

SUPPORTING INFORMATION

for

Diastereoselective synthesis of nitroso acetals from (S,E)- γ -aminated nitroalkenes via multicomponent [4 + 2]/[3 + 2] cycloadditions promoted by LiCl or LiClO₄

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1 EXPERIMENTAL SECTION AND CHARACTERIZATION

Typical procedure 1 - Multicomponent [4 + 2]/[3 + 2] cycloadditions performed without lithium salt solution (Table 1, entry 4).

(1'S,2R,3aR,4R,6S)-4-(1'-N,N-Dibenzylaminoethyl)-6-ethoxy-2-methoxycarbonylperhydro-

isoxazolidino[2,3-*b*]-1,2-oxazine (6a): To a solution of **5a** (85.0 mg, 0.287 mmol) in ethanol (3.75 mL) were added EVE (0.69 mL, ~25 equiv) and methyl acrylate (0.64 mL, ~25 equiv). The reaction mixture was kept in a sealed glass tube at 25 °C and under constant stirring for 20 days. After, the organic solution was evaporated to dryness under reduced pressure at 25 °C and the resulting crude oil was purified rapidly by chromatography on a short silica-gel column using ethyl acetate-hexane (15% v/v) as eluent. A mixture of two diastereoisomers was obtained in 67% yield (d.r. = 1.2:1.0) where **6a** is majority diastereoisomer. Pale yellow oil. $[\alpha]_D^{25} = +27.1^\circ$ (c 1.16, CHCl₃); IR (film) 3061–2804, 1746 (C=O), 1448, 1375, 1221, 1107, 1066, 1026 (N-O), 929, 744 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.34-7.20 (m, 10H), 4.99 (dd, *J* = 9.9, 4.2 Hz, 1H, HC(2)), 4.73 (dd, *J* = 7.9, 7.1 Hz, 1H, HC(6)), 3.91 (dq, *J* = 9.5, 7.1 Hz, 1H), 3.76 (d, *J* = 13.7 Hz, 2H), 3.74 (s, 3H), 3.51 (dq, *J* = 9.5, 7.1 Hz, 1H), 3.32 (d, *J* = 13.7 Hz, 2H), 3.25 (m, 1H, HC(3a)), 2.69 (ddd, *J* = 13.2, 9.5, 6.6 Hz, 1H), 2.55 (ddd, *J* = 13.8, 6.8, 3.3 Hz, 1H), 2.38 (ddd, *J* = 12.2, 7.9, 4.3 Hz, 1H), 2.27 (ddd, *J* = 12.3, 9.6, 9.6 Hz, 1H), 1.75 (m, 1H, HC(4)), 1.55 (ddd, *J* = 13.67, 13.67, 8.38 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.05 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 170.6, 139.4, 128.7, 128.3, 127.0, 100.5, 80.8, 72.0, 63.1, 55.4, 53.8, 52.4, 42.5, 36.7, 29.5, 15.1, 9.8; HRMS (ESI) calcd. for C₂₆H₃₅N₂O₅ [M + H]⁺ 455.2546 found 455.2541.

Typical procedure 2 - Multicomponent [4 + 2]/[3 + 2] cycloadditions promoted by lithium salt solutions (Table 2, entry 5).

(1'S,2R,3aR,4R,6S)-4-(1'-N,N-Dibenzylamino-2'-phenylethyl)-6-ethoxy-2-methoxycarbonylperhydro-isoxazolidino[2,3-b]-1,2-oxazine (7b) and (1'S,2S,3aR,4R,6S)-4-(1'-N,N-dibenzylamino-2'-phenylethyl)-6-ethoxy-2-methoxycarbonylperhydro-isoxazolidino[2,3-b]-1,2-oxazine (7b'): In a sealed glass tube **5b** (154.4 mg, 0.414 mmol) was dissolved in LiClO₄ solution 4.0 M in anhydrous THF (4.13 mL), and EVE (0.99 mL, ~25 equiv) and methyl acrylate (0.93 mL, ~25 equiv) were added under constant stirring. Next, LiClO₄ solution 6.84 M in water (1.26 mL) was slowly dripped into the reaction medium, in order to keep it homogeneous and free from solid particles. The reaction mixture was kept at 25 °C and under constant stirring for 3 days. Afterward, dichloromethane (15 mL) was added to the reaction medium, precipitating the lithium salt in the solution. The heterogenic mixture was filtered and washed with DCM to extract the desired product. The organic solution was reserved and the recovered lithium salt was contained in a round-bottom flask and maintained under reduced pressure at 25 °C for 5 hours. After this procedure the recycled salt could be reused. The reserved organic solution was directly evaporated to dryness under reduced pressure at 25 °C to avoid decomposition. The resulting crude oil was purified carefully by chromatography on a silica-gel column using ethyl acetate-hexane gradient (5–15% v/v) to furnish **7a** (112.0 mg) in 51% yield and **7b** (46.1 mg) in 21% yield. Compound **7b**: Pale yellow oil. $[\alpha]_D^{25} = +100.8^\circ$ (c 1.01, CHCl₃); IR (film) 3084–2802, 1743 (C=O), 1494, 1454, 1209, 1109, 1058, 1028 (N-O), 929 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.36-7.11 (m, 15H), 4.78 (dd, *J* = 10.1, 5.0 Hz, 1H, HC(2)), 4.62 (dd, *J* = 7.9, 6.8 Hz, 1H, HC(6)), 3.89 (m, 1H), 3.86 (d, *J* = 14.0 Hz, 2H), 3.76 (m, 1H, HC(3a)), 3.73 (s, 3H), 3.46 (m, 1H), 3.41 (d, *J* = 13.4 Hz, 2H), 3.21 (dd, *J* = 13.5, 4.2 Hz, 1H), 2.93 (m, 1H), 2.68 (dd, *J* = 13.3, 10.4 Hz, 1H), 2.22 (ddd, *J* = 12.8, 6.4, 2.4 Hz, 1H), 1.88 (ddd, *J* = 13.5, 13.5, 8.4 Hz, 1 H), 1.54 (m, 1H), 1.47 (m, 1H, HC(4)), 1.32 (m, 1H), 1.21 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 170.3, 139.8, 139.3, 129.1-126.2, 100.3, 80.5, 70.5, 63.2, 59.2, 55.5, 52.1, 40.3, 35.1, 31.5, 27.7, 15.0; HRMS (ESI) calcd. for C₃₂H₃₉N₂O₅ [M + H]⁺ 531.2859 found 531.2854. Compound **7b'**: Pale yellow oil. $[\alpha]_D^{25} = +80.2^\circ$ (c 2.33, CHCl₃); IR (film) 3084–2802, 1737 (C=O), 1492, 1454, 1217, 1209, 1105, 1056, 1030 (N-O), 914 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.33-7.13 (m, 15H), 4.63 (dd, *J* = 7.44, 7.21 Hz, 1 H, HC(6)), 4.38 (t, *J* = 8.4 Hz, 1H, HC(2)),

3.93 (m, 1H), 3.85 (d, $J = 13.3$ Hz, 2H), 3.67 (s, 3H), 3.57 (m, 1H, HC(3a)), 3.47 (m, 1H), 3.42 (d, $J = 13.7$ Hz, 2H), 3.22 (dd, $J = 13.6, 4.1$ Hz, 1H), 2.97 (m, 1H), 2.70 (dd, $J = 13.4, 10.0$ Hz, 1H), 2.21 (m, 1H), 1.86 (m, 1H), 1.69 (m, 1H), 1.56 (m, 1H, HC(4)), 1.42 (m, 1H), 1.21 (t, $J = 7.0$ Hz, 3H)); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 171.2, 139.9, 139.5, 129.2-126.3, 100.5, 81.5, 71.1, 63.3, 59.3, 55.5, 52.3, 40.1, 34.0, 31.9, 27.9, 15.0; HRMS (ESI) calcd. for $\text{C}_{32}\text{H}_{39}\text{N}_2\text{O}_5$ $[\text{M} + \text{H}]^+$ 531.2859 found 531.2878.

(1'S,2R,3aR,4R,6S)-4-(1'-N,N-dibenzylamino-3'-methylbutyl)-6-ethoxy-2-methoxycarbonylperhydroisoxazolidino[2,3-b]-1,2-oxazine (9c) and **(1'S,2S,3aR,4R,6S)-4-(1'-N,N-dibenzylamino-3'-methylbutyl)-6-ethoxy-2-methoxycarbonylperhydroisoxazolidino[2,3-b]-1,2-oxazine (9c')**. Nitroalkene **5c** (235.7 mg, 0.696 mmol) was reacted with EVE (1.66 mL, ~25 equiv) and methyl acrylate (1.56 mL, ~25 equiv) for 3 days following the typical procedure 2. Compound **9c**: Yield = 121.0 mg (35%) as pale yellow oil. $[\alpha]_{\text{D}}^{25} = +17.3^\circ$ (c 2.50, CHCl_3); IR (film) 3084–2802, 1743 (C=O), 1493, 1452, 1371, 1111, 1058, 1028 (N-O), 914 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.33-7.19 (m, 10H), 4.93 (dd, $J = 10.0, 4.9$ Hz, 1H, HC(2)), 4.72 (dd, $J = 8.0, 6.7$ Hz, 1 H, HC(6)), 3.92 (dq, $J = 9.6, 7.1$, 1 H), 3.78 (s, 3H), 3.76 (m, 1H, HC(3a)), 3.72 (d, $J = 13.4$ Hz, 2H), 3.48 (dq, $J = 9.6, 7.0$, 1 H), 3.36 (d, $J = 13.4$ Hz, 2H), 2.70 (m, 1H), 2.06 (ddd, $J = 12.9, 6.6, 2.8$ Hz, 1H), 1.87 (m, 2 H), 1.64 (m, 1H, HC(4)), 1.54 (m, 3H), 1.42 (m, 1H), 1.21 (t, $J = 7.1$ Hz, 3H), 0.93 (d, $J = 6.11$ Hz, 3 H); 0.89 (d, $J = 6.11$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 170.4, 139.7, 129.1, 128.3, 126.9, 100.5, 80.6, 70.6, 63.2, 55.3, 54.8, 52.2, 41.0, 35.5, 34.5, 27.9, 25.4, 23.7, 21.9, 15.0. Compound **9c'**: Yield = 65.7 mg (19%). Pale yellow oil. $[\alpha]_{\text{D}}^{25} = +61.2^\circ$ (c 1.50, CHCl_3); IR (film) 3084–2800, 1737 (C=O), 1494, 1454, 1371, 1219, 1109, 1058, 1028 (N-O), 914 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.32-7.21 (m, 10H), 4.70 (dd, $J = 7.9, 6.6$ Hz, 1H, HC(6)), 4.49 (dd, $J = 9.0, 7.1$ Hz, 1H, HC(2)), 3.93 (dq, $J = 9.7, 7.1$ Hz, 1H), 3.75 (s, 3H), 3.71 (d, $J = 13.5$ Hz, 2H), 3.63 (m, 1H, HC(3a)), 3.47 (dq, $J = 9.7, 7.1$ Hz, 1H), 3.37 (d, $J = 13.5$ Hz, 2H), 2.71 (m, 1H), 2.04 (ddd, $J = 12.7, 6.5, 2.4$ Hz, 1H), 1.98 (m, 1H), 1.81 (m, 1H), 1.69 (m, 1H, HC(4)), 1.56 (m, 3H), 1.42 (m, 1H), 1.21 (t, $J = 7.1$ Hz, 3H), 0.92 (d, $J = 5.1$ Hz, 3H), 0.91 (d, $J = 5.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 171.5, 139.9, 129.2-127.1, 100.6, 81.5, 71.3, 63.4, 55.4, 54.9, 52.4, 40.7, 34.8, 34.1, 28.1, 25.5, 23.8, 22.0, 15.0; HRMS (ESI) calcd. for $\text{C}_{29}\text{H}_{41}\text{N}_2\text{O}_5$ $[\text{M} + \text{H}]^+$ 497.3015 found 497.3012.

(1'S,2S,3aR,4R,6S)-4-(1'-N,N-dibenzylaminoethyl)-2-cyano-6-ethoxyperhydroisoxazolidino[2,3-b]-1,2-oxazine (10a'). Nitroalkene **5a** (141.9 mg, 0.479 mmol) was reacted with EVE (1.15 mL, ~25 equiv) and acrylonitrile (0.79 mL, ~25 equiv) for 1 day following the typical procedure 2. Yield = 63.2 mg (31%) as a yellow pale oil. $[\alpha]_D^{25} = +49.4^\circ$ (*c* 1.55, CHCl₃); IR (film) 3061–2804, 1492, 1452, 1377, 1211, 1107, 1057, 1022 (N-O), 914 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.34-7.21 (m, 10H), 4.81 (m, 2H, HC(6,2)), 3.95 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.75 (d, *J* = 13.7 Hz, 2H), 3.56 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.32 (d, *J* = 13.5 Hz, 2H), 3.23 (m, 1H, HC(3a)), 2.70 (m, 1H), 2.52 (m, 2H), 2.32 (ddd, *J* = 12.3, 9.1, 6.6 Hz, 1H), 1.83 (m, 1H, HC(4)), 1.55 (*J* = 13.7, 13.7, 8.4 Hz, 1H), 1.26 (t, 6.9 Hz, 3H), 1.05 (d, 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 139.3, 128.8-127.1, 118.6, 100.7, 72.9, 68.8, 63.6, 55.0, 54.0, 42.8, 38.4, 29.3, 15.0, 9.9; HRMS (ESI) calcd. for C₂₅H₃₂N₃O₃ [M + H]⁺ 422.24437 found 422.2437.

(1'S,2R,3aR,4R,6S)-4-(1'-N,N-dibenzylamino-2'-phenylethyl)-2-cyano-6-ethoxyperhydroisoxazolidino[2,3-b]-1,2-oxazine (11b). Nitroalkene **5b** (132.0 mg, 0.354 mmol) was reacted with EVE (0.84 mL, ~25 equiv) and acrylonitrile (0.58 mL, ~25 equiv) for 3 days following the typical procedure 2. Yield = 52.9 mg (30%). White crystalline solid. Mp = 183–185 °C. For X-ray experiments only 10 mg of the purified material was recrystallized in DCM in a small assay tube, which was kept in a closed flask containing pentane for 7 days at 15 °C. $[\alpha]_D^{25} = +75.5^\circ$ (*c* 1.78, CHCl₃); IR (film) 3086–2806, 1494, 1452, 1371, 1271, 1217, 1107, 1078, 1030 (N-O), 933 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ ppm 7.41-7.13 (m, 15H), 4.83 (dd, *J* = 9.8, 4.9 Hz, 1H, HC(2)), 4.58 (dd, *J* = 8.3, 6.6 Hz, 1H, HC(6)), 3.86 (m, 4H, HC(3a), NCH₂-Ph, CH₃HC(O)), 3.44 (m, 1H), 3.43 (d, *J* = 13.5 Hz, 2H), 3.25 (dd, *J* = 13.2, 3.9 Hz, 1H), 2.92 (ddd, *J* = 10.76, 3.91, 1 H), 2.70 (dd, *J* = 13.3, 10.9 Hz, 1H), 2.19 (ddd, *J* = 13.0, 6.5, 2.6 Hz, 1H), 1.88 (ddd, *J* = 13.6, 13.6, 8.4 Hz, 1H), 1.48 (ddd, *J* = 12.04, 9.38, 9.38 Hz, 1 H), 1.38 (m, 1H, HC(4)), 1.26 (ddd, *J* = 12.4, 8.4, 4.9 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ ppm 139.7, 139.2, 129.2-126.5, 116.6, 100.7, 71.4, 69.0, 63.7, 58.8, 55.8, 40.0, 36.0, 31.4, 27.2, 15.0; HRMS (ESI) calcd. for C₃₁H₃₆N₃O₃ [M + H]⁺ 498.2757 found 498.2748

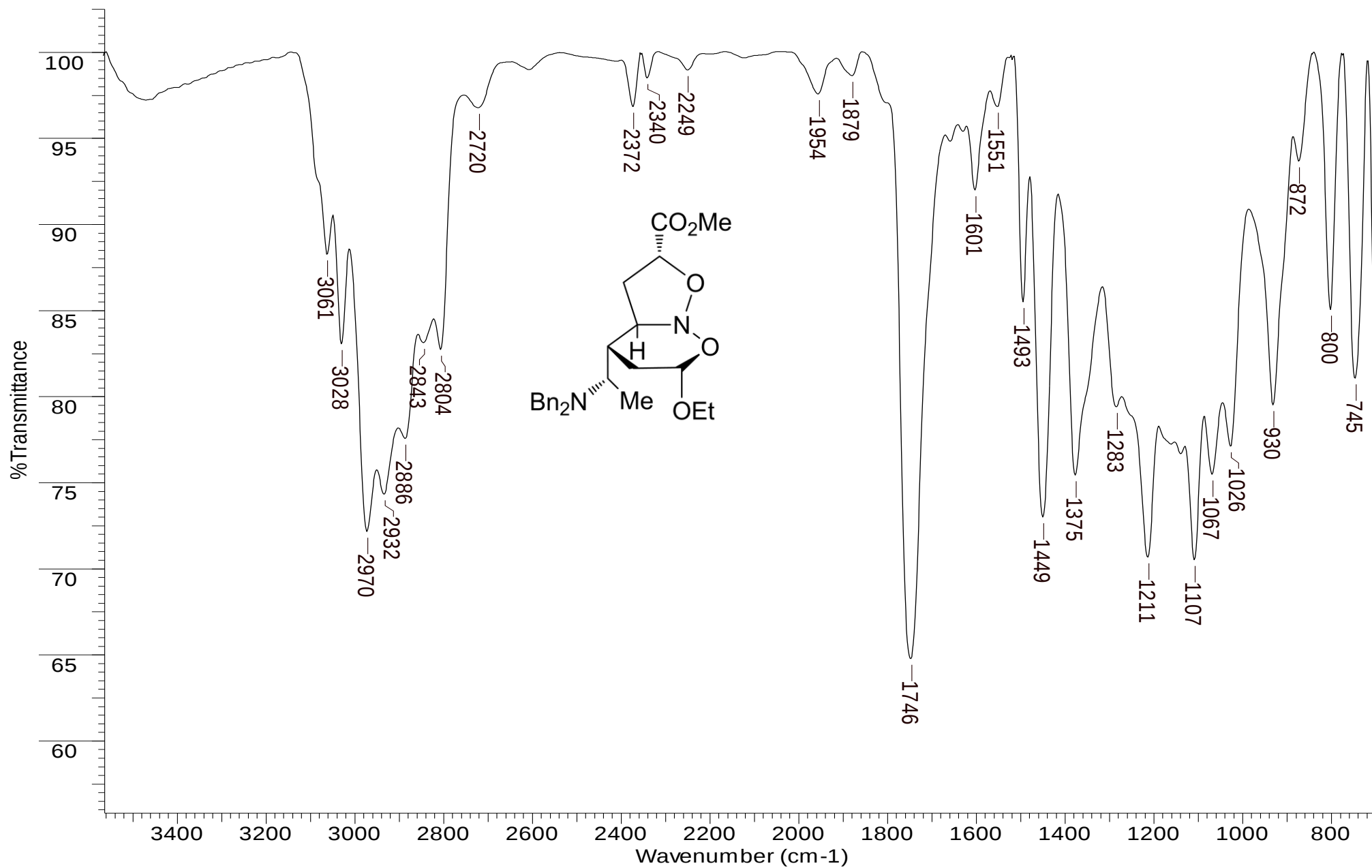
(1'S,2R,3aR,4R,6S)-2-acetyl-4-(1'-N,N-dibenzylamino-2'-phenylethyl)-6-ethoxyperhydroisoxazolidino[2,3-b]-1,2-oxazine (12b) and **(1'S,2S,3aR,4R,6S)-2-acetyl-4-(1'-N,N-dibenzylamino-2'-phenylethyl)-6-ethoxyperhydroisoxazolidino[2,3-b]-1,2-oxazine (12b')**. Nitroalkene **5b** (117.8 mg, 0.316 mmol) was

reacted with EVE (0.75 mL, ~25 equiv) and methyl vinyl ketone (0.65 mL, ~25 equiv) for 3 days following the typical procedure 2. Compound **12b**: Yield = 30.0 mg (18%) as pale yellow oil. $[\alpha]_{\text{D}}^{25} = +41.2^{\circ}$ (*c* 1.65, CHCl₃); IR (film) 3082–2804, 1720 (C=O), 1492, 1454, 1357, 1107, 1058, 1033 (N-O), 923 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.37-7.13 (m, 15H), 4.64 (dd, *J* = 8.0, 6.7 Hz, 1H, HC(6)), 4.61 (dd, *J* = 10.5, 5.6 Hz, 1H, HC(2)), 3.91 (m, 1H), 3.87 (d, *J* = 13.9 Hz, 2H), 3.54 (m, 1H, HC(3a)), 3.47 (ddd, *J* = 7.1, 7.1, 2.4 Hz, 1H), 3.42 (d, *J* = 13.5 Hz, 2H), 3.25 (dd, *J* = 13.5, 3.7 Hz, 1H), 2.93 (ddd, *J* = 10.7, 3.9, 3.7 Hz, 1H), 2.69 (dd, *J* = 13.5, 10.8 Hz, 1H), 2.22 (ddd, *J* = 12.84, 6.23, 2.98 Hz, 1H), 2.06 (s, 3H), 1.86 (m, 1H), 1.47 (m, 1H, HC(4)), 1.42 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.10 (ddd, *J* = 12.2, 8.8, 5.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 207.0, 139.8, 139.4, 129.2-126.4, 100.4, 87.2, 70.7, 63.5, 59.3, 55.7, 40.3, 34.6, 31.6, 27.6, 26.2, 15.0; HRMS (ESI) calcd. for C₃₂H₃₉N₂O₄ [M + H]⁺ 515.2909 found 515.2912. Compound **12b'**: Yield = 57.7 mg (35%). Pale yellow oil. $[\alpha]_{\text{D}}^{25} = +57.8^{\circ}$ (*c* 1.60, CHCl₃); IR (film) 3061-2804, 1716 (C=O), 1492, 1452, 1357, 1109, 1064, 1039 (N-O), 920 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.32-7.13 (m, 15H), 4.56 (dd, *J* = 8.3, 6.5 Hz, 1H, HC(6)), 4.28 (dd, *J* = 9.7, 6.4 Hz, 1H, HC(2)), 3.86 (m, 1H), 3.84 (d, *J* = 12.6 Hz, 2H), 3.55 (m, 1H, HC(3a)), 3.46 (m, 1H), 3.41 (d, *J* = 13.4 Hz, 2H), 3.21 (dd, *J* = 13.8, 4.7 Hz, 1H), 2.98 (ddd, *J* = 9.54, 4.82, Hz, 1H), 2.68 (dd, *J* = 13.7, 9.7 Hz, 1H), 2.23 (s, 3H), 2.20 (m, 1H), 1.84 (ddd, *J* = 13.5, 13.5, 8.3 Hz, 1H), 1.58 (ddd, *J* = 12.0, 9.0, 6.5 Hz, 1H), 1.49 (m, 1H, HC(4)), 1.42 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 209.1, 139.8, 139.4, 129.3-126.2, 100.5, 88.6, 71.2, 63.4, 59.3, 55.5, 40.5, 32.6, 32.1, 27.9, 26.8, 15.0; HRMS (ESI) calcd. for C₃₂H₃₉N₂O₄ [M + H]⁺ 515.2909 found 515.2903

(1'S,2R,3aR,4R,6S)-2-acetyl-4-(1'-N,N-dibenzylamino-3'-methylbutyl)-6-ethoxyperhydroisoxazolidino[2,3-b]-1,2-oxazine (13c) and **(1'S,2S,3aR,4R,6S)-2-acetyl-4-(1'-N,N-dibenzylamino-3'-methylbutyl)-6-ethoxyperhydroisoxazolidino[2,3-b]-1,2-oxazine (13c')**. Nitroalkene **5c** (211.2 mg, 0.624 mmol) was reacted with EVE (1.50 mL, ~25 equiv) and methyl vinyl ketone (1.30 mL, ~25 equiv) for 2 days following the typical procedure 2. Compound **13c**: Yield = 20.5 mg, (7%) as a pale yellow oil. $[\alpha]_{\text{D}}^{25} = +35.9^{\circ}$ (*c* 1.58, CHCl₃); IR (film) 3084–2802, 1720 (C=O), 1494, 1454, 1357, 1109, 1028 (N-O), 920 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.31-7.21 (m, 10H), 4.77 (dd, *J* = 10.4, 5.7 Hz, 1H, HC(2)), 4.73 (dd, *J* = 7.9, 6.8 Hz, 1H, HC(6)), 3.94 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.72 (d, *J* = 13.2 Hz, 2H), 3.63 (m, 1H, HC(3a)), 3.50 (dq, *J* =

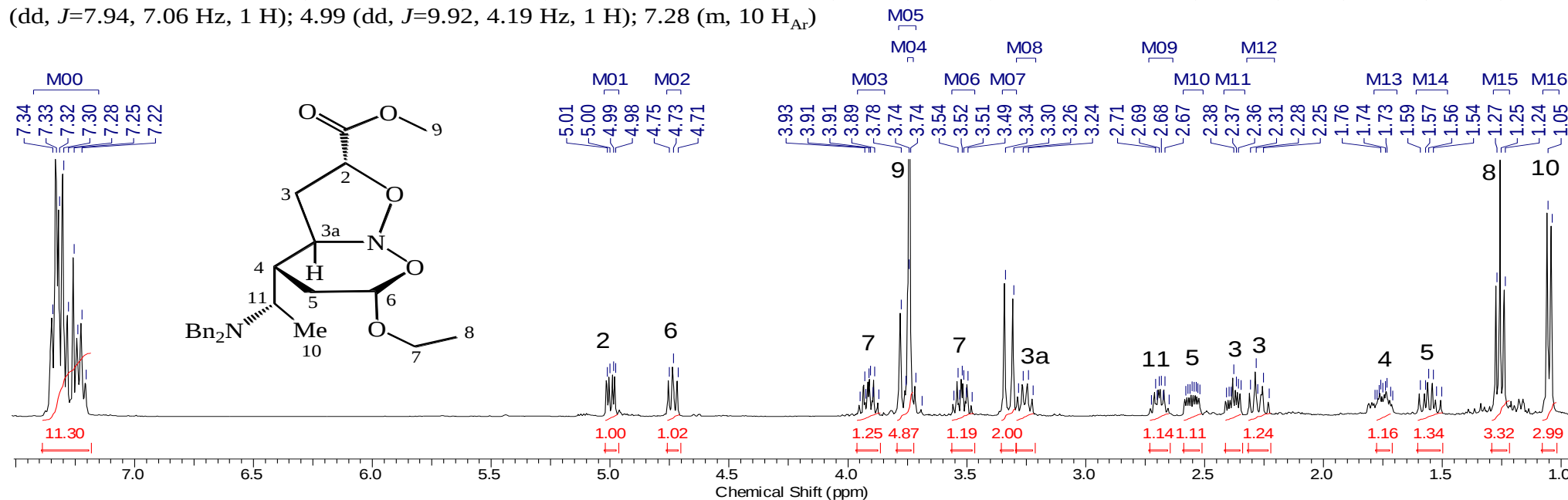
9.7, 7.1 Hz, 1H), 3.33 (d, $J = 13.5$ Hz, 2H), 2.70 (m, 1H), 2.14 (s, 3H), 2.06 (ddd, $J = 12.8, 6.7, 2.5$ Hz, 1H), 1.85 (m, 1H), 1.78 (m, 1H), 1.61 (m, 1H, HC(4)), 1.51 (m, 3H), 1.27 (m, 1H), 1.23 (t, $J = 7.2$ Hz, 3H), 0.97 (d, $J = 6.0$ Hz, 3H), 0.92 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 207.1, 139.8, 129.3-127.2, 100.6, 87.2, 70.8, 63.6, 55.5, 54.6, 41.2, 35.0, 34.3, 27.7, 26.4, 25.6, 24.0, 21.8, 15.0; HRMS (ESI) calcd. for $\text{C}_{29}\text{H}_{41}\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$ 481.3066 found 481.3057. Compound **13c'**: Yield = 80.3 mg (27%). Pale yellow oil. $[\alpha]_{\text{D}}^{25} = +44.4^\circ$ (c 1.99, CHCl_3); IR (film) 3084–2800, 1720, (C=O), 1494, 1454, 1355, 1111, 1028 (N-O), 916 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.31-7.21 (m, 10H), 4.65 (t, $J = 7.7$ Hz, 1H, HC(6)), 4.37 (dd, $J = 9.7, 6.0$ Hz, 1H, HC(2)), 3.88 (dq, $J = 9.6, 7.1$ Hz, 1H), 3.70 (d, $J = 13.2$, 2H), 3.61 (q, $J = 8.4$ Hz, 1H, HC(3a)), 3.47 (m, 1H), 3.37 (d, $J = 13.5$, 2H), 2.70 (ddd, $J = 8.9, 4.2, 3.8$ Hz, 1H), 2.31 (s, 3H), 2.02 (ddd, $J = 12.7, 6.4, 2.7$ Hz, 1H), 1.88 (ddd, $J = 12.0, 8.5, 6.2$ Hz, 1H), 1.79 (m, 1H), 1.61 (m, 1H, HC(4)), 1.52 (m, 3H), 1.40 (m, 1H), 1.23 (t, $J = 7.1$ Hz, 3H), 0.91 (d, $J = 5.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 209.2, 139.8, 129.2, 128.2, 127.0, 100.6, 88.6, 71.3, 63.4, 55.3, 54.9, 40.9, 34.8, 32.6, 28.0, 26.8, 25.4, 23.7, 22.0, 15.0

(1'S,2R,7R,7aR)-7-(1'-N,N-dibenzylamino-3'-methylbutyl)-2-hydroxypyrrolizin-3-one (14c). To a solution of **9c** (39.6 mg, 0.079 mmol) in MeOH (9.5 mL) was added a slurry of Raney Ni (previously activated to level W-2 and washed with water and subsequently with MeOH) (151 mg in 3.0 mL of MeOH). This mixture was shaken at room temperature under an atmosphere of H_2 (70 PSI) for 48 h, filtered through a short column of Celite eluted with MeOH (15 mL), concentrated in vacuum, and purified by silica gel chromatography eluted with EtOAc to afford **14c** (16.2 mg) in 50% yield as a pale yellow oil. $[\alpha]_{\text{D}}^{25} = +27.6^\circ$ (c 0.7, CHCl_3); IR (film) 3370 (O-H), 3084–3026, 2924-2803, 2363, 2340, 1686 (C=O), 1454, 1115, 1028, 962 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.29 (m, 10 H), 4.46 (dd, $J = 10.37, 7.63$ Hz, 1 H, HC(2)), 3.70 (d, $J = 13.69$ Hz, 2 H), 3.48 (d, $J = 13.69$ Hz, 2 H), 3.43 (m, 2 H, HC(7a), $\text{HCH}(5)$), 3.15 (dd, $J = 10.96, 9.78$ Hz, 1 H), 2.65 (ddd, $J = 6.95, 4.89$ Hz, 1 H), 2.43 (m, 1 H), 2.26 (ddd, $J = 11.74, 7.82, 5.87$ Hz, 1 H), 1.89 (m, 1 H), 1.80 (m, 1 H, HC(7)), 1.67 (m, 1 H), 1.62 (m, 1 H), 1.52 (ddd, $J = 11.93, 10.56, 8.80$ Hz, 1 H), 1.18 (ddd, $J = 13.30, 7.24, 5.67$ Hz, 1 H), 0.91 (d, $J = 6.26$ Hz, 3 H), 0.86 (d, $J = 6.26$ Hz, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 173.9, 139.9, 129.0, 128.2, 127.1, 73.1, 59.3, 55.9, 54.7, 49.8, 40.6, 38.1, 37.9, 31.0, 25.7, 23.2, 22.7; HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{35}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 407.2699 found 407.2701.

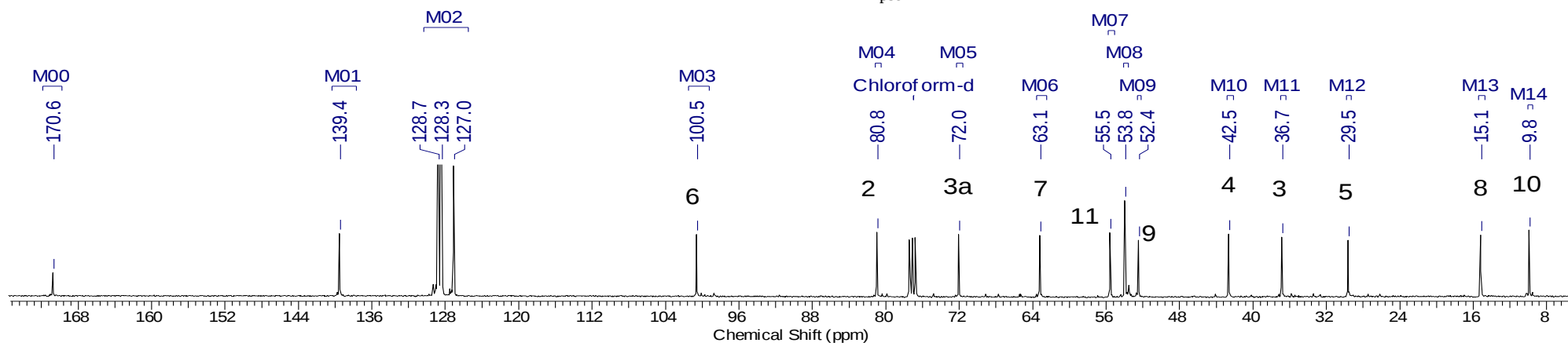


Spectrum 1 – Infrared of **6a**

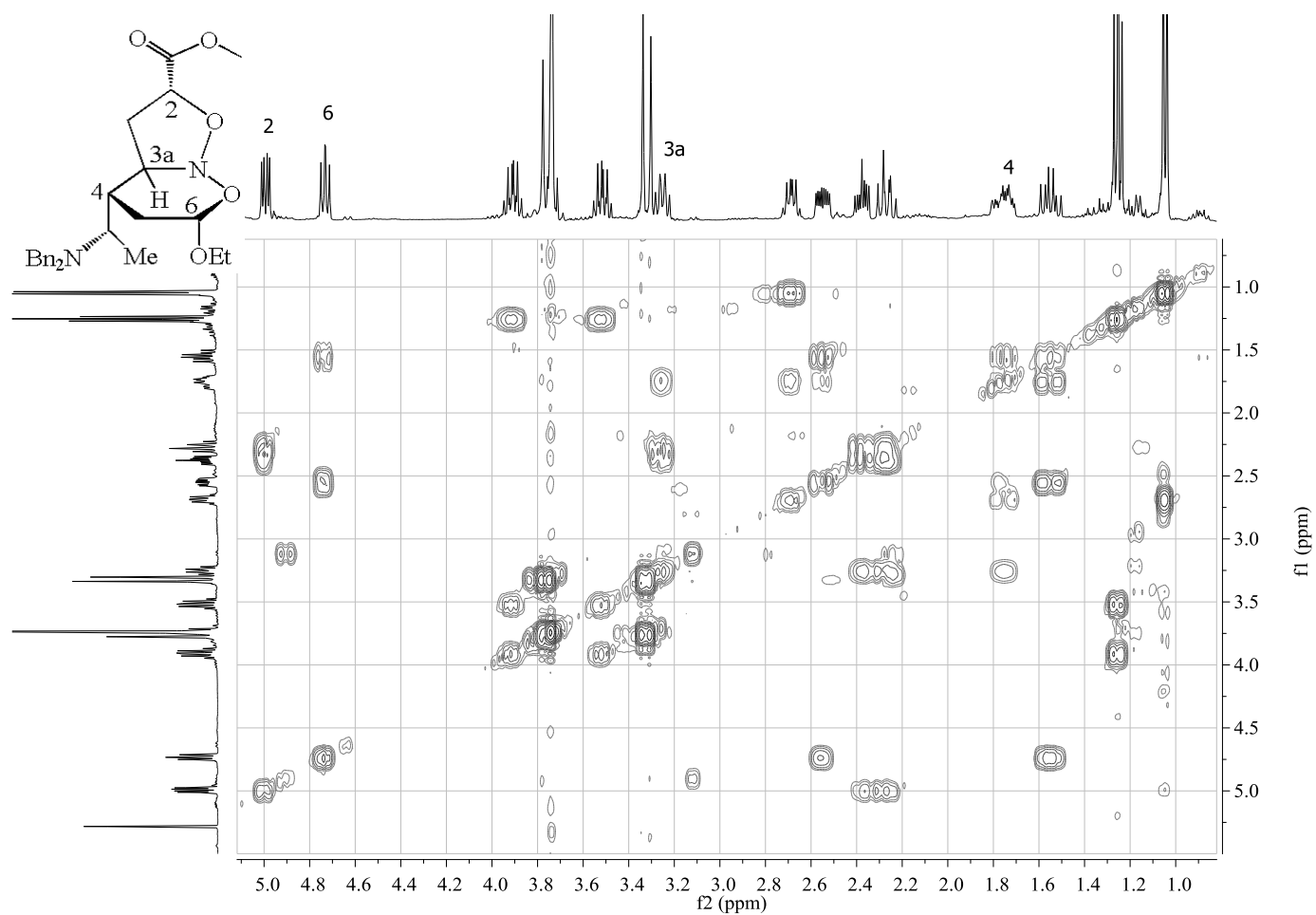
^1H NMR (400 MHz, CHCl_3 - d) δ ppm 1.05 (d, $J=6.62$ Hz, 3 H); 1.25 (t, $J=7.06$ Hz, 3 H); 1.55 (ddd, $J=13.67, 13.67, 8.38$ Hz, 1 H); 1.75 (m, 1 H); 2.27 (ddd, $J=12.29, 9.62, 9.62$ Hz, 1 H); 2.38 (ddd, $J=12.18, 7.99, 4.30$ Hz, 1 H); 2.55 (ddd, $J=13.84, 6.67, 3.31$ Hz, 1 H); 2.69 (ddd, $J=13.18, 9.54, 6.62$ Hz, 1 H); 3.25 (m, 1 H); 3.32 (d, $J=13.67$ Hz, 2 H); 3.52 (m, 1 H); 3.76 (d, $J=13.67$ Hz, 2 H); 3.74 (s, 3 H); 3.91 (m, 1 H); 4.73 (dd, $J=7.94, 7.06$ Hz, 1 H); 4.99 (dd, $J=9.92, 4.19$ Hz, 1 H); 7.28 (m, 10 H_{Ar})



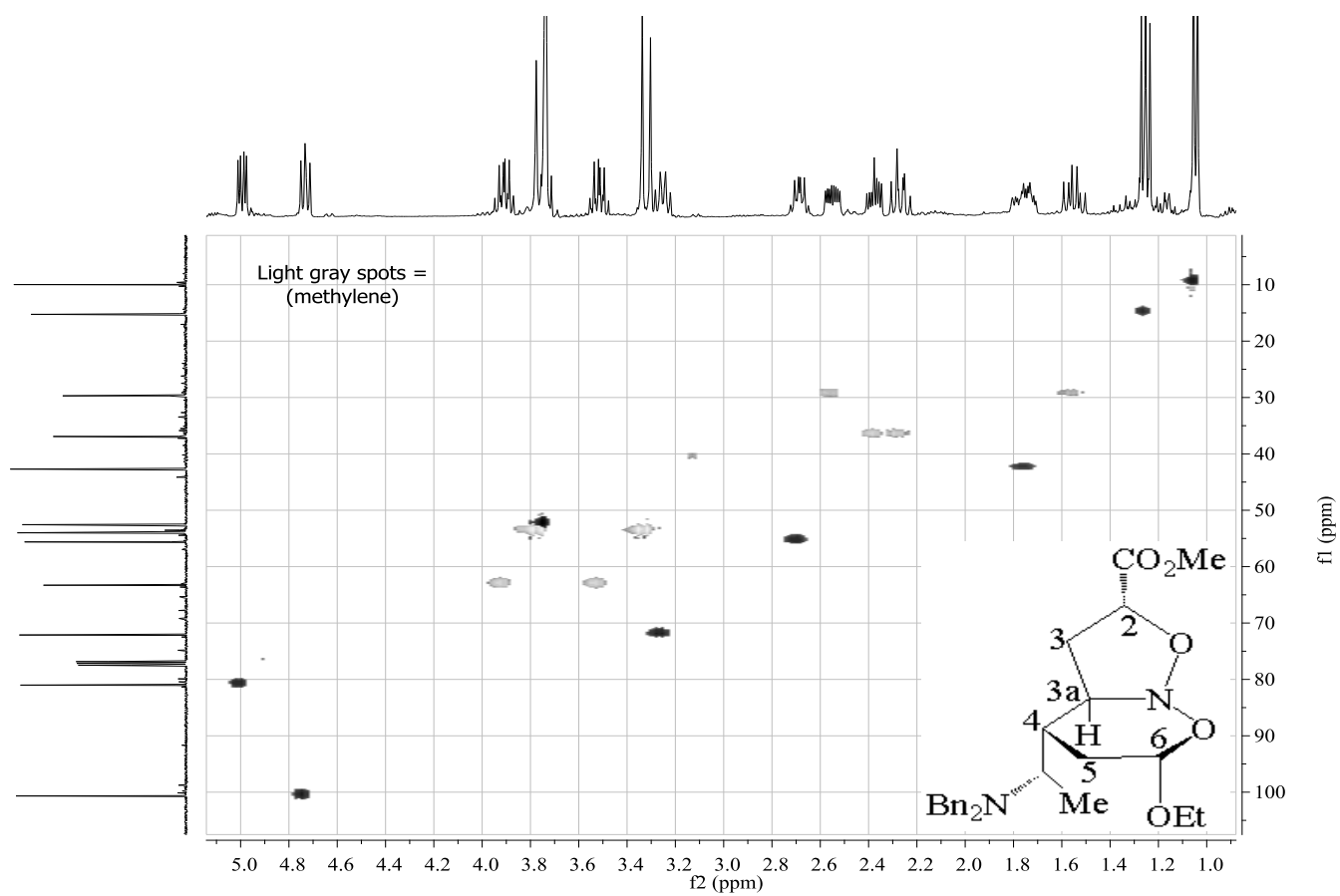
^{13}C NMR (101 MHz, CHCl_3 - d) δ ppm 9.8 (CH_3) 15.1 (CH_3) 29.5 (CH_2) 36.7 (CH_2) 42.5 (CH) 52.4 (CH_3) 53.8 (2x CH_2) 55.5 (CH) 63.1 (CH_2) 72.0 (CH) 80.8 (CH) 100.5 (CH) 127.0-128.7 (10x CH_{Ar}) 139.4 (2x C_{ipso}) 170.6 ($\text{C}=\text{O}$)



