Supplementary Material

New insights in the mechanism of amine catalysed epoxidation: dual role of protonated ammonium salts as both phase transfer catalysts and activators of Oxone®

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Melting points were measured on a Reichert melting point apparatus. ^1H and ^{13}C were recorded using Lambda 300 and Delta 400 instruments in CDCl_3 unless otherwise stated and are referenced to the appropriate solvent signal or using Me_4Si as internal standard. IR spectra were obtained using a Perkin–Elmer Spectrum-One FT-IR instrument. Mass spectra were recorded on KRATOS MS25, MS80 mass spectrometers using electron impact (EI, 20–50 eV), chemical ionization (CI) or fast atom bombardment (FAB) technicals. Optical rotations were determined using a Perkin–Elmer 241 MC instrument. Absolute configurations were determined by optical rotations, by chiral HPLC (Helwett Packard Series 1100) using a chiralcel OD column and by chiral GC (Shimadzu GC-17A) using a chiraldex γ -TA column. The enantioselectivities were determined by chiral GC (Perkin-Elmer Autosystem XL) using a β -CD column. Elemental analyses were performed by the microanalytical department of the University of Bristol.

Synthesis of (5S)-[3.3.0]-1-aza-2-oxo-3-oxa-4,4-di- β -naphthyl-bicyclooctane (4):

(S)-Proline-*N*-ethyl carbamate methyl ester was prepared according to literature procedures^[1] and was purified by distillation before use to afford a colourless oil. Cerium chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) (1.86 g, 5.00 mmol) was finely ground, placed in a 100 mL two-necked flask with a magnetic stirrer bar and dried according to Dimitrov's procedure.^[2] While the flask was still hot, nitrogen gas was introduced and the flask was cooled at room temperature. To the dry cerium chloride was added a solution of diester (1.00 g, 4.97 mmol) in dry THF (30 mL) and the resulting suspension was stirred for 3 h at room temperature. The organomagnesium solution was prepared in a two necked flask (25 mL) equipped with a magnetic stirrer bar and a condenser, containing magnesium (0.27 g, 2.21 mmol) and one crystal of iodine. To the magnesium, was added slowly a solution of 1-bromonaphthalene dried by distillation over 4 Å molecular sieves prior to use (2.28 g, 2.21 mmol) in 15 mL of anhydrous THF. The reaction mixture refluxed spontaneously and was stirred for 1.3 h at room temperature. To the solution of CeCl_3 and diester cooled at 0 °C with an ice bath, was added dropwise the organomagnesium bromide solution. The solution was stirred for 2.5 h at 0 °C. Under a flow of nitrogen, the flask was equipped with a condenser and the reaction was heated at 60 °C overnight. The reaction mixture was treated with brine (250 mL). The aqueous phase was extracted with EtOAc (5•200 mL) and the combined extracts were washed with brine (2•100 mL) and dried over MgSO_4 . After filtration, the solvent was removed under reduced pressure to give a yellow solid, which was purified by column chromatography on silica gel (EtOAc/petroleum ether; 30/70 then 50/50) and by recrystallisation from EtOAc/petroleum ether. The white solid was dried under high vacuum at 70 °C overnight (1.13 g, 60%). R_f = 0.33 (EtOAc/petroleum ether; 30/70). M.p. 207–209 °C; $[\alpha]_D^{20}$ = –640.0 (c = 0.50 in CHCl_3); ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 1.10–1.18 (m, 2 H; CH_2), 1.76–2.10 (m, 2 H; CH_2), 3.36–3.45 (m, 1 H; NC(H)H), 3.76–3.86 (m, 1 H; NC(H)H), 5.27 (dd, $^3J(\text{H,H})$ = 6.0 and 10.0 Hz; 1 H; NCH), 7.10–7.17 (m, 2 H; aromatic H), 7.25–7.32 (m, 2 H; aromatic H), 7.52–7.89 (m, 7 H; aromatic H), 8.11 (d, $^3J(\text{H,H})$ = 7.2 Hz; 1 H; aromatic H), 8.25 (d, $^3J(\text{H,H})$ = 8.8 Hz; 1 H; aromatic H), 8.31 (d, $^3J(\text{H,H})$ = 7.3 Hz; 1 H; aromatic H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 24.4, 27.9 (2 CH_2), 46.3 (NCH_2), 67.1 (NCH), 86.3 (C-O), 124.1, 124.2, 124.3, 124.5, 124.9, 125.4, 125.5, 125.7, 125.8, 125.9, 128.7, 129.0, 129.1, 129.5, 130.6, 131.6, 134.1, 134.9, 136.3, 137.1 (aromatic C), 160.5 (C=O); IR(neat): ν = 778, 1735, 2899, 2975, 3051 cm^{-1} ; MS (EI): m/z (%): 379 (22) [M^+], 335 (49), 282 (45), 265 (100), 155 (34), 127 (28). Elemental analysis: $\text{C}_{26}\text{H}_{21}\text{NO}_2$ requires: C, 82.30; H, 5.58; N, 3.69. Found: C, 82.11; H, 5.59; N, 3.65.

Synthesis of (S)-2-(Di- β -naphthylmethyl)pyrrolidine (2) and its corresponding hydrochloride (2•HCl):

A solution of (S)-4 (1.51 g, 4.00 mmol) in EtOH (150 mL) containing 5% triethylamine was hydrogenated over 10% Pd/C (664 mg) at 40 °C for 16 h. After removing the catalyst by filtration through Celite, the solvent was removed under reduced pressure to give a pale white solid, which was purified by column chromatography on silica gel ($\text{CHCl}_3/\text{MeOH}/\text{Et}_3\text{N}$; 96.5/2.5/1) and by recrystallisation from CH_2Cl_2 /petroleum ether to afford a white solid (0.93 g, 69%). R_f = 0.08 ($\text{CHCl}_3/\text{MeOH}/\text{Et}_3\text{N}$; 96.5/2.5/1). M.p. 159–161 °C; $[\alpha]_D^{20}$ = –106.6 (c = 1.04 in CHCl_3); ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 1.54–1.92 (m, 5 H; NH and CH_2CH_2), 2.84–2.94 (m, 1 H; NC(H)H), 3.01–3.09 (m, 1 H; NC(H)H), 3.99–4.08 (m, 1 H, NCH), 5.52 (d, $^3J(\text{H,H})$ = 9.4 Hz; 1 H; CH), 7.34–7.86 (m, 12 H; aromatic H), 8.27–8.42 (m, 2 H; aromatic H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 24.8, 30.5 (2 CH_2), 46.0 (NCH_2), 46.2 (CH), 64.3 (NCH), 123.5, 123.8, 125.2, 125.3, 125.3, 125.4, 125.5, 125.7, 126.1, 126.2, 126.9, 127.1,

