

Supporting Information

Reusable cobalt-copper catalyzed cross-coupling of (hetero)aryl halides with primary amides under air: investigating a new Co⁰/Co^{II}-based catalytic cycle

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1. General experimental

All reactions were carried out in open-air conditions in a dry reaction vessel and the reactants were transferred *via* syringes or spatulas. Analytical TLC was performed on a TLC Silica gel 60 F₂₅₄ (Merck, #1.05554.0007) and the TLC plates were visualized by exposure to UV light (254 nm) followed by an iodine chamber. Organic parts were extracted by simple filtration using ethyl acetate which was further concentrated using rotary evaporation (BUCHI Rotavapor R-100) under reduced pressure. Column chromatography was performed on 60-120 mesh silica gel (Spectrochem Co.) using EtOAc/hexane solvent according to the desired ratio.

Instrumentation

NMR spectroscopy

¹H and ¹³C NMR spectra were obtained using Bruker Avance-400 (400 MHz) NMR spectrometer. The proton chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane (TMS) and are referenced to TMS (δ 0.0) and CHCl₃ (δ 7.26). The chemical shifts of the carbon atoms are reported in parts per million (ppm, δ scale) downfield from TMS and referenced to the carbon resonance of CDCl₃ (δ 77.16). The data are presented as chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiple resonances, and br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers.

IR analysis

IR spectra were recorded using an Agilent Cary 630 FTIR Spectorometer; characteristic IR absorptions are reported in cm⁻¹.

HRMS

High-resolution mass spectra (HRMS) were recorded using fast atom bombardment (FAB) ionization with a Q-TOF mass spectrometer (serial no. YA 263).

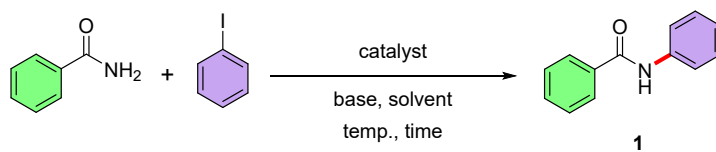
Materials

All the reactions were performed in a dry round bottom flask of glass connecting to condenser on a magnetic stirrer in oil-bath. Used amides and halides were purchased from Sigma-AldrichCo., Tokyo Chemical Industry (India) Pvt. Ltd., Spectrochem Pvt. Ltd., Sisco Research Laboratory Pvt. Ltd., ThermoFisher Scientific, BLDpharm etc. All other chemicals were also purchased from the same. The used catalysts Co(acac)₂ (\geq 99.0%), and copper iodide (powder, 99.999%) were purchased from the Sigma-Aldrich Co. The solvents used for filtration and column chromatography were purchased from RANKEM Co., and other commercial suppliers, and were used after appropriate purification, unless otherwise stated.

2. Optimization of reaction conditions for the synthesis of anilides^a

To achieve the optimized reaction conditions, a series of experiments were executed with a variation of the reaction parameters, such as catalyst, base, solvent, temperature, etc. We initiated our investigation by taking a representative reaction of benzamide with iodobenzene. The results are summarized in Table S1. The use of different solvents in the presence of $\text{Co}(\text{acac})_2/\text{CuI}$ catalyst with cesium carbonate as a base, at 110 °C temperature under an argon atmosphere, for 24 hours reaction time provided the benzanilide product **1** in moderate to excellent yields (entries 1-9). The reaction was also performed without using any solvent (neat), producing the product **1** with an 80% yield (entry 10). This yield is almost similar to that obtained using NMP as the solvent (entry 1). Based on this observation, we performed the reaction using a reduced amount of NMP (100 μL for 1.0 mmol scale of reaction) and achieved an improved yield of 88% (entry 11). By taking this condition forward, we tested $\text{Co}(\text{OAc})_2$, CoBr_2 and CoI_2 instead of $\text{Co}(\text{acac})_2$ as catalyst, but it significantly decreased the yield of the desired product (entries 12-14). Subsequently, variations of the base were tested (entries 15 and 16), and potassium carbonate stood out the best for the reaction. Lowering the reaction temperature to 90 °C and to 60 °C did not improve the yield of the desired product (entry 17 and 18). Next, to check the effect of both catalysts, we performed the reaction omitting CuI and $\text{Co}(\text{acac})_2$ catalysts one at a time (entries 19 and 20). Each case either resulted in trace amounts of the desired product or no desired product at all. This outcome reveals the involvement of both catalysts in the reaction system. In entries 21 and 22 of the optimization process, we examined the reaction by decreasing the time and it was found that the best yield of 91% was obtained after 15 hours duration of the reaction. Finally, the reaction was carried out under a nitrogen atmosphere and in open air (entries 23 and 24). The experiment in open air furnishes the desired product with a 93% yield, indicating that open-air condition can be effectively used in the reaction and hence it has been chosen as the standard one for the protocol (entry 24). After that, to our delight, we examined the reaction altering the amounts of catalysts and reactants which did not provide better results (entry 25-29).

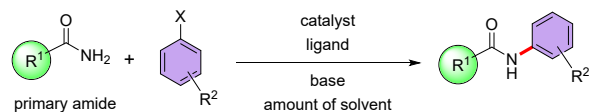
Table S1 Optimization of the reaction conditions^a



Entry	Catalyst	Base	Solvent	Temp.(°C)	Time	Yield(%) ^b
1	Co(acac) ₂ /CuI	Cs ₂ CO ₃	NMP	110	24h	86
2	Co(acac) ₂ /CuI	Cs ₂ CO ₃	DMF	110	24h	45
3	Co(acac) ₂ /CuI	Cs ₂ CO ₃	DMSO	110	24h	76
4	Co(acac) ₂ /CuI	Cs ₂ CO ₃	THF	90	24h	72
5	Co(acac) ₂ /CuI	Cs ₂ CO ₃	PEG-600	110	24h	70
6	Co(acac) ₂ /CuI	Cs ₂ CO ₃	toluene	110	24h	31
7	Co(acac) ₂ /CuI	Cs ₂ CO ₃	PhCl	110	24h	55
8	Co(acac) ₂ /CuI	Cs ₂ CO ₃	H ₂ O	110	24h	40
9	Co(acac) ₂ /CuI	Cs ₂ CO ₃	NMP+H ₂ O	110	24h	60
10	Co(acac) ₂ /CuI	Cs ₂ CO ₃	—	110	24h	80
11 ^c	Co(acac) ₂ /CuI	Cs ₂ CO ₃	NMP	110	24h	88
12 ^c	Co(OAc) ₂ /CuI	Cs ₂ CO ₃	NMP	110	24h	67
13 ^c	CoBr ₂ /CuI	Cs ₂ CO ₃	NMP	110	24h	43
14 ^c	CoI ₂ /CuI	Cs ₂ CO ₃	NMP	110	24h	51
15 ^c	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	24h	90
16 ^c	Co(acac) ₂ /CuI	Na ₂ CO ₃	NMP	110	24h	70
17 ^c	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	90	24h	58
18 ^c	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	60	24h	0
19 ^c	Co(acac) ₂ /-	K ₂ CO ₃	NMP	110	24h	0
20 ^c	-/CuI	K ₂ CO ₃	NMP	110	24h	11
21 ^c	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	15h	91
22 ^c	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	12h	81
23 ^{c,d}	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	15h	90
24^{c,e}	Co(acac)₂/CuI	K₂CO₃	NMP	110	15h	93
25 ^{c,f}	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	15h	74
26 ^{c,g}	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	15h	87
27 ^{c,h}	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	15h	81
28 ^{c,i}	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	15h	72
29 ^{c,j}	Co(acac) ₂ /CuI	K ₂ CO ₃	NMP	110	15h	93

^a Reaction conditions: amide (0.5 mmol), aryl halide (0.5 mmol), Co-catalyst (10 mol%), CuI (10 mol%), base (0.75 mmol), solvent (1 mL) under argon atmosphere. ^b Isolated yields. ^cNMP was used 100 μL for 1.0 mmol scale of reaction. ^d Reaction was carried out under nitrogen atmosphere. ^e Reaction was carried out in open air. ^fCo(acac)₂ (5 mol%) and CuI (5 mol%) were used. ^gCo(acac)₂ (5 mol%) and CuI (10 mol%) were used. ^hCo(acac)₂ (10 mol%) and CuI (5 mol%) were used. ⁱamide (0.75 mmol), aryl halide (0.5 mmol) were used. ^jamide (0.5 mmol), aryl halide (0.75 mmol) were used.

Table S2a. Comparison of the results of the present work with those of the previously reported cross-coupling reactions of primary amides with aryl halides employing cobalt catalysis.



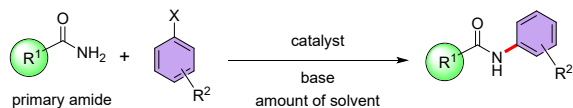
Entry	R ¹	X	Catalyst	Ligand	Base	Amount of solvent for 1.0 mmol scale of reaction	Yield (%)	Mechanistic study	Mechanistic cycle	Reuseability of catalyst	Substrate scope	Gram-scale synthesis	Conventional work-up required	Ref
1	R ¹ = Ph ✗ Aliphatic ✗ Heteroaryl	X = I ✗ X = Br, Cl ✗ Heteroaryl	CoCl ₂ ·6H ₂ O (20 mol%)	DMEDA	K ₃ PO ₄ ·H ₂ O	0.7 mL	24-28	No	not provided	No	2	No	Yes	14a
2	R ¹ = Aryl ✗ Aliphatic ✗ Heteroaryl	X = I ✗ X = Br, Cl ✗ Heteroaryl	Co(C ₂ O ₄) ₂ ·2H ₂ O (10-20 mol%)	DMEDA	Cs ₂ CO ₃	0.2 mL	18-92	No	Co(II)/Co(IV)	No	29	No	Yes	14b
3	R ¹ = Aliphatic ✗ Aryl ✗ Heteroaryl	X = I ✗ X = Br, Cl ✗ Heteroaryl	Co(C ₂ O ₄) ₂ ·2H ₂ O (20 mol%)	DMEDA	Cs ₂ CO ₃	0.2 mL	trace-75	No	not provided	No	16	No	Yes	14c
4	R ¹ = C ₃ H ₇ ✗ Aryl ✗ Heteroaryl	X = I ✗ X = Br, Cl ✗ Heteroaryl	Co(acac) ₂ (10 mol%) CuI (10 mol%)	—	Cs ₂ CO ₃	4.0 mL	82 (for R ² = 4-Cl) 90 (for R ² = 1-naphthyl)	No	Co(I)/Co(III)	No	2	No	Yes	13e
5	R ¹ = Aliphatic, Aryl, Heteroaryl	X = Br, I, Cl Aryl and Heteroaryl halides	Co(acac) ₂ (10 mol%) CuI (10 mol%)	—	K ₂ CO ₃	0.1 mL or Solvent-free	43-94 (for X = I, Br) 10-80 (for X = Cl)	Yes	Co(0)/Co(II)	Yes	51	Yes	No	Our Work

"✗" indicates "not applicable", which are significant disadvantages with respect to our present method.

Red colour indicates significant disadvantage with respect to our present method.

Blue colour indicates minor disadvantage with respect to our present method.

Table S2b. Comparison of the results of the present work with those of the previously reported ligand-free copper-catalyzed cross-coupling reactions of primary amides with aryl halides.



Entry	R ¹	X	Catalyst	Base	Amount of solvent for 1.0 mmol scale of reaction	Yield (%)	Mechanistic study	Mechanistic cycle	Reusability of catalyst	Substrate scope	Gram-scale synthesis	Conventional work-up required	Ref
1	R ¹ = CH ₃ , Aryl, heteroaryl	X = I ✗ X = Br, Cl ✗ Heteroaryl	CuI	K ₃ PO ₄ or, CsF	0.4 mL	39-97	No	not provided	No	5	Yes	Yes	8a
2	R ¹ = Pentyl, Ph ✗ Heteroaryl	X = I ✗ X = Br, Cl ✗ Heteroaryl	CuO NPs	Cs ₂ CO ₃	0.8 mL	25-88	No	provided but not mentioned the oxidation state of Cu species either in the text or in the catalytic cycle	Yes	6	No	Yes	8b
3	R ¹ = CH ₃ , Pentyl, Ph ✗ Heteroaryl	X = I ✗ X = Br, Cl ✗ Heteroaryl	Cu ₂ O NPs	KOH	0.7 mL	70-80	No	provided but not mentioned the oxidation state of Cu species either in the text or in the catalytic cycle	Yes	9	No	Yes	8c
4	R ¹ = 4-BrPh, Ph ✗ Aliphatic ✗ Heteroaryl	X = I ✗ X = Br, Cl ✗ Heteroaryl	Cu/Al ₂ O ₃	KOH	2.0 mL	78-81	No	not provided	Yes	2	No	Yes	8e
5	R ¹ = CH ₃ , Ph ✗ Heteroaryl	X = I, Br ✗ X = Cl ✗ Heteroaryl	Pre-prepared biogenic CuONP	K ₂ CO ₃	3.0 mL	85-96	Yes	provided but no redox process shown at the Cu center	Yes	13	No	Yes	7j
6	R ¹ = Ph ✗ Aliphatic ✗ Heteroaryl	X = Br (only bromobenzene) ✗ X = Cl ✗ Heteroaryl	CuI	K ₃ PO ₄	0.5 mL	49	No	not provided	No	1	No	Yes	8g
7	R ¹ = Aliphatic, Aryl, Heteroaryl	X = Br, I, Cl Aryl and Heteroaryl halides	Co(acac) ₂ /CuI	K ₂ CO ₃	0.1 mL or Solvent-free	43-94 (for X = I, Br) 10-80 (for X = Cl)	Yes	Co(0)/Co(II)	Yes	51	Yes	No	Our Work

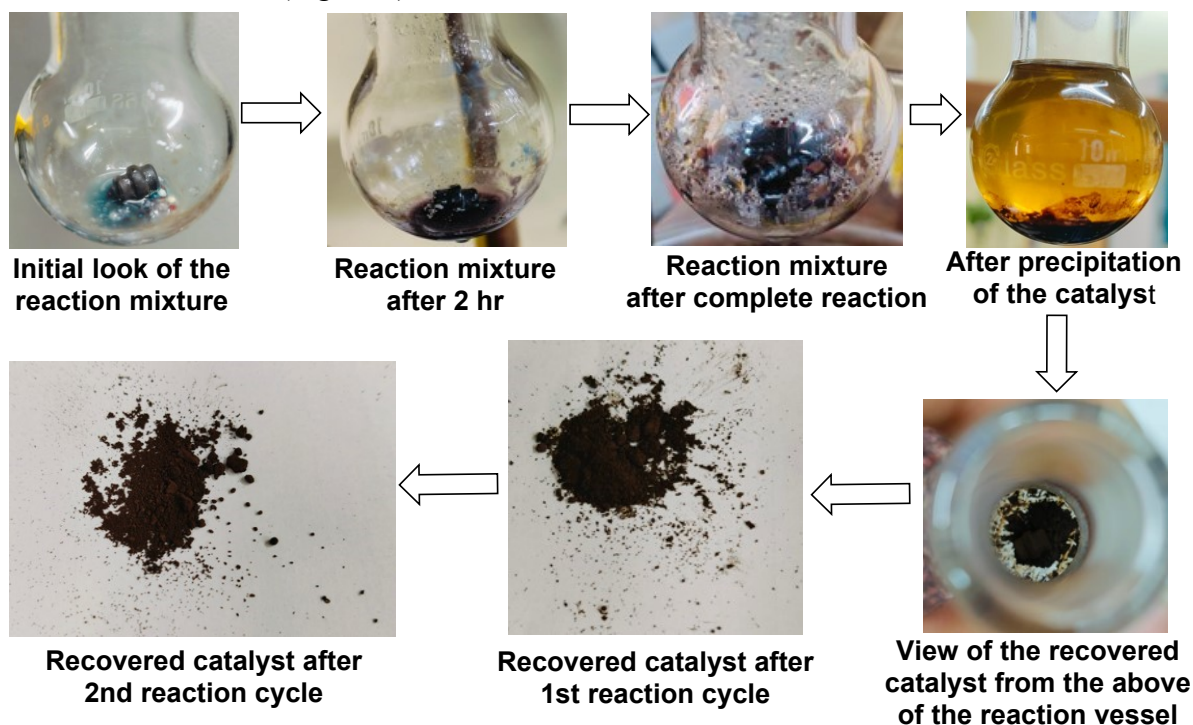
"✗" indicates "not applicable", which are significant disadvantages with respect to our present method.

Red colour indicates significant disadvantage with respect to our present method.

Blue colour indicates minor disadvantage with respect to our present method.

3. Experimental procedure for catalyst recovery:

After completion of the reaction, the reaction mixture was allowed to cool to room temperature. Then ethyl acetate (10 mL) was added to the mixture and stirred for 10 min to ensure product removal from the catalyst. Next, the catalyst was allowed to precipitate and the above-layered ethyl acetate containing the organic part was poured in a separate round-bottom flask. The same procedure was followed at least three times to ensure the complete removal of the organic part (monitored by TLC). After that, the reaction vessel containing the catalyst was properly dried under a high vacuum to obtain the powdered catalyst (Scheme 1) which was used further for consecutive reactions (Figure 2).



Scheme S1 Photographs at different stages of the experimental procedure for catalyst recovery.

4. EDS (energy dispersive X-ray spectroscopy) and CV study:

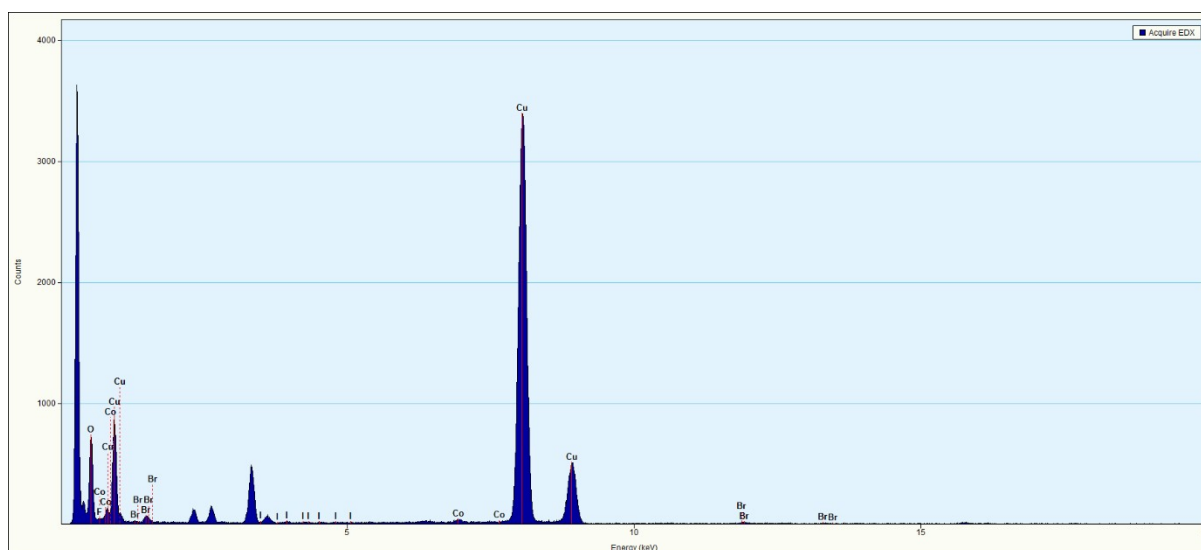


Fig. S1 EDS image of Co-nanoparticles formed in the reaction mixture.

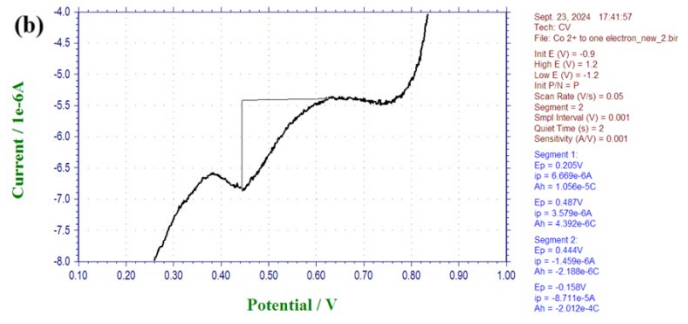
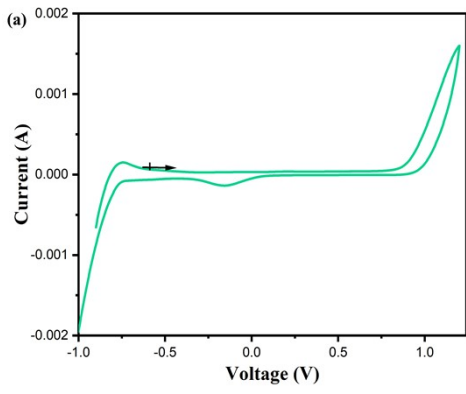
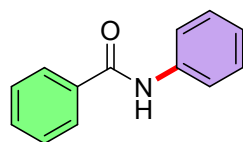


Fig. S2 (a) Cyclic voltammogram of $\text{Co}(\text{acac})_2$ in $\text{H}_2\text{O}/0.1 \text{ M K}_2\text{CO}_3$ with a Pt working electrode and a saturated Ag/AgCl reference electrode, (b) A zoomed-in picture of a Cyclic voltammogram of $\text{Co}(\text{acac})_2$ in $\text{H}_2\text{O}/0.1 \text{ M K}_2\text{CO}_3$ with a Pt working electrode and a saturated Ag/AgCl reference electrode.

5. Experimental procedures and characterization data of products

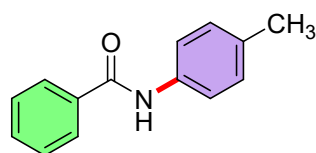
General Procedure A: synthesis of synthesis of *N*-arylamides: Representative Experimental Procedure for the synthesis of *N*-phenylbenzamide (1):



A mixture of benzamide **1i** (122 mg, 1.0 mmol), bromobenzene **2i'** (157 mg, 1.0 mmol) or iodobenzene **2i** (204 mg, 1.0 mmol), K_2CO_3 (208 mg, 1.5 mmol), $\text{Co}(\text{acac})_2$ (26 mg, 10 mol%), CuI (19 mg, 10 mol%) and NMP (100 μL per 1.0 mmol scale of reaction) was heated at 130°C (for bromobenzene) or 110°C (for iodobenzene) in open air for 15 h. Then the reaction mixture was allowed to cool and filtration was done by ethyl acetate. Then the organic part (filtrate) was evaporated under reduced pressure to give the crude product which was purified by column chromatography over silica gel (hexane/ethyl acetate 90:10) to provide the pure product as a white solid (140.0 mg, 71 % yield: for bromobenzene and 183.4 mg, 93 % yield: for iodobenzene).¹

White solid; mp $162\text{-}164^\circ\text{C}$; IR (neat, cm^{-1}) ν 3320, 2915, 2841, 1625, 1595, 1502; ^1H NMR (400 MHz, CDCl_3) δ 7.15 (t, $J = 7.4$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.44-7.54 (m, 3H), 7.64 (d, $J = 7.7$ Hz, 2H), 7.85 (t, $J = 7.0$ Hz, 2H), 7.97 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 120.4 (2C), 124.7, 127.2 (2C), 128.9 (2C), 129.2 (2C), 132.0, 135.0, 138.0, 166.0; HRMS (EI⁺) m/z [M]⁺ Calcd for $\text{C}_{13}\text{H}_{11}\text{NO}$: 197.0841, Found 197.0841. All analytical data are in good accordance with those reported in the literature.¹

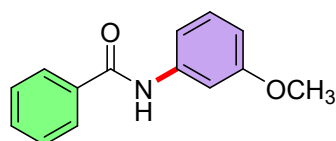
Synthesis of *N*-(*p*-tolyl)benzamide (2):



The reaction was carried out according to the general procedure A for 15 h at 110°C using benzamide (122 mg, 1.0 mmol) and 4-Iodotoluene (218 mg, 1.0 mmol). The title compound (164.8 mg, 78% yield) was obtained as a white solid after silica gel column chromatography.¹

White solid; mp $148^\circ\text{C}\text{-}149^\circ\text{C}$; ^1H NMR (400MHz, CDCl_3) δ 2.34 (s, 3H), 7.18 (d, $J = 8\text{Hz}$, 2H), 7.47-7.55 (m, 5H), 7.78 (s, 1H), 7.86 (d, $J = 8\text{Hz}$, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 120.4, 127.1(2C), 128.9 (2C), 129.8 (2C), 131.9 (2C), 134.4, 135.2, 135.4, 165.8. All analytical data are in good accordance with those reported in the literature.¹

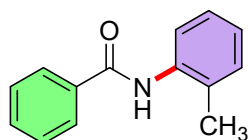
Synthesis of *N*-(3-methoxyphenyl)benzamide (3):



The reaction was carried out according to the general procedure A for 15 h at 110°C using benzamide (122 mg, 1.0 mmol) and 3-Iodoanisole (234 mg, 1.0 mmol). The title compound (138.6 mg, 61% yield) was obtained as a white solid after silica gel column chromatography.²

White solid; mp 160-162 °C; ¹H NMR (400MHz, CDCl₃) δ 3.79 (s, 3H), 6.69 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.21-7.26 (m, 1H), 7.41-7.52 (s, 4H), 7.84 (d, *J* = 7.2 Hz, 2H), 8.14 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 55.4, 106.0, 110.6, 112.5, 127.2 (2C), 128.8 (2C), 129.8, 131.9, 135.0, 139.3, 160.3, 166.1. All analytical data are in good accordance with those reported in the literature.²

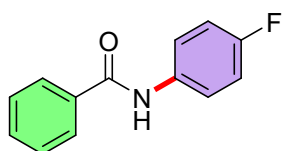
Synthesis of *N*-(*o*-tolyl)benzamide (4):



The reaction was carried out according to the general procedure A for 15 h at 110°C using benzamide (122 mg, 1.0 mmol) and 2-Iodotoluene (218 mg, 1.0 mmol). The title compound (190.1 mg, 90% yield) was obtained as a white solid after silica gel column chromatography.¹

White solid; mp 145-146°C; ¹H NMR (400MHz, CDCl₃) δ 2.30 (s, 3H), 7.12 (t, *J* = 6.7 Hz, 1H), 7.21-7.26 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.81-7.93 (m, 4H); ¹³C NMR (100MHz, CDCl₃) δ 17.9, 123.7, 125.6, 126.8, 127.2 (2C), 128.8 (2C), 130.0, 130.6, 131.9, 134.9, 135.8, 165.9. All analytical data are in good accordance with those reported in the literature.¹

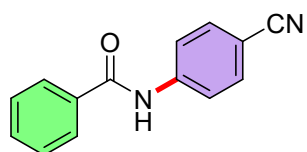
Synthesis of *N*-(4-fluorophenyl)benzamide (5):



The reaction was carried out according to the general procedure A for 15 h at 110°C using benzamide (122 mg, 1.0 mmol) and 4-Fluoriodobenzene (222 mg, 1.0 mmol). The title compound (174.3 mg, 81% yield) was obtained as a white solid after silica gel column chromatography.³

Light brown solid; mp 184-185 °C; ¹H NMR (400MHz, CDCl₃) δ 7.06 (t, *J* = 8.6 Hz, 3H), 7.47-7.50 (t, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.58-7.62 (m, 2H), 7.86 (d, *J* = 7.4 Hz, 3H); ¹³C NMR (100MHz, CDCl₃) δ 115.9 (d, *J* = 23.0 Hz, 2C), 122.2 (d, *J* = 7.0 Hz, 2C), 127.2, 129.0 (2C), 132.1 (2C), 134.0 (d, *J* = 2.0 Hz, 1C), 134.9, 159.7 (d, *J* = 243.0 Hz, 1C), 165.0. All analytical data are in good accordance with those reported in the literature.³

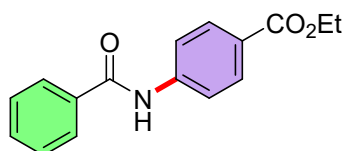
Synthesis of *N*-(4-cyanophenyl)benzamide (6):



The reaction was carried out according to the general procedure A for 15 h at 110°C using benzamide (122 mg, 1.0 mmol) and 4-iodobenzonitrile (229 mg, 1.0 mmol). The title compound (166.7 mg, 75% yield) was obtained as a white solid after silica gel column chromatography.⁴

White solid; mp 165-166 °C; ¹H NMR (400MHz, CDCl₃) δ 7.49 (t, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 8.81 (d, *J* = 8.8 Hz, 2H), 8.87 (d, *J* = 7.2 Hz, 2H), 8.33 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 107.3, 116.5, 119.0, 120.2, 124.7, 127.3, 128.6, 129.1, 130.3, 132.6, 133.4, 134.2, 142.3, 166.3. All analytical data are in good accordance with those reported in the literature.⁴

Synthesis of ethyl 4-benzamidobenzoate (7):

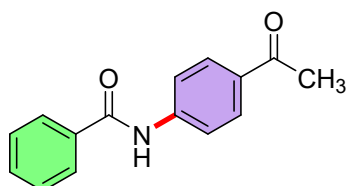


The reaction was carried out according to the general procedure A for 15 h at 110°C using benzamide (122 mg, 1.0 mmol) and ethyl

4-iodobenzoate (269.3 mg, 1.0 mmol). The title compound (193.9 mg, 72% yield) was obtained as a white solid after silica gel column chromatography.¹

White solid; mp 149-150°C; ¹H NMR (400MHz, CDCl₃) δ 2.71 (s, 1H), 2.99 (s, 1H), 4.31-4.40 (m, 3H), 7.48-7.59 (m, 3H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 8.02 (s, 1H), 8.06 (d, *J* = 8.6 Hz, 2H); ¹³C NMR (100MHz, CDCl₃) δ 14.5, 61.1, 115.3, 119.3, 126.4, 127.2, 129.1 (2C), 131.0 (2C), 131.9, 132.4, 134.7, 142.2, 165.9, 166.3. All analytical data are in good accordance with those reported in the literature.¹

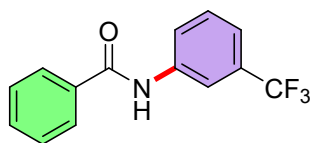
Synthesis of *N*-(4-acetylphenyl)benzamide (8):



The reaction was carried out according to the general procedure A for 15 h at 130°C using benzamide (122 mg, 1.0 mmol) and 1-(4-bromophenyl)ethan-1-one (199.0 mg, 1.0 mmol). The title compound (150.7 mg, 63% yield) was obtained as a white solid after silica gel column chromatography.¹

White solid; mp 203-204 °C; ¹H NMR (400MHz, CDCl₃) δ 2.59 (s, 3H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 8.15 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 26.6, 119.4 (2C), 127.3 (2C), 129.1 (2C), 130.0 (2C), 132.4, 133.2, 134.6, 142.5, 166.0, 197.2. All analytical data are in good accordance with those reported in the literature.¹

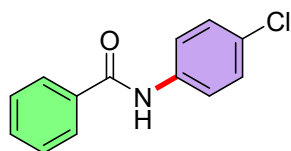
Synthesis of *N*-(4-(trifluoromethyl)phenyl)benzamide (9):



The reaction was carried out according to the general procedure A for 15 h at 110°C using benzamide (122 mg, 1.0 mmol) and 1-iodo-3-(trifluoromethyl)benzene (272 mg, 1.0 mmol). The title compound (190.9 mg, 72% yield) was obtained as a white solid after silica gel column chromatography.³

White solid; mp 88–89 °C; ¹H NMR (400MHz, CDCl₃) δ 7.27-7.35 (m, 4H), 7.43 (t, *J* = 11.4 Hz, 1H), 7.75 (d, *J* = 7.56 Hz, 3H), 7.85 (s, 1H), 8.29 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 117.3 (d, *J* = 4.0 Hz, 1C), 121.2 (d, *J* = 4.0 Hz, 1C), 123.6, 124.5 (d, *J* = 273.0 Hz, 1C), 127.2 (2C), 128.9 (2C), 129.7, 131.5 (d, *J* = 2.0 Hz, 1C), 132.3, 134.5, 138.6, 166.4. All analytical data are in good accordance with those reported in the literature.³

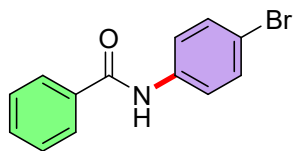
Synthesis of *N*-(4-chlorophenyl)benzamide (10):



The reaction was carried out according to the general procedure A for 15 h at 130°C using benzamide (122 mg, 1.0 mmol) and 1-bromo-4-chlorobenzene (208 mg, 1.0 mmol). The title compound (231.7 mg, 72% yield) was obtained as a white solid after silica gel column chromatography.

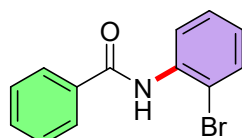
White solid; mp 198-200 °C; ¹H NMR (400MHz, CDCl₃) δ 7.33 (d, *J* = 8.8 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100MHz, CDCl₃) δ 121.6 (2C), 127.2 (2C), 129.0 (2C), 129.3 (2C), 129.7, 132.2, 134.8, 136.6, 165.8. All analytical data are in good accordance with those reported in the literature.⁵

Synthesis of *N*-(4-bromophenyl)benzamide (11):



chromatography.⁵

White solid; mp 175-178 °C; ¹H NMR (400MHz, CDCl₃) δ 7.40-7.47 (m, 3H), 7.55 (td, *J* = 6.4, 0.8 Hz, 1H), 7.80-7.84 (m, 5H), 8.11 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 121.9 (2C), 123.2, 127.2 (2C), 129.0 (2C), 130.1 (2C), 132.5, 134.1, 140.1, 166.0. All analytical data are in good accordance with those reported in the literature.⁵

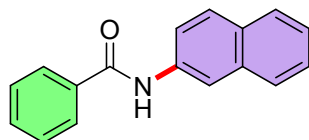


Synthesis of *N*-(2-bromophenyl)benzamide (12):

The reaction was carried out according to the general procedure A for 15 h at 130°C using benzamide (122 mg, 1.0 mmol) and 1,2-dibromobenzene (236 mg, 1.0 mmol). The title compound (168.4 mg, 61% yield) was obtained as a white solid after silica gel column chromatography.⁶

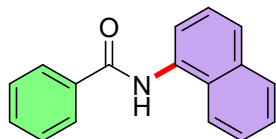
White solid; mp 168-170 °C; ¹H NMR (400MHz, CDCl₃) δ 7.38 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 6.8 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 6.8 Hz, 2H); ¹³C NMR (100MHz, CDCl₃) δ 120.3, 124.8, 127.2 (2C), 127.8, 128.9 (2C), 129.1, 129.3, 132.0, 135.1, 138.1, 165.9; All analytical data are in good accordance with those reported in the literature.⁶

Synthesis of *N*-(naphthalen-2-yl)benzamide (13):



chromatography.¹

White solid; mp 164-165°C; ¹H NMR (400MHz, CDCl₃) δ 7.41-7.52 (m, 4H), 7.55-7.61 (m, 2H), 7.81 (q, *J* = 8.4, 4.4 Hz, 3H), 7.92 (d, *J* = 7.2 Hz, 2H), 8.06 (s, 1H), 8.35 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 117.2, 120.2, 125.5, 126.7, 127.2 (2C), 127.7, 127.9, 128.9 (2C), 129.0, 130.9, 132.1, 134.0, 135.1, 135.5, 166.1. All analytical data are in good accordance with those reported in the literature.¹



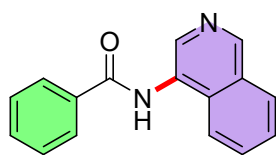
Synthesis of *N*-(naphthalen-1-yl)benzamide (14):

The reaction was carried out according to the general procedure A for 15 h at 110°C using benzamide (122 mg, 1.0 mmol) and 1-iodonaphthalene (254.1 mg, 1.0 mmol). The title compound (168.2 mg, 68% yield) was obtained as a white solid after silica gel column chromatography.¹

White solid; mp 158-160 °C; ¹H NMR (400MHz, CDCl₃) δ 7.43-7.51 (m, 5H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.86-7.95 (m, 5H), 8.39 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 121.1, 121.7, 125.8, 126.1, 126.3, 126.4, 127.3 (2C), 127.8, 128.8, 128.9 (2C), 132.0, 132.5,

134.2, 134.8, 166.6. All analytical data are in good accordance with those reported in the literature.¹

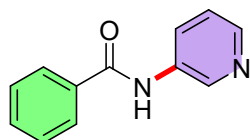
Synthesis of *N*-(quinolin-3-yl)benzamide (15):



The reaction was carried out according to the general procedure A for 15 h at 130°C using benzamide (122 mg, 1.0 mmol) and 4-bromoisoquinoline (184.9 mg, 1.0 mmol). The title compound (186.2 mg, 75% yield) was obtained as a white solid after silica gel column chromatography.⁷

Yellow solid; mp 123-125 °C; ¹H NMR (400MHz, CDCl₃) δ 7.64 (s, 1H), 7.33-7.38 (m, 3H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100MHz, CDCl₃) δ 125.2, 127.4 (2C), 127.6, 127.9, 128.1, 128.6 (2C), 128.7, 132.1, 132.4, 133.2, 134.2, 144.3, 144.5, 167.0. All analytical data are in good accordance with those reported in the literature.⁷

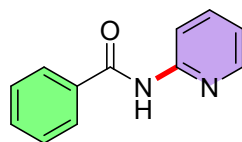
Synthesis of *N*-(pyridin-3-yl)benzamide (16):



The reaction was carried out according to the general procedure A for 15 h at 110°C using benzamide (122 mg, 1.0 mmol) and 3-iodopyridine (205 mg, 1.0 mmol). The title compound (154.6 mg, 78% yield) was obtained as a white solid after silica gel column chromatography.¹

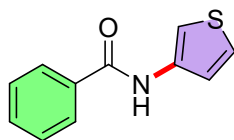
White solid; mp 116-118°C; ¹H NMR (400MHz, CDCl₃) δ 6.58 (s, *J* = 7.4 Hz, 1H), 7.16 (q, *J* = 4.8 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.77-7.81 (m, 3H), 8.49 (d, *J* = 4.8 Hz, 1H), 8.64 (d, *J* = 4.8 Hz, 1H); ¹³C NMR (100MHz, CDCl₃) δ 119.9, 123.8, 126.4 (2C), 127.5 (2C), 130.9, 132.5, 137.7, 146.8, 149.9, 169.0; All analytical data are in good accordance with those reported in the literature.¹

Synthesis of *N*-(pyridin-2-yl)benzamide (17):



The reaction was carried out according to the general procedure A for 15 h at 130°C using benzamide (122 mg, 1.0 mmol) and 2-bromopyridine (105.3 mg, 1.0 mmol). The title compound (99.1 mg, 50% yield) was obtained as a light yellow solid after silica gel column chromatography.⁸

Light yellow solid; mp 114-116°C; ¹H NMR (400MHz, CDCl₃) δ 7.11 (t, *J* = 6.0 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.81 (t, *J* = 7.2 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 2H), 8.27 (s, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 9.20 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 114.8, 120.1, 127.5 (2C), 129.0 (2C), 132.5, 134.1, 139.4, 147.0, 151.6, 166.0. All analytical data are in good accordance with those reported in the literature.⁸



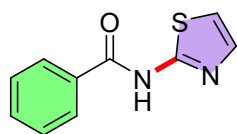
Synthesis of *N*-(thiophen-3-yl)benzamide (18):

The reaction was carried out according to the general procedure A for 15 h at 110°C using benzamide (122 mg, 1.0 mmol) and 3-iodothiophene (210 mg, 1.0 mmol). The title compound (111.7 mg, 55% yield) was obtained as a light yellow solid after silica gel column chromatography.

Light yellow solid; mp 118-120°C; IR (neat, cm⁻¹) ν 3108, 2918, 1710, 1602, 1563, 1460, 1246, 1024. ¹H NMR (400MHz, CDCl₃) δ 7.12 (d, *J* = 5.2 Hz, 1H), 7.27-7.30 (m, 1H), 7.47-7.56 (m, 4H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 8.15 (brs, 1H); ¹³C NMR

(100MHz, CDCl₃) δ 110.9, 121.3, 124.9, 127.1 (2C), 129.0 (2C), 132.1, 134.5, 152.2, 171.4; HRMS (FAB⁺) m/z [M]⁺ Calcd for C₁₁H₉NOS: 203.0405, Found 203.0405.

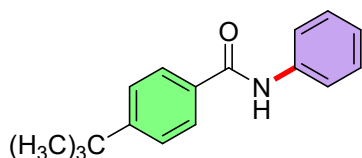
Synthesis of *N*-(thiazol-2-yl)benzamide (19):



The reaction was carried out according to the general procedure A for 15 h at 130°C using benzamide (122 mg, 1.0 mmol) and 2-bromothiazole (164 mg, 1.0 mmol). The title compound (106.2 mg, 52% yield) was obtained as a yellow solid after silica gel column chromatography.

