Note

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Synthesis of 1-Amino-*1H*-Indenes via a Sequential Suzuki–Miyaura Coupling/Petasis Condensation Sequence

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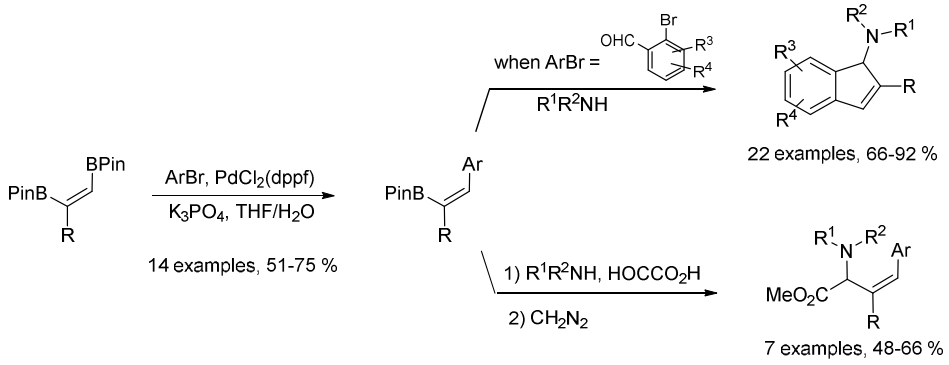
Abstract:

An efficient and straightforward synthesis of 1-amino-*1H*-indenes is reported from 1,2-bis(boronates) via a sequential Suzuki–Miyaura coupling / Petasis cyclisation reactions. Starting from the same monoboronic ester intermediates, an intermolecular version of this approach also afforded (*Z*)- α,β-unsaturated amino esters in moderate to good yields.

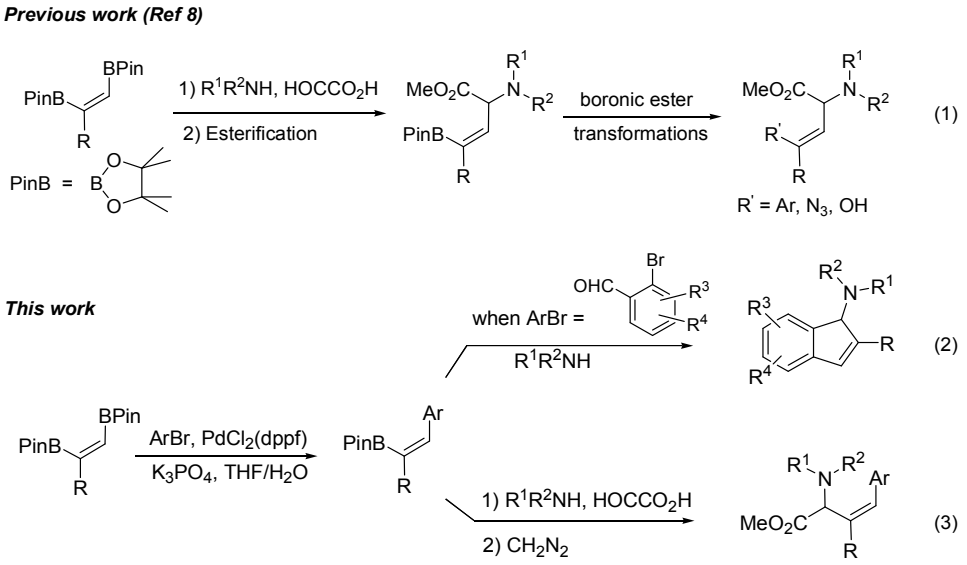


The significance of organoboron chemistry has been amply demonstrated in diverse areas of organic synthesis.[1] In particular, alkenyl boronic acids and derivatives were recognized as versatile buildings blocks in a variety of chemical transformations being engaged in a range of C-C and C-heteroatom bond formation,[2] Diels Alder cycloadditions,[3] sigmatropic rearrangements,[4] olefin metathesis,[5] and conjugate additions.[6] In the field of multicomponent process, the three-component reactions of carbonyl compounds, amines, and unsaturated organoboronic acids, referred as "Petasis reaction", give access to a variety of structurally and functionally diverse amino compounds and heterocycles.[7] In this context, we recently demonstrated that this Borono-Mannich reaction occurred regio- and stereo-selectively at the terminal C−B bond of (*E*)-alkenyl 1,2-bis(boronates) (Scheme 1, eq 1).[8,9]

Indenes and their corresponding hydrogenated derivatives, indanes, have found multiple applications as synthetic targets or building blocks, whether for their biological properties, as ligands of metal complexes or in material science.[10] The hitherto reported strategies mainly based on: transition-metal catalyzed [3+2]annulation,[11] reaction of metallacyclo-pentadienes with thiourea,[12] metathesis,[13] α-amidoalkylation of enolizable aldehydes,[14] nitrene insertion,[15] cascade reaction from propargyl alcohols,[16] and intramolecular cyclization of *N*-sulfonyl aldimines,[17] or *o*-ethynylbenzaldehyde.[18]

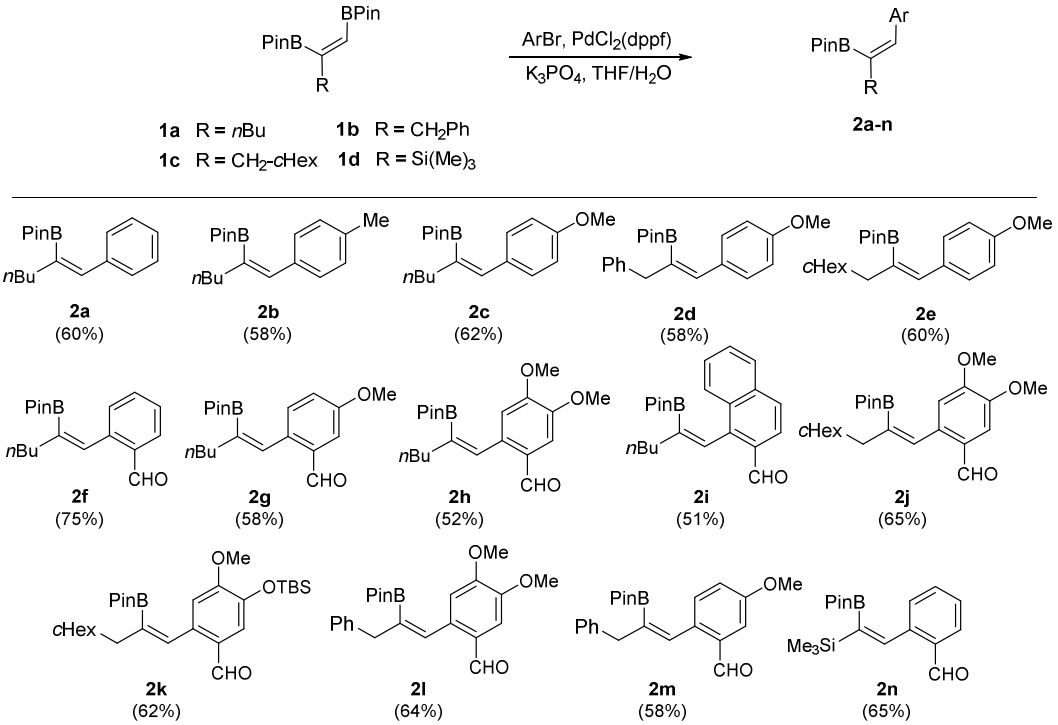
Herein, we report an attractive and complementary alternative to these approaches based on a two steps sequence starting with Suzuki-Miyaura couplings of (*E*)-alkenyl 1,2-bis(boronic esters) and substituted 2-bromobenzaldehydes. Further cyclization *via* a Petasis reaction provides access to substituted 1-amino-*1H*-indenes (Scheme 1, eq 2). When the coupling partner is devoid of an aldehyde group, the monoboronic ester intermediates can be engaged in an intermolecular Borono Mannich condensation with glyoxylic acid and amines to afford (*E*)- α,β-unsaturated amino esters (Scheme 1, eq 3).

Scheme 1. Multistep sequences involving a Petasis reaction and a Suzuki-Miyaura coupling.



(*E*)-Alkenyl 1,2-bis(boronates) **1a-d**, selected as model compounds, were first prepared in good yields from the corresponding 1-alkynes: 1-hexyne, 3-phenyl-1-propyne, 3-cyclohexyl-1-propyne and propargyl trimethylsilane, and bis(pinacolato)diboron in the presence of tetrakis(triphenylphosphine)platinum as catalyst, according to reported procedures.[19] These boronic esters were then engaged in Suzuki–Miyaura cross-couplings with aromatic halides in the presence of [1,1′-bis(diphenylphosphino) ferrocene]dichloro palladium(II) and potassium phosphate tribasic monohydrate in THF/H_2O at reflux.[20] As previously reported, this reaction occurred regioselectively at the terminal C-B bond that indicates that the coupling of a second aryl moiety is unfavorable. Yields are good to moderate with the formation of a single (*E*)-stereoisomer **2** (Scheme 2).

