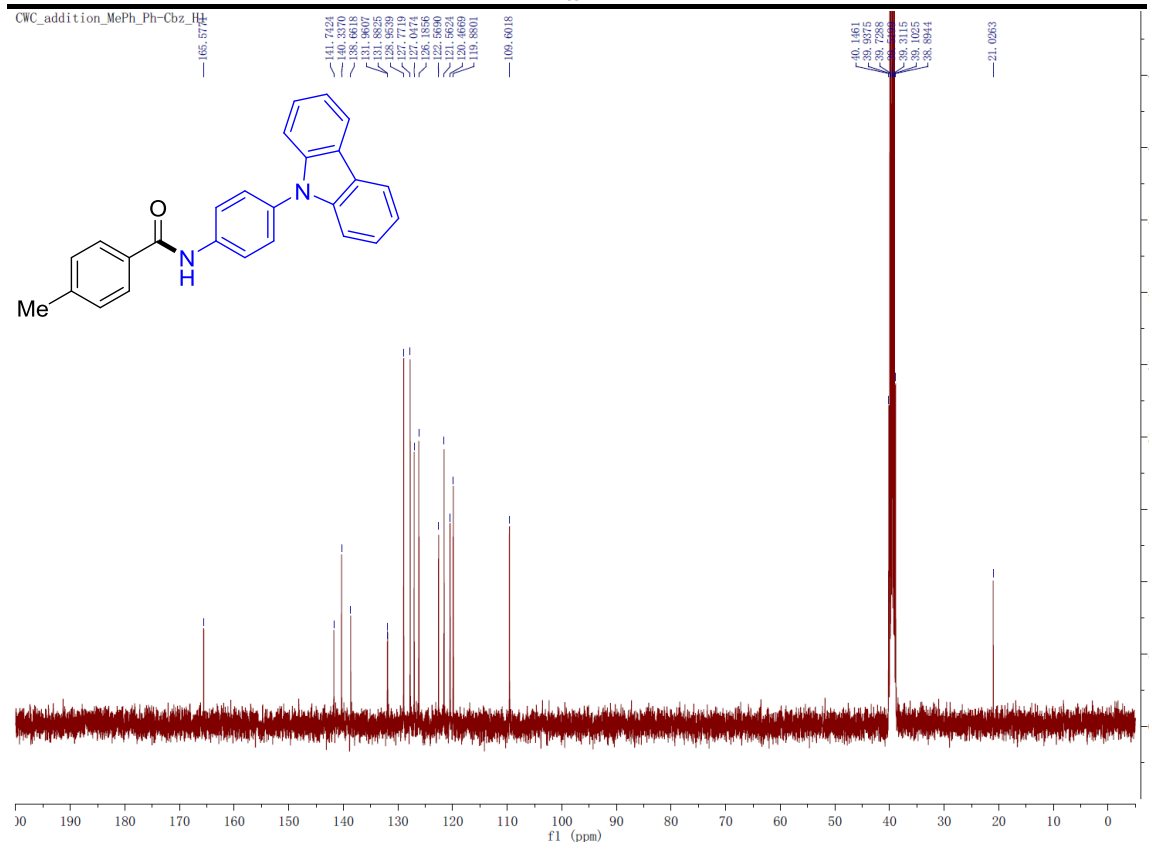
^{1}H and ^{13}C NMR of 4-fluoro-*N*-(4-(phenylamino)phenyl)benzamide (3v).



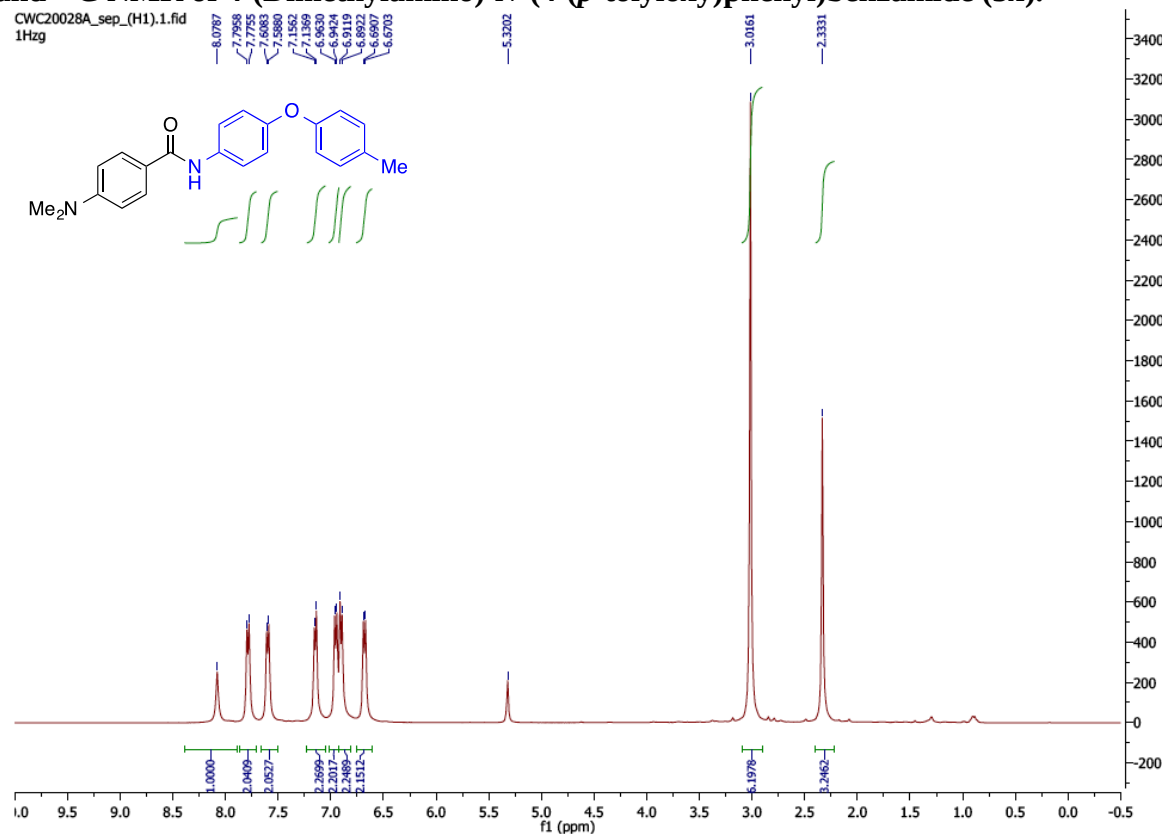


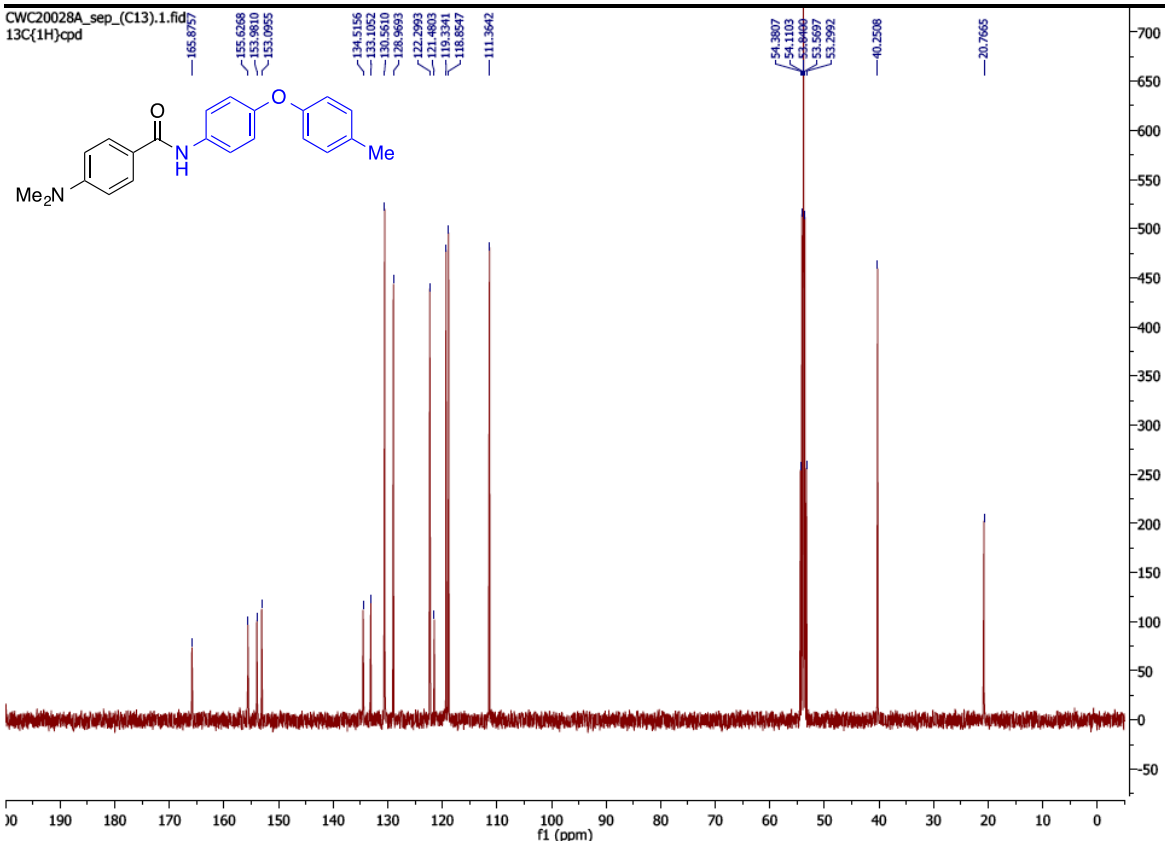
^{1}H and ^{13}C NMR of *N*-(4-(9*H*-Carbazol-9-yl)phenyl)-4-methylbenzamide (3w).



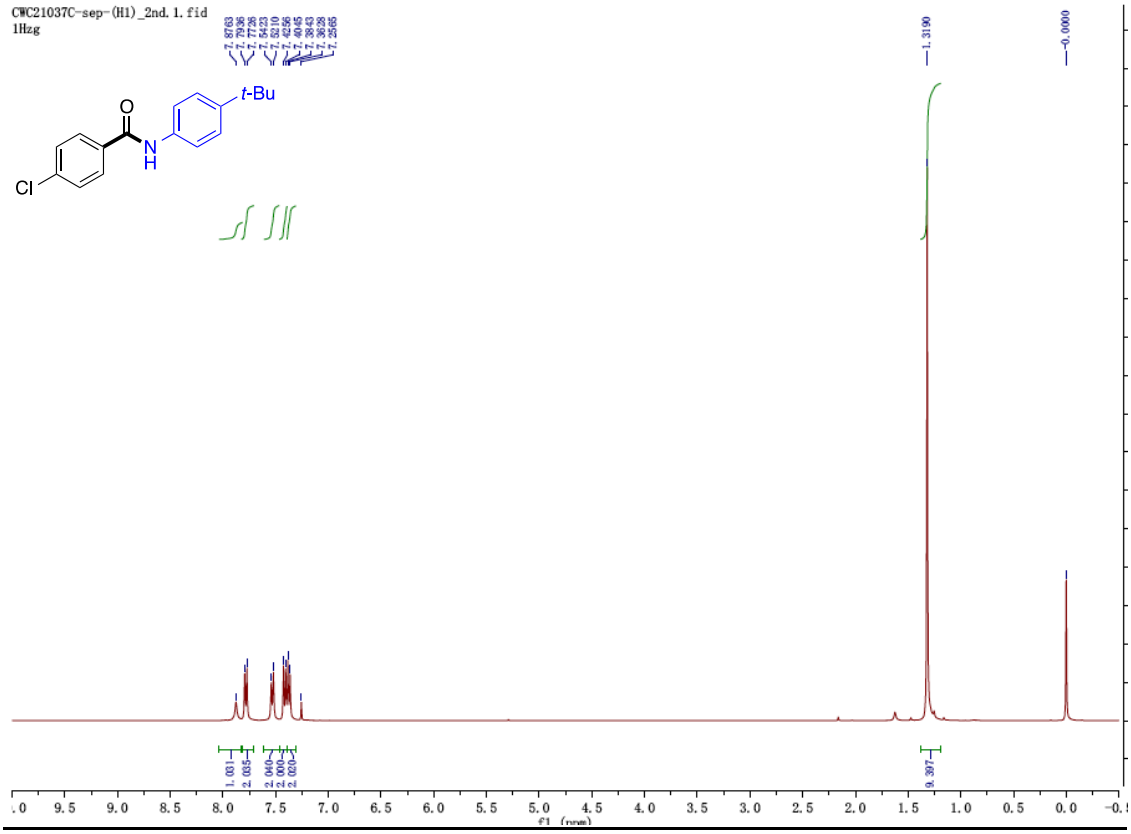


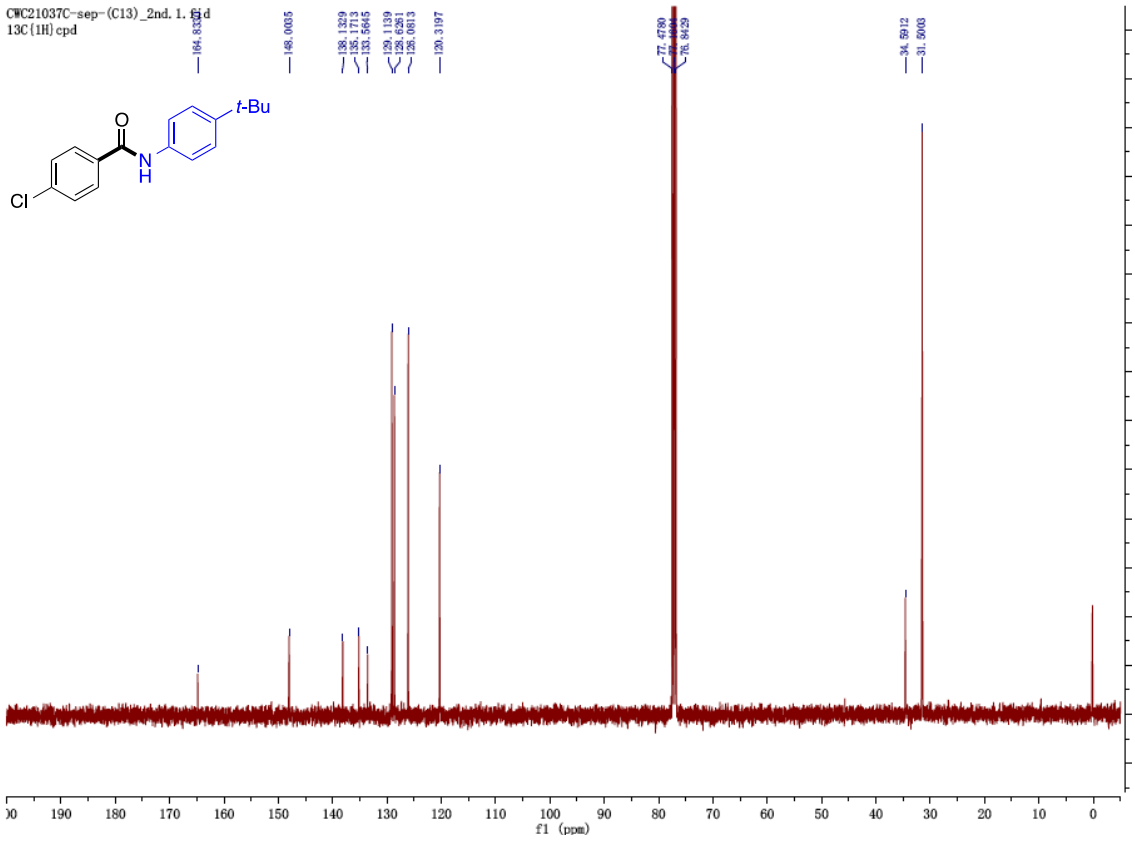
^{1}H and ^{13}C NMR of 4-(Dimethylamino)-*N*-(4-(*p*-tolyloxy)phenyl)benzamide (3x).



