

Facile Electrochemical Intramolecular Amination of Urea-Tethered Terminal Alkenes for the Synthesis of Cyclic Ureas

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Facile intramolecular amination of unactivated alkenes has been achieved by using electricity as a catalyst that helps to generate an intermediate and accelerates formation of cyclic ureas in high yields. Using this method, no metal catalysts were used. During electrolysis, a nitrogen radical was formed at the urea substrate that cyclized with the alkene and generated a terminal carbon radical which further formed a bond

with the 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO). This method of electrolysis not only gives cyclic ureas but also functionalizes terminal unactivated alkenes. This method can be considered to be environmentally friendly given that it avoids the issues of toxicity or complicated metal ligands and could therefore be potentially employed in green chemistry.

1. Introduction

The 1,2-difunctionalization of alkenes with heteroatoms is a powerful organic transformation to prepare molecules with diverse new functionalities.^[1] These functionalized hetero molecules can be used further to investigate prominent biological activities as well as in the synthesis of chiral reagents and natural products. Vicinal difunctionalization of alkenes and amination reactions mainly depend on transition metal catalysis, hypervalent iodine reagents and photocatalysis.^[2–5] The well-known Sharpless asymmetric aminohydroxylation and dihydroxylation^[6] catalysed by osmium metal is a famous route for difunctionalisation of alkenes and this method has been followed several decades. Palladium catalysts have been used for intramolecular aminations of unfunctionalized alkenes to the synthesis of bicyclic ureas [Eq. (1)].^[7] Progress has been made in the application of expensive Pt^[8a] and Ag^[8b] catalysts or by using excess amounts of Lewis acids^[9] [Eq. (2)] to synthesize fused bicyclic isoureas through intramolecular amino-oxylation of alkenes. In 2015, Shi et al. reported the efficient chemoselective synthesis of ureas and isoureas in high yields by control-

ling O/N nucleophilic addition in urea-tethered alkenes by using PhI(OAc)₂ as the oxidant in the presence of Pd or Cu catalyst [Eq. (3)].^[10] Amination and functionalisation of unactivated alkenes in synthesis is a continuing challenge. Several reagents and reagent combinations have been developed for such reactions, but most of them are dependent on oxidants and catalysts. Moreover, electrochemical intramolecular amination of urea-tethered terminal alkenes has not been reported.^[11] However, a few cyclization reactions have been reported employing allylcarbamates and amides as the substrates.^[11b–f] Xu et al. have been involved in developing sustainable C–N bond-forming reactions by employing electrochemically generated nitrogen-centered radical (NCR) intermediates. Difunctionalization of a variety of alkenes with carbamates/amides and TEMPO affords aminooxygenation products in good yields.^[11b] Furthermore, they envisioned this approach for electrochemical intramolecular oxidative amination reaction of hindered tri- and tetrasubstituted alkenes to synthesis alkene-bearing cyclic carbamates, ureas and lactams [Eq. (4)].^[11a] Wirth et al. developed an electrochemical flow method for the intramolecular oxidative amination of alkenes with TEMPO. They have demonstrated the facile synthesis of amidyl radicals used in intramolecular hydroaminations to produce isoindolinones.^[11c] The electrically catalysed organic reactions occur at the interface of electrodes and an electrolyte. These reactions serve as powerful methods for the synthesis of complex organic molecules as they provide for an easy generation of highly reactive species, even under very mild conditions, and can be consequently applied in green chemistry.^[12]

Cyclic ureas are heterocyclic motifs frequently observed in biologically active molecules.^[13] They are also involved in important organic transformations and are important precursors for the synthesis of vicinal diamines and amino alcohols.^[14] Despite their extensive utility, the development of a new method allowing efficient preparation of these heterocycles continues

