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Mild Double Allylboration Reactions of Nitriles and Acid Anhydrides Using Potassium Allyltrifluoroborate

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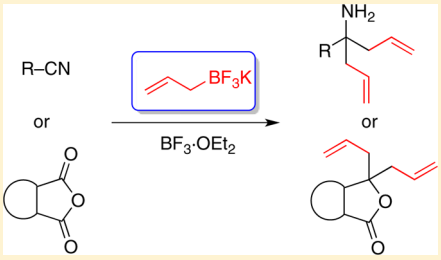
Supporting Information

ABSTRACT: The double allylboration of nitriles and acid anhydrides to form bisallyl amines and esters, respectively, can be achieved through the use of potassium allyltrifluoroborate in the presence of boron trifluoride etherate at room temperature. The method described is relatively mild, exhibits chemoselectivity to other electrophiles present, avoids the use of metals, and features the use of an operationally stable and robust potassium organotrifluoroborate reagent.



The double allylation of electrophiles at the carboxyl oxidation state provides a manner to access bisallylic compounds. These substrates can form the basis to obtain synthetically interesting compounds, including spirocycles through ring closing metathesis (RCM).[1] Typically, functionalities in the carboxyl oxidation state are intrinsically less reactive toward nucleophilic attack than functional groups at the carbonyl oxidation state, such as aldehydes, ketones, and imines, due to heteroatomic mesomeric stabilization of the electrophilic carboxylate center, or through additional π-electron stabilization as observed in nitriles. As a result, methods to allylate functional groups such as nitriles and acid anhydrides typically involve the overstoichiometric use of reactive allyl metal species, including Grignard reactions,[2] Grignard-type conditions using samarium,[3,4] indium,[5] or zinc,[6] or Barbier reactions using aluminum/lead,[7] zinc/copper,[8] or indium.[9,10]

It was envisaged that allylboration could afford a mild, inexpensive, and environmentally benign metal-free method to allylate nitriles and acid anhydrides, especially for substrates with functional groups that may not be tolerant of metal-based allylating reagents. The allylboration of acid anhydrides was investigated by Kramer and Brown using the sensitive *B*-allyl-9-BBN reagent.[11] Additionally, the allylboration of nitriles has been reported by Bubnov and co-workers;[12] however, the method employs triallylborane, which is inconvenient to use, and required forcing thermal conditions to form the diaza-2,4-diboretidine product, which could presumably be further reacted to furnish the bisallylamine. While operationally simpler organoboronic ester derivatives can be used for the allylation of carbonyl[13] and imine[13f,14] compounds, to the best of our knowledge, there is no precedence for the direct implementation of these reagents toward the allylation of nitriles or acid anhydrides. Our laboratory has previously demonstrated that potassium allyltrifluoroborate (allyl-BF_3K) and related salts[15] act as surrogates for allylboronic acids and esters, achieving the mild and selective allylation of aldehydes and ketones[16] or imines.[17] More recently, allyl-BF_3K has been shown to allylate the C2 position of indoles in very good yields.[18] Given the success of allyl-BF_3K addition to indoles, we believed that these reagents could exhibit reactivity toward other similarly less reactive electrophiles. Herein, we disclose the application of these reagents toward the mild and chemoselective metal-free allylation of nitriles and acid anhydrides.

The reaction of allyl-BF_3K with $BF_3{\cdot}OEt_2$ and carbonyl compounds and imines under anhydrous conditions presumably occurs via in situ-generated allyl-BF_2 as the active allylating agent.[16a,b,17−19] We considered that such an in situ-generated allyl-BF_2 species would be much more reactive than allylboronic ester equivalents and could have sufficient reactivity to add to functionalities at the carboxyl oxidation state. A general strategy involving the allylation of acid anhydrides or nitriles using allyl-BF_3K with $BF_3{\cdot}OEt_2$ activation was therefore envisioned. At least 2 equiv of the allyl-BF_3K reagent would be required, as previously observed for other systems,[16a,b,17,18] because the in situ-generated allyl-BF_2 may decompose during the course of the reaction, and an excess may ensure that enough active allylating reagent is available. Accordingly, reactions of nitriles could be achieved using 4 equiv of allyl-BF_3K and 5 equiv of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 for 6 h. The parent benzonitrile (**1a**) substrate was doubly allylated to furnish **2a** in 87% yield (Table 1).

The method is tolerant of a variety of substituents on the aromatic ring. Notably, the ester (**1i**), isothiocyanate (**1j**), and sulfonamide (**1k**) functional groups can withstand the reaction conditions. However, lower yields are observed for substrates bearing either mesomerically electron-donating substituents on the para position of the aromatic ring or ortho-substituents, as observed for the reactions of **1d**, **1f**, and **1h**. Yields were also

