1. General remarks

Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Solvents were dried and purified according to the standard procedures before use. Reactions were monitored by TLC. Flash column chromatography was performed on silica gels (200-300 mesh). $^1$H NMR and $^{13}$C NMR (300 and 75 MHz, respectively) spectra were recorded on a Bruker 300 MHz NMR spectrometer in CDCl$_3$. $^1$H NMR chemical shifts are reported in ppm ($\delta$) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl$_3$, $\delta$ 7.26 ppm, DMSO-$d_6$ at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, td = triplet of doublets, q = quartet, m = multiplet), coupling constants (Hz) and integration. $^{13}$C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl$_3$, $\delta$ 77.0 ppm). HRMS data were obtained on a Bruker Daltonics. Inc mass instrument (ESI).

2. Procedures and characterizations data of compounds

2.1 Synthesis of quinone monoacetals 1a-1j:

Quinone monoacetals 1a-1j were prepared according to known procedures. Quinone imine ketals 1k and 1l were prepared according to known procedures.\textsuperscript{1b,2}

2.2 Synthesis of vinylcarbamates 2a-2c:

![Reaction equation]

Benzyl vinylcarbamate (2a) was prepared according to a known procedure\textsuperscript{3} with minor modification: Acryloyl chloride (5.2 mL, 64 mmol) diluted with 50 mL of toluene was added dropwise to a cooled (0°C) solution of sodium azide (5 g, 77 mmol) in 50 mL of distilled water. The mixture was stirred vigorously at 0°C for 5 h. The organic layer was separated and washed with 10 mL of 10% aqueous sodium carbonate (3 x 50 mL) and then with cold distilled water (3 x 50 mL). The organic solution was dried over NaSO$_4$ before using in the subsequent step.
The toluene solution of acryloyl azide was added dropwise to a stirred and heated (100°C) mixture of hydroquinone (330 mg, 3 mmol), pyridine (300 µL, 3.8 mmol), and benzyl alcohol (8 mL, 77 mmol). The mixture was stirred for 30 min at 120°C after completion of addition, the solvent was removed by rotary evaporation to give the crude product which was purified by flash column chromatography (PE : EA = 50 : 1) to give a colorless solid (60%). It was stored at low temperature (< 0 °C)

Vinylcarbamates 2b and 2c were prepared following the same procedure.

2.3 General procedure for the [3+2] coupling of quinone monoacetals or quinone imine ketal 1 with vinylcarbamates 2:

Quinone monoacetal or quinone imine ketal 1 (0.30 mmol) and vinylcarbamate 2 (0.20 mmol) were added to a flame-dried vial equipped with a magnetic stirring bar. Then 2 mL of CH3CN was added to dissolve the mixture. Afterwards Cu(OTf)2 (10.8 mg, 0.02 mmol) was introduced in the solution. The reaction mixture was stirred at 25 °C for 12h. Then the solvent was evaporated and the residue was subjected to chromatography (silica gel, petroleum ether/EtOAc: 20/1 to 10/1) to afford the desired product 3.

2.4 Characterizations of compounds 3a-3n

**Benzyl (5-methoxy-2,3-dihydrobenzofuran-2-yl)carbamate (3a):** Yield 84%.

White solid. 1H NMR (300 MHz, CDCl3): δ 7.26-7.35 (m, 5H), 6.65-6.74 (m, 3H), 6.26 (brs, 1H), 5.75 (d, J = 8.8 Hz, 1H), 5.08-5.18 (m, 2H), 3.74 (s, 3H), 3.49 (dd, J1 = 8.3 Hz, J2 = 16.4 Hz, 1H), 2.89 (dd, J1 = 16.5 Hz, J2 = 4.5 Hz, 1H).


**Benzyl (7-bromo-5-methoxy-2,3-dihydrobenzofuran-2-yl)carbamate (3b):** Yield: 82%. Colorless oil. 1H NMR (300 MHz, CDCl3): δ 7.35-7.26 (m, 5 H), 6.83 (d, J = 2.1 Hz, 1H), 6.68 (s, 1H), 6.32 (brs, 1H), 5.75 (brs,
1H), 5.10-5.20 (m, 2H), 3.72 (s, 3H), 3.55 (dd, \( J_1 = 8.5 \text{ Hz} \), \( J_2 = 16.7 \text{ Hz} \), 1H), 3.00 (dd, \( J_1 = 16.6 \text{ Hz} \), \( J_2 = 5.3 \text{ Hz} \), 1H). \(^{13}\text{C} \) NMR (75 Hz, CDCl\(_3\)): \( \delta \) 154.9, 154.7, 149.6, 135.8, 128.5, 128.3, 128.2, 126.4, 116.1, 110.7, 102.1, 85.7, 67.3, 56.1, 37.1. HRMS (ESI) Calcd for \( \text{C}_{17}\text{H}_{16}\text{BrNO}_2\text{Na}^+ \) [M+Na]\(^{+}\) 400.0155; Found: 400.0145.