128.8, 129.1, 131.9, 132.5, 133.9, 134.1, 139.7 (aromatic C); IR(neat): $\nu \sim 774, 1595, 1509, 1393, 2867, 2954, 3045 \text{ cm}^{-1}$; MS (CI): m/z (%): 338 (56) [$M^+ + H$], 268 (16), 141 (50), 70 (100). Elemental analysis: $C_{25}H_{23}N$ requires: C, 88.98; H, 6.87; N, 4.15. Found: C, 89.10; H, 7.31; N, 4.10. The corresponding hydrochloride salt was synthesized by addition of HCl (35-38%) (~1eq.) to a solution of amine in MeOH. After stirring the solution for 30 min. at room temperature, the solvent was evaporated and a pale white solid was obtained. The solid was dried under high vacuum overnight to give the hydrochloride salt **2**•HCl quantitatively. M.p. > 230 °C; $[\alpha]_D^{20} = -396.0$ ($c = 1.32$ in EtOH); 1H NMR (400 MHz, d_4 -MeOH, 25 °C): $\delta = 1.50\text{--}2.05$ (m, 4 H; CH_2CH_2), 3.27–3.30 (m, 2 H; NCH_2), 4.62–4.64 (m, 1 H; NCH), 5.93 (d, $^3J(H,H) = 11.2$ Hz; 1 H; CH), 7.20–7.82 (m, 13 H; aromatic H), 8.66 (d, $^3J(H,H) = 8.3$ Hz; 1 H; aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 23.6, 30.3$ (2 CH_2), 41.7 (CH), 45.3 (NCH_2), 64.0 (NCH), 123.6, 124.2, 125.1, 125.5, 125.7, 125.8, 125.9, 126.5, 127.2, 127.9, 128.0, 128.5, 129.3, 131.4, 132.1, 134.1, 134.2, 136.0, 137.6 (aromatic C); IR(neat): $\nu \sim 777, 1394, 1511, 1597, 2946, 3400 \text{ cm}^{-1}$; MS (CI): m/z (%): 338 (48) [$M^+ - Cl$], 267 (16), 141 (41), 129 (29), 70 (100). Exact mass calcd for $C_{25}H_{24}N$ requires: 338.1909. Found: 338.1911.

Hydrochloride salt of (S)-2-(diphenylmethyl)pyrrolidine (1•HCl) and (S)-diphenylprolinol (3•HCl):

The hydrochloride salt was synthesized by addition of aqueous HCl (35-38%) (~1eq.) to a solution of amine in MeOH. After stirring the solution for 30 min. at room temperature, the solvent was evaporated and a white solid was obtained. The solid was dried under high vacuum overnight to give the hydrochloride salt quantitatively. Purification can be performed by recrystallisation from, or trituration with CH_2Cl_2 /petroleum ether. Hydrochloride salt of (S)-2-(diphenylmethyl)pyrrolidine (**1**•HCl): M.p. 281–282 °C; $[\alpha]_D^{20} = +1.8$ ($c = 1.15$ in $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.58\text{--}1.97$ (m, 4 H; CH_2CH_2), 2.75 (broad s, 2 H; NCH_2), 4.21 (broad s, 1 H; NCH), 4.30 (d, $^3J(H,H) = 11.7$ Hz; 1 H; CH), 7.15–7.37 (m, 8 H; aromatic H), 7.52 (d, $^3J(H,H) = 7.3$ Hz; 2 H; aromatic H), 9.00 and 9.42 (broad s, 2 H, N^+H_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 23.7, 31.0, 45.7$ (3 CH_2), 54.6, 62.7 (2 CH), 127.2, 127.3, 127.9, 128.5, 129.0, 129.1 (aromatic C), 140.2 and 141.5 (aromatic C quat.); IR(neat): $\nu \sim 699, 747, 766, 1393, 2712, 2864 \text{ cm}^{-1}$; MS (CI): m/z (%): 238 (100) [$M^+ - Cl$], 91 (20) [$C_7H_7^+$], 70 (78). Elemental analysis: $C_{17}H_{20}ClN$ requires: C, 74.57; H, 7.36; N, 5.15. Found: C, 74.29; H, 7.15; N, 5.31.

Hydrochloride salt of (S)-diphenylprolinol (**3**•HCl): M.p. > 285 °C (decomp); $[\alpha]_D^{20} = +63.5$ ($c = 0.57$ in MeOH); 1H NMR (400 MHz, D_2O , 25 °C): $\delta = 1.79\text{--}2.23$ (m, 4 H; CH_2CH_2), 3.10–3.33 (m, 2 H; NCH_2), 4.77 (t, $^3J(H,H) = 8.4$ Hz; 1 H; NCH), 7.21–7.51 (m, 10 H; aromatic H); ^{13}C NMR (100 MHz, D_2O , 25 °C): $\delta = 24.2, 25.7, 46.7$ (3 CH_2), 67.2 (2 NCH), 77.7 (C-OH), 125.6, 127.9, 128.1, 129.1, 129.3 (aromatic C), 143.5 and 143.7 (aromatic C quat.); IR(neat): $\nu \sim 695, 749, 1392, 1446, 2719, 2878, 3248 \text{ cm}^{-1}$; MS (FAB): m/z (%): 254 (100) [$M^+ - Cl$], 236 (38). Elemental analysis: $C_{17}H_{20}ClNO$ requires: C, 70.46; H, 6.96; N, 4.83. Found: C, 70.32; H, 6.96; N, 4.91.

