

Titanium Catalysts for Enantioselective Diamination of Alkenes with Imidoosmium Reagents

Kilian Muñiz and Martin Nieger

Kekulé-Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Str. 1,
D-53121 Bonn, Germany

Institut für Anorganische Chemie, Gerhard-Domagk-Str. 1, D-53121 Bonn,
Germany.

E-mail: kilian.muniz@uni-bonn.de

E-mail: nieger@joyx.joensuu.fi

Supporting Information

Experimental Details

Characterisation of Reaction Products

Spectral Characterisation

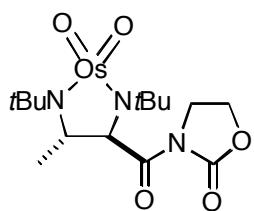
Elementary Cell from Solid State Structure of (+)-3

General procedure for enantioselective diamination:

Under an argon atmosphere, a portion of the respective olefin (0.1 mmol) is dissolved in freshly distilled toluene. The preformed Ti catalyst is added as a 1M-stock solution in toluene (0.01 mL) and the resulting solution is stirred at room temperature. Molecular sieves (ca. 1g) are introduced and the reaction mixture is cooled to 5°C before addition of the bisimido osmium compound **2** (0.11 mmol). The reaction is stirred for a period of 16h before it is placed directly on top of a small pad of silica. The product is obtained as the last fraction by changing to ethyl acetate as eluent. The pure products were obtained after removal of the solvent under reduced pressure. HPLC determinations were carried out on a Knauer Wellchrome (injection valve A0258, pump K-100, solvent organizer K-1500, UV-detector K-2600).

Characterisation of reaction products:

[*(4S/5R)*]-1,3-Bis-(*tert*-butyl)-2,2-dioxo-4-methyl-5-(oxazolidinon-3-yl-carbonyl)osma(VI)imidazolidine (3**)**



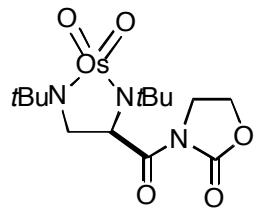
¹H nmr (CDCl₃, 300 MHz): δ = 1.23 (d, J = 6.0 Hz, 3H), 1.30 (s, 9H), 1.32 (s, 9H), 3.80-3.94 (m, 2H), 3.96 -4.07 (m, 2H), 4.43 (q, J = 6.0 Hz, 1H), 5.32 (s, 1H).

¹³C nmr (CDCl₃, 75 MHz): δ = 24.28, 30.17, 30.65, 42.79, 62.73, 67.06, 67.25, 74.56, 79.90, 153.85, 172.28.

HRMS: Calcd. for C₁₅H₂₇N₃O₅¹⁸⁸Os: 579.1664. Found: 579.1669.

HPLC: Chiralpak AD, n-hexane/2-propanol, 90/10 (v/v), 0.7 mL/min. Retention times: 24.8 and 28.2 min.

[(5*R*)]-1,3-Bis-(*tert*-butyl)-2,2-dioxo-5-(oxazolidinon-3-yl-carbonyl)osma(VI)imidazolidine (4)



¹H nmr (CDCl₃, 300 MHz): δ = 1.32 (s, 9H), 1.33 (s, 9H), 3.70 (d, J = 13.1 Hz, 1H), 3.94 (dt, J = 4.2, 8.1 Hz, 2H), 4.09 (dd, J = 6.8, 13.1 Hz, 1H), 4.44 (t, J = 8.1 Hz, 2H), 5.69 (d, J = 6.8 Hz, 1H).

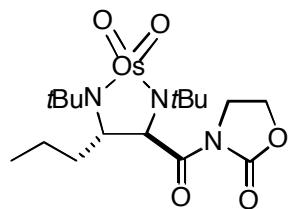
¹³C nmr (CDCl₃, 75 MHz): δ = 29.47, 30.10, 42.79, 62.73, 67.22, 67.34, 68.57, 73.11, 154.22, 172.98.

MS (eI): 507 ([M+], 492 (3), 393 (100), 337 (41), 281 (62), 149 (33), 57 (61).

HRMS: Calcd. for C₁₄H₂₅N₃O₅¹⁸⁸Os: 503.1353. Found: 503.1353.

HPLC: Chiralpak AD, n-hexane/2-propanol, 90/10 (v/v), 0.7 mL/min. Retention times: 45.6 and 69.4 min.

[(4*S*/5*R*)]-1,3-Bis-(*tert*-butyl)-2,2-dioxo-4-propyl-5-(oxazolidinon-3-yl-carbonyl)osma(VI)imidazolidine (5)



¹H nmr (CDCl₃, 300 MHz): δ = 0.82 (t, J = 7.0 Hz, 3H), 1.27-1.88 (m, 4H), 1.28 (s, 9H), 1.29 (s, 9H), 3.75 (d, dd, J = 2.0, 9.8 Hz, 1H), 3.80-3.88 (m, 1H), 3.91-3.98 (m, 1H), 4.36-4.41 (m, 2H), 5.62 (s, 1H).

