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Graphical Abstract

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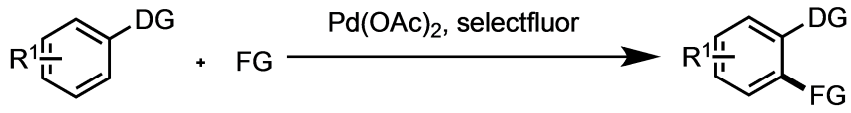

R^1 = Me, OMe, Cl, NO_2
DG=NHCOR^2, NR'COMe, NHTs

FG = aryl, 19 examples, yield up to 91%
FG = vinyl, 14 examples, yield up to 91%
FG = carbonyl, 5 examples, yield up to 81%

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ABSTRACT

The C–H activation of aryl amide using readily available $Pd(OAc)_2$ in the presence of selectfluor is reported. The highly mono-selective introduction of sp^2 hybridized functional groups have been realized. A broad range of aryl-, alkenyl- and keto-aryl amides were prepared using unactivated coupling partners under mild conditions.

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1. Introduction

Pd catalyzed coupling reactions of aryl halides to form a new Csp2–Csp2 bonds have become one of the most powerful strategies for stitching two arenes together.[1] Arene direct C–H activation as the improvement has attracted much attention for the engineering of the two aromatic systems.[2] The former transformation utilized electron rich Pd(0) catalysts while Pd(II) catalysts are preferred for the latter direct C–H functionalization reactions.[3] However, the reactivities of potential more reactive Pd(IV) species have not been very well explored.[4,5] In this communication, reactions using reactive Pd(IV) intermediates are reported and the new reactivities towards the syntheses of arene anilides, alkenyl anilides as well as keto-anilides have been demonstrated.

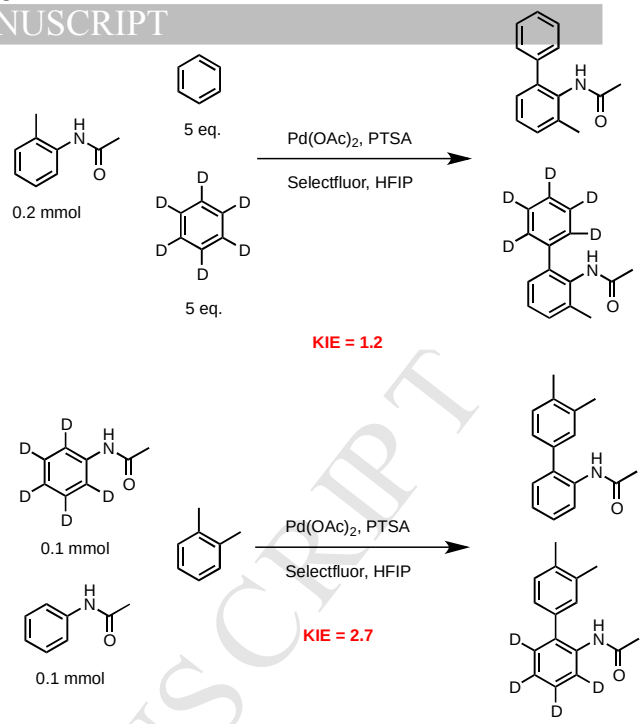
During our previous studies, we have proposed that Pd catalysts/intermediates at high oxidation state reacts much faster than the corresponding Pd catalysts/intermediates under mild conditions.[6] Inspired by Vigalok's Pt(IV),[7] Sanford,[8] Ritter's[9] isolation of Pd(IV) species using F-containing oxidants, we were interested in the utilization of Pd catalyst exploring reactions undergoing high oxidative Pd intermediates. Under similar conditions, fluorination or C–H activations have been also studied by Yu and Michael.[10,11]

Inspired by Sanford, Ritter and Yu, we are currently trying to explore the double C–H activation under Pd(IV)/(II) system. Knowing the oxidation of Pd(II) by a common oxidation reagent-selectfluor could provide Pd(IV) adduct, we started the investigation of reactions of common directed arene-acetanilide and *ortho*-xylene.[12,13] As a close reference, similar reactions by You had revealed that the reaction may undergo cationic Pd catalyzed conditions as they have shown that Pd (II) dimer **1a-Pd** can react with *ortho*-xylene **2a** to give the desired **3a** in 92% yield.[14]

2. Results and discussion

Preliminary results suggested that polar less-coordinating solvent hexafluoro isopropanol (HFIP) is a good solvent. When sub-stoichiometric amount of F-containing oxidant selectfluor was used, the desired product **3a** was obtained in a good yield of 62% (**SI, table 1**, entry 1). Selectfluor prior to other oxidants has shown the best reactivity towards the anilide synthesis, even other oxidants such as $K_2S_2O_8$, $(NH_4)_2S_2O_8$ are also promising oxidants for the reaction (**SI, Table 1**, entries 2-5). Other F-containing reagents are also potential good oxidants and the desired product was isolated in 75% and 55% respectively (**SI, table 1**, entries 12 and 13). The reactions in the absence of selectfluor did not provide any of our desired products. Further screening on the additives showed that sulfonic acids such as p-TSA, CSA or H_2SO_4 are good additives for the reaction while less strong acids such as HOAc and PivOH are less efficient. (**SI Table 2**).[15] Very interestingly, reaction using Pd(0) catalyst Pd_2dba_3 also provided the desired product in excellent yield.

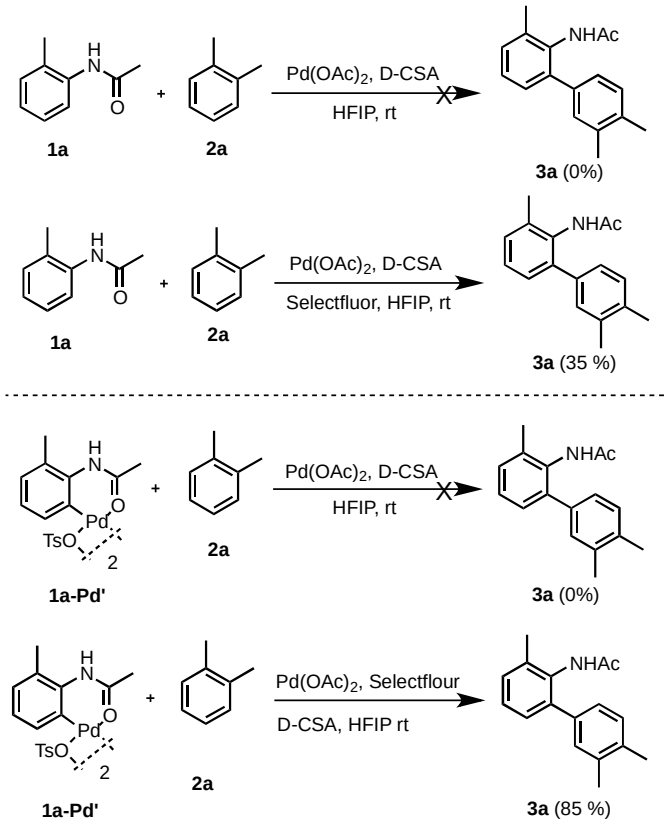
The KIE studies for both substrates revealed that the C–H activation processes are rate-determining step rather than the activation of arenes as shown in **Scheme 1**.



Scheme 1. KIE studies

These implied that if the reaction undergoes Friedel-Craft type of arylation forming Pd(IV) with benzene or xylene as one of the substituents then the reaction would be very favored comparing to the corresponding Pd(II) analogue.

The control experiments of **1a** and **1a-Pd'** were carried out in the presence and absence of selectfluor. As shown in **Scheme 2**, reactions of **1a** and **1a-Pd'** did not provide any our desired product while reactions in the presence of oxidant gave the corresponding amide **3a** in 35% and 85% yields respectively.



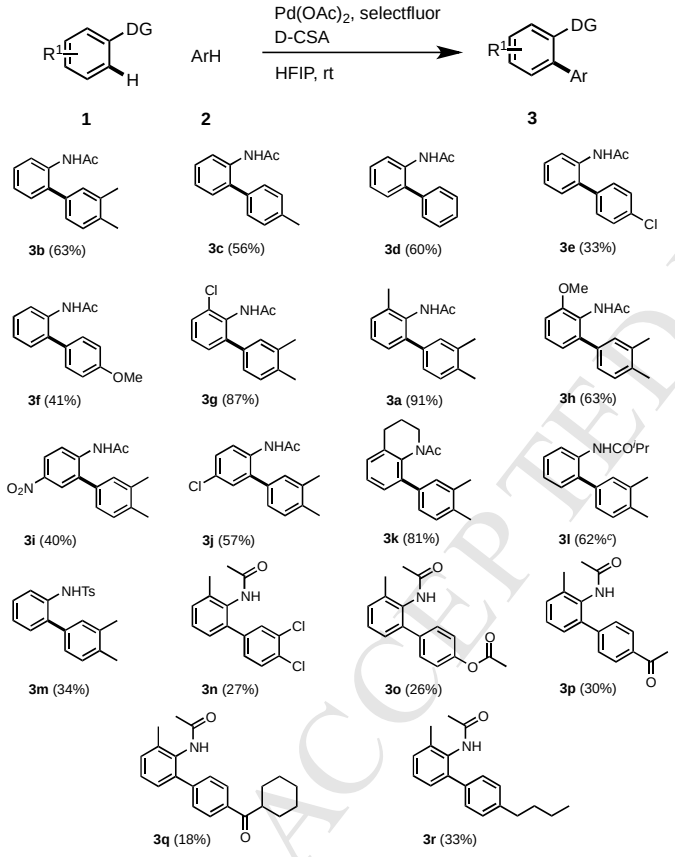
Scheme 2. Control experiments with/without selectfluor

In addition, as shown in **Figure 1 in SI**, we have observed the F signal in the ^{19}F NMR when subjecting the reaction mixture for NMR analysis, which may indicate that Pd(IV)-F species were formed in the reaction.

The scope of the Pd-catalyzed reaction with various anilides and unactivated arenes is summarized in **Table 1**.[16]

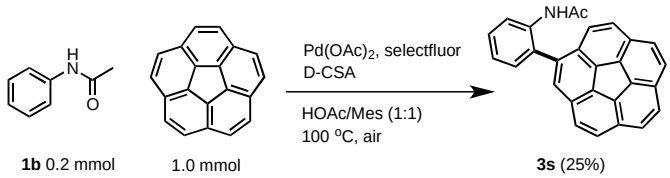
The reactions of anilide with arenes such as xylene, toluene and benzene went smoothly the desired products **3b-3f** were isolated in good yields. The substituted anilides were also good substrates for this type of transformation and a number substituted aryl anilides such as **3g-3j** have been prepared. The reactions with anilides other than acetanilide have also been studies and the desired products **3k** and **3l** were isolated in 81% and 62% yields respectively. The reaction of N-Ts aniline is also very successful and the corresponding product **3m** was obtained in 34% yield. The regio-selectivity was excellent for this type of reaction due to both steric and electronic reasons. Reactions with xylene and toluene, no other regio-isomers were detected by the 1H NMR of the crude reaction mixtures.

