# *ortho* C-H Arylation of Arenes at Room Temperature Using Visible Light Ruthenium C-H Activation

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#### **Experimental section**

General: All reactions were conducted under an atmosphere of nitrogen with oven-dried glassware. All photochemical reactions were conducted using a blue light-emitting diode (LED) as the visible-light source (90 W blue LED lamps (Kessil KSH150B Blue LED Grow Light; 5-7 cm away, with cooling fan to maintain the reaction at room temperature, 25-30 °C). Solvents were purchased in anhydrous quality and used as received. Starting materials were commercially available (Sigma-Aldrich or Alfa-Aesar or TCI-chemicals) and used as received or starting materials, with the exception of 2-phenylpyridines<sup>[s1]</sup> being synthesized according to literature procedures. For the scope, all the yields refer to isolated compounds. Column chromatography was conducted by manual column (silica gel) or using Biotage Snap Ultra cartridges on a Biotage Isolera automated columning machine. <sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded at 298 K on either 400 or 500 MHz Bruker NMR spectrometers as stated. Signal positions were recorded in  $\delta$  ppm and measured from the centre of the signal, excluding multiples, which are given as a range. Splitting patterns are reported using the abbreviations s, br. s, d, t, q, quin, sept and m (or combinations thereof) denoting singlet, broad singlet, doublet, triplet, quartet, quintet, septet and multiplet respectively. The use of the app abbreviation refers to apparent. All <sup>1</sup>H NMR and 13C chemical shifts were referenced to the residual solvent peak of CDCl<sub>3</sub> (<sup>1</sup>H referenced to 7.26 ppm and <sup>13</sup>C referenced to 77.16 ppm). All coupling constants, J, are quoted in Hz and reported to the nearest 0.1 Hz as observed in the spectra. Thin layer chromatography (TLC) was performed on commercially available pre-coated TLC plates (Alugram® Sil G/UV254). The visualisation was achieved under UV light at 254 nm. All mass spectrometry was carried out by the mass spectrometry service at the University of Manchester. Highresolution mass spectrometry (HRMS) was completed on a Waters QTOF micro with ESI/APCI ionisation. Low-resolution mass spectrometry was performed on Waters SQD2 Q-MS, Agilent 5975C Triple Axis GCMS or Hewlett Packard 5971 MSD.

#### General arylation procedure:

Scheme S1



A 5 mL microwave vial was charged with a magnetic stirring bar,  $[RuCl_2(p-cymene)]_2$ , (10 mol %), KOAc (2.0 eq), aryl halides **2** (1.5 eq), and phenylpyridines **1** (0.25 – 0.3 mmol, 1.0 eq) (*if phenylpyridine I is solid then added at this point before sealing the vial*). The vial was then sealed and evacuated under vacuum for 15-20 minutes and backfilled with nitrogen five times. 2-Methyl tetrahydrofuran (1 mL), H<sub>2</sub>O (5.0 equiv) and finally 2-phenylpyridines **1** (0.25 – 0.3 mmol, 1.0 equiv) (*if phenylpyridine I is liquid then added last via syringe*) were added via syringe through the septum. The reaction mixture (in microwave vial) was sonicated 2-3 minutes at 25 °C and a yellow-orange suspension was formed. The reaction mixture was then irradiated with blue LEDs (90 W blue LED lamps (Kessil KSH150B Blue LED Grow Light; 5-7 cm away, with a cooling fans to maintain the reaction at room temperature, 25-30 °C) under N<sub>2</sub> (1 atm) until completion of the reaction (monitored by TLC). The mixture was filtered through celite and silica gel pads and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to collect the expected *ortho* C-H arylation products.

#### **Radical trap experiment**

Scheme S2



A 25 mL microwave vial was charged with a magnetic stirring bar,  $[RuCl_2(p-cymene)]_2$ , (0.025 mmol, 10 mol %, 15.3 mg), KOAc (2.0 eq, 0.51 mmol) and the radical scavenger (1.5 eq, 0.37 mmol). The vial was then sealed and evacuated under vaccum for 30 minutes and backfilled with nitrogen three times. 2-MeTHF (1 mL), H<sub>2</sub>O (5.0 eq), *p*-bromoanisole **2a** (1.5 eq, 0.37 mmol) and 3-methyl-2-phenylpyridine (1.0 eq, 0.25 mmol) were added with a syringe through a septum. The reaction mixture was sonicated for 5 min at 25 °C and a yellow-orange suspension was formed. It was then irradiated with blue LEDs under N<sub>2</sub> atmosphere for 24 h. The solvent was evaporated and the residue was purified by column chromatography on silica gel.

*Light on-off experiment:* two separate 5 mL microwave vials were charged with a magnetic stirring bar,  $[RuCl_2(p-cymene)]_2$ , (0.03 mmol, 10 mol %), and KOAc (2.0 eq, 0.6 mmol). The two vials were then sealed and evacuated under vaccum for 15-20 minutes and backfilled with nitrogen five times. 2-Methyltetrahydrofuran (1 mL), 4-bromoanisole **2a** (0.45 mmol, 1.5 eq), H<sub>2</sub>O (5.0 eq) and finally 2-phenylpyridine **1a** (0.3 mmol, 1.0 eq) were added via syringe using the septum. The reaction mixtures (in microwave vials) were sonicated 2-3 minutes at 25 °C and and a yellow-orange suspension was formed. The reaction mixtures were then irradiated with blue LEDs (90 W blue LED lamps (Kessil KSH150B Blue LED Grow Light; 5-7 cm away, with the cooling fan to maintain the reaction at room temperature, 25-30 °C) under N<sub>2</sub> (1 atm).

