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ORIGINAL PAPER

Gold-catalyzed oxidative aminoesterification of unactivated alkenes

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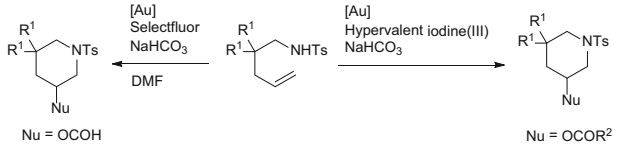
Abstract This paper describes an efficient aminoesterification of unactivated alkenes through Au(I)/Au(III) redox catalytic cycles using Selectfluor or hypervalent iodine(III) reagents.

Graphical abstract



Keywords Selectfluor · Hypervalent iodine(III) reagents · Heterocycles · Homogeneous catalysis · Redox reactions

Introduction

New methodologies to access highly important motifs in organic chemistry such as diols, diamines, and aminoalcohols have been developed during the past decades [1–14]. Palladium catalysts have been employed together with $PhI(OAc)_2$ in the aminooxygenation and diamination of unactivated alkenes in both an intra- [15–20] as well as in an intermolecular fashion [21–26]. In these transformations, the oxidation of Pd(II) to Pd(IV) species is crucial for the formation of the new carbon–heteroatom bonds [27–33]. Copper catalysts have also been used in similar transformations [34–43]. In addition, metal-free methodologies have also been developed [44–47]. A combination of carbophilic gold complexes and Au(I)/Au(III) redox catalytic cycles was employed in the past years by several groups to design new transformations along these lines [48–55]. In this context, our group reported a gold-catalyzed difunctionalization of alkenes to yield aminoalcohols, aminoesters, aminoethers, and diamines in a highly flexible manner (Scheme 1) [56–58].

To further expand the scope of these transformations, we envisaged the combination of Selectfluor as oxidant and DMF as solvent to attain the synthesis of aminoformate derivatives. Furthermore, we considered that the use of different hypervalent iodine(III) reagents could enable the introduction of other nucleophiles, thus expanding the scope of this reaction towards the synthesis of new aminoesters (Scheme 2).

Results and discussion

We started to investigate the formation of aminoformates using *N*-tosyl-2,2-diphenyl-4-pentenylamine (**1a**) as substrate. When ten equivalents of DMF were used in a reaction performed in nitromethane, 5,5-diphenyl-1-tosylpiperidin-3-yl formate **2a** could be obtained in 45% yield (Table 1, entry 1). Reducing the equivalents of DMF from 10 to 5, delivered the same amount of aminoaldehyde **2a** together with 13% of 5,5-diphenyl-1-tosylpiperidin-3-ol **2′a** (Table 1, entry 2). We envisaged that a faster hydrolysis of the iminium intermediate might prevent formation of byproduct **2′a**. Remarkably, the addition of 2 equivalents of water to hydrolyze the iminium ion in situ afforded 79% of aminoaldehyde **2a** and 13% of aminoalcohol **2′a** (Table 1, entry 3). These conditions (Table 1, entry 3) were

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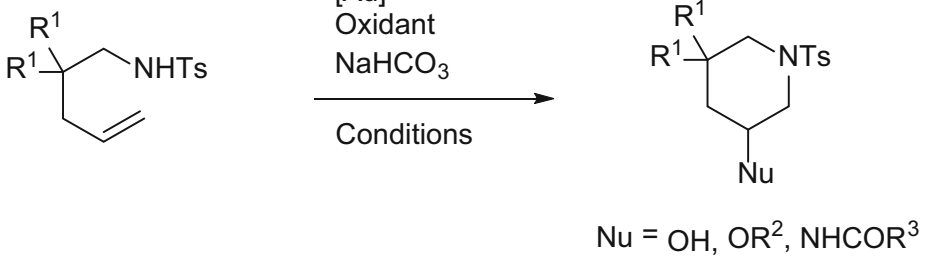
Scheme 1



