## Selective mono-alkylation of N-methoxybenzamides

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## **General Information**

Flash chromatography was performed on silica gel 100-200 µm. The solvent system used was a gradient of petroleum ether/ethyl acetate, increasing in polarity to ethyl acetate. Thin layer chromatography (TLC) was performed on glass-backed plates pre-coated with silica (GF254), which were developed using standard visualizing agents. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 400 MHz BRUKER AVANCE spectrometer at 25 °C. <sup>1</sup>H: Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CHCl<sub>3</sub>:  $\delta$  7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, sept = septet), integration, coupling constants (J) in Hz.  $^{13}$ C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl<sub>3</sub>:  $\delta$  77.16 ppm). Low resolution mass spectra were recorded on Micromass Autospec, operating in Agilent GC-MS operating in either E.I. or C.I mode. High-resolution mass spectrometry recorded for accurate mass analysis, was performed on a Q-TOF micro spectrometer. Melting points were performed on recrystallized solids and recorded on a national standard melting point apparatus and are uncorrected.

## **General Procedures**

All the known amides *N*-methoxybenzamides, *N*-benzyloxybenzamide, *N*-methybenzamide were prepared following literature procedure and the analytical data were agreed with those data which have been reported previously.

### General Procedure A: Synthesis of N-alkoxybenzamides



To a solution of the carboxylic acid (10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.3 M) at 0 °C under N<sub>2</sub>,

oxalyl chloride (12 mmol) was added dropwise followed by a catalytic amount of DMF (2 drops). The reaction was allowed to stir at room temperature until completion (typically 4 h). The solvent was then removed under reduced pressure to afford the corresponding crude acid chloride. Alkoxyamine hydrochloride (11 mmol) was added to a biphasic mixture of  $K_2CO_3$  (20 mmol) in a 2 : 1 mixture of EtOAc :  $H_2O$  (0.2 M). The resulting solution was cooled to 0  $\mathbb{C}$  followed by addition of a solution unpurified acid chloride in a minimum amount of EtOAc dropwise. The flask containing the acid chloride was then rinsed with additional EtOAc. The reaction was stirring for 4 h and slowly warmed up to room temperature. The two layers were separated and extracted with EtOAc (20 mL x 2). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel. <sup>[1]</sup>

#### **General Procedure B: Synthesis of ligand 8**



To a vigorously stirred solution containing 1, 2-bis (2-chlorethoxy) ethane (1.9 g, 10.3 mmol), NaI (1.5 g, 10.3 mmol) and Na<sub>2</sub>CO<sub>3</sub> (5.2 g, 49.4 mmol) in refluxing CH<sub>3</sub>CN (20 mL) was added a solution of benzylamine (1.1 g, 10.3 mmol) in CH<sub>3</sub>CN (12 mL). After being heated at reflux for 30 h, the mixture was cooled, filtered, and concentrated in vacuo. The crude solid product was dissolved in a refluxing solution of acetone:dioxane (1 : 1) and allowed to crystallize. The crystal is compound A. <sup>[3]</sup>

In a 500mL two-neck flask equipped with a condenser, the Na (6.25 g, 540 mmol) was dissolved in liquid ammonia (150 mL) and THF (100 mL) and then compound A (5 g, 11 mmol) dissolved in THF (50 mL) was added dropwise at -78 °C. After further 2 h, the reaction was quenched with EtOH (20 mL). After warming to room temperature and filtration, the solvent was evaporated, get the compound B. <sup>[4]</sup>

#### **General Procedure C: Synthesis of ligand 11**



A 250 mL well-dried round-bottomed flask was charged with nitrogen through Schlenk line. To a solution of 1, 2-dibromobenzene (9.44 g, 40 mmol), freshly distilled cyclopentadiene (2.64 g, 40 mmol) in toluene (40 mL) at 0 °C, a solution of <sup>n</sup>BuLi (c = 2.4 mol/L in hexanes, 40 mmol) was added dropwise over a period of 30 min. After the resulting white suspension had been stirred at 0 °C for additional 10 min, the mixture was allowed to reach 25 °C and stir overnight. Water (30 mL) was added and the layers were separated. The aqueous layer was extracted with petroleum ether (20 mL x 3) and the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The crude product was purified by flash chromatography to give product as a colorless oil.<sup>[2]</sup>

#### **General Procedure D: Synthesis of ligand 12 and ligand 13**



Triethylamine (6.6 mmol, 0.92 mL) and the desired anhydride (6 mmol) were added to a solution of amine (6 mmol) in 5 mL of N, N-dimethylformamide (DMF). The solution was heated for 16 h at 120 °C. After it was cooled down to room temperature, the resulting mixture was treated with water (30 mL), and extracted with diethyl ether