Table 1. The synthesis of *ortho*-aryl anilides



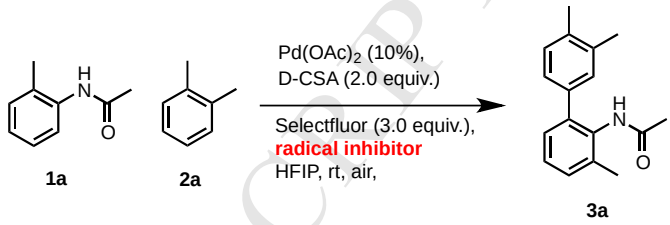
[a]Reaction conditions: anilide (0.2 mmol), arene (2.0 mmol), $Pd(OAc)_2$ (10 mol%), selectfluor (3.0 equiv.), D-CSA (2.0 equiv.), HFIP (1.0 mL).
[b]at 50 °C
[c]selectfluor (1.5 equiv.)

More interestingly, the reaction with curved aromatic system such as corannuele is also working and the desired corannulene **3n** was isolated in 25% yield after column chromatography. This approach has provided an excellent way of functionalizing synthetically challenging curved aromatic hydrocarbon like corannulene, even though the reaction gave slight disappointing yield.



Scheme 3. Direct arylation using corannulene **2n**

Reactions with radical inibitors such as TEMPO, BHT as well as hydroquinone were used. The reactions seemed to be strongly affected and only a trace amount of product was observed under our standard reaction conditions. (**Scheme 4**)

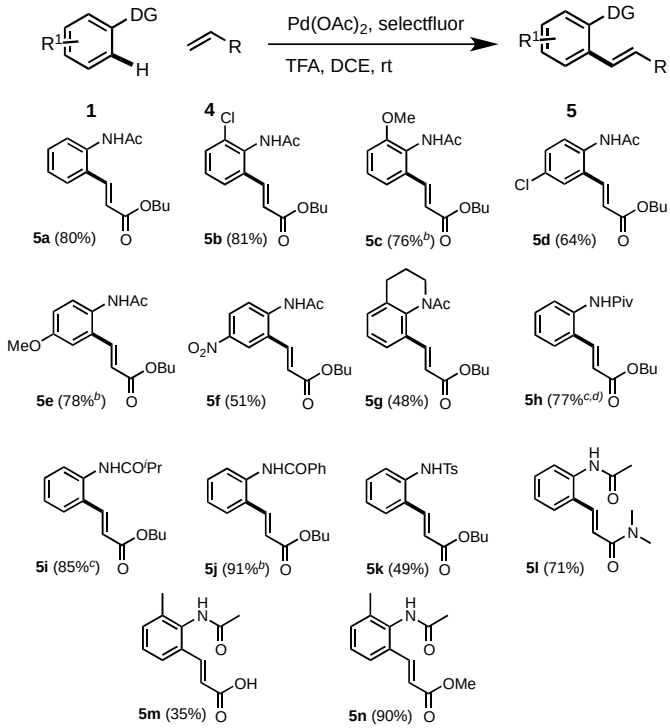


entry	radical inhibitor (3.0 equiv.)	yield of **3a** (%)
1	TEMPO	trace
2	BHT	trace
3	Hydroquinone	trace

Scheme 4. Reactions with radical inhibitors

With the optimal reaction conditions in hand, we have also utilized similar conditions see if coupling reactions with other partners would be possible.

Table 2. The synthesis of *ortho*-alkenyl anilides

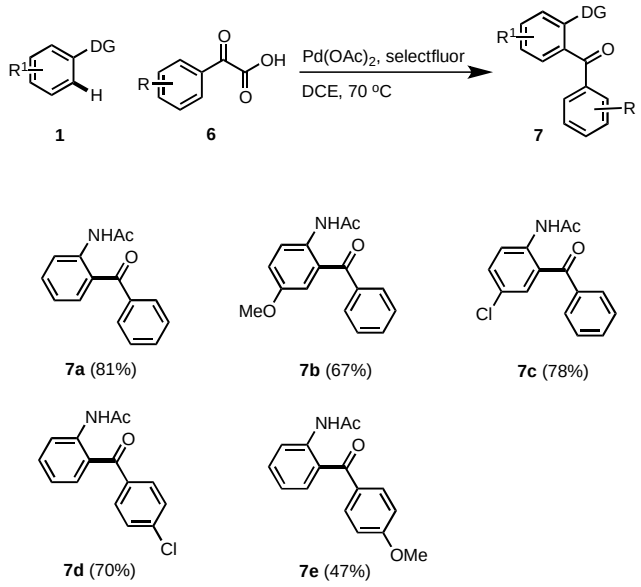


[a]Reaction conditions: anilide (0.2 mmol), alkene (3.0 equiv.), $Pd(OAc)_2$ (10 mol%), Selectfluor (0.4 mmol), DCE (1.0 mL), TFA (10 mmol)
[b]TFA (6.0 mmol)
[c]MsOH (2.0 equiv.) instead of TFA
[d]at 60 °C

Reactions of anilides with alkenes under similar conditions are fruitful and the results are shown in **Table 2**.[17] Similar to the reactions with arenes, reactions in the absence of selectfluor did not give any coupling product.

The synthesis of aryl ketoanilides was also straightforward as shown in **Table 3**. Both electron rich and deficient anilides as well as electron rich and poor keto carboxylic acids have shown good reactivity during the reactions.[18]

Table 3. ketoanilide synthesis



Reaction conditions: anilide **1** (0.2 mmol), keto carboxylic acid **6** (5.0 equiv.), $Pd(OAc)_2$ (10 mol%), Selectflour (0.6 mmol), DCE (1.0 mL)

3. Conclusion

In conclusion, we have reported three Pd-catalyzed syntheses of substituted anilides *via* aryl amide directed C–H activation reactions. A range of representative of aryl-, alkenyl- and keto-aryl amides were prepared using unactivated coupling partners under mild conditions.

4. Experimental section

4.1. General Information

Flash chromatography was performed on silica gel 100-200 mesh. The solvent system used was a gradient of petroleum ether/EtOAc, increasing in polarity to EtOAc or DCM/MeOH, increasing in polarity to MeOH. Thin layer chromatography (TLC) was performed on glass backed plates pre-coated with silica (GF254), which were developed using standard visualizing agents. ^{1}H and ^{13}C NMR spectra were recorded on a 600 MHz BRUKER AVANCE or 400 MHz BRUKER AVANCE spectrometer at 25 ^{o}C. ^{1}H: Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = sepetet, br = broad, m = multiplet), 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 ($CDCl_3$: δ 77.0 ppm). High-resolution mass spectra (HRMS) recorded for accurate mass analysis, were performed on either a Q-TOF micro (Bruker Compass Data Analysis 4.0) spectrometer. Melting points were performed on recrystallized solids and recorded on a national standard melting point apparatus and are uncorrected.

4.2. General Procedure A: Procedure for the arylation reactions

A solution of Anilide, arene, Selectfluor, $Pd(OAc)_2$, D-CSA in solvent was stirred at room temperature. After the reaction was completed, the mixture was extracted with EtOAc (10 mL x 3). The organic phase was dried over Na_2SO_4. Then the solvent was removed under reduced pressure to provide the crude product. The purification was performed by flash column chromatography on silica gel.

*4.2.1 N-(3,3',4'-Trimethyl-[1,1'-biphenyl]-2-yl)acetamide **(3a)***

Following the general procedure A, a solution of N-(o-tolyl)acetamide (0.2 mmol, 30 mg), dimethylbenzene (2 mmol, 240 µl), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA (0.6 mmol, 139 mg) in 1.0 mL HFIP was stirred at room temperature for 8 h. The desired amide **3a** (46 mg, 91%) was isolated as a white solid: Mp: 130-132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (m, 2 H), 7.16 (m, 2 H), 7.11-7.03 (m, 2 H), 6.62 (s, 1 H), 2.30 (s, 6 H), 2.29 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 139.3, 137.0, 136.7, 136.7, 135.8, 132.6, 130.2, 129.9, 129.6, 127.9, 127.4, 126.3, 23.2, 19.8, 19.5, 18.7. HRMS (ESI) m/z calcd for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1545; found 254.1545.

*4.2.2 N-(3',4'-Dimethyl-[1,1'-biphenyl]-2-yl)acetamide **(3b)***

Following the general procedure A, a solution of *N*-phenylacetamide (0.2 mmol, 27 mg), dimethylbenzene (2 mmol, 240 µl), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA (0.6 mmol, 139 mg) in 1.0 mL solvent (acetone: HFIP=1:1) was stirred at room temperature for 8 h. The desired amide **3b** (30 mg, 63%) was isolated as a white solid: Mp: 87-89 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1 H), 7.33 (t, *J* = 8.0 Hz, 1 H), 7.25-7.18 (m, 3 H), 7.17-7.11 (m, 2 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 2.33 (s, 3 H), 2.32 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 137.5, 136.5, 135.6, 134.8, 132.1, 130.5, 130.3, 130.1, 128.1, 126.5, 124.2, 121.4, 24.6, 19.8, 19.5. HRMS (ESI) *m/z* calcd for $C_{16}H_{17}NO$ $[M+H]^+$ 240.1383; found 240.1385.

*4.2.3 N-(4'-Methyl-[1,1'-biphenyl]-2-yl)acetamide **(3c)***

Following the general procedure A, a solution of *N*-phenylacetamide (0.2 mmol, 27 mg), toluene (2 mmol, 211 µl), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA (0.6 mmol, 139 mg) in 1.0 mL solvent (acetone: HFIP=1:1) was stirred at room temperature for 8 h. The desired amide **3c** (25 mg, 56%) was isolated as a white solid: Mp: 103-105 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1 H), 7.33 (t, *J* = 8.0 Hz, 1 H), 7.27 (t, *J* = 8.0 Hz, 4 H), 7.23-7.11 (m, 3 H), 2.42 (s, 3 H), 2.00 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2, 137.8, 135.2, 134.8, 132.2, 130.1, 129.8, 129.1, 128.2, 124.3, 121.6, 24.6, 21.2. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}NO$ $[M+H]^+$ 226.1226; found 226.1226.

