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Oxidative Route to Indoles via Intramolecular Amino-Hydroxylation of *o*-Allenyl Anilines

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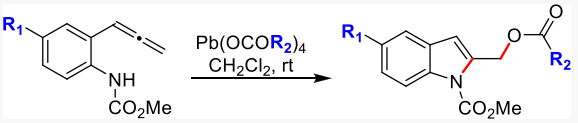
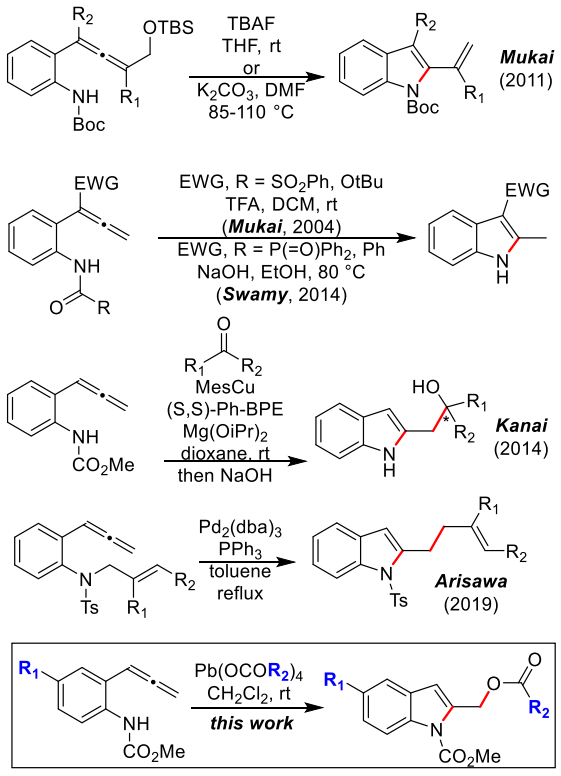
ABSTRACT: A new intramolecular oxidative amino-hydroxylation of *o*-allenyl anilines is reported. Treatment of carbamate-protected anilines with lead(IV) carboxylates in dichloromethane at room temperature results in facile tandem C−N (allene cyclization) and C−O bond formation (carboxylate trapping) to form indole products. Detailed reaction scope, mechanistic and kinetic studies suggest a reaction pathway involving an initial Wessely dearomatization step followed by cyclization and rearomatization.



INTRODUCTION

Indole is one of nature's privileged nitrogen heterocycles, and among U.S. FDA-approved drugs, indole ranks as the ninth most frequently occurring nitrogen heterocycle.[1] We recently reported a dearomatization−rearomatization approach for forming indoles from carbamate-protected aniline precursors.[2] This effort prompted us to explore alternative oxidative indole-forming approaches, wherein the starting aniline was substituted with an unsaturated group in its *ortho* position. We became drawn to anilines containing *o*-allene substituents, which as a class of compounds has not received much attention. Summarized in Scheme 1 are reported indole-forming approaches employing *o*-allenyl aniline starting materials. Mukai has demonstrated that carbamate-protected anilines can cyclize under base-mediated conditions to displace a silyl ether in an intramolecular S_N2' fashion to form indoles,[3] or alternatively using either an acid or a base can undergo an intramolecular conjugate addition if the allene is substituted with a sulfone activating group.[4] Swamy has shown that this same Michael approach can be realized with a phosphine oxide Michael acceptor.[5] We have uncovered only two reports in which from the starting *o*-allenyl aniline precursor two new bonds (colored red), including the indole N1−C2 bond, are made as part of the cyclization process. Kanai has impressively developed a copper-catalyzed asymmetric protocol in which after cyclization to form the indole the resulting chiral allyl copper intermediate can be effectively intercepted with aldehyde and ketone electrophiles.[6] Most recently, Arisawa has reported a palladium-mediated approach in which an *N*-allyl aniline substituent is first deprotected, and following cyclization of the nitrogen atom onto the allene facilitated by palladium activation, the resulting palladium species undergoes a reductive elimination to form a C−C bond to complete the butenyl side chain.[7] We proposed that by using either hypervalent iodine or lead(IV) carboxylate oxidants we should be able achieve a net amino-hydroxylation by cyclizing in an

Scheme 1. *o*-Allenyl Aniline Indole-Forming Cyclizations



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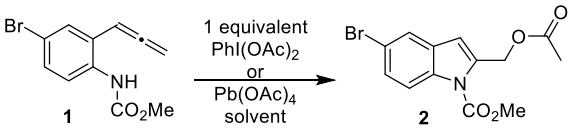
exo fashion onto the allene and capturing the intermediate with the oxidant's carboxylate ligand.

RESULTS AND DISCUSSION

Our hypervalent iodine oxidant-mediated aniline dearomatization−rearomatization indole-forming reaction served as the primary inspiration for this reaction design, which is why we first evaluated classical hypervalent iodine oxidations such as (diacetoxyiodo)benzene (PIDA) and its stronger cousin, [bis(trifluoroacetoxy)iodo]benzene (PIFA). These oxidations were performed in dichloromethane (DCM), trifluoroethanol (TFE), and hexafluoroisopropanol (HFIP), with the latter two being inspired by the seminal work of Kita,[8−10] who demonstrated their unique potential as solvents for hypervalent iodine oxidations (Table 1).[11] These studies revealed that

Table 1. Optimization of Intramolecular Indole-Forming Oxidative Amino-Hydroxylation[a]



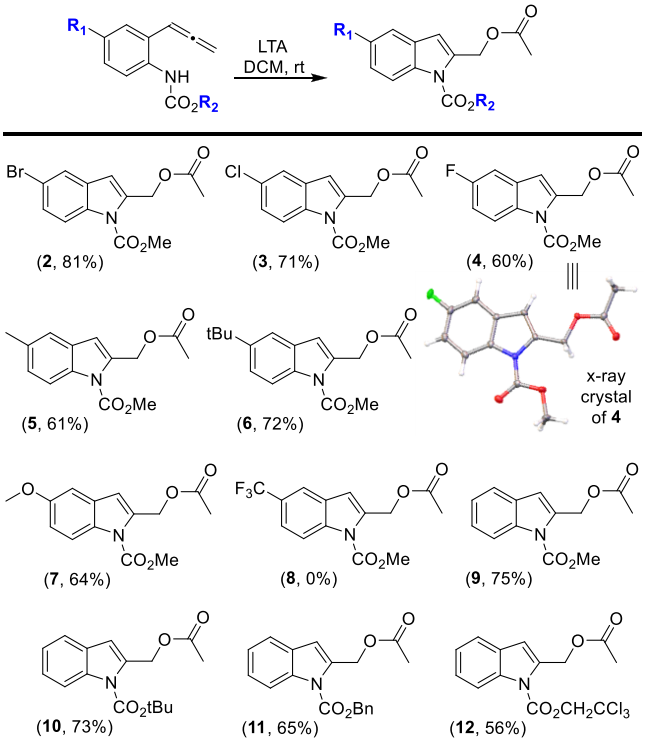
entry	oxidant	solvent	temp	yield (%)
1	PIDA (1.2 equiv)	TFE	rt	0
2	PIDA (1.2 equiv)	HFIP	rt	0
3	PIDA (1.2 equiv)	DCM	rt	4
4	LTA (0.5 equiv)	DCM	rt	21
5	LTA (1.0 equiv)	DCM	rt	40
6	LTA (1.2 equiv)	DCM	rt	51
7	LTA (1.5 equiv)	DCM	rt	81
8	LTA (1.2 equiv)	DCM[b]	40 °C	63
9	LTA (1.2 equiv)	DCE[b]	60 °C	52
10	LTA (1.5 equiv)	DCM[c]	rt	44
11	LTA (1.5 equiv)	DCM[d]	rt	50
12	LTA (1.5 equiv)	DCM[e]	rt	51
13	LTA (1.5 equiv)	benzene	rt	33
14	LTA (1.5 equiv)	DCM/AcOH	rt	55

[a]Reactions were run at 0.3 M overnight. [b]Reactions were run for 4 h. [c]At 0.1 M. [d]At 0.2 M. [e]At 0.4 M.

hypervalent iodine reagents formed **2** in only 4% yield (entries 1−3). Our past experiences with phenolic oxidative dearomatization transformations suggested to us that a stronger oxidant such as lead(IV) carboxylates, represented with lead(IV) acetate (LTA), could potentially facilitate the proposed reaction. We were encouraged by a rare example of an aniline aryl oxidation precedent from Yamamoto.[12] Toward that end, we were delighted to learn that upon treatment of 4-bromo *o*-allenyl aniline **1** with LTA in DCM at room temperature an efficient reaction took place forming a single product, which we confirmed to be indole **2**. The highest yield was obtained by performing the reaction at room temperature with 1.5 equiv of LTA (entry 3). Higher temperatures (entries 8 and 9), different concentrations (entries 10−12), and different solvents (entries 13 and 14) resulted in diminished yields.

We next turned our attention to investigating the impact of *p*-aniline substitution on this new reaction as well as exploring alternative synthetically attractive carbamate protecting groups. Halogen substituents were well tolerated with bromine (**2**) being superior followed by chlorine (**3**) and then fluorine (**4**) (Scheme 2). It is most instructive to compare the performance

Scheme 2. Scope and Limitation for Indole Formation with Unsubstituted Allenes



of 4-methyl (**5**) and 4-trifluoromethyl (**8**) substituents, with the former affording the indole product in 61% yield and the latter affording no product. Like the methyl case, other electron-donating substituents such as 4-*tert*-butyl (**6**) and 4-methoxy (**7**) both form indole products in good yields. For the unsubstituted aryl allene substrate, we also evaluated commonly employed carbamate protecting groups such as *tert*-butoxycarbonyl (Boc, **10**), carboxybenzyl (Cbz, **11**), and 2,2,2-trichloroethoxycarbonyl (Troc, **12**), all of which formed the indole products in fair to good yields, with the electron-withdrawing Troc carbamate giving the lowest yield.

We next decided to explore if we could employ lead(IV) carboxylates containing ligands other than acetates. Toward that end, we have explored benzoate and cinnamate ligands and have learned that this new oxidative indole-forming reaction can indeed also be realized with these oxidants (Scheme 3). The parent $Pb(OBz)_4$ furnished the indole product in 57% yield (**13**), with 4-fluoro and 4-trifloromethyl lead(IV) benzoates performing similarly to afford indoles **14** and **16** in 44% and 54% yields, respectively. Interestingly, the electron-donating 4-methoxy lead benzoate oxidant was the worst performer in this series (**15**). When lead(IV) cinnamate was utilized as the oxidant, the expected indole product was formed in 67% yield (**17**).

We next focused our investigations on elucidating how substituting the allene moiety would impact the performance of the indole reaction (Scheme 4). We decided to synthesize a pair of allene substrates, wherein in addition to the terminus of the allene being substituted, two different 4-aniline substituents that performed well in Table 1 (bromine and hydrogen) were also selected. In the case of allenes containing a single terminal methyl group (Scheme 4, **18** and **19**), both substrates underwent the new oxidative indole-forming reaction to afford the expected products in 48% and 49% yields, respectively.