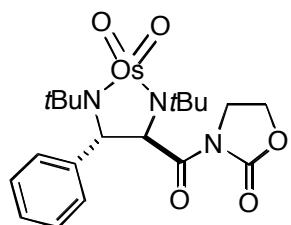
¹³C nmr (CDCl₃, 75 MHz): δ = 14.27, 19.79, 30.27, 30.70, 40.52, 43.02, 62.55, 67.26, 67.36, 76.18, 79.24, 153.45, 172.96.

MS (eI): 549 ([M+], 534 (21), 450 (38), 435 (100), 379 (89), 323 (41), 149 (19), 57 (67).

HRMS: Calcd. for C₁₇H₃₁N₃O₅¹⁸⁸Os: 545.1823. Found: 545.1804.

HPLC: Chiralpak AD, n-hexane/2-propanol, 90/10 (v/v), 0.7 mL/min. Retention times: 33.8 and 36.1 min.

[(4*S*/5*R*)]-1,3-Bis-(*tert*-butyl)-2,2-dioxo-4-phenyl-5-(oxazolidinon-3-yl-carbonyl)osma(VI)imidazolidine (6)



¹H nmr (CDCl₃, 300 MHz): δ = 1.17 (s, 9H), 1.24 (s, 9H), 3.94-4.01 (m, 2H), 4.44-4.51 (m, 2H), 4.91 (s, 1H), 5.74 (s, 1H), 7.16-7.29 (m, 5H).

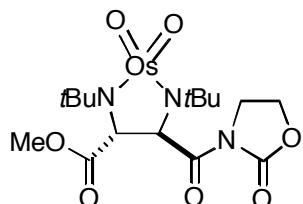
¹³C nmr (CDCl₃, 75 MHz): δ = 30.12, 30.72, 43.03, 62.66, 67.34, 68.08, 81.50, 81.62, 127.08, 127.86, 128.35, 144.20, 153.48, 172.66.

MS (eI): 583 ([M+1], 568 (5), 469 (57), 413 (71), 357 (43), 146 (50), 1044 (36), 57 (100).

HRMS: Calcd. for C₂₀H₂₉N₃O₅¹⁸⁸Os: 579.1664. Found: 579.1669.

HPLC: Chiralpak AD, n-hexane/ethanol, 90/10 (v/v), 1.0 mL/min. Retention times: 10.6 and 12.3 min.

[(4*R*/5*R*)]-1,3-Bis-(*tert*-butyl)-2,2-dioxo-4-methyloxycarbonyl-5-(oxazolidinon-3-yl-carbonyl)osma(VI)imidazolidine (7)

