Supporting Information

Highly Enantioselective [4+2] Cyclization of Chloroaldehydes and 1-Azadiene

Catalyzed by N-Heterocyclic Carbenes

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Part I  Experimental part

General Information

Unless otherwise indicated, all reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring. Anhydrous THF, ether, toluene were distilled from sodium and benzophenone, CH$_2$Cl$_2$ was distilled from CaH$_2$. Chiral triazolium salts $4a$-$4c$, $^{1a-d}5a$-$5b$, $^{1e}$ and chloroaldehydes$^2$ were synthesized according to our previous reports and the literatures. The commercially available NCS was recrystallized from AcOH. 1-Azadienes were prepared from $\alpha$, $\beta$-unsaturated ketones or $\alpha$, $\beta$-unsaturated aldehydes and sulfonamide according to literature procedures.$^3$ Column chromatograph was performed on silica gel 200~300 mesh. All $^1$H NMR (300 MHz), $^{13}$C NMR (75 MHz) spectra were recorded on a Bruker-DMX 300 spectrometer in CDCl$_3$, with tetramethylsilane as an internal standard and reported in parts per million (ppm, $\delta$). $^1$H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). Infrared spectra were recorded on a JASCO FT/IR-480 spectrophotometer and reported as wave number (cm$^{-1}$). Optical rotations were measured on Perkin Elmer/Model-343 digital polarimeter operating at the sodium D line with a 100 mm path cell, and are reported as follows: $[\alpha]_D^T$ (concentration (g/100 mL), solvent).
1.1 Preparation of the 1-azadienes

**Typical procedure.** To a solution of sulfonamide (5.0 mmol) and α, β-unsaturated aldehyde or α, β-unsaturated ketone (5.0 mmol) in DCM (15 mL), at 0 °C, were successively added Et₃N (10.0 mmol) and TiCl₄ (5.0 mmol). The reaction mixture was heated at reflux overnight. Then the solution was cooled to room temperature, quenched with water (100 mL) and extracted with CH₂Cl₂ (3 × 30 mL). The combined organic phase was dried (Na₂SO₄) and evaporated. The residue was purified by flash chromatography to afford pure 1-azadiene.

![Chemical structure](image)

4-Methyl-N-[3-(2-nitro-phenyl)-allylidene]-benzenesulfonamide (2e)

Yield: 1.17 g (71%), yellow solid. mp 136-138 °C, Rᶠ = 0.2 (petroleum ether/ethyl acetate, 2:1). ¹H NMR (300 MHz, CDCl₃) δ 8.79 (d, J = 9.3 Hz, 1H), 8.09-7.99 (m, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.75-7.59 (m, 3H), 7.36 (d, J = 7.8 Hz, 2H), 6.90 (dd, J = 9.0 Hz, J = 15 Hz, 1H), 2.45 (s, 3H); ¹³C NMR (300 MHz, CDCl₃) δ 169.9, 147.8, 144.8, 134.4, 133.8, 133.2, 131.2, 129.8, 128.8, 128.0, 125.1, 21.5. IR (KBr) ν 2984, 1718, 1600, 1456, 845, 775. HRMS (EI) m/z: M⁺ Calc. for C₁₆H₁₄N₂O₄S, 330.0674, Found 330.0680.
1.2 Optimization of reaction conditions for \( \alpha,\beta \)-unsaturated ketimine 6a (Table S1)

Table S1. Optimization of reaction conditions (\( \alpha,\beta \)-unsaturated ketimines)

<table>
<thead>
<tr>
<th>entry</th>
<th>4 or 5</th>
<th>solvent</th>
<th>T (°C)</th>
<th>( 7a )</th>
<th>yield (%)(^a)</th>
<th>ee (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>DCM</td>
<td>RT</td>
<td>(-)-7a</td>
<td>31</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>5a</td>
<td>DCM</td>
<td>RT</td>
<td>(+)-7a</td>
<td>77</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>5b</td>
<td>DCM</td>
<td>RT</td>
<td>(+)-7a</td>
<td>56</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>5a</td>
<td>THF</td>
<td>RT</td>
<td>(+)-7a</td>
<td>56</td>
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<td>(+)-7a</td>
<td>71</td>
<td>65</td>
</tr>
<tr>
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<td>DCM</td>
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<td>(+)-7a</td>
<td>84</td>
<td>81</td>
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<tr>
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<td>(+)-7a</td>
<td>27</td>
<td>61</td>
</tr>
<tr>
<td>8</td>
<td>5a</td>
<td>DCM</td>
<td>-60</td>
<td>(+)-7a</td>
<td>trace</td>
<td>/</td>
</tr>
</tbody>
</table>

\(^a\) Isolated yield. \(^b\) Determined by HPLC on chiral column.

Typical results of the condition optimization for the model reaction of \( \alpha \)-chloroaldehyde 1a and \( \alpha,\beta \)-unsaturated ketimine 6a was summarized in Table S1. Both NHCs derived L-pyroglutamic acid and aminoundanol worked for the reaction but with varied yields and enantioselectivities (entries 1-3). In contrast with the reaction of \( \alpha,\beta \)-unsaturated aldimines, NHC 5a with \( N \)-phenyl group worked better than NHC 5b with \( N \)-mesityl group for the reaction of \( \alpha,\beta \)-unsaturated ketimine 6a, giving the desired 7a in 77% yield with 78% ee at room temperature (entry 2 vs 3). No improvement was observed when the reaction was carried out in THF or toluene (entries 2, 4-5). Lowering the reaction temperature to 0 °C lead to improved yield (84%) and enantioselectivity (81% ee) (entry 6).
However, further lowering the temperature to -20 or -60 °C resulted in very low conversion (entries 7 and 8).

1.3 NHC-catalyzed reaction with α,β-unsaturated aldimines (Table 2)

Typical procedure. To an oven-dried 50 mL Schlenk tube equipped with a stir bar was charged with trazolium salt 5b (12 mg, 0.025 mmol) and anhydrous Cs₂CO₃ (17 mg, 0.05 mmol). This tube was closed with a septum, evacuated, and back-filled with argon. To this mixture was added freshly distilled DCM (5 mL) and stirred for 30 minutes at room temperature. Then Chloroaldehyde 1a (132 mg, 1 mmol), α, β-unsaturated aldimines 2a (143 mg, 0.5 mmol) and DIPEA (0.55 mL, 3 mmol) was added. After stirring for 24 h, the mixture was diluted with diethyl ether and passed through a short silica pad. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (ethyl acetate /petroleum ether, typically 1/50) to give the desired product.

