Electronic Supplementary Information (ESI) for:

Synergic Copper/TEMPO-Catalysed Benzylic C-H Imidation with N-Fluorobenzenesulfonimide at Room Temperature and Tandem Conversions with Alcohols or Arenes

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General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, TCI, Acros, J&K Chemicals and Adamas-beta. CuCl (99.99%, trace metal basis, extra pure, CAS No. 7758-89-6) were purchased from Acros. TEMPO was purchased from TCI (98.0% purity, CAS No. 2564-83-2). N-Fluorobenzenesulfonimide (NFSI) (97.0% purity, CAS No. 133745-75-2), ethyl acetate (EtOAc) (99.8%, SafeDry, water < 50 ppm), 1,4-dioxane (99.7%, SafeDry, water < 50 ppm), acetonitrile (MeCN) (99.9%, SafeDry, water < 50 ppm), 1,2-dichloroethane (DCE) (99.5%, SafeDry, water < 50 ppm) and THF (99.8%, SafeDry, water < 50 ppm) was purchased from Adamas-beta. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Carbamate substrates 2 were prepared through base-mediated condensation reactions between corresponding alcohols and isocyanates,^[1] or between corresponding anilines and chloroformates,^[2] according to literature reported methods.^[1-2] Products were purified by flash chromatography on silica gel using petroleum ether, ethyl acetate and dichloromethane as the eluents. ¹H-NMR spectra were recorded on Bruker AVANCE III-400 spectrometers. Chemical shifts (in ppm) were referenced with TMS in $CDCl_3$ (0 ppm); s = singlet, d = doublet, t = triplet, q = quartet, p = pentad, se = sextet, h = heptet, o = octet. 13 C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ ($\delta = 77.00$ ppm). High resolution mass spectra were obtained from an Agilent 6520B Q-TOF mass spectrometer with electron spray ionization (ESI) as the ion source.

Preparation and ¹H-NMR data of Substrate 1a-1k

1) Preparation and ¹H-NMR data of 1a-1f and 1j-1k

 $R \stackrel{H}{=} NH_2 + O \stackrel{NaHCO_3 (1.5 eq)}{(1 eq)} R \stackrel{H}{=} O \stackrel{NaHCO_3 (1.5 eq)}{THF, 0 °C to r.t.} R \stackrel{H}{=} O \stackrel{O}{H} OEt \\ H OEt \\ 1a-1f, 1j-1k$

Typical Procedure: To a solution of corresponding aniline (10 mmol) in THF (20 mL) was added sodium bicarbonate (15 mmol, 1.5 eq) at 0 °C. After stirring for 15 minutes, ethyl chloroformate (10 mmol, 1 eq) was added slowly at 0 °C, and the mixture was stirred at room temperature overnight. Then the reaction was quenched with saturated NH₄Cl (aq.), extracted with ethyl acetate, washed with water, and dried over Na₂SO₄. After removal of Na₂SO₄ by filtration, the organic phase was concentrated *in vacuo*, and purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford corresponding substrate **1a-1f** and **1j-1k**.

Ethyl *p*-tolylcarbamate (1a)

¹**H** NMR (CDCl₃, 400 MHz): δ = 7.25 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.64 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

Ethyl (3,4-dimethylphenyl)carbamate (1b)

¹H NMR (CDCl₃, 400 MHz): δ = 7.15 (s, 1H), 7.11 (d, J = 8.3 Hz, 1H), 6.99 (d, J = 8.3 Hz, 1H), 6.94 (s, 1H),
4.19 (q, J = 7.1 Hz, 2H), 2.17 (s, 3H), 2.16 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H) ppm.

Ethyl (2-methoxy-4-methylphenyl)carbamate (1c)

¹**H** NMR (CDCl₃, 400 MHz): δ = 7.92 (d, *J* = 8.1 Hz, 1H), 7.10 (s, 1H), 6.74 (dd, *J* = 8.1 Hz, 1.9 Hz, 1H), 6.65 (d, *J* = 1.9 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.30 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

Ethyl (2,4-dimethylphenyl)carbamate (1d)

¹**H** NMR (CDCl₃, 400 MHz): δ = 7.56 (s, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.96 (s, 1H), 6.33 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 2.20 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

Ethyl (3-fluoro-4-methylphenyl)carbamate (1e)

F N OEt 1e

¹**H** NMR (CDCl₃, 400 MHz): δ = 7.26-7.23 (m, 1H), 7.05 (t, *J* = 8.3 Hz, 1H), 6.93 (dd, *J* = 8.3 Hz, 2.2 Hz, 1H), 6.77 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.20 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

Ethyl (3-iodo-4-methylphenyl)carbamate (1f)

¹**H** NMR (CDCl₃, 400 MHz): δ = 7.85 (d, *J* = 2.4 Hz, 1H), 7.27 (dd, *J* = 8.2 Hz, 2.4 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.63 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm.

Butyl *p*-tolylcarbamate (1j)

¹**H** NMR (CDCl₃, 400 MHz): δ = 7.26 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.82 (s, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 2.28 (s, 3H), 1.63 (p, *J* = 7.1 Hz, 2H), 1.39 (se, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

Phenyl *p*-tolylcarbamate (1k)

¹**H** NMR (CDCl₃, 400 MHz): δ = 7.37 (t, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.92 (s, 1H), 2.31 (s, 3H) ppm.

2) Preparation and ¹H-NMR data of 1g-1i



Typical Procedure: To a solution of 1-isocyanato-4-methylbenzene (5 mmol) and Et_3N (5.5 mmol, 1.1 eq) in CH₂Cl₂ (25 mL) was added corresponding alcohol (5 mmol, 1 eq) slowly at 0 °C, and the mixture was stirred at room temperature for 2 hours. Then the reaction was quenched with saturated NH₄Cl (aq.), extracted with ethyl acetate, washed with water, and dried over Na₂SO₄. After removal of Na₂SO₄ by filtration, the organic phase was concentrated *in vacuo*, and purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford corresponding substrate **1g-1i**.

Propyl p-tolylcarbamate (1g)

N O 19

¹H NMR (CDCl₃, 400 MHz): δ = 7.46-7.45 (m, 2H), 7.15-7.07 (m, 2H), 6.77 (s, 1H), 4.11 (t, J = 6.7 Hz, 2H),
2.30 (s, 3H), 1.68 (se, J = 7.1 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H) ppm.

Isopropyl *p*-tolylcarbamate (1h)

N O Ih

¹**H** NMR (CDCl₃, 400 MHz): $\delta = 7.25$ (d, J = 8.1 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H), 6.66 (s, 1H), 5.01 (h, J = 6.3 Hz, 1H), 2.28 (s, 3H), 1.27 (d, J = 6.3 Hz, 6H) ppm.

Tert-Pentyl p-tolylcarbamate (1i)

¹H NMR (CDCl₃, 400 MHz): δ = 7.23 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 6.43 (s, 1H), 2.28 (s, 3H),
1.83 (q, J = 7.5 Hz, 2H), 1.48 (s, 6H), 0.92 (t, J = 7.5 Hz, 3H) ppm.

Experimental Procedure and Characterization Data

1) Synergic copper/TEMPO-catalysed benzylic C-H imidation of *p*-tolylcarbamates (Table 3)



Typical Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of *p*-tolylcarbamate (**1a-1k**, 0.3 mmol) and TEMPO (4.7 mg, 0.03 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, the mixture was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford corresponding benzylic imidated products **2a-2k**.

Ethyl (4-((*N*-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (2a)

The reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (53.7 mg, **1a**) and NFSI (189 mg) with CuCl (1.5mg) and TEMPO (4.7 mg) at 25 °C in argon afforded 129.6 mg of **2a** (91%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent.

White solid, m.p. 148.0-148.6 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.80-7.78$ (m, 4H), 7.57-7.53 (m, 2H), 7.43-7.39 (m, 4H), 7.30-7.24 (m, 4H), 6.87 (s, 1H), 4.88 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.30$, 139.71, 137.77, 133.44, 129.85, 128.98, 128.63, 127.83, 118.19, 61.07, 51.80, 14.34 ppm. HRMS m/z (ESI) calcd for $[C_{22}H_{22}N_2O_6S_2+Na]^+$ 497.0812, found 497.0816.

Ethyl (3-methyl-4-((*N*-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (2b)



The reaction of 0.3 mmol of ethyl (3,4-dimethylphenyl)carbamate (57.9 mg, **1b**) and NFSI (189 mg) with CuCl (1.5mg) and TEMPO (4.7 mg) at 25 °C in argon afforded 139.6 mg of **2b** (95%) after flash

chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent.

Light yellow solid, m.p. 148.2-148.5 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 7.81-7.79 (m, 4H), 7.58-7.55 (m, 2H), 7.45-7.41 (m, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.89 (dd, *J* = 8.4 Hz, 1.9 Hz, 1H), 6.62 (s, 1H), 4.97 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 153.46, 139.96, 137.56, 137.52, 133.54, 130.24, 128.73, 127.95, 126.92, 120.05, 116.07, 61.19, 49.80, 19.27, 14.48 ppm. HRMS *m*/z (ESI) calcd for [C₂₃H₂₄N₂O₆S₂+Na]⁺ 511.0968, found 511.0964.

Ethyl (2-methoxyl-4-((*N*-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (2c)

The reaction of 0.3 mmol of ethyl (2-methoxy-4-methylphenyl)carbamate (62.7 mg, **1c**) and NFSI (189 mg) with CuCl (1.5mg) and TEMPO (4.7 mg) at 25 °C in argon afforded 129.8 mg of **2c** (86%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent. Light yellow solid, m.p. 96.9-97.7 °C. **¹H NMR (CDCl₃, 400 MHz)**: δ = 7.99 (d, *J* = 8.2 Hz, 1H), 7.82-7.80 (m, 4H), 7.58-7.55 (m, 2H), 7.45-7.41 (m, 4H), 7.18 (s, 1H), 6.94 (dd, *J* = 8.2 Hz, 1.5 Hz, 1H), 6.80 (d, *J* = 1.5 Hz, 1H), 4.90 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.61 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, **100 MHz**): δ = 153.24, 147.27, 139.83, 133.41, 128.60, 128.43, 127.88, 127.42, 121.91, 117.22, 110.14, 61.03, 55.32, 52.35, 15.39 ppm. HRMS *m/z* (ESI) calcd for [C₂₃H₂₄N₂O₇S₂+Na]⁺ 527.0917, found 527.0912.

