

Versatile Chemoselectivity in Ni-Catalyzed Multiple Bond Carbonylations and Cyclocarbonylations in CO₂-Expanded Liquids

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Supporting Information

General Information

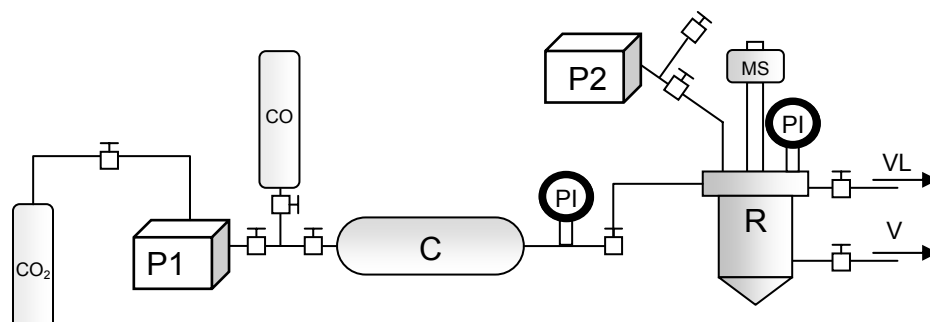
¹H NMR and ¹³C NMR spectra were recorded in CDCl₃, on a Bruker ARX 300 (300 and 75.5 MHz) spectrometer or on a Bruker AC 250. Chemical shifts are given in ppm relative to TMS (¹H, 0.0 ppm) or CDCl₃ (¹³C, 77.0 ppm). IR spectra were taken on a Perkin Elmer Spectrum One FT-IR spectrometer using CH₂Cl₂ as the solvent. Mass spectra were obtained on an AutoSpec-Q mass spectrometer. Elemental analyses were performed using a Carlo Erba 1106 apparatus.

Acetone was distilled under Ar just before use. Iron powder, 10 μm diameter (reduced by hydrogen), was provided by Merck-Darmstadt, product 1.03819.0100. Unless otherwise stated, all common reagents and solvents were used as obtained from commercial suppliers without further purification.

The CO₂ and CO contents in the liquid phase, where the reaction takes place, were estimated with flash separation calculations using the Peng Robinson EoS, assuming a ternary system CO-CO₂-acetone, and neglecting the effect of reactants and water. The values of the binary interactions parameters employed were reported by Lopez-Castillo et al., who reliably used the PR-EoS to model CO-CO₂-expanded solvent systems before. The software used for the calculations was Hysys Plant.

Equipment

A new apparatus was designed and built in order to run the high pressure reactions. This apparatus consists essentially in a 50 ml (internal volume) stainless steel high pressure cell (MAWP = 23 MPa at 295 K). CO₂ is introduced in the cell by means of a high pressure pump (ISCO 260D). Other gases, CO and/or N₂, are directly introduced from high pressure cylinders through pressure regulators. For each reaction, CO₂ and CO are previously mixed in a 163 ml cylinder, connected to the reactor. The substrates and solvent are added by means of a high-pressure liquid pump (Shimadzu LC-10AT). A stainless steel coil surrounding the cell is connected to a temperature controller (HAAKE F3), allowing to keep constant the temperature inside the reactor. The pressure inside the reactor is controlled by a low (0-4 bar) or high (0-100 bar) pressure gauge, depending on the reaction pressure conditions. The homogeneity of the reaction mixture is achieved by a mechanical stirrer. The components of this apparatus are connected by 1/8" stainless steel (external diameter) tubing and high pressure valves.



Schematic representation of the equipment used for the cyclocarbonylation reactions at high pressure, (P1) high-pressure CO₂ pump, (R) chemical reactor, (C) Cylinder, (P2) high-pressure liquid pump, (PI) pressure indicator, (MS) mechanical stirrer, (VL) vent line, (V) vacuum line.

Procedure

All experiments were carried out batchwise in the apparatus described above, and the kinetics was controlled, when possible, by the decrease in total pressure. We chose the readily available norbornene, phenylacetylene and allyl bromide as model substrates. The catalyst employed for the cyclocarbonylation reaction is prepared in-situ by a single electron reduction of a Ni(II) salt.