After irradiation for 5 h, the lamp was switched off and the first reaction mixture was worked up and purified to give the *ortho* C-H arylation product **5a** & **5aa** in 48% total yield (column chromatography). The second vial was left stirring for a further 19 hours in the dark (30 °C), giving 24-hour total reaction time. Work-up and purification gave ortho products **5a** & **5aa** in total yield of 53% (see Scheme S3). *The* 

light on-off-experiment suggests that the observed photochemical ortho-C-H action of arenes is not a chain reaction, and requires constant irradiation for complete reaction.

Scheme S3



A 5 mL microwave vial was charged with a magnetic stirring bar,  $[RuCl_2(p-cymene)]_2$ , (0.025 mmol, 10 mol %) and KOAc (2.0 eq, 0.50 mmol). The vial was then sealed and evacuated under vacuum for 15-20 minutes and backfilled with nitrogen five times. 2-Methyltetrahydrofuran (1 mL), 4-bromoanisole **2a** (0.50 mmol, 2.0 eq), ethyl 4-bromobenzoate **2b** (0.50 mmol, 2.0 eq), H<sub>2</sub>O (5.0 eq) and finally 3-methyl-2-phenylpyridine (0.25 mmol, 1.0 eq) were added via syringe using the septum. The reaction mixture (in microwave vial) was sonicated 2-3 minutes at 25 °C and a yellow-orange suspension was formed. The

reaction mixture was then irradiated with blue LEDs (90 W blue LED lamps (Kessil KSH150B Blue LED Grow Light; 5-7 cm away, with the cooling fan to maintain the reaction at room temperature, 25-30 °C) under  $N_2$  (1 atm) for 24 h. The solvent was evaporated and the residue was purified by column chromatography on silica gel to afford a 3:1 mixture of **6i** and **6j**. The ratio of the products was determined by <sup>1</sup>H NMR using 1,3,5-trimethylbenzene (mesitylene) as internal standard.

#### **Detection of free** *p***-cymene**

Scheme S5



Under an atmosphere of N<sub>2</sub>, a Schlenk-tube was charged with 2-phenylpyridine **1a** (232.8 mg, 1.50 mmol), 4-bromoanisole **2a** (420.8 mg, 2.25 mmol),  $[RuCl_2(p-cymene)]_2$  (92.0 mg, 150 µmol, 10.0 mol %), KOAc (294.0 mg, 3.00 mmol) and water (135 µL). 2-MeTHF (5.0 mL) was added and the reaction mixture was sonicated 2-3 minutes at 25 °C and a yellow-orange suspension was formed. The reaction mixture was then irradiated with blue LEDs. During the course of the reaction aliquots (100 µL) were removed via a syringe after, diluted with DCM, filtered through a short plug of silica gel and analyzed by gas chromatography.



Ambient light	Blue	LED light
<b>[7]</b> ,mg/ml	t/min	<b>[7]</b> ,mg/ml
3.17	1	4.99
3.24	2	5.49
3.46	4	6.09
3.55	5	6.17
3.61	10	6.39
3.65	20	6.46
3.68	60	6.54
4.29	180	7.65
	Ambient light [7],mg/ml 3.17 3.24 3.46 3.55 3.61 3.65 3.68 4.29	Ambient light     Blue       [7],mg/ml     t/min       3.17     1       3.24     2       3.46     4       3.55     5       3.61     10       3.65     20       3.68     60       4.29     180

**Spectroscopic Data** 

Scheme 2 products:

#### 2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)pyridine (5a)<sup>1</sup>



White solid; <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.64 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.49 – 7.36 (m, 4H), 7.14 – 7.04 (m, 3H), 6.90 (dt, J = 8.0, 1.1 Hz, 1H), 6.81 – 6.74 (m, 2H), 3.79 (s, 3H). <sup>13</sup>**C** NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 159.6, 158.6, 149.6, 140.3, 139.5, 135.4, 133.8, 130.9, 130.62, 130.56, 128.6, 127.4, 125.6, 121.4, 113.7, 55.3 (q, J = 5.0 Hz). **HRMS** (ESI) Calcd for [C<sub>18</sub>H<sub>15</sub>ON+Na]<sup>+</sup> 284.1046, Found 284.1038.

## **2-(4,4''-Dimethoxy-[1,1':3',1''-terphenyl]-2'-yl)pyridine (5aa)**<sup>2</sup>



Off-white solid; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.35 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 7.48 (dd, J = 8.5, 6.6 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.33 (td, J = 7.7, 1.8 Hz, 1H), 7.04 – 6.98 (m, 4H), 6.93 (ddd, J = 7.6, 4.9, 1.2 Hz, 1H), 6.88 (dt, J = 7.8, 1.1 Hz, 1H), 6.72 – 6.66 (m, 4H), 3.74 (s, 6H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.4, 158.2, 148.7, 141.5, 138.6, 135.1, 134.2, 130.8, 129.3, 128.2,

126.9, 120.9, 113.2, 55.3. **HRMS** (ESI) Calcd for  $[C_{25}H_{21}O_2N+Na]^+$  390.1465, Found 390.1455.

