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Efficient Cross-Coupling of Aryl/Alkenyl Triflates with Acyclic Secondary Alkylboronic Acids†

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Aryl-secondary alkyl cross-coupling with aryl sulfonate esters as coupling partners remains a significant challenge. Efficient cross-coupling between aryl/alkenyl triflates and acyclic secondary alkylboronic acids is realized for the first time to provide a series of sterically congested acyclic secondary alkyl arenes/olefins in good to excellent yields. The employment of sterically bulky P,P=O ligand **L1/L2** is crucial for the high yields and selectivities. The method has enabled a concise and 4-step synthesis of a key intermediate of male contraceptive agent and PAF antagonist gossypol.

Introduction

Sterically congested secondary alkyl/isopropyl arenes exist in numerous biologically important natural products or drugs (Figure 1).[1] Their preparation often requires a multi-step sequence i.e. an initial formation of an acyl arene by Friedel-Crafts acylation or nucleophilic substitution with a metal reagent, followed by methylation with a lithium/Grignard reagent, and finally hydrogenolysis to remove a benzylic hydroxyl group. Alternatively, the sterically hindered aryl-secondary alkyl cross-coupling in particular the Suzuki-Miyaura[2,3] cross-coupling has provided an attractive and straightforward method. Nevertheless, there remain many limitations in the substrate scope of aryl-secondary alkyl cross-coupling.[4] Besides the critical chemo-selectivity issue (inhibition of isomerization and reduction side-products), the current substrate scope is mostly limited to aryl halides. Because of the ready availability and abundance of phenol and ketone derivatives, it is of significant importance to develop efficient cross-couplings between aryl/alkenyl triflates and acyclic secondary alkylboronic acids. Herein we report our progress in cross-coupling between aryl/alkenyl triflates and acyclic secondary alkylboronic acids to provide a series of sterically congested acyclic secondary alkyl arenes in good to excellent yields.

Despite the numerous applications of aryl sulfonate esters in aryl-aryl[5] and aryl-primary alkyl[6] cross-coupling, few successes have been achieved in aryl-secondary alkyl cross-coupling with aryl sulfonate esters as starting materials. Only a few examples with very low yields (4% and 12%) are reported on such couplings (Scheme 1a and 1b).[7] The challenges mainly reside

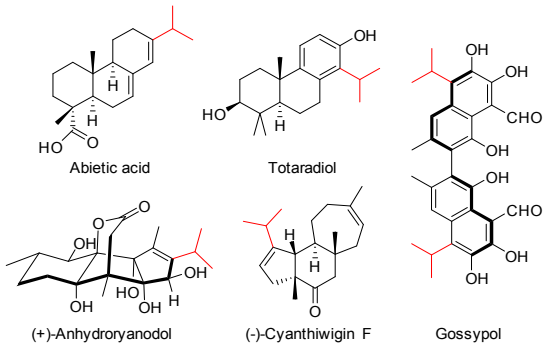

Figure 1. Biologically interesting natural products with isopropyl aryl moieties.

in two folds: (a) The aryl-secondary alkyl Suzuki-Miyaura cross-couplings often complicate with reduction and isomerization side-reactions due to the presence of β-hydrogen in the alkyl group;[4a](b) The aryl/alkenyl triflates tend to be hydrolyzed during the reaction. Our research group aimed to address these issues by designing and developing effective phosphorus ligands. By employing a sterically bulky P,P=O ligand **L1** or **L2**, we developed an efficient cross-coupling between sterically hindered aryl halides and acyclic secondary alkylboronic acids in high yields and excellent chemo-selectivity.[8] The role of P=O moiety in ligand **L1**/**L2** was to provide a hemilabile coordination to the palladium so that the isomerization and reduction side-products could be effectively inhibited. The success in our previous study with **L1**/**L2** as the ligand prompted us to investigate the challenging cross-

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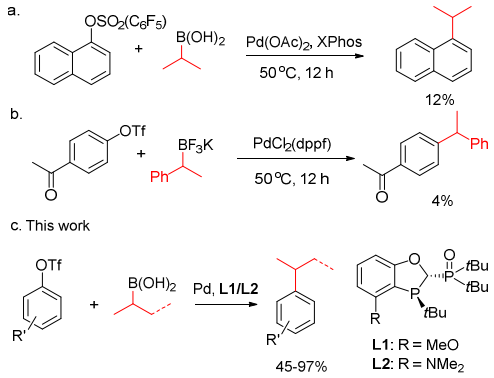
coupling between aryl/alkenyl triflates and secondary alkyl boronic acids. Herein we detailed our results.

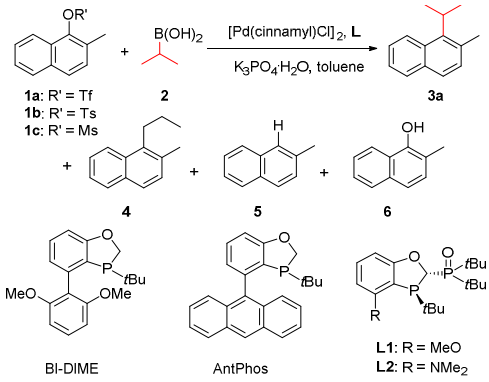


Scheme 1. Cross-coupling of aryl sulfonate ester with secondary alkyl boron reagents.