Scheme 2. Suzuki–Miyaura cross-couplings with 1,2-bis(boronates) **1a-1d** [a,b]

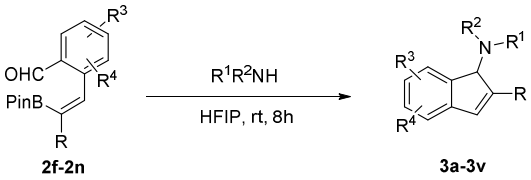


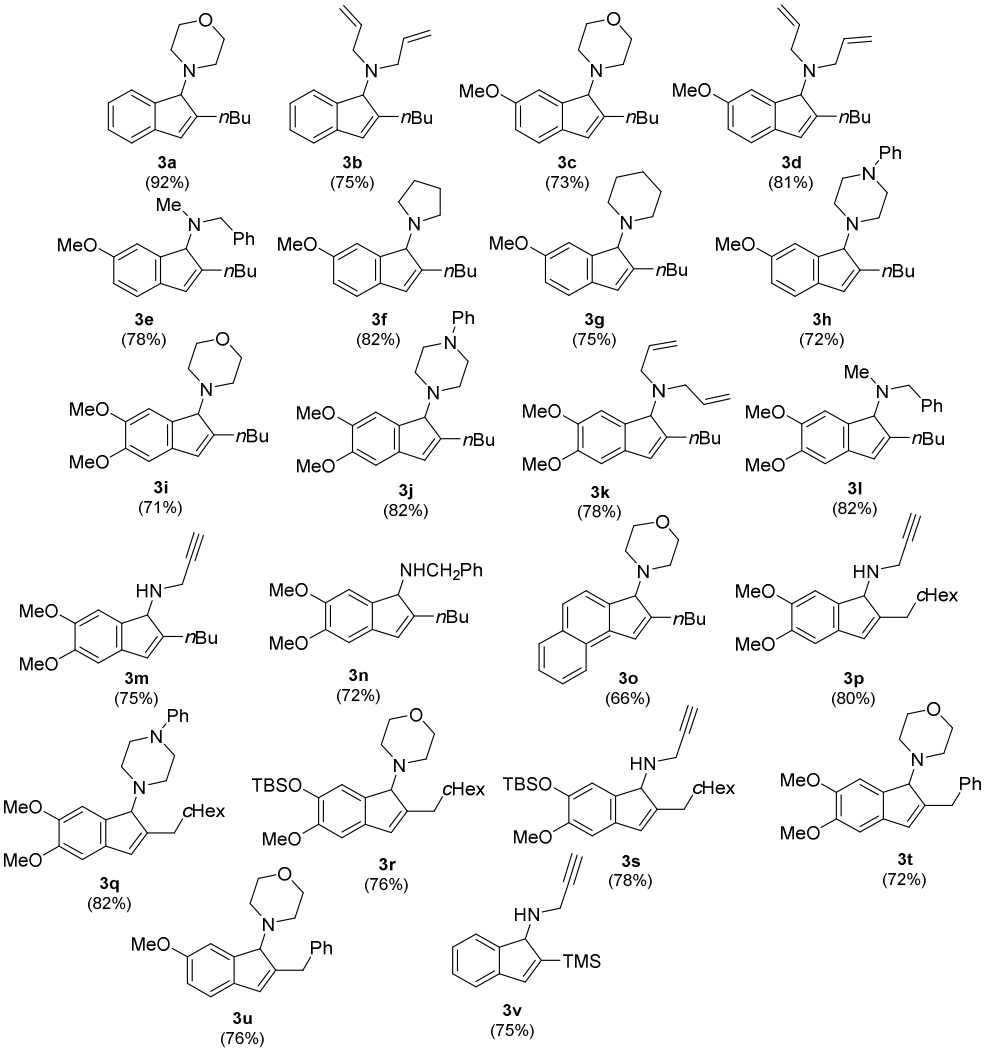
[a] General conditions: **1** (0.5 mmol), [1, 1'-bis (diphenyl phosphino)ferrocene] dichloropalladium(II) (0.01 mmol), potassium phosphate tribasic monohydrate (1.5 mmol) and arylbromide (0.5 mmol), THF (5 mL)/water (0.1 mL), reflux, 1h. [b] Yields of isolated products.

We then decided to explore the cyclization of compounds **2f-2n**, which have an aldehyde function in proper position for a Petasis condensation. While aryl aldehydes and pinacol boronic esters are usually poor substrates for such reaction, we expected that, in our case, entropic factors should greatly favor the formation of an indenyl substructure.[21] To our delight, the treatment of boronates **2f-2n** with amines afforded the corresponding 1-amino-*1H*-indenes in yields ranging from 66% to 92% (Scheme 3). Best results were obtained in HFIP (1,1,1,3,3,3-hexafluoropropan-2-ol) as solvent, probably due to the beneficial effect of HFIP on charged intermediates and stabilization of polar transition states (see proposed mechanism, Scheme 5). By comparison, with MeOH and trifluoroethanol as solvents, we observed the formation of 1-amino-*1H*-indene **3a** in 58% and 37% respectively under the same experimental conditions. Secondary amines, cyclic or acyclic, are good partners for this cyclization, as primary amine, with no significant influence of the presence of one or two methoxy groups on the aryl moiety. Moreover, the reaction was proven to be scalable with 1,2-bis(boronates) **1d** as model substrate, delivering the desired product **3v** in 45% isolated yield over two steps (Scheme 4).

The postulated mechanism is outlined in the Scheme 54. The formation of an iminium ion was followed by the quaternarization of the boronate function to give the corresponding ate complex. The migration of the alkenyl moiety afforded the 1-amino-*1H*-indene.

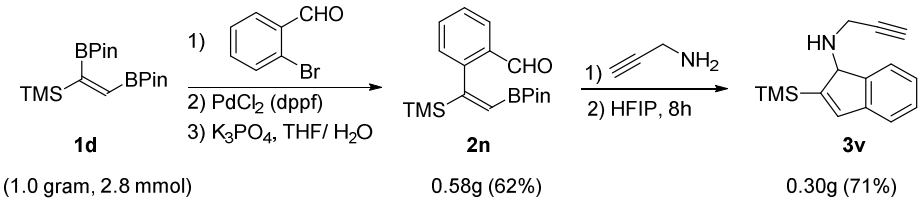
Scheme 3. Petasis reactions from boronates **2f-n.** Synthesis of 1-amino-*1H*-indenes **3a-3v**.[a,b]



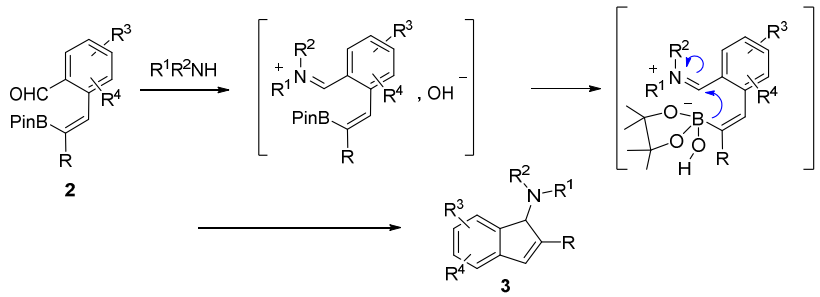


[a]General conditions: Amine (0.5 mmol), boronate **2f-n** (0.3 mmol) in 1,1,1,3,3,3-hexafluoropropan-2-ol (1 mL) rt, 8h.[b] Yields of isolated products.

Scheme 4. Gram scale synthesis of a 1-amino-*1H*-indene

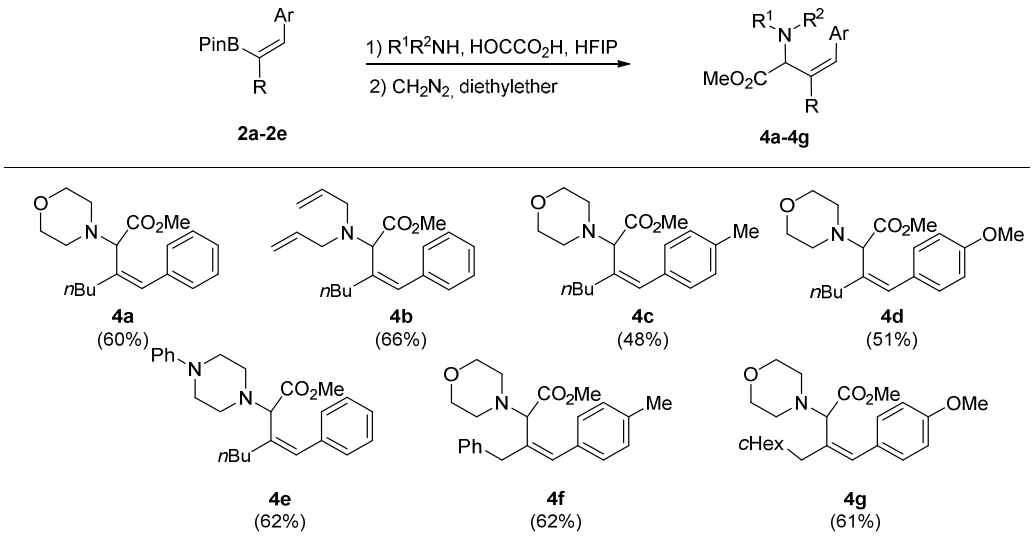


Scheme 5. Postulated mechanism for the formation of 1-amino-*1H*-indenes **3**



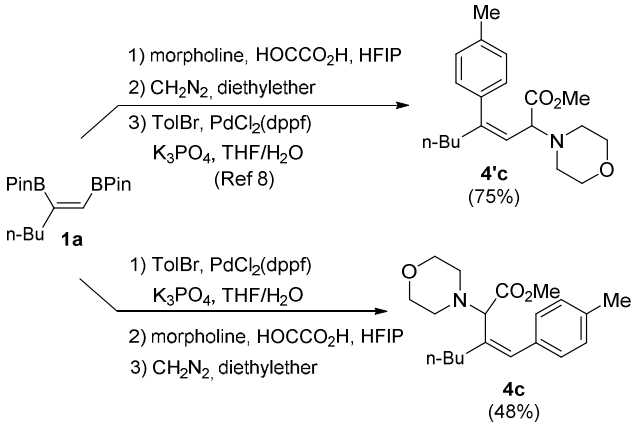
Due to the crucial role of amino acids and derivatives in biological processes, we also engaged the trisubstituted alkenyl boronates **2a-e** in intermolecular Petasis reactions to synthesize (*Z*)- α,β-unsaturated amino esters **4**. Various amines and glyoxylic acid reacted in HFIP at room temperature. The crude material was directly subjected to esterification with an ethereal solution of CH_2N_2. Cyclic secondary amines, as morpholine or *N*-phenylpiperazine, can be used, as the acyclic diallylamine, with yields ranging from 48 to 66% (Scheme 6). These results, in addition to our precedent study,[8] reveal that the simple inversion of the two reactions allows the divergent synthesis of structurally diverse α,β–unsaturated amino esters from a common precursor, as illustrated in Scheme 7.

