

## Supporting Information

### Replacing Pd(OAc)<sub>2</sub> with supported palladium nanoparticles in *ortho*-directed CDC reaction of alkylbenzenes

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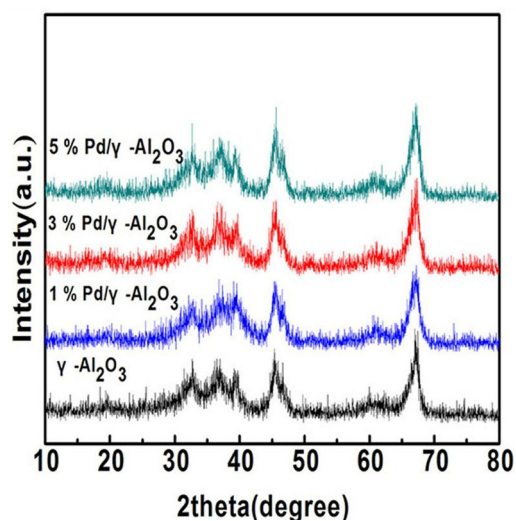
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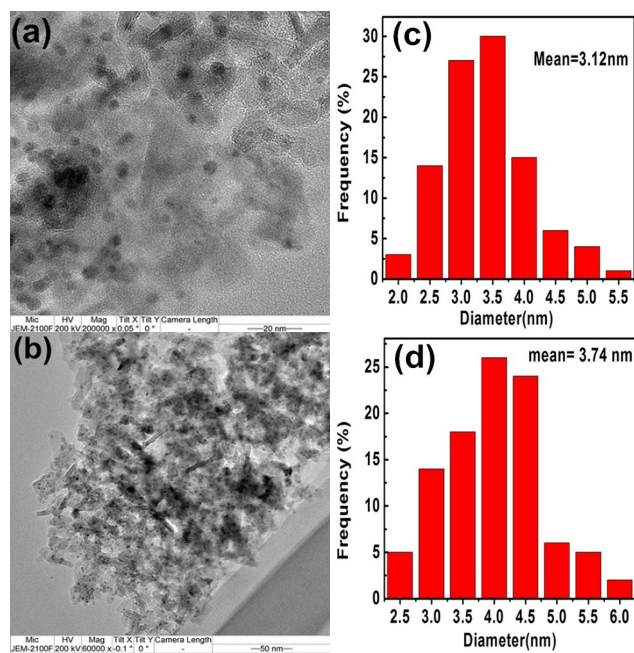
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## 1. Figures S1–S2



**Figure S1.** XRD patterns of catalysts with different loadings

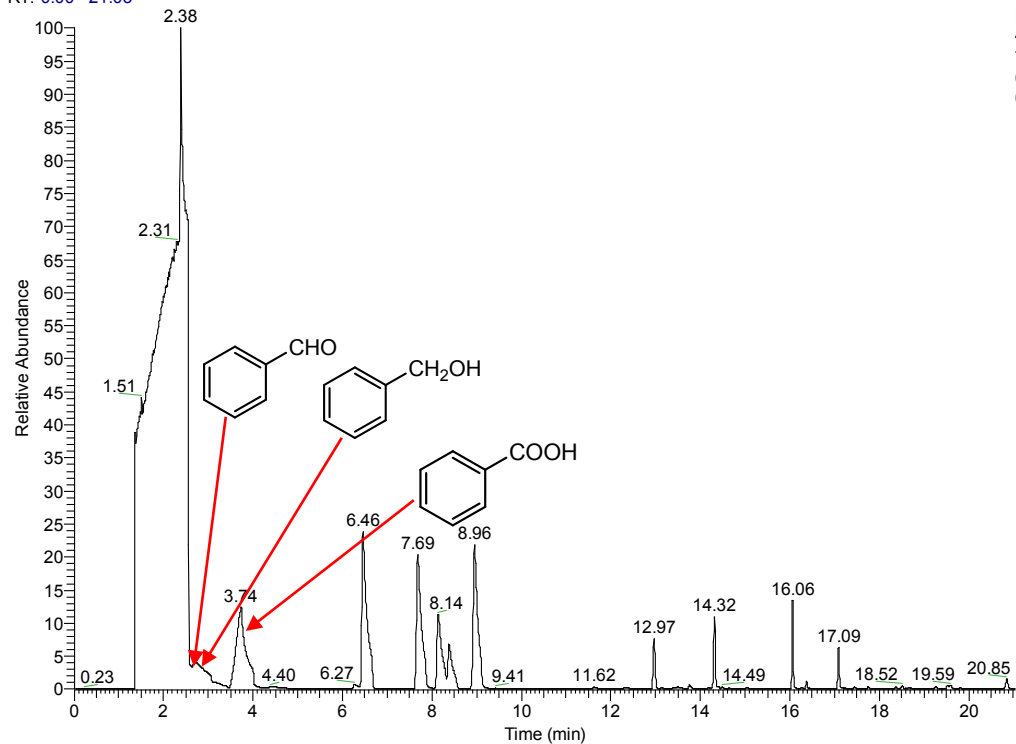


**Figure S2.** TEM images of catalysts: (a) 1 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and (b) 5 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (c, d) PdNPs size distributions of 1 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 5 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively.

## 2.GC-MS Analysis of Reaction of 1a with 2a and 1a with 2e

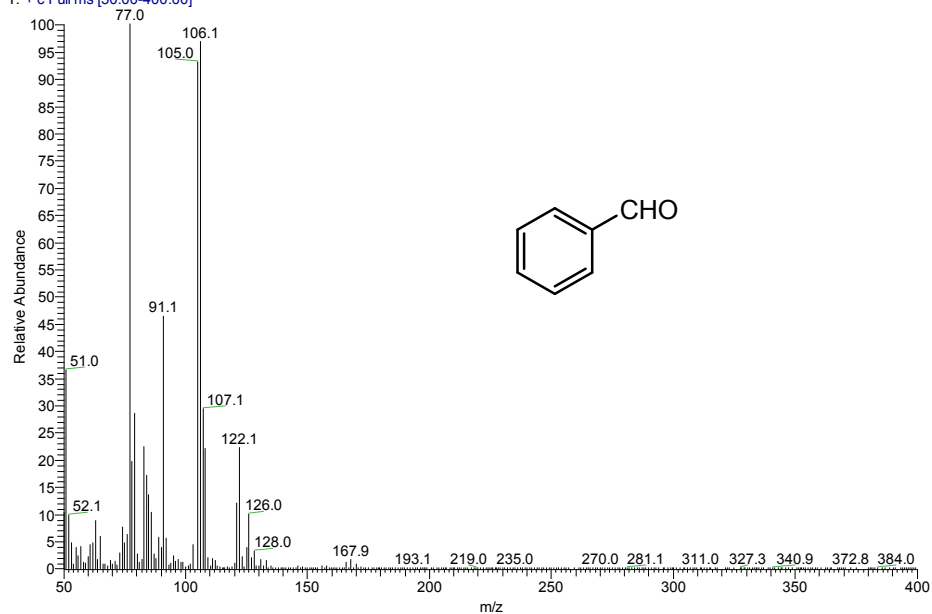
The GC spectra of reaction solution of **1a** with **2a** :

