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Preparation of Amino-Substituted Indenes and 1,4-Dihydronaphthalenes Using a One-Pot Multireaction Approach: Total Synthesis of Oxybenzo[*c*]phenanthridine Alkaloids

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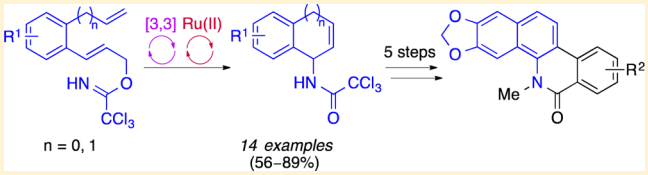
Supporting Information

ABSTRACT: Allylic trichloroacetimidates bearing a 2-vinyl or 2-allylaryl group have been designed as substrates for a one-pot, two-step multi-bond-forming process leading to the general preparation of aminoindenes and amino-substituted 1,4-dihydronaphthalenes. The synthetic utility of the privileged structures formed from this one-pot process was demonstrated with the total synthesis of four oxybenzo[*c*]phenanthridine alkaloids, oxychelerythrine, oxysanguinarine, oxynitidine, and oxyavicine. An intramolecular biaryl Heck coupling reaction, catalyzed using the Hermann−Beller palladacycle was used to effect the key step during the synthesis of the natural products.



INTRODUCTION

Naturally occurring benzo[*c*]phenanthridines belong to an extensive family of isoquinoline alkaloids, many of which have important biological activities.[1] In particular, the tetracyclic, fully aromatic oxybenzo[*c*]phenanthridine alkaloids have received much attention due to the discovery of wide-ranging and significant medicinal properties. For example, oxychelerythrine (**1**) isolated from the root bark of *Zanthoxylum integrifoliolum*[1b] displays cytotoxic effects against P-388 and HT-29 cell lines,[2] while oxysanguinarine (**2**) from the tuberless biennial herb *Corydalis tashiroi* possesses anti-platelet aggregation activity (Figure 1).[3] The related oxybenzo[*c*]phenanthridines, oxynitidine (**3**)[4] and oxyavicine (**4**),[5] isolated from various *Zanthoxylum* plant species inhibit DNA replication in hepatitis B virus[4c] and exhibit analgesic and anti-inflammatory activities.[5] Oxyavicine (**4**) is also used for the treatment of ophthalmic disorders.[5]

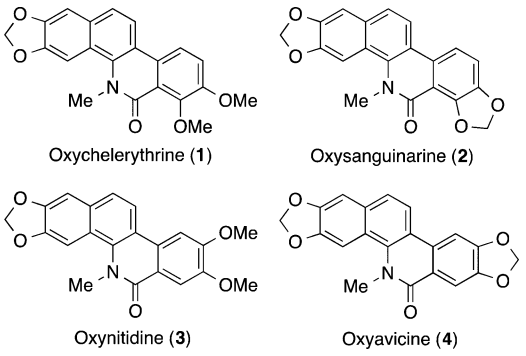


Figure 1. Structures of oxychelerythrine (**1**), oxysanguinarine (**2**), oxynitidine (**3**), and oxyavicine (**4**).

As a result of these wide-ranging pharmacological activities, methods for the synthesis of oxybenzo[*c*]phenanthridines have received considerable attention.[6−10] For example, Clark and Jahangir reported the synthesis of oxynitidine (**3**) by forming the benzo[*c*]phenanthridine skeleton through cycloaddition of a lithiated toluamide with a benzaldimine.[9b] In an analogous approach, Cho and co-workers showed that cycloaddition between lithiated toluamides and benzonitriles could be used for the general synthesis of this class of natural product.[6c−e,7e,f] The research group of Harayama prepared a number of oxybenzo[*c*]phenanthridines by initial formation of amide intermediates via coupling of aminonaphthalenes with *o*-halogenated benzoic acids.[6h] The key step, a challenging intramolecular biaryl Heck coupling reaction, was then optimized to complete the synthesis of the oxybenzo[*c*]phenanthridine skeleton.[6a,b,7b−d,9c] Cheng and co-workers reported the preparation of a range of oxybenzo[*c*]phenanthridines using a nickel-catalyzed annulation and regioselective cyclization of *o*-halobenzaldimines with a benzo[*d*][1,3]dioxol-5-yl substituted alkyne.[6f] Further development of this process showed that a halide-free benzaldimine could be subjected to a similar reaction through C−H activation resulting in a highly efficient synthesis of oxychelerythrine (**1**).[7g]

We recently reported the synthesis of amino-substituted indanes and tetrahydronaphthalenes from alkyne-derived allylic trichloroacetimidates using two consecutive one-pot multireaction processes (Scheme 1a).[11] The first of these involved an Overman rearrangement and ring-closing enyne metathesis (RCEYM) reaction to give cyclic *exo*-dienes. The amino-

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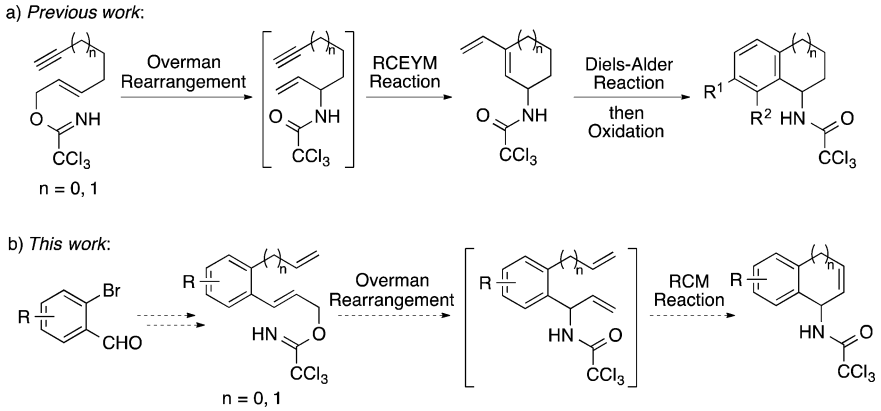
Scheme 1. One-Pot Multireaction Processes for the Preparation of Amino-Substituted Indane and Naphthalene Ring Systems

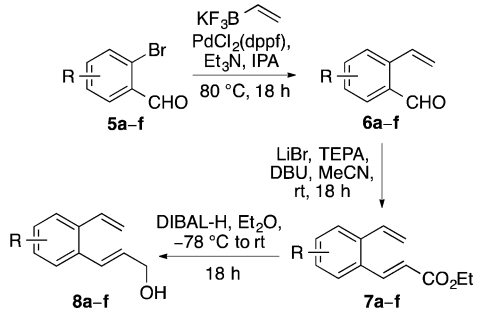


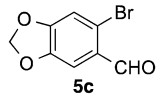
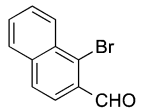
substituted indanes and tetrahydronaphthalenes were then formed following a one-pot Diels–Alder reaction and oxidation step using alkynes and 1,4-quinones as dienophiles. While this approach allowed the flexible synthesis of various ring sizes and the late stage incorporation of aromatic ring substituents, we found that only a limited number of electron-deficient alkynes participated in the Diels–Alder reaction, restricting the variety of compounds produced. To overcome this limitation, a new strategy for the preparation of these types of ring systems was devised (Scheme 1b). It was proposed that substituted 2-bromobenzaldehydes could be used as starting materials for the rapid preparation of allylic trichloroacetimidates bearing a 2-vinyl- or 2-allylaryl group. A one-pot, two-step multireaction process involving an Overman rearrangement and a ring-closing metathesis (RCM) reaction would then allow a more direct synthesis of these ring systems.[12] In addition, the general availability of 2-bromobenzaldehydes would result in the preparation of a wider range of potential products, and the formation of cyclic allylic amides from this particular one-pot process (cf. Scheme 1a) would give an additional functional handle for further transformations of these compounds. We now report the general synthesis of aminoindenes and amino-substituted 1,4-dihydronaphthalenes using a one-pot, two-step multireaction process. As well as demonstrating the scope of this process, we also describe its application for the total synthesis of the oxybenzo[*c*]phenanthridine alkaloids oxychelerythrine (**1**), oxysanguinarine (**2**), oxynitidine (**3**), and oxyavicine (**4**).

RESULTS AND DISCUSSION

Our studies began with the development of a short and efficient synthesis of (*E*)-(2-vinyl)cinnamyl alcohols that would ultimately generate amino-substituted indenes. Having identified 2-bromobenzaldehydes as suitable starting materials, we initially investigated the incorporation of a vinyl group using a Stille coupling with tri-*n*-butyl(vinyl)tin under standard conditions.[13] While this did give the coupled products in good yields, the reactions were not always reproducible and purification was complicated by the presence of the proto-debrominated benzaldehydes and organotin residues. Instead, a highly efficient, reproducible, and scalable synthesis of 2-vinylbenzaldehydes **6a–f** was achieved using a Suzuki–Miyaura coupling with potassium vinyltrifluoroborate and catalyzed by [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) [$PdCl_2$(dppf), 5 mol %] (Table 1).[14] A Horner–Wadsworth–Emmons (HWE) reaction of benzaldehydes **6a–f** with triethyl

Table 1. Synthesis of (*E*)-(2-Vinyl)cinnamyl Alcohols 8a–f



Entry	5	6 (%)	7 (%)	8 (%)
1	**5a** R = H	**6a** (84)	**7a** (98)	**8a** (97)
2	**5b** R = 4-Me	**6b** (90)	**7b** (100)	**8b** (92)
3	 **5c**	**6c** (96)	**7c** (94)	**8c** (99)
4	**5d** R = 5-F	**6d** (91)	**7d** (89)	**8d** (97)
5	 **5e**	**6e** (89)	**7e** (87)	**8e** (92)
6	**5f** R = 5-OMe	**6f** (89)	**7f** (99)	**8f** (89)

phosphonoacetate (TEPA) under mild Masamune–Roush conditions gave (*E*)-*α*,*β*-unsaturated esters **7a–f** as the sole products in excellent yields (87–100%).[15] Subsequent reduction of esters **7a–f** with DIBAL-H completed the three-step synthesis of desired (*E*)-(2-vinyl)cinnamyl alcohols **8a–f** in high overall yields.

Optimization of the one-pot Overman rearrangement and RCM reaction focused on the preparation of amino-substituted indene **11a** (Scheme 2). (2-Vinyl)cinnamyl alcohol **8a** (R = H) was converted to the corresponding allylic trichloroacetimidate using trichloroacetonitrile and a catalytic amount of DBU, and without purification this was subjected to a thermally mediated Overman rearrangement at 160 °C.[16] Grubbs first generation catalyst was initially investigated for the RCM step.[17] However,

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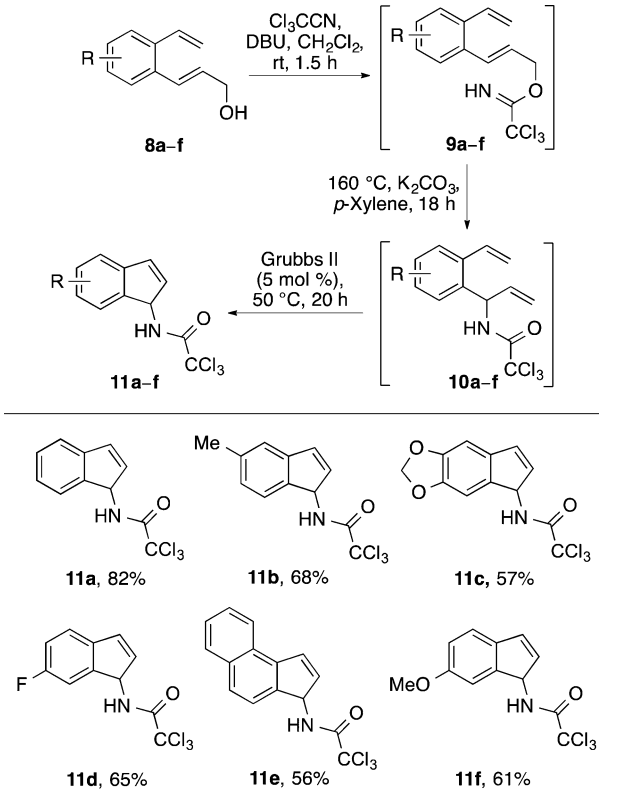
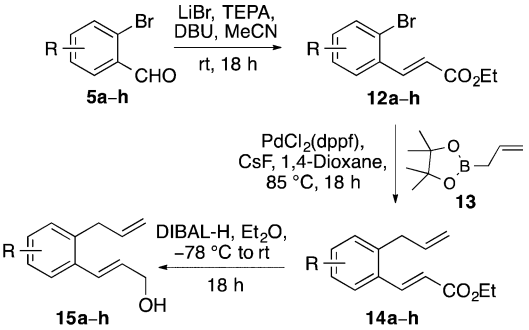
Scheme 2. Synthesis of Amino-Substituted Indenes 11a–f

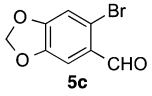
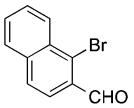
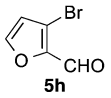


for complete conversion, a high catalyst loading (25 mol %) and long reaction time (96 h) were required, giving indene **11a** in 42% yield over the three steps. This stage of the one-pot process was significantly improved using Grubbs second generation catalyst.[18] After 20 h, complete conversion was achieved using a 5 mol % catalyst loading that gave indene **11a** in 82% overall yield from allylic alcohol **8a** (Scheme 2).[19] Using these optimized conditions, the scope of the one-pot process for the synthesis of a small library of amino-substituted indenes was explored. Overall, the one-pot process was found to be general for a range of allylic trichloroacetimidates **9b–f** bearing electron-rich or electron-deficient substituents, giving the aminoindenes **11b–f** in good yields from allylic alcohols **8b–f**.

Attention then turned to the development of a short route for the preparation of (*E*)-(2-allyl)cinnamyl alcohols that would allow the preparation of dihydronaphthalene analogues. Some optimization was required for incorporation of the allyl side-chain. For this reason, the aldehyde moiety was initially converted to the more stable (*E*)-α,β-unsaturated esters **12a–g** using a HWE reaction with TEPA (Table 2). Conditions for an efficient allylation were then explored. The use of a Suzuki–Miyaura reaction with allylboronic acid pinacol ester (**13**) and $Pd(PPh_3)_4$ (10 mol %) as a catalyst at high temperature (>100 °C) gave the coupled products in high yields.[20] However, these were often contaminated with up to 30% of the proto-debrominated (*E*)-α,β-unsaturated ester. This issue was overcome with the use of $PdCl_2$(dppf) (10 mol %) as a catalyst and a lower reaction temperature (85 °C), which gave allylated products **14a–g** very cleanly and in essentially quantitative yields.[21] DIBAL-H reduction of esters **14a–g** then completed the three-step synthesis of (*E*)-(2-allyl)-cinnamyl alcohols **15a–g**. This series of allylic alcohols was extended to include a heteroaromatic analogue. Allylic alcohol

Table 2. Synthesis of Allylic Alcohols 15a–h



Entry	5	12 (%)	14 (%)	15 (%)
1	**5a** R = H	**12a** (82)	**14a** (100)	**15a** (81)
2	**5b** R = 4-Me	**12b** (96)	**14b** (99)	**15b** (88)
3	 **5c**	**12c** (100)	**14c** (100)	**15c** (97)
4	**5d** R = 5-F	**12d** (95)	**14d** (98)	**15d** (92)
5	 **5e**	**12e** (100)	**14e** (98)[a]	**15e** (93)
6	**5f** R = 5-OMe	**12f** (93)	**14f** (99)	**15f** (82)
7	**5g** R = 4-CF_3	**12g** (88)	**14g** (100)	**15g** (93)
8	 **5h**	**12h** (93)	**14h** (100)	**15h** (96)

[a]Reaction performed at 100 °C.

15h bearing an allylfuran side-chain was prepared in four steps from 3-bromofuran. Initially, 3-bromofuran was formylated at the 2-position using Rieche conditions ($MeOCHCl_2/TiCl_4$), which gave 3-bromo-2-furaldehyde (**5h**) in 96% yield.[22] Application of the previously described three-step sequence involving a HWE reaction, allylation, and DIBAL-H reduction gave allylic alcohol **15h** in 89% overall yield (Table 2).

With a series of (*E*)-(2-allyl)cinnamyl alcohols in hand, conditions for the one-pot synthesis of amino-substituted 1,4-dihydronaphthalenes were optimized. Overman rearrangement of the allylic trichloroacetimidate derived from allylic alcohol **15a** was found to proceed to full conversion after 18 h at 160 °C. Lower temperatures (120–140 °C) resulted in incomplete conversion (~80%) even after 24 h. A comparison of catalysts for the RCM step showed again that a relatively high catalyst loading of Grubbs first generation catalyst (15 mol %) was required for complete conversion to the 1,4-dihydronaphthalene, while under the same conditions, only 5 mol % of Grubbs second generation catalyst was necessary. Using these optimized conditions as a one-pot process gave 1,4-dihydronaphthalene **16a** in 89% yield from allylic alcohol **15a** (Scheme 3). The scope of this process for the general synthesis

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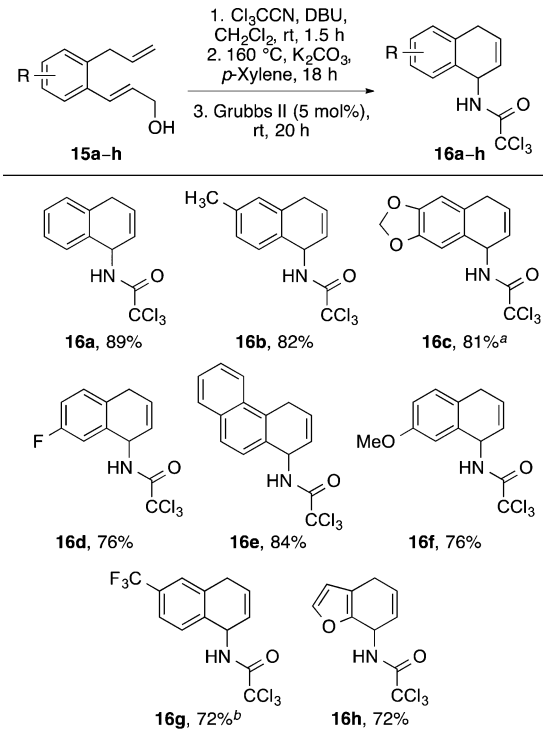
Scheme 3. Synthesis of Amino-Substituted 1,4-Dihydronaphthalenes 16a–h[a,b]



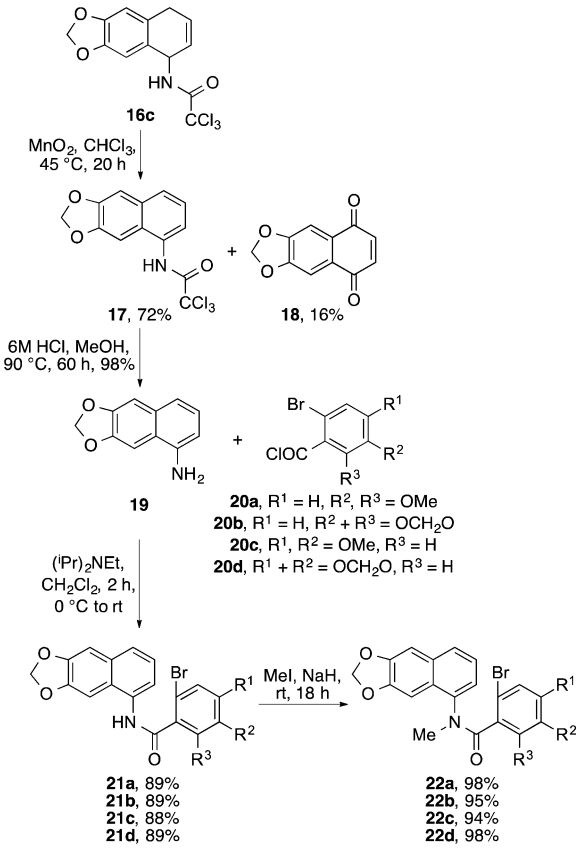
[a]The RCM step was performed using 2.5 mol % of Grubbs second generation catalyst.[23] [b]The RCM step required 10 mol % of Grubbs second generation catalyst and was performed at 50 °C over 48 h.

of amino-substituted 1,4-dihydronaphthalenes **16b–g** with electron-rich or electron-deficient groups as well as various substitution patterns was then explored and found to be particularly robust for the high-yielding synthesis of this series of compounds. In a similar fashion, conversion of the furan-derived allylic alcohol **15h** to the corresponding allylic trichloroacetimidate and implementation of the one-pot two-step process gave amino-substituted 1,4-dihydrobenzofuran **16h** in 72% yield.