Results and discussion

We studied the Suzuki-Miyaura coupling between 2-methylnaphthalen-1-yl triflate (**1a**) and isopropylboronic acid (**2**)

Table 1. Cross-coupling between aryl triflate **1** and isopropylboronic acid **2**



Entry[a]	L	R'	Conv. (%)[b]	Yield (%) 3[c]	4[c]	3:4[d]	5[b]	6[c]
1	BI-DIME	Tf	100	<1	28	1:28	11	58
2	AntPhos	Tf	100	2	35	1:17	9	50
3	**L1**	Tf	100	83	6	14:1	0	5
4	**L2**	Tf	100	69	23	3:1	0	6
5	BINAP	Tf	100	0	0	--	25	75
6	DPPF	Tf	100	0	13	--	19	68
7	DPPP	Tf	88	0	0	--	0	80
8	DPPB	Tf	100	0	0	--	5	93
9	SPhos	Tf	100	0	1	--	12	87
10	XPhos	Tf	95	0	3	--	11	80
11	XantPhos	Tf	86	0	0	--	0	12
12	PCy_3	Tf	100	0	14	--	25	57
13	PPh_3	Tf	100	0	4	--	51	44
14	**L1**	Ts	10	5	0	--	1	4
15	**L1**	Ms	20	0	0	--	0	18

[a]The reactions were performed under nitrogen in toluene (2 mL) at 110 °C for 12 h in the presence of 1 mol % [$Pd(cinnamyl)Cl]_2$ and 4 mol % **L1** with **1** (0.25 mmol), **2** (0.5 mmol), and $K_3PO_4·H_2O$ (0.75 mmol). [b]Conversions were analyzed by reversed phase HPLC on a C-18 column. [c]Isolated yields. [d]*i*Pr/*n*Pr ratios were determined by ^1H NMR spectroscopy.

by employing various commercially available phosphorus ligands (Table 1). The reactions were performed under nitrogen in toluene at 110 °C for 12 h at 2 mol % palladium loading. As shown in Table 1, various phosphorus ligands provided dramatically different results. Not surprisingly, the desired coupling product **3** was isolated in <5% yield with BI-DIME[9] or AntPhos[10] as the ligand (entry 1-2). Besides the isomerization and the reduction side-products **4** and **5**, severe formation of the hydrolysis product **6** was also observed. Excitingly, ligand **L1** provided the desired coupling product **3** in 83% yield (entry 3), once again demonstrating the special property of the P,P=O ligand in promoting the aryl-alkyl cross-coupling. A related ligand **L2**, however, provided an inferior yield and regioselectivity (entry 4). For comparison, a series of phosphorus ligands which were often applied in aryl-aryl Suzuki-Miyaura coupling were employed for study (entries 5-13). Under similar conditions, none of these ligands provided the desired product **3**, further indicating the uniqueness and power of **L1** for the success of this reaction. While some ligands such as DPPF, SPhos[11], XPhos[12], PCy_3[13], and PPh_3 provided low yields of the isomerization side-product **4** (entries 6, 9-10, 12-13), the rest only led to the formation of **5** and **6**. The employment of aryl triflate **1a** was crucial for the reactivity, while a low yield or no formation of product was observed with tosylate **1b** and mesylate **1c** (entries 14-15).

We then examined the substrate scope of the aryl-secondary alkyl cross-coupling. As can be seen in Table 2, a series of mono- or di-ortho-substituted aryl triflates were successfully coupled with isopropylboronic acid or sec-butylboronic acid with the Pd-**L1**/**L2** catalyst to form the corresponding coupling products in good yields (45-92%) and excellent iPr/nPr ratios. Moderate to high yields (50-92%) were achieved for a range of mono-ortho-substituted isopropyl arenes (**3c-3l**). A variety of ortho-substituents such as methyl, ethyl, isopropyl, methoxy, trifluoromethyl, and formyl groups were compatible. Functional groups such as cyano, Boc, and indole moieties were well tolerated. A series of di-ortho-substituted acyclic secondary alkyl arenes with various substituents and functionalities were also formed successfully in high yields and excellent iPr/nPr selectivities (**3a**, **3m-3q**). Importantly, product **3p** was isolated in 85% yield at a gram scale, demonstrating the practicality of the coupling. For 2-methoxy-1-naphthyl triflate (**3q**), ligand **L1** formed a low iPr/nPr ratio (1.5:1) most likely due to the coordinative ability of the ortho-methoxy group. Fortunately, ligand **L2** containing the dimethylamino moiety in its structure provided a good iPr/nPr selectivity (12:1), which was consistent with our previous report[6] on cross-coupling of aryl halides. Sec-Butylboronic acids were also employed successfully to form the corresponding secondary alkyl arenes in high yields and excellent selectivities (**3r-3t**). However, no desired coupling product was formed in the cases of a substrate containing an

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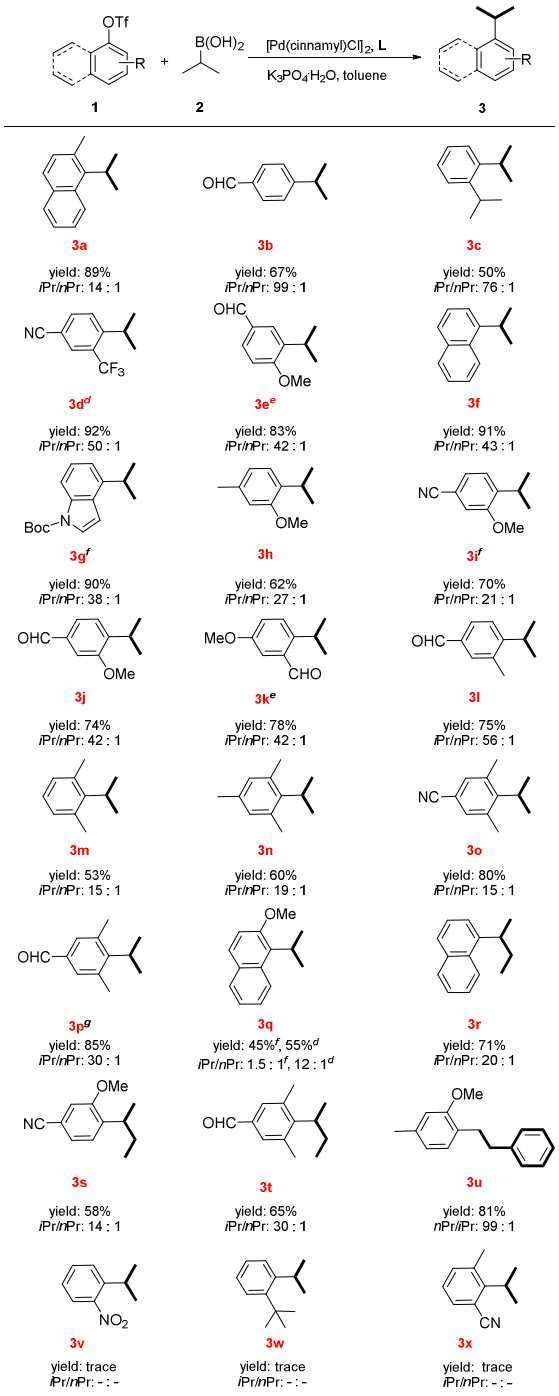
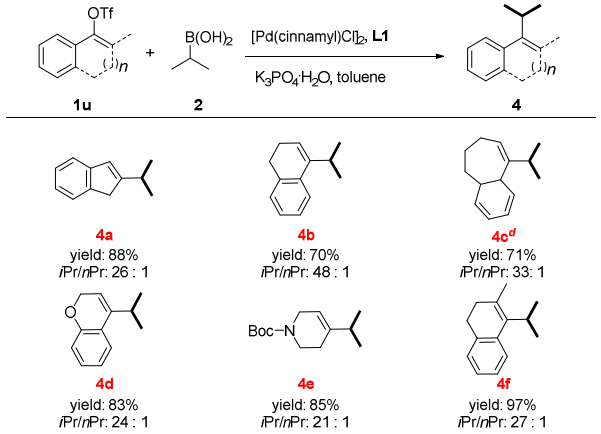
ortho-nitro (**3v**) or -*tert*-butyl group (**3w**), or both an *ortho*-methyl and an *ortho*-cyano substituents (3**x**).

Table 2. Cross-coupling between aryl triflates and secondary alkyl boronic acids: substrate scope[a,b,c]



[a]Unless otherwise specified, the reactions were performed under nitrogen in toluene (2 mL) at 110 °C for 12 h in the presence of 1 mol % $[Pd(cinnamyl)Cl]_2$ and 4 mol % **L1** with triflate (0.25 mmol), boronic acid (0.5 mmol), and $K_3PO_4.H_2O$ (0.75 mmol). [b]Isolated yields. [c]*i*Pr/*n*Pr or *sec*Bu/*n*Bu (3r-3t) ratios were determined by HPLC on a C18 reverse-phase column or by ^{1}H NMR spectroscopy. [d]2 mol % $[Pd(cinnamyl)Cl]_2$ and 8 mol % **L2**. [e]4 mol % **L2**. [f]2 mol % $[Pd(cinnamyl)Cl]_2$ and 8 mol % **L1**. [g]Gram scale.