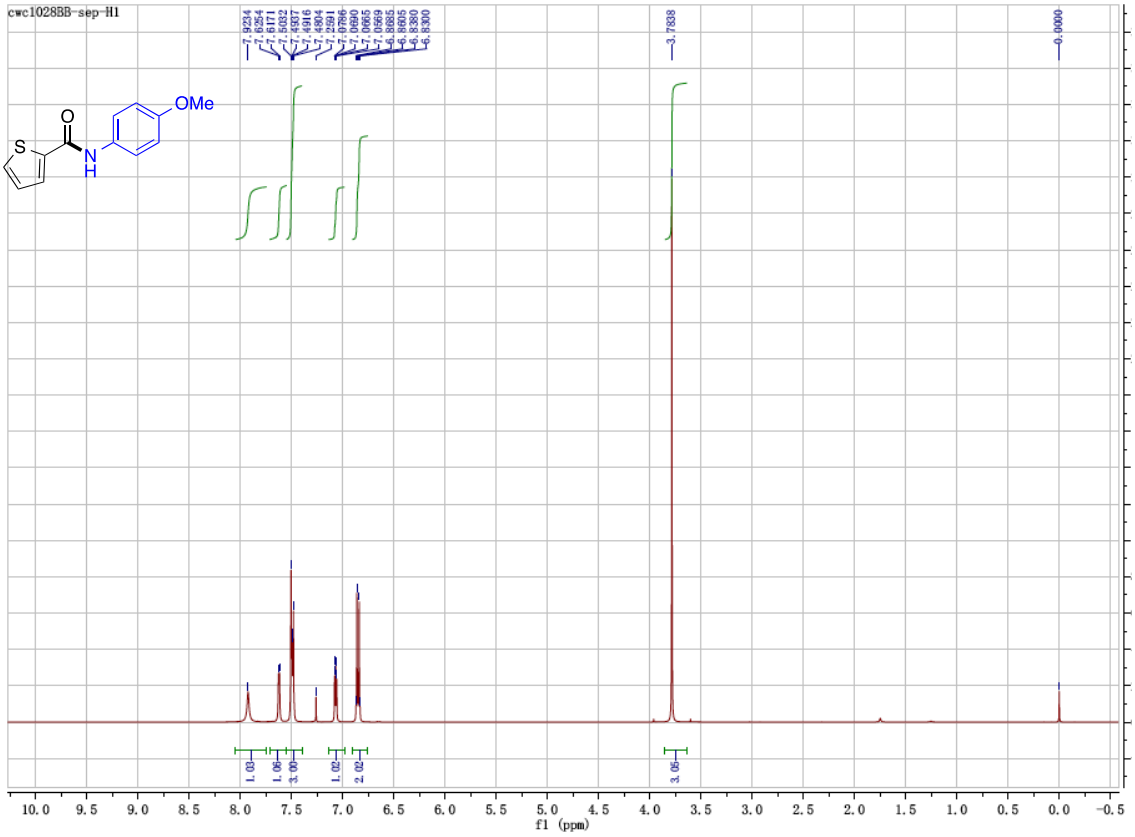


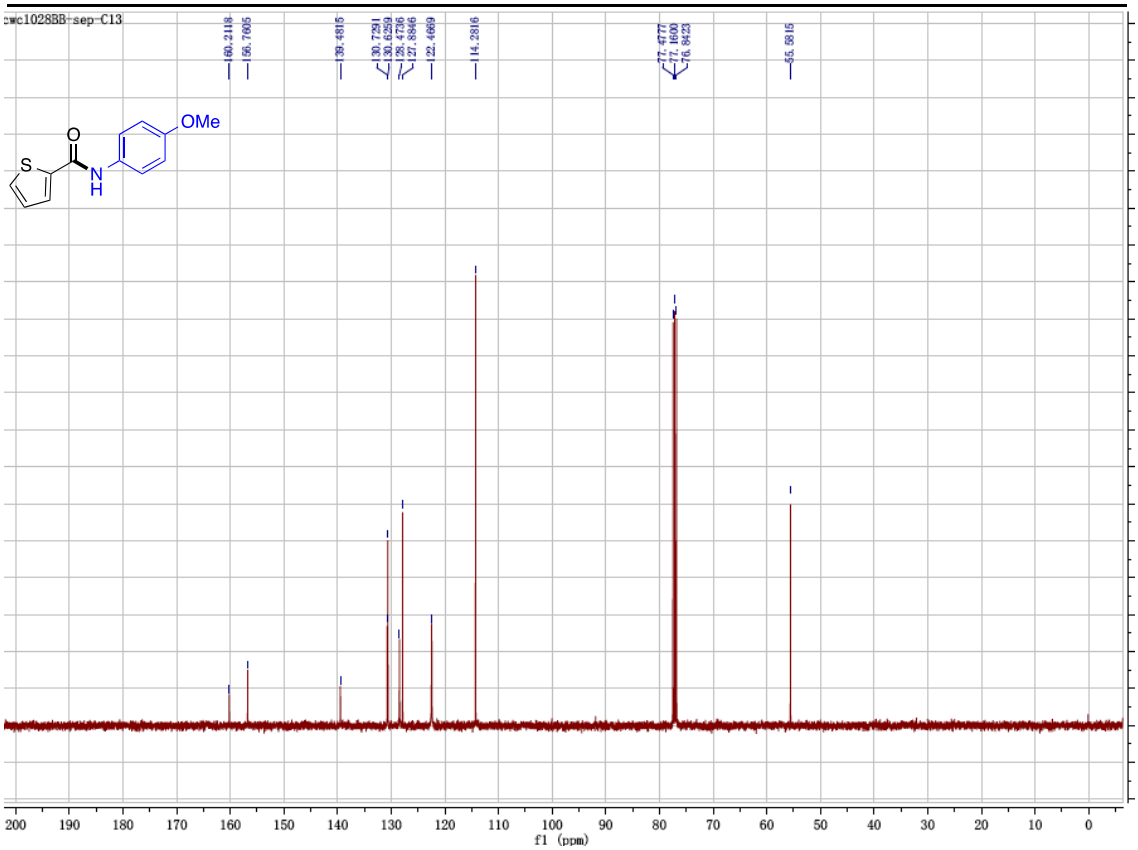
^{1}H and ^{13}C NMR of *N*-(4-(*tert*-butyl)phenyl)-4-chlorobenzamide (3y).



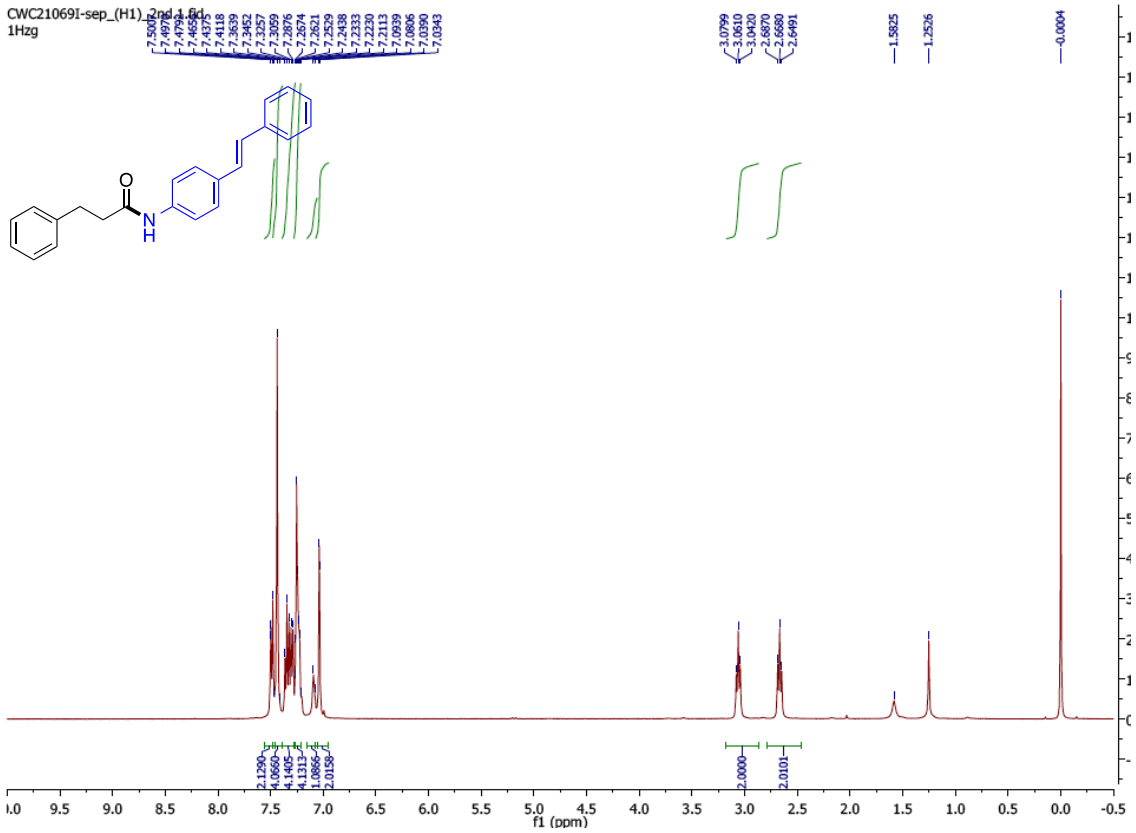


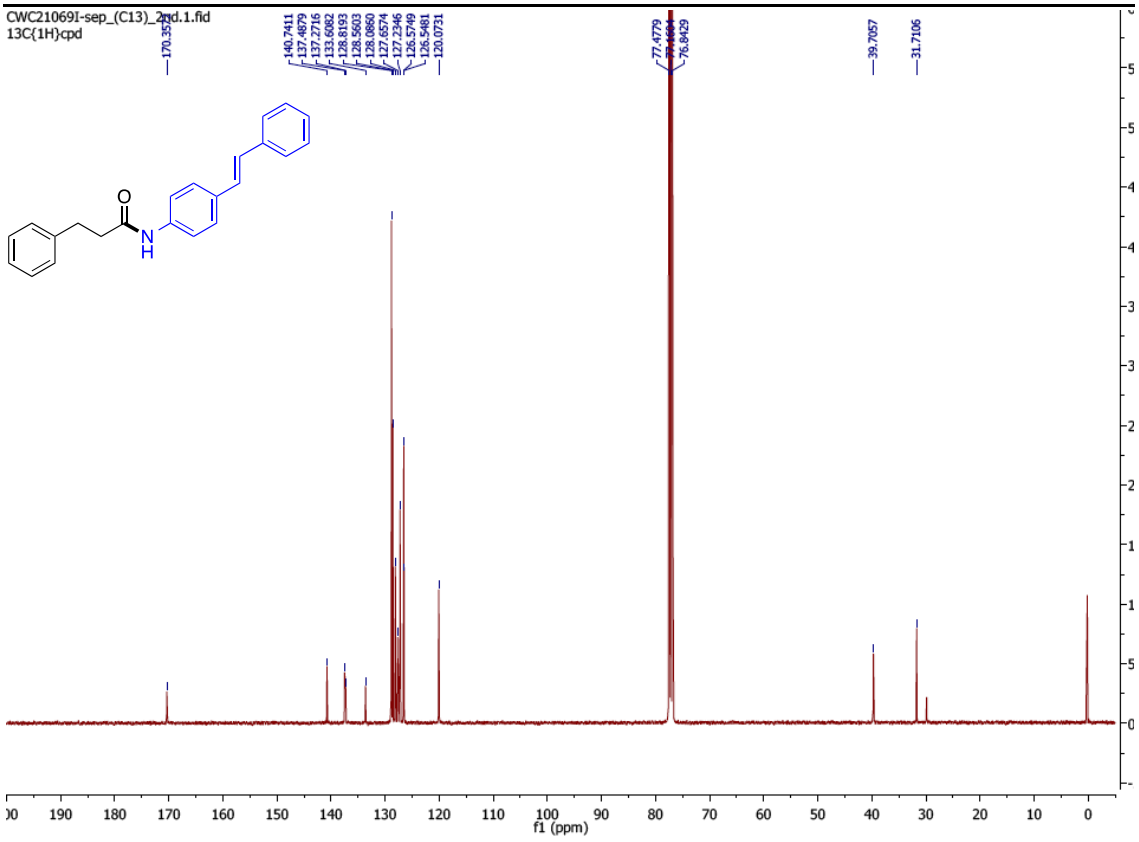
^{1}H and ^{13}C NMR of *N*-(4-methoxyphenyl)thiophene-2-carboxamide (3z).