Indane and tetrahydronaphthalene ring systems with C-1 amino functionality are privileged structures found within a range of pharmaceutically important agents used for the treatment of diseases associated with neurology and cardiology.[24] However, in this study, we wanted to demonstrate the synthetic utility of the compounds generated from the one-pot multistep approach by application to the total synthesis of natural products. In particular, 1,4-dihydronaphthalene **16c**, which was prepared in 75% overall yield from commercially available 2-bromo-4,5-methylenedioxybenzaldehyde (**5c**), was chosen as a key intermediate for the total synthesis of the oxybenzo[*c*]phenanthridine alkaloids oxychelerythrine (**1**), oxysanguinarine (**2**), oxynitidine (**3**), and oxyavicine (**4**). It was proposed that aromatization of **16c** followed by coupling of the amino group with a suitably derived 2-bromobenzoic acid and then an intramolecular biaryl Heck coupling reaction would allow access to the oxybenzo[*c*]phenanthridine alkaloids in relatively few steps.

For this part of the program, multigram quantities of 1,4-dihydronaphthalene **16c** were produced by scale-up of the one-pot two-step process. During these reactions, it was found that the total loading of Grubbs second generation catalyst could be lowered to 2.5 mol %, while still maintaining consistently high yields over the three steps (Scheme 3). For conversion of **16c** to the corresponding naphthalene **17**, various oxidizing agents were screened (Scheme 4).[25] While the use of manganese

Scheme 4. Synthesis of Amides 22a–d



dioxide did produce a quinone byproduct **18** (16%), the reaction gave the best yield of naphthalene **17** (72%). Acid-mediated hydrolysis of trichloroacetamide **17** was then followed by coupling of the resulting amine **19** with various 2-bromobenzoyl chlorides **20a–d** under standard conditions. Methylation with sodium hydride and iodomethane gave the penultimate compounds **22a–d** in excellent yields.

The last step for the synthesis of the oxybenzo[*c*]-phenanthridine alkaloids required an intramolecular Heck coupling reaction of aryl bromides **22a–d**. Building on initial work by Ames and Opalko,[26] the research group of Harayama has studied extensively this type of amide-tethered biaryl coupling for the synthesis of oxychelerythrine (**1**), oxynitidine (**3**), and other oxybenzo[*c*]phenanthridine alkaloids.[6h] They found that Heck coupling of **22a** using palladium(II) acetate (20 mol %) in the presence of P(*o*-tol)$_3$ and silver carbonate gave oxychelerythrine (**1**) in 96% yield.[7b–d] While this is a sterically demanding coupling, the transformation is assisted by the presence of a substituent *ortho* to the amide (R^3 = OMe), which helps position the bromide for reaction. To produce oxynitidine (**3**) using a similar coupling process is more challenging as the Heck precursor for this reaction has no directing group (R^3 = H) to preorganize the substrate. Therefore, in their synthesis of oxynitidine (**3**), Harayama and co-workers found that a high-yielding reaction (89%) could be achieved only by using a more reactive iodide analogue of

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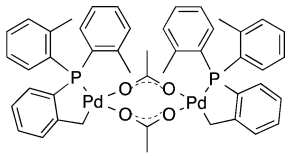
22c and high loading of palladium(II) acetate (100 mol %).[9c] By repeating the Harayama conditions in the Heck reaction of **22a**, we were able to isolate oxychelerythrine (**1**) in a similar yield of 97%. However, attempted Heck coupling of aryl bromides **22b**, **22c**, and **22d** using the same reagents and conditions with various catalyst loadings (30−100 mol %) gave oxysanguinarine (**2**), oxynitidine (**3**), and oxyavicine (**4**) respectively, in low yields (19−29%) with substantial amounts of starting material recovered even after extended reaction times (24 h). It was observed during repeated attempts of the coupling reactions that palladium(0) precipitated at an early stage from the reaction mixture. To develop a more general and efficient intramolecular biaryl Heck reaction for the synthesis of the oxybenzo[*c*]phenanthridine alkaloids using aryl bromide precursors and at the high temperatures typically required, a more stable palladium catalyst was required. The Hermann−Beller palladacycle **23** is well-known for its reactivity at high temperatures (Figure 2).[27,28] This is due to the slow release of



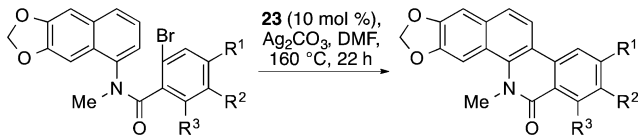
23

Figure 2. Hermann−Beller palladacycle **23**.

active Pd(0) during the reaction, which prevents deactivation processes.[29] Furthermore, palladacycle **23** has been utilized for a number of challenging Heck reactions,[30] including the efficient intramolecular coupling of amine-tethered aryl bromides with cyclic alkenes for the preparation of phenanthridine ring systems.[30d]

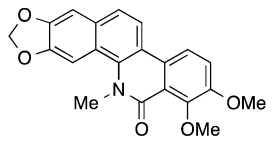
Palladacycle **23** was initially investigated for Heck coupling of aryl bromide **22a** (Scheme 5). Using 10 mol % loading of

Scheme 5. Synthesis of Oxybenzo[*c*]phenanthridine Alkaloids 1−4[*a,b*]

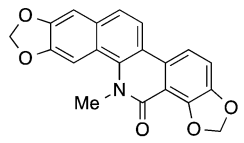


22a, R^1 = H, R^2, R^3 = OMe
22b, R^1 = H, R^2 + R^3 = OCH_2O
22c, R^1, R^2 = OMe, R^3 = H
22d, R^1 + R^2 = OCH_2O, R^3 = H

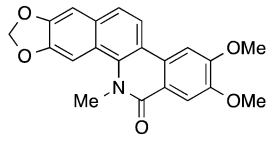
1−4



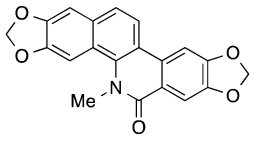
Oxychelerythrine (**1**), 95%



Oxysanguinarine (**2**), 90%[a]



Oxynitidine (**3**), 83%[b]



Oxyavicine (**4**), 78%[b]

[a]Reaction time was 3 h. [b]Catalyst loading of **23** was 20 mol %.

catalyst in the presence of silver carbonate at 160 °C, conversion was complete after 22 h. This allowed the isolation of oxychelerythrine (**1**) in 95% yield. Using the same conditions for aryl bromide **22b**, the reaction was complete after 3 h, giving oxysanguinarine (**2**) in 90% yield. The more challenging Heck couplings of **22c** and **22d** required a higher catalyst loading (20 mol %) for complete conversion and, after 22 h, oxynitidine (**3**) and oxyavicine (**4**) were isolated in 83% and 78% yield, respectively. In all four cases, the use of the Hermann−Beller palladacycle gave the natural products from aryl bromide substrates in excellent yields and at substantially lower catalyst loading compared to the combination of palladium(II) acetate and P(*o*-tol)$_3$.

■ CONCLUSIONS

In summary, short, flexible, and efficient synthetic routes for the preparation of allylic alcohols bearing 2-vinylaryl and 2-allylaryl side-chains have been developed. On conversion to the corresponding allylic trichloroacetamides, these compounds were found to be excellent substrates for a one-pot Overman rearrangement and RCM reaction process, generating a diverse library of aminoindenes and amino-substituted 1,4-dihydronaphthalenes in high overall yields. The synthetic utility of these privileged structures was demonstrated by the use of 1,4-dihydronaphthalene **16c** for the synthesis of four oxybenzo[*c*]-phenanthridine alkaloids. Optimization of the key step, an intramolecular biaryl Heck coupling reaction using the Hermann−Beller palladacycle, completed the total synthesis of oxychelerythrine (**1**), oxysanguinarine (**2**), oxynitidine (**3**), and oxyavicine (**4**) in 11 steps and in 46%, 42%, 38%, and 38% overall yields, respectively. Work is currently underway to investigate further synthetic applications of the aminoindenes and amino-1,4-dihydronaphthalenes generated from this study as well as extending the range of polycyclic classes of compound that can be prepared using one-pot multireaction processes.

■ EXPERIMENTAL SECTION

All reagents and starting materials were obtained from commercial sources and used as received. All dry solvents were purified using a solvent purification system. All reactions were performed under an atmosphere of argon unless otherwise mentioned. Brine refers to a saturated solution of sodium chloride. Flash column chromatography was performed using silica gel 60 (35−70 μm). Aluminum-backed plates precoated with silica gel 60F_{254} were used for thin layer chromatography and were visualized with a UV lamp or by staining with potassium permanganate. ^{1}H NMR spectra were recorded on a NMR spectrometer at either 400 or 500 MHz, and data are reported as follows: chemical shift in ppm relative to tetramethylsilane or the solvent as the internal standard ($CDCl_3$, δ 7.26 ppm or DMSO-d_6, δ 2.50 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances, integration). ^{13}C NMR spectra were recorded on a NMR spectrometer at either 101 or 126 MHz, and data are reported as follows: chemical shift in ppm relative to tetramethylsilane or the solvent as internal standard ($CDCl_3$, δ 77.2 ppm or DMSO-d_6, δ 39.5 ppm), multiplicity with respect to proton (deduced from DEPT experiments, C, CH, CH_2, or CH_3). Infrared spectra were recorded on a FTIR spectrometer; wavenumbers are indicated in cm^{-1}. Mass spectra were recorded using electron impact, chemical ionization, or electrospray techniques. High resolution mass spectra were recorded using a dual-focusing magnetic analyzer mass spectrometer. Melting points are uncorrected.

2-Vinylbenzaldehyde (6a).[31] Potassium vinyltrifluoroborate (0.904 g, 6.75 mmol) and [1,1′-bis(diphenylphosphino)ferrocene]-

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palladium(II) dichloride (0.276 g, 0.337 mmol) were added to a degassed solution of 2-bromobenzaldehyde (**5a**) (0.624 g, 3.37 mmol) and triethylamine (1.40 mL, 10.1 mmol) in propan-2-ol (34 mL). The solution was then heated to 80 °C for 18 h. The reaction mixture was cooled to room temperature, concentrated *in vacuo*, and purified by filtration through a pad of silica (elution with 20% diethyl ether in petroleum ether) to yield 2-vinylbenzaldehyde (**6a**) (0.374 g, 84%) as a yellow oil. Spectroscopic data were in accordance with literature values.[31] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (dd, *J* 11.0, 1.2 Hz, 1H), 5.71 (dd, *J* 17.4, 1.2 Hz, 1H), 7.40−7.48 (m, 1-H), 7.49−7.60 (m, 3H), 7.81−7.86 (m, 1H), 10.30 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.6 (CH_2), 127.6 (CH), 128.1 (CH), 131.4 (CH), 133.1 (C), 133.5 (CH), 133.9 (CH), 140.7 (C), 192.6 (CH); MS (EI) *m*/*z* 132 (M^+, 60), 131 (20), 104 (53), 103 (52), 86 (92), 84 (100), 78 (42).

4-Methyl-2-vinylbenzaldehyde (6b).[31] The reaction was carried out according to the previously described procedure for 2-vinylbenzaldehyde (**6a**) using 2-bromo-4-methylbenzaldehyde (**5b**) (0.400 g, 2.01 mmol). This gave 4-methyl-2-vinylbenzaldehyde (**6b**) (0.264 g, 90%) as a yellow oil. Spectroscopic data were in accordance with literature values.[31] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 5.49 (dd, *J* 11.0, 1.2 Hz, 1H), 5.69 (dd, *J* 17.4, 1.2 Hz, 1H), 7.24 (d, *J* 7.9 Hz, 1H), 7.37 (s, 1H), 7.53 (dd, *J* 17.4, 11.0 Hz, 1H), 7.73 (d, *J* 7.9 Hz, 1H), 10.23 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.0 (CH_3), 119.2 (CH_2), 128.2 (CH), 128.9 (CH), 130.9 (C), 131.7 (CH), 133.7 (CH), 140.7 (C), 144.9 (C), 192.2 (CH); MS (EI) *m*/*z* 146 (M^+, 100), 117 (71), 115 (37), 91 (25), 84 (11).

4,5-Methylenedioxy-2-vinylbenzaldehyde (6c).[32] The reaction was carried out according to the previously described procedure for 2-vinylbenzaldehyde (**6a**) using 2-bromo-4,5-methylenedioxybenzaldehyde (**5c**) (0.400 g, 1.75 mmol). This gave 4,5-methylenedioxy-2-vinylbenzaldehyde (**6c**) (0.296 g, 96%) as a yellow solid. Mp 50−53 °C (lit.[32] 52−54 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (dd, *J* 10.9, 0.8 Hz, 1H), 5.62 (dd, *J* 17.3, 0.8 Hz, 1H), 6.05 (s, 2H), 6.98 (s, 1H), 7.31 (s, 1H), 7.41 (dd, *J* 17.3, 10.9 Hz, 1H), 10.21 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 102.2 (CH_2), 106.8 (CH), 108.1 (CH), 119.2 (CH_2), 128.2 (C), 132.4 (CH), 138.5 (C), 148.1 (C), 152.7 (C), 189.6 (CH); MS (EI) *m*/*z* 176 (M^+, 100), 147 (91), 84 (90), 49 (68).

5-Fluoro-2-vinylbenzaldehyde (6d).[31] The reaction was carried out according to the previously described procedure for 2-vinylbenzaldehyde (**6a**) using 2-bromo-5-fluorobenzaldehyde (**5d**) (0.500 g, 2.46 mmol) and potassium vinyltrifluoroborate (0.396 g, 2.96 mmol). This gave 5-fluoro-2-vinylbenzaldehyde (**6d**) (0.336 g, 91%) as a yellow oil. Spectroscopic data were in accordance with literature values.[31] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 (d, *J* 11.0 Hz, 1H), 5.62 (d, *J* 17.4 Hz, 1H), 7.18−7.26 (m, 1H), 7.38 (dd, *J* 17.4, 11.0 Hz, 1H), 7.44−7.54 (m, 2H), 10.24 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 116.1 (CH, d, $^2J_{CF}$ 22.1 Hz), 119.9 (CH_2), 121.1 (CH, d, $^2J_{CF}$ 21.9 Hz), 129.7 (CH, d, $^3J_{CF}$ 7.3 Hz), 132.0 (CH), 134.4 (C, d, $^3J_{CF}$ 5.9 Hz), 137.0 (C, d, $^4J_{CF}$ 3.4 Hz), 162.3 (C, d, $^1J_{CF}$ 249.5 Hz), 190.6 (CH); MS (EI) *m*/*z* 150 (M^+, 79), 122 (100), 121 (63), 101 (61), 96 (52), 75 (32).

1-Vinyl-2-naphthaldehyde (6e).[31] The reaction was carried out according to the previously described procedure for 2-vinylbenzaldehyde (**6a**) using 1-bromo-2-naphthaldehyde (**5e**) (0.400 g, 1.70 mmol). This gave 1-vinyl-2-naphthaldehyde (**6e**) (0.275 g, 89%) as a yellow solid. Spectroscopic data were in accordance with literature values.[31] Mp 68−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (dd, *J* 17.5, 1.6 Hz, 1H), 6.01 (dd, *J* 11.3, 1.6 Hz, 1H), 7.38 (dd, *J* 17.5, 11.3 Hz, 1H), 7.58 (ddd, *J* 8.4, 6.9, 1.4 Hz, 1H), 7.63 (ddd, *J* 8.4, 6.9, 1.3 Hz, 1H), 7.83 (d, *J* 8.4 Hz, 1H), 7.87 (dd, *J* 8.4, 1.3 Hz, 1H), 8.00 (d, *J* 8.4 Hz, 1H), 8.18 (dd, *J* 8.4, 0.7 Hz, 1H), 10.46 (d, *J* 0.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 123.1 (CH_2), 126.0 (CH), 126.2 (CH), 127.1 (CH), 128.2 (CH), 128.6 (CH), 129.0 (CH), 130.8 (CH), 131.5 (C), 131.7 (C), 135.9 (C), 143.4 (C), 192.8 (CH); MS (EI) *m*/*z* 182 (M^+, 57), 153 (100), 152 (52), 127 (14), 84 (11), 76 (13).

