Note

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*J. Org. Chem.*, **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b02819 • Publication Date (Web): 05 Dec 2019

# Enantioselective Synthesis of Pyrrolizin-1-ones via Lewis Base Catalyzed N-Allylation of *N*-Silyl Pyrrole Latent Nucleophiles

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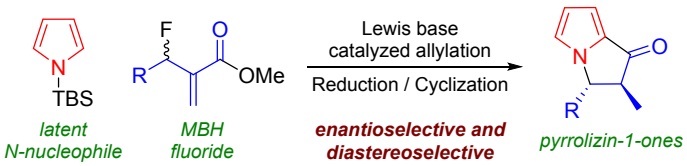


**Abstract**

Pyrrolizidine alkaloids and their derivatives often feature interesting biological activities. A class of substituted 2,3-dihydro-1*H*-pyrrolizin-1-one derivatives has been explored as a potential treatment for Alzheimer's disease but enantioselective synthesis of these molecules is still elusive. We report that enantioselective N-allylation of N-silyl pyrrole latent nucleophiles with allylic fluorides followed by hydrogenation and diastereoselective Friedel-Crafts cyclization constitute an efficient synthetic route to access enantioenriched substituted 2,3-dihydro-1*H*-pyrrolizin-1-ones.

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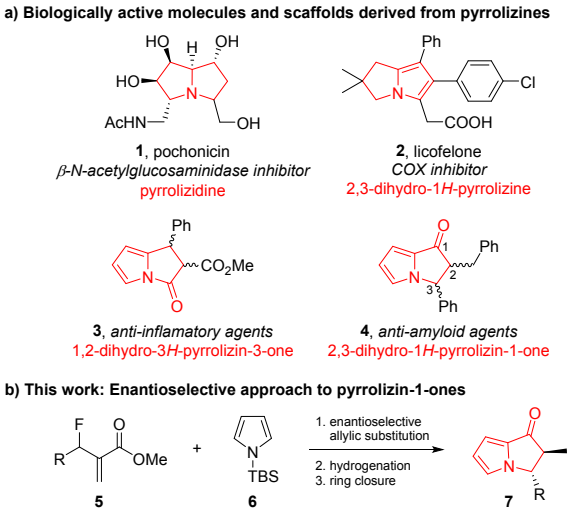
Pyrrolizidine alkaloids are a large group of plant natural products with 1-azabicyclo[3.3.0]octane core.[1] Many of these are toxic to humans and livestock and pose a significant threat to food safety. Other members of the group exhibit medicinally relevant biological activity such as pochonicine (**1**, Scheme 1a) which has been identified as a potent β-N-acetylglucosaminidase inhibitor.[2] Among synthetic derivatives with different levels of unsaturation and oxidation of the pyrrolizidine core, the derivatives with 2,3-dihydro-1*H*-pyrrolizine, such as the dual COX/LOX inhibitor licofelon (**2**),[3] have been under intense investigation and clinical development. The ease of access to 1,2-dihydro-3*H*-pyrrolizin-3-ones (**3**) has prompted numerous SAR studies of this scaffold.[4] In contrast to this, synthetic approaches to 2,3-dihydro-1*H*-pyrrolizin-1-ones (**4**) remain scarce despite the fact that this scaffold, due to its radical scavenging and anti-amyloid properties, has recently been identified as a promising platform for treatment of Alzheimer's disease.[5] The reported

synthetic approaches to this scaffold lack the control of stereoselectivity; the reactions proceed with low diastereoselectivity and the products have not been prepared in enantioenriched form.[5-6]

**Scheme 1.** a) Some biologically active molecules/scaffolds derived from pyrrolizidine; b) Outline of our approach to enantioselective synthesis of substituted 2,3-dihydro-1H-pyrrolizin-1-ones



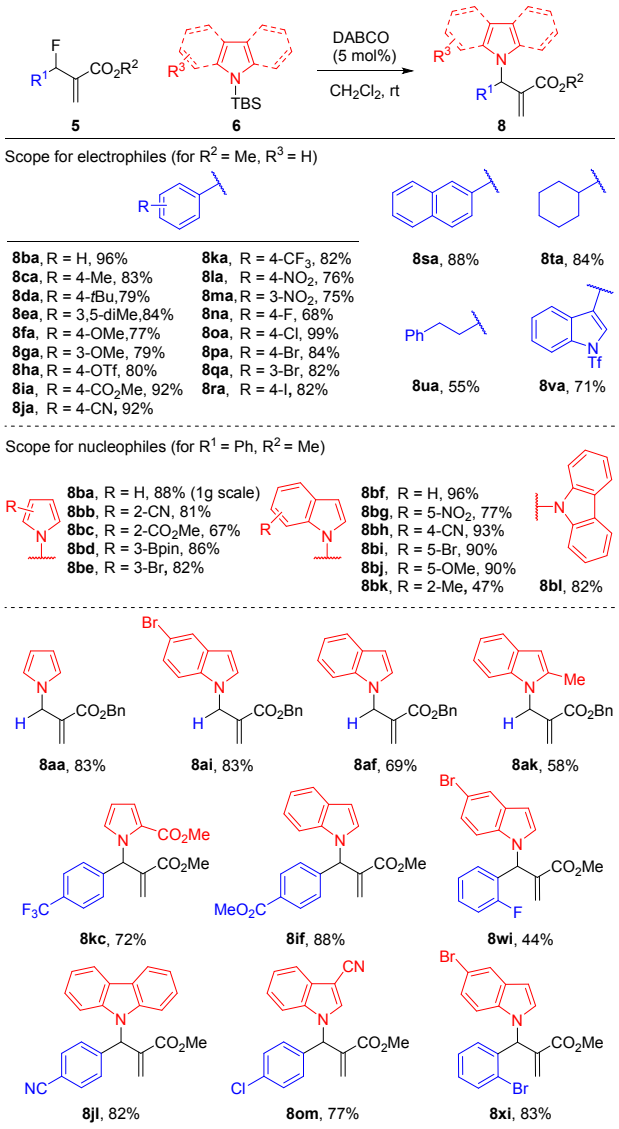

Considering the possibility of easy epimerization at C2, we presumed that a successful enantioselective approach to substituted 2,3-dihydro-1*H*-pyrrolizin-1-ones would have to effectively construct the C3 stereogenic center and allow for good control of diastereoselectivity at the C2 center. We have recently reported a Lewis base catalyzed enantioselective N-allylation of pyrroles, indoles and carbazoles which benefits from the concept of latent nucleophiles in Lewis base catalysis.[7] As these reactions construct a stereogenic center α to the nitrogen of the pyrrole and install the carbonyl group of the ester in an appropriate position, we saw this as an opportunity to develop a short enantioselective synthesis of substituted 2,3-dihydro-1*H*-pyrrolizin-1-ones. Here, we report the development of a short route to this scaffold that consists of enantioselective N-allylation of *N*-silyl pyrroles followed by reduction and diastereoselective cyclization (Scheme 1b).

Our work on Lewis base catalyzed N-allylation commenced as a proof of concept study for the use of latent nucleophiles in Lewis base catalysis. This concept is aimed at expanding the scope for nucleophile and allowing for better control of chemo-, regio- and stereoselectivity in Lewis base catalyzed reactions.[8] It is a

common occurrence that heteroatom nucleophiles compete and outperform the Lewis base catalyst thus preventing the development of enantioselective Lewis base catalyzed reactions.[9] We hypothesized that lowering the nucleophilicity of the nucleophilic reaction partner would increase the reaction selectivity and allow flexibility in the choice of catalyst. For N-centered nucleophiles, introducing a silyl group at the nitrogen atom lowers the nucleophilicity of the derivative (compared to the corresponding N-H nucleophile).[10] Such latent nucleophiles require an appropriate trigger to participate in the reaction. If activation of the nucleophile depends on the activation of the electrophile, by mediacy of the leaving group from the electrophile, the activated nucleophile is produced only when the activated electrophile is already present in the reaction mixture allowing for the bimolecular reaction of the two activated reactants to outcompete other possible pathways.[7] If activation of *N*-silyl latent nucleophile is to be dependent on activation of electrophile, mediacy of a fluoride ion as a leaving group would be a suitable trigger which makes Morita-Baylis-Hillman derived allylic fluorides a fitting reaction partner.

The reactions of various substituted allylic fluorides with *N*-TBS pyrrole have been evaluated in the presence of catalytic amounts of DABCO (Scheme 2). This exercise demonstrated a broad electrophile scope with reactions proceeding with good yields for both primary (**8aa**) and secondary allylic fluorides regardless of their electronic properties (**8ba**-**8va**). The same is true for a variety of substituted pyrroles, indoles and carbazoles (**8ba**-**8bl**). Electronically matched and mismatched sets of nucleophiles and electrophiles performed equally well in these reactions with generally good yields (**8kc**, **8if**, **8wi**, **8jl**, **8om**, **8xi**). Even sterically demanding nucleophiles/electrophiles, previously reported not to be reactive in related reactions, performed reasonably well with yields of around 50% (**8bk** and **8wi**).[11] The reactions proceeded with excellent regioselectivity: C2/C3 allylation of N-heterocycles and $S_N2$' type products were not observed in any of the reactions.

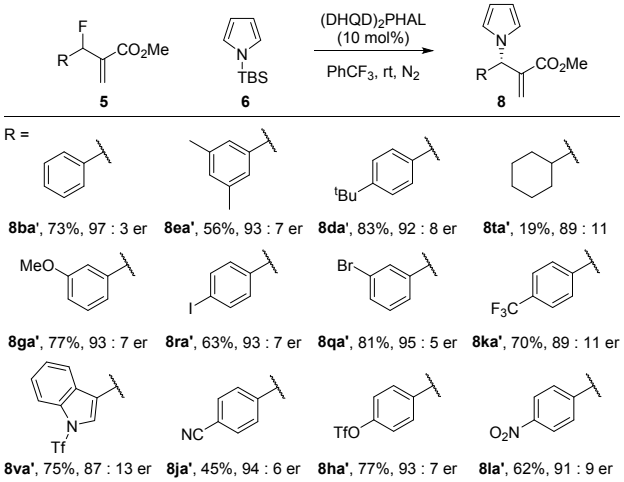
**Scheme 2** N-allylation of *N*-silyl latent nucleophiles **6** with various allylic fluorides **5** in the presence of DABCO. Isolated yields of the *N*-allyl pyrroles, indoles and carbazoles are shown. Conditions: 5 mol% DABCO, 1.1 equiv. **6**, $CH_2Cl_2$ (0.1 M). Numbering scheme follows the following formula: **5x** + **6y** gives **8xy**.