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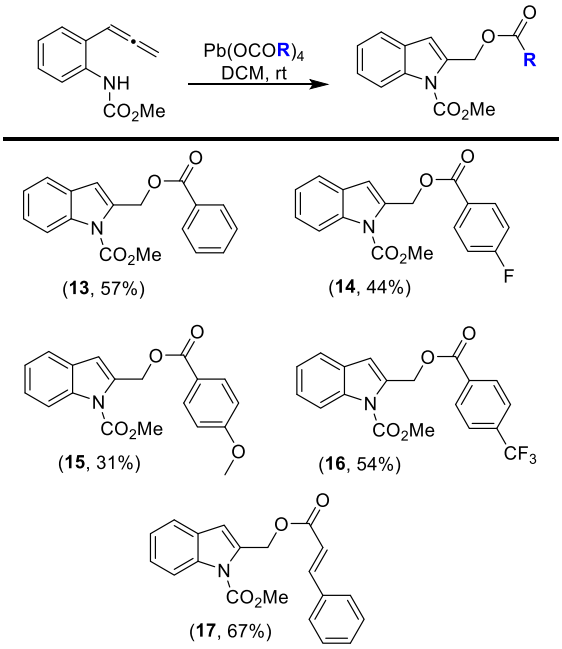
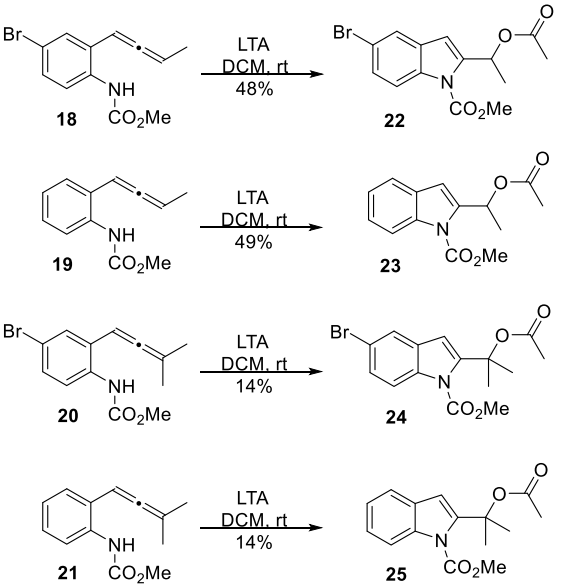
Scheme 3. Oxidations with Lead(IV) Benzoates



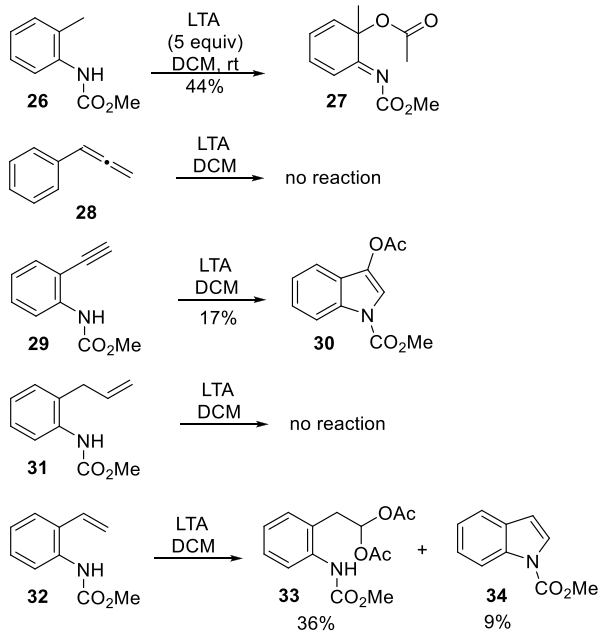
Scheme 4. Scope of Indole Formation with Terminally Substituted Allenes



Gratifyingly, dimethyl-substituted allenes **20** and **21** also participated and afforded the products, albeit in significantly diminished yields. Taken together, it is evident that size of the terminal allene substituents plays a significant role, with unsubstituted allenes like those detailed in Scheme 2 performing well, with yields dropping progressively when each of the terminal hydrogens is replaced with a methyl group.

Shown in Scheme 5 are the results of our control experiment investigations. When the allene is replaced with a simple methyl group (**26**), a more sluggish Wessely type oxidation[13] takes place to form imino quinol acetate **27** in 44% yield. Removal of the aniline carbamate (**28**) results in no reaction, and replacement of the allene with an allyl group (**31**) is also a

Scheme 5. Lead(IV) Acetate Control Experiments



dead end. Interestingly, in the case of an alkyne *ortho* substituent (**29**), the reaction is quite messy, but we did succeed in observing and isolating 3-acetoxy-substituted indole **30**, which as in the case of allenes is also a net amino-hydroxylation outcome. When styrene aniline carbamate **32** is used, an oxidation takes place to furnish unstable 1,1-bis-acetoxy product **33** and most intriguingly small amounts of indole product **34**.

Our substitution studies and control experiments have provided important mechanistic clues, wherein electron-donating (Me, tBu, H, and OMe) to weakly electron-withdrawing group (Br, Cl, and F) 4-aryl substituents perform well while a strong electron-withdrawing group (CF_3) shuts the reaction down. With respect to the carbamate group, diminished yields are observed when a more electron deficient carbamate is used (Scheme 2). With respect to the oxidant, we learned that yields suffered with more electron-rich benzoate oxidants compared to neutral or electro deficient (Scheme 3). Finally, sterics do play a role with yields dropping progressively as the terminal hydrogens of the allene are replaced with methyl groups (Scheme 4). The control experiments detailed in Scheme 5 highlight the uniqueness of the *o*-allenyl aniline carbamate combination for this new reaction. To learn more about the mechanism of this reaction, we embarked on assessing the kinetics for this reaction using proton NMR spectroscopy. Our proton NMR kinetic studies have established that the overall reaction is second-order. Specifically, it is first order with respect to the allene and LTA [rate = *k*[allene][LTA] (for more information, see the Supporting Information)]. Attempts were made to observe lead intermediates by lead NMR, but no useful signals were observed. To gather additional insight about the mechanism, we synthesized deuterium-labeled substrate **35**,[14] which proceeded to form deuterated allene product **36** in a yield nearly identical to that of proto cousin **9**. Comparing the kinetics for the formation of **36** and **9** revealed a kinetic isotope effect (KIE) of 0.87, which supports the proposed hybridization change and nucleophilic attack at the deuterated position (path b, formation of **E**). Kinetic studies were also

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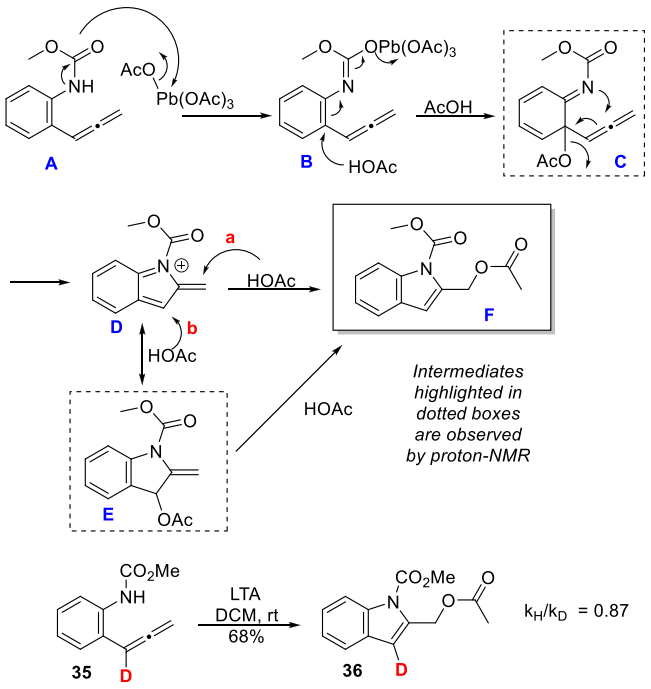
conducted with various 4-aryl-substituted substrates, with lower rates being observed for deactivated substituents (**2** and **3**), whereas rates for activated substrates like **7** were significantly higher. Our NMR kinetic analyses have been able to observe two intermediates, both of which are highlighted with dotted boxes in Scheme 6 (**C** and **E**). In general, the rates

Scheme 6. Mechanistic Proposal



of formation for the intermediates are approximately half the rate of the indole for the Wessely product, and one-tenth of the rate of the indole for the intermediate in path b. The mechanistic hypothesis we favor involves initial engagement of the carbamate with LTA, which results in a Wessely type dearomatization to form the first observable intermediate (**C**) followed by cyclization or more likely trapping of an activated carbocation (OAc leaves first). The resulting cyclized iminium ion (**D**) can then be attacked with acetic acid via path a to form the indole product (**F**) directly or alternatively attacked via path b to form NMR-observable indoline intermediate **E**, which can either regenerate the iminium ion or proceed to form the product. This last cyclization step would be significantly impacted by the size of the terminal allene substituents, which is what we observe; similarly, the more electron poor carbamates and strongly electron-withdrawing 4-aryl substituents would by this hypothesis be expected to perform worse, as well. Given that lead is acting as an electrophile, the results from the lead benzoate experiments seem also to be supportive. Intermediate **E** could also be envisioned to be formed directly from **A** as proposed by Moloney for acid-tethered[15,16] and alcohol-tethered[17] alkenes.

CONCLUSIONS

In conclusion, we report a new oxidative approach to indoles from carbamate-protected *o*-allenyl aniline starting materials. This new reaction is facilitated by lead(IV) acetate, resulting in the formation of new vicinal C−N and C−O bonds. Mechanistic investigations suggest that the aniline is first dearomatized, at which point cyclization and formation of the C−N bond take place to yield an iminium ion, which can be rearomatized upon attack by a carboxylate by one or two pathways.

EXPERIMENTAL SECTION

General Experimental. All reactions were performed using flame-dried glassware under an atmosphere of nitrogen with dry solvents, unless otherwise stated. Dry DCM was obtained by passing previously degassed solvents through activated alumina columns. LTA was recrystallized from and stored under glacial acetic acid and filtered immediately before use.[18] Lead tetrabenzoate, lead tetracinnamate, lead (4-methoxybenzoate), lead (4-fluorobenzoate), and lead (4-trifluoromethylbenzoate) were prepared according to a literature procedure.[16] All other commercial reagents were used as provided. Reactions were monitored by thin layer chromatography (TLC) carried out on EMD 250 μm silica gel 60-F254 plates. Visualization was performed by UV light irradiation, ceric ammonium molybdate, *p*-anisaldehyde, or potassium permanganate stain, and heat via a heat gun. Flash chromatography was performed on SiliaFlash F60 (particle size range of 40−63 μm). ^{1}H, ^{13}C, and ^{19}F NMR data were acquired on Bruker AVIII-400, NEO 500, and DRX 500 instruments, respectively, and the spectra were calibrated using residual solvent as the internal reference for ^{1}H and ^{13}C NMR ($CDCl_3$; 7.27 ppm for ^{1}H NMR, 77.16 for ^{13}C NMR). The following abbreviations were used to explain multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet. Infrared spectra were recorded on a Thermo Nicolet iS50R FT-IR instrument. High-resolution MS analysis was performed with a Thermo Fisher Scientific Q Exactive Plus Orbitrap MS with a resolution of 70000. X-ray diffraction data were acquired at the University of Arizona X-ray Diffraction Facility on a Bruker Kappa Apex II Duo instrument.