5-Methoxy-2-vinylbenzaldehyde (6f).[33] The reaction was carried out according to the previously described procedure for 2-vinylbenzaldehyde (**6a**) using 2-bromo-5-methoxybenzaldehyde (**5f**) (0.400 g, 1.86 mmol). This gave 5-methoxy-2-vinylbenzaldehyde (**6f**) (0.269 g, 89%) as a yellow oil. Spectroscopic data were in accordance with literature values.[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 5.45 (dd, *J* 10.9, 1.1 Hz, 1H), 5.61 (dd, *J* 17.3, 1.1 Hz, 1H), 7.13 (dd, *J* 8.6, 2.8 Hz, 1H), 7.34 (d, *J* 2.8 Hz, 1H), 7.42 (dd, *J* 17.3, 10.9 Hz, 1H), 7.51 (d, *J* 8.6 Hz, 1H), 10.32 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 55.7 (CH_3), 113.0 (CH), 118.3 (CH_2), 121.3 (CH), 129.0 (CH), 132.4 (CH), 133.9 (C), 134.0 (C), 159.5 (C), 191.8 (CH); MS (EI) *m*/*z* 162 (M^+, 66), 134 (100), 119 (42), 91 (41), 84 (39), 49 (28).

Ethyl (2*E*)-3-(2′-Vinylphenyl)prop-2-enoate (7a).[34] Lithium bromide (0.583 g, 6.70 mmol) was added to a solution of triethyl phosphonoacetate (1.13 mL, 5.69 mmol) and 1,8-diazabicyclo[5.4.0]-undec-7-ene (0.848 mL, 5.69 mmol) in acetonitrile (25 mL) and stirred at room temperature for 0.5 h. 2-Vinylbenzaldehyde (**6a**) (0.221 g, 1.67 mmol) was added, and the solution was stirred at room temperature for 18 h. The reaction was quenched by the addition of a saturated solution of ammonium chloride (30 mL), concentrated to half volume *in vacuo*, and extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with water (100 mL) and brine (100 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by filtration through a pad of silica (elution with 20% diethyl ether in petroleum ether) gave ethyl (2*E*)-3-(2′-vinylphenyl)-prop-2-enoate (**7a**) (0.331 g, 98%) as a yellow oil. Spectroscopic data were in accordance with literature values.[34] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* 7.2 Hz, 3H), 4.27 (q, *J* 7.2 Hz, 2H), 5.43 (dd, *J* 11.0, 1.2 Hz, 1H), 5.64 (dd, *J* 17.4, 1.2 Hz, 1H), 6.35 (d, *J* 15.9 Hz, 1H), 7.07 (dd, *J* 17.4, 11.0 Hz, 1H), 7.29 (td, *J* 7.5, 1.2 Hz, 1H), 7.36 (td, *J* 7.5, 1.2 Hz, 1H), 7.46−7.55 (m, 2H), 8.04 (d, *J* 15.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5 (CH_3), 60.7 (CH_2), 118.2 (CH_2), 120.5 (CH), 127.1 (CH), 127.2 (CH), 128.1 (CH), 130.1 (CH), 132.7 (C), 134.4 (CH), 138.1 (C), 142.5 (CH), 167.0 (C); MS (EI) *m*/*z* 202 (M^+, 10), 173 (4), 157 (10), 129 (100), 128 (58), 102 (5), 83 (12).

Ethyl (2*E*)-3-(4′-Methyl-2′-vinylphenyl)prop-2-enoate (7b). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 4-methyl-2-vinylbenzaldehyde (**6b**) (0.258 g, 1.77 mmol). This gave ethyl (2*E*)-3-(4′-methyl-2′-vinylphenyl)prop-2-enoate (**7b**) (0.385 g, 100%) as a yellow oil. IR (neat) 2980, 1710, 1631, 1313, 1266, 1176, 1158, 1037 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* 7.1 Hz, 3H), 2.37 (s, 3H), 4.26 (q, *J* 7.1 Hz, 2H), 5.40 (dd, *J* 11.0, 1.3 Hz, 1H), 5.62 (dd, *J* 17.3, 1.3 Hz, 1H), 6.32 (d, *J* 15.9 Hz, 1H), 7.06 (dd, *J* 17.3, 11.0 Hz, 1H), 7.09−7.12 (m, 1H), 7.30 (s, 1H), 7.45 (d, *J* 8.0 Hz, 1H), 8.01 (d, *J* 15.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (CH_3), 21.5 (CH_3), 60.6 (CH_2), 117.9 (CH_2), 119.4 (CH), 127.1 (CH), 127.7 (CH), 129.0 (CH), 129.9 (C), 134.5 (CH), 138.1 (C), 140.3 (C), 142.3 (CH), 167.2 (C); HRMS (ESI) calcd for $C_{14}H_{16}NaO_2$ (MNa^+), 239.1043, found 239.1035.

Ethyl (2*E*)-3-(4′,5′-Methylenedioxy-2′-vinylphenyl)prop-2-enoate (7c). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 4,5-methylenedioxy-2-vinylbenzaldehyde (**6c**) (0.279 g, 1.59 mmol). This gave ethyl (2*E*)-3-(4′,5′-methylenedioxy-2′-vinylphenyl)prop-2-enoate (**7c**) (0.367 g, 94%) as a white solid. Mp 82−84 °C; IR (neat) 2904, 1714, 1614, 1500, 1489, 1284, 1177 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (t, *J* 7.1 Hz, 3H), 4.26 (q, *J* 7.1 Hz, 2H), 5.35 (dd, *J* 10.9, 1.0 Hz, 1H), 5.53 (dd, *J* 17.2, 1.0 Hz, 1H), 5.98 (s, 2H), 6.21 (d, *J* 15.7 Hz, 1H), 6.95 (s, 1H), 7.00 (s, 1H), 7.03 (dd, *J* 17.2, 10.9 Hz, 1H), 7.98 (d, *J* 15.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (CH_3), 60.6 (CH_2), 101.7 (CH_2), 106.1 (CH), 106.6 (CH), 116.9 (CH_2), 118.6 (CH), 126.9 (C), 133.8 (C), 133.9 (CH), 141.7 (CH), 148.1 (C), 149.8 (C), 167.1 (C); MS *m*/*z* 246 (M^+, 76), 217 (30), 201 (30), 173 (100), 143 (38), 115 (96); HRMS (EI) calcd for $C_{14}H_{14}O_4$ (M^+), 246.0892, found 246.0889.

Ethyl (2*E*)-3-(5′-Fluoro-2′-vinylphenyl)prop-2-enoate (7d). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 5-fluoro-2-vinylbenzaldehyde (**6d**) (0.190 g, 1.27 mmol). This gave ethyl (2*E*)-3-(5′-fluoro-2′-vinylphenyl)prop-2-enoate (**7d**) (0.247 g, 89%) as a yellow oil. IR (neat) 2982, 2932, 1712, 1636, 1486, 1316, 1237, 1176, 1034 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, *J* 7.1

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Hz, 3H), 4.26 (q, *J* 7.1 Hz, 2H), 5.38 (dd, *J* 10.9, 0.7 Hz, 1H), 5.56 (dd, *J* 17.2, 0.7 Hz, 1H), 6.31 (d, *J* 15.9 Hz, 1H), 6.92−7.06 (m, 2H), 7.18 (dd, *J* 9.2, 2.7 Hz, 1H), 7.43 (dd, *J* 9.2, 5.7 Hz, 1H), 7.94 (dd, *J* 15.9, 1.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.4 (CH_3), 60.8 (CH_2), 113.2 (CH, d, $^2J_{CF}$ 22.3 Hz), 117.1 (CH, d, $^2J_{CF}$ 21.6 Hz), 118.0 (CH_2), 121.4 (CH), 128.9 (CH, d, $^3J_{CF}$ 8.1 Hz), 133.3 (CH), 134.3 (C, d, $^4J_{CF}$ 3.2 Hz), 134.4 (C, d, $^3J_{CF}$ 7.6 Hz), 141.1 (CH, d, $^4J_{CF}$ 2.3 Hz), 162.3 (C, d, $^1J_{CF}$ 247.3 Hz), 166.5 (C); HRMS (ESI) calcd for $C_{13}H_{13}FNaO_2$ (MNa^+), 243.0792, found 243.0789.

Ethyl (2*E*)-3-(1′-Vinylnaphthalen-2′-yl)prop-2-enoate (7e). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 1-vinyl-2-naphthaldehyde (**6e**) (0.271 g, 1.49 mmol). This gave ethyl (2*E*)-3-(1′-vinylnaphthalen-2′-yl)prop-2-enoate (**7e**) (0.327 g, 87%) as a yellow oil. IR (neat) 2978, 1711, 1627, 1293, 1256, 1175, 1038 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (t, *J* 7.1 Hz, 3H), 4.28 (q, *J* 7.1 Hz, 2H), 5.43 (dd, *J* 17.7, 1.8 Hz, 1H), 5.93 (dd, *J* 11.4, 1.8 Hz, 1H), 6.48 (d, *J* 16.0 Hz, 1H), 7.21 (dd, *J* 17.7, 11.4 Hz, 1H), 7.49−7.55 (m, 2H), 7.71 (d, *J* 8.7 Hz, 1H), 7.77 (d, *J* 8.7 Hz, 1H), 7.80−7.85 (m, 1H), 8.10−8.14 (m, 1H), 8.24 (d, *J* 16.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (CH_3), 60.6 (CH_2), 119.1 (CH_2), 123.6 (CH), 124.4 (CH), 126.2 (CH), 126.8 (CH), 127.1 (CH), 128.0 (CH), 128.4 (CH), 129.6 (C), 131.9 (C), 132.7 (CH), 134.1 (C), 138.2 (C), 144.0 (CH), 167.3 (C); HRMS (ESI) calcd for $C_{17}H_{16}NaO_2$ (MNa^+), 275.1043, found 275.1037.

Ethyl (2*E*)-3-(5′-Methoxy-2′-vinylphenyl)prop-2-enoate (7f). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 5-methoxy-2-vinylbenzaldehyde (**6f**) (0.266 g, 1.64 mmol). This gave ethyl (2*E*)-3-(5′-methoxy-2′-vinylphenyl)prop-2-enoate (**7f**) (0.376 g, 99%) as a yellow oil. IR (neat) 2980, 1709, 1634, 1603, 1493, 1314, 1236, 1167, 1035, 980 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (t, *J* 7.1 Hz, 3H), 3.83 (s, 3H), 4.27 (q, *J* 7.1 Hz, 2H), 5.32 (dd, *J* 11.0, 1.1 Hz, 1H), 5.54 (dd, *J* 17.3, 1.1 Hz, 1H), 6.33 (d, *J* 15.8 Hz, 1H), 6.92 (dd, *J* 8.6, 2.7 Hz, 1H), 7.00 (dd, *J* 17.3, 11.0 Hz, 1H), 7.02 (d, *J* 2.7 Hz, 1H), 7.43 (d, *J* 8.6 Hz, 1H), 8.01 (d, *J* 15.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.3 (CH_3), 55.4 (CH_3), 60.6 (CH_2), 111.1 (CH), 116.2 (CH_2), 116.5 (CH), 120.4 (CH), 128.2 (CH), 130.9 (C), 133.5 (CH), 133.6 (C), 142.3 (CH), 159.2 (C), 166.8 (C); MS *m*/*z* 232 (M^+, 53), 203 (47), 187 (24), 159 (100), 144 (83), 115 (53); HRMS (EI) calcd for $C_{14}H_{16}O_3$ (M^+), 232.1099, found 232.1099.

(2*E*)-3-(2′-Vinylphenyl)prop-2-en-1-ol (8a). Diisobutylaluminum hydride (3.33 mL, 3.33 mmol, 1 M solution in hexanes) was added dropwise with stirring to a solution of ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) (0.269 g, 1.33 mmol), in diethyl ether (27 mL) at −78 °C. The solution was stirred at −78 °C for 3 h and then warmed to room temperature over 15 h. The reaction was quenched with 10% aqueous potassium sodium tartrate solution (30 mL), extracted with diethyl ether (2 × 20 mL), washed with water (100 mL) and brine (100 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by column chromatography (elution with 50% diethyl ether in petroleum ether) yielded (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) (0.207 g, 97%) as a colorless oil. IR (neat) 3329, 2922, 1624, 1476, 1414, 1099, 966 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (br s, 1H), 4.35 (d, *J* 5.4 Hz, 2H), 5.34 (dd, *J* 11.0, 1.2 Hz, 1H), 5.63 (dd, *J* 17.4, 1.2 Hz, 1H), 6.24 (dt, *J* 15.7, 5.4 Hz, 1H), 6.92 (d, *J* 15.7 Hz, 1H), 7.02 (dd, *J* 17.4, 11.0 Hz, 1H), 7.23−7.27 (m, 2H), 7.41−7.47 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 64.0 (CH_2), 116.5 (CH_2), 126.5 (CH), 126.7 (CH), 127.9 (CH), 128.0 (CH), 128.9 (CH), 131.2 (CH), 135.0 (CH), 135.1 (C), 136.3 (C); MS *m*/*z* 160 (M^+, 5), 141 (13), 129 (100), 115 (21), 91 (9); HRMS (EI) calcd for $C_{11}H_{12}O$ (M^+), 160.0888, found 160.0882.

(2*E*)-3-(4′-Methyl-2′-vinylphenyl)prop-2-en-1-ol (8b). The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(4′-methyl-2′-vinylphenyl)prop-2-enoate (**7b**) (0.286 g, 1.32 mmol). This gave (2*E*)-3-(4′-methyl-2′-vinylphenyl)prop-2-en-1-ol (**8b**) (0.213 g, 92%) as a colorless oil. IR (neat) 3333, 2921, 1488, 1238, 1201, 1005, 910 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (t, *J* 5.7 Hz, 1H), 2.35 (s, 3H), 4.33 (td, *J* 5.7, 1.0 Hz, 2H), 5.31 (dd, *J* 11.0, 1.4 Hz, 1H), 5.61 (dd, *J* 17.4, 1.4 Hz, 1H), 6.20 (dt, *J* 15.7, 5.7 Hz, 1H), 6.88 (d, *J* 15.7 Hz, 1H), 7.00 (dd, *J* 17.4, 11.0 Hz, 1H), 7.06 (d, *J* 7.9 Hz, 1H), 7.26 (s, 1H), 7.33 (d, *J* 7.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.3 (CH_3), 64.2 (CH_2), 116.3 (CH_2), 126.7 (CH), 127.1 (CH), 128.9 (CH), 128.9 (CH), 130.3 (CH), 132.3 (C), 135.0 (CH), 136.2 (C), 137.6 (C); MS *m*/*z* 157 ($MH^+ - H_2O$, 98), 113 (31), 97 (38), 85 (85), 71 (100), 69 (90); HRMS (CI) calcd for $C_{12}H_{13}$ ($MH^+ - H_2O$), 157.1017, found 157.1021.

(2*E*)-3-(4′,5′-Methylenedioxy-2′-vinylphenyl)prop-2-en-1-ol (8c). The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(4′,5′-methylenedioxy-2′-vinylphenyl)prop-2-enoate (**7c**) (0.357 g, 1.45 mmol). This gave (2*E*)-3-(4′,5′-methylenedioxy-2′-vinylphenyl)prop-2-en-1-ol (**8c**) (0.292 g, 99%) as a white solid. Mp 73−76 °C; IR (neat) 3332, 2896, 1622, 1501, 1478, 1245, 1039 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.65 (s, 1H), 4.30 (dd, *J* 5.7, 1.5 Hz, 2H), 5.23 (dd, *J* 10.9, 1.0 Hz, 1H), 5.49 (dd, *J* 17.3, 1.0 Hz, 1H), 5.93 (s, 2H), 6.10 (dt, *J* 15.6, 5.7 Hz, 1H), 6.84 (dt, *J* 15.6, 1.5 Hz, 1H), 6.89 (s, 1H), 6.93 (s, 1H), 6.94 (dd, *J* 17.3, 10.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 62.9 (CH_2), 100.2 (CH_2), 105.0 (CH), 105.2 (CH), 113.9 (CH_2), 127.6 (CH), 128.5 (C), 128.8 (CH), 129.7 (C), 133.4 (CH), 146.8 (C), 146.8 (C); MS *m*/*z* 204 (M^+, 30), 173 (78), 115 (41), 82 (100); HRMS (EI) calcd for $C_{12}H_{12}O_3$ (M^+), 204.0786, found 204.0790.

(2*E*)-3-(5′-Fluoro-2′-vinylphenyl)prop-2-en-1-ol (8d). The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(5′-fluoro-2′-vinylphenyl)prop-2-enoate (**7d**) (0.223 g, 1.01 mmol). This gave (2*E*)-3-(5′-fluoro-2′-vinylphenyl)prop-2-en-1-ol (**8d**) (0.174 g, 97%) as a colorless oil. IR (neat) 3329, 2868, 1605, 1574, 1483, 1096, 964, 912 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.54 (br s, 1H), 4.36 (dd, *J* 5.4, 1.5 Hz, 2H), 5.31 (dd, *J* 11.0, 0.9 Hz, 1H), 5.56 (dd, *J* 17.4, 0.9 Hz, 1H), 6.25 (dt, *J* 15.8, 5.4 Hz, 1H), 6.87 (dd, *J* 15.8, 1.5 Hz, 1H), 6.91−6.98 (m, 2H), 7.11 (dd, *J* 9.3, 2.7 Hz, 1H), 7.41 (dd, *J* 9.3, 5.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 63.7 (CH_2), 112.9 (d, $^2J_{CF}$ 22.0 Hz, CH), 114.9 (d, $^2J_{CF}$ 21.6 Hz, CH), 116.4 (CH_2), 127.6 (d, $^4J_{CF}$ 2.2 Hz, CH), 128.3 (d, $^3J_{CF}$ 8.3 Hz, CH), 132.2 (CH), 132.5 (d, $^4J_{CF}$ 3.1 Hz, C), 133.9 (CH), 137.0 (d, $^3J_{CF}$ 7.7 Hz, C), 162.6 (d, $^1J_{CF}$ 246.2 Hz, C); MS *m*/*z* 178 (M^+, 4), 160 (11), 147 (100), 133 (13), 127 (10), 84 (5); HRMS (EI) calcd for $C_{11}H_{11}FO$ (M^+), 178.0794, found 178.0791.