Scheme 2

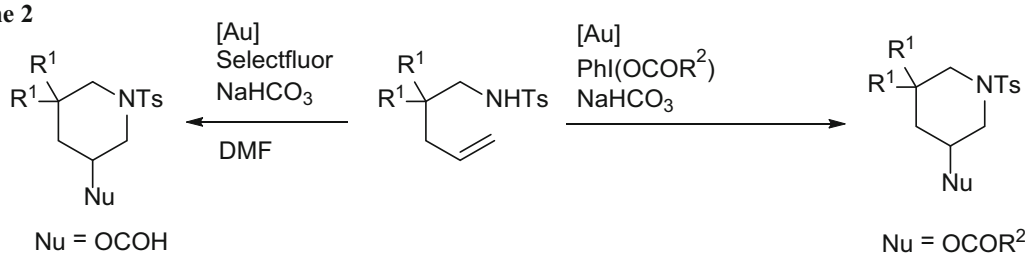
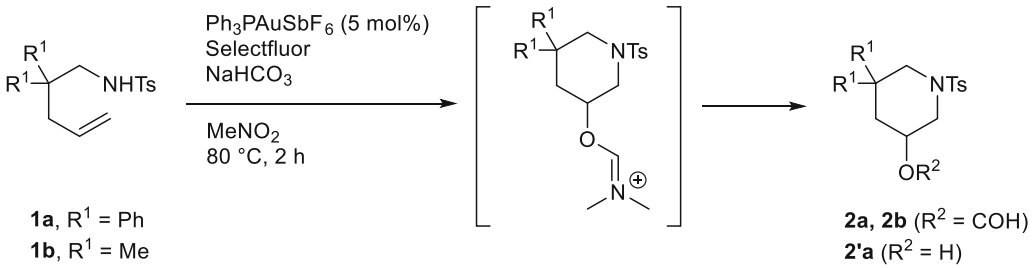


Table 1 Optimization of the gold-catalyzed synthesis of aminoaldehydes **2a**, **2b**



Entry	Substrate	Reaction conditions[a]	Product, yield/%[b]	Product, yield/%[b]
1	**1a**	[Au], Selectfluor, $NaHCO_3$, DMF (10 equiv.)	**2a**, 45	–
2	**1a**	[Au], Selectfluor, $NaHCO_3$, DMF (5 equiv.)	**2a**, 45	**2′a**, 13
3	**1a**	[Au], Selectfluor, $NaHCO_3$, DMF (10 equiv.), H_2O (2 equiv.)	**2a**, 79	**2′a**, 13
4	**1b**	[Au], Selectfluor, $NaHCO_3$ (1 equiv.), DMF (5 equiv.), H_2O (2 equiv.), $MeNO_2$, 80 °C, 2 h	**2b**, 67	–

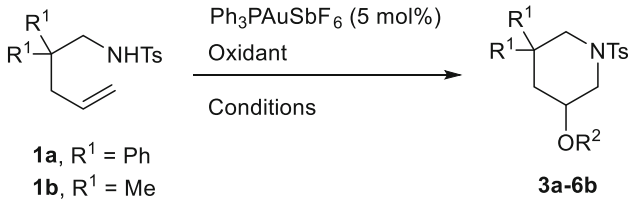
[a]Reaction conditions: [Au] = $Ph_3PAuSbF_6$ (5 mol%), Selectfluor (2 equiv.), $NaHCO_3$ (1 equiv.), $MeNO_2$ (0.1 M), 80 °C

[b]Isolated yield after column chromatography

applied also to *N*-(2,2-dimethylpent-4-en-1-yl)-4-methylbenzenesulfonamide (**1b**) furnishing 5,5-dimethyl-1-tosylpiperidin-3-yl formate **2b** in 67% yield (Table 1, entry 4).