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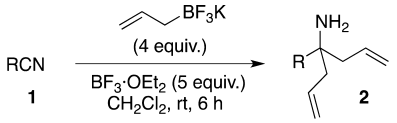
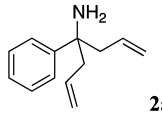
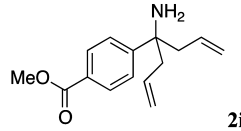
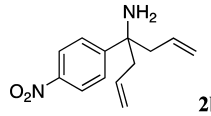
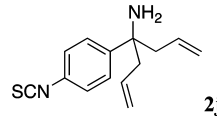
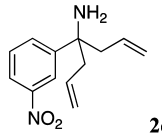
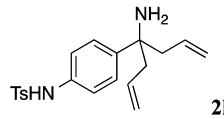
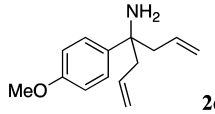
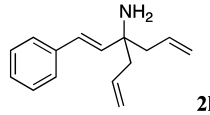
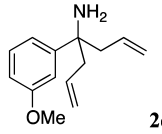
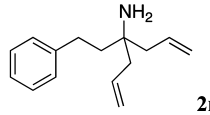
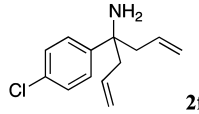
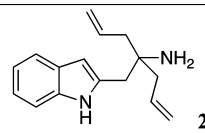
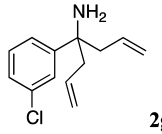
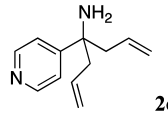
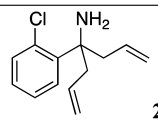
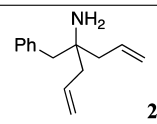
Table 1. Double Allylboration of Nitriles



Substrate	Product	Yield	Substrate	Product	Yield
1a	 **2a**	87%	**1i**	 **2i**	80%
1b	 **2b**	78%	**1j**	 **2j**	83%
1c	 **2c**	79%	**1k**	 **2k**	96%
1d	 **2d**	47%	**1l**	 **2l**	44%
1e	 **2e**	68%	**1m**	 **2m**	48%
1f	 **2f**	56%	**1n**	 **2n**	65%
1g	 **2g**	71%	**1o**	 **2o**	85%
1h	 **2h**	28%	**1p**	 **2p**	35%

lower for substrates where the nitrile group was not directly appended to an aryl ring (e.g., **1l**, **1m**, **1p**). An indole-based nitrile substrate (**1n**) was also suitable for reaction, and double allylboration of the nitrile functionality was successful in the presence of a pyridine ring (**1o**).

The formation of in situ-generated allyl-BF_2 is necessary as shown by a control allylation experiment involving nitrile **1a**, where water was added to form allyl-$B(OH)_2$, and for which none of the bis-allylated product **2a** was observed (Scheme 1). An attempt to adapt and apply previously reported allylation conditions using Montmorillonite K10 activation[16e] on nitrile **1a** was made (double the quantity of Montmorillonite K10 and CH_2Cl_2/H_2O solvent from the reported ketone allylation conditions were employed). Compound **2a** was obtained, but the yield was much lower (21%) than that obtained through $BF_3{\cdot}OEt_2$ activation.

Given the observed success with nitrile substrates, focus was then placed upon the use of acid anhydride substrates. It was observed that a modification of the conditions employed for double allylboration of nitriles, using 5 equiv of allyl-BF_3K and 5 equiv of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 solvent for 2 h, allowed for the successful double allylboration of phthalic anhydride (**3a**) in excellent yield to furnish **4a** (92%) (Table 2). Other aliphatic

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Scheme 1. Control Double Allylboration Experiment of a Nitrile Using H_2O (above) and Montmorillonite K10 Activation (below)

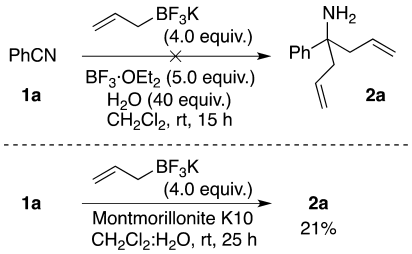
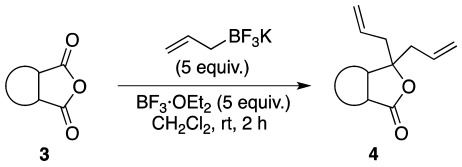
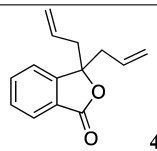
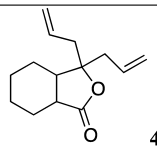
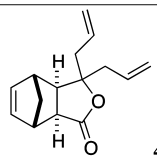
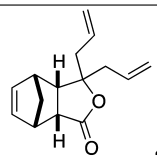


Table 2. Double Allylboration of Acid Anhydrides



Substrate	Product	Yield
3a	 **4a**	92%
3b	 **4b**	99%
3c	 **4c**	96%
3d	 **4d**	99%

cyclic acid anhydrides underwent bis-allylation in excellent yields using the same mild conditions.[20]

In conclusion, the double allylboration of nitriles and acid anhydrides can be achieved under mild conditions using potassium allyltrifluoroborate in the presence of $BF_3{\cdot}OEt_2$. This method circumvents some of the operational disadvantages of previous allylborane-based approaches and occurs at ambient temperature, rather than the elevated temperatures required for triallylboron, using a much more stable and conveniently handled potassium allyltrifluoroborate reagent. It is likely that the $BF_3{\cdot}OEt_2$ Lewis acid generates allyldifluoroborane as the reactive allylating species. Overall, the method is tolerant of other electrophilic functional groups that may be present in the substrate at ambient temperature. It is envisaged that this approach will either complement or serve as a suitable alternative for the previously reported Barbier or Grignard-based double allylation procedures. Finally, this method illustrates the general concept of using Lewis acid activation to achieve the addition of allyltrifluoroborate salts to electrophiles of low intrinsic reactivity.

