Palladium-Catalyzed [4+2] Annulation of Aryl and Alkenyl Carboxamides with 1,3-Dienes via C–H Functionalization: Synthesis of 3,4-Dihydroisoquinolones and 5,6-Dihydropyridinones

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General data:

$^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker Avance 400, and tetramethylsilane (TMS) or CDCl$_3$ (7.26 ppm for $^1$H NMR, 77.0 ppm for $^{13}$C NMR) was used as a reference. Data for $^1$H were reported as follows: chemical shift (ppm), and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet). Data for $^{13}$C NMR were reported as ppm. High resolution mass spectra analysis was performed on Waters SYNAPT G2-Si mass spectrometer. Melting points were determined using a X-4 digital micro melting point apparatus. X-ray structural analysis was conducted on the Gemini A Ultra instrument.

Materials:

Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone prior to use; CH$_2$Cl$_2$ was distilled from CaH$_2$. Other purchased reagents and solvents from commercial sources (Aldrich, Alfa, TCI, Adamas, Aladdin, innochem, Bide Pharmatech Ltd.) were used without further purification, if not stated otherwise. All start substrates including amides 1, 4 and dienes 2 were prepared according to the known literature. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography.

Experimental Procedure

(1) General procedure for the preparation of products 3 and 5.

An oven-dried Schlenk tube equipped with a Teflon valve was charged with a magnetic stir bar, substrate 1 or 4 (0.2 mmol), Pd(TFA)$_2$ (6.6 mg, 0.02 mmol, 10 mol%), Cu(OAc)$_2$ (7.3 mg, 0.04 mmol, 20 mol%), p-xylene (2 ml) and dienes 2 (0.4 mmol). The reaction mixture was stirred at 120 °C for 18 h under air. Then resulting suspension was cooled to room temperature and filtered through a pad of filter paper with the help of 50 mL of ethyl acetate. After evaporating the solvent under reduced
pressure, the residue was purified by column chromatography on silica gel to give the pure product 3 or 5.

(2) Procedure for scale-up synthesis of compound 3aa.

An oven-dried Schlenk tube equipped with a Teflon valve was charged with a magnetic stir bar, substrate 1a (1.1 g, 4 mmol), Pd(TFA)$_2$ (132.8 mg, 0.4 mmol, 10 mol%), Cu(OAc)$_2$ (145.6 mg, 0.8 mmol, 20 mol%), $p$-xylene (40 ml) and diene 2a (1.04 g, 8 mmol). The reaction mixture was stirred at 120 °C for 18 h under air. Then resulting suspension was cooled to room temperature and filtered through a pad of silica gel with the help of 200 mL of ethyl acetate. After evaporating the solvent under reduced pressure, the residue was purified by silica gel chromatography (PE/EA = 5:1) to give the pure product 3aa (1.52 g, 94% yield).

(3) General procedures for further synthetic transformations.

An oven-dried Schlenk tube equipped with a Teflon valve was charged with a magnetic stir bar and substrate 3aa (40.3 mg, 0.1 mmol). The tube was evacuated and backfilled with N$_2$ (this procedure was repeated 3 times). Then anhydrous THF (2.0 mL) and SmI$_2$ (3 ml, 0.3 mmol, 0.1 M in THF) were added by syringe at 0 °C. After stirred at 0 °C for 10 minutes, the reaction mixture was warmed to ambient temperature for 15 h. Then, saturated aqueous sodium bicarbonate (10 ml) was added. The aqueous phases were extracted three times with ethyl acetate (10 ml), and the combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by silica gel chromatography (PE/EA = 2:1) to afford the desired product 6 (14.5 mg, 59% yield).

A suspension of sodium hydride (60% dispersion in mineral oil, 16 mg, 0.24 mmol) in DMF (1 ml) at 0 °C, under nitrogen, was treated dropwise over 15 min with a solution of 6 (24.9 mg, 0.1 mmol) in anhydrous DMF (1 ml), stirred at 0 °C for an additional 20 min, treated with allyl bromide (18 mg, 0.15 mmol) at 0 °C, allowed to warm to room temperature, and stirred overnight. The reaction mixture was
partitioned between water (10 ml) and methylene chloride (10 ml). The aqueous layer was extracted with methylene chloride (10 ml). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel chromatography (PE/EA = 5:1) to afford the desired product 7 (27.2 mg, 95% yield).⁵

An oven-dried Schlenk tube under an N₂ atmosphere was charged with 7 (28.9 mg, 0.1 mmol), Grubbs II catalyst (17 mg, 0.02 mmol). Methylene chloride (2 ml) was added under an N₂ atmosphere. Then the mixture was refluxed for 4 h. After removed the solvent, the residue was purified by silica gel chromatography (PE/EA = 2:1) to afford the product 8 (14.4 mg; 78% yield).

An oven-dried Schlenk tube was charged with substrate 3aa (40.3 mg, 0.1 mmol), 5% Pd/C (10 mg, 0.005 mmol). Anhydrous EtOH (2.0 ml) were added under a H₂ atmosphere. The mixture was stirred at room temperature for 3 h, then filtrated with silica gel and concentrated in vacuo. The residue was purified by silica gel chromatography (PE/EA = 5:1) to afford the desired product 9 (38.1 mg; 97% yield).

To an oven-dried Schlenk tube, in a 0 °C bath, equipped with a magnetic stir bar under a N₂ atmosphere, was added the 3aa (40.3 mg, 0.1 mmol) and CH₂Cl₂ (2 mL). m-CPBA (34.4 mg, 0.2 mmol) was then added in one portion. After being stirred for 16 h, during which time the bath was allowed to expire, the reaction mixture was quenched by the sequential addition of sat. Na₂S₂O₅(aq) solution (1 mL) along with 10% NaOH solution (1 mL). The aqueous layer was extracted with CH₂Cl₂ (2 × 10 mL). The organic layers were combined, washed with 10% NaOH (2 × 5 mL) and with brine. It was then dried with MgSO₄, filtered, and concentrated in vacuo to

⁵
afford the crude epoxide. The residue was purified by silica gel chromatography (PE/EA = 5:1) to afford the desired product 10 (34.8 mg; 83% yield).\(^6\)

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\begin{array}{c}
\text{O} \\
\text{N} \\
\text{ Ts} \\
\text{Ph} \\
\text{Ph}
\end{array} \xrightarrow{\text{LiAlH}_4 / \text{AlCl}_3} 
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{ Ts} \\
\text{Ph} \\
\text{Ph}
\end{array} 
\]

An oven-dried Schlenk tube under an N\(_2\) atmosphere was charged with LiAlH\(_4\) (38 mg, 1 mmol) and AlCl\(_3\) (160.2 mg, 1.2 mmol), mixed solvents anhydrous THF (0.2 ml) and anhydrous Et\(_2\)O (1.0 ml) were added at 0 °C and the mixture was stirred at 0 °C for 30 minutes. Substrate 3aa (40.3 mg, 0.1 mmol) were dissolved in anhydrous THF (0.8 ml), and added to the above mixture by syringe. The reaction was stirred at 0 °C for 12 h, then the sat. aq. NH\(_4\)Cl (1 ml) was added. The aqueous layer was extracted with EtOAc (5 ml), dried over Na\(_2\)SO\(_4\), and concentrated in vacuo. The residue was purified by silica gel chromatography (PE/EA = 5:1) to afford the desired product 11 (37.0 mg; 95% yield).\(^7\)

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\begin{array}{c}
\text{O} \\
\text{N} \\
\text{ Ts} \\
\text{Ph} \\
\text{Ph}
\end{array} \xrightarrow{\text{NBS / AIBN} / \text{CCl}_4} 
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{ Ts} \\
\text{Br} \\
\text{Ph}
\end{array} 
\]

An oven-dried Schlenk tube was charged with substrate 3aa (40.3 mg, 0.1 mmol), NBS (21.4 mg, 0.12 mmol) and AIBN (3.3 mg, 0.02 mmol). CCl\(_4\) (1 mL) was added an N\(_2\) atmosphere. The reaction was refluxed for 1 h. After removed the solvent, the residue was purified by silica gel chromatography (PE/EA = 5:1) to afford the product 12 (42.8 mg; 89% yield).