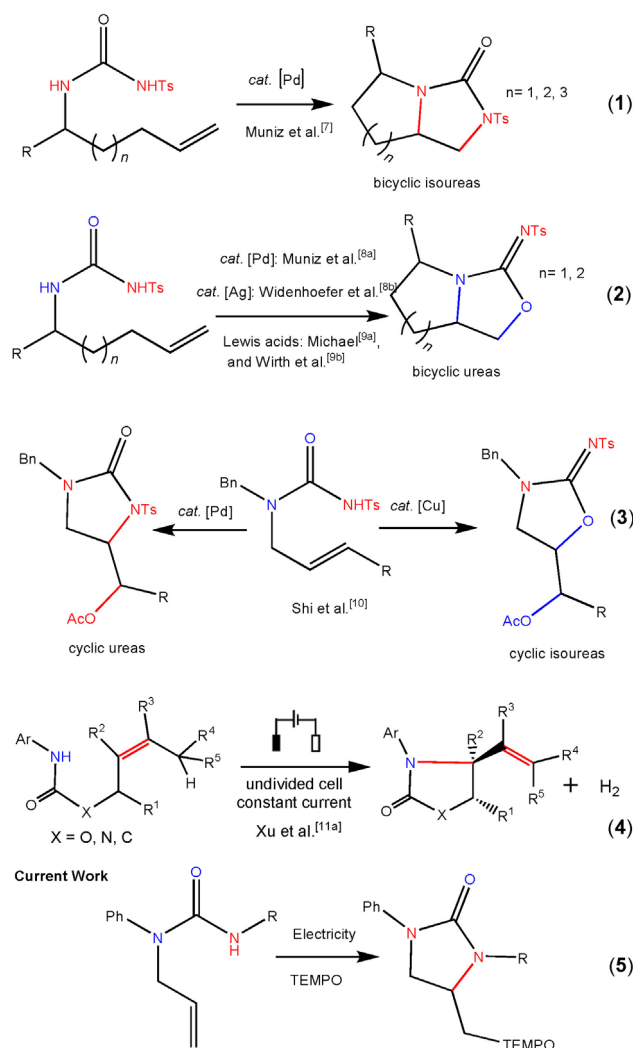
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Previous Work

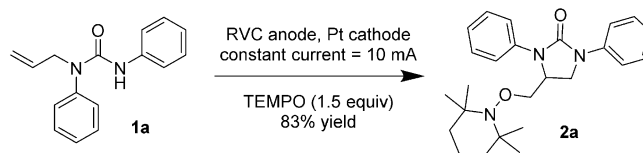


to be a stimulating challenge in organic synthesis. Herein, we have developed an electrochemical method for difunctionalisation of urea-tethered alkenes and report an economic, environmentally friendly controlled intramolecular amination. This method allows the construction of cyclic ureas in high yields from urea nucleophiles [Eq. (5)]. In this electrochemical reaction, the addition of the anodically generated nitrogen radical^[15] to a tethered alkene leads to a new terminal carbon radical, which is trapped with 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO) to afford the final cyclic urea. This electrochemical method precludes the use of stoichiometric quantities of chemical oxidants. The interception of this carbon radical with a trapping reagent (TEMPO)^[11] would also lead to difunctionalization of the alkene. Since no second oxidation would be required in such a situation, the reaction might work with an unactivated olefin.

2. Result and Discussion

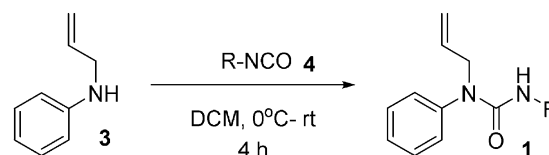
N-allylic urea **1a** was used as the first example and submitted to electrochemical difunctionalization. The reaction was run at

60 °C and a constant current of 10 mA in a three-necked round-bottom flask equipped with a reticulated vitreous carbon (RVC) anode and a platinum wire cathode. A solution of 0.1 M Bu₄NBF₄ in CH₃CN/H₂O (19:1 v/v) was used as the supporting electrolyte and 1.5 equivalents of TEMPO were included. After 1.8 F mol⁻¹ of electricity was passed through the electrolysis process, the precursor was consumed and the desired product **2a** was isolated in 83% yield (Scheme 1). 1.1 equivalents of Na₂CO₃ was used as a base in this reaction.



Scheme 1. Difunctionalization of alkenes. Reaction conditions: **1a** (0.35 mmol), TEMPO (0.53 mmol), H₂O (0.5 mL), CH₃CN (9.5 mL), 60 °C. **2a** was isolated in 83% yield.

After setting optimized conditions in electrolysis, the substrate scope was examined on the anodically catalysed difunctionalization of alkenes. The NH-phenyl ring of **1a** was modified with various functional groups to investigate their effects on alkene difunctionalization. All substrates were synthesized in high yields (Scheme 2, Figure 1). For their synthesis, allylamine



Scheme 2. Substrates synthesis (1 a–j). Reaction conditions: aryl isocyanate (1.0 equiv), dry CH_2Cl_2 (25 mL), allylamine (1.1 equiv), 0°C to rt, 4 h; yields of isolated products are given in Figure 1.

(**3**, 1.1 equiv) was added to a stirred solution of corresponding aryl isocyanate (**4**, 1.0 equiv) in dry CH₂Cl₂ (DCM) at 0 °C and then reaction was allowed to warm to room temperature and stirred for 4 h to obtain the desired urea substrate **1**. The substrate bearing functional groups, such as mono- and di-substituted Me, MeO, CF₃, NO₂, fluoro and benzyl, could proceed smoothly in the electrochemical system (see Table 1, **2a–e**, **2i,j**). The introduction of a tosyl and naphthyl groups, however, led to dissatisfactory results, which was probably caused by the decomposition of the product **2f–h** during the electrolysis (Table 1) or due to the steric hindrance of bulky tosyl and naphthyl groups which block the addition of TEMPO radical to form a bond at the terminal carbon radical of alkenes. The other possible reason could be the failure of **1f–h** to cyclize due to the difficulty in forming the requisite nitrogen radical.

