Diastereoselective Synthesis of Dibenzo[\textit{b,d}]azepines by Pd(II)-Catalyzed [5+2] Annulation of \(o\)-Arylanilines with Dienes

Lu Bai,† Yan Wang,† Yicong Ge, Jingjing Liu, Xinjun Luan*

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi’an, 710127 China

Email: xluan@nwu.edu.cn

†L. B. and Y. W. contributed equally to this work.

Supporting Information

Table of Contents:

A. General information: .................................................................................................................. 1
B. General procedure of the synthesis starting materials: ................................................................. 2
C. Catalytic results: ......................................................................................................................... 4
D. Kinetic isotope experiment: ........................................................................................................ 12
E. Large-scale preparation of 3a: ...................................................................................................... 13
F. References: .................................................................................................................................. 14
G. NMR spectra: .............................................................................................................................. 15

A. General information:

All reactions were carried out under an argon atmosphere using standard Schlenk-Lines or a glovebox (Innovative Technology). All reagents were used as received unless otherwise noted. CH\(_3\)CN, DMF, DMA and DMSO were dried over CaH\(_2\). 1,4-dioxane were dried over sodium. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F\(_{254}\)); visualization of the developed chromatogram was performed by fluorescence. Flash chromatography was performed with silica gel (300-400 mesh). Proton nuclear magnetic resonance (\(^1\)H NMR) data were acquired on Varian Unity Inova-400 (400 MHz) or Bruker Ascend 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (\(\delta\)) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; m, multiplet, br, broad. Coupling constants \(J\) are quoted in Hz. Carbon-13 nuclear magnetic resonance (\(^{13}\)C NMR) data were acquired at 100 MHz on Varian Unity Inova-400 or Bruker Ascend 400 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-\(d_2\). Fluorine nuclear magnetic resonance (\(^{19}\)F NMR) data were acquired at 376 MHz on a Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported relative to inter standard CFCl\(_3\) at 0.0 ppm. Infrared (IR) data were recorded as films on potassium bromide plates on a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm\(^{-1}\)). Mass spectra were acquired on a Bruker Daltonics
MicroTof-Q II mass spectrometer. 2-arylanilines 1a, 1c, 1e, 1i, 1j, 1n-o, 1p-r, 2a, 2b, 2c, 2d, 2e-j, 2k, 2m were prepared according to literature methods.

B. General procedure of the synthesis starting materials:

Pyridine (1.19 g, 15.0 mmol) was added dropwise to a solution of o-arylaniline (3.0 mmol) in dichloromethane (15 mL), then DMAP (73.3 mg, 0.6 mmol) was added, and then the solution was stirred for 10 min at room temperature, TsCl (629.1 mg 3.3 mmol) was added slowly, The reaction mixture was then stirred at room temperature overnight. Then the reaction mixture was quenched with water and extracted with dichloromethane (10 mL × 3), and the combined organic layer was washed with saturated aqueous CuSO$_4$ (20 mL × 3), dried over MgSO$_4$, filtered, concentrated in vacuo. The crude products were purified by flash chromatography on silica gel to afford desired product 1.

N-(5-fluoro-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide (1b)

White solid (0.91 g, 89% yield). PE/EA = 5:1, R$_f$ = 0.37. Mp: 77-78 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.76-7.68 (m, 1H), 7.43-7.32 (m, 5H), 7.20 (d, J = 8.0 Hz, 2H), 7.11-7.04 (m, 1H), 6.87-6.82 (m, 1H), 6.79 (d, J = 7.0 Hz, 2H), 6.51 (s, 1H), 2.43 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 159.9 (d, J = 246.0 Hz), 144.0, 136.6 (d, J = 8.0 Hz), 136.2, 135.9, 129.7 (d, J = 2.9 Hz), 129.6, 129.1, 128.6, 128.5, 127.2, 124.5 (d, J = 8.3 Hz), 116.9 (d, J = 22.8 Hz), 115.4 (d, J = 22.3 Hz), 21.5. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -116.92 (s). IR (KBr): 3062, 2924, 2229, 1603, 1490, 1399, 1341, 1272, 1245, 1166, 906, 757, 666 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{19}$H$_{16}$NSFO$_2$Na [M+Na]$^+$ 364.0783, found 364.0776.

N-(5-cyano-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide (1d)

White solid (0.92 g, 88% yield). PE/EA = 5:1, R$_f$ = 0.37. Mp: 77-78 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.70 (d, J = 8.6 Hz, 1H), 7.51 (d, J = 7.9 Hz, 3H), 7.41-7.32 (m, 4H), 7.20 (d, J = 8.4 Hz, 2H), 6.93-6.88 (m, 2H), 6.73 (s, 1H), 2.35 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 144.8, 138.2, 135.6, 134.8, 134.1, 133.3, 132.6, 130.0, 129.7, 129.3, 128.8, 127.2, 119.5, 118.4, 107.7, 21.6. IR (KBr): 3060, 2924, 2229, 1603, 1399, 1341, 1271, 1166, 906, 757, 666 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{20}$H$_{16}$N$_2$SO$_2$Na [M+Na]$^+$ 371.0830, found 371.0819.

Ethyl 6-((4-methylphenyl)sulfonamido)-[1,1'-biphenyl]-3-carboxylate (1f)

White solid (0.97 g, 82% yield). PE/EA = 5:1, R$_f$ = 0.26. Mp: 115-116 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.04-7.98 (m, 1H), 7.82 (d, J = 1.4 Hz, 1H), 7.78 (d, J = 8.6 Hz, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.47-7.39 (m, 3H), 7.26 (d, J = 8.0 Hz, 2H), 7.02-6.93 (m, 2H), 6.80 (s, 1H), 4.35 (q, J = 7.1 Hz, 2H), 2.42
(s, 3H), 1.37 (t, \( J = 7.1 \) Hz, 3H). \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)): \( \delta 165.9, 144.4, 138.0, 136.2, 135.8, 132.6, 131.7, 130.1, 129.8, 129.4, 129.0, 128.7, 127.2, 126.3, 119.1, 61.1, 21.6, 14.3. \) IR (KBr): 2985, 1711, 1605, 1250, 1165, 908, 757, 665, 548 cm\(^{-1}\). HRMS (ESI) m/z calculated for C\(_{22}\)H\(_{21}\)NSO\(_4\)Na [M+Na]\(^+\) 418.1089, found 418.1077.