EXPERIMENTAL SECTION

General Information. Reagents obtained from commercial suppliers were used as received. CH_2Cl_2 was distilled under nitrogen from calcium hydride through standard techniques. Compounds were typically purified using silica gel flash chromatography (silica: 60 Å, 230−400 mesh). Analytical thin layer chromatography (TLC) was performed on precoated UV-active aluminum backed silica plates, visualized with a UV254 lamp, and stained with 20% phosphomolybdic acid in ethanol. IR spectra were run as thin films (neat or with $CDCl_3$) on NaCl plates. Mass spectral data were obtained through DART (direct analysis in real time) or ESI methods. All melting points that were obtained are uncorrected. The ^1H and ^{13}C NMR spectra of all compounds were obtained at 400 and 100 MHz, respectively. Chemical shifts are reported in parts per million (δ) and coupling constants (J) are reported in hertz (Hz). The ^1H NMR spectra were referenced to the TMS internal standard, while ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 73.23). NMR experiments were performed at 25 °C unless otherwise stated. The multiplicities of the signals are indicated via the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. If a coupling pattern can be assigned as a combination of multiplicities, then the listed abbreviations are combined to provide an appropriate descriptor for the observed patterns (e.g., dt, doublet of triplets). Signals that have singlet multiplicity and are deemed as broad are prefixed with "br".

*N-(4-Cyanophenyl)-4-methylbenzenesulfonamide (**1k**).*[21] To a round-bottom flask were added 4-aminobenzonitrile (0.49 g, 4.1 mmol), 4-toluenesulfonyl chloride (0.79 g, 4.1 mmol), pyridine (20 mL), and a magnetic stirrer. The solution was heated to reflux for 3 days and stirred under an atmosphere of nitrogen. The solution was subsequently concentrated in vacuo, and the crude mixture was dissolved in EtOAc (75 mL). The organic phase was washed with HCl (aq, 3 N, 4 × 50 mL) and with a saturated $NaHCO_3$ solution (2 × 50 mL). The organic phase was then dried with Na_2SO_4, and the solvent was removed under reduced pressure to afford **1k** (0.74 g, 65%) as a light brown solid that did not require further purification. Mp 184−186 °C (EtOAc); ^1H NMR (400 MHz, DMSO-d_6): δ 10.97 (1H, br s), 7.73−7.67 (4H, m), 7.38 (2H, d, J = 8.0 Hz), 7.25−7.22 (2H, m), 2.34 (3H, s); ^{13}C NMR (100 MHz, DMSO-d_6): δ 143.9, 142.3, 136.2, 133.6, 129.9, 126.7, 118.7, 118.4, 105.3, 21.0.

Double Allylboration of Nitriles. To a round-bottom flask equipped with a magnetic stirrer and charged with potassium allyltrifluoroborate (2.0 mmol, 4.0 equiv) were added CH_2Cl_2 (5 mL) and nitrile **1** (0.50 mmol, 1.0 equiv). $BF_3{\cdot}OEt_2$ (2.5 mmol, 5.0 equiv) was subsequently added dropwise, and the mixture was stirred at room temperature under an N_2 atmosphere. After 6 h, starting material conversion was confirmed through TLC analysis, and approximately five drops of HCl (aq, 1 N) was added to facilitate hydrolysis of any potential amino-borate adduct present, followed by saturated $NaHCO_3$ solution (5 mL). Deionized water (~5−10 mL) was added as necessary to facilitate phase separation, and the organic phase was obtained. The aqueous phase was subsequently extracted with CH_2Cl_2 (3 × 5 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude mixture was purified through silica gel flash chromatography.

*4-Phenylhepta-1,6-dien-4-amine (**2a**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (45% EtOAc/hexanes + 0.5% NEt_3) afforded **2a** (0.082 g, 87%) as a yellow oil. R_f = 0.23 (40% EtOAc/hexanes); IR (thin film) ν_{max} 3374, 3312, 3075, 3024, 3005, 2977, 2914, 2855, 1700, 1637, 1601, 999, 917, 832, 765, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.44−7.41 (2H, m), 7.36−7.31 (2H, m), 7.24−7.20 (1H, m), 5.52 (2H, dddd, J = 17.0, 10.0, 8.5, 6.0 Hz), 5.10−5.02 (4H, m), 2.66 (2H, dddd, J = 13.5, 6.0, 1.5, 1.5 Hz), 2.44−2.38 (2H, m), 1.60 (2H, br s); ^{13}C NMR (100

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MHz, $CDCl_3$): δ 146.8, 134.1, 128.3, 126.4, 126.0, 118.8, 57.1, 48.3; LRMS ($DART^+$) m/z (rel intensity) 188.1 (60) $[M + H]^+$, 171.1 (100); HRMS ($DART^+$) m/z calcd for $C_{13}H_{18}N$ $[M + H]^+$: 188.1439. Found: 188.1438.