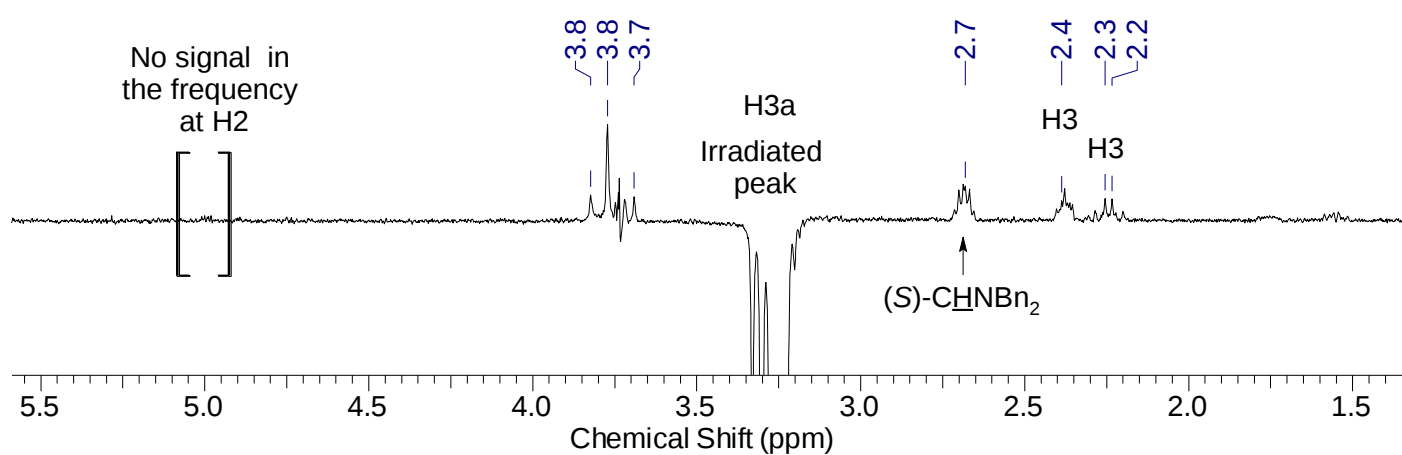
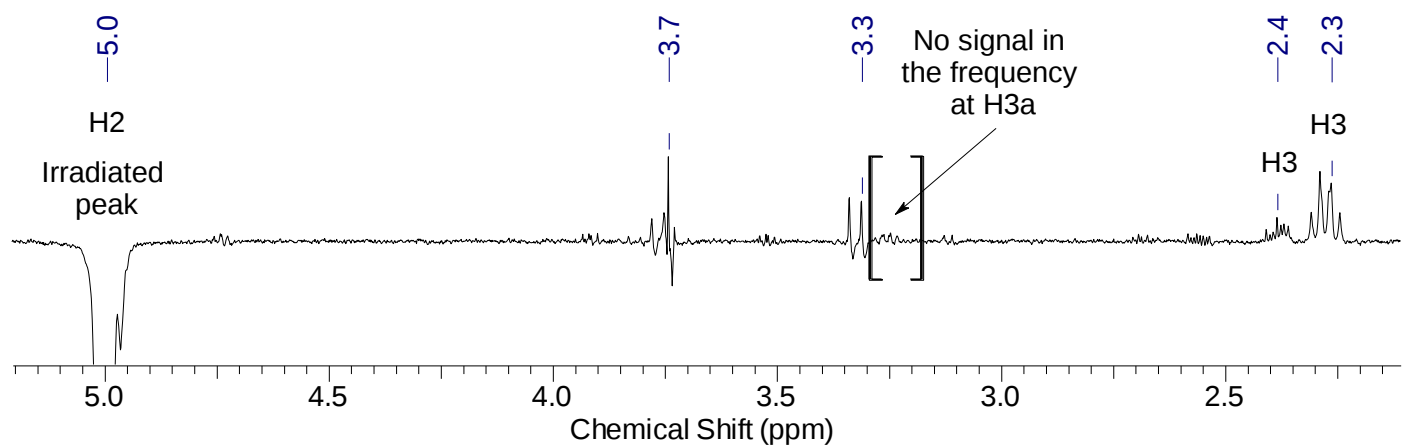
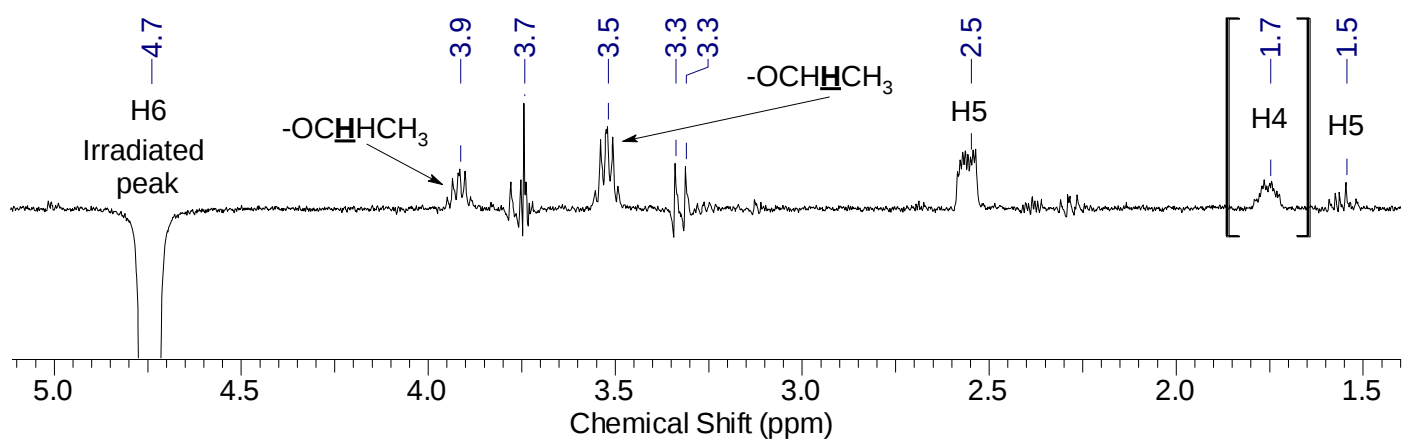
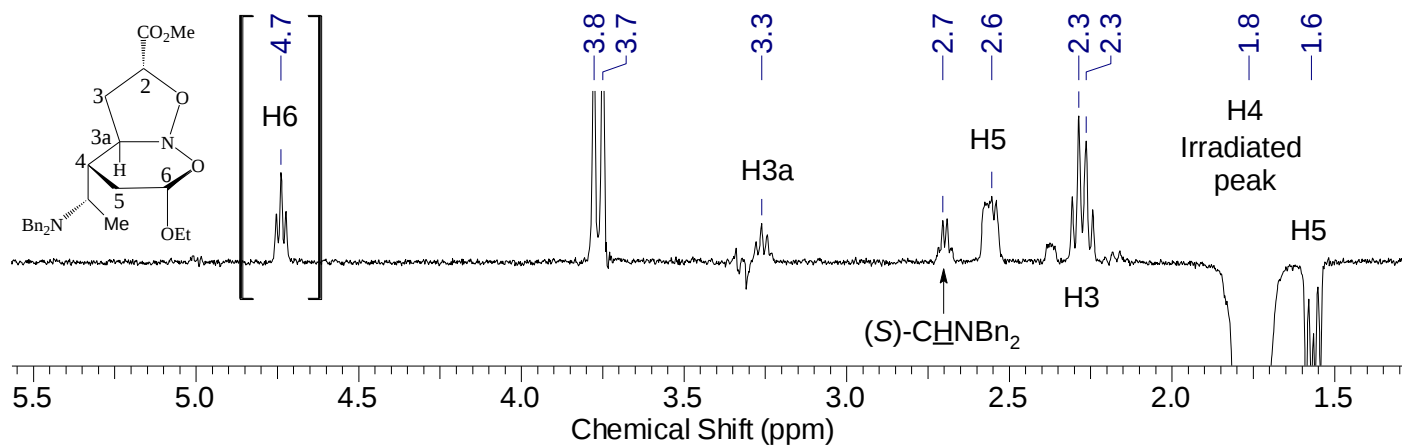
Spectrum 2 – ^1H and ^{13}C NMR of **6a**



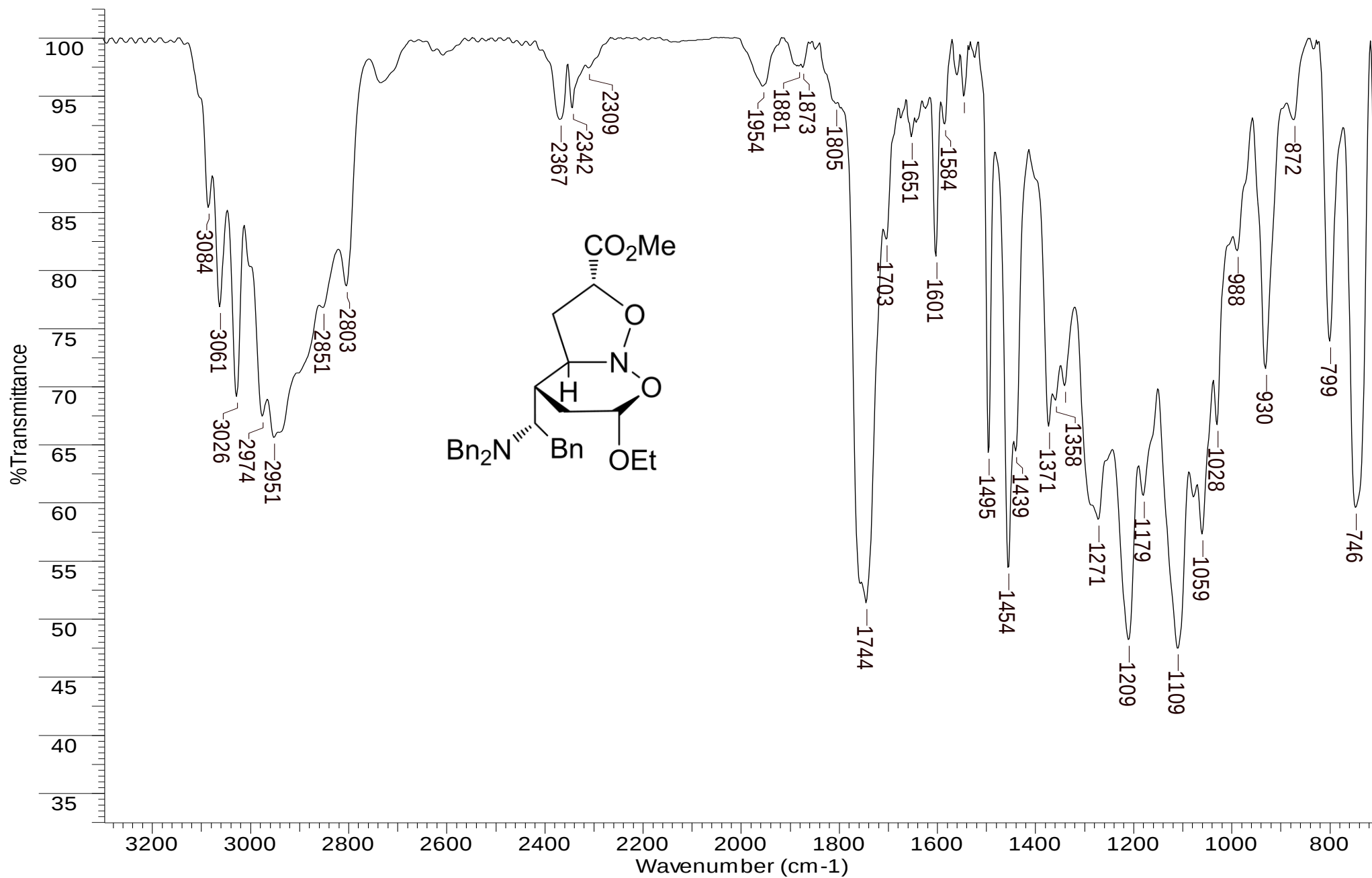
Spectrum 3 – 2D COSY of **6a**



Spectrum 4 – HSQC of **6a**

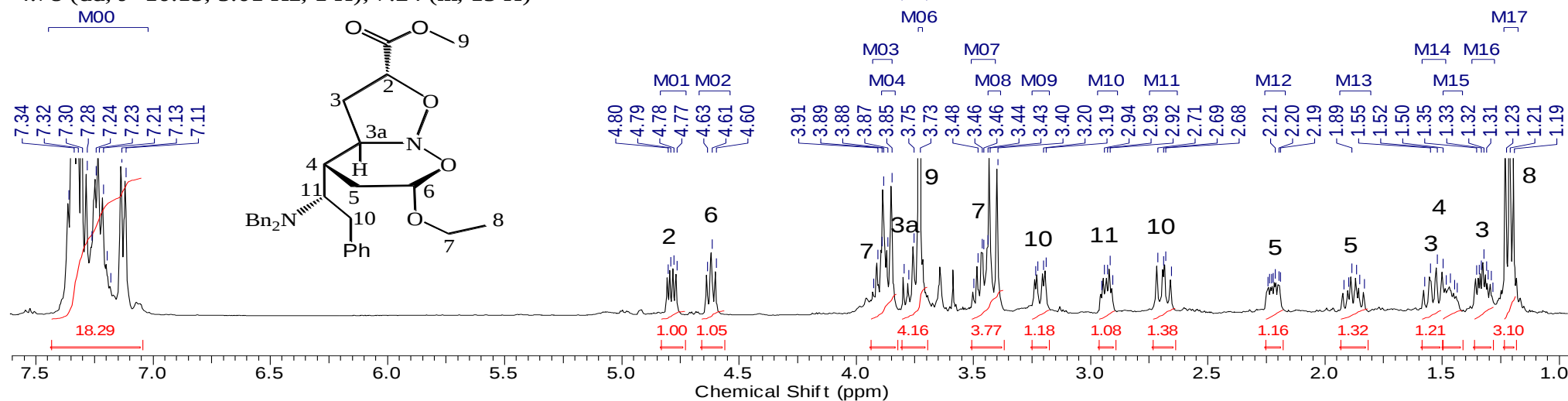


Spectrum 5 – 2D NOESY of **6a**

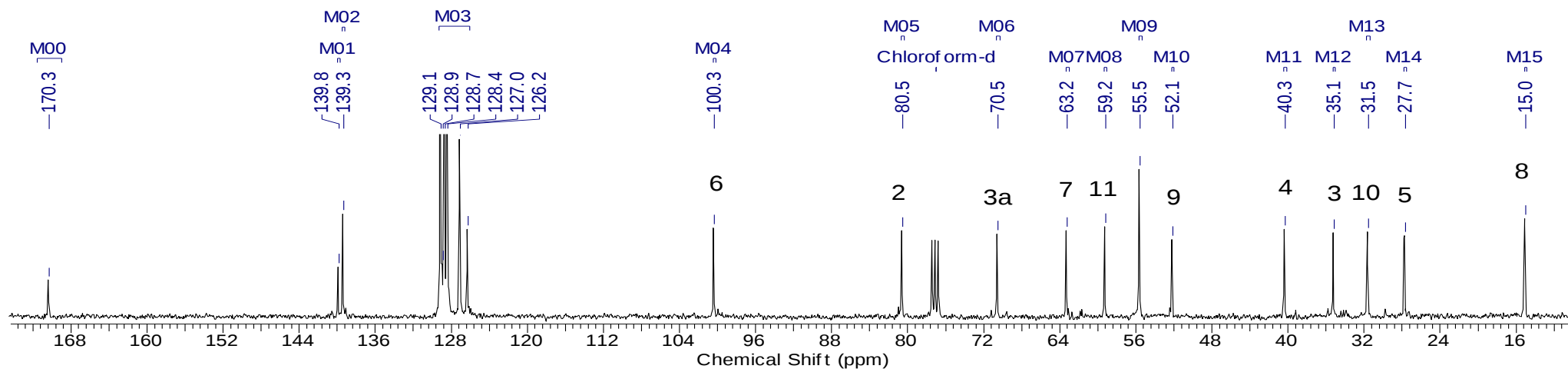


Spectrum 6 – Infrared of **7b**

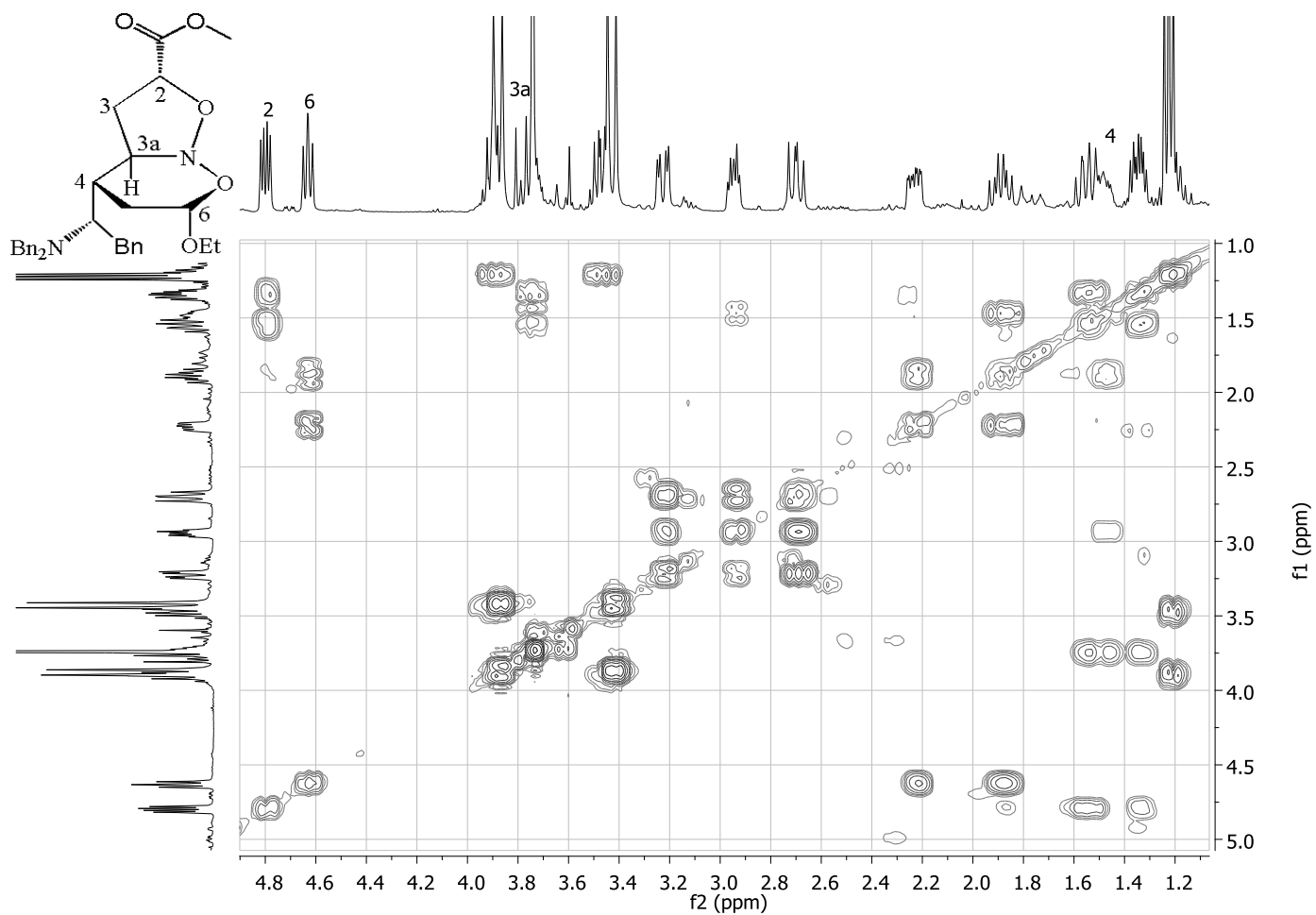
^1H NMR (400 MHz, CHLOROFORM-D) δ ppm 1.21 (t, $J=7.03$ Hz, 3 H); 1.32 (m, 1 H); 1.47 (m, 1 H); 1.54 (m, 1 H); 1.88 (ddd, $J=13.51$, 13.51, 8.44 Hz, 1 H); 2.22 (ddd, $J=12.81$, 6.45, 2.38 Hz, 1 H); 2.68 (dd, $J=13.33$, 10.39 Hz, 1 H); 2.93 (m, 1 H); 3.21 (dd, $J=13.51$, 4.22 Hz, 1 H); 3.41 (d, $J=13.45$ Hz, 2 H); 3.46 (m, 1 H); 3.76 (m, 1 H); 3.73 (s, 3 H); 3.86 (d, $J=14.06$ Hz, 2 H); 3.89 (m, 1 H); 4.62 (dd, $J = 7.95$, 6.85 Hz, 1 H); 4.78 (dd, $J=10.15$, 5.01 Hz, 1 H); 7.24 (m, 15 H)



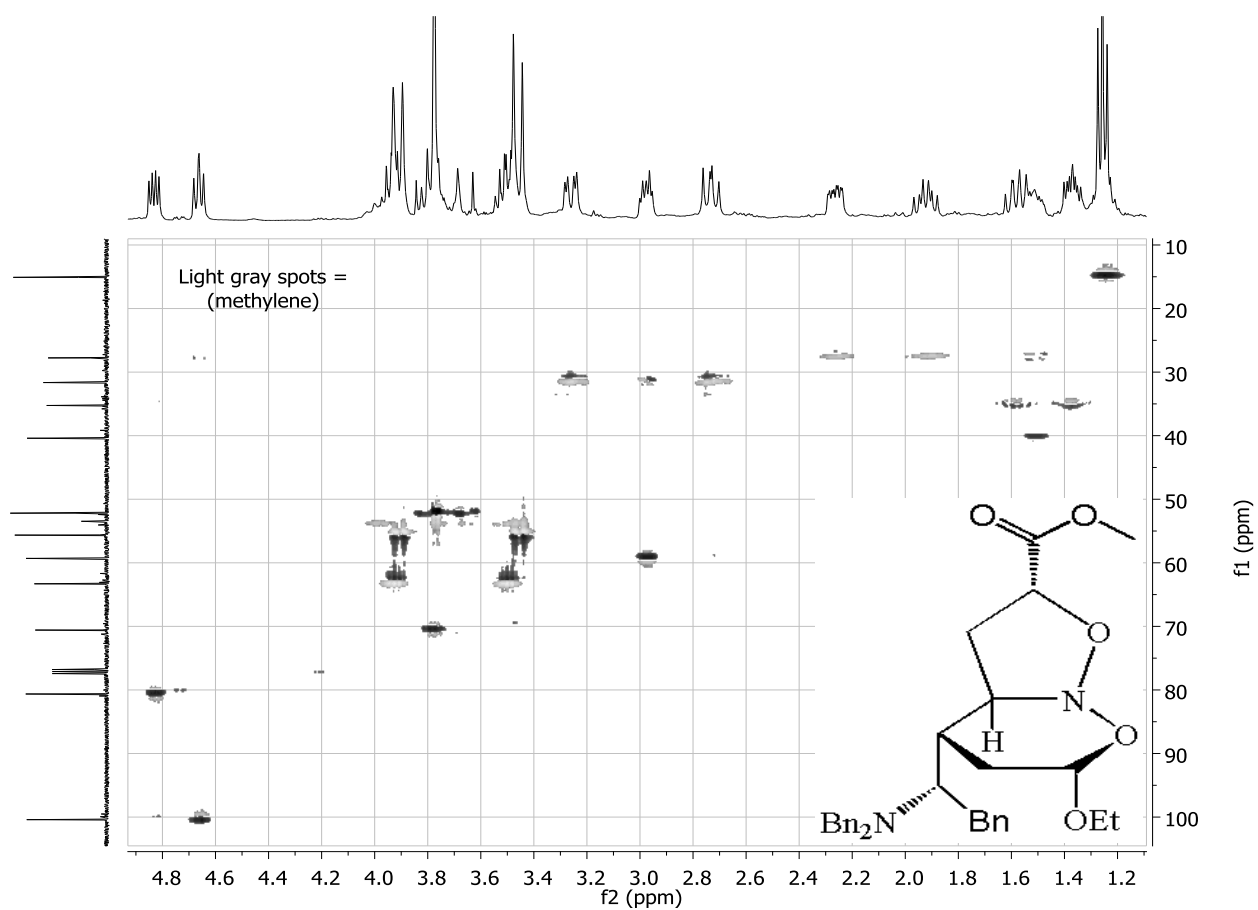
^{13}C NMR (101 MHz, CHLOROFORM-D) δ ppm 15.0 (CH_3); 27.7 (CH_2); 31.5 (CH_2); 35.1 (CH_2); 40.3 (CH); 52.1 (CH_3); 55.5 (2x CH_2); 59.2 (CH); 63.2 (CH_2); 70.5 (CH); 80.5 (CH); 100.3 (CH); 126.2-129.1 (15x CH_{Ar}); 139.3 (2x C_{ipso}); 139.8 (C_{ipso}); 170.3 ($\text{C}=\text{O}$)



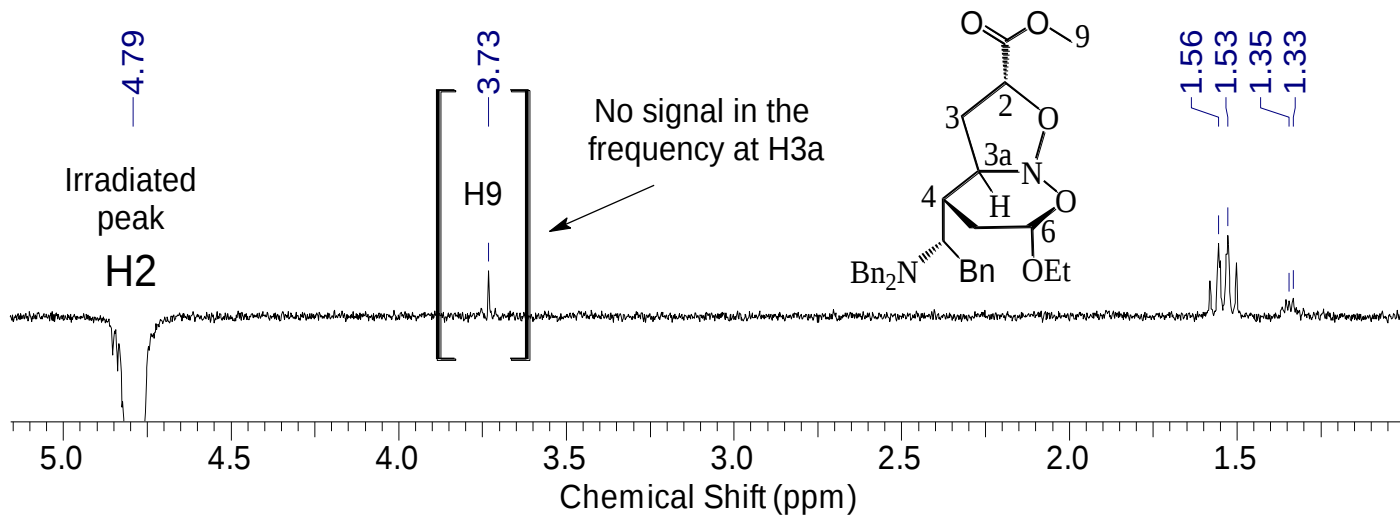
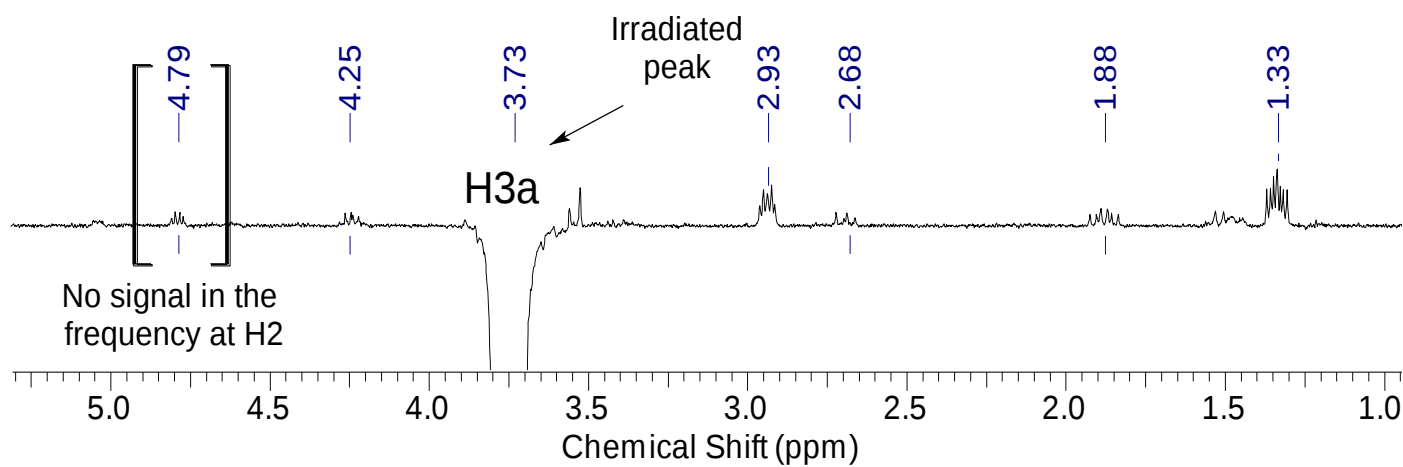
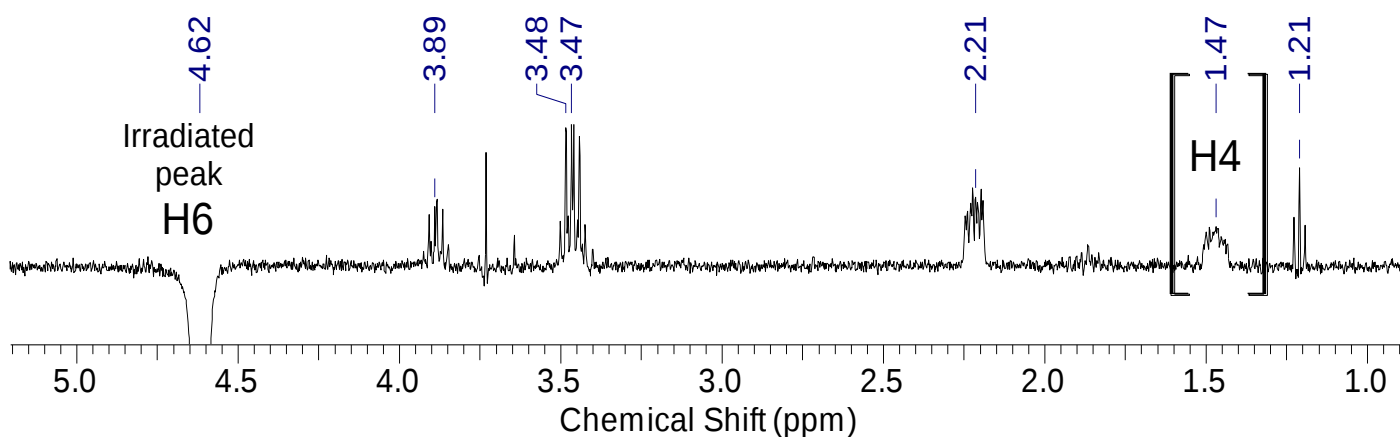
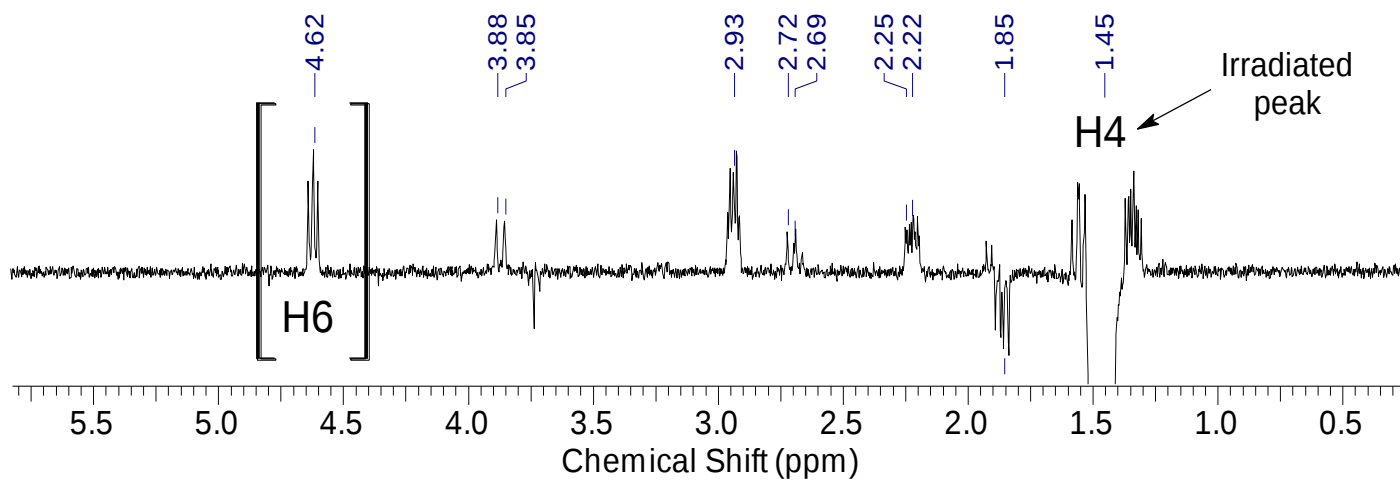
Spectrum 7 - ^1H and ^{13}C NMR of **7b**



