

Supporting Information

**Graphene Oxide: A Convenient Metal-Free Carbocatalyst for Facilitating
Amidation of Esters with Amines**

Khushbu P. Patel^[a], Eknath M. Gayakwad^[a], and Ganapati S. Shankarling^[a]*

*^[a]Department of Dyestuff Technology, Institute of Chemical Technology, N. P. Marg, Matunga,
Mumbai, India.*

E-mail: gs.shankarling@ictmumbai.edu.in. gsshankarling@gmail.com

Table of contents:

i.	Characterization of Graphene Oxide (GO):	S2
ii.	Spectral data of the compounds	S8
iii.	^1H , ^{13}C NMR Spectra of synthesized compounds	S20
iv.	References	S97

Characterization of Graphene Oxide (GO):

GO was synthesized from natural graphite powder by following improved hummer's method. [1]

Next, synthesized GO was thoroughly characterized by various spectral techniques (**Fig. S1A-S1F**).

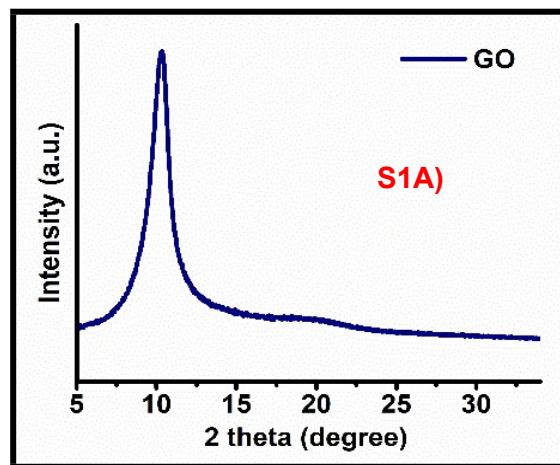


Figure S1A: X-ray diffraction pattern of GO;

The X-ray diffraction (XRD) pattern of GO exhibited a characteristic peak at 9.8° with intercalation distance of 0.90 nm (**Fig. S1A**).[2]

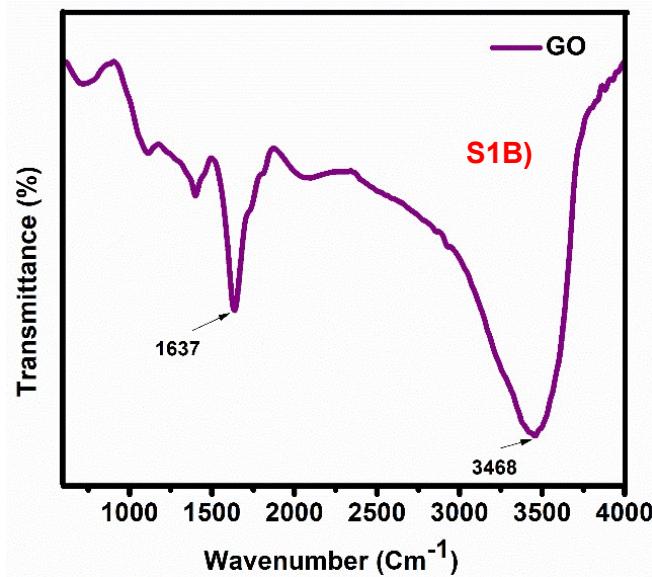


Figure S1B: FTIR spectra of GO;

The Fourier transform infrared spectra of the synthesized GO showed peaks at 3468, 1637, and 1050 cm^{-1} indicating the presence of hydroxy (-OH) carbonyl (-C=O) carboxyl (-COOH) epoxy(-O-) respectively (**Fig. S1B**).^[1] In overall, the GO surface contains four different oxygenated functional groups on graphene sheets.

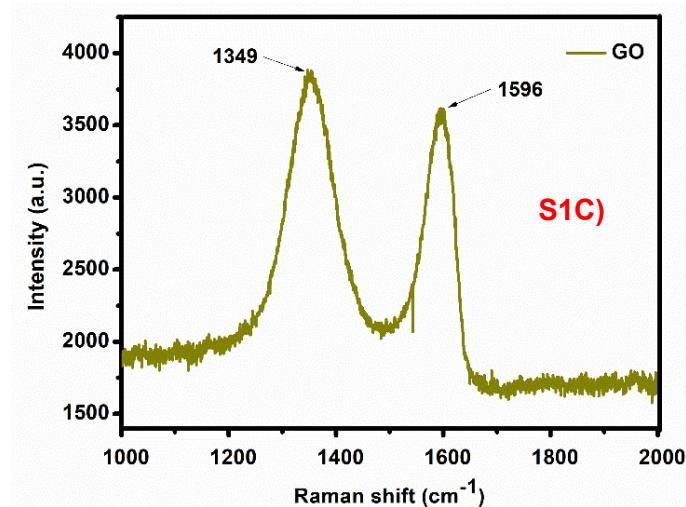


Figure S1C: Raman spectra of GO;

The synthesized GO was further analyzed by Raman analysis (**Fig. S1C**) as it is used to monitor the 2D, G (“graphenic”) and D (“defects”) bands present in the carbonaceous material. A D-band at 1349.0 cm^{-1} demonstrating defects in the graphene sheet and a G-band at 1596.0 cm^{-1} correspondings to the C–C bond stretching which is common to a sp^2 carbon network. The relative intensity ratio (I_D/I_G) of GO was also calculated. The calculated I_D/I_G value was found to be 1.06, which is due to randomness in the π -network of the graphene sheet. [1]

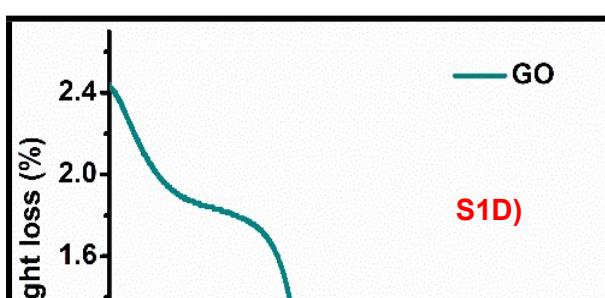


Figure S1D: Thermogravimetric analysis (TGA) of GO;

The thermogravimetric analysis (TGA) is depicted in **Fig S1D** was recorded under a nitrogen atmosphere. The thermogram reveals initial weight loss (~10%) at a temperature around 100°C due to the vaporization of the water molecules. The second weight loss (~85%) in the range of 180-200°C is due to decomposition of different oxygenated functionalities present on GO sheet.[3]

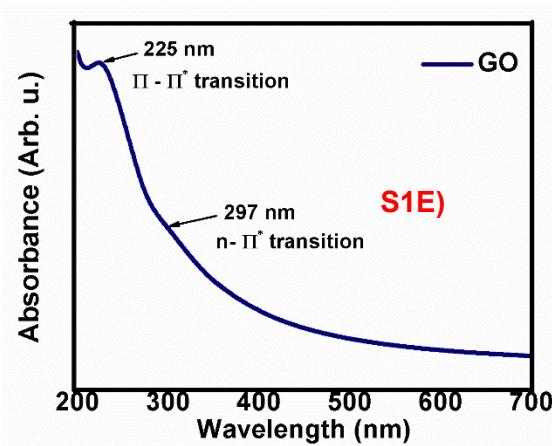


Figure S1E: UV-visible spectra of GO;

The UV-visible spectra of GO display two absorption peaks, a characteristic peak at 225 nm is due to $\pi-\pi^*$ transitions of aromatic C–C bonds and a peak at 297 nm ascribed to n– π^* transitions of carbonyl (**Fig. 1E**). [3]

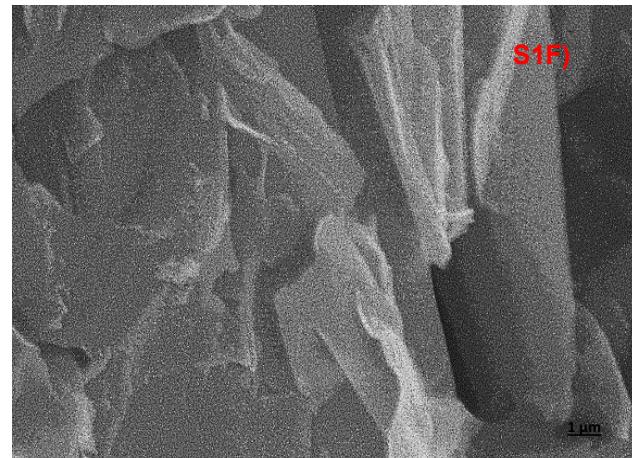


Figure S1F: Scanning electron microscopy (SEM),



Figure S1G: transmission electron microscopy (TEM)

The Scanning electron microscopy (SEM) analysis showed wrinkled and crumpled structure due to the presence of sp^3 carbon atoms associated with oxygen functionalities and various defects in the basal plane of GO (**Fig. S1F**).^[3] The transmission electron microscopy (TEM) analysis showed a layered sheet of GO (**Fig. S1G**).^[4] From the above analysis results, it can be concluded that GO is successfully synthesized from Natural graphite powder.

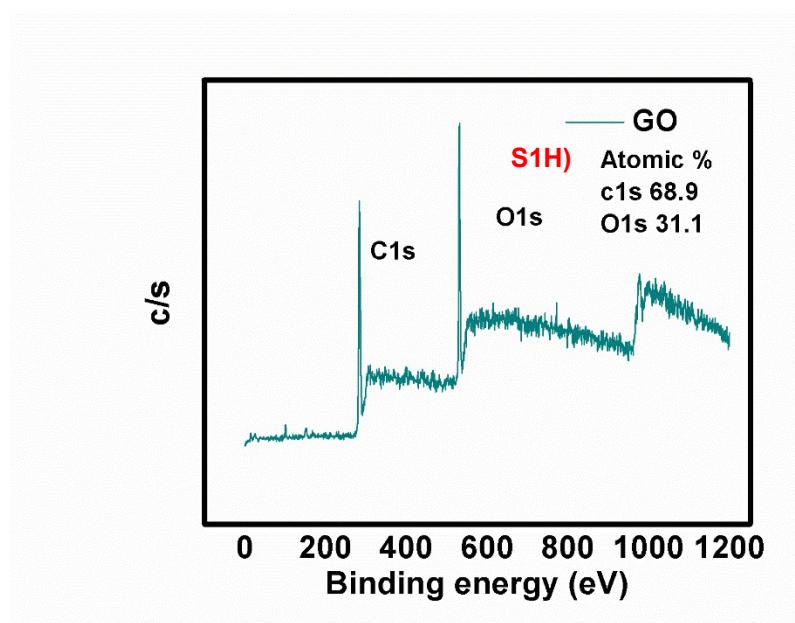


Figure S1H: XPS Survey spectrum of GO;

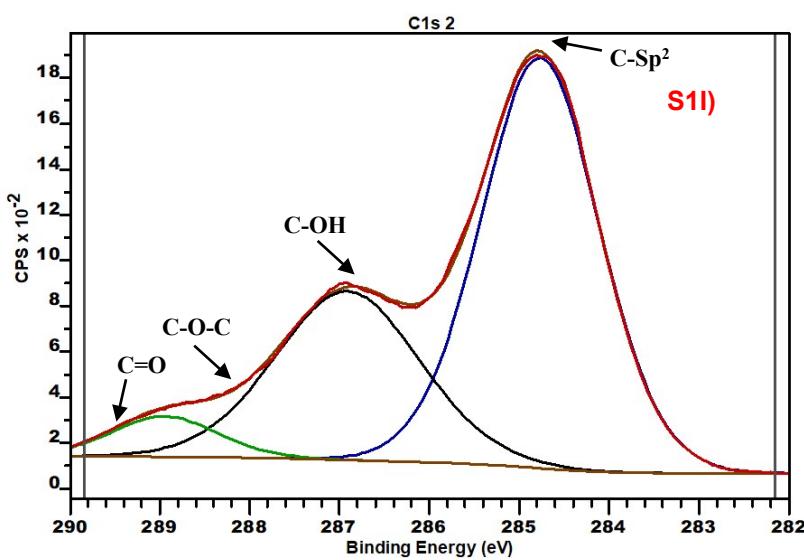


Figure S1I: C1s XPS Spectrum of recovered GO

X-ray photoelectron spectroscopy (XPS) survey spectrum of GO displayed two prominent peaks at 284.6 and 532.2, which corresponds to C1s and O1s respectively confirming the oxidation of graphite to GO (**Fig. S1H**). [5] In C1s core level spectrum of GO peak at 284.6 corresponds to sp² hybridized carbon and other components at 286.6, 287.8, and 288.6 eV is due to hydroxyl (C–OH), epoxide (C–O–C) and carboxyl (HO–C=O) groups, respectively(**Fig. S1I**).[3]

Spectral data of the compounds:

1. N-Benzyl benzamide (3a):

White crystals. Yield: 133 mg, 95%. MP: 106-108°C (lit[6] 108-109°C).

¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.39 – 7.27 (m, 5H), 6.41 (s, 1H), 4.65 (d, J = 5.6 Hz, 2H).

2. 4-Chloro-N-benzyl benzamide (3b):

White solid. 125 mg, 94%. MP: 159-161 °C (lit[7] 161-163 °C).

¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.34 – 7.28 (m, 5H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.38 (s, 1H), 4.63 (d, *J* = 5.3 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 166.90, 162.25, 138.39, 128.78, 127.94, 127.59, 126.63, 113.79, 44.10.

3. 4-Nitro-*N*-benzyl benzamide (3c):

Off white solid. 115 mg, 95%. MP: 140-141 °C (lit[8] 137-138 °C).

¹H NMR (500 MHz, CDCl₃) δ 8.29 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.42 – 7.30 (m, 5H), 6.66 (d, *J* = 8.7 Hz, 1H), 4.67 (d, *J* = 5.5 Hz, 2H).

4. 4-Hydroxy-*N*-benzyl benzamide (3d):

Buff solid. 111 mg, 82%. MP: 152-154°C (lit[7] 157-163 °C).

5. 4-Methoxy-*N*-benzyl benzamide (3e):

White solid. 115 mg, 87%. MP: 121-122°C (lit[9] 119-121 °C).

¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 4.4 Hz, 4H), 7.30 (dd, *J* = 8.9, 4.5 Hz, 1H), 6.92 (m, 2H), 6.30 (s, 1H), 4.64 (d, *J* = 5.6 Hz, 2H), 3.85 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 164.56, 138.38, 128.80, 128.76, 127.95, 127.61, 126.64, 113.80, 55.43, 44.12.

6. 4-Amino-*N*-benzyl benzamide (3f):

Buff solid. Yield: 106 mg, 78%. MP: 88-90 °C (lit[10] 89-91°C)

7. 2-Amino-*N*-benzyl benzamide (3g):

White crystal. Yield: 103 mg, 76%. MP: 122-123 °C (lit[11] 121-123°C)

¹H NMR (300 MHz, DMSO) δ 8.87 (t, *J* = 5.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.35 (m, 5H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.60 (d, *J* = 7.4 Hz, 1H), 6.55 (d, *J* = 6.2 Hz, 2H), 4.52 (d, *J* = 5.9 Hz, 2H).

¹³C NMR (75 MHz, DMSO) δ 168.93, 149.82, 139.95, 131.78, 128.16, 127.14, 126.62, 116.46, 114.57, 42.23.

8. 2-Hydroxy-N-benzyl benzamide (3h):

White crystal. 107 mg, 79%. MP: 134-136 °C (lit[10] 137 °C).

¹H NMR (300 MHz, DMSO) δ 12.53 (s, 1H), 9.36 (t, J = 5.8 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.45 – 7.22 (m, 6H), 6.90 (t, J = 7.4 Hz, 2H), 4.52 (d, J = 6.0 Hz, 2H).

¹³C NMR (75 MHz, DMSO) δ 168.88, 160.00, 138.93, 133.77, 128.34, 127.73, 127.22, 126.89, 118.63, 117.37, 115.13, 42.29.

9. *N¹,N³,N⁵- tribenzylbenzene-1,3,5-tricarboxamide (3i):*

Buff solid. Yield: 176 mg, 92%. MP: above 300 °C (lit[12] 319 °C).

¹H NMR (400 MHz, DMSO) δ 9.28 (t, J = 5.8 Hz, 3H), 8.51 (s, 3H), 7.34 (d, J = 4.4 Hz, 12H), 7.25 (m, 3H), 4.50 (d, J = 5.8 Hz, 6H).

¹³C NMR (100 MHz, DMSO) δ 165.92, 139.85, 135.36, 129.23, 128.77, 127.84, 127.30, 43.30.

10. N-benzyl-2-phenylacetamide (3j):

White crystals. Yield: 130 mg, 96%. MP: 124-125 °C (lit[13] 124-125 °C).

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.11 (m, 10H), 5.64 (s, 1H), 4.40 (d, J = 5.4 Hz, 2H), 3.62 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 170.87, 138.13, 134.77, 129.48, 129.09, 128.68, 127.50, 127.45, 127.44, 43.87, 43.60.

11. N-benzyl-2-(4-methoxyphenyl)acetamide (3k):

White solid. Yield: 143 mg, 92%. MP: 134-135 °C (lit[14] 134-135 °C).

12. N-benzyl-2-(o-tolyl)acetamide (3l):

White solid. Yield: 130 mg, 97%. MP: 108-110 °C (lit[15] 110 °C).

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.14 (m, 9H), 5.61 (s, 1H), 4.41 (d, *J* = 5.9 Hz, 2H), 3.65 (s, 2H), 2.28 (s, 3H).

¹³C NMR (100 MHz, DMSO) δ 165.94, 133.44, 132.50, 128.44, 126.12, 125.81, 123.90, 123.18, 122.67, 121.94, 38.74, 37.15, 14.75.

13. N-benzyl-2-(2-chlorophenyl)acetamide (3m):

White solid. Yield: 119 mg, 91%. MP: 120-122 °C

14. N-benzyl-2-(naphthalen-1-yl)acetamide (3n)

White solid. Yield: 128 mg, 94%. MP: 156-158 °C

¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.97 (m, 1H), 7.88 (dd, *J* = 7.0, 2.3 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.47 – 7.38 (m, 2H), 7.22 – 7.14 (m, 3H), 7.00 (dd, *J* = 6.8, 2.5 Hz, 2H), 5.62 (s, 1H), 4.35 (d, *J* = 5.9 Hz, 2H), 4.09 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 170.87, 138.05, 134.01, 132.07, 130.99, 128.84, 128.61, 128.51, 128.45, 127.28, 127.25, 126.86, 126.27, 125.66, 123.90, 43.38, 41.92.

15. N-benzyl-2-hydroxy-2-phenylacetamide (3o):

Buff solid. Yield: 109 mg, 82%. MP: 133-134 °C (lit[7] 134-135[16] °C).

¹H NMR (300 MHz, DMSO) δ 8.57 (t, *J* = 6.1 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.37 – 7.19 (m, 8H), 6.24 (d, *J* = 4.1 Hz, 1H), 4.98 (d, *J* = 3.1 Hz, 1H), 4.28 (d, *J* = 6.1 Hz, 2H).

¹³C NMR (75 MHz, DMSO) δ 172.21, 141.28, 139.55, 128.11, 127.89, 127.35, 127.07, 126.61, 126.51, 73.53, 41.70.

16. N-benzylcinnamamide (3p):

White solid. 151mg, 89%. MP: 109-111 °C (lit[17] 108-110°C).

¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 15.6 Hz, 1H), 7.50 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.38 (m, 8H), 6.40 (d, *J* = 15.6 Hz, 1H), 5.86 (s, 1H), 4.59 (d, *J* = 5.7 Hz, 2H).

17. *N*-(2-(benzylamino)-2-oxoethyl)benzamide (3q):

Buff solid. 137mg, 94%. MP: 158-159°C (lit[18] 158 °C).

¹H NMR (400 MHz, DMSO) δ 8.80 (t, *J* = 5.6 Hz, 1H), 8.45 (d, *J* = 5.5 Hz, 1H), 7.92-7.87 (t, 2H), 7.57-7.52 (m, 3H), 7.34-7.22 (m, 5H), 4.31 (d, *J* = 5.9 Hz, 2H), 3.93 (d, *J* = 5.9 Hz, 2H).

¹³C NMR (100 MHz, DMSO) δ 169.49, 166.96, 139.94, 134.50, 131.78, 128.71, 128.68, 127.86, 127.63, 127.17, 43.22, 42.49.

18. *N¹,N⁴-dibenzylsuccinamide (3r):*

White solid. Yield: 182mg, 93%. MP: 210-212 °C (lit[6] 212-212.5 °C).

¹H NMR (300 MHz, DMSO) δ 8.38 (t, *J* = 5.8 Hz, 2H), 7.31-7.22 (m, 11H), 4.27 (d, *J* = 5.9 Hz, 4H), 2.43 (s, 4H).

¹³C NMR (75 MHz, DMSO) δ 171.32, 139.58, 128.19, 127.10, 126.62, 41.98, 30.71.

19. *N*-benzyl-2-(2-formylphenoxy)acetamide (3s):

Buff solid. Yield: 170mg, 76%. MP: 69°C

¹H NMR (300 MHz, CDCl₃) δ 10.13 (s, 1H), 7.97 (s, 1H), 7.76 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.60 (dd, *J* = 11.4, 4.3 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 1H), 4.64 (s, 2H), 4.60 (d, *J* = 6.0 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 190.13, 167.43, 157.84, 137.86, 136.11, 134.03, 128.72, 127.65, 125.03, 122.05, 113.13, 67.66, 43.10.

20. *N*-(4-Methoxybenzyl) acetamide (3t):

White crystals. Yield: 227 mg, 95%. MP: 96-98°C (lit[12] 95°C).

¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 5.66 (s, 1H), 4.35 (d, *J* = 5.2 Hz, 2H), 3.78 (s, 3H), 1.99 (s, 3H).

21. *N*-Benzylformamide (3u):

White crystals. Yield: 196 mg, 96%. MP: 62-63°C (lit[6] 61-63 °C).
¹H NMR (500 MHz, cdcl3) δ 8.22 (s, 1H), 7.36-7.21 (m, 5H), 5.87 (s, 1H), 4.45 (d, *J* = 5.8 Hz, 2H).

22. *N*-benzylbutyramide (3v):

Off white solid. Yield: 155 mg, 98%. MP: 49-51°C (lit[19] 47-48°C).
¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.25 (m, 5H), 5.82 (s, 1H), 4.43 (d, *J* = 5.7 Hz, 2H), 2.19 (t, *J* = 7.5 Hz, 2H), 1.72 – 1.67 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).
¹³C NMR (100 MHz, DMSO) δ 168.10, 133.69, 123.96, 123.08, 122.75, 38.82, 33.95, 14.44, 9.06.

23. *N*-benzylisobutyramide (3w):

White crystal. Yield: 159 mg, 96%. MP: 85-86 °C (lit[20] 84-86°C).

24. *N*-benzyl-2,2,2-trifluoroacetamide (3x):

White crystals. Yield: 150 mg, 95%. MP: 96-98°C (lit¹⁰ 95°C).
¹H NMR (400 MHz, DMSO) δ 10.03 (s, 1H), 7.38 (m, 5H), 4.39 (d, *J* = 6.0 Hz, 2H).
¹³C NMR (100 MHz, DMSO) δ 156.66, 137.94, 129.30, 128.99, 127.82, 117.93, 43.02.

25. *N*-(2-Methoxybenzyl) benzamide (5a):

White crystals. Yield: 137mg, 94%. MP: 78-80 °C (lit[21] 77°C).

26. *N*-(4-Methoxybenzyl) benzamide (5b):

White crystals. Yield: 171mg, 95%. MP: 94-95°C (lit[22] 94-96°C).

27. *N*-(4-Methylbenzyl) benzamide (5c):

White solid. Yield: 182mg, 94%. MP: 136-137 °C (lit[22] 138-140°C).

28. *N*-(4-Tertbutylbenzyl) benzamide (5d):

White solid. Yield: 191mg, 93%. MP: 108-110 °C (lit[23] 105-106 °C).

29. *N*-(4-Fluorobenzyl) benzamide (5e):

White crystals. Yield: 188mg, 81%. MP: 113-115°C (lit[23] 114-116 °C).

30. (S)-*N*-(1-Phenylethyl) benzamide (5f):

White crystals. Yield: 189 mg, 79%. MP: 116-118°C (lit[23] 116°C).

¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.46 – 7.35 (m, 6H), 7.29 (t, *J* = 7.1 Hz, 1H), 6.31 (s, 1H), 5.35 (p, *J* = 7.1 Hz, 1H), 1.62 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 166.61, 143.15, 134.60, 131.48, 128.66, 127.47, 126.95, 126.28, 49.22, 21.73.

31. *N*-Octylbenzamide (5g):

White crystals. 114mg, 95%. MP: 40-42 °C (lit[24]39-41 °C).

¹H NMR (500 MHz, CDCl₃) δ 7.76 – 7.73 (m, 2H), 7.49 – 7.45 (m, 1H), 7.43 – 7.38 (m, 2H), 6.16 (s, 1H), 3.43 (td, *J* = 7.2, 5.8 Hz, 2H), 1.60 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.39 – 1.28 (m, 6H), 1.28 – 1.21 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 167.61, 134.88, 131.24, 128.47, 126.91, 40.15, 31.80, 29.68, 29.31, 29.23, 27.04, 22.64, 14.09.

32. *N*-Butylbenzamide (5h):

Yellow liquid.129 mg, 91%. MP:38-39 °C (lit[10]39 °C).

33. *N*-(tert-butyl)benzamide (5i):

White crystals. Yield: 176mg, 67%. MP: 101-103°C (lit[10] 102 °C).

¹H NMR (300 MHz, DMSO) δ 7.87 (d, J = 7.7 Hz, 2H), 7.31 (d, J = 7.0 Hz, 3H), 1.25 (s, 9H).

¹³C NMR (75 MHz, DMSO) δ 169.24, 129.27, 128.91, 127.30, 49.97, 27.81.

34. *N*-(2-hydroxyethyl)benzamide (5j):

White solid. Yield: 125mg, 88%. MP: 60-61°C (lit[25] 60-62 °C).

¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 6.3 Hz, 2H), 7.46 (d, J = 3.8 Hz, 1H), 7.39 (d, J = 6.9 Hz, 2H), 6.80 (s, 1H), 3.79 (s, 2H), 3.59 (s, 2H), 3.06 (s, 1H).

35. *N*-Cyclohexylbenzamide (5k):

White solid. Yield: 152 mg, 89%. MP: 151-153°C (lit[26] 153-155 °C).

¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.3 Hz, 2H), 7.48 (d, J = 6.7 Hz, 1H), 7.47 – 7.37 (m, 2H), 5.95 (s, 1H), 3.98 (s, 1H), 2.03 – 2.06 (m, 2H), 1.80 – 1.69 (m, 2H), 1.39 – 1.45 (m, 2H), 1.31 – 1.15 (m, 4H).

¹³C NMR (100 MHz, DMSO) δ 161.88, 130.39, 126.50, 123.78, 122.07, 43.92, 28.52, 20.85, 20.17.

36. *N*-cyclopropylbenzamide (5l):

White solid. Yield: 135 mg, 79%. MP: 93-95 °C (lit[27] 92-94 °C).

¹H NMR (400 MHz, DMSO) δ 8.18 (s, 1H), 7.58 (s, 2H), 7.27-7.21 (d, 3H), 2.61 (s, 1H), 0.46 (s, 2H), 0.34 (s, 2H).

37. *N*-(4-Nitrobenzyl) formamide (5m):

White solid. Yield: 276 mg, 72%. MP: 122-123 °C.

¹H NMR (400 MHz, DMSO) δ 8.63 (s, 1H), 8.16 (s, 1H), 8.08 (d, J = 6.2 Hz, 2H), 7.73 – 7.58 (m, 2H), 4.40 (d, J = 6.1 Hz, 2H).

38. *N*-(4-Cyanobenzyl) formamide (5n):

White crystals. Yield: 256 mg, 76%. MP: 126-127°C (lit[12] 127°C).

¹H NMR (500 MHz, CDCl₃) δ 8.32 (s, 1H), 7.62 (d, J = 6.7 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 5.98 (s, 1H), 4.54 (d, J = 6.3 Hz, 2H).

39. Morpholino(phenyl)methanethione (5o):

Buff solid. Yield: 184 mg, 69%. MP: 73-75°C (lit[28] 73-74.2 °C).

40. 2-phenyl-1-(pyrrolidin-1-yl)ethan-1-one (5p):

Yellow oil. Yield: 145 mg, 79%. MP: 45-47 °C (lit[29] 47-48°C).

¹H NMR (400 MHz, CDCl₃) δ 7.28 (dq, J = 8.5, 7.2 Hz, 5H), 3.66 (s, 2H), 3.47 – 3.40, 4H), 1.92 (m, 2H), 1.83 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 169.68, 134.89, 128.97, 128.60, 126.72, 46.92, 45.98, 42.27, 26.14, 24.35.

41. 4-(2-hydroxyethyl)piperazin-1-yl)(phenyl)methanone (5q):

Yellow oil. Yield: 205 mg, 76%.

¹H NMR (300 MHz, DMSO) δ 7.40 (ddd, J = 9.7, 7.0, 3.2 Hz, 5H), 3.42 – 3.20 (m, 4H), 2.57 – 2.28 (m, 8H).

¹³C NMR (75 MHz, DMSO) δ 168.87, 135.89, 129.42, 128.37, 126.81, 59.95, 58.35, 53.62.

42. piperazine-1,4-diylbis(phenylmethanone (5r):

Buff solid. Yield: 422 mg, 81%.

¹H NMR (300 MHz, DMSO) δ 7.90-7.43 (m, 10H), 3.50 (s, 8H).

¹³C NMR (75 MHz, DMSO) δ 169.23, 135.53, 129.65, 128.42, 126.98, 47.11, 41.52.

43. N-benzyl-N-methyl-2-phenylacetamide (5s):

Yellow oil. Yield: 167 mg, 87%.

¹H NMR[30] (400 MHz, CDCl₃, mixture of rotamers in a ratio of 3[†]:2[‡]) δ 7.42-7.22^{‡†} (m, 9H, ArH), 7.10[†] (d, J = 7.3 Hz, 1.2H, ArH), 7.08[‡] (d, J = 7.3 Hz, 0.8H, ArH), 4.61[†] (s,

1.14H, CH₂), 4.52‡ (s, 0.9H, CH₂), 3.78† (s, 1.2H, CH₂), 3.75‡ (s, 0.8H, CH₂), 2.95‡ (s, 1.19H, CH₃), 2.90† (s, 1.74H, CH₃)

¹³C NMR (100 MHz, CDCl₃, mixture of rotamers in a ratio of 3:2) δ 171.52, 171.17, 137.31, 136.50, 135.11, 134.97, 128.94, 128.85, 128.80, 128.73 128.70, 128.59, 128.08, 127.67, 127.37, 126.86, 126.81, 126.40, 53.68, 50.99, 41.24, 40.89, 35.24, 34.05.

44. *N,N*-Dibenzylformamide (5t)

Pale yellow solid. Yield: 167 mg, 84%. MP: 51-52 °C (lit[13] 50-53 °C).

¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 4.5 Hz, 1H), 7.39 – 7.28 (m, 8H), 7.15 (s, 1H), 4.70 (s, 2H), 4.40 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 172.29, 136.17, 129.68, 128.74, 128.51, 128.51, 127.67, 127.06, 126.90, 51.55, 46.85.

45. *N*-Phenylbenzamide (5u):

White crystals. Yield: 185 mg, 71%. MP: 164-166°C (lit[10] 162-164 °C).

¹H NMR (500 MHz, CDCl₃) δ 7.91 – 7.86 (m, 2H), 7.84 (s, 1H), 7.65 (d, J = 7.7 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.38 (t, J = 8.0 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 165.77, 137.93, 135.02, 131.87, 129.12, 128.81, 127.03, 124.60, 120.22.

46. *N*-Phenylacetamide (5v):

White crystals. Yield: 201 mg, 76%. MP: 113-114 °C (lit[6] 112-113 °C).

¹H NMR (500 MHz, DMSO) δ 9.90 (s, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.01 (t, J = 7.4 Hz, 1H), 2.03 (s, 3H).

¹³C NMR (100 MHz, DMSO) δ 167.96, 153.56, 131.49, 121.25, 115.44, 24.20.

47. *N*-(4-Hydroxyphenyl) acetamide (5w):

White crystals. Yield: 392 mg, 72%. MP: 169-170 °C (lit[14] 169-170 °C).

48. *N,N*-Diphenylformamide (5x):

Buff solid. Yield: 63 mg, 52%. MP: 70-72 °C (lit[10] 71-73 °C).

¹H NMR (300 MHz, CDCl₃) δ 8.67 (s, 1H), 7.40 (ddd, *J* = 7.3, 6.1, 3.1 Hz, 4H), 7.35 – 7.24 (m, 4H), 7.18 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 161.67, 142.03, 139.63, 129.65, 129.13, 127.00, 126.81, 126.07, 125.07.

49. *N*-benzylpicolinamide (7a):

Buff solid. Yield: 167 mg, 91%. MP: 87-88 °C (lit[13] 87-90 °C).

50. *N*-benzylnicotinamide (7b):

Buff solid. Yield: 163 mg, 92%. MP: 71-73 °C (lit[31] 70-72 °C).

¹H NMR (400 MHz, DMSO) δ 9.27 (t, *J* = 5.5 Hz, 1H), 9.06 (d, *J* = 1.4 Hz, 1H), 8.72 (d, *J* = 4.7 Hz, 1H), 8.24 (m, 1H), 7.52 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.34 (d, *J* = 4.4 Hz, 4H), 7.26 (dd, *J* = 8.7, 4.5 Hz, 1H), 4.52 (d, *J* = 6.0 Hz, 2H).

¹³C NMR (100 MHz, DMSO) δ 165.29, 152.39, 148.89, 139.75, 135.49, 130.26, 128.81, 127.74, 127.32, 123.97, 43.10.

51. *N*-isobutylpiconamide (7c):

White solid. Yield: 187 mg, 72%. MP: 52-54 °C (lit[32] 54.5-55.5 °C).

¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, *J* = 4.7 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 7.84 (td, *J* = 7.7, 1.7 Hz, 2H), 7.41 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 4.15 – 4.05 (m, 1H), 1.61 (p, *J* = 7.3 Hz, 2H), 1.25 (d, *J* = 6.6 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 163.60, 150.21, 147.95, 137.33, 125.98, 122.22, 46.66, 29.80, 20.51.

52. N-benzylfuran-2-carboxamide (7d):

Buff solid. Yield: 154 mg, 91%. MP: 108-109°C (lit[31] 108-110°C).

¹H NMR (300 MHz, CDCl₃) δ 7.42 – 7.35 (m, 5H), 7.29 (dd, J = 11.2, 6.1 Hz, 2H), 7.15 (d, J = 3.2 Hz, 1H), 6.53 – 6.48 (m, 1H), 4.62 (d, J = 5.9 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 158.26, 147.90, 143.88, 137.99, 129.39, 128.34, 127.64, 114.43, 112.19, 43.18.

53. pyrrolidin-2-one (9):

Colorless liquid. Yield: 154 mg, 76%.

¹H NMR (300 MHz, CDCl₃) δ 7.65 (s, 1H), 3.41 (d, J = 5.9 Hz, 2H), 2.30 (dd, J = 7.3, 6.4 Hz, 2H), 2.24 – 2.03 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 179.77, 42.49, 30.32, 20.72.

54. Tert-butyl (S)-(1-(benzylamino)-1-oxopropan-2-yl)carbamate (11)

White solid. Yield: 175mg, 84%. MP: 129-130°C.

¹H NMR (400 MHz, DMSO) δ 8.37 (s, 1H), 7.26 – 7.22 (m, 5H), 6.95 (d, J = 7.2 Hz, 1H), 4.25 (d, J = 5.8 Hz, 2H), 4.19 – 4.13 (m, 1H), 1.28 (s, 9H), 1.19 (d, J = 6.2 Hz, 3H).

55. Tert-butyl (S)-(1-(benzylamino)-1-oxo-3-phenylpropan-2-yl)carbamate (13)

White solid. Yield: 179 mg, 79%. MP 136–139 °C (lit[13] 134–135 °C).

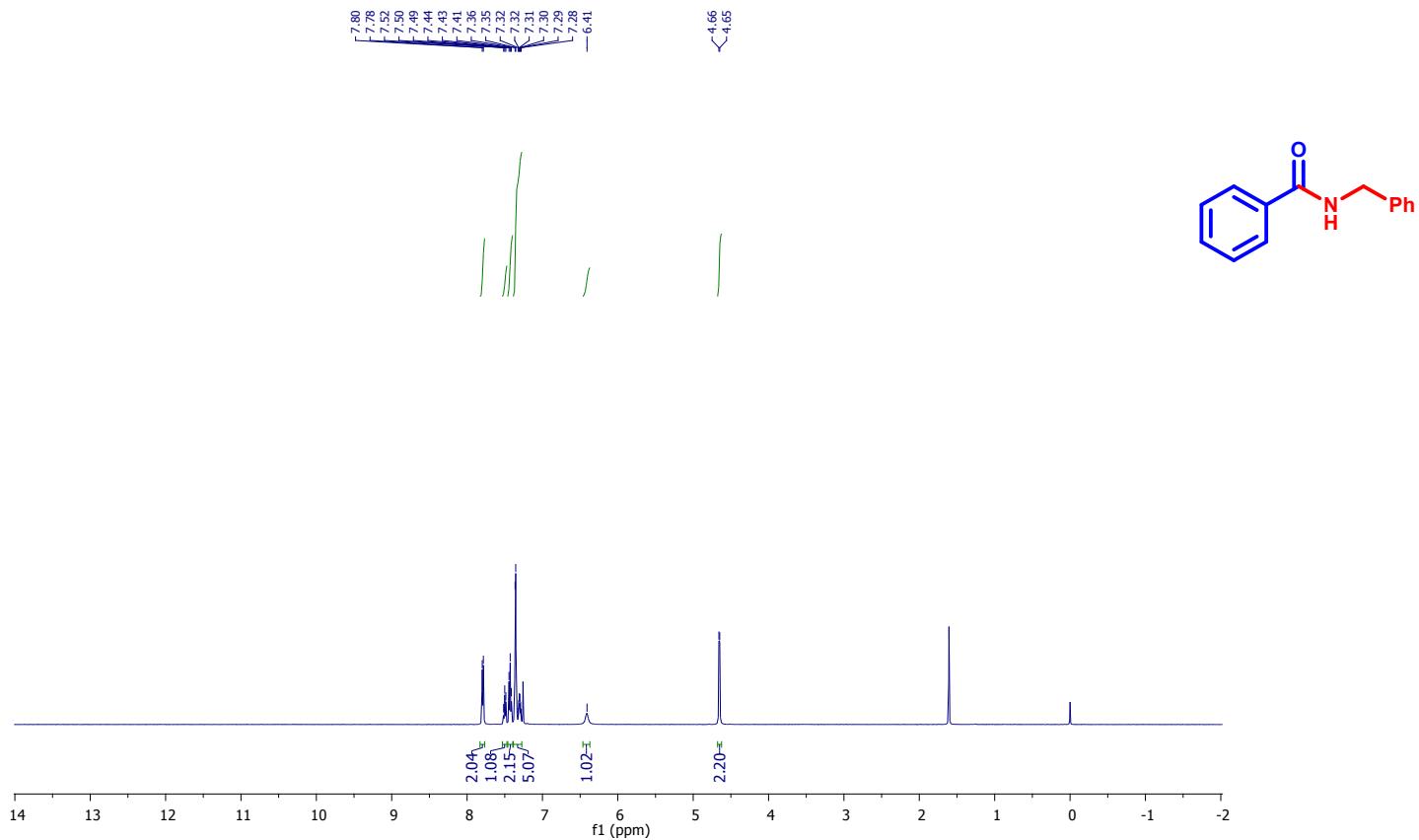
¹H NMR (400 MHz, DMSO) δ 8.42 (d, J = 6.0 Hz, 1H), 7.30– 7.18 (m, 10H), 6.98 (d, J = 5.8 Hz, 1H), 4.28 (d, J = 5.6 Hz, 2H), 4.20–4.16 (m, 1H), 3.99 (t, J = 7.0 Hz, 1H), 3.82 (s, 1H), 1.31 (s, 9H).