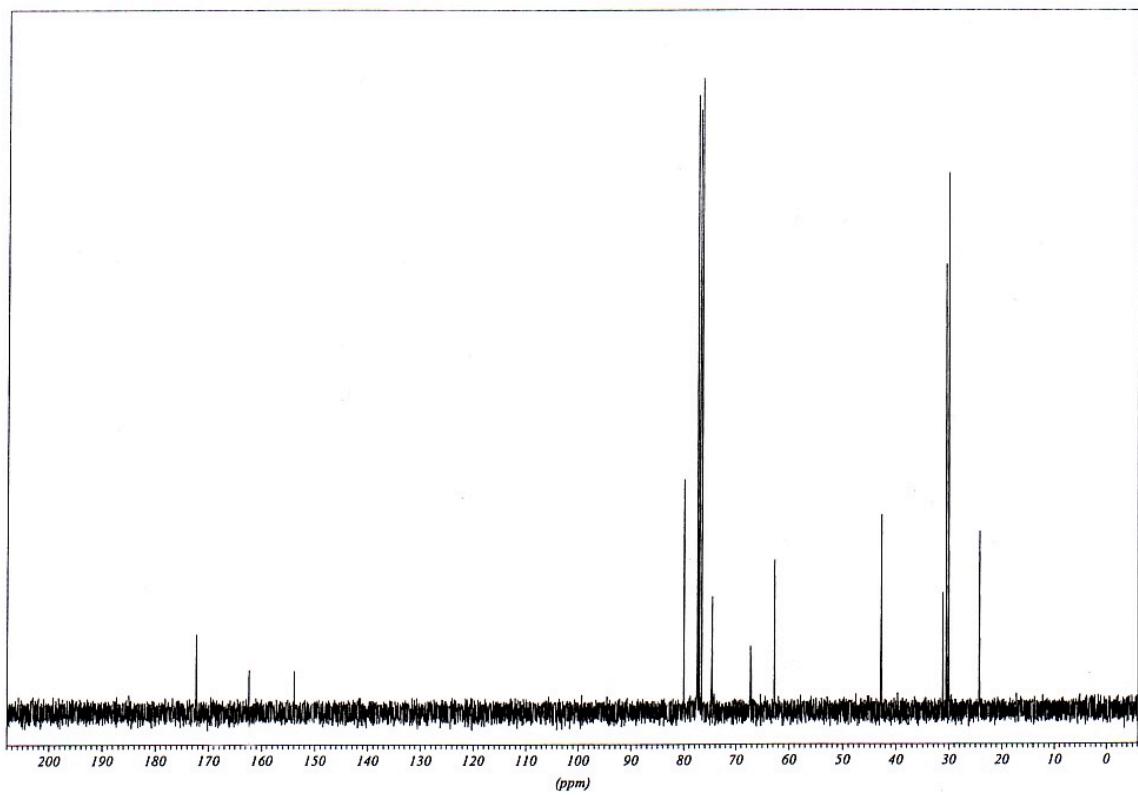
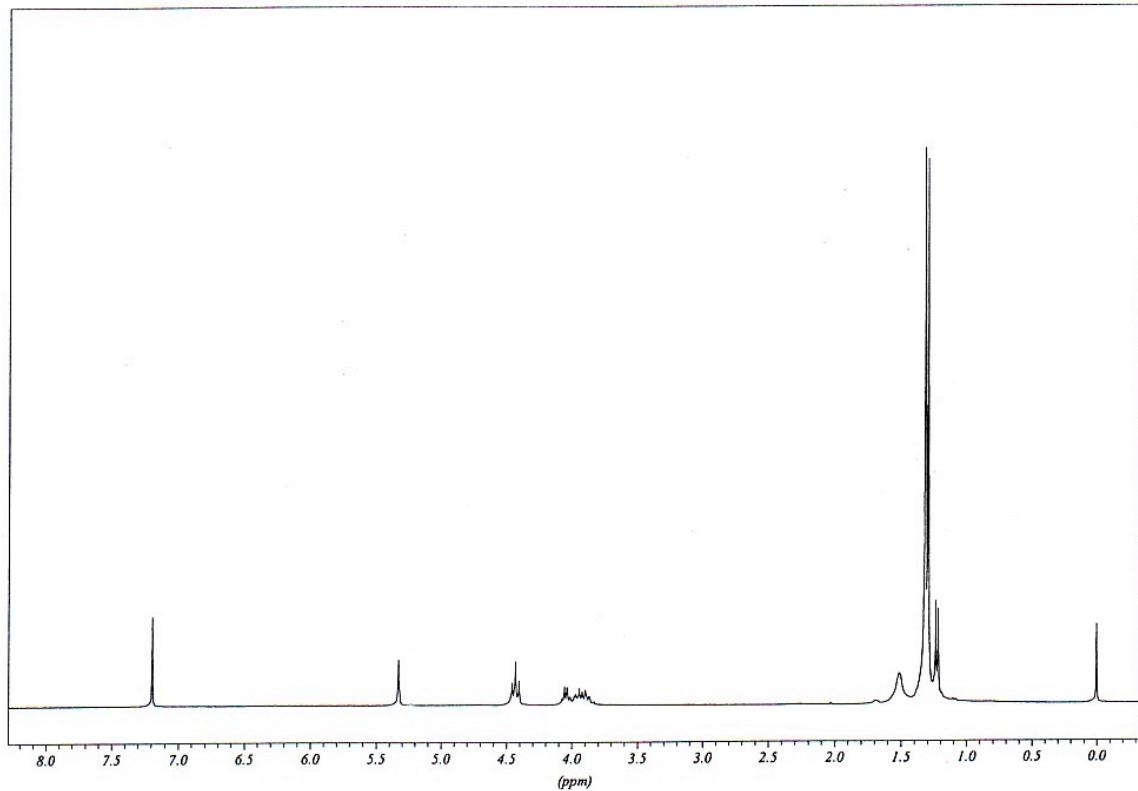
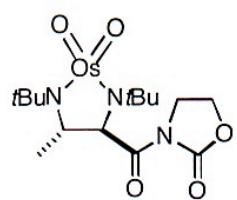


