JOC The Journal of Organic Chemistry

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Development of a Suzuki Cross-Coupling Reaction between 2-Azidoarylboronic Pinacolate Esters and Vinyl Triflates To Enable the Synthesis of [2,3]-Fused Indole Heterocycles

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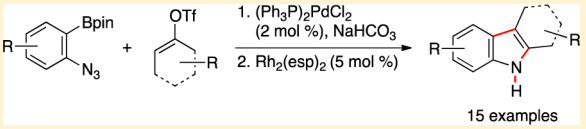
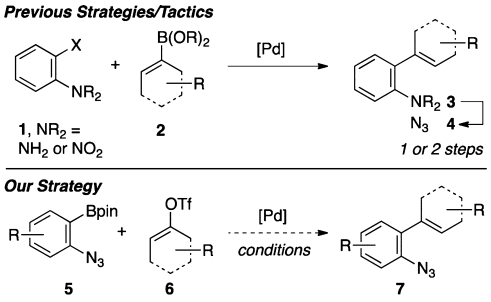
Supporting Information

ABSTRACT: The scope and limitations of a Suzuki reaction between 2-azidoarylboronic acid pinacolate esters and vinyl triflates are reported. This cross-coupling reaction enables the regioselective synthesis of indoles after a subsequent Rh^{II}_2-catalyzed sp^2-C−H bond amination reaction.



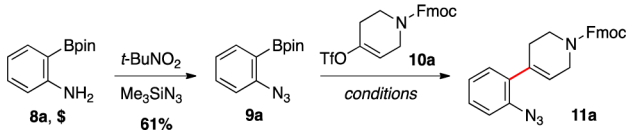
The ubiquity of the indole scaffold in compounds that exhibit promising biological and electronic properties continues to inspire research into developing efficient methods for their construction.[1,2] Our group has developed the use of rhodium(II) carboxylates to access this important scaffold through C−H bond amination from vinyl or aryl azides.[3] While our method worked to access a diverse array of functionalized N-heterocycles, the number of steps required to access the requisite aryl azide substrates diminished the overall synthetic efficiency of our process, and we felt that the development of new reactions to construct our aryl azide substrates would improve the overall synthetic efficiency of our C−H bond amination process.[4,5] In particular, we envisioned a cross-coupling reaction that minimized functional group manipulation could be achieved by pairing *o*-azidoarylboronic acid pinacolate esters with vinyl triflates, which are readily available from functionalized ketones (Scheme 1).[6] Despite the burgeoning use of aryl azides in synthetic and biological processes,[7−9] we found sparse examples of their use in cross-coupling reactions and no successful examples of *o*-azidoarylboronates or trifluoroborates.[10,11] To address this gap, herein we report the development of a cross-coupling reaction involving an *o*-azidoarylboronic acid pinacolate ester to enable the step-economical synthesis of functionalized 2-alkenylaryl azides from readily available starting materials.

Scheme 1. Cross-Coupling Strategies That Synthesize 2-Alkenyl Aryl Azides



Our reaction development began by examining the reactivity of *o*-azidophenylboronic acid pinacolate **9a** and vinyl triflate **10a** toward cross-coupling conditions (Table 1). Our first attempts were centered on using 2-azidophenyl trifluoroborate[12] or the 2-azidophenyl MIDA-boronate[13] in this transformation. Despite our best efforts, we were unable to synthesize either the 2-amino-MIDA-boronate or the 2-azidophenyl trifluoroborate. Undaunted by these failures, the pinacolate ester, which has never been reported, was examined next.[14] Its synthesis was surprisingly simple: diazotization using

Table 1. Optimization of Suzuki Cross-Coupling Reaction of 9a



entry	catalyst (amt, mol %)	base (*x* equiv)	*T*, °C	yield, %[a]
1[b]	$Pd(PPh_3)_4$ (10)	Na_2CO_3	100	72
2[b]	$Pd(PPh_3)_4$ (10)	$NaHCO_3$	100	74
3[b]	$Pd(PPh_3)_4$ (10)	K_2CO_3	100	60
4[b]	$Pd(PPh_3)_4$ (10)	Et_3N	100	37
5[b]	$Pd(OAc)_2$ + PCy_3 (3)	KF	25	83
6[c]	$PdCl_2(PPh_3)_2$ (10)	Na_2CO_3	80	83
7[c]	$PdCl_2(PPh_3)_2$ (10)	$NaHCO_3$	80	99
8[c]	$PdCl_2(PPh_3)_2$ (10)	$NaHCO_3$	70	90
9[c]	$PdCl_2(PPh_3)_2$ (5)	$NaHCO_3$	80	96
10[c]	$PdCl_2(PPh_3)_2$ (2)	$NaHCO_3$	80	94
11[c]	$PdCl_2(PPh_3)_2$ (1)	$NaHCO_3$	80	93

[a]As determined using ^{1}H NMR spectroscopy. [b]Reaction performed in DME. [c]Reaction performed in THF.

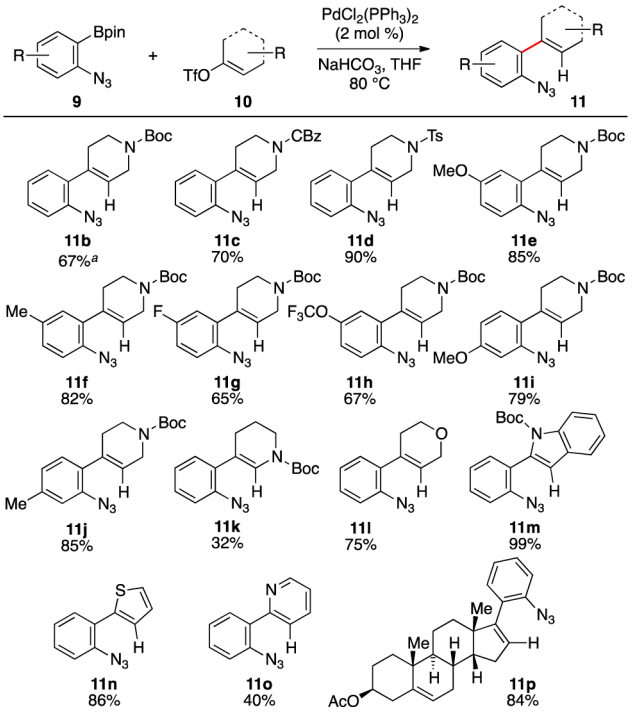
Received: February 1, 2014
Published: February 27, 2014

   dx.doi.org/10.1021/jo500252e | J. Org. Chem. 2014, 79, 2781−2791

the method reported by Moses and co-workers[15] of the commercially available aniline **8a** proved to be both reproducible and high yielding, and **9a** could be purified using silica gel chromatography to provide an air-stable yellow oil. We chose to couple this boronate with the vinyl triflate derived from FMOC-protected 4-piperidinone in order to find functional group tolerant optimal conditions. To our surprise, we found that simply employing 10 mol % of $Pd(PPh_3)_4$ at 100 °C led to the desired cross-coupling product **11a** (entry 1). Aryl azide **11a** was formed in 72% yield despite the potential for Staudinger reduction of the azide group with the excess phosphine ligand.[16] Surveying different bases, however, did not result in the yield using $Pd(PPh_3)_4$ (entries 2−4). We anticipated the yield might be improved by examining palladium catalysts that contained a smaller number of phosphine ligands. To our delight, the combination of $Pd(OAc)_2$ and PCy_3—conditions reported by Fu and co-workers[17]—improved the yield to 83% (entry 5). We were curious if similar conversions could be obtained using a less expensive phosphine source, and after a brief survey we found $PdCl_2(PPh_3)_2$ matched this result (entry 6). Changing the identity of the base from Na_2CO_3 to $NaHCO_3$ further improved the yield of the cross coupling to 99% (entry 7). Reducing the temperature from 80 to 70 °C, however, resulted in a smaller yield (entry 8). At 80 °C, the catalyst loading could be reduced to 1 mol % without attenuation of the yield (entries 9−11).

The scope and limitations of our cross-coupling reaction were examined using a variety of different aryl azides and vinyl triflates (Scheme 2). First, the identity of the nitrogen substituent was examined, and vinyl triflates bearing a variety of common N-protecting groups were successfully converted to the corresponding aryl azides **11b−d**. The cross-coupling reaction to produce aryl azide **11b** could be scaled to 4 mmol without significant diminishment of the yield. Second, the effect of substitution on the 2-azidoarylboron pinacolate ester on the yield of the cross-coupling reaction was surveyed. We found that while our reaction tolerated ethereal and alkyl substitution on this coupling partner (**11e−j**) the yield of the reaction was attenuated with fluorinated substituents (**11g,h**). Changing the position of the nitrogen in the vinyl triflate, however, adversely affected the outcome of the cross-coupling reaction: the vinyl triflate derived from 3-piperidone produced **11k** in 32% yield—a significant drop in yield in comparison to **11h**. In contrast, the nitrogen atom at the 4-position could be replaced by an oxygen atom without consequence to produce aryl azide **11l** in 75% yield. Next, a few heteroaromatic triflates were briefly surveyed to determine if our conditions could be extended to this class of cross-coupling partners. We found that while indole and thiophene triflates were competent to produce **11m,n**, reduced yields were observed using pyridine triflates. Finally, we demonstrated the synthetic utility of our cross-coupling reaction by successfully converting the 5,6-dehydroandrosterone-derived vinyl triflate to aryl azide **11p** in 84% yield. Together, these results illustrate the generality of our cross-coupling 2-azidoarylboron pincolate esters with vinyl triflates to efficiently access a range of complex, functionalized 2-alkenyl-substituted aryl azides.

Scheme 2. Investigation of the Scope and Limitations of the Cross-Coupling of 2-Azidoarylboron Pincolate Esters with Vinyl Triflates[a]



[a]Reaction performed on a 4 mmol scale.

To demonstrate the efficiency of our cross-coupling reaction, the aryl azide products were exposed to our Rh^{II}_2- catalyzed sp^2-C−H bond amination reaction to access a diverse range of N-heterocycles (Table 2).[3,18] We chose Du Bois's $Rh_2(esp)_2$ complex as the catalyst because of its robust nature[19] and found the identity of the nitrogen atom substituent influenced the yield of the amination reaction, with the Boc group providing the highest yield (entries 1−4). In contrast, our amination reaction was insensitive to the electronic nature of the aryl azide, enabling access to tetrahydracarbazoles **11e−j** (entries 1−4). To our delight, 5-substituted aryl azides **11i,j** were smoothly converted to tetrahydrocarbolines; these products cannot be accessed as single regioisomers using the Fischer−indole reaction (entries 6 and 7).[20] To our surprise, a higher yield was observed with aryl azide **11k** when the nitrogen atom was moved into conjugation (entry 11). Uniformly high yields were also observed with heteroaromatic ortho substituents (entries 12−14). Finally, the conversion of androsterone-derived **11p** to indole **12p** demonstrated that our C−H bond amination reaction works on complex functionalized substrates, albeit in reduced yield (entry 15).

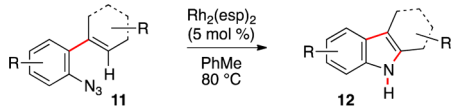
In conclusion, we have discovered a mild cross-coupling reaction that accesses complex, functionalized ortho-substituted aryl azides in one step from readily available 2-azidoarylboron pincolate esters and vinyl triflates using a palladium catalyst with inexpensive phosphine ligands. The resulting 2-substituted aryl azides can be easily transformed to N-heterocycles using our Rh^{II}_2-catalyzed sp^2-C−H bond amination reaction.