(2*E*)-3-(1′-Vinylnaphthalen-2′-yl)prop-2-en-1-ol (8e). The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(1′-vinylnaphthalen-2′-yl)prop-2-enoate (**7e**) (0.325 g, 1.29 mmol). This gave (2*E*)-3-(1′-vinylnaphthalen-2′-yl)prop-2-en-1-ol (**8e**) (0.248 g, 92%) as a yellow oil. IR (neat) 3327, 3056, 2859, 1508, 1418, 1094, 994, 970 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.49 (t, *J* 5.7 Hz, 1H), 4.38 (t, *J* 5.7 Hz, 2H), 5.43 (dd, *J* 17.8, 2.0 Hz, 1H), 5.84 (dd, *J* 11.4, 2.0 Hz, 1H), 6.41 (dt, *J* 15.9, 5.7 Hz, 1H), 7.07−7.15 (m, 2H), 7.43−7.50 (m, 2H), 7.69 (d, *J* 8.7 Hz, 1H), 7.74 (d, *J* 8.7 Hz, 1H), 7.79−7.82 (m, 1H), 8.08−8.11 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 64.3 (CH_2), 122.9 (CH_2), 123.8 (CH), 125.9 (CH), 125.9 (CH), 126.4 (CH), 127.6 (CH), 128.2 (CH), 129.6 (CH), 130.4 (CH), 131.5 (C), 132.0 (C), 133.1 (C), 133.5 (CH), 134.8 (C); MS *m*/*z* 210 (M^+, 10), 179 (100), 165 (29), 152 (19), 139 (6), 115 (5), 67 (21); HRMS (EI) calcd for $C_{15}H_{14}O$ (M^+), 210.1045, found 210.1049.

(2*E*)-3-(5′-Methoxy-2′-vinylphenyl)prop-2-en-1-ol (8f). The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(5′-methoxy-2′-vinylphenyl)prop-2-enoate (**7f**) (0.321 g, 1.38 mmol). This gave (2*E*)-3-(5′-methoxy-2′-vinylphenyl)prop-2-en-1-ol (**8f**) (0.233 g, 89%) as a colorless oil. IR (neat) 3345, 2936, 1603, 1491, 1288, 1246, 1167, 1105, 1024 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.96 (br s, 1H), 3.81 (s, 3H), 4.33 (d, *J* 5.4 Hz, 2H), 5.22 (dd, *J* 11.0, 1.3 Hz, 1H), 5.52 (dd, *J* 17.4, 1.3 Hz, 1H), 6.22 (dt, *J* 15.7, 5.4 Hz, 1H), 6.81 (dd, *J* 8.6, 2.7 Hz, 1H), 6.89 (d, *J* 15.7 Hz, 1H), 6.91−6.98 (m, 2H), 7.40 (d, *J* 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.5 (CH_3), 63.9 (CH_2), 111.4 (CH), 114.1 (CH), 114.7 (CH_2), 127.7 (CH), 128.9 (CH), 129.3 (C), 131.4 (CH), 134.3 (CH),

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136.3 (C), 159.4 (C); MS *m*/*z* 190 (M^+, 19), 172 (8), 159 (100), 144 (48), 115 (28), 83 (21); HRMS (EI) calcd for $C_{12}H_{14}O_2$ (M^+), 190.0994, found 190.0991.

1-(2′,2′,2′-Trichloromethylcarbonylamino)-1*H*-indene (11a). (2*E*)-3-(2′-Vinylphenyl)prop-2-en-1-ol (**8a**) (0.051 g, 0.32 mmol) was dissolved in dry dichloromethane (8 mL) and cooled to 0 °C with stirring. Trichloroacetonitrile (0.048 mL, 0.48 mmol) was added to the solution, followed by 1,8-diazabicyclo[5.4.0]undec-7-ene (0.024 mL, 0.16 mmol), and the reaction mixture was warmed to room temperature over 1.5 h. The reaction mixture was filtered through a short pad of neutral alumina with diethyl ether (150 mL) and concentrated *in vacuo* to yield the crude allylic trichloroacetimidate **9a** as a yellow oil, which was used without further purification. Allylic trichloroacetimidate **9a** was transferred to a dry Schlenk tube containing a stirrer bar and potassium carbonate (15 mg, 3 mg/mL) to which *p*-xylene (5 mL) was then added. The tube was purged with argon, sealed, and heated to 160 °C for 18 h. The mixture was allowed to cool to room temperature, Grubbs second generation catalyst (0.011 g, 0.015 mmol) was added, and the solution was heated to 50 °C for 20 h. The reaction mixture was concentrated *in vacuo* and purified by filtration through a short pad of silica (elution with 20% diethyl ether in petroleum ether) to yield 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) (0.072 g, 82%) as a white solid. Mp 73−75 °C; IR (neat) 3325, 2927, 1697, 1506, 1235, 819 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.62−5.68 (m, 1H), 6.42 (dd, *J* 5.6, 1.9 Hz, 1H), 6.66 (br d, *J* 5.2 Hz, 1H), 6.91 (ddd, *J* 5.6, 1.9, 0.8 Hz, 1H), 7.23−7.28 (m, 1H), 7.33−7.36 (m, 2H), 7.47−7.51 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 58.5 (CH), 92.5 (C), 122.0 (CH), 123.7 (CH), 126.7 (CH), 129.0 (CH), 134.0 (CH), 134.8 (CH), 142.9 (C), 143.2 (C), 162.8 (C); MS *m*/*z* 276 (MH^+, 100), 242 (62), 208 (32), 172 (10), 85 (17), 69 (27); HRMS (CI) calcd for $C_{11}H_9{}^{35}Cl_3NO$ (MH^+), 275.9750, found 275.9753.

5-Methyl-1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (11b). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(4′-methyl-2′-vinylphenyl)prop-2-en-1-ol (**8b**) (0.063 g, 0.36 mmol). This gave 5-methyl-1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11b**) (0.072 g, 68%) as a white solid. Mp 88−92 °C; IR (neat) 3321, 2923, 1695, 1505, 1239, 837, 809 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.39 (s, 3H), 5.58−5.63 (m, 1H), 6.40 (dd, *J* 5.6, 2.0 Hz, 1H), 6.65 (br d, *J* 6.1 Hz, 1H), 6.86 (ddd, *J* 5.6, 1.8, 0.6 Hz, 1H), 7.07 (d, *J* 7.5 Hz, 1H), 7.16 (s, 1H), 7.37 (d, *J* 7.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.6 (CH_3), 58.2 (CH), 92.5 (C), 122.8 (CH), 123.5 (CH), 127.3 (CH), 134.2 (CH), 134.8 (CH), 139.0 (C), 140.0 (C), 143.5 (C), 162.8 (C); HRMS (ESI) calcd for $C_{12}H_{10}{}^{35}Cl_3NNaO$ (MNa^+), 311.9720, found 311.9707.

5,6-Methylenedioxy-1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (11c). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(4′,5′-methylenedioxy-2′-vinylphenyl)prop-2-en-1-ol (**8c**) (0.057 mg, 0.28 mmol). This gave 5,6-methylenedioxy-1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11c**) (0.050 g, 57%) as a white solid. Mp 106−108 °C; IR (neat) 3325, 2901, 1696, 1502, 1472, 1337, 1276, 1039, 939, 838, 820 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.47−5.52 (m, 1H), 5.95 (d, *J* 1.4 Hz, 1H), 5.96 (d, *J* 1.4 Hz, 1H), 6.30 (dd, *J* 5.6, 2.0 Hz, 1H), 6.71 (br d, *J* 8.4 Hz, 1H), 6.76 (dd, *J* 5.6, 1.3 Hz, 1H), 6.78 (s, 1H), 6.96 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 58.1 (CH), 92.5 (C), 101.5 (CH_2), 103.0 (CH), 105.4 (CH), 132.8 (CH), 134.4 (CH), 136.8 (C), 137.0 (C), 147.0 (C), 148.3 (C), 162.7 (C); MS *m*/*z* 321 (M^+, 58), 284 (68), 248 (100), 218 (21), 202 (32), 174 (80), 159 (61), 116 (52), 103 (58), 89 (58); HRMS (EI) calcd for $C_{12}H_8{}^{35}Cl_2{}^{37}ClNO_3$ (M^+), 320.9542, found 320.9539.

6-Fluoro-1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (11d). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(5′-fluoro-2′-vinylphenyl)prop-2-en-1-ol (**8d**) (0.048 g, 0.27 mmol). This gave 6-fluoro-1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11d**) (0.052 g, 65%) as a white solid. Mp 92−94 °C; IR (neat) 3321, 2916, 1695, 1506, 1477, 1270, 1234, 839, 821 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.58−5.64 (m, 1H), 6.38 (dd, *J* 5.6, 2.0 Hz, 1H), 6.69 (br s, 1H), 6.87 (dd, *J* 5.6, 1.6 Hz, 1H), 7.03 (td, *J* 8.4, 2.4 Hz, 1H), 7.21 (dd, *J* 8.4, 2.4 Hz, 1H), 7.26 (dd, *J* 8.4, 4.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 58.4 (CH, d, $^4J_{CF}$ 2.1 Hz), 92.4 (C), 112.0 (CH, d, $^2J_{CF}$ 24.1 Hz), 115.7 (CH, d, $^2J_{CF}$ 22.8 Hz), 122.7 (CH, d, $^3J_{CF}$ 8.6 Hz), 133.7 (CH, d, $^5J_{CF}$ 4.1 Hz), 134.2 (CH), 138.9 (C, d, $^4J_{CF}$ 2.6 Hz), 145.2 (C, d, $^3J_{CF}$ 8.3 Hz), 162.3 (C, d, $^1J_{CF}$ 246.5 Hz), 162.8 (C); HRMS (ESI) calcd for $C_{11}H_7{}^{35}Cl_3FNNaO$ (MNa^+), 315.9469, found 315.9461.

3-(2′,2′,2′-Trichloromethylcarbonylamino)-3*H*-benz[*e*]-indene (11e). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(1′-vinylnaphth-2′-yl)prop-2-en-1-ol (**8e**) (0.055 g, 0.26 mmol). This gave 3-(2′,2′,2′-trichloromethylcarbonylamino)-3*H*-benz[*e*]indene (**11e**) (0.048 g, 56%) as a white solid. Mp 130−134 °C (decomposition); IR (neat) 3270, 3050, 1698, 1685, 1533, 1514, 1260, 841, 822 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.79−5.84 (m, 1H), 6.61 (dd, *J* 5.6, 1.8 Hz, 1H), 6.72 (br d, *J* 6.7 Hz, 1H), 7.47−7.59 (m, 3H), 7.63 (d, *J* 8.2 Hz, 1H), 7.79 (d, *J* 8.2 Hz, 1H), 7.91 (d, *J* 7.9 Hz, 1H), 8.06 (d, *J* 7.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 59.4 (CH), 92.5 (C), 121.3 (CH), 123.9 (CH), 126.3 (CH), 126.7 (CH), 127.2 (CH), 127.8 (C), 128.8 (CH), 132.1 (CH), 134.1 (C), 134.3 (CH), 139.7 (C), 140.4 (C), 163.0 (C); MS *m*/*z* 325 (M^+, 58), 290 (54), 254 (91), 208 (46), 180 (91), 165 (100), 152 (83), 88 (40), 70 (70), 61 (57); HRMS (EI) calcd for $C_{15}H_{10}{}^{35}Cl_3NO$ (M^+), 324.9828, found 324.9829.

6-Methoxy-1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (11f). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(5′-methoxy-2′-vinylphenyl)prop-2-en-1-ol (**8f**) (0.049 g, 0.26 mmol). This gave 6-methoxy-1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11f**) (0.048 g, 61%) as a white solid. Mp 69−71 °C; IR (neat) 3314, 2940, 1697, 1505, 1234, 1026, 818, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 5.58−5.63 (m, 1H), 6.27 (dd, *J* 5.6, 2.1 Hz, 1H), 6.67 (br d, *J* 7.8 Hz, 1H), 6.80−6.88 (m, 2H), 7.07 (d, *J* 2.1 Hz, 1H), 7.23 (d, *J* 8.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 55.8 (CH_3), 58.5 (CH), 92.5 (C), 110.7 (CH), 113.9 (CH), 122.4 (CH), 131.7 (CH), 134.5 (CH), 135.9 (C), 145.0 (C), 159.3 (C), 162.8 (C); MS *m*/*z* 307 (M^+, 59), 270 (82), 234 (48), 192 (15), 160 (60), 145 (64), 130 (40), 115 (42), 83 (100); HRMS (EI) calcd for $C_{12}H_{10}{}^{35}Cl_2{}^{37}ClNO_2$ (M^+), 306.9749, found 306.9751.

Ethyl (2*E*)-3-(2′-Bromophenyl)prop-2-enoate (12a).[35] The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 2-bromobenzaldehyde (**5a**) (0.492 g, 2.66 mmol). This gave ethyl (2*E*)-3-(2′-bromophenyl)prop-2-enoate (**12a**) (0.558 g, 82%) as a colorless oil. Spectroscopic data were in accordance with literature values.[35] ^1H NMR (500 MHz, $CDCl_3$) δ 1.35 (t, *J* 7.1 Hz, 3H), 4.28 (q, *J* 7.1 Hz, 2H), 6.39 (d, *J* 15.9 Hz, 1H), 7.22 (td, *J* 7.6, 1.6 Hz, 1H), 7.32 (t, *J* 7.6 Hz, 1H), 7.60 (dd, *J* 7.6, 1.6 Hz, 1H), 7.61 (dd, *J* 7.6, 1.6 Hz, 1H), 8.05 (d, *J* 15.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (CH_3), 60.8 (CH_2), 121.3 (CH), 125.4 (C), 127.8 (CH), 127.9 (CH), 131.3 (CH), 133.6 (CH), 134.7 (C), 143.1 (CH), 166.5 (C); MS (EI) *m*/*z* 254 (M^+, 25), 209 (45), 175 (86), 147 (100), 102 (62), 83 (31), 75 (21).

Ethyl (2*E*)-3-(2′-Bromo-4′-methylphenyl)prop-2-enoate (12b). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 2-bromo-4-methylbenzaldehyde (**5b**) (0.500 g, 2.51 mmol). This gave ethyl (2*E*)-3-(2′-bromo-4′-methylphenyl)prop-2-enoate (**12b**) (0.648 g, 96%) as a white solid. Mp 37−41 °C; IR (neat) 2980, 1709, 1634, 1603, 1312, 1263, 1165, 1040, 978, 814 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* 7.1 Hz, 3H), 2.34 (s, 3H), 4.27 (q, *J* 7.1 Hz, 2H), 6.35 (d, *J* 15.9 Hz, 1H), 7.12 (d, *J* 7.9 Hz, 1H), 7.44 (s, 1H), 7.50 (d, *J* 7.9 Hz, 1H), 8.02 (d, *J* 15.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5 (CH_3), 21.1 (CH_3), 60.8 (CH_2), 120.2 (CH), 125.4 (C), 127.5 (CH), 128.8 (CH), 131.7 (C), 134.0 (CH), 142.1 (C), 143.0 (CH), 166.7 (C); MS *m*/*z* 291 (MNa^+, 100), 271

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(6), 236 (22), 223 (64), 144 (19); HRMS (ESI) calcd for $C_{12}H_{13}{}^{79}BrNaO_2$ (MNa^+), 290.9991, found 290.9981.

Ethyl (2*E*)-3-(2′-Bromo-4′,5′-methylenedioxyphenyl)prop-2-enoate (12c).[36] The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 2-bromo-4,5-methylenedioxybenzaldehyde (**5c**) (0.600 g, 2.62 mmol). This gave ethyl (2*E*)-3-(2′-bromo-4′,5′-methylenedioxyphenyl)prop-2-enoate (**12c**) (0.781 g, 100%) as a white solid. Spectroscopic data were in accordance with literature values.[36] Mp 101−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, *J* 7.1 Hz, 3H), 4.25 (q, *J* 7.1 Hz, 2H), 6.01 (s, 2H), 6.22 (d, *J* 15.9 Hz, 1H), 7.03 (s, 1H), 7.04 (s, 1H), 7.96 (d, *J* 15.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.4 (CH_3), 60.7 (CH_2), 102.3 (CH_2), 106.5 (CH), 113.2 (CH), 117.9 (C), 119.1 (CH), 127.8 (C), 142.8 (CH), 148.0 (C), 150.1 (C), 166.7 (C); MS (EI) *m*/*z* 298 (M^+, 22), 219 (83), 191 (100), 174 (41), 133 (27), 84 (10).

Ethyl (2*E*)-3-(2′-Bromo-5′-fluorophenyl)prop-2-enoate (12d).[37] The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 2-bromo-5-fluorobenzaldehyde (**5d**) (0.300 g, 1.48 mmol). This gave ethyl (2*E*)-3-(2′-bromo-5′-fluorophenyl)prop-2-enoate (**12d**) (0.384 g, 95%) as a colorless oil. Spectroscopic data were in accordance with literature values.[37] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, *J* 7.1 Hz, 3H), 4.29 (q, *J* 7.1 Hz, 2H), 6.37 (d, *J* 15.9 Hz, 1H), 6.97 (ddd, *J* 8.8, 7.7, 3.0 Hz, 1H), 7.30 (dd, *J* 9.3, 3.0 Hz, 1H), 7.57 (dd, *J* 8.8, 5.3 Hz, 1H), 7.97 (dd, *J* 15.9, 1.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.4 (CH_3), 61.0 (CH_2), 114.6 (d, $^2J_{CF}$ 23.7 Hz, CH), 118.6 (d, $^2J_{CF}$ 22.7 Hz, CH), 119.6 (C), 122.4 (CH), 134.8 (d, $^3J_{CF}$ 7.9 Hz, CH), 136.4 (d, $^3J_{CF}$ 7.7 Hz, C), 142.1 (d, $^4J_{CF}$ 1.9 Hz, CH), 162.1 (d, $^1J_{CF}$ 247.4 Hz, C), 166.2 (C); MS (EI) *m*/*z* 272 (M^+, 14), 229 (23), 193 (36), 165 (100), 120 (47), 84 (20).

Ethyl (2*E*)-3-(1′-Bromonaphthalen-2′-yl)prop-2-enoate (12e). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 1-bromo-2-naphthaldehyde (**5e**) (0.500 g, 2.13 mmol). This gave ethyl (2*E*)-3-(1′-bromonaphthalen-2′-yl)prop-2-enoate (**12e**) (0.647 g, 100%) as a white solid. Mp 117−119 °C; IR (neat) 2976, 1707, 1632, 1308, 1283, 1180, 1157, 980 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, *J* 7.1 Hz, 3H), 4.32 (q, *J* 7.1 Hz, 2H), 6.50 (d, *J* 15.9 Hz, 1H), 7.53−7.69 (m, 3H), 7.77−7.88 (m, 2H), 8.35−8.43 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5 (CH_3), 60.9 (CH_2), 121.8 (CH), 124.1 (CH), 126.9 (C), 127.9 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 132.4 (C), 132.8 (C), 135.1 (C), 144.1 (CH), 166.7 (C); MS *m*/*z* 304 (M^+, 31), 225 (100), 197 (43), 152 (15), 76 (4); HRMS (EI) calcd for $C_{15}H_{13}{}^{79}BrO_2$ (M^+), 304.0099, found 304.0101.