Scheme 6. Intermolecular Petasis reactions from boronates **2a-e**. Synthesis of α,β-unsaturated amino esters **4a-4g** [a,b]



[a] General conditions: 1) Glyoxylic acid monohydrate (0.5 mmol), amine (0.5 mmol), **2a-e** (0.3 mmol) in HFIP (1 mL), rt, 78h. 2) Crude acid, CH_2N_2 in ether (2 mL, 0.5M), 0°C, 2h. [b] Yields of isolated products.

Scheme 7. Divergent synthesis of amino esters **4c** and **4'c**.



In conclusion, an efficient preparation of 1-amino-*1H*-indenes from easily accessible or commercially available reactants was described. The key features of this method are a regioselective Suzuki coupling at the terminal C-B bond of a (*E*)-1-alkene-1,2-diboronic ester and an Petasis condensation. We have also demonstrated the divergent approach to α,β–unsaturated aminoesters via an intermolecular version of this sequence starting from a common bis-boronate precursor.

EXPERIMENTAL SECTION

General Information and Materials. All commercially available chemicals were used without further purification. Tetrahydrofuran (THF), diethylether and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) were used as received. Analytical thin layer chromatography was performed on Silica Gel 60 F254 plates. The compounds were characterized by ^{1}H, ^{13}C NMR and ^{11}B techniques. ^{1}H and ^{13}C spectra were recorded in $CDCl_3$ (internal standard: 7.26 ppm, ^{1}H; 77.00 ppm, ^{13}C) and ^{11}B NMR chemical shifts to external $BF_3 \cdot OEt_2$ (0.0 ppm). High-resolution mass spectra (HMRS) were recorded on a micro-TOF-Q II mass analyzer or Q-TOF 2 using positive ion electrospray. Compounds **1a,**[22] **1b,**[23] **1c,**[24] and **1d** [25] have been prepared according to known protocol.[19] The ethereal solution of CH_2N_2 was generated from N-nitroso-N-methylurea according to the literature.[26]

General procedure for the Suzuki–Miyaura cross-couplings with 1,2-bis(boronates) 1a-1d. Synthesis of compounds 2a-2n. A solution of bispinacolate ester **1** (0.5 mmol) in THF (5 mL) and water (0.1 mL) was degassed under argon atmosphere, before the addition of [1, 1'-bis (diphenyl phosphino)ferrocene] dichloropalladium(II) (7.5 mg, 0.01 mmol), potassium phosphate tribasic monohydrate (346 mg, 1.5 mmol) and arylbromide (0.5 mmol). The reaction mixture was heated at reflux for 1h, cooled to room temperature, diluted with water and extracted with Et_2O (2 x 15 mL). The combined organic extracts were dried over $MgSO_4$ and evaporated under vacuum. The residue was purified by column chromatography (230-400 mesh Silica gel, EtOAc in cyclohexane) to give the corresponding Suzuki products.

(E)-4,4,5,5-tetramethyl-2-(1-phenylhex-1-en-2-yl)-1,3,2-dioxaborolane (**2a**): 86 mg (60%). Colourless oil, R_f = 0.10 (EtOAc/Hexane 10:90); ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.33-7.31 (m, 2H), 7.25-7.22 (m, 2H), 7.20-7.16 (s, 1H), 6.87 (s, 1H), 2.31-2.28 (m, 2H,), 1.49-1.43 (m, 2H), 1.38-1.34 (m, 2H), 1.25 (s, 12H), 0.90 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 139.0, 128.0, 127.7, 126.7, 83.4, 37.7, 31.8, 24.7, 22.4, 14.0 (The carbon α to boron was not found); ^{11}B NMR (96 MHz, $CDCl_3$): δ 31.1 (br); IR (neat); 3746, 3395, 3060, 3026, 2957, 2925, 2854, 1713, 1622, 1599, 1454, 1373, 1303, 1252, 1213, 1143, 1078, 1032, 1007, 982, 964, 919, 854, 750, 697, 672, 620, 577; HRMS (ESI+): *m/z* (M^++H) calculated for $C_{18}H_{28}BO_2$ 287.2176, found 287.2161.

(E)-4,4,5,5-tetramethyl-2-(1-p-tolylhex-1-en-2-yl)-1,3,2-dioxaborolane (**2b**). 87 mg (58%). Colourless oil, R_f = 0.10 (EtOAc/Hexane 10:90). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21 (d, 2H, *J* = 7.9 Hz), 7.04 (d, 2H, *J* = 7.7 Hz), 6.83 (s, 1H), 2.34-2.25 (m, 5H), 1.51-1.41 (m, 2H), 1.34-1.26 (m, 2H), 1.27 (s, 12H), 0.89 (t, 3H, *J* = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.6, 136.4, 136.1, 128.4, 128.0, 83.3, 38.1, 31.5, 24.7, 22.5, 21.1, 14.0 (The carbon α to boron was not found). ^{11}B NMR (96 MHz, $CDCl_3$): δ 31.1 (br) IR (neat): 3861, 3745, 3611, 2956, 2923, 2853, 1728, 1624, 1567, 1549, 1511, 1462, 1392, 1374, 1338, 1302, 1253, 1215, 1144, 1071, 1037, 964, 945, 860, 828, 804, 772, 708, 670, 574. HRMS (ESI+): *m/z* (M^++Na) calculated for $C_{19}H_{29}O_2BNa$ 323.2158, found 323.2156.

(E)-2-(1-(4-methoxyphenyl)-hex-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2c**). 98 mg (62%). Colourless oil, R_f = 0.15 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (d, 2H, *J* = 8.4 Hz), 6.81 (s, 1H), 6.78 (d, 2H, *J* = 8.8 Hz), 3.79 (s, 3H), 2.28-2.24 (m, 2H), 1.50-1.42 (m, 2H), 1.35-1.30 (m, 2H), 1.27 (s, 12H), 0.89 (t, 3H, *J* = 6.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6, 138.9, 131.5, 129.1, 113.2, 83.2, 55.1, 38.1, 31.0, 25.0, 22.5, 13.8 (The carbon α to boron was not found). IR (neat); 3746, 3611, 2955, 2924, 2853, 1729, 1607, 1573, 1510, 1462, 1374, 1298, 1245, 1175, 1143, 1035, 965, 941, 859, 831, 771, 705, 671, 577. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{19}H_{30}BO_3$ 317.2282, found 317.2287.

(E)-2-(1-(4-methoxyphenyl)-3-phenylprop-1en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2d**). 101 mg (58%). Colourless oil, R_f = 0.10 (EtOAc/Hexane 10:90). ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.32 (d, 2H, *J* = 8.6 Hz), 7.25-7.15 (m, 5H), 6.90 (s, 1H), 6.80 (d, 2H, *J* = 8.6 Hz), 3.79 (s, 3H), 3.63 (s, 2H), 1.08 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 141.1, 140.6, 131.3, 129.4, 129.3, 128.1, 125.9, 113.2, 83.4, 55.3, 44.2, 25.0 (The carbon α to boron was not found). IR (neat); 3429, 3028, 2978, 2930, 2838, 1714, 1605, 1511, 1456, 1392, 1304, 1249, 1173, 1143, 1111, 1077, 1032, 965, 832, 737, 700, 672. HRMS (ESI+): *m/z* (M^++Na) calculated for $C_{22}H_{28}BO_3Na$ 373.1945, found 373.1945.

(E)-2-(3-cyclohexyl-1-(4-methoxyphenyl)prop-1en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2e**). 107 mg (60%). Colorless oil, R_f = 0.10 (EtOAc/Hexane 10:90)**.** ^{1}H NMR

(500 MHz, $CDCl_3$): δ 7.31-7.27 (m, 2H), 6.81-6.77 (m, 3H), 3.79 (s, 1H), 2.16 (dt, 2H, *J* = 10.3, 5.2 Hz), 1.82-1.61 (m, 6H), 1.47-1.33 (m, 1H), 1.27 (s, 12H), 1.24-1.08 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7, 140.6, 131.8, 129.4, 113.2, 83.3, 55.3, 46.2, 38.2, 33.3, 26.7, 26.4, 24.8 (The carbon α to boron was not found). IR (neat); 3445, 2976, 2921, 2850, 1707, 1607, 1511, 1444, 1393, 1373, 1346, 1302, 1243, 1174, 1135, 1080, 1038, 964, 886, 859, 829, 767, 713, 667. HRMS (ESI+): *m/z* (M^++Na) calculated for $C_{22}H_{33}BO_3Na$ 379.2415, found 379.2414.