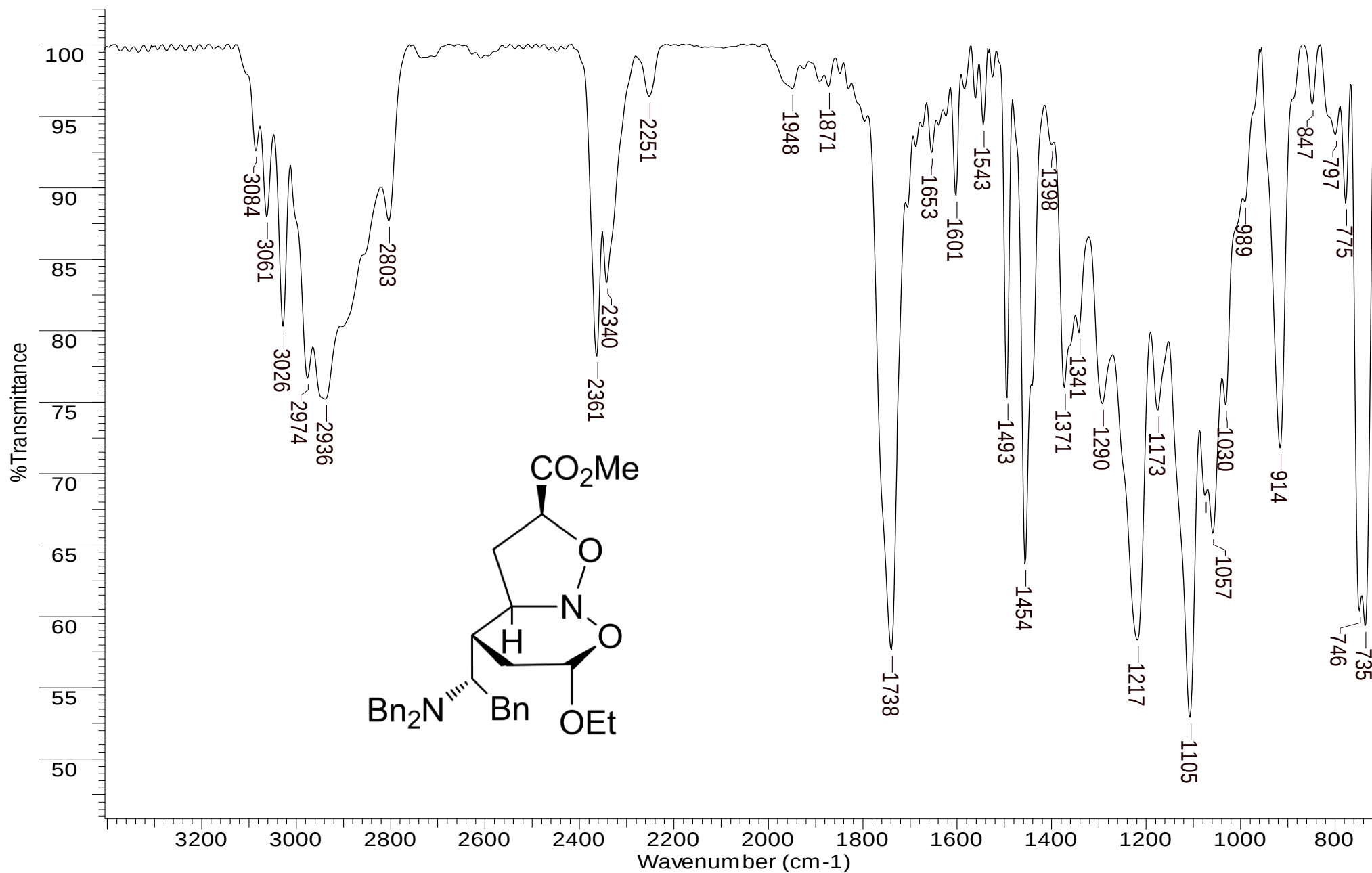
Spectrum 8 – 2D COSY of **7b**



Spectrum 9 – HSQC of **7b**

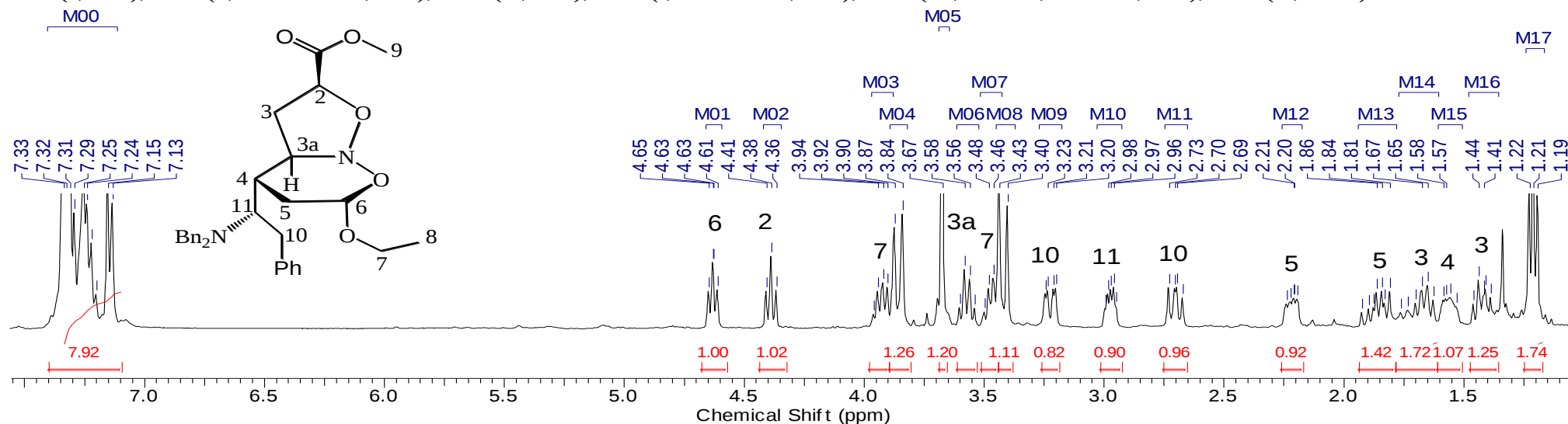


Spectrum 10 – 2D NOESY of **7b**

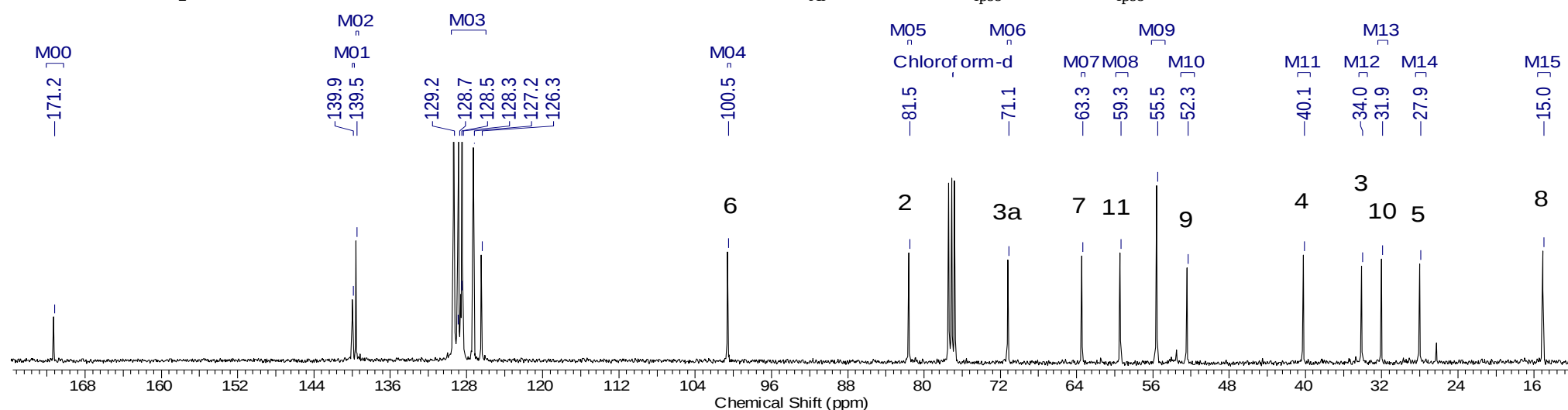


Spectrum 11 – Infrared of **7b'**

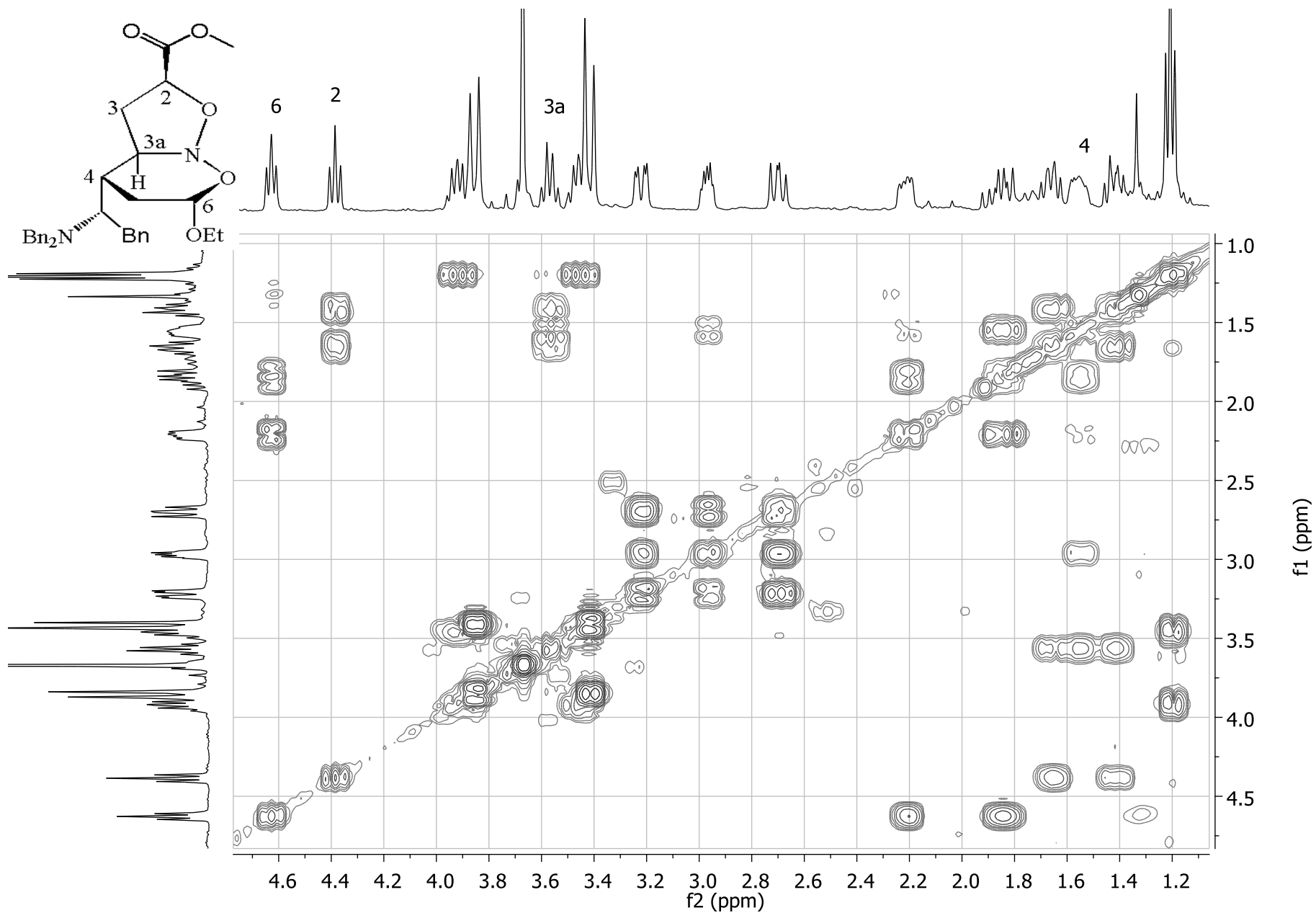
^1H NMR (400 MHz, CHCl_3 - d) δ ppm 1.21 (t, $J=6.98$ Hz, 3 H); 1.42 (m, 1 H); 1.56 (m, 1 H); 1.69 (m, 1 H); 1.86 (m, 1 H); 2.21 (m, 1 H); 2.70 (dd, $J=13.38, 10.12$ Hz, 1 H); 2.97 (m, 1 H); 3.22 (dd, $J=13.61, 4.07$ Hz, 1 H); 3.42 (d, $J=13.72$ Hz, 2 H); 3.47 (m, 1 H); 3.57 (m, 1 H); 3.67 (s, 3 H); 3.85 (d, $J=13.26$ Hz, 2 H); 3.93 (m, 1 H); 4.38 (t, $J=8.37$ Hz, 1 H); 4.63 (dd, $J=7.44, 7.21$ Hz, 1 H); 7.24 (m, 15 H)



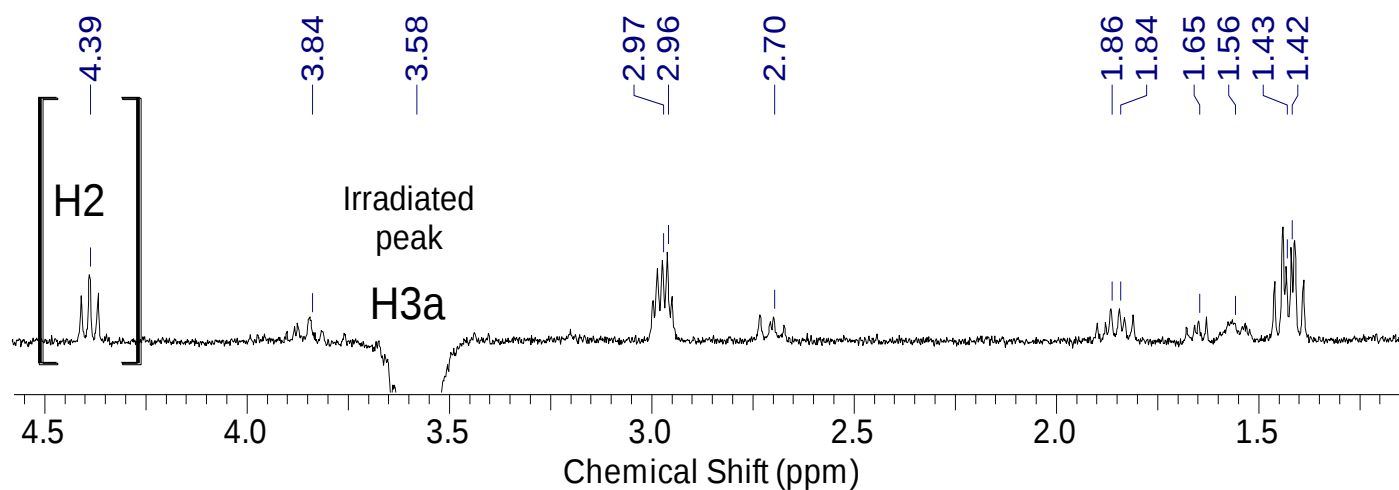
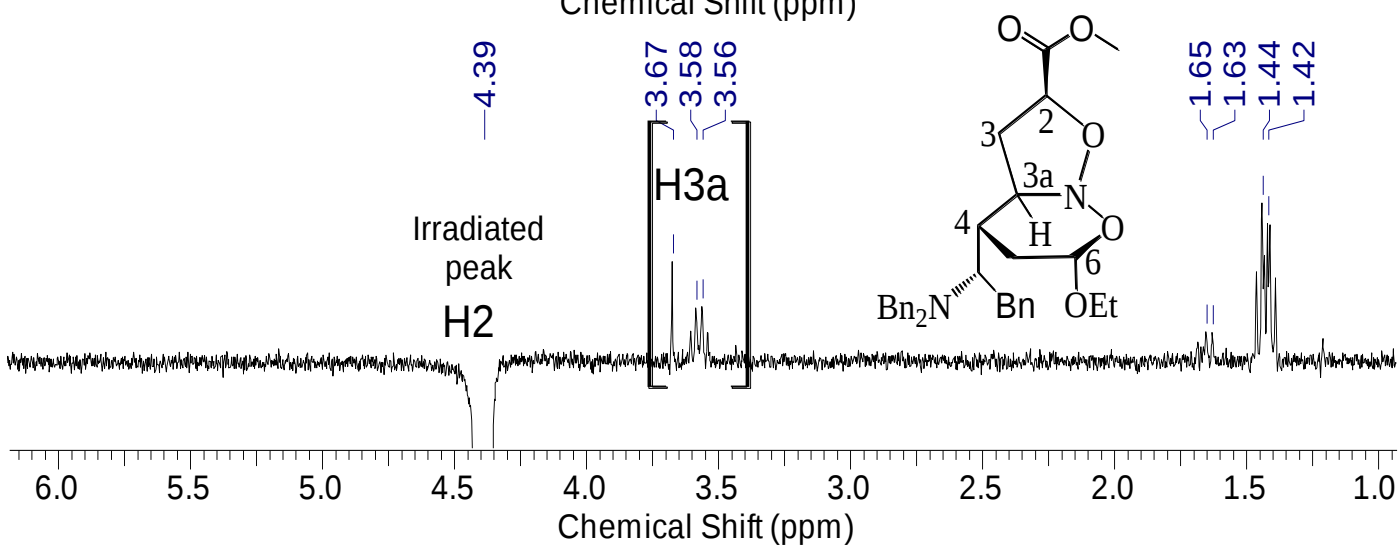
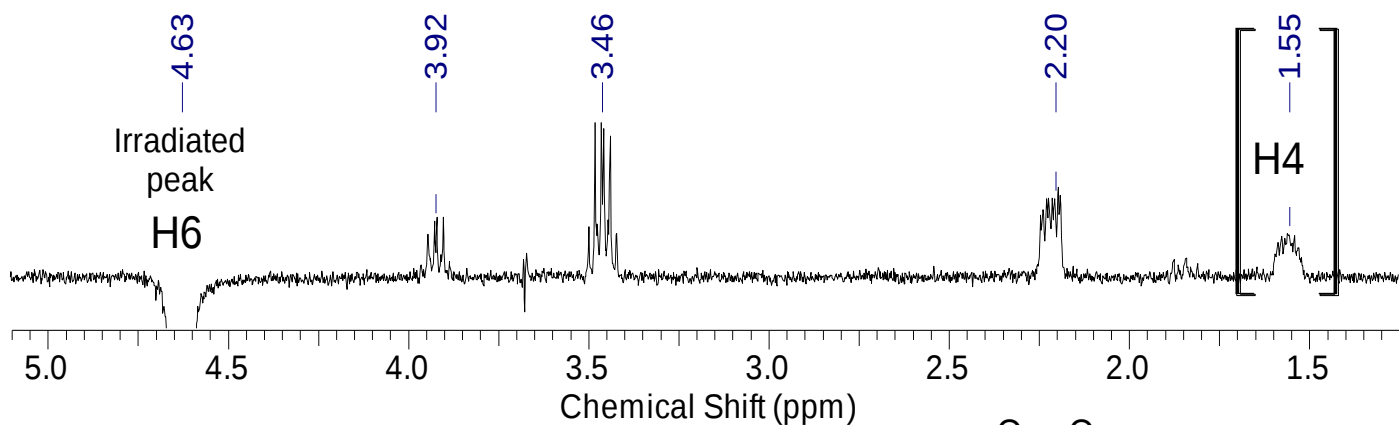
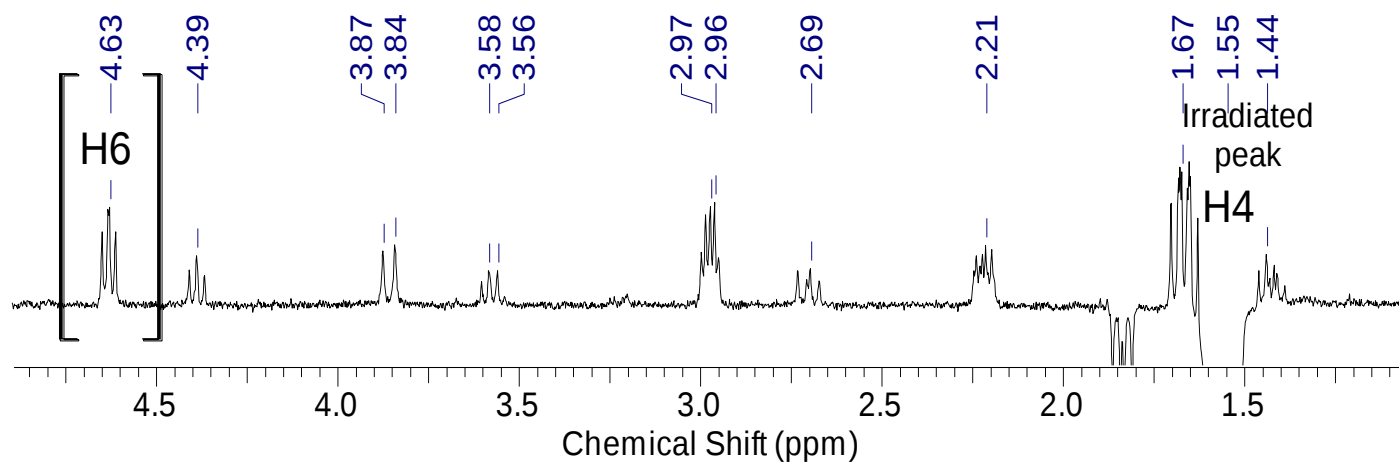
^{13}C NMR (101 MHz, CHCl_3 - d) δ ppm 15.0 (CH_3); 27.9 (CH_2); 31.9 (CH_2); 34.0 (CH_2); 40.1 (CH); 52.3 (CH_3); 55.5 ($2 \times \text{CH}_2$); 59.3 (CH); 63.3 (CH_2); 71.1 (CH); 81.5 (CH); 100.5 (CH); 126.3-129.2 ($15 \times \text{CH}_{\text{Ar}}$); 139.5 ($2 \times \text{C}_{\text{ipso}}$); 139.9 (C_{ipso}); 171.2 ($\text{C}=\text{O}$)



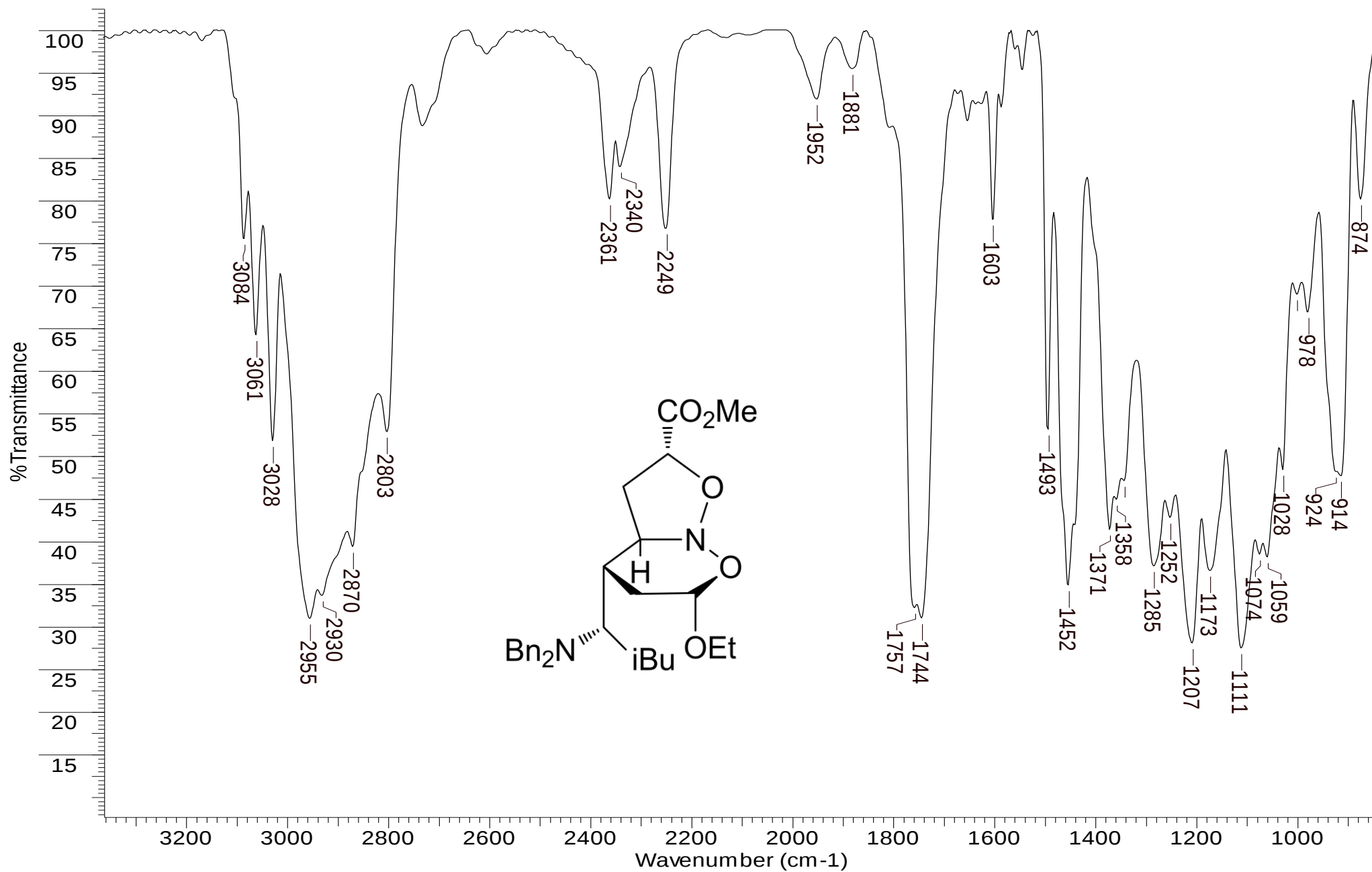
Spectrum 12 - ^1H and ^{13}C NMR of **7b'**



Spectrum 13 – 2D COSY of **7b'**

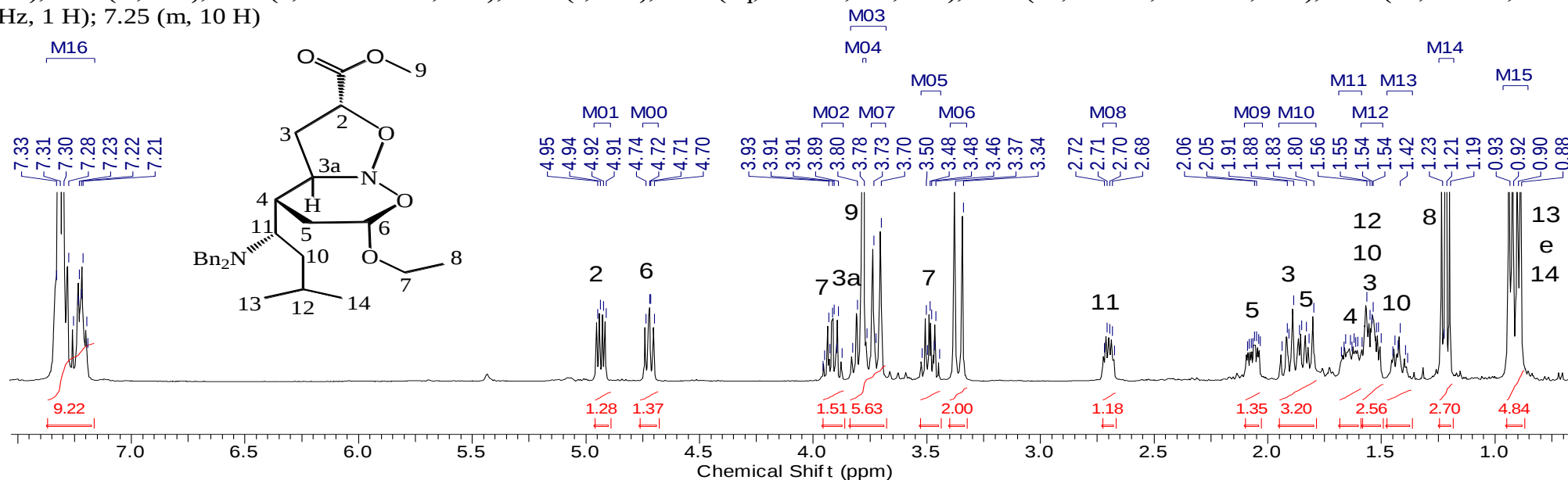


Spectrum 14 – 2D NOESY of **7b'**

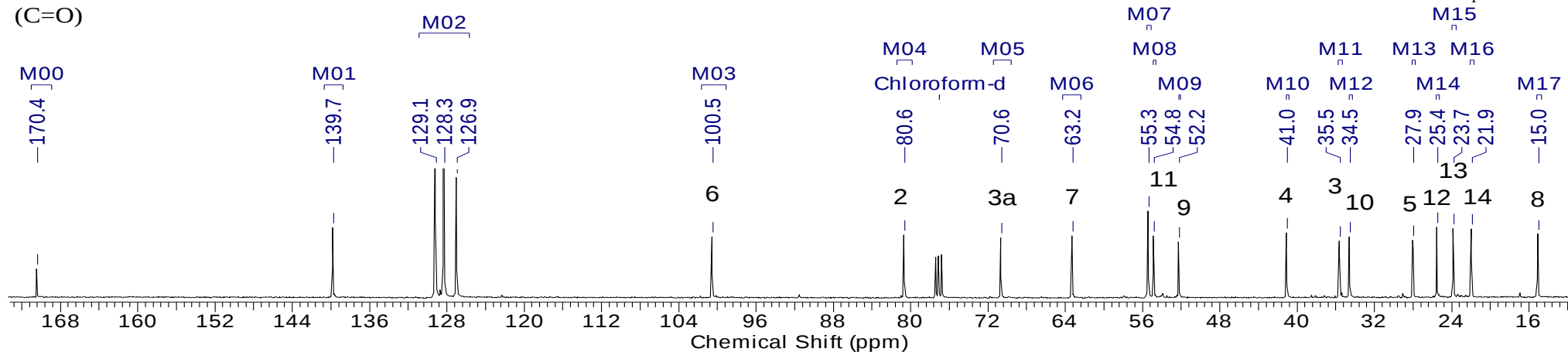


Spectrum 15 – Infrared of **9c**

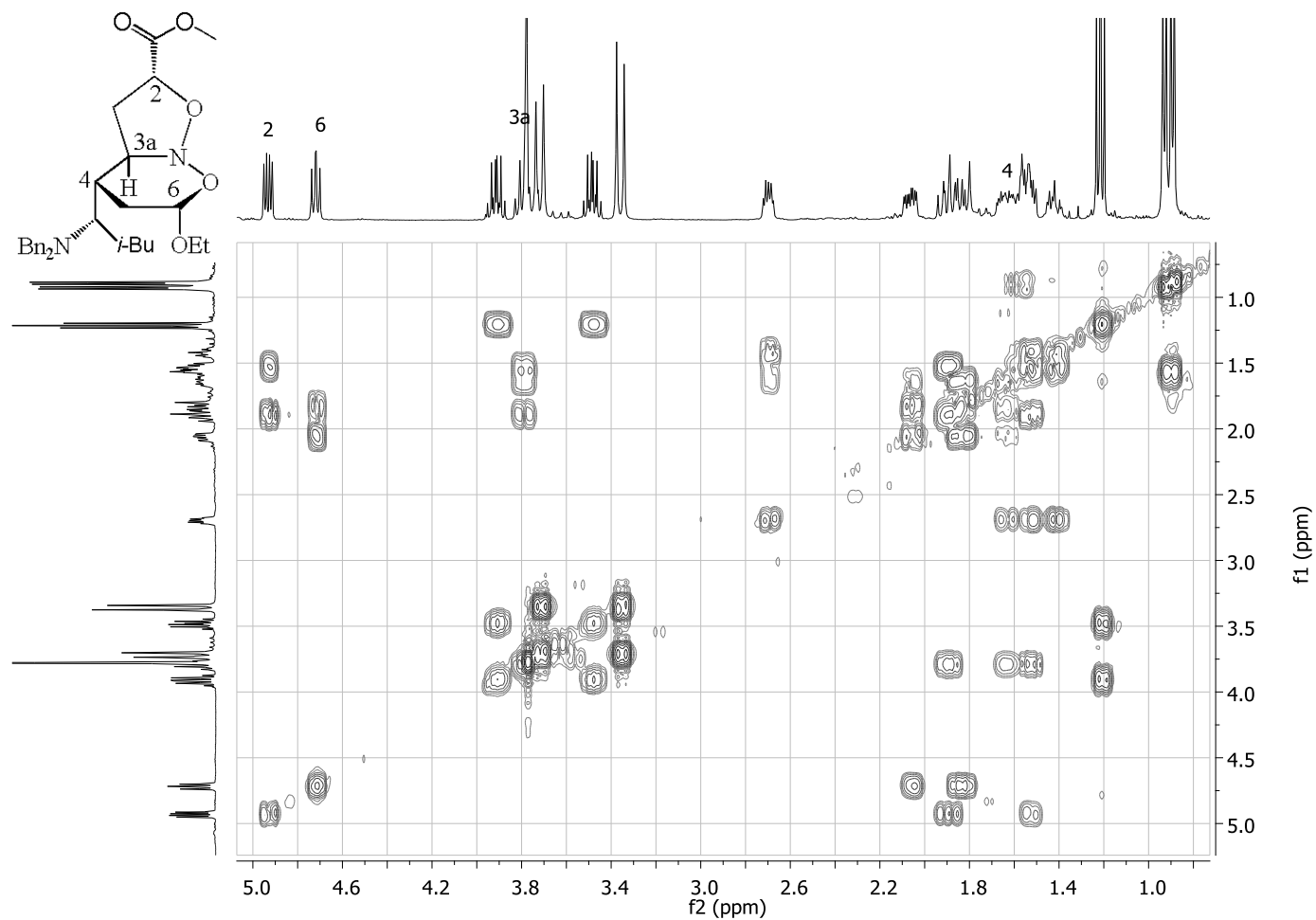
^1H NMR (400 MHz, CHLOROFORM-D) δ ppm 0.89 (d, $J=6.11$ Hz, 3 H); 0.93 (d, $J=6.11$ Hz, 3 H); 1.21 (t, $J=7.08$ Hz, 3 H); 1.42 (m, 1 H); 1.54 (m, 3 H); 1.64 (m, 1 H); 1.87 (m, 2 H); 2.06 (ddd, $J=12.93, 6.59, 2.83$ Hz, 1 H); 2.70 (m, 1 H); 3.36 (d, $J=13.41$ Hz, 2 H); 3.48 (dq, $J = 9.6, 7.0$, 1H); 3.76 (m, 1 H); 3.72 (d, $J=13.41$ Hz, 2 H); 3.78 (s, 3 H); 3.92 (dq, $J = 9.6, 7.1$, 1 H); 4.72 (dd, $J=8.05, 6.71$ Hz, 1 H); 4.93 (dd, $J=9.98, 4.92$ Hz, 1 H); 7.25 (m, 10 H)



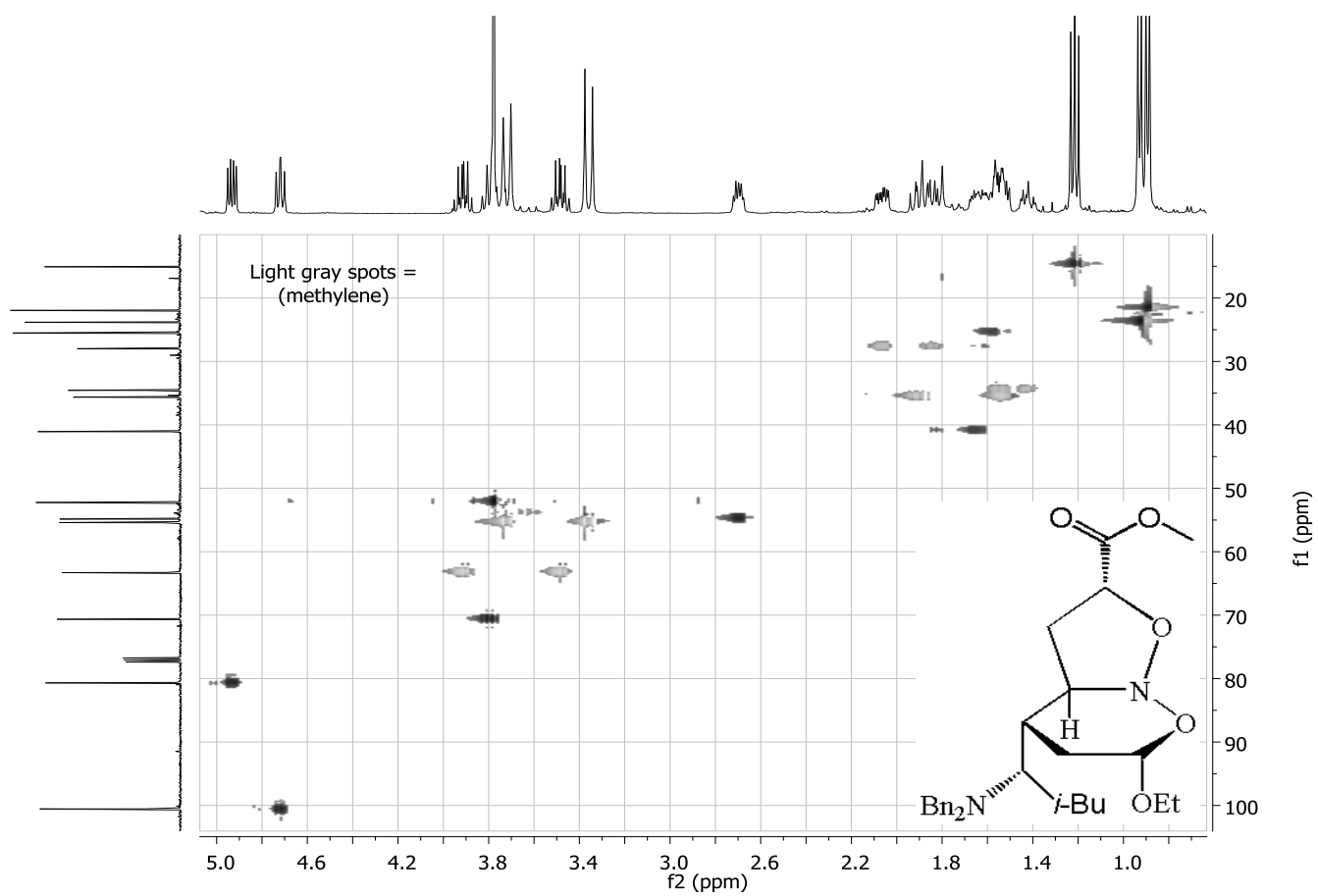
^{13}C NMR (101 MHz, CHLOROFORM-D) δ ppm 15.0 (CH_3); 21.9 (CH_3); 23.7 (CH_3); 25.4 (CH); 27.9 (CH_2); 34.5 (CH_2); 35.5 (CH_2); 41.0 (CH); 52.2 (CH_3); 54.8 (CH); 55.3 (2x CH_2); 63.2 (CH_2); 70.6 (CH); 80.6 (CH); 100.5 (CH); 126.9; 128.3; 129.1 (10x CH_{Ar}); 139.7 (2x C_{ipso}); 170.4 ($\text{C}=\text{O}$)



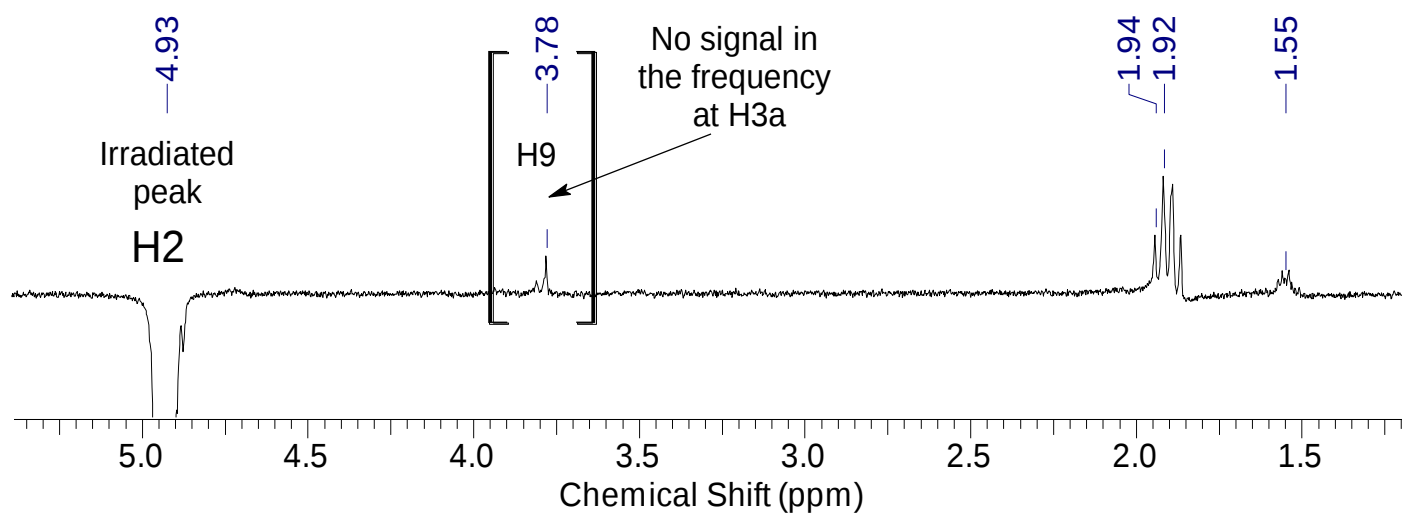
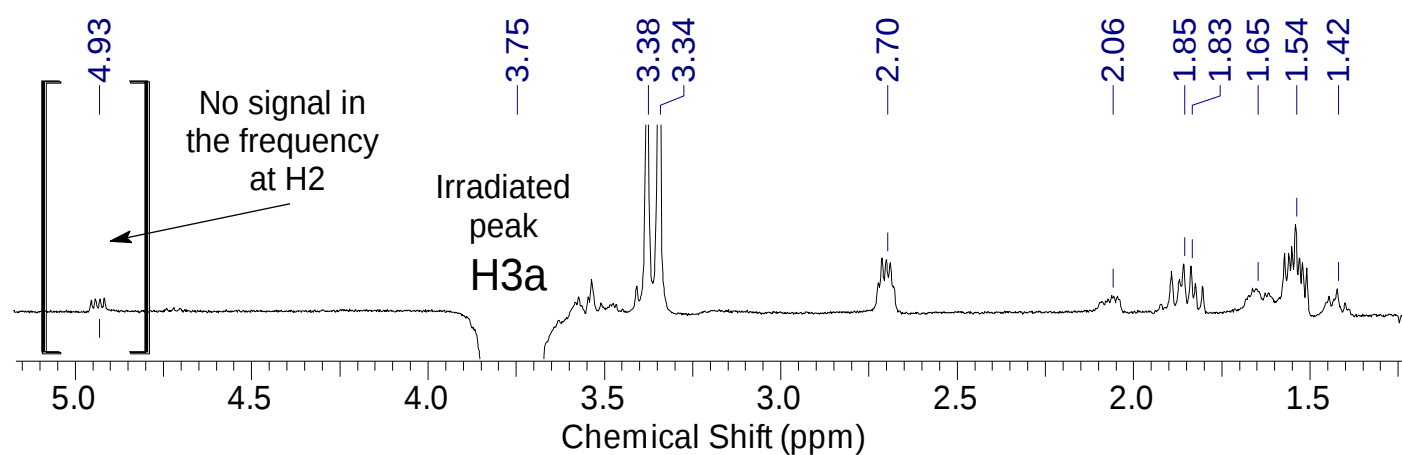
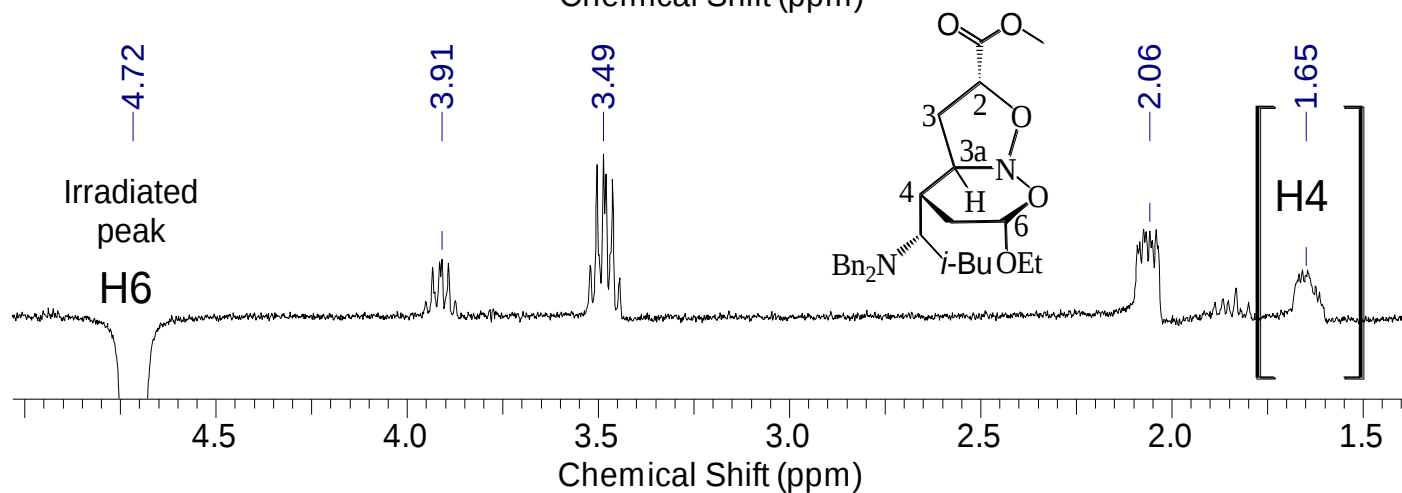
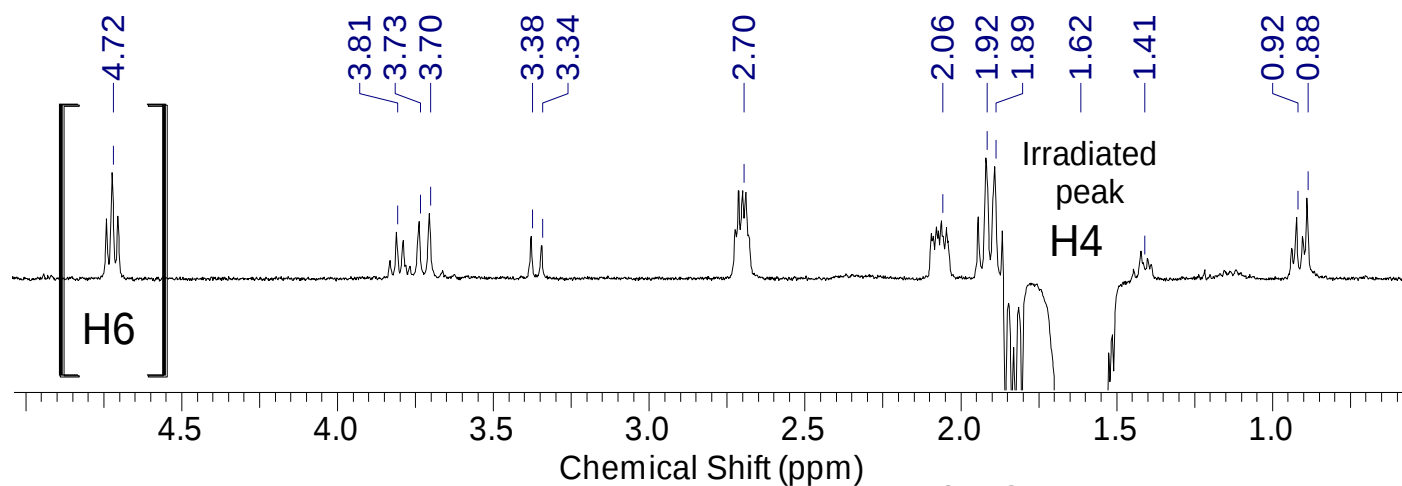
Spectrum 16 - ^1H and ^{13}C NMR of **9c**