Ethyl (2*E*)-3-(2′-Bromo-5′-methoxyphenyl)prop-2-enoate (12f). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 2-bromo-5-methoxybenzaldehyde (**5f**) (0.500 g, 2.33 mmol). This gave ethyl (2*E*)-3-(2′-bromo-5′-methoxyphenyl)prop-2-enoate (**12f**) (0.619 g, 93%) as a yellow oil. IR (neat) 2987, 1710, 1637, 1465, 1288, 1177, 1017 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (t, *J* 7.1 Hz, 3H), 3.81 (s, 3H), 4.28 (q, *J* 7.1 Hz, 2H), 6.37 (d, *J* 15.9 Hz, 1H), 6.81 (dd, *J* 8.8, 3.0 Hz, 1H), 7.11 (d, *J* 3.0 Hz, 1H), 7.49 (d, *J* 8.8 Hz, 1H), 8.00 (d, *J* 15.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (CH_3), 55.7 (CH_3), 60.9 (CH_2), 112.7 (CH), 116.1 (C), 117.8 (CH), 121.4 (CH), 134.1 (CH), 135.4 (C), 143.2 (CH), 159.2 (C), 166.5 (C); MS *m*/*z* 307 (MNa^+, 100), 285 (6), 264 (32), 239 (43), 160 (100); HRMS (ESI) calcd for $C_{12}H_{13}{}^{79}BrNaO_3$ (MNa^+), 306.9940, found 306.9936.

Ethyl (2*E*)-3-(2′-Bromo-4′-trifluoromethylphenyl)prop-2-enoate (12g). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 2-bromo-4-trifluoromethylbenzaldehyde (**5g**) (0.500 g, 1.98 mmol). This gave ethyl (2*E*)-3-(2′-bromo-4′-trifluoromethylphenyl)prop-2-enoate (**12g**) (0.562 g, 88%) as a yellow oil. IR (neat) 2984, 1717, 1640, 1393, 1316, 1265, 1171, 1125, 1078 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, *J* 7.1 Hz, 3H), 4.30 (q, *J* 7.1 Hz, 2H), 6.45 (d, *J* 16.0 Hz, 1H), 7.58 (br d, *J* 8.2 Hz, 1H), 7.69 (d, *J* 8.2 Hz, 1H), 7.87 (br s, 1H), 8.01 (d, *J* 16.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.3 (CH_3), 61.0 (CH_2), 123.0 (C, q, $^1J_{CF}$ 272.7 Hz), 123.5 (CH), 124.7 (CH, q, $^3J_{CF}$ 3.6 Hz), 125.1 (C), 128.1 (CH), 130.4 (CH, q, $^3J_{CF}$ 3.9 Hz), 132.8 (C, q, $^2J_{CF}$ 33.4 Hz), 138.2 (C), 141.4 (CH), 165.9 (C); MS *m*/*z* 345 (MNa^+, 100), 301 (65), 275 (40), 258 (26), 243 (19), 236 (49), 201 (28); HRMS (ESI) calcd for $C_{12}H_{10}{}^{79}BrF_3NaO_2$ (MNa^+), 344.9708, found 344.9693.

3-Bromofuran-2-carboxaldehyde (5h).[38] Titanium tetrachloride (17.0 mL, 1.0 M in dichloromethane, 17.0 mmol) was added to dichloromethane (70 mL) and cooled to −78 °C. Dichloromethyl methyl ether (1.53 mL, 17.0 mmol) was added dropwise and stirred for 0.1 h before 3-bromofuran (0.300 mL, 3.39 mmol) was added dropwise with vigorous stirring. The reaction mixture was stirred at −78 °C for 2 h, then warmed to 0 °C, quenched with water (20 mL), and stirred as a slurry for a further 1 h. A saturated solution of sodium hydrogen carbonate was added until gas evolution ceased. The biphasic reaction mixture was filtered through a pad of Celite and then extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with water (50 mL) and then brine (50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo* to yield 3-bromofuran-2-carboxaldehyde (**5h**) (0.567 g, 96%) as a light brown oil. Spectroscopic data were in accordance with literature values.[38] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (dd, *J* 1.8, 0.7 Hz, 1H), 7.63 (dd, *J* 1.8, 0.7 Hz, 1H), 9.71−9.73 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 112.8 (C), 116.8 (CH), 148.1 (CH), 148.3 (C), 176.5 (CH); MS (EI) *m*/*z* 175 (M^+, 95), 173 (74), 149 (39), 111 (53), 97 (72), 85 (78), 71 (98), 57 (100).

Ethyl (2*E*)-3-(3′-Bromofuran-2′-yl)prop-2-enoate (12h). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-vinylphenyl)prop-2-enoate (**7a**) using 3-bromofuran-2-carboxaldehyde (**5h**) (0.550 g, 3.14 mmol). This gave ethyl (2*E*)-3-(3′-bromofuran-2′-yl)prop-2-enoate (**12h**) (0.718 g, 93%) as an orange solid. Mp 44−46 °C; IR (neat) 2986, 1713, 1636, 1304, 1258, 1173, 1026, 964 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (t, *J* 7.1 Hz, 3H), 4.25 (q, *J* 7.1 Hz, 2H), 6.39 (d, *J* 15.8 Hz, 1H), 6.53 (d, *J* 2.0 Hz, 1H), 7.42 (d, *J* 2.0 Hz, 1H), 7.48 (d, *J* 15.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.4 (CH_3), 60.8 (CH_2), 105.5 (C), 116.0 (CH), 117.7 (CH), 128.1 (CH), 144.7 (CH), 148.2 (C), 166.8 (C); MS *m*/*z* 267 (MNa^+, 100), 242 (8), 236 (36), 200 (4), 171 (4); HRMS (ESI) calcd for $C_9H_9{}^{79}BrNaO_3$ (MNa^+), 266.9627, found 266.9628.

Ethyl (2*E*)-3-(2′-Allylphenyl)prop-2-enoate (14a).[39] Cesium fluoride (0.238 g, 1.57 mmol), [1,1′-bis(diphenylphosphino)-ferrocene]palladium(II) dichloride (0.0320 g, 0.0392 mmol), and allylboronic acid pinacol ester (**13**) (0.147 mL, 0.784 mmol) were added to a degassed solution of ethyl (2*E*)-3-(2′-bromophenyl)prop-2-enoate (**12a**) (0.100 g, 0.329 mmol) in 1,4-dioxane (5 mL). The solution was heated to 85 °C for 18 h, cooled to room temperature, and concentrated *in vacuo*. The reaction mixture was purified by filtration through a pad of silica (elution with 20% diethyl ether in petroleum ether) to yield ethyl (2*E*)-3-(2′-allylphenyl)prop-2-enoate (**14a**) (0.0844 g, 100%) as a yellow oil. Spectroscopic data were in accordance with literature values.[39] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (t, *J* 7.1 Hz, 3H), 3.53 (br d, *J* 6.2 Hz, 2H), 4.27 (q, *J* 7.1 Hz, 2H), 5.00 (dq, *J* 17.1, 1.6 Hz, 1H), 5.09 (dq, *J* 10.1, 1.6 Hz, 1H), 5.96 (ddt, *J* 17.1, 10.1, 6.2 Hz, 1H), 6.36 (d, *J* 15.8 Hz, 1H), 7.20−7.27 (m, 2H), 7.32 (td, *J* 7.5, 1.3 Hz, 1H), 7.58 (dd, *J* 7.5, 1.3 Hz, 1H), 7.99 (d, *J* 15.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.4 (CH_3), 37.6 (CH_2), 60.6 (CH_2), 116.5 (CH_2), 119.8 (CH), 126.7 (CH), 127.0 (CH), 130.2 (CH), 130.4 (CH), 133.6 (C), 136.7 (CH), 139.4 (C), 142.3 (CH), 167.1 (C); MS (EI) *m*/*z* 216 (M^+, 68), 187 (24), 171 (30), 143 (100), 142 (99), 128 (94), 115 (97), 84 (42).

Ethyl (2*E*)-3-(2′-Allyl-4′-methylphenyl)prop-2-enoate (14b). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-allylphenyl)prop-2-enoate (**14a**) using ethyl (2*E*)-3-(2′-bromo-4′-methylphenyl)prop-2-enoate (**12b**) (0.050 g, 0.19 mmol). This gave ethyl (2*E*)-3-(2′-allyl-4′-methylphenyl)prop-2-enoate (**14b**) (0.042 g, 99%) as a colorless oil. IR (neat) 2980, 1709, 1632, 1609, 1312, 1173, 1155 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, *J* 7.1 Hz, 3H), 2.34 (s, 3H), 3.50 (br d, *J* 6.2 Hz, 2H), 4.26 (q, *J*

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7.1 Hz, 2H), 5.00 (dq, *J* 17.0, 1.6 Hz, 1H), 5.08 (dq, *J* 10.1, 1.6 Hz, 1H), 5.95 (ddt, *J* 17.0, 10.1, 6.2 Hz, 1H), 6.33 (d, *J* 15.8 Hz, 1H), 7.03 (s, 1H), 7.06 (d, *J* 7.9 Hz, 1H), 7.49 (d, *J* 7.9 Hz, 1H), 7.96 (d, *J* 15.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5 (CH_3), 21.5 (CH_3), 37.6 (CH_2), 60.5 (CH_2), 116.4 (CH_2), 118.6 (CH), 126.7 (CH), 127.8 (CH), 130.6 (C), 131.1 (CH), 136.8 (CH), 139.4 (C), 140.6 (C), 142.2 (CH), 167.3 (C); MS *m*/*z* 253 (MNa^+, 100), 236 (8), 157 (36), 142 (28); HRMS (ESI) calcd for $C_{15}H_{18}NaO_2$ (MNa^+), 253.1199, found 253.1198.

Ethyl (2*E*)-3-(2′-Allyl-4′,5′-methylenedioxyphenyl)prop-2-enoate (14c). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-allylphenyl)prop-2-enoate (**14a**) using ethyl (2*E*)-3-(2′-bromo-4′,5′-methylenedioxyphenyl)prop-2-enoate (**12c**) (0.270 g, 0.903 mmol). This gave ethyl (2*E*)-3-(2′-allyl-4′,5′-methylenedioxyphenyl)prop-2-enoate (**14c**) (0.235 g, 100%) as a white solid. Mp 63−67 °C; IR (neat) 2982, 1694, 1499, 1476, 1256, 1036, 974 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, *J* 7.1 Hz, 3H), 3.45 (dt, *J* 6.2, 1.5 Hz, 1H), 4.24 (q, *J* 7.1 Hz, 2H), 4.99 (dq, *J* 17.0, 1.5 Hz, 1H), 5.07 (dq, *J* 10.1, 1.5 Hz, 1H), 5.91 (ddt, *J* 17.0, 10.1, 6.2 Hz, 1H), 5.97 (s, 2H), 6.21 (d, *J* 15.7 Hz, 1H), 6.68 (s, 1H), 7.05 (s, 1H), 7.89 (d, *J* 15.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5 (CH_3), 37.4 (CH_2), 60.5 (CH_2), 101.5 (CH_2), 105.8 (CH), 110.3 (CH), 116.4 (CH_2), 117.4 (CH), 126.8 (C), 134.9 (C), 136.7 (CH), 141.6 (CH), 146.9 (C), 149.6 (C), 167.3 (C); HRMS (ESI) calcd for $C_{15}H_{16}NaO_4$ (MNa^+), 283.0941, found 283.0935.

Ethyl (2*E*)-3-(2′-Allyl-5′-fluorophenyl)prop-2-enoate (14d). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-allylphenyl)prop-2-enoate (**14a**) using ethyl (2*E*)-3-(2′-bromo-5′-fluorophenyl)prop-2-enoate (**12d**) (0.254 g, 0.930 mmol). This gave ethyl (2*E*)-3-(2′-allyl-5′-fluorophenyl)prop-2-enoate (**14d**) (0.214 g, 98%) as a yellow oil. IR (neat) 2982, 1711, 1636, 1489, 1314, 1269, 1233, 1173, 1034, 976, 860 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* 7.1 Hz, 3H), 3.48 (br d, *J* 6.1 Hz, 2H), 4.27 (q, *J* 7.1 Hz, 2H), 4.96 (dq, *J* 17.1, 1.6 Hz, 1H), 5.09 (dq, *J* 10.1, 1.6 Hz, 1H), 5.93 (ddt, *J* 17.1, 10.1, 6.1 Hz, 1H), 6.33 (d, *J* 15.8 Hz, 1H), 7.02 (td, *J* 8.3, 2.7 Hz, 1H), 7.18 (dd, *J* 8.3, 5.8 Hz, 1H), 7.26 (dd, *J* 9.8, 2.7 Hz, 1H), 7.90 (dd, *J* 15.8, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5 (CH_3), 36.9 (CH_2), 60.8 (CH_2), 113.1 (d, $^2J_{CF}$ 22.1 Hz, CH), 116.7 (CH_2), 117.1 (d, $^2J_{CF}$ 21.2 Hz, CH), 120.9 (CH), 132.0 (d, $^3J_{CF}$ 7.9 Hz, CH), 135.1 (d, $^4J_{CF}$ 3.3 Hz, C), 135.3 (d, $^3J_{CF}$ 7.5 Hz, C), 136.5 (CH), 141.1 (d, $^4J_{CF}$ 2.2 Hz, CH), 161.7 (d, $^1J_{CF}$ 244.9 Hz, C), 166.8 (C); MS *m*/*z* 234 (M^+, 32), 205 (12), 189 (15), 161 (95), 146 (100), 133 (54), 84 (16), 69 (20); HRMS (EI) calcd for $C_{14}H_{15}FO_2$ (M^+), 234.1056, found 234.1053.

Ethyl (2*E*)-3-(1′-Allylnaphthalen-2′-yl)prop-2-enoate (14e). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-allylphenyl)prop-2-enoate (**14a**) using ethyl (2*E*)-3-(1′-bromonaphthalen-2′-yl)prop-2-enoate (**12e**) (0.415 g, 1.36 mmol) at 100 °C. This gave ethyl (2*E*)-3-(1′-allylnaphthalen-2′-yl)prop-2-enoate (**14e**) (0.355 g, 98%) as a yellow oil. IR (neat) 2978, 1707, 1626, 1256, 1173, 1153, 1036, 812 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (t, *J* 7.1 Hz, 3H), 4.01 (br d, *J* 5.6 Hz, 2H), 4.30 (q, *J* 7.1 Hz, 2H), 4.93 (dq, *J* 17.1, 1.7 Hz, 1H), 5.08 (dq, *J* 10.2, 1.7 Hz, 1H), 6.08 (ddt, *J* 17.1, 10.2, 5.6 Hz, 1H), 6.48 (d, *J* 15.8 Hz, 1H), 7.48−7.56 (m, 2H), 7.67 (d, *J* 8.7 Hz, 1H), 7.74 (d, *J* 8.7 Hz, 1H), 7.80−7.85 (m, 1H), 8.08 (d, *J* 8.1 Hz, 1H), 8.22 (d, *J* 15.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (CH_3), 32.3 (CH_2), 60.7 (CH_2), 116.6 (CH_2), 120.5 (CH), 123.8 (CH), 125.1 (CH), 126.8 (CH), 126.8 (CH), 127.6 (CH), 128.8 (CH), 130.8 (C), 132.5 (C), 134.5 (C), 136.0 (CH), 136.1 (C), 142.7 (CH), 167.2 (C); MS *m*/*z* 289 (MNa^+, 100), 236 (6), 193 (3), 178 (2); HMRS (ESI) calcd for $C_{18}H_{18}NaO_2$ (MNa^+), 289.1199, found 289.1190.

Ethyl (2*E*)-3-(2′-Allyl-5′-methoxyphenyl)prop-2-enoate (14f). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-allylphenyl)prop-2-enoate (**14a**) using ethyl (2*E*)-3-(2′-bromo-5′-methoxyphenyl)prop-2-enoate (**12f**) (0.619 g, 2.17 mmol). This gave ethyl (2*E*)-3-(2′-allyl-5′-methoxyphenyl)prop-2-enoate (**14f**) (0.529 g, 99%) as a yellow oil. IR (neat) 2980, 1709, 1634, 1495, 1233, 1165, 1036 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (t, *J* 7.1 Hz, 3H), 3.46 (br d, *J* 6.2 Hz, 2H), 3.81 (s, 3H), 4.27 (q, *J* 7.1 Hz, 2H), 4.97 (dq, *J* 17.1, 1.6 Hz, 1H), 5.06 (dq, *J* 10.0, 1.6 Hz, 1H), 5.93 (ddt, *J* 17.1, 10.0, 6.2 Hz, 1H), 6.34 (d, *J* 15.8 Hz, 1H), 6.89 (dd, *J* 8.4, 2.7 Hz, 1H), 7.09 (d, *J* 2.7 Hz, 1H), 7.12 (d, *J* 8.4 Hz, 1H), 7.94 (d, *J* 15.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (CH_3), 36.8 (CH_2), 55.5 (CH_3), 60.6 (CH_2), 111.4 (CH), 116.1 (CH_2), 116.4 (CH), 119.9 (CH), 131.5 (CH), 131.8 (C), 134.4 (C), 137.2 (CH), 142.3 (CH), 158.5 (C), 167.0 (C); HRMS (ESI) calcd for $C_{15}H_{18}NaO_3$ (MNa^+), 269.1148, found 269.1141.