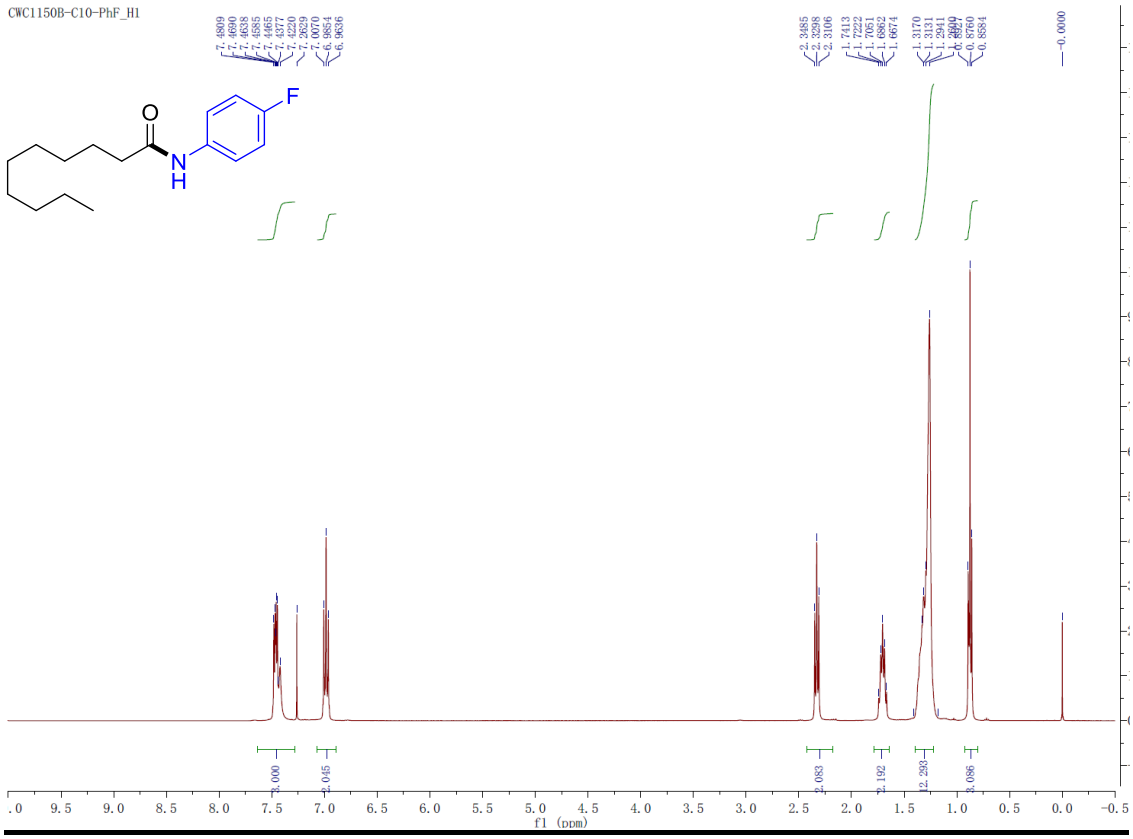


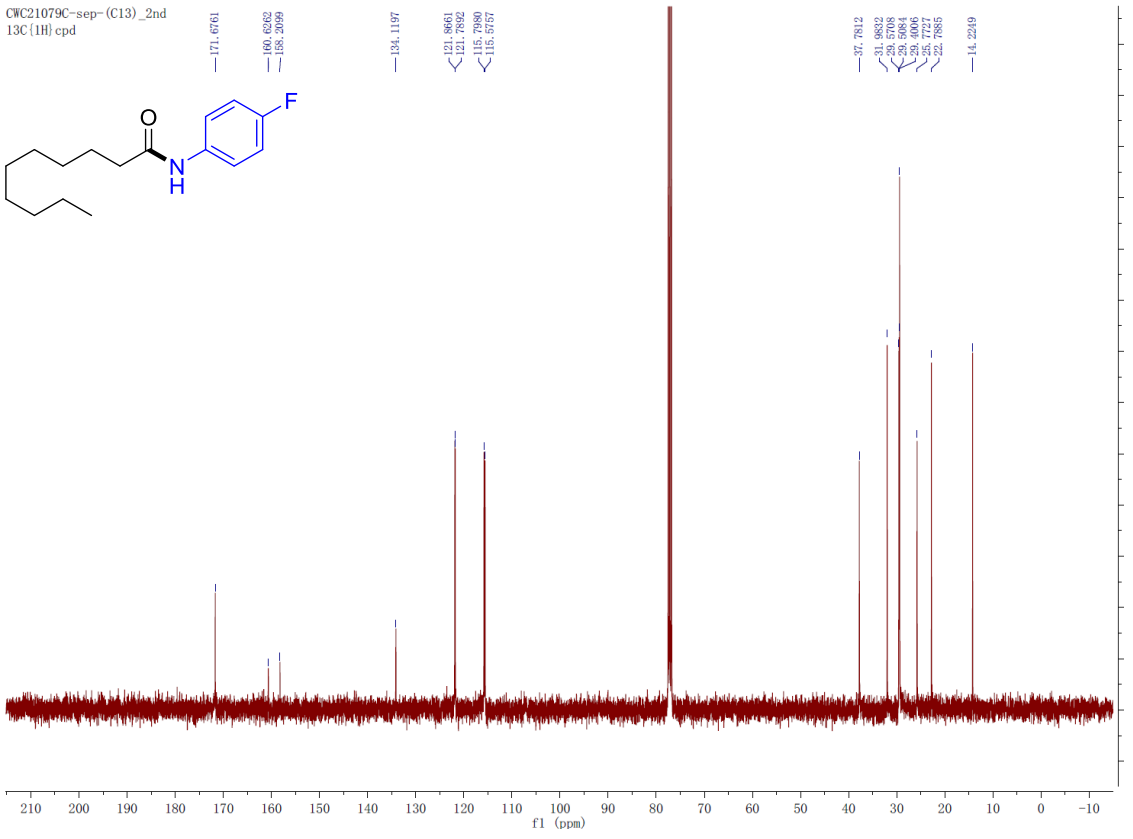
^{1}H and ^{13}C NMR of (*E*)-3-phenyl-*N*-(4-styrylphenyl)propanamide (3aa).



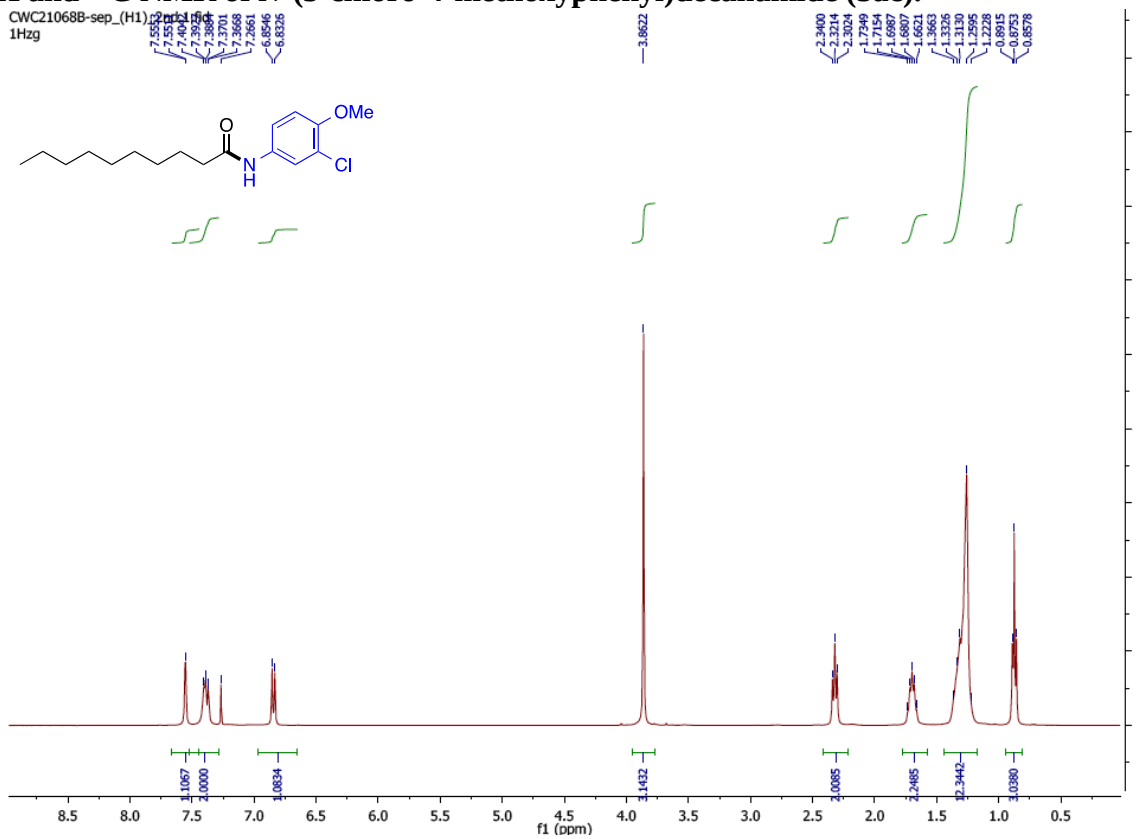


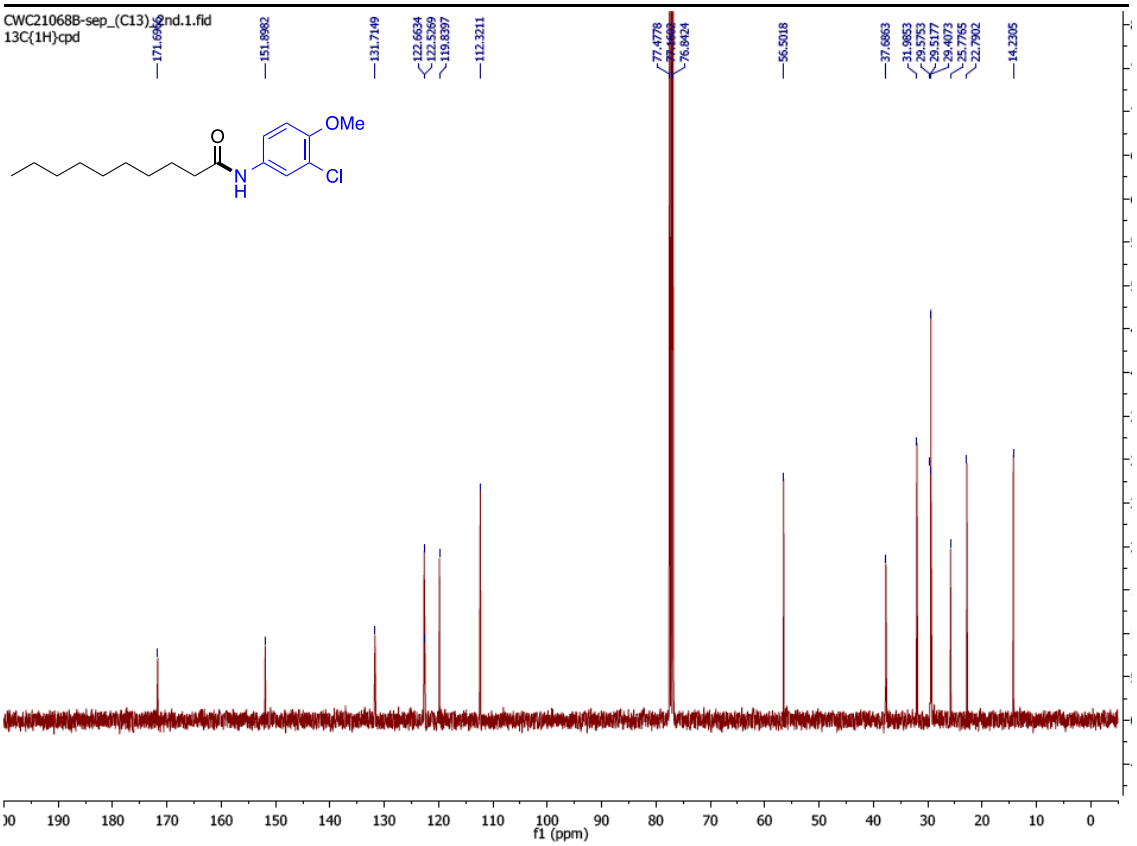
^{1}H and ^{13}C NMR of *N*-(4-fluorophenyl)decanamide (3ab).