(E)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-hex-1-enyl)benzaldehyde (**2f**). 118 mg (75%), colourless oil, R_f = 0.20 (EtOAc/Hexane 10:90). ^1H NMR (400 MHz, $CDCl_3$): δ 10.28 (s, 1H), 7.85 (dd, 1H, *J* = 1.8, 7.7 Hz), 7.45 (dd, IH, *J* = 1.6, 7.5 Hz), 7.38-7.31 (m, 1H), 7.31-7.27 (m, 2H), 2.36 (td, 2H, *J* = 1.5, 7.5 Hz), 1.54-1.46 (m, 2H), 1.41-1.34 (m, 2H), 1.09 (s, 12H), 0.94 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 143.2, 141.2 (br), 135.9, 133.6, 133.0, 130.4, 127.7, 127.4, 83.0, 37.2, 31.7, 24.55, 24.4, 13.6. ^{11}B NMR (96 MHz, $CDCl_3$): δ 30.4 (br. HRMS (ESI+): *m/z* (M^++Na) calculated for $C_{19}H_{27}O_3BNa$ 337.1950, found 337.1951.

(E)-5-methoxy-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-hex-1-enyl)benzaldehyde (**2g**). 100 mg (58%). Colourless oil, R_f = 0.40 (EtOAc/Hexane 20:80). ^1H NMR (500 MHz, $CDCl_3$): δ 10.25 (s, 1H), 7.36 (d, 1H, *J* = 2.8 Hz), 7.23-7.21 (m, 2H), 7.04 (dd, 1H, *J* = 2.8 , 8.5 Hz), 3.85 (s, 3H), 2.37-2.33 (m, 2H), 1.52-1.46 (m, 2H), 1.41-1.34 (m, 2H), 1.11 (s, 12H), 0.93 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 158.7, 136.2, 135.6, 134.5, 131.6, 120.7, 109.8, 83.4, 55.4, 37.2, 31.8, 24.5, 22.4, 13.9 (The carbon α to boron was not found). IR (neat): 2956, 2924, 2853, 1741, 1691, 1602, 1564, 1493, 1463, 1392, 1308, 1262, 1220, 1161, 1144, 1037, 964, 862, 836, 772, 706. HRMS (ESI+): *m/z* (M^++Na) calculated for $C_{20}H_{29}BO_4Na$ 367.2051, found 367.2059.

(E)-4,5-dimethoxy-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-enyl) benzaldehyde (**2h**). 97 mg (52%). Colourless oil, R_f = 0.60 (EtOAc/Hexane 20:80). ^1H NMR (500 MHz, $CDCl_3$): δ 10.11 (s, 1H), 7.38 (s, 1H), 7.17 (s, 1H), 6.78 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 2.36 (dd, 2H, *J* = 11.0, 4.1 Hz), 1.53-1.47 (m, 2H), 1.43-1.35 (m, 2H), 1.09 (s, 12H), 0.94 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 152.9, 148.1, 141.3 (br), 138.7, 135.3, 127.3, 112.1, 108.1, 83.3, 55.7, 55.6, 37.0, 31.7, 24.5, 22.3, 13.8. IR (neat):

2956, 2924, 2853, 1678, 1594, 1564, 1507, 1462, 1391, 1340, 1308, 1268, 1217, 1143, 1108, 1034, 1003, 964, 858, 772, 700, 671. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{21}H_{32}BO_5$ 375.2337, found 375.2323.

(E)-1-(2-(4,4,5,5-tetramethyl-1,2,3-dioxaborolan-2-yl)-hex-1-enyl)-2-naphthaldehyde (**2i**). 93 mg (51%). Colourless oil, R_f = 0.15 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.43 (s, 1H), 8.12 (d, 1H, *J* = 8.3 Hz), 7.96 (d, 1H, *J* = 8.5 Hz), 7.83 (d, 1H, *J* = 7.9 Hz), 7.80 (d, 1H, *J* = 8.6 Hz), 7.60-7.57 (m, 1H), 7.54-7.51 (m, 1H), 7.36 (s, 1H), 2.54 (dd, 2H, *J* = 16.9, 7.8 Hz), 1.64-1.58 (m, 2H), 1.50-1.44 (m, 2H), 0.99 (t, 3H, *J* = 7.3 Hz), 0.87 (s, 6H), 0.80 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): 193.0, 144.2, 135.6, 133.5, 132.4, 131.5, 128.4, 128.1, 127.3, 126.8, 126.4, 121.9, 83.2, 36.9, 31.9, 24.2, 22.6, 14.0 (The carbon α to boron was not found). IR (neat): 3059, 2957, 2924, 2853, 1681, 1617, 1595, 1461, 1427, 1397, 1374, 1314, 1256, 1225, 1142, 1029, 964, 857, 818, 747, 705, 668. . HRMS (ESI+): m/z (M^++Na) calculated for $C_{23}H_{29}BO_3Na$ 386.2138, found 386. 2146.

(E)-2-(3-cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-enyl)-4,5-dimethoxybenzaldehyde (**2j**). 135 mg (65%). Colourless oil, R_f = 0.60 (EtOAc/Hexane 20:80). ^{1}HNMR (500 MHz, $CDCl_3$): δ 10.13 (s, 1H), 7.39 (s, 1H), 7.13 (s, 1H), 6.77 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 2.26 (d, 2H, *J* = 7.1 Hz), 1.88-1.62 (m, 6H), 1.55-1.38 (m, 1H), 1.31-1.13 (m, 4H), 1.08 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.8, 153.0, 148.3, 138.8, 136.5, 127.4, 112.3, 108.2, 83.4, 56.0, 45.6, 37.9, 33.4, 26.5, 26.4, 24.5 (The carbon α to boron was not found). IR (neat); 3860, 3812, 3669, 3610, 3593, 4370, 3396, 3342, 3287, 3245, 2977, 2921, 2847, 1785, 1752, 1678, 1595, 1566, 1522, 1510, 1449, 1388, 1337, 1309, 1270, 1216, 1137, 1109, 1034, 1004, 965, 852, 772. HRMS (ESI+): m/z (M^++H) calculated for $C_{24}H_{36}BO_5$ 415.2650, found 415. 2647.

(E)-5-(tert-butyldimethylsilyloxy)-2-(3-cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-enyl)-4-methoxybenzaldehyde (**2k**). 159 mg (62%). Colourless oil, R_f = 0.20 (EtOAc/Hexane 10:90). ^{1}HNMR (500 MHz, $CDCl_3$): δ 10.18 (s, 1H), 7.36(s, 1H), 7.13 (s, 1H), 6.73 (s, 1H), 3.87 (s, 3H), 2.25 (d, 2H, *J* = 7.1 Hz), 1.82-1.61 (m, 6H), 1.51-1.40 (m, 1H), 1.32-1.16 (m, 4H), 1.08 (s, 12H), 0.99 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (101 MHz,

$CDCl_3$): δ 190.9, 155.2, 139.2, 137.0, 118.9, 112.8, 83.3, 77.36, 70.0, 76.7, 55.5, 45.5, 38.0, 33.4, 26.4 (The carbon α to boron was not found). IR (neat); 3744, 3609, 3394, 3338, 3308, 3246, 2925, 2853, 1657, 1642, 1550, 1513, 1448, 1389, 1325, 1286, 1219, 1140, 1064, 1012, 898, 838. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{29}H_{48}O_5BSi$ 515.3358, found 515.3347.

(E)-4,5-dimethoxy-2-(3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-enyl)benzaldehyde (**2l**). 130 mg (64%). R_f = 0.60 (EtOAc/Hexane 20:80). ^{1}HNMR (400 MHz, $CDCl_3$): δ 10.11 (s, 1H), 7.38 (s, 1H), 7.33-7.27 (m, 4H), 7.24-7.17 (m, 2H), 6.80(s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.69 (d, 2H, *J* =1.2 Hz), 0.97 (s, 12H). ^{13}C NMR (101MHz, $CDCl_3$): δ 190.6, 153.0, 148.4, 139.9, 138.3, 137.0, 129.2, 128.3, 127.4, 126.2, 112.3, 108.5, 83.5, 56.1, 43.3, 24.5 (The carbon α to boron was not found). IR (neat); 3448, 3066, 2978, 2929, 2832, 2718, 1686, 1594, 1557, 1508, 1451, 1397, 1343, 1263, 1218, 1112, 1031, 1000, 960, 886, 858, 777, 699. HRMS (ESI+): *m/z* (M^++Na) calculated for $C_{24}H_{29}BO_5Na$, 431.2000; found, 431.1981.

(E)-5-methoxy-2-(3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-enyl)benzaldehyde (**2m**). 109 mg (58%). Colourless oil, R_f = 0.30 (EtOAc/Hexane 10:90). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.24 (s, 1H), 7.36 (d, 1H, *J* = 2.8 Hz), 7.32-7.22 (m, 6H), 7.21-7.16 (m, 1H), 7.04 (dd, 1H, *J* = 8.5, 2.8 Hz), 3.86 (s, 3H), 3.69 (d, 2H, *J* = 1.2 Hz), 0.98 (s, 12H). ^{13}C NMR (101MHz, $CDCl_3$): δ 191.8, 159.0, 140.0, 137.2, 135.6, 134.6, 131.7, 129.2, 128.3, 126.1, 120.6, 110.4, 83.5, 55.5, 43.4, 24.4 (The carbon α to boron was not found). IR (neat): 3420, 2980, 2934, 2100, 1666, 1521, 1452, 1374, 1220, 1166, 1113, 1078, 1020, 854, 769, 697. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{23}H_{28}BO_4$, 379.2075; found, 379.2070, (M^++Na) calculated for $C_{23}H_{27}BO_4Na$, 401.1894; found, 401.1890.