Table 3. Sterically hindered alkenyl-alkyl cross-couplings[a,b,c]



[a]Unless otherwise specified, the reactions were performed under nitrogen in toluene (2 mL) at 110 °C for 12 h in the presence of 1 mol % $[Pd(cinnamyl)Cl]_2$ and 4 mol % **L1** with triflate (0.25 mmol), isopropylboronic acid (0.5 mmol), and $K_3PO_4•H_2O$ (0.75 mmol). [b]Isolated yields. [c]*i*Pr/*n*Pr ratios were determined by HPLC on a C18 reverse-phase column or by ^{1}H NMR spectroscopy. [d]2 mol % $[Pd(cinnamyl)Cl]_2$ and 8 mol % **L1**.

Because of the ready accessibility of alkenyl triflates from corresponding ketones, the cross-coupling between alkenyl triflates and isopropylboronic acids can provide an important method for the synthesis of sterically hindered tri- or tetra-substituted olefins, which are otherwise tedious to prepare.[4] As shown in Table 3, a series of alkenyl triflates were coupled smoothly with isopropylboronic acid to give the corresponding alkenes in moderate to good yields. Cyclic olefinic triflates with **5**, **6**, and **7**-membered rings were all applicable to form the corresponding coupling products in high yields and excellent selectivities (**4a-4c**). Substrates bearing oxygen- or nitrogen-containing heterocycles were well tolerable (**4d-4e**). A tetrasubstituted olefin was also formed successfully in 97% yield with a high *i*Pr/*n*Pr ratio (**4f**).

The cross-coupling method enabled a concise and 4-step synthesis of compound **11**, the key intermediate of male contraceptive agent and PAF antagonist gossypol (Scheme 2).[14] Thus, Diels-Alder reaction between diene **7** and dimethoxyquinone **8** provided benzoquinone **9** in 82% yield. Reduction of 9 under action of $BF_3.Et_2O$ and Et_3SiH followed by triflate formation provided **10** in 60% overall yield through 2 steps. Cross-coupling of **10** with isopropylboronic acid with Pd-**L2** as the catalyst provided the key gossypol intermediate **11** in 62% yield with the iPr/nPr ratio of 5.5 /1, which constituted the shortest sequence to date to prepare gossypol intermediate **11**.

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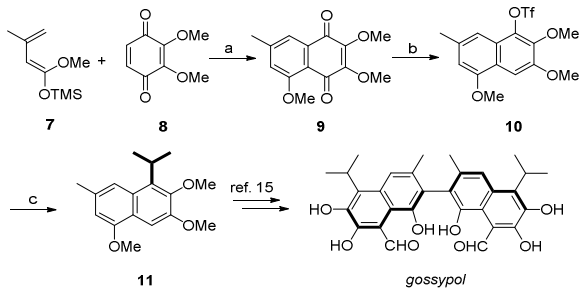

Scheme 2. Synthesis of gossypol intermediate **11** through aryl alkyl cross-coupling strategy. a) AcOH, DCM, rt, 82%; b) i) $BF_3.Et_2O$, Et_3SiH; ii) Tf_2O, Et_3N, DCM; 60% (2 steps); c) *i*PrB(OH)$_2$, [Pd(cinnamyl)Cl]$_2$ (1 mol %), **L2** (4 mol %), toluene, 62%, (*i*Pr:*n*Pr = 5.5 :1).

Conclusions

In summary, we demonstrated for the first time the cross-coupling between various sterically hindered aryl/alkenyl triflates and acyclic secondary boronic acids to form a series of sterically congested acyclic secondary alkyl arenes and olefins in moderate to good yields and excellent chemoselectivities. Ligands **L1**/**L2** played a crucial role in enabling the high yields and selectivities of this aryl/alkenyl-secondary alkyl Suzuki-Miyaura cross-coupling. This method enabled a concise and 4-step synthesis of gossypol intermediate **11**. Because of the ready accessibility of aryl/alkenyl triflates from corresponding phenol/ketone precursors, this method provides expedite access to sterically hindered secondary alkyl arene and olefin moieties, which should be highly valuable for the synthesis of natural products and drugs.

Experimental section

General

All reactions were carried out under nitrogen atmosphere unless otherwise specified. Unless otherwise noted, commercialized reagents were used without further purifications. Toluene was purchased from Sigma-Aldrich Chemical Co. All other solvents were purified and dried according to standard methods prior to use. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR data were recorded on a Bruker-Ultrashield PLUS400 NMR or a 500 MHz Agilent spectrometer with $CDCl_3$ as the solvent. ^{1}H chemical shifts were referenced to $CDCl_3$ at 7.26 ppm. ^{13}C chemical shifts were referenced to $CDCl_3$ at 77.14 ppm and obtained with 1H decoupling. ^{31}P chemical shifts were referenced to 85% H_3PO_4 in D_2O at 0.0 ppm as external standard and obtained with ^{1}H decoupling. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), triplet - doublet (td), quintet (quint), sextet (sextet), septet (septet), multiplet (m), and broad (br). MS was measured on Agilent 7890A/5975C Series GC/MSD mass spectrometer. HPLC yield were determined on Agilent 1200 Infinity Series.