(20 mL x 3) and washed with 1 N HCl (20 mL). The combined organic layer was washed with brine, dried over magnesium sulfate and concentrated in vacuo, purified by chromatography on a column of silica gel with PE/EA = 3/1 to afford the pure products as a white solid.<sup>[5]</sup>

## General Procedure E: Synthesis of alkylated aryl amides

A solution of amide (0.2 mmol), alkyl halide (1.2 mmol), Pd(OAc)<sub>2</sub> (10 mol%), PivOH (0.4 mmol), CsOAc (0.6 mmol), L-12 (0.2 mmol), toluene (2 mL) was heated in 100 °C under air for 7-24 h. After the reaction completed, the reaction mixture was allowed to cool down to room temperature and saturated aqueous NaHCO<sub>3</sub> (20 mL) was added. The resulting mixture was extracted with EtOAc (20 mL x 3). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure to provide the crude product. The purification was performed by flash column chromatography on silica gel.

### Table 1. Reaction condition screening



Entries <sup>a</sup>	Base	PivOH	8aa yield <sup>b</sup> (%)	8aa' yield <sup>b</sup> (%)
1			0	0
2	KOAc		0	0
3	K <sub>2</sub> HPO <sub>4</sub>		0	0
4	K <sub>2</sub> CO <sub>3</sub>		0	0
5	CsOAc		25	5
6	$Cs_2CO_3$		0	0
7	CsOAc	0.5 eq	34	15
8	CsOAc	1 eq	47	21
9	CsOAc	2 eq	53	43
10	CsOAc	4 eq	40	22

<sup>a</sup>Conditions: Benzamide (0.2 mmol), <sup>*n*</sup>BuI (1.2 mmol), Pd(OAc)<sub>2</sub> (10 mol%), base (0.6 mmol), toluene (2 mL), 100 °C, 24 h, under air. <sup>b</sup>Isolate yield.

## References

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- [4] Crossley, R.; Goolamali, Z.; Gosper, J. J.; Sammes, P. G. J. Chem. Soc., Perkin Trans. 2, 1994, 513.
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#### 2-Butyl-N-methoxybenzamide (8aa)

Following the general procedure E, the compound **8aa** was isolated as a colorless oil (31.0 mg, 75% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.40 (br s, 1H), 7.36 (t, *J* = 7.0 Hz, 1H), 7.30 (d, *J* = 7.0 Hz, 1H), 7.25 (d, *J* = 7.0 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 3.88 (s, 3H), 2.76 (t, *J* = 8.0 Hz, 2H), 1.63-1.55 (m, 2H), 1.41-1.32 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>):  $\delta$  166.4, 141.2, 134.3, 130.3, 130.2, 127.9, 126.0, 63.5, 33.7, 32.6, 22.5, 14.2. HRMS (ESI) m/z Calcd for C<sub>12</sub>H<sub>17</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 208.1338, found: 208.1335.



#### 2, 6-Dibutyl-N-methoxybenzamide (8aa')

Following the general procedure E, the compound **8aa'** was isolated as a colorless oil (4.2 mg, 8% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.28 (br s, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 2H), 3.91 (s, 3H), 2.6 (t, *J* = 8.0 Hz, 4H), 1.64-1.54 (m, 4H), 1.41-1.32 (m, 4H), 0.91 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  167.6 140.4, 132.7, 129.6, 126.6, 64.5, 33.9, 33.0, 22.8, 13.9. HRMS (ESI) m/z Calcd for C<sub>16</sub>H<sub>25</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 264.1964, found: 264.1965.



#### 2-Butyl-4-fluoro-N-methoxybenzamide (8ba)

Following the general procedure E, the compound **8ba** was isolated as a colorless oil (30.2 mg, 67% yield). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  11.44 (br s, 1H), 7.35-7.31 (m, 1H), 7.14 (dd, J = 10.5, 2.5 Hz, 1H), 7.07 (td, J = 8.5, 2.5 Hz, 1H), 3.70 (s, 3H), 2.69 (t, J = 8.0 Hz, 2H), 1.59-1.45 (m, 2H), 1.33-1.24 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>):  $\delta$  165.6, 163.1 ( $J_{C-F} = 246.5$  Hz), 144.8 ( $J_{C-F} = 8.0$  Hz), 130.7 ( $J_{C-F} = 3.0$  Hz), 130.3 ( $J_{C-F} = 9.0$  Hz), 116.9 ( $J_{C-F} = 21.0$  Hz), 112.8 ( $J_{C-F} = 21.5$  Hz), 63.6, 33.3, 32.5, 22.5, 14.2. HRMS (ESI) m/z Calcd for C<sub>12</sub>H<sub>16</sub>FNO<sub>2</sub>