Perchlorate salt of (S)-2-(diphenylmethyl)pyrrolidine (1•HClO₄):

The perchlorate salt was synthesized by addition of aqueous $HClO_4$ (60-72%) (~1eq.) to a solution of amine in CH_2Cl_2 . After stirring the solution for 30 min. at room temperature, the solvent was evaporated and a white solid was obtained. After purification by recrystallisation in CH_2Cl_2 /petroleum ether, the solid was dried under high vacuum overnight to give the salt **1**• $HClO_4$ quantitatively. M.p. 198–199 °C; $[\alpha]_D^{20} = -1.9$ ($c = 0.51$ in MeOH); 1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.75\text{--}2.17$ (m, 4 H; CH_2CH_2), 3.32 (broad s, 2 H; NCH_2), 4.17 (d, $^3J(H,H) = 11.7$ Hz; 1 H; CH), 4.45 (broad s, 1 H; NCH), 6.74 (broad s, 1 H, N^+H), 7.16–7.48 (m, 11 H; aromatic H and N^+H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 23.6, 30.0, 47.3$ (3 CH_2), 54.5, 64.7 (2 CH), 127.7, 127.9, 129.2, 129.6 (aromatic C), 139.3 and 140.2 (aromatic C quat.); IR(neat): $\nu \sim 701, 745, 756, 1047$ (Broad and strong), 3091 cm^{-1} ; MS (FAB): m/z (%): 238 (100) [$M^+ - ClO_4$]. Elemental analysis: $C_{17}H_{20}ClNO_4$ requires: C, 60.45; H, 5.97; N, 4.15. Found: C, 60.65; H, 5.90; N, 4.07.

Hydrogen sulfate salt (1•H₂SO₄) and sulfate salt of (S)-2-(diphenylmethyl)pyrrolidine:

The hydrogen sulfate and sulfate salt was synthesized by addition of 1.0 or 0.5 equivalent of H₂SO₄ (98%) respectively to a solution of (*S*)-2-(diphenylmethyl)pyrrolidine **1** in CH₂Cl₂. After purification by recrystallisation in MeOH/Et₂O, the solid was dried under high vacuum overnight to give the salt quantitatively. Hydrogen sulfate salt: M.p. 197–199 °C; [α]_D²⁰ = –2.6 (*c* = 0.58 in MeOH); ¹H NMR (400 MHz, *d*₄-MeOH, 25 °C): δ = 1.65–2.16 (m, 4 H; CH₂CH₂), 3.26–3.42 (m, 2 H; NCH₂), 4.17 (d, ³*J*(H,H) = 11.7 Hz, 1 H; CH), 4.49–4.60 (m, 1 H; NCH), 7.17–7.55 (m, 10 H; aromatic H); ¹³C NMR (100 MHz, *d*₄-MeOH, 25 °C): δ = 23.1, 29.9, 46.0 (3 CH₂), 54.5, 63.9 (2 CH), 127.0, 127.4, 127.5, 127.7, 128.7, 129.0 (aromatic C), 140.8 and 141.7 (aromatic C quat.); IR(neat): ν = 697, 747, 854, 1029, 1151, 3029 cm^{–1}; MS (CI): *m/z* (%): 238 (100) [*M*⁺– HSO₄]. Elemental analysis: C₁₇H₂₁NO₄S requires: C, 60.87; H, 6.31; N, 4.18. Found: C, 60.98; H, 6.48; N, 4.08. Sulfate salt: M.p. 239–242 °C; [α]_D²⁰ = –9.6 (*c* = 0.53 in MeOH); ¹H NMR (400 MHz, *d*₄-MeOH, 25 °C) and ¹³C NMR (100 MHz, *d*₄-MeOH, 25 °C): identical to the NMR of hydrosulfate salt. IR(neat): ν = 697, 749, 760, 1023, 1065, 1148, 2422, 2980 cm^{–1}; MS (FAB): *m/z* (%): 574 (32) [*M*⁺+2 H], 238 (100) [*M*⁺–SO₄]. Elemental analysis: C₃₄H₄₀N₂O₄S requires: C, 71.30; H, 7.04; N, 4.89. Found: C, 71.20; H, 7.03; N, 4.86.

Synthesis of the nitrone **5**:

The reaction was carried out in a flat bottomed glass vial (diameter 15mm) equipped with a magnetic stirrer flea. In the vial, was placed the amine **1** (50 mg, 0.212 mmol) which was dissolved in CH₃CN/H₂O (95/5) (0.5 mL) and finely ground NaHCO₃ (178 mg, 2.12 mmol) and Oxone[®] (260 mg, 0.424 mmol) were added. The reaction was stirred at room temperature for 1 hour. Salts were removed by filtration with a sinter over MgSO₄. The cake was washed with CH₂Cl₂ (25 mL). After evaporation, the crude mixture was analyzed by ¹H NMR. Yield was determined by ¹H NMR relative to an internal standard (*para*-dimethoxybenzene). The nitrone **5** was purified by column chromatography on silica gel (EtOAc/petroleum ether; 40/60 then MeOH/CHCl₃; 10/90). R_f = 0.9 (.MeOH/CHCl₃; 10/90).

The analytical data (¹H and ¹³C NMR spectroscopy) showed that the nitrone exists as two isomers **5a** and **5b**.

IR(neat): ν = 700, 1210, 1591, 3388 cm^{–1}; MS (CI): *m/z* (%): 252 (100) [*M*⁺+H], 236 (60), 193 (30), 167 (40).

Isomer **5a**:

¹H NMR (300 MHz, *d*₄-MeOH, 25 °C): δ = 2.1–2.2 (m, 2H; CH₂), 2.6–2.8 (m, 2H; CH₂), 4.1–4.2 (m, 2H; NCH₂), 5.7 (s, 1H; CH), between 7.1 and 7.4 (10H; aromatic H); ¹³C NMR (75 MHz, *d*₄-MeOH, 25 °C): δ = 17.8 (CH₂), 28.3 (CH₂), 50.7 (CH), 63.6 (CH₂), between 127.9 and 130.8 (aromatic C), 139.7 (Cquat).