56. Tert-butyl 2-(benzylcarbamoyl)pyrrolidine-1-carboxylate (15)

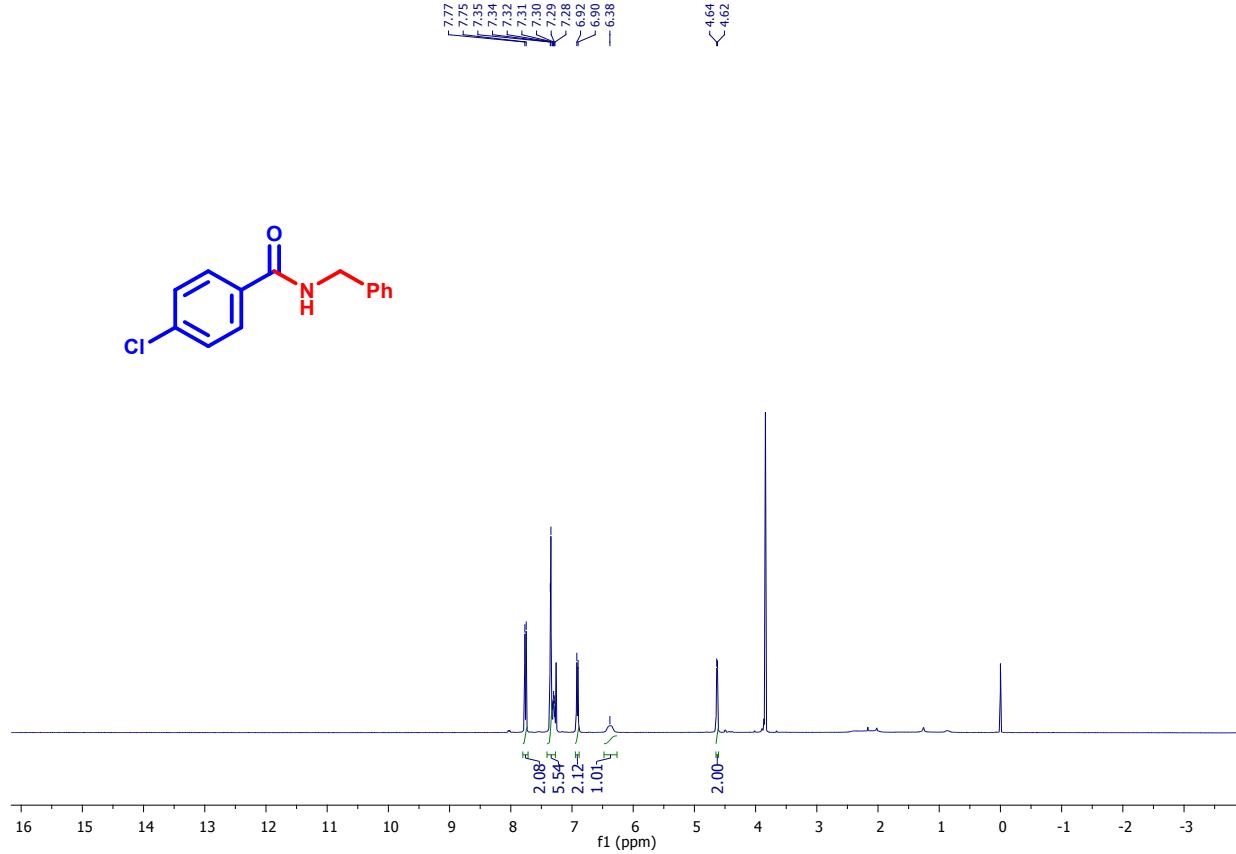
White solid. Yield: 189 mg, 91%. MP: 130–131 °C (lit[13] 129–131 °C).

¹H NMR (400 MHz, DMSO) δ 8.33 (d, J = 4.9 Hz, 1H), 7.33 – 7.14 (m, 5H), 4.34 – 4.26 (m, 1H), 4.12 (d, J = 5.1 Hz, 2H), 3.30– 3.26 (m, 2H), 2.31 – 1.93 (m, 2H), 1.78– 1.74 (m, 2H), 1.39 (s, 3H), 1.25 (s, 6H).

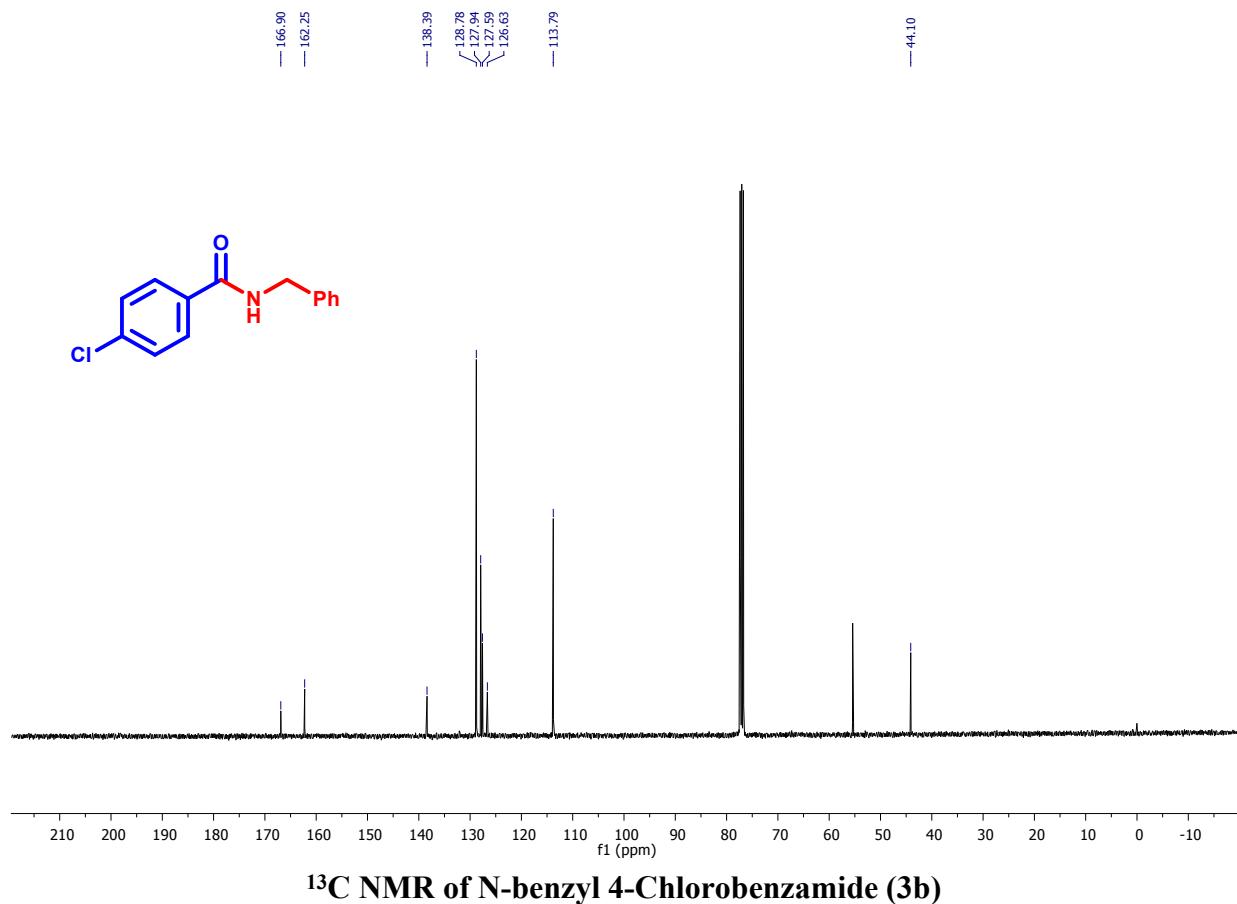
Copies of ^1H , ^{13}C NMR and GC-MS spectra



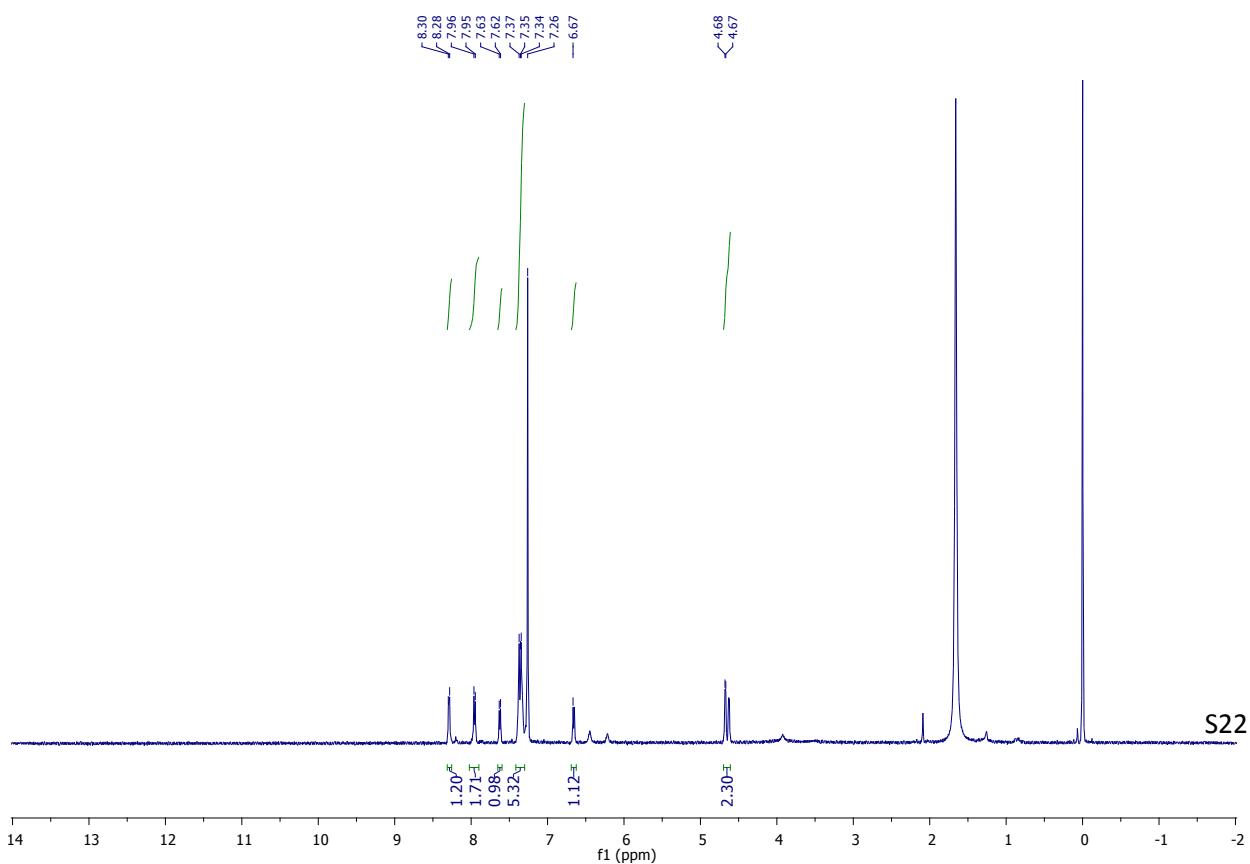
^1H NMR of N-Benzyl benzamide (3a)

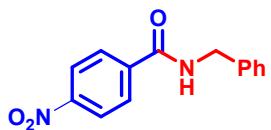


^1H NMR of N-benzyl 4-Chlorobenzamide (3b)

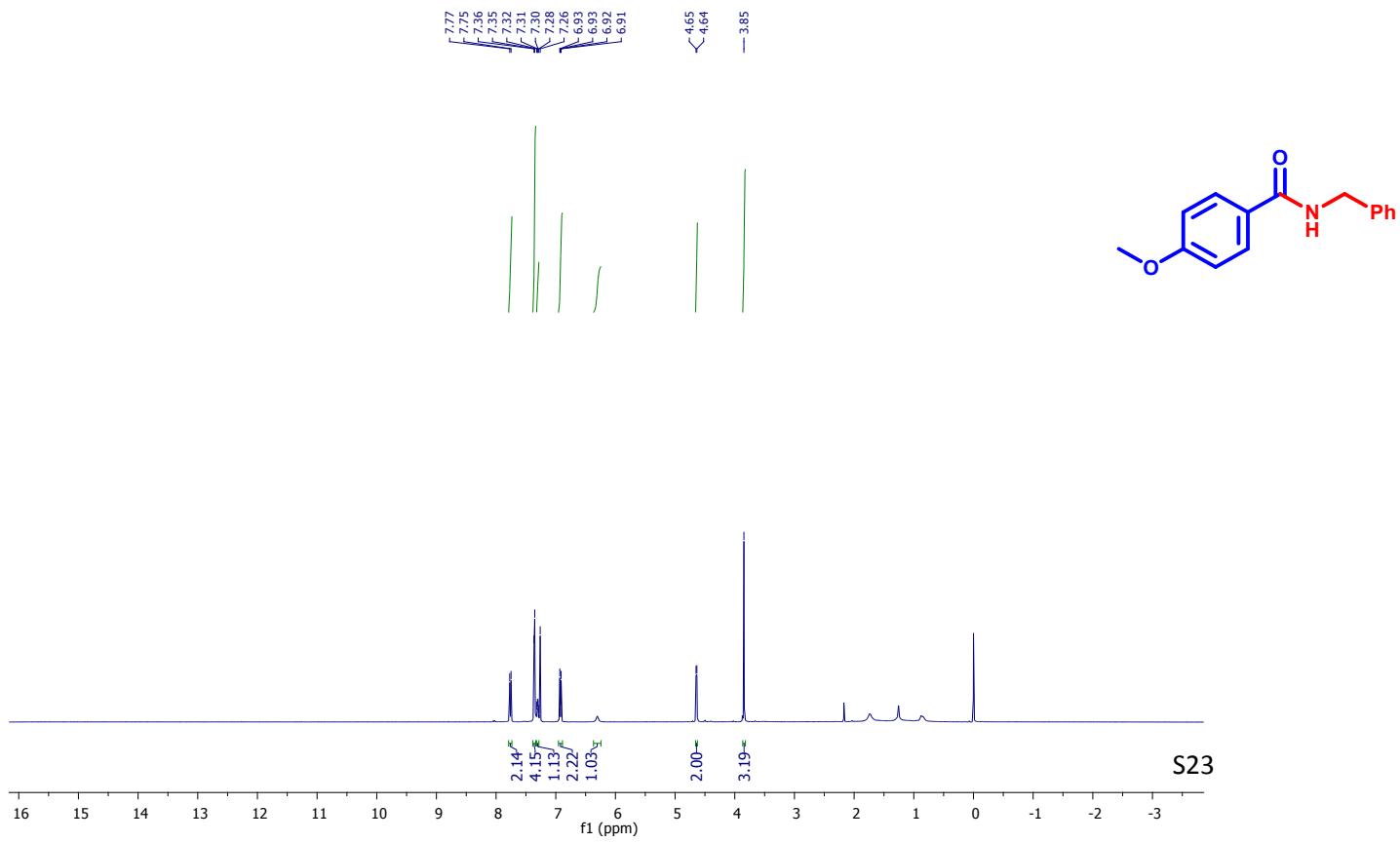


¹³C NMR of N-benzyl 4-Chlorobenzamide (3b)

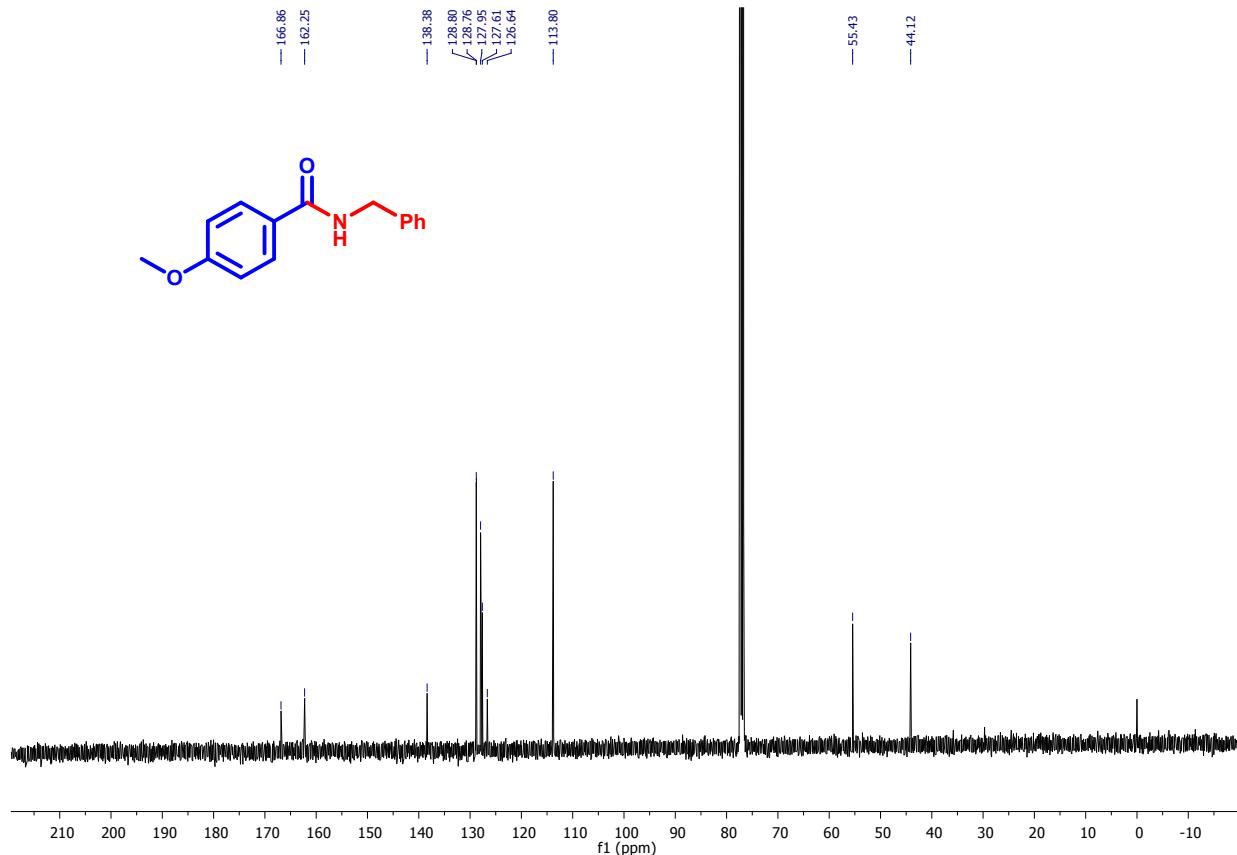




¹H NMR of N-benzyl 4-Nitrobenzamide (3c)

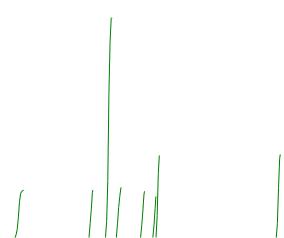


^1H NMR of N-benzyl 4-Methoxybenzamide (3e)

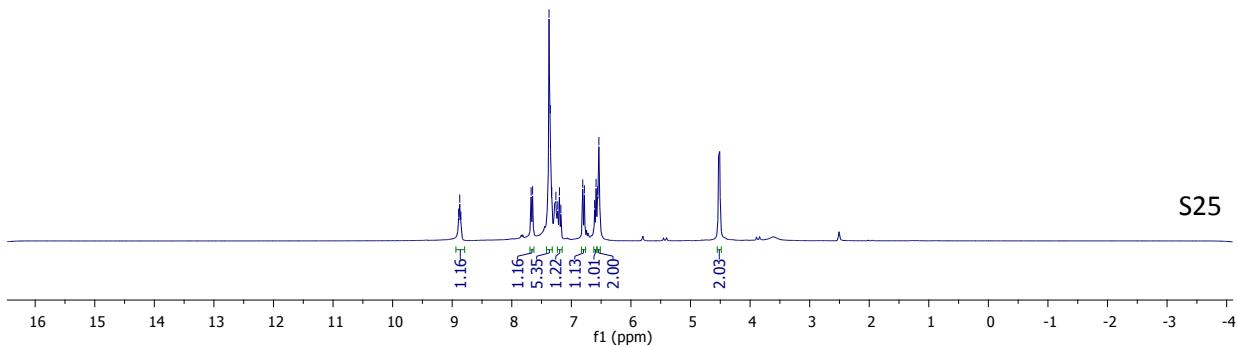


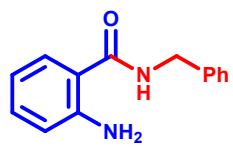
¹³C NMR of N-benzyl 4-Methoxybenzamide (3e)

8.89
8.87
7.68
7.65
7.35
7.33
7.26
7.23
7.20
7.18
6.81
6.78
6.61
6.58
6.56
6.54

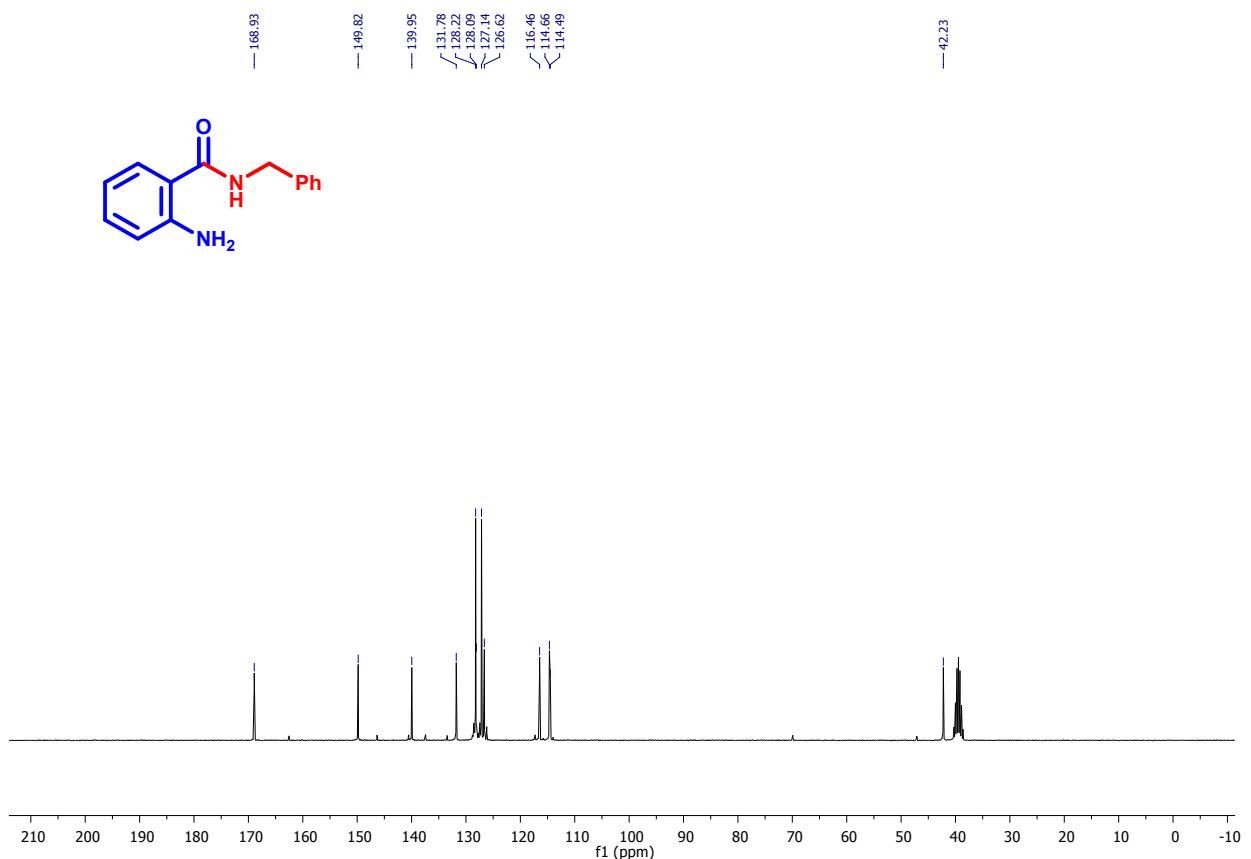


S25

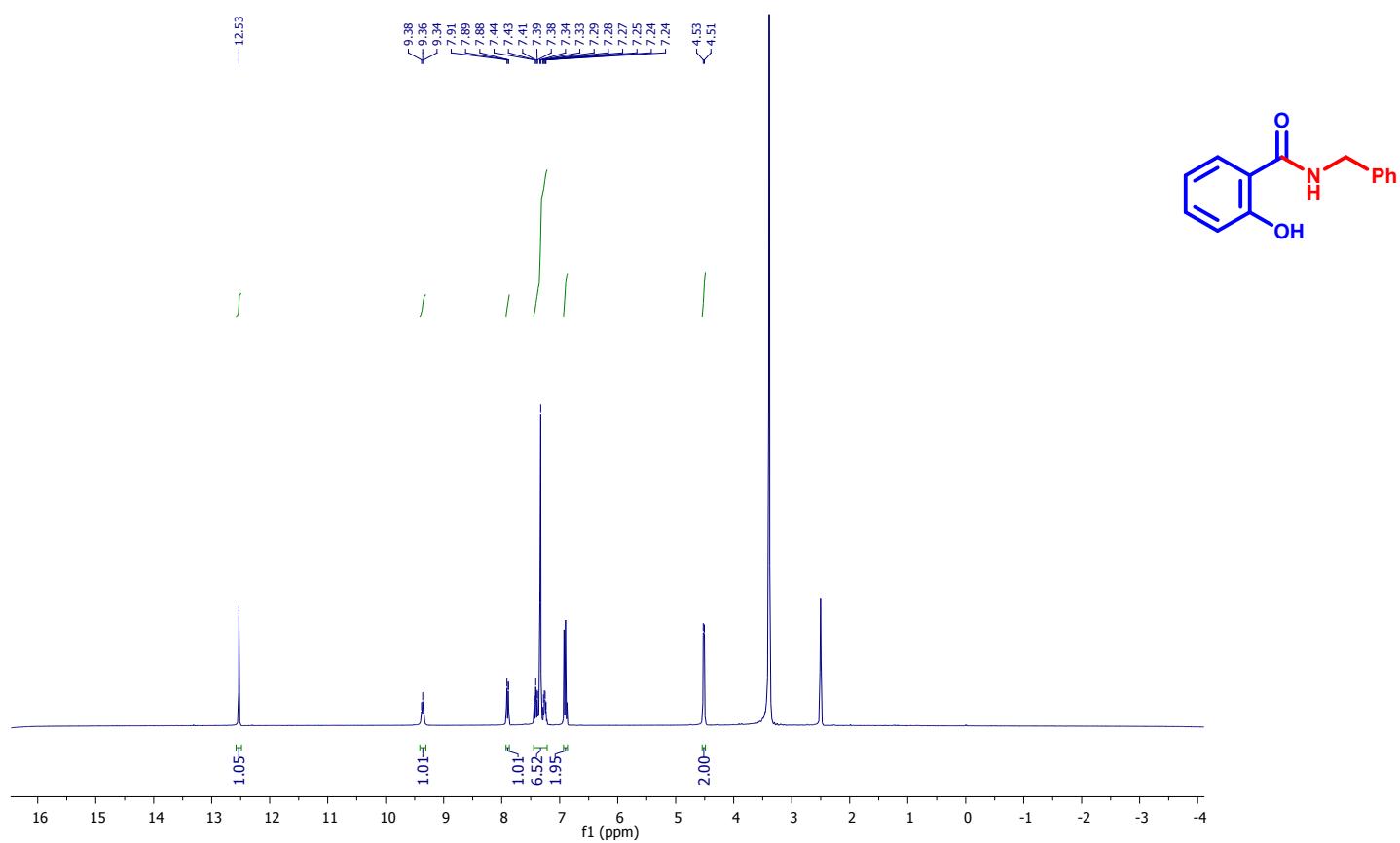




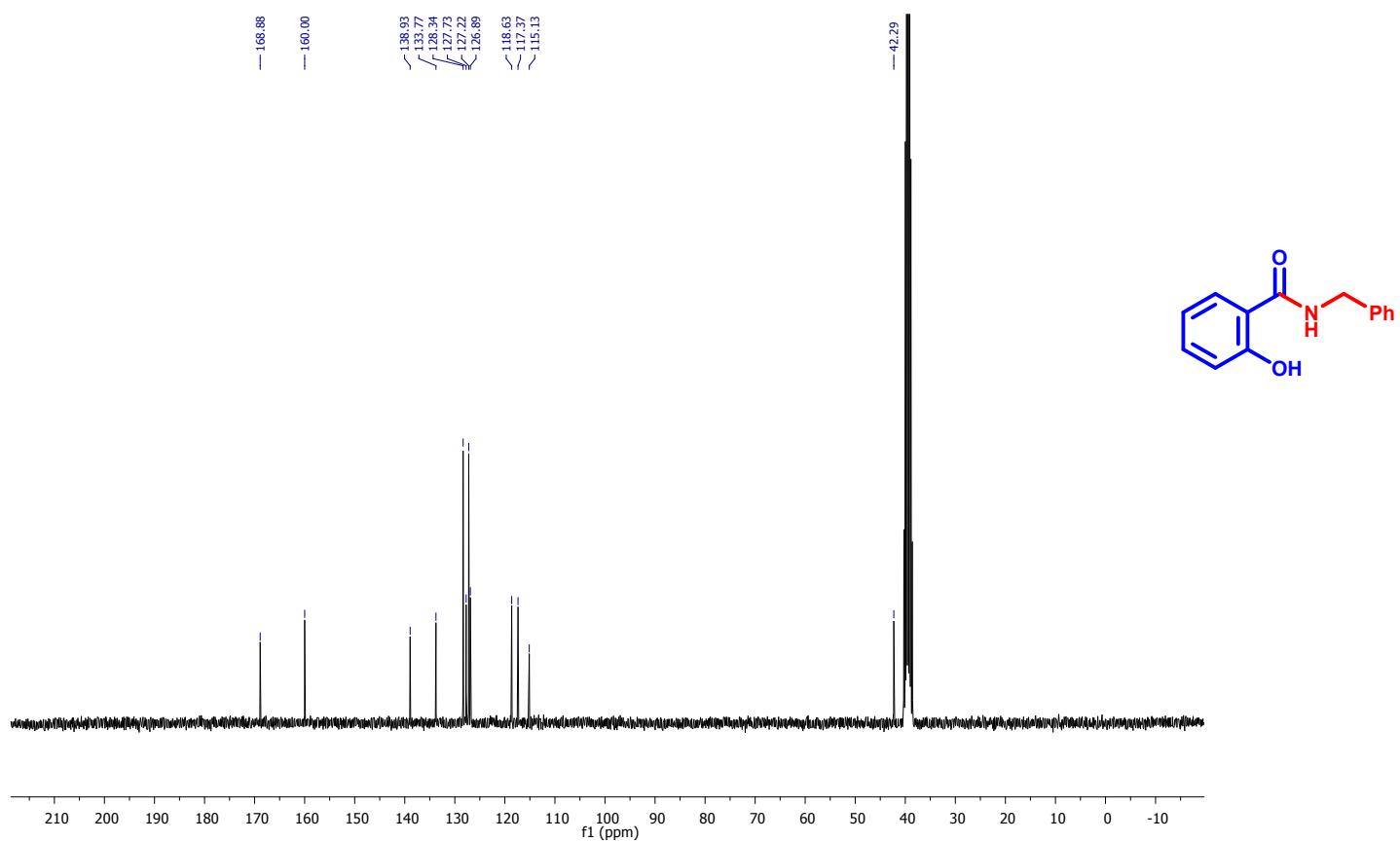
^1H NMR of 2-Amino-N-benzyl benzamide (3g)



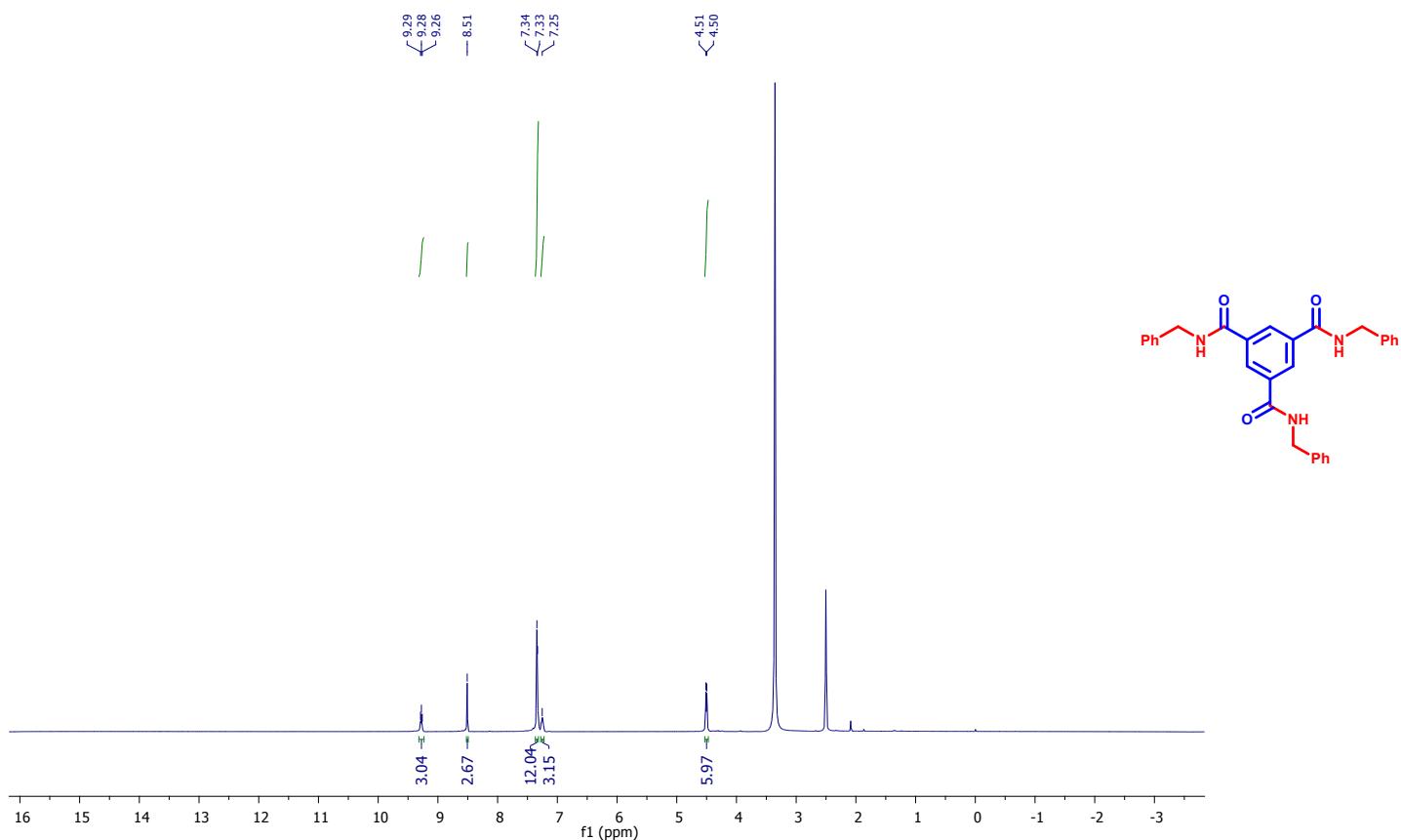
¹³C NMR of 2-Amino-N-benzyl benzamide (3g)



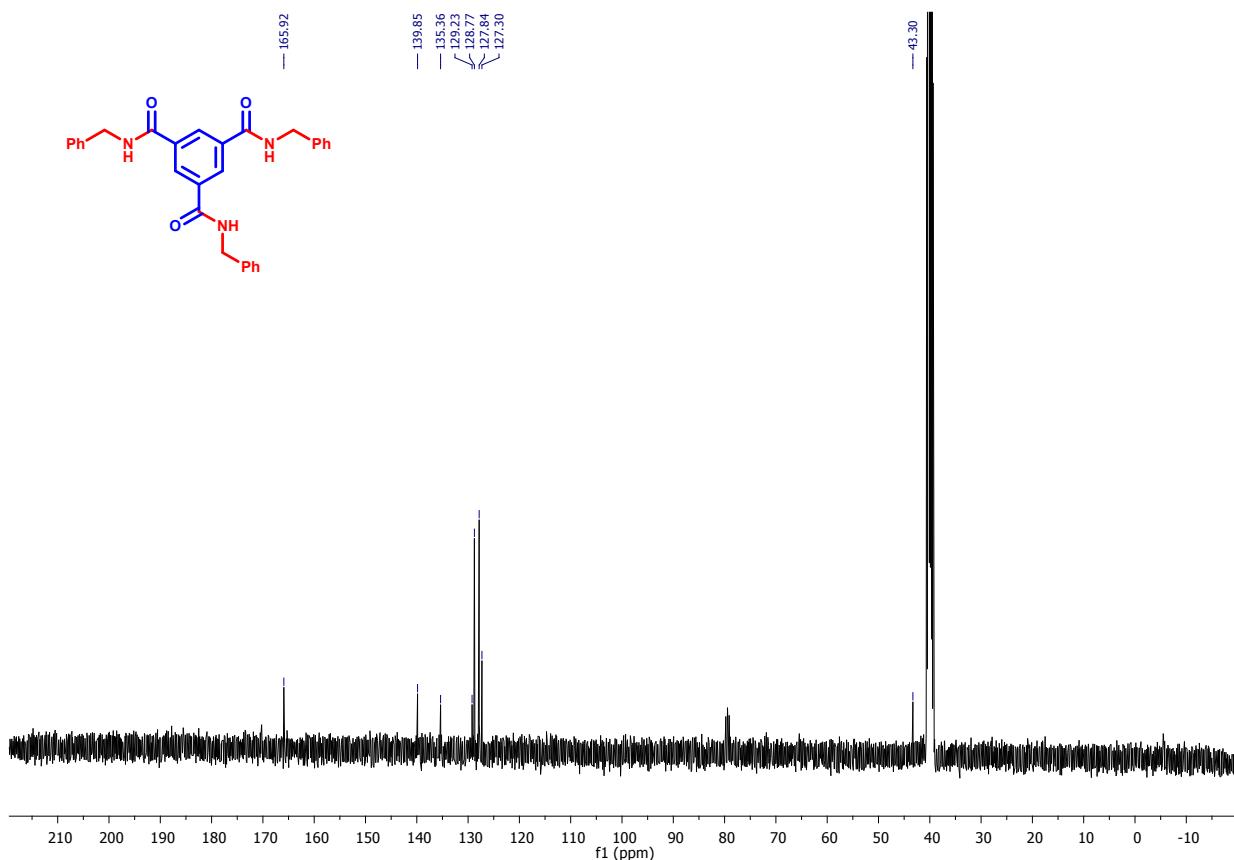
¹H NMR of 2-hydroxy-N-benzyl benzamide (3h)