*4-(4-Nitrophenyl)hepta-1,6-dien-4-amine (**2b**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (80% EtOAc/hexanes + 0.5% NEt_3) afforded **2b** (0.090 g, 78%) as an orange oil. R_f = 0.53 (EtOAc); IR (thin film) ν_{max} 3374, 3312, 3077, 3005, 2978, 2916, 2853, 1640, 1601, 1514, 1491, 1441, 1348, 1109, 997, 920, 854, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.21−8.17 (2H, m), 7.66−7.62 (2H, m), 5.54−5.44 (2H, m), 5.10−5.06 (4H, m), 2.67 (2H, dddd, J = 14.0, 6.5, 1.0, 1.0 Hz), 2.47−2.42 (2H, m), 1.55 (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 146.7, 132.9, 127.3, 123.5, 119.8, 57.7, 46.2; LRMS (ESI^+) m/z (rel intensity) 233.1 (52) $[M + H]^+$, 216.1 (100); HRMS (ESI^+) m/z calcd for $C_{13}H_{17}N_2O_2$ $[M + H]^+$: 233.1284. Found: 233.1279.

*4-(3-Nitrophenyl)hepta-1,6-dien-4-amine (**2c**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (60% EtOAc/hexanes + 0.5% NEt_3) afforded **2c** (0.092 g, 79%) as a yellow oil. R_f = 0.56 (80% EtOAc/hexanes); IR (thin film) ν_{max} 3374, 3312, 3077, 3005, 2978, 2916, 2861, 1640, 1527, 1443, 1348, 1314, 1288, 1099, 1078, 998, 920, 807, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (1H, dd, J = 2.0, 2.0 Hz), 8.09 (1H, ddd, J = 8.0, 2.0, 1.0 Hz), 7.82 (1H, ddd, J = 8.0, 2.0, 1.0 Hz), 7.52 (1H, dd, J = 8.0, 8.0 Hz), 5.56−5.46 (2H, m), 5.11−5.07 (4H, m), 2.67 (2H, dddd, J = 13.5, 6.5, 1.5, 1.5 Hz), 2.44 (2H, m), 1.73 (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 148.5, 132.9, 132.5, 129.2, 121.6, 121.3, 119.8, 57.3, 48.0; LRMS ($DART^+$) m/z (rel intensity) 233.1 (100) $[M + H]^+$, 216.1 (19); HRMS ($DART^+$): m/z $[M + H]^+$ calcd for $C_{13}H_{17}N_2O_2$: 233.1290; found: 233.1292.

*4-(4-Methoxyphenyl)hepta-1,6-dien-4-amine (**2d**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (60% EtOAc/hexanes + 0.5% NEt_3) afforded **2d** (0.052 g, 47%) as a yellow oil. R_f = 0.30 (70% EtOAc/hexanes); IR (thin film) ν_{max} 3370, 3312, 3074, 3002, 2976, 2933, 2912, 2835, 1640, 1607, 1511, 1505, 1301, 1249, 1180, 1037, 999, 916, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36−7.32 (2H, m), 6.89−6.85 (2H, m), 5.53 (2H, dddd, J = 17.0, 10.0, 8.5, 6.5 Hz), 5.10−5.02 (4H, m), 3.80 (3H, s), 2.61 (2H, dddd, J = 13.5, 6.5, 1.0, 1.0 Hz), 2.42−2.36 (2H, m), 1.70 (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 138.9, 134.2, 127.1, 118.8, 113.6, 56.7, 55.4, 48.3; LRMS ($DART^+$) m/z (rel intensity) 218.2 (57) $[M + H]^+$, 201.1 (100), 176.1 (7); HRMS ($DART^+$) m/z calcd for $C_{14}H_{20}NO$ $[M + H]^+$: 218.1545. Found: 218.1542.

*4-(3-Methoxyphenyl)hepta-1,6-dien-4-amine (**2e**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (60% EtOAc/hexanes + 0.5% NEt_3) afforded **2e** (0.074 g, 68%) as a yellow oil. R_f = 0.46 (80% EtOAc/hexanes); IR (thin film) ν_{max} 3372, 3302, 3075, 3002, 2976, 2935, 2914, 2834, 1640, 1607, 1582, 1484, 1464, 1432, 1290, 1248, 1170, 1051, 997, 917, 782, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28−7.23 (1H, m), 7.01−6.98 (2H, m), 6.76 (1H, ddd, J = 8.0, 2.5, 1.0 Hz), 5.53 (2H, dddd, J = 17.0, 10.0, 8.5, 6.0 Hz), 5.11−5.02 (4H, m), 3.81 (3H, s), 2.64 (2H, dddd, J = 13.5, 6.0, 1.5, 1.5 Hz), 2.42−2.36 (2H, m), 1.62 (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 148.8, 134.0, 129.2, 118.8, 118.4, 112.5, 111.2, 57.1, 55.4, 48.2; LRMS ($DART^+$) m/z (rel intensity) 218.2 (81) $[M + H]^+$, 201.1 (100), 176.1 (25); HRMS ($DART^+$) m/z calcd for $C_{14}H_{20}NO$ $[M + H]^+$: 218.1545. Found: 218.1552.