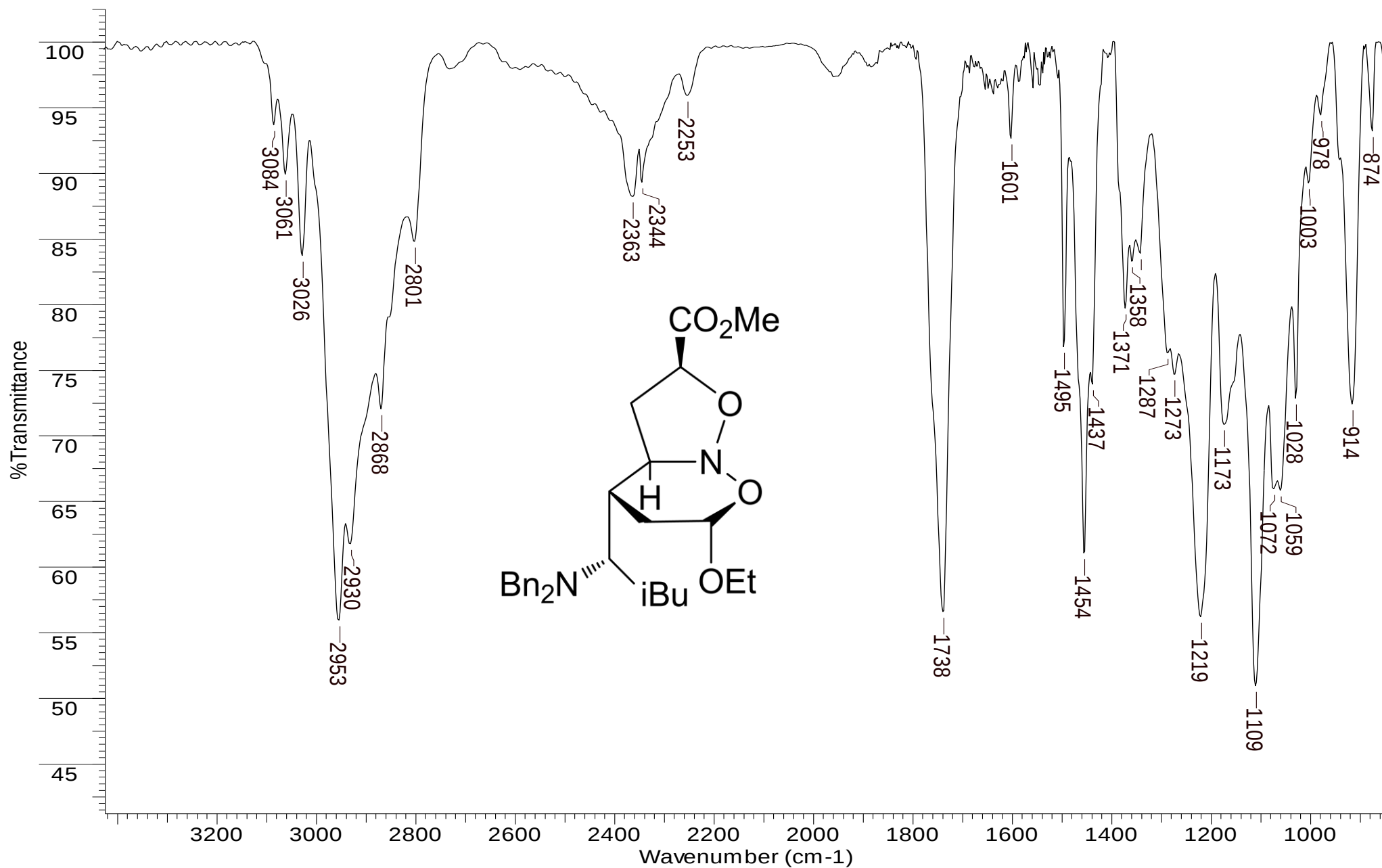
Spectrum 17 – 2D COSY of **9c**



Spectrum 18 – HSQC of **9c**

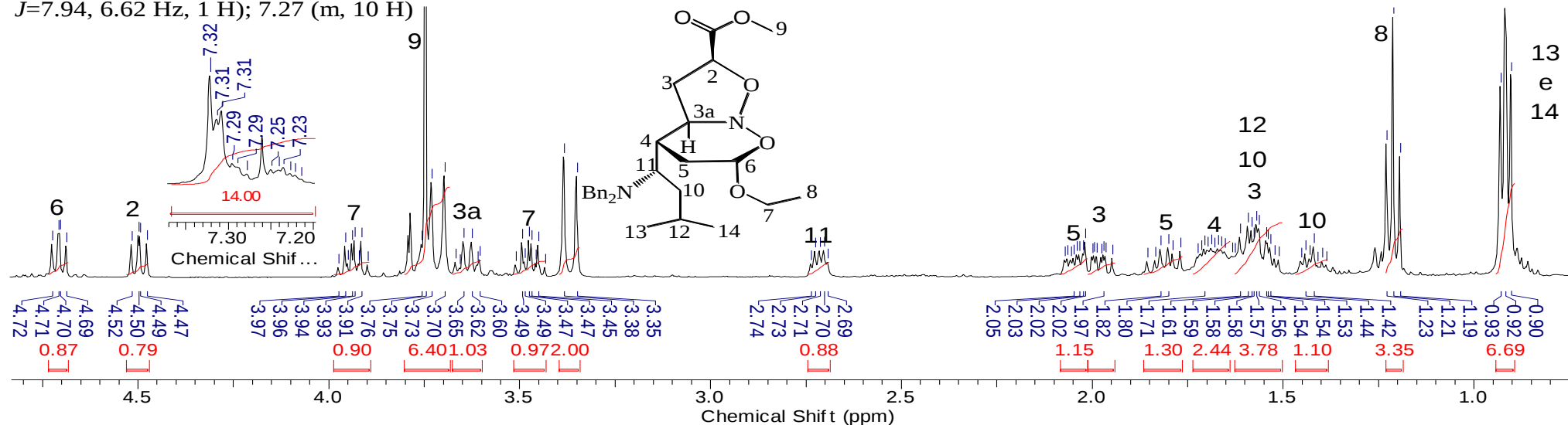


Spectrum 19 – 2D NOESY of **9c**

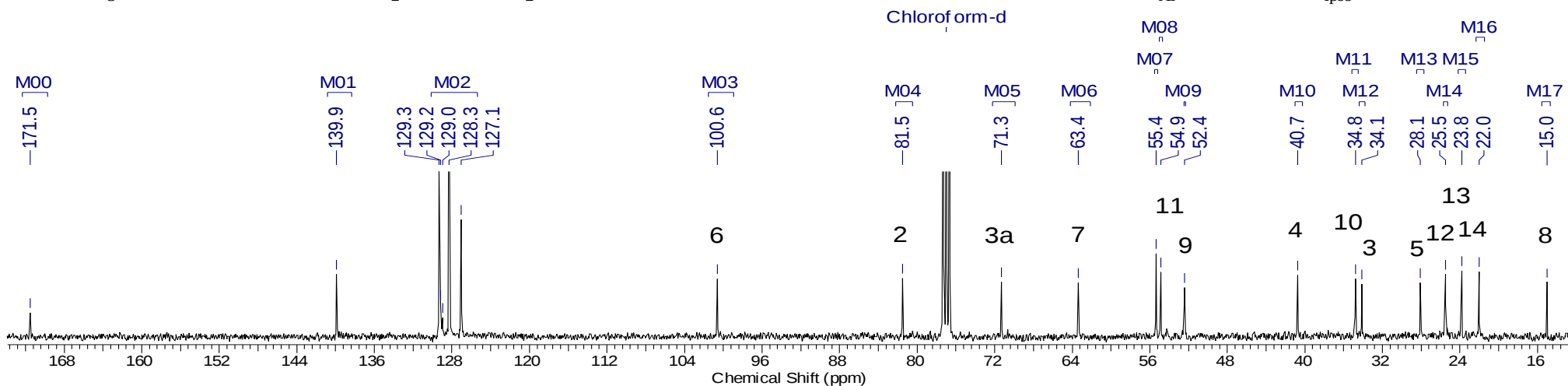


Spectrum 20 – Infrared of **9c'**

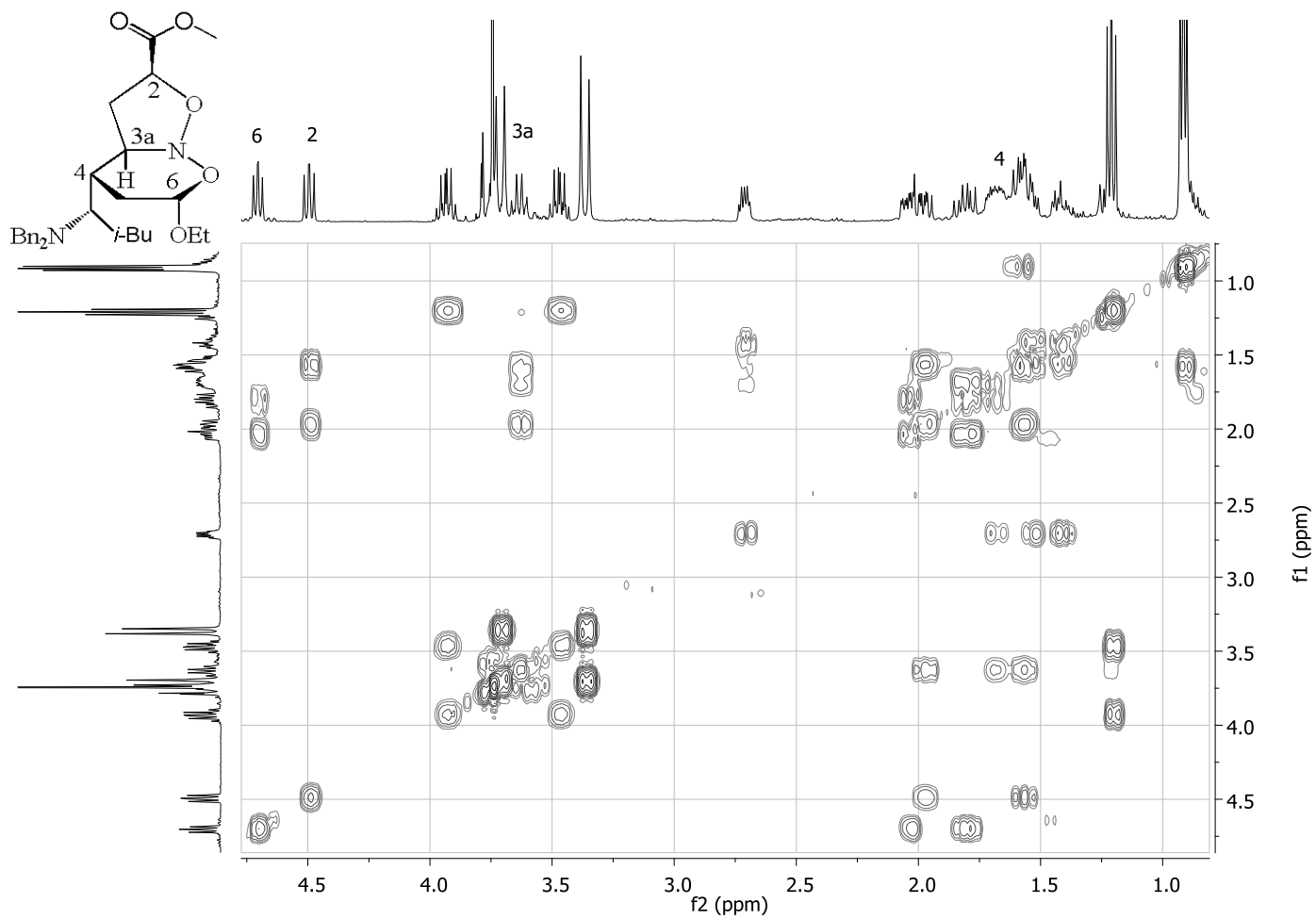
^1H NMR (400 MHz, CHCl_3 - d) δ ppm 0.91 (d, $J = 5.29$ Hz, 3 H); 0.92 (d, $J = 5.07$ Hz, 3 H); 1.21 (t, $J = 7.06$ Hz, 3 H); 1.56 (m, 3 H); 1.69 (m, 1 H); 1.81 (m, 1 H); 1.98 (m, 1 H); 2.04 (ddd, $J = 12.68, 6.51, 2.43$ Hz, 1 H); 2.71 (m, 1 H); 3.37 (d, $J = 13.45$ Hz, 2 H); 3.47 (dq, $J = 9.67, 7.07$ Hz, 1 H); 3.63 (m, 1 H); 3.73 (m, 1 H); 3.71 (d, $J = 13.45$ Hz, 2 H); 3.75 (s, 3 H); 3.93 (m, 1 H); 4.49 (dd, $J = 9.04, 7.06$ Hz, 1 H); 4.70 (d, $J = 7.94, 6.62$ Hz, 1 H); 7.27 (m, 10 H)



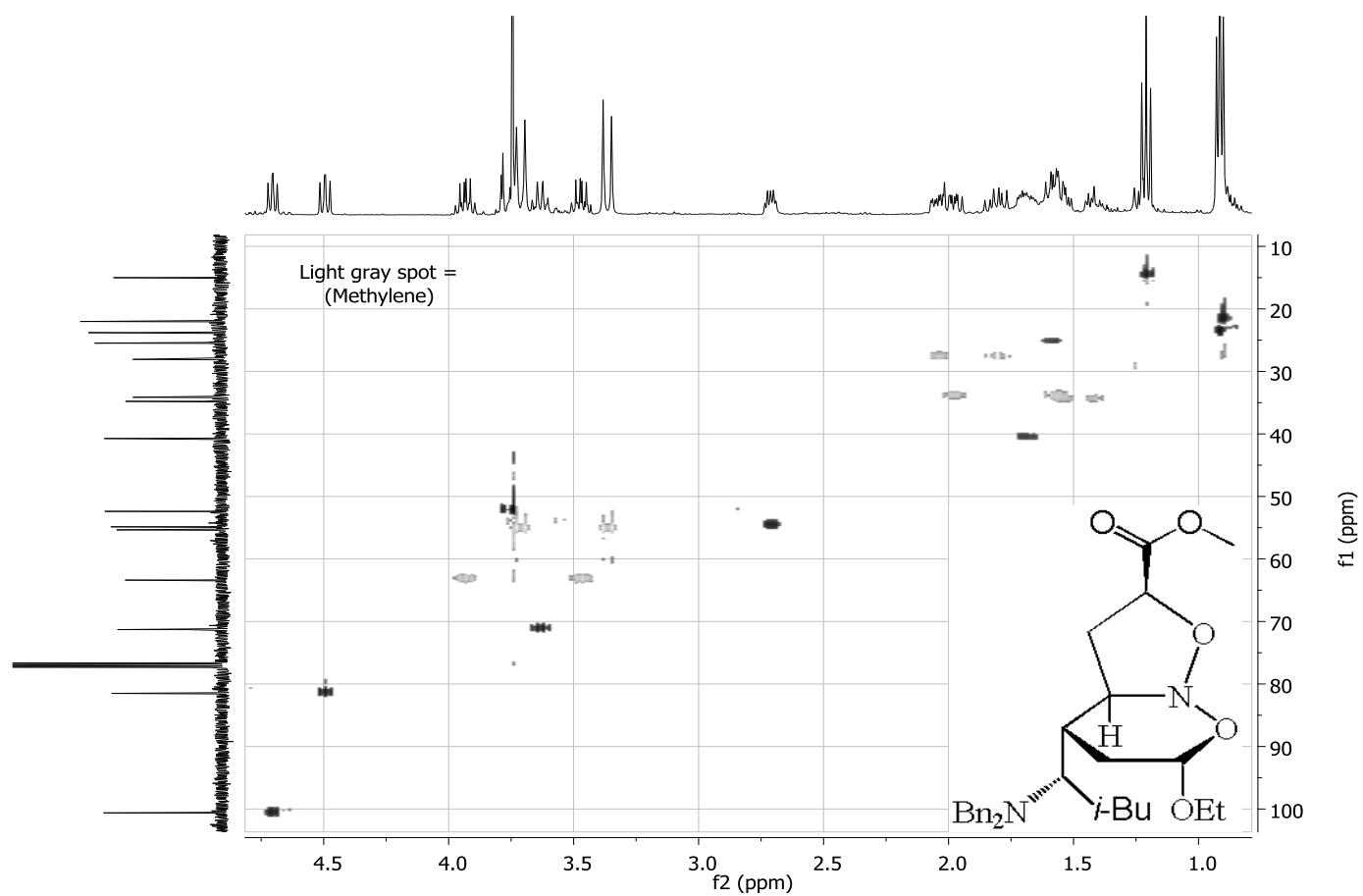
^{13}C NMR (101 MHz, CHCl_3 - d) δ ppm 15.0 (CH_3); 22.0 (CH_3); 23.8 (CH_3); 25.5 (CH); 28.1 (CH_2); 34.1 (CH_2); 34.8 (CH_2); 40.7 (CH); 52.4 (CH_3); 54.9 (CH); 55.4 (2x CH_2); 63.4 (CH_2); 71.3 (CH); 81.5 (CH); 100.6 (CH); 127.1-129.3 (10x CH_{Ar}); 139.9 (2x C_{ipso}); 171.5 ($\text{C}=\text{O}$)



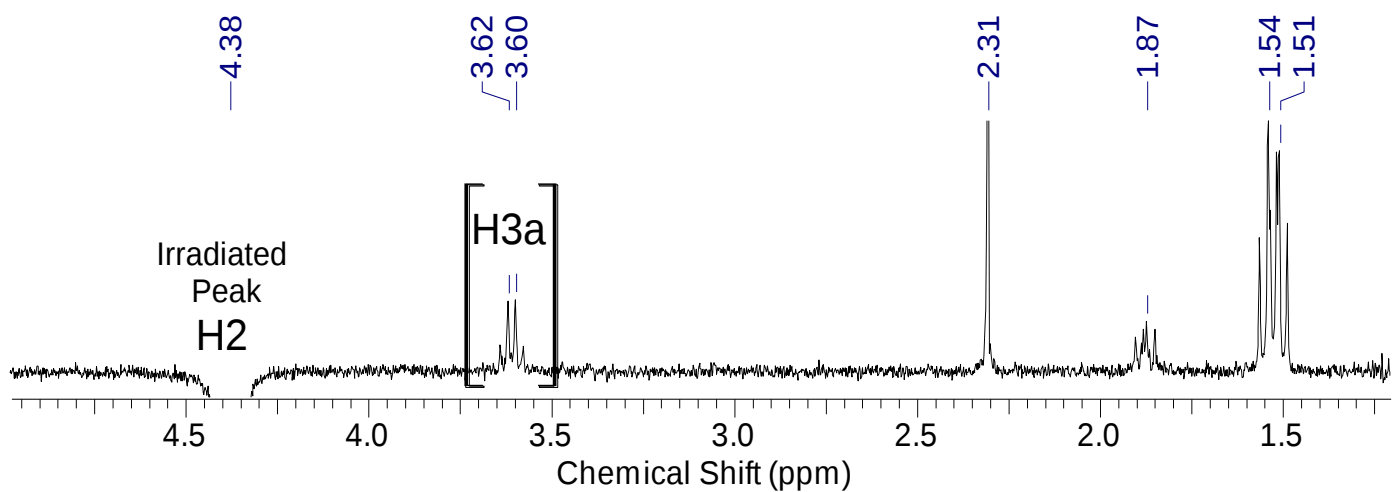
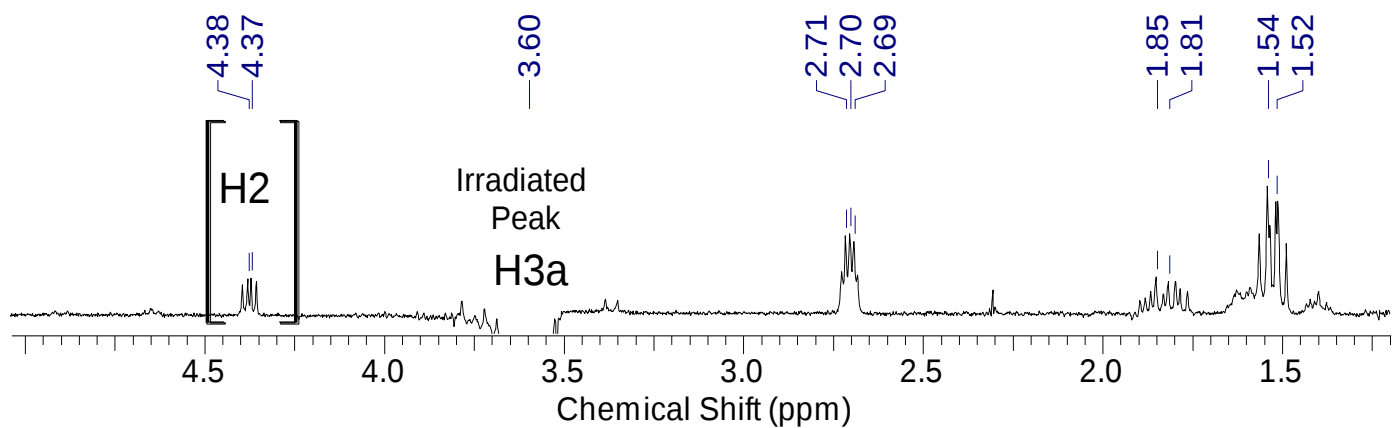
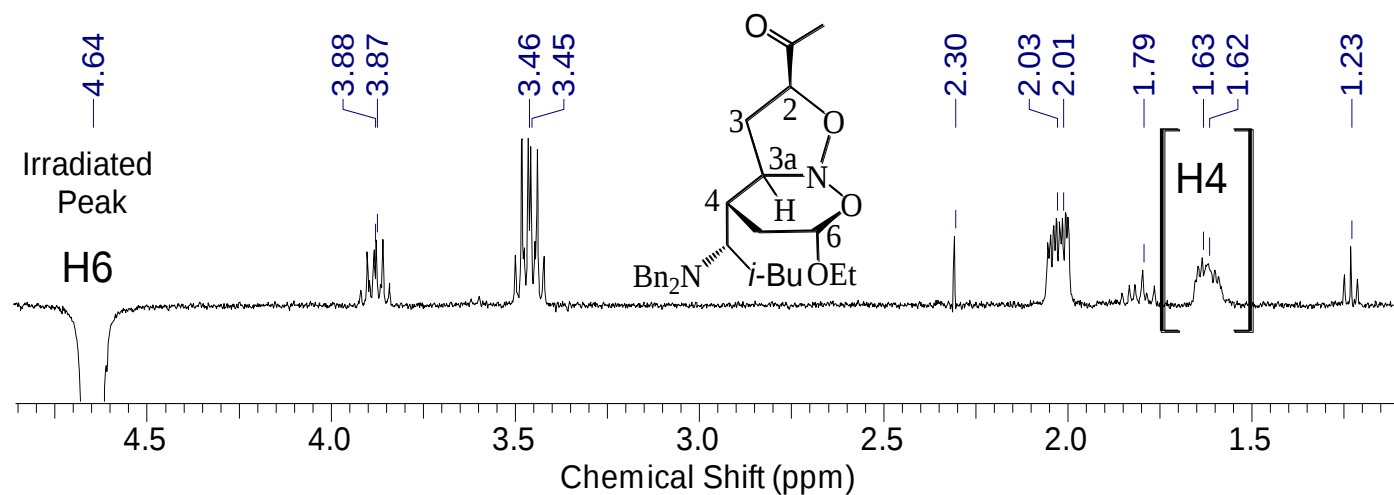
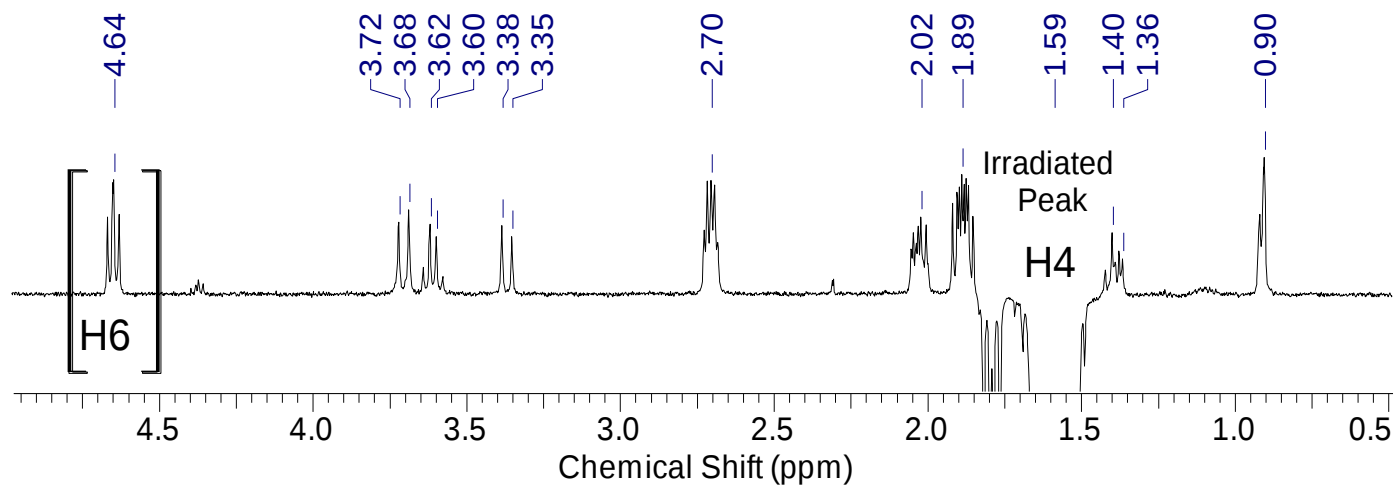
Spectrum 21 - ^1H and ^{13}C NMR of **9c'**



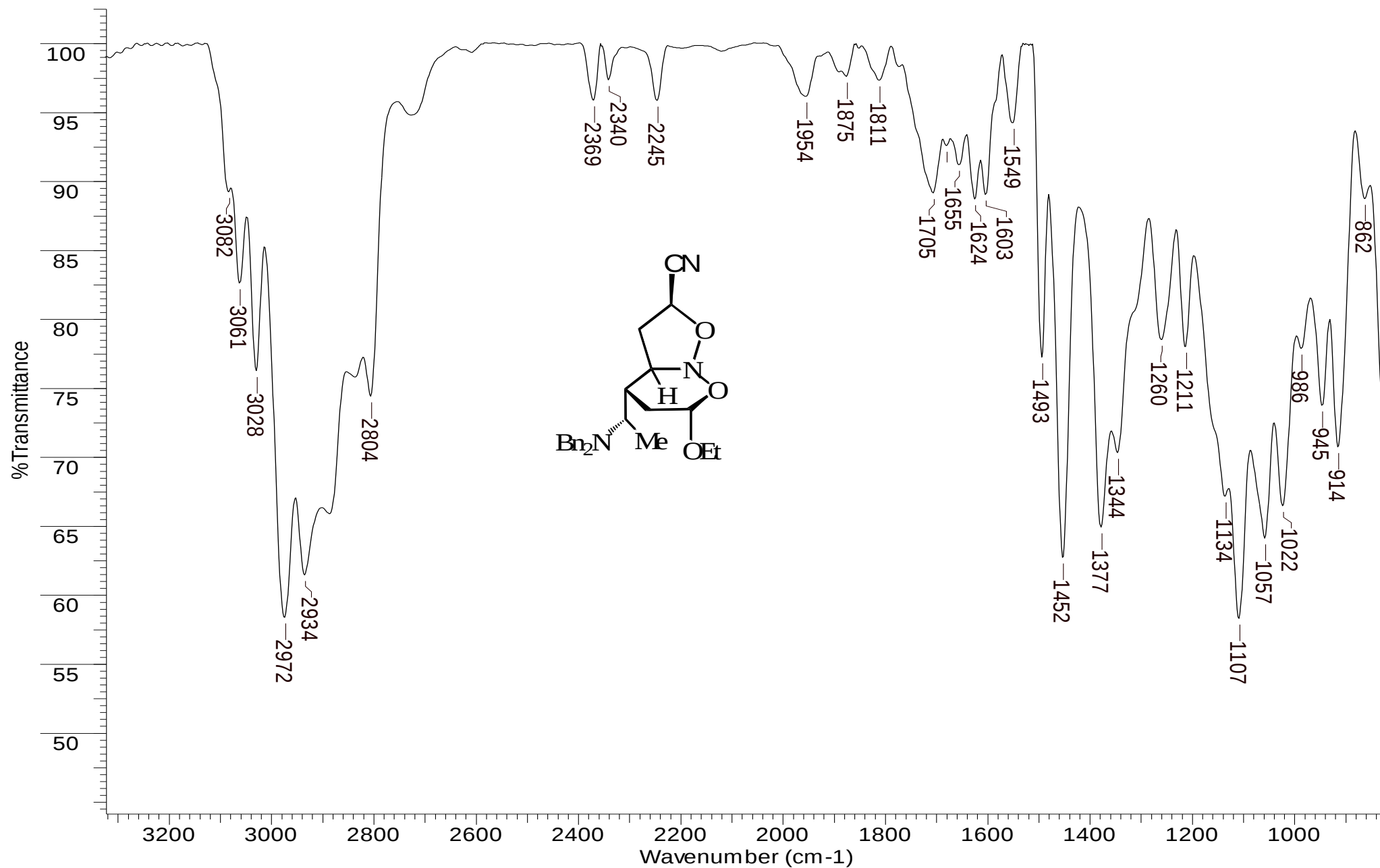
Spectrum 22 – 2D COSY of **9c'**



Spectrum 23 – HSQC of **9c'**

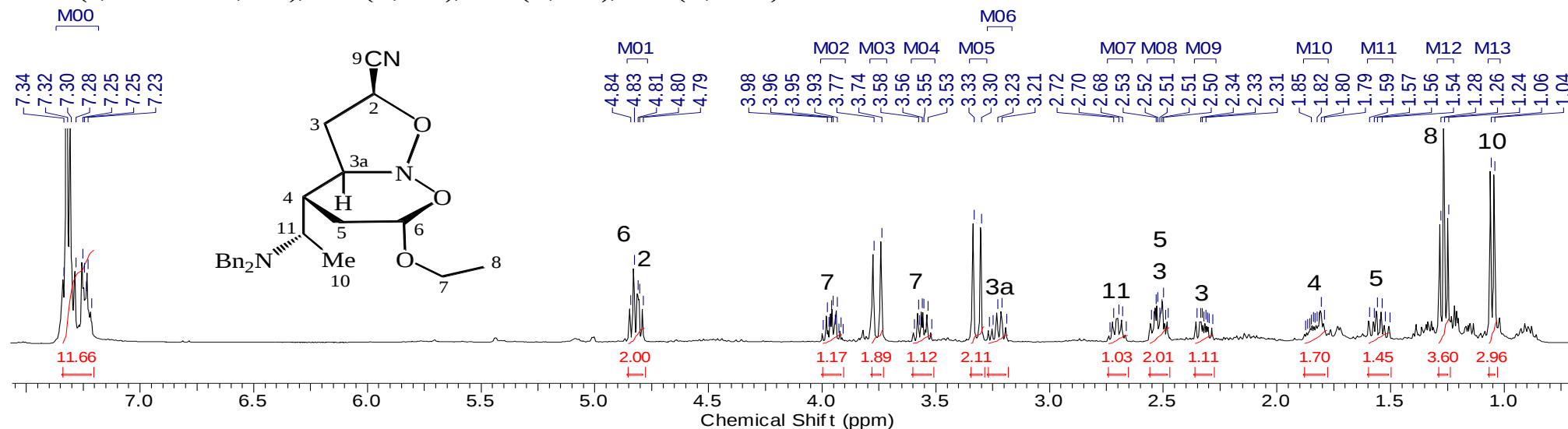


Spectrum 24 – 2D NOESY of **9c'**

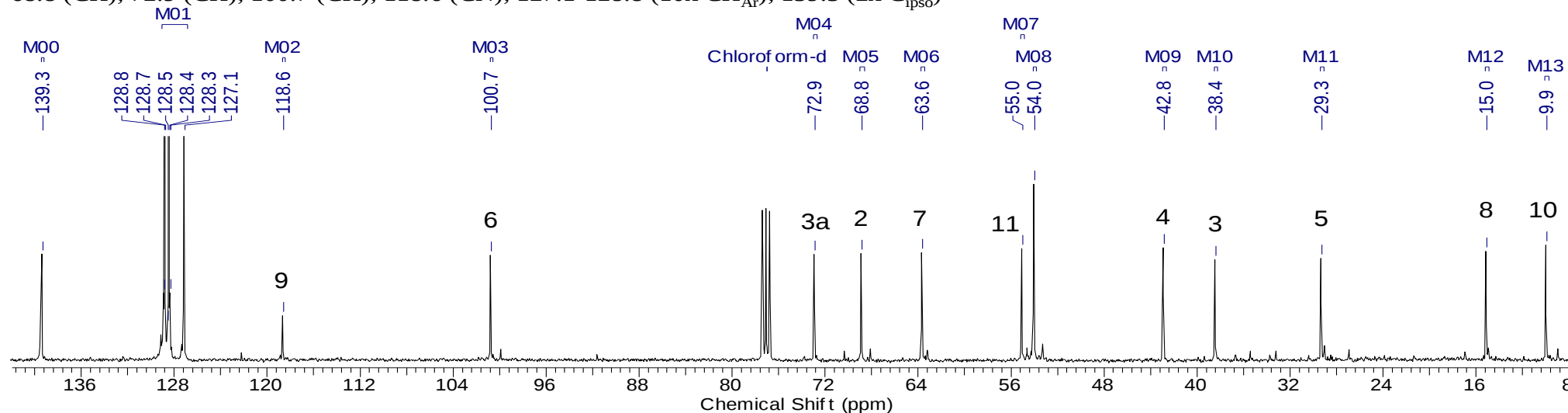


Spectrum 25 – Infrared of **10a'**

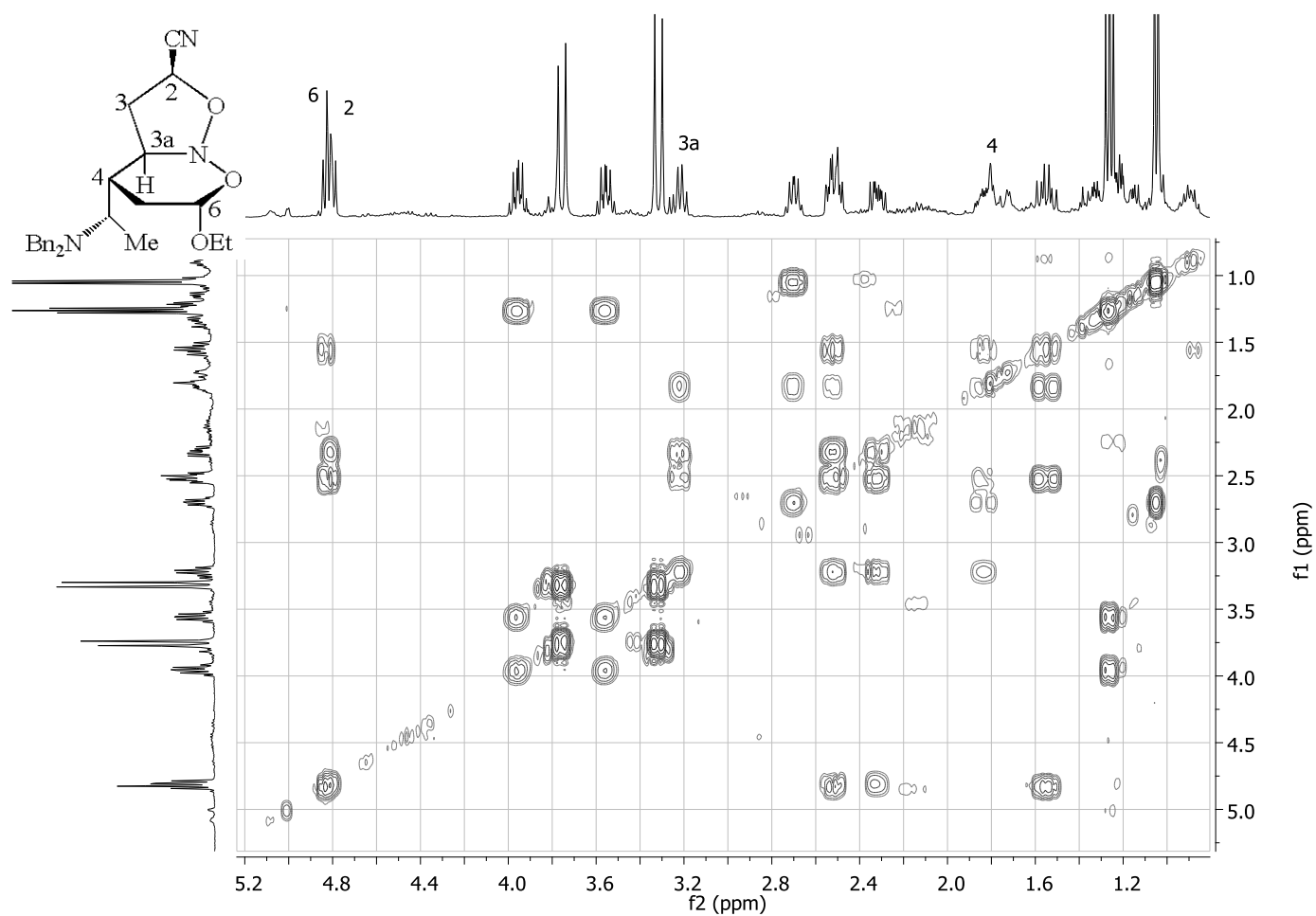
^1H NMR (400 MHz, CHLOROFORM-D) δ ppm 1.05 (d, $J=6.62$ Hz, 3 H); 1.26 (t, $J=6.95$ Hz, 3 H); 1.55 (ddd, $J=13.67$, 13.67, 8.38 Hz, 1 H); 1.83 (m, 1 H); 2.32 (ddd, $J=12.29$, 9.10, 6.62 Hz, 1 H); 2.52 (m, 2 H); 2.70 (m, 1 H); 3.23 (m, 1 H); 3.32 (d, $J=13.45$ Hz, 2 H); 3.56 (m, 1 H); 3.75 (d, $J=13.67$ Hz, 2 H); 3.95 (m, 1 H); 4.81 (m, 2 H); 7.27 (m, 10 H)