#### 2, 6-Dibutyl-4-fluoro-N-methoxybenzamide (8ba')

Following the general procedure E, the compound **8ba'** was isolated as a colorless oil (6.2 mg, 11% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.35 (br s, 1H), 6.76 (s, 1H), 6.74 (s, 1H), 3.90 (s, 3H), 2.58 (t, *J* = 8.0 Hz, 4H), 1.64-1.49 (m, 4H), 1.44-1.29 (m, 4H), 0.91 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  166.9, 163.3 (*J*<sub>C-F</sub> = 248.0 Hz), 143.3 (*J*<sub>C-F</sub> = 8.0 Hz), 128.8 (*J*<sub>C-F</sub> = 3.0 Hz), 113.3 (*J*<sub>C-F</sub> = 21.5 Hz), 64.4, 33.5, 32.9 (*J*<sub>C-F</sub> = 1.5 Hz), 22.6, 13.9. HRMS (ESI) m/z Calcd for C<sub>16</sub>H<sub>24</sub>FNO<sub>2</sub> [M+H]<sup>+</sup>: 282.1869, found: 282.1866.



#### 2-Butyl-4-chloro-N-methoxybenzamide (8ca)

Following the general procedure E, the compound **8ca** was isolated as a colorless oil (35.7 mg, 74% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.67 (br s, 1H), 7.23-7.20 (m, 2H), 7.14 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.85 (s, 3H), 2.70 (t, *J* = 8.0 Hz, 2H), 1.59-1.52 (m, 2H), 1.39-1.29 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  167.1, 144.1, 136.5, 130.8, 130.2, 128.6, 125.8, 64.6, 33.5, 32.7, 22.6, 13.9. HRMS (ESI) m/z Calcd for C<sub>12</sub>H<sub>16</sub><sup>35</sup>ClNO<sub>2</sub> [M+H]<sup>+</sup>: 242.0948, found: 242.0949.



### 2, 6-Dibutyl-4-chloro-N-methoxybenzamide (8ca')

Following the general procedure E, the compound **8ca'** was isolated as a colorless oil (7.1 mg, 12% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.33 (br s, 1H), 7.04 (s, 2H), 3.90 (s, 3H), 2.56 (t, *J* = 8.0 Hz, 4H), 1.61-1.54 (m, 4H), 1.40-1.30 (m, 4H), 0.91 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  166.7, 142.4, 135.5, 131.1, 126.6, 64.5, 33.6, 32.8, 22.7, 13.9. HRMS (ESI) m/z Calcd for C<sub>16</sub>H<sub>24</sub><sup>35</sup>ClNO<sub>2</sub> [M+H]<sup>+</sup>: 298.1574,

found: 298.1574.



#### 4-Bromo-2-butyl-N-methoxybenzamide (8da)

Following the general procedure E, the compound **8da** was isolated as a colorless oil (40.4 mg, 71% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.65 (br s, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.31 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 2.69 (t, *J* = 8.0 Hz, 2H), 1.59-1.52 (m, 2H), 1.39-1.29 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  167.1, 144.3, 133.2, 131.3, 128.8, 128.7, 124.9, 64.5, 33.5, 32.7, 22.6, 13.9. HRMS (ESI) m/z Calcd for C<sub>12</sub>H<sub>16</sub><sup>79</sup>BrNO<sub>2</sub> [M+H]<sup>+</sup>: 286.0443, found: 286.0446.



#### 4-Bromo-2, 6-dibutyl-N-methoxybenzamide (8da')

Following the general procedure E, the compound **8da'** was isolated as a colorless oil (10.9 mg, 16% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.29 (br s, 1H), 7.20 (s, 2H), 3.90 (s, 3H), 2.56 (t, *J* = 8.0 Hz, 4H), 1.61-1.54 (m, 4H), 1.40-1.30 (m, 4H), 0.92 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  166.7, 142.6, 131.6, 129.5, 123.9, 64.5, 33.6, 32.8, 22.7, 13.9. HRMS (ESI) m/z Calcd for C<sub>16</sub>H<sub>24</sub><sup>79</sup>BrNO<sub>2</sub> [M+H]<sup>+</sup>: 342.1069, found: 342.1066.