The possible mechanism for the electrosynthesis was proposed using urea substrate **R** (Scheme 3). The process originates from anodic oxidation of TEMPO to oxoammonium ion, and cathodic reduction of water (H_2O) to hydroxide (OH^-) and H_2 . Then deprotonation of substrate **R** by electrogenerated hy-

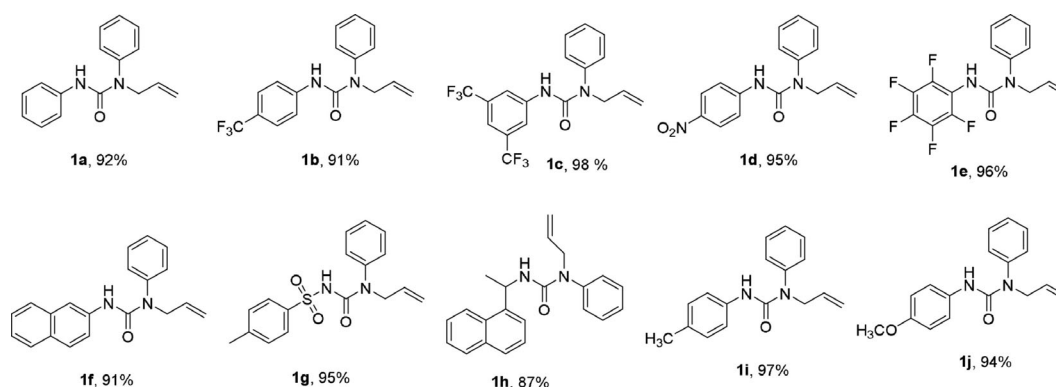
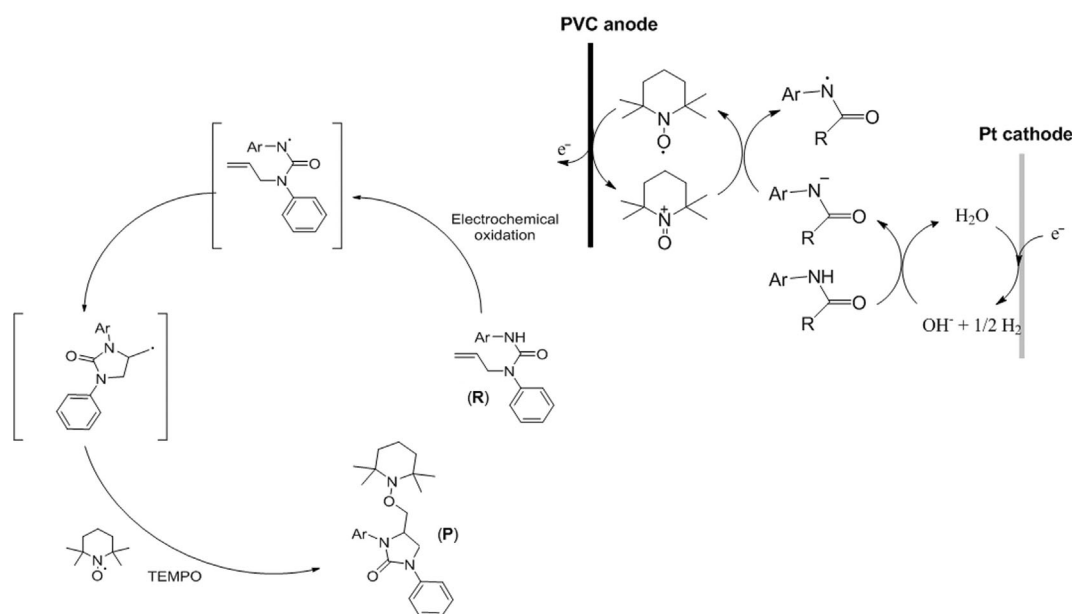


Figure 1. Substrates scope for the synthesis of urea-tethered alkenes (1 a–j).



