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Reaction of Papaverine with Baran Diversinates™
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![H NMR Spectrum for Compound 6 in CD$_3$OD]

S32: $^{13}$C NMR Spectrum for Compound 6 in CD$_3$OD

![13C NMR Spectrum for Compound 6 in CD$_3$OD]
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**S43**: COSY NMR Spectrum for Compound 8 in CD$_3$OD

![COSY NMR Spectrum for Compound 8 in CD$_3$OD](image)

**S44**: HSQC NMR Spectrum for Compound 8 in CD$_3$OD

![HSQC NMR Spectrum for Compound 8 in CD$_3$OD](image)
S45: HMBC NMR Spectrum for Compound 8 in CD$_3$OD
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S61: $^1$H NMR Spectrum for Compound 12 in CDCl$_3$

![H NMR Spectrum](image1)

S62: $^{13}$C NMR Spectrum for Compound 12 in CDCl$_3$

![C NMR Spectrum](image2)
S63: COSY NMR Spectrum for Compound 12 in CDCl₃

S64: HSQC NMR Spectrum for Compound 12 in CDCl₃
S65: HMBC NMR Spectrum for Compound 12 in CDCl₃
S66: $^1$H NMR Spectrum for Compound 12 in CD$_3$OD

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S70: HMBC NMR Spectrum for Compound 12 in CD$_3$OD
**S71:** Diversinate optimisation reactions with papaverine HCl (1) and the free-base of papaverine (1b)

| Cmpd | Solvent          | Eq. diversinate | Eq. TBHP | Time  | % yield of 2 | % of recovered starting material |
|------|------------------|-----------------|----------|-------|--------------|---------------------------------|
| 1a   | CH₂Cl₂/H₂O       | 3               | 3        | 16 h  | 15%          | 8%                              |
| 1a   | CH₂Cl₂/H₂O       | 6               | 6        | 16 h  | 24%          | 7%                              |
| 1a   | DMSO/H₂O         | 3               | 3        | 16 h  | 10%          | 5%                              |
| 1a   | DMSO/H₂O         | 6               | 6        | 16 h  | 11%          | 8%                              |
| 1b   | CH₂Cl₂/H₂O       | 6               | 6        | 16 h  | 15%          | 5%                              |
| 1b   | DMSO/H₂O         | 6               | 6        | 16 h  | 12%          | 7%                              |
| 1b   | CH₂Cl₂/TFA/H₂O   | 6               | 6        | 16 h  | 10%          | 9%                              |
| 1b   | DMSO/TFA/H₂O     | 6               | 6        | 16 h  | 9%           | 8%                              |

**S72:** Stacked ¹H NMR (800 MHz) spectra of the HCl salt (top) and free base (bottom) of papaverine in CD₃OD.
S73: $^1$H (800 MHz) and $^{13}$C (200 MHz) NMR data for papaverine HCl (1a) and the free base of papaverine (1b) in CD$_3$OD at 25 °C.

| Position | HCl salt of papaverine (1a) | Free base of papaverine (1b) |
|----------|-----------------------------|-----------------------------|
|          | $\delta_C$, type $\delta_H$, mult. ($J$ in Hz) | $\delta_C$, type $\delta_H$, mult. ($J$ in Hz) |
| 1        | 155.8, C                     | 159.1, C                     |
| 2        |                              |                              |
| 3        | 130.4, CH 8.26, d, $J = 6.5$ Hz | 140.5, CH 8.22, d, $J = 5.8$ Hz |
| 4        | 123.3, CH 8.13, d, $J = 6.5$ Hz | 120.5, CH 7.59, d, $J = 5.8$ Hz |
| 4a       | 138.9, C                     | 135.4, C                     |
| 5        | 107.5, CH 7.63, s            | 106.5, CH 7.25, s            |
| 6        | 159.2, C                     | 154.6, C                     |
| 7        | 154.5, C                     | 151.7, C                     |
| 8        | 106.2, CH 7.74, s            | 105.6, CH 7.44, s            |
| 8a       | 123.9, C                     | 124.3, C                     |
| 9        | 37.8, CH$_2$ 4.84, s         | 42.0, CH$_2$ 4.53, s         |
| 6-OMe    | 57.4, CH$_3$ 4.10, s         | 56.48, CH$_3$ 3.97, s        |
| 7-OMe    | 57.1, CH$_3$ 4.00, s         | 56.45, CH$_3$ 3.87, s        |
| 12-OMe   | 56.5*, CH$_3$ 3.79, s        | 56.36, CH$_3$ 3.74, s        |
| 13-OMe   | 56.6*, CH$_3$ 3.79, s        | 56.39, CH$_3$ 3.77, s        |
| 10       | 129.1, C                     | 133.6, C                     |
| 11       | 113.9, CH 7.03, d, $J = 2.1$ Hz | 113.6, CH 6.92, d, $J = 2.0$ Hz |
| 12       | 151.1, C                     | 150.6, C                     |
| 13       | 150.3, C                     | 149.1, C                     |
| 14       | 113.5, CH 6.92, d, $J = 8.3$ Hz | 113.2, CH 6.84, d, $J = 8.3$ Hz |
| 15       | 122.4, CH 6.83, dd, $J = 8.3, 2.1$ Hz | 121.9, CH 6.79, dd, $J = 8.3, 2.0$ Hz |

*interchangeable signals.
S74: Expansion of $^{13}$C NMR spectrum of compound 2 showing the quartet of the CF$_3$ group.

S75: Expansion of HMBC spectrum of compound 3.