The use of different hypervalent iodine(III) reagents to introduce additional nucleophiles was studied next. The previously optimized conditions had to be adapted. It was found that, changing the solvent from nitromethane to 1,2-dichloroethane, was beneficial for the reaction outcome. Specifically, when $PhI(OPiv)_2$ was employed as oxidant, both **1a** and **1b** could be efficiently converted into the desired products **3a** and **3b** in 86 and 80% yields, respectively (Table 2, entries 1 and 2). Other hypervalent iodine reagents such as $PhI(OCOCF_3)_2$ could also be successfully used to introduce the trifluoroacetoxy moiety delivering both products **4a** and **4b** in 80% yield (Table 2, entries 3 and 4). Encouraged by these results, $PhI(OCO(4\text{-}NO_2C_6H_4))_2$ was tested providing product formation in rather

Table 2 Gold-catalyzed intramolecular difunctionalization of **1a** and **1b**



1a, R^1 = Ph
1b, R^1 = Me

3a-6b

Entry	Substrate	Oxidant[a]	Product	Yield/%[c]
1	**1a**	$PhI(OPiv)_2$	**3a**, $R^2 = COt$-Bu	86
2	**1b**	$PhI(OPiv)_2$	**3b**, $R^2 = COt$-Bu	80
3	**1a**	$PhI(OCOCF_3)_2$	**4a**, $R^2 = COCF_3$	80
4	**1b**	$PhI(OCOCF_3)_2$	**4b**, $R^2 = COCF_3$	80
5	**1a**	$PhI(OCO(4\text{-}NO_2\text{-}C_6H_4))_2$	**5a**, $R^2 = CO(4\text{-}NO_2C_6H_4)$	42
6	**1b**	$PhI(OCO(4\text{-}NO_2\text{-}C_6H_4))_2$	**5b**, $R^2 = CO(4\text{-}NO_2C_6H_4)$	44
7	**1a**	$PhI(CO_2(3,5\text{-}MeO\text{-}C_6H_3))_2$[b]	**6a**, $R^2 = CO(3,5\text{-}MeOC_6H_3)$	21
8	**1b**	$PhI(CO_2(3,5\text{-}MeO\text{-}C_6H_3))_2$[b]	**6b**, $R^2 = CO(3,5\text{-}MeOC_6H_3)$	72

[a]Oxidant (2 equiv.), $NaHCO_3$ (1 equiv.), DCE, 80 °C, 2 h

[b]17 h

[c]Isolated yield after column chromatography

moderate yields (**5a** and **5b**, Table 2, entries 5 and 6). When $PhI(CO_2(3,5\text{-}MeOC_6H_3))_2$ was used, the desired products **6a** and **6b** could be isolated in 21 and 72% yields, respectively (Table 2, entries 7 and 8).

Conclusion

A new protocol for the efficient aminoesterification of unactivated alkenes is reported here. Taking advantage of Au(I)/Au(III) redox catalytic cycles in the presence of either Selectfluor or hypervalent iodine(III) reagents, aminoformate and aminoester derivatives have been respectively formed from 5-N-tosyl-4-pentenylamine substrates. The reactions are operationally simple and offer a flexible entry to previously unreported piperidine derivatives.

Experimental

Unless otherwise stated, starting materials were purchased from Aldrich and/or Fluka. All reagents were used as received. Substrates **1a** and **1b** were prepared according to previously reported procedures [34, 59]. IR and ^1H NMR spectra of the products **2b** [57] and **4b** [47] were found to be identical with the ones described. $PhI(OPiv)_2$, $PhI(OCO(4\text{-}NO_2\text{-}C_6H_4))_2$, and $PhI(OCO(3,5\text{-}MeO\text{-}C_6H_3))_2$ were synthesized in analogy to a previously reported procedure [60]. $Ph_3PAuSbF_6$ was prepared from Ph_3PAuCl (1 equiv.) and $AgSbF_6$ (1 equiv.) in DCE (0.05 M). Except acetonitrile, solvents were purchased in HPLC quality, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). Unless otherwise stated, reactions were not run under inert atmosphere. Conversion was monitored by thin-layer chromatography (TLC) using Merck TLC silica gel 60 F 254. Flash column chromatography was performed over silica gel (230–400 mesh). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). High-resolution electrospray ionization mass spectra were measured on a Bruker ESQUIRE-LC quadrupole ion trap instrument (Bruker Daltonik GmbH, Bremen, Germany) with accurate mass acquisition below 2 ppm.