*4.2.4 N-([1,1'-Biphenyl]-2-yl)acetamide **(3d)***

Following the general procedure A, a solution of *N*-phenylacetamide (0.2 mmol, 27 mg), benzene (2 mmol, 177 µl), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA (0.6 mmol, 139 mg) in the 1.0 mL solvent (acetone : HFIP=1:1) was stirred at room temperature for 8 h. The desired amide **3d** (25 mg, 60%) was isolated as a white solid: Mp: 118-119 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 1 H), 7.48 (t, *J* = 8.0 Hz, 2 H), 7.43-7.40 (m, 1 H), 7.39-7.34 (m, 3 H),

7.24 (d, *J* = 8.0 Hz, 1 H), 7.18-7.14 (m, 2 H), 2.00 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 138.2, 134.7, 132.3, 130.1, 129.2, 129.1, 128.4, 128.0, 124.4, 121.8, 24.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{13}NO$ $[M+Na]^+$ 234.0889; found 234.0890.

4.2.5 N-(4'-Chloro-[1,1'-biphenyl]-2-yl)acetamide ***(3e)***

Following the general procedure A, a solution of *N*-phenylacetamide (0.2 mmol, 27 mg), chlorobenzene (2 mmol, 205 μl), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA (0.6 mmol, 139 mg) in the 1.0 mL HFIP was stirred at room temperature for 8 h. The desired amide **3e** (16 mg, 33%) was isolated as a white solid: Mp: 124-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 7.42-7.34 (m, 1 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.19 (m, 2 H), 7.00 (s, 1 H), 2.03 (s, 3 H). The analytical data are consistently agreed with those had been previously reported in the literature. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}{}^{35}ClNO$ $[M+H]^+$ 246.0680; found 246.0678.

4.2.6 N-(4'-Methoxy-[1,1'-biphenyl]-2-yl)acetamide ***(3f)***

Following the general procedure A, a solution of *N*-phenylacetamide (0.2 mmol, 27 mg), anisole (2 mmol, 218 μl), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA (0.6 mmol, 139 mg) in 1.0 mL HFIP was stirred at room temperature for 6 h. The desired amide **3f** (20 mg, 41%) was isolated as a white solid: Mp: 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1 H), 7.39-7.26 (m, 3H), 7.23-7.10 (m, 3 H), 7.01 (d, *J* = 8.0 Hz, 2 H), 3.86 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 159.4, 134.9, 131.9, 130.4, 130.3, 130.2, 128.13, 124.3, 121.6, 114.5, 55.4, 24.7. HRMS (ESI) *m/z* calcd for $C_{15}H_{15}NO_2$ $[M+H]^+$ 242.1176; found 242.1176.

4.2.7 N-(3-Chloro-3',4'-dimethyl-[1,1'-biphenyl]-2-yl)acetamide ***(3g)***

Following the general procedure A, a solution of *N*-(2-chlorophenyl)acetamide (0.2 mmol, 34 mg), dimethylbenzene (2 mmol, 240 μl), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA (0.6 mmol, 139 mg) in the 1.0 mL HFIP was stirred at room temperature for 10 h. The desired amide **3g** (50 mg, 87%) was isolated as a white solid: Mp: 107-108 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.23 (m, 2 H), 7.13 (d, *J* = 7.5 Hz, 1 H), 7.10 (s, 1 H), 7.06 (d, *J* = 7.5 Hz, 1 H), 6.94 (s, 1 H), 2.27 (s, 3 H), 2.26 (s, 3 H), 1.99 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.3, 142.1, 136.6, 136.3, 136.22, 133.0, 131.7, 129.8, 129.64, 129.0, 128.8, 128.3, 126.0, 23.0, 19.8, 19.5. HRMS (ESI) *m/z* calcd for $C_{16}H_{16}Cl^{35}NO$ $[M+H]^+$ 274.0993; found 274.0992.

4.2.8 N-(3-Methoxy-3',4'-dimethyl-[1,1'-biphenyl]-2-yl)acetamide ***(3h)***

Following the general procedure A, A solution of *N*-(2-methoxyphenyl)acetamide (0.2 mmol, 33 mg), dimethylbenzene (2 mmol, 240 μl), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA (0.6 mmol, 139 mg) in 1.0 mL HFIP was stirred at room temperature for 5 h. The desired amide **3h** (34 mg, 63%) was isolated as a white solid: Mp: 137-139 °C; ^{1}H NMR (600 MHz, DMSO) δ 8.98 (s, 1 H), 7.31 (t, *J* = 8.0 Hz, 1 H), 7.13 (m, 3 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 6.91 (d, *J* = 8.0 Hz, 1 H), 3.78 (s, 3 H), 2.25 (s, 6 H), 1.84 (s, 3 H). ^{13}C NMR (151 MHz, DMSO) δ 168.8, 155.8, 141.1, 136.9, 135.6, 134.9, 129.7, 129.0, 127.7, 125.8, 123.8, 121.6, 110.4, 55.6, 22.5, 19.4, 19.0. HRMS (ESI) *m/z* calcd for $C_{17}H_{19}NO_2$ $[M+H]^+$ 270.1489; found 270.1487.

4.2.9 N-(3',4'-Dimethyl-5-nitro-[1,1'-biphenyl]-2-yl)acetamide ***(3i)***

Following the general procedure A, a solution of *N*-(4-nitrophenyl)acetamide (0.2 mmol, 36 mg), dimethylbenzene (2 mmol, 240 μl), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA (0.6 mmol, 139 mg) in 1.0 mL HFIP was stirred at room temperature for 18 h. The desired amide **3i** (23 mg, 40%) was isolated as a white solid: Mp: 157-158 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.5 Hz, 1 H), 8.19 (dd, *J* = 8.5, 2.5 Hz, 1 H), 8.09 (d, *J* = 2.5 Hz, 1 H), 7.56 (s, 1 H), 7.29 (d, *J* = 8.0 Hz, 1 H), 7.15 (s, 1 H), 7.11 (d, *J* = 8.0 Hz, 1 H), 2.35 (s, 3 H), 2.35 (s, 3 H), 2.08 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.4, 143.1, 140.9, 138.4, 137.9, 133.1, 131.8, 130.8, 130.2, 126.2, 125.4, 123.9, 119.9, 25.0, 19.9, 19.6. HRMS (ESI) *m/z* calcd for $C_{16}H_{16}N_2O_3$ $[M+H]^+$ 285.1233; found 285.1231.

4.2.10 N-(5-Chloro-3',4'-dimethyl-[1,1'-biphenyl]-2-yl)acetamide ***(3j)***

Following the general procedure A, A solution of *N*-(4-chlorophenyl)acetamide (0.2 mmol, 34 mg), dimethylbenzene (2 mmol, 240 μl), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA (0.6 mmol, 139 mg) in the 1.0 mL solvent (acetone: HFIP=2:8) was stirred at room temperature for 7 h. The desired amide **3j** (31 mg, 57%) was isolated as a white solid: Mp: 118-119 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 9.0 Hz, 1 H), 7.29 (dd, *J* = 9.0, 2.5 Hz, 1 H), 7.24 (d, *J* = 8.0 Hz, 1 H), 7.20 (d, *J* = 2.5 Hz, 1 H), 7.18 (s, 1 H), 7.11 (s, 1 H), 7.07 (d, *J* = 8.0 Hz, 1 H), 2.33 (s, 3 H), 2.32 (s, 3 H), 2.01 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2, 137.8, 137.1, 134.3, 133.6, 133.5, 130.4, 130.3, 129.8, 129.1, 128.0, 126.3, 122.4, 24.6, 19.8, 19.6. HRMS (ESI) *m/z* calcd for $C_{16}H_{16}{}^{35}ClNO$ $[M+H]^+$ 274.0993; found 274.0996.

4.2.11 1-(8-(3,4-Dimethylphenyl)-3,4-dihydroquinolin-1(2H)-yl)ethanone ***(3k)***

Following the general procedure A, A solution of *N*-(1,2,3,4-tetrahydronaphthalen-1-yl)acetamide (0.2 mmol, 38 mg), dimethylbenzene (2 mmol, 240 μl), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA (0.6 mmol, 139 mg) in 1.0 mL HFIP was stirred at room temperature for 4 h. The desired amide **3k** (45 mg, 81%) was isolated as a white solid: Mp: 83-85 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 1 H), 7.25 (t, *J* = 8.0 Hz, 1 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.11 (s, 1 H), 7.07 (d, *J* = 8.0 Hz, 1H), 4.78-4.74 (m, 1 H), 3.09-3.01 (m, 1 H), 2.74-2.70 (m, 1 H), 2.51-2.42 (m, 1 H), 2.36-2.28 (m, 1 H), 2.28 (s, 3 H), 2.27 (s, 3 H), 1.82-1.69 (m, 1 H), 1.46 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 138.1, 137.9, 137.6, 137.1, 136.6, 136.0, 130.3, 129.44, 128.7, 126.8, 126.4, 125.6, 41.7, 26.9, 24.4, 22.0, 20.0, 19.5. HRMS (ESI) *m/z* calcd for $C_{19}H_{21}NO$ $[M+H]^+$ 280.1696; found 280.1698.

4.2.12 N-(3',4'-dimethyl-[1,1'-biphenyl]-2-yl)isobutylramide ***(3l)***

Following the general procedure B, a solution of *N*-phenylisobutyramide (0.2 mmol, 32.6 mg), arene (2 mmol, 240 μl), selectfluor (0.3 mmol, 106 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA(0.6 mmol, 139 mg) in 1.0 mL HFIP was stirred at room temperature for 3 h. The desired amide **3l** (33 mg, 62%) was isolated as a white solid: Mp: 88-89 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.0 Hz, 1 H), 7.36-7.30 (m, 1 H), 7.28 (s, 1 H), 7.26-7.19 (m, 2 H), 7.16-7.11 (m, 2 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 2.36-2.31 (m, 7 H), 1.12 (s, 3 H), 1.11 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.8, 137.4, 136.4, 135.5, 135.0, 132.1, 130.6, 130.3, 129.9, 128.2, 126.6, 124.0, 121.1, 36.8, 19.8, 19.5, 19.4. HRMS (ESI) *m/z* calcd for $C_{18}H_{21}NO$ $[M+H]^+$ 268.1696; found 268.1695.