Isomer **5b**:

¹H NMR (300 MHz, *d*₄-MeOH, 25 °C): δ = 1.5–1.6 and 2.2–2.7 (m, 4H; CH₂CH₂), 4.7–4.8 (m, 1H; NCH), 5.1 (d, ³*J*(H,H) = 2.7 Hz, 1H; CH), 7.0 (s, 1H; N=CH), between 7.1 and 7.4 (10H; aromatic H); ¹³C NMR (75 MHz, *d*₄-MeOH, 25 °C): δ = 22.8 (CH₂), 32.2 (CH₂), 49.4 (CH), 76.8 (CH), between 127.9 and 130.8 (aromatic C), 140.2 (CH).

Synthesis of *N*-Methyl-(*S*)-2-(diphenylmethyl)pyrrolidine (**7**) and its corresponding hydrochloride salt (**7•HCl**):

Formaldehyde (37% aqueous solution) (150 μ l) was added to a refluxing solution containing (*S*)-2-(diphenylmethyl)pyrrolidine **1** (0.13 g, 0.56 mmol), formic acid (0.5 mL) and water (75 μ l) over a period of 5 minutes and reflux was continued for 4 h. The mixture was cooled and made alkaline (pH = 11) with NaOH 1M followed by extraction with CH₂Cl₂. The extracts were dried over MgSO₄ and evaporated *in vacuo* to yield the *N*-methyl-(*S*)-2-(diphenylmethyl)pyrrolidine (120 mg, 86%) which was directly used in the ammonium salt synthesis. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.6–2.0 (m, 4 H; CH₂CH₂), 2.0 (s, 3 H; NCH₃), 2.3–2.4 (m, 1 H; NC(*H*)H), 3.2–3.3 (m, 2 H; NCH and NC(*H*)H), 4.1 (d, ³*J*(H,H) = 9.2 Hz; 1 H; CH), 7.1–7.6 (m, 10 H; aromatic H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 22.6, 31.2 (2 CH₂), 42.6 (CH₃), 56.8 (CH), 58.6 (CH₂), 69.9 (CH), 126.3, 126.6, 128.4, 128.6 (aromatic C), 143.7 and 143.5 (aromatic C quat.).

The hydrochloride salt **7•HCl** was synthesized by addition of HCl (35–38%) (~1eq.) to a solution of crude amine in MeOH. After stirring the solution for 30 min. at room temperature, the solvent was evaporated and a white solid was obtained. The solid was dried under high vacuum overnight to give the hydrochloride salt **7•HCl** quantitatively. Purification can be performed by titration with Et₂O. M.p. 239–241 °C; [α]_D²⁰ = +76.7 (*c* = 0.55 in CHCl₃); ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.9–2.2 (m, 4 H; CH₂CH₂), 2.2 (s, 3 H; NCH₃), 2.9–3.0 (m, 1 H; NC(*H*)H), 3.9–4.1 (m, 2 H; NCH and NC(*H*)H), 4.9 (d, ³*J*(H,H) = 8.8 Hz; 1 H; CH), 7.2–7.4 (m, 10 H; aromatic H), 12.3 (m, 1 H; NH); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 21.5, 31.7 (2 CH₂), 41.9 (CH₃),

53.2 (CH), 58.9 (CH₂), 73.0 (CH), 127.3, 127.8, 128.6, 129.1, 129.4 (aromatic C), 140.8 and 141.7 (aromatic C quat.); IR (neat): ν = 700, 710, 750, 1007, 1452, 1493, 2427, 2951 cm⁻¹; MS (CI): m/z (%): 252 (90) [M^+ -Cl], 84 (100). Elemental analysis: C₁₈H₂₂ClN requires: C, 75.11; H, 7.70; N, 4.87. Found: C, 74.54; H, 7.87; N, 4.95.

Synthesis of *N,N*-dimethyl-(*S*)-2-(diphenylmethyl)pyrrolidine tetrafluoroborate salt **8:**

A solution of (*S*)-2-(diphenylmethyl)pyrrolidine **1** (256 mg, 1.10 mmol), methyl iodide (270 μ l, 4.30 mmol) and K₂CO₃ (150 mg, 1.10 mmol) in 5 mL of dry CH₃CN was refluxed under N₂ for 21 h. After cooling, the white precipitate was filtered and the filtrate was evaporated under reduced pressure to yield a white solid. The solid was triturated with Et₂O, collected by filtration and washed several times with Et₂O. The solid was dried under high vacuum to afford 280 mg (67%) of *N,N*-dimethyl-(*S*)-2-(diphenylmethyl)pyrrolidine iodide salt. M.p. 239 °C; $[\alpha]_D^{20}$ = +12.9 (c = 0.64 in MeOH); ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.8–2.4 (m, 4 H; CH₂CH₂), 2.9 (s, 3 H; NCH₃), 3.2 (s, 3 H; NCH₃), 3.8–3.9 (m, 1 H; NC(*H*)H), 4.2–4.3 (m, 2 H; CH and NC(*H*)H), 5.7–5.8 (m, 1 H; NCH), 7.3–7.7 (m, 10 H; aromatic H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 18.9, 29.1 (2 CH₂), 46.3, 53.2 (2 CH₃), 53.5 (CH), 69.4 (CH₂), 77.3 (CH), 127.1, 127.6, 128.0, 128.9, 129.2 (aromatic C), 139.8 and 141.1 (aromatic C quat.); IR (neat): ν = 701, 716, 753, 1450, 1475, 2160; MS (CI): m/z (%): 266 (25) [M^+ -I], 252 (50), 84 (100). Exact mass calcd for C₁₉H₂₄N requires: 266.1909. Found: 266.1899.