**Benzyl (6-methoxy-4-methyl-2,3-dihydro-1H-inden-2-yl)carbamate (3c):**

Yield: 50%. Colorless oil. \(^1\text{H} \) NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.26-7.35 (m, 5H), 6.54 (d, \( J = 11.8 \text{ Hz} \), 2H), 6.25 (d, \( J = 3.7 \text{ Hz} \), 1H), 5.83 (d, \( J = 8.0 \text{ Hz} \), 1H), 5.08-5.19 (m, 2H), 3.72 (s, 3H), 3.45 (dd, \( J_1 = 8.4 \text{ Hz} \), \( J_2 = 16.5 \text{ Hz} \), 1H), 2.88 (dd, \( J_1 = 16.5 \text{ Hz} \), \( J_2 = 4.8 \text{ Hz} \), 1H), 2.18 (s, 3H). \(^{13}\text{C} \) NMR (75 Hz, CDCl\(_3\)): \( \delta \) 155.2, 154.2, 150.5, 136.0, 128.5, 128.2, 128.1, 124.3, 120.3, 115.0, 107.9, 85.0, 67.1, 55.9, 36.5 15.4. HRMS (ESI) Calcd for \( \text{C}_{18}\text{H}_{19}\text{NO}_2\text{Na}^+ \) [M+Na]\(^{+}\) 336.1206; Found: 336.1201.

**Benzyl (5-methoxy-6-methyl-2,3-dihydro-1H-inden-2-yl)carbamate (3d):**

Yield 74%. White solid. \(^1\text{H} \) NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.26-7.35 (m, 5H), 6.68 (s, 1H), 6.62 (s, 1H), 6.23 (brs, 1H), 5.72 (d, \( J = 8.5 \text{ Hz} \), 1H), 5.08-5.18 (m, 2H), 3.76 (s, 3H), 3.48 (dd, \( J_1 = 8.3 \text{ Hz} \), \( J_2 = 16.2 \text{ Hz} \), 1H), 2.87 (dd, \( J_1 = 16.3 \text{ Hz} \), \( J_2 = 4.5 \text{ Hz} \), 1H), 2.17 (s, 3H). \(^{13}\text{C} \) NMR (75 Hz, CDCl\(_3\)): \( \delta \) 155.3, 152.5, 151.5, 135.9, 128.5, 128.2, 128.1, 127.0, 121.4, 111.9, 107.6, 85.4, 67.2, 56.3, 36.3, 16.4. HRMS (ESI) Calcd for \( \text{C}_{18}\text{H}_{19}\text{NO}_2\text{Na}^+ \) [M+Na]\(^{+}\) 336.1206; Found: 336.1201.

**Benzyl (5-methoxy-6-methyl-2,3-dihydro-1H-inden-2-yl)carbamate (3e):**

Yield 52%; Yellow oil; \(^1\text{H} \) NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.35-7.26 (m, 5H), 6.57 (d, \( J = 4.0 \text{ Hz} \), 2H), 6.25 (brs, 1H), 5.8 (d, \( J = 9.3 \text{ Hz} \), 1H), 5.08-5.19 (m, 2H), 3.73 (s, 3H), 3.46 (dd, \( J_1 = 8.4 \text{ Hz} \), \( J_2 = 16.5 \text{ Hz} \), 1H), 2.88 (dd, \( J_1 = 16.4 \text{ Hz} \), \( J_2 = 4.4 \text{ Hz} \), 1H), 2.57 (qd, \( J = 7.5 \text{ Hz} \), 2 H), 1.10-1.28 (m, 3 H). \(^{13}\text{C} \) NMR (75 Hz, CDCl\(_3\)): \( \delta \) 155.3, 154.3, 149.9, 135.9, 128.5, 128.2, 126.7, 124.4, 113.4, 107.7, 84.9, 67.0, 55.9, 36.4, 29.6, 23.0, 13.9. HRMS (ESI) Calcd for \( \text{C}_{19}\text{H}_{21}\text{NO}_2\text{Na}^+ \) [M+Na]\(^{+}\) 350.1363; Found: 350.1359.
**Benzyl (5-methoxy-6-methyl-2,3-dihydro-1H-inden-2-yl) carbamate (3f):**