General Procedures for the Protection of 2-Iodoaniline Derivatives and Compound Characterization Data. *General Procedure A: Methyl Carbamate Protection.* Following a modified reported procedure for a similar compound,[19] the 2-iodoaniline derivative (10.00 mmol, 1.0 equiv) was added to a flame-dried round-bottom flask equipped with a stir bar and septum. The flask was purged and maintained under nitrogen. The aniline was dissolved in DCM (20 mL, 1.0 M), followed by addition of pyridine (2.66 mL, 33.00 mmol, 3.3. equiv), and the solution was cooled in an ice bath to 0 °C. Methyl chloroformate (2.32 mL, 3.0 equiv) was added to the cooled solution over 15 min with a vent needle. The solution was then allowed to warm to room temperature and stirred for an additional 4 h. The crude mixture was quenched with 40 mL of distilled water and then extracted three times with 40 mL of DCM. The combined organic layers were washed with brine before being dried over Na_2SO_4 and filtered. The organic layer was concentrated in vacuo and then purified by silica gel flash column chromatography (15:85 EtOAc/hexanes).

*Methyl (2-Iodophenyl)carbamate (**S1**).* Compound **S1** was prepared on a 10 mmol scale with commercially available 2-iodoaniline using general procedure A. The product was obtained as a white solid (2.64 g, 95%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 1H), 7.76 (dd, J = 7.9, 1.5 Hz, 1H), 7.47−7.31 (m, 1H), 6.97 (br, 1H), 6.81 (td, J = 7.6, 1.6 Hz, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.0, 139.0, 138.5, 129.4, 125.2, 120.4, 89.0, 52.7; IR (NaCl) 3385, 1741 cm^{-1}; HRMS (ESI)$^{+}$ m/z calcd for $C_8H_9INO_2$ $[M + H]^{+}$ 277.9678, found 277.9673.

*Methyl (4-Fluoro-2-iodophenyl)carbamate (**S2**).* Compound **S2** was prepared on a 10.0 mmol scale with 4-fluoro-2-iodoaniline using general procedure A. The product was obtained as a white solid (2.77 g, 94%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, J = 9.1, 4.6 Hz, 1H), 7.15 (dd, J = 8.5, 2.6 Hz, 1H), 7.02 (td, J = 9.1, 2.6 Hz, 1H), 6.61 (d, J = 1.1 Hz, 1H), 5.43 (d, J = 1.1 Hz, 2H), 4.03 (s, 3H), 2.12 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.5, 159.5 (d, J = 239.9 Hz), 151.7, 136.6, 133.0, 129.6 (d, J = 10.1 Hz), 116.7, 112.6 (d, J = 24.9 Hz), 110.2 (d, J = 4.0 Hz), 106.2 (d, J = 23.8 Hz), 60.4, 54.0, 21.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ −120.16 (d, J = 5.0 Hz);

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IR (NaCl) 3266, 1694 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_8H_8FINO_2$ $[M + H]^+$ 295.9584, found 295.9578.

*Methyl (4-Chloro-2-iodophenyl)carbamate (**S3**).* Compound **S3** was prepared on a 10.00 mmol scale with 4-chloro-2-iodoaniline using general procedure A. The product was obtained as a white solid (2.99 g, 96%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 2.4 Hz, 1H), 7.32 (dd, J = 8.9, 2.4 Hz, 1H), 6.93 (br, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.8, 138.0, 137.4, 129.5, 129.2, 120.7, 88.6, 52.8; IR (NaCl) 3385, 1733 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_8H_8ClINO_2$ $[M + H]^+$ 311.9288, found 311.9283.

*Methyl (4-Bromo-2-iodophenyl)carbamate (**S4**).* Compound **S4** was prepared on a 10.00 mmol scale with 4-bromo-2-iodoaniline using general procedure A. The product was obtained as a white solid (3.41 g, 96%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 8.9 Hz, 1H), 7.88 (d, J = 2.3 Hz, 1H), 7.45 (dd, J = 8.8, 2.3 Hz, 1H), 6.94 (br, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.8, 140.7, 137.8, 132.4, 121.1, 116.5, 89.0, 52.9; IR (NaCl) 3384, 1733 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_8H_8BrINO_2$ $[M + H]^+$ 355.8783, found 355.8778.

*Methyl (2-Iodo-4-methylphenyl)carbamate (**S5**).* Compound **S5** was prepared on a 10.00 mmol scale with 2-iodo-4-methylaniline using general procedure A. The product was obtained as a tan solid (2.75 g, 95%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 8.5 Hz, 1H), 7.65−7.48 (m, 1H), 7.15 (dd, J = 8.5, 2.0 Hz, 1H), 6.85 (br, 1H), 3.80 (s, 3H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.1, 139.2, 136.0, 135.2, 130.1, 120.5, 89.3, 52.6, 20.3; IR (NaCl) 3379, 1747 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_9H_{11}INO_2$ $[M + H]^+$ 291.9834, found 291.9829.

*Methyl [4-(tert-Butyl)-2-iodophenyl]carbamate (**S6**).* Compound **S6** was prepared on a 7.22 mmol scale with methyl (2-iodophenyl)-carbamate (**S1**) following a known procedure.[20] The product was obtained as a colorless oil (819 mg, 34%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.3 Hz, 1H), 7.75 (d, J = 2.3 Hz, 1H), 7.37 (dd, J = 8.6, 2.3 Hz, 1H), 6.88 (br, 1H), 3.80 (s, 3H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.1, 148.6, 135.9, 135.8, 126.5, 120.3, 89.5, 52.6, 34.3, 31.3; IR (NaCl) 3391, 2962, 1744 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{17}INO_2$ $[M + H]^+$ 334.0304, found 334.0299.

*Methyl (2-Iodo-4-methoxyphenyl)carbamate (**S7**).* Compound **S7** was prepared on a 10.00 mmol scale with 2-iodo-4-methoxyaniline using general procedure A. The product was obtained as a tan solid (2.91 g, 95%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (br, 1H), 7.31 (d, J = 2.9 Hz, 1H), 6.91 (dd, J = 9.0, 2.9 Hz, 1H), 6.68 (br, 1H), 3.79 (s, 3H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.5, 154.5, 132.0, 123.9, 122.2, 115.1, 55.8, 52.6; IR (NaCl) 3382, 1743 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_9H_{11}INO_3$ $[M + H]^+$ 307.9784, found 307.9778.

*Methyl [2-Iodo-4-(trifluoromethyl)phenyl]carbamate (**S8**).* Compound **S8** was prepared on a 10.00 mmol scale with 2-iodo-4-(trifluoromethyl)aniline using a modified general procedure A. The reaction mixture was heated to 45 °C in an oil bath for 24 h before the reaction was quenched. The product was obtained as a white solid (3.26 g, 95%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.7 Hz, 1H), 7.99−7.95 (m, 1H), 7.57 (dd, J = 8.7, 2.1 Hz, 1H), 7.13 (s, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.5, 141.51, 135.9 (d, J = 3.8 Hz), 126.5 (q, J = 3.7 Hz), 123.0 (d, J = 272.1 Hz), 119.0, 87.19, 52.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ −62.15; IR (NaCl) 3314, 1707 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_9H_8F_3INO_2$ $[M + H]^+$ 345.9552, found 345.9546.

*tert-Butyl (2-Iodophenyl)carbamate (**S9**).* Compound **S9** was prepared on an 18.202 mmol scale with 2-iodoaniline following a literature procedure.[21] The product was obtained as a light-yellow oil (5.76 g, 99%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09−8.03 (m, 1H), 7.75 (dd, J = 7.9, 1.5 Hz, 1H), 7.31 (ddd, J = 8.6, 7.4, 1.5 Hz, 1H), 6.83 (br, 1H), 6.77 (td, J = 7.6, 1.6 Hz, 1H), 1.54 (d, J = 5.8 Hz, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.7, 146.8, 138.9, 129.3, 124.8, 120.3, 88.8, 81.2, 28.4; IR (NaCl) 3395, 2979, 1735 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{11}H_{15}INO_2$ $[M + H]^+$ 320.0147, found 320.0142.

*Benzyl (2-Iodophenyl)carbamate (**S10**).* Compound **S10** was prepared on a 16.13 mmol scale with 2-iodobenzoic acid following a literature procedure.[22] The product was obtained as a white solid (2.14 g, 62%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.3 Hz, 1H), 7.77 (dd, J = 7.9, 1.5 Hz, 1H), 7.49−7.31 (m, 6H), 7.05 (br, 1H), 6.82 (td, J = 7.6, 1.6 Hz, 1H), 5.25 (s, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.4, 139.0, 138.4, 136.0, 129.4, 128.8, 128.6, 128.5, 125.3, 120.5, 89.0, 67.4; IR (NaCl) 3384, 1739 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{14}H_{13}INO_2$ $[M + H]^+$ 353.9991, found 353.9986.

*2,2,2-Trichloroethyl (2-Iodophenyl)carbamate (**S11**).* Compound **S11** was prepared on a 16.13 mmol scale with 2-iodobenzoic acid following a literature procedure.[22] The product was obtained as a white solid (4.32 g, 68%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 1H), 7.80 (dd, J = 8.0, 1.5 Hz, 1H), 7.38 (ddd, J = 8.5, 7.4, 1.5 Hz, 1H), 7.16 (br, 1H), 6.87 (td, J = 7.6, 1.6 Hz, 1H), 4.86 (s, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.7, 139.2, 137.7, 129.5, 126.1, 121.0, 95.2, 89.6, 74.8; IR (NaCl) 3381, 2953, 1754 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_9H_8C_{l3}INO_2$ $[M + H]^+$ 393.8665, found 393.8660.

General Coupling Procedure of Carbamate-Protected *o*-Alkynyl Anilines and Compound Characterization Data. *General Procedure B: Sonogashira Coupling of Protected 2-Iodoaniline Derivatives.* Following a modified reported procedure for a similar compound,[23] the protected 2-iodoaniline derivative (1.00 equiv), $PdCl_2(PPh_3)_2$ (0.02 equiv), and CuI (0.03 equiv) were transferred to a flame-dried flask equipped with a stir bar and septum and dissolved in a THF/NEt_3 mixture (4:1, 0.5 M). Nitrogen was bubbled through the solution followed by dropwise addition of the alkyne (1.20 equiv). The reaction mixture was stirred at room temperature for 3−6 h, and then the reaction quenched with saturated aqueous NH_4Cl. The crude mixture was extracted three times with ethyl acetate, and then the combined organic layers were washed with brine and dried over Na_2SO_4. The organic layer was concentrated in vacuo and then purified by silica gel flash column chromatography (20:80 to 40:60 EtOAc/hexanes). **Note** that products were commonly isolated as a yellow solid. Flushing with a large volume of 20% EtOAc in hexanes allowed for separation of the yellow impurity.

*Methyl [2-(3-Hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S12**).* Compound **S12** was prepared on a 10.83 mmol scale with methyl (2-iodophenyl)carbamate (**S1**) and propargyl alcohol using general procedure B. The product was obtained as a yellow to off-white solid (1.78 g, 80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (br, 1H), 7.49 (s, 1H), 7.32 (dd, J = 7.7, 1.6 Hz, 1H), 7.30−7.25 (m, 1H), 6.94 (t, J = 7.6 Hz, 1H), 4.53 (s, 2H), 3.75 (s, 3H), 3.49 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.0, 139.0, 132.0, 129.8, 122.7, 118.0, 111.1, 94.5, 80.5, 52.5, 51.3; IR (NaCl) 3395, 2211, 1740 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{11}H_{12}NO_3$ $[M + H]^+$ 206.0817, found 206.0812.