Scheme 3. Proposed mechanism for alkene difunctionalization.

dioxide leads to a nitrogen-containing anion, which is a much better electron donor than its neutral precursor. Single-electron transfer (SET) between the nitrogen-containing anion substrate R^- and the oxoammonium ion affords the electron-deficient nitrogen-centered radical and regenerates the TEMPO radical molecule. Subsequently, the nitrogen radical intermediate can cyclize onto the cyclic urea group to give another radical at the terminal carbon that reacts with the TEMPO radical molecule to form the difunctionalized product **P**.^[11f]

3. Conclusions

In conclusion, this is a facile and green approach to generate a radical at the nitrogen center without the use of expensive metal catalysts and by using only electricity, which is economically excellent. Then this nitrogen radical on addition to unactivated/unsubstituted terminal alkenes in the presence of TEMPO constitutes a general and mild approach to alkene difunctionalization and construction of cyclic ureas in high yields. In this procedure, TEMPO plays the dual role of redox

facilitator and in radical trapping. This intramolecular amination of urea-tethered alkenes represents an environmentally friendly method that avoids the issues of toxicity or the complicated ligands of many transition-metal-based systems. In this procedure, catalyst- and oxidant-free conditions are used, which deserves significant attention from the viewpoint of green chemistry.

Experimental Section

All the solvent and chemicals were purchased from Sigma Aldrich, Alfa Aesar, Acros Organic and FluoroChem and were used without further purification. All air sensitive reactions were carried out under an argon or nitrogen atmosphere. Thin-layer chromatography (TLC) was performed on pre-coated aluminium sheets of Merck silica gel 60 F254 (0.20 mm) and visualised by UV radiation (254 nm). Automated column chromatography was performed on a Biotage® Isolera Four. ¹H NMR and ¹³C NMR spectra were measured on Bruker DPX 300, 400 or 500 apparatus. Mass spectrometric measurements were performed by the EPSRC Mass Spectrometry Facility in Swansea University on a Waters Xevo G2-S and on a

Table 1. Difunctionalization of alkenes.

Entry	Substrate	Product	¹ H NMR Conversion [%]	Yield [%; isolated] (Current [F mol ⁻¹])
1	1a	2a	100%	83% (1.8)
2	1b	2b	100%	85% (2.1)
3	1c	2c	100%	79% (3.0)
4	1d	2d	100%	83% (2.8)
5	1e	2e	100%	77% (2.2)
6	1f	2f	25%	mixture of 1f and 2f (3.0)
7	1g	2g	7%	minor traces (3.5)
8	1h	2h	2%	minor traces (4.0)
9	1i	2i	100%	80% (2.4)
10	1j	2j	100%	85% (2.4)

Thermo Scientific LTQ Orbitrap XL machine for high-resolution mass spectroscopy (HRMS). The electrochemical reactions were carried out in a galvanostatic mode using a GWINSTEK GPR-30H10D.

General Procedure for the Preparation of Allyl Ureas

To a stirred solution of an aryl isocyanate (1.0 equiv) in dry CH₂Cl₂ at 0 °C under N₂, the corresponding allylamine (1.1 equiv) was added. The reaction was allowed to warm to room temperature

and stirred for 4 hours. The reaction mixture was then diluted with CH₂Cl₂, washed with water, HCl (1 N), NaHCO₃ (sat.) and brine, dried with anhydrous MgSO₄. The mixture was filtered, and the filtrate was concentrated under vacuum. The residue was purified through silica gel flash chromatography (eluent: hexanes and ethyl acetate).

General Procedure for the Electrolysis

The substrate (0.35 mmol, 1 equiv), TEMPO (0.53 mmol, 1.5 equiv), Bu₄NBF₄ (1.0 mmol), Na₂CO₃ (0.39 mmol, 1.1 equiv) were placed in a 25 mL three-necked round-bottom flask equipped with a RVC anode and a platinum wire cathode. The flask was flushed with argon. Acetonitrile (9.5 mL) and water (0.5 mL) were added. The resulting mixture was sonicated for 0.5 min. The electrolysis was carried out at 60 °C and a constant current of 10 mA until complete consumption of the substrate (monitored by TLC or ¹H NMR). The reaction mixture was cooled to RT. Water (25 mL) and ethyl acetate (25 mL) were added. The phases were separated and the aqueous phase was extracted with ethyl acetate (2 × 25 mL). The combined organic solution was dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product. Automated column chromatography was also performed on a Biotage® Isolera Four for purification of few products.

1-Allyl-1,3-diphenylurea (1 a)

White crystalline solid, mp = (110–112) °C; ¹H NMR (300 MHz, CDCl₃) δ = 7.43–7.00 (m, 10H), 6.84 (t, *J* = 6.8 Hz, 1H), 6.16 (s, 1H), 5.82 (ddt, *J* = 16.4, 10.5, 6.1 Hz, 1H), 5.14–4.90 (m, 2H), 4.21 ppm (d, *J* = 6.1 Hz, 2H); ¹³C NMR (101 MHz, Acetone) δ = 153.93, 142.06, 140.16, 134.93, 129.80, 128.68, 128.36, 128.15, 127.21, 122.11, 119.27, 118.50, 116.22, 52.09 ppm; ESI HRMS *m/z*: calcd 252.1263 g mol⁻¹. Observed 253.1352 g mol⁻¹.