General protocol A

A mixture of aminopent-4-ene (**1**, 1 equiv.), Selectfluor (2 equiv.), $NaHCO_3$ (1 equiv.), and DMF (5 equiv.) was dissolved in $MeNO_2$ (0.1 M) followed by addition of $Ph_3PAuSbF_6$ (0.05 equiv.). The reaction was stirred for 2 h at 80 °C and was monitored by TLC. Upon consumption of the starting material, the mixture was diluted with 5 cm^3

DCM and 2 cm^3 water was added. The mixture was extracted with DCM (3 × 5 cm^3) and the combined organic phases were dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was purified through silica gel flash column chromatography (hexane/EtOAc = 6/1) to yield the desired aminoaldehydes **2**.

5,5-Diphenyl-1-tosylpiperidin-3-yl formate
(**2a**, $C_{25}H_{25}NO_4S$)
Following the general protocol A, compound **2a** was isolated in 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (s, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 7.7 Hz, 2H), 7.38–7.14 (m, 10H), 4.92 (tt, J = 9.8, 4.1 Hz, 1H), 4.46 (d, J = 12.5 Hz, 1H), 3.91–3.86 (m, 1H), 2.93 (dt, J = 12.6, 1.7 Hz, 1H), 2.63 (d, J = 12.5 Hz, 1H), 2.43 (s, 3H), 2.40 (d, J = 7.1 Hz, 1H), 2.18–2.10 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.3, 146.2, 144.7, 143.6, 133.1, 130.5, 129.4, 129.2, 128.4, 128.3, 127.4, 127.3, 127.1, 67.6, 54.6, 49.8, 47.0, 40.4, 22.2 ppm; IR (film): $\bar{\nu}$ = 2925, 2366, 1723, 1598, 1496, 1447, 1345, 1162, 1090, 1011, 908, 779, 730, 699, 661, 578, 562, 550 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{25}H_{25}NNaO_4S$ 458.13965, found 458.13970.

5,5-Dimethyl-1-tosylpiperidin-3-yl formate
(**2b**, $C_{15}H_{21}NO_4S$)
Following the general protocol A, compound **2b** was isolated in 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (s, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.14 (tt, J = 8.8, 4.5 Hz, 1H), 3.65 (dd, J = 11.2, 4.4 Hz, 1H), 3.07 (d, J = 11.5 Hz, 1H), 2.48–2.44 (m, 1H), 2.43 (s, 3H), 2.31 (d, J = 11.5 Hz, 1H), 1.73 (dd, J = 13.2, 4.5 Hz, 1H), 1.22 (dd, J = 13.2, 9.5 Hz, 1H), 1.07 (s, 3H), 1.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.6, 144.4, 134.2, 130.4, 128.2, 67.5, 57.5, 49.7, 42.6, 32.5, 28.7, 26.1, 22.2 ppm; IR (film): $\bar{\nu}$ = 2958, 1721, 1598, 1469, 1343, 1307, 1158, 1092, 993, 966, 916, 815, 660, 583, 551 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{15}H_{21}NNaO_4S$ 334.10835, found 334.10830.

General protocol B

A mixture of aminopent-4-ene (**1**, 1 equiv.), oxidant (2 equiv.), and $NaHCO_3$ (1 equiv.) was dissolved in 1,2-dichloroethane (0.1 M) followed by addition of $Ph_3PAuSbF_6$ (0.05 equiv.). The reaction was stirred for 2 h at 80 °C and was monitored by TLC. Upon consumption of the starting material, the mixture was diluted with 5 cm^3 DCM and filtered over celite. The solvent was evaporated under reduced pressure and the residue was purified through silica gel flash column chromatography (hexane/EtOAc = 10/1) to yield the desired aminoesters **3**–**6**.