In a typical experiment, the reactor (R) is manually charged with NiBr₂ (0.43 mmol), NaI (2.55 mmol), Fe powder (8.5 mmol, reducing agent) and granulated Fe (10.8 mmol, for efficient mixing), and then sealed. The air inside the reactor and the cylinder is vented through the vacuum line (VL) and, after that, 1.5 ml of acetone are introduced in the reactor. Carbon monoxide and carbon dioxide are mixed in the gas cylinder (C) under different conditions (different partial pressures) for each reaction, and then a valve connecting the cylinder and the reactor is opened allowing equilibrium. This valve is kept opened during all the reaction, as well as the mechanical stirring. After 30 minutes of reduction, 8.5 mmol of each one of the substrates (norbornene + allyl bromide, or acetylene + allyl bromide) are slowly added by means of a high-pressure liquid pump (P2), for 3 hours. After that, the reaction is left running overnight (approx. 15h).

The following day, the stirring is stopped, and gases inside the reactor are vented to atmosphere. The product is collected with acetone. The solvent is removed, and the contents of the flask are transferred to a separation funnel washing the flask (with the remaining iron) with dichloromethane. The reaction mixture darkens deeply in contact with the air, due to the oxidation of the remaining iron. The solution is treated with portions of 5M HCl solution until no further discoloration is observed. After washing the organic phase with water to neutralization, the organic layer is treated with a solution of Na₂S₂O₃ (to remove any I₂ produced by oxidation), washed again with water, and dried on MgSO₄. The solvent is removed in a rotatory evaporator. After this work up, the reaction products are separated by flash chromatography, and identified and quantified by ¹H and ¹³C NMR.

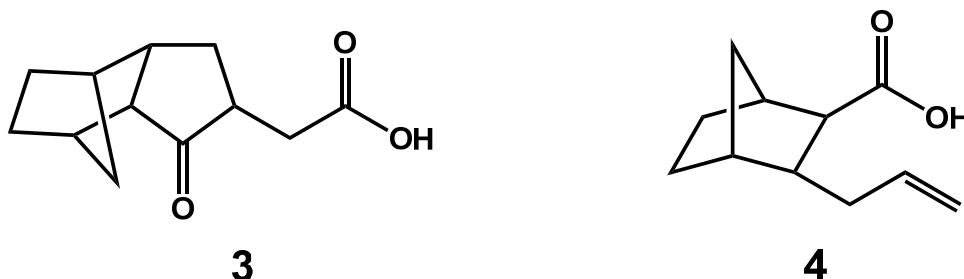
Compound characterization

Reactions with Norbornene and Allyl Bromide:

These compounds were previously synthesized, characterized and reported in this article:

D. del Moral, J.M. Moretó, E. Molins, S. Ricart, *Tetrahedron Lett.*, published ASAP.

Following the general procedure, setting the CO and CO₂ partial pressures required for each reaction and using norbornene (800 mg, 8.5 mmol) and allyl bromide (740 μ l, 8.5 mmol) as the reagents, products **3** and **4** are obtained after flash chromatography (99:1 CH₂Cl₂/CH₃OH).



3. IR (CH₂Cl₂) ν (cm⁻¹): 3600-3000 (O-H), 1734 (C=O), 1710 (C=O).

¹H-NMR (300 MHz, CDCl₃): δ 0.90-1.10 (m, 3H, CH₂); 1.16 (d, J (H,H) = 8 Hz, 2H, CH₂); 1.20 (d, J (H,H) = 20 Hz, 1H, CH₂); 1.53 (bd, J (H,H) = 8 Hz, 2H, CH₂); 2.16 (d, J (H,H) = 11 Hz, 2H, CH); 2.24 (t, J (H,H) = 9 Hz, 1H, CH); 2.58 (bs, 1H, CH₂); 2.40-2.80 (m, 3H, CH, CH₂).

¹³C-NMR (75 MHz, CDCl₃): δ 27.7 (t); 27.8 (t); 31.6 (t); 32.8 (t); 33.9 (t); 38.7 (d); 40.5 (d); 42.0 (d); 44.9 (d); 54.0 (d); 178.1 (s); 218.5 (s).

HRMS (E.I.) (M^+): 208.1092 (theoretical: 208.1095).

Elemental analysis: C, 69.33%; H, 7.91% (calculated: C, 69.21%; H, 7.74%).