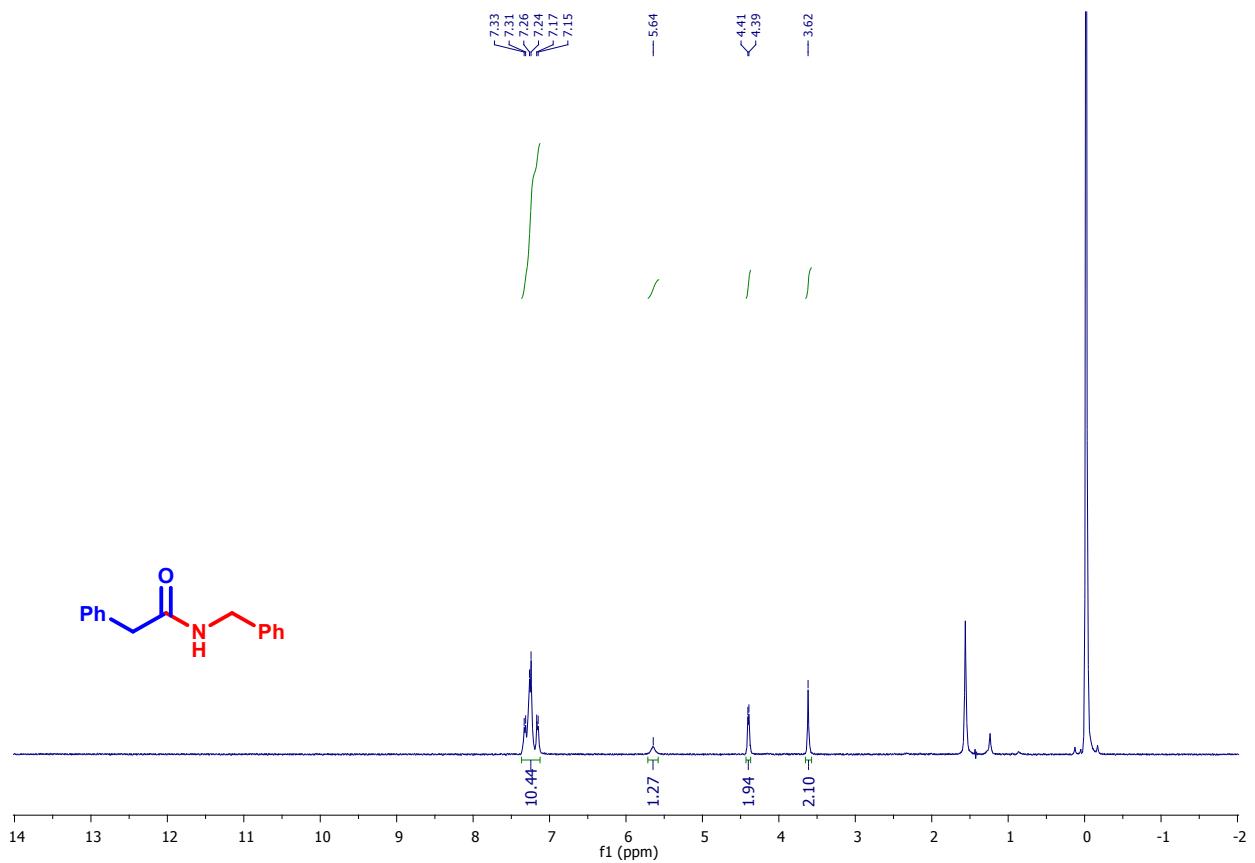
¹³C NMR of 2-Hydroxy-N-benzyl benzamide (3h)



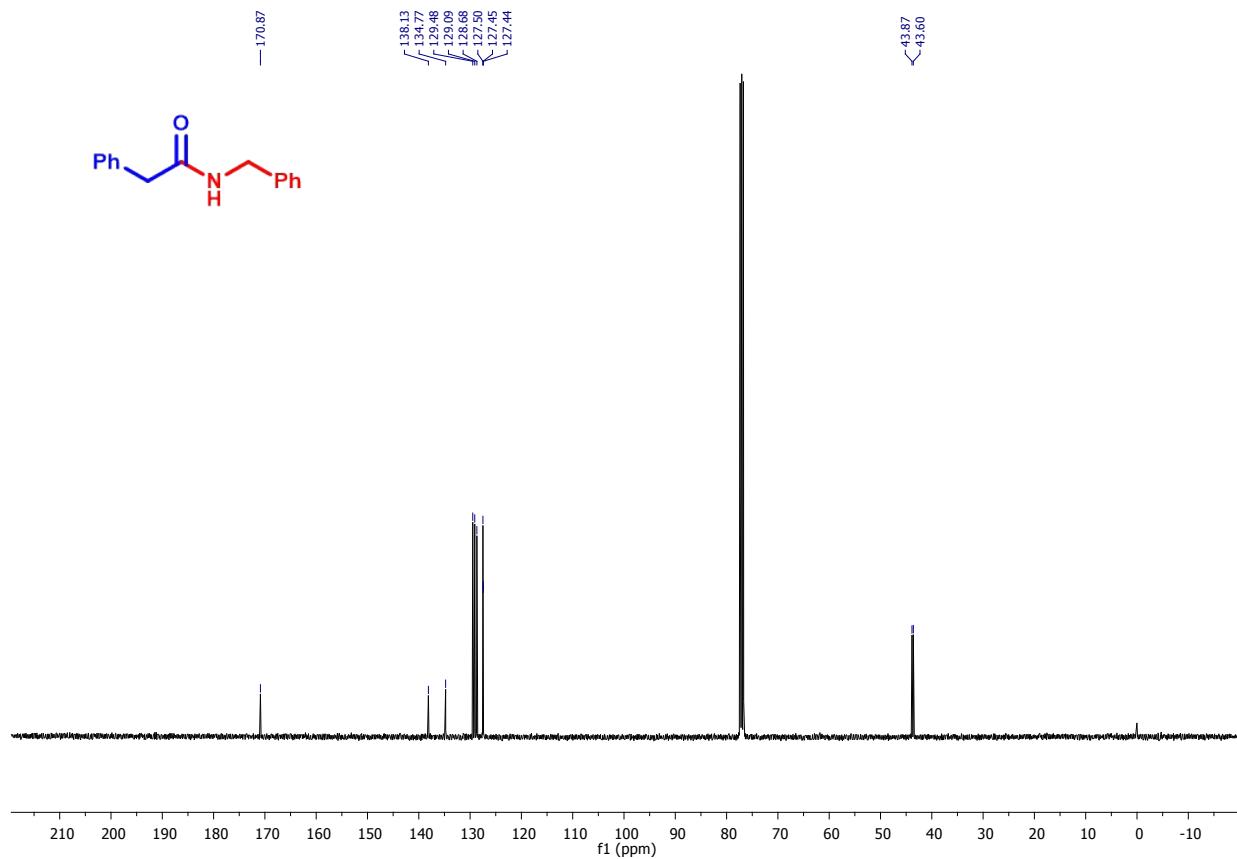
^1H NMR of $\text{N}^1,\text{N}^3,\text{N}^5$ -tribenzylbenzene-1,3,5-tricarboxamide (3i)



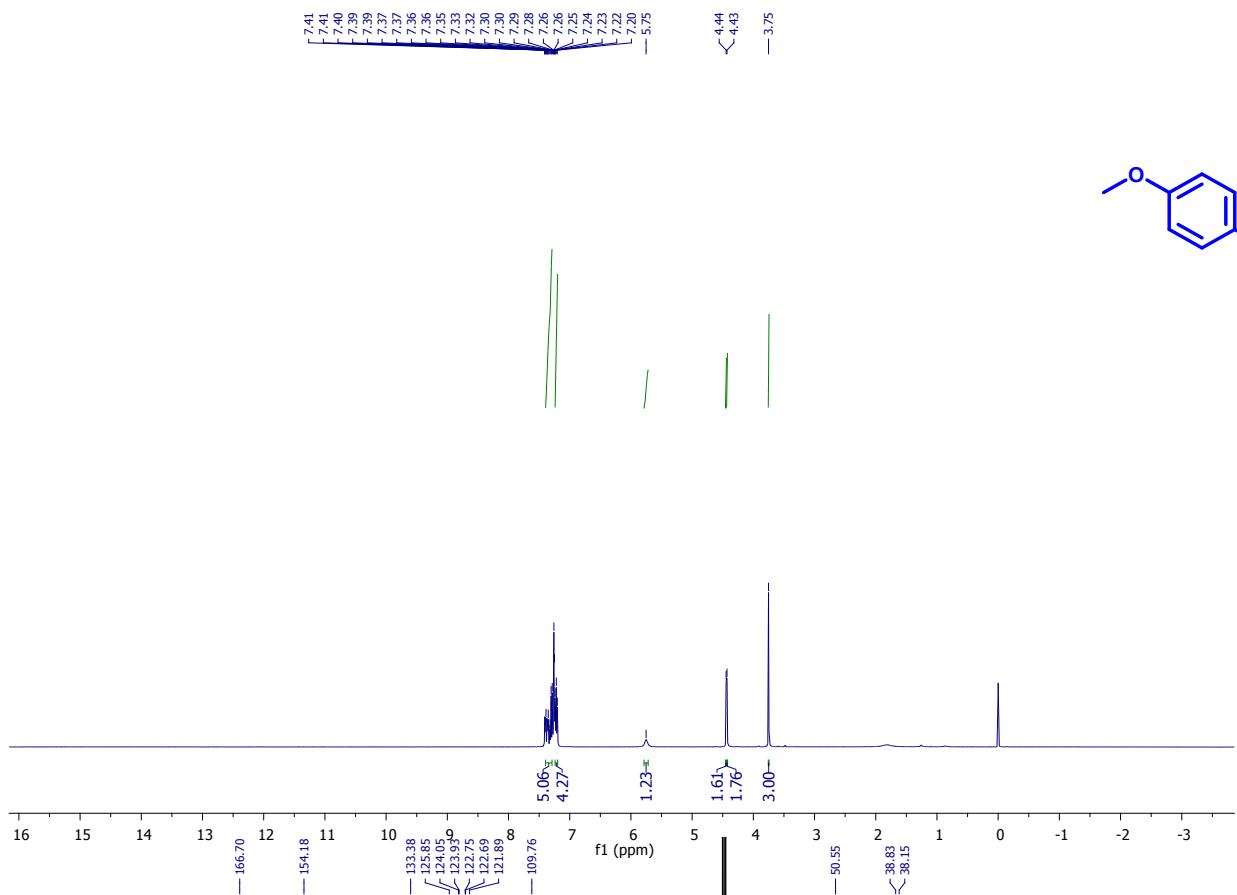
^{13}C NMR of $\text{N}^1,\text{N}^3,\text{N}^5$ -tribenzylbenzene-1,3,5-tricarboxamide (3i)



¹H NMR of *N*-benzyl-2-phenylacetamide (3j)

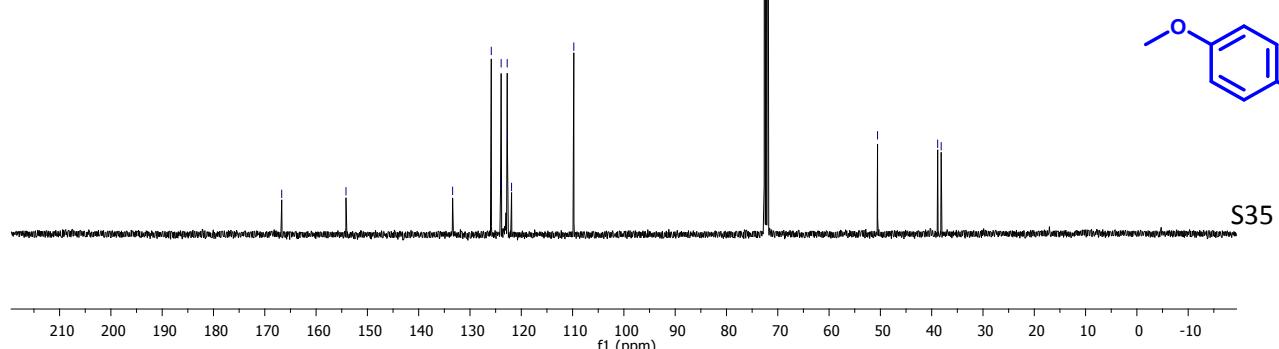


^{13}C NMR of *N*-benzyl-2-phenylacetamide (3j)

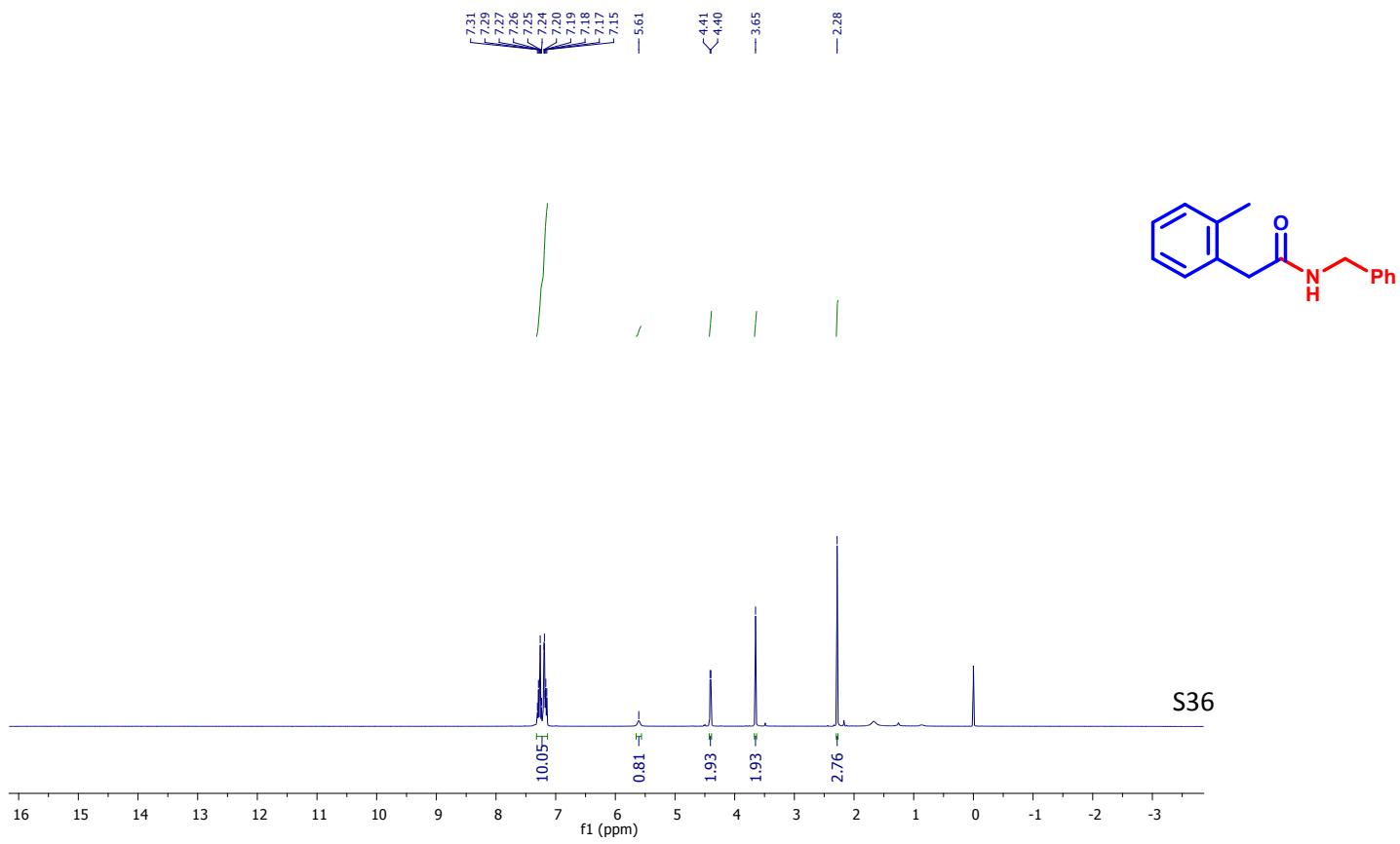


¹H NMR of N-benzyl-2-(4-

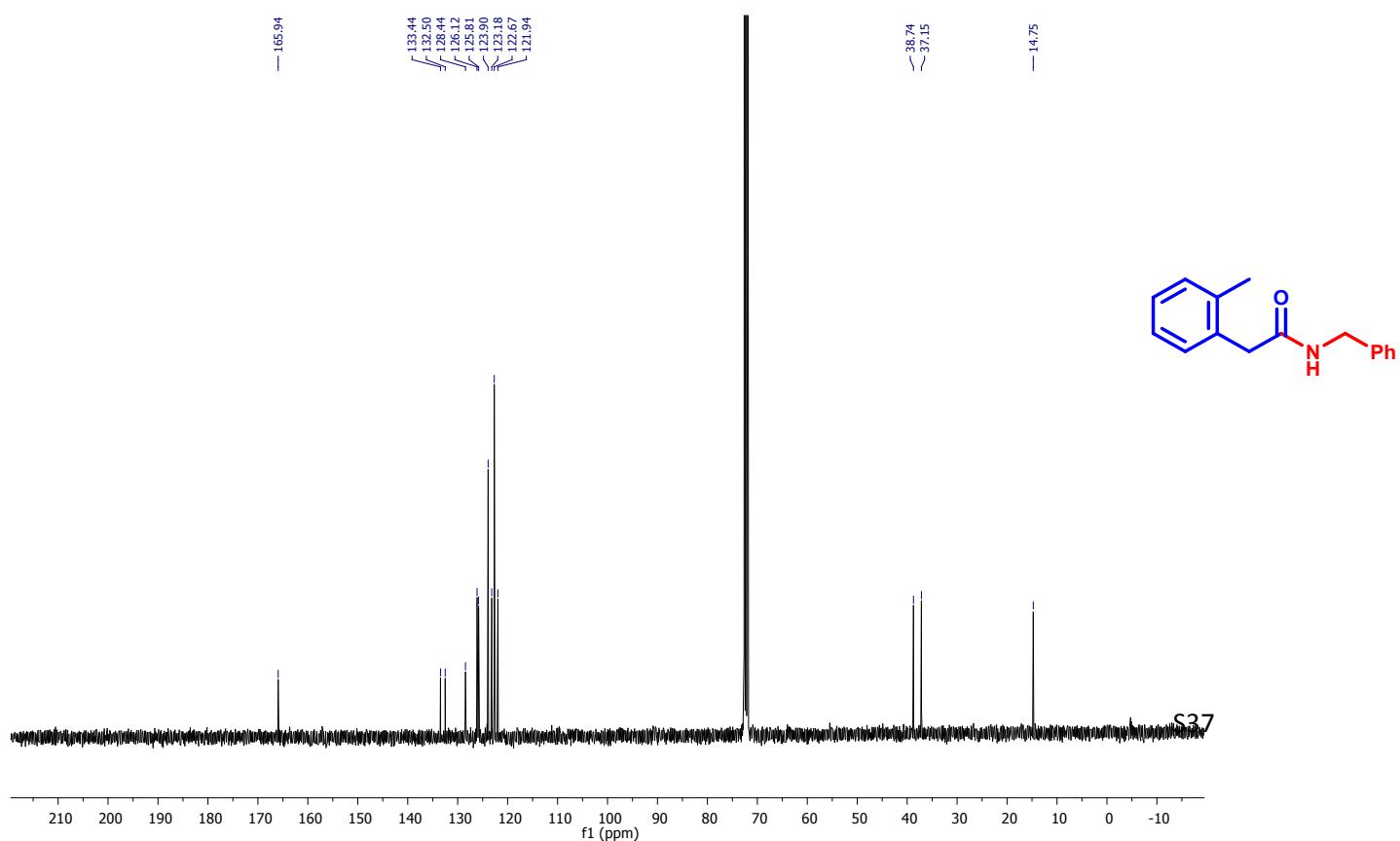
methoxyphenyl)acetamide (3k)



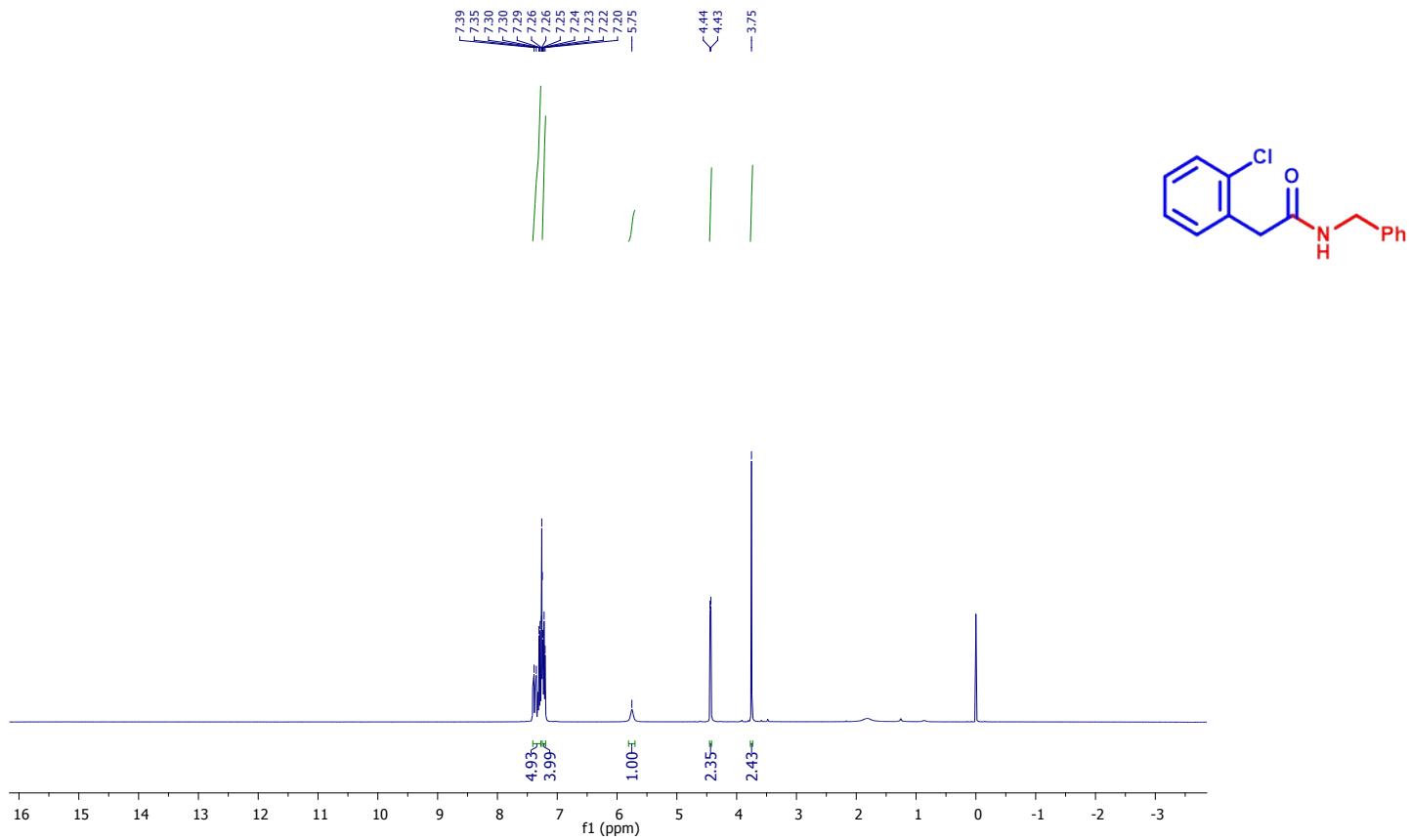
¹³C NMR of N-benzyl-2-(4-methoxyphenyl)acetamide (3k)



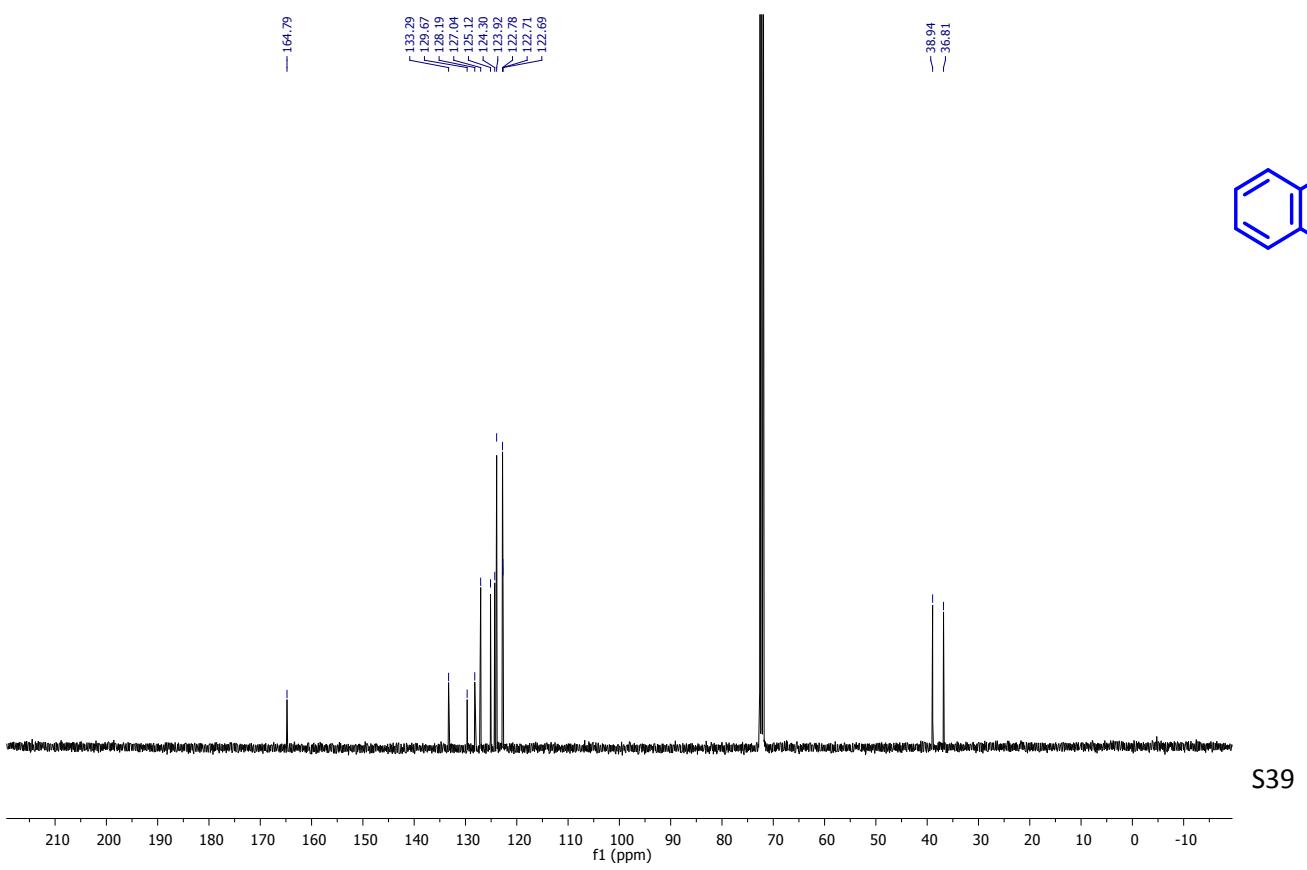
¹H NMR of N-benzyl-2-(o-tolyl)acetamide (3l)



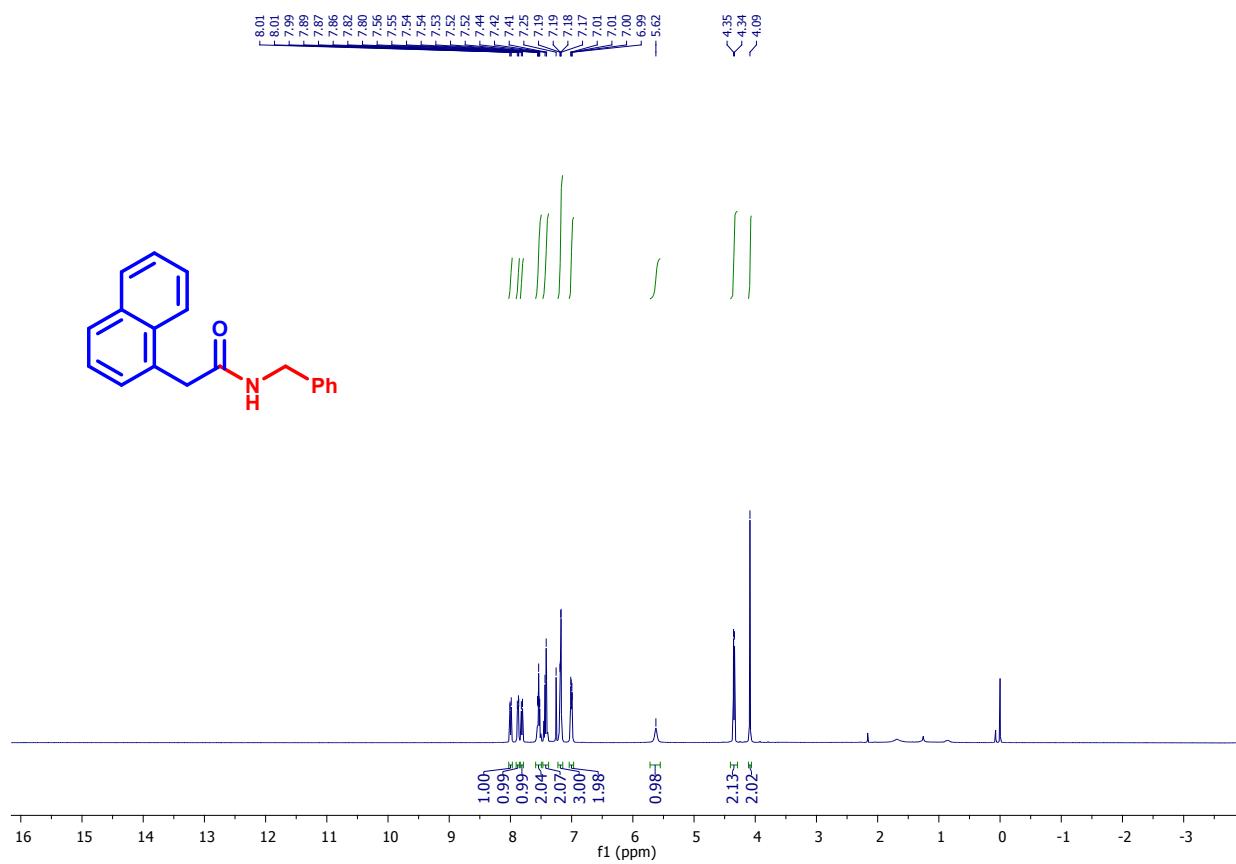
¹³C NMR of N-benzyl-2-(o-tolyl)acetamide (3l)



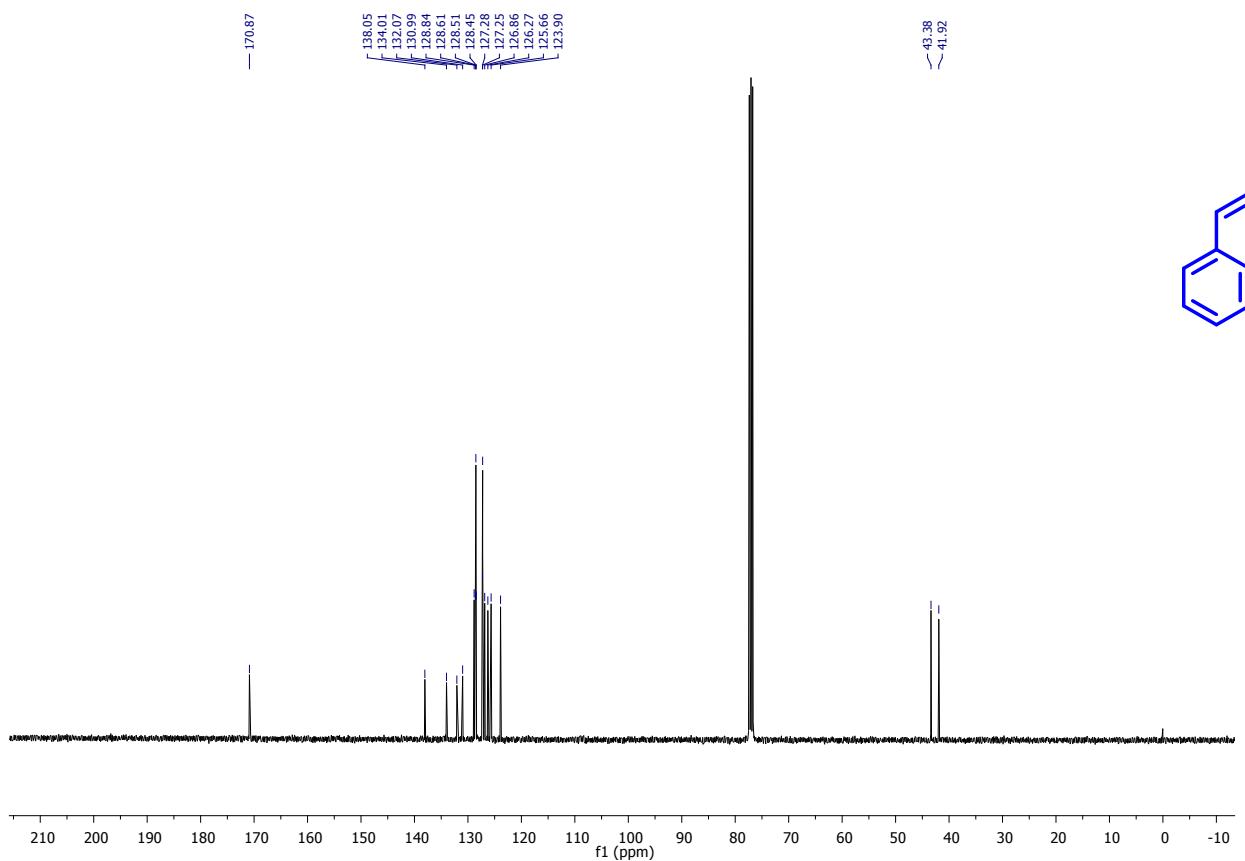
¹³C NMR of N-benzyl-2-(2-chlorophenyl)acetamide (3m)



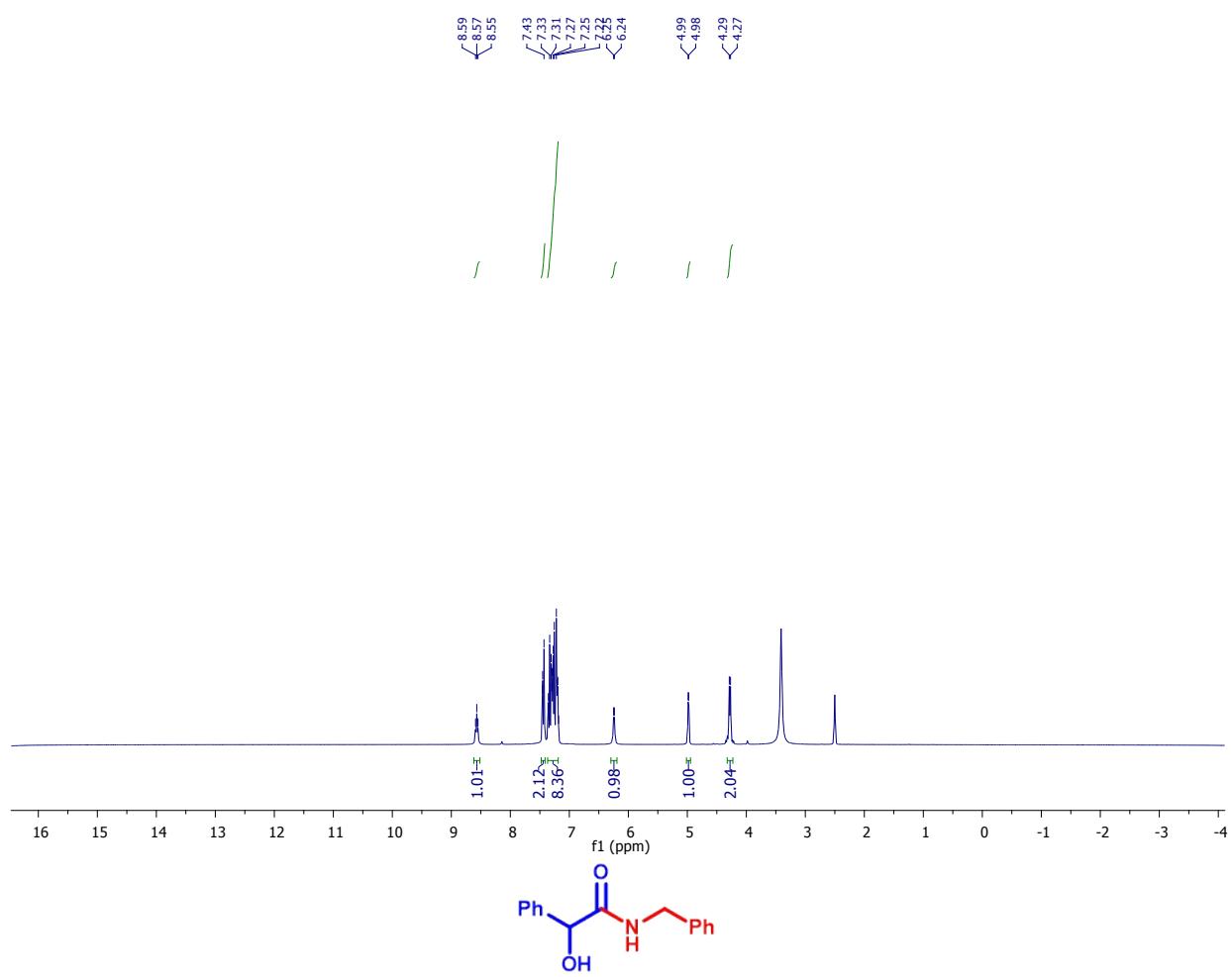
¹³C NMR of N-benzyl-2-(2-chlorophenyl)acetamide (3m)