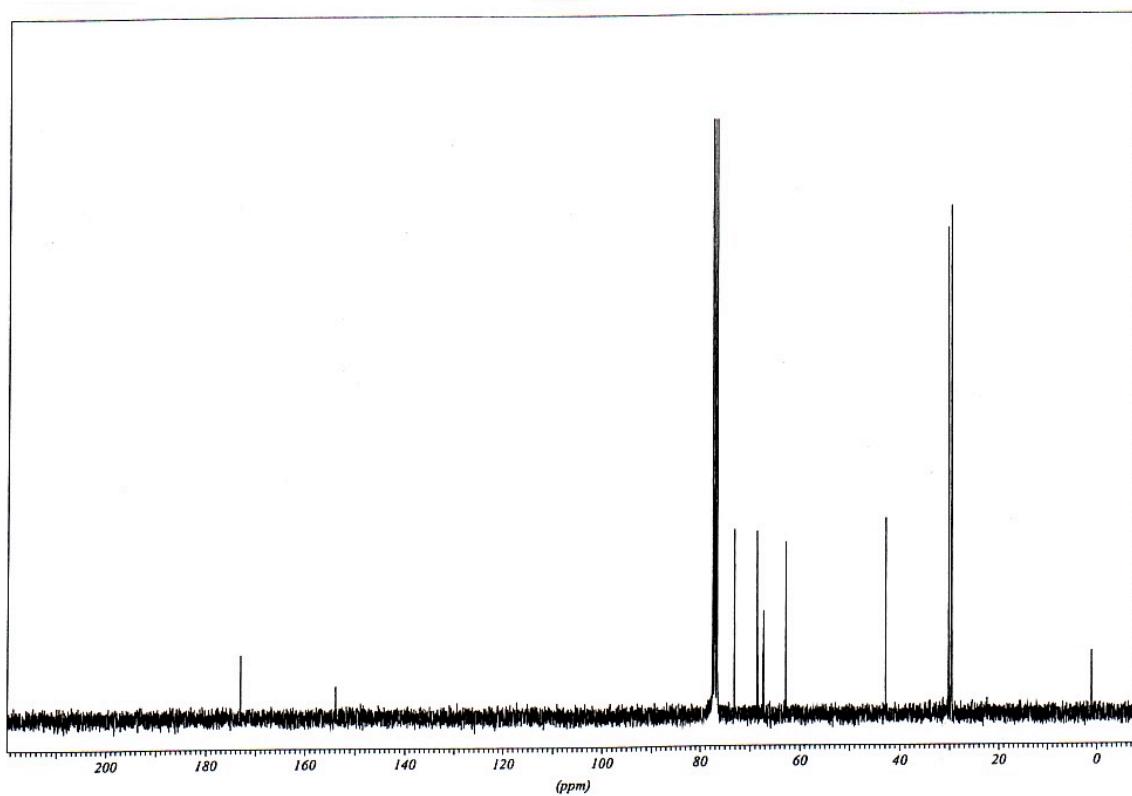
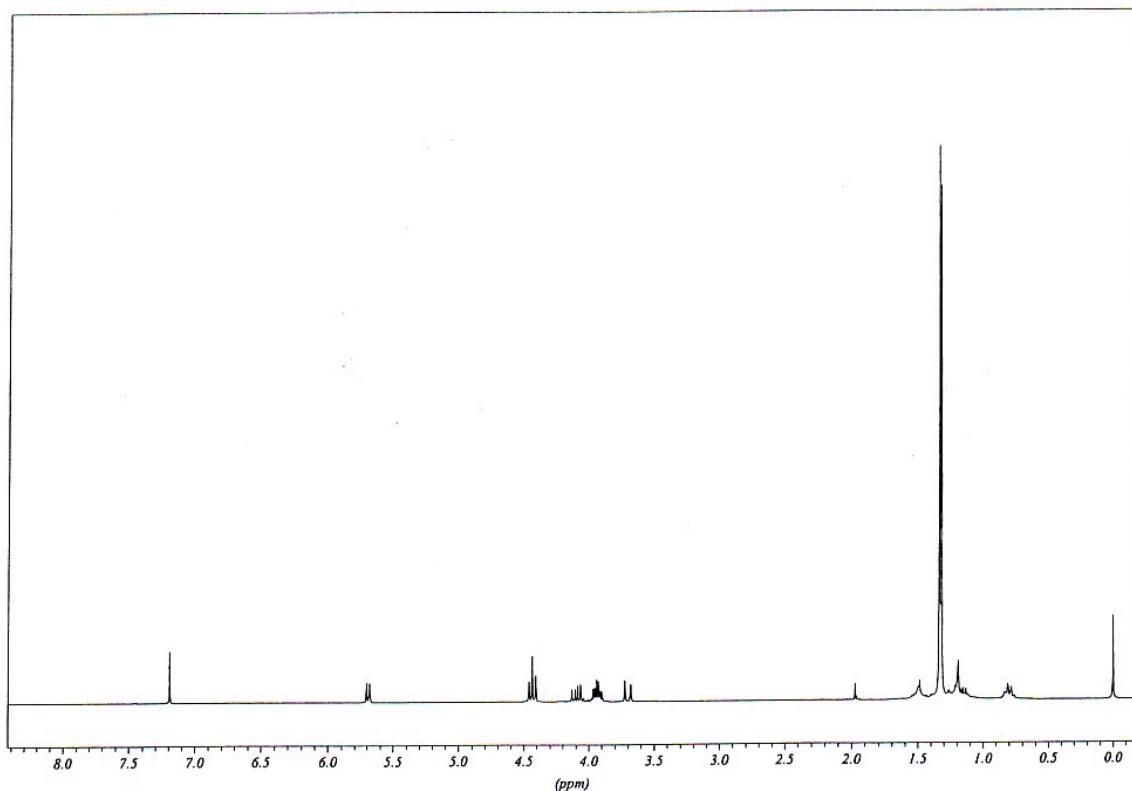
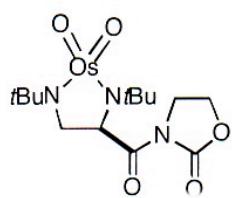
¹H nmr (CDCl₃, 300 MHz): δ = 1.29 (s, 9H), 1.30 (s, 9H), 3.67 (s, 3H), 3.86-3.99 (m, 2H), 4.39 (s, 1H), 4.45 (t, J = 8.1 Hz, 2H), 5.89 (s, 1H).