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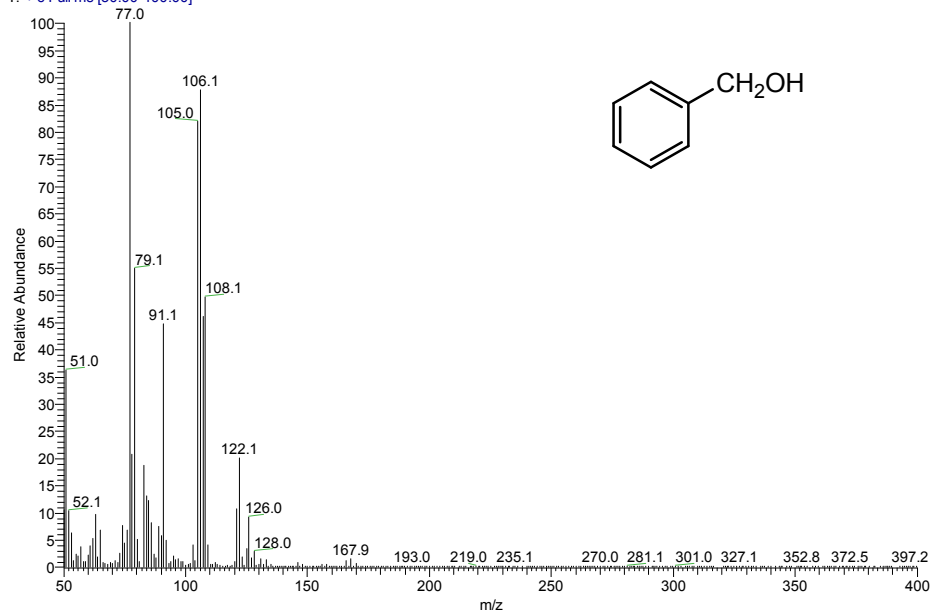


NL:  
4.89E9  
TIC MS  
01\_150515  
093237

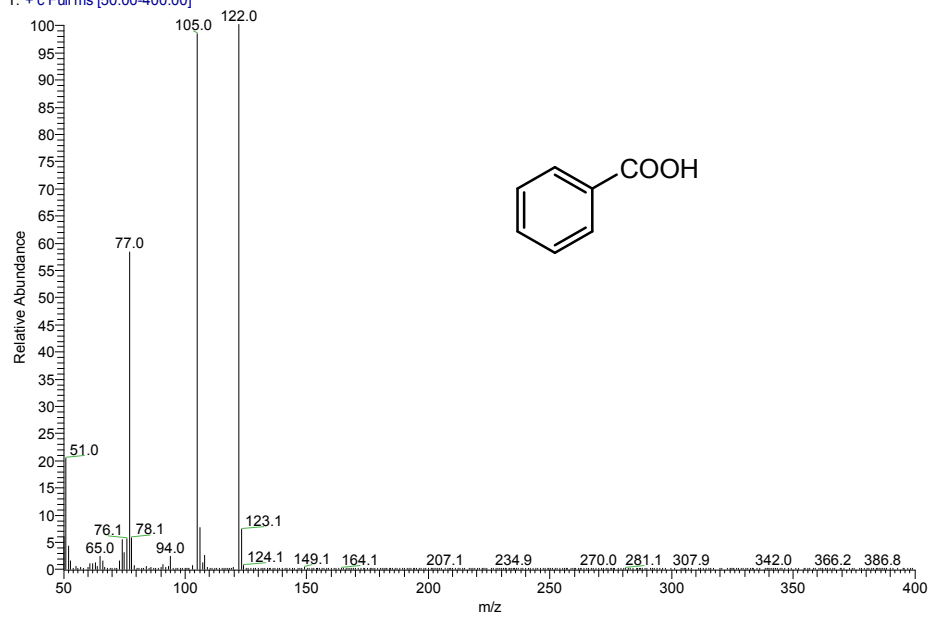
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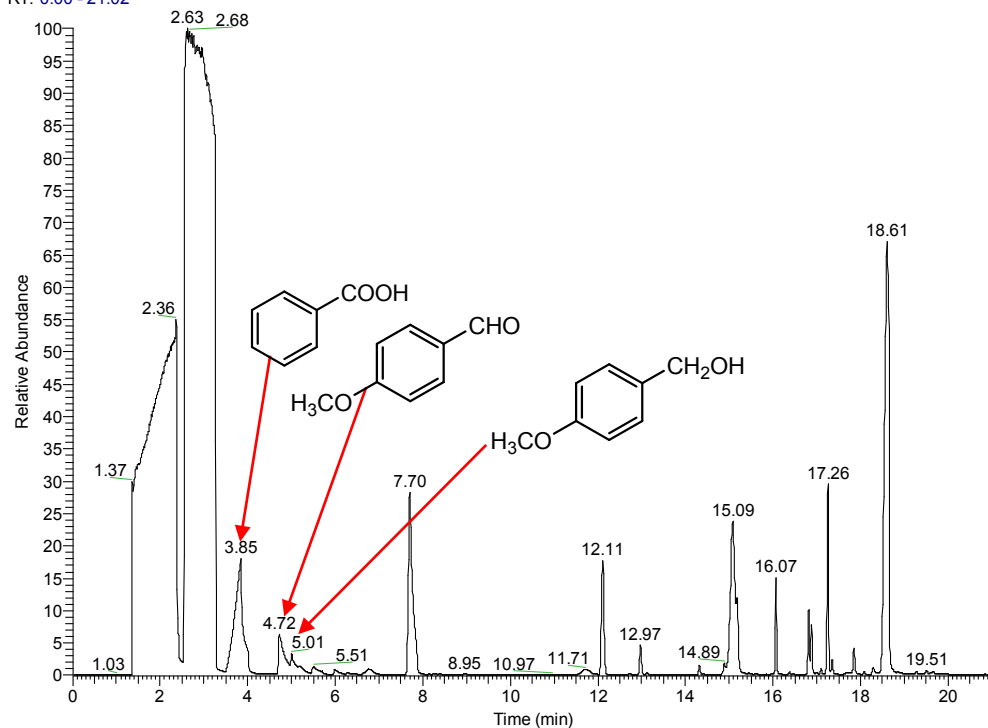


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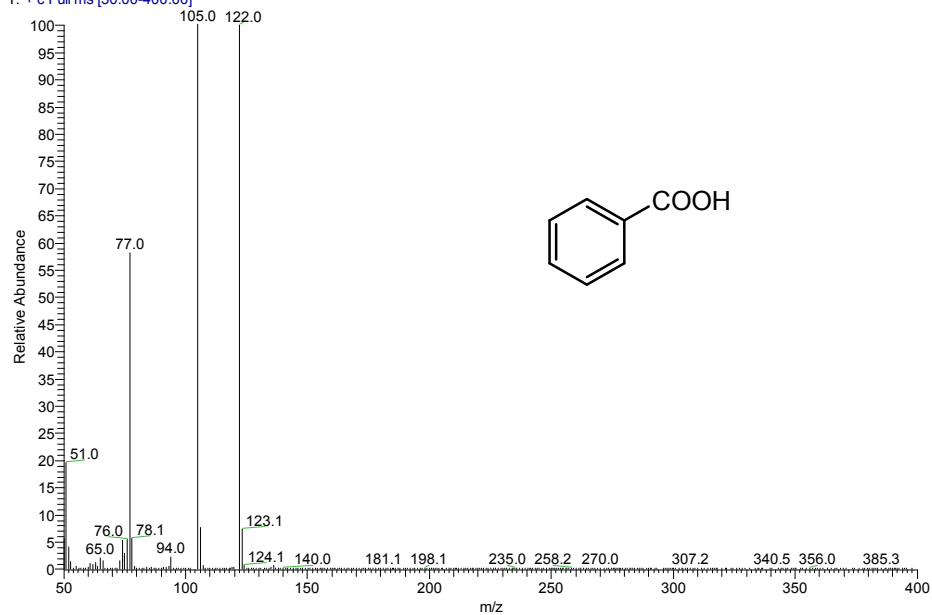
The GC spectra of reaction solution of **1a** with **2e** :