Ethyl (2-methyl-4-((N-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (2d)

The reaction of 0.3 mmol of ethyl (2,4-dimethylphenyl)carbamate (57.9 mg, **1d**) and NFSI (189 mg) with CuCl (1.5mg) and TEMPO (4.7 mg) at 25 °C in argon afforded 74.9 mg of **2d** (51%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent.

White solid, m.p. 112.4-113.0 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 7.81-7.79 (m, 4H), 7.71-7.70 (m, 1H), 7.59-7.56 (m, 2H), 7.46-7.42 (m, 4H), 7.19 (dd, *J* = 8.3 Hz, 1.6 Hz, 1H), 7.07 (s, 1H), 6.37 (s, 1H), 4.88 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.10 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 153.68, 139.94, 135.80, 133.54, 130.93, 129.65, 128.74, 128.03, 127.77, 61.34, 52.09, 17.43, 14.52 ppm. HRMS *m/z* (ESI) calcd for [C₂₃H₂₄N₂O₇S₂+Na]⁺ 511.0968, found 511.0969.

Ethyl (3-fluoro-4-((*N*-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (2e)

The reaction of 0.3 mmol of ethyl (3-fluoro-4-methylphenyl)carbamate (59.1 mg, **1e**) and NFSI (189 mg) with CuCl (1.5mg) and TEMPO (4.7 mg) at 25 °C in argon afforded 111.6 mg of **2e** (76%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent. White solid, m.p. 83.6-84.5 °C. **¹H NMR (CDCl₃, 400 MHz)**: $\delta = 7.87-7.85$ (m, 4H), 7.61-7.57 (m, 2H), 7.48-7.44 (m, 4H), 7.33-7.30 (m, 1H), 7.17 (t, J = 8.0 Hz, 1H), 6.74-6.72 (m, 2H), 5.00 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 160.63$ (d, J = 245.5 Hz), 153.21, 139.64, 139.43 (d, J = 11.2 Hz), 133.76, 130.62 (d, J = 4.5 Hz), 128.44 (d, J = 84.6 Hz), 127.58, 116.10 (d, J = 13.9 Hz), 113.69, 105.49 (d, J = 28.9 Hz), 61.49, 45.38 (d, J = 4.1 Hz), 14.42 ppm. HRMS *m*/z (ESI) calcd for [C₂₂H₂₁FN₂O₆S₂+Na]⁺ 515.0717, found 515.0716.

Ethyl (3-iodo-4-((N-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (2f)

The reaction of 0.3 mmol of ethyl (3-iodo-4-methylphenyl)carbamate (91.5 mg, **1f**) and NFSI (189 mg) with CuCl (1.5mg) and TEMPO (4.7 mg) at 25 °C in argon afforded 129.1 mg of **2f** (72%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent. White solid, m.p. 144.8-145.0 °C. **¹H NMR (CDCl₃, 400 MHz)**: $\delta = 7.98$ (s, 1H), 7.90-7.88 (m, 4H), 7.63-7.59 (m, 2H), 7.49-7.45 (m, 4H), 7.01 (d, J = 7.7 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 6.68 (s, 1H), 5.00 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.27$, 139.35, 138.09, 133.79, 131.00, 128.81, 128.63, 128.51, 128.12, 118.08, 97.44, 61.33, 56.68, 14.34 ppm. HRMS *m*/z (ESI) calcd for [C₂₂H₂₁IN₂O₆S₂+Na]⁺ 622.9778, found 622.9777.

Propyl (4-((*N*-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (2g)

The reaction of 0.3 mmol of propyl p-tolylcarbamate (57.9 mg, 1g) and NFSI (189 mg) with CuCl (1.5 mg)

and TEMPO (4.7 mg) at 25 °C in argon afforded 123.13 mg of 2g (84%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent.

White solid, m.p. 109.9-110.6 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.80-7.78$ (m, 4H), 7.57-7.54 (m, 2H), 7.43-7.40 (m, 4H), 7.29-7.25 (m, 4H), 4.88 (s, 2H), 4.12 (t, J = 6.6 Hz, 2H), 1.69 (se, J = 7.1 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.30$, 139.53, 137.67, 133.30, 129.66, 128.77, 128.47, 127.65, 118.08, 66.52, 51.65, 21.87, 10.01 ppm. HRMS *m/z* (ESI) calcd for [C₂₃H₂₄N₂O₆S₂+Na]⁺ 511.0968, found 511.0970.

Isopropyl (4-((N-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (2h)

$$\begin{array}{c} PhO_2S \\ PhO_2S \\ PhO_2S \end{array} \begin{array}{c} H \\ 0 \end{array} \begin{array}{c} 2h \\ (83\%) \end{array}$$

The reaction of 0.3 mmol of isopropyl *p*-tolylcarbamate (57.9 mg, **1h**) and NFSI (189 mg) with CuCl (1.5mg) and TEMPO (4.7 mg) at 25 °C in argon afforded 121.3 mg of **2h** (83%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent.

White solid, m.p. 107.8-109.1 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.80-7.78$ (m, 4H), 7.58-7.54 (m, 2H), 7.44-7.40 (m, 4H), 7.31-7.24 (m, 4H), 6.77 (s, 1H), 5.02 (h, J = 6.2 Hz, 1H), 4.88 (s, 2H), 1.30 (d, J = 6.2 Hz, 6H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.00$, 139.80, 138.02, 133.52, 129.92, 128.93, 128.71, 127.92, 118.18, 68.69, 51.89, 21.98 ppm. HRMS *m*/*z* (ESI) calcd for [C₂₃H₂₄N₂O₆S₂+Na]⁺ 511.0968, found 511.0961.

Tert-Pentyl (4-((N-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (2i)

PhO₂S PhO₂S N PhO₂S N O O (86%)

The reaction of 0.3 mmol of *tert*-pentyl *p*-tolylcarbamate (66.3 mg, **1i**) and NFSI (189 mg) with CuCl (1.5mg) and TEMPO (4.7 mg) at 25 °C in argon afforded 133.5 mg of **2i** (86%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent.

White solid, m.p. 70.1-70.9 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 7.82-7.80 (m, 4H), 7.58-7.55 (m, 2H), 7.45-7.41 (m, 4H), 7.30-7.22 (m, 4H), 6.63 (s, 1H), 4.88 (s, 2H), 1.85 (q, *J* = 7.5 Hz, 2H), 1.50 (s, 6H), 0.94 (t, *J* = 7.5 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 152.48, 139.92, 138.36, 133.51, 129.92, 128.73, 127.96, 118.12, 83.03, 51.95, 33.54, 25.69, 8.22 ppm. HRMS *m/z* (ESI) calcd for [C₂₅H₂₈N₂O₆S₂+Na]⁺ 539.1281, found 539.1281.

Butyl (4-((N-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (2j)



The reaction of 0.3 mmol of butyl *p*-tolylcarbamate (62.1 mg, **1j**) and NFSI (189 mg) with CuCl (1.5mg) and TEMPO (4.7 mg) at 25 °C in argon afforded 104.8 mg of **2j** (70%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent.

White solid, m.p. 68.8-69.3 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 7.80-7.78 (m, 4H), 7.57-7.54 (m, 2H), 7.44-7.40 (m, 4H), 7.31-7.23 (m, 4H), 6.76 (s, 1H), 4.88 (s, 2H), 4.17 (t, *J* = 6.7 Hz, 2H), 1.65 (p, *J* = 7.1 Hz, 2H), 1.41 (se, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 153.55, 139.91, 137.96, 133.55, 129.97, 129.14, 128.75, 127.97, 118.29, 65.11, 51.94, 30.86, 18.99, 13.65 ppm. HRMS *m/z* (ESI) calcd for [C₂₄H₂₆N₂O₆S₂+Na]⁺ 525.1125, found 525.1124.

Phenyl (4-((N-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (2k)



The reaction of 0.3 mmol of phenyl *p*-tolylcarbamate (68.1 mg, **1k**) and NFSI (189 mg) with CuCl (1.5mg) and TEMPO (4.7 mg) at 25 °C in argon afforded 77.8 mg of **2k** (50%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent.

White solid, m.p. 132.5-133.1 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 7.81-7.79 (m, 4H), 7.58-7.54 (m, 2H), 7.44-7.38 (m, 6H), 7.34-7.31 (m, 4H), 7.29-7.18 (m, 4H), 4.89 (s, 2H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 150.39, 139.81, 137.33, 133.66, 130.04, 129.86, 129.41, 129.15, 128.81, 128.00, 127.42, 125.76, 121.58, 118.52, 51.89 ppm. HRMS *m/z* (ESI) calcd for [C₂₆H₂₂N₂O₆S₂+Na]⁺ 545.0812, found 545.0811.

2) Subsequent alkoxylation of benzylic imidated *p*-tolylcarbamate 2a with alcohols (Table 4, 6a-60)



Typical Procedure: To a reaction tube charged with imidated *p*-tolylcarbamate **2a** (142.2 mg, 0.3 mmol) was added a suspension of KOH (67.2 mg, 1.2 mmol) in alcohols (**5a-5o**, 1 mL) under argon (1 atm). After stirring at 25°C for 4 hours, the mixture was concentrated *in vacuo*, followed by purification via flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford corresponding benzylic ethers **6a-6o**.

Ethyl (4-(methoxymethyl)phenyl)carbamate (6a)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in methanol (**5a**, 1 mL) at 25 °C in argon afforded 60.4 mg of **6a** (96%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.36$ (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 6.78 (s, 1H), 4.40 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.36 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.61$, 137.47, 132.96, 128.66, 118.50, 74.20, 61.17, 57.84, 14.50 ppm. HRMS *m*/z (ESI) calcd for [C₁₁H₁₅NO₃+Na]⁺ 232.0944, found 232.0944.