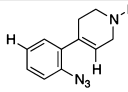
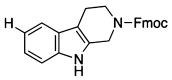
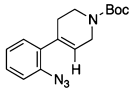
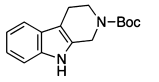
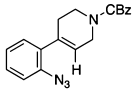
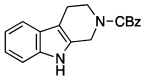
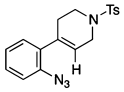
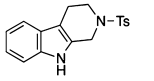
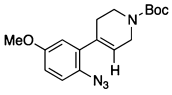
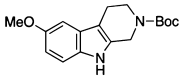
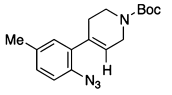
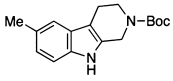
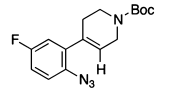
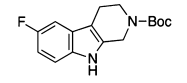
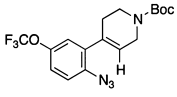
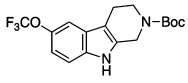
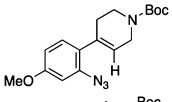
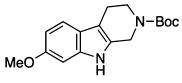
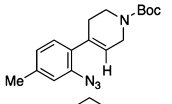
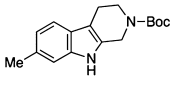
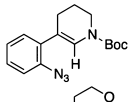
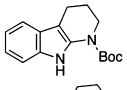
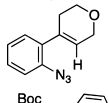
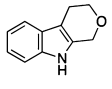
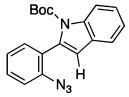
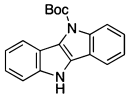
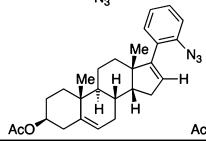
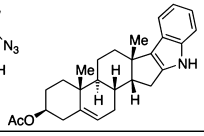
EXPERIMENTAL SECTION

General Considerations. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperature using 500 or 300 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra were acquired on a LTQ FT spectrometer using electrospray

dx.doi.org/10.1021/jo500252e | J. Org. Chem. 2014, 79, 2781−2791

Table 2. Conversion of Ortho-Substituted Aryl Azides to N-Heterocycles through Rh^{II}_2-Catalyzed C−H Bond Amination



entry	#	aryl azide **11**	indole **12**	yield (%)[a]
1	**a**			54
2	**b**			77
3	**c**			51
4	**d**			47
5	**e**			75
6	**f**			80
7	**g**			65
8	**h**			75
9	**i**			60
10	**j**			81
11	**k**			91
12	**l**			83
11	**m**			96
14	**n**			98
15	**p**			25

[a]After purification by silica gel chromatography.

to ionize the sample and were obtained by peak matching. Melting points are reported uncorrected. Infrared spectroscopy was obtained using a diamond attenuated total reflectance (ATR) accessory. Analytical thin-layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on 60 Å (40−60 μm) mesh silica gel (SiO_2). Medium-pressure liquid chromatography (MPLC) was performed to force flow the indicated solvent system down columns that had been packed with 60 Å (40−60 μm) mesh silica gel (SiO_2). All reactions were carried out under an atmosphere of nitrogen in glassware which had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Acetonitrile, methanol, toluene, THF, Et_2O, and CH_2Cl_2 were dried by filtration through alumina according to the procedure of Grubbs.[21] Metal salts were stored in a nitrogen atmosphere drybox.

General Synthesis of 2-Aminoarylboronic Acid Pinacolate Esters. To a mixture of 1.0 g of 2-bromoaniline (5.8 mmol), 3.22 mL of Et_3N (23.2 mmol), and 0.208 g of (dppf)$PdCl_2$ (0.25 mmol) in 20 mL of 1,4-dioxane was added dropwise 2.53 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17.4 mmol). The resultant mixture was refluxed at 120 °C. After 12 h, the mixture was cooled to room temperature and diluted with 20 mL of NH_4Cl. The resulting aqueous phase was extracted with an additional 2 × 20 mL of CH_2Cl_2. The combined organic phases were washed with 1 × 30 mL of brine. The resulting organic phase was dried over Na_2SO_4 and filtered, and the filtrate was concentrated in vacuo. Purification via MPLC afforded the 2-aminoarylboronic acid pinacolate ester.

2-Aminophenylboronic Acid Pinacolate Ester.[22] The general procedure for the Pd-catalyzed borylation reaction was followed using 3.40 g of 2-bromoaniline (20.0 mmol), 8.7 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (60.0 mmol), 0.816 g of (dppf)$PdCl_2$ (1.00 mmol), and 8.4 mL of Et_3N (80.0 mmol) in 100 mL of 1,4-dioxane. Purification by MPLC (2/100 to 10/90 EtOAc/hexanes) afforded the product as a light yellow solid (3.02 g, 69%): mp 62−64 °C; spectral data matched those reported by Driver and co-workers, and this compound is also available commercially;[22] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 7.5 Hz, 1H), 7.24 (t, J = 7.0 Hz, 1H), 6.70 (t, J = 7.0 Hz, 1H), 6.61 (d, J = 8.5 Hz, 1H), 4.76 (s, 2H), 1.36 (s, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 153.7 (C), 136.8 (CH), 132.8 (CH), 116.9 (CH), 114.8 (CH), 83.5 (C), 25.0 (CH_3) only visible peaks; IR (thin film) 3486, 3380, 1624, 1605,1352, 1311, 1244, 1135, 1086, 847, 758, 654 cm^{-1}.

2-Amino-5-methoxyphenylboronic Acid Pinacolate Ester.[23] The general procedure for the Pd-catalyzed borylation reaction was followed using 0.850 g of 2-bromo-4-methoxyaniline (4.20 mmol), 1.83 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12.6 mmol), 0.170 g of (dppf)$PdCl_2$ (0.210 mmol), and 2.34 mL of Et_3N (16.8 mmol) in 42 mL of 1,4-dioxane. Purification by MPLC (2/100 to 10/90 EtOAc/hexanes) afforded the product as a brown liquid (0.670 g, 64%): spectral data matched those reported by Driver and co-workers;[23] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.85 (dd, J = 8.5, 3.0 Hz, 1H), 6.57 (d, J = 8.5 Hz, 1H), 4.47 (s, 2H), 3.76 (s, 3H), 1.34 (s, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 151.4 (C), 148.0 (C), 120.6 (CH), 119.6 (CH), 116.5 (CH), 83.6 (C), 56.0 (CH_3), 25.0 (CH_3) only visible peaks; IR (thin film) 3456, 3366, 1494, 1421, 1359, 1304, 1226, 1037, 855, 829, 750 cm^{-1}.

2-Amino-5-methylphenylboronic Acid Pinacolate Ester.[23b] The general procedure for the Pd-catalyzed borylation reaction was followed using 0.930 g of 2-bromo-4-methylaniline (5.00 mmol), 2.20 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15.0 mmol), 0.204 g of (dppf)$PdCl_2$ (0.250 mmol), and 2.78 mL of Et_3N (20.0 mmol) in 25 mL of 1,4-dioxane. Purification by MPLC (2/100 to 10/90 EtOAc/hexanes) afforded the product as a light yellow solid (0.490 g, 42%): mp 60 °C; spectral data matched those reported by Driver and co-workers;[23b] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.08 (d, J = 8.0 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 4.65 (s, 2H), 2.26 (s, 3H), 1.38 (s, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 151.5 (C), 136.8 (CH), 133.7 (CH), 125.8 (C), 115.1 (CH), 83.5 (C), 67.1 (C), 25.0 (CH_3), 20.3 (CH_3); IR (thin film) 3500, 2980, 2244, 1618, 1576, 1496 cm^{-1}.

2-Amino-5-fluorophenylboronic Acid Pinacolate Ester.[24] The general procedure for the Pd-catalyzed borylation reaction was followed using 0.950 g of 2-bromo-4-fluoroaniline (5.00 mmol), 2.2

dx.doi.org/10.1021/jo500252e | J. Org. Chem. 2014, 79, 2781−2791

mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15.0 mmol), 0.204 g of (dppf)$PdCl_2$ (0.250 mmol), and 2.78 mL of Et_3N (20.0 mmol) in 25 mL of 1,4-dioxane. Purification by MPLC (2/100 to 10/90 EtOAc/hexanes) afforded the product as a light yellow solid (0.900 g, 76%): spectral data matched those reported by Driver and co-workers;[24] ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, J = 9.0 Hz, 3.0 Hz, 1H), 6.92 (dt, J = 8.5 Hz, 3.0 Hz, 1H), 6.53 (dd, J = 9.0 Hz, 4.5 Hz, 1H), 4.59 (s, 2H), 1.34 (s, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.2 (d, J_{CF} = 233.2 Hz, C), 149.8 (C), 121.6 (d, J_{CF} = 20.1 Hz, CH), 119.7 (d, J_{CF} = 23.7 Hz, CH), 116.0 (CH), 83.9 (C), 24.9 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ −129.5; IR (thin film) 3470, 3371, 2975, 2931, 1624, 1492, 1434, 1380, 1347, 1198, 1190, 1135, 1081, 963, 912 cm^{-1}.

2-Amino-5-trifluoromethoxyphenylboronic Acid Pinacolate Ester. The general procedure for the Pd-catalyzed borylation reaction was followed using 1.28 g of 2-bromo-4-trifluoromethoxyaniline (5.00 mmol), 2.20 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15.0 mmol), 0.204 g of (dppf)$PdCl_2$ (0.250 mmol), and 2.78 mL of Et_3N (20.0 mmol) in 25 mL of 1,4-dioxane. Purification by MPLC (2/100 to 10/90 EtOAc/hexanes) afforded the product as a light yellow solid (0.970 g, 59%): mp 63−67 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.06 (d, J = 8.5 Hz, 1H), 6.54 (d, J = 9.0 Hz, 1H), 4.80 (s, 2H), 1.34 (s, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 152.5 (C), 140.0 (C), 129.0 (CH), 126.0 (CH), 122.8 (q, J_{CF} = 253.5 Hz, C), 115.5 (CH), 84.0 (C), 24.9 (CH_3), only visible peaks; ^{19}F NMR (282 MHz, $CDCl_3$) δ −58.8; IR (thin film) 3477, 3374, 2992, 2980, 1627, 1492, 1436, 1532, 1211, 1163, 1094, 965, 852, 825 cm^{-1}.

2-Amino-4-methoxyphenylboronic Acid Pinacolate Ester. The general procedure for the Pd-catalyzed borylation reaction was followed using 1.01 g of 2-bromo-5-methoxyaniline (5.00 mmol), 2.20 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15.0 mmol), 0.204 g of (dppf)$PdCl_2$ (0.250 mmol), and 2.78 mL of Et_3N (20.0 mmol) in 25 mL of 1,4-dioxane. Purification by MPLC (2/100 to 10/90 EtOAc/hexanes) afforded the product as a light yellow oil (0.632 g, 46%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5 Hz, 1H), 6.27 (dd, J = 8.5 Hz, 2.0 Hz, 1H), 6.11 (d, J = 2.0 Hz, 1H), 4.82 (br s, 2H), 3.75 (s, 3H), 1.34 (s, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 163.7 (C), 155.6 (C), 138.4 (CH), 103.8 (CH), 99.4 (CH), 83.3 (C), 54.9 (CH_3), 24.9 (CH), only visible peaks; IR (thin film) 2976, 2934, 2832, 2101, 1601, 1565, 1345, 1035, 836 cm^{-1}.