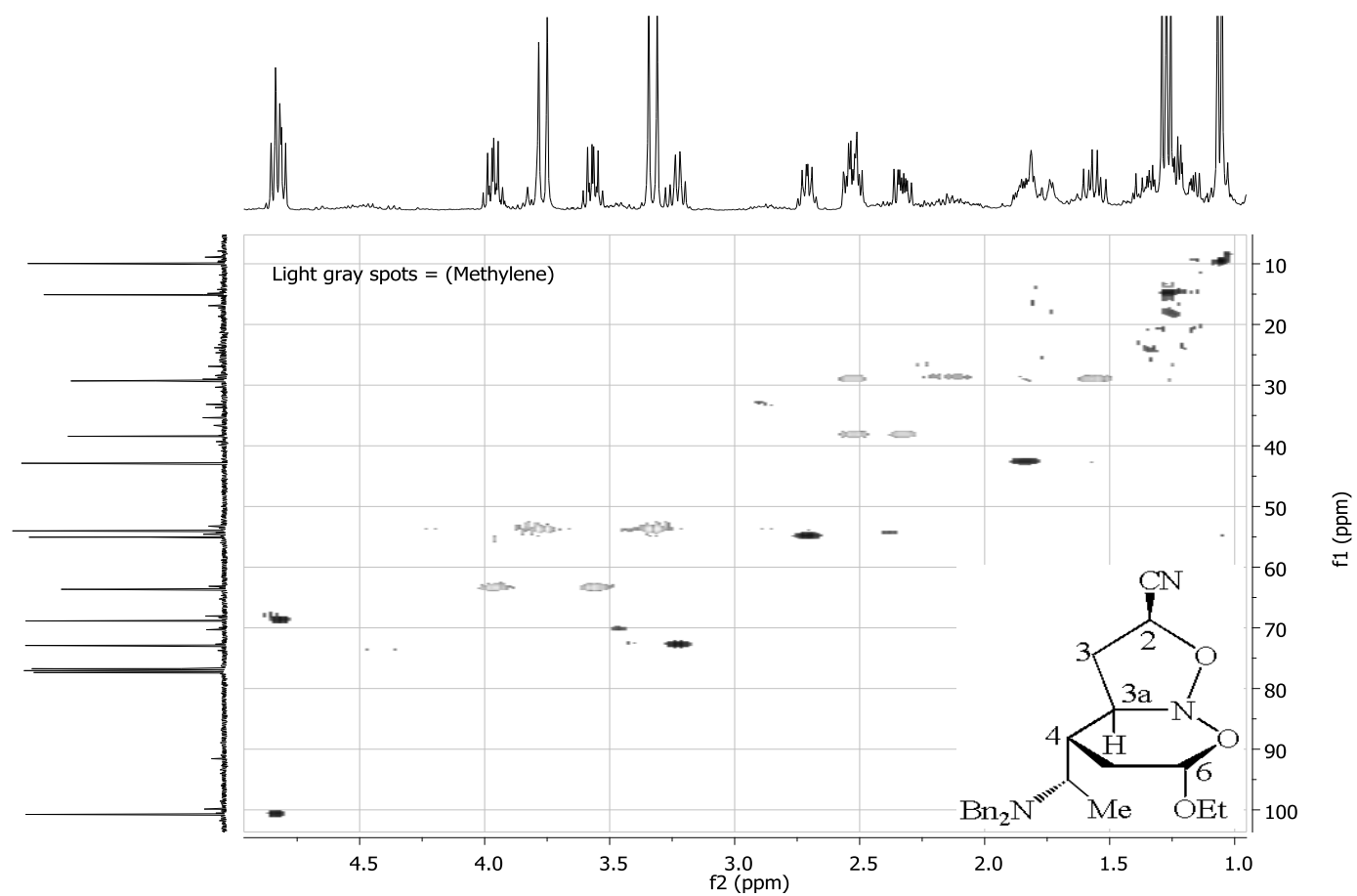
^{13}C NMR (101 MHz, CHLOROFORM-D) δ ppm 9.9 (CH_3); 15.0 (CH_3); 29.3 (CH_2); 38.4 (CH_2); 42.8 (CH); 54.0 (2x CH_2); 55.0 (CH); 63.6 (CH_2); 68.8 (CH); 72.9 (CH); 100.7 (CH); 118.6 (CN); 127.1-128.8 (10x CH_{Ar}); 139.3 (2x C_{ipso})



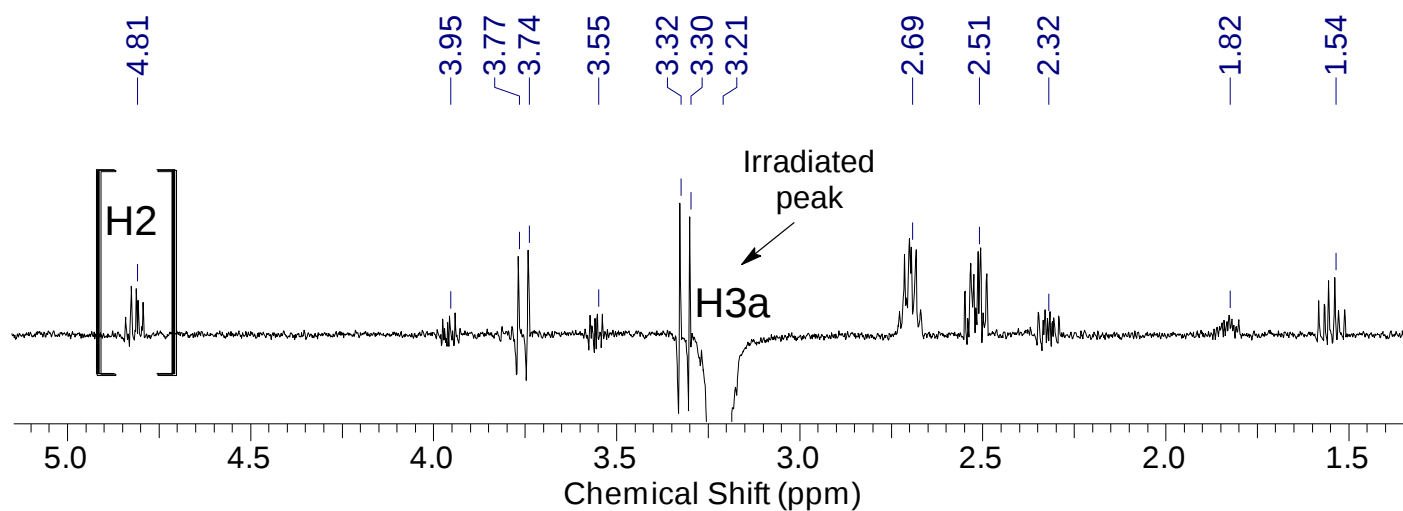
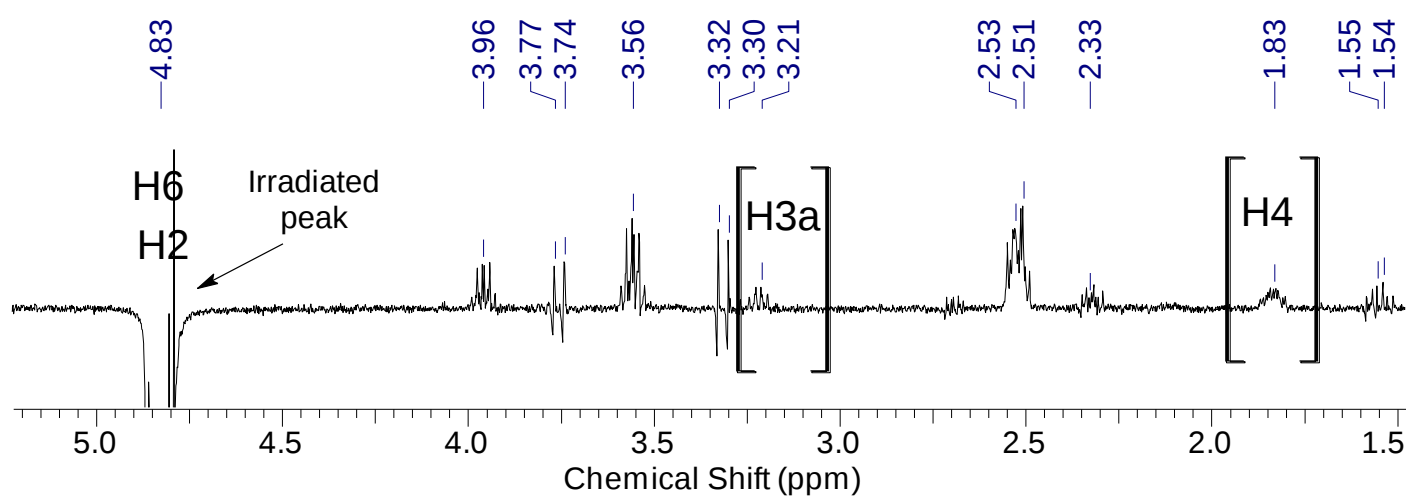
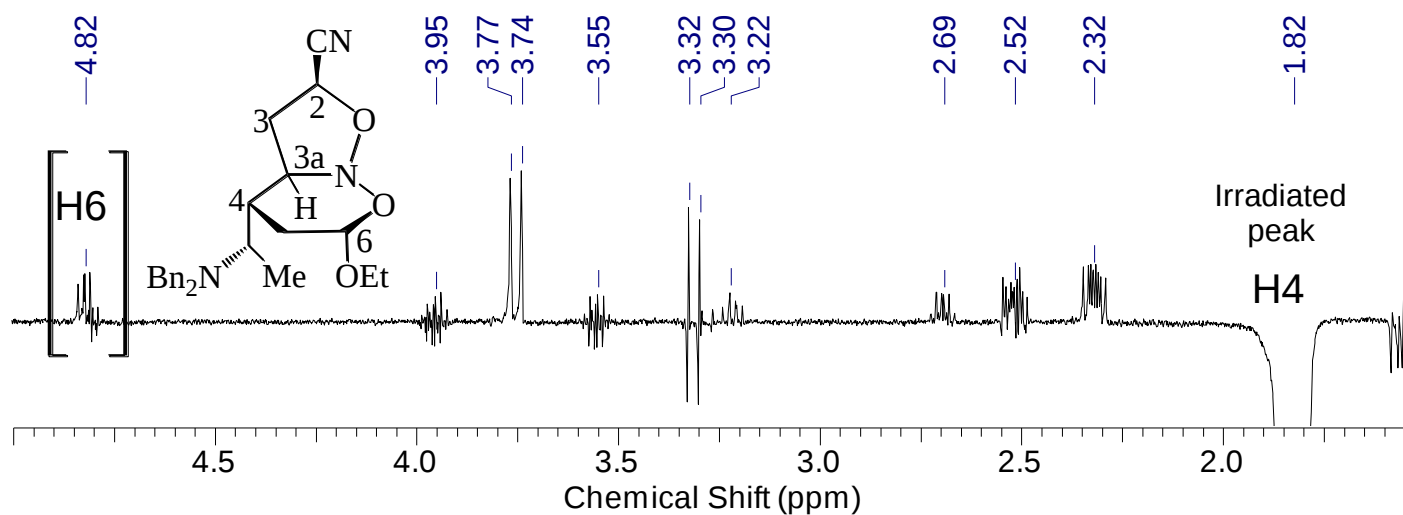
Spectrum 26 - ^1H and ^{13}C NMR of **10a'**



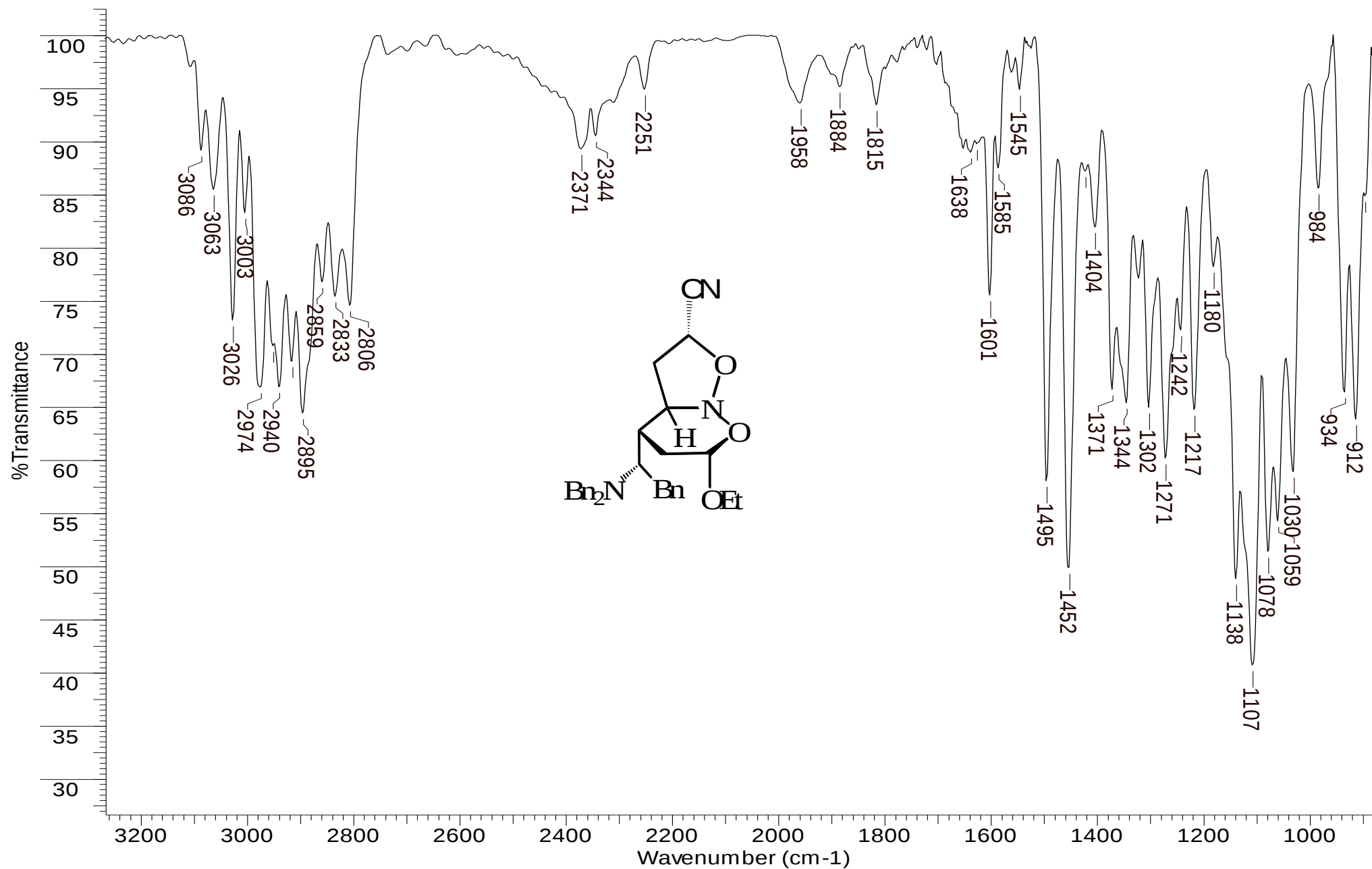
Spectrum 27 – 2D COSY of **10a'**



Spectrum 28 – HSQC of **10a'**

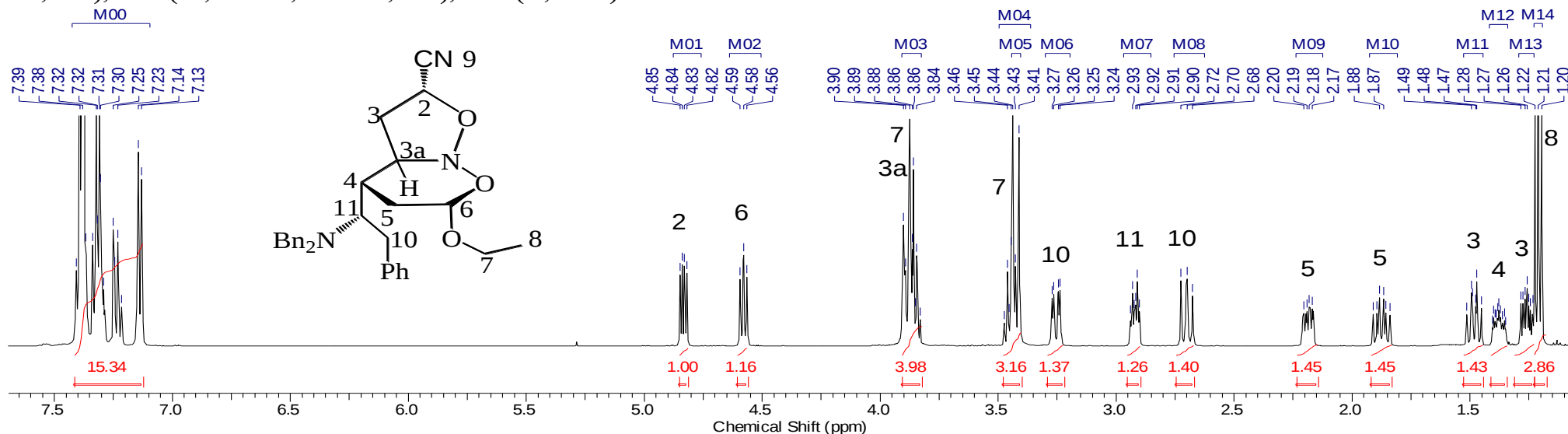


Spectrum 29 – 2D NOESY of **10a'**

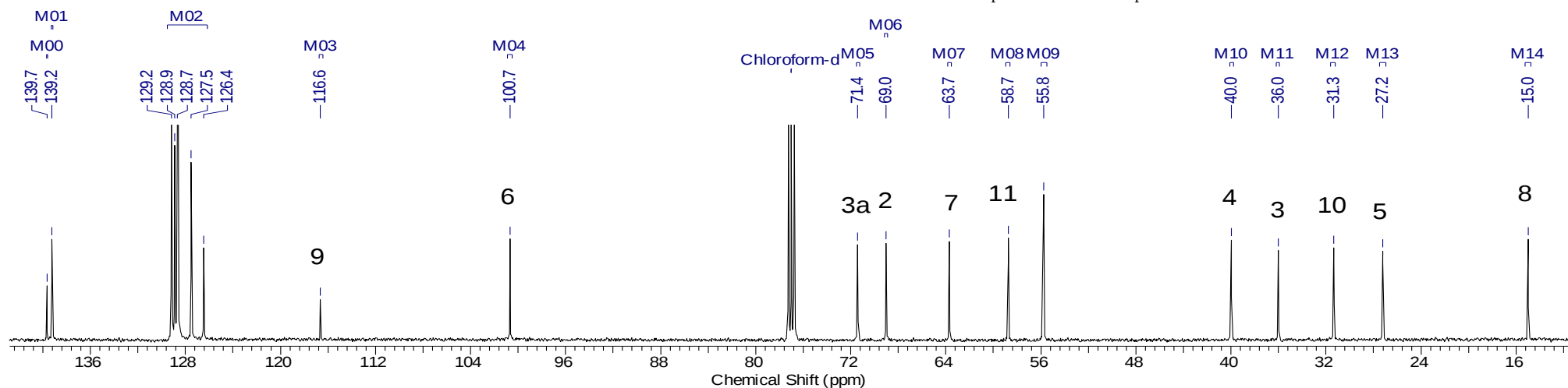


Spectrum 30 – Infrared of **11b**

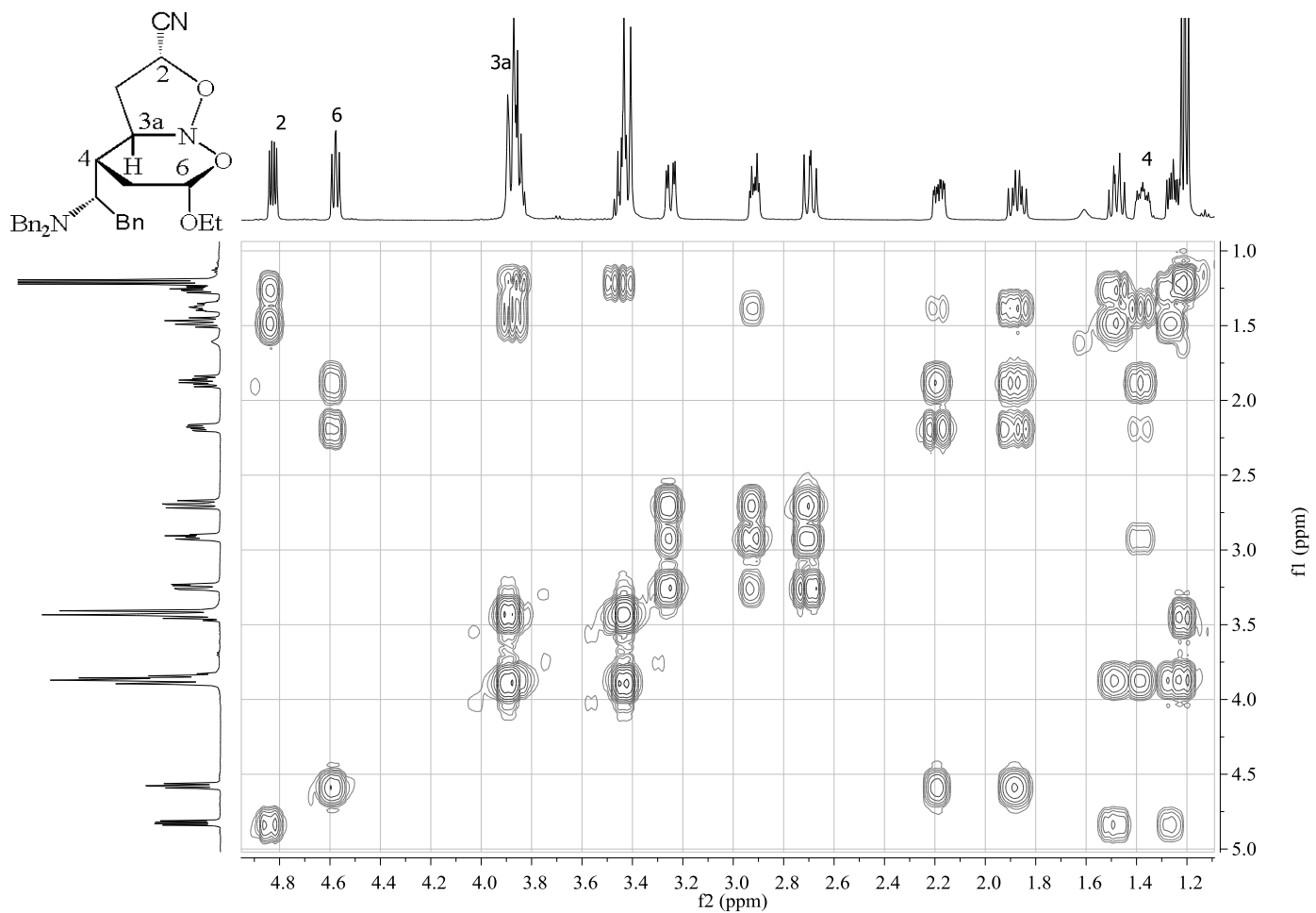
^1H NMR (500 MHz, CHCl_3 - d) δ ppm 1.21 (t, $J=7.09$ Hz, 3 H); 1.26 (ddd, $J=12.10, 8.44, 4.89$ Hz, 1 H); 1.38 (m, 1 H); 1.48 (ddd, $J=12.04, 9.38, 9.38$ Hz, 1 H); 1.88 (ddd, $J=13.63, 13.63, 8.44$ Hz, 1 H); 2.19 (ddd, $J=12.96, 6.48, 2.57$ Hz, 1 H); 2.70 (dd, $J=13.33, 10.88$ Hz, 1 H); 2.92 (ddd, $J=10.76, 3.91, 1$ H); 3.25 (dd, $J=13.45, 3.91$ Hz, 1 H); 3.44 (m, 1 H); 3.43 (d, $J=13.45$ Hz, 2 H); 3.86 (m, 4 H); 4.58 (dd, $J=8.31, 6.60$ Hz, 1 H); 4.83 (dd, $J=9.78, 4.89$ Hz, 1 H); 7.29 (m, 15 H)



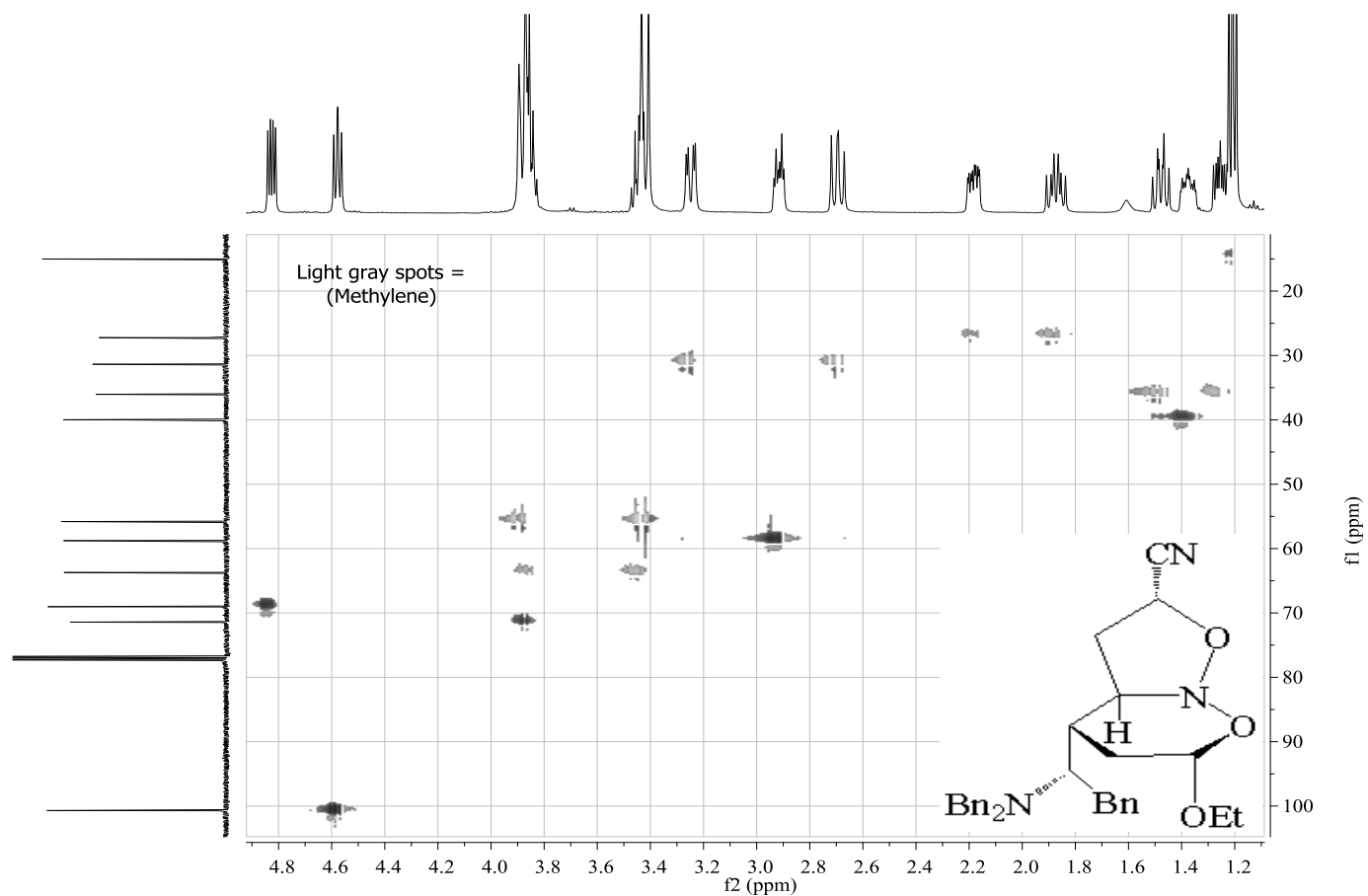
^{13}C NMR (126 MHz, CHCl_3 - d) δ ppm 15.0 (CH_3); 27.2 (CH_2); 31.3 (CH_2); 36.0 (CH_2); 40.0 (CH); 55.8 ($2 \times \text{CH}_2$); 58.7 (CH); 63.7 (CH_2); 69.0 (CH); 71.4 (CH); 100.7 (CH); 116.6 (CN); 126.4-129.2 (15 CH_{Ar}); 139.2 ($2 \times \text{C}_{\text{ipso}}$); 139.7 (C_{ipso})



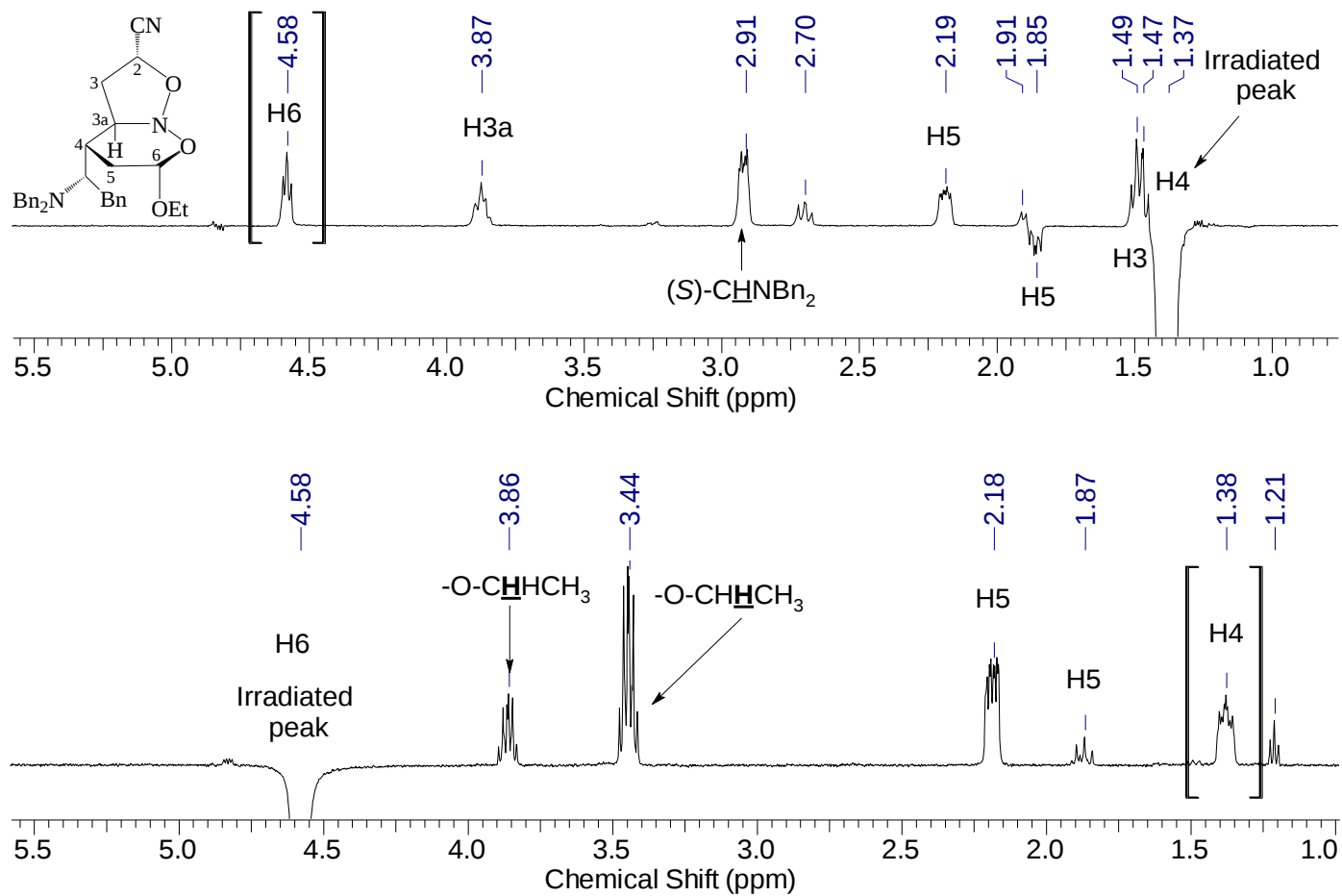
Spectrum 31 - ^1H and ^{13}C NMR of **11b**

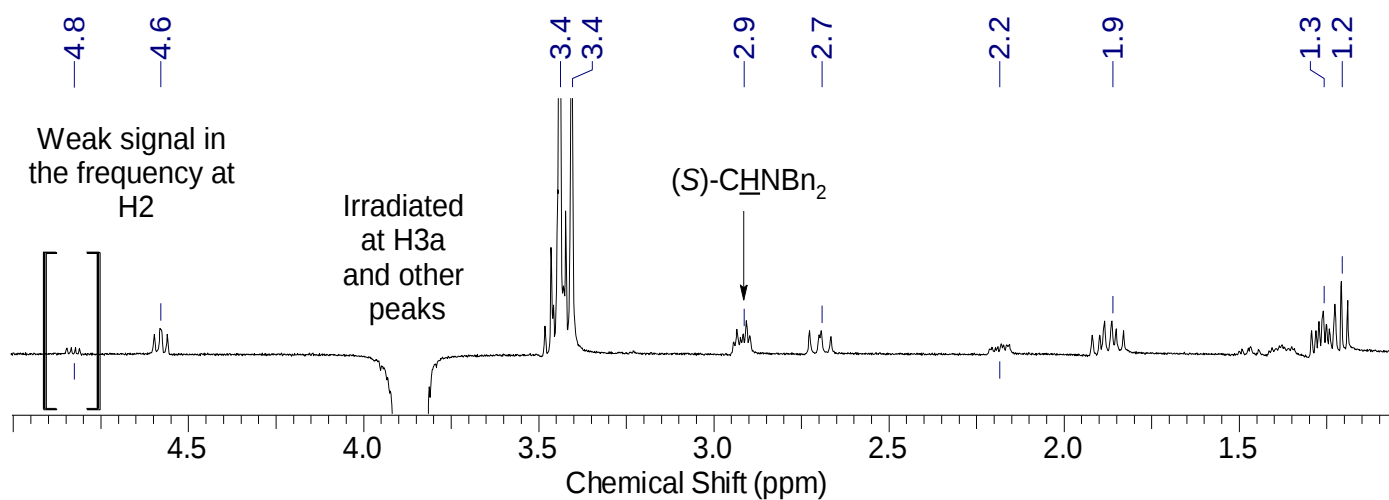
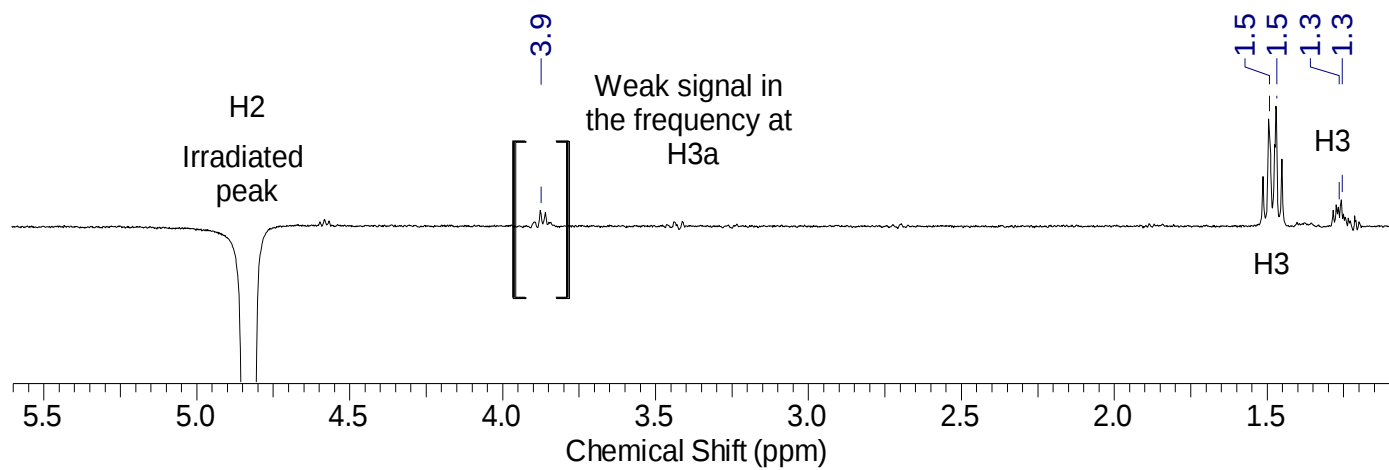