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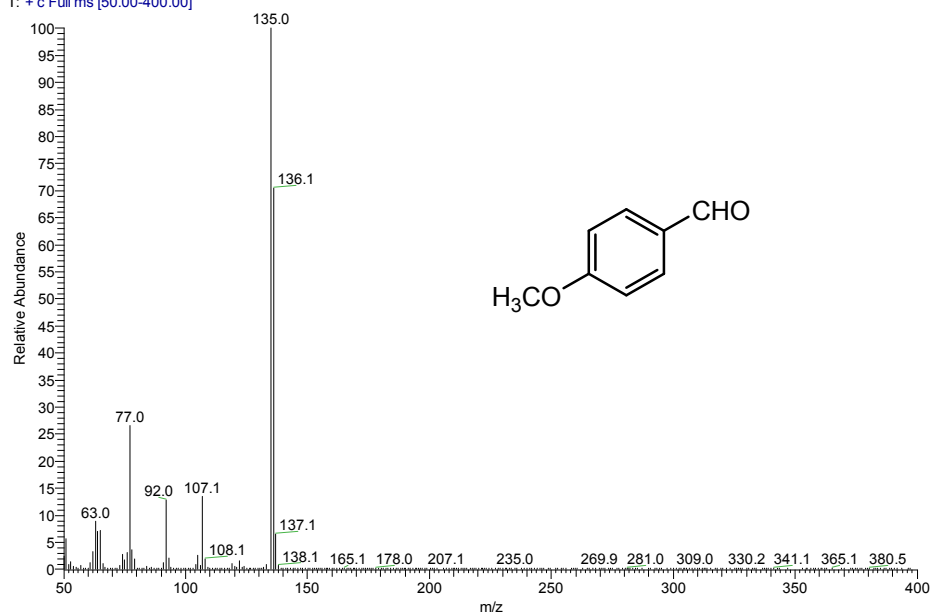


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6.00E9  
TIC MS  
02\_150515  
100250

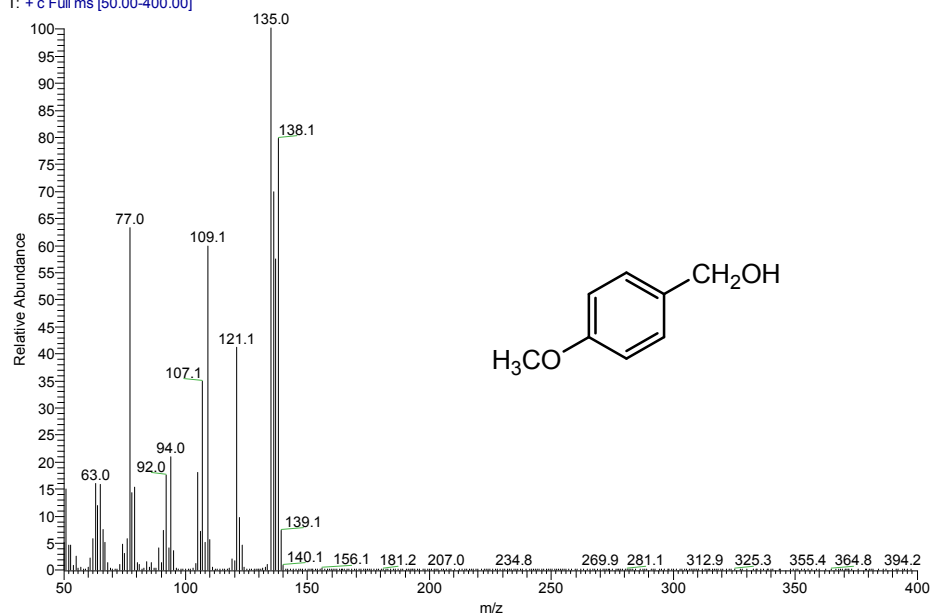
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02\_150515100250 #1172 RT: 5.01 AV: 1 NL: 2.54E7  
T: + c Full ms [50.00-400.00]



### 3. Characterization Data for the Products

phenyl(2-(pyridin-2-yl)phenyl)methanone **3aa**.<sup>1</sup> Conversion: 83% (GC). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.39 (d, *J* = 4.0 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.57 – 7.49 (m, 3H), 7.41 – 7.35 (m, *J* = 7.4 Hz, 1H), 7.30 – 7.24 (m, *J* = 7.7 Hz, 2H), 7.09 – 6.99 (m, 1H).

(2-(pyridin-2-yl)phenyl)(p-tolyl)methanone **3ab**.<sup>1</sup> Yield: 80% (43.7 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.40 (d, *J* = 4.5 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.54 (m, 4H), 7.52 – 7.47 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.03 (dd, *J* = 7.1, 5.4 Hz, 1H), 2.32 (s, 3H).

(2-(pyridin-2-yl)phenyl)(*o*-tolyl)methanone **3ac**.<sup>1</sup> Yield: 64% (35.0 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.43 (d, *J* = 4.6 Hz, 1H), 7.67 – 7.50 (m, 5H), 7.41 (d, *J* = 7.8 Hz,

1H), 7.16 (d,  $J = 7.4$  Hz, 2H), 7.08 (d,  $J = 7.6$  Hz, 1H), 7.05 – 6.98 (m, 1H), 6.97 – 6.90 (m, 1H), 2.57 (s, 3H).

(2-(pyridin-2-yl) phenyl) (m-tolyl) methanone **3ad**.<sup>2</sup> Yield: 76% (41.5 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.40 (d,  $J = 4.4$  Hz, 1H), 7.77 (d,  $J = 7.7$  Hz, 1H), 7.63 – 7.57 (m, 2H), 7.55 – 7.44 (m, 5H), 7.23 – 7.18 (m, 1H), 7.16 (t,  $J = 7.6$  Hz, 1H), 7.08 – 7.02 (m, 1H), 2.29 (s, 3H).

(4-methoxyphenyl)(2-(pyridin-2-yl)phenyl)methanone **3ae**.<sup>1</sup> Yield: 81% (46.9 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.44 (d,  $J = 3.8$  Hz, 1H), 7.77 (d,  $J = 7.9$  Hz, 1H), 7.68 (d,  $J = 8.8$  Hz, 2H), 7.62 – 7.56 (m, 2H), 7.51 (d,  $J = 4.0$  Hz, 2H), 7.48 (d,  $J = 7.8$  Hz, 1H), 7.10 – 7.03 (m, 1H), 6.76 (d,  $J = 8.8$  Hz, 2H), 3.79 (s, 3H).

(4-chlorophenyl)(2-(pyridin-2-yl)phenyl)methanone **3af**.<sup>1</sup> Yield: 69% (40.5 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.35 (d,  $J = 4.4$  Hz, 1H), 7.78 (d,  $J = 7.7$  Hz, 1H), 7.65 – 7.57 (m, 4H), 7.56 – 7.49 (m, 3H), 7.23 (d,  $J = 8.5$  Hz, 2H), 7.09 – 7.02 (m, 1H).

(2-chlorophenyl)(2-(pyridin-2-yl) phenyl)methanone **3ag**.<sup>2</sup> Yield: 57% (33.5 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (d,  $J = 2.6$  Hz, 1H), 7.75 – 7.50 (m, 5H), 7.46 (d,  $J = 6.9$  Hz, 1H), 7.35 – 7.27 (m, 1H), 7.25 – 7.20 (m, 1H), 7.18 (t,  $J = 7.0$  Hz, 1H), 7.11 – 6.97 (m, 2H).

(3-chlorophenyl)(2-(pyridin-2-yl)phenyl)methanone **3ah**.<sup>3</sup> Yield: 65% (38.2 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (s, 1H), 7.79 (d,  $J = 7.7$  Hz, 1H), 7.69 – 7.61 (m, 3H), 7.58 (d,  $J = 9.5$  Hz, 1H), 7.56 – 7.51 (m, 3H), 7.35 (d,  $J = 7.9$  Hz, 1H), 7.20 (t,  $J = 7.8$  Hz, 1H), 7.11 – 7.03 (m, 1H).

(4-bromophenyl)(2-(pyridin-2-yl)phenyl)methanone **3ai**.<sup>4</sup> Yield: 63% (42.6 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (s, 1H), 7.78 (d,  $J = 7.6$  Hz, 1H), 7.66 – 7.59 (m, 2H), 7.58 – 7.50 (m, 5H), 7.41 (d,  $J = 8.5$  Hz, 2H), 7.11 – 7.05 (m, 1H).