The comprehensive study of the reaction scope led into investigation of enantioselective N-allylation of pyrrole in the presence of chiral Lewis base catalyst (Scheme 3). The cinchona alkaloid based catalysts, well-established in similar allylic substitutions,[12] performed well in these reactions too. $(DHQD)_2PHAL$, $(DHQD)_2AQN$ and $(DHQ)_2PHAL$ all gave the desired products in good yields and good enantioselectivities. The reactions proceed as kinetic resolutions of the racemic allylic fluorides,[13] which is why the optimized conditions included an excess of the allylic fluoride in the presence of 10 mol% of $(DHQD)_2PHAL$ in

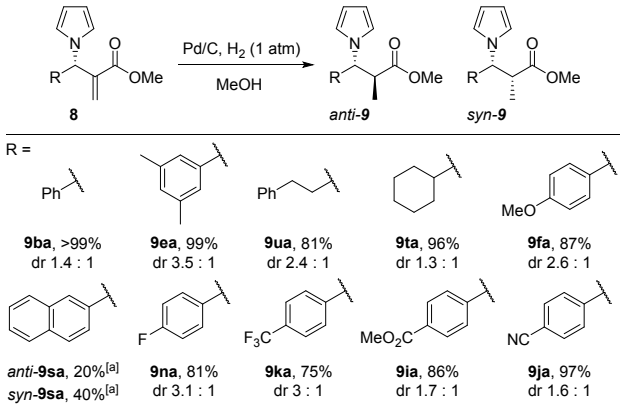
trifluorotoluene at ambient temperature. The excess of allylic fluoride was required to offset the low reaction rates caused by the significantly lower reactivity of the chiral catalysts and not to increase the enantioselectivities suggesting that the reactions of the two enantiomeric allylic fluorides are enantioconvergent. The enantiomeric ratios for pyrrole nucleophiles were generally higher than 90:10 and a short, focused optimization of the reaction conditions for a specific substrate can be conducted to improve enantioselectivity.[7] The yields remained good regardless of electronic properties of the allylic fluoride (45 - 83%, Scheme 3). The lowered reactivity of the catalyst also allowed for competitive elimination of the fluoride from alkyl substituted allylic fluorides which led to lower yields (**8ta'**).

**Scheme 3.** Enantioselective allylic substitution with *N*-TBS pyrrole **6a**. Isolated yields and enantiomeric ratios determined by HPLC on chiral stationary phase are shown. Absolute configuration of the *N*-allyl pyrroles **8** is assigned based analogy to previously reported material. Conditions: 10 mol% $DHQD_2(PHAL)$, 2 equiv. of **5**, $PhCF_3$ (0.2 M).




The further investigation was focused on the alkene reduction and the cyclization to produce the desired pyrrolizinones. Main concerns while developing the two-step procedure were the preservation of the C3 stereogenic center, the control of diastereoselectivity at C2 and the operational simplicity of the sequence. Attempts to carry out cyclization followed by reduction failed due to the lability of Michael acceptor under acidic conditions. This prompted exploration of the reverse sequence: reduction followed by cyclization.

**Scheme 4.** Hydrogenation of *N*-allyl pyrroles **8**. Isolated yields for the inseparable mixtures of *anti* and *syn* diastereomers and the diastereomeric ratio determined by $^1$H NMR are shown. Relative stereochemistry is tentatively assigned based on $^1$H NMR and the results of cyclization experiments. Reactions were performed with both racemic material and enantioenriched material (for **8ba** and **8ea**). Conditions: 10 mol% Pd/C, 1 atm. $H_2$, MeOH. [a]Isolated yields of *anti*-**9sa** and *syn*-**9sa** which do not account for losses of each isomer during purification

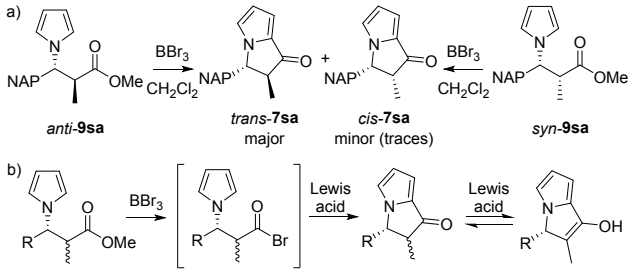



With a large pool of methods for 1,4-reduction to choose from,[14] we opted for the simplest heterogeneous hydrogenation of **8** over palladium catalyst which provided the desired reduction product in excellent yield but with low diastereoselectivity (Scheme 4). This was not seen as a setback as it allowed access to both diastereomers of the reduced products which were of interest in subsequent cyclization attempts. The difficulties in separating the two diastereomers, however, brought about the search for a substrate that would allow the easier separation of the two isomers. All attempted reductions proceeded with good yields and low diastereoselectivities ranging from 1.3:1 to 3.5:1 without an obvious trend (Scheme 4).[4] It was only the *syn*- and *anti*-isomers of naphthyl substituted ester **9sa** that could be separated by column chromatography.

Having access to both *syn*- and *anti*-diastereomers of **9sa**, the conditions for cyclization reactions became a focal point. In the presence of a pyrrole and an aryl substituent at the C3, Friedel-Crafts-type cyclization was a logical choice for cyclization as we expected the electron rich pyrrole to outperform the aryl substituent. On the other hand, mild reaction conditions were desired in order to minimize the epimerization

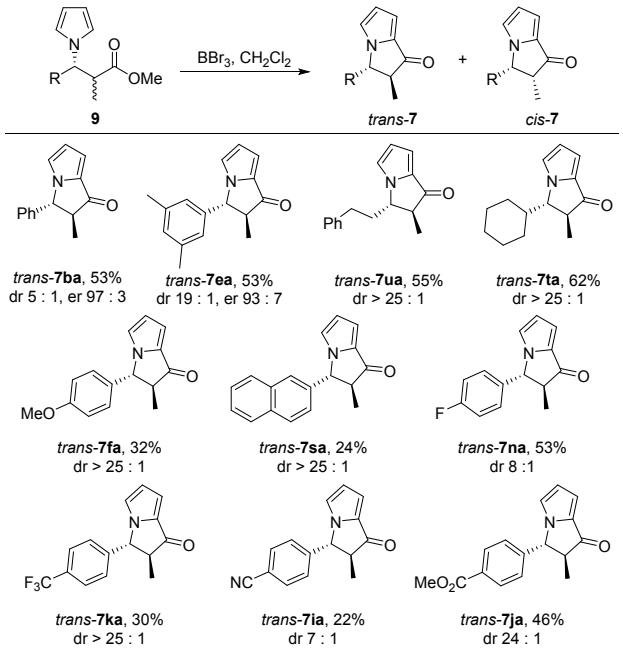
at C2. To reconcile these requirements, numerous Lewis and Brønsted acids ($AlCl_3$, $Ti(O^iPr)_4$, $BF_3$, TMSOTf and TfOH among others) were tested as potential promotors of the cyclization to no avail. Only the treatment with $BBr_3$ afforded the desired cyclization product, albeit in moderate yield.[15] This suggested the *in-situ* formation of an acyl bromide which further reacts to form the pyrrolizinone (see Scheme 5). To test this, the ester was hydrolyzed, and the corresponding acid was treated with $PBr_3$ to form the cyclization product although in lower yields.

**Scheme 5.** a) Evaluation of the diastereoselectivity for cyclizations of *anti*-**9sa** and *syn*-**9sa** and plausible mechanism for the isomerization. b) Proposed mechanism for cyclization and isomerization of **9**.




Independent cyclization of *syn*-**9sa** and *anti*-**9sa**, somewhat surprisingly, afforded the same isomer of **7sa** as the major cyclization product tentatively assigned as *trans*-**7sa** based on the $^3J_{H\text{-}H}$ coupling constants for C2 and C3 protons. When these reactions were stopped at ~50% conversion, the re-isolated starting material was unchanged suggesting that isomerization happens upon cyclization. With three $sp^2$ atoms in the pyrrolidinone ring, we expected the low energy conformations to be rather flat which would cause significant *gauche* interactions between C2 and C3 substituents in the *cis* isomer of **7** making the *trans* isomer increasingly more stable than the *cis* as the substituents become larger (like in the case of naphthyl derivative **7sa**).

**Scheme 6.** Diastereoselective cyclization of mixtures of *anti*-**9** and *syn*-**9** to pyrrolizinones **7**. Isolated yields for the major diastereomer and the diastereomeric ratio are shown. Conditions: 1.05 equiv. $BBr_3$, $CH_2Cl_2$ (0.1 M)




Since the configuration of **9** does not appear to significantly influence the diastereoselectivity in the cyclization to form *cis*- and *trans*-**7** (although it may influence the reaction rates and overall yield), we carried out $BBr_3$ promoted cyclization using mixtures of diastereomers for a series of *N*-allyl pyrroles **9** (Scheme 6). The desired pyrrolizinones (Scheme 6) were isolated with good to excellent diastereoselectivity between 5:1 and >25:1. The diastereomers could be separated in each case with *trans*-isomer being the major product in all attempted cyclizations. Assignment of the *cis* and *trans* isomers was made based on $^1$H NMR spectra and the $^3J_{H\text{-}H}$ coupling constants for C2 and C3 protons which were consistent across the series with values of around 4.8 Hz for the *trans*-**7** and around 7.7 Hz for *cis*-**7**, the latter being indicative of the close to *syn*-periplanar arrangement of these protons in *cis*-**7**. The isolated yields for the major diastereomers range from 22% to 62% (Scheme 6). These moderate yields are likely a consequence of the rather harsh reaction conditions and the side reactions which include competitive degradation of ether, ester, trifluoromethyl and nitrile substituents (**7fa**, **7ka**, **7ia** and **7ja**),[16] and intramolecular electrophilic aromatic substitution on the C3-aryl substituent. The substrates with alkyl substituents, and therefore with

no opportunity for the competing Friedel-Crafts involving the C3 substituent, performed much better in the cyclization reactions to produce **7ua** and **7ta**. Finally, when enantioenriched *N*-allyl pyrroles **8** were used in the two-step sequence, the yields and diastereoselectivity in both hydrogenation and cyclization reactions remained unaffected. Same is true for the configuration at C3 and therefore the enantiomeric ratios of the *trans*-**7** products. Products *trans*-**7ba** and *trans*-**7ea**, for example, were isolated with enantiomeric ratios of 97:3 and 93:7, respectively, which matches that of the of starting materials **8ba'** and **8ea'**.