Ethyl (4-(ethoxymethyl)phenyl)carbamate (6b)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in ethanol (**5b**, 1 mL) at 25 °C in argon afforded 56.7 mg of **6b** (85%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.35$ (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 6.79 (s, 1H), 4.45 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.52 (q, J = 7.0 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.0 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.61$, 137.34, 133.38, 128.56, 118.52, 72.21, 65.47, 61.13, 15.15, 14.49 ppm. HRMS *m/z* (ESI) calcd for [C₁₂H₁₇NO₃+Na]⁺ 246.1101, found 246.1107.

Ethyl (4-(butoxymethyl)phenyl)carbamate (6c)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in butanol (**5c**, 1 mL) at 25 °C in argon afforded 61.4 mg of **6c** (82%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.35$ (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 6.84 (s, 1H), 4.44 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 3.45 (t, J = 6.6 Hz, 2H), 1.62-1.55 (m. 2H), 1.43-1.33 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.63$, 137.31, 133.48, 128.47, 118.51, 72.33, 69.95, 61.10, 31.73, 19.29, 14.48, 13.85 ppm. HRMS *m/z* (ESI) calcd for [C₁₄H₂₁NO₃+Na]⁺ 274.1414, found 274.1717.

Ethyl (4-((hexyloxy)methyl)phenyl)carbamate (6d)



The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in hexanol (**5d**, 1 mL) at 25 °C in argon afforded 75.1 mg of **6d** (90%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.35$ (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 6.79 (s, 1H), 4.44 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.44 (t, J = 6.7 Hz, 2H), 1.60 (p, J = 7.0 Hz, 2H), 1.36-1.26 (m. 9H), 0.88 (t, J = 6.8 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.62$, 137.30, 133.50, 128.49, 118.49, 72.34, 70.29, 61.12, 31.63, 29.64, 25.80, 22.56, 14.49, 13.99 ppm. HRMS *m*/z (ESI) calcd for [C₁₆H₂₅NO₃+Na]⁺ 302.1727, found 302.1724.

Ethyl (*E*)-(4-((but-2-en-1-yloxy)methyl)phenyl)carbamate (6e)

OCE 66 (84%)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in (*E*)-but-2-en-1-ol (crotonyl alcohol, **5e**, 1 mL) at 25 °C in argon afforded 62.5 mg of **6e** (84%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.35$ (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 6.81 (s,

1H), 5.75-5.68 (m, 1H), 5.64-5.57 (m, 1H), 4.44 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 3.93 (d, J = 6.2 Hz, 2H), 1.71 (dd, J = 6.2 Hz, 0.8 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.61$, 137.35, 133.23, 129.68, 128.65, 127.43, 118.49, 71.38, 70.63, 61.11, 17.73, 14.48 ppm. HRMS *m*/*z* (ESI) calcd for [C₁₄H₁₉NO₃+Na]⁺ 272.1257, found 272.1255.

Ethyl (E)-(4-((hex-2-en-1-yloxy)methyl)phenyl)carbamate (6f)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in (*E*)-hex-2-en-1-ol (**5f**, 1 mL) at 25 °C in argon afforded 64.6 mg of **6f** (78%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Light-yellow oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.35$ (d, J = 8.1 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 6.75 (s, 1H), 5.74-5.67 (m, 1H), 5.61-5.54 (m, 1H), 4.44 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.95 (d, J = 6.1 Hz, 2H), 2.03 (q, J = 7.0 Hz, 2H), 1.41 (se, J = 7.4 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.57$, 137.33, 134.86, 133.29, 128.70, 126.24, 118.49, 71.32, 70.72, 61.15, 34.34, 22.18, 14.51, 13.67 ppm. HRMS *m/z* (ESI) calcd for [C₁₆H₂₃NO₃+Na]⁺ 300.1570, found 300.1577.

Ethyl (4-(((3-methylbut-2-en-1-yl)oxy)methyl)phenyl)carbamate (6g)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in 3-methylbut-2-en-1-ol (**5g**, 1 mL) at 25 °C in argon afforded 69.6 mg of **6g** (78%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.35$ (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 6.79 (s, 1H), 5.38 (tt, J = 6.9 Hz, 1.2 Hz, 1H), 4.44 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.97 (d, J = 6.9 Hz, 2H), 1.74 (s, 3H), 1.64 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.59$, 137.34, 137.17, 133.36, 128.67, 120.96, 118.45, 71.50, 66.29, 61.11, 25.73, 17.98, 14.49 ppm. HRMS *m/z* (ESI) calcd for [C₁₅H₂₁NO₃+Na]⁺ 286.1414, found 286.1414.

Ethyl (4-(((2-methylallyl)oxy)methyl)phenyl)carbamate (6h)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in 2-methylprop-2-en-1-ol (**5h**, 1 mL) at 25 °C in argon afforded 67.7 mg of **6h** (91%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.36$ (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 6.80 (s, 1H), 4.99 (d, J = 0.6 Hz, 1H), 4.92 (s, 1H), 4.44 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.91 (s, 2H), 1.76 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.61$, 142.09, 137.37, 133.20, 128.57, 118.50, 112.29, 73.83, 71.29, 61.13, 19.48, 14.49 ppm. HRMS m/z (ESI) calcd for $[C_{14}H_{19}NO_3+Na]^+$ 272.1257, found 272.1258.

Ethyl (4-((but-2-yn-1-yloxy)methyl)phenyl)carbamate (6i)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in but-2-yn-1-ol (**5i**, 1 mL) at 25 °C in argon afforded 64.3 mg of **6i** (87%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.36$ (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 6.88 (s, 1H), 4.52 (s, 2H), 4.32 (q, J = 7.1 Hz, 2H), 4.10 (q, J = 2.3 Hz, 2H), 1.87 (t, J = 2.3 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.59$, 137.58, 132.31, 128.92, 118.45, 82.59, 74.96, 70.87, 61.10, 57.38, 14.44, 3.53 ppm. HRMS *m/z* (ESI) calcd for [C₁₄H₁₇NO₃+Na]⁺ 270.1101, found 270.1100.

Ethyl (4-((2-cyanoethoxy)methyl)phenyl)carbamate (6j)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in 3-hydroxypropanenitrile (**5j**, 1 mL) at 25 °C in argon afforded 56.7 mg of **6j** (76%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.38$ (d, J = 8.2 Hz, 2H), 7.28 (d, J = 7.4 Hz, 2H), 6.77 (s, 1H), 4.52 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.65 (t, J = 6.4 Hz, 2H), 2.61 (t, J = 6.4 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.56$, 137.81, 131.94, 128.68, 118.60, 117.79, 72.81, 64.29, 61.21, 18.85, 14.48 ppm. HRMS *m*/z (ESI) calcd for [C₁₃H₁₆N₂O₃+Na]⁺ 271.1053, found 271.1054.

Ethyl (4-((3-methoxypropoxy)methyl)phenyl)carbamate (6k)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in 3-methoxypropan-1-ol (**5k**, 1 mL) at 25 °C in argon afforded 63.6 mg of **6k** (79%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.36$ (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.01 (s, 1H), 4.44 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 3.53 (t, J = 6.4 Hz, 2H), 3.48 (t, J = 6.4 Hz, 2H), 3.32 (s, 3H), 1.87 (p, J = 6.4 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.65$, 137.43, 133.16, 128.44, 118.47, 72.43, 69.63, 66.99, 61.02, 58.47, 29.85, 14.44 ppm. HRMS *m/z* (ESI) calcd for [C₁₄H₂₁NO₄+Na]⁺ 290.1363, found 290.1362.

Ethyl (4-(((3,7-dimethyloct-6-en-1-yl)oxy)methyl)phenyl)carbamate (6l)



The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in 3,7-dimethyloct-6-en-1-ol (citronellol, **5l**, 1 mL) at 25 °C in argon afforded 71.3 mg of **6l** (71%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.35$ (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 6.72 (s, 1H), 5.11-5.07 (m, 1H), 4.44 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.51-3.43 (m, 2H), 2.03-1.91 (m, 2H), 1.70-1.55 (m, 8H), 1.45-1.34 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.19-1.12 (m, 1H), 0.88 (d, J = 6.6 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.58$, 137.28, 133.52, 131.10, 128.51, 124.77, 118.46, 72.41, 68.50, 61.15, 37.15, 36.63, 29.50, 25.68, 25.41, 19.49, 17.59, 14.51 ppm. HRMS *m*/*z* (ESI) calcd for [C₂₀H₃₁NO₃+Na]⁺ 356.2196, found 356.2194.

Ethyl (E)-(4-(((3,7-dimethylocta-2,6-dien-1-yl)oxy)methyl)phenyl)carbamate (6m)

The reaction of 0.3 mmol of imidated p-tolylcarbamate 2a (142.2 mg) with KOH (67.2 mg) in

(*E*)-3,7-dimethylocta-2,6-dien-1-ol (geraniol, **5m**, 1 mL) at 25 °C in argon afforded 72.3 mg of **6m** (73%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, *v/v*) as the eluent. Light-yellow oil. ¹H NMR (CDCl₃, 400 MHz): δ = 7.35 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.73 (s, 1H), 5.38 (t, *J* = 6.6 Hz, 1H), 5.10 (t, *J* = 6.5 Hz, 1H), 4.45 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.00 (d, *J* = 6.8 Hz, 2H), 2.12-2.02 (m, 4H), 1.68 (s, 3H), 1.63 (s, 3H), 1.60 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 153.57, 140.40, 137.33, 133.45, 131.61, 128.73, 123.96, 120.73, 118.49, 71.42, 66.33, 61.16, 39.55, 26.31, 25.66, 17.64, 16.45, 14.51 ppm. HRMS *m/z* (ESI) calcd for [C₂₀H₂₉NO₃+Na]⁺ 354.2040, found 354.2042.

Ethyl (Z)-(4-(((3,7-dimethylocta-2,6-dien-1-yl)oxy)methyl)phenyl)carbamate (6n)



The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in (*Z*)-3,7-dimethylocta-2,6-dien-1-ol (nerol, **5n**, 1 mL) at 25 °C in argon afforded 57.4 mg of **6n** (58%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, ν/ν) as the eluent. Light-yellow oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.35$ (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 6.65 (s, 1H), 5.39 (t, J = 6.5 Hz, 1H), 5.07 (s, 1H), 4.44 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.98 (d, J = 6.8 Hz, 2H), 2.05-2.04 (m, 4H), 1.75 (s, 3H), 1.67 (s, 3H), 1.58 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.55$, 140.60, 137.30, 133.45, 131.88, 128.69, 123.81, 121.74, 118.43, 71.61, 66.19, 61.16, 32.21, 26.65, 25.66, 23.46, 17.60 14.52 ppm. HRMS *m/z* (ESI) calcd for [C₂₀H₂₉NO₃+Na]⁺ 354.2040, found

354.2037.