*Methyl [4-Fluoro-2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S13**).* Compound **S13** was prepared on a 6.79 mmol scale with methyl (4-fluoro-2-iodophenyl)carbamate (**S2**) and propargyl alcohol using general procedure B. The product was obtained as a yellow to off-white solid (1.30 g, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.05 (dd, J = 8.8, 2.8 Hz, 1H), 4.54 (s, 2H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.7 (d, J = 243.1 Hz), 153.8, 135.5, 119.6, 118.3 (d, J = 24.0 Hz), 117.1 (d, J = 22.2 Hz), 95.0, 79.9 (d, J = 3.1 Hz), 52.55, 51.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ −120.05; IR (NaCl) 3301, 2227, 1747 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{11}H_{11}FNO_3$ $[M + H]^+$ 224.0723, found 234.0718.

*Methyl [4-Chloro-2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S14**).* Compound **S14** was prepared on a 6.43 mmol scale with methyl (4-chloro-2-iodophenyl)carbamate (**S3**) and propargyl alcohol using general procedure B. The product was obtained as a yellow to off-white solid (1.19 g, 77%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.7 Hz, 1H), 7.34 (s, 1H), 7.32 (d, J = 2.5 Hz, 1H), 7.30−7.22 (m, 1H), 4.56 (d, J = 3.9 Hz, 2H), 3.80 (s, 3H), 2.38 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.8, 137.9, 131.5, 130.1, 127.6, 119.2, 112.4, 95.5, 79.7, 52.8, 51.5; IR (NaCl) 3322, 2222, 1705 cm^{-1};

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HRMS (ESI)$^+$ m/z calcd for $C_{11}H_{11}ClNO_3$ $[M + H]^+$ 240.0427, found 240.0422.

*Methyl [4-Bromo-2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S15**).* Compound **S15** was prepared on a 4.12 mmol scale with methyl (4-bromo-2-iodophenyl)carbamate (**S4**) and propargyl alcohol using general procedure B. The product was obtained as a yellow to off-white solid (1.04 g, 89%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (br, 1H), 7.46 (d, J = 2.3 Hz, 1H), 7.41 (dd, J = 8.9, 2.4 Hz, 1H), 7.35 (s, 1H), 4.56 (d, J = 3.2 Hz, 2H), 3.80 (s, 3H), 2.51 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.7, 138.3, 134.4, 132.9, 119.5, 114.8, 112.8, 95.6, 79.5, 52.8, 51.5; IR (NaCl) 3305, 2194, 1707 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{11}H_{11}BrNO_3$ $[M + H]^+$ 283.9922, found 283.9917.

*Methyl [2-(3-Hydroxyprop-1-yn-1-yl)-4-methylphenyl]carbamate (**S16**).* Compound **S16** was prepared on a 4.12 mmol scale with methyl (4-methyl-2-iodophenyl)carbamate (**S5**) and propargyl alcohol using general procedure B. The product was obtained as a tan to white solid (613 mg, 67%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (br, 1H), 7.34 (s, 1H), 7.15 (d, J = 2.1 Hz, 1H), 7.10 (dd, J = 8.6, 2.1 Hz, 1H), 4.54 (s, 2H), 3.77 (s, 3H), 2.91 (br, 1H), 2.23 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.1, 136.7, 132.3, 130.7, 118.1, 111.0, 94.1, 81.0, 52.5, 51.5, 20.5; IR (NaCl) 3322, 2226, 1712 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{14}NO_3$ $[M + H]^+$ 220.0974, found 220.0968.

*Methyl [4-(tert-Butyl)-2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S17**).* Compound **S17** was prepared on a 2.45 mmol scale with methyl [4-(*tert*-butyl)-2-iodophenyl]carbamate (**S6**) and propargyl alcohol using general procedure B. The product was obtained as a light tan to white solid (552 mg, 88%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (br, 1H), 7.39 (d, J = 2.4 Hz, 1H), 7.36−7.32 (m, 2H), 4.56 (s, 2H), 3.78 (s, 3H), 2.60 (br, 1H), 1.27 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.1, 145.7, 136.7, 128.9, 127.2, 117.9, 110.7, 93.8, 81.4, 52.5, 51.6, 34.3, 31.3; IR (NaCl) 3399, 2225, 1741 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{15}H_{20}NO_3$ $[M + H]^+$ 262.1443, found 262.1438.

*Methyl [2-(3-Hydroxyprop-1-yn-1-yl)-4-methoxyphenyl]carbamate (**S18**).* Compound **S18** was prepared on a 4.40 mmol scale with methyl (2-iodo-4-methoxyphenyl)carbamate (**S7**) and propargyl alcohol using general procedure B. The product was obtained as a tan to white solid (855 g, 83%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (br, 1H), 7.21 (s, 1H), 6.88 (dq, J = 6.1, 3.0 Hz, 2H), 4.59−4.39 (m, 2H), 3.77 (s, 3H), 3.74 (s, 3H), 2.74 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.9, 154.2, 132.7, 119.9, 116.5, 116.2, 94.2, 80.9, 55.6, 52.5, 51.5; IR (NaCl) 3400, 2225, 1733 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{14}NO_4$ $[M + H]^+$ 236.0923, found 236.0917.

*Methyl [2-(3-Hydroxyprop-1-yn-1-yl)-4-(trifluoromethyl)phenyl]carbamate (**S19**).* Compound **S19** was prepared on a 4.12 mmol scale with methyl [2-iodo-4-(trifluoromethyl)phenyl]carbamate (**S8**) and propargyl alcohol using general procedure B. The product was obtained as a tan to white solid (1.04 g, 95%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 2.2 Hz, 1H), 7.54 (dd, J = 8.9, 2.2 Hz, 1H), 7.48 (s, 1H), 4.56 (d, J = 5.7 Hz, 2H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.5, 142.1, 129.4−129.2 (m), 127.0 (d, J = 3.7 Hz), 124.7 (d, J = 33.6 Hz), 117.7, 110.9, 95.8, 79.7, 52.9, 51.6, 29.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ −62.34; IR (NaCl) 3345, 3205, 2193, 1717 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{11}F_3NO_3$ $[M + H]^+$ 274.0691, found 274.0686.

*tert-Butyl [2-(3-Hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S20**).* Compound **S20** was prepared on a 3.23 mmol scale with *tert*-butyl (2-iodophenyl)carbamate (**S9**) and propargyl alcohol using general procedure B. The product was obtained as a brown oil (765 mg, 97%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, J = 8.5 Hz, 1H), 7.35 (dd, J = 7.8, 1.6 Hz, 1H), 7.32−7.26 (m, 1H), 7.24 (s, 1H), 6.93 (td, J = 7.6, 1.1 Hz, 1H), 4.56 (s, 2H), 2.79 (br, 1H), 1.54 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.7, 139.7, 132.2, 122.2, 117.9, 110.7, 94.3, 81.0, 51.5, 28.4; IR (NaCl) 3404, 2234, 1732 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{14}H_{18}NO_3$ $[M + H]^+$ 248.1287, found 248.1281.

*Benzyl [2-(3-Hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S21**).* Compound **S21** was prepared on a 4.25 mmol scale with benzyl (2-iodophenyl)carbamate (**S10**) and propargyl alcohol using general procedure B. The product was obtained as a tan solid (951 mg, 80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.3 Hz, 1H), 7.78−7.27 (m, 8H), 6.98 (td, J = 7.6, 1.2 Hz, 1H), 5.23 (s, 2H), 4.51 (d, J = 4.6 Hz, 2H), 2.45 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.2, 139.1, 135.9, 132.2, 130.0, 128.8, 128.6, 128.6, 122.8, 118.0, 111.0, 94.5, 80.8, 67.4, 51.6; IR (NaCl) 3395, 2235, 1736 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{17}H_{16}NO_3$ $[M + H]^+$ 282.1130, found 282.1125.

*2,2,2-Trichloroethyl [2-(3-Hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S22**).* Compound **S22** was prepared on a 2.55 mmol scale with 2,2,2-trichloroethyl (2-iodophenyl)carbamate (**S11**) and propargyl alcohol using general procedure B. The product was obtained as a tan solid (707 mg, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, J = 8.3 Hz, 1H), 7.63 (s, 1H), 7.40 (dd, J = 7.7, 1.6 Hz, 1H), 7.34 (ddd, J = 8.7, 7.6, 1.6 Hz, 1H), 7.03 (td, J = 7.6, 1.1 Hz, 1H), 4.86 (s, 2H), 4.59 (s, 2H), 2.55 (br, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.5, 138.3, 132.3, 130.1, 123.5, 118.5, 111.7, 95.3, 94.7, 80.7, 74.7, 51.6; IR (NaCl) 3395, 2235, 1748 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{11}Cl_3NO_3$ $[M + H]^+$ 321.9805, found 321.9799.

*Methyl [2-(3-Hydroxybut-1-yn-1-yl)phenyl]carbamate (**S23**).* Compound **S23** was prepared on a 5.56 mmol scale with methyl (2-iodophenyl)carbamate (**S1**) and but-3-yn-2-ol using general procedure B. The product was obtained as a tan solid (1.21 g, 99%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.7 Hz, 1H), 7.42 (s, 1H), 7.32 (dd, J = 7.7, 1.6 Hz, 1H), 7.28 (ddd, J = 8.7, 7.5, 1.6 Hz, 1H), 6.95 (td, J = 7.6, 1.2 Hz, 1H), 4.80 (dt, J = 8.1, 4.0 Hz, 1H), 3.77 (s, 3H), 3.20 (br, 1H), 1.58 (d, J = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.9, 139.0, 131.9, 129.8, 122.6, 117.9, 111.0, 98.3, 79.0, 58.7, 52.5, 24.4; IR (NaCl) 3396, 2226, 1743 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{14}NO_3$ $[M + H]^+$ 220.0974, found 220.0968.

*Methyl [2-(3-Hydroxy-3-methylbut-1-yn-1-yl)phenyl]carbamate (**S24**).* Compound **S24** was prepared on a 10.83 mmol scale with methyl (2-iodophenyl)carbamate (**S1**) and 2-methylbut-3-yn-2-ol using general procedure B. The product was obtained as a tan solid (2.49 g, 98%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.35 (s, 1H), 7.28 (dd, J = 7.7, 1.6 Hz, 1H), 7.26−7.22 (m, 1H), 6.91 (td, J = 7.6, 1.1 Hz, 1H), 3.74 (s, 3H), 3.05 (br, 1H), 1.62 (s, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.9, 138.9, 131.7, 129.7, 122.6, 117.9, 111.1, 101.3, 84.1, 77.3, 65.7, 52.5, 31.5; IR (NaCl) 3397, 2224, 1742 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{13}H_{16}NO_3$ $[M + H]^+$ 234.1130, found 234.1125.