5,5-Diphenyl-1-tosylpiperidin-3-yl pivalate
(**3a**, $C_{29}H_{33}NO_4S$)
Following the general protocol B, compound **3a** was isolated in 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 7.5 Hz, 2H), 7.36–7.29 (m, 4H), 7.26–7.15 (m, 6H), 4.80 (tt, J = 9.4, 4.5 Hz, 1H), 4.30 (d, J = 12.2 Hz, 1H), 3.69 (dd, J = 10.5, 4.3 Hz, 1H), 2.90 (dt, J = 12.7, 1.8 Hz, 1H), 2.82 (d, J = 12.2 Hz, 1H), 2.49 (t, J = 9.9 Hz, 1H), 2.42 (s, 3H), 2.05 (dd, J = 12.8, 10.2 Hz, 1H), 1.10 (s, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.1, 146.5, 144.5, 144.0, 133.4, 130.5, 129.4, 129.2, 128.5, 128.3, 127.3, 127.2, 127.2, 54.8, 49.9, 46.9, 40.3, 39.3, 27.8, 27.7, 27.7, 22.2 ppm; IR (film): $\bar{\nu}$ = 2971, 1728, 1598, 1496, 1479, 1447, 1346, 1282, 1161, 1090, 1038, 1020, 991, 910, 804, 783, 732, 699, 663, 570, 549 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{33}NNaO_4S$ 514.20225, found 514.20233.

5,5-Dimethyl-1-tosylpiperidin-3-yl pivalate
(**3b**, $C_{19}H_{29}NO_4S$)
Following the general procedure for the gold-catalyzed difunctionalization of alkenes, compound **2b** was isolated in 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 5.02–4.91 (m, 1H), 3.40 (dd, J = 11.4, 3.9 Hz, 1H), 2.90 (d, J = 11.4 Hz, 1H), 2.62 (dd, J = 11.3, 7.8 Hz, 1H), 2.50 (d, J = 11.4 Hz, 1H), 2.43 (s, 3H), 1.64 (dd, J = 13.3, 4.3 Hz, 1H), 1.23 (dd, J = 13.4, 8.2 Hz, 1H), 1.18 (s, 9H), 1.04 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.7, 143.6, 134.0, 129.8, 127.7, 66.7, 57.0, 49.2, 41.8, 38.8, 31.7, 27.9, 27.2, 26.2, 21.7 ppm; IR (film): $\bar{\nu}$ = 2969, 1736, 1455, 1366, 1348, 1307, 1282, 1228, 1216, 1206, 1161, 1092, 1036, 992, 916, 813, 767, 752, 685, 660, 549 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{29}NNaO_4S$ 390.1715, found 390.17130.

5,5-Diphenyl-1-tosylpiperidin-3-yl 2,2,2-trifluoroacetate
(**4a**, $C_{16}H_{20}F_3NO_4S$)
Following the general protocol B, compound **4a** was isolated in 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.56–7.49 (m, 4H), 7.46–7.30 (m, 6H), 5.14 (tt, J = 9.9, 4.3 Hz, 1H), 4.65 (d, J = 12.5 Hz, 1H), 4.12 (dd, J = 10.5, 4.8 Hz, 1H), 3.16 (dt, J = 12.6, 1.8 Hz, 1H), 2.81 (d, J = 12.5 Hz, 1H), 2.64 (t, J = 10.2 Hz, 1H), 2.61 (s, 3H), 2.40 (dd, J = 12.5, 10.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.0 (q, J = 42.7 Hz), 145.7, 144.9, 143.1, 133.0, 130.7, 129.6, 129.4, 128.5, 128.3, 127.8, 127.5, 127.0, 114.9 (q, J = 285.8 Hz), 72.2, 54.6, 49.3, 47.1, 40.0, 22.2 ppm; IR (film): $\bar{\nu}$ = 2852, 1784, 1598, 1496, 1448, 1347, 1221, 1158, 1091, 1009, 908, 864, 816, 803, 781, 733, 698, 662, 578, 550 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{24}F_3NNaO_4S$ 526.12703, found 526.12763.