#### 2-Butyl-N-methoxy-4-(trifluoromethyl)benzamide (8ea)

Following the general procedure E, the compound **8ea** was isolated as a colorless oil (33.5 mg, 61% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.89 (br s, 1H), 7.48 (s, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H), 2.75 (t, J = 8.0 Hz, 2H), 1.59-1.52 (m, 2H), 1.39-1.29 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  166.7, 143.0, 135.8, 132.2 (q,  $J_{C-F} = 19.5$  Hz), 127.7, 126.8, 123.7 (q,

 $J_{C-F} = 273.5 \text{ Hz}$ , 122.6, 64.6, 33.5, 32.8, 22.6, 13.8. HRMS (ESI) m/z Calcd for  $C_{13}H_{16}F_3NO_2 [M+H]^+$ : 276.1211, found: 276.1213.



#### 2, 6-Dibutyl-N-methoxy-4-(trifluoromethyl)benzamide (8ea')

Following the general procedure E, the compound **8ea'** was isolated as a colorless oil (7.3 mg, 11% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.38 (br s, 1H), 7.30 (s, 2H), 3.92 (s, 3H), 2.64 (t, *J* = 8.0 Hz, 4H), 1.64-1.56 (m, 4H), 1.42-1.33 (m, 4H), 0.93 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  166.3, 141.6, 135.9, 131.8 (q, *J*<sub>C-F</sub> = 32.5 Hz), 123.8 (q, *J*<sub>C-F</sub> = 273.5 Hz), 123.3(q, *J*<sub>C-F</sub> = 3.5 Hz), 64.6, 33.7, 33.0, 22.7, 13.9. HRMS (ESI) m/z Calcd for C<sub>17</sub>H<sub>24</sub>F<sub>3</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 332.1837, found: 332.1835.



#### 2-Butyl-N-methoxy-4-methylbenzamide (8fa)

Following the general procedure E, the compound **8fa** was isolated as a colorless oil (38.4 mg, 79% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.35 (br s, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.06 (s, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 3.87 (s, 3H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.33 (s, 3H), 1.62-1.50 (m, 2H), 1.43-1.30 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  168.3, 142.0, 140.6, 131.0, 129.5, 127.3, 126.3, 64.4, 33.9, 32.8, 22.7, 21.4, 13.9. HRMS (ESI) m/z Calcd for C<sub>13</sub>H<sub>19</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 222.1494, found: 222.1494.



#### 2, 6-Dibutyl-N-methoxy-4-methylbenzamide (8fa')

Following the general procedure E, the compound **8fa'** was isolated as a colorless oil (7.7 mg, 14% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.17 (br s, 1H), 6.87 (s, 2H), 3.92 (s, 3H), 2.57 (t, J = 8.0 Hz, 4H), 2.30 (s, 3H), 1.62-1.55 (m, 4H), 1.41-1.32 (m, 4H), 0.92 (t, J = 7.5 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  167.9, 140.3, 139.5,

129.9, 127.3, 64.5, 34.0, 33.0, 22.8, 21.4, 14.0. HRMS (ESI) m/z Calcd for  $C_{17}H_{27}NO_2 [M+H]^+$ : 278.2120, found: 278.2122.



#### 2-Butyl-N, 4-dimethoxybenzamide (8ga)

Following the general procedure E, the compound **8ga** was isolated as a colorless oil (29.8 mg, 63% yield). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  11.30 (br s, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.81 (d, *J* = 2.5 Hz, 1H), 6.77 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.76 (s, 3H), 3.68 (s, 3H), 2.68 (t, *J* = 8.0 Hz, 2H), 1.57-1.44 (m, 2H), 1.34-1.23 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>):  $\delta$  166.4, 160.7, 143.6, 129.6, 126.5, 115.9, 111.0, 63.5, 55.6, 33.7, 32.8, 22.6, 14.3. HRMS (ESI) m/z Calcd for C<sub>13</sub>H<sub>19</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 238.1443, found: 238.1442.



#### 2, 6-Dibutyl-N, 4-dimethoxybenzamide (8ga')

Following the general procedure E, the compound **8ga'** was isolated as a colorless oil (12.9 mg, 22% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.18 (br s, 1H), 6.58 (s, 2H), 3.91 (s, 3H), 3.79 (s, 3H), 2.58 (t, *J* = 8.0 Hz, 4H), 1.68-1.52 (m, 4H), 1.44-1.30 (m, 4H), 0.92 (t, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  167.8, 160.3, 142.3, 125.5, 112.0, 64.4, 55.2, 33.8, 33.2, 22.8, 13.9. HRMS (ESI) m/z Calcd for C<sub>17</sub>H<sub>27</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 294.2069, found: 294.2066.



#### **3-Butyl-N-methoxy-2-naphthamide (8ha)**

Following the general procedure E, the compound **8ha** was isolated as a colorless oil (38.6 mg, 75% yield). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  11.61 (br s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.5 Hz, 2H), 7.77 (s, 1H), 7.59-7.46 (m, 2H), 3.76 (s, 3H), 2.86 (t, J = 8.0 Hz, 2H), 1.63-1.56 (m, 2H), 1.38-1.29 (m, 2H), 0.90 (t, J = 7.5 Hz,

3H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>): δ 166.4, 138.3, 133.9, 132.8, 131.1, 128.3, 128.3, 127.7, 127.7, 127.6, 126.5, 63.6, 33.5, 32.7, 22.6, 14.3. HRMS (ESI) m/z Calcd for C<sub>16</sub>H<sub>19</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 258.1494, found: 258.1495.



#### 2-Butyl-6-chloro-N-methoxybenzamide (8ia)

Following the general procedure E, the compound **8ia** was isolated as a colorless oil (24.1 mg, 50% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.34 (br s, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 3.93 (s, 3H), 2.64 (t, *J* = 8.0 Hz, 2H), 1.63-1.56 (m, 2H), 1.40-1.31 (m, 2H), 0.91 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  164.7, 143.4, 132.4, 131.4, 130.8, 127.8, 126.8, 64.5, 33.6, 33.0, 22.6, 13.9. HRMS (ESI) m/z Calcd for C<sub>12</sub>H<sub>16</sub><sup>35</sup>ClNO<sub>2</sub> [M+H]<sup>+</sup>: 242.0948, found: 242.0948.



#### 2-Butyl-N-methoxy-6-methylbenzamide (8ja)

Following the general procedure E, the compound **8ja** was isolated as a colorless oil (36.2 mg, 82% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.32 (br s, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.06-7.01 (m, 2H), 3.92 (s, 3H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.34 (s, 3H), 1.62-1.55 (m, 2H), 1.41-1.32 (m, 2H), 0.91 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  167.6, 140.4, 135.3, 133.0, 129.6, 127.6, 126.6, 64.5, 33.9, 32.9, 22.7, 19.1, 13.9. HRMS (ESI) m/z Calcd for C<sub>13</sub>H<sub>19</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 222.1494, found: 222.1495.



#### 2-Benzyl-N-methoxy-6-methylbenzamide (8jh)

Following the general procedure E, the compound 8jh was isolated as a colorless oil

(40.3 mg, 79% yield). 1H NMR (400 MHz, CDCl3) δ 8.20 (br s, 1H), 7.33-7.12 (m, 6H), 7.06 (d, J = 7.5 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 4.01 (s, 2H), 3.75 (s, 3H), 2.34 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 167.3, 140.4, 138.2, 135.8, 133.4, 129.8, 128.8, 128.6, 128.3, 127.8, 126.3, 64.3, 38.8, 19.1. HRMS (ESI) m/z Calcd for C16H17NO2 [M+H]+: 256.1338, found: 256.1337.



#### 2-Butyl-N, 6-dimethoxybenzamide (8ka)

Following the general procedure E, the compound **8ka** was isolated as a colorless oil (37.9 mg, 80% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.39 (br s, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 2.64 (t, *J* = 8.0 Hz, 2H), 1.62-1.55 (m, 2H), 1.39-1.30 (m, 2H), 0.90 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  166.4, 156.6, 143.5, 130.8, 122.3, 122.0, 108.3, 64.4, 55.8, 33.6, 32.8, 22.7, 13.9. HRMS (ESI) m/z Calcd for C<sub>13</sub>H<sub>19</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 238.1443, found: 238.1441.



#### 2-Butyl-5-chloro-N-methoxybenzamide (8la)

Following the general procedure E, the compound **8**Ia was isolated as a colorless oil (38.6 mg, 80% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.81 (br s, 1H), 7.31 (dd, J = 8.0, 2.0 Hz, 1H), 7.28-7.25 (m, 1H), 7.17 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H), 2.70 (t, J = 8.0 Hz, 2H), 1.58-1.51 (m, 2H), 1.39-1.27 (m, 2H), 0.90 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  166.5, 140.4, 133.9, 131.6, 131.3, 130.5, 127.2, 64.5, 33.6, 32.3, 22.6, 13.9. HRMS (ESI) m/z Calcd for C<sub>12</sub>H<sub>16</sub><sup>35</sup>ClNO<sub>2</sub> [M+H]<sup>+</sup>: 242.0948, found: 242.0945.



#### 5-Bromo-2-butyl-N-methoxybenzamide (8ma)

Following the general procedure E, the compound **8ma** was isolated as a colorless oil (53.9 mg, 91% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.51 (br s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 2.69 (t, *J* = 8.0 Hz, 2H), 1.59-1.51 (m, 2H), 1.38-1.29 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  166.4, 140.9, 134.2, 133.4, 131.9, 130.1, 119.0, 64.5, 33.5, 32.3, 22.6, 13.9. HRMS (ESI) m/z Calcd for C<sub>12</sub>H<sub>16</sub><sup>79</sup>BrNO<sub>2</sub> [M+H]<sup>+</sup>: 286.0443, found: 286.0445.