4. IR (CH₂Cl₂) ν (cm⁻¹): 3600-3000 (O-H), 3077 (C=CH), 1702 (C=O).

¹H-NMR (300 MHz, CDCl₃): δ 1.05-1.20 (m, 3H, CH₂); 1.45-1.60 (m, 2H, CH₂); 1.83 (d, J (H,H) = 10 Hz, 1H, CH₂); 1.85-2.00 (m, 2H, CH, CH₂); 2.13 (bs, 1H, CH); 2.10-2.20 (m, 1H, CH₂); 2.43 (bs, 1H, CH); 2.51 (d, J (H,H) = 9 Hz, 1H, CH); 4.97 (d, J (H,H) = 10 Hz, 1H, CH₂); 4.99 (d, J (H,H) = 17 Hz, 1H, CH₂); 5.75 (ddt, J (H,H) = 7, 10, 17 Hz, 1H, CH).

¹³C-NMR (75 MHz, CDCl₃): δ 28.6 (t); 28.9 (t); 34.2 (t); 34.8 (t); 38.8 (d); 40.1 (d); 45.5 (d); 50.7 (d); 115.6 (t); 137.3 (d); 180.5 (s).

HRMS (E.I.) (M^+): 180.1146 (theoretical: 180.1146).

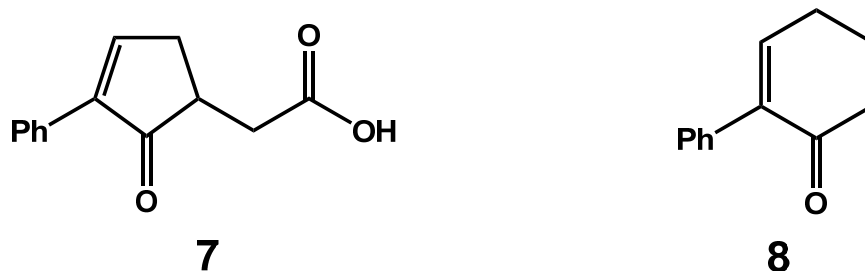
Elemental analysis: C, 73.87%; H, 9.20% (calculated: C, 73.30%; H, 8.95%).

Reactions with Phenylacetylene and Allyl Bromide:

Compound **7** was previously synthesized, characterized and reported in this article:

M.Ll. Nadal, J. Bosch, J.M. Vila, G. Klein, S. Ricart, J.M. Moretó, *J. Am. Chem. Soc.*, **2005**, *127*, 10476.

Following the general procedure, setting the CO and CO₂ partial pressures required for each reaction and using phenylacetylene (960 μ l, 8.5 mmol) and allyl bromide (740 μ l, 8.5 mmol) as the reagents, products **7** and **8** are obtained after flash chromatography (99:1 CH₂Cl₂/CH₃OH).



7. IR (CH₂Cl₂) ν (cm⁻¹): 3600-3000 (O-H), 3055 (C=CH), 1737 (C=O), 1704 (C=O).

¹H-NMR (300 MHz, CDCl₃): δ 2.47 (ddd, J (H,H) = 19, 3, 3 Hz, 1H, CH₂); 2.58 (dd, J (H,H) = 17, 9 Hz, 1H, CH₂); 2.85-2.95 (m, 1H, CH); 2.97 (dd, J (H,H) = 17, 3 Hz, 1H, CH₂); 3.02 (ddd, J (H,H) = 19, 6, 3 Hz, 1H, CH₂); 7.30-7.45 (m, 3H, Ph); 7.65-7.75 (m, 2H, Ph); 7.80 (dd, J (H,H) = 3, 3 Hz, 1H, CH).

¹³C-NMR (75 MHz, CDCl₃): δ 33.3 (t); 35.1 (t); 42.6 (d); 127.0 (d); 128.5 (d); 128.6 (d); 131.4 (s); 142.6 (s); 157.6 (d); 177.5 (s); 207.5 (s).

8. IR (CH₂Cl₂) ν (cm⁻¹): 30xx (C=CH), 17xx (C=O).

¹H-NMR (300 MHz, CDCl₃): δ 2.11 (tt, J (H,H) = 7, 7 Hz, 2H, CH₂); 2.54 (dt, J (H,H) = 7, 5 Hz, 2H, CH₂); 2.61 (t, J (H,H) = 7 Hz, 2H, CH₂); 7.04 (t, J (H,H) = 5 Hz, 1H, CH); 7.20-7.50 (m, 5H, Ph).