General procedure for the synthesis of compounds 3a–u (Table 2) and 4a-f (Table 3)

To a mixture of aryl/alkenyl triflates (0.25 mmol), alkylboronic acid (0.5 mmol), potassium phosphate tribasic monohydrate (0.75 mmol), [Pd(cinnamyl)Cl]$_2$ (0.0013 mmol, 2.0 mol % Pd), phosphorus ligand (**L1** or **L2**, 4.0 mol %, Pd : **L** = 1 : 2) was charged dry toluene (2 mL). The mixture was pumped and refilled with nitrogen for three times. The resulting mixture was stirred at 110℃ under nitrogen for 12 h, and then cooled to room temperature, partitioned with water (2 mL) and dichloromethane (3 mL). The organic layer was separated, dried over sodium sulfate, concentrated, and purified by silica gel column chromatography (hexanes/EtOAc as eluent) to provide the coupling product. The *i*Pr/*n*Pr ratios were determined by HPLC on a C18 reversed phase HPLC column or by ^{1}H NMR.

Characterization data for the products 3a–u , 4a–f and 11

1-Isopropyl-2-methylnaphthalene(3a): ^{1}H NMR (500 MHz, CDCl3) δ 8.30 (d, J = 8.1 H_Z, 1H), 7.83 (d, J = 8.0 H_Z, 1H), 7.63 (d, J = 8.3 H_Z, 1H), 7.40~7.49 (dt, J = 29.3, 7.2 H_Z, 2H), 7.30 (d, J = 8.4 H_Z, 1H), 3.90 (s, 1H), 2.58 (s, 3H), 1.60 (d, J = 7.0 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 133.0, 132.5, 131.85, 129.5, 125.6, 124.2, 29.4, 21.8(d, J = 20.3 Hz); EI-MS: *m/z* 184.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{14}H_{16}$ (M): 184.1252, found: 184.1246.

4-Isopropylbenzaldehyde(3b): ^{1}H NMR (500 MHz, CDCl3) δ 9.97 (s, 1H), 7.81 (d, J =8.0 Hz, 2H), 7.39 (d, J =8.1 Hz, 2H), 2.99 (septet, J = 6.9 H_Z,1H), 1.29 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 192.0, 156.2, 134.5, 130.0, 127.1, 34.5, 23.6; EI-MS: *m/z* 148.0 $[M]^+$; HRMS (EI) *m/z* calcd for C10H12O (M): 148.0837, found: 148.0838.

1,2-Diisopropylbenzene(3c) : ^{1}H NMR (500 MHz, CDCl3) δ7.26~7.29 (m, 2H), 7.18~7.21 (m, 2H), 3.31 (septet, J = 6.8 H_Z,2H), 1.26 (d, J = 6.9 Hz, 12H); ^{13}C NMR (125 MHz, CDCl3) δ 145.5, 125.8, 125.0, 28.1, 24.1; EI-MS: *m/z* 162.0 $[M]^+$; HRMS (EI) *m/z* calcd for$C_{12}H_{18}$ (M): 162.1409, found: 162.1415.

4-Isopropyl-3-(trifluoromethyl)benzonitrile (3d): ^{1}H NMR (500 MHz, CDCl3) δ 7.89 (t, J = 0.7 H_Z,1H), 7.79 (dd, J = 8.2, 1.4 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 3.40 (septet, J = 6.6 H_Z,1H), 1.28 (d, J = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 153.9, 135.4, 129.7 (q, J = 6.1 Hz), 128.7, 122.4, 117.9, 110.3, 29.9, 24.0 ; ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.9; EI-MS: *m/z* 213.1 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{11}H_{10}F_3N$ (M): 213.0765, found: 213.0773.

3-Isopropyl-4-methoxybenzaldehyde(3e): ^{1}H NMR (500 MHz, CDCl3) δ 9.87 (s, 1H), 7.76 (d, J = 2H_Z, 1H), 7.69~7.71 (m, 1H), 6.94 (d, J = 8.4 H_Z, 1H), 3.91 (s, 1H), 3.32 (septet, J = 6.8 H_Z, 1H), 1.23 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 191.3, 162.0, 137.9, 130.5, 129.7, 127.1, 110.0, 55.6, 26.7, 22.4; EI-MS: *m/z* 178.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{11}H_{14}O_2$ (M): 178.0994, found: 178.1000.

1-Isopropylbenzene(3f): ^{1}H NMR (500 MHz, CDCl3) δ 8.23 (d, 1H), 7.93~7.96 (m, 1H), 7.79 (d, 1H), 7.50~7.62 (m, 4H), 3.85 (septet, J = 6.8 H_Z, 1H), 1.50 (d, J = 6.9 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.59, 133.90, 131.35, 128.89, 127.85, 126.26, 125.78, 125.63, 125.61, 125.19, 123.27, 121.66, 28.50, 23.53 ; EI-

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MS: *m/z* 170.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{13}H_{14}$ (M): 170.1096, found: 170.1100.