(3-bromophenyl)(2-(pyridin-2-yl)phenyl)methanone **3aj**.<sup>3</sup> Yield: 68% (46.0 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 (d,  $J = 4.1$  Hz, 1H), 7.82 (s, 1H), 7.78 (d,  $J = 7.7$  Hz, 1H), 7.62 (t,  $J = 6.8$  Hz, 2H), 7.59 – 7.51 (m, 5H), 7.49 (d,  $J = 7.9$  Hz, 1H), 7.13 (t,  $J = 7.8$  Hz, 1H), 7.06 – 7.00 (m, 1H).

benzo[*h*]quinolin-10-yl(phenyl)methanone **3ba**.<sup>1</sup> Yield: 84% (47.6 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (dd,  $J = 4.4, 1.7$  Hz, 1H), 8.11 (dd,  $J = 8.0, 1.7$  Hz, 1H), 8.06 (dd,  $J = 8.0, 0.9$  Hz, 1H), 7.91 (d,  $J = 8.8$  Hz, 1H), 7.83 – 7.73 (m, 4H), 7.63 (dd,  $J = 7.2, 1.1$  Hz, 1H), 7.45 – 7.39 (m, 1H), 7.34 (dd,  $J = 8.0, 4.4$  Hz, 1H), 7.30 (t,  $J = 7.7$  Hz, 2H).

(2-(1H-pyrazol-1-yl)phenyl)(phenyl)methanone **3ca**.<sup>5</sup> Yield: 70% (34.7 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 – 7.60 (m, 5H), 7.60 – 7.56 (m, 1H), 7.51 – 7.47 (m, 1H), 7.45 – 7.41 (m, 1H), 7.40 (d,  $J = 1.6$  Hz, 1H), 7.32 – 7.27 (m, 2H), 6.21 – 6.14 (m, 1H).

(5-methyl-2-(pyridin-2-yl)phenyl)(phenyl)methanone **3da**.<sup>1</sup> Yield: 81% (44.3 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (d,  $J = 4.8$  Hz, 1H), 7.73 – 7.67 (m, 3H), 7.58 – 7.53 (m, 1H), 7.49 (d,  $J = 7.9$  Hz, 1H), 7.45 – 7.36 (m, 3H), 7.29 – 7.25 (m, 2H), 7.00 (dd,  $J = 6.9, 5.4$  Hz, 1H), 2.47 (s, 3H).

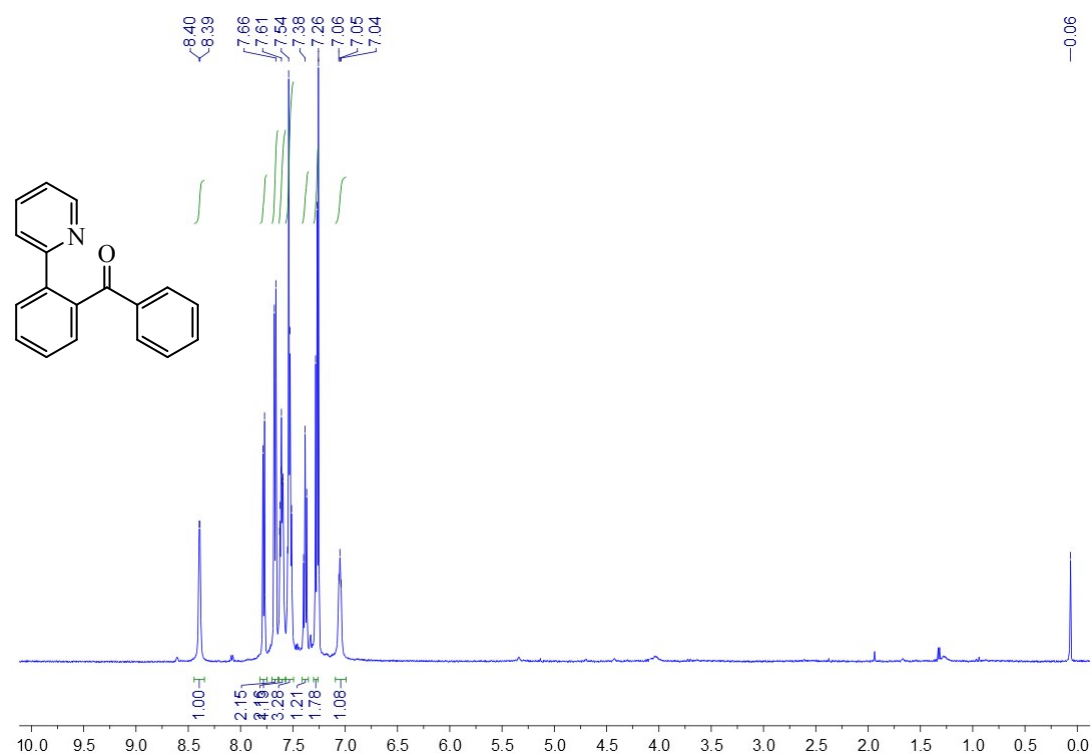
## References

- (1) Zhou, W.; Li, H. J.; Wang, L. Direct Carbo-Acylation Reactions of 2-Arylpyridines with  $\alpha$ -Diketones via Pd-Catalyzed C-H Activation and Selective C(sp<sup>2</sup>)-C(sp<sup>2</sup>) Cleavage. *Org. Lett.*, **2012**, *14*, 4594-4597.
- (2) Xiao, F. H.; Qi, S.; Zhao, F.; Baslé, O.; Deng, G. J.; Li, C.-J. Palladium-Catalyzed Oxidative sp<sup>2</sup> C-H Bond Acylation with Alcohols. *Org. Lett.* **2011**, *13*, 1614-1617.
- (3) Khemnar, A. B.; Bhanage, B. M. Palladium-Catalyzed Oxidative Synthesis of Aromatic Ketones Using Olefins as Acyl Equivalents through Selective *ortho* Aromatic C-H Bond Activation. *Eur. J. Org. Chem.* **2014**, *2014*, 6746-6752.
- (4) Jia, X. F.; Zhang, S. H.; Wang, W. H.; Luo, F.; Cheng, J. Palladium-Catalyzed Acylation of sp<sup>2</sup> C-H Bond: Direct Access to Ketones from Aldehydes. *Org. Lett.* **2009**, *11*, 3120-3123.
- (5) Ashok, B. K.; Bhalchandra, M. B. Palladium-Catalyzed Oxidative Synthesis of Aromatic Ketones Using Olefins as Acyl Equivalents through Selective *ortho* Aromatic C-H Bond Activation. *Eur. J. Org. Chem.* **2014**, 6746-6752.