Spectrum 32 – 2D COSY of **11b**

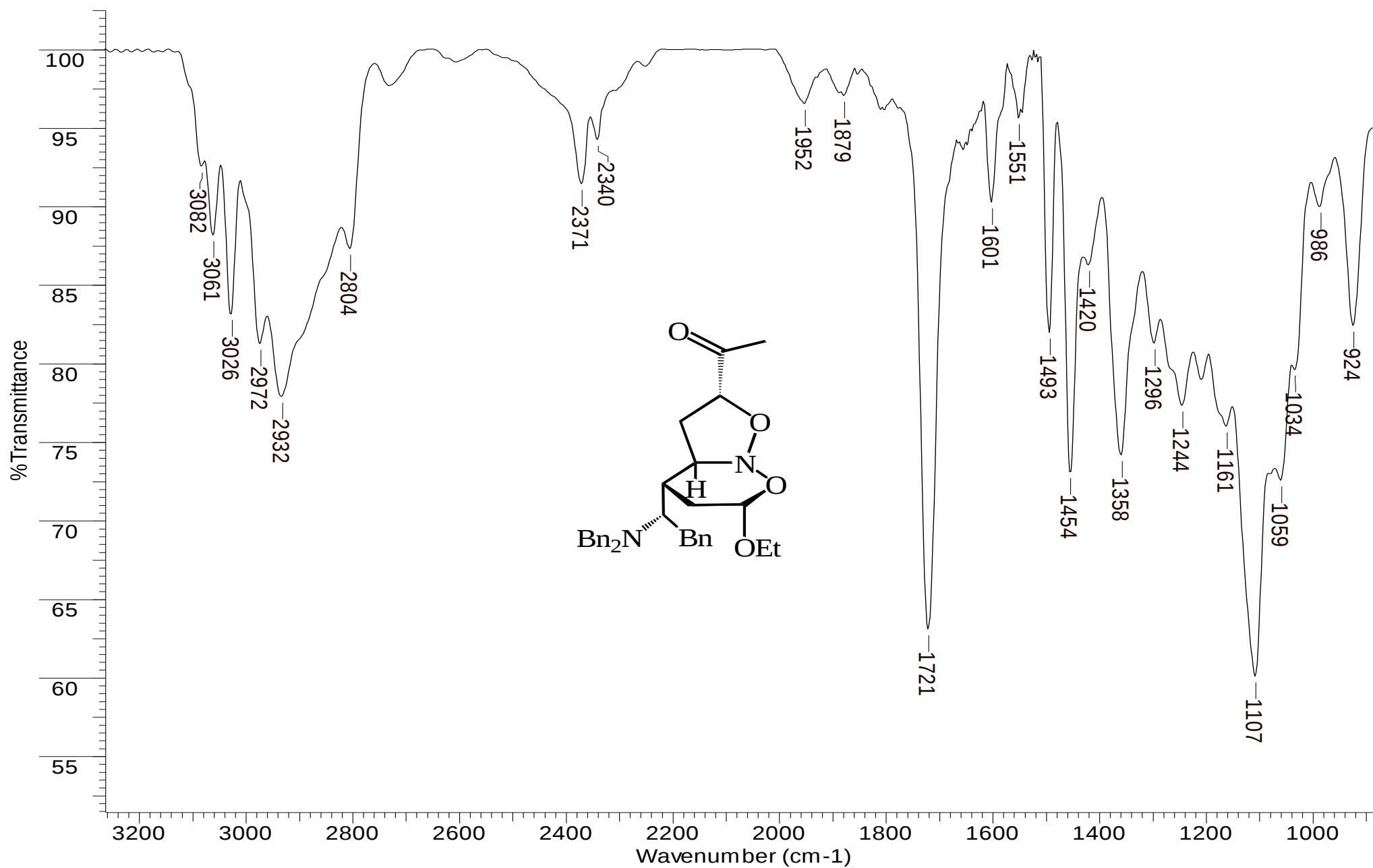


Spectrum 33 – HSQC of **11b**



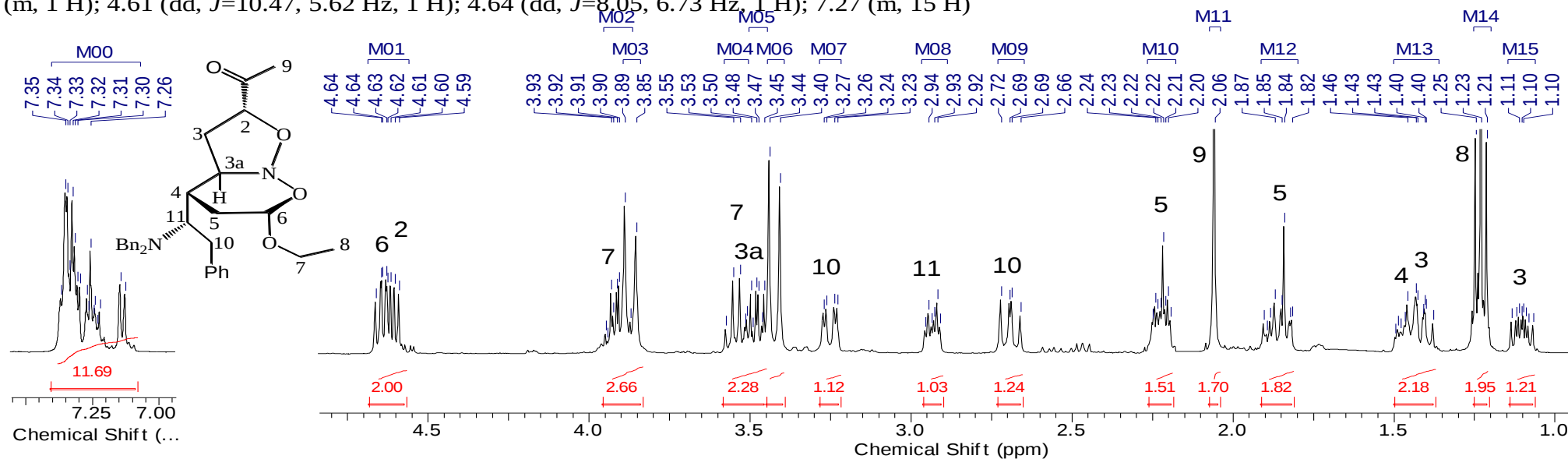


Spectrum 34 – 2D NOESY of **11b**

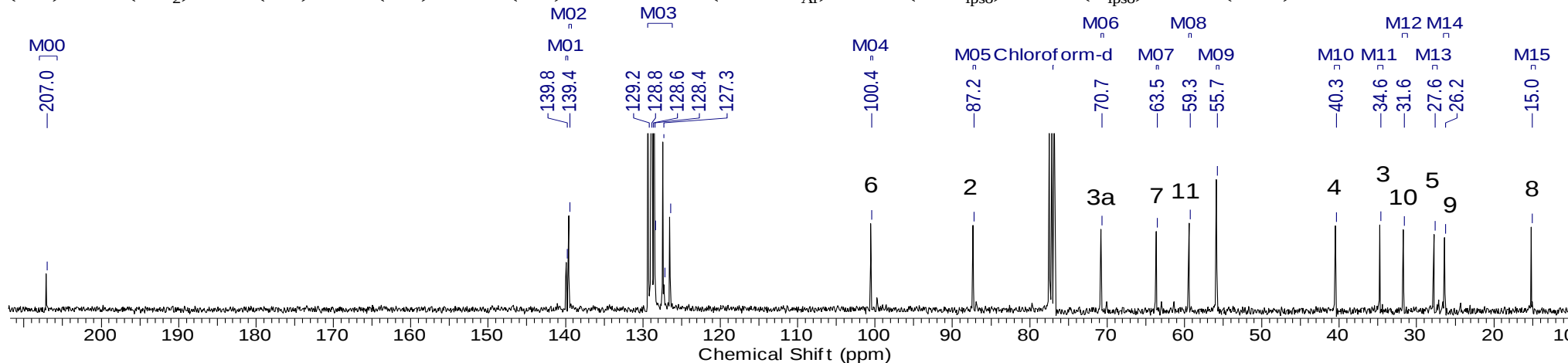


Spectrum 35 – Infrared of **12b**

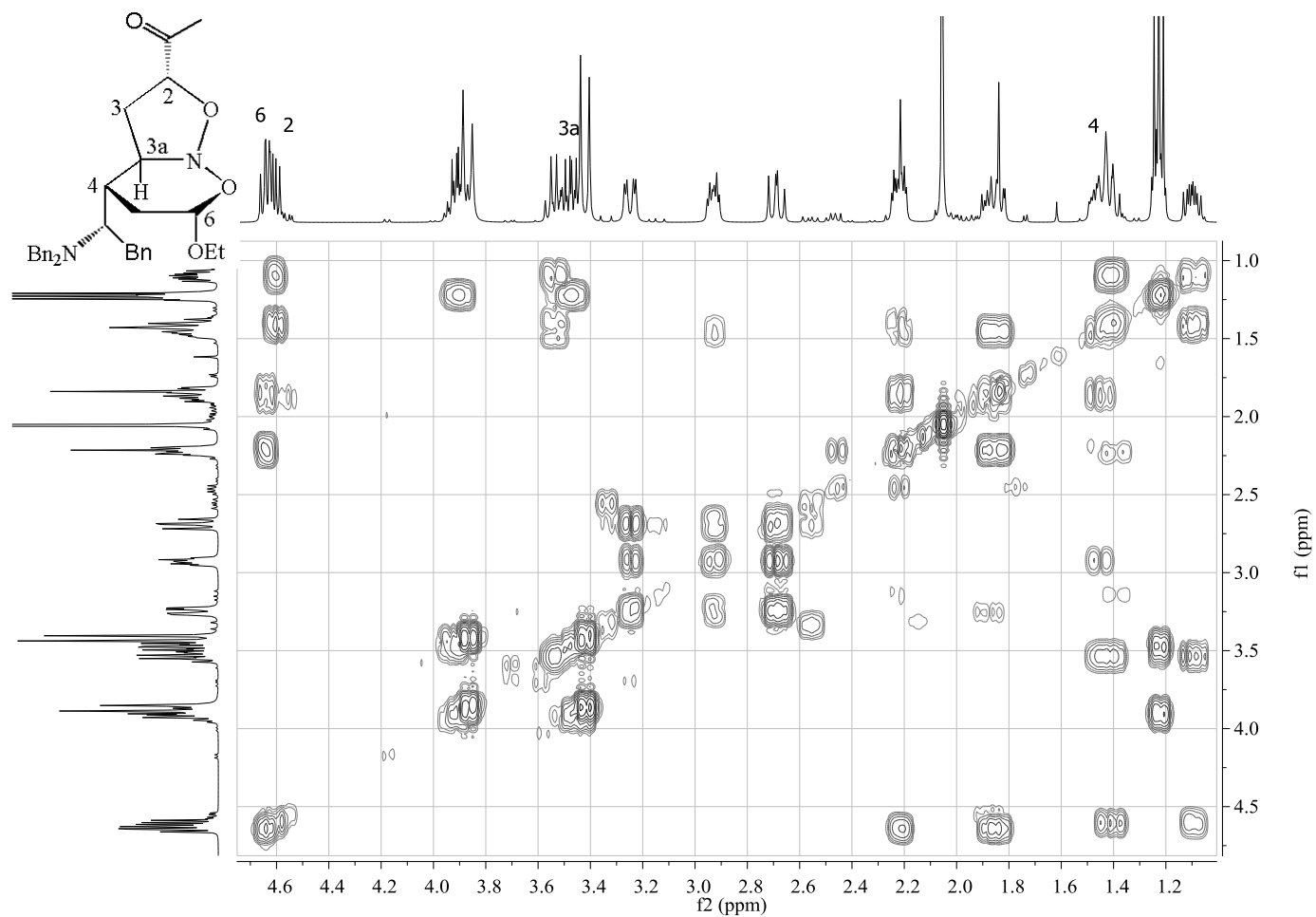
^1H NMR (400 MHz, CHCl_3 - d) δ ppm 1.10 (ddd, $J=12.18, 8.77, 5.73$ Hz, 1 H); 1.23 (t, $J=7.06$ Hz, 3 H); 1.42 (m, 1 H); 1.47 (m, 1 H); 1.86 (m, 1 H); 2.06 (s, 3 H); 2.22 (ddd, $J=12.84, 6.23, 2.98$ Hz, 1 H); 2.69 (dd, $J=13.45, 10.80$ Hz, 1 H); 2.93 (ddd, $J=10.69, 3.86, 3.75$ Hz, 1 H); 3.25 (dd, $J=13.45, 3.75$ Hz, 1 H); 3.42 (d, $J=13.45$ Hz, 2 H); 3.47 (ddd, $J=7.06, 7.06, 2.43$ Hz, 1 H); 3.54 (m, 1 H); 3.87 (d, $J=13.89$ Hz, 2 H); 3.91 (m, 1 H); 4.61 (dd, $J=10.47, 5.62$ Hz, 1 H); 4.64 (dd, $J=8.05, 6.73$ Hz, 1 H); 7.27 (m, 15 H)



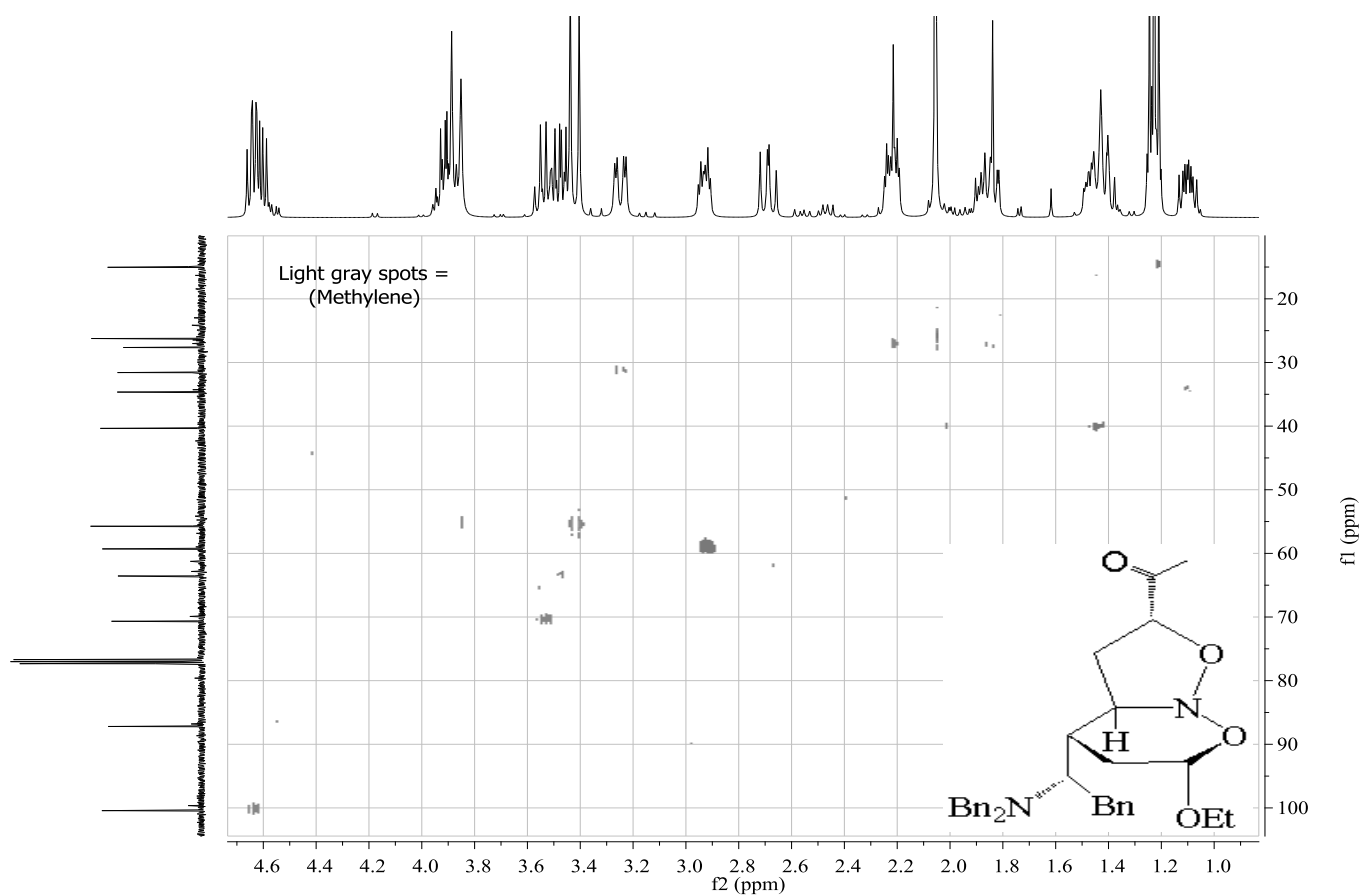
^{13}C NMR (101 MHz, CHCl_3 - d) δ ppm 15.0 (CH_3); 26.2 (CH_3); 27.6 (CH_2); 31.6 (CH_2); 34.6 (CH_2); 40.3 (CH); 55.7 (2x CH_2); 59.3 (CH); 63.5 (CH_2); 70.7 (CH); 87.2 (CH); 100.4 (CH); 126.4-129.2 (15x CH_{Ar}); 139.4 (2x C_{ipso}); 139.8 (C_{ipso}); 207.0 ($\text{C}=\text{O}$)



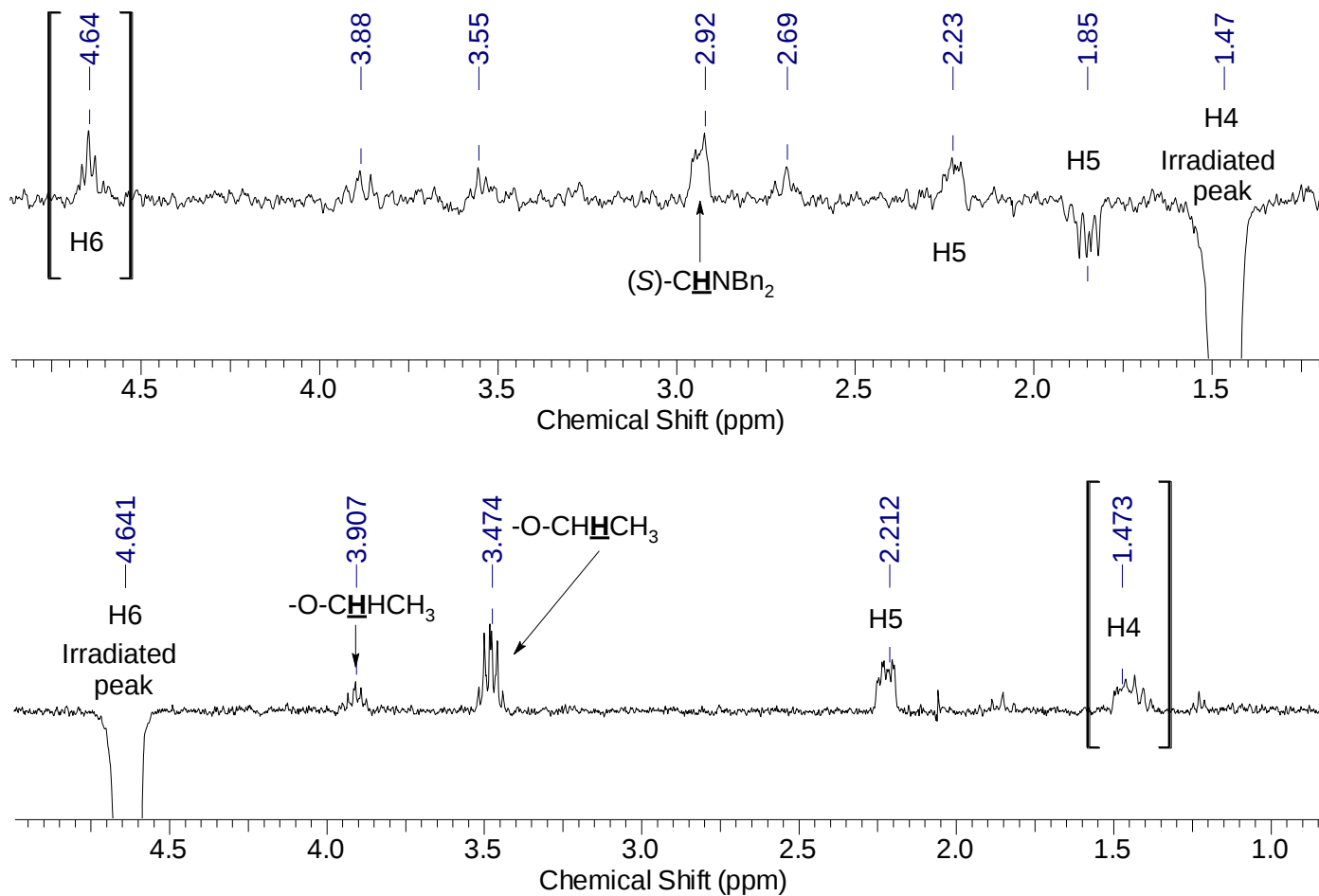
Spectrum 36 - ^1H and ^{13}C NMR of **12b**

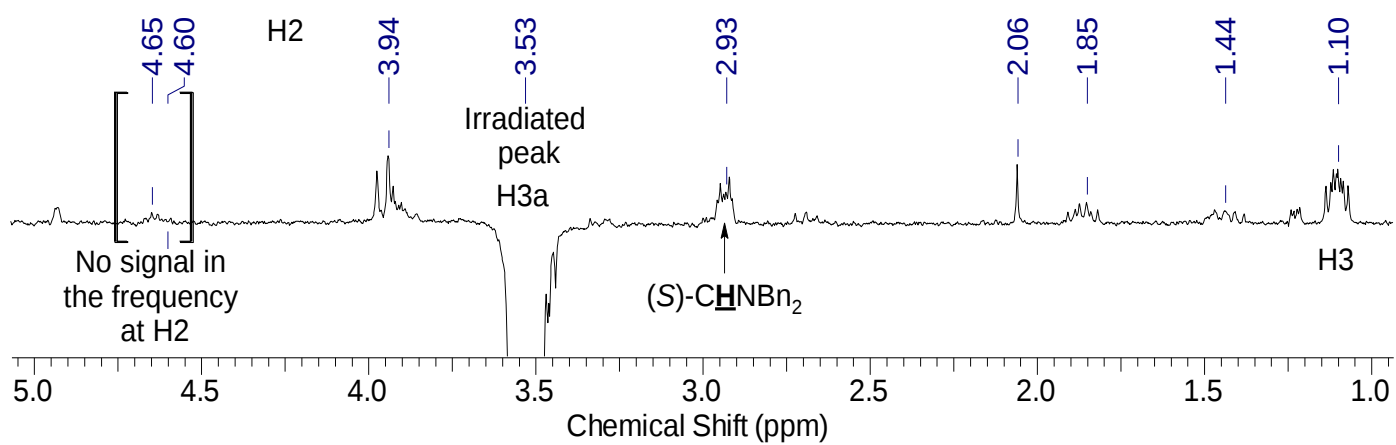
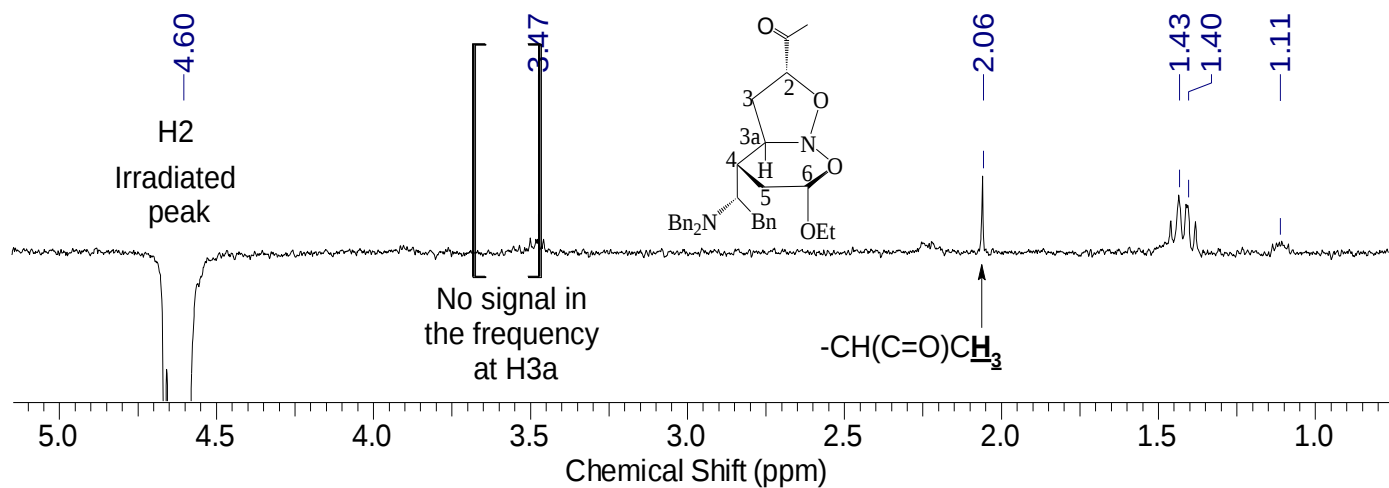


Spectrum 37 – 2D COSY of **12b**

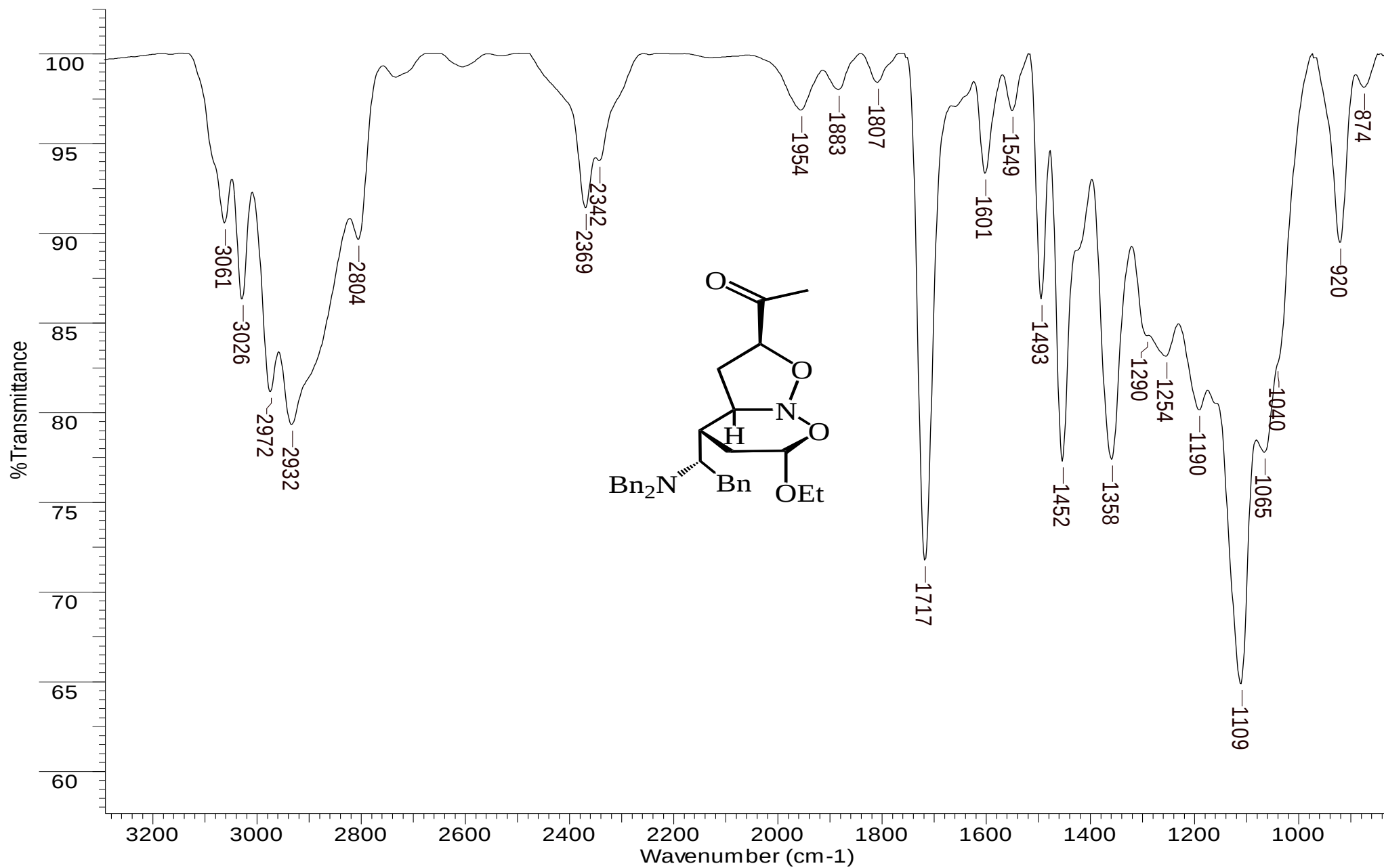


Spectrum 38 – HSQC of **12b**



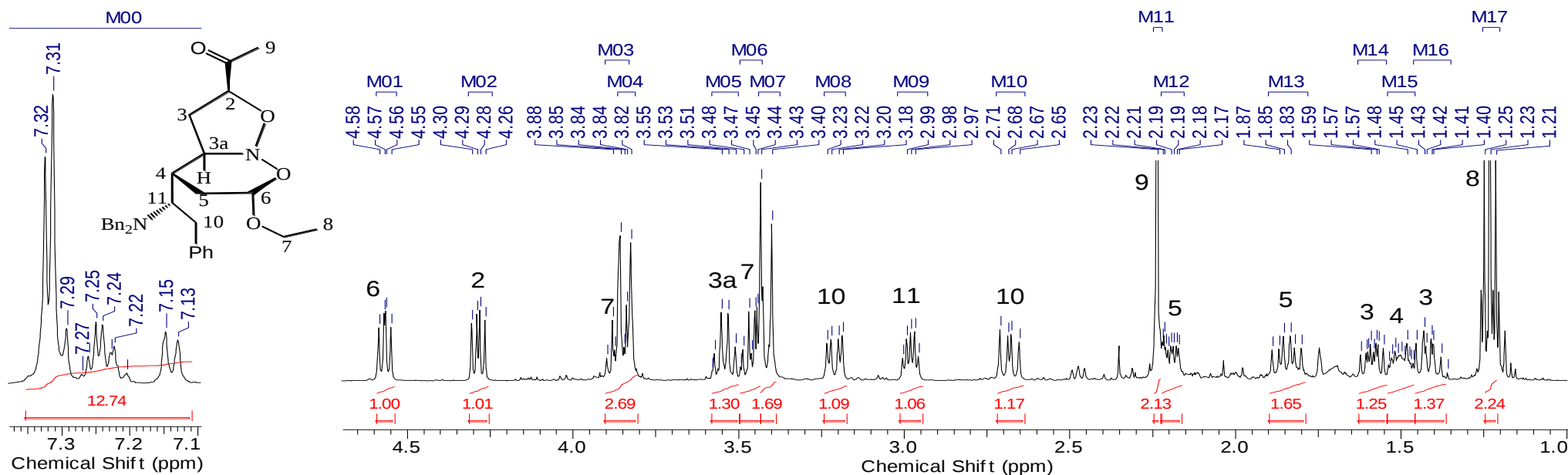


Spectrum 39 – 2D NOESY of **12b**

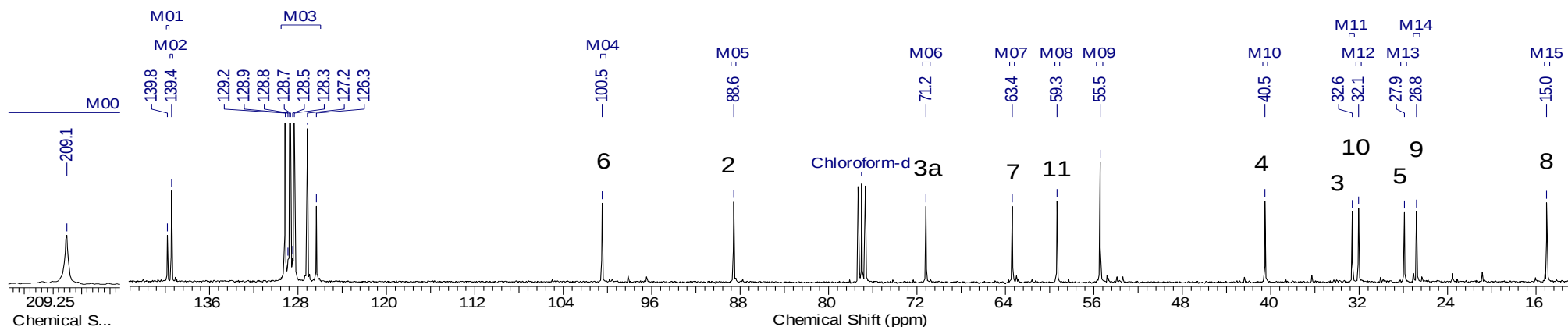


Spectrum 40 – Infrared of **12b'**

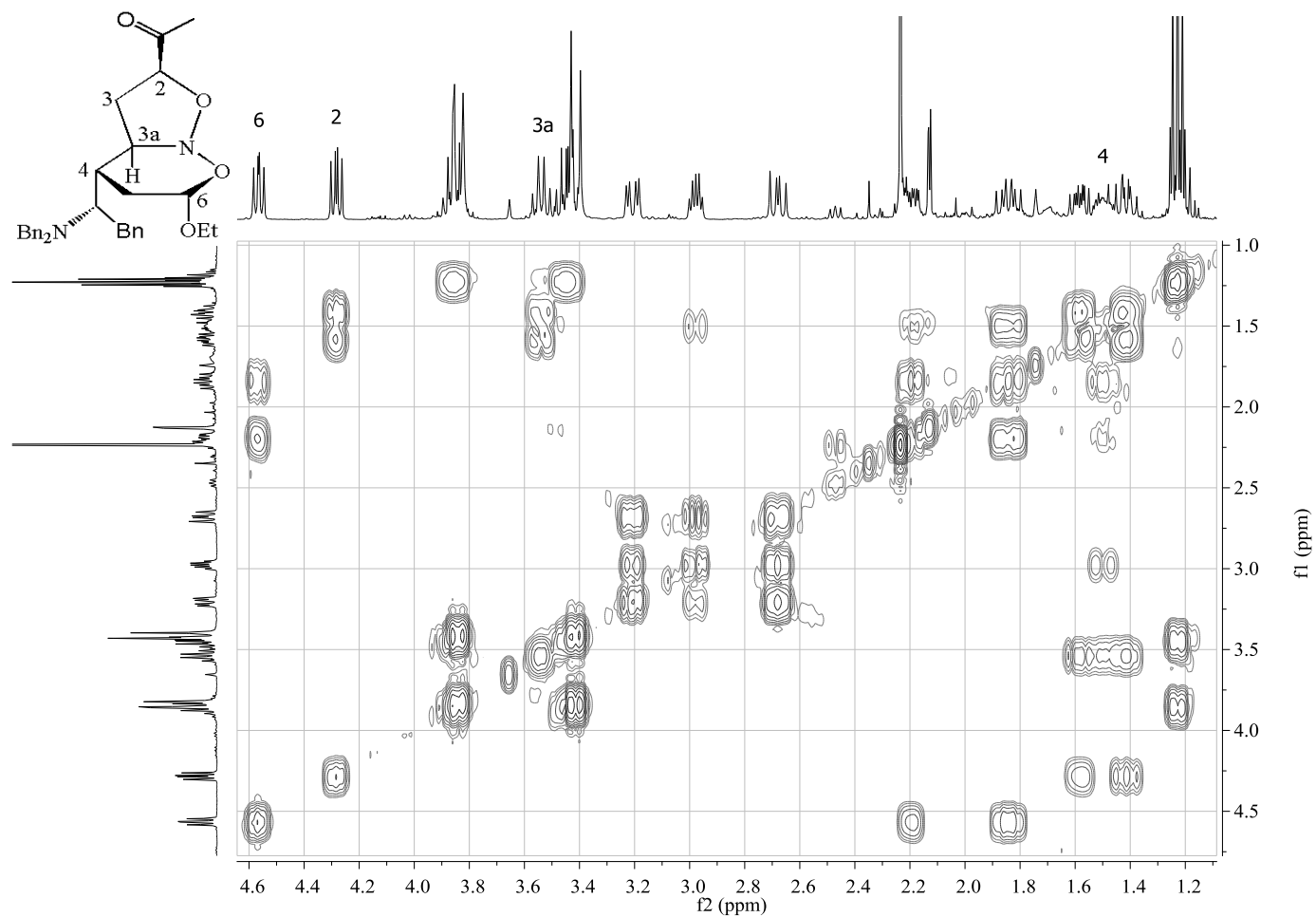
^1H NMR (400 MHz, CHCl_3 - d) δ ppm 1.23 (t, $J=7.06$ Hz, 3 H); 1.42 (m, 1 H); 1.49 (m, 1 H); 1.58 (ddd, $J=12.02, 9.04, 6.51$ Hz, 1 H); 1.84 (ddd, $J=13.51, 13.51, 8.27$ Hz, 1 H); 2.20 (m, 1 H); 2.23 (s, 3 H); 2.68 (dd, $J=13.67, 9.70$ Hz, 1 H); 2.98 (ddd, $J=9.54, 4.82$ Hz, 1 H); 3.21 (dd, $J=13.78, 4.74$ Hz, 1 H); 3.41 (d, $J=13.45$ Hz, 2 H); 3.46 (m, 1 H); 3.55 (m, 1 H); 3.84 (d, $J=12.57$ Hz, 2 H); 3.86 (m, 1 H); 4.28 (dd, $J=9.70, 6.39$ Hz, 1 H); 4.56 (dd, $J=8.27, 6.50$ Hz, 1 H); 7.24 (m, 15 H)



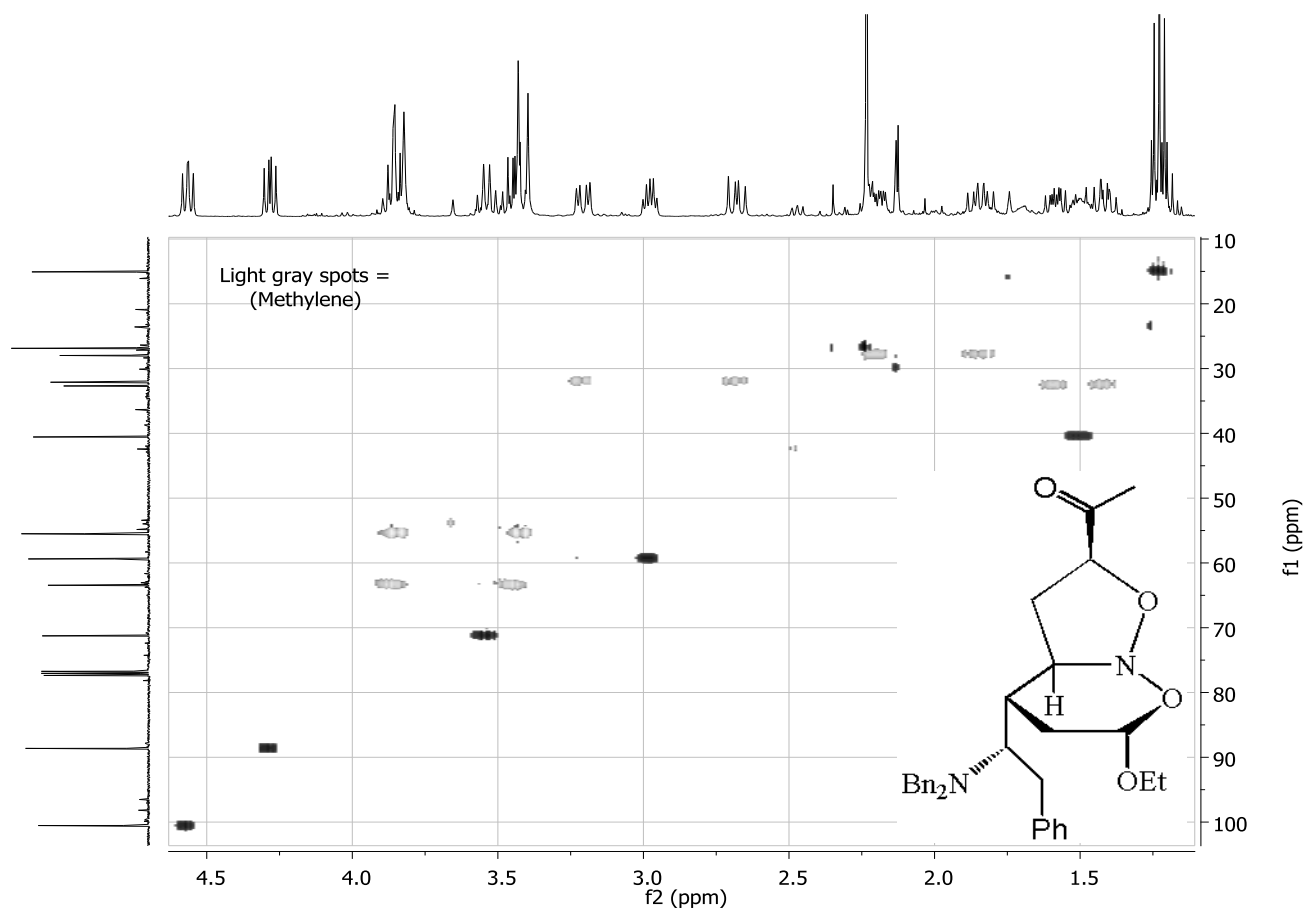
^{13}C NMR (101 MHz, CHCl_3 - d) δ ppm 15.0 (CH_3); 26.8 (CH_3); 27.9 (CH_2); 32.1 (CH_2); 32.6 (CH_2); 40.5 (CH); 55.5 (2x CH_2); 59.3 (CH); 63.4 (CH_2); 71.2 (CH); 88.6 (CH); 100.5 (CH); 126.2-129.3 (15x CH_{Ar}); 139.4 (2x C_{ipso}); 139.8 (C_{ipso}); 209.1 ($\text{C}=\text{O}$)