Racemic samples for the standard of chiral HPLC spectra were prepared using the triazolium salts $\text{S1}$ as the catalyst.
(3S,4S)-3-benzyl-4-phenyl-1-tosyl-3,4-dihydropyridin-2(1H)-one (3a)

Yield: 193.5 mg (93%), white solid. mp 115-117 °C, R_f = 0.41 (petroleum ether/ethyl acetate, 5:1); [α]_D^{25} +104.2 (c 1.1, CHCl_3), HPLC analysis: 99% ee [Daicel CHIRALPAK AS-H column, 20 °C, 254 nm hexane/i-PrOH = 90:10, 1.0 mL /min, 254 nm, 13.4 min (minor), 17.8 min (major)]. ^1H NMR (300 MHz, CDCl_3) δ 8.01 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.27-7.15 (m, 4H), 7.08 (d, J = 8.1 Hz, 1H), 7.01-6.96 (m, 4H), 6.46 (d, J = 7.5 Hz, 2H), 5.52 (dd, J = 6.3 Hz, J = 8.1 Hz, 1H), 3.36 (t, J = 6.6 Hz, 1H ), 3.29-3.26 (m, 1H), 3.16 (dd, J = 4.2 Hz, J = 14.4 Hz, 1H), 2.51 (s, 3H), 2.13 (dd, J = 4.2 Hz, J = 14.4 Hz, 1H ). ^13C NMR (300 MHz, CDCl_3) δ 169.0, 145.3, 138.6, 137.3, 134.8, 129.6, 128.9, 128.6, 128.5, 128.0, 127.5, 126.5, 123.9, 114.2, 48.8, 41.1, 31.4, 21.8. IR (KBr) ν 2970, 1720, 1538, 1356, 1162, 770.

HRMS (EI) m/z: M^+ Calc. for C_{25}H_{23}NO_3S, 417.1399, Found 417.1403.

(3S,4S)-3-benzyl-4-(4-methoxyphenyl)-1-tosyl-3,4-dihydropyridin-2(1H)-one (3b)

Yield: 206.5 mg (93%), white solid. mp 106-108 °C, R_f = 0.40 (petroleum ether/ethyl acetate, 5:1 ); [α]_D^{25} +217.4 (c 1.5, CHCl_3), HPLC analysis: 99% ee [Daicel CHIRALPAK AS-H column, 20 °C, 254 nm hexane/i-PrOH = 95:5, 1.0 mL /min, 254 nm, 32.3 min (minor), 35.7 min (major)]. ^1H NMR (300 MHz, CDCl_3) δ 7.90 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.17-7.08 (m, 3H), 6.96 (d, J = 7.2 Hz, 1H), 6.90 (d, J = 7.2 Hz, 2H), 6.42 (d, J = 8.7 Hz, 2H), 6.32 (d, J = 8.4 Hz, 2H), 5.41 (t, J = 6.6 Hz, 1H), 3.62 (s, 3H), 3.24-3.03 (m, 3H ), 2.40 (s, 3H), 2.05 (dd, J = 9.2 Hz, J =
14.4 Hz, 1H). $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ 169.8, 158.6, 145.2, 138.5, 134.6, 129.4, 129.0, 128.8, 128.8, 128.3, 126.3, 123.4, 114.5, 113.7, 55.0, 48.8, 40.1, 31.2, 21.6. IR (KBr) v 2987, 1738, 1658, 1540, 1203, 1060, 759. HRMS (EI) $m/z$: M$^+$ Calc. for C$_{26}$H$_{25}$NO$_4$S, 447.1504, Found 447.1509.

$^{(3S,4S)}$-3-benzyl-4-(furan-2-yl)-1-tosyl-3,4-dihydropyridin-2(1H)-one (3c)

Yield: 176.5 mg (87%), yellow solid. mp 95-97 °C, R$_f$ = 0.51 (petroleum ether/ethyl acetate, 5:1); $[\alpha]_D^{25}$ +194.4 (c 1.5, CHCl$_3$), HPLC analysis: 99% ee [Daicel CHIRALPAK AS-H column, 20 °C, 254 nm hexane/i-PrOH = 90:10, 1.0 mL /min, 254 nm, 16.0 min (minor), 25.7 min (major)]. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.87 ($d$, $J = 8.1$ Hz, 2H), 7.27 ($d$, $J = 8.1$ Hz, 2H), 7.18-7.10 ($m$, 3H), 6.99-6.96 ($m$, 3H), 6.74 ($d$, $J = 0.9$ Hz, 1H), 6.05 ($t$, $J = 3.0$ Hz, 1H), 5.72 ($d$, $J = 3.3$ Hz, 1H), 5.32 ($t$, $J = 7.8$ Hz, 1H), 3.30 ($t$, $J = 6.3$ Hz, 1H), 3.18 ($dd$, $J = 4.2$ Hz, $J = 14.4$ Hz, 1H ), 3.02-2.98 ($m$, 1H), 2.38 ($s$, 3H), 2.05 ($dd$, $J = 10.5$ Hz, $J = 15.0$ Hz, 1H ). $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ 169.4, 150.4, 144.9, 141.9, 138.5, 135.1, 129.2, 128.9, 128.7, 128.4, 126.4, 125.1, 110.7, 109.9, 107.8, 48.1, 33.6, 31.4, 21.6. IR (KBr) v 2980, 1838, 1654, 1530, 1183, 1060, 780. HRMS (EI) $m/z$: M$^+$ Calc. for C$_{23}$H$_{21}$NO$_4$S, 407.1191, Found 407.1198.
**(3S,4S)-3-benzyl-4-(4-nitrophenyl)-1-tosyl-3,4-dihydropyridin-2(1H)-one (3d)**

Yield: 87.5 mg (42%), yellow solid. mp 114-115 °C, R_f = 0.43 (petroleum ether/ethyl acetate, 5:1); [\(\alpha\)]_D^{25} +121.9 (c 1.3, CHCl_3), HPLC analysis: 92% ee [Daicel CHIRALPAK AS-H column, 20 °C, 254 nm hexane/i-PrOH = 80:20, 1.2 mL /min, 254 nm, 17.6 min (minor), 25.7 min (major)]. \(^1\)H NMR (300 MHz, CDCl_3) δ 7.94 (d, \(J = 8.4 \) Hz, 2H), 7.88-7.82 (m, 1H), 7.78 (d, \(J = 8.7 \) Hz, 2H), 7.39 (d, \(J = 8.1 \) Hz, 2H), 7.23-7.07 (m, 4H), 6.89 (d, \(J = 6.9 \) Hz, 2H), 6.57 (d, \(J = 8.7 \) Hz, 2H), 5.45 (t, \(J = 6.9 \) Hz, 1H), 3.42 (t, \(J = 6.6 \) Hz, 1H), 3.32-3.28 (m, 2H), 3.20-3.13 (m, 1H), 2.51 (s, 3H), 2.20 (dd, \(J = 4.5 \) Hz, \(J = 14.4 \) Hz, 1H). \(^13\)C NMR (300 MHz, CDCl_3) δ 169.3, 146.0, 144.9, 137.7, 134.5, 129.8, 129.6, 129.0, 128.8, 127.9, 126.8, 125.1, 124.0, 123.7, 112.7, 48.1, 40.5, 31.4, 21.8.IR (KBr) ν 3080, 2995, 1850, 1554, 1430, 1083, 1030, 780. HRMS (EI) m/z: M⁺ Calc. for C_{25}H_{22}NO_5S, 462.1249, Found 462.1255.