1-Allyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)urea (1 b)

White crystalline solid, mp = (116–117) °C; ¹H NMR (300 MHz, DMSO) δ = 8.56 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.50–7.39 (m, 2H), 7.31 (ddd, *J* = 8.4, 4.9, 1.6 Hz, 3H), 5.93 (dtd, *J* = 15.8, 10.6, 5.5 Hz, 1H), 5.29–5.02 (m, 2H), 4.37 ppm (d, *J* = 5.5 Hz, 2H); ¹³C NMR (75 MHz, DMSO) δ = 192.51, 154.51, 144.39, 142.56, 134.95, 129.81, 127.50, 126.82, 125.99, 125.94, 122.55, 122.12, 119.68, 117.10, 52.53 ppm; ¹⁹F NMR (376 MHz, Acetone) δ = –62.08 ppm; ESI HRMS *m/z* [M+H]⁺ calcd 320.1136 g mol⁻¹. Observed 321.1210 g mol⁻¹.

1-Allyl-3-(3,5-bis(trifluoromethyl)phenyl)-1-phenylurea (1 c)

White crystalline solid, mp = (128–130) °C; ¹H NMR (400 MHz, DMSO) δ = 8.83 (s, 1H), 8.28 (s, 2H), 7.64 (s, 1H), 7.54–7.44 (m, 2H), 7.44–7.33 (m, 3H), 6.09–5.73 (m, 1H), 5.24–4.97 (m, 2H), 4.37 ppm (d, *J* = 5.6 Hz, 2H); ¹³C NMR (101 MHz, DMSO) δ = 154.40, 142.76, 141.87, 134.70, 131.16, 130.83, 130.51, 130.19, 129.95, 128.01, 127.36, 125.23, 122.52, 119.70, 117.33, 114.81, 114.77, 52.71 ppm; ¹⁹F NMR (376 MHz, Acetone) δ = –63.59 ppm; ESI HRMS *m/z*: calcd 388.1010 g mol⁻¹. Observed 389.1108 g mol⁻¹.

1-Allyl-3-(4-nitrophenyl)-1-phenylurea (1 d)

Yellow crystalline solid, mp=(123–125) °C; ¹H NMR (400 MHz, Acetone) δ=8.00–7.95 (m, 1H), 7.89 (s, 1H), 7.61–7.54 (m, 1H), 7.38–7.16 (m, 2H), 5.82 (ddt, *J*=17.2, 10.2, 6.0 Hz, 1H), 4.98 (ddq, *J*=13.2, 10.2, 1.5 Hz, 1H), 4.23 ppm (dt, *J*=6.0, 1.4 Hz, 1H); ¹³C NMR (75 MHz, Acetone) δ=153.39, 146.67, 141.86, 141.31, 134.29, 129.88, 128.17, 127.61, 124.43, 118.39, 116.62, 52.46 ppm; ESI HRMS *m/z*: calcd 297.1113 g mol⁻¹. Observed 298.1210 g mol⁻¹

1-Allyl-3-(perfluorophenyl)-1-phenylurea (1 e)

White crystalline solid, mp=(72–73) °C; ¹H NMR (300 MHz, CDCl₃) δ=7.43–7.00 (m, 10H), 6.84 (t, *J*=6.8 Hz, 1H), 6.16 (s, 1H), 5.82 (ddt, *J*=16.4, 10.5, 6.1 Hz, 1H), 5.14–4.90 ppm (m, 2H), 4.21 (d, *J*=6.1 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ=153.34, 140.80, 133.24, 130.37, 128.63, 128.38, 118.12, 77.47, 77.04, 76.62, 52.89 ppm; ¹⁹F NMR (376 MHz, DMSO) δ=–146.47, –146.52, –146.53, –160.07, –160.13, –160.19, –164.14, –164.20, –164.25, –164.26 ppm; ESI HRMS *m/z* [M+H]⁺ calcd 342.0792 g mol⁻¹ Observed 343.0866 g mol⁻¹.

