Brønsted Acid Catalyzed Intramolecular Friedel-Crafts Addition of Tertiary Allylic Alcohols to Indoles

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An intermolecular Friedel-Crafts alkylation of indole and tertiary allylic alcohols has been developed. The allylic alcohols were synthesized using a two-step procedure, then exposure of these alcohols to diphenyl phosphate facilitated the desired annulation reaction. This reaction tolerated a variety of indole substitutions to yield 1H,2H,3H,4H-pyrido[1,2-a]indoles.

Introduction

Due to their importance in natural products and pharmaceuticals,[1-4] the reactivity of indole and indole-containing compounds is frequently studied.[4-12] In particular, indoles readily undergo electrophilic aromatic substitution reactions. The electrophiles used in these reactions can be generated from many different stable precursors, including allylic alcohols.[13-17] Recent reports have shown that allylic alcohols readily undergo Friedel-Crafts reactions with indoles in the presence of catalytic amounts of $InCl_3$, $InBr_3$, $FeCl_3$, Au_2Cl_2 or $C_6F_5B(OH)_2$.[13-17] While Brønsted acids have been shown to be effective catalysts for this transformation and others,[18, 19] the use of diphenyl phosphoric acid as a catalyst has not been reported. [12, 20-26] Furthermore, these examples focus on intermolecular reactions though there is one example of an intramolecular reaction.[27] We sought to develop a method for the synthesis of 1H,2H,3H,4H-pyrido[1,2-a]indoles and related structural motifs which could be used in the synthesis of natural products, such as flinderole A-C, and their analogues (Figure 1).[28-36] This could be accomplished by tethering the allylic alcohol to the indole nitrogen and promoting the electrophilic addition at the C-2 position. Herein, we report diphenyl phosphate-catalyzed intramolecular Friedel-Crafts reactions of indoles with tertiary allylic alcohols.

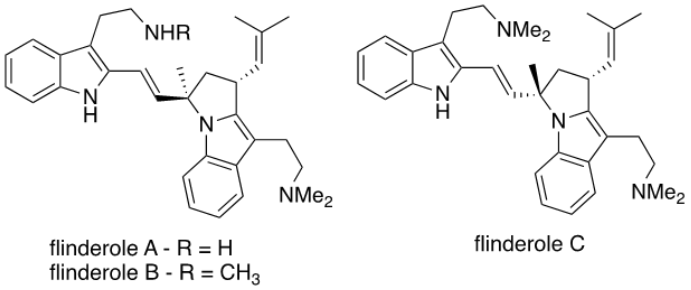
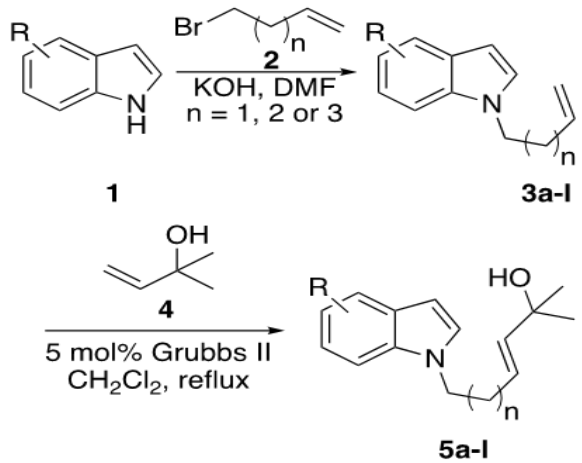


Figure 1. Structure of the flinderoles

Chemistry

The allylic alcohols required for this study were synthesized in two steps (Scheme 1). First, treatment of indoles with different substituents with KOH and 5-bromo-1-pentene provided the *N*-alkylation product (n = 2) in moderate to good yield (Table 1, Entries 1-10).[37-39]The chain length could be changed to n = 1 or n = 3 by using 4-bromo-1-butene or 6-bromo-1-hexene, respectively. (Table 1, Entries 11-12). Cross-metathesis with Grubbs second generation catalyst and 2-methyl-3-buten -2-ol provided the allylic alcohols, **5**.[40] This two-step procedure was effective in constructing indole-tethered allylic alcohols with different functionality on the indole ring.