#### 2-Butyl-N, 5-dimethoxybenzamide (8na)

Following the general procedure E, the compound **8na** was isolated as a colorless oil (35.6 mg, 75% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.64 (br s, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 6.88 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.81 (d, *J* = 2.5 Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 2.65 (t, *J* = 8.0 Hz, 2H), 1.57-1.49 (m, 2H), 1.37-1.27 (m, 2H), 0.89 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  167.7, 157.3, 133.6, 133.2, 131.3, 116.2, 112.7, 64.5, 55.4, 34.0, 32.0, 22.6, 13.9. HRMS (ESI) m/z Calcd for C<sub>13</sub>H<sub>19</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 238.1443, found: 238.1442.



#### 2-Butyl-N-methoxy-1-naphthamide (80a)

Following the general procedure E, the compound **80a** was isolated as a colorless oil (36.0 mg, 70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.42 (br s, 1H), 7.85-7.79 (m, 3H), 7.55-7.41 (m, 2H), 7.34 (d, *J* = 8.5 Hz, 1H), 3.99 (s, 3H), 2.78 (t, *J* = 8.0 Hz, 2H), 1.71-1.64 (m, 2H), 1.48-1.33 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  167.2, 138.7, 131.6, 130.6 129.9, 129.2, 128.0, 127.2, 127.2, 125.7, 124.3, 64.7, 33.9, 33.4, 22.8, 14.0. HRMS (ESI) m/z Calcd for C<sub>16</sub>H<sub>19</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 258.1494, found: 258.1492.



#### 6-Butyl-N, 2, 3-trimethoxybenzamide (8pa)

Following the general procedure E, the compound **8pa** was isolated as a colorless oil (42.7 mg, 80% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.58 (br s, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 2.60 (t, *J* = 8.0 Hz, 2H), 1.64-1.47 (m, 2H), 1.40-1.28 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  165.7, 150.2, 145.9, 134.2, 128.0, 125.2, 113.8, 64.3, 62.0, 55.9, 33.7, 32.1, 22.6, 13.9. HRMS (ESI) m/z Calcd for C<sub>14</sub>H<sub>21</sub>NO<sub>4</sub> [M+H]<sup>+</sup>: 268.1549, found: 268.1548.



#### 2-Butyl-N, 4, 5-trimethoxybenzamide (8qa)

Following the general procedure E, the compound **8qa** was isolated as a colorless oil (40.0 mg, 75% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.32 (br s, 1H), 6.84 (s, 1H), 6.71 (s, 1H), 3.89 (s, 6H), 3.85 (s, 3H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.61-1.53 (m, 2H), 1.41-1.32 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  168.1, 150.5, 146.5, 135.3, 124.1, 112.9, 110.7, 64.4, 56.1, 55.9, 34.2, 32.7, 22.7, 13.9. HRMS (ESI) m/z Calcd for C<sub>14</sub>H<sub>21</sub>NO<sub>4</sub> [M+H]<sup>+</sup>: 268.1549, found: 268.1549.



#### Methyl 5-(2-(methoxycarbamoyl)phenyl)pentanoate (8ab)

Following the general procedure E, the compound **8ab** was isolated as a colorless oil (37 mg, 73% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.68 (br s, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 3.86 (s, 3H), 3.63 (s, 3H), 2.77 (s, 2H), 2.30 (dd, *J* = 9.0, 4.5 Hz, 2H), 1.67-1.59 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  174.3, 168.2, 141.3, 132.7, 130.7, 130.4, 127.4, 126.0, 77.0, 64.6, 51.6, 33.9, 32.8, 30.9, 24.7. HRMS (ESI) m/z Calcd for C<sub>14</sub>H<sub>20</sub>NO<sub>4</sub>

[M+H]<sup>+</sup>: 266.1392, found: 266.1391.



Dimethyl 5, 5'-(2-(methoxycarbamoyl)-1, 3-phenylene)dipentanoate (8ab')

Following the general procedure E, the compound **8ab'** was isolated as a colorless oil (7.6 mg, 10% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.91 (br s, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 3.87 (s, 3H), 3.61 (s, 6H), 2.59 (s, 4H), 2.27 (d, *J* = 5.5 Hz, 4H), 1.61 (s, 8H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  174.3, 167.4, 139.7, 133.02, 129.7, 126.9, 64.4, 51.6, 33.8, 32.9, 30.9, 24.7. HRMS (ESI) m/z Calcd for C<sub>20</sub>H<sub>29</sub>NO<sub>6</sub> [M+H]<sup>+</sup>: 380.2073, found: 380.2070.