Ethyl (2*E*)-3-(2′-Allyl-4′-trifluoromethylphenyl)prop-2-enoate (14g). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-allylphenyl)prop-2-enoate (**14a**) using ethyl (2*E*)-3-(2′-bromo-4′-trifluoromethylphenyl)prop-2-enoate (**12g**) (0.321 g, 1.00 mmol). This gave ethyl (2*E*)-3-(2′-allyl-4′-trifluoromethylphenyl)prop-2-enoate (**14g**) (0.282 g, 100%) as a yellow oil. IR (neat) 2984, 1715, 1638, 1333, 1314, 1279, 1163, 1123, 1078 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (t, *J* 7.1 Hz, 3H), 3.56 (br d, *J* 6.2 Hz, 2H), 4.28 (q, *J* 7.1 Hz, 2H), 5.01 (dq, *J* 16.8, 1.5 Hz, 1H), 5.14 (dq, *J* 10.3, 1.5 Hz, 1H), 5.94 (ddt, *J* 16.8, 10.3, 6.2 Hz, 1H), 6.40 (d, *J* 15.9 Hz, 1H), 7.47 (s, 1H), 7.50 (d, *J* 8.2 Hz, 1H), 7.65 (d, *J* 8.2 Hz, 1H), 7.95 (d, *J* 15.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.3 (CH_3), 37.4 (CH_2), 60.8 (CH_2), 117.3 (CH_2), 122.1 (CH), 123.7 (CH, q, $^3J_{CF}$ 3.7 Hz), 123.9 (C, q, $^1J_{CF}$ 272.3 Hz), 127.0 (CH, q, $^3J_{CF}$ 3.8 Hz), 127.1 (CH), 131.7 (C, q, $^2J_{CF}$ 32.5 Hz), 135.5 (CH), 137.1 (C), 139.8 (C), 140.7 (CH), 166.4 (C); MS *m*/*z* 307 (MNa^+, 100), 301 (43), 236 (36), 209 (72); HRMS (ESI) calcd for $C_{15}H_{15}F_3NaO_2$ (MNa^+), 307.0916, found 307.0907.

Ethyl (2*E*)-3-(3′-Allylfuran-2′-yl)prop-2-enoate (14h). The reaction was carried out according to the previously described procedure for ethyl (2*E*)-3-(2′-allylphenyl)prop-2-enoate (**14a**) using ethyl (2*E*)-3-(3′-bromofuran-2′-yl)prop-2-enoate (**12h**) (0.230 g, 0.939 mmol). This gave ethyl (2*E*)-3-(3′-allylfuran-2′-yl)prop-2-enoate (**14h**) (0.193 g, 100%) as a yellow oil. IR (neat) 2924, 1705, 1636, 1304, 1258, 1165, 1042, 972 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (t, *J* 7.1 Hz, 3H), 3.29 (br d, *J* 6.3 Hz, 2H), 4.24 (q, *J* 7.1 Hz, 2H), 5.06−5.11 (m, 2H), 5.88 (ddt, *J* 16.2, 10.0, 6.3 Hz, 1H), 6.27 (d, *J* 15.6 Hz, 1H), 6.35 (d, *J* 1.6 Hz, 1H), 7.40 (d, *J* 1.6 Hz, 1H), 7.47 (d, *J* 15.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (CH_3), 29.4 (CH_2), 60.5 (CH_2), 113.9 (CH), 114.9 (CH), 116.5 (CH_2), 128.0 (C), 129.1 (CH), 135.6 (CH), 144.3 (CH), 147.1 (C), 167.5 (C); HRMS (ESI) calcd for $C_{12}H_{14}NaO_3$ (MNa^+), 229.0835, found 229.0838.

(2*E*)-3-(2′-Allylphenyl)prop-2-en-1-ol (15a).[40] The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(2′-allylphenyl)prop-2-enoate (**14a**) (0.700 g, 3.24 mmol). This gave (2*E*)-3-(2′-allylphenyl)prop-2-en-1-ol (**15a**) (0.456 g, 81%) as a colorless oil. Spectroscopic data were in accordance with literature values.[40] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (t, *J* 5.4 Hz, 1H), 3.45 (dt, *J* 6.2, 1.7 Hz, 2H), 4.30−4.35 (m, 2H), 4.97 (dq, *J* 17.1, 1.7 Hz, 1H), 5.06 (dq, *J* 10.1, 1.7 Hz, 1H), 5.97 (ddt, *J* 17.1, 10.1, 6.2 Hz, 1H), 6.26 (dt, *J* 15.7, 5.7 Hz, 1H), 6.85 (dt, *J* 15.7, 1.5 Hz, 1H), 7.14−7.23 (m, 3H), 7.46−7.49 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.6 (CH_2), 64.1 (CH_2), 116.0 (CH_2), 126.3 (CH), 126.8 (CH), 128.0 (CH), 128.9 (CH), 129.9 (CH), 130.4 (CH), 135.9 (C), 137.0 (CH), 137.3 (C); MS (EI) *m*/*z* 174 (M^+, 8), 156 (31), 143 (62), 128 (100), 115 (70), 91 (23), 84 (12), 74 (5).

(2*E*)-3-(2′-Allyl-4′-methylphenyl)prop-2-en-1-ol (15b). The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(2′-allyl-4′-methylphenyl)prop-2-enoate (**14b**) (0.483 g, 2.10 mmol). This gave (2*E*)-3-(2′-allyl-4′-methylphenyl)prop-2-en-1-ol (**15b**) (0.348 g, 88%) as a colorless oil. IR (neat) 3325, 2918, 1638, 1611, 1495, 1086, 995, 966 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39 (t, *J* 5.9 Hz, 1H), 2.32 (s, 3H), 3.42 (dt, *J* 6.2, 1.6 Hz, 2H), 4.32 (td, *J* 5.9, 1.5 Hz, 2H), 4.98 (dq, *J* 17.0, 1.6 Hz, 1H), 5.06 (dq, *J* 10.1, 1.6 Hz, 1H), 5.95 (ddt, *J* 17.0, 10.1, 6.2 Hz, 1H), 6.22 (dt, *J* 15.7, 5.9 Hz, 1H), 6.81 (d, *J* 15.7 Hz, 1H), 6.97 (br s, 1H), 7.02 (d, *J* 7.9 Hz, 1H), 7.38 (d, *J* 7.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.3 (CH_3), 37.6

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(CH_2), 64.2 (CH_2), 115.9 (CH_2), 126.2 (CH), 127.6 (CH), 128.9 (CH), 129.4 (CH), 130.6 (CH), 133.0 (C), 137.1 (CH), 137.2 (C), 137.8 (C); MS *m*/*z* 211 (MNa^+, 24), 190 (22), 171 (29), 143 (100), 128 (46); HRMS (ESI) calcd for $C_{13}H_{16}NaO$ (MNa^+), 211.1093, found 211.1096.

(2*E*)-3-(2′-Allyl-4′,5′-methylenedioxyphenyl)prop-2-en-1-ol (15c). The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(2′-allyl-4′,5′-methylenedioxyphenyl)prop-2-enoate (**14c**) (1.14 g, 4.37 mmol). This gave (2*E*)-3-(2′-allyl-4′,5′-methylenedioxyphenyl)prop-2-en-1-ol (**15c**) (0.920 g, 97%) as a white crystalline solid. Mp 45−49 °C; IR (neat) 3262, 2866, 1636, 1503, 1481, 1244, 1165, 1044, 1017, 995 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.30 (dt, *J* 6.1, 1.5 Hz, 2H), 3.68 (br s, 1H), 4.25 (br d, *J* 5.7 Hz, 2H), 4.95 (dq, *J* 17.0, 1.5 Hz, 1H), 5.02 (dq, *J* 10.1, 1.5 Hz, 1H), 5.85 (s, 2H), 5.88 (ddt, *J* 17.0, 10.1, 6.1 Hz, 1H), 6.08 (dt, *J* 15.6, 5.7 Hz, 1H), 6.60 (s, 1H), 6.71 (dt, *J* 15.6, 1.2 Hz, 1H), 6.94 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.4 (CH_2), 64.1 (CH_2), 101.1 (CH_2), 106.0 (CH), 109.9 (CH), 116.0 (CH_2), 128.6 (CH), 128.7 (CH), 129.2 (C), 131.4 (C), 137.0 (CH), 146.6 (C), 147.5 (C); MS *m*/*z* 218 (M^+, 100), 200 (20), 173 (80), 160 (44), 149 (23), 115 (48), 103 (19), 83 (73), 77 (12); HRMS (EI) calcd for $C_{13}H_{14}O_3$ (M^+), 218.0943, found 218.0945.

(2*E*)-3-(2′-Allyl-5′-fluorophenyl)prop-2-en-1-ol (15d). The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(2′-allyl-5′-fluorophenyl)prop-2-enoate (**14d**) (0.190 g, 0.812 mmol). This gave (2*E*)-3-(2′-allyl-5′-fluorophenyl)prop-2-en-1-ol (**15d**) (0.144 g, 92%) as a colorless oil. IR (neat) 3300, 2857, 1609, 1582, 1489, 1267, 1155, 964, 912, 870 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.61 (br s, 1H), 3.41 (br d, *J* 6.1 Hz, 2H), 4.34 (td, *J* 5.8, 1.6 Hz, 2H), 4.94 (dq, *J* 17.0, 1.6 Hz, 1H), 5.07 (dq, *J* 10.1, 1.6 Hz, 1H), 5.93 (ddt, *J* 17.0, 10.1, 6.1 Hz, 1H), 6.25 (dt, *J* 15.7, 5.8 Hz, 1H), 6.80 (dq, *J* 15.7, 1.6 Hz, 1H), 6.90 (td, *J* 8.3, 2.7, Hz, 1H), 7.10 (dd, *J* 8.3, 5.9 Hz, 1H), 7.16 (dd, *J* 10.2, 2.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 36.8 (CH_2), 63.7 (CH_2), 112.6 (CH, d, $^2J_{CF}$ 21.9 Hz), 114.6 (CH, d, $^2J_{CF}$ 21.2 Hz), 116.2 (CH_2), 127.7 (CH, d, $^4J_{CF}$ 2.2 Hz), 131.4 (CH, d, $^3J_{CF}$ 8.7 Hz), 131.5 (CH), 132.9 (C, d, $^4J_{CF}$ 3.0 Hz), 136.8 (CH), 137.7 (C, d, $^3J_{CF}$ 7.5 Hz), 161.8 (C, d, $^1J_{CF}$ 243.7 Hz); MS *m*/*z* 175 ($MH^+ - H_2O$, 100), 147 (25), 113 (6), 85 (5), 73 (14); HRMS (CI) calcd for $C_{12}H_{12}F$ ($MH^+ - H_2O$), 175.0923, found 175.0919.

(2*E*)-3-(1′-Allylnaphthalen-2′-yl)prop-2-en-1-ol (15e). The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(1′-allylnaphthalen-2′-yl)prop-2-enoate (**14e**) (0.326 g, 1.23 mmol). This gave (2*E*)-3-(1′-allylnaphthalen-2′-yl)prop-2-en-1-ol (**15e**) (0.256 g, 93%) as a yellow oil. IR (neat) 3320, 3055, 2859, 1636, 1510, 1449, 1373, 1090, 966, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.58 (br s, 1H), 3.92 (dt, *J* 5.5, 1.8 Hz, 2H), 4.40 (d, *J* 5.7, 2H), 4.91 (dq, *J* 17.2, 1.8 Hz, 1H), 5.06 (dq, 10.2, 1.8 Hz, 1H), 6.08 (ddt, *J* 17.2, 10.2, 5.5 Hz, 1H), 6.39 (dt, *J* 15.7, 5.7 Hz, 1H), 7.07 (d, *J* 15.7 Hz, 1H), 7.45 (ddd, *J* 8.0, 7.0, 1.1 Hz, 1H), 7.50 (ddd, *J* 8.4, 7.0, 1.2 Hz, 1H), 7.63 (d, *J* 8.7 Hz, 1H), 7.72 (d, *J* 8.7 Hz, 1H), 7.81 (dd, *J* 8.0, 1.2 Hz, 1H), 8.03 (d, *J* 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 32.3 (CH_2), 64.2 (CH_2), 116.1 (CH_2), 124.5 (CH), 124.6 (CH), 125.6 (CH), 126.4 (CH), 127.2 (CH), 128.6 (CH), 129.4 (CH), 131.2 (CH), 132.5 (C), 132.6 (C), 133.0 (C), 133.5 (C), 136.2 (CH); MS *m*/*z* 247 (MNa^+, 100), 236 (49), 227 (40), 207 (29), 179 (100), 166 (17), 159 (11); HRMS (ESI) calcd for $C_{16}H_{16}NaO$ (MNa^+), 247.1093, found 247.1093.

(2*E*)-3-(2′-Allyl-5′-methoxyphenyl)prop-2-en-1-ol (15f). The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(2′-allyl-5′-methoxyphenyl)prop-2-enoate (**14f**) (0.461 g, 1.87 mmol). This gave (2*E*)-3-(2′-allyl-5′-methoxyphenyl)prop-2-en-1-ol (**15f**) (0.313 g, 82%) as a yellow oil. IR (neat) 3228, 2909, 1605, 1572, 1495, 1285, 1198, 1163, 1040, 964 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.46 (t, *J* 5.3 Hz, 1H), 3.39 (dt, *J* 6.2, 1.7 Hz, 2H), 3.81 (s, 3H), 4.33 (t, *J* 5.3 Hz, 2H), 4.95 (dq, *J* 16.9, 1.7 Hz, 1H), 5.04 (dq, *J* 10.2, 1.7 Hz, 1H), 5.94 (ddt, *J* 16.9, 10.2, 6.2 Hz, 1H), 6.25 (dt, *J* 15.7, 5.3 Hz, 1H), 6.78 (dd, *J* 8.4, 2.8 Hz, 1H), 6.81 (dt, *J* 15.7, 1.6 Hz, 1H), 7.02 (d, *J* 2.8 Hz, 1H), 7.07 (d, *J* 8.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 36.8 (CH_2), 55.4 (CH_3), 64.0 (CH_2), 111.4 (CH), 113.7 (CH), 115.7 (CH_2), 128.9 (CH), 129.7 (C), 130.5 (CH), 131.0 (CH), 136.9 (C), 137.4 (CH), 158.4 (C); MS *m*/*z* 204 (M^+, 74), 173 (100), 159 (74), 158 (73), 115 (53), 103 (18), 91 (23), 77 (13), 51 (10); HRMS (EI) calcd for $C_{13}H_{16}O_2$ (M^+), 204.1150, found 204.1152.

(2*E*)-3-(2′-Allyl-4′-trifluoromethylphenyl)prop-2-en-1-ol (15g). The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(2′-allyl-4′-trifluoromethylphenyl)prop-2-enoate (**14g**) (0.326 g, 1.23 mmol). This gave (2*E*)-3-(2′-allyl-4′-trifluoromethylphenyl)prop-2-en-1-ol (**15g**) (0.256 g, 93%) as a colorless oil. IR (neat) 3320, 2928, 1640, 1616, 1420, 1332, 1160, 1118, 1091 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.98 (br s, 1H), 3.48 (dt, *J* 6.2, 1.5 Hz, 2H), 4.36 (dd, *J* 5.4, 1.6 Hz, 2H), 4.98 (dq, *J* 16.7, 1.5 Hz, 1H), 5.11 (dq, *J* 10.1, 1.5 Hz, 1H), 5.94 (ddt, *J* 16.7, 10.1, 6.2 Hz, 1H), 6.32 (dt, *J* 15.8, 5.4 Hz, 1H), 6.86 (d, *J* 15.8 Hz, 1H), 7.41 (s, 1H), 7.44 (d, *J* 8.2 Hz, 1H), 7.54 (d, *J* 8.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 37.4 (CH_2), 63.6 (CH_2), 116.9 (CH_2), 123.5 (CH, q, $^3J_{CF}$ 3.8 Hz), 124.3 (C, q, $^1J_{CF}$ 272.0 Hz), 126.6 (CH), 126.7 (CH, q, $^3J_{CF}$ 3.8 Hz), 127.2 (CH), 129.7 (C, q, $^2J_{CF}$ 32.3 Hz), 132.8 (CH), 135.9 (CH), 137.9 (C), 139.6 (C); MS *m*/*z* 225 ($MH^+ - H_2O$, 100), 197 (12), 125 (3), 81 (13), 69 (15); HRMS (CI) calcd for $C_{13}H_{12}F_3$ ($MH^+ - H_2O$), 225.0891, found 225.0892.

(2*E*)-3-(3′-Allylfuran-2′-yl)prop-2-en-1-ol (15h). The reaction was carried out according to the previously described procedure for (2*E*)-3-(2′-vinylphenyl)prop-2-en-1-ol (**8a**) using ethyl (2*E*)-3-(3′-allylfuran-2′-yl)prop-2-enoate (**14h**) (0.235 g, 1.14 mmol). This gave (2*E*)-3-(3′-allylfuran-2′-yl)prop-2-en-1-ol (**15h**) (0.180 g, 96%) as a yellow oil. IR (neat) 3323, 2924, 1640, 1499, 1433, 1148, 1092, 1053, 993, 959 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.37−1.44 (m, 1H), 3.20 (br d, *J* 6.3 Hz, 2H), 4.31 (td, *J* 5.6, 1.2 Hz, 2H), 5.02−5.09 (m, 2H), 5.88 (ddt, *J* 16.7, 10.3, 6.3 Hz, 1H), 6.23−6.29 (m, 2H), 6.46 (dt, *J* 15.7, 1.2 Hz, 1H), 7.29 (d, *J* 1.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.2 (CH_2), 63.7 (CH_2), 113.1 (CH), 115.8 (CH_2), 117.6 (CH), 120.6 (C), 126.3 (CH), 136.4 (CH), 141.6 (CH), 148.0 (C); MS *m*/*z* 147 ($MH^+ - H_2O$, 16), 137 (100), 113 (6), 89 (22), 73 (12); HRMS (CI) calcd for $C_{10}H_{11}O$ ($MH^+ - H_2O$), 147.0810, found 147.0807.

1-(2′,2′,2′-Trichloromethylcarbonylamino)-1,4-dihydronaphthalene (16a). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(2′-allylphenyl)prop-2-en-1-ol (**15a**) (0.049 g, 0.28 mmol). The RCM step was performed at room temperature. This gave 1-(2′,2′,2′-trichloromethylcarbonylamino)-1,4-dihydronaphthalene (**16a**) (0.073 g, 89%) as a white solid. Mp 87−89 °C; IR (neat) 3271, 3032, 1682, 1520, 1250, 1018, 826, 741, 648 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.39−3.54 (m, 2H), 5.71−5.77 (m, 1H), 5.93 (ddt, *J* 10.0, 3.6, 2.2 Hz, 1H), 6.20 (dtd, *J* 10.0, 3.6, 1.8 Hz, 1H), 6.83 (br d, *J* 5.7 Hz, 1H), 7.18−7.23 (m, 1H), 7.27−7.31 (m, 2H), 7.37−7.41 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.5 (CH_2), 48.0 (CH), 92.9 (C), 124.4 (CH), 127.3 (CH), 128.1 (CH), 128.4 (CH), 128.6 (CH), 128.7 (CH), 133.2 (C), 134.1 (C), 161.6 (C); HRMS (ESI) calcd for $C_{12}H_{10}{}^{35}Cl_3NNaO$ (MNa^+), 311.9720, found 311.9719.