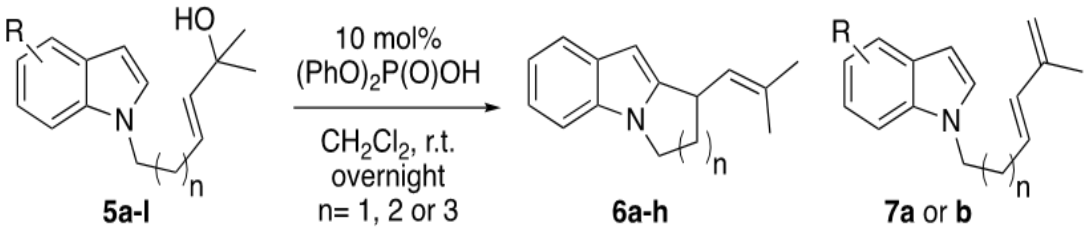


Scheme 1. Synthesis of allylic alcohols from indoles

With the allylic alcohols in hand, the diphenyl phosphate-catalyzed Friedel-Crafts reaction could be explored (Scheme 2). Treatment of **5a** with 10 mol% diphenyl phosphate in dichloromethane yielded the desired product in 73% yield. Introduction of various electron-donating groups on the indole ring was tolerated. Substitution at the C-3 position of the ring provided an increase in yield (Figure 1, **6b** and **6c**). Methyl or methoxy substituents could be added to the indole ring and the reaction proceeded in moderate to good yield in most cases, **6d-i**. Use of allylic alcohol **5k**, which contains bromine, led to the generation of an inseparable mixture of non-polar compounds, indicating that electron-withdrawing groups are not compatible with these reaction conditions. The effects of changing the tether length from n = 2 to n = 1 (**5k**) or 3 (**5l**) to provide access to 5- or 7-membered rings, respectively, were also examined. This change provided little of the desired annulation product, but instead yielded the dehydration products, **7a** or **b**, in low yield. Compound **7a** was isolated as a 4:5:1 of mixture with desired cyclization product. The yield was the annulation product could not be improved. The dehydration reaction was not

Table 1. Results of alkylation and cross-metathesis reactions

Entry	n	R	Compound (Yield %)	Compound (Yield %)
1	2	H	**3a** (81)	**5a** (82)
2	2	3-methyl	**3b** (56)	**5b** (56)
3	2	3 $CH_2CH_2OTBDPS$	**3c** (32)	**5c** (68)
4	2	4-methoxy	**3d** (76)	**5d** (72)
5	2	5-methoxy	**3e**(61)	**5e** (61)
6	2	5-methyl	**3f** (57)	**5f** (87)
7	2	6-methyl	**3g** (79)	**5g** (55)
8	2	7-methoxy	**3h** (65)	**3h** (53)
9	2	7-methyl	**3i** (49)	**3i** (37)
10	2	5-bromo	**3j** (62)	**5j** (74)
11	1	H	**3k** (9)	**5k** (57)
12	3	H	**3l** (33)	**5l** (61)