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**(3S,4S)-3-benzyl-4-(2-nitrophenyl)-1-tosyl-3,4-dihydropyridin-2(1H)-one (3e)**

Yield: 131.5 mg (57%), yellow solid. mp 104-105 °C, R_f = 0.43 (petroleum ether/ethyl acetate, 5:1); [\(\alpha\)]_D^{25} +101.7 (c 1.3, CHCl_3), HPLC analysis: 96% ee [Daicel CHIRALPAK AS-H column, 20 °C, 254 nm hexane/i-PrOH = 80:20, 1.2 mL /min, 254 nm, 17.6 min (minor), 21.4 min (major)]. \(^1\)H NMR (300 MHz, CDCl_3) δ 7.97 (d, \(J = 8.1 \) Hz, 2H), 7.78 (d, \(J = 7.2 \) Hz, 1H), 7.42-7.33 (m, 3H), 7.17-7.13 (m, 3H), 7.09 (d, \(J = 8.4 \) Hz, 2H), 6.70 (t, \(J = 3.3 \) Hz, 2H), 6.52 (d, \(J = 7.8 \) Hz, 1H), 5.72
(dd, J = 6.6 Hz, J = 9.3 Hz 1H), 3.85 (t, J = 3.9 Hz, 1H), 3.30-3.24 (m, 2H), 2.53 (s, 3H), 2.16 (dd, J = 8.4 Hz, J = 14.4 Hz, 1H). ^{13}C NMR (300 MHz, CDCl$_3$) δ 169.8, 149.7, 145.5, 137.3, 134.7, 133.1, 133.0, 129.6, 128.9, 128.8, 128.3, 128.2, 128.2, 126.8, 124.8, 124.1, 112.6, 47.5, 35.0, 31.6, 21.8. IR (KBr) v 3078, 2985, 1850, 1554, 1430, 1083, 780. HRMS (EI) m/z: M$^+$ Calc. for C$_{25}$H$_{22}$NO$_5$S, 462.1249, Found 462.1255.

![Diagram](image.png)

(3S,4S)-4-phenyl-3-propyl-1-tosyl-3,4-dihydropyridin-2(1H)-one (3f)

Yield: 159.2 mg (87%), white solid. Mp 77-79 °C, R$_f$ = 0.61 (petroleum ether/ethyl acetate, 5:1); $[\alpha]_D^{25}$ +271.2 (c 1.3, CHCl$_3$), HPLC analysis: 99% ee [Daicel CHIRALPAK AD-H column, 20 °C, 254 nm hexane/i-PrOH = 95:5, 0.9 mL /min, 254 nm, 16.1 min (major), 17.9 min (minor)]. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.91 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.04 (d, J = 8.1 Hz, 2H), 6.91 (t, J = 7.5 Hz, 2H), 6.56 (d, J = 4.5 Hz, 2H), 5.50 (dd, J = 6.3 Hz, J = 8.4 Hz, 1H), 3.50 (t, J = 6.6 Hz, 1H), 2.76 (q, J = 8.1 Hz, 1H), 2.42 (s, 3H), 1.47-1.42 (m, 1H), 1.26-1.18 (m, 2H), 1.00-0.82 (m, 1H), 0.72 (t, J = 7.5 Hz, 3H). ^{13}C NMR (300 MHz, CDCl$_3$) δ 170.4, 145.2, 137.4, 134.9, 129.5, 128.8, 128.5, 127.8, 127.3, 124.2, 113.6, 47.3, 42.2, 27.9, 21.8, 20.4, 13.9. IR (KBr) v 2985, 1816, 1458, 1170, 875. HRMS (EI) m/z: M$^+$ Calc. for C$_{21}$H$_{23}$NO$_3$S, 369.1399, Found 369.1403.

![Diagram](image.png)

(3S,4S)-3-octyl-4-phenyl-1-tosyl-3,4-dihydropyridin-2(1H)-one (3g)

Yield: 177.4 mg (81%), white solid. mp 88-90 °C, R$_f$ = 0.60 (petroleum ether/ethyl
acetate, 5:1 ); \([\alpha]_D^{25} +241.3 (c 1.5, \text{CHCl}_3)\), HPLC analysis: 99% ee [Daicel CHIRALPAK AD-H column, 20 °C, 254 nm hexane/\text{i-PrOH} = 95:5, 0.9 mL /min, 254 nm, 12.6 min (major), 16.1 min (minor)]. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.99 (\(d, J = 8.1 \text{ Hz}, 2\text{H}\)), 7.39 (\(d, J = 8.1 \text{ Hz}, 2\text{H}\)), 7.13 (\(t, J = 7.8 \text{ Hz}, 2\text{H}\)), 7.00 (\(t, J = 7.5 \text{ Hz}, 2\text{H}\)), 6.63 (\(d, J = 7.8 \text{ Hz}, 2\text{H}\)), 5.57 (\(dd, J = 6.0 \text{ Hz}, J =9.0 \text{ Hz}, 1\text{H}\)), 3.59 (\(t, J = 6.3 \text{ Hz}, 1\text{H}\)), 2.83 (\(q, J = 6.9 \text{ Hz}, 1\text{H}\)), 2.50 (\(s, 3\text{H}\)), 1.63-1.54 (\(m, 1\text{H}\)), 1.27-1.18 (\(br, 12\text{H}\)), 0.97-0.95 (\(m, 1\text{H}\)), 0.92-0.87 (\(m, 3\text{H}\)). \(^13\)C NMR (300 MHz, CDCl\(_3\)) \(\delta\) 170.3, 150.6, 145.1, 137.4, 134.9, 131.2, 129.5, 129.1, 128.8, 128.4, 127.7, 127.3, 127.2, 124.2, 113.5, 47.5, 42.1, 31.8, 29.4, 29.2, 29.1, 27.1, 25.6, 22.6, 21.7, 14.1. IR (KBr) \(\nu\) 2977, 1616, 1078, 547. HRMS (EI) \(m/z\): M\(^+\) Calc. for C\(_{26}\)H\(_{33}\)NO\(_3\)S, 439.2181, Found 439.2187.

### 1.4 NHC-catalyzed reaction with \(\alpha, \beta\)-unsaturated ketimines (Table 3)

![Chemical structure](image)

**Typical procedure.** To an oven-dried 50 mL Schlenk tube equipped with a stir bar was charged with trazolium salt \(5a\) (18 mg, 0.05 mmol) and anhydrous Cs\(_2\)CO\(_3\) (17 mg, 0.05 mmol). This tube was closed with a septum, evacuated, and back-filled with argon. To this mixture was added freshly distilled DCM (5 mL) and stirred for 30 minutes at room temperature. After further stirring at 0 °C for 10 min, chloroaldehyde \(1a\) (132 mg, 1 mmol), \(\alpha, \beta\)-unsaturated ketimines \(2a\) (0.5 mmol) and DIPEA (0.55 ml, 3 mmol) was added. After stirring for 24 h, the mixture was diluted with diethyl ether and passed through a short silica pad. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel.

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(ethyl acetate /petroleum ether, typically 1/50) to give the desired product.

Racemic samples for the standard of chiral HPLC spectra were prepared using the triazolium salts S1 as the catalyst.

(3S,4S)-ethyl-3-benzyl-6-(naphthalen-2-yl)-2-oxo-1-tosyl-1,2,3,4-tetrahydropyridine-4-carboxylate (7a) Yield: 234.1 mg (87%), white solid. mp 129-131 °C, Rf = 0.40 (petroleum ether/ethyl acetate, 5:1 ); [α]D25 +97.3 (c 1.0, CHCl3), HPLC analysis: 81% ee [Daicel CHIRALPAK AD-H column, 20 °C, 254 nm hexane/i-PrOH = 80:20, 1.0 mL /min, 254 nm, 21.3 min (major), 25.7 min (minor)]. 1H NMR (300 MHz, CDCl3) δ 7.85 (d, J = 6.0 Hz, 2H), 7.78-7.72 (m, 4H), 7.56-7.55 (m, 1H), 7.53-7.52 (m, 2H), 7.24-7.18 (m, 5H), 7.06-7.03 (m, 2H), 5.80 (d, J = 6.6Hz, 1H), 4.12 (q, J = 3.0 Hz, 2H), 3.16-3.11 (m, 1H), 3.16-3.11 (m, 2H), 2.98 (dd, J = 8.1 Hz, J = 8.1 Hz, 1H), 2.43 (s, 3H), 1.25 (t, J = 3.0 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H), 0.66 (t, J = 7.5 Hz, 3H). 13C NMR (300 MHz, CDCl3) δ 172.4, 170.8, 145.0, 141.3, 137.0, 136.2, 134.2, 133.3, 132.8, 129.4, 129.0, 128.0, 128.6, 128.2, 128.1, 127.8, 126.8, 126.5, 126.4, 124.7, 124.0, 114.3, 61.7, 48.2, 40.5, 34.3, 21.7, 14.0. IR (KBr) ν 3038, 1742, 1576, 1456, 1362, 669. HRMS (EI) m/z: M+ Calc. for C32H29NO5S, 539.1766, Found 539.1772

(3S,4S)-ethyl-3-benzyl-2-oxo-6-phenyl-1-tosyl-1,2,3,4-tetrahydropyridine-4-carboxylate (7b). Yield: 212.5 mg (87%), white solid. mp 81-83 °C, Rf = 0.45 (petroleum ether/ethyl acetate, 5:1 ); [α]D25 +128 (c 1.3, CHCl3), HPLC analysis: 82% ee [Daicel CHIRALPAK AD-H column, 20 °C, 254 nm hexane/i-PrOH = 80:20, 1.0 mL /min, 254 nm, 10.8 min (major), 16.3 min (minor)]. 1H NMR (300 MHz, CDCl3) δ 7.78 (d,
\( J = 8.4 \text{ Hz}, 2H \), \( 7.42-7.32 \text{ (m, 6H)} \), \( 7.27-7.18 \text{ (m, 4H)} \), \( 7.04-7.01 \text{ (m, 2H)} \), \( 5.68 \text{ (d, } J = 6.3 \text{ Hz, 1H)} \), \( 4.09 \text{ (q, } J = 4.2 \text{ Hz, 2H)} \), \( 3.16-3.11 \text{ (m, 1H)} \), \( 3.10-3.04 \text{ (m, 2H)} \), \( 2.88 \text{ (dd, } J = 8.1 \text{ Hz, } J = 8.1 \text{ Hz, 1H)} \), \( 2.85 \text{ (s, 3H)} \), \( 1.23 \text{ (s, 7.2 Hz, 3H)} \). \(^{13}\text{C NMR (300 MHz, CDCl}_3\) \( \delta 172.2, 170.9, 145.0, 141.2, 137.1, 136.2, 129.4, 129.1, 129.0, 128.7, 128.4, 126.9, 126.0, 113.8, 61.7, 48.1, 40.5, 34.3, 21.7, 14.0. \) IR (KBr) \( \nu \) 3048, 1732, 1558, 1456, 1362, 775. HRMS (EI) \( m/z \): M\(^+\) Calc. for C\(_{28}\)H\(_{27}\)NO\(_5\)S, 489.1610, Found 489.1618

\((3S,4S)\)-ethyl-3-benzyl-6-(4-methoxyphenyl)-2-oxo-1-tosyl-1,2,3,4-tetrahydropyridine-4-carboxylate \((7c)\). Yield: 205.7 mg (79%), white solid. mp 102-104 °C, \( R_f = 0.38 \) (petroleum ether/ethyl acetate, 5:1 ); \([\alpha]_D^{25} +169 \text{ (c 1.5, CHCl}_3\) ), HPLC analysis: 83% ee [Daicel CHIRALPAK OD-H column, 20 °C, 254 nm hexane/i-ProH = 80:20, 1.0 mL /min, 254 nm, 14.6 min (minor), 19.2 min (major)]. \(^1\)H NMR (300 MHz, CDCl\(_3\) ) \( \delta 7.79 \text{ (d, } J = 8.4 \text{ Hz, 2H)} \), \( 7.35 \text{ (d, } J = 9.0 \text{ Hz, 2H)} \), \( 7.27-7.25 \text{ (m, 3H)} \), \( 7.21-7.19 \text{ (m, 3H)} \), \( 7.04-7.01 \text{ (m, 2H)} \), \( 6.90 \text{ (d, } J = 8.7 \text{ Hz, 2H)} \), \( 5.60 \text{ (d, } J = 6.6 \text{ Hz, 1H)} \), \( 4.10 \text{ (q, } J = 3.3 \text{ Hz, 2H)} \), \( 3.84 \text{ (s, 3H)} \), \( 3.16-3.11 \text{ (m, 1H)} \), \( 3.10-3.03 \text{ (m, 2H)} \), \( 2.88 \text{ (dd, } J = 8.1 \text{ Hz, } J = 8.1 \text{ Hz, 1H)} \), \( 2.45 \text{ (s, 3H)} \), \( 1.23 \text{ (s, 7.2 Hz, 3H)} \). \(^{13}\)C NMR (300 MHz, CDCl\(_3\) ) \( \delta 172.3, 170.9, 159.9, 144.9, 140.9, 137.1, 136.2, 129.7, 129.4, 129.1, 129.0, 128.6, 128.4, 127.3, 126.8, 113.8, 112.4, 61.6, 55.3, 48.2, 40.3, 34.2, 21.7, 14.0. IR (KBr) \( \nu \) 2980, 1772, 1558, 1362, 775, 669. HRMS (EI) \( m/z \): M\(^+\) Calc. for C\(_{29}\)H\(_{29}\)NO\(_5\)S, 519.1716, Found 519.1723.

\((3S,4S)\)-ethyl-3-benzyl-2-oxo-6-p-tolyl-1-tosyl-1,2,3,4-tetrahydropyridine-4-carboxylate \((7d)\). Yield: 208.5 mg (83%), white solid. mp 121-123 °C, \( R_f = 0.49 \)
(petroleum ether/ethyl acetate, 5:1); [α]D^25 +128 (c 1.5, CHCl3), HPLC analysis: 78% ee [Daicel CHIRALPAK OD-H column, 20 °C, 254 nm hexane/i-PrOH = 80:20, 1.0 mL /min, 254 nm, 9.8 min (minor), 12.4 min (major)]. ^1H NMR (300 MHz, CDCl3) δ 7.72 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.20-7.18 (m, 3H), 7.13-7.10 (m, 4H), 6.96-6.93 (m, 2H), 5.58 (d, J = 6.3 Hz, 1H), 4.04-3.98 (m, 2H), 3.14-3.11 (m, 1H), 3.03-2.96 (m, 2H), 2.78 (dd, J = 8.1 Hz, J = 8.1 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H). ^13C NMR (300 MHz, CDCl3) δ 172.2, 170.9, 144.9, 141.2, 138.6, 137.1, 136.2, 134.2, 129.5, 129.1, 129.0, 128.6, 126.8, 125.8, 112.9, 61.6, 48.1, 40.3, 34.2, 21.7, 21.3, 14.0. IR (KBr) ν 3038, 1762, 1558, 1360, 775, 669. HRMS (El) m/z: M^+ Calc. for C_{29}H_{29}NO_{5}S, 503.1766, Found 503.1774.

(3S,4S)-ethyl-6-(naphthalen-2-yl)-2-oxo-3-propyl-1-tosyl-1,2,3,4-tetrahydropyridine-4-carboxylate (7e). Yield: 173.5 mg (71%), white solid. mp 121-123 °C, R_f = 0.61 (petroleum ether/ethyl acetate, 5:1); [α]D^25 +87.3 (c 1.0, CHCl3), HPLC analysis: 78% ee [Daicel CHIRALPAK AD-H column, 20 °C, 254 nm hexane/i-PrOH = 80:20, 1.0 mL /min, 254 nm, 11.7 min (minor), 19.0 min (major)]. ^1H NMR (300 MHz, CDCl3) δ 7.85-7.71 (m, 7H), 7.53-7.48 (m, 3H), 7.22 (s, 1H), 5.85 (d, J = 6.0 Hz, 1H), 4.22 (q, J = 4.2 Hz, 2H), 3.36 (t, J = 6.0 Hz, 1H), 2.94 (q, J = 6.3 Hz, 1H), 2.43 (s, 3H), 1.56-1.58 (m, 2H), 1.32-1.22 (m, 5H), 0.87 (t, J = 7.1 Hz, 3H). ^13C NMR (300 MHz, CDCl3) δ 173.0, 171.2, 145.0, 141.1, 136.4, 134.3, 133.3, 132.9, 129.4, 129.3, 129.0, 128.3, 127.8, 126.5, 126.4, 124.0, 115.3, 61.7, 46.9, 42.0, 31.0, 21.7, 19.6, 14.2, 13.9. IR (KBr) ν 3030, 1832, 1558, 1455, 1262, 665. HRMS (El) m/z: M^+ Calc. for C_{28}H_{29}NO_{5}S, 491.1766, Found 491.1772.
(3S,4S)-ethyl-6-(naphthalen-2-yl)-3-octyl-2-oxo-1-tosyl-1,2,3,4-tetrahydropyridine-4-carboxylate (7f). Yield: 21.5 mg (75%), white solid. mp 81-83 °C, Rf = 0.61 (petroleum ether/ethyl acetate, 5:1 ); [α]D25 +176.5 (c 1.3, CHCl3), HPLC analysis: 80% ee [Daicel CHIRALPAK AD-H column, 20 °C, 254 nm hexane/i-PrOH = 80:20, 1.0 mL /min, 254 nm, 16.3 min (minor), 19.5 min (major)]. 1H NMR (300 MHz, CDCl3) δ 7.85-7.72 (m, 6H), 7.54-7.47 (m, 3H), 7.24 (d, J = 8.7 Hz, 2H), 5.85 (d, J = 5.7Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 3.36 (t, J = 6.3 Hz, 1H), 2.92 (q, J = 6.3 Hz, 1H), 2.42 (s, 3H), 1.62-1.60 (br, 2H), 1.32-1.21 (m, 15H), 0.87 (t, J = 6.0 Hz, 3H). 13C NMR (300 MHz, CDCl3) δ 172.8, 171.2, 144.9, 141.0, 136.3, 134.3, 133.2, 132.9, 129.4, 129.0, 128.2, 128.1, 127.7, 126.5, 126.4, 124.7, 123.9, 115.2, 61.6, 47.0, 41.8, 31.8, 29.4, 29.3, 29.1, 28.7, 26.1, 22.6, 21.7, 14.1, 14.06. IR (KBr) ν 2998, 1830, 1568, 1446, 1362, 775, 669. HRMS (EI) m/z: M+ Calc. for C33H39NO5S, 561.2549, Found 561.2557.

(3S,4S)-ethyl-3-benzyl-2-oxo-6-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine-4-carboxylate (7g). Yield: 185.5 mg (78%), yellow solid. mp 71-73 °C, Rf = 0.51 (petroleum ether/ethyl acetate, 5:1 ); [α]D25 +98.3 (c 1.0, CHCl3), HPLC analysis: 74% ee [Daicel CHIRALPAK AD-H column, 20 °C, 254 nm hexane/i-PrOH = 80:20, 1.0 mL /min, 254 nm, 12.2 min (major), 17.6 min (minor)]. 1H NMR (300 MHz, CDCl3) δ 7.89 (d, J = 8.1 Hz, 2H), 7.63-7.58 (m, 1H), 7.47-7.25 (m, 7H), 7.23-7.18 (m, 3H), 7.03-7.00 (m, 2H), 5.69 (d, J = 6.3 Hz, 1H), 4.10 (q, J = 4.2 Hz, 2H), 3.24-3.20
(m, 1H), 3.10-3.04 (m, 2H), 2.88 (dd, J = 8.1 Hz, J = 8.1 Hz, 1H), 1.22 (t, J = 6.9 Hz, 3H). $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ 172.1, 170.6, 141.0, 138.9, 136.9, 136.7, 133.8, 129.2, 128.9, 128.6, 128.3, 128.3, 126.8, 125.9, 113.8, 61.6, 48.0, 40.3, 34.2, 13.9. IR (KBr) v 3030, 1632, 1362, 775, 669. HRMS (EI) m/z: M$^+$ Calc. for C$_{27}$H$_{25}$NO$_5$S, 475.1453, Found 475.1461.

(3S,4S)-isopropyl-3-benzyl-2-oxo-6-phenyl-1-tosyl-1,2,3,4-tetrahydropyridine-4-carboxylate (7i). Yield: 156.1 mg (62%), white solid. mp 124-126 °C, R$_f$ = 0.42 (petroleum ether/ethyl acetate, 5:1 ); [α]$_D^{25}$ +22.5 (c 1.0, CH$_2$Cl$_2$), HPLC analysis: 81% ee [Daicel CHIRALPAK AD-H column, 20 °C, 254 nm hexane/i-PrOH = 80:20, 1.0 mL /min, 254 nm, 14.4 min (minor), 17.1 min (major)]. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.76 (d, J = 8.3 Hz, 2H), 7.39-7.32 (m, 5H), 7.25-7.18 (m, 5H), 7.04-7.01 (m, 2H), 5.64 (d, J = 6.2 Hz, 1H), 5.01-4.93 (m, 1H), 3.26-3.19 (m, 1H), 3.07-3.01 (m, 2H), 2.89 (dd, J = 8.0 Hz, J = 5.6 Hz, 1H), 2.44 (s, 3H), 1.26 (d, J = 6.2 Hz, 3H), 1.20 (d, J = 6.3 Hz, 3H). $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ 172.4, 170.5, 145.1, 141.2, 141.0, 137.3, 137.0, 136.4, 129.5, 129.2, 129.1, 128.7, 128.5, 126.9, 126.2, 114.1, 69.5, 48.1, 40.7, 34.3, 21.84, 21.76, 21.7. IR (KBr) v 3073, 1726, 1454, 1369, 1171, 760, 671. HRMS (EI) m/z: M$^+$ Calc. for C$_{29}$H$_{29}$NO$_5$S, 503.1766, Found 503.1722.

(3S,4S)-tert-butyl-3-benzyl-2-oxo-6-phenyl-1-tosyl-1,2,3,4-tetrahydropyridine-4-carboxylate (7j). Yield: 191.5 mg (74%), white solid. mp 100-102 °C, R$_f$ = 0.49 (petroleum ether/ethyl acetate, 5:1 ); [α]$_D^{25}$ +29.5 (c 1.0, CH$_2$Cl$_2$), HPLC analysis:
90% ee [Daicel CHIRALPAK AD-H column, 20 °C, 254 nm hexane/i-PrOH = 80:20, 1.0 mL /min, 254 nm, 12.8 min (minor), 23.7 min (major)]. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.78-7.75 (m, 2H), 7.35-7.32 (m, 5H), 7.25-7.18 (m, 5H), 7.05-7.02 (m, 2H), 5.62 (d, \(J = 6.3\) Hz, 1H), 3.22-3.16 (m, 1H), 3.01-2.98 (m, 2H), 2.90 (dd, \(J = 7.9\)Hz, \(J = 5.9\) Hz, 1H), 2.44 (s, 3H), 1.45 (s, 9H). \(^{13}\)C NMR (300 MHz, CDCl\(_3\)) \(\delta\) 172.6, 170.2, 145.1, 141.0, 1374, 137.2, 136.4, 129.6, 129.3, 129.1, 128.7, 1286, 128.5, 126.9, 126.3, 114.5, 82.5, 48.2, 41.4, 34.3, 28.1, 21.9. IR (KBr) \(\nu\) 3019, 1730, 1368, 1149, 669, 541, 455. HRMS (EI) m/z: M\(^+\) Calc. for C\(_{30}\)H\(_{31}\)NO\(_5\)S, 517.1923, Found 517.1923.

1.5 Synthesis of piperidinones (Scheme 1)

![Scheme 1](image)

**Typical procedure.** A glass flask (10 mL) with a magnetick stirring bar was charged with 3 (0.1 mmol), Pd/C (0.02 mmol), and ethyl acetate (2 mL) and placed in a steel autoclave. The reaction mixture was stirred overnight at room temperature under 50 bar H\(_2\). Then the mixture was diluted with diethyl ether and passed through a short silica pad. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (ethyl acetate /petroleum ether, typically 1/50) to give the desired product.
(3S,4S)-3-benzyl-4-phenyl-1-tosylpiperidin-2-one (8a)

Yield: 39.5 mg (94%), white solid. mp 125-127 °C, R_f = 0.41 (petroleum ether/ethyl acetate, 5:1 ); [α]_D^{25} +176 (c 0.9, CHCl_3), HPLC analysis: 99% ee [Daicel CHIRALPAK AS-H column, 20 °C, 254 nm hexane/i-PrOH = 90:10, 1.0 mL /min, 254 nm, 11.6 min (minor), 12.2 min (major)]. ^1H NMR (300 MHz, CDCl_3) δ 7.98 (d, J = 8.4 Hz , 2H), 7.40 (d, J = 8.4 Hz ,2H), 7.22-7.14 (m, 6H), 6.82 (d, J = 5.1 Hz, 2H), 6.66 (d, J = 7.2 Hz, 2H), 3.96-3.94 (m, 1H ), 3.85-3.82 (m, 1H), 3.27 (dd, J = 4.2 Hz, J = 14.4 Hz, 1H), 3.16-3.14 (m, 1H ), 2.93-2.90 (m, 1H ), 2.51 (s, 3H), 2.29 (dd, J = 10.2 Hz, J = 14.4 Hz, 1H ), 2.00-1.95 (m, 1H). ^13C NMR (300 MHz, CDCl_3) δ 172.5, 144.8, 139.8, 139.1, 135.7, 129.4, 129.0, 128.8, 128.6, 128.3, 128.1, 127.0, 126.3, 49.0, 43.8, 39.6, 32.4, 31.0, 21.7. IR (KBr) ν 3010, 1816, 1788, 1362, 775. HRMS (EI) m/z: M^+ Calc. for C_{25}H_{25}NO_3S, 419.1555, Found 419.1560.

(3S,4S)-3-benzyl-4-(4-methoxyphenyl)-1-tosylpiperidin-2-one (8b)

Yield: 42.7 mg (95%), white solid. mp 101-103 °C, R_f = 0.49 (petroleum ether/ethyl acetate, 5:1 ); [α]_D^{25} +172.3 (c 1.0, CHCl_3), HPLC analysis: 99% ee [Daicel CHIRALPAK AS-H column, 20 °C, 254 nm hexane/i-PrOH = 90:10, 1.0 mL /min, 254 nm, 16.7 min (minor), 17.8 min (major)]. ^1H NMR (300 MHz, CDCl_3) δ 7.98 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.20-7.16 (m, 3H), 6.85 (t, 2H), 6.68 (d, J = 8.4 Hz, 2H), 6.57 (d, J = 8.4 Hz, 2H), 3.97-3.91 (m, 1H), 3.85-3.82 (m, 1H), 3.79 (s,
(3S,4S)-3-benzyl-4-(furan-2-yl)-1-tosylpiperidin-2-one (8c)

Yield: 42.7 mg (93%), white solid. mp 88-90 °C, R_f = 0.52 (petroleum ether/ethyl acetate, 5:1); [α]_D^25 +121.7 (c 1.0, CHCl_3), HPLC analysis: 97% ee [Daicel CHIRALPAK AS-H column, 20 °C, 254 nm hexane/i-PrOH = 90:10, 1.0 mL/min, 254 nm, 15.4 min (minor), 21.8 min (major)]. ^1H NMR (300 MHz, CDCl_3) δ 7.98 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.5 Hz, 2H), 7.19-7.13 (m, 4H), 6.97(s, 1H), 6.88 (d, J = 6.9 Hz, 2H), 6.16 (s, 1H), 5.77 (s, 1H), 3.00-3.96 (m, 1H), 3.72-3.63 (m, 1H), 3.26 (d, J = 14.4 Hz, 1H), 3.13 (d, J = 4.5 Hz, 1H), 2.77-2.74 (m, 1H), 2.41 (s, 3H), 2.15-2.02 (m, 3H). ^13C NMR (300 MHz, CDCl_3) δ 136.8, 151.4, 142.8, 139.9, 137.3, 134.1, 127.5, 127.2, 126.8, 126.6, 124.6, 108.4, 105.9, 47.1, 42.7, 31.6, 30.8, 27.1, 19.9. IR (KBr) v 3010, 1738, 1538, 1260, 750. HRMS (EI) m/z: M^+ Calc. for C_{26}H_{27}NO_4S, 449.1661, Found 449.1668.

(3S,4S)-4-phenyl-3-propyl-1-tosylpiperidin-2-one (8f)

Yield: 42.7 mg (93%), white solid. mp 85-87 °C, R_f = 0.65 (petroleum ether/ethyl acetate, 5:1); [α]_D^25 +272.3 (c 1.0, CHCl_3), HPLC analysis: 99% ee [Daicel CHIRALPAK AS-H column, 20 °C, 254 nm hexane/i-PrOH = 90:10, 1.0 mL/min,
254 nm, 21.5 min (minor), 29.6 min (major)]. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.88 ($d, J = 8.4$ Hz, 2H), 7.29 ($d, J = 7.5$ Hz, 2H), 7.08-7.05 ($m$, 3H), 6.68 ($d, J = 7.5$ Hz, 2H), 4.01-3.80 ($m$, 1H), 3.78-3.77 ($m$, 1H), 3.29-3.27 ($m$, 1H), 2.55-2.53 ($m$, 1H), 2.40 ($s$, 3H), 2.29-2.24 ($m$, 1H), 1.98-1.95 ($m$, 1H), 1.54-1.50 ($m$, 1H), 1.19-1.09 ($m$, 1H), 0.95-0.93 ($m$, 1H), 0.65 ($t$, $J = 7.5$ Hz, 3H). $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ 173.2, 144.7, 140.5, 136.0, 129.3, 128.8, 127.7, 126.8, 47.1, 44.2, 40.9, 29.9, 28.9, 21.7, 20.5, 13.8. IR (KBr) $\nu$ 2998, 1768, 1558, 1440, 1260, 750. HRMS (EI) $m/z$: M$^+$ Calc. for C$_{21}$H$_{25}$NO$_3$S, 371.1555, Found 371.1563

1.6 X-ray crystal structure of cis-3a

![Figure S1 X-ray crystal structure of cis-3a](image)

The structure of 3a was determined by X-ray. The crystal was prepared from the solution of 3a in DCM/ether (90/10) with trace of petroleum ether.

CCDC 887864 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
References


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PL12             22.33 dB
PL13             23.00 dB
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### Table 1: Experimental Parameters

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- **SI:** 32768

### Channel f2 Parameters

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- **PL12:** -22.33 dB
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- **SFO2:** 75.4677490 MHz

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**Figure 1:** 1H NMR spectrum of compound 3d showing chemical shifts and peak assignments.

**Figure 2:** 13C NMR spectrum of compound 3d showing chemical shifts and peak assignments.
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**NS**  16  
**DS**  0  
**SNH**  8992.866 Hz  
**FIDRES**  0.137219 Hz  
**AQ**  3.6438515 sec  
**RG**  128  
**GW**  55.600 usec  
**DE**  8.00 usec  
**TE**  297.0 K  
**D1**  1.00000000 sec  
**TDD**  1  

**NAME**  jty-655B  
**EXPNO**  11  
**PROCNO**  1  
**Date**  20101209  
**Time**  8.17  
**INSTRUM**  spect  
**PROBHD**  5 mm DUL 13C-1  
**FUPLOP**  zgpg30  
**TD**  65536  
**SOLVENT**  CDCl3  
**NS**  101  
**DS**  4  
**SNH**  17985.611 Hz  
**FIDRES**  0.274439 Hz  
**AQ**  1.8219508 sec  
**RG**  5160.6  
**GW**  27.800 usec  
**DE**  8.00 usec  
**TE**  297.3 K  
**D1**  2.00000000 sec  
**D11**  0.03000000 sec  
**TDD**  1  

**NAME**  jty-655B  
**EXPNO**  12  
**PROCNO**  1  
**Date**  20101209  
**Time**  8.19  
**INSTRUM**  spect  
**PROBHD**  5 mm DUL 13C-1  
**FUPLOP**  zgpg30  
**TD**  65536  
**SOLVENT**  CDCl3  
**NS**  101  
**DS**  4  
**SNH**  17985.611 Hz  
**FIDRES**  0.274439 Hz  
**AQ**  1.8219508 sec  
**RG**  5160.6  
**GW**  27.800 usec  
**DE**  8.00 usec  
**TE**  297.3 K  
**D1**  2.00000000 sec  
**D11**  0.03000000 sec  
**TDD**  1  

**NAME**  jty-655B  
**EXPNO**  13  
**PROCNO**  1  
**Date**  20101209  
**Time**  8.21  
**INSTRUM**  spect  
**PROBHD**  5 mm DUL 13C-1  
**FUPLOP**  zgpg30  
**TD**  65536  
**SOLVENT**  CDCl3  
**NS**  101  
**DS**  4  
**SNH**  17985.611 Hz  
**FIDRES**  0.274439 Hz  
**AQ**  1.8219508 sec  
**RG**  5160.6  
**GW**  27.800 usec  
**DE**  8.00 usec  
**TE**  297.3 K  
**D1**  2.00000000 sec  
**D11**  0.03000000 sec  
**TDD**  1  

**NAME**  jty-655B  
**EXPNO**  14  
**PROCNO**  1  
**Date**  20101209  
**Time**  8.22  
**INSTRUM**  spect  
**PROBHD**  5 mm DUL 13C-1  
**FUPLOP**  zgpg30  
**TD**  65536  
**SOLVENT**  CDCl3  
**NS**  101  
**DS**  4  
**SNH**  17985.611 Hz  
**FIDRES**  0.274439 Hz  
**AQ**  1.8219508 sec  
**RG**  5160.6  
**GW**  27.800 usec  
**DE**  8.00 usec  
**TE**  297.3 K  
**D1**  2.00000000 sec  
**D11**  0.03000000 sec  
**TDD**  1

---

**NAME**  jty-655B  
**EXPNO**  15  
**PROCNO**  1  
**Date**  20101209  
**Time**  8.23  
**INSTRUM**  spect  
**PROBHD**  5 mm DUL 13C-1  
**FUPLOP**  zgpg30  
**TD**  65536  
**SOLVENT**  CDCl3  
**NS**  101  
**DS**  4  
**SNH**  17985.611 Hz  
**FIDRES**  0.274439 Hz  
**AQ**  1.8219508 sec  
**RG**  5160.6  
**GW**  27.800 usec  
**DE**  8.00 usec  
**TE**  297.3 K  
**D1**  2.00000000 sec  
**D11**  0.03000000 sec  
**TDD**  1