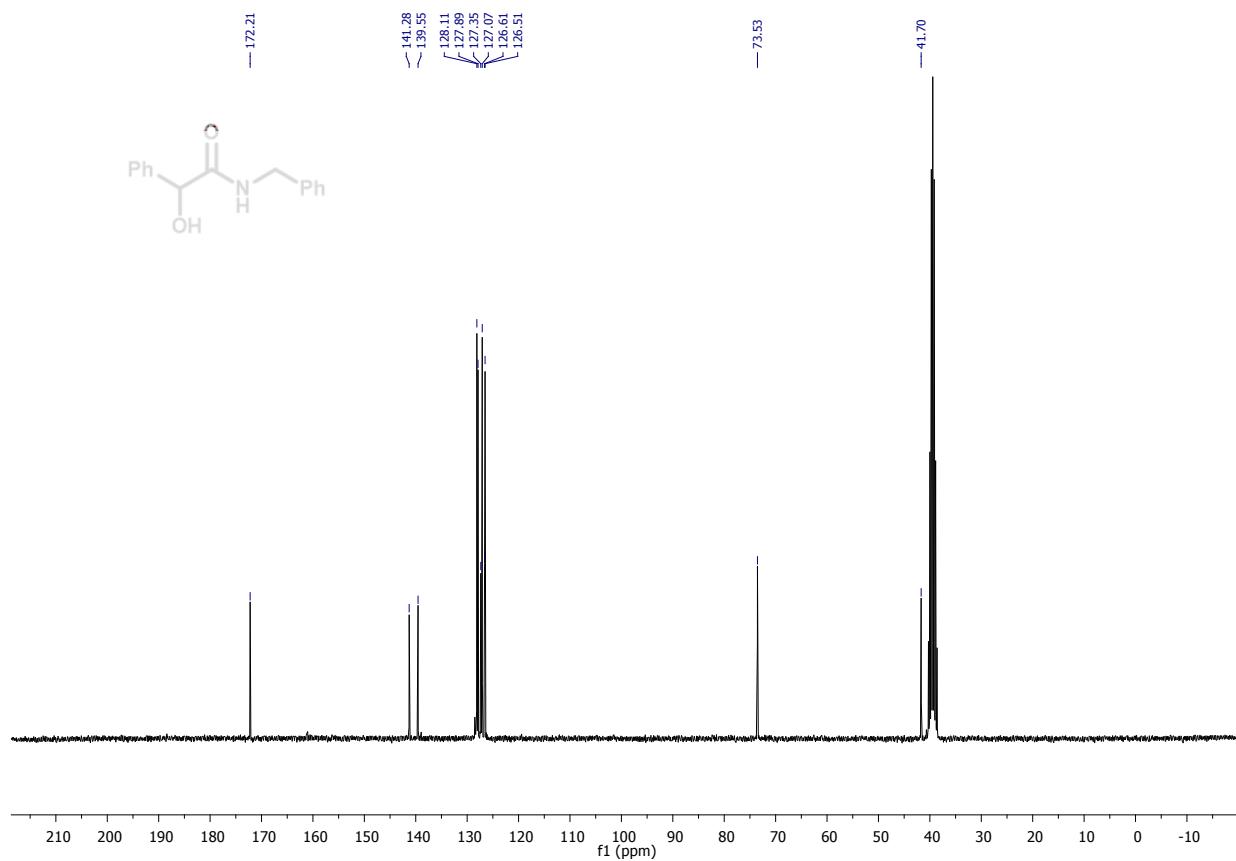
¹H NMR of N-benzyl-2-(naphthalen-1-yl)acetamide (3n)



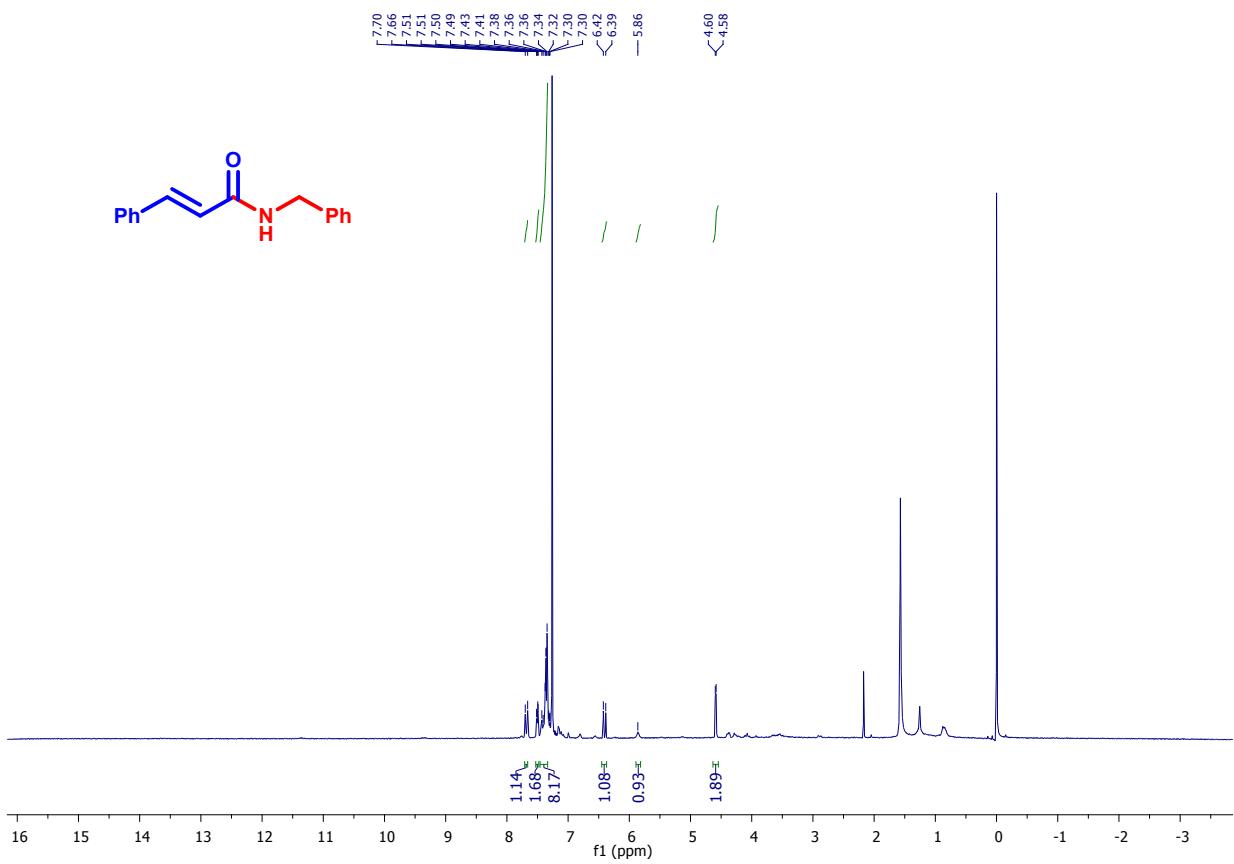
¹³C NMR of N-benzyl-2-(naphthalen-1-yl)acetamide (3n)



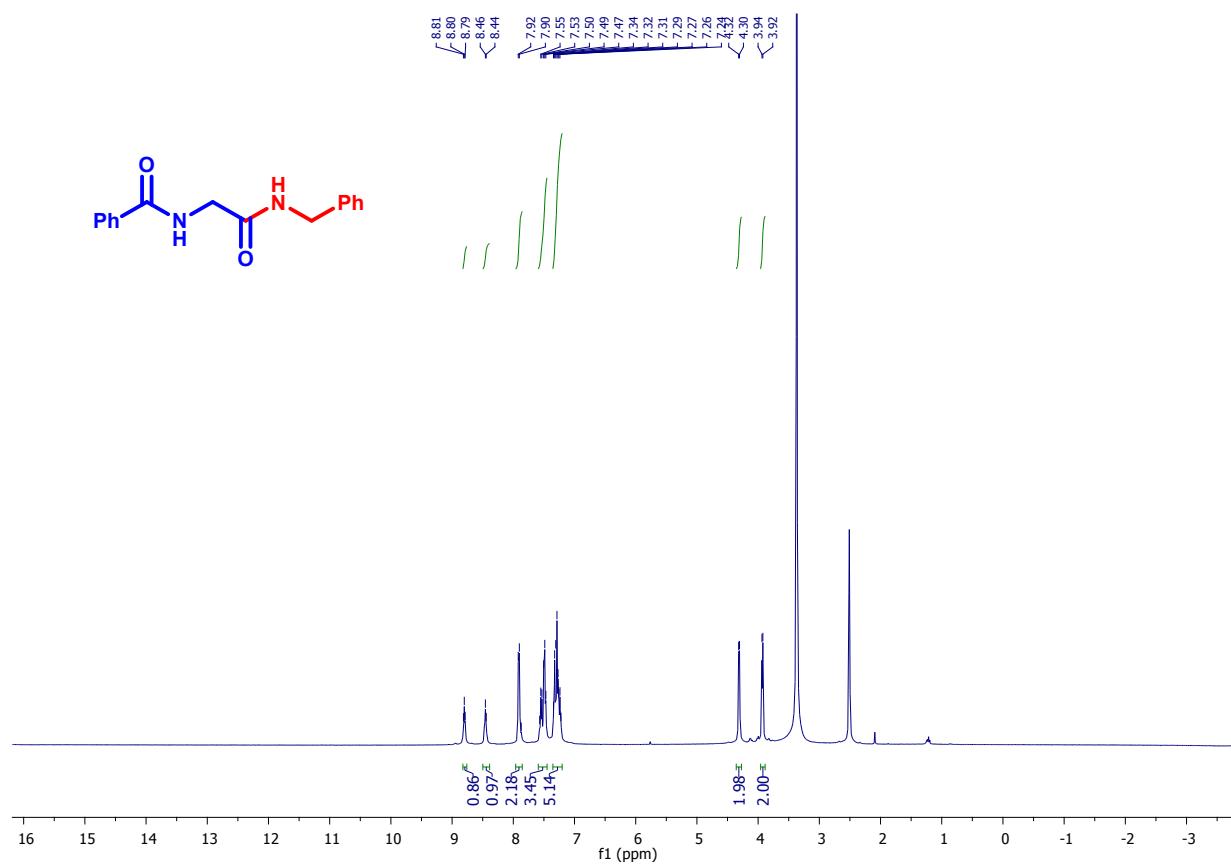
¹H NMR of N-benzyl-2-hydroxy-2-phenylacetamide (3o)



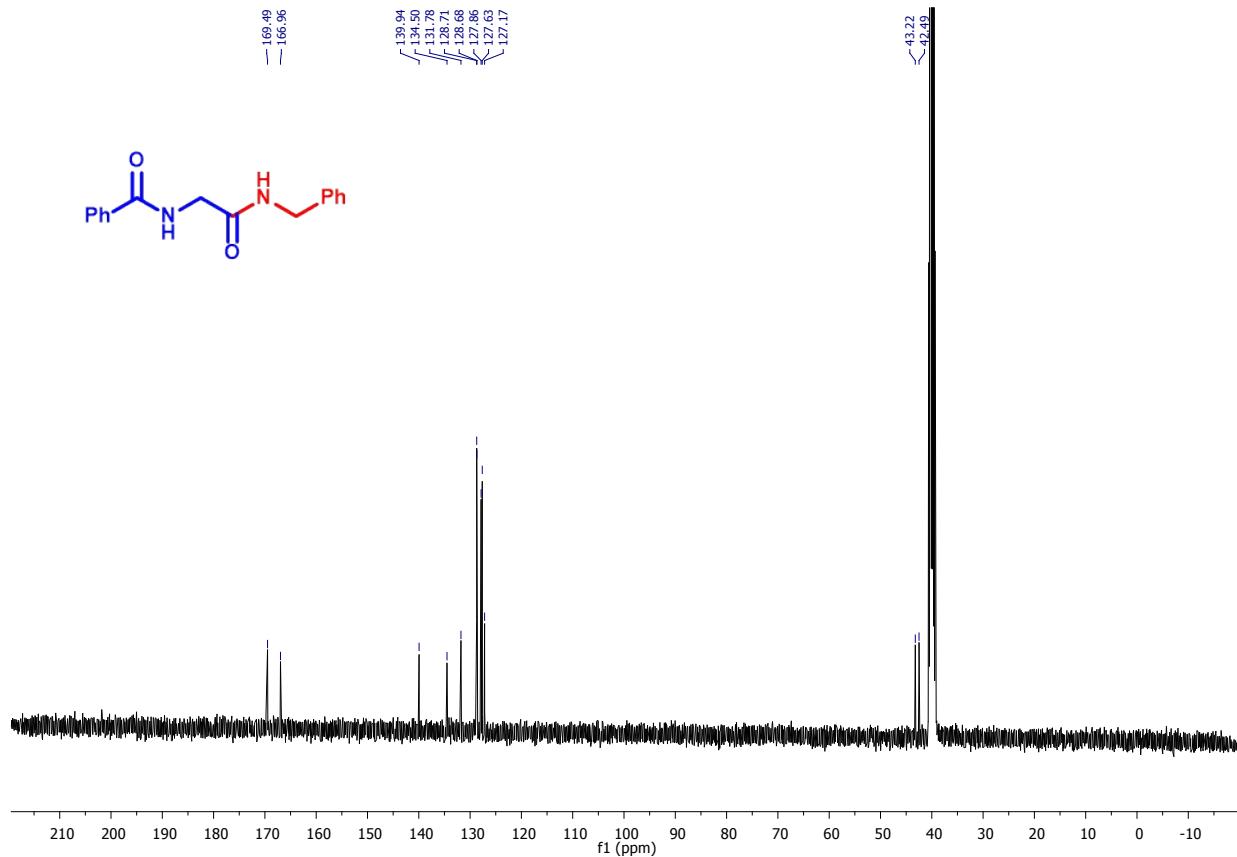
¹³C NMR of N-benzyl-2-hydroxy-2-phenylacetamide (3o)

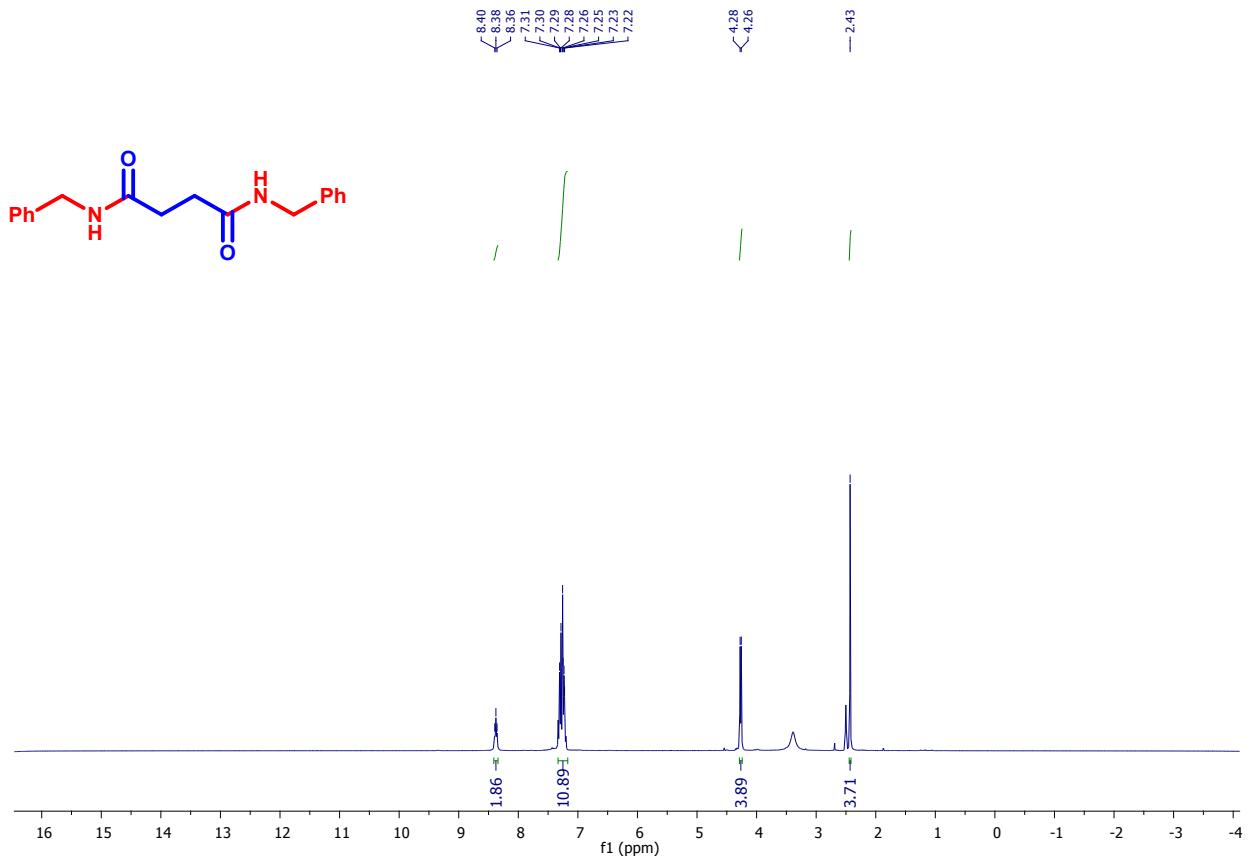


¹H NMR of *N*-benzylcinnamamide (3p)

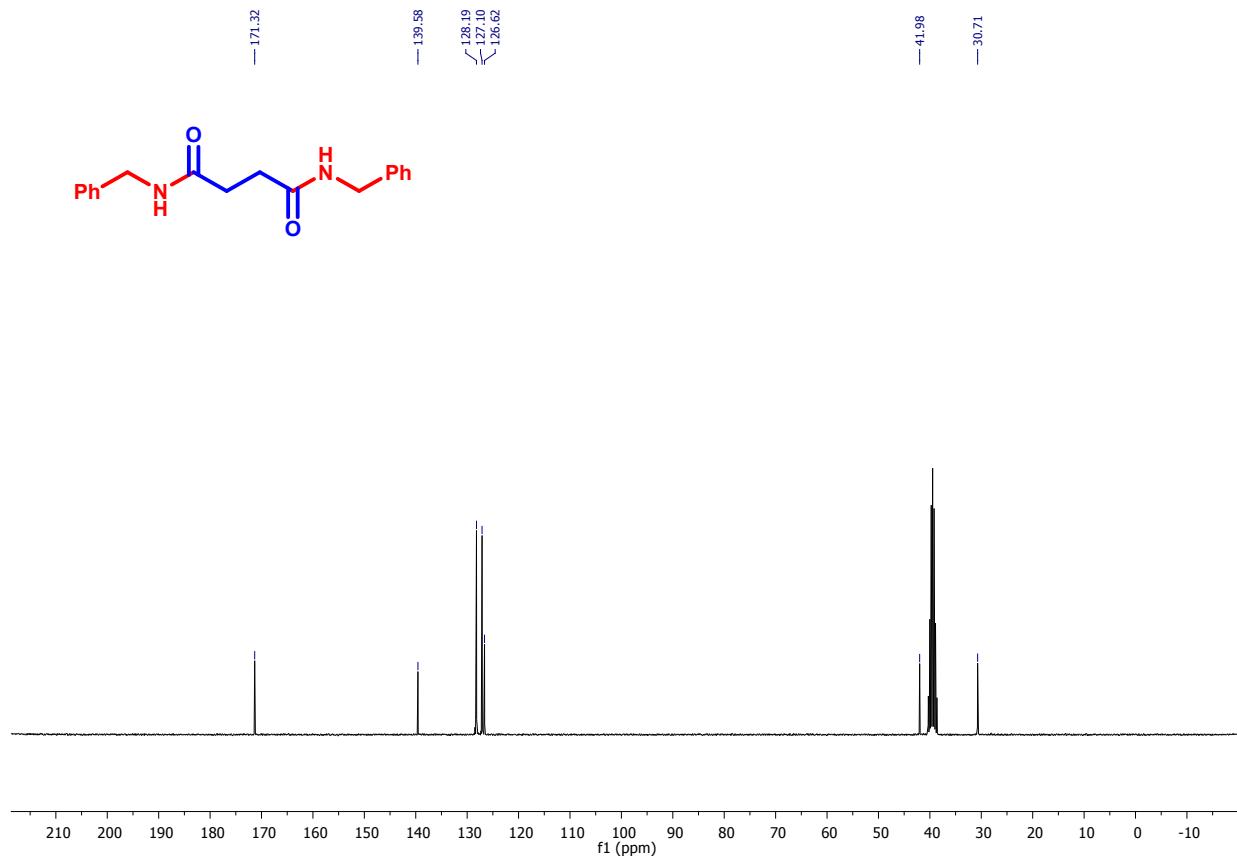


¹H NMR of N-(2-(benzylamino)-2-oxoethyl)benzamide (3q)

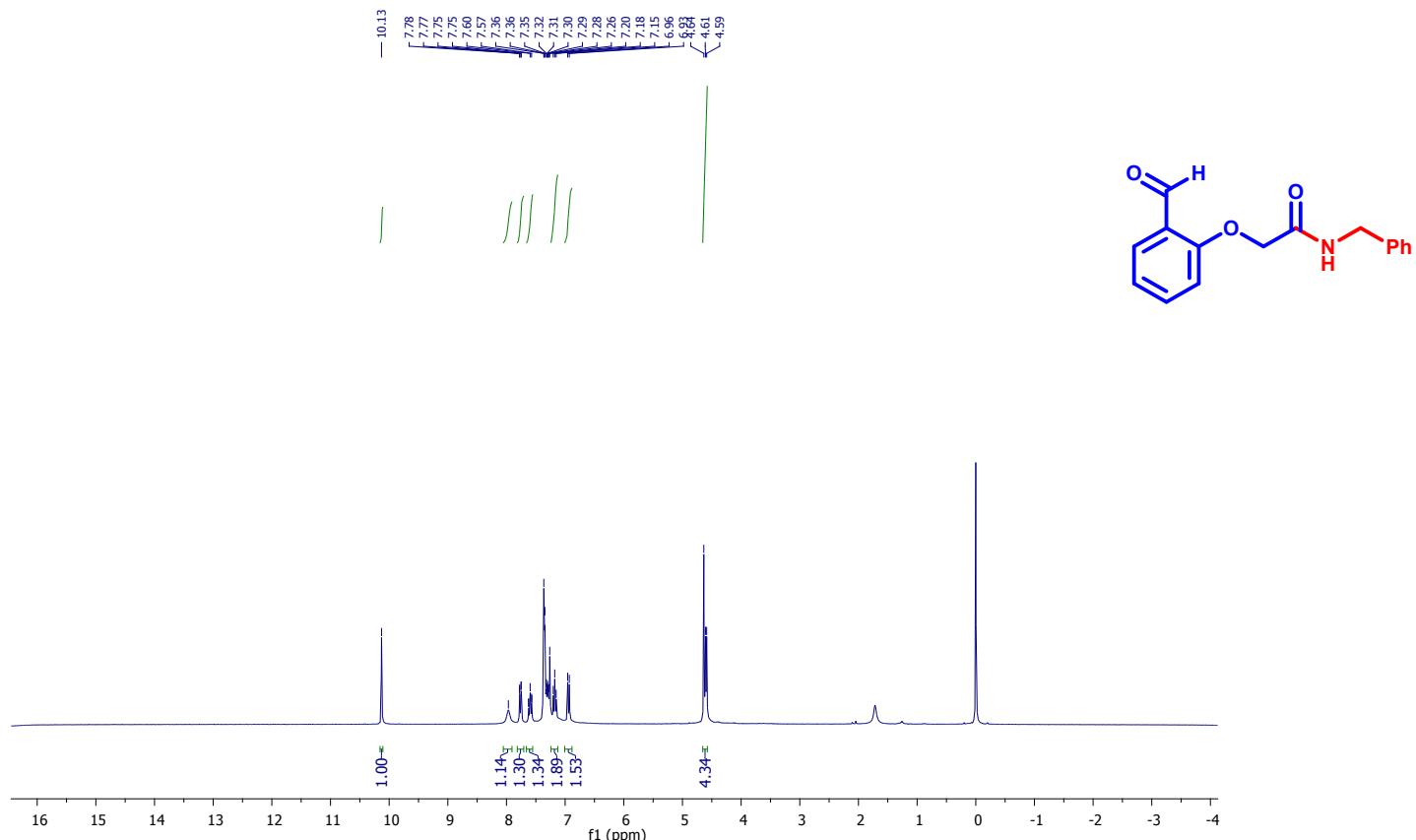




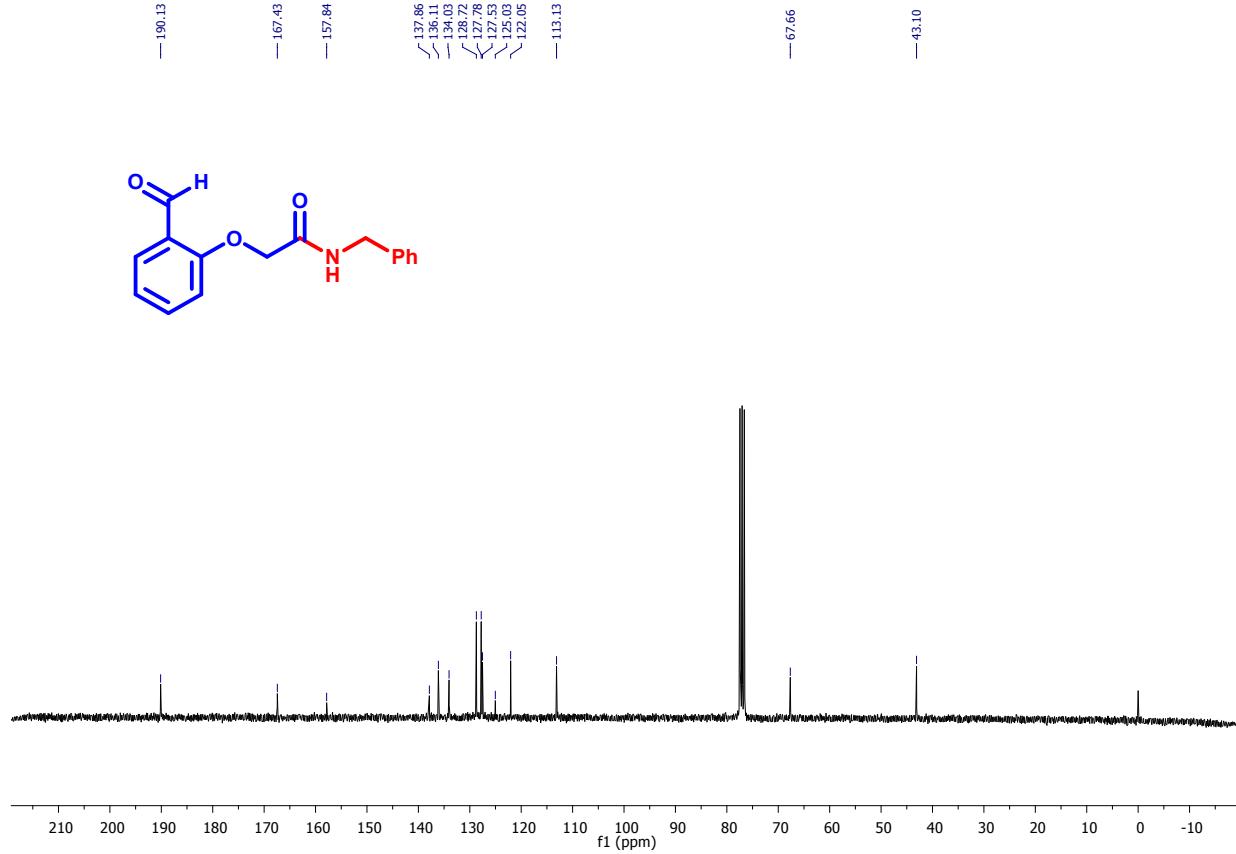
^1H NMR of *N*₁,*N*₄-dibenzylsuccinamide (3r)

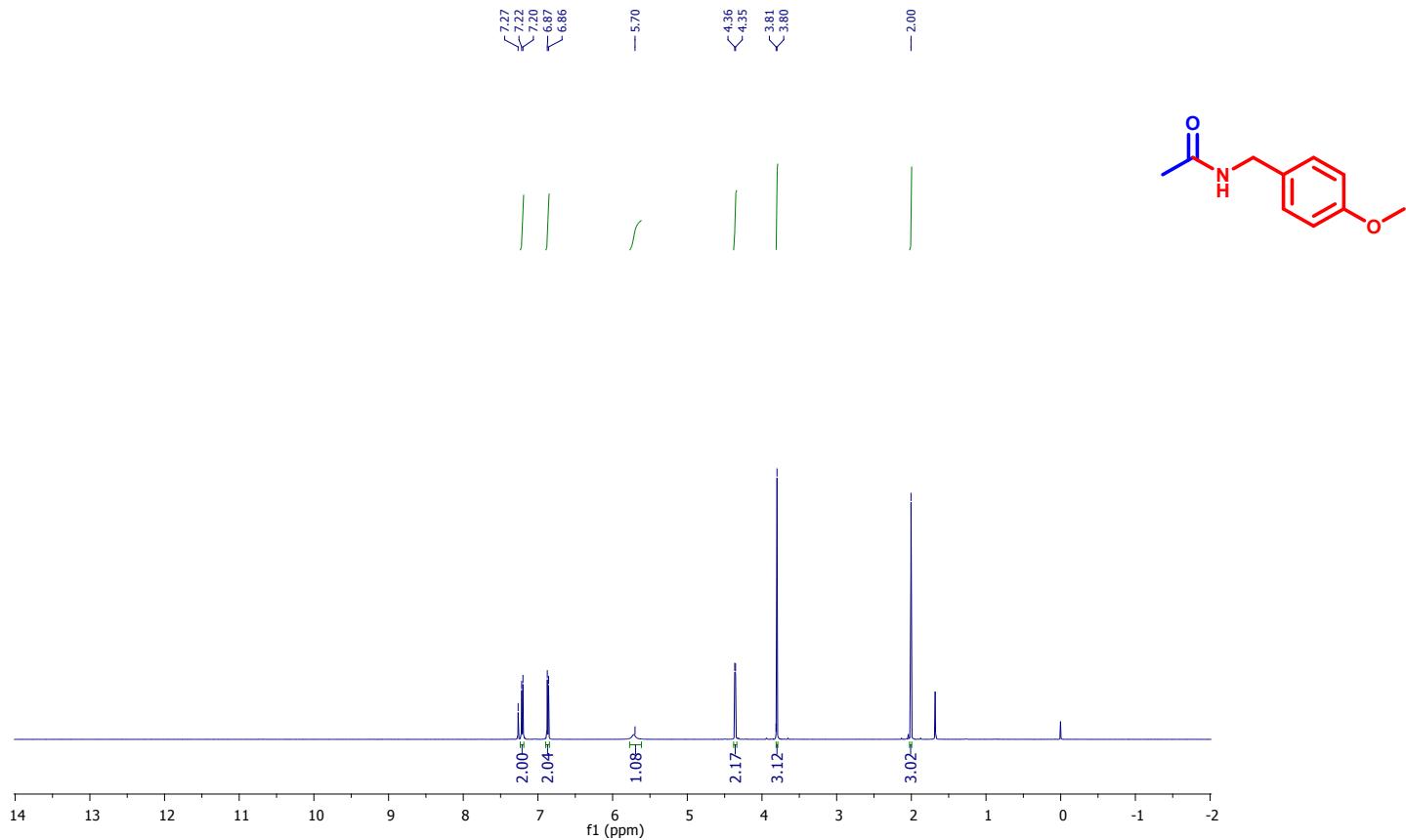


¹³C NMR of N1,N4-dibenzylsuccinamide (3r)

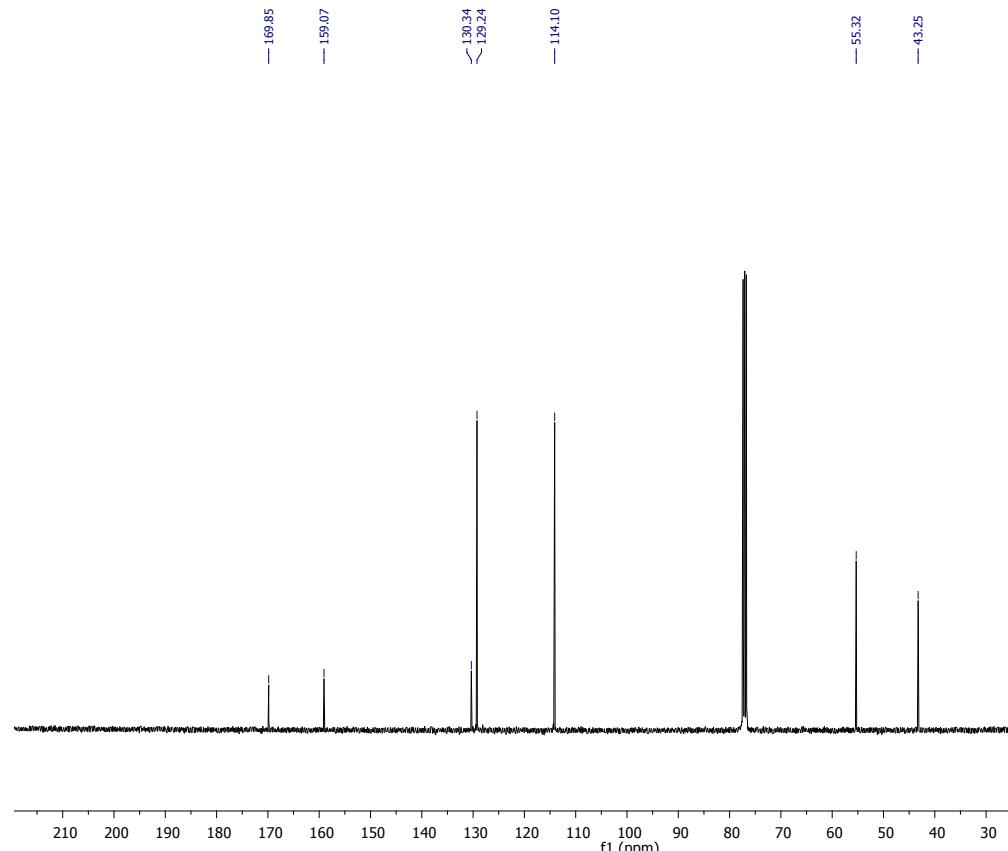


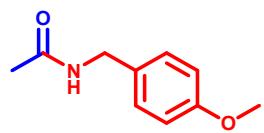
¹H NMR of N-benzyl-2-(2-formylphenoxy)acetamide (3s)



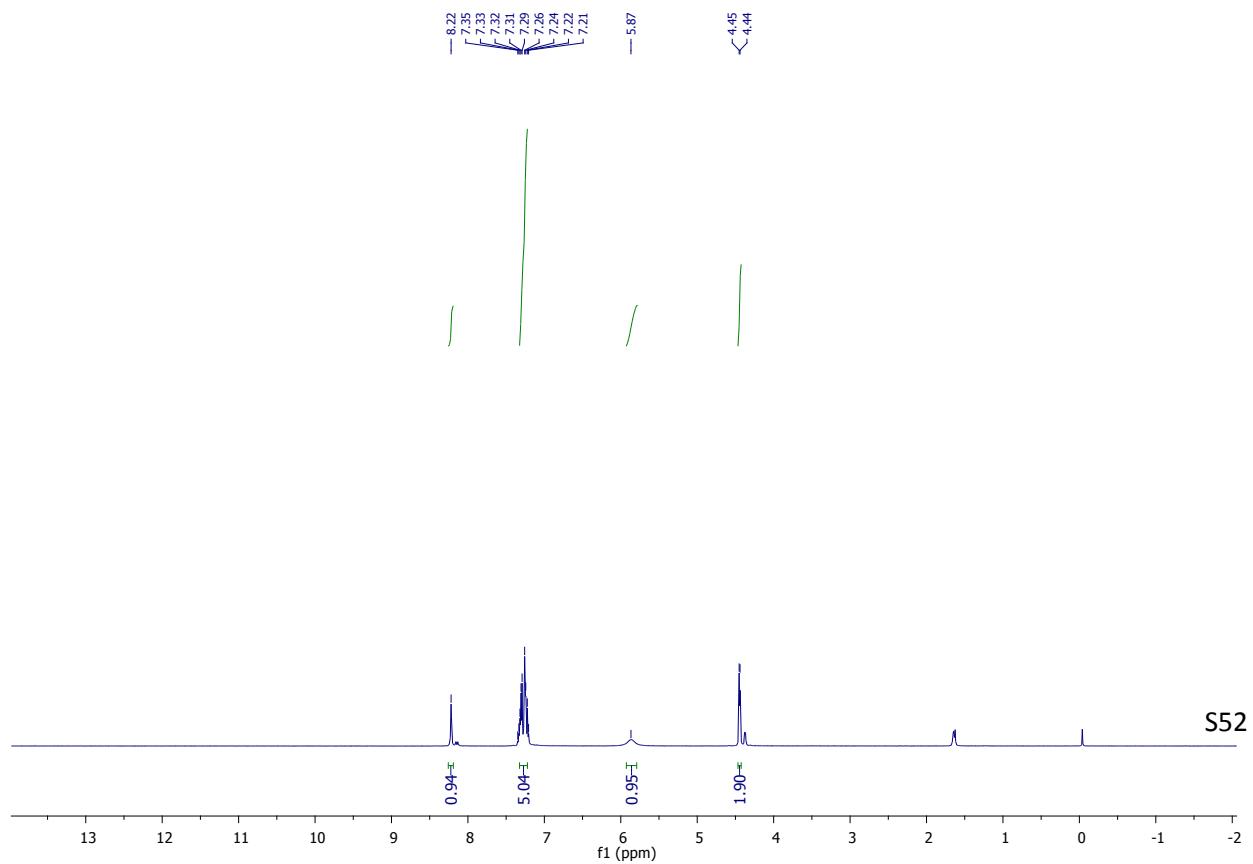


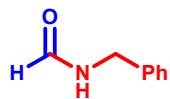
¹H NMR of N-(4-Methoxybenzyl) acetamide (3t)