Scheme 2. Brønsted Acid catalyzed intramolecular Friedel-Crafts Addition

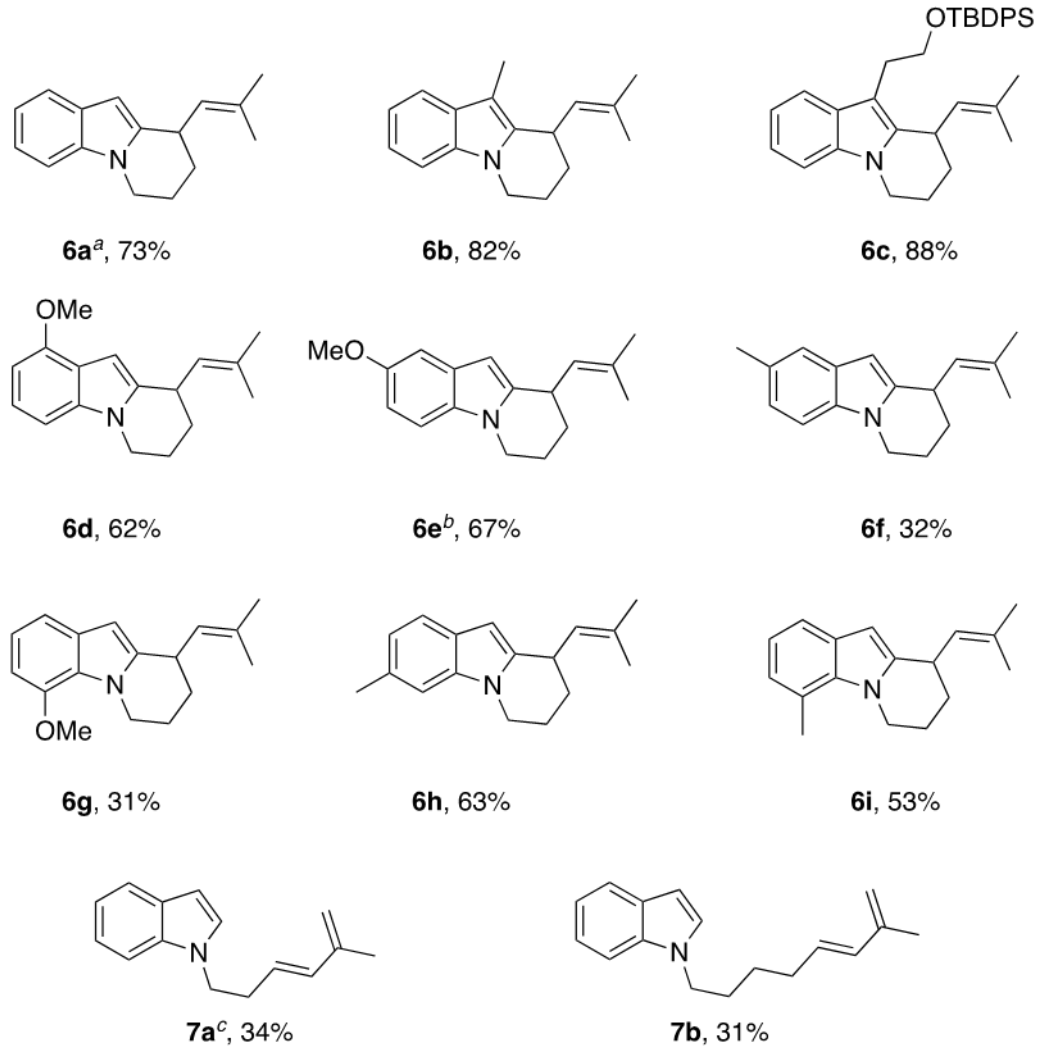


Figure 2. Products from the Friedel-Crafts Addition. Reaction time 8 h [b] 10% dehydration product isolated [c] 1:4.5 Ratio of **6**:**7**

unique to n = 1 and 3 tether lengths and was isolated in a 10% yield in the synthesis of **6e**. This elimination results from slow cyclization of **5k** and **5l**. Overall, the reaction proceeds in good to moderate yield to provide 1H,2H,3H,4H-pyrido[1,2-a]indoles with alkyl and methoxy substituents around the ring.

Experimental Methods

Sample Indole Alkylation Procedures

3-(2-[(tert-butyldiphenylsilyl)oxy]ethyl)-1-(pent-4-en-1-yl)-1H-indole (3c): To a solution of TBDPS-tryptophol[4c] in 2 mL of DMF was added 32 mg (.57 mmol) of freshly crushed KOH and 86 mg (.57 mmol) of 5-bromo-1-pentene. The mixture was stirred for 24 h then quenched with water, extracted with ether (3x). The combined organic layers were washed with brine (3x), dried ($MgSO_4$) filtered and concentrated *in vacuo*. The residue was purified by chromatography on SiO_2 (0®5% EtOAc/Hex) to yield **3c** (32%) as a colorless oil: IR (Neat) 3070, 2930, 2856, 1490, 1427 cm^{-1}, ^1H NMR (300 MHz, $CDCl_3$) d 7.68-7.61 (m, 4 H), 7.44-7.31 (m, 8 H), 7.14 (ddd, 1 H, *J* = 8.3, 7.1, 1.4 Hz), 7.02 (ddd, 1 H, *J* = 7.7, 6.9, 0.8 Hz), 6.90 (s, 1 H), 5.79 (dddd, 1 H, *J* = 17.0, 10.7, 6.6, 6.6 Hz), 5.04 (dddd, 1 H, *J* = 7.7, 1.4, 1.4, 1.4 Hz), 4.99 (dd, 1 H, *J* = 1.4, 1.4 Hz), 4.05 (t, 2 H, *J* = 6.9 Hz), 3.92 (t, 2 H, *J* = 7.4 Hz), 3.03 (t, 2 H, *J* = 7.1 Hz), 2.05 (ddd, 2 H, *J* = 6.9, 6.9, 6.9 Hz), 1.89 (dddd, 2 H, *J* = 6.9, 6.9, 6.9, 6.9 Hz), 1.06 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) d 137.6, 136.3, 135.8, 134.2, 129.7, 128.3, 127.8, 126.2, 121.4, 119.2, 118.7, 115.7, 111.6, 109.4, 64.7, 45.5, 31.0, 29.4, 28.8, 27.0, 19.4; MS (EI) *m/z* (rel intensity) 467 (M^+, 15), 412 (10), 411 (35), 410 (100), 332 (30), 212 (30), 198 (25), 158 (10), 144 (25), 130 (10); HRMS (EI) Calcd for $C_{31}H_{37}NOSi$ 467.2644, found 467.2635.