5,5-Dimethyl-1-tosylpiperidin-3-yl 4-nitrobenzoate (**5b**, $C_{21}H_{24}N_2O_6S$)

Following the general protocol B, compound **5b** was isolated in 44% yield. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.28$ (d, $J = 12.0$ Hz, 2H), 8.16 (d, $J = 9.0$ Hz, 2H), 7.65 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 5.28 (dt, $J = 7.8$, 4.0 Hz, 1H), 3.57 (dd, $J = 11.4$, 3.7 Hz, 1H), 2.97 (d, $J = 11.5$ Hz, 1H), 2.84 (dd, $J = 11.3$, 7.7 Hz, 1H), 2.60 (d, $J = 11.5$ Hz, 1H), 2.43 (s, 3H), 1.78 (dd, $J = 13.5$, 4.2 Hz, 1H), 1.46 (dd, $J = 13.6$, 8.3 Hz, 1H), 1.10 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 164.4$, 151.5, 144.4, 136.0, 134.5, 131.5, 130.5, 128.2, 124.3, 69.4, 57.5, 49.8, 42.4, 32.4, 28.4, 26.9, 22.2 ppm; IR (film): $\bar{\nu} = 2958$, 1724, 1600, 1526, 1468, 1346, 1309, 1274, 1162, 1117, 1092, 993, 912, 813, 720, 661, 593, 572, 550 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{24}N_2NaO_6S$ 455.12473, found 455.12468.

5,5-Diphenyl-1-tosylpiperidin-3-yl 3,5-dimethoxybenzoate (**6a**, $C_{33}H_{33}N_2O_6S$)

Following the general protocol B, compound **6a** was isolated in 21% yield. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.65$ (d, $J = 8.2$ Hz, 2H), 7.50 (d, $J = 8.2$ Hz, 2H), 7.36 (t, $J = 7.8$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 7.27–7.08 (m, 6H), 7.03 (d, $J = 2.4$ Hz, 2H), 6.63 (t, $J = 2.3$ Hz, 1H), 5.04 (tt, $J = 9.1$, 4.6 Hz, 1H), 4.37 (d, $J = 12.3$ Hz, 1H), 3.87 (dd, $J = 10.4$, 3.6 Hz, 1H), 3.81 (s, 6H), 3.01 (d, $J = 12.5$ Hz, 1H), 2.83 (d, $J = 12.3$ Hz, 1H), 2.58 (t, $J = 9.9$ Hz, 1H), 2.42 (s, 3H), 2.27 (dd, $J = 12.7$, 10.3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 165.8$, 161.3, 146.3, 144.6, 144.0, 133.3, 132.2, 130.5, 129.4, 129.2, 128.5, 128.3, 127.3, 127.3, 127.1, 108.0, 106.4, 68.4, 56.3, 54.7, 50.0, 46.9, 40.3, 22.2 ppm; IR (film): $\bar{\nu} = 2958$, 1718, 1596, 1458, 1347, 1231, 1205, 1158, 1091, 1048, 767, 699, 665, 576, 549 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{33}H_{33}NNaO_6S$ 594.19208, found 594.19180.

5,5-Dimethyl-1-tosylpiperidin-3-yl 3,5-dimethoxybenzoate (**6b**, $C_{23}H_{29}N_2O_6S$)

Following the general protocol B, compound **6b** was isolated in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.65$ (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 7.14 (d, $J = 2.4$ Hz, 2H), 6.64 (t, $J = 2.3$ Hz, 1H), 5.22 (tt, $J = 8.4$, 4.3 Hz, 1H), 3.82 (s, 6H), 3.63 (dd, $J = 11.3$, 4.1 Hz, 1H), 3.03 (d, $J = 11.5$ Hz, 1H), 2.71 (dd, $J = 11.2$, 8.2 Hz, 1H), 2.50 (d, $J = 11.5$ Hz, 1H), 2.42 (m, 3H), 1.78 (dd, $J = 13.3$, 4.3 Hz, 1H), 1.39 (dd, $J = 13.3$, 8.7 Hz, 1H), 1.10 (s, 3H), 1.07 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 166.0$, 161.3, 144.2, 134.6, 132.5, 130.4, 128.2, 108.0, 106.4, 68.4, 57.5, 56.3, 49.9, 42.6, 32.4, 28.6, 26.6, 22.2 ppm; IR (film): $\bar{\nu} = 2958$, 1716, 1596, 1461, 1428, 1345, 1303, 1233, 1205, 1158, 1092, 1049, 990, 916, 813, 767, 731, 661, 587, 571, 551 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{23}H_{29}NNaO_6S$ 470.16078, found 470.16067.

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