**Characterization Data:**

\((E)-3\text{-styryl-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (3aa)}\) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 79.8 mg (99%); mp 112–113 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.01–8.98 (m, 3H), 7.47 (t, \(J = 7.5\) Hz, 1H), 7.31 (t, \(J = 7.6\) Hz, 1H), 7.26–7.17 (m, 8H), 6.63 (d, \(J = 15.9\) Hz, 1H), 6.01 (dd, \(J = 15.7, 7.4\) Hz, 1H), 5.71–5.67 (m, 1H),
3.66 (dd, J = 16.2, 5.9 Hz, 1H), 3.05 (dd, J = 16.3, 1.9 Hz, 1H), 2.38 (s, 3H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.9, 144.7, 136.8, 136.2, 135.7, 133.8, 133.8, 129.4, 129.2, 129.0, 128.6, 128.2, 128.2, 127.9, 127.6, 126.6, 126.2, 57.4, 34.9, 21.7; HRMS (ESI-TOF) \(m/z\) calcd for [M + H]\(^+\) (C\(_{24}\)H\(_{22}\)NO\(_3\)S) 404.1320, found 404.1328.

\((E)-6\)-methyl-3-styryl-2-tosyl-3,4-dihydroisoquinolin-1(2\(H\))-one (3ba) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 80.1 mg (96%); mp 164–165 °C; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.25–7.17 (m, 7H), 7.10 (d, J = 8.0 Hz, 1H), 6.98 (s, 1H), 6.62 (d, J = 15.7 Hz, 1H), 6.01 (dd, J = 15.8, 7.4 Hz, 1H), 5.69–5.64 (m, 1H), 3.62 (dd, J = 16.2, 5.9 Hz, 1H), 2.99 (dd, J = 16.2, 2.0 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.9, 144.8, 144.6, 137.4, 135.7, 134.7, 133.8, 133.6, 129.4, 129.2, 129.0, 128.8, 128.6, 128.5, 128.2, 126.6, 125.3, 34.9, 21.7, 21.6; HRMS (ESI-TOF) \(m/z\) calcd for [M + H]\(^+\) (C\(_{25}\)H\(_{24}\)NO\(_3\)S) 418.1477, found 418.1480.

\((E)-7\)-methyl-3-styryl-2-tosyl-3,4-dihydroisoquinolin-1(2\(H\))-one (3ca) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 79.2 mg (95%); mp 85–86 °C; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 (d, J = 8.3 Hz, 2H), 7.81 (s, 1H), 7.28–7.15 (m, 8H), 7.07 (d, J = 7.7 Hz, 1H), 6.662 (d, J = 15.7 Hz, 1H), 6.01 (dd, J = 15.7, 7.2 Hz, 1H), 5.68–5.65 (m, 1H), 3.60 (dd, J = 16.1, 5.9 Hz, 1H), 3.01 (dd, J = 16.2, 1.9 Hz, 1H), 2.37 (s, 3H), 2.30 (s, 3H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.1, 144.6, 137.4, 136.3, 135.7, 134.7, 133.8, 133.6, 129.4, 129.3, 129.1, 128.6, 128.1, 128.1, 127.6, 126.6, 126.4, 57.5, 34.4, 21.6, 21.0; HRMS (ESI-TOF) \(m/z\) calcd for [M + H]\(^+\) (C\(_{25}\)H\(_{24}\)NO\(_3\)S) 418.1477, found 418.1486.
(E)-8-methyl-3-styryl-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (3da) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 80.9 mg (97%); mp 158–159 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, $J = 8.4$ Hz, 2H), 7.35–7.17 (m, 8H), 7.09 (d, $J = 7.6$ Hz, 1H), 7.01 (d, $J = 7.5$ Hz, 1H), 6.66 (d, $J = 15.8$ Hz, 1H), 6.02 (dd, $J = 15.8$, 7.1 Hz, 1H), 5.64–5.60 (m, 1H), 3.58 (dd, $J = 15.9$, 5.7 Hz, 1H), 3.01 (dd, $J = 16.0$, 2.2 Hz, 1H), 2.56 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.2, 144.4, 142.4, 137.8, 136.8, 135.9, 133.7, 132.7, 131.4, 129.2, 129.0, 128.5, 128.1, 126.6, 126.3, 126.3, 126.2, 56.9, 35.8, 22.6, 21.6; HRMS (ESI-TOF) m/z calcd for [M + H]$^+$ (C$_{25}$H$_{24}$NO$_3$S) 418.1477, found 418.1485.

(3da)

(E)-6-ethyl-3-styryl-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (3ea) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 81.9 mg (95%); mp 75–76 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, $J = 8.4$ Hz, 2H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.27–7.17 (m, 7H), 7.13 (d, $J = 8.1$ Hz, 1H), 7.00 (s, 1H), 6.63 (dd, $J = 15.8$, 7.5 Hz, 1H), 6.02 (dd, $J = 15.8$, 7.1 Hz, 1H), 5.69–5.65 (m, 1H), 3.64 (dd, $J = 16.2$, 5.9 Hz, 1H), 3.01 (dd, $J = 16.2$, 2.0 Hz, 1H), 2.64 (q, $J = 7.6$ Hz, 2H), 2.37 (s, 3H), 1.21 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.9, 150.9, 144.6, 136.9, 136.4, 135.8, 133.6, 129.4, 129.2, 129.1, 128.6, 128.1, 127.5, 127.3, 126.6, 126.4, 125.5, 57.5, 34.9, 28.9, 21.6, 14.9; HRMS (ESI-TOF) m/z calcd for [M + H]$^+$ (C$_{23}$H$_{26}$NO$_3$S) 432.1633, found 432.1634.

(3ea)

(3fa) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 88.1 mg (96%); mp 182–183 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, $J = 8.4$ Hz, 2H), 7.93 (d, $J = 8.3$ Hz, 1H), 7.33 (d, $J = 8.3$ Hz, 1H), 7.28–7.20 (m, 7H), 7.16 (s, 1H), 6.65 (d, $J = 15.8$ Hz, 1H), 6.04 (dd, $J = 15.8$, 7.5 Hz, 1H), 5.70–5.66 (m, 1H), 3.66 (dd, $J = 16.2$, 6.0 Hz, 1H), 2.56 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.9, 150.9, 144.6, 136.9, 136.4, 135.8, 133.6, 129.4, 129.2, 129.1, 128.6, 128.1, 127.5, 127.3, 126.6, 126.4, 125.5, 57.5, 34.9, 28.9, 21.6, 14.9; HRMS (ESI-TOF) m/z calcd for [M + H]$^+$ (C$_{26}$H$_{26}$NO$_3$S) 432.1633, found 432.1634.
1H), 3.03 (dd, J = 16.2, 2.0 Hz, 1H), 2.37 (s, 3H), 1.29 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl₃) δ 162.9, 157.8, 144.5, 136.6, 136.4, 135.8, 133.6, 129.4, 129.1, 128.9, 128.6, 128.1, 126.6, 126.6, 125.2, 125.0, 124.9, 57.5, 35.2, 35.1, 31.0, 21.6; HRMS (ESI-TOF) \(m/z\) calcd for [M + H]⁺ (C\(_{23}\)H\(_{30}\)NO\(_3\)S ) 460.1946, found 460.1953.