2-Amino-4-methylphenylboronic Acid Pinacolate Ester.[25] The general procedure for the Pd-catalyzed borylation reaction was followed using 0.930 g of 2-bromo-5-methylaniline (5.00 mmol), 2.20 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15.0 mmol), 0.204 g of (dppf)$PdCl_2$ (0.250 mmol), and 2.78 mL of Et_3N (20.0 mmol) in 25 mL of 1,4-dioxane. Purification by MPLC (2/100 to 10/90 EtOAc/hexanes) afforded the product as a light yellow solid (0.791 g, 68%): mp 68 °C; spectral data of the product matched those reported by Marsden, Nelson, and co-workers;[25] ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 7.5 Hz, 1H), 6.51 (d, J = 7.5 Hz, 1H), 6.4 (s, 1H), 4.64 (br s, 2H), 2.26 (s, 3H), 1.34 (s, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 153.7 (C), 143.1 (C), 136.8 (CH), 118.2 (CH), 115.4 (CH), 83.4 (C), 24.9 (CH_3), 21.7 (CH_3), only visible peaks; IR (thin film) 3473, 3370, 2972, 1617, 1563, 1507, 1435, 1357, 1305, 1247, 1143, 1305, 1247, 1143, 1098, 1052, 857 cm^{-1}.

General Procedure for the Synthesis of 2-Azidoarylboronic Acid Pinacolate Esters. The azidation of 2-aminoarylboronic acid pinacolate esters was performed using the conditions reported by Zhang and Moses.[15] To a cooled solution (0 °C) of aniline in MeCN (0.2 M) were added dropwise t-$BuNO_2$ (4.0 equiv) and Me_3SiN_3 (3.0 equiv). The resulting solution was warmed to room temperature. After 1.5 h, the reaction mixture was concentrated *in vacuo*. Purification of the residue by MPLC (0/100 to 5/95 EtOAc/hexanes) afforded the 2-azidoarylboronic acid pinacolate ester.

2-Azidophenylboronic Acid Pinacolate Ester 9a.[26] The general procedure for azidation was followed by using 1.60 g of 2-aminophenylboronic acid pinacolate ester (7.30 mmol), 3.47 mL of t-$BuNO_2$ (29.2 mmol) and 2.90 mL of Me_3SiN_3 (21.9 mmol) in 36 mL of MeCN. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a yellow oil (1.091 g, 61%); spectral data matched those reported by Driver and co-workers;[26] ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 7.0 Hz, 1H), 7.15−7.10 (m, 2H), 1.36 (s, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 144.8 (C), 137.0 (CH), 132.4 (CH), 124.2 (CH), 118.2 (CH), 84.0 (C), 24.8 (CH_3) only visible signals; ATR-FTIR (thin film) 2976, 2112, 2076, 1594, 1572, 1487, 1432, 1351, 1316, 1279, 1143, 1110, 1058, 1036, 836, 747 cm^{-1}.

2-Azido-5-methoxyphenylboronic Acid Pinacolate Ester 9b. The general procedure for azidation was followed by using 0.550 g of 2-amino-5-methoxyphenylboronic acid pinacolate ester (2.00 mmol), 0.95 mL of t-$BuNO_2$ (8.0 mmol), and 0.80 mL of Me_3SiN_3 (6.0 mmol) in 10 mL of MeCN. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a yellow solid (0.396 g, 72%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 2.5 Hz, 1H), 7.07 (d, J = 9.0 Hz, 1H), 6.98 (dd, J = 8.5 Hz, 3.0 Hz, 1H), 3.81 (s, 3H), 1.36 (s, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.3 (C), 137.3 (C), 120.9 (CH), 119.7 (CH), 118.6 (CH), 80.1 (C), 55.6 (CH_3), 24.8 (CH_3) only visible peaks; ATR-FTIR (thin film) 2976, 2934, 2118, 1484, 1409, 1341, 1231, 1143, 1052, 906, 724 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{18}BN_3O_3Na$ $(M + Na)^+$ 298.1339, found 298.1345.

2-Azido-5-methylphenylboronic Acid Pinacolate Ester 9c. The general procedure for azidation was followed by using 0.518 g of 2-amino-5-methylphenylboronic acid pinacolate ester (2.00 mmol), 0.95 mL of t-$BuNO_2$ (8.0 mmol), and 0.80 mL of Me_3SiN_3 (6.0 mmol) in 10 mL of MeCN. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as an orange oil (0.253 g, 49%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 1.5 Hz, 1H), 7.26 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 2.31 (s, 3H), 1.36 (s, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 142.1 (C), 137.4 (CH), 133.8 (C), 133.0 (CH), 118.2 (CH), 84.0 (C), 24.8 (CH_3), 20.7 (CH_3) only visible peaks; ATR-FTIR (thin film) 2979, 2924, 2118, 2092, 1579, 1487, 1400, 1345, 1312, 1269, 1146, 906, 730 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{18}BN_3O_2Na$ $(M + Na)^+$ 282.1390, found 282.1391.

2-Azido-5-fluorophenylboronic Acid Pinacolate Ester 9d. The general procedure for azidation was followed by using 0.526 g of 2-amino-5-fluorophenylboronic acid pinacolate ester (2.00 mmol), 0.95 mL of t-$BuNO_2$ (8.0 mmol), and 0.80 mL of Me_3SiN_3 (6.0 mmol) in 10 mL of MeCN. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a red oil (0.373 g, 71%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, J = 8.5 Hz, 3.0 Hz, 1H), 7.10 (ddd, J = 10.5 Hz, 7.5 Hz, 3.0 Hz, 1H), 7.05 (dd, J = 8.5 Hz, 4.0 Hz, 1H), 1.34 (s, 12 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 159.4 (d, J_{CF} = 242.9 Hz, C), 140.5 (C), 123.0 (d, J_{CF} = 20.5 Hz, CH), 119.9 (d, J_{CF} = 7.5 Hz, 1H), 119.1 (d, J_{CF} = 23.5 Hz, CH), 84.3 (C), 24.8 (CH_3) only visible peaks; ^{19}F NMR (282 MHz, $CDCl_3$) δ −119.4; ATR-FTIR (thin film) 2989, 2121, 2092, 1485, 1416, 1319, 1200, 1143, 1126, 966, 916, 807, 763 cm^{-1}. HRMS (EI) m/z calcd for $C_{12}H_{15}BN_3O_2F$ $[M]^+$ 263.1241, found 263.1233.

2-Azido-5-trifluoromethoxyphenylboronic Acid Pinacolate Ester 9e. The general procedure for azidation was followed by using 0.658 g of 2-amino-5-trifluoromethoxyphenylboronic acid pinacolate ester (2.0 mmol), 0.95 mL of t-$BuNO_2$ (8.0 mmol), and 0.8 mL of Me_3SiN_3 (6.0 mmol) in 10 mL of MeCN. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a brown oil (0.467 g, 71%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.27 (d, J = 9.0 Hz, 1H), 7.13 (d, J = 9.0 Hz, 1H), 1.36 (s, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 145.5 (C), 143.5 (C), 129.4 (CH), 124.9 (CH), 120.5 (q, J_{CF} = 255.2 Hz, C), 119.6 (CH), 84.4 (C), 24.7 (CH_3) only visible peaks; ^{19}F NMR (282 MHz, $CDCl_3$) δ −58.5; ATR-FTIR (thin film) 2979, 2934, 2125, 2092, 1487, 1416, 1345, 1243, 1214, 1136, 1055, 956, 851 cm^{-1}. HRMS (EI) m/z calcd for $C_{13}H_{15}BN_3O_3F_3$ $[M]^+$ 329.1159, found 329.1158.

2-Azido-4-methoxyphenylboronic Acid Pinacolate Ester 9f. The general procedure for azidation was followed by using 0.550 g of 2-amino-4-methoxyphenylboronic acid pinacolate ester (2.00 mmol), 0.95 mL of t-$BuNO_2$ (8.0 mmol), and 0.80 mL of Me_3SiN_3 (6.0 mmol) in 10 mL of MeCN. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a yellow oil (0.253 g, 46%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.5 Hz, 1H), 6.67 (d, J = 2.0 Hz, 1H), 6.64 (m, 1H), 3.81 (s, 3H), 1.33 (s, 12H); $^{13}C\{^1H\}$ NMR (125

dx.doi.org/10.1021/jo500252e | J. Org. Chem. 2014, 79, 2781−2791

MHz, $CDCl_3$) δ 163.1 (C), 146.6 (C), 138.8 (CH), 110.0 (CH), 104.3 (CH), 83.7 (C), 55.3 (CH_3), 24.8 (CH_3) only visible peaks; ATR-FTIR (thin film) 2979, 2973, 2101, 1601, 1565, 136, 1228, 1151, 1111, 1035, 837, 649 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{18}BN_3O_3Na$ $(M + Na)^+$ 298.1339, found 298.1342.

2-Azido-4-methylphenylboronic Acid Pinacolate Ester 9g. The general procedure for azidation was followed by using 0.518 g of 2-amino-4-methylphenylboronic acid pinacolate ester (0.200 mmol), 0.95 mL of *t*-$BuNO_2$ (8.0 mmol), and 0.80 mL of Me_3SiN_3 (6.0 mmol) in 10 mL of MeCN. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as an orange oil (0.321 g, 62%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 7.5 Hz, 1H), 6.94 (s, 1H), 6.93 (s, 1H), 2.63 (s, 3H), 1.35 (s, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 144.8 (C), 142.9 (C), 137.1 (CH), 125.3 (CH), 118.8 (CH), 83.8 (C), 24.8 (CH_3), 21.6 (CH_3), only peaks visible; ATR-FTIR (thin film) 2979, 2931, 2102, 1615, 1556, 1341, 1257, 1153, 1120, 1055, 961, 863, 815 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{18}BN_3O_2Na$ $(M + Na)^+$ 282.1390, found 282.1394.

General Procedure for the Preparation of Vinyl Triflates. To a cooled solution (−78 °C) of 2.38 g of LHMDS (16.9 mmol, 1.1 equiv) in 75 mL of THF was added the ketone (15.4 mmol, 1 equiv). After addition, the resulting mixture was warmed to room temperature. After 1 h, the reaction mixture was cooled to −78 °C, and a solution of 6.60 g of $PhNTf_2$ (18.5 mmol, 1.2 equiv) in 20 mL of THF was added. The solution was stirred overnight. After 15 h, the reaction mixture was evaporated to dryness. The resulting residue was extracted with 3 × 30 mL of ethyl acetate. The combined organic phases were dried over Na_2SO_4, and filtered, and the filtrate was concentrated in vacuo. The resulting residue was purified by MPLC to afford the triflate as a colorless oil. Because of the sensitivity of several of the vinyl triflates toward water, these products were characterized only using ^1H NMR and were immediately used in the subsequent cross-coupling reaction.

