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# $MnI_2$-catalyzed regioselective intramolecular iodoamination of unfunctionalized olefins

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ABSTRACT

$MnI_2$-catalyzed intramolecular iodoamination of unfunctionalized olefins was reported. Interaction of $MnI_2$ with *N*-alkenyl amine/sulfonamide gave −NRMnI which produced a $-CH_2MnI$ intermediate via intramolecular aminometallation of C=C double bond. Reductive elimination of $-CH_2I$ from $-CH_2MnI$ produced iodomethyl heterocycle with the release of Mn(0) which was confirmed by XPS and XRD experiments.

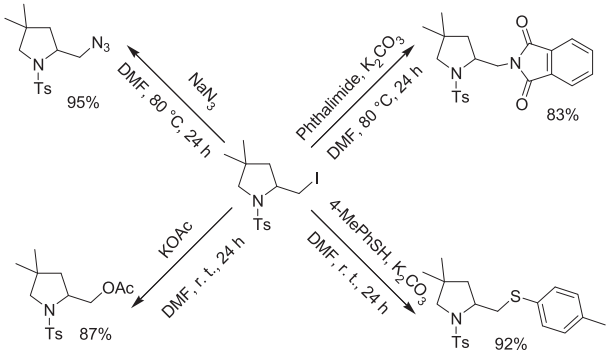


## 1. Introduction

Vicinal haloamines have played important role in organic chemistry and medicinal chemistry. They have appeared as subunits of several natural products[1] and have been used as key functional groups in mechanism-based antitumor drugs.[2] Under certain conditions, vicinal haloamines can be converted to aziridines[3] from which different structures can be constructed,[4] and dehalogenation of the vicinal haloamines can also be a useful supplemental method for hydroamination reactions.[5] In addition, vicinal haloamines especially 3-halo- and 2-halomethylheterocycles have been used as key intermediates for the synthesis of a variety of alkaloids[6] and pharmaceuticals.[7] Further, a variety of chiral ligands[8] and organocatalysts[9] can be prepared using 3-halo- and 2-halomethylheterocycles as important starting materials. For these reasons, continued efforts have been made toward the chemo- and stereoselective synthesis of vicinal haloamines.[10]

While haloamination of activated C=C double bond has been realized both chemo- and stereoselectively,[11] there still exists the space of development for intramolecular haloamination of unfunctionalized olefins. In addition to the well-developed conventional functional group transformation reactions,[12] a variety of cyclization reactions have also been developed for the construction of 2-halomethyl- and 3-haloheterocycles. These methods include free radical cyclization of N-chloramines,[13] electrophilic cyclization of alkeneamines(imines),[14] organocatalytic bromoamination[15] as well as transition metal-catalyzed intramolecular haloamination reactions.[16]

In our previous studies we found that Cu(II) alone was able to promote chloro- and bromoamination of unfunctionalized olefins, leading to chlorine and bromine-containing heterocycles in good to excellent isolated yields.[17] Functionalized heterocycles could be obtained via subsequent nucleophilic substitution reactions. However, the derivatization would require high temperature due to the poor leaving group properties of both chloride and bromide anions. Later, we found that $PhI(OAc)_2$ was a viable promoter for the reactions, and iodoamination of different substrates were realized in high isolated yields. The iodo-group could be readily derivatized under mild conditions (Scheme 1).[18]




**Scheme 1.** Derivatization of 2-iodomethylpyrrolidine compounds.

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0040-4020/

The problem associated with our previous methods is the amount of reaction promoters used. So far, it is difficult to carry out these reactions catalytically, and stoichiometric amount Cu(II) or $PhI(OAc)_2$ would have to be applied irrespective of whatever halide sources were used. Considering the potential application of iodine-containing heterocycles in the construction of biologically interesting structures, we decided to develop a new method for intramolecular iodoamination of unfunctionalized olefins. In this paper we wish to report our recent progress on Mn(II)-catalyzed intramolecular iodoamination of unfunctionalized olefins.

## 2. Results and discussion

Based on our understanding of transition metal-mediated amination reactions, a variety of metal iodides were screened and $MnI_2$ gave the most promising results.[19] In the presence of stoichiometric amount of $MnI_2$, cyclization of *N*-benzyl 2,2-diphenyl-4-penten-1-amine (**1a**) proceeded readily, giving 6-*endo*-trig product 1-benzyl-3,3-diphenyl-5-iodopiperidine (**2a**) and 5-*exo*-trig product 1-benzyl-2-iodomethyl-4,4-diphenylpyrrolidine (**3a**) in a ratio of 88:12. Isolation of **2a** and **3a** was difficult due to the easy inter-conversion of these two isomers via aziridium intermediate.[20]

Different control experiments were then carried out to verify if the reaction was promoted by $MnI_2$, or by $I_2$ formed via possible oxidation of $I^-$ (Table 1).[21] Iodine was indeed able to promote the reaction. However, the reaction was significantly suppressed after the addition of potassium thiosulfate. When $MnI_2$ was used as the reaction promoter, complete conversion of the substrate was observed either in argon atmosphere or in open air, and potassium thiosulfate showed less effect on the course of the reaction. These results indicated that the reactions were promoted by $MnI_2$ rather than molecular iodine.

After the validation of Mn(II)-promoted intramolecular iodoamination reaction, different solvents were tested to find a suitable medium for the reaction.[19] Preliminary results indicated that toluene, alcoholic solvents (methanol, ethanol), acetonitrile, dichloroethane and diethyl ether could all be used as reaction media (Table 2). Ethanol was used for further study due to the safety issue and its good performance.

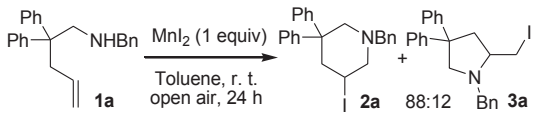
Next, studies were carried out to develop an Mn(II)-catalyzed intramolecular iodoamination reaction. Reactions with catalytic amount of $MnI_2$ and different iodide sources were carried out, and NaI was found to be the most suitable iodide source.[19] Both anhydrous and sodium iodide dihydrate were tested as the iodide source, and no significant difference was observed in the presence of 20 mol % of $MnI_2$ (Table 2, entries 11 and 12). Other iodide sources such as potassium iodide or pyridine hydroiodic acid salt gave low conversions under this condition (Table 2, entries 13 and 14). Reducing the amount of iodide source $NaI\cdot 2H_2O$ resulted in the decrease of the conversion of the substrate (Table 2, entry 16). Sodium iodide alone was unable to promote the reaction (Table 2, entry 17), indicating the important role played by $MnI_2$.

After establishing a general method for Mn(II)-catalyzed intramolecular iodoamination of **1a**, different substrates were tested to study the scope of the reaction. Up to 96% yields were observed for 4-penten-1-amine substrates, and up to 95% isolated yields were observed for 5-hexen-1-amine substrates.[19]

During the study we found that gray powder was always formed when the reaction was carried out with stoichiometric amount of $MnI_2$. This gray powder was not soluble in any organic solvents, nor was it soluble in any aqueous alkaline solutions. However, the solid was soluble in acidic solutions, along with the release of gas bubbles. XPS experiment on the obtained gray powder indicated that it contained manganese (0).[19] Further XRD experiment confirmed that this gray solid was manganese (0).

Further reducing the catalyst loading led to a drop of substrate conversion, and only 20% of **1a** was converted (**2a**:**3a**=9:1) when the reaction was carried out with 10 mol % of $MnI_2$ under otherwise identical conditions. We reasoned that this was possibly due to the slow conversion of Mn(0) to Mn(II), and this problem would be tackled with the addition of acid additive. The acid additive should be such that it could react with Mn(0) to regenerate Mn(II), and strong interaction of the additive with the substrate should be avoided. To this end, several solid acid additives were tested for their capability to convert Mn(0) to Mn(II), and sodium bisulfate gave the most promising results.[19] In the presence of 10 mol % of $MnI_2$, 2.5 equiv of sodium bisulfate, and 4 equiv of $NaI\cdot 2H_2O$, intramolecular iodoamination of **1a** proceeded readily, leading to 6-*endo*-trig product **2a** and 5-*exo*-trig product **3a** in 95% yield (**2a**:**3a**=7:1) (Scheme 2a). A control experiment with 10 mol % of Mn powder under otherwise identical conditions also provided products in 81% yield (**2a**:**3a**=10:1) (Scheme 2b).