Tert-butyl 4-isopropyl-1H-indole-1-carboxylate (3g): ^{1}H NMR (500 MHz, CDCl3) δ 8.04 (d, J = 7.9 H_Z, 1H), 7.63 (d, J = 3.6 H_Z, 1H), 7.31 (t, J = 7.9 H_Z, 1H), 7.14 (d, J = 7.5H_Z, 1H), 6.70 (d, J = 3.7H_Z, 1H), 3.35 (septet, J = 6.9 H_Z, 1H), 1.70 (d, J = 3.8H_Z, 9H), 1.38 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 141.2, 128.9, 125.2, 124.4, 118.5, 115.1, 112.8, 105.5, 83.4, 30.9, 28.2, 23.2; EI-MS: *m/z* 259.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{16}H_{21}NO_2$ (M): 259.1572, found: 259.1569.

1-Isopropyl-2-methoxy-4-methylbenzene(3h): ^{1}H NMR (500 MHz, CDCl3) δ 7.11 (d, J = 7.7 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 6.68 (s, 1H), 3.82 (s, 3H), 3.29 (septet, J = 6.9 H_Z, 1H), 2.34 (s, 3H), 1.21 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 156.6, 136.3, 134.0, 125.8, 121.0, 111.4, 55.3, 26.4, 22.8, 21.4; EI-MS: *m/z* 164.1 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{11}H_{16}O$ (M): 164.1201, found: 164.1208.

4-Isopropyl-3-methoxybenzonitrile(3i): ^{1}H NMR (500 MHz, CDCl3) δ 7.29~7.35 (m, 2H), 7.12 (d, J =1.3Hz, 1H), 3.92 (s, 1H), 3.41 (septet, J = 6.9 H_Z,1H), 2.27 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 156.8, 143.1, 126.8, 124.9, 119.2, 113.0, 110.0, 55.6, 27.0, 22.2; EI-MS: *m/z* 175.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{11}H_{13}NO$ (M): 175.0997, found: 175.0994.

4-Isopropyl-3-methoxybenzaldehyde(3j): ^{1}H NMR (500 MHz, CDCl3) δ 9.93 (s, 1H), 7.35~7.42(m, 3H), 3.90 (s, 3H), 3.38 (septet, J = 6.9 H_Z,1H), 1.23 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 192.0, 157.3, 144.90, 135.4, 126.4, 124.7, 108.4, 55.5, 27.2, 22.3; EI-MS: *m/z* 178.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{11}H_{14}O_2$ (M): 178.0994, found: 178.0993.

2-Isopropyl-5-methoxybenzaldehyde(3k): ^{1}H NMR (500 MHz, CDCl3) δ 9.88 (s, 1H), 7.76 (d, J = 2.1 Hz, 1H), 7.70 (d, J = 8.4, 2.1 Hz, 1H), 6.95 (d, J = 8.4 Hz , 1H), 3.92 (s, 3H), 3.33 (septet, J = 7.0 H_Z,1H), 1.23 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 191.4, 162.1, 138.1, 130.6, 129.8, 127.3, 110.2, 55.8, 26.8, 22.5; EI-MS: *m/z* EI-MS: *m/z* 178.0 $[M]^+$; HRMS (EI) *m/z* calcd for C11H14O2 (M): 178.0994, found: 178.0993.

4-Isopropyl-3-methylbenzaldehyde(3l): ^{1}H NMR (500 MHz, CDCl3) δ 9.94 (s, 1H), 7.67~7.70(m, 1H), 7.65(s, 1H), 7.40 (d, J = 7.9 Hz, 1H), 3.20 (septet, J = 6.9 Hz, 1H), 2.41 (s, 3H), 1.25 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 192.2, 154.4, 136.0, 134.1, 131.4, 128.0, 125.4, 29.7, 22.9, 19.2; EI-MS: *m/z* 162.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{11}H_{14}O$ (M): 162.1045, found: 162.1046.

2-Isopropyl-1,3-dimethylbenzene(3m): ^{1}H NMR (500 MHz, CDCl3) δ 6.90 (s, 2H), 3.50(septet, J = 7.3 H_Z,1H), 2.45 (s, 6H), 2.33 (s, 3H), 1.42 (d, J = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 144.1, 136.0, 128.0, 125.4, 29.5, 21.5, 20.8 ; EI-MS: *m/z* 148.0 $[M]^+$; HRMS (EI) *m/z* calcd for C11H16 (M): 148.1252, found: 148.1250.

2-Isopropyl-1,3,5-trimethylbenzene(3n): ^{1}H NMR (500 MHz, CDCl3) δ 6.90 (s, 2H), 3.50(septet, J = 7.3 H_Z, 1H), 2.45 (s, 6H), 2.33 (s, 3H), 1.42 (d, J = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 141.2, 136.0, 134.8, 130.1, 29.3, 21.5, 21.0, 20.7; EI-MS: *m/z* 162.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{12}H_{18}$ (M): 162.1409, found: 162.1411.

