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Palladium-Catalyzed Ligand-Controlled Regio-selective Nucleophilic Aromatic Substitution of 1-(Chloromethyl)naphthalenes with Arylacetonitriles

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ABSTRACT: The palladium-catalyzed reaction of 1-(chloromethyl)naphthalenes **1** with (hetero)arylacetonitriles **2** gives either *para*- or *ortho*-acylated naphthalenes (**3** or **4**) in good to high yields. The regioselectivity can be controlled by the ligand of palladium catalyst. A sterically bulky ligand, ^{t}BuPPh$_2$, affords *para*-acylated products **3**, whereas a sterically less bulky ligand, Me$_2$PPh, provides *ortho*-acylated products **4**. Further, direct substitution product **5** at benzylic position is not obtained essentially, although such a reaction at benzylic position is favorable in ordinary nucleophilic substitutions. In this paper, it was revealed that the

benzylpalladium intermediate could react through different mode (η^3-benzylpalladium intermediate or η^1-benzylpalladium intermediate) in nucleophilic aromatic substitution. In addition to interesting mechanistic aspect, the present reaction provides a facile synthetic method for a wide range of diaryl ketones, some of which are not easily available through the previously known procedures.

KEYWORDS: Ligand-control, Regio-selective, Nucleophilic substitution, Palladium catalysis, Diaryl ketones

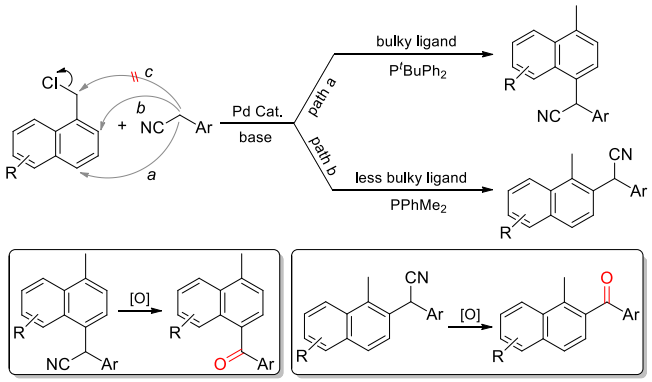
INTRODUCTION

Aromatic rings are important structural frameworks frequently found in various bioactive molecules, organic materials, and pharmaceuticals.[1] Therefore, numerous methods for the functionalization of aromatic rings have been reported over the past decades.[2] Among these methods, electrophilic substitution reaction of arenes, namely the Friedel-Crafts reaction, is well known and frequently used as a standard and important approach. The transition-metal-catalyzed direct functionalization of aromatic C–H bonds has recently emerged as a powerful tool for the synthesis of aromatic ring-containing complex organic molecules.[3] In comparison with Rh,[4] Ru,[5] Ir,[6] Co,[7] and Cu[8] catalysts, Pd catalysts are specifically widely used for the functionalization mainly due to the following reasons: many Pd(II) catalysts are compatible with oxidants and the directed C–H bond functionalization reactions usually can be performed in the presence of ambient air and moisture.[9] In comparison with the above-mentioned two methods, the nucleophilic substitution reaction is rarely reported; this method required a leaving group linked on aromatic ring[10] or a metal atom coordinated to aromatic π-system.[11] Palladium-catalyzed aromatic substitution via η^3-benzylpalladium intermediate is recently reported by Tunge,[12]

Kuwano,[13] and our group[14] as a novel complement to the method of nucleophilic substitution reaction. Tunge and co-worker succeeded in the control of product generation (dearomatized alicyclic ketones or α-monoarylated ketones) by using different palladium catalyst and ligand. Kuwano and co-workers successfully proved that intramolecular aromatic nucleophilic substitution of η^3-benzylpalladium intermediates could exclusively occur at *para*-position.

Herein, we report ligand-controlled regio-selective nucleophilic aromatic substitution of 1-(chloromethyl)naphthalenes with arylacetonitriles (Scheme 1). The ordinary nucleophilic substitution reaction of 1-(chloromethyl)naphthalenes with a nucleophile normally occurs on the benzylic position to afford benzylated products.[15] However, palladium-catalyzed reaction of 1-(chloromethyl)naphthalenes with arylacetonitriles does not give substitution products at benzylic position, instead it affords regio-divergently either *para*- or *ortho*-substituted products; a sterically bulky ligand provides *para*- whereas a less bulky ligand gives *ortho*-substituted products. The *para*- or *ortho*-substituted products could easily converted to diaryl ketones through aerobic oxidation (Scheme 1).

Scheme 1. Palladium-catalyzed regio-selective nucleophilic substitution reaction of 1-(chloromethyl)naphthalenes with arylacetonitriles: a novel method for the synthesis of diaryl ketones.

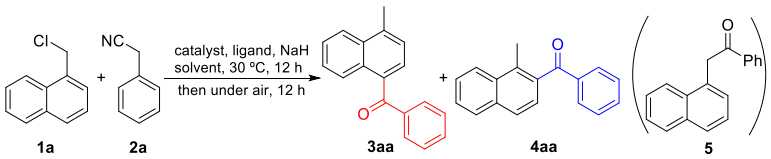


RESULTS AND DISCUSSION

Screening of Reaction Conditions for Regioselective Acylation of 1-Chloromethylnaphthalenes. In our initial studies, we selected the reaction of 1-(chloromethyl)naphthalene (**1a**) with phenylacetonitrile (**2a**) as a model to optimize the reaction conditions. The optimization included the selection of the most suitable catalyst or precatalyst, solvent, and ligand. Table 1 shows the results. The *para*-acylated product (**3aa**) was obtained as a sole product when tetrahydrofuran (THF), hexane, and 1,4-dioxane were used as solvents in the presence of $Pd(PPh_3)_4$ (entries 1–3, 60%, 27%, and 70%, respectively). However, the nucleophilic substitution reaction of **2a** occurred on the benzylic position of **1a** to produce 2-(naphthalen-1-yl)-1-phenylethanone (**5**) in 60% yield when a strong polar solvent dimethyl sulfoxide (DMSO) was tested (entry 4). To control the reaction regioselectivity, other phosphine ligands were then employed in the presence of a palladium precatalyst in 1,4-dioxane. The combinations of $Pd_2(dba)_3$ and PPh_3, $Pd(OAc)_2$ and PPh_3, $Pd(OAc)_2$ and P(*p*-tol)$_3$, and $Pd(OAc)_2$ and P(*o*-tol)$_3$ afforded **3aa** as a sole product (entries 5–8, 32%, 76%, 65%, and 24%, respectively). No reaction was observed when a bidentate ligand, 1,1'-bis(diphenylphosphino)ferrocene (DPPF), was examined (entry 9). The highest yield of **3aa** was obtained by combining $Pd(OAc)_2$ and Ph_2P^tBu, a more sterically hindered phosphine ligand (entry 10, 85%). The regioselectivity was switched

by utilizing smaller phosphine ligands PMe_3 and Me_2PPh. An *ortho*-acylated product **4aa** was obtained in a relatively high yield (64%) and high selectivity (**3aa**:**4aa** = 9/91) with the increased loading of Me_2PPh (entry 13 vs. entries 11 and 12).

Table 1. Optimization of palladium-catalyzed ligand-controlled regio-divergent acylation[a]



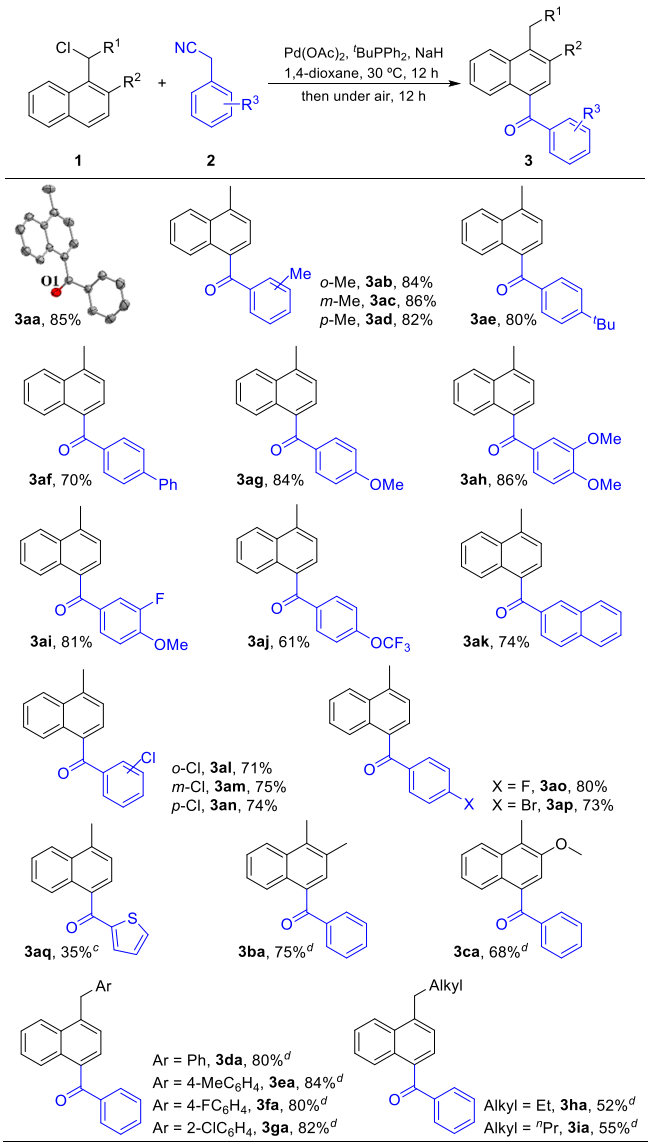
Entry	Catalyst	Ligand	Solvent	Yield (%)[b]	Ratio of **3aa** to **4aa**[c]
1	$Pd(PPh_3)_4$	none	THF	60	100/0
2	$Pd(PPh_3)_4$	none	hexane	27[d]	100/0
3	$Pd(PPh_3)_4$	none	dioxane	70	100/0
4	$Pd(PPh_3)_4$	none	DMSO	60[e]	--
5	$Pd_2(dba)_3$	PPh_3	dioxane	32[f]	100/0
6	$Pd(OAc)_2$	PPh_3	dioxane	76	100/0
7	$Pd(OAc)_2$	P(*p*-tol)$_3$	dioxane	65	100/0
8	$Pd(OAc)_2$	P(*o*-tol)$_3$	dioxane	24	100/0
9	$Pd(OAc)_2$	DPPF	dioxane	NR[g]	--
10	$Pd(OAc)_2$	Ph_2P^tBu	dioxane	85	100/0
11	$Pd(OAc)_2$	PMe_3	dioxane	30[h]	10/90
12	$Pd(OAc)_2$	Me_2PPh	dioxane	56	12/88
13[i]	$Pd(OAc)_2$	Me_2PPh	dioxane	64	9/91

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), NaH (1.2 mmol), catalyst (5 mol%), and ligand (10 mol%) in solvent (5 mL) at 30 °C under N_2 atmosphere for 12 h; then, the reaction mixture was stirred under air for 12 h. [b]Isolated yields. [c]Ratio of **3aa** to **4aa** was determined by ^{1}H NMR. [d]The starting material **1a** was recovered in 43% yield. [e]Nucleophilic substitution reaction occurred on the benzylic position to produce 2-(naphthalen-1-yl)-1-phenylethanone (**5**). [f]The starting material **1a** was recovered in 40% yield. [g]No reaction; **1a** was recovered in 70% yield. [h]By-product **5** was also separated in 42% yield. [i]20 mol% of Me_3PPh was used.

***Para*-acylation of 1-(chloromethyl)naphthalenes.** The scope and limitation of this type of *para*-substitution reaction was explored under the optimal reaction conditions. Scheme 2 summarizes the results. When arylacetonitriles **2b**–**2d** bearing a methyl group on *ortho*-, *meta*- or *para*-position were tested in the reaction of **1a**, 84%, 86%, and 82% yields of diaryl ketones **3ab**–**3ad** were obtained, respectively. The reactions of arylacetonitriles bearing an alkyl (*tert*-butyl) or aryl (phenyl) group on the *para*-position of the benzene ring also proceeded smoothly to produce *para*-acylated products **3ae** and **3af** in satisfactory yields. High yields were obtained in the reactions of methoxyl-substituted arylacetonitriles **2g**–**2i**. In addition, the desired product **3aj** was obtained in satisfactory yield (61%) when the *para*-(trifluoromethoxy)phenylacetonitrile (**2j**) was examined. The reaction of 2-(naphthalen-2-yl)acetonitrile (**2k**) with **1a** proceeded also smoothly to produce the corresponding product **3ak** in 74% yield. Halogen-substituted arylacetonitriles **2l**–**2p** were demonstrated to be suitable substrates in this reaction. The desired products **3al**–**3ap** were obtained in 71%–80% yields. Notably, the bromo atom linked to the aromatic ring were tolerated under the reaction conditions, suggesting that further manipulation based on C–Br bond may produce useful compounds. A relatively low yield (35%) was observed when 2-(thiophen-2-yl)acetonitrile (**2q**), was examined. Here, 1-methylnaphthalene, a dechlorinated product, was obtained as a major product (50% yield). The reactions of **1b**–**1i** with **2a** were examined under the abovementioned optimal conditions using ^{t}BuPPh$_2$ ligand, but the

reaction did not proceed and the starting substrates were recovered. However, the *para*-substitution reaction successfully occurred by simply changing the phosphine ligand from sterically quite bulky Ph_2P^tBu to PPh_3. The *para*-acylated products **3ba** and **3ca** were obtained in satisfactory yields in the reaction of 1-(chloromethyl)naphthalene **1b** or **1c** bearing an *ortho*-methyl or methoxy group. Good to high yields were observed in the reactions of **1d–1g** bearing an aryl substituent on the benzylic position. However, the alkyl-substituted 1-(chloromethyl)naphthalenes **1h** and **1i** provided the desired products in moderate yields because the β-hydride elimination occurred competitively.

Scheme 2. Palladium-catalyzed ligand-controlled *para*-acylation of 1-(chloromethyl)naphthalenes.[a,b]

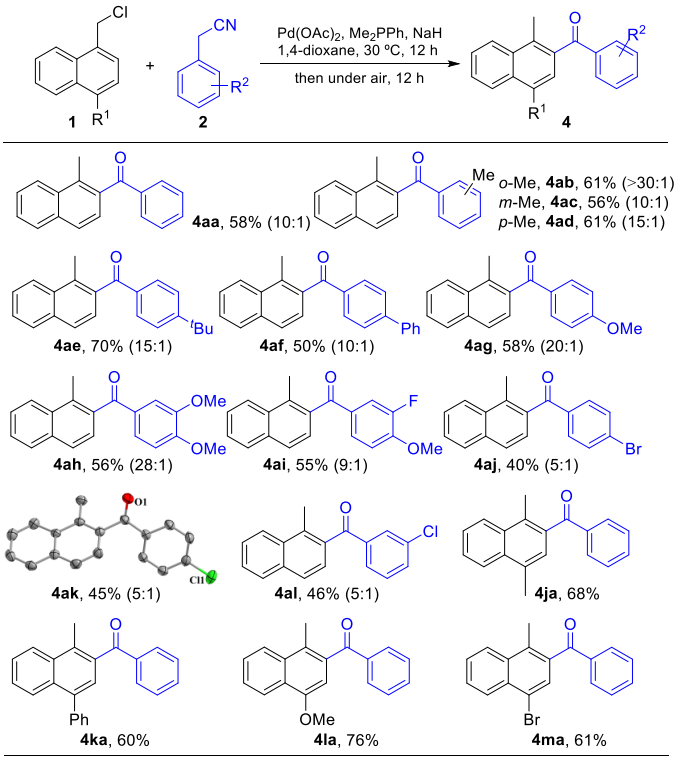


[a]Reaction conditions: **1** (0.3 mmol), **2** (0.6 mmol), NaH (60% in oil, 1.2 mmol), $Pd(OAc)_2$ (5 mol%), and Ph_2P^tBu (10 mol%) in 1,4-dioxane (5 mL) at 30 °C under N_2 atmosphere for 12 h; then, the reaction mixture was stirred at 30 °C under air for an additional 12 h. [b]Isolated yield. [c]1-Methylnaphthalene was isolated in 50% yield. [d]PPh_3 was used as ligand.

***Ortho*-acylation of 1-(chloromethyl)naphthalenes.** Next, we examined the nucleophilic aromatic substitution reaction of 1-(chloromethyl)naphthalenes by using smaller Me_2PPh as a ligand. Scheme 3 shows the results. The reactions of **1a** with various arylacetonitriles having

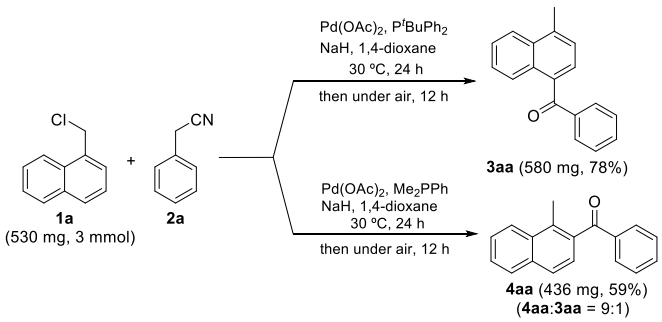
methyl, *tert*-butyl, phenyl, methoxyl, and a halogen atom on the benzene ring proceeded smoothly to give the *ortho*-acylated products **4aa–4al** in moderate to satisfactory yields (40%–70%). Arylacetonitriles bearing electron-donating groups gave higher regioselectivity than which bearing electron-withdrawing groups. Interestingly, steric effect seemed positive for controlling regioselectivity, no *para*-acylated product was produced when 2-(*o*-tolyl)acetonitrile was used as nucleophile. Relatively high yields were observed when the *para*-position of 1-(chloromethyl)naphthalene was blocked by a substituent such as methyl, phenyl, methoxyl, or bromine atom (**4ja–4ma**, 60%–76% yields). The halogen atoms (F, Cl, and Br) linked on the benzene rings of substrates were tolerated under the reaction conditions. The *ortho*-acylated products **4** cannot be regioselectively synthesized through the Friedel–Crafts acylation reaction.[16] In comparison with the *para*-acylation reaction, the *ortho*-acylation provided the desired products in relatively lower yields even when the starting materials were completely consumed.

Scheme 3. Palladium-catalyzed ligand-controlled *ortho*-acylation of 1-(chloromethyl)naphthalenes.[a,b]



[a]Reaction conditions: **1** (0.3 mmol), **2** (0.6 mmol), NaH (60% in oil, 1.2 mmol), $Pd(OAc)_2$ (5 mol%), and Me_2PPh (20 mol%) in 1,4-dioxane (5 mL) at 30 °C under N_2 atmosphere for 12 h; then, the reaction mixture was stirred at 30 °C under air for an additional 12 h. [b]Isolated yield; the ratio of **4** to **3** is shown within parenthesis.

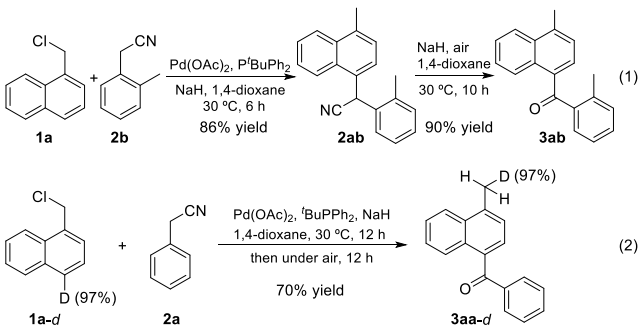
Scheme 4. Scale-up reaction.



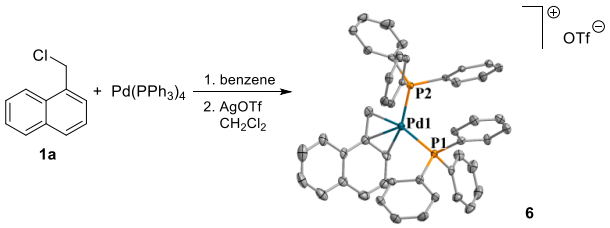
Scale-up reaction. To demonstrate the practicality of this method, scale-up reactions were performed under the standard conditions. The results are shown in Scheme 4. The *para*-acylated

product **3aa** and the *ortho*-acylated product **4aa** were obtained in 78% and 59% yileds, respectively. These results indicated that the scale-up reactions also proceeded smoothly without loss of efficiency.

Scheme 5. Mechanistic study.



Scheme 6. η^3-Benzylpalladium intermediate (the structure of counter anion in complex **6** was omitted for clear).

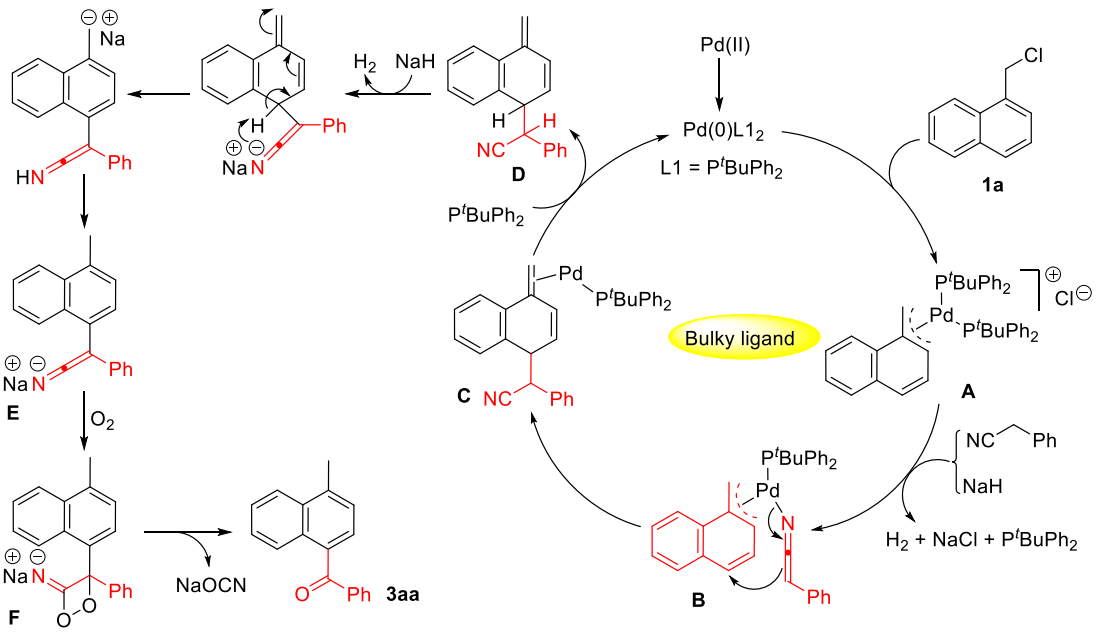


Mechanistic study. We performed control experiments (Scheme 5) to gain insights into the mechanism of this type of nucleophilic substitution reaction. The reaction of **1a** with **2b** under the standard conditions (^{t}BuPPh$_2$, NaH, 1,4-dioxane), without aftertreatment using aerobic oxygen, gave *para*-substituted product **2ab** in 86% yield. Then, **2ab** was converted to **3ab** in 90% yield upon treatment with air as oxidant under basic conditions (Eq. 1). The deuterium-labeling experiment revealed that D atom linked on the *para*-position of **1a**-*d* migrated completely to the benzylic position of product **3aa**-*d* (Eq. 2).

In order to confirm possibility of the formation of a η^3-benzylpalladium intermediate during this type of substitution reaction, we synthesized it according to reported literature. The addition of **1a** to a suspension of $Pd(PPh_3)_4$ in benzene at room temperature resulted in a yellow solution. Then, dechlorination was carried out with AgOTf in CH_2Cl_2. Indeed, η^3-benzylpalladium intermediate **6** was obtained and its structure was confirmed by X-ray analysis (Scheme 6).

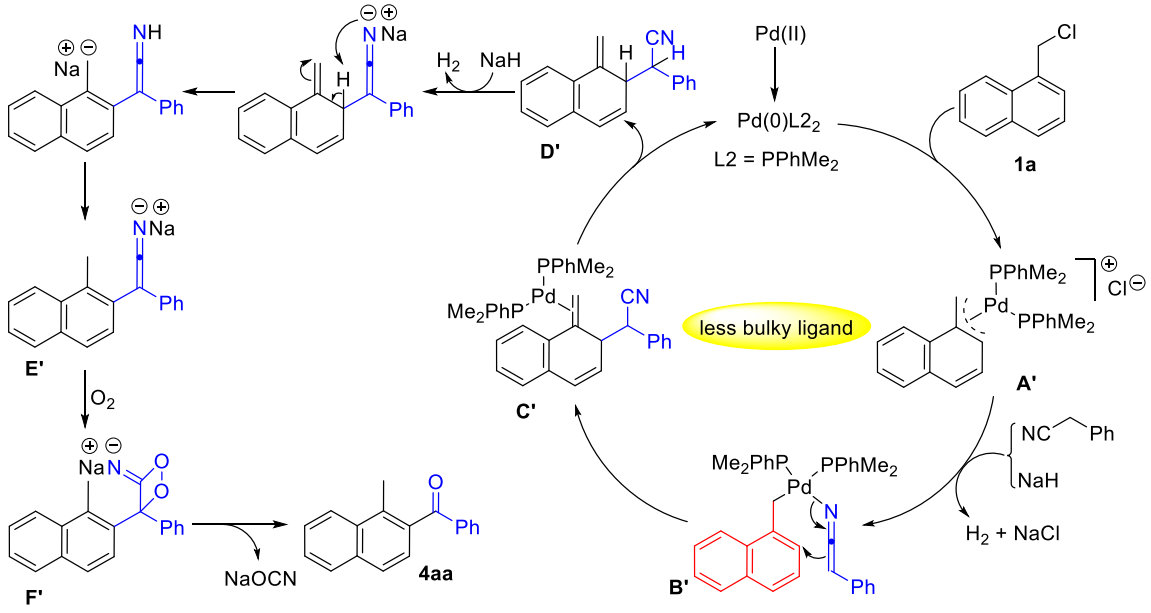
Based on our experimental outcomes and previous computational studies,[17] we propose plausible catalytic cycles to account for the present regio-selective aromatic substitution reaction. Scheme 7 illustrates the mechanism for *para*-substitution reaction. The oxidative addition of Pd(0) species [$Pd(P^tBuPh_2)_2$] to **1a** produces cationic palladium complex **A** in a polar solvent.[18] The complex subsequently undergoes a ligand-exchange reaction due to the steric effect of P^tBuPh_2 to generate η^3-benzylpalladium intermediate **B** with phenylethenimine anion ligand derived from phenylacetonitrile in the presence of NaH. C–C bond formation, as shown in **B**, produces **C**. Ligand-exchange reaction occurs again for the production of intermediate **D**, a dearomatization product, and Pd(0) species. The intermediate **K** subsequently undergoes deprotonation reaction in the presence of NaH, followed by re-aromatization to generate intermediate **E**, which is finally oxidated to the *para*-acylated product **3aa** via peroxide intermediate **F** in the presence of oxygen as the oxidant.[19]

Scheme 7. Proposed mechanism for *para*-acylation reaction.



Scheme 8 illustrates a possible mechanism for *ortho*-substitution reaction. Similarly, cationic palladium complex **A′** is generated in a polar solvent through the oxidative addition of Pd(0) species [Pd(PPhMe$_2$)$_2$] to **1a**. Phenylethenimine anion coordinated to the palladium atom in **A′** generates η^1-benzylpalladium intermediate **B′**, which then undergoes C–C bond formation at the *ortho*-position for the production of intermediate **C′**. The dearomatization product **D′** is then released from **C′** and finally converted to a *ortho*-acylated product **4aa** through deprotonation, re-aromatization, and oxidation.

Scheme 8. Proposed mechanism for *ortho*-acylation reaction.



CONCLUSIONS

We have developed a novel ligand-controlled regio-selective nucleophilic aromatic substitution reaction of 1-(chloromethyl)naphthalenes. The *para*-acylated products are obtained in the presence of a bulky ligand, whereas the *ortho*-acylated products are obtained in the presence of a less bulky ligand. In this paper, it was revealed that the benzylpalladium intermediate could react through different mode (η^3-benzylpalladium intermediate or η^1-benzylpalladium intermediate) in nucleophilic aromatic substitution. In addition to interesting mechanistic aspect, the present reaction provides a facile synthetic method for a wide range of diaryl ketones, some of which are not easily available through the previously known procedures.

EXPERIMENTAL SECTION

General Information

All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Solvents were purified by standard techniques without special instructions. ^{1}H and ^{13}C{^{1}H} NMR spectra

were recorded on Varian Inova-400 spectrometer (400 MHz for ^{1}H, 100 MHz for $^{13}C\{^{1}H\}$), Bruker Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for $^{13}C\{^{1}H\}$), and Varian Inova-500 spectrometer (500 MHz for ^{1}H, 125 MHz for $^{13}C\{^{1}H\}$); $CDCl_3$ and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on either a Q-TOF mass spectrometry or a GC-TOF mass spectrometry. TLC was carried out on SiO_2 (silica gel 60 F_{254}, Merck), and the spots were located with UV light, iodoplatinate reagent or 1% aqueous $KMnO_4$. Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 mesh). Diffraction intensity data were collected on a Bruker Smart APEX CCD area detector diffractometer (graphite monochrometer, MoKα radiation, λ = 0.71073 Å) at 296(2) K. All the (hetero)arylacetonitriles are commercially available.

General procedure

To a suspension of NaH (48.0 mg, 60% dispersion in mineral oil, 1.2 mmol) in 1, 4-dioxane (5 mL), 2-phenylacetonitrile (**2a**, 70.3 mg, 0.6 mmol) was added at 30 ºC. After the colour of the resulting mixture was changed to purple, 1-(chloromethyl)naphthalene (**1a**, 53.0 mg, 0.3 mmol) was added, followed by $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), P^tBuPh_2 (7.3 mg, 0.03 mmol). The reaction mixture was stirred for 12 h under a N_2 atmosphere, followed by stirred the solution under the air for another 12 h. Then quenched by water (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified via silica gel chromatography (eluent:

hexane/ethyl acetate = 50:1) to afford (4-methylnaphthalen-1-yl)(phenyl)methanone (**3aa**) in 85% yield (62.8 mg) as a white solid.

(4-Methylnaphthalen-1-yl)(phenyl)methanone (**3aa**)[20]: White solid (62.80 mg, 85% yield), mp 69–70 ˚C (lit. 67–69 ˚C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74 (s, 3H), 7.33 (d, J = 7.2 Hz, 1H), 7.41–7.57 (m, 6H), 7.85 (d, J = 7.6 Hz, 2H), 8.06 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.1, 124.5, 125.2, 126.4, 127.0, 128.2, 128.5, 130.5, 131.2, 133.0, 133.1, 134.8, 138.4, 138.8, 198.2.

(4-Methylnaphthalen-1-yl)(o-tolyl)methanone **(3ab)**: Yellowish oil (65.60 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 2.73 (s, 3H), 7.18 (dd, J = 7.2, 7.6 Hz, 1H), 7.27 (dd, J = 7.6, 8.8 Hz, 2H), 7.34–7.40 (m, 2H), 7.44 (d, J = 7.2 Hz, 1H), 7.56–7.61 (m, 2H), 8.06–8.08 (m, 1H), 8.66–8.68 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.3, 20.7, 124.6, 125.4, 125.5, 126.5, 126.6, 127.7, 130.3, 130.9, 131.0, 131.3, 131.4, 133.1, 134.8, 138.1, 140.0, 140.1, 200.4; IR (neat) 3064, 2962, 2925, 1656, 1590, 1514, 1456, 1292, 1248, 1045, 975, 877, 761, 738 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{16}O$: 260.1201 $[M]^+$; found: 260.1203.

(4-Methylnaphthalen-1-yl)(m-tolyl)methanone **(3ac)**: Yellowish oil (67.16 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.74 (s, 3H), 7.28–7.33 (m, 2H), 7.37 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.49–7.57 (m, 2H), 7.60 (d, J = 7.6 Hz, 1H), 7.71 (s, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.0, 21.4, 124.5, 125.2, 126.4, 126.5, 127.0, 127.9, 128.1, 128.3, 130.8, 131.2, 132.9, 134.0, 135.0, 138.30, 138.34, 138.8, 198.4; IR (neat) 3060, 2922, 1655, 1589, 1513, 1287, 1260, 1180, 976, 761, 741 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{16}O$: 260.1201 $[M]^+$; found: 260.1211.

(4-Methylnaphthalen-1-yl)(p-tolyl)methanone **(3ad)**: Yellowish oil (64.04 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.74 (s, 3H), 7.22 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.44–7.50 (m, 2H), 7.54 (dd, J = 6.8, 7.6 Hz, 1H), 7.75 (d, J = 8.0 Hz, 2H), 8.06 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.0, 21.9, 124.5, 125.3, 126.4, 126.5, 126.9, 127.7, 129.2, 130.7, 131.2, 132.9, 135.2, 136.1, 138.1, 144.1, 197.9; IR (neat) 2955, 2924, 2854, 1656, 1604, 1513, 1456, 1284, 1254, 1178, 973, 833, 762 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{16}O$: 260.1201 $[M]^+$; found: 260.1194.

(4-(tert-Butyl)phenyl)(4-methylnaphthalen-1-yl)methanone **(3ae)**: Yellowish oil (72.58 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 9H), 2.75 (s, 3H), 7.33 (d, J = 7.2 Hz, 1H), 7.44–7.51 (m, 4H), 7.53–7.57 (m, 1H), 7.80 (d, J = 8.4 Hz, 2H), 8.07 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.1, 31.3, 35.3, 124.5, 125.2, 125.5, 126.4, 126.5, 126.9, 127.8, 130.6, 131.2, 133.0, 135.2, 136.0, 138.1, 157.0, 197.9; IR (neat) 3069, 2963, 2904, 2868, 1657, 1604, 1513, 1284, 1257, 1187, 1108, 974, 878, 851, 834, 785, 771, 758, 711 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{22}H_{22}O$: 302.1671 $[M]^+$; found: 302.1672.

[1,1'-Biphenyl]-4-yl(4-methylnaphthalen-1-yl)methanone **(3af)**: Yellowish solid (67.70 mg, 70% yield), mp 106–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (s, 3H), 7.36–7.60 (m, 8H), 7.63 (d, J = 7.2 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 8.09 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.1, 124.6, 125.3, 126.48, 126.51, 127.1, 127.2, 127.4, 128.0, 128.4, 129.1, 131.16, 131.24, 133.0, 135.0, 137.4, 138.4, 140.0, 145.9, 197.8; IR (KBr) 3059, 2924, 1653, 1601, 1514, 1422, 1284, 1256, 1111, 1007, 974, 878, 760, 746, 697 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{24}H_{18}O$: 322.1358 $[M]^+$; found: 322.1365.

(4-Methoxyphenyl)(4-methylnaphthalen-1-yl)methanone **(3ag)**: Yellowish solid (69.64 mg, 84% yield), mp 77–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.73 (s, 3H), 3.83 (s, 3H), 6.89 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.2 Hz, 1H), 7.42–7.48 (m, 2H), 7.53 (dd, J = 7.2, 8.0 Hz, 1H), 7.83 (d, J = 8.8 Hz, 2H), 8.06 (dd, J = 7.6, 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.0, 55.6, 113.7, 124.5, 125.3, 126.3, 126.5, 126.8, 127.1, 131.1, 131.4, 132.9, 135.5, 137.7, 163.8, 196.9; IR (KBr) 3071, 2932, 2839, 1651, 1598, 1509, 1254, 1170, 1029, 973, 878, 845, 768 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{16}O_2$: 276.1150 $[M]^+$; found: 276.1151.

(3,4-Dimethoxyphenyl)(4-methylnaphthalen-1-yl)methanone **(3ah)**: Yellowish solid (79.04 mg, 86% yield), mp 104–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76 (s, 3H), 3.92 (s, 3H), 3.94 (s, 3H), 6.79 (d, J = 8.4 Hz, 1H), 7.29 (dd, J = 2.0, 8.4 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.45–7.51 (m, 2H), 7.54–7.57 (m, 1H), 7.64 (d, J = 2.0 Hz, 1H), 8.07 (d, J = 8.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.0, 56.16, 56.21, 109.9, 111.6, 124.5, 125.2, 126.35, 126.41, 126.5, 126.8, 127.1, 131.2, 131.5, 132.9, 135.3, 137.7, 149.2, 153.6, 197.0; IR (KBr) 3077, 2935, 2838, 1651, 1592, 1511, 1463, 1416, 1264, 1126, 1023, 979, 914, 879, 809, 765 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{20}H_{18}O_3$: 306.1256 $[M]^+$; found: 306.1263.

(3-Fluoro-4-methoxyphenyl)(4-methylnaphthalen-1-yl)methanone **(3ai)**: Yellowish solid (71.52 mg, 81% yield), mp 92–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 (s, 3H), 3.92 (s, 3H), 6.93 (dd, J = 8.0, 8.4 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.47–7.58 (m, 3H), 7.67 (dd, J = 2.0, 11.6 Hz, 1H), 8.06 (d, J = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.0, 56.4, 112.3 (d, $^4J_{C\text{-}F}$ = 1.6 Hz), 117.8 (d, $^2J_{C\text{-}F}$ = 18.9 Hz), 124.6, 125.3, 126.3, 126.5, 127.0, 127.4, 128.2 (d, $^3J_{C\text{-}F}$ = 3.3 Hz), 131.1, 131.7 (d, $^3J_{C\text{-}F}$ = 5.0 Hz), 133.0, 134.7, 138.2, 152.0 (d, $^1J_{C\text{-}F}$ = 246.5 Hz), 152.1 (d, $^2J_{C\text{-}F}$ = 10.9 Hz), 196.0; IR (KBr) 3072, 2936, 2843, 1652, 1609, 1513, 1434, 1282, 1174, 1114, 1021, 763 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{15}O_2F$: 294.1056 $[M]^+$; found: 294.1051.

(4-Methylnaphthalen-1-yl)(4-(trifluoromethoxy)phenyl)methanone **(3aj)**: Yellow oil (60.44 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76 (s, 3H), 7.27 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.51–7.60 (m, 2H), 7.90 (d, J = 8.8 Hz, 2H), 8.08 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.1, 120.5 (q, $^1J_{C\text{-}F}$ = 257.2 Hz), 124.6, 125.2, 126.3, 126.5, 126.6, 127.3, 128.3, 131.1, 132.5, 133.0, 134.2, 137.1, 139.0, 152.7, 196.5; IR (neat) 3074, 2926, 2861, 1660, 1601, 1591, 1514, 1503, 1254, 1167,

1017, 975, 877, 837, 767 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{13}O_2F_3$: 330.0868 $[M]^+$; found: 330.0869.

(4-Methylnaphthalen-1-yl)(naphthalen-2-yl)methanone **(3ak)**: Yellow oil (65.79 mg, 74% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 2.77 (s, 3H), 7.36 (d, J = 7.2 Hz, 1H), 7.46–7.59 (m, 5H), 7.79 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 8.05–8.10 (m, 2H), 8.20 (d, J = 8.4 Hz, 1H), 8.24 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 20.1, 124.6, 125.3, 125.7, 126.50, 126.53, 126.9, 127.1, 127.9, 128.1, 128.5, 128.7, 129.8, 131.3, 132.5, 132.9, 133.0, 135.1, 135.8, 136.1, 138.4, 198.2; IR (neat) 3057, 1655, 1626, 1591, 1513, 1464, 1289, 1185, 1118, 978, 821, 762 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{22}H_{16}O$: 296.1201 $[M]^+$; found: 296.1208.

(2-Chlorophenyl)(4-methylnaphthalen-1-yl)methanone **(3al)**: Yellow oil (59.80 mg, 71% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 2.73 (s, 3H), 7.24 (d, J = 7.6 Hz, 1H), 7.33–7.36 (m, 1H), 7.41–7.43 (m, 2H), 7.47 (d, J = 7.2 Hz, 2H), 7.58–7.68 (m, 2H), 8.07 (d, J = 8.4 Hz, 1H), 8.98 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 20.4, 124.6, 125.4, 126.7, 126.76, 126.82, 128.2, 130.2, 130.4, 131.2, 131.5, 132.1, 132.4, 132.8, 133.2, 140.4, 141.4, 197.1; IR (neat) 3065, 2923, 2855, 1660, 1590, 1515, 1433, 1289, 1245, 1075, 977, 877, 763, 745 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{18}H_{13}OCl$: 280.0655 $[M]^+$; found: 280.0663.

(3-Chlorophenyl)(4-methylnaphthalen-1-yl)methanone **(3am)**: White solid (63.17 mg, 75% yield), mp 93–94 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.76 (s, 3H), 7.34–7.39 (m, 2H), 7.47 (d, J = 7.2 Hz, 1H), 7.51–7.58 (m, 3H), 7.69 (d, J = 7.6 Hz, 1H), 7.85 (dd, J = 1.6, 2.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 20.1, 124.6, 125.2, 126.3, 126.6, 127.3, 128.6, 128.7, 129.8, 130.3, 131.2, 133.0, 133.1, 133.9, 134.8, 139.2, 140.5, 196.7; IR (KBr) 3066, 2923, 2859, 1660, 1589, 1568, 1514, 1423, 1285, 1250, 1201, 977, 838, 762, 743 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{18}H_{13}OCl$: 280.0655 $[M]^+$; found: 280.0656.

(4-Chlorophenyl)(4-methylnaphthalen-1-yl)methanone **(3an)**: Yellowish oil (62.33 mg, 74% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 2.76 (s, 3H), 7.35 (d, J = 7.2 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 7.2 Hz, 1H), 7.50–7.59 (m, 2H), 7.79 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 20.1, 124.6, 125.3, 126.3, 126.4, 126.6, 127.2, 128.2, 128.9, 131.1, 131.9, 133.0, 134.3, 137.2, 138.8, 139.7, 196.9; IR (neat) 3069, 2923, 1657, 1587, 1514, 1422, 1284, 1254, 1089, 1013, 974, 875, 843, 764 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{18}H_{13}OCl$: 280.0655 $[M]^+$; found: 280.0659.

(4-Fluorophenyl)(4-methylnaphthalen-1-yl)methanone **(3ao)**: Yellow oil (63.43 mg, 80% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 2.76 (s, 3H), 7.10 (dd, J = 8.8, 8.8 Hz, 2H), 7.34 (dd, J = 0.8, 7.2 Hz, 1H), 7.45 (d, J = 7.2 Hz, 1H), 7.48–7.59 (m, 2H), 7.86–7.89 (m, 2H), 8.07 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 20.1, 115.7 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 124.6, 125.3, 126.4, 126.6, 127.1, 127.9, 131.1, 133.0, 133.1 (d, $^3J_{C\text{-}F}$ =9.3 Hz), 134.6, 135.1 (d, $^4J_{C\text{-}F}$ = 2.9 Hz), 138.6, 165.9 (d, $^1J_{C\text{-}F}$ = 253.5 Hz), 196.6; IR (neat) 3072, 2924, 1659, 1596,

1504, 1284, 1254, 1231, 1155, 973, 851, 766, 584 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{18}H_{13}OF$: 264.0950 $[M]^+$; found: 264.0953.

(4-Bromophenyl)(4-methylnaphthalen-1-yl)methanone **(3ap)**: Yellow solid (71.22 mg, 73% yield), mp 75–76 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.76 (s, 3H), 7.34 (d, J = 7.2 Hz, 1H), 7.45 (d, J = 7.2 Hz, 1H), 7.50–7.59 (m, 4H), 7.71 (d, J = 8.0 Hz, 2H), 8.08 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 20.1, 124.6, 125.2, 126.3, 126.6, 127.2, 128.3, 128.4, 131.1, 131.8, 132.0, 133.0, 134.2, 137.5, 138.4, 138.9, 197.0; IR (KBr) 3067, 2923, 2860, 1656, 1583, 1514, 1396, 1283, 1254, 1070, 1010, 974, 875, 841, 763 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{18}H_{13}OBr$: 324.0150 $[M]^+$; found: 324.0148.

(4-Methylnaphthalen-1-yl)(thiophen-2-yl)methanone **(3aq)**: Yellow oil (26.49 mg, 35% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 2.75 (s, 3H), 7.08 (dd, J = 3.6, 5.2 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.47 (dd, J = 1.2, 3.6 Hz, 1H), 7.50–7.59 (m, 2H), 7.63 (d, J = 7.2 Hz, 1H), 7.71 (dd, J = 1.2, 5.2 Hz, 1H), 8.06 (d, J = 7.6 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 20.1, 124.5, 125.2, 126.2, 126.5, 127.0, 127.4, 128.2, 130.8, 134.7, 135.0, 135.6, 138.5, 145.7, 189.9; IR (neat) 3076, 2923, 1635, 1589, 1514, 1411, 1352, 1291, 1258, 1232, 1057, 967, 809, 763, 726 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{16}H_{12}OS$: 252.0609 $[M]^+$; found: 252.0604.

(3,4-Dimethylnaphthalen-1-yl)(phenyl)methanone **(3ba)**: Yellowish solid (58.57 mg, 75% yield), mp 90–91 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 2.66 (s, 3H), 7.40–7.46 (m, 4H), 7.50–7.59 (m, 2H), 7.85 (d, J = 7.6 Hz, 2H), 8.07 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 15.2, 20.9, 124.2, 125.9, 126.3, 126.4, 128.5, 129.9, 130.5, 131.1, 132.0, 133.17, 133.21, 134.2, 135.4, 138.8, 198.4; IR (KBr) 3061, 2923, 1656, 1560, 1578, 1511, 1447, 1280, 1253, 1207, 1024, 866, 753, 715 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{16}O$: 260.1201 $[M]^+$; found: 260.1198.

(3-Methoxy-4-methylnaphthalen-1-yl)(phenyl)methanone **(3ca)**: Yellowish solid (56.37 mg, 68% yield), mp 66–67 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.62 (s, 3H), 3.89 (s, 3H), 7.32 (d, J = 7.6 Hz, 1H), 7.35 (s, 1H), 7.45 (dd, J = 7.2, 8.0 Hz, 2H), 7.51 (dd, J = 7.6, 7.6 Hz, 1H), 7.58 (dd, J = 7.2, 7.6 Hz, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.96 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 11.2, 56.9, 115.3, 123.4, 124.0, 124.6, 126.3, 126.7, 128.6, 130.6, 133.4, 134.1, 135.8, 138.4, 153.1, 198.0; IR (KBr) 3067, 2936, 2842, 1660, 1593, 1512, 1462, 1448, 1339, 1237, 1174, 1113, 1055, 1028, 862, 756, 716 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{16}O_2$: 276.1150 $[M]^+$; found: 276.1148.

(4-Benzylnaphthalen-1-yl)(phenyl)methanone **(3da)**: Yellowish solid (77.37 mg, 80% yield), mp 92–93 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 4.49 (s, 2H), 7.21 (d, J = 7.2 Hz, 3H), 7.28 (dd, J = 7.6, 8.0 Hz, 3H), 7.41–7.51 (m, 5H), 7.57 (dd, J = 7.2, 7.6 Hz, 1H), 7.88 (d, J = 7.6 Hz, 2H), 8.07–8.09 (m, 1H), 8.14–8.16 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 39.5, 124.7, 125.9, 126.5, 126.6, 126.7, 127.0, 127.8, 128.6, 128.7, 128.9, 130.6, 131.6, 132.5, 133.3, 135.5, 138.5, 140.0,

140.5, 198.2; IR (KBr) 3060, 3026, 2920, 1658, 1595, 1580, 1513, 1494, 1448, 1282, 1254, 876, 849, 765, 710 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{24}H_{18}O$: 322.1358 $[M]^+$; found: 322.1349.

(4-(4-Methylbenzyl)naphthalen-1-yl)(phenyl)methanone **(3ea)**: Yellow oil (84.78 mg, 84% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 4.46 (s, 2H), 7.10 (br, 4H), 7.30 (d, J = 7.2 Hz, 1H), 7.42–7.51 (m, 5H), 7.57 (dd, J = 7.2, 7.6 Hz, 1H), 7.87 (d, J = 7.6 Hz, 2H), 8.08–8.10 (m, 1H), 8.13–8.16 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 21.2, 39.0, 124.7, 125.8, 126.5, 126.7, 127.0, 127.9, 128.5, 128.8, 129.4, 130.6, 131.6, 132.5, 133.3, 135.4, 136.0, 136.9, 138.5, 140.8, 198.2; IR (neat) 3048, 3022, 2920, 1658, 1595, 1579, 1513, 1448, 1283, 1253, 876, 853, 766, 714 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{25}H_{20}O$: 336.1514 $[M]^+$; found: 336.1511.

(4-(4-Fluorobenzyl)naphthalen-1-yl)(phenyl)methanone **(3fa)**: White solid (81.69 mg, 80% yield), mp 103–104 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 4.45 (s, 2H), 6.96 (dd, J = 8.4, 8.8 Hz, 2H), 7.13–7.17 (m, 2H), 7.28 (d, J = 7.2 Hz, 1H), 7.41–7.51 (m, 5H), 7.57 (dd, J = 7.2, 7.6 Hz, 1H), 7.87 (d, J = 7.2 Hz, 2H), 8.02–8.05 (m, 1H), 8.13–8.15 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 38.6, 115.5 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 124.6, 125.9, 126.6, 126.8, 127.1, 127.7, 128.6, 130.3 (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 130.6, 131.6, 132.4, 133.4, 135.6 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 135.7, 138.5, 140.2, 161.6 (d, $^1J_{C\text{-}F}$ = 243.0 Hz), 198.1; IR (KBr) 3065, 2919, 1657, 1597, 1580, 1509, 1448, 1283, 1254, 1221, 1158, 912, 877, 826, 788, 714 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{24}H_{17}OF$: 340.1263 $[M]^+$; found: 340.1259.

(4-(2-Chlorobenzyl)naphthalen-1-yl)(phenyl)methanone **(3ga)**: Yellow oil (87.78 mg, 82% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 4.58 (s, 2H), 6.92 (dd, J = 1.6, 7.6 Hz, 1H), 7.08–7.12 (m, 1H), 7.16–7.20 (m, 2H), 7.42–7.46 (m, 3H), 7.48–7.52 (m, 3H), 7.55–7.59 (m, 1H), 7.86–7.89 (m, 2H), 7.99–8.01 (m, 1H), 8.15–8.18 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 36.7, 124.5, 125.7, 126.6, 126.9, 127.1, 127.2, 127.8, 128.0, 128.6, 129.6, 130.6, 130.9, 131.5, 132.5, 133.3, 134.3, 135.7, 137.6, 138.5, 139.1, 198.1; IR (neat) 3062, 2913, 1659, 1595, 1579, 1514, 1446, 1283, 1253, 1177, 1051, 909, 878, 799 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{24}H_{17}OCl$: 356.0968 $[M]^+$; found: 356.0962.

Phenyl(4-propylnaphthalen-1-yl)methanone **(3ha)**: Yellow oil (42.80 mg, 52% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, J = 7.4 Hz, 3H), 1.79–1.85 (m, 2H), 3.11 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 7.2 Hz, 1H), 7.44 (dd, J = 7.6, 8.0 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.53–7.60 (m, 2H), 7.86 (d, J = 7.2 Hz, 2H), 8.13 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.5, 24.0, 35.7, 124.4, 124.6, 126.4, 126.6, 126.9, 128.1, 128.5, 130.6, 131.6, 132.3, 133.2, 134.8, 138.7, 142.8, 198.3; IR (neat) 3060, 2959, 2930, 2870, 1658, 1560, 1579, 1514, 1448, 1275, 1252, 1176, 878, 799, 763, 714 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{20}H_{18}O$: 274.1358 $[M]^+$; found: 274.1359.

(4-Butylnaphthalen-1-yl)(phenyl)methanone **(3ia)**: Yellow oil (47.58 mg, 55% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.4 Hz, 3H), 1.44–1.53 (m, 2H), 1.73–1.81 (m, 2H), 3.13 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 7.2 Hz, 1H), 7.42–7.50 (m, 4H), 7.53–7.59 (m, 2H), 7.86 (d, J = 6.8 Hz,

2H), 8.13 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 14.2, 23.1, 33.0, 33.4, 124.4, 124.5, 126.4, 126.7, 126.9, 128.1, 128.5, 130.6, 131.6, 132.3, 133.2, 134.8, 138.8, 143.1, 198.3; IR (neat) 3060, 2956, 2930, 2870, 1658, 1560, 1580, 1514, 1448, 1282, 1254, 841, 764 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{21}H_{20}O$: 288.1514 $[M]^+$; found: 288.1512.

(1-Methylnaphthalen-2-yl)(phenyl)methanone **(4aa)**: Yellowish oil (42.85 mg, 58% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 3H), 7.37 (d, J = 8.4 Hz, 1H), 7.45 (dd, J = 7.2, 8.0 Hz, 2H), 7.55–7.63 (m, 3H), 7.77 (d, J = 8.4 Hz, 1H), 7.84 (dd, J = 1.2, 8.0 Hz, 2H), 7.89 (dd, J = 2.4, 7.6 Hz, 1H), 8.12 (d, J = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.5, 124.79, 124.84, 126.3, 126.87, 126.93, 128.7, 128.8, 130.4, 132.8, 132.9, 133.5, 134.0, 136.6, 137.9, 199.6; IR (neat) 3056, 2924, 1665, 1595, 1448, 1277, 1248, 1167, 933, 813, 750, 719 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{18}H_{14}O$: 246.1045 $[M]^+$; found: 246.1042.

(1-Methylnaphthalen-2-yl)(o-tolyl)methanone **(4ab)**: White solid (47.64 mg, 61% yield), mp 64–65 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 3H), 2.67 (s, 3H), 7.16 (dd, J = 7.2, 7.6 Hz, 1H), 7.30–7.42 (m, 4H), 7.54–7.61 (m, 2H), 7.71 (d, J = 8.8 Hz, 1H), 7.87 (d, J = 7.2 Hz, 1H), 8.14 (d, J = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.1, 21.2, 125.0, 125.4, 125.6, 126.1, 126.7, 127.0, 128.6, 131.5, 131.7, 131.8, 132.8, 134.0, 134.1, 137.5, 138.5, 139.1, 201.6; IR (KBr) 3055, 2925, 1662, 1597, 1569, 1453, 1242, 930, 820, 773, 751, 737 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{16}O$: 260.1201 $[M]^+$; found: 260.1206.

(1-Methylnaphthalen-2-yl)(m-tolyl)methanone **(4ac)**: Yellow oil (43.74 mg, 56% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.61 (s, 3H), 7.31–7.41 (m, 3H), 7.58–7.62 (m, 3H), 7.68 (s, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.5, 21.5, 124.8, 124.9, 126.2, 126.8, 126.9, 127.8, 128.6, 128.8, 130.7, 132.76, 132.83, 134.0, 134.4, 136.8, 138.0, 138.6, 199.9; IR (neat) 3054, 2922, 1664, 1600, 1584, 1280, 1257, 1161, 954, 825, 754 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{16}O$: 260.1201 $[M]^+$; found: 260.1197.

(1-Methylnaphthalen-2-yl)(p-tolyl)methanone **(4ad)**: Yellowish solid (47.64 mg, 61% yield), mp 95–96 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 2.60 (s, 3H), 7.24 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 1H), 7.55–7.62 (m, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.5, 21.9, 124.7, 124.8, 126.2, 126.8, 128.8, 129.5, 130.5, 132.5, 132.8, 133.9, 135.4, 136.9, 144.5, 199.3; IR (KBr) 3053, 2922, 1661, 1603, 1446, 1277, 1250, 1166, 933, 815, 757 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{16}O$: 260.1201 $[M]^+$; found: 260.1207.

(4-(tert-Butyl)phenyl)(1-methylnaphthalen-2-yl)methanone **(4ae)**: Yellowish oil (63.51 mg, 70% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 9H), 2.61 (s, 3H), 7.36 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.8 Hz, 2H), 7.53–7.61 (m, 2H), 7.74–7.79 (m, 3H), 7.88 (d, J = 7.6 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.3, 31.1, 35.2, 124.6, 124.7, 125.6, 126.0, 126.7, 128.7, 130.3, 132.5, 132.7, 133.8, 135.1, 136.8, 157.3, 199.1; IR (neat) 3054, 2963, 2905, 2868,

1663, 1604, 1463, 1278, 1253, 1169, 1108, 936, 812, 771, 748 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{22}H_{22}O$: 302.1671 $[M]^+$; found: 302.1676.

[1,1'-Biphenyl]-4-yl(1-methylnaphthalen-2-yl)methanone **(4af)**: Yellow solid (48.36 mg, 50% yield), mp 100–101 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.64 (s, 3H), 7.37–7.40 (m, 2H), 7.46 (dd, J = 7.2, 7.6 Hz, 2H), 7.55–7.61 (m, 4H), 7.66 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.0 Hz, 3H), 8.12 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.5, 124.75, 124.84, 126.3, 126.88, 126.91, 127.4, 127.5, 128.5, 128.8, 129.1, 131.0, 132.78, 132.83, 134.0, 136.57, 136.64, 140.0, 146.2, 199.2; IR (KBr) 3055, 3032, 1662, 1601, 1448, 1279, 1252, 1168, 935, 814, 753, 697 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{24}H_{18}O$: 322.1358 $[M]^+$; found: 322.1357.

(4-Methoxyphenyl)(1-methylnaphthalen-2-yl)methanone **(4ag)**: Yellow oil (48.08 mg, 58% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 3H), 3.85 (s, 3H), 6.91 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.4 Hz, 1H), 7.53–7.59 (m, 2H), 7.76 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 9.2 Hz, 2H), 7.88 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.4, 55.7, 114.0, 124.6, 124.7, 126.2, 126.7, 126.8, 128.8, 130.9, 132.2, 132.7, 132.8, 133.9, 137.0, 164.0, 198.3; IR (neat) 3053, 2933, 2839, 1656, 1598, 1508, 1420, 1253, 1163, 1028, 934, 816, 767 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{16}O_2$: 276.1150 $[M]^+$; found: 276.1148.

(3,4-Dimethoxyphenyl)(1-methylnaphthalen-2-yl)methanone **(4ah)**: White solid (51.47 mg, 56% yield), mp 93–94 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 3H), 3.94 (s, 3H), 3.95 (s, 3H), 6.81 (d, J = 8.4 Hz, 1H), 7.23 (dd, J = 2.0, 8.4 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.55–7.63 (m, 3H), 7.77 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.3, 56.07, 56.13, 109.9, 111.0, 124.5, 124.6, 126.0, 126.4, 126.6, 126.7, 128.7, 130.8, 132.2, 132.7, 133.7, 136.8, 149.2, 153.7, 198.2; IR (KBr) 2935, 2838, 1654, 1594, 1583, 1510, 1417, 1273, 1262, 1133, 1022, 765 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{20}H_{18}O_3$: 306.1256 $[M]^+$; found: 306.1250.

(3-Fluoro-4-methoxyphenyl)(1-methylnaphthalen-2-yl)methanone **(4ai)**: White solid (48.56 mg, 55% yield), mp 100–101 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 3H), 3.94 (s, 3H), 6.94 (dd, J = 8.0, 8.4 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.53–7.60 (m, 3H), 7.64 (dd, J = 2.4, 12.0 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.4, 56.5, 112.4, 117.4 (d, $^2J_{C\text{-}F}$ = 18.7 Hz), 124.5, 124.8, 126.3, 126.9, 128.2 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 128.8, 131.1, 132.5, 132.8, 133.9, 136.3, 152.2 (d, $^1J_{C\text{-}F}$ = 247.0 Hz), 152.4 (d, $^3J_{C\text{-}F}$ = 10.8 Hz), 197.4; IR (KBr) 3059, 2936, 2846, 1660, 1608, 1514, 1433, 1281, 1117, 1022, 798, 761 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{15}O_2F$: 294.1056 $[M]^+$; found: 294.1050.

(4-Bromophenyl)(1-methylnaphthalen-2-yl)methanone **(4aj)**: White solid (39.03 mg, 40% yield), mp 130–131 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 3H), 7.34 (d, J = 8.4 Hz, 1H), 7.56–7.63 (m, 4H), 7.69 (d, J = 8.8 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 7.2 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.5, 124.6, 124.9, 126.4, 127.0, 127.1, 128.8, 128.9, 131.8, 132.1, 132.8, 133.0, 134.1, 135.9, 136.7, 198.5; IR (KBr) 3053, 1660, 1582, 1276,

1247, 1165, 1068, 1008, 934, 810, 757 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{18}H_{13}OBr$: 324.0150 $[M]^+$; found: 324.0142.

(4-Chlorophenyl)(1-methylnaphthalen-2-yl)methanone **(4ak)**: White solid (37.90 mg, 45% yield), mp 128–129 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 3H), 7.35 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.56–7.64 (m, 2H), 7.77 (d, J = 8.4 Hz, 3H), 7.90 (d, J =7.6 Hz, 1H), 8.12 (d, J = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.5, 124.6, 124.9, 126.4, 127.0, 127.1, 128.9, 129.1, 131.7, 132.8, 133.0, 134.1, 136.0, 136.3, 140.1, 198.3; IR (KBr) 3056, 1659, 1583, 1277, 1248, 1089, 935, 811, 759 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{18}H_{13}OCl$: 280.0655 $[M]^+$; found: 280.0659.

(3-Chlorophenyl)(1-methylnaphthalen-2-yl)methanone **(4al)**: Yellowish oil (38.74 mg, 46% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 3H), 7.34–7.41 (m, 2H), 7.54–7.61 (m, 3H), 7.68 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.82 (s, 1H), 7.90 (d, J = 7.2 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.5, 124.6, 124.9, 126.4, 127.0, 127.2, 128.5, 128.8, 130.08, 130.12, 132.8, 133.3, 133.4, 134.1, 135.1, 135.7, 139.6, 198.2; IR (neat) 3063, 1667, 1569, 1422, 1277, 1244, 1171, 1072, 945, 819, 757, 736 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{18}H_{13}OCl$: 280.0655 $[M]^+$; found: 280.0649.

(1,4-Dimethylnaphthalen-2-yl)(phenyl)methanone **(4ja)**: Yellowish solid (53.11 mg, 68% yield), mp 86–87 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3H), 2.68 (s, 3H), 7.21 (s, 1H), 7.45 (dd, J = 7.6, 7.6 Hz, 2H), 7.56–7.62 (m, 3H), 7.84 (d, J = 8.0 Hz, 2H), 8.05–8.07 (m, 1H), 8.11–8.14 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.5, 19.6, 124.9, 125.2, 125.3, 126.4, 126.7, 128.7, 130.3, 130.7, 132.5, 132.9, 133.3, 133.5, 136.3, 137.9, 199.9; IR (KBr) 3067, 2925, 2866, 1666, 1597, 1449, 1387, 1308, 1245, 1167, 929, 757, 718 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{16}O$: 260.1201 $[M]^+$; found: 260.1197.

(1-Methyl-4-phenylnaphthalen-2-yl)(phenyl)methanone **(4ka)**: Yellow oil (58.03 mg, 60% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 2.66 (s, 3H), 7.33 (s, 1H), 7.39–7.64 (m, 10H), 7.88 (d, J = 7.6 Hz, 2H), 7.97 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.6, 125.1, 125.5, 126.7, 126.98, 126.99, 127.6, 128.5, 128.8, 130.3, 130.4, 132.2, 132.3, 133.2, 133.6, 136.3, 137.9, 138.6, 140.3, 199.5; IR (neat) 3059, 2924, 2856, 1666, 1596, 1449, 1387, 1244, 1073, 944, 768, 702 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{24}H_{18}O$: 322.1358 $[M]^+$; found: 322.1348.

(4-Methoxy-1-methylnaphthalen-2-yl)(phenyl)methanone **(4la)**: Yellowish solid (63.00 mg, 76% yield), mp 82–83 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H), 3.94 (s, 3H), 6.70 (s, 1H), 7.45 (dd, J = 7.6, 7.6 Hz, 2H), 7.54–7.63 (m, 3H), 7.86 (d, J = 7.2 Hz, 2H), 8.03 (d, J = 7.6 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.0, 55.7, 102.7, 122.7, 124.2, 124.6, 126.2, 126.4, 127.3, 128.8, 130.3, 133.6, 133.7, 136.3, 137.8, 153.8, 199.7; IR (KBr) 3068, 2934, 2844, 1667, 1595, 1510, 1450, 1371, 1347, 1275, 1239, 1112, 937, 810, 763, 720 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{19}H_{16}O_2$: 276.1150 $[M]^+$; found: 276.1151.

(4-Bromo-1-methylnaphthalen-2-yl)(phenyl)methanone **(4ma)**: Yellow solid (59.51 mg, 61% yield), mp 96–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3H), 7.47 (dd, J = 7.6, 8.0 Hz, 2H), 7.59–7.71 (m, 4H), 7.83 (d, J = 6.8 Hz, 2H), 8.12 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 16.6, 121.0, 125.3, 127.7, 128.1, 128.3, 128.4, 128.9, 130.4, 132.4, 132.8, 133.9, 134.1, 137.1, 137.4, 197.9; IR (KBr) 3068, 2924, 1668, 1596, 1449, 1325, 1270, 1244, 1176, 943, 903, 801, 757, 725 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{18}H_{13}OBr$: 324.0150 [M]$^+$; found: 324.0154.

2-(Naphthalen-1-yl)-1-phenylethan-1-one **(5)**[21]: White solid (44.34 mg, 60% yield), mp 105–106 °C (lit. 105–107 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (s, 2H), 7.36 (d, J = 7.2 Hz, 1H), 7.44–7.51 (m, 5H), 7.56–7.60 (m, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.86–7.88 (m, 2H), 8.08 (d, J = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 43.1, 123.9, 125.5, 125.8, 126.3, 127.9, 128.0, 128.5, 128.7, 128.8, 131.4, 132.3, 133.3, 133.9, 136.7, 197.6.

2-(4-Methylnaphthalen-1-yl)-2-(o-tolyl)acetonitrile **(2ab)**: Colorless oil (70.01 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.69 (s, 3H), 5.88 (s, 1H), 7.13–7.17 (m, 1H), 7.21–7.25 (m, 3H), 7.29 (d, J = 7.2 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H), 7.48–7.56 (m, 2H), 7.78 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 19.5, 19.7, 36.8, 119.6, 123.3, 125.4, 126.2, 126.4, 126.6, 126.9, 127.0, 128.5, 128.58, 128.64, 130.7, 131.2, 133.4, 133.7, 135.9, 136.0; IR (neat) 3071, 3021, 2973, 2864, 2241, 1600, 1516, 1488, 1460, 1389, 1164, 1032, 910, 838, 748 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{20}H_{17}N$: 271.1361 [M]$^+$; found: 271.1356.

Deuterated (4-methylnaphthalen-1-yl)(phenyl)methanone **(3aa-*d*)**: Yellowish oil (51.94 mg, 70% yield, 97% D). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74 (s, 2H), 7.34 (d, J = 7.2 Hz, 1H), 7.42–7.58 (m, 6H), 7.85 (d, J = 8.0 Hz, 2H), 8.07 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 19.8 (t, J = 19.4 Hz), 124.6, 125.3, 126.47, 126.49, 127.1, 128.2, 128.5, 130.6, 131.2, 133.0, 133.2, 134.8, 138.5, 138.8, 198.2; IR (neat) 3060, 2922, 1656, 1590, 1579, 1513, 1448, 1274, 1250, 1202, 1074, 897, 828, 757, 716, 700 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{18}H_{13}DO$: 247.1107 [M]$^+$; found: 247.1116.

Supporting Information.

Detailed descriptions of preparation of deuterium-labeled substrate and X-ray data for **3aa**, **4ak** and **6** as well as copies of ^{1}H and ^{13}C{^{1}H} NMR spectra are presented in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) For selected reviews, see: (a) Vilums, M.; Heuberger, J.; Heitman, L. H.; IJzerman, A. P. Indanes–Properties, Preparation, and Presence in Ligands for G Protein Coupled Receptors. *Med. Res. Rev.* **2015**, *35*, 1097–1126. (b) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. Semiconducting π–Conjugated Systems in Field–Effect Transistors: A Material Odyssey of Organic Electronics. *Chem. Rev.* **2012**, *112*, 2208–2267. (c) Thomas, R. A Biosynthetic Classification of Fungal and Streptomycete Fused–Ring Aromatic Polyketides. *ChemBioChem* **2001**, *2*, 612–627.

(2) For selected a book, see: (a) Mortier, J. Arene Chemistry: Reaction Mechanisms and Methods for Aromatic Compounds; John Wiley & Sons, Inc., **2015**. For selected reviews, see: (b) Yan, M.; Kawamata, Y.; Baran, P. S. Synthetic Organic Electrochemical Methods Since 2000: On the Verge of a Renaissance. *Chem. Rev.* **2017**, *117*, 13230–13319. (c) Shi, J.; Li, Y.; Li, Y. Aryne multifunctionalization with benzdiyne and benztriyne equivalents. *Chem. Soc. Rev.*

2017, *46*, 1707–1719. (d) Yuzawa, H.; Yoshida, H. Direct Functionalization of Aromatic Rings on Platinum–loaded Titanium Oxide Photocatalyst. *Chem. Lett.* **2013**, *42*, 1336–1343. (e) Sartori, G.; Maggi, R. Use of Solid Catalysts in Friedel–Crafts Acylation Reactions. *Chem. Rev.* **2006**, *106*, 1077–1104.

(3) For a book, see: (a) Dixneuf, P. H.; Doucet, H. C–H Bond Activation and Catalytic Functionalization; Springer, Switzerland, **2016**. For selected recent reviews, see: (b) Qin, Y.; Zhu, L.; Luo, S. Organocatalysis in Inert C–H Bond Functionalization. *Chem. Rev.* **2017**, *117*, 9433–9520. (c) Murakami, K.; Yamada, S.; Kaneda, T.; Itami, K. C–H Functionalization of Azines. *Chem. Rev.* **2017**, *117*, 9302–9332. (d) Wei, Y.; Hu, P.; Zhang, M.; Su, W. Metal-Catalyzed Decarboxylative C–H Functionalization. *Chem. Rev.* **2017**, *117*, 8864–8907. (e) Neufeldt, S. R.; Sanford, M. S. Controlling Site Selectivity in Palladium-Catalyzed C–H Bond Functionalization. *Acc. Chem. Res.* **2012**, *45*, 936–946.

(4) Colby, D. A,; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. Rhodium Catalyzed Chelation-Assisted C–H Bond Functionalization Reactions. *Acc. Chem. Res.* **2012**, *45*, 814–825.

(5) (a) Leitch, J. A.; Frost, C. G. Ruthenium-catalysed σ-activation for remote meta-selective C ‑ H functionalization. *Chem. Soc. Rev.* **2017**, *46*, 7145–7153. (b) Ackermann, L. Carboxylate-Assisted Ruthenium-Catalyzed Alkyne Annulations by C–H/Het–H Bond Functionalizations. *Acc. Chem. Res.* **2014**, *47*, 281–295.

(6) Haldar, C.; Hoque, Md E.; Bisht, R.; Chattopadhyay, B. Concept of Ir-catalyzed C–H bond activation/borylation by noncovalent interaction. *Tetrahedron Lett.* **2018**, *59*, 1269–1277.

(7) Gao, K.; Yoshikai, N. Low-Valent Cobalt Catalysis: New Opportunities for C–H Functionalization. *Acc. Chem. Res.* **2014**, *47*, 1208–1219.

(8) (a) Liu, J.; Chen, G.; Tan, Z. Copper-Catalyzed or -Mediated C–H Bond Functionalizations Assisted by Bidentate Directing Groups. *Adv. Synth. Catal.* **2016**, *358*, 1174–1194. (b) Guo, X.-X.; Gu, D.-W.; Wu, Z.; Zhang, W. Copper-Catalyzed C–H Functionalization Reactions: Efficient Synthesis of Heterocycles. *Chem. Rev.* **2015**, *115*, 1622–1651.

(9) For selected reviews, see: (a) He, J.; Wasa, M.; Chan, K. S. L.; Shao, Q.; Yu, J.-Q. Palladium-Catalyzed Transformations of Alkyl C–H Bonds. *Chem. Rev.* **2017**, *117*, 8754–8786. (b) Musaev, D. G.; Figg, T. M.; Kaledin, A. L. Versatile reactivity of Pd-catalysts: mechanistic features of the mono-N-protected amino acid ligand and cesium-halide base in Pd-catalyzed C–H bond functionalization. *Chem. Soc. Rev.* **2014**, *43*, 5009–5031. (c) Sigman, M. S.; Werner, E. W. Imparting Catalyst Control upon Classical Palladium-Catalyzed Alkenyl C–H Bond Functionalization Reactions. *Acc. Chem. Res.* **2012**, *45*, 874–884.

(10) Terrier, F. Modern Nucleophilic Aromatic Substitution; Wiley-VCH Verlag GmbH & Co. KGaA, **2013**.

(11) For selected a review, see: (a) Rose-Munch, F.; Rose, E. Application of (eta(6)-arene) chromium tricarbonyl complexes in organic synthesis: Nucleophilic aromatic substitution and lithiation. *Curr. Org. Chem.* **1999**, *3*, 445–467. For selected recent references, see: (b) Ricci, P. Krämer, K. Larrosa, I. Tuning Reactivity and Site Selectivity of Simple Arenes in C‑H Activation: Ortho-Arylation of Anisoles via Arene‑Metal π-Complexation. *J. Am. Chem. Soc.* **2014**, *136*, 18082–18086. (c) Pigge, F. C.; Coniglio, J. J.; Dalvi, R. Exploiting Phosphonate Chemistry in Metal-Mediated Dearomatization: Stereoselective Construction of Functionalized Spirolactams from Arene Ruthenium Complexes. *J. Am. Chem. Soc.* **2006**, *128*, 3498–3499.

(12) Mendis, S. N.; Tunge, J. A. Decarboxylative dearomatization and mono-α-arylation of ketones. *Chem. Commun.* **2016**, *52*, 7695–7698.

(13) Ueno, S.; Komiya, S.; Tanaka, T.; Kuwano, R. Intramolecular SN′–Type Aromatic Substitution of Benzylic Carbonates at their Para-Position. *Org. Lett.* **2012**, *14*, 338–341.

(14) (a) Zhang, S.; Wang, Y.; Feng, X.; Bao, M. Palladium-Catalyzed Amination of Chloromethylnaphthalene and Chloromethylanthracene Derivatives with Various Amines. *J. Am. Chem. Soc.* **2012**, *134*, 5492–5495. (b) Peng, B.; Zhang, S.; Yu, X.; Feng, X.; Bao, M. Nucleophilic Dearomatization of Chloromethyl Naphthalene Derivatives via η^3-Benzylpalladium Intermediates: A New Strategy for Catalytic Dearomatization. *Org. Lett.* **2011**, *13*, 5402–5405.

(15) The direct nucleophilic substitution reaction of 1-(chloromethyl)naphthalenes with a nucleophile appeared in supporting informations of literatures, see: (a) Zhao, X.; Zhou, J.; Lin, S.; Jin, X.; Liu, R. C–H Functionalization via Remote Hydride Elimination: Palladium Catalyzed Dehydrogenation of ortho-Acyl Phenols to Flavonoids. *Org. Lett.* **2017**, *19*, 976–979. (b) Yan, H.; Li, Z.-F.; Guo, Z.-F.; Lu, Z.-L.; Wang, F.; Wu, L.-Z. Effective and reversible DNA condensation induced by bifunctional molecules containing macrocyclic polyamines and naphthyl moieties. *Bioorg. Med. Chem.* **2012**, *20*, 801–808.

(16) (a) Khodaei, M. M.; Alizadeh, A.; Nazari, E. Tf_2O as a rapid and efficient promoter for the dehydrative Friedel–Crafts acylation of aromatic compounds with carboxylic acids. *Tetrahedron Lett.* **2007**, *48*, 4199–4202. (b) Gmouh, S.; Yang, H.; Vaultier, M. Activation of Bismuth(III) Derivatives in Ionic Liquids: Novel and Recyclable Catalytic Systems for Friedel–Crafts Acylation of Aromatic Compounds. *Org. Lett.* **2003**, *5*, 2219–2222.

(17) (a) Xie, H.; Zhang, H; Lin, Z. DFT Studies on the Palladium-Catalyzed Dearomatization Reaction between Chloromethylnaphthalene and the Cyclic Amine Morpholine. *Organometallics* **2013**, *32*, 2336–2343. (b) Ariafard, A.; Lin, Z. DFT Studies on the

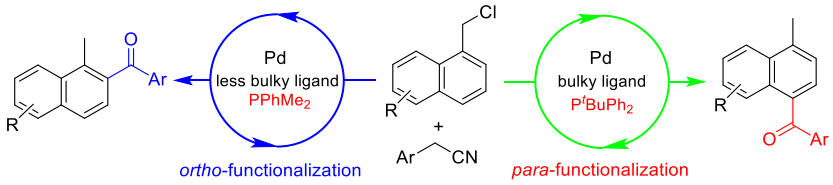
Mechanism of Allylative Dearomatization Catalyzed by Palladium. *J. Am. Chem. Soc.* **2006**, *128*, 13010–13016.

(18) Johns, A. M.; Utsunomiya, M.; Incarvito, C. D.; Hartwig, J. F. A Highly Active Palladium Catalyst for Intermolecular Hydroamination. Factors that Control Reactivity and Additions of Functionalized Anilines to Dienes and Vinylarenes. *J. Am. Chem. Soc.* **2006**, *128*, 1828–1839.

(19) Ye, J.; Wu, J.; Lv, T.; Wu, G.; Gao, Y.; Chen, H. Oxidative Rearrangement Coupling Reaction for the Functionalization of Tetrahydro-β-carbolines with Aromatic Amines. *Angew. Chem., Int. Ed.* **2017**, *56*, 14968–14972.

(20) Zhu, S.; Zhang, Z.; Huang, X.; Jiang, H.; Guo, Z. Gold-Catalyzed Reactions of Enynals/Enynones with Norbornenes: Generation and Trapping of Cyclic *o*-Quinodimethanes (*o*-QDMs) *Chem.-Eur. J.*, **2013**, *19*, 4695–4700.

(21) Fu, W. C.; So, C. M.; Yuen, O. Y.; Lee, I. T. C.; Kwong, F. Y. Exploiting Aryl Mesylates and Tosylates in Catalytic Mono-α-arylation of Aryl- and Heteroarylketones. *Org. Lett.*, **2016**, *18*, 1872–1875.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