*Methyl [4-Bromo-2-(3-hydroxybut-1-yn-1-yl)phenyl]carbamate (**S25**).* Compound **S25** was prepared on a 4.21 mmol scale with methyl (4-bromo-2-iodophenyl)carbamate (**S4**) and but-3-yn-2-ol using general procedure B. The product was obtained as a tan solid (1.23 g, 98%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.9 Hz, 1H), 7.45 (d, J = 2.4 Hz, 1H), 7.40 (dd, J = 9.0, 2.4 Hz, 1H), 7.32 (s, 1H), 4.81 (q, J = 6.8 Hz, 1H), 3.79 (s, 3H), 2.68 (br, 1H), 1.59 (d, J = 6.6 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.7, 138.2, 134.2, 132.8, 119.4, 114.8, 112.8, 99.4, 77.9, 58.8, 52.8, 24.4; IR (NaCl) 3399, 2981, 2944, 2928, 1743 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{13}BrNO_3$ $[M + H]^+$ 298.0079, found 298.0073.

*Methyl [4-Bromo-2-(3-hydroxy-3-methylbut-1-yn-1-yl)phenyl]carbamate (**S26**).* Compound **S26** was prepared on a 1.40 mmol scale with methyl (4-bromo-2-iodophenyl)carbamate (**S4**) and 2-methylbut-3-yn-2-ol using general procedure B. The product was obtained as a tan solid (275 mg, 62%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03−7.98 (m, 1H), 7.45 (d, J = 2.3 Hz, 1H), 7.39 (dd, J = 8.9, 2.4 Hz, 1H), 7.30 (s, 1H), 3.79 (s, 3H), 2.58 (br, 1H), 1.65 (s, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.7, 138.2, 134.1, 132.7, 119.3, 114.8, 112.9, 102.4, 76.1, 65.8, 52.8, 31.5; IR (NaCl) 3396, 2984, 2944, 2932, 1743 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{13}H_{15}BrNO_3$ $[M + H]^+$ 312.0235, found 312.0230.

General Procedure for Allene Synthesis and Compound Characterization Data. *General Procedure C: Synthesis of*

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Carbamate-Protected o-Allenyl Aniline Derivatives. Following a modified reported procedure,[24] the propargyl alcohol derivative (1.00 equiv), PPh_3 (1.50 equiv), and *N*-isopropylidene-*N*′-2-nitrobenzenesulfonyl hydrazine (IPNBSH) (1.50 equiv) were transferred to a flame-dried round-bottom flask equipped with a septum and dissolved in THF (0.2 M). The solution was cooled to 0 °C followed by dropwise addition of DIAD (1.50 equiv). After 5 min, the solution was then allowed to warm to room temperature and stirred for 2 h. A 1:1 TFE/H_2O mixture was added to allow for diazene formation, and the mixture was stirred for an additional 2 h. The crude mixture was partitioned between Et_2O and H_2O, and the organic layer was washed with water four times. The organic layer was washed with brine and dried over $MgSO_4$ before being concentrated in vacuo and then purified by silica gel flash column chromatography (15:85 EtOAc/hexanes).

General Procedure D: Synthesis of Dimethyl-Substituted Carbamate-Protected o-Allenyl Aniline Derivatives. Following a modified reported procedure,[25] propargyl alcohol (1.00 equiv) was transferred to a flame-dried 20 mL vial equipped with a septum and dissolved in nitromethane (0.167 M). The septum was removed; 2-nitrobenzenesulfonylhydrazide (NBSH) (1.20 equiv) was added, followed by flushing with argon, and the mixture was spun until NBSH dissolved. The septum was removed again, and AgOTf (0.20 equiv) was added followed by flushing with argon. TfOH (0.10 equiv) was added, and the septum was then removed and replaced with a Teflon cap. The mixture was heated to 35 °C in an oil bath and spun for 1 h. The reaction was then quenched with $NaHCO_3$, and the mixture extracted three times with Et_2O, washed with brine, and dried over $MgSO_4$. The organic layer was concentrated in vacuo and then purified by silica gel flash column chromatography (10:90 EtOAc/hexanes).

*Methyl [2-(Propa-1,2-dien-1-yl)phenyl]carbamate (**S27**).* Compound **S27** was prepared on a 2.03 mmol scale with methyl [2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S12**) using general procedure C. The product was obtained as a white solid (305 mg, 79%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (br, 1H), 7.26−7.21 (m, 3H), 7.08 (td, J = 7.6, 1.29 Hz, 1H), 6.29 (t, J = 7.0 Hz, 1H), 5.22 (d, J = 7.0, 2H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.1, 154.5, 135.4, 129.0, 128.1, 124.3, 122.0, 90.8, 78.9, 52.5; IR (NaCl) 3387, 3307, 1940, 1709 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{11}H_{12}NO_2$ [M + H]$^+$ 190.0868, found 190.0863.

*Methyl [4-Fluoro-2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S28**).* Compound **S28** was prepared on a 1.35 mmol scale with methyl [4-fluoro-2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S13**) using general procedure C. The product was obtained as a white solid (181 mg, 65%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (br, 1H), 7.19−6.63 (m, 3H), 6.23 (t, J = 6.9 Hz, 1H), 5.22 (d, J = 6.9 Hz, 2H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.4, 154.9, 130.8, 125.0, 114.8, 114.6, 89.9, 79.4, 52.6, 22.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −118.11; IR (NaCl) 3296, 1941, 1710 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{11}H_{11}FNO_2$ [M + H]$^+$ 208.0774, found 208.0768.

*Methyl [4-Chloro-2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S29**).* Compound **S29** was prepared on a 1.67 mmol scale with methyl [4-chloro-2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S14**) using general procedure C. The product was obtained as a white solid (188 mg, 50%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (br, 1H), 7.23−7.08 (m, 3H), 6.21 (t, J = 7.0 Hz, 1H), 5.25 (d, J = 6.9 Hz, 2H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.3, 154.4, 133.8, 129.6, 128.4, 127.9, 125.3, 123.4, 89.9, 79.5, 52.7; IR (NaCl) 3374, 3282, 1937, 1697 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{11}H_{11}ClNO_2$ [M + H]$^+$ 224.0478, found 224.0473.

*Methyl [4-Bromo-2-(propa-1,2-dien-1-yl)phenyl]carbamate (**1**).* Compound **1** was prepared on a 0.42 mmol scale with methyl [4-bromo-2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S15**) using general procedure C. The product was obtained as a white solid (24 mg, 43%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (br, 1H), 7.40−7.29 (m, 2H), 7.18 (br, 1H), 6.20 (t, J = 7.0 Hz, 1H), 5.25 (d, J = 7.0 Hz, 2H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.2, 154.3, 134.4, 131.3, 130.8, 123.5, 117.1, 89.8, 79.6, 52.7, 52.6; IR (NaCl) 3278, 1940, 1696 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{11}H_{11}BrNO_2$ [M + H]$^+$ 267.9973, found 267.9968.

*Methyl [4-Methyl-2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S30**).* Compound **S30** was prepared on a 1.83 mmol scale with methyl [2-(3-hydroxyprop-1-yn-1-yl)-4-methylphenyl]carbamate (**S16**) using general procedure C. The product was obtained as a white solid (263 mg, 71%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (br, 1H), 7.18−6.94 (m, 3H), 6.26 (t, J = 7.0 Hz, 1H), 5.20 (d, J = 7.0 Hz, 2H), 3.77 (s, 3H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.2, 154.7, 134.2, 132.7, 129.2, 128.8, 122.5, 90.6, 78.8, 52.5, 20.8; IR (NaCl) 3386, 3310, 1941, 1719 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{14}NO_2$ [M + H]$^+$ 204.1025, found 204.1019.

*Methyl [4-(tert-Butyl)-2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S31**).* Compound **S31** was prepared on a 1.38 mmol scale with methyl [4-(*tert*-butyl)-2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S17**) using general procedure C. The product was obtained as an off-white solid (257 mg, 76%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (br, 1H), 7.28−7.20 (m, 3H), 6.28 (t, J = 7.0 Hz, 1H), 5.18 (d, J = 7.0 Hz, 2H), 3.75 (d, J = 1.0 Hz, 3H), 1.29 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.1, 154.7, 147.3, 132.8, 129.0, 128.1, 125.7, 125.3, 122.1, 91.1, 78.8, 52.5, 34.4, 31.4; IR (NaCl) 3392, 3316, 1941, 1721 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{15}H_{20}NO_2$ [M + H]$^+$ 246.1494, found 246.1489.

*Methyl [4-Methoxy-2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S32**).* Compound **S32** was prepared on a 1.28 mmol scale with methyl [2-(3-hydroxyprop-1-yn-1-yl)-4-methoxyphenyl]carbamate (**S18**) using general procedure C. The product was obtained as a white solid (149 mg, 73%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (br, 1H), 6.83 (d, J = 3.0 Hz, 1H), 6.78 (dd, J = 8.8, 3.0 Hz, 1H), 6.26 (t, J = 6.9 Hz, 1H), 5.18 (d, J = 6.9 Hz, 2H), 3.79 (s, 3H), 3.75 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.4, 157.0, 155.2, 127.9, 125.4, 113.7, 113.1, 90.3, 78.9, 55.5, 52.5; IR (NaCl) 3388, 3305, 1941, 1712 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{14}NO_3$ [M + H]$^+$ 220.0974, found 220.0968.

*Methyl [2-(Propa-1,2-dien-1-yl)-4-(trifluoromethyl)phenyl]carbamate (**S33**).* Compound **S33** was prepared on a 0.85 mmol scale with methyl [2-(3-hydroxyprop-1-yn-1-yl)-4-(trifluoromethyl)-phenyl]carbamate (**S19**) using general procedure C. The product was obtained as a white solid (190 mg, 87%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.6 Hz, 1H), 7.57 (br, 1H), 7.47 (dd, J = 8.7, 2.2 Hz, 1H), 7.44 (d, J = 2.2 Hz, 1H), 6.29 (t, J = 7.0 Hz, 1H), 5.30 (d, J = 7.0 Hz, 2H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.1, 153.9, 138.8, 125.1 (q), 125.1 (d, J = 3.7 Hz), 124.1 (d, J = 271.5 Hz), 120.7, 90.4, 79.9, 52.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ −62.26; IR (NaCl) 3288, 1942, 1698 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{11}F_3NO_2$ [M + H]$^+$ 258.0742, found 258.0736.

*tert-Butyl [2-(Propa-1,2-dien-1-yl)phenyl]carbamate (**S34**).* Compound **S34** was prepared on a 0.89 mmol scale with *tert*-butyl [2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S20**) using general procedure C. The product was obtained as a colorless oil that upon standing in the freezer for 1 week solidified to an off-white solid (101 mg, 49%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 1H), 7.22 (td, J = 7.0, 6.5, 1.8 Hz, 2H), 7.13−7.01 (m, 2H), 6.29 (t, J = 7.0 Hz, 1H), 5.20 (d, J = 7.0 Hz, 2H), 1.53 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.2, 153.2, 135.8, 128.9, 128.0, 123.9, 122.8, 122.0, 90.8, 80.4, 78.6, 28.4; IR (NaCl) 3397, 3333, 1941, 1698 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{14}H_{18}NO_2$ [M + H]$^+$ 232.1338, found 232.1332.