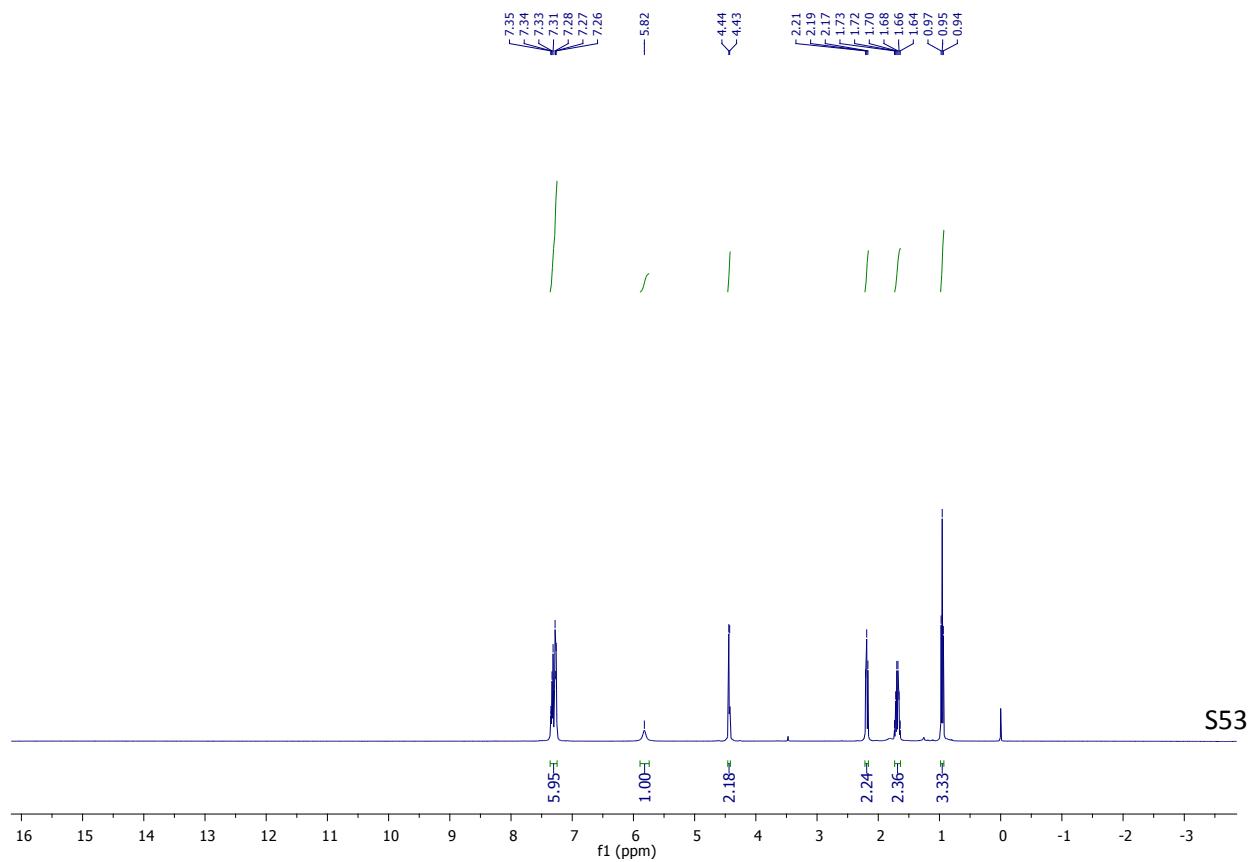


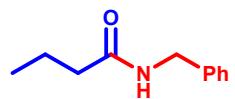
¹³C NMR of N-(4-Methoxybenzyl) acetamide (3t)



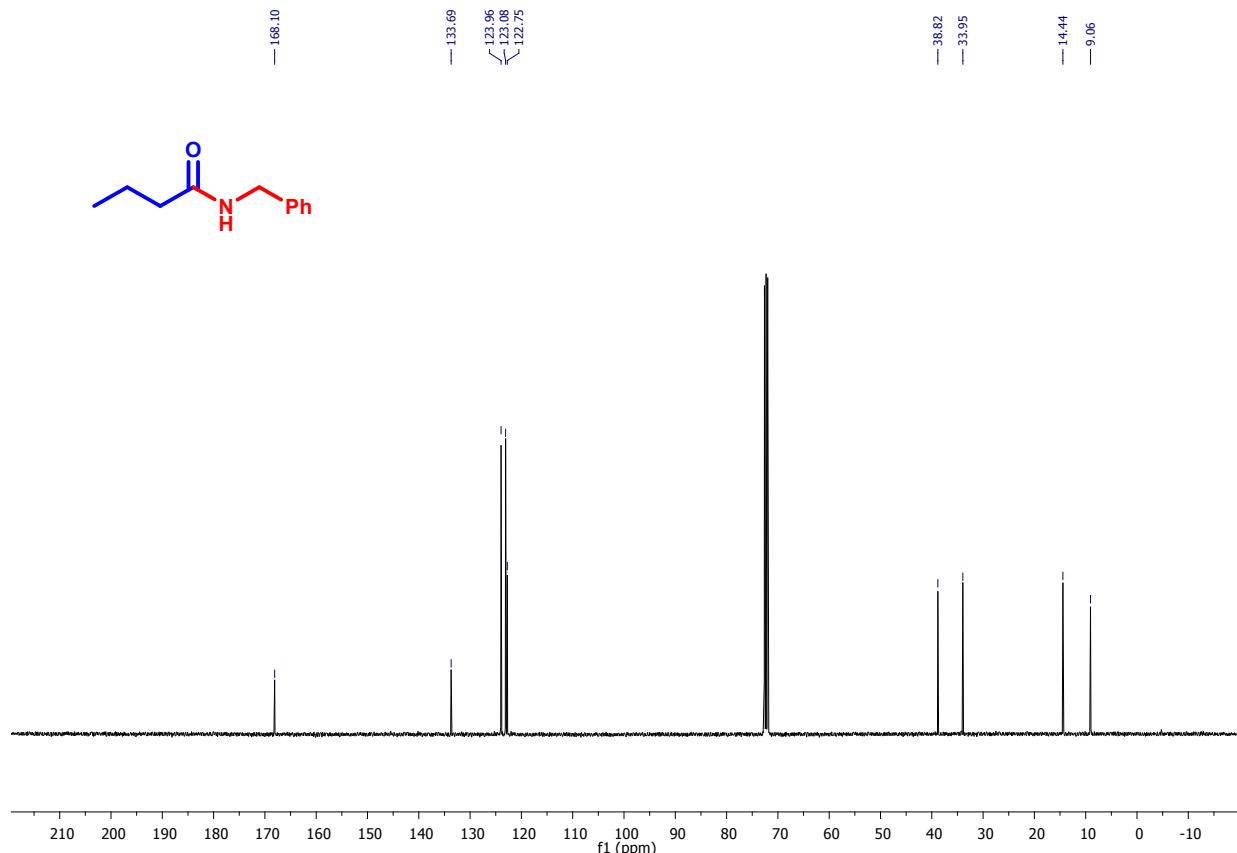


¹H NMR of N-Benzylformamide (3u)

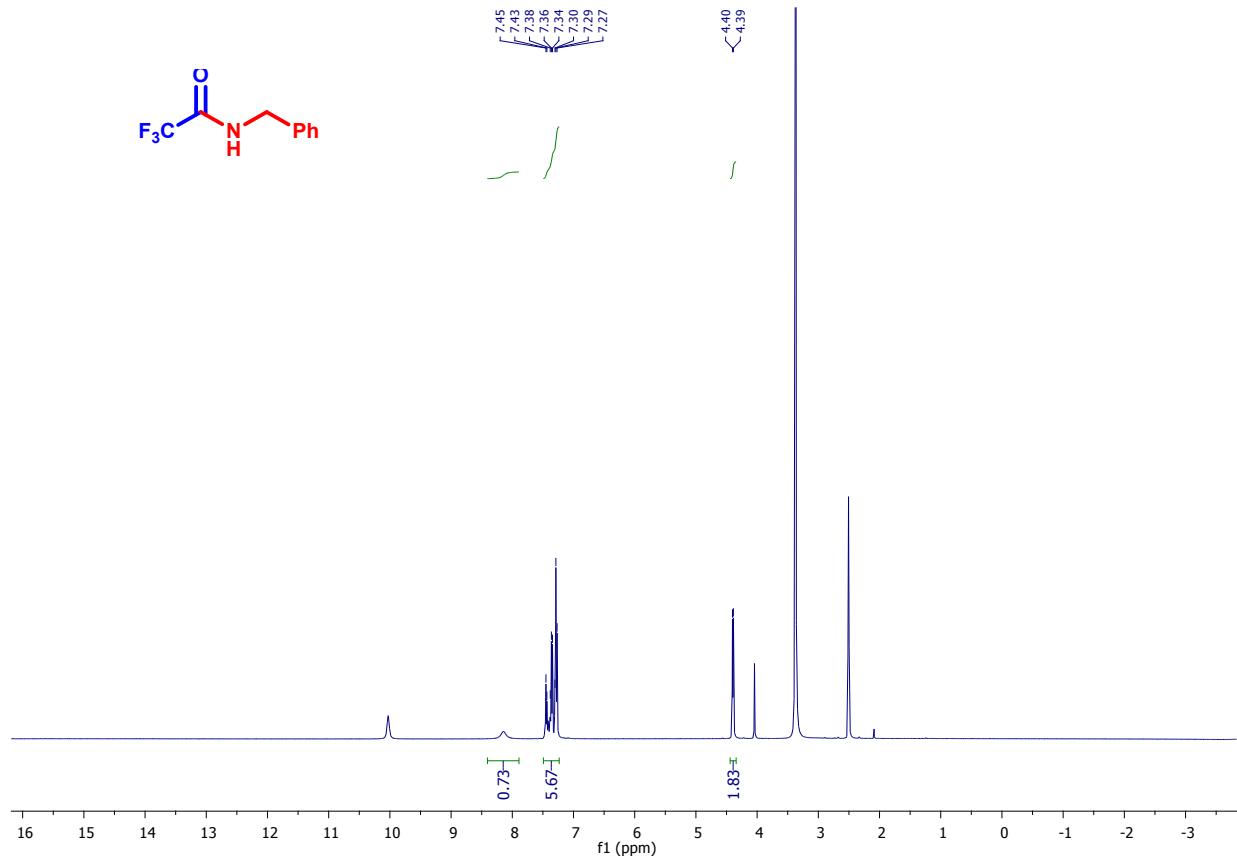




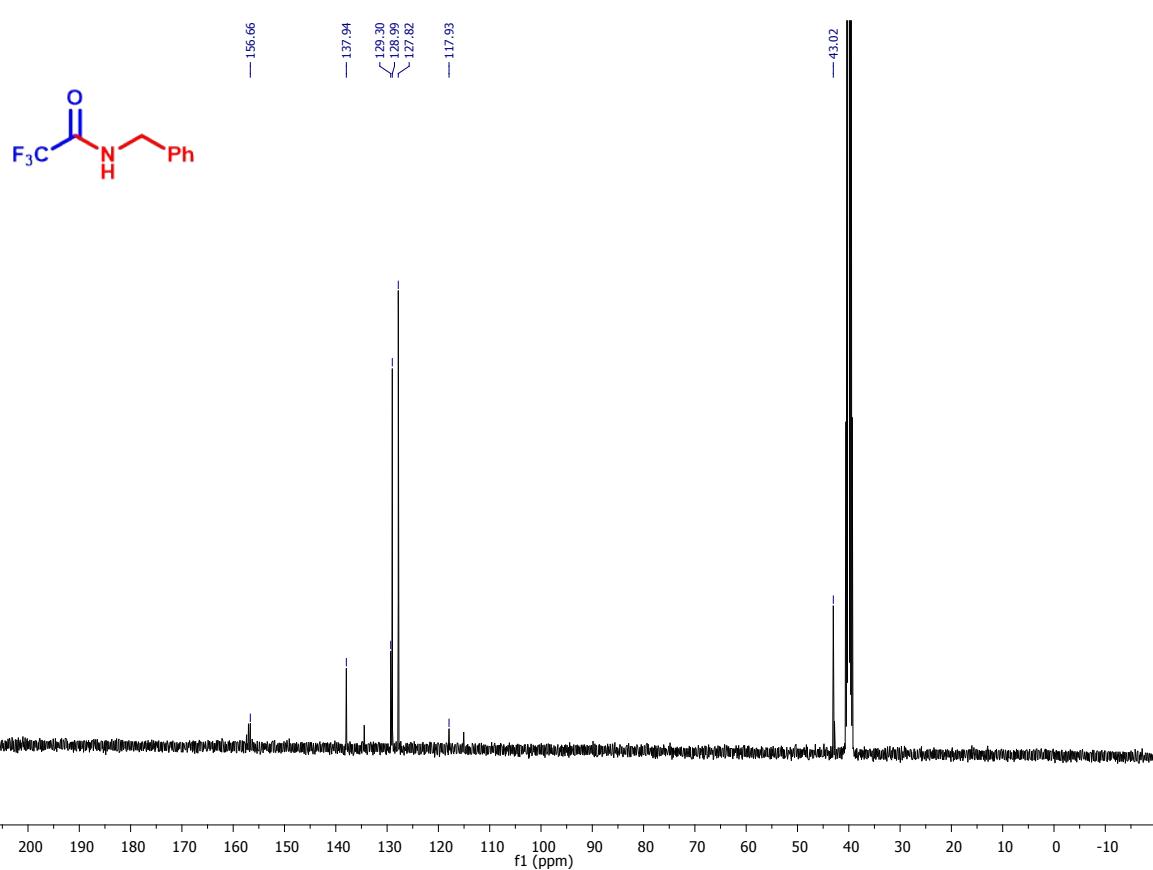
¹H NMR of N-benzylbutyramide (3v)



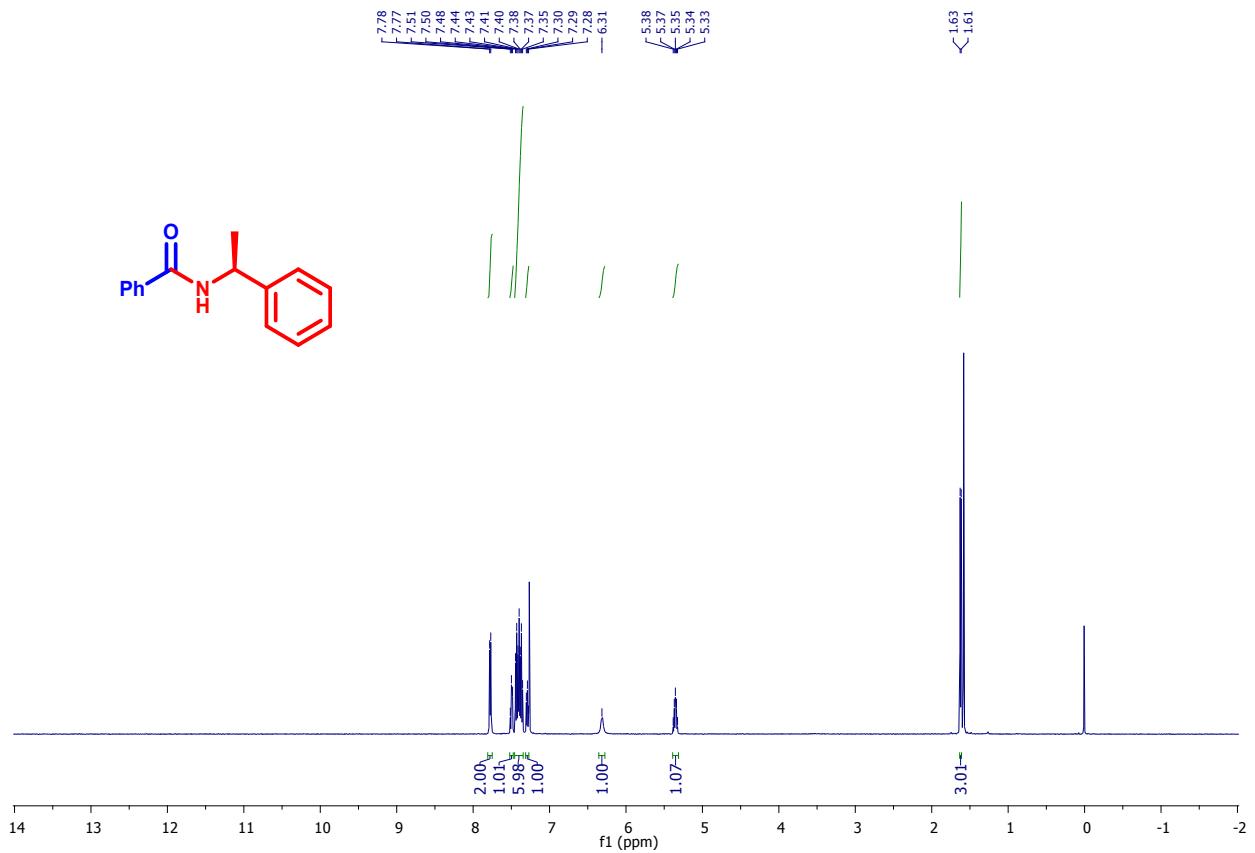
^{13}C NMR of N-benzylbutyramide (3v)



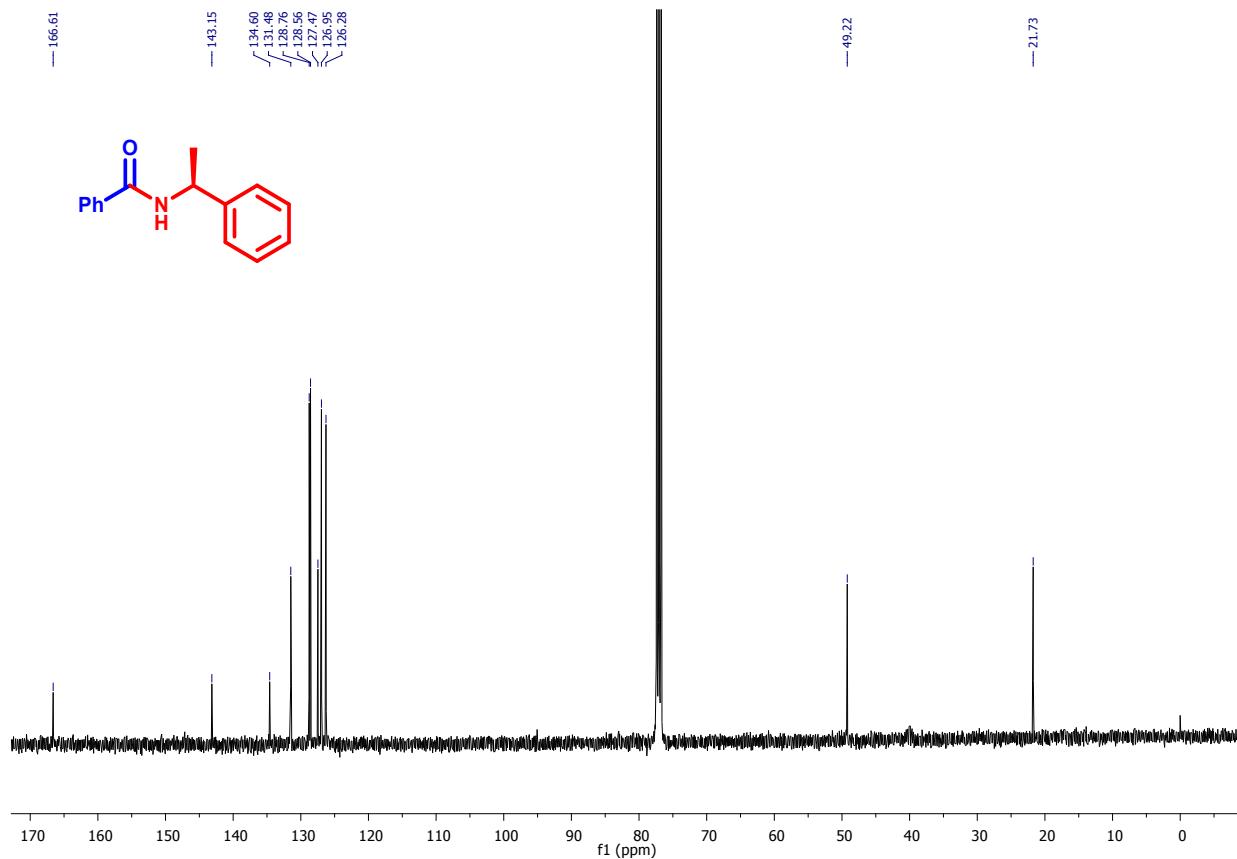
¹H NMR of *N*-benzyl-2,2,2-trifluoroacetamide (3x)



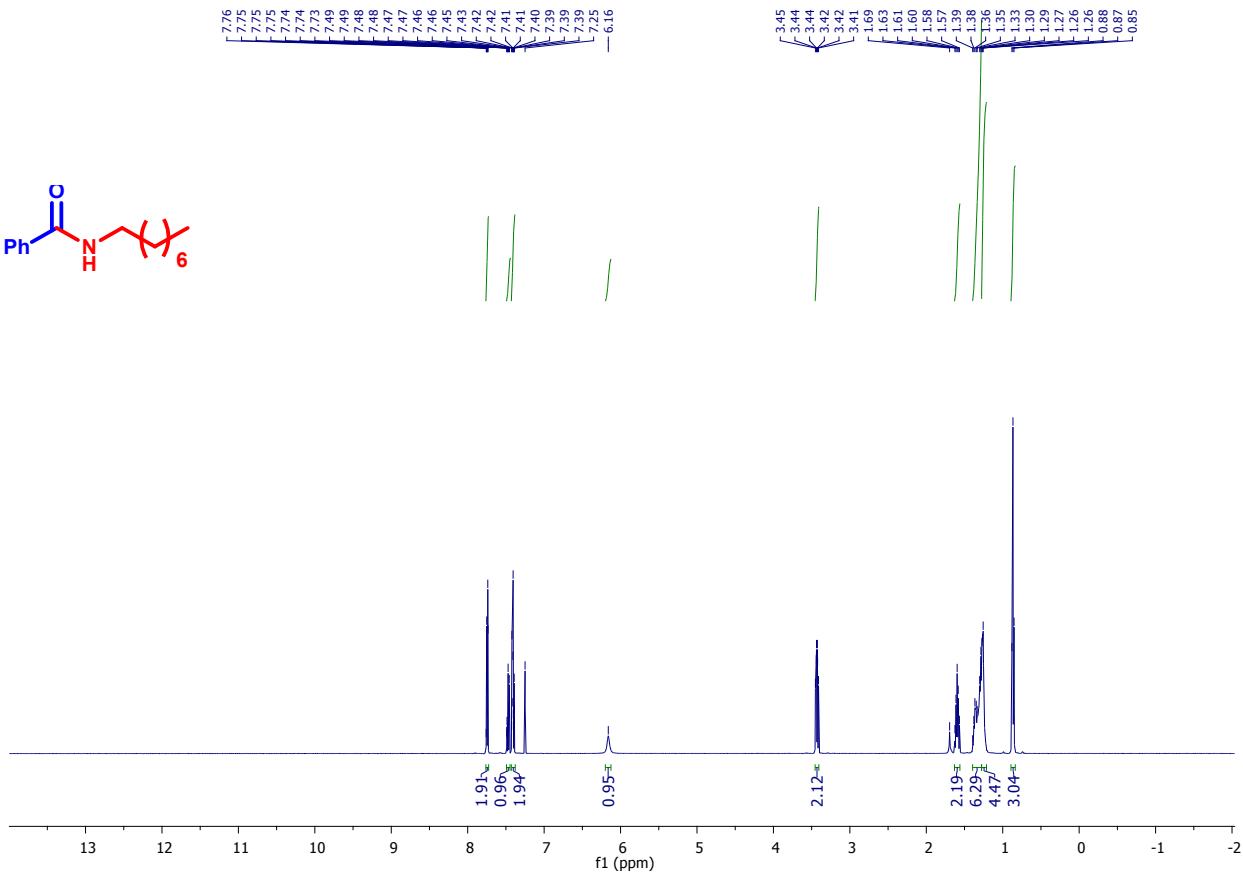
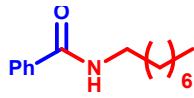
¹³C NMR of *N*-benzyl-2,2,2-trifluoroacetamide (3x)



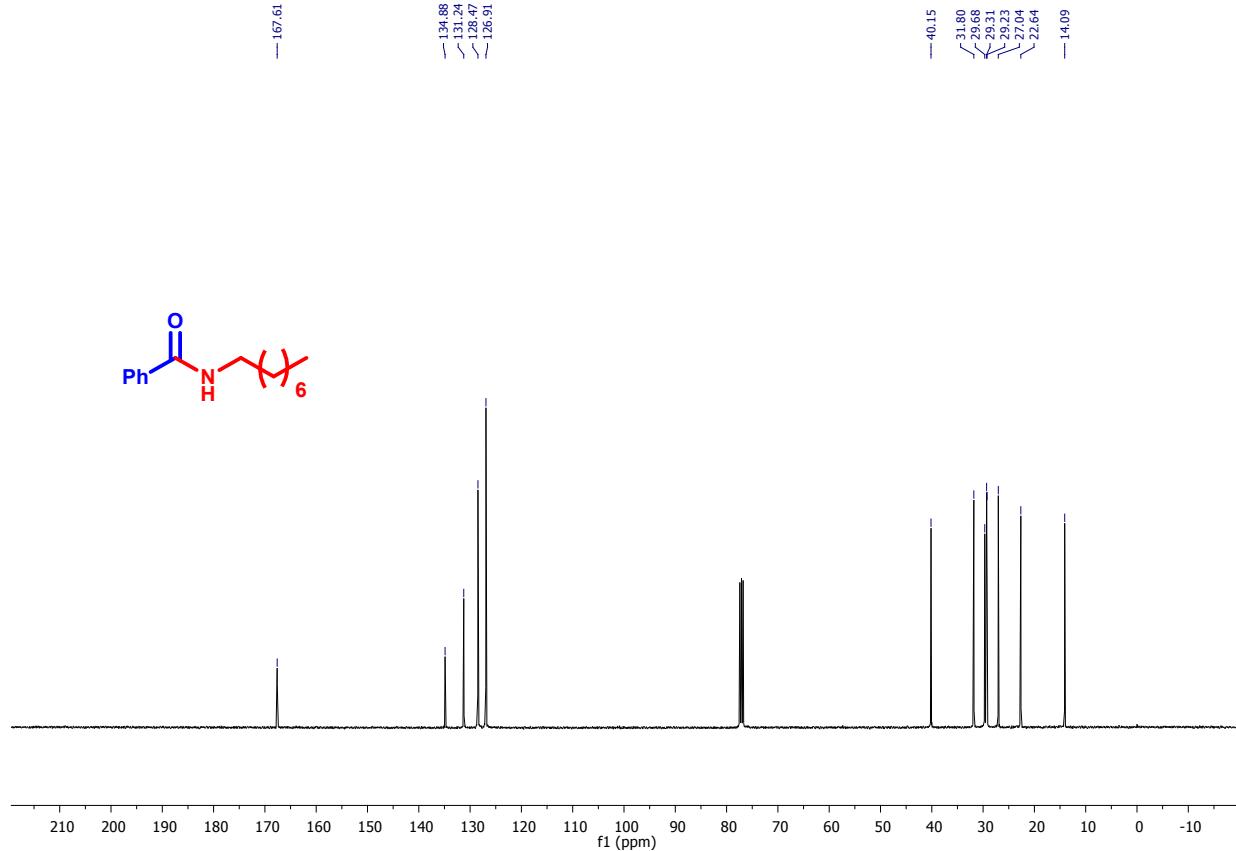
¹H NMR of (S)-N-(1-Phenylethyl) benzamide (5f)



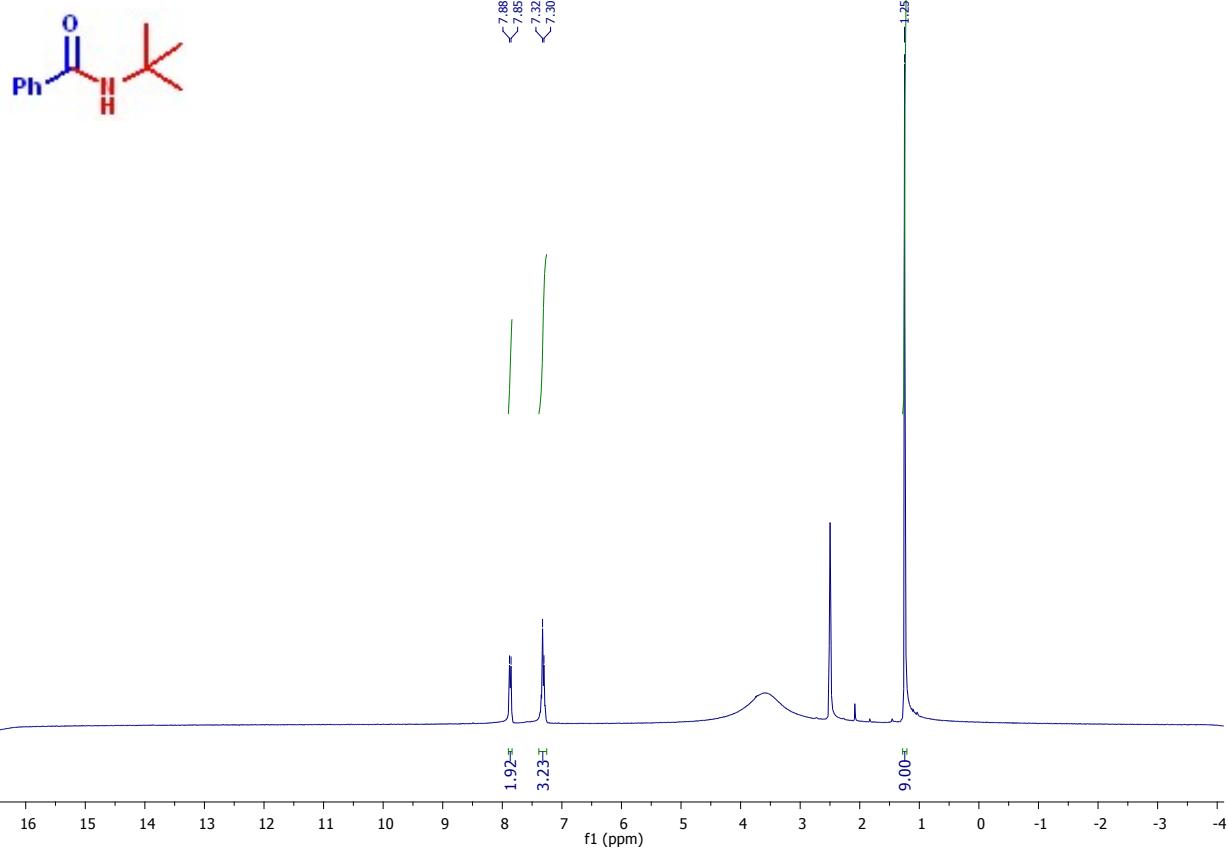
¹³C NMR of (S)-N-(1-Phenylethyl) benzamide (5f)



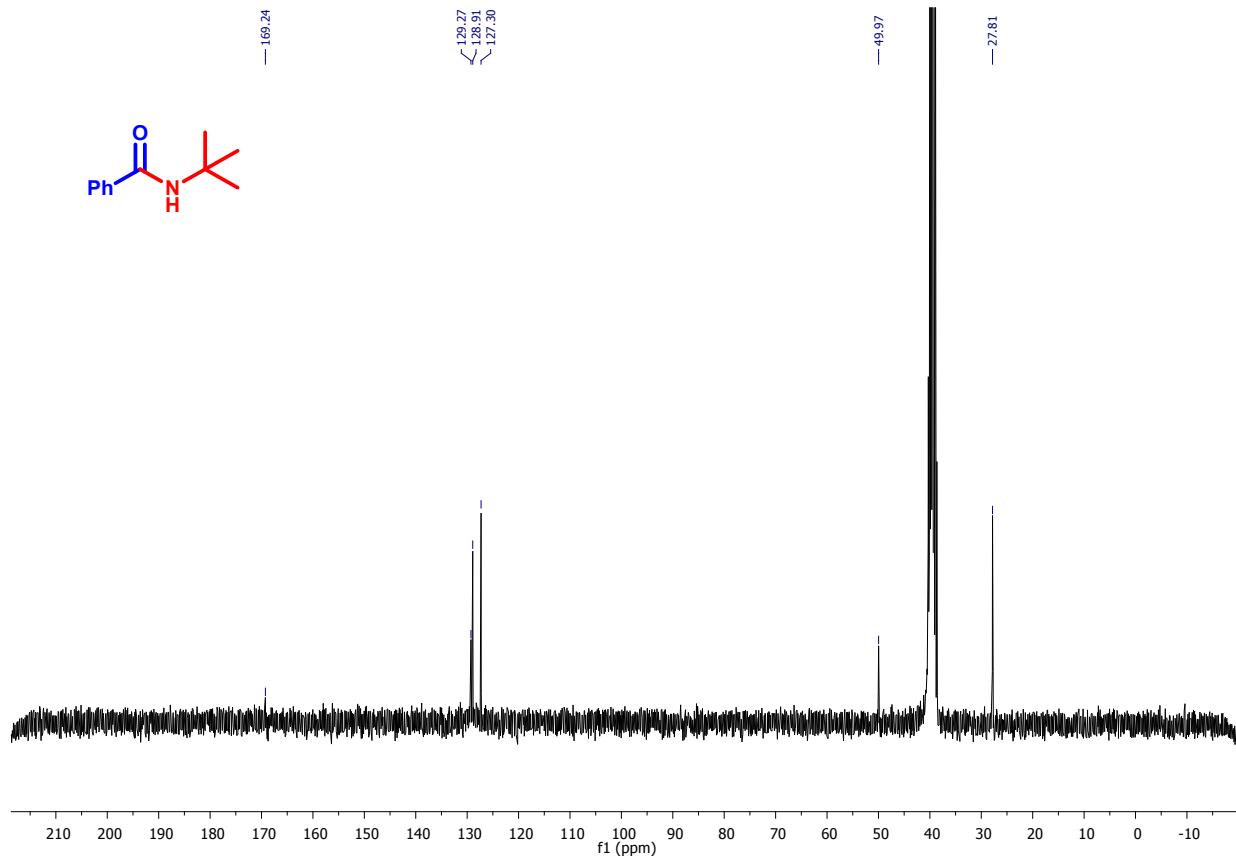
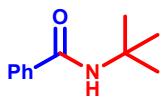
¹H NMR of N-Octylbenzamide(5g)



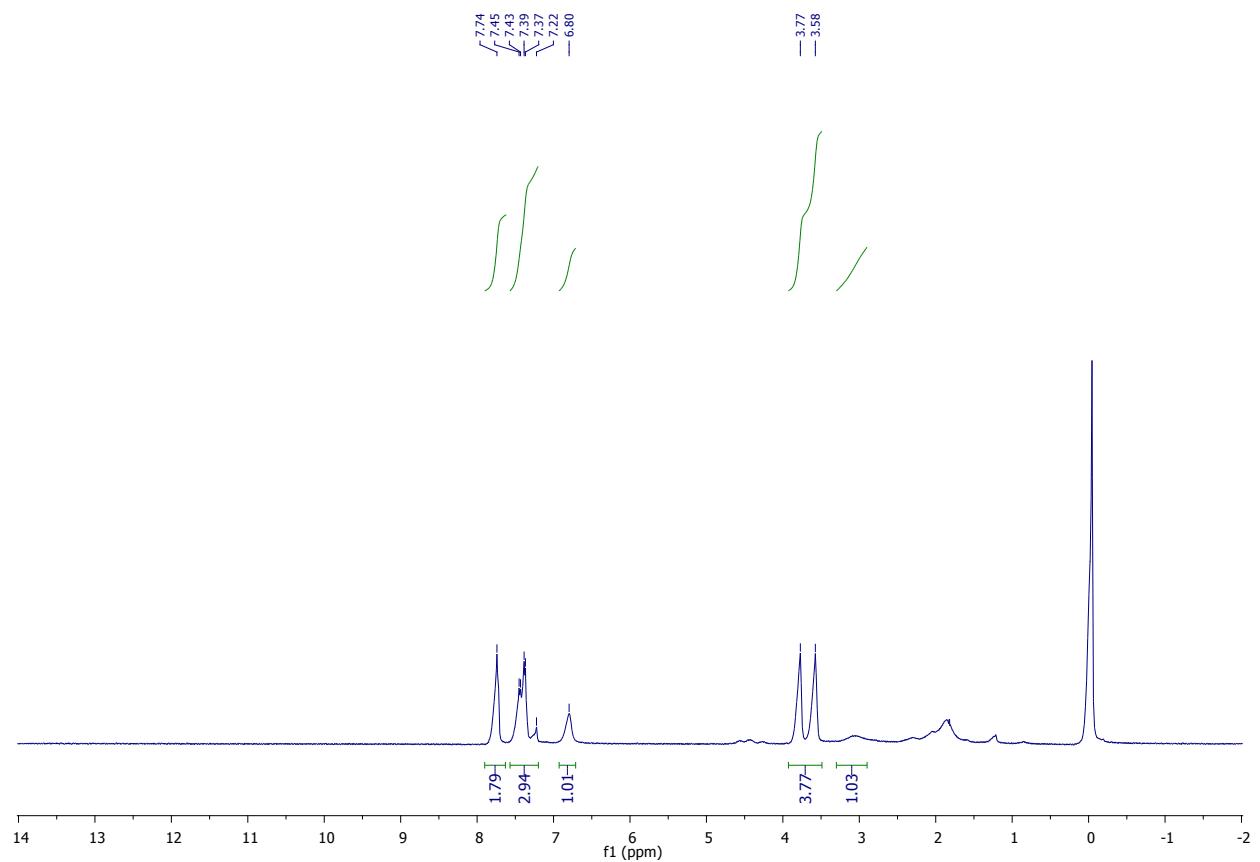
¹³C NMR of N-Octylbenzamide (5g)