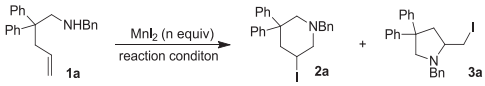
**Table 1**
Validation of $MnI_2$-catalyzed intramolecular iodoamination of **1a**[a]




| Entry | Promoter | Condition | Additive | (**2a**+**3a**):**1a**/**2a**:**3a**[b] |
|---|---|---|---|---|
| 1 | $MnI_2$ | Ar | — | >99:1 (8:1) |
| 2 | $MnI_2$ | Air | — | >99:1 (7:1) |
| 3 | $MnI_2$ | Ar | $K_2S_2O_3$ | 72:28 (8:1) |
| 4 | $I_2$ | Air | — | 93:7 (8:1) |
| 5 | $I_2$ | Ar | $K_2S_2O_3$ | 24:76 (7:1) |

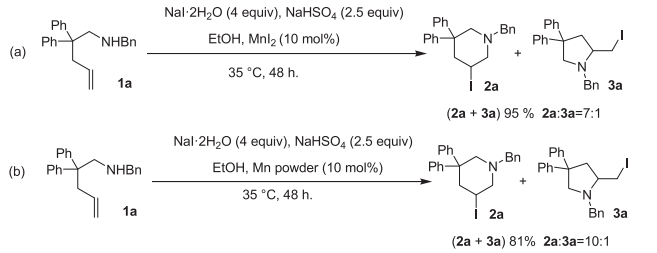
[a] Reaction conditions: **1a** (0.25 mmol), promoter (1 equiv), additive (1 equiv), toluene (1 mL), room temperature, 24 h.
[b] Based on $^1H$ NMR analysis of the reaction mixtures.

**Table 2**
Screening of solvents and iodide sources[a]




| Entry | Solvent | $MnI_2$ (equiv) | Iodide source (equiv) | (**2a**+**3a**):**1a**/**2a**:**3a**[b] |
|---|---|---|---|---|
| 1 | Toluene | 1 | — | >99:1 (7:1) |
| 2 | MeOH | 1 | — | 94:6 (7:1) |
| 3 | EtOH | 1 | — | >99:1 (8:1) |
| 4 | MeCN | 1 | — | 97:3 (8:1) |
| 5 | DCE | 1 | — | 97:3 (7:1) |
| 6 | $Et_2O$ | 1 | — | 98:2 (8:1) |
| 7 | $CH_2Cl_2$ | 1 | — | 55:45 (8:1) |
| 8 | THF | 1 | — | 65:35 (6:1) |
| 9 | EtOAc | 1 | — | 79:21 (6:1) |
| 10 | EtOH | 0.5 | — | 98:2 (8:1) |
| 11 | EtOH | 0.2 | $NaI\cdot 2H_2O$ (4) | 97:3 (10:1) |
| 12 | EtOH | 0.2 | NaI(4) | 90:10 (8:1) |
| 13 | EtOH | 0.2 | KI(4) | 77:23 (8:1) |
| 14 | EtOH | 0.2 | Py·HI(4) | 32:68 (7:1) |
| 15[c] | EtOH | 0.2 | $NaI\cdot 2H_2O$(4) | 97:3 (10:1) |
| 16[c] | EtOH | 0.2 | $NaI\cdot 2H_2O$(2) | 65:35 (7:1) |
| 17[d] | EtOH | — | $NaI\cdot 2H_2O$ | NR. |

[a] Reactions were carried out with 0.25 mmol of **1a** at room temperature for 24 h. Iodide sources: 4 equiv, solvent (1 mL).
[b] Based on crude $^1H$ NMR analysis of the reaction mixtures.
[c] Reaction temperature=35 °C.
[d] NR.=no reaction.

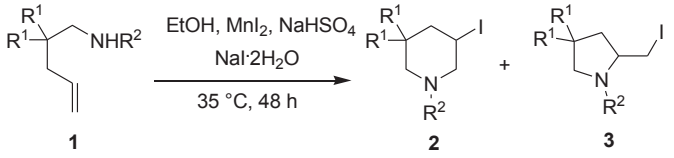



**Scheme 2.** Control reaction of **1a** in the presence of $MnI_2$/Mn powder and sodium bisulfate.

This result led to the optimized reaction condition with 10 mol % of $MnI_2$ as the catalyst, and sodium bisulfate as the additive to assist the conversion of Mn(0) to Mn(II). In the presence 10 mol % of $MnI_2$, 4 equiv of sodium iodide dihydrate and 2.5 equiv of sodium bisulfate, both 4-penten-1-amine substrates and 5-hexen-1-amine substrates could be converted to the corresponding products with good isolated yields (Tables 3 and 4).

As shown in Table 3, the reactions generally proceeded readily, leading to iodoamination products in good to excellent isolated yields. When *N*-benzyl substrates were used, 6-*endo*-trig compounds (*N*-benzyl-3-iodopiperidines, **2a**-**2i**) were obtained as the final products, along with small amount of 5-*exo*-trig *N*-benzyl-2-iodomethylpyrrolidines (entries 1–9). The amount of 5-*exo*-trig products decreased with the reduce of the size of 3,3-disubstituents, and in some cases the 6-*endo*-trig products could be isolated as the sole isomers (entries 10 and 11). When the amino groups in the substrates were tosylated, only 5-*exo*-trig products (2-iodomethylpyrrolidines, **3l**-**3o**) were obtained (entries 12–15). These results also indicated that the 5-*exo*-trig products were formed at first. When the nitrogen atoms contained *N*-alkyl substituents, the products underwent fast isomerization through aziridinium intermediates, giving thermodynamically stable 6-*endo*-trig 3-iodopiperidines as the final products. When the amino groups were tosylated, the nucleophilicity of the nitrogen atoms was reduced, and the conversion of 5-*exo*-trig 2-iodomethylpyrrolidines to 6-*endo*-trig 3-iodopiperidines was difficult. Under such conditions, 5-*exo*-trig *N*-tosyl 2-iodomethylpyrrolidines could be isolated as the final products of the reactions. Further, when *o*-allylaniline *N*-sulfonamide **1p** was used, *N*-sulfonyl 2-iodomethylindoline **3p** could also be obtained in moderate isolated yield (entry 16). Substrates with acetoxyl, benzoyl or Boc groups on nitrogen atoms failed to react.[19] Thorpe-Ingold effect[22] showed some impact on the reactions, but most reactions still produced the corresponding cyclization products in good to excellent isolated yields.

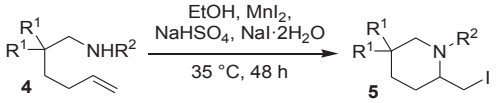
**Table 3**
$MnI_2$-catalyzed intramolecular iodoamination of 4-penten-1-amine substrates[a]




| Entry | Substrate | $R^1$ | $R^2$ | Yield (**2**+**3**)[b]/(**2**:**3**)[c] |
|---|---|---|---|---|
| 1 | **1a** | Ph | Bn | 95 (7:1) |
| 2 | **1b** | Ph | 4-FBn | 60 (7:1) |
| 3 | **1c** | Ph | 4-ClBn | 74 (6:1) |
| 4 | **1d** | Ph | 4-BrBn | 83 (8:1) |
| 5 | **1e** | Ph | 4-MeBn | 87 (10:1) |
| 6 | **1f** | Ph | 4-MeOBn | 94 (7:1) |
| 7 | **1g** | Ph | 4-CNBn | 94 (7:1) |
| 8 | **1h** | Ph | 4-$NO_2$Bn | 96 (7:1) |
| 9 | **1i** | $-(CH_2)_5-$ | Bn | 85 (20:1) |
| 10 | **1j** | Me | Bn | 91 (**2j** only) |
| 11 | **1k** | H | Bn | 85 (**2k** only) |
| 12[d] | **1l** | Ph | Ts | 94 (**3l** only) |
| 13[d] | **1m** | $-(CH_2)_5-$ | Ts | 93 (**3m** only) |
| 14[d] | **1n** | Me | Ts | 87 (**3n** only) |
| 15[d] | **1o** | H | Ts | 81 (**3o** only) |
| 16[d] | **1p** | | | 67 (**3p** only) |

[a] Reactions were carried out with 0.25 mmol of **1**, 0.025 mmol $MnI_2$ (10 mol %), 1 mmol NaI·$2H_2O$ (4 equiv) and 0.625 mmol $NaHSO_4$ (2.5 equiv) in EtOH (1 mL) at 35 °C for 48 h.
[b] Isolated yields.
[c] Based on NMR integration of the isolated products.
[d] Reaction time=96 h.

**Table 4**
$MnI_2$-catalyzed intramolecular iodoamination of 5-hexen-1-amine substrates[a]




| Entry | Substrate | $R^1$ | $R^2$ | Yield (%)[b] |
|---|---|---|---|---|
| 1 | **4a** | Ph | Bn | 93 |
| 2 | **4b** | Ph | 4-MeOBn | 91 |
| 3 | **4e** | Ph | 4-*i*-PrBn | 94 |
| 4 | **4f** | Ph | 4-MeBn | 81 |
| 5 | **4g** | Ph | 4-FBn | 85 |
| 6 | **4h** | Ph | 4-ClBn | 88 |
| 7 | **4i** | Ph | 4-BrBn | 88 |
| 8 | **4j** | Ph | *p*-MeOOCBn | 64 |
| 9 | **4k** | Ph | 4-CNBn | 88 |
| 10 | **4l** | Ph | 4-$NO_2$Bn | 89 |
| 11 | **4m** | Ph | *i*-Pr | 83 |
| 12 | **4n** | $-(CH_2)_5-$ | Bn | 94 |
| 13 | **4o** | Me | Bn | 83 |
| 14 | **4p** | Ph | Ts | 87[c] (92)[d] |
| 15 | **4q** | $-(CH_2)_5-$ | Ts | 81[c] (91)[d] |
| 16 | **4r** | Me | Ts | 73[c] (83)[d] |
| 17 | **4s** | H | Ts | 53[c] (64)[d] |

[a] All reactions were carried out with 0.25 mmol of **4**, 0.025 mmol $MnI_2$ (10% mol), 1 mmol NaI·$2H_2O$ (4 equiv) and 0.625 mmol $NaHSO_4$ (2.5 equiv) in EtOH (1 mL) at 35 °C for 48 h.
[b] Isolated yields.
[c] Reaction time=96 h, reaction temperature=45 °C.
[d] Reaction time=96 h, reaction temperature=35 °C, catalyst loading=20 mol %.