Ethyl (Z)-(4-(((3,7-dimethylocta-2,6-dien-1-yl)oxy)methyl)phenyl)carbamate (60)

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The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) with KOH (67.2 mg) in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP, **5o**, 1 mL) at 40 °C in argon afforded 94.5 mg of **6o** (91%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent. White solid, m.p. 74.1-74.7 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 7.42 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.78 (s, 1H), 4.77 (s, 2H), 4.23 (q, J = 7.1 Hz, 2H), 4.10 (h, J = 6.0 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.56$, 138.81, 129.79, 129.24, 121.55 (q, J = 282.1 Hz), 118.64, 75.45, 73.90 (p, J = 32.2 Hz), 61.36, 14.43 ppm. HRMS *m*/*z* (ESI) calcd for [C₁₃H₁₃F₆NO₃+Na]⁺ 368.0692, found 368.0697.

3) Subsequent acyloxylation of benzylic imidated *p*-tolylcarbamate 2a with carboxylate (Table 4, 6p)



Typical Procedure: To a reaction tube charged with imidated *p*-tolylcarbamate **2a** (142.2 mg, 0.3 mmol) and KOH (33.6 mg, 0.6 mmol) was added a suspension of sodium acetate (NaOAc, **5p**, 49.2 mg, 0.6 mmol) in HFIP (2 mL) under argon (1 atm). After stirring at 40°C for 4 hours, the mixture was concentrated *in vacuo*, followed by purification via flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford 46.6 mg of benzyl acetate **6p** (66%).

4-((Ethoxycarbonyl)amino)benzyl acetate (6p)

White solid, m.p. 104.8-105.2 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 7.39 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.77 (s, 1H), 5.05 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.08 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 170.95, 153.50, 138.07, 130.67, 129.35, 118.53, 65.95, 61.25, 21.01, 14.49 ppm. HRMS *m/z* (ESI) calcd for [C₁₂H₁₅NO₄+Na]⁺ 260.0893, found 260.0890.

4) Subsequent arylation of benzylic imidated *p*-tolylcarbamate 2a with arenes (Table 5)



Typical Procedure: To a reaction tube charged with imidated *p*-tolylcarbamate **2a** (142.2 mg, 0.3 mmol) and KOH (33.6 mg, 0.6 mmol) was added a solution of arenes (**7a-7p**, 0.6 mmol) in HFIP (2 mL) under argon (1 atm). After stirring at 40°C for 4 hours, the mixture was concentrated *in vacuo*, followed by purification via flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford corresponding benzylated arenes **8a-8p**.

Ethyl (4-((1*H*-indol-3-yl)methyl)phenyl)carbamate (8a)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and 1*H*-indole (**7a**, 70.2 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 75.5 mg of **8a** (86%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent.

White solid, m.p. 89.6-89.8 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 7.98 (s, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.27-7.14 (m, 5H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.84 (s, 1H), 6.57 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.04 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 153.78, 136.39, 136.31, 135.70, 129.16, 127.30, 122.31, 121.92, 119.22, 119.03, 118.87, 115.66, 111.06, 102.21, 61.13, 30.87, 14.51 ppm. HRMS *m*/z (ESI) calcd for [C₁₈H₁₈N₂O₂+Na]⁺ 217.1261, found 217.2157.

Ethyl (4-((5-chloro-1*H*-indol-3-yl)methyl)phenyl)carbamate (8b)



The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and 5-chloro-1*H*-indole (**7b**, 90.6 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 86.8 mg of **8b** (88%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1 to 6:1, v/v) as the eluent.

White solid, m.p. 122.7-123.0 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 8.10 (s, 1H), 7.43 (d, *J* = 1.7 Hz, 1H), 7.25-7.07 (m, 6H), 6.84 (s, 1H), 6.60 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 153.76, 135.84, 134.73, 129.66, 129.10, 128.40, 124.96, 123.72, 122.24, 118.91, 118.49, 115.50, 112.08, 101.83, 61.17, 30.68, 14.52 ppm. HRMS *m/z* (ESI) calcd for $[C_{18}H_{17}CIN_2O_2+Na]^+$ 351.0871, found 351.0869.

Ethyl (4-((5-cyano-1*H*-indol-3-yl)methyl)phenyl)carbamate (8c)



The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and 1*H*-indole-5-carbonitrile (**7c**, 85.2 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 69.7 mg of **8c** (73%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent. White solid, m.p. 148.5-148.9 °C. ¹H NMR (DMSO-d₆, 400 MHz): $\delta = 11.45$ (s, 1H), 9.50 (s, 1H), 7.96 (s, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.42-7.36 (m, 4H), 7.22 (d, J = 8.4 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 4.02 (s, 2H), 1.25 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): $\delta = 153.56$, 138.08, 137.06, 135.05, 128.69, 126.76, 125.68, 124.27, 123.68, 120.87, 118.27, 115.60, 112.69, 100.29, 60.01, 29.90, 14.53 ppm. HRMS *m*/z (ESI) calcd for [C₁₉H₁₇N₃O₂+Na]⁺ 342.1213, found 342.1216.

Ethyl 3-(4-((ethoxycarbonyl)amino)benzyl)-1H-indole-5-carboxylate (8d)

EtO₂C

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and ethyl 1*H*-indole-5-carboxylate (**7d**, 113.4 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 99.0 mg of **8d** (90%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, *v/v*) as the eluent. White solid, m.p. 144.7-145.1 °C. ¹H NMR (DMSO-d₆, 400 MHz): $\delta = 11.25$ (s, 1H), 9.49 (s, 1H), 8.12 (s, 1H), 7.72 (dd, J = 8.6 Hz, 1.4 Hz, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 1.8 Hz, 1H), 7.18 (d, J = 8.4 Hz, 2H), 4.28 (q, J = 7.1 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 4.03 (s, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): $\delta = 166.85$, 153.63, 139.11, 137.11, 135.21, 128.67, 126.61, 125.03, 122.05, 121.25, 120.12, 118.25, 115.69, 111.38, 60.10, 60.07, 30.17, 14.59, 14.37 ppm. HRMS *m/z* (ESI) calcd for [C₂₁H₂₂N₂O₄+Na]⁺ 389.1472, found 389.1475.

Ethyl (4-((6-fluoro-1*H*-indol-3-yl)methyl)phenyl)carbamate (8e)

F N OEt 8e (89%)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate 2a (142.2 mg) and 6-fluoro-1*H*-indole (7e, 81.0 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 83.4 mg of **8e** (89%) after flash

chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent.

White solid, m.p. 210.5-211.0 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.01$ (s, 1H), 7.35 (dd, J = 8.6 Hz, 5.4 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.99 (dd, J = 9.7 Hz, 2.1 Hz, 1H), 6.83-6.79 (m, 2H), 6.56 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 4.01 (s, 2H), 1.29 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 159.97$ (d, J = 236.1 Hz), 153.77, 136.35 (d, J = 12.4 Hz), 135.93 (d, J = 19.7 Hz), 129.15, 123.93, 122.52 (d, J = 3.5 Hz), 119.78 (d, J = 10.2 Hz), 118.90, 115.83, 108.01 (d, J = 24.4 Hz), 102.33, 97.34 (d, J = 26.0 Hz), 61.18, 30.87, 14.53 ppm. HRMS *m*/z (ESI) calcd for [C₁₈H₁₇FN₂O₂+Na]⁺ 335.1166, found 335.1170.

Ethyl (4-((6-chloro-1*H*-indol-3-yl)methyl)phenyl)carbamate (8f)



The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and 6-chloro-1*H*-indole (**7f**, 90.6 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 72.1 mg of **8f** (73%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, *v/v*) as the eluent. White solid, m.p. 127.1-127.7 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.03$ (s, 1H), 7.36-7.25 (m, 4H), 7.18-7.13 (m, 2H), 7.02-7.00 (m, 1H), 6.85 (s, 1H), 6.55 (s, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 4.01 (s, 2H), 1.29 (t, *J* = 7.0 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.75$, 136.77, 135.85, 129.50, 129.13, 127.91, 125.94, 122.93, 120.01, 119.96, 118.88, 115.91, 110.99, 61.19, 30.78, 14.53 ppm. HRMS *m/z* (ESI) calcd for [C₁₈H₁₇ClN₂O₂+Na]⁺ 351.0871, found 351.0877.

Ethyl 3-(4-((ethoxycarbonyl)amino)benzyl)-1H-indole-6-carboxylate (8g)

EtO₂C H OEt 8g (78%)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and ethyl 1*H*-indole-6-carboxylate (**7g**, 113.4 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 85.2 mg of **8g** (78%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, *v/v*) as the eluent. White solid, m.p. 141.4-141.7 °C. ¹H NMR (DMSO-d₆, 400 MHz): $\delta = 11.24$ (s, 1H), 9.47 (s, 1H), 8.03 (s, 1H), 7.57 (dd, J = 8.4 Hz, 1.3 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.38-7.34 (m, 3H), 7.18 (d, J = 8.4 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 4.10 (q, J = 7.1 Hz, 2H), 3.99 (s, 2H), 1.33 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): $\delta = 166.84$, 153.61, 137.05, 135.67, 135.31, 130.42, 128.69, 127.19, 122.26, 119.03, 118.40, 118.24, 114.88, 113.43, 60.24, 60.06, 30.21, 14.58, 14.36 ppm. HRMS *m/z* (ESI) calcd

for [C₂₁H₂₂N₂O₄+Na]⁺ 389.1472, found 389.1476.