6-Methyl-1-(2′,2′,2′-trichloromethylcarbonylamino)-1,4-dihydronaphthalene (16b). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(2′-allyl-4′-methylphenyl)prop-2-en-1-ol (**15b**) (0.059 g, 0.31 mmol). The RCM step was performed at room temperature. This gave 6-methyl-1-(2′,2′,2′-trichloromethylcarbonylamino)-1,4-dihydronaphthalene (**16b**) (0.078 g, 82%) as a white solid. Mp 118−122 °C; IR (neat) 3253, 3036, 1685, 1529, 1300, 1249, 1025, 823 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.33−3.49 (m, 2H), 5.65−5.73 (m, 1H), 5.92 (ddt, *J* 10.1, 3.6, 2.2 Hz, 1H), 6.18 (dtd, *J* 10.1, 3.6, 1.8 Hz, 1H), 6.82 (br d, *J* 8.4 Hz, 1H), 7.02 (s, 1H), 7.09 (d, *J* 8.0 Hz, 1H), 7.28 (d, *J* 8.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.2 (CH_3), 29.4 (CH_2), 47.9 (CH), 93.0 (C), 124.4 (CH), 128.2 (CH), 128.3 (CH),

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128.7 (CH), 129.0 (CH), 130.2 (C), 134.0 (C), 137.8 (C), 161.5 (C); MS *m*/*z* 326 (MNa^+, 100), 319 (14), 297 (6), 236 (10), 184 (14), 175 (14), 143 (36), 128 (7); HRMS (ESI) calcd for $C_{13}H_{12}{}^{35}Cl_3NNaO$ (MNa^+), 325.9877, found 325.9864.

6,7-Methylenedioxy-1-(2′,2′,2′-trichloromethylcarbonylamino)-1,4-dihydronaphthalene (16c). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(2′-allyl-4′,5′-methylenedioxy phenyl)prop-2-en-1-ol (**15c**) (1.96 g, 8.99 mmol). Grubbs second generation catalyst (0.114 g, 0.135 mmol) was added, and the reaction mixture was stirred at room temperature for 3 h before a second portion of Grubbs second generation catalyst (0.0763 g, 0.0899 mmol) was added and allowed to stir for a further 17 h. This gave 6,7-methylenedioxy-1-(2′,2′,2′-trichloromethylcarbonylamino)-1,4-dihydronaphthalene (**16c**) (2.43 g, 81%) as a white solid. Mp 114−116 °C; IR (neat) 3334, 2894, 1699, 1502, 1482, 1233, 1038, 819 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.24−3.39 (m, 2H), 5.53−5.60 (m, 1H), 5.85 (ddt, *J* 10.0, 3.9, 2.2 Hz, 1H), 5.88 (d, *J* 1.3 Hz, 1H), 5.89 (d, *J* 1.3 Hz, 1H), 6.13 (dtd, *J* 10.0, 3.5, 1.7 Hz, 1H), 6.55 (s, 1H), 6.75 (s, 1H), 6.87 (d, *J* 8.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.6 (CH_2), 48.2 (CH), 92.8 (C), 101.1 (CH_2), 107.5 (CH), 107.7 (CH), 123.8 (CH), 125.9 (C), 127.6 (C), 128.5 (CH), 146.8 (C), 147.5 (C), 161.4 (C); MS *m*/*z* 356 (MNa^+, 85), 346 (7), 242 (100), 236 (14), 184 (18), 173 (18), 142 (4); HRMS (ESI) calcd for $C_{13}H_{10}{}^{35}Cl_3NNaO_3$ (MNa^+), 355.9618, found 355.9602.

7-Fluoro-1-(2′,2′,2′-trichloromethylcarbonylamino)-1,4-dihydronaphthalene (16d). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(2′-allyl-5′-fluorophenyl)-prop-2-en-1-ol (**15d**) (0.053 g, 0.28 mmol). The RCM step was performed at room temperature. This gave 7-fluoro-1-(2′,2′,2′-trichloromethylcarbonylamino)-1,4-dihydronaphthalene (**16d**) (0.076 g, 76%) as a white solid. Mp 123−127 °C; IR (neat) 3268, 3040, 1687, 1503, 1249, 1226, 1023, 815 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.34−3.50 (m, 2H), 5.66−5.73 (m, 1H), 5.80 (ddt, *J* 10.1, 3.5, 1.9 Hz, 1H), 6.21 (dtd, *J* 10.1, 3.6, 1.9 Hz, 1H), 6.84 (br d, *J* 6.2 Hz, 1H), 6.99 (td, *J* 8.3, 2.6, Hz, 1H), 7.09 (dd, *J* 9.6, 2.6 Hz, 1H), 7.17 (dd, *J* 8.3, 5.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 28.9 (CH_2), 48.0 (CH, d, $^4J_{CF}$ 1.4 Hz), 92.8 (C), 114.5 (CH, d, $^2J_{CF}$ 21.6 Hz), 115.6 (CH, d, $^2J_{CF}$ 21.6 Hz), 123.8 (CH), 128.8 (CH), 129.7 (C, d, $^4J_{CF}$ 3.1 Hz), 130.2 (CH, d, $^3J_{CF}$ 7.8 Hz), 135.1 (C, d, $^3J_{CF}$ 7.0 Hz), 161.7 (C), 161.8 (C, d, $^1J_{CF}$ 245.5 Hz); HRMS (ESI) calcd for $C_{12}H_9{}^{35}Cl_2{}^{37}ClFNNaO$ (MNa^+), 331.9597, found 331.9588.

1-(2′,2′,2′-Trichloromethylcarbonylamino)-1,4-dihydrophenanthrene (16e). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(1′-allylnaphthalen-2′-yl)-prop-2-en-1-ol (**15e**) (0.059 g, 0.31 mmol). The RCM step was performed at room temperature. This gave 1-(2′,2′,2′-trichloromethylcarbonylamino)-1,4-dihydrophenanthrene (**16e**) (0.081 g, 84%) as a white solid. Mp 150−152 °C (decomposition); IR (neat) 3250, 3042, 1678, 1510, 1308, 1248, 1020, 818 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.72−3.89 (m, 2H), 5.87−5.94 (m, 1H), 6.04 (ddt, *J* 10.0, 3.6, 2.5 Hz, 1H), 6.37 (dtd, *J* 10.0, 3.6, 1.6 Hz, 1H), 6.85 (d, *J* 8.3 Hz, 1H), 7.46 (d, *J* 8.5 Hz, 1H), 7.52−7.61 (m, 2H), 7.79 (d, *J* 8.5 Hz, 1H), 7.86 (dd, *J* 8.1, 0.9 Hz, 1H), 7.98 (d, *J* 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) 26.8 (CH_2), 48.7 (CH), 92.9 (C), 123.4 (CH), 123.7 (CH), 126.0 (CH), 126.4 (CH), 126.8 (CH), 128.0 (CH), 128.4 (CH), 128.7 (CH), 129.7 (C), 130.1 (C), 131.3 (C), 133.0 (C), 161.6 (C); MS *m*/*z* 362 (MNa^+, 56), 320 (61), 307 (10), 301 (7), 242 (7), 179 (100), 141 (3); HRMS (ESI) calcd for $C_{16}H_{12}{}^{35}Cl_3NNaO$ (MNa^+), 361.9877, found 361.9866.

7-Methoxy-1-(2′,2′,2′-trichloromethylcarbonylamino)-1,4-dihydronaphthalene (16f). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(2′-allyl-5′-methoxyphenyl)prop-2-en-1-ol (**15f**) (0.052 g, 0.26 mmol). The RCM step was performed at room temperature. This gave 7-methoxy-1-(2′,2′,2′-trichloromethylcarbonylamino)-1,4-dihydronaphthalene (**16f**) (0.063 g, 76%) as a white solid. Mp 92−96 °C; IR (neat) 3293, 2935, 1704, 1613, 1501, 1261, 1241, 1033, 1021, 816 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.31−3.46 (m, 2H), 3.77 (s, 3H), 5.67−5.74 (m, 1H), 5.89 (ddt, *J* 10.1, 3.6, 2.3 Hz, 1H), 6.20 (dtd, *J* 10.1, 3.6, 1.8 Hz, 1H), 6.86 (dd, *J* 8.4, 3.0 Hz, 1H), 6.87−6.91 (m, 2H), 7.10 (d, *J* 8.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 28.7 (CH_2), 48.3 (CH_3), 55.5 (CH), 92.9 (C), 111.8 (CH), 115.4 (CH), 123.9 (CH), 126.1 (C), 129.1 (CH), 129.6 (CH), 134.1 (C), 158.6 (C), 161.6 (C); MS *m*/*z* 342 (MNa^+, 100), 319 (83), 307 (7), 297 (6), 236 (10), 218 (6), 184 (11), 159 (22), 144 (4); HRMS (ESI) calcd for $C_{13}H_{12}{}^{35}Cl_3NNaO_2$ (MNa^+), 341.9826, found 341.9811.

1-(2′,2′,2′-Trichloromethylcarbonylamino)-6-trifluoromethyl-1,4-dihydronaphthalene (16g). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(2′-allyl-4′-trifluoromethylphenyl)prop-2-en-1-ol (**15g**) (0.061 g, 0.25 mmol). Grubbs second generation catalyst (0.011 g, 0.013 mmol) was added, and the reaction mixture was stirred at 50 °C for 24 h before a second portion of Grubbs second generation catalyst (0.011 g, 0.013 mmol) was added and allowed to stir at 50 °C for a further 24 h. This gave 1-(2′,2′,2′-trichloromethylcarbonylamino)-6-trifluoromethyl-1,4-dihydronaphthalene (**16g**) (0.065 g, 72%) as a colorless oil. IR (neat) 3268, 2924, 1684, 1525, 1329, 1160, 1119, 822 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.43−3.59 (m, 2H), 5.74−5.80 (m, 1H), 5.94 (ddt, *J* 10.0, 3.5, 2.0 Hz, 1H), 6.24 (dtd, *J* 10.0, 3.5, 1.5 Hz, 1H), 6.86 (d, *J* 8.3 Hz, 1H), 7.47 (s, 1H), 7.51−7.53 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.3 (CH_2), 47.5 (CH), 92.6 (C), 123.9 (CH, q, $^3J_{CF}$ 3.6 Hz), 124.0 (C, q, $^1J_{CF}$ 272.3 Hz), 124.0 (CH), 125.6 (CH, q, $^3J_{CF}$ 3.8 Hz), 128.4 (CH), 128.9 (CH), 130.4 (C, q, $^2J_{CF}$ 32.5 Hz), 134.7 (C), 137.0 (C), 161.6 (C); MS *m*/*z* 380 (MNa^+, 100), 301 (19), 236 (26), 199 (3), 136 (2); HRMS (ESI) calcd for $C_{13}H_9{}^{35}Cl_3F_3NNaO$ (MNa^+), 379.9594, found 379.9581.

7-(2′,2′,2′-Trichloromethylcarbonylamino)-4,7-dihydrobenzo[*b*]furan (16h). The reaction was carried out according to the previously described procedure for 1-(2′,2′,2′-trichloromethylcarbonylamino)-1*H*-indene (**11a**) using (2*E*)-3-(3′-allylfuran-2′-yl)prop-2-en-1-ol (**15h**) (0.055 g, 0.33 mmol). The RCM step was performed at room temperature. This gave 7-(2′,2′,2′-trichloromethylcarbonylamino)-4,7-dihydrobenzo[*b*]furan (**16h**) (0.052 g, 72%) as a white solid. Mp 102−104 °C; IR (neat) 3275, 2886, 1686, 1517, 1244, 1036, 821 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.14−3.28 (m, 2H), 5.66−5.73 (m, 1H), 5.88 (ddt, *J* 9.9, 3.7, 2.1 Hz, 1H), 6.14 (dtd, *J* 9.9, 3.4, 1.7 Hz, 1H), 6.32 (d, *J* 1.9 Hz, 1H), 6.73 (br s, 1H), 7.41 (d, *J* 1.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 25.1 (CH_2), 44.8 (CH), 92.7 (C), 109.6 (CH), 118.4 (C), 123.7 (CH), 129.2 (CH), 143.0 (CH), 145.3 (C), 161.5 (C); MS *m*/*z* 302 (MNa^+, 100), 236 (10), 218 (2), 184 (10); HRMS (ESI) calcd for $C_{10}H_8{}^{35}Cl_3NNaO_2$ (MNa^+), 301.9513, found 301.9512.

6,7-Methylenedioxy-1-(2′,2′,2′-trichloromethylcarbonylamino)naphthalene (17). Manganese(IV) oxide (0.521 g, 5.99 mmol) was added to a solution of 6,7-methylenedioxy-1-(2′,2′,2′-trichloromethylcarbonylamino)-1,4-dihydronaphthalene (**16c**) (0.200 g, 0.597 mmol) in chloroform (6 mL) and heated at 45 °C for 20 h. The crude reaction mixture was filtered through a short pad of Celite with chloroform (100 mL) and then concentrated *in vacuo*. Purification by column chromatography (elution with 100% toluene) yielded 6,7-methylenedioxy-1-(2′,2′,2′-trichloromethylcarbonylamino)naphthalene (**17**) (0.143 g, 72%) as a white solid. Further elution gave 6,7-methylenedioxy-1,4-naphthoquinone (**18**) (0.019 g, 16%) as an orange solid. Data for **17**: Mp 139−140 °C; IR (neat) 3302, 2913, 1686, 1489, 1462, 1242, 1034, 849, 814 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.05 (s, 2H), 7.05 (s, 1H), 7.13 (s, 1H), 7.32 (t, *J* 7.9 Hz, 1H), 7.55 (d, *J* 7.9 Hz, 1H), 7.60 (d, *J* 7.9 Hz, 1H), 8.46 (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 93.1 (C), 97.6 (CH), 101.6 (CH_2), 104.8 (CH), 121.4 (CH), 124.2 (CH), 125.3 (C), 127.0 (CH), 130.0 (C), 131.6 (C), 148.1 (C), 148.9 (C), 160.6 (C); MS *m*/*z* 354 (MNa^+, 100), 301 (3), 236 (7), 227 (4), 159 (1); HRMS (ESI) calcd for $C_{13}H_8{}^{35}Cl_3NNaO_3$ (MNa^+), 353.9462, found 353.9452. Data for **18**: Mp 196−200 °C; IR (neat) 2928, 1655, 1586, 1485, 1316, 1026, 976, 833 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.14 (s, 2H), 6.88 (s, 2H), 7.45 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

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102.6 (CH_2), 105.9 (CH), 129.0 (C), 138.2 (CH), 152.3 (C), 184.0 (C); MS *m*/*z* 202 (M^+, 100), 174 (37), 148 (22), 120 (29), 105 (20), 84 (41), 77 (19), 62 (24); HRMS (EI) calcd for $C_{11}H_6O_4$ (M^+), 202.0266, found 202.0264.

6,7-Methylenedioxy-1-aminonaphthalene (19).[41] Hydrochloric acid (6 M, 15 mL) was added to a solution of 6,7-methylenedioxy-1-(2′,2′,2′-trichloromethylcarbonylamino)-naphthalene (**17**) (0.330 g, 0.991 mmol) in methanol (20 mL) and heated with stirring to 90 °C for 60 h. The reaction mixture was cooled to room temperature and washed with dichloromethane (2 × 10 mL). The aqueous layer was basified to pH ≈ 10 with 12 M sodium hydroxide solution and extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo* to yield 6,7-methylenedioxy-1-aminonaphthalene (**19**) (0.182 g, 98%) as a white solid. Mp 151−152 °C (lit.[41] 151−153 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.85 (s, 2H), 6.03 (s, 2H), 6.69 (dd, *J* 6.6, 1.9 Hz, 1H), 7.09 (s, 1H), 7.13 (s, 1H), 7.14−7.18 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 97.9 (CH), 101.2 (CH_2), 104.8 (CH), 109.7 (CH), 118.9 (CH), 120.3 (C), 125.0 (CH), 131.7 (C), 141.5 (C), 147.3 (C), 147.6 (C); MS (ESI) *m*/*z* 188 (MH^+, 100), 158 (26), 146 (10), 130 (78).

6-Bromo-2,3-dimethoxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (21a).[7c] 6-Bromo-2,3-dimethoxybenzoic acid (0.024 g, 0.10 mmol) was suspended in thionyl chloride (0.5 mL) and heated with stirring to 65 °C for 1 h. The reaction mixture was cooled and concentrated *in vacuo* to yield the acid chloride **20a**, which was used without further purification. In a second flask, *N*,*N*-diisopropylethylamine (0.14 mL, 0.80 mmol) was added to a solution of 6,7-methylenedioxy-1-aminonaphthalene (**19**) (0.015 g, 0.080 mmol) in dichloromethane (0.4 mL) and cooled to 0 °C. Acid chloride **20a** was dissolved in dichloromethane (0.4 mL) and added dropwise to the cooled, stirring solution of amines. The reaction mixture was stirred at 0 °C for 1 h and then allowed to return to room temperature over 1 h. The reaction was quenched with 1 M hydrochloric acid (1 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with a saturated solution of sodium hydrogen carbonate (20 mL) and then brine (30 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting solid was washed with a minimal volume of ice cold chloroform to yield 6-bromo-2,3-dimethoxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**21a**) (0.031 g, 89%) as a white solid. Mp 227−229 °C (lit.[7c] 237.5−239 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (s, 3H), 3.98 (s, 3H), 6.05 (s, 2H), 6.88 (d, *J* 8.8 Hz, 1H), 7.15 (s, 1H), 7.34 (d, *J* 8.8 Hz, 1H), 7.38 (t, *J* 7.8 Hz, 1H), 7.47−7.52 (m, 2H), 7.61 (d, *J* 7.8 Hz, 1H), 7.69 (d, *J* 7.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.3 (CH_3), 62.5 (CH_3), 99.0 (CH), 101.4 (CH_2), 104.5 (CH), 110.0 (C), 114.6 (CH), 122.1 (CH), 124.4 (CH), 126.3 (C), 126.4 (CH), 128.6 (CH), 131.4 (C), 131.7 (C), 134.2 (C), 147.2 (C), 148.0 (C), 148.7 (C), 152.5 (C), 164.8 (C); MS (ESI) *m*/*z* 452 (MNa^+, 100), 430 (1), 413 (3), 243 (1).