Yellow solid; mp 120-122 °C; IR (neat, cm⁻¹) ν 3103, 2925, 2851, 1707, 1599, 1564, 1461, 1290, 1244, 1021, 1027. ¹H NMR (400MHz, CDCl₃) δ 6.80 (d, J = 5.2 Hz, 1H), 7.40 (d, J = 3.6 Hz, 1H), 7.51-7.57 (m, 2H), 7.67 (d, J = 3.6 Hz, 1H), 8.30 (d, J = 4.8 Hz, 1H), 8.45 (q, J = 8.0, 1.6 Hz, 2H); ¹³C NMR (100MHz, CDCl₃) δ 110.1, 118.7, 123.3, 128.5, 130.0, 132.5, 138.4, 144.0, 156.2, 165.2; HRMS (FAB⁺) m/z [M+Na]⁺ Calcd for C₁₀H₈N₂OSNa: 227.0249, Found 227.0247.

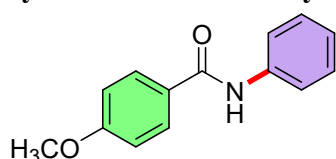
Synthesis of 4-(tert-butyl)-*N*-phenylbenzamide (20):



The reaction was carried out according to the general procedure A for 15 h at 130°C using 4-(tert-butyl)benzamide (177.2 mg, 1.0 mmol) and bromobenzene (157 mg, 1.0 mmol). The title compound (202.7 mg, 80% yield) was obtained as a yellow solid after silica gel column chromatography.

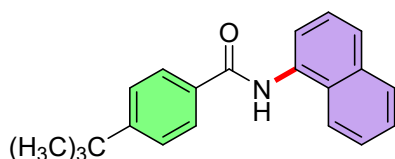
Yellow solid; mp 123-125 °C; IR (neat, cm⁻¹) ν 3099, 2926, 1707, 1601, 1563, 1460, 1245, 1021, 1024. ¹H NMR (400MHz, CDCl₃) δ 1.35 (s, 9H), 7.14 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 7.88 (brs, 1H); ¹³C NMR (100MHz, CDCl₃) δ 31.3 (3C), 35.1, 120.3 (2C), 124.6, 125.9 (2C), 127.0 (2C), 129.2 (2C), 132.2, 138.2, 155.6, 165.9; HRMS (FAB⁺) m/z [M]⁺ Calcd for C₁₇H₁₉NO: 253.1467, Found 253.1467.

Synthesis of 4-methoxy-*N*-phenylbenzamide (21):



The reaction was carried out according to the general procedure A for 15 h at 110°C using benzamide (122 mg, 1.0 mmol) and iodobenzene (204.0 mg, 1.0 mmol). The title compound (154.5 mg, 68% yield) was obtained as a white solid after silica gel column chromatography.⁵

White solid; mp 160-162 °C; ¹H NMR (400MHz, CDCl₃) δ 3.87 (s, 3H), 6.96 (d, J = 8.8 Hz, 2H), 7.14 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 8.4 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.8 Hz, 3H); ¹³C NMR (100MHz, CDCl₃) δ 55.6, 114.1 (2C), 120.3 (2C), 124.5, 127.2, 129.1 (2C), 129.2 (2C), 138.2, 162.6, 165.4. All analytical data are in good accordance with those reported in the literature.⁵

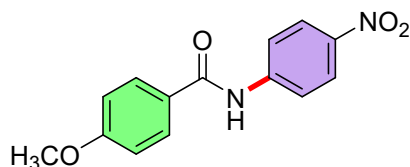


Synthesis of 4-(tert-butyl)-*N*-(naphthalen-1-yl)benzamide (22):

The reaction was carried out according to the general procedure A for 15 h at 130°C using 4-(tert-butyl)benzamide (177.2 mg, 1.0 mmol) and 1-bromonaphthalene (207 mg, 1.0 mmol). The title compound (218.5 mg, 72% yield) was obtained as a yellow solid after silica gel column chromatography.⁹

White solid; mp 110-112 °C; ¹H NMR (400MHz, CDCl₃) δ 1.38 (s, 9H), 7.50-7.56 (m, 5H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.89-7.94 (m, 4H), 8.03 (d, *J* = 6.8 Hz, 1H), 8.25 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 31.3, 35.2 (3C), 120.8, 121.3, 126.0 (2C), 126.1, 126.2, 126.5, 127.2 (2C), 127.6, 129.0, 130.0, 132.1, 132.6, 134.3, 155.7, 166.3. All analytical data are in good accordance with those reported in the literature.⁹

Synthesis of 4-methoxy-*N*-(4-nitrophenyl)benzamide (23):

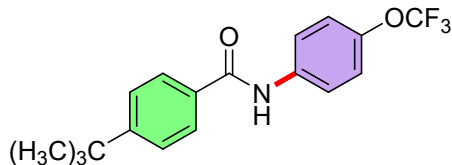


The reaction was carried out according to the general procedure A for 15 h at 130°C using 4-methoxybenzamide (151.2 mg, 1.0 mmol), 1-bromo-4-nitrobenzene (202 mg, 1.0 mmol). The title compound (136.1 mg, 50% yield) was obtained as a yellow solid after silica gel column

chromatography.¹⁰

Yellow solid; mp 210-212 °C; ¹H NMR (400MHz, CDCl₃) δ 3.79 (s, 3H), 6.69 (d, *J* = 8.4 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.21-7.26 (m, 1H), 7.41-7.52 (m, 3H), 7.84 (d, *J* = 7.2 Hz, 2H), 8.07-8.14 (m, 1H); ¹³C NMR (100MHz, CDCl₃) δ 55.7, 114.4 (2C), 119.5 (2C), 125.3 (2C), 126.2, 129.3 (2C), 143.6, 144.2, 163.2, 165.5. All analytical data are in good accordance with

those reported in the literature.¹⁰

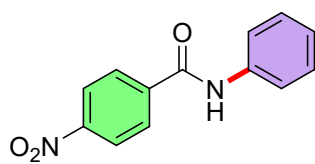


Synthesis of 4-(tert-butyl)-*N*-(4-(trifluoromethoxy)phenyl)benzamide (24):

The reaction was carried out according to the general procedure A for 15 h at 110°C using 4-(tert-butyl)benzamide (177.2 mg, 1.0 mmol), 1-iodo-4-(trifluoromethoxy)benzene (288.0 mg, 1.0 mmol). The title compound (263.1 mg, 78% yield) was obtained as a white solid after silica gel column chromatography.

White solid; mp 122-124°C; IR (neat, cm⁻¹) ν 3308, 2965, 2868, 1644, 1541, 1507, 1416, 1215, 1152, 1021; ¹H NMR (400MHz, CDCl₃) δ 1.30 (s, 9H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.9 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 8.28 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 31.2, 35.1, 119.3, 121.6 (2C), 121.8 (2C), 125.8 (2C), 127.1 (2C), 131.7, 136.9, 145.5, 155.8, 166.2; HRMS (FAB⁺) *m/z* [M+H]⁺ Calcd for C₁₈H₁₉F₃NO₂: 338.1363, Found 338.1363.

Synthesis of 4-nitro-*N*-phenylbenzamide (25):



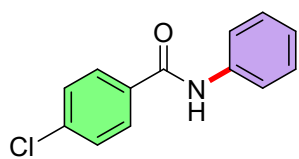
The reaction was carried out according to the general procedure A for 15 h at 110°C using 4-nitrobenzamide (166.1 mg, 1.0 mmol) and iodobenzene (204.0 mg, 1.0 mmol). The title compound (169.6 mg, 70% yield) was obtained as a yellow solid after silica gel column

chromatography.¹¹

Yellow solid; mp 200-202 °C; ¹H NMR (400MHz, CDCl₃) δ 6.52 (d, *J* = 9.2 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.90 (s, 1H), 8.04-8.16 (m, 3H), 8.35 (d, *J* = 8.8 Hz, 1H); ¹³C NMR (100MHz, CDCl₃) δ 116.5,

120.6, 124.2 (2C), 125.5 (2C), 128.4 (2C), 129.4 (2C), 137.3, 140.7, 163.8. All analytical data are in good accordance with those reported in the literature.¹¹

Synthesis of 4-chloro-*N*-phenylbenzamide (26):

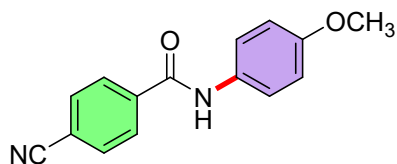


chromatography.¹

The reaction was carried out according to the general procedure A for 15 h at 110°C using 4-chlorobenzamide (155.6 mg, 1.0 mmol) and iodobenzene (204.0 mg, 1.0 mmol). The title compound (185.3 mg, 80% yield) was obtained as a white solid after silica gel column

White solid; mp 187-188°C; ¹H NMR (400MHz, CDCl₃) δ 7.17 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 3H); ¹³C NMR (100MHz, CDCl₃) δ 120.4 (2C), 125.0 (2C), 128.6 (2C), 129.3 (2C), 132.8, 133.5, 137.8, 138.3, 164.8. All analytical data are in good accordance with those reported in the literature.¹

Synthesis of 4-cyano-*N*-(4-methoxyphenyl)benzamide (27):

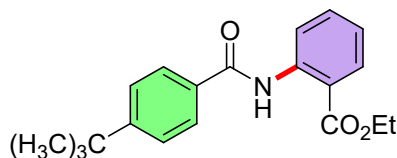


was obtained as a red solid after silica gel column chromatography.¹²

The reaction was carried out according to the general procedure A for 15 h at 130°C using 4-cyanobenzamide (155.6 mg, 1.0 mmol), 1-bromo-4-methoxybenzene (187.0 mg, 1.0 mmol). The title compound (206.9 mg, 82% yield)

Red solid; mp 186-188°C; ¹H NMR (400MHz, CDCl₃) δ 3.81 (s, 3H), 6.89 (d, *J* = 8.9 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 3H); ¹³C NMR (100MHz, CDCl₃) δ 55.7, 114.5, 115.4, 118.1, 122.5, 127.9, 130.4, 132.7, 139.1, 157.2, 164.0. All analytical data are in good accordance with those reported in the literature.¹²

Synthesis of ethyl 2-(4-(tert-butyl)benzamido)benzoate (28):

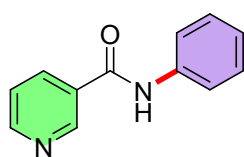


obtained as a yellow solid after silica gel column chromatography.

The reaction was carried out according to the general procedure A for 15 h at 130°C using 4-(tert-butyl)benzamide (177.2 mg, 1.0 mmol), ethyl 2-bromobenzoate (229.1 mg, 1.0 mmol). The title compound (175.7 mg, 54% yield) was

Yellow solid; mp 176-178 °C; IR (neat, cm⁻¹) ν 3125, 3068, 2959, 2857, 1702, 1655, 1604, 1582, 1541, 1507, 1450, 1387, 1330, 1307, 1227, 1130, 1073; ¹H NMR (400MHz, CDCl₃) δ 1.27-1.31 (m, 2H), 1.34 (s, 12H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.64 (td, *J* = 7.6, 0.8 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 8.17 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.95 (d, *J* = 8.4 Hz, 1H), 11.96 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 29.8, 31.3 (3C), 35.1, 60.7, 100.0, 114.7, 120.7, 122.9, 125.9 (2C), 127.4 (2C), 132.0, 135.7, 142.4, 155.9, 166.3, 172.1; HRMS (FAB⁺) *m/z* [M+NH₄]⁺ Calcd for C₂₀H₂₇N₂O₃: 343.2016, Found 343.2014.

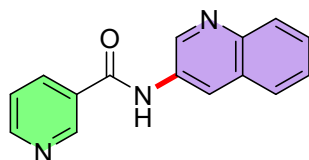
Synthesis of *N*-phenylnicotinamide (29):



The reaction was carried out according to the general procedure A for 15 h at 130°C using nicotinamide (122.1 mg, 1.0 mmol), bromobenzene (157.1 mg, 1.0 mmol). The title compound (101.1 mg, 51% yield) was obtained as a yellow solid after silica gel column chromatography.¹³

Yellow solid; mp 130–132°C; ¹H NMR (400MHz, CDCl₃) δ 7.50 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 3H), 7.62 (t, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 7.6 Hz, 1H), 8.67 (s, 1H), 8.71 (s, 1H), 9.06 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 120.8, 123.9, 125.1 (2C), 129.2 (2C), 131.1, 135.9, 137.7, 147.9, 152.1, 164.2. All analytical data are in good accordance with those reported in the literature.¹³

Synthesis of *N*-(quinolin-3-yl)nicotinamide (30):

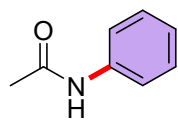


chromatography.¹⁴

The reaction was carried out according to the general procedure A for 15 h at 130°C using nicotinamide (122.1 mg, 1.0 mmol), 3-bromoquinoline (208.1 mg, 1.0 mmol). The title compound (107.2 mg, 43% yield) was obtained as a yellow solid after silica gel column

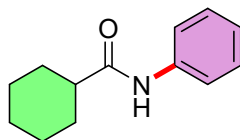
White solid; mp 141-143°C; ¹H NMR (400MHz, CDCl₃) δ 7.51 (t, *J* = 7.2 Hz, 1H), 7.60-7.67 (m, 2H), 7.77-7.85 (m, 2H), 7.93-8.03 (m, 1H), 8.10 (d, *J* = 2.4 Hz, 1H), 8.37 (t, *J* = 8.4 Hz, 1H), 8.86 (d, *J* = 2.4 Hz, 1H), 9.19-9.27 (m, 2H); ¹³C NMR (100MHz, CDCl₃) δ 127.1, 127.6, 127.8, 128.5, 128.6, 128.8, 129.3, 129.8, 133.1, 137.4, 140.1, 145.2, 146.7, 148.3, 149.8. All analytical data are in good accordance with those reported in the literature.¹⁴

Synthesis of *N*-phenylacetamide (31):



The reaction was carried out according to the general procedure A for 15 h at 130°C using acetamide (59.1 mg, 1.0 mmol), bromobenzene (157.1 mg, 1.0 mmol). The title compound (118.9 mg, 88% yield) was obtained as a white solid after silica gel column chromatography.¹⁵

White solid, mp 112-114 °C; ¹H NMR (400MHz, CDCl₃) δ 2.72 (s, 3H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.29-7.35 (m, 3H), 7.49 (d, *J* = 7.6 Hz, 2H); ¹³C NMR (100MHz, CDCl₃) δ 24.6, 120.0 (2C), 124.5, 129.1 (2C), 138.0, 168.5. All analytical data are in good accordance with those reported in the literature.¹⁵

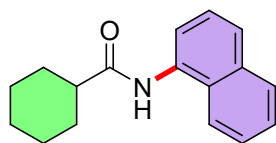


Synthesis of *N*-phenylcyclohexanecarboxamide (32):

The reaction was carried out according to the general procedure A for 15 h at 130°C using cyclohexanecarboxamide (127.2 mg, 1.0 mmol), bromobenzene (157.1 mg, 1.0 mmol). The title compound (162.6 mg, 80% yield) was obtained as a white solid after silica gel column chromatography.¹⁶

White solid; mp 120-122 °C; ¹H NMR (400MHz, CDCl₃) δ 1.43-1.58 (m, 3H), 1.65-1.75 (m, 2H), 1.82 (d, *J* = 11.6 Hz, 2H), 1.95 (d, *J* = 12.4 Hz, 2H), 2.18-2.26 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.24 (s, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100MHz, CDCl₃) δ 25.8 (2C), 29.7 (2C), 29.8, 46.7, 119.9 (2C), 124.2, 129.1 (2C), 138.2, 174.6. All analytical data are in good accordance with those reported in the literature.¹⁶

Synthesis of *N*-(naphthalen-1-yl)cyclohexanecarboxamide (33):

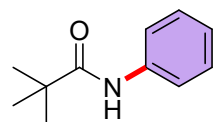


chromatography.¹⁷

The reaction was carried out according to the general procedure A for 15 h at 110°C using cyclohexanecarboxamide (127.2 mg, 1.0 mmol), 1-iodonaphthalene (254.1 mg, 1.0 mmol). The title compound (192.5 mg, 76% yield) was obtained as a white solid after silica gel column

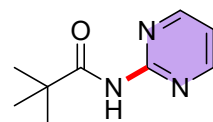
White solid; mp 130-132°C; ¹H NMR (400MHz, CDCl₃) δ 1.26-1.39 (m, 4H), 1.60 (q, *J* = 12.0 Hz, 2H), 1.85 (d, *J* = 10.8 Hz, 2H), 2.05 (d, *J* = 7.6 Hz, 2H), 2.38 (t, *J* = 11.6 Hz, 1H), 7.40-7.49 (m, 3H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.80-7.88 (m, 3H); ¹³C NMR (100MHz, CDCl₃) δ 25.8 (2C), 29.8, 30.0 (2C), 46.4, 120.8, 121.3, 125.7, 125.8, 126.0, 126.3, 127.4, 128.8, 132.4, 134.2, 175.1. All analytical data are in good accordance with those reported in the literature.¹⁷

Synthesis of *N*-phenylpivalamide (34):



The reaction was carried out according to the general procedure A for 15 h at 130°C using pivalamide (101.2 mg, 1.0 mmol), bromobenzene (157.1 mg, 1.0 mmol). The title compound (152.4 mg, 86% yield) was obtained as a white solid after silica gel column chromatography.¹⁸

White solid; mp 126-128 °C; ¹H NMR (400MHz, CDCl₃) δ 1.32 (s, 9H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 8.4 Hz, 3H), 7.52 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100MHz, CDCl₃) δ 27.8, 39.7 (3C), 120.1 (2C), 124.3, 129.0 (2C), 138.1, 176.7. All analytical data are in good accordance with those reported in the literature.¹⁸

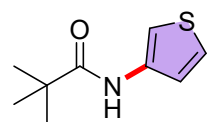


Synthesis of *N*-(pyrimidin-2-yl)pivalamide (35):

The reaction was carried out according to the general procedure A for 15 h at 130°C using pivalamide (101.2 mg, 1.0 mmol), 2-bromopyrimidine (159.0 mg, 1.0 mmol). The title compound (168.5 mg, 94% yield) was obtained as a white solid after silica gel column chromatography.¹⁹

White solid; mp 132-134 °C; ¹H NMR (400MHz, CDCl₃) δ 1.31 (s, 9H), 7.00 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.22 (q, *J* = 3.8 Hz, 1H), 7.61 (dd, *J* = 3.3, 1.1 Hz, 2H); ¹³C NMR (100MHz, CDCl₃) δ 21.3 (3C), 42.7, 110.9, 158.0 (2C), 162.8, 175.9. All analytical data are in good accordance with those reported in the literature.¹⁹

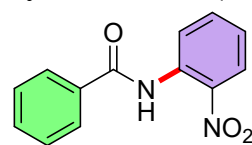
Synthesis of *N*-(thiophen-3-yl)pivalamide (36):



The reaction was carried out according to the general procedure A for 15 h at 110°C using 4-chlorobenzamide (155.6 mg, 1.0 mmol) and 3-iodothiophene (210.0 mg, 1.0 mmol). The title compound (155.8 mg, 85% yield) was obtained as a white solid after silica gel column chromatography.

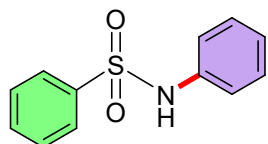
White solid; mp 152-154°C; IR (neat, cm⁻¹) ν 3343, 2954, 2919, 2868, 1650, 1519, 1485, 1364, 1198, 1141; ¹H NMR (400MHz, CDCl₃) δ 1.30 (s, 9H), 6.99 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.22 (q, *J* = 3.6 Hz, 1H), 7.61 (dd, *J* = 3.2, 1.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 27.8 (3C), 39.4, 110.2, 121.2, 124.5, 135.8, 176.1; HRMS (FAB⁺) *m/z* [M+H]⁺ Calcd for C₉H₁₄NOS: 184.0791, Found 184.0791.

Synthesis of *N*-(2-nitrophenyl)benzamide (37):



The reaction was carried out according to the general procedure A for 15 h at 130°C using benzamide (122 mg, 1.0 mmol), 1-chloro-2-nitrobenzene (236.4 mg, 1.5 mmol). The title compound (193.8 mg, 80% yield) was obtained as a yellow solid after silica gel column chromatography.²⁰

Yellow solid; mp 182-184 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.07 (d, *J* = 8.4 Hz, 2H), 7.33 (td, *J* = 8.0, 0.8 Hz, 3H), 7.61 (td, *J* = 7.2, 0.8 Hz, 3H), 8.05 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100



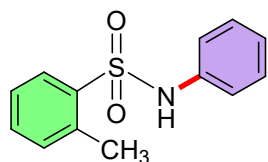
MHz, CDCl₃) δ 123.7, 125.6, 126.8, 127.2 (2C), 128.8 (2C), 130.0, 130.6, 131.9, 134.9, 135.8, 165.9. All analytical data are in good accordance with those reported in the literature.²⁰

Synthesis of *N*-phenylbenzenesulfonamide (38):

The reaction was carried out according to the general procedure A for 15 h at 130°C using benzenesulfonamide (157 mg, 1.0 mmol), bromobenzene (236 mg, 1.5 mmol). The title compound (142.3 mg, 61% yield) was obtained as a yellow solid after silica gel column chromatography.²¹

Yellow solid; mp 110-112 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.0-7.05 (m, 3H), 7.08 (s, 1H), 7.14-7.19 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.44-7.97 (m, 1H), 7.71 (d, *J* = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 122.0 (2C), 125.7, 127.3 (2C), 129.2 (2C), 129.5 (2C), 133.2, 136.4, 139.1. All analytical data are in good accordance with those reported in the literature.²¹

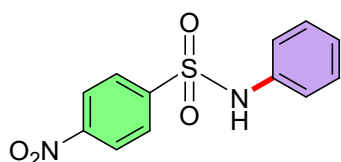
Synthesis of 2-methyl-*N*-phenylbenzenesulfonamide (39):



The reaction was carried out according to the general procedure A for 15 h at 130°C using 2-methylbenzenesulfonamide (171 mg, 1.0 mmol), bromobenzene (236 mg, 1.5 mmol). The title compound (103.9 mg, 42% yield) was obtained as a yellow solid after silica gel column chromatography.²¹

Yellow solid; mp 116-118 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.58 (s, 3H), 6.94-6.99 (m, 4H), 7.12-7.14 (m, 2H), 7.18 (q, *J* = 3.6 Hz, 2H), 7.34-7.36 (m, 1H), 7.90 (d, *J* = 4.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 20.5, 120.7, 125.1, 126.4, 129.5 (2C), 130.1, 132.7 (2C), 133.3, 136.6, 137.3, 137.5. All analytical data are in good accordance with those reported in the literature.²¹

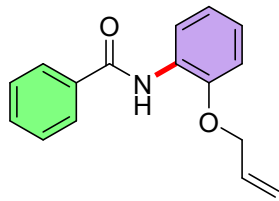
Synthesis of 4-nitro-*N*-phenylbenzenesulfonamide (40):



The reaction was carried out according to the general procedure A for 15 h at 130°C using 4-nitrobenzenesulfonamide (202 mg, 1.0 mmol), bromobenzene (236 mg, 1.5 mmol). The title compound (136.4 mg, 49% yield) was obtained as a yellow solid after silica gel column chromatography.²²

Yellow solid; mp 132-134 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.14 (d, *J* = 8.4 Hz, 2H), 7.36 (q, *J* = 1.2 Hz, 4H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 8.06 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 113.8 (2C), 122.1 (2C), 124.8, 126.4 (2C), 129.9 (2C), 139.6, 139.9, 150.3. All analytical data are in good accordance with those reported in the literature.²²

Synthesis of *N*-(2-(allyloxy)phenyl)benzamide (41):

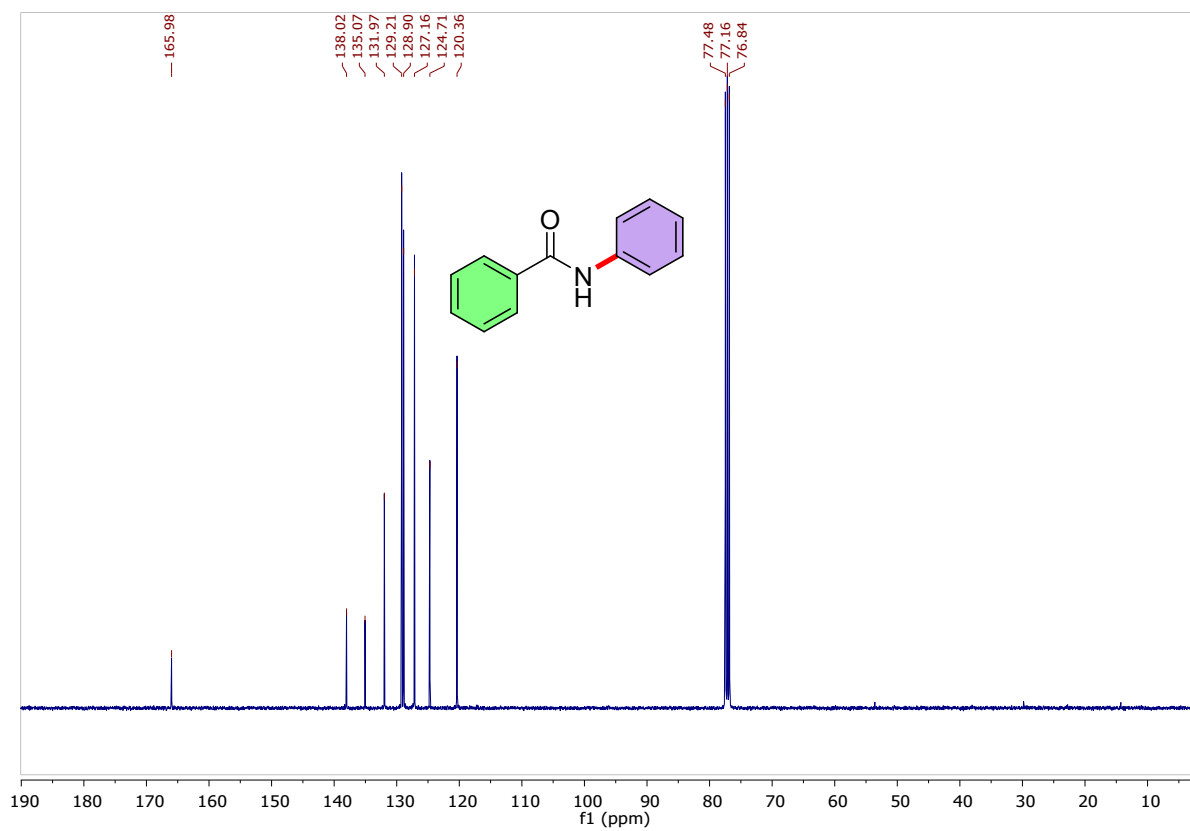
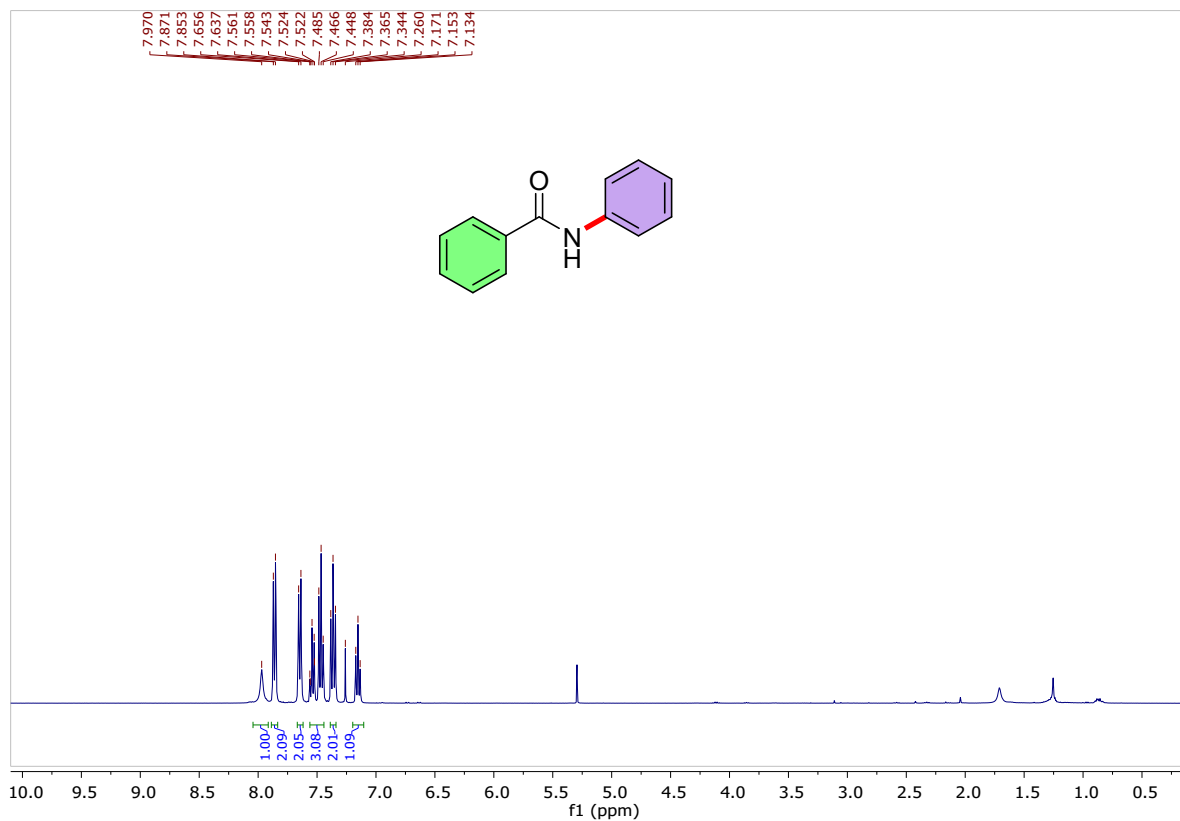


The reaction was carried out according to the general procedure A for 15 h at 130°C using benzamide (122 mg, 1.0 mmol), 1-(allyloxy)-2-bromobenzene (213.1 mg, 1.0 mmol). The title compound (164.6 mg, 65% yield) was obtained as a yellow liquid after silica gel column chromatography.

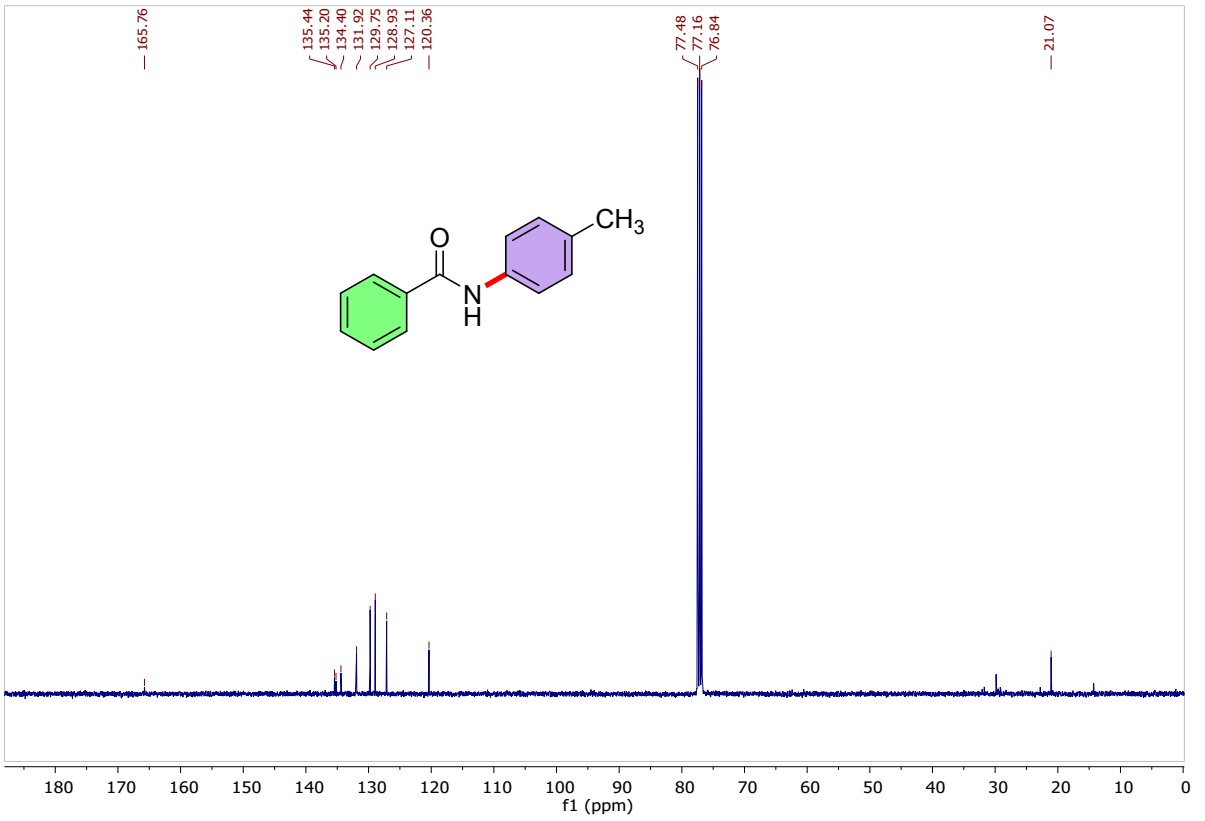
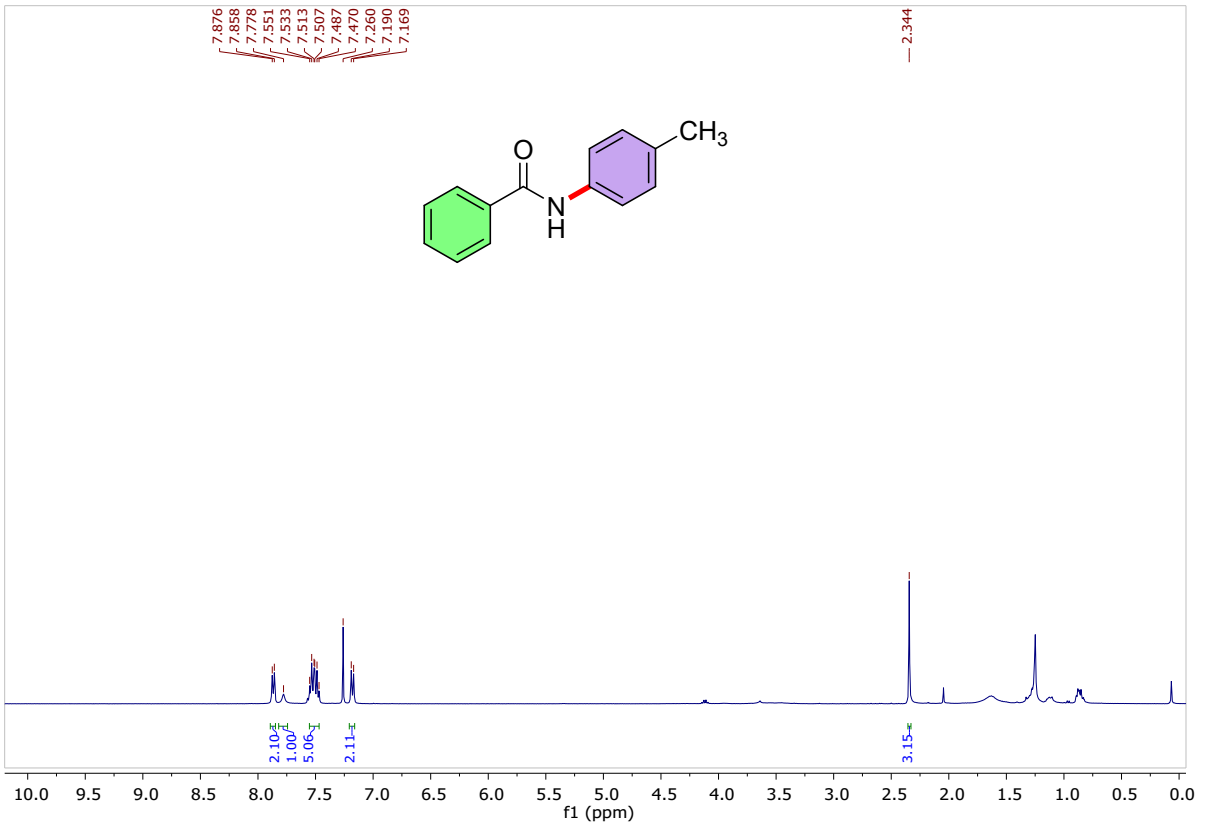
Yellow liquid; ¹H NMR (400MHz, CDCl₃) δ 4.65 (t, *J* = 3.4 Hz, 2H), 5.34 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.43 (dd, *J* = 17.2, 1.6 Hz, 1H), 6.05-6.14 (m, 1H), 6.93 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.05 (td, *J* = 7.6, 2.0 Hz, 1H), 7.48-7.56 (m, 4H), 7.86-7.91 (m, 2H), 8.55 (dd, *J* = 7.6, 2.0 Hz,

1H), 8.63 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 69.7, 111.6, 118.3, 120.1, 121.7, 123.9, 125.7, 127.1 (2C), 128.9 (2C), 131.9, 132.9, 135.4, 147.3, 165.3; HRMS (FAB^+) m/z $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_2$: 253.1103, Found 253.1103.