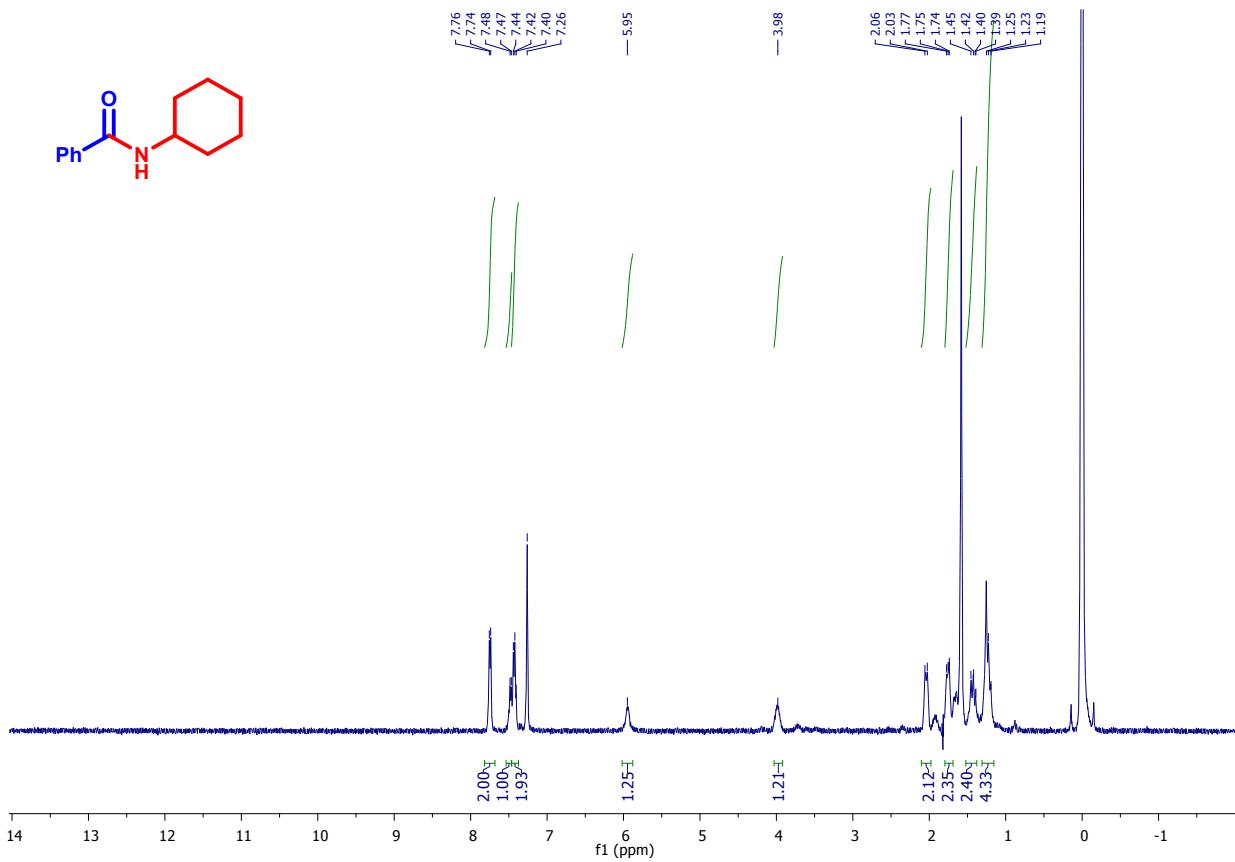
¹H NMR of N-(tert-butyl)benzamide (5i)



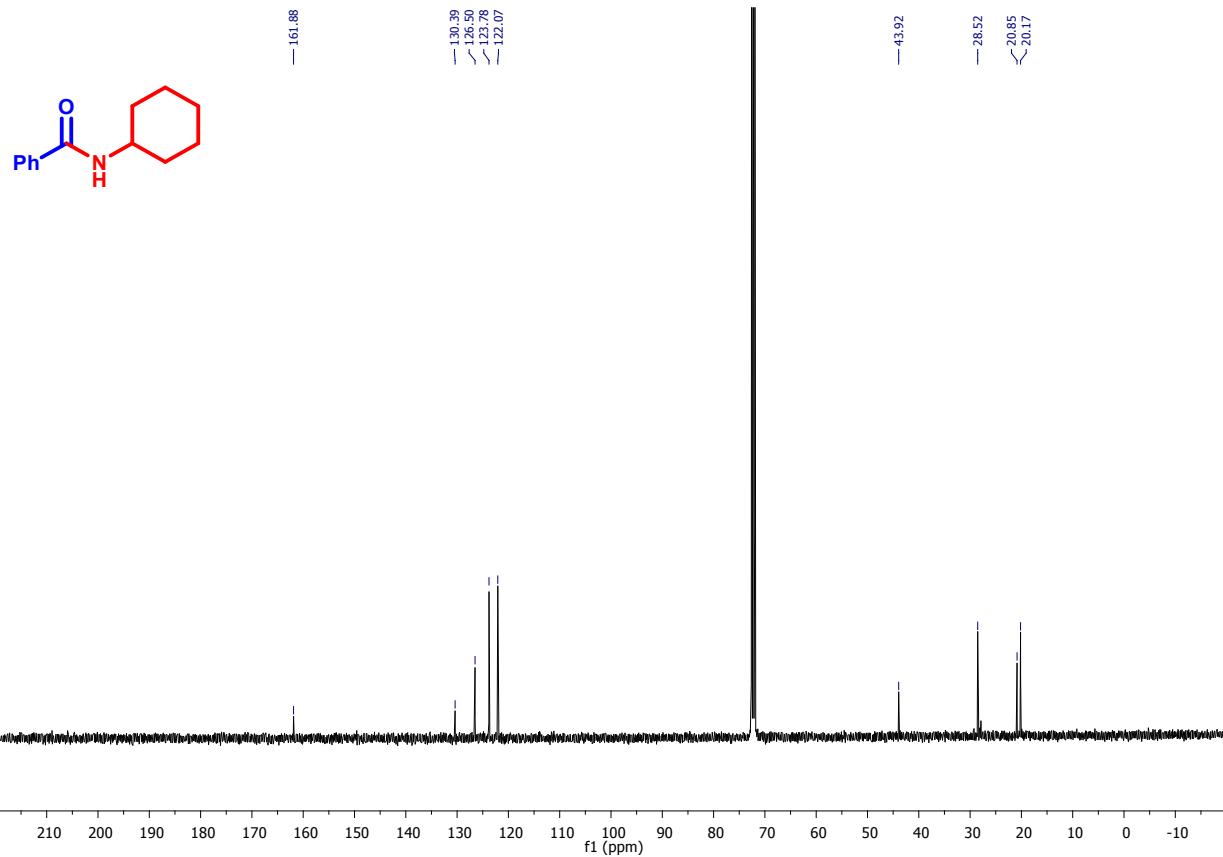
¹³C NMR of N-(tert-butyl)benzamide (5i)



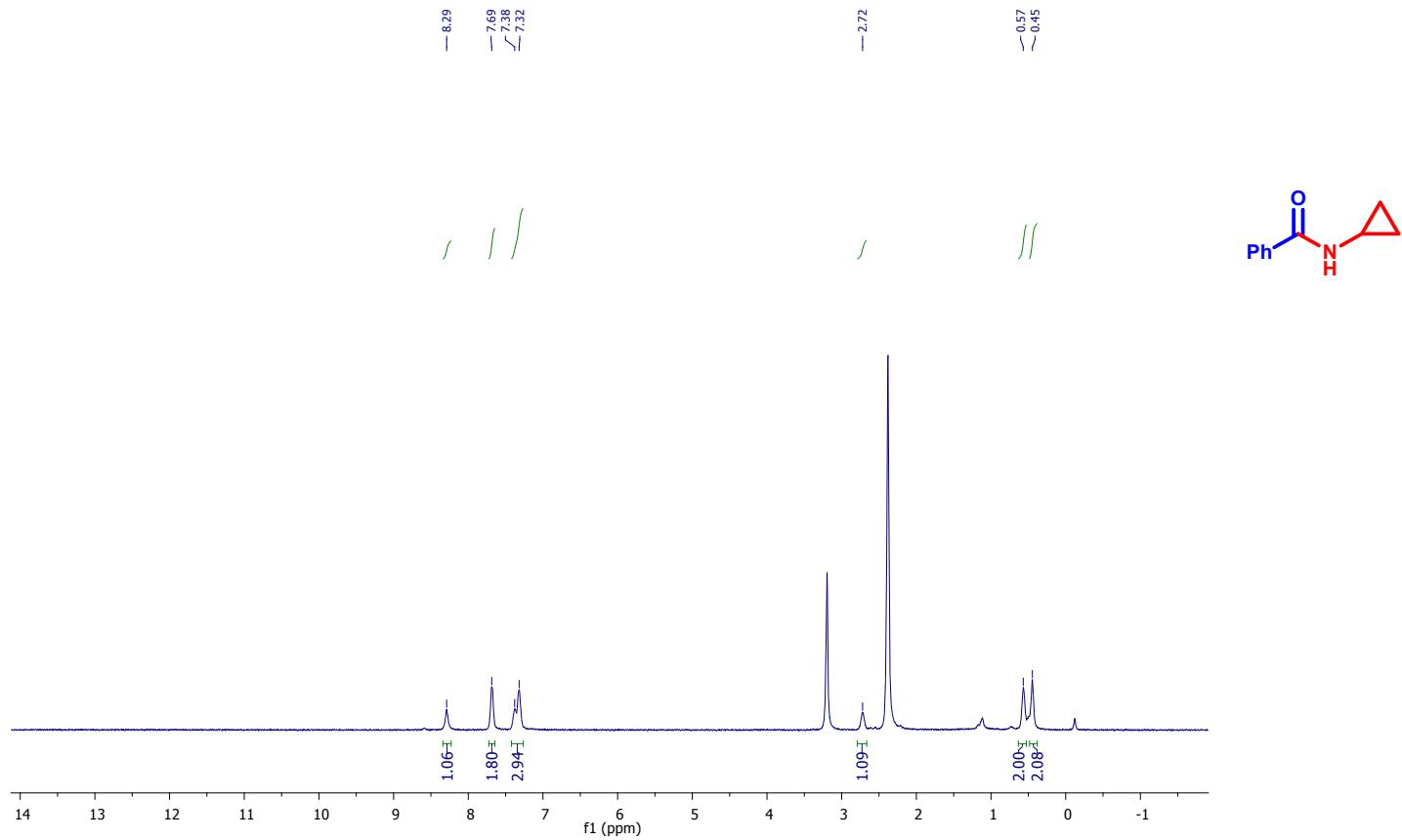
¹H NMR of N-(2-hydroxyethyl)benzamide (5j)



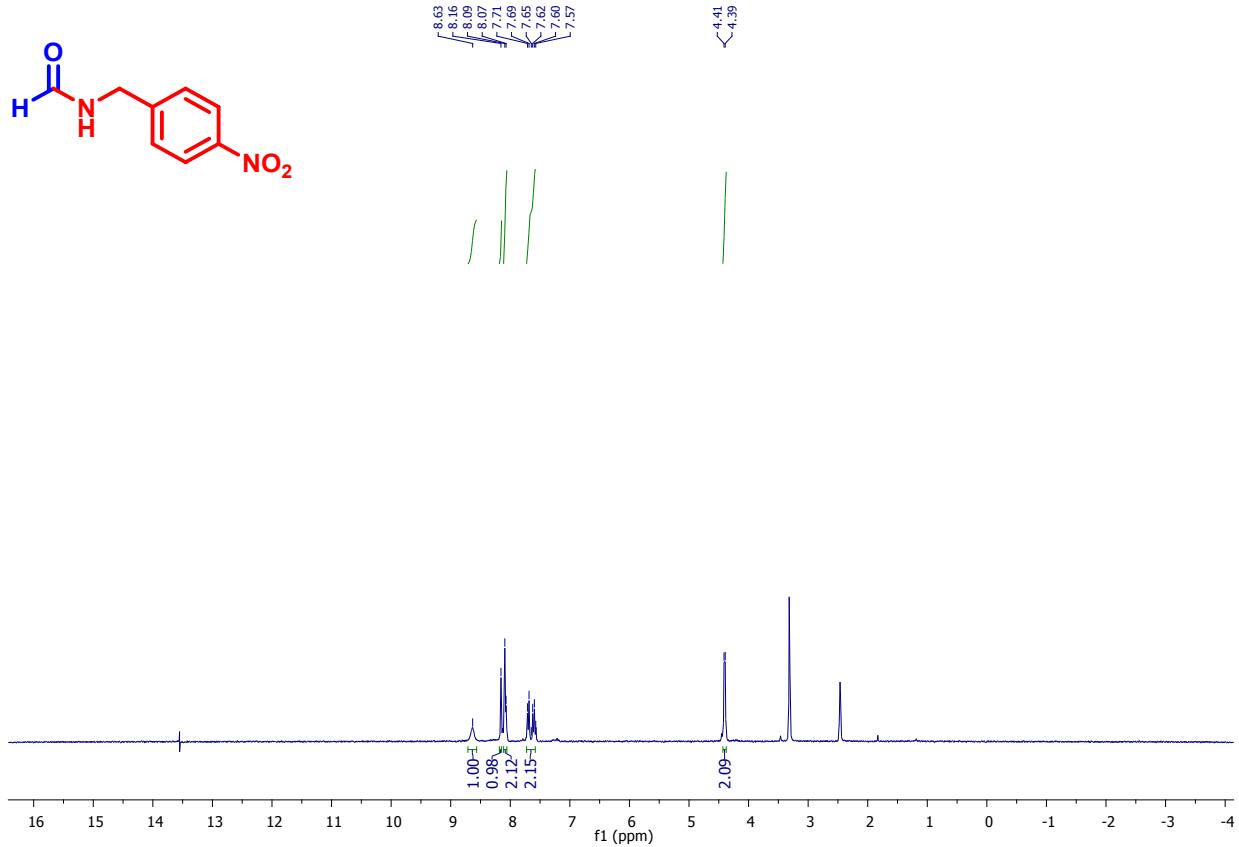
¹H NMR of N-Cyclohexylbenzamide (5k)



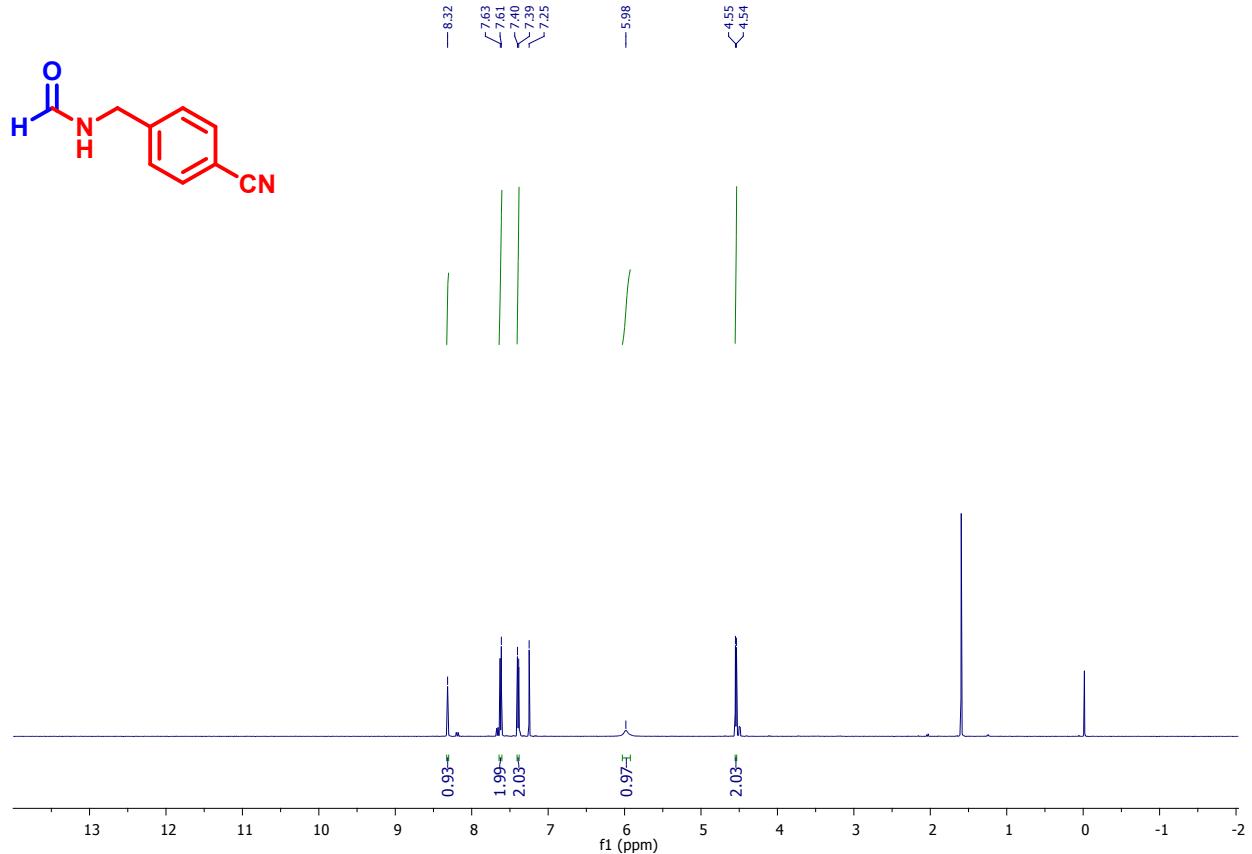
^{13}C NMR of N-Cyclohexylbenzamide (5k)



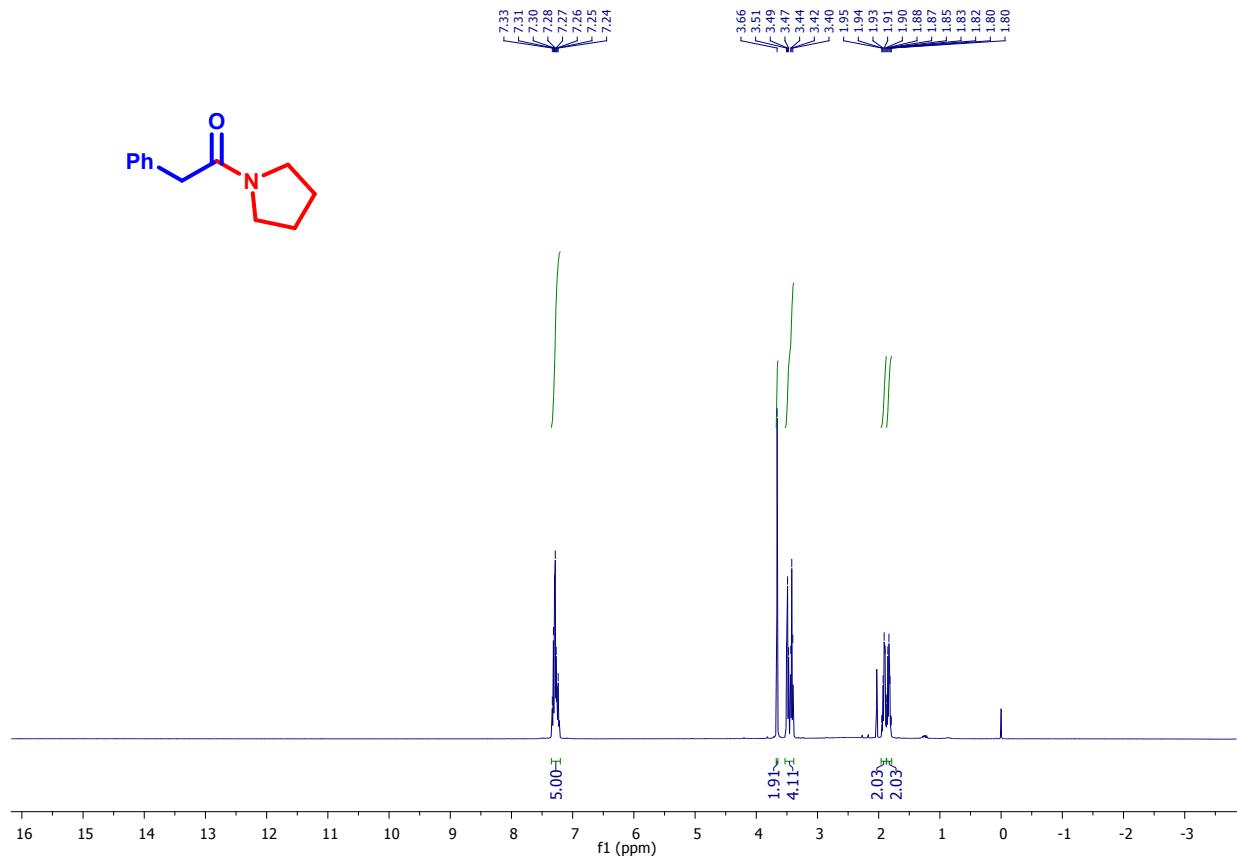
¹H NMR of N-Cyclopropylbenzamide (5l)



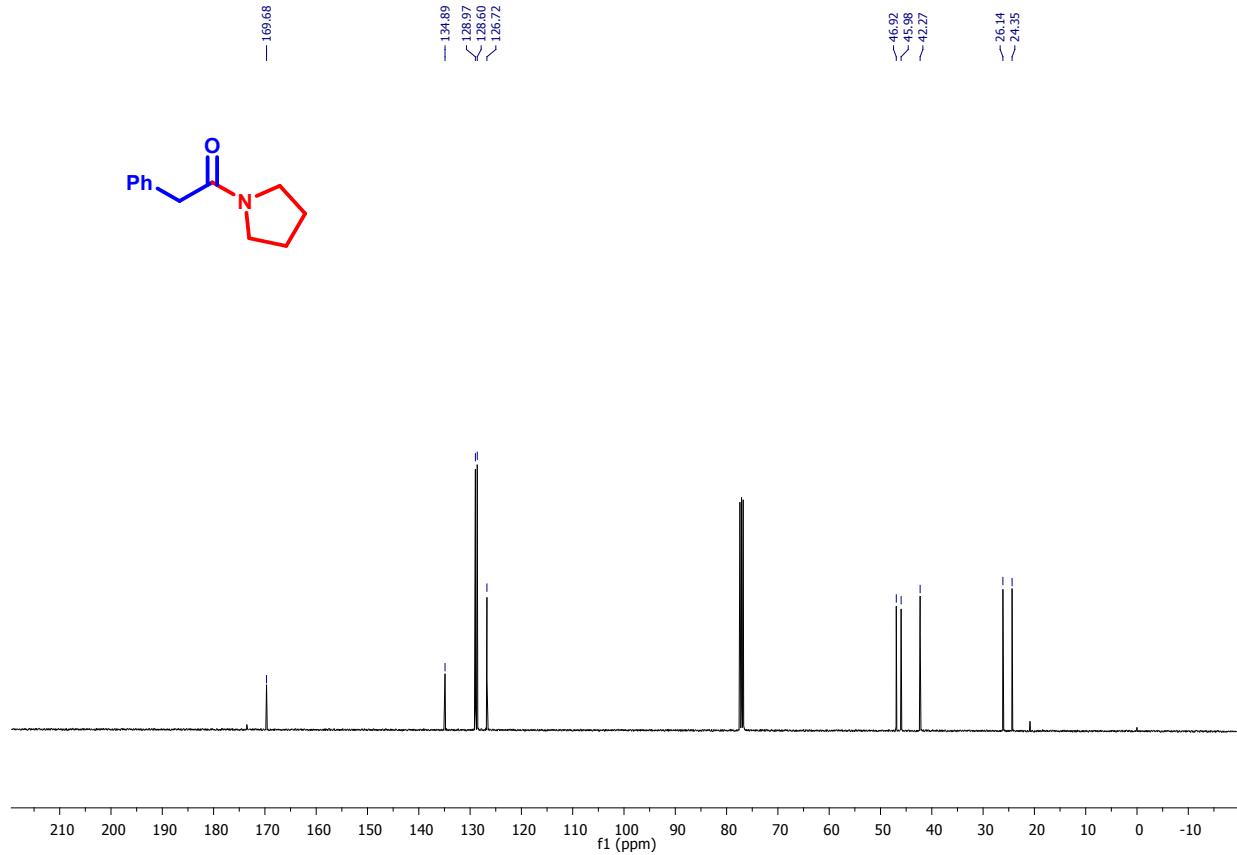
¹H NMR of N-(4-Nitrobenzyl) formamide (5m)



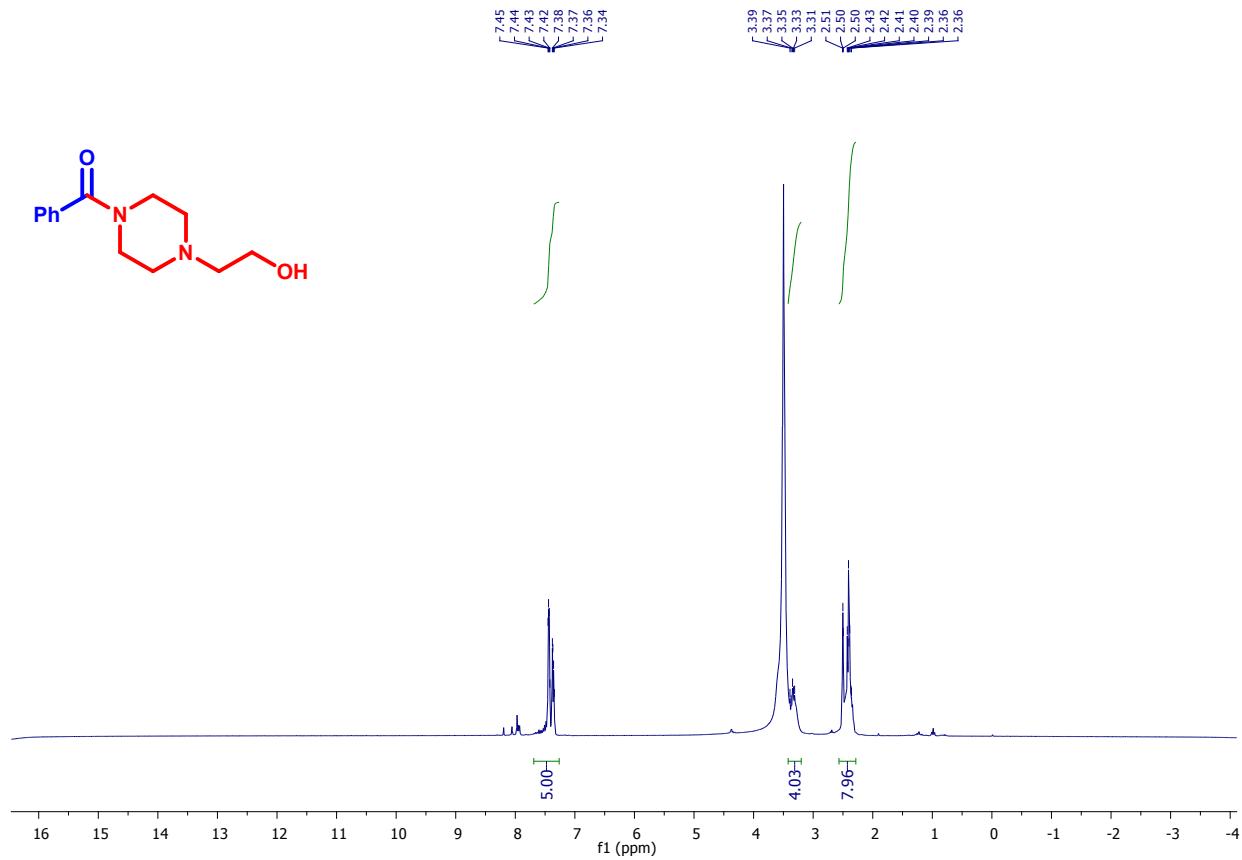
¹H NMR of N-(4-Cyanobenzyl) formamide (5n)



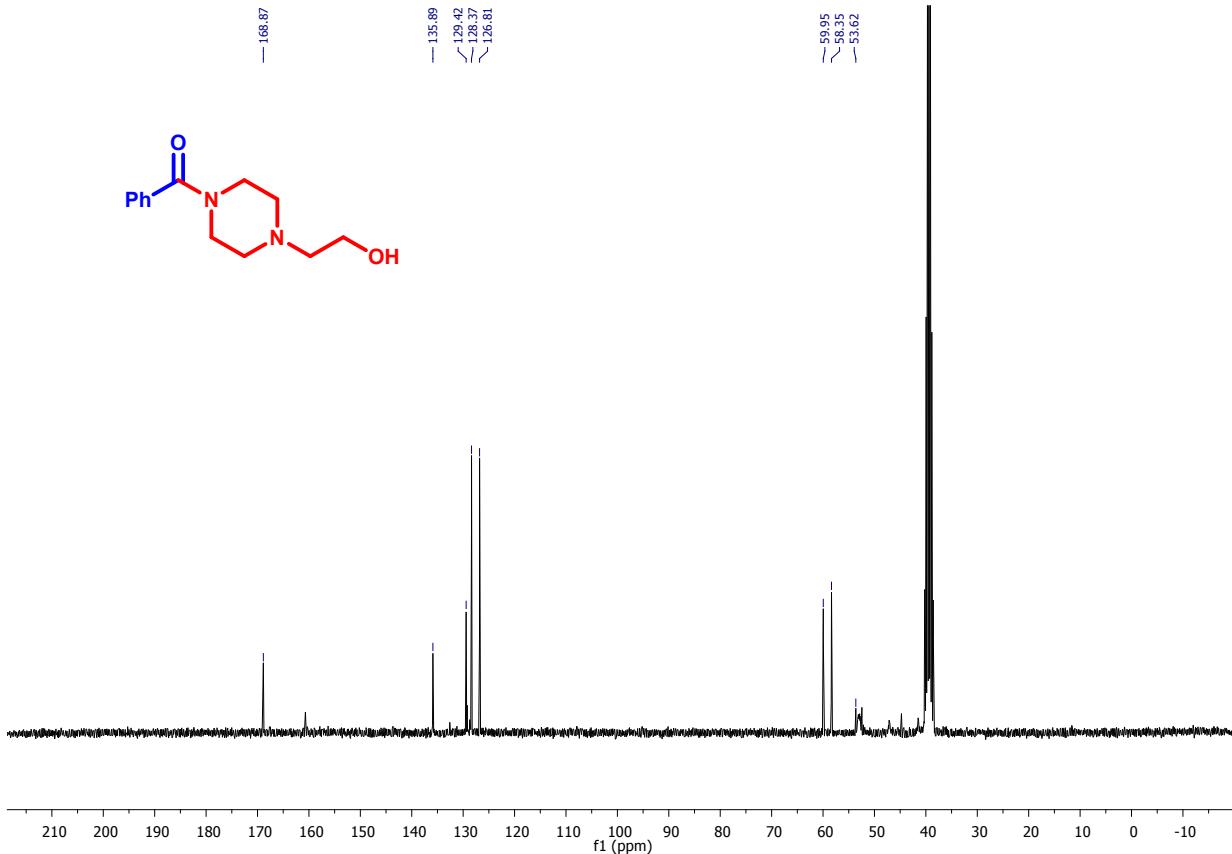
¹H NMR of 2-phenyl-1-(pyrrolidin-1-yl)ethan-1-one (5p)



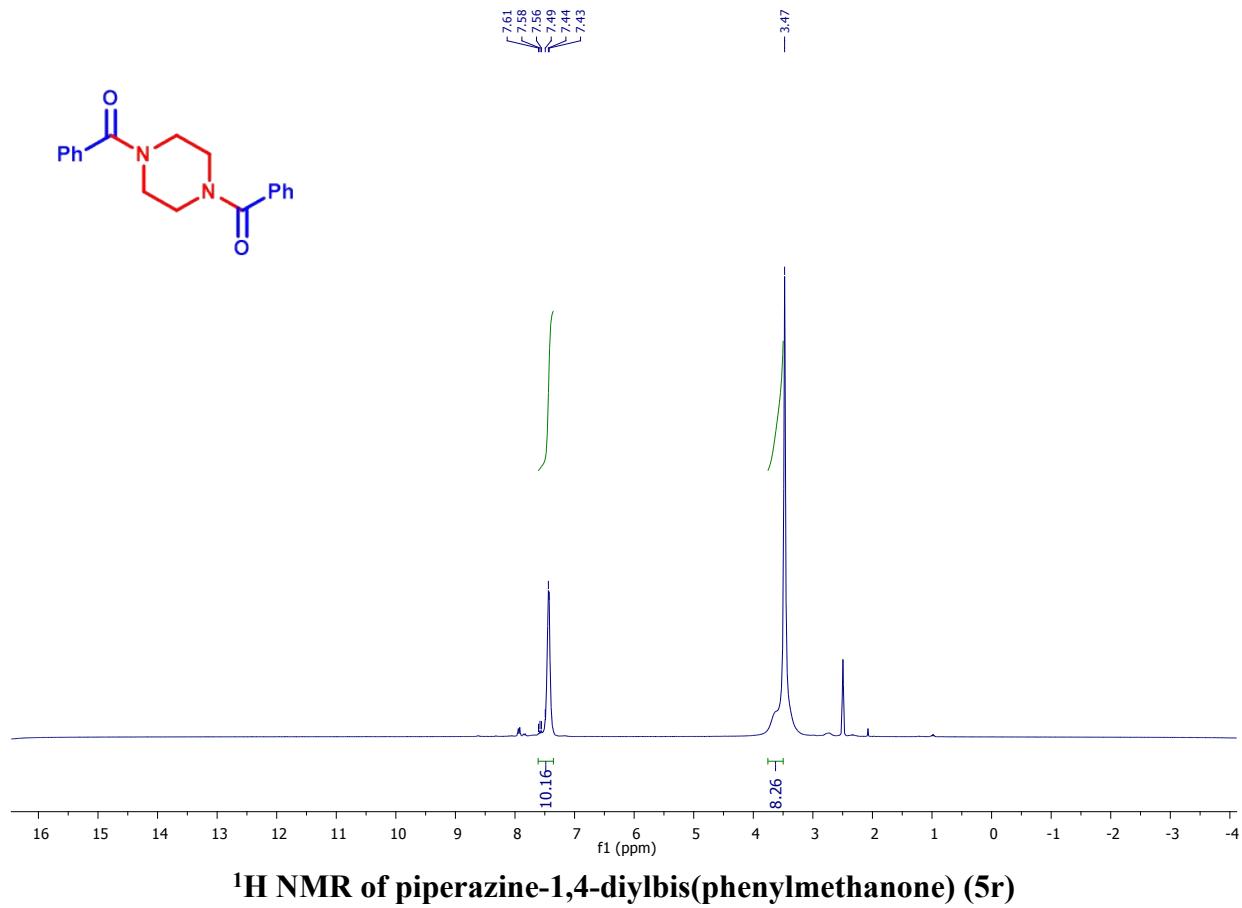
^{13}C NMR of 2-phenyl-1-(pyrrolidin-1-yl)ethan-1-one (**5p**)

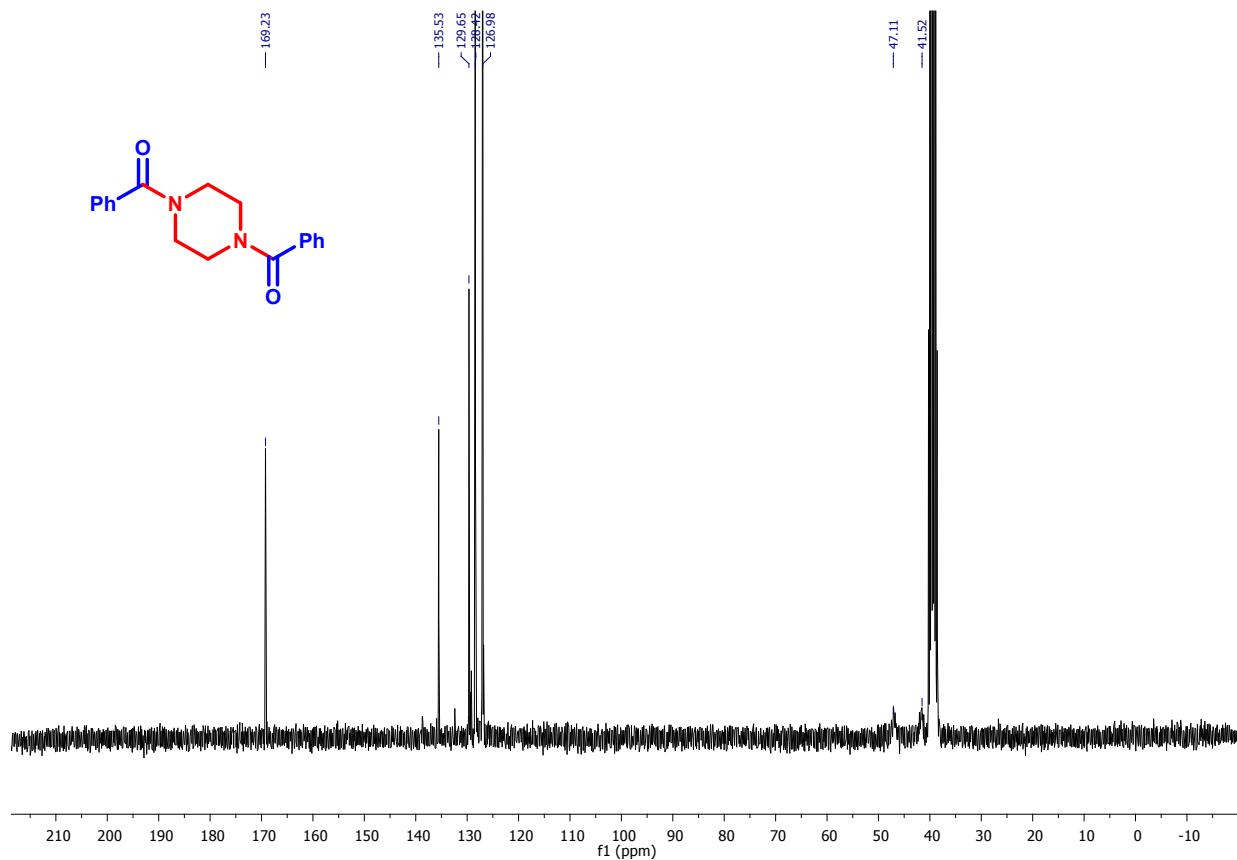


¹H NMR of (4-(2-hydroxyethyl)piperazin-1-yl)(phenyl)methanone (5q)