To determine the skeleton of the products, compound **2c** was subjected to X-ray diffraction experiment. The ORTEP drawing clearly showed a typical chair conformation with two phenyl groups at both *e*- and *a*-positions of the six-membered ring. Iodo- and *p*-chlorobenzyl groups also resided at the *e*-positions of the six-membered ring (Fig. 1).

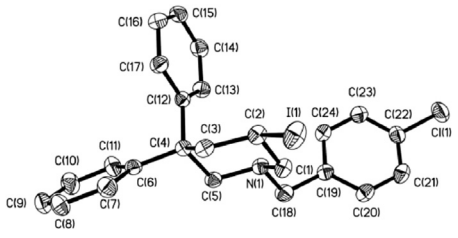



**Fig. 1.** ORTEP drawing of compound **2c** with thermal ellipsoids at 30% probability. Hydrogen atoms were omitted for clarity.

Next, our attention turned to the 5-hexen-1-amine substrates, and the results were presented in Table 4. The reactions showed high selectivity for 6-*exo*-trig products. 2-Iodomethylpiperidines were obtained in all cases, and conversion of 2-iodomethylpiperidines to the corresponding 3-iodoazepanes

was not observed. The 2-iodomethylpiperidine structure was also confirmed with X-ray diffraction experiment (Fig. 2). When *N*-sulfonamides were subjected to the same reaction, longer reaction time and higher reaction temperature were generally required (entries 14–17).

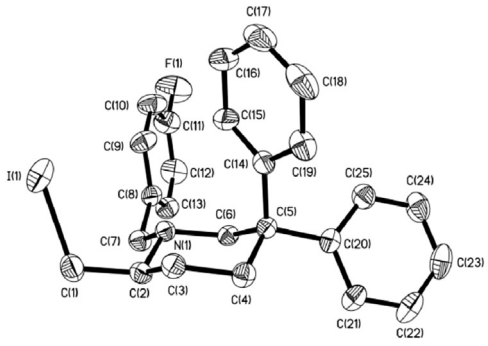
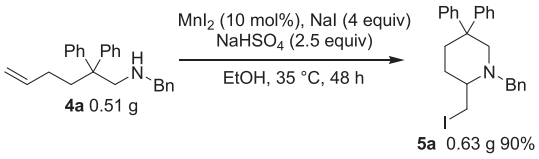


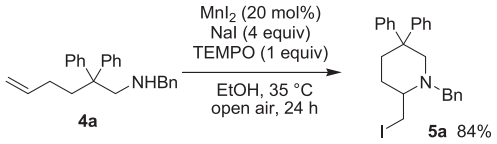

**Fig. 2.** ORTEP drawing of compound **5g** with thermal ellipsoids at 30% probability. Hydrogen atoms were omitted for clarity.

Iodoamination of **4a** was also scaled up to prove the scalability of the current protocol. The reaction was carried out under the optimized reaction conditions, and the expected product **5a** was obtained in 90% isolated yield (Scheme 3).



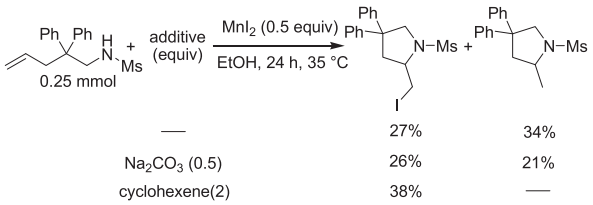

**Scheme 3.** Scale-up of the reaction.

Mn(III) was known to promote free radical carbolactonization and related reactions.[23] To study the possible pathway of the current reaction, iodoamination of **4a** was carried out in the presence of TEMPO (Scheme 4). Preliminary results indicated that this additive showed no impact on the reaction, and the free radical capture was also not observed, possibly ruling out the free radical pathway of the reaction.




**Scheme 4.** Reaction of **4a** in the presence of free radical capturer.

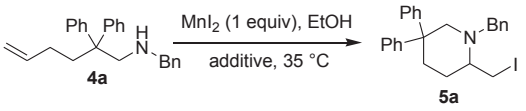
Tilley et al. showed that a Brønsted acid could be released when sulfonamide coordinated to a metal salt.[24] Bergman et al. pointed out that acid catalysis was more likely in many metal-catalyzed hydroamination and hydroarylation reactions.[25] Szolcsányi et al. detailed the intramolecular hydroamination of N-tosylalkenylamines using a variety of metal triflate as catalysts, and concluded that triflic acid could be the true catalyst for these reactions.[26] Sarpong et al. showed that HI could be used as a viable promoter for intramolecular hydroamination of unfunctionalized olefins.[27] To test if HI was released in the current reactions, different sulfonamide substrates were subjected to the same iodoamination reactions. While only iodoamination product was observed for *N*-tosyl substrate, iodoaminadtion product along with intramolecular hydroamination product was observed when *N*-mesyl substrate was subjected to the reaction under otherwise identical conditions (Scheme 5). Further, the intramolecular hydroamination product was significantly suppressed when cyclohexene was added to clear any possible HI formed during the reaction (Scheme 5). These results supported the possible release of HI during the interaction of $MnI_2$ with the substrate.




**Scheme 5.** Possible formation of HI during the reaction.

To further study the possible release of HI, control reactions of **4a** in the absence and presence of bases were carried out (Table 5). While sodium carbonate was ineffective to accelerate the intramolecular iodoamination reaction of **4a** (Table 5, entry 2), significant rate enhancement was observed when the reaction was carried out in the presence of potassium phosphate (Table 5 entry 3).

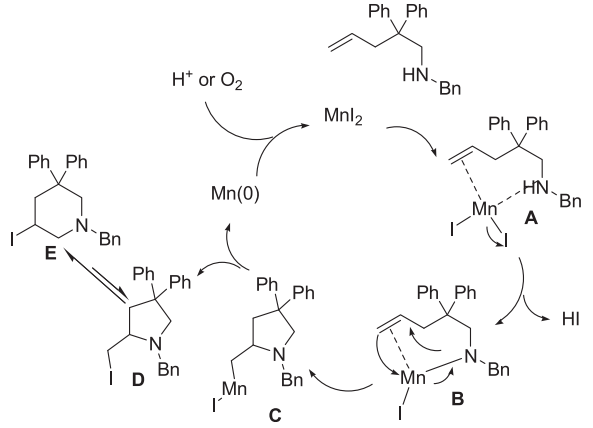
**Table 5**
The effect of base on the course of the reaction[a]




| Entry | Additive (equiv) | **5a**:**4a**[b] |
|---|---|---|
| 1 | — | 1.6:1 |
| 2 | $Na_2CO_3$ (1) | 1.2:1 |
| 3 | $K_3PO_4$ (2/3) | 6:1 |

[a] Reactions were carried out with 0.25 mmol of substrate and 1 equiv of $MnI_2$ in EtOH (1 mL). Reaction time=5 h.
[b] Based on NMR analysis of the reaction mixtures.

Based on the current results, a preliminary reaction mechanism was proposed as shown in Scheme 6. Interaction of Mn(II) with substrate gave intermediate **A**. HI was released at this stage and this step could be enhanced upon addition of a suitable base (Table 5, entry 3). Interaction of Mn with C=C double bond led to the activation of the latter, and intramolecular nucleophilic attack of nitrogen atom on activated C=C double bond proceeded as shown in **B**, yielding an aminometallation intermediate **C**. Reductive elimination of product **D** from **C** occurred, releasing Mn(0), which could be proved by XPS and XRD experiments. Product **D** underwent fast




**Scheme 6.** A plausible mechanism for $MnI_2$-catalyzed intramolecular iodoamination reaction.

equilibrium with **E**, leading to the formation of **E** as the final product, and Mn(0) was converted to Mn(II) by the action of oxygen or via reaction with an acid additive, thus completing the catalysis cycle.