Ethyl (4-((1-methyl-1*H*-indol-3-yl)methyl)phenyl)carbamate (8h)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and 1-methyl-1*H*-indole (**7h**, 78.6 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 82.5 mg of **8h** (89%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, *v/v*) as the eluent. White solid, m.p. 105.9-106.3 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.48$ (d, J = 7.9 Hz, 1H), 7.27-7.18 (m, 6H), 7.07-7.03 (m, 1H), 6.70 (s, 1H), 6.56 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.03 (s, 2H), 3.68 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.68$, 137.12, 136.45, 135.74, 129.16, 127.71, 127.05, 121.52, 119.13, 118.71, 114.29, 109.09, 100.56, 61.09, 32.52, 30.81, 14.53 ppm. HRMS *m/z* (ESI) calcd for [C₁₉H₂₀N₂O₂+Na]⁺ 331.1417, found 331.1418.

Methyl 3-(4-((ethoxycarbonyl)amino)benzyl)-1-methyl-1*H*-indole-5-carboxylate (8i)



The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and methyl 1-methyl-1*H*-indole-5-carboxylate (**7i**, 113.4 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 99.8 mg of **8i** (91%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1 to 6:1, v/v) as the eluent.

White solid, m.p. 130.6-130.8 °C. ¹H NMR (DMSO-d₆, 400 MHz): $\delta = 9.50$ (s, 1H), 8.10 (t, J = 1.1 Hz, 1H), 7.73 (dd, J = 8.7 Hz, 1.6 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.14-7.12 (m, 3H), 4.06 (q, J = 7.1 Hz, 2H), 3.96 (s, 2H), 3.78 (s, 3H), 3.71 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): $\delta = 167.24$, 153.61, 139.24, 137.13, 134.99, 129.38, 128.62, 126.82, 122.09, 121.35, 119.88, 118.31, 115.26, 109.65, 60.04, 51.67, 32.44, 29.90, 14.54 ppm. HRMS *m*/*z* (ESI) calcd for [C₂₁H₂₂N₂O₄+Na]⁺ 389.1472, found 389.1472.

Ethyl (4-((2,3-dimethyl-3H-indol-3-yl)methyl)phenyl)carbamate (8j)



The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and 2,3-dimethyl-1*H*-indole (**7j**, 87.1 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 70.3 mg of **8j** (73%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1 to 1:1, v/v) as the eluent.

White solid, m.p. 96.7-97.0 °C. ¹H NMR (DMSO-d₆, 400 MHz): δ = 9.40 (s, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.24-7.16 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.16 (d, *J* = 13.6 Hz, 1H), 2.95 (d, *J* = 13.6 Hz, 1H), 2.27 (s, 3H), 1.31 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): δ = 185.94, 154.30, 153.44, 143.49, 137.41, 130.42, 129.24, 127.39, 124.42, 122.65, 119.08, 117.18, 60.04, 58.58, 41.04, 22.08, 16.00, 14.54 ppm. HRMS *m*/z (ESI) calcd for [C₂₀H₂₂N₂O₂+Na]⁺ 345.1574, found 345.1572.

Ethyl (4-((1,2,3,4-tetrahydro-4aH-carbazol-4a-yl)methyl)phenyl)carbamate (8k)



The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and 2,3,4,9-tetrahydro-1*H*-carbazole (**7k**, 102.6 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 77.4 mg of **8k** (74%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1 to 1:1, ν/ν) as the eluent. Light-yellow solid, m.p. 219.4-219.7 °C. ¹H NMR (DMSO-d₆, 400 MHz): $\delta = 9.39$ (s, 1H), 7.38 (dt, J = 7.2 Hz, 0.8 Hz, 1H), 7.28 (dt, J = 7.7 Hz, 1.8 Hz, 1H), 7.23-7.13 (m, 2H), 7.04 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 8.6 Hz, 2H), 4.05 (q, J = 7.1 Hz, 2H), 3.22 (d, J = 13.6 Hz, 1H), 3.11 (d, J = 13.6 Hz, 1H), 2.84-2.79 (m, 1H), 2.71-2.67 (m, 1H), 2.44-2.40 (m, 1H), 2.17-1.99 (m, 2H), 1.66-1.63 (m, 1H), 1.31-1.27 (m, 1H), 1.19 (t, J = 7.1 Hz, 3H), 1.04-0.98 (m, 1H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): $\delta = 187.91$, 154.78, 153.40, 144.65, 137.24, 130.31, 129.19, 127.25, 124.10, 122.54, 119.34, 117.14, 59.98, 58.73, 37.77, 29.98, 28.96, 28.31, 20.72, 14.51 ppm. HRMS *m/z* (ESI) calcd for [C₂₂H₂₄N₂O₂+Na]⁺ 371.1730, found 371.1733.

Ethyl (4-((3,4-dimethoxythiophen-2-yl)methyl)phenyl)carbamate (8l)

MeO S OMe N OEt 81 (62%) The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and 3,4-dimethoxythiophene (**71**, 86.4 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 60.0 mg of **81** (62%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

White solid, m.p. 101.6-101.9 °C. ¹H NMR (DMSO-d₆, 400 MHz): δ = 9.51 (s, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.30 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 2H), 3.70 (s, 3H), 3.64 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): δ = 153.54, 150.11, 143.00, 137.52, 133.76, 128.64, 125.66, 118.28, 93.90, 60.19, 60.04, 56.97, 31.13, 14.51 ppm. HRMS *m/z* (ESI) calcd for [C₁₆H₁₉NO₄S+Na]⁺ 344.0927, found 344.0928.

Ethyl (4-((2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)methyl)phenyl)carbamate (8m)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and 2,3-dihydrothieno[3,4-*b*][1,4] dioxine (**7m**, 85.2 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 57.7 mg of **8m** (60%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1 to 6:1, v/v) as the eluent.

White solid, m.p. 81.3-81.9 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.29$ (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 6.58 (s, 1H), 6.13 (s, 1H), 4.23-4.16 (m, 6H), 3.91 (s, 2H), 1.29 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 141.47$, 137.80, 136.20, 134.97, 129.05, 118.78, 116.72, 96.26, 64.66, 64.60, 61.15, 31.24, 14.53 ppm. HRMS *m/z* (ESI) calcd for [C₁₆H₁₇NO₄S+Na]⁺ 342.0771, found 342.0771.

Ethyl (4-((1*H*-pyrrol-2-yl)methyl)phenyl)carbamate (8n)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and 1*H*-pyrrole (**7n**, 40.2 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 61.8 mg of **8n** (84%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent.

Light-yellow solid, m.p. 50.8-51.4 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.86$ (s, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 1.5 Hz, 1H), 6.59 (s, 1H), 6.13 (q, J = 2.8 Hz, 1H), 5.97 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.92 (s, 2H), 1.30 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.70$,

136.26, 134.51, 130.69, 129.23, 119.04, 116.93, 108.28, 106.31, 61.20, 33.35, 15.52 ppm. **HRMS** *m/z* (**ESI**) calcd for [C₁₄H₁₆N₂O₂+Na]⁺ 267.1104, found 267.1108.

Ethyl (4-((5-pivalamidoquinolin-8-yl)methyl)phenyl)carbamate (80)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and *N*-(quinolin-5-yl)pivalamide (**7o**, 136.8 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 68.4 mg of **8o** (56%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1 to 6:1, v/v) as the eluent.

White solid, m.p. 173.2-174.0 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 10.29$ (s, 1H), 8.77 (d, J = 4.0 Hz, 1H), 8.73 (d, J = 7.9 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.38-7.35 (m, 2H), 7.26 (d, J = 7.8 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 6.63 (s, 1H), 4.31 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.42 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 177.17$, 153.67, 147.68, 139.29, 136.18, 135.28, 133.60, 133.15, 130.29, 128.88, 128.39, 126.70, 121.24, 118.86, 115.77, 61.07, 40.26, 37.61, 27.68, 14.48 ppm. HRMS *m/z* (ESI) calcd for [C₂₄H₂₇N₃O₃+Na]⁺ 406.2125, found 406.2130.

Ethyl (4-(2,4,6-trimethoxybenzyl)phenyl)carbamate (8p)

The reaction of 0.3 mmol of imidated *p*-tolylcarbamate **2a** (142.2 mg) and 1,3,5-trimethoxybenzene (**7p**, 100.8 mg) with KOH (33.6 mg) in HFIP (2 mL) at 40 °C in argon afforded 60.3 mg of **8p** (58%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent. White solid, m.p. 350.6-351.0 °C. ¹H NMR (CDCl₃, **400** MHz): δ = 7.20-7.14 (m, 4H), 6.51 (s, 1H), 6.13 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 2H), 3.79 (s, 3H), 3.77 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 159.52, 158.68, 153.71, 137.39, 135.14, 128.83, 118.52, 110.17, 90.50, 60.93, 55.60, 55.23, 27.53, 14.49 ppm. HRMS *m/z* (ESI) calcd for [C₁₉H₂₃NO₅+Na]⁺ 368.1468, found 368.1467.

5) Tandem imidation-alkoxylation from *p*-tolylcarbamates 1 without isolation of 2 (Table <u>6, 6a-6t)</u>



Typical Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of *p*-tolylcarbamate (**1**, 0.3 mmol) and TEMPO (4.7 mg, 0.03 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, the reaction was quenched with Na₂CO₃ (2M, aq., 2 mL) and extracted with EtOAc (4 mL). The organic layer was concentrated *in vacuo*, dissolved in alcohols (**5**, 1 mL), and added to a reaction tude charged with KOH (67.2 mg, 1.2 mmol) under argon (1 atm). After stirring at 25°C for another 4 hours, the mixture was concentrated *in vacuo*, followed by purification via flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford corresponding benzylic ethers **6**.

Ethyl (4-(methoxymethyl)phenyl)carbamate (6a)

MeO OEt 6a 83% (87%)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with methanol (**5a**, 1 mL) afforded 51.8 mg of **6a** (83%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent. For comparison, the 87% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 96% yield of **6a** in Table 4.

Ethyl (4-((hexyloxy)methyl)phenyl)carbamate (6d)

H₃C(H₂C)₅O H₃C(H₂C)₅O OEt 6d 76% (82%)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with hexanol (**5d**, 1 mL) afforded 63.5 mg of **6d** (76%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent. For comparison, the 82% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 90% yield of **6d** in Table 4.