---

**NAME**  jty-655B  
**EXPNO**  16  
**PROCNO**  1  
**Date**  20101209  
**Time**  8.24  
**INSTRUM**  spect  
**PROBHD**  5 mm DUL 13C-1  
**FUPLOP**  zgpg30  
**TD**  65536  
**SOLVENT**  CDCl3  
**NS**  101  
**DS**  4  
**SNH**  17985.611 Hz  
**FIDRES**  0.274439 Hz  
**AQ**  1.8219508 sec  
**RG**  5160.6  
**GW**  27.800 usec  
**DE**  8.00 usec  
**TE**  297.3 K  
**D1**  2.00000000 sec  
**D11**  0.03000000 sec  
**TDD**  1

---

**NAME**  jty-655B  
**EXPNO**  17  
**PROCNO**  1  
**Date**  20101209  
**Time**  8.25  
**INSTRUM**  spect  
**PROBHD**  5 mm DUL 13C-1  
**FUPLOP**  zgpg30  
**TD**  65536  
**SOLVENT**  CDCl3  
**NS**  101  
**DS**  4  
**SNH**  17985.611 Hz  
**FIDRES**  0.274439 Hz  
**AQ**  1.8219508 sec  
**RG**  5160.6  
**GW**  27.800 usec  
**DE**  8.00 usec  
**TE**  297.3 K  
**D1**  2.00000000 sec  
**D11**  0.03000000 sec  
**TDD**  1
NAME           jty-695B
EXPNO                10
PROCNO                1
Date_          20110318
Time              16.12
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
FULPROC          zg30
TD                65536
SOLVENT           CDCl3
NS                  1
DS                  0
SNW              8992.806 Hz
FIDRES          0.137219 Hz
AQ                3.6438515 sec
RG                128
DW                55.600 usec
DE                8.00 usec
TE                296.2 K
D1          1.00000000 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                1H
P1                10.80 usec
PL1                3.00 dB
SFO1          300.1324010 MHz
SI                 32768
SF          300.1300112 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

NAME           jty-695B
EXPNO                10
PROCNO                1
Date_          20110318
Time              16.12
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
FULPROC          zg30
TD                65536
SOLVENT           CDCl3
NS                  1
DS                  0
SNW              8992.806 Hz
FIDRES          0.137219 Hz
AQ                3.6438515 sec
RG                128
DW                55.600 usec
DE                8.00 usec
TE                296.2 K
D1          1.00000000 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                1H
P1                10.80 usec
PL1                3.00 dB
SFO1          300.1324010 MHz
SI                 32768
SF          300.1300112 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

NAME           jty-695B
EXPNO                10
PROCNO                1
Date_          20110318
Time              16.12
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
FULPROC          zg30
TD                65536
SOLVENT           CDCl3
NS                  1
DS                  0
SNW              8992.806 Hz
FIDRES          0.137219 Hz
AQ                3.6438515 sec
RG                128
DW                55.600 usec
DE                8.00 usec
TE                296.2 K
D1          1.00000000 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                1H
P1                10.80 usec
PL1                3.00 dB
SFO1          300.1324010 MHz
SI                 32768
SF          300.1300112 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

NAME           jty-695B
EXPNO                10
PROCNO                1
Date_          20110318
Time              16.12
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
FULPROC          zg30
TD                65536
SOLVENT           CDCl3
NS                  1
DS                  0
SNW              8992.806 Hz
FIDRES          0.137219 Hz
AQ                3.6438515 sec
RG                128
DW                55.600 usec
DE                8.00 usec
TE                296.2 K
D1          1.00000000 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                1H
P1                10.80 usec
PL1                3.00 dB
SFO1          300.1324010 MHz
SI                 32768
SF          300.1300112 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

NAME           jty-695B
EXPNO                40
PROCNO                1
Date_          20110914
Time               8.12
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                434
DS                  4
SNW            17985.611 Hz
FIDRES          0.274439 Hz
AQ                1.8219508 sec
RG                1625.5
DW                27.800 usec
DE                6.50 usec
TE                298.8 K
D1          2.00000000 sec
D11          0.03000000 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                13C
P1                12.50 usec
PL2                2.00 dB
SFO2          75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 usec
PL2                2.00 dB
SF           75.4677490 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
NAME : jty-822
EXPN0 : 30
PROCNO : 0
Date_ : 20120315
Time : 16.18
INSTRUM : spect
PROBHD : 5 mm DUL 13C-1
PULPROG : zgpg30
TD : 65536
SOLVENT : CDCl3
DS : 49
SN : 17985.611 Hz
FIDRES : 0.274439 Hz
AQ : 1.8219508 sec
RG : 512
DW : 27.800 usec
TE : 295.3 K
T1 : 2.03000000 sec
T11 : 2.03000000 sec
TD0 : 1
======== CHANNEL f1 ========
NUC1 : 1H
P1 : 12.50 usec
PL1 : 3.00 dB
SFO1 : 75.4752953 MHz
SI : 32768
SF : 75.4677490 MHz
WDW : EM
SSB : 0
LB : 0.40 Hz
PC : 1.40

NAME : jty-822
EXPN0 : 20
PROCNO : 1
Date_ : 20120314
Time : 8.34
INSTRUM : spect
PROBHD : 5 mm DUL 13C-1
PULPROG : zg30
TD : 65536
SOLVENT : CDCl3
DS : 0
SN : 8992.806 Hz
FIDRES : 0.137219 Hz
AQ : 3.6438515 sec
RG : 181
DN : 55.600 usec
DE : 8.00 usec
TE : 294.9 K
T1 : 1.00000000 sec
TD0 : 1
======== CHANNEL f1 ========
NUC1 : 1H
P1 : 10.80 usec
PL1 : 3.00 dB
SFO1 : 300.1324010 MHz
SI : 32768
SF : 300.1300082 MHz
WDW : EM
SSB : 0
LB : 0.30 Hz
GB : 0
PC : 1.00
Part III  HPLC Spectra

3a

---

### Area Percent Report

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<th>1 Signal</th>
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Signal 1: VM01 A, Wavelength=254 nm

| Peak RetTime Type Width Area Height Area |  |
|------------------------------------------|--|---|---|
| 1 13.349 min | Width | 0.5687 | 298.57534 | 6.93765 | 0.5029 |
| 2 17.798 min | Height | 1.6666 | 5.0952444 | 711.3110 | 98.4971 |

Totals: 5.1039e4 719.42038
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Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

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Totals: 1.67658e4 730.61956
Signal 1: VWD1 A, Wavelength=254 nm

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Signal 1: VWD1 A, Wavelength=254 nm

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<th>Area [mAU]</th>
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**Area Percent Report**

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<th>VK01 A, Wavelength=254 nm</th>
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<td>Use Multiplier &amp; Dilution Factor with ISIDs</td>
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Totals : 164.83940 3.29749