Yield: 74%. White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.35-7.26 (m, 5H), 6.67 (d, $J = 15.1$ Hz, 2H), 6.26 (brs, 1H), 5.63 (d, $J = 8.8$ Hz, 1H), 5.10-5.20 (m, 2H), 3.76 (s, 3H), 3.51 (dd, $J_1 = 8.7$ Hz, $J_2 = 16.3$ Hz, 1H), 2.88 (dd, $J_1 = 16.3$ Hz, $J_2 = 4.7$ Hz, 1H), 2.57 (q, $J = 7.4$ Hz, 2H), 1.15 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (75 Hz, CDCl$_3$): $\delta$ 155.3, 152.0, 151.6, 135.8, 133.2, 128.5, 128.3, 121.3, 110.3, 107.7, 85.2, 67.2, 56.2, 36.2, 23.3, 14.3. HRMS (ESI) Calcd for C$_{19}$H$_{21}$NO$_4$Na$^+$ [M+Na]$^+$ 350.1363; Found: 350.1359.

**Benzyl (7-(tert-butyl)-5-methoxy-2,3-dihydrobenzofuran-2-yl) carbamate (3g):** Yield: 62%. Yellow solid. $^1$H NMR (300 MHz, CDCl$_3$):

$\delta$ 7.35-7.26 (m, 5H), 6.70 (d, $J = 2.4$ Hz, 1H), 6.61 (d, $J = 2.3$ Hz, 1H), 6.25 (brs, 1H), 5.99 (d, $J = 9.1$ Hz, 1H), 5.13 (s, 2H), 3.76 (s, 3H), 3.42 (dd, $J_1 = 8.3$ Hz, $J_2 = 16.3$ Hz, 1H), 2.85 (dd, $J_1 = 16.3$ Hz, $J_2 = 3.4$ Hz, 1H), 1.35 (s, 9H). $^{13}$C NMR (75 Hz, CDCl$_3$): $\delta$ 155.3, 153.9, 149.6, 136.0, 134.0, 128.4, 128.0, 127.9, 125.2, 111.7, 107.0, 84.6, 66.8, 55.7, 35.8, 34.1, 29.0. HRMS (ESI) Calcd for C$_{21}$H$_{25}$NO$_4$Na$^+$ [M+Na]$^+$ 378.1676; Found: 378.1686.

**Benzyl (6-(tert-butyl)-5-methoxy-2,3-dihydrobenzofuran-2-yl) carbamate (3h):** Yield: 81%. White solid. $^1$H NMR (300 MHz, CDCl$_3$):

$\delta$ 7.35-7.26 (m, 5H), 6.78 (d, $J = 21.1$ Hz, 2H), 6.26 (brs, 1H), 5.67 (d, $J = 7.9$ Hz, 1H), 5.09-5.19 (m, 2H), 3.78 (s, 3H), 3.50 (dd, $J_1 = 8.2$ Hz, $J_2 = 16.2$ Hz, 1H), 2.88 (dd, $J_1 = 16.2$ Hz, $J_2 = 4.1$ Hz, 1H), 1.33 (s, 9H). $^{13}$C NMR (75 Hz, CDCl$_3$): $\delta$ 155.3, 153.5, 151.6, 139.1, 135.9, 128.5, 128.2, 128.2, 128.1, 121.3, 108.9, 108.3, 85.3, 67.2, 55.9, 36.2, 35.0, 29.7. HRMS (ESI) Calcd for C$_{21}$H$_{25}$NO$_4$Na$^+$ [M+Na]$^+$ 378.1676; Found: 378.1686.

**Benzyl (5-ethoxy-2,3-dihydrobenzofuran-2-yl) carbamate (3i):** Yield: 81%.

White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.26-7.35 (m, 5H), 6.65-6.74 (m, 3 H), 6.26 (d, $J = 4.0$ Hz, 1H), 5.68 (d, $J = 7.6$ Hz, 1H), 5.17 (d, $J = 11.6$ Hz, 2H),...
3.95 (q, J = 7.0 Hz, 2 H), 3.49 (dd, J1 = 8.3 Hz, J2 = 16.5 Hz, 1 H), 2.88 (dd, J1 = 16.6 Hz, J2 = 4.7 Hz, 1 H), 1.37 (t, J = 7.0 Hz, 3 H). 13C NMR (75 Hz, CDCl3): δ 155.3, 153.7, 151.8, 135.9, 128.5, 128.3, 128.2, 125.1, 114.3, 111.8, 109.9, 85.4, 67.2, 64.4, 36.2, 14.9. HRMS (ESI) Calcd for C19H23NO4Na+[M+Na]+ 336.1206; Found: 336.1198.