7-methyl-1-(pent-4-en-1-yl)-1H-indole (3i): To a solution of 500 mg (3.8 mmol) of 7-methylindole in 11 mL of DMF was added 320 mg (5.7 mmol) of freshly crushed KOH and 852 mg (5.7 mmol) of 5-bromo-1-pentene. The mixture was stirred overnight then quenched with water, extracted with ether (3x). The combined organic layers were washed with brine (3x), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on SiO_2 (0®3% EtOAc/ Hexanes) to yield 375 mg (49% yield) of **3i** as a colorless oil: IR (Neat) 3076, 3047, 2974, 2934, 2866, 1640, 1522 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) d 7.49 (d, 1 H, *J* = 7.7 Hz), 7.10-6.90 (m, 3 H), 6.49 (d, 1 H, *J* = 3.3 Hz), 5.83 (dddd, 1 H, *J* = 17.0, 10.1, 6.0, 6.0 Hz), 5.14-5.01 (m, 2 H), 4.35 (t, 2 H, *J* = 7.4 Hz), 2.73 (s, 3 H), 2.13 (ddd, 2 H, *J* = 6.9, 6.9, 6.9 Hz), 1.92 (dddd, 2 H, *J* = 7.4, 7.4, 7.4, 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) d 137.5, 134.7, 130.0, 129.6, 124.7, 120.8, 119.6, 119.3, 115.7, 101.6, 48.3, 31.9, 30.9, 20.1; MS (EI) *m/z* (rel intensity) 199 (M^+,65), 184 (10), 145 (45), 144 (100), 130 (15); HRMS (EI) Calcd for $C_{14}H_{17}N$ 199.1361, found 199.1358.

Sample Cross Metathesis Procedures

(3E)-7-(3-(2-[(tert-butyldiphenylsilyl)oxy]ethyl)-1H-indol-1-yl)-2-methylhept-3-en-2-ol (5c): To a solution of 60 mg (.12 mmol) of **3c** in 1.2 mL of CH_2Cl_2 was added 144 mg (1.7 mmol) of 2-methyl-3-butene-2-ol (**4**) and 5.5 mg (0.0064 mmol) of Grubbs II. The mixture was then heated to 40 °C overnight. The mixture was cooled, filtered through a pad of a 1:1 mixture of silica gel and celite, which was washed with ethyl acetate. The filtrate was concentrated *in vacuo.* The residue was purified by chromatography on SiO_2 (0®10% EtOAc/Hex) to yield 43 mg (68%) of **5c** as a colorless oil: IR (Neat) 3390, 3070, 3048, 2960, 2929, 2856, 1613, 1589, 1468, 1428 cm^{-1}, ^1H NMR (300 MHz, Acetone-d_6) d 7.68-7.62 (m, 4 H), 7.47-7.33 (m, 8 H), 7.11 (ddd, 2 H, *J* = 6.9, 6.9, 0.8 Hz), 6.94 (ddd, 1 H, *J* = 8.0, 8.0, 1.1 Hz), 5.59 (dd, 2 H, *J* = 4.7, 2.8 Hz), 4.13 (t, 2 H, *J* = 6.9 Hz), 3.93 (t, 2 H, *J*= 7.1 Hz), 3.38 (s, 1 H), 3.03 (t, 2 H, *J* = 7.1 Hz), 1.99 (ddd, 2 H, *J* = 7.7, 7.7, 3.3 Hz), 1.85 (dddd, 2 H, *J* = 6.9, 6.9, 6.9, 6.9 Hz), 1.21 (s, 6 H), 1.04 (s, 9 H), ^{13}C NMR (75 MHz, Acetone-d_6) d 141.0, 137.4, 136.4, 134.7, 130.6, 129.2, 128.7, 127.3, 125.6, 121.9, 119.7, 119.3, 111.9, 110.3, 70.1, 65.4, 45.9, 30.9, 30.5, 30.1, 29.5, 27.3, 19.7; MS (EI) *m/z* (rel intensity) 525 (M^+, 2), 509 (10), 508 (35), 507 (75), 451 (25), 450 (65), 252 (30), 239 (15), 238 (100), 225 (10), 199 (10), 183 (10), 144 (10), 67 (10); HRMS (EI) Calcd for $C_{34}H_{43}NO_2Si$ 525.3063, found 525.3058.