When *N*-benzyl 4-penten-1-amine substrate was subjected to the reaction, 5-*exo*-trig product could easily isomerize to 6-*endo*-trig product via aziridium iodide intermediate. When *N*-sulfonyl 4-penten-1-amine substrate was subjected to the same reaction, conversion of 5-*exo*-trig product **D** to 6-*endo*-trig product **E** was difficult due to the low nucleophilicity of the sulfonylated nitrogen atom. Under such circumstance, 5-*exo*-trig 2-iodomethyl heterocyclic product was obtained as the final product. When 5-hexen-1-amine substrate was subjected to the same reaction, conversion of 6-*exo*-trig product to 7-*endo*-trig product was difficult, and 6-*exo*-trig compound **5** was obtained as the only product.

## 3. Conclusion

In summary, intramolecular iodoamination of unfunctionalized olefins were realized in the presence of catalytic amount of $MnI_2$, a suitable iodide source and an acid additive. Both N-substituted pent-4-en-1-amines and *N*-substituted hex-5-en-1-amines could be easily cyclized, leading to 3-iodopiperidines or 2-iodomethylpyrrolidines in good to excellent isolated yields. The advantages of the current system include mild and easy-to-operate reaction conditions, and the easy availability of both the catalyst and the iodide source. To the best of our knowledge, this is the first report for reductive elimination of alkyliodide from Mn(II) center. Development of Mn(II)-catalyzed asymmetric iodohaloamination and preparation of related heterocycles are in good progress and the results will be reported in due time.

## 4. Experimental section

### 4.1. General information

Reactions were carried out using commercially available reagents in oven-dried apparatus. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DRX 400 spectrometer at 298 K using deuterated chloroform as solvent and TMS as the internal reference. Column chromatography was performed employing 200–300 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel $GF_{254}$. HRMS analyses were carried out with Varian FTICR-MS 7.0 T.

### 4.2. General procedure for intramolecular iodoamination

To a solution of $MnI_2$ (7.72 mg, 0.025 mmol, 10 mol %) in EtOH (0.5 mL) was added **1a** (81.75 mg, 0.25 mmol, 1 equiv), $NaI{\cdot}2H_2O$ (185.9 mg, 1 mmol, 4.0 equiv) and $NaHSO_4$ (87.0 mg, 0.625 mmol, 2.5 equiv), followed by another portion of EtOH (0.5 mL). The resulting mixture was stirred at 35 °C and the reaction was monitored by TLC. After completion of the reaction (48 h), the solvent was evaporated and the residue was purified by flash column chromatography to give **2a** as colorless oil.

### 4.3. Scaled-up iodoamination of 4a

To a solution of $MnI_2$ (0.046 mg, 0.15 mmol, 10 mol %) in EtOH (6 mL) was added **4a** (0.5118 g, 1.5 mmol, 1 equiv), $NaI{\cdot}2H_2O$ (1.118 g, 6 mmol, 4.0 equiv) and $NaHSO_4$ (0.522 g, 3.75 mmol, 2.5 equiv). The resulting mixture was stirred at 35 °C and the reaction was monitored by TLC. After completion of the reaction (48 h), water (20 mL) was added and the aqueous portion was extracted with $CH_2Cl_2$ (50 mL×3). The organic portion was washed with brine, dried over anhydrous sodium sulfate, and concentrated in vacuo. The solvent was evaporated and the residue was purified by flash column chromatography to give **5a** (0.63 g, 90%) as colorless oil.

*4.3.1. 1-Benzyl-5-iodo-3,3-diphenylpiperidine (**2a**).* White solid, m. p. 47 °C–50 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.31–6.95 (m, 15H), 3.99 (t, $J$=11.68 Hz, 1H), 3.58 (d, $J$=12.1 Hz, 1H), 3.48 (s, 2H), 3.23 (d, $J$=10.2 Hz, 1H), 3.09 (t, $J$=17.6 Hz, 1H), 2.57 (t, $J$=12.6 Hz, 1H), 2.43 (t, $J$=10.8 Hz, 1H), 2.25 (t, $J$=13.9 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 146.2, 143.6, 135.9, 133.3, 128.2, 127.9, 127.7, 127.2, 127.0, 126.7, 125.3, 124.8, 62.8, 61.0, 60.7, 49.1, 47.7, 22.2, 20.1. HRMS–ESI ($m/z$): $[M+H]^+$ calcd for $C_{24}H_{24}IN$: 454.1032; found: 454.1028. The NMR data were in agreement with reported results.[18]

*4.3.2. 1-(4-Fluorobenzyl)-5-iodo-3,3-diphenylpiperidine (**2b**).* White solid, mp 105 °C–107 °C. 1H NMR (400 MHz, $CDCl_3$) $\delta$ 7.21–6.88 (m, 14H), 3.99 (t, $J$=11.5 Hz, 1H), 3.55 (d, $J$=11.9 Hz, 1H), 3.49–3.37 (m, 2H), 3.20 (d, $J$=8.5 Hz, 1H), 3.12 (d, $J$=12.4 Hz, 1H), 2.56 (t, $J$=12.6 Hz, 1H), 2.42 (t, $J$=10.8 Hz, 1H), 2.26 (d, $J$=12.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 147.2, 144.6, 133.4, 133.3, 130.9, 130.8, 128.7, 128.4, 128.2, 126.5, 126.4, 126.1, 115.4, 115.2, 63.9, 61.8, 61.6, 50.2, 48.8, 22.9. $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ −115.2. HRMS–ESI ($m/z$): $[M+H]^+$ calcd for $C_{24}H_{23}FIN$: 472.0937; found: 472.0929. The NMR data were in agreement with reported results.[18]

*4.3.3. 1-(4-Chlorobenzyl)-5-iodo-3,3-diphenylpiperidine (**2c**).* White solid, mp 122 °C–124 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.23–6.94 (m, 14H), 4.05–3.93 (m, 1H), 3.54 (d, $J$=12.0 Hz, 1H), 3.46–3.38 (m, 2H), 3.19 (d, $J$=8.6 Hz, 1H), 3.12 (d, $J$=12.7 Hz, 1H), 2.55 (t, $J$=12.7 Hz, 1H), 2.42 (t, $J$=10.9 Hz, 1H), 2.27 (d, $J$=12.1 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 146.0, 143.4, 135.0, 132.0, 129.4, 127.5, 127.4, 127.3, 127.1, 125.3, 125.2, 124.9, 62.8, 60.9, 60.5, 49.0, 47.5, 21.6. IR (KBr): 3084, 3046, 3025, 2961, 2930, 2815, 2787, 2713, 1951, 1894, 1596, 1491, 1445, 1340, 1184, 1137, 1072, 1061, 1016, 909, 839, 804, 754, 701, 631, 580, 538, 460 $cm^{-1}$;HRMS–ESI ($m/z$): $[M+H]^+$ calcd for $C_{24}H_{23}ClIN$: 488.0642; found: 488.0635.

Crystal data for **2c**: $C_{24}H_{23}ClIN$, $M$=487.78, monoclinic, $a$=12.325(3) Å, $b$=10.604(2) Å, $c$=16.287(3) Å, $\alpha$=90.00°, $\beta$=91.13(3)°, $\gamma$=90.00°, $V$=2128.2(7) Å$^3$, $T$=293(2) K, space group $P2(1)/c$, $Z$=4, μ(MoKα)=1.639 $mm^{-1}$, 21,190 reflections measured, 5083 independent reflections ($R_{int}$=0.0391). The final $R_1$ values were 0.0496 ($I>2\sigma(I)$). The final $wR(F^2)$ values were 0.1262 ($I>2\sigma(I)$). The final $R_1$ values were 0.0655 (all data). The final $wR(F^2)$ values were 0.1384 (all data). The goodness of fit on $F^2$ was 1.074. CCDC 1451292.

*4.3.4. 1-(4-Bromobenzyl)-5-iodo-3,3-diphenylpiperidine (**2d**).* White solid, mp 83 °C–86 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.37 (d, $J$=8.0 Hz, 2H), 7.25–7.06 (m, 11H), 6.99 (d, $J$=7.9 Hz, 2H), 4.05–3.95 (m, 1H), 3.56 (d, $J$=12.0 Hz, 1H), 3.49–3.39 (m, 2H), 3.23–3.17 (m, 1H), 3.14 (d, $J$=12.6 Hz, 1H), 2.56 (t, $J$=12.7 Hz, 1H), 2.44 (t, $J$=10.9 Hz, 1H), 2.29 (d, $J$=12.1 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 147.1, 144.5, 136.6, 131.5, 130.9, 128.6, 128.4, 128.4, 128.2, 126.5, 126.3, 126.0, 63.9, 61.9, 61.6, 50.2, 48.6, 22.7. IR (KBr): 3084, 3058, 3026, 2926, 2883, 2813, 2760, 1591, 1490, 1468, 1445, 1332, 1300, 1263, 1100, 1070, 1053, 1012, 965, 840, 802, 768, 749, 697, 630, 566, 526 $cm^{-1}$; HRMS–ESI ($m/z$): $[M+H]^+$ calcd for $C_{24}H_{23}BrIN$: 532.0137; found: 532.0116.