**Benzyl (5-methoxy-2,3-dihyronaphtho[1,2-b]furan-2-yl)carbamate (3j)**: Yield: 77%. blue oil. 1H NMR (300 MHz, CDCl3): δ 8.17-8.19 (m, 1 H), 7.91 (d, J = 7.2 Hz, 1 H), 7.40-7.49 (m, 2 H), 7.26-7.35 (m, 5 H), 6.64 (s, 1 H), 6.44 (brs, 1 H), 5.86 (d, J = 8.1 Hz, 1 H), 5.11-5.23 (m, 2H), 3.92 (s, 3 H), 3.63 (dd, J1 = 8.7 Hz, J2 = 16.3 Hz, 1 H), 3.02 (dd, J1 = 16.2 Hz, J2 = 4.6 Hz, 1 H). 13C NMR (75 Hz, CDCl3): δ 155.4, 150.4, 146.8, 136.0, 128.5, 128.3, 128.2, 126.2, 125.5, 125.2, 122.4, 121.3, 120.9, 116.0, 101.0, 85.5, 67.2, 56.0, 37.4. HRMS (ESI) Calcd for C21H19NO3Na+[M+Na]+ 350.1387; Found: 350.1379.

**tert-Butyl 5-methoxy-2,3-dihydrobenzofuran-2-ylcarbamate (3k)**: Yield: 84%; White solid. 1H NMR (300 MHz, CDCl3): δ 6.65-6.74 (m, 3 H), 6.21 (brs, 1H), 5.45 (d, J = 1.9 Hz, 1H), 3.74 (s, 3H), 3.48 (dd, J1 = 8.4 Hz, J2 = 16.4 Hz, 1H), 2.87 (dd, J1 = 16.5 Hz, J2 = 5.0 Hz, 1H), 1.47 (s, 9 H); 13C NMR (75 Hz, CDCl3): δ 154.5, 154.3, 152.0, 125.4, 113.3, 111.0, 109.8, 85.2, 80.6, 56.0, 36.1, 28.2. HRMS (ESI) Calcd for C14H16NO3[M+] 265.1314; Found: 265.1336.

**Benzyl (5-methoxy-1-tosylindolin-2-yl)carbamate (3m)**: Yield: 86%. Colorless oil. 1H NMR (300 MHz, CDCl3): δ 7.62 (d, J = 7.2 Hz, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.26-7.34 (m, 6H), 7.17 (d, J = 7.8 Hz, 2H), 6.74 (dd, J1 = 8.8 Hz, J2 = 2.5 Hz, 1H), 6.60 (s, 1H), 5.83 (dd, J1 = 7.4 Hz, J2 = 5.5 Hz, 1H), 5.67 (brs, 1H), 5.07-5.16 (m, 2H), 3.73 (s, 3H), 3.03 (dd, J1 = 8.5 Hz, J2 = 17.0 Hz, 1H), 2.76-2.82 (m, 1H), 2.34 (s, 3H). 13C NMR (75 Hz, CDCl3): δ 157.1, 154.9, 144.1, 136.0, 134.4, 133.8, 130.9, 129.6, 128.4, 128.1, 128.0, 127.2, 116.9, 113.1, 110.7, 70.0, 66.9, 55.5, 37.1, 21.4. HRMS (ESI) Calcd for C23H24N2O5SNa+[M+Na]+ 476.1337; Found: 476.1327.
benzyl (5-methoxy-1-((4-nitrophenyl)sulfonyl)indolin-2-yl)carbamate (3n):

Yield: 80%. Yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.22 (d, $J = 7.6$ Hz, 2 H), 7.97 (d, $J = 7.0$ Hz, 2 H), 7.54 (d, $J = 8.8$ Hz, 1 H), 7.26-7.35 (m, 5 H), 6.77 (d, $J = 8.9$ Hz, 1 H), 6.63 (s, 1 H), 5.90 (brs, 1 H), 5.62 (d, $J = 7.4$ Hz, 1 H), 5.13 (s, 2 H), 3.74 (s, 3 H), 3.13 (dd, $J_1 = 8.7$ Hz, $J_2 = 17.1$ Hz, 1 H), 2.83 (dd, $J_1 = 17.1$ Hz, $J_2 = 2.5$ Hz, 1 H). $^{13}$C NMR (75 Hz, CDCl$_3$): $\delta$ 157.5, 154.9, 150.3, 143.0, 135.7, 132.8, 130.5, 128.6, 128.5, 128.4, 128.2, 124.3, 116.5, 113.5, 111.0, 70.1, 67.2, 55.6, 37.0. HRMS (ESI) Calcd for C$_{23}$H$_{21}$N$_3$O$_7$SNa$^+$ [M+Na]$^+$ 506.0992; Found: 506.0978.

3. References


4. $^1$H NMR and $^{13}$C NMR spectra: