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Rh(II)-Catalyzed Synthetic Strategy for Diverse and Functionalized Halonaphthalenyl Ethers and Esters from Diazo Compounds and Its Application to Polyaromatic Compounds

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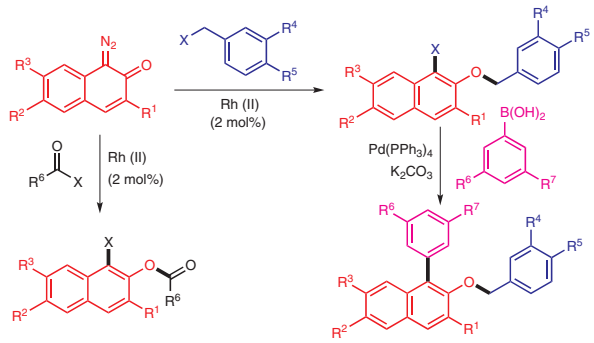

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Abstract An efficient and simple synthesis of various functionalized halonaphthalenyl ethers and esters in moderate to good yield was achieved via rhodium(II)-catalyzed reaction of readily available diazo compounds with benzyl halides or acid halides. This methodology has several advantages, such as ease of handling, mild reaction conditions, bromine- or chlorine-free route, and the use of an effective catalyst. The synthesized compounds were further converted into valuable polyaromatic compounds using the Suzuki reaction.

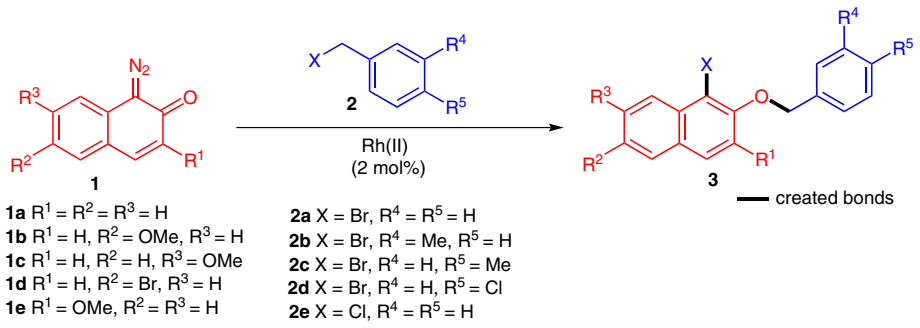
Key words diazo compounds, rhodium(II) catalyst, halonaphthalenyl ethers, halonaphthalenyl esters, polyaromatic compounds

The halogenation of aromatic compounds provides important chemical precursors for the synthesis of valuable drugs, pharmaceuticals, agrochemicals, bioactive natural products, and photographic materials.[1] In addition, halogenated aromatic compounds have been widely used as key intermediates in the preparation of organometallic reagents for the synthesis of a wide variety of biologically active molecules and functional materials.[2] They have also found widespread utility as vital starting materials in transition-metal-catalyzed coupling reactions for the preparation of new molecules.[3] Typical approaches for the halogenation of aromatic molecules include direct electrophilic aromatic substitution using Cl_2 and Br_2 in the presence of Lewis acids, Brønsted acids, and ionic liquids as catalysts and promoters.[4] These methods are quite cumbersome because of their toxicity and hazardous nature. To avoid these problems, other methods using *N*-halosuccinimide/catalysts,[5] HX/peroxides,[6] MX/peroxides,[7] and MX/hypervalent iodines[8] as halogenating reagents have been developed. In addition, a variety of other effective approaches for halogenation have also been reported, which include iron-mediated photolytic reaction,[9] palladium- or copper-catalyzed reactions,[10,11] and Cu-Mn spinel oxide catalyzed reaction,[12] and further reactions using a non-heme iron halide complex[13] and iron(III) *meso*-chloro-isoporphyrin.[14]

Despite their merits, many of the reported methods suffer from drawbacks, including toxic reagents, harsh reaction conditions, side reactions of overhalogenation, low yields, and low chemo- and regioselectivity. Therefore, more environmentally benign and efficient methods are needed to overcome these limitations, which prompted this study to develop new approaches for the halogenation of aromatic compounds via the decomposition of diazo compounds.

The decomposition of diazo compounds has been used widely in organic synthesis, and it is an important tool for the synthesis of a wide range of organic molecules.[15] Previous studies examined the decomposition of diazo compounds and various substrates, developing novel methodologies for the synthesis of heterocycles[16] and valuable molecules.[17] Among these, a methodology for preparing β-substituted α-haloenones and α,β-dihaloenones using rhodium(II)- or ruthenium(II)-catalyzed reactions of cyclic diazodicarbonyl compounds with acid chlorides, benzyl halides, or oxalyl halides was reported.[18,19] In related work, the transition-metal-catalyzed[20] and hypervalent iodine-based halogenations of diazo compounds have been reported by other groups.[21]

As a result of an ongoing study in this area, herein we report rhodium(II)-catalyzed reactions of 1-diazonaphthalen-2(1*H*)-ones with benzyl halides to form diverse and functionalized halonaphthalenyl ethers. This is the first example of the synthesis of diverse and functionalized halonaphthalenyl ethers starting from diazo compounds **1a**–**e** and benzyl halides **2a**–**e** by rhodium(II)-catalyzed reactions (Scheme 1).



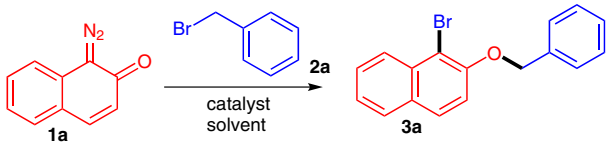
1a $R^1 = R^2 = R^3 = H$
1b $R^1 = H$, $R^2 = OMe$, $R^3 = H$
1c $R^1 = H$, $R^2 = H$, $R^3 = OMe$
1d $R^1 = H$, $R^2 = Br$, $R^3 = H$
1e $R^1 = OMe$, $R^2 = R^3 = H$

2a X = Br, $R^4 = R^5 = H$
2b X = Br, $R^4 = Me$, $R^5 = H$
2c X = Br, $R^4 = H$, $R^5 = Me$
2d X = Br, $R^4 = H$, $R^5 = Cl$
2e X = Cl, $R^4 = R^5 = H$

Scheme 1 Rhodium(II)-catalyzed synthesis of various halonaphthalenyl ethers from 1-diazonaphthalen-2(1*H*)-ones

The diazo compounds **1a**–**e** and **6** were prepared from the corresponding naphthols using 2-azido-1,3-dimethylimidazolinium chloride according to the reported procedure.[22] This study commenced by optimizing the reaction conditions for the synthesis of **3a** using various catalysts and solvents (Table 1).

Table 1 Optimization for the Synthesis of **3a** from **1a** and **2a** Using Various Catalysts and Solvents[a]



Entry	Catalyst	Solvent	Conditions	Yield[b] (%)
1	$In(OAc)_3$ (5 mol%)	PhF	r.t., 24 h	0
2	$Cu(OAc)_2$ (5 mol%)	PhF	r.t., 24 h	0
3	$FeCl_3$ (5 mol%)	PhF	r.t., 24 h	0
4	$Au(PPh_3)_3Me$ (5 mol%)	PhF	r.t., 24 h	0
5	$Pd(OAc)_2$ (5 mol%)	PhF	r.t., 24 h	0
6	$Ru(PPh_3)_3Cl_2$ (2 mol%)	PhF	r.t., 24 h	10
7	$Rh_2(OAc)_4$ (2 mol%)	PhF	r.t., 24 h	35
8	$Rh_2(OPiv)_4$ (2 mol%)	PhF	r.t., 15 h	70
9	$Rh_2(OPiv)_4$ (2 mol%)	benzene	r.t., 15 h	60
10	$Rh_2(OPiv)_4$ (2 mol%)	toluene	r.t., 15 h	65
11	$Rh_2(OPiv)_4$ (2 mol%)	CH_2Cl_2	r.t., 15 h	40
12	$Rh_2(OPiv)_4$ (1 mol%)	PhF	r.t., 15 h	48
13	$Rh_2(OPiv)_4$ (5 mol%)	PhF	r.t., 15 h	52

[a] Reactions were carried out using **1a** (1.0 mmol) and **2a** (10 mmol) in solvent (5 mL) under N_2.
[b] Isolated yield after column chromatography.

No products were formed when **1a** was treated with **2a** in the presence of 5 mol% of indium(III) acetate, copper(II) acetate, iron(III) chloride, methyltris(triphenylphosphine)gold(I), and palladium(II) acetate in fluorobenzene at room temperature for 24 hours (entries 1–5). With 2 mol% of tris(triphenylphosphine)ruthenium(II) dichloride in fluorobenzene at room temperature for 24 hours, product **3a** was obtained in 10% yield (entry 6). With 2 mol% of rhodium(II) acetate at room temperature for 24 hours, the yield of product **3a** increased to 35% (entry 7). The best yield (70%) was obtained with 2 mol% of rhodium(II) pivalate in fluorobenzene at room temperature for 15 hours (entry 8). The yield of **3a** did not increase using other solvents, such as benzene, toluene, and dichloromethane (entries 9–11). Increasing or decreasing the rhodium(II) pivalate loading did not improve the yield (entries 12 and 13). The structure of **3a** was determined by analysis of the spectral data and by comparison with the spectra of a reported compound.[23] The ^1H NMR spectrum of **3a** showed a benzylic signal at δ = 5.20 as a singlet. The structure was further confirmed by the ^{13}C NMR spectrum, which showed the benzylic carbon at δ = 71.8.

Under the optimized conditions, the generality of this decomposition reaction was explored further by employing different diazo compounds and benzyl halides (Figure 1). Reactions of **1a** with 3-methyl- or 4-methylbenzyl bromide bearing electron-donating group in fluorobenzene afforded the expected products **3b** and **3c** in 65 and 62% yield, respectively. In addition, the reactions of diazo compound **1b**–**d** bearing electron-donating or -withdrawing groups, such as OMe or Br, on the benzene ring were also successful. The reaction of **1b** or **1c** bearing an electron-donating group with **2a**–**c** provided the desired products **3d**–**h** in 60–70% yield, and that of **1d** bearing an electron-withdrawing group afforded **3i**–**k** in 55–72% yield. Similarly, the diazo **1d** yielded the product **3l** in 60% when treated with 4-chlorobenzyl bromide bearing electron-withdrawing group in the *para* position. The combination of the other diazo compound **1e** with benzyl or 3-methylbenzyl bromide afforded **3m** (69%) and **3n** (63%), respectively. The combination of diazo compounds **1d** or **1e** with benzyl chloride provided the corresponding products **3o** and **3p** in 57 and 60% yield, respectively.

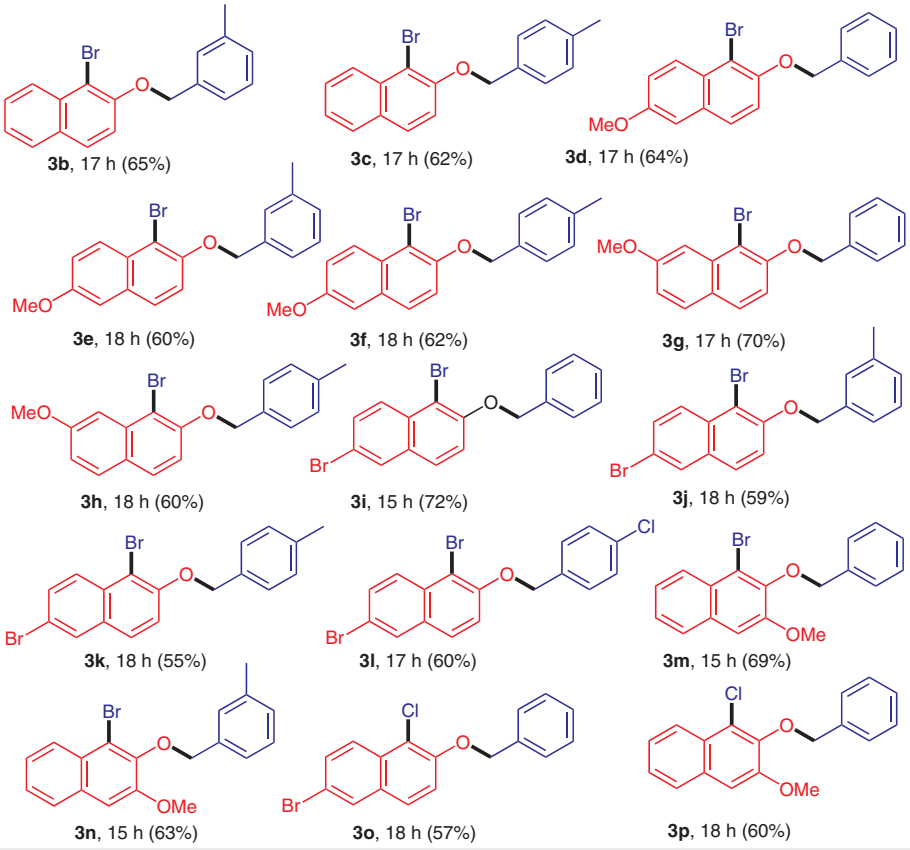
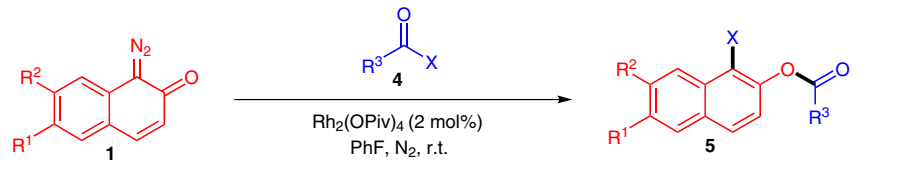


Figure 1 Formation of various halonaphthalenyl ethers **3b–p** from the 1-diazonaphthalene-2(1*H*)-ones **1a–e** and benzyl halides **2a–e**

To further demonstrate the versatility of this reaction, other decomposition reactions using acid halides, which will lead to the formation of halonaphthalenyl esters, were next examined (Scheme 2). For example, the decomposition of **1a–d** with acetyl chloride (**4a**) in fluorobenzene at room temperature for 17 hours provided the corresponding chloronaphthalenyl chlorides **5a–d** in 52–60% yield. Similarly, the reaction of **1b** with benzoyl bromide (**4b**) in fluorobenzene afforded bromonaphthalenyl ester **5e** in 52% yield after 17 hours.

Considering the general applicability for the synthesis of 1-halonaphthalenyl ethers **3a–p** and 1-halonaphthalenyl esters **5a–e** using 1-diazonaphthalen-2(1*H*)-ones **1a–e** as the starting materials, this study examined whether this approach was suitable using 2-diazonaphthalen-1(2*H*)-one (**6**), which will allow the formation of the 2-halonaphthalenyl ether and 2-halonaphthalenyl ester (Scheme 3). Reaction of **6** with **2a** in the presence of 2 mol% of rhodium(II) pivalate in fluorobenzene at room temperature for 18 hours

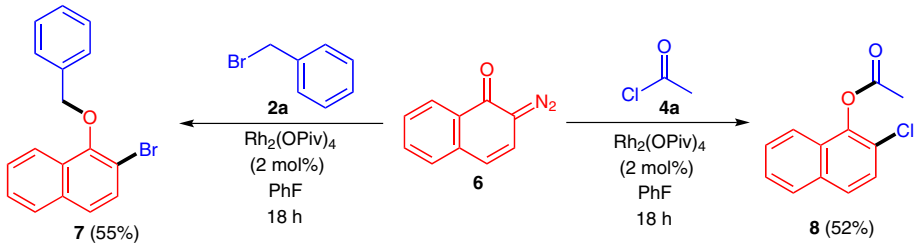


1a $R^1 = R^2 = H$
1b $R^1 = OMe$, $R^2 = H$
1c $R^1 = H$, $R^2 = OMe$
1d $R^1 = Br$, $R^2 = H$

4a $R^3 = Me$, X = Cl
4b $R^3 = Ph$, X = Br

5a $R^1 = R^2 = H$, $R^3 = Me$, X = Cl, 52%
5b $R^1 = OMe$, $R^2 = H$, $R^3 = Me$, X = Cl, 56%
5c $R^1 = H$, $R^2 = OMe$, $R^3 = Me$, X = Cl, 58%
5d $R^1 = Br$, $R^2 = H$, $R^3 = Me$, X = Cl, 60%
5e $R^1 = OMe$, $R^2 = H$, $R^3 = Ph$, X = Br, 52%

Scheme 2 Reaction of diazo compounds **1a–d** with acetyl chloride (**4a**) or benzoyl bromide (**4b**) for the formation of chloro or bromonaphthalenyl esters **5a–e**



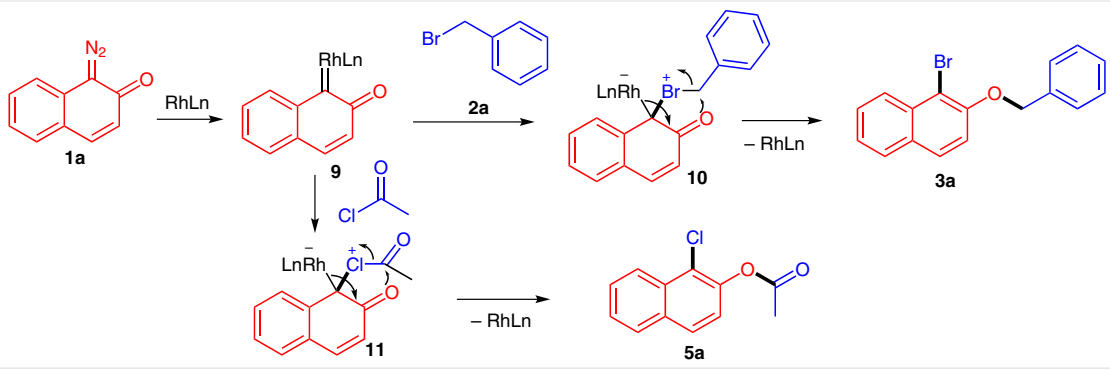
Scheme 3 Reaction of 2-diazonaphthalen-1(2*H*)-one (**6**) with **2a** and **4a** for the synthesis of bromonaphthalenyl ether **7** and chloronaphthalenyl ester **8**

provided 2-bromonaphthalenyl ether **7** (55%), and the reaction with acetyl chloride (**4a**) afforded 2-chloronaphthalenyl ester **8** (52%).

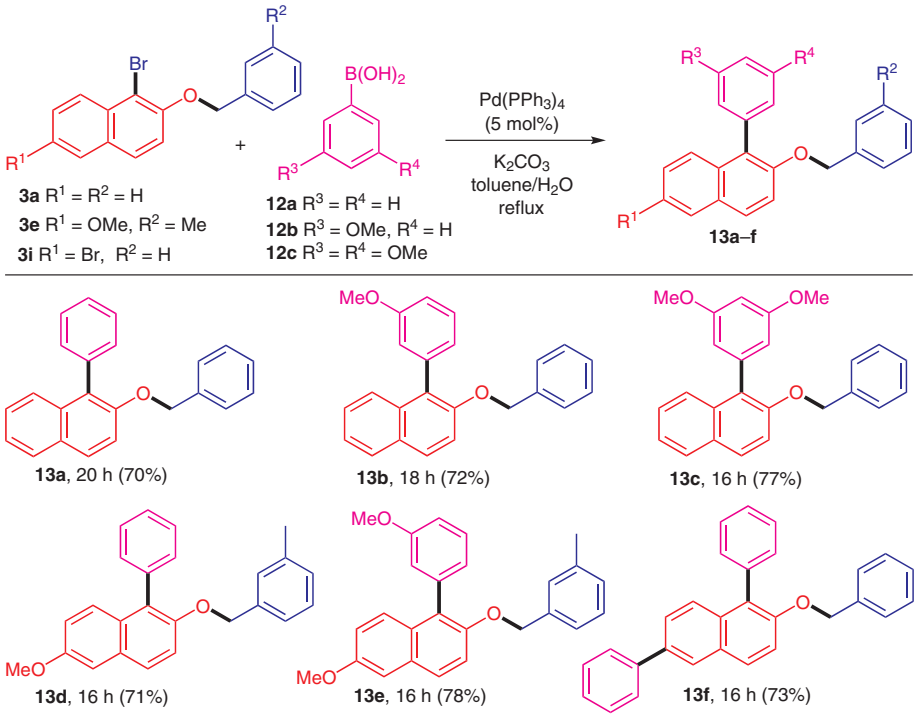
The proposed reaction mechanism for the formation of **3a** and **5a** can be explained, as shown in Scheme 4. The diazo compound **1a** in the presence of rhodium(II) catalyst first formed rhodium carbenoid **9** by loss of nitrogen. The nucleophilic attack of the bromine atom of benzyl bromide to **9** provided another intermediate **10**. The intramolecular nucleophilic attack of oxygen to carbon on the benzylic position followed by C–Br bond cleavage provided the final product **3a**. In the case of ester formation of **5a**, nucleophilic attack of the chlorine atom of the acid chloride to rhodium carbenoid **9** provided intermediate **11**, which underwent intramolecular nucleophilic attack followed by cleavage of the C–Cl bond to produce the product **5a**.

As an application of this methodology, the conversion of the synthesized compounds **3a**, **3e**, and **3i** into polyaromatic compounds was next attempted using the Suzuki reactions, as shown in Scheme 5. Recently, naphthalenyl group based polyaromatic molecules have attracted considerable interest in the fields of light emitting diodes (LEDs) and organic light emitting diodes (OLEDs) because they are used widely as highly efficient and stable-light emitting materials.[24] The reaction of **3a** with 1.1 equivalents of phenyl- (**12a**), 3-methoxyphenyl- (**12b**) or 3,5-dimethoxyphenylboronic acid (**12c**) in the presence of 5 mol% of $Pd(PPh_3)_4$ in refluxing aqueous toluene for 16–20 hours gave **13a–c** in 70, 72, and 77% yield, respectively, whereas the treatment of **3e** bearing a methoxy group on the naphthalenyl ring with **12a** or **12b** formed **13d** and **13e** in 71 and 78% yield, respectively. Importantly, the reaction of **3i** bearing a Br group on the naphthalenyl ring with 2.2 equivalents of **12a** in refluxing aqueous toluene for 16 hours provided product **13f** in 73% yield. The formation of these products was confirmed by ^1H and ^{13}C NMR spectroscopy. The results show that this synthetic approach can be used widely to introduce benzene rings on the naphthalenyl nucleus.

An environmentally benign and efficient process for the synthesis of diverse halonaphthalenyl ethers and esters was developed by the rhodium(II)-catalyzed reaction of diazo compounds and benzyl halides or acid halides. This synthetic approach for various functionalized halonaphthalenyl ethers and esters involves simultaneous halogenation and ether or ester formation as a one-pot procedure. This novel protocol has important advantages, such as simple operation, bromine- or chlorine-free route, and mild catalyst, over the existing methodologies. The synthesized compounds were further transformed into valuable polyaromatic compounds using the Suzuki reaction.



Scheme 4 Proposed mechanism for the formation of **3a** and **5a**



Scheme 5 Formation of polyaromatic compounds **13a–f** by the Suzuki coupling reaction of the synthesized compounds **3a**, **3e**, and **3i**

All experiments were carried out under a N_2 atmosphere. Merck, precoated silica gel plates (Art. 5554) with a fluorescent indicator were used for analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). ^{1}H NMR spectra were recorded on Varian VNS 300 or 600 MHz or DPX (Bruker) 300 MHz spectrometers relative to TMS (δ = 0) as internal standard or relative to the resonance of the residual protonated solvent (^{1}H: $CDCl_3$, δ = 7.24). ^{13}C NMR spectra were obtained at 75 MHz or 150 MHz spectrometers and referenced to the internal solvent signals (^{13}C: $CDCl_3$, δ = 77.0). IR spectra were recorded on a Jasco FTIR 5300 spectrophotometer. Melting points were measured with a Fisher-Johns melting point apparatus and are uncorrected. HRMS were measured using a Jeol JMS-600 mass spectrometer (positive ion EI mode) at the Korean Basic Science Institute.

Halonaphthalenyl Ethers 3a–p and 7; General Procedure

To a solution of diazo compound **1a–e** or **6** (1 mmol) and benzyl halide **2a–e** (10 mmol) in PhF (5 mL) was added $Rh_2(OPiv)_4$ (2 mol%). The mixture was stirred under N_2 at r.t. for 15–18 h. Then, the solvent was evaporated on a rotary evaporator under reduced pressure. The residue thus obtained was purified by flash column chromatography (silica gel) to isolate the product.

2-(Benzyloxy)-1-bromonaphthalene (3a)

Solid; yield: 218 mg (70%); mp 105–107 °C.

IR (KBr): 3061, 2364, 1625, 1501, 1343, 1266, 1052, 802, 749 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.7 Hz, 1 H), 7.68–7.64 (m, 2 H), 7.50–7.42 (m, 3 H), 7.30 (t, *J* = 6.9 Hz, 3 H), 7.24 (d, *J* = 7.2 Hz, 1 H), 7.16 (d, *J* = 8.7 Hz, 1 H), 5.20 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0, 136.6, 130.0, 129.2, 128.7, 128.5, 127.9, 127.7, 127.6, 127.1, 126.2, 124.4, 115.6, 110.0, 71.8.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{17}H_{13}BrO$: 312.0150; found: 312.0150.

1-Bromo-2-(3-methylbenzyloxy)naphthalene (3b)

Solid; yield: 212 mg (65%); mp 46–48 °C.

IR (KBr): 2922, 2368, 1622, 1502, 1459, 1341, 1267, 1074, 821, 753 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.4 Hz, 1 H), 7.69 (q, *J* = 8.4 Hz, 2 H), 7.49 (t, *J* = 7.8 Hz, 1 H), 7.32 (t, *J* = 8.4 Hz, 1 H), 7.26 (d, *J* = 7.2 Hz, 1 H), 7.21–7.17 (m, 3 H), 7.06 (d, *J* = 7.8 Hz, 1 H), 5.19 (s, 2 H), 2.30 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0, 138.2, 136.6, 133.2, 130.0, 128.7, 128.7, 128.4, 128.0, 127.8, 127.6, 126.2, 124.5, 124.2, 115.7, 110.0, 71.9, 21.4.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{15}BrO$: 326.0306; found: 326.0307.

1-Bromo-2-(4-methylbenzyloxy)naphthalene (3c)

Solid; yield: 196 mg (62%); mp 112–114 °C.

IR (KBr): 2923, 2372, 1622, 1504, 1452, 1340, 1268, 1070, 805, 742 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.4 Hz, 1 H), 7.68 (t, *J* = 8.4 Hz, 2 H), 7.48 (t, *J* = 7.8 Hz, 1 H), 7.33–7.30 (m, 2 H), 7.19 (d, *J* = 9.0 Hz, 2 H), 7.12 (d, *J* = 7.2 Hz, 2 H), 5.19 (s, 2 H), 2.28 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0, 137.7, 133.6, 133.1, 130.0, 129.2, 128.7, 127.9, 127.6, 127.3, 126.2, 124.4, 115.7, 110.0, 71.8, 21.1.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{15}BrO$: 326.0306; found: 326.0304.

2-(Benzyloxy)-1-bromo-6-methoxynaphthalene (3d)

Solid; yield: 219 mg (64%); mp 99–101 °C.

IR (KBr): 2925, 2371, 1597, 1497, 1456, 1344, 1256, 1029, 740, 693 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 9.0 Hz, 1 H), 7.62 (d, *J* = 8.4 Hz, 1 H), 7.50 (d, *J* = 7.8 Hz, 2 H), 7.37 (t, *J* = 7.8 Hz, 2 H), 7.32 (t, *J* = 8.4 Hz, 1 H), 7.22–7.20 (m, 2 H), 7.06 (d, *J* = 2.4 Hz, 1 H), 5.24 (s, 2 H), 3.89 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.7, 151.4, 136.8, 131.1, 128.6, 128.5, 127.9, 127.9, 127.3, 127.2, 120.3, 116.5, 110.5, 105.9, 72.1, 55.3.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{18}H_{15}BrO_2$: 342.0255; found: 342.0253.

1-Bromo-6-methoxy-2-(3-methylbenzyloxy)naphthalene (3e)

Solid; yield: 214 mg (60%); mp 83–85 °C.

IR (KBr): 2915, 2369, 1598, 1498, 1456, 1372, 1252, 1167, 1071, 851, 793, 691 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 9.0 Hz, 1 H), 7.63 (d, *J* = 9.0 Hz, 1 H), 7.33 (t, *J* = 7.8 Hz, 2 H), 7.28 (t, *J* = 7.8 Hz, 1 H), 7.25–7.22 (m, 2 H), 7.14 (d, *J* = 7.2 Hz, 1 H), 7.08 (d, *J* = 1.8 Hz, 1 H), 5.22 (s, 2 H), 3.91 (s, 3 H), 2.38 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.7, 151.5, 138.2, 136.7, 131.0, 128.6, 128.5, 128.4, 127.9, 127.9, 127.3, 124.3, 120.3, 116.6, 110.4, 105.9, 72.2, 55.3, 21.4.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{19}H_{17}BrO_2$: 356.0412; found: 356.0410.

1-Bromo-6-methoxy-2-(4-methylbenzyloxy)naphthalene (3f)

Solid; yield: 221 mg (62%); mp 105–107 °C.

IR (KBr): 2924, 2370, 1598, 1458, 1372, 1252, 1125, 1028, 798, 640 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 9.6 Hz, 1 H), 7.65 (d, *J* = 8.7 Hz, 1 H), 7.43 (d, *J* = 7.8 Hz, 2 H), 7.28–7.27 (m, 1 H), 7.24–7.21 (m, 3 H), 7.10 (d, *J* = 2.4 Hz, 1 H), 5.24 (s, 2 H), 3.93 (s, 3 H), 2.38 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.7, 151.5, 137.7, 133.8, 131.0, 129.2, 128.6, 127.9, 127.4, 127.2, 120.2, 116.7, 110.5, 106.0, 72.2, 55.3, 21.1.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{19}H_{17}BrO_2$: 356.0412; found: 356.0408.

2-(Benzyloxy)-1-bromo-7-methoxynaphthalene (3g)

Solid; yield: 239 mg (70%); mp 84–86 °C.

IR (KBr): 2927, 2380, 1627, 1509, 1455, 1381, 1264, 1221, 1030, 824, 732 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.65 (q, *J* = 5.4 Hz, 2 H), 7.52–7.50 (m, 3 H), 7.40–7.28 (m, 3 H), 7.10 (d, *J* = 8.7 Hz, 1 H), 7.03 (dd, *J* = 8.7, 2.1 Hz, 1 H), 5.27 (s, 2 H), 3.96 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 153.5, 136.7, 134.6, 129.7, 128.5, 128.5, 128.4, 127.9, 127.1, 125.3, 117.4, 112.7, 104.6, 71.6, 55.3.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{18}H_{15}BrO_2$: 342.0255; found: 342.0257.

1-Bromo-7-methoxy-2-(4-methylbenzyloxy)naphthalene (3h)

Solid; yield: 213 mg (60%); mp 76–78 °C.

IR (KBr): 2924, 2372, 1628, 1510, 1482, 1381, 1261, 1032, 816, 618 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.64 (q, *J* = 4.5 Hz, 2 H), 7.50 (d, *J* = 2.1 Hz, 1 H), 7.39 (d, *J* = 7.8 Hz, 2 H), 7.18 (q, *J* = 7.8 Hz, 2 H), 7.10 (d, *J* = 8.7 Hz, 1 H), 7.02 (dd, *J* = 8.7, 2.4 Hz, 1 H), 5.23 (s, 2 H), 3.95 (s, 3 H), 2.34 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 153.3, 137.4, 134.4, 133.4, 129.5, 129.0, 128.8, 128.2, 127.0, 125.1, 117.1, 112.6, 104.4, 71.4, 55.1, 20.9.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{19}H_{17}BrO_2$: 356.0412; found: 356.0414.

2-(Benzyloxy)-1,6-dibromonaphthalene (3i)

Solid; yield: 280 mg (72%); mp 83–85 °C.

IR (KBr): 3064, 2369, 1582, 1490, 1456, 1334, 1272, 1060, 799, 732 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 9.0 Hz, 1 H), 7.82 (s, 1 H), 7.57–7.50 (m, 2 H), 7.42 (d, *J* = 6.9 Hz, 2 H), 7.33–7.24 (m, 3 H), 7.17 (d, *J* = 9.0 Hz, 1 H), 5.20 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.1, 136.3, 131.7, 130.8, 129.7, 128.6, 128.1, 127.8, 127.4, 127.1, 126.7, 118.3, 115.6, 109.8, 71.6.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{17}H_{12}Br_2O$: 389.9255; found 389.9256.

1,6-Dibromo-2-(3-methylbenzyloxy)naphthalene (3j)

Solid; yield: 210 mg (59%); mp 63–65 °C.

IR (KBr): 2922, 2371, 1584, 1490, 1389, 1272, 1071, 802, 691 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 9.3 Hz, 1 H), 7.90 (d, *J* = 1.8 Hz, 1 H), 7.65–7.57 (m, 2 H), 7.30–7.26 (m, 4 H), 7.13–7.11 (m, 1 H), 5.24 (s, 2 H), 2.36 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.3, 138.3, 136.3, 130.8, 129.8, 128.8, 128.5, 128.2, 127.8, 127.8, 126.7, 124.2, 118.3, 117.6, 116.5, 113.4, 71.8, 21.4.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{18}H_{14}Br_2O$: 403.9411; found: 403.9410.

1,6-Dibromo-2-(4-methylbenzyloxy)naphthalene (3k)

Solid; yield: 222 mg (55%); mp 127–129 °C.

IR (KBr): 2926, 2357, 1556, 1510, 1451, 1382, 1265, 757, 661 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.4 Hz, 1 H), 7.90 (s, 1 H), 7.65–7.57 (m, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 7.27–7.16 (m, 3 H), 5.24 (s, 2 H), 2.33 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.2, 137.8, 133.3, 131.8, 130.8, 130.8, 129.8, 129.3, 128.2, 127.7, 127.2, 118.3, 116.5, 109.9, 71.7, 21.2.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{18}H_{14}Br_2O$: 403.9411; found: 403.9409.

1,6-Dibromo-2-(4-chlorobenzyloxy)naphthalene (3l)

Solid; yield: 255 mg (60%); mp 134–136 °C.

IR (KBr): 2923, 2368, 1564, 1511, 1472, 1380, 1260, 769, 651 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 9.0 Hz, 1 H), 7.93 (d, *J* = 1.2 Hz, 1 H), 7.67 (d, *J* = 8.4 Hz, 1 H), 7.61 (dd, *J* = 8.4, 1.2 Hz, 1 H), 7.45 (d, *J* = 9.0 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 7.25 (d, *J* = 1.2 Hz, 1 H), 5.25 (s, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.9, 134.9, 133.9, 131.8, 131.0, 130.9, 129.8, 128.8, 128.5, 128.2, 127.9, 118.6, 116.3, 110.1, 71.0.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{17}H_{11}Br_2ClO$: 425.8865; found: 425.8865.

2-(Benzyloxy)-1-bromo-3-methoxynaphthalene (3m)

Liquid; yield: 236 mg (69%).

IR (neat): 2960, 2359, 1463, 1490, 1257, 1119, 1027, 749, 696 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.17–8.14 (m, 1 H), 7.72–7.69 (m, 1 H), 7.61 (d, *J* = 6.6 Hz, 2 H), 7.47–7.34 (m, 5 H), 7.16 (s, 1 H), 5.12 (s, 2 H), 3.97 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.5, 146.0, 137.0, 131.6, 128.5, 128.3, 128.1, 127.8, 126.7, 126.7, 126.0, 125.0, 116.8, 106.9, 74.8, 55.8.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{15}BrO_2$: 342.0255; found: 342.0255.

1-Bromo-3-methoxy-2-(3-methylbenzyloxy)naphthalene (3n)

Liquid; yield: 224 mg (63%).

IR (neat): 2926, 2359, 1645, 1537, 1452, 1342, 1268, 804, 755 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25–8.22 (m, 1 H), 7.79–7.76 (m, 1 H), 7.54–7.46 (m, 4 H), 7.39–7.31 (m, 1 H), 7.24–7.22 (m, 2 H), 5.15 (s, 2 H), 4.06 (s, 3 H), 2.47 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.6, 146.1, 137.9, 137.0, 131.6, 129.1, 128.8, 128.2, 127.9, 126.7, 126.7, 126.0, 125.5, 125.0, 116.8, 106.9, 74.9, 55.9, 21.4.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{19}H_{17}BrO_2$: 356.0412; found: 356.0408.

2-(Benzyloxy)-6-bromo-1-chloronaphthalene (3o)

Solid; yield: 197 mg (57%); mp 66–68 °C.

IR (KBr): 2926, 2359, 1645, 1537, 1452, 1342, 1268, 804, 755 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.7 Hz, 1 H), 7.91 (d, *J* = 1.8 Hz, 1 H), 7.60 (d, *J* = 8.7 Hz, 2 H), 7.49–7.46 (m, 2 H), 7.40–7.27 (m, 4 H), 5.28 (s, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.8, 136.2, 130.4, 130.3, 129.6, 128.7, 128.5, 128.4, 127.9, 126.9, 126.6, 125.3, 118.2, 116.4, 71.5.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{17}H_{12}BrClO$: 345.9760; found: 345.9761.

2-(Benzyloxy)-1-chloro-3-methoxynaphthalene (3p)

Liquid; yield: 179 mg (60%).

IR (neat): 2930, 2354, 1643, 1463, 1329, 1260, 761, 645 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15–8.12 (m, 1 H), 7.72–7.67 (m, 1 H), 7.57 (d, *J* = 6.6 Hz, 2 H), 7.45–7.29 (m, 5 H), 7.11 (s, 1 H), 5.11 (s, 2 H), 3.97 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.6, 144.7, 137.0, 131.2, 128.6, 128.5, 128.3, 128.1, 126.7, 126.0, 124.8, 124.1, 116.1, 106.0, 75.1, 55.9.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{15}ClO_2$: 298.0761; found: 298.0758.

1-(Benzyloxy)-2-bromonaphthalene (7)

Solid; yield: 172 mg (55%); mp 48–50 °C.

IR (KBr): 3059, 2367, 1604, 1510, 1368, 1210, 1017, 820, 750 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12–8.09 (m, 1 H), 7.80 (s, 1 H), 7.62–7.59 (m, 3 H), 7.53–7.37 (m, 6 H), 5.12 (s, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.9, 136.8, 133.9, 130.1, 129.3, 128.5, 128.3, 128.2, 128.0, 126.7, 126.5, 125.4, 122.1, 113.1, 75.6.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{17}H_{13}BrO$: 312.0150; found: 312.0149.

Chloronaphthalenyl Esters 5a–e and 8; General Procedure

To a solution of diazo compounds **1a**–**d**, or **6** (1 mmol) and acetyl chloride (**4a**) or benzoyl bromide (**4b**) (10 mmol) in PhF (5 mL) was added $Rh_2(OPiv)_4$ (2 mol%). The mixture was stirred under N_2 for 17 h. Then, the remaining acetyl chloride was evaporated on a rotary evaporator under reduced pressure. The residue thus obtained was purified by flash column chromatography (silica gel) to isolate the product.

1-Chloronaphthalen-2-yl Acetate (5a)

Solid; yield: 114 mg (52%); mp 62–64 °C.

IR (KBr): 3060, 2931, 2369, 1758, 1509, 1370, 1212, 1017, 820, 754 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82–7.73 (m, 3 H), 7.51 (d, *J* = 2.1 Hz, 1 H), 7.45–7.41 (m, 1 H), 7.21–7.17 (m, 1 H), 2.31 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.6, 148.2, 133.7, 131.4, 129.3, 127.7, 127.6, 126.5, 125.6, 121.0, 118.4, 21.1.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{12}H_9ClO_2$: 220.0291; found: 220.0292.

1-Chloro-6-methoxynaphthalen-2-yl Acetate (5b)

Solid; yield: 140 mg (56%); mp 79–81 °C.

IR (KBr): 2999, 2940, 2834, 1750, 1602, 1365, 1198, 1018, 853, 816, 711 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 9.0 Hz, 1 H), 7.56 (d, *J* = 9.0 Hz, 1 H), 7.27 (dd, *J* = 9.0, 2.4 Hz, 1 H), 7.21 (d, *J* = 9.0 Hz, 1 H), 7.13 (d, *J* = 2.4 Hz, 1 H), 3.92 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.9, 158.0, 142.9, 133.7, 129.0, 126.6, 126.4, 125.9, 122.2, 120.2, 106.2, 55.4, 20.7.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{13}H_{11}ClO_3$: 250.0397; found: 250.0400.

1-Chloro-7-methoxynaphthalen-2-yl Acetate (5c)

Solid; yield: 145 mg (58%); mp 69–71 °C.

IR (KBr): 3009, 2905, 2855, 1763, 1628, 1510, 1360, 1188, 1023, 896, 846, 677 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 9.0 Hz, 1 H), 7.67 (d, *J* = 8.4 Hz, 1 H), 7.49 (d, *J* = 2.4 Hz, 1 H), 7.15 (dd, *J* = 9.0, 2.4 Hz, 1 H), 7.10 (d, *J* = 9.0 Hz, 1 H), 3.94 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.6, 159.1, 145.2, 132.8, 129.7, 127.7, 127.5, 121.6, 119.2, 119.0, 102.5, 55.3, 20.7.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{13}H_{11}ClO_3$: 250.0397; found: 250.0399.

6-Bromo-1-chloronaphthalen-2-yl Acetate (5d)

Solid; yield: 178 mg (60%); mp 110–112 °C.

IR (KBr): 3057, 2928, 2364, 1750, 1512, 1372, 1213, 1019, 820, 753 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (s, 1 H), 7.74 (d, *J* = 9.0 Hz, 1 H), 7.65 (d, *J* = 9.0 Hz, 1 H), 7.53 (td, *J* = 9.0, 1.8 Hz, 2 H), 2.33 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.4, 148.5, 132.4, 132.1, 129.9, 129.8, 129.2, 128.5, 122.2, 119.6, 118.6, 21.1.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{12}H_8BrClO_2$: 297.9396; found: 297.9394.

1-Bromo-6-methoxynaphthalen-2-yl Benzoate (5e)

Solid; yield: 185 mg (52%); mp 149–151 °C.

IR (KBr): 3009, 2936, 2851, 1763, 1628, 1506, 1452, 1375, 1172, 1126, 1018, 896, 835, 712, 677 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 7.2 Hz, 2 H), 8.16 (d, *J* = 9.0 Hz, 1 H), 7.73 (d, *J* = 9.0 Hz, 1 H), 7.65 (t, *J* = 7.2 Hz, 1 H), 7.53 (t, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 9.0 Hz, 1 H), 7.26 (dd, *J* = 9.0, 2.4 Hz, 1 H), 7.14 (d, *J* = 2.4 Hz, 1 H), 3.92 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.6, 157.9, 144.7, 133.8, 133.7, 130.4, 129.1, 128.6, 128.5, 127.9, 127.4, 122.3, 120.4, 114.9, 106.2, 55.4.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{13}BrO_3$: 356.0048; found: 356.0048.

2-Chloronaphthalen-1-yl Acetate (8)

Solid; yield: 114 mg (52%); mp 42–44 °C.

IR (KBr): 3058, 2930, 2366, 1752, 1504, 1372, 1210, 1019, 820, 750 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.81 (t, *J* = 9.3 Hz, 2 H), 7.68 (d, *J* = 8.7 Hz, 1 H), 7.56–7.46 (m, 3 H), 2.49 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.1, 142.8, 132.9, 128.0, 127.9, 127.3, 126.9, 126.6, 123.6, 121.9, 121.0, 20.5.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{12}H_9ClO_{23}$: 220.0291; found: 220.0290.