*4.3.5. 5-Iodo-1-(4-methylbenzyl)-3,3-diphenylpiperidine (**2e**).* White solid, mp 123 °C–124 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.31–6.91 (m, 14H), 4.04–3.95 (m, 1H), 3.59 (d, $J$=12.1 Hz, 1H), 3.46 (d, $J$=3.8 Hz, 2H), 3.28–3.21 (m, 1H), 3.12 (d, $J$=12.5 Hz, 1H), 2.56 (d, $J$=12.6 Hz, 1H), 2.43 (t, $J$=11.0 Hz, 1H), 2.26 (d, $J$=13.4 Hz, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 146.3, 143.6, 135.9, 133.4, 128.2, 127.9, 127.7, 127.3, 127.0, 125.3, 125.3, 124.8, 62.8, 61.0, 60.8, 49.1, 47.8, 22.2, 20.1. IR (KBr): 3047, 3020, 2958, 2930, 2786, 2753, 1596,

1494, 1445, 1340, 1262, 1207, 1106, 1061, 1024, 909, 805, 751, 701, 632, 588, 557, 485 $cm^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for C25H26IN: 468.1188; found: 468.1180.

*4.3.6. 5-Iodo-1-(4-methoxybenzyl)-3,3-diphenylpiperidine (**2f**).* White solid, mp 105 °C–107 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.26–7.03 (m, 10H), 6.99 (d, *J*=7.5 Hz, 2H), 6.79 (d, *J*=8.4 Hz, 2H), 4.06–3.92 (m, 1H), 3.73 (s, 3H), 3.58 (d, *J*=12.1 Hz, 1H), 3.50–3.34 (m, 2H), 3.28–3.17 (m, 1H), 3.12 (d, *J*=12.6 Hz, 1H), 2.57 (t, *J*=12.7 Hz, 1H), 2.42 (t, *J*=11.0 Hz, 1H), 2.23 (d, *J*=12.1 Hz, 1H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 157.9, 146.2, 143.6, 129.4, 128.5, 127.7, 127.3, 127.0, 125.8, 125.3, 124.8, 112.6, 62.8, 60.6, 54.2, 49.1, 47.8, 22.19. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{26}INO$: 484.1137; found: 484.1124. The NMR data were in agreement with reported results.[18]

*4.3.7. 4-((5-Iodo-3,3-diphenylpiperidin-1-yl)methyl)benzonitrile (**2g**).* White solid, mp 145 °C–148 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.53 (d, *J*=8.1 Hz, 2H), 7.31 (d, *J*=8.1 Hz, 2H), 7.23–7.04 (m, 8H), 7.00 (d, *J*=7.4 Hz, 2H), 4.08–3.97 (m, 1H), 3.59–3.45 (m, 2H), 3.20–3.12 (m, 1H), 2.56 (t, *J*=12.8 Hz, 1H), 2.47 (t, *J*=11.1 Hz, 1H), 2.39 (d, *J*=12.0 Hz, 1H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 146.9, 144.3, 143.4, 132.3, 129.7, 128.5, 128.5, 128.3, 126.6, 126.3, 126.2, 118.9, 111.3, 63.8, 62.2, 61.8, 50.2, 48.5, 22.2. IR (KBr): 3083, 3053, 3019, 2949, 2907, 2817, 2797, 2227, 1950, 1811, 1606, 1496, 1467, 1444, 1262, 1197, 1132, 1106, 1063, 1032, 911, 816, 757, 700, 631, 581, 548 $cm^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{23}IN_2$: 479.0984; found: 479.0981.

*4.3.8. 5-Iodo-1-(4-nitrobenzyl)-3,3-diphenylpiperidine (**2h**).* White solid, mp 149 °C–150 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.12 (d, *J*=7.5 Hz, 2H), 7.38 (d, *J*=7.6 Hz, 2H), 7.26–7.07 (m, 8H), 7.01 (d, *J*=7.5 Hz, 2H), 4.05 (t, *J*=10.1 Hz, 1H), 3.65–3.52 (m, 3H), 3.18 (d, *J*=10.6 Hz, 2H), 2.57 (t, *J*=13.0 Hz, 1H), 2.50 (t, *J*=11.1 Hz, 1H), 2.42 (d, *J*=12.0 Hz, 1H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 146.3, 145.8, 144.4, 143.2, 128.6, 127.4, 127.2, 127.1, 125.5, 125.2, 125.1, 122.6, 62.7, 61.1, 60.4, 49.1, 47.4, 20.9. IR (KBr): 3067, 3026, 2962, 2943, 2910, 2843, 2802, 2450, 1955, 1727, 1601, 1508, 1445, 1344, 1262, 1183, 1107, 1055, 1033, 861, 805, 759, 699, 630, 568, 536 $cm^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{23}IN_2O_2$: 499.0882; found: 499.0875.

*4.3.9. 2-Benzyl-4-iodo-2-azaspiro[5.5]undecane (**2i**).* Brownish oil. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.36–7.01 (m, 5H), 4.36–4.26 (m, 1H), 3.49 (d, *J*=13.4 Hz, 1H), 3.31 (d, *J*=13.4 Hz, 1H), 3.24–3.17 (m, 1H), 2.71 (d, *J*=11.3 Hz, 1H), 2.30 (dd, *J*=14.5, 7.4 Hz, 2H), 1.63–1.41 (m, 4H), 1.38–1.13 (m, 8H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 137.5, 127.5, 127.2, 126.0, 64.0, 61.1, 48.4, 37.3, 37.1, 31.3, 25.6, 23.7, 20.5. IR (KBr): 3083, 3060, 3026, 2924, 2851, 2792, 2756, 1736, 1668, 1602, 1494, 1452, 1345, 1262, 1144, 1028, 911, 875, 800, 739, 699, 679, 614 $cm^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{24}IN$:370.1032; found: 370.1023.

*4.3.10. 1-Benzyl-5-iodo-3,3-dimethylpiperidine (**2j**).* Brownish oil. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.26–7.09 (m, 5H), 4.36–4.19 (m, 1H), 3.46 (d, *J*=13.4 Hz, 1H), 3.32 (d, *J*=13.4 Hz, 1H), 3.23–3.15 (m, 1H), 2.39 (d, *J*=11.1 Hz, 1H), 2.23 (t, *J*=11.1 Hz, 1H), 2.09–1.99 (m, 1H), 1.72 (d, *J*=11.1 Hz, 1H), 1.64 (t, *J*=12.7 Hz, 1H), 0.98 (s, 3H), 0.76 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 137.4, 127.5, 127.2, 126.0, 63.4, 63.3, 61.0, 50.3, 34.3, 28.1, 23.5. IR (KBr): 3647, 3084, 3061, 3027, 2952, 2796, 2755, 2714, 1601, 1455, 1363, 1306, 1255, 1115, 1074, 1037, 909, 878, 785, 740, 698, 613, 546, 462 $cm^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{20}IN$:330.0719; found: 330.0717.

*4.3.11. 1-Benzyl-3-iodopiperidine (**2k**).* Brownish oil. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.45–7.05 (m, 5H), 4.35–4.04 (m, 1H), 3.45 (q, *J*=13.3 Hz, 2H), 3.05–2.88 (m, 1H), 2.70 (d, *J*=8.7 Hz, 1H), 2.43 (t, *J*=10.5 Hz, 1H), 2.17 (t, *J*=24.6 Hz, 2H), 1.86–1.71 (m, 1H), 1.65–1.53 (m, 2H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 137.9, 129.0, 128.3, 127.2, 63.5, 62.5, 52.9, 37.5, 27.1, 22.4. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{16}IN$:302.0406; found: 302.0399.

*4.3.12. 2-(Iodomethyl)-4,4-diphenyl-1-tosylpyrrolidine (**3l**).* White solid, mp 177 °C–178 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.52 (d, *J*=8.1 Hz, 2H), 7.27–6.96 (m, 12H), 4.37 (d, *J*=10.3 Hz, 1H), 3.84–3.74 (m, 1H), 3.67 (d, *J*=10.3 Hz, 1H), 3.60 (dd, *J*=9.5, 3.0 Hz, 1H), 2.81–2.67 (m, 2H), 2.58 (dd, *J*=13.1, 5.2 Hz, 1H), 2.32 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 144.6, 144.4, 143.7, 133.9, 129.8, 128.7, 128.7, 127.4, 126.8, 126.6, 126.5, 126.3, 60.4, 59.2, 52.2, 43.8, 21.6, 11.4. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{22}INO_2S$:518.0651; found: 518.0640. The NMR data were in agreement with reported results.[18]

*4.3.13. 3-(Iodomethyl)-2-tosyl-2-azaspiro[4.5]decane (**3m**).* White solid, mp 50 °C–51 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.66 (d, *J*=8.3 Hz, 2H), 7.25 (d, *J*=8.0 Hz, 2H), 3.70–3.65 (m, 1H), 3.57–3.48 (m, 1H), 3.34–3.27 (m, 2H), 3.09 (d, *J*=11.0 Hz, 1H), 2.35 (s, 3H), 1.98–1.84 (m, 1H), 1.48–1.41 (m, 1H), 1.41–1.22 (m, 4H), 1.22–1.06 (m, 3H), 1.06–0.98 (m, 1H), 0.76–0.60 (m, 1H), 0.55–0.46 (m, 1H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 143.7, 134.7, 129.7, 127.5, 59.3, 41.4, 36.1, 33.9, 25.8, 23.7, 22.7, 21.6, 13.7. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{24}INO_2S$:434.0651; found: 434.0642. The NMR data were in agreement with reported results.[18]

*4.3.14. 2-(Iodomethyl)-4,4-dimethyl-1-tosylpyrrolidine (**3n**).* White solid, mp 86 °C–87 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.67 (d, *J*=8.2 Hz, 2H), 7.26 (d, *J*=8.0 Hz, 2H), 3.70 (dd, *J*=9.5, 2.8 Hz, 1H), 3.66–3.56 (m, 1H), 3.30 (t, *J*=9.2 Hz, 1H), 3.20–3.07 (m, 2H), 2.36 (s, 3H), 1.85 (dd, *J*=12.8, 7.1 Hz, 1H), 1.52 (dd, *J*=12.8, 8.5 Hz, 1H), 0.97 (s, 3H), 0.42 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 143.7, 134.9, 129.8, 127.5, 62.0, 60.1, 47.8, 37.5, 26.0, 25.9, 21.6, 13.3. The NMR data were in agreement with reported results.[28]

*4.3.15. 2-(Iodomethyl)-1-tosylpyrrolidine (**3o**).* White solid, mp 89 °C–90 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.66 (d, *J*=8.2 Hz, 2H), 7.27 (d, *J*=8.1 Hz, 2H), 3.72–3.60 (m, 1H), 3.55 (dd, *J*=9.7, 3.0 Hz, 1H), 3.47–3.37 (m, 1H), 3.20–3.03 (m, 2H), 2.37 (s, 3H), 1.88–1.68 (m, 3H), 1.52–1.40 (m, 1H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 143.8, 134.1, 129.9, 127.5, 60.7, 50.1, 32.0, 23.9, 21.6, 11.6. The NMR data were in agreement with reported results.[16i]

*4.3.16. 2-(Iodomethyl)-1-tosylindoline (**3p**).* White solid, mp 148 °C–149 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.57 (d, *J*=8.1 Hz, 1H), 7.48 (d, *J*=8.2 Hz, 2H), 7.21–7.05 (m, 3H), 7.01–6.91 (m, 2H), 4.33–4.20 (m, 1H), 3.58 (dd, *J*=9.7, 3.4 Hz, 1H), 3.17 (t, *J*=9.9 Hz, 1H), 2.97–2.80 (m, 1H), 2.76 (dd, *J*=16.7, 3.0 Hz, 1H), 2.26 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 144.3, 141.2, 134.4, 130.4, 129.8, 128.0, 127.1, 125.3, 125.0, 116.8, 62.5, 34.8, 21.6, 11.6. The NMR data were in agreement with reported results.[16i]

*4.3.17. 1-Benzyl-2-(iodomethyl)-5,5-diphenylpiperidine (**5a**).* White solid, mp 125 °C–127 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.42–6.86 (m, 14H), 3.93 (d, *J*=12.8 Hz, 1H), 3.38 (dd, *J*=10.5, 6.6 Hz, 1H), 3.31–3.20 (m, 2H), 3.04 (d, *J*=12.8 Hz, 1H), 2.42 (d, *J*=12.4 Hz, 1H), 2.33 (dd, *J*=8.4, 4.7 Hz, 1H), 2.24–2.14 (m, 1H), 2.10 (s, 1H), 1.66–1.50 (m, 2H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 148.0, 146.4, 138.2, 129.8, 128.6, 128.3, 128.1, 127.8, 127.4, 127.1, 125.9, 125.6, 60.0, 59.6, 58.9, 46.4, 33.3, 28.1, 11.7. IR (KBr): 3084, 3057, 3028, 2949, 2856, 2790, 2742, 1596, 1492, 1445, 1360, 1328, 1262, 1198, 1164, 1095, 1061, 1028, 960, 803, 750, 699, 586, 558 $cm^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{26}IN$: 468.1188; found: 468.1182.

*4.3.18. 2-(Iodomethyl)-1-(4-methoxybenzyl)-5,5-diphenylpiperidine (**5b**).* White solid, mp 75 °C–78 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.26

(t, *J*=10.7 Hz, 2H), 7.17–7.06 (m, 6H), 7.06–6.95 (m, 4H), 6.82 (d, *J*=8.6 Hz, 2H), 3.89 (t, *J*=10.9 Hz, 1H), 3.74 (s, 3H), 3.40 (dd, *J*=10.5, 6.5 Hz, 1H), 3.34–3.19 (m, 2H), 2.98 (d, *J*=12.7 Hz, 1H), 2.39 (d, *J*=12.4 Hz, 1H), 2.33 (dd, *J*=8.5, 4.6 Hz, 1H), 2.24–2.14 (m, 1H), 2.07 (s, 1H), 1.61–1.48 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 157.8, 146.9, 145.3, 129.8, 129.0, 127.5, 127.0, 126.6, 126.0, 124.8, 124.4, 112.5, 58.5, 58.3, 56.9, 54.2, 45.3, 32.2, 27.0, 10.8. IR (KBr): 3644, 3056, 3018, 2960, 2934, 2906, 2835, 2800, 1663, 1611, 1513, 1445, 1302, 1256, 1177, 1035, 805, 753, 700, 638, 579, 522 cm$^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{28}INO$: 498.1294; found:498.1274.

*4.3.19. 2-(Iodomethyl)-1-(3-methoxybenzyl)-5,5-diphenylpiperidine (**5c**).* White solid, mp 138 °C–139 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.34–6.65 (m, 15H), 3.88 (d, *J*=12.9 Hz, 1H), 3.71 (s, 3H), 3.35 (dd, *J*=10.4, 6.5 Hz, 1H), 3.25 (t, *J*=12.7 Hz, 2H), 2.97 (d, *J*=12.9 Hz, 1H), 2.39 (d, *J*=12.4 Hz, 1H), 2.29 (t, *J*=14.6 Hz, 1H), 2.23–2.11 (m, 1H), 2.04 (s, 1H), 1.64–1.43 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 159.8, 148.1, 146.4, 140.1, 129.3, 128.7, 128.2, 127.8, 127.2, 126.0, 125.7, 122.0, 114.7, 113.5, 60.3, 59.6, 59.0, 55.4, 46.5, 33.5, 28.2, 12.2. IR (KBr): 3563, 3327, 3247, 3161, 3061, 3027, 2944, 2838, 2482, 2378, 2277, 2055, 1950, 1887, 1812, 1757, 1638, 1506, 1493, 1460, 1290, 1245, 1183, 1117, 1036, 912, 840, 761, 712 cm$^{-1}$HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{28}INO$: 498.1294; found:498.1294.

*4.3.20. 2-(Iodomethyl)-1-(2-methoxybenzyl)-5,5-diphenylpiperidine (**5d**).* White solid, mp 128 °C–129 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.47–6.74 (m, 15H), 3.74 (d, *J*=14.0 Hz, 4H), 3.51 (d, *J*=13.5 Hz, 1H), 3.42 (t, *J*=12.9 Hz, 1H), 3.31 (t, *J*=9.1 Hz, 1H), 3.23 (d, *J*=12.4 Hz, 1H), 2.63 (d, *J*=12.4 Hz, 1H), 2.43–2.25 (m, 2H), 2.14 (dd, *J*=16.1, 6.2 Hz, 1H), 1.73–1.47 (m, 2H) $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 158.0, 147.9, 146.9, 131.5, 128.4, 128.3, 127.9, 127.8, 127.4, 126.4, 125.7, 125.6, 120.3, 110.5, 59.7, 59.5, 55.4, 52.4, 46.4, 32.7, 27.5, 10.6. IR (KBr): 3559, 3320, 3246, 3150, 3052, 2914, 2829, 2741, 2382, 2281, 1954, 1887, 1827, 1751, 1637, 1603, 1490, 1450, 1376, 1279, 1153, 1124, 1045, 1002, 962, 913, 877, 754, 703 cm$^{-1}$HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{28}INO$: 498.1294; found:498.1292.

*4.3.21. 2-(Iodomethyl)-1-(4-isopropylbenzyl)-5,5-diphenylpiperidine (**5e**).* White solid, mp 73 °C–77 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.27 (d, *J*=7.8 Hz, 2H), 7.20–7.08 (m, 9H), 7.07–6.98 (m, 4H), 3.90 (d, *J*=12.9 Hz, 1H), 3.44–3.37 (m, 1H), 3.35–3.23 (m, 2H), 3.10 (d, *J*=12.9 Hz, 1H), 2.91–2.81 (m, 1H), 2.48 (d, *J*=12.4 Hz, 1H), 2.34 (d, *J*=13.3 Hz, 1H), 2.25–2.11 (m, 2H), 1.67–1.52 (m, 2H), 1.21 (d, *J*=6.9 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 147.9, 147.9, 146.5, 135.4, 129.6, 128.5, 128.0, 127.7, 127.2, 126.2, 125.8, 125.6, 59.7, 59.4, 58.5, 46.4, 33.8, 33.2, 27.9, 24.1, 24.1, 11.4. IR (KBr): 3053, 3027, 2960, 2926, 2872, 1660, 1598, 1495, 1448, 1362, 1276, 1057, 920, 812, 759, 701, 638, 588 cm$^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{28}H_{32}IN$:510.1658; found: 510.1652.

*4.3.22. 2-(Iodomethyl)-1-(4-methylbenzyl)-5,5-diphenylpiperidine (**5f**).* White solid, mp 99 °C–102 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.26 (t, *J*=13.3 Hz, 2H), 7.20–7.07 (m, 8H), 7.07–6.98 (m, 4H), 3.91 (d, *J*=12.8 Hz, 1H), 3.45–3.06 (m, 1H), 3.35–3.22 (m, 2H), 3.04 (d, *J*=12.8 Hz, 1H), 2.41 (t, *J*=10.5 Hz, 1H), 2.37–2.26 (m, 4H), 2.26–2.16 (m, 1H), 2.12 (d, *J*=5.0 Hz, 1H), 1.66–1.52 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 148.0, 146.4, 136.9, 135.0, 129.6, 128.9, 128.6, 128.0, 127.7, 127.1, 125.8, 125.5, 59.8, 59.4, 58.5, 46.4, 33.2, 28.0, 21.2, 11.6. IR (KBr): 3084, 3051, 3027, 2955, 2944, 2922, 2780, 2729, 2702, 1805, 1661, 1597, 1494, 1444, 1359, 1325, 1271, 1201, 1164, 1092, 1034, 955, 910, 886, 842, 793, 754, 700, 583, 543 cm$^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{28}IN$:482.1345; found: 482.1339.

*4.3.23. 1-(4-Fluorobenzyl)-2-(iodomethyl)-5,5-diphenylpiperidine (**5g**).* White solid, mp 110 °C–112 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.34–7.27 (m, 2H), 7.17–6.86 (m, 12H), 3.87 (d, *J*=12.8 Hz, 1H), 3.40–3.32 (m, 1H), 3.23 (t, *J*=10.5 Hz, 2H), 2.96 (d, *J*=12.8 Hz, 1H), 2.42–2.27 (m, 2H), 2.26–2.12 (m, 1H), 2.04 (s, 1H), 1.75–1.44 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 163.5, 161.1, 148.0, 146.3, 133.9, 133.9, 131.4, 131.3, 128.6, 128.2, 127.8, 127.1, 126.0, 125.7, 59.9, 59.6, 58.0, 46.4, 33.3, 28.2, 11.9. $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ −115.5. IR (KBr): 3058, 3027, 2959, 2935, 2792, 2753, 2730, 1602, 1507, 1494, 1444, 1363, 1321, 1262, 1221, 1086, 1028, 960, 820, 802, 761, 700, 565 cm$^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{25}FIN$:486.1094; found: 486.1092.

Crystal data for **5g**: $C_{25}H_{25}FIN$, *M*=485.36, monoclinic, *a*=18.309(4) Å, *b*=10.301(2) Å, *c*=24.854(5) Å, $\alpha$=90.00°, $\beta$=111.12(3)°, $\gamma$=90.00°, *V*=4372.4(15) Å$^3$, *T*=293(2) K, space group *C2/c*, *Z*=8, $\mu$(MoK$\alpha$)=1.483 mm$^{-1}$, 20,834 reflections measured, 5167 independent reflections ($R_{int}$=0.0366). The final $R_1$ values were 0.0447 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1222 ($I>2\sigma(I)$). The final $R_1$ values were 0.0579 (all data). The final $wR(F^2)$ values were 0.1333 (all data). The goodness of fit on $F^2$ was 1.080. CCDC 1451293.

*4.3.24. 1-(4-Chlorobenzyl)-2-(iodomethyl)-5,5-diphenylpiperidine (**5h**).* White solid, mp 108 °C–110 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.37–6.91 (m, 15H), 3.89 (d, *J*=12.9 Hz, 1H), 3.41–3.33 (m, 1H), 3.29–3.15 (m, 2H), 2.98 (d, *J*=12.9 Hz, 1H), 2.45–2.28 (m, 2H), 2.25–2.14 (m, 1H), 2.06 (s, 1H), 1.71–1.50 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 146.8, 145.0, 135.6, 132.0, 130.0, 127.4, 127.3, 127.0, 126.7, 125.9, 124.9, 124.6, 58.9, 58.4, 57.0, 45.3, 32.2, 27.0, 10.6. IR (KBr):3087, 3055, 3031, 2963, 2815, 2733, 2609, 1662, 1595, 1491, 1447, 1359, 1323, 1197, 1096, 1023, 801, 744, 696, 580, 557 cm$^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{25}ClIN$:502.0798; found: 502.0792.

*4.3.25. 1-(4-Bromobenzyl)-2-(iodomethyl)-5,5-diphenylpiperidine (**5i**).* Brownish oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.77–6.84 (m, 14H), 3.86 (d, *J*=13.0 Hz, 1H), 3.42–3.33 (m, 1H), 3.27–3.19 (m, 2H), 2.95 (d, *J*=13.0 Hz, 1H), 2.44–2.28 (m, 2H), 2.25–2.12 (m, 1H), 2.04 (d, *J*=7.5 Hz, 1H), 1.68–1.48 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 147.8, 146.1, 137.3, 132.5, 131.4, 130.1, 128.5, 128.1, 127.8, 127.0, 125.7, 121.2, 60.1, 59.6, 58.1, 46.4, 38.3, 28.1, 11.6. IR (KBr): 3055, 3028, 2961, 2926, 2882, 1658, 1595, 1491, 1448, 1360, 1316, 1277, 1071, 1012, 919, 800, 758, 701, 639, 587, 478 cm$^{-1}$; HRMS–ESI (*m/z*): [M+H]+ calcd for $C_{25}H_{25}BrIN$:546.0293; found: 546.0275.

*4.3.26. Methyl 4-((2-(iodomethyl)-5,5-diphenylpiperidin-1-yl) methyl)benzoate (**5j**).* Mp 153 °C–155 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.95 (d, *J*=7.9 Hz, 2H), 7.43 (d, *J*=7.9 Hz, 2H), 7.19–6.88 (m, 10H), 3.96 (d, *J*=13.1 Hz, 1H), 3.83 (s, 3H), 3.39–3.32 (m, 1H), 3.29–3.17 (m, 2H), 3.06 (d, *J*=13.1 Hz, 1H), 2.41 (d, *J*=12.3 Hz, 1H), 2.34 (d, *J*=12.9 Hz, 1H), 2.25–2.13 (m, 1H), 2.08 (s, 1H), 1.69–1.49 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 167.1, 147.8, 146.1, 143.8, 129.7, 129.6, 129.3, 128.5, 128.2, 127.8, 127.0, 126.0, 125.7, 60.3, 59.8, 58.6, 52.2, 46.4, 33.3, 28.1, 11.6. IR (KBr): 3084, 3062, 3022, 2946, 2884, 2861, 2810, 2783, 2737, 2702, 1953, 1716, 1607, 1494, 1438, 1310, 1198, 1171, 1106, 1017, 958, 874, 796, 768, 699, 564, 496 cm$^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{27}H_{28}INO_2$:526.1243; found:526.1236.

*4.3.27. 4-((2-(Iodomethyl)-5,5-diphenylpiperidin-1-yl)methyl)benzonitrile (**5k**).* White solid, mp 104 °C–107 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.54 (d, *J*=8.2 Hz, 2H), 7.45 (d, *J*=8.1 Hz, 2H), 7.17–6.90 (m, 10H), 3.94 (d, *J*=13.4 Hz, 1H), 3.39–3.32 (m, 1H), 3.26–3.17 (m, 2H), 3.05 (d, *J*=13.4 Hz, 1H), 2.45 (d, *J*=12.2 Hz, 1H), 2.36 (d, *J*=13.3 Hz, 1H), 2.29–2.13 (m, 1H), 2.07 (s, 1H), 1.72–1.45 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 147.7, 145.9, 144.2, 132.1, 130.3, 128.4, 128.2, 127.9, 126.9, 126.1, 125.8, 119.0, 111.2, 60.5, 59.6, 58.5, 46.4, 33.3, 28.2, 11.6. IR (KBr): 3085, 3053, 3020, 2946, 2903, 2873, 2851, 2806, 2228, 1607, 1496, 1446, 1368, 1340, 1296, 1268, 1177, 1129, 1093,

1021, 811, 754, 637, 580 $cm^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{25}IN_2$:493.1141; found: 493.1129.