4-Isopropyl-3,5-dimethylbenzonitrile(3o): ^{1}H NMR (500 MHz, CDCl3) δ 7.24 (s, 2H), 3.45 (septet, J = 7.3 H_Z,1H), 2.39 (s, 6H), 1.33 (d, J = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 149.9, 137.3, 132.5, 119.2, 109.0, 29.8, 21.3, 20.3; EI-MS: *m/z* 173.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{12}H_{15}N$ (M): 173.1204, found: 173.1201.

Isopropyl-2-methoxynaphthalene(3q): ^{1}H NMR (500 MHz, CDCl3) δ 8.21 (d, J = 8.7 H_Z, 1H), 7.83 (d, J = 8.2 H_Z, 1H), 7.75 (d, J = 9.0 H_Z, 1H), 7.50 (t, J = 8.0 H_Z, 1H), 7.37 (t, J = 7.8 H_Z, 1H), 7.31 (d, J = 9.0 H_Z, 1H), 4.01 (s, 1H), 3.98 (s, 3H), 1.54 (d, J = 7.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.6, 129.7, 129.3, 128.8, 127.7, 125.9, 123.4, 123.1, 114.8, 56.6, 26.6, 21.3; EI-MS: *m/z* 200.1 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{14}H_{16}O$ (M): 200.1201, found: 200.1197.

(S)-1-(sec-butyl)naphthalene(3r): ^{1}H NMR (500 MHz, CDCl3) δ8.13 (d, J = 8.9 H_Z, 1H), 8.13 (dd, J = 7.9, 0.7 H_Z, 1H), 7.70 (d, J = 8.1 H_Z, 1H), 7.43~7.53 (m, 3H), 7.37~7.40 (m, 1H), 3.52 (sextet, J = 7.0 H_Z,1H), 1.82~1.90 (m, 1H), 1.67~1.77 (m, 1H), 1.38 (d, J = 6.9 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 143.7, 133.9, 131.8, 128.9, 126.1, 125. 6,125.5, 125.2, 123.2, 122.4, 35.3, 30.6, 21.2, 12.3; EI-MS: *m/z* 184.0 $[M]^+$; HRMS (EI) *m/z* calcd for C14H16 (M): 184.1252, found: 184.1251.

(S)-4-(sec-butyl)-3-methoxybenzonitrile(3s): ^{1}H NMR (500 MHz, CDCl3) δ 7.22 (s, 2H), 7.05 (s, 1H), 3.84 (s, 3H), 3.13 (sextet, J = 7.1 H_Z, 1H), 1.52~1.64 (m, 2H), 1.17 (d, J = 7.0 H_Z, 3H), 0.82 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 157.2, 142.2, 127.6, 124.9, 119.4, 113.3, 110.0, 55.7, 33.8, 29.5, 20.1, 12.1; EI-MS: *m/z* 189.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{12}H_{15}NO$ (M): 189.1154, found: 189.1158.

(S)-4-(sec-butyl)-3,5-dimethylbenzaldehyde(3t): ^{1}H NMR (500 MHz, CDCl3) δ 9.88~9.95 (d, 1H), 7.48 (d, J = 7.5 Hz, 2H), 3.22 (sextet, J = 7.4 H_Z,1H), 2.45 (s, 6H), 1.40 (dd, J = 7.3, 0.4 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 192.4, 150.8, 137.4, 133.8, 129.4, 37.4, 27.8, 21.7, 18.3, 13.0; EI-MS: *m/z* 190.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{13}H_{18}O$ (M): 190.1358, found: 190.1361.

2-methoxy-4-methyl-1-phenethylbenzene (3u): ^{1}H NMR (500 MHz, CDCl3) δ 7.32~7.36 (m, 2H), 7.22~7.29 (m, 3H), 7.05 (d, J = 7.3 Hz, 1H), 6.76 (d, J = 7.5 Hz, 2H), 3.87 (s, 3H), 2.90~2.98 (m, 4H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, CDCl3) δ157.5, 142.7, 137.1, 129.7, 128.6, 128.3, 127.3, 125.8, 121.0, 111.4, 55.3, 36.5, 32.3, 21.6; EI-MS: *m/z* 226.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{16}H_{18}O$ (M): 226.1358, found: 226.1355.

2-Isopropyl-1*H*-indene(4a): ^{1}H NMR (500 MHz, CDCl3) δ 7.38 (d, J = 7.4 H_Z, 1H), 7.28 (d, J = 6.7 H_Z, 1H), 7.22 (t, J = 7.5 H_Z, 1H), 7.10 (t, J = 7.4 H_Z, 1H), 6.51 (s, 1H), 3.35 (s, 2H), 2.88 (septet, J = 6.8 H_Z, 1H), 1.23 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 145.7, 143.1, 126.4, 124.2, 123.7, 123.6, 120.1, 39.3, 30.2, 22.7; EI-MS: *m/z* 158.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{12}H_{14}$ (M): 158.1096, found: 158.1102.