Vinyl Triflate 10a. The general procedure for triflate formation was followed by using 4.95 g of Fmoc-protected 4-piperidinone (15.4 mmol), 2.83 g of LHMDS (16.9 mmol) in 75 mL of THF, and 6.60 g of $PhNTf_2$ (18.5 mmol) in 20 mL of THF. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a white solid (6.14 g, 88%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 7.5 Hz, 2H), 7.41 (t, J = 7.0 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 5.77−5.73 (br m, 1H), 4.50 (d, J = 5.5 Hz, 2H), 4.25 (t, J = 6.5 Hz, 1H), 4.12−4.00 (m, 2H), 3.68−3.56 (m, 2H), 2.44−2.34 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.0 (C), 147.1 (C), 143.8 (C), 141.4 (C), 127.9 (CH), 127.2 (CH), 124.9 (CH), 120.1 (CH), 118.5 (q, J_{CF} = 318.9 Hz, CF_3), 115.2 (CH), 67.4 (CH_2), 47.3 (CH), 41.7 (CH_2), 40.4 (CH_2), 27.8 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.20; ATR-FTIR (thin film) 3067, 2943, 2355, 2332, 1692, 1417, 1199, 1136, 1121, 1047, 857 cm^{-1}.

Vinyl Triflate 10b.[27] The general procedure for triflate formation was followed by using 2.00 g of Boc-protected 4-piperidinone (10.03 mmol), 1.847 g of LHMDS (11.0 mmol) in 50 mL of THF, and 4.29 g of $PhNTf_2$ (12.0 mmol) in 15 mL of THF. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a colorless oil (2.76 g, 83%): spectral data of the product matched those reported by Fürstner and co-workers;[27] ^1H NMR (500 MHz, $CDCl_3$) δ 5.75 (br s, 1H), 4.03 (m, 2H), 3.62 (t, J = 6.0 Hz, 2H), 2.42 (m, 2H), 1.46 (s, 9H); ATR-FTIR (thin film) 2982, 2927, 1669, 1491, 1419, 1271, 1246, 1203, 1137, 1065, 1010, 865 cm^{-1}.

Vinyl Triflate 10c.[28] The general procedure for triflate formation was followed by using 0.250 g of Cbz-protected 4-piperidinone (1.07 mmol), 0.197 g of LHDMS (1.18 mmol) in 5 mL of THF, and 0.459 g of $PhNTf_2$ (1.28 mmol) in 3 mL of THF. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a colorless oil (0.297 g, 76%): spectral data of the product matched those reported by Patel and co-workers;[28] ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 5H), 5.78 (br m, 1H), 5.16 (s, 2H), 4.13 (br m, 2H), 3.72 (br m, 2H), 2.46 (br m, 2H); ATR-FTIR (thin film) 3076, 2849, 1698, 1666, 1416, 1236, 1137, 1062, 866, 752 cm^{-1}.

Vinyl Triflate 10d.[29] The general procedure for triflate formation was followed by using 0.253 g of Ts-protected 4-piperidinone (1.00 mmol), 0.197 g of LHDMS (1.18 mmol) in 5 mL of THF, and 0.459 g of $PhNTf_2$ (1.28 mmol) in 3 mL of THF. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a colorless oil (0.297 g, 76%): spectral data of the product matched those reported by Dantale and Söderberg;[29] ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.72 (m, 1H), 3.78 (q, J = 3.0 Hz, 2H), 3.34 (t, J = 6.0 Hz, 2H), 2.47 (m, 2H), 2.43 (s, 3H); ATR-FTIR (thin film) 3076, 2849, 1698, 1666, 1416, 1236, 1137, 1062, 866, 752 cm^{-1}.

Vinyl Triflate 10e.[30] To a stirred solution of 0.948 mL of diisopropylamine (7.03 mmol) in 15 mL of THF at 0 °C under an atmosphere of argon was added slowly 2.81 mL of a 2.5 M solution of *n*-butyllithium in hexane (7.03 mmol). After 10 min, the solution was cooled to −78 °C, and 1.00 g of *N*-Boc-3-piperidone (5.02 mmol) in 5 mL of THF was added dropwise to this solution. After 30 min, 1.59 g of *N*-Phenylbis(trifluoromethanesulfonimide) (5.02 mmol) in 5 mL of THF was added dropwise, and the solution was warmed slowly to room temperature overnight. The volatiles were removed under reduced pressure, and purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product, a 30/70 mixture of rotamers, as a brown oil (0.698 g, 44%): spectral data matched those reported by Wang and co-workers;[30] ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (s, 0.46H), 7.06 (s, 0.54H), 3.52 (br s, 2H), 2.43 (t, J = 6.5 Hz, 2H), 1.92 (quint, J = 6.0 Hz, 2H), 1.49 (s, 9H); ATR-FTIR (thin film) 2982, 2931, 2872, 1710, 1417, 1391, 1352, 1244, 1203, 1160, 910 cm^{-1}.

Vinyl Triflate 10f.[31] To a stirred solution of 0.760 mL of diisopropylamine (5.49 mmol) in 15 mL of THF at 0 °C under an atmosphere of argon was added slowly 2.19 mL of a 2.5 M solution of *n*-butyllithium in hexane (5.49 mmol). After 10 min, the solution was cooled to −78 °C, and 0.500 g of tetrahydro-4*H*-pyran-4-one (4.99 mmol) in 5 mL of THF was added dropwise to this solution. After 30 min, 1.96 g of *N*-phenyl-bis(trifluoromethanesulfonimide) (5.49 mmol) in 5 mL of THF was added dropwise, and the solution was warmed slowly to room temperature overnight. The volatiles were removed under reduced pressure, and purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a brown oil (0.787 g, 68%): spectral data of the product matched those reported by Hall and co-workers;[31] ^1H NMR (500 MHz, $CDCl_3$) δ 5.81 (m, 1H), 4.25 (q, J = 3.0 Hz, 2H), 3.88 (t, J = 5.5 Hz, 2H), 2.45 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 145.7 (C), 118.5 (q, J = 317.7 Hz, CF_3), 116.9 (CH), 64.2 (CH_2), 63.9 (CH_2), 28.4 (CH_2) ; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.3; ATR-FTIR (thin film) 2943, 2865, 2843, 1692, 1415, 1248, 1201, 1129, 1061, 1007, 868, 840 cm^{-1}.

Vinyl Triflate 10g.[32] To a stirred solution of 0.280 g of Boc-protected 2-oxindole (1.20 mmol) and 0.345 g of 2,6-di-*tert*-butyl-4-methylpyridine (1.68 mmol) in 5 mL of dry dichloroethane was slowly added 0.260 mL of Tf_2O (1.56 mmol) under a nitrogen atmosphere at 0 °C. The reaction mixture was then slowly warmed to room temperature. After 2 h, the reaction mixture was diluted with 20 mL of Et_2O. The resulting mixture was washed with NH_4OH and brine. The resulting organic phase was dried over Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a colorless oil (0.372 g, 85%): this product was reported by Shibata and co-workers;[32] ^1H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.0 Hz, 1H), 6.45 (s, 1H), 1.71 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 148.2 (C), 138.2 (C), 132.9 (C), 125.6 (CH), 125.1 (C), 123.7 (CH), 121.3 (CH), 118.9 (q, J_{CF} = 319.5 Hz), 115.6 (CH), 98.2 (CH), 86.3 (C), 28.1 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.4; ATR-FTIR (thin film) 2979, 1745, 1594, 1433, 1318, 1212, 1156, 969 cm^{-1}.

Vinyl Triflate 10h.[33] Under a nitrogen atmosphere, 0.40 g of 2(5*H*)-thiophenone (4.0 mmol), 1.12 g of Tf_2O (4.00 mmol) and 1.40 mL of triethylamine (10.0 mmol) was dissolved in 5.8 mL of CH_2Cl_2. After 5 h, volatiles were removed under reduced pressure, and purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a colorless oil (0.371 g, 40%); spectral data of the product matched those reported by Tsuchimoto and co-workers:[33] ^1H NMR (500 MHz, $CDCl_3$) δ 7.05 (dd, J = 6 Hz, 1 Hz, 1H), 6.90 (m, 1H), 6.86 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 149.4 (C), 124.5

dx.doi.org/10.1021/jo500252e | J. Org. Chem. 2014, 79, 2781−2791

(CH), 121.2 (CH), 119.3 (q, J = 319.5 Hz, CF_3), 118.4 (CH); ATR-FTIR (thin film) 3112, 1591, 1542, 1426, 1247, 1206, 1127, 819 cm^{-1}.

Vinyl Triflate 10i.[34] To a cooled solution (0 °C) of 1.00 g of 2-hydroxypyridine (10.5 mmol) in 40 mL of dry pyridine was added 2.12 mL of Tf_2O (12.6 mmol) dropwise. The resulting solution was then stirred at room temperature overnight, diluted with water, and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by MPLC (0/100 to 10/90 EtOAc/hexanes) to afford the product as a colorless oil (1.80 g, 76%): spectral data of the product matched those reported by Umemoto and Tomizawa;[34] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, J = 5.0 Hz, 1H), 7.89 (t, J = 8.0 Hz, 1H), 7.38 (t, J = 7.0 Hz, 1H), 7.17 (d, J = 8.5 Hz, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 155.9 (C), 148.7 (CH), 141.0 (CH), 124.3 (CH), 118.6 (q, J_{CF} = 319 Hz, C), 115.2 (CH).

Vinyl Triflate 10j. To a stirred solution of 0.500 g of dehydroisoandrosterone 3-acetate (1.51 mmol) in CH_2Cl_2 (15 mL) was added 0.280 mL of Tf_2O (1.66 mmol), and the reaction mixture was stirred at room temperature for 5 min. A solution of 0.21 mL of triethylamine (1.51 mmol) in 5 mL of CH_2Cl_2 was then added slowly. The resulting solution was stirred at room temperature for 3.5 h. The reaction was quenched by addition of water and extracted with 2 × 10 mL of CH_2Cl_2 followed by 1 × 10 mL of brine. The resulting organic phase was dried over Na_2SO_4 and was concentrated in vacuo. Purification by MPLC (0/100 to 10/90 EtOAc/hexanes) afforded the product as a yellow oil (0.450 g, 64%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.58 (s, 1H), 5.39 (s, 1H), 4.60 (m, 1H), 3.46 (br s, 1H), 2.33−2.21 (m, 3H), 2.03 (s, 3H), 1.98 (m, 2H), 1.86 (m, 2H), 1.77 (m, 2H), 1.65 (m, 2H), 1.49 (t, J = 8.0 Hz, 2H), 1.25 (t, J = 7.0 Hz, 2H), 1.14 (m, 1H), 1.05 (s, 3H), 0.99 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.5 (C), 159.2 (C), 140.2 (C), 121.8 (CH), 118.6 (q, J_{CF} = 317.7 Hz, CF_3), 114.5 (CH), 73.7 (CH), 54.2 (CH), 50.4 (CH), 44.7 (C), 38.1 (CH_2), 36.9 (CH_2), 36.8 (C), 32.7 (CH_2), 30.5 (CH_2), 29.9 (CH_3), 28.6 (CH_2), 27.7 (CH_2), 21.4 (CH), 20.1 (CH_2), 19.2 (CH_3), 15.1 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.02; ATR-FTIR (thin film) 2946, 2908, 2862, 1419, 1213, 1140, 906, 728 cm^{-1}.