Polyaromatic Compounds 13a–f; General Procedure

To a solution of halonaphthalenyl ether **3a**, **3e**, and **3i** (1 mmol) and phenylboronic acid **12a–c** (1.1 mmol or 2.2 mmol) in toluene (5 mL) and K_2CO_3 (2 M) was added $Pd(PPh_3)_4$ (5 mol%) and the mixture was refluxed for 16–20 h. The mixture was quenched with sat. NH_4Cl solution (10 mL) and extracted with EtOAc (3 × 10 mL). The solvent was evaporated on a rotary evaporator under reduced pressure. The residue thus obtained was purified by flash column chromatography (silica gel) to isolate the product.

2-(Benzyloxy)-1-phenylnaphthalene (13a)

Liquid; yield: 217 mg (70%).

IR (neat): 3050, 2922, 2344, 1723, 1596, 1455, 1257, 1057, 742 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.7 Hz, 2 H), 7.34–7.26 (m, 4 H), 7.21–7.11 (m, 5 H), 7.05–7.03 (m, 3 H), 6.96 (d, *J* = 7.2 Hz, 2 H), 4.87 (s, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.8, 137.3, 136.3, 133.6, 131.0, 129.4, 129.1, 128.9, 128.3, 128.0, 127.8, 127.5, 127.0, 126.9, 126.2, 125.4, 123.8, 116.3, 71.7.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{23}H_{18}O$: 310.1358; found: 310.1359.

2-(Benzyloxy)-1-(3-methoxyphenyl)naphthalene (13b)

Liquid; yield: 205 mg (72%).

IR (neat): 3052, 2925, 2340, 1720, 1596, 1450, 1250, 1053, 743 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.67 (m, 2 H), 7.44–7.42 (m, 1 H), 7.28 (t, *J* = 7.8 Hz, 1 H), 7.22–7.21 (m, 3 H), 7.15–7.11 (m, 3 H), 7.07 (d, *J* = 7.8 Hz, 2 H), 6.87 (d, *J* = 7.2 Hz, 2 H), 6.82 (s, 1 H), 4.97 (s, 2 H), 3.69 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.4, 152.7, 137.7, 137.3, 133.5, 129.3, 129.0, 129.0, 128.3, 127.7, 127.5, 127.0, 126.7, 126.2, 125.4, 123.8, 123.5, 116.3, 116.3, 113.0, 71.7, 55.2.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{24}H_{20}O_2$: 340.1463; found: 340.1462.

2-(Benzyloxy)-1-(3,5-dimethoxyphenyl)naphthalene (13c)

Solid; yield: 285 mg (77%); mp 85–87 °C.

IR (KBr): 3050, 2920, 2340, 1724, 1590, 1450, 1251, 1052, 742 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.70 (m, 2 H), 7.52–7.51 (m, 1 H), 7.26–7.25 (m, 3 H), 7.20–7.17 (m, 2 H), 7.15 (d, *J* = 7.8 Hz, 3 H), 6.47 (s, 3 H), 5.03 (s, 2 H), 3.70 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.5, 152.6, 138.4, 137.3, 133.5, 132.3, 129.3, 128.9, 128.4, 128.3, 127.7, 127.5, 127.0, 126.7, 126.3, 125.5, 123.8, 116.2, 108.9, 99.6, 71.7, 55.2.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{25}H_{22}O_3$: 370.1569; found: 370.1567.

6-Methoxy-2-(3-methylbenzyloxy)-1-phenylnaphthalene (13d)

Liquid; yield: 251 mg (71%).

IR (neat): 3048, 2935, 2301, 1725, 1598, 1501, 1371, 1240, 1039, 772, 969 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 9.0 Hz, 1 H), 7.50–7.31 (m, 7 H), 7.16–7.11 (m, 2 H), 7.02 (d, *J* = 9.0 Hz, 2 H), 6.94 (d, *J* = 7.8 Hz, 2 H), 4.98 (s, 2 H), 3.89 (s, 3 H), 2.26 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2, 151.5, 137.9, 137.3, 136.5, 131.0, 130.5, 128.9, 128.2, 128.1, 128.0, 127.8, 127.5, 127.5, 127.1, 127.0, 124.0, 118.9, 117.3, 105.7, 72.3, 55.3, 21.3.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{25}H_{22}O_2$: 354.1620; found: 354.1619.

6-Methoxy-1-(3-methoxyphenyl)-2-(3-methylbenzyloxy)naphthalene (13e)

Solid; yield: 299 mg (78%); mp 72–74 °C.

IR (KBr): 3052, 2925, 2340, 1714, 1596, 1449, 1250, 1056, 749 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 9.0 Hz, 1 H), 7.53 (d, *J* = 9.3 Hz, 1 H), 7.43 (t, *J* = 8.1 Hz, 1 H), 7.35 (d, *J* = 8.7 Hz, 1 H), 7.20–7.14 (m, 2 H), 7.08–6.99 (m, 7 H), 5.03 (s, 2 H), 3.91 (s, 3 H), 3.83 (s, 3 H), 2.30 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 156.2, 151.4, 137.9, 137.8, 137.3, 130.4, 128.9, 128.8, 128.2, 128.0, 127.8, 127.5, 127.2, 127.1, 124.0, 123.4, 118.9, 117.2, 116.3, 112.8, 105.7, 72.1, 55.2, 55.1, 21.2.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{26}H_{24}O_3$: 384.1725; found: 384.1726.

2-(Benzyloxy)-1,6-diphenylnaphthalene (13f)

Solid; yield: 282 mg (73%); mp 128–130 °C.

IR (KBr): 3052, 2940, 2354, 1722, 1560, 1443, 1260, 1043, 749 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.94 (s, 1 H), 7.82 (d, *J* = 9.0 Hz, 1 H), 7.61 (d, *J* = 7.2 Hz, 2 H), 7.53 (s, 2 H), 7.46–7.25 (m, 10 H), 7.20–7.19 (m, 2 H), 7.12–7.09 (m, 2 H), 5.02 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.9, 141.0, 137.2, 136.5, 136.3, 132.8, 131.0, 129.6, 129.2, 128.8, 128.3, 128.1, 127.5, 127.2, 127.1, 127.1, 126.9, 126.8, 126.0, 125.9, 125.6, 116.7, 71.7.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{29}H_{22}O$: 386.1671; found: 386.1668.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561295.

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