#### 2-(4-Cyanobutyl)-N-methoxybenzamide (8ac)

Following the general procedure E, the compound **8ac** was isolated as a colorless oil (30.2 mg, 65% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.88 (br s, 1H), 7.36 (dd, J = 12.0, 4.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.25-7.15 (m, 2H), 3.82 (s, 3H), 2.76 (dd, J = 10.0, 5.0 Hz, 2H), 2.38-2.27 (m, 2H), 1.81-1.59 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.8, 140.8, 132.4, 130.9, 130.3, 127.4, 126.2, 119.9, 64.8, 32.2, 30.5, 25.1, 17.0. HRMS (ESI) m/z Calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 233.1290, found: 233.1290.



#### 2, 6-Dis(4-cyanobutyl)-N-methoxybenzamide (8ac')

Following the general procedure E, the compound **8ac'** was isolated as a colorless oil (10.0 mg, 16% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.70 (br s, 1H), 7.33-7.24 (m,

1H), 7.08 (d, J = 7.5 Hz, 2H), 3.90 (s, 3H), 2.68-2.60 (m, 4H), 2.34 (t, J = 7.0 Hz, 4H), 1.83-1.76 (m, 4H), 1.67 (tt, J = 7.0, 4.0 Hz, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.2, 139.1, 133.1, 130.1, 127.1, 119.8, 64.6, 32.3, 30.4, 25.0, 17.1. HRMS (ESI) m/z Calcd for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 314.1869, found: 314.1866.



#### N-methoxy-2, 6-dimethylbenzamide (8ad')

Following the general procedure E, the compound **8ad'** was isolated as a colorless oil (34.0 mg, 19% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.66 (br s, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 2H), 3.86 (s, 3H), 2.28 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  167.5, 135.3, 133.4, 129.5, 127.5, 64.4, 19.0. HRMS (ESI) m/z Calcd for C<sub>10</sub>H<sub>13</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 180.1025, found: 180.1024.



#### 2-Isobutyl-N-methoxybenzamide (8ae)

Following the general procedure E, the compound **8ae** was isolated as a colorless oil (19.5mg, 47% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.68 (br s, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 6.5 Hz, 1H), 7.11 (m, 2H), 3.76 (s, 3H), 2.57 (d, *J* = 7.5 Hz, 2H), 1.82 (dt, J = 13.5, 7.0 Hz, 1H), 0.80 (d, *J* = 6.5 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.1, 139.7, 131.8, 130.0, 129.2, 126.3, 124.7, 63.4, 41.0, 29.1, 21.4. HRMS (ESI) m/z Calcd for C<sub>12</sub>H<sub>17</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 208.1338, found: 208.1338.



#### 2, 6-Diisobutyl-N-methoxybenzamide (8ae')

Following the general procedure E, the compound 8ae' was isolated as a colorless oil

(2.0mg, 4% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.14 (br s, 1H), 7.25 (t, *J* = 10.0, 5.0 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 2H), 3.93 (s, 3H), 2.50 (d, *J* = 7.5 Hz, 4H), 1.94 (m, 2H), 0.90 (d, *J* = 6.5 Hz, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.7, 139.4, 133.6, 129.2, 127.6, 64.6, 42.5, 30.1, 22.7. HRMS (ESI) m/z Calcd for C<sub>16</sub>H<sub>25</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 264.1964, found: 264.1962.



#### N-Methoxy-2-(3, 3, 3-trifluoropropyl)benzamide (8af)

Following the general procedure E, the compound **8af** was isolated as a colorless oil (22mg, 45% yield). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  11.54 (br s, 1H), 7.46-7.37 (m, 2H), 7.36-7.28 (m, 2H), 3.71 (s, 3H), 2.91 (dd, *J* = 10.0, 6.5 Hz, 2H), 2.56 (d, *J* = 11.0, 8.5, 5.5 Hz, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>)  $\delta$  137.7, 134.2, 130.7, 130.6, 128.1, 127.6 (*J*<sub>C-F</sub> = 278.0 Hz), 127.1, 63.6, 34.9 (*J*<sub>C-F</sub> = 27.5Hz), 25.7 (*J*<sub>C-F</sub> = 3.0Hz). HRMS (ESI) m/z Calcd for C<sub>11</sub>H<sub>12</sub>F<sub>3</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 248.0898, found: 248.0899.



#### N-Methoxy-2, 6-bis(3, 3, 3-trifluoropropyl)benzamide (8af')

Following the general procedure E, the compound **8af'** was isolated as a colorless oil (5.3 mg, 8% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (br s, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 3.93 (s, 3H), 2.92-2.84 (m, 4H), 2.49-2.35 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.4, 137.1, 130.6, 127.8, 129.2 (*J*<sub>C-F</sub> = 279.0), 127.8, 64.6, 35.7 (*J*<sub>C-F</sub> = 28.5), 26.0 (*J*<sub>C-F</sub> = 3.0). HRMS (ESI) m/z Calcd for C<sub>14</sub>H<sub>15</sub>F<sub>6</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 344.1085, found: 344.1084.



#### 2-Hexyl-N-methoxybenzamide (8ag)

Following the general procedure E, the compound **8ag** was isolated as a colorless oil (28.7 mg, 61% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.42 (br s, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 3.88 (s, 3H), 2.81-2.67 (m, 2H), 1.64-1.54 (m, 2H), 1.36-1.23 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.1, 142.0, 132.4, 130.6, 130.2, 127.2, 125.7, 64.6, 33.2, 31.7, 29.3, 22.6, 14.1. HRMS (ESI) m/z Calcd for C<sub>14</sub>H<sub>17</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 236.1651, found: 236.1650.



#### 2, 6-Dihexyl-N-methoxybenzamide (8ag')

Following the general procedure E, the compound **8ag'** was isolated as a colorless oil (6.4 mg, 10% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (br s, 1H), 7.29-7.23 (t, 1H), 7.06 (d, J = 7.5 Hz, 2H), 3.93 (s, 3H), 2.66-2.56 (m, 4H), 1.65-1.58 (m, 4H), 1.37-1.25 (m, 12H), 0.88 (t, J = 7.0 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.6, 140.4, 132.6, 129.7, 128.0, 126.6, 64.5, 33.3, 31.8, 31.7, 29.4, 22.6, 14.1. HRMS (ESI) m/z Calcd for C<sub>20</sub>H<sub>33</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 320.2590, found: 320.2590.



#### 2, 6-Dibenzyl-N-methoxybenzamide (8ah')

Following the general procedure E, the compound **8ah'** was isolated as a white solid: MP: 145-147 °C (21.8 mg, X= Br, 33%; X= Cl, 7% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (br s, 1H), 7.29 (m, 5H), 7.21 (t, *J* = 5.0 Hz, 2H), 7.17 (d, *J* = 7.0 Hz, 4H), 7.06 (d, *J* = 7.5 Hz, 2H), 4.05 (s, 4H), 3.65 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.2, 140.3, 138.7, 133.7, 123.0, 128.9, 128.6, 128.5, 126.8, 64.3, 38.9. HRMS (ESI) m/z Calcd for C<sub>20</sub>H<sub>33</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 332.1651, found: 332.1650.



#### Palladacycle 9

A solution of benzamide **7a** (0.05 mmol), Pd(OAc)<sub>2</sub> (0.05 mmol), PivOH (0.1 mmol), and L-12 or L-13 (0.01-0.25 mmol) in toluene (5 mL) was heated at 100 °C under air for 4-8 h. After the reaction completed, the reaction mixture was allowed to cool down to room temperature then filtered to give the crude product. The further purification was carried out by washing with EtOAc (3 mL x 3). The compound **9** was isolated as a yellow solid (L-12/L-13: 62%-96% yield, no ligand: 96% yield). MP: 278 °C (decomposed). <sup>1</sup>H NMR (400 MHz, DMSO-d6)  $\delta$  7.62 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 6.5 Hz, 1H), 7.02 (t, *J* = 7.0 Hz, 1H), 6.95 (d, *J* = 7.0 Hz, 1H), 3.62 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-d6)  $\delta$  174.6, 143.0, 138.5, 131.0, 128.7, 126.5, 125.2, 61.9. HRMS (ESI) m/z Calcd for C<sub>8</sub>H<sub>7</sub>NO<sub>2</sub>Pd [M+H]<sup>+</sup>: 254.9512, found: 254.9510.

# <sup>1</sup>H and <sup>13</sup>C NMR Spectra















$$-8.331$$

$$-7.040$$

$$-7.040$$

$$-7.040$$

$$-7.154$$

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$$-3.899$$

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190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1 f1 (ppm)













190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1 f1 (ppm)





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130 120 110 100 fl (ppm) 



















-8.156 7.274 7.260 7.255 7.255 7.255 7.255 7.255 7.267 -3.932 -3.932 -3.932 -3.607 -3.607 -3.607 -3.607 -1.304 -1.304 -1.304 -1.304 -0.885 -0.8856