(E)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)vinyl)benzaldehyde (**2n**). 117 mg (65%). Colourless oil, R_f = 0.10 (EtOAc/Hexane 10:90). ^{1}HNMR (400 MHz, $CDCl_3$): δ 10.28 (s, 1H), 7.85 (dt, 1H, *J* = 12.3, 6.1 Hz), 7.79 (s, 1H), 7.53-7.46 (m, 1H), 7.44-7.35 (m, 2H), 1.12(s, 12H), 0.23(s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.9, 146.7, 144.5, 133.1, 129.2, 128.7, 127.6, 83.4, 24.7, -1.0 (The carbon α to boron was not found). IR

(neat); 3743, 3438, 3396, 3064, 2954, 2897, 2837, 1696, 1587, 1557, 1466, 1370, 1317, 1245, 1215, 1138, 1096, 1008, 984, 951, 838, 760, 719, 690, 630. HRMS (ESI+): *m/z* (M^++Na) calculated for $C_{18}H_{27}BO_3SiNa$ 353.1714, found 353.1721.

General Procedure for Petasis cyclization from Boronates 2f-2n. Synthesis of Compounds 3a-3v. Amine (0.5 mmol) was added to a stirred solution of boronate **2** (0.3 mmol) in 1,1,1,3,3,3-hexafluoropropan-2-ol (1 mL) under argon atmosphere at room temperature. The reaction mixture was stirred during 8 h. The solvent was removed under reduced pressure to give a residue that was purified by column chromatography (230-400 mesh Silica gel, EtOAc in cyclohexane) to afford amino indenes **3**.

4-(2-Butyl-1H-inden-1-yl) morpholine (**3a**). 71 mg (92%). Colourless oil, R_f = 0.10 (EtOAc/Hexane 10:90). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, 1H, *J* = 7.3 Hz), 7.23-7.15 (m, 2H), 7.09-7.04 (m, 1H), 6.41 (s, 1H), 4.12 (s, 1H), 3.71-3.62 (m, 4H), 2.72-2.69 (m, 2H), 2.59-2.54 (m, 2H), 2.44-2.38 (m, 2H), 1.68-1.52 (m, 2H), 1.44-1.35 (m, 2H), 0.95 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 144.3, 143.1, 127.5, 126.55, 124.5, 123.8, 120.2, 72.9, 67.75, 49.3, 30.6, 29.0, 22.6, 14.0. IR (neat):3062, 2955, 2924, 2852, 1718, 1616, 1508, 1458, 1376, 1318, 1290, 1271, 1244, 1168, 1115, 1011, 929, 888, 848, 752, 732, 690. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{17}H_{24}NO$, 258.1852; found, 258.1854.

N,N-Diallyl-2-butyl-1H-inden-1-amine (**3b**)**.** 66 mg (75%). Colourless oil, R_f = 0.10 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, 1H, *J* = 7.3 Hz), 7.23-7.13 (m, 2H), 7.06 (td, 1H, *J* = 7.2, 1.4 Hz), 6.39 (s, 1H), 5.88-5.78 (m, 2H), 5.22, (dd, 2H, *J* = 17.2, 1.1 Hz), 5.10 (d, 2H, *J* = 10.1 Hz, CH=$\underline{H_2}$), 4.38 (s, 1H), 3.14-3.01 (m, 4H), 2.46-2.33 (m, 2H), 1.66-1.46 (m, 2H), 1.44-1.33 (m, 2H), 0.94 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.8, 144.6, 144.35, 137.3, 127.3, 125.9, 124.2, 123.6, 120.3, 116.8, 67.2, 53.3, 30.3, 29.0, 22.45, 14.1. IR (neat): 3072, 2957, 2924, 2854, 1721, 1644, 1620, 1462, 1399, 1377, 1287, 1261, 1118, 1074, 995, 919, 876, 803, 751, 733. HRMS (ESI+): *m/z* (M^++Na) calculated for $C_{19}H_{25}NNa$ 290.1879, found 290.1883.

4-(2-Butyl-6-methoxy-1H-inden-1-yl) morpholine (**3c**). 63 mg (73%). Colourless oil, R_f = 0.25 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (s, 1H), 7.04 (d, 1H, *J* = 8.2 Hz), 6.75 (dd, 1H, *J* = 2.2, 8.0 Hz), 6.34 (s, 1H), 4.09 (s, 1H), 3.81 (s, 3H), 3.70-3.63 (m, 4H), 2.71-2.70 (m, 2H), 2.60-2.55 (m, 2H), 2.40-2.34 (m, 2H), 1.63-1.51 (m, 2H), 1.43-1.35 (m, 2H), 0.94 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.0, 149.7, 144.9, 137.2, 126.2, 120.4, 112.1, 111.8, 72.8, 67.8, 55.9, 49.4, 30.6, 29.0, 22.5, 14.2. IR (neat): 2955, 2922, 2852, 1728, 1609, 1581, 1468, 1318, 1284, 1219, 1115, 1034, 1010, 854, 771 cm^{-1}. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{18}H_{26}NO_2$, 288.1958; found, 288.1949.

N,N-Diallyl-2-butyl-6-methoxy-1H-inden-1-amine (**3d**)**.** 72 mg (81%). Colourless oil, R_f = 0.10 (EtOAc/Hexane 10:90). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (dd, 1H, *J* = 3.9, 2.9 Hz), 7.05 (d, 1H, *J* = 8.1 Hz), 6.74 (dd, 1H, *J* = 8.1, 2.4 Hz), 6.33 (d, 1H, *J* = 0.9 Hz), 5.90-5.80 (m, 2H), 5.23 (dd, 2H, *J* = 17.2, 1.3 Hz), 5.13-5.08 (m, 2H), 4.30 (s, 1H), 3.81 (s, 3H), 3.15-3.04 (m, 4H), 2.40-2.34 (m, 2H), 1.63-1.51 (m, 2H), 1.43-1.35 (m, 2H), 0.93 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 151.5, 146.3, 137.3, 125.3, 120.1, 116.7, 112.0, 111.1, 67.4, 55.5, 53.4, 30.6, 28.8, 22.6, 14.0. IR (neat): 3745, 3076, 2955, 2923, 2853, 2832, 1641, 1607, 1581, 1471, 1429, 1355, 1282, 1258, 1153, 1136, 1092, 1035, 995, 918, 859, 804, 772, 726. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{20}H_{28}NO$, 298.2165; found, 298.2155.

N-Benzyl-2-butyl-6-methoxy-N-methyl-1H-inden-1-amine (**3e**)**.** 75 mg (78%). Colourless oil, R_f = 0.25 (EtOAc/Hexane 10:90). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, 2H, *J* = 7.2 Hz), 7.31 (dd, 2H, *J* = 10.2, 4.7 Hz, Ar-), 7.23 (dd, 1H, *J* = 8.3, 6.2 Hz), 7.16 (d, 1H, *J* = 2.1 Hz), 7.08-7.05 (m, 1H), 6.75 (dd, 1H, *J* = 8.1, 2.4 Hz), 6.35 (d, 1H, *J* = 0.8 Hz), 4.30 (s, 1H), 3.81 (s, 3H), 3.76-3.67 (m, 2H), 2.45.2.41 (m, 2H), 2.20 (s, 3H), 1.63-1.51 (m, 2H), 1.43-1.35 (m, 2H), 0.93 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.1, 151.0, 145.6, 140.1, 137.5, 128.7, 128.3, 126.9, 125.6, 120.2, 112.4, 111.4, 71.8, 58.2, 55.6, 37.8, 30.8, 28.7, 23.0, 13.5. IR (neat): 3060, 3027, 2953, 2927, 2855, 2833, 2794, 1705, 1605, 1581, 1471, 1438, 1359, 1310, 1282, 1255, 1230, 1133, 1103, 1034, 976, 923, 861, 806, 771, 739, 698, 603. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{22}H_{28}NO$, 322.2165; found, 322.2152.

1-(2-Butyl-6-methoxy-1H-indene-1-yl) pyrrolidine (**3f**). 66 mg (82%). Colourless oil, R_f = 0.10 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (s, 1H), 7.04 (d, 1H, *J* = 8.2 Hz), 6.73 (dd, 1H, *J* = 2.4 , 8.1 Hz), 6.30 (s, 1H), 4.42 (s, 1H), 3.80 (s, 3H), 2.83-2.81 (m, 2H), 2.60-2.56 (m, 2H), 2.40-2.33 (m, 2H), 1.75-1.70 (m, 4H), 1.64-1.51 (m, 2H), 1.43-1.36 (m, 2H), 0.94 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.9, 151.4, 145.7, 137.7, 124.6, 119.8, 112.5, 111.3, 68.2, 55.5, 48.2, 30.6, 29.1, 24.0, 22.6, 14.0. IR (neat): 3448, 3027, 2594, 2853, 1742, 1605, 1509, 1452, 1385, 1247, 1175, 1116, 1072, 1028, 873, 829, 771, 699. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{18}H_{26}NO$, 272.2014; found, 272.2003.