General Procedure for the Screening of Reaction Conditions To Synthesize 2-Alkenylaryl Azides 11. To a mixture of vinyl triflate **9a** (0.1 mmol), 2-azidophenylboronic acid pinacolate ester **10a** (0.12 mmol), and palladium catalyst in the appropriate solvent (0.1M) was added a saturated solution of base (2 mL/mmol of **10**). The resulting solution was heated to reflux. After 1.5 h, the mixture was cooled to room temperature and quenched with 5 mL of cold water. The solution was extracted with 2 × 10 mL of ether followed by 1 × 10 mL of brine. The resulting organic phase was dried over Na_2SO_4 and was concentrated in vacuo. Dibromomethane (0.7 μL, 0.1 mmol) was added, and the mixture was analyzed using ^{1}H NMR spectroscopy to determine the outcome of the reaction. The results of this screen are given in Table 1.

Optimized Conditions for 2-Alkenylaryl Azide Formation from Suzuki Cross-Coupling Reaction. To a mixture of vinyl triflate (0.1 mmol), 2-azidoarylboronic acid pinacolate ester (0.12 mmol), and $PdCl_2(PPh_3)_2$ (2 mol %) in THF (0.1 M) was added a saturated solution of $NaHCO_3$ (2 mL/mmol of boronic ester). The resulting solution was heated to reflux. After 1.5 h, the mixture was cooled to room temperature and diluted with 5 mL of cold water. The solution was extracted with 2 × 10 mL of ether followed by 1 × 10 mL of brine. The resulting organic phase was dried over Na_2SO_4 and was concentrated in vacuo. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product.

(9*H*-Fluoren-9-yl)methyl 4-(2-Azidophenyl)-5,6-dihydropyridine-1(2*H*)-carboxylate 11a. The optimal procedure was followed by using 0.045 g of vinyl triflate **10a** (0.099 mmol), 0.029 g of 2-azidophenylboronic acid pinacolate ester **9a** (0.12 mmol), 0.0014 g of $PdCl_2(PPh_3)_2$ (2 mol %), 1.0 mL of THF, and 0.24 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a colorless liquid (0.032 g, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 7.0 Hz, 2H), 7.44−7.41 (m, 2H), 7.36−7.32 (m, 4H), 7.18−7.13 (m, 2H), 5.74 (br s, 1H), 4.49 (d, J = 6.5 Hz, 2H), 4.30 (t, J = 7.0 Hz, 1H), 4.15 (br s, 2H), 3.71 (br s, 2H), 2.51 (br s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.1 (C), 141.4 (C), 137.0 (C), 135.2 (C), 134.4 (C), 129.5 (CH), 128.6 (CH), 127.7 (CH), 127.1 (CH), 125.1 (CH), 123.3 (CH), 120.1 (CH), 118.6 (CH), 67.5 (CH_2), 47.4 (CH_2), 43.6 (CH), 40.6 (CH_2), 29.1 (CH_2) only visible peaks; diagnostic data for the minor rotamer 129.8 (CH), 124.9 (CH), 123.9 (CH); ATR-FTIR (thin film) 3064, 2950, 2125, 2089, 1696, 1678, 1423, 1286, 1228, 1191, 1110, 737 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{23}N_4O_2$ $(M + H)^+$ 423.1820, found 423.1821.

***tert*-Butyl 4-(2-Azidophenyl)-5,6-dihydropyridine-1(2*H*)-carboxylate 11b.** The optimal procedure was followed by using 0.662 g of vinyl triflate **10b** (4.00 mmol), 1.18 g of 2-azidophenylboronic acid pinacolate ester **9a** (4.80 mmol), 0.028 g of $PdCl_2(PPh_3)_2$ (2 mol %), 40 mL of THF, and 9.6 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a colorless liquid (0.805 g, 67%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dt, J = 8.0 Hz, 1.5 Hz, 1H), 7.14 (t, J = 6.0 Hz, 2H), 7.09 (t, J = 7.5 Hz, 1H), 5.70 (br s, 1H), 4.04 (br s, 2H), 3.60 (br s, 2H), 2.46 (br s, 2H), 1.49 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.9 (C), 136.9 (C), 134.6 (C), 129.8 (CH), 128.5 (CH), 127.2 (C), 123.9 (C) 124.8 (CH), 118.6 (CH), 79.7 (C), 43.7 (CH_2), 39.9 (CH_2), 29.4 (CH_2), 28.5 (CH_3); ATR-FTIR (thin film) 2976, 2927, 2120, 2089, 1692, 1484, 1415, 1235, 1112, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{21}N_4O_2$ $(M + H)^+$ 301.1664, found 301.1665.

Benzyl 4-(2-Azidophenyl)-5,6-dihydropyridine-1(2*H*)-carboxylate 11c. The optimal procedure was followed by using 0.365 g of vinyl triflate **10c** (1.00 mmol), 0.294 g of 2-azidophenylboronic acid pinacolate ester **9a** (1.20 mmol), 0.014 g of $PdCl_2(PPh_3)_2$ (2 mol %), 1.0 mL of THF, and 0.24 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a colorless liquid (0.234 g, 70%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40−7.28 (m, 6H), 7.18−7.13 (m, 3H), 5.75−5.70 (m, 1H), 5.22 (s, 2H), 4.16 (d, J = 2.5 Hz, 2H), 3.73 (t, J = 5.5 Hz, 2H), 2.52 (br s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.9 (C), 137.0 (C), 135.5 (C), 134.7 (C), 129.5 (CH), 128.6 (CH), 128.2 (CH), 127.0 (CH), 124.9 (CH), 123.7 (C), 123.3 (CH), 121.3 (CH), 118.6 (CH), 67.5 (CH_2), 43.6 (CH_2), 40.6 (CH_2), 29.1 (CH_2); diagnostic data for minor rotamer no characteristic peaks; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 136.6 (C), 135.2 (C), 129.8 (CH), 128.7 (CH), 128.0 (CH); ATR-FTIR (thin film) 3080, 3028, 2839, 2121, 2092, 1672, 1487, 1428, 1377, 1290, 1234, 1195, 1143, 1110, 951, 747 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{19}N_4O_2$ $(M + H)^+$ 335.1505, found 335.1508.

4-(2-Azidophenyl)-1-tosyl-1,2,3,6-tetrahydropyridine 11d. The optimal procedure was followed by using 0.0385 g of vinyl triflate **10d** (0.099 mmol), 0.029 g of 2-azidophenylboronic acid pinacolate ester **9a** (0.12 mmol), 0.0014 g of $PdCl_2(PPh_3)_2$ (2 mol %), 1.0 mL of THF, and 0.24 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a yellow solid (0.0320 g, 90%): mp 106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.30−7.27 (m, 1H), 7.1 (d, J = 8.0 Hz, 1H), 7.08−7.05 (m, 2H), 5.62 (br s, 1H), 3.75 (d, J = 3.0 Hz, 2H), 3.30 (t, J = 6.0 Hz, 2H), 2.54 (br s, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.7 (C), 136.9 (C), 135.1 (C), 133.8 (C), 133.3 (C), 129.8 (CH), 128.8 (CH), 127.8 (CH), 124.9 (CH), 123.4 (C), 122.3 (CH), 118.5 (CH), 45.1 (CH_2), 43.0 (CH_2), 29.2 (CH_2), 21.6 (CH_3); ATR-FTIR (thin film) 2924, 2852, 2111, 2075, 1491, 1445, 1338, 1286, 1156, 1094, 919, 814, 730 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{19}N_4O_2S$ $(M + H)^+$ 355.1226, found 355.1229.

(9*H*-Fluoren-9-yl)methyl 4-(2-Azido-5-methoxyphenyl)-5,6-dihydropyridine-1(2*H*)-carboxylate 11e. The optimal procedure was followed by using 0.165 g of vinyl triflate **10b** (0.500 mmol), 0.166 g of 2-azido-5-methoxyphenylboronic acid pinacolate ester **9b** (0.600 mmol), 0.0070 g of $PdCl_2(PPh_3)_2$ (2 mol %), 5.0 mL of THF, and 1.2 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a yellow liquid (0.140 g, 85%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (d, J = 8.5 Hz, 1H), 6.80 (dd, J = 8.5 Hz, 3.0 Hz, 1H), 6.67 (d, J = 3.0 Hz, 1H), 5.67 (br s, 1H), 4.01 (br s, 2H), 3.75 (s, 3H), 3.57 (t, J = 5.0 Hz,

dx.doi.org/10.1021/jo500252e | J. Org. Chem. 2014, 79, 2781−2791

2H), 2.42 (br s, 2H), 1.47 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.8 (C), 154.9 (C), 135.6 (C), 135.1 (C), 129.3 (C), 123.9 (CH), 119.6 (CH), 115.1 (CH), 113.8 (CH), 79.6 (C), 55.5 (CH_3), 43.7 (CH_2), 39.8 (CH_2), 29.2 (CH_2), 28.5 (CH_2); ATR-FTIR (thin film) 2977, 2924, 2827, 2112, 1595, 1484, 1415, 1364, 1284, 1238, 1163, 1109, 1033, 954 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}N_4O_3$ $(M + H)^+$ 331.1770, found 331.1771.

(9*H*-Fluoren-9-yl)methyl 4-(2-Azido-5-methylphenyl)-5,6-dihydropyridine-1(2*H*)-carboxylate 11f. The optimal procedure was followed by using 0.165 g of vinyl triflate **10b** (0.500 mmol), 0.155 g of 2-azido-5-methylphenylboronic acid pinacolate ester **9c** (0.600 mmol), 0.0070 g of $PdCl_2(PPh_3)_2$ (2 mol %), 5.0 mL of THF, and 1.20 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a yellow liquid (0.135 g, 82%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, J = 8.0 Hz, 1H), 7.00 (d, 8.0 Hz, 1H), 6.96 (s, 1H), 5.66 (br m, 1H), 4.02 (d, J = 2.0 Hz, 2H), 3.59 (t, J = 5.0 Hz, 2H), 2.43 (br m, 2H), 2.29 (s, 3H), 1.48 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.9 (C), 135.3 (C), 134.6 (C), 134.4 (C), 134.4 (C), 130.4 (CH), 129.0 (CH), 123.9 (CH), 118.5 (CH), 79.6 (C), 43.7 (CH_2), 39.8 (CH_2), 29.4 (CH_2), 28.5 (CH_3), 20.7 (CH_3); ATR-FTIR (thin film) 3080, 3054, 3025, 2918, 2114, 1698, 1603, 1494, 1458, 1170, 1112, 1080 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}N_4O_2$ $(M + H)^+$ 315.1821, found 315.1821.

(9*H*-Fluoren-9-yl)methyl 4-(2-Azido-5-fluorophenyl)-5,6-dihydropyridine-1(2*H*)-carboxylate 11g. The optimal procedure was followed by using 0.165 g of vinyl triflate **10b** (0.500 mmol), 0.157 g of 2-azido-5-fluorophenylboronic acid pinacolate ester **9d** (0.600 mmol), 0.0070 g of $PdCl_2(PPh_3)_2$ (2 mol %), 5.0 mL of THF, and 1.20 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a colorless liquid (0.103 g, 65%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.07 (dd, J = 6.0, 5.0 Hz, 1H), 6.99 (dt, J = 8.5, 2.5 Hz, 1H), 6.88 (dd, J = 9.0, 3.0 Hz, 1H), 5.74 (s, 1H), 4.04 (s, 2H), 3.60 (t, J = 5.0 Hz, 2H), 2.44 (s, 2H), 1.49 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 159.6 (d, J_{CF} = 243.7 Hz, C), 154.9 (C), 136.2 (d, J = 7.5 Hz, C), 132.8 (C), 125.2 (CH), 119.9 (d, J = 7.8 Hz, CH), 116.5 (d, J = 22.2 Hz, CH), 115.1 (d, J = 22 Hz, CH), 79.8 (C), 43.5 (CH_2), 39.6 (CH_2), 29.1 (CH_2), 28.5 (CH_3), only visible peaks; ^{19}F NMR (282 MHz, $CDCl_3$) δ −118.26; ATR-FTIR (thin film) 2979, 2931, 2830, 2120, 1685, 1481, 1420, 1169, 1116, 907, 728 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{20}FN_4O_2$ $(M + H)^+$ 319.1571, found 319.1570.