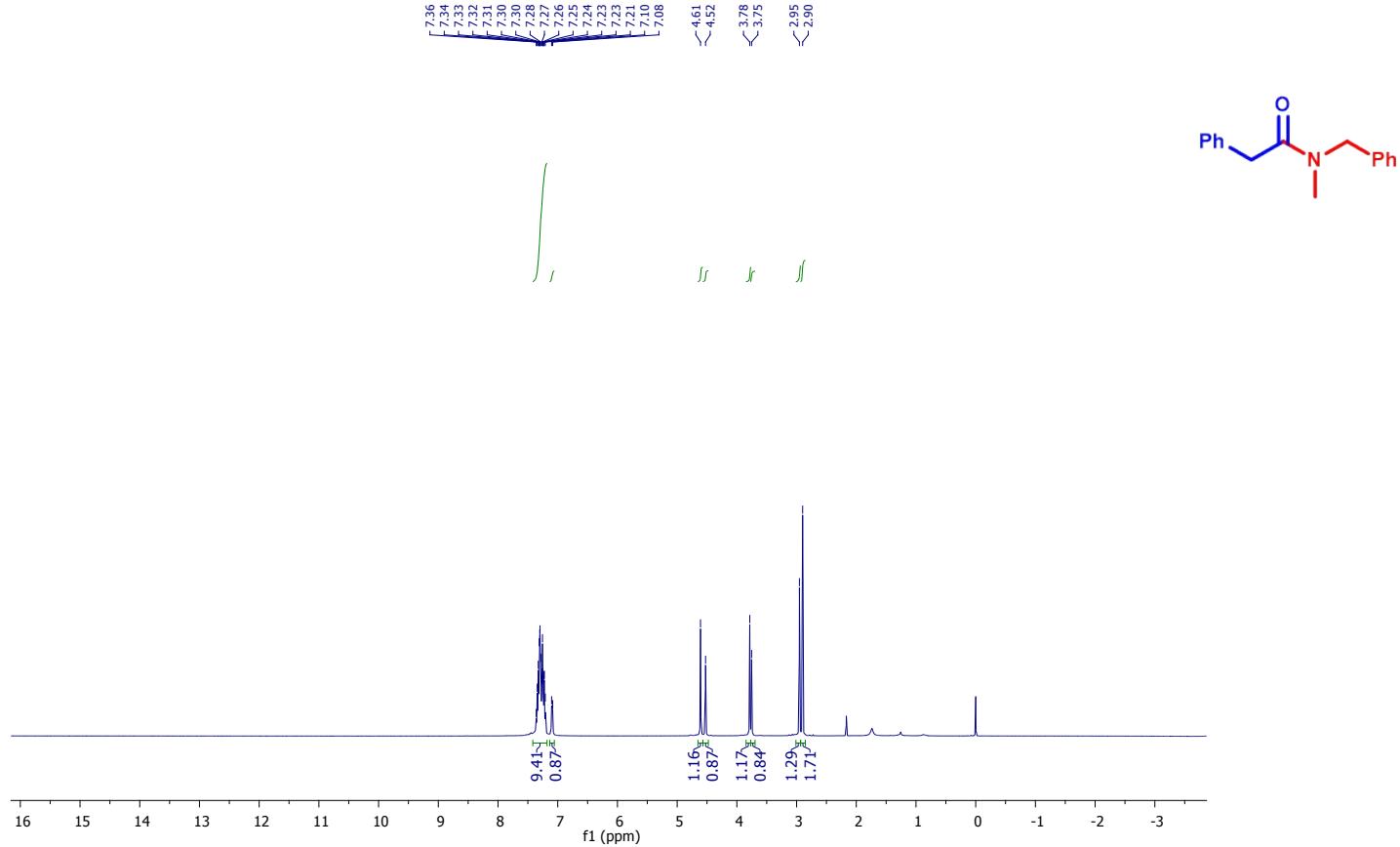


^{13}C NMR of (4-(2-hydroxyethyl)piperazin-1-yl)(phenyl)methanone (**5q**)

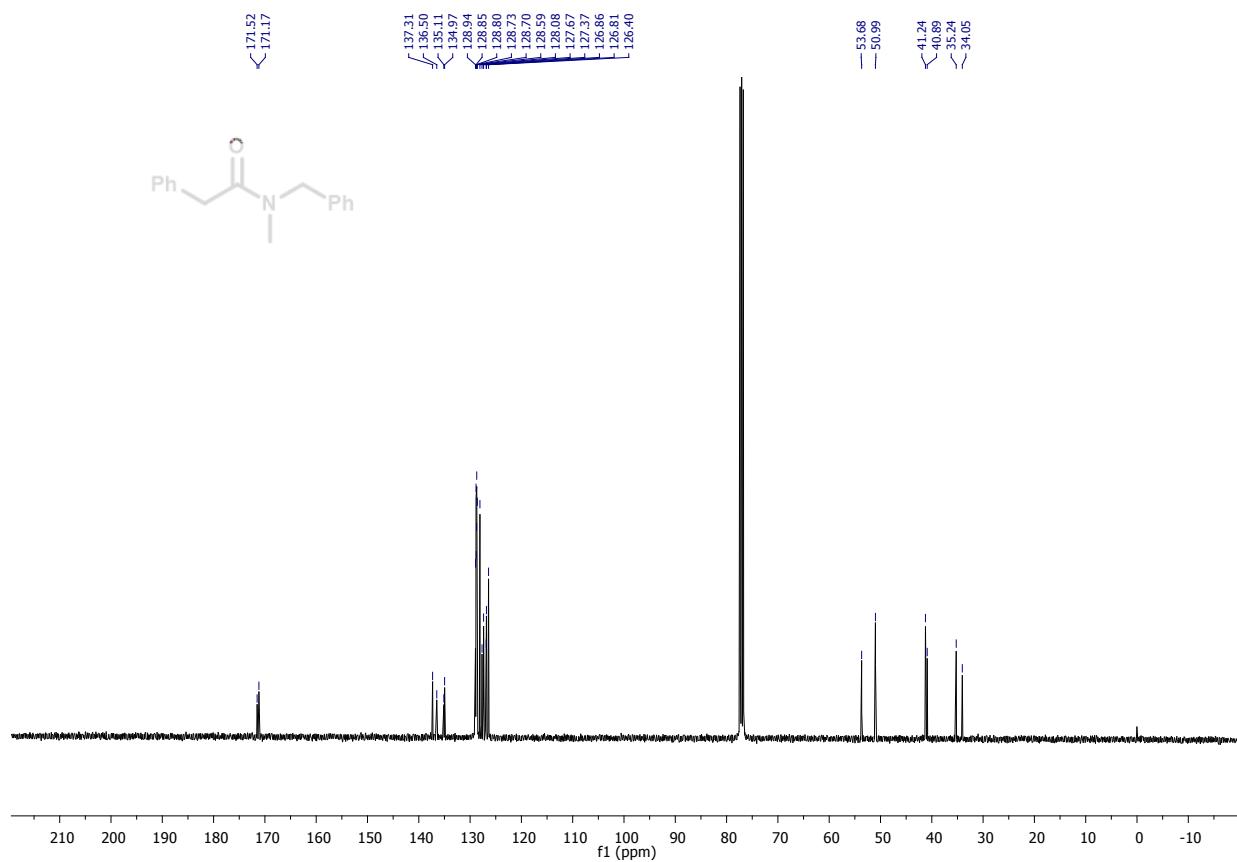




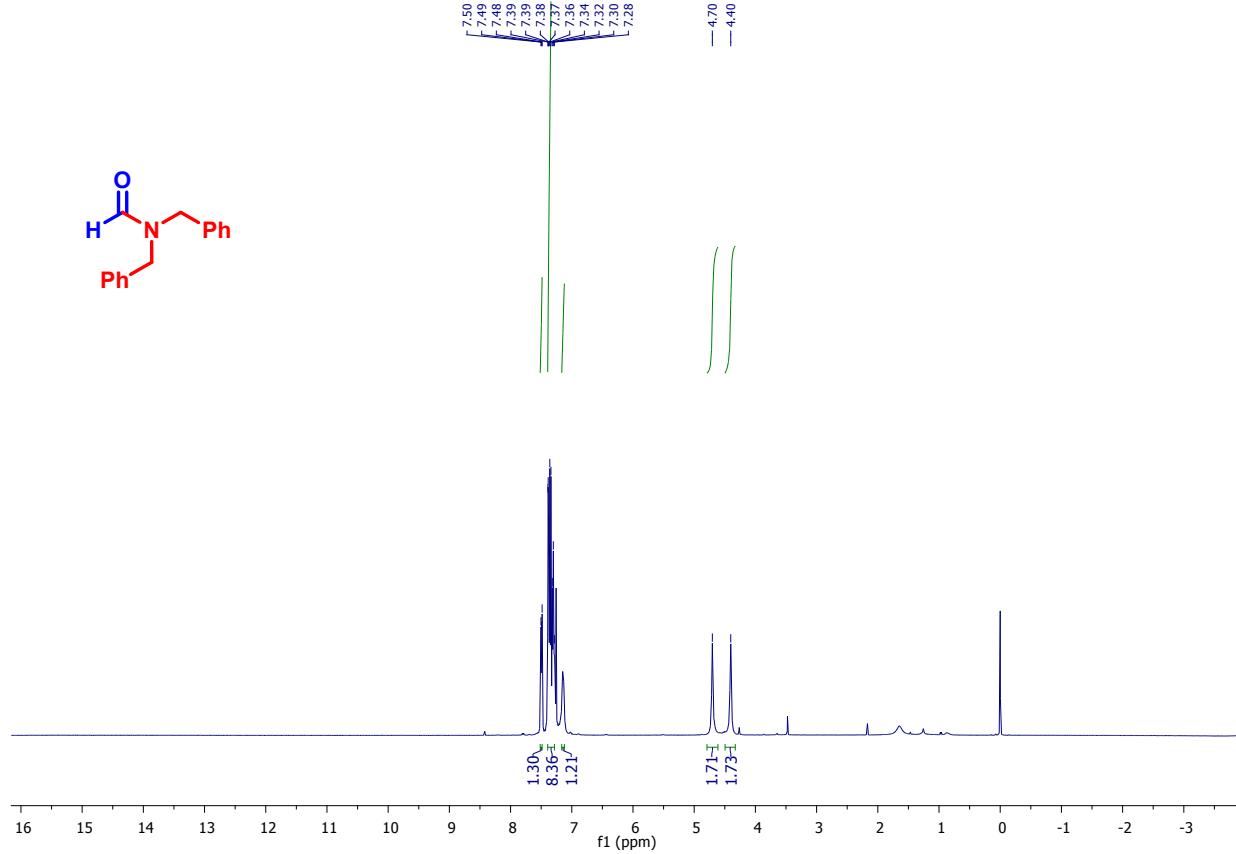
¹³C NMR of piperazine-1,4-diylbis(phenylmethanone) (5r)



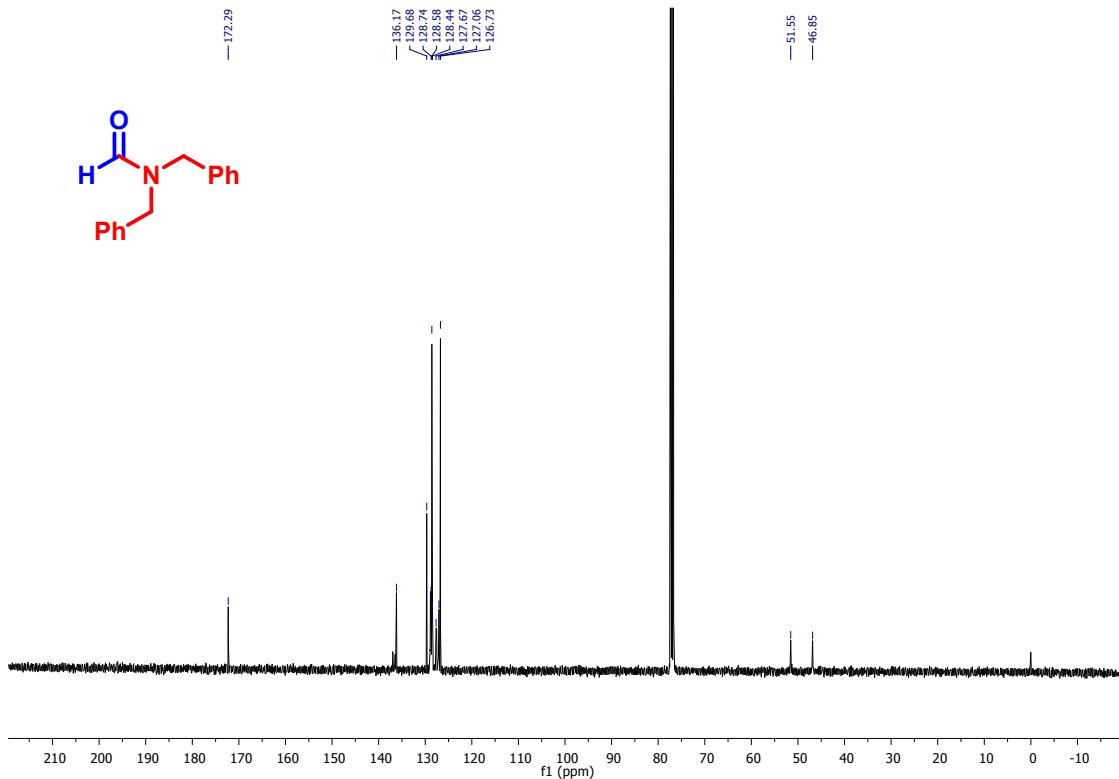
¹H NMR of N-benzyl-N-methyl-2-phenylacetamide (5s)



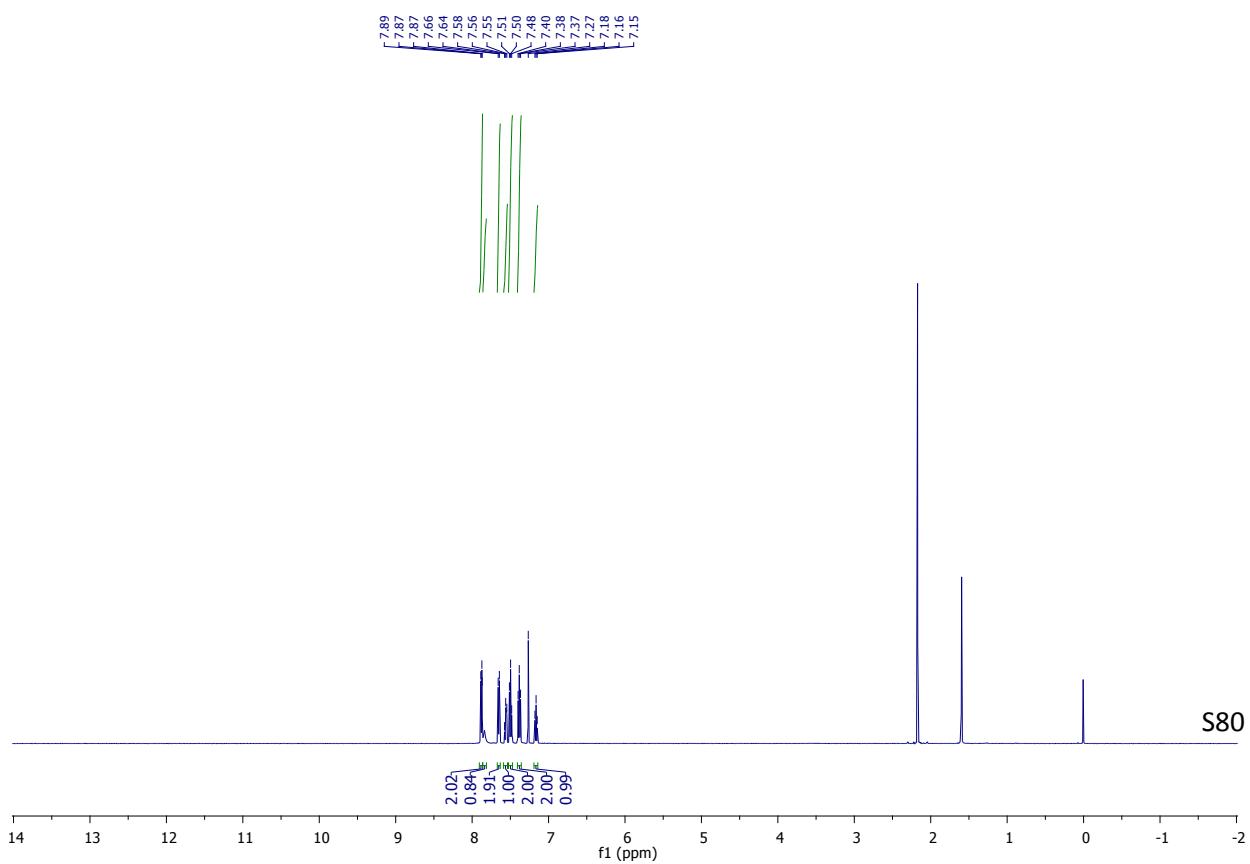
¹³C NMR of N-benzyl-N-methyl-2-phenylacetamide (5s)

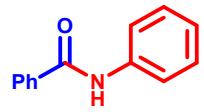


¹H NMR of N,N-dibenzylformamide (5t)

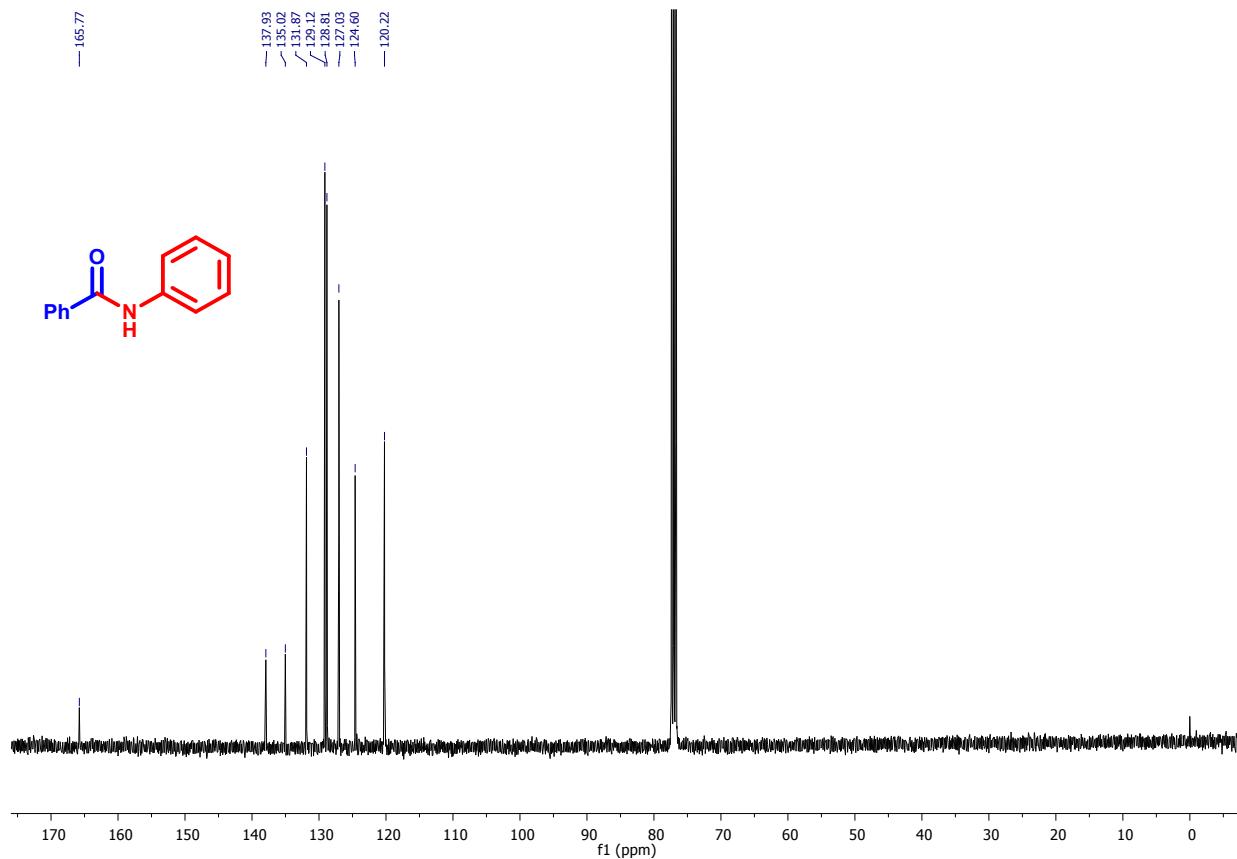


^{13}C NMR of N,N -dibenzylformamide (5t)

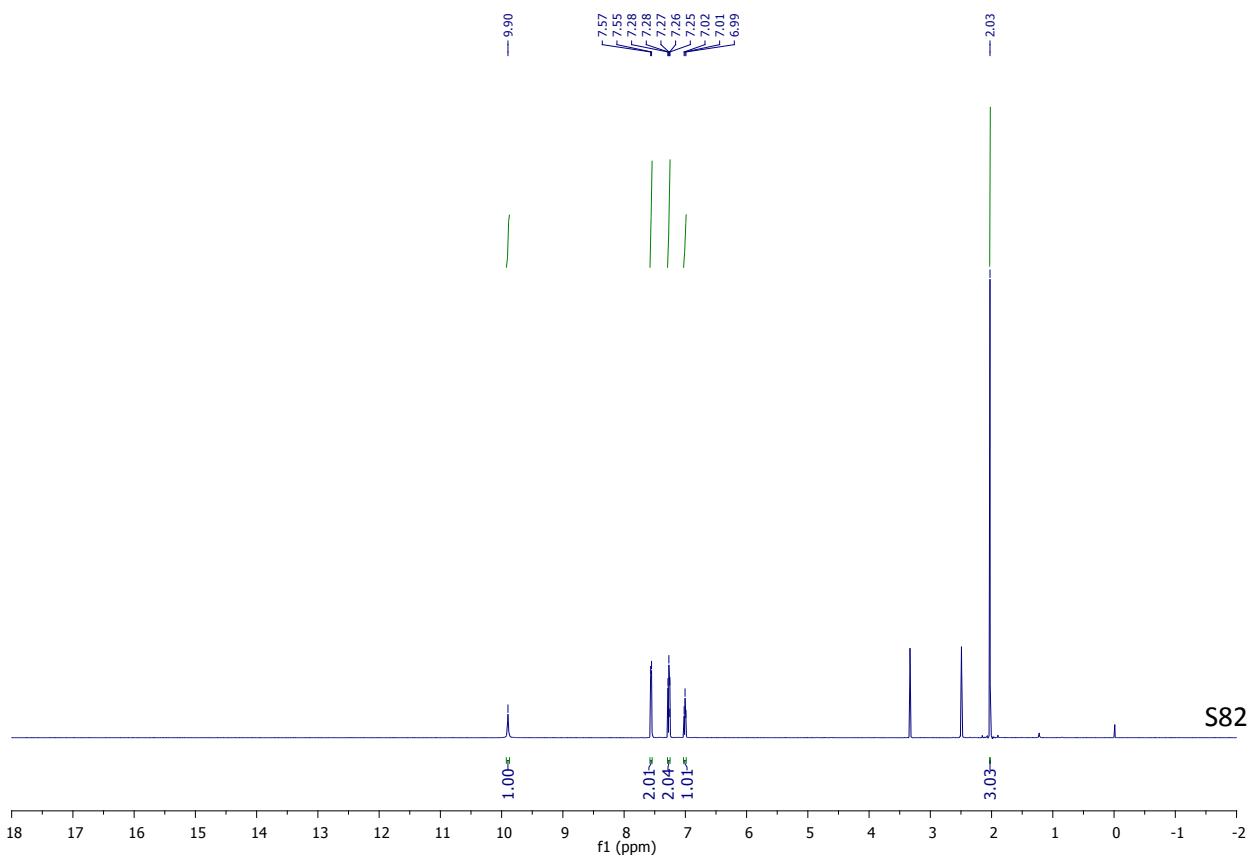




¹H NMR of N-Phenylbenzamide (5u)

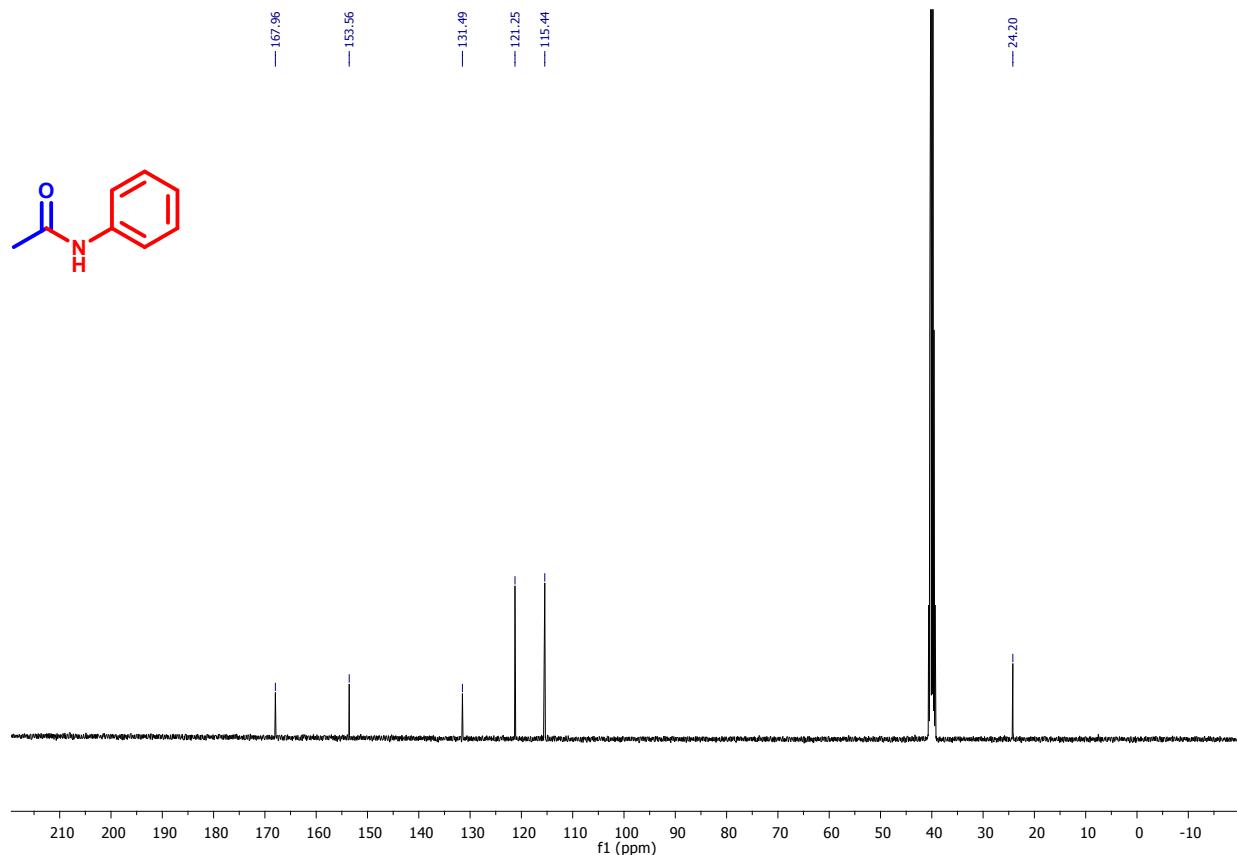


^{13}C NMR of N-Phenylbenzamide (5u)

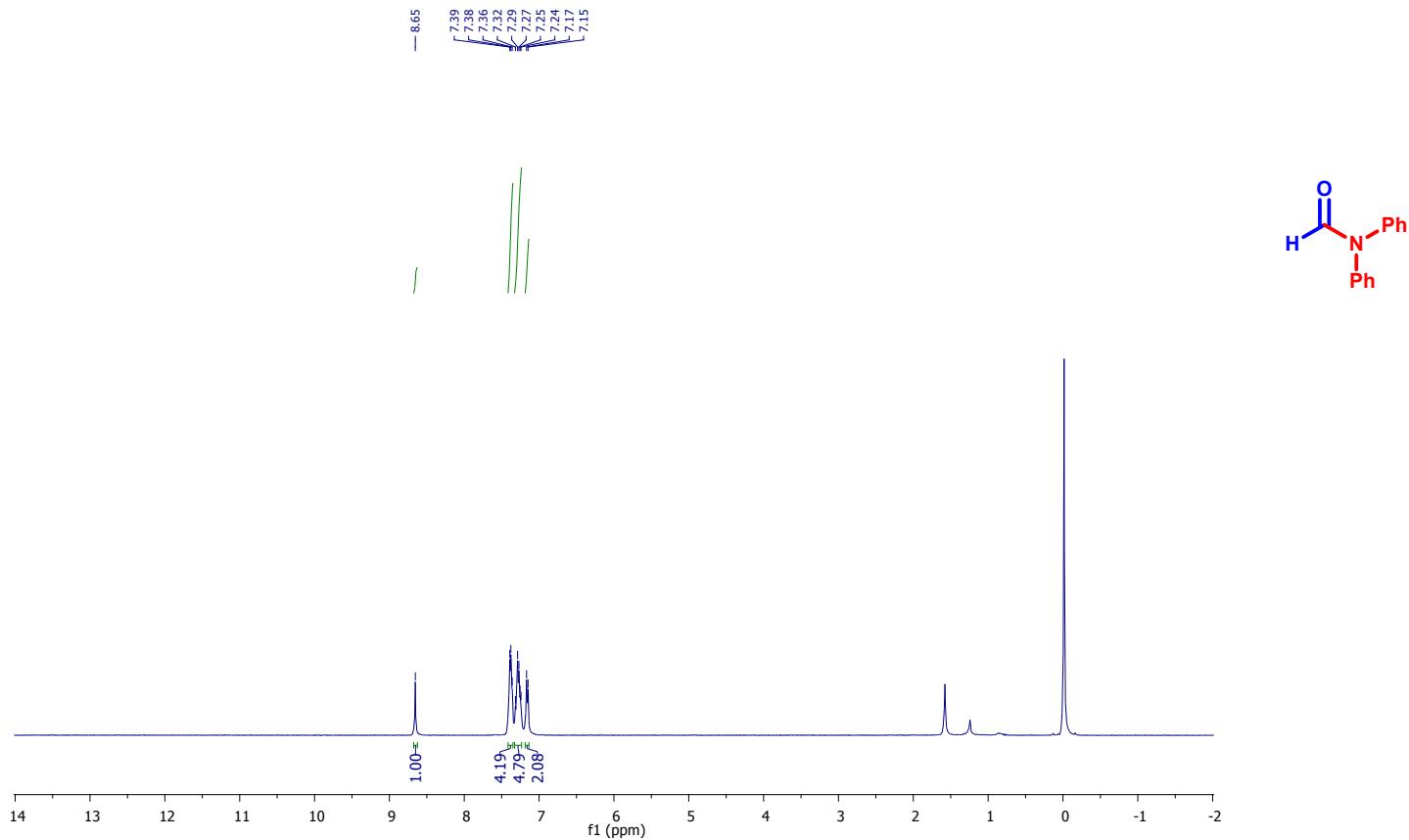




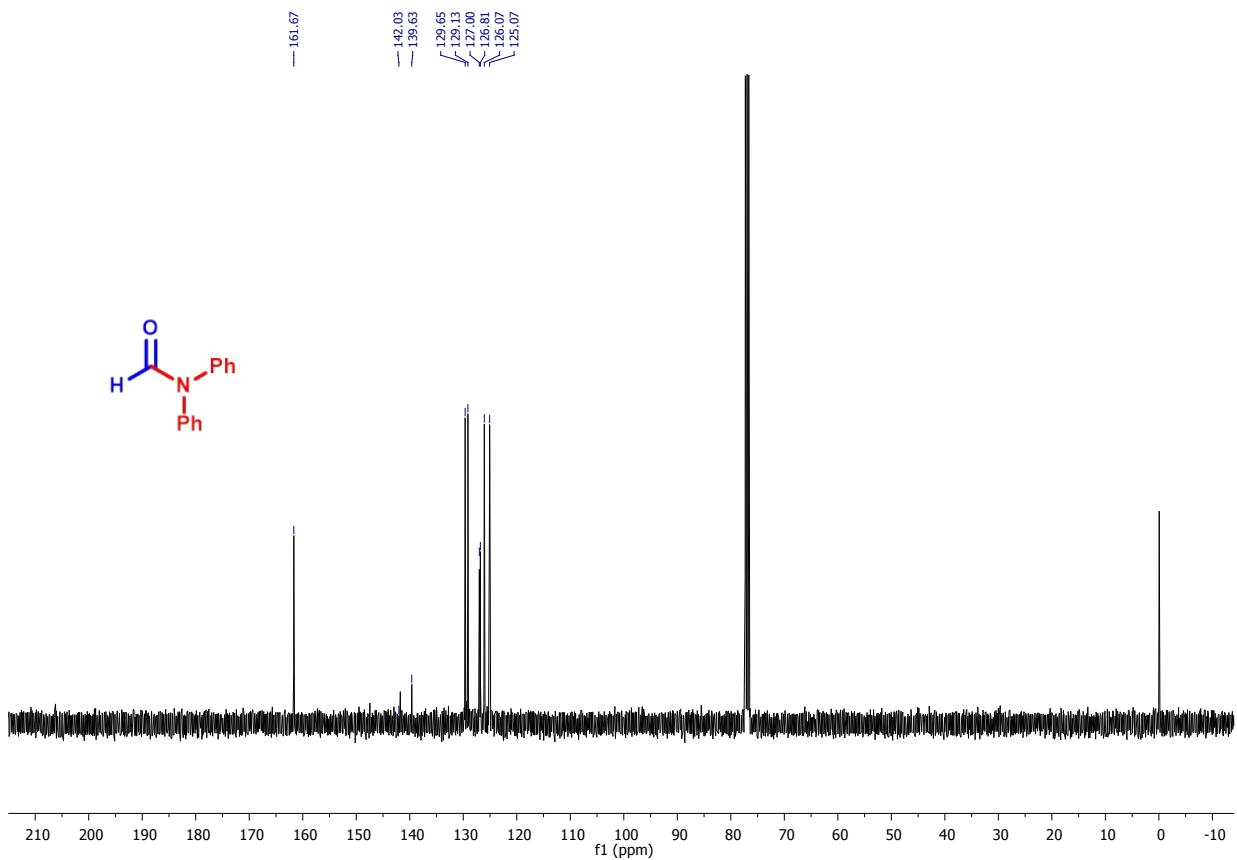
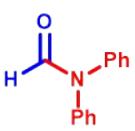
¹H NMR of N-Phenylacetamide (5v)



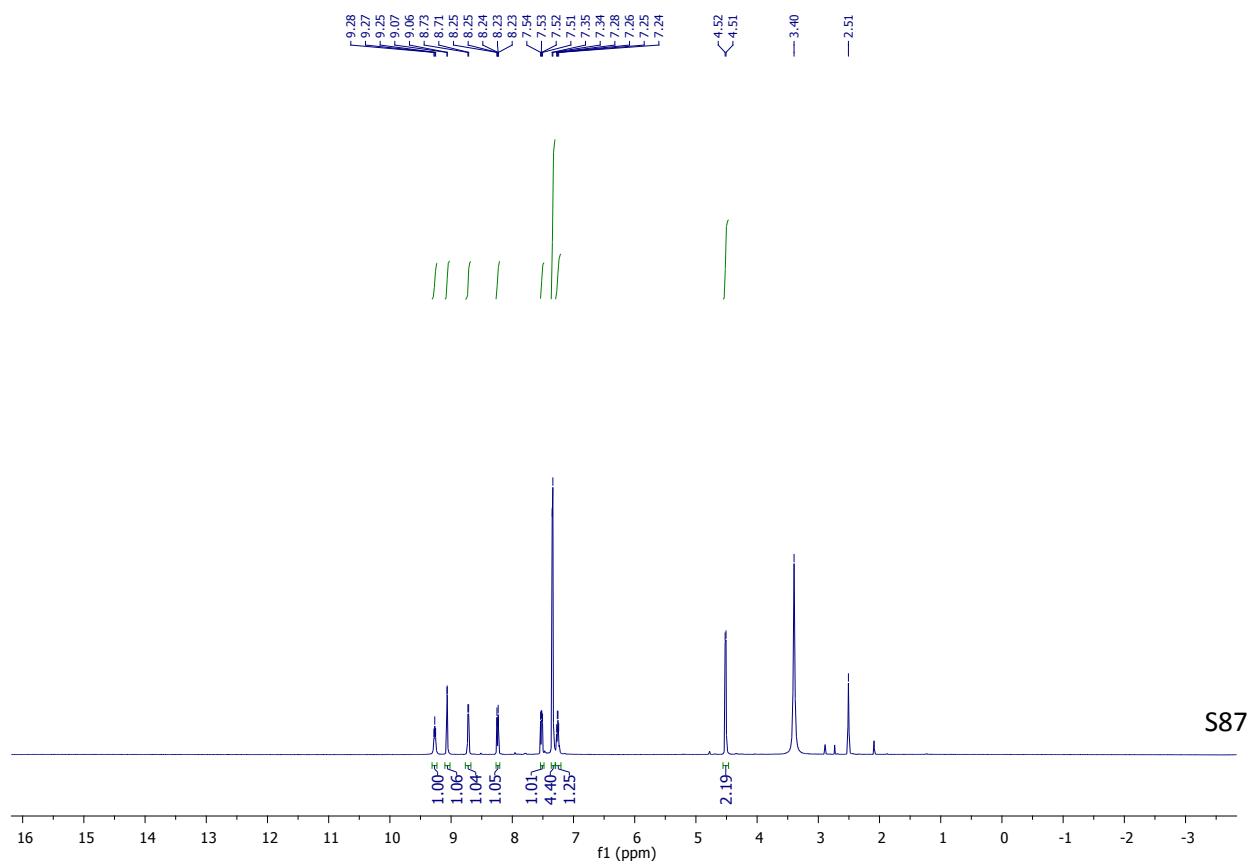
^{13}C NMR of N-Phenylacetamide (5v)

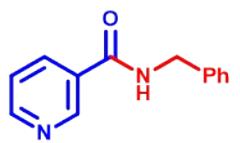


^1H NMR of N,N-Diphenylformamide (5x)