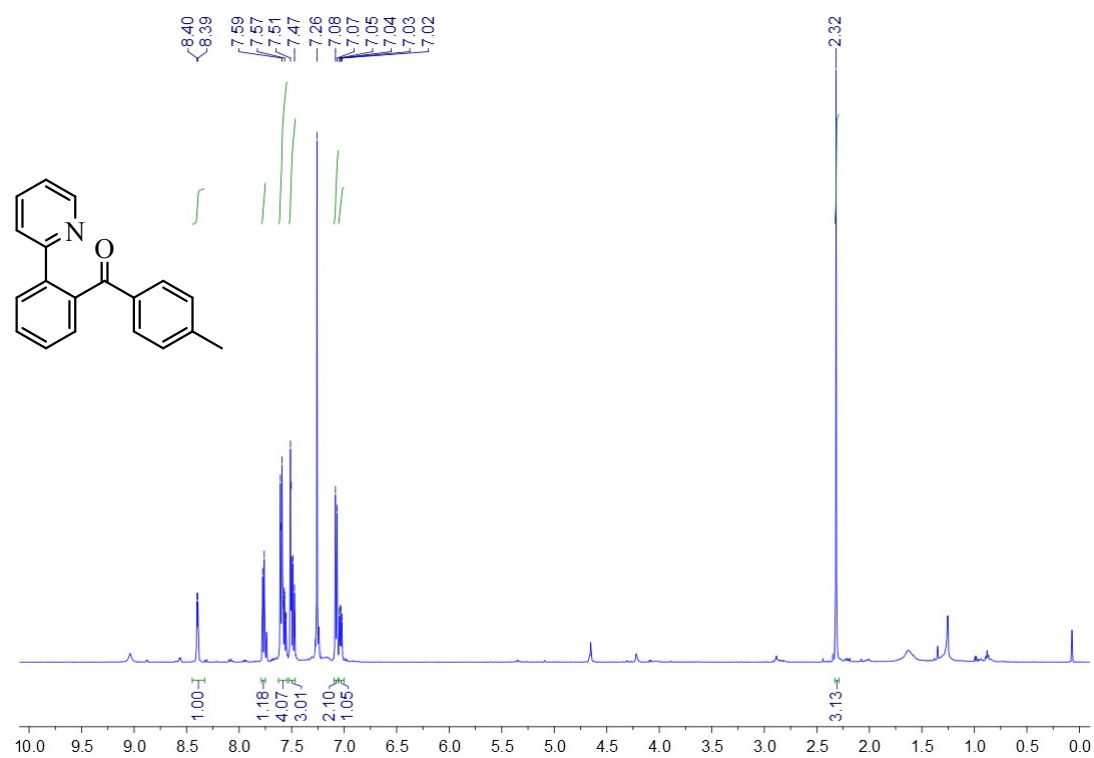


#### 4. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra of the Products

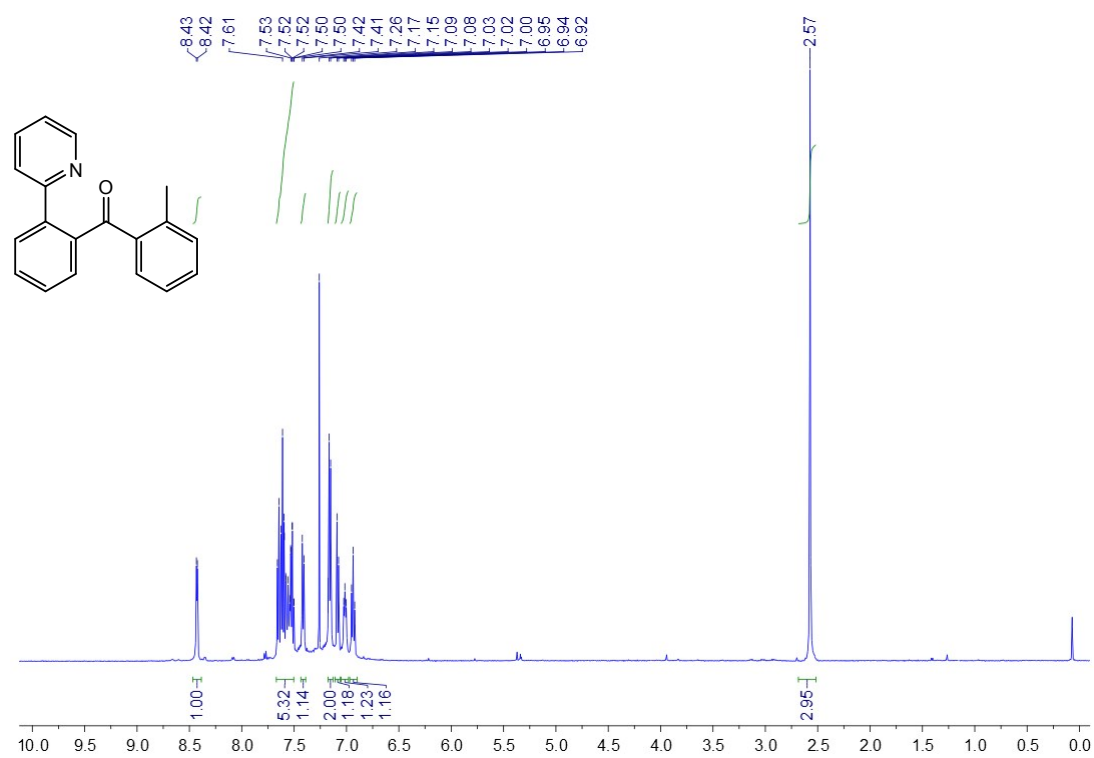
##### $^1\text{H}$ NMR of phenyl(2-(pyridin-2-yl)phenyl)methanone **3aa**



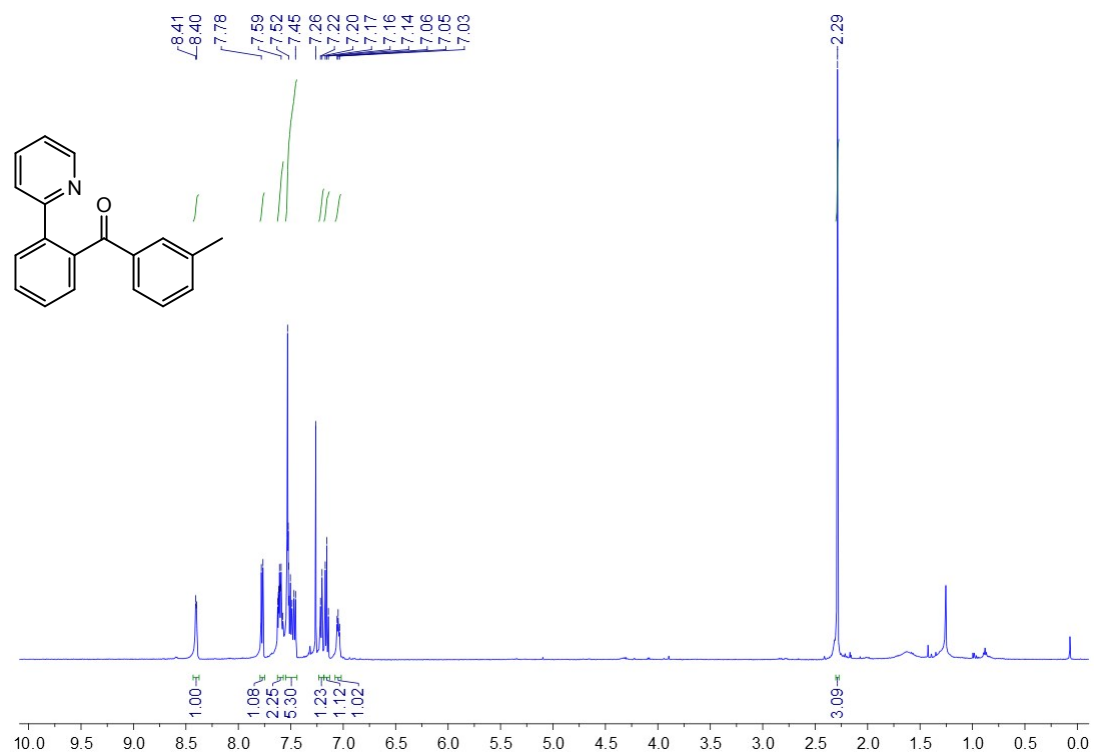
##### $^1\text{H}$ NMR of (2-(pyridin-2-yl)phenyl)(p-tolyl)methanone **3ab**



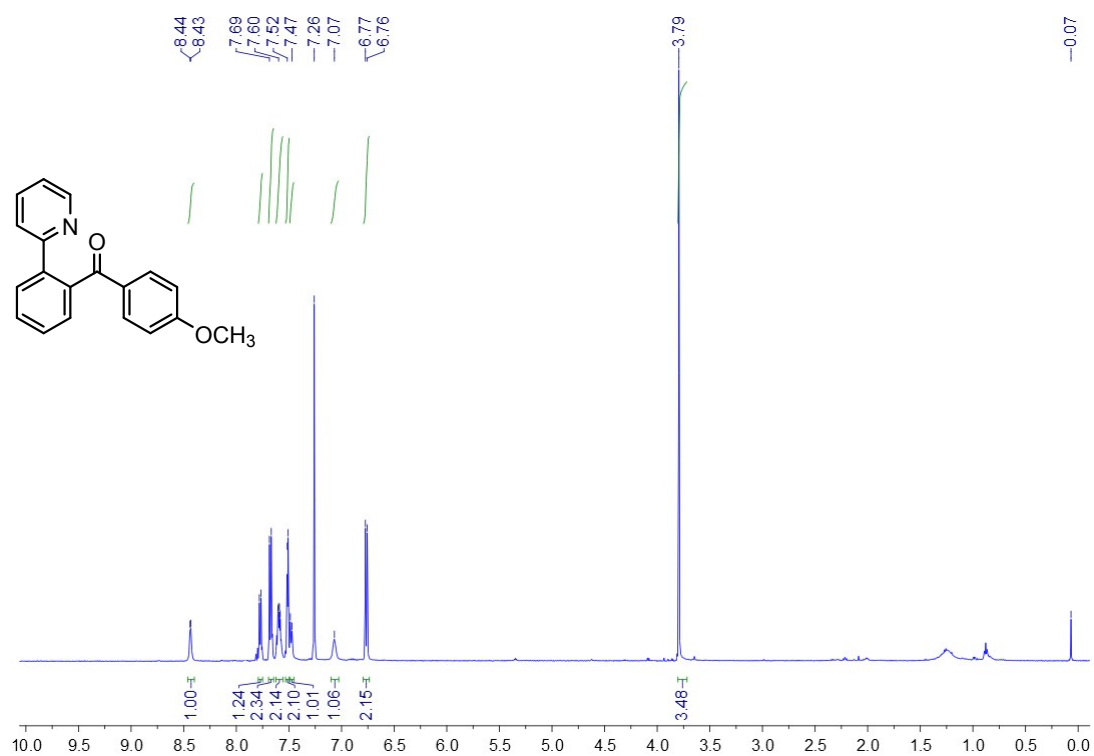
<sup>1</sup>H NMR of (2-(pyridin-2-yl)phenyl)(*o*-tolyl)methanone **3ac**