1-(2-Butyl-6-methoxy-1H-indene-1-yl) piperidine (**3g**). 64 mg (75%). Colourless oil, R_f = 0.10 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (s, 1H), 7.02 (d, 1H, *J* = 8.2 Hz), 6.72 (dd, 1H, *J* = 2.3, 8.7 Hz), 6.31 (s, 1H), 4.08 (s, 1H), 3.81 (s, 3H), 2.65-2.61 (m, 2H), 2.50-2.48 (m, 2H), 2.35 (t, 2H, *J* = 7.6 Hz), 1.64-1.50 (m, 6H), 1.43-1.36 (m, 4H), 0.94 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 151.0, 145.7, 137.4, 125.0, 120.0, 112.3, 111.2, 73.6, 55.5, 50.1, 30.6, 29.0, 26.8, 24.7, 22.6, 14.0. IR (neat): 3051, 2929, 2854, 2802, 2744, 1711, 1607, 1582, 1471, 1432, 1379, 1357, 1308, 1281, 1207, 1166, 1134, 113, 1090, 1034, 1002, 858, 770, 602. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{19}H_{28}NO$, 286.2165; found, 286.21.

1-(2-Butyl-6-methoxy-1H-indene-1-yl)-4-phenyl piperazine (**3h**). 78 mg (72%). Colourless oil, R_f = 0.10 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25-7.22 (m, 2H, 7.10 (s, 1H), 7.05 (d, 1H, *J* = 8.0 Hz), 6.90 (d, 2H, *J* = 7.9 Hz), 6.83 (t, 1H, *J* = 7.3 Hz), 6.74 (dd, 1H, *J* = 2.2, 8.0 Hz), 6.36 (s, 1H), 4.20 (s, 1H), 3.80 (s, 3H), 3.20-3.10 (m, 4H), 2.90-2.80 (m, 2H), 2.75-2.71 (m, 2H), 2.42-2.36 (m, 2H), 1.64-1.51 (m, 2H), 1.45-1.36 (m, 2H), 0.94 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.0, 151.5, 149.9, 144.9, 137.2, 128.9, 125.8, 120.1, 119.5, 116.0, 1112.2, 111.8, 72.6, 55.5, 50.0, 48.7, 30.6, 29.0, 22.6, 14.0. IR (neat): 3745, 3639, 3017, 2925, 2852, 1730, 1694, 1694, 1600, 1499, 1470, 1380, 1282, 1216, 1140, 1033, 1013, 926, 858, 770, 667. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{24}H_{31}N_2O$, 363.2430; found, 363.2421.

4-(2-Butyl-5,6-dimethoxy-1H-inden-1-yl) morpholine (**3i**). 67 mg (71%). Colourless oil, R_f = 0.80 (EtOAc/Hexane 20:80). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (s, 1H), 6.76 (s, 1H), 6.32 (s, 1H), 4.07 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.75-3.64 (m, 4H), 2.74-2.70 (m, 2H), 2.60-2.57 (m, 2H), 2.41-2.33 (m, 2H), 1.63-1.50 (m, 2H), 1.44-1.35 (m, 2H), 0.95 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 148.7, 146.0, 137.1, 135.1, 125.9, 109.5, 104.2, 72.8, 67.7, 56.4, 55.9, 49.2, 30.7, 29.0, 22.5, 13.9. IR (neat): 3745, 3611, 3396, 2954, 2923, 2852, 1694, 1602, 1582, 1490, 1461, 1411, 1315, 1216, 1140, 1114, 1089, 1012, 992, 933, 861, 772. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{19}H_{28}NO_3$, 318.2063; found, 318.2051.

1-(2-Butyl-5,6-dimethoxy-1H-indene-1-yl)-4-phenyl piperazine (**3j**). 96 mg (82%). Colourless oil, R_f = 0.70 (EtOAc/Hexane 20:80). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26-7.22 (m, 2H), 7.09 (s, 1H), 6.92 (dd, 2H, *J* = 8.7, 0.8 Hz), 6.84 (t, 1H, *J* = 7.3 Hz), 6.79 (s, 1H), 6.34 (s, 1H), 4.17 (s, 1H), 3.88 (s, 6H), 3.20-3.11 (m, 4H), 2.88-2.83 (m, 2H), 2.77-2.72 (m, 2H), 2.41-2.37 (m, 2H), 1.64-1.51 (m, 2H), 1.44-1.34 (m, 2H), 0.94 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.4, 151.0, 148.7, 145.9, 137.1, 135.2, 128.9, 125.8, 119.5, 116.0, 109.5, 104.2, 72.6, 56.3, 55.9, 49.9, 48.7, 30.7, 29.0, 22.5, 13.9. IR (neat): 3057, 2953, 2926, 2854, 2827, 1677, 1599, 1492, 1455, 1410, 1380, 1304, 1232, 1143, 1085, 1101, 992, 927, 863, 814, 760. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{25}H_{33}N_2O_2$, 393.2536; found, 393.2524.

N,N-Diallyl-2-butyl-5,6-dimethoxy-1H-inden-1-amine (**3k**). 78 mg (78%). Colourless oil, R_f = 0.60 (EtOAc/Hexane 20:80). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (s, 1H), 6.75 (s, 1H), 6.30 (s, 1H), 5.88-5.80 (m, 2H), 5.22 (dd, 2H, *J* = 17.2, 1.2 Hz), 5.11 (d, 2H, *J* = 10.1 Hz), 4.31 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.15-3.04 (m, 4H), 2.42-2.35 (m, 2H), 1.63-1.46 (m, 2H), 1.42-1.32 (m, 2H), 0.94 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.6, 148.6, 145.9, 137.2, 136.6, 125.4, 116.6, 109.3, 104.2, 67.6, 56.5, 55.9, 53.5, 30.7, 29.0, 22.6, 14.0. IR (neat): 3360, 2926, 2833, 1742, 1659, 1487, 1453, 1415, 1336, 1218, 1112, 1017, 918, 772. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{21}H_{30}NO_2$, 328.2271; found, 328.2259.

N-Benzyl- 2-butyl-5, 6- dimethoxy-N-methyl-1H-inden-1-amine (**3l**). 86 mg (82%). Colourless oil, R_f = 0.50 (EtOAc/Hexane 20:80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.37 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.22 (m, 1H), 7.13 (s, 1H), 6.80 (s, 1H), 6.33 (s, 1H), 4.21 (s, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.71-3.62 (m, 2H), 2.50-2.43 (m, 2H), 2.33 (s, 3H, NCH_3), 1.65-1.50 (m, 2H, CH_2), 1.46-1.37 (m, 2H, CH_2), 0.95 (t, 3H, *J* = 7.3 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 148.7, 146.0, 139.9, 137.3, 135.8, 128.5, 128.1, 126.8, 125.5, 109.5, 104.2, 71.8, 57.9, 56.5, 55.9, 37.9, 30.8, 29.1, 22.7, 14.0. IR (neat): 2924, 2853, 1679, 1491, 1463, 1335, 1218, 1099, 1027, 772.HRMS (ESI+): *m/z* (M^++H) calculated for $C_{23}H_{30}NO_2$, 352.2271; found, 352.224760.

2-Butyl-5,6-dimethoxy-N-(prop-2-ynyl)-1H-inden-1-amine (**3m**)**.** 64 mg (75%). Colourless oil, R_f = 1.50 (EtOAc/Hexane 20:80). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (s, 1H), 6.77 (s, 1H), 6.36 (s, 1H), 4.27 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.04 (d, 2H, *J* = 2.5 Hz), 2.42-2.31 (m, 2H), 2.18 (t, 1H, *J* = 2.4 Hz), 1.94 (s, 1H), 1.66-1.50 (m, 2H), 1.45-1.37 (m, 2H), 0.95 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.3, 148.7, 146.6, 136.5, 135.6, 126.0, 107.8, 104.1, 82.4, 71.1, 65.3, 56.1, 55.9, 32.4, 30,5, 28.0, 22.4, 13.8. IR (neat): 3745, 3610, 3286, 3062, 2954, 2927, 2857, 1673, 1645, 1605, 1496, 1312, 1265, 1215, 1125, 1030, 864, 771, 668. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{18}H_{24}NO_2$, 286.1801; found, 286.1791.

N-Benzyl-2-butyl-5,6-dimethoxy-1H-inden-1-amine (**3n**). 73 mg (72%). Colourless oil, R_f = 0.70 (EtOAc/Hexane 20:80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.17 (m, 5H), 7.06 (s, 1H), 6.80 (s, 1H), 6.40 (s, 1H), 4.30 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.40 (d, 1H, *J* = 12.8 Hz), 3.34 (d, 1H, *J* = 12.8 Hz) 2.47-2.33 (m, 2H), 1.85 (br, 1H), 1.67-1.51 (m, 2H), 1.46-1.37 (m, 2H), 0.95 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 148.7, 146.7, 140.8, 136.8, 128.2, 128.1, 126.8, 125.7, 107.9, 104.2, 66.2, 56.3, 56.0, 47.4, 30.7, 28.2, 22.6, 13.9. IR (neat): 2924, 2923, 2853, 1652, 1604, 1492, 1460, 1312, 1264, 1217, 1126, 1028, 993, 863, 771, 700. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{22}H_{28}NO_2$, 338.2114; found, 338.2103.