Ethyl (4-(((3-methylbut-2-en-1-yl)oxy)methyl)phenyl)carbamate (6g)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with 3-methylbut-2-en-1-ol (**5g**, 1 mL) afforded 59.4 mg of **6g** (75%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent. For comparison, the 80% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 88% yield of **6g** in Table 4.

Ethyl (4-((but-2-yn-1-yloxy)methyl)phenyl)carbamate (6i)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with but-2-yn-1-ol (**5i**, 1 mL) afforded 50.7 mg of **6i** (68%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent. For comparison, the 79% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 87% yield of **6i** in Table 4.

Ethyl (4-((2-cyanoethoxy)methyl)phenyl)carbamate (6j)

NC(H₂C)₂O

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with 3-hydroxypropanenitrile (**5j**, 1 mL) afforded 42.7 mg of **6j** (57%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent. For comparison, the 69% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 76% yield of **6j** in Table 4.

Ethyl (E)-(4-(((3,7-dimethylocta-2,6-dien-1-yl)oxy)methyl)phenyl)carbamate (6m)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with (*E*)-3,7-dimethylocta-2,6-dien-1-ol (geraniol, **5m**, 1 mL) afforded 60.9 mg of **6m** (61%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent. For comparison, the 66% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 73% yield of **6m** in Table 4.

4-((Ethoxycarbonyl)amino)benzyl acetate (6p)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with sodium acetate (**5p**, 49.2 mg, 0.6 mmol) and KOH (33.6 mg, 0.6 mmol) afforded 49.6 mg of **6p** (70%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent. For comparison, the 60% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 66% yield of **6m** in Table 4.

Isopropyl (4-(methoxymethyl)phenyl)carbamate (6q)

The tandem reaction of 0.3 mmol of isopropyl *p*-tolylcarbamate (57.9 mg, **1h**) as the starting material with methanol (**5a**, 1 mL) afforded 47.7 mg of **6q** (71%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent.

Light-yellow oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.36$ (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 6.68 (s, 1H), 5.02 (h, J = 6.3 Hz, 1H), 4.40 (s, 2H), 3.36 (s, 3H), 1.29 (d, J = 6.3 Hz, 6H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.18$, 137.59, 132.85, 128.66, 118.42, 74.22, 68.68, 57.83, 22.05 ppm. HRMS *m*/z (ESI) calcd for [C₁₂H₁₇NO₃+Na]⁺ 246.1101, found 246.1099.

Tert-Pentyl (4-(methoxymethyl)phenyl)carbamate (6r)

The tandem reaction of 0.3 mmol of *tert*-pentyl *p*-tolylcarbamate (66.3 mg, **1i**) as the starting material with methanol (**5a**, 1 mL) afforded 64.3 mg of **6r** (85%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent.

Light-yellow oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.34$ (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 6.58 (s, 1H), 4.40 (s, 2H), 3.35 (s, 3H), 1.84 (q, J = 7.5 Hz, 2H), 1.48 (s, 6H), 0.93 (t, J = 7.5 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 152.66$, 137.87, 132.60, 128.62, 118.34, 82.92, 74.24, 57.80, 33.57, 25.76, 8.27 ppm. HRMS *m*/z (ESI) calcd for [C₁₄H₂₁NO₃+Na]⁺ 274.1414, found 274.1416.

Ethyl (4-(methoxymethyl)-3-methylphenyl)carbamate (6s)

The tandem reaction of 0.3 mmol of ethyl (3,4-dimethylphenyl)carbamate (57.9 mg, **1b**) as the starting material with methanol (**5a**, 1 mL) afforded 44.4 mg of **6s** (66%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent.

Light-yellow oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.23-7.21$ (m, 2H), 7.26 (dd, J = 8.3 Hz, 2.0 Hz, 1H), 6.66 (s, 1H), 4.40 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 3.37 (s, 3H), 2.31 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 153.57$, 137.88, 137.51, 131.05, 129.61, 120.28, 115.68, 72.59, 61.1, 57.91, 18.84, 14.52 ppm. HRMS *m/z* (ESI) calcd for [C₁₂H₁₇NO₃+Na]⁺ 246.1101, found 246.1101.

Ethyl (3-fluoro-4-(methoxymethyl)phenyl)carbamate (6t)

The tandem reaction of 0.3 mmol of ethyl (3-fluoro-4-methylphenyl)carbamate (59.1 mg, **1e**) as the starting material with methanol (**5a**, 1 mL) afforded 28.9 mg of **6t** (42%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent.

Light-yellow oil. ¹**H NMR (CDCl₃, 400 MHz)**: $\delta = 9.89$ (s, 1H), 7.38 (dd, J = 10.6 Hz, 2.1 Hz, 1H), 7.30 (t, J = 8.4 Hz, 1H), 7.20 (dd, J = 8.4 Hz, 2.1 Hz, 1H), 4.36 (s, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.25 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H) ppm. ¹³**C NMR (CDCl₃, 100 MHz)**: $\delta = 160.44$ (d, J = 241.9 Hz), 153.41, 140.72 (d, J = 11.2 Hz), 131.03 (d, J = 6.0 Hz), 118.24 (d, J = 15.3 Hz), 113.55, 104.58 (d, J = 26.4 Hz), 67.08 (d, J = 2.6 Hz), 60.43, 57.35, 14.45 ppm. **HRMS** *m/z* (**ESI**) calcd for [C₁₁H₁₄FNO₃+Na]⁺ 228.1031, found 228.1031.

6) Tandem imidation-arylation from *p*-tolylcarbamates 1 without isolation of 2 (Table 6, <u>8a-8s)</u>



Typical Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of *p*-tolylcarbamate (**1**, 0.3 mmol) and TEMPO (4.7 mg, 0.03 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, the reaction was quenched with Na₂CO₃ (2M, aq., 2 mL) and extracted with EtOAc (4 mL). The organic layer was concentrated *in vacuo*, dissolved in HFIP (2 mL), and added to a reaction tude charged with KOH (34.6 mg, 0.6 mmol) and arene (**7**, 0.9 mmol) at 25 °C under argon (1 atm). After stirring at 40°C for another 4 hours, the mixture was concentrated *in vacuo*, followed by purification via flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford corresponding benzylated arene **8**.

Ethyl (4-((1*H*-indol-3-yl)methyl)phenyl)carbamate (8a)

H OEt 8a 69% (78%)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with 1*H*-indole (**7a**, 105.3 mg) afforded 61.1 mg of **8a** (69%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent. For comparison, the 78% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 86% yield of **8a** in Table 5.

Ethyl (4-((6-fluoro-1*H*-indol-3-yl)methyl)phenyl)carbamate (8e)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with 6-fluoro-1*H*-indole (**7e**, 121.5 mg) afforded 61.2 mg of **8e** (65%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent. For comparison, the 81% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 89% yield of **8e** in Table 5.

Ethyl (4-((6-fluoro-1*H*-indol-3-yl)methyl)phenyl)carbamate (8g)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with ethyl 1*H*-indole-6-carboxylate (**7g**, 170.1 mg) afforded 80.4 mg of **8g** (73%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent. For comparison, the 71% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 78% yield of **8g** in Table 5.

Ethyl (4-((1-methyl-1*H*-indol-3-yl)methyl)phenyl)carbamate (8h)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with 1-methyl-1*H*-indole (**7h**, 117.9 mg) afforded 58.6 mg of **8h** (63%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent. For comparison, the 81% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 89% yield of **8h** in Table 5.

Ethyl (4-((2,3-dimethyl-3H-indol-3-yl)methyl)phenyl)carbamate (8j)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with 2,3-dimethyl-1*H*-indole (**7j**, 130.6 mg) afforded 69.8 mg of **8j** (72%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1 to 1:1, v/v) as the eluent. For comparison, the 66% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 73% yield of **8j** in Table 5.

Ethyl (4-((3,4-dimethoxythiophen-2-yl)methyl)phenyl)carbamate (8l)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with 3,4-dimethoxythiophene (**7l**, 129.6 mg) afforded 51.4 mg of **8l** (53%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v/v) as the eluent. For comparison, the 56% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 62% yield of **8l** in Table 5.

Ethyl (4-((8-pivalamidoquinolin-5-yl)methyl)phenyl)carbamate (80)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with *N*-(quinolin-5-yl)pivalamide (**7o**, 205.2 mg) afforded 63.5 mg of **8o** (52%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1 to 6:1, v/v) as the eluent. For comparison, the 51% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 56% yield of **8o** in Table 5.

Ethyl (4-(2,4,6-trimethoxybenzyl)phenyl)carbamate (8p)

The tandem reaction of 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg) as the starting material with 1,3,5-trimethoxybenzene (**7p**, 151.2 mg) afforded 53.1 mg of **8p** (51%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent. For comparison, the 53% yield in parenthesis is calculated by multiplying the 91% yield of **2a** in Table 3 with the 58% yield of **8p** in Table 5.

Isopropyl (4-((1*H*-indol-3-yl)methyl)phenyl)carbamate (8q)

₩ 0 (74%)

The tandem reaction of 0.3 mmol of isopropyl *p*-tolylcarbamate (**1h**, 57.9 mg) as the starting material with 1*H*-indole (**7a**, 105.3 mg) afforded 68.7 mg of **8q** (74%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent.

White solid, m.p. 129.1-130.0 °C. ¹H NMR (DMSO-d₆, 400 MHz): δ =10.78 (s, 1H), 9.39 (s, 1H), 7.36-7.28 (m, 4H), 7.14-7.07 (m, 3H), 7.00 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 4.82 (h, *J* = 6.2 Hz, 1H), 3.92 (s, 2H), 1.19 (d, *J* = 6.2 Hz, 6H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): δ = 153.18, 136.97, 136.42, 135.56, 128.62, 126.95, 122.97, 120.90, 118.57, 118.21, 114.13, 111.36, 67.23, 30.47, 22.00 ppm. HRMS *m/z* (ESI) calcd for [C₁₉H₂₀N₂O₂+Na]⁺ 331.1417, found 331.1425.