In conclusion, the three-step sequence of pyrrole N-allylation followed by simple Pd-catalyzed hydrogenation and $BBr_3$ promoted cyclization is an effective route for the synthesis of substituted 2,3-dihydro-1*H*-pyrrolizin-1-ones. The concept of latent nucleophiles in Lewis base catalysis is a powerful tool for the development of enantioselective allylic substitutions with the broad scope for both reaction partners. The use of *N*-TBS pyrrole as a latent nucleophile in combination with allylic fluorides and common chiral Lewis base catalysts allows for the enantioselective N-allylation of pyrrole and, for the first time, enables the synthesis of enantioenriched pyrrolizin-1-ones *via* the said three step sequence. These enantioenriched materials are required for further biological evaluation of their radical scavenging and anti-amyloid properties which will be reported in due course.

## Experimental section

**General remarks.** All the chemicals that are not mentioned in the subsequent parts were purchased from Merck, Alfa Aesar, Acros Organics, ABCR, Fluorochem or TCI and used without further purification. The solvents if needed were dried according to standard laboratory practices. For column chromatography and TLC ($SiO_2$, 60M, pore size 0.04 – 0.063 mm), products of Machery-Nagel were used. The TLC-glass-plates DURASIL consisted of a 0.25 mm layer of silica 60 with Fluorescence indicator UV254. TLCs were checked under UV-light (254 nm or 365 nm) and stained with an aq. $KMnO_4$-solution, PMA-stain, DNP or PAA solution. Reaction monitoring using GC-MS was performed using HP 6890, capillary column DB5-MS and Agilent 5973 MSD. The default method was 70 °C (2 min), ramp 20 °C/min to 270 °C, hold 10 min. Injector temperature 250 °C, Aux temperature 275 °C. All $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra were measured with a BRUKER 250 ($^{13}C$), BRUKER Fourier 300 ($^{1}H$, $^{13}C$) or a BRUKER Avance 400 spectrometer ($^{1}H$, $^{13}C$, $^{19}F$). The chemical shift of each signal was registered in ppm. For $^{1}H$ and $^{13}C$ measurements, the chemical shift refers to TMS, showing a signal at 0 ppm. As an internal standard, the remaining protons or respectively the carbons of the

corresponding deuterated solvent were used ($CDCl_3$, 7.26 ppm ($^1$H-NMR), 77.16 ppm ($^{13}$C-NMR)). The chemical shift of the fluorine NMR was determined indirectly. For carbon spectra, a broadband decoupling was performed. Enantiomeric excess was determined by HPLC analysis on Phenomenex Lux Cellulose-1 columns. High-resolution mass spectra (HRMS) were measured with EI or ESI ionization by the MS platform. A chromatographic purification was performed before each measurement. The Thermo Q-Exactive plus device for ESI-mass spectra was coupled to a binary UHPLC system using orbitrap as mass analyzer. For EI-measurement, a GC-system was coupled to the Thermo Q-Exactive (quadrupole) GC Orbitrap device. All the IRs were measured using the Shimadzu IR-Affinity-1 (FTIR) device.

**Synthesis of Morita Baylis Hillman (MBH) Fluorides 5.** DAST (1.1 or 1.2 equiv.) was added to $CH_2Cl_2$ at -78 °C. To this, a precooled solution of MBH adduct (1 equiv.) in $CH_2Cl_2$ was added slowly (overall concentration MBH 0.25 M in $CH_2Cl_2$). The mixture was stirred for 30 minutes and then quenched with sat. $NaHCO_3$ solution. The mixture was extracted twice with $CH_2Cl_2$. The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography using either ethyl acetate in petroleum ether or ether in petroleum ether. The data for the known compounds **5a**, **5b**, **5c**, **5g**, **5k**, **5l**, **5m**, **5n**, **5o**, **5p**, **5q**, **5s**, **5t**, **5v**[13] and **5d**, **5e**, **5f**, **5h**, **5i**, **5j** and **5u**[7] are consistent with previous reports.

**methyl 2-((4-iodophenyl)fluoromethyl)acrylate (5r).** 4-iodo-benzaldehyde (2.00 g, 8.60 mmol mmol) was treated with DABCO (0.48 g, 4.30 mmol) in methyl acrylate (1.48 g, 17.2 mmol) and stirred at ambient temperature till judged completed by TLC. The crude mixture was directly subjected to column chromatography (silica) using ethyl acetate and petroleum ether (15:85) as solvent system to give the corresponding alcohol, methyl 2-(hydroxy(4-iodo)methyl)acrylate as a colorless solid. Yield: 1.34 g, 4.21 mmol, 49%. $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (d, $J$ = 8.8 Hz, 2H), 7.19 – 7.10 (d, $J$ = 8.8 Hz, 2H), 6.36 (s, 1H), 5.85 (s, 1 H), 5.51 (d, $J$ = 4.5 Hz, 1H), 3.75 (s, 3H), 3.16 (s. 1H). $^{13}$C{1H}-NMR (63 MHz, $CDCl_3$) δ 167.5, 142.4, 141.9, 138.4, 129.4, 127.4, 94.4, 73.8, 53.0. HRMS [EI]: m/z calculated for $C_{11}H_{11}IO_3$ $[M]^+$ 317.9747; found 317.9746. IR (ATR): $\nu$ = 3441 (br, w), 1709, (vs), 1420 (m), 1146 (vs), 1138 (s), 1007 (vs) $cm^{-1}$. The corresponding MBH fluoride was prepared by general procedure for synthesis of Morita Baylis Hillman fluorides. Yield: colorless solid, 434 mg, 1.36 mmol, 44%. $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.74 (d, $J$ = 7.8 Hz, 2H), 7.16 (d, $^3J_{H,H}$ = 9.4 Hz, 2H), 6.48 (d, $J$ = 2.8 Hz, 1H ), 6.24 (d, $J$ = 45.8 Hz, 1H), 6.05 (s, 1H), 3.74 (s, 3H). $^{13}$C{1H}-NMR (101 MHz, $CDCl_3$) δ 165.0 (d, $J$ = 6.4 Hz), 138.9 (d, $J$ = 22.9 Hz), 137.7, 137.1 (d, $J$ = 20.8 Hz), 128.9 (d, i = 5.6 Hz), 126.2 (d, $J$ = 8.8 Hz), 90.2 (d, $J$ = 174.9 Hz), 52.1 .$^{19}$F-NMR (377 MHz, $CDCl_3$) δ -172.54 (d, $J$ = 45.8 Hz). HRMS [EI]: m/z calculated for $C_{11}H_{10}FIO_2$ $[M]^+$ 319.9704, found 319.9702. IR (ATR): $\nu$ = 2959(w), 1713 (s), 1273 (s) 1165 (m), 964 (s), 806 (s) $cm^{-1}$.

**Synthesis of N-silyl-N-heterocycles 6.**[7] Under nitrogen atmosphere, the heterocycle (1 equiv.) was dissolved in THF cooled to -78°C and then n-BuLi (1.1 equiv.) or NaH (1.1 equiv) was added and stirred at this temperature for 15 minutes. TBS-chloride (1.2 equiv.) was added portion-wise. The reaction mixture was allowed to warm to room temperature. The reaction was quenched with water and then extracted with diethyl ether. The combined organic layers were dried over $Na_2SO_4$ and the solvent was removed under reduced pressure. The crude mixtures were either distilled or subjected to column chromatography using ethyl acetate in petroleum ether. The analytical data for known compounds **6b**, **6c**, **6h**, **6l**,[7] **6f**, **6k**, and **6j**[19] matched the previously reported data. Compounds **6a**, **6d** (TIPS derivative), **6e** (TIPC derivative), **6g** and **6i** are commercially available.

**Substitution of Allylic fluorides.** The TBS protected pyrrole, indole or carbazole **6** (for **6a**: 1.04 g, 5.67 mmol) and DABCO (28.9 mg, 0.26 mmol) were dissolved in $CH_2Cl_2$ (15 mL). To this, a solution of allylic fluoride (for **5b**: 1.00 g, 5.15 mmol) in $CH_2Cl_2$ (15 mL) was added slowly. After the completion of the reaction (monitored by TLC), the mixture was concentrated and purified by flash column chromatography using ethyl acetate in petroleum ether.

**benzyl 2-((1*H*-pyrrol-1-yl)methyl)acrylate (8aa).** Yield: colorless oil, 23.8 mg, 0.100 mmol, 83%. Chromatography: ethyl acetate: petroleum ether 10:90. $^1$H-NMR (250 MHz, $CDCl_3$) δ 7.41 (s, 5H), 6.69 (t, *J* = 2.1 Hz, 2H), 6.36 (d, *J* = 1.1 Hz, 1H), 6.22 (t, J = 2.1 Hz, 2H), 5.35 (d, *J* = 0.9 Hz, 1H), 5.26 (s, 2H), 4.80 (s, 2H). $^{13}$C{1H}-NMR (63 MHz, CDCl3) δ 166.2, 138.8, 136.5, 129.5, 129.3, 129.1, 127.5, 122.1, 109.5, 67.7, 50.9. HRMS [ESI]: m/z calculated for $C_{15}H_{15}NO_2$ $[M]^+$ 241.1097, found 241.1097. IR (ATR): $\nu$ = 2924 (w), 1713 (s), 1288 (m), 1134 (m), 1088 (m), 725 (s) cm$^{-1}$.

**methyl 2-(phenyl(1*H*-pyrrol-1-yl)methyl)acrylate (8ba).**[7] Yield: colorless solid, 1.09 g, 5.15 mmol, 88%. Chromatography: ethyl acetate: petroleum ether 5:95.

**methyl 2-((1*H*-pyrrol-1-yl)(p-tolyl)methyl)acrylate (8ca).** Yield: colorless oil, 65.2 mg, 0.255 mmol, 83%. Chromatography: ethyl acetate: petroleum ether 5:95. $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.51 (t, *J* = 2.1 Hz, 2H), 6.37 (d, *J* = 1.0 Hz, 1H), 6.23 (s, 1H), 6.07 (t, *J* = 2.2 Hz, 2H), 5.13 (dd, *J* = 1.6, 0.8 Hz, 1H), 3.63 (s, 3H), 2.26 (s, 3H). $^{13}$C{1H}-NMR (101 MHz, $CDCl_3$) δ 166.1, 141.2, 138.0, 135.1, 129.4, 127.9, 127.5, 120.7, 108.3, 62.6, 52.2, 21.1. HRMS [ESI]: m/z calculated for $C_{16}H_{17}NO_2$ $[M]^+$ 255.1254, found 255.1255. IR (ATR): $\nu$ = 2951 (w), 1721 (vs), 1435 (m), 1273 (s), 1138 (vs), 721 (vs) cm$^{-1}$.

**methyl 2-((4-(tert-butyl)phenyl)(1*H*-pyrrol-1-yl)methyl)acrylate (8da).**[7] Yield: colorless oil, 63.3 mg, 0.210 mmol, 79%. Chromatography: ethyl acetate: petroleum ether 7.5:92.5.

**methyl 2-((3,5-dimethylphenyl)(1*H*-pyrrol-1-yl)methyl)acrylate (8ea).**[7] Yield: colorless oil, 77.0 mg, 0.29 mmol, 84%. Chromatography: diethyl ether : petroleum ether 5:95

**methyl 2-((4-methoxyphenyl)(1*H*-pyrrol-1-yl)methyl)acrylate (8fa).**[7] Yield: colorless solid, 35.7 mg, 0.130 mmol, 77%. Chromatography: ethyl acetate: petroleum ether 10:90

**methyl 2-((3-methoxyphenyl)(1*H*-pyrrol-1-yl)methyl)acrylate (8ga).**[7] Yield: colorless oil, 49.0 mg, 0.18 mmol, 84%. Chromatography: ethyl acetate: petroleum ether 10:90

**methyl 2-((1*H*-pyrrol-1-yl)(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)methyl)acrylate (8ha).**[7] Yield: colorless oil, 65.5 mg, 0.17 mmol, 80%. Chromatography: ethyl acetate: petroleum ether 20:80

**methyl 4-(2-(methoxycarbonyl)-1-(1*H*-pyrrol-1-yl)allyl)benzoate (8ia).** [7] Yield: colorless solid, 88.2 mg, 0.29 mmol, 92%. Chromatography: ethyl acetate: petroleum ether 15:85.

**methyl 2-((4-cyanophenyl)(1*H*-pyrrol-1-yl)methyl)acrylate (8ja).** Yield: colorless oil, 41.0 mg, 0.15 mmol, 92%. Chromatography: ethyl acetate: petroleum ether 10:90 $^{1}$H-NMR (250 MHz, $CDCl_3$) δ 7.73 – 7.60 (d, *J* =8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.61 (t, *J* = 2.1 Hz, 1H), 6.57 (s, 1H), 6.42 (s, 1H), 6.23 (t, *J* = 2.2 Hz) *5*.30 (s, 1H), 3.77 (s, 3H). $^{13}$C{1H}-NMR (63 MHz, $CDCl_3$) δ 166.5, 144.8, 140.8, 133.5, 130.0, 129.4, 121.5, 119.3, 113.1, 110.1, 63.1, 53.4. HRMS [EI]: m/z calculated for $C_{16}H_{14}N_2O_2$ $[M]^+$ 266.1050, found 266.1052. IR (ATR): $\nu$ = 2955 (w), 2230 (w), 1721 (s), 1273 (m), 1142 (s), 725 (vs) $cm^{-1}$.

**methyl 2-((4-(trifluormethyl)-phenyl)(1*H*-pyrrol-1-yl)methyl)acrylate (8ka).**[7] Yield: colorless solid, 60.5 mg, 0.20 mmol, 82%. %. Chromatography: ethyl acetate: petroleum ether 10:90

**methyl 2-((4-nitrophenyl)(1*H*-pyrrol-1-yl)methyl)acrylate (8la).**[7] Yield: colorless oil, 30.6 mg, 0.11 mmol, 79%. Chromatography: diethyl ether : petroleum ether 30:70

**methyl 4-((3-nitrophenyl)(1*H*-pyrrol-1-yl)allyl)benzoate (8ma).** Yield: colorless oil, 30.0 mg, 0.10 mmol, 71%. Chromatography: ethyl acetate: petroleum ether 10:90 $^{1}$H-NMR (250 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.0, 1.9 Hz, 1H), 8.06 (d, *J* = 2.0 Hz, 1H), 7.68 – 7.39 (m, 2H), 6.62 (dd, *J* = 5.0, 2.7 Hz, 3H), 6.47 (s, 1H), 6.24 (d, *J* = 2.1 Hz, 2H), 5.33 (s, 1H), 3.77 (d, *J* = 1.6 Hz, 3H). $^{13}$C{1H}-NMR (63 MHz, $CDCl_3$) δ 166.4, 149.5, 141.6, 140.8, 134.8, 130.8, 123.0, 124.2, 123.7, 121.5, 110.2, 62.9, 53.4. HRMS [ESI]: m/z calculated for $C_{15}H_{14}N_2O_4$ $[M]^+$ 286.0954, found 286.0948. IR (ATR): $\nu$ = 2955 (w), 1721 (s), 1528 (vs), 1346 (vs), 1273 (s), 725 (vs) $cm^{-1}$.

**methyl 2-((4-fluorophenyl)(1*H*-pyrrol-1-yl)methyl)acrylate (8na).** Yield: colorless solid, 62.1 mg, 0.24 mmol, 68%. Chromatography: ethyl acetate: petroleum ether 10:90. $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 6.61 (t, *J* = 2.1 Hz, 2H), 6.50 (s, 1H), 6.36 (s, 1H), 6.20 (t, *J* = 2.1 Hz, 2H), 5.25 (d, *J* = 2.0 Hz, 1H), 3.75 (s, 3H). $^{13}$C{1H}- NMR (101 MHz, ) δ 165.9 , 162.5 (d, $J_{C\text{-}F}$ = 247.2 Hz), 141.0 , 134.0 (d, $J_{C\text{-}F}$ = 3.3 Hz), 129.7 (d, $J_{C\text{-}F}$ = 8.2 Hz), 127.9, 120.6, 115.7 (d, $J_{C\text{-}F}$ = 21.7 Hz), 108.6, 62.1, 52.3. $^{19}$F-NMR (377 MHz, $CDCl_3$) δ -113.82. HRMS [ESI]: m/z calculated for $C_{15}H_{14}FNO_2$ $[M]^+$ 259.1003, found 259.1007. IR (ATR): $\nu$ = 2951 (w), 1717 (s), 1508 (s), 1265 (m), 1219 (m) 1134 (m), 733 (vs) $cm^{-1}$.

**methyl 2-((4-chlorophenyl)(1*H*-pyrrol-1-yl)methyl)acrylate (8oa).**[7] Yield: colorless oil, 40.0 mg, 0.14 mmol, >99%. Chromatography: ethyl acetate: petroleum ether 15:85.

**methyl 2-((4-bromophenyl)(1*H*-pyrrol-1-yl)methyl)acrylate (8pa).** Yield: colorless solid, 61.7 mg, 0.19 mmol, 84%. Chromatography: ethyl acetate: petroleum ether 10:90 $^{1}$H-NMR (250 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.58 (t, *J* = 2.2 Hz, 2H), 6.49 (s, 1H), 6.30 (s, 1H), 6.17 (t, *J* = 2.2 Hz, 2H), 5.23 (s, 1H), 3.72 (s, 3H). $^{13}$C{1H}-NMR (63 MHz, $CDCl_3$) δ 166.7, 141.5, 138.3, 132.8, 130.5, 129.1, 123.2, 121.5, 109.6, 63.1, 53.2. HRMS [EI]: m/z calculated for $C_{15}H_{14}NO_2BrNa$ $[M+Na]^+$ 342.0106, found 342.0106. IR (ATR): $\nu$ = 2951 (w), 1721 (vs), 1489 (m), 1273 (s), 1142 (s), 1072 (m), 725 (vs) $cm^{-1}$.

**methyl 2-((3-bromophenyl)(1*H*-pyrrol-1-yl)methyl)acrylate (8qa).**[7] Yield: colorless oil, 58.0 mg, 0.18 mmol, 82%. Chromatography: ethyl acetate: petroleum ether 10:90.

**methyl 2-((4-iodophenyl)(1*H*-pyrrol-1-yl)methyl)acrylate (8ra).** Yield: colorless solid, 69.0 mg, 0.19 mmol, 82%. Chromatography: diethyl ether : petroleum ether 10:90 $^{1}$H-NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.50 (m, 2H), 6.96 – 6.80 (m, 2H), 6.57 (t, *J* = 2.1 Hz, 2H), 6.48 (t, *J* = 0.8 Hz, 1H), 6.29 (s, 1H), 6.17 (t, *J* = 2.2 Hz, 2H), 5.24 (d, *J* = 1.5 Hz, 1H), 3.72 (s, 3H). $^{13}$C{1H}-NMR (75 MHz, $CDCl_3$) δ 165.8, 140.6, 138.1, 137.9, 129.9, 128.3, 120.7, 108.8, 94.1, 62.3, 52.4. HRMS [ESI]: m/z calculated for $C_{15}H_{14}INO_2$ $[M]^+$ 367.0064, found 367.0066. IR (ATR): $\nu$ = 2947 (w), 1697 (vs), 1481 (m), 1439 (m), 1269 (m), 1142 (s), 1084 (s), 737 (vs) $cm^{-1}$.

**methyl 2-(naphthalen-2-yl(1*H*-pyrrol-1-yl)methyl)acrylate (8sa).**[7] Yield: yellow solid, 61.4 mg, 0.21 mmol, 88%. Chromatography: ethyl acetate: petroleum ether 10:90.

**methyl 2-(cyclohexyl(1*H*-pyrrol-1-yl)methyl)acrylate (8ta).**[7] Yield: colorless oil, 26.5 mg, 0.11 mmol, 84%. Chromatography: diethy lether: petroleum ether 5:95.

**methyl 2-methylene-5-phenyl-3-(1*H*-pyrrol-1-yl)pentanoate (8ua).**[7] Yield: colorless oil, 45.5 mg, 0.169 mmol, 55%. Chromatography: ethyl acetate: petroleum ether 2.5:97.5.

**methyl 2-((1*H*-pyrrol-1-yl)(1-((trifluoromethyl)sulfonyl)-1*H*-indol-3-yl)methyl)acrylate (8va).**[7] Yield: colorless wax, 38.3 mg, 0.09 mmol, 71%. Chromatography: diethyl ether: petroleum ether 5:95.

**methyl 2-((2-cyano-1*H*-pyrrol-1-yl)(phenyl)methyl)acrylate (8bb).**[7] Yield: colorless oil, 26.6 mg, 0.100 mmol, 67%. Chromatography: ethyl acetate: petroleum ether 10:90.

**methyl 1-(2-(methoxycarbonyl)-1-phenylallyl)-1*H*-pyrrole-2-carboxylate (8bc).**[7] Yield: brown oil, 37.5 mg, 0.125 mmol, 67%. Chromatography: ethyl acetate: petroleum ether 10:90.

**methyl 2-((1*H*-indol-1-yl)(phenyl)methyl)acrylate (8bf).**[12c] Yield: colorless solid, 86.2 mg, 0.285 mmol, 96%. Chromatography: ethyl acetate: petroleum ether 10:90.

**methyl 2-((5-nitro-1*H*-indol-1-yl)(phenyl)methyl)acrylate (8bg).**[7] Yield: brown solid, 49.3 mg, 0.147mmol, 77%. Chromatography: ethyl acetate: petroleum ether 15:85.

**methyl 2-((4-cyano-1*H*-indol-1-yl)(phenyl)methyl)acrylate (8bh).** [7] Yield: colorless oil, 7.8 mg, 0.025 mmol, 93%. Chromatography: ethyl acetate: petroleum ether 15:85.

**methyl 2-((5-bromo-1*H*-indol-1-yl)(phenyl)methyl)acrylate (8bi).**[12c] Yield: colorless oil, 60.7 mg, 0.163 mmol, 90%. Chromatography: ethyl acetate: petroleum ether 15:85.

**methyl 2-((5-methoxy-1*H*-indol-1-yl)(phenyl)methyl)acrylate (8bj).**[7] Yield: colorless solid, 74.0 mg, 0.22 mmol, 88%. Chromatography: ethyl acetate: petroleum ether 15:85.

**methyl 2-((2-methyl-1*H*-indol-1-yl)(phenyl)methyl)acrylate (8bk).**[7] Yield: colorless oil, 37.6 mg, 0.123 mmol, 47%. Chromatography: ethyl acetate: petroleum ether 5:95.

**methyl 2-((9*H*-carbazol-9-yl)(phenyl)methyl)acrylate (8bl).**[7] Yield: colorless solid, 52.4 mg, 0.15 mmol, 82%. Chromatography: ethyl acetate: petroleum ether 10:90.

**benzyl 2-((5-bromo-1*H*-indol-1-yl)methyl)acrylate (8ai).** Yield: colorless solid, 23.7 mg, 0.064 mmol, 89%. Chromatography: ethyl acetate: petroleum ether 10:90 $^{1}$H-NMR (400 MHz, $CDCl_3$ ) δ 7.78 (d, *J* = 1.8 Hz, 1H), 7.39 (dd, *J* = 5.0, 3.3 Hz, 5H), 7.32 – 7.25 (m, 1H), 7.20 – 7.09 (m, 2H), 6.54 – 6.46 (m, 1H), 6.33 (s, 1H), 5.25 (s, 2H), 5.21 (s, 1H), 5.01 (s, 2H). $^{13}$C{1H}-NMR (101 MHz, $CDCl_3$) δ 165.2, 136.1, 135.4, 134.7, 130.3, 129.5, 128.7, 128.5, 128.3, 126.7, 124.7, 123.5, 113.0, 111.1, 101.6, 67.0, 47.0. HRMS [EI]: m/z calculated for $C_{19}H_{16}NO_2Br$ $[M]^+$ 369.0365, found 369.0364. IR (ATR): $\nu$ = 2928 (w), 1721 (s), 1466 (m), 1258 (vs), 1157 (vs), 736 (vs) $cm^{-1}$.

**benzyl 2-((1*H*-indol-1-yl)methyl)acrylate (8af).** Yield: colorless oil, 24.4 mg, 0.084 mmol, 69%. Chromatography: ethyl acetate: petroleum ether 10:90 $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 1H), 7.41 (d, *J* = 3.4 Hz, 5H), 7.35 – 7.12 (m, 4H), 6.61 – 6.53 (m, 1H), 6.33 (s, 1H), 5.28 (s, 2H), 5.22 (s, 1H), 5.06 (s, 2H). $^{13}$C{1H}-NMR (101 MHz, $CDCl_3$) δ 165.4, 136.4, 136.0, 135.6, 128.7, 128.6, 128.5, 128.4, 128.3, 126.6, 121.8, 121.0, 119.7, 109.6, 102.0, 66.9, 46.8. HRMS [ESI]: m/z calculated for $C_{19}H_{17}NO_2$ $[M]^+$ 291.1259, found 291.1253. IR (ATR): $\nu$ = 2951 (w), 1712 (s), 1462 (m), 1258 (vs), 1130 (s), 737 (vs) $cm^{-1}$.

**benzyl 2-((2-methyl-1*H*-indol-1-yl)methyl)acrylate (8ak).** Yield: colorless oil, 20.0 mg, 0.070 mmol, 69%. Chromatography: ethyl acetate: petroleum ether 10:90 $^{1}$H-NMR (250 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 1H), 7.50 – 7.40 (m, 5H), 7.25 – 7.04 (m, 3H), 6.40 – 6.32 (m, 1H), 6.26 (s, 1H), 5.33 (s, 2H), 5.00 (t, *J* = 2.0 Hz, 2H), 4.87 (d, *J* = 2.1 Hz, 1H), 2.40 (s, 3H).). $^{13}$C{1H}-NMR (101 MHz, $CDCl_3$) δ 165.5, 136.7, 136.4, 136.1, 135.6, 128.7, 128.5, 128.3, 128.2, 125.6, 120.9, 119.8, 119.7, 109.0, 100.7, 66.9, 43.3, 12.4. HRMS [ESI]: m/z calculated for $C_{20}H_{19}NO_2$ $[M]^+$ 305.1416, found 305.1416. IR (ATR): $\nu$ = 1708 (s), 1454 (m), 1369 (m), 1292 (vs), 1130 (s), 737 (vs) $cm^{-1}$.

**methyl 1-(2-(methoxycarbonyl)-1-(4-(trifluoromethyl)phenyl)allyl)-1*H*-pyrrole-2-carboxylate (8kc).**[7] Yield: colorless oil, 26.6 mg, 0.072 mmol, 72%. Chromatography: diethyl ether: petroleum ether 20:80.

**methyl 4-(1-(1*H*-indol-1-yl)-2-(methoxycarbonyl)allyl)benzoate (8if).**[7] Yield: colorless solid, 74.0 mg, 0.22 mmol, 88%. Chromatography: ethyl acetate: petroleum ether 20:80.

**methyl 2-((5-bromo-1*H*-indol-1-yl)(2-fluorophenyl)methyl)acrylate (8wi).**[7] Yield: colorless oil, 30.5 mg, 0.08 mmol, 44%. Chromatography: diethyl ether: petroleum ether 10:90.

**methyl 2-((9*H*-carbazol-9-yl)(4-cyanophenyl)methyl)acrylate (8jl).**[7] Yield: colorless solid, 81.2 mg, 0.22 mmol, 82%. Chromatography: ethyl acetate: petroleum ether 15:85.

**methyl 2-((4-chlorophenyl)(3-cyano-1*H*-indol-1-yl)methyl)acrylate (8om).**[7] Yield: wax, 65.0 mg, 0.19 mmol, 77%. Chromatography: ethyl acetate: petroleum ether 15:85

**methyl 2-((5-bromo-1*H*-indol-1-yl)(2-bromophenyl)methyl)acrylate (8xi).**[7] Yield: colorless oil, 58.0 mg, 0.13 mmol, 84%. Chromatography: diethyl ether: petroleum ether 10:90

**General procedure for enantioselective allylation of *N*-heterocycles.** To a flask with N-silyl heterocycle (0.1 mmol) and $(DHQD)_2PHAL$ (7.8 mg, 10 mol %) were added successively and the flask was then evacuated and refilled with nitrogen. This procedure was repeated three times. Dry $PhCF_3$ (0.5 mL), dissolving MBH fluorides (0.2 mmol) was then added. The reaction mixture was stirred at room temperature. After stirring for 40 h or the completion of the reaction (monitored by TLC), the mixture was concentrated and purified by flash column chromatography with ethyl acetate in petroleum ether to afford the corresponding product. NMR Data was compared with the racemic material. The ratio of enantiomers was determined by HPLC on chiral stationary phase.

**General procedure Hydrogenation of Substitution products.** The substrate (1.equiv.) was dissolved in MeOH (1mL) and degassed with nitrogen for 5 minutes. Pd/C (10 mol%) was added and hydrogen was bubbled through the mixture until observed to be completed (by GC-MS). The reaction mixture was filtered on a plug of silica eluting with ethyl acetate if not stated differently.

**methyl 2-methyl-3-phenyl-3-(1*H*-pyrrol-1-yl)propanoate (9ba).** Yield: colorless solid, 166 mg, 0.68 mmol, >99%. Mixture of diastereomers. $^1$H NMR (250 MHz, $CDCl_3$) δ 7.45 – 7.22 (m, 5H), 6.79 (m, 2H), 6.22 – 6.08 (m, 2H), 5.21 (m, 1H), 3.62 (s, 3H (major)), 3.62 (s, 3H (minor)) 3.55 – 3.40 (m, 1H), 1.16 (m, 3H).$^{13}$C{1H} NMR (63 MHz, $CDCl_3$) δ 175.7, 175.4, 140.3, 139.5, 129.8, 129.6, 129.1, 129.0, 128.3, 127.9, 120.6, 120.3, 109.4, 109.2, 67.2, 66.6, 53.0, 52.8, 46.0, 45.8, 16.9, 165. HRMS [ESI]: m/z calculated for $C_{15}H_{17}NNaO_2$ $[M+Na]^+$ 266.1157, found 266.1161. IR (ATR): $\tilde{\nu}$= 2935 (w), 1728 (vs), 1454 (m), 1261 (m), 1092 (m), 725 (vs); 702 (vs) $cm^{-1}$.

**methyl 3-(3,5-dimethylphenyl)-2-methyl-3-(1*H*-pyrrol-1-yl)propanoate (9ea).** Yield: colorless solid, 24.3 mg, 0.09 mmol, >99%. Mixture of diastereomers. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.96 (m, 3H), 6.78 (m, 2H), 6.17 (m, 2H (minor)), 6.11 (m, 2H (major)), 5.12 (m, 1H), 3.59 (s, 3H, (major)), 3.52 – 3.40 (s, 3H (minor)), 2.31 (m, 6H), 1.13 (m, 3H).$^{13}$C{1H} NMR (101 MHz, $CDCl_3$) δ 175.0, 174.5, 139.2, 138.38, 138.37, 138.1, 129.9, 129.8, 125.2, 124.8,

119.7, 119.4, 108.4, 108.1, 66.4, 65.6, 52.0, 51.8, 45.0, 44.9, 21.4, 16.1, 15.6, 15.5. HRMS [ESI]: m/z calculated for $C_{17}H_{21}NO_2$ $[M]^+$ 271.1567, found 271.1570. IR (ATR): $\tilde{\nu}$= 3951 (w), 1753 (vs), 1458 (m), 1265(m), 1165 (m), 718 (vs), 698 (s) $cm^{-1}$.

**methyl 2-methyl-5-phenyl-3-(1*H*-pyrrol-1-yl)pentanoate (9ua).** Yield: colorless oil, 22 mg, 0.08 mmol. Mixture of diastereomers. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 2H), 7.27 – 7.18 (m, 2H), 7.17 – 7.06 (m, 2H), 6.70 (m, 2H), 6.23 (t, 2H (minor)), 6.19 (t, 2H (major)), 4.1 (m, 1H (major)) , 4.05 (m, 1H (minor)), 3.72 (s, 1H (minor)), 3.54 (3H (major)), 2.88 (1H), 2.52 – 2.34 (2H), 2.30 – 1.98 (2H), 1.23 (3H (major)), 0.94 (3H (minor)). $^{13}$C{1H} NMR (101 MHz, $CDCl_3$) δ 175.0, 174.5, 141.02, 140.97, 128.5, 128.4, 126.1, 126.0, 119.5, 119.4, 108.3, 108.0, 61.5, 61.4, 51.9, 51.8, 46.7, 46.5, 35.9, 33.8, 32.2, 32.0, 14.6, 14.4. HRMS [EI]: m/z calculated for $C_{17}H_{21}NO_2$ $[M]^+$ 271.1567, found 271.1568. IR (ATR): $\tilde{\nu}$= 2951 (w), 1732 (s), 1265 (m), 1161 (m), 721 (vs), 698 (vs) $cm^{-1}$.

**methyl 3-cyclohexyl-2-methyl-3-(1*H*-pyrrol-1-yl)propanoate (9ta).** Yield: colorless oil, 59 mg, 0.237 mmol. Mixture of diastereomers. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.61 (m, 2H), 6.12 (m, 2H), 3.99 (dd, J = 8.6, 7.0 Hz, 1H (minor)), 3.89 (dd, J = 8.2, 6.6 Hz, 01H (major)), 3.71 (s, 3H (minor)), 3.57 (s, 3H (major)), 3.22 – 2.95 (m, 1H), 1.89 (dddd, J = 11.7, 8.7, 6.5, 3.3 Hz, 1H), 1.82 – 1.44 (m, 6H), 1.22 (d, J = 7.0 Hz, 3H), 1.18 – 1.07 (m, 2H (major)), 1.01 (d, J = 7.0 Hz, 2H(minor)), 0.96 – 0.77 (m, 1H). $^{13}$C{1H} NMR (101 MHz, $CDCl_3$) δ 175.3, 174.7, 120.8, 120.6, 107.5, 107.1, 67.4, 66.8, 51.9, 51.7, 42.5, 42.0, 41.2, 39.4, 30.9, 30.6, 28.7, 28.0, 26.3, 26.24, 26.21, 26.17, 26.12, 15.0, 13.49.HRMS [EI]: m/z calculated for $C_{15}H_{23}NO_2$ $[M]^+$ 249.1729, found 249.1724. IR (ATR): $\tilde{\nu}$= 2973 (m), 2855 (m), 1735 (s), 1261 (m), 1165 (m), 721 (vs) $cm^{-1}$.

**methyl 3-(4-methoxyphenyl)-2-methyl-3-(1*H*-pyrrol-1-yl)propanoate (9fa).** Yield: colorless oil, 20.2 mg, 0.074 mmol. Mixture of diastereomers. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 2H), 6.99 – 6.82 (m, 2H), 6.76 (m, 2H), 6.16 (m, 2H (minor)), 6.11 (m, 2H (major)), 5.16 (m, 1H), 3.80 (m, 3H), 3.60 (s, 3H (major)), 3.56 (s, 3H (minor)), 3.43 (m, 1H), 1.14 (m, 3H). $^{13}$C{1H} NMR (101 MHz, $CDCl_3$) δ 174.9, 174.5, 159.4, 159.2, 131.7, 130.8, 129.9, 128.6, 128.2, 119.5, 119.3, 114.2, 114.0, 113.8, 108.5, 108.2, 65.7, 65.1, 55.3, 55.2, 52.1, 51.9, 45.3, 45.1, 29.7, 16.0, 15.6. HRMS [EI]: m/z calculated for $C_{16}H_{19}NO_3$ $[M]^+$ 273.1359, found 273.1355. IR (ATR): $\tilde{\nu}$= 2951 (w), 1735 (s), 1512 (s), 1250 (m), 1165 (s), 723 (vs), 629 (s) $cm^{-1}$.

**methyl (*syn*)-2-methyl-3-(naphthalen-2-yl)-3-(1*H*-pyrrol-1-yl)propanoate (*syn* 9sa).** Yield: colorless solid, 47.4 mg, 0.162 mmol, 41%. $^1$H NMR (400 MHz, $CDCl_3$ ) δ 7.86 – 7.79 (m, 3H), 7.58 – 7.42 (m, 3H), 6.84 (t, J = 2.2 Hz, 2H), 6.20 (t, *J* = 2.1 Hz, 2H), 5.39 (d, *J* = 11.0 Hz, 1H), 3.67 – 3.59 (m, 1H), 3.55 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 3H).$^{13}$C{1H} NMR (101 MHz, $CDCl_3$) δ 174.5, 136.8, 133.2, 133.0, 128.7, 128.2, 127.6, 126.3, 126.3, 125.6, 125.3, 119.8, 108.7, 65.6, 52.0, 44.9, 15.7. HRMS [EI]: m/z calculated for $C_{19}H_{19}NO_2$ $[M]^+$ 293.1410, found 293.1414. IR (ATR): $\tilde{\nu}$= 2935 (w), 1720 (vs), 1357 (m), 1269 (m), 1177 (m), 725 (vs), 383 (vs) $cm^{-1}$.

**methyl (*anti*)-2-methyl-3-(naphthalen-2-yl)-3-(1*H*-pyrrol-1-yl)propanoate (*anti* 9sa).** Yield: colorless solid, 25.0 mg, 0.085 mmol, 21%. $^1$H NMR (400 MHz, $CDCl_3$ ) δ 7.92 – 7.78 (m, 4H), 7.55 – 7.49 (m, 2H), 7.44 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.86 (t, *J* = 2.2 Hz, 2H), 6.14 (t, *J* = 2.2 Hz, 2H), 5.40 (d, *J* = 11.2 Hz, 1H), 3.65 (s, 3H), 3.62 – 3.54 (m, 1H), 1.17 (d, J = 7.0 Hz, 3H).$^{13}$C{1H} NMR (101 MHz, 0$CDCl_3$) δ 174.9, 136.0, 133.2, 133.1, 129.0, 128.03, 128.02, 127.7, 126.8, 126.5, 126.4, 124.6, 119.5, 108.4, 66.4, 52.2, 44.8, 16.1. HRMS [EI]: m/z calculated for $C_{19}H_{19}NO_2$ $[M]^+$ 293.1410, found 293.1413. IR (ATR): ῦ= 2936 (w), 1728 (s), 1258 (m), 1161 (m), 725 (vs), 687 (m) $cm^{-1}$.

**methyl 3-(4-fluorophenyl)-2-methyl-3-(1*H*-pyrrol-1-yl)propanoate (9na).** Yield: colorless oil, 18.9 mg, 0.07 mmol. Mixture of diastereomers. $^1$H NMR (400 MHz,$CDCl_3$) δ 7.32 (m, 2H), 7.14 – 6.96 (m, 2H), 6.76 (m, 2H), 6.18 (m, 2H), 5.19 (m, 1H), 3.61 (s, 3H (major)), 3.56 (s, 3H (minor)), 3.42 (m, 1H), 1.13 (m, 3H). $^{13}$C{1H} NMR (101 MHz, $CDCl_3$) δ 174.6, 174.3, 162.4 (d, *J* = 247.4 Hz), 134.6, 134.6, 129.0 (d, *J* = 8.3 Hz), 128,7 (d, *J* = 8.2 Hz), 119.5, 119.3, 115.8 (d, *J* = 21.4 Hz), 115.6 (d, *J* = 21.6 Hz), 108.8, 108.5, 65.5, 65.0, 52.2, 52.0, 45.2, 45.0, 16.0. 19F NMR (377 MHz, $CDCl_3$) δ -113.74, -114.01. HRMS [EI]: m/z calculated for $C_{15}H_{16}NFO_2$ $[M]^+$ 261.1160, found 261.1162. IR (ATR): ῦ= 2951 (w), 1753 (s), 1512 (s), 1265 (m), 1161 (s), 721 (vs), 623 (s) $cm^{-1}$.

**methyl 3-(4-trifluoromethyl)-2-methyl-3-(1*H*-pyrrol-1-yl)propanoate (9ka).** Yield: colorless oil, 46.5 mg, 0.15 mmol. Mixture of diastereomers.$^1$H NMR (250 MHz, $CDCl_3$) δ 7.62 (m, 2H), 7.46 (m, 2H), 6.78 (m, 2H), 6.18 (m, 2H), 5.28 (m, 1H), 3.64 (s, 3H (major)), 3.58 (s, 3H (minor)), 3.55 – 3.39 (m, 1H), 1.17 (m, 3H). $^{13}$C{1H} NMR (63 MHz, $CDCl_3$) δ 175.2, 175.0, 143.6, 131.4 (q, $J_{C\text{-}F}$ = 32.4 Hz) 128.6, 128.3, 126.8 (q, $J_{C\text{-}F}$ = 3.8 Hz), 120.5, 120.3, 110.0, 109.7, 66.6, 66.0, 53.2, 53.0, 45.7, 45.5, 16.8, 16.4. 19F NMR (377 MHz, $CDCl_3$) δ -62.72. HRMS [EI]: m/z calculated for $C_{16}H_{16}NF_3O_2$ $[M]^+$ 311.1128, found 311.1131. IR (ATR): ῦ= 2954 (w), 1736 (s), 1250 (m), 1323 (vs), 1165 (s), 1068 (vs) $cm^{-1}$.

**methyl 4-(3-methoxy-2-methyl-3-oxo-1-(1*H*-pyrrol-1-yl)propyl)benzoate (9ia)**. Yield: colorless solid, 45 mg, 0.15 mmol, >99%. Mixture of diastereomers. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.86 (m, 2H), 7.38 – 7.26 (m, 2H), 6.66 (m, 2H), 6.07 (m, 2H (minor)), 6.02 (m, 2H (major)), 5.15 (m, 1H), 3.81 (m, 3H), 3.51 (s, 3H (major)), 3.44 (s, 3H (minor)), 3.36 (m, 1H) 1.07 (2H (minor)), 1.02 (2H (major)). $^{13}$C{1H} NMR (101 MHz, $CDCl_3$) δ 174.4, 174.1, 166.5, 166.5, 144.3, 143.6, 130.2, 130.1, 130.0, 129.9, 127.4, 127.0, 119.6, 119.4, 108.9, 108.7, 65.8, 65.3, 52.2, 52.1, 52.0, 44.9, 44.6, 15.9, 15.5. HRMS [ESI]: m/z calculated for $C_{17}H_{19}NO_4$ $[M]^+$ 301.1317 found 301.1314. IR (ATR): ῦ= 2951 (w), 1720 (vs), 1435 (m), 1276 (vs), 1168 (m), 725 (m) $cm^{-1}$.

**methyl 3-(4-cyanophenyl)-2-methyl-3-(1*H*-pyrrol-1-yl)propanoate (9ja).** Yield: colorless oil, 41.2 mg, 0.153 mmol. Mixture of diastereomers. $^1$H NMR (250 MHz, $CDCl_3$) δ 7.65 (m, 2H), 7.44 (m, 2H), 6.75 (m, 2H), 6.27 – 6.08 (m, 2H), 5.39 – 5.18 (m, 1H), 3.63 (s, 3H (major)), 3.58 (s, 3H (minor)), 3.44 (m, 1H), 1.17 (3H). $^{13}$C{1H} NMR (63 MHz, $CDCl_3$) δ 175.0, 174.9, 145.5, 144.7, 133.7, 133.5, 128.9, 128.6, 120.5, 120.3, 119.2, 113.2, 113.0, 110.2, 110.0, 66.5, 66.0,

53.2, 53.1, 45.6, 45.3, 30.6, 16.8, 16.4. HRMS [EI]: m/z calculated for $C_{16}H_{16}N_2O_2$ $[M]^+$ 268.1206, found 268.1208. IR (ATR): $\tilde{\nu}$= 2955 (w), 2230 (w), 1732 (s), 1269 (m), 1168 (m), 721 (vs) $cm^{-1}$.

**General procedure for intramolecular Friedel craft acylation.** Under nitrogen, the substrate (1.equiv.) was dissolved in $CH_2Cl_2$ (0.1M) and $BBr_3$ (1.05 eq.) was added slowly. The reaction was monitored by TLC and when judged completed, poured onto sat. $NaHCO_3$ solution. The organic phase was separated, and the aqueous phase was extracted twice with $CH_2Cl_2$. The combined organic phases were dried over $Na_2SO_4$ and after evaporation subjected to column chromatography to yield the desired compound.

**(2S,3R)-2-methyl-3-phenyl-2,3-dihydro-1*H*-pyrrolizin-1-one (*trans*-7ba).** Yield: colorless oil, 74.9 mg, 0.35 mmol, 53%. Chromatography: ethyl acetate: petroleum ether 15:85 $^1$H NMR (250 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 3H), 7.26 – 7.17 (m, 2H), 6.82 (d, *J* = 2.1 Hz, 2H), 6.56 (dd, *J* = 3.8, 2.5 Hz, 1H), 5.02 (d, *J* = 4.8 Hz, 1H), 2.98 (qd, *J* = 7.4, 4.8 Hz, 1H), 1.44 (d, *J* = 7.4 Hz, 3H). $^{13}$C{1H} NMR (63 MHz, $CDCl_3$) δ 192.0, 140.3, 133.7, 130.2, 129.6, 127.3, 123.2, 118.1, 108.9, 67.5, 57.1, 15.1. HRMS [ESI]: m/z calculated for $C_{14}H_{13}NNaO$ $[M+Na]^+$ 234.0894, found 234.0896. IR (ATR): $\tilde{\nu}$= 2966 (w), 1693 (vs), 1523 (m), 1454 (m), 1307 (s), 736 (vs), 798 (vs) $cm^{-1}$.

**(2S,3S)-2-methyl-3-phenyl-2,3-dihydro-1*H*-pyrrolizin-1-one (*cis*-7ba).** Yield: colorless solid, 13.0 mg, 0.06 mmol, 10%. Chromatography: ethyl acetate: petroleum ether 15:85 $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 5.8, 1.6 Hz, 3H), 6.92 (dd, *J* = 2.3, 1.1 Hz, 1H), 6.85 (dd, *J* = 3.8, 1.2 Hz, 3H), 6.61 (dd, *J* = 4.0, 2.3 Hz, 1H), 5.72 (d, *J* = 8.0 Hz, 1H), 3.50 (p, *J* = 7.7 Hz, 1H), 0.86 (d, *J* = 7.6 Hz, 3H). $^{13}$C{1H} NMR (63 MHz, CDCl3) δ 191.6, 138.3, 132.7, 128.8, 128.4, 126.9, 122.8, 117.2, 107.5, 62.6, 50.5, 12.1. IR (ATR): $\tilde{\nu}$= 2970 (w), 2018 (w), 1693 (vs), 1524 (m), 1369 (m), 1307 (m), 741 (s), 698 (s) in $cm^{-1}$.

**(2S,3R)-3-(3,5-dimethylphenyl)-2-methyl-2,3-dihydro-1*H*-pyrrolizin-1-one (*trans*-7ea).** Yield: colorless oil, 11.3 mg, 0.047 mmol, 53%. Chromatography: ethyl acetate: petroleum ether 15:85 $^1$H NMR (250 MHz, $CDCl_3$) δ 7.03 (s, 1H), 6.91 – 6.77 (m, 4H), 6.58 (dd, *J* = 3.7, 2.6 Hz, 1H), 4.94 (d, *J* = 4.8 Hz, 1H), 2.99 (qd, *J* = 7.4, 4.8 Hz, 1H), 2.34 (s, 6H), 1.44 (d, *J* = 7.4 Hz, 3H). $^{13}$C{1H} NMR (63 MHz, $CDCl_3$) δ 186.9, 134.9, 134.5, 128.3, 125.9, 119.8, 117.9, 112.6, 103.5, 62.2, 51.7, 16.9, 9.8. HRMS [ESI]: m/z calculated for $C_{16}H_{18}NO$ $[M+H]^+$ 240.1383, found 240.1338. IR (ATR): $\tilde{\nu}$= 2924 (w), 1697 (vs), 1527 (m), 1369 (m), 1307 (m), 848 (m), 741 (vs) $cm^{-1}$. This compound was subjected to the conventional self-disproportionation of enantiomers (SDE) test described in the literature.[20] We did not observe significant SDE for this compound and there were no indications of significant SDE with other pyrrolizin-1-one and *N*-allyl pyrroles reported here.

***trans*-2-methyl-3-phenethyl-2,3-dihydro-1*H*-pyrrolizin-1-one (*trans*-7ua)**. Yield: colorless solid, 7.5 mg, 0.040 mmol, 55% (brsm). Chromatography: ethyl acetate: petroleum ether 10:90 $^1$H NMR (400 MHz, $CDCl_3$ ) δ 7.34 (dd, *J* = 8.0, 6.6 Hz, 2H), 7.30 – 7.20 (m, 3H), 7.05 (dd, *J* = 2.3, 1.0 Hz, 1H), 6.76 (dd, *J* = 4.0, 1.0 Hz, 1H), 6.56

(dd, *J* = 4.0, 2.3 Hz, 1H), 4.15 (dt, *J* = 8.1, 4.2 Hz, 1H), 2.87 (qd, *J* = 7.4, 3.9 Hz, 1H), 2.82 – 2.66 (m, 2H), 2.46 – 2.30 (m, 1H), 2.24 – 2.05 (m, 1H), 1.42 (d, *J* = 7.4 Hz, 3H).$^{13}$C{1H} NMR (101 MHz, $CDCl_3$) δ 191.9, 140.4, 132.2, 128.7, 128.2, 126.4, 121.5, 116.9, 107.8, 62.1, 51.7, 37.2, 31.4, 15.9. HRMS [EI]: m/z calculated for $C_{16}H_{17}NO$ $[M]^+$ 239.1305, found 239.1303. IR (ATR): $\tilde{\nu}$= 2928(w), 1693 (vs), 1523 (vs), 1307 (s), 736 (vs) $cm^{-1}$.

***trans*-3-cyclohexyl-2-methyl-2,3-dihydro-1*H*-pyrrolizin-1-one (*trans*-7ta)**. Yield: colorless oil, 24.6 mg, 0.113 mmol, 62%. Chromatography: ethyl acetate: petroleum ether 10:90 $^1$H NMR (300 MHz, $CDCl_3$) δ 7.01 (s, 1H), 6.70 (d, *J* = 4.0 Hz, 1H), 6.52 (dd, *J* = 4.0, 2.3 Hz, 1H), 4.00 (t, J = 3.8 Hz, 2H), 2.85 (qd, *J* = 7.5, 3.3 Hz, 2H), 1.99 – 1.63 (m, 4H), 1.35 (d, *J* = 7.5 Hz, 3H), 1.31 – 1.14 (3H) 1.12 - 0.97 (m, 3H), 0.87 (m, 2H). $^{13}$C{1H} NMR (75 MHz, $CDCl_3$) δ 192.6, 132.4, 122.0, 116.61, 107.3, 67.4, 48.1, 42.4, 29.7, 28.9, 26.8, 26.3, 26.1, 25.9, 17.0. HRMS [EI]: m/z calculated for $C_{14}H_{19}NO$ $[M]^+$ 217.1467, found 217.1463. IR (ATR): $\tilde{\nu}$= 2824 (m), 2855 (m), 1693 (vs), 1527 (m), 1369 (m), 1307 (m), 733 (vs) $cm^{-1}$.

***trans*-3-(4-methoxyphenyl)-2-methyl-2,3-dihydro-1*H*-pyrrolizin-1-one (*trans*-7fa).** Yield: colorless oil, 5.0 mg, 0.023 mmol, 32%. Chromatography: ethyl acetate: petroleum ether 30:70 $^1$H NMR (600 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.73 (dd, *J* = 3.9, 1.1 Hz, 1H), 6.71 (dd, *J* = 2.4, 1.0 Hz, 1H), 6.46 (dd, *J* = 3.9, 2.3 Hz, 1H), 4.87 (d, *J* = 5.0 Hz, 1H), 3.75 (s, 3H), 2.88 (qd, *J* = 7.4, 5.0 Hz, 1H), 1.33 (d, *J* = 7.4 Hz, 3H).$^{13}$C{1H} NMR (151 MHz, $CDCl_3$) δ 191.3, 159.9, 132.7, 131.2, 127.8, 122.1, 117.1, 114.6, 107.9, 66.2, 56.2, 55.4, 14.0.. HRMS [EI]: m/z calculated for $C_{15}H_{15}NO_2$ $[M]^+$ 241.1097, found 241.1095. IR (ATR): $\tilde{\nu}$= 2931 (w), 1693 (vs), 1512 (vs), 1249 (vs), 1030 (m), 736 (s), 613 (m) $cm^{-1}$.

***trans*-2-methyl-3-(naphthalen-2-yl)-2,3-dihydro-1*H*-pyrrolizin-1-one (*trans*-7sa).** Yield: colorless solid, 4.8 mg, 0.018 mmol, 24% (brsm). Chromatography: ethyl acetate: petroleum ether 15:85 $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.84 (m, 3H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.63 – 7.50 (m, 2H), 7.22 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.89 (dd, *J* = 3.9, 1.1 Hz, 1H), 6.84 (dd, *J* = 2.3, 1.1 Hz, 1H), 6.60 (dd, *J* = 4.0, 2.3 Hz, 1H), 5.19 (d, *J* = 4.9 Hz, 1H), 3.10 (qd, *J* = 7.4, 4.9 Hz, 1H), 1.49 (d, *J* = 7.4 Hz, 3H).$^{13}$C{1H} NMR (101 MHz, $CDCl_3$) δ 191.1, 136.5, 133.3, 133.2, 129.6, 127.9, 127.9, 126.8, 126.8, 126.1, 123.4, 122.3, 117.3, 108.1, 66.9, 56.0, 14.2. HRMS [EI]: m/z calculated for $C_{18}H_{15}NO$ $[M]^+$ 261.1148, found 261.1152. IR (ATR): $\tilde{\nu}$= 2928 (w), 1693 (m), 1527 (m), 1572 (m), 1366 (m), 1308 (s), 736 (vs) $cm^{-1}$.

***trans*-3-(4-fluorophenyl)-2-methyl-2,3-dihydro-1*H*-pyrrolizin-1-one (*trans*-7na).** Yield: colorless solid, 9.4 mg, 0.041 mmol, 53%. Chromatography: ethyl acetate: petroleum ether 20:80 $^1$H NMR (400 MHz, $CDCl_3$) δ 7.19 (m 2H), 7.11 (m2H), 6.84 (dd, *J* = 4.0, 1.1 Hz, 1H), 6.82 – 6.79 (m, 1H), 6.58 (dd, *J* = 4.0, 2.3 Hz, 1H), 5.01 (d, *J* = 4.8 Hz, 1H), 2.95 (qd, *J* = 7.4, 4.9 Hz, 1H), 1.44 (d, *J* = 7.4 Hz, 3H). $^{13}$C{1H} NMR (101 MHz, $CDCl_3$) δ 190.8, 162.8 (d, $J_{C\text{-}F}$ = 247.9 Hz), 135.2 (d, $J_{C\text{-}F}$ = 3.1 Hz), 132.7, 128.2 (d, $J_{C\text{-}F}$ = 8.4 Hz), 122.1, 117.3, 116.3 (d, $J_{C\text{-}F}$ = 21.7 Hz), 108.1,

66.0, 56.2, 14.2. HRMS [EI]: m/z calculated for $C_{14}H_{12}NFO$ $[M]^+$ 229.0897, found 229.0899. IR (ATR): $\tilde{\nu}$= 2931 (w), 1705 (s), 1512 (m), 1288 (m), 1010 (m), 829 (vs), 775 (s) $cm^{-1}$.

***cis*-3-(4-fluorophenyl)-2-methyl-2,3-dihydro-1*H*-pyrrolizin-1-one (*cis*-7na).** Yield: colorless solid, 1.2 mg, 0.005 mmol, 7%. Chromatography: ethyl acetate: petroleum ether 20:80 $^1$H NMR (300 MHz, $CDCl_3$) δ 7.03 (m, 2H), 6.90 (m, 1H), 6.89 – 6.77 (m, 2H), 6.60 (dd, *J* = 4.0, 2.3 Hz, 1H), 5.71 (d, *J* = 8.0 Hz, 1H), 3.48 (p, *J* = 7.7 Hz, 1H), 0.85 (d, *J* = 7.6 Hz, 3H). $^{19}$F NMR (377 MHz, $CDCl_3$) δ -113.37. HRMS [EI]: m/z calculated for $C_{14}H_{12}NFO$ $[M]^+$ 229.0897, found 229.0900.

***trans*-3-(4-trifluormethylphenyl)-2-methyl-2,3-dihydro-1*H*-pyrrolizin-1-one (*trans*-7ka).** Yield: colorless solid, 12.2 mg, 0.044 mmol, 30%. Chromatography: ethyl acetate: petroleum ether 15:85 $^1$H NMR (250 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.89 – 6.86 (m, 1H), 6.83 (dd, *J* = 2.4, 1.0 Hz, 1H), 6.61 (dd, *J* = 3.9, 2.4 Hz, 1H), 5.11 (d, *J* = 4.8 Hz, 1H), 2.97 (qd, *J* = 7.4, 4.8 Hz, 1H), 1.48 (d, *J* = 7.4 Hz, 3H).).$^{13}$C{1H} NMR (63 MHz, CDCl3) δ 191.2, 144.4, 133.7, 132.0 (q, $J_{C-F}$=32.5 Hz), 127.6, 127.2 (q, $J_{C-F}$ = 3.76Hz), 124.7 (q, $J_{C-F}$ = 272 Hz), 118.5, 109.3, 67.0, 57.1, 15.2. $^{19}$F NMR (377 MHz, $CDCl_3$) δ -62.72. HRMS [EI]: m/z calculated for $C_{15}H_{12}NF_3O$ $[M]^+$ 279.0866, found 279.0862. IR (ATR): $\tilde{\nu}$= 2970 (w), 1697 (m), 1528 (vs), 1312 (vs), 1065 (vs), 1018 (m), 734 (m) $cm^{-1}$.

***trans*-3-(4-cyanophenyl)-2-methyl-2,3-dihydro-1*H*-pyrrolizin-1-one (*trans*-7ia).** Yield: colorless solid, 7.2 mg, 0.030 mmol, 22% (brsm). Chromatography: ethyl acetate: petroleum ether 20:80 $^1$H NMR (400 MHz, $CDCl_3$ ) δ 7.72 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.86 (dd, *J* = 4.0, 1.1 Hz, 1H), 6.82 (dd, *J* = 2.4, 1.0 Hz, 1H), 6.61 (dd, *J* = 4.0, 2.4 Hz, 1H), 5.10 (d, *J* = 4.7 Hz, 1H), 2.92 (qd, *J* = 7.4, 4.7 Hz, 1H), 1.47 (d, *J* = 7.4 Hz, 3H). $^{13}$C{1H} NMR (101 MHz, $CDCl_3$) δ 189.9, 144.8, 133.2, 132.7, 127.0, 122.1, 118.1, 117.9, 112.8, 108.5, 66.0, 56.1, 14.5. HRMS [EI]: m/z calculated for $C_{15}H_{12}N_2O$ $[M]^+$ 236.0944, found 236.0945. IR (ATR): $\tilde{\nu}$= 2927 (w), 1701 (vs), 1458 (m), 1369 (m), 1281 (vs), 744 (m) $cm^{-1}$.

***trans*-methyl 4-(*trans*)-2-methyl-1-oxo-2,3-dihydro-1*H*-pyrrolizin-3-yl)benzoate (*trans*-7ja).** Yield: colorless solid, 16.9 mg, 0.063 mmol, 46% (brsm). Chromatography: ethyl acetate: petroleum ether 20:80 $^1$H NMR (600 MHz, $CDCl_3$) δ 8.07 – 7.96 (m, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.76 (d, *J* = 4.0 Hz, 1H), 6.73 (d, *J* = 1.3 Hz, 1H), 6.50 (dd, *J* = 4.0, 2.3 Hz, 1H), 5.00 (d, *J* = 4.8 Hz, 1H), 3.86 (s, 3H), 2.87 (qd, *J* = 7.4, 4.8 Hz, 1H), 1.37 (d, *J* = 7.4 Hz, 3H). $^{13}$C{1H} NMR (151 MHz, $CDCl_3$) δ 190.5, 166.4, 144.4, 132.7, 130.6, 130.6, 126.3, 122.2, 117.5, 108.3, 66.2, 56.1, 52.3, 14.4. HRMS [EI]: m/z calculated for $C_{16}H_{15}NO_3$ $[M]^+$ 269.1052, found 269.1053.

## Associated Content: Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.XXXXXXX. $^{1}H$, $^{13}C$, and $^{19}F$ NMR of new compounds, $^{1}H$ NMR spectra of known compounds and HPLC chromatograms for compounds prepared in enantioenriched form.

**Acknowledgment**

Financial support from the Carl-Zeiss Foundation (endowed professorship to I.V.), Friedrich Schiller University Jena and the State of Thuringia (graduate fellowship to M.L.) is gratefully acknowledged. We thank Philipp Schüler, Dr. Peter Bellstedt, and Dr. Nico Ueberschaar for their support with HPLC, NMR, and MS analysis, respectively. The help of Constanze Schultz, Lea Klepsch and Hannah Zeihe in the synthesis of starting materials is greatly appreciated.

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