**N-[(1,1’:3’,1”-terphenyl]-4’-yl)-4-methylbenzenesulfonamide (1g)**

White solid (1.03 g, 86% yield). PE/EA = 5:1, \( R_f \) = 0.39. Mp: 132-133 °C. \( ^{1} \text{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta 7.82 (d, \( J = 8.5 \) Hz, 1H), 7.62-7.54 (m, 5H), 7.46-7.34 (m, 7H), 7.24 (d, \( J = 8.1 \) Hz, 2H), 6.98-6.91 (m, 2H), 6.65 (s, 1H), 2.44 (s, 3H). \) \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)): \( \delta 144.0, 139.8, 137.7, 137.2, 136.2, 134.3, 133.0, 130.8, 129.7, 129.2, 128.9, 128.8, 128.2, 127.5, 127.2, 127.1, 126.8, 121.7, 21.6. \) IR (KBr): 3051, 2924, 1599, 1481, 1395, 1337, 1268, 1164, 756, 548 cm\(^{-1}\). HRMS (ESI) m/z calculated for C\(_{25}\)H\(_{21}\)NSO\(_2\)Na [M+Na]\(^+\) 422.1191, found 422.1188.

**4-methyl-N-(1-phenylnaphthalen-2-yl)benzenesulfonamide (1h)**

White solid (0.89 g, 79% yield). PE/EA = 5:1, \( R_f \) = 0.38. Mp: 187-188 °C. \( ^{1} \text{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta 8.02 (d, \( J = 9.0 \) Hz, 1H), 7.89-7.81 (m, 2H), 7.48-7.36 (m, 6H), 7.32-7.28 (m, 1H), 7.20-7.08 (m, 3H), 6.72 (d, \( J = 7.1 \) Hz, 2H), 6.41 (s, 1H), 2.37 (s, 3H). \) \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)): \( \delta 144.0, 135.9, 134.6, 132.8, 131.7, 131.0, 129.2, 128.6, 127.9, 127.3, 126.6, 126.0, 125.5, 121.3, 21.6. \) IR (KBr): 3060, 2921, 1621, 1404, 1369, 1328, 1167, 763, 747, 704, 675, 556 cm\(^{-1}\). HRMS (ESI) m/z calculated for C\(_{23}\)H\(_{19}\)NSO\(_2\)Na [M+Na]\(^+\) 396.1034, found 396.1028.

**N-(5-methoxy-[1,1’-biphenyl]-2-yl)-4-methylbenzenesulfonamide (1k)**

White solid (0.90 g, 85% yield). PE/EA = 5:1, \( R_f \) = 0.35. Mp: 98-99 °C. \( ^{1} \text{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta 7.64 (d, \( J = 8.9 \) Hz, 1H), 7.35 (d, \( J = 8.1 \) Hz, 2H), 7.32-7.25 (m, 3H), 7.13 (d, \( J = 8.0 \) Hz, 2H), 6.93-6.87 (m, 1H), 6.78 (d, \( J = 6.9 \) Hz, 2H), 6.65 (d, \( J = 2.7 \) Hz, 1H), 6.61 (s, 1H), 3.75 (s, 3H), 2.39 (s, 3H). \) \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)): \( \delta 157.3, 143.6, 137.4, 137.3, 136.1, 129.5, 128.8, 128.7, 127.9, 127.1, 126.3, 125.7, 115.5, 113.8, 55.5, 21.6. \) IR (KBr): 3058, 2950, 2842, 1604, 1492, 1394, 1331, 1214, 1163, 1034, 668, 548 cm\(^{-1}\). HRMS (ESI) m/z calculated for C\(_{20}\)H\(_{19}\)NSO\(_3\)Na [M+Na]\(^+\) 376.0983, found 376.0976.

**4-methyl-N-(4-methyl-[1,1'-biphenyl]-2-yl)benzenesulfonamide (1l)**

White solid (0.84 g, 83% yield). PE/EA = 5:1, \( R_f \) = 0.35. Mp: 104-105 °C. \( ^{1} \text{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta 7.48-7.45 (m, 1H), 7.41-7.35 (m, 2H), 7.27-7.22 (m, 3H), 7.11 (d, \( J = 8.0 \) Hz, 2H), 6.92-6.86 (m, 2H), 6.77-6.71 (m, 2H), 6.47 (s, 1H), 2.32 (s, 3H), 2.31 (s, 3H). \) \( ^{13} \text{C} \) NMR (100 MHz, CDCl\(_3\)): \( \delta 143.8,
Catalytic results: In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with Pd(TFA)$_2$ (3.3 mg, 0.01 mmol), Cu(OAc)$_2$ (76.3 mg, 0.42 mmol), 1 (0.20 mmol) and 1,3-dienes 2 (0.40 mmol), followed by sequential addition of MeCN (1.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 120 °C for 36 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO$_4$, filtered, and concentrated in vacuo. The residue was then purified on silica gel to afford the desired product 3.

Ethyl (E)-3-(5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3a)
White solid (73.4 mg, 82% yield). PE/EA = 5:1, R$_f$ = 0.35. Mp: 115-116 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.66-7.56 (m, 1H), 7.41-7.33 (m, 2H), 7.18-7.13 (m, 1H), 7.09-7.02 (m, 2H), 6.99-6.90 (m, 2H), 6.79 (d, $J$ = 8.3 Hz, 2H), 6.61 (d, $J$ = 8.1 Hz, 2H), 6.53 (d, $J$ = 7.4 Hz, 1H), 6.30-6.16 (m, 1H), 5.35-5.25 (m, 1H), 4.16 (q, $J$ = 7.1 Hz, 2H), 2.70-2.59 (m, 1H), 2.50 (t, $J$ = 13.4 Hz, 1H), 2.21 (s, 3H), 1.25 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.3, 146.4, 142.4, 140.8, 138.5, 136.0, 135.3, 134.0, 133.1, 129.5, 129.4, 129.0, 128.7, 128.1, 127.8, 127.3, 126.4, 122.0, 68.7, 60.6, 37.2, 21.4, 14.3. IR (KBr): 3061, 2982, 2927, 1718, 1657, 1600, 1482, 1446, 1346, 1275, 1168, 1101, 979, 746 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{26}$H$_{25}$NSO$_4$Na [M+Na]$^+$ 470.1402, found 470.1390.

Ethyl (E)-3-(2-fluoro-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3b)
White solid (66.1 mg, 71% yield), PE/EA = 5:1, R$_f$ = 0.38. Mp: 134-135 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.77-7.59 (m, 1H), 7.23-7.12 (m, 3H), 7.09-6.99 (m, 2H), 6.98-6.93 (m, 1H), 6.89 (d, $J$ = 8.2 Hz, 2H), 6.82 (d, $J$ = 8.4 Hz, 2H), 6.59 (d, $J$ = 7.5 Hz, 1H), 6.31 (d, $J$ = 15.6 Hz, 1H), 5.48-5.32 (m, 1H), 4.26
(q, J = 7.1 Hz, 2H), 2.76 (dd, J = 13.9, 4.9 Hz, 1H), 2.59 (t, J = 13.4 Hz, 1H), 2.32 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.3, 162.8 (d, J = 249.7 Hz), 146.1, 143.0 (d, J = 8.7 Hz), 142.6, 137.5, 135.9, 135.8, 135.4, 129.1, 129.0 (d, J = 3.0 Hz), 128.3 (d, J = 4.9 Hz), 128.0, 127.4, 126.4, 122.1, 116.0 (d, J = 23.1 Hz), 115.5 (d, J = 22.3 Hz), 68.6, 60.7, 37.1, 21.4, 14.3. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -111.33 (s). IR (KBr): 2985, 1717, 1653, 1485, 1347, 1269, 1167, 1098, 980, 754 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{26}$H$_{24}$NFSO$_4$Na [M+Na]$^+$ 488.1308, found 488.1295.