(3E)-2-methyl-7-(7-methyl-1H-indol-1-yl)hept-3-en-2-ol (5i): To a solution of 200 mg (0.99 mmol) of **3i** in 10 mL of CH_2Cl_2 was added 1.17g (13.7 mmol) of 2-methyl-3-butene-2-ol (**4**) and 42.2 mg (.0497 mmol) of Grubbs II. The mixture was then heated to 40 °C overnight. The mixture was cooled, filtered through a pad of a 1:1 mixture of silica gel and celite, which was washed with ethyl acetate. The filtrate was concentrated *in vacuo.* The residue was purified by chromatography on SiO_2 (0®30% EtOAc/Hexanes) to yield 95 mg (37% yield) of **5i** as a yellow-brown oil: IR (Neat) 3381, 3045, 3020, 2971, 2927, 2866, 1669, 1582 cm^{-1}, ^1H NMR (300 MHz, DMSO-d_6) d 7.35 (dd, 1 H, *J* = 7.2, 1.4 Hz), 7.26 (d, 1 H, *J* = 3.0 Hz), 6.90-6.81 (m, 2 H), 6.38 (d, 1 H, *J* = 3.3 Hz), 5.59-5.45 (m, 2 H), 4.41 (s, 1 H), 4.31 (t, 2 H, *J* = 7.1 Hz), 2.65 (s, 3 H), 1.97 (ddd, 2 H, *J* = 7.4, 7.4, 7.4 Hz), 1.75 (dddd, 2 H, *J* = 7.4, 7.4, 7.4, 7.4 Hz), 1.14 (s, 6 H); ^{13}C NMR (75 MHz, DMSO-d_6) d 140.1, 134.0, 130.1, 129.3, 124.1, 123.9, 120.4, 119.0, 118.6, 100.7, 68.8, 47.3, 32.0, 30.0, 28.6, 19.5; MS (EI) *m/z* (rel intensity) 245 (M^+, 45), 239 (10), 198 (15), 145 (45), 144 (100), 131(10); HRMS (EI) Calcd for $C_{17}H_{23}NO$ 257.1780, found 257.1785.

Sample Procedures for the Intramolecular Friedel-Crafts Reaction

10-(2-[(tert-butyldiphenylsilyl)oxy]ethyl)-1-(2-methylprop-1-en-1-yl) -1H,2H,3H,4H-pyrido[1,2-a]indole (6c): To a solution of 20 mg (0.038 mmol) of **5c** in 0.5 mL of CH_2Cl_2 was added 1.0 mg (0.0038mmol) of $(PhO)_2P(O)OH$. The mixtures was stirred overnight then quenched with sat. aq. $NaHCO_3$. The solution was extracted with CH_2Cl_2 (3x), the combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on SiO_2 (0®2% EtOAc/Hexanes) to yield 17 mg (88% yield) of **6c** as a colorless oil: IR (Neat) 3070, 3048, 2929, 2856, 1462, 1428 cm^{-1}, ^1H NMR d 7.68-7.62 (m, 2 H), 7.61-7.57 (m, 2 H), 7.45-7.31 (m, 6 H), 7.24 (d, 2 H, *J* = 8.2 Hz), 7.03 (ddd, 1 H, *J*= 7.1, 7.1, 1.1 Hz), 6.90 (ddd, 1 H, *J* = 8.0, 8.0, 1.1 Hz), 5.26 (ddq, 1 H, *J* = 9.9, 1.7, 1.7 Hz), 4.16-3.99 (m, 2 H), 3.95 (ddd, 1 H, *J* = 11.6, 8.3, 5.2 Hz), 3.78 (t, 2 H, *J* = 7.7 Hz), 3.08-2.87 (m, 2 H), 2.22-2.07 (m, 1 H), 2.02-1.87 (m, 2 H), 1.81 (d, 3 H, *J* = 1.1 Hz), 1.77-1.65 (m, 1 H), 1.68 (d, 3 H, *J* = 1.1 Hz), 1.02 (s, 9 H); ^{13}C NMR (75 MHz, Acetone-d_6) d 137.0, 136.9, 136.4, 134.8, 134.7, 131.0, 130.6, 130.5, 129.5, 128.6, 128.57, 128.2, 121.0, 119.7, 118.6, 109.5, 107.8, 65.4, 43.0, 33.3, 28.4, 27.3, 26.0, 21.3, 19.8, 18.1; MS (EI) *m/z* (rel intensity) 507 (M^+, 50), 451 (10), 450 (25), 252 (10), 239 (15), 238 (100) HRMS (EI) Calcd for $C_{34}H_{41}NOSi$ 507.2957, found 507.2958.

6-methyl-1-(2-methylprop-1-en-1-yl)-1H,2H,3H,4H-pyrido[1,2-a] indole (6i): To a solution of 47 mg (0.18 mmol) of **5i** in 2 mL of DCM was added 4.6 mg (0.018 mmol) of $(PhO)_2P(O)OH$. The mixture was stirred overnight then quenched with sat. aq. $NaHCO_3$. The solution was extracted with CH_2Cl_2 (3x), the combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on SiO_2 (0®2% Et_2O/Hexanes) to yield 23 mg (53% yield) of **6i** as a white crystalline solid: Mp 84.0-88.1 °C; IR (Neat) 2925, 2858 cm^{-1}, ^1H NMR (300 MHz, Acetone-d_6) d 7.24 (d, 1 H, *J* = 7.1 Hz), 6.82 (dd, 1 H, *J* = 7.4, 7.1 Hz), 6.74 (d, 1 H, *J* = 7.1 Hz) 6.03 (d, 1 H, *J* = 1.4 Hz), 5.24 (ddq, 1 H, *J* = 9.1, 1.4, 1.4 Hz), 4.74 (dddd, 1 H, *J* = 11.6, 5.5, 2.8, 0.8 Hz), 4.17 (ddd, 1 H, *J* = 11.3, 11.3, 5.0 Hz), 3.78 (dddd, 1 H, *J* = 9.6, 9.6, 5.2, 1.1 Hz), 2.70 (s, 3 H), 2.21-2.13 (m, 1 H), 2.09-2.01 (m, 1 H), 1.99-1.88 (m, 1 H), 1.79 (d, 3 H, *J* = 1.4 Hz), 1.78 (d, 3 H, *J* = 1.4 Hz), 1.48 (dddd, 1 H, *J* = 12.3, 11.3, 11.3, 3.0 Hz); ^{13}C NMR (75 MHz, Acetone-d_6) d 141.5, 136.8, 132.8, 130.0, 128.1, 124.2, 121.8, 120.1, 118.6, 99.9, 46.4, 36.4, 28.9, 26.0, 24.2, 20.6, 18.1; MS (EI) *m/z* (rel intensity) 239 (M^+, 100), 224 (50), 184 (20), 144 (15); HRMS (EI) Calcd for $C_{17}H_{21}N$ 239.1674, found 239.1674.

Results and Conclusion

In conclusion, diphenyl phosphate-catalyzed intramolecular Friedel-Crafts reactions of tertiary allylic alcohols and indoles has been reported. Nine examples of 1H,2H,3H,4H-pyrido[1,2-a]indoles were synthesized bearing electron-donating groups in a yield of 32-88%. More work is required to expand the scope of this transformation to allow for the

formations of 5 and 7-membered rings. In the addition, this approach could extend to pyrrole or other heterocycles or the use of chiral phosphoric acid catalysts could render this reaction enantioselective.

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