To a oven-dried flask was placed, under N₂, silver tetrafluoroborate (38 mg, 0.195 mmol) and a solution of *N,N*-dimethyl-(*S*)-2-(diphenylmethyl)pyrrolidine iodide salt (75 mg, 0.19 mmol) in 1.3 mL of dry CH₃CN was added. The precipitation of silver iodide was observed immediately. The solution was stirred at room temperature for 1 hour in the dark, filtered through celite and evaporated under reduced pressure to yield a white solid. The solid was triturated with Et₂O, collected by filtration and washed several times with Et₂O. The solid was dried under high vacuum to afford 58 mg (87%) of *N,N*-dimethyl-(*S*)-2-(diphenylmethyl)pyrrolidine tetrafluoroborate salt **8**. M.p. 205 °C; $[\alpha]_D^{20}$ = +89.1 (c = 0.45 in DMSO); ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C): δ = 1.6–2.1 (m, 4 H; CH₂CH₂), 2.5 (s, 3 H; NCH₃), 2.9 (s, 3 H; NCH₃), 3.3–3.6 (m, 2 H; NCH₂), 4.3 (d, ³*J*(H,H) = 11.5 Hz; 1 H; CH), 4.8–4.9 (m, 1 H; NCH), 7.1–7.6 (m, 10 H; aromatic H); ¹³C NMR (75 MHz, DMSO-*d*₆, 25 °C): δ = 18.0, 28.4 (2 CH₂), 44.1 (CH₃), 51.1 (CH), 52.6 (CH₃), 68.3 (CH₂), 75.7 (CH), 127.1, 127.5, 127.6, 128.0, 128.9, 129.2 (aromatic C), 140.8 and 142.2 (aromatic C quat.); IR(neat): ν = 704, 716, 761, 1034, 1046, 1453, 2032, 2160; MS (CI): m/z (%): 266 (85) [M^+ -BF₄], 84 (100). Exact mass calcd for C₁₉H₂₄N requires: 266.1909. Found: 266.1901.

Complex **6 formation:** To a solution of (*S*)-2-(diphenylmethyl)pyrrolidine **1** (0.424–2.96 mmol) in CH₃CN/H₂O (95/5) (c = 0.422 mol.l⁻¹) (1–7 mL) cooled to –10 °C, was added Oxone[®] (4 eq., 1.04–7.27 g). The mixture was stirred for 30 min. at this temperature. A quick filtration was then performed over MgSO₄ using a sinter funnel and a Millipore (CAT NO; GVWP 047 00) to remove salts. The cake was washed with CH₂Cl₂ and the solvent was partially evaporated. A second filtration under the same conditions was then performed and the filtrate evaporated to dryness. This crude complex is quite clean by ¹H NMR in CDCl₃ and only a trace of the corresponding nitron was detected (less than 5%). On large scale (2.96 mmol), the nitron can be mostly removed by trituration with CH₂Cl₂/Et₂O. The presence of trace solvent (CH₂Cl₂ and CH₃CN) is often present in the crude and facilitates dissolution of the complex in CDCl₃. Solvents can be removed by dissolution of the pale white solid in CH₂Cl₂ and evaporation *in vacuo* three times. The complex is then left under high vacuum for 10 hours to remove all solvents. When the complex is completely dry, its solubility in CDCl₃ is reduced and ¹H NMR in *d*₄-MeOH or CD₃CN is then carried out. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.67–2.06 (m, 4 H; CH₂CH₂), 3.30 (broad s, 2 H; NCH₂), 4.22 (d, ³*J*(H,H) = 11.7 Hz 1 H; CH), 4.41 (broad s, 1 H; NCH), 6.70 (broad s, 1 H, N⁺H), 7.10–7.52 (m, 10 H; aromatic H), 7.82 (broad s, 1 H, N⁺H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 23.6, 30.2, 47.0 (3 CH₂), 54.3, 63.8 (2 CH), 127.2, 127.5, 127.8, 128.1, 129.0, 129.3 (aromatic C), 139.9 and 141.0 (aromatic C quat.); The ¹H NMR of **6** in CDCl₃ shows a characteristic broad signal at 7.82 ppm and a large broad signal at around 6.70 ppm, which each integrate for 1H and could correspond to the N⁺(H)₂ (these signals disappear in *d*₄-MeOH). The corresponding perchlorate salt (**1**•HClO₄) shows very similar signals although the corresponding hydrochloride salt (**1**•HCl) is slightly different. The ¹H NMR and ¹³C NMR in *d*₄-MeOH or CD₃CN of the complex is similar to the NMR with hydrogen sulfate salt (**1**•H₂SO₄). IR(neat): ν = 697, 747, 856 (Broad and weak), 1052 (Broad and strong), 1215 (Broad and strong), 3030 cm⁻¹.

Comparison of complex's stretching vibrations of S=O with different salts

Salt	Stretching vibrations of S=O	
Complex 6	1052 (Broad and strong)	856 (Broad and weak)
	1215 (Broad and strong)	
KHSO ₅ •H ₂ O ^[3]	1070 (Broad and strong)	
	1250 (Broad and strong)	
Hydrosulfate salt I	1029 (Broad and strong)	854 (Broad and strong)
	1151 (Broad and strong)	
Sulfate salt II	1065 (Sharp and strong)	1023 (Sharp and strong)
	1148 (Sharp and weak)	

Comparison of ¹H and ¹³C NMR of the complex **6** with the NMR of the perchlorate and hydrochloride salt in CDCl₃

	CH ₂ CH ₂ (¹ H and ¹³ C NMR)	NCH ₂ (¹ H and ¹³ C NMR)	NCH (¹ H and ¹³ C NMR)	CH (¹ H and ¹³ C NMR)	N ⁺ (H) ₂ (¹ H and ¹³ C NMR)
Complex 6	Δ = 1.7–2.1 ppm (m) δ=23.6, 30.2 ppm	δ=3.3 ppm (Broad s) δ=47.0 ppm	δ=4.4 ppm (Broad s) δ=63.8 ppm	δ=4.2 ppm (d) δ=54.3 ppm	δ=6.7 and 7.8 ppm (Broad s)
1•HClO₄	δ=1.7–2.2 ppm (m) δ=23.6, 30.0 ppm	δ=3.3 ppm (Broad s) δ=47.3 ppm	δ=4.4 ppm (Broad s) δ=64.7 ppm	δ=4.1 ppm (d) δ=54.5 ppm	δ=6.7 and 7.3 ppm (Broad s)
1•HCl	δ=1.6–2.0 ppm (m) δ=23.7, 31.0 ppm	δ=2.7 ppm (Broad s) δ=45.7 ppm	δ=4.2 ppm (Broad s) δ=62.7 ppm	δ=4.3 ppm (d) δ=54.6 ppm	δ=9.0 and 9.4 ppm (Broad s)

Titration: To a 120–150 mg sample was added 0.5 mL of glacial acetic acid and 1 mL of 10% aqueous NaI. After dilution to 5 mL with THF, it was titrated with a 0.100–0.110 M solution of sodium sulfite in deionized water to the yellow endpoint (NaI was dried under high vacuum overnight prior to preparing the solution with deionized water. Freshly prepared solutions of NaI and sodium sulfite have to be used). After complex formation and titration, an average of 57–62% by weight of active oxidizing agent was found (peroxymonosulfate salt **6b**, C₁₇H₂₁NO₅S, FW=351.42). For example, after complex formation with 2.96 mmol of (*S*)-2-(diphenylmethyl)pyrrolidine **1**, trituration of the complex with CH₂Cl₂/Et₂O and drying under vacuum overnight, titration gave 62.2% by weight of active oxidizing agent. The titration of the same batch left for six weeks at 0 °C give 51.1%.