*4.2.13 N-(3',4'-dimethyl-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide **(3m)***

Following the general procedure A, a solution of 4-methyl-*N*-phenylbenzenesulfon amide (0.2 mmol, 49.4mg), dimethylbenzene (2 mmol, 240 μl), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA (0.6 mmol, 139 mg) in 1.0 mL HFIP was stirred at room temperature for 36 h. The desired amide **3m** (24 mg, 34%) was isolated as a white solid: Mp: 97-98 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2 H), 7.16-7.07 (m, 6 H), 6.97 (s, 1 H), 6.93 (d, *J* = 8.0 Hz, 1 H), 6.85 (d, *J* = 8.0 Hz, 1 H), 2.28 (s, 3 H), 2.08 (s, 3 H), 2.07 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.5, 141.9, 139.1, 137.9, 137.8, 136.4, 130.4, 130.0, 129.5, 129.2, 128.0, 127.9, 127.2, 125.9, 21.6, 19.9, 19.4. (2 peaks were overlapped); HRMS (ESI) *m/z* calcd for $C_{21}H_{21}NO_2S$ $[M+H]^+$ 352.1366; found 351.1364.

*4.2.14 N-(3',4'-Dichloro-3-methyl-[1,1'-biphenyl]-2-yl)acetamide **(3n)***

Following the general procedure A, a solution of *N*-(*o*-tolyl)acetamide (0.2 mmol, 30 mg), 1,2-dichlorobenzene (2 mmol, 294 mg), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA(0.4 mmol, 93 mg) in the 1.0 mL HFIP was stirred at room temperature for 3 h. The desired amide **3n** (16 mg, 27%) was isolated as a white solid: Mp: 171-173 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51-7.39 (m, 2H), 7.29-7.26 (m, 2H), 7.16 (dd, *J* = 15.0, 7.5 Hz, 2H), 6.57 (s, 1H), 2.30 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 139.7, 137.7, 137.2, 132.5, 132.4, 131.7, 130.9, 130.7, 130.3, 128.3, 127.8, 127.7, 23.0, 18.5. HRMS (ESI) *m/z* calcd for $C_{15}H_{14}{}^{35}Cl_2NO$ $[M+H]^+$ 294.0452; found 294.0453.

*4.2.15 2'-Acetamido-3'-methyl-[1,1'-biphenyl]-4-yl acetate **(3o)***

Following the general procedure A, a solution of *N*-(*o*-tolyl)acetamide (0.2 mmol, 30 mg), phenyl acetate (2 mmol, 272 mg), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA(0.4 mmol, 93 mg) in the 1.0 mL HFIP was stirred at room temperature for 3 h. The desired amide **3o** (15 mg, 26%) was isolated as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 6.5, 4.5 Hz, 2H), 7.28-7.24 (m, 2H), 7.18-7.14 (m, 1H), 7.13 (dd, *J* = 6.5, 4.5 Hz, 2H), 6.61 (s, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 169.4, 150.1, 138.8, 137.3, 137.0, 132.7, 130.4, 130.0, 127.9, 127.6, 121.5, 23.1, 21.2, 18.6. HRMS (ESI) *m/z* calcd for $C_{17}H_{18}NO_3$ $[M+H]^+$ 284.1287; found 284.1285.

*4.2.16 N-(4'-acetyl-3-methyl-[1,1'-biphenyl]-2-yl)acetamide **(3p)***

Following the general procedure A, a solution of *N*-(*o*-tolyl)acetamide (0.2 mmol, 30 mg), acetophenone (2 mmol, 240 mg), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA(0.4 mmol, 93 mg) in the 1.0 mL HFIP was stirred at room temperature for 3 h. The desired amide **3p** (16 mg, 30%) was isolated as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 2H), 7.52 (dt, *J* = 15.0, 7.5 Hz, 2H), 7.31-7.28 (m, 2H), 7.19 (dd, *J* = 5.5, 3.5 Hz, 1H), 6.66 (s, 1H), 2.61 (s, 3H), 2.32 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 169.2, 140.3, 139.0, 137.3, 137.1, 133.5, 132.6, 130.6, 128.8, 128.6, 127.9, 127.8, 127.2, 26.7, 23.0, 18.5. HRMS (ESI) *m/z* calcd for $C_{17}H_{18}NO_2$ $[M+H]^+$ 268.1338; found 268.1337.

*4.2.17 N-(4'-(cyclohexanecarbonyl)-3-methyl-[1,1'-biphenyl]-2-yl)acetamide **(3q)***

Following the general procedure A, a solution of *N*-(*o*-tolyl)acetamide (0.2 mmol, 30 mg), cyclohexyl(phenyl)methanone (2 mmol, 376 mg), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA(0.6 mmol, 139 mg) in the 1.0 mL HFIP was stirred at room temperature for 8 h. The desired amide **3q** (12 mg, 18%) was isolated as a yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.94-7.90 (m, 1H), 7.53-7.49 (m, 1H), 7.32-7.29 (m, 1H), 7.19 (dd, *J* = 6.0, 3.0 Hz, 1H), 6.60 (s, 1H), 3.26 (tt, *J* = 11.5, 3.0 Hz, 1H), 2.32 (s, 3H), 2.00 (s, 3H), 1.90-1.83 (m, 2H), 1.54-1.47 (m, 2H), 1.46-1.34 (m, 2H), 1.32-1.22 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 203.8, 169.3, 140.2, 139.1, 137.1, 136.6, 133.1, 130.6, 128.7, 128.0, 127.8, 127.3, 45.7, 29.5, 25.9, 25.8, 23.1, 18.6. HRMS (ESI) *m/z* calcd for $C_{22}H_{26}NO_2$ $[M+H]^+$ 336.1964; found 336.1965.

*4.2.18 N-(4'-butyl-3-methyl-[1,1'-biphenyl]-2-yl)acetamide **(3r)***

Following the general procedure A, a solution of *N*-(*o*-tolyl)acetamide (0.2 mmol, 30 mg), butylbenzene (2 mmol, 268 mg), selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), D-CSA(0.4 mmol, 93 mg) in the 1.0 mL HFIP was stirred at room temperature for 8 h. The desired amide **3r** (18.5 mg, 33%) was isolated as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26-7.19 (m, 6H), 7.16 (dd, *J* = 8.5, 4.0 Hz, 1H), 6.67 (s, 1H), 2.66-2.60 (m, 2H), 2.29 (s, 3H), 2.00 (s, 3H), 1.67-1.59 (m, 2H), 1.39 (dq, *J* = 14.5, 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 142.2, 139.4, 136.8, 136.8, 132.7, 129.9, 128.8, 128.4, 127.9, 127.4, 35.4, 33.6, 23.1, 22.5, 18.7, 14.0. HRMS (ESI) *m/z* calcd for $C_{19}H_{24}NO$ $[M+H]^+$ 282.1858; found 282.1858.

*4.2.19N-(2-(dibenzo[ghi,mno]fluoranthen-1-yl)phenyl)acetamide **(3s)***

Following the general procedure A, a solution of *N*-phenylacetamide (0.2 mmol, 27 mg), corannulene (1 mmol, 250 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), PTSA (0.4 mmol, 76 mg) in 0.5 mL HOAc and 0.5 mL mesitylene was stirred at room temperature for 12 h. The desired amide **3s** (19 mg, 25%) was isolated as a white solid: Mp: 179-181 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1 H), 7.39-7.26 (m, 3 H), 7.23-7.10 (m, 3 H), 7.01 (d, *J* = 8.0 Hz, 2 H), 3.86 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 136.8, 136.2, 135.9, 135.9, 135.8, 135.7, 135.6, 131.3, 131.1, 131.01131.1, 130.7, 130.0, 129.6, 129.1, 128.2, 127.9, 127.7, 127.6, 127.4, 127.2, 127.1, 126.9, 126.1, 124.5, 122.0, 29.7. HRMS (ESI) *m/z* calcd for $C_{28}H_{18}NO$ $[M+H]^+$ 384.1388; found 384.1390.

4.3. General Procedure B: Procedure for the alkenylation reaction

A solution of anilides, alkene, Selectfluor, $Pd(OAc)_2$, TFA or methanesulfonic acid in DCE was stirred at room temperature. After the reaction was completed, the mixture was extracted with EtOAc (10 mL x 3). The organics were dried over Na_2SO_4. Then the solvent was removed under reduced pressure to provide the crude product. The purification was performed by flash column chromatography on silica gel.

*4.3.1 (E)-butyl 3-(2-acetamidophenyl)acrylate **(5a)***

Following the general procedure B: a solution of *N*-phenylacetamide (0.2 mmol, 27 mg), butyl acrylate (0.6 mmol, 86 μl), selectfluor (0.4 mmol, 142 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), TFA (10 mmol, 740 μl) in DCE (1.0 mL) was stirred at room temperature for 30 min. The desired amide **5a** (42 mg, 80%) was isolated as a white solid: Mp: 88-89 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 16.0 Hz, 1 H), 7.69-7.67(m, 2 H) 7.53 (d, *J* = 7.5 Hz, 1 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 7.18 (t, *J* = 7.5 Hz, 1 H), 6.37 (d, *J* = 16.0 Hz, 1 H), 4.18 (t, *J* = 7.0 Hz, 2 H), 2.20 (s, 3 H), 1.70-1.59 (m, 2 H), 1.49-1.34 (m, 2 H), 0.95 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 16.0, 139.5,

136.0, 130.7, 127.8, 127.0, 125.9, 125.5, 120.4, 64.6, 30.7, 24.0, 19.2, 13.7. HRMS (ESI) *m/z* calcd for $C_{15}H_{19}NO_3$ $[M+Na]^+$ 284.1257; found 284.1260.

4.3.2 (E)-butyl 3-(2-acetamido-3-chlorophenyl)acrylate ***(5b)***

Following the general procedure B, a solution of *N*-(2-chlorophenyl)acetamide (0.2 mmol, 33.7 mg), Butyl acrylate (0.6 mmol, 86 µl), selectfluor (0.4 mmol, 142 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), TFA (10 mmol, 740 µl) in DCE (1.0 mL) was stirred at room temperature for 6 h. The desired amide **5b** (47 mg, 81%) was isolated as a white solid: Mp: 115-116 ^oC; ^1H NMR (600 MHz, $CDCl_3$): δ 7.68 (d, *J* = 16.0 Hz, 1 H), 7.55 (d, *J* = 8.0 Hz, 1 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 7.24 (t, *J* = 8.0 Hz, 1 H), 7.20 (s, 1 H), 6.41 (d, *J* = 16.0 Hz, 1 H), 4.19 (t, *J* = 7.0 Hz, 2 H), 2.26 (s, 3 H), 1.67 (m, 2 H), 1.49-1.32 (m, 2 H), 0.96 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.2, 166.7, 140.0, 134.3, 133.1, 132.1, 130.8, 128.1, 125.4, 120.7, 64.6, 30.7, 23.3, 19.2, 13.7. HRMS (ESI) *m/z* calcd for $C_{15}H_{18}{}^{35}ClNO_3$ $[M+Na]^+$ 318.0867; found 318.0869.