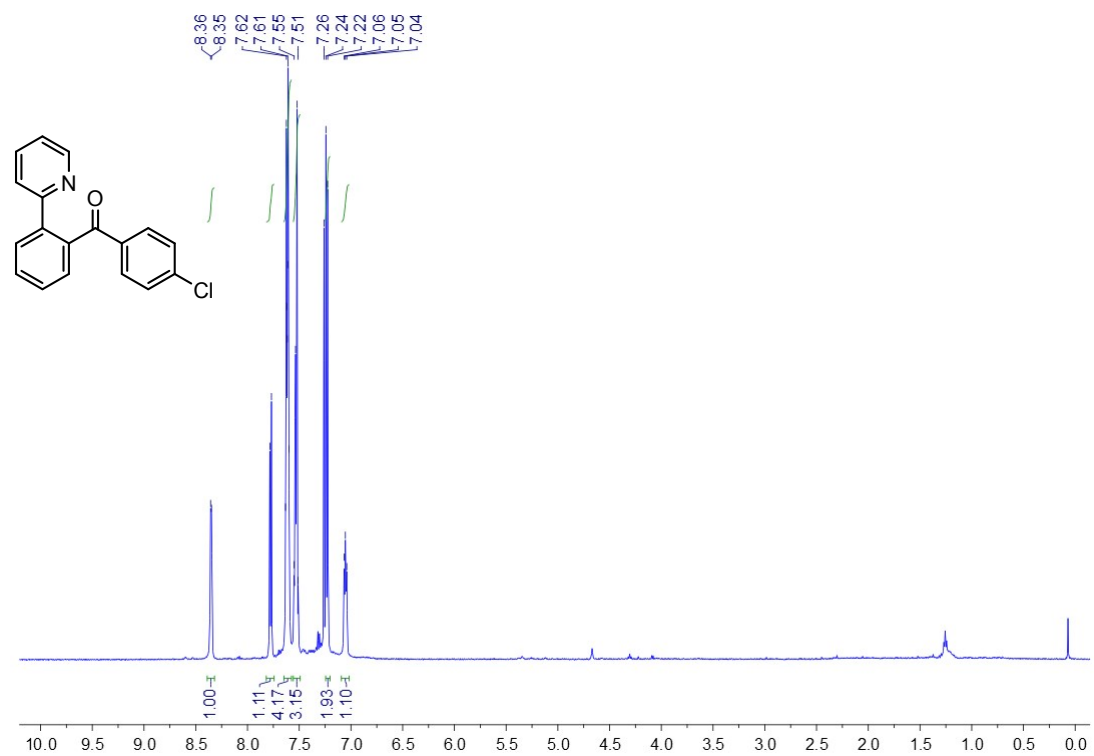
<sup>1</sup>H NMR of (2-(pyridin-2-yl) phenyl) (*m*-tolyl) methanone **3ad**



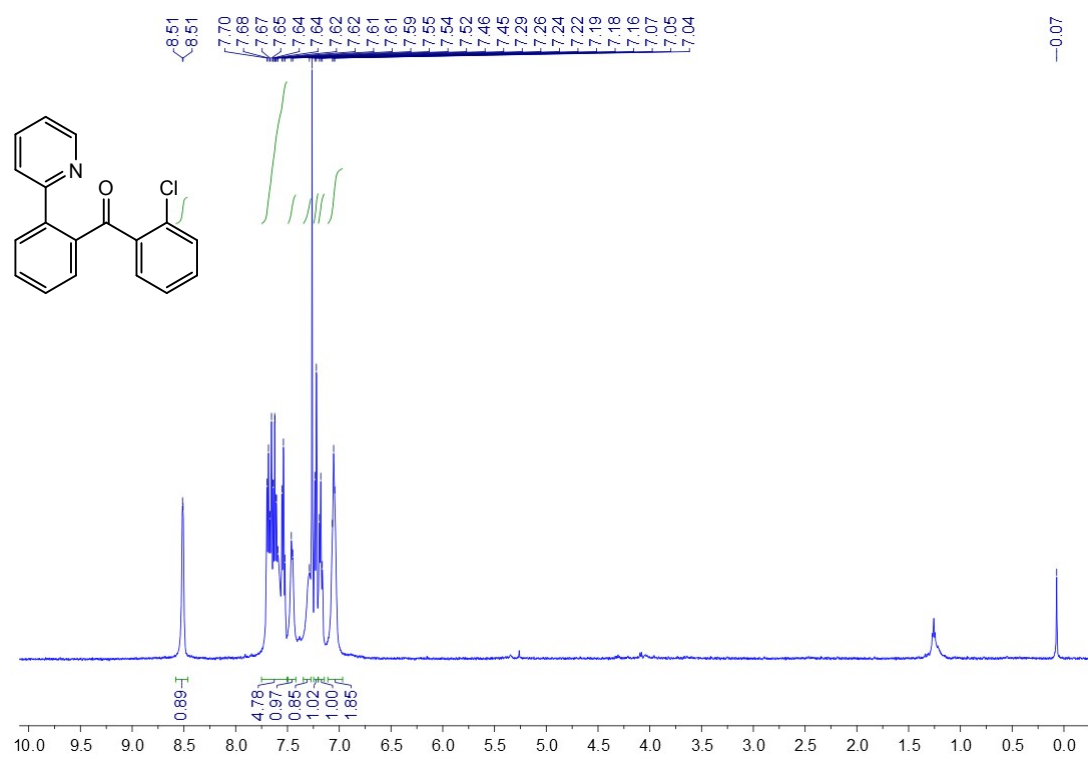
<sup>1</sup>H NMR of (4-methoxyphenyl)(2-(pyridin-2-yl)phenyl)methanone **3ae**