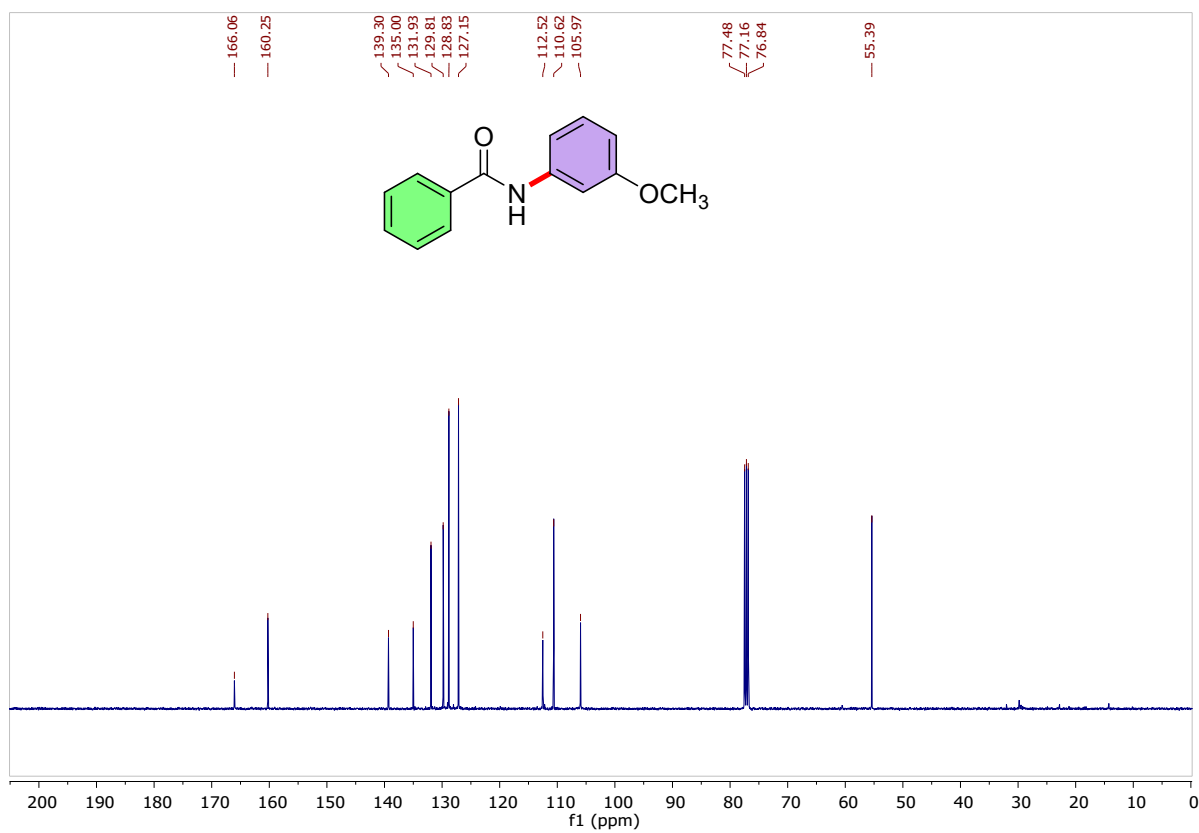
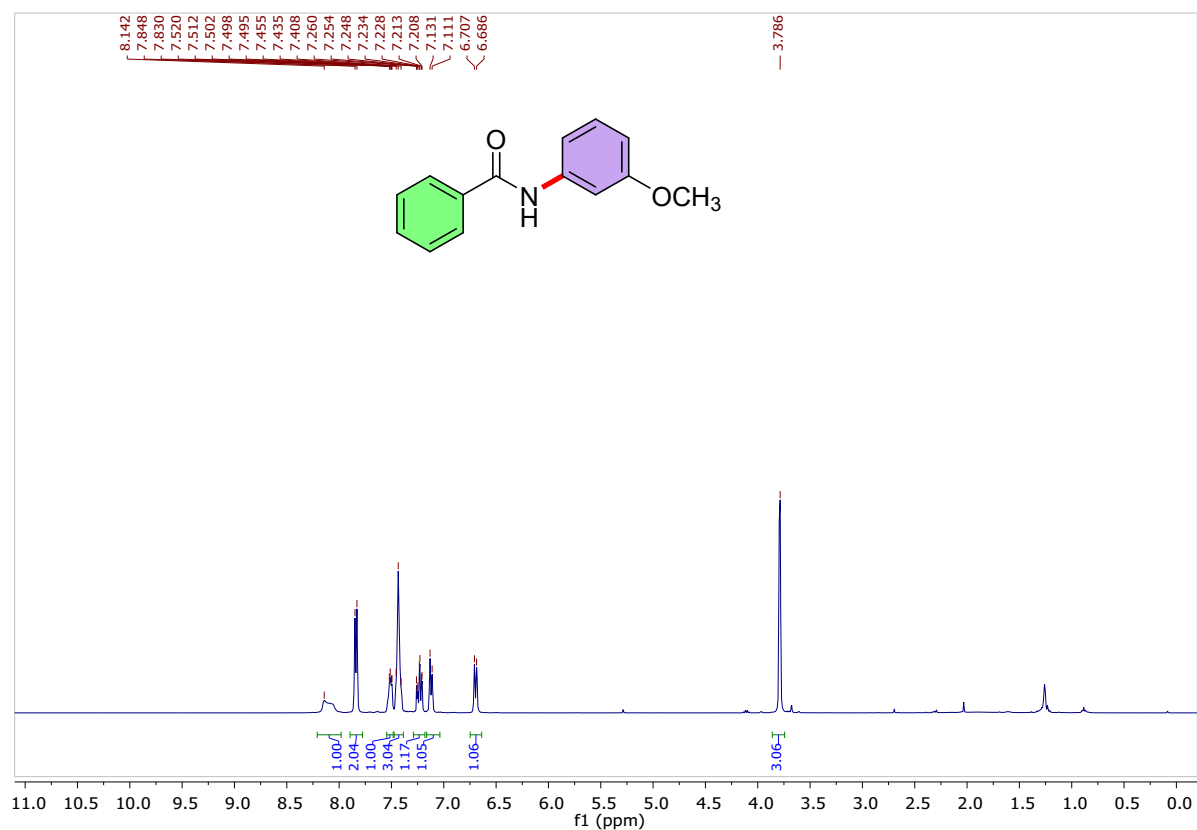
6. ^1H and ^{13}C NMR Spectra
***N*-phenylbenzamide (1)**



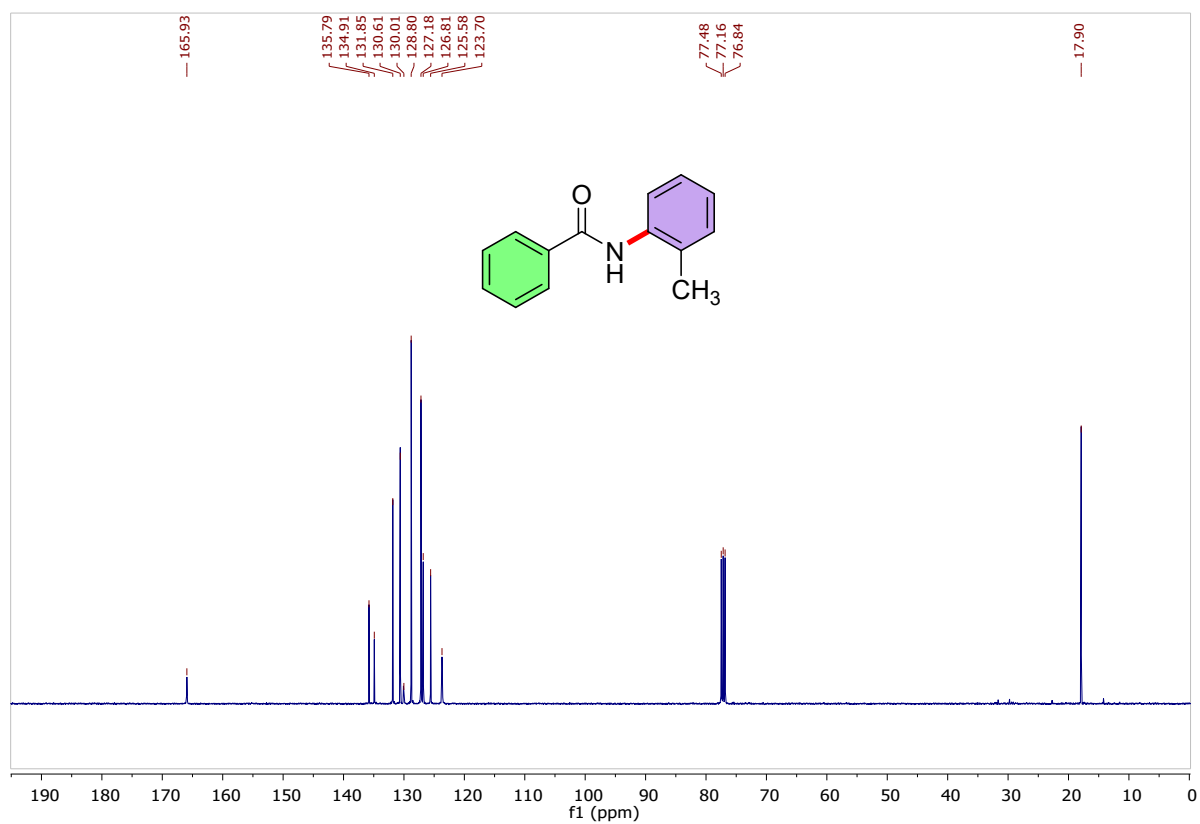
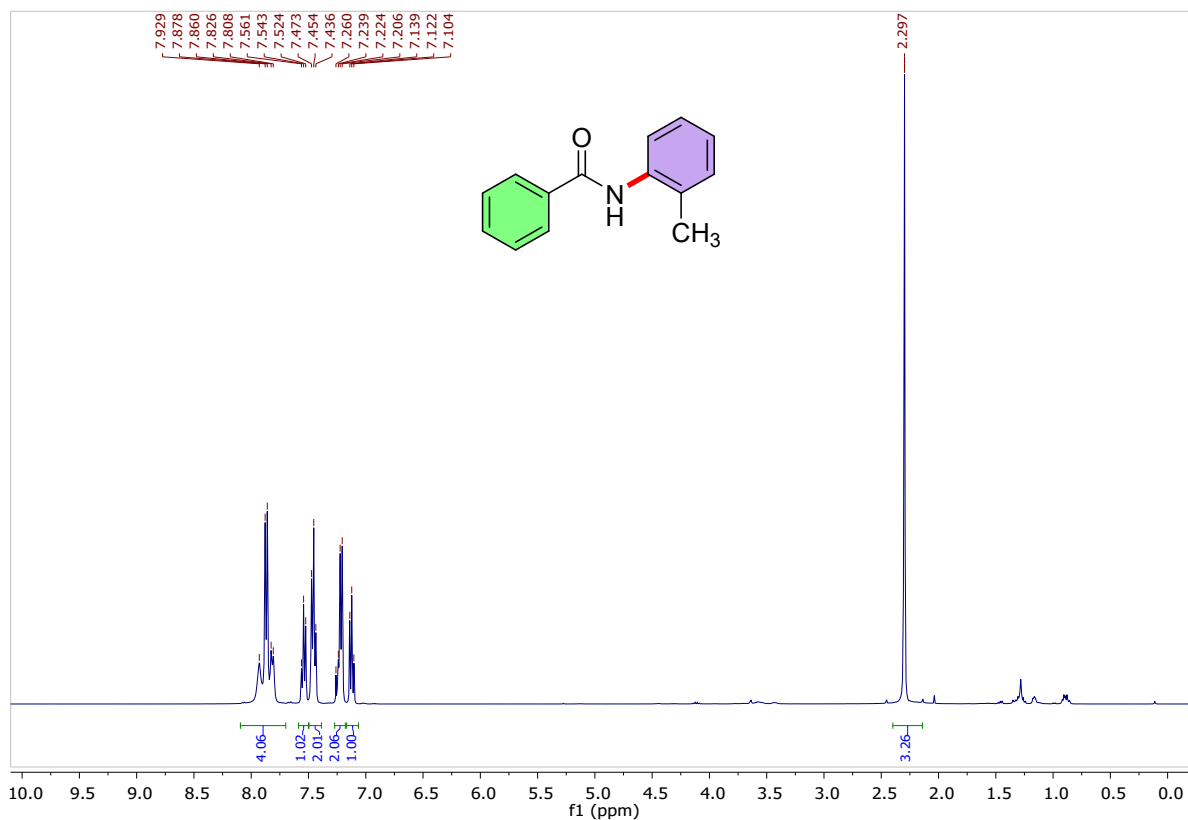
***N*-(*p*-tolyl)benzamide (2)**



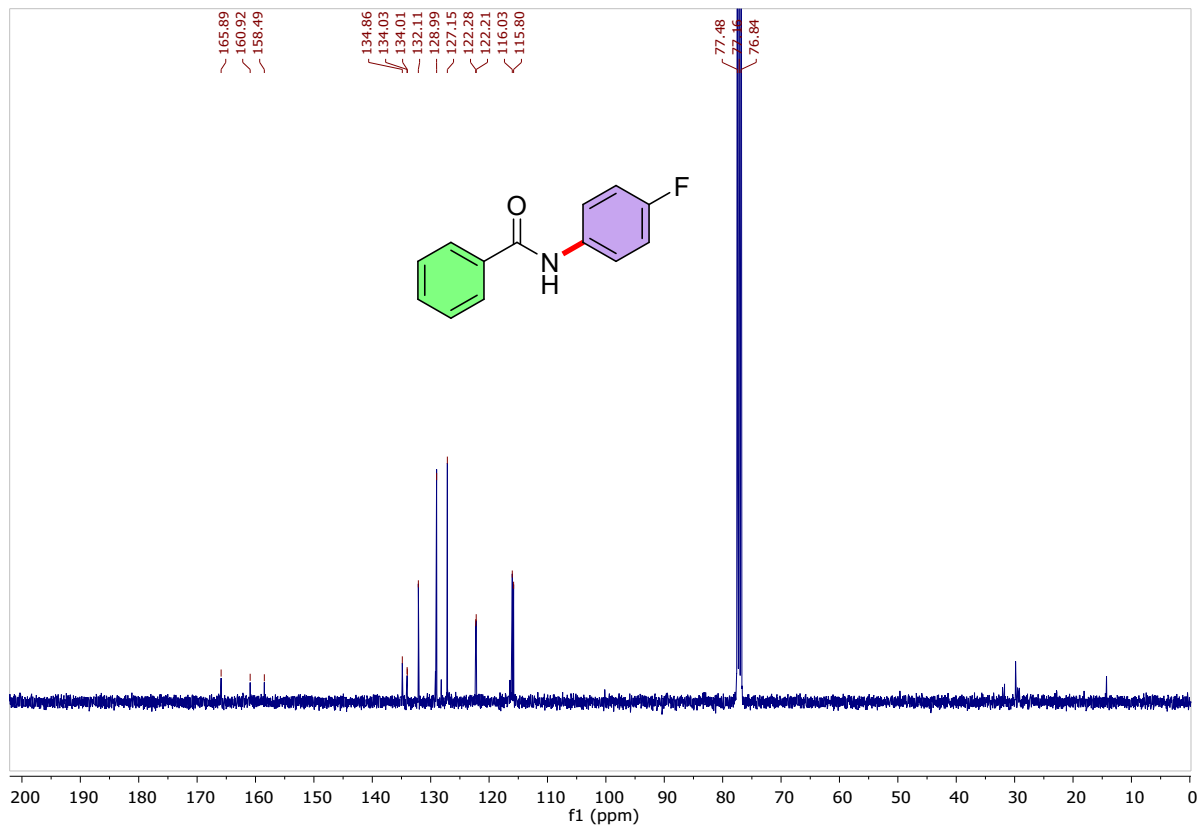
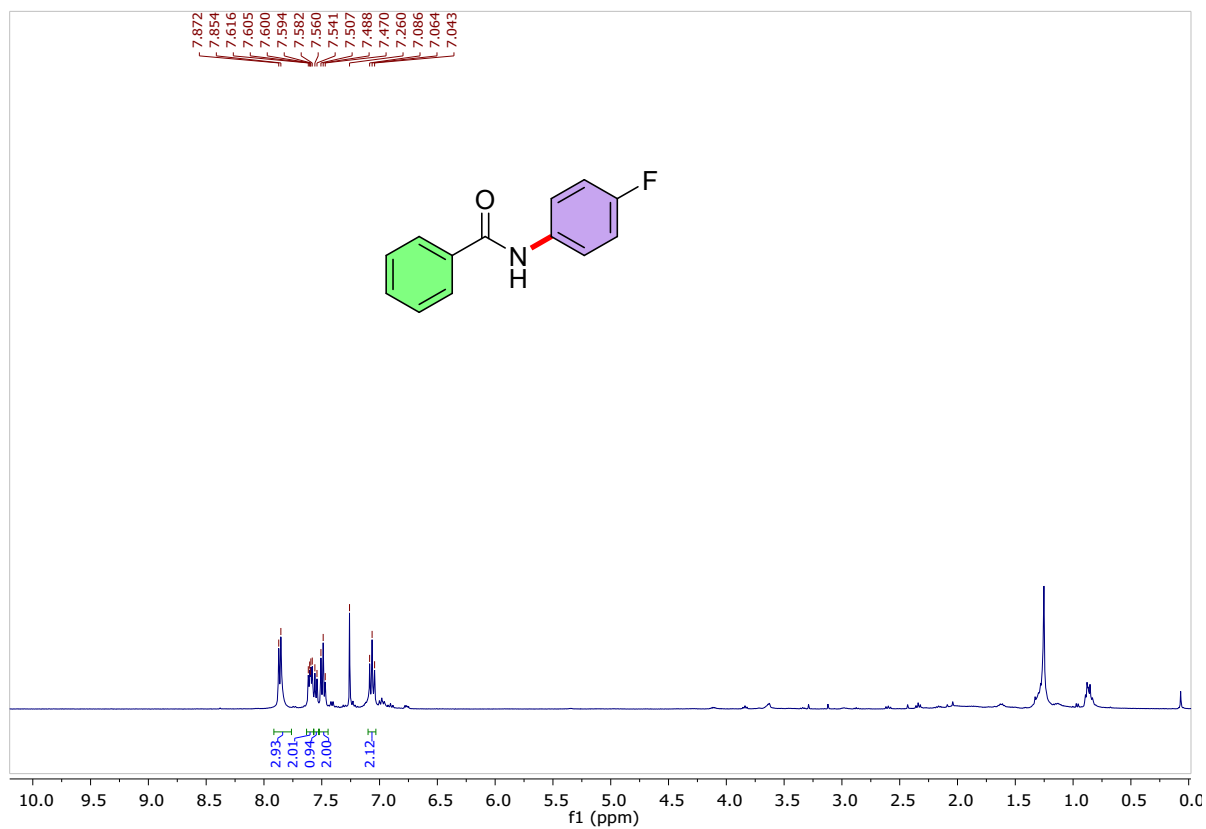
N-(3-methoxyphenyl)benzamide (3)



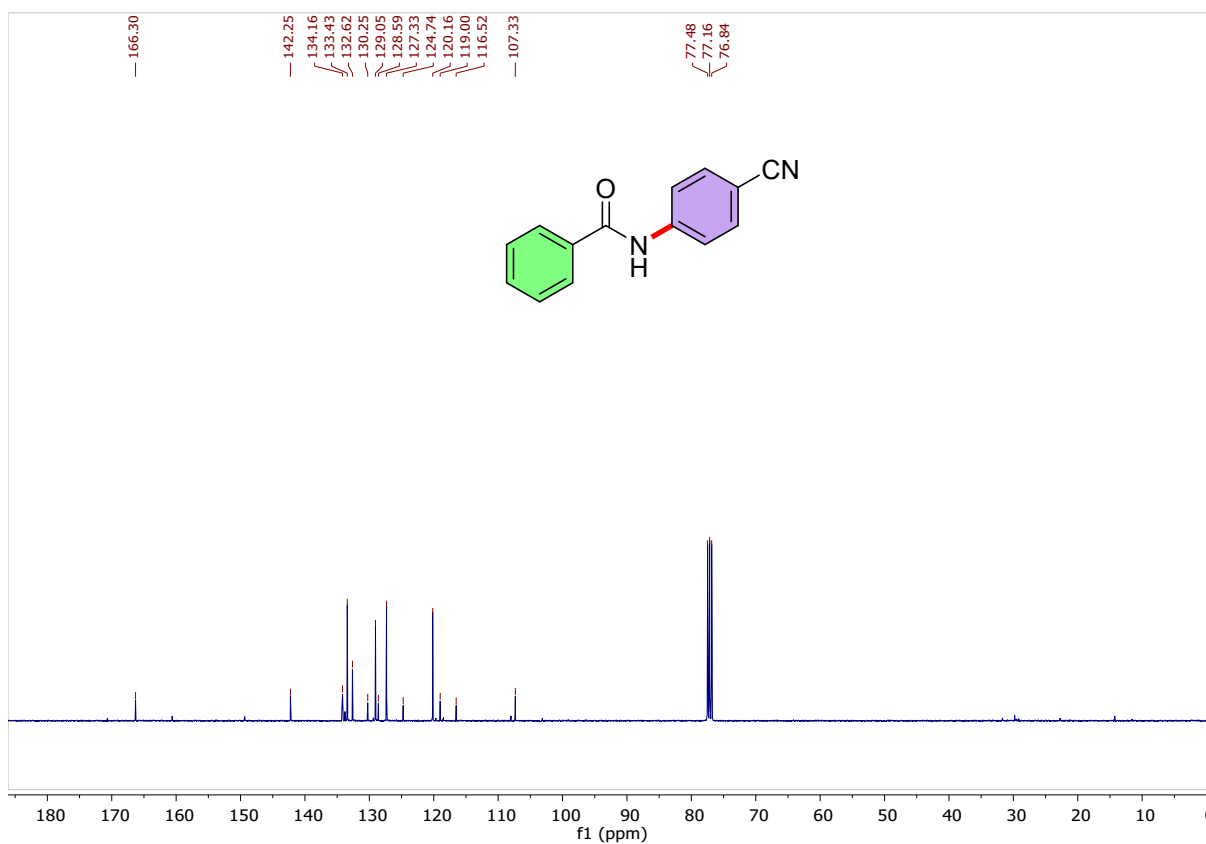
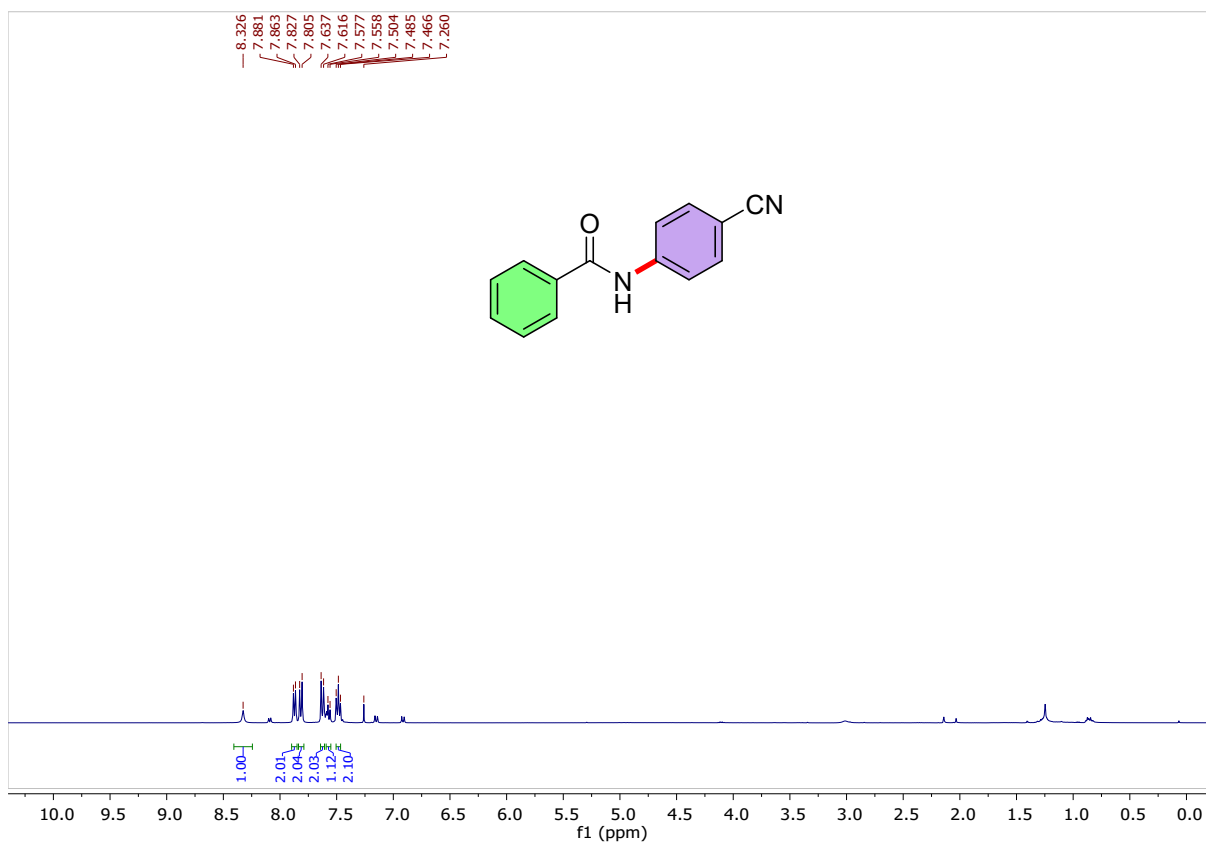
N-(*o*-tolyl)benzamide (4)



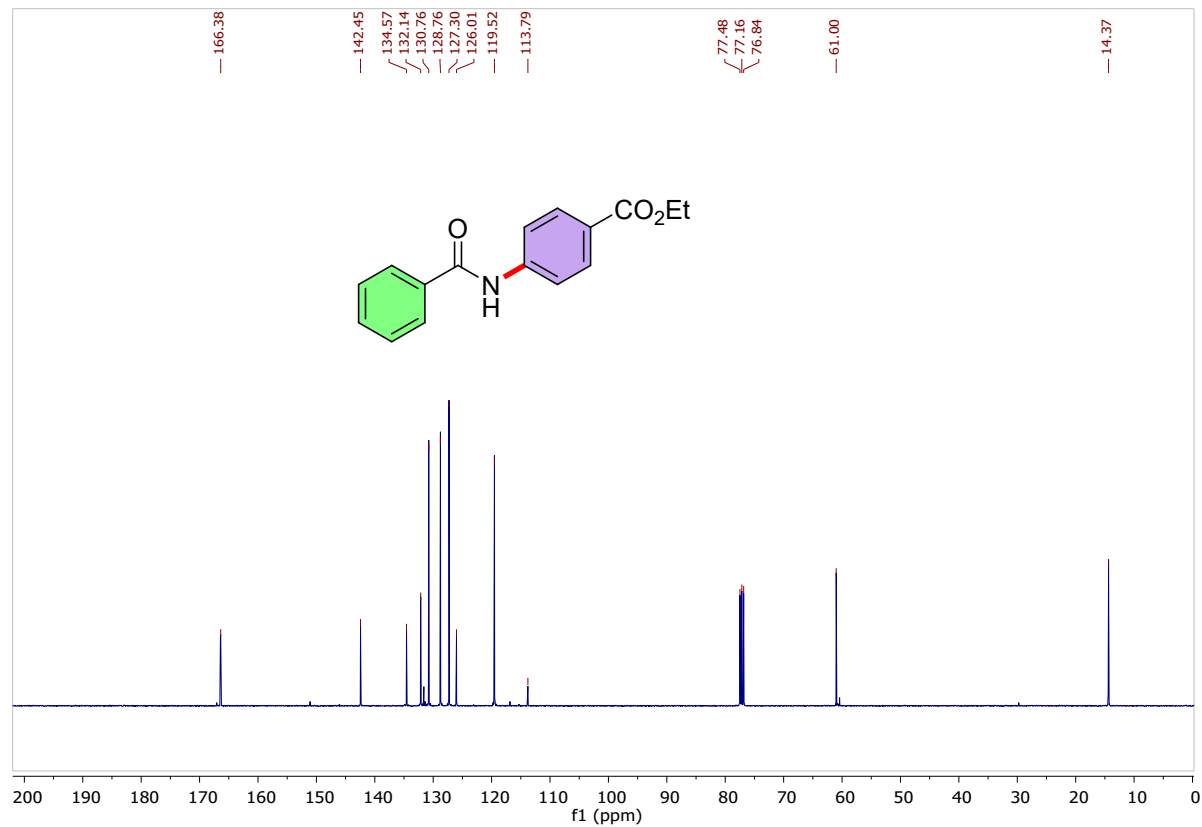
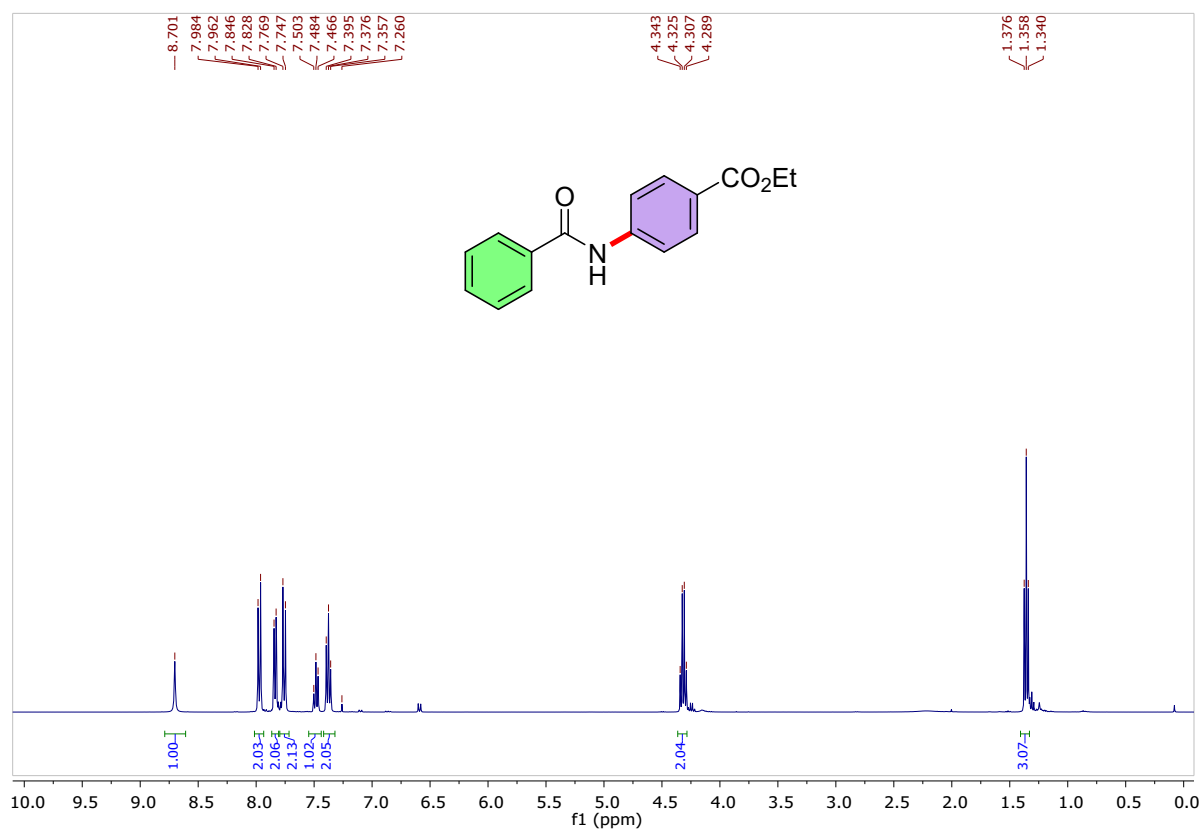
N-(4-fluorophenyl)benzamide (5)



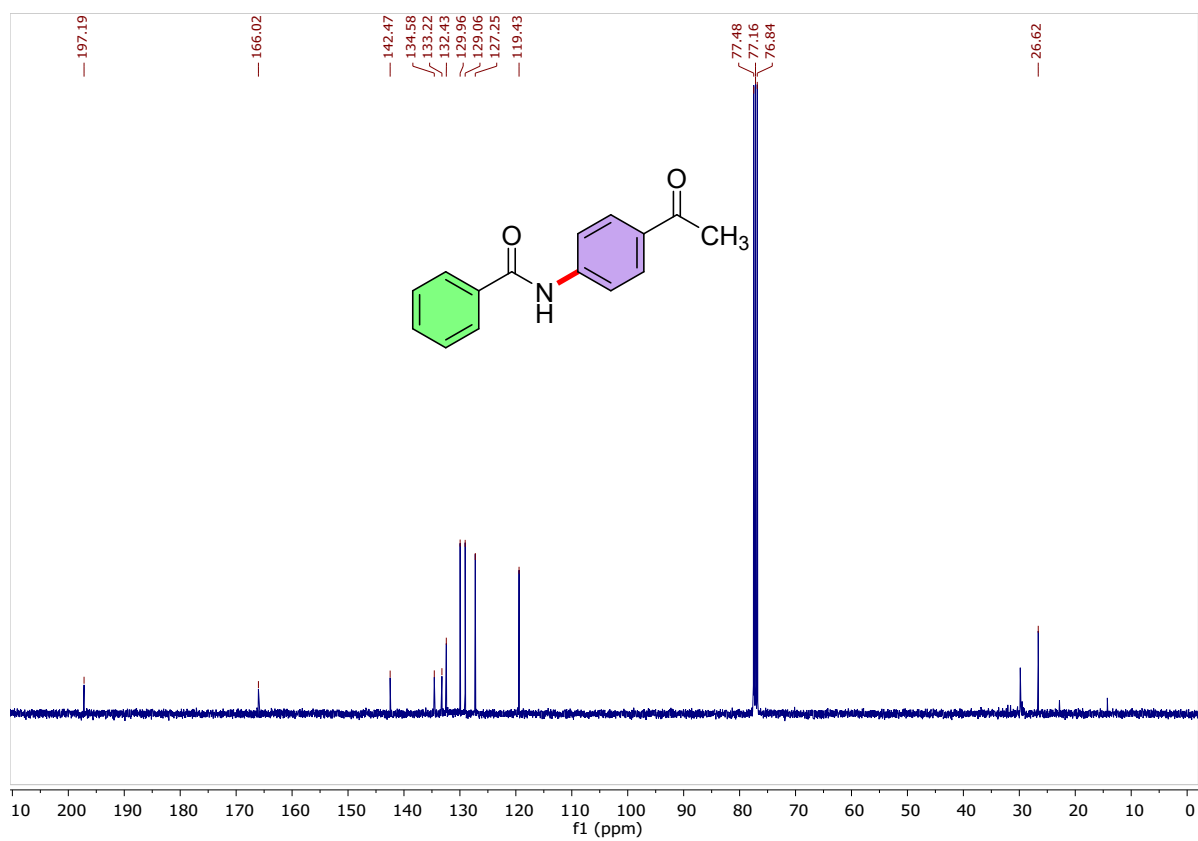
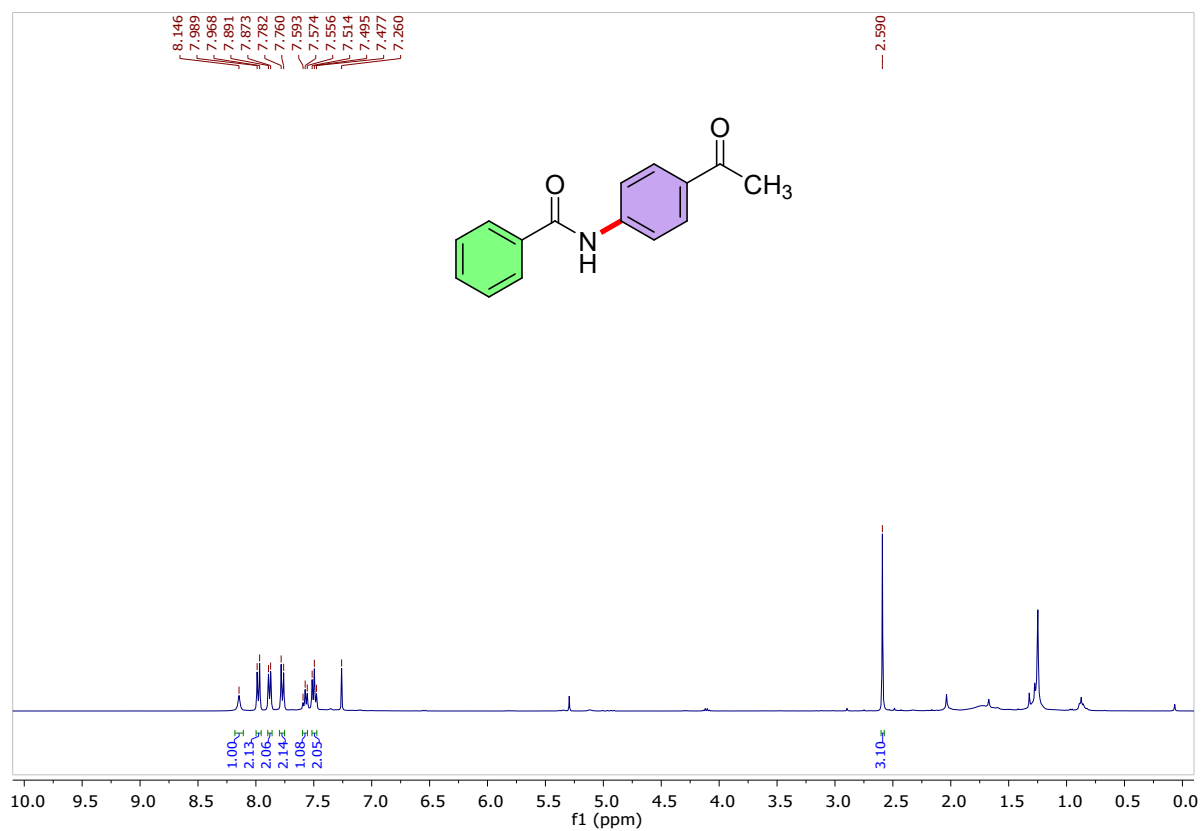
N-(4-cyanophenyl)benzamide (6)



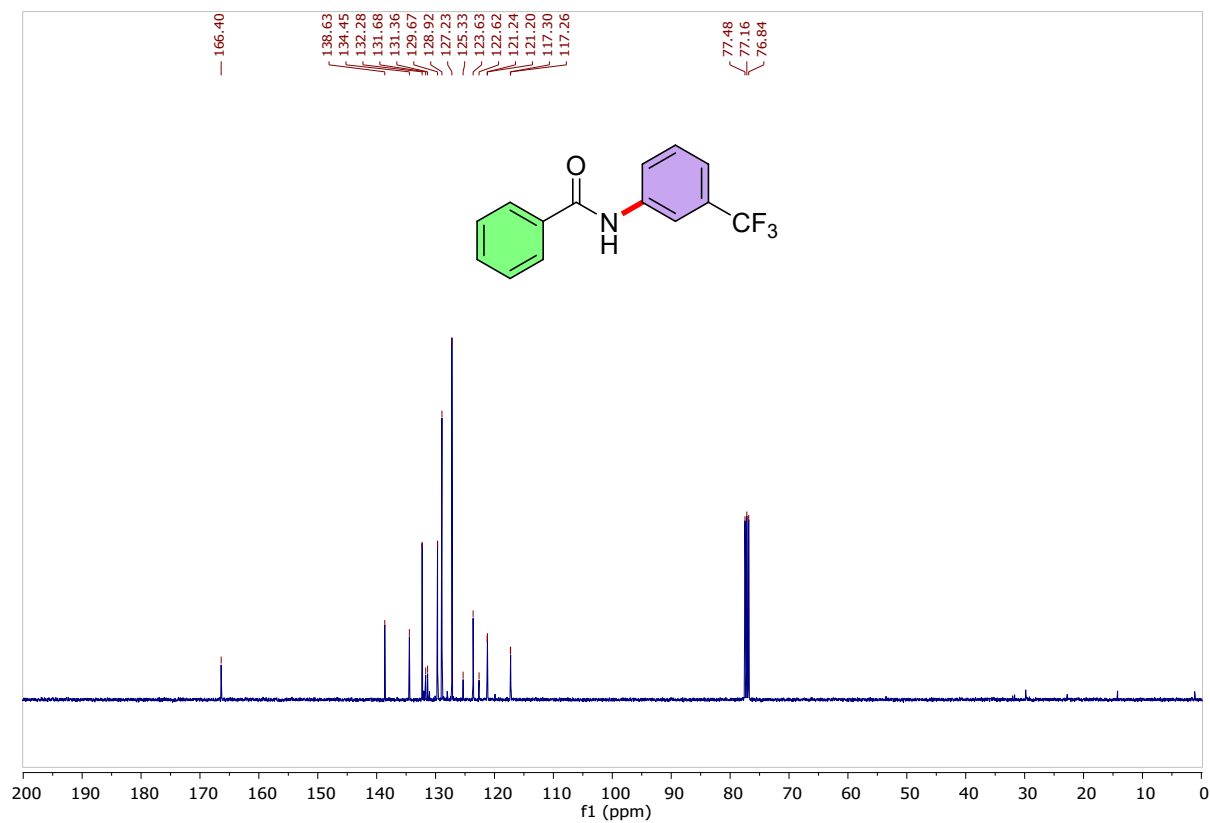
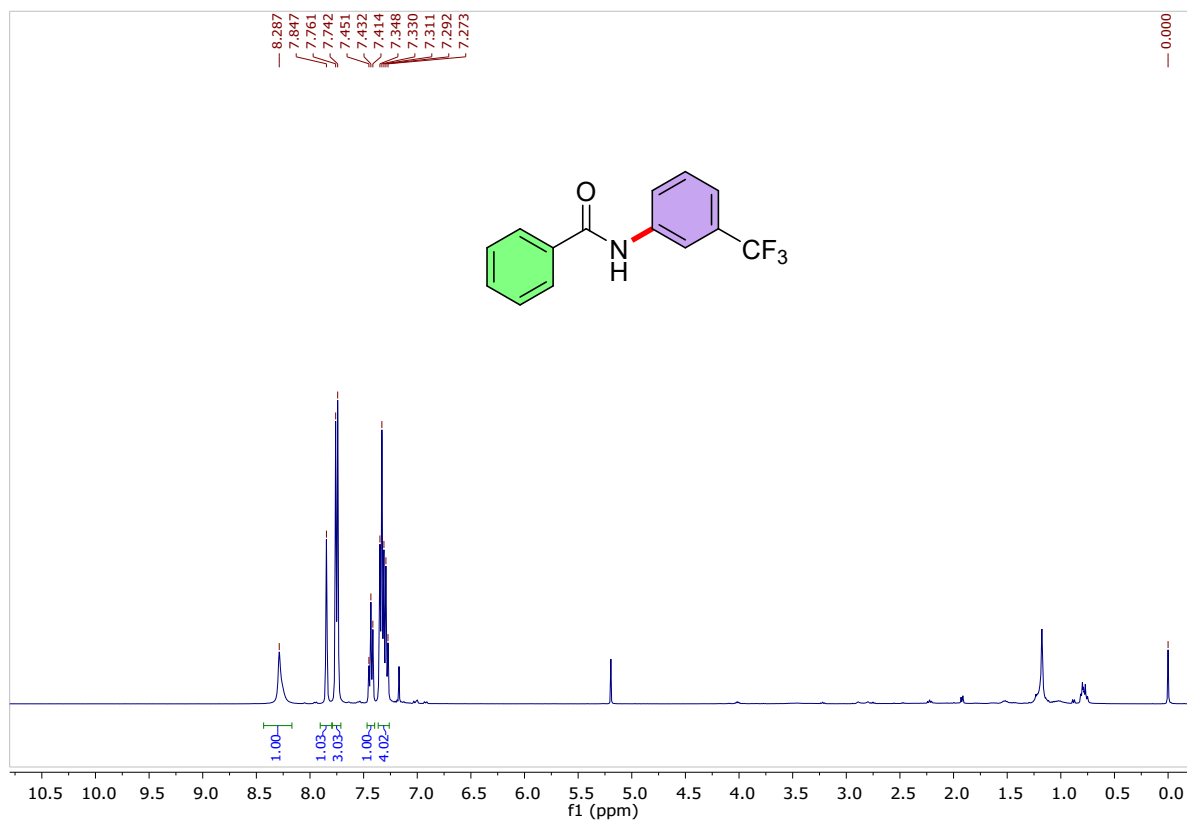
ethyl 4-benzamidobenzoate (7)