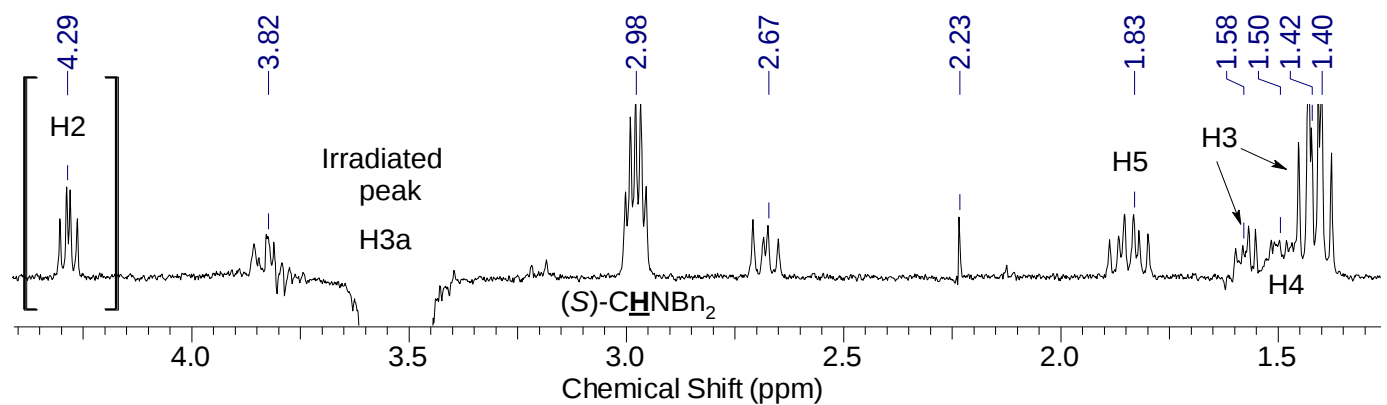
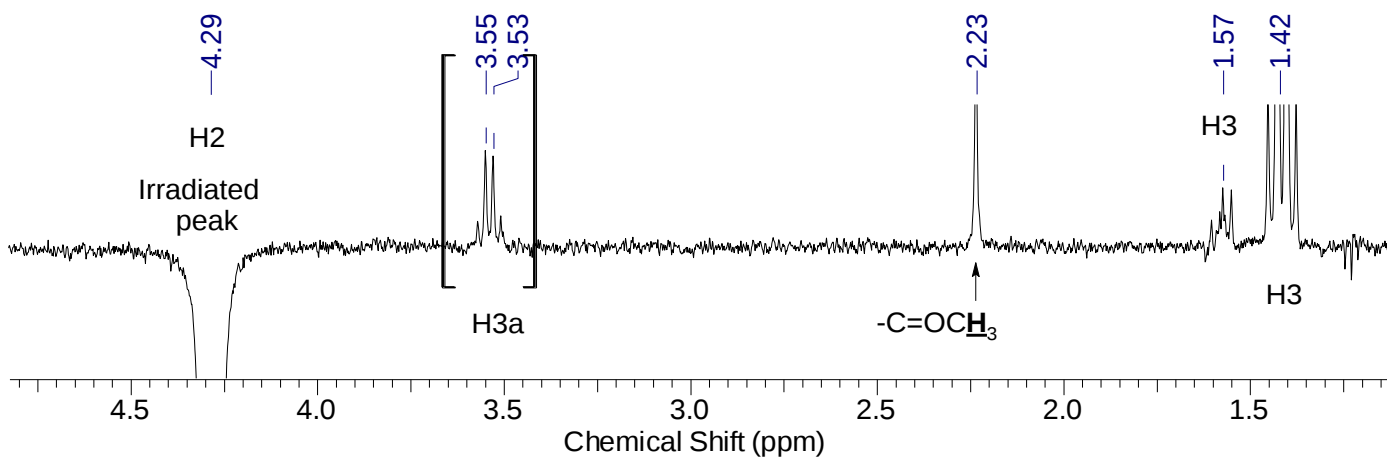
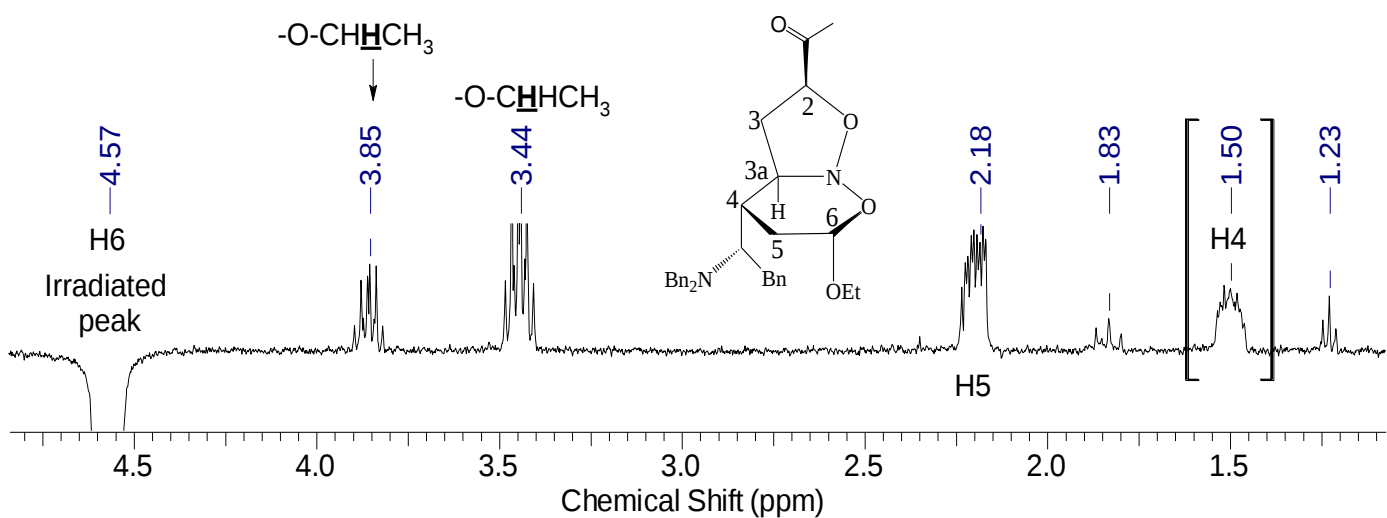
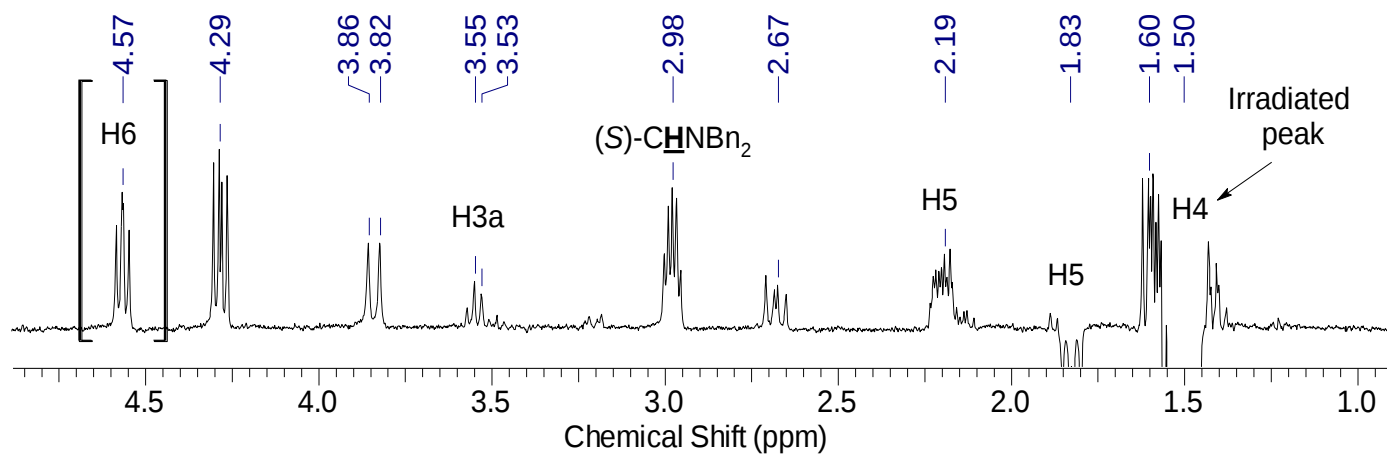
Spectrum 41 - ^1H and ^{13}C NMR of **12b'**



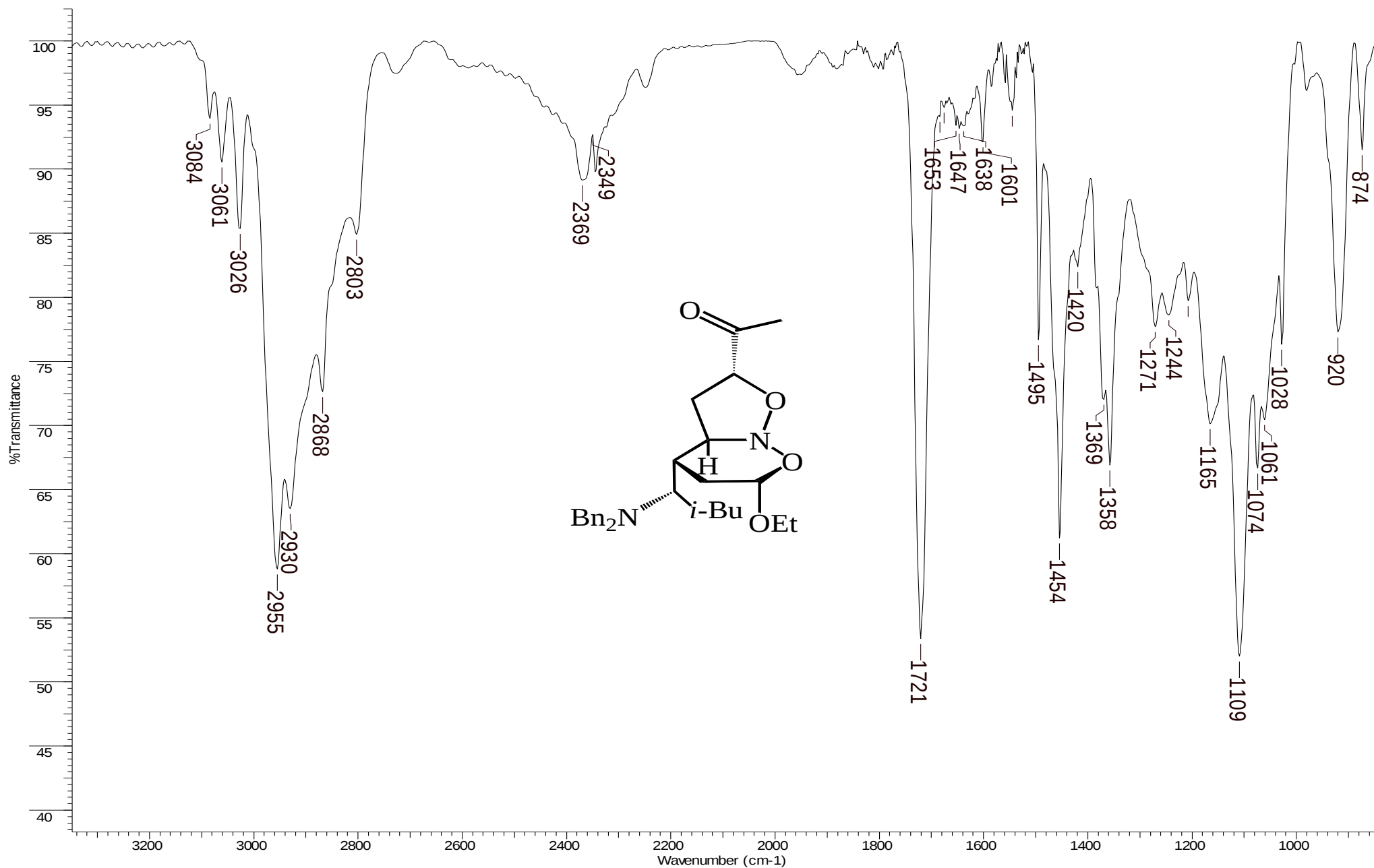
Spectrum 42 – 2D COSY of **12b'**



Spectrum 43 – HSQC of **12b'**

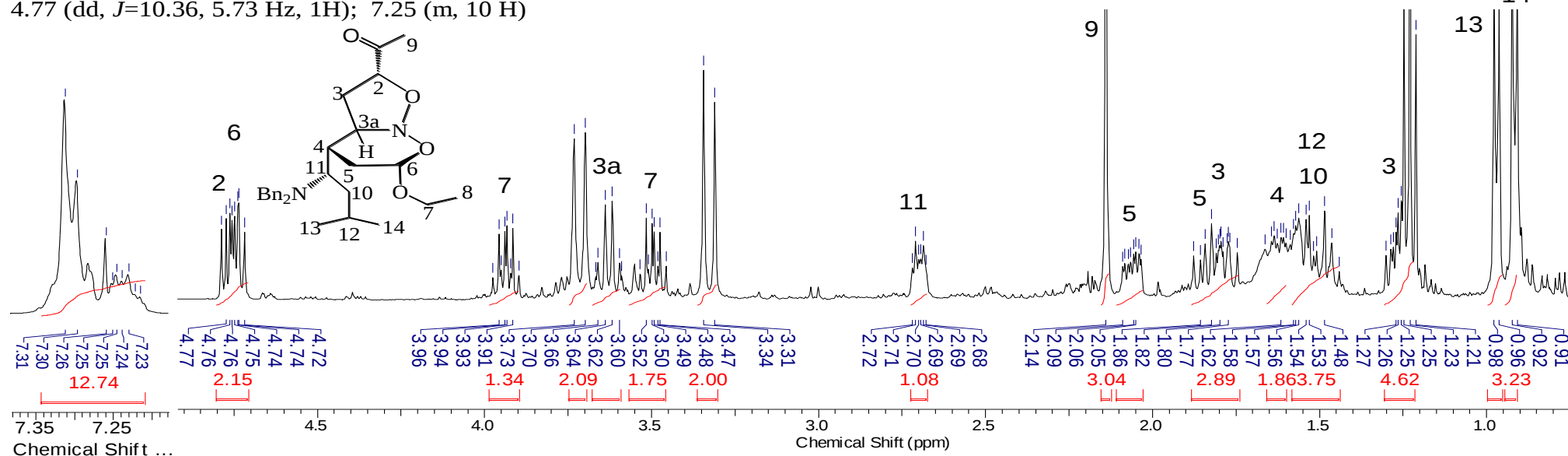


Spectrum 44 – 2D NOESY of **12b'**

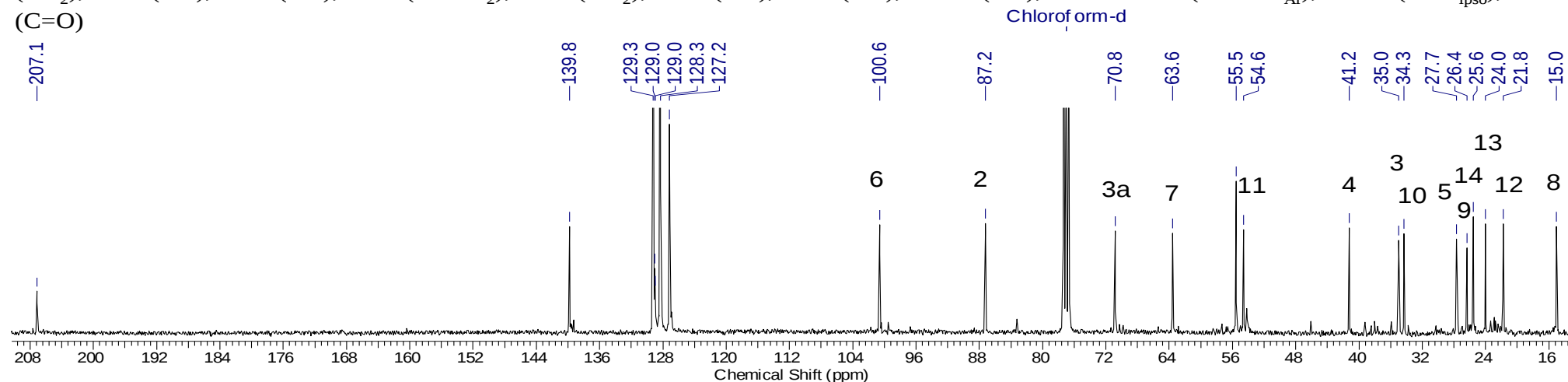


Spectrum 45 – Infrared of **13c**

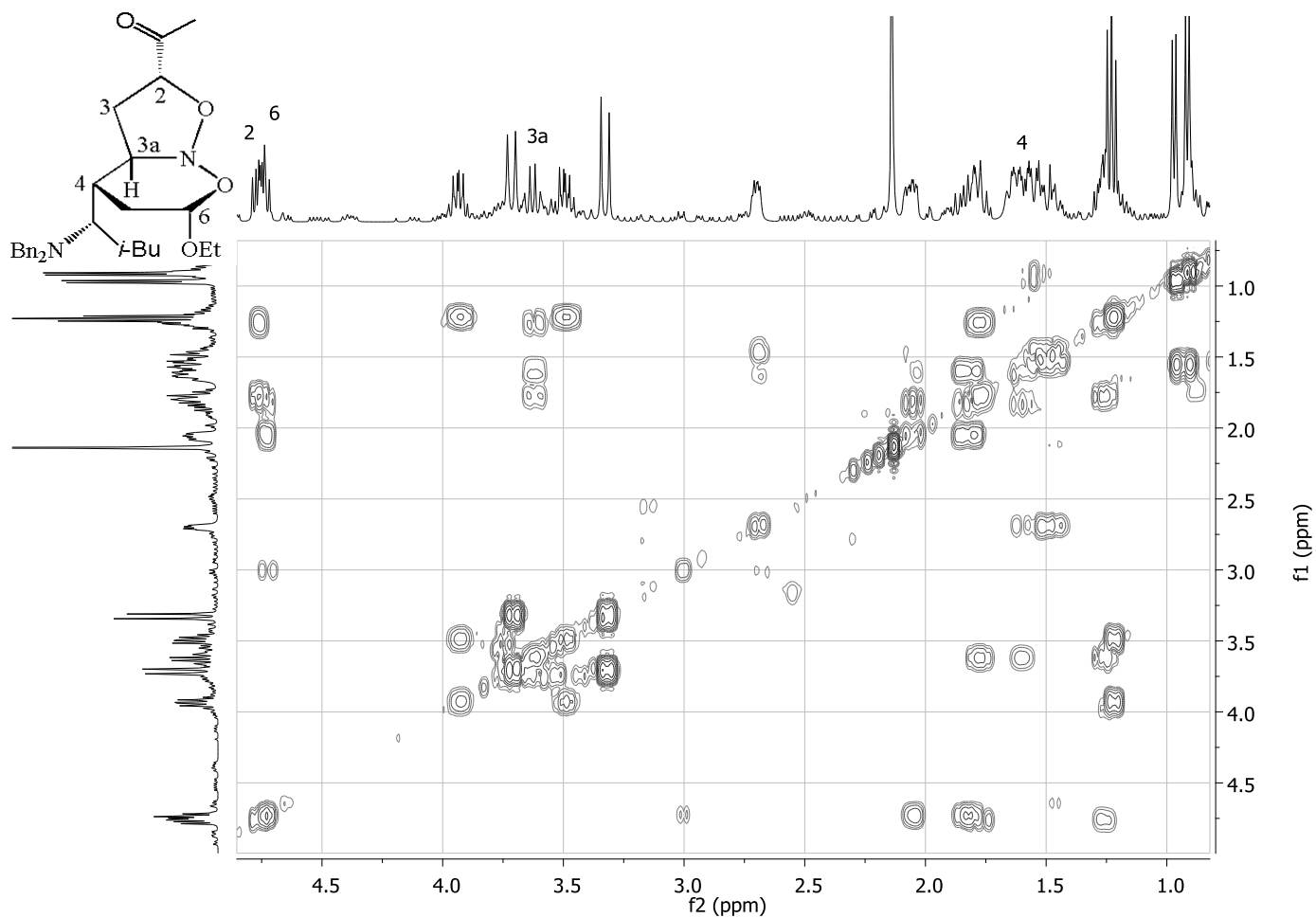
^1H NMR (400 MHz, CHLOROFORM-D) δ ppm 0.92 (d, $J=5.95$ Hz, 3 H); 0.97 (d, $J=5.95$ Hz, 3 H); 1.23 (t, $J=7.17$ Hz, 3 H); 1.27 (m, 1 H); 1.51 (m, 3 H); 1.61 (m, 1 H); 1.78 (m, 1 H); 1.85 (m, 1 H); 2.06 (ddd, $J=12.84, 6.67, 2.54$ Hz, 1 H); 2.14 (s, 3 H); 2.70 (m, 1 H); 3.33 (d, $J=13.45$ Hz, 2 H); 3.50 (m, 1 H); 3.63 (m, 1 H); 3.72 (d, $J=13.23$ Hz, 2 H); 3.94 (m, $J=14.22, 9.59, 7.06$ Hz, 1 H); 4.73 (dd, $J=7.94, 6.84$ Hz, 1H); 8.47 (dd, $J=10.36, 5.73$ Hz, 1H); 7.25 (m, 10 H)



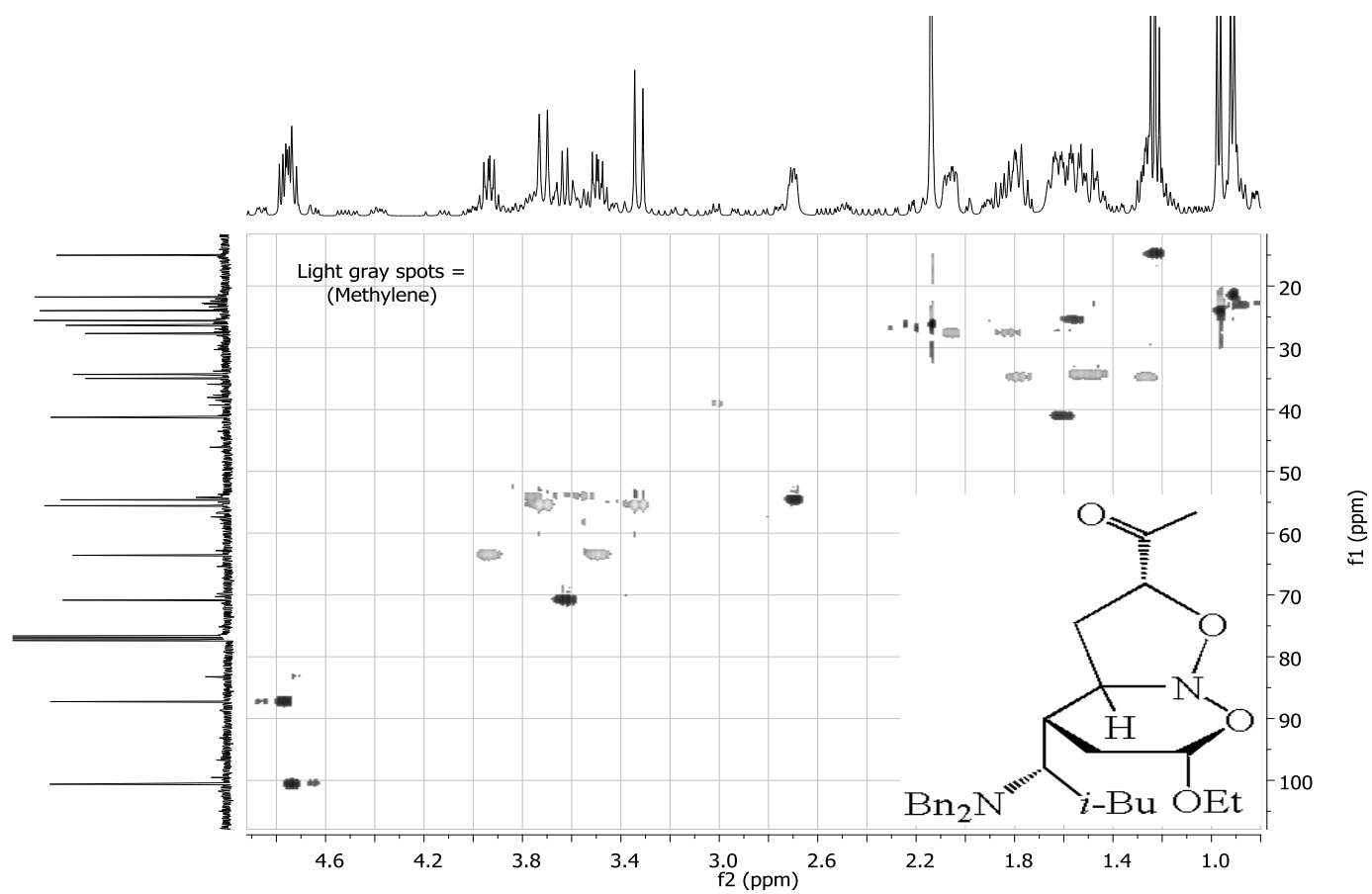
^{13}C NMR (101 MHz, CHLOROFORM-D) δ ppm 15.0 (CH_3); 21.8 (CH); 24.0 (CH_3); 25.6 (CH_3); 26.4 (CH_3); 27.7 (CH_2); 34.3 (CH_2); 35.0 (CH_2); 41.2 (CH); 54.6 (CH); 55.5 (2x CH_2); 63.6 (CH_2); 70.8 (CH); 87.2 (CH); 100.6 (CH); 127.2-129.3 (10x CH_{Ar}); 139.8 (2x C_{ipso}); 207.1 ($\text{C}=\text{O}$)



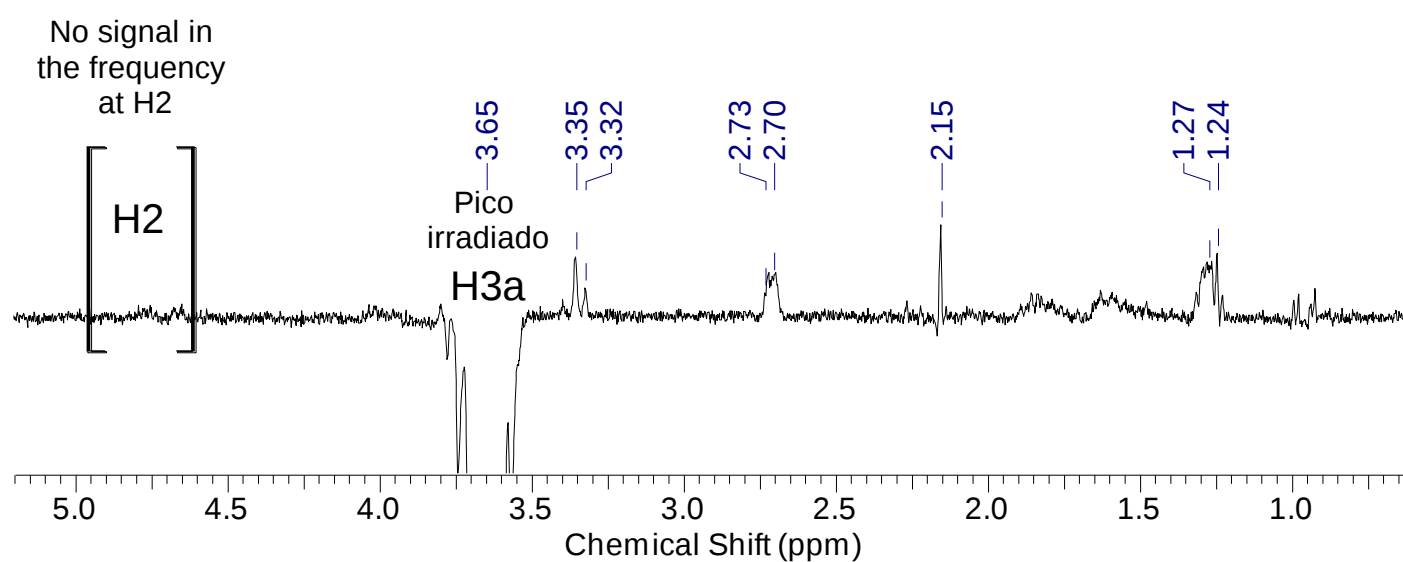
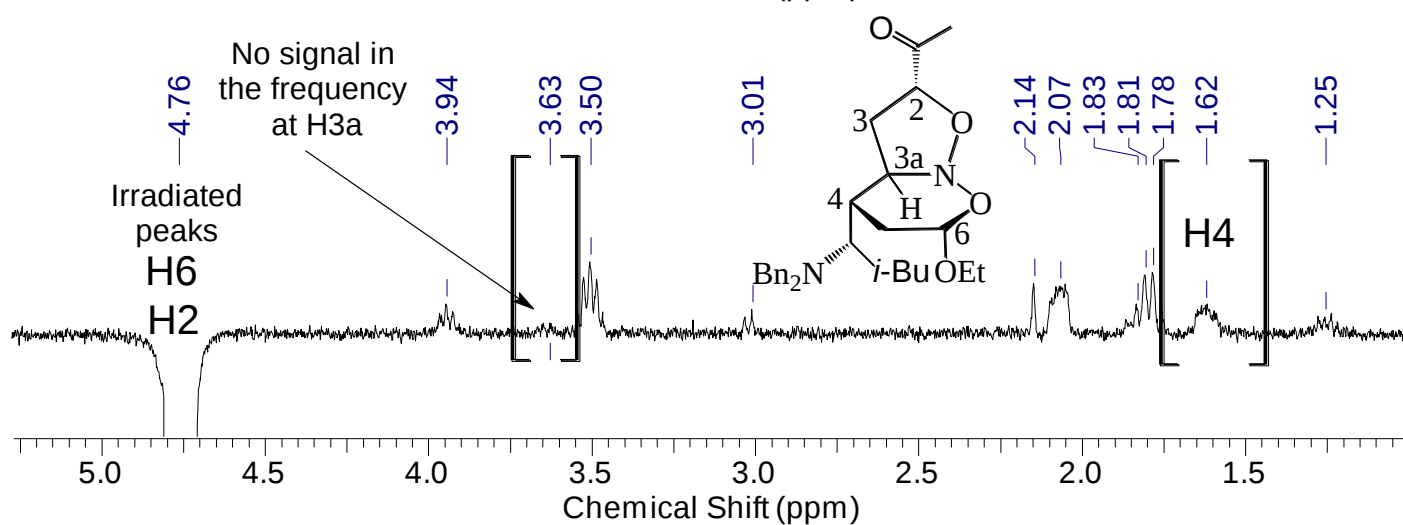
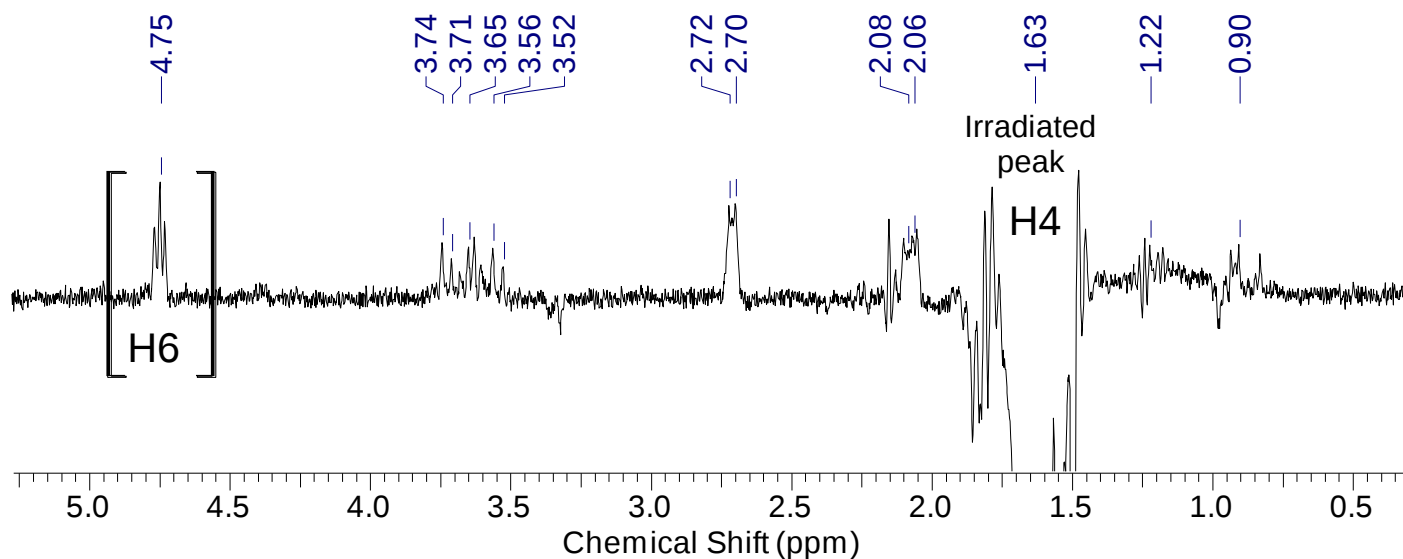
Spectrum 46 - ^1H and ^{13}C NMR of 13c



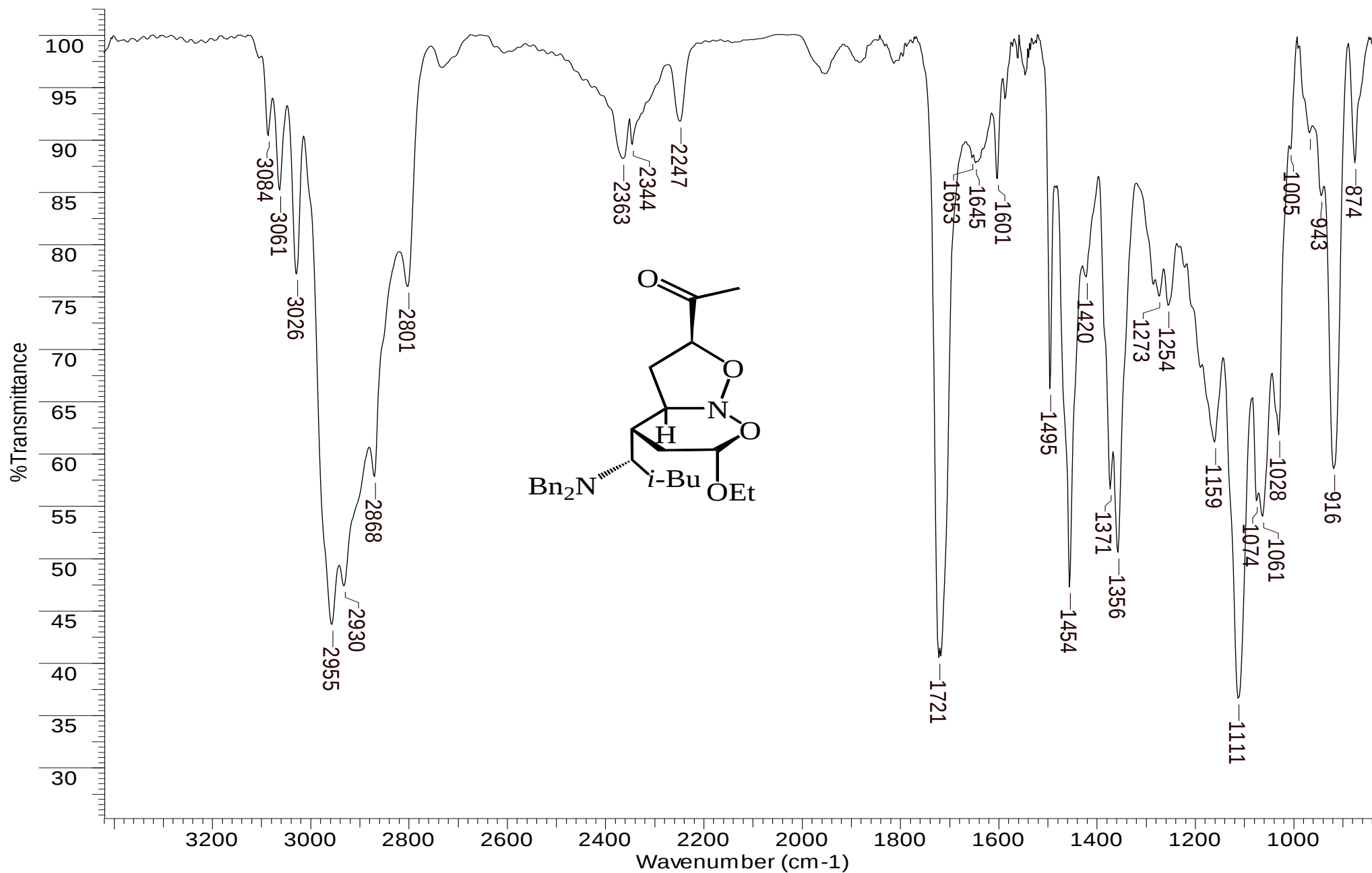
Spectrum 47 – 2D COSY of **13c**



Spectrum 48 – HSQC of **13c**

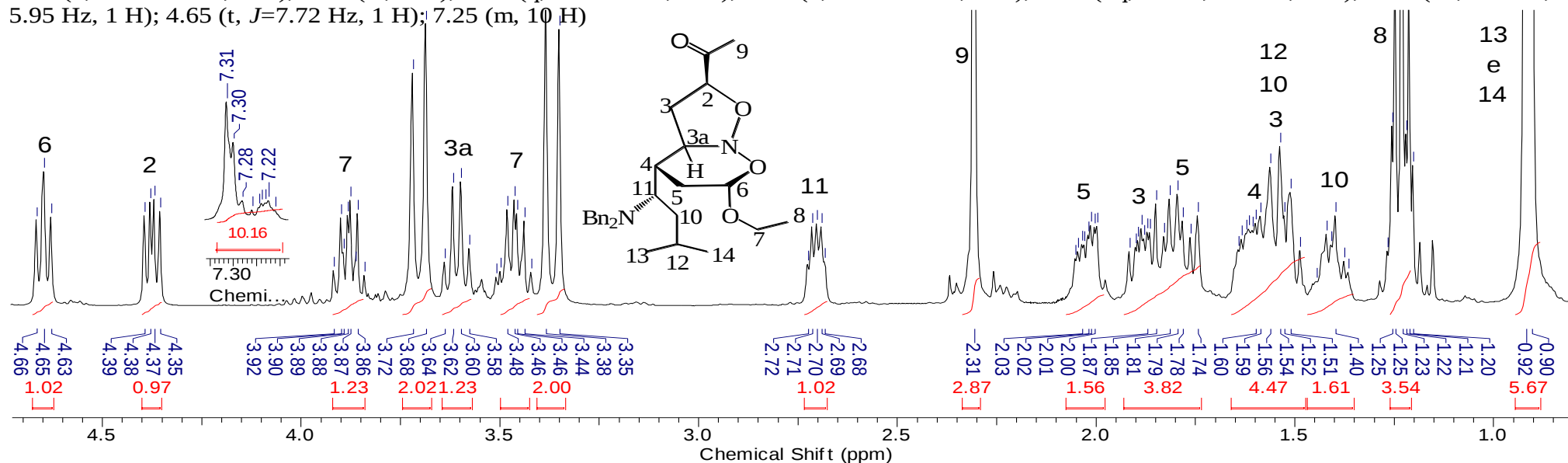


Spectrum 49 – 2D NOESY of **13c**

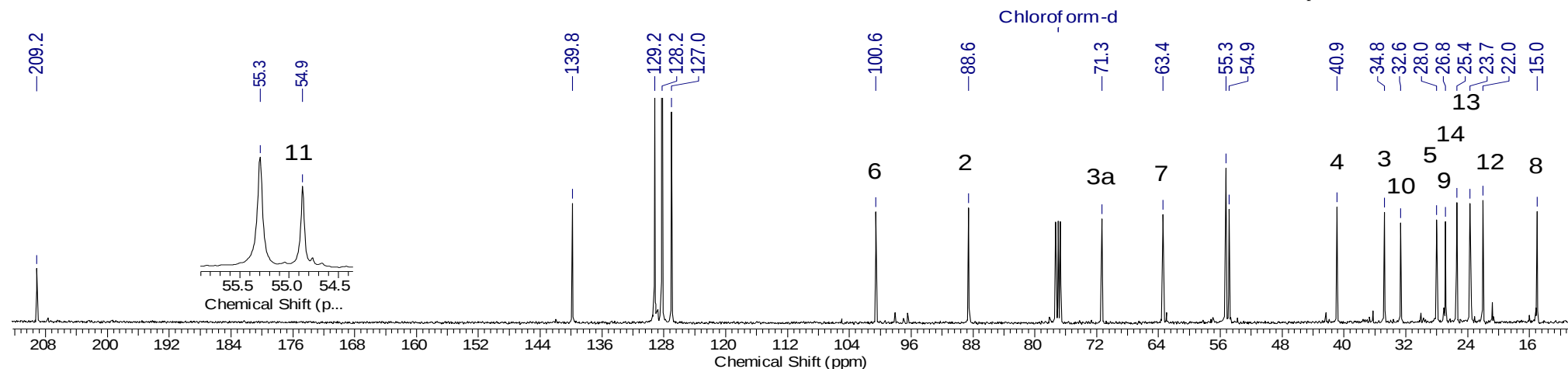


Spectrum 50 – Infrared of **13c'**

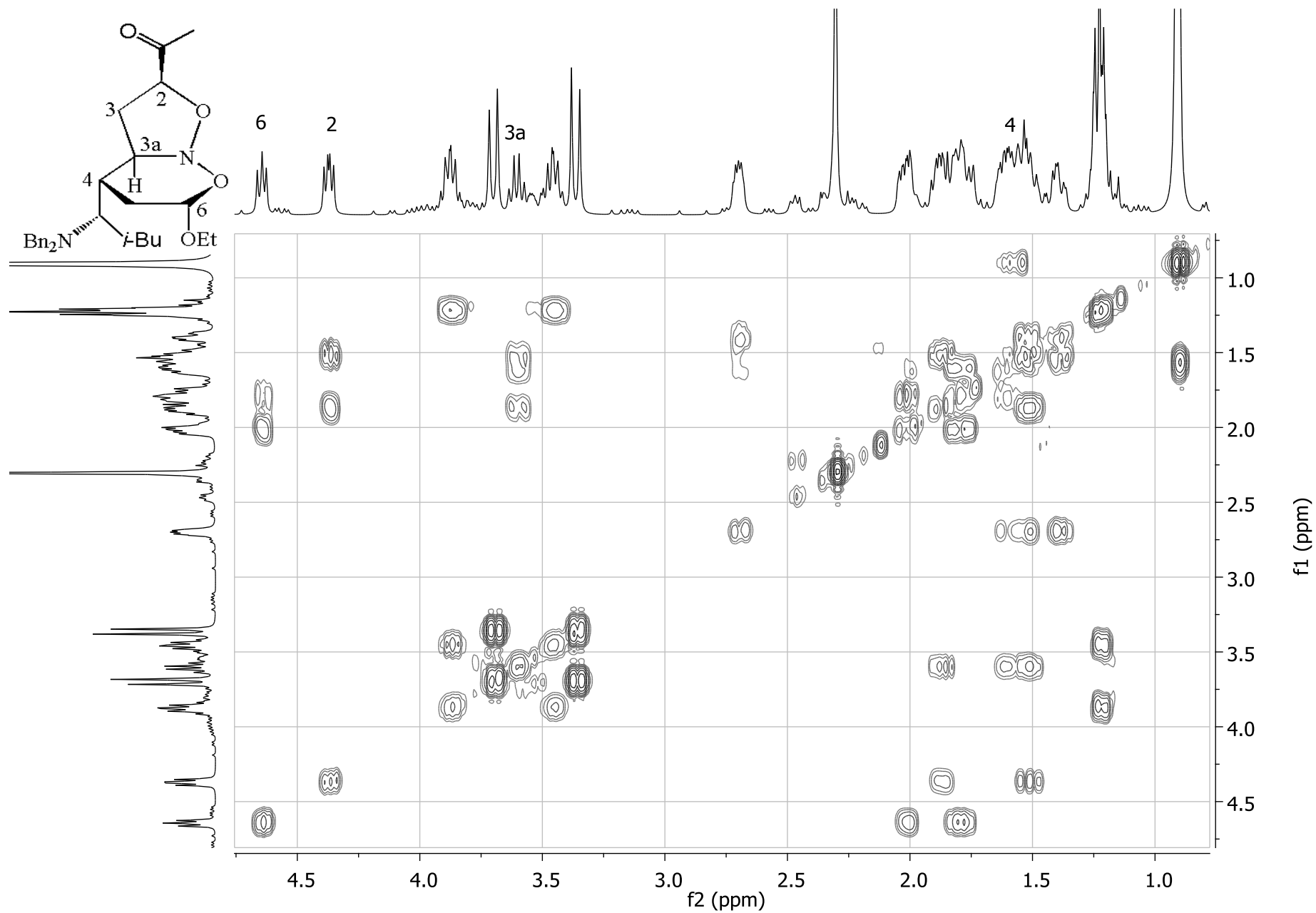
^1H NMR (400 MHz, CHLOROFORM-D) δ ppm 0.91 (d, $J=5.95$ Hz, 6 H); 1.23 (t, $J=7.06$ Hz, 3 H); 1.40 (m, 1 H); 1.52 (m, 3 H); 1.61 (m, 1 H); 1.79 (m, 1 H); 1.88 (ddd, $J=12.02, 8.49, 6.17$ Hz, 1 H); 2.02 (ddd, $J=12.79, 6.39, 2.65$ Hz, 1 H); 2.31 (s, 3 H); 2.70 (ddd, $J=8.9, 4.2, 3.8$ Hz, 1 H); 3.37 (d, $J=13.45$ Hz, 2 H); 3.47 (m, 1 H); 3.61 (q, $J=8.45$ Hz, 1 H); 3.70 (d, $J=13.23$ Hz, 2 H); 3.88 (dq, $J=9.6, 7.1$ Hz, 1 H); 4.37 (dd, $J=9.70, 5.95$ Hz, 1 H); 4.65 (t, $J=7.72$ Hz, 1 H); 7.25 (m, 10 H)