Tert-Pentyl (4-((1*H*-indol-3-yl)methyl)phenyl)carbamate (8r)



The tandem reaction of 0.3 mmol of *tert*-pentyl *p*-tolylcarbamate (66.3 mg, **1i**) as the starting material with 1*H*-indole (**7a**, 105.3 mg) afforded 61.5 mg of **8r** (61%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent.

Colourless oil. ¹H NMR (DMSO-d₆, 400 MHz): $\delta = 10.78$ (s, 1H), 9.17 (s, 1H), 7.35 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.30-7.28 (m, 3H), 7.11 (d, J = 8.6 Hz, 2H), 7.07 (d, J = 2.4 Hz, 1H), 7.00 (td, J = 8.2 Hz, 1.1 Hz, 1H), 6.87 (td, J = 8.0 Hz, 1.0 Hz, 1H), 3.91 (s, 2H), 1.74 (q, J = 7.5 Hz, 2H), 1.37 (s, 6H), 0.84 (t, J = 7.5 Hz, 3H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): $\delta = 152.77$, 137.21, 136.43, 135.29, 128.55, 126.95, 122.96, 120.89, 118.58, 118.19, 114.17, 111.36, 80.99, 32.97, 30.47, 25.71, 8.18 ppm. HRMS *m*/z (ESI) calcd for [C₂₁H₂₄N₂O₂+Na]⁺ 357.1730, found 359.1727.

Ethyl (4-((1*H*-indol-3-yl)methyl)-3-methylphenyl)carbamate (8s)

Me H OEt 8s (66%)

The tandem reaction of 0.3 mmol of ethyl (3,4-dimethylphenyl)carbamate (57.9 mg, **1b**) as the starting material with 1*H*-indole (**7a**, 105.3 mg) afforded 61.6 mg of **8s** (66%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 8:1, v/v) as the eluent.

Colourless oil. ¹**H NMR (DMSO-d₆, 400 MHz)**: δ =10.77 (s, 1H), 9.40 (s, 1H), 7.38 (dd, *J* = 7.9 Hz, 1.0 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.22-7.14 (m, 2H), 7.03-6.99 (m, 2H), 6.91-6.87 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 2.20 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm. ¹³**C NMR (DMSO-d₆, 100 MHz)**: δ = 153.59, 137.00, 136.41, 136.12, 133.48, 129.33, 127.09, 123.13, 120.91, 119.91, 118.55, 118.22, 115.75, 113.13, 111.40, 59.97, 28.23, 19.45, 14.57 ppm. **HRMS** *m*/*z* (**ESI**) calcd for [C₁₉H₂₀N₂O₂+Na]⁺ 331.1417, found 331.1419.

7) Applications to the preparation of key intermediates for the synthesis of bioactive molecules (Scheme 2)



Typical Procedure for deprotection: To a reaction tube charged with benzyl ether **6** or benzylated arene **8** (0.3 mmol) was added a solution of Bu_4NF (1.5 mL of 1.0 M solution in THF, 1.5mmol) under argon (1 atm). After stirring under reflux for 12 hours, the mixture was concentrated *in vacuo*, followed by purification via flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford corresponding aniline **9**.

4-(Methoxymethyl)aniline (9a)

MeO (96%)

The deprotection of 0.3 mmol of ethyl (4-(methoxymethyl)phenyl)carbamate (62.7 mg, **6a**) afforded 39.6 mg of **9a** (96%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1, v/v) as the eluent.

White solid, m.p. 166.8-167.4 °C. ¹H NMR (DMSO-d₆, 400 MHz): $\delta = 6.92$ (d, J = 8.4 Hz, 2H), 6.48 (d, J = 8.4 Hz, 2H), 5.01 (s, 2H), 4.14 (s, 2H), 3.15 (s, 3H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): $\delta = 148.22$, 129.26, 124.96, 113.48, 73.94, 56.72 ppm. HRMS *m*/*z* (ESI) calcd for [C₈H₁₁NO+H]⁺ 138.0913, found 138.0910.

4-(Ethoxymethyl)aniline (9b)

Eto NH₂ 9b (92%)

The deprotection of 0.3 mmol of ethyl (4-(ethoxymethyl)phenyl)carbamate (66.9 mg, **6b**) afforded 41.9 mg of **9b** (92%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1, v/v) as the eluent.

Colourless oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.12$ (d, J = 8.3 Hz, 2H), 6.63 (d, J = 8.4 Hz, 2H), 4.37 (s, 2H), 3.58 (brs, 2H), 3.49 (q, J = 7.0 Hz, 2H), 1.21 (t, J = 7.0 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 145.89$, 129.32, 128.27, 114.85, 72.52, 65.08, 15.15 ppm. HRMS *m*/z (ESI) calcd for [C₉H₁₃NO+H]⁺ 152.1070, found 152.1067.

4-(2,4,6-Trimethoxybenzyl)aniline (9p)

The deprotection of 0.3 mmol of ethyl (4-(2,4,6-trimethoxybenzyl)phenyl)carbamate (103.5 mg, **8p**) afforded 78.1 mg of **9p** (95%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, v/v) as the eluent.

Light-yellow solid, m.p. 110.0-110.7 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.04$ (d, J = 8.4 Hz, 2H), 6.55 (d, J = 8.3 Hz, 2H), 6.14 (s, 2H), 3.82 (s, 2H), 3.79 (s, 3H), 3.77 (s, 6H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 159.35$, 158.70, 143.67, 132.42, 129.09, 115.03, 110.86, 90.55, 55.64, 55.63, 55.25, 27.27 ppm. HRMS *m*/z (ESI) calcd for [C₉H₁₃NO+H]⁺ 152.1070, found 152.1067.



Typical Procedure: To a reaction tube charged with CuCl (9.9 mg, 0.1 mmol) and NFSI (1.26 g, 4 mmol) was added a solution of ethyl *p*-tolylcarbamate (**1a**, 358.2 mg, 2 mmol) and TEMPO (31.3 mg, 0.2 mmol) in anhydrous acetonitrile (10 mL) under argon (1 atm). After stirring at 25°C for 12 hours, the reaction was quenched with Na₂CO₃ (2M, aq., 2 mL) and extracted with EtOAc (4 mL). The organic layer was concentrated *in vacuo*, dissolved in HFIP (12 mL), and added to a reaction tude charged with KOH (224.4 mg, 4 mmol) and methyl 1-methyl-1*H*-indole-5-carboxylate (**7i**, 756.3 mg, 4 mmol) at 25 °C under argon (1 atm). After stirring at 40°C for another 4 hours, the mixture was concentrated *in vacuo*, followed by purification via flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford 556.4 mg of methyl 3-(4-((ethoxycarbonyl)amino)benzyl)-1-methyl-1*H*-indole-5-carboxylate (**8i**, 76%).

Subsequently, to a reaction tube charged with the above **8i** (556.4 mg, 1.52 mmol) was added a solution of Bu_4NF (10 mL of 1.0 M solution in THF, 10 mmol) under argon (1 atm). After stirring under reflux for 12 hours, the mixture was concentrated *in vacuo*, followed by purification via flash chromatography on silica gel using petroleum ether and ethyl acetate as the effluent to afford 420.6 mg of methyl 3-(4-aminobenzyl)-1-methyl-1*H*-indole-5-carboxylate (**11**, 94%).

Methyl 3-(4-aminobenzyl)-1-methyl-1H-indole-5-carboxylate (11)



Synthesis of key intermediate **11** from 0.3 mmol of ethyl *p*-tolylcarbamate (**1a**, 358.2 mg, 2 mmol) afforded 420.6 mg of **11** (71% total yield from **1a**) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, v/v) as the eluent. For comparison, the literature reported total yield of the identical intermediate from the same amount of starting material is 53%.

White solid, m.p. 149.4-150.0 °C. ¹H NMR (DMSO-d₆, 400 MHz): δ = 8.08 (d, *J* = 1.6 Hz, 1H), 7.71 (dd, *J* = 8.6 Hz, 1.6 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.13 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.44 (d, *J* = 8.4 Hz, 2H), 4.80 (s, 2H), 3.85 (s, 2H), 3.78 (s, 3H), 3.73 (s, 3H) ppm. ¹³C NMR (DMSO-d₆, 100 MHz): δ = 167.23, 146.54, 139.20, 129.17, 128.75, 127.95, 126.87, 121.95, 121.40, 119.69, 116.05, 113.94, 109.59, 51.65, 32.43, 29.74 ppm. HRMS *m/z* (ESI) calcd for [C₁₈H₁₈N₂O₂+H]⁺ 317.1261, found 317.1261.
Control Experiments

1) To demonstrate the crucial role of the carbamate directing group (Scheme 3)



Experimental Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of TEMPO (4.7 mg, 0.03 mmol) and ethyl *m*-tolylcarbamate (**11**, 53.7 mg, 0.3 mmol) or ethyl *o*-tolylcarbamate (**1m**, 53.7 mg, 0.3 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, no corresponding benzylic imidated product **2l** or **2m** could be observed on GC-MS.



Experimental Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of ethyl methyl(*p*-tolyl)carbamate (**1n**, 57.9 mg, 0.3 mmol) and TEMPO (4.7 mg, 0.03 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, the mixture was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford 23.6 mg of **2n** (16%).

To a reaction tube charged with imidated *p*-tolylcarbamate **2n** (146.4 mg, 0.3 mmol) was added a suspension of KOH (67.2 mg, 1.2 mmol) in methanol (**5a**, 1 mL) under argon (1 atm). After stirring at 25°C for 4 hours, no corresponding benzyl ether **6u** could be observed on GC-MS.

To a reaction tube charged with imidated *p*-tolylcarbamate **2n** (146.4 mg, 0.3 mmol) and KOH (33.6 mg, 0.6 mmol) was added a solution of 1*H*-indole (**7a**, 70.2 mg, 0.6 mmol) in HFIP (2 mL) under argon (1 atm). After stirring at 40°C for 4 hours, no corresponding benzylated indole **8u** could be observed on GC-MS.

Ethyl methyl(4-((*N*-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (2n)

The reaction of 0.3 mmol of ethyl methyl(*p*-tolyl)carbamate (**1n**, 57.9 mg) and NFSI (189 mg) with CuCl (1.5 mg) and TEMPO (4.7 mg) at 25 °C in argon afforded 23.6 mg of **2n** (16%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent.

