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Multidirectional Synthesis of Substituted Indazoles via Iridium-Catalyzed C−H Borylation

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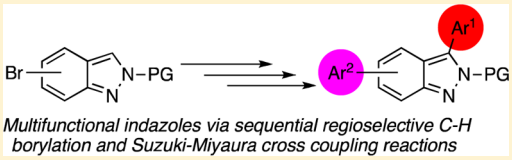
Supporting Information

ABSTRACT: In the absence of a steric directing group, iridium-catalyzed C−H borylation of N-protected indazoles occurs rapidly and selectively at C-3 and the resulting boronate esters can be utilized in a range of downstream conversions. The functional group tolerance of the iridium-catalyzed C−H borylation reaction enables simple and efficient multidirectional syntheses of substituted indazoles to be realized.



Multifunctional indazoles via sequential regioselective C-H borylation and Suzuki-Miyaura cross coupling reactions

Organoboronic acids and esters are of great importance in organic, medicinal, and materials chemistry.[1] Reflecting this, methods for the preparation of functionalized boronic acids and their derivatives are of great interest. Although boronate esters have been classically prepared via transmetalation and trapping with boron electrophiles, recent developments in their synthesis have focused on milder, more functional group tolerant approaches. Foremost among these are metal-catalyzed C−X and C−H borylation.[2−5] Of these, the direct C−H borylation of aromatic C−H bonds catalyzed by boryl iridium complexes is particularly attractive, as it enables late-stage functionalization of molecules. However, many important basic heterocycles are not well tolerated, giving slow reactions with low conversions.[6] These characteristics can be related to the ability for the basic nitrogen to coordinate to, and thus inhibit, the Ir catalyst and the related presence of the proximal azinyl nitrogen lone pair, which provides an inhibitory repulsive interaction with the developing negative charge of the ortho carbon during the C−H activation step and also a low-energy pathway for protodeboronation.[7,8] We have recently demonstrated that the introduction of a strongly electron withdrawing group at the 2-position of a pyridine lowers the basicity of the azinyl nitrogen (pK_a: pyridine, 5.25; 2-chloropyridine, 0.7; 2-fluoropyridine, −0.44), facilitating borylation at the 6-position and providing the resulting boronate ester with much enhanced stability (Figure 1).[7] Other substituents can have a similar effect, with the presence of a second azinyl nitrogen atom also leading to lower pK_a values and enhanced reactivity in the C−H borylation process (Figure 2). We then considered azole systems and noted that

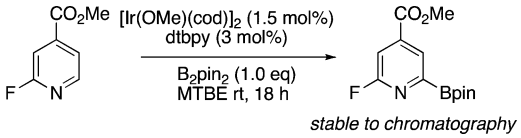


Figure 1. C−H borylation of 2-fluoropyridines.

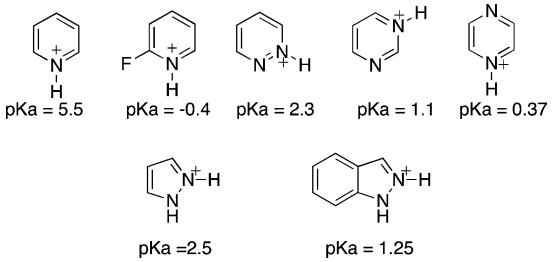


Figure 2. pK_a values for azinyl ring systems.[11]

Harrity has previously demonstrated that 3-pyrazole boronate esters, in which there is a nitrogen atom adjacent to the azine moiety, are stable entities.[9] In addition, Smith and Malezcka have shown that protected pyrazoles are viable substrates for borylation and, in these cases, reaction occurs exclusively at C-4, remote from the azinyl nitrogen.[6e] Consequently, reflecting their importance in a variety of medicinal chemistry applications, we became interested in the reactivity and selectivity of indazole borylation in which the NR group adjacent to the azinyl nitrogen reduces the basicity of the nitrogen atom (pK_a: indazole, 1.25; 2-methoxypyridine, 3.3; 2-chloropyridine, 0.7). Prompted by a recent disclosure from a group at Syngenta,[10] we now describe the development of simple, multidirectional syntheses of indazoles based on selective C−H borylation of this heterocycle.

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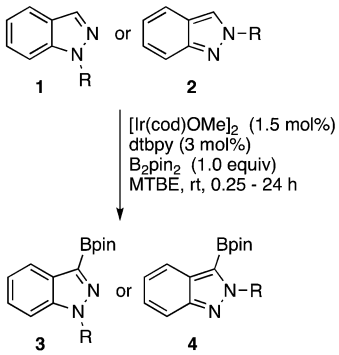
Our initial experiments explored the borylation of the parent indazole. Consistent with attempts to borylate other heterocycles which contain an unencumbered azinyl nitrogen, no reaction was observed. Smith and Maleczka have recently shown that the N−H group of various heterocycles can be temporarily protected by N−H borylation with HBpin.[12] However, we were not able to achieve the borylation of indazole following this protocol. Consequently, a series of different, less labile nitrogen protecting groups were explored (Table 1). Borylation of 1-protected indazole with 1 equiv of

Table 1. Borylation of N-Protected Indazoles



R = **a** H; **b** Boc; **c** Me; **d** THP; **e** SEM[a]; **f** (3,5)-$Me_2C_6H_4CH_2$; **g** Ms

entry	SM	time (h)	conversn (%)[b]
1	**1a**	24	0
2	**1b**	2	100
3	**1c**	24	67
4	**1d**	24	83
5	**1e**	24	63
6	**1f**	24	61
7	**1g**	1	100 (62)[c]
8	**2c**	1	100
9	**2d**	20	100
10	**2e**	6	100
11	**2f**	0.25	100

[a]SEM = trimethylsilylethoxymethoxy. [b]Determined by ^{1}H NMR. [c]Isolated yield.