¹³C-NMR (75 MHz, CDCl₃): δ 23.0 (t); 26.6 (t); 39.1 (t); 127.5 (d); 128.0 (d); 128.7 (d); 136.7 (s); 140.3 (s); 148.1 (d); 197.8 (s).

HRMS (E.I.) (M^+): 172.0881 (theoretical: 172.0885).

Crystal data and structure refinement for compound 3

| | | |
|-----------------------------------|---|-------------------------------|
| Identification code | Sr2 | |
| Empirical formula | C12 H16 O3 | |
| Formula weight | 208.25 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 5.836(14) Å | $\alpha = 90.82(12)^\circ$. |
| | b = 5.865(7) Å | $\beta = 97.58(15)^\circ$. |
| | c = 17.00(2) Å | $\gamma = 109.87(12)^\circ$. |
| Volume | 541.5(16) Å ³ | |
| Z | 2 | |
| Density (calculated) | 1.277 Mg/m ³ | |
| Absorption coefficient | 0.091 mm ⁻¹ | |
| F(000) | 224 | |
| Crystal size | 0.44 x 0.33 x 0.18 mm ³ | |
| Theta range for data collection | 2.42 to 25.02° | |
| Index ranges | -6 ≤ h ≤ 6, -6 ≤ k ≤ 6, 0 ≤ l ≤ 16 | |
| Reflections collected | 2315 | |
| Independent reflections | 1791 [R(int) = 0.0184] | |
| Completeness to theta = 25.02° | 94.6 % | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 1791 / 0 / 137 | |
| Goodness-of-fit on F ² | 1.072 | |
| Final R indices [I > 2σ(I)] | R1 = 0.1067, wR2 = 0.2744 | |
| R indices (all data) | R1 = 0.2596, wR2 = 0.3580 | |
| Largest diff. peak and hole | 0.267 and -0.243 e.Å ⁻³ | |

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for sr2.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | x | y | z | U(eq) |
|-------|-----------|-----------|---------|--------|
| C(1) | 2275(13) | -1209(14) | 2766(5) | 70(2) |
| C(2) | 2880(20) | -329(17) | 3594(7) | 99(4) |
| C(3) | 2453(17) | -2408(18) | 4176(7) | 118(4) |
| C(4) | -343(16) | -3627(15) | 4046(6) | 80(3) |
| C(5) | -1251(16) | -2134(16) | 3419(6) | 81(3) |
| C(6) | -504(12) | -2523(13) | 2639(5) | 64(2) |
| C(7) | -1483(13) | -1299(15) | 1940(5) | 79(3) |
| C(8) | 664(12) | 95(12) | 1528(5) | 60(2) |
| C(9) | 2750(13) | 772(14) | 2179(5) | 67(2) |
| C(10) | 750(30) | 447(17) | 3703(6) | 128(5) |
| C(11) | 380(14) | 2195(14) | 1055(5) | 75(3) |
| C(12) | 2406(15) | 3406(16) | 606(5) | 67(2) |
| O(1) | 4454(11) | 2605(12) | 2223(4) | 128(3) |
| O(2) | 3554(11) | 2280(10) | 297(4) | 86(2) |
| O(3) | 2857(10) | 5719(10) | 542(4) | 84(2) |

Bond lengths [\AA] and angles [$^\circ$] for sr2

| | |
|-------------|-----------|
| C(1)-C(2) | 1.449(14) |
| C(1)-C(9) | 1.519(10) |
| C(1)-C(6) | 1.525(10) |
| C(2)-C(10) | 1.493(14) |
| C(2)-C(3) | 1.556(12) |
| C(3)-C(4) | 1.526(12) |
| C(4)-C(5) | 1.542(11) |
| C(5)-C(6) | 1.488(12) |
| C(5)-C(10) | 1.585(14) |
| C(6)-C(7) | 1.543(10) |
| C(7)-C(8) | 1.510(10) |
| C(8)-C(9) | 1.473(11) |
| C(8)-C(11) | 1.524(9) |
| C(9)-O(1) | 1.184(8) |
| C(11)-C(12) | 1.472(11) |

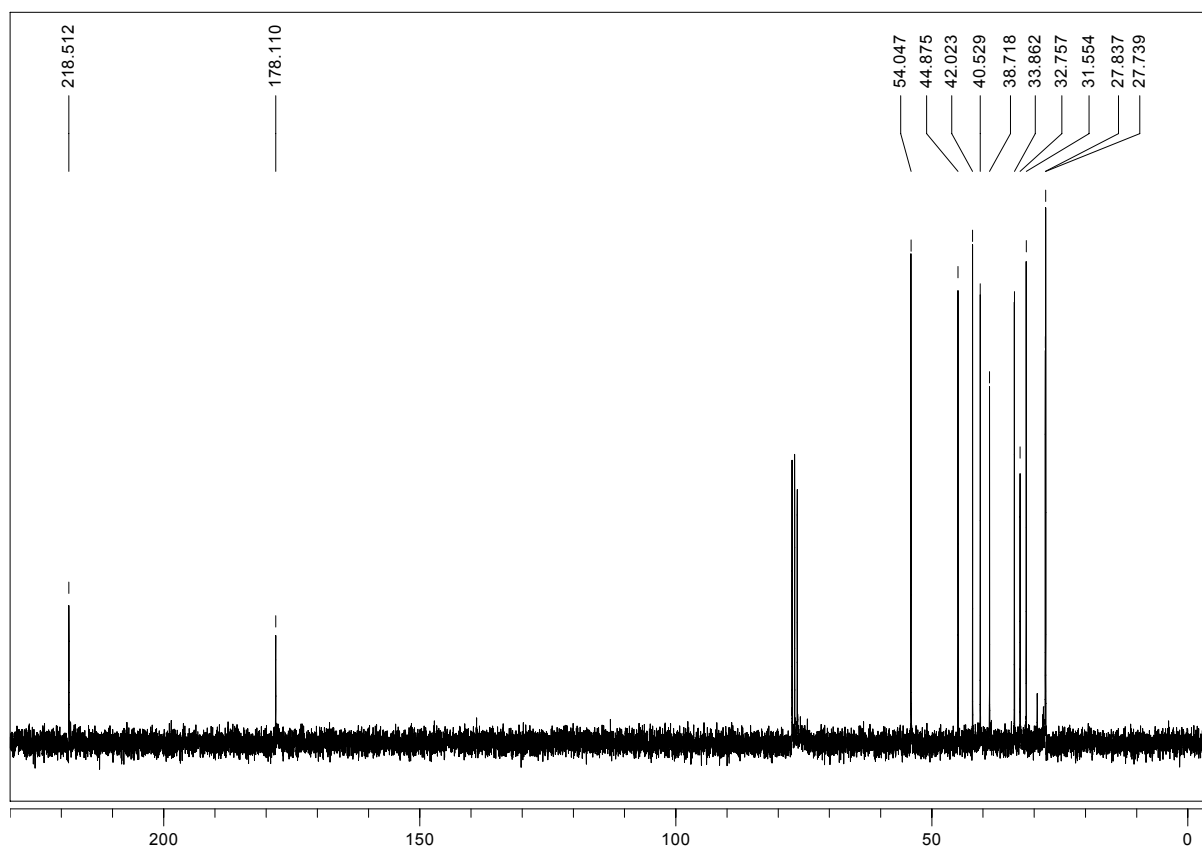
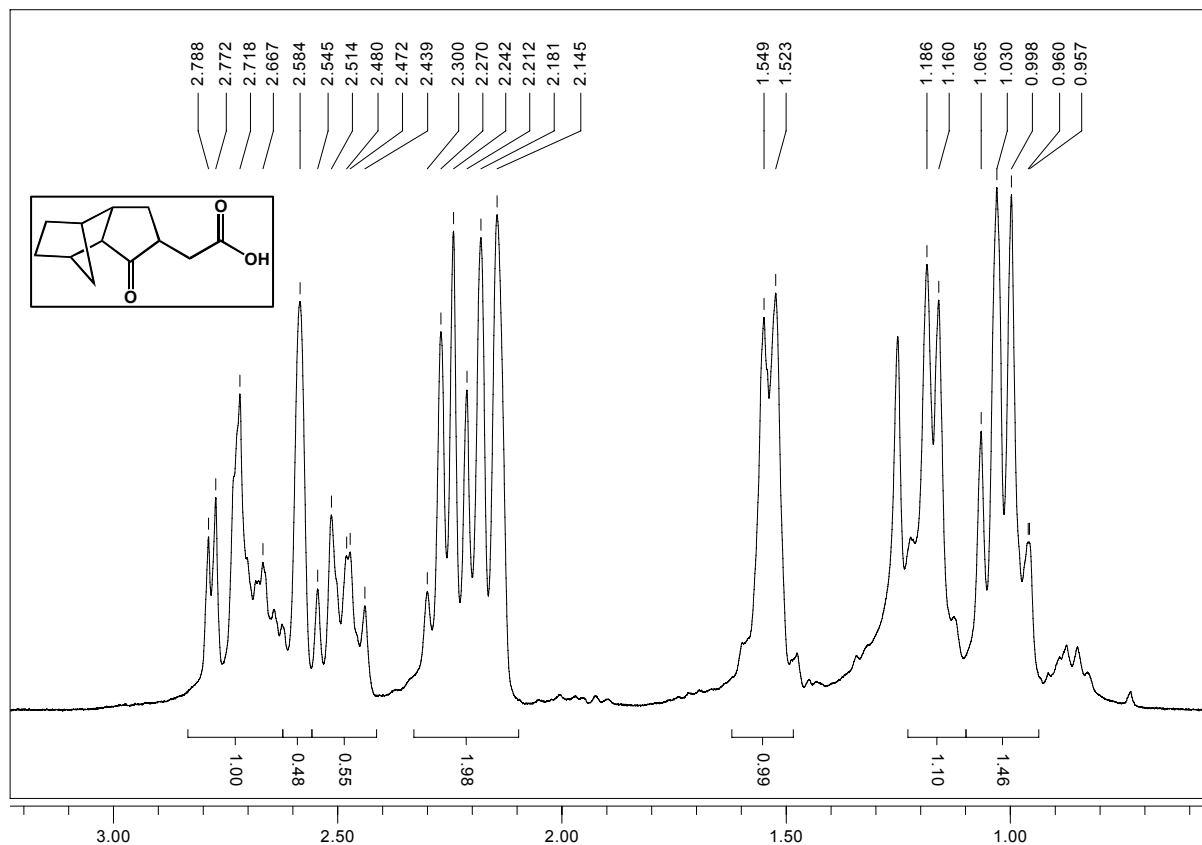
| | |
|------------------|-----------|
| C(12)-O(2) | 1.243(10) |
| C(12)-O(3) | 1.300(9) |
| | |
| C(2)-C(1)-C(9) | 114.6(8) |
| C(2)-C(1)-C(6) | 104.8(8) |
| C(9)-C(1)-C(6) | 105.8(6) |
| C(1)-C(2)-C(10) | 101.6(8) |
| C(1)-C(2)-C(3) | 113.1(9) |
| C(10)-C(2)-C(3) | 99.3(10) |
| C(4)-C(3)-C(2) | 102.9(8) |
| C(3)-C(4)-C(5) | 104.2(7) |
| C(6)-C(5)-C(4) | 110.2(8) |
| C(6)-C(5)-C(10) | 99.9(7) |
| C(4)-C(5)-C(10) | 97.9(8) |
| C(5)-C(6)-C(1) | 103.9(7) |
| C(5)-C(6)-C(7) | 115.6(7) |
| C(1)-C(6)-C(7) | 104.6(6) |
| C(8)-C(7)-C(6) | 108.1(6) |
| C(9)-C(8)-C(7) | 102.6(6) |
| C(9)-C(8)-C(11) | 115.1(6) |
| C(7)-C(8)-C(11) | 116.4(7) |
| O(1)-C(9)-C(8) | 123.7(7) |
| O(1)-C(9)-C(1) | 127.6(8) |
| C(8)-C(9)-C(1) | 108.7(6) |
| C(2)-C(10)-C(5) | 94.1(7) |
| C(12)-C(11)-C(8) | 115.6(7) |
| O(2)-C(12)-O(3) | 122.8(7) |
| O(2)-C(12)-C(11) | 122.2(8) |
| O(3)-C(12)-C(11) | 115.0(9) |

Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for sr2. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^2 U^{11} + \dots + 2 h k a^* b^* U^{12}]$

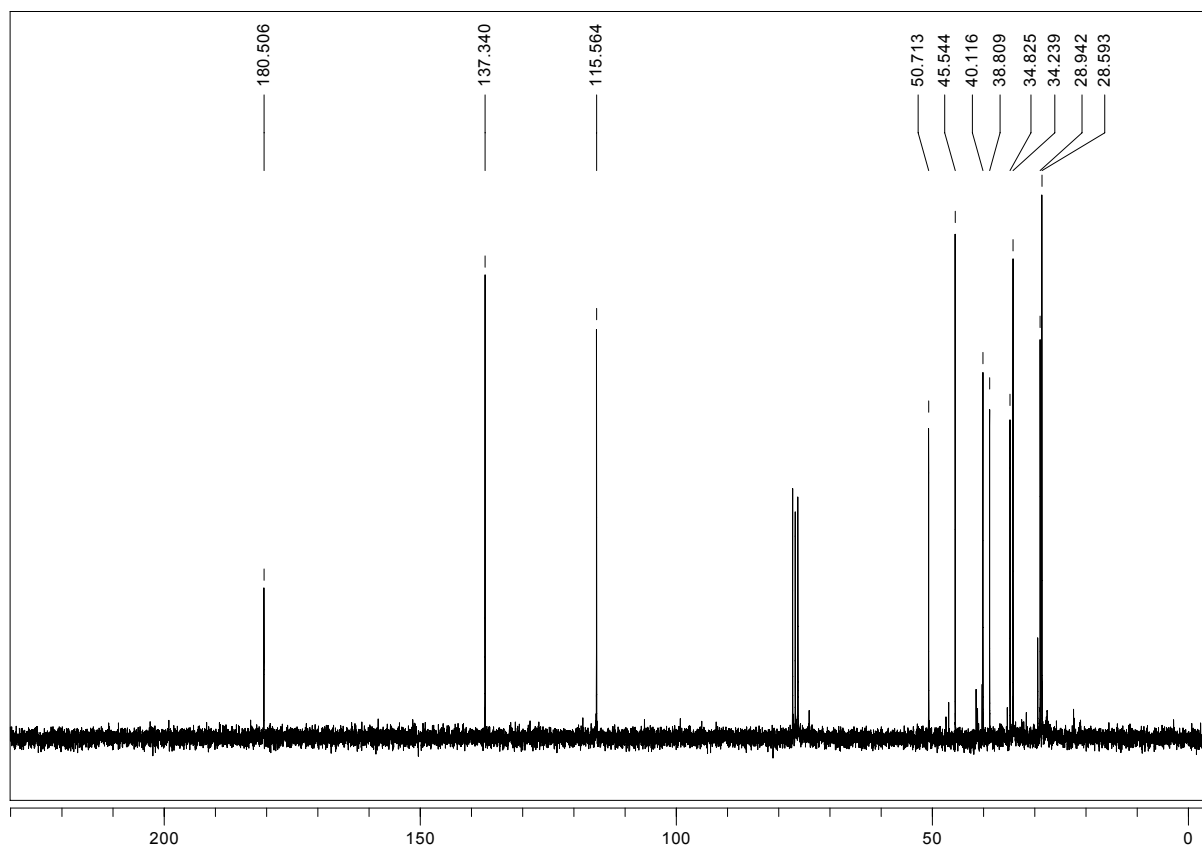
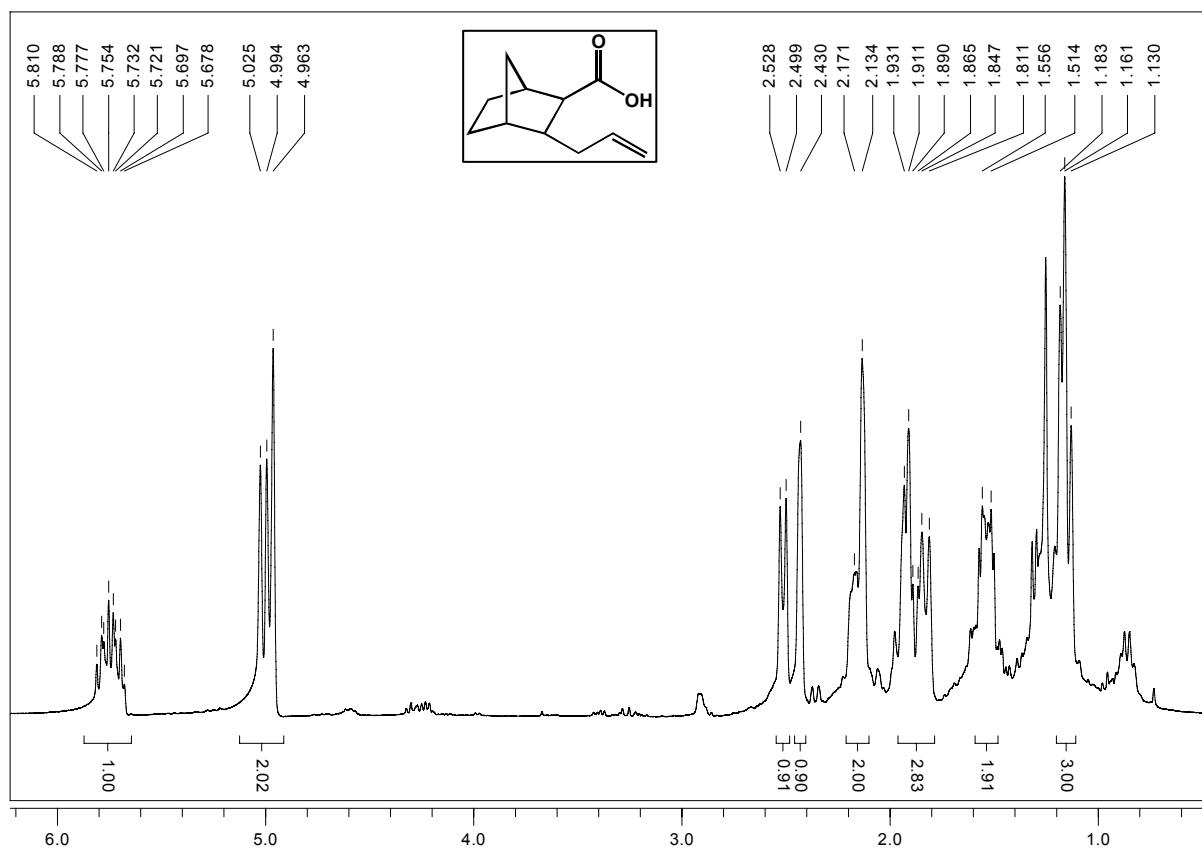
| | U11 | U22 | U33 | U23 | U13 | U12 |
|-------|---------|--------|---------|-------|--------|--------|
| C(1) | 58(4) | 83(5) | 79(7) | 7(5) | 12(5) | 37(4) |
| C(2) | 107(8) | 67(5) | 99(9) | 1(5) | -20(7) | 11(5) |
| C(3) | 95(7) | 127(8) | 114(10) | 47(7) | -13(6) | 24(6) |
| C(4) | 94(6) | 77(5) | 82(7) | 5(5) | 24(5) | 44(5) |
| C(5) | 75(5) | 112(7) | 83(7) | 23(5) | 26(5) | 63(5) |
| C(6) | 54(4) | 66(4) | 63(6) | -2(4) | 5(4) | 11(3) |
| C(7) | 55(4) | 98(6) | 72(6) | 18(5) | -7(4) | 15(4) |
| C(8) | 60(4) | 71(5) | 52(5) | 2(4) | 4(4) | 27(4) |
| C(9) | 50(4) | 81(5) | 71(6) | 14(4) | 8(4) | 22(4) |
| C(10) | 265(16) | 78(7) | 69(8) | -1(5) | 58(9) | 85(9) |
| C(11) | 73(5) | 83(5) | 75(6) | 6(5) | 4(5) | 35(4) |
| C(12) | 66(5) | 73(5) | 58(6) | -2(4) | 6(4) | 20(4) |
| O(1) | 90(4) | 123(5) | 112(6) | 36(4) | -23(4) | -26(4) |
| O(2) | 104(4) | 75(3) | 91(5) | -1(3) | 38(4) | 37(3) |
| O(3) | 91(4) | 73(4) | 92(5) | 12(3) | 18(3) | 32(3) |

^1H -RMN and ^{13}C -RMN spectra:

Compound 3



Compound 4



^1H - ^1H RMN COSY spectrum (compound 4)