4-Isopropyl-1,2-dihydronaphthalene(4b): ^{1}H NMR (500 MHz, CDCl3) δ 7.33 (d, J = 7.8 H_Z, 1H), 7.22 (td, J = 6.9, 2.2 H_Z, 1H), 7.12~7.17 (m, 2H), 5.90 (td, J = 4.6 H_Z, 1.0 1H), 2.91~3.00 (m, 1H), 2.72 (t, J = 7.8 H_Z, 2H), 2.23~2.28 (m, 2H),1.18 (d, J = 6.8 H_Z, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 137.1, 135.0, 127.6, 126.2 (d, J = 5.5 Hz), 122.4, 121.4, 28.6, 28.2, 23.0, 22.3; EI-MS: *m/z* 172.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{13}H_{16}$ (M): 172.1252, found: 172.1253.

9-Isopropyl-6,7-dihydro-5*H*-benzo[7]annulene(4c): ^{1}H NMR (500 MHz, CDCl3) δ 7.23~7.17 (m, 2H), 7.14~7.20 (m, 2H), 5.88 (td, J = 7.3, 1.4 H_Z, 1H), 2.80 (septet, J = 6.8 H_Z, 1H), 2.51 (t, J = 7.1 H_Z, 2H), 2.03 (m, 2H), 1.77 (q, J = 7.2 H_Z, 2H), 1.07 (d, J = 6.8 H_Z, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 141.9, 141.4, 128.5, 126.4, 126.0, 125.9, 121.8, 34.6, 33.3, 32.1, 24.2, 22.3; EI-MS: *m/z* 186.1 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{14}H_{18}$ (M): 186.1409, found: 186.1408.

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4-Isopropyl-2*H*-chromene(4d): ^{1}H NMR (500 MHz, CDCl3) δ 7.24 (d, J = 7.7 H_Z, 1H), 7.10~7.15 (m, 1H), 6.93 (t, J = 7.6 H_Z, 1H), 6.85 (d, J = 8.1 H_Z, 1H), 5.61 (t, J = 3.8 H_Z, 1H), 4.74 (d, J = 3.8 H_Z, 2H), 2.88 (septet, J = 6.4 H_Z, 1H), 1.17 (d, J = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 140.4, 128.5, 123.5, 123.1, 121.1, 116.2, 114.9, 65.4, 27.6, 21.7; EI-MS: *m/z* 174.1 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{12}H_{14}O$ (M): 174.1056, found: 174.1051.

Tert-butyl 4-isopropyl-3,6-dihydropyridine-1(2H)-carboxylate (4e): ^{1}H NMR (500 MHz, CDCl3) δ 5.30 (d, J = 16.2 Hz, 1H), 3.84 (s, 2H), 3.46 (t, J = 5.5 Hz, 2H), 2.20 (septet, J = 7.1 H_Z,1H), 2.04 (d, J = 5.7 Hz, 2H), 1.46 (s, 9H), 0.99 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 142.5, 115.4, 79.4, 43.6, 40.0, 34.8, 28.6, 26.4, 21.1; EI-MS: *m/z* 225.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{13}H_{23}NO_2$ (M): 225.1025, found: 225.1023.

4-Isopropyl-3-methyl-1,2-dihydronaphthalene(4f): ^{1}H NMR (500 MHz, CDCl3) δ 7.41 (d, J = 7.9 H_Z, 1H), 7.19 (t, J = 7.3 H_Z, 1H), 7.14 (d, J = 6.7 H_Z, 1H), 7.09 (t, J = 7.3 H_Z, 1H), 3.25 (septet, J = 7.4 H_Z, 1H), 2.66 (t, J = 7.6 H_Z, 2H), 2.16 (d, J = 7.8 H_Z, 2H), 1.98 (s, 3H), 1.35 (d, J = 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 136.4, 135.4, 133.1, 127.3, 125.8, 125.2, 123.7, 31.8, 29.2, 29.0, 21.5, 20.7; EI-MS: *m/z* 186.0 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{14}H_{18}$ (M): 186.1456, found: 186.1361.

compound 11: ^{1}H NMR (500 MHz, CDCl3) δ 7.47 (s, 2H), 6.61 (s, 1H), 3.98~3.97 (m, 4H), 3.88 (d, J = 2.7 Hz,3H), 2.49 (s, 3H), 1.50 (d, J = 6.0 Hz, 6H); 13C NMR (100 MHz, CDCl3) δ 154.9, 151.2, 135.0, 133.4, 128.9, 121.3, 115.7, 105.4, 100.1, 61.2, 55.6, 55.6, 28.1, 22.8, 22.3; EI-MS: m/z 274.4 [M]+; HRMS (EI) m/z calcd for C17H22O3(M): 274.1569, found: 274.1570.

Conflicts of interest

There are no conflicts to declare.

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