4.3.3 (E)-Butyl 3-(2-acetamido-3-methoxyphenyl)acrylate ***(5c)***

Following the general procedure B, a solution of *N*-(2-methoxyphenyl)acetamide (0.2 mmol, 33 mg), butyl acrylate (0.6 mmol, 86 µl), Selectfluor (0.4 mmol, 142 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), TFA (6 mmol, 446 µl) in DCE (1.0 mL) was stirred at room temperature for 4 h. The desired amide **5c** (44 mg, 76%) was isolated as a white solid: Mp: 95-96 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 16.0 Hz, 1 H), 7.42-7.05 (m, 3 H), 6.90 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.17 (t, *J* = 8.0 Hz, 2 H), 3.81 (s, 3 H), 2.21 (s, 3 H), 1.70-1.63 (m, 2 H), 1.47-1.37 (m, 2 H), 0.95 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 167.1, 153.9, 140.9, 132.5, 127.4, 125.2, 119.3, 118.5, 112.1, 64.4, 55.8, 30.7, 23.4, 19.2, 13.8. HRMS (ESI) *m/z* calcd for $C_{17}H_{23}NO_4$ $[M+H]^+$ 292.1543; found 292.1541.

4.3.4 (E)-Butyl 3-(2-acetamido-5-chlorophenyl)acrylate ***(5d)***

Following the general procedure B, a solution of *N*-(4-chlorophenyl)acetamide (0.2 mmol, 33.7 mg), butyl acrylate (0.6 mmol, 86 µl), selectfluor (0.4 mmol, 142 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), TFA (10 mmol, 740 µl) in DCE (1.0 mL) was stirred at room temperature for 4 h. The desired amide **5d** (38 mg, 64%) was isolated as a white solid: Mp: 135-137 ^oC; ^1H NMR (600 MHz, $CDCl_3$): δ 7.76 (s, 1 H), 7.70 (d, *J* = 16.0 Hz, 1 H), 7.63 (d, *J* = 8.5 Hz, 1 H), 7.48 (s, 1 H), 7.28 (d, *J* = 8.5 Hz, 1 H), 6.35 (d, *J* = 16.0 Hz, 1 H), 4.18 (t, *J* = 7.0 Hz, 2 H), 2.20 (s, 3 H), 1.80-1.63 (m, 2 H), 1.52-1.32 (m, 2 H), 0.95 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.2, 166.6, 138.1, 134.4, 131.3, 130.5, 129.2, 126.7, 126.7, 121.6, 64.8, 30.7, 24.0, 19.2, 13.7. HRMS (ESI) *m/z* calcd for $C_{15}H_{18}{}^{35}ClNO_3$ $[M+Na]^+$ 318.0867; found 318.0869.

4.3.5 (E)-Butyl 3-(2-acetamido-5-methoxyphenyl)acrylate ***(5e)***

Following the general procedure B, a solution of *N*-(4-methoxyphenyl)acetamide (0.2 mmol, 33 mg), butyl acrylate (0.6 mmol, 86 µl), selectfluor (0.4 mmol, 142 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), TFA (6 mmol, 446µl) in DCE (1.0 mL) was stirred at room temperature for 50 min. The desired amide **5e** (45 mg, 78%) was isolated as a white solid: Mp: 130-131 ^oC; ^1H NMR (600 MHz, $CDCl_3$): δ 7.78 (s, 1 H), 7.73 (d, *J* = 16.0 Hz, 1 H), 7.37 (d, *J* = 8.5 Hz, 1 H), 7.01 (d, *J* = 3.0 Hz, 1H), 6.87 (dd, *J* = 8.5, 3.0 Hz, 1 H), 6.32 (d, *J* = 16.0 Hz, 1 H), 4.16 (t, *J* = 7.0 Hz, 2 H), 3.79 (s, 3 H), 2.15 (s, 3 H), 1.76-1.53 (m, 2 H), 1.47-1.32 (m, 2 H), 0.95 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.6, 166.9, 157.6, 139.6, 130.2, 129.2, 127.9, 120.0, 116.8, 111.0, 64.6, 55.5, 30.7, 23.6, 19.2, 13.7. HRMS (ESI) *m/z* calcd for $C_{16}H_{21}NO_4[M+H]^+$ 292.1543; found 292.1541.

4.3.6 (E)-Butyl 3-(2-acetamido-5-nitrophenyl)acrylate ***(5f)***

Following the general procedure B, a solution of *N*-(4-nitrophenyl)acetamide (0.2 mmol, 36 mg), butyl acrylate (0.6 mmol, 86 µl), selectfluor (0.4 mmol, 142 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), TFA (10 mmol, 740 µl) in DCE (1.0 mL) was stirred at room temperature for 6 h. The desired amide **5f** (31 mg, 51%) was isolated as a white solid: Mp:157-159 ^oC; ^1H NMR (600 MHz, $CDCl_3$): δ 8.38 (d, *J* = 2.0 Hz, 1 H), 8.31 (d, *J* = 8.0 Hz, 1 H), 8.21 (dd, *J* = 8.0, 2.5 Hz, 1 H), 7.89 (s, 1 H), 7.81 (d, *J* = 16.0 Hz, 1 H), 6.53 (d, *J* = 16.0 Hz, 1 H), 4.22 (t, *J* = 7.0 Hz, 2 H), 2.29 (s, 3 H), 1.77-1.57 (m, 2 H), 1.56-1.31 (m, 2 H), 0.97 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6, 166.2, 144.1, 141.3, 136.7, 125.5, 124.3, 123.0, 122.8, 122.8, 65.2, 30.7, 24.6, 19.1, 13.6. HRMS (ESI) *m/z* calcd for $C_{15}H_{18}N_2O_5$ $[M+Na]^+$ 329.1108; found 329.1106.

4.3.7 (E)-Butyl 3-(1-acetyl-1,2,3,4-tetra-hydroquinolin-8-yl)acrylate ***(5g)***

Following the general procedure B, a solution of 1-(3, 4-dihydroquinolin-1(2H)-yl)ethanone (0.2 mmol, 35 mg), butyl acrylate (0.6 mmol, 86 µl), selectfluor (0.3 mmol, 106 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), MsOH (0.4 mmol, 26 µl) in DCE (1.0 mL) was stirred at room temperature for 16 h. The desired amide **5g** (29 mg, 48%) was isolated as a brown oil; ^1H NMR (600 MHz, $CDCl_3$): δ 7.69 (d, *J* = 16.0 Hz, 1 H), 7.56-7.51 (m, 1 H), 7.24 (d, *J* = 4.6 Hz, 2 H), 6.49 (d, *J* = 16.0 Hz, 1 H), 4.83-4.79 (m, 1 H), 4.21 (t, *J* = 7.0 Hz, 2 H), 2.96-2.91 (m, 1 H), 2.75-2.71 (m, 1 H), 2.55-2.49 (m, 1 H), 2.32-2.23 (m, 1 H), 1.96-1.94 (m, 1 H), 1.82 (s, 3 H), 1.71-1.68 (m, 2 H), 1.49-1.32 (m, 2 H), 0.96 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.9, 166.6, 140.3, 139.7, 137.5, 130.4, 129.5, 126.7, 125.0, 120.2, 64.6, 42.0, 30.7, 26.5, 23.8, 22.2, 19.2, 13.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{23}NO_3$ $[M+H]^+$ 302.1751; found 302.1753.

4.3.8 (E)-Butyl 3-(2-pivalamidophenyl)acrylate ***(5h)***

Following the general procedure B, a solution of *N*-phenylpivalamide (0.2 mmol, 35.4 mg), butyl acrylate (0.6 mmol, 86 µl), selectfluor (0.4 mmol, 142 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), TFA (6 mmol, 446 µl) in DCE (1.0 mL) was stirred at 60 ^oC for 30 min. The desired amide **5h** (47 mg, 77%) was isolated as a white solid: Mp: 99-101 ^oC; ^1H NMR (600 MHz, $CDCl_3$): δ 7.71 (d, *J* = 16.0 Hz, 1 H), 7.61 (s, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 7.36-7.30 (m, 1 H), 7.18 (t, *J* = 7.5 Hz, 1 H), 6.34 (d, *J* = 16.0 Hz, 1 H), 4.15 (t, *J* = 7.0 Hz, 2 H), 1.65 (m, 2 H), 1.41 (m, 2 H), 1.34 (s, 9 H), 0.95 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 177.2, 166.7, 139.3, 136.1, 130.6, 128.6, 127.0, 126.0, 125.7, 120.4, 64.5, 39.6, 30.7, 27.6, 19.2, 13.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{25}NO_3$ $[M+H]^+$ 304.1911; found 304.1910.

4.3.9 (E)-Butyl 3-(2-isobutyramidophenyl)acrylate ***(5i)***

Following the general procedure B, a solution of *N*-phenylisobutyramide (0.2 mmol, 32.6 mg), butyl acrylate (0.6 mmol, 86 µl), selectfluor (0.4 mmol, 142 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), TFA (6 mmol, 446 µl) in DCE (1.0 mL) was stirred at room temperature for 5 h. The desired amide **5i** (49 mg, 85%) was isolated as a white solid: Mp: 93-94 ^oC; ^1H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 16.0 Hz, 1 H), 7.69-7.57 (m, 2 H), 7.52 (d, *J* = 7.0 Hz, 1 H), 7.34 (t, *J* = 7.0 Hz, 1 H), 7.17 (s, 1 H), 6.35 (d, J = 16.0 Hz, 1 H), 4.16 (t, *J* = 7.0 Hz, 2 H), 2.60-2.58 (m, 1 H), 1.67-1.63 (m, 2 H), 1.403-1.38 (m, 2H), 1.26 (d, *J* = 7.0 Hz,

6 H), 0.94 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 175.9, 166.8, 139.4, 136.0, 130.6, 128.2, 127.0, 125.9, 125.5, 120.3, 64.6, 36.2, 30.7, 19.6, 19.2, 13.7. HRMS (ESI) *m/z* calcd for $C_{17}H_{23}NO_3$ $[M+Na]^+$ 312.1570; found 312.1571.