*4-(4-Chlorophenyl)hepta-1,6-dien-4-amine (**2f**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (60% EtOAc/hexanes + 0.5% NEt_3) afforded **2f** (0.62 g, 56%) as a yellow oil. R_f = 0.49 (80% EtOAc/hexanes); IR (thin film) ν_{max} 3373, 3312, 3076, 3005, 2977, 2916, 2854, 1640, 1593, 1492, 1441, 1398, 1094, 998, 918, 828 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39−7.36 (2H, m), 7.31−7.28 (2H, m), 5.51 (2H, dddd, J = 17.0, 10.0, 8.5, 6.5 Hz), 5.10−5.03 (4H, m), 2.61 (2H, dddd, J = 13.5, 6.5, 1.5, 1.5 Hz), 2.41−2.36 (2H, m), 1.53 (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 133.7, 132.3, 128.4, 127.6, 119.2, 57.0, 48.3; LRMS ($DART^+$) m/z (rel intensity) 224.1 (24), 222.1 (78) $[M + H]^+$, 207.1 (29), 205.1 (100); HRMS ($DART^+$) m/z calcd for $C_{13}H_{17}ClN$ $[M + H]^+$: 222.1050. Found: 222.1050.

*4-(3-Chlorophenyl)hepta-1,6-dien-4-amine (**2g**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (60% EtOAc/hexanes + 0.5% NEt_3) afforded **2g** (0.079 g, 71%) as a yellow oil. R_f = 0.58 (80% EtOAc/hexanes); IR (thin film) ν_{max} 3375, 3314, 3076, 3005, 2978, 2914, 2854, 1640, 1595, 1570, 1478, 1442, 1417, 1341, 1296, 1184, 1080, 998, 919, 840, 784, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.44 (1H, dd, J = 1.5, 1.5 Hz), 7.32−7.18 (3H, m), 5.50 (2H, dddd, J = 16.5, 10.0, 8.0, 6.0 Hz), 5.11−5.04 (4H, m), 2.62 (2H, dddd, J = 12.5, 6.0, 1.5, 1.5 Hz), 2.43−2.35 (2H, m), 1.74 (2H, br s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.2, 134.4, 133.5, 129.5, 126.6, 126.5, 124.3, 119.3, 57.1, 48.1; LRMS ($DART^+$) m/z (rel intensity) 224.1 (30), 222.1 (99) $[M + H]^+$, 207.1 (24), 205.1 (100); HRMS ($DART^+$) m/z calcd for $C_{13}H_{17}ClN$ $[M + H]^+$: 222.1050. Found: 222.1056.

*4-(2-Chlorophenyl)hepta-1,6-dien-4-amine (**2h**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (45% EtOAc/hexanes + 0.5% NEt_3) afforded **2h** (0.031 g, 28%) as a yellow oil. R_f = 0.65 (50% EtOAc/hexanes); IR (thin film) ν_{max} 3372, 3312, 3074, 2977, 2925, 2870, 1640, 1591, 1464, 1432, 1291, 1036, 997, 917, 757, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (1H, dd, J = 7.5, 2.0 Hz), 7.36 (1H, dd, J = 7.5, 1.5 Hz), 7.23 (1H, ddd, J = 7.5, 7.5, 1.5 Hz), 7.17 (1H, ddd, J = 7.5, 7.5, 2.0 Hz), 5.48 (2H, dddd, J = 17.0, 10.0, 8.5, 6.5 Hz), 5.11−5.06 (2H, m), 5.02−4.99 (2H, m), 3.23 (2H, dddd, J = 14.0, 6.5, 1.5, 1.5 Hz), 2.52−2.47 (2H, m), 1.93 (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 134.1, 132.1, 131.9, 129.6, 128.3, 126.9, 118.7, 58.3, 44.6; LRMS ($DART^+$) m/z (rel intensity) 224.1 (33), 222.1 (100) $[M + H]^+$, 205.1 (21), 186.1 (18), 182.1 (21), 180.1 (68); HRMS ($DART^+$) m/z calcd for $C_{13}H_{17}ClN$ $[M + H]^+$: 222.1050. Found: 222.1059.

*Methyl 4-(4-Aminohepta-1,6-dien-4-yl)benzoate (**2i**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (50% EtOAc/hexanes + 0.5% NEt_3) afforded **2i** (0.098 g, 80%) as a yellow oil. R_f = 0.33 (50% EtOAc/hexanes); IR (thin film) ν_{max} 3375, 3317, 3076, 3003, 2977, 2950, 2914, 2844, 1723, 1640, 1610, 1435, 1407, 1280, 1191, 1108, 1018, 918, 854, 827, 775, 712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.02−7.99 (2H, m), 7.53−7.50 (2H, m), 5.49 (2H, dddd, J = 17.0, 10.0, 8.5, 6.5 Hz), 5.09−5.03 (4H, m), 3.91 (3H, s), 2.66 (2H, dddd, J = 13.5, 6.5, 1.5, 1.5 Hz), 2.45−2.39 (2H, m), 1.62 (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 152.3, 133.5, 129.6, 128.4, 126.2, 119.3, 57.5, 52.2, 48.2; LRMS ($DART^+$) m/z (rel intensity) 246.2 (100) $[M + H]^+$, 229.1 (49); HRMS ($DART^+$) m/z calcd for $C_{15}H_{20}NO_2$ $[M + H]^+$: 246.1494. Found: 246.1498.