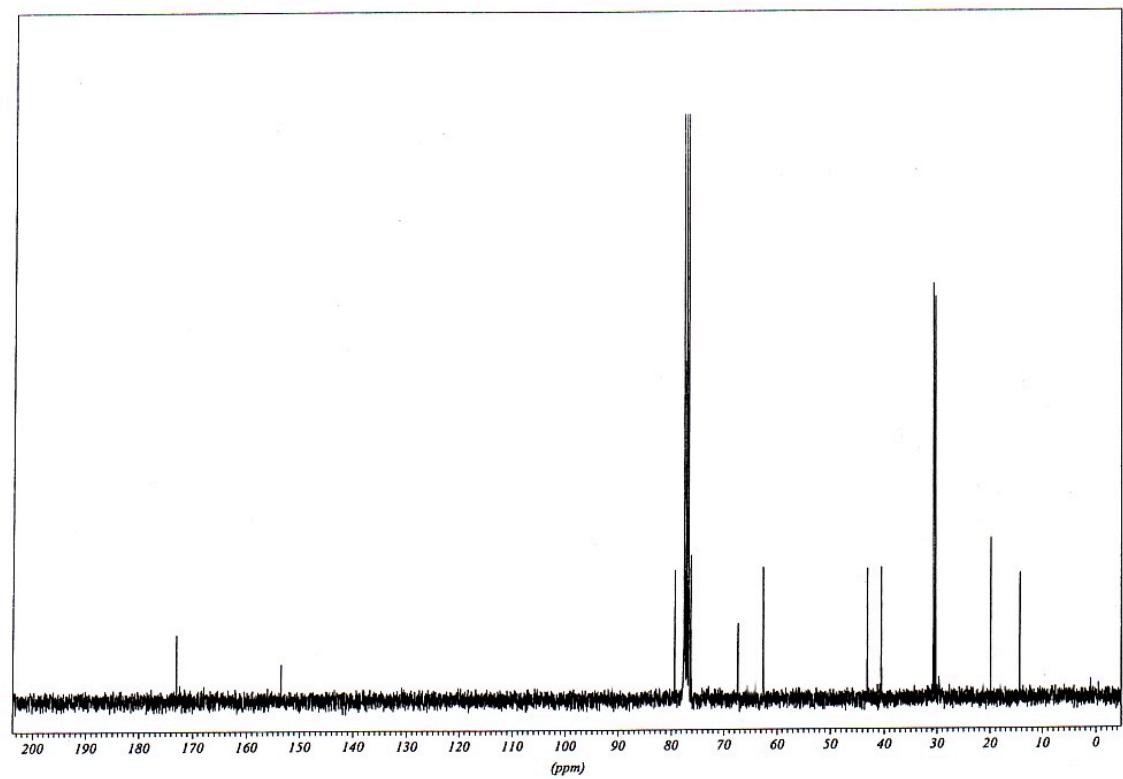
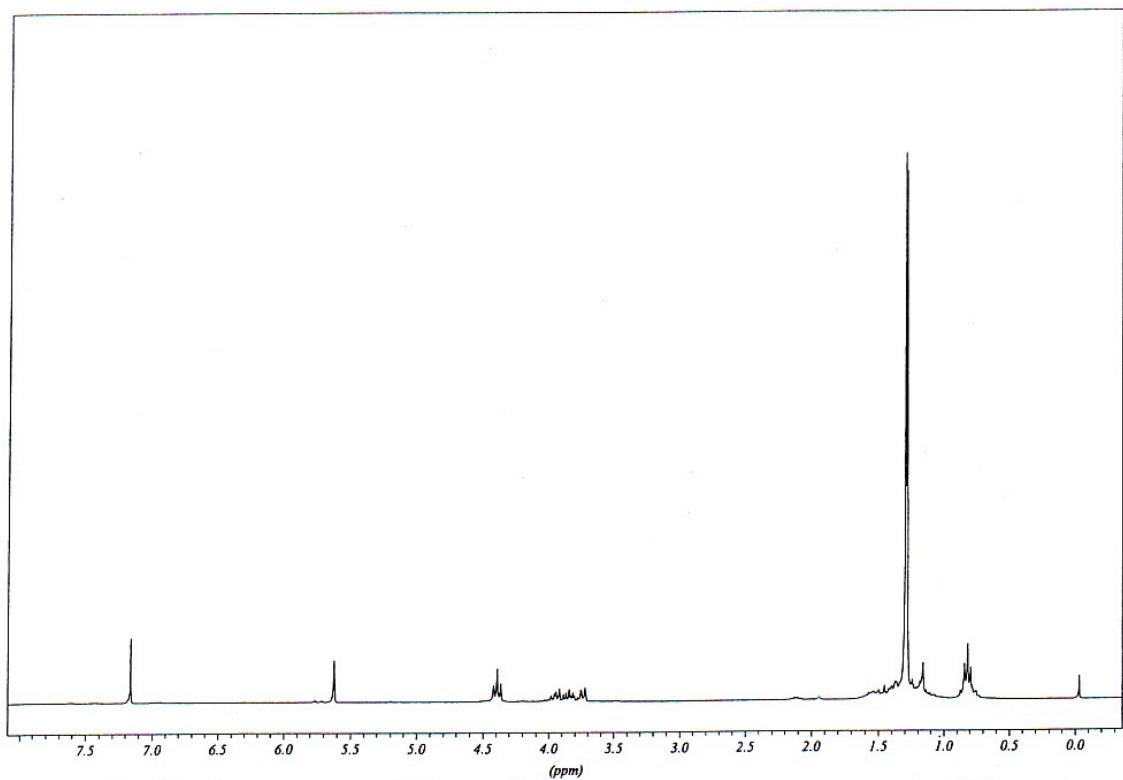
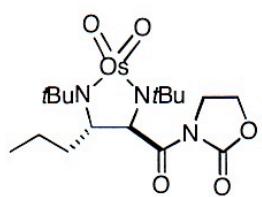
¹³C nmr (CDCl₃, 75 MHz): δ = 29.91, 30.02, 42.80, 52.63, 62.66, 67.20, 67.33, 77.84, 80.08, 153.48, 171.38, 171.44.