4.3.10 (E)-Butyl 3-(2-benzamidophenyl)acrylate ***(5j)***

Following the general procedure B, a solution of *N*-phenylbenzamide (0.2 mmol, 39.4 mg), butyl acrylate (0.6 mmol, 86 μl), selectfluor (0.4 mmol, 142 mg), $Pd(OAc)_2$ (10 mol%, 4.5mg), MsOH (0.4 mmol, 26 μl) in DCE (1.0 mL) was stirred at room temperature for 4 h. The desired amide **5j** (59 mg, 91%) was isolated as a white solid: Mp：142-143 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.16 (s, 1 H), 7.89 (d, *J* = 16.0 Hz, 2 H), 7.85 (d, *J* = 7.5 Hz, 1 H), 7.79 (d, *J* = 7.5 Hz, 1 H), 7.57 (d, *J* = 7.5 Hz, 1 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 2 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.23 (t, *J* = 7.5 Hz, 1 H), 6.39 (d, *J* = 16.0 Hz, 1 H), 4.13 (t, *J* = 7.0 Hz, 2 H), 1.69 -1.50 (m, 2 H), 1.46 -1.28 (m, 2 H), 0.91 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 166.8, 166.2, 139.4, 136.0, 134.2, 132.1, 130.8, 128.8, 128.3, 127.3, 127.2, 126.1, 125.5, 120.7, 64.6, 30.7, 19.2, 13.7. HRMS (ESI) *m/z* calcd for $C_{20}H_{21}NO_3$ $[M+H]^+$ 324.1594; found 324.1592.

4.3.11 Butyl (E)-butyl 3-(2-(4-methylphenylsulfonamido) phenyl)acrylate ***(5k)***

Following the general procedure B, a solution of 4-methyl-N-phenylbenzene sulfonamide (0.2 mmol, 49.4 mg), butyl acrylate (0.6 mmol, 86 μl), selectfluor (0.4 mmol, 142 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), TFA (10 mmol, 740 μl) in DCE (1.0 mL) was stirred at room temperature for 10 h. The desired amide **5k** (37 mg, 49%) was isolated as a white solid: Mp: 82-83 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.36 (d, *J* = 16.0 Hz, 1 H), 7.56 (d, *J* = 8.0 Hz, 2 H), 7.43-7.39 (m, 1 H), 7.40-7.35 (m, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 7.04-6.62 (m, 2 H), 4.62 (d, *J* = 16.0 Hz, 1 H), 4.08 (t, *J* = 7.0 Hz, 2 H), 2.44 (s, 3 H), 1.60-1.58 (m, 2 H), 1.38-1.34 (m, 2 H), 0.92 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 167.2, 144.9, 143.9, 135.1, 134.8, 129.88, 129.85, 129.82, 129.7, 127.8, 100.0, 64.0, 30.8, 21.7, 19.2, 13.7. (2 peaks were overlapped). HRMS (ESI) *m/z* calcd for $C_{20}H_{23}NO_4S$ $[M+Na]^+$ 392.1240; found 392.1238.

4.3.12 (E)-3-(2-Acetamidophenyl)-N, N-dimethylacrylamide ***(5l)***

Following the general procedure B, a solution of *N*-phenylacetamide (0.2 mmol, 27 mg), *N, N*-dimethylacrylamide (0.6 mmol, 62 μl), Selectfluor (0.4 mmol, 142 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), TFA (10 mmol, 740 μl) in DCE (1.0 mL) was stirred at room temperature for 11 h. The desired amide **5l** (33 mg, 71%) was isolated as a white solid: Mp: 134-135 °C; ^{1}H NMR (400 MHz, DMSO) δ 9.79 (s, 1 H), 7.84 (d, *J* = 16.0 Hz, 1 H), 7.62 (d, *J* = 8.0 Hz, 1 H), 7.36 (m, 2 H), 7.23 (t, *J* = 8.0 Hz, 1 H), 7.11 (d, *J* = 16.0 Hz, 1 H), 3.15 (s, 3 H), 2.93 (s, 3 H), 2.07 (s, 3 H). ^{13}C NMR (101 MHz, DMSO) δ 169.3, 166.2, 137.14, 137.05, 130.4, 130.0, 127.24, 127.18, 126.1, 120.0, 37.4, 35.8, 23.6. HRMS (ESI) *m/z* calcd for $C_{13}H_{16}N_2O_2$ $[M+H]^+$ 255.1104; found 255.1103.

4.3.13 (E)-3-(2-acetamido-3-methylphenyl)acrylic acid ***(5m)***

Following the general procedure B, *N*-(*o*-tolyl)acetamide (0.2 mmol, 30 mg), acrylic acid (0.6 mmol, 72 mg), Selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), TFA (10 mmol, 740 μl) in DCE (1.0 mL) was stirred at room temperature for 3 h. The desired amide **5m** (15 mg, 35%) was isolated as a white solid: Mp: 257-259 °C; ^{1}H NMR (600 MHz, DMSO) δ 12.41 (s, 1H), 9.55 (s, 1H), 7.67-7.60 (m, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 2.15 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 168.8, 167.7, 140.3, 136.3, 135.9, 132.0, 131.7, 127.0, 124.2, 120.0, 22.5, 18.0. HRMS (ESI) *m/z* calcd for $C_{12}H_{14}NO_3$ $[M+H]^+$ 220.0974; found 220.0975.

4.3.14 (E)-Methyl 3-(2-acetamido-3-methylphenyl)acrylate ***(5n)***

Following the general procedure B, *N*-(*o*-tolyl)acetamide (0.2 mmol, 30 mg), methyl acrylate (0.6 mmol, 52 mg), Selectfluor (0.6 mmol, 212 mg), $Pd(OAc)_2$ (10 mol%, 4.5 mg), TFA (10 mmol, 740 μl) in DCE (1.0 mL) was stirred at room temperature for 8 h. The desired amide **5n** (45.9 mg, 90%) was isolated as a white solid; The compound exists as a 70:30 mixture of amide rotamers. Signals corresponding to the major rotamer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 16.0 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.29-7.19 (m, 2H), 6.98 (s, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 2.25 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 167.3, 140.7, 136.7, 134.4, 132.5, 132.3, 127.8, 124.6, 119.7, 51.7, 23.2, 18.3. Representative signals corresponding to the minor rotamer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 16.0 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.34-7.30 (m, 2H), 6.92 (s, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 3.80 (d, *J* = 4.6 Hz, 3H), 2.31 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 167.3, 139.7 , 132.7, 128.6, 125.2, 121.0, 51.7, 23.3, 20.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{15}NO_3Na$ $[M+Na]^+$ 256.0950; found 256.0948.

4.4. General Procedure C: Procedure for the decarboxylative acylation recations

A solution of anilides (0.2 mmol), α-oxocarboxylic acids (1 mmol), selectfluor (0.6 mmol), $Pd(OAc)_2$ (10 mol%) in DCM (1.0 mL) was stirred at 70 °C. After the reaction was completed, the mixture was extracted with EtOAc (10 mL x 3). The organic phase was dried over Na_2SO_4. Then the solvent was removed under reduced pressure to provide the crude product. The purification was performed by flash column chromatography on silica gel.

4.4.1 N-(2-Benzoylphenyl)acetamide ***(7a)***

Following the general procedure C, the reaction was stirred at 70 °C for 4.5 h. The desired amide **7a** (39 mg, 81%) was isolated as a white solid: Mp: 125-127 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.81 (s, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.62-7.58 (m, 1H), 7.58-7.54 (m, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.0, 169.2, 140.5, 138.7, 134.3, 133.6, 132.5, 129.9, 128.4, 123.3, 122.1, 121.5, 25.3. HRMS (ESI) *m/z* calcd for $C_{15}H_{13}NO_2$ $[M+Na]^+$ 262.0839; found 262.0840.

4.4.2 N-(2-Benzoyl-4-methoxyphenyl)acetamide ***(7b)***

Following the general procedure C, the reaction was stirred at 70 °C for 16 h. *N*-(2-Benzoyl-4-methoxyphenyl)acetamide **7b** (36 mg, 67%) was isolated as a white solid: Mp: 129-131 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.30 (s, 1 H), 8.47 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.13 (dd, *J* = 8.0, 3.0 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 3.74 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.0, 168.9, 154.2, 138.3, 133.4, 132.7, 130.0, 128.4, 125.2, 123.5, 119.3, 118.2, 55.7, 25.0. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}NO_3$ $[M+Na]^+$ 292.0944; found 292.0944.

4.4.3 N-(2-Benzoyl-4-chlorophenyl)acetamide ***(7c)***

Following the general procedure C, the reaction was stirred at 70 °C for 48 h. The desired amide **7c** (43 mg, 78%) was isolated as a white solid: Mp: 115-117 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.61 (d, *J* = 8.5 Hz, 1H), 7.73-7.68 (m, 2H), 7.66-7.61 (m, 1H), 7.55-7.48 (m, 4H), 2.22 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.4, 169.1, 138.9, 137.9, 133.9, 133.0, 132.6,

129.9, 128.6, 127.3, 124.6, 123.1, 25.2. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}{}^{35}ClNO_2$ $[M+Na]^+$ 296.0449; found 296.0448.

4.4.4 N-(2-(4-Chlorobenzoyl)phenyl)acetamide ***(7d)***

Following the general procedure C, the reaction was stirred at 70 °C for 12 h. The desired amide **7d** (38 mg, 70%) was isolated as a white solid: Mp: 125-127 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.69 (s, 1 H), 8.61 (d, *J* = 8.0 Hz, 1 H), 7.65 (d, *J* = 8.5 Hz, 2 H), 7.60-7.55 (m, 1 H), 7.50 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2 H), 7.12-7.07 (m, 1 H), 2.22 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.3, 169.2, 140.5, 139.0, 136.9, 134.5, 133.1, 131.3, 128.7, 123.1, 122.2, 121.7, 25.2. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}{}^{35}ClNO_2$ $[M+Na]^+$ 296.0449; found 296.0449.

4.4.5 N-(2-(4-Methoxybenzoyl)phenyl)acetamide ***(7e)***

Following the general procedure C, the reaction was stirred at 70 °C for 16 h. The desired amide **7e** (25 mg, 47%) was isolated as a white solid: Mp: 119-121 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.52 (s, 1 H), 8.56 (d, *J* = 8.5 Hz, 1 H), 7.74 (d, *J* =8.5, 2 H), 7.55 (m, 2 H), 7.12-7.06 (m, 1 H), 6.97 (d, *J* =8.5, 2 H), 3.89 (s, 3 H), 2.20 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 169.0, 163.5, 139.9, 133.5, 132.7, 132.6, 131.0, 124.29, 122.1, 121.7, 113.7, 55.5, 25.2. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}NO_3$ $[M+Na]^+$ 292.0944; found 292.0944.