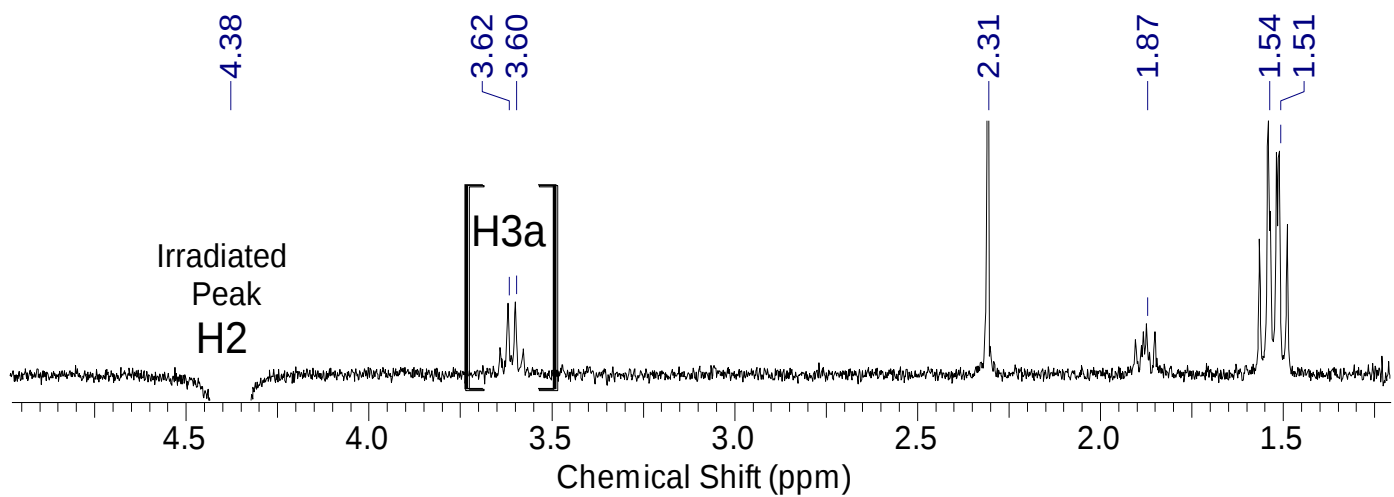
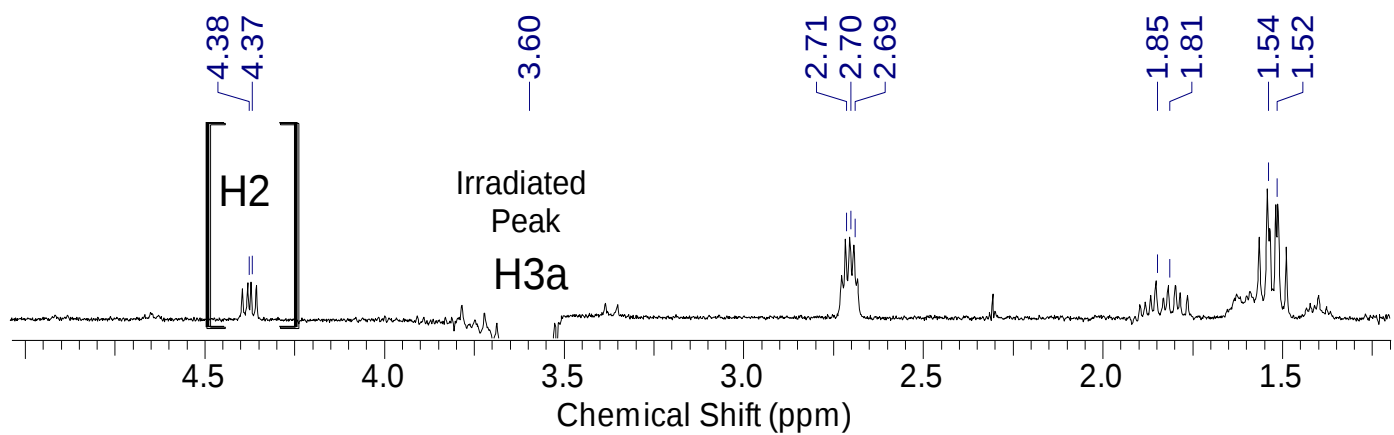
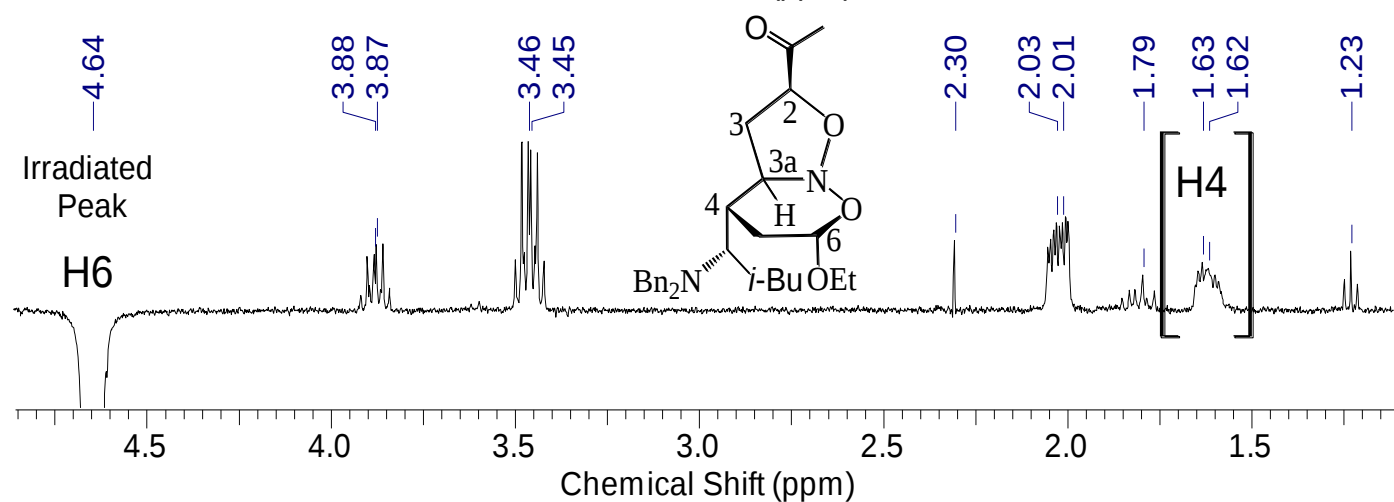
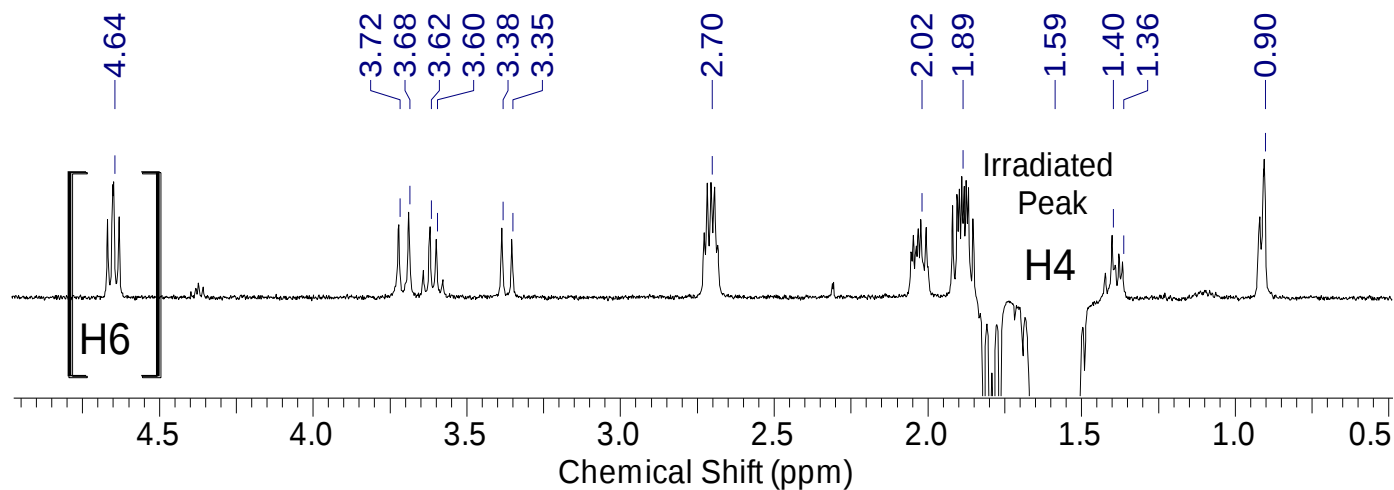
^{13}C NMR (101 MHz, CHLOROFORM-D) δ ppm 15.0 (CH_3); 22.0 (CH); 23.7 (CH_3); 25.4 (CH_3); 26.8 (CH_3); 28.0 (CH_2); 32.6 (CH_2); 34.8 (CH_2); 40.9 (CH); 54.9 (CH); 55.3 (2x CH_2); 63.4 (CH_2); 71.3 (CH); 88.6 (CH); 100.6 (CH); 127.0-129.2 (10x CH_{Ar}); 139.8 (2x C_{ipso}); 209.2 ($\text{C}=\text{O}$)



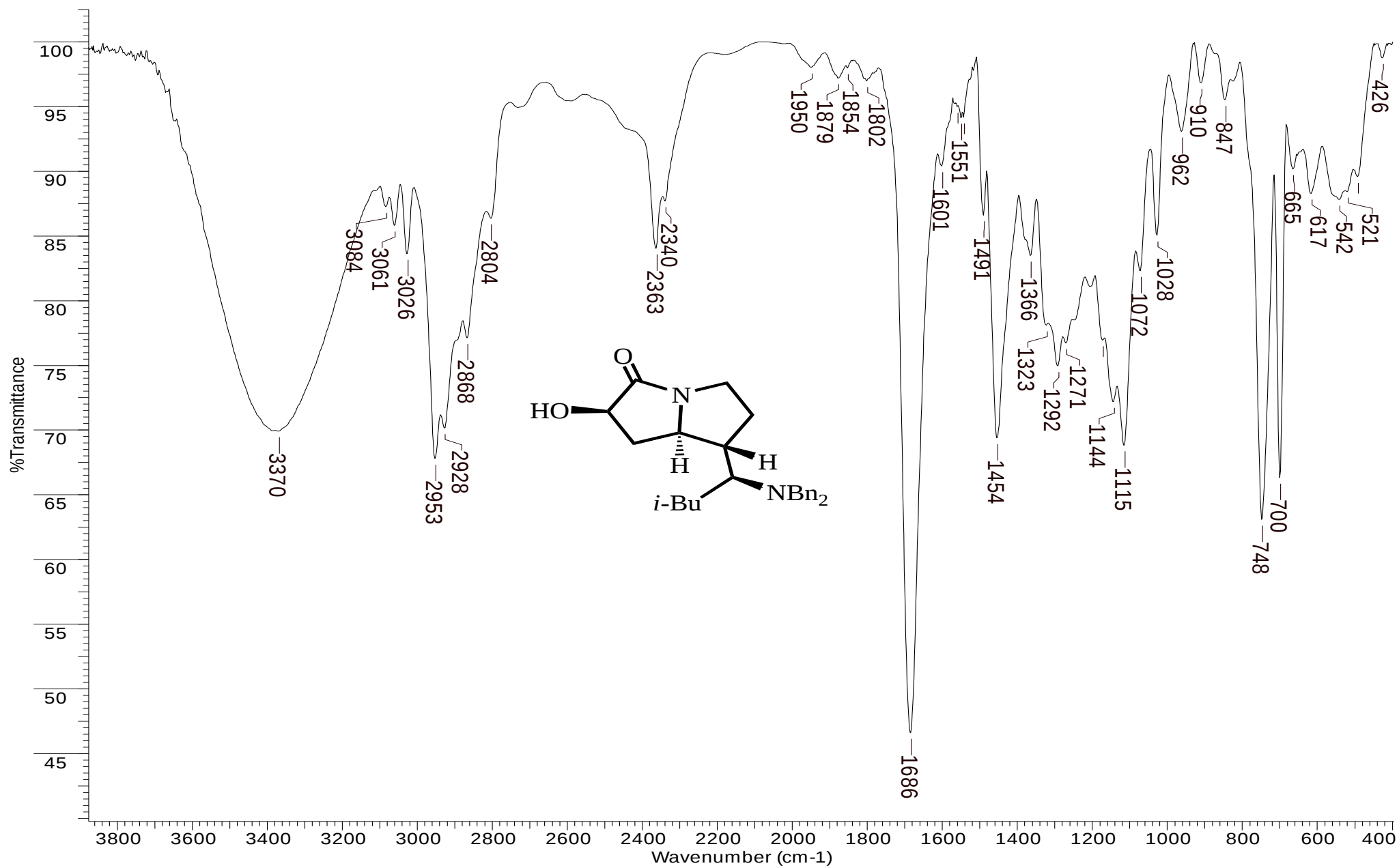
Spectrum 51 - ^1H and ^{13}C NMR of 13c'



Spectrum 52 – 2D COSY of **13c'**

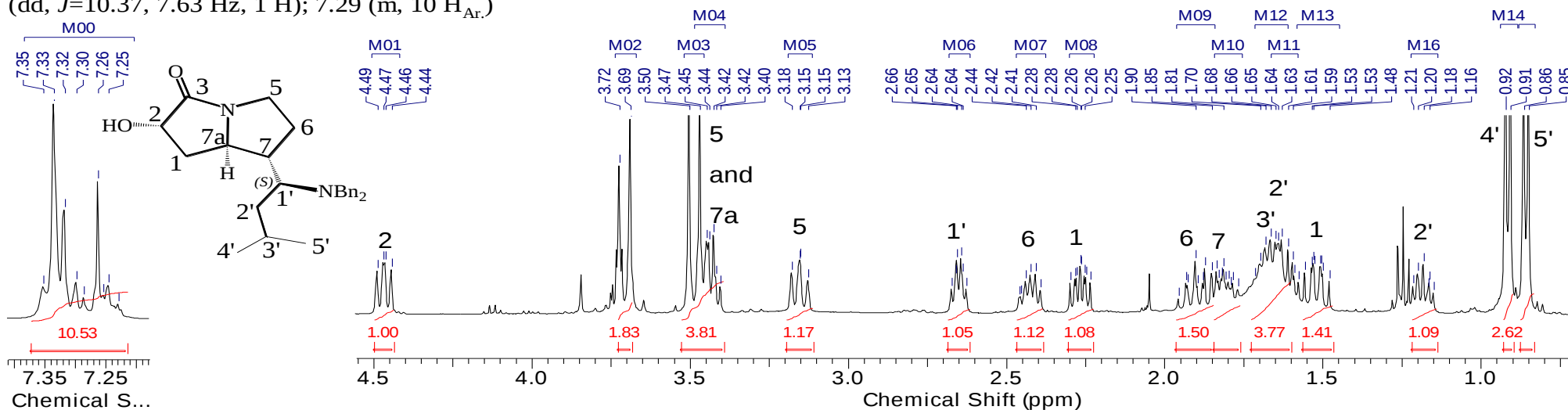


Spectrum 53 – 2D NOESY of **13c'**

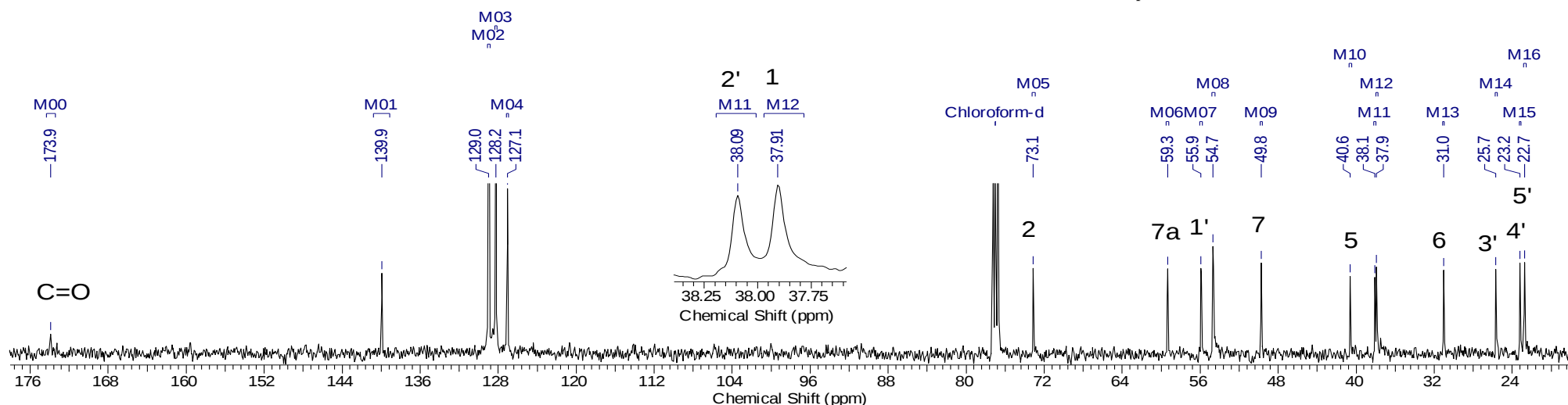


Spectrum 54 – Infrared of **14c**

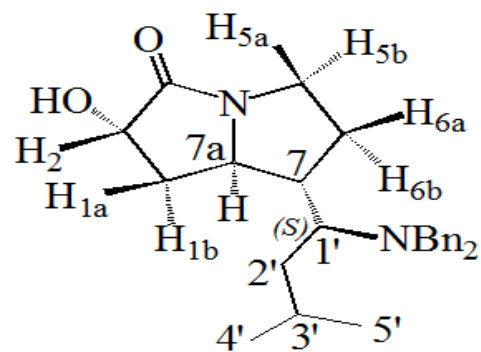
^1H NMR (400 MHz, CHCl_3 - D) δ ppm 0.86 (d, $J=6.26$ Hz, 3 H); 0.91 (d, $J=6.26$ Hz, 3 H); 1.18 (ddd, $J=13.30, 7.24, 5.67$ Hz, 1 H); 1.52 (ddd, $J=11.93, 10.56, 8.80$ Hz, 1 H); 1.62 (m, 1 H); 1.67 (m, 1 H); 1.80 (m, 1 H); 1.89 (m, 1 H); 2.26 (ddd, $J=11.74, 7.82, 5.87$ Hz, 1 H); 2.43 (m, 1 H); 2.65 (ddd, $J=6.95, 4.89$ Hz, 1 H); 3.15 (dd, $J=10.96, 9.78$ Hz, 1 H); 3.43 (m, 2 H); 3.48 (d, $J=13.69$ Hz, 2 H); 3.70 (d, $J=13.69$ Hz, 2 H); 4.46 (dd, $J=10.37, 7.63$ Hz, 1 H); 7.29 (m, 10 H_{Ar} .)



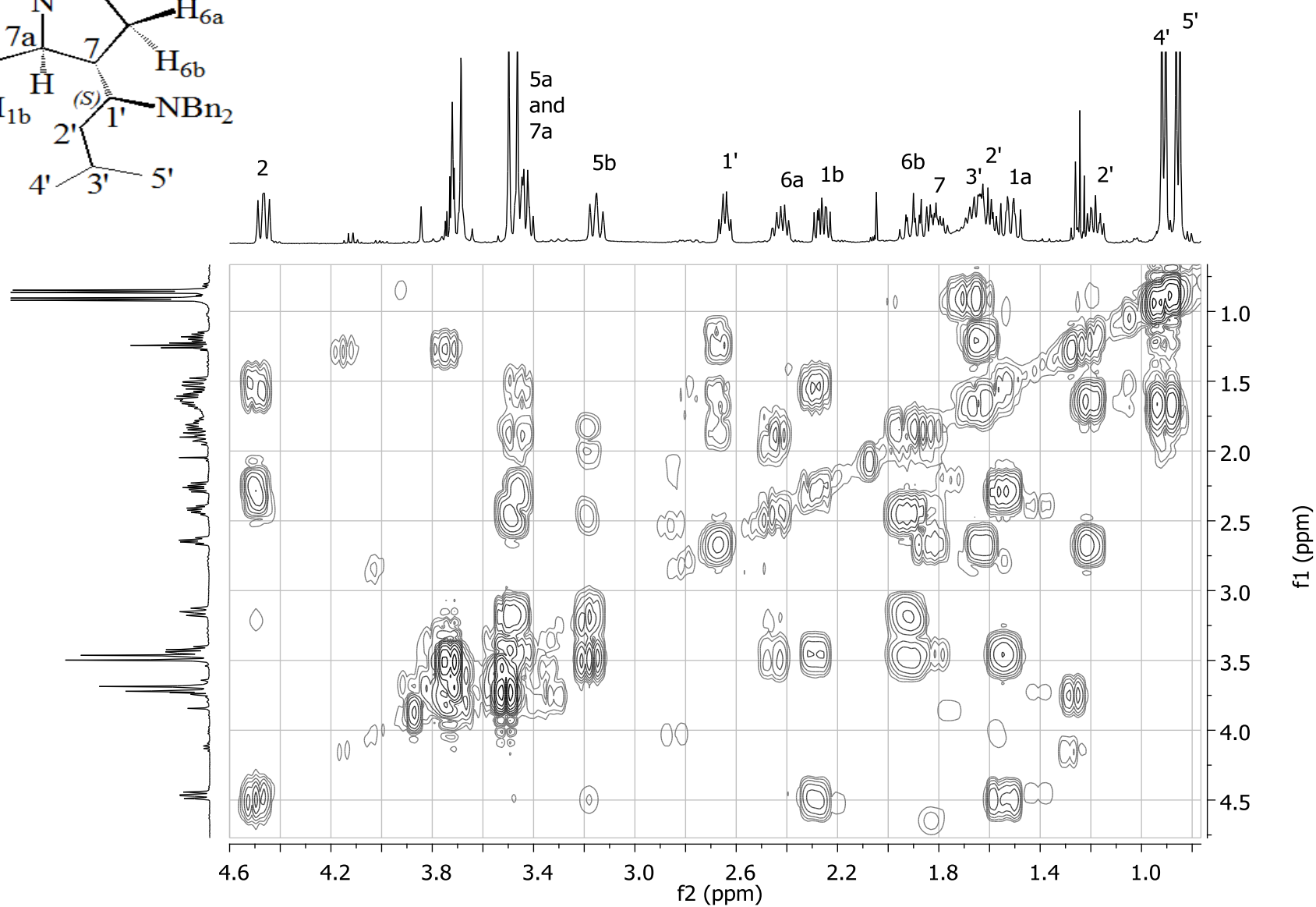
^{13}C NMR (126 MHz, CHCl_3 - D) δ ppm 22.7 (CH_2); 23.2 (CH_2); 25.7 (CH); 31.0 (CH_2); 37.9 (CH_2); 38.1 (CH_2); 40.6 (CH_2); 49.8 (CH); 54.7 (2 x CH_2); 55.9 (CH); 59.3 (CH); 73.1 (CH); 127.1 (CH_{Ar}); 128.2 (CH_{Ar}); 129.0 (CH_{Ar}); 139.9 (2x C_{ipso}); 173.9 (C=O)



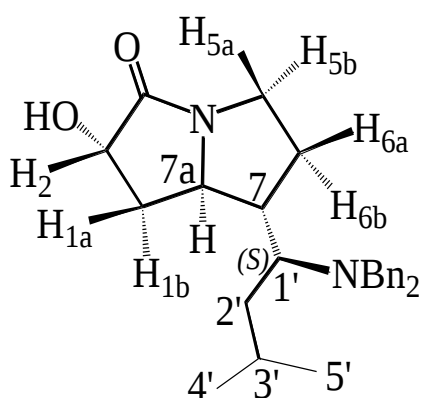
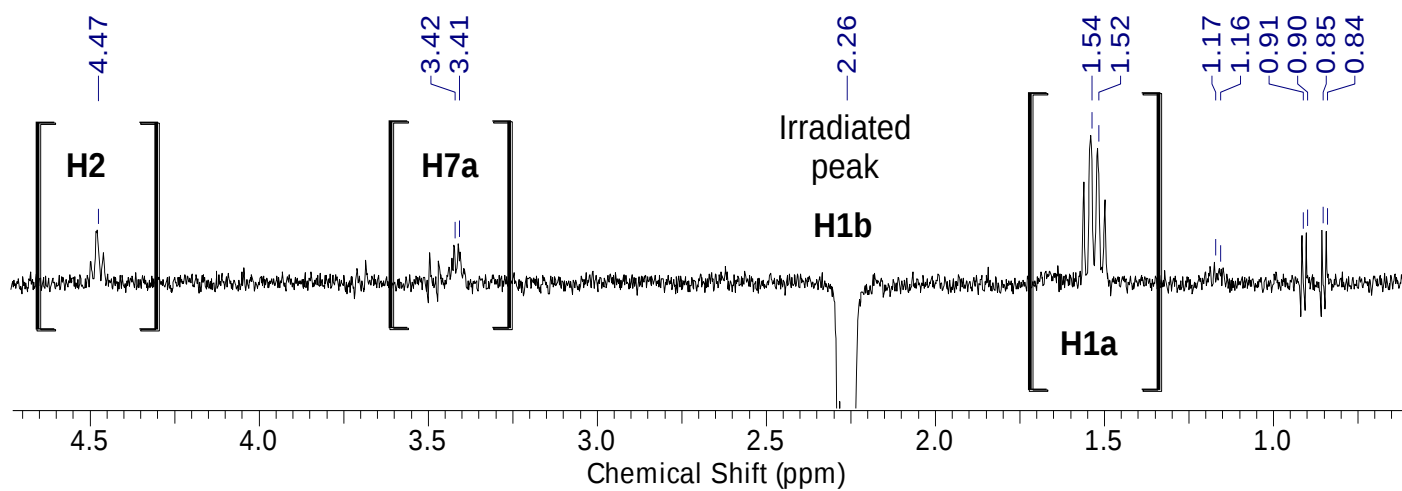
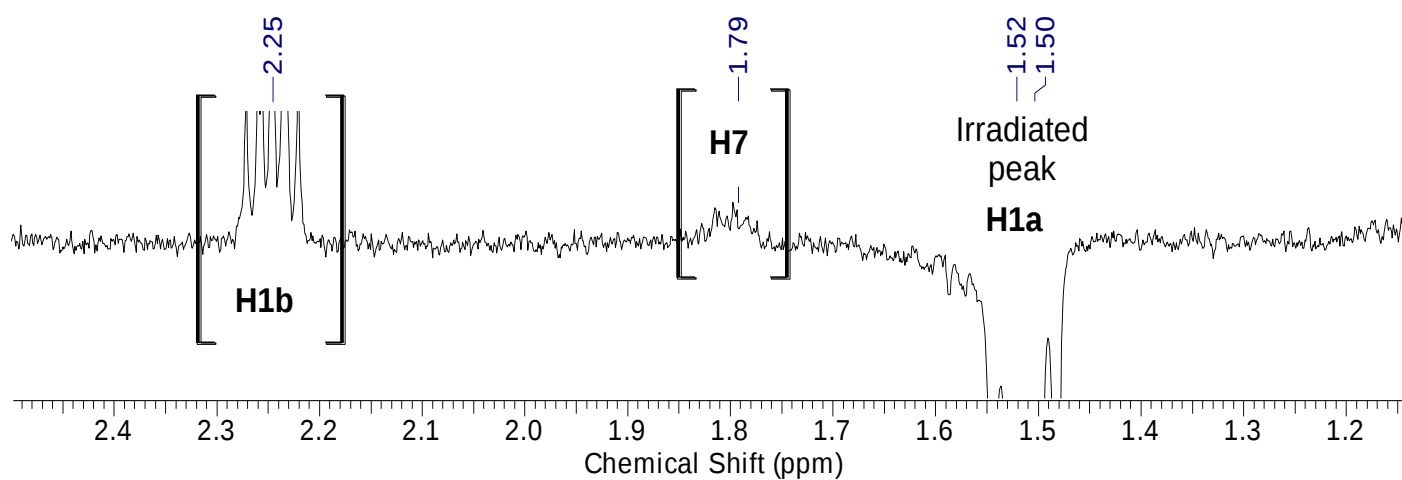
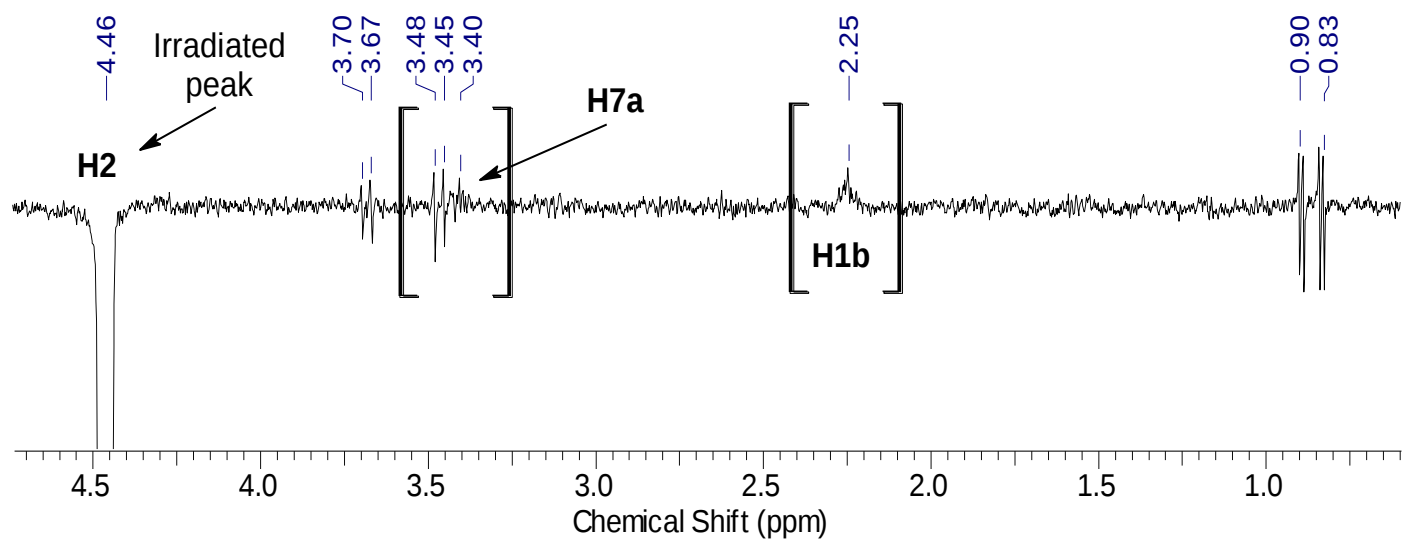
Spectrum 55 - ^1H and ^{13}C NMR of **14c**

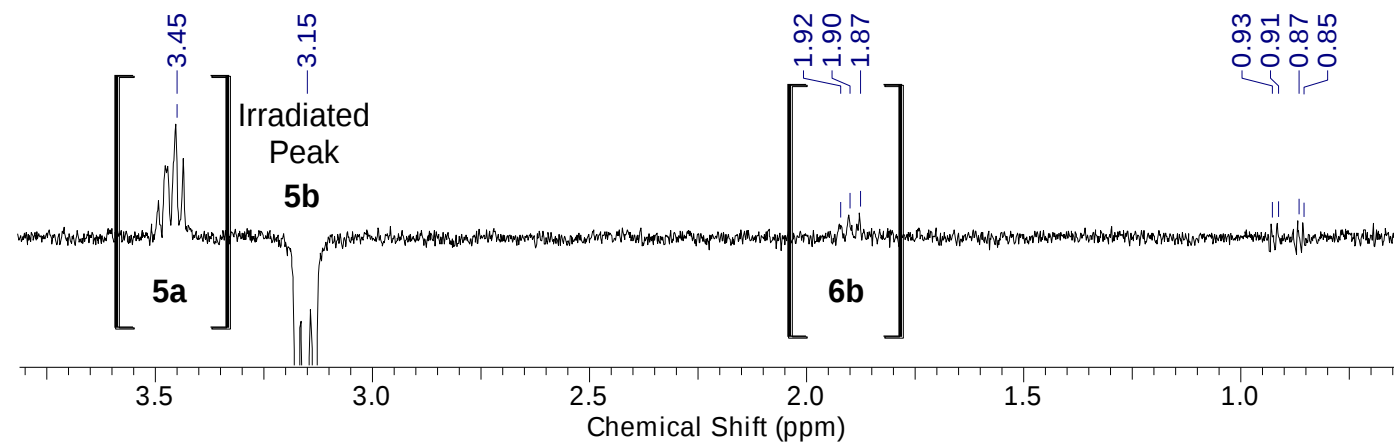
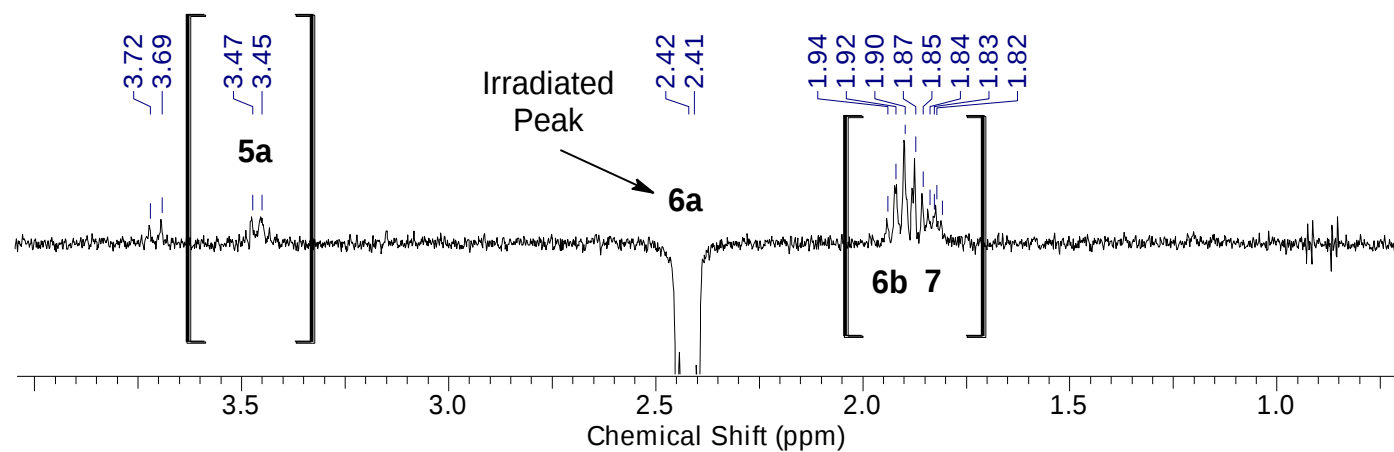
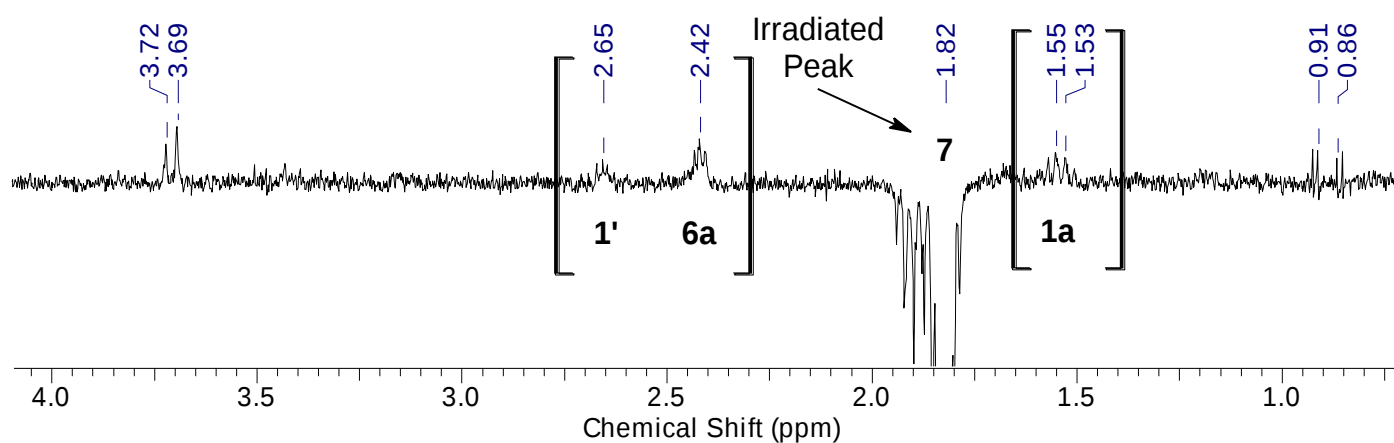
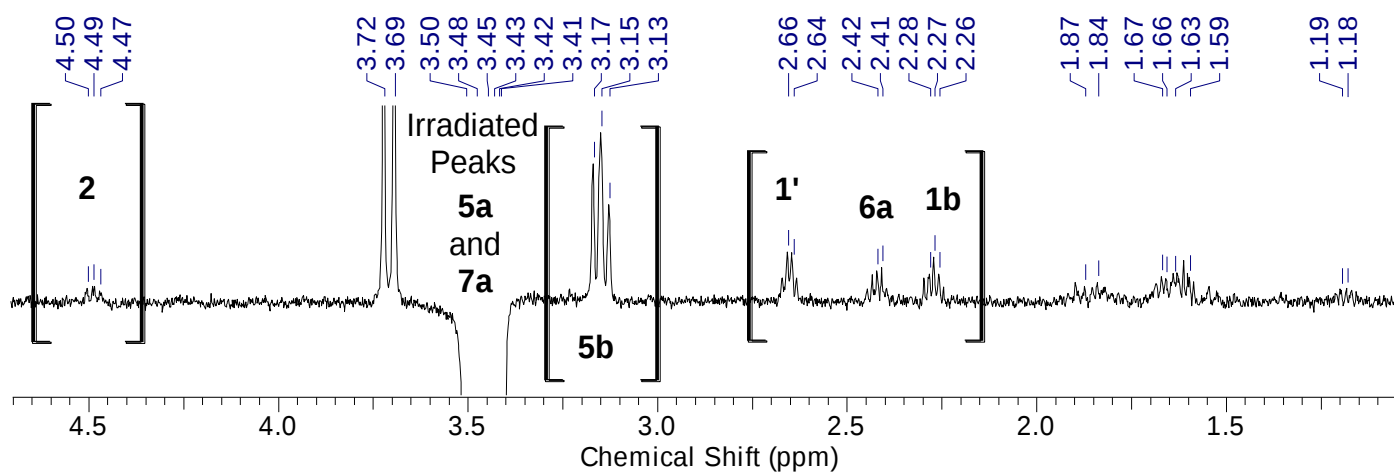


The Chemical shift of H-H^b were inferred by 1D NOESY experiments



Spectrum 56 – 2D COSY of **14c**





Spectrum 57 – 2D NOESY of **14c**