*4-(4-Isothiocyanatophenyl)hepta-1,6-dien-4-amine (**2j**).* The standard nitrile double allylboration procedure was used with the following exceptions in regards to workup: (i) no HCl was used, and (ii) water was used instead of a saturated solution of $NaHCO_3$. Additionally, on account of the instability of this compound toward silica gel flash chromatography, purification was achieved through trituration using hexanes and 5% CH_2Cl_2/hexanes to afford **2j** (0.101 g, 83%) as a viscous orange oil. IR (thin film) ν_{max} 3579, 3171, 2926, 2102, 1609, 1514, 1451, 1344, 1062, 936, 834, 731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38−7.36 (2H, m), 7.25−7.22 (2H, m), 5.55−5.44 (2H, m), 5.29−5.22 (4H, m), 2.88−2.83 (2H, m), 2.79−2.73 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 136.3, 132.1, 129.0, 127.0, 126.5, 123.4, 62.2, 42.6; LRMS ($DART^+$) m/z (rel intensity) 245.1 (12) $[M + H]^+$, 228.1 (100); HRMS ($DART^+$) m/z calcd for $C_{14}H_{17}N_2S$ $[M + H]^+$: 245.1112. Found: 245.1121.

*N-(4-(4-Aminohepta-1,6-dien-4-yl)phenyl)-4-methylbenzenesulfonamide (**2k**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (80% EtOAc/hexanes + 0.5% NEt_3) afforded **2k** (0.172 g, 96%) as a light beige solid. Mp 132−134 °C ($CDCl_3$); R_f = 0.33 (EtOAc); IR (thin film in $CDCl_3$) ν_{max} 3353, 3257, 3075, 3029, 3006, 2978, 2921, 2850, 1639, 1599, 1511, 1444, 1335, 1161, 1093, 919, 813, 732, 663 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.63−7.60 (2H, m), 7.31−7.28 (2H, m), 7.22−7.19 (2H, m), 7.02−7.00 (2H, m), 6.31 (1H, br s), 5.44 (2H, dddd, J = 17.0, 11.0, 8.5, 6.5 Hz), 5.05−5.00 (4H, m), 2.59−2.54 (2H,

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m), 2.38 (3H, s), 2.38−2.33 (2H, m), 1.49 (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): rotameric mixture: δ 144.3, 144.2, 144.0, 136.4, 134.8, 134.7, 133.8, 129.7, 127.5, 127.07, 127.06, 122.0, 121.9, 119.0, 56.9, 48.2, 21.8; LRMS (ESI$^+$) m/z (rel intensity) 379.1 (1) $[M + Na]^+$, 357.2 (1) $[M + H]^+$, 340.1 (100); HRMS (ESI$^+$) m/z calcd for $C_{20}H_{25}N_2O_2S$ $[M + H]^+$: 357.1631. Found: 357.1644.

*(E)-4-Styrylhepta-1,6-dien-4-amine (**2l**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel EtOAc + 0.5% NEt_3) afforded **2l** (0.092 g, 44%) as a yellow oil. R_f = 0.23 (EtOAc); IR (thin film) ν_{max} 3370, 3293, 3075, 3025, 3003, 2976, 2921, 2856, 1640, 1600, 1494, 1449, 1436, 1415, 1071, 997, 971, 915, 749, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.37 (2H, m), 7.33−7.29 (2H, m), 7.23−7.20 (1H, m), 6.49 (1H, d, J = 16.0 Hz), 6.27 (1H, d, J = 16.0 Hz), 5.80 (2H, dddd, J = 16.0, 9.5, 8.0, 6.5 Hz), 5.10−5.16 (4H, m), 2.36 (2H, dddd, J = 13.5, 6.5, 6.5, 1.0 Hz), 2.29−2.24 (2H, m), 1.59 (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 137.3, 134.0, 128.8, 128.1, 127.5, 126.5, 119.0, 55.7, 46.7; LRMS (DART$^+$) m/z (rel intensity) 214.2 (22) $[M + H]^+$, 197.1 (100); HRMS (DART$^+$) m/z calcd for $C_{15}H_{20}N$ $[M + H]^+$: 214.1596. Found: 214.1592.

*4-Phenethylhepta-1,6-dien-4-amine (**2m**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (15% MeOH/EtOAc + 0.5% NEt_3) afforded **2m** (0.053 g, 48%) as a yellow oil. R_f = 0.38 (15% MeOH/EtOAc); IR (thin film) ν_{max} 3360, 3187, 3074, 3026, 3002, 2927, 2860, 1638, 1603, 1496, 1456, 998, 915, 847, 824, 746, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.25 (2H, m), 7.19−7.15 (3H, m), 5.92−5.82 (2H, dddd, J = 16.0, 11.0, 7.5, 7.5 Hz), 5.17−5.12 (4H, m), 2.68−2.63 (2H, m), 2.23−2.21 (4H, m), 1.90 (2H, br s), 1.69−1.65 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 133.8, 128.6, 128.5, 126.0, 119.0, 54.2, 44.6, 42.1, 30.2; LRMS (DART$^+$) m/z (rel intensity) 216.2 (100) $[M + H]^+$; HRMS (DART$^+$) m/z calcd for $C_{15}H_{22}N$ $[M + H]^+$: 216.1752. Found: 216.1759.

