Supporting Information
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A Synthesis of (±)-γ-Lycorane using an Intramolecular Friedel-Crafts Reaction

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<chemistry>
\[
\text{MeO} \quad \text{O} \quad \text{OMe} \quad \overset{\text{TsNH}_2, \text{AcOH}, \uparrow}{\longrightarrow} \quad \overset{\text{Ac}_2\text{O}, \text{AlCl}_3, \text{CH}_2\text{Cl}_2}{\longrightarrow} \quad \overset{\text{NaBH}_4, \text{MeOH}, 0 ^\circ \text{C}}{\longrightarrow} \quad \overset{\text{DMSO}, 160 ^\circ \text{C}}{\longrightarrow}
\]
</chemistry>

1. Synthesis of N-tosyl pyrrole 4

A mixture of p-toluenesulfonamide (20 g, 116.8 mmol) and 2,5-dimethoxytetrahydrofuran (20 mL, 154 mmole) in acetic acid (100 mL) was heated at reflux for 2 hours. The mixture was allowed to cool to room temperature, then poured into water (1 L). The mixture was allowed to stand for 1 hour, then the precipitate was isolated by filtration and recrystallised from ethanol to give N-tosylpyrrole (19.72 g, 76%) as colourless crystals.

2. Synthesis of 3-acetyl-N-tosylpyrrole SI-1

Acetic anhydride (39.4 mmol, 3.70 ml, 3 eq) was added dropwise to a suspension of anhydrous AlCl₃ (78.8 mmol, 10.5 g, 6 eq) in CH₂Cl₂ (80 ml). The mixture was stirred for 15 minutes until a clear solution was obtained. A solution of N-tosyl pyrrole 4 (13.1 mmol, 2.73 g, 1 eq) in CH₂Cl₂ (20 ml) was then added slowly, and the mixture was stirred at room temperature for 2 hours until TLC showed completion. The reaction was quenched with ice water. The organic layer was separated and the aqueous layer was further extracted with CH₂Cl₂ (30 ml x 2). The combined organic layers were washed with saturated NaHCO₃ solution (20 ml), brine (20 ml), dried over MgSO₄ and concentrated to give pyrrole SI-1 as a pale yellow solid (3.0 g), which was used without further purification.

^1H NMR (400 MHz, CDCl₃): δ 7.80 (d, J = 8.0 Hz, 2H), 7.72 (app t, J = 2.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.13 (dd, J = 2.0, 3.2Hz, 1H), 6.68 (dd, J = 2.0, 3.2Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H).

^13C NMR (100 MHz, CDCl₃): δ 192.8, 145.9, 135.0, 130.3, 129.2, 127.1, 124.5, 121.5, 112.2, 27.2, 21.6.

NaBH₄ (34.5 mmol, 1.30 g) was added portionwise to a solution of Pyrrole SI-1 (3.03 g, 11.5 mmol) in methanol (50 ml) at 0°C. The mixture was stirred for 30 minutes until TLC showed completion. The mixture was diluted with water (20 ml) and the methanol was removed under reduced pressure. The remaining aqueous phase was extracted with EtOAc (30 ml x 3). The combined organic layers were washed with brine (30 ml) and dried over Na₂SO₄. The solvent was removed in vacuo to give pyrrole SI-2 as pale yellow oil (3.03 g) which was used without further purification.

\[ ^{1}H \text{ NMR (400 MHz, CDCl}_3) : \delta 7.74 \text{ (d, J = 8 Hz, 2H), 7.29 \text{ (d, J = 8 Hz, 2H), 7.11 \text{ (dd, J = 2.4, 3.2 Hz, 1H), 7.07 \text{ (dd, J = 1.6, 2.4 Hz, 1H), 6.30 \text{ (dd, J = 1.6, 3.2 Hz, 1H), 4.77 \text{ (m, 1H), 2.40 \text{ (s, 3H), 1.69 \text{ (app br d, J = 4 Hz, 1H), 1.43 \text{ (d, J = 6Hz, 3H).}} \]}

\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3) : \delta 145.0, 136.0, 133.0, 130.0, 127.9, 121.2, 116.5, 111.8, 64.1, 24.0, 21.6. \]

4. Synthesis of N-tosyl-3-vinylpyrrole 5

A solution of pyrrole SI-2 (3.03 g, 11.4 mmol) in DMSO (50 ml) was stirred at 160 °C for 3 hours until TLC showed completion. The reaction was allowed to cool to room temperature and was then poured into water (300 ml). The mixture was extracted with Et₂O (20 ml x 6). The combined organic layers were washed with brine (25 ml), dried over MgSO₄ and concentrated. The residue was purified by flash chromatography, eluting with 10% EtOAc/hexane to give pyrrole 5 as a colorless solid (2.35 g, 73% over 3 steps)

\[ ^{1}H \text{ NMR (400 MHz, CDCl}_3) : \delta 7.74 \text{ (d, J = 8 Hz, 2H), 7.28 \text{ (d, J = 8 Hz, 2H), 7.10 \text{ (m, 2H), 6.49 \text{ (dd, J = 11, 18 Hz, -CH\text{-}, 1H), 6.44 \text{ (app dd, J = 2.0, 3.0 Hz, 1H), 5.44 \text{ (dd, J = 1.2, 18 Hz, 1H), 5.10 \text{ (dd, J = 1.2, 11 Hz, 1H), 2.40 \text{ (s, 3H).}}} \]}

\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3) : \delta 145.0, 135.8, 129.9, 128.3, 127.8, 126.8, 121.5, 118.4, 113.3, 110.8, 21.5. \]
$^1$H and $^{13}$C NMR spectra of 3-acetyl-1-tosylpyrrole SI 1
$^1$H and $^{13}$C NMR spectra of pyrrole SI 2
$^1$H and $^{13}$C NMR spectra of 1-tosyl-3-vinylpyrrole 5
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