1-Allyl-3-(naphthalen-2-yl)-1-phenylurea (1 f)

White crystalline solid, mp=(117–118) °C; ¹H NMR (400 MHz, Acetone) δ=7.93 (d, *J*=2.0 Hz, 1H), 7.62 (d, *J*=8.5 Hz, 1H), 7.60–7.56 (m, 2H), 7.40–7.14 (m, 9H), 5.84 (ddt, *J*=17.2, 10.2, 6.0 Hz, 1H), 5.07–4.86 (m, 2H), 4.24 ppm (dt, *J*=6.0, 1.4 Hz, 2H); ¹³C NMR (101 MHz, Acetone) δ=154.02, 142.01, 137.82, 134.89, 134.11, 129.84, 129.82, 128.21, 127.91, 127.40, 127.29, 127.11, 126.08, 123.99, 120.46, 116.28, 114.85, 52.17 ppm; ESI HRMS *m/z*: calcd 302.1419 g mol⁻¹. Observed 303.1493 g mol⁻¹

N-(Allyl(phenyl)carbamoyl)-4-methylbenzenesulfonamide (1 g)

White crystalline solid, mp=(114–115) °C; ¹H NMR (400 MHz, Acetone) δ=8.78 (s, 1H), 7.78–7.70 (m, 2H), 7.35–7.08 (m, 7H), 5.76–5.54 (m, 1H), 5.02–4.78 (m, 2H), 4.04 (dt, *J*=6.1, 1.4 Hz, 2H), 2.30 ppm (s, 3H); ¹³C NMR (126 MHz, Acetone) δ=150.73, 143.89, 140.53, 137.78, 133.43, 129.72, 129.10, 128.28, 128.26, 127.85, 117.12, 52.32, 20.65 ppm.; ESI HRMS *m/z*: calcd 330.1038 g mol⁻¹. Observed 331.1118 g mol⁻¹

1-(2-Allylphenyl)-3-(1-(naphthalen-1-yl)ethyl)urea (1 h)

Off white liquid; ¹H NMR (300 MHz, CDCl₃) δ=8.09 (d, *J*=8.4 Hz, 1H), 7.75 (d, *J*=7.8 Hz, 1H), 7.65 (d, *J*=8.1 Hz, 1H), 7.52–7.35 (m, 2H), 7.34–7.04 (m, 7H), 5.92–5.66 (m, 2H), 5.02 (dd, *J*=2.9, 1.5 Hz, 1H), 4.97 (dt, *J*=4.6, 1.4 Hz, 1H), 4.52 (d, *J*=7.9 Hz, 1H), 4.22 (dt, *J*=6.0, 1.3 Hz, 2H), 1.46 ppm (d, *J*=6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ=155.92, 141.79, 139.63, 134.62, 133.92, 130.99, 129.89, 128.71, 128.23, 127.91, 127.50, 126.28, 125.70, 125.17, 123.65, 122.09, 116.89, 52.32, 46.28, 21.94 ppm.; ESI HRMS *m/z*: calcd 330.1732 g mol⁻¹. Observed 331.1807 g mol⁻¹

1-Allyl-1-phenyl-3-(*p*-tolyl)urea (1 i)

White crystalline solid, mp=(113–114) °C; ¹H NMR (500 MHz, [D₆]DMSO) δ=7.89 (s, 1H), 7.42–7.01 (m, 9H), 5.88 (m, 1H), 5.11 (ddq, *J*=17.1, 10.3, 1.5 Hz, 2H), 4.31 (dt, *J*=5.5, 1.4 Hz, 2H), 2.22 ppm (s, 3H); ¹³C NMR (126 MHz, [D₆]DMSO) δ=154.80, 143.04,

137.84, 135.34, 131.35, 129.76, 129.12, 127.46, 126.53, 120.44, 116.87, 52.29, 20.79 ppm; ESI HRMS *m/z* [M+H]⁺ calcd 266.1419 g mol⁻¹. Observed 367.1509 g mol⁻¹.

1-Allyl-3-(4-methoxyphenyl)-1-phenylurea (1 j)

White crystalline solid, mp=(111–112) °C; ¹H NMR (500 MHz, [D₆]DMSO) δ=7.85 (s, 1H), 7.42–7.23 (m, 7H), 6.82–6.79 (m, 2H), 5.88 (ddd, *J*=22.6, 10.6, 5.5 Hz, 1H), 5.11 (ddd, *J*=13.7, 11.4, 1.3 Hz, 2H), 4.31 (d, *J*=5.5 Hz, 2H) 3.68 ppm (s, 3H); ¹³C NMR (126 MHz, [D₆]DMSO) δ=154.98, 143.07, 135.41, 133.41, 129.74, 127.49, 126.47, 122.31, 116.83, 113.91, 55.59, 52.28 ppm; ESI HRMS *m/z* [M+H]⁺ calcd 282.1368 g mol⁻¹. Observed 283.1452 g mol⁻¹.