# 2-(4',5-Dimethoxy-[1,1'-biphenyl]-2-yl)pyridine (5b)<sup>1,3</sup>



Colorless pasty solid; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.61 (ddd, J = 4.8, 1.9, 1.0 Hz, 1H), 7.64 (dd, J = 8.5, 1.6 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.10 – 7.04 (m, 3H), 6.99 (dt, J = 8.5, 2.2 Hz, 1H), 6.93 (t, J = 2.5 Hz, 1H), 6.84 – 6.81 (m, 1H), 6.80 – 6.77 (m, 2H), 3.88 (d, J = 1.8 Hz, 3H), 3.79 (d, J = 1.9 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.6, 159.1, 158.6, 149.3, 141.5, 135.1, 133.7, 132.2, 131.9, 130.7, 125.4, 120.8, 115.6, 113.5, 112.9, 55.4, 55.2. **HRMS** (ESI) Calcd for [C<sub>19</sub>H<sub>18</sub>O<sub>2</sub>N+K]<sup>+</sup> 292.1320, Found 292.1332.

<sup>&</sup>lt;sup>1</sup> C. Binnani, R. K. Rai, D. Tyagi, S. M. Mobin and S. K. Singh, *Eur. J. Inorg. Chem.*, **2018**, *12*, 1435-1445.

<sup>&</sup>lt;sup>2</sup> C. K. Rank, T. Wall, F. Dietrich, M. Vidovic, M. P. Klein, Y. Sun, G. Niedner-Schatteburg, M. Gerhards and F. W. Patureau, *Eur. J. Inorg. Chem.*, **2018**, *12*, 1394-1398.

<sup>&</sup>lt;sup>3</sup> L. Su, D.-D. Guo, B. Li, S.-H. Guo, G.-F. Pan, Y.-R. Gao and Y.-Q. Wang, Chem. *ChemCatChem.*, **2017**, *9*, 2001-2008.

**2-(4,4'',5'-Trimethoxy-[1,1':3',1''-terphenyl]-2'-yl)pyridine (5bb)**<sup>1,4</sup>



White solid; <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.32 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.30 (td, J = 7.7, 1.8 Hz, 1H), 7.03 – 7.00 (m, 4H), 6.94 (s, 2H), 6.90 (ddd, J = 7.7, 4.9, 1.1 Hz, 1H), 6.84 (d, J = 7.9, 1H), 6.71 – 6.67 (m, 4H), 3.89 (s, 3H), 3.74 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.1, 158.8, 158.1, 148.5, 142.8, 134.9, 134.1, 131.6, 130.5, 127.1, 120.5, 114.5, 113.0, 55.4, 55.1. **HRMS** 

(ESI) Calcd for  $[C_{26}H_{23}O_3N+K]^+$  397.1662, Found 397.1672.

#### 2-(5-(Tert-butyl)-4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine (5c)<sup>1,4</sup>



Pasty light yellow oil; <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.62 (d, J = 4.7 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.10 – 7.07 (m, 3H), 6.89 (d, J = 7.9 Hz, 1H), 6.79 (d, J = 8.2 Hz, 2H), 3.79 (s, 3H), 1.38 (s, 9H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$  159.4, 158.4, 151.5, 149.4, 139.7, 136.6, 135.1, 134.3, 130.8, 130.2, 127.5, 125.3, 124.5, 121.0, 113.5, 55.2, 34.7, 31.3. **HRMS** (ESI) Calcd for [C<sub>22</sub>H<sub>23</sub>ON+K]<sup>+</sup> 356.1398, Found 356.1411.

## **2-(5'-(Tert-butyl)-4,4''-dimethoxy-[1,1':3',1''-terphenyl]-2'-yl)pyridine (5cc)**<sup>1,4</sup>

White solid; <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.35 (d, J = 4.4 Hz, 1H), 7.43 (s, 2H), 7.32 (t, J = 7.6 Hz,



1H), 7.04 (d, J = 8.3 Hz, 4H), 6.91 (t, J = 8.4 Hz, 2H), 6.71 (d, J = 8.3 Hz, 4H), 3.75 (s, 6H), 1.42 (s, 9H). ). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  159.4, 157.9, 150.9, 148.5, 140.9, 135.7, 134.8, 134.6, 130.7, 126.7, 126.4, 120.6, 113.0, 55.1, 34.7, 31.3. **HRMS (ESI)** Calcd for  $[C_{29}H_{29}O_2N+K]^+$  462.1816, Found 462.1830.

<sup>&</sup>lt;sup>4</sup> T.-T. Zhao, W.-H. Xu, Z.-J. Zheng, P.-F. Xu and H. Wei, *J. Am. Chem. Soc.*, **2018**, *140*, 586-589.

# 2-(4'-Methoxy-5-methyl-[1,1'-biphenyl]-2-yl)pyridine (5d)<sup>1,4</sup>



Yellow oil; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.63 (d, J = 4.7 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.37 (td, J = 7.7, 1.9 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.11 – 7.03 (m, 3H), 6.91 – 6.83 (m, 1H), 6.82 – 6.73 (m, 2H), 3.78 (s, 3H), 2.44 (s, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.6, 158.6, 149.5, 140.1, 138.4, 136.8, 135.3, 134.0, 131.3, 130.9, 130.6, 128.2, 125.5, 121.2, 113.6, 55.3, 21.4. **HRMS** (ESI) Calcd for [C<sub>19</sub>H<sub>17</sub>NO+Na]<sup>+</sup> 298.1192, found 298.1202.

## 2-(4,4"-Dimethoxy-5'-methyl-[1,1':3',1"-terphenyl]-2'-yl)pyridine (5dd)<sup>1,4</sup>



Off-white solid; <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 (d, J = 4.4 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.23 (s, 2H), 7.05 – 6.97 (m, 4H), 6.91 (ddd, J = 7.6, 4.9, 1.2 Hz, 1H), 6.86 (dd, J = 7.8, 1.2 Hz, 1H), 6.72 – 6.65 (m, 4H), 3.74 (s, 6H), 2.46 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.5, 158.1, 148.7, 141.4, 137.8, 135.9, 135.0, 134.3, 130.8, 130.0,

127.0, 120.8, 113.2, 55.2, 21.4. **HRMS** (ESI) Calcd for  $[C_{26}H_{23}NO_2+Na]^+$  404.1604, found 404.1621.

#### 2-(4,4"-Dimethoxy-5'-phenyl-[1,1':3',1"-terphenyl]-2'-yl)pyridine (5ee)<sup>1,4</sup>



Light yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.40 – 8.38 (m, 1H), 7.72 (d, J = 7.4 Hz, 2H), 7.673 (s, 1H), 7.671 (s, 1H), 7.49 – 7.45 (m, 2H), 7.41 – 7.34 (m, 2H), 7.11 – 7.07 (m, 4H), 7.00 – 6.93 (m, 2H), 6.80 – 6.68 (m, 4H), 3.76 (s, 6H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.0, 158.1, 148.6, 141.9, 140.8, 140.5, 137.4, 135.0, 134.0, 130.6, 128.8, 127.9, 127.5, 127.2, 126.8, 120.8, 113.1, 55.1. HRMS (ESI)

Calcd for [C<sub>31</sub>H<sub>25</sub>O<sub>2</sub>N+K]<sup>+</sup> 482.1503, Found 482.1517.

**Methyl 4,4''-dimethoxy-2'-(pyridin-2-yl)-[1,1':3',1''-terphenyl]-5'-carboxylate (5ff)**<sup>1,4</sup>



Light yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.28 (d, J = 4.8 Hz, 1H), 8.00 (s, 2H), 7.26 (td, J = 7.7, 1.8 Hz, 1H), 6.95 – 6.92 (m, 4H), 6.87 (ddd, J = 7.6, 4.9, 1.2 Hz, 1H), 6.79 (d, J = 7.8, 1H), 6.62 – 6.61 (m, 4H), 3.86 (s, 3H), 3.65 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  166.8, 158.4, 158.3, 148.7, 142.5, 141.8, 135.1, 133.0, 130.6, 130.1,

129.6, 126.4, 121.2, 113.2, 55.1, 52.2. **HRMS** (ESI) Calcd for  $[C_{22}H_{17}ON+Na]^+$  448.1501, Found 448.1519.

# **2-(4,4'-Dimethoxy-[1,1'-biphenyl]-2-yl)pyridine (5g)**<sup>1,4</sup>



Light yellow oil; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.65 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 7.39 (td, J = 7.7, 1.8 Hz, 1H), 7.33 (d, J = 8.5 Hz, 1H), 7.23 (d, J = 2.7 Hz, 1H), 7.11 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 7.05 – 6.99 (m, 3H), 6.89 (dt, J = 7.9, 1.1 Hz, 1H), 6.79 – 6.73 (m, 2H), 3.89 (s, 3H), 3.77 (s, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 158.8, 158.1, 149.3, 140.3, 135.2, 133.4, 132.8, 131.6, 130.7, 125.4, 121.4, 115.0, 114.8, 113.4, 55.4,

55.1. **HRMS (ESI)** Calcd for  $[C_{19}H_{17}O_2N+K]^+$  330.0875, Found 330.0891.

## 2-(4'-Methoxy-4-methyl-[1,1'-biphenyl]-2-yl)pyridine (5h)<sup>1,4</sup>



Yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.64 – 8.63 (m, 1H), 7.54 (s, 1H), 7.37 (td, J = 7.7, 1.9 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.08 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 7.06 – 7.03 (m, 2H), 6.87 (d J = 7.9 Hz, 1H), 6.77 – 6.74 (m, 2H), 3.76 (s, 3H), 2.43 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  159.5, 158.3, 149.4, 139.1, 137.3, 137.0, 135.1, 133.6, 131.0, 130.7, 130.3, 129.2, 125.4, 121.2, 113.5, 55.1, 21.0. HRMS

(ESI) Calcd for  $[C_{19}H_{17}ON+K]^+$  314.0927, Found 314.0942.

## 2-(4-Chloro-4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine (5i)<sup>1,4</sup>



Light yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.61 – 8.51 (m, 1H), 7.65 – 7.56 (m, 1H), 7.36 – 7.29 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.08 – 7.00 (m, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 2H), 3.69 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  158.7, 158.0, 149.5, 140.7, 138.6, 135.4, 133.2, 132.4, 131.7, 130.6, 130.4, 128.4, 125.2, 121.7, 113.6, 55.2. **HRMS (ESI)** Calcd for [C<sub>18</sub>H<sub>14</sub>ON<sup>35</sup>Cl+K]<sup>+</sup> 334.0382,

Found 334.0396.