*4.3.28. 2-(Iodomethyl)-1-(4-nitrobenzyl)-5,5-diphenylpiperidine (**5l**).* Mp 135 °C–136 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.14 (d, *J*=8.6 Hz, 2H), 7.54 (d, *J*=8.5 Hz, 2H), 7.27–6.88 (m, 10H), 4.02 (t, *J*=11.8 Hz, 1H), 3.43–3.36 (m, 1H), 3.33–3.19 (m, 2H), 3.13 (d, *J*=13.5 Hz, 1H), 2.50 (t, *J*=14.3 Hz, 1H), 2.39 (d, *J*=13.3 Hz, 1H), 2.26–2.17 (m, 1H), 2.10 (s, 1H), 1.81–1.54 (m, 2H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 146.6, 146.3, 145.2, 144.7, 129.2, 127.2, 127.1, 126.8, 125.8, 125.0, 124.7, 122.4, 59.6, 58.6, 57.1, 45.3, 32.2, 27.1, 10.3. IR (KBr):3081, 3054, 3022, 2961, 2905, 2852, 2805, 1805, 1602, 1517, 1446, 1351, 1263, 1178, 1129, 1106, 1032, 1020, 857, 809, 753, 700, 634, 581 $cm^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{25}INO_2$:513.1039; found: 513.1031.

*4.3.29. 2-(Iodomethyl)-1-isopropyl-5,5-diphenylpiperidine (**5m**).* White solid, mp 82 °C–83 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.43–7.00 (m, 10H), 3.43–3.37 (m, 1H), 3.33–3.27 (m, 1H), 3.20–3.08 (m, 2H), 2.49 (d, *J*=12.2 Hz, 1H), 2.34–2.24 (m, 1H), 2.24–2.13 (m, 1H), 2.13–2.05 (m, 1H), 1.60–1.38 (m, 2H), 1.25 (d, *J*=6.7 Hz, 3H), 0.83 (d, *J*=6.6 Hz, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 147.9, 145.9, 128.1, 127.0, 126.6, 126.1, 124.9, 124.4, 54.9, 51.6, 47.0, 45.0, 33.0, 27.6, 19.9, 12.6, 11.9. IR (KBr): 3083, 3060, 3023, 2965, 2859, 2010, 1737, 1653, 1598, 1493, 1446, 1360, 1316, 1264, 1194, 1168, 1093, 1017, 802, 758, 702, 630, 559 $cm^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{26}IN$: 420.1188; found: 420.1180.

*4.3.30. 2-Benzyl-3-(iodomethyl)-2-azaspiro[5.5]undecane (**5n**).* Brownish oil. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.33 (d, *J*=7.4 Hz, 2H), 7.23 (t, *J*=7.4 Hz, 2H), 7.16 (t, *J*=5.2 Hz, 1H), 3.96 (d, *J*=13.1 Hz, 1H), 3.48–3.42 (m, 1H), 3.33 (d, *J*=10.5 Hz, 1H), 2.97 (d, *J*=13.1 Hz, 1H), 2.53 (d, *J*=11.5 Hz, 1H), 1.92–1.78 (m, 2H), 1.73 (d, *J*=11.5 Hz, 1H), 1.64–1.07 (m, 13H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 138.5, 127.7, 127.1, 125.7, 59.0, 56.7, 36.3, 32.6, 32.3, 32.0, 26.8, 25.8, 20.6, 12.5. IR (KBr): 3640, 3059, 3026, 2922, 2852, 2786, 2734, 2610, 1734, 1668, 1602, 1494, 1450, 1359, 1322, 1261, 1196, 1180, 1106, 1072, 1027, 979, 801, 739, 699, 651, 480 $cm^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{26}IN$:384.1188; found: 384.1181.

*4.3.31. 1-Benzyl-2-(iodomethyl)-5,5-dimethylpiperidine (**5o**).* Brownish oil. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.37–7.03 (m, 5H), 3.89 (d, *J*=13.2 Hz, 1H), 3.48–3.41 (m, 1H), 3.27 (d, *J*=10.5 Hz, 1H), 2.94 (d, *J*=13.2 Hz, 1H), 2.31–2.20 (m, 1H), 1.90–1.74 (m, 2H), 1.71 (d, *J*=11.3 Hz, 1H), 1.50–1.43 (m, 1H), 1.38–1.28 (m, 1H), 1.26–1.13 (m, 1H), 0.88 (s, 3H), 0.72 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 138.3, 127.6, 127.1, 125.7, 61.3, 58.4, 56.7, 34.9, 29.7, 27.5, 27.4, 24.2, 12.2. IR (KBr): 3301, 3028, 2957, 2870, 2745, 1664, 1605, 1495, 1454, 1402, 1367, 1313, 1263, 1237, 1082, 1031, 915, 804, 751, 701, 651, 600, 534 $cm^{-1}$; HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{22}IN$:344.0875; found: 344.0873.

*4.3.32. 2-(Iodomethyl)-5,5-diphenyl-1-tosylpiperidine (**5p**).* White solid, mp 61 °C–62 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.57 (d, *J*=8.3 Hz, 2H), 7.35 (d, *J*=7.6 Hz, 2H), 7.30–7.21 (m, 6H), 7.21–7.12 (m, 4H), 4.58 (dd, *J*=13.3, 1.9 Hz, 1H), 4.13–4.03 (m, 1H), 3.37 (dd, *J*=11.8, 10.0 Hz, 1H), 3.21–3.10 (m, 1H), 2.51–2.36 (m, 4H), 2.29–2.13 (m, 2H), 1.76–1.62 (m, 1H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 146.9, 143.8, 143.3, 136.6, 129.9, 128.6, 128.5, 127.8, 127.5, 126.7, 126.4, 126.2, 53.8, 48.1, 45.7, 28.3, 23.0, 21.6, 2.4. IR (KBr):3057, 3028, 2960, 2869, 1725, 1597, 1495, 1446, 1339, 1261, 1185, 1156, 1090, 1030, 947, 878, 803, 754, 701, 669, 580, 546 $cm^{-1}$. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{26}INO_2S$:532.0807; found: 532.0803.

*4.3.33. 3-(Iodomethyl)-2-tosyl-2-azaspiro[5.5]undecane (**5q**).* $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.63 (d, *J*=8.3 Hz, 2H), 7.23 (d, *J*=8.1 Hz, 2H), 4.23–4.11 (m, 1H), 3.52 (d, *J*=13.1 Hz, 1H), 3.32–3.19 (m, 1H), 2.94–2.87 (m, 1H), 2.47 (d, *J*=13.2 Hz, 1H), 2.36 (s, 3H), 1.95–1.87 (m, 1H), 1.79–1.63 (m, 1H), 1.42–1.06 (m, 12H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 142.2, 136.7, 128.7, 125.9, 52.9, 37.0, 31.4, 29.6, 25.4, 20.7, 20.5, 20.4, 20.2, 2.2. IR (KBr): 3029, 2926, 2854, 2668, 1916, 1728, 1598, 1494, 1452, 1341, 1263, 1887, 1160, 1092, 1032, 967, 939, 813, 668, 602, 547 $cm^{-1}$. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{26}INO_2S$:448.0807; found: 448.0806.

*4.3.34. 2-(Iodomethyl)-5,5-dimethyl-1-tosylpiperidine (**5r**).* White solid, mp 90 °C–91 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.63 (d, *J*=8.3 Hz, 2H), 7.23 (d, *J*=8.0 Hz, 2H), 4.23–4.15 (m, 1H), 3.27–3.13 (m, 2H), 2.94–2.86 (m, 1H), 2.58 (d, *J*=13.0 Hz, 1H), 2.36 (s, 3H), 2.02–1.92 (m, 1H), 1.80–1.68 (m, 1H), 1.26–1.16 (m, 2H), 0.83 (s, 3H), 0.76 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 142.3, 136.7, 128.7, 125.9, 52.4, 49.9, 30.1, 29.2, 27.8, 22.0, 21.6, 20.5, 1.9. IR (KBr): 3062, 2963, 2868, 1728, 1596, 1469, 1368, 1335, 1307, 1262, 1156, 1106, 1089, 1054, 974, 908, 803, 664, 600, 546 $cm^{-1}$. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{22}INO_2S$:408.0494; found: 408.0492.

*4.3.35. 2-(Iodomethyl)-1-tosylpiperidine (**5s**).* Yellowish oil. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.65 (d, *J*=8.2 Hz, 2H), 7.23 (d, *J*=8.1 Hz, 2H), 4.20 (dd, *J*=10.5, 5.2 Hz, 1H), 3.68–3.60 (m, 1H), 3.32–3.25 (m, 1H), 3.15 (dd, *J*=9.9, 5.1 Hz, 1H), 2.92–2.82 (m, 1H), 2.36 (s, 3H), 2.05–1.97 (m, 1H), 1.50–1.29 (m, 4H), 1.28–1.11 (m, 1H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 143.3, 137.9, 129.8, 127.0, 53.9, 40.6, 26.2, 24.3, 21.6, 17.7, 4.1. IR (KBr):3030, 2941, 2863, 1919, 1726, 1597, 1494, 1447, 1337, 1160, 1091, 1047, 989, 929, 882, 815, 726, 664, 588, 548 $cm^{-1}$. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{18}INO_2S$: 380.0181; found: 380.0169.

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## Supplementary data

Supplementary data (Copies of NMR spectra of the products and X-ray diffraction data of compounds **2c** and **5g**.) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.09.038.

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