Microanalysis: Four possible structures can be present after complexation. These structures are represented below. The sample, which was submitted for analysis had 59.4% by weight of active oxidizing agent (structure **6b**). Microanalysis results obtained from two different sources are reported in Table 1, together with the theoretical microanalysis of each possible structures and the sum of the differences with microanalysis results. The best result was obtained with structure **6b** (• = 1.52). However, the titration showed us that only 59% of active oxidizing agent could be present after complexation. It is difficult to know which other counterions (hydrogen sulfate or sulfate) can be involve and in which ratio. A good result was obtained with the mixture **6b/I** (59.4/40.6) with • = 1.54.

Table 1: Microanalysis results

	Analysis 1				•	Independent Analysis 2				•
	C	H	N	S		C	H	N	S	
Found	58.90	6.20	4.00	8.22		58.27	6.32	3.92	8.14	
Structure I (calc.)	60.87	6.31	4.18	9.56	3.6	60.87	6.31	4.18	9.56	4.29
Structure II (calc.)	71.30	7.04	4.89	5.60	16.75	71.30	7.04	4.89	5.60	17.26
Structure 6a (calc.)	54.6	5.40	3.75	8.59	5.65	54.6	5.40	3.75	8.59	5.14
Structure 6b (calc.)	58.10	6.02	3.99	9.12	1.89	58.10	6.02	3.99	9.12	1.52
6b/I (59.4/40.6) (calc.)	59.22	6.13	4.07	9.30	1.54	59.22	6.13	4.07	9.30	2.45
6b/6a (59.4/40.6) (calc.)	56.70	5.76	3.89	8.59	3.43	56.70	5.76	3.89	8.59	2.91

Typical experimental procedure for the epoxidation reactions described in Table 1, Table 3 and Scheme 10:

The reaction was carried out in a flat bottomed glass vial (diameter 15mm) equipped with a magnetic stirrer flea. In the vial, were placed the amine **1** or the hydrochloride salt of amine **1**, **2**, **3**, **7** or **8** (5 or 10 mol %, 0.0212 or 0.042 mmol), and 1-phenylcyclohexene (67 mg, 0.424 mmol). The mixture was dissolved in CH₃CN/H₂O (0.5 mL) and pyridine (0.5 eq., 0.212 mmol, 17 μ L) was added followed by finely ground NaHCO₃ (356 mg, 4.24 mmol) and Oxone[®] (521 mg, 0.848 mmol). The reaction was stirred at room temperature or at –10°C and followed by TLC. If the reaction was not complete, stirring was continued for a maximum of 2 hours. Salts were removed by filtration with a sinter over MgSO₄. The cake was washed with CH₂Cl₂ (25 mL). When the reaction was performed at –10°C (Table 1, entries 4, 7 and 9), the organic phase was extracted with a saturated solution of NaHCO₃ (to recover the amine). After evaporation of the dried organic phase, the crude mixture was analyzed by ¹H NMR. Yields and conversions are determined by ¹H NMR relative to an internal standard (*para*-dimethoxybenzene). The enantioselectivities were determined by chiral GC using a α -CD column.

Procedure for reaction described in Scheme 5:

The reaction has been performed following the procedure described above for Table 1 with CD₃CN/D₂O. After 5 min. of stirring at room temperature, the reaction mixture was diluted with CDCl₃ (2 mL) in the presence of an internal standard. After 5 min. of stirring, the salts were allowed to settle. Solvent was decanted for NMR analysis. Yields are determined by ¹H NMR relative to an internal standard (*para*-dimethoxybenzene).

Procedure for reaction described in Scheme 7:

The reaction was carried out in a flat bottomed glass vial (diameter 15mm) equipped with a magnetic stirrer flea. In the vial, were placed the amine **1** (50 mg, 0.212 mmol) and pyridine (17 μ L, 0.212 mmol). The mixture was dissolved in CH₃CN/H₂O (95/5) (0.5 mL) and placed in a bath at –10°C. Finely ground NaHCO₃ (178 mg, 4.24 mmol) and Oxone[®] (521 mg, 0.848 mmol) were added. After 30 min. of stirring at –10°C, a quick filtration over MgSO₄ was performed. The cake was washed with CH₂Cl₂ (20 mL) and the organic phase was extracted with a saturated solution of NaHCO₃ (5 mL) (to recover the amine). The organic layer was dried over MgSO₄. After filtration, the solvent was removed and the crude mixture was analyzed by ¹H NMR relative to an internal standard (*para*-dimethoxybenzene).

Typical experimental procedure for the epoxidation reaction described in Table 2 with peroxymonosulfate ammonium **6b** (method A) or using the corresponding hydrochloride in catalytic amount at room temperature (method B) or at –10 °C (method C):

Method A: The reaction was carried out in a flat bottomed glass vial (diameter 15mm) equipped with a magnetic stirrer flea. Alkene (0.212 mmol) was placed in the vial, followed by addition of the complex (FW=351.42), 223 mg, which corresponds to 0.36-0.39 mmol (1.71–1.86 equivalent) of active oxygen after titration). The mixture was then dissolved in CH₃CN/H₂O (95/5) (1 mL) with pyridine (1 eq., 17 μ L). The reaction was stirred at room temperature (reaction times given in the table 1). The reaction was then dissolved in Et₂O (3 mL) and pyridine (2 eq., 34 μ L) was added before hydrolysis with H₂O (3 mL). The aqueous phase was extracted with Et₂O (4x3 mL). The organic phase was dried over MgSO₄ and after filtration and evaporation, the crude mixture was analyzed by ¹H NMR. Yields and conversions were determined by ¹H NMR relative to an internal standard (*para*-dimethoxybenzene). The enantioselectivities were determined by chiral GC using a α -CD column.