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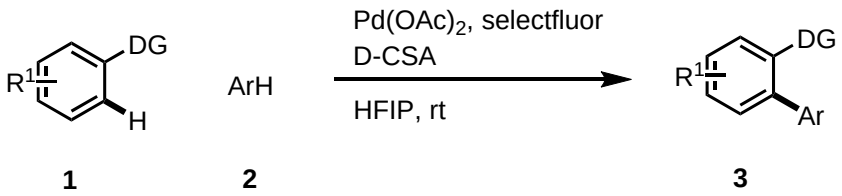
References and notes

1. For selected reviews see: (a) Jana, R.; Pathak, T. P.; Sigman, M. S. *Chem. Rev.*, **2011**, *111*, 1417-1492; (b) Johansson Seechurn C. C.; Kitching M. O.; Colacot T. J.; Snieckus V. *Angew. Chem. Int. Ed.*, **2012**, *51*, 5062-5085.
2. For selected examples, see: (a) Stuart, D. R.; Fagnou, K. *Science*, **2007**, *316*, 1172-1175; (b) Stuart, D. R.; Villemure, E.; Fagnou, K. *J. Am. Chem. Soc.*, **2007**, *129*, 12072-12073; (c) Neufeldt, S. R.; Sanford, M. S. *Acc. Chem. Res.*, **2012**, *45*, 936-946.
3. For selected reviews see: (a) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem. Int. Ed.*, **2009**, *48*, 5094-5115; (b) Ackermann, L. *Acc. Chem. Res.*, **2014**, *47*, 281-295; (c) Yu, J.-Q.; Shi, Z.-J. *Top. Curr. Chem.*, **2010**, *292*, 57-84; **2010**, *292*, 165-194.
4. (a) Sehnal, P.; Taylor, R. J. K.; Fairlamb, I. J. S. *Chem. Rev.*, **2010**, *110*, 824-889; (b) Lyons, T. W.; Sanford, M. S. *Chem. Rev.*, **2010**, *110*, 1147-1169; (c) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.*, **2010**, *39*, 712-733. (d) Topczewski, J. J.; Sanford, M. S. *Chem. Sci.*, **2015**, *6*, 70-76.
5. (a) Uson, R.; Fornies, J.; Navarro, R. *J. Organometallic Chem.*, **1975**, *96*, 307-312; (b) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.*, **1986**, 1722-1724; (c) Dick, A. R.; K. Hull, L.; Sanford, M. S. *J. Am. Chem. Soc.*, **2004**, *126*, 2300-2301; (d) Alexanian, E. J.; Lee, C.; Sorensen, E. J. *J. Am. Chem. Soc.*, **2005**, *127*, 7690-7691; (e) Powers, D. C.; Geibel, M. A. L.; Klein, J. E. M. N.; Ritter, T. *J. Am. Chem. Soc.*, **2009**, *131*, 17050-17051.
6. (a) Yu, Q.; Zhang, N.; Huang, J.; Lu, S.; Zhu, Y.; Yu, X.; Zhao, K. *Chem. Eur. J.*, **2013**, *19*, 11184-11188; (b) Liu, W.; Yu, Q.; Hu, L.; Chen, Z.; Huang, J. *Chem. Sci.*, **2015**, *6*, 5768-5772.
7. (a) Yahav-Levi, A.; Goldberg, I.; Vigalok, A. *J. Am. Chem. Soc.*, **2003**, *125*, 13634-13635; *(b) Yahav-Levi, A.; Goldberg, I.; Vigalok, A. J. Am. Chem. Soc.*, **2006**, *128*, *8710-8711;* (c) Kaspi, A. W.; Yahav-Levi, A.; Goldberg, I.; Vigalok, A. *Inorganic Chemistry*, **2008**, *47*, 5-7.
8. (a) Hull, K. L.; Anani, W. Q.; Sanford, M. S. *J. Am. Chem. Soc.*, **2006**, *128*, 7134-7135; (b) Hull, K. L.; Lanni, E. L.; Sanford, M. S. *J. Am. Chem. Soc.*, **2006**, *128*, 14047-14049; (c) Ball, N. D.; Sanford, M. S. *J. Am. Chem. Soc.*, **2009**, *131*, 3796-3797; (d) Racowski, J. M.; Gary, J. B.; Sanford, M. S. *Angew. Chem.Int. Ed.*, **2012**, *124*, 3470-3479.
9. (a) Furuya, T.; Ritter, T. *J. Am. Chem. Soc.*, **2008**, *130*, 10060-10061; (b) Furuya, T.; Kaiser, H. M.; Ritter, T. *Angew. Chem. Int. Ed.*, **2008**, *47*, 5993-5996.
10. (a) Engle, K. M.; Mei, T.; Wang, X.; Yu, J.-Q. *Angew. Chem. Int. Ed.*, **2011**, *50*, 1478-1491; (b) Wang, X.; Mei, T.; Yu, J.-Q. *J. Am. Chem. Soc.*, **2009**, *131*, 7520-7521; (c) Mei, T.; Wang, X; Yu, J.-Q. *J. Am. Chem. Soc.*, **2009**, *131*, 10806-10807; (d) Wang, X.; Lu, Y.; Dai, H.; Yu, J.-Q. *J. Am. Chem. Soc.*, **2010**, *132*, 12203-12205.
11. Rosewall, C. F.; Sibbald, P. A.; Liskin, D. V.; Michael, F. E. *J. Am. Chem. Soc.*, **2009**, *131*, 9488-9489.
12. For transition metal-mediated *ortho*-directed C-H activations, see: (a) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.*, **2010**, *110*, 624-655; (b) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. *Chem. Rev.*, **2012**, *112*, 5879-5918; (c) Li, B.-J.; Shi, Z.-J. *Chem. Soc. Rev.*, **2012**, *41*, 5588-5598; (d) Yu, D.-G.; Suri, M.; Glorius, F. *J. Am. Chem. Soc.*, **2013**, *135*, 8802-8805; (e) Cheng, X.-F.; Li, Y.; Su, Y.-M.; Yin, F.; Wang, J.-Y.; Sheng, J.; Vora, H. U.; Wang, X.-S.; Yu, J.-Q. *J. Am. Chem. Soc.*, **2013**, *135*, 1236-1239; (f) Hesp, K. D.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.*, **2011**, *133*, 11430-11433; (g) Wang, H.; Schrçder, N.; Glorius, F. *Angew. Chem., Int. Ed.*, **2013**, *52*, 5386-5389; (h) Tsai, A. S.; Tauchert, M. E.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.*, **2011**, *133*, 1248-1250; (i) Basl, O.; Bidange, J.; Shuai, Q.; Li, C.-J. *Adv. Synth. Catal.*, **2010**, *352*, 1145-1149; (j) Yang, Y.; Zhou, B.; Li, Y. *Adv. Synth. Catal.*, **2012**, *354*, 2916-2920; (k) Li, C.; Wang, L.; Li, P.; Zhou, W. *Chem. Eur. J.*, **2011**, *17*, 10208-10212; (l) Park, J.; Park, E.; Kim, A.; Lee, Y.; Chi, K.-W.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Org. Lett.*, **2011**, *13*, 4390-4393; (m) Li, M.; Ge, H. *Org. Lett.*, **2010**, *12*, 3464-3467; (n) Kim, M.; Park, J.; Sharma, S.; Kim, A.; Park, E.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Chem. Commun.*, **2013**, *49*, 925-927; (o) Wang, H.; Guo, L.-N.; Duan, X.-H. *Org. Lett.*, **2012**, *14*, 4358-4361; (p) Park, J.; Kim, M.; Sharma, S.; Park, E.; Kim, A.; Lee, S. H.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Chem. Commun.*, **2013**, *49*, 1654-1656; (q) Guin, S.; Rout, S. K.; Banerjee, A.; Nandi, S.; Patel, B. K. *Org. Lett.*, **2012**, *14*, 5294-5297. (r) Lou, S.-J.; Mao, Y.-J.; Xu, D.-Q.; He, J.-Q.; Chen, Q.; Xu, Z.-Y. *ACS catalysis*, **2016**, *6*, 3890-3894.
13. (a) Brasche, G.; Garcia-Fortanet, J.; Buchwald, S. L. *Org. Lett.*, **2008**, *10*, 2207-2210; (b) Daugulis, O.; Zaitsev, V. G. *Angew. Chem. Int. Ed.*, **2005**, *44*, 4046-4048; (c) Lazareva, A.; Daugulis, O. *Org. Lett.*, **2006**, *8*, 5211-5213; (d) Yeung, C. S.; Zhao, X.; Borduas, N.; Dong, V. M. *Chem. Sci.*, **2010**, *1*, 331-336; (e) Wan, C.; Zhao, J.; Xu, M.; Huang, J. *J. Org. Chem.*, **2014**, *79*, 4751-4756; (f) Li, B.; Tian, S.; Fang, Z.; Shi, Z. -J. *Angew. Chem. Int. Ed.*, **2008**, *47*, 1115-1118; (g) Yang, S.; Li, B.; Wan, X.; Shi, Z. -J. *J. Am. Chem. Soc.*, **2007**, *129*, 6066-6067; (h) Li, D.; Xu, N.; Zhang, Y.; Wang, L. *Chem. Commun.*, **2014**, *50*, 14862-14865.
14. Yang, F.; Song, F.; Li, W.; Lan, J.; You, J. *RSC Adv.*, **2013**, *3*, 9649-9652.
15. (a) Bedford, R. B.; Haddow, M. F.; Mitchell C. J.; Webster, R. L. *Angew. Chem. Int. Ed.*, **2011**, *50*, 5524-5527; (b) Houlden, C. E.; Hutchby, M.; Bailey, C. D.; Gair Ford, J.; Tyler, S. N. G.; Gagne, M. R.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. *Angew. Chem. Int. Ed.*, **2009**, *48*, 1830-1833; (c) Houlden, C. E.; Bailey, C. D.; Gair Ford, J.; Gagne, M. R.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. *J. Am. Chem. Soc.*, **2008**, *130*, 10066-10067; (d) Rauf, W.; Thompson, A. L.; Brown, J. M. *Dalton Trans.*, **2010**, *39*, 10414-10421; (e) Wang, L.; Liu, S.; Li, Z.; Yu, Y. *Org. Lett.*, **2011**, *13*, 6137-6139; (f) Xu, Y.; Yan, G.; Ren, Z.; Dong, G. *Nat. Chem.*, **2015**, *7*, 829-834.
16. Huang, J.; Lu S.; Zhu, R.; Zhu, D. CN. Patent 104557589 A, 2015.
17. (a) Liu, X.; Hii, K. K. *J. Org. Chem.*, **2011**, *76*, 8022-8026; (b) Boele, M. D. K.; van Strijdonck, G. P. F.; de Vries, A. H. M.; Kamer, P. C. J.; de Vries, J. G.; van Leeuwen, P. W. N. M. *J. Am. Chem. Soc.*, **2002**, *124*, 1586-1587; (c) Schmidt, B.; Elizarov, N. *Chem. Commun.*, **2012**, *48*, 4350-4352; (d) Chng, L. L.; Zhang, J.; Yang, J.; Amoura, M.; Ying, J. Y. *Adv. Synth. Catal.*, **2011**, *353*, 2988-2998.
18. (a) Fang, P.; Li, M.; Ge, H. *J. Am. Chem. Soc.*, **2010**, *132*, 11898-11899; (b) Wu, Y.; Choy, P. Y.; Mao, F.; Kwong, F. Y. *Chem. Commun.*, **2013**, *49*, 689-691; (c) Wu, Y.; Li, B.; Mao, F.; Li, X.; Kwong, F. Y. *Org. Lett.*, **2011**, *12*, 3258-3261; (d) Szabo, F.; Simko, D.; Novak, Z. *RSC Adv.*, **2014**, *4*, 3883-3886; (e) Yin, Z.; Sun, P. *J. Org. Chem.*, **2012**, *77*, 11339-11344; (f) Li, C.; Wang, L.; Li, P.; Zhou, W. *Chem. Eur. J.*, **2011**, *17*, 10208-10212; (g)