White solid, m.p. 137.0-137.9 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 7.77-7.75 (m, 4H), 7.55-7.51 (m, 2H), 7.41-7.37 (m, 4H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 4.89 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.25 (s, 1H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 155.33, 143.16, 139.77, 133.52, 129.55, 129.35, 128.69, 127.89, 125.26, 61.63, 51.84, 37.41, 14.50 ppm. HRMS *m/z* (ESI) calcd for [C₂₃H₂₄N₂O₆S₂+Na]⁺ 511.0968, found 511.0964.



Experimental Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of TEMPO (4.7 mg, 0.03 mmol) and toluene, *N*,4-dimethylaniline, *N*,*N*,4-trimethylaniline, 1-methoxy-4-methylbenzene or *p*-xylene (0.3 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, no corresponding benzylic imidated product could be observed on GC-MS.

To a reaction tube charged with *N*-benzyl-*N*-(phenylsulfonyl)benzenesulfonamide, *N*-(4-methylbenzyl)-*N*-(phenylsulfonyl)benzenesulfonamide or *N*-(4-methoxybenzyl)-*N*-(phenylsulfonyl)benzenesulfonamide (0.3 mmol) was added a suspension of KOH (67.2 mg, 1.2 mmol) in methanol (**5a**, 1 mL) under argon (1 atm). After stirring at 25°C for 4 hours, no corresponding benzyl ether could be observed on GC-MS.

To a reaction tube charged with *N*-benzyl-*N*-(phenylsulfonyl)benzenesulfonamide, *N*-(4-methylbenzyl)-*N*-(phenylsulfonyl)benzenesulfonamide or *N*-(4-methoxybenzyl)-*N*-(phenylsulfonyl)benzenesulfonamide (0.3 mmol) and KOH (33.6 mg, 0.6 mmol) was added a solution of 1*H*-indole (**7a**, 70.2 mg, 0.6 mmol) in HFIP (2 mL) under argon (1 atm). After stirring at 40°C for 4 hours, no corresponding benzylated indole could be observed on GC-MS.



Experimental Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of ethyl mesitylcarbamate (**1o**, 62.1 mg, 0.3 mmol) and TEMPO (4.7 mg, 0.03 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, the mixture was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford 19.3 mg of **2o** (13%).

Ethyl (2,6-dimethyl-4-((*N*-(phenylsulfonyl)phenylsulfonamido)methyl)phenyl)carbamate (20)

The reaction of 0.3 mmol of ethyl methyl(*p*-tolyl)carbamate (**10**, 62.1 mg) and NFSI (189 mg) with CuCl (1.5 mg) and TEMPO (7.0 mg) at 25 °C in argon afforded 19.3 mg of **20** (13%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (6:1 to 3:1, v/v) as the eluent.

Light-yellow oil. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.80-7.78$ (m, 4H), 7.60-7.56 (m, 2H), 7.48-7.44 (m, 4H), 6.98 (s, 2H), 5.96 (s, 1H), 4.87 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 2.14 (s, 6H), 1.25 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 154.26$, 139.84, 135.88, 133.57, 132.83, 128.74, 128.58, 128.03, 60.30, 52.13, 18.11, 14.59 ppm. HRMS *m/z* (ESI) calcd for [C₂₄H₂₆N₂O₆S₂+Na]⁺ 525.1125, found 525.1129.

1a (0.3 mmol)	NFSI	CuCl (0.015 mmol) TEMPO (0.03 mmol)	1a (31%)
1d (0.3 mmol)	+ (0.3 mmol)	MeCN (2 mL) 25 °C, 12 h	+ 1d (14%)

Experimental Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (94.6 mg, 0.3 mmol) was added a solution of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg, 0.3 mmol), ethyl (2,4-dimethylphenyl)carbamate (**1d**, 57.9 mg, 0.3 mmol) and TEMPO (4.7 mg, 0.03 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, the mixture was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford 44.3 mg of **2a** (31%) and 20.7 mg of **2d** (14%).

1a (0.3 mmol)	NFSI	CuCl (0.015 mmol) TEMPO (0.03 mmol)	1a (40%) + 1o (0%)
1o (0.3 mmol)	• (0.3 mmol)	MeCN (2 mL) 25 °C, 12 h	

Experimental Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (94.6 mg,

0.3 mmol) was added a solution of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg, 0.3 mmol), ethyl mesitylcarbamate (**1o**, 62.1 mg, 0.3 mmol) and TEMPO (4.7 mg, 0.03 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, the mixture was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford 57.2 mg of **2a** (40%), whereas no **2o** could be observed on GC-MS.

2) To indicate some key differences compared to the previous palladium-catalysed benzylic C-H imidation with NFSI (Scheme 4)



Experimental Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (94.6 mg, 0.3 mmol) was added a solution of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg, 0.3 mmol), *N*-(p-tolyl)acetamide (**3a**, 44.7 mg, 0.3 mmol) and TEMPO (4.7 mg, 0.03 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, the mixture was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford 62.9 mg of **2a** (44%) and 27.6 mg of **4a** (21%).

N-(4-((N-(Phenylsulfonyl)phenylsulfonamido)methyl)phenyl)acetamide (4a)

White solid, m.p. 164.5-165.0 °C. ¹H NMR (DMSO-d₆, 400 MHz): $\delta = 9.99$ (s, 1H), 7.80-7.71 (m, 6H), 7.59-7.52 (m, 6H), 7.25 (d, J = 8.5 Hz, 2H), 4.97 (s, 2H), 2.08 (s, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 168.73$, 139.69, 137.92, 133.71, 130.06, 129.75, 128.83, 127.94, 119.61, 51.95, 24.44 ppm. HRMS *m*/*z* (ESI) calcd for [C₂₁H₂₀N₂O₅S₂+H]⁺ 445.0886, found 445.0884.



Experimental Procedure: To a reaction tube charged with the imidated *p*-tolylcarbamate **2a** (142.2 mg, 0.3 mmol) and the imidated *p*-tolylacetamide **4a** (133.2 mg, 0.3 mmol) was added a suspension of KOH (50.5 mg, 0.9 mmol) in methanol (**5a**, 1 mL) under argon (1 atm). After stirring at 25°C for 4 hours, the mixture was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford 52.9 mg of **6a** (84%) and 13.8 mg of **4b** (26%).

N-(4-(Methoxymethyl)phenyl)acetamide (4b)

White solid, m.p. 98.0-98.5 °C. ¹H NMR (CDCl₃, 400 MHz): $\delta = 7.48$ (d, J = 8.3 Hz, 2H), 7.36 (s, 1H), 7.28 (d, J = 8.3 Hz, 2H), 4.41 (s, 2H), 3.37 (s, 3H), 2.17 (s, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta = 168.31$,

137.34, 134.05, 128.53, 119.75, 74.21, 57.96, 24.58 ppm. **HRMS** *m*/*z* (**ESI**) calcd for [C₁₀H₁₃NO₂+Na]⁺ 202.0839, found 202.0837.



Experimental Procedure: To a reaction tube charged with the imidated *p*-tolylcarbamate **2a** (142.2 mg, 0.3 mmol), the imidated *p*-tolylacetamide **4a** (133.2 mg, 0.3 mmol) and KOH (33.6 mg, 0.6 mmol) was added a solution of 1*H*-indole (**7a**, 70.2 mg, 0.6 mmol) in HFIP (2 mL) under argon (1 atm). After stirring at 40°C for 4 hours, the mixture was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford 55.7 mg of **8a** (63%), whereas no **4c** could be observed on GC-MS.



Experimental Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg, 0.3 mmol), H₂O (6 μ L, 0.3 mmol) and TEMPO (4.7 mg, 0.03 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, the mixture was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford corresponding 72.8 mg of the benzylic imidated *p*-tolylcarbamate **2a** (51%).

To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg, 0.3 mmol), H₂O (11 μ L, 0.6 mmol) and TEMPO (4.7 mg, 0.03 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, the mixture was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford corresponding 55.2 mg of the benzylic imidated *p*-tolylcarbamate **2a** (39%).

To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg, 0.3 mmol), H₂O (22 μ L, 1.2 mmol) and TEMPO (4.7 mg,

0.03 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, the mixture was concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to afford corresponding 37.3 mg of the benzylic imidated *p*-tolylcarbamate **2a** (26%).

To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of ethyl *p*-tolylcarbamate (**1a**, 53.7 mg, 0.3 mmol), H₂O (54 μ L, 3 mmol) and TEMPO (4.7 mg, 0.03 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, no benzylic imidated *p*-tolylcarbamate **2a** could be observed on GC-MS.

3) To support the radical pathway proposed in Scheme 5



Experimental Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of TEMPO (93.8 mg, 0.6 mmol) and ethyl *p*-tolylcarbamate (**1a**, 53.7 mg, 0.3 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, only trace amount of benzylic imidated product **2a** could be observed on TLC.

To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of TEMPO (187.5 mg, 1.2 mmol) and ethyl *p*-tolylcarbamate (**1a**, 53.7 mg, 0.3 mmol) in anhydrous acetonitrile (2 mL) under argon (1 atm). After stirring at 25°C for 12 hours, only trace amount of benzylic imidated product **2a** could be observed on TLC.



Experimental Procedure: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189 mg, 0.6 mmol) was added a solution of TEMPO (4.7 mg, 0.03 mmol) and ethyl *p*-tolylcarbamate (**1a**, 53.7 mg, 0.3 mmol) in anhydrous acetonitrile (1 mL) under argon (1 atm). Then a solution of DMPO (101.8 mg, 0.9 mmol) in anhydrous acetonitrile (1 mL) was added immediately. After stirring at 25°C for 30 minutes, the reaction mixture was investigated by ESI-HRMS.

The DMPO adduct of the benzylic radical: calcd for $[C_{16}H_{23}N_2O_3]^+$ 291.1703, found 291.1715. The DMPO adduct of TEMPO: calcd for $[C_{15}H_{29}N_2O_2]^+$ 269.2224, found 269.2226. The TEMPO adduct of the benzylic radical: calcd for $[C_{19}H_{30}N_2O_3+H]^+$ 335.2329, found 335.2325.







S48













S54











S59































































































































S122













S128
































