4-(2-Butyl-3H-cyclopenta[α]napthalen-3-yl) morpholine (**3o**). 61 mg (66%). Colourless oil, R_f = 0.10 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, 1H, *J* = 8.3 Hz), 7.84 (d, 1H, *J* = 7.9 Hz), 7.68 (d, 1H, *J* = 8.2 Hz), 7.61 (d, 1H, *J* = 8.2 Hz), 7.48-7.40 (m, 2H), 7.00 (s, 1H), 4.25 (s, 1H), 3.73-3.64 (m, 4H), 2.77 (br, 2H, C_2), 2.65-2.61 (m, 2H), 1.73-1.60 (m, 2H), 1.69-1.56 (m, 2H), 1.49-1.36 (m, 2H), 0.98 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 140.6, 140.3, 133.3, 128.3, 127.1, 125.4, 125.1, 123.8, 123.7, 123.6, 122.9, 73.8, 67.8, 49.6, 31.0, 29.4, 22.7, 14.1. IR (neat): 3056, 2956, 2924, 2853, 1682, 1620, 1595, 1563, 1515, 1459, 1374, 1315, 1255, 1226, 1143, 1116, 1071, 1015, 963, 858, 820, 766, 670. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{21}H_{25}NO$, 308.2008; found, 308.2010.

2-(Cyclohexylmethyl)-5,6-dimethoxy-N-(prop-2-ynyl)-1H-1-amine (**3p**). 78 mg (80%). Colourless oil, R_f = 0.60 (EtOAc/Hexane 10:90). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 1H), 6.78 (s, 1H), 6.36 (s, 1H), 4.25 (s, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.02 (d, 2H, *J* = 2.5 Hz), 2.29 (ddd, 1H, *J* = 14.7, 5.5, 1.3 Hz), 2.25 – 2.17 (m, 2H), 1.91-1.70 (m, 5H), 1.61-1.47 (m, 1H), 1.34-1.15 (m, 4H), 1.10-0.96 (m, 1H), 0.94-0.80 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.8, 146.8, 136.7, 135.8, 127.6, 108.0, 104.3, 82.6, 71.2, 65.5, 56.4, 56.1, 37.5, 36.4, 34.1, 32.9, 32.5, 26.5, 26.4, 26.2. IR (neat); 3855, 3744, 3611, 3525, 3416, 3395, 3285, 3116, 3051, 2995, 2920, 2847, 1695, 1608, 1579, 1490, 1448, 1410, 1315, 1286, 1215, 1125, 1085, 1028, 991, 868, 845, 760, 694, 670, 642. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{21}H_{28}NO_2$, 326.2114; found, 326.2108.

1-(2-(Cyclohexylmethyl)-5,6-dimethoxy-1H-inden-1-yl)-4-phenylpiperazine (**3q**)**.** 106 mg (82%). Colourless oil, R_f = 0.30 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.20 (m, 2H), 7.10 (d, 1H, *J* = 8.1 Hz), 6.92 (d, 2H, *J* = 8.1 Hz), 6.83 (dd, 1H, *J* = 13.3, 6.0 Hz), 6.78 (s, 1H), 6.33 (s, 1H), 4.14 (s, 1H), 3.88 (s, 6H), 3.22-3.09 (m, 4H), 2.86 (dd, 2H, *J* = 10.5, 5.2 Hz), 2.80-2.68 (m, 2H), 2.37 (dd, 1H, *J* = 14.7, 4.6 Hz), 2.27-2.14 (m, 1H), 1.80-1.62 (m, 5H), 1.29-1.18 (m, 4H), 1.07-0.96 (m, 1H), 0.93- 0.82 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.6, 149.5, 148.8, 146.0, 137.1, 135.4, 129.0, 127.1, 119.6, 116.1, 109.6, 104.3, 72.6, 56.5, 56.0, 50.0, 48.9, 37.3, 34.2, 33.1, 26.6, 26.4, 26.3. IR (neat); 3315, 2925, 2848, 1637, 1493, 1450, 1232, 1143, 1014. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{28}H_{37}N_2O_2$ 433.2855, found 433.2856.

4-(6-(Tert-butyldimethylsilyloxy)-2-(cyclohexylmethyl)-5-methoxy-1H-inden-1-yl) morpholine (**3r**). 104 mg (76%). Colourless oil, R_f = 0.20 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.71 (s, 1H), 6.29 (s, 1H), 4.02 (s, 1H), 3.79 (s, 3H), 3.72–3.56 (m, 4H), 2.64 (br s, 2H), 2.54 (dd, 2H, *J* = 7.3, 4.0 Hz), 2.32 (dt, 1H, *J* = 17.1, 8.6 Hz), 2.22-2.11 (m, 1H), 1.87-1.64 (m, 4H), 1.60-1.49 (m, 1H), 1.33-1.12 (m, 4H), 1.01 (s, 9H), 0.93-0.81 (m, 2H), 0.17 (s, 3H), 0.15 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.4, 149.3, 141.6, 138.0, 135.3, 127.3, 118.2, 104.7, 72.6, 67.8, 55.6, 49.3, 37.3, 37.2, 34.2, 33.0, 26.6, 26.4, 26.3, 25.8, 18.5, -4.4, -4.5. IR (neat); 3317, 2951, 2926, 2847, 1645, 1484, 1450, 1412, 1343, 1294, 1250, 1213, 1115, 1013, 906. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{27}H_{44}NO_3Si$ 458.3090, found 458.3094.

6-(Tert-butyldimethylsilyloxy)-2-(cyclohexylmethyl)-5-methoxy-N-(prop-2-ynyl)-1H-inden-1-amine (**3s**). 99 mg (78%). Colourless oil, R_f = 0.60 (EtOAc/Hexane 30:70). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 1H), 6.73 (s, 1H), 6.33 (s, 1H), 4.23 (s, 1H), 3.80 (s, 3H), 3.03-3.01 (m, 2H), 2.28 (dt, 1H, *J* = 16.1, 8.0 Hz), 2.24–2.13 (m, 2H), 1.82 (d, 1H, *J* = 12.8 Hz), 1.72 (dd, 4H, *J* = 12.8, 3.3 Hz), 1.60–1.47 (m, 1H), 1.35–1.10 (m, 4H), 1.00 (s, 9H), 0.88 (ddd, 2H, *J* = 11.6, 10.2, 3.2 Hz), 0.16 (s, 3H), 0.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.7, 149.0, 142.4, 137.7, 136.1, 127.6, 116.8, 104.8, 82.6, 71.1, 65.2, 55.7, 37.4, 36.4, 34.1, 33.0, 32.6, 26.5, 26.4, 26.2, 25.8, 18.5, -4.5, -4.6. IR (neat); 3744, 3671, 3609, 3395, 3341, 3310, 3282, 2993, 2925, 2853, 1785, 1752, 1645, 1577, 1549, 1487, 1451, 1415, 1344, 1296, 1252, 1215, 1126, 1086, 1014, 908, 839, 780, 631. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{26}H_{40}NO_2Si$ 426.2828, found 426.2836.

4-(2-Benzyl-5,6-dimethoxy-1H-inden-1-yl) morpholine (**3t**). 76 mg (72%). Colourless oil, R_f = 0.50 (EtOAc/Hexane 30:70). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–7.24 (m, 4H), 7.21 (t, 1H, *J* = 7.0 Hz, 7.04 (s, 1H), 6.74 (s, 1H), 6.25 (s, 1H), 4.02 (s, 1H), 3.87 (s, 3H), 3.85 (s, 1H,, 3.77-3.62 (m, 6H), 2.74-2.63 (m, 2H), 2.63 -2.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.4, 148.8, 146.3, 140.2, 136.8, 135.3, 129.1, 128.3, 127.7, 126.0, 109.5, 104.7, 72.4, 67.8, 56.4, 56.0, 49.3, 36.0. IR (neat): 3451, 2952, 2850, 1627, 1490, 1457, 1410, 1314, 1288, 1244, 1214, 1140, 1113, 1088, 991, 861, 769, 702. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{22}H_{26}NO_3$ 352.1907; found, 352.1894.

4-(2-Benzyl-6-methoxy-1H-inden-1-yl) morpholine (**3u**). 73 mg (76%). Colourless oil, R_f = 0.30 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.23 (m, 5H), 7.21 (t, 1H, *J* = 7.0 Hz), 7.08-7.00 (m, 1H), 6.73 (dd, 1H, *J* = 8.1, 1.9 Hz), 6.28 (s, 1H), 4.05 (s, 1H, N-C), 3.79 (s, 3H), 3.76-3.60 (m, 6H), 2.80-2.66 (m, 2H), 2.64- 2.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.3, 148.3, 144.9, 140.2, 136.9, 129.1, 128.3, 127.7, 126.0, 120.7, 112.2, 111.9, 72.3, 67.8, 55.5, 49.2, 36.0. IR (neat): 3445, 3058, 3025, 2929, 2822, 2741, 1606, 1576, 1468, 1428, 1349, 1316, 1282, 1233, 1147, 1106, 1022, 921, 852, 809, 755, 695. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{21}H_{24}NO_2$, 322.1801; found, 322.1793.

N-(Prop-2-ynyl)-2-(trimethylsilyl)-1H-inden-1-amine (**3v**). 54 mg (75%). Colourless oil, R_f = 0.10 (EtOAc/Hexane 10:90). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, 1H, *J* = 7.2 Hz), 7.30-7.22 (m, 2H), 7.21-7.15 (m, 1H), 7.00 (d, 1H, *J* = 1.8 Hz), 4.66 (d, 1H, *J* = 1.6 Hz), 3.13-3.01 (m, 2H), 2.16 (t, 1H, *J* = 2.5 Hz), 1.76 (br s, 1H), 0.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.8, 148.3, 145.1, 142.6, 128.6, 126.5, 124.1, 122.1, 83.5, 72.0, 69.9, 34.1, 0.02. IR (neat): 3299, 3067, 2926, 2099, 1710, 1650, 1605, 1541, 1461, 1327, 1282, 1248, 1208, 1118, 1083, 1023, 841, 758, 635. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{15}H_{20}NSi$ 242.1365, found, 242.1378.

