

# Nickel-Catalyzed Cross-Coupling of Potassium Aryl- and Heteroaryltrifluoroborates with Unactivated Alkyl Halides

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## Supporting Information

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## General Considerations.

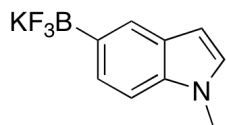
The following chemicals were purchased and used as received: NiBr<sub>2</sub>•glyme, NiCl<sub>2</sub>•glyme, LiHMDS, NaHMDS, KHMDS, *L*-prolinol, bathophenanthroline, 3-(4-bromophenyl)propionic acid, triphenylphosphine, carbon tetrabromide, borane dimethylsulfide, benzyl 2-bromoethyl ether, cyclohexyl iodide, 5-bromo-1-pentene, 1-bromo-6-chlorohexane, 1-iodo-4-chlorobutane, tetrahydrofurfuryl chloride, 4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane, cyclohexyl chloride, 2-bromomethyl-1,3-dioxolane and ethyl 6-bromohexanoate. 1-Bromo-3-phenylpropane, 2-(bromomethyl)-tetrahydro-2*H*-pyran, cyclopentyl bromide, cycloheptyl bromide and 3-bromoheptane were distilled under reduced pressure prior to use. The aryl and heteroarylboronic acids were converted to trifluoroborates according to known literature procedures.<sup>1</sup> *sec*-Butanol and dichloromethane were distilled over CaH<sub>2</sub> prior to use. Standard benchtop techniques were employed for handling air-sensitive reagents.

Melting points (°C) are uncorrected. <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F spectra were recorded at 500.39, 125.75, and 470.55 MHz, respectively. <sup>19</sup>F NMR chemical shifts were referenced to external CFCl<sub>3</sub> (0.0 ppm). <sup>11</sup>B NMR spectra at 128.4 MHz were obtained on a spectrometer equipped with the appropriate decoupling accessories. All <sup>11</sup>B NMR chemical shifts were referenced to external BF<sub>3</sub>•OEt<sub>2</sub> (0.0 ppm) with a negative sign indicating an upfield shift. Analytical thin-layer chromatography (TLC) was performed on TLC silica gel plates (0.25 mm) precoated with a fluorescent indicator. Standard flash chromatography procedures<sup>2</sup> were followed using 40–63 μm silica gel. Visualization was effected with ultraviolet light, KMnO<sub>4</sub>, cerium molybdate (CAM) or phosphomolybdic acid (PMA).

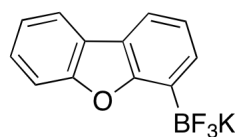
## Procedure for Preparation of Starting Materials.

### General procedure for the conversion of organoboronic acids to potassium organotrifluoroborates.

To a solution of organoboronic acid (1 equiv) in MeOH (3.5 M or enough to give a free flowing suspension) under N<sub>2</sub> was added KHF<sub>2</sub> (3 equiv) in one portion at 0 °C. H<sub>2</sub>O (4.5 M) was added dropwise. The ice-water bath was removed and the reaction was stirred until the full conversion of the organoboronic acid as indicated by <sup>11</sup>B NMR (5–30 min). The crude mixture was concentrated under reduced pressure and left under vacuum overnight. The crude solid was purified using continuous Soxhlet extraction (6–24 h) with acetone. The solution obtained was concentrated under reduced pressure and then redissolved in a minimal amount of MeOH, then the solid was precipitated by addition of Et<sub>2</sub>O. The product was filtered, concentrated and dried under vacuum to afford the pure potassium organotrifluoroborate as a solid.

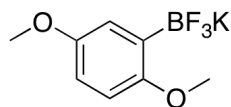


**Potassium *N*-methylindole-6-yltrifluoroborate.** The general procedure was used employing *N*-methylindole-6-ylboronic acid (1.00 g, 5.71 mmol) to provide the desired product as a light orange-pink solid (1.10 g, 81%). mp > 200 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.47 (s, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 3.0 Hz, 1H), 6.22 (d, *J* = 3.0 Hz, 1H), 3.70 (s, 3H); <sup>13</sup>C NMR (125.8 MHz, DMSO-*d*<sub>6</sub>) δ 136.49, 128.41, 126.50, 123.81; 123.79, 108.10, 100.72, 33.16; <sup>19</sup>F NMR (470.8 MHz, DMSO-*d*<sub>6</sub>) δ -137.29; <sup>11</sup>B NMR (128.4 MHz, DMSO-*d*<sub>6</sub>) δ 3.19; IR (KBr) 3097, 2945, 1611, 1514, 1428, 1325, 1250, 1159, 981, 815, 724 cm<sup>-1</sup>; HRMS (ESI) calcd. for C<sub>9</sub>H<sub>8</sub>NBF<sub>3</sub> (M-K) 198.0702, found 198.0687.

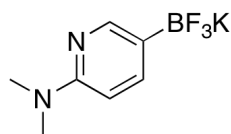


**Potassium dibenzofuran-4-yltrifluoroborate.** The general procedure was used employing dibenzofuran-4-ylboronic acid (1.00 g, 4.72 mmol) to provide the desired product as a white solid (1.17 g, 90%). mp > 200 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.04-8.00 (m, 1H), 7.84 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.50 (dd, *J* = 7.0, 0.9 Hz, 1H), 7.46-7.39 (m, 1H), 7.33-7.27 (m, 1H), 7.18

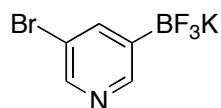
(t,  $J = 7.3$  Hz, 1H);  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  160.27, 156.19, 132.25, 127.20, 125.37, 122.84, 122.65, 122.33, 121.33, 118.99, 112.25;  $^{19}\text{F}$  NMR (470.8 MHz, DMSO- $d_6$ )  $\delta$  -136.97;  $^{11}\text{B}$  NMR (128.4 MHz, DMSO- $d_6$ )  $\delta$  2.28; IR (KBr) 3050, 1602, 1451, 1394, 1180, 1155, 989, 857, 757  $\text{cm}^{-1}$ ; HRMS (ESI) calcd. for  $\text{C}_{12}\text{H}_7\text{OBF}_3$  (M-K) 235.0542, found 235.0540.



**Potassium 2,5-dimethoxyphenyltrifluoroborate.** The general procedure was used employing 2,5-dimethoxyphenylboronic acid (1.00 g, 5.49 mmol) to provide the desired product as a white solid (1.11 g, 83%). mp > 200 °C.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  6.87 (d,  $J = 3.2$  Hz, 1H), 6.59 (d,  $J = 8.6$  Hz, 1H), 6.54 (dd,  $J = 8.6, 3.2$  Hz, 1H), 3.62 (s, 3H), 3.57 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  157.64, 153.67, 120.05, 111.96, 111.72, 56.71, 55.91;  $^{19}\text{F}$  NMR (470.8 MHz, DMSO- $d_6$ )  $\delta$  -137.14;  $^{11}\text{B}$  NMR (128.4 MHz, DMSO- $d_6$ )  $\delta$  2.11; IR (KBr) 2996, 2952, 2831, 1489, 1403, 1301, 1210, 981, 871, 728  $\text{cm}^{-1}$ ; HRMS (ESI) calcd. for  $\text{C}_8\text{H}_9\text{O}_2\text{BF}_3$  (M-K) 205.0648, found 205.0648.



**Potassium 2-(*N,N*-dimethylamino)pyridyltrifluoroborate.** The general procedure was used employing 2-(*N,N*-dimethylamino)pyridine-5-boronic acid monohydrate (1.00 g, 6.02 mmol) to provide the desired product as a brown solid (1.17 g, 90%). mp > 200 °C.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.96 (s, 1H), 7.41 (d,  $J = 8.3$  Hz, 1H), 6.44 (d,  $J = 8.3$  Hz, 1H), 2.92 (s, 6H);  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  158.93, 151.13, 141.61, 105.53, 38.85;  $^{19}\text{F}$  NMR (470.8 MHz, DMSO- $d_6$ )  $\delta$  -137.73;  $^{11}\text{B}$  NMR (128.4 MHz, DMSO- $d_6$ )  $\delta$  2.62; IR (KBr) 2996, 2952, 2831, 1489, 1403, 1301, 1210, 981, 871, 728  $\text{cm}^{-1}$ ; HRMS (ESI) calcd. for  $\text{C}_7\text{H}_9\text{N}_2\text{BF}_3$  (M-K) 189.0811, found 189.0809.

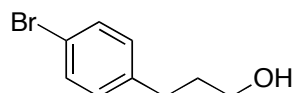
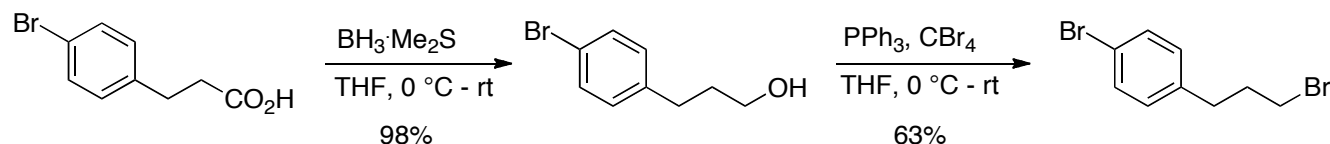


**Potassium 3-bromopyridyltrifluoroborate.** The general procedure was used employing 3-bromopyridine-5-boronic acid (1.00 g, 4.95 mmol) to provide the desired product as a yellow solid (0.82 g, 63%). mp > 200 °C.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.96 (s, 1H),

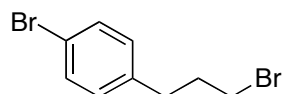


7.41 (dd,  $J = 8.3, 1.7$  Hz, 1H), 6.44 (d,  $J = 8.3$  Hz, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  151.56, 147.73, 142.17, 121.27;  $^{19}\text{F}$  NMR (470.8 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -139.64;  $^{11}\text{B}$  NMR (128.4 MHz,  $\text{DMSO-}d_6$ )  $\delta$  1.49; IR (KBr) 3042, 1581, 1404, 1226, 973, 881, 768, 708  $\text{cm}^{-1}$ ; HRMS (ESI) calcd. for  $\text{C}_5\text{H}_3\text{O}_2\text{NBrBF}_3$  (M-K) 223.9494, found 223.9485.

### Preparation of 1-bromo-4-(3-bromopropyl)benzene



**3-(4-Bromophenyl)propan-1-ol.**<sup>3</sup> To a solution of 4-bromophenyl propionic acid (2.00 g, 8.73 mmol) in dry THF (30 mL) at  $0\text{ }^\circ\text{C}$  was added  $\text{BH}_3\cdot\text{SMe}_2$  (3.52 g, 43.6 mmol) dropwise. After complete addition the mixture was maintained at  $0\text{ }^\circ\text{C}$  for an additional 1 h, then allowed to reach rt and stirred for 6 h. The reaction was quenched by the dropwise addition of MeOH (20 mL) at  $0\text{ }^\circ\text{C}$ . The mixture was allowed to warm to rt and then stirred for 1 h. The solvent was concentrated under reduced pressure to afford a cloudy oil.  $\text{Et}_2\text{O}$  (50 mL) was added to the crude oil and the organic layer was washed consecutively with 10% aq. NaOH (2x20 mL) and brine (2x20 mL), then dried ( $\text{MgSO}_4$ ) and concentrated under reduced pressure. The compound was passed through a short plug of silica gel and washed with EtOAc/hexanes (20/80) to afford a colorless oil (1.84 g, 98%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 8.4$  Hz, 2H), 7.10 (d,  $J = 8.4$  Hz, 2H), 3.75-3.63 (t,  $J = 6.1$  Hz, 2H), 2.75-2.64 (t,  $J = 7.7$  Hz, 2H), 1.96-1.82 (m, 2H), 1.30 (broad s, 1H).



**1-Bromo-4-(3-bromopropyl)benzene.**<sup>4</sup> Triphenylphosphine (1.93 g, 7.34 mmol) and then  $\text{CBr}_4$  (2.43 g, 7.34 mmol) were added to a solution of bromo-4-(3-hydroxypropyl)benzene (1.25 g, 5.81 mmol) in dry THF (30 mL) at  $0\text{ }^\circ\text{C}$  under a nitrogen atmosphere. The mixture was stirred at  $0\text{ }^\circ\text{C}$  for 15 min and then at rt for 8 h. The solvent was removed under reduced pressure and the crude mixture was purified by flash chromatography (EtOAc/hexanes = 3/97) to afford the title compound as a colorless oil (1.02 g,

63%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.40 (t, *J* = 6.5 Hz, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.24-2.07 (m, 2H).

## HTE OPTIMIZATION

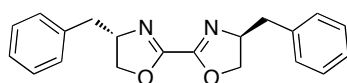
### General Procedure for Parallel Microscale Experimentation. Reactions of Potassium Phenethyltrifluoroborate with 2-Chloroanisole or 3-Chloropyridine.

The following procedure is representative of the parallel microscale experimentation reactions run in this publication. The ligands (1 μmol of each bidentate ligand) were dosed into the 96-well reactor vial as solutions (50 μL of a 0.02 M solution in EtOH or 1,2-dimethoxyethane depending upon the solubility of the ligand). Plates of these ligands are typically dosed in advance of the reaction, the solvent is removed by evacuation on a Genovac, and the plates are stored in the glovebox. Ni pre-catalyst (1 μmol, 50 μL of a 0.02 M solution in DME) was then added to the reaction vials and this was evacuated to dryness on a Genovac. LiHMDS or NaHMDS (30 μmol, 50 μL of a 0.6 M solution in THF) was then added added to the ligand/catalyst mixture, and this was evacuated to dryness on the Genovac. A parylene stir-bar was then added to each reaction. The alkyl bromide (10 μmol/reaction), potassium aryltrifluoroborate (12.5 μmol/reaction) and biphenyl (1 μmol/reaction) (used as an internal standard to measure HPLC yield) were then dosed together in the desired reaction solvents (2-butanol or 2-methyl-2-butanol) using a single-tip pipettor. The reactions were then sealed and heated at 60 °C for 18 h. After cooling to ambient temperature, the reactions were diluted with 500 μL of MeCN, a silicon-rubber storage mat was added, and the contents were shaken to homogenize. Into a separate 96-well-plate LC plate with 1 mL vials was then added 750 μL of MeCN, and then 20 μL of the diluted reaction mixtures. The 96-well plate LC block was then sealed with a silicon rubber storage mat, and an aluminum cover was attached to the block with screws. The reactions were then analyzed using an Agilent Chemstation on an HPLC modified with a 96-well plate auto-sampler.

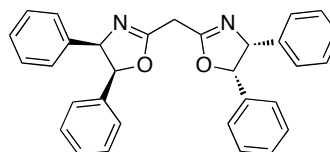
**Table 1: Ligand effects**

Ligand	Average <sup>*</sup>
4,4'- <i>t</i> -Bu-bipyridine	2.53
4,4'-MeO-bipyridine	2.15
phenanthroline	2.03
4,4'-Ph-bipyridine	1.96
4,4'-Me-bipyridine	1.92
<i>L</i> -tert-leucinol	1.59
<i>cis</i> -1,2-cyclohexanediamine	1.53
4,7-Ph-phen (bathophenanthroline)	1.49

5-Cl-phenanthroline	1.41
(1 <i>S</i> ,2 <i>R</i> )-(+)-2-amino-1,2-diphenylethanol	1.40
3,4,7,8-Me-phenanthroline	1.40
5-NH <sub>2</sub> -phenanthroline	1.39
4,7-MeO-phenanthroline	1.26
ligand A	1.12
(-)- <i>N</i> -methylephedrine	1.10
(1 <i>R</i> ,2 <i>R</i> )- <i>N,N'</i> -dimethyl-1,2-cyclohexanediamine	1.00
<i>trans</i> -2-aminocyclohexanol hydrochloride	0.99
(1 <i>S</i> ,2 <i>S</i> )-(+)- <i>trans</i> -1-amino-2-indanol	0.95
( <i>S,S</i> )- diphenylethylenediamine	0.88
diphenylglyoxime	0.84
2,2'-bis(2-oxazoline)	0.77
4,5-diazafluoren-9-one	0.75
nioxime	0.75
5,6-oxo-phenanthroline	0.73
2,9-Me-phenanthroline (neocuproine)	0.72
dimethylglyoxime	0.70
ligand B	0.67
2,2'-bis(4,5-Me-imidazole)	0.66
5,5'-Me-bipy	0.58
5-NO <sub>2</sub> -phen	0.49
( <i>R</i> )-(+)-1,1'-binaphthyl-2,2'-diamine	0.48
2,9-Me-4,7-Ph-phenanthroline (bathocuproine)	0.47
pybox	0.45
bipyridine	0.41
2,9-Bu-phenanthroline	0.40
2,2'-biquinoline	0.32



ligand A



ligand B

**Table 2: Ni Effects**

Solvent	Nickel cat.	Base	Average <sup>*</sup>
<i>t</i> -amylOH	NiI <sub>2</sub>	NaHMDS	0.83
2-BuOH	NiI <sub>2</sub>	NaHMDS	1.01
<i>t</i> -amylOH	NiI <sub>2</sub>	LiHMDS	0.93
2-BuOH	NiI <sub>2</sub>	LiHMDS	1.08
			<b>0.96</b>
<i>t</i> -amylOH	NiBr <sub>2</sub> •glyme	NaHMDS	1.16
2-BuOH	NiBr <sub>2</sub> •glyme	NaHMDS	1.09
<i>t</i> -amylOH	NiBr <sub>2</sub> •glyme	LiHMDS	1.20
2-BuOH	NiBr <sub>2</sub> •glyme	LiHMDS	1.22
			<b>1.17</b>

**Table 3: Solvent Effects**

Solvent	Nickel cat.	Base	Average <sup>*</sup>
<i>t</i> -amylOH	NiI <sub>2</sub>	NaHMDS	0.83
<i>t</i> -amylOH	NiI <sub>2</sub>	LiHMDS	0.93
<i>t</i> -amylOH	NiBr <sub>2</sub> •glyme	NaHMDS	1.16
<i>t</i> -amylOH	NiBr <sub>2</sub> •glyme	LiHMDS	1.20
			<b>1.03</b>
2-BuOH	NiI <sub>2</sub>	NaHMDS	1.01
2-BuOH	NiI <sub>2</sub>	LiHMDS	1.08
2-BuOH	NiBr <sub>2</sub> •glyme	NaHMDS	1.09
2-BuOH	NiBr <sub>2</sub> •glyme	LiHMDS	1.22
			<b>1.10</b>

**Table 4: Base Effects**

Solvent	Nickel cat.	Base	Average <sup>*</sup>
<i>t</i> -amylOH	NiI <sub>2</sub>	NaHMDS	0.83
<i>t</i> -amylOH	NiBr <sub>2</sub> •glyme	NaHMDS	1.16
2-BuOH	NiI <sub>2</sub>	NaHMDS	1.01
2-BuOH	NiBr <sub>2</sub> •glyme	NaHMDS	1.09
			<b>1.02</b>
<i>t</i> -amylOH	NiI <sub>2</sub>	LiHMDS	0.93
<i>t</i> -amylOH	NiBr <sub>2</sub> •glyme	LiHMDS	1.20
2-BuOH	NiI <sub>2</sub>	LiHMDS	1.08
2-BuOH	NiBr <sub>2</sub> •glyme	LiHMDS	1.22
			<b>1.11</b>

<sup>\*</sup> ratio product/internal standard

**Table 5: Top Conditions on micromolar scale on model substrate**

Top	Solvent	Ligand	Ni cat.	Base	Anisole <sup>1</sup>	Alkyl -Br <sup>2</sup>	Prod <sup>3</sup>	Prod/IS
1	<i>t</i> -amylOH	4,4'- <i>t</i> Bu-bipy	NiBr <sub>2</sub> •glyme	NaHMDS	29	259	860	3.15
2	2-BuOH	4,4'-OMe-bipy	NiBr <sub>2</sub> •glyme	NaHMDS	0	267	776	2.93
3	2-BuOH	4,4'- <i>t</i> -Bu-bipy	NiBr <sub>2</sub> •glyme	NaHMDS	0	277	692	2.86
4	2-BuOH	Phenanthroline	NiI <sub>2</sub>	NaHMDS	108	234	882	2.84
5	2-BuOH	4,4'-OMe-bipy	NiI <sub>2</sub>	NaHMDS	9	296	869	2.72
6	2-BuOH	4,4'- <i>t</i> Bu-bipy	NiBr <sub>2</sub> •glyme	LiHMDS	6	251	784	2.64
7	2-BuOH	4,4'-OMe-bipy	NiBr <sub>2</sub> •glyme	LiHMDS	11	280	790	2.63
8	2-BuOH	4,4'-Ph-bipy	NiBr <sub>2</sub> •glyme	LiHMDS	64	300	717	2.57
9	<i>t</i> -amylOH	4,4'- <i>t</i> -Bu-bipy	NiI <sub>2</sub>	NaHMDS	6	319	806	2.50
10	<i>t</i> -amylOH	4,4'- <i>t</i> -Bu-bipy	NiBr <sub>2</sub> •glyme	LiHMDS	68	399	839	2.48

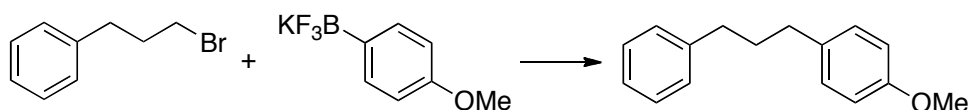
11	<i>t</i> -amyLOH	4,4'- <i>t</i> -Bu-bipy	NiBr <sub>2</sub> •glyme	LiHMDS	66	515	926	2.42
12	2-BuOH	Phenanthroline	NiBr <sub>2</sub> •glyme	LiHMDS	85	437	827	2.38
13	2-BuOH	<i>cis</i> -1,2-Cy-diamine	NiBr <sub>2</sub> •glyme	LiHMDS	95	276	828	2.32
14	2-BuOH	4,7-Ph-phen	NiBr <sub>2</sub> •glyme	LiHMDS	0	347	793	2.32

<sup>1</sup> Product obtained by protodeboronation of the potassium organotrifluoroborate starting material

<sup>2</sup> Starting material recovered

<sup>3</sup> Cross-coupling product

The reactions in Table 5 were ran on a model substrate (eq. 1):



On large scale, the top conditions from Table 5 provided high yields (70-80%) for electron rich or non-substituted aryltrifluoroborates. However, for a general substrate scope, conditions in entry 14 (Table 5) were chosen as they provided average best yield in average for various substrates, including electron poor aryl- and heteroaryltrifluoroborates.

## **Procedure for the Suzuki–Miyaura Cross-Coupling of Aryl- and Heteroaryltrifluoroborates with Alkyl Halides**

### **General procedure for the cross-coupling of alkyl iodides and bromides on 0.5 mmol scale**

Outside the glovebox, bathophenanthroline (16.6 mg, 0.05 mmol) and potassium organotrifluoroborate (0.51 mmol) were added to a Biotage microwave tube equipped with a stir bar. NiBr<sub>2</sub>•glyme (15.4 mg, 0.05 mmol) and LiHMDS (251 mg, 1.5 mmol) were then added in the glove box. The vial was sealed and removed from the glove box, then *s*-BuOH (1 mL) was added *via* syringe. The mixture was stirred for 15-30 min and alkyl halide (0.5 mmol) was added to the resulting solution. The reaction was stirred at 60 °C for 5-26 h outside the glovebox, then passed through a short plug of silica, which was washed thoroughly with EtOAc (30 mL). The filtrate was concentrated under reduced pressure, then purified by column chromatography on silica gel.

### **General procedure for the cross-coupling of alkyl chlorides on 0.5 mmol scale**

Outside the glovebox, potassium organotrifluoroborate (0.51 mmol) was added to a Biotage microwave tube equipped with a stir bar. L-Prolinol (10.1 mg, 0.1 mmol), NiCl<sub>2</sub>•glyme (10.9 mg, 0.05 mmol) and NaHMDS (275 mg, 1.5 mmol) or KHMDS (275 mg, 1.5 mmol) were then added in the glove box. The vial was sealed and removed from the glove box, then *s*-BuOH (1 mL) was added *via* syringe. The mixture was stirred for 15-30 min and alkyl halide (0.5 mmol) was added to the resulting solution. The reaction was stirred at 80 °C for 24-48 h, then passed through a short plug of silica, which was washed thoroughly with EtOAc (30 mL). The filtrate was concentrated under reduced pressure, then purified by column chromatography on silica gel.

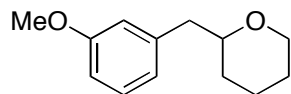
### **General procedure for the cross-coupling of alkyl bromides on 5 mmol scale**

Outside the glovebox, potassium 2-thiophenyltrifluoroborate (0.97 g, 5.10 mmol) or potassium 3-methylphenyltrifluoroborate (1.01 g, 5.10 mmol), bathophenanthroline (16.6 mg, 0.05 mmol), NiBr<sub>2</sub>•glyme (15.4 mg, 0.05 mmol) and LiHMDS (2.51 g, 1.50 mmol) were added added to a Schlenk tube equipped with a stir bar. The Schlenk tube was purged with Ar (five cycles vacuum/Ar) then *s*-BuOH (8 mL) was added *via* syringe under Ar. The mixture was stirred for 15 min and 2-(bromomethyl)tetrahydro-2*H*-pyran (895 mg, 0.50 mmol) was added to the resulting solution under Ar.

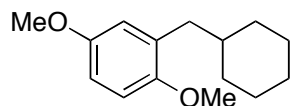
S10

The reaction was stirred at 60 °C for 30 h outside the glovebox, then passed through a short plug of silica, which was washed thoroughly with EtOAc (100 mL). The filtrate was concentrated under reduced pressure, then purified by column chromatography on silica gel to provide 2-(3-methylbenzyl)tetrahydro-2*H*-pyran (0.72 g, 76%) or 2-(thiophen-3-ylmethyl)tetrahydro-2*H*-pyran (0.67 g, 74%).

## Compound Characterization for the Suzuki–Miyaura Cross-Coupling of Aryl- and Hetero-aryltrifluoroborates with Alkyl Halides

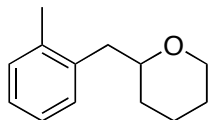


**2-(3-Methoxybenzyl)tetrahydro-2H-pyran (Table 1, entry 1, R = H).** The general procedure was employed using potassium 3-methoxyphenyltrifluoroborate (109.2 mg, 0.51 mmol) and 2-(bromomethyl)-tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 6 h and the compound was obtained as a colorless oil (88.5 mg, 86%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 (t,  $J = 7.8$  Hz, 1H), 6.83-6.72 (m, 3H), 4.01-3.94 (m, 1H), 3.80 (s, 3H), 3.53-3.45 (m, 1H), 3.41 (dt,  $J = 11.7, 2.3$  Hz, 1H), 2.85 (dd,  $J = 13.8, 6.6$  Hz, 1H), 2.61 (dd,  $J = 13.8, 6.6$  Hz, 1H), 1.85-1.76 (m, 1H), 1.57 (s, 2H), 1.52-1.37 (m, 2H), 1.34-1.23 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.64, 140.58, 129.27, 121.94, 115.27, 111.53, 78.84, 68.78, 55.28, 43.37, 31.63, 26.18, 23.63; IR (neat) = 2935, 2838, 1602, 1488, 1258, 1088, 1044, 776  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{13}\text{H}_{19}\text{O}_2$  ( $\text{MH}^+$ ) 207.1385, found 207.1384.

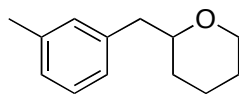


**2-(2,5-Dimethoxybenzyl)tetrahydro-2H-pyran (Table 1, entry 1, R = OMe).** The general procedure was employed using potassium 2,5-dimethoxyphenyltrifluoroborate (124.5 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 5 h and the compound was obtained as a colorless oil (84.1 mg, 72%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.80-6.74 (m, 2H), 6.71 (dd,  $J = 8.8, 3.0$  Hz, 1H), 4.02-3.93 (m, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.57-3.49 (m, 1H), 3.42 (t,  $J = 11.7, 2.1$  Hz, 1H), 2.84 (dd,  $J = 13.4, 6.6$  Hz, 1H), 2.68 (dd,  $J = 13.4, 6.6$  Hz, 1H), 1.79 (d,  $J = 14.5$  Hz, 1H), 1.64-1.52 (m, 2H), 1.51-1.37 (m, 2H), 1.35-1.25 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.42, 152.13, 128.55, 117.61, 111.54, 111.40, 77.57, 68.70, 56.13, 55.78, 37.54, 31.67, 26.28, 23.67; IR (neat) = 2935, 2843, 1499, 1225, 1048, 804  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{14}\text{H}_{21}\text{O}_3$  ( $\text{MH}^+$ ) 237.1491, found 237.1497.

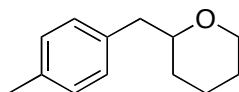




**2-(2-Methylbenzyl)tetrahydro-2H-pyran (Table 1, entry 2, R = *o*-Me).** The general procedure was employed using potassium 2-methylphenyltrifluoroborate (101.3 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 8 h and the compound was obtained as a colorless oil (72.0 mg, 76%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20-7.06 (m, 4H), 4.02-3.94 (m, 1H), 3.54-3.37 (m, 2H), 2.92 (dd,  $J$  = 13.8, 6.3 Hz, 1H), 2.67 (dd,  $J$  = 13.8, 7.0 Hz, 1H), 2.34 (s, 3H), 1.86-1.76 (m, 1H), 1.66-1.54 (m, 2H), 1.53-1.29 (m, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  137.13, 136.65, 130.34, 130.29, 126.38, 125.84, 78.11, 68.81, 40.48, 31.74, 26.24, 23.70, 19.88; IR (neat) = 3017, 2934, 2843, 1090, 1048, 742  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{13}\text{H}_{19}\text{O}$  ( $\text{MH}^+$ ) 191.1436, found 191.1437.

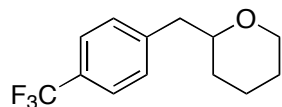


**2-(3-Methylbenzyl)tetrahydro-2H-pyran (Table 1, entry 2, R = *m*-Me).** The general procedure was employed using potassium 3-methylphenyltrifluoroborate (100.9 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 8 h and the compound was obtained as a colorless oil (77.1 mg, 81%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (t,  $J$  = 7.6 Hz, 1H), 7.03-6.98 (m, 3H), 4.01-3.92 (m, 1H), 3.50-3.43 (m, 1H), 3.43-3.36 (m, 1H), 2.84 (dd,  $J$  = 13.6, 6.6 Hz, 1H), 2.60 (dd,  $J$  = 13.6, 6.6 Hz, 1H), 2.32 (s, 3H), 1.84-1.74 (m, 1H), 1.64-1.51 (m, 2H), 1.51-1.36 (m, 2H), 1.33-1.21 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  139.01, 137.97, 130.40, 128.30, 127.05, 126.58, 79.05, 68.86, 43.38, 31.71, 26.28, 23.72, 21.62; IR (neat) = 2934, 2842, 1088, 1041  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{13}\text{H}_{19}\text{O}$  ( $\text{MH}^+$ ) 191.1436, found 191.1429.

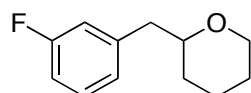


**2-(4-Methylbenzyl)tetrahydro-2H-pyran (Table 1, entry 2, R = *p*-Me).** The general procedure was employed using potassium 4-methylphenyltrifluoroborate (101.0 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 8 h and the compound was obtained as a colorless oil (77.1 mg, 81%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.09 (s, 4H), 4.01-3.94 (m, 1H), 3.49-

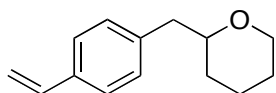
3.36 (m, 2H), 2.84 (dd,  $J = 13.7, 6.6$  Hz, 1H), 2.60 (dd,  $J = 13.7, 6.6$  Hz, 1H), 2.32 (s, 3H), 1.85-1.74 (m, 1H), 1.65-1.52 (m, 2H), 1.51-1.36 (m, 2H), 1.34-1.19 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  135.63, 135.43, 129.16, 128.82, 78.83, 68.60, 42.68, 31.35, 25.98, 23.46, 20.90; IR (neat) = 2934, 2846, 1091, 1042  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{13}\text{H}_{19}\text{O}$  ( $\text{MH}^+$ ) 191.1436, found 191.1436, found 191.1444.



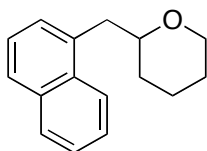
**2-(4-(Trifluoromethyl)benzyl)tetrahydro-2H-pyran (Table 1, entry 3).** The general procedure was employed using potassium 4-(trifluoromethyl)phenyltrifluoroborate (128.5 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 24 h and the compound was obtained as a colorless oil (78.1 mg, 64%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 8.0$  Hz, 2H), 7.32 (d,  $J = 7.9$  Hz, 2H), 3.98-3.88 (m, 1H), 3.54-3.47 (m, 1H), 3.38 (td,  $J = 11.7$  Hz, 2.2 Hz, 1H), 2.88 (dd,  $J = 13.8, 7.3$  Hz, 1H), 2.72 (dd,  $J = 13.8, 5.5$  Hz, 1H), 1.86-1.77 (m, 1H), 1.63-1.39 (m, 4H), 1.36-1.30 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  143.24, 129.79, 128.54 (qd,  $J = 32.3$  Hz, 2C), 125.21 (qd,  $J = 3.8$  Hz, 1C), 124.5 (qd,  $J = 271.8$  Hz, 1C), 78.39, 68.77, 43.03, 31.70, 26.06, 23.58;  $^{19}\text{F}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -62.34; IR (neat) = 2939, 2846, 1326, 1162, 1123  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{13}\text{H}_{15}\text{OF}_2$  ( $\text{M-F}^+$ ) 225.1091, found 225.1097.



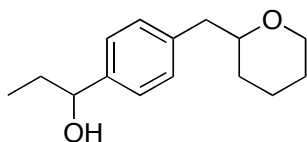
**2-(3-Fluorobenzyl)tetrahydro-2H-pyran (Table 1, entry 4).** The general procedure was employed using potassium 3-fluorophenyltrifluoroborate (102.9 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 24 h and the compound was obtained as a colorless oil (70.7 mg, 73%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.21 (m, 1H), 7.02-6.87 (m, 3H), 4.02-3.95 (m, 1H), 3.53-3.46 (m, 1H), 3.41 (td,  $J = 10.5, 2.4$  Hz, 1H), 2.86 (dd,  $J = 13.8, 7.0$  Hz, 1H), 2.66 (dd,  $J = 13.8, 5.9$  Hz, 1H), 1.87-1.79 (m, 1H), 1.64-1.40 (m, 4H), 1.36-1.23 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.68 (d,  $J = 244.8$  Hz, 1C), 141.35 (d,  $J = 7.3$  Hz, 1C), 129.42 (d,  $J = 8.2$  Hz, 1C), 124.91 (d,  $J = 2.6$  Hz, 1C), 116.14 (d,  $J = 20.9$  Hz, 1C), 112.85 (d,  $J = 21.7$  Hz, 1C), 78.28, 68.52, 42.71, 31.39, 25.87, 23.36;  $^{19}\text{F}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -114.02 Hz; IR (neat) = 2936, 2847, 1589, 1487, 1450, 1249, 1088, 1043, 780  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{12}\text{H}_{16}\text{OF}$  ( $\text{M-H}^+$ ) 195.1185, found 195.1187.



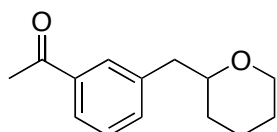
**2-(4-Vinylbenzyl)tetrahydro-2H-pyran (Table 1, entry 5).** The general procedure was employed using potassium 4-vinylphenyltrifluoroborate (107.1 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (54.0 mg, 53%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J$  = 8.1 Hz, 1H), 7.17 (d,  $J$  = 8.1 Hz, 3H), 6.69 (dd,  $J$  = 17.6, 10.9 Hz, 1H), 5.70 (d,  $J$  = 17.6 Hz, 1H), 5.19 (d,  $J$  = 10.9 Hz, 1H), 4.00-3.94 (m 1H), 3.50-3.43 (dd,  $J$  = 9.9, 5.5 Hz, 1H), 3.40 (td,  $J$  = 11.8, 2.4 Hz, 1H), 2.85 (dd,  $J$  = 13.7, 6.7 Hz, 1H), 2.63 (dd,  $J$  = 13.7, 6.4 Hz, 1H), 1.84-1.76 (m, 1H), 1.63-1.51 (m, 2H), 1.51-1.37 (m, 2H), 1.34 - 1.22 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  138.49, 136.60, 135.43, 129.44, 125.99, 112.97, 78.64, 68.56, 42.81, 31.38, 25.94, 23.41; IR (neat) = 2934, 2847, 1089, 1718, 1041  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{14}\text{H}_{19}\text{O}$  ( $\text{MH}^+$ ) 204.1436, found 204.1436.



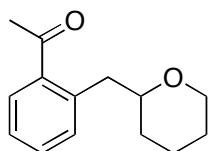
**2-(Naphthalen-1-ylmethyl)tetrahydro-2H-pyran (Table 1, entry 6).** The general procedure was employed using potassium naphthalen-1-yltrifluoroborate (119.4 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (77.0 mg, 68%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d,  $J$  = 8.5 Hz, 1H), 7.88 (d,  $J$  = 7.5 Hz, 1H), 7.76 (d,  $J$  = 8.0 Hz, 1H), 7.57-7.46 (m, 2H), 7.45-7.35 (m, 2H), 4.06-3.99 (m, 1H), 3.73-3.65 (m, 1H), 3.49-3.40 (m, 2H), 3.10 (dd,  $J$  = 13.9, 7.3 Hz, 1H), 1.88-1.77 (m, 1H), 1.69-1.33 (m, 5H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  134.90, 133.99, 132.41, 128.87, 127.71, 127.11, 125.90, 125.55, 125.53, 124.18, 78.08, 68.84, 40.43, 31.97, 26.23, 23.60. IR (neat) = 3043, 2934, 2843, 2360, 1086, 1046, 788, 774  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{16}\text{H}_{19}\text{O}$  ( $\text{MH}^+$ ) 227.1436, found 227.1436.



**2-(4-(1-Hydroxypropyl)benzyl)tetrahydro-2H-pyran (Table 1, entry 7).** The general procedure was employed using potassium 4-(1-hydroxypropyl)phenyltrifluoroborate (123.4 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (94.5 mg, 81%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (d,  $J$  = 8.1 Hz, 2H), 7.19 (d,  $J$  = 8.1 Hz, 2H), 4.57 (t,  $J$  = 6.6 Hz, 1H), 4.01-3.94 (s, 1H), 3.51-3.44 (s, 1H), 3.44-3.36 (d,  $J$  = 11.7 Hz, 1H), 2.87 (dd,  $J$  = 13.7, 6.6 Hz, 1H), 2.64 (dd,  $J$  = 13.7, 6.6 Hz, 1H), 1.93 (s, 1H), 1.87-1.70 (m, 3H), 1.63-1.52 (m, 2H), 1.52-1.37 (m, 2H), 1.34-1.23 (d,  $J$  = 14.7 Hz, 1H), 0.92 (t,  $J$  = 7.4 Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  142.28, 138.00, 129.29, 125.79, 78.65, 75.78, 68.52, 42.72, 31.71, 31.35, 25.93, 23.39, 10.13; IR (neat) = 3400, 2931, 2847, 1084, 1039, 785, 700  $\text{cm}^{-1}$ ; HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Na}$  ( $\text{MNa}^+$ ) 257.1517, found 257.1507.

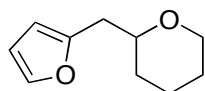


**2-(3-Acetylbenzyl)tetrahydro-2H-pyran (Table 1, entry 8).** The general procedure was employed using potassium 3-acetylphenyltrifluoroborate (115.2 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 26 h at 80 °C and the compound was obtained as a colorless oil (72.1 mg, 66%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83-7.76 (m, 2H), 7.42 (d,  $J$  = 7.5 Hz, 1H), 7.38 (t,  $J$  = 7.5 Hz, 1H), 4.01-3.91 (m, 1H), 3.54-3.46 (m, 1H), 3.39 (td,  $J$  = 11.8, 2.3 Hz, 1H), 2.89 (dd,  $J$  = 13.8, 7.2 Hz, 1H), 2.72 (dd,  $J$  = 13.8, 5.7 Hz, 1H), 2.59 (s, 3H), 1.86-1.76 (m, 1H), 1.63-1.38 (m, 4H), 1.36-1.23 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  198.53, 139.65, 137.28, 134.40, 129.24, 128.55, 126.44, 78.58, 68.76, 43.07, 31.67, 26.84, 26.10, 23.59; IR (neat) = 2935, 2848, 1684, 1439, 1357, 1267, 1088, 695  $\text{cm}^{-1}$ ; HRMS (ESI) calcd. for  $\text{C}_{14}\text{H}_{19}\text{O}_2$  ( $\text{MH}^+$ ) 219.1385, found 219.1379.

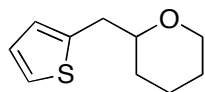


**2-(2-Acetylbenzyl)tetrahydro-2H-pyran (Table 1, entry 9).** The general procedure was employed using potassium 2-acetylphenyltrifluoroborate (115.2 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 26 h at 80 °C and the compound was obtained as a colorless oil (74.2 mg, 68%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J$  = 7.7 Hz, 1H), 7.41-7.34 (m,

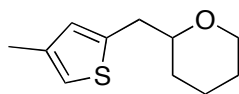
1H), 7.32-7.23 (m, 2H), 3.93- 3.85 (m, 1H), 3.49-3.41 (m, 1H), 3.30 (td,  $J = 11.7, 1.9$  Hz, 1H), 3.04 (dd,  $J = 13.5, 4.3$  Hz, 1H), 2.95 (dd,  $J = 13.4, 7.8$  Hz, 1H), 2.57 (s, 3H), 1.84-1.74 (m, 1H), 1.66-1.59 (m, 1H), 1.57-1.38 (m, 3H), 1.37-1.26 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  202.68, 138.90, 138.75, 132.61, 131.12, 128.90, 126.21, 78.73, 68.59, 40.80, 31.98, 30.06, 26.19, 23.71; IR (neat) = 2934, 2846, 1685, 1441, 1354, 1251, 1089, 1045, 759  $\text{cm}^{-1}$ ; HRMS (ESI) calcd. for  $\text{C}_{14}\text{H}_{19}\text{O}_2$  ( $\text{MH}^+$ ) 219.1385, found 219.1385.



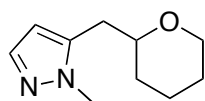
**2-(Furan-2-ylmethyl)tetrahydro-2H-pyran (Table 2, entry 1, X = O).** The general procedure was employed using potassium 2-furanyltrifluoroborate (88.7 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 15 h and the compound was obtained as a colorless oil (56.51 mg, 68%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (dd,  $J = 1.8, 0.8$  Hz, 1H), 6.29 (dd,  $J = 3.1, 1.8$  Hz, 1H), 6.06 (dd,  $J = 3.1, 0.8$  Hz, 1H), 4.02-3.95 (m, 1H), 3.60-3.53 (m, 1H), 3.43 (td,  $J = 11.7, 2.3$  Hz, 1H), 2.86 (dd,  $J = 15.0, 6.7$  Hz, 1H), 2.70 (dd,  $J = 15.0, 6.3$  Hz, 1H), 1.86-1.78 (m, 1H), 1.64-1.42 (m, 4H), 1.35-1.25 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  152.84, 141.00, 110.11, 106.35, 76.36, 68.55, 35.27, 31.44, 25.83, 23.33; IR (neat) = 2935, 2847, 1087, 1044, 1008, 735  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{10}\text{H}_{15}\text{O}_2$  ( $\text{MH}^+$ ) 167.1072, found 167.1084.



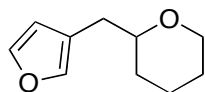
**2-(Thiophen-2-ylmethyl)tetrahydro-2H-pyran (Table 2, entry 1, X = S).** The general procedure was employed using potassium 2-thiophenyltrifluoroborate (96.9 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 15 h and the compound was obtained as a colorless oil (57.4 mg, 63%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14 (dd,  $J = 5.1$  Hz, 1.1 Hz, 1H), 6.93 (dd,  $J = 5.1, 3.4$  Hz, 1H), 6.83 (dd,  $J = 3.4$  Hz, 1.1 Hz, 1H), 4.04-3.97 (d,  $J = 11.4$  Hz, 1H), 3.54-3.38 (m, 2H), 3.04 (dd,  $J = 14.8, 6.9$  Hz, 1H), 2.90 (dd,  $J = 14.8, 5.8$  Hz, 1H), 1.87-1.78 (m, 1H), 1.68-1.53 (m, 2H), 1.53-1.42 (m, 2H), 1.37-1.23 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.04, 126.58, 125.54, 123.73, 78.48, 68.62, 37.09, 31.33, 25.95, 23.42; IR (neat) = 2934, 2845, 1439, 1090, 1045, 692  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{10}\text{H}_{15}\text{OS}$  ( $\text{MH}^+$ ) 183.0844, found 183.0840.



**2-((4-Methylthiophen-2-yl)methyl)tetrahydro-2H-pyran (Table 2, entry 2).** The general procedure was employed using potassium 4-methylthiophen-2-yltrifluoroborate (104.0 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 15 h and the compound was obtained as a colorless oil (64.7 mg, 66%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.69 (s, 1H), 6.63 (s, 1H), 4.03-3.96 (m, 1H), 3.51-3.39 (m, 2H), 2.97 (dd,  $J$  = 14.8, 6.9 Hz, 1H), 2.82 (dd,  $J$  = 14.8, 5.9 Hz, 1H), 2.20 (s, 3H), 1.86-1.78 (m, 1H), 1.68-1.62 (m, 1H), 1.60-1.52 (m, 1H), 1.52-1.41 (m, 2H), 1.33-1.23 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.06, 137.32, 128.18, 119.00, 78.63, 68.76, 37.40, 31.51, 26.09, 23.56, 15.84; IR (neat) = 2928, 1601, 1454, 1252, 750, 698  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{11}\text{H}_{17}\text{OS}$  ( $\text{MH}^+$ ) 197.1000, found 197.1004.

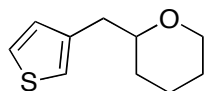


**1-Methyl-5-(tetrahydro-2H-pyran-2-yl)methyl-1H-pyrazole (Table 2, entry 3).** The general procedure was employed using potassium 1-methyl-1H-pyrazol-5-yltrifluoroborate (88.7 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 20 h and the compound was obtained as a colorless oil (31.6 mg, 35%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (s, 1H), 6.30 (s, 1H), 4.02-3.94 (m, 1H), 3.84 (s, 3H), 3.46-3.36 (m, 2H), 2.63 (dd,  $J$  = 14.6, 6.8 Hz, 1H), 2.49 (dd,  $J$  = 14.6, 5.9 Hz, 1H), 1.86-1.77 (m, 1H), 1.66-1.39 (m, 4H), 1.34-1.21 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  142.41, 139.73, 121.38, 111.53, 77.72, 68.48, 31.99, 31.36, 25.91, 23.37; IR (neat) = 2936, 2845, 1090, 1044, 1023, 778  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{10}\text{H}_{17}\text{ON}_2$  ( $\text{MH}^+$ ) 181.1341, found 181.1349.