B_2pin_2 afforded the 3-borylated product, as confirmed by a distinct shift of the 4-H resonance to higher frequency in the ^{1}H NMR spectrum. Significantly, and consistent with our previous results, more strongly electron withdrawing protecting groups led to faster reactions and higher conversions. Somewhat surprisingly, borylation of the corresponding N2-protected indazoles also proceeds exclusively at the 3-position even in the presence of relatively bulky benzyl or THP protecting groups at N-2 (Table 1, entries 8−11). The higher reactivity of these isomers was most notably seen with complete borylation of the bulky 3,5-dimethylbenzyl derivative being observed in minutes, in contrast to the many hours required for the analogous 1-N-protected isomer. We attribute this higher reactivity of the 2-protected isomers to the fact that the site of C−H activation is no longer adjacent to an azinyl lone pair. This also mirrors the more rapid reaction of a pyrrole in comparison with a 2-substituted pyridine and the preference for C−H borylation in a pyrazole to occur at C-4, not C-3. Most of these α-azinyl boronate esters, although considerably more stable than simple 2-pyridyl boronates, proved to be prone to protodeboronation, and attempts to purify them using column chromatography were complicated by partial reversion to the starting indazole. The incorporation of a more electron deficient sulfonyl group (Table 1, entry 7) overcame this challenge, and these boronate esters were amenable to standard chromatographic purification. Reflecting this decomposition pathway, for all other substrates, following characterization of the crude borylation reaction mixture by a combination of NMR spectroscopy and GCMS, each indazole boronate ester was subjected to a standard Suzuki−Miyaura cross-coupling reaction. For the 1-protected substrates CuCl was added to enhance the rate of transmetalation and thus reduce protodeborylation of the α-azinyl boronate.[13] However, for the 2-protected substrates, presumably reflecting the fact that these are not α-azinyl boronates, this proved not to have any significant effect. Given that C−H borylation is an ideal strategy for late-stage functionalization, we opted to use the indazole as the limiting reagent and adopted a standard reaction stoichiometry using 1 equiv of aryl electrophile with respect to starting indazole. Under these conditions, the desired 3-arylindazoles could be obtained in moderate to good overall yields (Table 2) from both N-1- and N-2-protected indazoles. Although cross-coupling of simple aryl chlorides proved not to be viable under these standard cross-coupling conditions, a range of aryl and heteroaryl iodides and bromides, both electron rich and electron poor, proved to be effective partners. Importantly, the tolerance of the Ir-catalyzed C−H borylation sequence enables an alternative approach to be employed and permits the easy generation of multiply substituted indazole cores to be established (Scheme 1). For example, borylation of 7-bromo-2-(2′-trimethsilylethoxymethyl)indazole **10a** occurs selectively at the 3-position to afford boronate ester **11a**. With this product it is possible to cross-couple the boronate ester selectively with aryl iodides and more reactive heteroaryl bromides while leaving the carbocyclic bromide available for subsequent transformations. While initial attempts using $Pd(dppf)Cl_2$ led to small but detectable amounts of homocoupling products, using $Pd(Ph_3P)_4$ as the catalyst precursor led to exclusive formation of the desired 3-arylbromondazole **12**, with no evidence for oligomerization of the bifunctional indazole being detected in the crude reaction mixture. A subsequent second cross-coupling reaction then enabled differentially 3,7-disubstituted indazoles to be accessed. Similar sequences are possible with the isomeric bromoindazoles **10b−d**. As with other C−H borylation processes, the regiochemistry of the borylation reaction is strongly influenced by steric parameters, and a bromine substituent at C-4 is sufficient to inhibit C-3 borylation and result in selective borylation at C-6. Sequential Suzuki−Miyaura cross-coupling reactions, as described above, afford 4,6-disubstituted indazoles e.g. **14e**. In an alternative second stage of this sequence, reduction of the C−Br bond using ammonium formate afforded the formal product of selective indazole C-6 borylation and cross-coupling (Scheme 2). Borylation of **2e** and **10a** with an excess of B_2pin_2 afforded the diborylated indazoles **16** and **17**, respectively (Scheme 3).[14] Disappointingly, attempts to achieve site-selective Suzuki−Miyaura coupling reactions with these polyborylated products proved to be challenging, leading to complex mixtures of mono- and bis-arylated products.[15] However, by exploitation of the greater lability toward protodeborylation of the 3-boronate ester, simple treatment of the crude reaction mixture with aqueous KOH selectively afforded the C-5 borylated indazole **17**.[16] Without additional purification, this compound could be selectively cross-coupled

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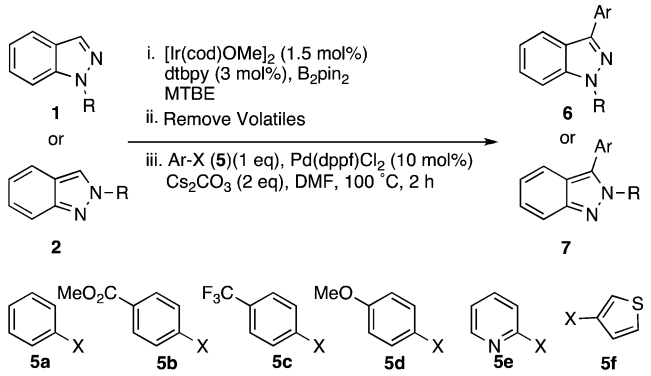
Table 2. Sequential One-Pot Ir-Catalyzed C−H Borylation Suzuki−Miyaura Cross-Coupling Reaction of N-Protected Indazoles 1 and 2[a]



		5						5			
entry	indazole[b]	Ar	X	product	yield (%)[c]	entry	indazole[b]	Ar	X	product	yield (%)[c]
1[a]	**1c**	**5a**	I	**6ca**	43	7[a]	**1e**	**5f**	Br	**6ef**	32
2[a]	**1d**	**5b**	I	**6db**	50	8	**2c**	**5a**	I	**7ca**	44
3[a]	**1d**	**5b**	CI		0	9	**2e**	**5e**	Br	**7ee**	47
4[a]	**1d**	**5c**	Br	**6dc**	42	10	**2e**	**5b**	I	**7eb**	51
5[a]	**1d**	**5d**	I	**6dd**	42	11	**2e**	**5f**	Br	**7ef**	41
6[a]	**1d**	**5e**	Br	**6de**	48						

[a]1 equiv of CuCI added. [b]For the structures of **1c−e** and **2c,e**, see Table 1 [c]Yield of purified isolated product based on starting indazole **1** or **2**.

with an aryl iodide, providing entry to 5,7-disubstituted indazoles **19**.

In summary, provided coordination of the azinyl nitrogen to the iridium catalyst is inhibited, the borylation of N-protected indazoles proceeds readily to afford selectively the corresponding 3-borylindazole. The presence of the second (azole) nitrogen reduces the basicity of the azinyl nitrogen atom, facilitating the isolation of these boronate esters to the extent that, when an electron-withdrawing protecting group is employed, the α-azinyl boronate ester is stable to column chromatography. Moreover, in spite of the increased steric demand, but consistent with a lack of the inhibitory effect of an azinyl lone pair ortho to the site of C−H activation, borylation of N-2-protected indazoles occurs significantly more quickly than that of the equivalent N-1-protected analogue. The resulting borylated indazoles are viable substrates for a variety of subsequent transformations, providing easy routes for late-stage modification of this valuable heterocycle. In particular, the functional group tolerance of C−H borylation enables a halogen to serve as both a blocking and directing group, providing access to regiocontrolled multisubstituted indazoles.