(9*H*-Fluoren-9-yl)methyl 4-(2-Azido-5-trifluoromethoxyphenyl)-5,6-dihydropyridine-1(2*H*)-carboxylate 11h. The optimal procedure was followed by using 0.165 g of vinyl triflate **10b** (0.500 mmol), 0.197 g of 2-azido-5-trifluoromethoxyphenylboronic acid pinacolate ester **9e** (0.600 mmol), 0.0070 g of $PdCl_2(PPh_3)_2$ (2 mol %), 5.0 mL of THF, and 1.20 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a brown liquid (0.129 g, 67%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.15 (dd, J = 8.5, 2.0 Hz, 1H), 7.12 (d, J = 9.0 Hz, 1H), 7.03 (d, J = 1.5 Hz, 1H), 5.74 (s, 1H), 4.05 (s, 2H), 3.60 (t, J = 5.0 Hz, 2H), 2.45 (s, 2H), 1.49 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.8 (C), 145.8 (C), 136.0 (C), 135.7 (C), 125.1 (C), 122.5 (CH), 120.9 (CH), 120.4 (q, J_{CF} = 255.2 Hz, C), 119.7 (CH), 79.8 (C), 43.8 (CH_2), 39.6 (CH_2), 29.1 (CH_2), 28.5 (CH_3), only visible peaks; ^{19}F NMR (282 MHz, $CDCl_3$) δ −58.5; ATR-FTIR (thin film) 3025, 2918, 2119, 1699, 1604, 1494, 1457, 1256, 1218, 1168, 1081, 1029 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{20}F_3N_4O_3$ $(M + H)^+$ 385.1486, found 385.1488.

(9*H*-Fluoren-9-yl)methyl 4-(2-Azido-4-methoxyphenyl)-5,6-dihydropyridine-1(2*H*)-carboxylate 11i. The optimal procedure was followed by using 0.165 g of vinyl triflate **10b** (0.500 mmol), 0.165 g of 2-azido-4-methoxyphenylboronic acid pinacolate ester **9f** (0.600 mmol), 0.0070 g of $PdCl_2(PPh_3)_2$ (2 mol %), 5.0 mL of THF, and 1.20 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a yellow liquid with 83% purity (0.158 g, 79%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, J = 8.5 Hz, 1H), 6.69 (m, 1H), 6.68 (d, J = 2.5 Hz, 1H), 5.79−5.68 (br m, 1H), 4.06 (d, J = 2.0 Hz, 2H), 3.85 (s, 3H), 3.62 (t, J = 5.5 Hz, 2H), 2.45 (br s, 2H), 1.52 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 159.8 (C), 155.0 (C), 137.9 (C), 134.7 (C), 130.6 (CH), 127.4 (C), 123.5 (CH), 110.3 (CH), 104.6 (CH), 79.8 (C), 55.5 (CH_3), 43.8 (CH_2), 39.9 (CH_2), 29.6 (CH_2), 28.6 (CH_3); ATR-FTIR (thin film) 2969, 2927, 2846, 2122, 2090, 1690, 1575, 1485, 1415, 1364, 1289, 1235, 1162, 1112, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}N_4O_3$ $(M + H)^+$ 331.1770, found 331.1771.

(9*H*-Fluoren-9-yl)methyl 4-(2-Azido-4-methylphenyl)-5,6-dihydropyridine-1(2*H*)-carboxylate 11j. The optimal procedure was followed by using 0.165 g of vinyl triflate **10b** (0.500 mmol), 0.155 g of 2-azido-4-methylphenylboronic acid pinacolate ester **9g** (0.600 mmol), 0.0070 g of $PdCl_2(PPh_3)_2$ (2 mol %), 5.0 mL of THF, and 1.20 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a colorless liquid (0.133 g, 85%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.03 (d, J = 8.0 Hz, 1H), 6.92 (s, 1H), 6.89 (d, J = 7.5 Hz, 1H), 5.66 (br s, 1H), 4.02 (br s, 2H), 3.59 (br s, 2H), 2.44 (br s, 2H), 2.34 (s, 3H), 1.49 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.9 (C), 138.6 (C), 136.6 (C), 135.0 (C), 131.7 (C), 129.6 (CH), 125.7 (CH), 123.5 (CH), 119.1 (CH), 79.6 (C), 53.5 (CH_2), 43.8 (CH_2), 39.8 (CH_2), 28.5 (CH_3), 21.1 (CH_3); ATR-FTIR (thin film) 2972, 2924, 2103, 1691, 1412, 1363, 1292, 1235, 1163, 1110, 1054, 973, 808 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}N_4O_2$ $(M + H)^+$ 315.1821, found 315.1821.

***tert*-Butyl 2-(2-Azidophenyl)-5,6-dihydropyridine-1(2*H*)-carboxylate 11k.** The optimal procedure was followed by using 0.123 g of vinyl triflate **10e** (0.372 mmol), 0.110 g of 2-azidophenylboronic acid pinacolate ester **9a** (0.450 mmol), 0.0052 g of $PdCl_2(PPh_3)_2$ (2 mol %), 1.0 mL of THF, and 0.90 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a colorless liquid (0.036 g, 32%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, J = 8.0 Hz, 1H), 7.21−7.19 (m, 1H), 7.15−7.11 (m, 2H), 7.08−7.06 (m, 0.38H), 6.93 (br s, 0.58H), 3.62 (br s, 2H), 2.40 (t, J = 6.0 Hz, 2H), 1.94 (br s, 2H), 1.49 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 152.3 (C), 133.8 (C) 130.1 (CH), 127.8 (CH), 124.8 (CH), 121.0 (C), 118.7 (CH), 117.8 (CH), 115.0 (C), 80.9 (C), 42.4 (CH_2), 28.4 (CH_3), 26.2 (CH_2), 21.7 (CH_2); ATR-FTIR (thin film) 2924, 2852, 2111, 2075, 1491, 1445, 1338, 1286, 1156, 1094, 919, 814, 730 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{20}N_4O_2Na$ $(M + Na)^+$ 323.1481, found 323.1484.

4-(2-Azidophenyl)-3,6-dihydro-2*H*-pyran 11l. The optimal procedure was followed by using 0.0230 g of vinyl triflate **10f** (0.099 mmol), 0.029 g of 2-azidophenylboronic acid pinacolate ester **9a** (0.12 mmol), 0.0014 g of $PdCl_2(PPh_3)_2$ (2 mol %), 1.0 mL of THF, and 0.24 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a yellow solid (0.015 g, 75%): mp 37 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, J = 6.5 Hz, 1H), 7.18−7.11 (m, 3H), 5.79 (br s, 1H), 4.31−4.30 (m, 2H), 3.91 (t, J = 5.5 Hz, 2H), 2.48 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 137.0 (C), 134.3 (C), 134.0 (C), 129.7 (CH), 128.5 (CH), 126.0 (CH), 124.9 (CH), 118.6 (CH), 65.6 (CH_2), 64.4 (CH_2), 29.2 (CH_2); ATR-FTIR (thin film) 2957, 2927. 2846, 2817, 2121, 2082, 1575, 1487, 1439, 1380, 1290, 1130, 845, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{11}H_{11}N_3O$ $(M)^+$ 201.0900, found 201.0902.

***tert*-Butyl 2-(2-Azidophenyl)-1*H*-indole-1-carboxylate 11m.** The optimal procedure was followed by using 0.0360 g of vinyl triflate **10g** (0.099 mmol), 0.029 g of 2-azidophenylboronic acid pinacolate ester **9a** (0.12 mmol), 0.0014 g of $PdCl_2(PPh_3)_2$ (2 mol %), 1.0 mL of THF, and 0.24 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a yellow solid (0.030 g, 99%): mp 87 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, J = 8.5 Hz, 1H), 5.70 (d, J = 7.5 Hz, 1H), 7.42 (t. J = 7.5 Hz, 1H), 7.40 (d, J = 6.5 Hz, 1H), 7.35 (t, J = 8.5 Hz, 1H), 7.26 (t, J = 8.0 Hz, 1H), 7.23−7.20 (m, 2H), 6.53 (s, 1H), 1.35 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 149.9 (C), 138.9 (C), 136.9 (C), 136.0 (C), 130.8 (CH), 129.4 (CH), 128.9 (C), 127.3 (C), 124.5 (CH), 122.8 (CH), 120.6 (CH), 117.9 (CH), 117.8 (CH), 115.4 (CH), 110.5 (CH), 83.2 (C), 27.7 (CH_3); ATR-FTIR (thin film) 3070, 2979, 2937, 2115, 2089, 1734, 1455, 1328, 1302, 1224,

dx.doi.org/10.1021/jo500252e | J. Org. Chem. 2014, 79, 2781−2791

1153, 1130, 1020, 740 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{19}N_4O_2$ $(M + H)^+$ 335.1505, found 335.1508.

2-(2-Azidophenyl)thiophene 11n. The optimal procedure was followed by using 0.0940 g of vinyl triflate **10h** (0.400 mmol), 0.119 g of 2-azidophenylboronic acid pinacolate ester **9a** (0.485 mmol), 0.0014 g of $PdCl_2(PPh_3)_2$ (2 mol %), 1.0 mL of THF, and 0.24 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a colorless liquid (0.0590g, 86%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 3.5 Hz, 1H), 7.39 (d, J = 5.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 7.5 Hz, 1 H), 7.18 (t, J = 7.5 Hz, 1H), 7.12 (dd, J = 5.0, 3.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 139.1 (C), 136.4 (C), 130.1 (C), 128.6 (CH), 127.2 (CH), 126.8 (CH), 126.2 (CH), 125.0 (CH), 119.1 (CH), only visible signals; ATR-FTIR (thin film) 3106, 3070, 2128, 2089, 1572, 1489, 1295, 1267, 733 cm^{-1}; HRMS (ESI) m/z calcd for $C_{10}H_7N_3S$ $(M)^+$ 201.0360, found 201.0361.

2-(2-Azidophenyl)pyridine 11o. The optimal procedure was followed by using 0.110 g of vinyl triflate **10i** (0.480 mmol), 0.143 g of 2-azidophenylboronic acid pinacolate ester **9a** (0.580 mmol), 0.0068 g of $PdCl_2(PPh_3)_2$ (2 mol %), 4.8 mL of THF, and 0.96 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a colorless liquid (0.037 g, 40%): ^1H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, J = 4.5 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.69–7.66 (m, 2H), 7.43 (t, J = 7.0 Hz, 1H), 7.27–7.23 (m, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.8 (C), 149.6 (CH), 137.3 (C), 135.9 (CH), 132.3 (C), 131.5 (CH), 129.9 (CH), 125.1 (CH), 124.9 (CH), 122.2 (CH), 118.9 (CH); ATR-FTIR (thin film) 3051, 2920, 2363, 1652, 1620, 1592, 1495, 1449, 1339, 1187, 1099, 980, 766 cm^{-1}; HRMS (EI) m/z calcd for $C_{11}H_8N_4$ $(M)^+$ 196.07489, found 196.07403.