## 2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)-4-methylpyridine (5j)<sup>1,4</sup>



Light yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.47 (d, J = 5.0 Hz, 1H), 7.64 – 7.63 (m, 1H), 7.44 – 7.39 (m, 3H), 7.08 – 7.06 (m, 2H), 6.93 (d, J =4.6, 1H), 6.78 – 6.75 (m, 3H), 3.79 (s, 3H), 2.13 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 158.4, 149.0, 146.2, 140.2, 139.5, 133.8, 130.7, 130.4, 130.3, 128.3, 127.2, 126.2, 122.3, 113.4, 55.2, 20.9. HRMS (ESI) Calcd for  $[C_{19}H_{17}ON+K]^+$  314.0928, Found 314.0942.

## 2-(4,4"-Dimethoxy-[1,1':3',1"-terphenyl]-2'-yl)-4-methylpyridine (5jj)<sup>1,4</sup>



Colourless oil; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.23 (dd, J = 5.0, 0.8 Hz, 1H), 7.48 (dd, J = 8.6, 6.5 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.09 – 7.02 (m, 4H), 6.79 – 6.75 (m, 1H), 6.75 – 6.69 (m, 5H), 3.76 (s, 6H), 2.10 (s, 3H).<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.8, 157.9, 148.1, 145.7, 141.3, 138.4, 134.1, 130.5, 129.0, 127.9, 127.6, 121.8, 112.9, 55.0, 20.8. **HRMS** (ESI) Calcd for [C<sub>26</sub>H<sub>23</sub>O<sub>2</sub>N+K]<sup>+</sup> 420.134,

Found 420.1360.

## 2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)-5-methylpyridine (5k)<sup>1,4</sup>



Yellow oil; <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.47 (s, 1H), 7.67 – 7.65 (m, 1H), 7.45 – 7.38 (m, 3H), 7.21 (dd, J = 8.1, 2.3 Hz, 1H), 7.10 – 7.06 (m, 2H), 6.80 – 6.76 (m, 3H), 3.80 (s, 3H), 2.30 (s, 3H). <sup>13</sup>**C** NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.4, 156.5, 149.8, 140.1, 139.3, 135.9, 133.9, 130.7, 130.6, 130.4, 130.3, 128.2, 127.3, 124.8, 113.5, 55.2, 18.1. **HRMS** (ESI) Calcd for [C<sub>19</sub>H<sub>17</sub>ON+K]<sup>+</sup> 314.0927, Found 314.0942.

#### **2-(4,4''-Dimethoxy-[1,1':3',1''-terphenyl]-2'-yl)-5-methylpyridine (5kk)**<sup>1,4</sup>



Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (s, 1H), 7.48 – 7.44 (m, 1H), 7.40 (s, 1H), 7.38 – 7.37 (m, 1H), 7.14 (dd, J = 8.0, 2.3 Hz, 1H), 7.04 – 7.00 (m, 4H), 6.77 (d, J = 7.9 Hz, 1H), 6.74 – 6.66 (m, 4H), 3.75 (s, 6H), 2.20 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  157.9, 156.1, 148.9, 141.4, 138.3, 135.6, 134.2, 130.6, 129.9, 129.1, 127.9, 126.1, 113.0, 55.1, 18.1. HRMS (ESI) Calcd for  $[C_{26}H_{23}O_2N+K]^+$ 

420.1346, Found 420.1360.

## 5-Methyl-2-(4,4'',5'-trimethoxy-[1,1':3',1''-terphenyl]-2'-yl)pyridine (5ll)



Light yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 – 8.15 (m, 1H), 7.11 (dd, J = 7.9, 1.8 Hz, 1H), 7.04 – 7.01 (m, 4H), 6.94 (s, 2H), 6.73 (d, J = 8.0 Hz, 1H), 6.72 – 6.68 (m, 4H), 3.88 (s, 3H), 3.75 (s, 6H), 2.18 (s, 3H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.6, 158.0, 156.0, 148.8, 142.8, 135.6, 134.2, 131.4, 130.5, 129.6, 126.4, 114.5,

113.0, 55.3, 55.0, 18.1. **HRMS (ESI)** Calcd for  $[C_{27}H_{25}O_3N+K]^+$  450.1449, Found 450.1466.

#### 2-(3-(4-Methoxyphenyl)naphthalen-2-yl)pyridine (5m)



White solid; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.69 (ddd, J = 4.9, 1.9, 1.0 Hz, 1H), 8.19 (s, 1H), 7.94 – 7.92 (m, 1H), 7.90 – 7.87 (m, 2H), 7.54 – 7.47 (m, 2H), 7.43 (td, J = 7.7, 1.9 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.14 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 6.98 (dt, J = 7.9, 1.1 Hz, 1H), 6.84 – 6.80 (m, 2H), 3.80 (s, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 158.5, 149.4, 138.1, 137.8, 135.2, 133.7, 133.2, 132.4, 130.8, 130.0, 129.2, 128.2, 127.5, 126.6, 126.1, 125.5, 121.3, 113.5, 55.2. **HRMS (ESI)** Calcd for [C<sub>22</sub>H<sub>17</sub>ON+K]<sup>+</sup> 350.0927,

Found 350.0942.

#### 2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)quinoline (5n)



Yellow oil; <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.54 (d, J = 5.7 Hz, 1H), 7.72 (d, J = 8.3, 1H), 7.60 – 7.45 (m, 7H), 7.32 – 7.26 (m, 1H), 7.02 – 6.99 (m, 2H), 6.65 – 6.53 (m, 2H), 3.61 (s, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$  161.5, 158.1, 141.9, 141.1, 138.1, 136.0, 133.5, 130.6, 130.1, 129.8, 129.7, 128.7, 127.5, 127.2, 126.8, 126.7, 126.5, 119.7, 113.2, 54.93. **HRMS** (**ESI**) Calcd for [C<sub>22</sub>H<sub>17</sub>ON+K]<sup>+</sup> 350.0929, Found 350.0942.

#### 1-(4'-Methoxy-[1,1'-biphenyl]-2-yl)isoquinoline (50):



Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.54 (d, J = 5.7 Hz, 1H), 7.73 (d, J = 8.3 Hz, 1H), 7.65 – 7.42 (m, 7H), 7.31 (t, J = 7.7 Hz, 1H), 7.00 (d, J = 8.2 Hz, 2H), 6.54 (d, J = 8.2 Hz, 2H), 3.63 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.6, 158.3, 142.1, 141.3, 138.2, 136.1, 133.6, 130.8, 130.2, 130.0, 129.9, 128.9, 127.6, 127.3, 127.0, 126.9, 126.7, 119.9, 113.3, 55.1 (d, J = 5.6 Hz). HRMS (ESI) Calcd for

 $[C_{22}H_{17}ON+H]^+$  312.1383, Found 312.1374.

#### 2-(3-(4-Methoxyphenyl)thiophen-2-yl)pyridine (5p)



Yellow oil; <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.58 (ddd, J = 4.9, 1.9, 1.1 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.30 – 7.27 (m, 2H), 7.09 – 7.05 (m, 3H), 6.93 – 6.90 (m, 2H), 3.85 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  159.0, 153.1, 149.5, 139.6, 138.7, 135.8, 131.2, 130.2, 129.3, 126.4, 121.8. 121.5, 114.1, 55.3. **HRMS (ESI)** Calcd for [C<sub>16</sub>H<sub>13</sub>ONS+K]<sup>+</sup> 306.0336, Found 306.0349.

## 1-(4'-Methoxy-[1,1'-biphenyl]-2-yl)-1H-pyrazole (5q)<sup>5,6</sup>



Colourless oil; <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (d, J = 1.9 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.49 – 7.39 (m, 3H), 7.10 (d, J = 2.4 Hz, 1H), 7.07 – 6.98 (m, 2H), 6.85 – 6.78 (m, 2H), 3.80 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  159.1, 140.3, 138.7, 136.5, 131.5, 131.1, 131.0, 129.8, 128.4, 128.1, 126.8, 114.1, 106.5 (d, J = 1.9 Hz), 55.4 (q, J = 4.9 Hz). **HRMS** (APCI) Calcd for [C<sub>16</sub>H<sub>14</sub>ON<sub>2</sub>+H]<sup>+</sup> 251.1179, Found 251.1168.

# **1-(4,4''-Dimethoxy-[1,1':3',1''-terphenyl]-2'-yl)-1H-pyrazole (5qq)**<sup>7</sup>



White solid (46 mg, 52%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 – 7.48 (m, 1H), 7.48 – 7.37 (m, 3H), 7.09 (s, 1H), 7.02 (d, J = 8.2 Hz, 4H), 6.76 (d, J = 8.3 Hz, 4H), 6.09 (s, 1H), 3.77 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.9, 140.2, 139.5, 136.4, 132.5, 131.3, 129.8, 129.5, 129.2, 113.6, 106.2, 55.3. HRMS (APCI) Calcd for [C<sub>23</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>+H]<sup>+</sup>

357.1598, Found 357.1587.

<sup>&</sup>lt;sup>5</sup> P. B. Arockiam, C. Fischmeister, C. Bruneau and P. H. Dixneuf, *Green Chem.*, **2013**, *15*, 67-71.

<sup>&</sup>lt;sup>6</sup> L. Ackermann, R, Vicente, H. K. Potukuchi and V. Pirovano, Org. Lett., **2010**, *12*, 5032-5035.

<sup>&</sup>lt;sup>7</sup> L. Ackermann, A. Althammer and R. Born, *Tetrahedron*, **2008**, *64*, 6115-6124.

#### Scheme 3 products:

## 2-(4'-(Tert-butyl)-[1,1'-biphenyl]-2-yl)-3-methylpyridine (6a)<sup>8</sup>



Colorless oil; <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (d, J = 4.7 Hz, 1H), 7.49 – 7.36 (m, 4H), 7.30 (d, J = 7.8 Hz, 1H), 7.18 (d, J = 8.4, 1.8 Hz, 2H), 7.14 – 7.08 (m, 1H), 7.04 (d, J = 7.3 Hz, 2H), 1.73 (s, 3H), 1.26 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.7, 149.6, 146.6, 140.6, 139.5, 138.1, 137.5, 131.8, 130.1, 129.8, 128.9, 128.4, 127.3, 124.8, 122.2, 34.5, 31.4, 19.0. **HRMS** (ESI) Calcd for (C<sub>22</sub>H<sub>23</sub>N+H)<sup>+</sup> 302.1903, Found 302.1897.

#### **3-Methyl-2-(4'-methyl-[1,1'-biphenyl]-2-yl)pyridine (6b)**

Yellow oil; <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (d, J = 4.9 Hz, 1H), 7.50 – 7.36 (m, 4H), 7.30 (d, J = 7.6



Hz, 1H), 7.10 (dd, J = 7.7, 4.8 Hz, 1H), 6.99 (q, J = 8.0 Hz, 4H), 2.27 (s, 3H), 1.75 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  159.8, 146.7, 140.7, 139.5, 138.3, 137.6, 136.4, 131.8, 130.0, 129.8, 129.2, 128.7, 128.4, 127.3, 122.2, 21.2, 19.0. HRMS (APCI) Calcd for  $[C_{19}H_{17}N+H]^+$  260.1434, Found 260.1428.

## 2-([1,1':4',1'':3'',1''':4''',1''''-Quinquephenyl]-2''-yl)pyridine (6cc)



White soild; <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.44 – 8.32 (m, 1H), 7.62 – 7.58 (m, 7H), 7.46 – 7.42 (m, 8H), 7.38 – 7.33 (m, 3H), 7.22 – 7.21 (m, 4H), 7.00 – 6.95 (m, 2H).<sup>13</sup>**C** NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.9, 148.6, 141.5, 140.6, 140.5, 138.9, 138.5, 135.0, 130.0, 129.5, 128.7, 128.3, 127.2, 126.9, 126.8, 126.3, 121.0. **HRMS (ESI)** Calcd for  $[C_{35}H_{25}N+K]^+$ 

498.1602, Found 498.1619.

#### 2-(2,6-Di(thiophen-2-yl)phenyl)pyridine (6dd)



White soild; <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.56 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 7.59 – 7.57 (m, 2H), 7.52 – 7.44 (m, 2H), 7.16 – 7.13 (m, 3H), 7.09 (dt, J = 7.7, 1.1 Hz, 1H), 6.82 (dd, J = 5.1, 3.6 Hz, 2H), 6.65 (dd, J = 3.6, 1.2 Hz, 2H).<sup>13</sup>**C** NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.5, 148.8, 142.6, 138.4, 135.7, 134.6, 130.0, 128.4,

<sup>&</sup>lt;sup>8</sup> C. K. Seigerman, T. M. Micyus, S. R. Neufeldt and M. S. Sanford, *Tetrahedron*, **2013**, *69*, 5580-5587.

127.1, 126.7, 126.2, 125.7, 122.1. **HRMS (ESI)** Calcd for  $[C_{19}H_{13}NS_2+K]^+$  358.0106, Found 358.0121.

# 2-(4'-Chloro-[1,1'-biphenyl]-2-yl)-3-methylpyridine (6e)<sup>9</sup>

Yellow solid; <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.49 (dd, J = 4.8, 1.5 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.44 –



7.37 (m, 2H), 7.33 (dd, J = 7.8, 1.6 Hz, 1H), 7.17 – 7.09 (m, 3H), 7.08 – 6.99 (m, 2H), 1.77 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 146.8, 139.7, 139.5 (d, J = 2.1 Hz), 137.8, 132.9, 131.6, 130.6, 130.1, 129.6, 128.6, 128.2, 127.9, 122.4, 19.0. **HRMS** (APCI) Calcd for  $[C_{18}H_{14}N^{35}Cl+H]^+$  280.0888, Found 280.0881.

## 2-(4'-Bromo-[1,1'-biphenyl]-2-yl)-3-methylpyridine (6f)

Yellow solid; <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.48 (dd, J = 4.8, 1.7 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.43 –



7.37 (m, 2H), 7.33 (dd, J = 7.8, 1.6 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.12 (dd, J = 7.7, 4.8 Hz, 1H), 7.01 – 6.95 (m, 2H), 1.77 (s, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 146.8, 140.2, 139.51, 139.46, 137.8, 131.6, 131.1, 131.0, 130.1, 129.6, 128.6, 127.9, 122.4, 121.2, 19.0. **HRMS** (ESI) Calcd for  $[C_{18}H_{14}N^{79}Br+H]^+$  324.0382, Found 324.0377.

#### 2-(4,4"-Difluoro-[1,1':3',1"-terphenyl]-2'-yl)pyridine (6gg)



White solid; <sup>1</sup>**H** NMR (400 MHz, , CDCl<sub>3</sub>)  $\delta$  8.34 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 7.51 (dd, J = 8.5, 6.8 Hz, 1H), 7.43 – 7.41 (m, 2H), 7.34 (td, J = 7.7, 1.8 Hz, 1H), 7.08 – 7.02 (m, 4H), 6.95 (ddd, J = 7.6, 4.9, 1.2 Hz, 1H), 6.88 – 6.80 (m, 5H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  161.5 (d,  $J_{C-F} = 244.3$  Hz), 158.6, 148.7, 140.8, 138.6, 137.3 (d,  $J_{C-F} = 3.4$  Hz), 135.1, 131.1 (d,

 $J_{C-F} = 7.9$  Hz), 129.5, 128.3, 126.7, 121.1, 114.6 (d,  $J_{C-F} = 21.1$  Hz). **HRMS** (ESI) Calcd for  $[C_{23}H_{16}NF_2+K]^+$  344.1240, Found 344.1245.

<sup>&</sup>lt;sup>9</sup> D. Kalyani, N. R. Deprez, L. V. Desai and M. S. Sanford, J. Am. Chem. Soc., 2005, 127, 7330-7331.

## 1-(2'-(3-Methylpyridin-2-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one (6h)<sup>10</sup>



Yellow-brown solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 – 8.45 (m, 1H), 7.81 – 7.70 (m, 2H), 7.55 – 7.39 (m, 4H), 7.32 (dd, J = 7.6, 0.9 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.11 (dd, J = 7.7, 4.8 Hz, 1H), 2.54 (s, 3H), 1.78 (s, 3H). <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>)  $\delta$  197.6, 160.1, 147.6, 146.9, 141.0, 140.6, 138.4, 136.5, 132.2, 131.1, 130.6, 130.3, 129.4, 128.9, 128.8, 123.4, 26.8 (q, J = 4.4 Hz), 19.2

(d, J = 1.4 Hz). HRMS (ESI) Calcd for  $[C_{20}H_{17}NO+H]^+$  288.1383, Found 288.1373. **HRMS** (ESI) Calcd for  $[C_{20}H_{17}NO+H]^+$  288.1383, Found 288.1373.

#### Ethyl 2'-(3-methylpyridin-2-yl)-[1,1'-biphenyl]-4-carboxylate (6i)



Yellow-brown solid; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.47 (d, J = 4.8 Hz, 1H), 7.84 (d, J = 7.9 Hz, 2H), 7.56 – 7.37 (m, 4H), 7.29 (d, J = 7.7 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.10 (dd, J = 7.7, 4.9 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 1.75 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.6, 159.0, 146.7, 145.8, 139.7, 139.5, 137.8, 131.6, 130.1,

129.7, 129.3, 129.2, 128.7, 128.6, 128.2, 122.4, 61.0, 18.9, 14.4 (d, J = 3.3 Hz). **HRMS** (ESI) Calcd for  $[C_{21}H_{19}O_2N+H]^+$  340.1308, Found 340.1295.

## 2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)-3-methylpyridine (6j)<sup>1,4</sup>



White solid; <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.50 (dd, J = 4.9, 1.6 Hz, 1H), 7.47 – 7.36 (m, 4H), 7.31 – 7.29 (m, 1H), 7.10 (dd, J = 7.7, 4.8 Hz, 1H), 7.05 – 7.02 (m, 2H), 6.72 – 6.68 (m, 2H), 3.74 (s, 3H), 1.74 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.6, 158.3, 146.5, 140.2, 139.2, 137.4, 133.5, 131.6, 130.2, 129.8, 129.5, 128.3, 127.0, 122.0, 113.2, 55.1, 18.8. **HRMS (ESI)** Calcd for [C<sub>19</sub>H<sub>17</sub>ON+K]<sup>+</sup> 314.0928, Found 314.0942.

<sup>&</sup>lt;sup>10</sup> N. R. Deprez and M. S. Sanford, *J. Am. Chem. Soc.*, **2009**, *131*, 11234-11241.

## 2-(2'-Methoxy-[1,1'-biphenyl]-2-yl)-3-methylpyridine (6k)



Yellow oil; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.42 – 8.33 (d, 1H), 7.46 – 7.40 (m, 4H), 7.33 – 7.29 (m, 1H), 7.15 (ddd, J = 8.2, 7.4, 1.8 Hz, 1H), 7.02 (dt, J = 7.7, 5.3 Hz, 2H), 6.81 – 6.75 (m, 1H), 6.72 (d, J = 8.2 Hz, 1H), 3.53 (s, 3H), 1.92 (s, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.6, 156.2, 146.2, 140.3, 137.7, 137.4, 132.3, 131.7, 131.1, 130.0, 129.7, 128.5, 127.8, 127.3, 121.7, 120.1, 110.4, 55.0, 19.0. **HRMS** (ESI) Calcd for [C<sub>19</sub>H<sub>17</sub>NO+Na]<sup>+</sup>

298.1202, found 298.1192.

S18

# **NMR Spectra**







S21

















S28



















![](_page_35_Figure_0.jpeg)

![](_page_36_Figure_0.jpeg)

![](_page_37_Figure_0.jpeg)

![](_page_38_Figure_0.jpeg)

![](_page_39_Figure_0.jpeg)

![](_page_40_Figure_0.jpeg)

S41

![](_page_41_Figure_0.jpeg)

![](_page_42_Figure_0.jpeg)

![](_page_43_Figure_0.jpeg)

![](_page_44_Figure_0.jpeg)

90 80 f1 (ppm) 

![](_page_45_Figure_0.jpeg)

![](_page_45_Figure_1.jpeg)

![](_page_45_Figure_2.jpeg)

![](_page_46_Figure_0.jpeg)

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![](_page_49_Figure_0.jpeg)

![](_page_50_Figure_0.jpeg)

![](_page_51_Figure_0.jpeg)

![](_page_51_Figure_1.jpeg)

![](_page_51_Figure_2.jpeg)

![](_page_52_Figure_0.jpeg)