EXPERIMENTAL SECTION

"One-Pot" C−H Borylation/Suzuki−Miyaura Cross-Coupling Sequence of Protected 1*H*- and 2*H*-Indazoles. In a glovebox, a thick-walled microwave synthesis vial was charged with the corresponding indazole (1 equiv) (vial A). A separate vial was charged with $[Ir(COD)OMe]_2$ (1.5 mol %), dtbpy (3.0 mol %), and B_2pin_2 (0.7 equiv) before MTBE was added. Once it was homogeneous, this solution was added to vial A. The vial was removed from the glovebox and heated to 80 °C for 1 h. Upon completion the volatiles were removed in vacuo to afford the crude boronate product. Palladium catalyst (10 mol %), base (2 equiv) and aryl halide (see schemes for details; 1.1 equiv) were added, and the vial was sealed and purged with three evacuation/refill (Ar) cycles. Solvent (DMF or DMAc) (5 mL) was added, and the mixture was heated to 100 °C for 1 h in a microwave reactor. The reaction mixture was diluted with water (10 mL) and extracted with Et_2O (3 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered through Celite, and concentrated in vacuo to afford the crude product. Purification was achieved by flash column chromatography using the stated solvent system.

Suzuki−Miyaura Cross-Coupling of 3-Arylbromoindazoles. A 5 mL microwave vial was charged with bromoindazole (1 equiv), $Pd(dppf)Cl_2$ (10 mol %), Na_2CO_3 (3 equiv), and arylboronic acid (2 equiv). The vial was evacuated and placed under N_2 with three evacuation/refill cycles. A 3.5 mL portion of degassed 6/1 dioxane/H_2O was added. The mixture was heated to 105 °C for 2 h. The reaction mixture was diluted with H_2O (30 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, filtered through Celite, and concentrated. The product was then purified by column chromatography.

*1-(Methanesulfonyl)-3-(Bpin)-1H-indazole (**3g**).* In a glovebox, a thick-walled microwave synthesis vial was charged with the indazole (0.15 g, 0.8 mmol) (vial A). A separate vial was charged with $[Ir(COD)OMe]_2$ (1.5 mol %), dtbpy (3.0 mol %), and B_2pin_2 (0.7 equiv) before MTBE was added. Once it was homogeneous, this solution was added to vial A. The vial was removed from the glovebox and heated to 80 °C for 1 h, after which time the volatiles were removed in vacuo and the crude boronate ester was adsorbed onto silica. Purification by flash column chromatography (0−5% MeOH in $CHCl_3$) afforded **3g** as an off-white solid (0.154 g, 62%). δ_H (400 MHz, $CDCl_3$): 8.13 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.53 (m, 1H), 7.38 (m, 1H), 3.33 (s, 3H), 1.42 (s, 12H). δ_c (176 MHz, $CDCl_3$): 140.2, 130.5, 129.0, 124.3, 123.2, 112.8, 85.0, 41.5, 25.0. δ_B (128 MHz, $CDCl_3$): 28.9 (s (br)). ν_{max} (ATR): 1503, 1373, 1325, 1266, 1176, 1142, 1078, 956, 907 cm^{-1}. Accurate mass (ASAP): $C_{14}H_{19}{}^{10}BN_2O_4S$ requires M, 321.1195, found $[M]^+$ 321.1177.

*1-Methyl-3-phenyl-1H-indazole (**6ca**).* Isolated following purification by chromatography (5% EtOAc in hexane) as a pale yellow oil (0.081 g, 43%). δ_H (700 MHz, $CDCl_3$): 8.03 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 7.6 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.42 (m, 3H), 7.22 (ddd, J = 8.0, 5.4, 2.2 Hz, 1H), 4.14 (s, 3H). δ_C (176 MHz, $CDCl_3$): 143.9, 141.6, 133.8, 128.9, 127.9, 127.5, 126.4, 121.8, 121.5, 121.0, 109.3, 35.7. m/z (GC/MS, EI): 208 $[M]^+$, 180, 131 $[M - C_6H_5]^+$, 104, 77 $[C_6H_5]^+$, 51. Accurate mass (ASAP): $C_{14}H_{12}N_2$ requires M, 208.1000, found $[M]^+$ 208.0995.

*1-(Tetrahydro-2H-pyran-2″-yl)-3-(4′-(methoxycarbonyl)phenyl)-1H-indazole (**6db**).* Isolated following purification by chromatography

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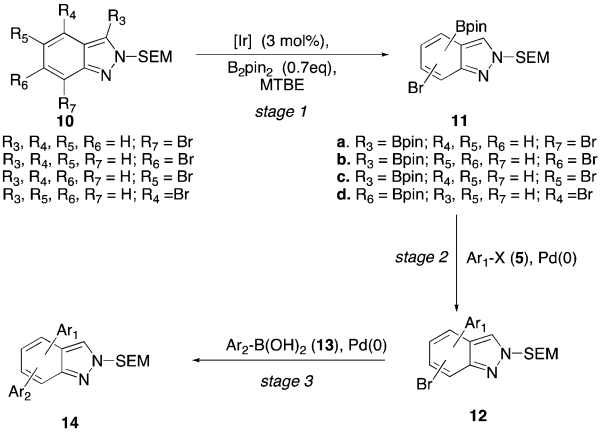
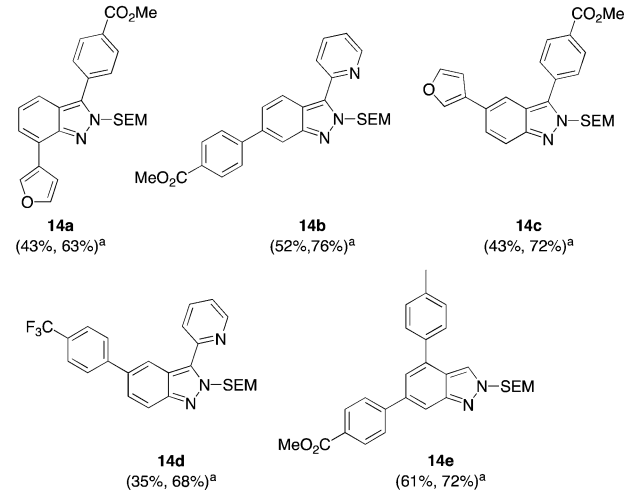
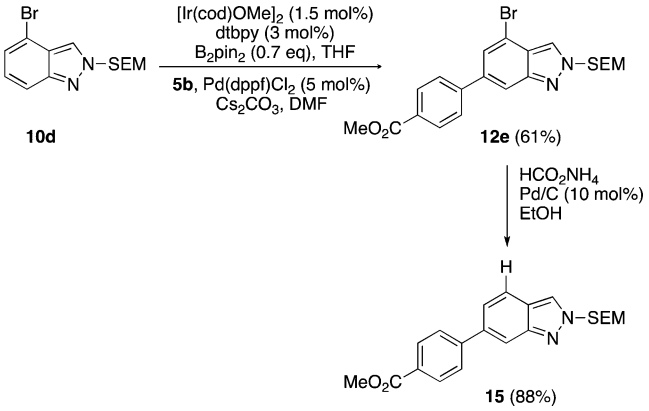
Scheme 1. Multiply Substituted Indazoles through Sequential Borylation and Cross-Coupling