*Benzyl [2-(Propa-1,2-dien-1-yl)phenyl]carbamate (**S35**).* Compound **S35** was prepared on a 1.71 mmol scale with benzyl [2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S21**) using general procedure C. The product was obtained as a white solid (306 mg, 68%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (br, 1H), 7.36 (m, 5H), 7.26−7.17 (m, 2H), 7.12−6.99 (m, 1H), 6.26 (t, J = 7.0 Hz, 1H), 5.20 (s, 2H), 5.17 (d, J = 7.0 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.2, 153.8, 136.4, 135.3, 129.0, 128.7, 128.4, 128.3, 128.1, 124.5, 122.1, 90.7, 78.9, 67.1; IR (NaCl) 3274, 1941, 1692 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{17}H_{15}NO_2$ [M + H]$^+$ 266.1181, found 266.1176.

*2,2,2-Trichloroethyl [2-(Propa-1,2-dien-1-yl)phenyl]carbamate (**S36**).* Compound **S36** was prepared on a 0.75 mmol scale with

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2,2,2-trichloroethyl [2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S22**) using general procedure C. The product was obtained as a white solid (138 mg, 61%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (br, 1H), 7.61 (s, 1H), 7.26 (m, 2H), 7.13 (t, J = 7.6 Hz, 1H), 6.32 (t, J = 7.0 Hz, 1H), 5.26 (d, J = 7.0 Hz, 2H), 4.83 (s, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.2, 152.0, 134.8, 129.2, 128.3, 125.0, 122.0, 95.5, 91.0, 79.3, 74.7; IR (NaCl) 3378, 3324, 1939, 1750 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{11}Cl_3NO_2$ [M + H]$^+$ 305.9855, found 305.9850.

*Methyl [2-(Buta-1,2-dien-1-yl)phenyl]carbamate (**19**).* Compound **19** was prepared on a 0.51 mmol scale with methyl [2-(3-hydroxybut-1-yn-1-yl)phenyl]carbamate (**S23**) using general procedure C. The product was obtained as a white solid (42 mg, 41%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (br, 1H), 7.59 (br, 1H), 7.23 (td, J = 8.2, 7.8, 1.6 Hz, 1H), 7.18 (dd, J = 7.8, 1.6 Hz, 1H), 7.05 (td, J = 7.5, 1.3 Hz, 1H), 6.23 (dq, J = 6.9, 3.5 Hz, 1H), 5.61 (p, J = 7.0 Hz, 1H), 3.78 (s, 3H), 1.84 (dd, J = 7.1, 3.5 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 206.1, 154.3, 135.7, 129.2, 127.9, 123.8, 121.2, 91.3, 89.9, 52.4, 14.5; IR (NaCl) 3287, 1947, 1697 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{14}NO_2$ [M + H]$^+$ 204.1025, found 204.1019.

*Methyl [2-(3-Methylbuta-1,2-dien-1-yl)phenyl]carbamate (**21**).* Compound **21** was prepared on a 0.64 mmol scale with methyl [2-(3-hydroxy-3-methylbut-1-yn-1-yl)phenyl]carbamate (**S24**) using general procedure D. The product was obtained as a light-yellow oil (58 mg, 41%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (br, 1H), 7.95 (br, 1H), 7.32 (t, J = 7.9 Hz, 1H), 7.25 (d, J = 7.7 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 6.25 (s, 1H), 3.88 (s, 3H), 1.98 (d, J = 3.7 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 202.8, 154.3, 135.9, 129.3, 127.6, 123.4, 120.4, 99.7, 90.3, 52.1, 20.6; IR (NaCl) 3354, 1952, 1740 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{13}H_{16}NO_2$ [M + H]$^+$ 218.1181, found 218.1176.

*Methyl [4-Bromo-2-(buta-1,2-dien-1-yl)phenyl]carbamate (**18**).* Compound **18** was prepared on a 1.21 mmol scale with methyl [4-bromo-2-(3-hydroxybut-1-yn-1-yl)phenyl]carbamate (**S25**) using general procedure C. The product was obtained as an off-white solid (134 mg, 47%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (br, 1H), 7.47 (br, 1H), 7.35−7.29 (m, 2H), 6.13 (dq, J = 6.8, 3.4 Hz, 1H), 5.65 (p, J = 7.0 Hz, 1H), 3.78 (s, 3H), 1.84 (dd, J = 7.2, 3.4 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 206.4, 154.2, 134.8, 131.6, 130.6, 122.7, 116.6, 90.7, 90.4, 52.6, 14.4; IR (NaCl) 3287, 1947, 1697 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{13}BrNO_2$ [M + H]$^+$ 282.0130, found 282.0124.

*Methyl [4-Bromo-2-(3-methylbuta-1,2-dien-1-yl)phenyl]-carbamate (**20**).* Compound **20** was prepared on a 0.32 mmol scale with methyl [4-bromo-2-(3-hydroxy-3-methylbut-1-yn-1-yl)-phenyl]carbamate (**S26**) using general procedure D. The product was obtained as an off-white solid (38 mg, 40%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (br, 1H), 7.71 (br, 1H), 7.29−7.21 (m, 2H), 6.03 (hept, J = 3.1 Hz, 1H), 3.77 (s, 3H), 1.86 (d, J = 3.2 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 203.3, 154.1, 135.1 (d, J = 31.2 Hz), 131.7, 130.4, 122.0, 116.2, 100.6, 89.5, 52.6, 20.7; IR (NaCl) 3353, 1953, 1741 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{13}H_{15}BrNO_2$ [M + H]$^+$ 296.0286, found 296.0281.

*Methyl [2-(Propa-1,2-dien-1-yl-1-d)phenyl]carbamate (**35**).* Compound **35** was prepared on a 1.35 mmol scale with methyl [2-(3-hydroxyprop-1-yn-1-yl)phenyl]carbamate (**S12**) using a modified general procedure C. TFE and H_2O were substituted for TFE-d_1 and D_2O, respectively, to form the deuterated allene. The product was obtained as a white solid (200 mg, 78%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (br, 1H), 7.30 (br, 1H), 7.27−7.17 (m, 2H), 7.08 (t, J = 7.5 Hz, 1H), 5.21 (s, 2H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.1, 154.5, 135.3, 128.9, 128.0, 124.3, 123.2, 122.1, 90.5 (t, J = 25.3 Hz), 79.0, 52.5; IR (NaCl) 3388, 3313, 1935, 1721 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{11}H_{11}DNO_2$ [M + H]$^+$ 191.0931, found 191.0925.

General Procedure for Oxidative Indole Synthesis and Compound Characterization Data. *General Procedure E: Indole Synthesis.* To a flame-dried 4 mL vial equipped with a Teflon septum and stir bar was added the desired lead tetracarboxylate (1.5 equiv), and the vial was purged and maintained under nitrogen. A separate solution of the desired 2-allenylaniline derivative (1.0 equiv) was added to a flame-dried 4 mL vial equipped with a Teflon septum and dissolved in dichloromethane (0.30 M). This solution was then loaded into a syringe and added to the lead tetracarboxylate over 30 s while the mixture was being stirred at room temperature and allowed to continue to stir overnight (approximately 15 h). The crude suspension was filtered through a basic alumina plug prepared in a 1.5 cm diameter column packed to 5 cm with alumina (basic, activity 5), using dichloromethane as the eluent. The crude material was then concentrated in vacuo and immediately purified by silica gel flash column chromatography (20:80 EtOAc/hexanes).

*Methyl 2-(Acetoxymethyl)-1H-indole-1-carboxylate (**9**).* Compound **9** was prepared on a 0.215 mmol scale with methyl [2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S27**) and lead tetraacetate using general procedure E. The product was obtained as a white solid (40 mg, 75%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dq, J = 8.4, 0.8 Hz, 1H), 7.53 (ddd, J = 7.7, 1.3, 0.7 Hz, 1H), 7.33 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 7.25 (ddd, J = 7.7, 7.2, 1.0 Hz, 1H), 6.68 (q, J = 0.9 Hz, 1H), 5.46 (d, J = 1.0 Hz, 2H), 4.05 (s, 3H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.8, 152.2, 136.9, 135.1, 128.9, 125.1, 123.5, 121.0, 115.9, 111.1, 60.6, 53.9, 21.0; IR (NaCl) 2956, 2915, 2853, 1735 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{13}H_{14}NO_4$ [M + H]$^+$ 248.0923, found 248.0917.

*Methyl 2-(Acetoxymethyl)-5-fluoro-1H-indole-1-carboxylate (**4**).* Compound **4** was prepared on a 0.096 mmol scale with methyl [4-fluoro-2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S28**) and lead tetraacetate using general procedure E. The product was obtained as a white solid (15.3 mg, 60%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, J = 9.1, 4.6 Hz, 1H), 7.15 (dd, J = 8.5, 2.6 Hz, 1H), 7.02 (td, J = 9.1, 2.6 Hz, 1H), 6.61 (d, J = 1.1 Hz, 1H), 5.43 (d, J = 1.1 Hz, 2H), 4.03 (s, 3H), 2.12 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.5, 159.5 (d, J = 239.9 Hz), 151.7, 136.6, 133.0, 129.6 (d, J = 10.1 Hz), 116.7, 112.6 (d, J = 24.9 Hz), 110.2 (d, J = 4.0 Hz), 106.2 (d, J = 23.8 Hz), 60.4, 54.0, 20.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ −120.16 (d, J = 5.0 Hz); IR (NaCl) 2956, 2921, 2853, 1743, 1721 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{13}H_{13}FNO_4$ [M + H]$^+$ 266.0829, found 266.0823.

*Methyl 2-(Acetoxymethyl)-5-chloro-1H-indole-1-carboxylate (**3**).* Compound **3** was prepared on a 0.088 mmol scale with methyl [4-chloro-2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S29**) and lead tetraacetate using general procedure E. The product was obtained as a white solid (17.4 mg, 71%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dt, J = 8.9, 0.7 Hz, 1H), 7.46 (dd, J = 2.1, 0.5 Hz, 1H), 7.24 (dd, J = 8.9, 2.1 Hz, 1H), 6.58 (q, J = 1.0 Hz, 1H), 5.42 (d, J = 1.0 Hz, 2H), 4.04 (s, 3H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.6, 151.8, 136.6, 135.2, 130.1, 129.1, 125.1, 120.4, 116.9, 109.8, 60.4, 54.1, 20.9; IR (NaCl) 2959, 2921, 2847, 1743, 1724 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{13}H_{13}ClNO_4$ [M + H]$^+$ 282.0533, found 282.0528.

*Methyl 2-(Acetoxymethyl)-5-bromo-1H-indole-1-carboxylate (**2**).* Compound **2** was prepared on a 0.062 mmol scale with methyl [4-bromo-2-(propa-1,2-dien-1-yl)phenyl]carbamate (**1**) and lead tetraacetate using general procedure E. The product was obtained as a white solid (16.2 mg, 81%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.9 Hz, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.39 (dd, J = 8.9, 2.0 Hz, 1H), 6.59 (q, J = 1.0 Hz, 1H), 5.43 (d, J = 1.0 Hz, 2H), 4.05 (s, 3H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.7, 151.9, 136.4, 135.6, 130.7, 127.8, 123.5, 117.3, 116.8, 109.8, 60.4, 54.1, 20.9; IR (NaCl) 2954, 2924, 2850, 1732 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{13}H_{13}BrNO_4$ [M + H]$^+$ 326.0028, found 326.0023.

