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Supporting Information

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Gold- and Platinum-Catalyzed Tandem Cycloisomerization-Prins Type Cyclization Reactions

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General. ^{1}H NMR spectra were recorded on a Bruker AV-600 (600 MHz), Bruker AMX-400 (400 MHz) or Bruker DPX-300 (300 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard ($CHCl_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, dd: double doublet, td: triplet of doublets, t: triplet, q: quartet, br: broad, m: multiplet), coupling constants (*J* in Hz), integration and assignment. ^{13}C NMR spectra were recorded on a Bruker AV-600 (150 MHz), Bruker AMX-400 (100 MHz) or Bruker DPX-300 (75 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 76.95). Bidimensional NMR experiments (COSY, HSQCED, HMBC and NOESY) were recorded on a Bruker AMX-400 (400 MHz). High-resolution mass spectrometry was carried out on a Finnigan-Mat 95 spectrometer. All reactions were conducted in dried glassware under an inert atmosphere of argon. The alcohols used as solvents (methanol, methanol-D_4, ethanol, propanol and 2-propanol) were distilled from calcium hydride. Acetic acid and propyonic acid were used without further purification.

General Procedure for the Tandem Cycloisomerization-Prins Type Reaction of ω-alkynols 1 Catalyzed by Gold- or Platinum-complexes. Synthesis of Compounds 2 and 8.

Method A. $AuCl_3$.

To a yellow solution of $AuCl_3$ (6 mg, 0.02 mmol) in methanol, ethanol, propanol or 2-propanol (2 mL) was added the corresponding ω-alkynol **1** (1 mmol). Instantaneously, the solution became into dark slurry, which was stirred at room temperature for an hour

until complete conversion (monitored by TLC). After removing of the solvent, the crude was purified by flash column chromatography on silica gel using hexane:ethyl acetate 10:1 as eluent to yield compounds **2**.

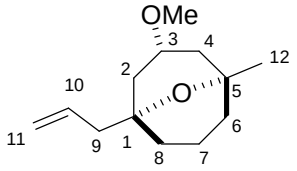
Method B. [(COD)$PtCl_2$].

To a white slurry of [(COD)$PtCl_2$] (7.5 mg, 0.02 mmol) in methanol, methanol-D_4, ethanol, propanol, 2-propanol, acetic acid or propyonic acid (2 mL) was added the corresponding ω-alkynol **1** (1 mmol). The resulting slurry was refluxed for twelve hours until complete conversion (monitored by TLC). Solvent was removed at reduced pressure and the residue was worked up as method A to obtain compounds **2** or **8**.

Method C. $PtCl_4$.

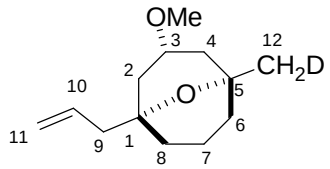
To an orange solution of $PtCl_4$ (6.7 mg, 0.02 mmol) in methanol, ethanol, propanol or 2-propanol (2 mL) was added the corresponding ω-alkynol **1** (1 mmol). The resulting slurry was refluxed for one hour until complete conversion (monitored by TLC). Solvent was removed at reduced pressure and the residue obtained was worked up as method A and B yielding compounds **2**.

(1*R,3*R**,5*R**)-1-Allyl-3-methoxy-5-methyl-9-oxabicyclo [3.3.1]nonane (2a).**



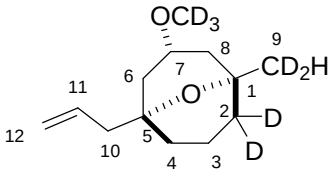
Colorless oil. R_f 0.45 (hexane:ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 6.48 (ddt, *J*= 16.0, 11.4, 7.1 Hz, 1H; H_{10}), 5.73-5.64 (m, 2H; H_{11}), 4.74 (tt, *J*= 10.9, 6.2 Hz, 1H; H_3), 3.30 (s, 3H; OCH_3), 2.87 (dt, *J*= 7.1, 1.1 Hz, 2H; H_9), 2.66 (dd, *J*= 12.9, 6.2 Hz, 1H; H_{2a}), 2.61 (dd, *J*= 13.0, 6.2 Hz, 1H; H_{4a}), 2.50-2.05 (m, 6H; $H_{6,7,8}$), 1.95 (dd, *J*= 12.9, 10.9 Hz, 1H; H_{2b}), 1.91 (dd, *J*= 13.0, 10.9 Hz, 1H; H_{4b}), 1.85 (s, 3H; CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 20.1, 31.8, 32.8, 35.0, 40.1, 42.4, 49.5, 55.3, 71.5, 73.2, 73.3, 117.6, 133.7. HRMS calcd. for $C_{13}H_{22}O_2$ 210.1620, found 210.1613.

(1*R,3*R**,5*R**)-1-Allyl-5-deuteromethyl-3-methoxy-9-oxabicyclo [3.3.1]nonane ([D_1]-2a).**



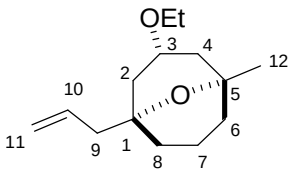
Colorless oil. R_f 0.42 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.80-5.64 (m, 1H; H_{10}), 4.98-4.83 (m, 2H; H_{11}), 4.10 (tt, *J*= 11.0, 6.3 Hz, 1H; H_3), 3.18 (s, 3H; OCH_3), 2.23 (dt, *J*= 7.4, 1.2 Hz, 2H; H_9), 2.02 (ddd, *J*= 12.9, 6.3, 1.0 Hz, 1H; H_{2a}), 1.97 (ddd, *J*= 12.9, 6.3, 1.0 Hz, 1H; H_{4a}), 1.83-1.43 (m, 8H), 1.35-1.19 (m, 3H), 0.91-0.83 (m, 2H; CH_2D). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 20.1, 31.5 (t, *J*= 19.4 Hz; CH_2D), 32.8, 34.9, 40.1, 42.3, 49.4, 55.2, 73.2, 73.2, 73.3, 117.6, 133.7. HRMS calcd. for $C_{12}H_{21}DO$ (M^+–CH_3OH) 180.1499, found 180.1485.