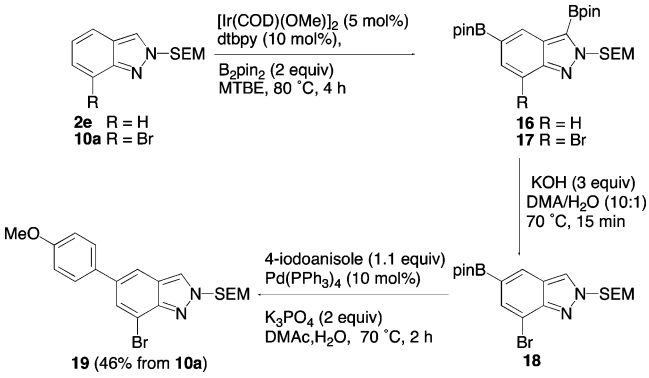
[a]Values given are the yields of stages 1 and 2 and the yield of stage 3, respectively. Yields are for purified, isolated products.

Scheme 2. Selective Synthesis of C-6-Substituted Indazoles



(0−25% EtOAc in hexane) as a white powder (0.168 g, 50%). δ_H (700 MHz): 8.16 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.0 Hz,1H), 7.66 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.26 (t, J = 8.0 Hz, 1H), 5.80 (dt, J = 9.1 Hz, 3.0 Hz, 1H), 4.07 (dt, J = 10.4 Hz, 3.5 Hz, 1H), 3.95 (s, 3H), 3.78 (td, J = 10.4 Hz, 2.5 Hz, 1H), 2.67 (m, 1H), 2.20 (m, 1H), 2.12 (m, 1H), 1.79 (m, 2H), 1.68 (m, 1H). δ_C (176 MHz): 170.0, 143.3, 141.0, 138.2, 130.0, 129.3, 127.3, 126.6, 122.5, 122.0, 121.1, 110.7, 85.6, 67.6, 52.2, 29.3, 25.2, 22.5. ν_{max}

Scheme 3. Selective Protodeborylation of Polyborylated Indazoles



(ATR): 2940, 2843, 1716, 1609, 1432, 1279, 1075, 1038, 748, 696 cm^{-1}. m/z (ASAP): 337.1 $[MH]^+$, 305.1 $[M - OMe]^+$, 271.1, 253.1 $[MH - THP]^+$. Accurate mass (ASAP): $C_{20}H_{21}N_2O_3$ requires M, 337.1552, found $[M + H]^+$ 337.1540.

*1′-Tetrahydropyran-2″-yl-3-(4-(trifluoromethyl)benzene)-1H-indazole (**6dc**).* Isolated following purification by chromatography (0−3% Et_2O in hexane) as an off-white solid (0.190 g, 42%). δ_H (600 MHz, $CDCl_3$): 8.11 (d, J = 8.2 Hz, 2H), 7.99 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 5.81 (dd, J = 9.3, 2.7 Hz, 1H), 4.07 (m, 1H), 3.79 (m, 1H), 2.68 (m, 1H), 2.21 (m, 1H), 2.13 (m, 1H), 1.79 (m, 2H), 1.69 (m, 1H). δ_C (151 MHz, $CDCl_3$): 143.2, 141.2, 137.4, 129.9 (q, J = 31.7 Hz), 127.9, 126.9, 125.8 (q, J = 3.0 Hz), 124.3 (q, J = 273.3 Hz), 122.5, 122.3, 121.1, 110.8, 85.7, 67.7, 29.5, 25.3, 22.7. δ_F (376 MHz, $CDCl_3$): −62.5. ν_{max} (ATR): 2948, 2866, 1615, 1332, 1066, 744 cm^{-1}. m/z (GCMS, EI): 346 $[MH^+]$ 10%, 262 $[M - THP]^+$ 100%. Accurate mass (ASAP): $C_{19}H_{18}F_3N_2O$ requires M, 347.1371, found $[M + H]^+$ 347.1363.

*3-(4′-Methoxyphenyl)-1-(tetrahydro-2H-pyran-2″-yl)-1H-indazole (**6dd**).* Isolated following purification by chromatography (0−40% Et_2O in hexane) as a white powder (0.127g, 42%). δ_H (700 MHz, $CDCl_3$): 7.96 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 8.1 Hz, 1H), 7.40 (t, J= 8.1 Hz, 1H), 7.21 (t, J = 8.1 Hz, 1H), 7.03 (d, J = 8.7 Hz, 2H), 5.76 (dd, J = 9.4 Hz, 2.8 Hz, 1H), 4.07 (d, J = 11.1 Hz, 1H), 3.87 (s, 3H), 3.76 (td, J = 11.1 Hz, 2.6 Hz, 1H), 2.67 (m, 1H), 2.19 (m, 1H), 2.10 (m, 1H), 1.78 (m, 2H), 1.66 (m, 1H) δ_C (176 MHz, $CDCl_3$): 159.5, 144.4, 140.9, 128.9, 126.5, 126.4, 122.6, 121.4, 120.1, 114.1, 110.3, 85.5, 67.5, 55.3, 29.5, 25.1, 22.7. ν_{max} (ATR) 2939, 2849, 1611, 1529, 1078, 1037, 833, 742 cm^{-1}. m/z (ASAP): 309.2 $[MH]^+$, 225.1 $[MH - THP]^+$. Accurate mass (ASAP): $C_{19}H_{21}N_2O_2$ requires M, 309.1603, found $[M + H]^+$ 309.1597.