3*S*,10*R*,13*S*-17-(2-Azidophenyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1*H*-cyclopenta[*a*]-phenanthren-3-yl Acetate 11p. The optimal procedure was followed by using 0.0460 g of vinyl triflate **10j** (0.099 mmol), 0.029 g of 2-azidophenylboronic acid pinacolate ester **9a** (0.12 mmol), 0.0014 g of $PdCl_2(PPh_3)_2$ (2 mol %), 1.0 mL of THF, and 0.24 mL of a saturated aqueous solution of $NaHCO_3$. Purification by MPLC (3/97 to 20/80 EtOAc/hexane) afforded the product as a yellow solid (0.036 g 84%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 1H), 7.17–7.12 (m, 2H), 7.09–7.06 (t, J = 7.0 Hz, 1H), 5.73 (br s, 1H), 5.41 (br s, 1H), 4.64–4.60 (m, 1H), 2.35–2.32 (m, 3H), 2.09–2.06 (m, 2H), 2.04 (s, 3H), 1.87–1.84 (m, 2H), 1.73–1.72 (m, 2H), 1.64–1.60 (m, 6H), 1.18–1.13 (m, 2H), 1.06 (s, 3H), 0.93 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 170.5 (C), 151.1 (C), 140.0 (C), 138.0 (C), 130.5 (CH), 130.0 (C), 129.9 (CH) 128.1 (CH), 124.1 (CH), 122.5 (CH), 118.6 (CH), 73.9 (CH), 56.9 (CH), 50.4 (CH), 49.1 (C), 38.2 (CH_2), 36.9 (CH_2), 36.8 (C), 34.9 (CH_2), 32.2 (CH_2), 31.6 (CH_2), 30.7 (CH), 27.8 (CH_2), 21.5 (CH_3), 20.8 (CH_2), 19.3 (CH_3), 16.3 (CH_3); ATR-FTIR (thin film) 2934, 2853, 2121, 2082, 1728, 1484, 1374, 1240, 1029, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{33}N_3O_2$ $(M + Na)^+$ 454.2475, found 454.2470.

General Procedure for the Rh^{II}_2-Catalyzed Synthesis of [2,3]-Fused Indole Heterocycles. To a mixture of 2-alkenylaryl azide **11** and $Rh_2(esp)_2$ (5 mol %) was added toluene (0.1 M). The resulting mixture was heated at 80 °C. After 16 h, the mixture was cooled to room temperature, diluted with CH_2Cl_2, and concentrated in vacuo. Purification of the residue by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product.

(9*H*-Fluoren-9-yl)methyl 3,4-Dihydro-1*H*-pyrido[3,4-*b*]-indole-2(9*H*)-carboxylate 12a. The general procedure was followed by using 0.020 g of aryl azide **4a** (0.045 mmol), 0.0029 g of $Rh_2(esp)_2$, and 0.45 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a white solid (0.010 g, 54%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.89–7.71 (m, 3H), 7.61–7.58 (m, 2H), 7.49 (d, J = 7.5 Hz, 1H), 7.42–7.29 (m, 5H), 7.17–7.13 (m, 2H), 4.71 (s, 1H), 4.60 (s, 1H), 4.50 (m, 2H), 4.30 (m, 1H), 3.81 (m, 2H), 2.80 (t, J = 8 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.7 (C), 144.0 (C), 141.4 (C), 136.3 (C), 130.1 (C), 127.7 (CH), 127.1 (CH), 124.9 (C), 121.9 (C), 120.0 (CH), 119.7 (CH), 118.0 (CH), 111.9 (C), 110.9 (CH), 67.7 (CH_2), 47.4 (CH), 42.2 (CH_2), 42.0 (CH_2), 21.0 (CH_2), only visible peaks; ATR-FTIR (thin film) 3285, 3045, 2917, 3045, 2917, 2853, 1687, 1448, 1422, 1224, 1099, 906, 735 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{23}N_2O_2$ $(M + H)^+$ 395.1766, found 395.1760.

***tert*-Butyl 3,4-Dihydro-1*H*-pyrido[3,4-*b*]indole-2(9*H*)-carboxylate 12b.**[35] The general procedure was followed by using 0.030 g of aryl azide **11b** (0.100 mmol), 0.0038 g of $Rh_2(esp)_2$, and 1 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a white solid (0.021 g, 77%): this product was previously reported by Kikuchi and co-workers;[35] ^1H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 0.48H), 7.91 (s, 0.32H), 7.48 (d, J = 7.5 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 4.67 (br s, 2H), 3.77 (br s, 2H), 2.80 (t, J = 5.5 Hz, 2H), 1.54 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.1 (C), 136.2 (C), 130.7 (C), 127.0 (C), 121.6 (CH), 119.4 (CH), 117.9 (CH), 110.9 (CH), 108.5 (C), 80.2 (C), 42.5 (CH_2), 41.8 (CH_2), 28.5 (CH_3), 21.5 (CH_2); ATR-FTIR (thin film) 3291, 3050, 2972, 2931, 1667, 1415, 1366, 1264, 1231, 1156, 1099, 731 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{21}N_2O_2$ $(M + H)^+$ 273.1603, found 273.1603.

Benzyl 3,4-Dihydro-1*H*-pyrido[3,4-*b*]indole-2(9*H*)-carboxylate 12c.[36] The general procedure was followed by using 0.030 g of aryl azide **11c** (0.081 mmol), 0.0034 g of $Rh_2(esp)_2$, and 0.81 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a white solid (0.014 g, 51%): this product was previously reported by Nolan and co-workers;[36] ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 0.48H), 7.79 (s, 0.39H), 7.48 (br s, 1H), 7.39–7.30 (m, 6H), 7.16 (t, J = 7.5 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 5.19 (m, 2H), 4.69 (m, 2H), 3.85 (m, 2H), 2.81 (br s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.8 (C), 136.2 (C), 130.2 (CH), 128.6 (CH), 128.1 (CH), 127.0 (CH), 121.8 (CH), 119.6 (CH), 118.9 (C), 117.9 (CH), 111.9 (C), 110.9 (CH), 108.5 (C), 67.5 (CH_2), 42.3 (CH_2), 42.1 (CH_2), 21.5 (CH_2); ATR-FTIR (thin film) 3405, 3054, 1689, 1447, 1426, 1264, 1224, 1098, 730 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{19}N_2O_2$ $(M + H)^+$ 307.1448, found 307.1448.

2-Tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole 12d.[37] The general procedure was followed by using 0.030 g of aryl azide **11d** (0.081 mmol), 0.0032 g of $Rh_2(esp)_2$, and 0.84 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a white solid (0.013 g, 47%): spectral data of this product matched those reported by Eilbracht and co-workers;[37] ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 3H), 7.42 (d, J = 8.0 Hz, 1H), 7.29 (dd, J = 8.0 Hz, 3.5 Hz, 3H), 7.15 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 4.40 (s, 2H), 3.49 (t, J = 6.0 Hz, 2H), 2.84 (t, J = 5.5 Hz, 2H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 143.7 (C), 136.1 (C), 134.1 (C), 129.8 (CH), 128.5 (C), 127.6 (CH), 126.7 (C), 122.1 (CH), 119.8 (CH), 118.1 (CH), 110.9 (CH), 108.4 (CH), 44.2 (CH_2), 43.5 (CH_2), 21.5 (CH_3), 21.4 (CH_2); ATR-FTIR (thin film) 3385, 3045, 2911, 2856, 1589, 1452, 1342, 1165, 744 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{19}N_2O_2S$ $(M + H)^+$ 327.1165, found 327.1167.

(9*H*-Fluoren-9-yl)methyl 3,4-Dihydro-1*H*-pyrido[3,4-*b*]-indole-2(9*H*)-carboxylate 12e.[38] The general procedure was followed by using 0.0730 g of aryl azide **11e** (0.220 mmol), 0.0083 g of $Rh_2(esp)_2$, and 2.20 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a white solid (0.050 g, 75%): this product was previously reported by Rawal and co-workers;[38] ^1H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 0.56H), 7.92 (s, 0.35 H), 7.19 (d, J = 9.0 Hz, 1H), 6.94 (s, 1H), 6.81 (d. J = 8.5 Hz, 1H), 4.65 (br m, 2H), 3.86 (s, 3H), 3.77 (br s, 2H), 2.77 (t, J = 5.0 Hz, 2H), 1.55 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.4 (C), 154.0 (C), 131.6 (C), 131.3 (C), 127.4 (C), 111.6 (CH), 111.2 (CH), 108.1 (C), 100.4 (CH), 80.2 (C), 56.0 (CH_3), 42.7 (CH_2), 41.9 (CH_2), 20.6 (CH_3), 21.5 (CH_2); ATR-FTIR (thin film) 3288, 2979, 2931, 2898, 2846, 2362, 1670, 1594, 1416, 1367, 1214, 1169, 1133, 1094, 902, 727 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}N_2O_3$ $(M + H)^+$ 303.1702, found 303.1709.

(9*H*-Fluoren-9-yl)methyl 3,4-Dihydro-1*H*-pyrido[3,4-*b*]-indole-2(9*H*)-carboxylate 12f. The general procedure was followed by using 0.0640 g of aryl azide **11f** (0.200 mmol), 0.0077 g of

dx.doi.org/10.1021/jo500252e | J. Org. Chem. 2014, 79, 2781–2791

$Rh_2(esp)_2$ and 2.0 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a white solid (0.046 g, 80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 0.58H), 7.81 (s, 0.39H), 7.27 (s, 1H), 7.19 (d, J = 8.5 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 4.65 (s, 2H), 3.76 (br s, 2H), 2.78 (t, J = 5.0 Hz, 2H), 2.46 (s, 3H), 1.54 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.2 (C), 134.5 (C), 130.9 (C), 128.6 (C), 127.3 (C), 123.1 (CH), 117.7 (CH), 110.5 (CH), 107.9 (C), 80.1 (C), 42.7 (CH_2), 41.9 (CH_2), 28.6 (CH_3), 21.5 (CH_3), 21.2 (CH_2); ATR-FTIR (thin film) 3288, 3005, 2914, 1676, 1579, 1409, 1361, 1250, 1231, 1162, 1091, 913 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}N_2O_2$ $(M + H)^+$ 287.1756, found 287.1760.

(9*H*-Fluoren-9-yl)methyl 3,4-Dihydro-1*H*-pyrido[3,4-*b*]indole-2(9*H*)-carboxylate 12g. The general procedure was followed by using 0.0320 g of aryl azide **11g** (0.100 mmol), 0.0038 g of $Rh_2(esp)_2$, and 1.0 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a white solid (0.019 g, 65%): mp 174 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (s, 0.63H), 7.95 (s, 0.32H), 7.26 (dd, J = 9.0 Hz, 4.0 Hz, 1H), 7.15 (d, J = 9.0 Hz, 1H), 6.92 (dt, J = 9.0 Hz, 2.0 Hz, 1H), 4.65 (m, 2H), 3.80 (s, 2H), 2.79 (t, J = 5.5 Hz, 2H), 1.58 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.9 (d, J_{CF} = 231 Hz, C), 155.5 (C), 132.7 (C), 127.4 (C), 111.4 (CH), 109.6 (d, J_{CF} = 22.9 Hz, CH), 108.6 (C), 102.9 (d, J_{CF} = 26.6 Hz, CH), 80.3 (C), 42.6 (CH_2), 41.9 (CH_2), 28.6 (CH_3), 21.4 (CH_2), only visible peaks; ^{19}F NMR (282 MHz, $CDCl_3$) δ −125.26; ATR-FTIR (thin film) 2972, 2934, 2836, 2117, 1691, 1481, 1416, 1237, 1113, 958 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{20}FN_2O_2$ $(M + H)^+$ 291.1508, found 291.1509.