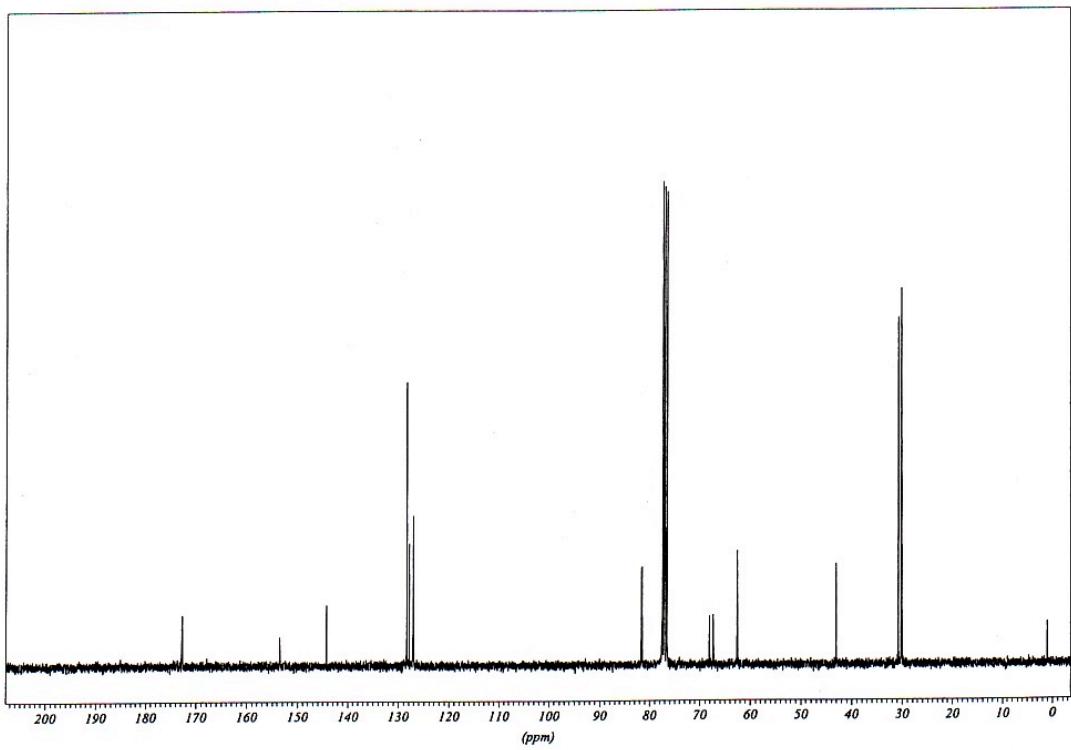
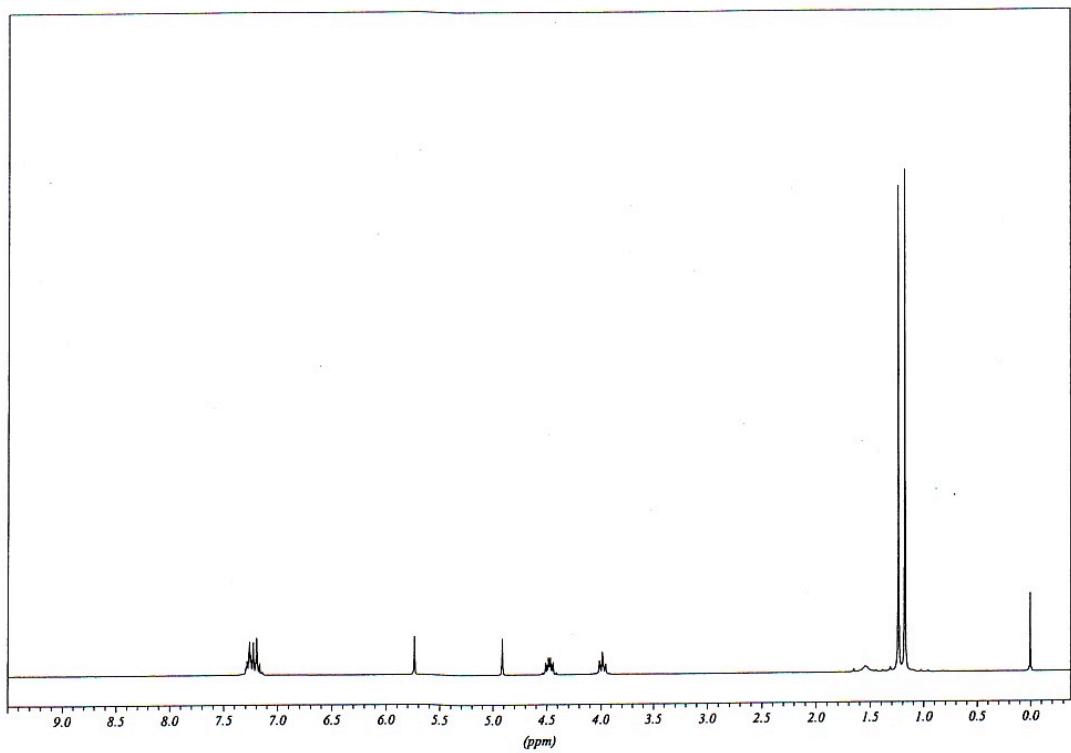
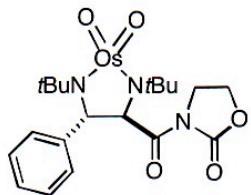
HRMS: Calcd. for C₁₆H₂₇N₃O₇¹⁸⁸Os: 561.1408. Found: 561.1414.