\((E)-6\text{-methoxy-3-styryl-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one}\) (3ga) (Flash column chromatography eluent, PE/EA = 3:1) Light yellow solid; yield: 84.9 mg (98%); mp 111–112 °C; \(^1\)H NMR (400 MHz, CDCl₃) δ 7.99–7.94 (m, 3H), 7.25–7.18 (m, 7H), 6.80 (dd, J = 8.8, 2.5 Hz, 1H), 6.65–6.60 (m, 2H), 6.03 (dd, J = 15.8, 7.4 Hz, 1H), 5.67–5.64 (m, 1H), 3.81 (s, 3H), 3.63 (dd, J = 16.1, 5.9 Hz, 1H), 2.99 (dd, J = 16.3, 2.0 Hz, 1H), 2.36 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃) δ 163.9, 162.6, 144.5, 139.2, 136.5, 135.7, 133.6, 131.3, 129.3, 129.1, 128.6, 128.2, 126.6, 126.3, 120.5, 113.3, 112.9, 57.4, 55.5, 35.2, 21.6; HRMS (ESI-TOF) \(m/z\) calcd for [M + H]⁺ (C\(_{25}\)H\(_{24}\)NO\(_4\)S ) 434.1426, found 434.1435.

\((E)-6\text{-phenyl-3-styryl-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one}\) (3ha) (Flash column chromatography eluent, PE/EA = 5:1) Yellow solid; yield: 89.1 mg (93%); mp 87–88 °C; \(^1\)H NMR (400 MHz, CDCl₃) δ 8.08–7.99 (m, 3H), 7.58–7.52 (m, 3H), 7.45–7.38 (m, 4H), 7.29–7.20 (m, 7H), 6.66 (d, J = 15.8 Hz, 1H), 6.06 (dd, J = 15.8, 7.4 Hz, 1H), 5.74–5.70 (m, 1H), 3.71 (dd, J = 16.1, 5.9 Hz, 1H), 3.12 (d, J = 16.2 Hz, 1H), 2.38 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃) δ 162.8, 146.6, 144.7, 139.5, 137.3, 136.3, 135.7, 133.8, 129.6, 129.4, 129.2, 129.0, 128.6, 128.5, 128.2, 127.3, 126.7, 126.7, 126.6, 126.3, 126.2, 57.5, 35.1, 21.7; HRMS (ESI-TOF) \(m/z\) calcd for [M + H]⁺ (C\(_{30}\)H\(_{26}\)NO\(_3\)S ) 480.1633, found 480.1640.
(E)-6-fluoro-3-styryl-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (3ia) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 76.6 mg (91%); mp 145–146 °C; ^1H NMR (400 MHz, CDCl₃) δ 8.03 (dd, J = 8.7, 5.7 Hz, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.30–7.23 (m, 5H), 7.21–7.16 (m, 2H), 6.99 (td, J = 8.5, 2.5 Hz, 1H), 6.89 (dd, J = 8.6, 2.4 Hz, 1H), 6.61 (d, J = 15.7 Hz, 1H), 6.00 (dd, J = 15.8, 7.3 Hz, 1H), 5.71–5.67 (m, 1H), 3.66 (dd, J = 16.3, 5.9 Hz, 1H), 3.04 (dd, J = 16.4, 2.0 Hz, 1H), 2.39 (s, 3H); ^13C NMR (100 MHz, CDCl₃) δ 165.9 (d, J = 254.8 Hz), 162.0, 144.8, 139.9 (d, J = 9.4 Hz), 136.1, 135.5, 134.0, 132.0 (d, J = 9.8 Hz), 129.4, 129.2, 128.6, 128.3, 126.6, 125.8, 124.3 (d, J = 2.8 Hz), 115.1 (d, J = 22.0 Hz), 115.0 (d, J = 22.2 Hz), 57.3, 34.9, 21.7; HRMS (ESI-TOF) m/z calcd for [M + H]^+ (C₂₄H₂₁NO₃SF) 422.1226, found 422.1232.

(E)-6-chloro-3-styryl-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (3ja) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 83.9 mg (96%); mp 188–189 °C; ^1H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 8.4 Hz, 1H), 7.30–7.18 (m, 9H), 6.60 (d, J = 15.7 Hz, 1H), 5.98 (dd, J = 15.8, 7.3 Hz, 1H), 5.71–5.67 (m, 1H), 3.64 (dd, J = 16.1, 6.0 Hz, 1H), 3.03 (dd, J = 16.3, 2.1 Hz, 1H), 2.39 (s, 3H); ^13C NMR (100 MHz, CDCl₃) δ 162.1, 144.9, 140.1, 138.5, 136.0, 135.5, 134.0, 130.6, 129.4, 129.2, 128.7, 128.6, 128.3, 128.2, 128.1, 126.6, 126.4, 125.7, 57.2, 34.7, 21.7; HRMS (ESI-TOF) m/z calcd for [M + H]^+ (C₂₄H₂₁NO₃SCl) 438.0931, found 438.0933.

(E)-6-bromo-3-styryl-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (3ka) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 58.7 mg (61%); mp 196–197 °C; ^1H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.37
(s, 1H), 7.27–7.23 (m, 5H), 7.20–7.18 (m, 2H), 6.60 (d, J = 15.7 Hz, 1H), 5.98 (dd, J = 15.8, 7.3 Hz, 1H), 5.70–5.67 (m, 1H), 3.65 (dd, J = 16.3, 5.9 Hz, 1H), 3.02 (dd, J = 16.3, 1.8 Hz, 1H), 2.39 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 162.2, 144.9, 138.6, 136.0, 135.4, 134.0, 131.1, 131.0, 130.6, 129.4, 129.2, 128.9, 128.6, 128.4, 126.8, 126.6, 125.7, 57.3, 34.6, 21.7; HRMS (ESI-TOF) m/z calcd for [M + H]+ (C24H21NO3SBr) 482.0426, found 482.0430.

(E)-3-styryl-2-tosyl-3,4-dihydrobenzo[g]isoquinolin-1(2H)-one (3la) (Flash column chromatography eluent, PE/EA = 5:1) Yellow solid; yield: 85.2 mg (94%); mp 206–207 °C; 1H NMR (400 MHz, CDCl3) δ 8.60 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.62 (s, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.26–7.13 (m, 7H), 6.65 (d, J = 15.7 Hz, 1H), 5.99 (dd, J = 15.8, 7.5 Hz, 1H), 5.80–5.71 (m, 1H), 3.78 (dd, J = 15.8, 2.2 Hz, 1H), 2.38 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 163.1, 144.7, 136.3, 135.8, 135.6, 133.8, 132.0, 131.9, 131.1, 129.6, 129.4, 129.2, 129.0, 128.5, 128.2, 127.2, 126.7, 126.6, 126.5, 126.3, 125.8, 57.3, 35.3, 21.7; HRMS (ESI-TOF) m/z calcd for [M + H]+ (C28H24NO3S) 454.1477, found 454.1473.

(E)-2-(methylsulfonyl)-3-styryl-3,4-dihydroisoquinolin-1(2H)-one (3ma) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 53.0 mg (81%); mp 73–74 °C; 1H NMR (400 MHz, CDCl3) δ 8.17 (d, J = 7.8 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.26–7.21 (m, 6H), 6.69 (d, J = 15.8 Hz, 1H), 6.08 (dd, J = 15.7, 8.0 Hz, 1H), 5.48–5.45 (m, 1H), 3.65 (dd, J = 16.3, 5.9 Hz, 1H), 3.39 (s, 3H), 3.05 (dd, J = 16.4, 1.9 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 164.0, 137.0, 135.5, 134.3, 134.2, 129.2, 128.6, 128.4, 127.8, 127.5, 126.7, 125.0, 57.0, 42.6, 34.4; HRMS (ESI-TOF) m/z calcd for [M + Na]+ (C18H17NO3SNa) 350.0827, found 350.0832.
\((E)-2-((4\text{-nitrophenyl})\text{sulfonyl})-3\text{-styril}-3,4\text{-dihydroisoquinolinin-1(2H)-one (3na)}\)

(Flash column chromatography eluent, PE/EA = 3:1)

Light yellow solid; yield: 81.6 mg (94%); mp 198–199 oC; \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 8.29–8.24 (m, 4H), 7.99 (d, \(J = 7.9\) Hz, 1H), 7.53 (t, \(J = 7.5\) Hz, 1H), 7.36 (t, \(J = 7.6\) Hz, 1H), 7.31–7.20 (m, 6H), 6.71 (d, \(J = 15.7\) Hz, 1H), 6.01 (dd, \(J = 15.8, 8.1\) Hz, 1H), 5.71–5.66 (m, 1H), 3.73 (dd, \(J = 16.3, 5.9\) Hz, 1H), 3.10 (dd, \(J = 16.4, 2.0\) Hz, 1H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 162.9, 150.5, 144.7, 136.8, 134.6, 134.4, 130.8, 129.1, 128.8, 128.7, 128.4, 127.8, 127.2, 126.6, 125.3, 123.7, 58.0, 34.9; \text{HRMS (ESI-TOF) } m/z \text{ calcld for } [\text{M} + \text{Na}]^+ (C\(_{23}\)H\(_{18}\)N\(_2\)O\(_5\)SNa) 457.0834, found 457.0836.