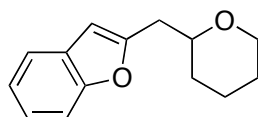


**2-(Furan-3-ylmethyl)tetrahydro-2H-pyran (Table 2, entry 4, X = O).** The general procedure was employed using potassium 3-furanyltrifluoroborate (88.7 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 15 h and the compound was obtained as a colorless oil (59.0 mg, 71%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (s, 1H), 6.30 (s, 1H), 4.02-3.94 (m, 1H), 3.46-3.36 (m, 2H), 2.63 (dd,  $J$  = 14.6, 6.8 Hz, 1H), 2.49 (dd,  $J$  = 14.6, 5.9 Hz, 1H), 1.86-1.77

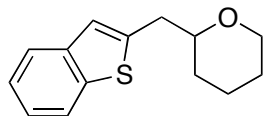
(m, 1H), 1.66-1.39 (m, 4H), 1.34-1.21 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  142.41, 139.73, 121.38, 111.53, 77.72, 68.48, 31.99, 31.36, 25.91, 23.37; IR (neat) = 2936, 2845, 1090, 1044, 1023, 778  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{10}\text{H}_{15}\text{O}_2$  ( $\text{MH}^+$ ) 167.1072, found 167.1077.



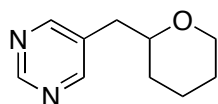
**2-(Thiophen-3-ylmethyl)tetrahydro-2H-pyran (Table 2, entry 4, X = S).** The general procedure was employed using potassium 3-thiophenyltrifluoroborate (96.9 mg, 0.51 mmol) and 2-(bromomethyl)-tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 6 h and the compound was obtained as a colorless oil (73.8 mg, 80%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (dd,  $J$  = 4.9, 3.0 Hz, 1H), 7.01 (dd,  $J$  = 3.0, 1.0 Hz, 1H), 6.98 (dd,  $J$  = 4.9, 1.0 Hz, 1H), 4.06-3.93 (m, 1H), 3.54-3.37 (m, 2H), 2.87 (dd,  $J$  = 14.3, 6.7 Hz, 1H), 2.70 (dd,  $J$  = 14.3, 6.1 Hz, 1H), 1.86-1.77 (m, 1H), 1.63-1.53 (m, 2H), 1.52-1.41 (m, 2H), 1.33-1.24 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  139.17, 129.00, 125.11, 121.62, 78.26, 68.73, 37.57, 31.64, 26.16, 23.61; IR (neat) = 3099, 2934, 2844, 1439, 1091, 1042, 771  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{10}\text{H}_{15}\text{OS}$  ( $\text{MH}^+$ ) 183.0844, found 183.0840.



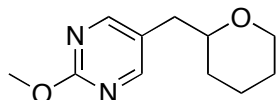
**2-((Tetrahydro-2H-pyran-2-yl)methyl)benzofuran (Table 2, entry 5, X = O).** The general procedure was employed using potassium 2-benzofuranyltrifluoroborate (114.3 mg, 0.51 mmol) and 2-(bromomethyl)-tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (86.0 mg, 80%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.45 (m, 1H), 7.41 (d,  $J$  = 8.0 Hz, 1H), 7.23-7.13 (m, 2H), 6.46 (s, 1H), 4.02-3.93 (m, 1H), 3.73-3.64 (m, 1H), 3.43 (td,  $J$  = 11.7, 2.3 Hz, 1H), 2.99 (dd,  $J$  = 15.0, 7.0 Hz, 1H), 2.83 (dd,  $J$  = 15.0, 5.9 Hz, 1H), 1.86-1.77 (m, 1H), 1.69-1.42 (m, 4H), 1.41-1.29 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.19, 154.82, 129.05, 123.31, 122.52, 120.44, 110.90, 103.74, 76.18, 68.77, 35.97, 31.77, 25.98, 23.49; IR (neat) = 2934, 2848, 1454, 1253, 1090, 1044, 750  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{14}\text{H}_{17}\text{O}_2$  ( $\text{MH}^+$ ) 217.1229, found 217.1219.



**2-(Benzo[b]thiophen-2-ylmethyl)tetrahydro-2H-pyran (Table 2, entry 5, X = S).** The general procedure was employed using potassium 2-benzothiophenyltrifluoroborate (114.3 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless gel (67.0 mg, 58%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J$  = 7.8 Hz, 1H), 7.69 (d,  $J$  = 7.7 Hz, 1H), 7.35-7.24 (m, 2H), 7.08 (s, 1H), 4.09-4.01 (m, 1H), 3.65-3.57 (m, 1H), 3.48 (td,  $J$  = 11.8, 2.3 Hz, 1H), 3.13 (dd,  $J$  = 14.7, 6.9 Hz, 1H), 3.00 (dd,  $J$  = 14.8, 5.5 Hz, 1H), 1.90-1.82 (m, 1H), 1.75-1.57 (m, 2H), 1.56-1.46 (m, 2H), 1.43-1.33 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  142.17, 139.92, 139.74, 123.92, 123.40, 122.71, 122.03, 121.96, 77.98, 68.58, 37.90, 31.36, 25.82, 23.33; IR (neat) = 3056, 2934, 2844, 1457, 1437, 1204, 1089, 1045, 745, 726  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{14}\text{H}_{16}\text{OS}$  ( $\text{M}^+$ ) 232.0922, found 232.0922.



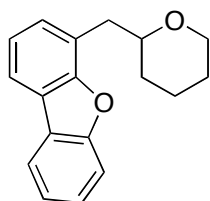
**5-((Tetrahydro-2H-pyran-2-yl)methyl)pyrimidine (Table 2, entry 6, R = H).** The general procedure was employed using potassium pyrimidine-5-yltrifluoroborate (94.8 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 16 h and the compound was obtained as a colorless oil (68.7 mg, 77%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.08 (s, 1H), 8.62 (s, 2H), 3.99-3.91 (m, 1H), 4.05-3.84 (m, 1H), 3.48-3.42 (m, 1H), 3.36 (td,  $J$  = 14.4, 7.8 Hz, 1H), 2.75 (dd,  $J$  = 14.4, 7.8 Hz, 1H), 2.69 (dd,  $J$  = 14.4, 4.5 Hz, 1H), 1.90-1.82 (m, 1H), 1.59-1.43 (m, 3H), 1.39-1.28 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.56, 156.95, 132.33, 77.31, 68.63, 37.54, 31.66, 25.85, 23.43; IR (neat) = 2936, 2845, 1603, 1416, 1352, 1206, 1089, 1043, 808, 789  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}$  ( $\text{MH}^+$ ) 179.1184, found 179.1191.



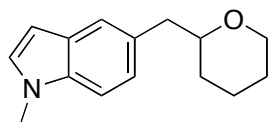
**2-Methoxy-5-((tetrahydro-2H-pyran-2-yl)methyl)pyrimidine (Table 2, entry 6, R = OMe).** The general procedure was employed using potassium 4-methoxypyrimidine-5-yltrifluoroborate (110.2 mg, 0.51 mmol) and 2-(bromo-methyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 16



h and the compound was obtained as a colorless oil (73.8 mg, 71%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (s, 2H), 3.99 (s, 3H), 3.98 (s, 1H), 3.43-3.31 (m, 2H), 2.68 (dd,  $J = 14.4, 7.6$  Hz, 1H), 2.61 (dd,  $J = 14.4, 4.7$  Hz, 1H), 1.87-1.80 (m, 1H), 1.64-1.42 (m, 4H), 1.35-1.25 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.67, 159.73, 125.23, 77.70, 68.65, 54.82, 36.56, 31.51, 25.92, 23.46; IR (neat) = 2935, 2848, 1599, 1561, 1471, 1407, 1322, 1088, 1043, 805  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{11}\text{H}_{17}\text{N}_2\text{O}_2$  ( $\text{MH}^+$ ) 209.1290, found 209.1290.

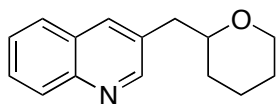


**4-((Tetrahydro-2H-pyran-2-yl)methyl)dibenzo[*b,d*]furan (Table 2, entry 7).** The general procedure was employed using potassium 4-dibenzofuranyltrifluoroborate (139.78 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (103.9 mg, 78%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.7$  Hz, 1H), 7.82 (dd,  $J = 7.6, 1.2$  Hz, 1H), 7.61 (d,  $J = 8.2$  Hz, 1H), 7.49-7.42 (m, 1H), 7.38-7.24 (m, 3H), 4.00 (d,  $J = 11.4$  Hz, 1H), 3.76 (s, 1H), 3.45 (td,  $J = 11.8, 2.3$  Hz, 1H), 3.22 (dd,  $J = 13.8, 6.8$  Hz, 1H), 3.08 (dd,  $J = 13.8, 6.5$  Hz, 1H), 1.86-1.78 (m, 1H), 1.67-1.56 (m, 2H), 1.53-1.37 (m, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.18, 155.13, 128.68, 127.06, 124.77, 123.97, 123.03, 122.79, 122.71, 120.82, 118.74, 111.89, 77.58, 68.80, 37.26, 31.78, 26.20, 23.61; IR (neat) = 3057, 2934, 2844, 1451, 1422, 1185, 1049, 752  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{18}\text{H}_{19}\text{O}_2$  ( $\text{MH}^+$ ) 267.1385, found 267.1380.

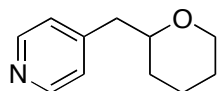


**1-Methyl-5-((tetrahydro-2H-pyran-2-yl)methyl)-1H-indole (Table 2, entry 8).** The general procedure was employed using potassium *N*-methyl-indol-4-yltrifluoroborate (120.9 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil, which turns into brick-red glassy solid upon standing (93.9 mg, 82%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.45 (m, 1H), 7.29-7.24 (m, 1H), 7.12 (dd,  $J = 6.9$  Hz, 1.5 Hz, 1H), 7.04 (d,  $J = 3.1$  Hz, 1H), 6.45 (d,  $J = 3.1$  Hz, 1H), 4.07-3.98 (m, 1H), 3.79 (s, 3H), 3.59-3.51 (m, 1H), 3.46 (td,  $J = 11.8, 2.4$  Hz, 1H), 3.04 (dd,  $J = 13.5, 6.2$  Hz, 1H), 2.76 (dd,  $J = 13.5, 7.1$  Hz,

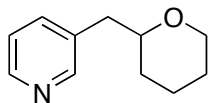
1H), 1.86-1.78 (m, 1H), 1.68-1.56 (m, 2H), 1.54-1.38 (m, 2H), 1.37-1.27 (m, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 135.66, 129.56, 128.99, 128.71, 123.46, 121.30, 108.92, 100.64, 79.70, 68.79, 43.43, 32.93, 31.49, 26.28, 23.66; IR (neat) = 2981, 2847, 1493, 1423, 1333, 1078, 1041, 899, 727 cm<sup>-1</sup>; HRMS (ESI) calcd. for C<sub>15</sub>H<sub>20</sub>NO (MH<sup>+</sup>) 230.1545, found 230.1552.



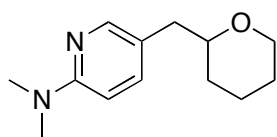
**3-((Tetrahydro-2H-pyran-2-yl)methyl)quinoline (Table 2, entry 9).** The general procedure was employed using potassium 4-isoquinolinyltrifluoroborate (119.87 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (79.6 mg, 70%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.81 (d, *J* = 2.1 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 1.5 Hz, 1H), 7.76 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.65 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.54-7.47 (m, 1H), 4.00-3.93 (m, 1H), 3.59-3.52 (m, 1H), 3.38 (td, *J* = 11.8, 2.3 Hz, 1H), 2.98 (dd, *J* = 14.1, 7.4 Hz, 1H), 2.86 (dd, *J* = 14.1, 5.3 Hz, 1H), 1.86-1.78 (m, 1H), 1.67-1.52 (m, 2H), 1.52-1.31 (m, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 152.42, 146.87, 135.40, 131.62, 129.06, 128.56, 127.97, 127.35, 126.37, 78.07, 68.52, 40.27, 31.49, 25.80, 23.34; IR (neat) = 2935, 2844, 1495, 1088, 1043, 786, 752 cm<sup>-1</sup>; HRMS (ESI) calcd. for C<sub>15</sub>H<sub>18</sub>NO (MH<sup>+</sup>) 228.1388, found 228.1389.



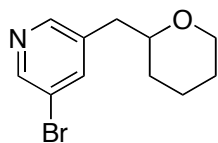
**4-((Tetrahydro-2H-pyran-2-yl)methyl)pyridine (Table 2, entry 10).** The general procedure was employed using potassium 3-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (62.92 mg, 71%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.49 (d, *J* = 5.8 Hz, 2H), 7.15 (d, *J* = 5.8 Hz, 2H), 3.99-3.92 (m, 1H), 3.54-3.48 (m, 1H), 3.38 (td, *J* = 11.7, 2.4 Hz, 1H), 2.81 (dd, *J* = 13.9, 7.5 Hz, 1H), 2.66 (dd, *J* = 13.9, 5.2 Hz, 1H), 1.87-1.79 (m, 1H), 1.62-1.41 (m, 4H), 1.37-1.27 (m, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 149.60, 148.05, 124.83, 77.67, 68.65, 42.41, 31.68, 25.91, 23.47; IR (neat) = 2936, 2845, 1423, 1199, 1090, 1043, 715 cm<sup>-1</sup>; HRMS (ESI) calcd. for C<sub>11</sub>H<sub>16</sub>NO (MH<sup>+</sup>) 178.1232, found 178.1237.



**3-((Tetrahydro-2H-pyran-2-yl)methyl)pyridine (Table 2, entry 11).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (52.28 mg, 59%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51-8.41 (m, 2H), 7.55 (d,  $J$  = 7.8 Hz, 1H), 7.20 (dd,  $J$  = 7.7, 4.8 Hz, 1H), 3.99-3.92 (m, 1H), 3.50-3.43 (m, 1H), 3.38 (td,  $J$  = 11.6, 2.4 Hz, 1H), 2.81 (dd,  $J$  = 14.0, 7.3 Hz, 1H), 2.67 (dd,  $J$  = 14.0, 5.4 Hz, 1H), 1.87-1.78 (m, 1H), 1.62-1.40 (m, 4H), 1.37-1.25 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  150.70, 147.65, 137.00, 134.44, 123.24, 78.19, 68.69, 40.24, 31.59, 26.00, 23.52; IR (neat) = 2936, 2847, 1560, 1409, 1089, 1043, 730  $\text{cm}^{-1}$ ; HRMS (ESI) calcd. for  $\text{C}_{11}\text{H}_{16}\text{NO}$  ( $\text{MH}^+$ ) 178.1232, found 178.1231.

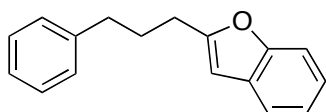


***N,N*-Dimethyl-5-((tetrahydro-2H-pyran-2-yl)methyl)pyridin-2-amine (Table 2, entry 12).** The general procedure was employed using potassium *N,N*-dimethylaminopyridin-5-yltrifluoroborate (116.3 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (56.12 mg, 51%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J$  = 2.3 Hz, 1H), 7.33 (dd,  $J$  = 8.7, 2.3 Hz, 1H), 6.47 (d,  $J$  = 8.7 Hz, 1H), 4.00-3.92 (m, 1H), 3.43-3.33 (m, 2H), 3.06 (s, 6H), 2.70 (dd,  $J$  = 14.0, 6.6 Hz, 1H), 2.51 (dd,  $J$  = 14.0, 6.3 Hz, 1H), 1.85-1.76 (m, 1H), 1.62-1.36 (m, 4H), 1.31-1.20 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.36, 148.12, 138.66, 121.47, 105.65, 78.90, 68.72, 39.34, 38.39, 31.37, 26.16, 23.60; IR (neat) = 2933, 2848, 1609, 1509, 1398, 1090, 1042  $\text{cm}^{-1}$ ; HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{21}\text{N}_2\text{O}$  ( $\text{MH}^+$ ) 221.1654, found 221.1657.

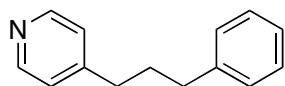


**3-Bromo-5-((tetrahydro-2H-pyran-2-yl)methyl)pyridine (Table 2, entry 13).** The general procedure was employed using potassium 3-bromopyridin-5-yltrifluoroborate (134.6 mg, 0.51 mmol) and 2-(bromomethyl)tetrahydro-2H-pyran (89.5 mg, 0.50 mmol). The reaction time was 12 h and the

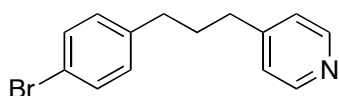
compound was obtained as a colorless oil (80.7 mg, 63%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.52 (s, 1H), 8.38 (s, 1H), 7.72 (s, 1H), 3.99-3.91 (m, 1H), 3.50-3.41 (m, 1H), 3.37 (td,  $J = 11.6, 2.5$  Hz, 1H), 2.76 (dd,  $J = 14.2, 7.7$  Hz, 1H), 2.66 (dd,  $J = 14.2, 4.8$  Hz, 1H), 1.88-1.79 (m, 1H), 1.63-1.42 (m, 4H), 1.36-1.26 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  148.81, 148.67, 139.51, 136.39, 120.50, 77.72, 68.64, 39.72, 31.65, 25.90, 23.45; IR (neat) = 2935, 2845, 1422, 1090, 1043, 708  $\text{cm}^{-1}$ ; HRMS (ESI) calcd. for  $\text{C}_{11}\text{H}_{15}\text{NOBr}$  ( $\text{MH}^+$ ) 256.0337, found 256.0327.



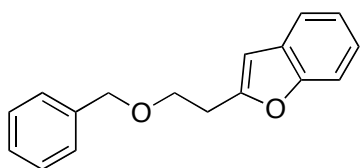
**2-(3-Phenylpropyl)benzofuran (Table 3, entry 1, 1).** The general procedure was employed using potassium 2-benzofuranyltrifluoroborate (114.3 mg, 0.51 mmol) and 1-bromo-3-phenylpropane (99.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (93.3 mg, 79%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.46 (m, 1H), 7.43-7.38 (m, 1H), 7.32-7.26 (m, 2H), 7.23-7.15 (m, 5H), 6.39 (s, 1H), 2.79 (t,  $J = 7.6$  Hz, 2H), 2.72 (t,  $J = 7.6$  Hz, 2H), 2.10 (quintet,  $J = 7.6$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.27, 154.82, 141.87, 129.09, 128.65, 128.54, 126.07, 123.27, 122.56, 120.35, 110.87, 102.25, 35.36, 29.41, 28.03; IR (neat) = 3061, 3027, 2931, 2859, 1601, 1454, 1252, 750, 699  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{17}\text{H}_{17}\text{O}$  ( $\text{MH}^+$ ) 237.1279, found 237.1283.



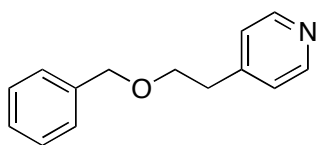
**4-(3-Phenylpropyl)pyridine (Table 3, entry 1, 2).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and 1-bromo-3-phenylpropane (99.5 mg, 0.50 mmol). The reaction time was 16 h and the compound was obtained as a colorless oil (79.8 mg, 81%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49 (d,  $J = 5.4$  Hz, 2H), 7.34-7.24 (m, 2H), 7.23-7.13 (m, 3H), 7.10 (d,  $J = 5.9$  Hz, 2H), 2.69-2.58 (m, 4H), 2.02-1.92 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  151.32, 149.84, 141.76, 128.57, 128.56, 126.14, 124.07, 35.42, 34.77, 31.91; IR (neat) = 3029, 2954, 2857, 1601, 1495, 1453, 1414, 791, 750, 699  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{14}\text{H}_{16}\text{N}$  ( $\text{MH}^+$ ) 198.1283, found 198.1283.



**4-(3-(4-Bromophenyl)propyl)pyridine (Table 3, entry 2, 2).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and 1-bromo-4-(3-bromopropyl)benzene (138.49 mg, 0.50 mmol). The reaction time was 16 h and the compound was obtained as a colorless oil (84.23 mg, 61%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49 (d,  $J = 5.5$  Hz, 2H), 7.40 (d,  $J = 8.3$  Hz, 2H), 7.09 (d,  $J = 5.5$  Hz, 2H), 7.04 (d,  $J = 8.3$  Hz, 2H), 2.64-2.56 (m, 4H), 1.99-1.89 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  150.94, 149.87, 140.63, 131.58, 130.26, 123.97, 119.83, 34.73, 34.59, 31.67; IR (neat) = 3064, 3028, 2938, 2857, 2360, 1601, 1487, 1414, 1071, 1010, 803  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{14}\text{H}_{15}\text{BrN}$  ( $\text{MH}^+$ ) 276.0388, found 276.0386.

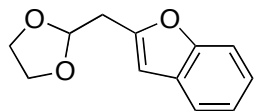


**2-(2-(Benzyloxy)ethyl)benzofuran (Table 3, entry 3, 1).** The general procedure was employed using potassium 2-benzofuranyltrifluoroborate (114.3 mg, 0.51 mmol) and benzyl 2-bromoethyl ether (107.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (100.9 mg, 80%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.46 (m, 1H), 7.42-7.37 (m, 1H), 7.33-7.24 (m, 5H), 7.22-7.14 (m, 2H), 6.46 (s, 1H), 4.54 (s, 2H), 3.82 (t,  $J = 6.7$  Hz, 2H), 3.08 (t,  $J = 6.7$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.36, 154.79, 138.26, 129.01, 128.52, 127.79, 123.43, 122.59, 120.48, 110.90, 103.25, 73.17, 67.94, 49.53, 29.50; IR (neat) = 3059, 3031, 2858, 1602, 1454, 1362, 1252, 1170, 1099, 798, 738, 696  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{17}\text{H}_{16}\text{O}_2$  ( $\text{M}^+$ ) 252.1150, found 252.1150.

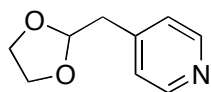


**4-(2-(Benzyloxy)ethyl)pyridine (Table 3, entry 3, 2).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and benzyl 2-bromoethyl ether (107.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (81.0 mg, 76%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (d,  $J = 5.4$  Hz, 2H), 7.35-7.30 (m, 2H), 7.29-7.25 (m, 3H), 7.15 (d,  $J = 5.9$  Hz, 2H), 4.51 (s, 2H), 3.71 (t,  $J = 6.6$  Hz, 2H), 2.90 (t,  $J = 6.6$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  149.81, 148.42, 138.17, 128.57, 127.84, 127.75, 124.50, 73.22, 69.77, 35.79; IR (neat) =

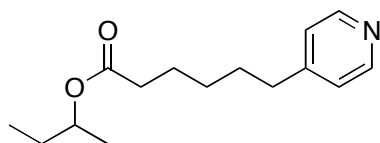
3029, 2925, 2859, 1602, 1453, 1415, 1363, 1103, 804, 737, 698  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{14}\text{H}_{16}\text{NO}$  ( $\text{MH}^+$ ) 214.1224, found 214.1232.



**2-((1,3-Dioxolan-2-yl)methyl)benzofuran (Table 3, entry 4, 1).** The general procedure was employed using potassium 2-benzofuranyltrifluoroborate (114.3 mg, 0.51 mmol) and 2-(bromoethyl)-1,3-dioxolane (83.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (77.6 mg, 76%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 7.2$  Hz, 1H), 7.45 (d,  $J = 8.3$  Hz, 1H), 7.27-7.16 (m, 2H), 6.57 (s, 1H), 5.26 (t,  $J = 4.8$  Hz, 1H), 4.03-3.96 (m, 2H), 3.94-3.86 (m, 2H), 3.16 (d,  $J = 4.8$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.00, 153.74, 128.90, 123.67, 122.70, 120.67, 111.12, 104.57, 102.52, 65.32, 34.20; IR (neat) = 2956, 2887, 1603, 1455, 1253, 1132, 1040, 804, 752  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{12}\text{H}_{13}\text{O}_3$  ( $\text{MH}^+$ ) 205.0865, found 205.0863.

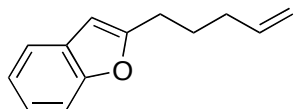


**4-((1,3-Dioxolan-2-yl)methyl)pyridine (Table 3, entry 4, 2).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and 2-(bromoethyl)-1,3-dioxolane (83.5 mg, 0.50 mmol). The reaction time was 16 h and the compound was obtained as a colorless oil (77.4 mg, 78%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49 (d,  $J = 4.9$  Hz, 2H), 7.18 (d,  $J = 4.9$  Hz, 2H), 5.07 (t,  $J = 4.5$  Hz, 1H), 3.92-3.77 (m, 4H), 2.93 (d,  $J = 4.5$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  149.70, 145.20, 125.33, 103.57, 65.20, 40.14, 11.83; IR (neat) = 2962, 2885, 1603, 1415, 1133, 1037, 994, 802, 732; HRMS (ES) calcd. for  $\text{C}_9\text{H}_{12}\text{O}_2\text{N}$  ( $\text{MH}^+$ ) 166.0867, found 166.0868.

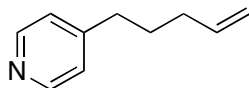


**sec-Butyl 6-(pyridin-4-yl)hexanoate (Table 3, entry 5, 2).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.3 mg, 0.51 mmol) and ethyl 6-bromohexanoate (111.6 mg, 0.50 mmol). The reaction time was 16 h and the compound was obtained as a light yellow oil (87.0 mg, 70%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (d,  $J = 5.2$  Hz, 2H), 7.09 (d,  $J = 5.8$  Hz, 2H), 4.88-4.78 (m,

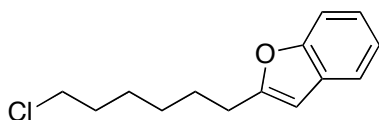
1H), 2.60 (app t,  $J = 7.7$  Hz, 2H), 2.28 (app t,  $J = 7.4$  Hz, 2H), 1.70-1.61 (m, 4H), 1.61-1.46 (m, 2H), 1.40-1.32 (m, 2H), 1.18 (d,  $J = 6.3$  Hz, 3H), 0.88 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  173.19, 151.24, 149.57, 123.77, 71.93, 34.90, 34.40, 29.81, 28.70, 28.50, 24.70, 19.38, 9.59; IR (neat) = 2966, 2936, 2359, 1729, 1602, 1190, 1125, 992  $\text{cm}^{-1}$ ; HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{24}\text{NO}_2$  ( $\text{MH}^+$ ) 250.1801, found 250.1807.



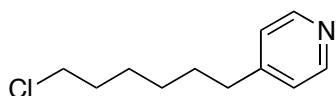
**2-(Pent-4-en-1-yl)benzofuran (Table 3, entry 6, 1).** The general procedure was employed using potassium 2-benzofuranyltrifluoroborate (114.3 mg, 0.51 mmol) and 5-bromo-1-pentene (74.51 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (58.7 mg, 63%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53-7.47 (m, 1H), 7.43 (d,  $J = 8.0$  Hz, 1H), 7.25-7.16 (m, 2H), 6.40 (s, 1H), 5.92-5.80 (m, 1H), 5.13-4.98 (m, 2H), 2.80 (app t,  $J = 7.5$  Hz, 2H), 2.22-2.14 (m, 2H), 1.92-1.82 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.42, 154.80, 138.16, 129.11, 123.23, 122.53, 120.32, 115.34, 110.86, 102.14, 33.25, 27.92, 26.99; IR (neat) = 3069, 2928, 2853, 1585, 1455, 1250, 1167, 1007, 946, 762, 750, 739  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{13}\text{H}_{15}\text{O}$  ( $\text{MH}^+$ ) 187.1123, found 187.1119.



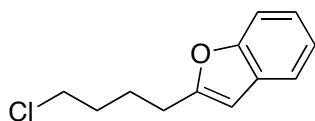
**4-(Pent-4-en-1-yl)pyridine (Table 3, entry 6, 2).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and 5-bromo-1-pentene (74.51 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a light yellow oil (50.1 mg, 68%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (br. s, 2H), 7.10 (br. s, 2H), 5.87-5.75 (m, 1H), 5.08-4.96 (m, 2H), 2.69-2.54 (t,  $J = 7.1$  Hz, 2H), 2.10 (m, 2H), 1.79-1.68 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  151.61, 150.02, 138.29, 124.26, 115.57, 34.85, 33.41, 29.71; IR (neat) = 3068, 2930, 1602, 1415, 992, 912, 795  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{10}\text{H}_{14}\text{N}$  ( $\text{MH}^+$ ) 148.1126, found 148.1123.



**2-(6-Chlorohexyl)benzofuran (Table 3, entry 7, 1).** The general procedure was employed using potassium 2-benzofuranyltrifluoroborate (114.3 mg, 0.51 mmol) and 1-bromo-6-chlorohexane (99.7 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (82.9 mg, 70%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.47 (m, 1H), 7.42 (d,  $J$  = 8.0 Hz, 1H), 7.24-7.16 (m, 2H), 6.38 (s, 1H), 3.54 (t,  $J$  = 6.7 Hz, 2H), 2.78 (t,  $J$  = 7.5 Hz, 2H), 1.84-1.73 (m, 4H), 1.54-1.39 (m, 4H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.51, 154.77, 129.11, 123.24, 122.55, 120.33, 110.86, 102.06, 45.20, 32.62, 28.54, 28.46, 27.67, 26.75; IR (neat) = 2933, 2858, 1455, 1251, 1172, 945, 796, 750  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{14}\text{H}_{18}\text{ClO}$  ( $\text{MH}^+$ ) 237.1046, found 237.1047.

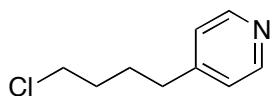


**2-(6-Chlorohexyl)pyridine (Table 3, entry 7, 2).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and 1-bromo-6-chlorohexane (99.7 mg, 0.50 mmol). The reaction time was 16 h and the compound was obtained as a yellow oil (60.2 mg, 61%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (d,  $J$  = 5.3 Hz, 2H), 7.09 (d,  $J$  = 5.3 Hz, 2H), 3.50 (t,  $J$  = 6.7 Hz, 2H), 2.59 (app t,  $J$  = 7.7 Hz, 2H), 1.79-1.70 (m, 2H), 1.66-1.57 (m, 2H), 1.49-1.41 (m, 2H), 1.37-1.31 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  151.71, 149.67, 124.06, 45.13, 35.21, 32.55, 30.21, 28.51, 26.73; IR (neat) = 2932, 2852, 1601, 1415, 803, 728; HRMS (CI) calcd. for  $\text{C}_{11}\text{H}_{17}\text{ClN}$  ( $\text{MH}^+$ ) 198.1050, found 198.1048.

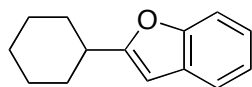


**2-(4-Chlorobutyl)benzofuran (Table 3, entry 8, 1).** The general procedure was employed using potassium 2-benzofuranyltrifluoroborate (114.3 mg, 0.51 mmol) and 1-iodo-4-butane (85.7 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (87.6 mg, 84%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J$  = 7.1 Hz, 1H), 7.41 (d,  $J$  = 8.1 Hz, 1H), 7.24-7.16 (m, 2H), 6.41 (s, 1H), 3.58 (t,  $J$  = 6.3 Hz, 2H), 2.82 (t,  $J$  = 6.8 Hz, 2H), 1.96-1.85 (m, 4H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.73, 154.81, 128.98, 123.39, 122.62, 120.40, 110.90, 102.40, 44.79, 32.04, 27.81, 25.14; IR (neat) = 2952, 1454, 1253, 1175, 941, 796, 750  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{12}\text{H}_{14}\text{ClO}$  ( $\text{MH}^+$ ) 209.0722, found 209.0733.

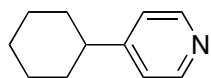




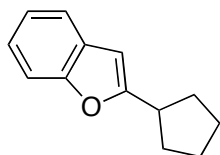
**4-(4-Chlorobutyl)pyridine (Table 3, entry 8, 2).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and 1-iodo-4-butane (85.7 mg, 0.50 mmol). The reaction time was 16 h and the compound was obtained as a light yellow oil (53.5 mg, 63%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (d,  $J = 6.0$  Hz, 2H), 7.10 (d,  $J = 5.7$  Hz, 2H), 3.54 (t,  $J = 6.0$  Hz, 2H), 2.63 (t,  $J = 7.1$  Hz, 2H), 1.81-1.75 (m, 4H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  150.87, 149.88, 123.98, 44.74, 34.51, 32.01, 27.51; IR (neat) = 2922, 2850, 1602, 1415, 953, 803, 732  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_9\text{H}_{13}\text{NCl}$  ( $\text{MH}^+$ ) 170.0737, found 170.0760.



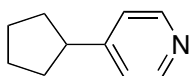
**2-Cyclohexylbenzofuran (Table 3, entry 9, 1).** The general procedure was employed using potassium 2-benzofuranyltrifluoroborate (114.3 mg, 0.51 mmol) and cyclohexyl iodide (74.51 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (60.1 mg, 60%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J = 6.7$  Hz, 1H), 7.43 (d,  $J = 8.0$  Hz, 1H), 7.25-7.16 (m, 2H), 6.36 (s, 1H), 2.82-2.73 (m, 1H), 2.18-2.10 (m, 2H), 1.91-1.82 (m, 2H), 1.80-1.72 (m, 1H), 1.57-1.38 (m, 4H), 1.37-1.26 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.99, 154.31, 128.81, 122.90, 122.20, 120.17, 110.63, 99.68, 37.51, 31.25, 26.01, 25.85; IR (neat) = 3074, 2930, 2857, 1601, 1455, 1251, 912, 795, 750  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{14}\text{H}_{16}\text{O}$  ( $\text{M}^+$ ) 200.1201, found 200.1220.



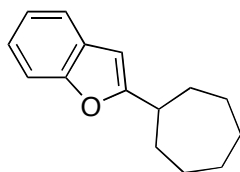
**4-Cyclohexylpyridine (Table 3, entry 9, 2).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and cyclohexyl iodide (105 mg, 0.50 mmol). The reaction time was 16 h and the compound was obtained as a light yellow oil (57.1 mg, 71%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (d,  $J = 6.0$  Hz, 2H), 7.12 (d,  $J = 6.0$  Hz, 2H), 2.56-2.41 (m, 1H), 1.95-1.80 (m, 4H), 1.80-1.71 (m, 1H), 1.47-1.33 (m, 4H), 1.33-1.18 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.66, 149.83, 122.46, 43.93, 33.63, 26.65, 26.05; IR (neat) = 2926, 2852, 1597, 1448, 814  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{11}\text{H}_{16}\text{N}$  ( $\text{MH}^+$ ) 162.1283, found 162.1283.



**2-Cyclopentylbenzofuran (Table 3, entry 10, 1).** The general procedure was employed using potassium 2-benzofuranyltrifluoroborate (114.3 mg, 0.51 mmol) and cyclopentyl bromide (74.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (62.2 mg, 67%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (dd,  $J = 7.0, 1.9$  Hz, 1H), 7.41 (d,  $J = 8.1$  Hz, 1H), 7.23-7.15 (m, 2H), 6.38 (s, 1H), 3.23 (s, 1H), 2.14-2.04 (m, 2H), 1.85-1.76 (m, 4H), 1.74-1.66 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.39, 154.79, 129.08, 123.13, 122.45, 120.31, 110.85, 100.43, 39.13, 31.86, 25.52; IR (neat) = 2958, 2870, 1454, 1253, 1169, 794, 750  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{13}\text{H}_{15}\text{O}$  ( $\text{MH}^+$ ) 187.1123, found 187.1117.

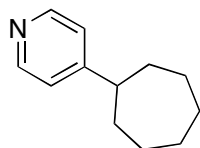


**4-Cyclopentylpyridine (Table 3, entry 10, 2).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and cyclopentyl bromide (74.5 mg, 0.50 mmol). The reaction time was 16 h and the compound was obtained as a light yellow oil (50.2 mg, 68%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (d,  $J = 5.8$  Hz, 2H), 7.14 (d,  $J = 5.8$  Hz, 2H), 2.98 (quintet,  $J = 8.6$  Hz, 1H), 2.16-2.03 (m, 2H), 1.89-1.66 (m, 4H), 1.66-1.53 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.66, 149.70, 122.72, 45.22, 34.01, 25.61; IR (neat) = 2954, 2869, 1598, 1410, 814  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{10}\text{H}_{14}\text{N}$  ( $\text{MH}^+$ ) 148.1126, found 148.1120.

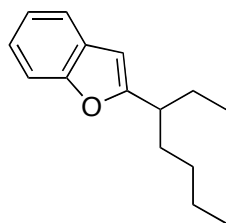


**2-Cycloheptylbenzofuran (Table 3, entry 11, 1).** The general procedure was employed using potassium 2-benzofuranyltrifluoroborate (114.3 mg, 0.51 mmol) and cyclopentyl bromide (74.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a colorless oil (76.1 mg, 71%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (dd,  $J = 7.0, 1.9$  Hz, 1H), 7.42 (d,  $J = 8.0$  Hz, 1H), 7.24-7.15 (m, 2H), 6.37 (s, 1H), 3.03-2.95 (m, 1H), 2.19-2.10 (m, 2H), 1.85-1.57 (m, 10H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.99, 154.58, 129.09, 123.14, 122.44, 120.39, 110.86, 100.07, 39.66, 33.19, 28.58, 26.41; IR

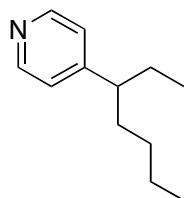
(neat) = 2925, 2865, 1583, 1455, 1255, 1175, 793, 749  $\text{cm}^{-1}$ ; HRMS (ES) calcd. for  $\text{C}_{15}\text{H}_{18}\text{O}$  ( $\text{M}^+$ ) 214.1358, found 214.1359.



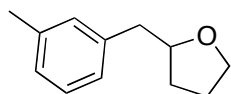
**4-Cycloheptylpyridine (Table 3, entry 11, 2).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and cycloheptyl bromide (88.6 mg, 0.50 mmol). The reaction time was 16 h and the compound was obtained as a light yellow oil (60.2 mg, 69%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.44 (d,  $J = 6.1$  Hz, 2H), 7.08 (d,  $J = 6.1$  Hz, 2H), 2.66-2.59 (m, 1H), 1.90-1.83 (m, 2H), 1.82-1.74 (m, 2H), 1.71-1.49 (m, 8H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.52, 149.82, 122.37, 46.37, 36.03, 27.97, 27.19; IR (neat) = 3021, 2924, 2854, 1596, 1460, 1411, 804  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{12}\text{H}_{18}\text{N}$  ( $\text{MH}^+$ ) 176.1439, found 176.1442.



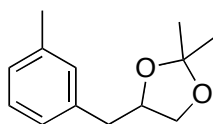
**2-(Heptan-3-yl)benzofuran (Table 3, entry 12, 1).** The general procedure was employed using potassium 2-benzofuranyltrifluoroborate (114.3 mg, 0.51 mmol) and 3-heptyl bromide (89.5 mg, 0.50 mmol). The reaction time was 12 h and the compound was obtained as a light yellow oil (66.8 mg, 62%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (dd,  $J = 6.8, 2.2$  Hz, 1H), 7.43 (d,  $J = 7.6$  Hz, 1H), 7.19 (dd,  $J = 8.0, 6.2$  Hz, 2H), 6.39 (s, 1H), 2.74-2.66 (m, 1H), 1.78-1.62 (m, 4H), 1.35-1.21 (m, 4H), 0.90-0.84 (m, 6H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.52, 154.72, 129.04, 123.01, 122.41, 120.29, 110.95, 102.27, 41.38, 33.40, 29.70, 27.00, 22.86, 14.16, 11.95; IR (neat) = 2959, 2930, 2859, 1584, 1455, 1253, 796, 750  $\text{cm}^{-1}$ ; HRMS (ES) calcd. for  $\text{C}_{15}\text{H}_{21}\text{O}$  ( $\text{MH}^+$ ) 217.1588, found 217.1592.



**4-(Heptan-3-yl)pyridine (Table 3, entry 12, 2).** The general procedure was employed using potassium 4-pyridinyltrifluoroborate (94.34 mg, 0.51 mmol) and 3-heptyl bromide (89.5 mg, 0.50 mmol). The reaction time was 16 h and the compound was obtained as a colorless oil (55.5 mg, 63%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (d,  $J = 4.8$  Hz, 2H), 7.05 (d,  $J = 4.8$  Hz, 2H), 2.45-2.29 (m, 1H), 1.74-1.59 (m, 2H), 1.59-1.47 (m, 2H), 1.31-1.18 (m, 2H), 1.16-1.01 (m, 2H), 0.82 (t,  $J = 7.1$  Hz, 3H), 0.75 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.33, 149.78, 123.49, 47.54, 35.65, 29.76, 29.19, 22.82, 14.08, 12.12; IR (neat) = 3024, 2928, 2858, 1598, 1461, 1414, 818  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{12}\text{H}_{20}\text{N}$  ( $\text{MH}^+$ ) 178.1596, found 178.1589.

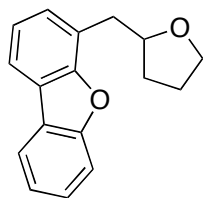


**2-(3-Methylbenzyl)tetrahydrofuran (Table 4, entry 1).** The general procedure was employed using potassium 3-methylphenyltrifluoroborate (100.9 mg, 0.51 mmol) and tetrahydrofurfuryl chloride (60.3 mg, 0.50 mmol). The reaction time was 24 h and the compound was obtained as a colorless oil (52.6 mg, 60%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (t,  $J = 7.5$  Hz, 1H), 7.06-6.98 (m, 3H), 4.09-4.01 (m, 1H), 3.92-3.85 (m, 1H), 3.76-3.68 (m, 1H), 2.87 (dd,  $J = 13.5, 6.5$  Hz, 1H), 2.69 (dd,  $J = 13.5, 6.6$  Hz, 1H), 2.31 (s, 3H), 1.95-1.77 (m, 3H), 1.59-1.50 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  138.83, 137.74, 129.88, 128.11, 126.81, 126.09, 80.04, 67.79, 41.79, 30.94, 25.47, 21.32; IR (neat) = 2924, 2856, 1604, 1459, 1063  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{12}\text{H}_{17}\text{O}$  ( $\text{MH}^+$ ) 177.1279, found 177.1283.

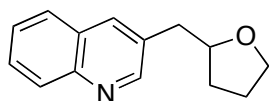


**2,2-Dimethyl-4-(3-methylbenzyl)-1,3-dioxolane (Table 4, entry 2).** The general procedure was employed using potassium 3-methylphenyltrifluoroborate (100.9 mg, 0.51 mmol) and 4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (75.3 mg, 0.50 mmol). The reaction time was 24 h and the compound was obtained as a colorless oil (55.5 mg, 54%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 (t,  $J = 7.5$  Hz, 1H), 7.04-6.97 (m, 3H), 4.34-4.26 (m, 1H), 3.94 (dd,  $J = 8.1, 5.9$  Hz, 1H), 3.62 (dd,  $J = 8.0, 7.0$  Hz, 1H), 2.97 (dd,  $J = 13.6, 6.0$  Hz, 1H), 2.71 (dd,  $J = 13.6, 7.4$  Hz, 1H), 2.31 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  137.97, 137.35, 129.84, 128.29, 127.19, 126.04, 108.99, 68.93,

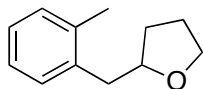
40.00, 26.94, 25.65, 21.30; IR (neat) = 2985, 2932, 2868, 1607, 1369, 1225, 1062  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{12}\text{H}_{19}\text{O}$  ( $\text{MH}^+$ ) 207.1385, found 207.1385.



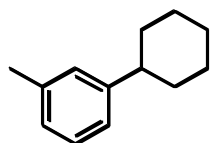
**4-((Tetrahydrofuran-2-yl)methyl)dibenzo[*b,d*]furan (Table 4, entry 3).** The general procedure was employed using potassium 4-dibenzofuranyltrifluoroborate (139.8 mg, 0.51 mmol) and tetrahydrofurfuryl chloride (60.3 mg, 0.50 mmol). The reaction time was 28 h and the compound was obtained as a colorless oil (59.3 mg, 47%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J$  = 7.6 Hz, 1H), 7.82 (d,  $J$  = 7.6 Hz, 1H), 7.59 (d,  $J$  = 8.2 Hz, 1H), 7.50-7.42 (m, 1H), 7.39-7.24 (m, 3H), 4.40-4.31 (m, 1H), 4.00-3.92 (m, 1H), 3.83-3.74 (m, 1H), 3.27 (dd,  $J$  = 13.7, 6.6 Hz, 1H), 3.16 (dd,  $J$  = 13.7, 6.6 Hz, 1H), 2.01-1.83 (m, 3H), 1.73-1.64 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.18, 155.07, 128.38, 127.08, 124.76, 124.01, 123.23, 122.93, 122.72, 120.83, 118.80, 111.83, 78.94, 68.16, 36.00, 31.31, 25.80; IR (neat) = 2971, 2867, 1450, 1184, 1061, 751  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{17}\text{H}_{17}\text{O}_2$  ( $\text{MH}^+$ ) 253.1235, found 253.1229.



**3-((Tetrahydrofuran-2-yl)methyl)quinoline (Table 4, entry 4).** The general procedure was employed using potassium 4-isoquinolinytrifluoroborate (119.8 mg, 0.51 mmol) and tetrahydrofurfuryl chloride (60.3 mg, 0.50 mmol). The reaction time was 28 h and the compound was obtained as a colorless oil (50.1 mg, 42%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (s, 1H), 8.08 (d,  $J$  = 8.4 Hz, 1H), 8.01 (d,  $J$  = 1.5 Hz, 1H), 7.78 (dd,  $J$  = 8.2, 1.2 Hz, 1H), 7.69-7.63 (m, 1H), 7.54-7.49 (m, 1H), 4.21-4.12 (m, 1H), 3.93-3.85 (m, 1H), 3.80-3.71 (m, 1H), 3.02 (2 dd,  $J$  = 12.1, 6.2 Hz, 2H), 2.04-1.95 (m, 1H), 1.93-1.82 (m, 2H), 1.66-1.56 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  152.53, 147.13, 135.64, 131.85, 129.29, 128.90, 128.24, 127.62, 126.69, 79.46, 68.21, 39.19, 31.11, 25.82; IR (neat) = 2938, 2853, 1463, 1065, 784  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{14}\text{H}_{16}\text{ON}$  ( $\text{MH}^+$ ) 214.1232, found 214.1223.



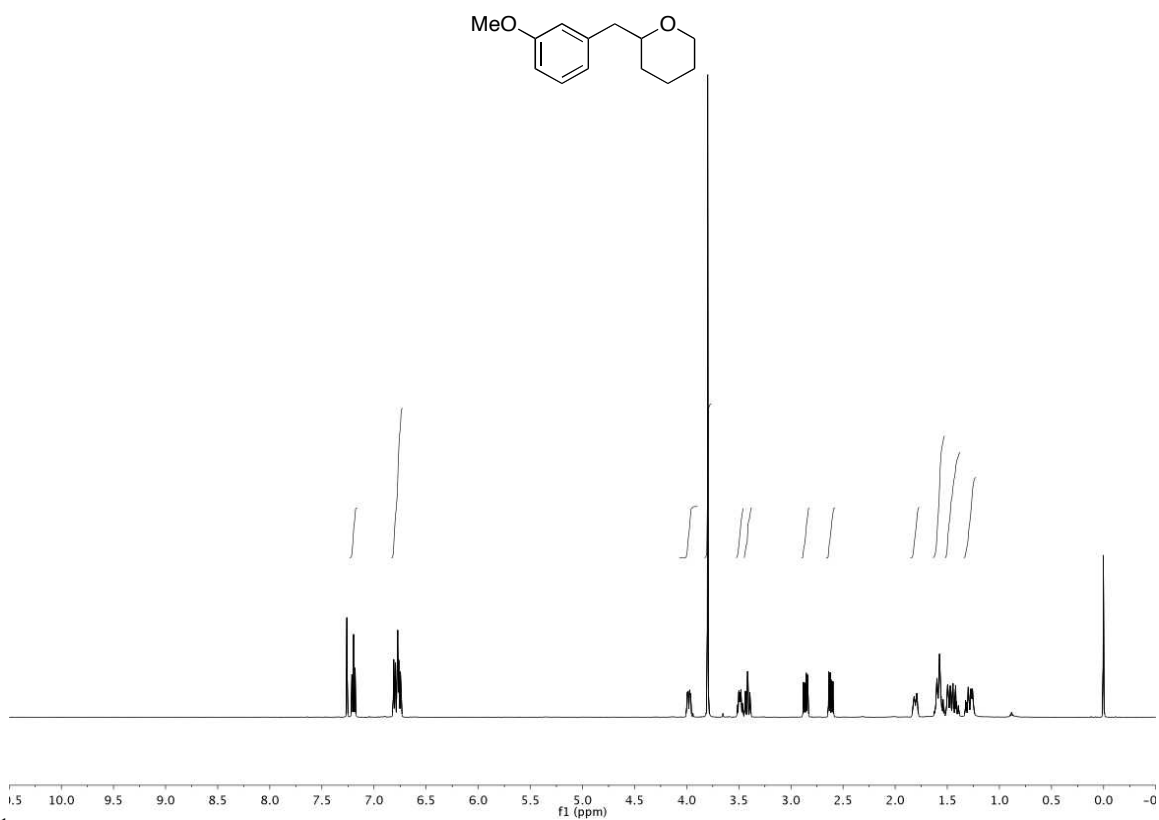
**2-(2-Methylbenzyl)tetrahydrofuran (Table 4, entry 5).** The general procedure was employed using potassium 2-methylphenyltrifluoroborate (100.9 mg, 0.51 mmol) and tetrahydrofurfuryl chloride (60.3 mg, 0.50 mmol). The reaction time was 26 h and the compound was obtained as a colorless oil (52.5 mg, 60%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22-7.18 (m, 1H), 7.17-7.10 (m, 3H), 4.14-4.06 (m, 1H), 3.96-3.89 (m, 1H), 3.79-3.72 (m, 1H), 2.97 (dd,  $J$  = 13.9, 6.5 Hz, 1H), 2.75 (dd,  $J$  = 13.9, 6.7 Hz, 1H), 2.35 (s, 3H), 1.99-1.83 (m, 3H), 1.66-1.57 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  137.42, 136.50, 130.33, 129.92, 126.44, 126.02, 79.27, 68.00, 39.20, 31.37, 25.78, 19.84; IR (neat) = 2969, 2866, 1489, 1060, 742  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{12}\text{H}_{16}\text{O}$  ( $\text{M}^+$ ) 176.1201, found 176.1203.



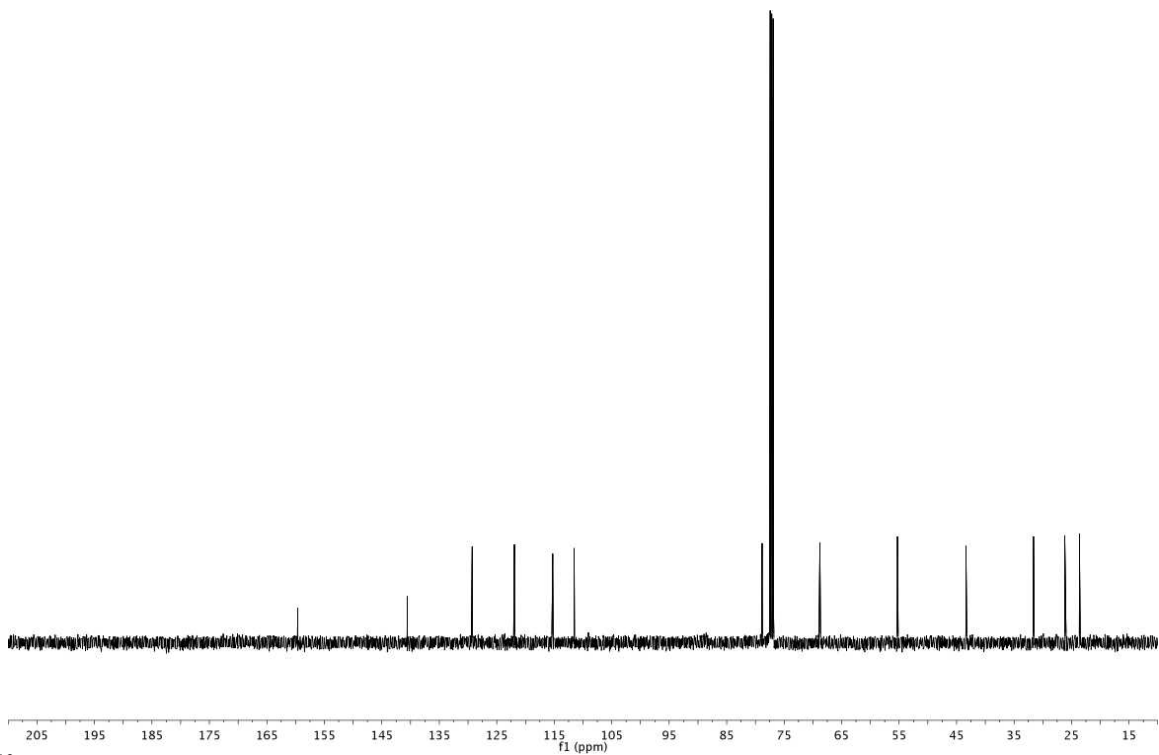
**Cyclohexyl-3-methylbenzene (Table 4, entry 6).** The general procedure was employed using potassium 3-methylphenyltrifluoroborate (100.9 mg, 0.51 mmol) and cyclohexyl chloride (59.3 mg, 0.50 mmol). The reaction time was 26 h and the compound was obtained as a colorless oil (42.5 mg, 49%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (t,  $J$  = 7.5 Hz, 1H), 7.08-7.01 (m, 3H), 2.53-2.46 (m, 1H), 2.37 (s, 3H), 1.95-1.84 (m, 4H), 1.82-1.75 (m, 1H), 1.51-1.37 (m, 4H), 1.35-1.24 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  148.27, 137.91, 128.36, 127.85, 126.70, 124.00, 44.76, 34.67, 27.14, 26.39, 21.68; IR (neat) = 2923, 2851, 1447, 779, 701  $\text{cm}^{-1}$ ; HRMS (CI) calcd. for  $\text{C}_{13}\text{H}_{19}$  ( $\text{M}^+$ ) 175.1487, found 175.1489.

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Fine, R.; Gritzen, C.; Hood, J. D.; Hu, S.; Kachi, S.; Kang, X.; Klebansky, B.; Kousba, A.; Lohse, D.; Mak, C. C.; Martin, M.; McPherson, A.; Pathak, V. P.; Renick, J.; Soll, R.; Umeda, N.; Yee, S.; Yokoi, K.; Zeng, B.; Zhu, H.; Noronha, G. *J. Med. Chem.* **2008**, *51*, 1546-1559.

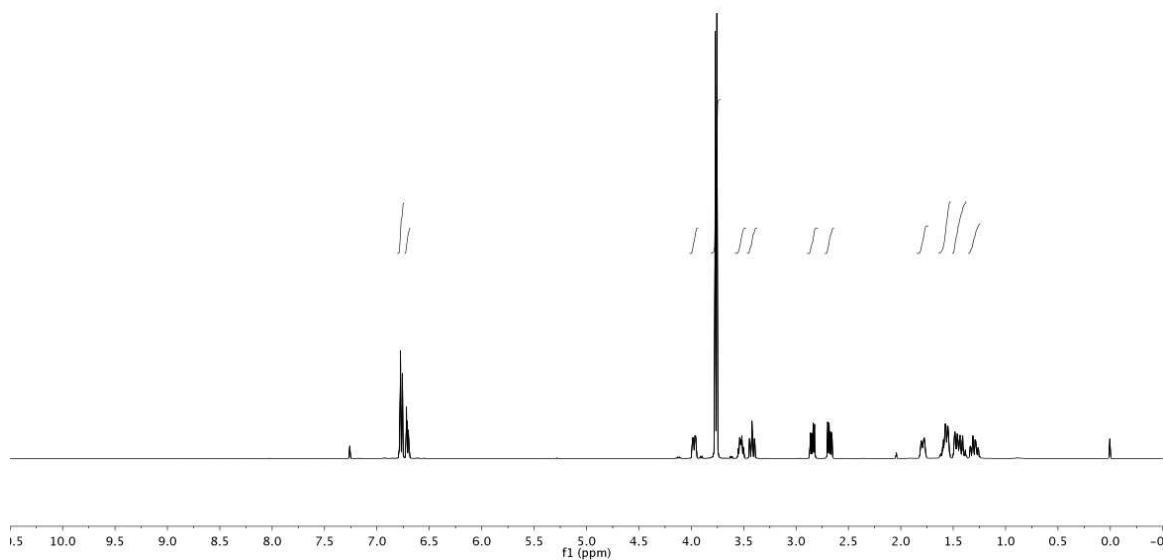
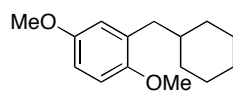


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-(3-methoxybenzyl)tetrahydro-2*H*-pyran (Table 1, entry 1, R = H)

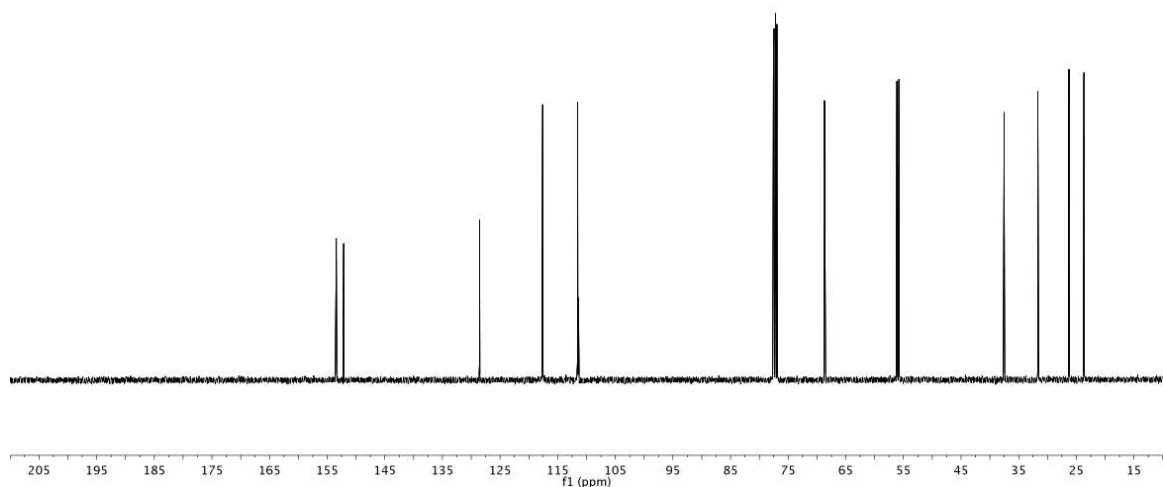


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 2-(3-methoxybenzyl)tetrahydro-2*H*-pyran (Table 1, entry 1, R = H)

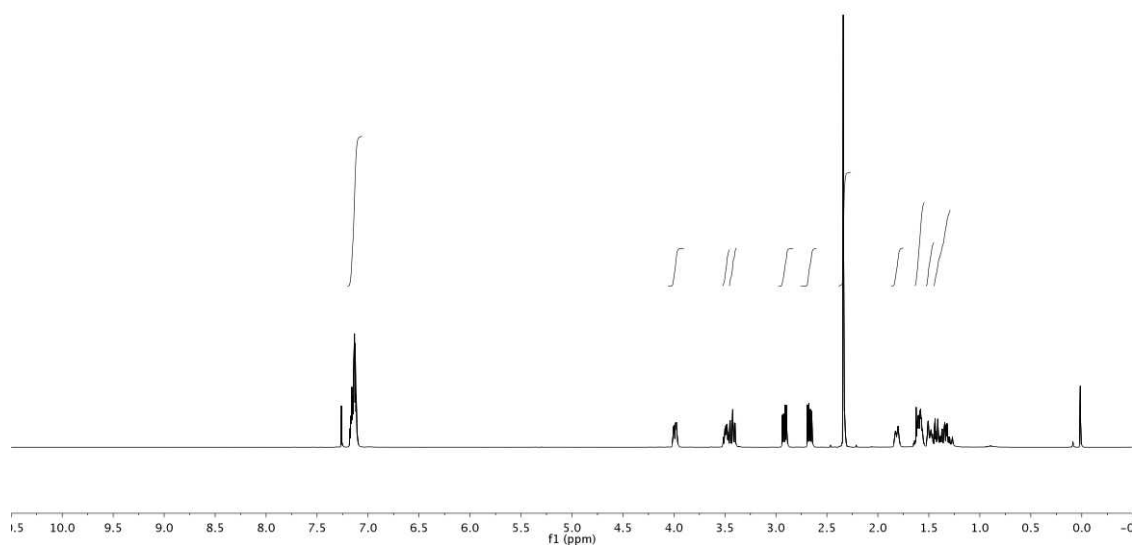
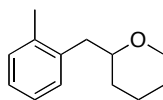




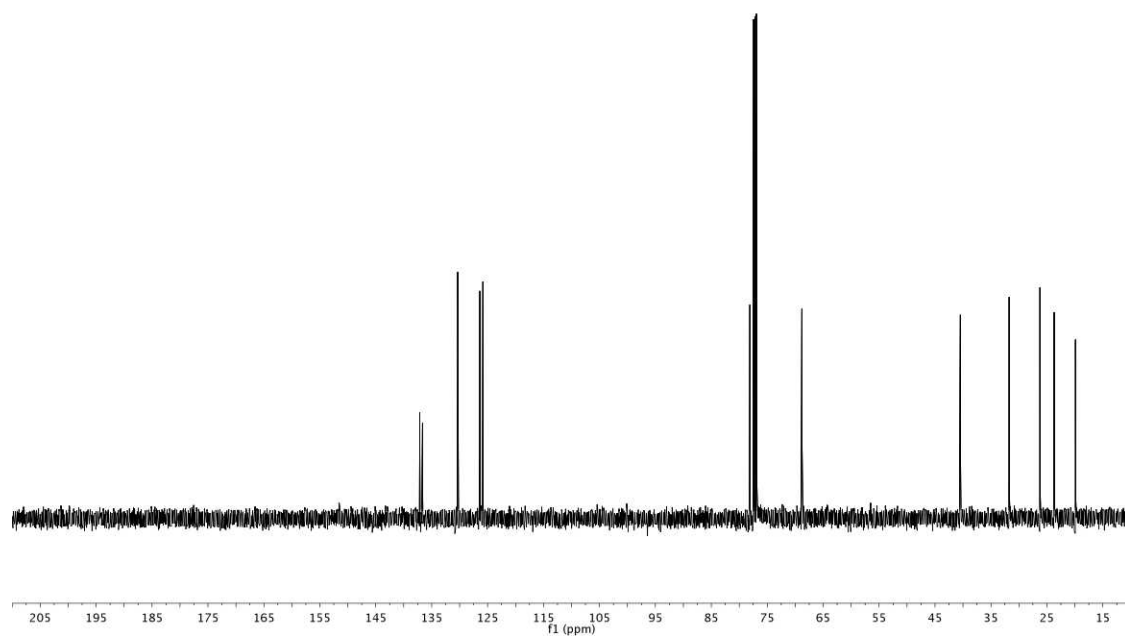
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-(2,5-dimethoxybenzyl)tetrahydro-2*H*-pyran (Table 1, entry 1, R = OMe)



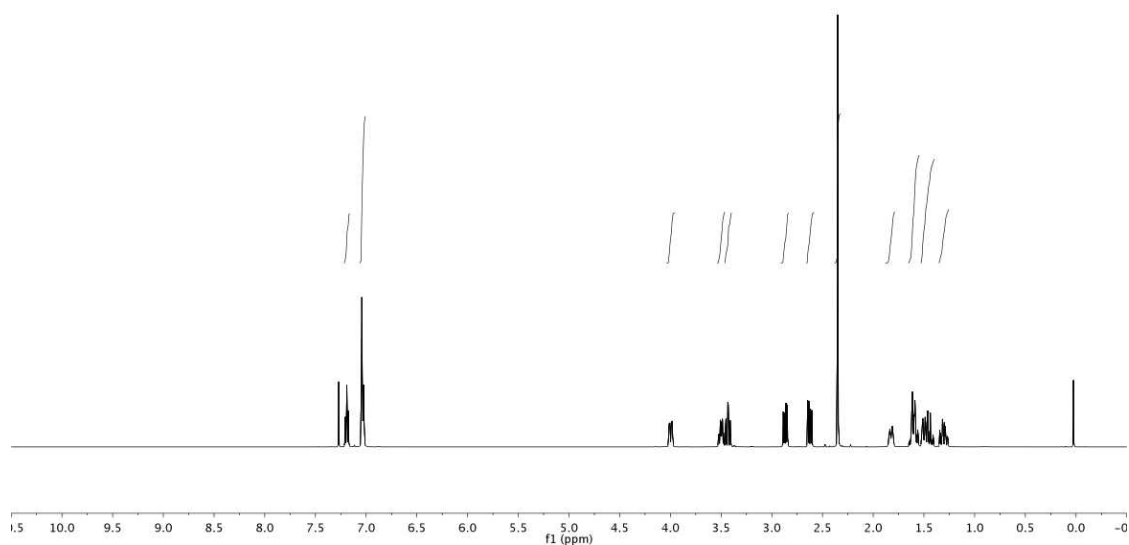
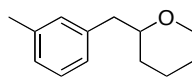
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-(2,5-dimethoxybenzyl)tetrahydro-2*H*-pyran (Table 1, entry 1, R = OMe)



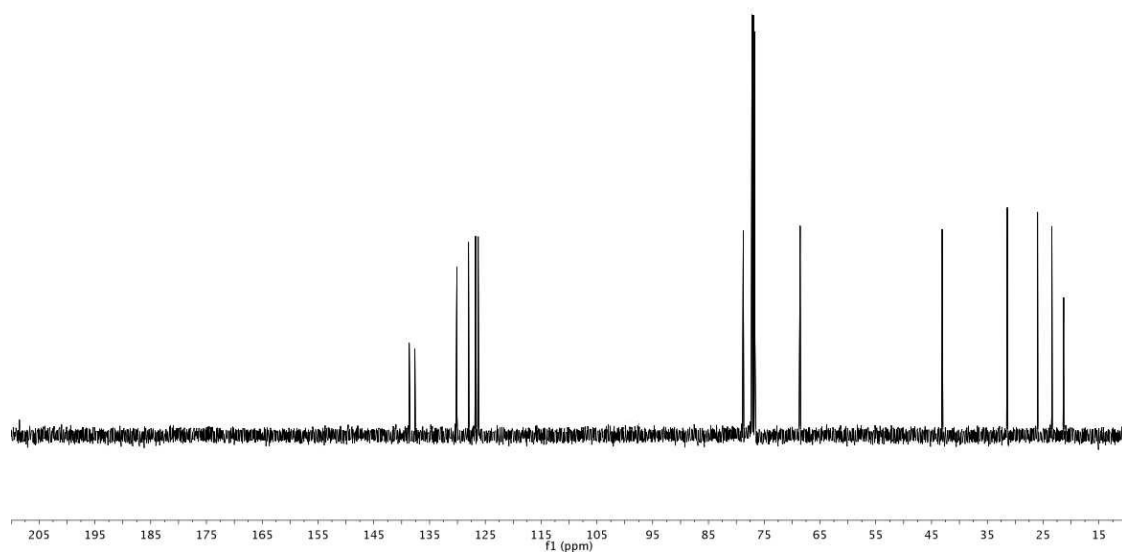
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-(2-methylbenzyl)tetrahydro-2*H*-pyran (Table 1, entry 2, R = *o*-Me)



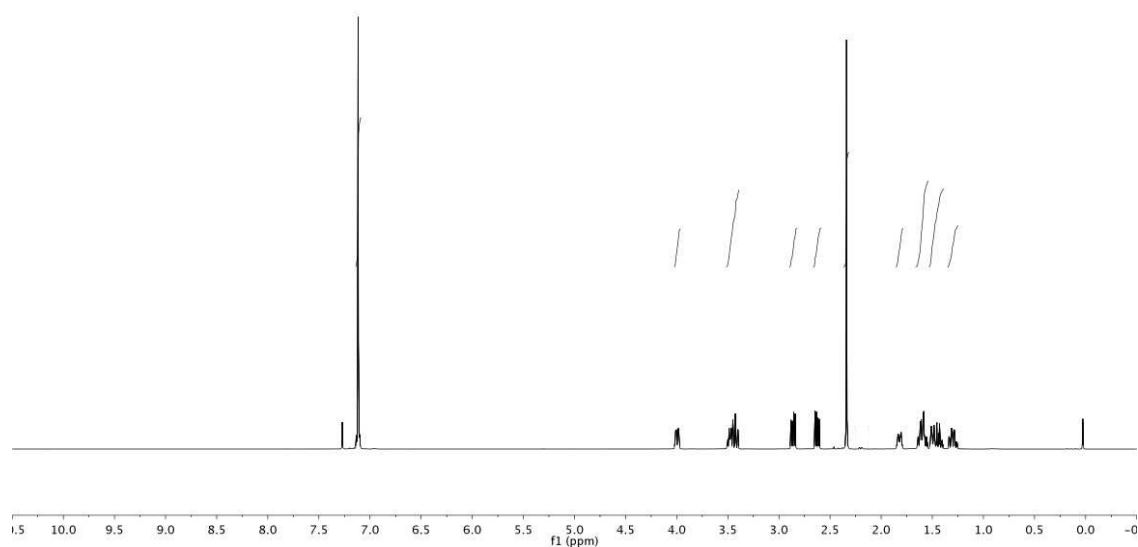
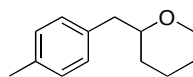
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-(2-methylbenzyl)tetrahydro-2*H*-pyran (Table 1, entry 2, R = *o*-Me)



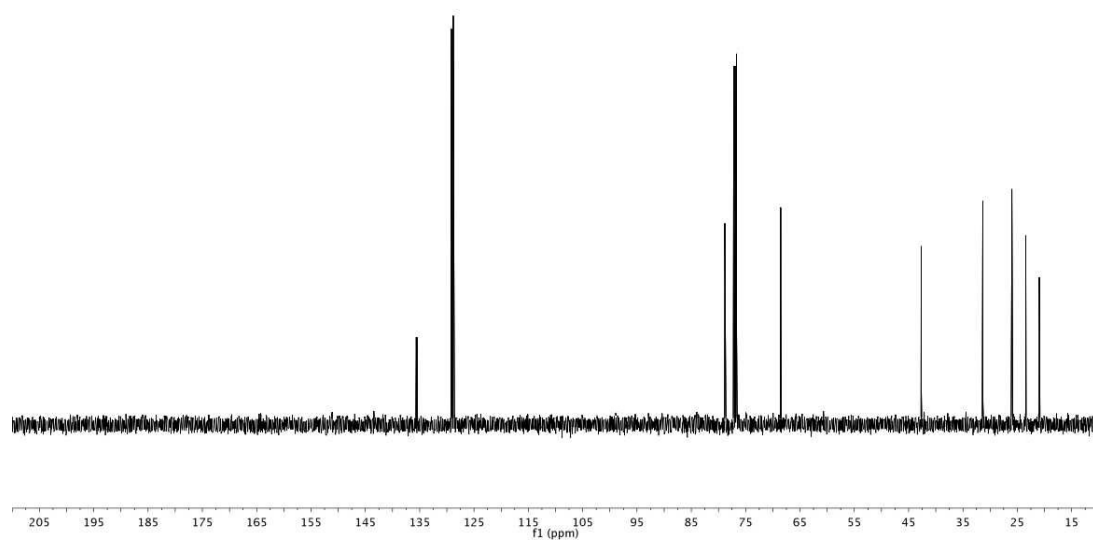
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-(3-methylbenzyl)tetrahydro-2*H*-pyran (Table 1, entry 2, R = *m*-Me)



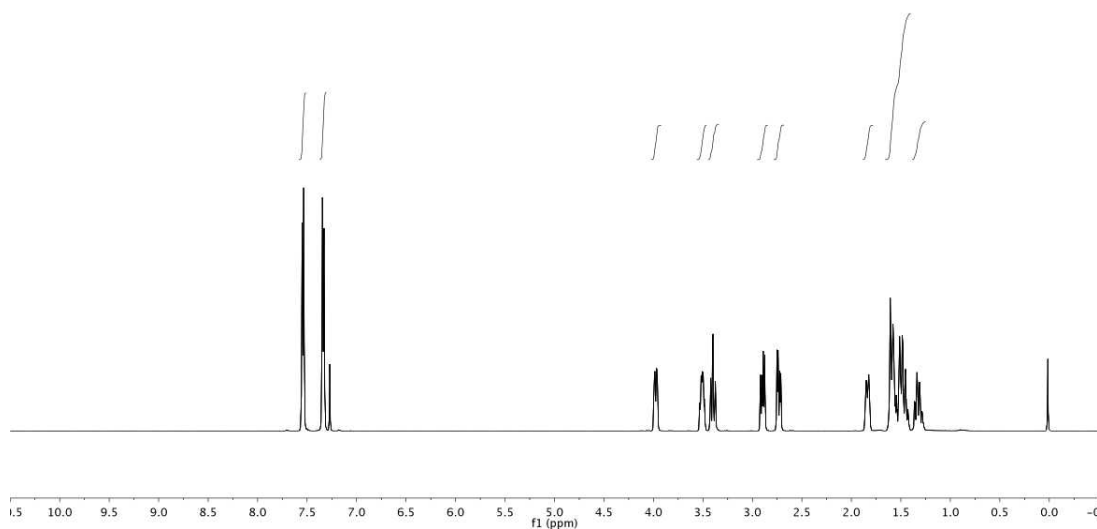
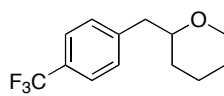
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-(3-methylbenzyl)tetrahydro-2*H*-pyran (Table 1, entry 2, R = *m*-Me)



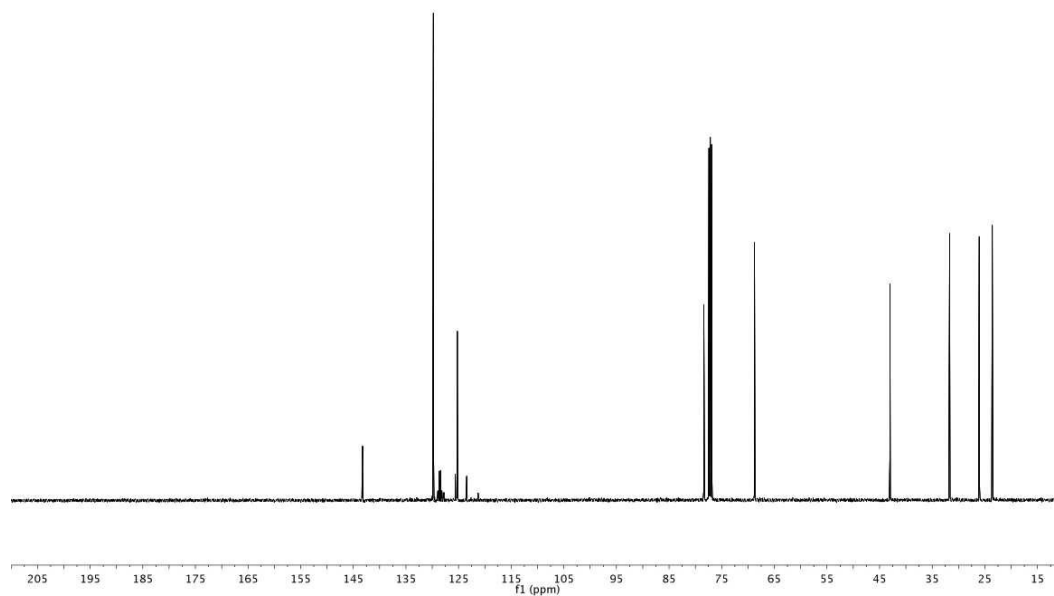
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-(4-methylbenzyl)tetrahydro-2*H*-pyran (Table 1, entry 2, R = *p*-Me)



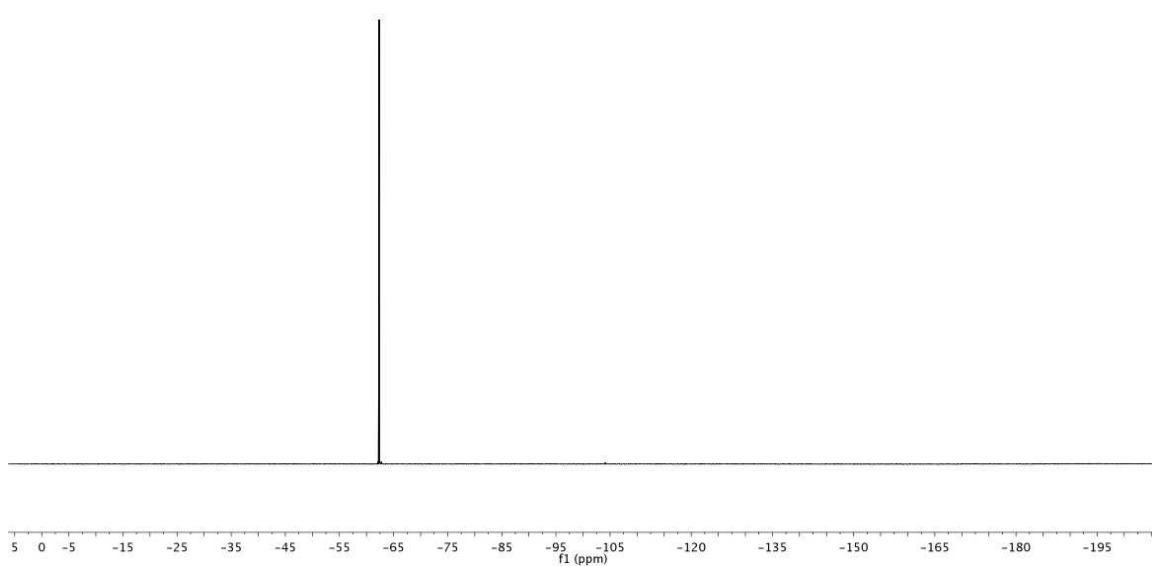
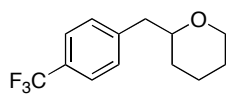
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-(4-methylbenzyl)tetrahydro-2*H*-pyran (Table 1, entry 2, R = *p*-Me)



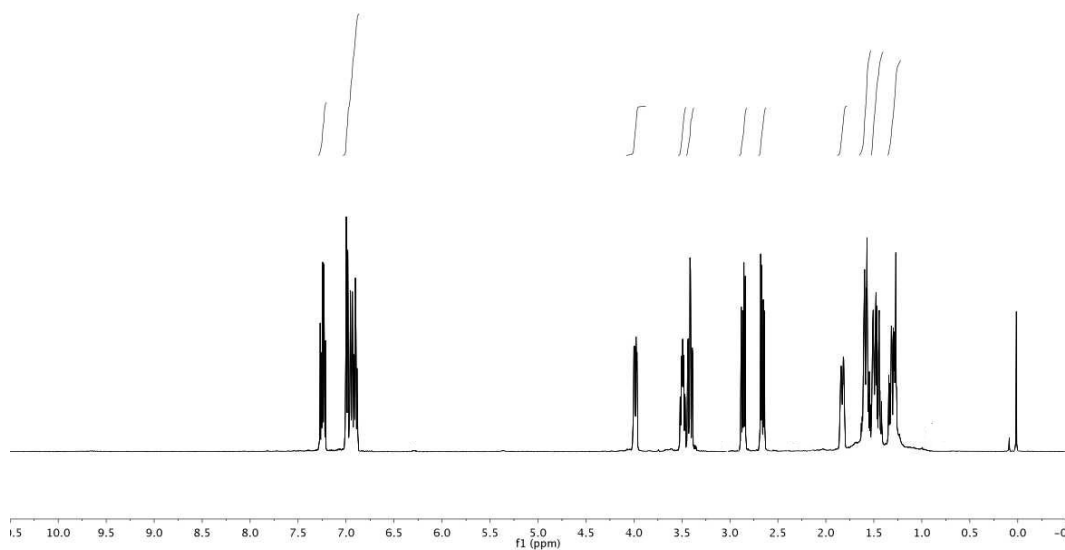
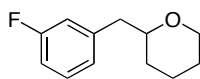
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-(4-(trifluoromethyl)benzyl)tetrahydro-2*H*-pyran (Table 1, entry 3)



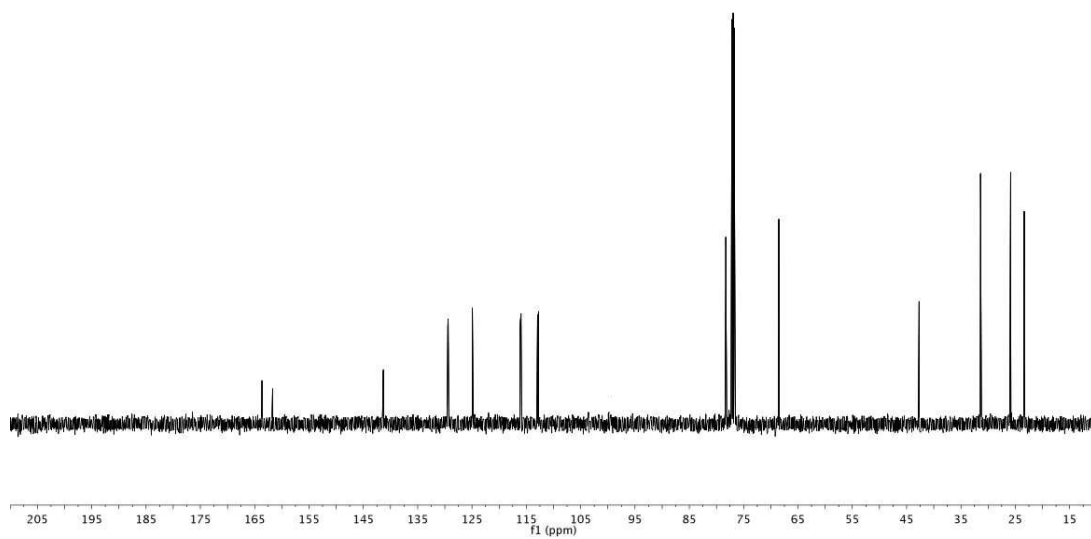
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-(4-(trifluoromethyl)benzyl)tetrahydro-2*H*-pyran (Table 1, entry 3)



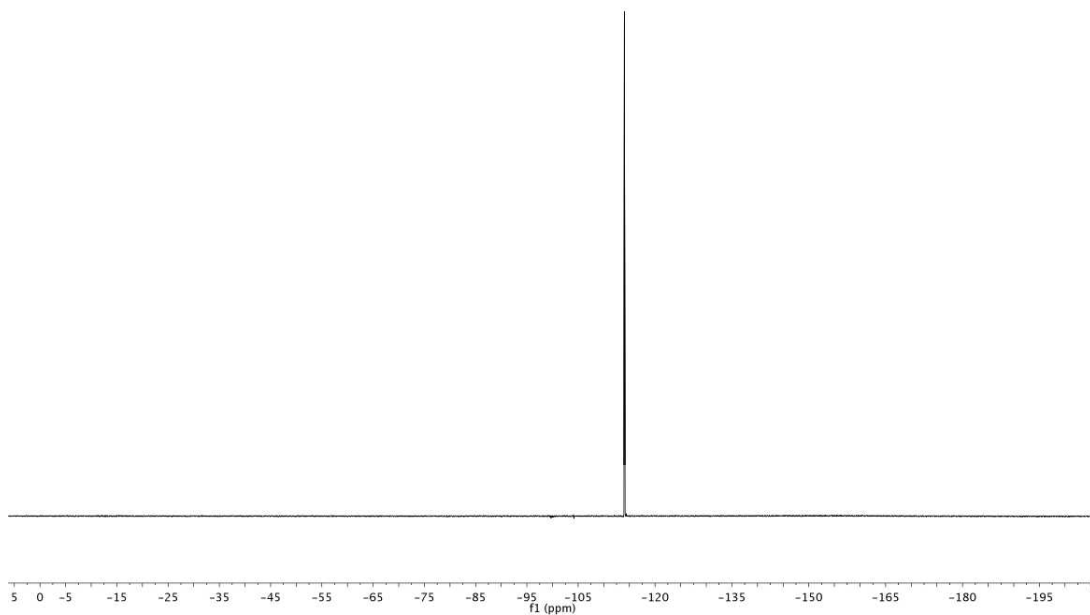
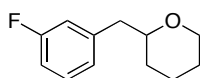
$^{19}\text{F}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ ) of 2-(4-(trifluoromethyl)benzyl)tetrahydro-2*H*-pyran (Table 1, entry 3)



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-(3-fluorobenzyl)tetrahydro-2H-pyran (Table 1, entry 4)

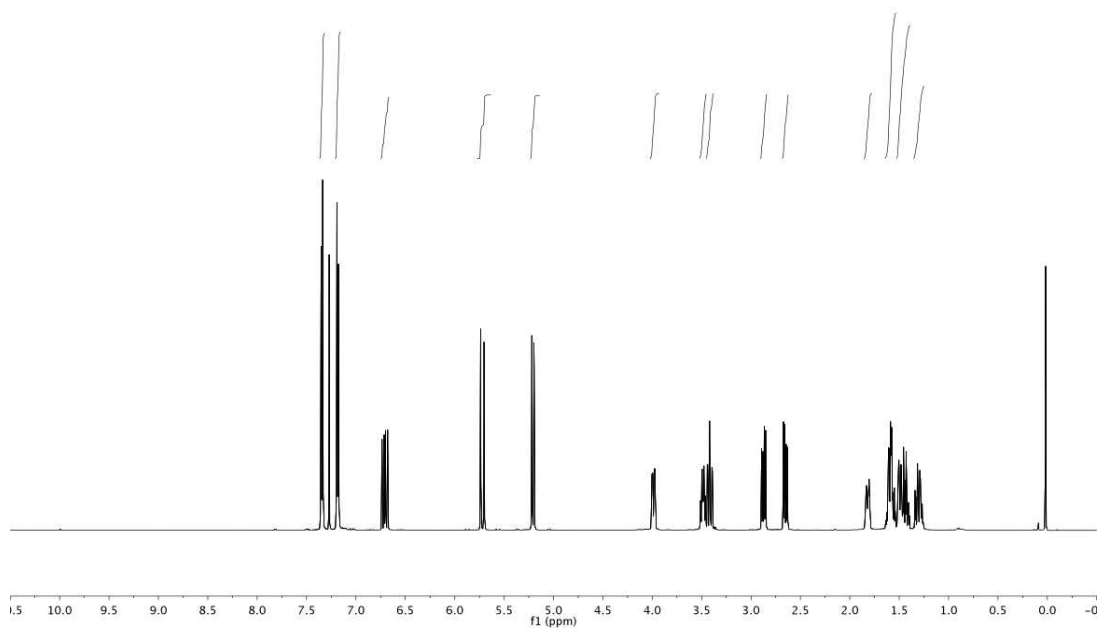
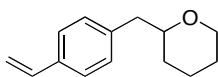


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 2-(3-fluorobenzyl)tetrahydro-2H-pyran (Table 1, entry 4)

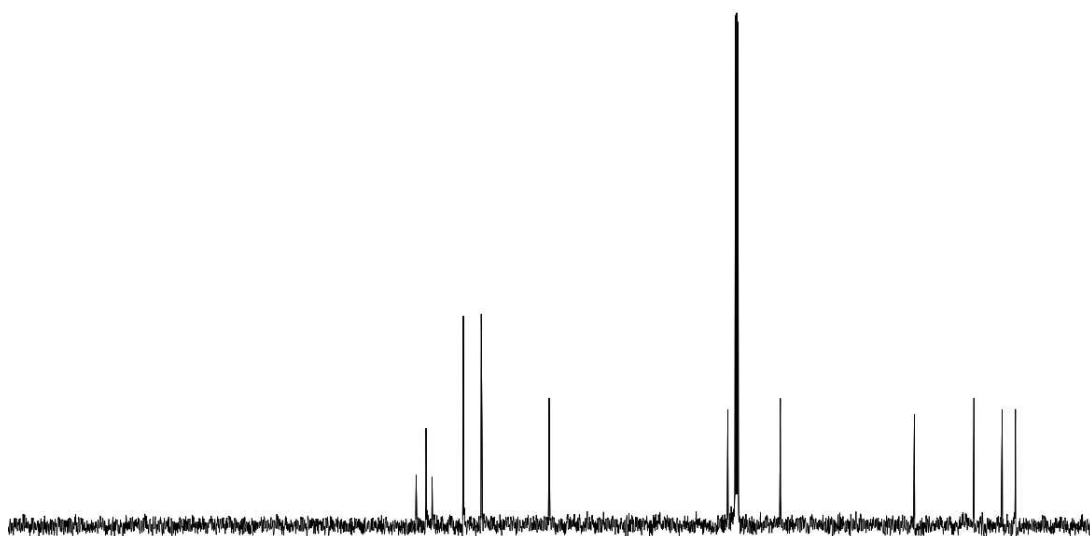


$^{19}\text{F}$  NMR (471 MHz,  $\text{C}_6\text{D}_6$ ) of 2-(3-fluorobenzyl)tetrahydro-2*H*-pyran (Table 1, entry 4)

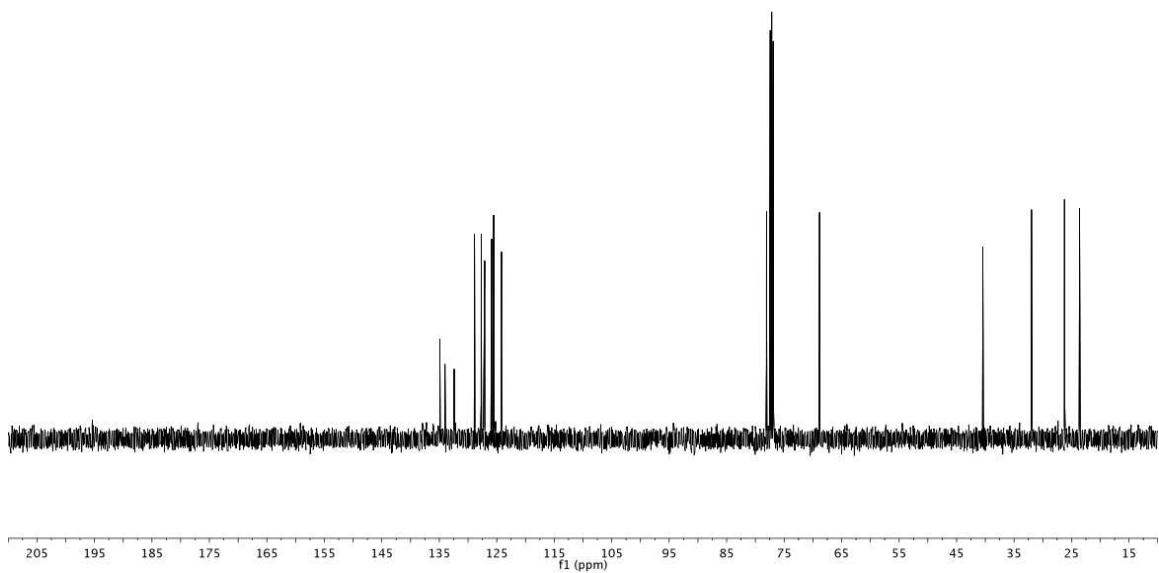
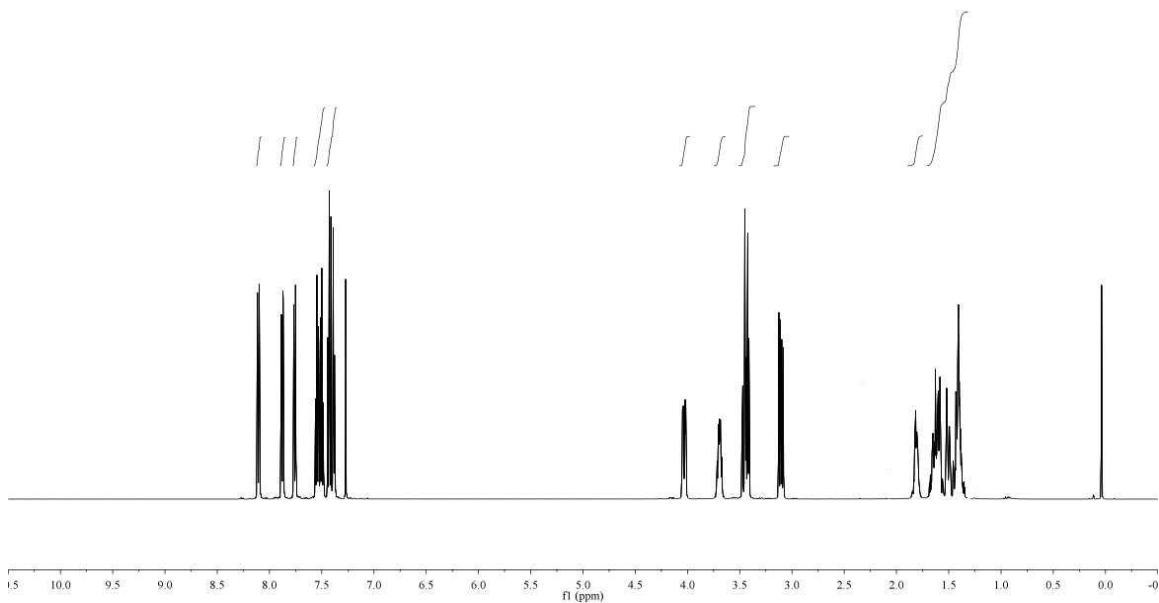
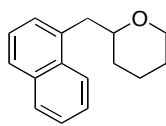