(9*H*-Fluoren-9-yl)methyl 3,4-Dihydro-1*H*-pyrido[3,4-*b*]indole-2(9*H*)-carboxylate 12h. The general procedure was followed by using 0.0390 g of aryl azide **11h** (0.101 mmol), 0.0038 g of $Rh_2(esp)_2$, and 1.00 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a white solid (0.027 g, 75%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (s, 0.66H), 8.02 (s, 0.30H), 7.31 (s, 1H), 7.27 (d, J = 9.0 Hz, 1H), 7.01 (d, J = 9.0 Hz, 1H), 4.69 (br m, 2H), 3.77 (t, J = 5.5 Hz, 2H), 2.78 (t, J = 5.5 Hz, 2H), 1.55 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.6 (C), 143.1 (C), 134.5 (C), 132.9 (C), 127.3 (C), 120.9 (q, J_{CF} = 253.4 Hz, C), 115.4 (CH), 111.3 (CH), 110.5 (CH), 108.9 (C), 80.4 (C), 42.5 (CH_2), 41.9 (CH_2), 28.5 (CH_3), 21.3 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ −58.5; ATR-FTIR (thin film) 3269, 2976, 2934, 2849, 1666, 1423, 1243, 1212, 1133, 1101, 896 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{20}F_3N_2O_3$ $(M + H)^+$ 357.1424, found 357.1426.

(9*H*-Fluoren-9-yl)methyl 3,4-Dihydro-1*H*-pyrido[3,4-*b*]indole-2(9*H*)-carboxylate 12i. The general procedure was followed by using 0.440 g of aryl azide **11i** (0.110 mmol, 83% pure), 0.0042 g of $Rh_2(esp)_2$, and 1.10 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a white solid (0.020 g, 60%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 0.52 H), 7.75 (s, 0.37H), 7.35 (d, J = 8.5 Hz, 1H), 6.83 (s, 1H), 6.79 (d, J = 8.5 Hz, 1H), 4.62 (br s, 2H), 3.83 (s, 3H), 3.75 (s, 2H). 2.76 (br s, 2H), 1.52 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.2 (C), 155.2 (C), 137.0 (C), 129.3 (C), 121.5 (C), 118.5 (C), 118.4 (CH), 108.9 (CH), 95.0 (CH_2), 80.1 (C), 55.8 (CH_3), 42.6 (CH_2), 41.7 (CH_2), 28.5 (CH_3), 21.5 (CH_2); ATR-FTIR (thin film) 3297, 3008, 2979, 2908, 2830, 1665, 1631, 1478, 1421, 1365, 1249, 1231, 1155, 1112, 1032, 909, 815 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}N_2O_3$ $(M + H)^+$ 303.1702, found 303.1709.

(9*H*-Fluoren-9-yl)methyl 3,4-Dihydro-1*H*-pyrido[3,4-*b*]indole-2(9*H*)-carboxylate 12j. The general procedure was followed by using 0.450 g of aryl azide **11j** (0.142 mmol), 0.0054 g of $Rh_2(esp)_2$, and 1.40 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a white solid (0.033 g, 81%): mp 176 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 0.57H), 7.76 (s, 0.39H), 7.36 (d, J = 8.0 Hz, 1H), 7.09 (s, 1H), 6.94 (d, J = 8.0 Hz, 1H), 4.63 (br s, 2H), 3.76 (br s, 2H), 2.77 (t, J = 5.5 Hz, 2H), 2.45 (s, 3H), 1.53 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.3 (C), 136.7 (C), 131.3 (C), 130.0 (C), 124.9 (C), 121.1 (CH), 117.5 (CH), 110.9 (CH), 108.2 (C), 80.1 (C), 42.6 (CH_2), 41.8 (CH_2), 28.5 (CH_3), 21.8 (CH_3), 21.5 (CH_2); ATR-FTIR (thin film) 3308, 2979, 2917, 2853, 1672, 1414, 1365, 1306, 1230, 1160, 1099, 899, 799 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}N_2O_2$ $(M + H)^+$ 287.1756, found 287.1760.

***tert*-Butyl 2,3,4,9-Tetrahydro-1*H*-pyrido[2,3-*b*]indole-1-carboxylate 12k.** The general procedure was followed by using 0.023 g of aryl azide **11k** (0.073 mmol), 0.0027 g of $Rh_2(esp)_2$, and 0.7 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a yellow solid (0.019 g, 91%): mp 87 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 0.75H), 7.39−7.38 (m, 1H), 7.27 (m, 1H), 7.07 (m, 2H), 3.81 (t, J = 5.5 Hz, 2H), 2.74 (t, J = 6.0 Hz, 2H), 2.05 (m, 2H), 1.57 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 152.7 (C), 133.8 (C), 132.0 (C), 129.4 (C), 126.6 (C), 119.9 (CH), 119.4 (CH), 116.7 (CH), 110.5 (CH), 81.7 (C), 45.1 (CH_2), 28.4 (CH_3), 22.7 (CH_2), 19.2 (CH_2); ATR-FTIR (thin film) 3396, 2972, 2953, 2924, 2843, 1682, 1582, 1494, 1387, 1351, 1260, 1159, 1130, 740 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{21}N_2O_2$ $(M + H)^+$ 273.1610, found 273.1603.

1,3,4,9-Tetrahydropyrano[3,4-*b*]indole 12l. The general procedure was followed by using 0.032 g of aryl azide **11l** (0.089 mmol), 0.006 g of $Rh_2(esp)_2$ and 1.0 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a brown solid (0.023 g, 83%): mp 111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 4.80 (s, 2H), 4.05 (t, J = 5.5 Hz, 2H), 2.86 (t, J = 5.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 135.9 (C), 131.5 (C), 127.2 (C), 121.7 (CH), 119.6 (CH), 118.0 (CH), 110.9 (CH), 107.6 (CH), 65.8 (CH_2), 63.7 (CH_2), 22.2 (CH_2); ATR-FTIR (thin film) 3382, 2957, 2843, 2810, 1452, 1238, 1088, 747 cm^{-1}; HRMS (ESI) m/z calcd for $C_{11}H_{12}NO$ $(M)^+$ 174.0916, found 174.0919.

***tert*-Butyl Indolo[3,2-*b*]indole-5(10*H*)-carboxylate 12m.** The general procedure was followed by using 0.030 g of aryl azide **11m** (0.089 mmol), 0.0034 g of $Rh_2(esp)_2$, and 0.9 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a brown solid (0.030 g, 96%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (m, 1H), 8.28 (br s, 1H), 8.18 (s, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.32−7.27 (m, 2H), 7.25−7.22 (m, 1H), 1.82 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 150.8 (C), 140.3 (C), 139.4 (C), 127.1 (C), 124.2 (CH), 124.0 (C), 122.9 (CH), 122.7 (CH), 121.5 (CH), 119.9 (CH), 118.7 (C), 117.4 (CH), 117.1 (C), 116.9 (CH), 111.8 (CH), 84.0 (C), 28.6 (CH_3); ATR-FTIR (thin film) 3425, 3402, 1725, 1449, 1364, 1348, 1302, 1243, 1141, 737 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{19}N_2O_2$ $(M + H)^+$ 307.1440, found 307.1447.

4*H*-Thieno[3,2-*b*]indole 12n.[10a] The general procedure was followed by using 0.025 g of aryl azide **11n** (0.012 mmol), 0.0047 g of $Rh_2(esp)_2$, and 1.4 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a white solid (0.021 g, 98%); spectral data of the product matched those reported by Sapi and co-workers:[10a] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 5.0 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 5.0 Hz, 1H); ^{13}C{^{1}H} NMR δ 143.2 (C), 141.3 (C), 127.1 (CH), 122.9 (CH), 122.3 (C), 119.9 (CH), 118.9 (CH), 118.1 (C), 112.0 (CH), 111.7 (CH); ATR-FTIR (thin film) 3396, 3076, 3047, 1528, 1452, 1049, 1302, 1238, 1091, 743 cm^{-1}; HRMS (ESI) m/z calcd for $C_{10}H_8NS$ $(M + H)^+$ 174.0376, found 174.0377.

(4*S*,6a*R*,8a*S*)-6a,8a-Dimethyl-1,3,4,5,6,6a,6b,7,8,8a,13,14,14a,14b-tetradecahydronaphtho[2′,1′:4,5]indeno[2,1-*b*]indol-4-yl Acetate 12p. The general procedure was followed by using 0.034 g of aryl azide **11p** (0.078 mmol), 0.0030 g of $Rh_2(esp)_2$, and 0.8 mL of toluene. Purification by MPLC (3/97 to 20/80 EtOAc/hexanes) afforded the product as a brown solid (0.0080 g, 25%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.48 (m, 1H), 7.30 (dd, J = 6.5, 2.5 Hz, 1H), 7.08−7.05 (m, 2H), 5.44 (br s, 1H), 4.62 (m, 1H), 2.69 (dd, J = 14.5, 6.5 Hz, 1H), 2.54−2.49 (m, 1H), 2.40−2.36 (m, 3H), 2.11 (m, 2H), 2.05 (s, 3H), 1.91−1.88 (m, 3H), 1.78−1.72 (m, 3H), 1.62−1.58 (m, 2H), 1.20−1.17 (m, 2H), 1.12 (s, 3H), 1.03 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.6 (C), 141.7 (C), 140.3 (C), 139.5 (C), 129.7 (C), 123.6 (C),

dx.doi.org/10.1021/jo500252e | J. Org. Chem. 2014, 79, 2781−2791

122.2 (CH), 120.3 (CH), 119.4 (C), 118.1 (CH), 111.5 (CH), 73.9 (CH), 61.4 (CH), 50.8 (CH), 41.9 (C), 38.2 (CH_2), 37.0 (C), 36.8 (CH_2), 36.1 (CH_2), 31.8 (CH_2), 30.5 (CH_3), 27.8 (CH_2), 27.3 (CH_2), 21.5 (C), 20.7 (CH_2), 19.3 (CH_3), 18.1 (CH_3); ATR-FTIR (thin film) 3370, 2946, 2898, 2846, 1708, 1452, 1364, 1250, 1036, 733 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{34}NO_2$ $(M + H)^+$ 404.2587, found 404.2590.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving spectroscopic data for the products. 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.

■ ACKNOWLEDGMENTS

We are grateful to the National Institutes of Health NIGMS (R01GM084945), National Science Foundation (CHE-1265630), and the University of Illinois at Chicago for their generous support. We also thank Mr. Furong Sun (UIUC) for mass spectrometry data.

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dx.doi.org/10.1021/jo500252e | *J. Org. Chem.* 2014, 79, 2781−2791