\((E)-3-(4\text{-methylstyril})-2\text{-tosyl}-3,4\text{-dihydroisoquinolinin-1(2H)-one (3ab)}\) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 81.7 mg (98%); mp 111–112 oC; \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 8.03–7.95 (m, 3H), 7.46 (t, \(J = 7.5\) Hz, 1H), 7.30 (t, \(J = 7.6\) Hz, 1H), 7.23 (d, \(J = 8.1\) Hz, 2H), 7.18 (d, \(J = 7.5\) Hz, 1H), 7.10–7.02 (m, 4H), 6.59 (d, \(J = 15.8\) Hz, 1H), 5.95 (dd, \(J = 15.7, 7.5\) Hz, 1H), 5.69–5.65 (m, 1H), 3.65 (dd, \(J = 16.2, 5.9\) Hz, 1H), 3.04 (dd, \(J = 16.2, 1.9\) Hz, 1H), 2.37 (s, 3H), 2.29 (s, 3H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 164.0, 137.0, 135.5, 134.3, 134.2, 129.2, 128.6, 128.4, 127.8, 127.5, 126.7, 125.0, 57.0, 42.6, 34.4; \text{HRMS (ESI-TOF) } m/z \text{ calcld for } [\text{M} + \text{H}]^+ (C\(_{23}\)H\(_{24}\)NO\(_3\)S) 418.1477, found 418.1478.

\((E)-3-(3\text{-methylstyril})-2\text{-tosyl}-3,4\text{-dihydroisoquinolinin-1(2H)-one (3ac)}\) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 74.2 mg (89%); mp 75–76 oC; \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 8.01–7.98 (m, 3H), 7.46 (t, \(J = 7.5\) Hz, 1H), 7.30 (t, \(J = 7.7\) Hz, 1H), 7.24 (d, \(J = 8.1\) Hz, 2H), 7.18 (d, \(J = 7.6\) Hz, 1H), 7.12 (d, \(J = 7.8\) Hz, 1H), 7.03 (d, \(J = 7.6\) Hz, 1H), 6.99 (s, 1H), 6.98 (d, \(J = 6.4\) Hz, 1H), 6.58 (d, \(J = 16.0\) Hz, 1H), 5.99 (dd, \(J = 15.8, 7.3\) Hz, 1H), 5.72–5.63 (m, 1H), 3.65 (dd, \(J = 16.2, 5.9\) Hz, 1H), 2.37 (s, 3H).
Hz, 1H), 3.05 (dd, \( J = 16.3, 1.9 \) Hz, 1H), 2.38 (s, 3H), 2.27 (s, 3H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \( \delta \) 162.9, 138.2, 136.8, 136.3, 135.6, 133.8, 133.8, 129.4, 129.2, 128.98, 128.96, 128.5, 128.2, 127.9, 127.5, 127.4, 126.0, 123.7, 57.4, 34.9, 21.6, 21.3; \( \text{HRMS (ESI-TOF)} \) \( m/z \) calcd for [M + H]\(^+\) (C\(_{25}\)H\(_{24}\)NO\(_3\)S) 418.1477, found 418.1486.

\((E)-3-(2\text{-methylstyryl})-2\text{-tosyl-3,4-dihydroisoquinolin-1(2H)-one} \ (3\text{ad})\)

(Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 81.7 mg (98%); mp 50–51 °C; \(^{1}\text{H NMR}\) (400 MHz, CDCl\(_3\)) \( \delta \) 8.01–7.98 (m, 3H), 7.46 (t, \( J = 7.5 \) Hz, 1H), 7.30 (t, \( J = 7.7 \) Hz, 1H), 7.25 (d, \( J = 8.1 \) Hz, 2H), 7.19 (d, \( J = 7.6 \) Hz, 1H), 7.15–7.03 (m, 4H), 6.85 (d, \( J = 7.6 \) Hz, 1H), 5.89 (dd, \( J = 15.6, 7.0 \) Hz, 1H), 5.72–5.69 (m, 1H), 3.66 (dd, \( J = 16.2, 2.0 \) Hz, 1H), 2.38 (s, 3H), 2.17 (s, 3H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \( \delta \) 162.9, 144.7, 136.8, 136.4, 135.8, 135.0, 133.8, 131.7, 130.3, 129.3, 129.2, 128.9, 128.1, 128.0, 127.6, 127.5, 126.0, 125.6, 57.4, 34.9, 21.6, 19.5; \( \text{HRMS (ESI-TOF)} \) \( m/z \) calcd for [M + H]\(^+\) (C\(_{25}\)H\(_{24}\)NO\(_3\)S) 418.1477, found 418.1487.

\((E)-3-(2\text{-methoxystyryl})-2\text{-tosyl-3,4-dihydroisoquinolin-1(2H)-one} \ (3\text{ae})\)

(Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 72.7 mg (84%); mp 74–75 °C; \(^{1}\text{H NMR}\) (400 MHz, CDCl\(_3\)) \( \delta \) 8.01–7.99 (m, 3H), 7.46 (t, \( J = 7.5 \) Hz, 1H), 7.30 (t, \( J = 7.6 \) Hz, 1H), 7.24–7.17 (m, 4H), 7.11 (d, \( J = 7.6 \) Hz, 1H), 7.04 (d, \( J = 15.8 \) Hz, 1H), 6.87–6.76 (m, 2H), 5.99 (dd, \( J = 15.9, 8.1 \) Hz, 1H), 5.73–5.64 (m, 1H), 3.79 (s, 3H), 3.67 (dd, \( J = 16.2, 5.8 \) Hz, 1H), 3.06 (dd, \( J = 16.2, 2.0 \) Hz, 1H), 2.37 (s, 3H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \( \delta \) 162.9, 156.9, 144.5, 137.1, 136.4, 133.7, 129.5, 129.1, 129.0, 128.2, 128.0, 127.4, 127.0, 126.5, 124.8, 120.5, 110.9, 58.0, 55.4, 35.1, 21.6; \( \text{HRMS (ESI-TOF)} \) \( m/z \) calcd for [M + H]\(^+\) (C\(_{25}\)H\(_{24}\)NO\(_4\)S) 434.1426, found 434.1436.
(E)-3-(4-fluorostyryl)-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (3af)  (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 73.2 mg (87%); mp 75–76 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01–7.97 (m, 3H), 7.47 (t, $J$ = 7.5 Hz, 1H), 7.32 (t, $J$ = 7.6 Hz, 1H), 7.25–7.14 (m, 5H), 6.95–6.91 (m, 2H), 6.61 (d, $J$ = 15.8 Hz, 1H), 5.94 (dd, $J$ = 15.8, 7.4 Hz, 1H), 5.69–5.65 (m, 1H), 3.65 (dd, $J$ = 16.2, 5.9 Hz, 1H), 3.05 (dd, $J$ = 16.3, 2.0 Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.8, 162.6 (d, $J$ = 246.3 Hz), 144.7, 136.7, 136.2, 133.8, 132.6, 131.8 (d, $J$ = 3.4 Hz), 129.4, 129.2, 129.0, 128.2 (d, $J$ = 8.1 Hz), 128.1, 127.9, 127.6, 126.0 (d, $J$ = 2.3 Hz), 115.5 (d, $J$ = 21.5 Hz), 57.3, 34.8, 21.6; HRMS (ESI-TOF) m/z calcd for [M + H]$^+$ (C$_{23}$H$_{21}$NO$_3$SF) 422.1226, found 422.1234.

(E)-3-(4-chlorostyryl)-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (3ag)  (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 81.3 mg (93%); mp 164–165 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01–7.96 (m, 3H), 7.46 (t, $J$ = 7.5 Hz, 1H), 7.31 (t, $J$ = 7.6 Hz, 1H), 7.25–7.18 (m, 5H), 7.11 (d, $J$ = 8.5 Hz, 2H), 6.58 (d, $J$ = 15.8 Hz, 1H), 6.00 (dd, $J$ = 15.8, 7.3 Hz, 1H), 5.69–5.66 (m, 1H), 3.64 (dd, $J$ = 16.3, 6.0 Hz, 1H), 3.05 (dd, $J$ = 16.3, 2.0 Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.8, 144.8, 136.7, 136.2, 134.2, 133.9, 132.5, 129.3, 129.2, 129.0, 128.7, 128.2, 127.9, 127.6, 126.9, 57.2, 34.7, 21.7; HRMS (ESI-TOF) m/z calcd for [M + H]$^+$ (C$_{24}$H$_{21}$NO$_3$SCI) 438.0931, found 438.0941.

(E)-3-(4-bromostyryl)-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (3ah)  (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 45.2 mg (47%); mp 190–191 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, $J$ = 7.8 Hz, 1H), 7.97 (d, $J$ = 8.4 Hz, 2H), 7.48 (t, $J$ = 7.5 Hz, 1H), 7.36 (d, $J$ = 8.4 Hz, 2H), 7.32 (t, $J$ = 7.6 Hz, 1H), 7.24 (d, $J$ = 8.1 Hz, 2H), 7.19 (d, $J$ = 7.6 Hz, 1H), 7.05 (d, $J$ = 8.5 Hz, 2H), 6.57 (d, $J$ = 15.8 Hz,
1H), 6.01 (dd, J = 15.8, 7.3 Hz, 1H), 5.71–5.62 (m, 1H), 3.65 (dd, J = 16.2, 5.9 Hz, 1H), 3.05 (dd, J = 16.2, 2.0 Hz, 1H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.8, 144.8, 136.6, 136.2, 134.6, 133.9, 132.6, 131.7, 129.3, 129.2, 129.0, 128.1, 127.8, 127.6, 127.0, 122.1, 57.2, 34.7, 21.7; HRMS (ESI-TOF) m/z calcd for [M + H]$^+$ (C$_{24}$H$_{21}$NO$_3$SBr) 482.0426, found 482.0434.

$^{(E)}$-ethyl 3-(1-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-3-yl)acrylate (3ai) (Flash column chromatography eluent, PE/EA = 3:1) White solid; yield: 78.2 mg (98%); mp 149–150 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.02–7.94 (m, 3H), 7.47 (t, J = 7.5 Hz, 1H), 7.34–7.31 (m, 3H), 7.17 (d, J = 7.6 Hz, 1H), 6.76 (dd, J = 15.6, 5.6 Hz, 1H), 5.94 (dd, J = 15.6, 1.6 Hz, 1H), 5.69–5.65 (m, 1H), 4.17–4.04 (m, 2H), 3.60 (dd, J = 16.3, 6.3 Hz, 1H), 3.05 (dd, J = 16.4, 2.0 Hz, 1H), 2.42 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.4, 162.5, 145.1, 144.1, 135.88, 135.87, 134.0, 129.33, 129.26, 129.1, 128.0, 127.8, 127.7, 124.4, 60.7, 55.6, 33.60, 21.7, 14.1; HRMS (ESI-TOF) m/z calcd for [M + H]$^+$ (C$_{21}$H$_{22}$NO$_5$S) 400.1219, found 400.1229.

$^{(E)}$-methyl 3-(1-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-3-yl)acrylate (3aj) (Flash column chromatography eluent, PE/EA = 3:1) White solid; yield: 57.8 mg (75%); mp 203–204 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99–7.96 (m, 3H), 7.48 (t, J = 7.5 Hz, 1H), 7.36–7.30 (m, 3H), 7.17 (d, J = 7.6 Hz, 1H), 6.78 (dd, J = 15.6, 5.7 Hz, 1H), 5.97 (dd, J = 15.6, 1.6 Hz, 1H), 5.70–5.66 (m, 1H), 3.66 (s, 3H), 3.60 (dd, J = 16.3, 6.2 Hz, 1H), 3.05 (dd, J = 16.4, 2.0 Hz, 1H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.9, 162.5, 145.1, 144.4, 135.8, 134.0, 129.4, 129.3, 129.1, 128.0, 127.9, 127.7, 124.0, 55.6, 51.8, 33.6, 21.7; HRMS (ESI-TOF) m/z calcd for [M + H]$^+$ (C$_{20}$H$_{20}$NO$_5$S) 386.1062, found 386.1070.
(E)-3-(3-oxo-3-phenylprop-1-en-1-yl)-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one

(3ak) (Flash column chromatography eluent, PE/EA = 3:1)
Colorless oil; yield: 69.8 mg (81%); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07–8.01 (m, 2H), 7.99 (dd, $J = 7.9$, 1.4 Hz, 1H), 7.76–7.74 (m, 2H), 7.57–7.51 (m, 1H), 7.47 (td, $J = 7.5$, 1.5 Hz, 1H), 7.43–7.37 (m, 2H), 7.34–7.28 (m, 3H), 7.18 (d, $J = 7.6$, 1H), 7.04 (dd, $J = 15.3$, 1.6 Hz, 1H), 6.89 (dd, $J = 15.3$, 4.9 Hz, 1H), 5.82–5.78 (m, 1H), 3.65 (dd, $J = 16.4$, 6.4 Hz, 1H), 3.15 (dd, $J = 16.4$, 2.0 Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 188.8, 162.8, 145.2, 144.0, 136.9, 134.0, 135.9, 134.1, 133.3, 129.5, 129.3, 129.0, 128.7, 128.6, 128.1, 127.9, 127.6, 127.4, 56.4, 33.7, 21.7; HRMS (ESI-TOF) m/z calcd for [M + H]$^+$ (C$_{25}$H$_{22}$NO$_4$S) 432.1270, found 432.1270.

(E)-diethyl (2-(1-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-3-yl)vinyl)phosphonate

(3al) (Flash column chromatography eluent, PE/EA = 1:1) White solid; yield: 88.9 mg (96%); mp 106–107 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01–7.97 (m, 2H), 7.96 (dd, $J = 7.9$, 1.4 Hz, 1H), 7.47 (td, $J = 7.5$, 1.4 Hz, 1H), 7.34–7.29 (m, 3H), 7.16 (d, $J = 7.6$ Hz, 1H), 6.70–6.60 (m, 1H), 5.80–5.66 (m, 2H), 4.03–3.91 (m, 2H), 3.80–3.68 (m, 1H), 3.64–3.52 (m, 2H), 3.08 (dd, $J = 16.3$, 2.0 Hz, 1H), 2.43 (s, 3H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.02 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.6, 148.8, 148.7, 145.1, 135.8, 134.0, 129.4, 129.3, 128.9, 128.0, 127.8, 121.6, 119.8, 62.0 (d, $J = 5.6$ Hz), 61.8 (d, $J = 5.1$ Hz), 56.8 (d, $J = 22.5$ Hz), 33.4 (d, $J = 1.4$ Hz), 21.7, 16.3 (d, $J = 6.4$ Hz), 16.0 (d, $J = 6.2$ Hz); HRMS (ESI-TOF) m/z calcd for [M + H]$^+$ (C$_{22}$H$_{27}$NO$_6$PS) 464.1297, found 464.1294.

(E)-ethyl 3-(4-methyl-1-oxo-2-tosyl-1,2,3,4-tetrahydroisoquinolin-3-yl)acrylate

(3am) (Flash column chromatography eluent, PE/EA = 3:1) Light yellow solid; yield: 28.9 mg (35%); mp 55–56 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ (4:1 mixture of diastereomers) 8.02–7.94 (m, 3 H), 7.54 (td, $J = 7.6$, 1.5 Hz, 0.8 H), 7.48 (td, $J = 7.6$, 1.6 Hz, 0.2 H), 7.35–7.29 (m, 3 H), 7.22 (d, $J = 7.6$ Hz, 0.8
H), 7.15 (d, J = 7.5 Hz, 0.2 H), 6.77 (dd, J = 15.6, 7.6 Hz, 0.2 H), 6.56 (dd, J = 15.5, 7.7 Hz, 0.8 H), 6.08 (dd, J = 15.6, 1.1 Hz, 0.8 H), 5.97 (dd, J = 15.6, 1.6 Hz, 0.2 H), 5.42–5.34 (m, 1 H), 4.17–4.07 (m, 2 H), 3.70–3.61 (m, 0.8 H), 3.25–3.19 (m, 0.2 H), 2.42 (s, 0.6 H), 2.41 (s, 2.4 H), 1.47 (d, J = 7.1 Hz, 2.4 H), 1.40 (d, J = 7.0 Hz, 0.6 H), 1.26–1.20 (m, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (4:1 mixture of diastereomers) 165.5, 165.3, 162.6, 162.1, 145.1, 145.0, 144.7, 141.9, 140.4, 140.1, 135.9, 135.7, 134.2, 129.4, 129.3, 129.2, 129.1, 127.8, 127.6, 127.5, 126.6, 126.4, 125.1, 123.9, 61.7, 61.3, 60.7, 60.7, 38.3, 36.1, 22.3, 21.7, 14.6, 14.1, 14.1; HRMS (ESI-TOF) m/z calcd for [M + Na]$^+$ (C$_{22}$H$_{23}$NO$_5$SNa) 436.1195, found 436.1195.

**(E)-3-(2-(naphthalen-1-yl)vinyl)-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (3aq)**

(Flash column chromatography eluent, PE/EA = 5:1)

Yellow solid; yield: 77.0 mg (85%); mp 152–153 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.08–7.99 (m, 3 H), 7.83–7.76 (m, 2 H), 7.73 (d, J = 7.6 Hz, 1 H), 7.50–7.42 (m, 3 H), 7.39 (d, J = 15.9 Hz, 1 H), 7.35–7.27 (m, 3 H), 7.21–7.19 (m, 3 H), 6.05 (dd, J = 15.5, 7.0 Hz, 1 H), 5.83–5.79 (m, 1 H), 3.70 (dd, J = 16.2, 5.8 Hz, 1 H), 3.13 (dd, J = 16.2, 2.0 Hz, 1 H), 2.33 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.0, 144.7, 136.8, 136.3, 133.8, 133.5, 133.5, 131.2, 131.0, 129.39, 129.36, 129.3, 129.0, 128.49, 128.46, 128.2, 128.1, 127.6, 126.3, 125.9, 125.4, 123.9, 123.6, 57.4, 34.8, 21.6; HRMS (ESI-TOF) m/z calcd for [M + H]$^+$ (C$_{28}$H$_{24}$NO$_5$S) 454.1477, found 454.1485.

**(E)-3-(3-phenylprop-1-en-1-yl)-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (3ar)**

(Flash column chromatography eluent, PE/EA = 5:1)

Light yellow solid; yield: 70.1 mg (84%); mp 171–172 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, J = 7.8 Hz, 1 H), 7.92 (d, J = 8.4 Hz, 2 H), 7.49 (t, J = 7.5 Hz, 1 H), 7.32 (t, J = 7.6 Hz, 1 H), 7.22–7.14 (m, 6 H), 6.92–6.89 (m, 2 H), 5.81 (dt, J = 14.2, 7.0 Hz, 1 H), 5.56–5.52 (m, 1 H), 5.44 (dd, J = 14.8, 6.8 Hz, 1 H), 3.56 (dd, J = 16.0, 5.7 Hz, 1 H), 3.31–3.12 (m, 2 H), 2.98 (dd, J = 16.1, 2.0 Hz, 1 H), 2.38 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.0, 144.6, 139.3, 137.0, 136.2, 133.7, 133.2, 129.3, 129.1, 128.9, 128.5, 128.3, 128.2, 128.1, 127.4, 126.2, 56.7, 38.3, 34.8, 21.7; HRMS (ESI-TOF) m/z calcd
for [M + Na]+ (C25H23NO3SNa) 440.1296, found 440.1300.

(E)-3-(4-phenylbut-1-en-1-yl)-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (3a)  
(Flash column chromatography eluent, PE/EA = 5:1)  
Yellowish oil; yield: 70.7 mg (82%); 1H NMR (400 MHz, CDCl3) δ 7.99–7.97 (m, 3H), 7.47 (td, J = 7.5, 1.4 Hz, 1H), 7.33–7.28 (m, 3H), 7.24–7.19 (m, 2H), 7.17–7.14 (m, 2H), 7.03–7.01 (m, 2H), 5.78 (dt, J = 14.0, 6.8 Hz, 1H), 5.48–5.45 (m, 1H), 5.34 (dd, J = 15.2, 7.0 Hz, 1H), 3.53 (dd, J = 16.1, 5.8 Hz, 1H), 2.89 (dd, J = 16.2, 2.0 Hz, 1H), 2.54 (t, J = 7.7 Hz, 2H), 2.41 (s, 3H), 2.26–2.16 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 161.8, 143.5, 140.2, 135.9, 135.3, 133.1, 132.6, 128.2, 128.1, 127.8, 127.3, 127.2, 127.1, 126.9, 126.6, 126.3, 124.8, 55.9, 34.2, 33.7, 32.8, 20.6; HRMS (ESI-TOF) m/z calcd for [M + Na]+ (C26H25NO3SNa) 454.1453, found 454.1451.

(E)-3-styryl-2-tosyl-3,4,5,6,7,8-hexahydroisoquinolin-1(2H)-one (5a)  
(Flash column chromatography eluent, PE/EA = 5:1)  
Yellowish oil; yield: 64.3 mg (79%); 1H NMR (400 MHz, CDCl3) δ 7.94–7.91 (m, 2H), 7.32–7.25 (m, 5H), 7.19 (d, J = 7.9 Hz, 2H), 6.58 (d, J = 15.8 Hz, 1H), 6.15 (dd, J = 15.8, 7.6 Hz, 1H), 5.45–5.40 (m, 1H), 3.08–3.02 (m, 1H), 2.37 (s, 3H), 2.28–2.23 (m, 2H), 2.18–2.05 (m, 3H), 1.73–1.65 (m, 2H), 1.55–1.43 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 163.5, 148.0, 144.3, 136.5, 135.9, 133.3, 129.4, 129.1, 128.6, 128.2, 126.7, 126.63, 126.61, 56.1, 36.1, 31.0, 22.6, 22.0, 21.6, 21.6; HRMS (ESI-TOF) m/z calcd for [M + Na]+ (C24H25NO3SNa) 430.1453, found 430.1457.

(E)-3-styryl-2-tosyl-2,3,4,5,6,7-hexahydro-1H-cyclopenta[c]pyridin-1-one (5b)  
(Flash column chromatography eluent, PE/EA = 5:1)  
Yellowish oil; yield: 24.4 mg (31%); 1H NMR (400 MHz, CDCl3) δ 7.93 (d, J = 8.4 Hz, 2H), 7.33–7.24 (m, 5H), 7.19 (d, J = 8.1 Hz, 2H), 6.54 (d, J = 15.8 Hz, 1H), 6.13 (dd, J = 15.8, 7.6 Hz, 1H), 5.58–5.54 (m, 1H), 3.14–2.97 (m, 1H), 2.61–2.43 (m, 5H), 2.36 (s, 3H), 2.01–1.85 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 62.1, 156.4, 144.3, 136.6, 135.8, 133.1, 132.1, 129.4, 129.0, 128.6, 128.2, 126.9,
126.6, 57.9, 36.9, 32.2, 29.7, 22.0, 21.6; **HRMS** (ESI-TOF) *m/z* calcd for [M + Na]$^+$ (C$_{23}$H$_{23}$NO$_3$SNa) 416.1296, found 416.1302.

**(E)-3-methyl-4-phenyl-6-styryl-1-tosyl-5,6-dihydropyridin-2(1H)-one** (5c) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 67.3 mg (76%); mp 73–74 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, $J$ = 8.4 Hz, 2H), 7.44–7.19 (m, 10H), 7.19–7.11 (m, 2H), 6.64 (d, $J$ = 15.7 Hz, 1H), 6.30 (dd, $J$ = 15.8, 7.2 Hz, 1H), 5.58–5.49 (m, 1H), 3.43–3.35 (m, 1H), 2.72 (d, $J$ = 17.7 Hz, 1H), 2.39 (s, 3H), 1.80 (d, $J$ = 2.5 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.3, 147.2, 144.5, 139.4, 136.3, 135.8, 133.7, 129.4, 129.2, 128.7, 128.6, 128.5, 128.3, 127.3, 126.7, 126.5, 126.2, 56.0, 37.5, 21.7, 13.6; **HRMS** (ESI-TOF) *m/z* calcd for [M + Na]$^+$ (C$_{27}$H$_{25}$NO$_3$SNa) 466.1453, found 466.1454.

**(E)-3,4-dimethyl-6-styryl-1-tosyl-5,6-dihydropyridin-2(1H)-one** (5d) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 57.2 mg (75%); mp 123–124 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, $J$ = 8.3 Hz, 2H), 7.37–7.23 (m, 5H), 7.20 (d, $J$ = 8.1 Hz, 2H), 6.57 (d, $J$ = 15.8 Hz, 1H), 6.15 (dd, $J$ = 15.9, 7.4 Hz, 1H), 5.42–5.39 (m, 1H), 3.17–3.04 (m, 1H), 2.37 (s, 3H), 2.35–2.29 (m, 1H), 1.88 (s, 3H), 1.78 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.7, 145.8, 145.8, 144.3, 136.5, 135.8, 133.2, 129.3, 129.1, 128.6, 128.2, 126.7, 126.6, 125.1, 55.7, 37.3, 21.6, 21.0, 11.8; **HRMS** (ESI-TOF) *m/z* calcd for [M + Na]$^+$ (C$_{22}$H$_{23}$NO$_3$SNa) 404.1296, found 404.1298.

**(E)-3-(2-methylstyryl)-2-tosyl-3,4,5,6,7,8-hexahydroisoquinolin-1(2H)-one** (5e) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 64.0 mg (76%); mp 110–111 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, $J$ = 8.4 Hz, 2H), 7.28–7.27 (m, 1H), 7.21 (d, $J$ = 8.2 Hz, 2H), 7.18–7.12 (m, 3H), 6.80 (d, $J$ = 15.6 Hz, 1H), 6.02 (dd, $J$ = 15.6, 7.3 Hz, 1H), 5.47–5.42 (m, 1H), 3.12–2.99 (m, 1H), 2.37 (s, 3H), 2.31–2.24 (m, 5H), 2.14–2.08 (m, 3H), 1.71–1.68 (m, 2H), 1.54–1.45 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.5,
(E)-3-(4-chlorostyryl)-2-tosyl-3,4,5,6,7,8-hexahydroisoquinolin-1(2H)-one (5f)

*(Flash column chromatography eluent, PE/EA = 5:1)*

Light yellow solid; yield: 52.0 mg (59%); mp 130–131 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91–7.89 (m, 2H), 7.29–7.27 (m, 2H), 7.23–7.19 (m, 4H), 6.54 (d, J = 15.8 Hz, 1H), 6.13 (dd, J = 15.8, 7.6 Hz, 1H), 5.43–5.39 (m, 1H), 3.11–2.98 (m, 1H), 2.38 (s, 3H), 2.27–2.22 (m, 2H), 2.17–2.08 (m, 3H), 1.73–1.69 (m, 2H), 1.54–1.46 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 147.9, 144.4, 136.4, 134.3, 133.9, 132.1, 129.3, 129.1, 128.8, 127.9, 127.3, 126.7, 55.9, 35.9, 30.9, 22.6, 21.9, 21.6, 21.6; HRMS (ESI-TOF) m/z calcd for [M + Na]⁺ (C₂₅H₂₇NO₃SNa) 444.1609, found 444.1609.

(E)-ethyl 3-(1-oxo-2-tosyl-1,2,3,4,5,6,7,8-octahydroisoquinolin-3-yl)acrylate (5g)

*(Flash column chromatography eluent, PE/EA = 3:1)*

White solid; yield: 56.4 mg (70%); mp 110–111 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 6.83 (dd, J = 15.6, 6.1 Hz, 1H), 5.92 (dd, J = 15.6, 1.5 Hz, 1H), 5.43–5.39 (m, 1H), 4.24–4.14 (m, 2H), 3.05–2.92 (m, 1H), 2.41 (s, 3H), 2.25–2.21 (m, 2H), 2.12–2.07 (m, 3H), 1.75–1.66 (m, 2H), 1.53–1.43 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.7, 163.0, 147.2, 144.7, 144.5, 136.2, 129.21, 129.19, 127.0, 123.9, 60.8, 54.3, 34.7, 30.8, 22.5, 21.8, 21.7, 21.5, 14.2; HRMS (ESI-TOF) m/z calcd for [M + Na]⁺ (C₂₃H₂₅NO₃SClNa) 464.1063, found 464.1068.

(E)-3-(2-(naphthalen-1-yl)vinyl)-2-tosyl-3,4,5,6,7,8-hexahydroisoquinolin-1(2H)-one (5h)

*(Flash column chromatography eluent, PE/EA = 5:1)*

Yellow oil; yield: 78.6 mg (86%); ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.4 Hz, 2H), 7.95–7.91 (m,
1H), 7.88–7.83 (m, 1H), 7.79 (dd, J = 7.0, 2.4 Hz, 1H), 7.52–7.46 (m, 2H), 7.44–7.34 (m, 3H), 7.16 (d, J = 8.1 Hz, 2H), 6.19 (dd, J = 15.6, 7.4 Hz, 1H), 5.58–5.54 (m, 1H), 3.14–3.06 (m, 1H), 2.35–2.26 (m, 5H), 2.16–2.13 (m, 3H), 1.73–1.67 (m, 2H), 1.53–1.45 (m, 2H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 163.6, 147.9, 144.4, 136.5, 133.7, 133.6, 131.1, 130.6, 129.8, 129.3, 129.1, 128.6, 128.5, 126.7, 126.3, 126.0, 125.5, 123.9, 123.6, 56.1, 36.1, 31.0, 22.7, 22.0, 21.6; \textbf{HRMS} (ESI-TOF) \(m/z\) calcd for \([M + Na]^+\) (C\(_{28}\)H\(_{27}\)NO\(_3\)\(\text{Na}\)) 480.1609, found 480.1609.

\((E)\)-3-styryl-3,4-dihydroisoquinolin-1(2H)-one (6) (Flash column chromatography eluent, PE/EA = 2:1) White solid; yield: 14.4 mg (59%); mp 164–165 °C; \(^{1}\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 8.10 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.39–7.25 (m, 6H), 7.22 (d, J = 7.5 Hz, 1H), 6.64 (d, J = 15.8 Hz, 1H), 6.23 (dd, J = 15.8, 7.4 Hz, 1H), 5.97 (s, 1H), 4.47–4.41 (m, 1H), 3.15 (dd, J = 15.7, 9.4 Hz, 1H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 166.0, 137.4, 135.9, 132.6, 132.5, 128.7, 128.4, 128.3, 128.2, 128.0, 127.5, 127.3, 126.6, 54.0, 35.0; \textbf{HRMS} (ESI-TOF) \(m/z\) calcd for \([M + Na]^+\) (C\(_{17}\)H\(_{15}\)NONa) 272.1051, found 272.1053.