*4-((1H-Indol-2-yl)methyl)hepta-1,6-dien-4-amine (**2n**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (20% MeOH/EtOAc + 0.5% NEt_3) afforded **2n** (0.078 g, 65%) as a light brown solid. Mp 78−80 °C ($CDCl_3$); R_f = 0.33 (20% MeOH/EtOAc); IR (thin film in $CDCl_3$) ν_{max} 3409, 3334, 3164, 3063, 2976, 2919, 2849, 1640, 1576, 1458, 1439, 1365, 1340, 1234, 1109, 997, 915, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (1H, br s), 7.63 (1H, d, J = 8.0 Hz), 2.20−2.02 (4H, m), 7.36 (1H, d, J = 8.0 Hz), 7.18 (1H, ddd, J = 7.0, 7.0, 1.0 Hz), 7.13−7.10 (1H, m), 7.08 (1H, d, J = 2.0 Hz), 5.94 (2H, dddd, J = 17.5, 10.0, 7.5, 7.5 Hz), 5.17−5.08 (4H, m), 2.87 (2H, s), 2.29−2.24 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 134.4, 128.9, 123.9, 122.1, 119.7, 119.6, 118.8, 111.6, 111.3, 54.9, 44.4, 35.8; LRMS (ESI$^+$) m/z (rel intensity) 241.2 (24) $[M + H]^+$, 224.1 (100), 130.1 (69); HRMS (ESI$^+$) m/z calcd for $C_{16}H_{21}N_2$ $[M + H]^+$: 241.1699. Found: 241.1695.

*4-(Pyridin-4-yl)hepta-1,6-dien-4-amine (**2o**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (10% MeOH/EtOAc) afforded **2o** (0.085 g, 85%) as a yellow oil. R_f = 0.30 (10% MeOH/EtOAc); IR (thin film) ν_{max} 3366, 3287, 3076, 2978, 2925, 2855, 1691, 1641, 1597, 1553, 1441, 1410, 1070, 995, 919, 822, 566 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56−8.55 (2H, m), 7.36−7.35 (2H, m), 5.49 (2H, dddd, J = 17.0, 10.5, 8.5, 6.5 Hz), 5.10−5.06 (4H, m), 2.62 (2H, dddd, J = 14.0, 6.5, 1.5, 1.5 Hz), 2.44−2.38 (2H, m), 1.94 (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 149.8, 132.9, 121.5, 119.8, 57.1, 47.7; LRMS (DART$^+$) m/z (rel intensity) 189.1 (100) $[M + H]^+$; HRMS (DART$^+$) m/z calcd for $C_{12}H_{17}N_2$ $[M + H]^+$: 189.1392. Found: 189.1389.

*4-Benzylhepta-1,6-dien-4-amine (**2p**).* Using the standard nitrile double allylboration procedure and flash chromatography on silica gel (EtOAc + 0.5% NEt_3) afforded **2p** (0.035 g, 35%) as a light yellow oil. R_f = 0.20 (EtOAc); IR (thin film) ν_{max} 3364, 3291, 3074, 3028, 3003, 2976, 2922, 2853, 1640, 1603, 1589, 1495, 1452, 1441, 1414, 1082, 1032, 997, 914, 745, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.28 (2H, m), 7.25−7.21 (3H, m), 5.92 (2H, dddd, J = 17.5, 10.0, 7.5, 7.5 Hz), 5.18−5.09 (4H, m), 2.69 (1H, s), 2.18 (2H, dddd, J = 14.0, 7.5, 1.0, 1.0 Hz), 2.09 (2H, dddd, J = 14.0, 7.5, 1.0, 1.0 Hz), 1.47 (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 134.3, 130.9, 128.3, 126.6, 118.9, 54.4, 46.5, 44.5; LRMS (ESI$^+$) m/z (rel intensity) 202 (18) $[M + H]^+$, 185 (26), 143 (84), 129 (59), 117 (36), 91 (100); HRMS (ESI$^+$) m/z calcd for $C_{14}H_{20}N$ $[M + H]^+$: 202.1590. Found: 202.1596.

Double Allylboration of Acid Anhydrides. To a round-bottom flask equipped with a magnetic stirrer and charged with potassium allyltrifluoroborate (0.370 g, 2.5 mmol, 5.0 equiv) were added CH_2Cl_2 (5 mL) and acid anhydride (0.50 mmol, 1.0 equiv). $BF_3{\cdot}OEt_2$ (310 μL, 2.5 mmol, 5.0 equiv) was subsequently added dropwise, and the mixture was stirred at room temperature under an N_2 atmosphere. After 2 h, starting material conversion was confirmed through TLC, and approximately five drops of HCl (aq, 1 N) was added followed by saturated $NaHCO_3$ solution (5 mL). Deionized water (~5−10 mL) was added as necessary to facilitate phase separation, and the organic phase was obtained. The aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude mixture was purified through silica gel flash chromatography.