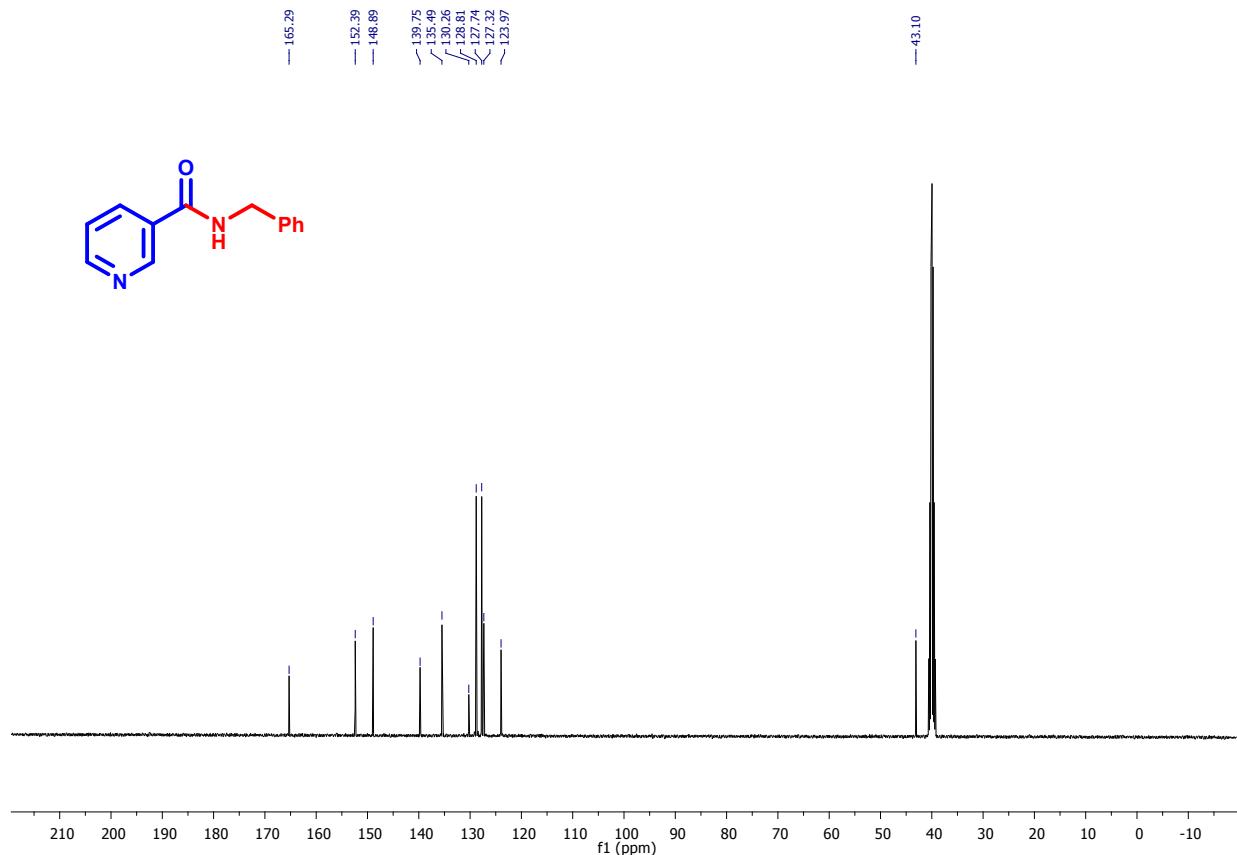


¹³C NMR of N,N-Diphenylformamide (5x)

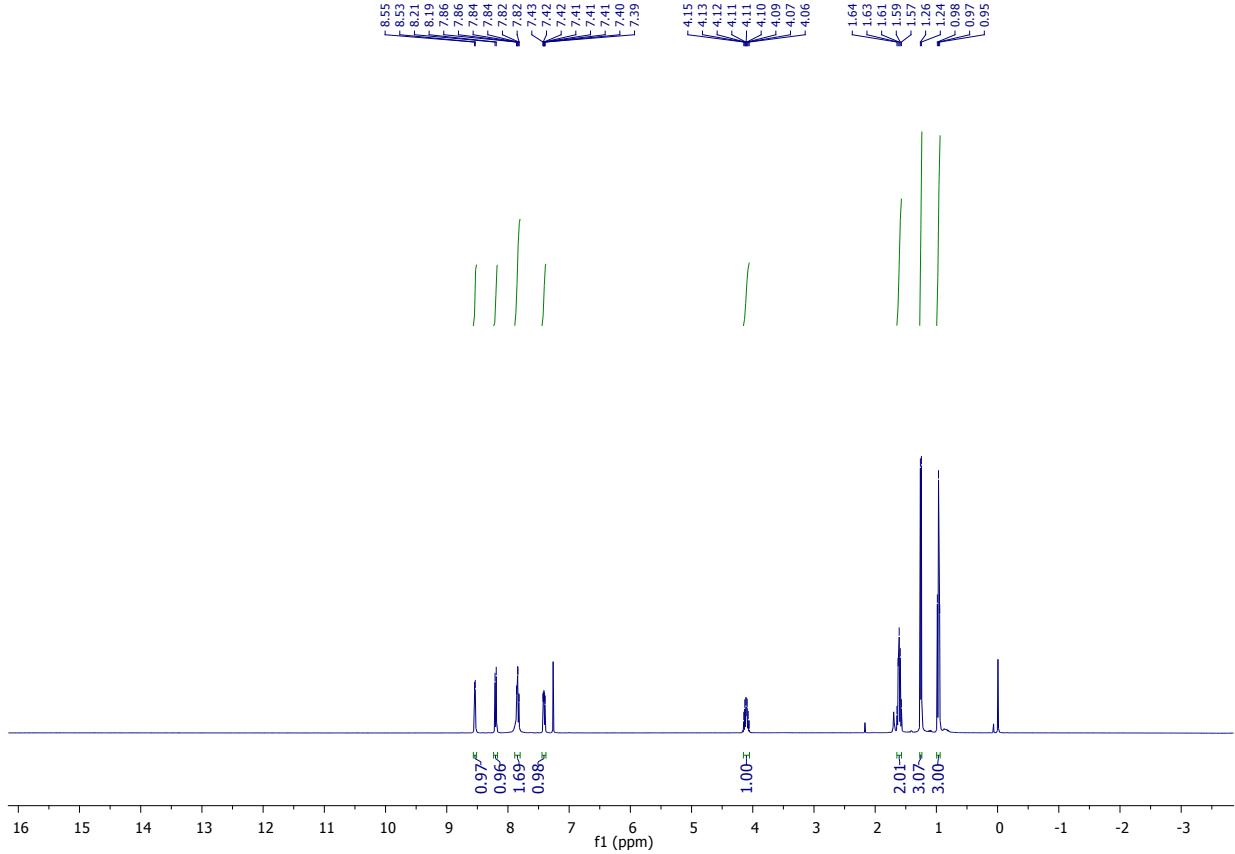




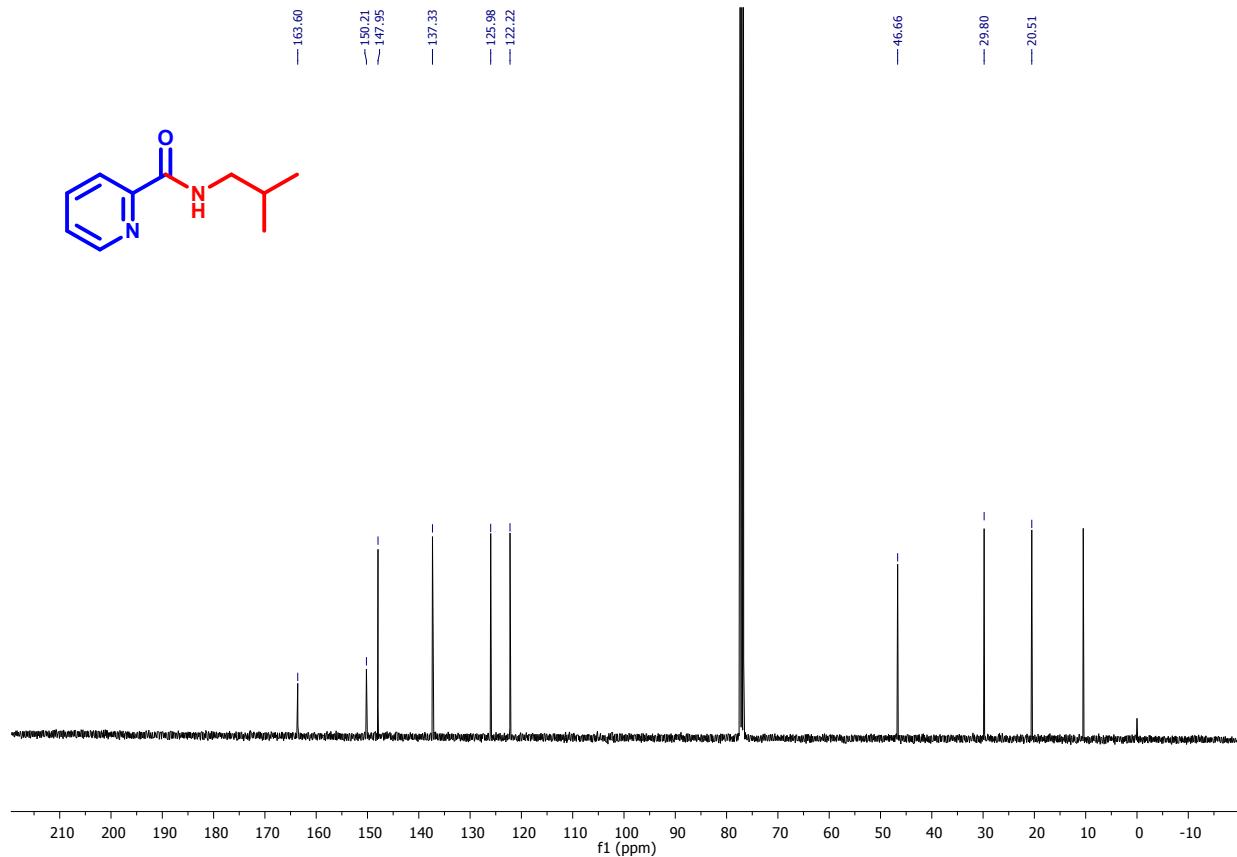
¹H NMR of N-benzylnicotinamide (7b)



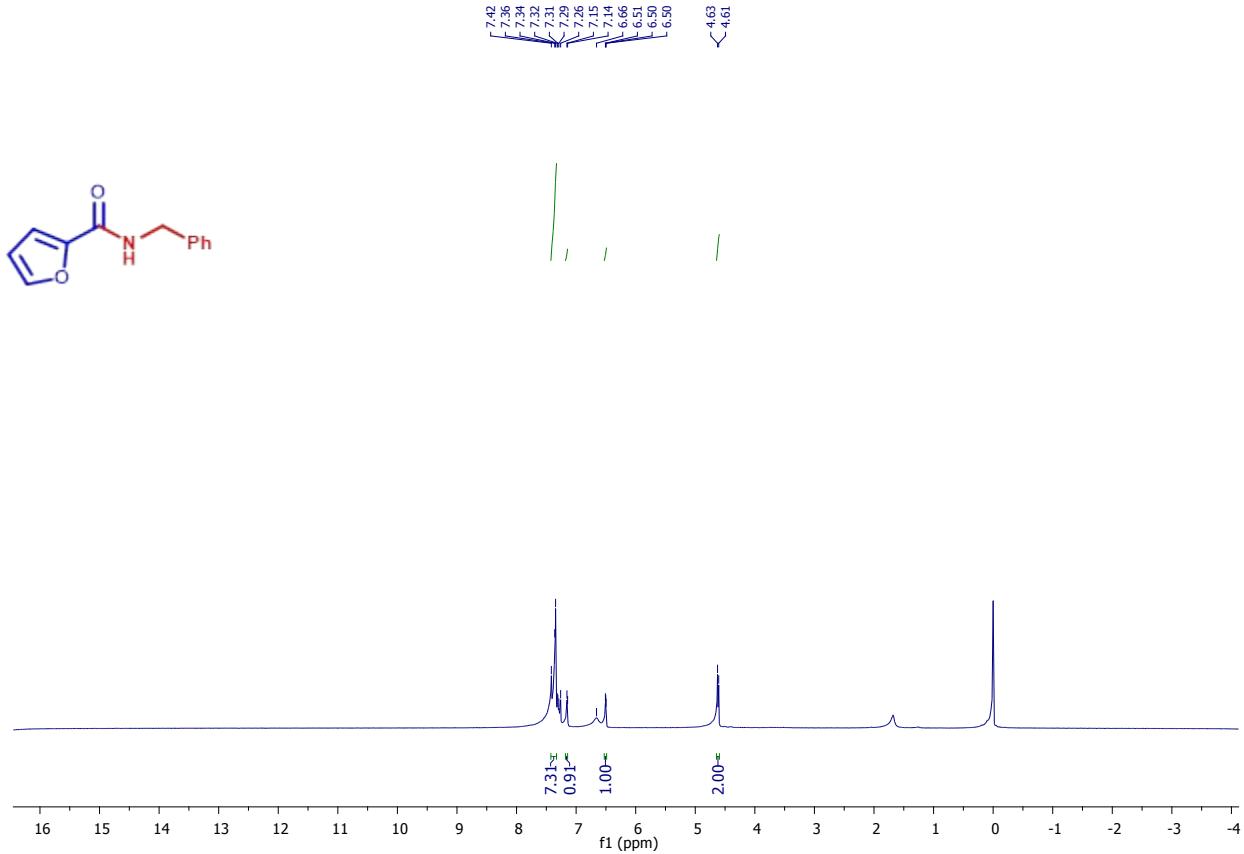
^{13}C NMR of N-benzylnicotinamide (7b)



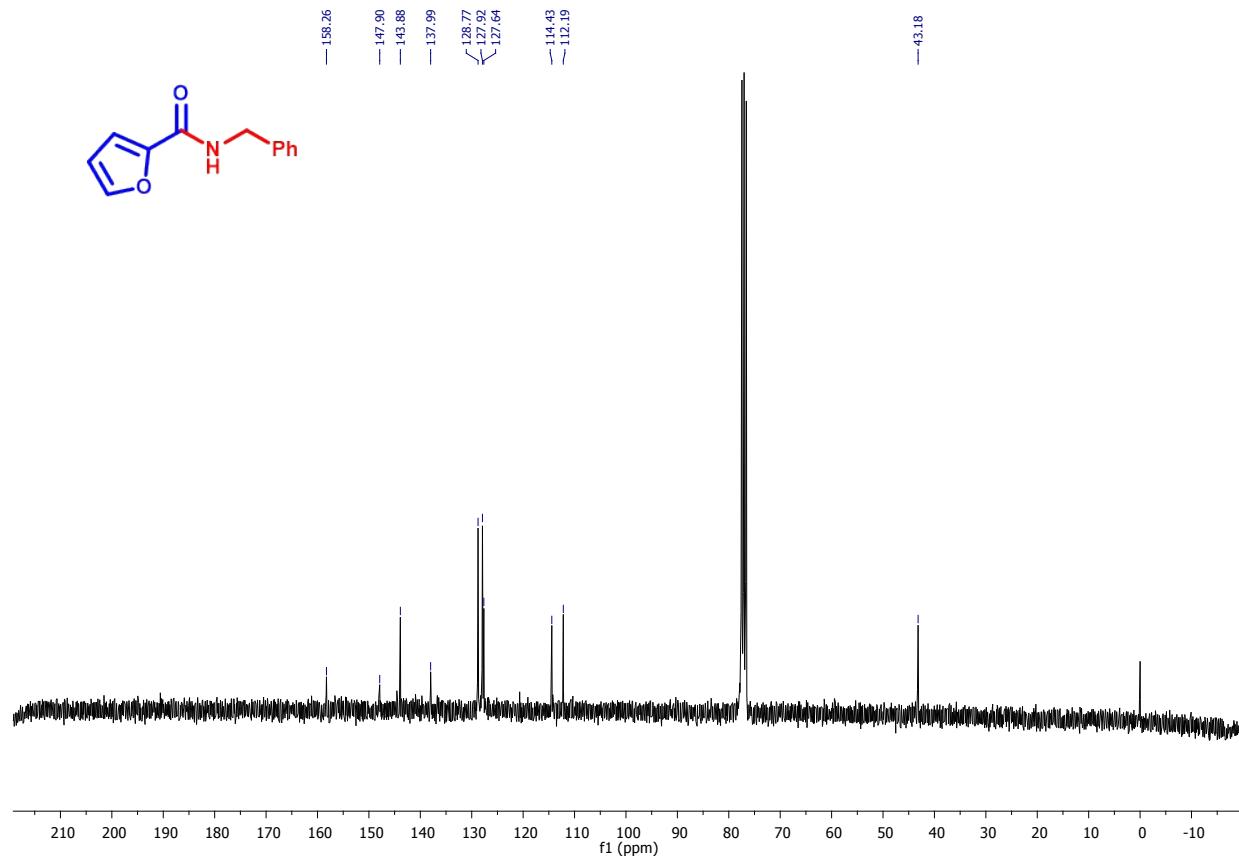
¹H NMR of *N*-Isobutylpicolinamide (7c)



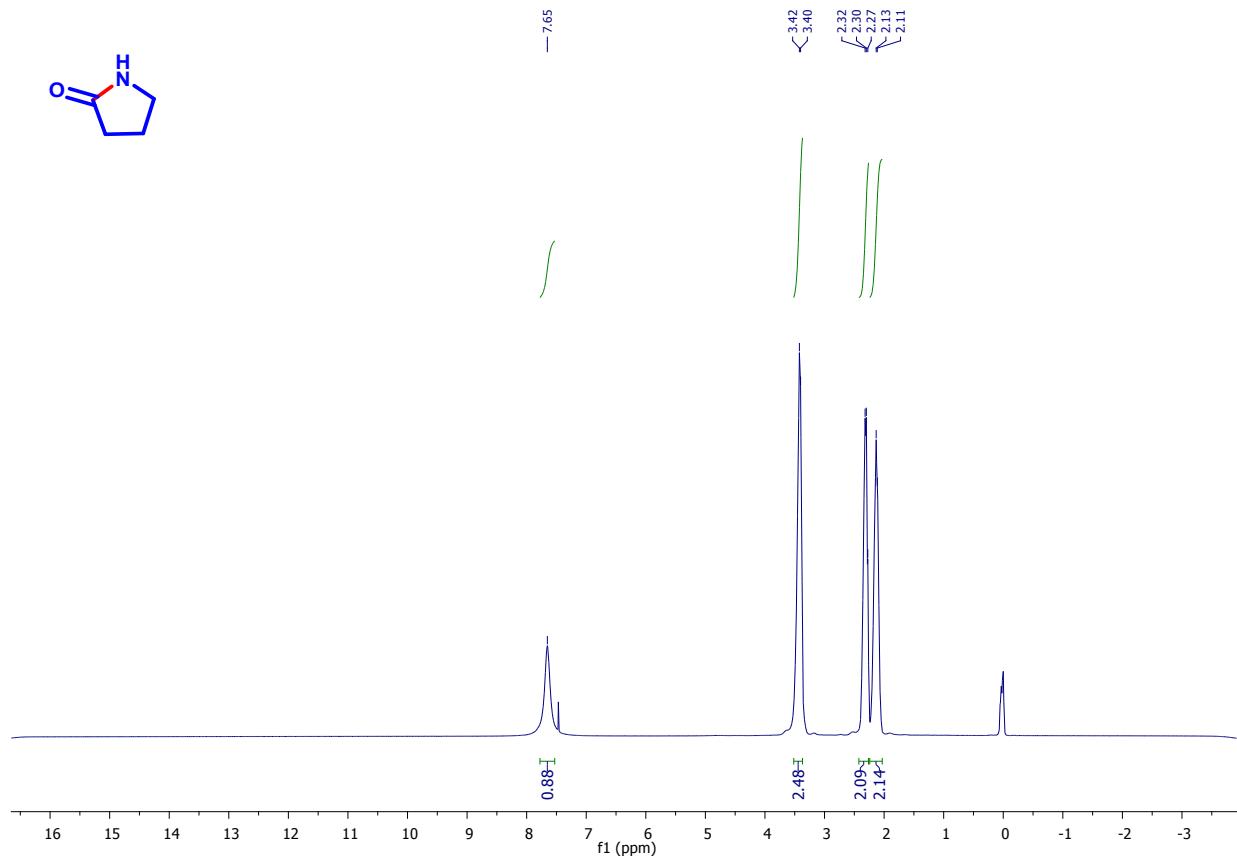
^{13}C NMR of *N*-Isobutylpicolinamide (7c)



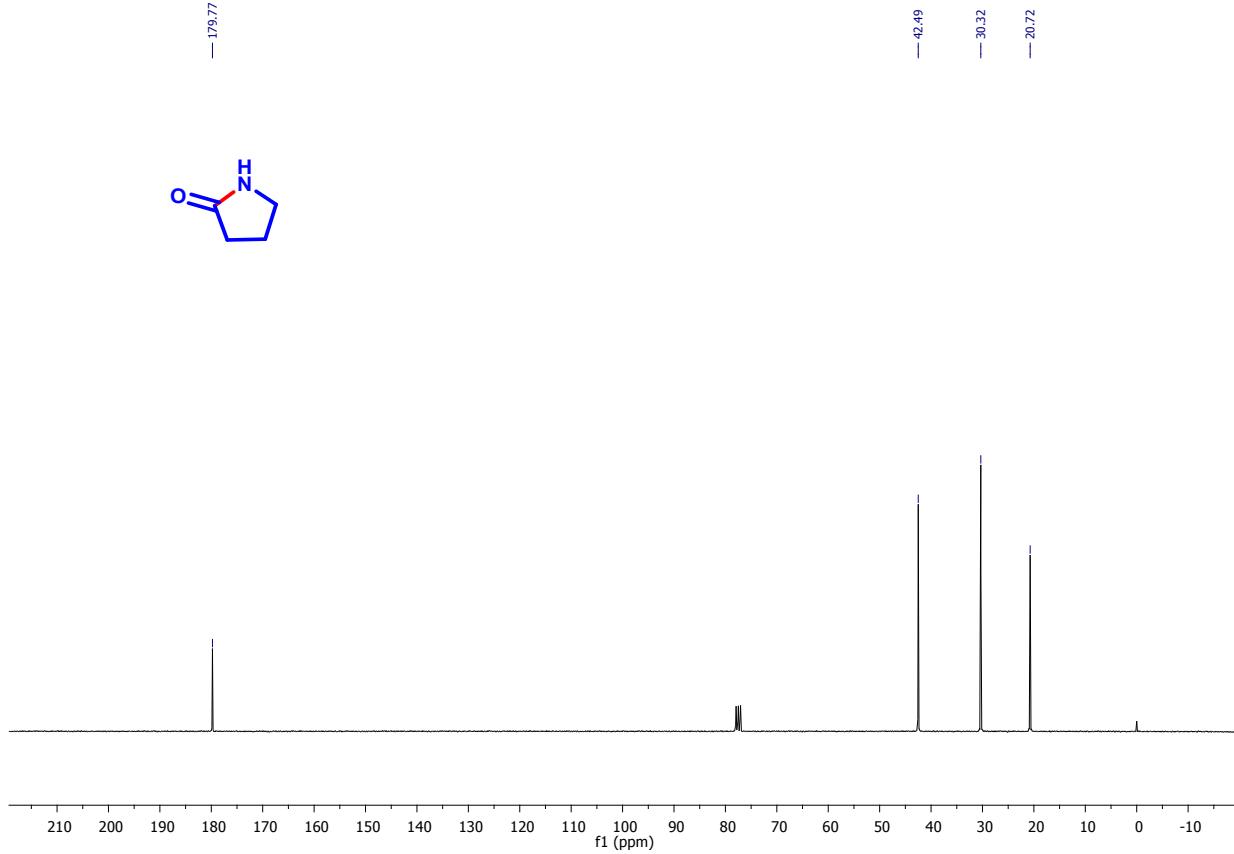
¹H NMR of N-benzylfuran-2-carboxamide (7d)



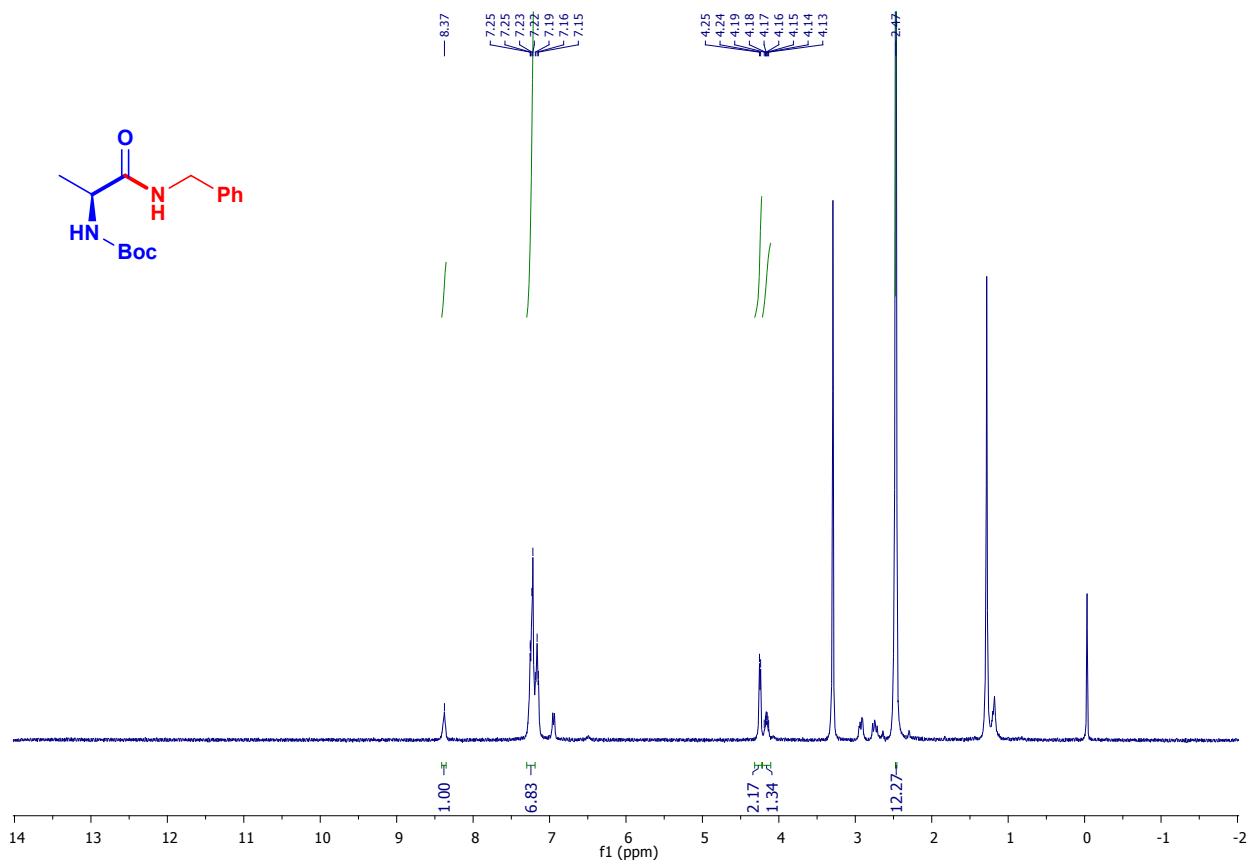
^{13}C NMR of N-benzylfuran-2-carboxamide (7d)



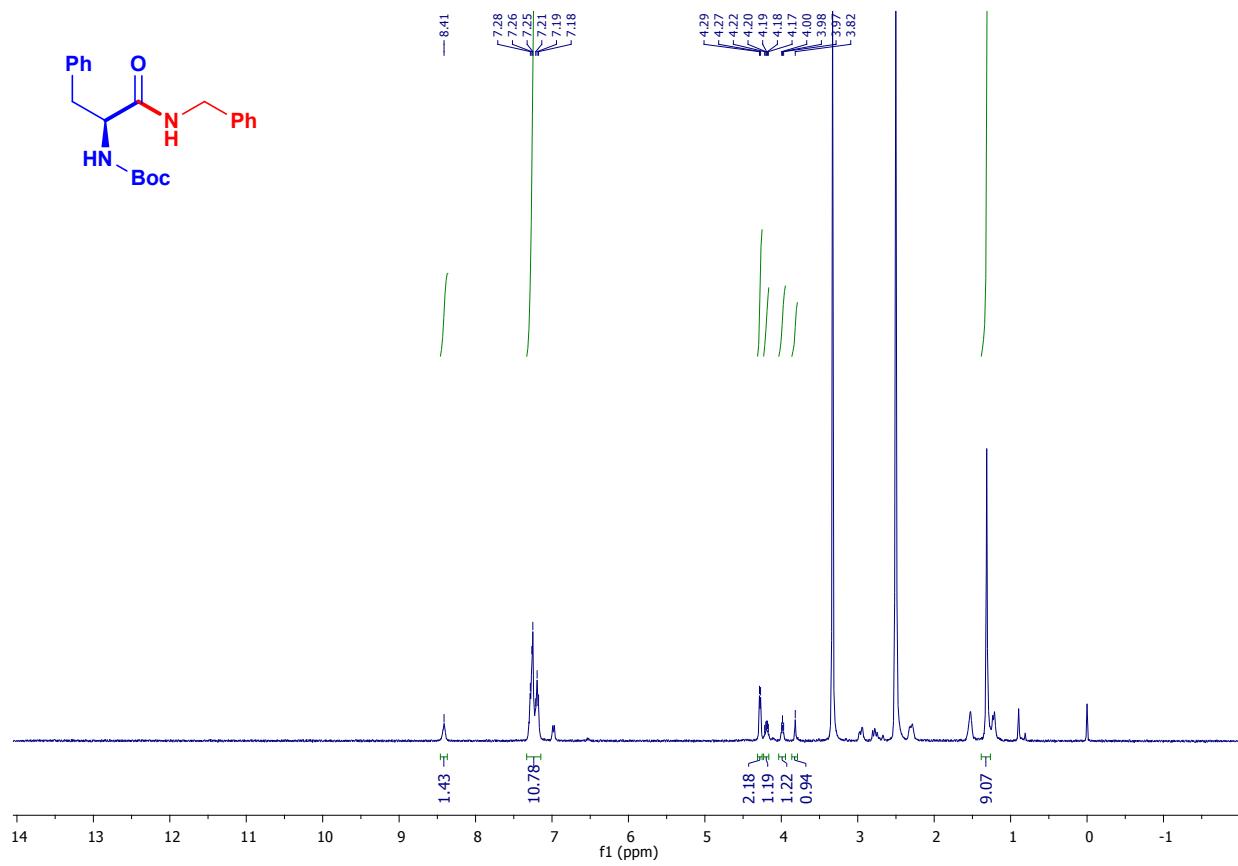
^1H NMR of pyrrolidin-2-one (9)



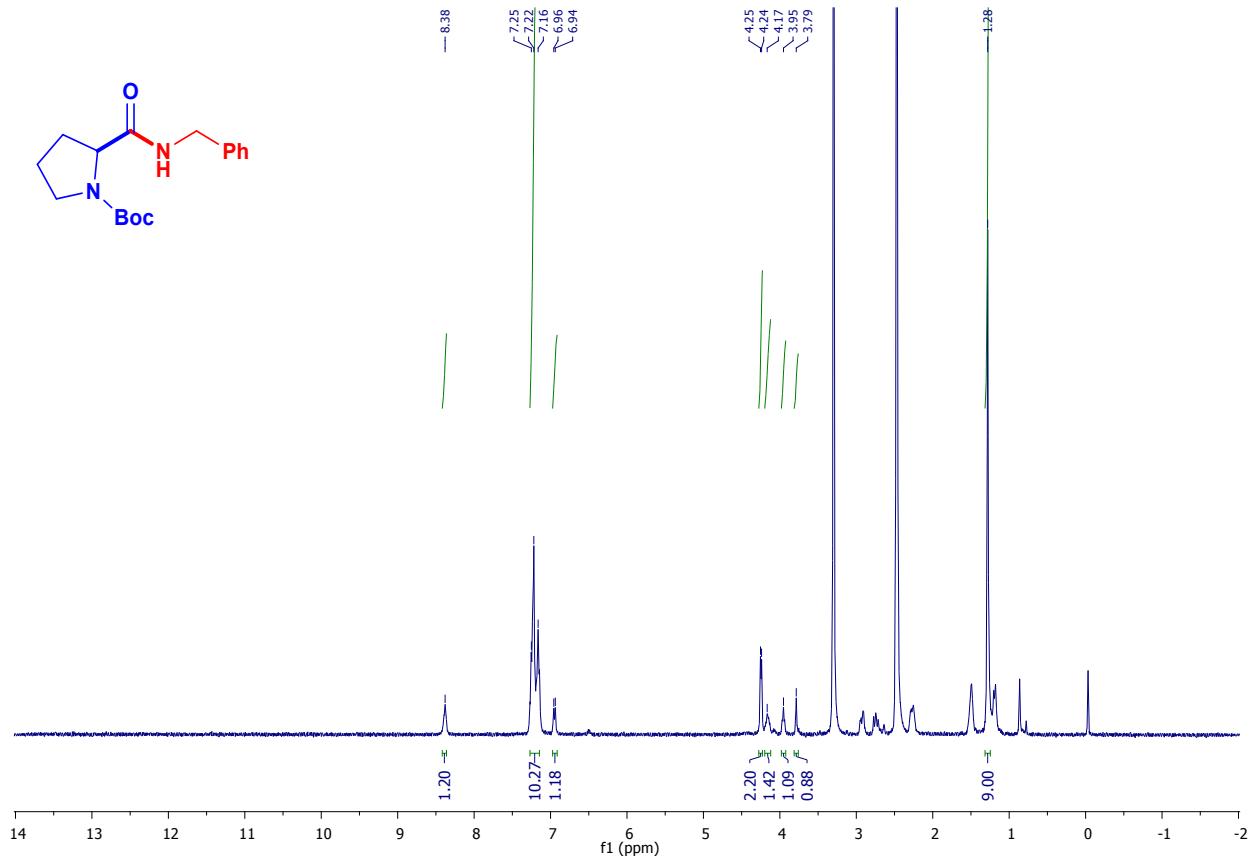
^{13}C NMR of pyrrolidin-2-one (9)



¹H NMR of tert-butyl (S)-(1-(benzylamino)-1-oxopropan-2-yl)carbamate (11)



¹H NMR of tert-butyl (S)-(1-(benzylamino)-1-oxo-3-phenylpropan-2-yl)carbamate (13)



¹H NMR of Tert-butyl 2-(benzylcarbamoyl)pyrrolidine-1-carboxylate (15)

Reference:

- [1] D.C. Marcano, D. V Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.B. Alemany, W. Lu, J.M. Tour, *ACS Nano* 4 (2010) 4806–4814.
- [2] X. Leng, R. Liu, J. Zou, X. Xiong, H. He, *Journal of Central South University* 23 (2016) 1823–1830.
- [3] Jamatia Ramen, A. Gupta, B. Dam, M. Saha, A.K. Pal, *Green Chemistry* 19 (2017) 1576–1585.
- [4] B. Majumdar, D. Sarma, T. Bhattacharya, T.K. Sarma, *ACS Sustainable Chemistry & Engineering* 5 (2017) 9286–9294.
- [5] H.-K. Jeong, Y.P. Lee, R.J.W.E. Lahaye, M.-H. Park, K.H. An, I.J. Kim, C.-W. Yang, C.Y. Park, R.S. Ruoff, Y.H. Lee, *Journal of the American Chemical Society* 130 (2008) 1362–1366.
- [6] L. Becerra-Figueroa, A. Ojeda-Porras, D. Gamba-Sánchez, *The Journal of Organic Chemistry* 79 (2014) 4544–4552.
- [7] K.L. Shepard, *Journal of the Chemical Society D: Chemical Communications* (1971) 928–929.
- [8] K. Pandey, M.K. Muthyalu, S. Choudhary, A. Kumar, *RSC Advances* 5 (2015) 13797–13804.
- [9] T.K. Houlding, K. Tchabanenko, M.T. Rahman, E. V Rebrov, *Organic and Biomolecular Chemistry* 11 (2013) 4171–4177.
- [10] A. Ojeda-Porras, A. Hernandez-Santana, D. Gamba-Sánchez, *Green Chemistry* 17 (2015)

3157–3163.

- [11] F.A. Cabrera-Rivera, C. Ortíz-Nava, J. Escalante, J.M. Hernández-Pérez, M. Hô, *Synlett* 23 (2012) 1057–1063.
- [12] P.B. Thale, P.N. Borase, G.S. Shankarling, *RSC Advances* 6 (2016) 52724–52728.
- [13] H. Morimoto, R. Fujiwara, Y. Shimizu, K. Morisaki, T. Ohshima, *Organic Letters* 16 (2014) 2018–2021.
- [14] R.M. Lanigan, P. Starkov, T.D. Sheppard, *The Journal of Organic Chemistry* 78 (2013) 4512–4523.
- [15] S.G. Sudrik, S.P. Chavan, K.R.S. Chandrakumar, S. Pal, S.K. Date, S.P. Chavan, H.R. Sonawane, *The Journal of Organic Chemistry* 67 (2002) 1574–1579.
- [16] G. Blay, I. Fernández, A. Marco-Aleixandre, J.R. Pedro, *Synthesis* 2007 (2007) 3754–3757.
- [17] F.D. King, S. Caddick, *Tetrahedron* 69 (2013) 487–491.
- [18] K.C. Nadimpally, K. Thalluri, N.B. Palakurthy, A. Saha, B. Mandal, *Tetrahedron Letters* 52 (2011) 2579–2582.
- [19] F. Li, J. Ma, L. Lu, X. Bao, W. Tang, *Catalysis Science & Technology* 5 (2015) 1953–1960.
- [20] E. Alonso, D.J. Ramón, M. Yus, *Tetrahedron* 53 (1997) 14355–14368.
- [21] Y. Sugiyama, Y. Kurata, Y. Kunda, A. Miyazaki, J. Matsui, S. Nakamura, H. Hamamoto, T. Shioiri, M. Matsugi, *Tetrahedron* 68 (2012) 3885–3892.

- [22] T.D. Apsunde, M.L. Trudell, *Synthesis* 46 (2014) 230–234.
- [23] A. Khalafi-Nezhad, H. ollah Foroughi, M.M. Doroodmand, F. Panahi, *Journal of Materials Chemistry* 21 (2011) 12842–12851.
- [24] L. Perreux, A. Loupy, F. Volatron, *Tetrahedron* 58 (2002) 2155–2162.
- [25] M.C. Mollo, L.R. Orelli, *Organic Letters* 18 (2016) 6116–6119.
- [26] S.M. Mali, R.D. Bhaisare, H.N. Gopi, *The Journal of Organic Chemistry* 78 (2013) 5550–5555.
- [27] J.-B. Gaultierotti, X. Schumacher, P. Fontaine, G. Masson, Q. Wang, J. Zhu, *Chemistry – A European Journal* 18 (2012) 14812–14819.
- [28] D.C. Braddock, P.D. Lickiss, B.C. Rowley, D. Pugh, T. Purnomo, G. Santhakumar, S.J. Fussell, *Organic Letters* 20 (2018) 950–953.
- [29] J.W. Comerford, J.H. Clark, D.J. Macquarrie, S.W. Breeden, *Chemical Communications* (2009) 2562–2564.
- [30] M.T. Sabatini, L.T. Boulton, T.D. Sheppard, *Science Advances* 3 (2017).
- [31] R.A. Green, D. Pletcher, S.G. Leach, R.C.D. Brown, *Organic Letters* 18 (2016) 1198–1201.
- [32] J. S. Foot, H. Kanno, G. Giblin, R. J. K. Taylor, *Esters and Amides from Activated Alcohols Using Manganese(IV) Dioxide: Tandem Oxidation Processes*, 2003.