6-Bromo-2,3-methylenedioxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (21b). The reaction was carried out according to the previously described procedure for 6-bromo-2,3-dimethoxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**21a**) using 6-bromo-2,3-methylenedioxybenzoic acid (0.13 g, 0.51 mmol) and 6,7-methylenedioxy-1-aminonaphthalene (**19**) (0.080 g, 0.43 mmol). This gave 6-bromo-2,3-methylenedioxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**21b**) (0.16 g, 89%) as a white solid. Mp 236−238 °C; IR (neat) 3237, 2905, 1655, 1543, 1493, 1451, 1238, 1038, 926, 849 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.15 (s, 2H), 6.22 (s, 2H), 7.01 (d, *J* 8.3 Hz, 1H), 7.20 (d, *J* 8.3 Hz, 1H), 7.36 (t, *J* 7.6 Hz, 1H), 7.37 (s, 1H), 7.46 (s, 1H), 7.47 (d, *J* 7.6 Hz, 1H), 7.67 (d, *J* 7.6 Hz, 1H), 10.52 (s, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 99.3 (CH), 101.4 (CH_2), 102.6 (CH_2), 103.9 (CH), 110.0 (C), 110.2 (CH), 121.3 (C), 121.5 (CH), 123.9 (CH), 125.2 (CH), 125.4 (CH), 125.4 (C), 131.1 (C), 132.1 (C), 145.7 (C), 147.2 (C), 147.4 (C), 147.7 (C), 162.2 (C); MS *m*/*z* 436 (MNa^+, 98), 413 (13), 335 (13), 289 (3), 236 (8), 159 (6); HRMS (ESI) calcd for $C_{19}H_{12}{}^{79}BrNNaO_5$ (MNa^+), 435.9791, found 435.9792.

2-Bromo-4,5-dimethoxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (21c).[42] The reaction was carried out according to the previously described procedure for 6-bromo-2,3-dimethoxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**21a**) using 2-bromo-4,5-dimethoxybenzoic acid (0.084 g, 0.32 mmol) and 6,7-methylenedioxy-1-aminonaphthalene (**19**) (0.050 g, 0.27 mmol). This gave 2-bromo-4,5-dimethoxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**21c**) (0.10 g, 88%) as a white solid. Mp 249−251 °C (lit.[42] 250−252 °C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.84 (s, 3H), 3.85 (s, 3H), 6.15 (s, 2H), 7.25 (s, 1H), 7.28 (s, 1H), 7.36 (t, *J* 7.7 Hz, 1H), 7.36 (s, 1H), 7.49 (s, 1H), 7.54 (d, *J* 7.7 Hz, 1H), 7.65 (d, *J* 7.7 Hz, 1H), 10.22 (s, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 56.0 (CH_3), 56.1 (CH_3), 99.8 (CH), 101.3 (CH_2), 103.8 (CH), 109.6 (C), 112.4 (CH), 115.7 (CH), 121.6 (CH), 123.9 (CH), 125.2 (CH), 125.6 (C), 131.1 (C), 131.1 (C), 132.8 (C), 147.3 (C), 147.6 (C), 148.0 (C), 150.1 (C), 166.4 (C); MS (ESI) *m*/*z* 452 (MNa^+, 100), 413 (6), 381 (10), 353 (10), 301 (3), 236 (3).

2-Bromo-4,5-methylenedioxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (21d). The reaction was carried out according to the previously described procedure for 6-bromo-2,3-dimethoxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**21a**) using 2-bromo-4,5-methylenedioxybenzoic acid (0.031 g, 0.13 mmol) and 6,7-methylenedioxy-1-aminonaphthalene (**19**) (0.020 g, 0.11 mmol). This gave 2-bromo-4,5-methylenedioxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**21d**) (0.039 g, 89%) as a white solid. Mp 236−238 °C; IR (neat) 3233, 2909, 1659, 1543, 1462, 1238, 1038, 934, 849 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.15 (s, 2H), 6.16 (s, 2H), 7.31−7.38 (m, 4H), 7.48 (s, 1H), 7.52 (d, *J* 7.7 Hz, 1H), 7.65 (d, *J* 7.7 Hz, 1H), 10.24 (s, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 99.7 (CH), 101.3 (CH_2), 102.3 (CH_2), 103.8 (CH), 108.9 (CH), 110.2 (C), 112.5 (CH), 121.6 (CH), 123.8 (CH), 125.2 (CH), 125.6 (C), 131.0 (2 × C), 132.6 (C), 146.9 (C), 147.3 (C), 147.6 (C), 148.8 (C), 166.2 (C); MS *m*/*z* 436 (MNa^+, 100), 413 (8), 370 (4), 236 (7), 227 (8), 198 (3); HRMS (ESI) calcd for $C_{19}H_{12}{}^{79}BrNNaO_5$ (MNa^+), 435.9791, found 435.9775.

6-Bromo-2,3-dimethoxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (22a).[7c] Sodium hydride (60% dispersion in mineral oil, 0.020 g, 0.51 mmol) was washed with hexane (3 × 3 mL) under argon and dried under reduced pressure. *N*,*N*′-Dimethylformamide (1 mL) was added to the sodium hydride followed slowly by a solution of 6-bromo-2,3-dimethoxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**21a**) (0.087 g, 0.20 mmol) in *N*,*N*′-dimethylformamide (1 mL). The reaction mixture was stirred at room temperature for 0.1 h, then methyl iodide (0.044 mL, 0.71 mmol) was added dropwise with vigorous stirring, and the mixture was stirred for 18 h at room temperature. The reaction was quenched by the slow addition of 1 M hydrochloric acid solution (3 mL), diluted with 5% lithium chloride solution (3 mL), and extracted with diethyl ether (3 × 5 mL). The combined organic layers were washed with brine (3 × 10 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude product was washed with cold hexane (5 × 1 mL), to yield 6-bromo-2,3-dimethoxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**22a**) (0.088 g, 98%) as a white solid. Mp 173−175 °C (lit.[7c] mp 178−179 °C); the NMR spectra showed the presence of rotomers; for simplification, only signals for the major rotomer are reported: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.20 (s, 3H), 3.93 (s, 3H), 4.03 (s, 3H), 6.04 (d, *J* 1.5 Hz, 1H), 6.05 (d, *J* 1.5 Hz, 1H), 6.87 (d, *J* 9.0 Hz, 1H), 7.17 (s, 1H), 7.34 (d, *J* 9.0 Hz, 1H), 7.38−7.42 (m, 1H), 7.44−7.48 (m, 1H), 7.53 (s, 1H), 7.64−7.69 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 39.6 (CH_3), 56.2 (CH_3), 61.9 (CH_3), 99.7 (CH), 101.3 (CH_2), 104.5 (CH), 109.4 (C), 114.0 (CH), 123.6 (CH), 124.7 (CH), 127.4 (CH), 128.2 (C), 128.5 (CH), 131.8 (C), 132.2 (C), 134.0 (C), 138.8 (C), 146.0 (C), 149.1 (C), 152.6 (C), 166.9 (C); MS (ESI) *m*/*z* 466 (MNa^+, 100), 446 (1), 243 (1), 227 (1).

6-Bromo-2,3-methylenedioxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (22b). The reaction was carried out according to the previously described procedure for 6-bromo-2,3-dimethoxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)-benzamide (**22a**) using 6-bromo-2,3-methylenedioxy-*N*-(6′,7′-methyl-

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enedioxynaphthalen-1-yl)benzamide (**21b**) (0.140 g, 0.338 mmol). This gave 6-bromo-2,3-methylenedioxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**22b**) (0.138 g, 95%) as a white solid. Mp 161−163 °C; IR (neat) 2901, 1651, 1462, 1447, 1373, 1246, 1038, 934 cm^{-1}; the NMR spectra showed the presence of rotomers; for simplification, only signals for the major rotomer are reported: ^1H NMR (500 MHz, $CDCl_3$) δ 3.52 (s, 3H), 5.13 (d, *J* 1.5 Hz, 1H), 5.79 (d, *J* 1.5 Hz, 1H), 6.04 (d, *J* 1.0 Hz, 1H), 6.08 (d, *J* 1.0 Hz, 1H), 6.36 (d, *J* 8.0 Hz, 1H), 6.82 (d, *J* 8.0 Hz, 1H), 7.07 (s, 1H), 7.13−7.17 (m, 1H), 7.34 (s, 1H), 7.51−7.55 (m, 1H), 7.66−7.71 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 37.3 (CH_3), 100.6 (CH), 101.4 (CH_2), 101.6 (CH_2), 104.3 (CH), 109.4 (CH), 111.2 (C), 121.1 (C), 124.2 (2 × CH), 125.3 (CH), 125.8 (C), 127.9 (CH), 138.7 (C), 144.9 (C), 146.6 (C), 146.7 (C), 147.9 (C), 148.1 (C), 165.7 (C); MS *m*/*z* 450 (MNa^+, 98), 430 (1), 413 (6), 236 (1), 227 (1); HRMS (ESI) calcd for $C_{20}H_{14}{}^{79}BrNNaO_5$ (MNa^+), 449.9948, found 449.9935.

2-Bromo-4,5-dimethoxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (22c).[42] The reaction was carried out according to the previously described procedure for 6-bromo-2,3-dimethoxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**22a**) using 2-bromo-4,5-dimethoxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**21c**) (0.085 g, 0.20 mmol). This gave 2-bromo-4,5-dimethoxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**22c**) (0.083 g, 94%) as a white solid. Mp 182−184 °C (lit.[42] 186−187 °C); the NMR spectra showed the presence of rotomers; for simplification, only signals for the major rotomer are reported: ^1H NMR (500 MHz, $CDCl_3$) δ 3.32 (s, 3H), 3.52 (s, 3H), 3.71 (s, 3H), 6.07 (s, 2H), 6.46 (s, 1H), 6.79 (s, 1H), 7.09 (s, 1H), 7.13 (dd, *J* 8.1, 7.5 Hz, 1H), 7.29 (dd, *J* 7.5, 1.1 Hz, 1H), 7.31 (s, 1H), 7.49 (br d, *J* 8.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 37.2 (CH_3), 55.6 (CH_3), 56.1 (CH_3), 99.2 (CH), 101.6 (CH_2), 104.9 (CH), 110.6 (CH), 110.8 (C), 115.4 (CH), 124.4 (2 × CH), 127.5 (C), 127.7 (CH), 130.2 (C), 131.8 (C), 139.4 (C), 147.2 (C), 148.0 (C), 149.1 (C), 149.5 (C), 169.7 (C); MS (ESI) *m*/*z* 466 (MNa^+, 100), 413 (1), 381 (4), 353 (4), 236 (2).

2-Bromo-4,5-methylenedioxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (22d). The reaction was carried out according to the previously described procedure for 6-bromo-2,3-dimethoxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**22a**) using 2-bromo-4,5-methylenedioxy-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**21d**) (0.010 g, 0.024 mmol). This gave 2-bromo-4,5-methylenedioxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**22d**) (0.010 g, 98%) as a white solid. Mp 193−196 °C; IR (neat) 2916, 1636, 1462, 1242, 1026, 934, 860 cm^{-1}; the NMR spectra showed the presence of rotomers; for simplification, only signals for the major rotomer are reported: ^1H NMR (500 MHz, $CDCl_3$) δ 3.48 (s, 3H), 5.74 (d, *J* 1.3 Hz, 1H), 5.78 (d, *J* 1.3 Hz, 1H), 6.08 (d, *J* 1.1 Hz, 1H), 6.11 (d, *J* 1.1 Hz, 1H), 6.42 (s, 1H), 6.80 (s, 1H), 7.09 (s, 1H), 7.15 (dd, *J* 8.1, 7.5 Hz, 1H), 7.24 (s, 1H), 7.34 (dd, *J* 7.5, 1.0 Hz, 1H), 7.51 (br d, *J* 8.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 37.2 (CH_3), 99.0 (CH), 101.5 (CH_2), 101.7 (CH_2), 104.6 (CH), 107.1 (CH), 111.5 (C), 112.9 (CH), 124.0 (CH), 124.2 (CH), 127.2 (C), 127.6 (CH), 131.5 (C), 131.7 (C), 139.0 (C), 146.3 (C), 148.1 (C), 148.3 (C), 149.1 (C), 169.3 (C); MS *m*/*z* 450 (MNa^+, 100), 413 (4), 301 (7), 257 (1), 236 (4), 199 (3); HRMS (ESI) calcd for $C_{20}H_{14}{}^{79}BrNNaO_5$ (MNa^+), 449.9948, found 449.9935.

Oxychelerythrine (1).[6g] 6-Bromo-2,3-dimethoxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**22a**) (0.020 g, 0.045 mmol), *trans*-bis(acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]-dipalladium(II) (**23**) (0.0042 g, 0.0045 mmol), and silver carbonate (0.025 g, 0.090 mmol) were combined with a stirrer bar in a sealed tube and placed under argon. Degassed *N*,*N*′-dimethylformamide (1.2 mL) was added, and the tube was sealed, heated to 160 °C for 22 h, and then cooled to room temperature. The reaction mixture was diluted with diethyl ether (4 mL) and filtered. The filtrate was then further diluted with diethyl ether (10 mL), washed with 5% lithium chloride solution (3 × 15 mL) and brine (15 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography (elution with 40% ethyl acetate in petroleum ether) and then washing the resulting solid with hexane (3 × 1 mL) yielded oxychelerythrine (**1**) (0.016 g, 95%) as a white solid. Mp 194−197 °C (lit.[6g] 198−200 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 3.89 (s, 3H), 3.98 (s, 3H), 4.08 (s, 3H), 6.09 (s, 2H), 7.15 (s, 1H), 7.38 (d, *J* 9.0 Hz, 1H), 7.52 (d, *J* 9.0 Hz, 1H), 7.53 (s, 1H), 7.98 (d, *J* 9.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.9 (CH_3), 56.8 (CH_3), 61.9 (CH_3), 101.6 (CH_2), 102.6 (CH), 104.8 (CH), 117.3 (C), 117.9 (CH), 118.0 (CH), 118.6 (CH), 119.9 (C), 121.2 (C), 123.4 (CH), 129.1 (C), 131.8 (C), 135.8 (C), 147.2 (C), 147.6 (C), 150.3 (C), 152.9 (C), 162.8 (C); MS (ESI) *m*/*z* 386 (MNa^+, 100), 371 (4), 227 (6).

Oxysanguinarine (2).[6g] The reaction was carried out according to the previously described procedure for the synthesis of oxychelerythrine (**1**) using 6-bromo-2,3-methylenedioxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**22b**) (0.020 g, 0.047 mmol). The reaction was complete after 3 h. Purification by column chromatography (20−100% ethyl acetate in petroleum ether, then 1% methanol in dichloromethane) and then washing the resulting solid with hexane (3 × 1 mL) gave oxysanguinarine (**2**) (0.015 g, 90%) as a white solid. Mp 356−358 °C (lit.[6g] 361−363 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 3.91 (s, 3H), 6.10 (s, 2H), 6.27 (s, 2H), 7.16 (s, 1H), 7.24 (d, *J* 8.7 Hz, 1H), 7.53 (d, *J* 8.7 Hz, 1H), 7.57 (s, 1H), 7.76 (d, *J* 8.7 Hz, 1H), 7.98 (d, *J* 8.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.0 (CH_3), 101.7 (CH_2), 102.7 (CH), 103.0 (CH_2), 104.9 (CH), 111.1 (C), 113.3 (CH), 115.6 (CH), 117.4 (C), 118.9 (CH), 121.3 (C), 123.7 (CH), 129.0 (C), 132.0 (C), 135.7 (C), 147.3 (C), 147.7 (C), 147.8 (C), 147.9 (C), 162.8 (C); MS (ESI) *m*/*z* 370 (MNa^+, 100), 354 (3), 342 (3), 236 (6), 227 (1).

Oxynitidine (3).[6g] The reaction was carried out according to the previously described procedure for the synthesis of oxychelerythrine (**1**) using 2-bromo-4,5-dimethoxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**22c**) (0.019 g, 0.043 mmol) and *trans*-bis(acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (**23**) (0.0080 g, 0.0086 mmol). Purification was performed by washing with hexane (5 × 2 mL) and then ice-cold diethyl ether (3 × 1 mL), which yielded oxynitidine (**3**) (0.013 g, 83%) as a white solid. Mp 268−270 °C (lit.[6g] 270−272 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 3.99 (s, 3H), 4.06 (s, 3H), 4.11 (s, 3H), 6.11 (s, 2H), 7.19 (s, 1H), 7.57 (d, *J* 8.7 Hz, 1H), 7.60 (s, 1H), 7.65 (s, 1H), 7.93 (s, 1H), 8.00 (d, *J* 8.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.4 (CH_3), 56.3 (CH_3), 56.4 (CH_3), 101.7 (CH_2), 102.8 (CH), 103.0 (CH), 104.9 (CH), 108.8 (CH), 116.9 (C), 118.5 (CH), 119.4 (C), 121.2 (C), 123.4 (CH), 129.1 (C), 132.0 (C), 136.1 (C), 147.2 (C), 147.7 (C), 149.9 (C), 153.7 (C), 164.4 (C); MS (EI) *m*/*z* 363 (M^+, 100), 334 (17), 305 (15), 290 (8), 262 (9), 182 (10), 84 (11).

Oxyavicine (4).[6g] The reaction was carried out according to the previously described procedure for the synthesis of oxychelerythrine (**1**) using 2-bromo-4,5-methylenedioxy-*N*-methyl-*N*-(6′,7′-methylenedioxynaphthalen-1-yl)benzamide (**22d**) (0.040 g, 0.093 mmol) and *trans*-bis(acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (**23**) (0.017 g, 0.019 mmol). Purification was performed by washing with hexane (5 × 2 mL) and then ice-cold diethyl ether (3 × 1 mL), which yielded oxyavicine (**4**) (0.025 g, 78%) as a white solid. Mp 265−268 °C (lit.[6g] 271−273 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 3.97 (s, 3H), 6.10 (s, 2H), 6.13 (s, 2H), 7.17 (s, 1H), 7.54 (d, *J* 8.8 Hz, 1H), 7.60 (s, 1H), 7.62 (s, 1H), 7.89 (s, 1H), 7.92 (d, *J* 8.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.4 (CH_3), 100.8 (CH), 101.7 (CH_2), 102.1 (CH_2), 102.8 (CH), 104.9 (CH), 106.8 (CH), 117.0 (C), 118.7 (CH), 121.0 (C), 121.1 (C), 123.4 (CH), 131.2 (C), 132.1 (C), 136.0 (C), 147.2 (C), 147.7 (C), 148.3 (C), 152.6 (C), 164.2 (C); MS *m*/*z* (ESI) 370 (MNa^+, 49), 357 (57), 343 (100), 321 (6), 236 (6).

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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