Chan, C.; Zhou, Z.; Yua, W. *Adv. Synth. Catal.*, **2011**, *353*, 2999-3006; (h) Luo, F.; Yang, J.; Li, Z.; Xiang, H.; Zhou, X. *Eur. J. Org. Chem.*, 2015, 2463-2469. (i) Li, Q.; Li, Z.; Wang, G.-W. *ACS Omega*, **2018**, *3*, 4187-4198; (j) Kim, B. S.; Jang, C.; Lee, D.; Youn, S. W. *Chem. Asian J.*, **2010**, *5*, 2336-2340; (k) Rauf, W.; Thompson, A. L.; Brown, J. M. *Chem. Comm.*, **2009**, 3874-3876; (l) Lee, G. T.; Jiang, X.; Prasad, K.; Repič, O.; Blacklock, T. J. *Adv. Syn. Catal.*, **2005**, *347*, 1921-1924.

Supplementary Material

Supplementary material that may be helpful in the review process should be prepared and provided as a separate electronic file. That file can then be transformed into PDF format and submitted along with the manuscript and graphic files to the appropriate editorial office.



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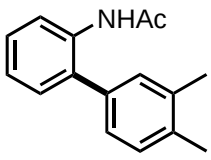

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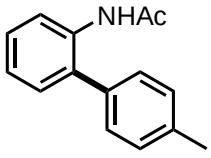

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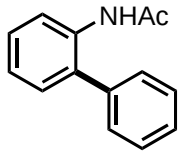

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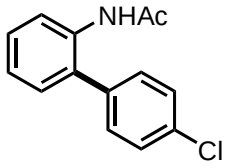

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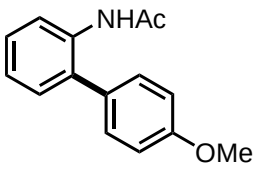

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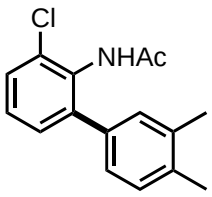

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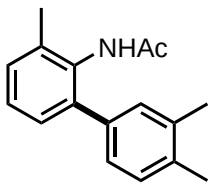

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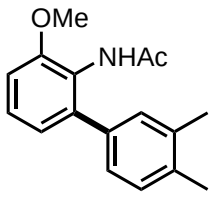

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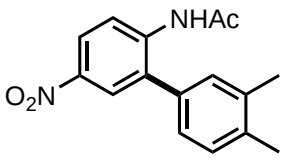

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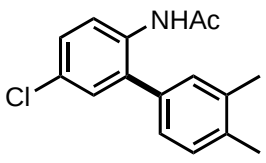

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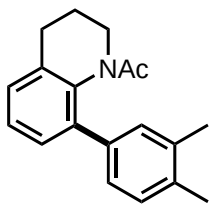

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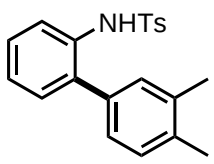
3l (62%[c])



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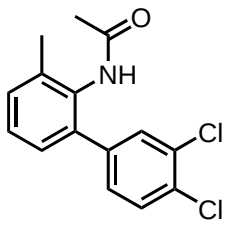

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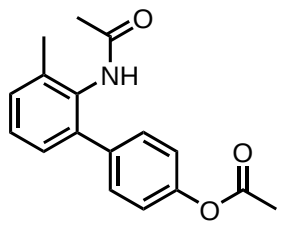

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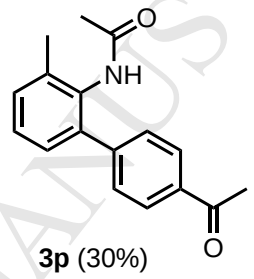

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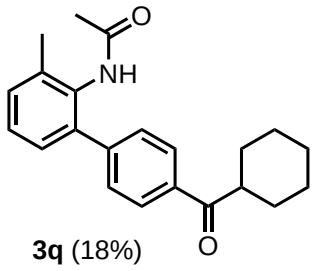

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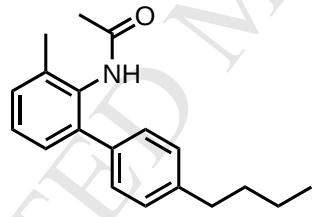

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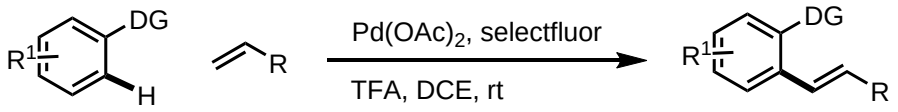

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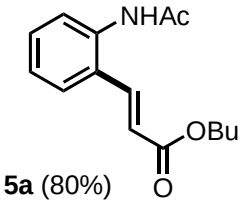

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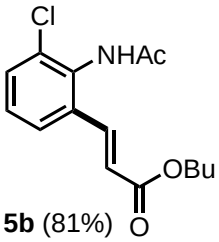

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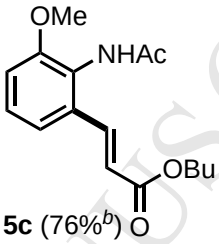

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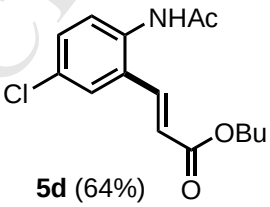

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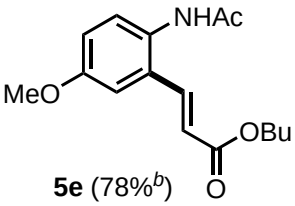

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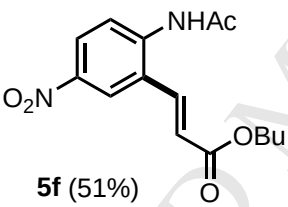

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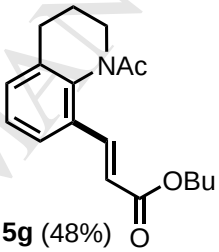

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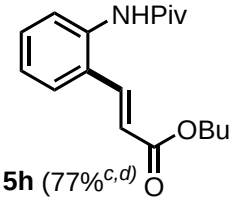

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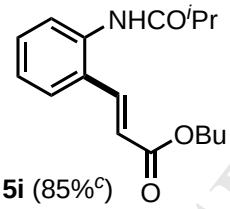

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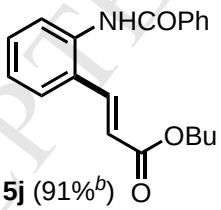

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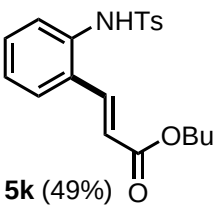

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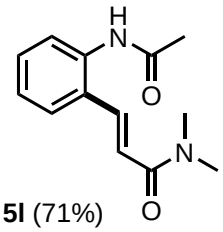

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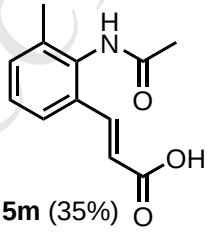

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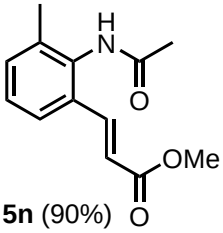

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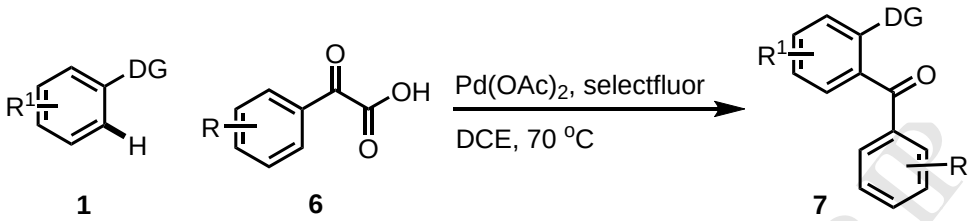

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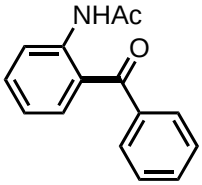

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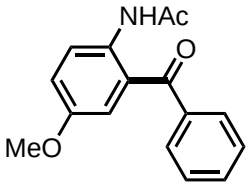

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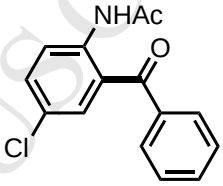

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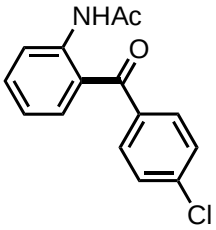

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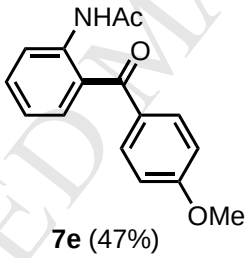

7e (47%)