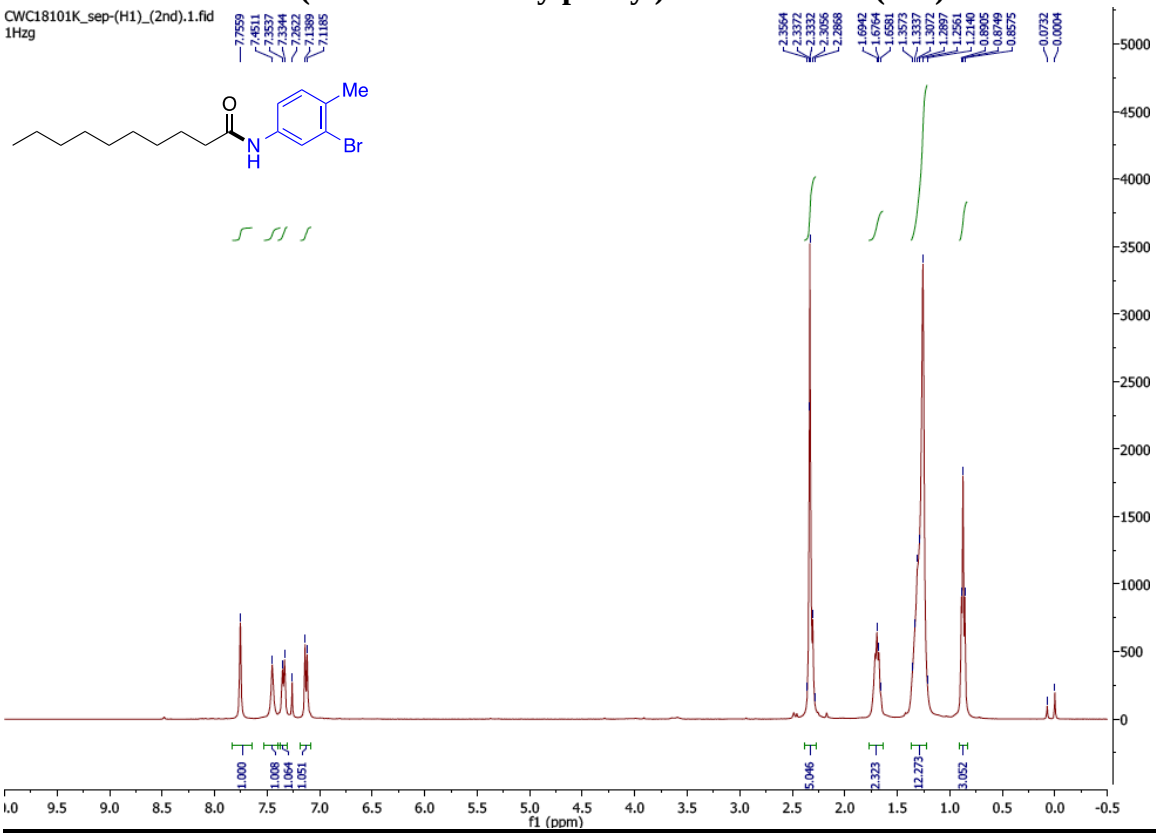


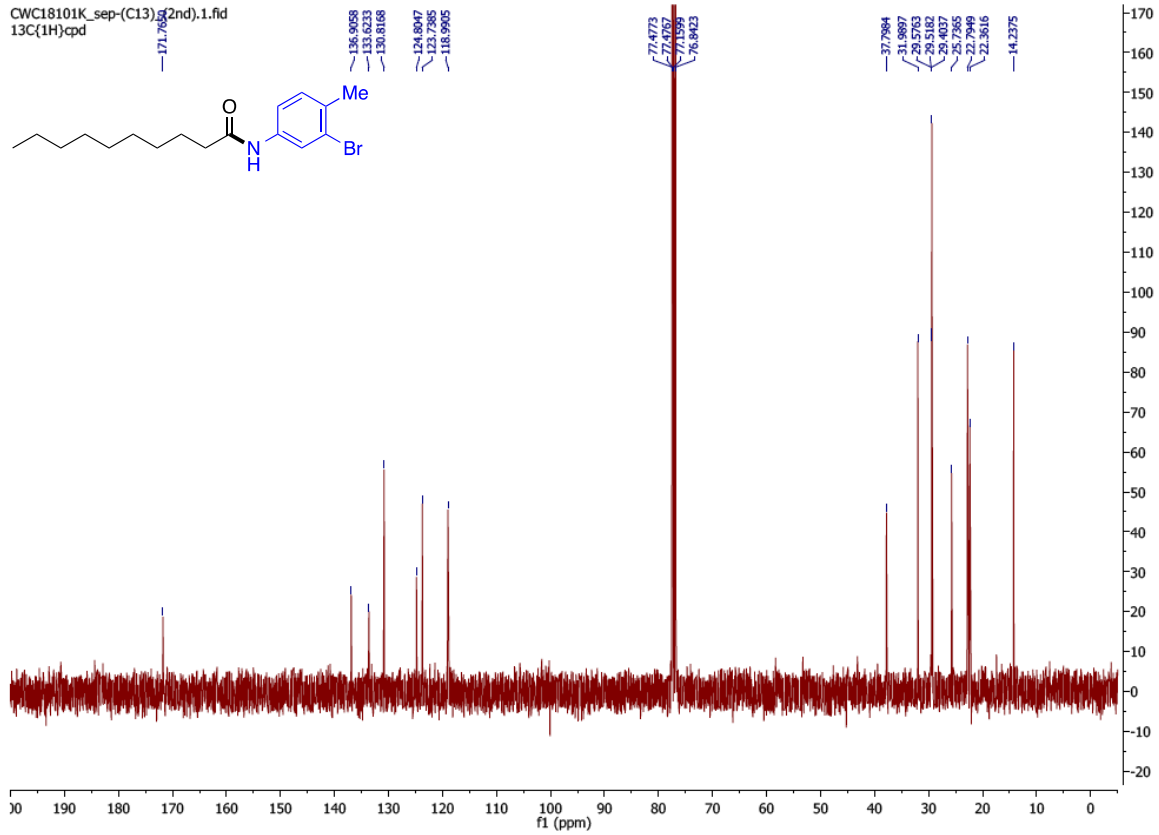
^{1}H and ^{13}C NMR of *N*-(3-chloro-4-methoxyphenyl)decanamide (3ac).



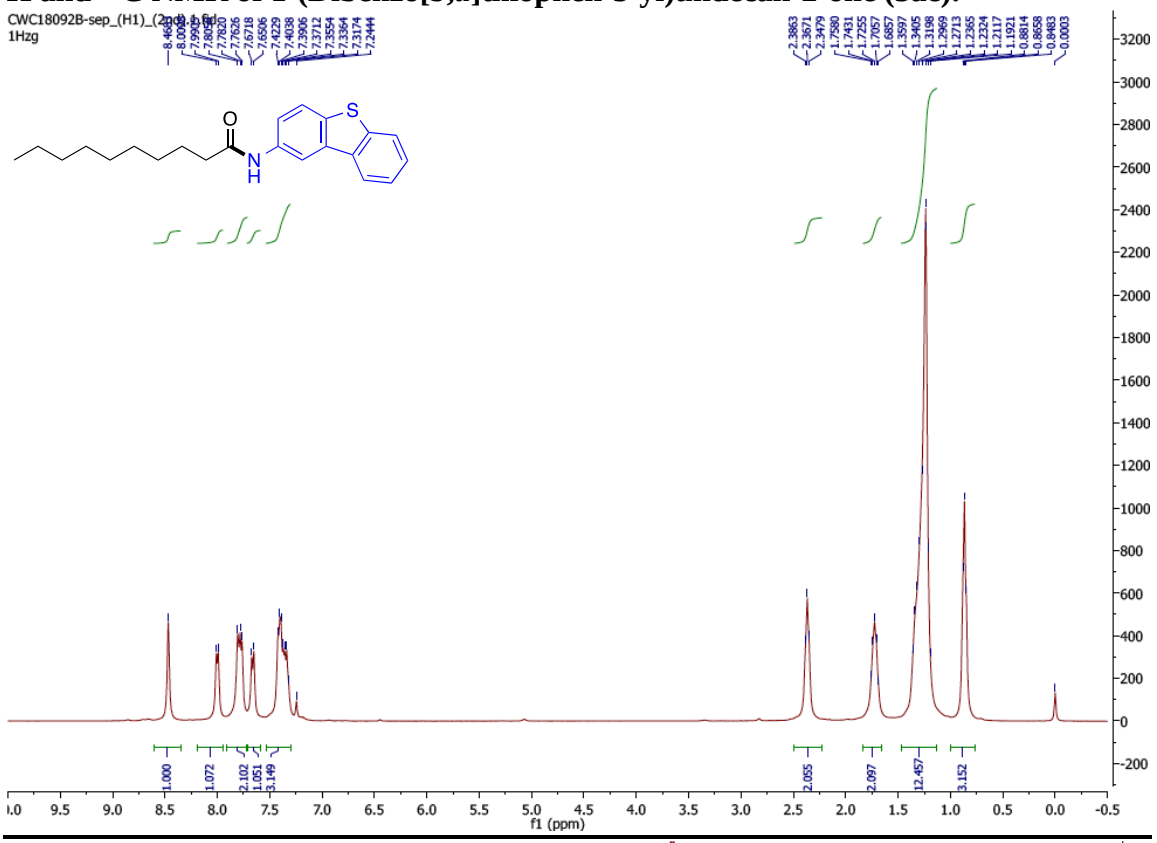


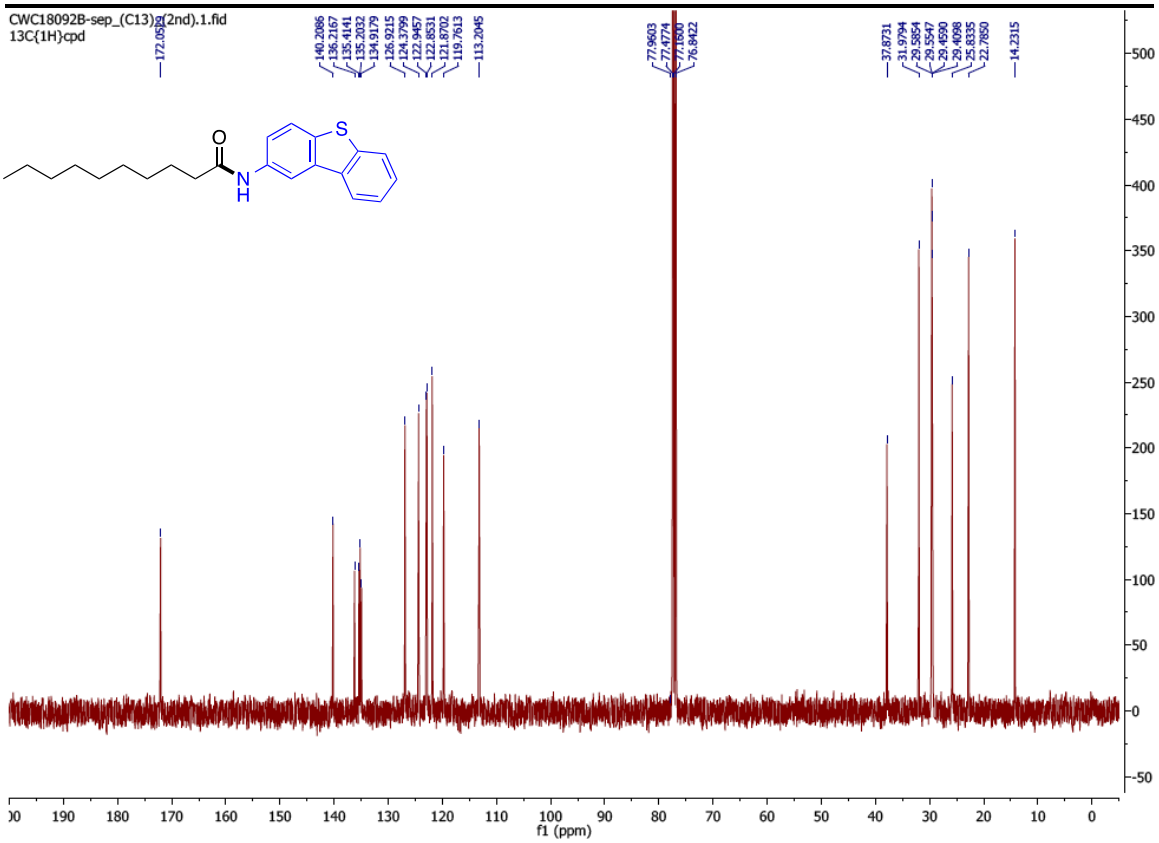
^{1}H and ^{13}C NMR of 1-(3-Bromo-4-methylphenyl)undecan-2-one (3ad).



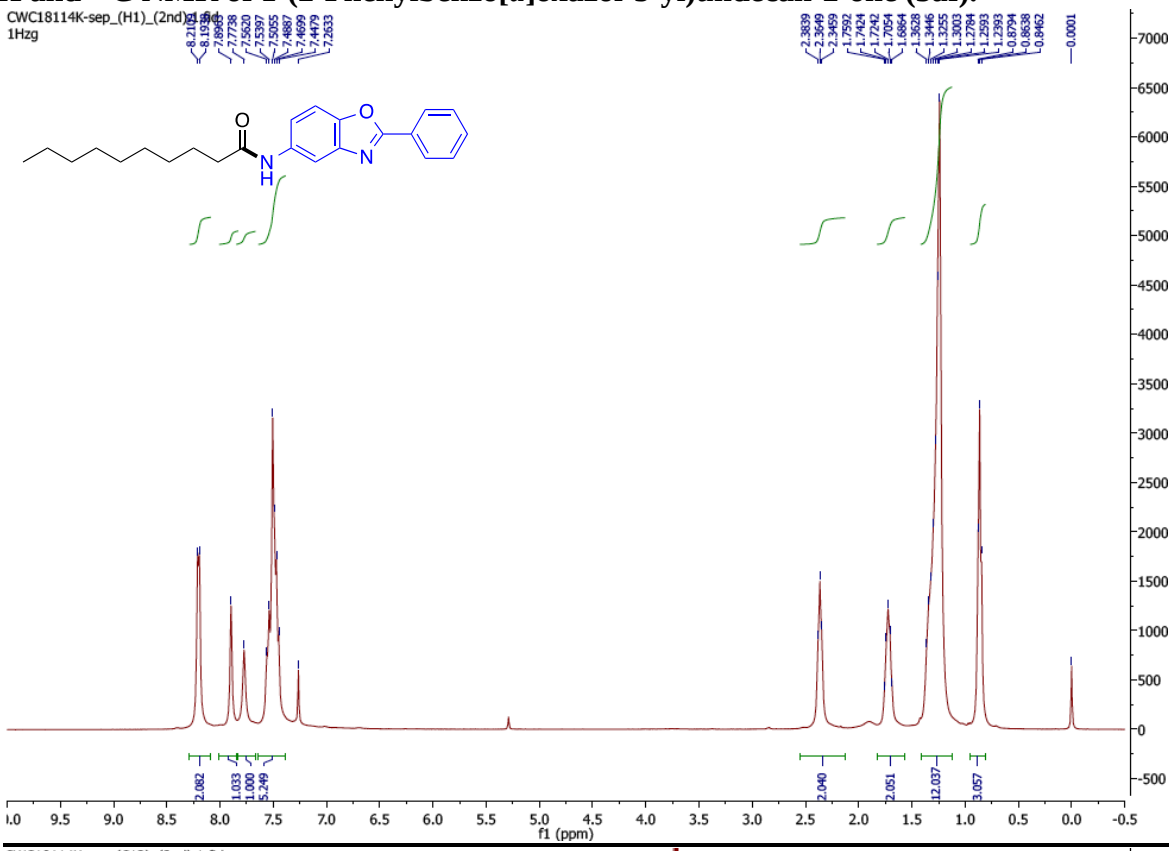


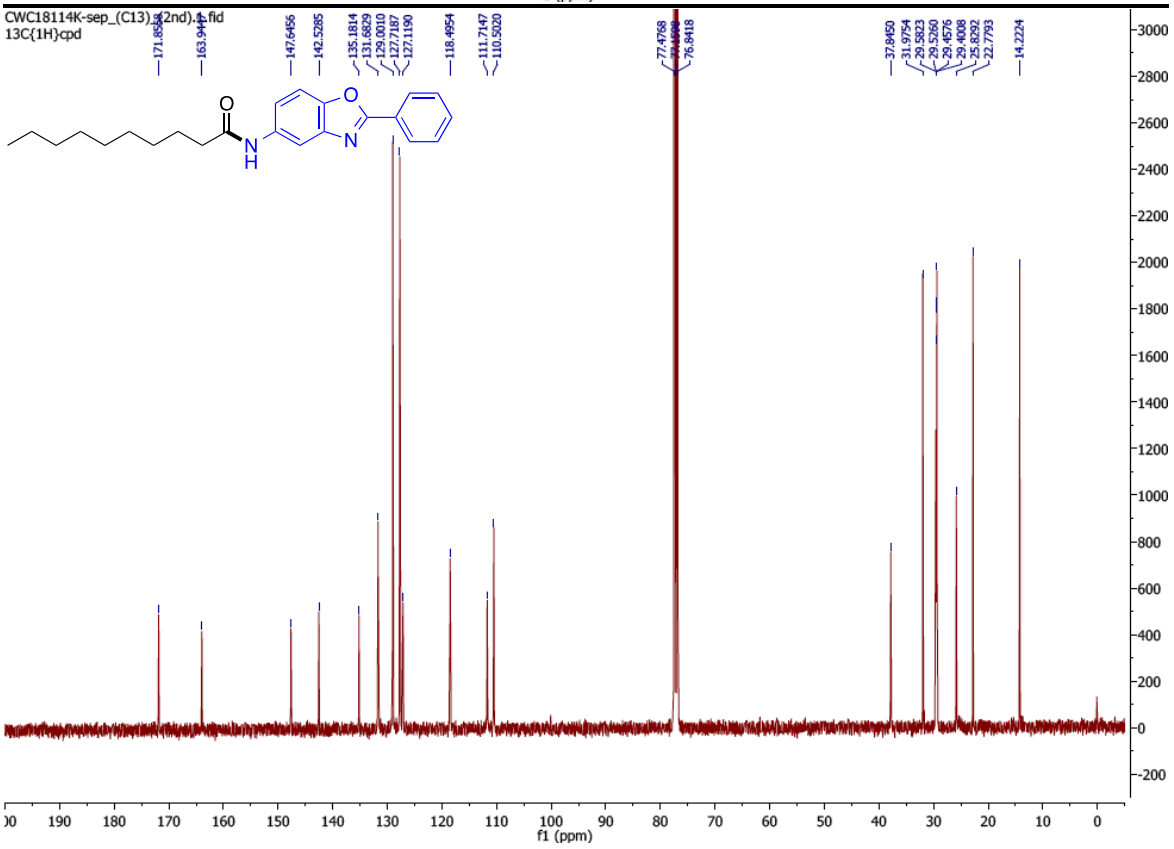
^{1}H and ^{13}C NMR of 1-(Dibenzo[*b*,*d*]thiophen-3-yl)undecan-2-one (3ae).



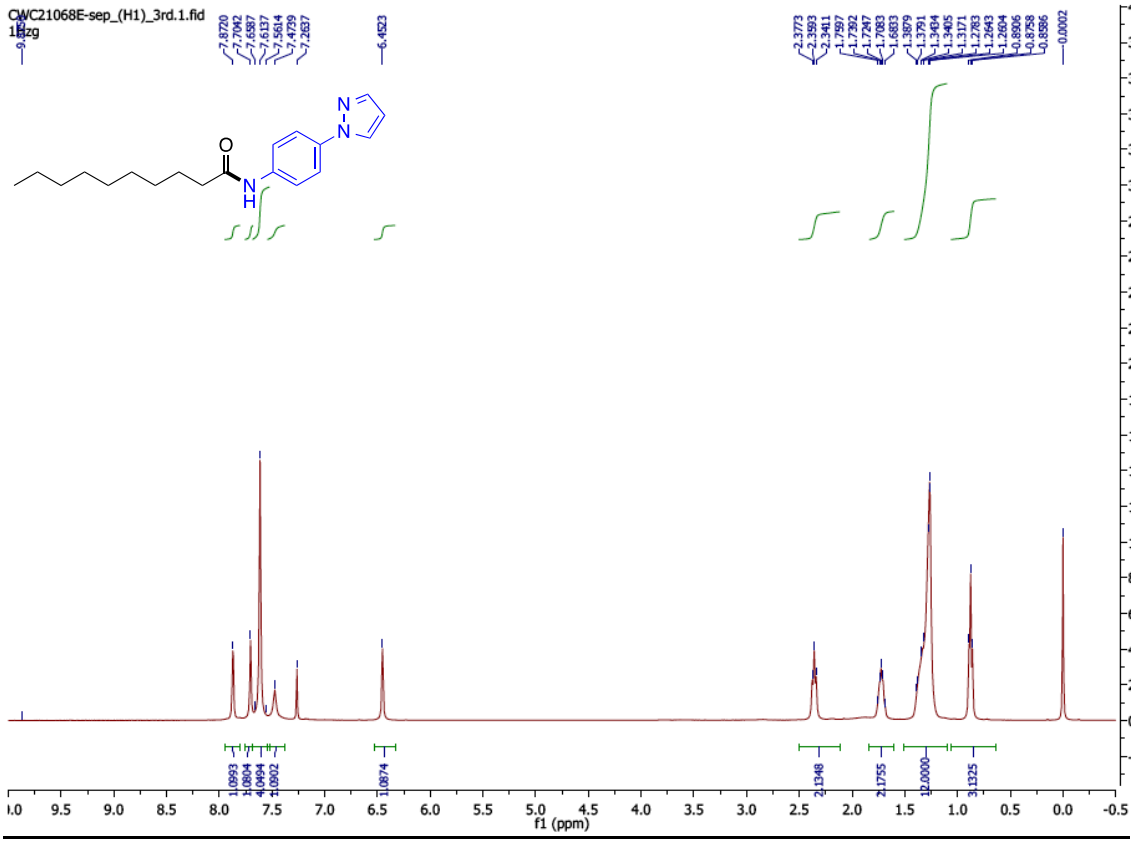


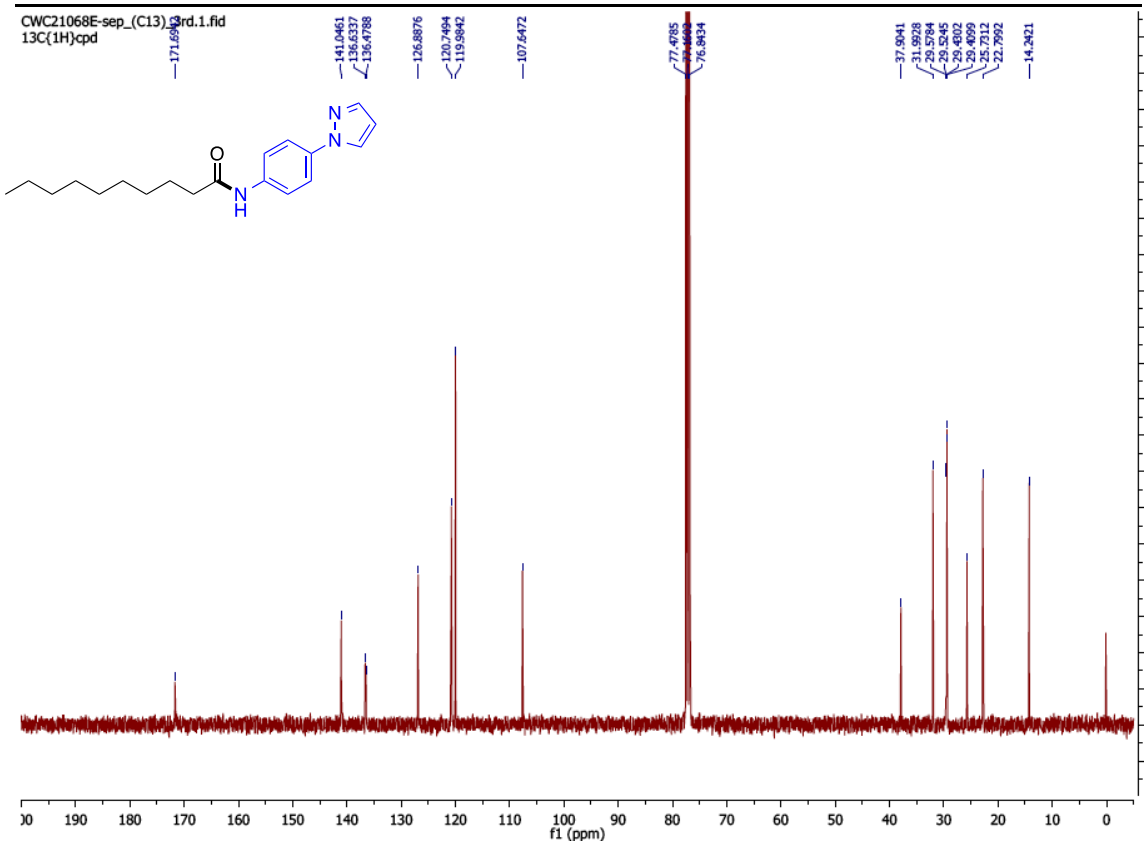
^{1}H and ^{13}C NMR of 1-(2-Phenylbenzo[*d*]oxazol-5-yl)undecan-2-one (3af).



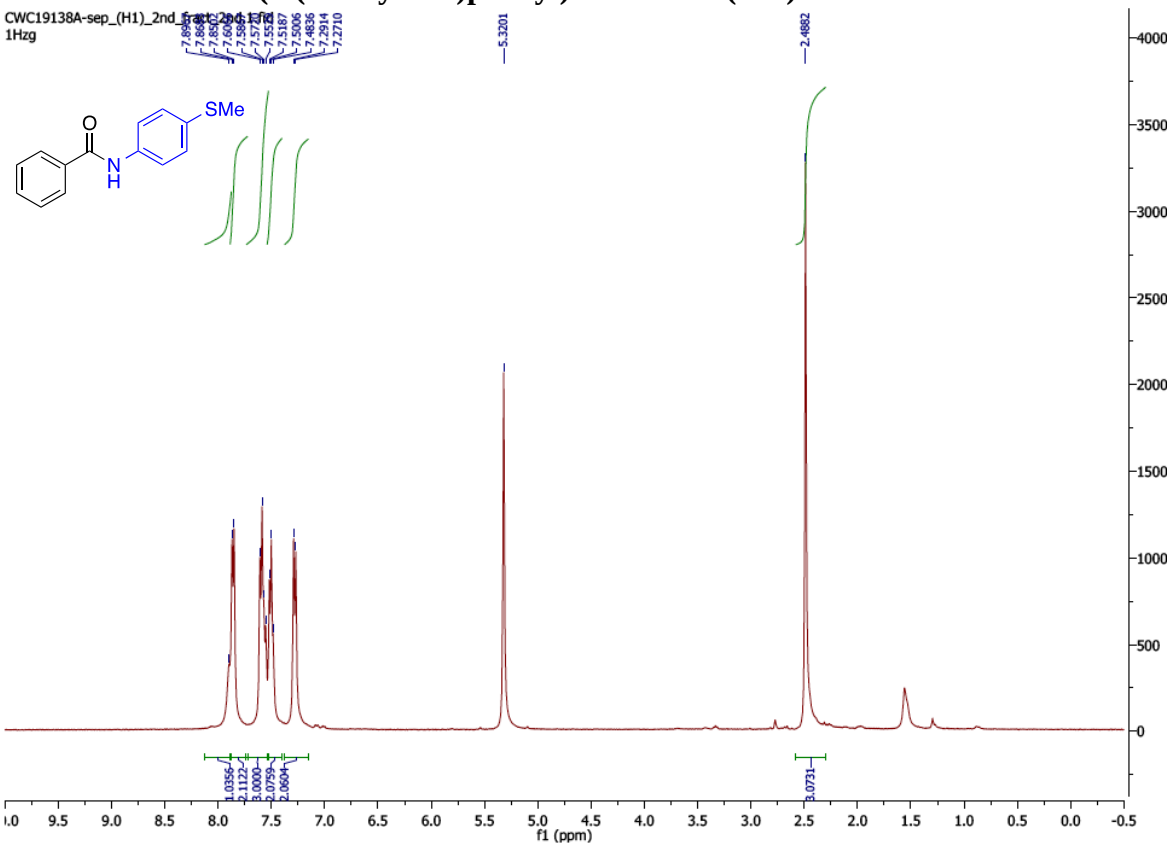


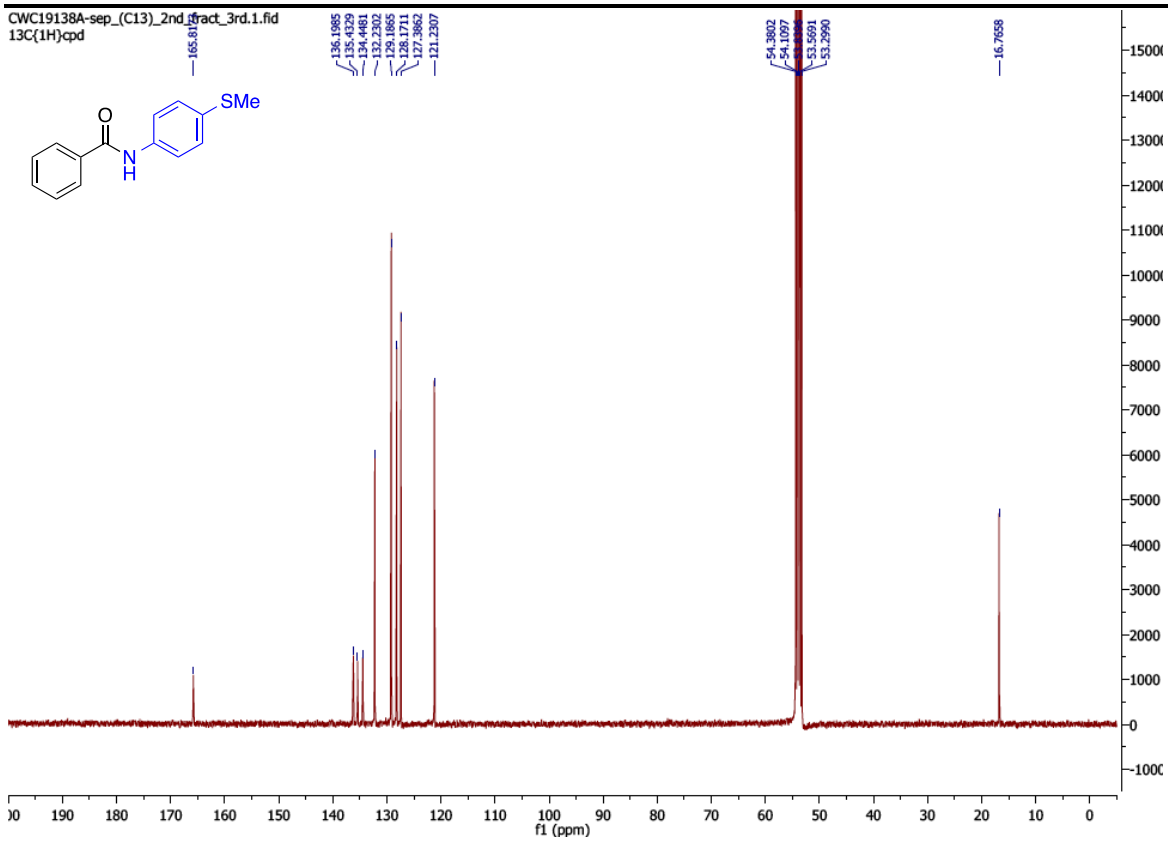
^{1}H and ^{13}C NMR of 1-(4-(1*H*-Pyrazol-1-yl)phenyl)undecan-2-one (3ag).



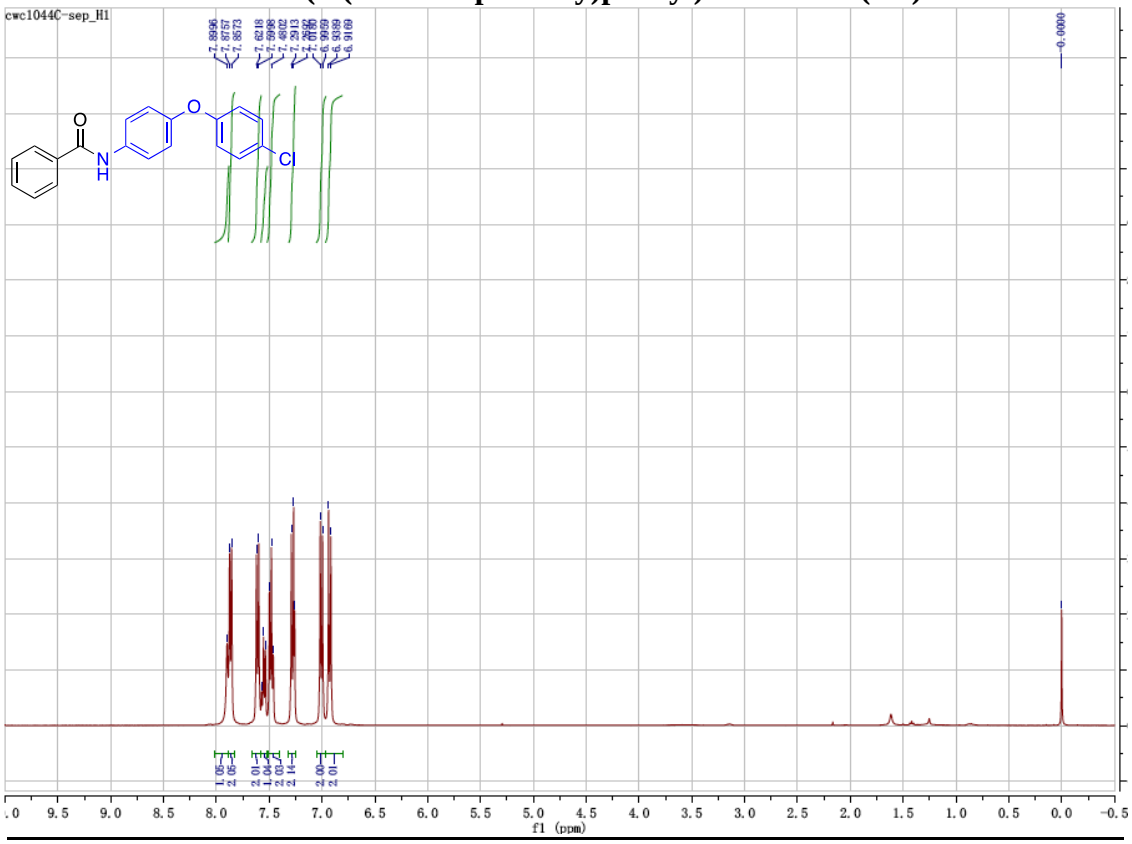


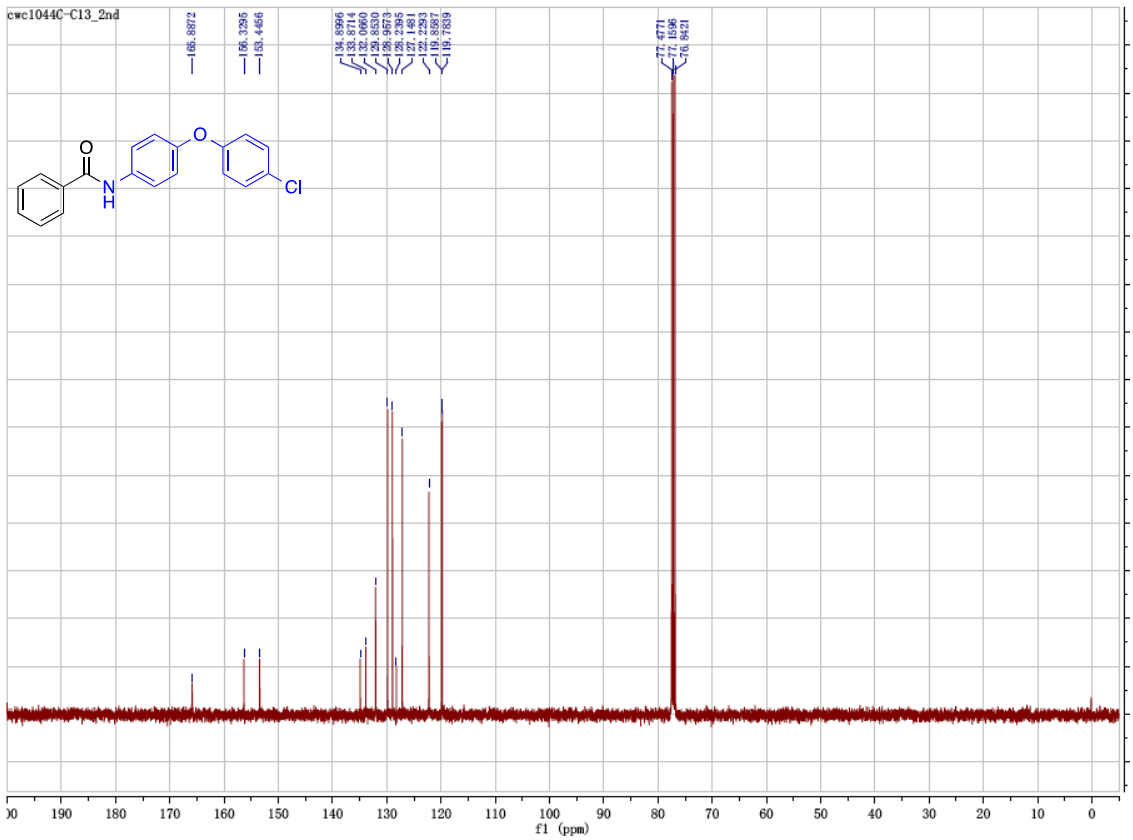
^{1}H and ^{13}C NMR of *N*-(4-(Methylthio)phenyl)benzamide (3ah).



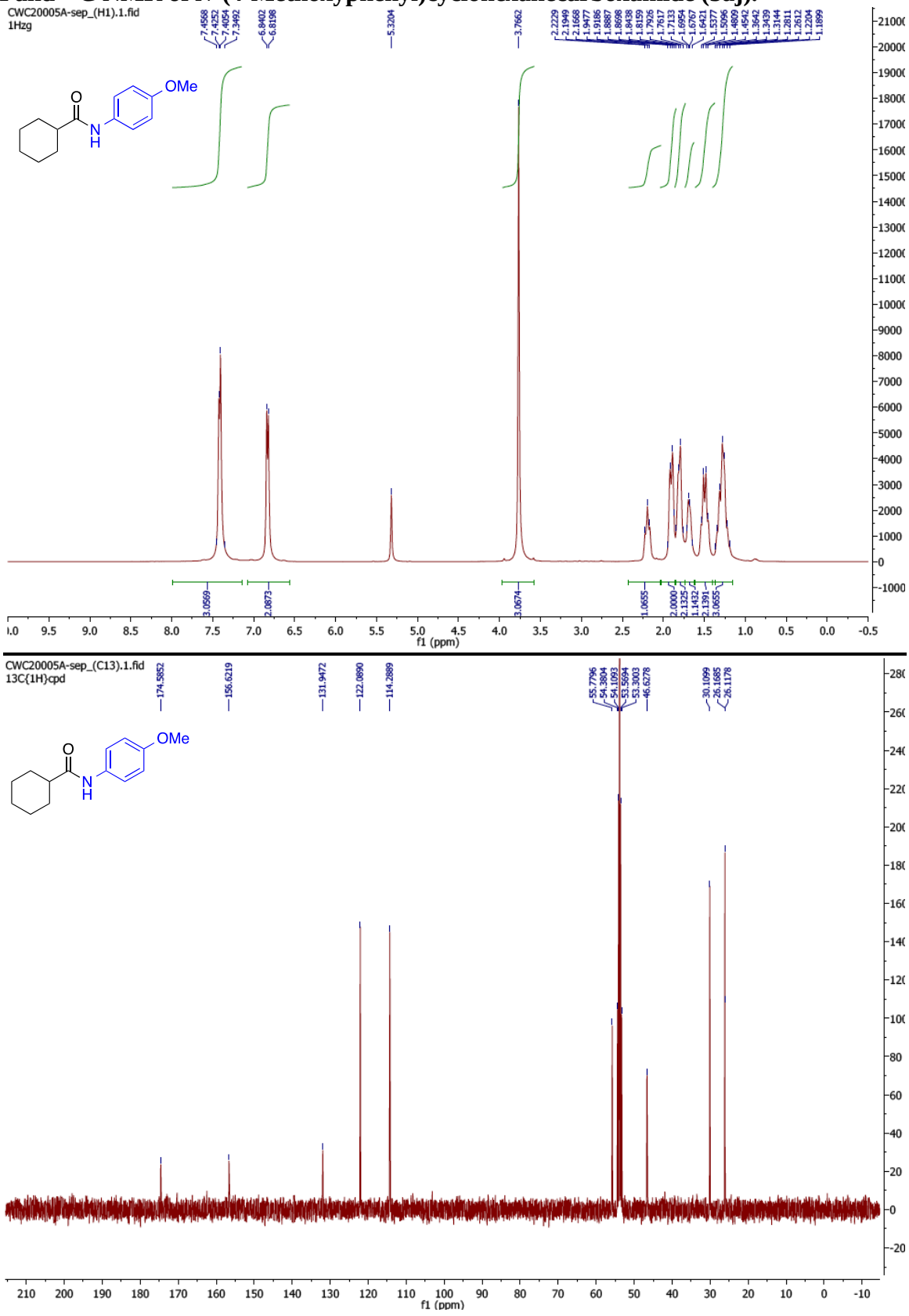


^{1}H and ^{13}C NMR of *N*-(4-(4-Chlorophenoxy)phenyl)benzamide (3ai).

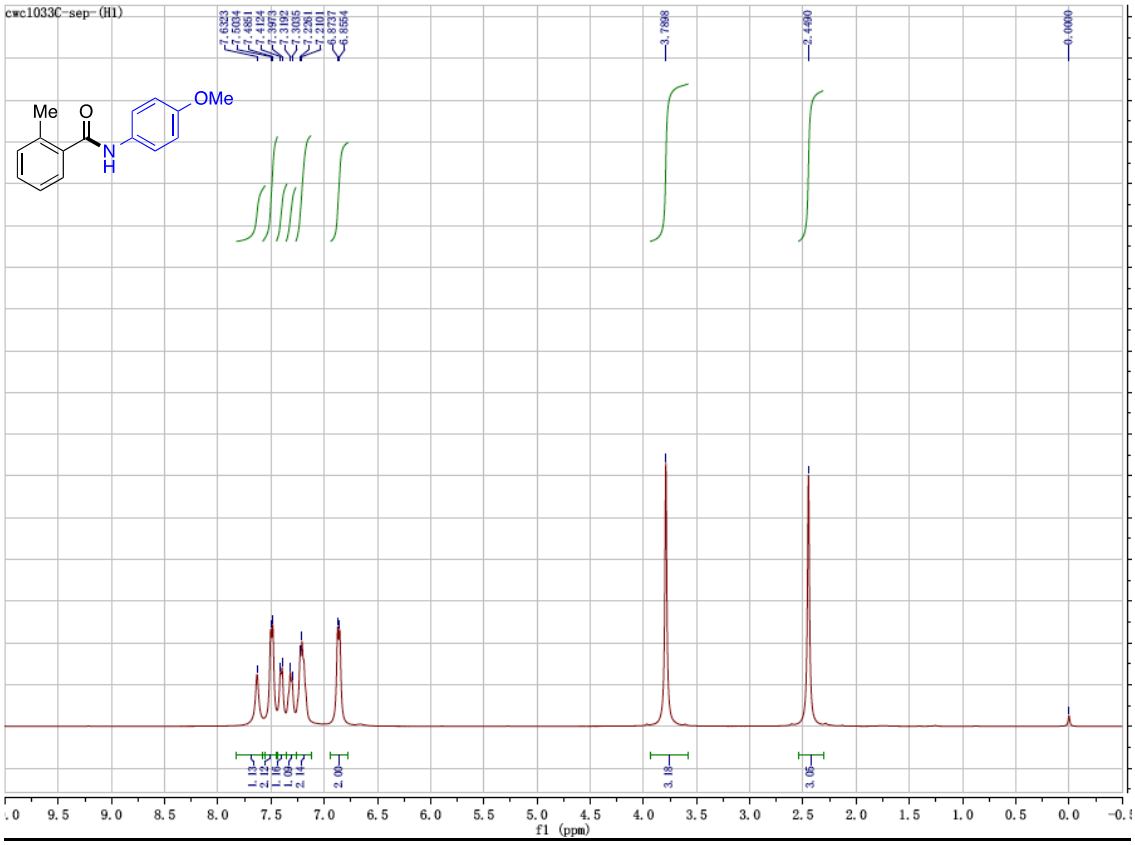


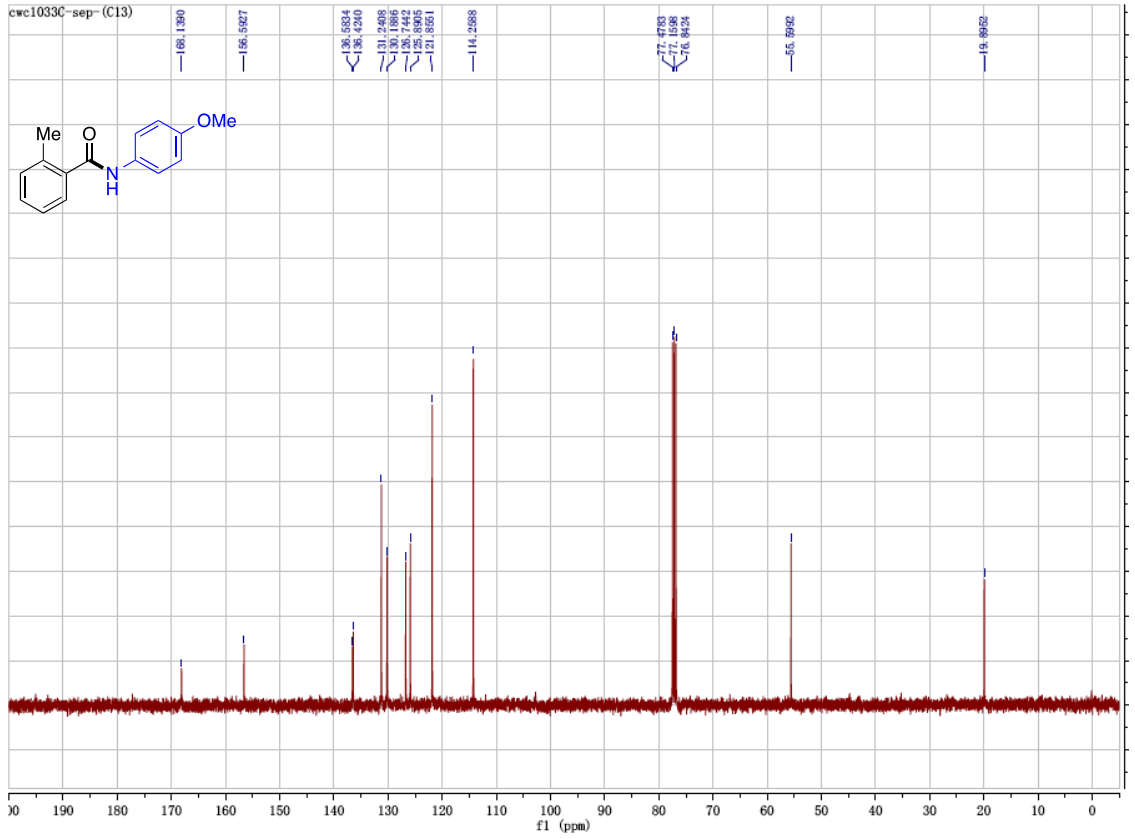


^{1}H and ^{13}C NMR of *N*-(4-Methoxyphenyl)cyclohexanecarboxamide (3aj).

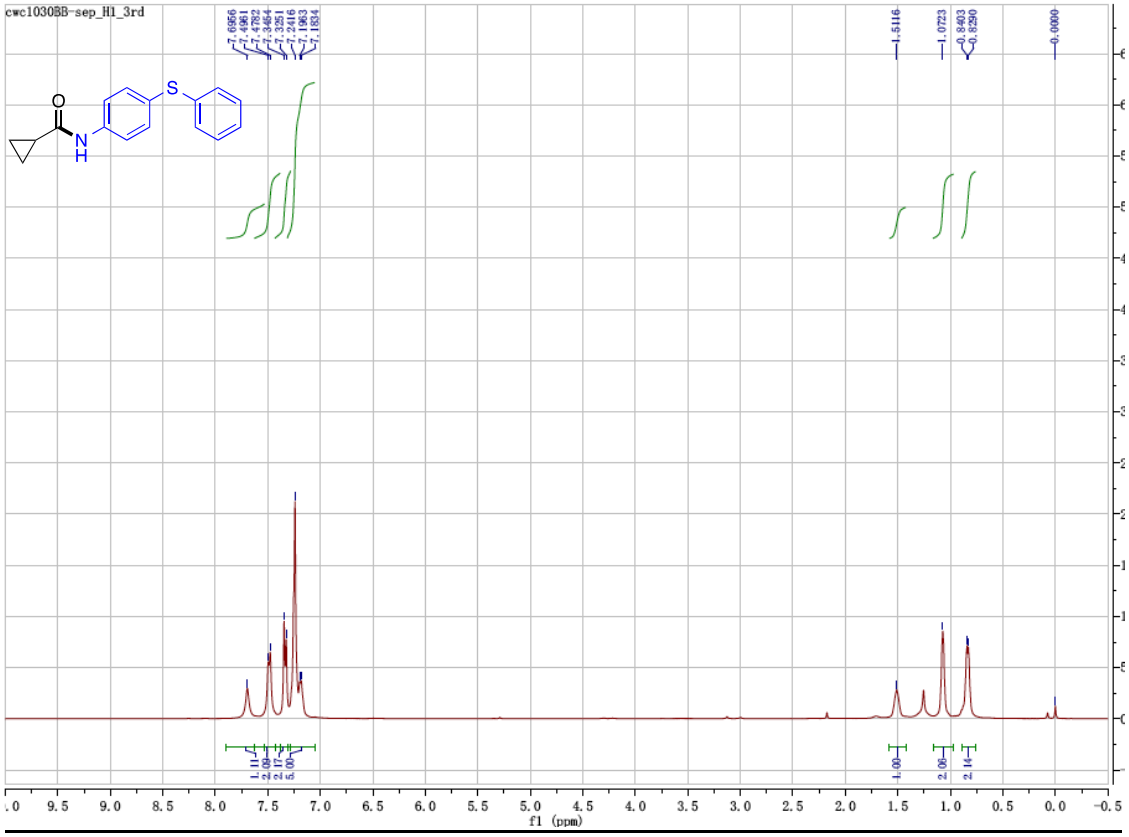


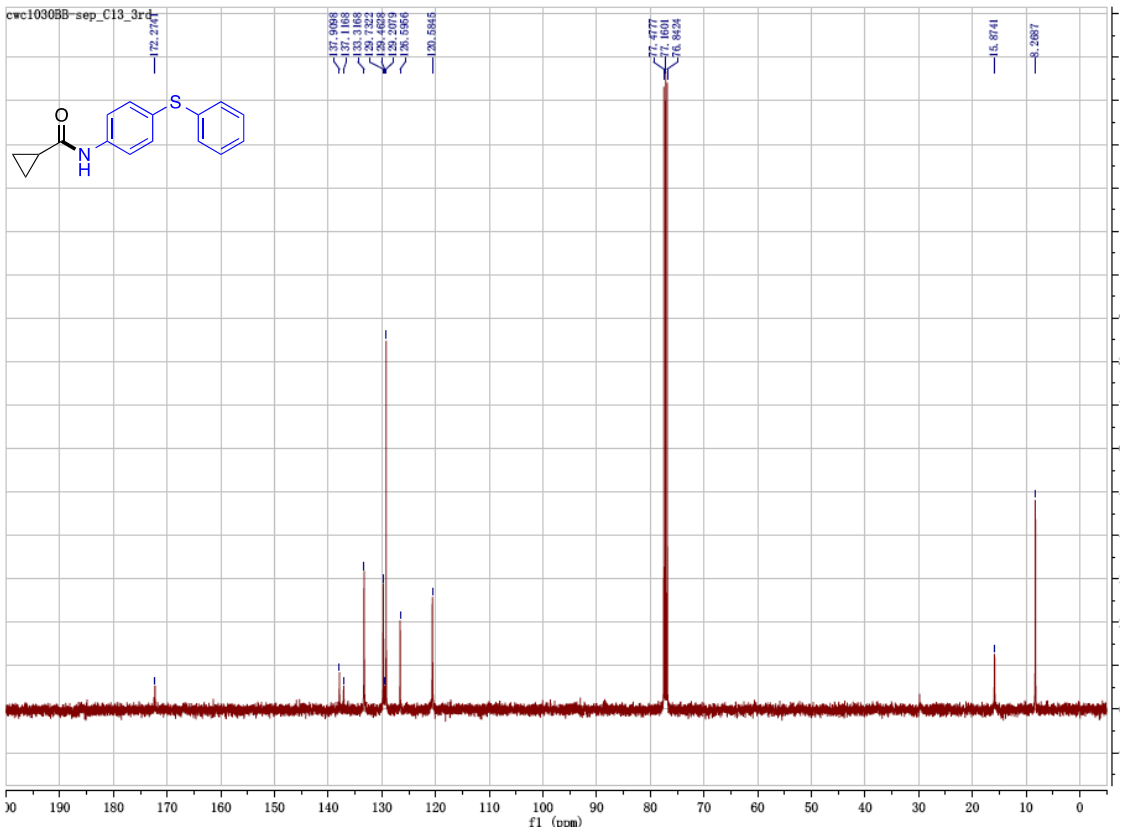
^{1}H and ^{13}C NMR of *N*-(4-methoxyphenyl)-2-methylbenzamide (3ak).



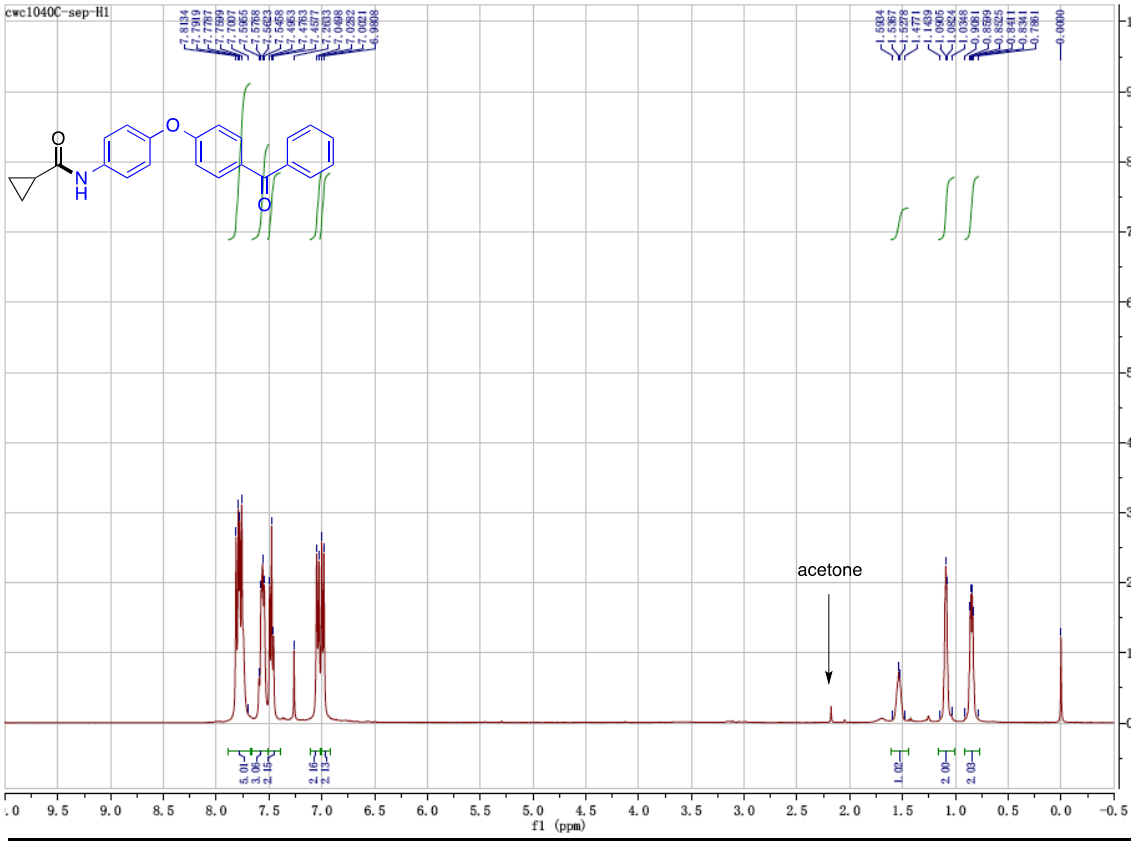


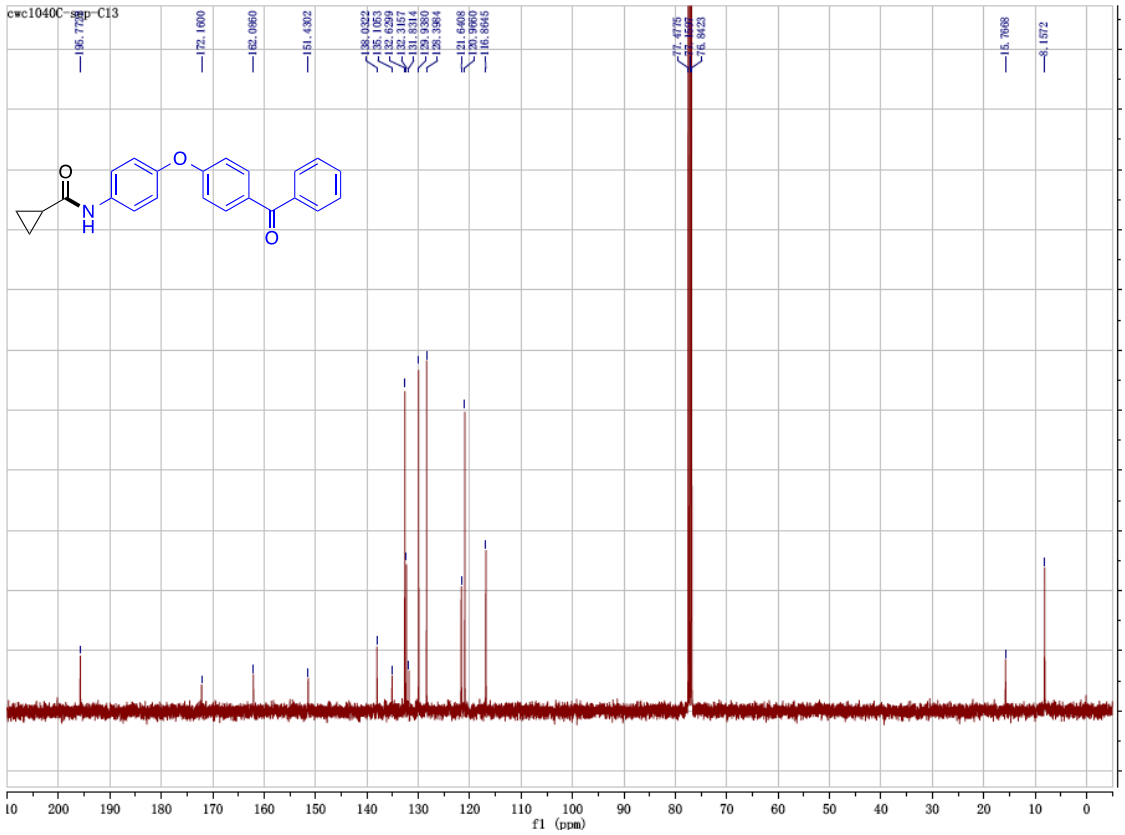
^{1}H and ^{13}C NMR of *N*-(4-(Phenylthio)phenyl)cyclopropanecarboxamide (3al).



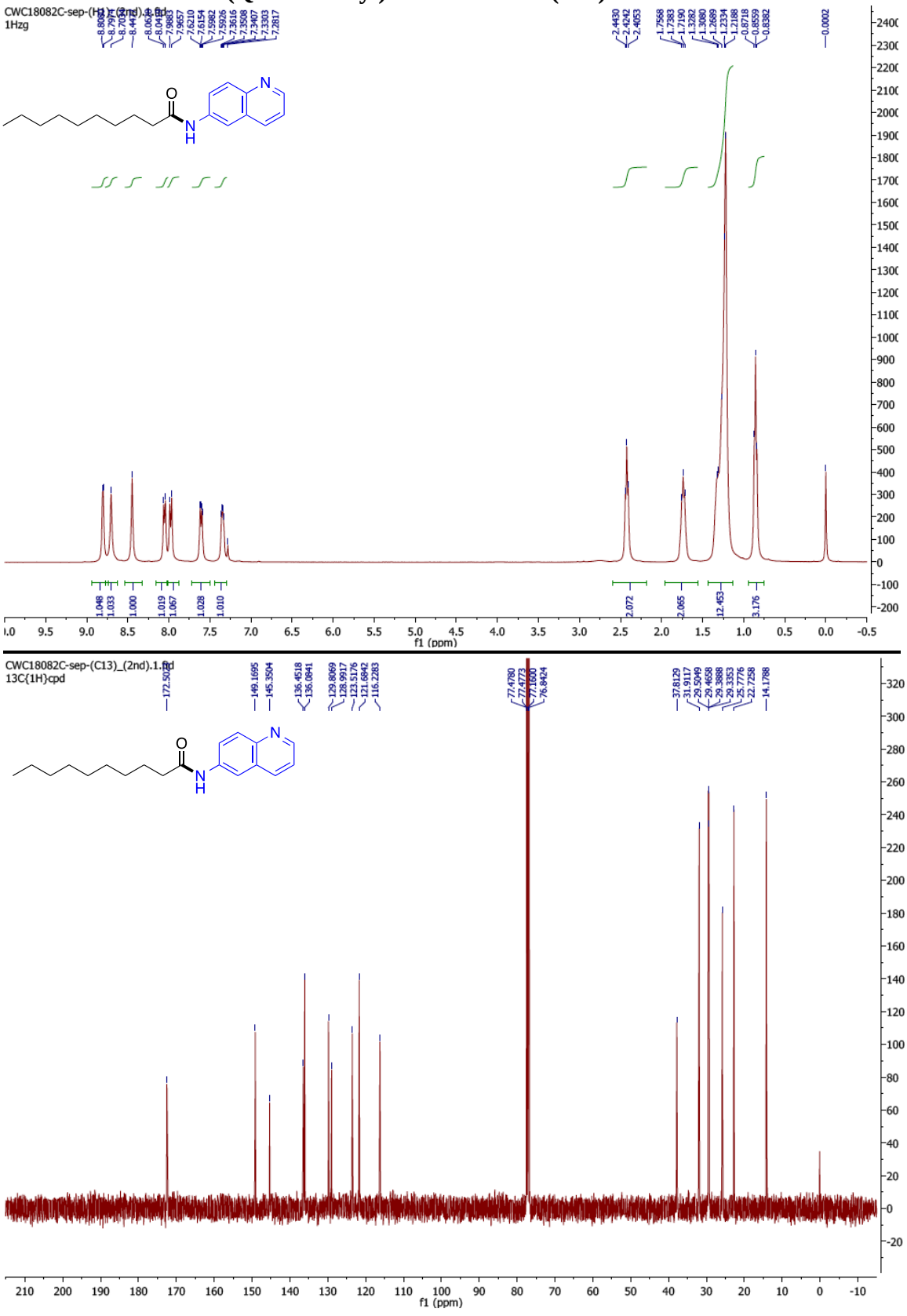


^{1}H and ^{13}C NMR of *N*-(4-(4-Benzoylphenoxy)phenyl)cyclopropanecarboxamide (3am).

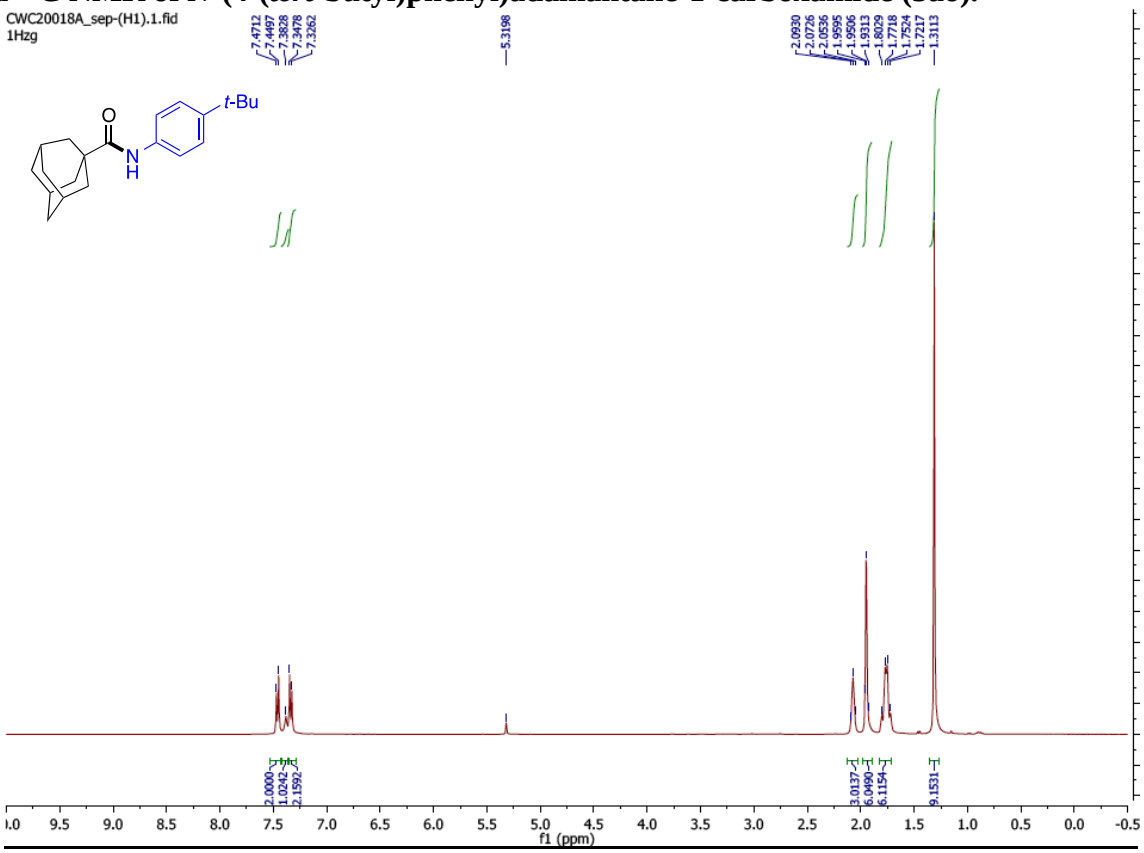


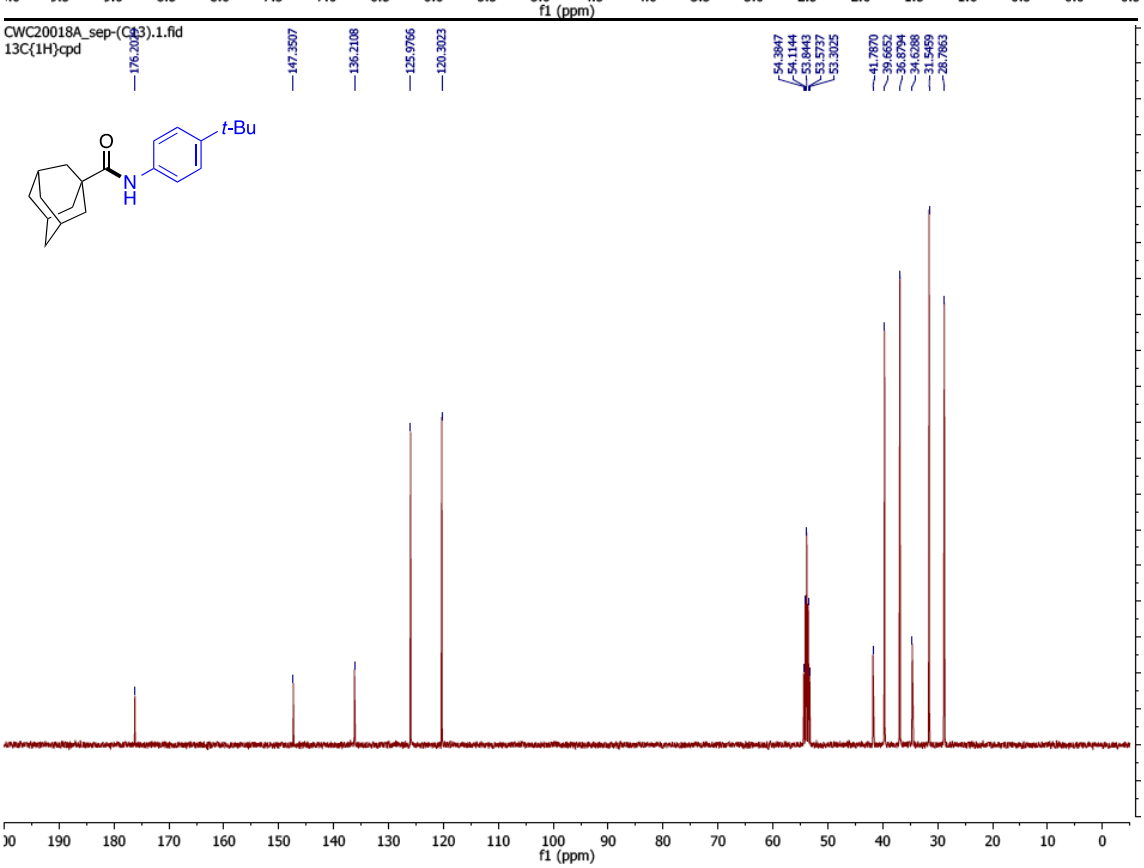


^{1}H and ^{13}C NMR of 1-(Quinolin-6-yl)undecan-2-one (3an).

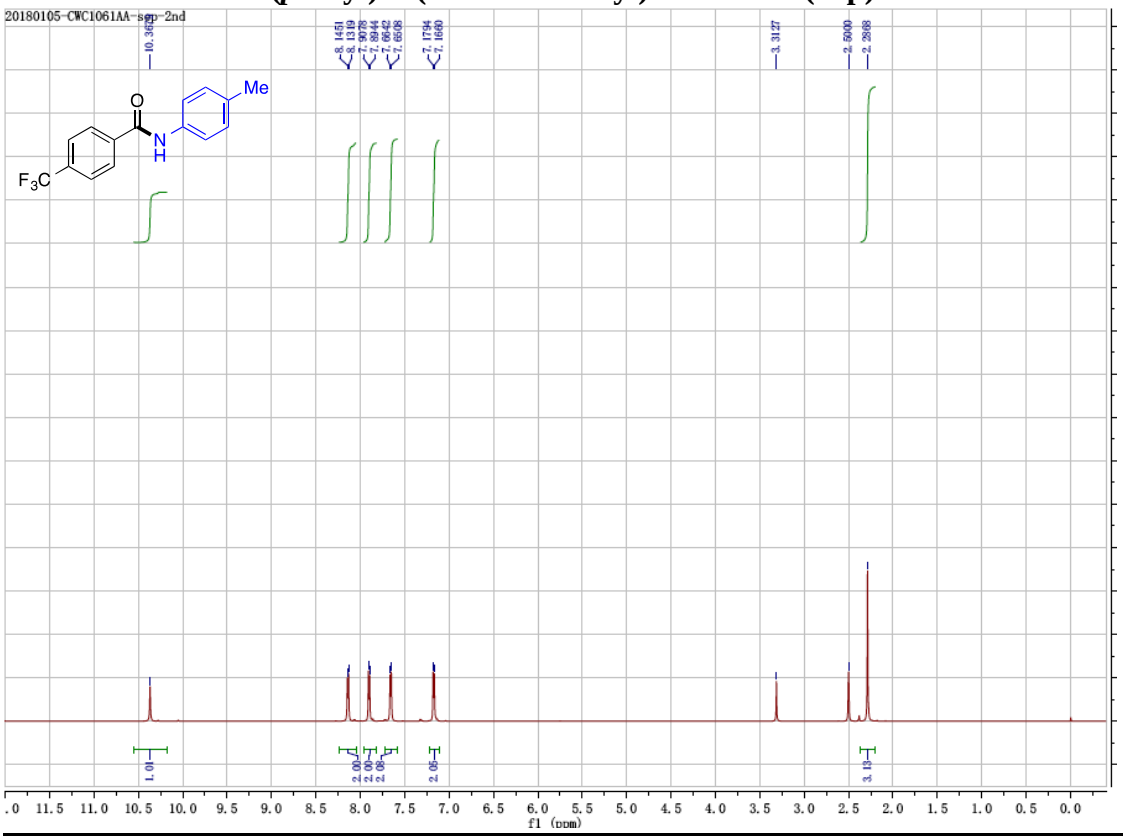


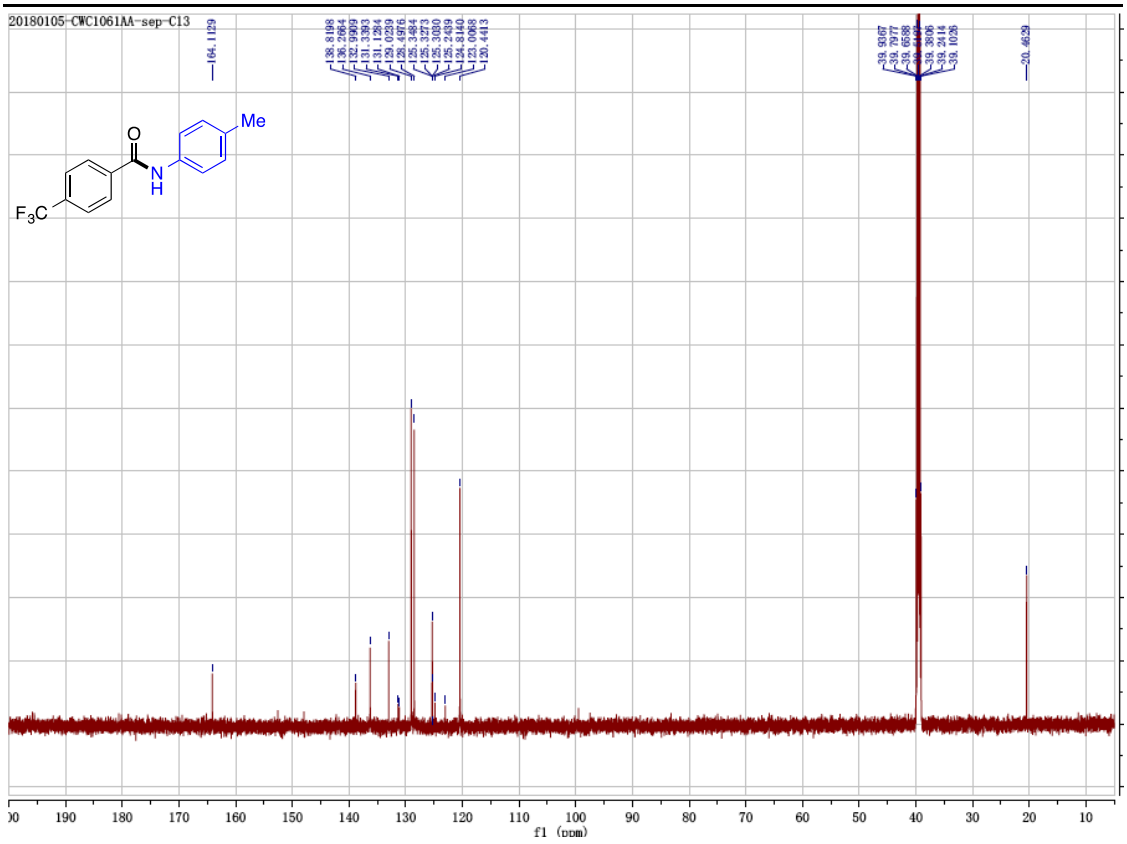
^{1}H and ^{13}C NMR of *N*-(4-(*tert*-butyl)phenyl)adamantane-1-carboxamide (3ao).





^{1}H and ^{13}C NMR of *N*-(*p*-tolyl)-4-(trifluoromethyl)benzamide (3ap).





^{1}H and ^{13}C NMR of *N*-(4-(*tert*-butyl)phenyl)-3,4,5-trimethoxybenzamide (4a).

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