*Methyl 2-(Acetoxymethyl)-5-methyl-1H-indole-1-carboxylate (**5**).* Compound **5** was prepared on a 0.167 mmol scale with methyl [4-methyl-2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S30**) and lead tetraacetate using general procedure E. The product was obtained as a white solid (18.6 mg, 61%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 1H), 7.30 (dp, J = 1.5, 0.8 Hz, 1H), 7.14 (ddd, J = 8.5, 1.8, 0.7 Hz, 1H), 6.59 (q, J = 0.9 Hz, 1H), 5.44 (d, J = 0.9 Hz, 2H), 4.03 (s, 3H), 2.43 (s, 3H), 2.13 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.8, 152.2, 135.1, 135.0, 133.0, 129.1, 126.4, 120.8, 115.5, 110.9, 60.6, 53.8, 21.2, 21.0; IR (NaCl) 2956, 2921, 2853, 1743 cm^{-1};

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HRMS (ESI)$^+$ m/z calcd for $C_{14}H_{16}NO_4$ $[M + H]^+$ 262.1079, found 262.1074.

*Methyl 2-(Acetoxymethyl)-5-(tert-butyl)-1H-indole-1-carboxylate (**6**).* Compound **6** was prepared on a 0.100 mmol scale with methyl [4-methoxy-2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S31**) and lead tetraacetate using general procedure E. The product was obtained as a white solid (21.3 mg, 72%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.9 Hz, 1H), 7.54 (d, J = 2.1 Hz, 1H), 7.41 (dd, J = 8.8, 2.0 Hz, 1H), 6.66 (s, 1H), 5.47 (s, 2H), 4.05 (s, 3H), 2.14 (s, 3H), 1.39 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.6, 152.1, 146.5, 134.9, 134.8, 128.7, 122.9, 117.1, 115.3, 111.4, 60.6, 53.8, 34.7, 31.8, 21.1; IR (NaCl) 2956, 2918, 2847, 1743, 1721 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{17}H_{22}NO_4$ $[M + H]^+$ 304.1549, found 304.1543.

*Methyl 2-(Acetoxymethyl)-5-methoxy-1H-indole-1-carboxylate (**7**).* Compound **7** was prepared on a 0.187 mmol scale with methyl [4-methoxy-2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S32**) and lead tetraacetate using general procedure E. The product was obtained as an off-white solid (33.2 mg, 64%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 9.1 Hz, 1H), 6.97 (d, J = 2.5 Hz, 1H), 6.92 (dd, J = 9.1, 2.6 Hz, 1H), 6.59−6.58 (m, 1H), 5.42 (d, J = 0.9 Hz, 2H), 4.01 (s, 3H), 3.83 (s, 3H), 2.13 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.7, 156.4, 152.0, 135.6, 131.4, 129.7, 116.6, 113.7, 110.8, 103.3, 60.5, 55.6, 53.8, 20.9; IR (NaCl) 2956, 2921, 2853, 2833, 1737 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{14}H_{16}NO_5$ $[M + H]^+$ 278.1028, found 278.1023.

*tert-Butyl 2-(Acetoxymethyl)-1H-indole-1-carboxylate (**10**).* Compound **10** was prepared on a 0.113 mmol scale with *tert*-butyl [2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S34**) and lead tetraacetate using general procedure E. The product was obtained as a white solid (23.8 mg, 73%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.35−7.28 (m, 1H), 7.23 (t, J = 7.5 Hz, 1H), 6.65 (s, 1H), 5.46 (s, 2H), 2.16 (s, 3H), 1.70 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.6, 150.1, 136.9, 135.0, 128.7, 124.7, 123.0, 120.8, 115.8, 110.0, 84.5, 61.0, 31.0, 21.1; IR (NaCl) 2981, 2935, 1738 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{16}H_{20}NO_4$ $[M + H]^+$ 290.1392, found 290.1387.

*Benzyl 2-(Acetoxymethyl)-1H-indole-1-carboxylate (**11**).* Compound **11** was prepared on a 0.100 mmol scale with benzyl [2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S35**) and lead tetraacetate using general procedure E. The product was obtained as a white solid (21.1 mg, 65%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.3 Hz, 1H), 7.53−7.47 (m, 3H), 7.39 (dd, J = 10.4, 7.1 Hz, 3H), 7.32−7.25 (m, 1H), 7.25−7.19 (m, 1H), 6.66 (s, 1H), 5.45 (s, 2H), 5.42 (s, 2H), 2.02 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.6, 151.4, 136.9, 130.4, 129.7, 129.0, 128.9, 128.8, 128.4, 125.0, 123.4, 120.9, 115.9, 111.2, 69.1, 60.7, 21.0; IR (NaCl) 2956, 2924, 2853, 1734 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{19}H_{18}NO_4$ $[M + H]^+$ 324.1236, found 324.1230.

*2,2,2-Trichloroethyl 2-(Acetoxymethyl)-1H-indole-1-carboxylate (**12**).* Compound **12** was prepared on a 0.077 mmol scale with 2,2,2-trichloroethyl [2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S36**) and lead tetraacetate using general procedure E. The product was obtained as a white solid (14.9 mg, 56%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (dq, J = 8.4, 0.9 Hz, 1H), 7.56−7.53 (m, 1H), 7.36 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 7.31−7.27 (m, 1H), 6.74 (q, J = 1.0 Hz, 1H), 5.52 (d, J = 1.0 Hz, 2H), 5.10 (s, 2H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.7, 150.1, 136.9, 135.2, 129.2, 125.5, 124.1, 121.2, 116.2, 112.2, 94.3, 76.3, 60.6, 21.0; IR (NaCl) 2959, 2924, 2850, 1734 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{14}H_{13}Cl_3NO_4$ $[M + H]^+$ 363.9910, found 363.9905.

*Methyl 2-(1-Acetoxyethyl)-1H-indole-1-carboxylate (**23**).* Compound **23** was prepared on a 0.197 mmol scale with methyl [2-(buta-1,2-dien-1-yl)phenyl]carbamate (**19**) and lead tetraacetate using general procedure E. The product was obtained as a colorless oil (25 mg, 49%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 1H), 7.55−7.49 (m, 1H), 7.31 (ddd, J = 8.4, 7.1, 1.4 Hz, 1H), 7.27−7.20 (m, 1H), 6.72 (s, 1H), 6.53 (q, J = 6.4 Hz, 1H), 4.03 (s, 3H), 2.09 (s, 3H), 1.66 (d, J = 6.5 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.2, 152.1, 140.6, 136.8, 128.8, 124.9, 123.4, 120.8, 115.9, 108.5, 66.6, 53.9, 21.4, 20.1; IR (NaCl) 2956, 2921, 2850, 1740 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{14}H_{16}NO_4$ $[M + H]^+$ 262.1079, found 262.1074.

*Methyl 2-(1-Acetoxyethyl)-5-bromo-1H-indole-1-carboxylate (**22**).* Compound **22** was prepared on a 0.071 mmol scale with methyl [4-bromo-2-(buta-1,2-dien-1-yl)phenyl]carbamate (**18**) and lead tetraacetate using general procedure E. The product was obtained as a white solid (11.6 mg, 48%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.9 Hz, 1H), 7.65 (s, 1H), 7.40 (d, J = 9.0 Hz, 1H), 6.65 (s, 1H), 6.51 (q, J = 6.5 Hz, 1H), 4.04 (s, 3H), 2.10 (s, 3H), 1.66 (d, J = 6.4 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.1, 151.8, 142.1, 135.5, 130.5, 127.7, 123.4, 117.4, 116.7, 107.5, 66.4, 54.2, 21.3, 20.2; IR (NaCl) 2959, 2926, 2844, 1740 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{14}H_{15}BrNO_4$ $[M + H]^+$ 340.0184, found 340.0179.

*Methyl 2-(2-Acetoxypropan-2-yl)-5-bromo-1H-indole-1-carboxylate (**24**).* Compound **24** was prepared on a 0.059 mmol scale with methyl [4-bromo-2-(3-methylbuta-1,2-dien-1-yl)phenyl]-carbamate (**20**) and lead tetraacetate using general procedure E. The product was obtained as a white solid (3 mg, 14%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 8.9 Hz, 1H), 7.63 (d, J = 2.1 Hz, 1H), 7.36 (dd, J = 8.9, 2.0 Hz, 1H), 6.61 (s, 1H), 4.06 (s, 3H), 2.03 (s, 3H), 1.92 (s, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 169.8, 152.0, 144.7, 136.1, 130.1, 127.4, 123.5, 117.0, 116.3, 108.0, 54.1, 28.3, 22.1; IR (NaCl) 2956, 2926, 2847, 1757, 1730 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{15}H_{17}BrNO_4$ $[M + H]^+$ 354.0341, found 354.0336.

*Methyl 2-(Acetoxymethyl)-1H-indole-1-carboxylate-3-d (**36**).* Compound **36** was prepared on a 0.110 mmol scale with methyl [2-(propa-1,2-dien-1-yl-1-d)phenyl]carbamate (**35**) and lead tetraacetate using general procedure E. The product was obtained as a white solid (18.7 mg, 68%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (dt, J = 8.4, 0.9 Hz, 1H), 7.54 (dt, J = 7.7, 1.1 Hz, 1H), 7.34 (ddd, J = 8.5, 7.2, 1.4 Hz, 1H), 7.28−7.23 (m, 1H), 5.47 (s, 2H), 4.06 (s, 3H), 2.15 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.7, 152.1, 136.8, 134.9, 128.8, 125.0, 123.5, 120.9, 115.8, 110.8 (t, J = 26.9 Hz), 60.6, 54.0, 21.1; IR (NaCl) 2960, 2921, 2853, 1746 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{13}H_{13}DNO_4$ $[M + H]^+$ 249.0986, found 249.0980.

*Methyl 2-[(Benzoyloxy)methyl]-1H-indole-1-carboxylate (**13**).* Compound **13** was prepared on a 0.108 mmol scale with methyl [2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S27**) and lead tetrabenzoate using general procedure E. The product was obtained as a white solid (20.1 mg, 57%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (dq, J = 8.4, 0.8 Hz, 1H), 8.12−8.09 (m, 2H), 7.60−7.56 (m, 1H), 7.54 (ddd, J = 7.8, 1.3, 0.8 Hz, 1H), 7.48−7.44 (m, 2H), 7.35 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 7.28−7.24 (m, 1H), 6.76 (q, J = 1.0 Hz, 1H), 5.72 (d, J = 1.0 Hz, 2H), 4.03 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.4, 152.2, 137.0, 135.1, 133.4, 130.2, 123.0, 129.0, 128.7, 125.1, 123.5, 121.0, 115.9, 111.0, 61.1, 54.0; IR (NaCl) 2956, 2926, 2855, 1743, 1724 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{18}H_{16}NO_4$ $[M + H]^+$ 310.1079, found 310.1074.