(1*R,5*R**,7*R**)-5-Allyl-2,2-dideuterio-1-dideuteriomethyl-7-trideuteriomethoxy-9-oxabicyclo[3.3.1]nonane ([D_7]-2a).**



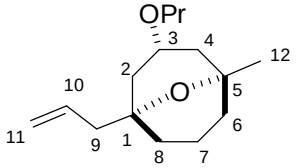
Colorless oil. R_f 0.45 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.79-5.65 (m, 1H; H_{11}), 4.96-4.87 (m, 2H; H_{12}), 3.96 (tt, *J*= 10.9, 6.2 Hz, 1H; H_7), 2.09 (dt, *J*= 7.3, 1.2 Hz, 2H; H_{10}), 1.87 (dd, *J*= 13.1, 6.2 Hz, 1H; H_{6a}), 1.83 (dd, *J*= 14.0, 6.2 Hz, 1H; H_{8a}), 1.68-1.27 (m, 4H; $H_{3,4}$), 1.15 (dd, *J*= 13.1, 10.9 Hz, 1H; H_{6b}), 1.13 (dd, *J*= 14.0, 10.9 Hz, 1H; H_{8b}), 1.06-1.02 (m, 1H; H_9). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 19.6, 31.1 (q, *J*= 19.3 Hz; CD_2H), 32.7, 34.8-33.5 (m, CD_2), 40.1, 42.3, 49.4, 54.4 (hept, *J*= 21.6 Hz; OCD_3), 71.2, 73.0, 73.1, 117.5, 133.6. HRMS calcd. for $C_{13}H_{14}O_2D$ (M^+-1) 216.1936, found 216.1934.

(1*R,3*R**,5*R**)-1-Allyl-3-ethoxy-5-methyl-9-oxabicyclo [3.3.1]nonane (2b).**



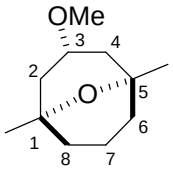
Colorless oil. R_f 0.43 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 6.60-6.47 (m, 1H; H_{10}), 5.76-5.62 (m, 2H; H_{11}), 4.85 (tt, *J*= 10.8, 6.2 Hz, 1H; H_3), 4.17 (c, *J*= 7.0 Hz, 2H; OCH_2), 2.88 (dd, *J*= 7.3, 1.0 Hz, 2H; H_9), 2.67 (dd, *J*= 14.0, 6.2 Hz, 1H; H_{2a}), 2.61 (dd, *J*= 13.1, 6.2 Hz, 1H; H_{4a}), 2.48-1.95 (m, 8H; $H_{2b,4b,6,7,8}$), 1.86 (s, 3H; H_{12}). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 15.6, 20.1, 31.8, 32.8, 34.9, 40.6, 42.9, 49.5, 62.8, 71.5, 71.6, 73.2, 117.5, 133.7. HRMS calcd. for $C_{14}H_{24}O_2$ 224.1776, found 224.1780.

(1*R,3*R**,5*R**)-1-Allyl-5-methyl-3-propoxy-9-oxabicyclo [3.3.1]nonane (2c).**



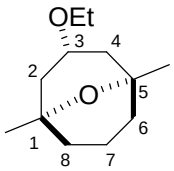
Colorless oil. R_f 0.57 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.90-5.78 (m, 1H; H_{10}), 5.12-4.96 (m, 2H; H_{11}), 4.15 (tt, *J*= 10.9, 6.2 Hz, 1H; H_3), 3.37 (t, *J*= 7.3 Hz, 2H; OCH_2), 2.19 (dd, *J*= 7.3 Hz, 2H; H_9), 1.98 (dd, *J*= 13.1, 6.2 Hz, 1H; H_{2a}), 1.93 (dd, *J*= 13.1, 6.2 Hz, 1H; H_{4a}), 1.80-1.58 (m, 9H), 1.53 (hex, *J*= 7.3 Hz, 2H; OCH_2CH_2), 1.35-1.24 (m, 2H; $H_{2b,4b}$), 1.18 (s, 3H; CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 10.5, 20.1, 23.2, 31.8, 32.7, 34.9, 40.5, 42.8, 49.4, 69.4, 71.4, 71.6, 73.2, 117.5, 133.6. HRMS calcd. for $C_{15}H_{26}O_2$ 238.1933, found 238.1935.

(1*S,3*R**,5*R**)-3-Methoxy-1,5-dimethyl-9-oxabicyclo [3.3.1]nonane (2d).**



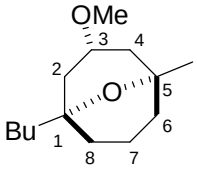
Colorless oil. R_f 0.42 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.08 (tt, *J*= 11.0, 6.3 Hz, 1H; H_3), 3.30 (s, 3H; OCH_3), 1.96 (dd, *J*= 13.3, 6.3 Hz, 2H; $H_{2a,4a}$), 1.84-1.38 (m, 6H; $H_{6,7,8}$), 1.32-1.21 (m, 2H; $H_{2b,4b}$), 1.18 (s, 6H; $2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 20.3, 31.8, 34.7, 42.1, 55.2, 71.6, 73.1. HRMS calcd. for $C_{11}H_{20}O_2$ 184.1463, found 184.1470.

(1*S,3*R**,5*R**)-3-Ethoxy-1,5-dimethyl-9-oxabicyclo [3.3.1]nonane (2e).**



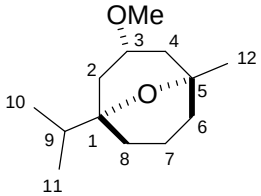
Colorless oil. R_f 0.45 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.21 (tt, *J*= 11.0, 6.2 Hz, 1H; H_3), 3.50 (c, *J*= 6.9 Hz, 2H; OCH_2), 1.99 (dd, *J*= 13.5, 6.2 Hz, 2H; $H_{2a,4a}$), 1.84-1.28 (m, 8H; $H_{6,7,8,2b,4b}$), 1.21 (s, 6H; $2CH_3$), 1.18 (t, *J*= 6.9 Hz, 3H; $CH_2C\mathit{H}_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 15.6, 20.4, 31.9, 34.8, 42.7, 62.8, 71.5, 71.6. HRMS calcd. for $C_{12}H_{22}O_2$ 198.1619, found 198.1620.

(1*S,3*R**,5*R**)-1-Butyl-3-methoxy-5-methyl-9-oxabicyclo [3.3.1]nonane (2f).**



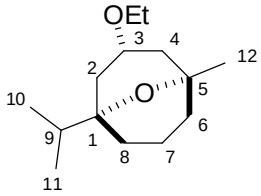
Colorless oil. R_f 0.55 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.96 (tt, *J*= 10.9, 6.2 Hz, 1H; H_3), 3.21 (s, *3*H; OCH_3), 1.93-1.82 (m, 2H; $H_{2a,4a}$), 1.71-1.12 (m, 14H), 1.08 (s, 3H; CH_3), 0.77 (t, *J*= 7.2 Hz, 3H; CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 13.9, 20.2, 23.2, 25.2, 31.9, 32.8, 35.0, 40.0, 42.4, 44.9, 55.2, 71.2, 73.3, 73.5. HRMS calcd. for $C_{14}H_{26}O_2$ 226.1933, found 226.1933.

(1*S,3*R**,5*R**)-1-*iso*-Propyl-3-methoxy-5-methyl-9-oxabicyclo[3.3.1]nonane (2g).**



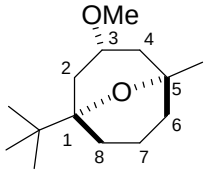
Colorless oil. R_f 0.45 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.95 (tt, *J*= 10.9, 6.1 Hz, 1H; H_3), 3.22 (s, *3*H; OCH_3), 1.87 (dd, *J*= 12.9, 6.1 Hz, 1H; H_{2a}), 1.84 (dd, *J*= 12.0, 6.1 Hz, 1H; H_{4a}),1.70-1.10 (m, 9H), 1.07 (s, 3H; CH_3), 0.78 (d, *J*= 6.8 Hz, 3H; CH_3), 0.75 (d, *J*= 6.8 Hz, 3H; CH_3).^{13}C NMR (75 MHz, $CDCl_3$) δ= 16.4, 16.6, 20.0, 29.5, 31.9, 34.9, 36.5, 39.9, 42.5, 55.3, 70.9, 73.6, 75.3. HRMS calcd. for $C_{13}H_{24}O_2$ 212.1776, found 212.1779.

(1*S,3*R**,5*R**)-3-Ethoxy-1-*iso*-propyl-5-methyl-9-oxabicyclo [3.3.1]nonane (2h).**



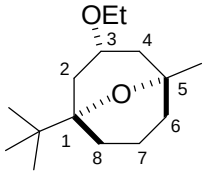
Colorless oil. R_f 0.49 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.18 (tt, *J*= 11.0, 6.1 Hz, 1H; H_3), 3.52 (c, *J*= 7.0 Hz, 2H; OCH_3), 1.98 (dd, *J*= 13.5, 6.1 Hz, 1H; H_{2a}), 1.92 (dd, *J*= 14.0, 6.1 Hz, 1H; H_{4a}), 1.82-1.24 (m, 9H), 1.21 (t *J*= 7.0 Hz, 3H; OCH_2CH_3), 1.18 (s, 3H; CH_3), 0.91 (d, *J*= 6.9 Hz, 3H; CH_3), 0.86 (d, *J*= 6.9 Hz, 3H; CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 15.5, 16.4, 16.6, 20.0, 29.6, 31.8, 34.9, 36.7, 39.9, 43.0, 62.8, 70.9, 71.9, 75.3. HRMS calcd. for $C_{14}H_{26}O_2$ 226.1933, found 226.1930.

(1*S,3*R**,5*R**)-1-*tert*-Butyl-3-methoxy-5-methyl-9-oxabicyclo[3.3.1]nonane (2i).**



Colorless oil. R_f 0.62 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.03 (tt, *J*= 10.8, 5.9 Hz, 1H; H_3), 3.34 (s, 3H; OCH_3), 1.94 (ddd, *J*= 12.7, 5.9, 1.2 Hz, 1H; H_{2a}), 1.85 (ddd, *J*= 12.5, 5.9, 1.2 Hz, 1H; H_{4a}), 1.77-1.30 (m, 8H), 1.15 (s, 3H; CH_3), 0.92 (s, 9H; $(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 19.8, 24.8, 27.0, 31.9, 34.5, 35.2, 38.1, 42.5, 55.2, 70.4, 74.0, 76.5. HRMS calcd. for $C_{14}H_{26}O_2$ 226.1933, found 226.1934.

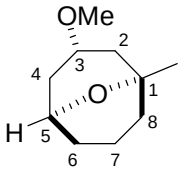
(1*S,3*R**,5*R**)-1-*tert*-Butyl-3-ethoxy-5-methyl-9-oxabicyclo [3.3.1]nonane (2j).**



Colorless oil. R_f 0.68 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.02 (tt, *J*= 10.9, 5.9 Hz, 1H; H_3), 3.41 (c, *J*= 7.0 Hz, 2H; OCH_2), 1.83 (ddd, *J*= 12.5, 5.9, 1.2 Hz, 1H; H_{2a}), 1.72 (ddd, *J*= 12.5, 5.9, 1.1 Hz, 1H; H_{4a}), 1.65-1.18 (m, 8H), 1.09 (t, *J*= 7.0 Hz, 3H; OCH_2CH_3), 1.03 (s, 3H; CH_3), 0.82 (s, 9H; $(CH_3)_3$). ^{13}C

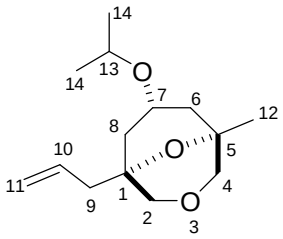
NMR (75 MHz, $CDCl_3$) δ= 15.7, 19.8, 24.8, 27.0, 31.9, 34.5, 35.7, 38.1, 43.1, 62.8, 70.4, 72.4, 76.3. HRMS calcd. for $C_{15}H_{28}O_2$ 240.1725, found 240.1725.

(1*R,3*S**,5*S**)-3-Methoxy-1-methyl-9-oxabicyclo [3.3.1]nonane (2k).**



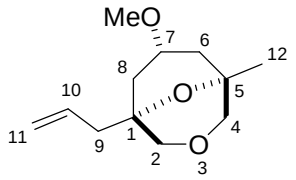
Colorless oil. R_f 0.43 (hexane:ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 4.12 (app. t, *J*= 5.8 Hz, 1H; H_5), 3.97 (tt, *J*= 11.0, 6.2 Hz, 1H; H_3), 3.23 (s, 3H; OCH_3), 1.93 (ddd, *J*= 13.0, 6.2, 1.2 Hz, 2H; H_{2a}), 1.87 (ddt, *J*= 13.0, 6.2, 1.4 Hz, 2H; H_{4a}), 1.82-1.22 (m, 6H), 1.06 (s, 3H; CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 20.0, 28.4, 31.8, 35.4, 36.0, 42.8, 55.2, 69.2, 70.6, 72.9. HRMS calcd. for $C_{10}H_{18}O_2$ 170.1307, found 170.1310.

(1*R,5*S**,7*R**)-1-Allyl-7-isopropoxy-5-methyl-3,9-dioxabicyclo[3.3.1]nonane (2l).**



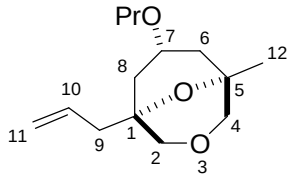
Colorless oil. R_f 0.42 (hexane:ethyl acetate, 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ= 5.85-5.65 (m, 1H; H_{10}), 5.14-5.07 (m, 2H; H_{11}), 4.61 (tt, *J*= 10.8, 5.9 Hz, 1H; H_7), 3.76 (hept, *J*= 6.1, 1H; OCH), 3.67 (d, *J*= 11.3 Hz, 1H; H_{2a}), 3.65 (d, *J*= 11.3 Hz, 1H; H_{4a}), 3.39 (dd, *J*= 11.3, 2.6 Hz, 1H; H_{2b}), 3.34 (dd, *J*= 11.3, 2.6 Hz, 1H; H_{4b}), 2.19 (dt, *J*= 7.6, 1.1 Hz, 2H; H_9), 2.05 (app. t, *J*= 5.9 Hz, 1H; H_{6a}), 2.01 (app. t, *J*= 5.9 Hz, 1H; H_{8a}), 1.44 (ddd, *J*= 10.8, 6.1, 2.6 Hz, 1H; H_{6b}), 1.41 (ddd, *J*= 10.8, 6.1, 2.6 Hz, 1H; H_{8b}), 1.14 (d, *J*= 6.1 Hz, 6H; $(CH_3)_2$), 1.12 (s, 3H; CH_3). ^{13}C NMR (200 MHz, $CDCl_3$) δ= 22.9, 23.0, 25.0, 40.3, 42.7, 43.7, 68.3, 68.4, 71.3, 72.7, 73.3, 74.4, 118.1, 132.1. HRMS calcd. for $C_{14}H_{24}O_3$ 240.1725, found 240.1727.

(1*R,5*S**,7*R**)-1-Allyl-7-methoxy-5-methyl-3,9-dioxabicyclo [3.3.1]nonane (2m).**



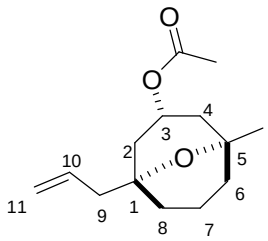
Colorless oil. R_f 0.45 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.87-5.70 (m, 1H; H_{10}), 5.08-4.96 (m, 2H; H_{11}), 4.29 (tt, *J*= 10.9, 5.9 Hz, 1H; H_7), 3.50 (d, *J*= 11.4 Hz, 1H; H_{2a}), 3.48 (d, *J*= 11.4 Hz, 1H; H_{4a}), 3.24 (dd, *J*= 11.4, 2.6 Hz, 1H; H_{2b}), 3.22 (s, 3H; OCH_3), 3.18 (dd, *J*= 11.4, 2.6 Hz, 1H; H_{4b}), 2.04 (d, *J*= 7.4 Hz, 2H; H_9), 2.01-1.90 (m, 2H; $H_{6a,8a}$), 1.23 (dt, *J*= 10.7, 2.6 Hz, 1H; H_{6b}), 1.18 (dt, *J*= 10.7, 2.6 Hz, 1H; H_{8b}), 0.96 (s, 3H; CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 25.0, 39.1, 41.5, 43.6, 55.3, 71.3, 72.5, 72.7, 73.2, 74.4, 118.2, 132.0. HRMS calcd. for $C_{12}H_{20}O_3$ 212.1412, found 212.1411.

(1*R,5*S**,7*R**)-1-Allyl-5-methyl-7-propoxy-3,9-dioxabicyclo [3.3.1]nonane (2n).**



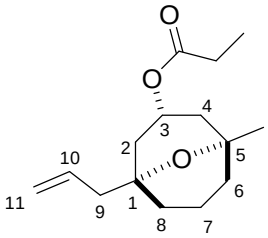
Colorless oil. R_f 0.42 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.75-5.58 (m, 1H; H_{10}), 4.97-4.86 (m, 2H; H_{11}), 4.35 (tt, *J*= 10.8, 5.9 Hz, 1H; H_7), 3.48 (d, *J*= 11.1 Hz, 1H; H_{2a}), 3.47 (d, *J*= 11.1 Hz, 1H; H_{4a}), 3.28 (t, *J*= 7.4 Hz, 2H; OCH_2), 3.21 (dd, *J*= 11.1, 2.4 Hz, 1H; H_{4b}), 3.16 (dd, *J*= 11.1, 2.4 Hz, 1H; H_{2b}), 2.02 (d, *J*= 7.3 Hz, 2H, H_9), 1.94 (app. t, *J*= 5.9 Hz, 1H; H_{6a}), 1.90 (app. t, *J*= 5.9 Hz, 1H; H_{8a}), 1.42 (hex, *J*= 7.4 Hz, 1H; OCH_2CH_2), 1.26 (dt, *J*= 11.1, 2.3 Hz, 1H; H_{6b}), 1.21 (dt, *J*= 11.1, 2.3 Hz, 1H; H_{8b}), 0.95 (s, 3H; CH_3), 0.77 (t, *J*= 7.3 Hz, 3H; CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 10.5, 23.3, 25.0, 39.6, 42.0, 43.7, 69.5, 70.9, 71.3, 72.7, 73.3, 74.4, 118.1, 132.1. HRMS calcd. for $C_{14}H_{24}O_3$ 240.1725, found 240.1730.

(1*R,3*R**,5*R**)-1-Allyl-5-methyl-9-oxabicyclo[3.3.1]nonan-3-yl acetate (8a).**



Colorless oil. R_f 0.42 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.90-5.75 (m, 1H, H_{10}), 5.63 (tt, *J*= 11.1, 6.2 Hz, 1H; H_3), 5.12-4.98 (m, 2H; H_{11}), 2.23 (d, *J*= 7.4 Hz, 2H; H_9), 2.01 (s, 3H; $C(O)CH_3$), 1.98-1.37 (m, 10 H), 1.20 (s, 3H; CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 19.9, 21.2, 31.6, 32.7, 34.7, 39.1, 41.4, 49.2, 67.9, 71.5, 73.2, 117.7, 133.4, 170.6. HRMS calcd. for $C_{14}H_{22}O_3$ 238.1569, found 238.1576.

(1*R,3*R**,5*R**)-1-Allyl-5-methyl-9-oxabicyclo[3.3.1]nonan-3-yl propionate (8b).**

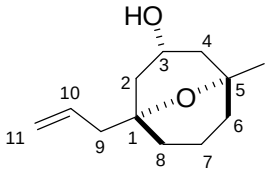


Colorless oil. R_f 0.60 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.92-5.77 (m, 1H, H_{10}), 5.64 (tt, *J*= 11.2, 6.3 Hz, 1H; H_3), 5.13-5.01 (m, 2H; H_{11}), , 2.27 (c, *J*= 7.5 Hz, 2H; $C(O)CH_2$), 2.22 (d, *J*= 7.5 Hz, 2H; H_9), 1.98 (dd, *J*= 12.7, 6.3 Hz, 1H; H_{2a}), 1.92 (dd, *J*= 12.9, 6.3 Hz, 1H; H_{4a}), 1.85-1.35 (m, 8H), 1.20 (s, 3H; CH_3), 1.11 (t, *J*= 7.5 Hz, 3H; $CH_2C\mathit{H}_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 9.1, 20.0, 27.8, 31.6, 32.7, 34.8, 39.2, 41.4, 49.3, 67.7, 71.5, 73.3, 117.7, 133.5, 174.1. HRMS calcd. for $C_{15}H_{24}O_3$ 252.1725, found 252.1732.

Solvolysis of compound 8a. Synthesis of compound 9.

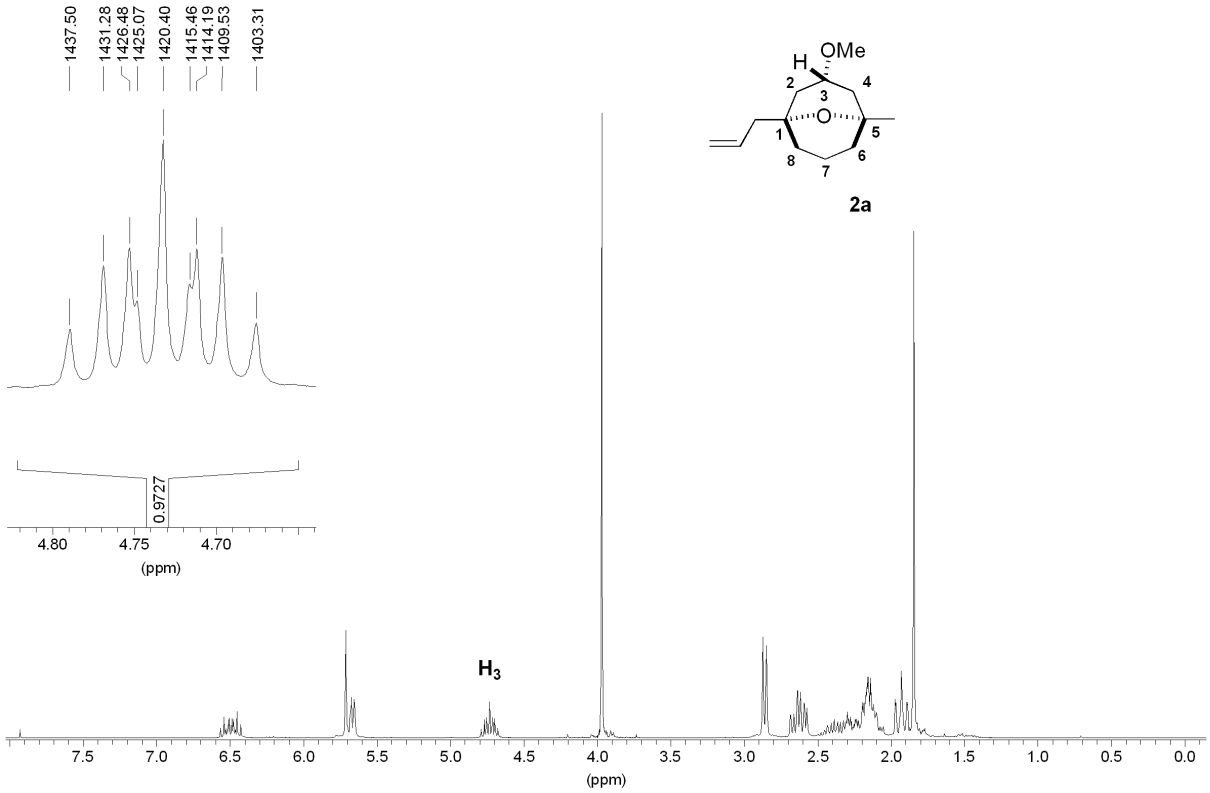
To a solution of compound **8a** (119 mg, 0.5 mmol) in methanol (5 mL) was added K_2CO_3 (14 mg, 0.1 mmol) at room temperature. After one hour the resulting slurry was filtered and the solvent was removed at reduced pressure. The crude obtained was purified by flash column chromatography on silica gel using hexane:ethyl acetate 5:1 as eluent to yield compound **9**.

(1*R,3*R**,5*R**)-1-Allyl-5-methyl-9-oxabicyclo[3.3.1]nonan-3-ol (9).**

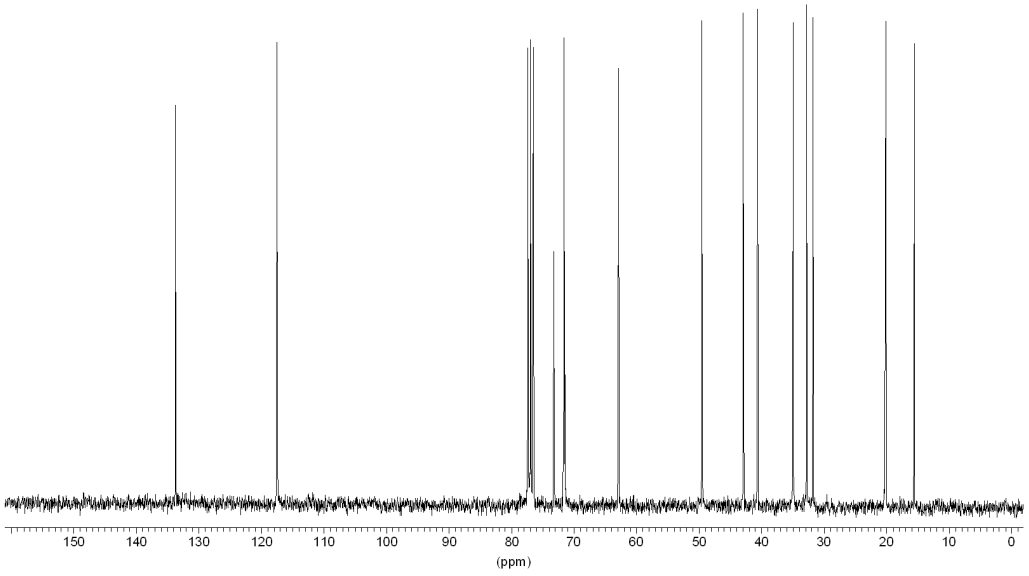


Colorless oil. R_f 0.15 (hexane:ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.91-5.76 (m, 1H, H_{10}), 5.08-4.97 (m, 2H; H_{11}), 4.46 (tt, *J*= 10.0, 5.8 Hz, 1H; H_3) , 2.21 (dd, *J*= 7.3, 0.9 Hz, 2H; H_9), 2.16 (s, 1H; OH), 1.92 (dd, *J*= 13.0, 5.8 Hz, 1H; H_{2a}), 1.87 (dd, *J*= 13.0, 5.8 Hz, 1H; H_{4a}), 1.78-1.29 (m, 8H), 1.18 (s, 3H; CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ= 19.5, 31.9, 32.9, 35.0, 42.8, 45.1, 49.4, 64.6, 71.5, 73.2, 117.7, 133.5. HRMS calcd. for $C_{12}H_{20}O_2$ 196.1463, found 196.1469.

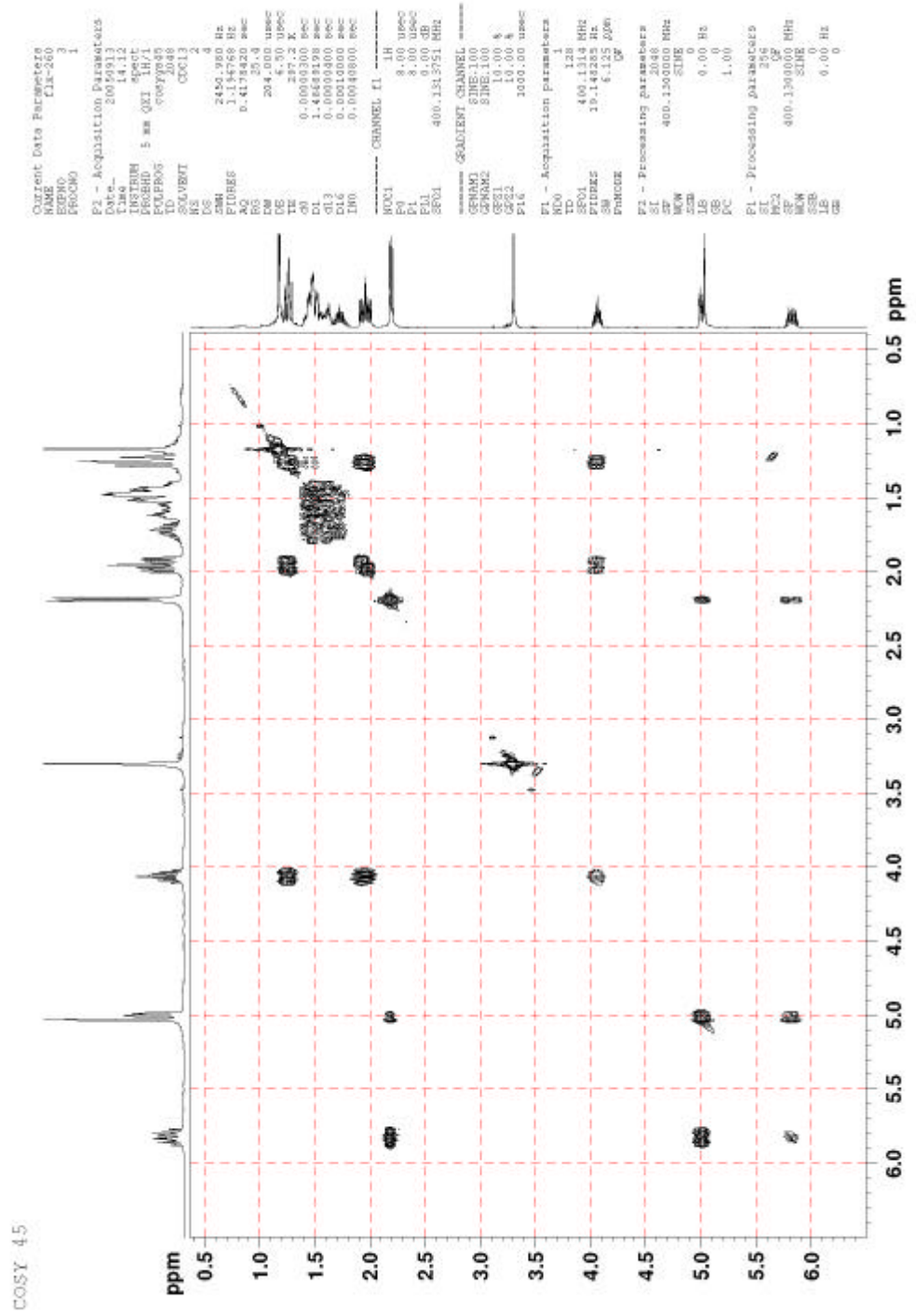
Characterization of compound 2a.



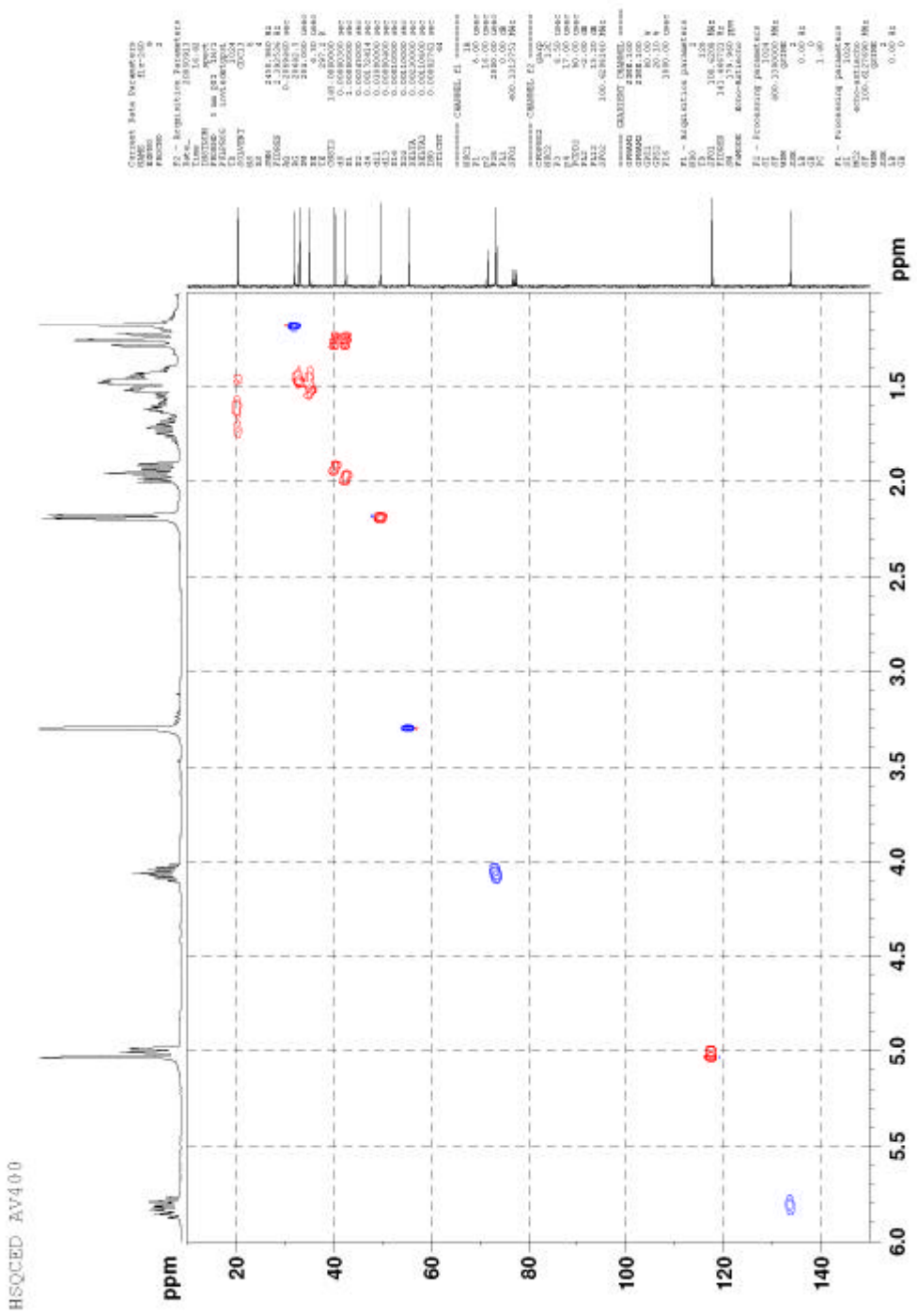
^{1}H-NMR(400 MHz, $CDCl_3$)



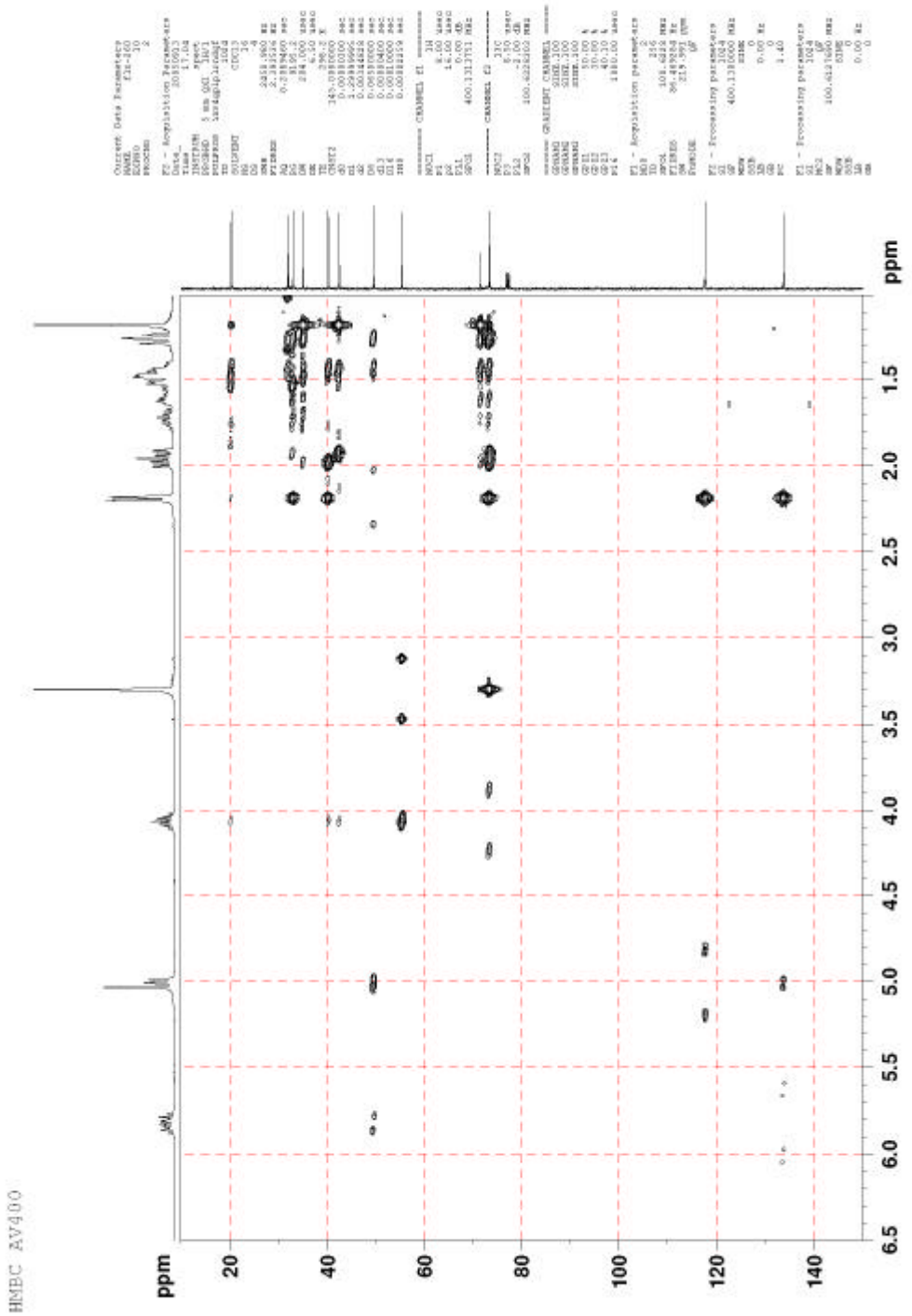
^{13}C-NMR (400 MHz, $CDCl_3$)



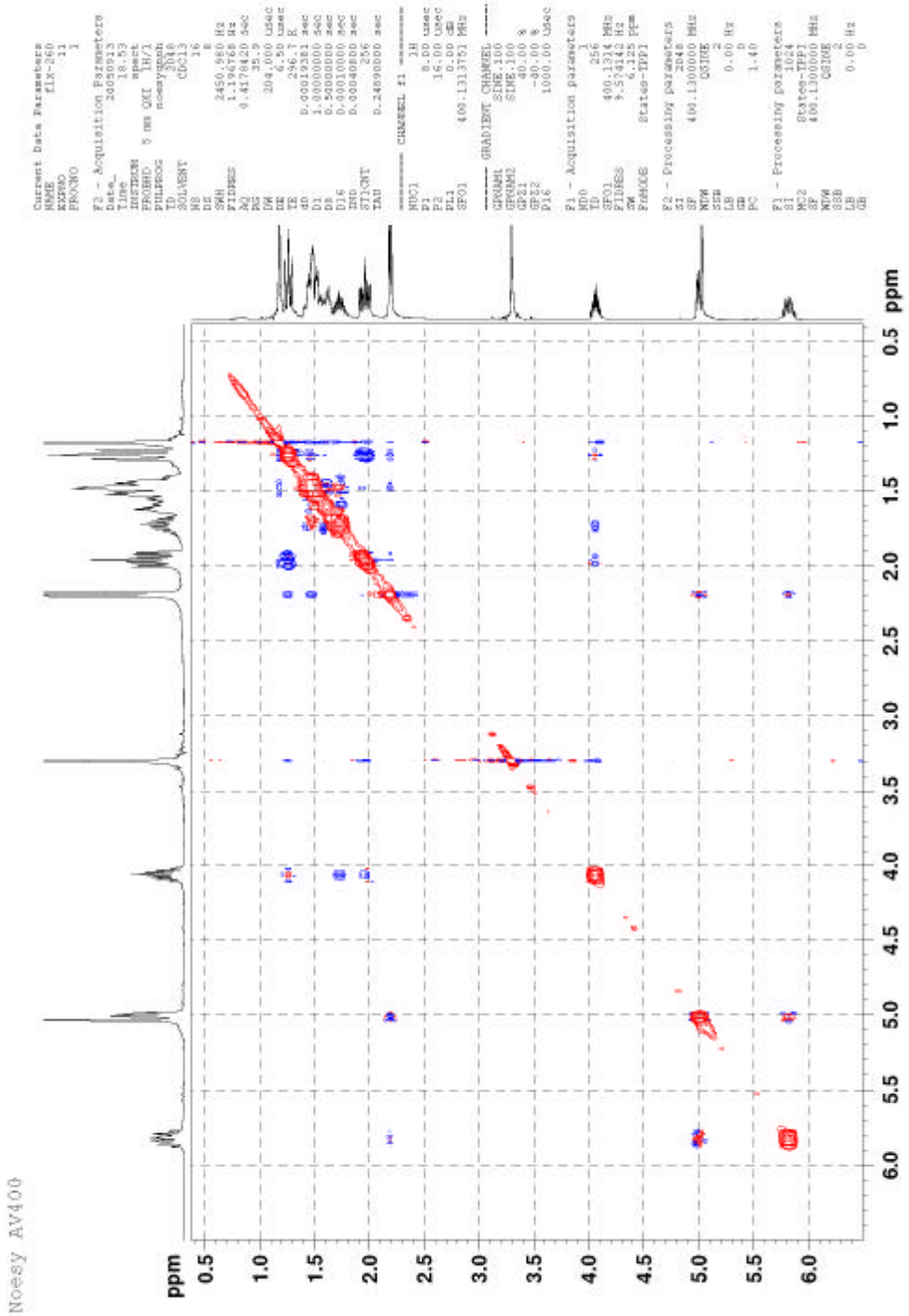
COSY 45 (400 MHz, $CDCl_3$)



HSQCED (400 MHz, $CDCl_3$)



HMBC (400 MHz, $CDCl_3$)



NOESY (400 MHz, $CDCl_3$)