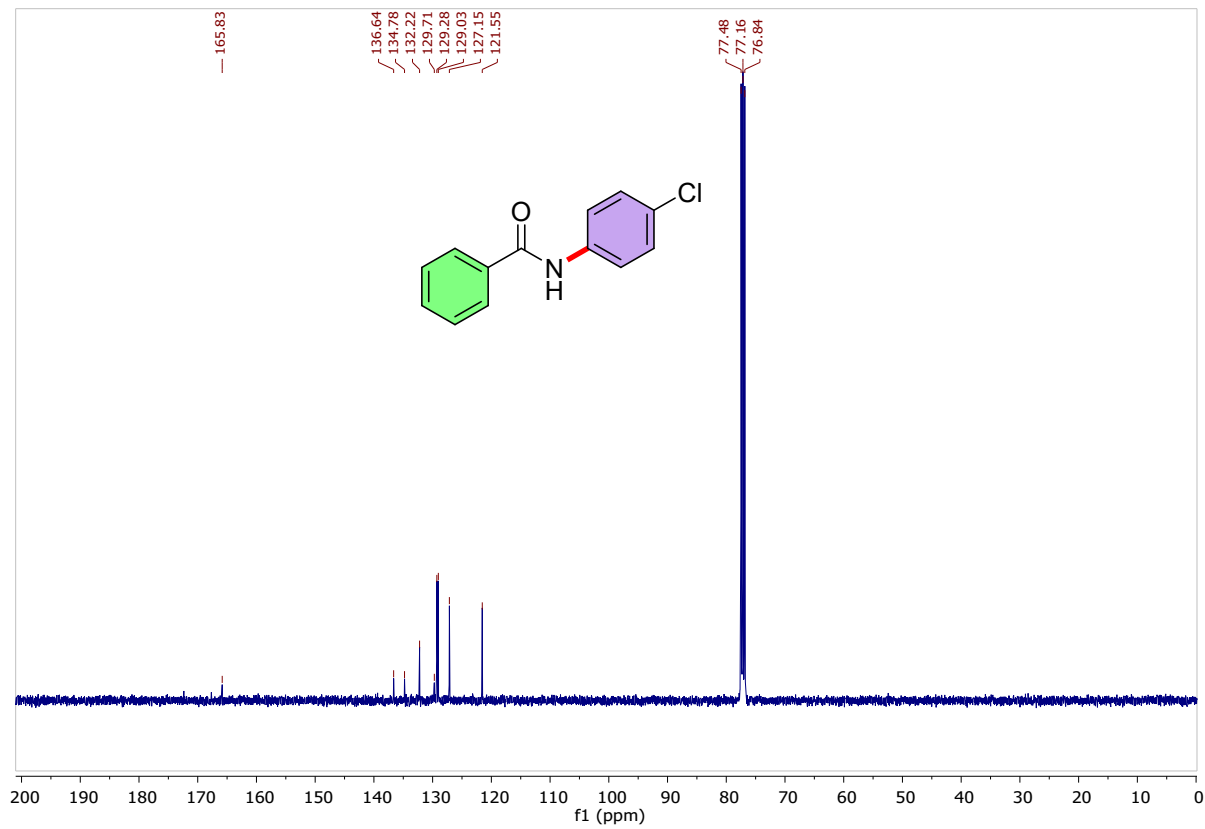
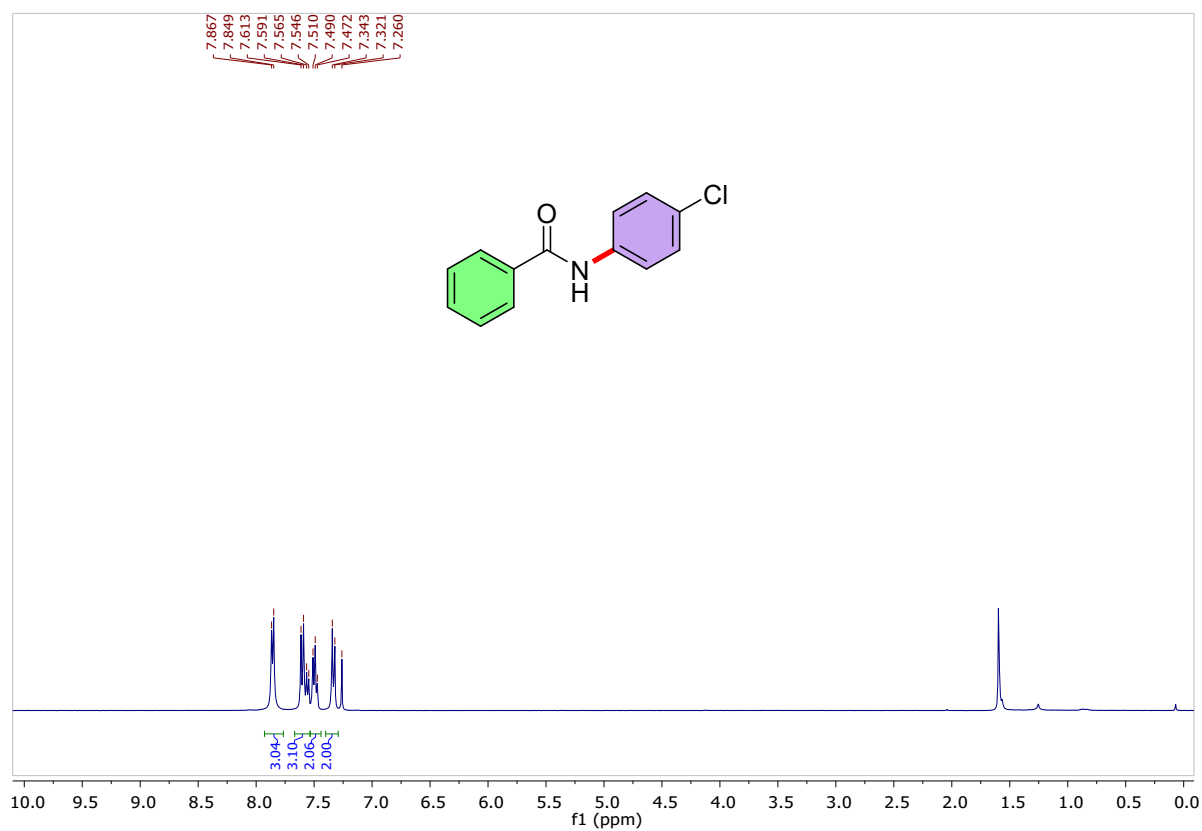
N-(4-acetylphenyl)benzamide (8)



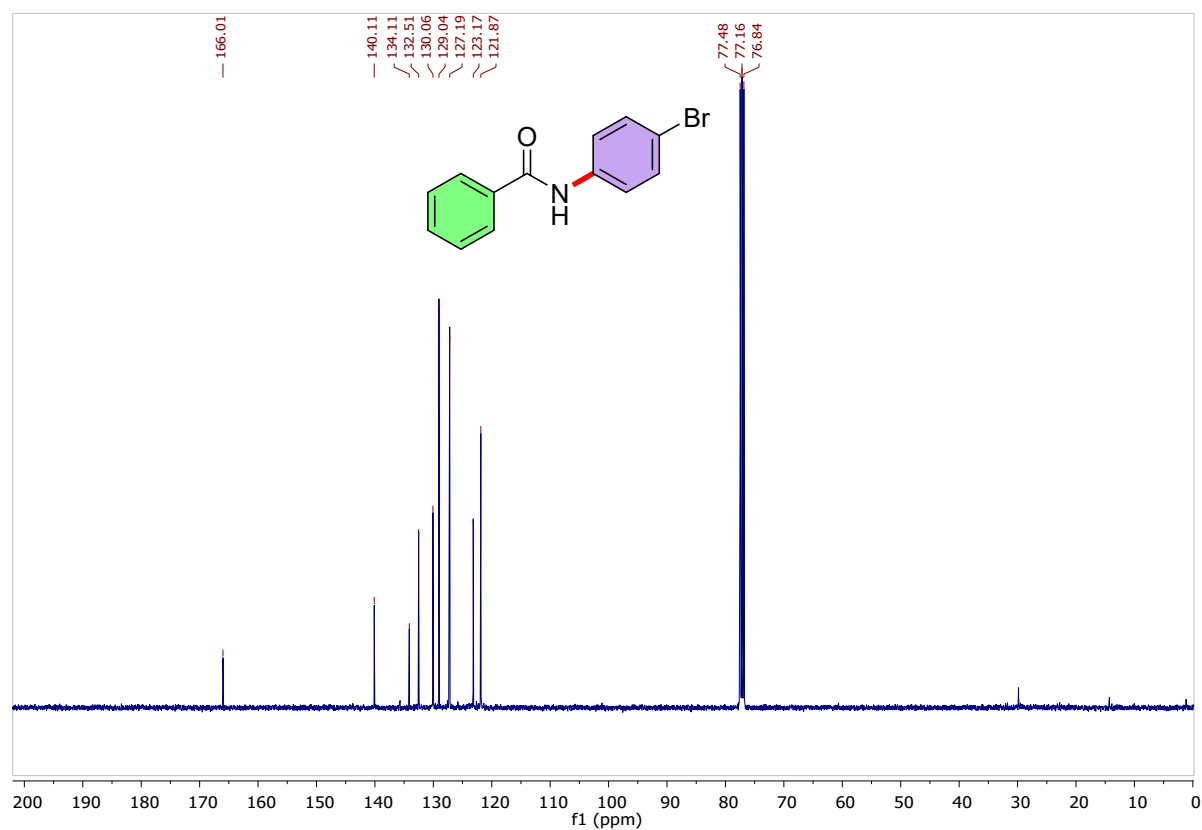
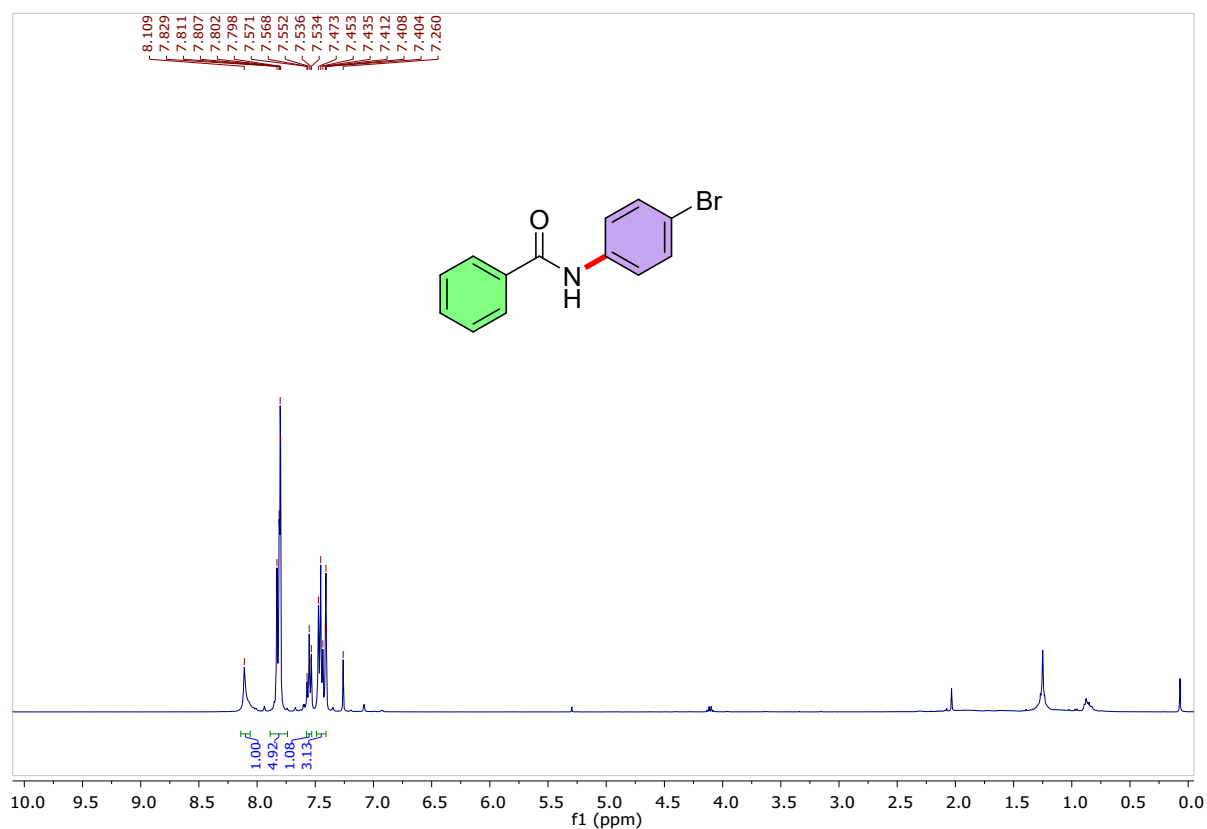
N-(3-(trifluoromethyl)phenyl)benzamide (9)



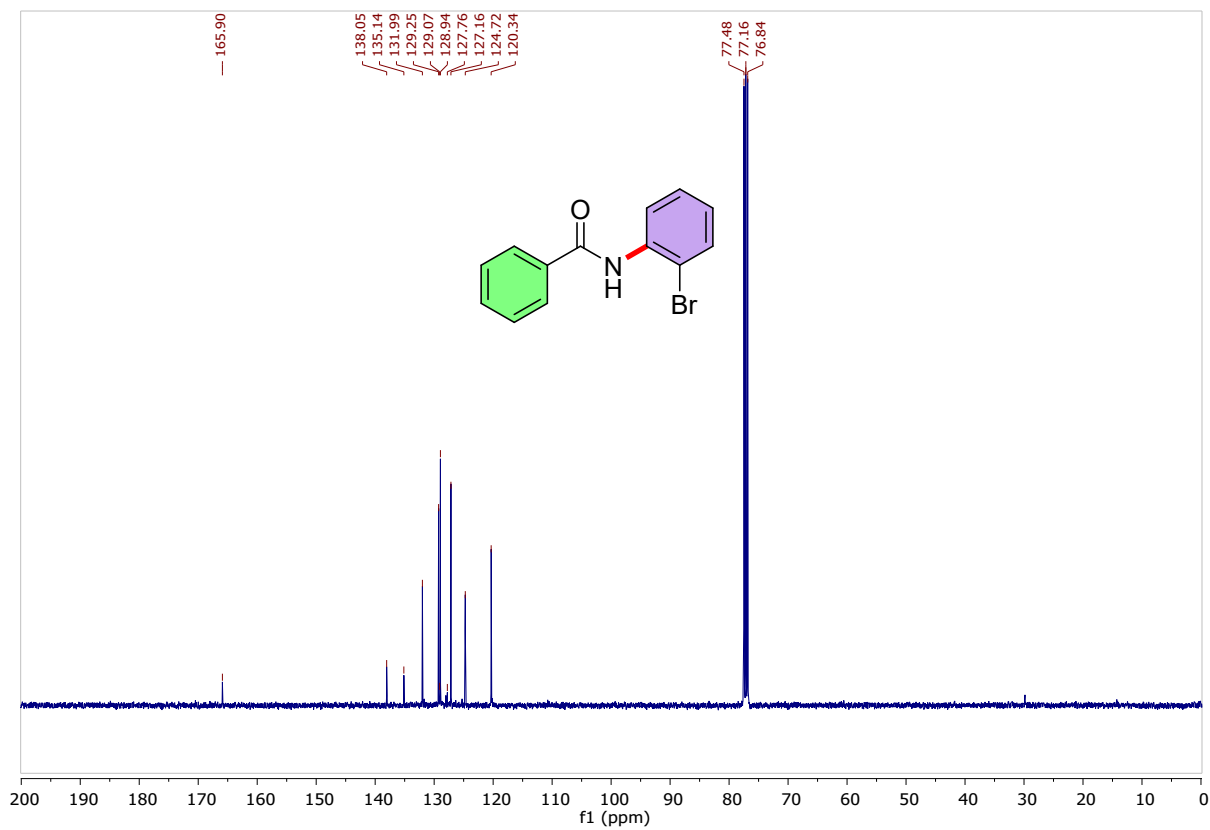
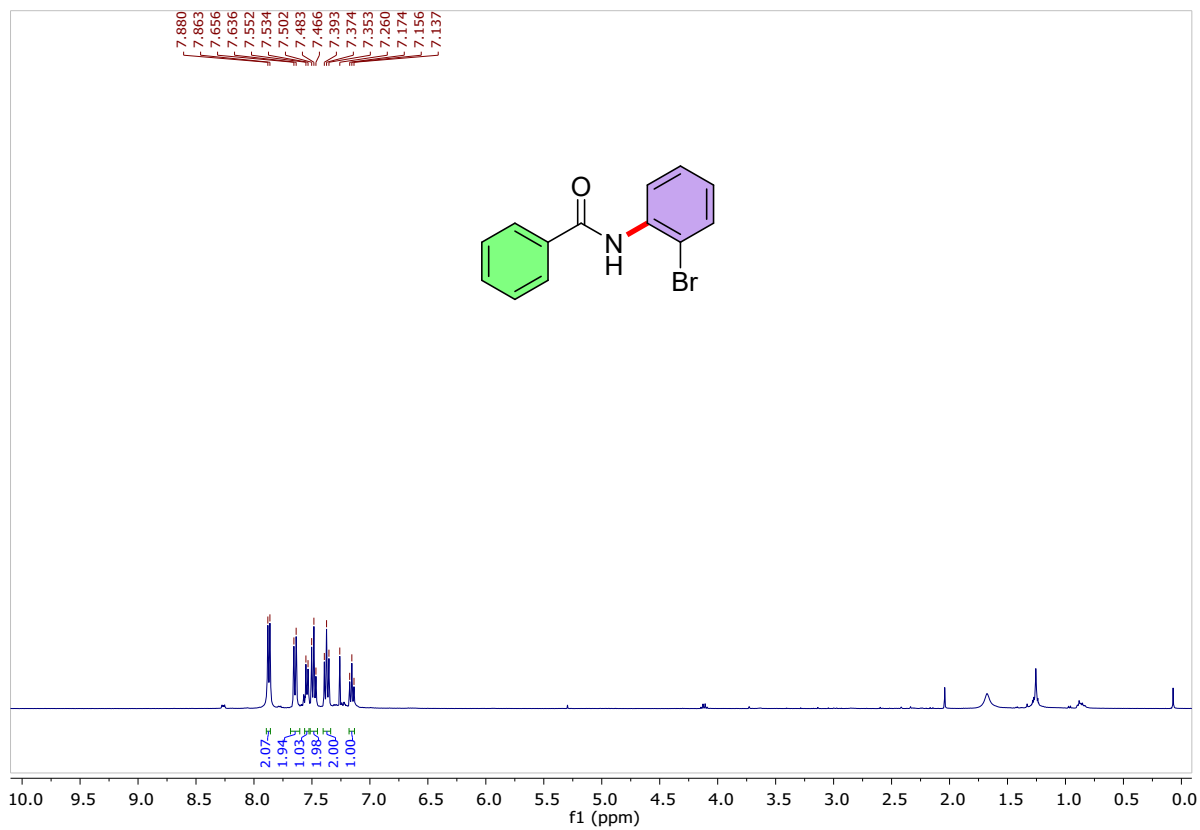
N-(4-chlorophenyl)benzamide (10)



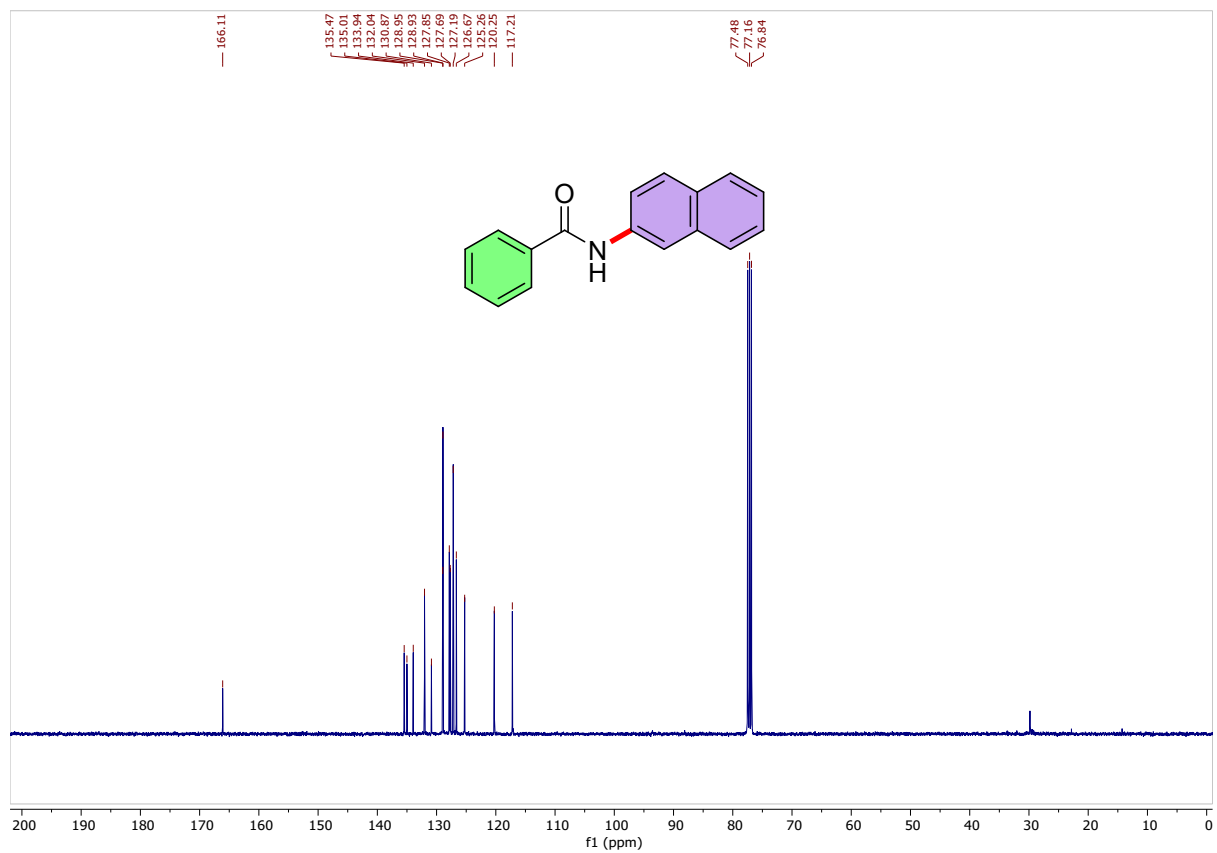
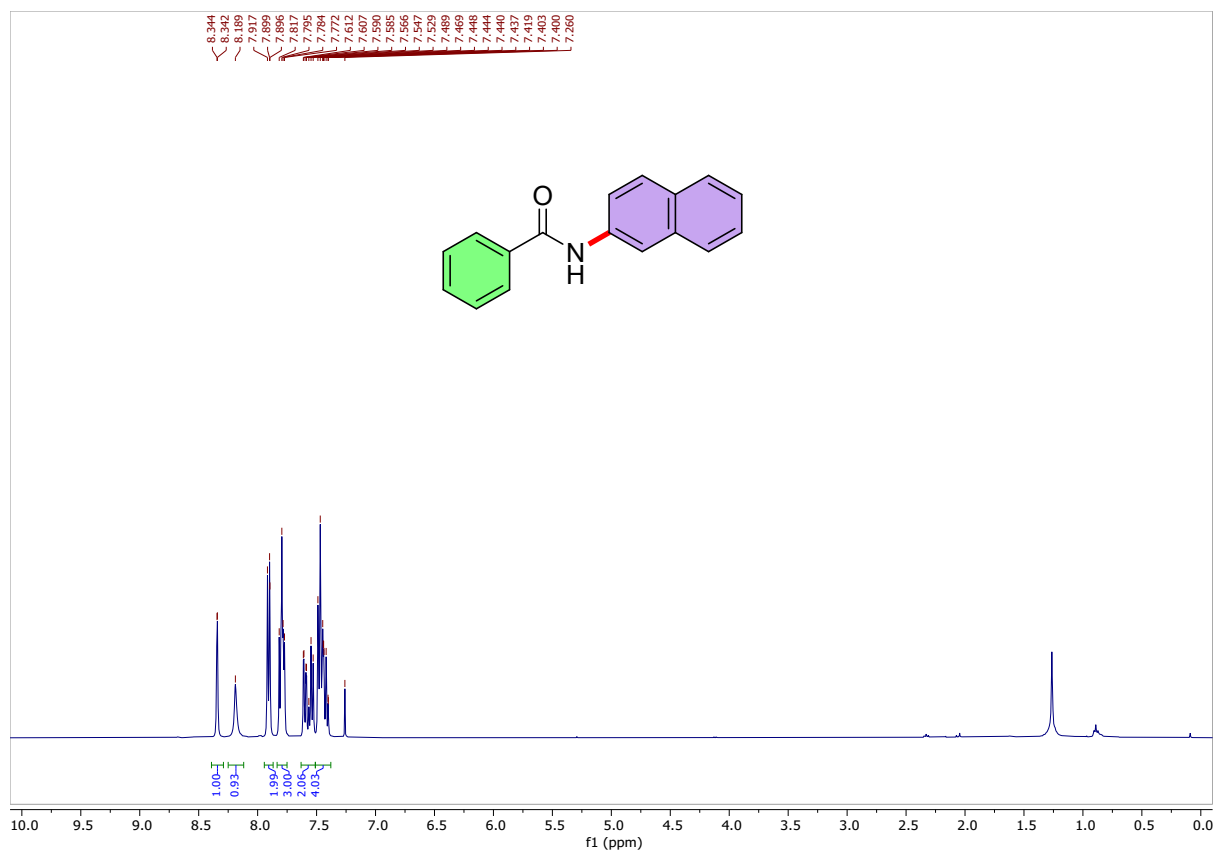
N-(4-bromophenyl)benzamide (11)



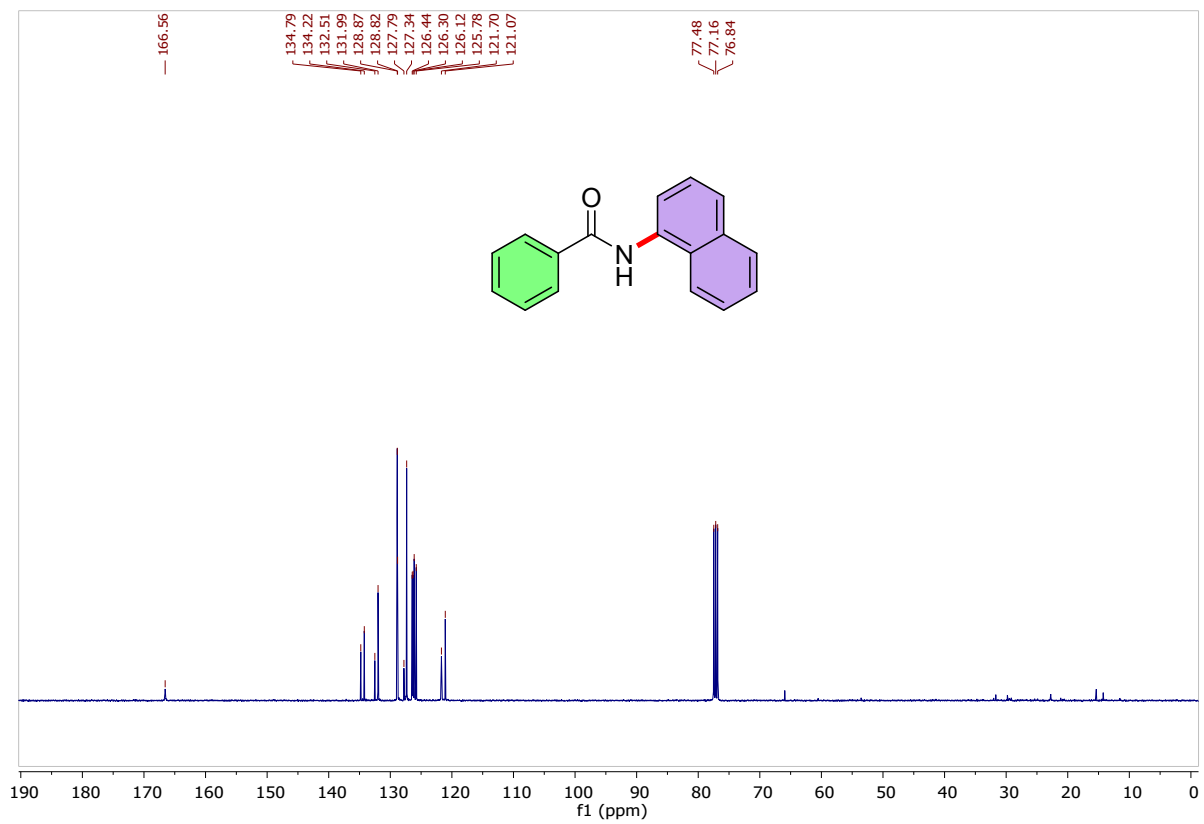
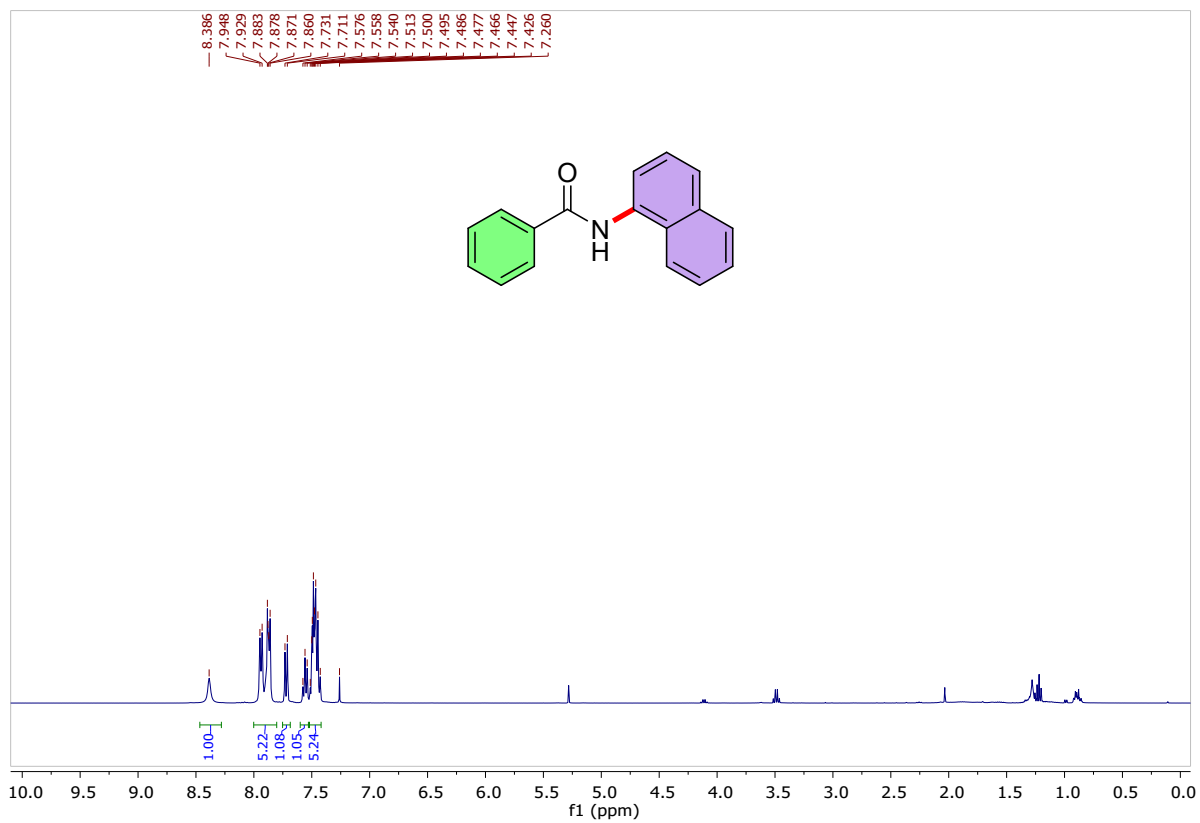
N-(2-bromophenyl)benzamide (12)



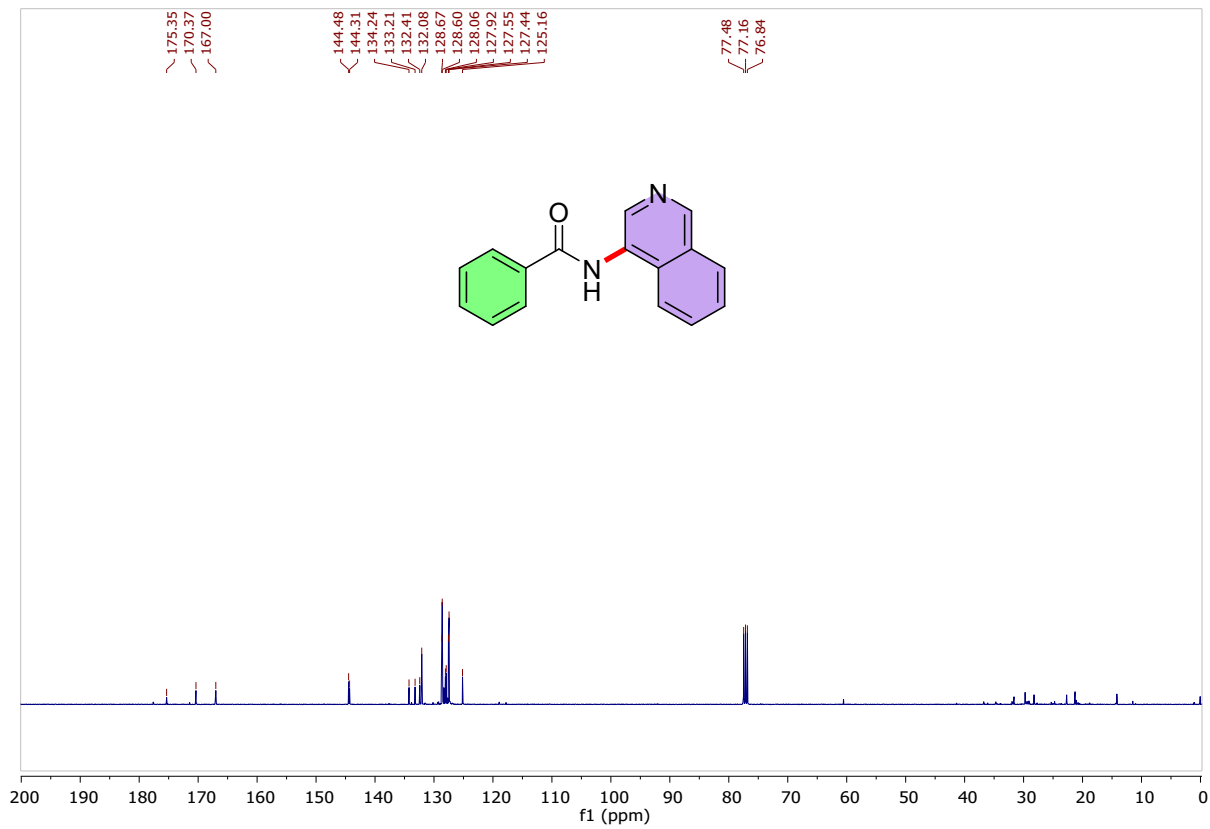
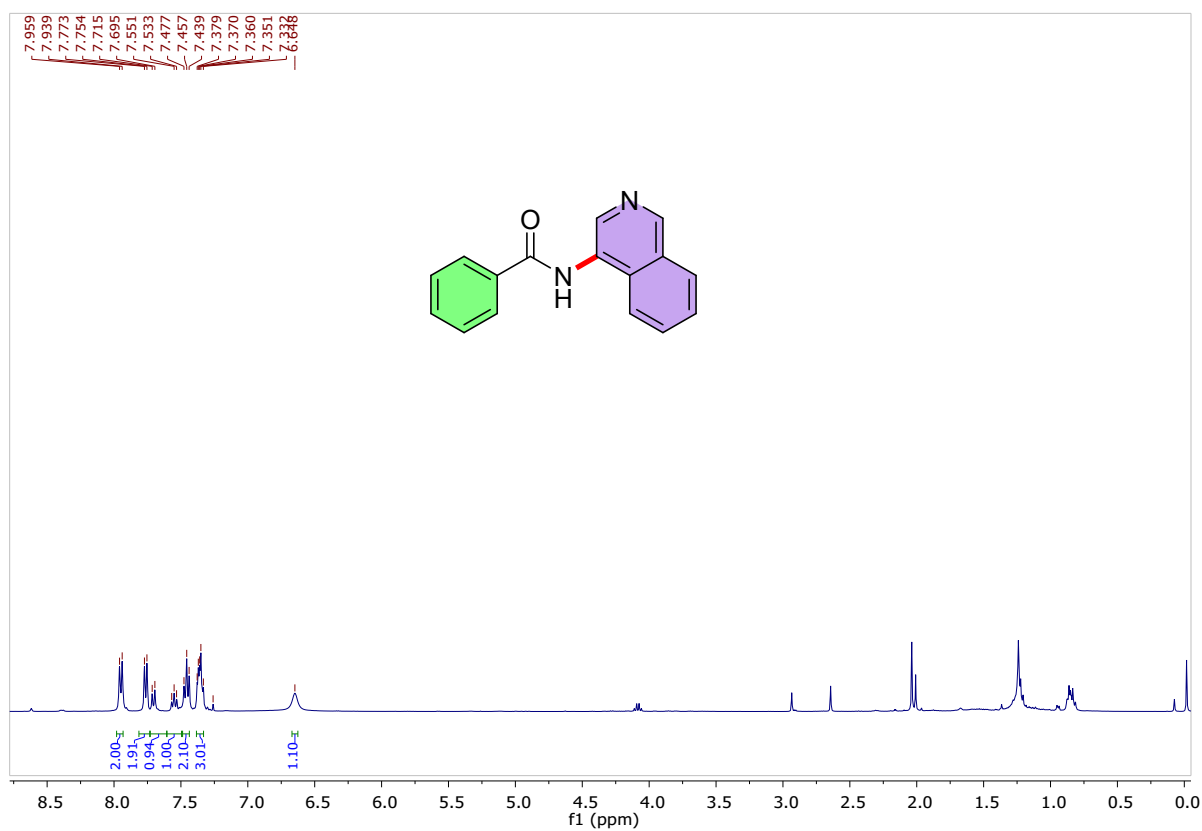
***N*-(naphthalen-2-yl)benzamide (13)**