![Ethyl (E)-3-(5-tosyl-2-(trifluoromethyl)-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3c)](image)

**Ethyl (E)-3-(5-tosyl-2-(trifluoromethyl)-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3c)**

White solid (81.5 mg, 79% yield). PE/EA = 5:1, R$_f$ = 0.32. Mp: 115-116 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.75 (d, J = 8.2 Hz, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.43 (s, 1H), 7.12 (t, J = 7.3 Hz, 1H), 7.07 (d, J = 7.0 Hz, 1H), 7.01-6.90 (m, 2H), 6.82 (d, J = 8.2 Hz, 2H), 6.74 (d, J = 8.1 Hz, 2H), 6.59 (d, J = 7.5 Hz, 1H), 6.21 (d, J = 15.6 Hz, 1H), 5.39-5.23 (m, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.69 (dd, J = 14.0, 4.9 Hz, 1H), 2.49 (t, J = 13.5 Hz, 1H), 2.23 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): 166.1, 145.8, 142.9, 141.7, 137.2, 136.5, 135.8, 135.3, 134.7, 131.48 (d, J = 32.7 Hz), 129.2, 128.6, 128.3, 128.1, 127.6, 126.4, 125.48 (dd, J = 6.9, 3.3 Hz), 122.3, 68.7, 60.7, 36.9, 21.4, 14.3. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -62.58 (s). IR (KBr): 2923, 2858, 1718, 1653, 1453, 1341, 1269, 1168, 1126, 978, 755 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{26}$H$_{24}$NFSO$_4$Na [M+Na]$^+$ 538.1276, found 538.1273.

![Ethyl (E)-3-(2-cyano-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3d)](image)

**Ethyl (E)-3-(2-cyano-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3d)**

White solid (67.1 mg, 71% yield). PE/EA = 5:1, R$_f$ = 0.25. Mp: 174-175 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.75 (d, J = 8.2 Hz, 1H), 7.67 (dd, J = 8.2, 2.0 Hz, 1H), 7.47 (d, J = 1.9 Hz, 1H), 7.17-7.13 (m, 1H), 7.08 (d, J = 6.5 Hz, 1H), 7.03-7.00 (m, 1H), 6.92 (dd, J = 15.6, 5.4 Hz, 1H), 6.80 (d, J = 8.4 Hz, 2H), 6.75 (d, J = 8.2 Hz, 2H), 6.58-6.49 (m, 1H), 6.20 (dd, J = 15.6, 1.5 Hz, 1H), 5.36-5.27 (m, 1H), 4.17 (q, J = 7.1 Hz, 2H), 2.71 (dd, J = 14.1, 5.0 Hz, 1H), 2.48 (t, J = 13.6 Hz, 1H), 2.24 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.1, 145.6, 143.1, 142.3, 137.6, 136.3, 135.6, 135.3, 135.1, 133.0, 132.0, 129.3, 129.0, 128.4, 128.1, 127.7, 126.3, 122.5, 118.0, 113.4, 68.9, 60.8, 36.8, 21.4, 14.3. IR (KBr): 3062, 2982, 2232, 1718, 1656, 1486, 1449, 1352, 1272, 1168, 1098, 977, 746 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{27}$H$_{24}$N$_2$SO$_4$Na [M+Na]$^+$ 495.1354, found 495.1350.

![Ethyl (E)-3-(2-chloro-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3e)](image)

**Ethyl (E)-3-(2-chloro-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3e)**

White solid (64.6 mg, 67% yield). PE/EA = 5:1, R$_f$ = 0.26. Mp: 124-125 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.59-7.52 (m, 1H), 7.38-7.30 (m, 1H), 7.17-7.13 (m, 1H), 7.12-7.04 (m, 2H), 6.97-6.88 (m, 2H), 6.81 (d, J = 6.9 Hz, 2H), 6.74 (d, J = 7.8 Hz, 2H), 6.52 (d, J = 7.6 Hz, 1H), 6.20 (d, J = 15.6 Hz, 1H), 5.35-5.24 (m, 1H), 4.17 (q, J = 7.1 Hz, 2H), 2.66 (dd, J = 14.0, 5.1 Hz, 1H), 2.50 (t, J = 13.4 Hz, 1H), 2.23 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.2, 146.0, 142.7, 142.4, 137.3, 135.8, 135.4, 135.3, 131.7, 129.3, 128.8, 128.4, 128.3, 128.0, 127.4, 126.4, 122.2, 68.6, 60.7, 37.0, 21.4.
14.3. IR (KBr): 3062, 2983, 1718, 1656, 1480, 1448, 1350, 1273, 1168, 1099, 979, 746 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{26}$H$_{24}$NClSO$_4$Na [M+Na]$^+$ 504.1012, found 504.1007.

**Ethyl (E)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepine-2-carboxylate (3f)**

White solid (55.1 mg, 53% yield). PE/EA = 5:1, $R_f = 0.26$. Mp: 150-151 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.04 (dd, $J = 8.2$, 2.0 Hz, 1H), 7.86 (d, $J = 2.0$ Hz, 1H), 7.71 (d, $J = 8.2$ Hz, 1H), 7.14-7.03 (m, 2H), 7.02-6.90 (m, 2H), 6.80 (d, $J = 8.3$ Hz, 2H), 6.73 (d, $J = 8.1$ Hz, 2H), 6.61 (d, $J = 7.5$ Hz, 1H), 6.22 (dd, $J = 15.6$, 1.4 Hz, 1H), 5.41-5.23 (m, 1H), 4.40-4.27 (m, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 2.68 (dd, $J = 14.0$, 5.0 Hz, 1H), 5.41-5.23 (m, 1H), 4.40-4.27 (m, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 2.68 (dd, $J = 14.0$, 5.0 Hz, 1H), 2.49 (t, $J = 13.5$ Hz, 1H), 2.23 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.26 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.2, 165.8, 146.0, 141.0, 137.6, 137.3, 135.8, 135.2, 134.1, 131.4, 130.6, 129.6, 129.1, 128.3, 127.4, 126.4, 122.2, 68.8, 61.4, 60.7, 37.0, 21.4, 14.4, 14.3. IR (KBr): 3062, 2982, 2923, 1718, 1654, 1451, 1353, 1274, 1166, 1103, 975, 752 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{29}$H$_{29}$NClSO$_4$Na [M+Na]$^+$ 542.1613, found 542.1615.

**Ethyl (E)-3-(2-phenyl-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3g)**

White solid (63.9 mg, 61% yield). PE/EA = 5:1, $R_f = 0.31$. Mp: 89-90 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.76 (d, $J = 8.2$ Hz, 1H), 7.70-7.66 (m, 1H), 7.65-7.60 (m, 2H), 7.49-7.44 (m, 3H), 7.47-7.36 (m, 1H), 7.20-7.11 (m, 2H), 7.09-7.00 (m, 2H), 6.92 (d, $J = 8.3$ Hz, 2H), 6.80 (d, $J = 8.1$ Hz, 2H), 6.69 (d, $J = 7.4$ Hz, 1H), 6.33 (dd, $J = 15.6$, 1.5 Hz, 1H), 5.47-5.33 (m, 1H), 4.24 (q, $J = 7.1$ Hz, 2H), 2.76 (dd, $J = 13.9$, 5.2 Hz, 1H), 2.66 (t, $J = 13.3$ Hz, 1H), 2.29 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.4, 146.4, 142.5, 142.2, 141.1, 139.8, 138.5, 136.1, 135.4, 134.3, 132.3, 129.1, 129.0, 128.2, 128.1, 128.0, 127.9, 127.8, 127.4, 127.3, 127.2, 126.4, 122.0, 68.6, 60.7, 37.2, 21.4, 14.3. IR (KBr): 3060, 2984, 1717, 1656, 1482, 1448, 1347, 1271, 1166, 1099, 979, 752 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{32}$H$_{29}$NClSO$_4$Na [M+Na]$^+$ 546.1715, found 546.1709.

**Ethyl (E)-3-(7-tosyl-8,9-dihydro-7H-benzo[d]naphtho[2,1-b]azepin-8-yl)acrylate (3h)**

White solid (71.7 mg, 72% yield). PE/EA = 5:1, $R_f = 0.32$. Mp: 173-174 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.86 (t, $J = 8.2$ Hz, 2H), 7.79-7.71 (m, 2H), 7.44 (t, $J = 7.4$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.18-7.10 (m, 2H), 6.98-6.88 (m, 2H), 6.84 (d, $J = 8.2$ Hz, 2H), 6.73 (d, $J = 8.1$ Hz, 2H), 6.63 (d, $J = 7.5$ Hz, 1H), 6.19 (d, $J = 15.7$ Hz, 1H), 5.33-5.24 (m, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 2.67 (dd, $J = 13.6$, 5.2 Hz, 1H), 2.49 (t, $J = 13.2$ Hz, 1H), 2.21 (s, 3H), 1.24 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.3, 146.1, 142.3, 137.2, 136.7, 136.4, 135.6, 134.1, 131.3, 131.0, 130.8, 130.6, 129.2, 128.9, 128.3, 128.2, 127.8, 126.6, 126.5, 126.3, 122.2, 69.2, 60.6, 37.2, 21.4, 14.3. IR (KBr): 3060, 2985, 1717, 1654, 1450, 1344, 1271, 1164, 1096, 982, 754 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{30}$H$_{27}$NSO$_4$Na [M+Na]$^+$ 520.1558, found 520.1556.
Ethyl (E)-3-(2-nitro-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3i)

White solid (39.4 mg, 40% yield). PE/EA = 5:1, Rf = 0.29. Mp: 175-176 °C. 1H NMR (400 MHz, CDCl3): δ 8.31 (dd, J = 8.7, 2.7 Hz, 1H), 8.14 (d, J = 2.7 Hz, 1H), 7.91 (d, J = 8.7 Hz, 1H), 7.28-7.23 (m, 1H), 7.19 (d, J = 6.6 Hz, 1H), 7.16-7.10 (m, 1H), 7.02 (dd, J = 15.6, 5.4 Hz, 1H), 6.91 (d, J = 8.3 Hz, 2H), 6.85 (d, J = 8.2 Hz, 2H), 6.72 (d, J = 7.6 Hz, 1H), 6.30 (dd, J = 15.6, 1.5 Hz, 1H), 5.50-5.38 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 2.82 (dd, J = 14.1, 5.0 Hz, 1H), 2.60 (t, J = 13.6 Hz, 1H), 2.33 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl3): δ 166.0, 148.0, 145.5, 143.2, 142.4, 139.2, 136.4, 135.6, 135.2, 129.3, 129.1, 128.4, 128.3, 127.7, 126.4, 124.3, 123.3, 122.5, 68.9, 60.8, 36.8, 21.5, 14.3. IR (KBr): 3066, 2924, 1718, 1657, 1526, 1450, 1350, 1272, 1168, 1097, 976, 745 cm⁻¹. HRMS (ESI) m/z calculated for C26H24N2SO6Na [M+Na]⁺ 515.1253, found 515.1246.

Ethyl (E)-3-(2-methyl-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3j)

White solid (76.6 mg, 83% yield). PE/EA = 5:1, Rf = 0.30. Mp: 157-158 °C. 1H NMR (400 MHz, CDCl3): δ 7.48 (d, J = 8.0 Hz, 1H), 7.19-7.15 (m, 1H), 7.07-7.00 (m, 2H), 6.97-6.89 (m, 3H), 6.81 (d, J = 8.2 Hz, 2H), 6.71 (d, J = 8.1 Hz, 2H), 6.54 (d, J = 7.5 Hz, 1H), 6.27-6.15 (m, 1H), 5.32-5.22 (m, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.62 (dd, J = 13.8, 5.0 Hz, 1H), 2.48 (t, J = 13.4 Hz, 1H), 2.32 (s, 3H), 2.21 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl3): δ 166.4, 146.5, 142.3, 140.5, 139.5, 138.6, 136.1, 135.3, 133.7, 130.4, 130.0, 129.5, 129.0, 128.1, 128.0, 127.7, 127.2, 126.4, 121.9, 68.5, 60.6, 37.2, 21.4, 21.3, 14.3. IR (KBr): 3066, 2984, 1718, 1657, 1450, 1345, 1392, 1364, 1356, 1352, 1293, 1284, 1283, 1277, 1264, 1243, 1233, 1225, 68.9, 60.8, 36.8, 21.5, 14.3. HRMS (ESI) m/z calculated for C27H27N5SO4Na [M+Na]⁺ 484.1558, found 484.1545.

Ethyl (E)-3-(2-methoxy-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3k)

White solid (43.0 mg, 45% yield). PE/EA = 5:1, Rf = 0.32. Mp: 127-128 °C. 1H NMR (400 MHz, CDCl3): δ 7.52 (d, J = 8.7 Hz, 1H), 7.09-7.00 (m, 2H), 6.98-6.86 (m, 3H), 6.80 (d, J = 7.8 Hz, 2H), 6.71 (d, J = 8.1 Hz, 2H), 6.65 (d, J = 2.8 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 6.22 (d, J = 15.6 Hz, 1H), 5.33-5.22 (m, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 2.63 (dd, J = 13.8, 5.0 Hz, 1H), 2.49 (t, J = 13.3 Hz, 1H), 2.21 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl3): δ 166.4, 146.5, 142.3, 140.5, 139.5, 138.6, 136.1, 135.4, 135.1, 129.0, 128.2, 127.9, 127.8, 127.2, 126.4, 125.6, 121.9, 114.8, 113.5, 68.4, 60.6, 55.5, 37.2, 21.4, 14.3. IR (KBr): 2928, 2853, 1718, 1657, 1450, 1345, 1272, 1167, 1100, 979, 745 cm⁻¹. HRMS (ESI) m/z calculated for C27H27N5SO5Na [M+Na]⁺ 500.1508, found 500.1498.

Ethyl (E)-3-(2-methyl-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3l)
White solid (48.0 mg, 52% yield). PE/EA = 5:1, Rf = 0.31. Mp: 69-70 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (s, 1H), 7.27-7.26 (m, 1H), 7.13-6.96 (m, 5H), 6.88 (d, J = 7.8 Hz, 2H), 6.78 (d, J = 7.6 Hz, 2H), 6.59 (d, J = 7.6 Hz, 1H), 6.29 (d, J = 15.7 Hz, 1H), 5.40-5.29 (m, 1H), 4.24 (q, J = 7.1 Hz, 2H), 2.69 (dd, J = 13.8, 4.9 Hz, 1H), 2.57 (t, J = 13.3 Hz, 1H), 2.46 (s, 3H), 2.29 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.4, 146.6, 142.4, 138.8, 138.5, 137.7, 136.1, 135.2, 132.9, 130.3, 129.1, 129.0, 128.0, 127.9, 127.5, 127.2, 126.4, 121.9, 68.6, 60.6, 37.2, 21.4, 21.2, 14.3. IR (KBr): 3058, 2924, 2863, 1718, 1657, 1449, 1345, 1272, 1168, 979, 742 cm⁻¹. HRMS (ESI) m/z calculated for C₂₇H₂₇NSO₄Na (M+Na)⁺ 484.1558, found 484.1553.

**Ethyl (E)-3-(1-methyl-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3m)**

White solid (60.9 mg, 66% yield). PE/EA = 5:1, Rf = 0.34. Mp: 147-148 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.56-7.50 (m, 1H), 7.38-7.33 (m, 2H), 7.19-7.12 (m, 2H), 7.02-6.94 (m, 4H), 6.88 (d, J = 8.2 Hz, 2H), 6.57 (d, J = 7.6 Hz, 1H), 6.23 (dd, J = 15.7, 1.4 Hz, 1H), 5.25-5.16 (m, 1H), 4.24 (q, J = 7.1 Hz, 2H), 2.70 (dd, J = 13.6, 5.2 Hz, 1H), 2.51 (t, J = 13.1 Hz, 1H), 2.34 (s, 3H), 2.22 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.3, 146.0, 142.3, 139.2, 136.7, 136.6, 136.5, 136.0, 133.3, 131.8, 131.2, 130.0, 129.2, 128.1, 127.9, 127.5, 126.5, 126.3, 122.1, 67.8, 60.6, 37.0, 21.4, 20.9, 14.3. IR (KBr): 3063, 2982, 1718, 1658, 1449, 1346, 1269, 1161, 1111, 974, 746 cm⁻¹. HRMS (ESI) m/z calculated for C₂₇H₂₇NSO₄Na (M+Na)⁺ 484.1553, found 484.1552.

**Ethyl (E)-3-(9-methyl-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3n)**

White solid (62.8 mg, 68% yield). PE/EA = 5:1, Rf = 0.35. Mp: 135-136 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.62-7.56 (m, 1H), 7.39-7.32 (m, 2H), 7.18-7.12 (m, 1H), 7.09-7.01 (m, 2H), 6.95 (d, J = 9.3 Hz, 3H), 6.47 (d, J = 7.7 Hz, 1H), 6.22 (dd, J = 15.6, 1.5 Hz, 1H), 5.32-5.22 (m, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.59 (dd, J = 13.8, 5.2 Hz, 1H), 2.48 (t, J = 13.3 Hz, 1H), 2.24 (s, 3H), 2.23 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.3, 146.0, 142.3, 139.2, 136.7, 136.6, 136.5, 136.0, 133.3, 131.8, 131.2, 130.0, 129.2, 128.1, 127.9, 127.5, 126.5, 126.3, 122.1, 67.8, 60.6, 37.0, 21.4, 20.9, 14.3. IR (KBr): 3063, 2982, 1718, 1658, 1449, 1346, 1269, 1161, 1111, 974, 746 cm⁻¹. HRMS (ESI) m/z calculated for C₂₇H₂₇NSO₄Na [M+Na]⁺ 484.1553, found 484.1552.

**Ethyl (E)-3-(10-methyl-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3o)**

White solid (47.1 mg, 51% yield). PE/EA = 5:1, Rf = 0.38. Mp: 155-156 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.74-7.66 (m, 1H), 7.51-7.43 (m, 2H), 7.27-7.21 (m, 1H), 7.09-7.01 (m, 2H), 6.98 (d, J = 7.6 Hz, 1H), 6.90 (d, J = 8.3 Hz, 2H), 6.85 (d, J = 8.1 Hz, 2H), 6.43 (s, 1H), 6.33 (dd, J = 15.6, 1.6 Hz, 1H), 5.44-5.33 (m, 1H), 4.26 (q, J = 7.1 Hz, 2H), 2.72 (dd, J = 13.9, 5.0 Hz, 1H), 2.56 (t, J = 13.4 Hz, 1H), 2.34 (s, 3H), 2.23 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 166.4, 146.5, 142.1, 141.1, 138.2, 137.2, 136.3, 134.1, 133.1, 132.3, 129.4, 129.3, 128.8, 128.6, 128.4, 128.0, 126.7, 121.9, 68.7, 60.6,
Ethyl (E)-3-(11-methoxy-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3p)
White solid (27.7 mg, 29% yield). PE/EA = 5:1, Rf = 0.24. Mp: 189-190 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.61-7.55 (m, 1H), 7.40-7.36 (m, 1H), 7.35-7.28 (m, 2H), 7.02 (d, J = 7.9 Hz, 1H), 6.97-6.88 (m, 3H), 6.75 (d, J = 8.1 Hz, 2H), 6.70 (d, J = 7.3 Hz, 1H), 6.44 (d, J = 8.3 Hz, 1H), 6.19 (dd, J = 15.7, 1.4 Hz, 1H), 5.25-5.15 (m, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.46 (s, 3H), 2.59 (s, 3H), 2.36 (t, J = 13.3 Hz, 1H), 2.23 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.4, 155.4, 146.2, 141.7, 137.3, 136.7, 136.4, 133.7, 133.2, 131.8, 128.9, 128.8, 128.3, 128.2, 126.5, 125.8, 122.0, 119.4, 68.2, 61.4, 59.2, 37.3, 21.6, 14.3. IR (KBr): 3060, 2924, 1717, 1654, 1460, 1344, 1267, 1165, 1090, 979, 742 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{27}$H$_{27}$NSO$_4$Na [M+Na]$^+$ 500.1508, found 500.1500.

Ethyl (E)-3-(9-methoxy-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3q)
White solid (48.7 mg, 51% yield). PE/EA = 5:1, Rf = 0.38. Mp: 149-150 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.61-7.52 (m, 1H), 7.40-7.28 (m, 2H), 7.15-7.08 (m, 1H), 6.94 (dd, J = 15.6, 5.3 Hz, 1H), 6.84 (d, J = 8.2 Hz, 2H), 6.74 (d, J = 8.1 Hz, 2H), 6.57 (d, J = 1.4 Hz, 1H), 6.52-6.29 (m, 2H), 6.22 (dd, J = 15.6, 1.3 Hz, 1H), 5.41-5.09 (m, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.72 (s, 3H), 2.58 (s, 3H), 2.48 (t, J = 13.3 Hz, 1H), 2.22 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.4, 155.4, 146.2, 141.7, 137.3, 136.7, 136.4, 134.0, 132.9, 131.0, 129.4, 129.3, 129.1, 128.9, 128.3, 128.2, 126.6, 122.1, 113.6, 112.5, 68.2, 60.7, 55.3, 37.4, 21.4, 14.3. IR (KBr): 3059, 2978, 2847, 1717, 1657, 1608, 1468, 1346, 1266, 1170, 1101, 980, 746 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{27}$H$_{27}$NSO$_5$Na [M+Na]$^+$ 500.1508, found 500.1500.

Ethyl (E)-3-(9-fluoro-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylate (3r)
White solid (31.7 mg, 34% yield). PE/EA = 5:1, Rf = 0.37. Mp: 115-116 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.63-7.56 (m, 1H), 7.42-7.34 (m, 2H), 7.15-7.07 (m, 1H), 6.92 (dd, J = 15.6, 5.4 Hz, 1H), 6.85 (d, J = 8.2 Hz, 2H), 6.77 (dd, J = 12.2, 5.5 Hz, 3H), 6.67-6.57 (m, 1H), 6.56-6.46 (m, 1H), 6.22 (dd, J = 15.6, 1.2 Hz, 1H), 5.38-5.25 (m, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.61 (dd, J = 13.8, 5.1 Hz, 1H), 2.49 (t, J = 13.4 Hz, 1H), 2.24 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.2, 162.1 (d, J = 247.5 Hz), 145.8, 142.7, 139.9, 137.4 (d, J = 7.7 Hz, 2H), 136.2, 134.5 (d, J = 3.1 Hz), 134.2, 133.0, 129.8 (d, J = 8.4 Hz), 129.6, 129.2, 128.9, 126.5, 122.3, 115.0 (d, J = 21.8 Hz), 113.9 (d, J = 21.3 Hz), 68.1, 60.7, 37.1, 21.4, 14.3. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -114.36 (s). IR (KBr): 3062, 2984, 2928, 1718, 1657, 1601, 1448, 1346, 1279, 1163, 1102, 977, 736 cm$^{-1}$. HRMS (ESI) m/z calculated for C$_{26}$H$_{26}$NFSO$_4$Na [M+Na]$^+$ 488.1308, found 488.1309.
Dimethyl-2-((5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)methylene)malonate (3a')

Compound 3a' was isolated by flash chromatography as a diastereomeric mixture (60.9 mg, 62% yield, dr = 5:1) in 62% yield. The pure analytical sample of the major diastereomer of 3a' was obtained by preparative TLC on silica gel as a yellow oil. PE/E A = 5:1, R\textsubscript{f} = 0.28. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.54-7.45 (m, 1H), 7.36-7.27 (m, 2H), 7.13-7.10 (m, 1H), 7.02-6.95 (m, 2H), 6.94-6.78 (m, 2H), 6.75 (d, J = 7.8 Hz, 2H), 6.65 (d, J = 7.5 Hz, 1H), 5.67-5.36 (m, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 2.63 (dd, J = 13.6, 4.5 Hz, 1H), 2.39 (t, J = 13.1 Hz, 1H), 2.13 (s, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 164.9, 164.4, 147.8, 142.5, 140.7, 138.4, 136.2, 134.7, 133.8, 133.0, 129.7, 129.5, 129.0, 128.8, 128.5, 128.0, 127.9, 127.4, 126.4, 126.3, 66.0, 52.7, 52.6, 36.6, 21.4. IR (KBr): 2955, 2922, 2852, 1724, 1645, 1599, 1478, 1267, 1160, 977, 747 cm\textsuperscript{-1}. HRMS (ESI) m/z calculated for C\textsubscript{27}H\textsubscript{25}N\textsubscript{2}O\textsubscript{6}Na [M+Na]+ 514.1300, found 514.1308.

(E)-N,N-dimethyl-3-(5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylamide (3b')

White solid (52.7 mg, 59% yield). PE/E A = 3:1, R\textsubscript{f} = 0.23. Mp: 190-191 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.69-7.60 (m, 1H), 7.46-7.36 (m, 2H), 7.25-7.20 (m, 1H), 7.17-7.07 (m, 2H), 7.05-6.98 (m, 1H), 6.94-6.81 (m, 4H), 6.81-6.66 (m, 2H), 6.60 (d, J = 7.4 Hz, 1H), 5.47-5.33 (m, 1H), 3.20 (s, 3H), 3.04 (s, 3H), 2.73 (dd, J = 13.9, 5.1 Hz, 1H), 2.59 (t, J = 13.4 Hz, 1H), 2.29 (s, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 166.4, 142.9, 142.4, 140.9, 138.5, 136.1, 135.7, 133.9, 133.2, 129.4, 129.0, 128.6, 128.1, 128.0, 127.8, 127.2, 126.4, 121.7, 69.4, 37.6, 37.5, 35.8, 21.4. IR (KBr): 3031, 2926, 1663, 1622, 1483, 1344, 1265, 1160, 1095, 972, 741 cm\textsuperscript{-1}. HRMS (ESI) m/z calculated for C\textsubscript{26}H\textsubscript{26}N\textsubscript{2}SO\textsubscript{3}Na [M+Na]+ 469.1562, found 469.1565.

(E)-3-(5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepin-6-yl)acrylic acid (3c')

Yellow solid (35.2 mg, 42% yield). PE/E A = 1:1, R\textsubscript{f} = 0.22. Mp: 224-225 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 11.07 (br s, 1H), 7.65-7.60 (m, 1H), 7.43-7.37 (m, 2H), 7.19-7.16 (m, 1H), 7.12-7.03 (m, 3H), 6.98-6.92 (m, 1H), 6.82 (d, J = 8.3 Hz, 2H), 6.73 (d, J = 8.2 Hz, 2H), 6.56 (d, J = 7.4 Hz, 1H), 6.26 (dd, J = 15.6, 1.4 Hz, 1H), 5.35-5.31 (m, 1H), 2.68 (dd, J = 13.9, 5.0 Hz, 1H), 2.53 (t, J = 13.4 Hz, 1H), 2.23 (s, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 171.4, 149.1, 142.5, 140.8, 138.5, 135.9, 135.2, 134.0, 133.0, 129.4, 129.0, 128.8, 128.1, 127.8, 127.3, 126.4, 121.2, 68.5, 37.0, 21.5. IR (KBr): 3063, 2924, 1698, 1655, 1480, 1346, 1266, 1161, 1098, 972, 742 cm\textsuperscript{-1}. HRMS (ESI) m/z calculated for C\textsubscript{24}H\textsubscript{21}N\textsubscript{2}SO\textsubscript{4}Na [M+Na]+ 442.1089, found 442.1088.

(E)-6-styryl-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepine (3d')
White solid (74.1 mg, 82% yield). PE/EA = 5:1, Rf = 0.36. Mp: 196-197 °C. 1H NMR (400 MHz, CDCl3): δ 7.74-7.67 (m, 1H), 7.51-7.45 (m, 4H), 7.37 (t, J = 7.5 Hz, 2H), 7.32-7.27 (m, 2H), 7.21-7.16 (m, 2H), 7.10-7.03 (m, 1H), 6.97 (d, J = 81. Hz, 2H), 6.88-6.79 (m, 3H), 6.71 (d, J = 7.5 Hz, 1H), 6.42 (dd, J = 15.9, 6.3 Hz, 1H), 5.52-5.43 (m, 1H), 2.80 (dd, J = 13.8, 5.2 Hz, 1H), 2.68 (t, J = 13.2 Hz, 1H), 2.33 (s, 3H). 13C NMR (100 MHz, CDCl3): δ 142.1, 141.2, 138.7, 136.7, 136.1, 133.9, 133.6, 130.9, 129.4, 129.3, 129.2, 129.0, 128.7, 128.6, 128.2, 128.0, 127.8, 127.7, 127.1, 126.7, 126.5, 126.5, 126.5, 30.0, 21.4. IR (KBr): 3031, 2925, 1601, 1486, 1443, 1342, 1267, 1160, 1095, 970, 747 cm⁻¹. HRMS (ESI) m/z calculated for C29H25NSO2Na [M+Na]+ 474.1504, found 474.1500.

(E)-6-(2-methoxystyryl)-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepine (3e)

White solid (88.6 mg, 92% yield). PE/EA = 5:1, Rf = 0.39. Mp: 147-148 °C. 1H NMR (400 MHz, CDCl3): δ 7.75-7.68 (m, 1H), 7.58-7.52 (m, 1H), 7.51-7.42 (m, 2H), 7.32-7.24 (m, 2H), 7.11-7.05 (m, 1H), 7.04-6.95 (m, 3H), 6.92 (d, J = 8.2 Hz, 1H), 6.84 (d, J = 7.5 Hz, 2H), 6.73 (d, J = 6.9 Hz, 1H), 6.50-6.36 (m, 1H), 5.56-5.40 (m, 1H), 3.90 (s, 3H), 2.87-2.79 (m, 1H), 2.74-2.63 (m, 1H), 2.33 (s, 3H). 13C NMR (100 MHz, CDCl3): δ 156.9, 142.1, 141.2, 138.7, 136.9, 136.3, 133.9, 133.7, 129.7, 129.2, 129.0, 128.9, 128.5, 128.2, 128.0, 127.7, 127.0, 126.9, 126.5, 125.7, 125.6, 126.0, 111.0, 70.4, 55.6, 38.2, 21.4. IR (KBr): 3060, 2949, 1594, 1484, 1450, 1340, 1249, 1164, 1100, 976, 743 cm⁻¹. HRMS (ESI) m/z calculated for C30H27NSO3Na [M+Na]+ 504.1609, found 504.1606.

(E)-6-(4-fluorostyryl)-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepine (3f)

White solid (83.6 mg, 89% yield). PE/EA = 5:1, Rf = 0.36. Mp: 221-222 °C. 1H NMR (400 MHz, CDCl3): δ 7.74-7.67 (m, 1H), 7.49-7.40 (m, 4H), 7.30-7.26 (m, 1H), 7.20-7.05 (m, 2H), 7.09-7.01 (m, 3H), 6.95 (d, J = 8.2 Hz, 2H), 6.86-6.76 (m, 3H), 6.69 (d, J = 7.6 Hz, 1H), 6.32 (dd, J = 15.9, 6.3 Hz, 1H), 5.49-5.40 (m, 1H), 2.79 (dd, J = 13.8, 5.2 Hz, 1H), 2.66 (t, J = 13.3 Hz, 1H), 2.32 (s, 3H). 13C NMR (100 MHz, CDCl3): δ 162.5 (d, J = 246.9 Hz, 10H), 142.1, 141.2, 138.7, 136.9, 136.3, 133.9, 133.7, 129.7, 129.2, 129.0, 128.9, 128.5, 128.2, 128.0, 127.7, 127.0, 126.9, 126.5, 125.7, 125.6, 126.0, 111.0, 70.4, 55.6, 38.2, 19F NMR (376 MHz, CDCl3): δ -114.24 (s). IR (KBr): 3058, 2924, 2924, 1594, 1484, 1450, 1340, 1249, 1164, 1100, 976, 743 cm⁻¹. HRMS (ESI) m/z calculated for C29H24NSFOSNa [M+Na]+ 492.1409, found 492.1399.

(E)-6-(3-nitrostyryl)-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepine (3g)

White solid (90.4 mg, 91% yield). PE/EA = 5:1, Rf = 0.36. Mp: 217-218 °C. 1H NMR (400 MHz, CDCl3): δ 8.31 (t, J = 1.8 Hz, 1H), 8.18-8.10 (m, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.75-7.68 (m, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.53-7.47 (m, 2H), 7.33-7.29 (m, 1H), 7.22-7.14 (m, 2H), 7.10-7.03 (m, 1H), 6.99-6.90 (m, 3H), 6.83 (d, J = 6.1 Hz, 2H), 6.68 (d, J = 7.5 Hz, 1H), 6.53 (dd, J = 15.9, 6.2 Hz, 1H), 5.52-5.41 (m, 1H), 2.81 (dd, J = 13.8, 5.2 Hz, 1H), 2.69 (t, J = 13.3 Hz, 1H), 2.33 (s, 3H). 13C NMR (100 MHz, CDCl3): δ 148.6, 142.3, 141.0, 138.6, 138.5, 136.3, 135.7, 133.8, 133.3, 132.7, 132.6, 129.5, 129.4, 129.3, 129.0,
128.8, 128.7, 128.2, 127.8, 127.2, 126.4, 122.4, 121.2, 69.7, 37.9, 21.4. IR (KBr): 3063, 2923, 1604, 1528, 1484, 1443, 1345, 1268, 1161, 1095, 972, 744 cm⁻¹. HRMS (ESI) m/z calculated for C₂₉H₂₄N₂SO₄Na [M+Na]⁺ 519.1354, found 519.1356.

(E)-6-(2-(thiophen-2-yl)vinyl)-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepine (3h')

White solid (37.5 mg, 41% yield). PE/EA = 5:1, Rₐ = 0.33. Mp: 165-166 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.73-7.65 (m, 1H), 7.50-7.44 (m, 2H), 7.30-7.28 (m, 1H), 7.20 (d, J = 4.9 Hz, 1H), 7.19-7.14 (m, 2H), 7.09-7.04 (m, 2H), 7.06-6.98 (m, 2H), 6.97-6.92 (m, 2H), 6.82 (d, J = 8.0 Hz, 2H), 6.68 (d, J = 7.4 Hz, 1H), 6.22 (dd, J = 15.7, 6.3 Hz, 1H), 5.48-5.37 (m, 1H), 2.78 (dd, J = 13.8, 5.2 Hz, 1H), 2.65 (t, J = 13.3 Hz, 1H), 2.32 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 142.1, 141.7, 141.1, 138.6, 136.6, 136.0, 133.9, 133.5, 129.3, 129.2, 128.9, 128.8, 128.6, 128.1, 128.0, 127.7, 127.4, 127.1, 126.5, 126.4, 124.5, 124.3, 69.8, 38.0, 21.4. IR (KBr): 3062, 2922, 1640, 1602, 1485, 1442, 1341, 1268, 1161, 1097, 957, 751 cm⁻¹. HRMS (ESI) m/z calculated for C₂₇H₂₃N₂O₂SNa [M+Na]⁺ 480.1068, found 480.1070.

(E)-6-(2-(furan-2-yl)vinyl)-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepine (3i')

White solid (52.1 mg, 59% yield). PE/EA = 5:1, Rₐ = 0.34. Mp: 137-138 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.71-7.63 (m, 1H), 7.48-7.39 (m, 2H), 7.36 (s, 1H), 7.26-7.23 (m, 1H), 7.19-7.10 (m, 2H), 7.06-6.97 (m, 1H), 6.90 (d, J = 8.2 Hz, 2H), 6.79 (d, J = 8.1 Hz, 2H), 6.66 (t, J = 12.9 Hz, 2H), 6.43-6.36 (m, 1H), 6.35-6.24 (m, 2H), 5.39 (m, 1H), 2.74 (dd, J = 13.8, 5.2 Hz, 1H), 2.61 (t, J = 13.3 Hz, 1H), 2.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 152.2, 142.1, 142.0, 141.0, 138.6, 136.5, 136.1, 134.0, 133.4, 129.3, 129.2, 128.9, 128.6, 128.1, 128.0, 127.8, 127.7, 127.0, 126.4, 119.4, 111.4, 108.8, 69.8, 38.1, 21.4. IR (KBr): 3060, 2922, 1603, 1485, 1444, 1342, 1266, 1161, 1097, 968, 747 cm⁻¹. HRMS (ESI) m/z calculated for C₂₇H₂₃NO₃SNa [M+Na]⁺ 464.1296, found 464.1294.

(E)-6-(4-phenylbut-1-en-1-yl)-5-tosyl-6,7-dihydro-5H-dibenzo[b,d]azepine

White solid (85.4 mg, 89% yield). PE/EA = 10:1, Rₐ = 0.45. Mp: 115-116 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.61-7.57 (m, 1H), 7.47-7.40 (m, 2H), 7.34-7.29 (m, 2H), 7.28-7.20 (m, 4H), 7.17-7.08 (m, 2H), 7.07-6.99 (m, 1H), 6.92 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.1 Hz, 2H), 6.67 (d, J = 7.5 Hz, 1H), 6.02-5.92 (m, 1H), 5.66 (dd, J = 15.4, 6.1 Hz, 1H), 5.27-5.19 (m, 1H), 2.77 (t, J = 7.7 Hz, 2H), 2.63 (dd, J = 13.9, 5.2 Hz, 1H), 2.53-2.47 (m, 1H), 2.46-2.38 (m, 2H), 2.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 142.0, 141.7, 141.1, 138.6, 136.8, 136.4, 133.8, 133.6, 131.1, 130.6, 129.1, 129.0, 128.9, 128.6, 128.4, 128.3, 128.1, 127.9, 127.6, 126.9, 126.4, 125.8, 69.8, 38.2, 35.6, 34.1, 21.4. IR (KBr): 3062, 2922, 1599, 1495, 1481, 1440, 1346, 1265, 1161, 1092, 978, 745 cm⁻¹. HRMS (ESI) m/z calculated for C₃₁H₂₉NO₃SNa [M+Na]⁺ 502.1817, found 502.1816.

D. Kinetic isotope experiment:

S12
In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with Pd(TFA)$_2$ (3.3 mg, 0.01 mmol), Cu(OAc)$_2$ (76.3 mg, 0.42 mmol), [D$_1$]-1a (0.20 mmol) and 1,3-dienes 2a (0.40 mmol), followed by sequential addition of MeCN (1.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 120 °C for 36 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO$_4$, filtered, and concentrated in vacuo. The residue was then purified on silica gel to afford the desired product. The residue was then purified on silica gel to afford a mixture of 3a and [D$_1$]-3a in 17% yield (15.3 mg). The KIE value ($K_H/K_D = 1.0$) was determined on the basis of $^1$H NMR analysis (see below).

E. Large-scale preparation of 3a:

In a glovebox, a 20.0 mL vial equipped with a stirring bar was charged with Pd(TFA)$_2$ (16.5 mg, 0.05 mmol), Cu(OAc)$_2$ (419.3 mg, 21.0 mmol), 1a (1.0 mmol) and 1,3-dienes 2a (2.0 mmol), followed by sequential addition of MeCN (5.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 120 °C for 36 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO$_4$, filtered, and concentrated in vacuo. The residue was then purified on silica gel using 10% ethyl acetate/petroleum ether eluent to afford the desired product 349.1 mg 3a (78% yield).
F. References:
G. NMR spectra:
(1m)