General procedure for the intermolecular Petasis reactions from boronates 2a-2e. Synthesis of compounds 4a-4g. Glyoxylic acid monohydrate (51 mg, 0.5 mmol) and amine (0.5 mmol) were added to a stirred solution of the boronate **2** (0.3 mmol) in 1,1,1,3,3,3-hexafluoropropan-2-ol) (1 mL) under argon atmosphere at room temperature. The reaction mixture was stirred during 78h. The solvent was removed under reduced pressure to give a residue which was directly used for further esterification reaction. To a solution of the crude acid in diethyl ether (5 mL) at 0 ^{o}C a solution of CH_2N_2 in ether (2 mL, 0.5M) (**Due to its explosiveness and toxicity**, diazomethane was directly generated in diethyl ether and used without further purification after simple decantation)[22] was added until the persistence of yellow color. After 2 h, the solvent was evaporated and residue was purified by column chromatography (230-400 mesh Silica gel, EtOAc in cyclohexane) to afford unsaturated amino esters **4.**

Methyl-(Z)-3-benzylidene-2-morpholinoheptanoate (**4a**). 57 mg (60%). Colourless oil, R_f = 0.50 (EtOAc/Hexane 30:70). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.31 (m, 4H), 7.27-7.24 (m, 1H), 6.69 (s, 1H), 4.07 (s, 1H), 3.75 (s, 3H), 3.73-3.64 (m, 4H), 2.31 (br, 4H) 2.27-2.24 (m, 2H), 1.55-1.46 (m, 2H), 1.43-1.37 (m, 2H), 0.94 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3, 137.0, 136.5, 131.7, 130.0, 128.1, 126.7, 69.1, 66.6, 52.0, 51.4, 30.5, 30.3, 22.5, 14.1. **I**R (neat): 3745, 3730, 3610, 3056, 3022, 2955, 2923, 2853, 2812, 2765, 1745, 1644, 1598, 1570, 1549, 1492, 1452, 1380, 1337, 1266, 1245, 1193, 1167, 1136, 1118, 1072, 1025, 989, 931, 905, 881, 860, 772, 744, 700, 667, 635, 585. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{19}H_{28}NO_3$ 318.2063, found 318.2062.

Methyl-(Z)-3-benzylidene-2-(diallylamino)heptanoate (**4b**). 65 mg (66%). Colourless oil, R_f = 0.20 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.32 (m, 4H), 7.26-7.22 (m, 1H), 6.64 (s, 1H), 5.71-5.63 (m, 2H), 5.04-5.00 (m, 4H), 4.48 (s, 1H), 3.69 (s, 3H), 3.17-3.05 (m, 4H), 2.32-2.28 (m, 2H), 1.53-1.47 (m, 2H), 1.43-1.37 (m, 2H), 0.94 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 138.0, 137.1, 134.7, 130.7, 129.0, 127.6, 126.6, 117.7, 64.5, 53.0, 51.7, 31.0, 31.0, 22.6, 14.1. IR (neat): 3859, 3825, 3746, 3610, 3076, 3019, 2955, 2923, 2853, 1743, 1642, 1549, 1493, 1461, 1372, 1261, 1214, 1193, 1163, 1122, 1073, 1013, 995, 919, 854, 747, 700, 667, 572. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{21}H_{29}NO_2Na$ 350.2091, found 350.2116.

Methyl-(Z)-3-(4-methylbenzylidene)-2-morpholinoheptanoate (**4c**). 48 mg (48%). Colourless oil, R_f = 0.40 (EtOAc/Hexane 30:70). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, 2H, *J* = 7.9 Hz), 7.16 (d, 2H, *J* = 7.9 Hz), 6.65 (s, 1H), 4.08 (s, 1H), 3.75 (s, 3H), 3.73-3.64 (m, 4H), 2.36 (s, 3H), 2.32 (br, 4H), 2.17 (t, 2H, *J* = 7.2 Hz), 1.55-1.44 (m, 2H), 1.43-1.36 (m, 2H), 0.93 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 136.4, 136.0, 134.1, 131.7, 128.8, 69.1, 66.6, 52.0, 51.4, 30.5, 30.3, 22.6, 21.1, 14.1. IR (neat): 3860, 3745, 3669, 3610, 2955, 2923, 2853, 2812, 1746, 1549, 1511, 1454, 1379, 1339, 1266, 1244, 1214, 1194, 1166, 1138, 1118, 1071, 1024, 990, 948, 905, 879, 810, 668, 640, 576. HRMS (ESI+): *m/z* (M^++Na) calculated for $C_{20}H_{29}NO_3Na$ 354.2045, found 354.2042.

Methyl-(Z)-3-(4-methoxybenzylidene)-2-morpholinoheptanoate (**4d**)**.** 53 mg (51%). Colourless oil, R_f = 0.40 (EtOAc/Hexane 30:70). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, 2H, *J* = 8.5 Hz), 6.90 (d, 2H, *J* = 8.6 Hz), 6.63 (s, 1H), 4.08 (s, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 3.73-3.64 (m, 4H), 2.35-2.28 (m, 4H) 2.24-2.12 (m, 2H), 1.54-1.44 (m, 2H), 1.38-1.31 (m,

2H), 0.90 (t, 3H, *J* = 6.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.0, 158.4, 135.5, 131.3, 130.2, 129.5, 113.5, 69.2, 66.6, 55.2, 52.0, 51.4, 31.7, 30.6, 22.6, 14.0. IR (neat): 3733, 3611, 2954, 2922, 2853, 2813, 1744, 1607, 1574, 1510, 1457, 1379, 1338, 1246, 1212, 1175, 1135, 1118, 1070, 1031, 990, 942, 866, 838, 766, 667, 595. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{20}H_{30}NO_4$ 348.2169, found 348.2168, *m/z* (M^++Na) calculated for $C_{20}H_{29}NO_4Na$ 370.1988, found 370.1987.

Methyl-(Z)-3-(4-methoxybenzylidene)-2-(4-phenylpiperazin-1-yl)heptanoate (**4e**). 78 mg (62%). Colourless oil, R_f = 0.30 (EtOAc/Hexane 10:90). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, 1H, *J* = 8.5 Hz), 7.23 (dd, 1H, *J* = 8.6, 7.4 Hz), 7.24-7.21 (m, 2H), 6.90-6.81 (m, 5H), 6.64 (s, 1H), 4.14 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.22-3.12 (m, 4H), 2.50 (br, 4H), 2.27 (t, 1H, *J* = 7.9 Hz), 1.53-1.47 (m, 2H), 1.42-1.37 (m, 2H), 0.94 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 158.4, 151.1, 136.0, 131.0, 130.2, 129.5, 129.0, 119.6, 116.0, 113.5, 69.0, 55.2, 52.0, 51.0, 50.0, 30.6, 30.4, 22.6, 14.1. IR (neat): 3020, 2928, 1743, 1602, 1509, 1452, 1384, 1214, 1023, 908, 746, 667, 625. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{26}H_{34}N_2O_3$ 423.26425, found 423.2645.

(Z)-Methyl 3-benzyl-4-(4-methoxyphenyl)-2-morpholinobut-3-enoate (**4f**). 71 mg (62%). Colourless oil, R_f = 0.40 (EtOAc/Hexane 30:70). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.21 (m, 7H), 6.87 (d, 2H, *J* = 8.6 Hz), 6.41 (s, 1H), 4.16 (s, 1H), 3.82 (s, 3H), 3.73-3.68 (m, 4H), 3.60 (s, 2H), 3.59 (s, 3H), 2.41-2.37 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 158.7, 139.3, 134.8, 134.7, 130.3, 129.6, 128.3, 126.2, 113.6, 68.9., 66.8, 55.3, 51.9, 51.5, 37.8. IR (neat); 3448, 3027, 2594, 2853, 1742, 1605, 1509, 1452, 1385, 1247, 1175, 1116, 1072, 1028, 873, 829, 771, 699**.** HRMS (ESI+): *m/z* (M^++Na) calculated for $C_{23}H_{27}NO_4Na$ 404.1832, found, 404.1850.

(Z)-methyl3-(cyclohexylmethyl)-4-(4-methoxyphenyl)-2-morpholinobut-3-enoate (**4g**). 71 mg (61%). Colourless oil, R_f = 0.50 (EtOAc/Hexane 30:70). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (d, 2H, *J* = 8.6 Hz), 6.90 (d, 2H, *J* = 8.6 Hz), 6.63 (s, 1H), 4.09 (s, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.68 (ddd, 4H, *J* = 16.0, 9.4, 4.7 Hz), 2.33 (s, 4H), 2.11 (dd, 2H, 15.6, 7.2 Hz), 1.88-1.66 (m, 4H), 1.58-1.39 (m, 1H), 1.38-1.05 (m, 4H), 0.94-0.82 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.5, 158.5, 133.1, 132.6, 130.3, 129.5, 113.6, 69.1, 66.7, 55.2, 51.8, 51.5, 38.8, 36.2, 33.5, 33.2, 26.6, 26.5. IR (neat); 3451, 2923, 2849, 1744, 1606, 1509, 1448, 1247, 1174,

1117, 1070, 1030, 945, 874, 830, 771. HRMS (ESI+): *m/z* (M^++H) calculated for $C_{23}H_{34}NO_4$ 388.2482, found 388.2490.

Supporting Information. ^{1}H and ^{13}C spectra of compounds **2a-n**, **3a-3v** and **4a-4g**. This material is available free of charge via the Internet at http://pubs.acs.org.

Notes

The authors declare no competing financial interest.

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