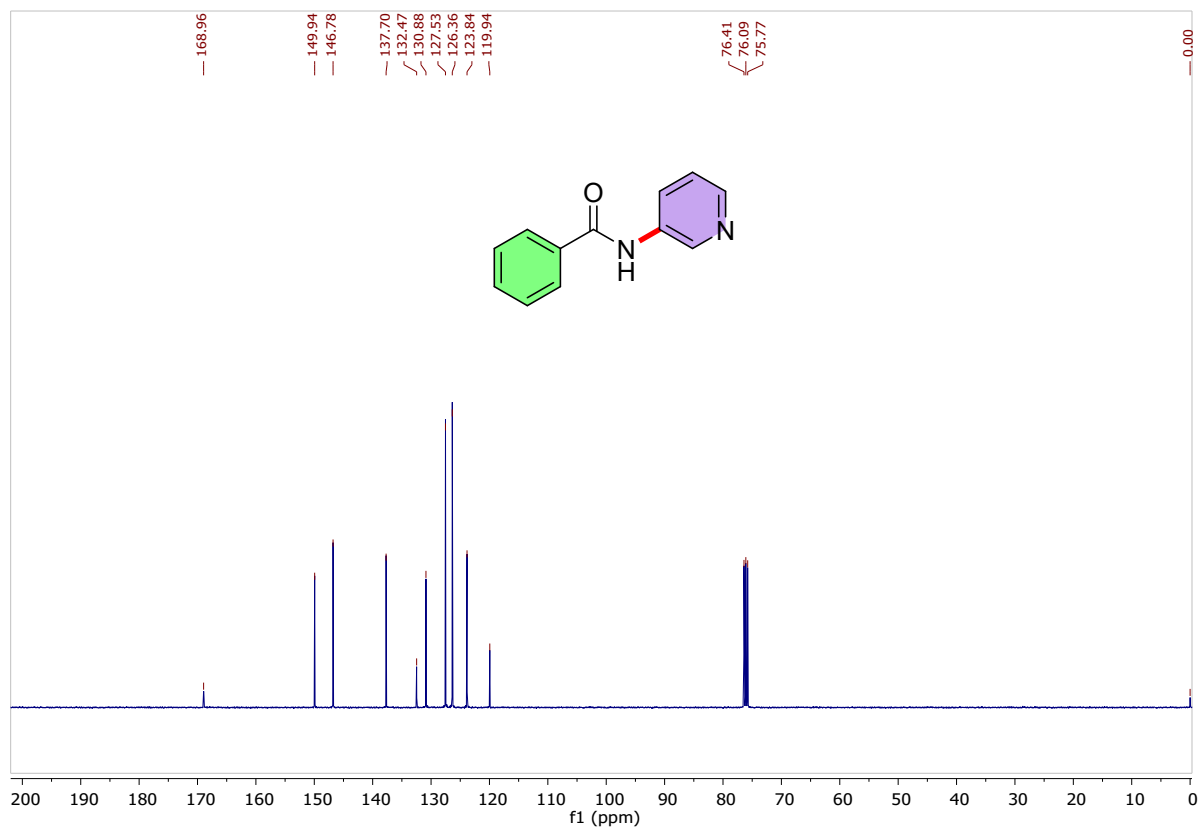
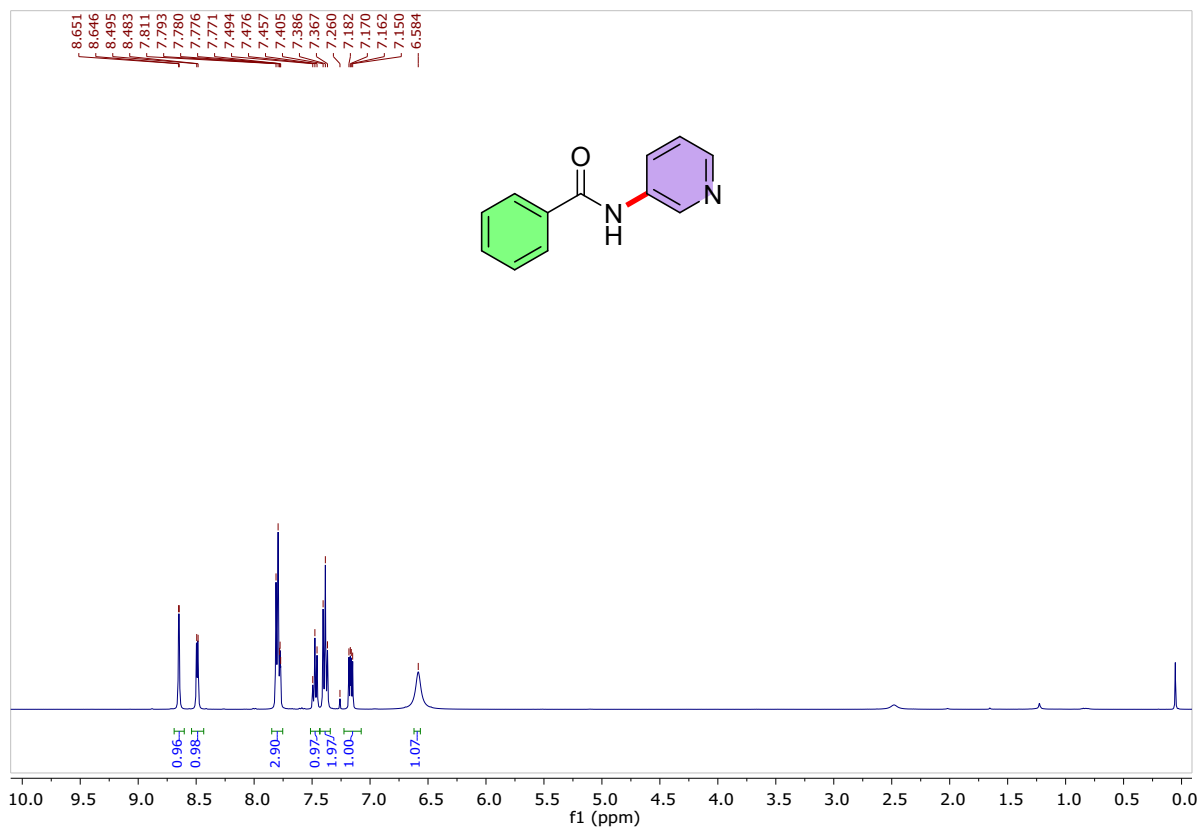
***N*-(naphthalen-1-yl)benzamide (14)**



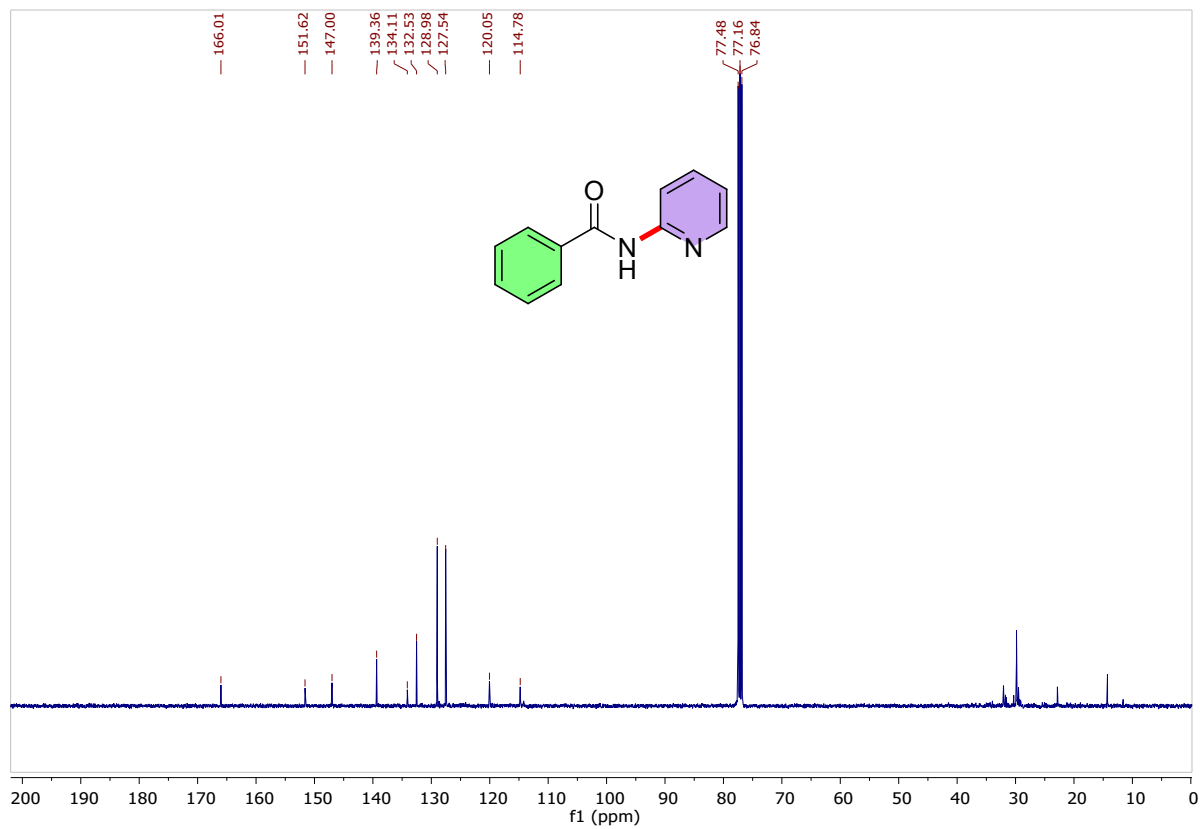
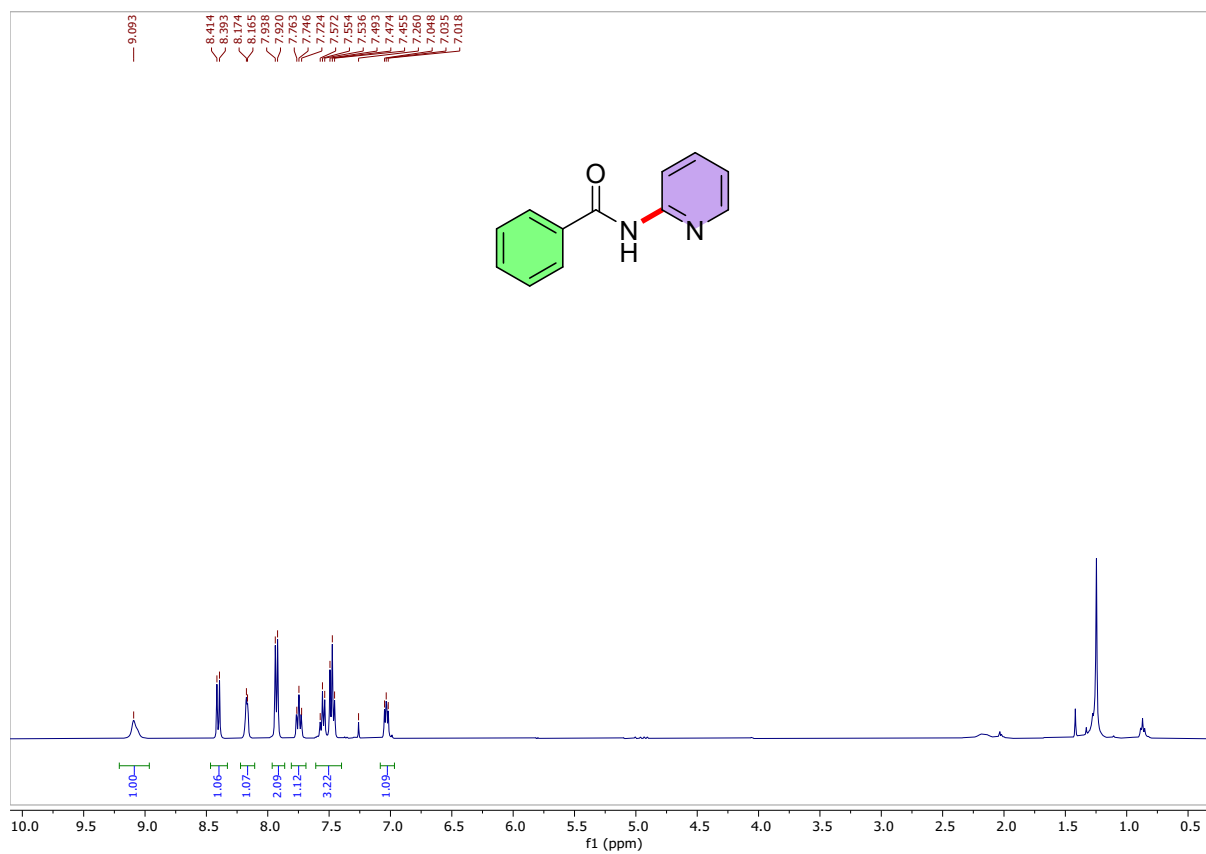
***N*-(quinolin-3-yl)benzamide (15)**



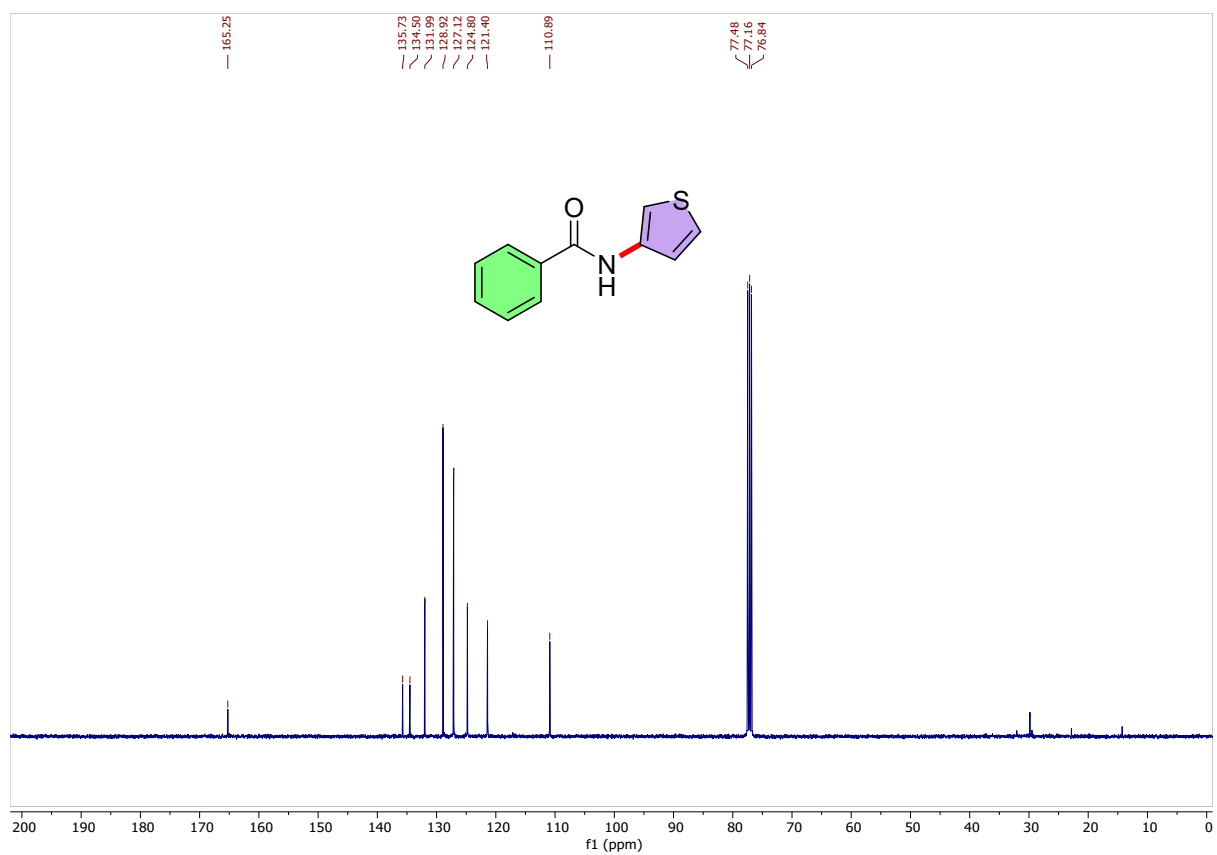
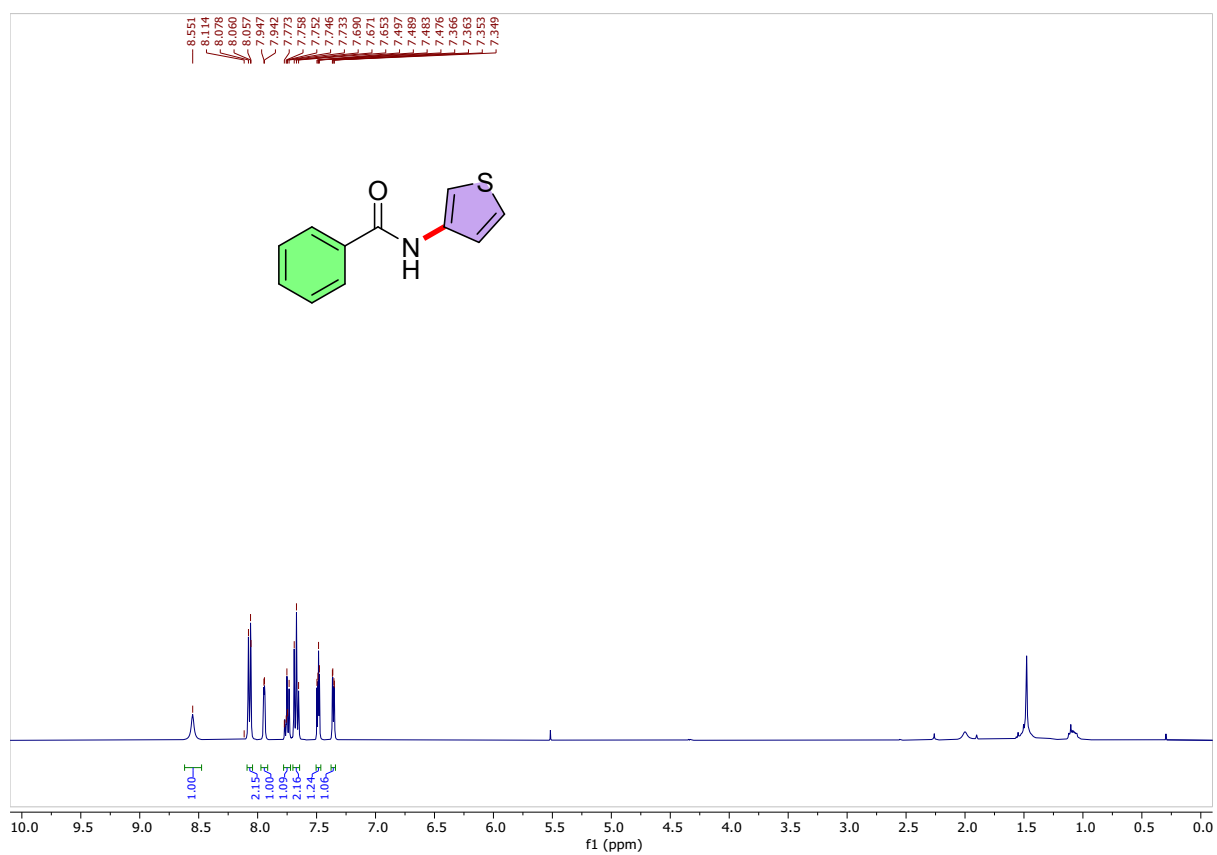
***N*-(pyridin-3-yl)benzamide (16)**



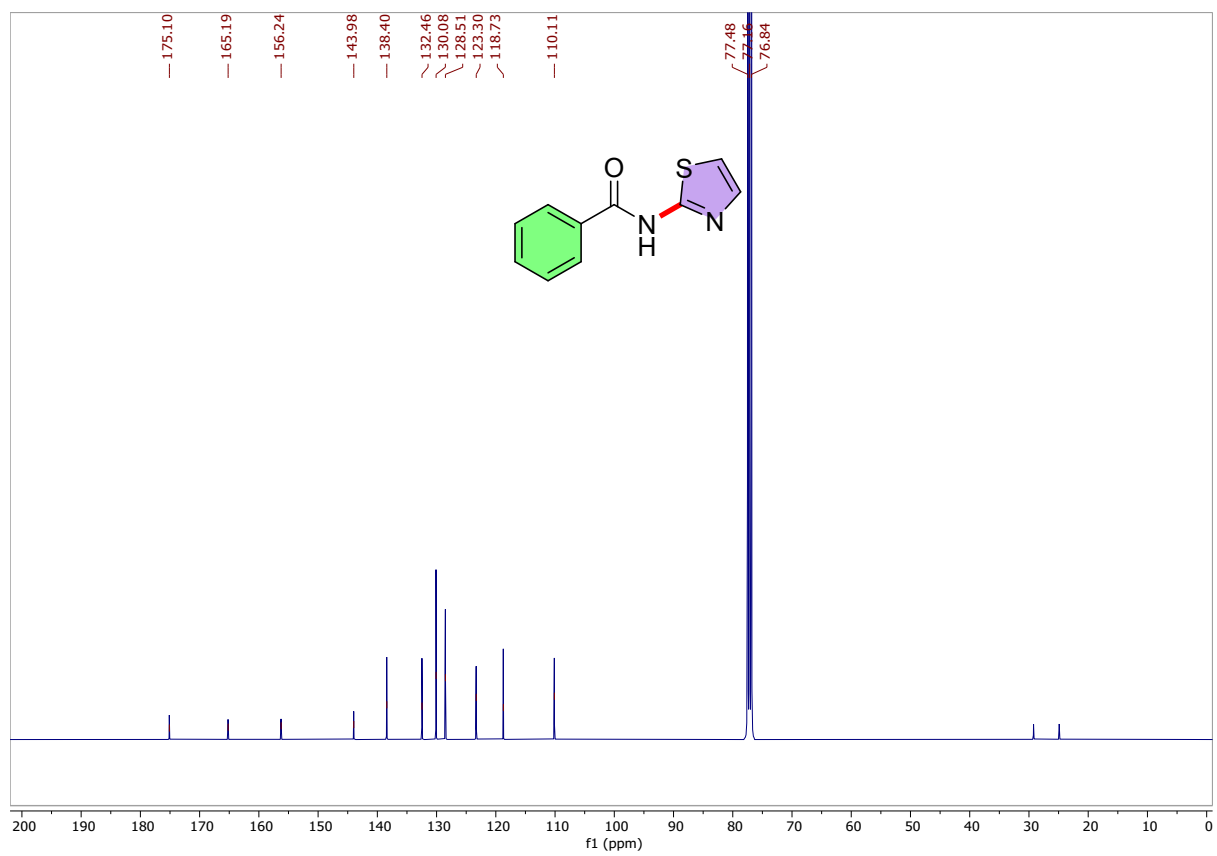
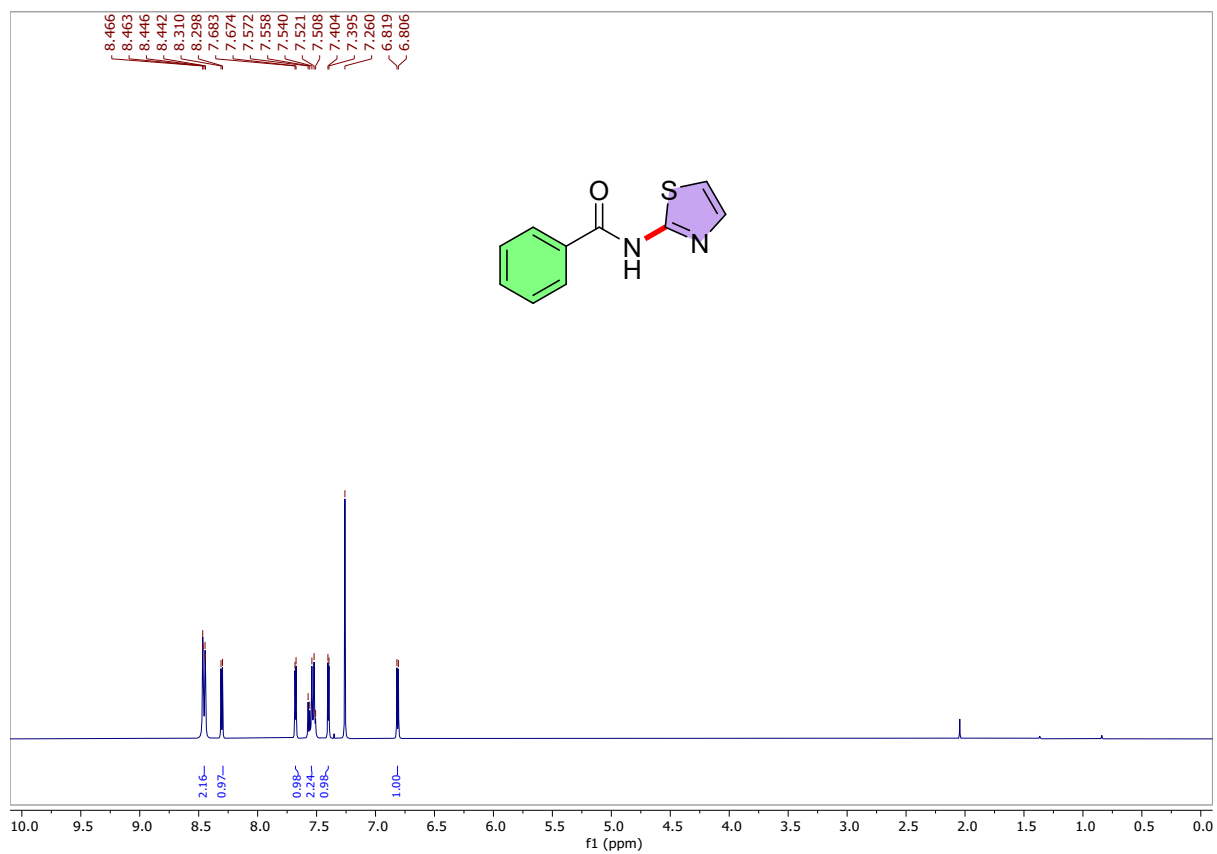
***N*-(pyridin-2-yl)benzamide (17)**



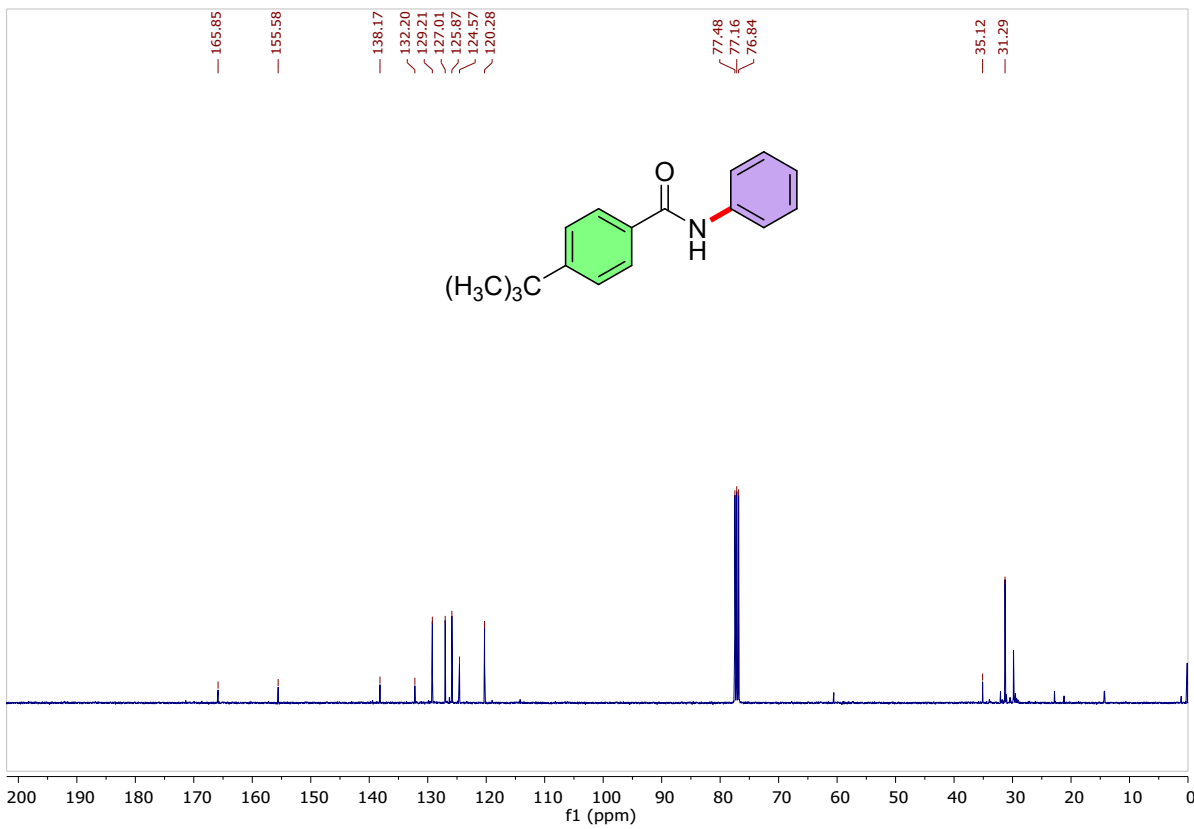
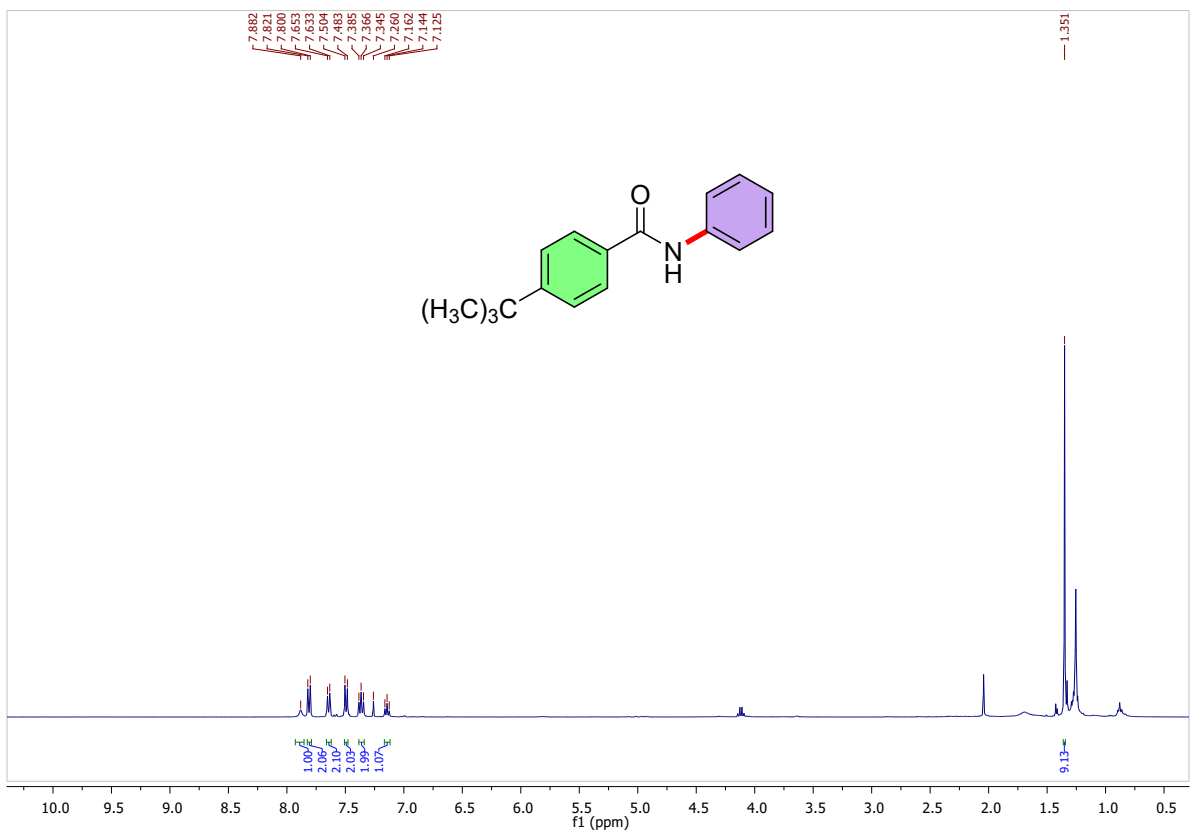
***N*-(thiophen-3-yl)benzamide (18)**



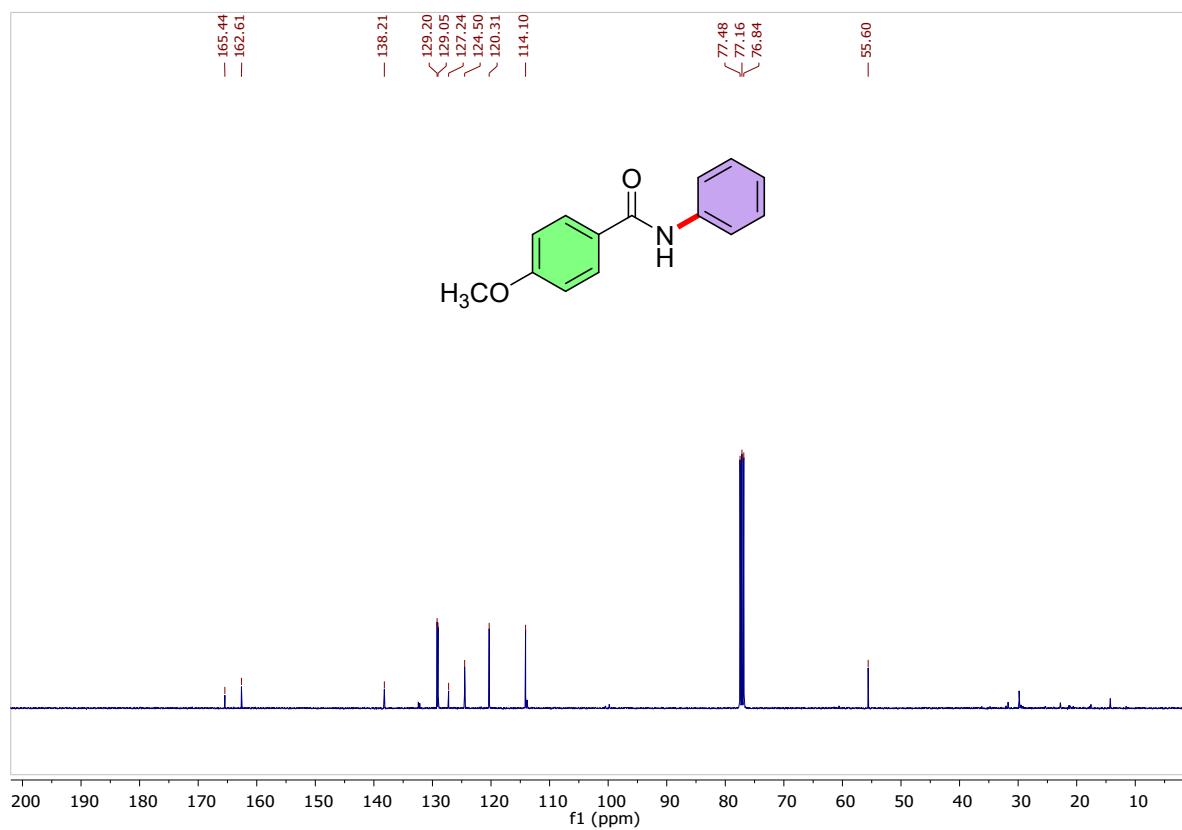
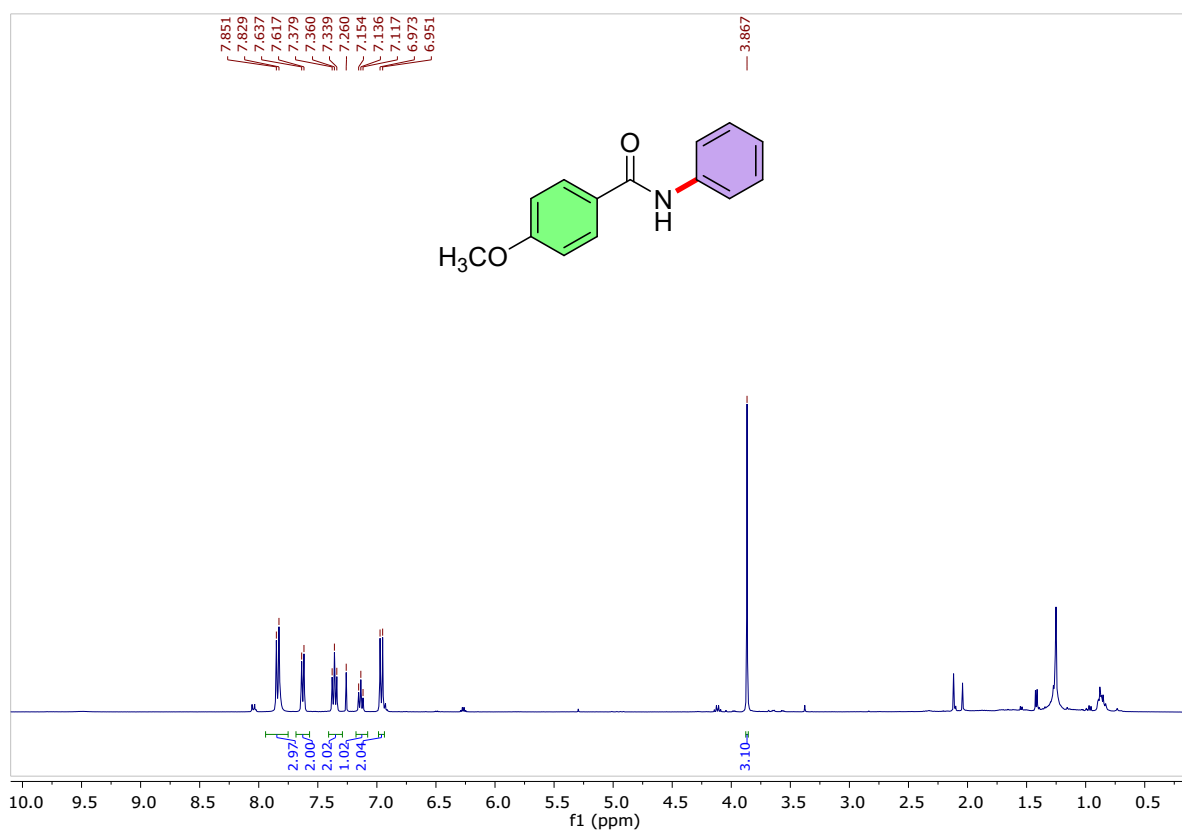
***N*-(thiazol-2-yl)benzamide (19)**



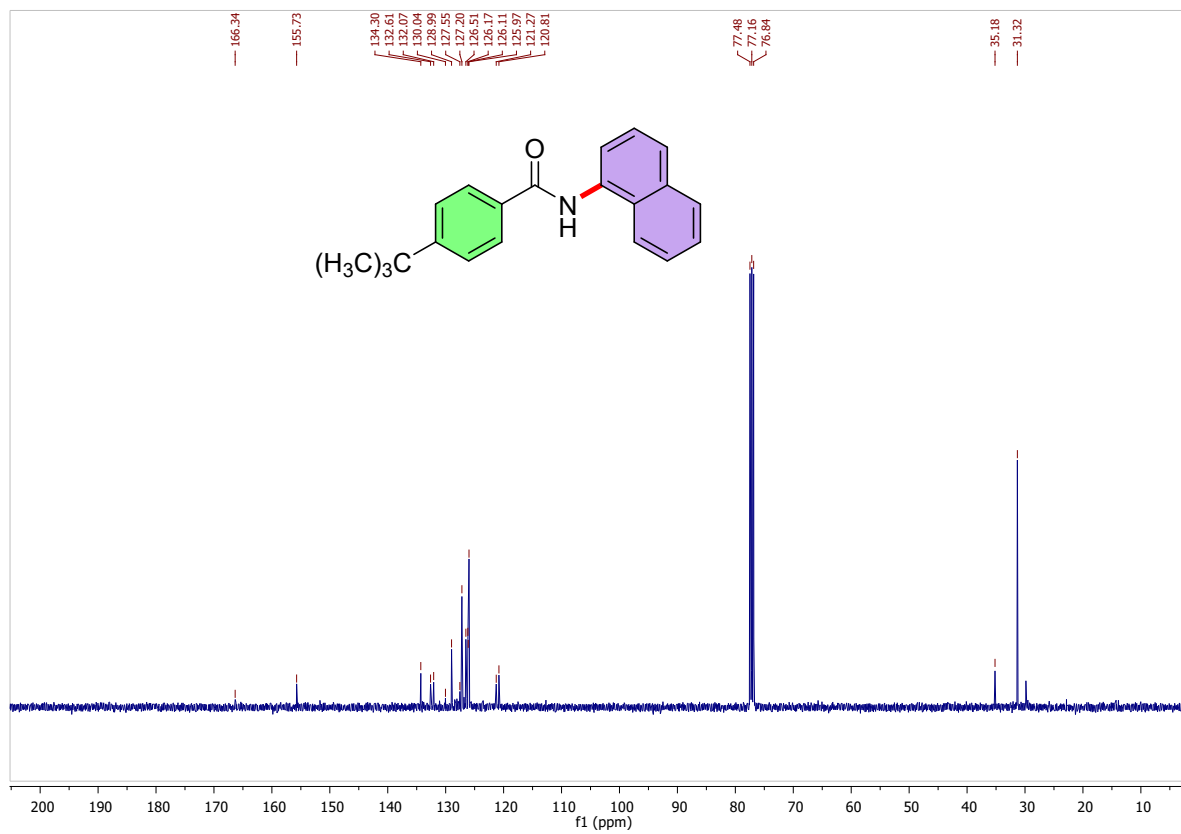
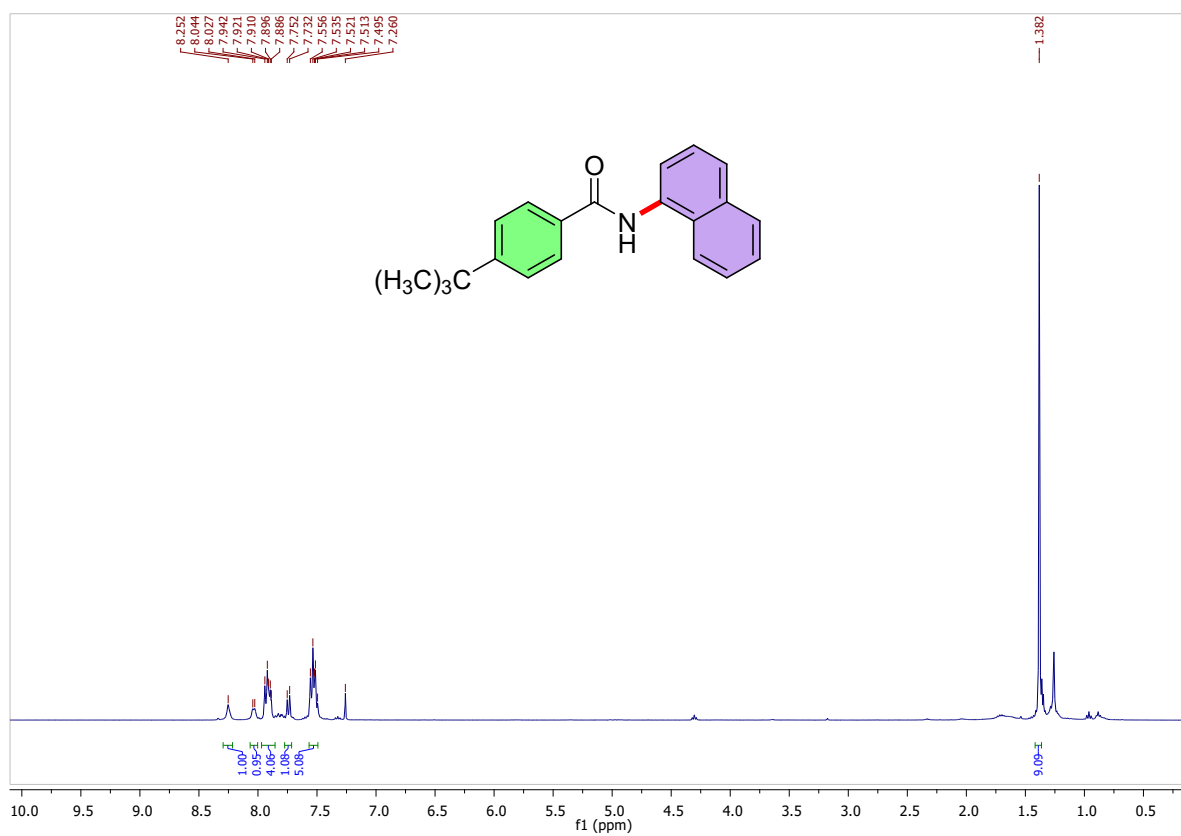
4-(tert-butyl)-*N*-phenylbenzamide (20)