As 1-methylcyclohexene is volatile, the reaction was performed in deuterated solvent. The reaction was diluted in CDCl₃ (2 mL) in the presence of internal standard and pyridine (2 eq., 34 μ L) before hydrolysis with H₂O (3 mL). The organic phase was separated from the aqueous phase and dried over MgSO₄ before performing analysis.

Method B: The reaction was carried out in a flat bottomed glass vial (diameter 15mm) equipped with a magnetic stirrer flea. In the vial, were placed the ammonium salt **1**•HCl (12 mg, 0.042 mmol), and the alkene (0.424 mmol). The mixture was dissolved in CH₃CN/H₂O (95/5) (0.5 mL) and pyridine (0.5 eq., 0.212 mmol, 17 μ L) was added followed by finely ground NaHCO₃ (356 mg,

4.24 mmol) and Oxone[®] (521 mg, 0.848 mmol). The reaction was stirred at room temperature and followed by TLC. If the reaction was not complete, stirring was continued for a maximum of 4 hours. had been fixed. Salts were removed by filtration with a sinter over MgSO₄. The cake was washed with CH₂Cl₂ (25 mL). After evaporation, the crude mixture was analyzed by ¹H NMR. Yields and conversions are determined by ¹H NMR relative to an internal standard (*para*-dimethoxybenzene). The enantioselectivities were determined by chiral GC using a α -CD column.

As 1-methylcyclohexene is volatile, the reaction was performed in deuterated solvent. The reaction was then diluted with CDCl₃ (2 mL) in the presence of internal standard. After 5 min. of stirring, the salts were allowed to settle. Solvent was decanted for analysis. Yields are determined by ¹H NMR relative to an internal standard (*para*-dimethoxybenzene).

Method C: (–10 °C, with recovery of amine) The reaction was carried out in a flat bottomed glass vial (diameter 15mm) equipped with a magnetic stirrer flea. In the vial, were placed the ammonium salt **1**·HCl (10 mol %, 0.042 mmol) and the alkene (0.424 mmol). The mixture was dissolved in CH₃CN/H₂O (95/5) (0.5 mL) and pyridine (0.5 eq., 0.212 mmol, 17 μ L) was added. The mixture was placed in a bath at –10 °C and finely ground NaHCO₃ (356 mg, 4.24 mmol) was added followed by the addition of Oxone[®] in three portions over 4 h 30. A quick filtration over MgSO₄ was then performed. The cake was washed with CH₂Cl₂ (20 mL) and the organic phase was extracted with a saturated solution of NaHCO₃ (5 mL) (to recover the amine). The organic layer was dried over MgSO₄. After filtration, the solvent was removed and the crude mixture was analyzed by ¹H NMR relative to an internal standard (*para*-dimethoxybenzene). The enantioselectivities were determined by chiral GC using a β -CD column.

As 1-methylcyclohexene is volatile, the reaction was performed in deuterated solvent and the extraction was not conducted. At the end of the reaction, the mixture was diluted with CDCl₃ (2 mL) in the presence of internal standard. After 5 min. of stirring, the salts were allowed to settle. Solvent was decanted for analysis. Yields are determined by ¹H NMR relative to an internal standard (*para*-dimethoxybenzene).

Data for epoxides in Table 2 and determination of absolute configuration:

(S,S)-1-phenylcyclohexene oxide^[4]: ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.20-1.71 (m, 4H; CH₂), 1.92-2.38 (m, 4H; CH₂), 3.01 (m, 1H; CHO), 7.21-7.53 (m, 5H; aromatic H).

The absolute configuration was determined by comparing the measured optical rotation with the reported one: $[\alpha]_D^{20}$ = –54.8 (*c* = 0.47 in toluene) [lit.^[5]] for the (*R,R*)-1-phenylcyclohex-1-ene oxide: $[\alpha]_D^{25}$ = +116.7 (*c* = 1.21 in benzene) for 98% ee].

(1R,2S)-1-methylcyclohexene oxide^[6]: ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.11-1.87 (m, 8H; CH₂), 1.25 (s, 3H; CH₃), 2.95 (m, 1H; CHO).

The absolute configuration was determined by chiral GC (Chiraldex γ -TA column) and compared with the literature data.^[5]

1-phenyl-1,2-epoxypropane^[7]: ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 1.45 (d, ³*J*(H,H) = 4.9 Hz, 3 H; CH₃), 3.06 (dq, ³*J*(H,H) = 5.4 Hz, ³*J*(H,H) = 2.0 Hz, 1H; CHO), 3.58 (d, ³*J*(H,H) = 2.0 Hz, 1H; CHO), 7.25-7.42 (m, 5H; aromatic H).

(S,S)-stilbene oxide^[8]: ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 3.85 (s, 2H; CHO), 7.21-7.43 (m, 10; aromatic H).

The absolute configuration was determined by chiral HPLC using an OD column and compared with the literature data.^[9]

Table of conditions for ee determination by chiral GC using a β -CD column

Epoxides	Pressure	T °C (oven)	R _f	R _t
20 psi	120 °C	15.9 min. (<i>S,S</i>)	16.4 min. (<i>R,R</i>)
20 psi	35 °C	12.3 min. (1 <i>R</i> ,2 <i>S</i>)	12.9 min. (1 <i>S</i> ,2 <i>R</i>)
20 psi	100 °C	5.1 min. (<i>S,S</i>)	5.4 min. (<i>R,R</i>)
20 psi	150 °C	21.6 min. (<i>S,S</i>)	22.9 min. (<i>R,R</i>)

Epoxidation reaction on 1-phenylcyclohexene using method B: comparison of amines 1, 2 and 3 with their corresponding ammonium chloride salts:

Entry	Catalyst	Time	Yield (%)	Ee (%)
1	10% amine 1	30 min.	87-99	32-38
2	10% 1 . HCl	20 min.	93 (5 ^a)	46
3	10% amine 2	75 min.	99	56
4	10% 2 . HCl	60 min.	89 (7 ^a)	59
5	10% amine 3	2 h.	80 (5 ^a)	60
6	10% 3 . HCl	2 h.	79 (11 ^a)	54

a: Yield of diol

Variation of amounts of Oxone[®] and NaHCO₃ in the epoxidation reaction of 1-phenylcyclohexene using the ammonium chloride salt of (S)-2-(diphenylmethyl)pyrrolidine **1 (method B):**

Entry	Oxone (eq.)	NaHCO ₃ (eq.)	Time	Yield (%)	Ee (%)
1	2	10	20 min.	93	46
2	1.5	10	30 min.	92	45
3	1	10	30 min.	94	45
4	1	5	30 min.	98	45
5	1	3	1 h.	94	46

Solvent study for the epoxidation following Method A: The epoxidation reaction was performed with 0.212 mmol of 1-phenylcyclohexene, 1.2 equivalent of active oxygen (150 mg of complex **6**) in 2 mL of solvent without pyridine (pyridine was added before work-up).

Solvent	Reaction time	Yield (%)	Ee (%)
CH ₃ CN	1h	67	47
CH ₃ CN/H ₂ O (95/5)	1h	65	46
CH ₃ CN/H ₂ O (50/50)	2h	21(31 ^a)	45
CH ₂ Cl ₂	1h	21	40
THF	1h	trace	-
THF/H ₂ O (4/1)	2h	7	46
DMF	2h	trace	-

a) Yield of diol

Solvent study for the epoxidation following Method B: The epoxidation was performed on 0.424 mmol of 1-phenylcyclohexene as described in procedure B.

Catalyst	Solvent	Reaction time	Yield (%)	Ee (%)
1	CH ₃ CN/H ₂ O (95/5)	20 min.	92	34
1	MeOH	40 min.	98	41
1	MeOH/H ₂ O (95/5)	40 min.	98	41
1	Dioxane/H ₂ O (95/5)	20 min.	54	7
1	MeOCH ₂ CH ₂ OMe/H ₂ O (95/5)	20 min.	52	2
1	CH ₂ Cl ₂ /H ₂ O (95/5), Bu ₄ NHSO ₄ (10%)	20 min.	65	7
1	CHCl ₃ /H ₂ O (95/5), Bu ₄ NHSO ₄ (10%)	20 min.	73	8
1 •HCl	CF ₃ CH ₂ OH	40 min.	75	46
1 •HCl	CF ₃ CH ₂ OH/CH ₃ CN (1/2)	30 min.	86	48
1 •ClO ₄ ⁻	CH ₃ CN/H ₂ O (95/5)	1h	96	45
1 •ClO ₄ ⁻ ^a	CH ₃ CN/H ₂ O (95/5)	3.5h	92	43
3 •HCl	CH ₃ CN/H ₂ O (95/5)	2h	79 (11 ^b)	54
3 •HCl	MeOH	2h	57	29

a) The reaction has been performed with 0.212 mmol of alkene in 2 mL of solvent (instead of 0.424 mmol in 0.5 mL). b) Yield of diol

These experiments show that alternative solvents can be employed. In particular, MeOH and CF₃CH₂OH show similar results to MeCN/H₂O (95/5).

Competition Reaction between the *trans* and *cis*-beta-methylstyrene:

Amine catalyst process: The competition experiment was performed with 1 equivalent of each alkene (each 0.424 mmol) using method **B** described above. After filtration and evaporation, the crude mixture was analyzed by ¹H NMR (see below), thus showed that the relative rates in oxidation of *cis* and *trans* •-methyl styrenes was 56:44.

m-CPBA oxidation: The *trans* and *cis*-beta-methylstyrene (each 0.424 mmol) were placed in a vial and were dissolved in 1 mL of CH₂Cl₂. *m*-CPBA (0.212 mmol) was added and the solution was stirred for 25 min. at room temperature. The mixture was filtrated over MgSO₄ and the cake was washed with CH₂Cl₂ (20 mL). After evaporation, the crude mixture was analyzed by ¹H NMR. By the same analysis, the relative rates of oxidation of *cis* and *trans* •-methyl styrenes was 58:42.

Hammett correlations: The relative reactivities of 1-phenylcyclohexene and four *para*-substituted 1-phenylcyclohexene towards epoxidation by amine catalyst process were measured by competition experiments and were used to construct Hammett correlations. Two substrates in equal quantities were paired in each competition experiment and submitted to epoxidation in the presence of 0.2 eq. of Oxone®. The reaction was stopped after 30 min. (Table 2). It was necessary to limit the amount of oxidant to keep conversion of the more reactive substrate as close as possible to 10%. The data presented is the average of 3 runs.

Table 2: Competition experiment between *p*-substituted 1-phenylcyclohexenes^a

Substrates	Conversion % ^b			
A/B	A+B	A	B	(A)/(B)
F/CF ₃	20	14	6	2.3
H/F	19	10	9	1.11
Me/H	17	12	5	2.4
OMe/Me	26	15	11	1.36

^a 1 eq. of each alkene is used in all experiments. Alkene (0.424 mmol; C_{substrate}=0.848 mol.l⁻¹), (S)-2-(diphenylmethyl)pyrrolidine **1** (5 Mol %, 0.021 mmol), Oxone® (0.085 mmol), NaHCO₃ (0.424 mmol), Pyridine (0.424 mmol), *d*-MeCN:D₂O (95:5) (0.5 ml). ^b Conversion determined by ¹H NMR relative to an internal standard (dichloromethane).

From the data obtained for k_H/k_X (Table 3), the Hammett equation gives y = -0.711x + 0.003 (r² = 0.930). As shown from the value of ρ = -0.71 this reaction is faster for electron donating substituents.

Table 3: observed values for k_H/k_X

X	k _H /k _X	Log ₁₀ k _H /k _X	σ ⁺
CF ₃	0.39	-0.409	0.58
F	0.90	-0.046	-0.07
H	1	0	0
Me	2.4	0.380	-0.31
OMe	3.2	0.505	-0.78

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