1,3-Diphenyl-4-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)imidazolidin-2-one (2 a)

White crystalline solid, mp=(133.4–134.7) °C; ¹H NMR (300 MHz, DMSO) δ=7.66–7.46 (m, 4H), 7.35–7.17 (m, 4H), 7.05–6.83 (m, 2H), 4.84–4.50 (m, 1H), 4.05 (t, *J*=9.4 Hz, 1H), 3.81 (dd, *J*=9.7, 3.4 Hz, 1H), 3.73–3.62 (m, 2H), 1.56–0.99 (m, 6H), 0.94 (s, 1H), 0.82 (s, 1H), 0.66 (s, 1H), 0.59 ppm (s, 1H). ¹³C NMR (75 MHz, DMSO) δ=154.88, 140.63, 139.09, 129.18, 128.97, 123.80, 122.69, 121.41, 117.98, 75.55, 59.93, 59.72, 51.60, 45.47, 33.22, 32.54, 19.91, 16.87 ppm. ESI HRMS *m/z* [M+H]⁺ calcd 407.2573 g mol⁻¹ Observed 408.2643 g mol⁻¹.

1-Phenyl-4-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-3-(4 (trifluoromethyl)phenyl)imidazolidin-2-one (2 b)

Off white crystalline solid, mp=(135–138) °C; ¹H NMR (300 MHz, CDCl₃) δ=7.64 (d, *J*=8.7 Hz, 2H), 7.56–7.48 (m, 4H), 7.35–7.27 (m, 2H), 7.08–6.99 (m, 1H), 4.61–4.46 (m, 1H), 4.04 (t, *J*=9.2 Hz, 1H), 3.90 (d, *J*=5.0 Hz, 2H), 3.79 (dd, *J*=9.1, 4.3 Hz, 1H), 1.50–1.11 (m, 6H), 1.03 (s, 3H), 0.95 (s, 3H), 0.82 ppm (s, 6H), ¹³C NMR (75 MHz, CDCl₃) δ=154.65, 141.84, 139.61, 130.40, 128.98, 128.49, 125.97, 125.92, 125.47, 125.04, 123.41, 122.44, 120.13, 118.48, 118.34, 75.80, 60.03, 51.37, 45.80, 39.57, 33.02, 32.82, 20.03, 19.86, 16.90 ppm, ¹⁹F NMR (376 MHz, Acetone) δ=–67.21 ppm. ESI HRMS *m/z* [M+H]⁺ calcd 475.2447 g mol⁻¹ Observed 476.2525 g mol⁻¹.

3-(3,5-Bis(trifluoromethyl)phenyl)-1-phenyl-4-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)imidazolidin-2-one (2 c)

White crystalline solid, mp=(151–153) °C; ¹H NMR (400 MHz, CDCl₃) δ=8.05 (s, 2H), 7.60–7.45 (m, 3H), 7.39–7.23 (m, 2H), 7.13–6.97 (m, 1H), 4.69–4.49 (m, 1H), 4.09 (t, *J*=9.2 Hz, 1H), 4.01–3.84 (m, 2H), 3.73 (dt, *J*=14.9, 7.5 Hz, 1H), 1.52–1.20 (m, 6H), 1.01 (s, 3H), 0.94 (s, 3H), 0.86 (s, 3H), 0.72 ppm (s, 3H), ¹³C NMR (101 MHz, Acetone) δ=154.27, 141.82, 139.99, 131.57, 131.24, 128.71, 125.01, 122.99, 122.30, 120.21, 120.18, 118.07, 115.49, 115.45, 115.41, 76.90, 59.71, 59.59, 51.19, 45.37, 39.46, 39.45, 32.51, 32.16, 19.21, 19.07, 16.65 ppm, ¹⁹F NMR (376 MHz, Acetone) δ=–68.15 ppm. ESI HRMS *m/z* [M+H]⁺ calcd 543.2320 g mol⁻¹ Observed 544.2419 g mol⁻¹.

3-(4-Nitrophenyl)-1-phenyl-4-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)imidazolidin-2-one (2 d)

Yellow crystalline solid, mp=(163.5–167) °C; ¹H NMR (300 MHz, Acetone) δ=8.13 (d, *J*=9.3 Hz, 2H), 7.95 (d, *J*=9.3 Hz, 2H), 7.61 (d, *J*=7.9 Hz, 2H), 7.26 (t, *J*=8.0 Hz, 2H), 6.97 (t, *J*=7.3 Hz, 1H), 4.88 (d, *J*=6.3 Hz, 1H), 4.20 (t, *J*=9.3 Hz, 1H), 4.05 (dd, *J*=9.9,

3.3 Hz, 1H), 3.96–3.82 (m, 2H), 1.47–1.09 (m, 6H), 0.99 (s, 3H), 0.88 (s, 3H), 0.69 ppm (s, 6H), ^{13}C NMR (101 MHz, Acetone) δ = 154.08, 145.84, 142.01, 140.03, 128.72, 124.35, 123.02, 118.76, 118.18, 75.61, 59.80, 59.61, 51.41, 45.44, 39.49, 32.74, 32.13, 29.74, 19.30, 19.23, 16.66, 12.99 ppm. ESI HRMS m/z $[M+H]^+$ calcd 452.2424 g mol $^{-1}$ Observed 453.2493 g mol $^{-1}$.