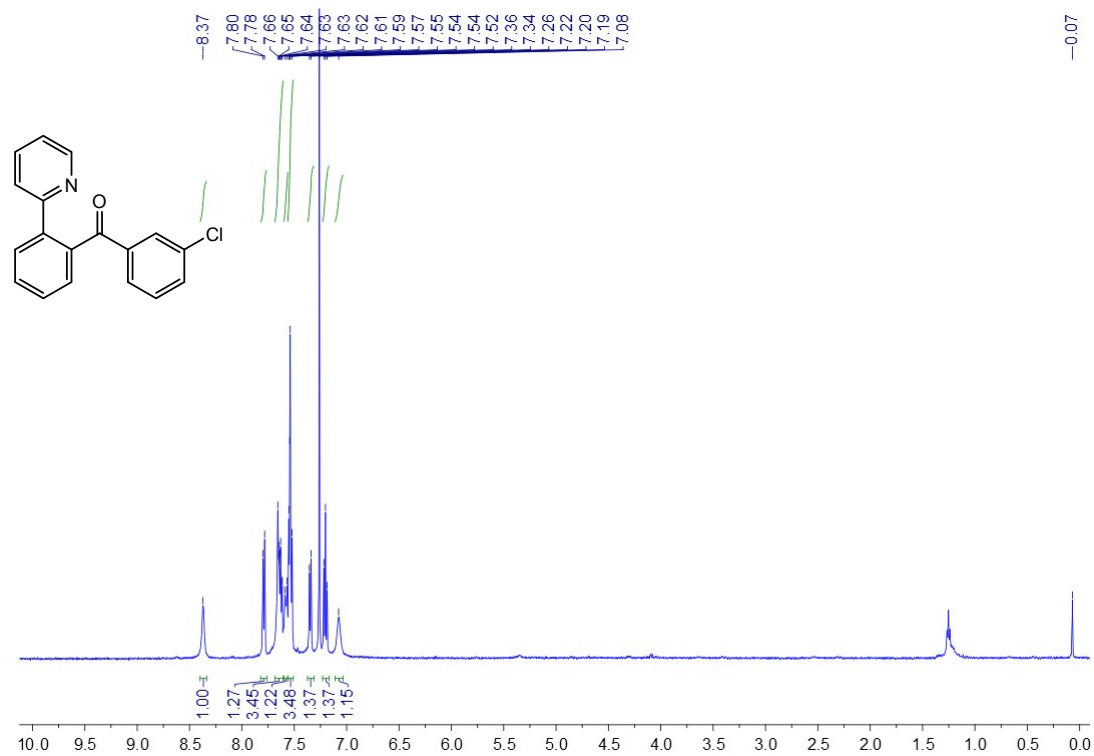
<sup>1</sup>H NMR of (4-chlorophenyl)(2-(pyridin-2-yl)phenyl)methanone **3af**



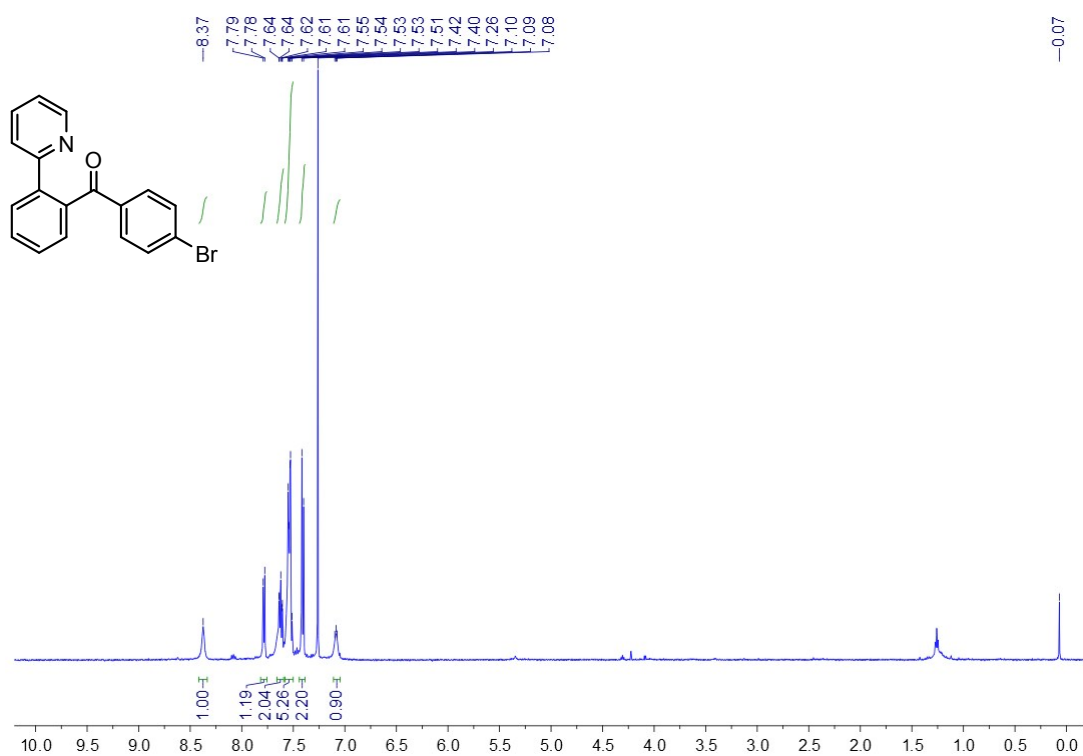
<sup>1</sup>H NMR of (2-chlorophenyl)(2-(pyridin-2-yl)phenyl)methanone **3ag**



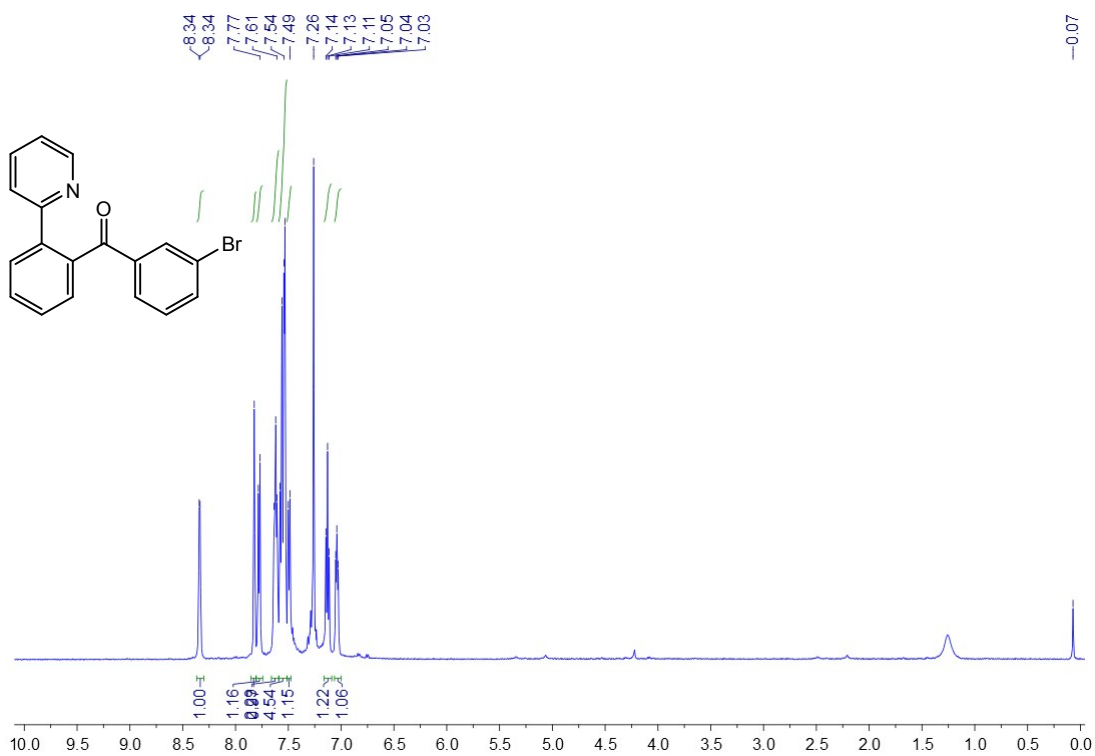
<sup>1</sup>H NMR of (3-chlorophenyl)(2-(pyridin-2-yl)phenyl)methanone **3ah**