*1-Tetrahydropyran-2′-yl-3-pyridin-2″-yl-1H-indazole (**6de**).* Isolated following purification by chromatography (0−10% EtOAc in hexane) as a colorless oil (0.15 g, 48%). δ_H (700 MHz, $CDCl_3$): 8.74 (d, J = 4.7 Hz, 1H), 8.67 (d, J = 8 Hz, 1H), 8.23 (d, J = 7.9 Hz, 1H), 7.76 (m, 1H), 7.62 (d, J = 8 Hz, 1H), 7.43 (t, J = 8 Hz, 1H), 7.29 (t, J = 8 Hz, 1H), 7.24 (m, 1H), 5.81 (dd, J = 9.2, 2.7 Hz, 1H), 4.07 (m, 1H), 3.78 (m, 1H), 2.68 (m, 1H), 2.21 (m, 1H), 2.12 (m, 1H), 1.79 (m, 2H), 1.69 (m, 1H). δ_C (176 MHz, $CDCl_3$): 153.7, 149.3, 143.6, 141.2, 136.4, 126.8, 123.9, 123.2, 122.4, 122.3, 121.4, 110.1, 85.7, 67.6, 29.5, 25.3, 22.7. ν_{max} (ATR): 2942, 1592, 1562, 1510, 1490, 1459, 1442, 1378, 1315, 1279, 1235, 1206, 1172, 1148, 1112, 1080, 1040, 1003, 906, 876, 795 cm^{-1}. Accurate mass (ASAP): $C_{17}H_{18}N_3O$ requires M, 280.1450, $[M + H]^+$ found 280.1441.

*3-(Thiophen-3′-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-indazole (**6ef**).* Isolated following purification by chromatography (0−40% Et_2O in hexane) as a yellow oil (0.106g, 32%). δ_H (700 MHz, $CDCl_3$): 7.99 (d, J = 8.2 Hz, 1H), 7.82 (m, 1H), 7.72 (d, J = 5.4 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H) 7.46 (m, 1H, 5′-*H*), 7.45 (m, 1H), 7.27 (t, J = 8.2 Hz, 1H), 5.77 (s, 2H), 3.61 (t, J = 8.1 Hz, 2H), 0.91 (t, J = 8.1 Hz, 2H), −0.06 (s, 9H). δ_C (176 MHz, $CDCl_3$): 141.3, 141.2, 134.6, 127.1, 126.9, 126.1, 122.7, 122.3, 121.8, 121.3, 110.1, 77.8, 66.6, 17.9, −1.3.

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ν_{max} (ATR): 2949, 2893, 1614, 1075, 856, 832, 741, 674 cm^{-1}. *m/z* (GCMS, EI): 330 $[M]^+$ 60%, 257 $[M - (CH_3)_3Si]^+$ 50%, 214 $[MH - (CH_3)_3SiCH_2CH_2O]^+$ 100%, 128 $[MH - SEM]^+$ 20%, 73 $[(CH_3)_3Si]^+$ 35%. Accurate mass (ASAP): $C_{17}H_{23}N_2OSSi$ requires *M*, 331.1300, found $[M + H]^+$ 331.1302.

*2-Methyl-3-phenyl-2H-indazole (**7ca**).* Isolated following purification by chromatography (0−10% Et_2O in hexane) as a pale yellow oil (0.064 g, 44%). δ_H (700 MHz, $CDCl_3$): 7.71 (d, *J* = 8.7 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.55 (m, 4H), 7.50 (m, 1H), 7.32 (m, 1H), 7.08 (m, 1H), 4.19 (s, 3H). δ_C (176 MHz, $CDCl_3$): 148.3, 136.2, 129.9, 129.8, 129.2, 128.9, 126.4, 122.0, 121.4, 120.3, 117.2, 38.7. *m/z* (GC/MS, EI): 208 $[M]^+$, 180, 165, 104, 77 $[C_6H_5]^+$. ν_{max} (ATR): 2363, 1500, 1361, 1287, 1009, 904 cm^{-1}. Accurate mass (ASAP): $C_{14}H_{13}N_2$ requires *M*, 209.1077, found $[M + H]^+$ 209.1079.

*2-((2-(Trimethylsilyl)ethoxy)methyl)-3-(4-(methoxycarbonyl)-phenyl)-2H-indazole (**7eb**).* Isolated following purification by chromatography (0−10% EtOAc in hexane) as a colorless oil (0.21 g, 51%). δ_H (700 MHz, $CDCl_3$): 8.22 (m, 2H), 7.86 (m, 2H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.36 (m, 1H), 7.15 (m, 1H), 5.71 (s, 2H), 3.97 (s, 3H), 3.87 (t, *J* = 8.3 Hz, 2H), 0.97 (t, *J* = 8.3 Hz, 2H), −0.01 (s, 9H). δ_C (176 MHz, $CDCl_3$): 166.7, 148.3, 135.7, 134.0, 130.3, 130.2, 129.8, 127.1, 123.1, 121.5, 120.5, 118.2, 79.6, 67.9, 52.5, 18.1, −1.3. ν_{max} (ATR): 2952, 1717, 1612, 1490, 1436, 1276, 1249, 1228, 1175, 1149, 1080, 1018, 906, 860, 835, 782 cm^{-1}. Accurate mass (ASAP): $C_{21}H_{27}N_2O_3Si$ requires *M*, 383.1791, found $[M + H]^+$ 383.1803.

*2-((2-(Trimethylsilyl)ethoxy)methyl)-3-pyridin-2′-yl-2H-indazole (**7ee**).* Isolated following purification by chromatography (20% Et_2O in hexanes) as a colorless oil (0.16 g, 47%). δ_H (700 MHz, $CDCl_3$): 8.80 (m, 1H), 7.88 (m, 3H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.34 (m, 2H), 7.18 (m, 1H), 6.15 (s, 2H), 3.68 (t, *J* = 8.3 Hz, 2H), 0.86 (t, *J* = 8.3 Hz, 2H), −0.10 (s, 9H). δ_C (176 MHz, $CDCl_3$): 150.3, 149.5, 148.3, 137.0, 134.4, 126.8, 124.4, 123.4, 122.7, 121.7, 120.8, 118.4, 80.3, 67.4, 18.0, −1.4. ν_{max} (ATR): 2953, 1586, 1490, 1459, 1364, 1306, 1249, 1152, 1088, 1021, 906, 859, 835, 786 cm^{-1}. Accurate mass (ASAP): $C_{18}H_{24}N_3OSi$ requires *M*, 326.1689, found $[M + H]^+$ 326.1692.

*2-((2-(Trimethylsilyl)ethoxy)methyl)3-thiophen-3′-yl-2H-indazole (**7ef**).* Isolated following purification by chromatography (0−5% EtOAc in hexane) as a pale yellow oil (0.13 g, 41%). δ_H (700 MHz, $CDCl_3$): 7.85 (m, 1H), 7.73 (m, 2H), 7.58 (m, 1H), 7.52 (m, 1H), 7.33 (m, 1H), 7.12 (m, 1H), 5.73 (s, 2H), 3.82 (t, *J* = 8.3 Hz, 2H), 0.96 (t, *J* = 8.3 Hz, 2H), −0.02 (m, 9H). δ_C (176 MHz, $CDCl_3$): 148.1, 132.4, 129.8, 128.3, 127.0, 126.7, 125.8, 122.4, 121.2, 120.9, 118.0, 79.6, 67.6, 18.2, −1.3. ν_{max} (ATR): 2953, 2224, 1627, 1478, 1408, 1293, 1267, 1249, 1080, 1021, 907, 856, 834, 790 cm^{-1}. Accurate mass (ASAP): $C_{17}H_{23}N_2OSSi$ requires *M*, 331.1300, found $[M + H]^+$ 331.1266.

*2-((2-(Trimethylsilyl)ethoxy)methyl)-3-(4′-(methoxycarbonyl)-phenyl)-7-bromo-2H-indazole (**12a**).* Isolated following purification by chromatography (0−30% Et_2O in hexane) as a white powder (0.198 g, 43%). δ_H (700 MHz, $CDCl_3$): 8.22 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.00 (dd, *J* = 8.4 Hz, 7.3 Hz, 1H), 5.74 (s, 2H), 3.97 (s, 3H), 3.88 (t, *J* = 8.3 Hz, 2H), 0.95 (t, *J* = 8.3 Hz, 2H), −0.01 (s, 9H), δ_C (176 MHz, $CDCl_3$): 166.5, 146.8, 137.1, 133.5, 130.5, 130.2, 129.7, 129.6, 123.5, 122.2, 119.9, 111.7, 79.5, 67.7, 52.4, 17.9, −1.4. ν_{max} (ATR): 2942, 2894, 1649, 1576, 1278, 1228, 1202, 1082, 1038, 744, 684 cm^{-1}. *m/z* (ASAP): 463.1 $[M(^{81}Br)H]^+$, 461.1 $[M(^{79}Br)H]^+$, 403.0 $[M(^{81}Br) - CO_2Me]^+$, 401.0 $[M(^{79}Br) - CO_2Me]^+$. Accurate mass (ASAP): $C_{21}H_{26}N_2O_3Si^{79}Br$ requires *M*, 461.0896, found $[M + H]^+$ 461.0911.

*2-(2-(Trimethylsilyl)ethoxymethyl)-3-(4′-methoxycarbonyl)-7-(furan-3″-yl)-2H-indazole (**14a**).* Isolated following purification by chromatography (0−20% Et_2O in hexane) as a yellow oil (0.127 g, 63%) δ_H (700 MHz, $CDCl_3$): 8.64 (dd, *J* = 1.5 Hz, 0.6 Hz, 1H), 8.22 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.57 (dd, *J* = 8.5 Hz, 0.8 Hz, 1H), 7.53 (t, *J* = 1.5 Hz, 1H), 7.51 (dd, *J* = 6.9 Hz, 0.8 Hz, 1H), 7.18 (dd, *J* = 8.5 Hz, 6.9 Hz, 1H), 7.01 (dd, *J* = 1.5 Hz, 0.6 Hz, 1H), 5.74 (s, 2H), 3.97 (s, 3H), 3.94 (t, *J* = 8.3 Hz, 2H), 1.00 (t, *J* = 8.3 Hz, 2H), 0.00 (s, 9H), δ_C (176 MHz, $CDCl_3$): 166.6, 145.9, 142.8, 142.5, 135.7, 134.0, 130.2, 130.1, 129.7, 123.2, 123.0, 122.5, 122.2, 121.9, 118.8, 108.4, 79.4, 67.8, 52.3, 18.0, −1.3. ν_{max} (ATR): 1721, 1610, 1435, 1202, 1085, 1001, 835, 751 cm^{-1}. *m/z* (ASAP): 449.2 $[MH]^+$, 421.1 $[MH - OMe]^+$, 391.1 $[MH - CO_2Me]^+$, 331.1 $[MH - (Me_3Si(CH_2)_2O)]^+$. Accurate mass (ASAP): $C_{25}H_{28}N_2O_4Si$ requires *M*, 448.1818, found $[M]^+$ 448.1808.

*6-Bromo-2-((2-(trimethylsilyl)ethoxy)methyl)-3-pyridin-2′-yl-2H-indazole (**12b**).* Isolated following purification by chromatography (15% EtOAc in hexanes) as a pale yellow oil (179 mg, 52%). δ_H (700 MHz, $CDCl_3$): 8.80 (d, *J* = 5.4 Hz, 1H), 7.95 (s, 1H), 7.87 (m, 2H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.35 (t, *J* = 5.4 Hz, 1H), 7.24 (d, *J* = 8.9 Hz, 1H), 6.08 (s, 2H) 3.68 (t, *J* = 8.3 Hz, 2H), 0.87 (t, *J* = 8.3 Hz, 2H), −0.09 (s, 9H). δ_C (176 MHz, $CDCl_3$): 150.4, 148.9, 148.8, 137.2, 135.1, 127.1, 124.4, 123.1, 122.5, 120.9, 120.7, 120.3, 80.3, 67.6, 18.0, −1.3. ν_{max} (ATR): 2951, 1584, 1470, 1244, 1092, 1014, 908, 832. Accurate mass (ASAP): $C_{18}H_{23}{}^{79}BrN_3OSi$ requires *M*, 404.0789, found $[M + H]^+$ 404.0794.

*2-((2-(Trimethylsilyl)ethoxy)methyl)-3-pyridin-2′-yl-6-(4″-(methoxycarbonyl)phenyl)-2H-indazole (**14b**).* Isolated following purification by chromatography (0−20% EtOAc in hexanes) to give **14b** (137 mg, 76%) as an off-white solid. δ_H (700 MHz, $CDCl_3$): 8.82 (d, *J* = 4.5 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 2H), 8.02 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.91 (m, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.35 (ddd, *J* = 6.6, 4.5, 1.4 Hz, 1H), 6.16 (s, 2H), 3.95 (s, 3H), 3.71 (t, *J* = 8.3 Hz, 2H), 0.88 (t, *J* = 8.3 Hz, 2H), −0.09 (s, 9H). δ_C (176 MHz, $CDCl_3$): 167.1, 150.4, 149.3, 148.6, 146.1, 138.7, 137.1, 134.6, 130.3, 129.1, 127.4, 124.4, 123.6, 122.9, 121.6, 121.4, 116.7, 80.4, 67.5, 52.3, 18.0, −1.3. ν_{max} (ATR): 2949, 1719, 1607, 1536, 1478, 1280, 1102 cm^{-1}. Accurate mass (ASAP): $C_{26}H_{30}N_3O_3Si$ requires 460.2056, found $[M + H]^+$ 460.2046.

*2-(2-(Trimethylsilyl)ethoxymethyl)-3-(4′-methoxycarbonylphenyl)-5-bromo-2H-indazole (**12c**).* Isolated following purification by chromatography (0−30% Et_2O in hexane) as a yellow oil (0.198 g, 43%). δ_H (700 MHz, $CDCl_3$): 8.23 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.70 (s, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 5.68 (s, 2H), 3.97 (s, 3H), 3.84 (t, *J* = 8.4 Hz, 2H), 0.95 (t, *J* = 8.4 Hz, 2H), 0.02 (s, 9H), δ_C (176 MHz, $CDCl_3$): 166.5, 135.7, 133.8, 130.2, 130.1, 129.6, 127.3, 126.7, 126.6, 121.7, 118.6, 116.0, 79.5, 67.6, 52.2, 18.0, −1.4. ν_{max} (ATR): 2953, 1764, 1610, 1436, 1201, 1093, 860, 836, 706 cm^{-1}. *m/z* (ASAP): 463.1 $[M(^{81}Br)H]^+$, 461.1 $[M(^{79}Br)H]^+$, 433.1 $[MH - OMe]^+$, 403.0 $[MH - CO_2Me]^+$, 376.0 $[MH - (Me_3SiCH_2)]^+$. Accurate mass (ASAP): $C_{21}H_{26}BrN_2O_3Si$ requires *M*, 461.0896, found $[M + H]^+$ 461.0898.

*2-(2-(Trimethylsilyl)ethoxymethyl)-3-(4′-methoxycarbonylphenyl)-5-(furan-3″-yl)-2H-indazole (**14c**).* Isolated following purification by chromatography (0−25% Et_2O in hexane) as a yellow oil (64 mg, 72%). δ_H (700 MHz, $CDCl_3$): 8.23 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.76 (dd, *J* = 9.0 Hz, 1.2 Hz, 1H), 7.74 (t, *J* = 1.3 Hz, 1H), 7.70 (t, *J* = 1.2 Hz, 1H)), 7.51 (dd, *J* = 9.0 Hz, 1.2 Hz, 1H), 7.47 (t, *J* = 1.3 Hz, 1H), 6.71 (m, 1H), 5.68 (s, 2H), 3.97 (s, 3H), 3.85 (t, *J* = 8.3 Hz, 2H), 0.96 (t, *J* = 8.3 Hz, 2H), −0.02 (s, 9H), δ_C (176 MHz, $CDCl_3$): 166.6, 147.6, 143.7, 138.4, 135.7, 133.9, 130.2, 130.1, 129.6, 127.3, 126.8, 126.6, 121.7, 118.6, 116.1, 108.8, 79.5, 67.8, 52.3, 17.9, −1.3. ν_{max} (ATR): 2953, 2918, 1764, 1610, 1457, 1200, 1089, 861, 835 cm^{-1}. *m/z* (ASAP): 449.2 $[MH]^+$, 391.1 $[MH - CO_2Me]^+$, 331.1 $[M - (Me_3Si(CH_2)_2O)]^+$, 287.1 $[M - (Me_3Si(CH_2)OCH_2)]^+$. Accurate mass (ASAP): $C_{25}H_{29}N_2O_4Si$ requires *M*, 449.1897, found $[M + H]^+$ 449.1889.

*2-(Trimethylsilylethoxymethyl)-3-(pyrid-2′-yl)-5-bromoindazole (**12d**).* Isolated following purification by chromatography (0−50% Et_2O in hexane) as a yellow oil (0.141 g, 35%). δ_H (700 MHz, $CDCl_3$): 8.80 (m, 1H, 6′-*H*), 8.08 (dd, *J* = 1.8 Hz, 0.8 Hz, 1H), 7.88 (m, 1H), 7.86 (m, 1H), 7.65 (dd, *J* = 9.2 Hz, 0.8 Hz, 1H), 7.39 (dd, *J* = 9.2 Hz, 1.8 Hz, 1H), 7.34 (m, 1H), 6.08 (s, 2H), 3.67 (t, *J* = 8.3 Hz, 2H), 0.86 (t, *J* = 8.3 Hz, 2H), −0.10 (s, 9H). δ_C (176 MHz, $CDCl_3$): 150.2, 148.7, 146.4, 137.0, 133.9, 130.3, 124.2, 123.1, 122.9, 122.7, 119.9, 116.9, 80.2, 67.3, 17.7, −1.6. ν_{max} (ATR): 2969, 1365, 1217, 908, 725 cm^{-1}. *m/z* (ASAP): 406.1 $[M(^{81}Br)H]^+$, 404.1 $[M(^{79}Br)H]^+$, 287.0 $[M + H - (Me_3Si(CH_2)_2O)]^+$. Accurate mass (ASAP): $C_{18}H_{23}BrN_3OSi$ requires *M*, 404.0794, found $[M + H]^+$ 404.0782.

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*2-(2-(Trimethylsilyl)ethoxymethyl)-3-(pyrid-2′-yl)-5-(4″-(trifluoromethyl)phenyl)-2H-indazole (**14d**).* Isolated following purification by chromatography (0−50% Et_2O in hexane) as a yellow oil (80 mg, 68%). δ_H (700 MHz, $CDCl_3$): 8.82 (m, 1H, 6′-*H*), 8.10 (dd, *J* = 1.7 Hz, 0.8 Hz, 1H), 7.92 (dt, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.89 (td, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.87 (dd, J =9.0 Hz, 0.8 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.60 (dd, *J* = 9.0 Hz, 1.7 Hz, 1H), 7.35 (m, 1H), 6.12 (s, 2H), 3.72 (t, *J* = 8.2 Hz, 2H), 0.88 (t, *J* = 8.2 Hz, 2H), −0.09 (s, 9H), δ_C (176 MHz, $CDCl_3$): 150.3, 149.0, 147.8, 145.2, 137.0, 135.2, 135.0, 129.0 (q, *J* = 32.5 Hz), 127.5, 126.9, 125.6 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 272.5 Hz), 124.3, 122.8, 121.9, 119.5, 118.9, 80.3, 67.6, 17.8, −1.4. ν_{max} (ATR): 1615, 1587, 1325, 1198, 1122, 1091, 839 cm^{-1}. *m/z* (ASAP): 470.2 $[M + H]^+$, 353.1 $[M - (Me_3Si(CH_2)_2O)]^+$, 335.1 $[M - (Me_3Si(CH_2)_2OCH_2)]^+$. Accurate mass (ASAP): $C_{25}H_{27}F_3N_3OSi$ requires *M*, 470.1875, found $[M + H]^+$ 470.1873.

*4-Bromo-2-((2-(trimethylsilyl)ethoxy)methyl)-6-(4-(methoxycarbonyl)phenyl)-2H-indazole (**12e**).* Isolated following purification by chromatography (0−25% Et_2O in hexane) as an off-white solid (267 mg, 61%). δ_H (700 MHz, $CDCl_3$): 8.16 (s(br), 1H), 8.13 (m, 2H), 7.89, (s(distorted), 1H), 7.71 (m, 2H), 7.57 (d, *J* = 1.1 Hz, 1H), 5.74 (s, 2H), 3.95 (s, 3H), 3.67, (t, *J* = 8.3 Hz, 2H), 0.97 (t, *J* = 8.3 Hz, 2H), −0.01 (s, 9H). δ_C (176 MHz, $CDCl_3$): 167.0, 149.1, 144.9, 139.6, 130.4, 129.5, 127.4, 125.1, 124.1, 124.0, 115.7, 114.2, 82.3, 68.0, 52.3, 18.0, −1.3. ν_{max} (ATR): 2953, 1723, 1610, 1555, 1436, 1369, 1285, 1250, 1197, 1104, 1079, 1018, 930, 836, 795, 772 cm^{-1}. Accurate mass (ASAP): $C_{21}H_{26}{}^{79}BrN_2O_3Si$ requires *M*, 461.0896, found $[M + H]^+$ 461.0893.

*2-((2-(Trimethylsilyl)ethoxy)methyl)-4-(4′-methylphenyl)-6-(4″-(methoxycarbonyl)phenyl)-2H-indazole (**14e**).* Isolated following purification by chromatography (0−10% ethyl acetate in hexane) as a colorless oil (85 mg, 72%). δ_H (700 MHz, $CDCl_3$): 8.27 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 2H), 7.93 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.45 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.75 (s, 2H), 3.95 (s, 3H), 3.67 (t, *J* = 8.3 Hz, 2H), 2.45 (s, 3H) 0.96 (t, *J* = 8.3 Hz, 2H), −0.02 (s, 9H). δ_C (176 MHz, $CDCl_3$): 167.2, 150.0, 146.3, 138.9, 138.0, 137.3, 135.6, 130.3, 129.8, 129.1, 128.1, 127.5, 123.2, 121.6, 121.2, 115.3, 82.2, 67.8, 52.3, 21.4, 18.0, −1.3. ν_{max} (ATR): 2949, 1719, 1612, 1511, 1435, 1278, 1102, 912 cm^{-1}. Accurate mass (ASAP): $C_{28}H_{33}N_2O_3Si$ requires *M*, 473.2260, found $[M + H]^+$ 473.2249.

*2-((2-(Trimethylsilyl)ethoxy)methyl)-6-(4-(methoxycarbonyl)-phenyl)-2H-indazole (**15**).* **12e** (130 mg, 0.28 mmol) was dissolved in ethanol (10 mL), and ammonium formate (353 mg, 5.6 mmol, 20 equiv) was charged. The reaction vessel was evacuated and back-filled with nitrogen (three cycles) before 10% Pd/C (15 mg, 0.014 mmol, 5 mol %) was slowly added under a positive pressure of nitrogen. The reaction mixture was stirred at room temperature for 2 h and then filtered through a plug of Celite and dry-loaded onto silica for purification by flash column chromatography (15% ethyl acetate in hexane), giving **15** as a viscous clear oil (94 mg, 88%). δ_H (700 MHz, $CDCl_3$): 8.13 (m, 2H), 7.97 (s, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.74 (m, 2H), 7.40 (dd, *J* = 8.7, 1.4 Hz, 1H), 5.75 (s, 2H), 3.95 (s, 3H), 3.66 (t, *J* = 8.3 Hz, 2H), 0.96 (t, *J* = 8.3 Hz, 2H), −0.02 (s, 9H). δ_C (176 MHz, $CDCl_3$): 167.2, 149.3, 146.2, 138.4, 130.3, 129.0, 127.4, 122.9, 122.6, 122.0, 121.3, 116.5, 82.1, 67.8, 52.3, 18.0, −1.3. ν_{max} (ATR): 2954, 1720, 1607, 1435, 1281, 1108, 932 cm^{-1}. Accurate mass (ASAP): $C_{21}H_{27}N_2O_3Si$ requires *M*, 383.1791, found $[M + H]^+$ 383.1787.

*2-(2-(Trimethylsilyl)ethoxymethyl)-5-(4′-methoxyphenyl)-7-bromo-2H-indazole (**19**).* In a glovebox, a thick-walled microwave synthesis vial was charged with **10a** (327 mg, 1 mmol) (vial A). A separate vial was charged with $[Ir(COD)OMe]_2$ (5 mol %), dtbpy (10 mol %), and B_2pin_2 (2 equiv) before MTBE (2.5 mL) was added. Once homogeneous, this solution was added to vial A. The vial was removed from the glovebox and heated to 80 °C for 2 h. Upon completion the volatiles were removed in vacuo to afford the crude boronate product. KOH (3 equiv) was added, and the vial was sealed and purged with three evacuation/refill (Ar) cycles. DMA (5 mL) and H_2O (0.5 mL) were added, and the mixture was heated to 70 °C for 15 min. The mixture was placed in a vial containing $Pd(PPh_3)_4$ (10 mol %), K_3PO_4 (2 equiv), and 4-iodoanisole (1.1 equiv), which had been purged with three evacuation/refill (Ar) cycles, and heated for a further 2 h at 70 °C. The reaction mixture was diluted with water (30 mL) and extracted with Et_2O (4 × 20 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered through Celite, and concentrated in vacuo to afford the crude product. Purification by flash column chromatography (0−40% Et_2O in hexane) afforded **19** as a white powder (0.199 g, 46%). δ_H (700 MHz, $CDCl_3$): 8.23 (s, 1H), 7.78 (s, 1H), 7.74 (s, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 5.77 (s, 2H), 3.85 (s, 3H), 3.66 (t, *J* = 8.5 Hz, 2H), 0.95 (t, *J* = 8.5 Hz, 2H), −0.02 (s, 9H). δ_C (176 MHz, $CDCl_3$): 159.1, 146.6, 136.1, 133.0, 129.8, 128.2, 124.0, 123.4, 116.8, 114.4, 111.7, 82.3, 67.8, 55.4, 17.9, −1.33. ν_{max} (ATR): 2190, 1981, 1502, 1246, 1096, 832, 743. *m/z* (ASAP): 434.1 $[(^{81}Br)M]^+$, 432.1 $[(^{79}Br)M]^+$, 350.0 $[(^{81}Br)M - (Me_3SiCH_2)]^+$, 348.0 $[(^{79}Br)M - (Me_3SiCH_2)]^+$. Accurate mass (ASAP): $C_{20}H_{25}{}^{79}BrN_2O_2Si$ requires *M*, 432.0869, found *m/z* $[M]^+$ 432.0865.

■ ASSOCIATED CONTENT

Supporting Information

Text giving general experimental details and figures giving ^1H, ^{13}C, and ^{11}B NMR spectra for all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00452.

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Notes

The authors declare no competing financial interest.

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