*3,3-Diallylisobenzofuran-1(3H)-one (**4a**).*[6] Using the standard acid anhydride double allylboration procedure and flash chromatography on silica gel (30% EtOAc/hexanes) afforded **4a** (0.099 g, 92%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (1H, ddd, J = 7.5, 1.0, 1.0 Hz), 7.60 (1H, ddd, J = 7.5, 7.5, 1.0 Hz), 7.50 (1H, ddd, J = 7.5, 7.5, 1.0 Hz), 7.38 (1H, ddd, J = 7.5, 1.0, 1.0 Hz), 5.60−5.49 (2H, m), 5.09−5.03 (4H, m), 2.76 (2H, dddd, J = 14.5, 7.5, 1.0, 1.0 Hz), 2.67 (2H, dddd, J = 14.0, 7.0, 1.0, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 151.8, 134.0, 130.9, 129.2, 127.1, 125.9, 121.7, 120.5, 88.4, 42.9.

*3,3-Diallylhexahydroisobenzofuran-1(3H)-one (**4b**).* Using the standard acid anhydride double allylboration procedure and flash chromatography on silica gel (15% EtOAc/hexanes) afforded **4.18** (0.110 g, 99%) as a clear oil. R_f = 0.50 (15% EtOAc/hexanes); IR (thin film) ν_{max} 3077, 2936, 2859, 1771, 1640, 1441, 1337, 1182, 1125, 976, 916 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86−5.71 (2H, m), 5.19−5.10 (4H, m), 2.99 (1H, dd, J = 6.5, 6.5 Hz), 2.61−2.53 (2H, m), 2.37−2.31 (2H, m), 2.28−2.19 (2H, m), 1.81−1.72 (2H, m), 1.62−1.52 (2H, m), 1.27−1.08 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 132.5, 132.5, 119.6, 119.5, 86.9, 41.1, 39.8, 39.5, 37.5, 24.9, 23.9, 23.2, 22.8; LRMS (DART$^+$) m/z (rel intensity) 238.2 (100) $[M + NH_4]^+$, 221.2 (44) $[M + H]^+$; HRMS (DART$^+$) m/z calcd for $C_{14}H_{21}O_2$ $[M + H]^+$: 221.1542. Found: 221.1545.

*(3aR(S),4S(R),7R(S),7aS(R))-3,3-Diallyl-3a,4,7,7a-tetrahydro-4,7-methanoisobenzofuran-1(3H)-one (**4c**).* Using the standard acid anhydride double allylboration procedure and flash chromatography on silica gel (20% EtOAc/hexanes) afforded **4c** (0.111 g, 96%) as a clear oil. R_f = 0.53 (20% EtOAc/hexanes); IR (thin film) ν_{max} 3076, 2982, 1750, 1641, 1336, 1328, 1205, 1145, 1016, 1000, 964, 920, 828 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.24−6.19 (2H, m), 5.88 (1H, dddd, J = 17.0, 10.5, 8.0, 6.0 Hz), 5.24 (1H, dddd, J = 17.5, 10.5, 7.5, 7.5 Hz), 5.22−5.13 (4H, m), 3.27−3.25 (1H, m), 3.05−3.03 (1H, m), 2.74−2.72 (1H, m), 2.63 (1H, dddd, J = 14.5, 6.0, 1.5, 1.5 Hz), 2.46−2.39 (2H, m), 2.30 (1H, dddd, J = 14.0, 7.0, 1.0, 1.0 Hz), 2.20 (1H, d, J = 8.0 Hz), 1.50−1.48 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.4, 139.1, 138.1, 132.7, 131.5, 121.0, 119.6, 86.7, 50.4, 49.5, 46.1, 45.4, 44.8, 44.0, 39.3; LRMS (DART$^+$) m/z (rel intensity) 248.2 (93) $[M + NH_4]^+$, 231.1 (100) $[M + H]^+$; HRMS (DART$^+$) m/z calcd for $C_{15}H_{19}O_2$ $[M + H]^+$: 231.1385. Found: 231.1394.

*(3aS(R),4S(R),7R(S),7aR(S))-3,3-Diallyl-3a,4,7,7a-tetrahydro-4,7-methanoisobenzofuran-1(3H)-one (**4d**).* Using the standard acid anhydride double allylboration procedure and flash chromatography on silica gel (30% EtOAc/hexanes) afforded **4d** (0.117 g, 99%) as a clear oil. R_f = 0.35 (20% EtOAc/hexanes); IR (thin film) ν_{max} 3076, 2979, 2944, 2871, 1767, 1641, 1436, 1338, 1201, 1129, 998, 918, 812, 721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29−6.23 (2H, m), 5.89−5.71 (2H, m), 5.21−5.15 (4H, m), 3.39 (1H, dd, J = 9.0, 5.0 Hz), 3.25−3.22 (1H, m), 3.13−3.09 (1H, m), 2.80 (1H, dd, J = 9.0, 3.5 Hz), 2.54−2.49 (1H, m), 2.38−2.33 (3H, m), 1.64 (1H, ddd, J = 8.5, 2.0, 2.0 Hz), 1.43−1.41 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 136.5, 134.8, 120.7, 119.4, 87.1, 53.1, 49.9, 45.9, 45.4, 45.1, 40.3; LRMS (DART$^+$) m/z (rel intensity) 248.2 (86) $[M + NH_4]^+$, 231.1

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(100) $[M + H]^+$; HRMS (DART$^+$) m/z calcd for $C_{15}H_{19}O_2$ $[M + H]^+$: 231.1385. Found: 231.1397.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectral images. 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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