3-(Perfluorophenyl)-1-phenyl-4-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)imidazolidin-2-one (2e)

White crystalline solid, mp = (118–120) °C; ^1H NMR (300 MHz, Acetone) δ = 7.57–7.50 (m, 2H), 7.28–7.19 (m, 2H), 7.00–6.91 (m, 1H), 4.68–4.51 (m, 1H), 4.20 (t, J = 9.5 Hz, 1H), 4.05–3.95 (m, 1H), 3.88 (dd, J = 10.3, 3.3 Hz, 1H), 3.66 (dd, J = 9.4, 7.1 Hz, 1H), 1.34–1.07 (m, 6H), 0.96 (s, 3H), 0.92 (s, 3H), 0.77 (s, 3H), 0.57 ppm (s, 3H), ^{13}C NMR (75 MHz, Acetone) δ = 153.96, 139.94, 128.74, 122.89, 117.52, 79.52, 59.57, 59.54, 53.12, 45.43, 39.41, 39.32, 32.59, 32.24, 26.63, 18.87, 18.70, 16.66 ppm, ^{19}F NMR (376 MHz, Acetone) δ = –143.50 (d, J = 17.8 Hz), –147.06 (d, J = 13.8 Hz), –159.14 (t, J = 21.0 Hz), –165.54 (s), –165.98 (s). ESI HRMS m/z $[M+H]^+$ calcd 497.2102 g mol $^{-1}$ Observed 498.2195 g mol $^{-1}$.

1-Phenyl-4-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-3-(p-tolyl)imidazolidin-2-one (2i)

White crystalline solid, mp = (137–138) °C; ^1H NMR (500 MHz, DMSO) δ = 7.42–7.26 (m, 9H), 4.60–4.58 (m, 1H), 4.09 (t, J = 7.5 Hz, 1H), 3.93 (m, 2H), 3.75 (dt, J = 13.3, 6.5 Hz, 1H), 2.22 (s, 3H, CH₃), 1.30 (m, 6H), 1.03 (s, 3H), 0.95 (s, 3H), 0.82 ppm (s, 6H). ^{13}C NMR (126 MHz, DMSO) δ = 155.11, 140.73, 138.89, 129.44, 123.90, 122.78, 121.27, 117.60, 75.80, 59.72, 51.60, 45.32, 33.59, 32.19, 21.49, 20.34, 17.08 ppm. ESI HRMS m/z $[M+H]^+$ calcd 421.2729 g mol $^{-1}$ Observed 422.2813 g mol $^{-1}$.

3-(4-Methoxyphenyl)-1-phenyl-4-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)imidazolidin-2-one (2j)

White crystalline solid, mp = (128–129) °C; ^1H NMR (500 MHz, DMSO) δ = 7.41–7.28 (m, 7H), 6.82–6.80 (m, 2H), 4.54 (m, 1H), 4.04 (t, J = 9.1 Hz, 1H), 3.91 (d, J = 5.6 Hz, 2H), 3.80 (dd, J = 9.2, 3.6 Hz, 1H), 3.70 (s, 3H, OCH₃), 1.31 (m, 6H), 1.03 (s, 3H), 0.95 (s, 3H), 0.82 ppm (s, 6H). ^{13}C NMR (126 MHz, DMSO) δ = 154.29, 140.43, 138.89, 129.72, 129.44, 123.51, 122.78, 120.54, 118.41, 76.50, 59.99, 55.61, 51.24, 45.32, 33.22, 32.19, 19.63, 16.38 ppm. ESI HRMS m/z $[M+H]^+$ calcd 437.2678 g mol $^{-1}$ Observed 438.2757 g mol $^{-1}$.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: amination • cyclic ureas • electrochemical oxidation • TEMPO • terminal alkenes

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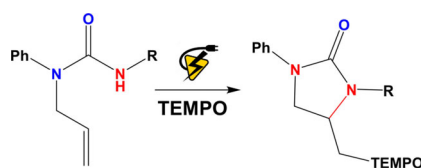
FULL PAPERS

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Facile Electrochemical Intramolecular Amination of Urea-Tethered Terminal Alkenes for the Synthesis of Cyclic Ureas



Go green: Several reagents and reagent combinations have been developed for the amination and functionalisation of unactivated alkenes. However, most of these are dependent on oxidants and catalysts. Herein, we report a green approach for the intramolecular amination of urea-tethered alkenes by generating radicals without using expensive catalysts and employing only electricity.