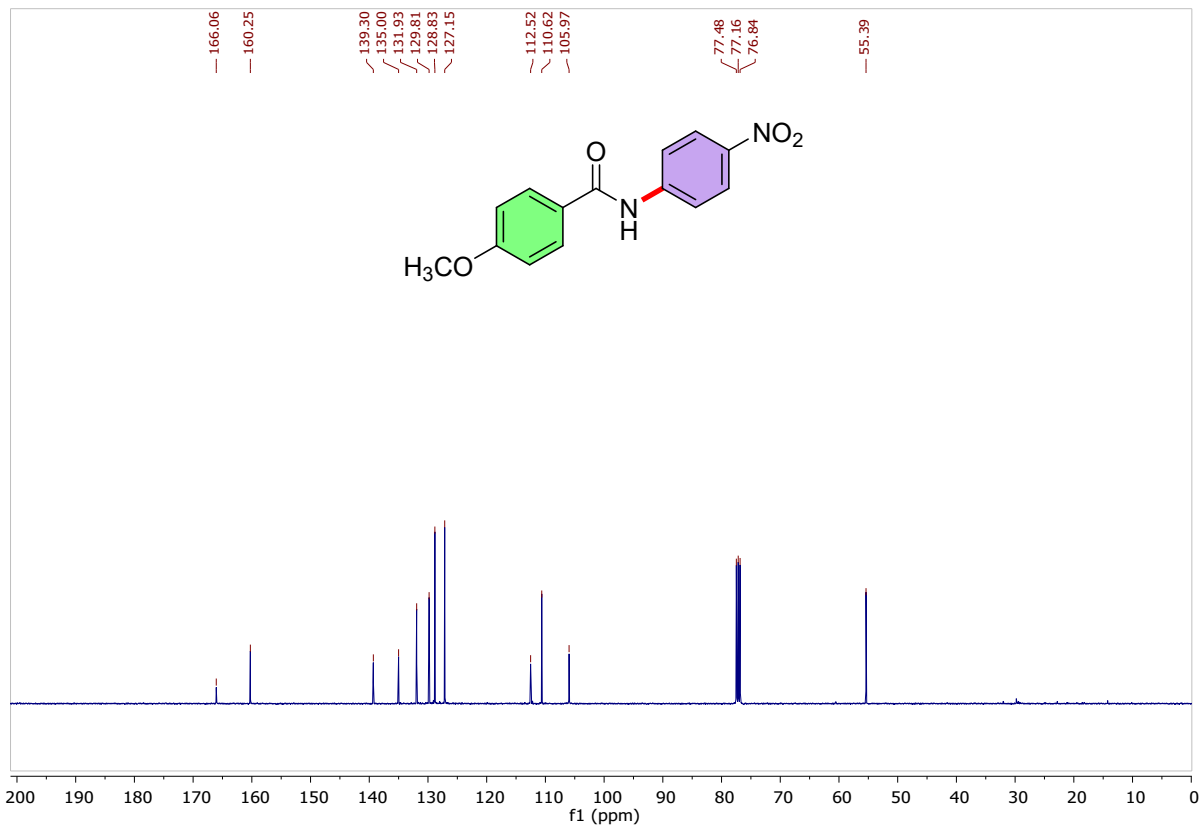
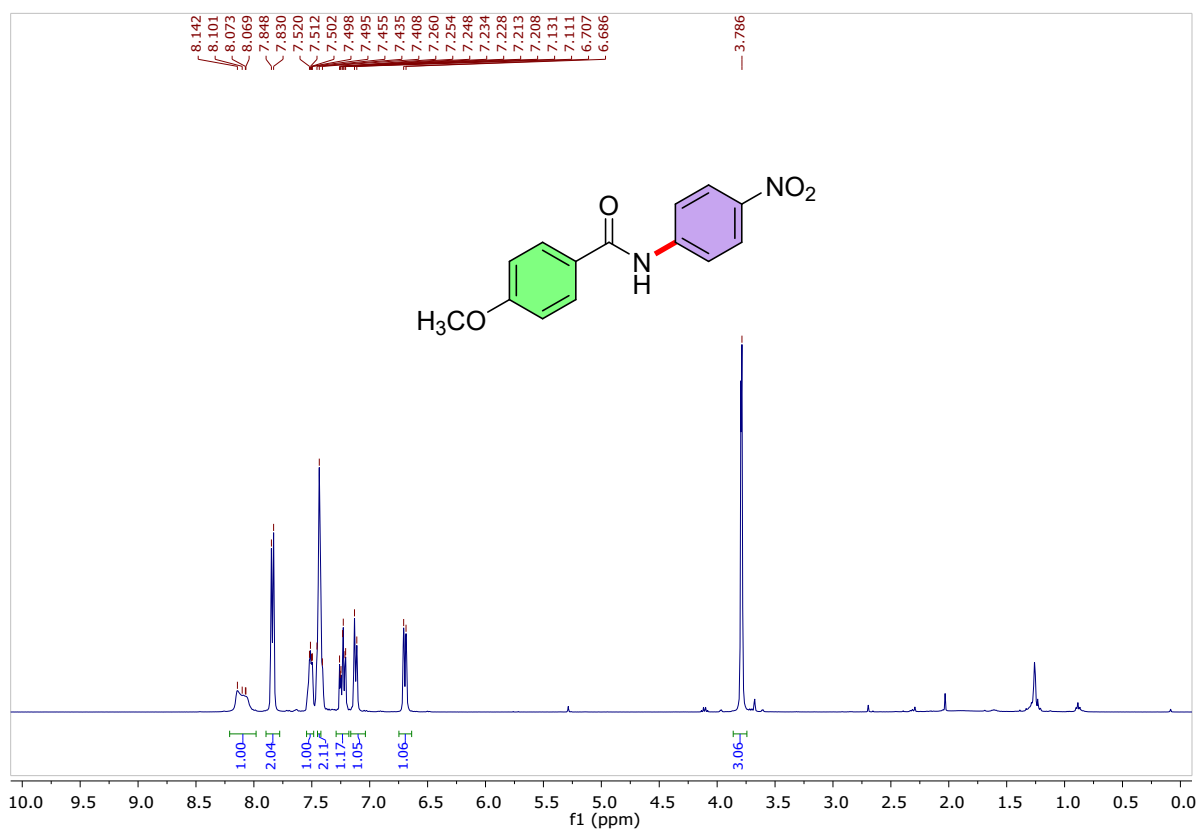
4-methoxy-*N*-phenylbenzamide (21)



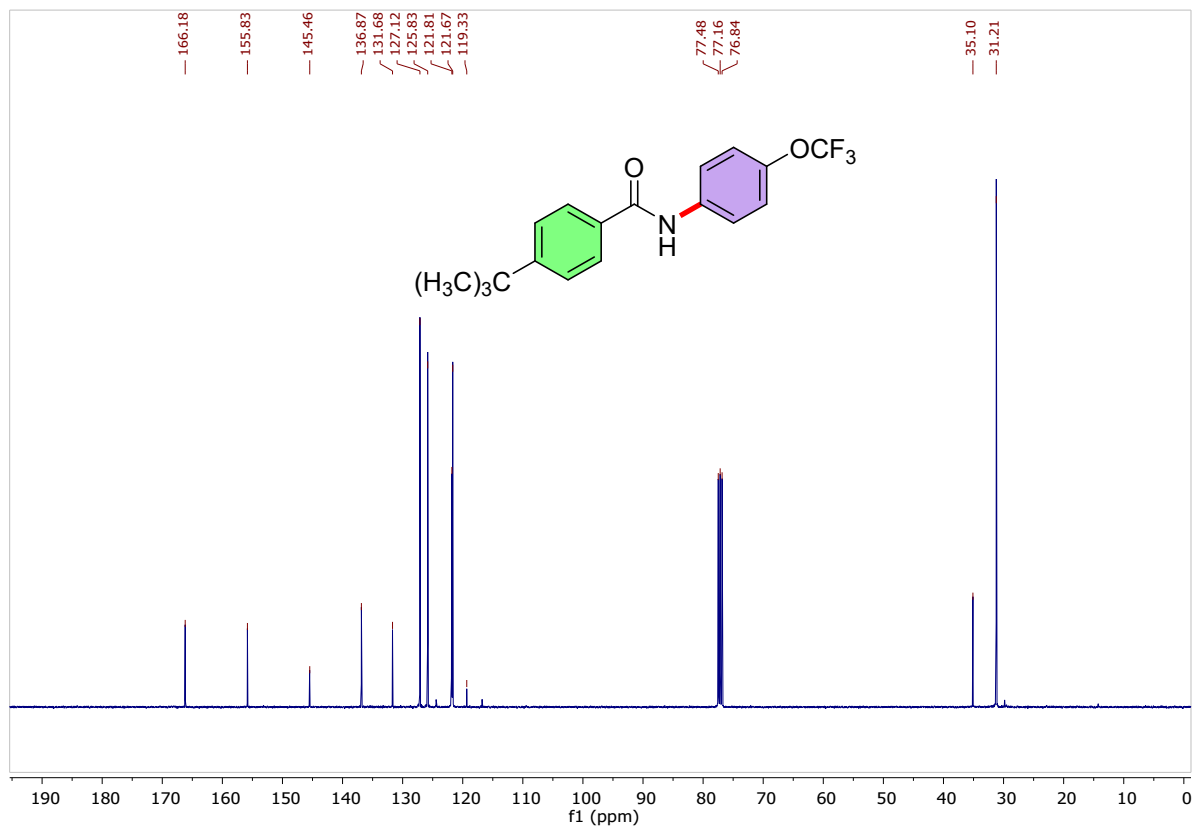
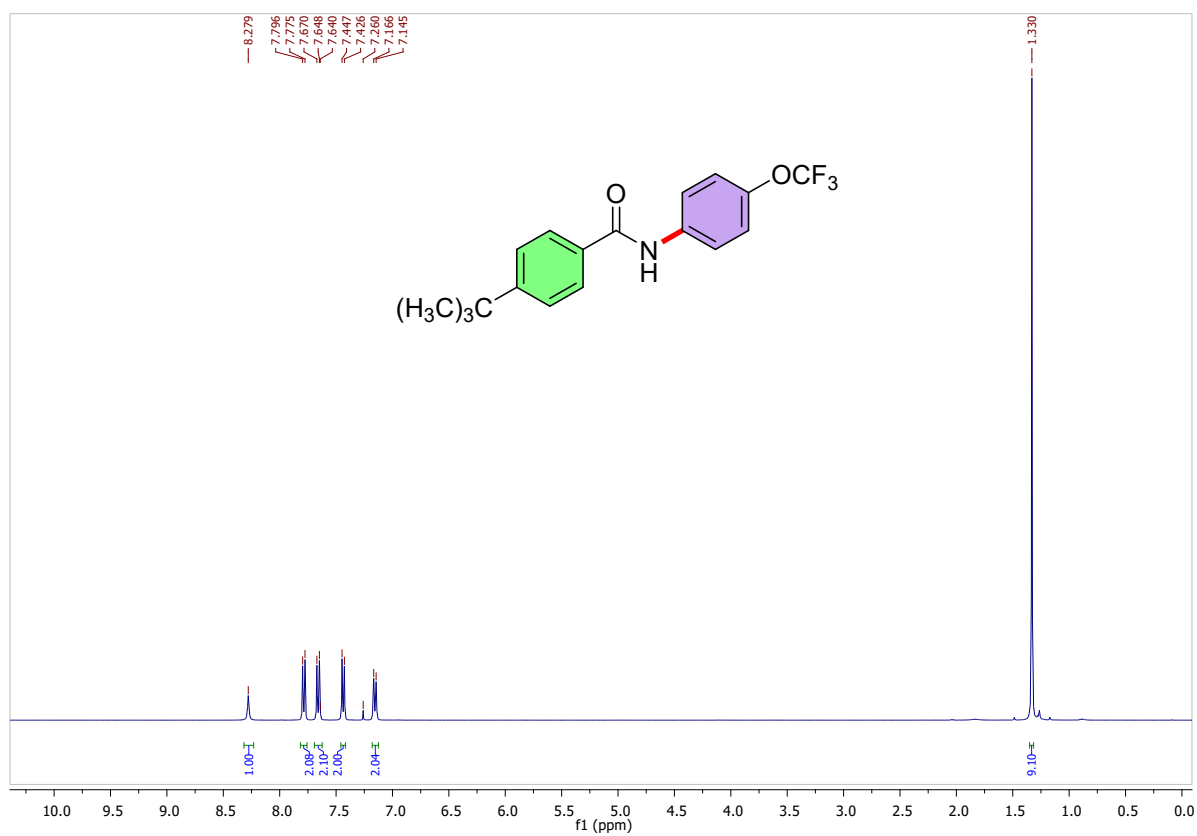
4-(tert-butyl)-*N*-(naphthalen-1-yl)benzamide (22)



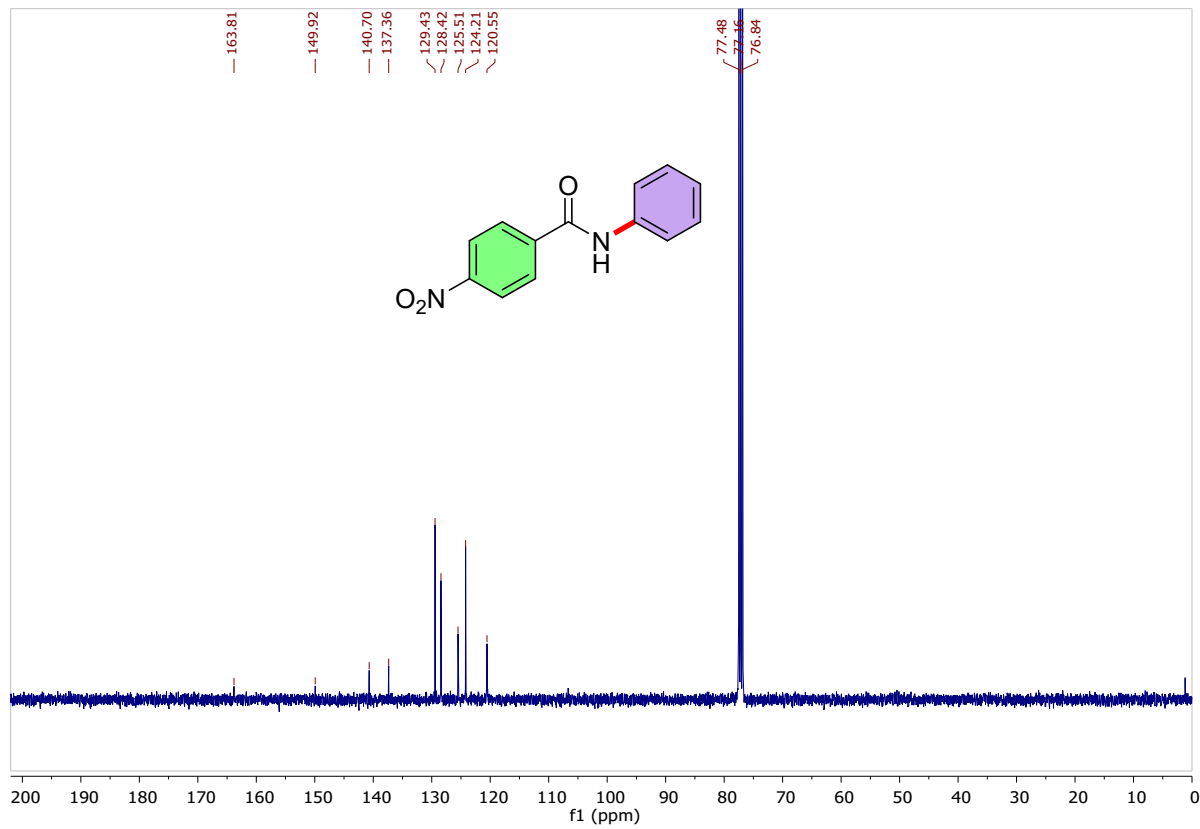
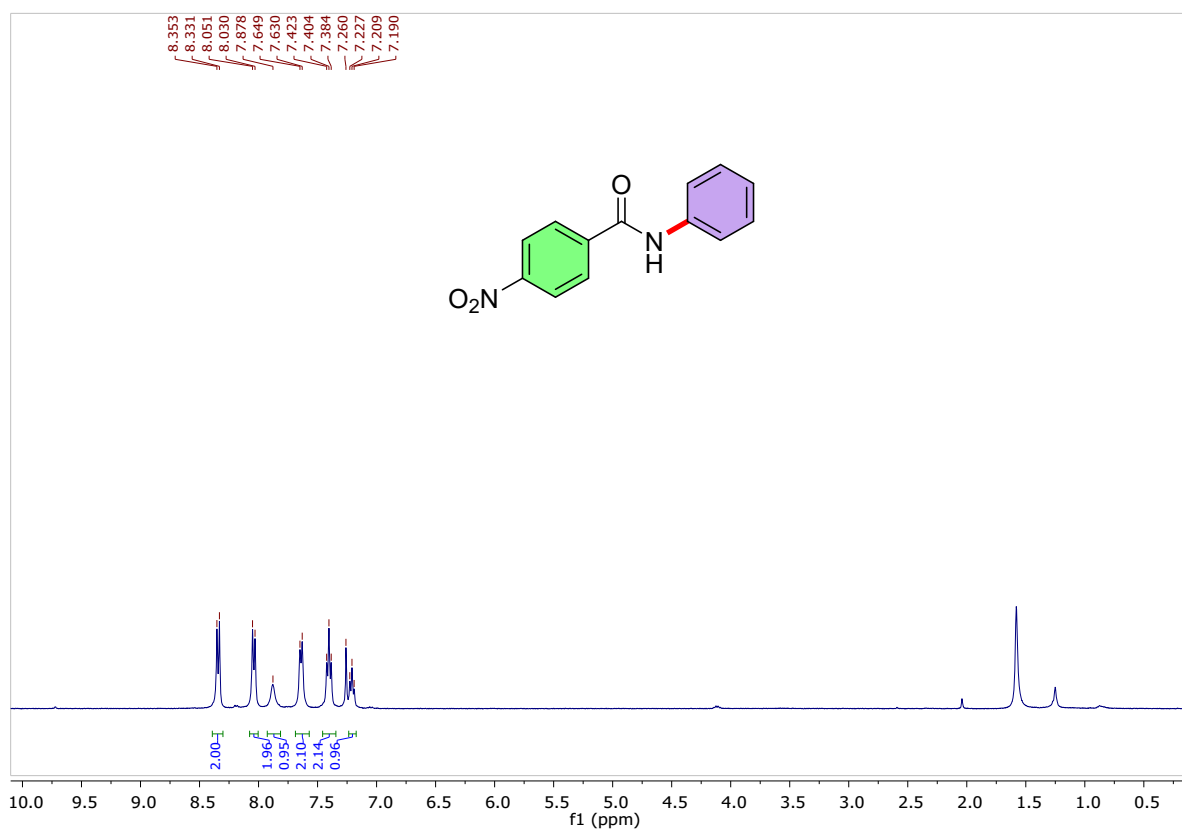
4-methoxy-*N*-(4-nitrophenyl)benzamide (23)



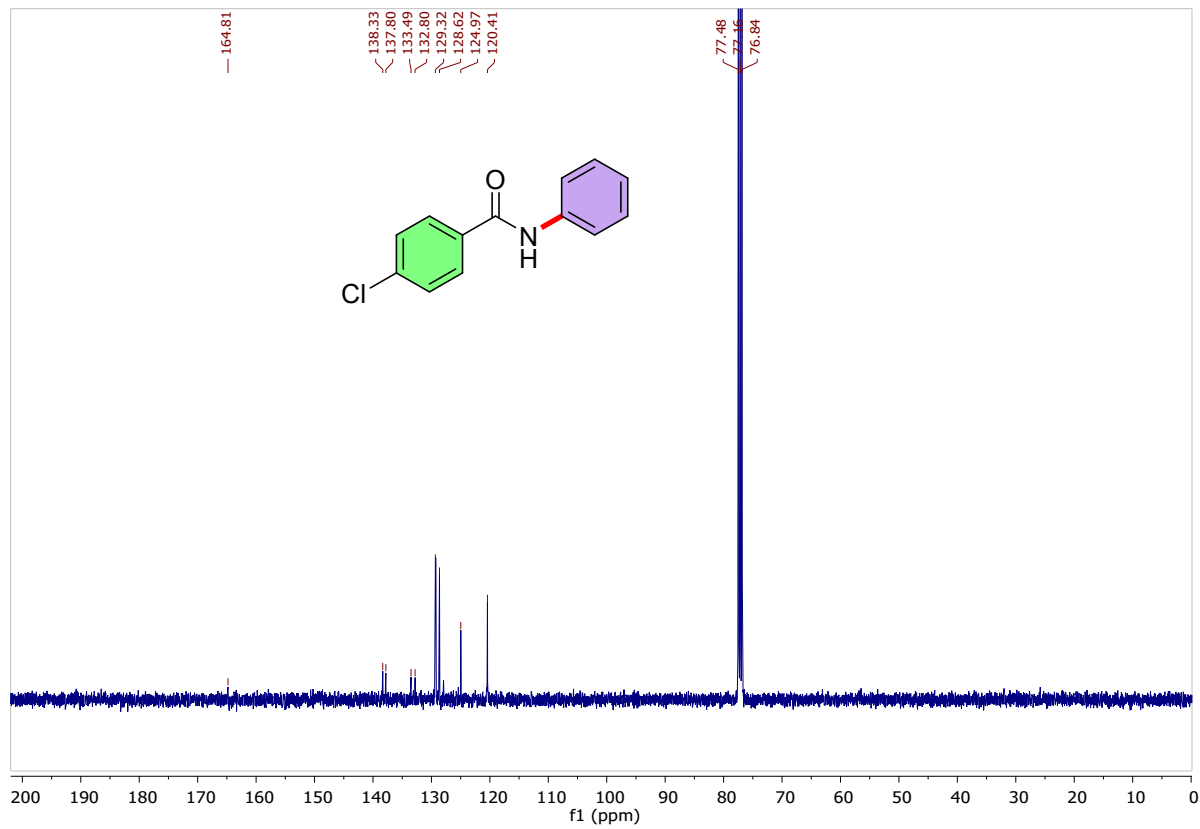
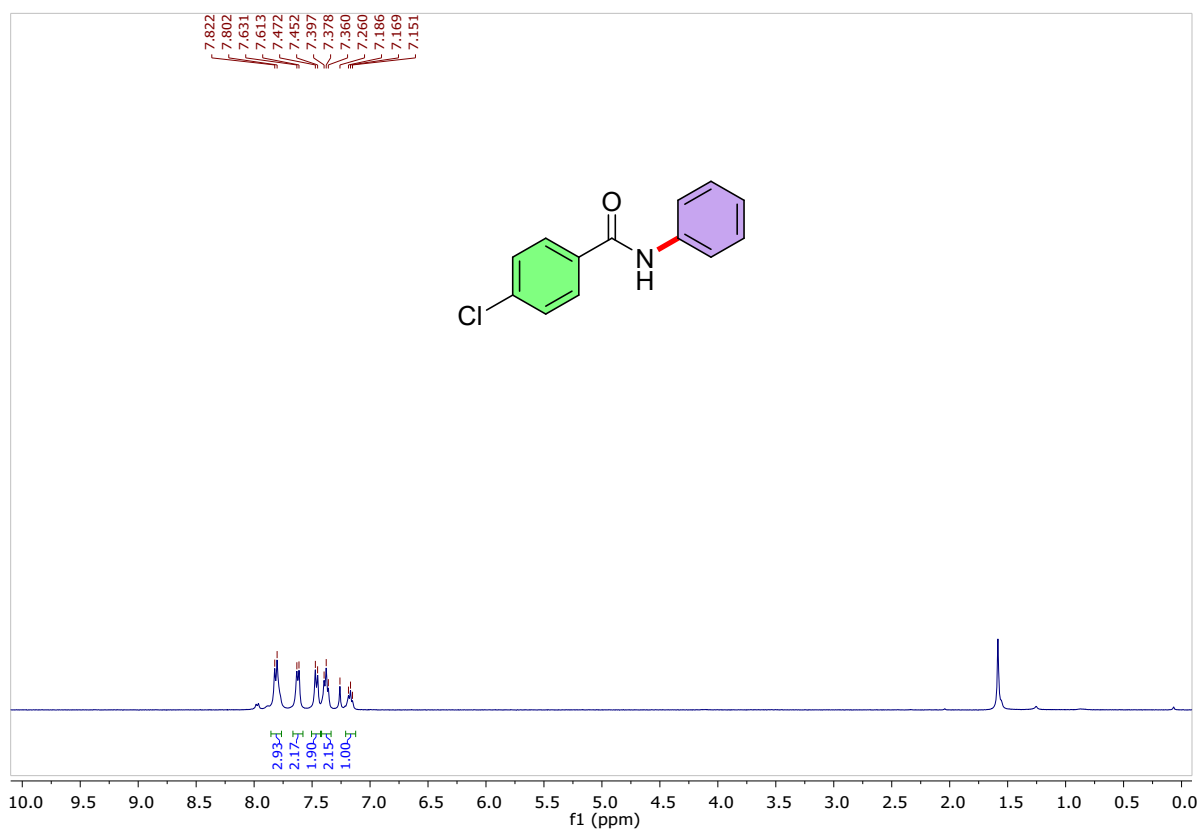
4-(tert-butyl)-N-(4-(trifluoromethoxy)phenyl)benzamide (24)



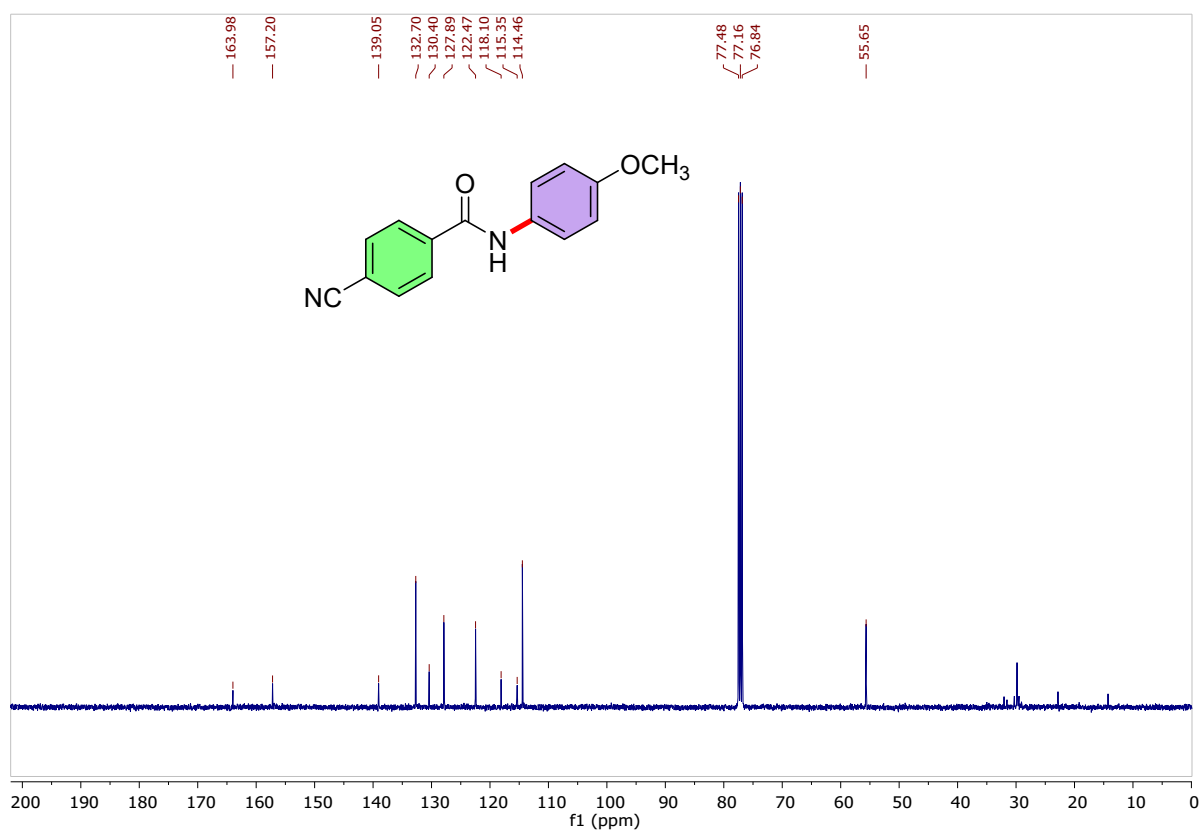
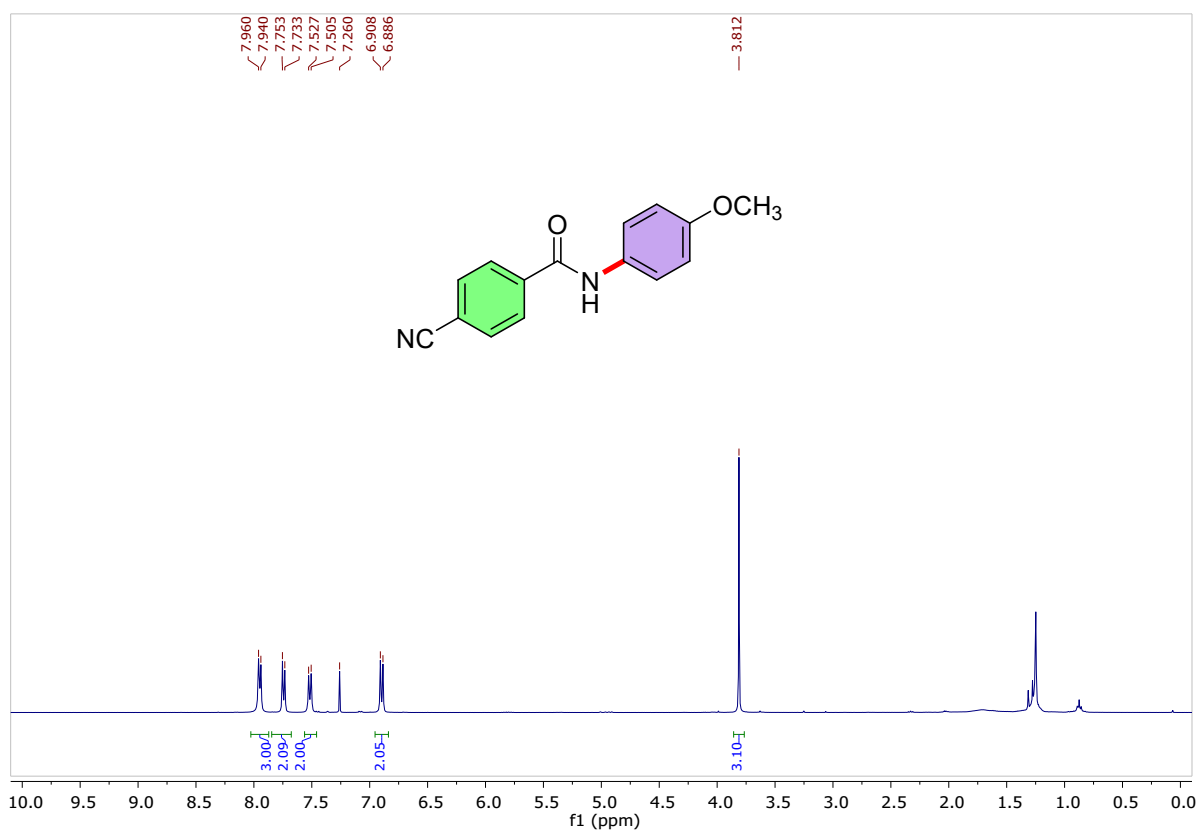
4-nitro-*N*-phenylbenzamide (25)



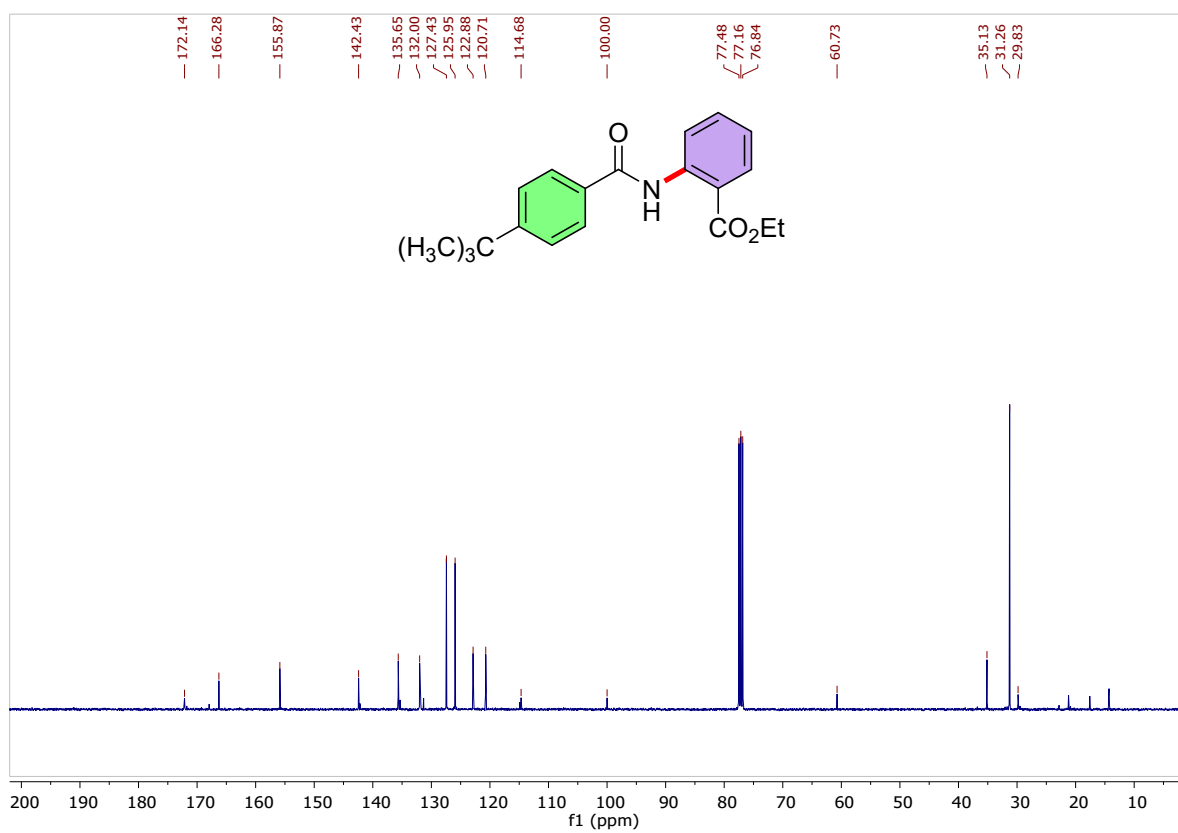
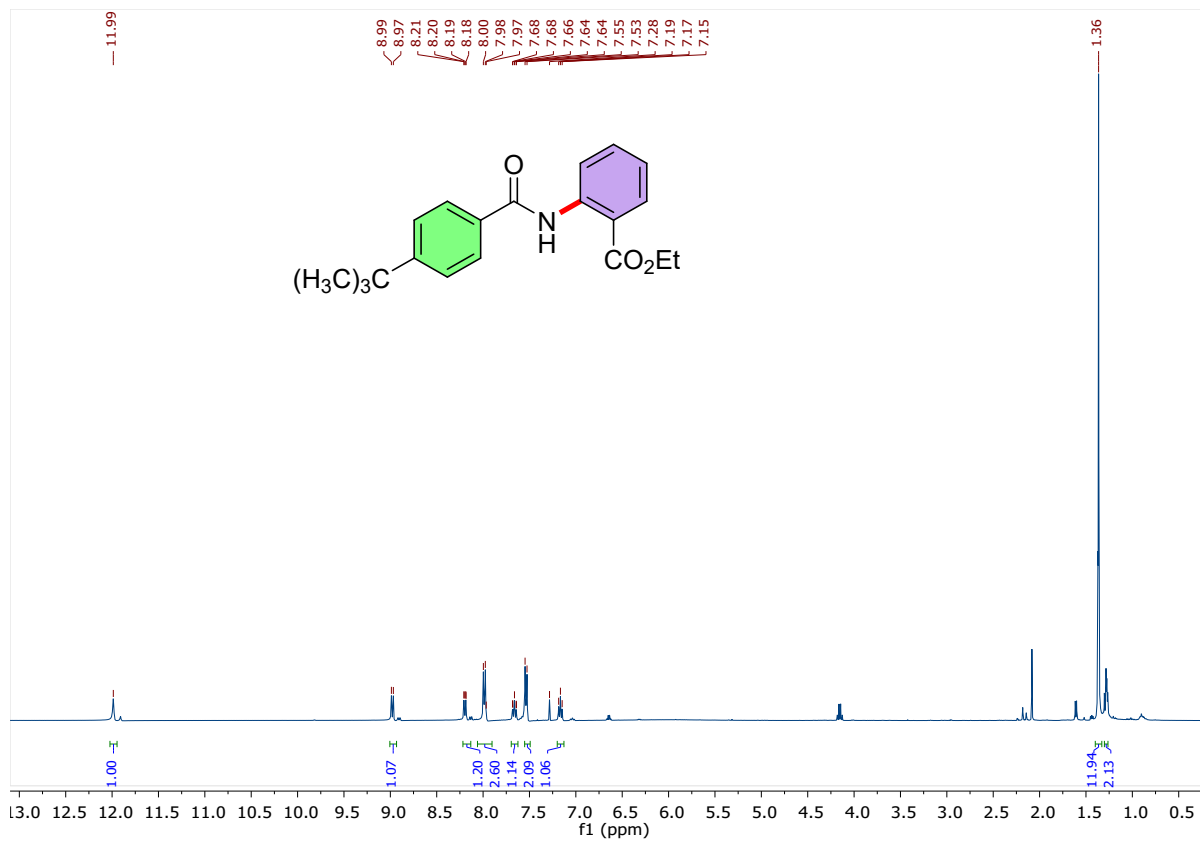
4-chloro-N-phenylbenzamide (26)



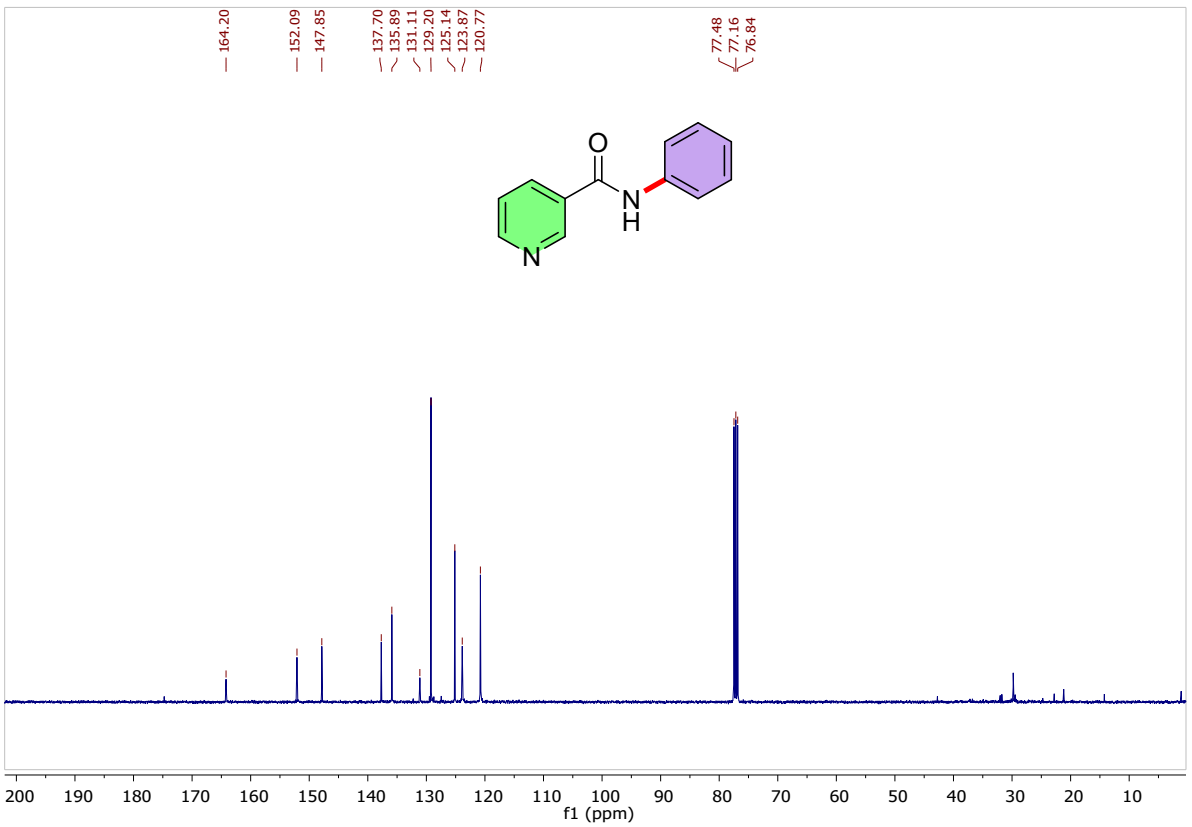
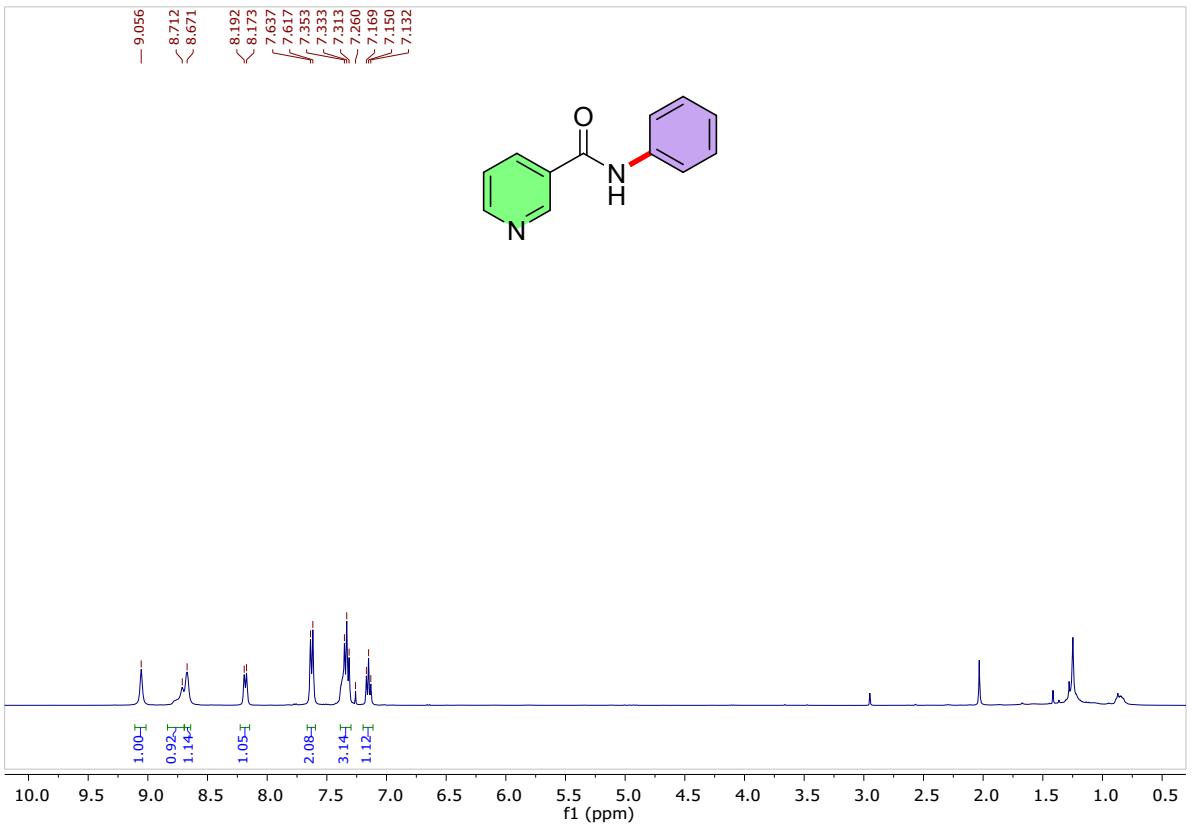
4-cyano-*N*-(4-methoxyphenyl)benzamide (27)



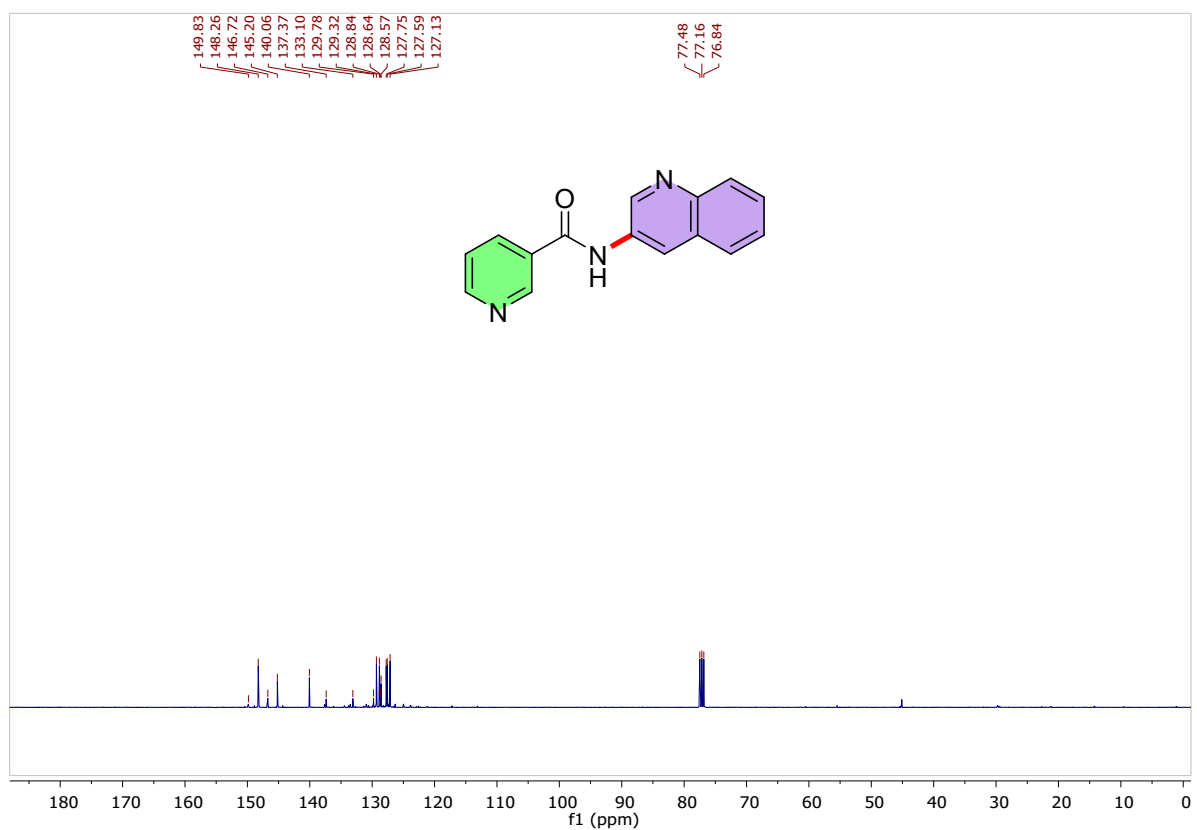
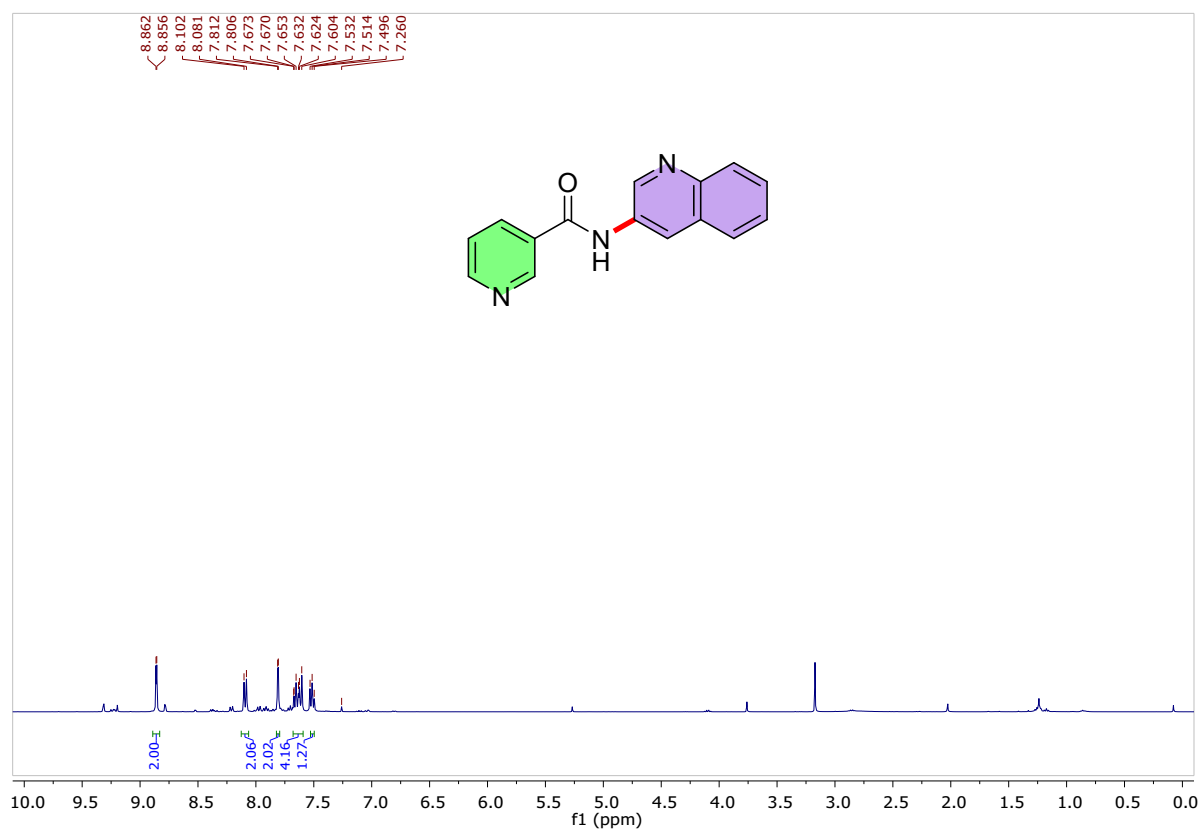
ethyl 2-(4-(tert-butyl)benzamido)benzoate (28)



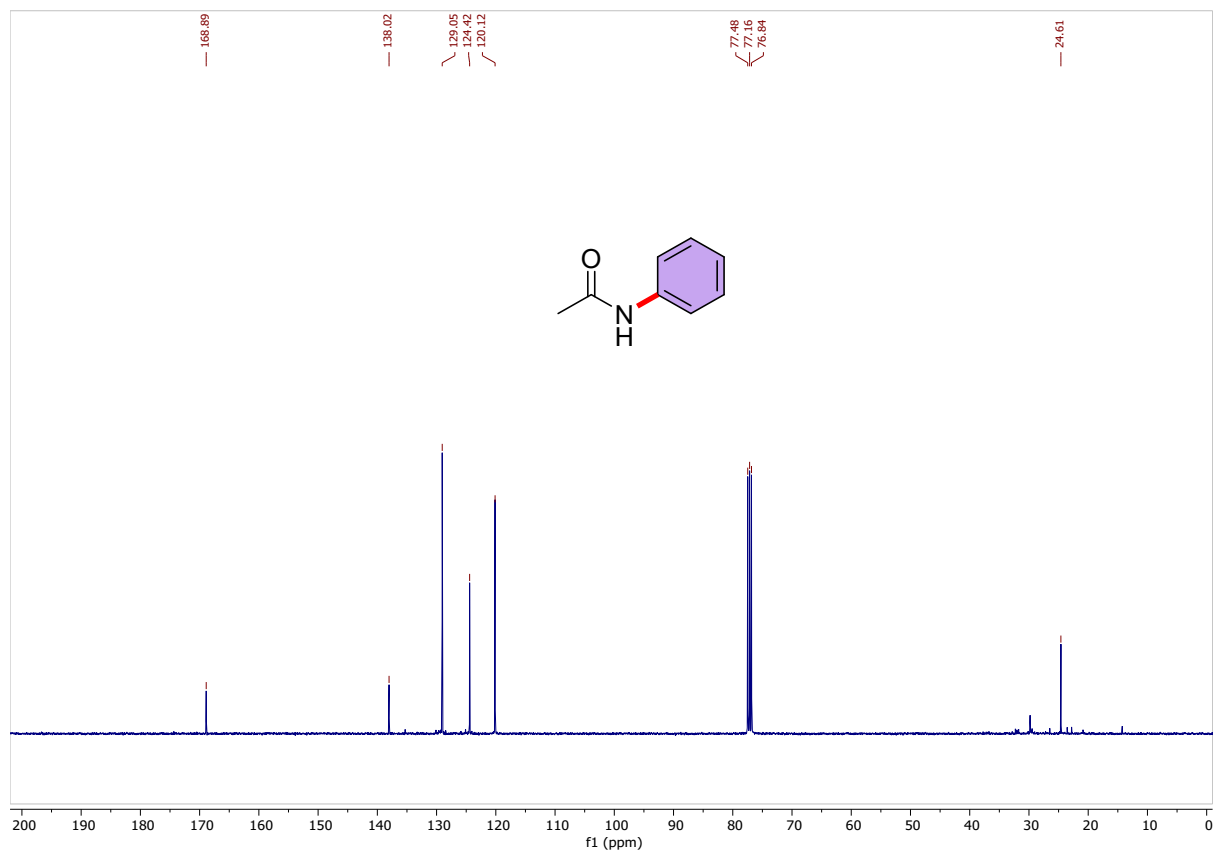
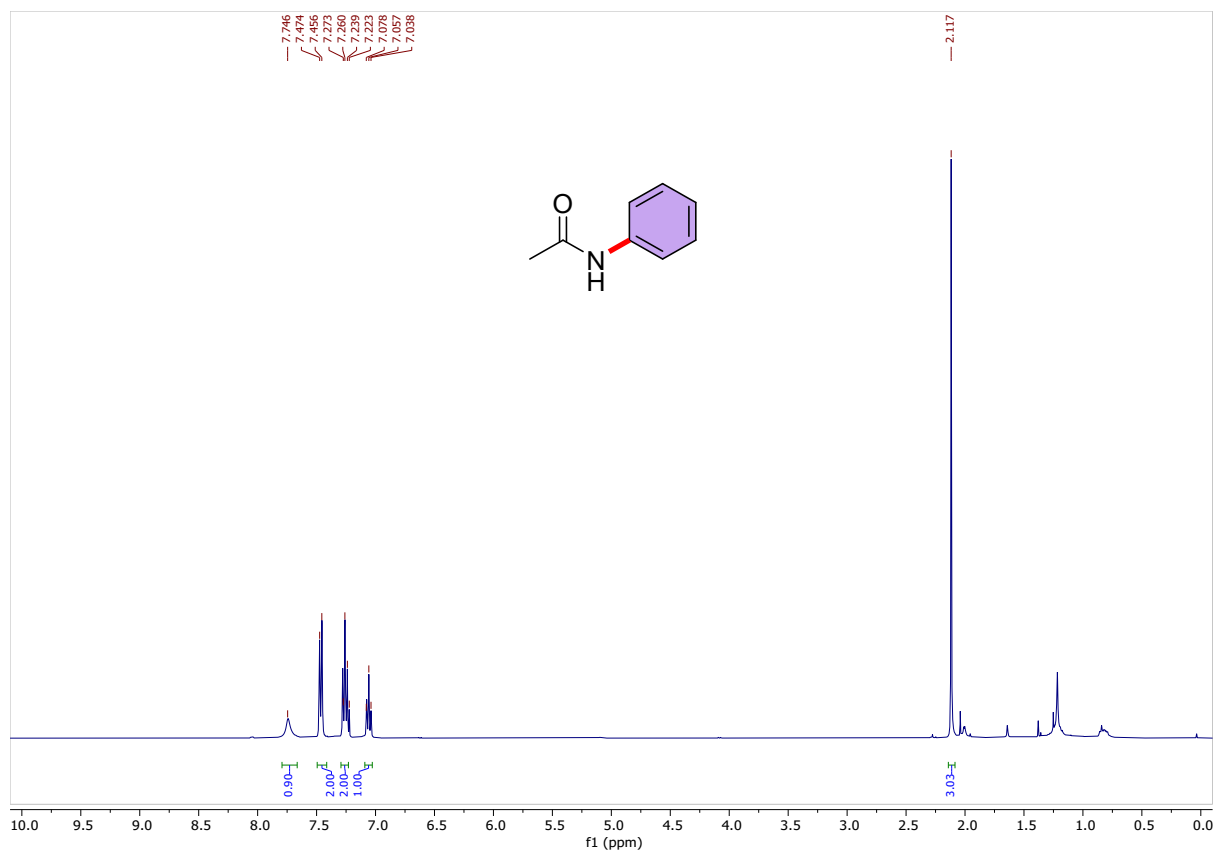
N-phenylnicotinamide (29)



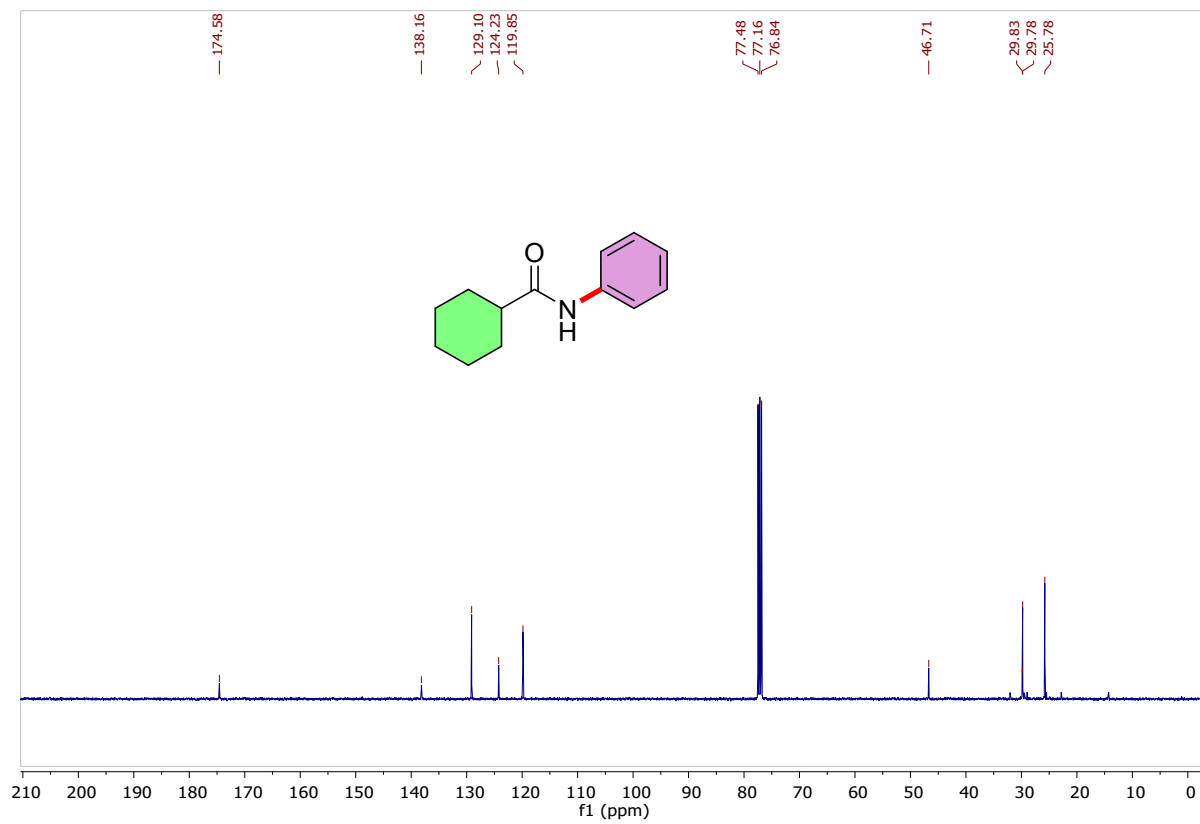
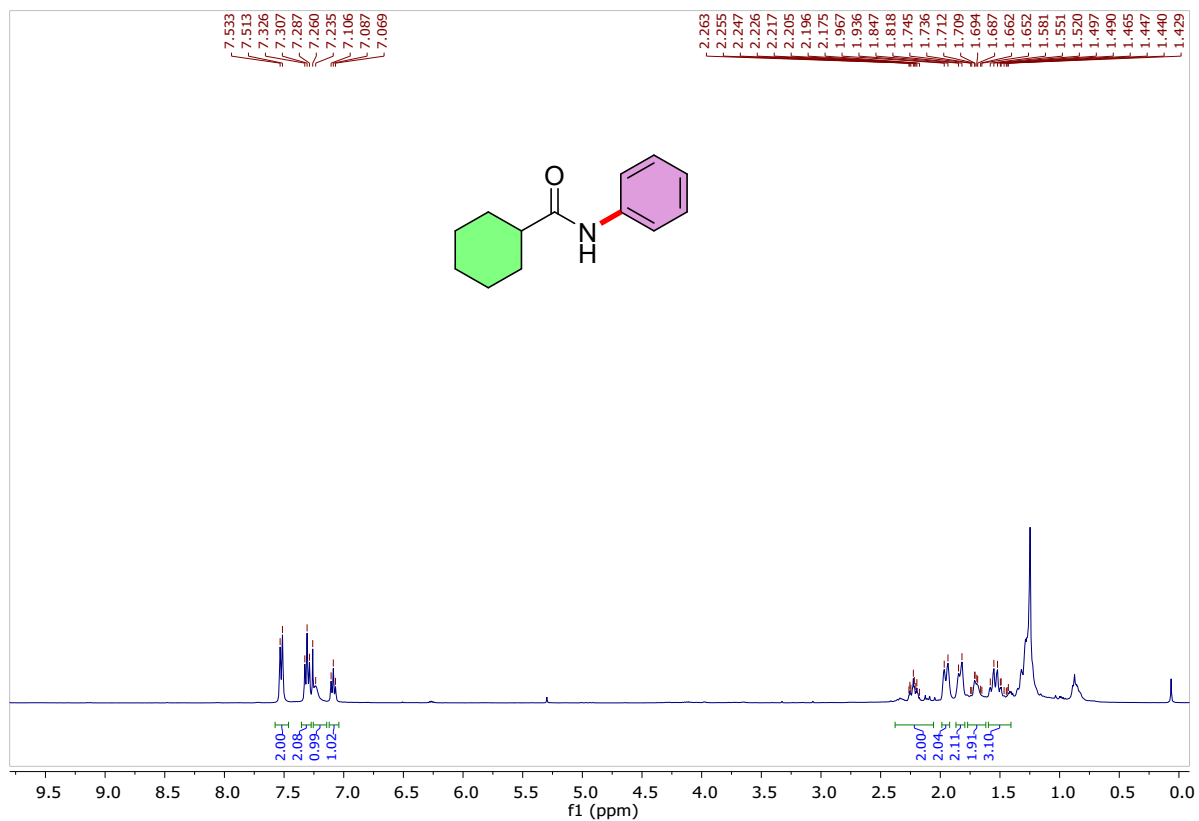
N-(quinolin-3-yl)nicotinamide (30)



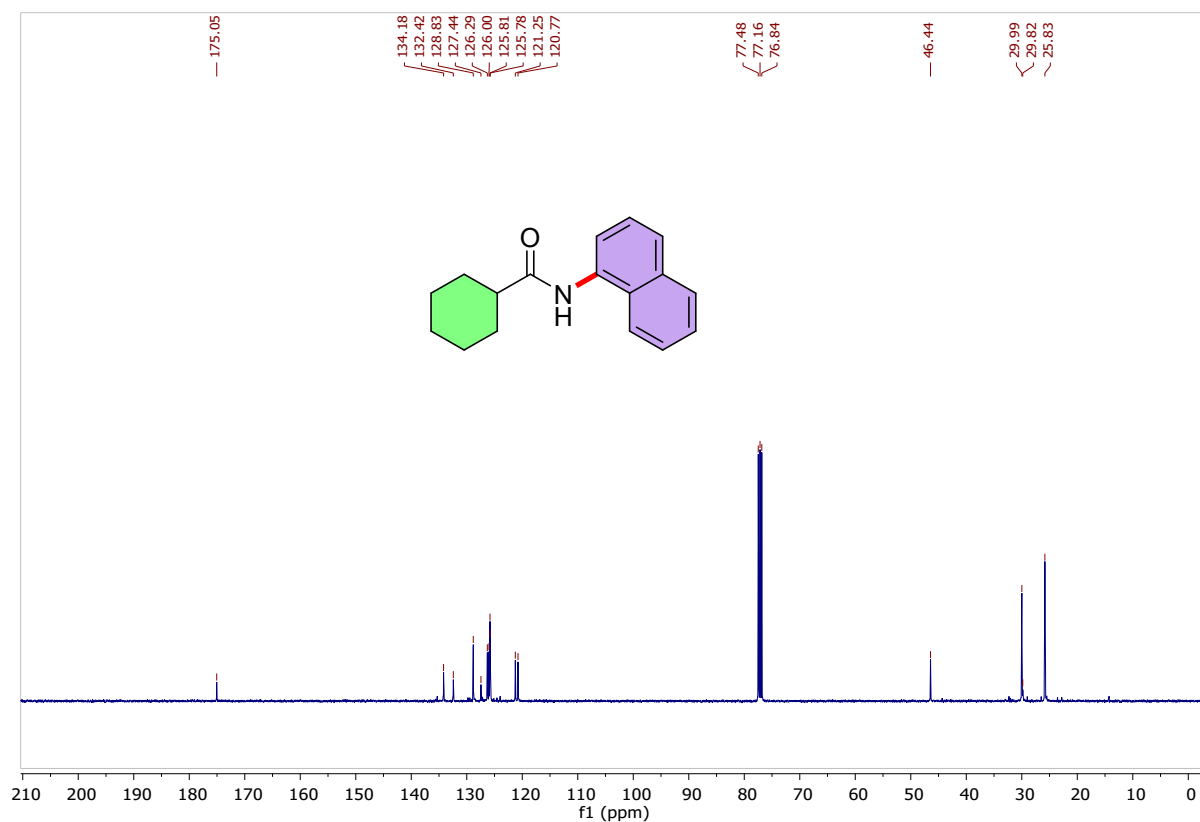
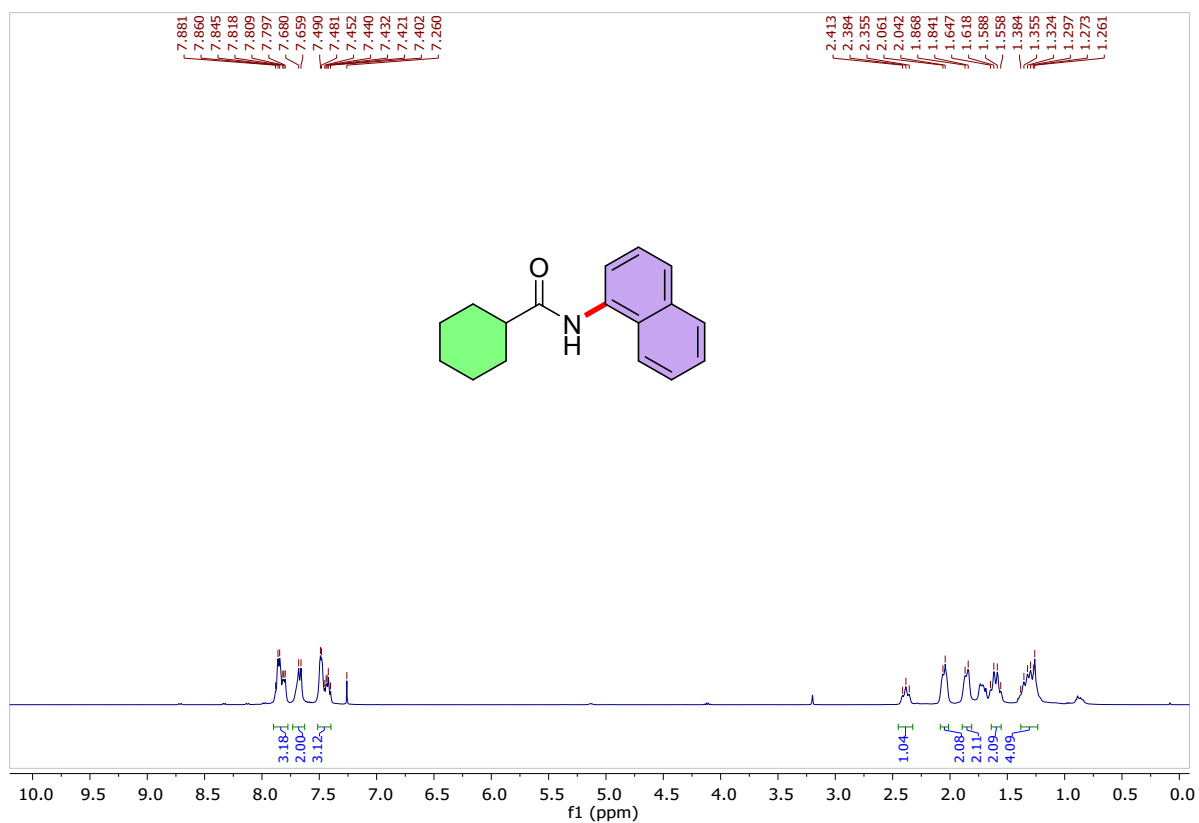
N-phenylacetamide (31)



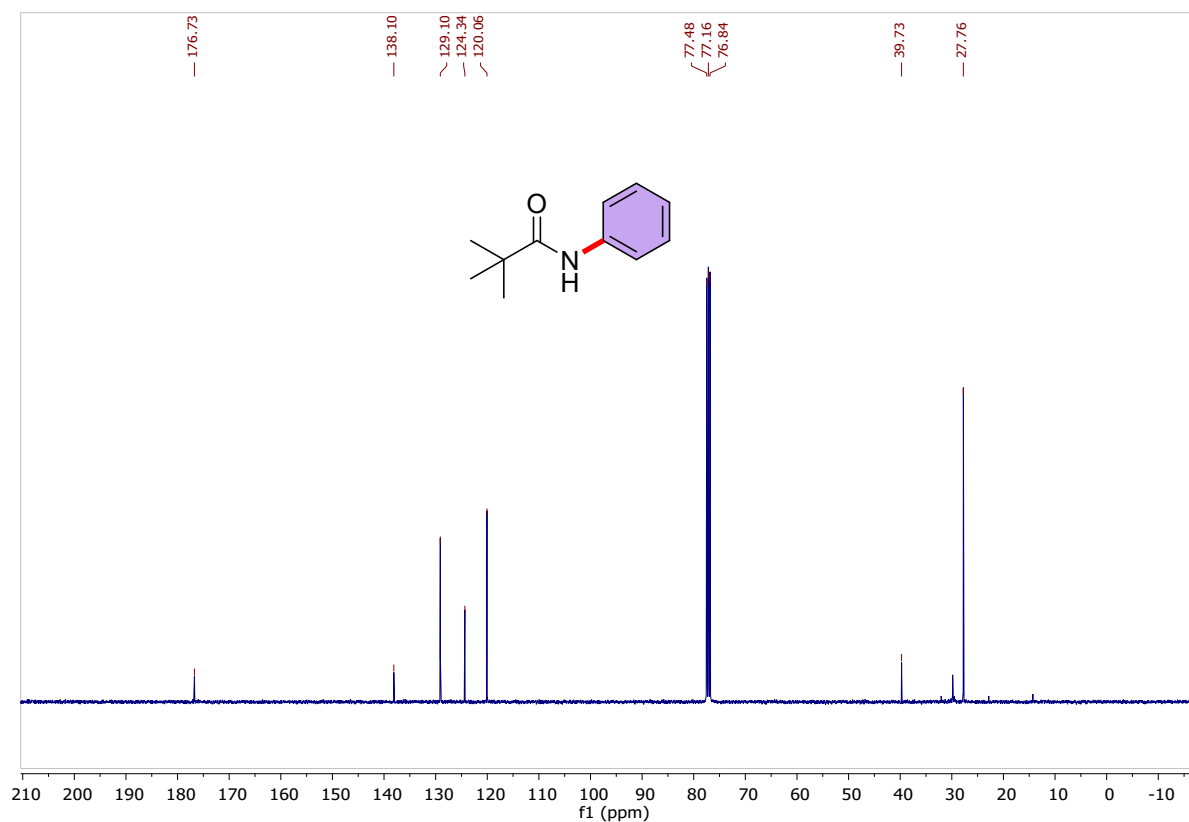
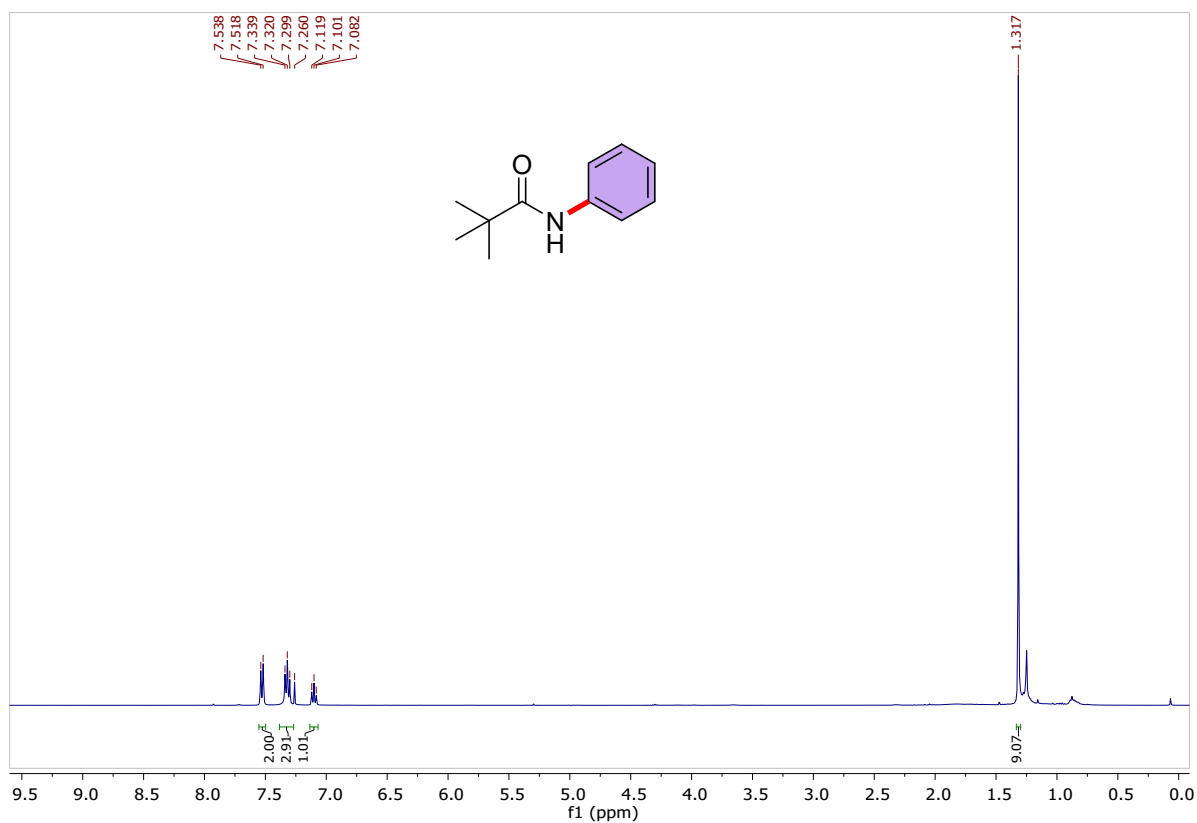
***N*-phenylcyclohexanecarboxamide (32)**



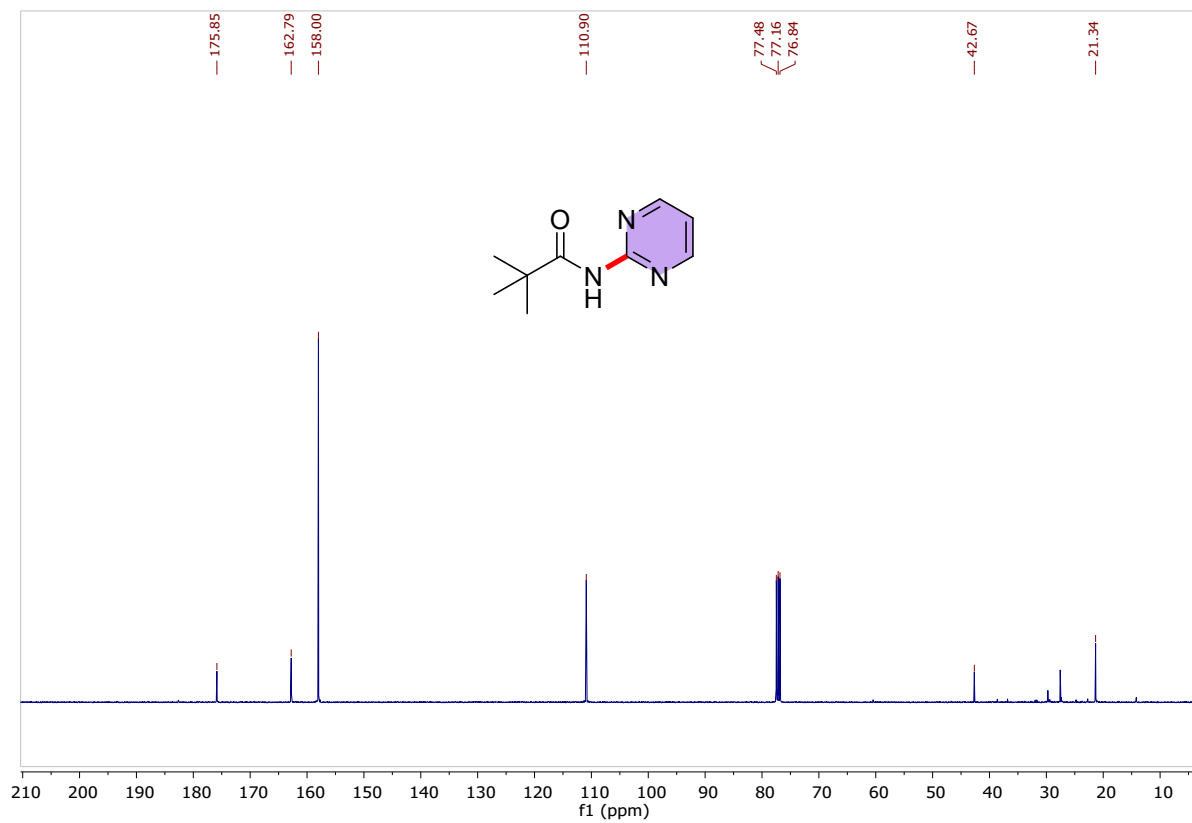
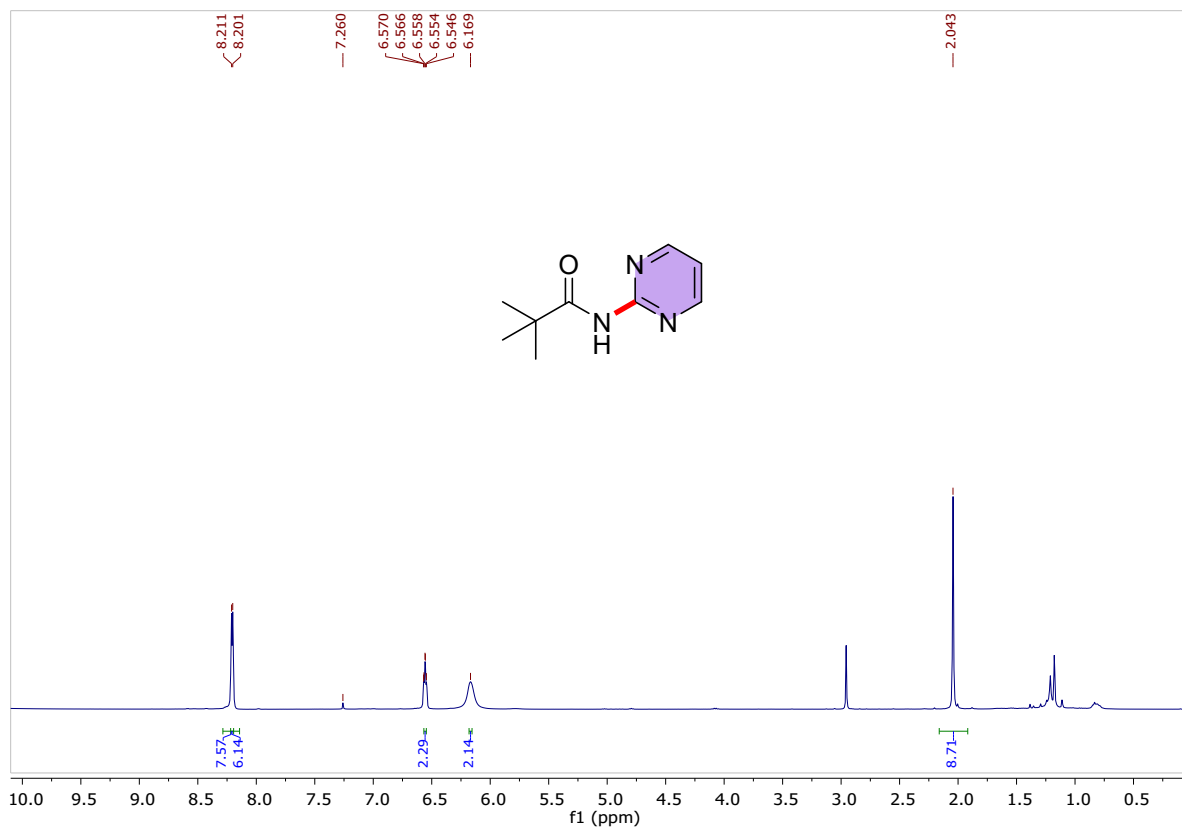
***N*-(naphthalen-1-yl)cyclohexanecarboxamide (33)**



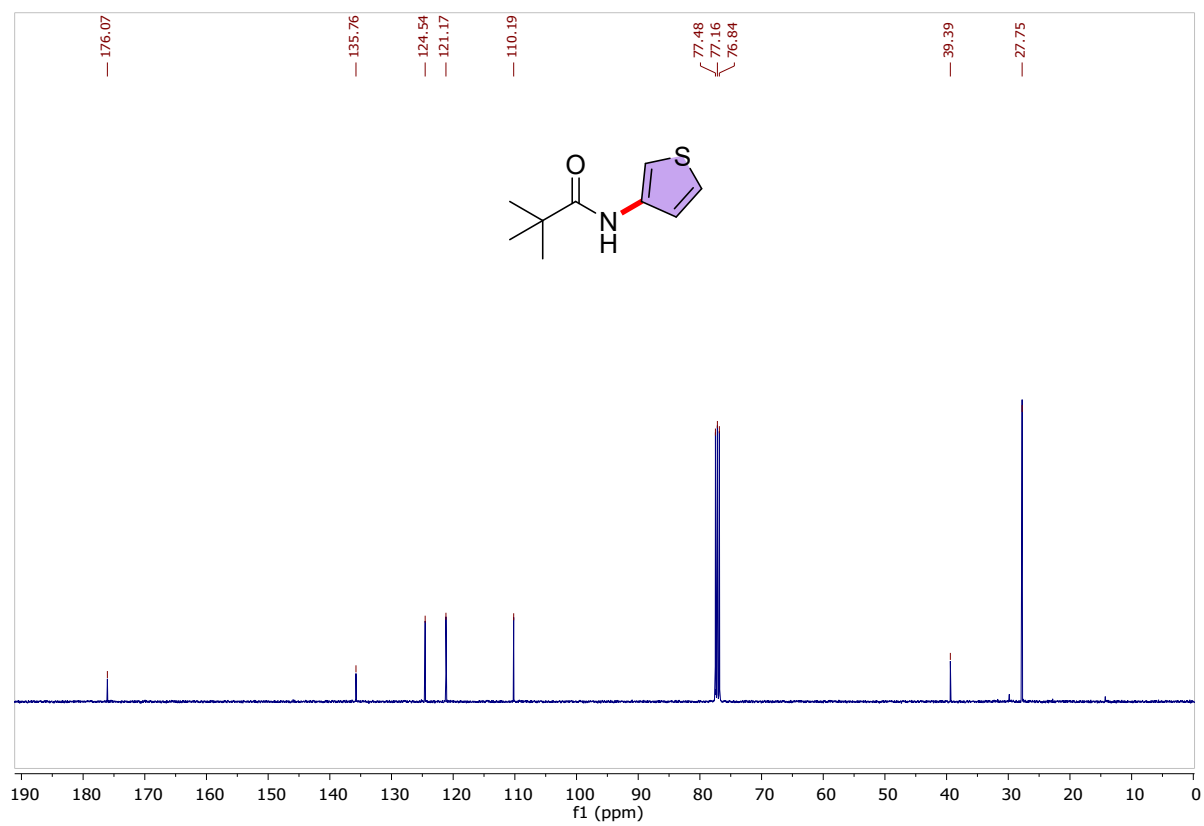
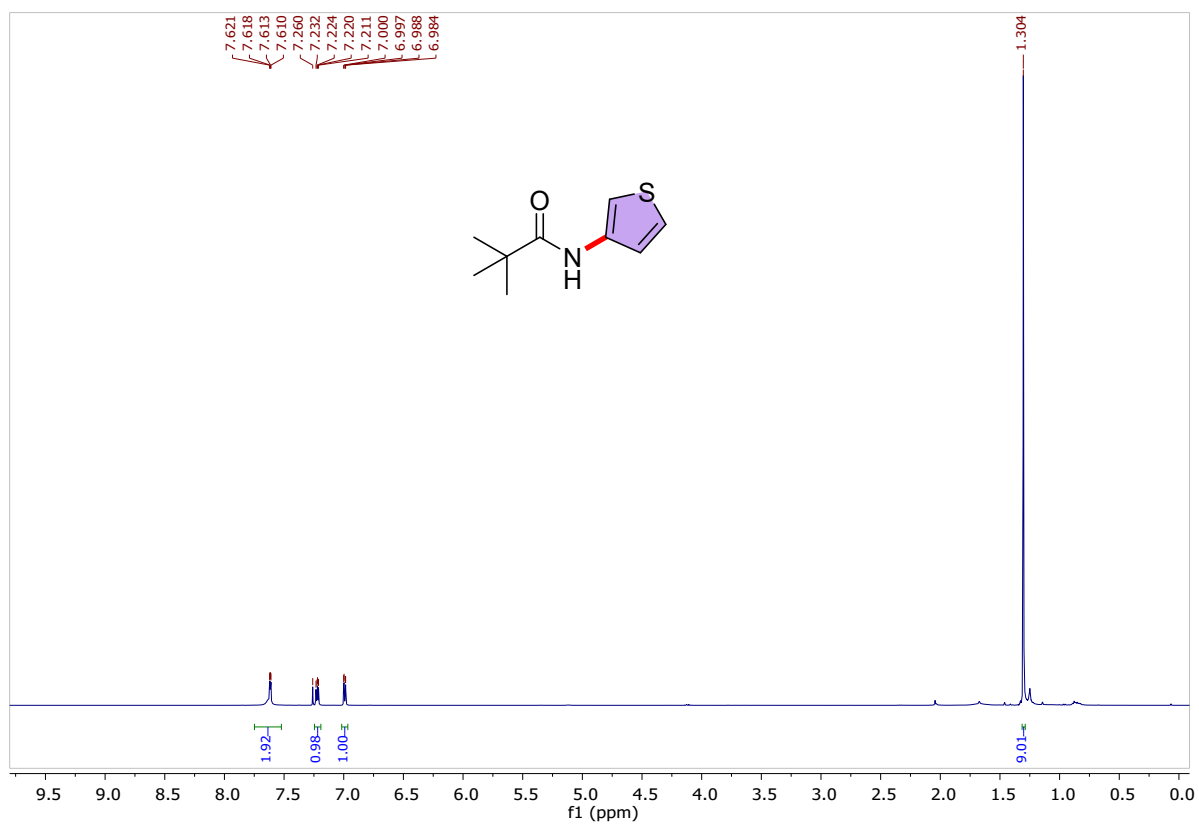
N-phenylpivalamide (34)



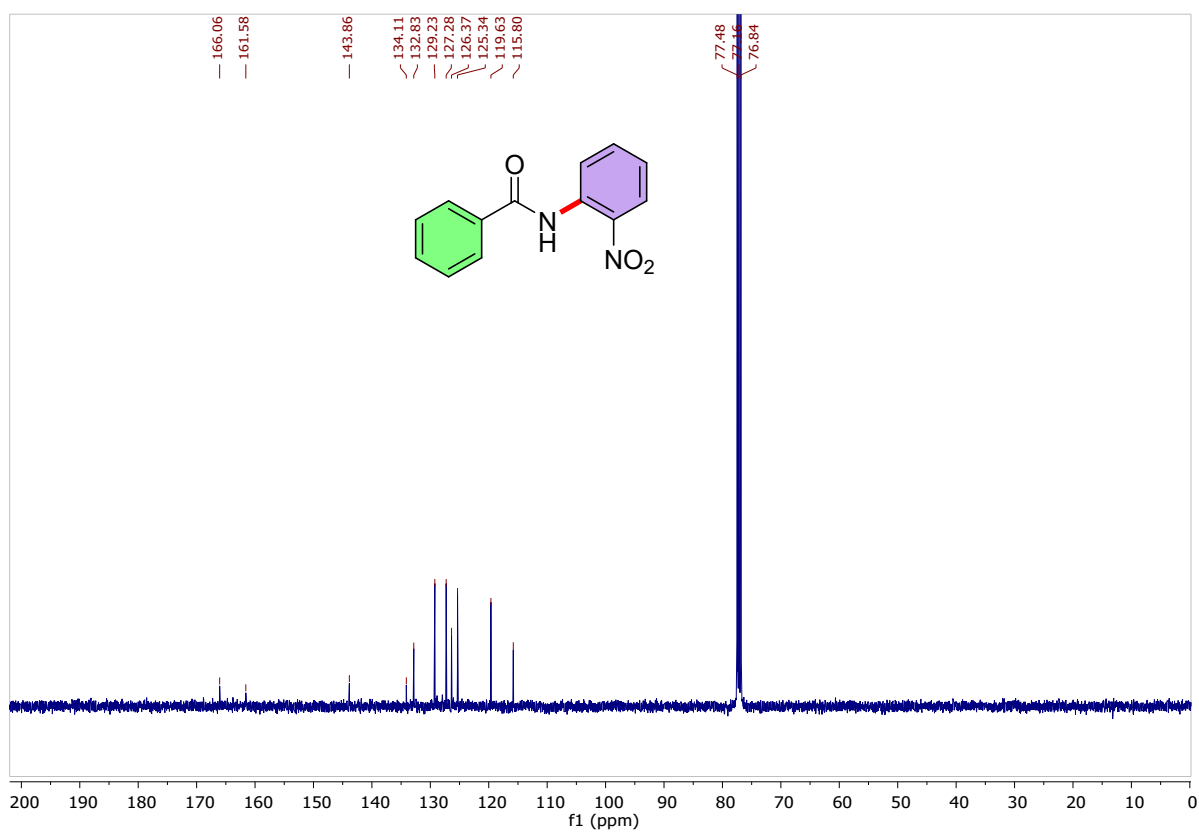
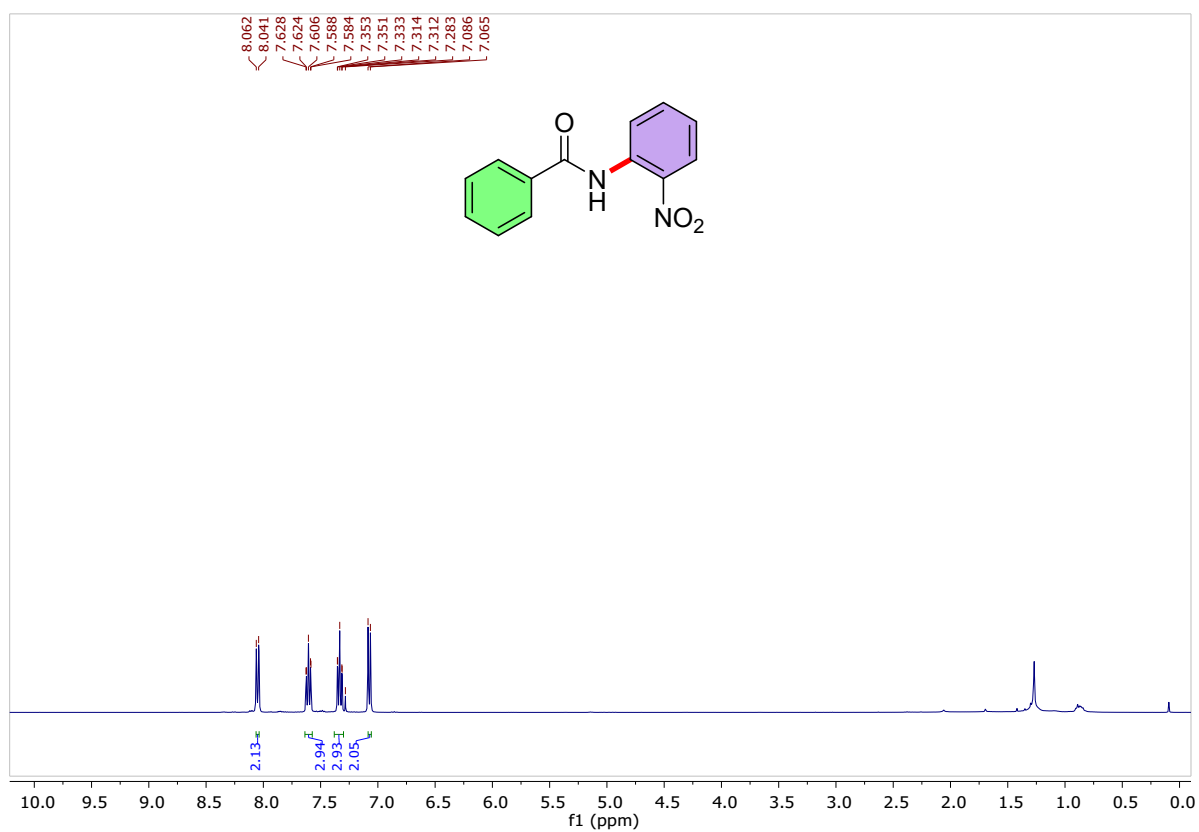
***N*-(pyrimidin-2-yl)pivalamide (35)**



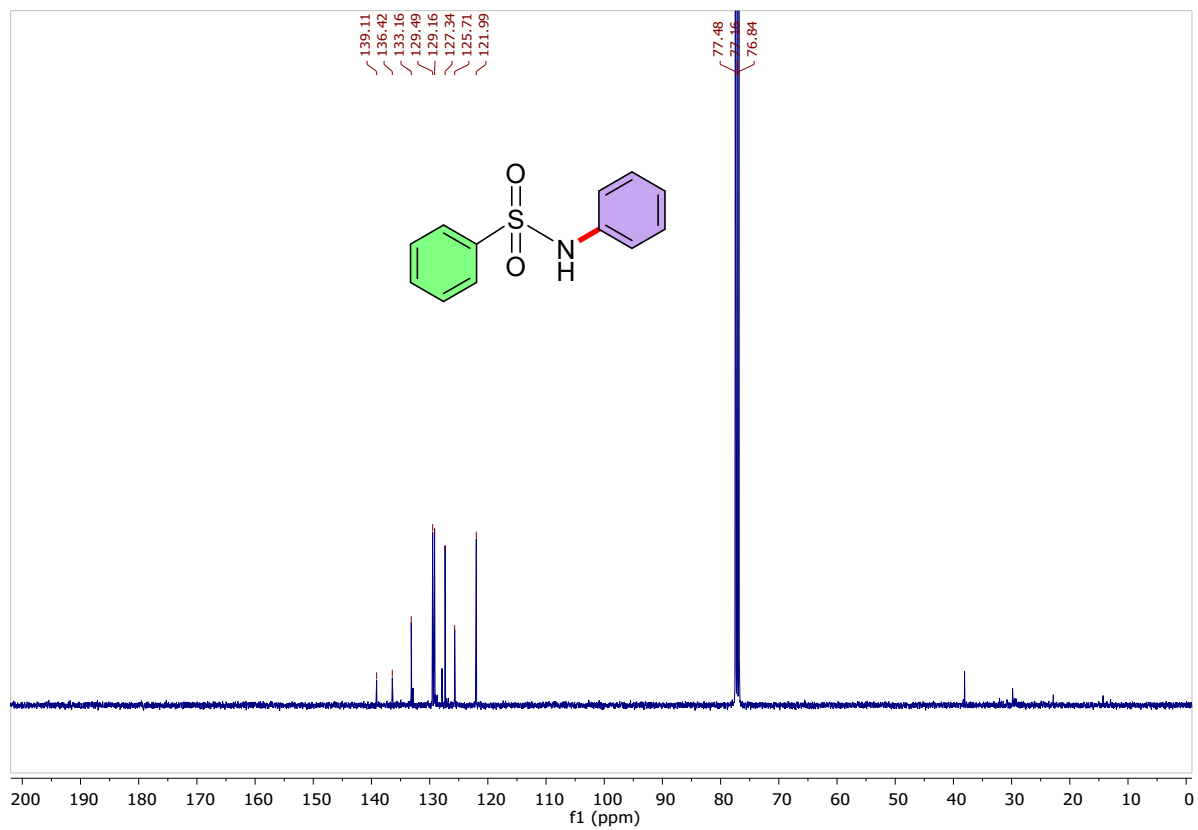
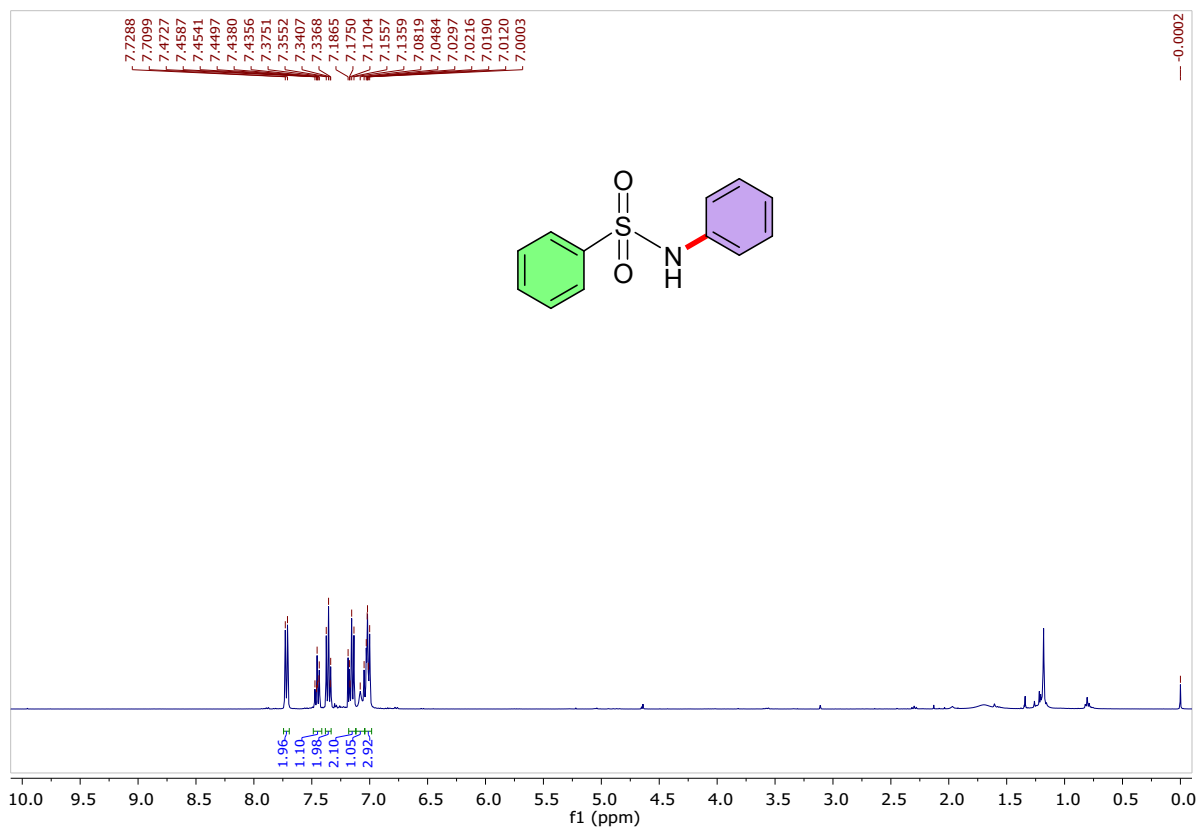
***N*-(thiophen-3-yl)pivalamide (36)**



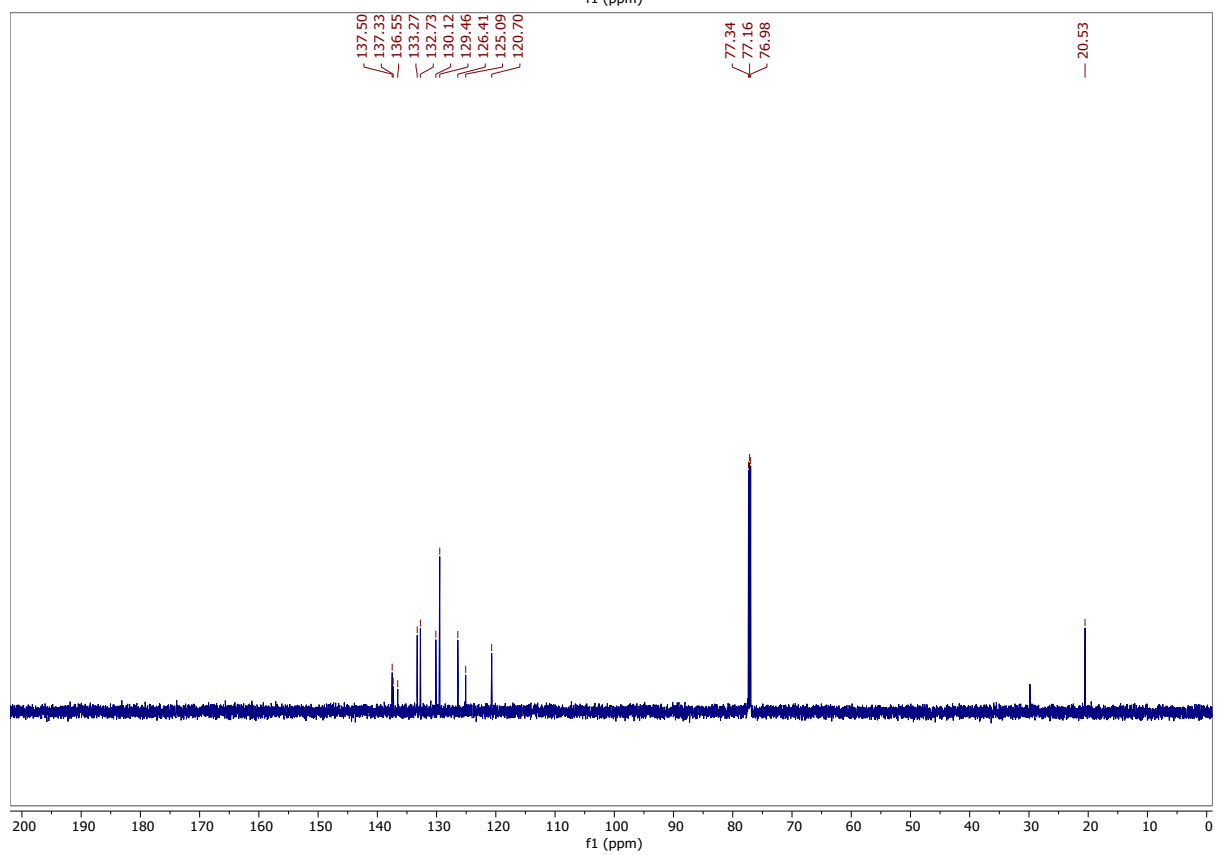
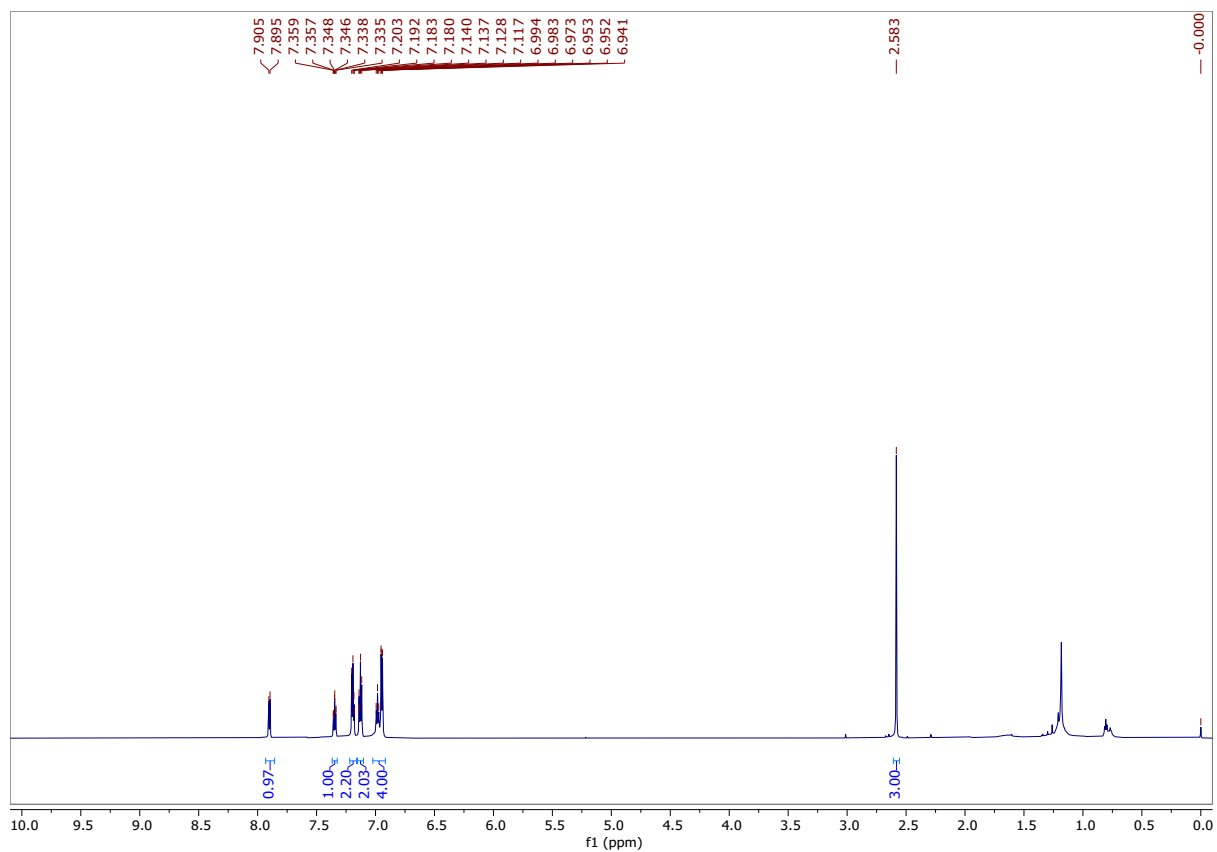
***N*-(2-nitrophenyl)benzamide (37)**



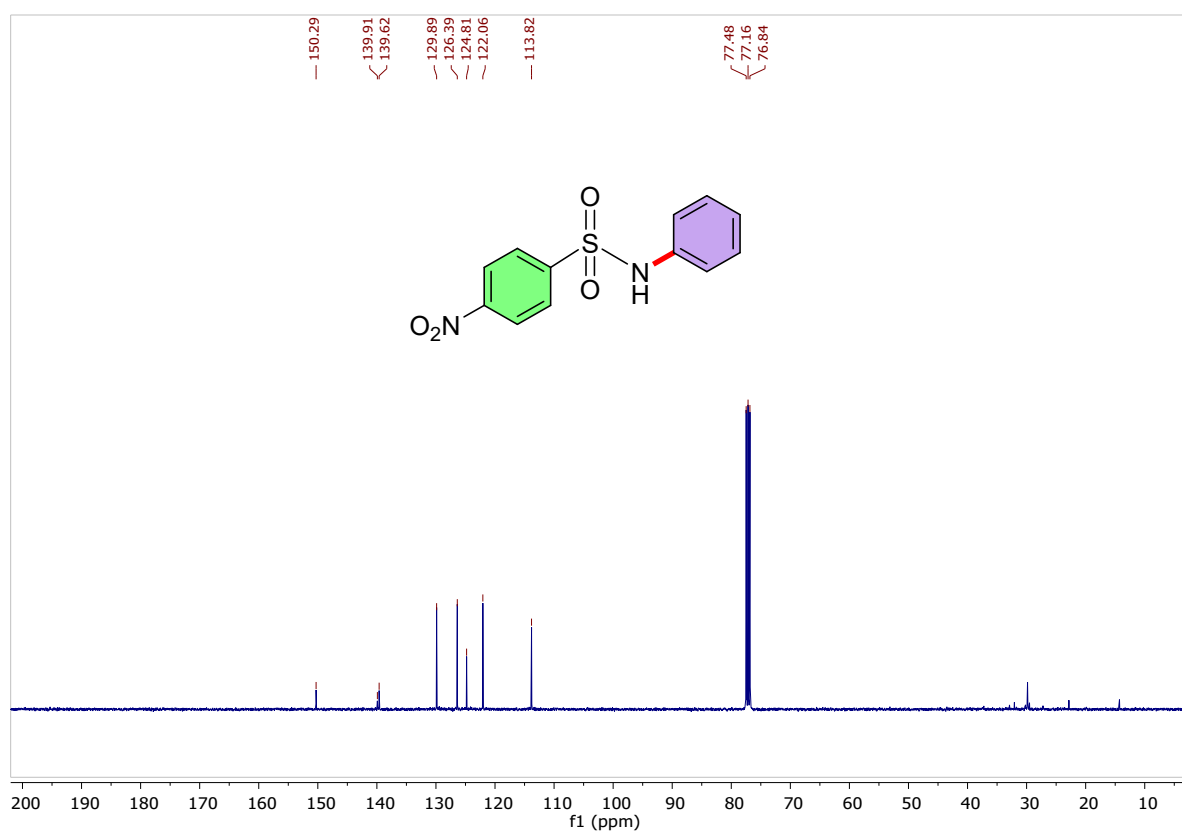
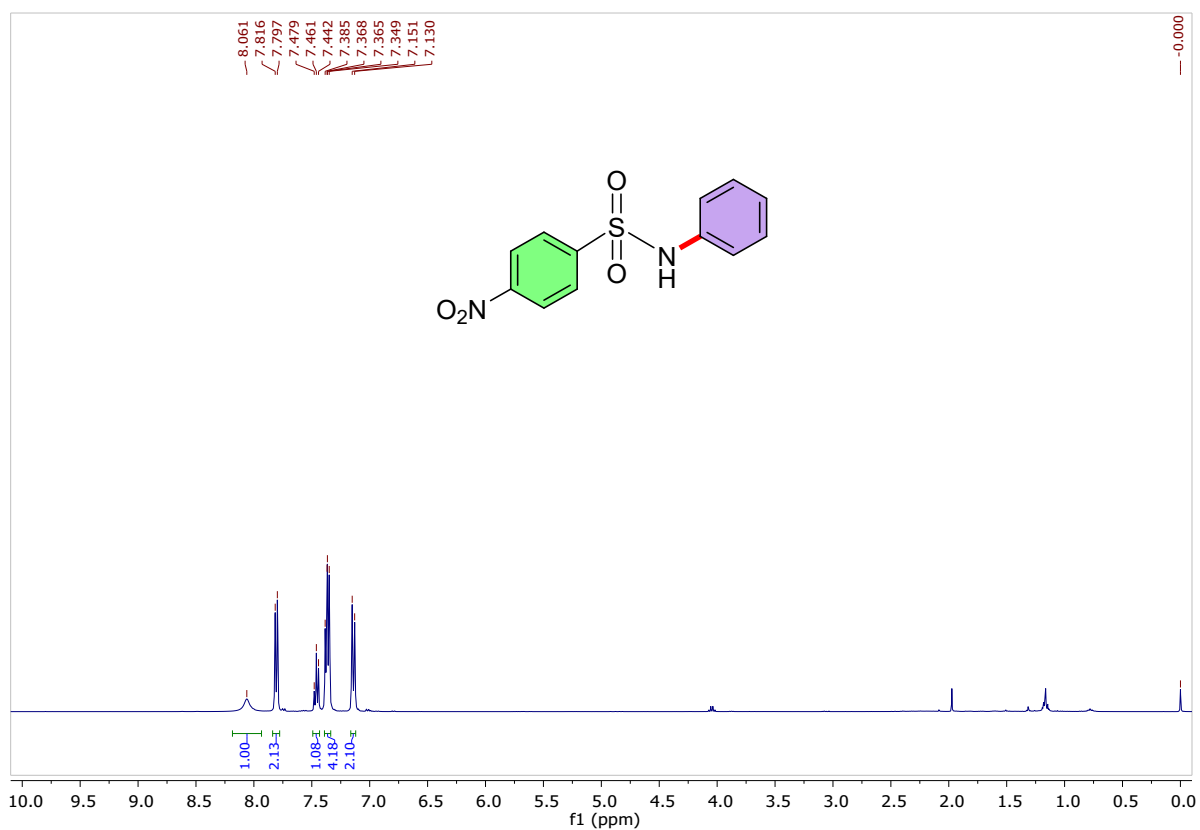
***N*-phenylbenzenesulfonamide (38):**



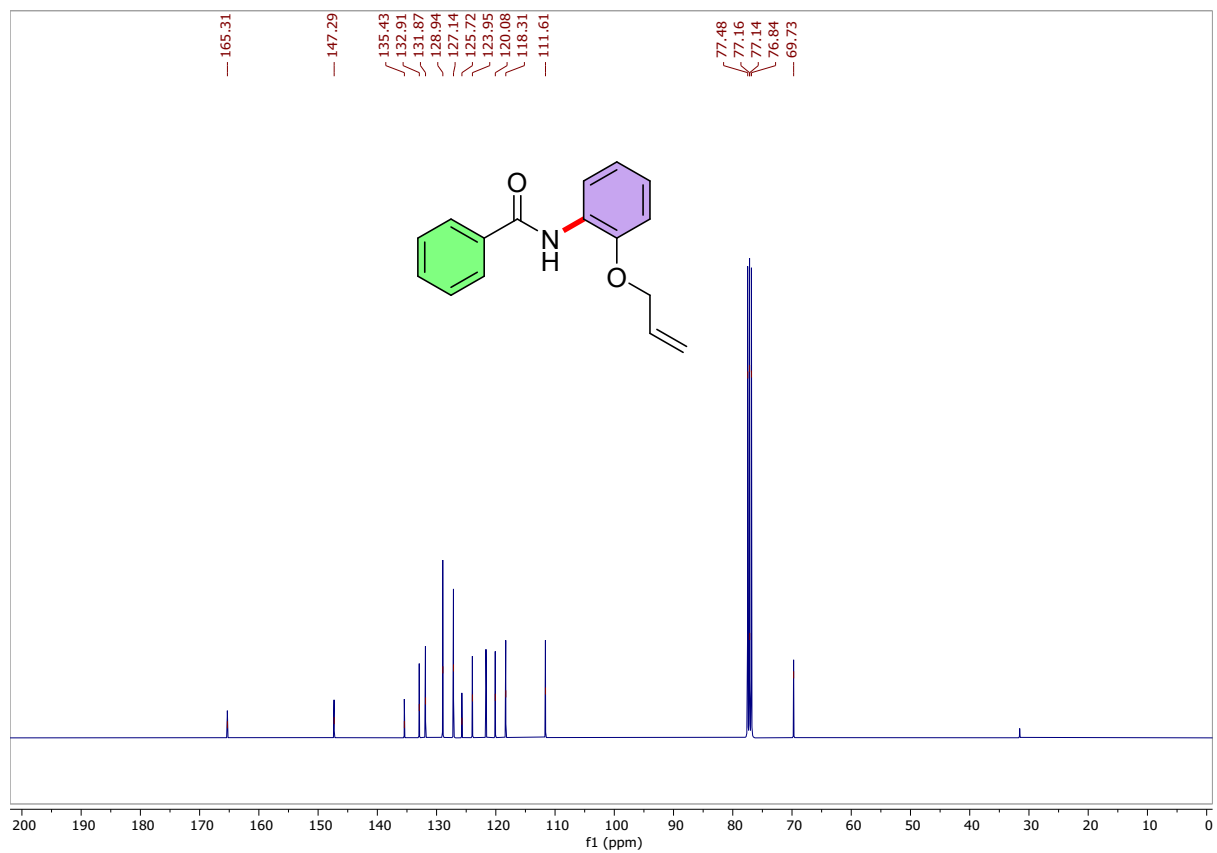
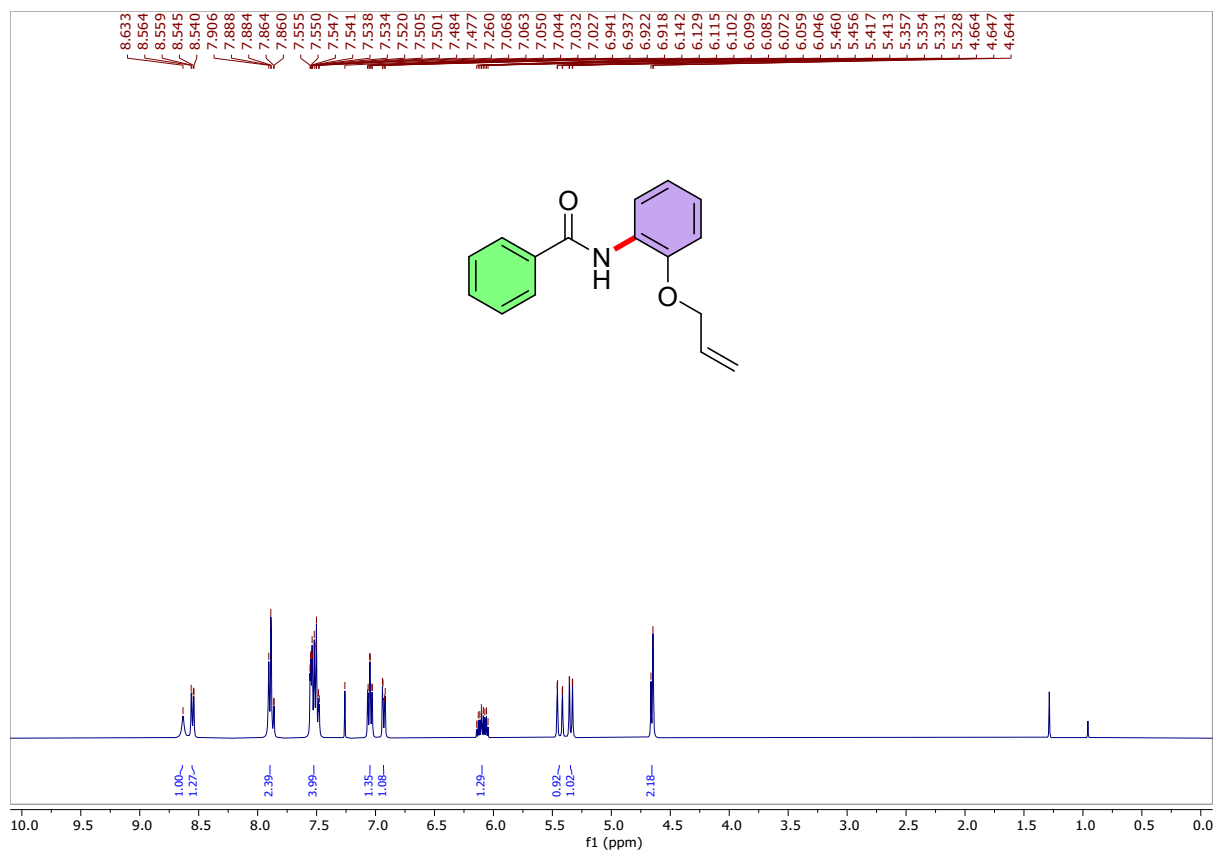
2-methyl-N-phenylbenzenesulfonamide (39):



4-nitro-*N*-phenylbenzenesulfonamide (40):



***N*-(2-(allyloxy)phenyl)benzamide (41)**



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