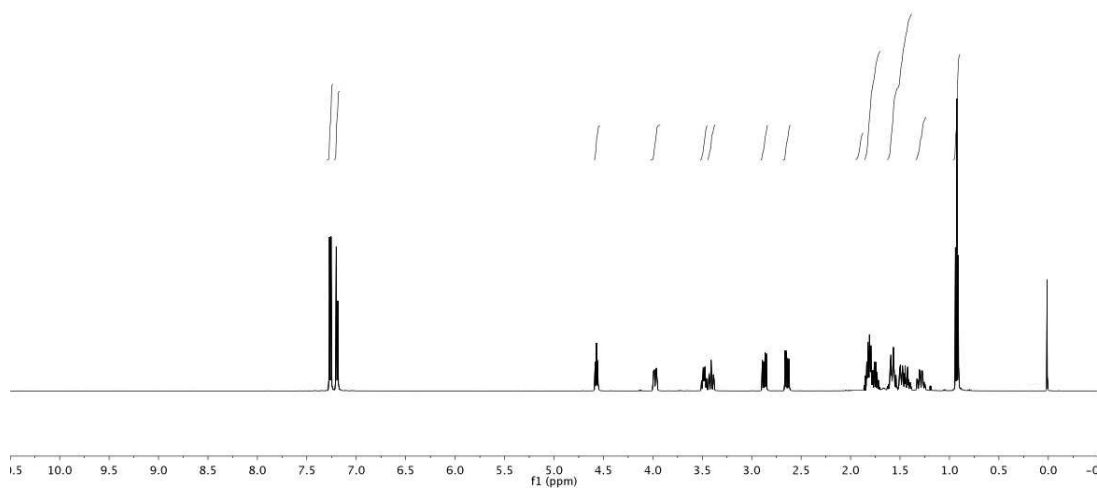
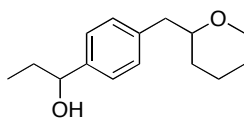


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-(4-Vinylbenzyl)tetrahydro-2*H*-pyran (Table 1, entry 5)

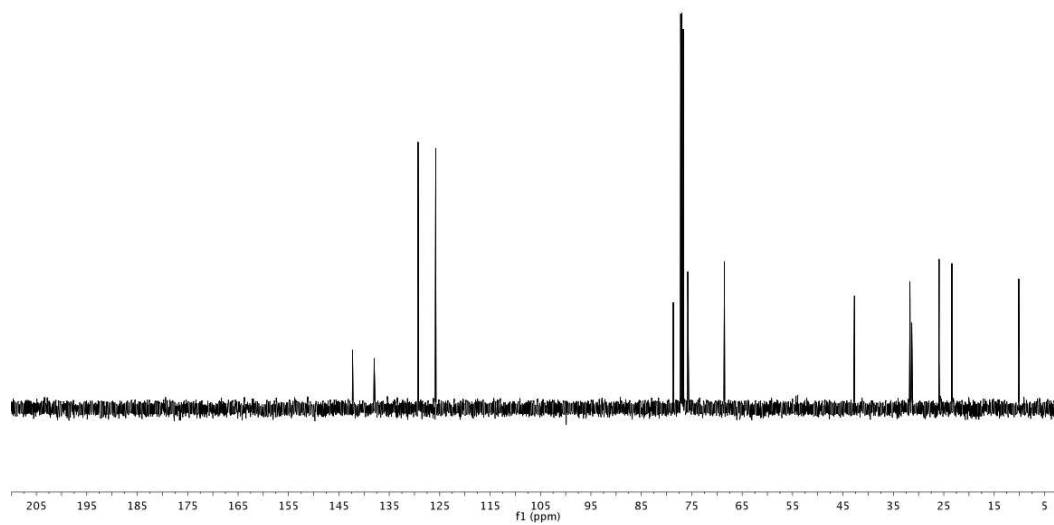


$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-(4-Vinylbenzyl)tetrahydro-2*H*-pyran (Table 1, entry 5)

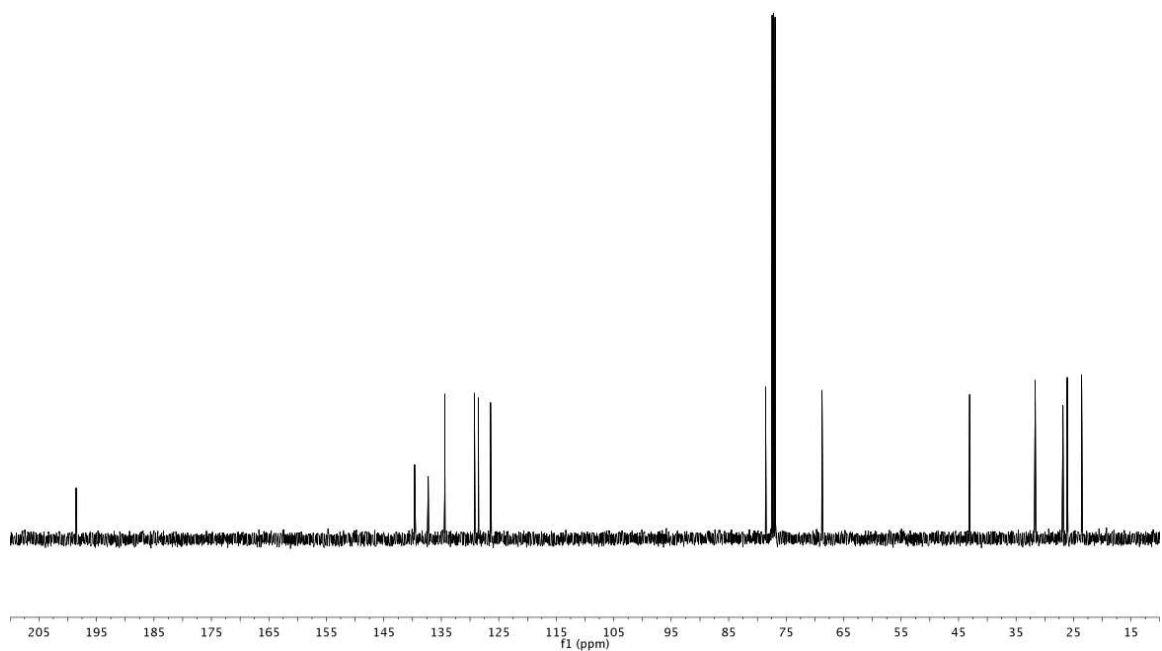
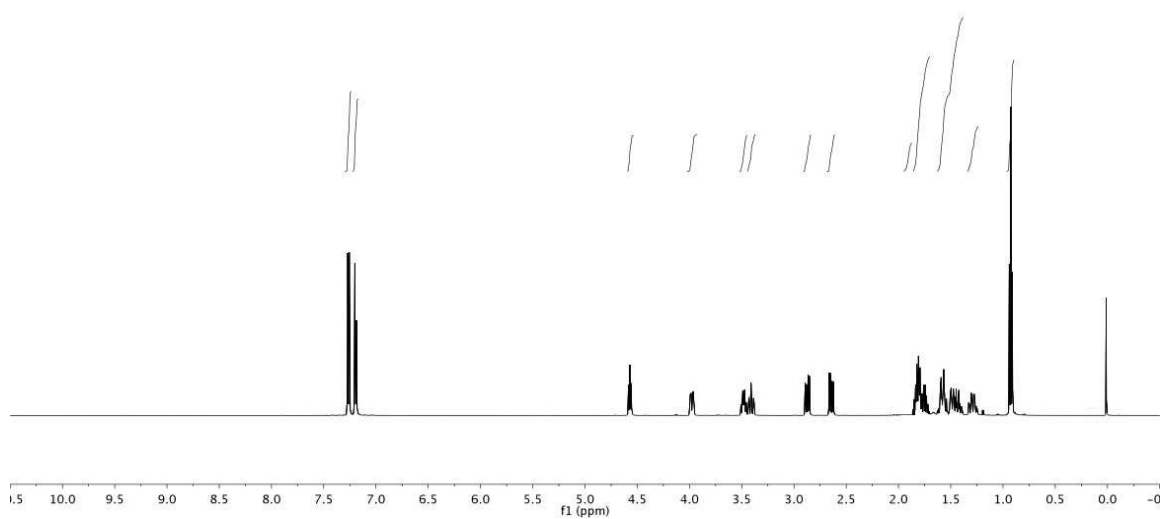
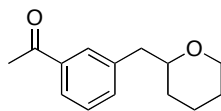


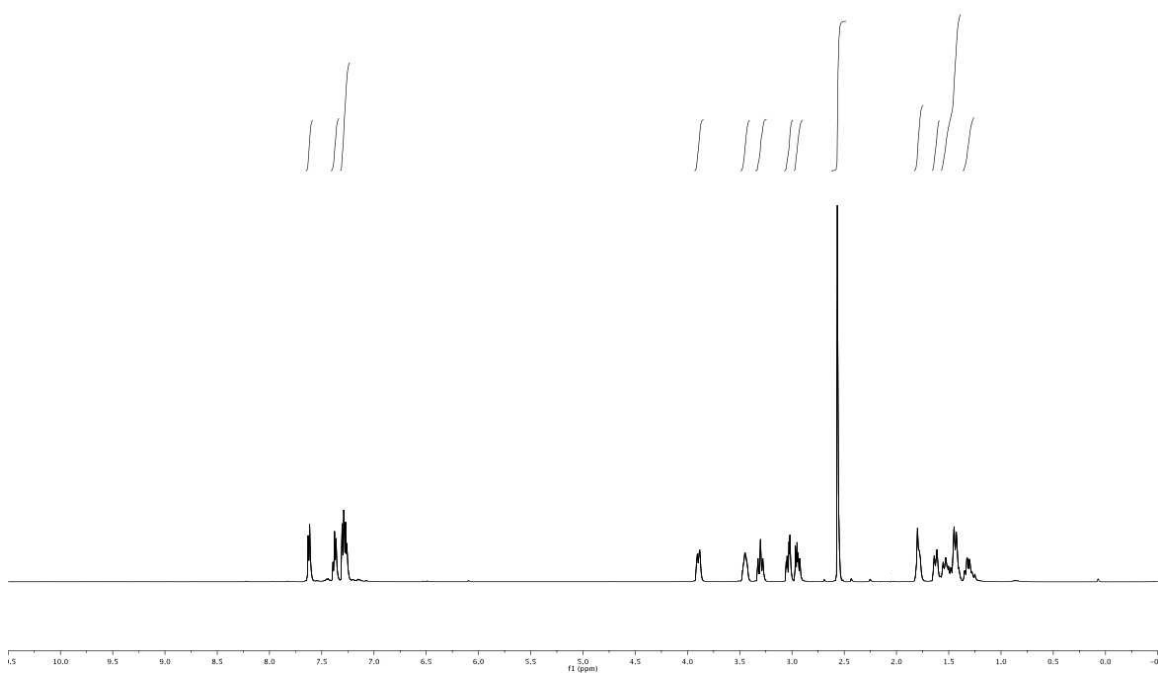
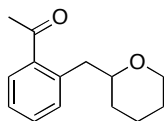


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-(4-(1-hydroxypropyl)benzyl)tetrahydro-2*H*-pyran (Table 1, entry 7)

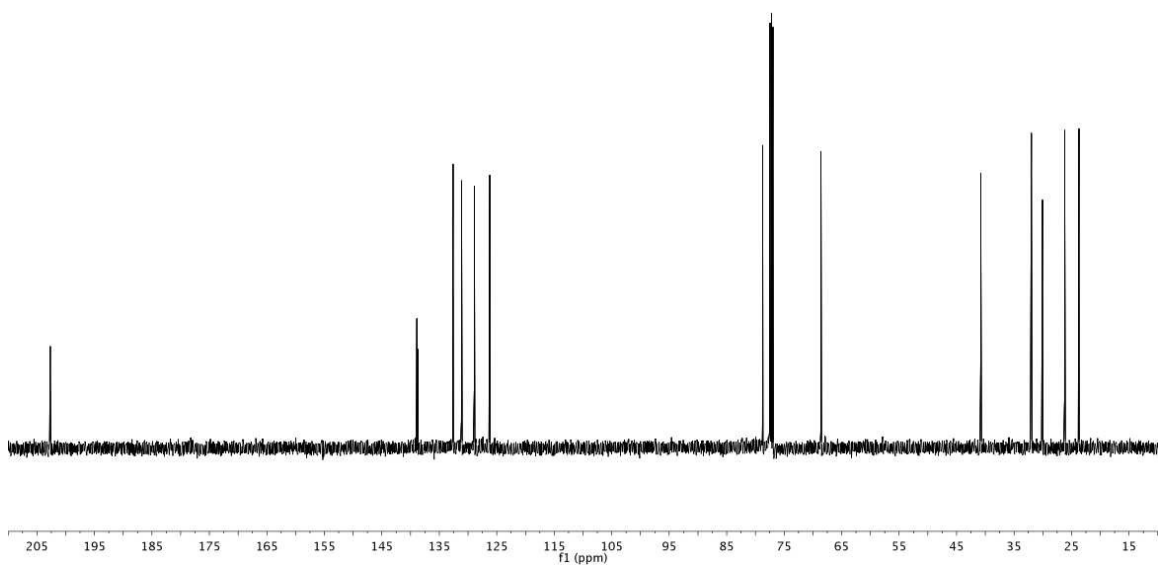


$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-(4-(1-hydroxypropyl)benzyl)tetrahydro-2*H*-pyran (Table 1, entry 7)

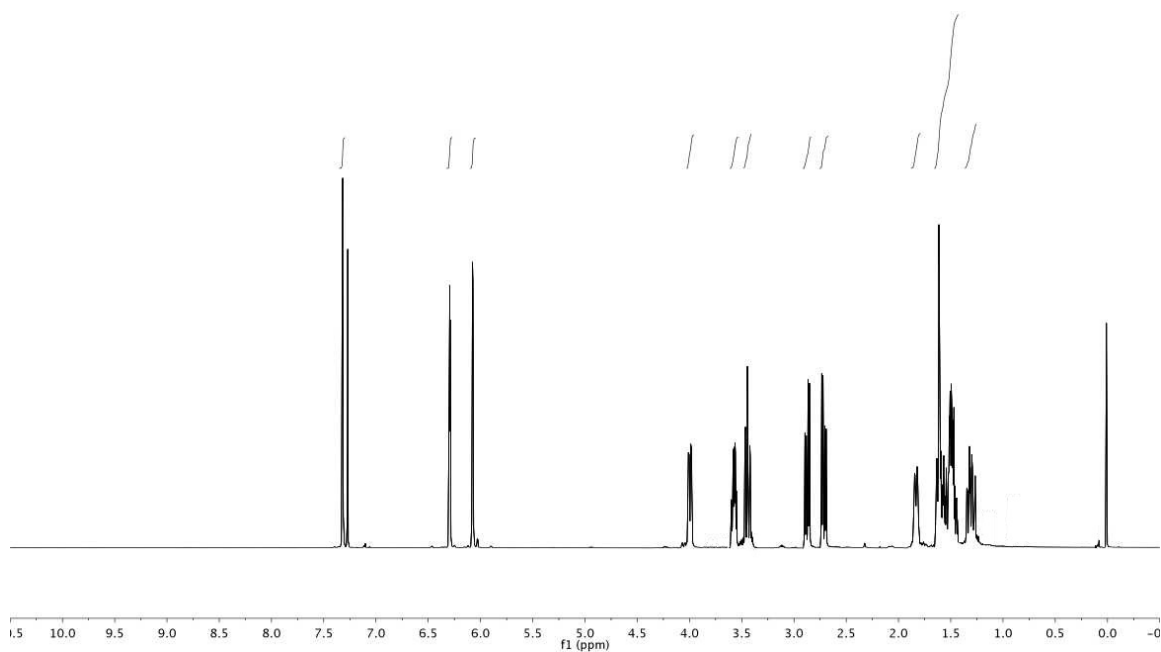
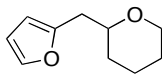




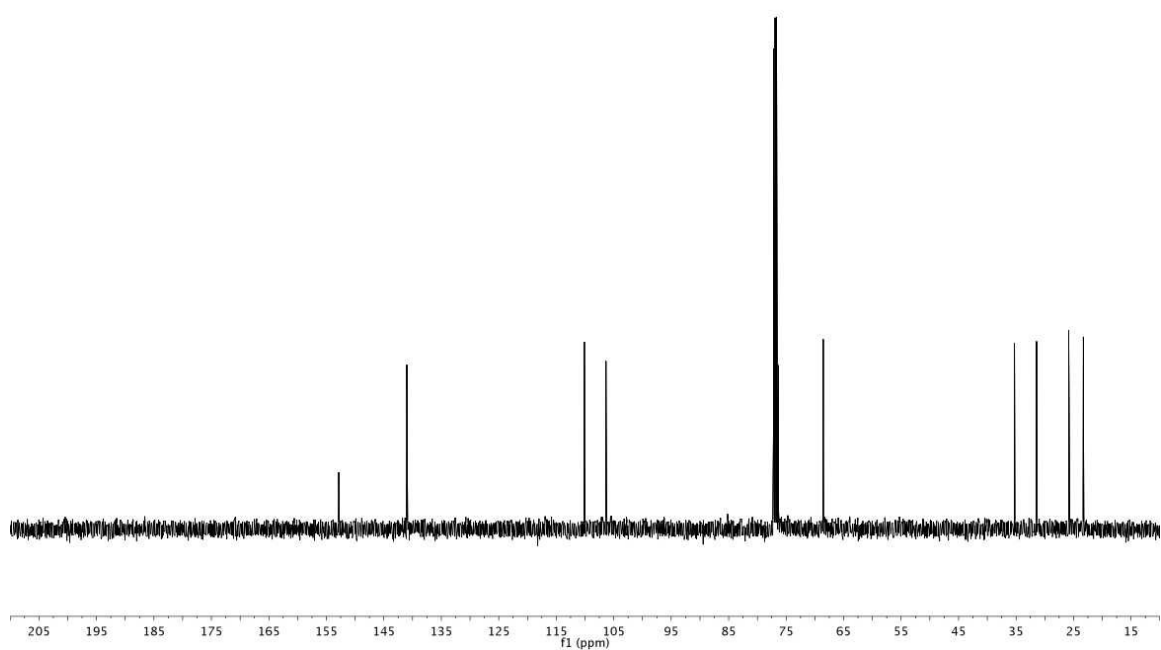
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-(2-acetylbenzyl)tetrahydro-2H-pyran (Table 1, entry 9)



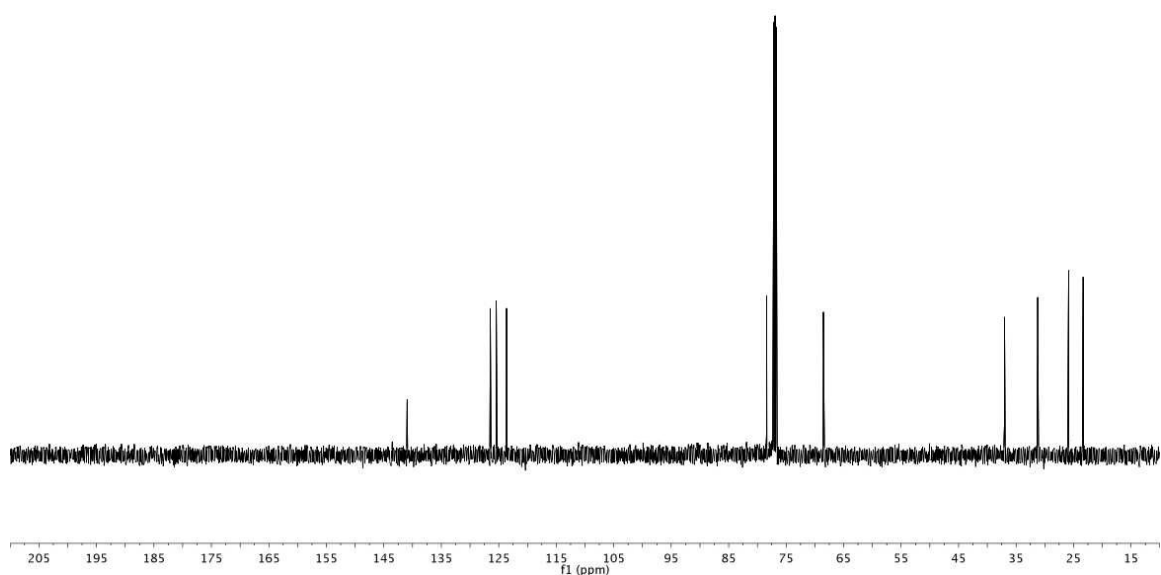
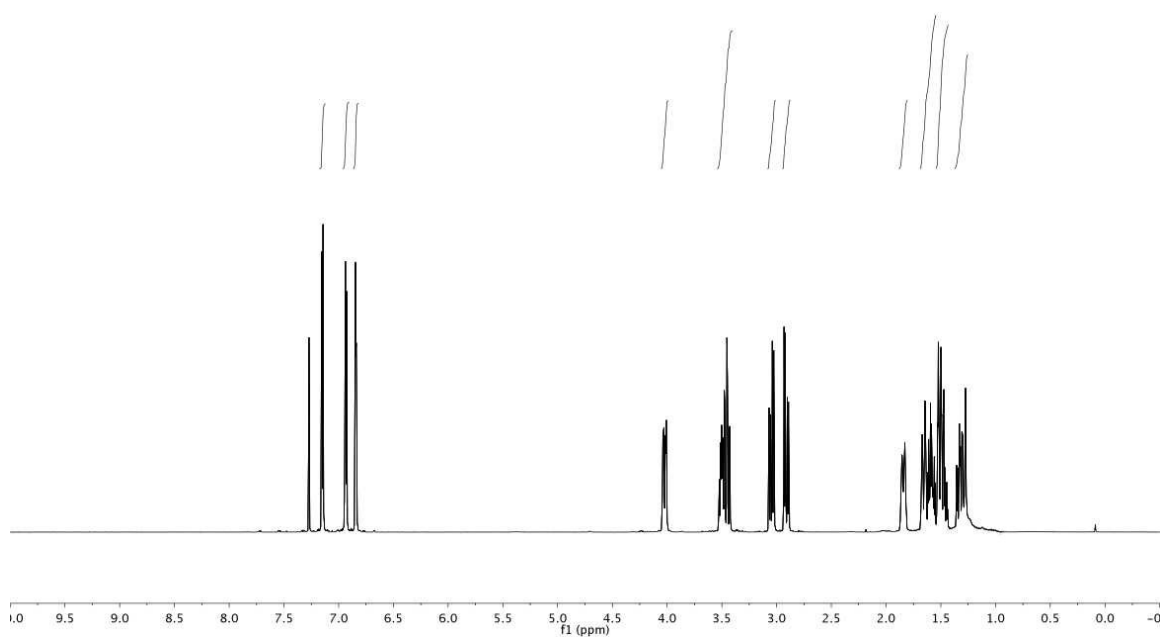
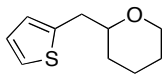
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 2-(2-acetylbenzyl)tetrahydro-2H-pyran (Table 1, entry 9)

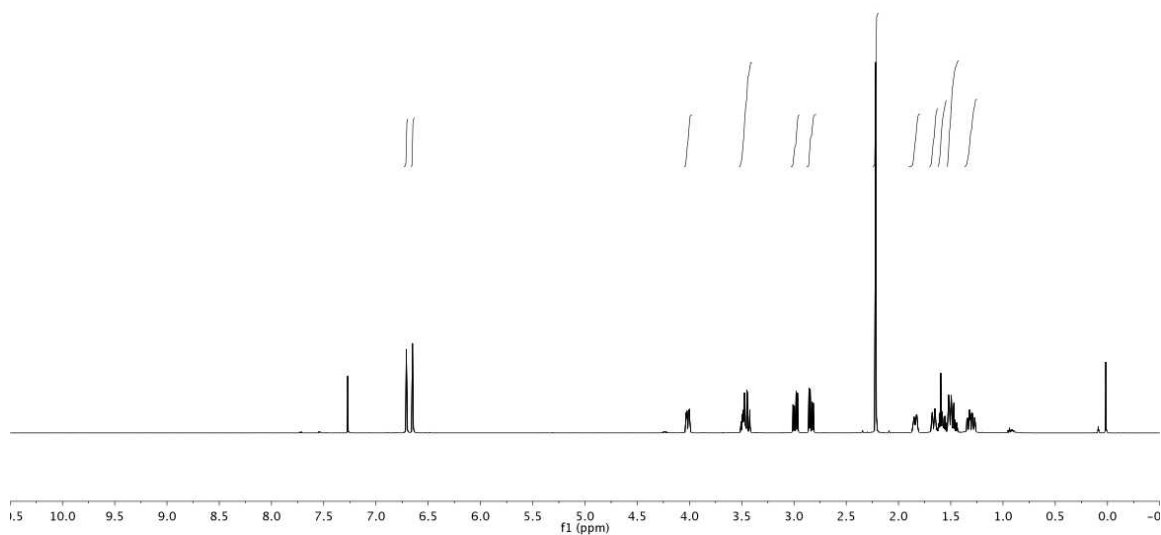
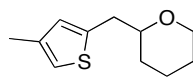


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-(furan-2-ylmethyl)tetrahydro-2*H*-pyran (Table 2, entry 1, X = O)

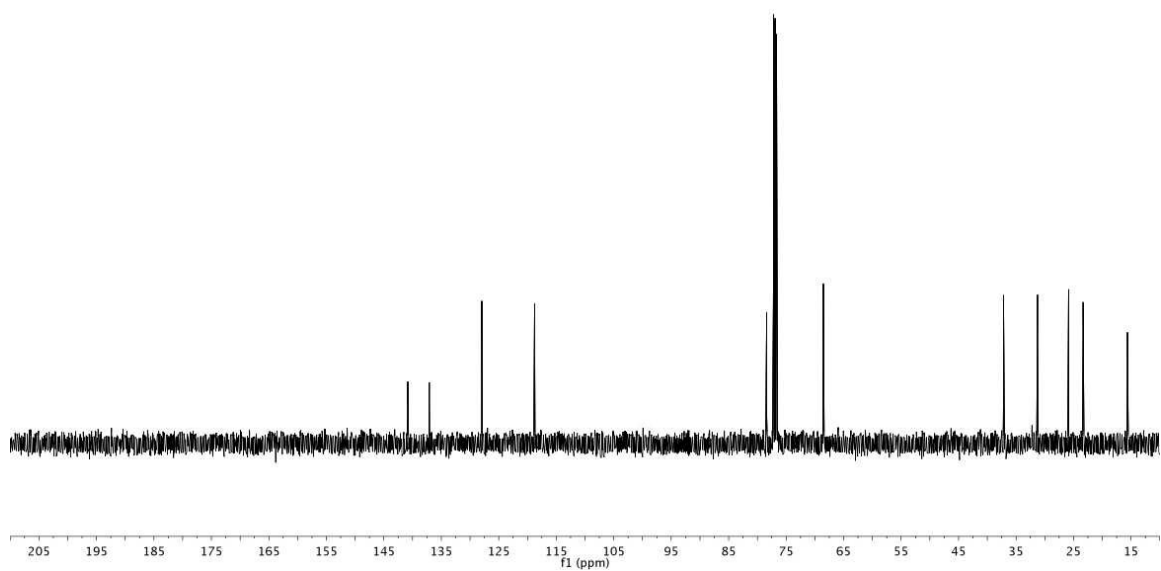


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 2-(furan-2-ylmethyl)tetrahydro-2*H*-pyran (Table 2, entry 1, X = O)



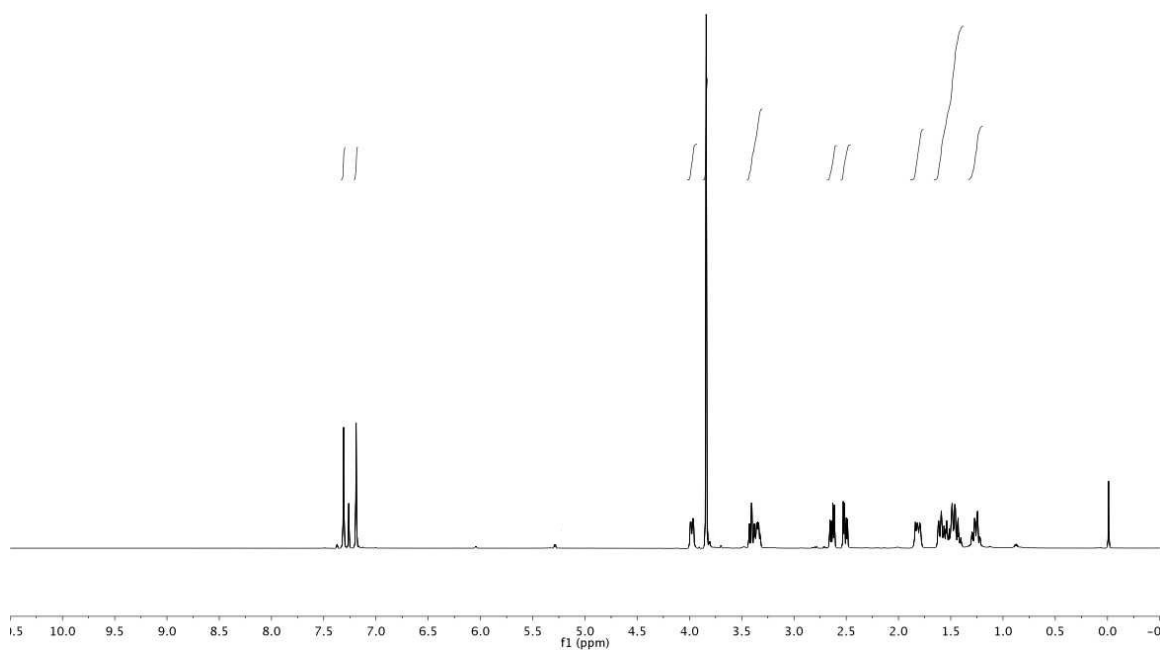
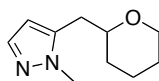


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-((4-methylthiophen-2-yl)methyl)tetrahydro-2*H*-pyran (Table 2, entry 2)

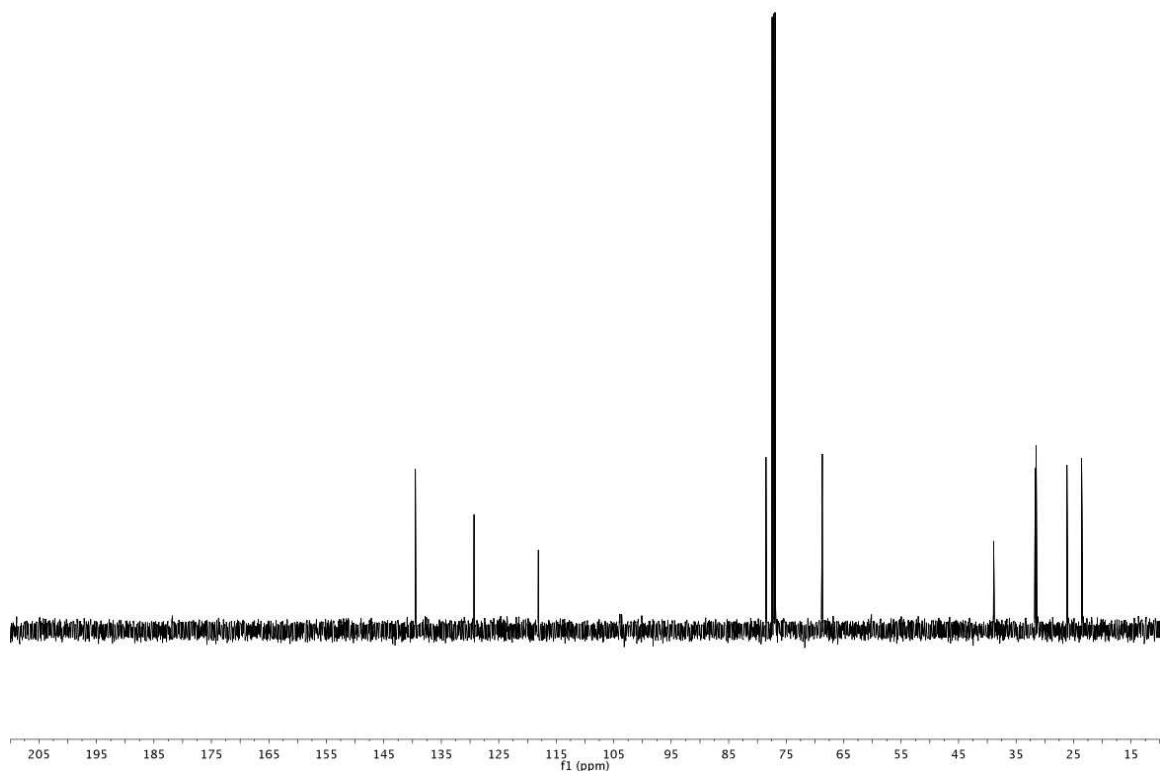


$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-((4-methylthiophen-2-yl)methyl)tetrahydro-2*H*-pyran (Table 2, entry 2)

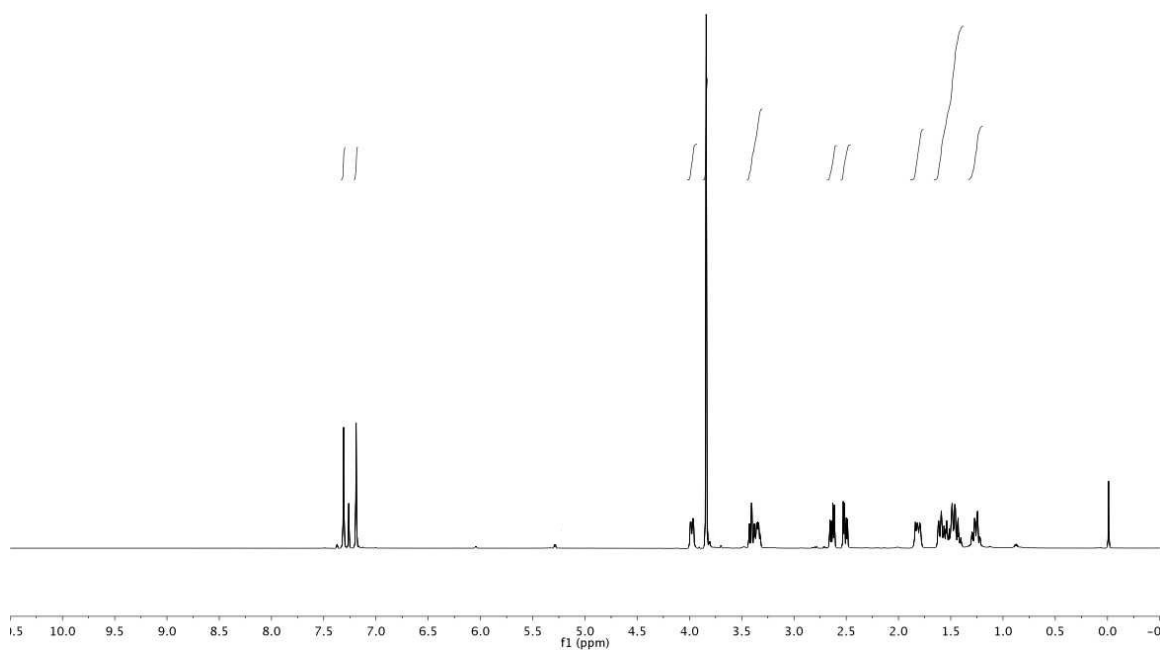




$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 1-methyl-5-(tetrahydro-2*H*-pyran-2-yl)methyl-1*H*-pyrazole (Table 2, entry 3)

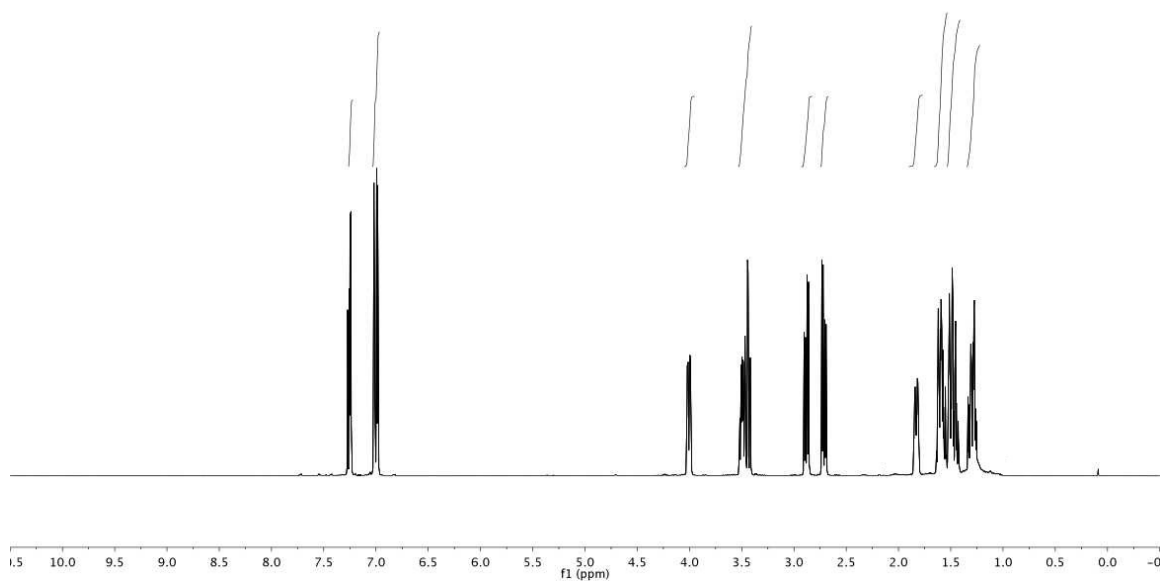
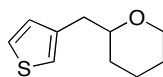


$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 1-methyl-5-(tetrahydro-2*H*-pyran-2-yl)methyl-1*H*-pyrazole (Table 2, entry 3)

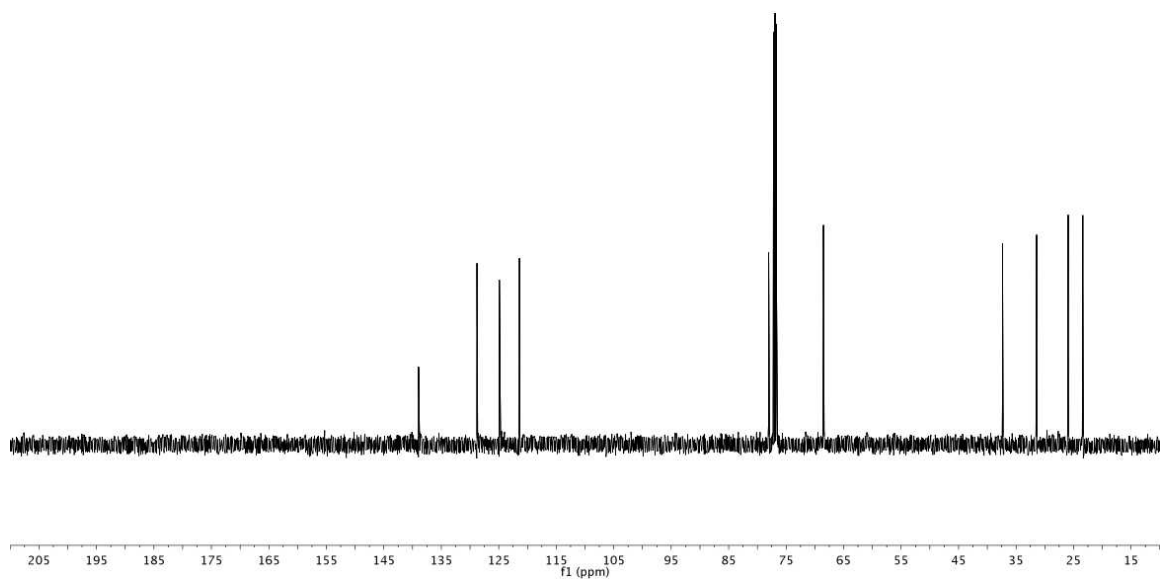


13C NMR spectrum of 1,4-dichlorobenzene in CDCl3. The x-axis is labeled 'f1 (ppm)' and ranges from 205 to 15. The spectrum shows several sharp peaks: a triplet for the solvent CDCl3 at 77.0 ppm, aromatic carbons at 128.5 and 133.0 ppm, and aliphatic carbons at 25.5 and 31.5 ppm. Integration values are shown below the baseline.