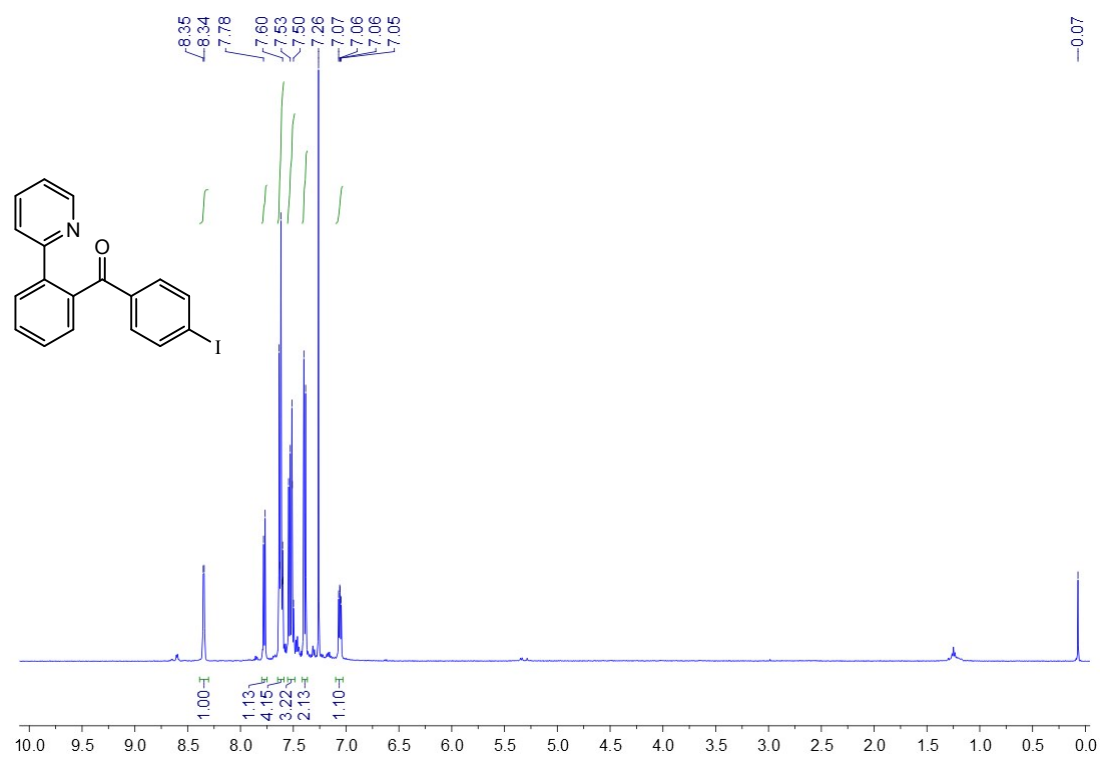
<sup>1</sup>H NMR of (4-bromophenyl)(2-(pyridin-2-yl)phenyl)methanone **3ai**



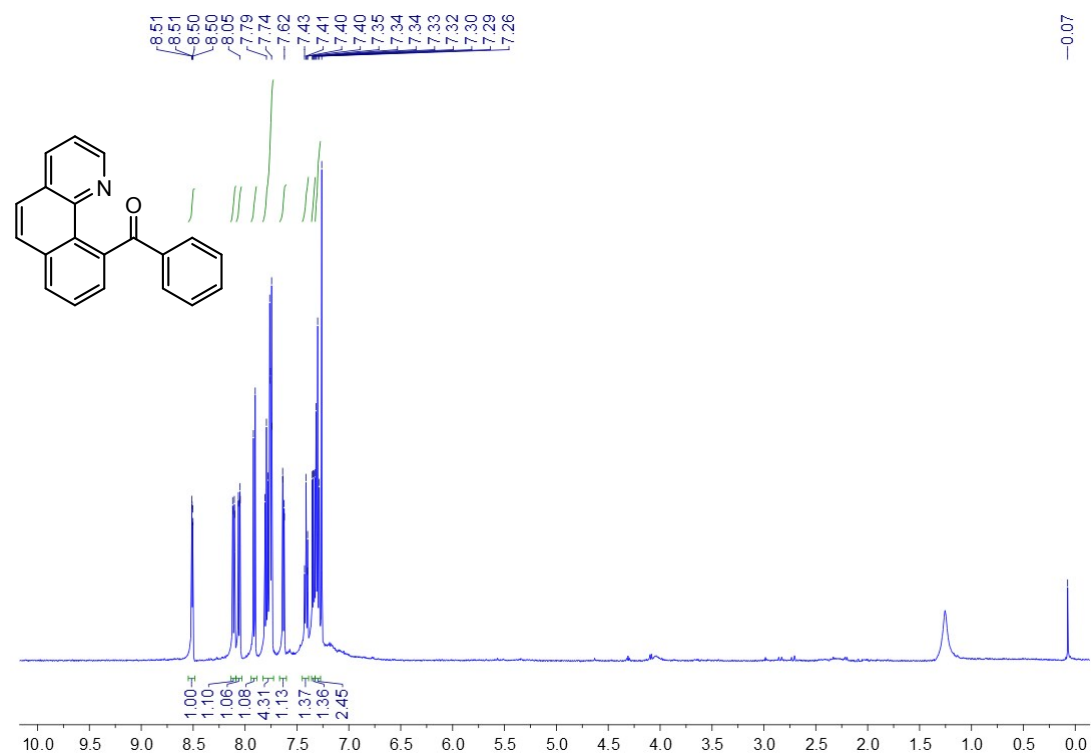
<sup>1</sup>H NMR of (3-bromophenyl)(2-(pyridin-2-yl)phenyl)methanone **3aj**



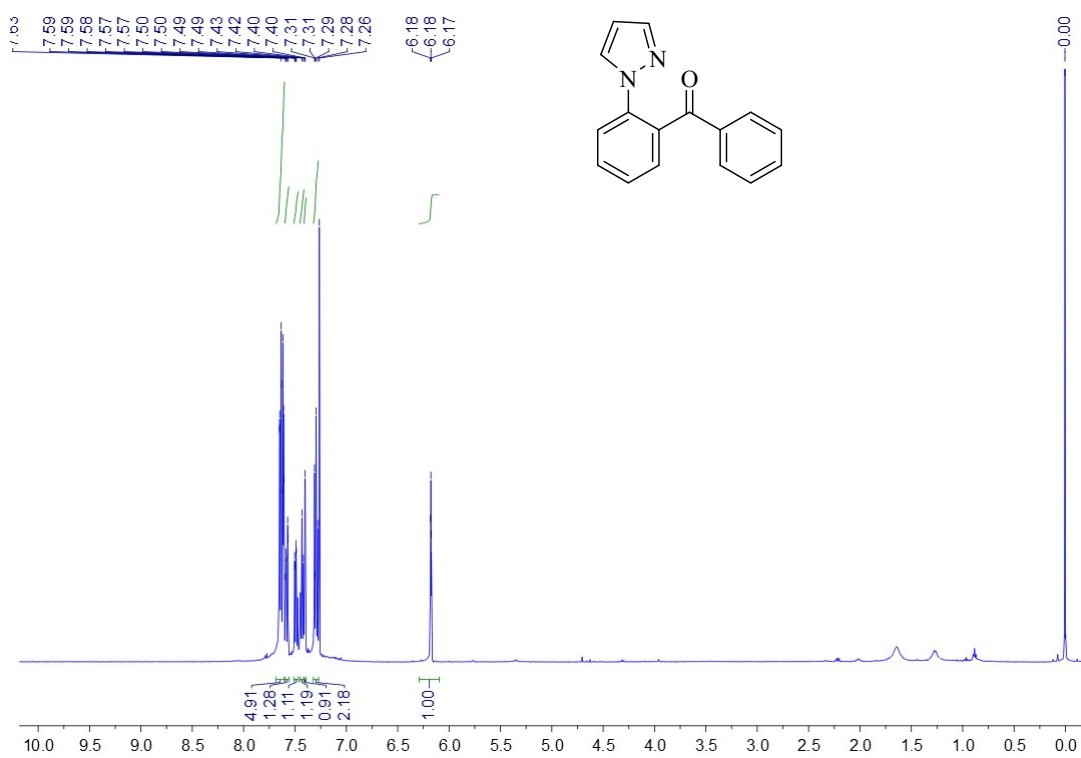
<sup>1</sup>H NMR of (4-iodophenyl)(2-(pyridin-2-yl)phenyl)methanone **3ak**



<sup>1</sup>H NMR of benzo[*h*]quinolin-10-yl(phenyl)methanone **3ba**



<sup>1</sup>H NMR of (2-(1H-pyrazol-1-yl)phenyl)(phenyl)methanone **3ca**



<sup>1</sup>H NMR of (5-methyl-2-(pyridin-2-yl)phenyl)(phenyl)methanone **3da**