\((E)\)-2-allyl-3-styryl-3,4-dihydroisoquinolin-1(2H)-one (7) (Flash column chromatography eluent, PE/EA = 5:1) Yellowish oil; yield: 27.2 mg (94%); \(^{1}\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 8.12 (d, J = 7.8 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.28–7.17 (m, 5H), 7.15 (d, J = 7.4 Hz, 1H), 6.43 (d, J = 15.8 Hz, 1H), 6.06 (dd, J = 15.8, 7.6 Hz, 1H), 5.96–5.86 (m, 1H), 5.32–5.20 (m, 2H), 4.98–4.92 (m, 1H), 4.36–4.26 (m, 1H), 3.53–3.43 (m, 2H), 2.93 (dd, J = 15.9, 2.6 Hz, 1H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 162.8, 134.9, 134.7, 132.6, 131.2, 130.9, 128.0, 127.5, 127.1, 126.9, 126.5, 126.1, 125.8, 125.4, 116.2, 56.1, 46.4, 32.8; \textbf{HRMS} (ESI-TOF) \(m/z\) calcd for \([M + Na]^+\) (C\(_{20}\)H\(_{19}\)NONa) 312.1364, found 312.1369.
10,10a-dihydropyrrolo[1,2-b]isoquinolin-5(3H)-one (8) (Flash column chromatography eluent, PE/EA = 2:1) White solid; yield: 14.4 mg (78%); mp 96–97 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J$ = 7.6 Hz, 1H), 7.43 (t, $J$ = 7.4 Hz, 1H), 7.36 (t, $J$ = 7.5 Hz, 1H), 7.21 (d, $J$ = 7.4 Hz, 1H), 6.05–6.02 (m, 1H), 5.91–5.89 (m, 1H), 4.80–4.73 (m, 1H), 4.66–4.59 (m, 1H), 4.33–4.27 (m, 1H), 3.04 (dd, $J$ = 15.0, 3.9 Hz, 1H), 2.94–2.86 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.6, 137.1, 131.7, 130.4, 129.1, 127.8, 127.4, 127.3, 129.8, 52.2, 34.4; HRMS (ESI-TOF) $m/z$ calcd for [M + H]$^+$ (C$_{12}$H$_{12}$NO) 186.0919, found 186.0925.

3-phenethyl-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (9) (Flash column chromatography eluent, PE/EA = 5:1) White solid; yield: 38.1 mg (97%); mp 99–100 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.02–7.93 (m, 3H), 7.47 (td, $J$ = 7.5, 1.4 Hz, 1H), 7.35–7.22 (m, 5H), 7.22–7.09 (m, 4H), 5.06–4.96 (m, 1H), 3.36 (dd, $J$ = 16.2, 5.5 Hz, 1H), 2.96 (dd, $J$ = 16.3, 1.6 Hz, 1H), 2.79–2.65 (m, 2H), 2.41 (s, 3H), 2.15–2.01 (m, 1H), 1.92–1.78 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.8, 144.7, 140.4, 136.8, 136.6, 133.7, 132.4, 128.9, 128.5, 128.3, 128.2, 128.1, 127.5, 126.2, 55.6, 35.1, 32.7, 32.6, 21.7; HRMS (ESI-TOF) $m/z$ calcd for [M + Na]$^+$ (C$_{24}$H$_{23}$NO$_3$SNa) 428.1296, found 428.1300.

3-(3-phenyloxiran-2-yl)-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (10) (Flash column chromatography eluent, PE/EA = 5:1) White solid; yield: 34.8 mg (83%); mp 95–96 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99–7.90 (m, 3H), 7.53 (td, $J$ = 7.5, 1.4 Hz, 1H), 7.37–7.27 (m, 5H), 7.21–7.13 (m, 4H), 4.80–4.76 (m, 1H), 4.12 (d, $J$ = 1.9 Hz, 1H), 3.49 (dd, $J$ = 16.5, 5.9 Hz, 1H), 3.32 (dd, $J$ = 16.5, 2.0 Hz, 1H), 2.91 (dd, $J$ = 7.7, 1.9 Hz, 1H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.5, 144.9, 136.2, 136.1, 135.9, 134.1, 129.3, 129.0, 128.5, 128.4, 127.8, 127.7, 125.6, 61.2, 59.8, 56.0, 30.9, 21.7; HRMS (ESI-TOF) $m/z$ calcd for [M + Na]$^+$ (C$_{24}$H$_{21}$NO$_3$SNa) 442.1089, found 442.1089.
(E)-3- styryl-2-tosyl-1,2,3,4-tetrahydroisoquinoline (11) (Flash column chromatography eluent, PE/EA = 5:1) White solid; yield: 37.0 mg (95%); mp 114–115 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77–7.69 (m, 2H), 7.23–7.14 (m, 7H), 7.10–7.03 (m, 4H), 6.42 (d, $J = 16.0$ Hz, 1H), 5.83 (dd, $J = 15.9$, 6.7 Hz, 1H), 5.03–4.99 (m, 1H), 4.73 (d, $J = 15.9$ Hz, 1H), 4.27 (d, $J = 15.9$ Hz, 1H), 3.19 (dd, $J = 16.1$, 5.9 Hz, 1H), 2.83 (dd, $J = 16.2$, 2.1 Hz, 1H), 2.33 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.4, 136.5, 136.2, 133.1, 131.9, 131.4, 129.6, 129.1, 128.4, 127.8, 127.5, 126.9, 126.4, 126.4, 126.1, 125.7, 53.5, 43.7, 34.0, 21.5; HRMS (ESI-TOF) $m/z$ calcd for [M + Na]$^+$ (C$_{24}$H$_{23}$NO$_2$SNa) 412.1347, found 412.1349.

(E)-4-bromo-3-styryl-2-tosyl-3,4-dihydroisoquinolin-1(2H)-one (12) (Flash column chromatography eluent, PE/EA = 5:1) Light yellow solid; yield: 42.8 mg (89%); mp 136–137 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11–8.05 (m, 3H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.33–7.25 (m, 8H), 6.81 (d, $J = 15.6$ Hz, 1H), 5.93 (dd, $J = 15.6$, 7.2 Hz, 1H), 5.84 (d, $J = 7.2$ Hz, 1H), 5.39 (s, 1H), 2.40 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.1, 145.1, 137.1, 135.7, 135.6, 135.2, 134.2, 130.0, 129.7, 129.6, 129.1, 128.7, 128.6, 127.9, 127.1, 126.9, 123.6, 64.9, 46.3, 21.7; HRMS (ESI-TOF) $m/z$ calcd for [M + H]$^+$ calcd for C$_{24}$H$_{21}$NO$_2$SBr: 482.0426; found: 482.0428.

References


522
Copies of $^1$H, $^{13}$C Spectra
$35$
X-Ray crystallographic data

X-ray structure of product 3ba (thermal ellipsoids are shown at 50% probability level). The crystal of product 3ba was obtained by slow evaporation in PE and EA. Crystal data have been deposited to CCDC, number 1912544.

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<td>$h, k, l_{\text{max}}$</td>
<td>15,7,29</td>
<td>15,7,29</td>
</tr>
<tr>
<td>$N_{\text{ref}}$</td>
<td>3614</td>
<td>3614</td>
</tr>
</tbody>
</table>
Tmin, Tmax 0.910, 0.961 0.910, 0.961
Tmin’ 0.910

Correction method = # Reported T Limits: Tmin = 0.928  Tmax = 1.000
AbsCorr = MULTI-SCAN
Data completeness = 0.996

Theta(max) = 25.344

R(reflections) = 0.0491 (2642)  wR2(reflections) = 0.1316 (3601)
S = 1.041

Npar = 255