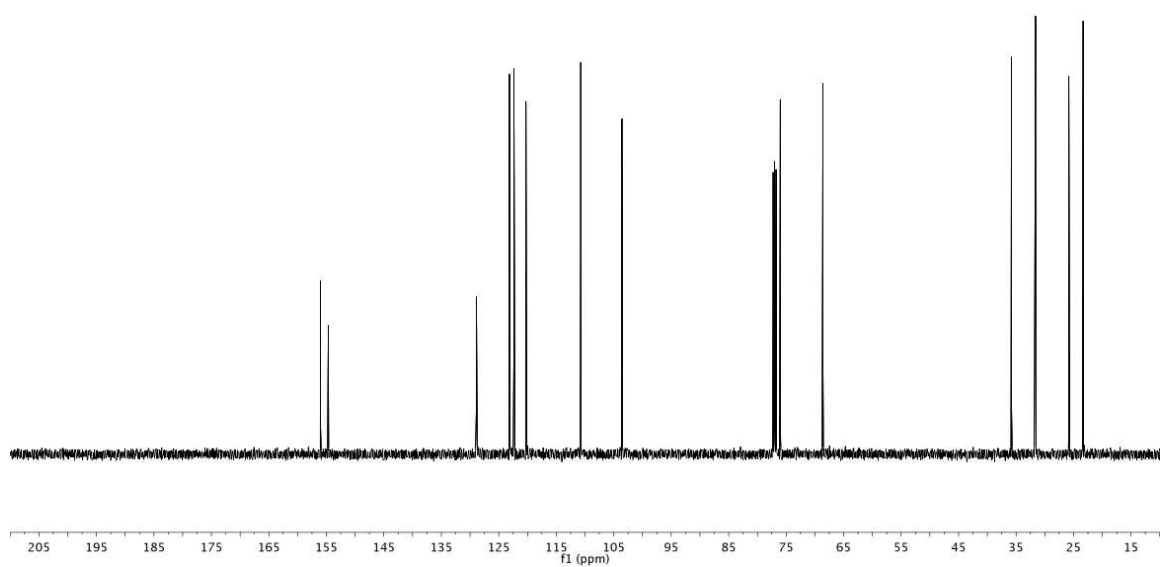
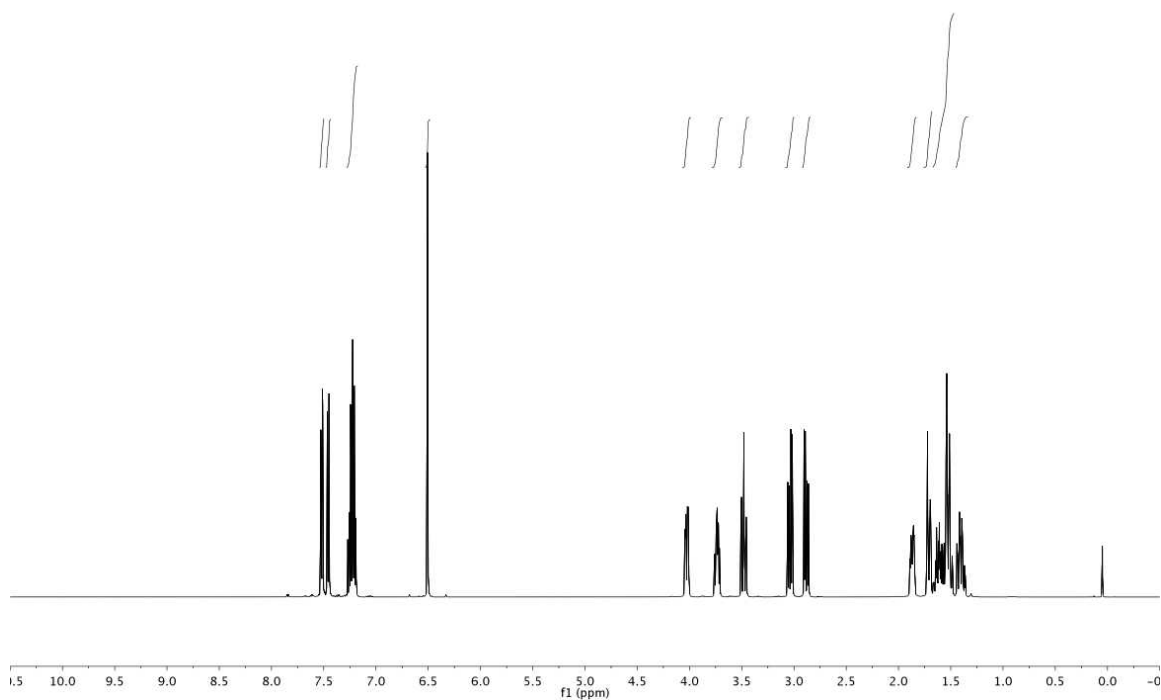
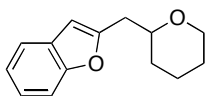
S54

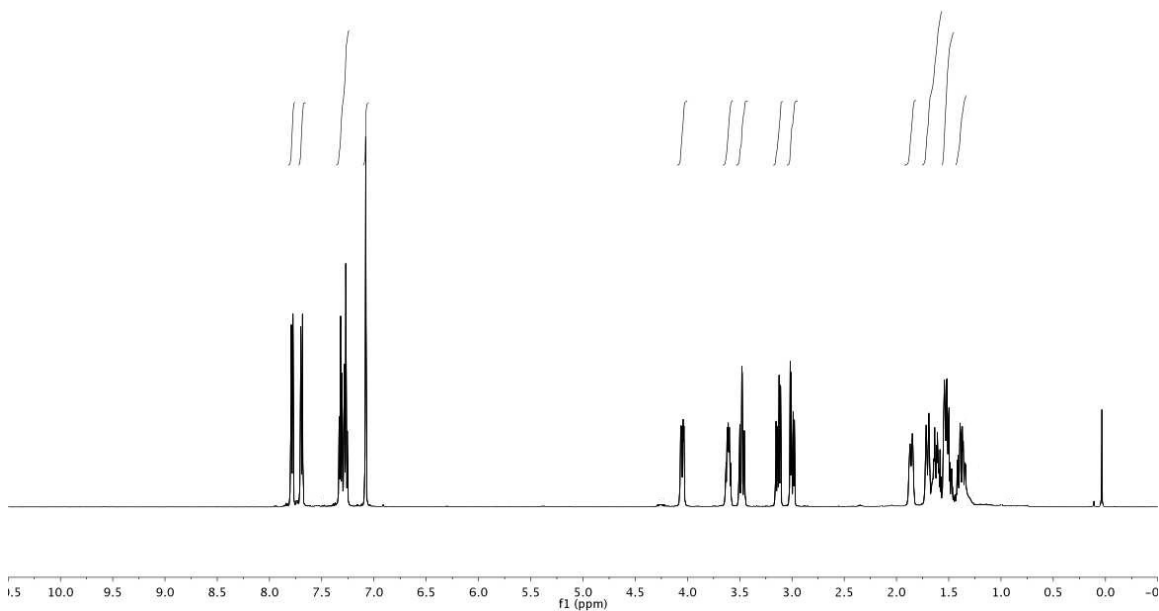
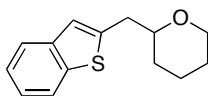


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-(thiophen-3-ylmethyl)tetrahydro-2H-pyran (Table 2, entry 4, X = S)

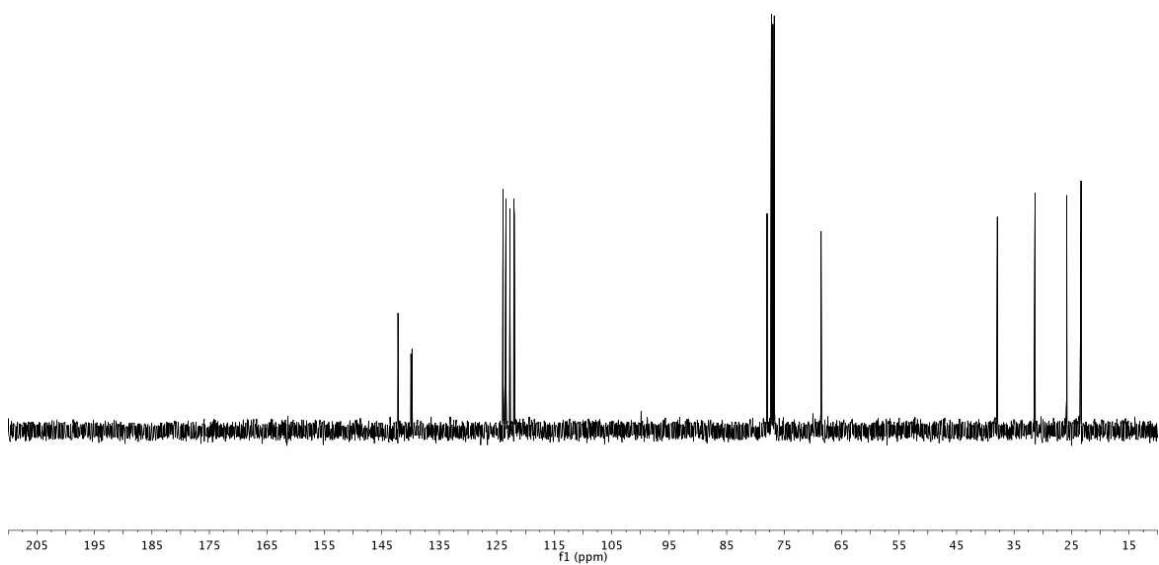


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 2-(thiophen-3-ylmethyl)tetrahydro-2H-pyran (Table 2, entry 4, X = S)





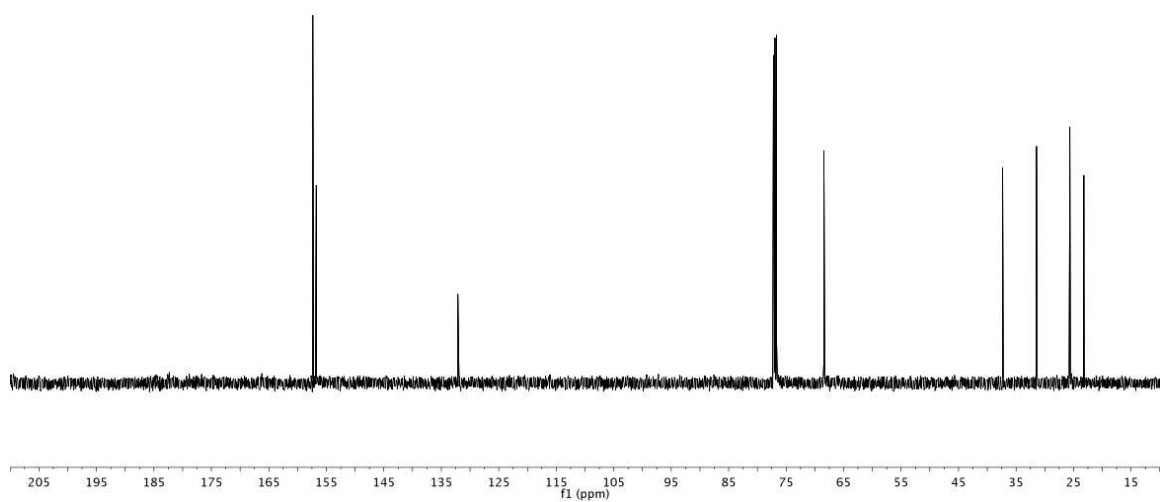
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-(benzo[*b*]thiophen-2-ylmethyl)tetrahydro-2*H*-pyran (Table 2, entry 5, X = S)



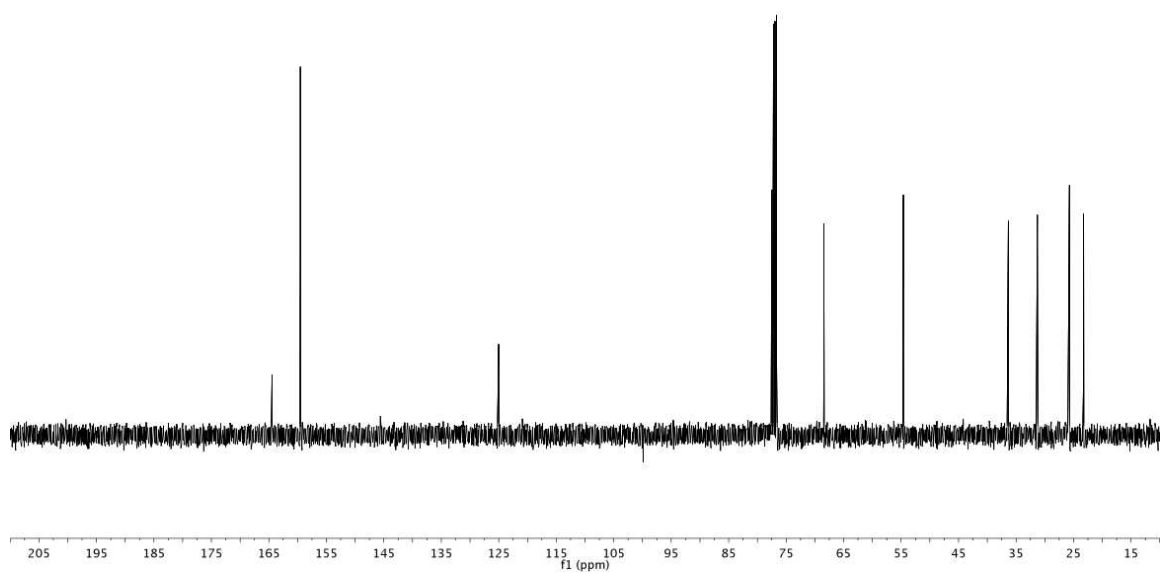
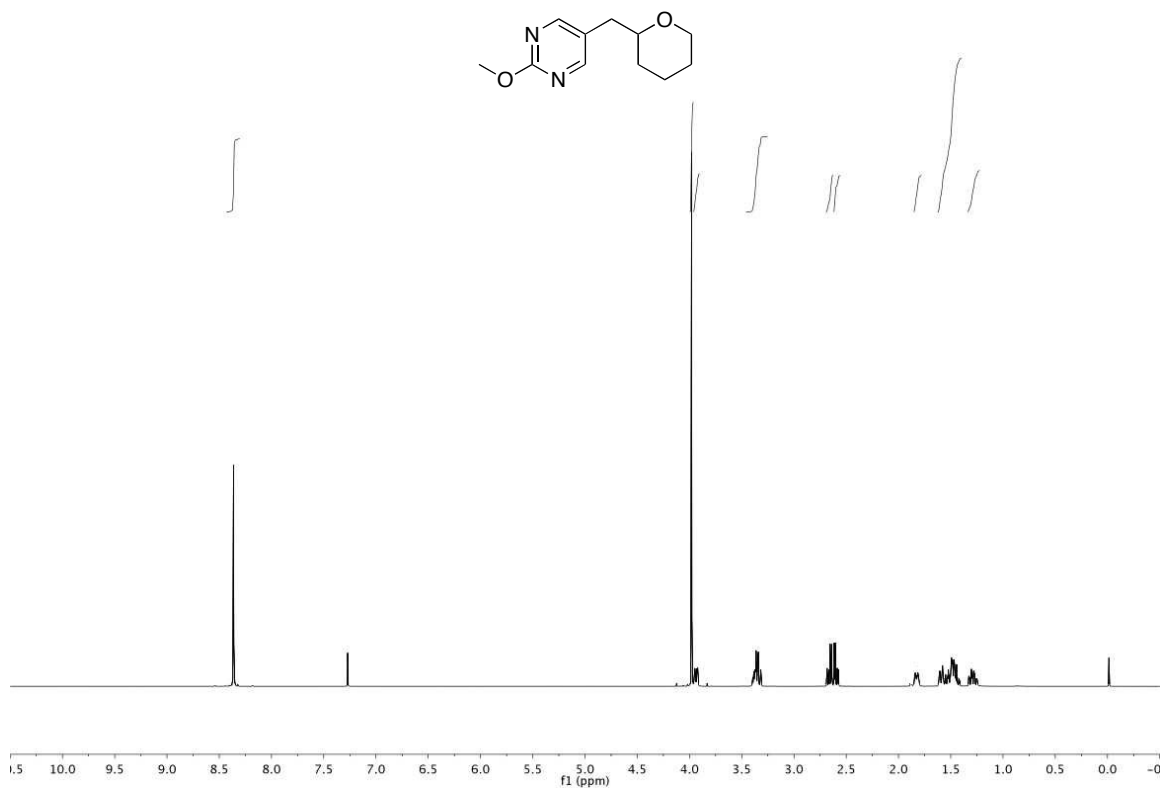
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-(benzo[*b*]thiophen-2-ylmethyl)tetrahydro-2*H*-pyran (Table 2, entry 5, X = S)

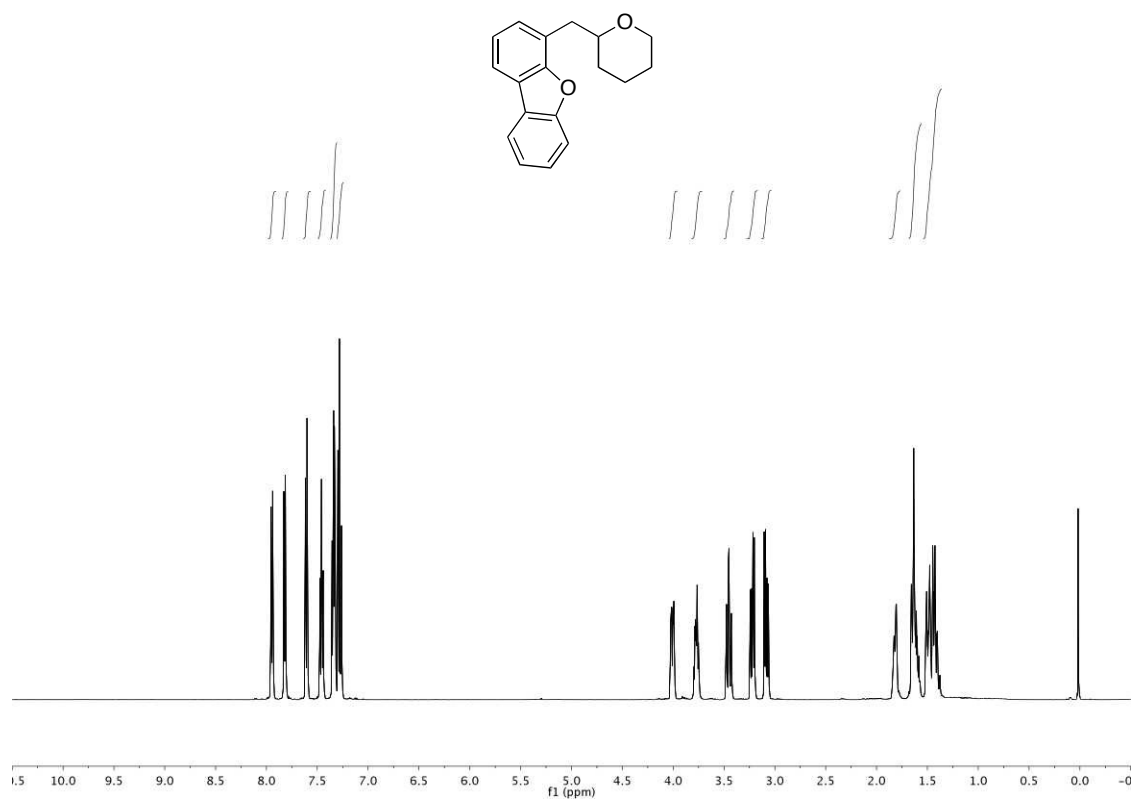


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 5-((tetrahydro-2*H*-pyran-2-yl)methyl)pyrimidine (Table 2, entry 6, X = H)

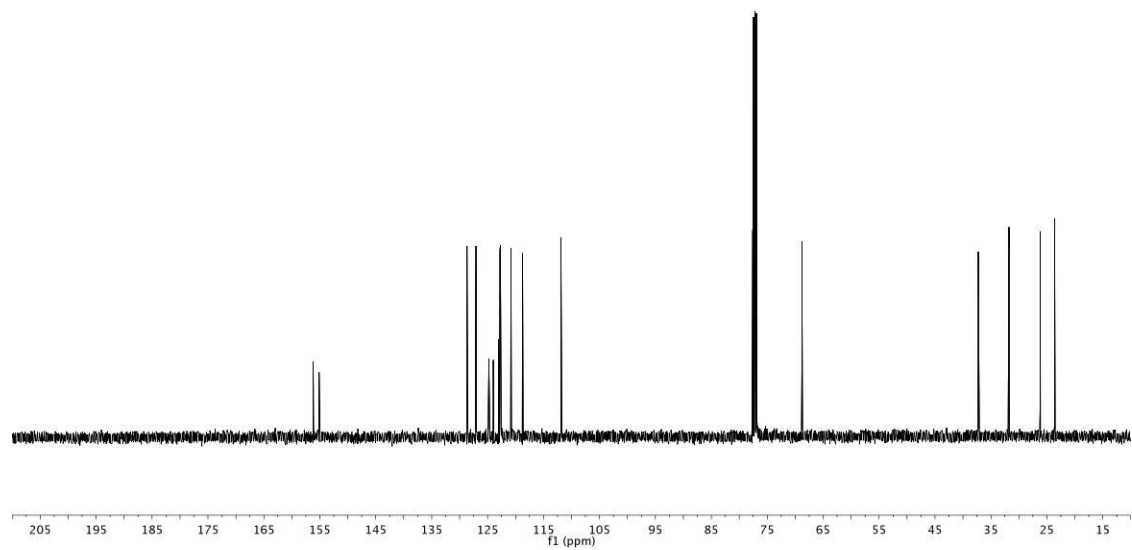


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 5-((tetrahydro-2*H*-pyran-2-yl)methyl)pyrimidine (Table 2, entry 6, X = H)



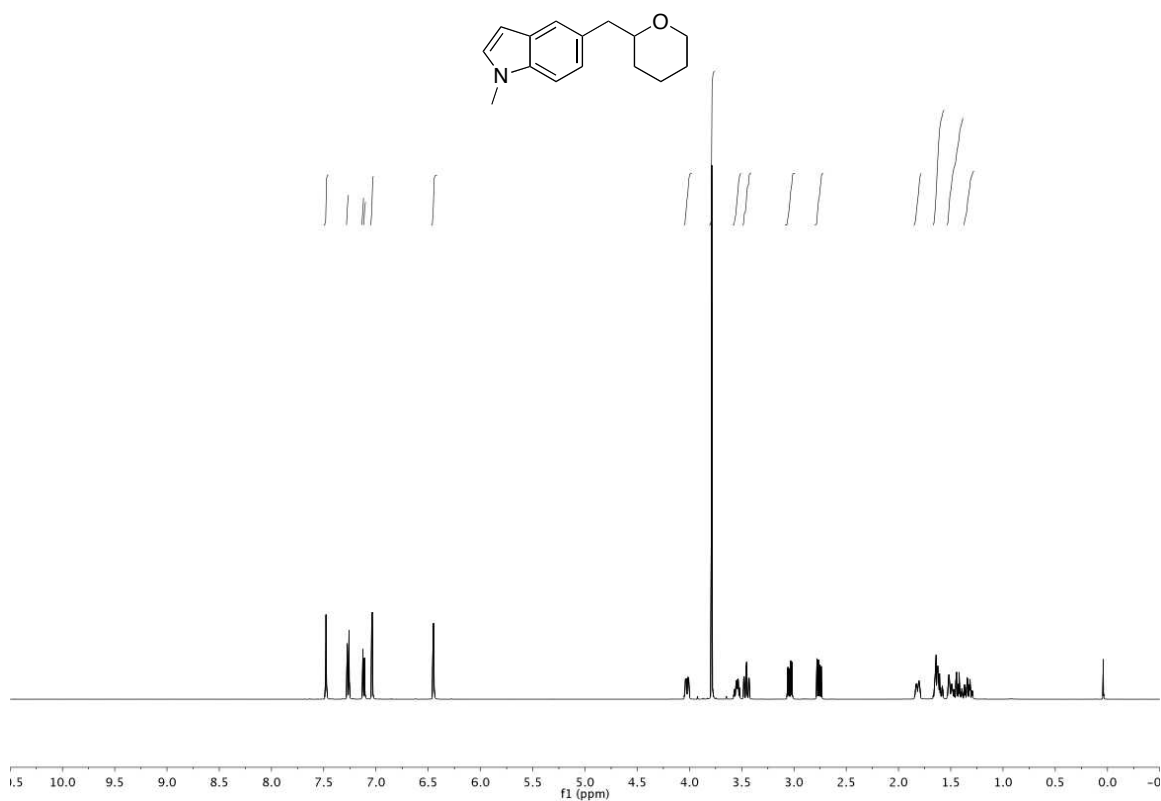


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 4-((tetrahydro-2*H*-pyran-2-yl)methyl)dibenzo[*b,d*]furan (Table 2, entry 7)

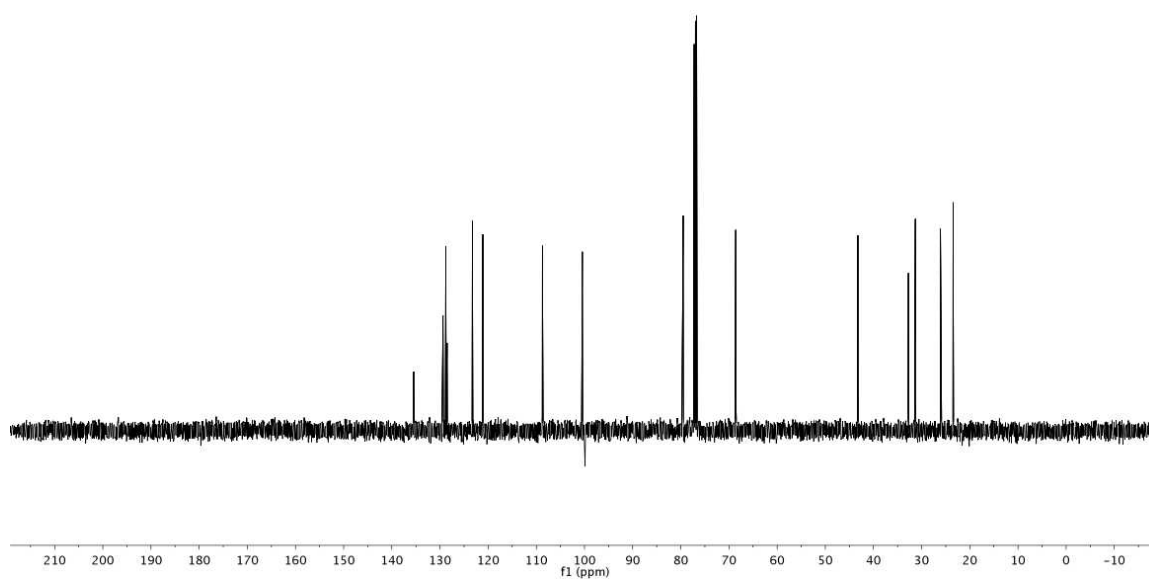


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 4-((tetrahydro-2*H*-pyran-2-yl)methyl)dibenzo[*b,d*]furan (Table 2, entry 7)

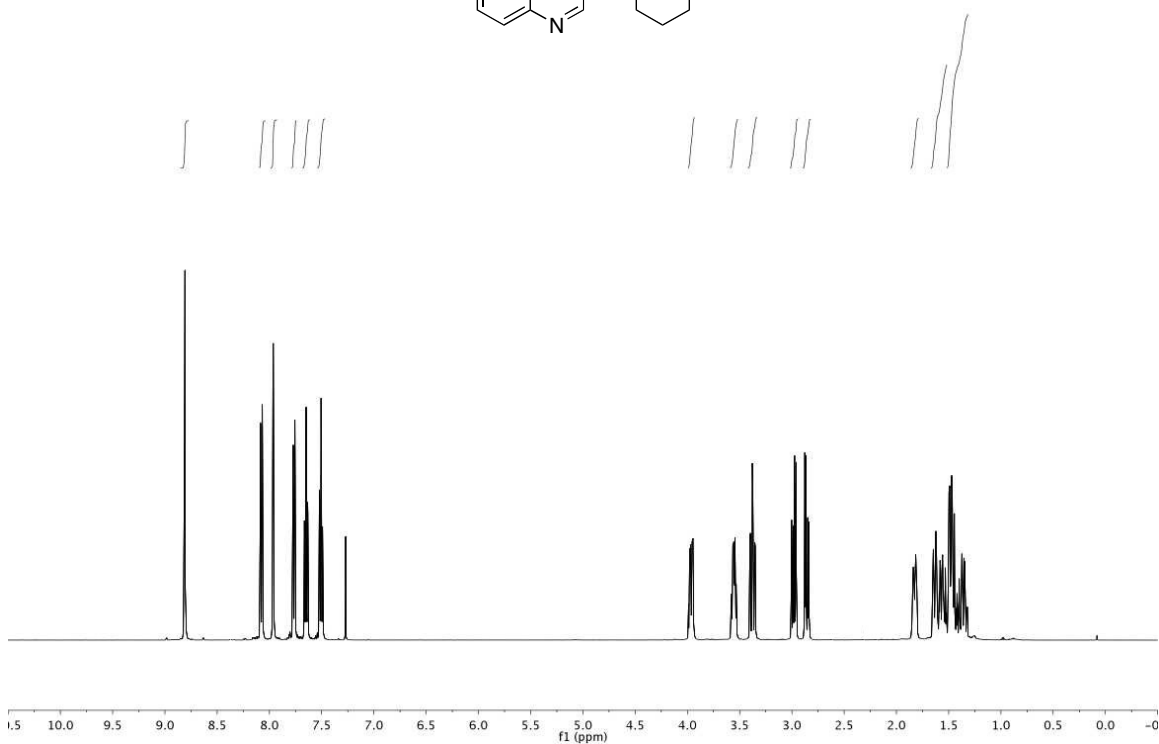




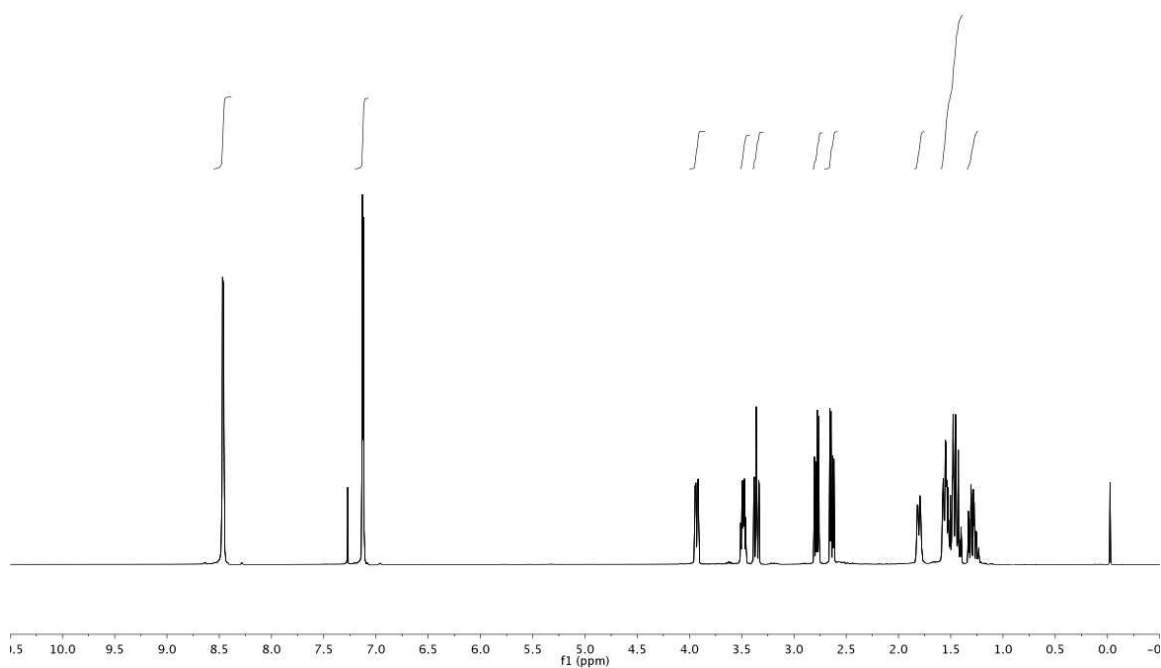
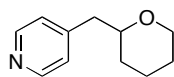
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 1-methyl-5-((tetrahydro-2*H*-pyran-2-yl)methyl)-1*H*-indole (Table 2, entry 8)



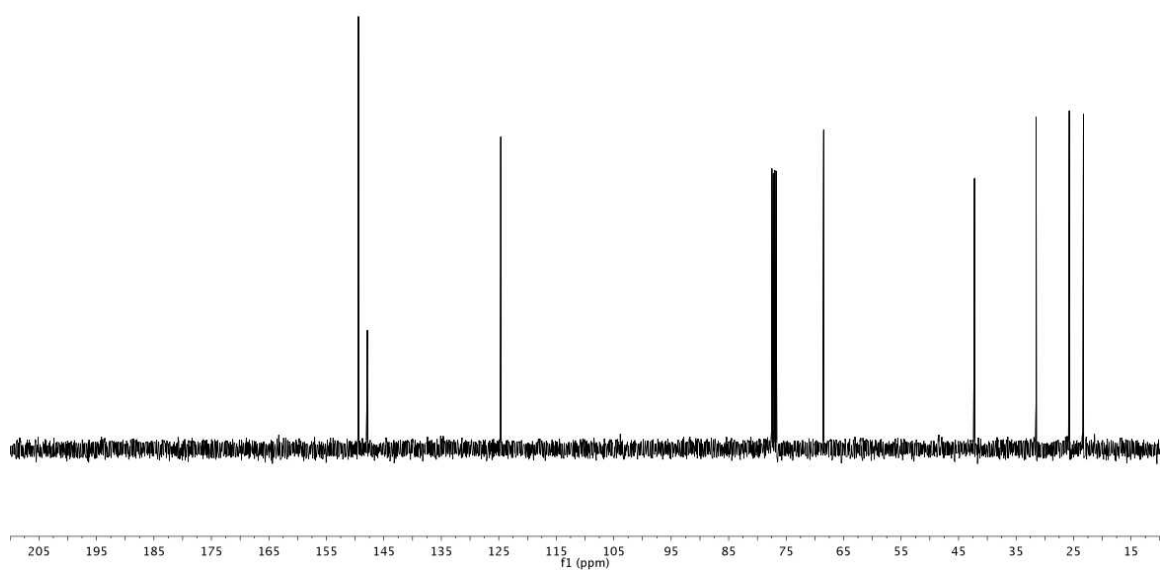
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 1-methyl-5-((tetrahydro-2*H*-pyran-2-yl)methyl)-1*H*-indole (Table 2, entry 8)



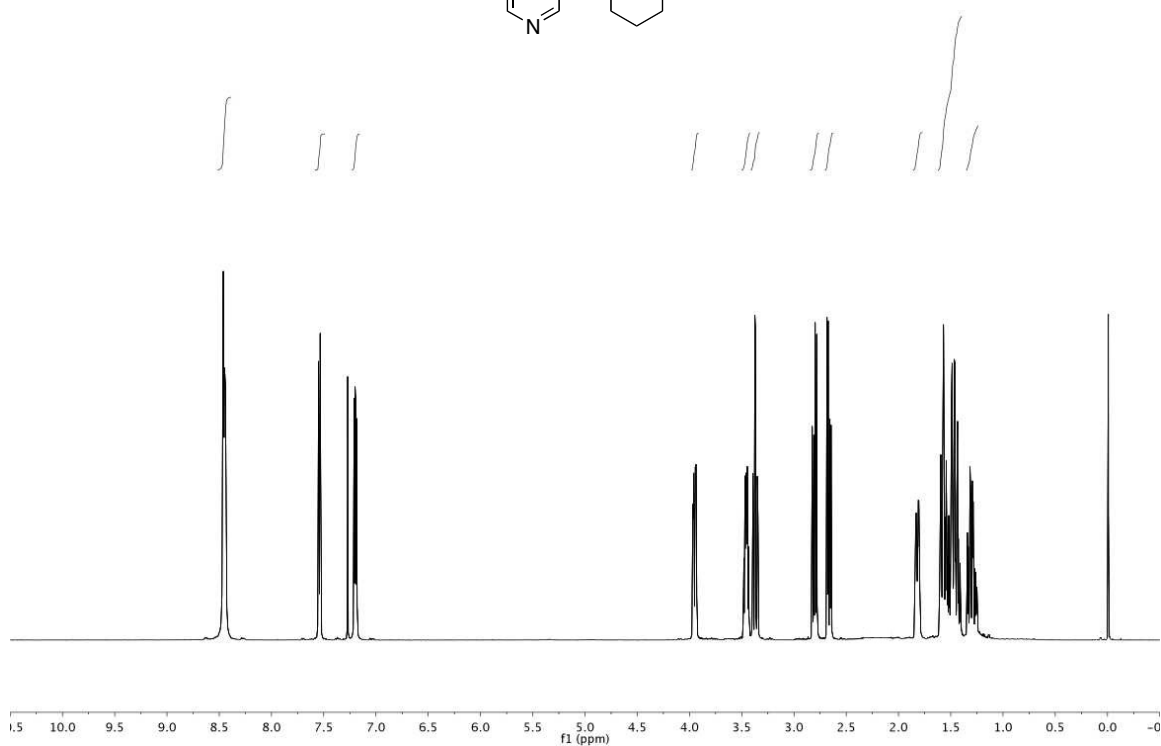
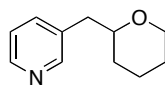
S62



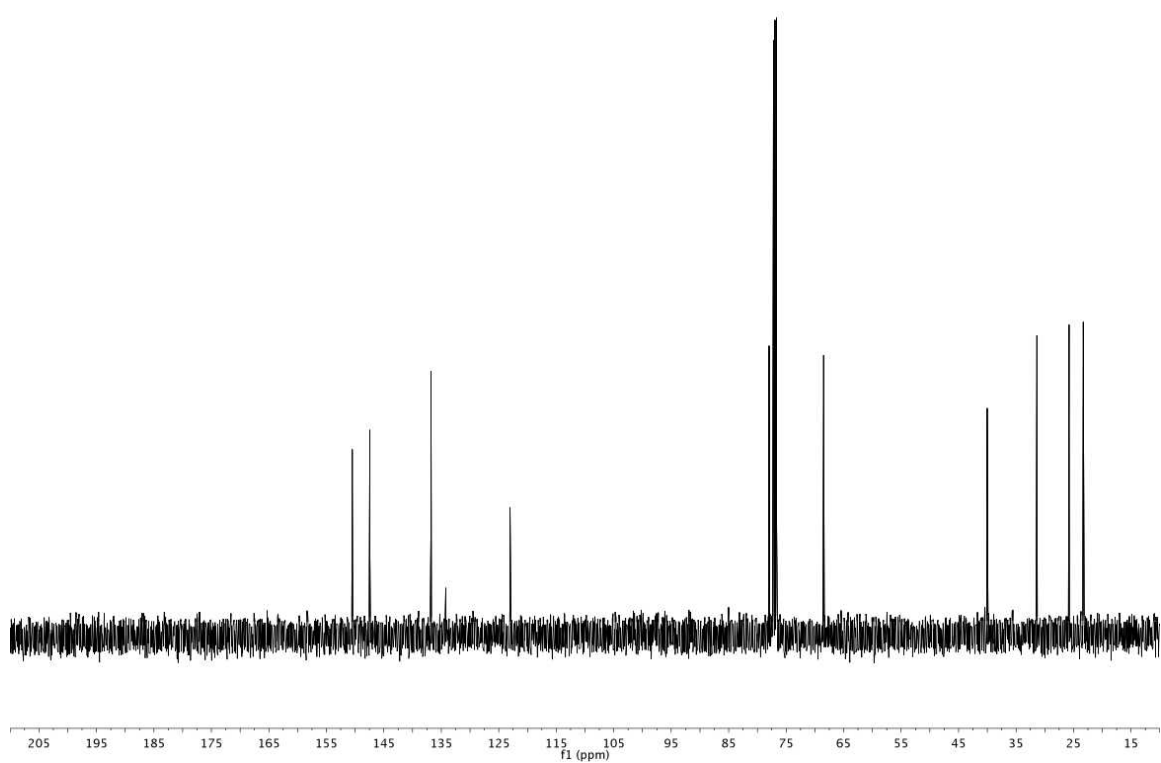
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 4-((tetrahydro-2*H*-pyran-2-yl)methyl)pyridine (Table 2, entry 10)



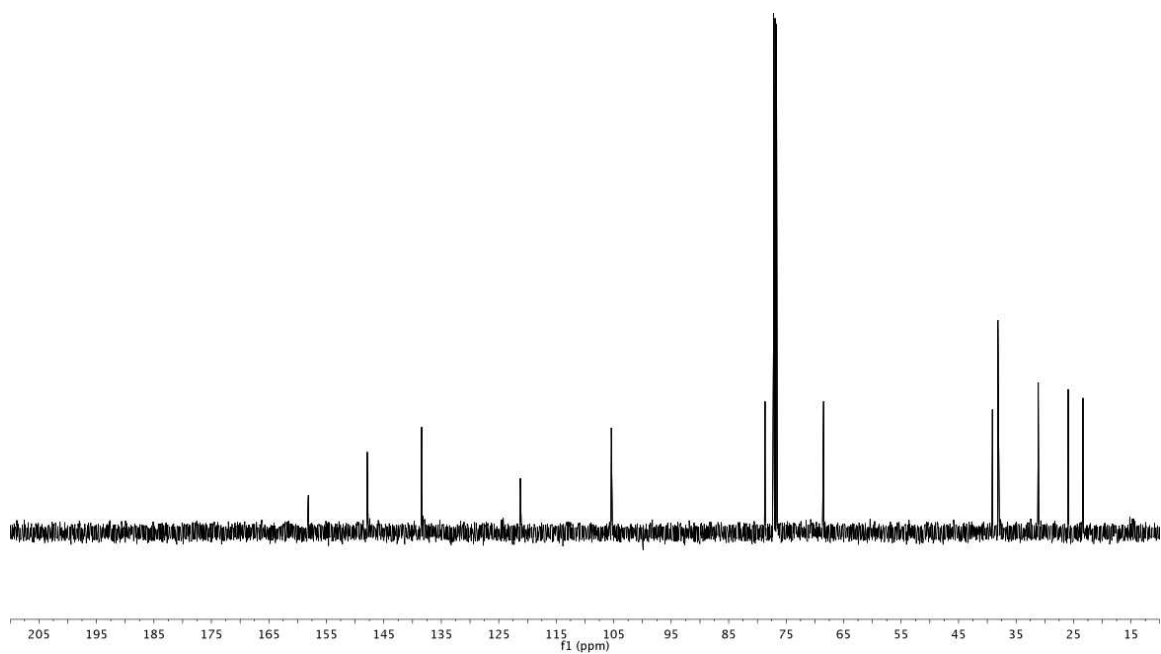
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 4-((tetrahydro-2*H*-pyran-2-yl)methyl)pyridine (Table 2, entry 10)

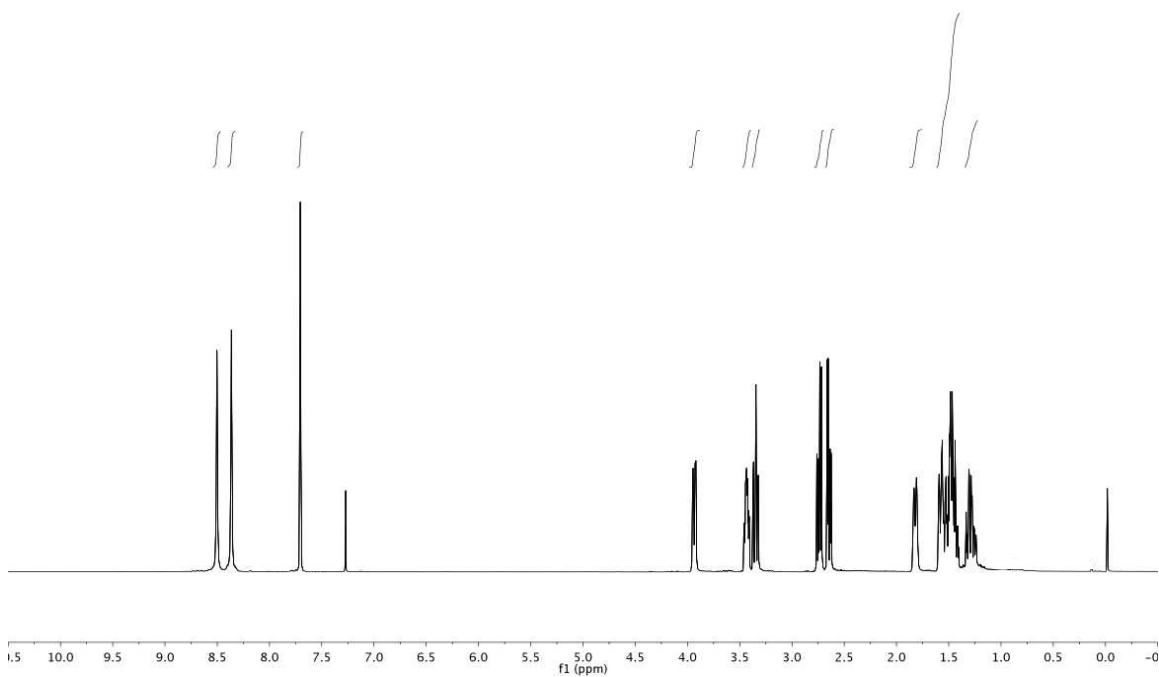
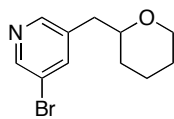


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 3-((tetrahydro-2*H*-pyran-2-yl)methyl)pyridine (Table 2, entry 11)

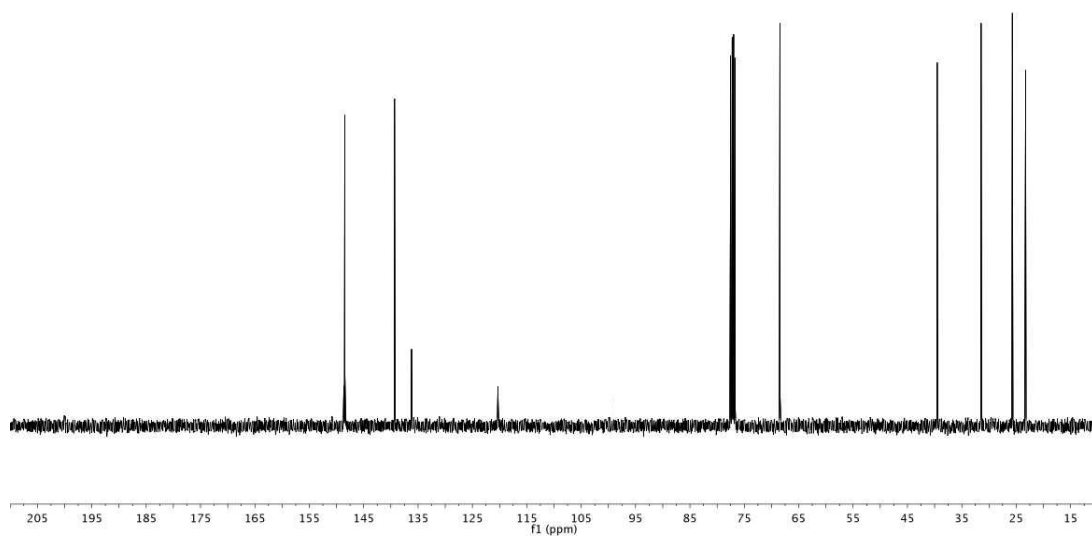


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 3-((tetrahydro-2*H*-pyran-2-yl)methyl)pyridine (Table 2, entry 11)

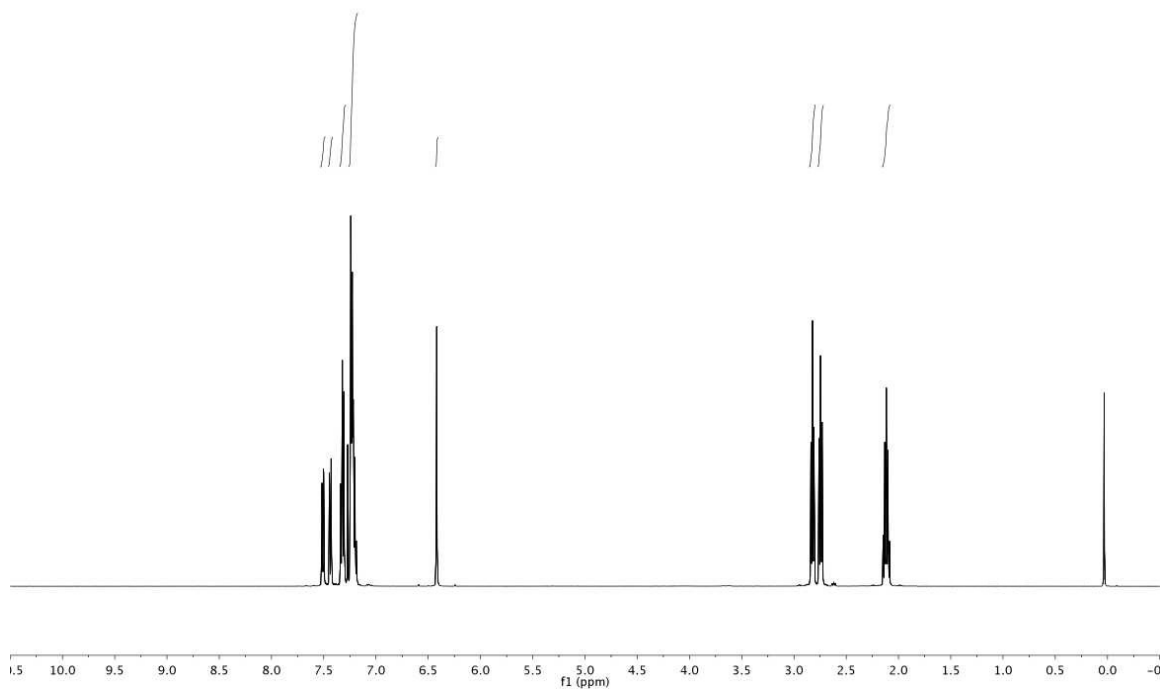
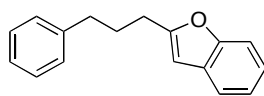




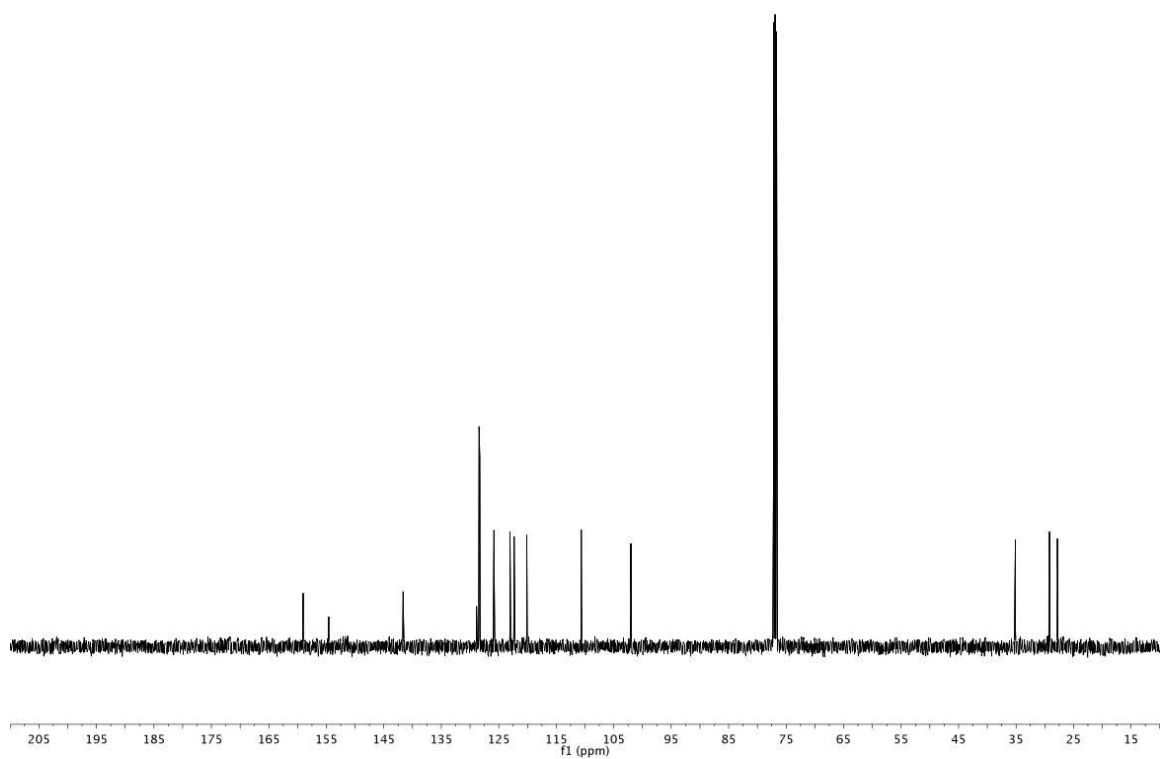
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 3-bromo-5-((tetrahydro-2H-pyran-2-yl)methyl)pyridine (Table 2, entry 13)



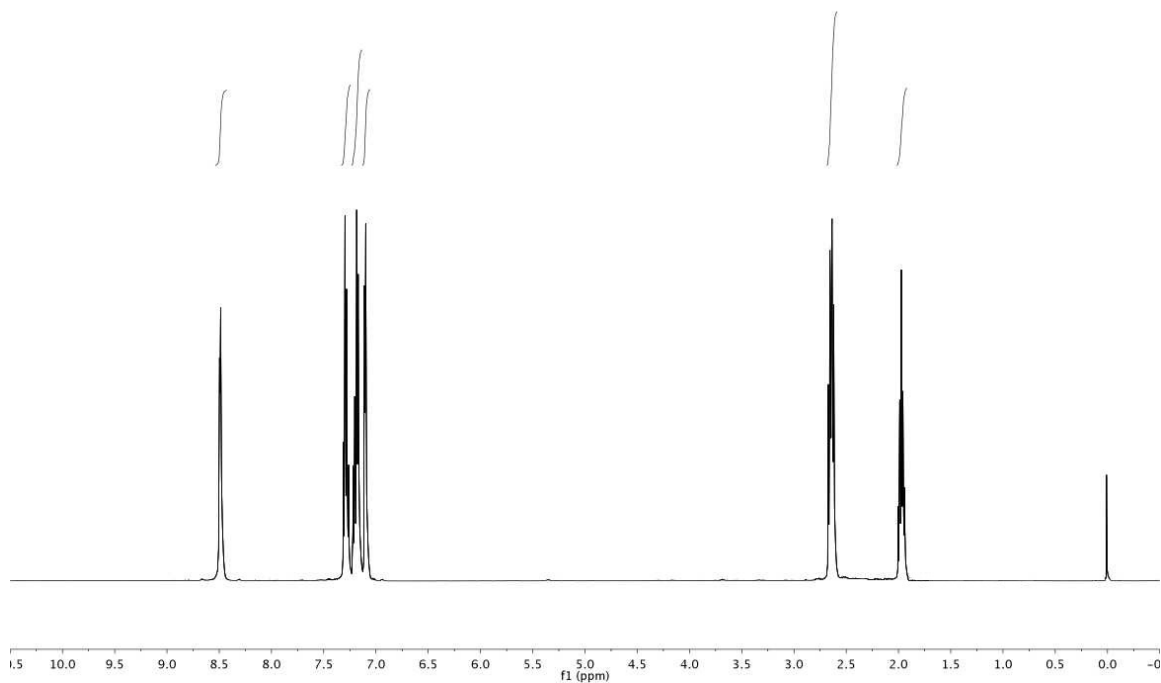
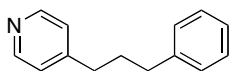
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 3-bromo-5-((tetrahydro-2H-pyran-2-yl)methyl)pyridine (Table 2, entry 13)



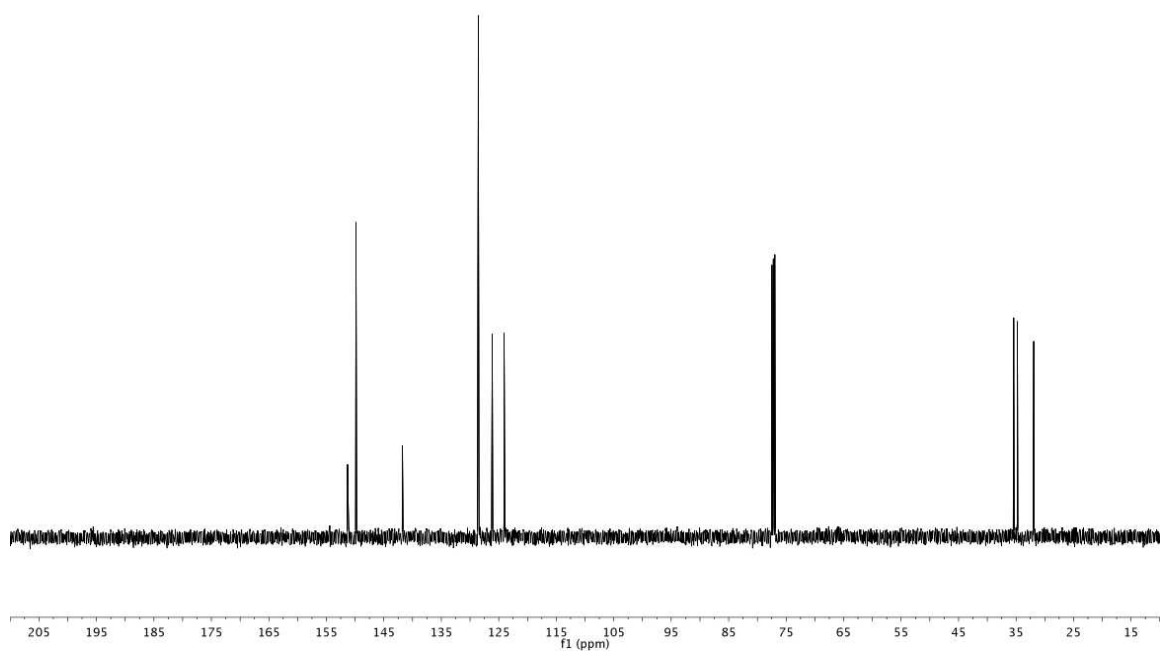
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-(3-phenylpropyl)benzofuran (Table 3, entry 1, 1)



<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 2-(3-phenylpropyl)benzofuran (Table 3, entry 1, 1)

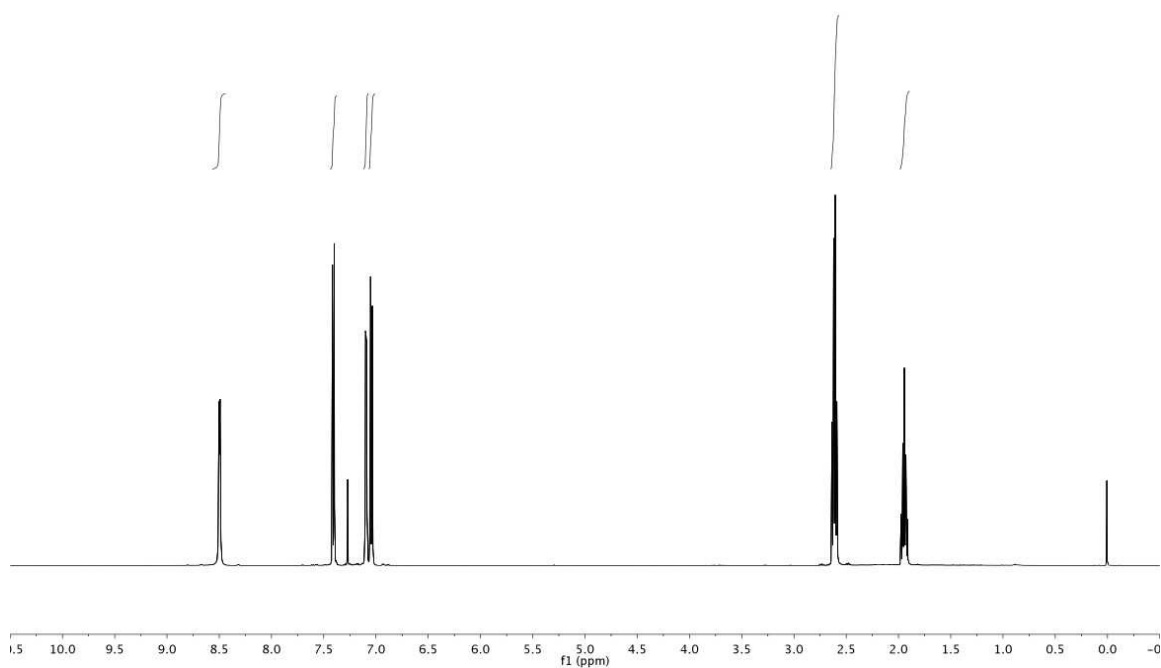
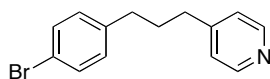


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 4-(3-phenylpropyl)pyridine (Table 3, entry 1, 2)

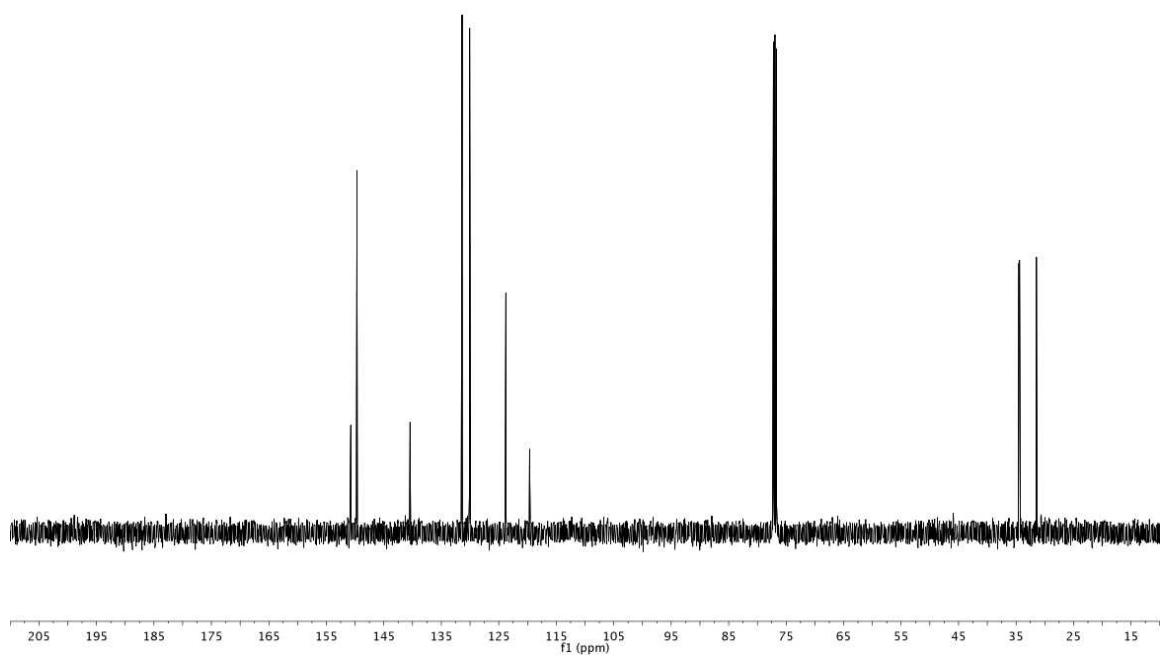


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 4-(3-phenylpropyl)pyridine (Table 3, entry 1, 2)

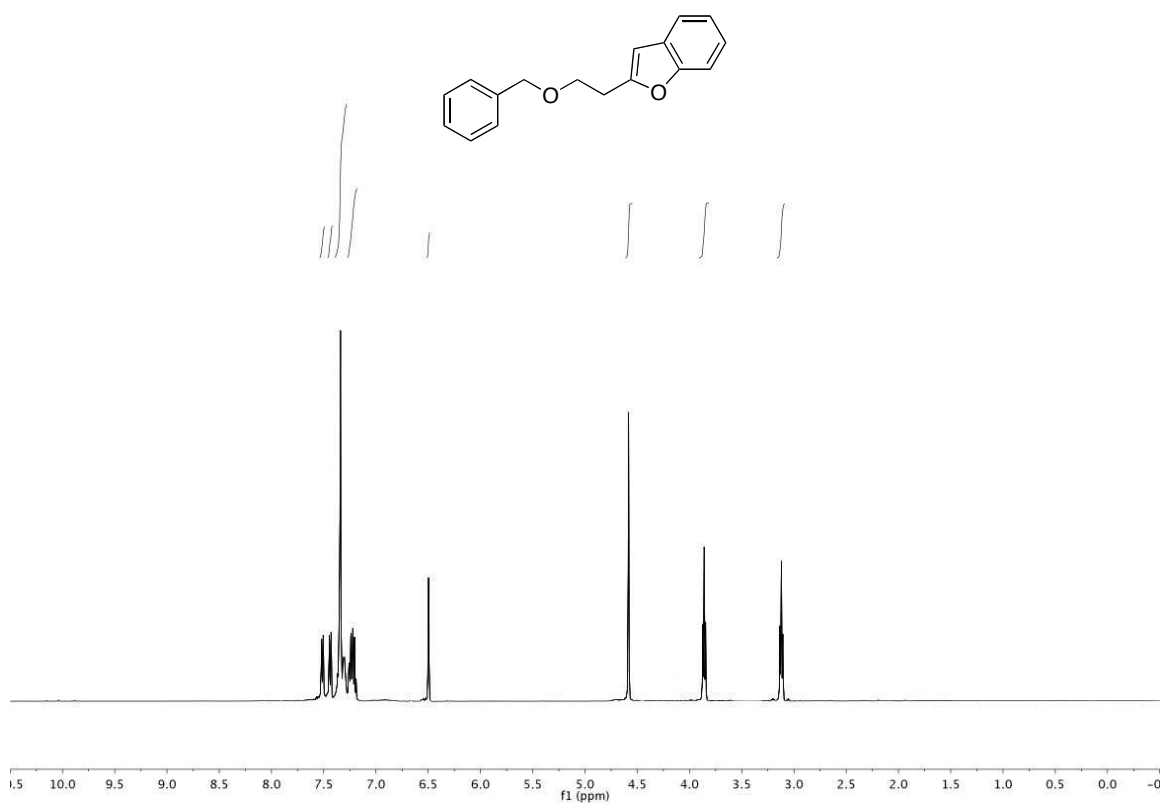




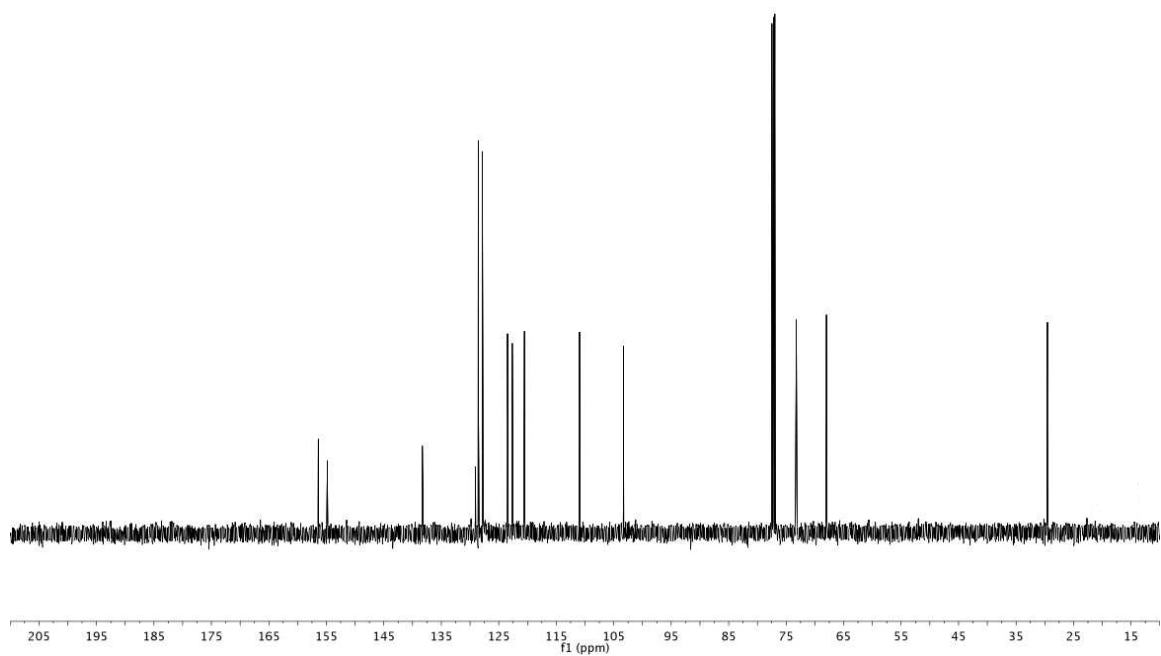
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 4-(3-(4-bromophenyl)propyl)pyridine (Table 3, entry 2, 2)



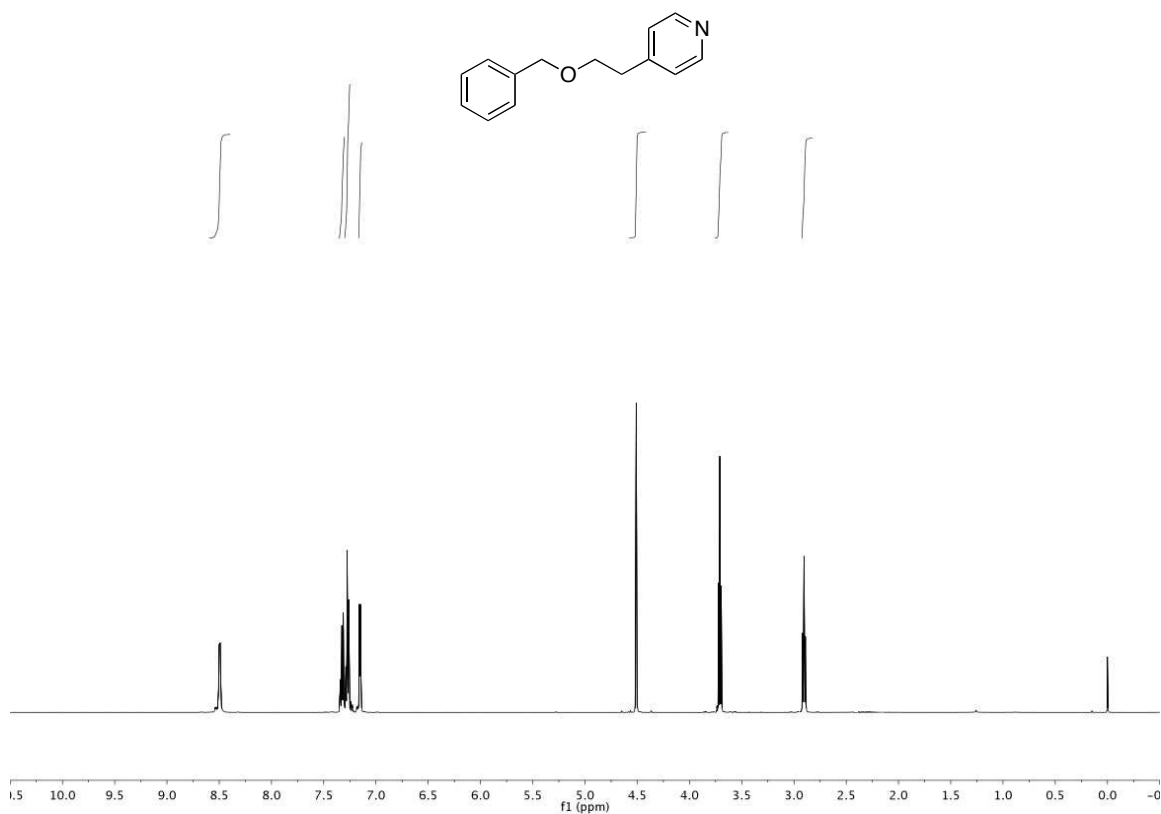
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 4-(3-(4-bromophenyl)propyl)pyridine (Table 3, entry 2, 2)



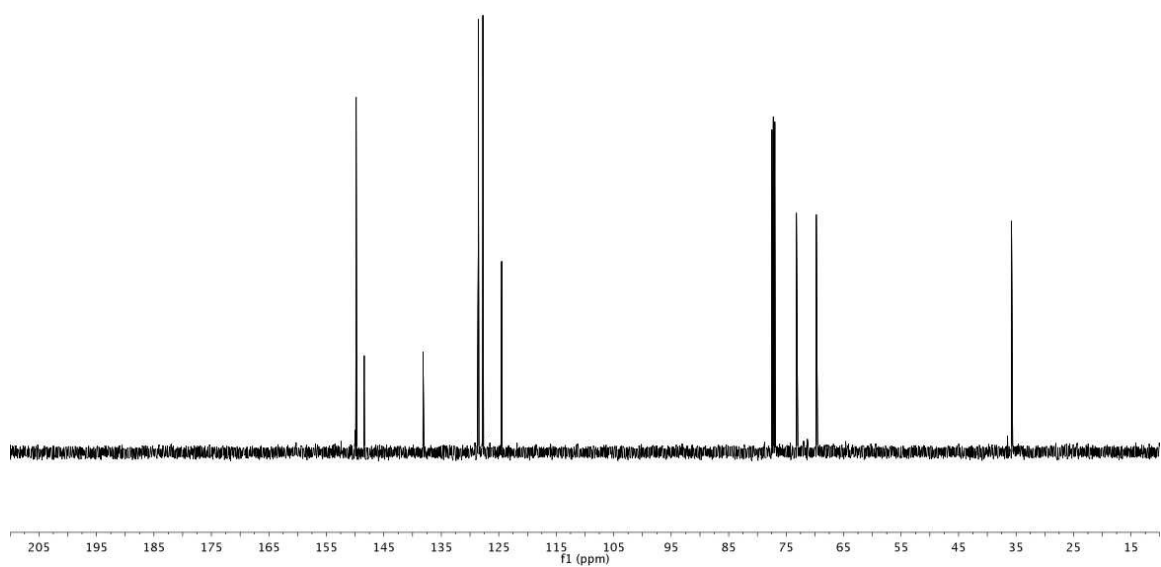
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-(2-(benzyloxy)ethyl)benzofuran (Table 3, entry 3, 1)



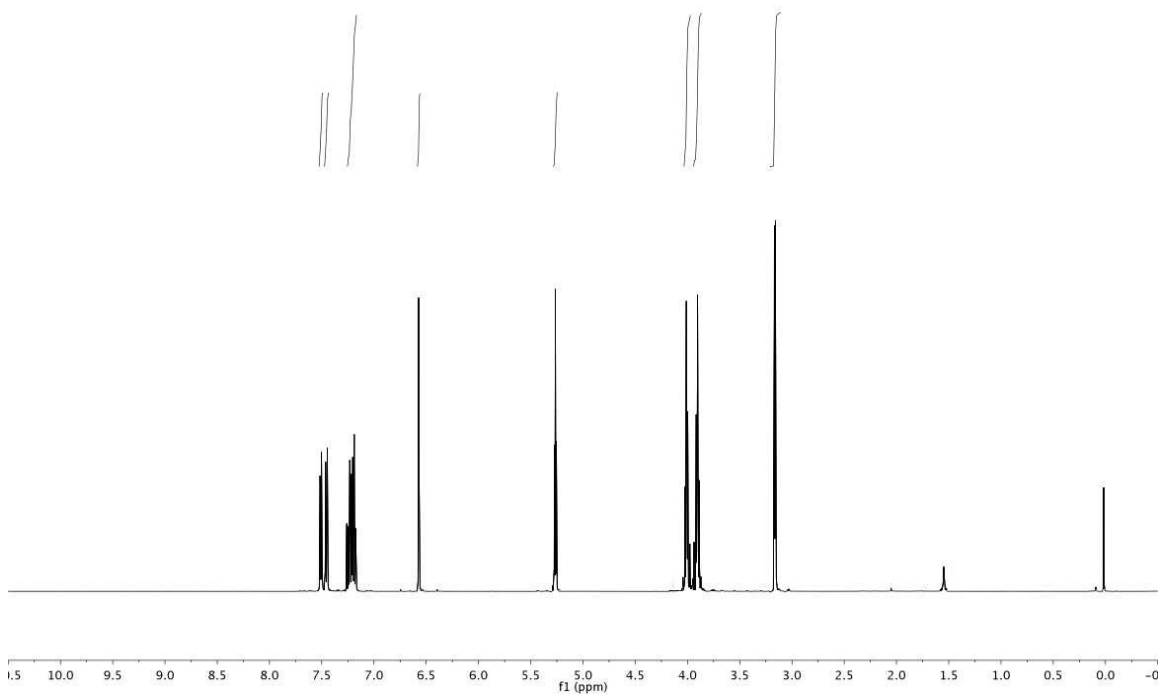
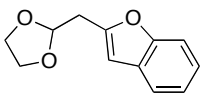
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 2-(2-(benzyloxy)ethyl)benzofuran (Table 3, entry 3, 1)



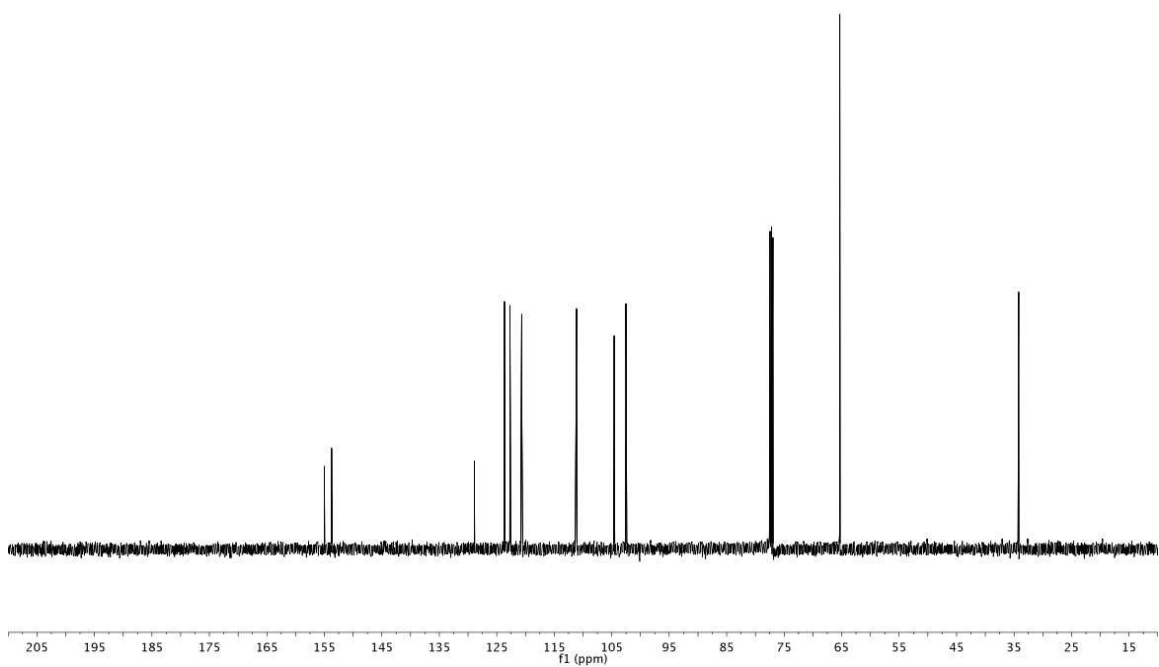
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 4-(2-(benzyloxy)ethyl)pyridine (Table 3, entry 3, 2)



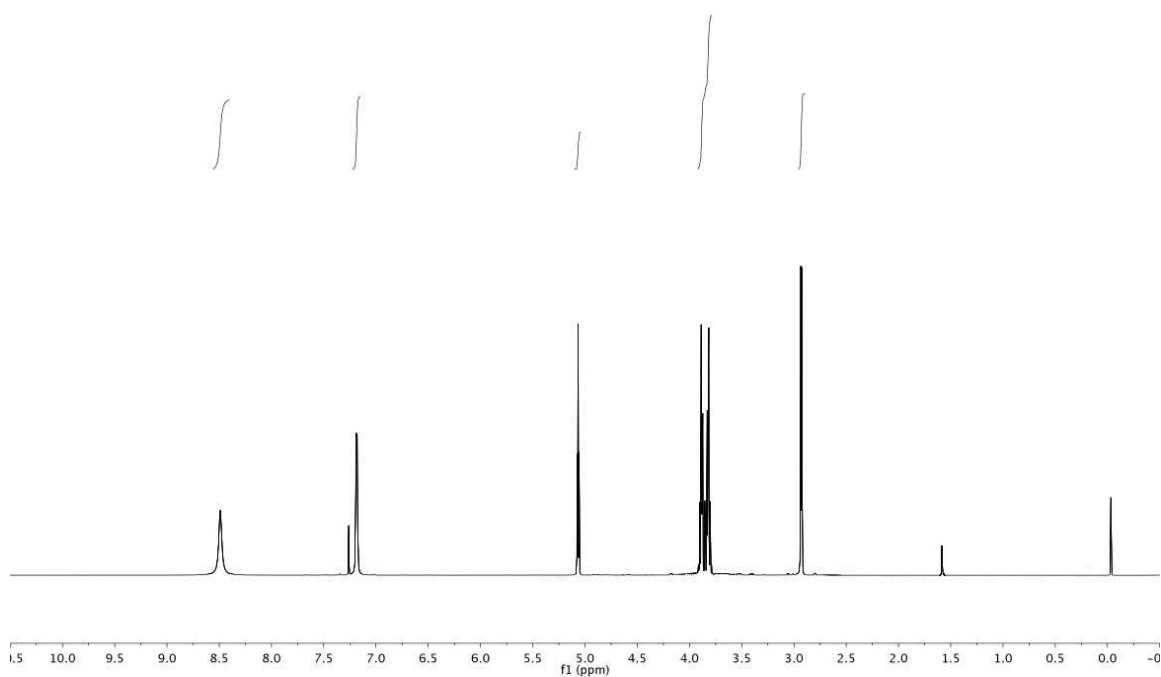
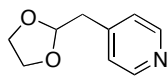
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 4-(2-(benzyloxy)ethyl)pyridine (Table 3, entry 3, 2)



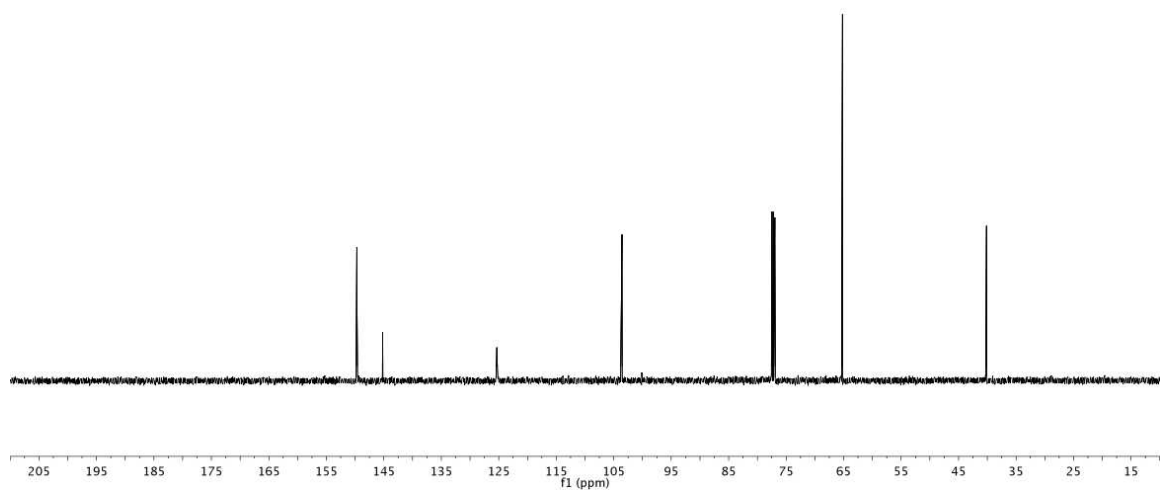
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-((1,3-dioxolan-2-yl)methyl)benzofuran (Table 3, entry 4, 1)



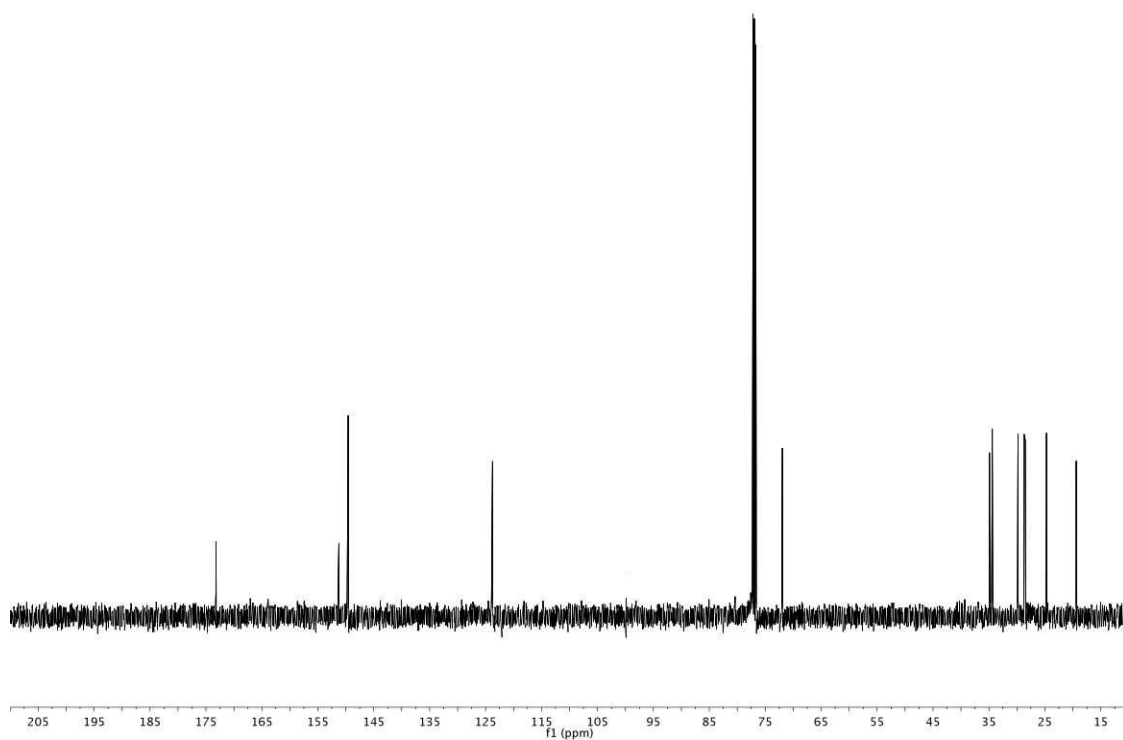
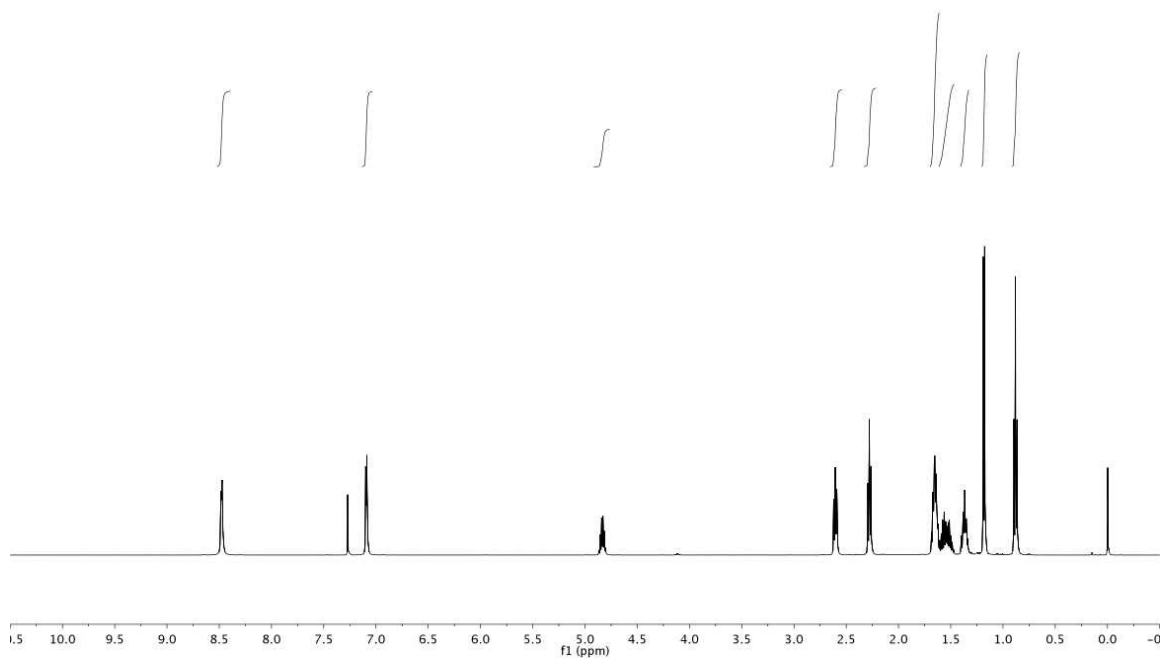
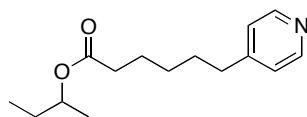
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-((1,3-dioxolan-2-yl)methyl)benzofuran (Table 3, entry 4, 1)

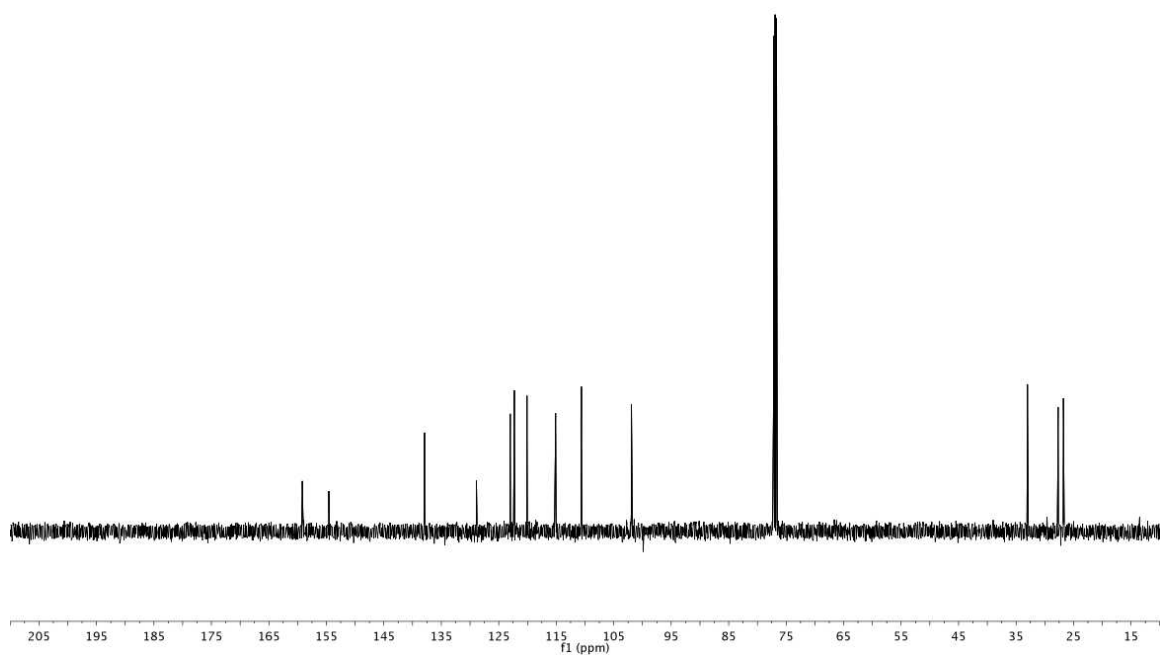
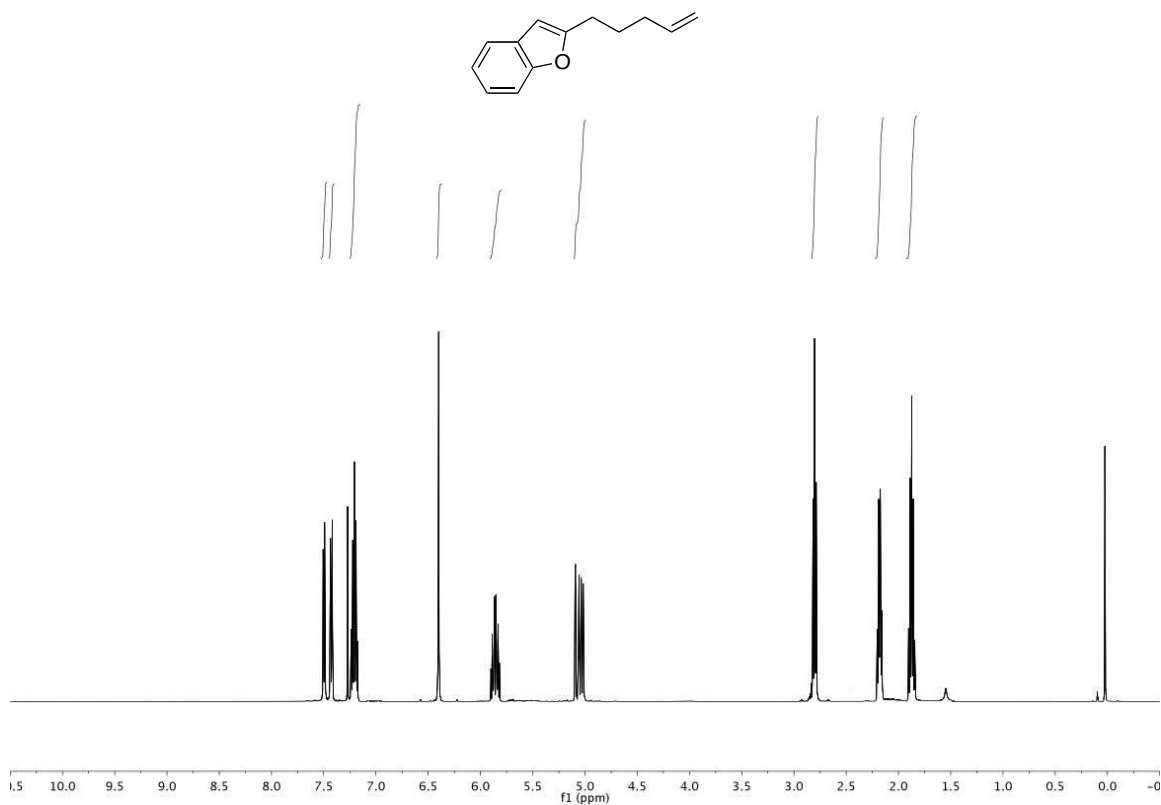


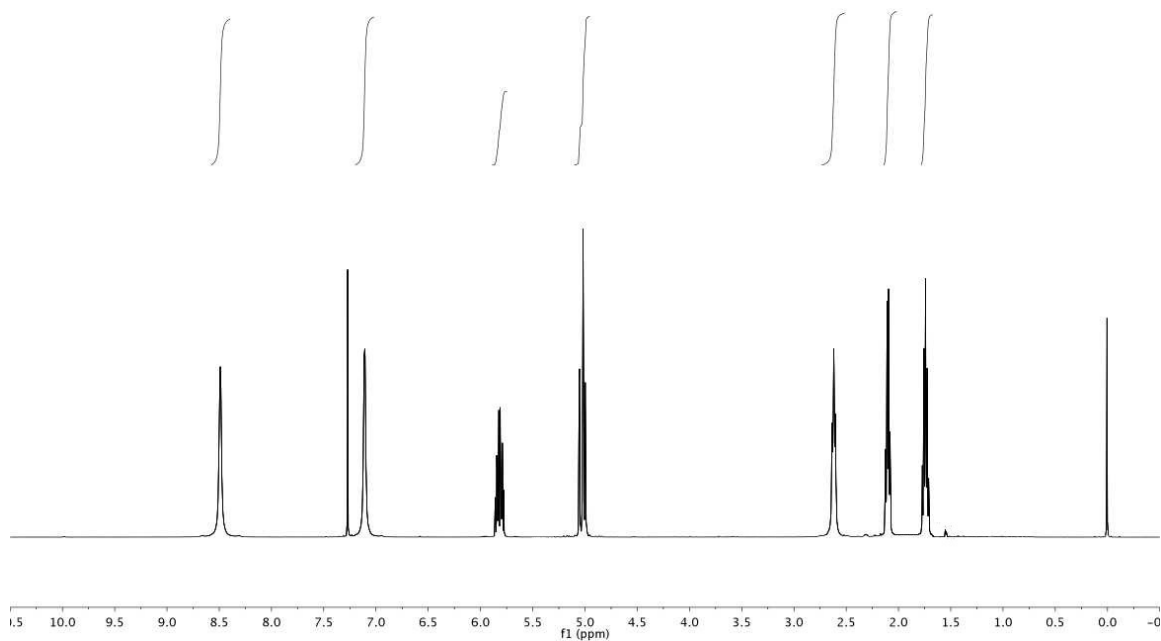
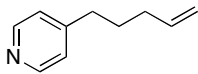
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 4-((1,3-dioxolan-2-yl)methyl)pyridine (Table 3, entry 4, 2)



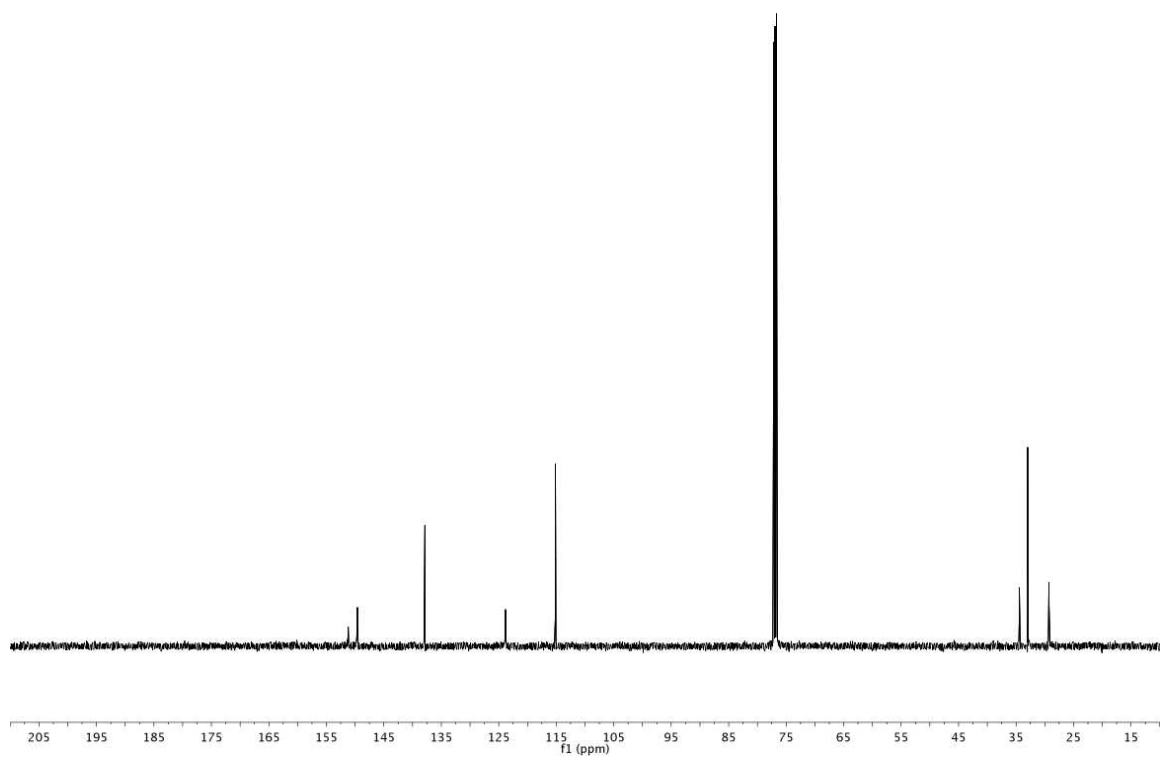
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 4-((1,3-dioxolan-2-yl)methyl)pyridine (Table 3, entry 4, 2)





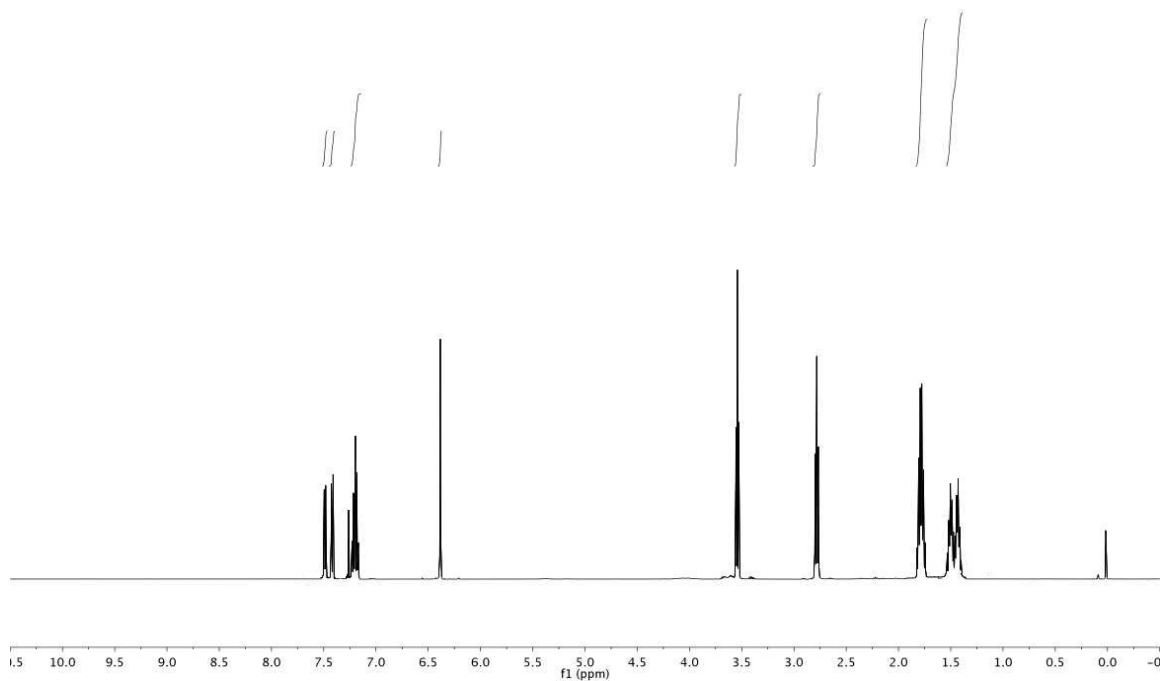
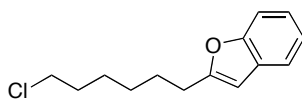


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 4-(pent-4-en-1-yl)pyridine (Table 3, entry 6, 2)

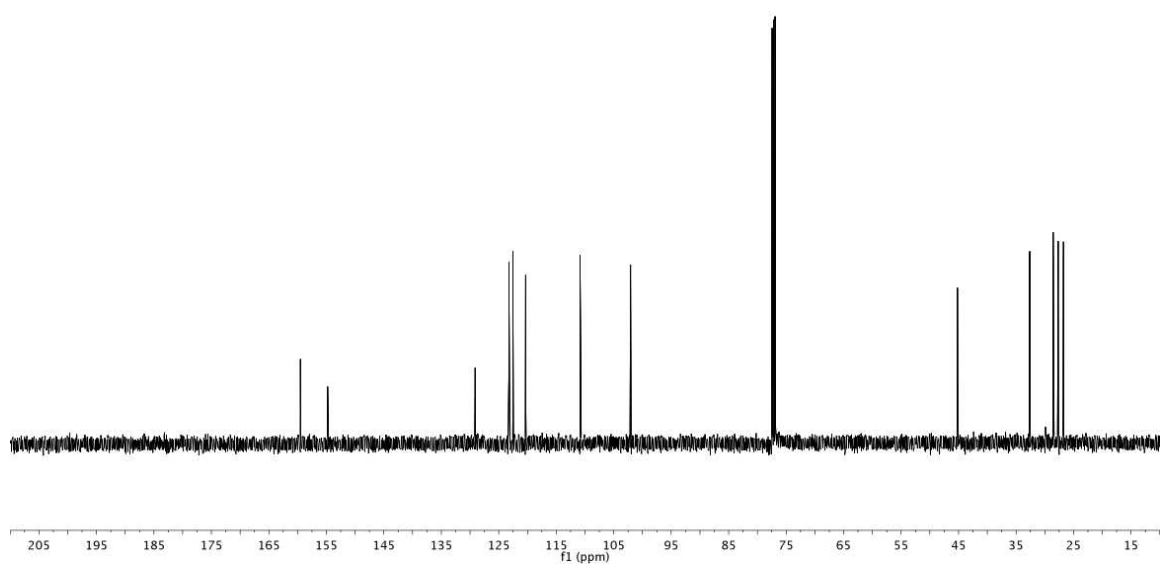


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 4-(pent-4-en-1-yl)pyridine (Table 3, entry 6, 2)

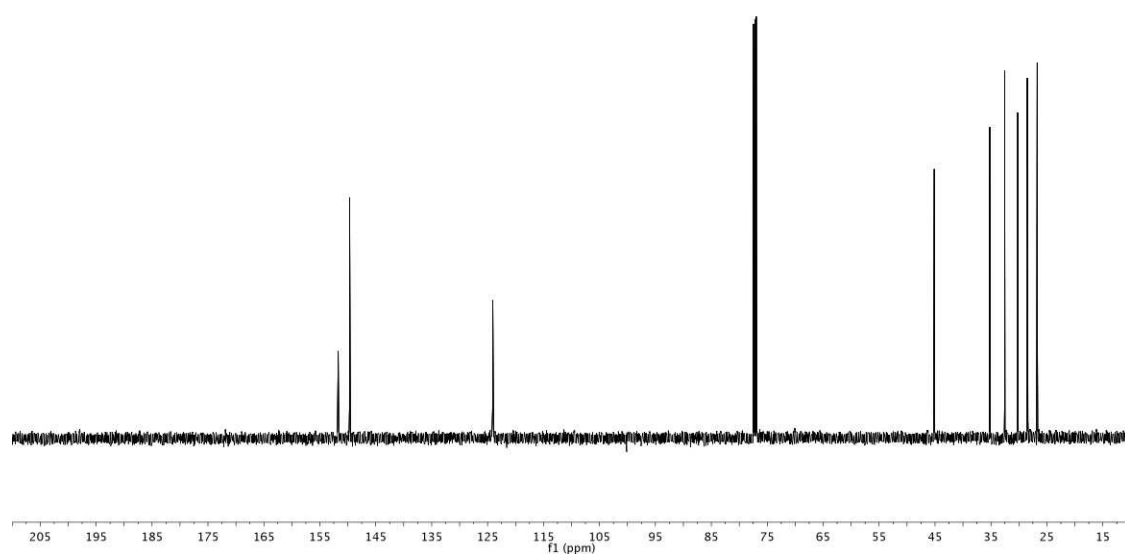
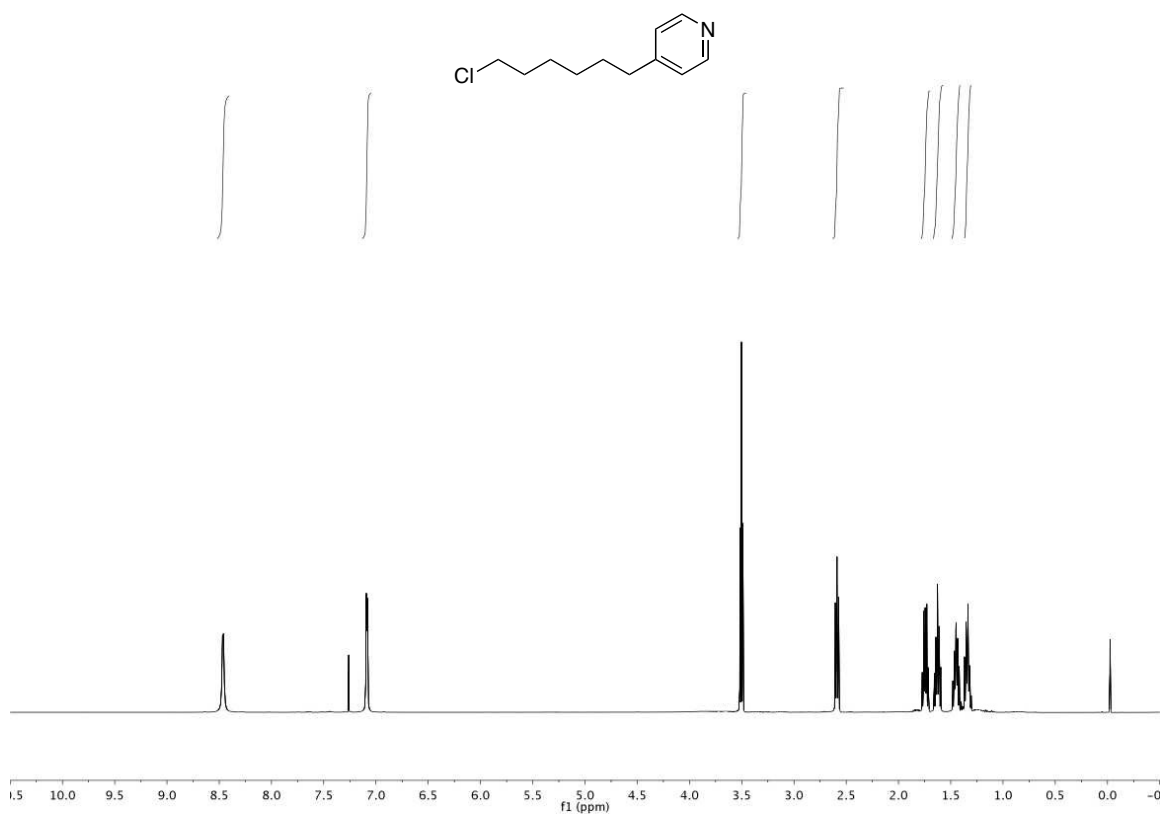


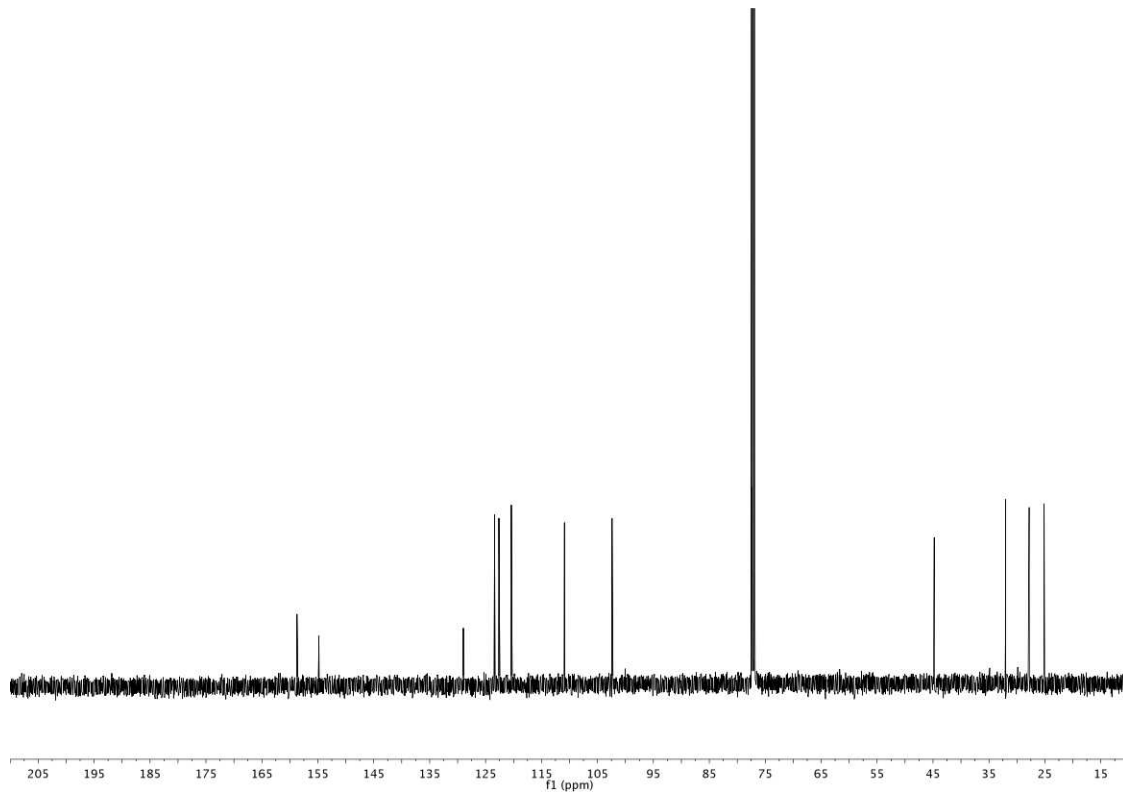
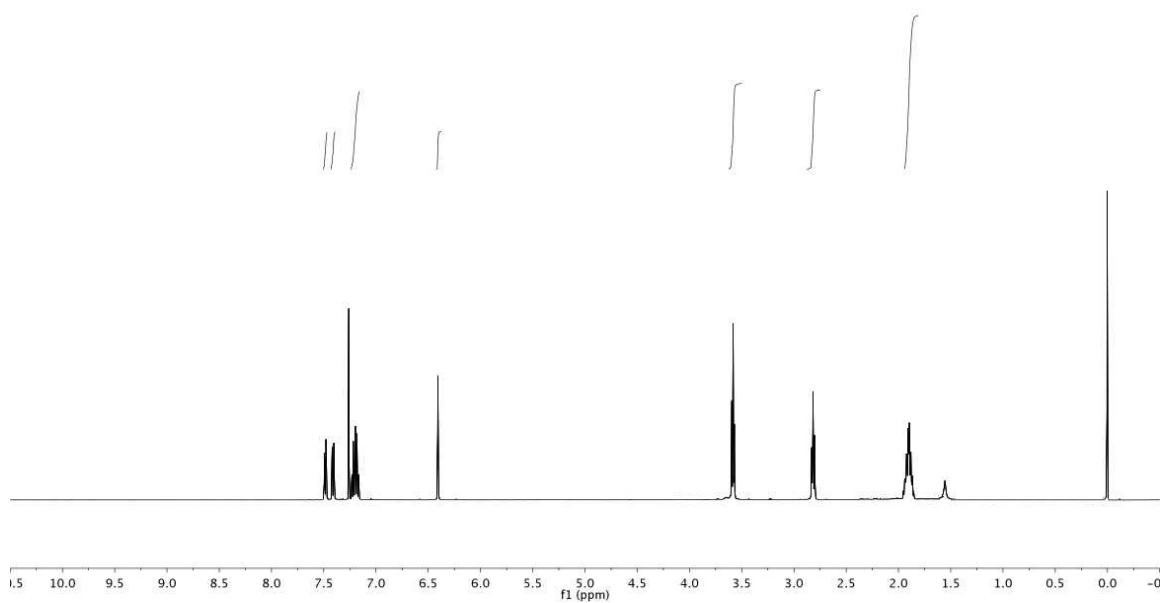
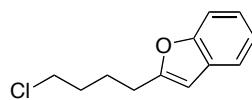


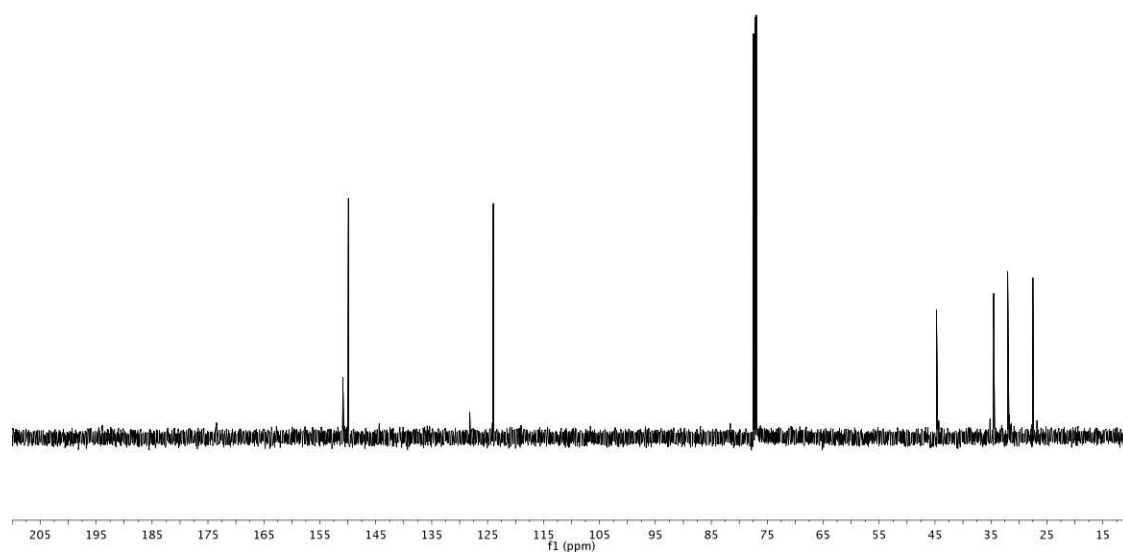
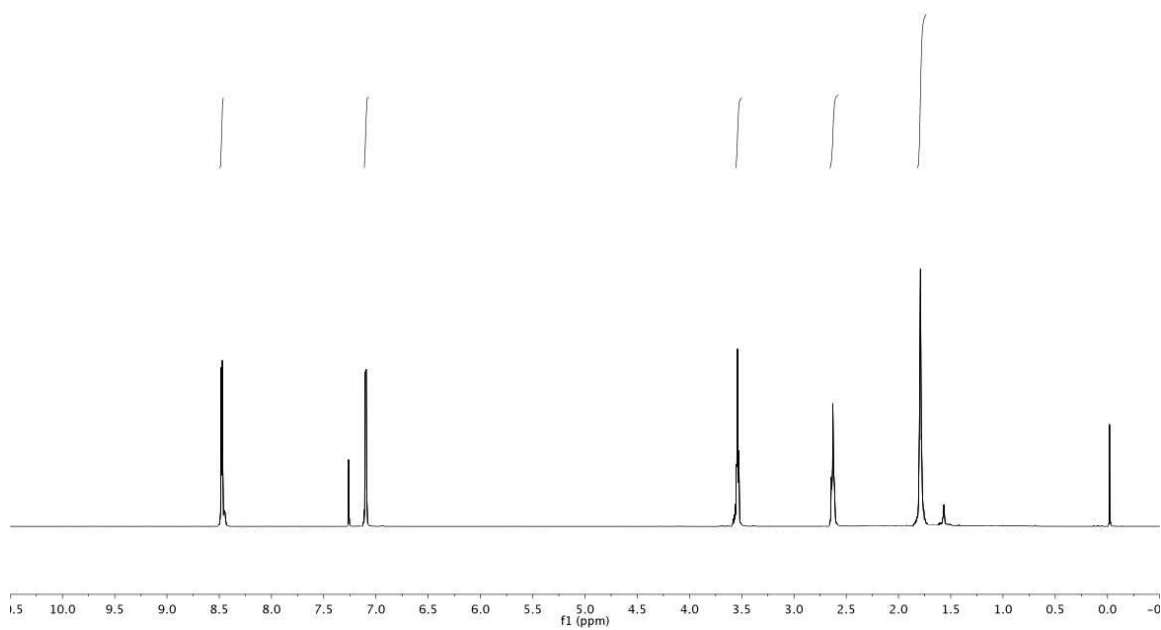
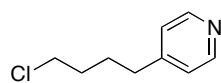
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-(6-chlorohexyl)benzofuran (Table 3, entry 7, 1)

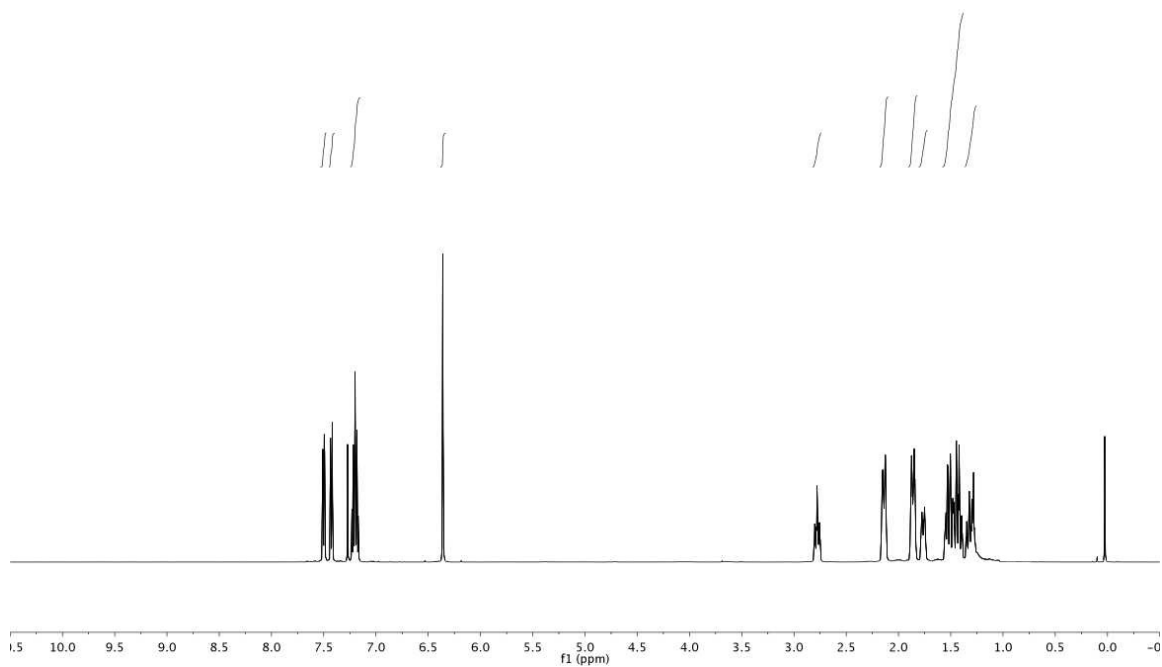
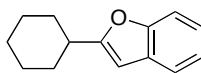


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 2-(6-chlorohexyl)benzofuran (Table 3, entry 7, 1)

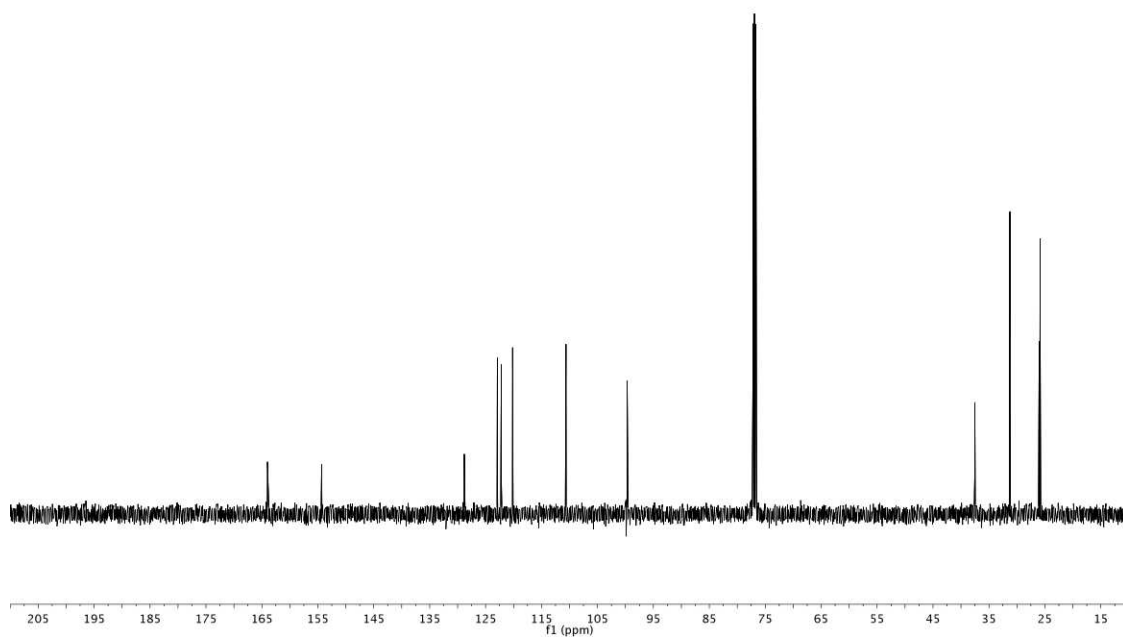




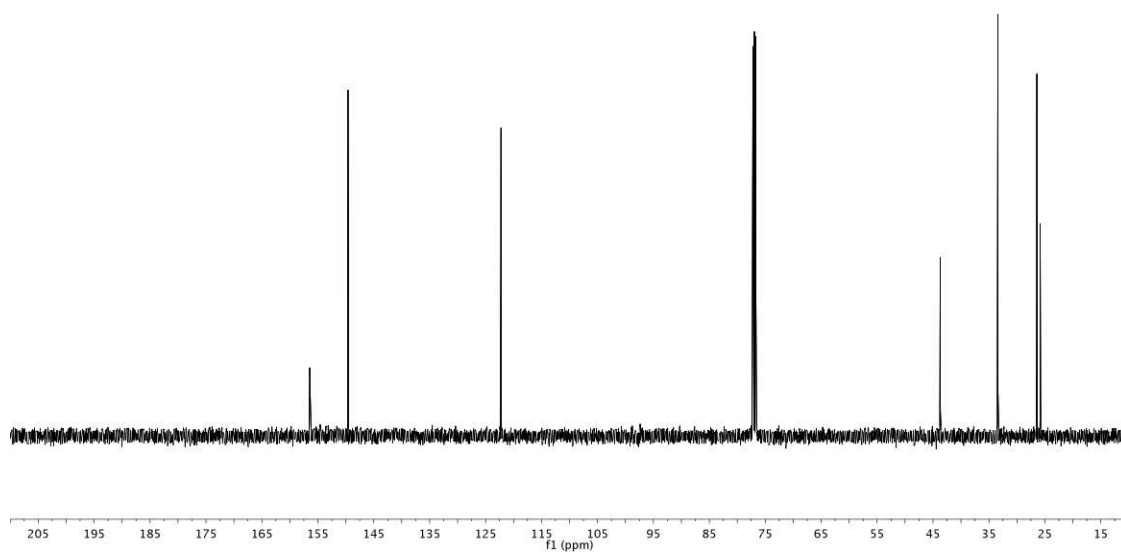
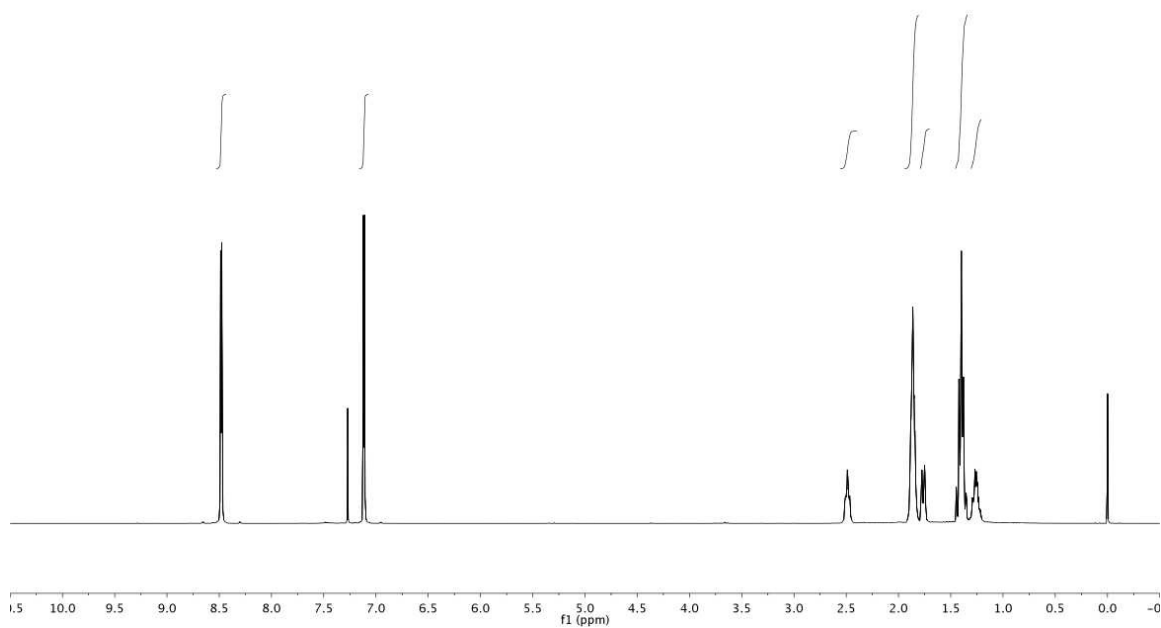
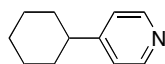


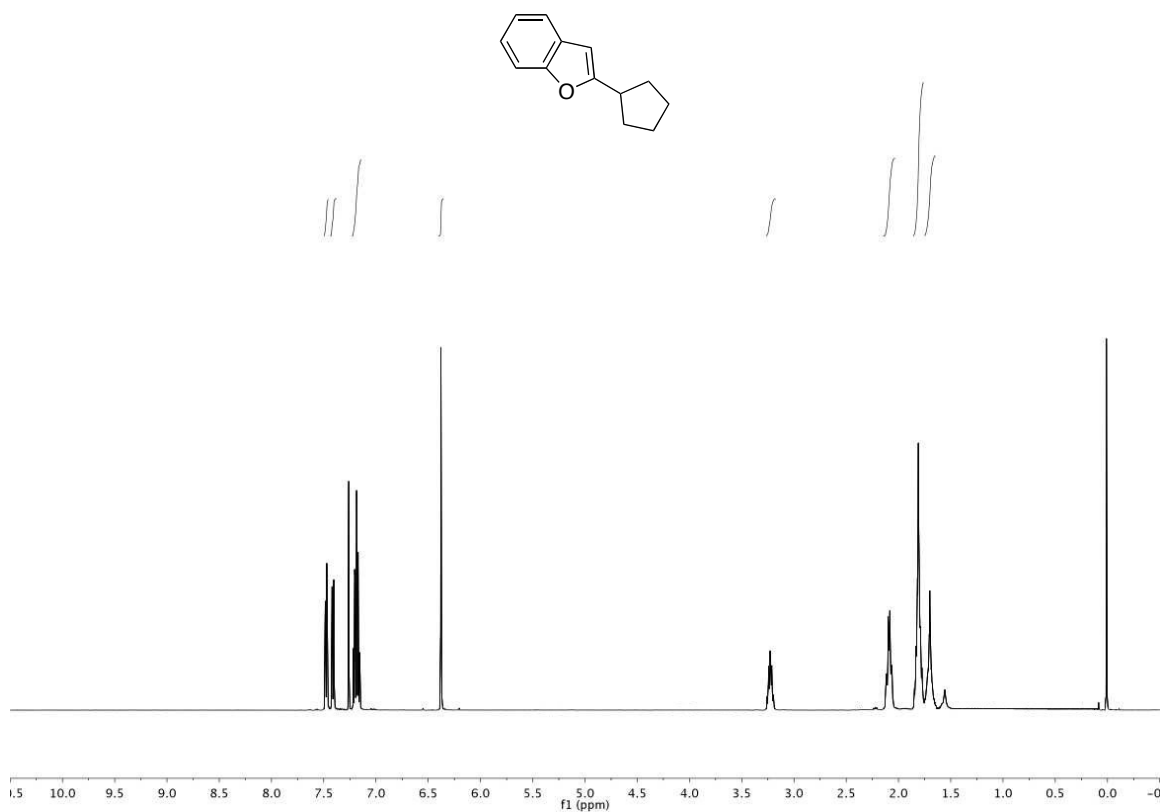


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-cyclohexylbenzofuran (Table 3, entry 9, 1)

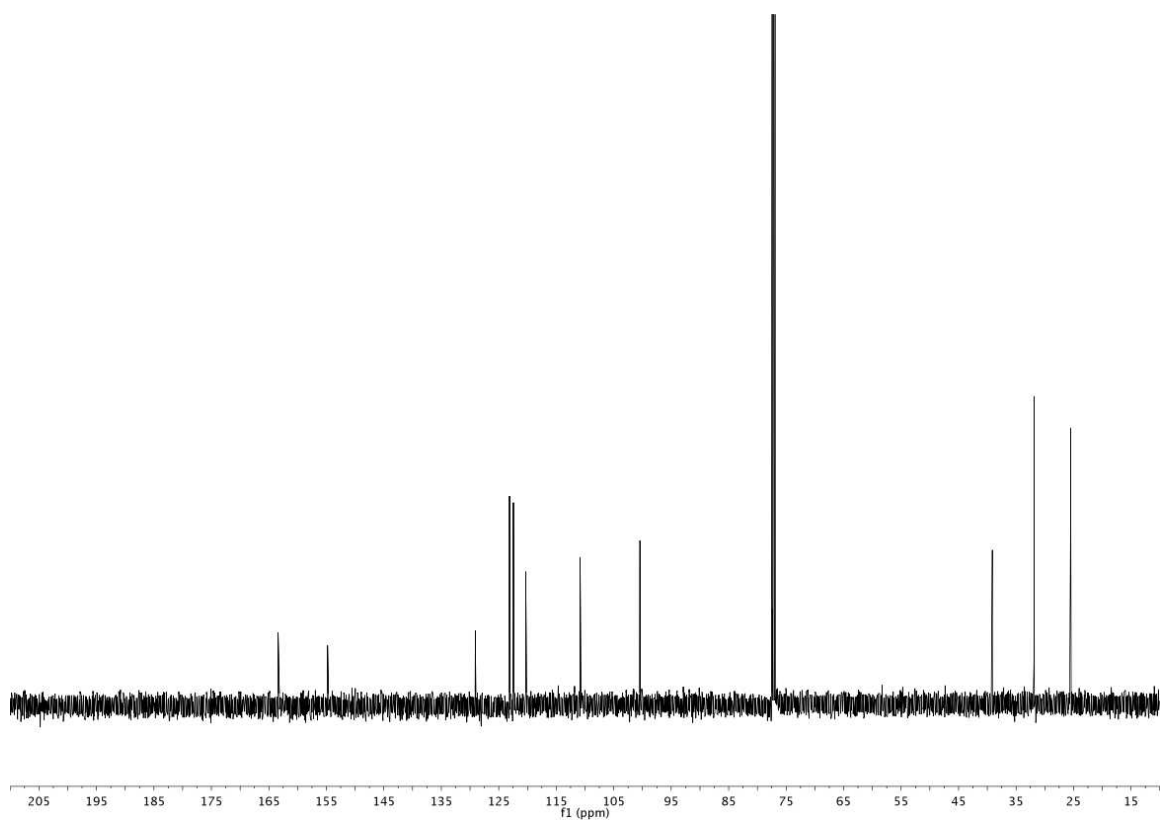


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 2-cyclohexylbenzofuran (Table 3, entry 9, 1)

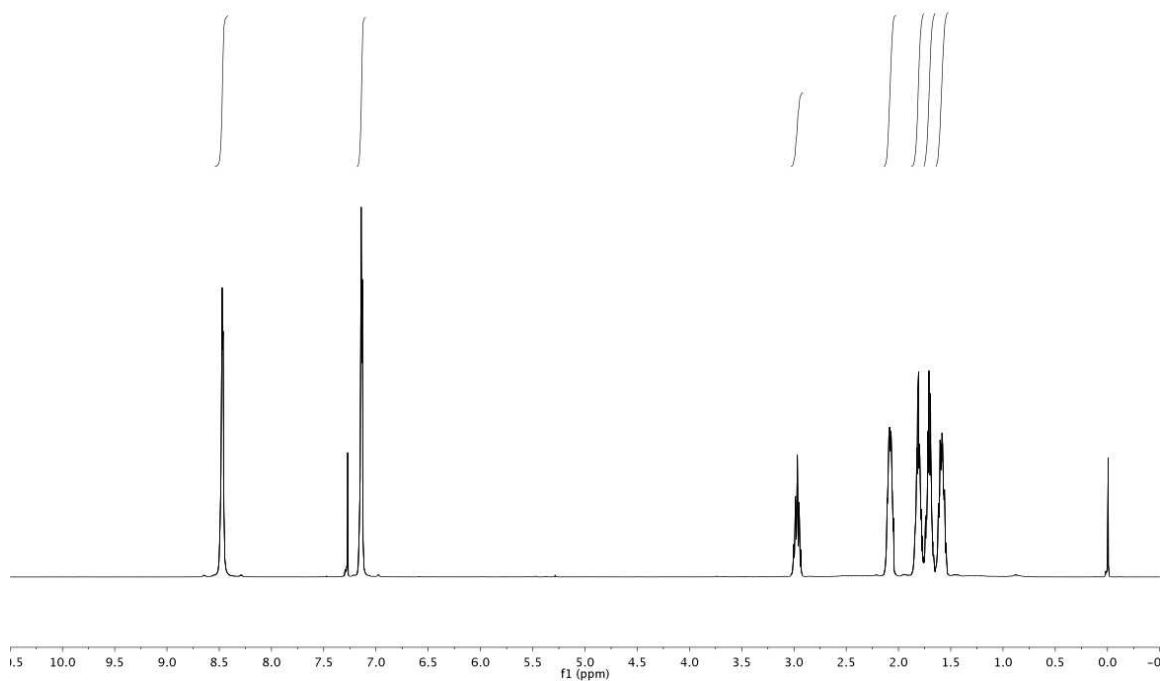
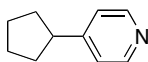




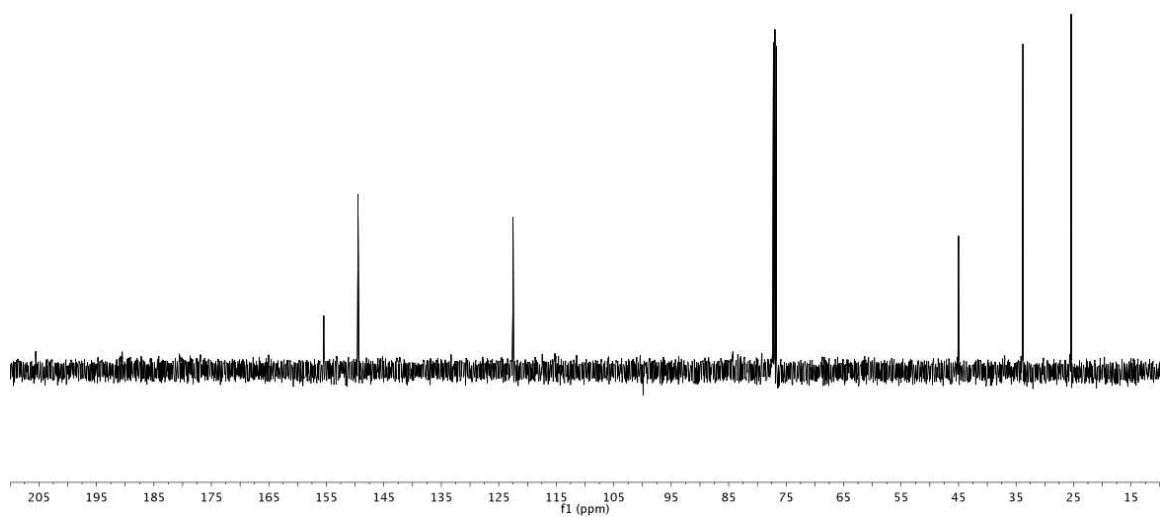
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-cyclopentylbenzofuran (Table 3, entry 10, 1)



$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-cyclopentylbenzofuran (Table 3, entry 10, 1)

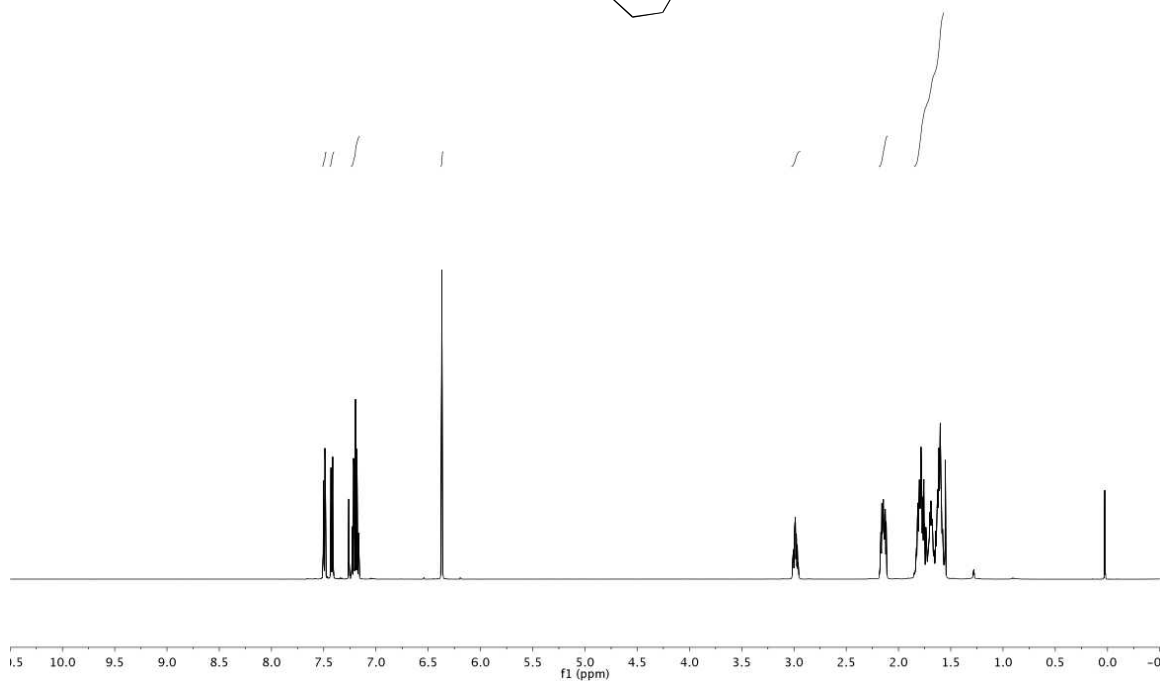
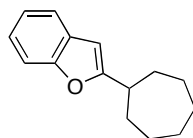


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 4-cyclopentylpyridine (Table 3, entry 10, 2)

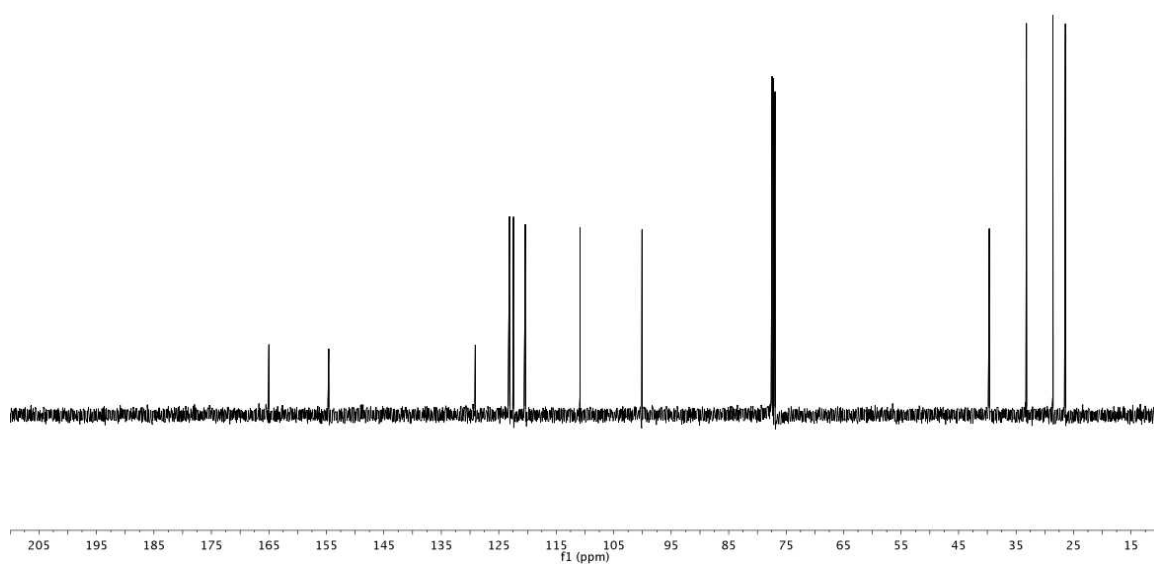


<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 4-cyclopentylpyridine (Table 3, entry 10, 2)

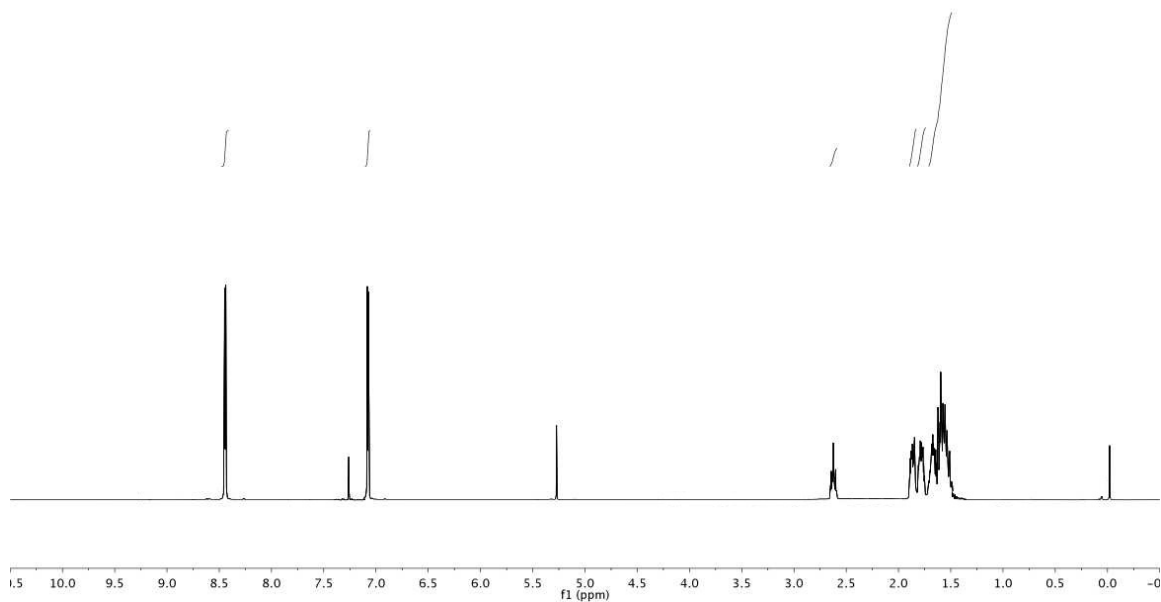
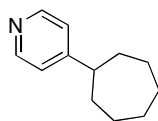




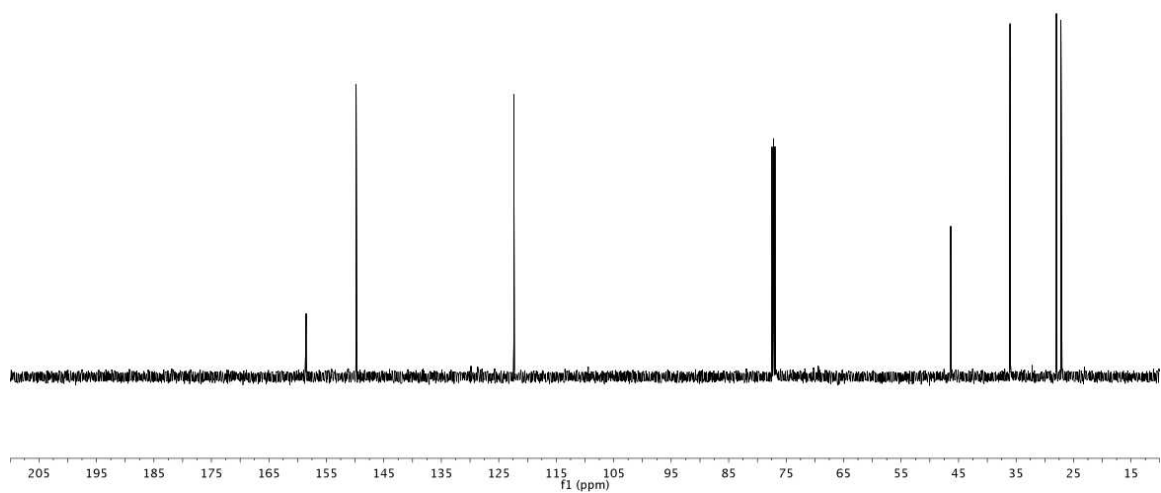
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-cycloheptylbenzofuran (Table 3, entry 11, 1)



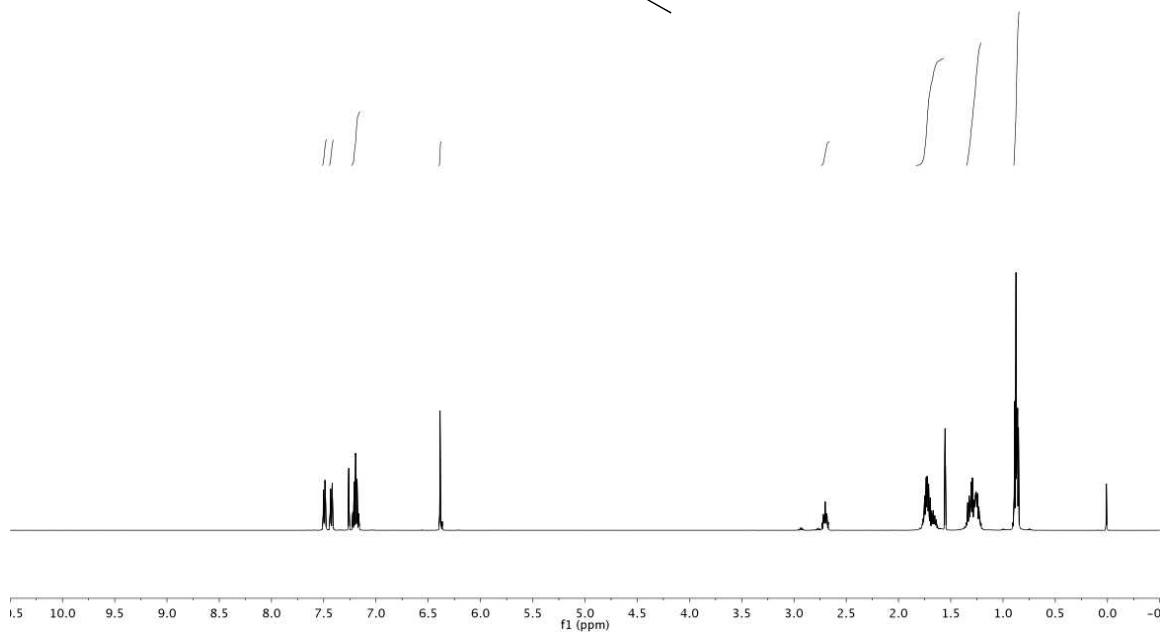
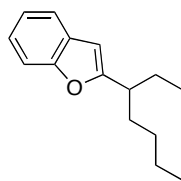
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-cycloheptylbenzofuran (Table 3, entry 11, 1)



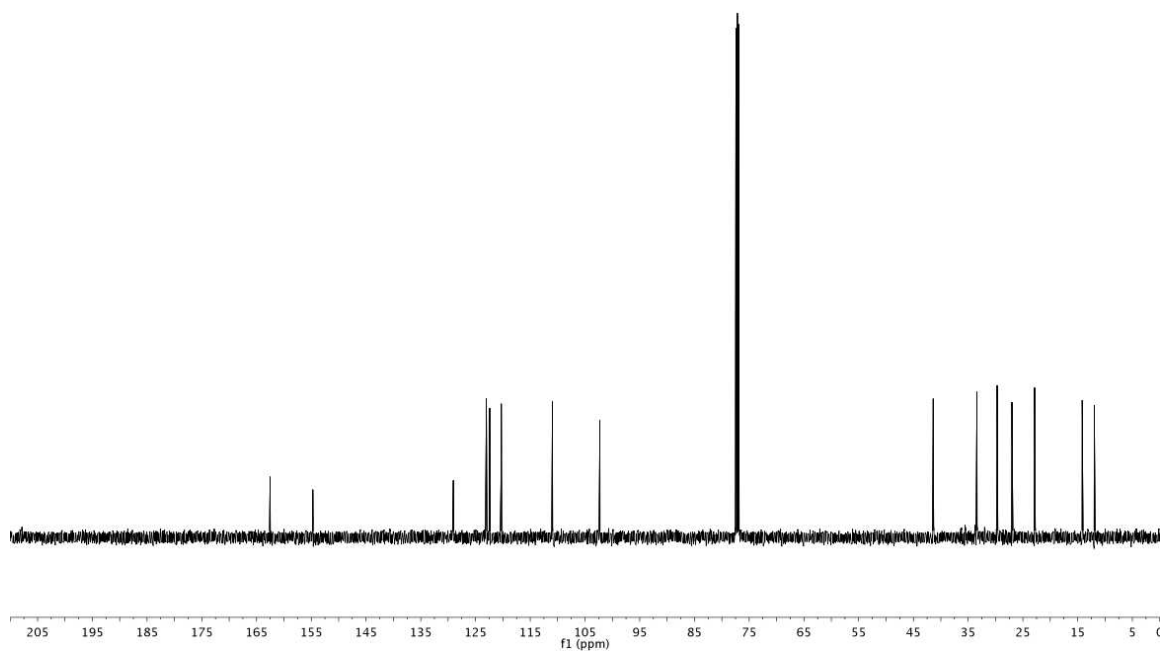
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-cycloheptylpyridine (Table 3, entry 11, 2)



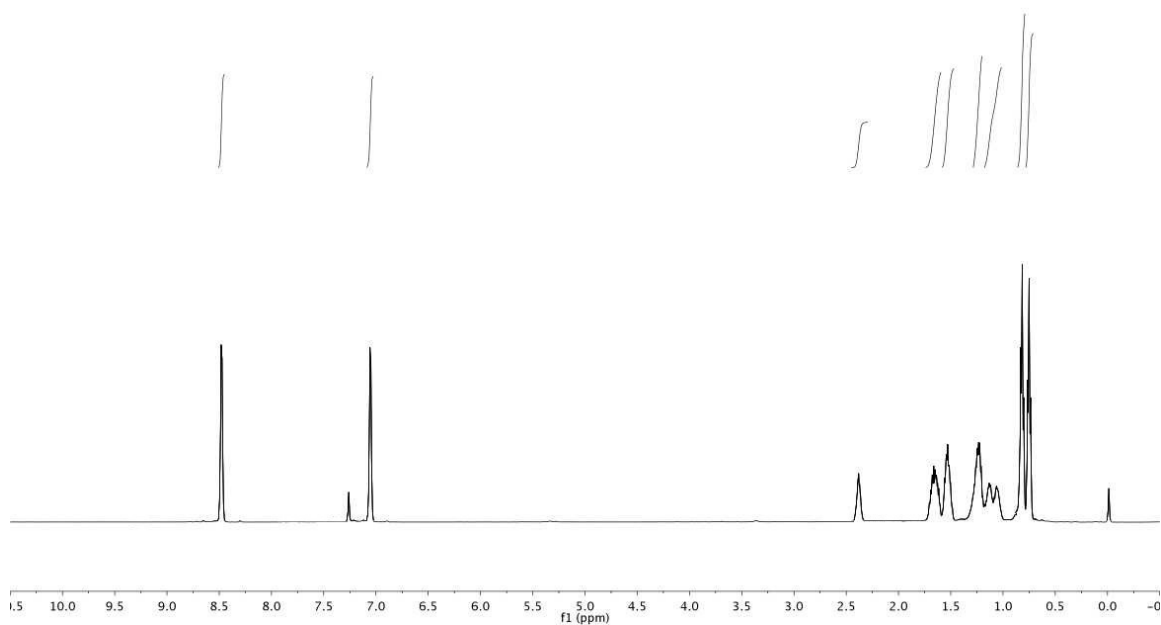
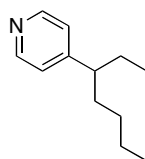
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 2-cycloheptylpyridine (Table 3, entry 11, 2)



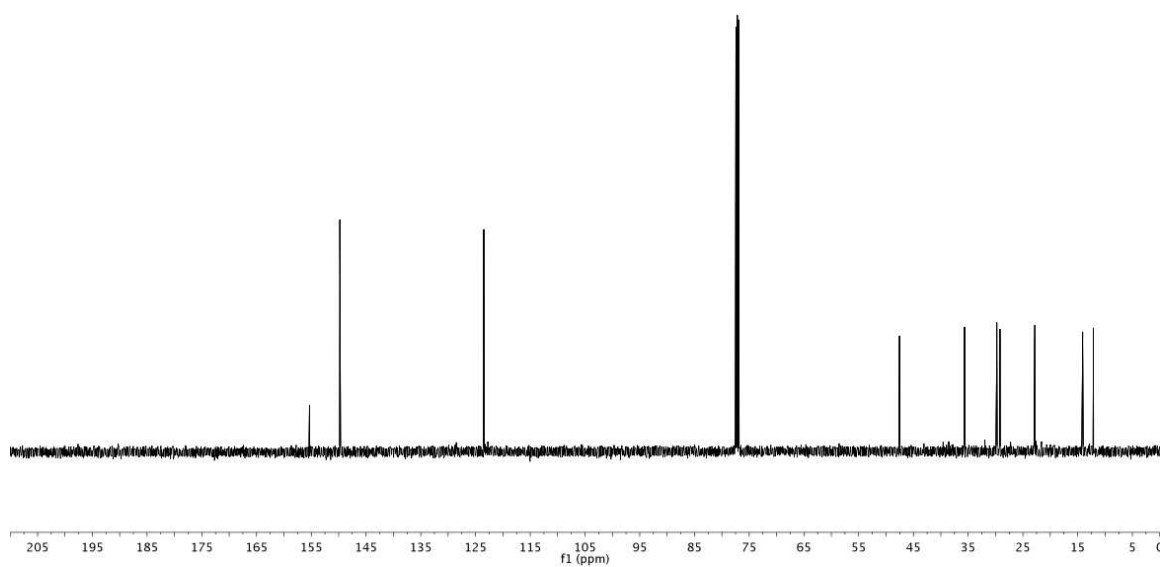
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-(heptan-3-yl)benzofuran (Table 3, entry 12, 1)



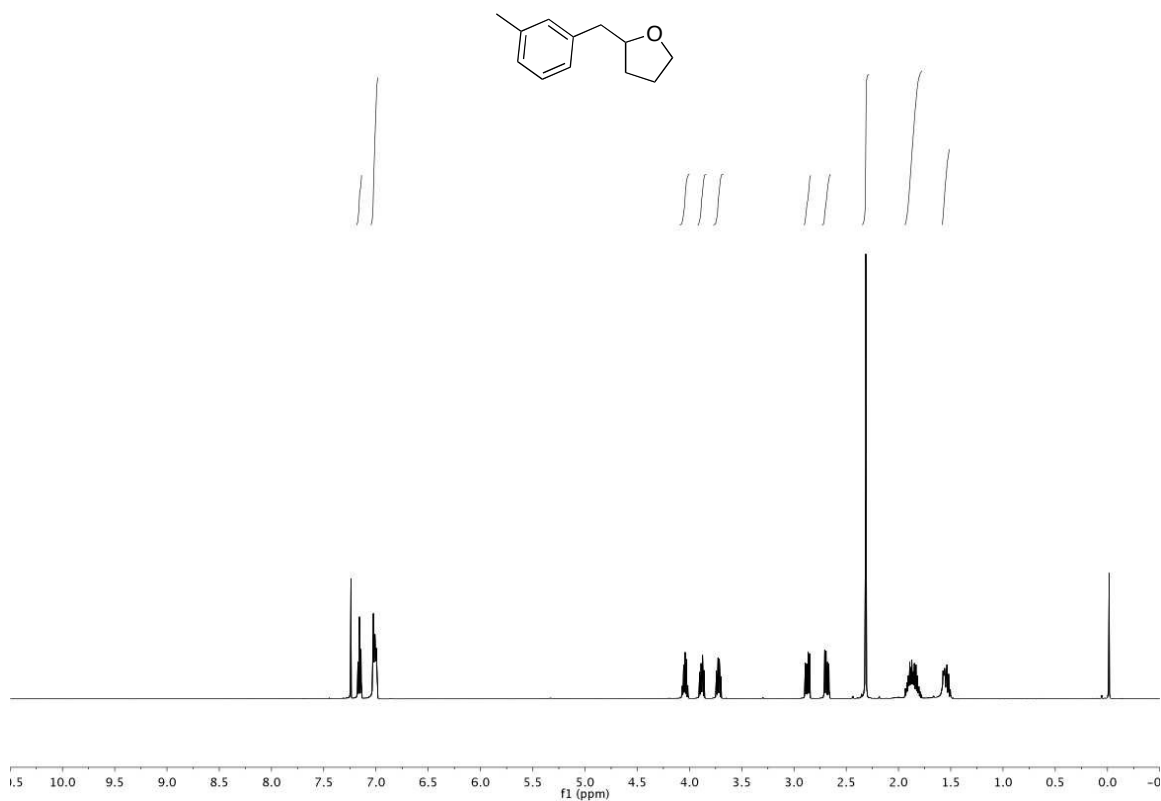
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-(heptan-3-yl)benzofuran (Table 3, entry 12, 1)



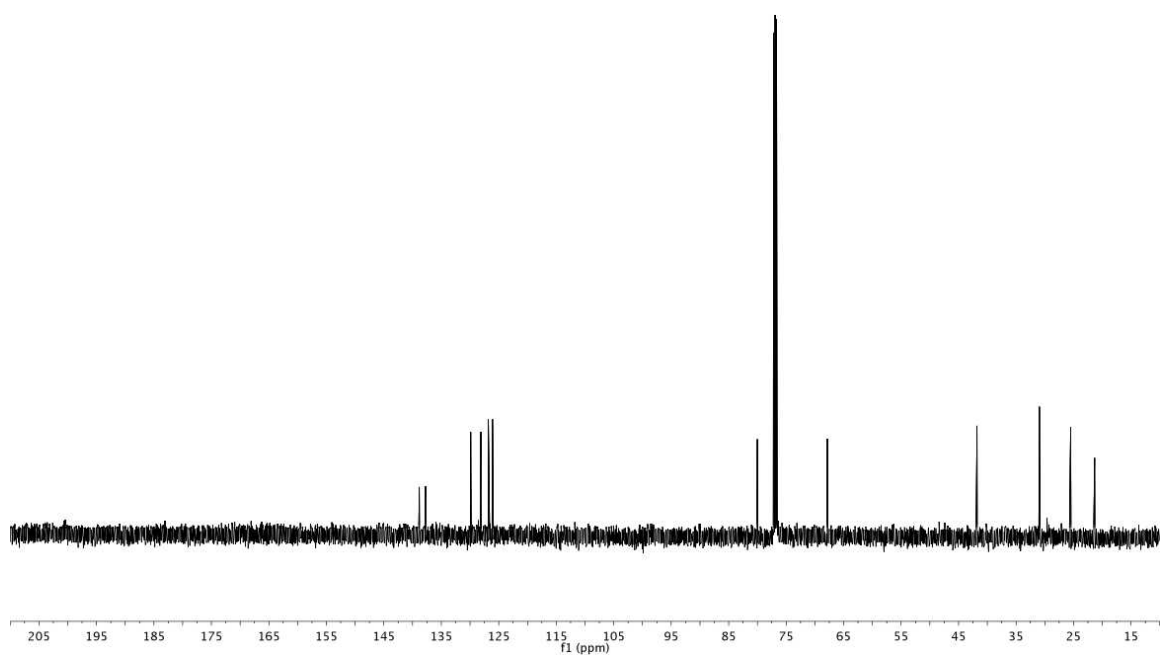
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 4-(heptan-3-yl)pyridine (Table 3, entry 12, 2)



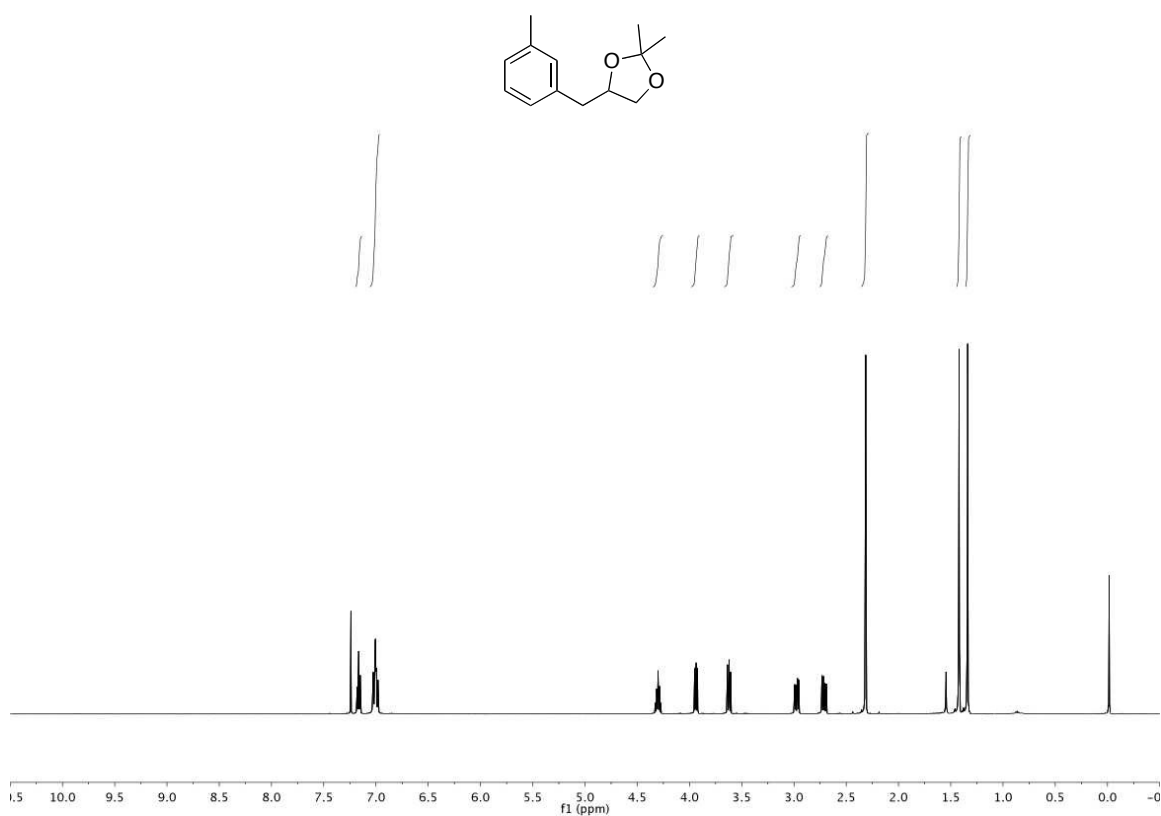
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 4-(heptan-3-yl)pyridine (Table 3, entry 12, 2)



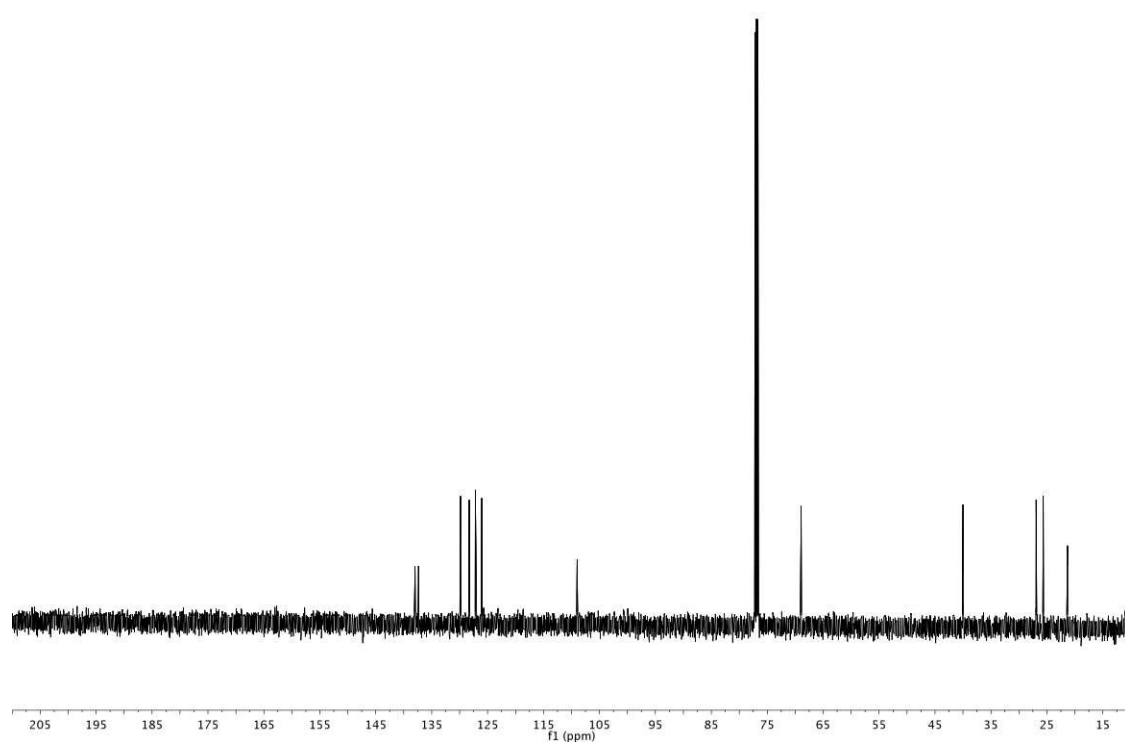
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 2-(3-methylbenzyl)tetrahydrofuran (Table 4, entry 1)



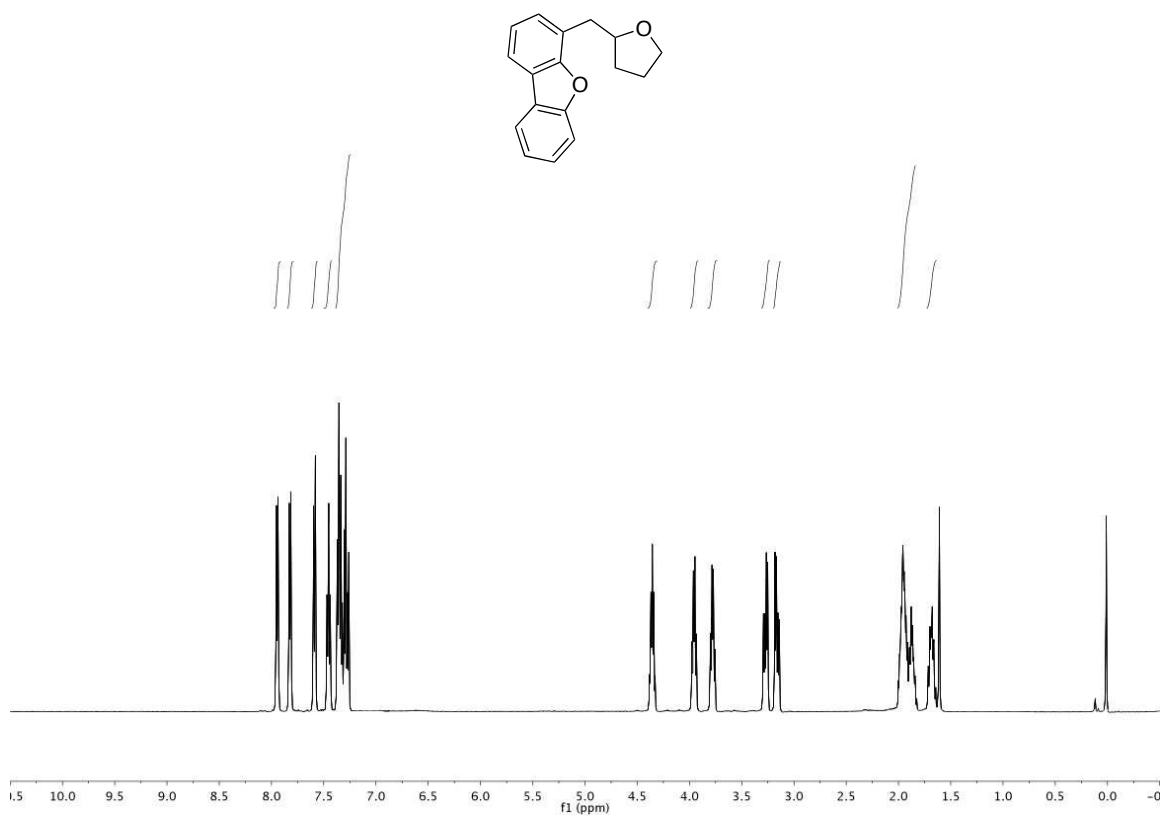
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of 2-(3-methylbenzyl)tetrahydrofuran (Table 4, entry 1)



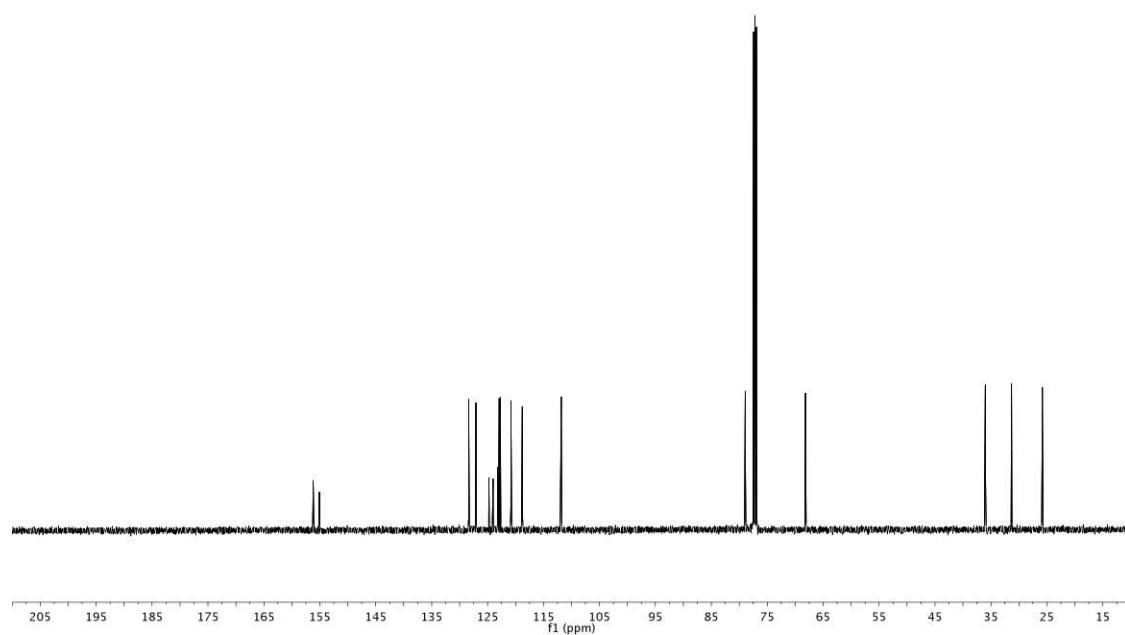
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2,2-dimethyl-4-(3-methylbenzyl)-1,3-dioxolane (Table 4, entry 2)



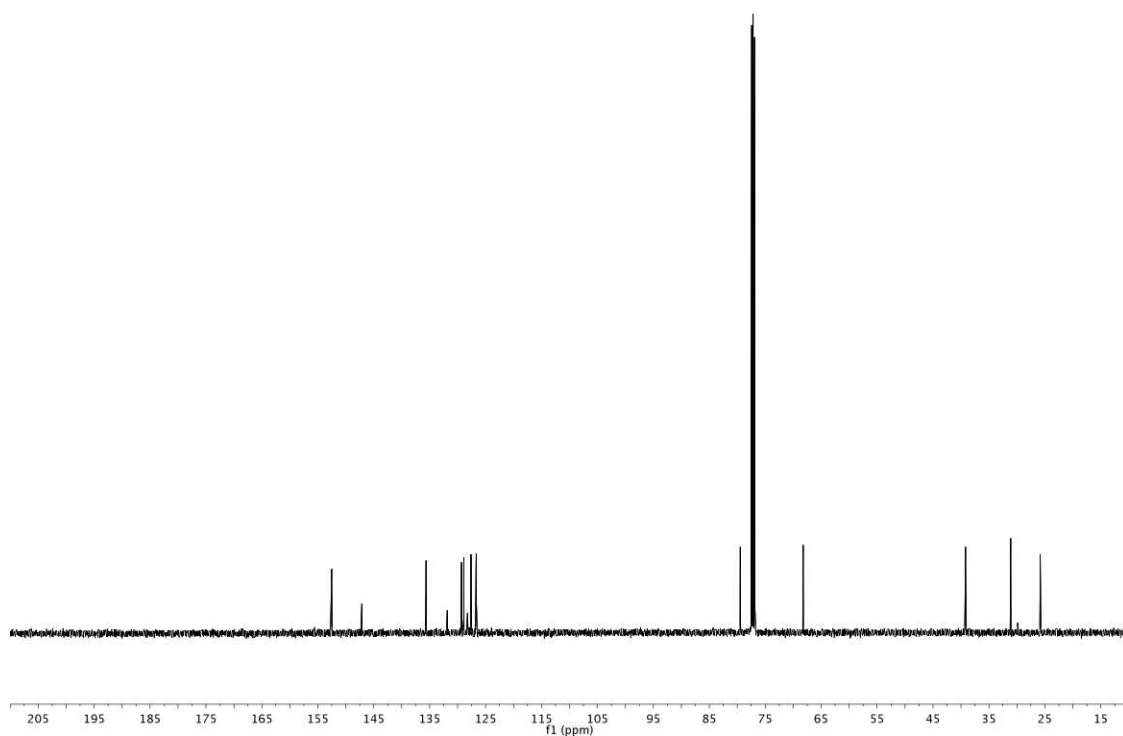
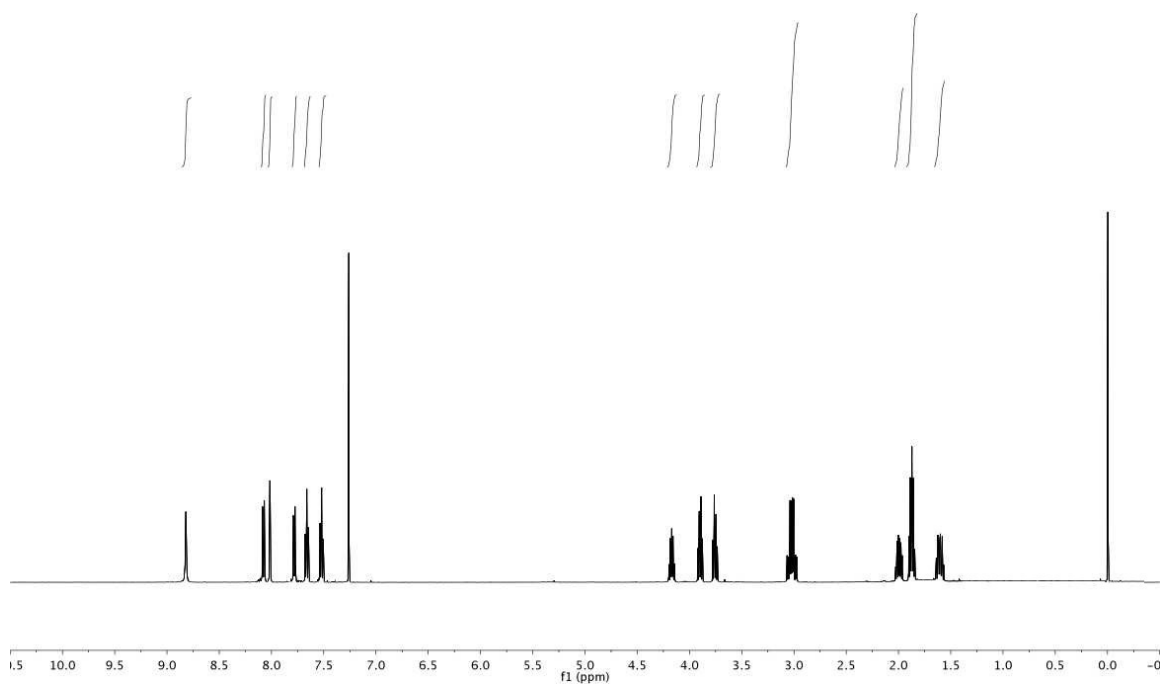
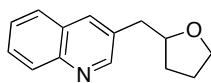
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 2,2-dimethyl-4-(3-methylbenzyl)-1,3-dioxolane (Table 4, entry 2)



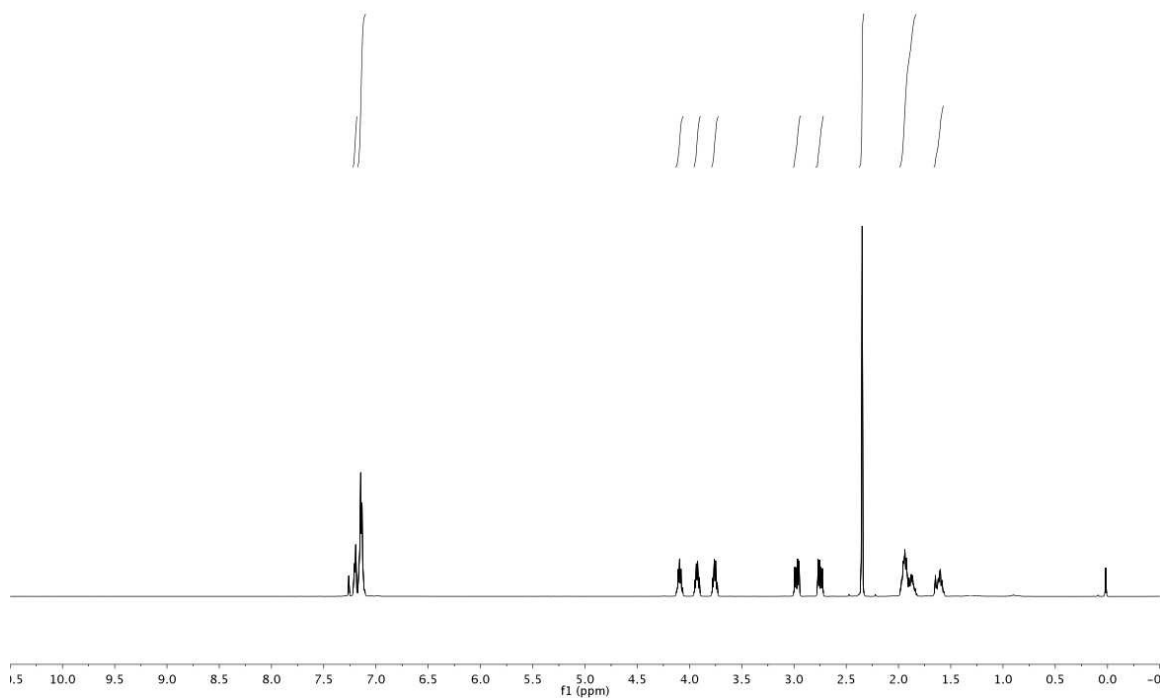
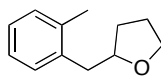
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 4-((tetrahydrofuran-2-yl)methyl)dibenzo[*b,d*]furan (Table 4, entry 3)



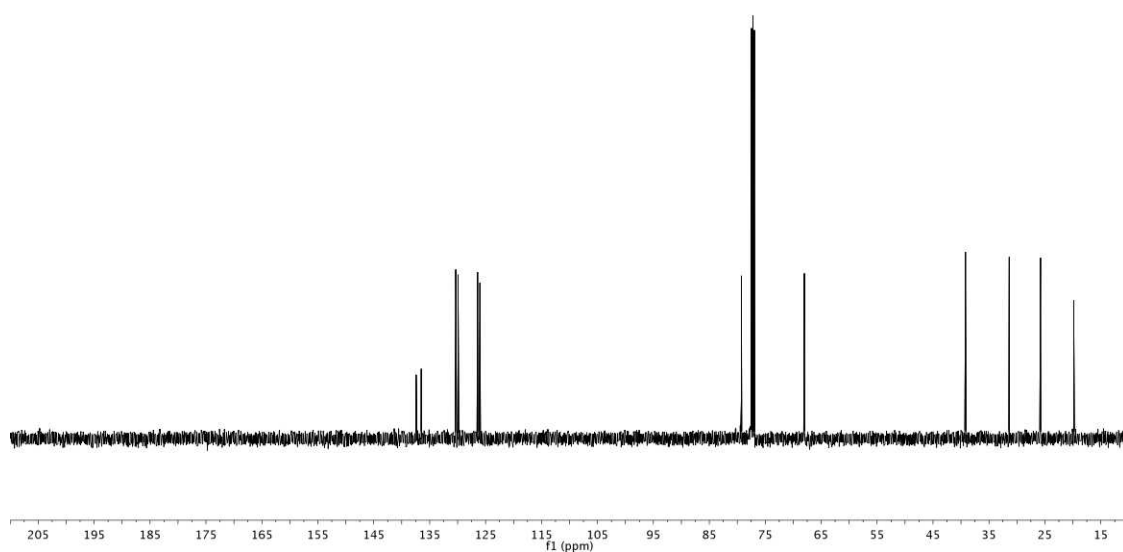
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 4-((tetrahydrofuran-2-yl)methyl)dibenzo[*b,d*]furan (Table 4, entry 3)



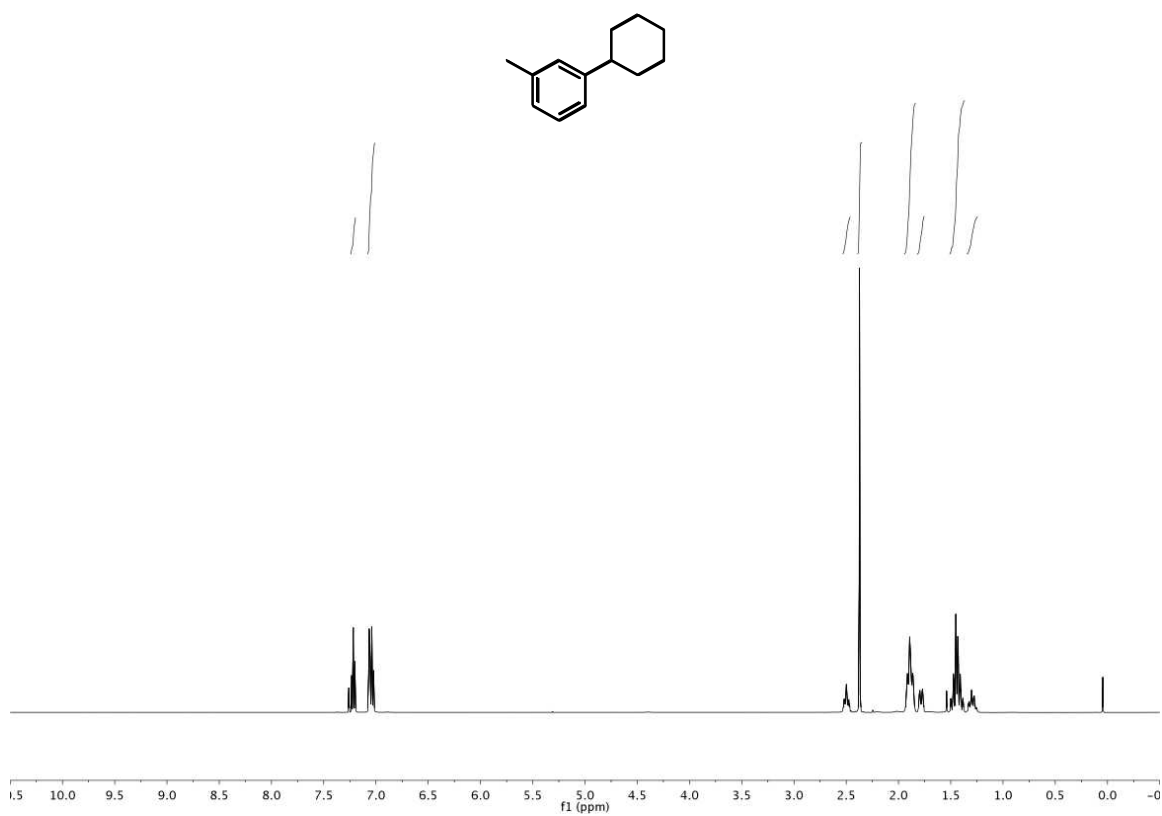




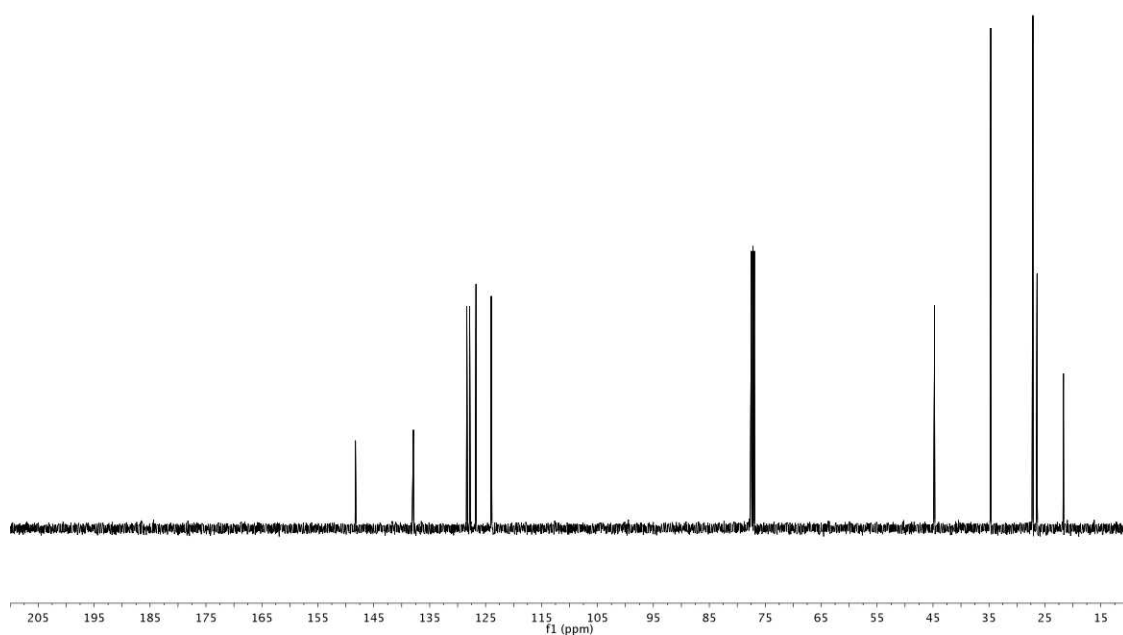
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of 2-(2-methylbenzyl)tetrahydrofuran (Table 4, entry 5)



<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) of 2-(2-methylbenzyl)tetrahydrofuran (Table 4, entry 5)



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of cyclohexyl-3-methylbenzene (Table 4, entry 6)



$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) of cyclohexyl-3-methylbenzene (Table 4, entry 6)