

Supplementary material

A General Synthesis of Aromatic Amides via Palladium-Catalyzed direct Aminocarbonylation of Aryl Chlorides

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Table of contents

1. Supplement to the experiments
2. NMR data for the main products

1. Supplement to the experiments

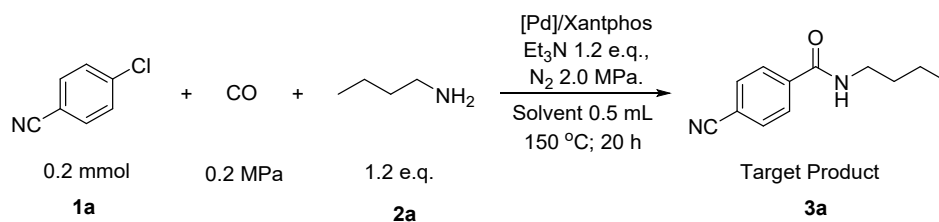
1.1 General considerations

The chemical reagents were purchased from Merck Chemicals, ABCR Chemicals or TCI Chemicals, which were used as received. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 300 spectrometer. Conversion and selectivity were determined by Agilent 6890N GC and Agilent 5973 Network GC-MS.

1.2 Supplement to Aminocarbonylation of Aryl Chlorides

All the palladium precursors and solvents in this part are commercially available.

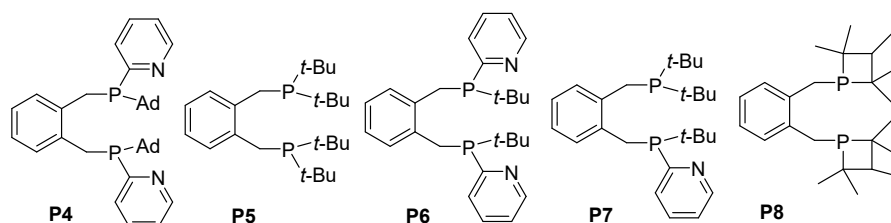
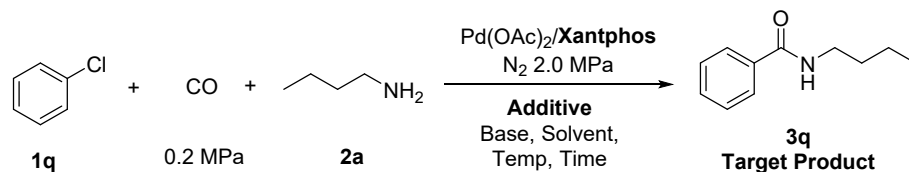
Table S1 Aminocarbonylation of 4-chlorobenzonitrile under different palladium precursors and solvents ^a



Entry	Pd catalyst	P-Ligand	Base	Solvent	Conv. (%) ^b	Sel. _{3a} (%) ^b
1	Pd(OAc)₂	Xantphos	Et₃N	1,4-dioxane	98	97
2	Pd(CH ₃ CN) ₂ Cl ₂	Xantphos	Et ₃ N	1,4-dioxane	90	90
3	Pd(PPh ₃) ₂ Cl ₂	Xantphos	Et ₃ N	1,4-dioxane	89	88
4	Pd(PPh ₃) ₄	Xantphos	Et ₃ N	1,4-dioxane	85	91
5	Pd/C (10 %)	Xantphos	Et ₃ N	1,4-dioxane	56	94
6	Pd(cod)Cl ₂	Xantphos	Et ₃ N	1,4-dioxane	84	89
7	Pd(PhCN) ₂ Cl ₂	Xantphos	Et ₃ N	1,4-dioxane	80	96
8	[Pd(allyl)Cl] ₂	Xantphos	Et ₃ N	1,4-dioxane	85	86
9	Pd(OAc) ₂	Xantphos	Et ₃ N	THF	83	80
10	Pd(OAc) ₂	Xantphos	Et ₃ N	DMSO	72	84
11	Pd(OAc) ₂	Xantphos	Et ₃ N	Toluene	92	90
12	Pd(OAc) ₂	Xantphos	Et ₃ N	MeCN	85	96
13	Pd(OAc) ₂	Xantphos	Et ₃ N	DMF	93	5
14	Pd(OAc) ₂	Xantphos	Et ₃ N	DMAc	95	38

^a 4-Chlorobenzonitrile (0.2 mmol, 27.5 mg), *n*-butylamine 0.24 mmol (17.52 mg, 1.2 e.q.), Pd precursor 0.004 mmol, S/[Pd] mol ratio = 50, 0.016 mmol Xantphos, Et₃N 0.24 mmol (1.2 e.q.), CO 0.2 MPa, N₂ 2.0 MPa, 150 °C, solvent 0.5 mL, time 20 h; ^b Determined by GC-MS, dodecane (C₁₂) as internal standard.

Table S2 Aminocarbonylation of chlorobenzene under different ligands, solvents and temperature ^a



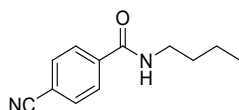
Entry	P-Ligand	Additive	Base	Temp (°C)	Solvent	Conv. (%) ^b	Sel. 3q (%) ^b
1	Xantphos	CsCl	Et₃N	150	1,4-dioxane	45	94
2	PPh₃	CsCl	Et ₃ N	150	1,4-dioxane	21	8
3	P4	CsCl	Et ₃ N	150	1,4-dioxane	1	Trace
4	P5	CsCl	Et ₃ N	150	1,4-dioxane	20	34
5	P6	CsCl	Et ₃ N	150	1,4-dioxane	18	38
6	P7	CsCl	Et ₃ N	150	1,4-dioxane	23	36
7	P8	CsCl	Et ₃ N	150	1,4-dioxane	14	27
8 ^c	Xantphos	CsCl	Et ₃ N	150	1,4-dioxane	21	94
9 ^d	Xantphos	CsCl	Et ₃ N	150	1,4-dioxane	6	96
10	Xantphos	CsCl	Et ₃ N	150	THF	43	86
11	Xantphos	CsCl	Et ₃ N	150	DMSO	35	56
12	Xantphos	CsCl	Et ₃ N	150	Toluene	23	96
13	Xantphos	CsCl	Et ₃ N	150	MeCN	23	5
14	Xantphos	CsCl	Et ₃ N	150	DMF	53	13
15	Xantphos	CsCl	Et ₃ N	150	DMAc	39	8
16	Xantphos	CsCl	Et ₃ N	140	1,4-dioxane	32	68
17	Xantphos	CsCl	Et ₃ N	100	1,4-dioxane	7	27

^a Chlorobenzene (0.2 mmol), butylamine 0.24 mmol (1.2 e.q.), Pd(OAc)₂ 0.004 mmol, [Pd]/[P] mol ratio = 1/8, base 0.24 mmol, additive 0.2 mmol, CO 0.2 MPa, N₂ 2.0 MPa, 150 °C, solvent 0.5 ml, time 20 h; ^b Determined by GC and GC-MS, dodecane (C₁₂) as internal standard; ^c [Pd] 1 % mol, S/[Pd] mol ratio = 100, Xantphos 4 % mol; ^d [Pd] 0.5 % mol, S/[Pd] mol ratio = 200, Xantphos 2 % mol.

2. NMR data of the main products

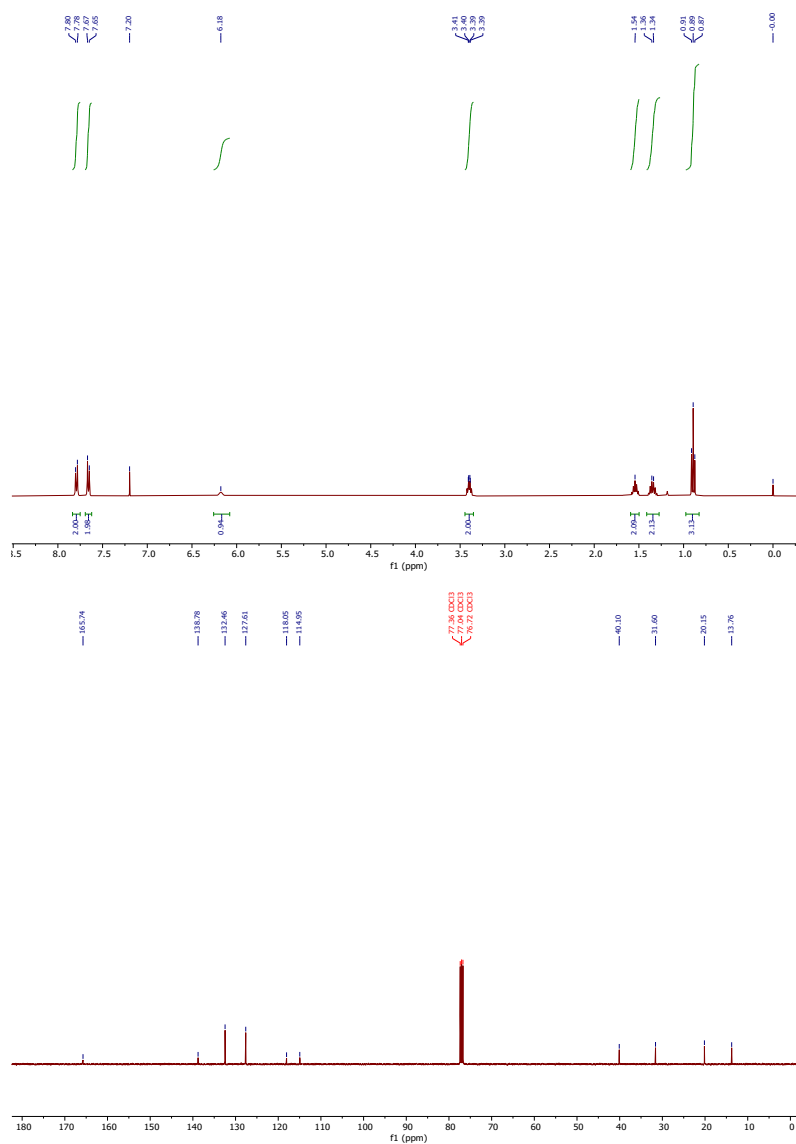
All the products separated are known products. Methods for the separation of all compounds are according to the references [1-5].

N-butyl-4-cyanobenzamide (3a)

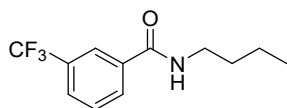


^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, $J = 8.1$ Hz, 2H), 7.66 (d, $J = 8.0$ Hz, 2H), 6.18 (s, 1H), 3.45-3.35 (m, 2H), 1.54 (s, 2H), 1.35 (d, $J = 7.7$ Hz, 2H), 0.89 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.74, 138.78, 132.46, 127.61, 118.05, 114.95, 40.10, 31.60, 20.15, 13.76.

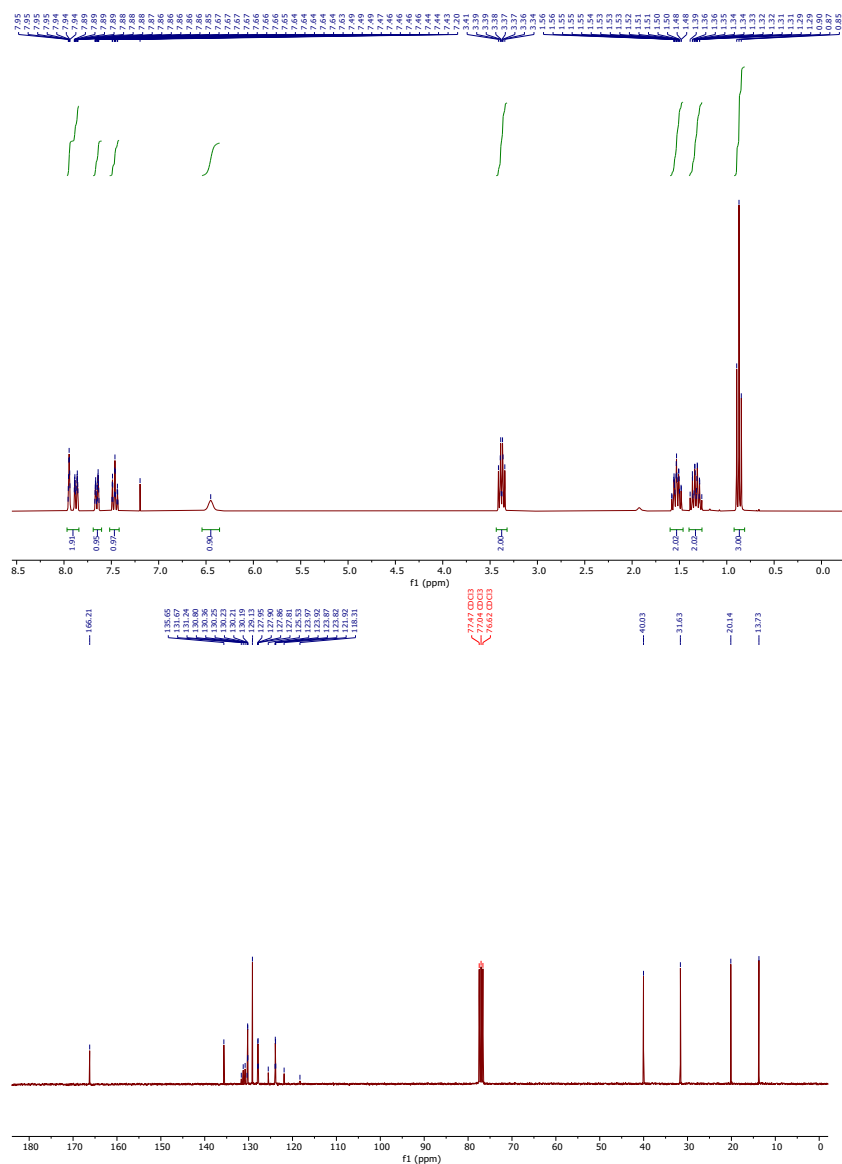


N-butyl-3-(trifluoromethyl)benzamide (3c)

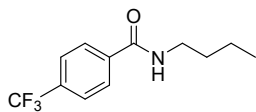


^1H NMR (300 MHz, Chloroform-*d*) δ 7.97-7.84 (m, 2H), 7.65 (dddd, $J = 7.8, 1.9, 1.2, 0.7$ Hz, 1H), 7.46 (tp, $J = 7.8, 0.8$ Hz, 1H), 6.45 (s, 1H), 3.38 (td, $J = 7.2, 5.7$ Hz, 2H), 1.60-1.46 (m, 2H), 1.40-1.26 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.21, 135.65, 131.67, 131.24, 130.80, 130.36, 130.25, 130.23, 130.21, 130.19, 129.13, 127.95, 127.90, 127.86, 127.81, 125.53, 123.97, 123.92, 123.87, 123.82, 121.92, 40.03, 31.63, 20.14, 13.73.

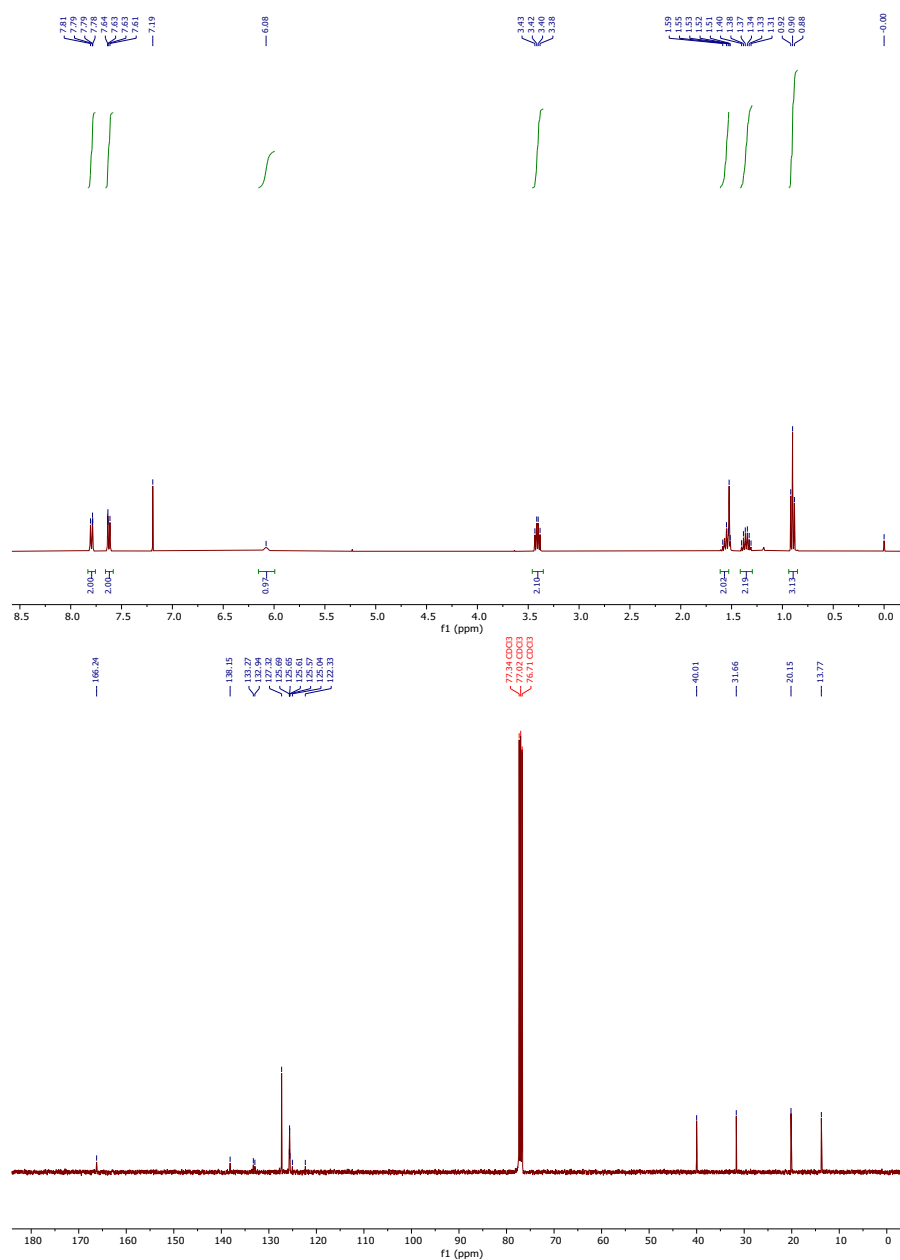


N-butyl-4-(trifluoromethyl)benzamide (**3d**)

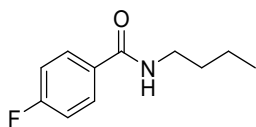


^1H NMR (400 MHz, Chloroform-*d*) δ 7.83-7.76 (m, 2H), 7.66-7.58 (m, 2H), 6.08 (s, 1H), 3.46-3.35 (m, 2H), 1.61-1.53 (m, 2H), 1.36 (dq, $J = 14.4, 7.3$ Hz, 2H), 0.90 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.24, 138.15, 133.27, 132.94, 127.32, 125.69, 125.65, 125.61, 125.57, 125.04, 122.33, 40.01, 31.66, 20.15, 13.77.

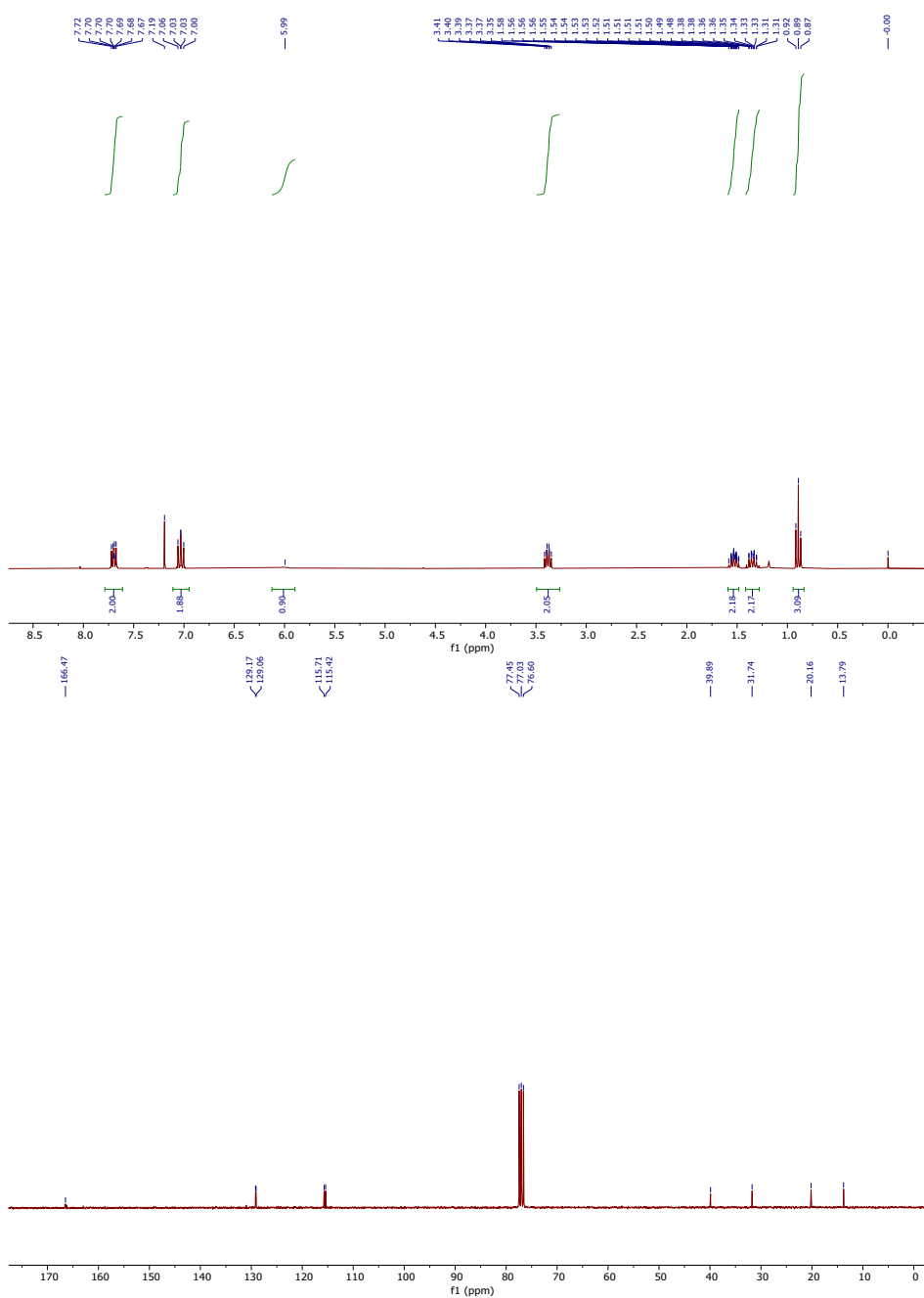


N-butyl-4-fluorobenzamide (**3e**)

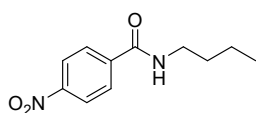


^1H NMR (300 MHz, Chloroform-*d*) δ 7.79-7.61 (m, 2H), 7.03 (dd, $J = 8.9, 8.4$ Hz, 2H), 5.99 (s, 1H), 3.38 (td, $J = 7.2, 5.7$ Hz, 2H), 1.59-1.48 (m, 2H), 1.42-1.28 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.47, 129.17, 129.06, 115.71, 115.42, 39.89, 31.74, 20.16, 13.79.

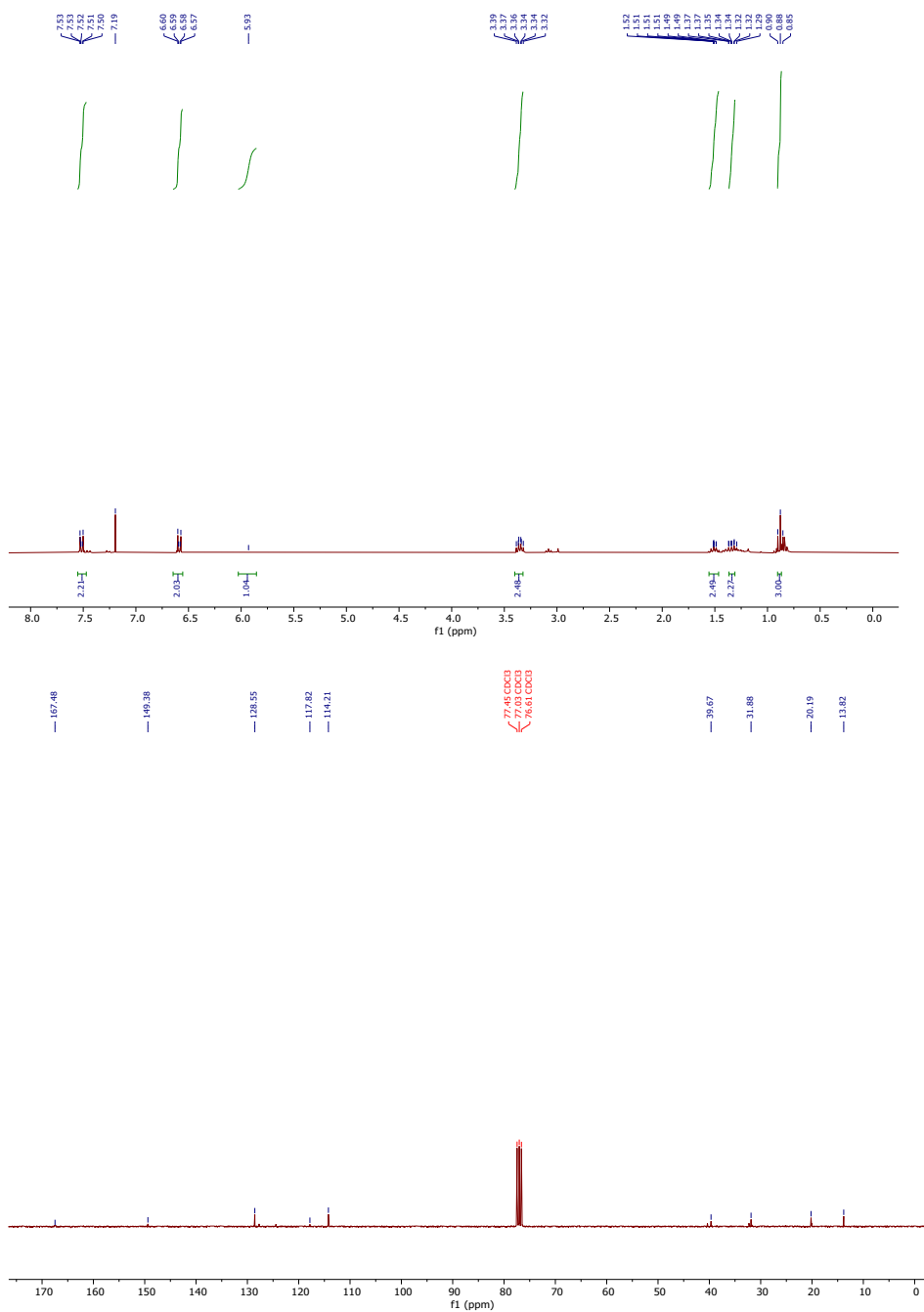


N-butyl-4-nitrobenzamide (**3f**)

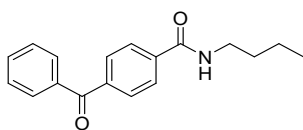


^1H NMR (300 MHz, Chloroform-*d*) δ 7.55-7.47 (m, 2H), 6.65-6.55 (m, 2H), 5.93 (s, 1H), 3.40-3.32 (m, 2H), 1.56-1.46 (m, 2H), 1.37-1.31 (m, 2H), 0.89 (d, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.48, 149.38, 128.55, 117.82, 114.21, 39.67, 31.88, 20.19, 13.82.

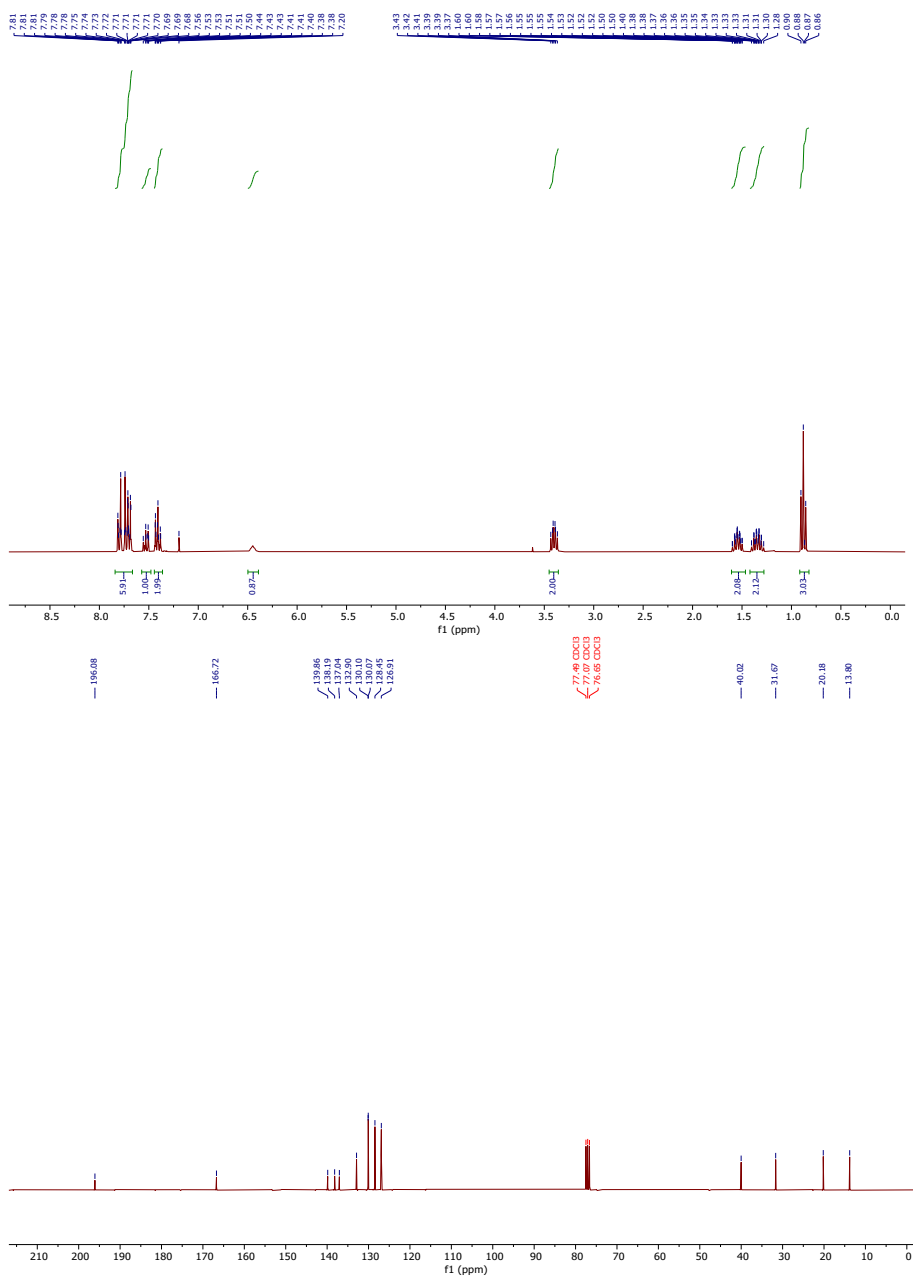


4-benzoyl-N-butylbenzamide (**3g**)

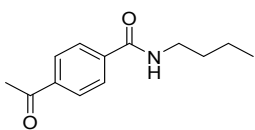


^1H NMR (300 MHz, Chloroform-*d*) δ 7.84-7.67 (m, 6H), 7.57-7.48 (m, 1H), 7.44-7.36 (m, 2H), 6.45 (t, $J = 5.7$ Hz, 1H), 3.40 (td, $J = 7.2, 5.7$ Hz, 2H), 1.61-1.47 (m, 2H), 1.42-1.28 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 196.08, 166.72, 139.86, 138.19, 137.04, 132.90, 130.10, 130.07, 128.45, 126.91, 40.02, 31.67, 20.18, 13.80.

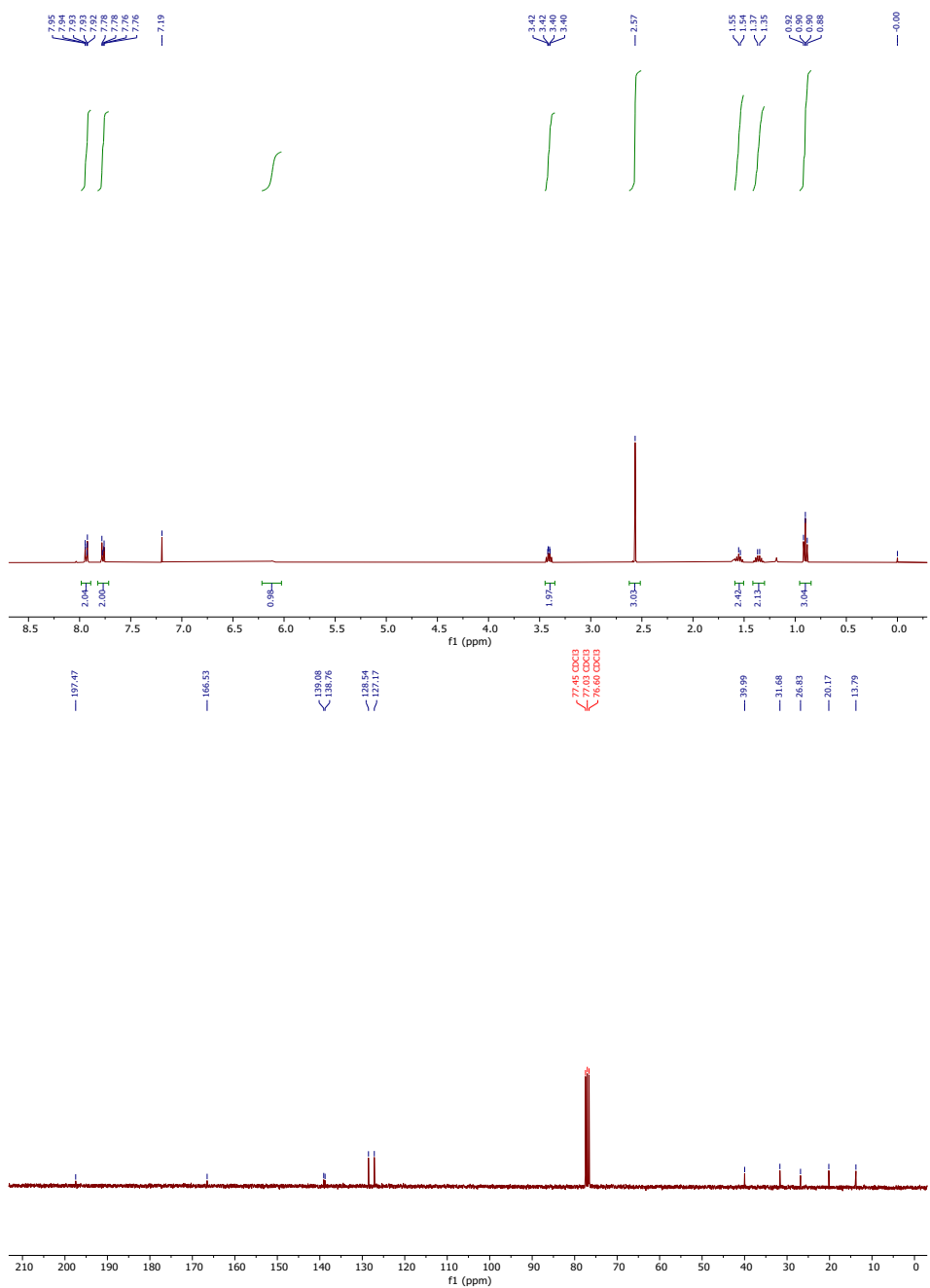


4-acetyl-N-butylbenzamide (**3h**)

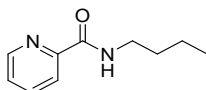


^1H NMR (400 MHz, Chloroform-*d*) δ 7.98-7.89 (m, 2H), 7.82-7.72 (m, 2H), 6.11 (s, 1H), 3.45-3.35 (m, 2H), 2.57 (s, 3H), 1.54 (d, $J = 6.9$ Hz, 2H), 1.36 (d, $J = 8.2$ Hz, 2H), 0.90 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.47, 166.53, 139.08, 138.76, 128.54, 127.17, 39.99, 31.68, 26.83, 20.17, 13.79.

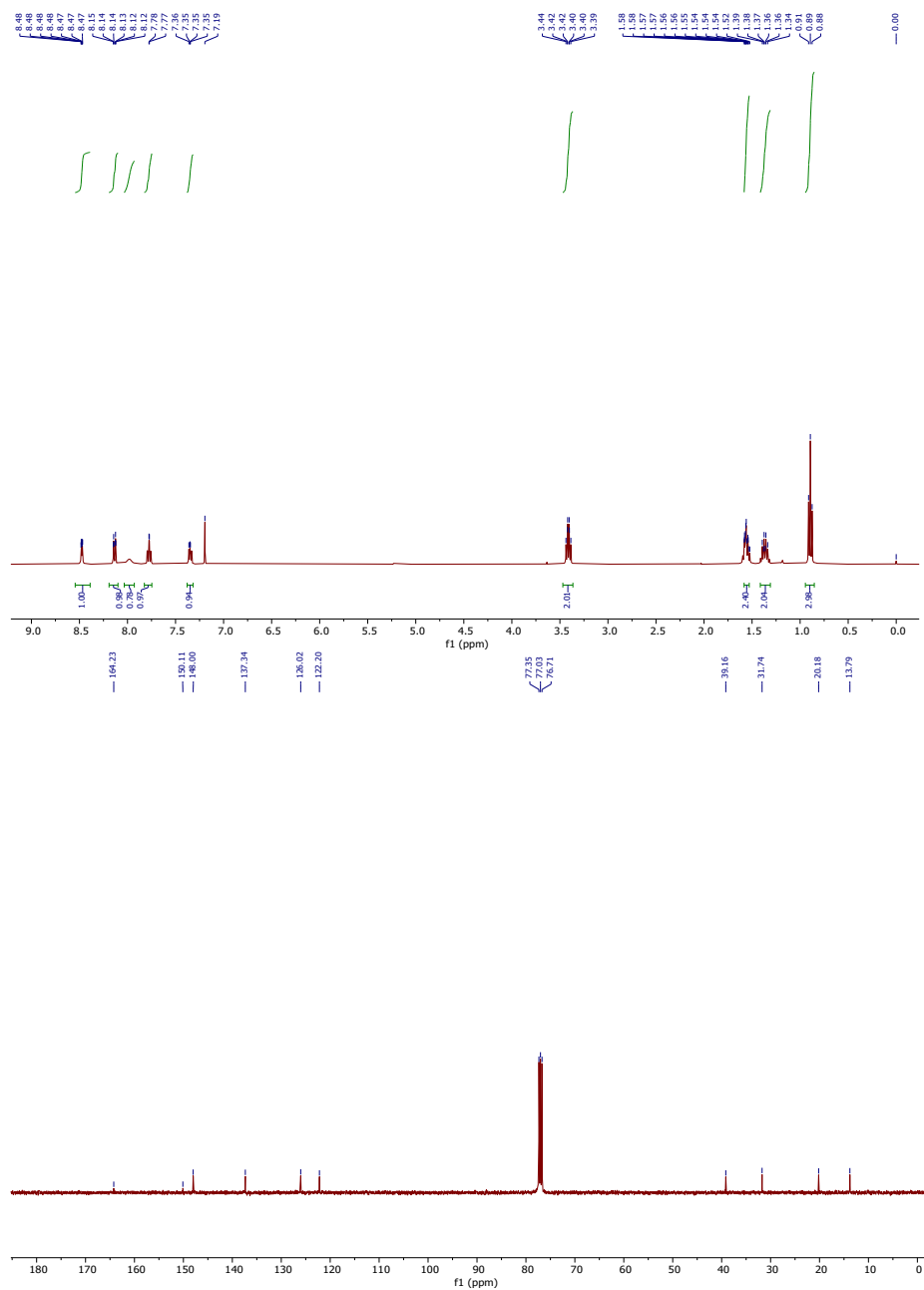


N-butylpicolinamide (**3i**)

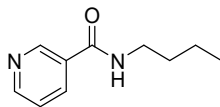


^1H NMR (400 MHz, Chloroform-*d*) δ 8.54-8.39 (m, 1H), 8.13 (dt, $J = 7.8, 1.1$ Hz, 1H), 7.98 (s, 1H), 7.77 (d, $J = 1.7$ Hz, 1H), 7.38-7.32 (m, 1H), 3.41 (td, $J = 7.1, 6.1$ Hz, 2H), 1.58-1.53 (m, 2H), 1.41-1.31 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.23, 148.00, 137.34, 126.02, 122.20, 39.16, 31.74, 20.18, 13.79.

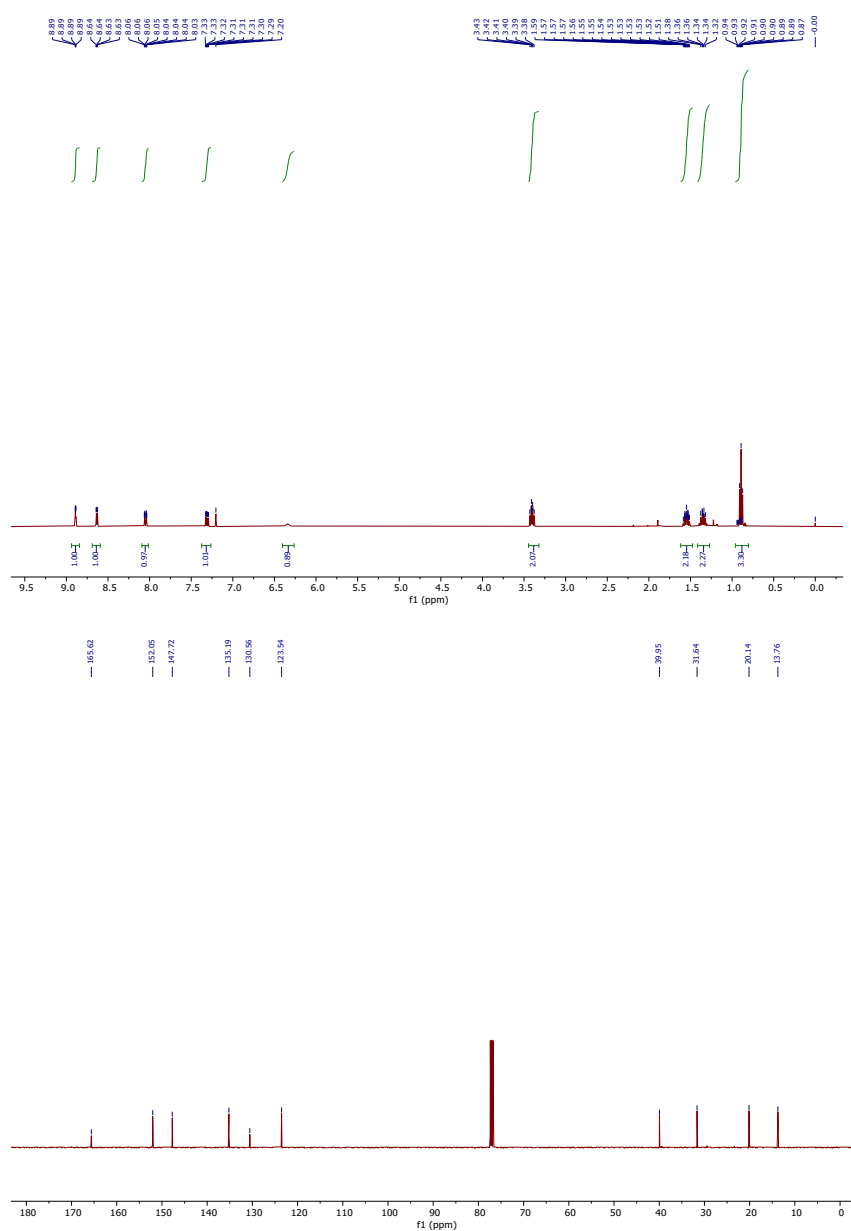


N-butylnicotinamide (**3j**)

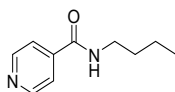


^1H NMR (400 MHz, Chloroform-*d*) δ 8.89 (dd, $J = 2.3, 0.9$ Hz, 1H), 8.63 (dd, $J = 4.9, 1.7$ Hz, 1H), 8.05 (ddd, $J = 7.9, 2.3, 1.7$ Hz, 1H), 7.31 (ddd, $J = 7.9, 4.8, 0.9$ Hz, 1H), 6.34 (s, 1H), 3.40 (td, $J = 7.2, 5.7$ Hz, 2H), 1.62-1.47 (m, 2H), 1.35 (dt, $J = 8.5, 7.2$ Hz, 2H), 0.89 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.62, 152.05, 147.72, 135.19, 130.56, 123.54, 39.95, 31.64, 20.14, 13.76.

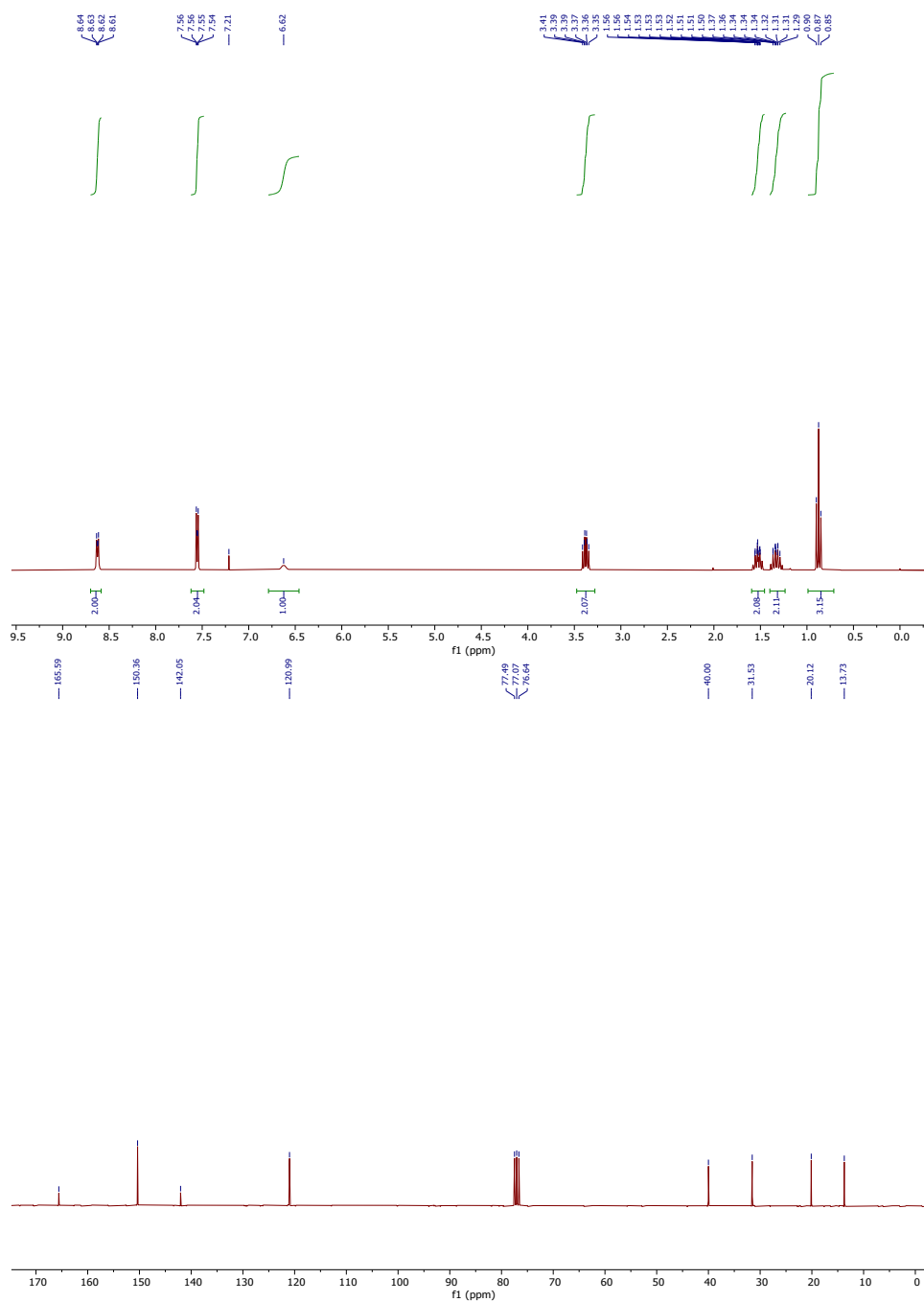


N-butylisonicotinamide (**3k**)

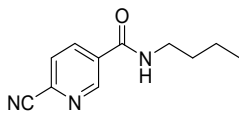


^1H NMR (300 MHz, Chloroform-*d*) δ 8.70-8.59 (m, 2H), 7.62-7.48 (m, 2H), 6.62 (s, 1H), 3.38 (td, J = 7.2, 5.7 Hz, 2H), 1.59-1.46 (m, 2H), 1.40-1.23 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.59, 150.36, 142.05, 120.99, 40.00, 31.53, 20.12, 13.73.

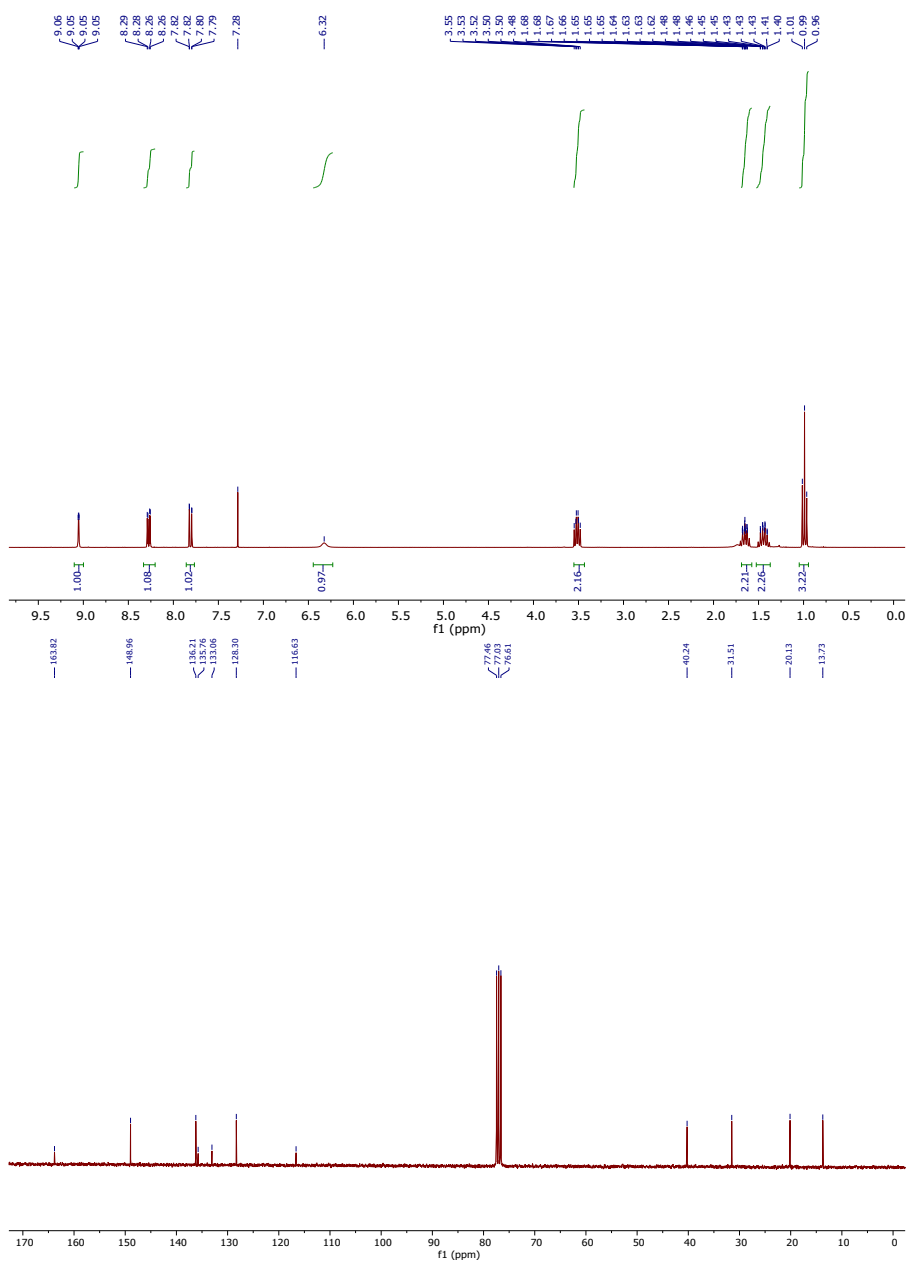


N-butylquinoline-2-carboxamide (**31**)

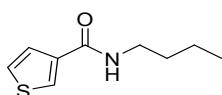


^1H NMR (300 MHz, Chloroform-*d*) δ 9.05 (dd, $J = 2.2, 0.9$ Hz, 1H), 8.27 (dd, $J = 8.0, 2.2$ Hz, 1H), 7.81 (dd, $J = 8.0, 0.9$ Hz, 1H), 6.32 (s, 1H), 3.51 (td, $J = 7.2, 5.7$ Hz, 2H), 1.69-1.61 (m, 2H), 1.50-1.40 (m, 2H), 0.99 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 163.82, 148.96, 136.21, 135.76, 133.06, 128.30, 116.63, 40.24, 31.51, 20.13, 13.73.

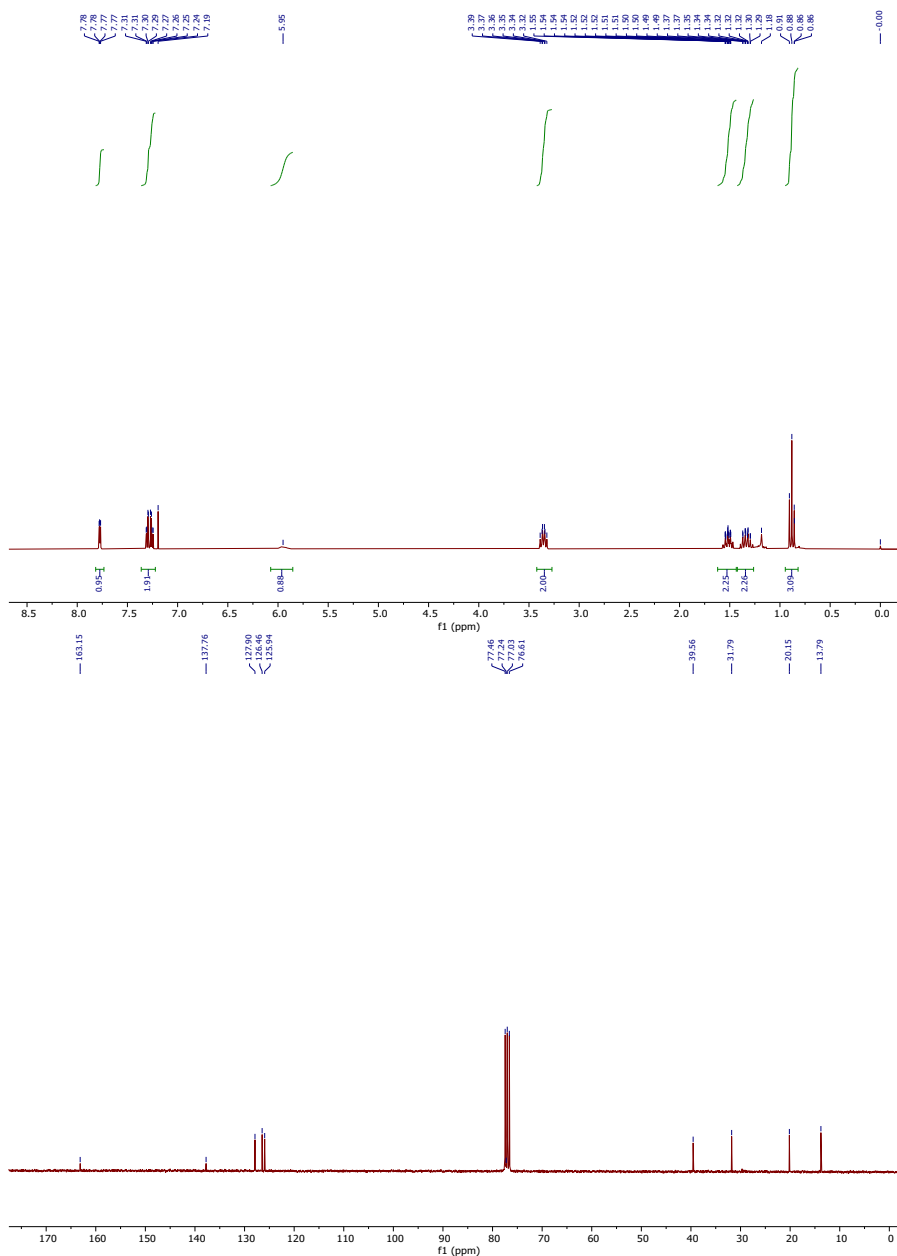


N-butyl-6-methoxypicolinamide (**3n**)

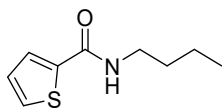


^1H NMR (300 MHz, Chloroform-*d*) δ 7.77 (dd, $J = 2.9, 1.4$ Hz, 1H), 7.36-7.22 (m, 2H), 5.95 (s, 1H), 3.36 (td, $J = 7.1, 5.7$ Hz, 2H), 1.62-1.43 (m, 2H), 1.42-1.26 (m, 2H), 0.95-0.82 (m, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 163.15, 137.76, 127.90, 126.46, 125.94, 39.56, 31.79, 20.15, 13.79.

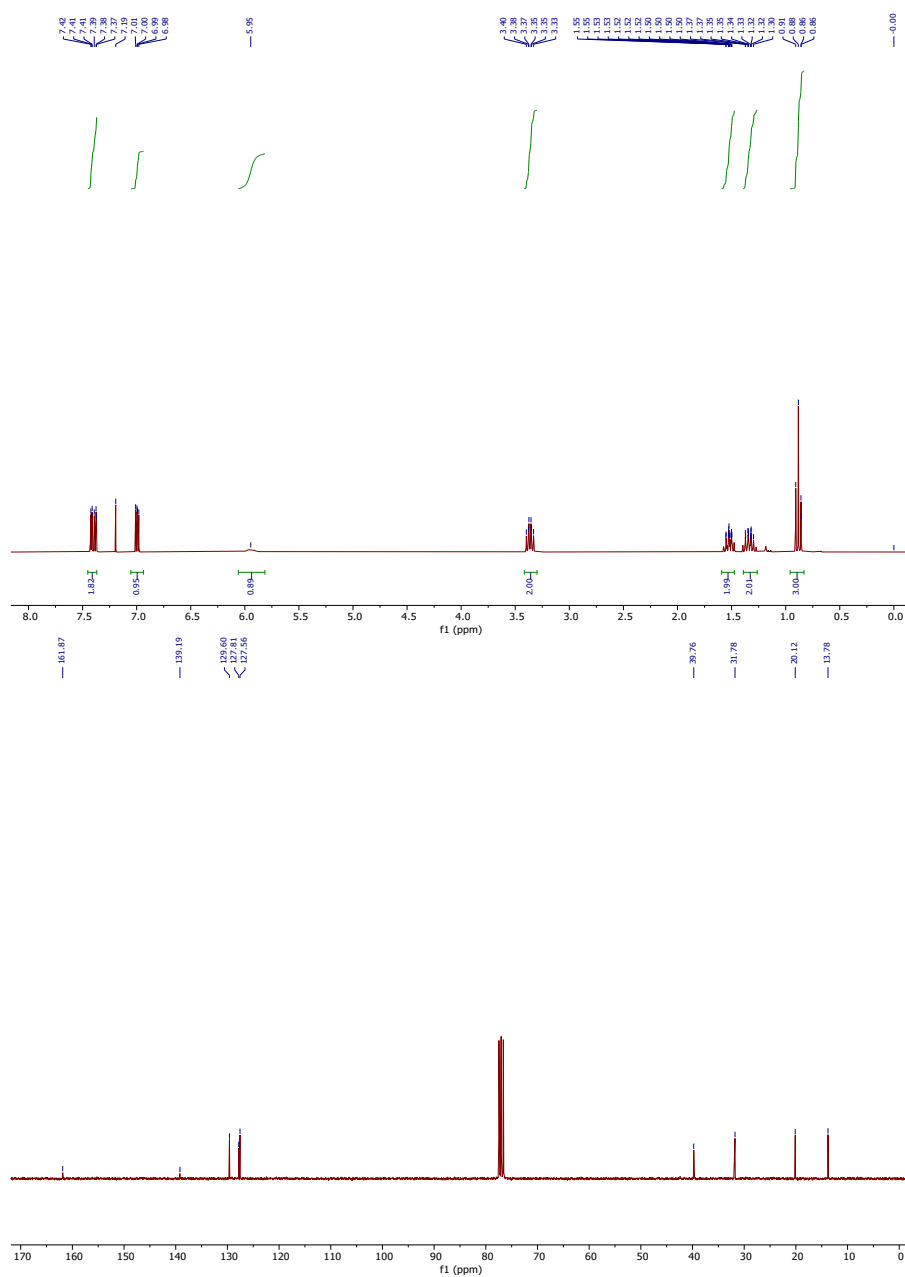


N-butylthiophene-2-carboxamide (**3p**)

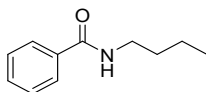


^1H NMR (300 MHz, Chloroform-*d*) δ 7.45-7.37 (m, 2H), 6.99 (dd, $J = 5.0, 3.7$ Hz, 1H), 5.95 (s, 1H), 3.36 (td, $J = 7.2, 5.7$ Hz, 2H), 1.59-1.47 (m, 2H), 1.39-1.26 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 161.87, 139.19, 129.60, 127.81, 127.56, 39.76, 31.78, 20.12, 13.78.

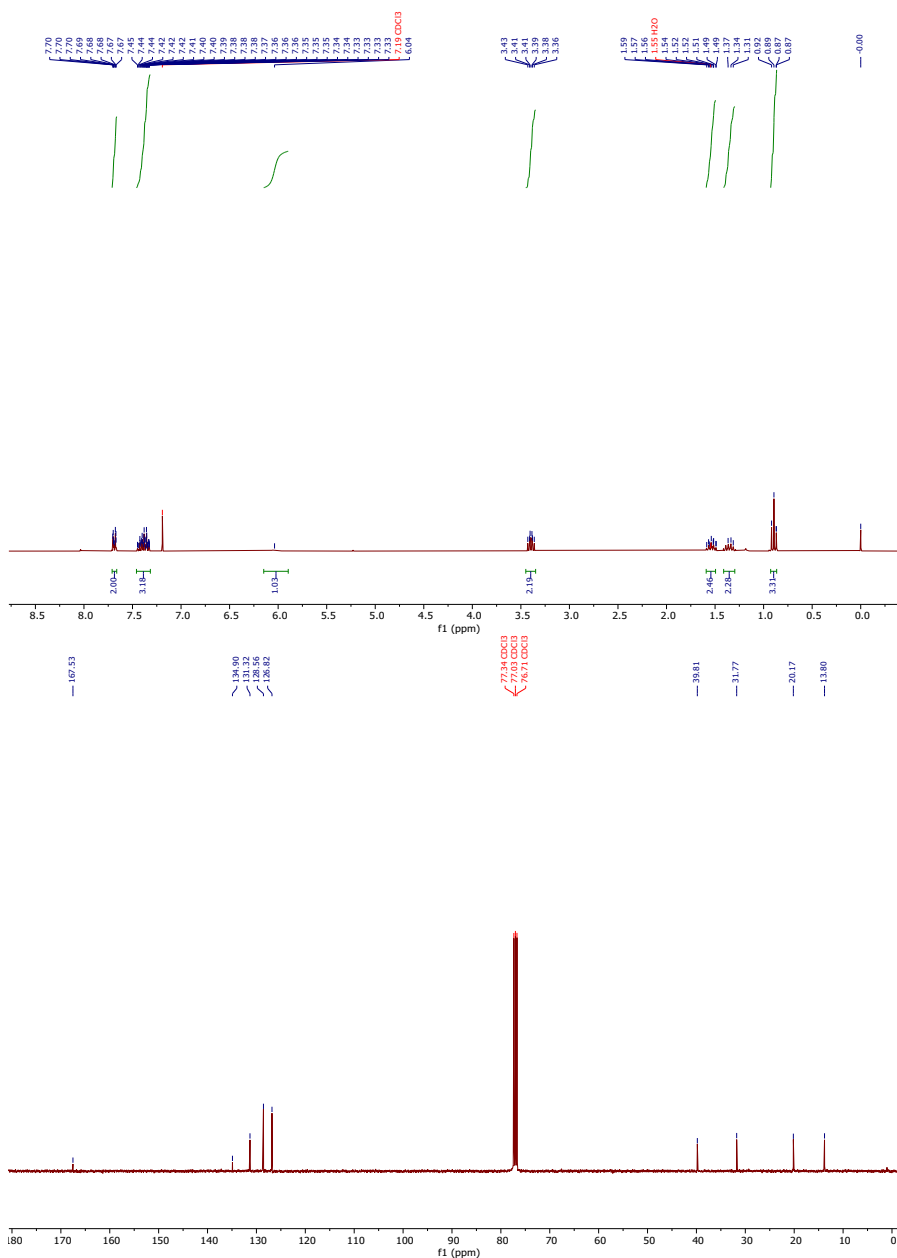


N-butylbenzamide (3q)

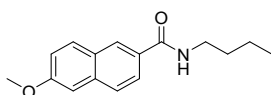


^1H NMR (300 MHz, Chloroform-*d*) δ 7.71-7.66 (m, 2H), 7.46-7.32 (m, 3H), 6.04 (s, 1H), 3.40 (td, J = 7.1, 5.7 Hz, 2H), 1.59-1.50 (m, 2H), 1.41-1.30 (m, 2H), 0.93-0.87 (m, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.53, 134.90, 131.32, 128.56, 126.82, 39.81, 31.77, 20.17, 13.80.

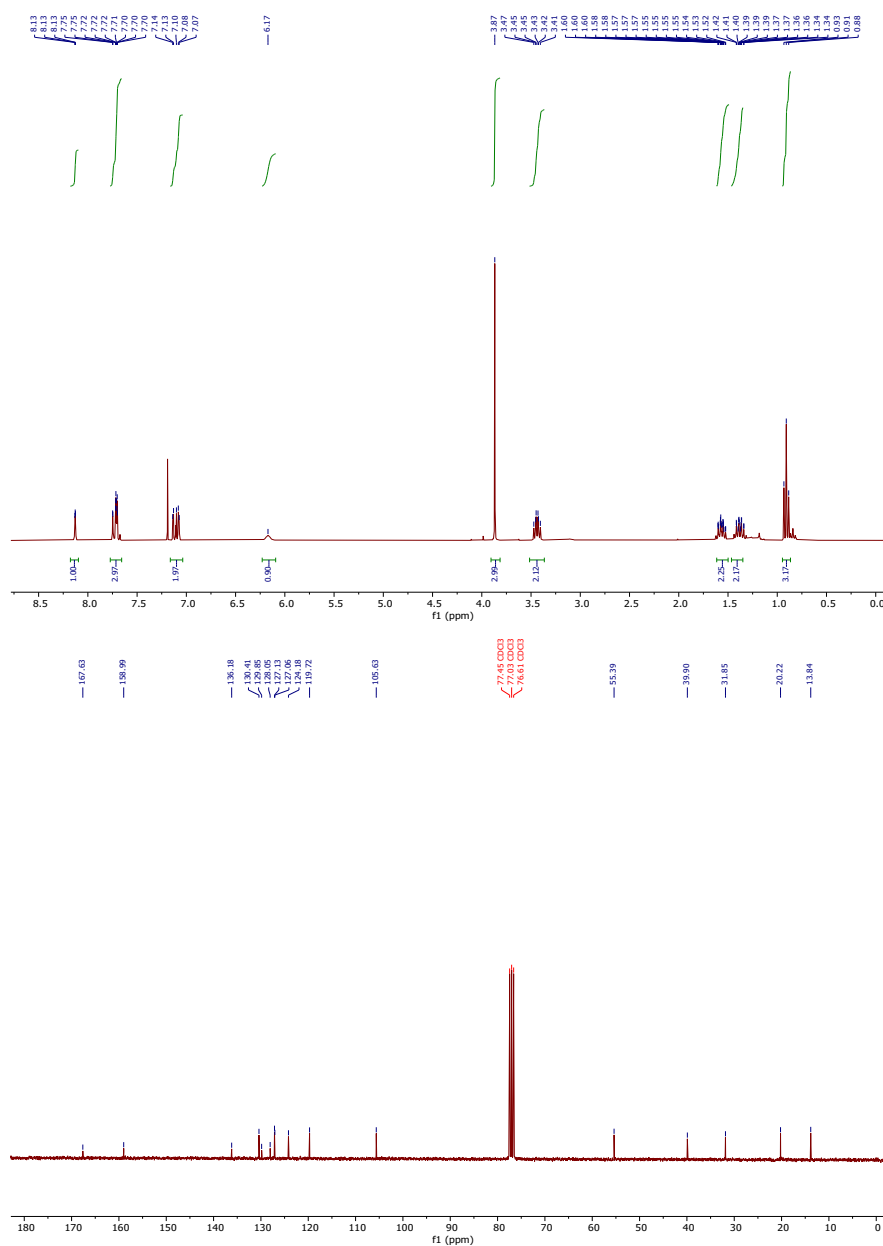


N-butyl-1-naphthamide (**3r**)

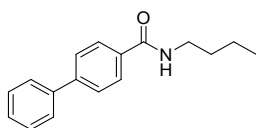


^1H NMR (300 MHz, Chloroform-*d*) δ 8.18-8.10 (m, 1H), 7.77-7.66 (m, 3H), 7.16-7.04 (m, 2H), 6.17 (s, 1H), 3.87 (s, 3H), 3.44 (td, $J = 7.2, 5.7$ Hz, 2H), 1.61-1.50 (m, 2H), 1.46-1.35 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H).

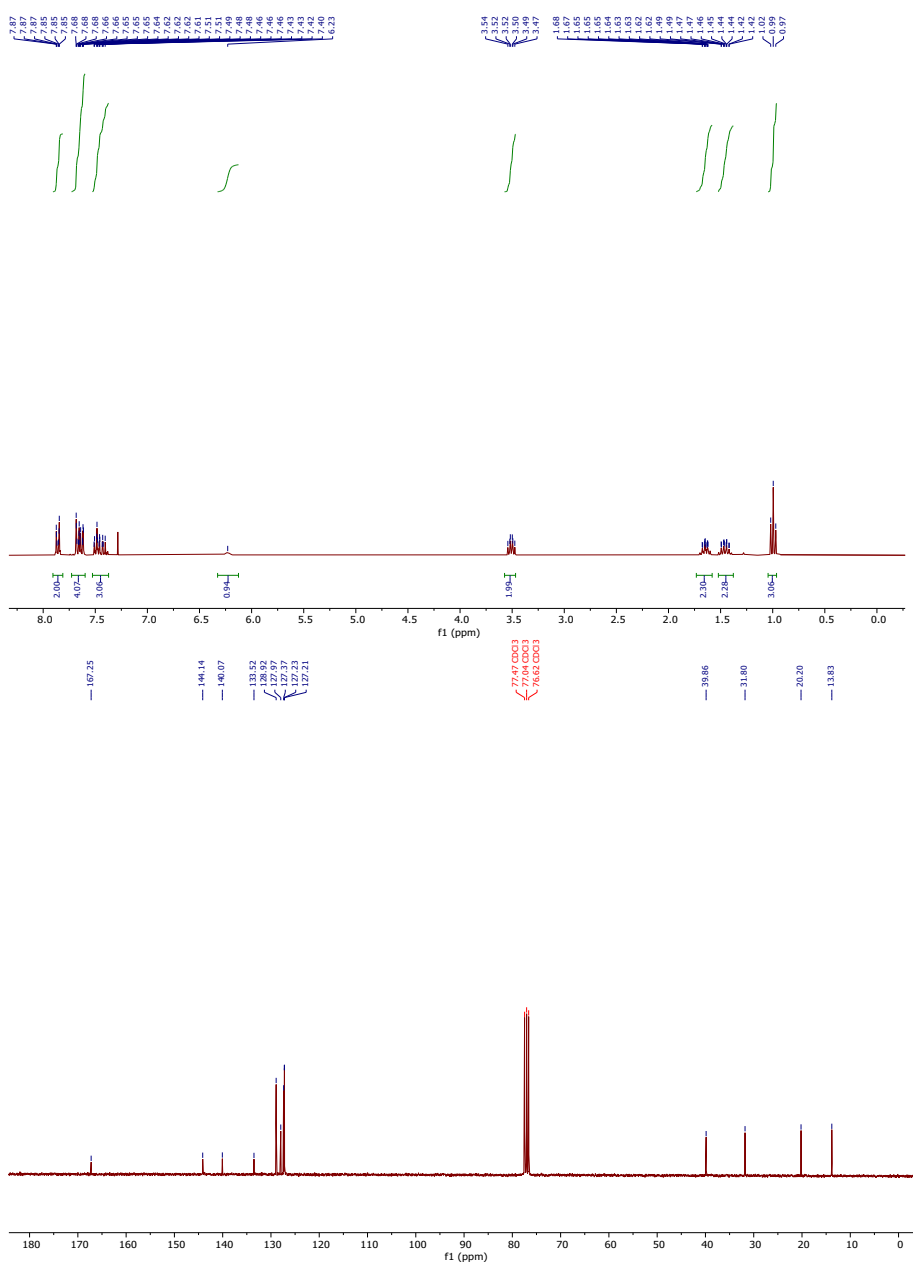
^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.63, 158.99, 136.18, 130.41, 129.85, 128.05, 127.13, 127.06, 124.18, 119.72, 105.63, 55.39, 39.90, 31.85, 20.22, 13.84.



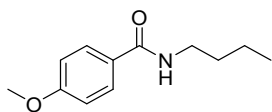
N-butyl-[1,1'-biphenyl]-4-carboxamide (**3t**)



^1H NMR (300 MHz, Chloroform-*d*) δ 7.91-7.81 (m, 2H), 7.73-7.60 (m, 4H), 7.53-7.37 (m, 3H), 6.23 (s, 1H), 3.51 (td, $J = 7.2, 5.7$ Hz, 2H), 1.73-1.58 (m, 2H), 1.52-1.38 (m, 2H), 0.99 (t, $J = 7.3$ Hz, 3H).
 ^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.25, 144.14, 140.07, 133.52, 128.92, 127.97, 127.37, 127.23, 127.21, 39.86, 31.80, 20.20, 13.83.

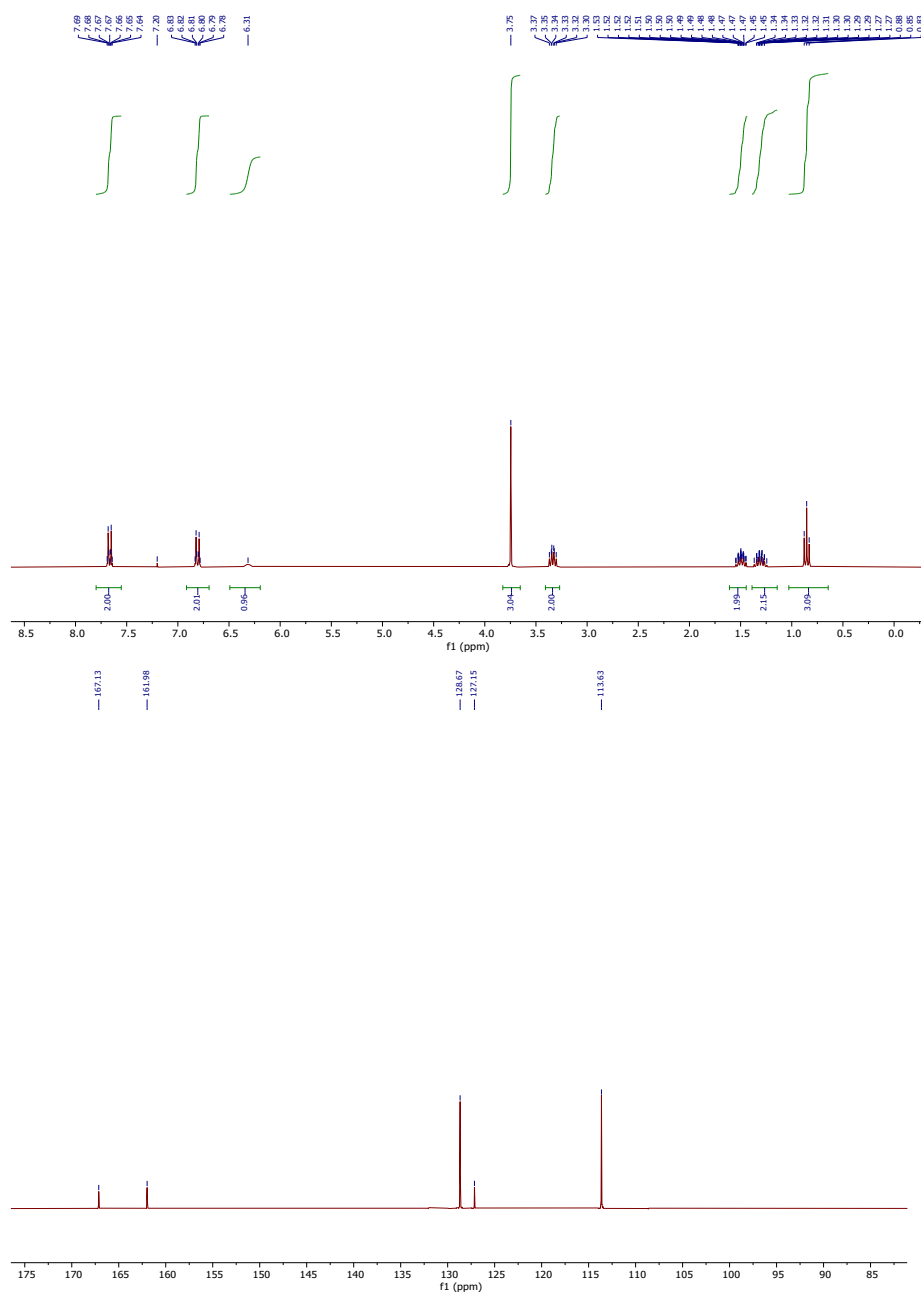


N-butyl-2-hydroxybenzamide (**3u**)

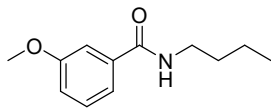


^1H NMR (300 MHz, Chloroform-*d*) δ 7.80-7.55 (m, 2H), 6.92-6.69 (m, 2H), 6.31 (s, 1H), 3.75 (s, 3H), 3.34 (td, $J = 7.2, 5.7$ Hz, 2H), 1.61-1.45 (m, 2H), 1.39-1.14 (m, 2H), 0.85 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.13, 161.98, 128.67, 127.15, 113.63, 55.36, 39.77, 31.80, 20.18, 13.80.

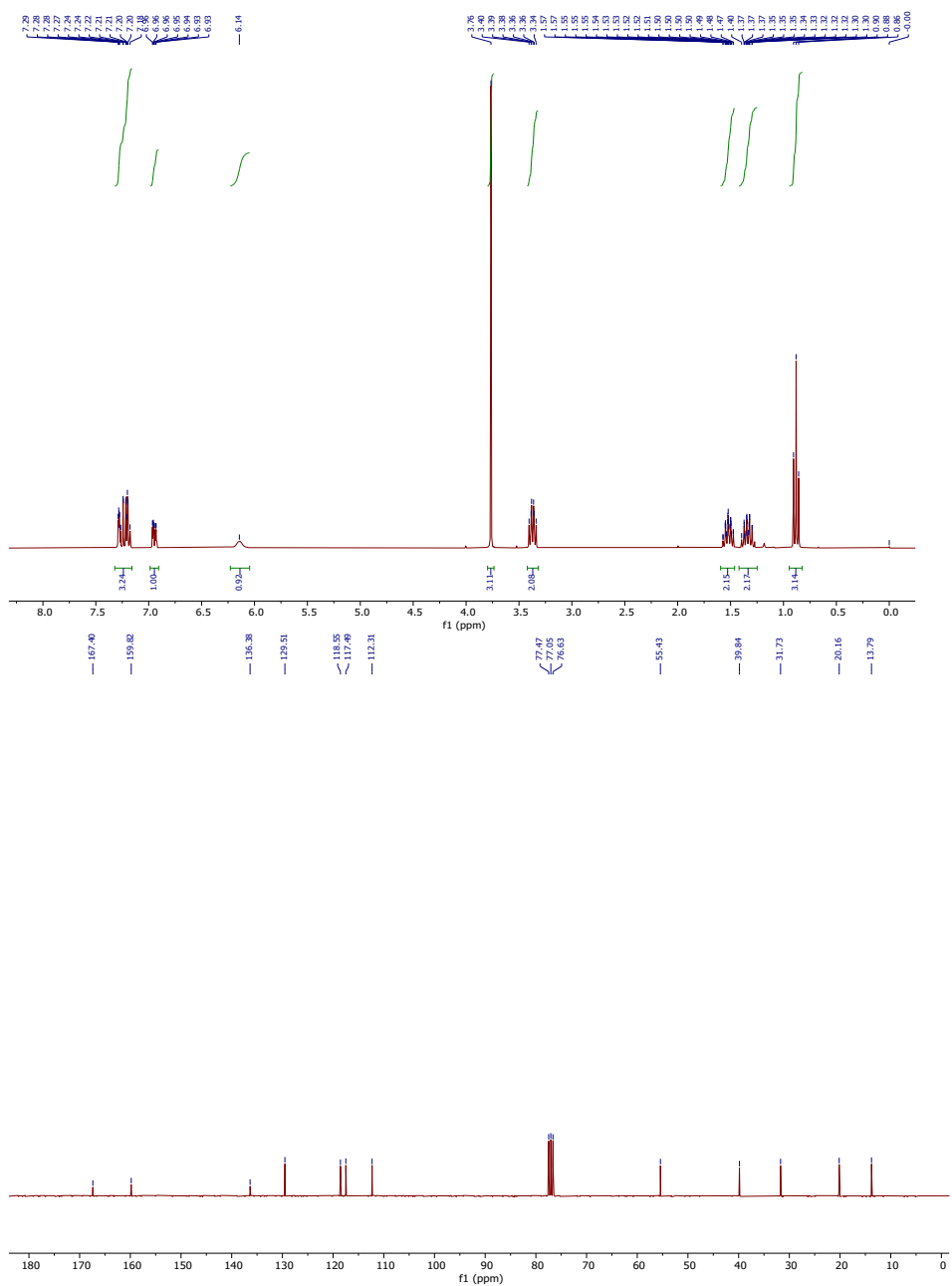


N-butyl-3-methoxybenzamide (**3w**)

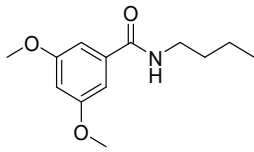


^1H NMR (300 MHz, Chloroform-*d*) δ 7.32-7.16 (m, 3H), 6.99-6.91 (m, 1H), 6.14 (s, 1H), 3.76 (s, 3H), 3.37 (td, $J = 7.1, 5.7$ Hz, 2H), 1.59-1.46 (m, 2H), 1.42-1.25 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.40, 159.82, 136.38, 129.51, 118.55, 117.49, 112.31, 55.43, 39.84, 31.73, 20.16, 13.79.

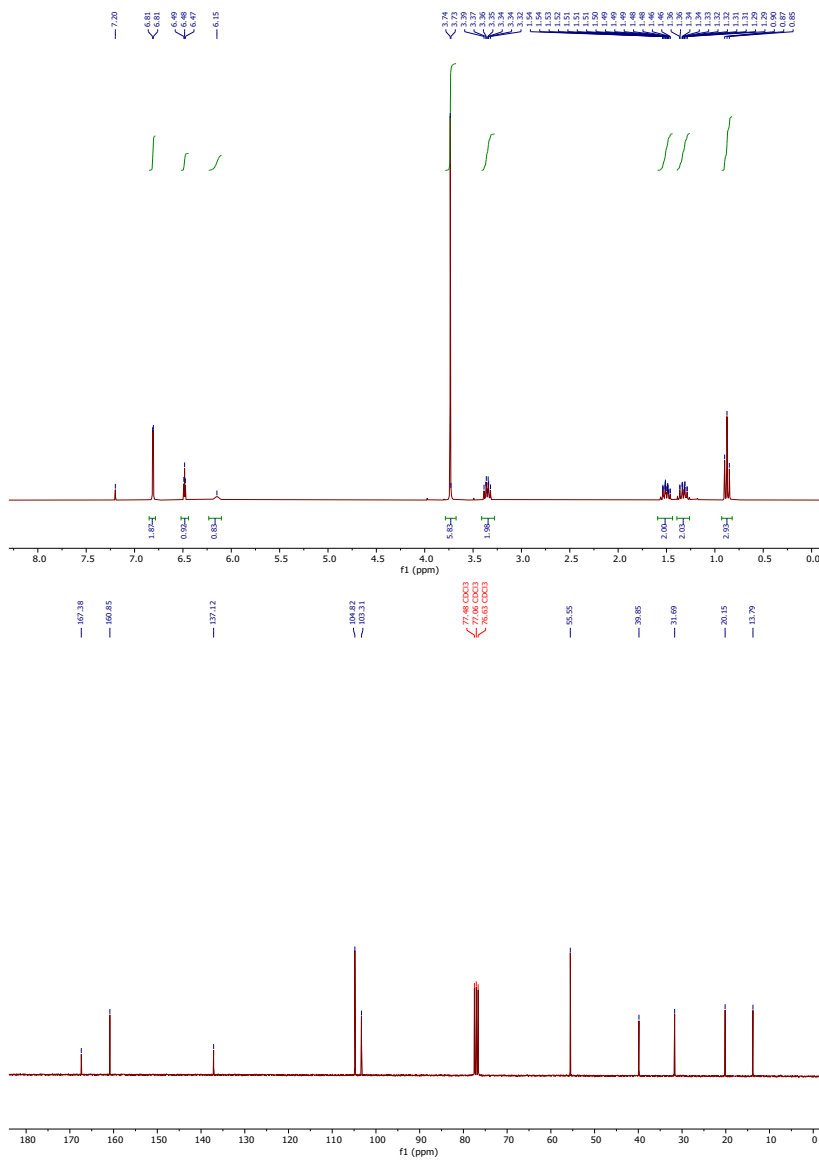


N-butyl-3,5-dimethoxybenzamide (**3x**)

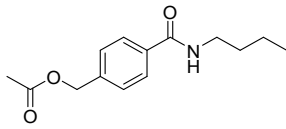


^1H NMR (300 MHz, Chloroform-*d*) δ 6.81 (d, $J = 2.3$ Hz, 2H), 6.48 (t, $J = 2.3$ Hz, 1H), 6.15 (s, 1H), 3.74 (s, 6H), 3.35 (td, $J = 7.1, 5.7$ Hz, 2H), 1.59-1.44 (m, 2H), 1.39-1.26 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.38, 160.85, 137.12, 104.82, 103.31, 55.55, 39.85, 31.69, 20.15, 13.79.

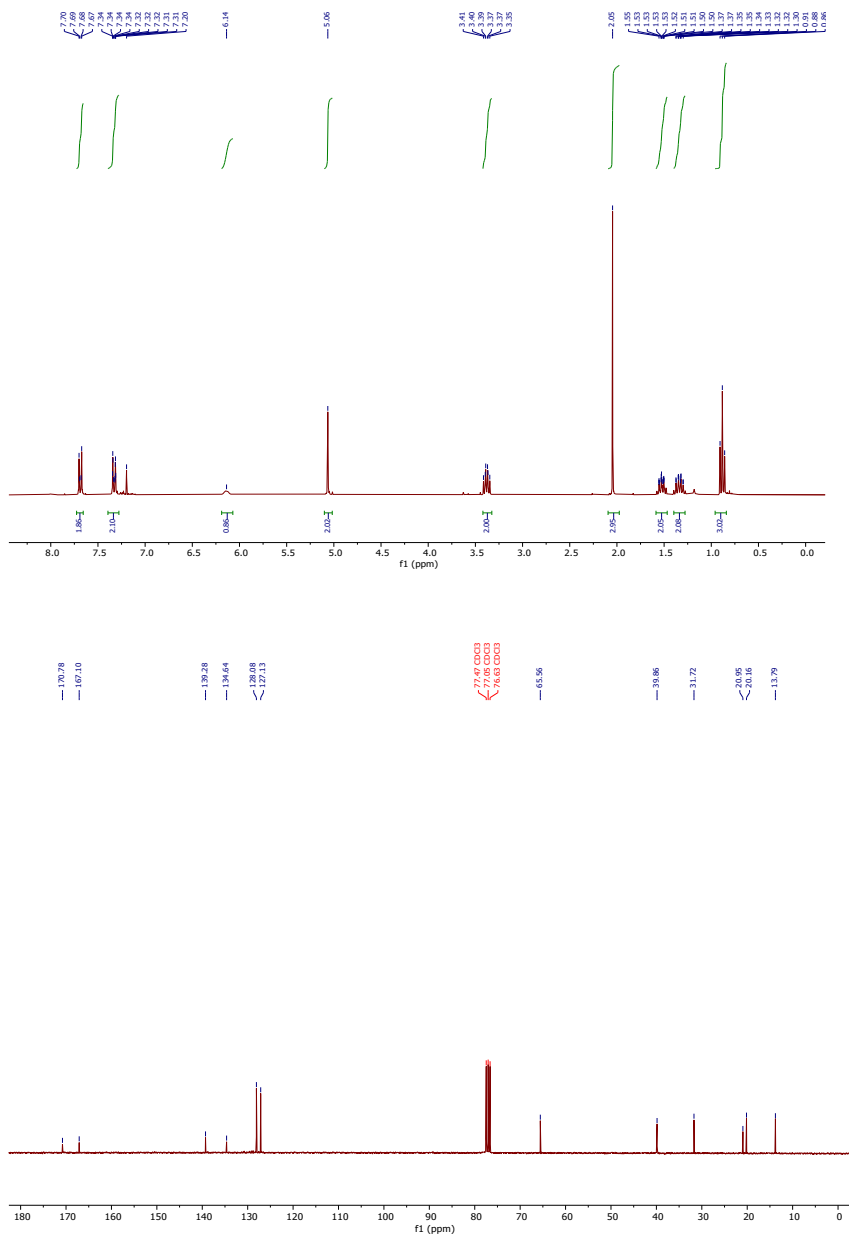


4-(butylcarbamoyl)benzyl acetate (**3y**)

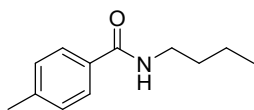


^1H NMR (300 MHz, Chloroform-*d*) δ 7.73-7.66 (m, 2H), 7.39-7.28 (m, 2H), 6.14 (s, 1H), 5.06 (s, 2H), 3.38 (td, $J = 7.1, 5.7$ Hz, 2H), 2.05 (s, 3H), 1.59-1.47 (m, 2H), 1.40-1.28 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H).

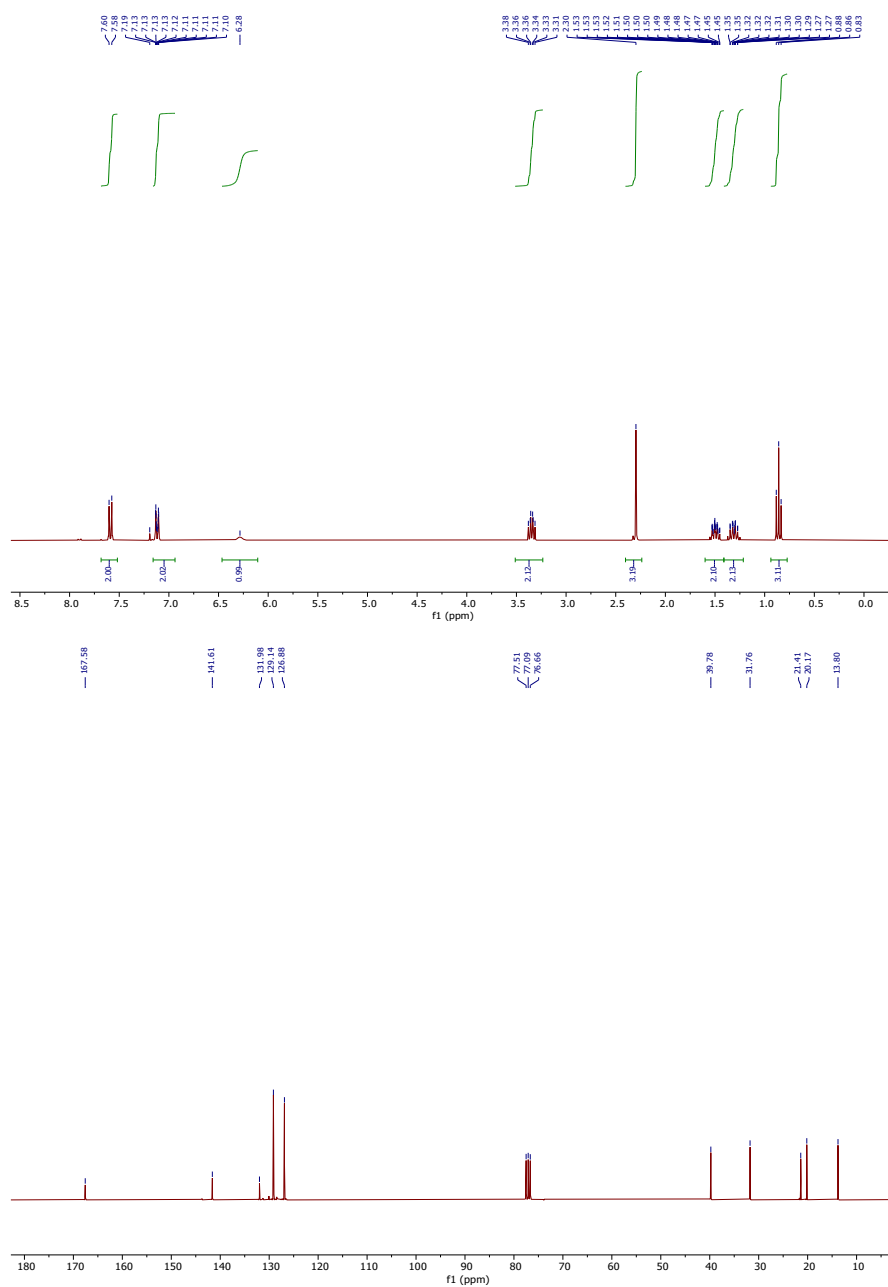
^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.78, 167.10, 139.28, 134.64, 128.08, 127.13, 65.56, 39.86, 31.72, 20.95, 20.16, 13.79.



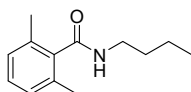
N-butyl-3-(methylthio)benzamide (**3z**)



^1H NMR (300 MHz, Chloroform-*d*) δ 7.59 (d, $J = 8.2$ Hz, 2H), 7.16-6.94 (m, 2H), 6.28 (s, 1H), 3.35 (td, $J = 7.2, 5.7$ Hz, 2H), 2.30 (s, 3H), 1.60-1.41 (m, 2H), 1.41-1.22 (m, 2H), 0.86 (t, $J = 7.3$ Hz, 3H).
 ^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.58, 141.61, 131.98, 129.14, 126.88, 39.78, 31.76, 21.41, 20.17, 13.80.

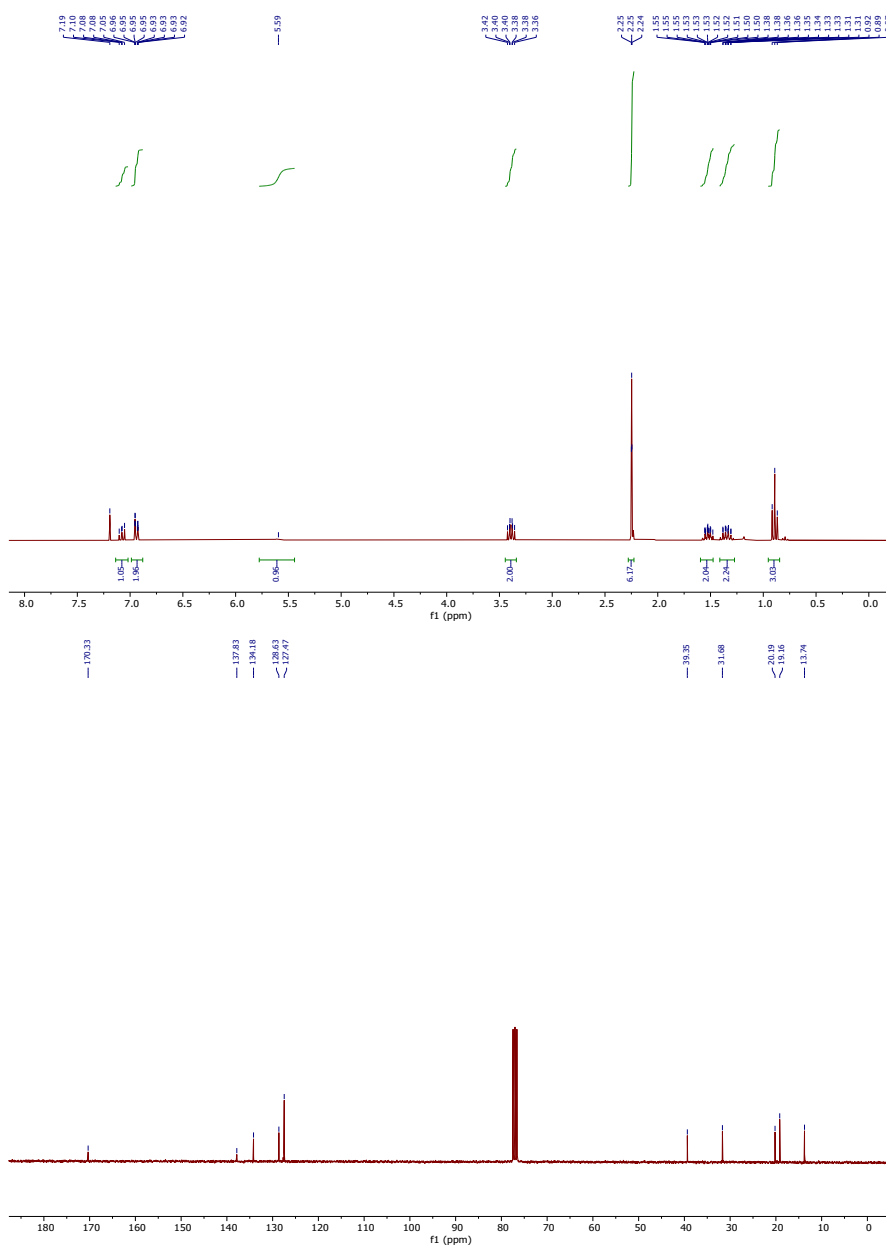


N-butyl-2-methylbenzamide (**3ab**)

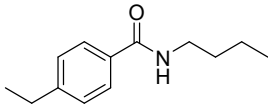


^1H NMR (300 MHz, Chloroform-*d*) δ 7.08 (dd, $J = 8.3, 6.9$ Hz, 1H), 6.94 (dq, $J = 7.6, 0.6$ Hz, 2H), 5.59 (s, 1H), 3.39 (td, $J = 7.1, 5.8$ Hz, 2H), 2.25 (d, $J = 0.7$ Hz, 6H), 1.60-1.48 (m, 2H), 1.41-1.27 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.33, 137.83, 134.18, 128.63, 127.47, 39.35, 31.68, 20.19, 19.16, 13.74.

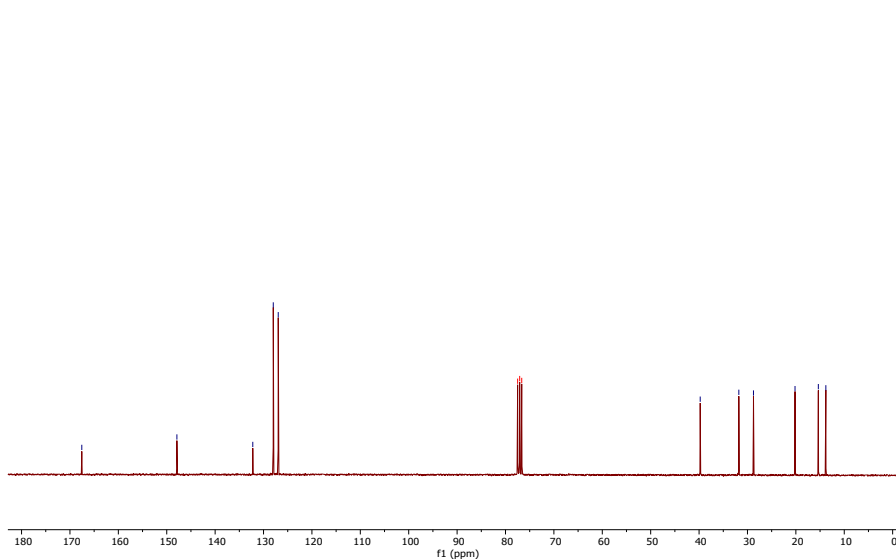
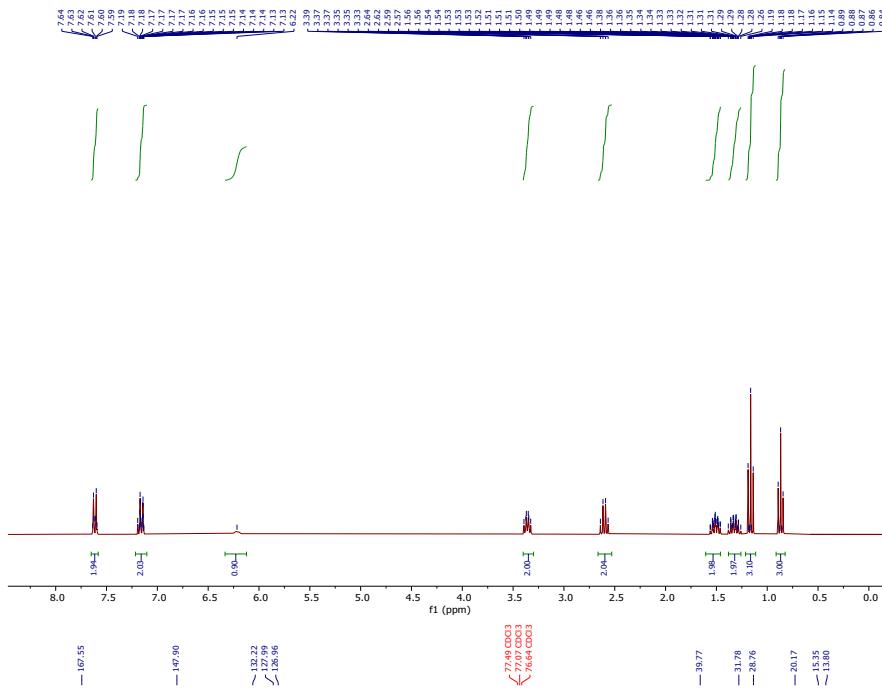


N-butyl-4-ethylbenzamide (**3ad**)

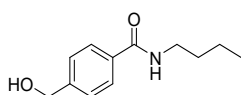


^1H NMR (300 MHz, Chloroform-*d*) δ 7.65-7.58 (m, 2H), 7.22-7.10 (m, 2H), 6.22 (s, 1H), 3.36 (td, $J = 7.1, 5.6$ Hz, 2H), 2.60 (q, $J = 7.6$ Hz, 2H), 1.61-1.46 (m, 2H), 1.38-1.26 (m, 2H), 1.16 (t, $J = 7.6$ Hz, 3H), 0.87 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.55, 147.90, 132.22, 127.99, 126.96, 39.77, 31.78, 28.76, 20.17, 15.35, 13.80.

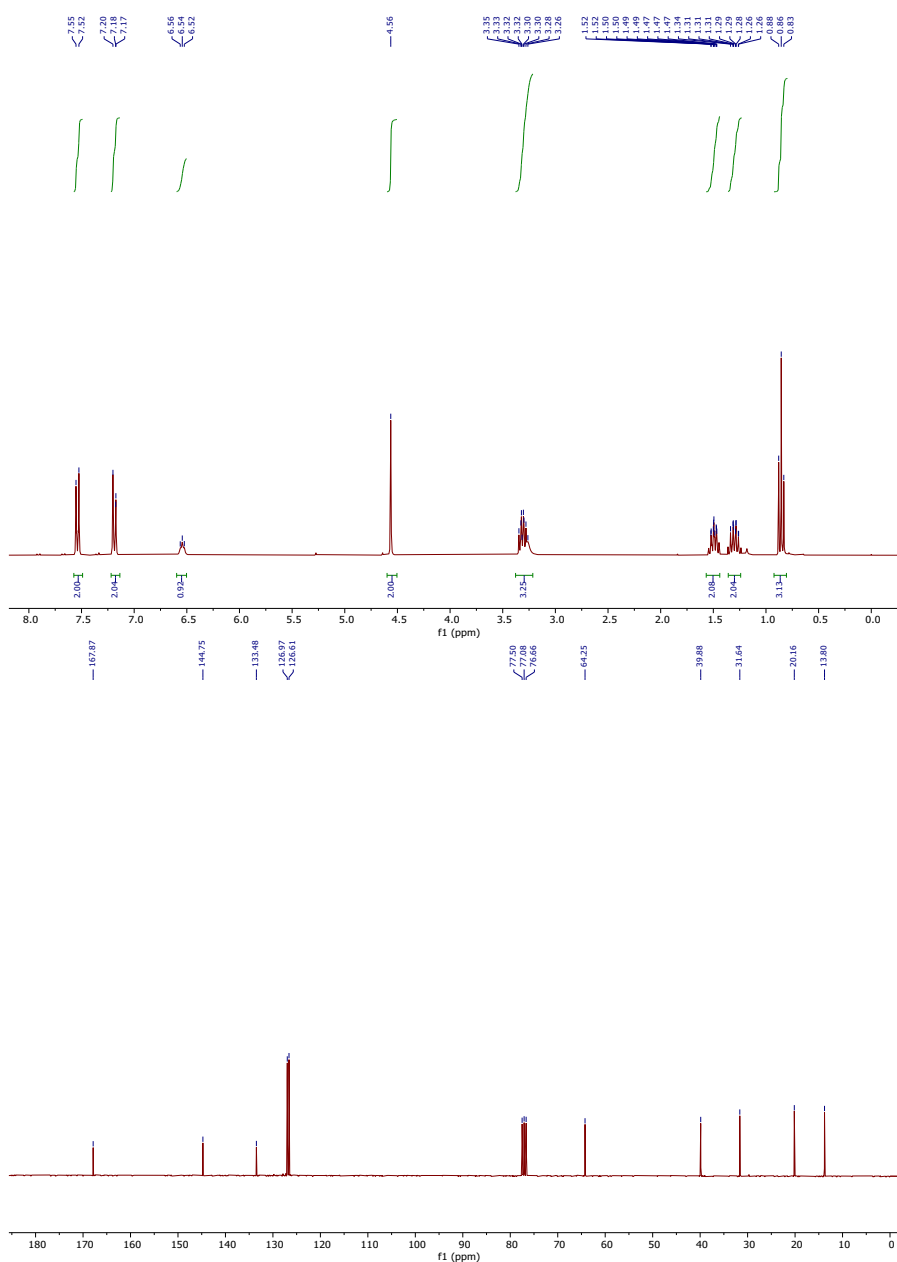


N-butyl-5-fluoro-2-methylbenzamide (**3ae**)

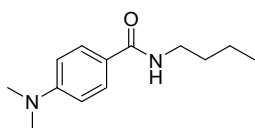


^1H NMR (300 MHz, Chloroform-*d*) δ 7.54 (d, $J = 8.3$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 6.54 (t, $J = 5.8$ Hz, 1H), 4.56 (s, 2H), 3.38-3.21 (m, 3H), 1.50 (ddd, $J = 9.2, 6.5, 1.3$ Hz, 2H), 1.36-1.24 (m, 2H), 0.86 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.87, 144.75, 133.48, 126.97, 126.61, 64.25, 39.88, 31.64, 20.16, 13.80.

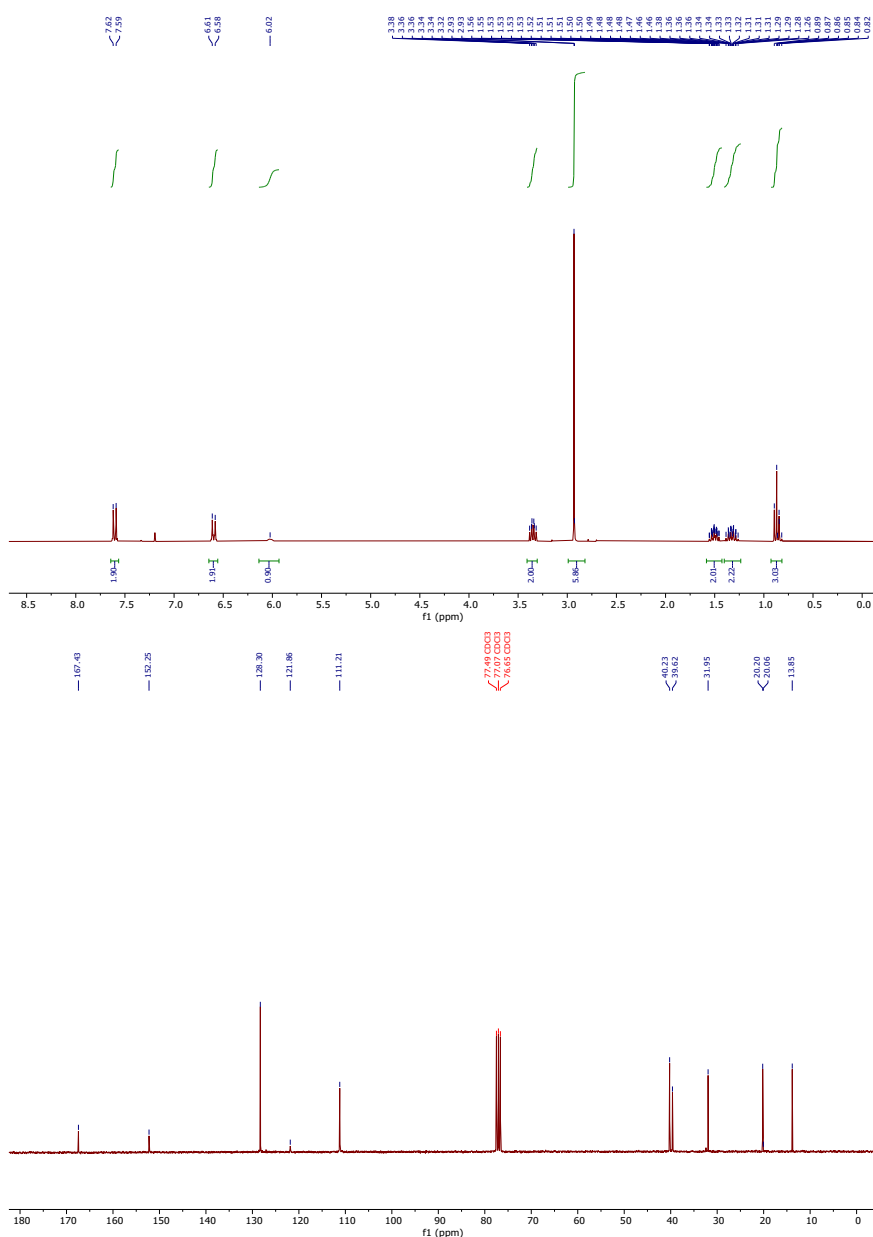


N-butyl-4-(dimethylamino)benzamide (**3ag**)

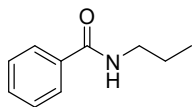


^1H NMR (300 MHz, Chloroform-*d*) δ 7.60 (d, $J = 9.0$ Hz, 2H), 6.60 (d, $J = 8.9$ Hz, 2H), 6.02 (s, 1H), 3.35 (td, $J = 7.1, 5.7$ Hz, 2H), 2.93 (s, 6H), 1.50 (dtdd, $J = 8.4, 6.8, 6.0, 0.8$ Hz, 2H), 1.40-1.23 (m, 2H), 0.93-0.82 (m, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.43, 152.25, 128.30, 121.86, 111.21, 40.23, 39.62, 31.95, 20.20, 13.85.

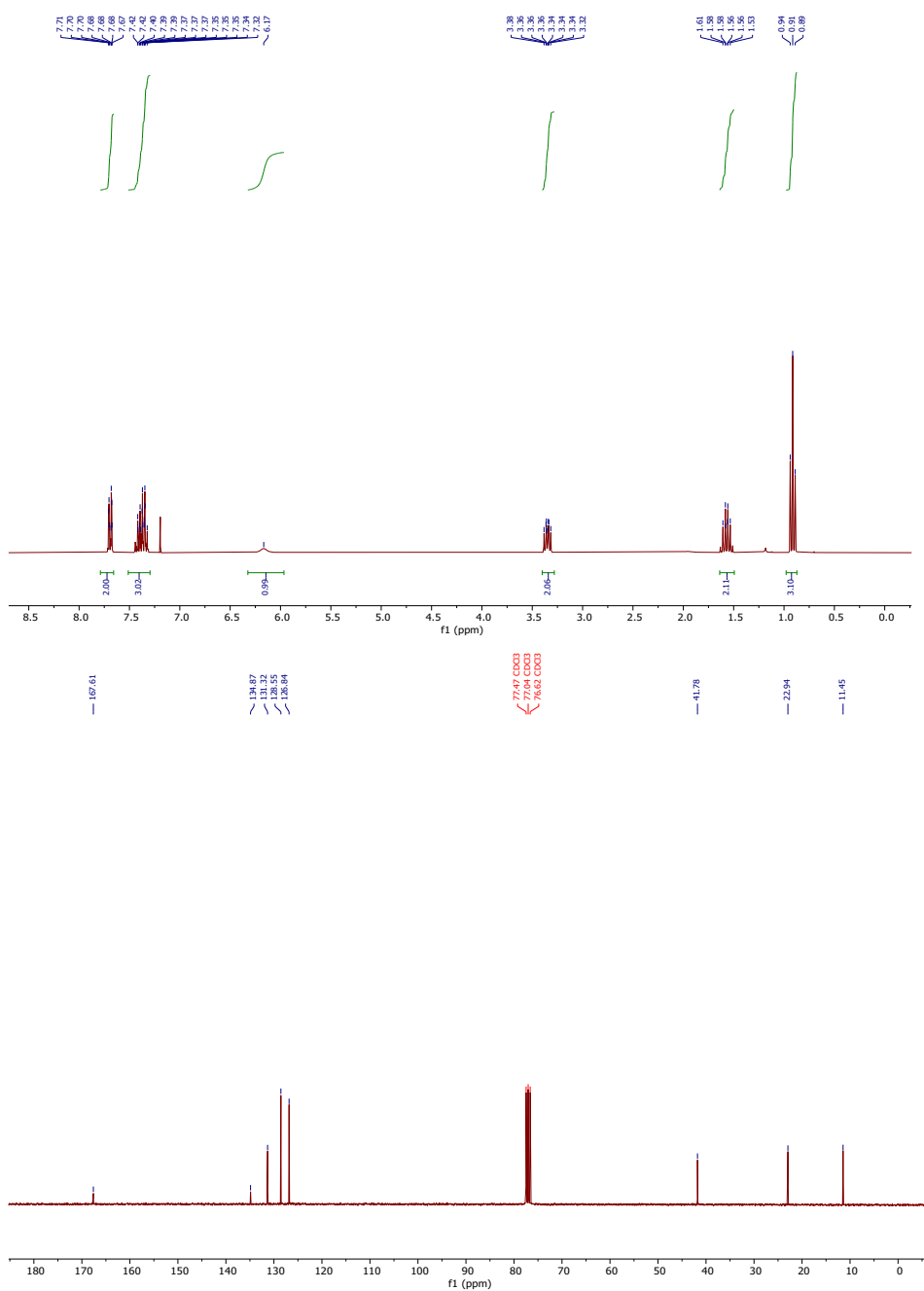


N-propylbenzamide (**3ah**)

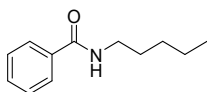


^1H NMR (300 MHz, Chloroform-*d*) δ 7.79-7.66 (m, 2H), 7.51-7.30 (m, 3H), 6.17 (s, 1H), 3.35 (ddd, $J = 7.9, 7.1, 5.8$ Hz, 2H), 1.64-1.49 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.61, 134.87, 131.32, 128.55, 126.84, 41.78, 22.94, 11.45.

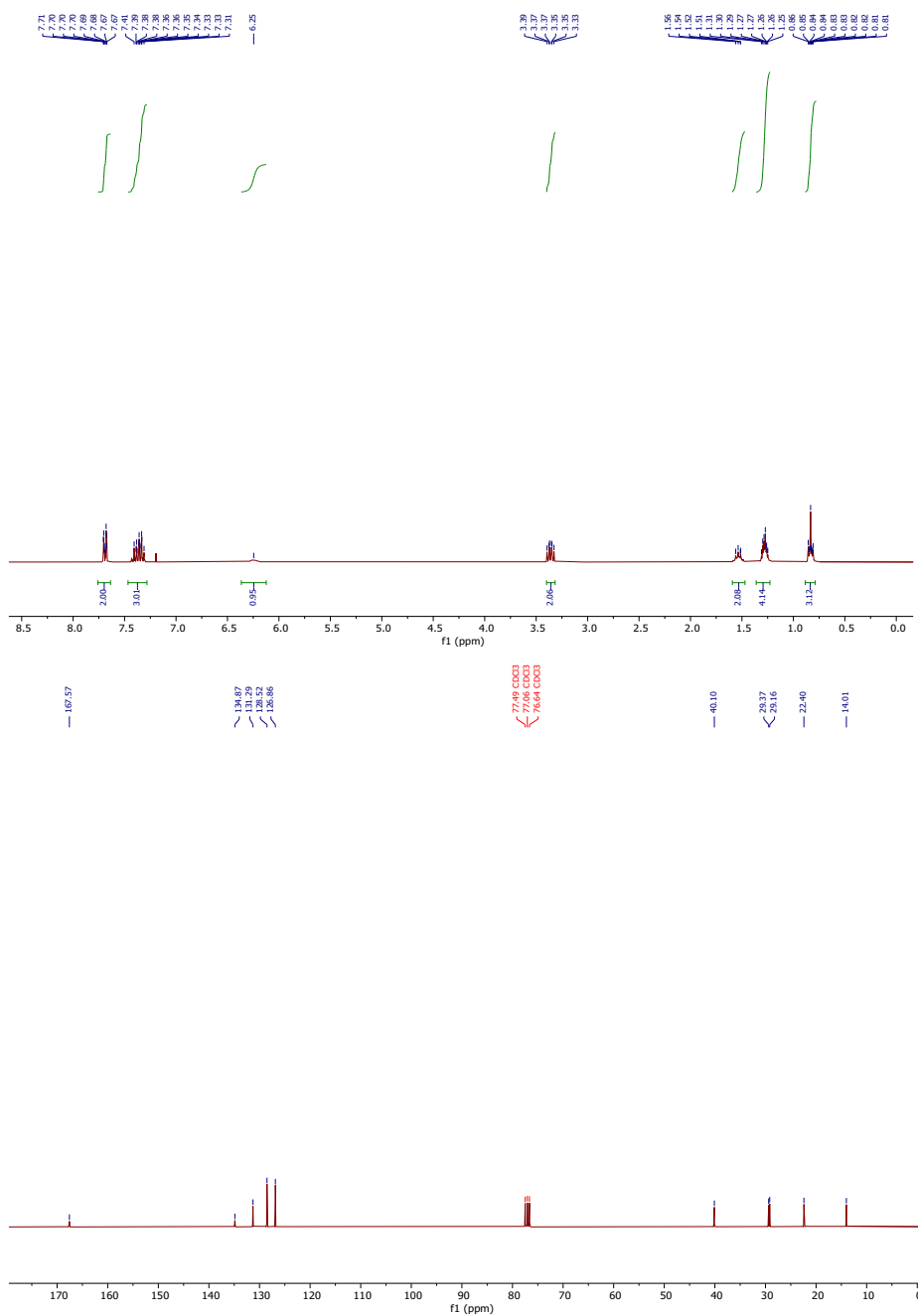


N-pentylbenzamide (**3ai**)

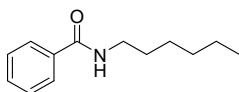


^1H NMR (300 MHz, Chloroform-*d*) δ 7.76-7.64 (m, 2H), 7.47-7.28 (m, 3H), 6.25 (s, 1H), 3.36 (td, J = 7.2, 5.8 Hz, 2H), 1.59-1.47 (m, 2H), 1.28 (dq, J = 7.1, 3.5 Hz, 4H), 0.88-0.79 (m, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.57, 134.87, 131.29, 128.52, 126.86, 40.10, 29.37, 29.16, 22.40, 14.01.

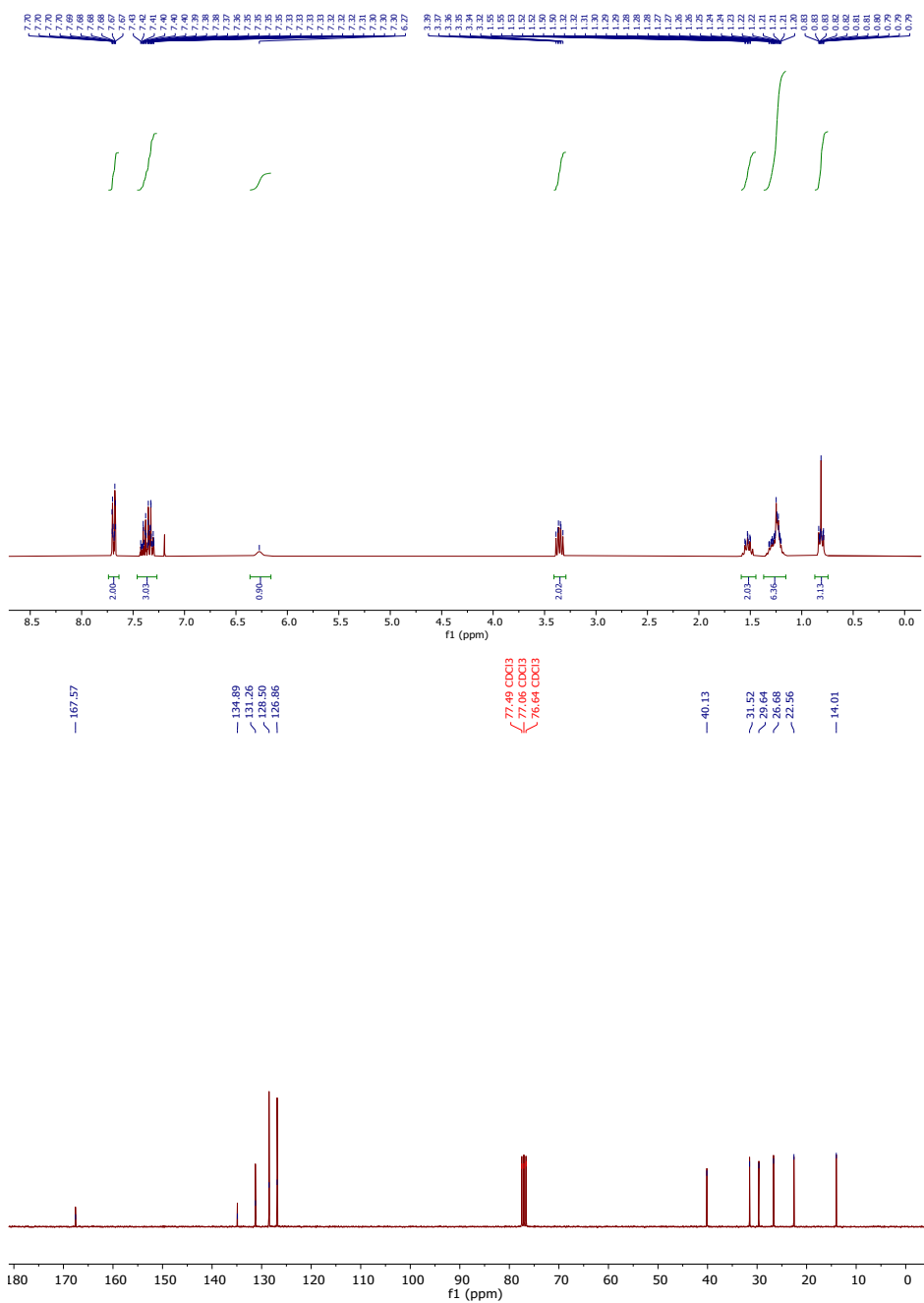


N-hexylbenzamide (**3aj**)

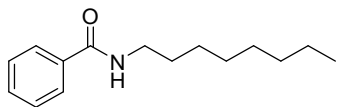


^1H NMR (300 MHz, Chloroform-*d*) δ 7.74-7.64 (m, 2H), 7.46-7.27 (m, 3H), 6.27 (s, 1H), 3.36 (td, J = 7.2, 5.7 Hz, 2H), 1.53 (td, J = 7.5, 1.7 Hz, 2H), 1.37-1.15 (m, 6H), 0.87-0.74 (m, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.57, 134.89, 131.26, 128.50, 126.86, 40.13, 31.52, 29.64, 26.68, 22.56, 14.01.

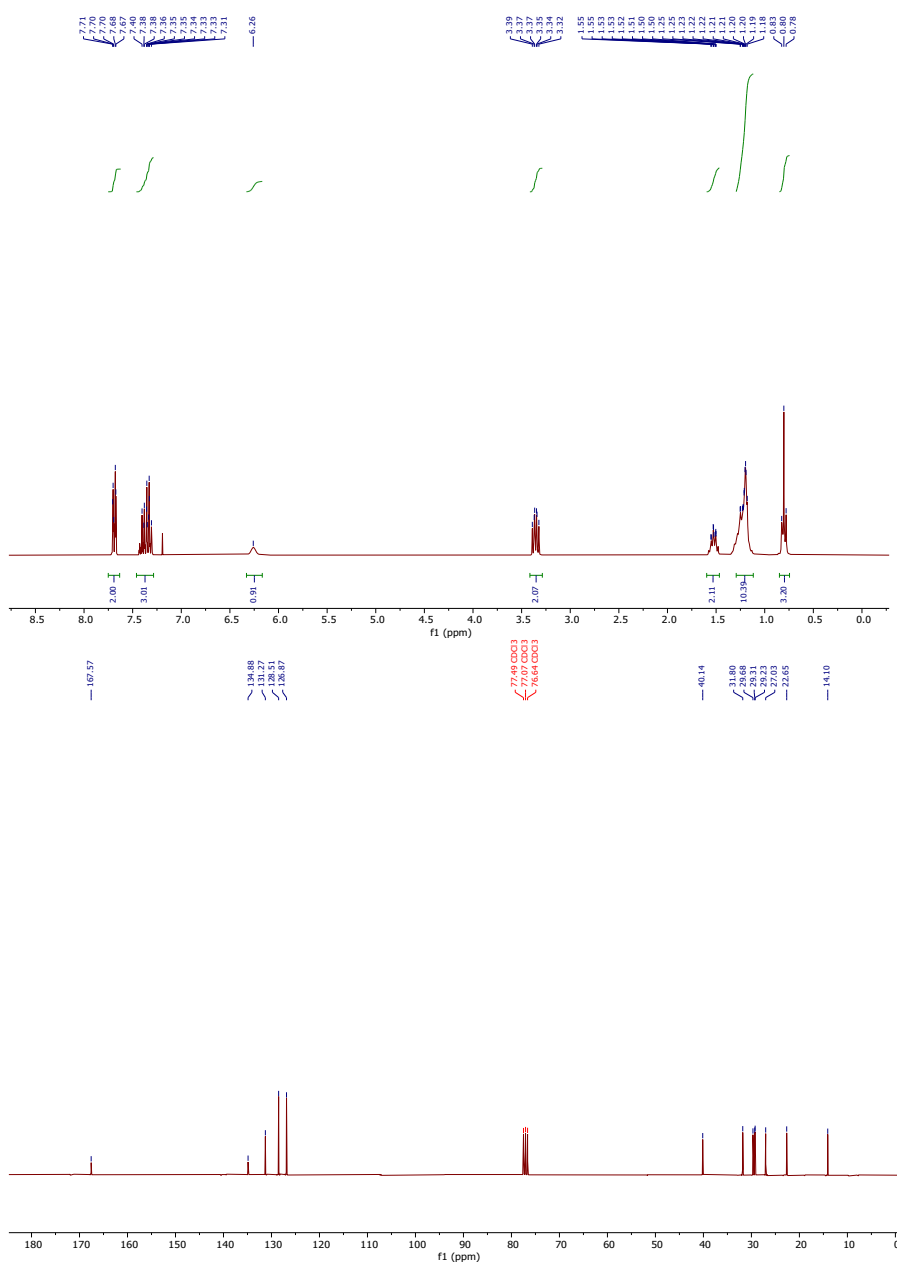


N-octylbenzamide (**3ak**)

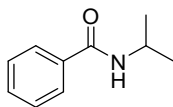


^1H NMR (300 MHz, Chloroform-*d*) δ 7.75-7.63 (m, 2H), 7.46-7.29 (m, 3H), 6.26 (s, 1H), 3.36 (td, J = 7.2, 5.7 Hz, 2H), 1.60-1.47 (m, 2H), 1.29-1.12 (m, 10H), 0.85-0.74 (m, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.57, 134.88, 131.27, 128.51, 126.87, 40.14, 31.80, 29.68, 29.31, 29.23, 27.03, 22.65, 14.10.

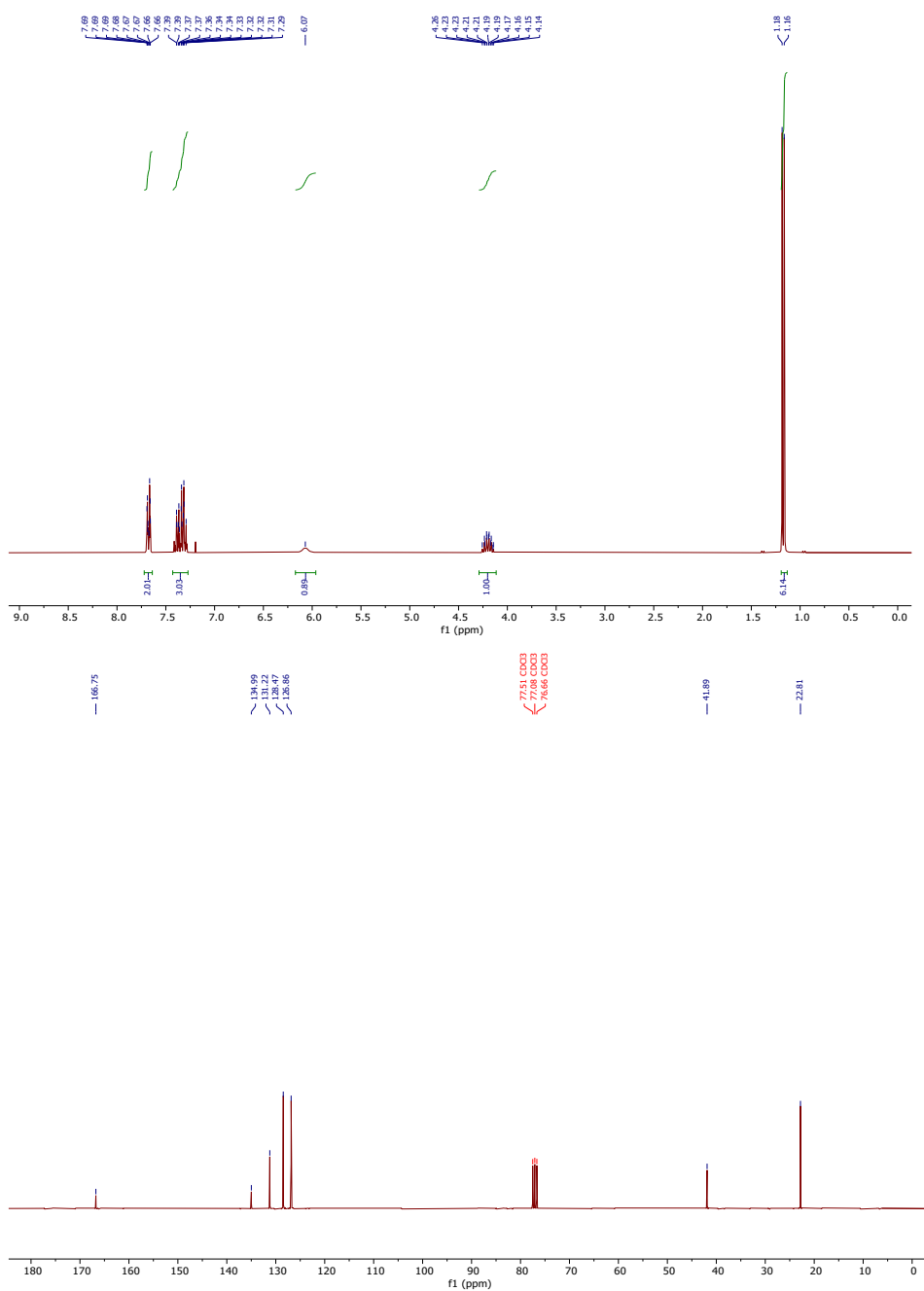


N-isopropylbenzamide (**3al**)

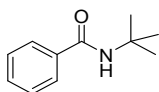


^1H NMR (300 MHz, Chloroform-*d*) δ 7.72-7.64 (m, 2H), 7.43-7.27 (m, 3H), 6.07 (s, 1H), 4.20 (dp, J = 7.9, 6.6 Hz, 1H), 1.17 (d, J = 6.5 Hz, 6H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.75, 134.99, 131.22, 128.47, 126.86, 41.89, 22.81.

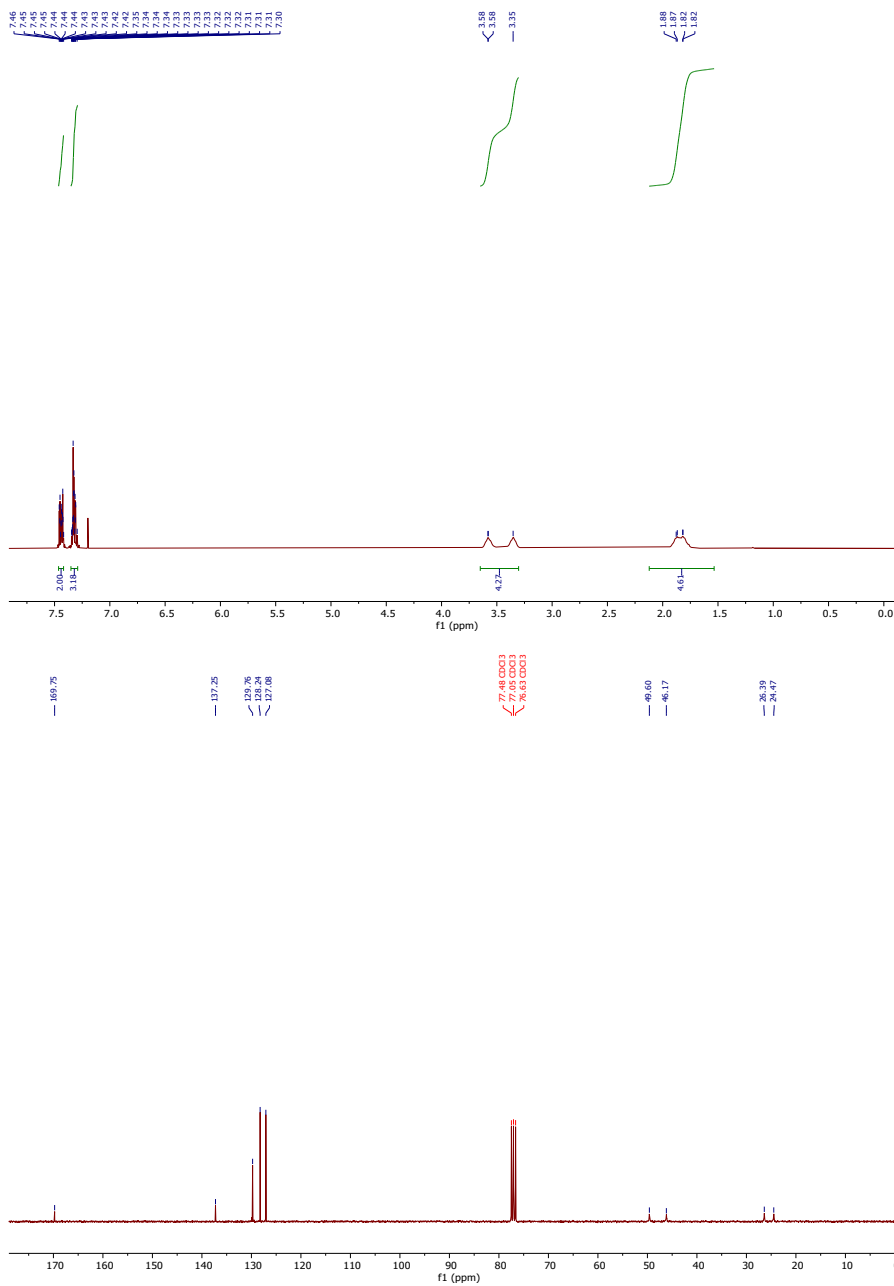


N-(tert-butyl)benzamide (**3am**)

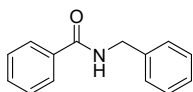


^1H NMR (300 MHz, Chloroform-*d*) δ 7.46-7.42 (m, 2H), 7.35-7.29 (m, 3H), 3.65-3.30 (m, 4H), 1.85 (d, $J = 18.0$ Hz, 5H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 169.75, 137.25, 129.76, 128.24, 127.08, 49.60, 46.17, 26.39, 24.47.

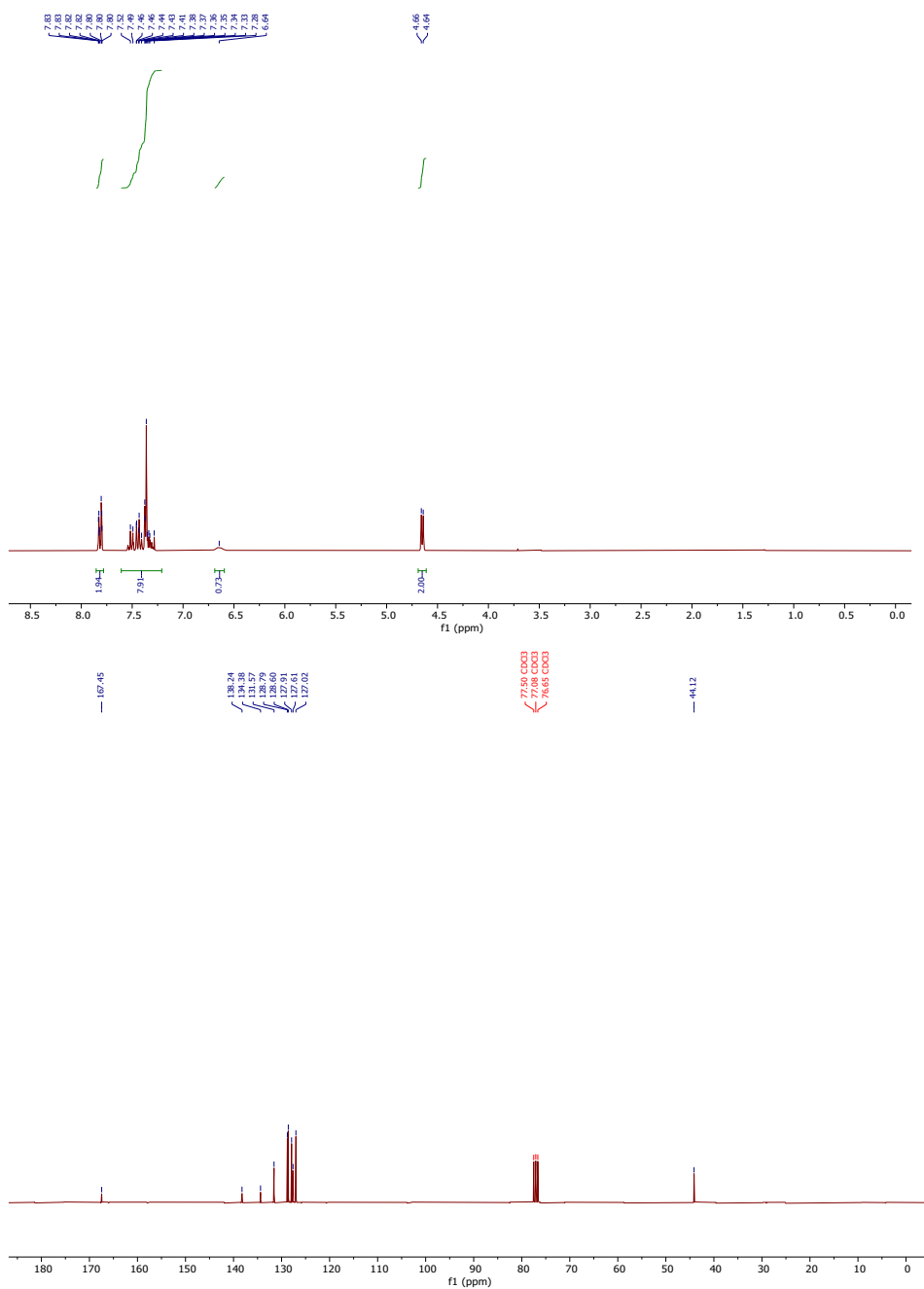


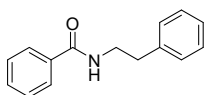
N-benzylbenzamide (**3an**)



^1H NMR (300 MHz, Chloroform-*d*) δ 7.85 – 7.78 (m, 2H), 7.61 – 7.21 (m, 8H), 6.64 (s, 1H), 4.65 (d, $J = 5.6$ Hz, 2H).

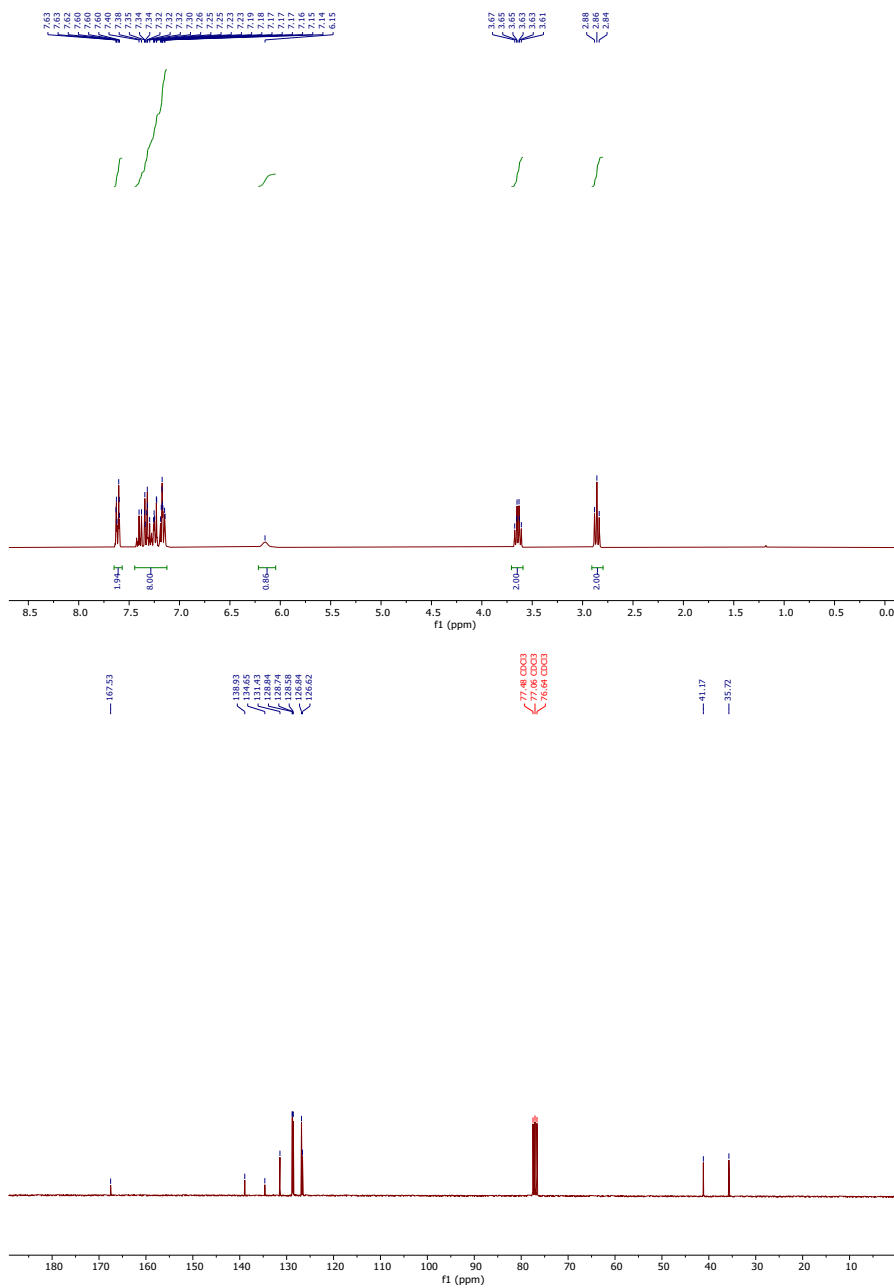
^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.45, 138.24, 134.38, 131.57, 128.79, 128.60, 127.91, 127.61, 127.02, 44.12.



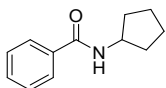


^1H NMR (300 MHz, Chloroform-*d*) δ 7.65-7.57 (m, 2H), 7.44-7.13 (m, 8H), 6.15 (s, 1H), 3.64 (td, J = 6.9, 5.8 Hz, 2H), 2.86 (t, J = 6.9 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.53, 138.93, 134.65, 131.43, 128.84, 128.74, 128.58, 126.84, 126.62, 41.17, 35.72.

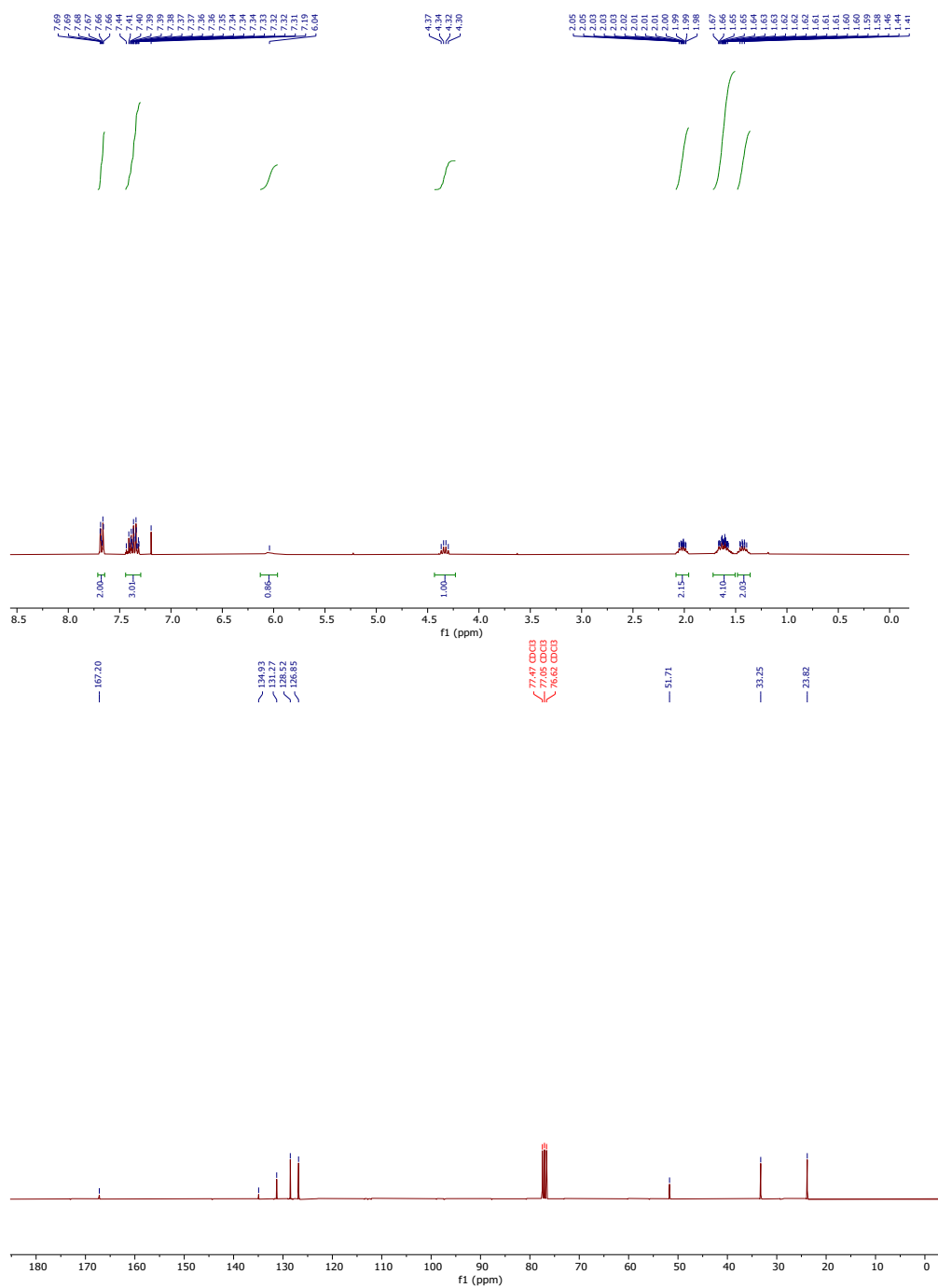


N-cyclopentylbenzamide (**3ap**)

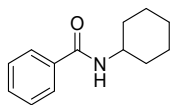


^1H NMR (300 MHz, Chloroform-*d*) δ 7.71-7.65 (m, 2H), 7.44-7.29 (m, 3H), 6.04 (s, 1H), 4.33 (q, $J = 6.9$ Hz, 1H), 2.08-1.96 (m, 2H), 1.72-1.51 (m, 4H), 1.48-1.36 (m, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.20, 134.93, 131.27, 128.52, 126.85, 51.71, 33.25, 23.82.

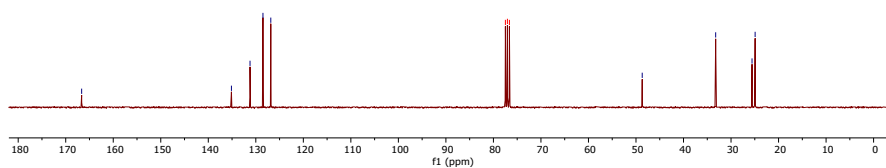
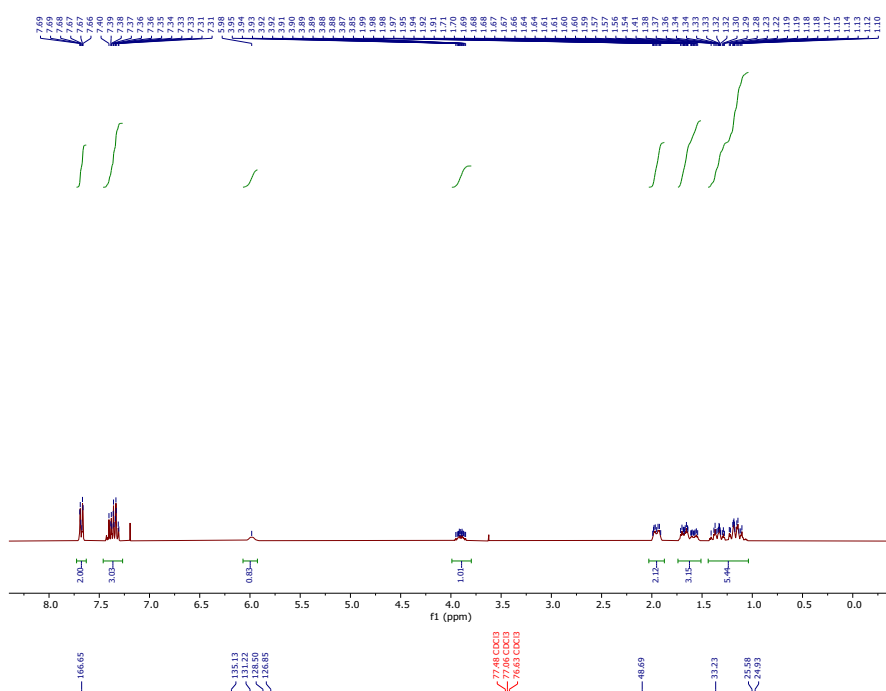


N-cyclohexylbenzamide (3aq)

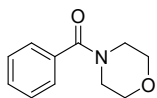


^1H NMR (300 MHz, Chloroform-*d*) δ 7.73-7.63 (m, 2H), 7.46-7.27 (m, 3H), 5.98 (s, 1H), 3.90 (dddd, $J = 10.6, 8.1, 6.6, 4.0$ Hz, 1H), 1.96 (dp, $J = 12.0, 3.9, 3.2$ Hz, 2H), 1.74-1.51 (m, 3H), 1.44-1.04 (m, 5H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.65, 135.13, 131.22, 128.50, 126.85, 48.69, 33.23, 25.58, 24.93.

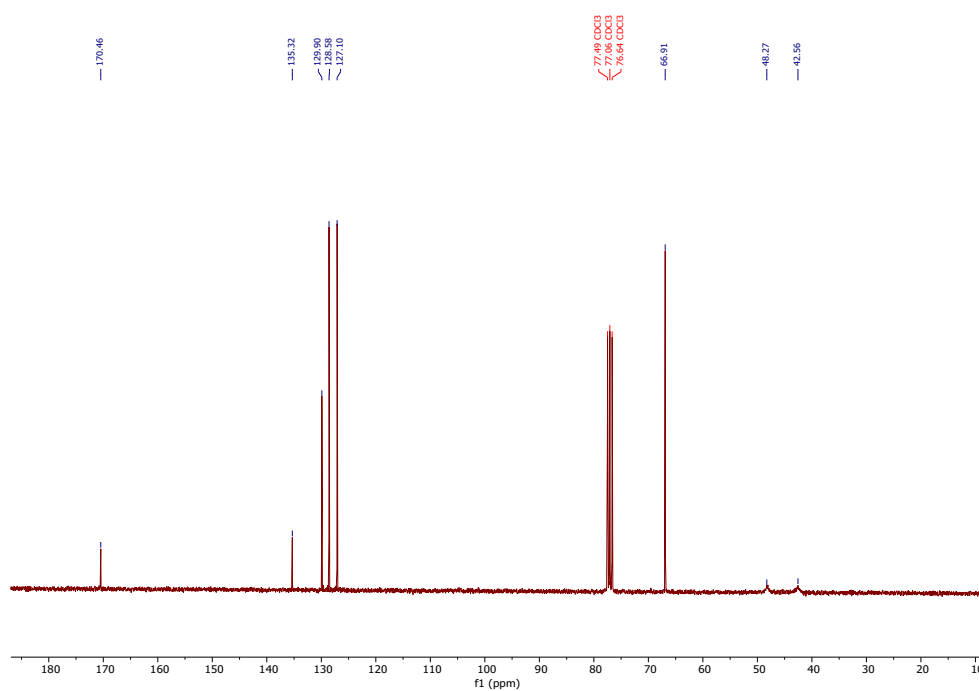
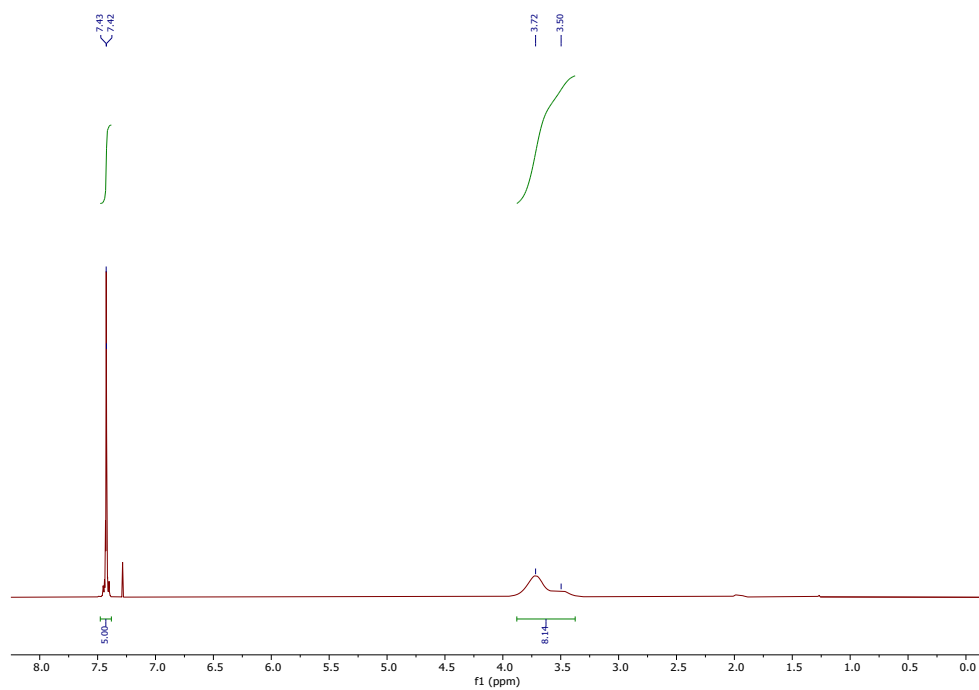


Morpholino(phenyl)methanone (**3ar**)

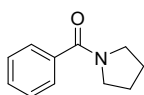


^1H NMR (300 MHz, Chloroform-*d*) δ 7.42 (d, $J = 0.8$ Hz, 5H), 3.61 (d, $J = 66.2$ Hz, 8H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.46, 135.32, 129.90, 128.58, 127.10, 66.91, 48.27, 42.56.

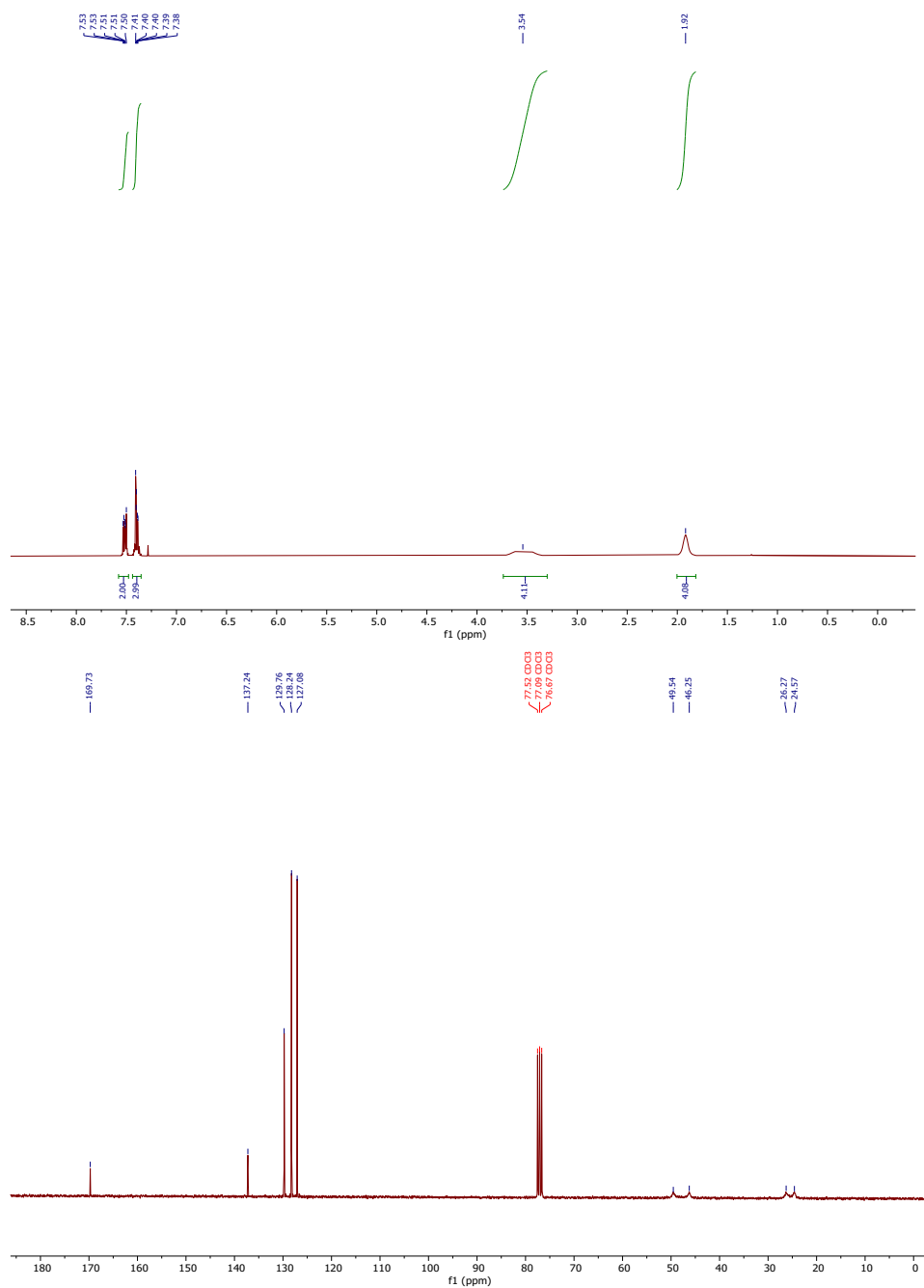


Phenyl(pyrrolidin-1-yl)methanone (**3as**)

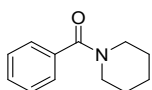


^1H NMR (300 MHz, Chloroform-*d*) δ 7.58-7.48 (m, 2H), 7.40 (dd, $J = 5.0, 1.9$ Hz, 3H), 3.54 (s, 4H), 1.92 (s, 4H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 169.73, 137.24, 129.76, 128.24, 127.08, 49.54, 46.25, 26.27, 24.57.

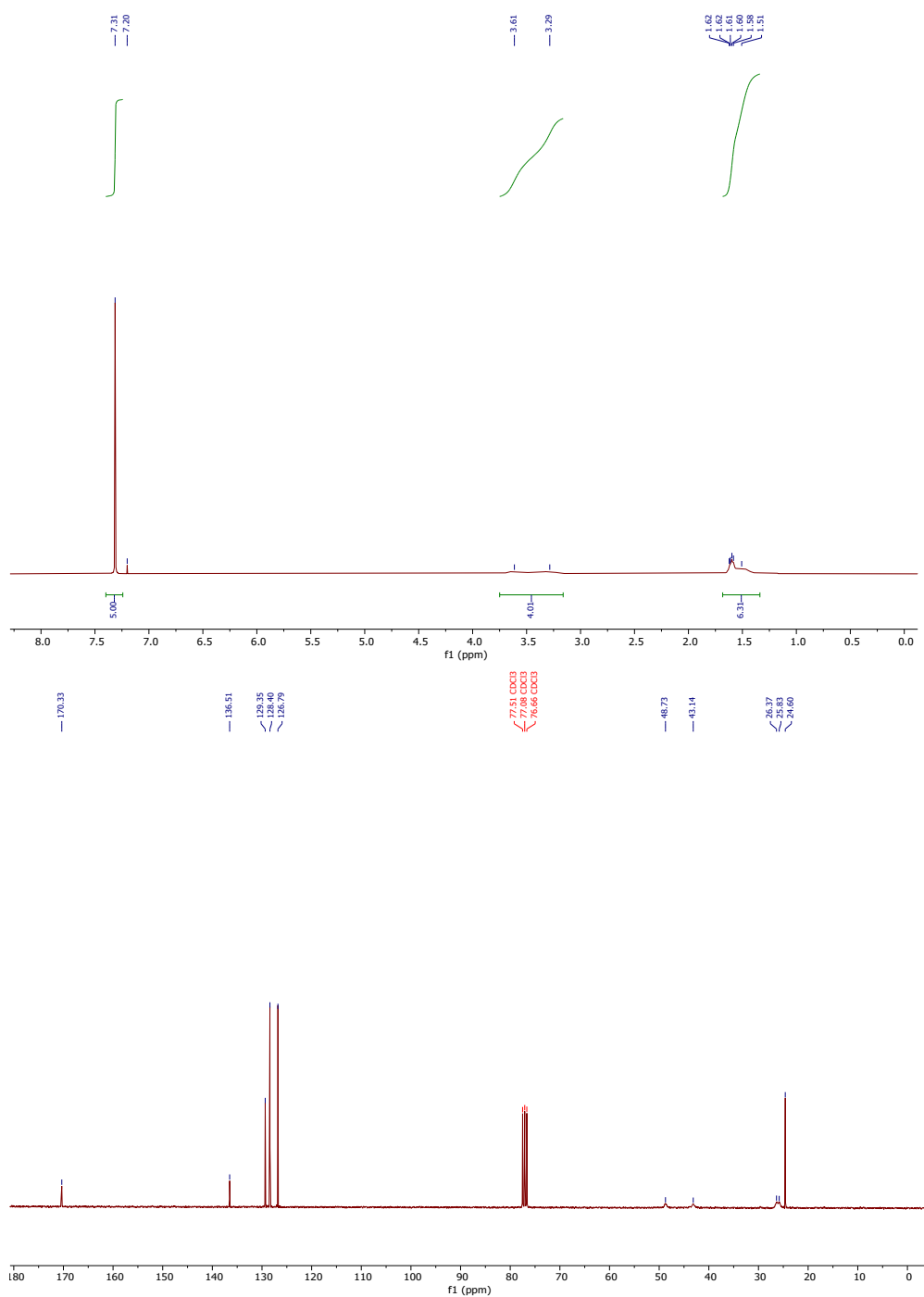


Phenyl(piperidin-1-yl)methanone (**3at**)

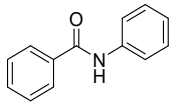


^1H NMR (300 MHz, Chloroform-*d*) δ 7.31 (s, 5H), 3.45 (d, $J = 98.4$ Hz, 4H), 1.68-1.34 (m, 6H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.33, 136.51, 129.35, 128.40, 126.79, 48.73, 43.14, 26.37, 25.83, 24.60.

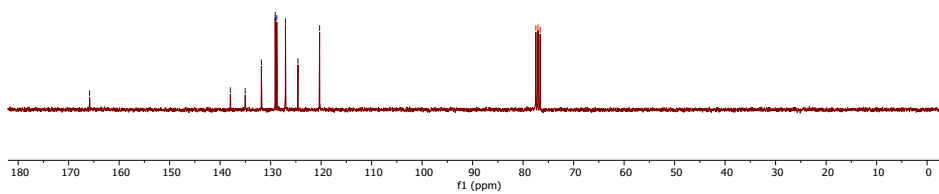
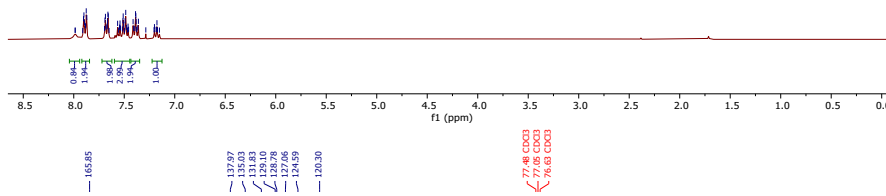
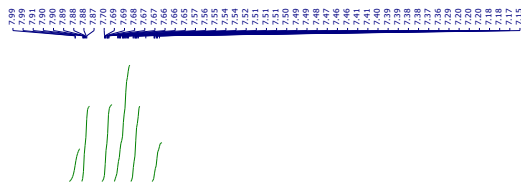


N-phenylbenzamide (**4a**)

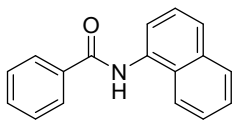


^1H NMR (300 MHz, Chloroform-*d*) δ 8.04-7.94 (m, 1H), 7.92-7.84 (m, 2H), 7.72-7.62 (m, 2H), 7.60-7.45 (m, 3H), 7.43-7.35 (m, 2H), 7.22-7.13 (m, 1H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.85, 137.97, 135.03, 131.83, 129.10, 128.78, 127.06, 124.59, 120.30.

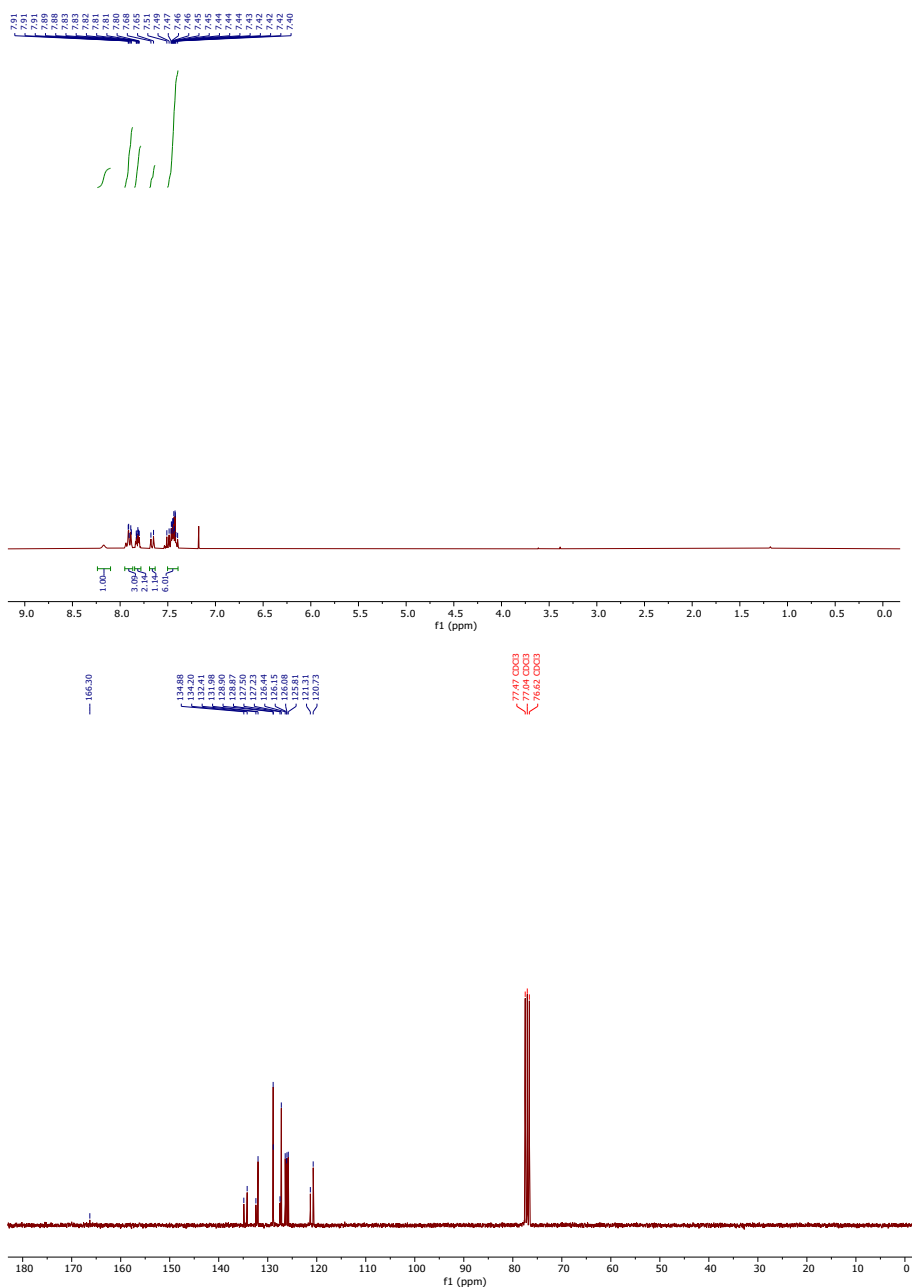


N-(naphthalen-1-yl)benzamide (**4b**)

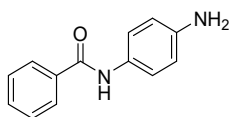


^1H NMR (300 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.90 (dd, $J = 8.3, 1.5$ Hz, 3H), 7.85-7.78 (m, 2H), 7.66 (d, $J = 8.2$ Hz, 1H), 7.50-7.39 (m, 6H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.30, 134.88, 134.20, 132.41, 131.98, 128.90, 128.87, 127.50, 127.23, 126.44, 126.15, 126.08, 125.81, 121.31, 120.73.

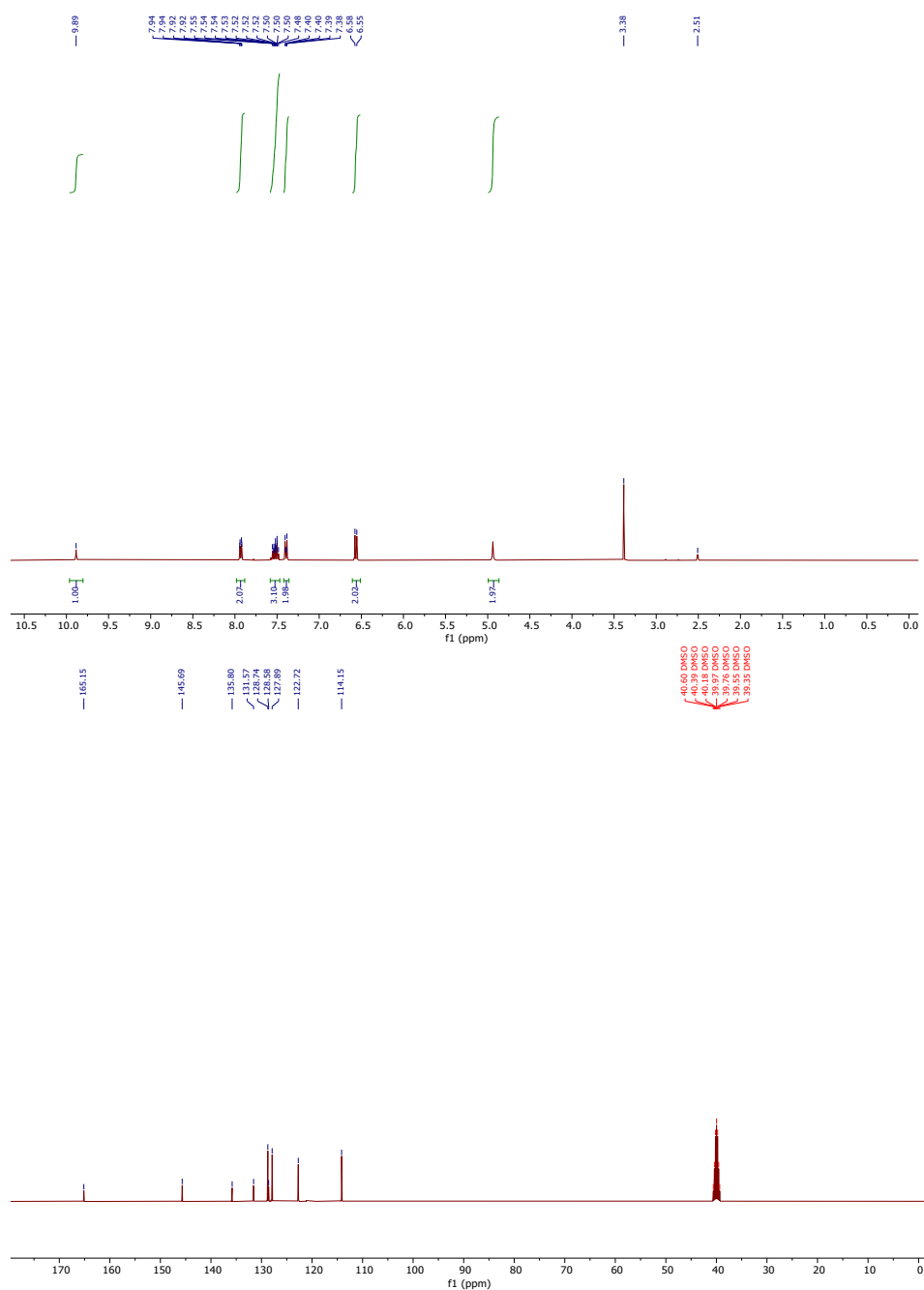


N-(4-aminophenyl)benzamide (**4c**)

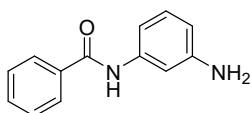


^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 9.89 (s, 1H), 7.98-7.88 (m, 2H), 7.58-7.47 (m, 3H), 7.42-7.36 (m, 2H), 6.56 (d, $J = 8.7$ Hz, 2H), 4.94 (s, 2H).

^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 165.15, 145.69, 135.80, 131.57, 128.74, 128.58, 127.89, 122.72, 114.15.

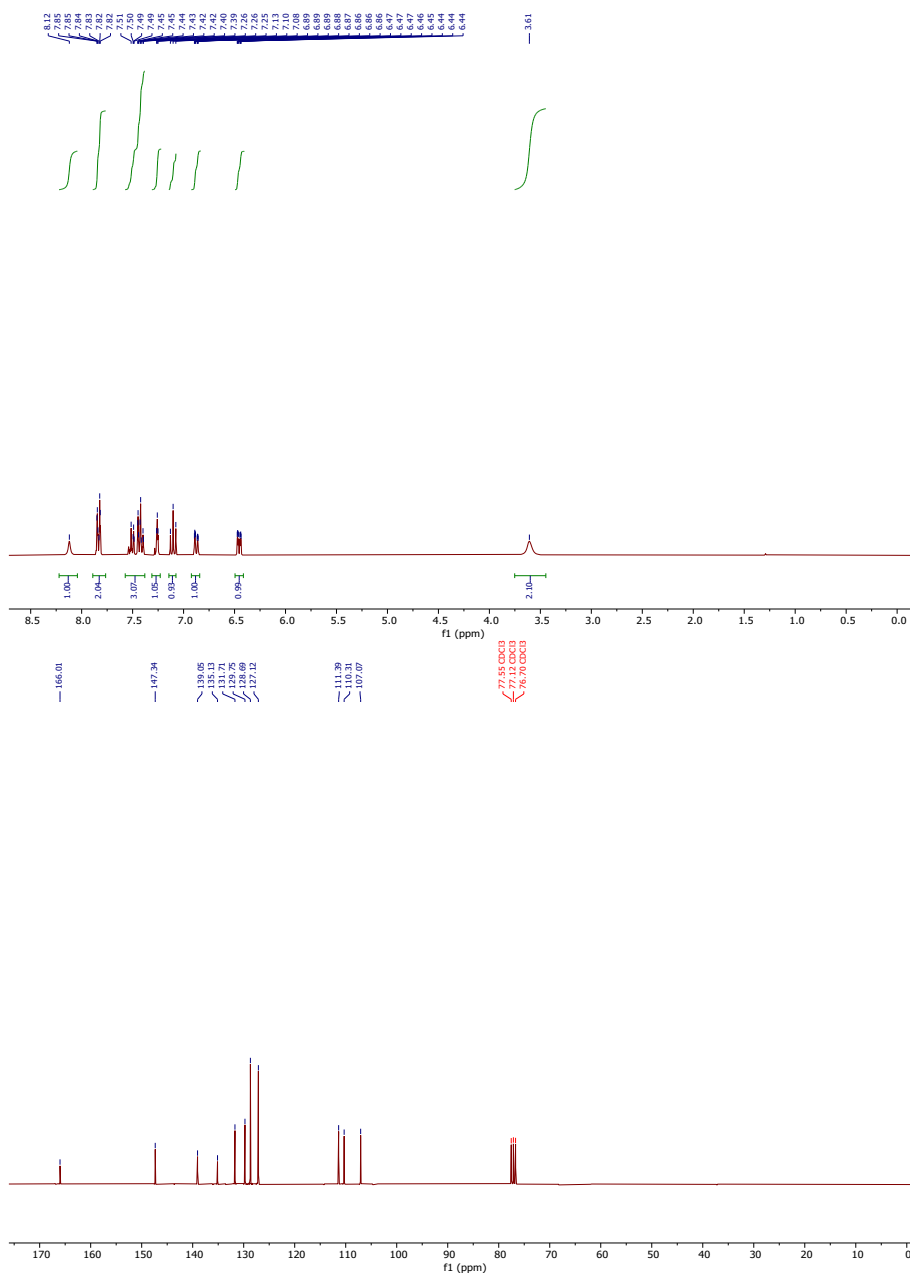


N-(3-aminophenyl)benzamide (**4d**)

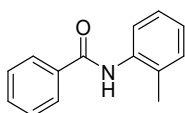


^1H NMR (300 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.89-7.76 (m, 2H), 7.57-7.38 (m, 3H), 7.26 (t, $J = 2.1$ Hz, 1H), 7.10 (t, $J = 8.0$ Hz, 1H), 6.88 (ddd, $J = 8.0, 2.1, 0.9$ Hz, 1H), 6.45 (ddd, $J = 8.0, 2.3, 1.0$ Hz, 1H), 3.61 (s, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.01, 147.34, 139.05, 135.13, 131.71, 129.75, 128.69, 127.12, 111.39, 110.31, 107.07.

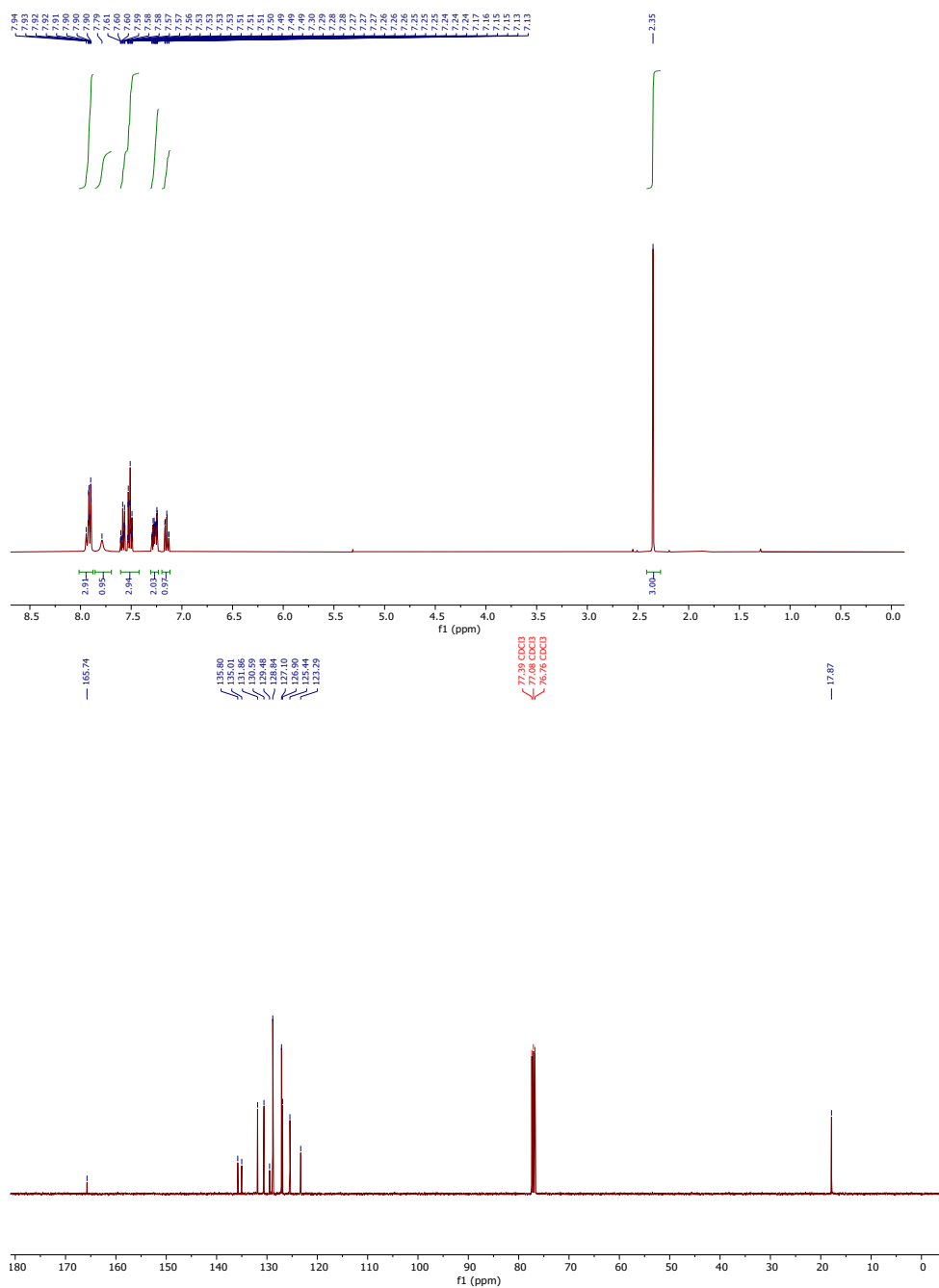


N-(o-tolyl)benzamide (**4e**)

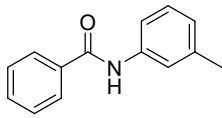


^1H NMR (400 MHz, Chloroform-*d*) δ 8.01-7.88 (m, 3H), 7.79 (s, 1H), 7.60-7.42 (m, 3H), 7.31-7.23 (m, 2H), 7.15 (td, $J = 7.5, 1.3$ Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.74, 135.80, 135.01, 131.86, 130.59, 129.48, 128.84, 127.10, 126.90, 125.44, 123.29, 17.87.

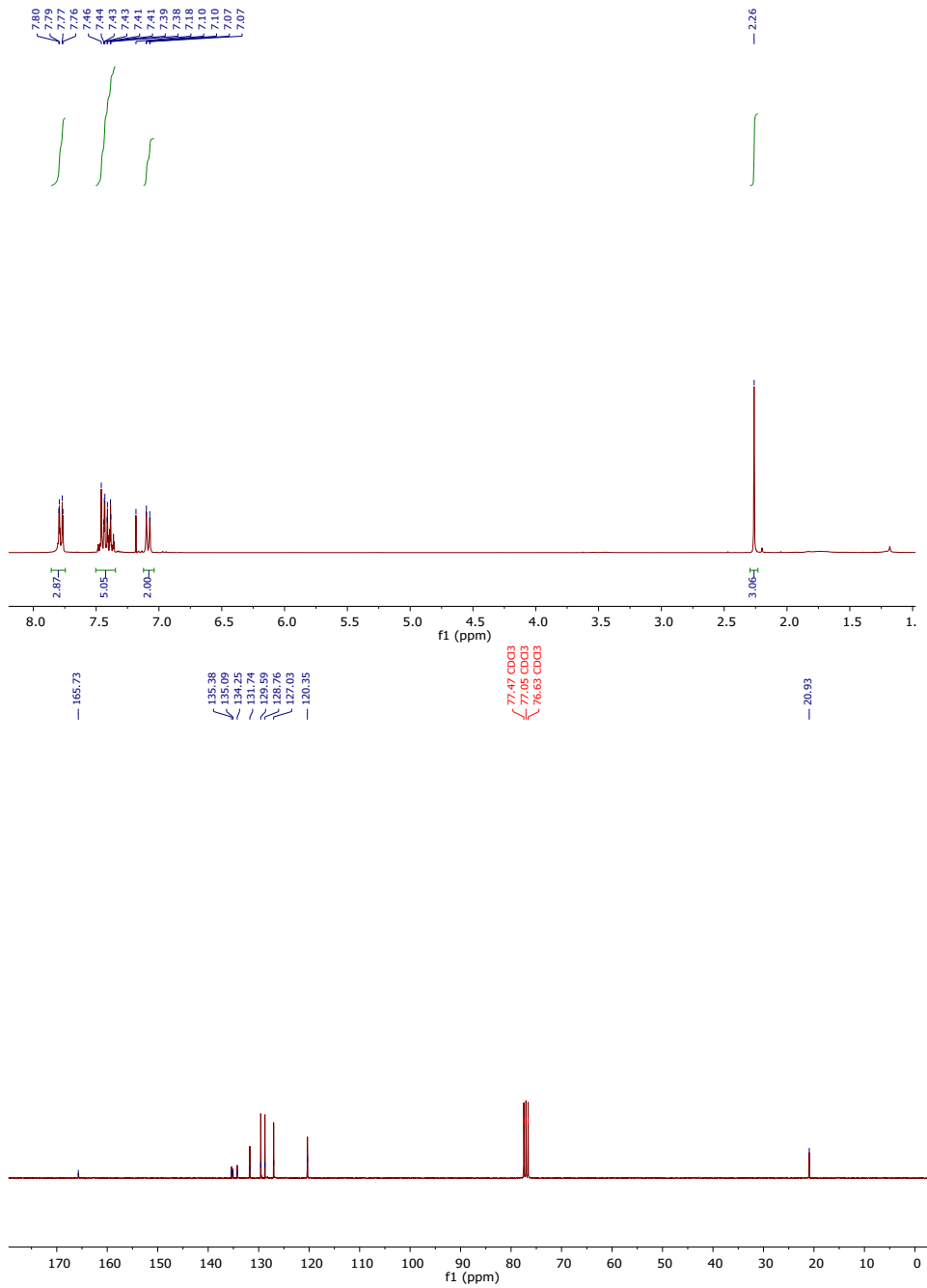


N-(m-tolyl)benzamide (**4f**)

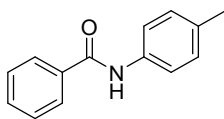


^1H NMR (300 MHz, Chloroform-*d*) δ 7.78 (dd, $J = 8.2, 1.4$ Hz, 3H), 7.50-7.35 (m, 5H), 7.09 (dd, $J = 8.7, 0.8$ Hz, 2H), 2.26 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.73, 135.38, 135.09, 134.25, 131.74, 129.59, 128.76, 127.03, 120.35, 20.93.

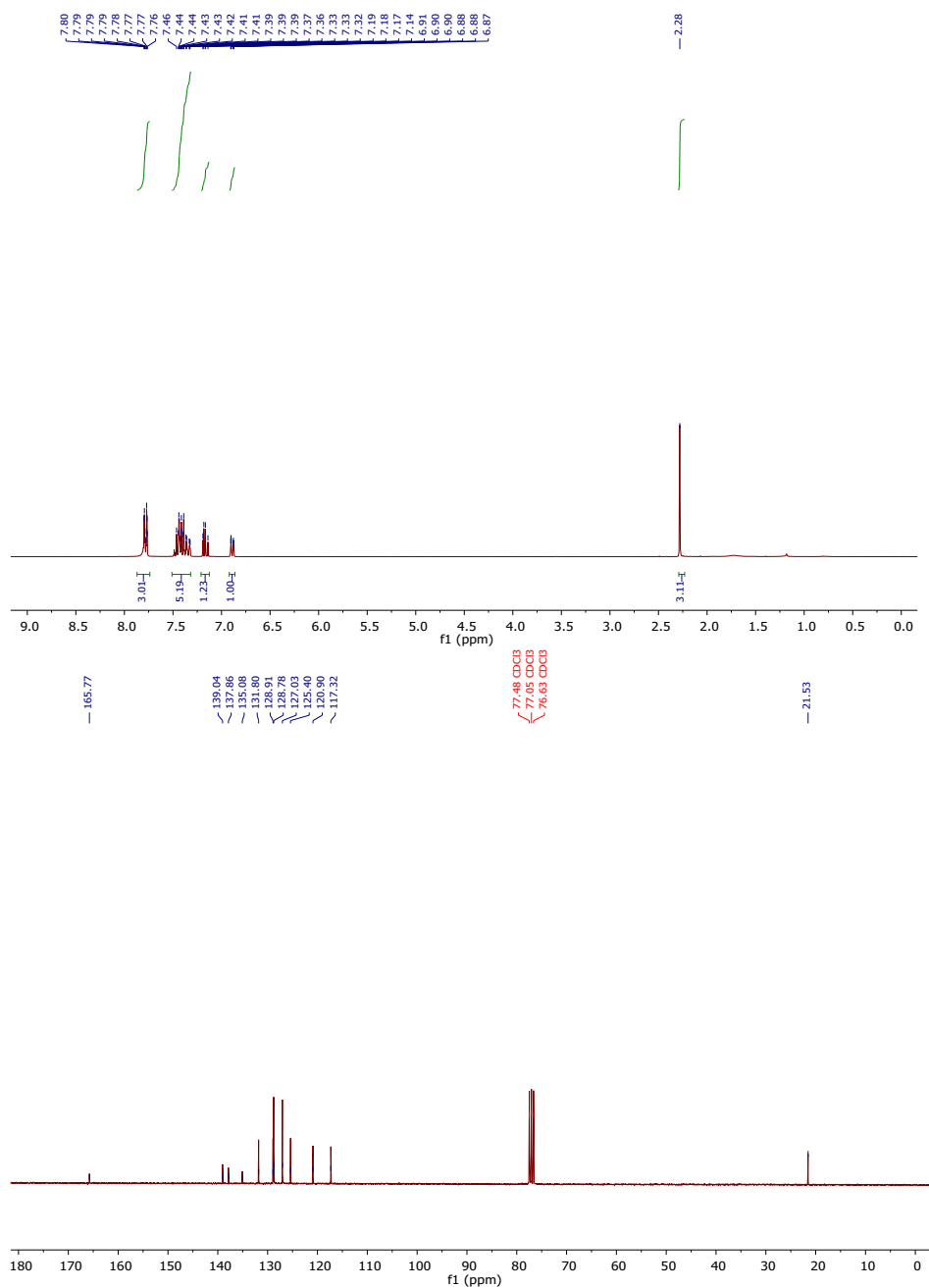


N-(p-tolyl)benzamide (**4g**)

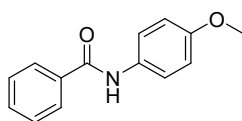


^1H NMR (300 MHz, Chloroform-*d*) δ 7.87-7.74 (m, 3H), 7.51-7.32 (m, 5H), 7.21-7.13 (m, 1H), 6.89 (dt, $J = 7.6, 0.9$ Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.77, 139.04, 137.86, 131.80, 128.91, 128.78, 127.03, 125.40, 120.90, 117.32, 21.53.

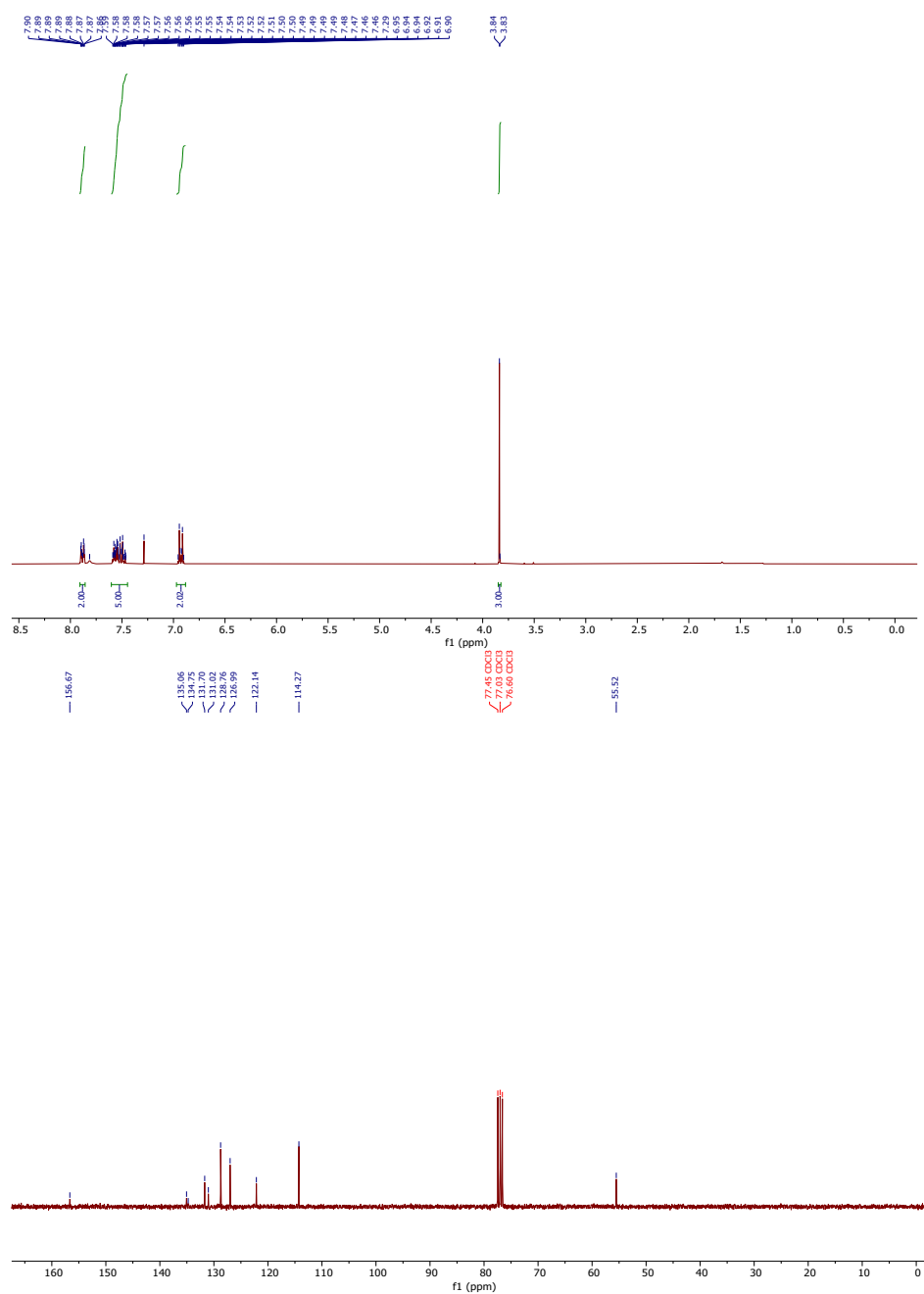


N-(4-methoxyphenyl)benzamide (**4h**)

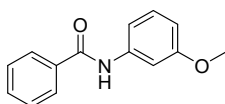


^1H NMR (300 MHz, Chloroform-*d*) δ 7.91-7.86 (m, 2H), 7.60-7.45 (m, 5H), 6.97-6.88 (m, 2H), 3.84 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 156.67, 135.06, 131.70, 131.02, 128.76, 126.99, 122.14, 114.27, 55.52.

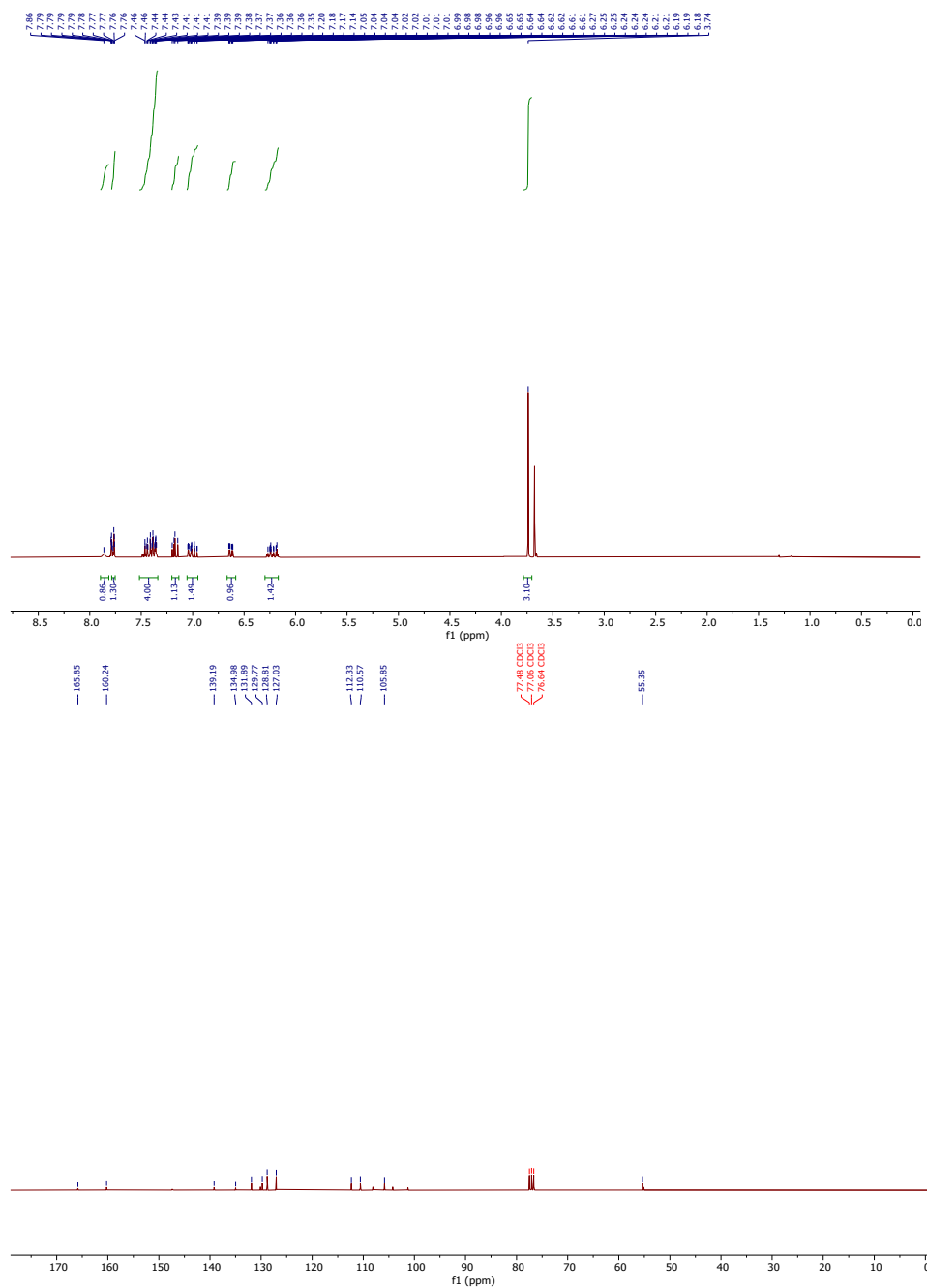


N-(3-methoxyphenyl)benzamide (**4i**)

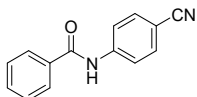


^1H NMR (300 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.79-7.75 (m, 1H), 7.52-7.34 (m, 4H), 7.20-7.13 (m, 1H), 7.05-6.95 (m, 1H), 6.63 (ddd, $J = 8.2, 2.5, 1.0$ Hz, 1H), 6.30-6.17 (m, 1H), 3.74 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.85, 160.24, 139.19, 134.98, 131.89, 129.77, 128.81, 127.03, 112.33, 110.57, 105.85, 55.35.

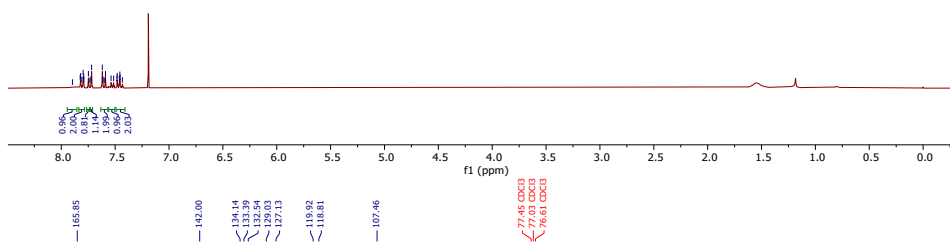
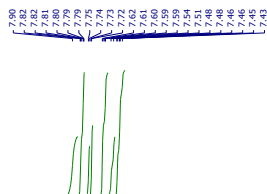


N-(4-cyanophenyl)benzamide (**4j**)

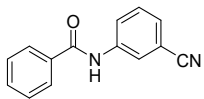


^1H NMR (300 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.84-7.79 (m, 2H), 7.74 (d, $J = 2.0$ Hz, 1H), 7.72 (d, $J = 2.1$ Hz, 1H), 7.63-7.57 (m, 2H), 7.53 (d, $J = 7.3$ Hz, 1H), 7.49-7.41 (m, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.85, 142.00, 134.14, 133.39, 132.54, 129.03, 127.13, 119.92, 118.81, 107.46.

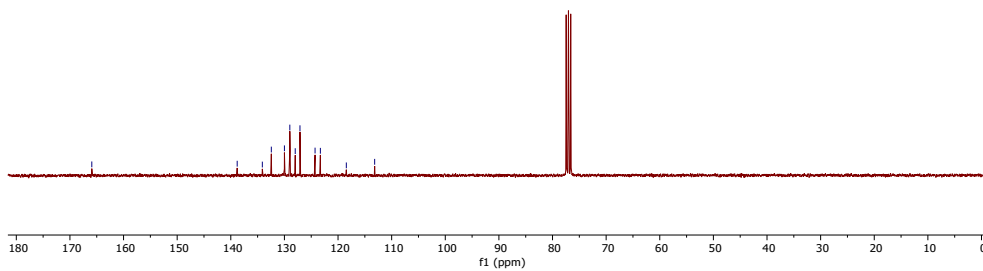
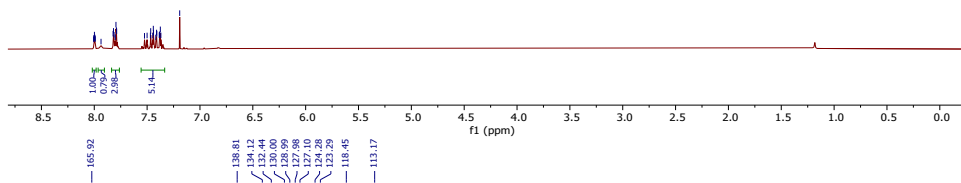
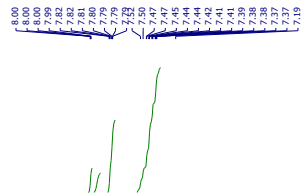


N-(3-cyanophenyl)benzamide (**4k**)

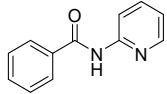


^1H NMR (300 MHz, Chloroform-*d*) δ 8.00 (ddd, $J = 2.2, 1.5, 0.6$ Hz, 1H), 7.94 (s, 1H), 7.84-7.76 (m, 3H), 7.56-7.33 (m, 5H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.92, 138.81, 134.12, 132.44, 130.00, 128.99, 127.98, 127.10, 124.28, 123.29, 118.45, 113.17.

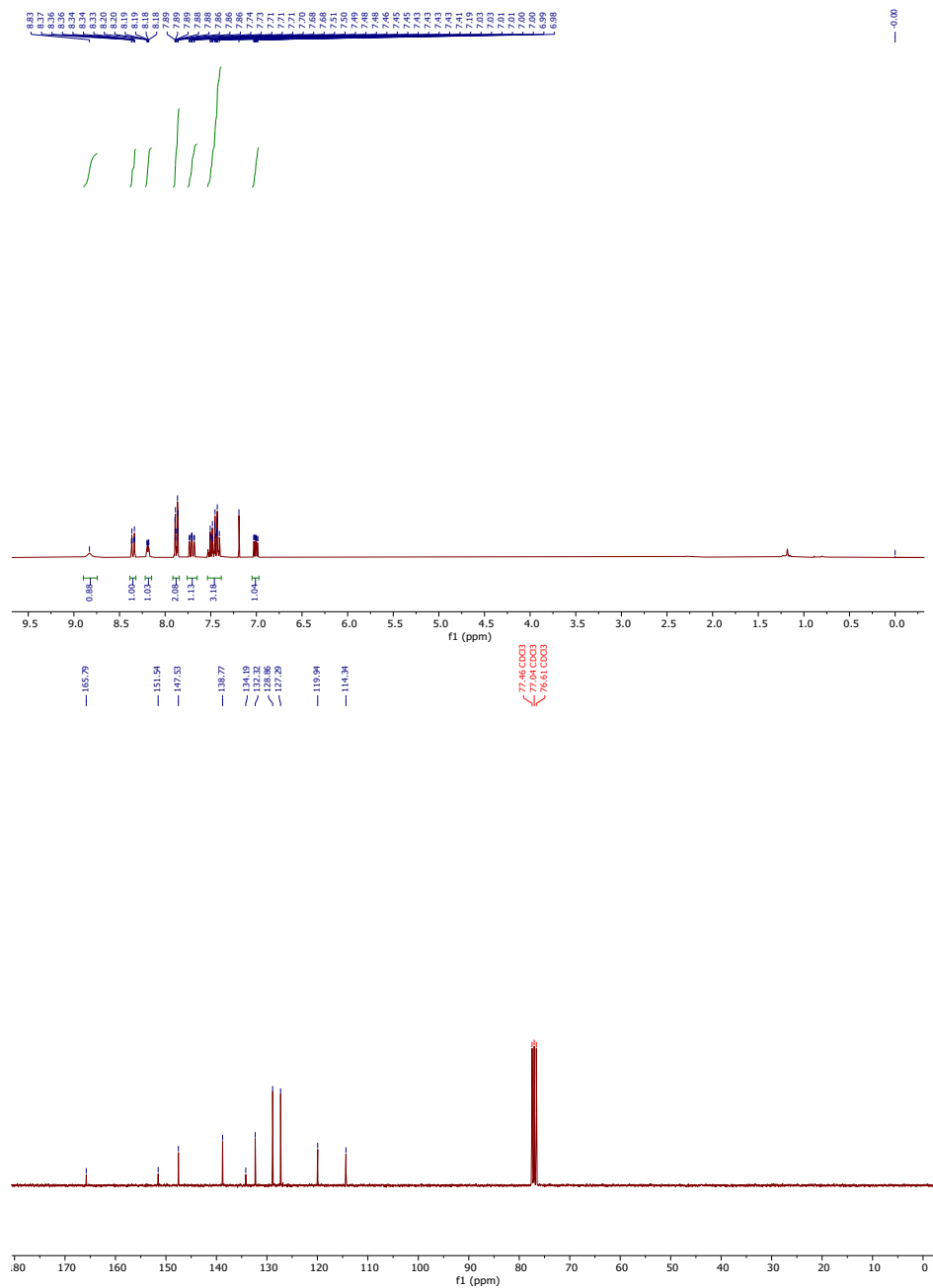


N-(pyridin-2-yl)benzamide (4I)

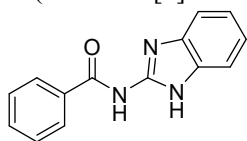


^1H NMR (300 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 8.35 (dt, $J = 8.4, 1.0$ Hz, 1H), 8.19 (dt, $J = 4.1, 1.1$ Hz, 1H), 7.92-7.84 (m, 2H), 7.71 (ddd, $J = 8.4, 7.4, 1.9$ Hz, 1H), 7.54-7.38 (m, 3H), 7.01 (ddd, $J = 7.4, 5.0, 1.0$ Hz, 1H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.79, 151.54, 147.53, 138.77, 134.19, 132.32, 128.86, 127.29, 119.94, 114.34.

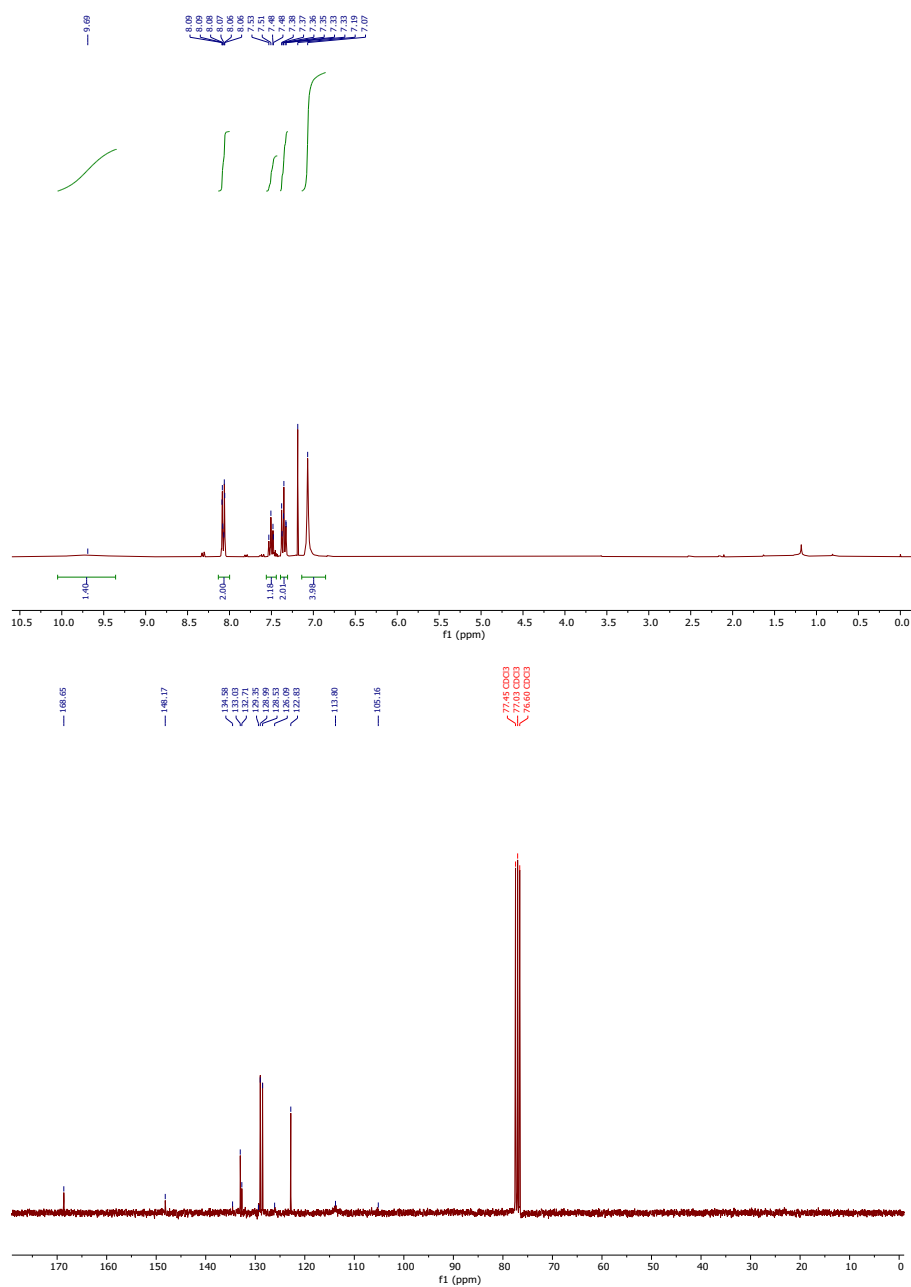


N-(1H-benzo[d]imidazol-2-yl)benzamide (**4m**)

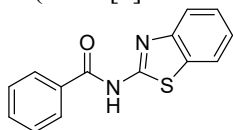


^1H NMR (300 MHz, Chloroform-*d*) δ 9.69 (s, 1H), 8.13-8.00 (m, 2H), 7.56-7.44 (m, 1H), 7.39-7.31 (m, 2H), 7.07 (s, 4H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 168.65, 148.17, 134.58, 133.03, 132.71, 129.35, 128.99, 128.53, 126.09, 122.83, 113.80, 105.16.

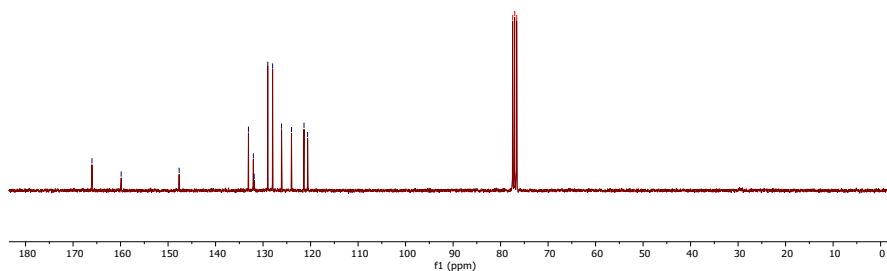
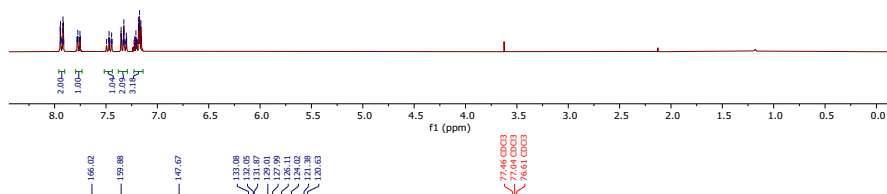
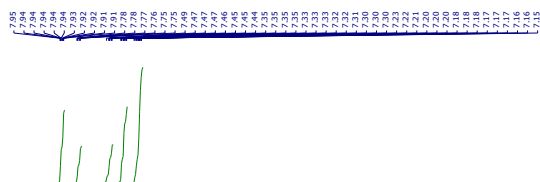


N-(benzo[d]thiazol-2-yl)benzamide (**4n**)



^1H NMR (300 MHz, Chloroform-*d*) δ 7.96-7.90 (m, 2H), 7.80-7.73 (m, 1H), 7.52-7.44 (m, 1H), 7.38-7.29 (m, 2H), 7.23-7.14 (m, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.02, 159.88, 147.67, 133.08, 132.05, 131.87, 129.01, 127.99, 126.11, 124.02, 121.38, 120.63.



References

- [1] X. F. Wu, H. Neumann, M. Beller, *Chem. Eur. J.*, **2010**, 16, 9750-9753.
- [2] J. Y. Wang, A. E. Strom, J. F. Hartwig, *J. Am. Chem. Soc.*, **2018**, 140, 7979-7993.
- [3] J. R. Martinelli, T. P. Clark, D. A. Watson, R. H. Munday, S. L. Buchwald, *Angew. Chem.*, **2007**, 119, 8612-8615.
- [4] P. L. L. Tremblay, A. Fabrikant, B. A. Arndtsen, *ACS Catal.*, **2018**, 8, 5350-5354.
- [5] Y. B.-David, M. Portnoy, D. Milstein, *J. Am. Chem. Soc.*, **1989**, 111, 8742-8744.