*Methyl 2-{[(4-Fluorobenzoyl)oxy]methyl}-1H-indole-1-carboxylate (**14**).* Compound **14** was prepared on a 0.159 mmol scale with methyl [2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S27**) and lead tetra(4-fluorobenzoate) using general procedure E. The product was obtained as a white solid (22.8 mg, 44%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 7.55 (dd, J = 7.7, 1.2 Hz, 1H), 7.36 (ddd, J = 8.5, 7.3, 1.4 Hz, 1H), 7.18−7.06 (m, 3H), 6.76 (d, J = 1.1 Hz, 1H), 5.71 (d, J = 1.1 Hz, 2H), 4.04 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.2 (d, J = 223.9 Hz), 165.0, 152.1, 136.9, 134.8, 132.4 (d, J = 9.5 Hz), 128.9, 126.4 (d, J = 2.9 Hz), 125.1, 121.0, 115.9 (d, J = 3.0 Hz), 115.7, 111.2, 61.2, 54.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −105.30; IR (NaCl) 2956, 2924, 2853, 1741, 1724 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{18}H_{15}FNO_4$ $[M + H]^+$ 328.0985, found 328.0980.

*Methyl 2-({[4-(Trifluoromethyl)benzoyl]oxy}methyl)-1H-indole-1-carboxylate (**16**).* Compound **16** was prepared on a 0.159 mmol scale with methyl [2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S27**) and lead tetra(4-trifluoromethylbenzoate) using general procedure E. The product was obtained as a white solid (32.4 mg, 54%): ^{1}H NMR

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(500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.1 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.37 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 6.78 (s, 0H), 5.76 (s, 1H), 4.05 (s, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 165.1, 152.1, 136.9, 134.5, 130.3, 128.8, 125.7 (d, J = 3.8 Hz), 125.3, 123.6, 121.1, 115.9, 111.5, 61.6, 54.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.14; IR (NaCl) 2959, 2924, 2855, 1743, 1727 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{19}H_{15}F_3NO_4$ $[M + H]^+$ 378.0953, found 378.0948.

*Methyl 2-{[(4-Methoxybenzoyl)oxy]methyl}-1H-indole-1-carboxylate (**15**).* Compound **15** was prepared on a 0.160 mol scale with methyl [2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S27**) and lead tetra(4-methoxybenzoate) using general procedure E. The product was obtained as a white solid (16.6 mg, 31%): ^1H NMR (500 MHz, $CDCl_3$) δ 8.17 (dd, J = 8.4, 0.9 Hz, 1H), 8.07−8.03 (m, 2H), 7.53 (ddd, J = 7.7, 1.3, 0.7 Hz, 1H), 7.34 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 7.28−7.24 (m, 1H), 6.95−6.92 (m, 2H), 6.74 (q, J = 1.0 Hz, 1H), 5.68 (d, J = 1.0 Hz, 2H), 4.02 (s, 3H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.0, 163.8, 152.2, 137.0, 135.3, 132.0, 129.0, 125.0, 123.5, 122.5, 120.9, 115.8, 113.9, 110.7, 60.8, 55.5, 53.9; IR (NaCl) 2956, 2924, 2853, 1743, 1716 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{19}H_{18}NO_5$ $[M + H]^+$ 340.1185, found 340.1180.

*Methyl 2-[(Cinnamoyloxy)methyl]-1H-indole-1-carboxylate (**17**).* Compound **17** was prepared on a 0.169 mmol scale with methyl [2-(propa-1,2-dien-1-yl)phenyl]carbamate (**S27**) and lead tetra[(*E*)-cinnamate] using general procedure E. The product was obtained as a white solid (38.1 mg, 67%): ^1H NMR (500 MHz, $CDCl_3$) δ 8.17 (dq, J = 8.4, 0.9 Hz, 1H), 7.77 (d, J = 16.0 Hz, 1H), 7.57−7.52 (m, 3H), 7.42−7.38 (m, 3H), 7.35 (ddd, J = 8.5, 7.2, 1.4 Hz, 1H), 7.28−7.25 (m, 1H), 6.74 (q, J = 1.0 Hz, 1H), 6.53 (d, J = 15.9 Hz, 1H), 5.61 (d, J = 1.0 Hz, 2H), 4.05 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.7, 152.2, 145.7, 137.0, 135.1, 134.5, 130.6, 129.1, 128.9, 128.3, 125.0, 123.5, 121.0, 117.8, 115.8, 111.1, 60.6, 53.9; IR (NaCl) 2959, 2915, 2850, 1735 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{20}H_{18}NO_4$ $[M + H]^+$ 336.1236, found 336.1230.

Specific Procedures for the Synthesis and Testing of All Controls and Compound Characterization Data. *Methyl o-Tolylcarbamate (**26**).* Compound **26** was prepared on a 9.33 mmol scale with *o*-toluidine using general procedure A. The product was obtained as a white solid (1.49 g, 97%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.22 (td, J = 7.8, 1.6 Hz, 1H), 7.17 (dd, J = 7.2, 1.3 Hz, 1H), 7.05 (td, J = 7.4, 1.3 Hz, 1H), 6.43 (s, 1H), 3.79 (s, 3H), 2.26 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 154.5, 135.9, 130.5, 127.0, 124.3, 121.3, 52.5, 17.7; IR (NaCl) 3314, 3025, 2995, 1719 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_9H_{12}NO_2$ $[M + H]^+$ 166.0868, found 166.0863.

*Methyl (2-Vinylphenyl)carbamate (**32**).* Methyl (2-iodophenyl)-carbamate (0.722 mmol, 1.00 equiv), copper iodide (0.058 mmol, 0.06 equiv), and palladium tetrakis(triphenylphosphine) (0.029 mmol, 0.04 equiv) were added to a flame-dried flask equipped with a stir bar. The reaction vessel was purged with nitrogen followed by addition of DMF (0.1M). Tributyl(vinyl)tin (0.87 mmol, 1.20 equiv) was then added dropwise, and the mixture was allowed to stir for 16 h. Once complete, the reaction was quenched with 5% NH_4OH, and the mixture was extracted with EtOAc. The combined organic layers were washed five times with H_2O and brine and dried over Na_2SO_4. The crude material was then concentrated in vacuo and immediately purified by silica gel flash column chromatography (15:85 EtOAc/hexanes). The product was obtained as a yellow oil that upon standing in the freezer overnight solidified to an off-white solid (124 mg, 97%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 8.2 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.72 (dd, J = 17.4, 11.0 Hz, 1H), 6.53 (s, 1H), 5.58 (d, J = 17.4 Hz, 1H), 5.32 (d, J = 11.0 Hz, 1H), 3.69 (d, J = 1.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 154.5, 134.6, 132.2, 128.7, 127.0, 124.6, 122.0, 118.2, 52.5; IR (NaCl) 3312, 2954, 2905, 2839, 1738, 1716 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{10}H_{12}NO_2$ $[M + H]^+$ 178.0868, found 178.0863.

*Methyl (2-Ethynylphenyl)carbamate (**29**).* Compound **29** was prepared on a 5.42 mmol scale with methyl (2-iodophenyl)carbamate (**S1**) and TMS/acetylene using general procedure B to afford a brown solid (1.36 g, 97%). This was reacted with K_2CO_3 and MeOH to afford the product as a white solid [856 mg, 90% (87% in two steps)]: ^1H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, J = 8.6 Hz, 1H), 7.48−7.34 (m, 3H), 7.00 (t, J = 7.6 Hz, 1H), 3.81 (s, 3H), 3.49 (s, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 153.7, 139.9, 132.3, 130.3, 122.6, 117.8, 110.2, 84.4, 79.2, 52.5; IR (NaCl) 3396, 3243, 3025, 3008, 2959, 1738 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{10}H_{10}NO_2$ $[M + H]^+$ 176.0712, found 176.0706.

*Methyl (2-Allylphenyl)carbamate (**31**).* Compound **31** was prepared on a 1.81 mmol scale with methyl (2-iodophenyl)carbamate following a known procedure.[26] The product was obtained as an off-white solid (174 mg, 50%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 6.98 (t, J = 7.4 Hz, 1H), 6.57 (d, J = 7.4 Hz, 1H), 5.85 (ddd, J = 16.5, 11.1, 5.5 Hz, 1H), 5.09−5.00 (m, 1H), 4.95 (d, J = 2.2 Hz, 1H), 3.66 (s, 3H), 3.27 (d, J = 6.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 154.5, 144.9, 136.2, 136.0, 130.2, 127.5, 124.3 (d, J = 62.9 Hz), 122.1, 116.7, 52.4, 36.6; IR (NaCl) 3413, 3325, 2954, 2907, 2836, 1738 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{11}H_{14}NO_2$ $[M + H]^+$ 192.1025, found 192.1019.

*6-[(Methoxycarbonyl)amino]-1-methylcyclohexa-2,4-dien-1-yl Acetate (**27**).* Compound **27** was prepared on a 0.60 mmol scale with methyl *o*-tolylcarbamate (**26**) and lead tetraacetate using a modified general procedure E, using 5 equiv of LTA. The product was obtained as a yellow oil (60 mg, 44%): ^1H NMR (500 MHz, $CDCl_3$) δ 6.67 (dd, J = 9.9, 5.8 Hz, 1H), 6.27 (d, J = 9.8 Hz, 1H), 6.19 (dd, J = 9.7, 5.8 Hz, 1H), 6.10 (d, J = 9.6 Hz, 1H), 3.81 (s, 3H), 2.07 (s, 3H), 1.50 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 171.6, 169.4, 162.9, 139.7, 136.1, 121.1, 77.4, 53.5, 26.4, 20.9; IR (NaCl) 3050, 1745, 1722, 1239 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{11}H_{14}NO_4$ $[M + H]^+$ 224.0923, found 224.0917.

*2-{2-[(Methoxycarbonyl)amino]phenyl}ethane-1,1-diyl Diacetate (**33**).* Compound **33** was prepared on a 0.60 mmol scale with methyl (2-vinylphenyl)carbamate (**32**) and lead tetraacetate using a modified general procedure E, using 5 equiv of LTA. The product was obtained as a yellow oil (62 mg, 36%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.36 (s, 1H), 7.32−7.22 (m, 1H), 7.14 (dd, J = 7.6, 1.7 Hz, 1H), 7.07−6.94 (m, 1H), 6.70 (t, J = 5.4 Hz, 1H), 3.77 (s, 3H), 3.06 (d, J = 5.5 Hz, 2H), 2.05 (s, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 169.0, 154.6, 136.7, 131.4, 128.5, 124.3, 122.5, 90.8, 52.5, 35.6, 20.7; IR (NaCl) 3350, 1765, 1736 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{14}H_{18}NO_6$ $[M + H]^+$ 296.1134, found 296.1129.

*Methyl 3-Acetoxy-1H-indole-1-carboxylate (**30**).* Compound **30** was prepared on a 0.60 mmol scale with methyl (2-ethynylphenyl)-carbamate (**29**) and lead tetraacetate using a modified general procedure E, using 5 equiv of LTA. The product was obtained as a colorless oil (24 mg, 17%): ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.77 (s, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.27−7.21 (m, 1H), 3.99 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.8, 151.5, 133.9, 126.6, 125.6, 123.6, 123.1, 117.7, 115.2, 113.8, 53.9, 21.0; IR (NaCl) 2962, 2926, 2953, 1782, 1738 cm^{-1}; HRMS (ESI)$^+$ m/z calcd for $C_{12}H_{12}NO_4$ $[M + H]^+$ 234.0766, found 234.0761.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01379.

Experimental procedures and characterization data for all new compounds (PDF)

Accession Codes

CCDC 2087886 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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