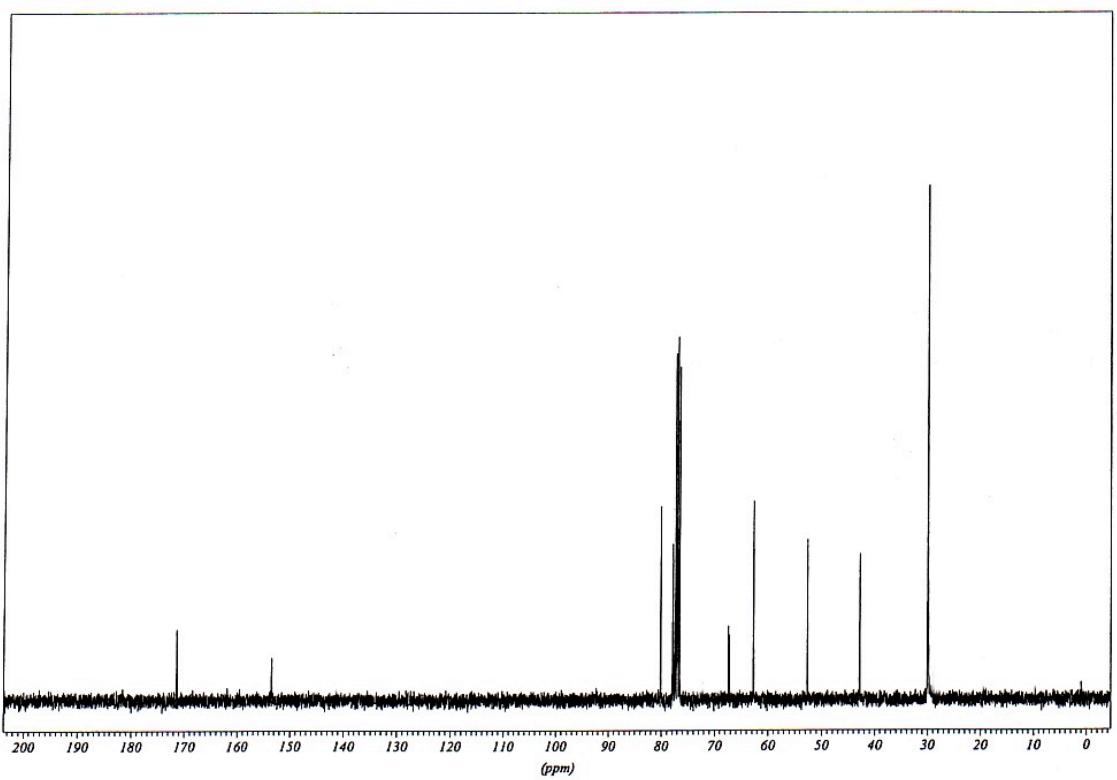
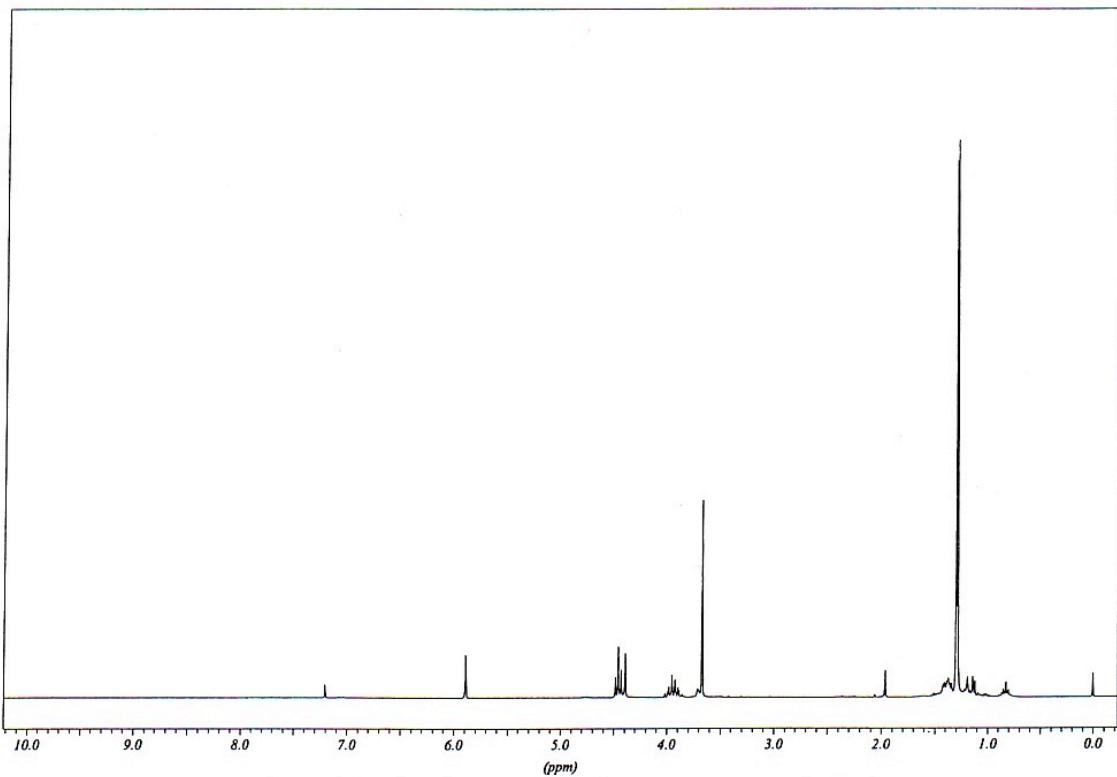
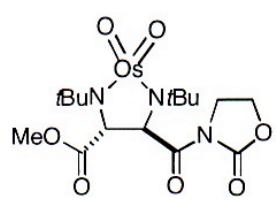
HPLC: Chiralpak AD, n-hexane/ethanol, 90/10 (v/v), 0.5 mL/min. Retention times: 70.4 and 81.8 min.











Elementary cell from solid state structure elucidation of (+)-3:

