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Supporting Information

Ruthenium-Olefin Complexes: Effect of Ligand Variation upon Geometry

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General Considerations

All reactions were carried out under a dry argon atmosphere using standard Schlenk techniques or in a nitrogen-filled glovebox, unless otherwise noted. Toluene, pentane, benzene, and benzene-d_6 were purified by passage through activated A-2 alumina solvent columns and were degassed with argon prior to use. Unless otherwise noted, all compounds were purchased from Aldrich or Fisher. Diethyl diallymalonate (**2.9**) was purchased from Aldrich and distilled prior to use. CD_2Cl_2 was purified by distillation from CaH_2 and degassed with argon prior to use. $CDCl_2CDCl_2$ was passed through a plug of alumina, degassed with nitrogen and stored over 4Å molecular sieves. Divinylbenzene (**9**),[1] catalyst **18**,[2] **19**,[3] and catalyst **14**[3,4] were prepared according to literature procedure. Complexes **7** and **14** were generously donated by Materia, Inc. High-resolution mass spectrometry (HRMS) data was obtained on a JEOL MSRoute mass spectrometer. ^1H and ^{13}C NMR spectra were recorded on Varian Inova (300 and 500) or on a Bruker Avance DPX 400 MHz NMR spectrometer equipped with a 5 mm dual $^1H/^{13}C$ Z-gradient probe. ^1H NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and referenced internally with respect to the protio solvent impurity. ^{13}C NMR spectra were referenced internally with respect to the solvent resonance.

NMR Spectroscopy Experiments

2D NMR spectra were obtained on a Bruker Avance DPX 400 MHz NMR spectrometer equipped with a 5 mm dual $^1H/^{13}C$ Z-gradient probe. Unless otherwise specified, spectra were obtained at room temperature. For experiments requiring elevated temperatures, the probe was calibrated with a sample of ethylene glycol containing a trace amount of gaseous HCl.[5] 1D ^1H and ^{13}C

spectra were acquired with standard pulse sequences and parameters. Details for the 2D experiments are as follows:

Gradient-enhanced 2D COSY experiment.[6] The **cosygs** pulse program was used with the following acquisition parameters: F2 and F1 sweep widths, 7184 Hz. F2 and F1 digital resolution, 7.01 Hz/pt. 256 FIDs recorded, each consisting of 4 scans and 1024 data points (AQ = 0.071 s). A recycle delay of (D1) of 1.5 s was employed. Processing parameters: unshifted sinusoidal apodization was applied in both dimensions prior to the Fourier transformation.

2D COSYLR experiment.[7] The **cosylr** pulse program was used with the following acquisition parameters: F2 and F1 sweep widths, 7184 Hz. F2 and F1 digital resolution, 7.01 Hz/pt. 128 FIDs recorded, each consisting of 8 scans and 1024 data points (AQ = 0.071 s). Refocussing delays of 100 ms and 200 ms were used in separate experiments. A recycle delay of (D1) of 2.0 s was employed. Zero-filling was applied once to achieve digital resolution of 3.5 Hz/pt in each dimension. Processing parameters: unshifted sinusoidal (SINE, SSB=0) apodization was applied in both dimensions prior to the Fourier transformation.

2D ROESY experiment.[8] The **roesytp.2** pulse program was used with the following acquisition parameters: F2 and F1 sweep widths, 7184 Hz. F2 and F1 digital resolution, 3.5 Hz/pt. 256 FIDs recorded, each consisting of 16 scans and 2048 data points (AQ = 0.142 s). The 800 ms spin lock consisted of 5404 cycles of phase-shifted pairs of 74 μs 180° pulses. A recycle delay of (D1) of 2.0 s was employed. Processing parameters: $\pi/2$ shifted sine^2 (QSINE, SSB=2) apodization was applied in both dimensions prior to the Fourier transformation.

Representative 2D NOESY/EXSY experiment.[9] The **noesytp** pulse program was used with the following acquisition parameters: F2 and F1 sweep widths, 2913 Hz. F2 and F1 digital resolution, 2.8 Hz/pt. 256 FIDs recorded, each consisting of 8 scans and 1024 data points (AQ = 0.176 s). A mixing time of 800 ms was set as a simple delay. A recycle delay of (D1) of 2.0 s was employed.

Processing parameters: π/2 shifted sine^2 (QSINE, SSB=2) apodization was applied in both dimensions prior to the Fourier transformation.

Gradient-enhanced 2D ^{1}H-^{13}C HMQC experiment.[10] The **inv4gp** pulse program was used with the following acquisition parameters: F2 sweep width, 7184 Hz, F1 sweep width, 32,895 Hz. F2 digital resolution, 7.01 Hz/pt, F1 digital resolution, 257 Hz/pt. 128 FIDs recorded, each consisting of 16 scans and 1024 data points (AQ = 0.071 s). The D2 delay was set to 3.57 ms (1/2J = 140 Hz). A recycle delay (D1) of 3.0 s was employed. Processing parameters: Zero-filling was applied once (SI = 2048) in F2 to achieve a digital resolution of 3.5 Hz/pt and eight times (SI = 1024) in F1 to achieve a digital resolution of 32 Hz/pt. Exponential (EM, LB = 5) apodization was applied in the F2 dimension and π/3 shifted sine^2 (QSINE, SSB=3) apodization was applied in the F1 dimension prior to the Fourier transformation.

Assignment of the ^{1}H NMR Spectra

The ^{1}H NMR spectra of each ruthenium-olefin complex was assigned utilizing a mixture of 1D and 2D NMR data. Due to the complexity of some samples, full proton assignment could not be made.

Complex **10**: To a 4-mL vial in the glovebox was added **7** (95 mg, 0.12 mmol) and toluene (ca. 2 mL). Vial capped with a screwcap containing a PTFE septum and removed from the glovebox. Divinylbenzene (17.5 μL, 0.12 mmol) added via syringe. Vial taken into the glovebox. The reaction stirred at 22 °C overnight, filtered through a pipette column and washed with toluene (ca. 1 mL) and pentane (2 x 2 mL). Solid eluted with CH_2Cl_2 and concentrated to yellow-green solid (37 mg, 56%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 16.57 (q, 1H, *J* = 0.9 Hz), 16.42 (q, 1H, *J* = 1.1 Hz), 7.60 (m, 2H), 7.47 (m, 4H), 7.37 (m, 2H), 7.22 (m, 6H), 7.23 (m, 4H), 6.68 (d, 1H, *J* = 7.8 Hz), 6.55 (d, 1H, *J* = 7.7 Hz), 6.4 (tt, 1H, *J* = 9.0, 1.4 Hz), 6.22 (br d, 1H, *J* = 11.3 Hz, H_a of **10a**), 6.10 (tt, 1H, *J* = 9.0, 1.4 Hz), 5.77 (dd, 1H, *J* = 9.1, 12.8 Hz, H_a of **10b**), 4.48-3.96 (m, 9H, H_b of **10a** is buried within), 3.73 (dt, 1H, *J* = 9.1, 1.4 Hz, H_b of **10b**), 3.40 (ddd, 1H, *J* = 0.65, 1.8, 12.8 Hz, H_c of **10b**), 3.33, (dd, 1H, *J* = 12.8, 1.1 Hz, H_c of **10a**); ^{19}F NMR (1:1 TCE-d_2/CD_2Cl_2, 376.5 MHz): δ = −111.5 ppm (br s), −113.7, −116.0, −118.2, −118.5. HRMS (FAB) *m*/*z* (%): 581.9824 $[M]^+$ (2). Calcd: 581.9827.

COSYLR NMR data for **10**: Benzylidene resonance at 16.57 has long-range COSY interaction with 3.73 ppm (H_b of **10b).** Benzylidene resonance at 16.42 has long-range COSY interaction with H_b of **10a** (resonance buried within NHC backbone). H_c of **10b** has COSYLR interactions with 3.73 ppm (H_b of **10b**), which is to be expected on account of a small geminal coupling.

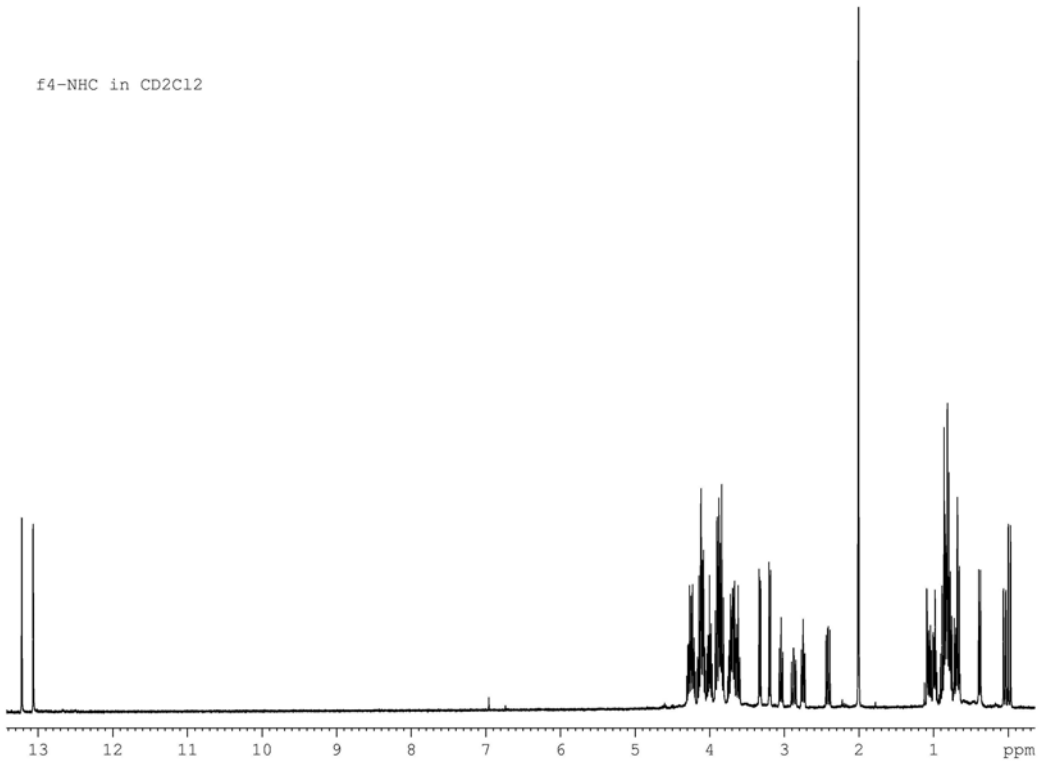

Figure A1. ^{1}H NMR spectrum of **10** in CD_2Cl_2 at 22 °C.

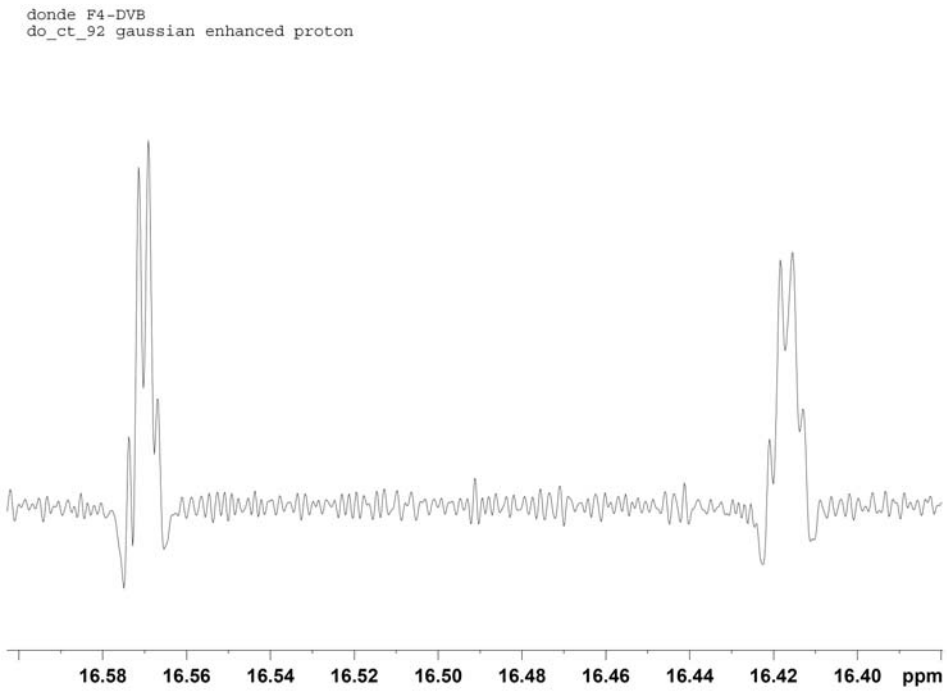

Figure A2. Gaussian-enhanced ^{1}H NMR spectrum of **10** in CD_2Cl_2 at 22 °C.

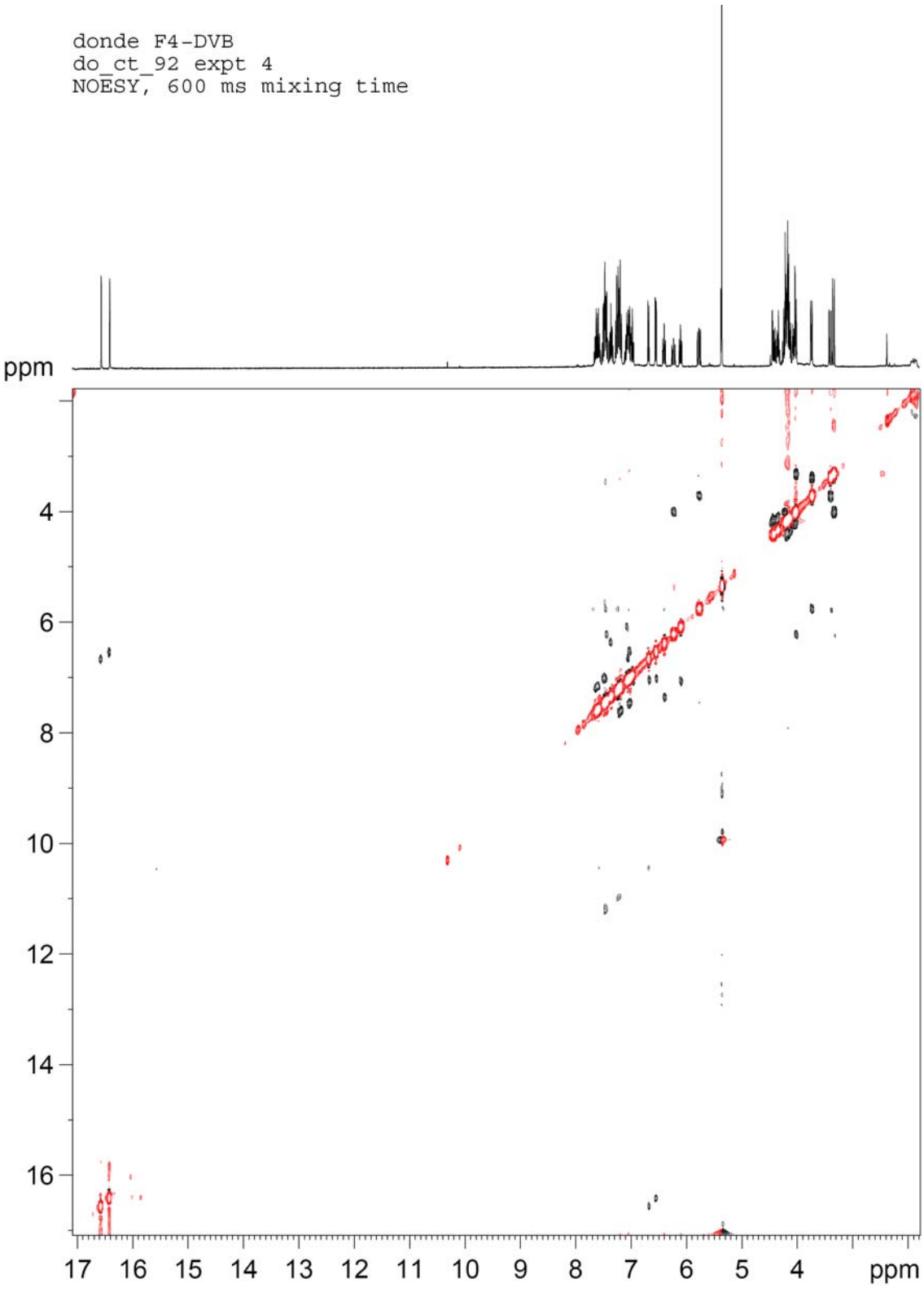

Figure A3. 2D-NOESY/EXSY spectrum of **10** in CD_2Cl_2 at 22 °C.

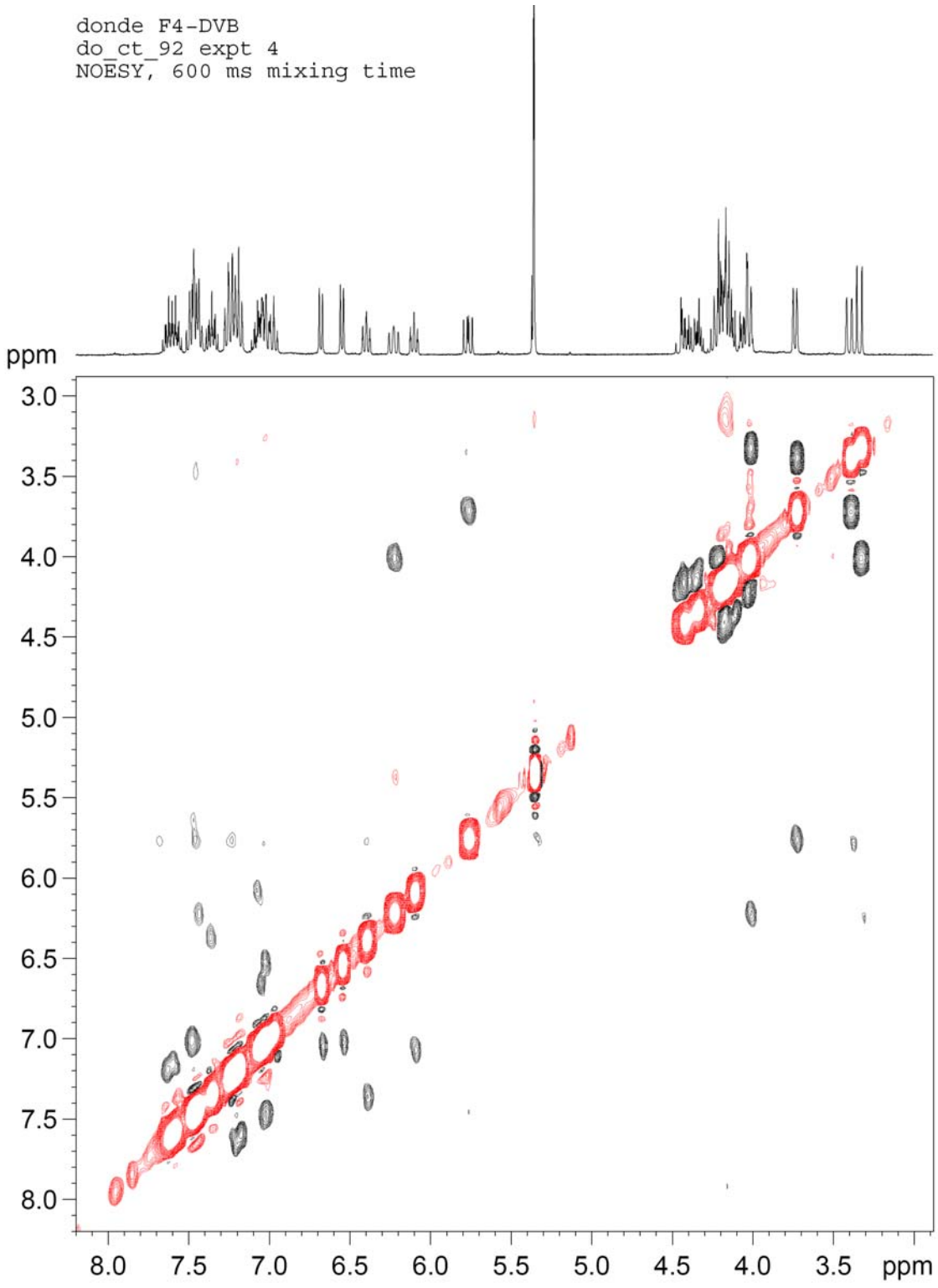

Figure A4. 2D-NOESY/EXSY spectrum of **10** in CD_2Cl_2 at 22 °C.

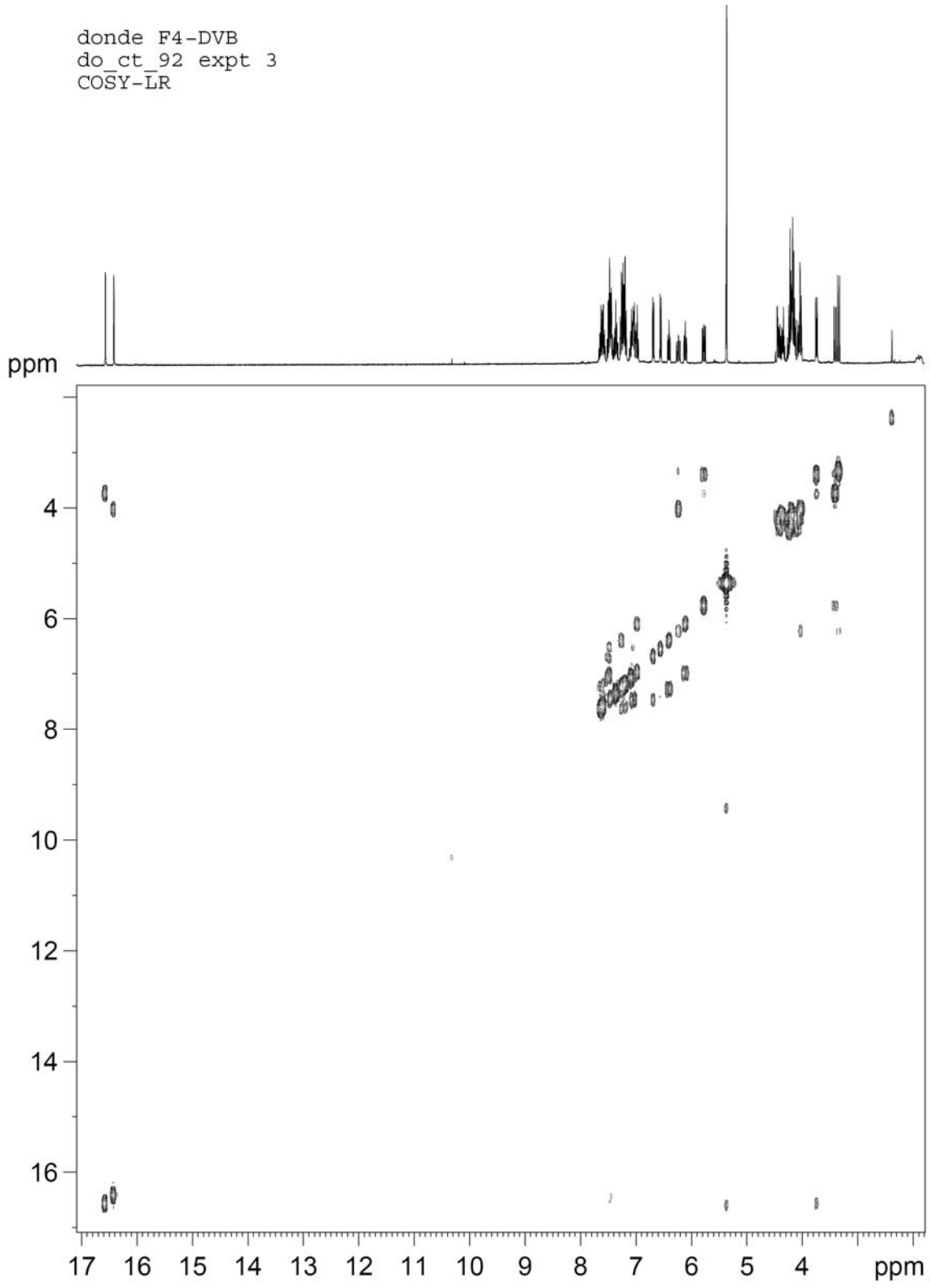

Figure A5. COSYLR spectrum of **10** in CD_2Cl_2 at 22 °C.

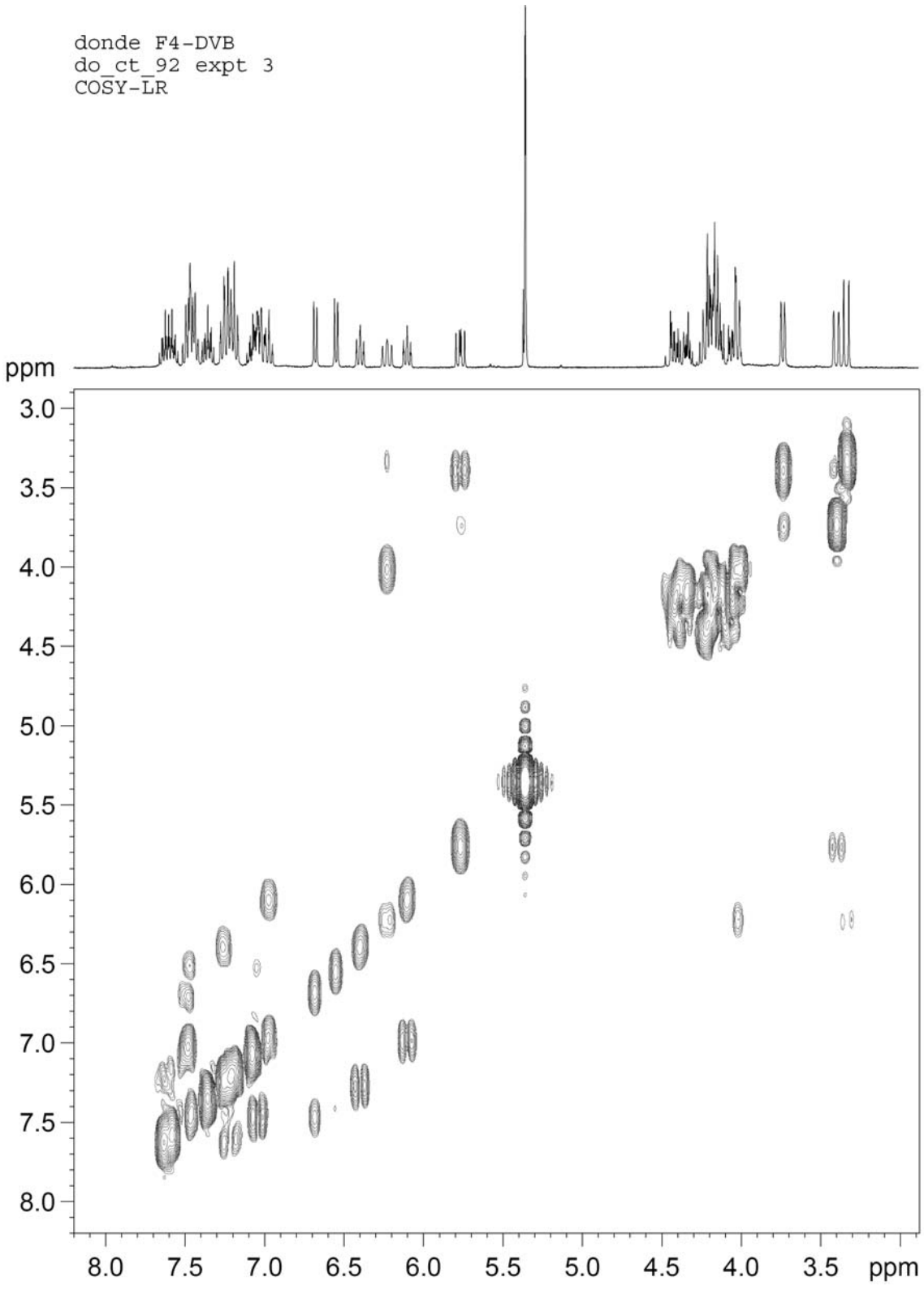

Figure A6. COSYLR spectrum of **10** in CD_2Cl_2 at 22 °C.

Complex **12**: To a 4-mL vial in the glovebox was added **11** (30 mg, 0.032 mmol) and benzene (ca. 1 mL). Vial capped with a screwcap containing a PTFE septum and removed from the glovebox. Divinylbenzene (4.5 μL, 0.032 mmol) added via syringe. Vial taken into the glovebox. The reaction stirred at 22 °C 2 h, concentrated and extracted with pentanes. The resulting solid was dissolved in benzene and precipitated with pentane. After filtration through a pipette column, elution with CH_2Cl_2, and concentration, a green solid (12 mg, 55%) was isolated. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 16.14 (br s, 1H, long range couples to 2.93 ppm, 7.32 ppm), 7.6-7.2 (m, 10 H), 7.00 (t, 1H, *J* = 7.7 Hz), 6.76 (d, 1H, *J* = 7.2 Hz), 6.24 (d, 1H, *J* = 7.5 Hz), 6.13 (dd, 1H, *J* = 9.9. 11.7 Hz, H_a of **12a**), 4.44 (m, 2H), 4.28 (m, 2H), 4.12 (m, 1H), 4.03 (m, 1H), 3.08 (sept, 1H, *J* = 6.7 Hz), 3.05 (d, 1H, *J* = 12.3 Hz, H_c of **12a**), 2.95 (d, 1H, *J* = 10.1 Hz, H_b of **12a**), 2.34 (septet, 1H, *J* = 7.2 Hz), 1.83 (d, 3H, *J* = 6.7 Hz), 1.53 (d, 3H, *J* = 6.7 Hz), 1.46 (d, 3H, *J* = 6.7 Hz), 1.37 (d, 3H, *J* = 6.7 Hz), 1.27 (d, 3H, *J* = 6.7 Hz), 1.21 (d, 3H, *J* = 6.7 Hz), 1.00 (d, 3H, *J* = 6.7 Hz), 0.09 (d, 3H, *J* = 6.7 Hz).

2D-NOESY data utilized to assign the major conformer in solution as **12a**: H_c shows an NOE with a Me resonance at 0.09 ppm, H_b shows an NOE to a Me resonance at 1.46 ppm, H_a shows one NOE to H_b. Additional NOE expts were run in C_6D_6 in order to resolve overlap between one olefin resonance and a methine resonance. In this experiment, H_b shows an NOE to a methyl resonance at 1.32 ppm, H_c shows NOEs to 0.11 ppm (Me), 1.32 ppm (Me), and 2.35 ppm (C-H). It is also interesting to note that a methine-methine NOE is readily observed in this data set (2.35/3.0 ppm)—this is likely the C-H/C-H interaction spanning the gap filled by the olefin.

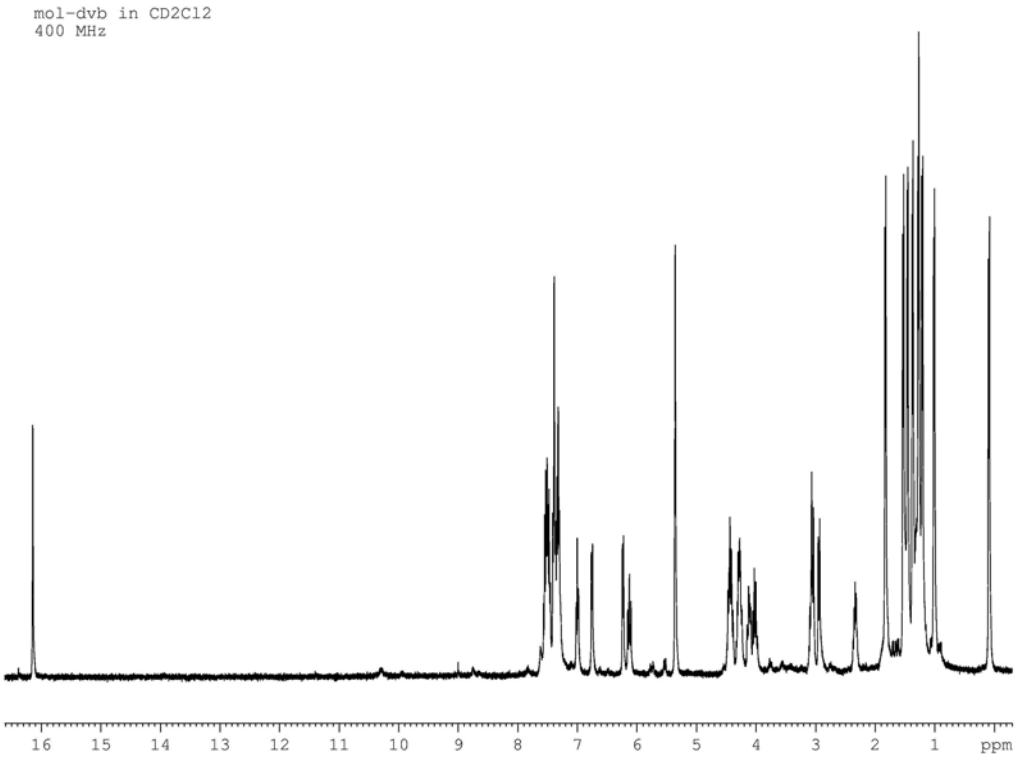

Figure A7. ^{1}H NMR spectrum of **12** in CD_2Cl_2 at 22 °C.

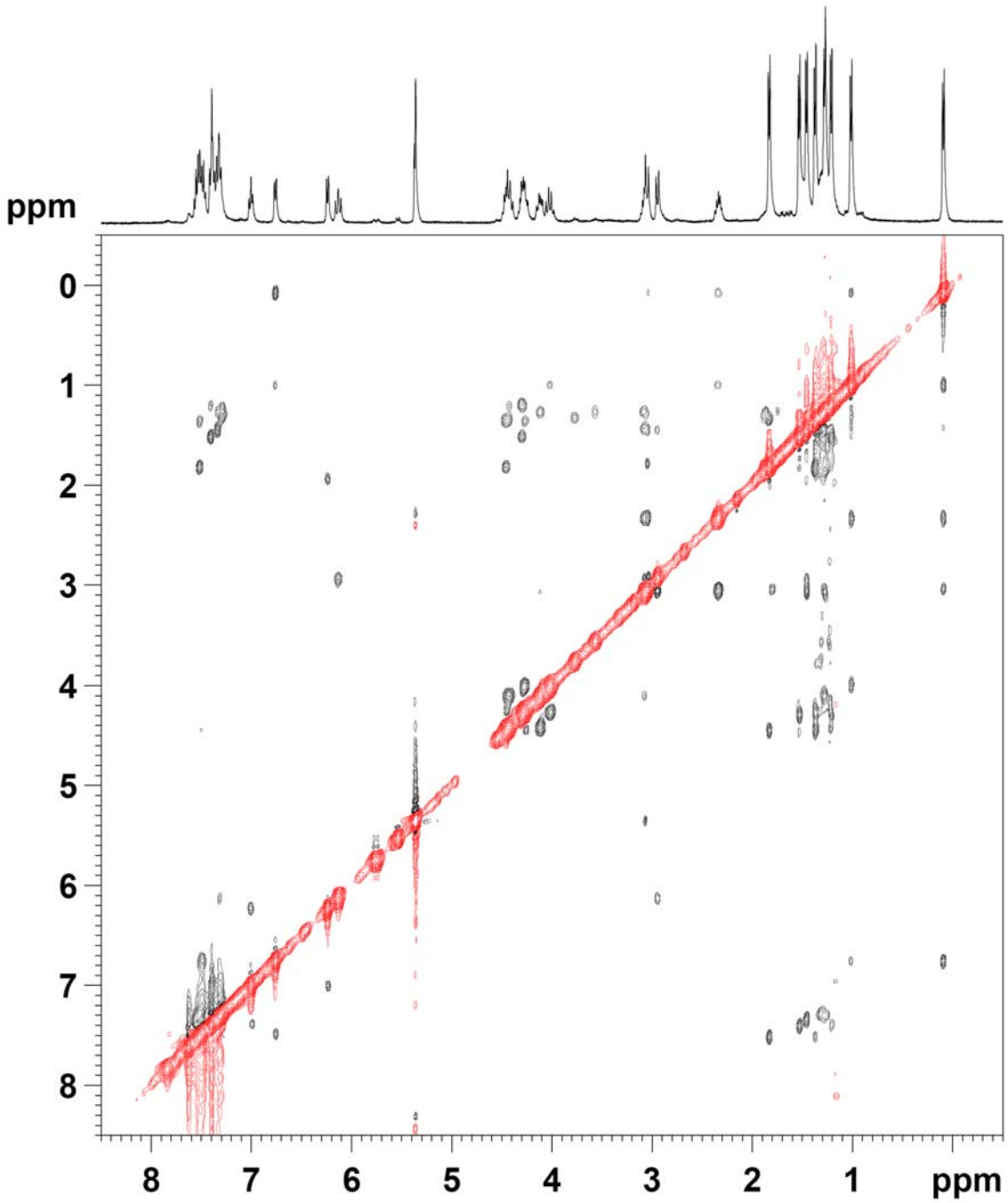

Figure A8. Alkyl and aromatic region of 2D-NOESY/EXSY spectrum of **12** in CD_2Cl_2 at 22 °C.

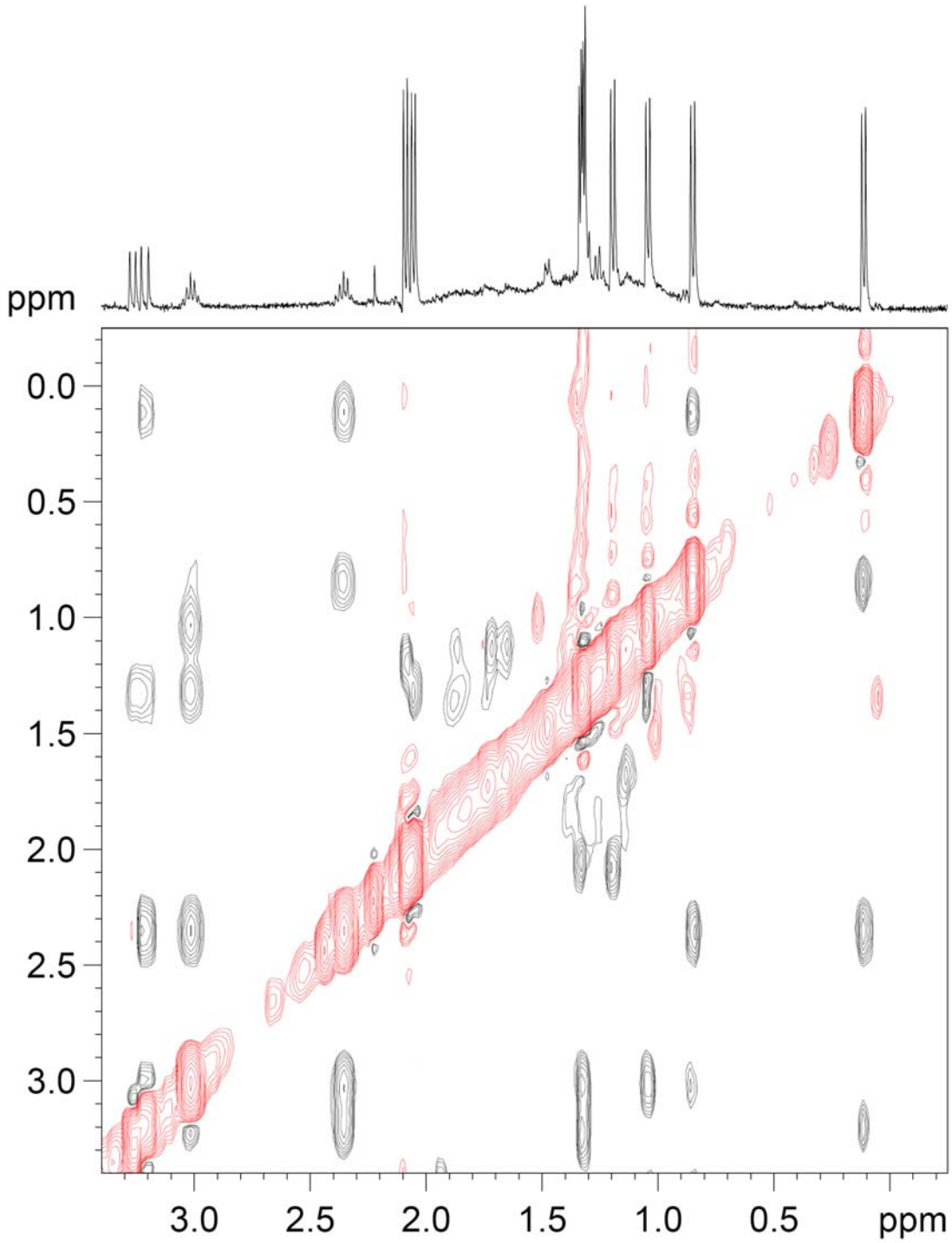

Figure A9. 2D-NOESY/EXSY spectrum of **12** in C_6D_6 at 22 °C.

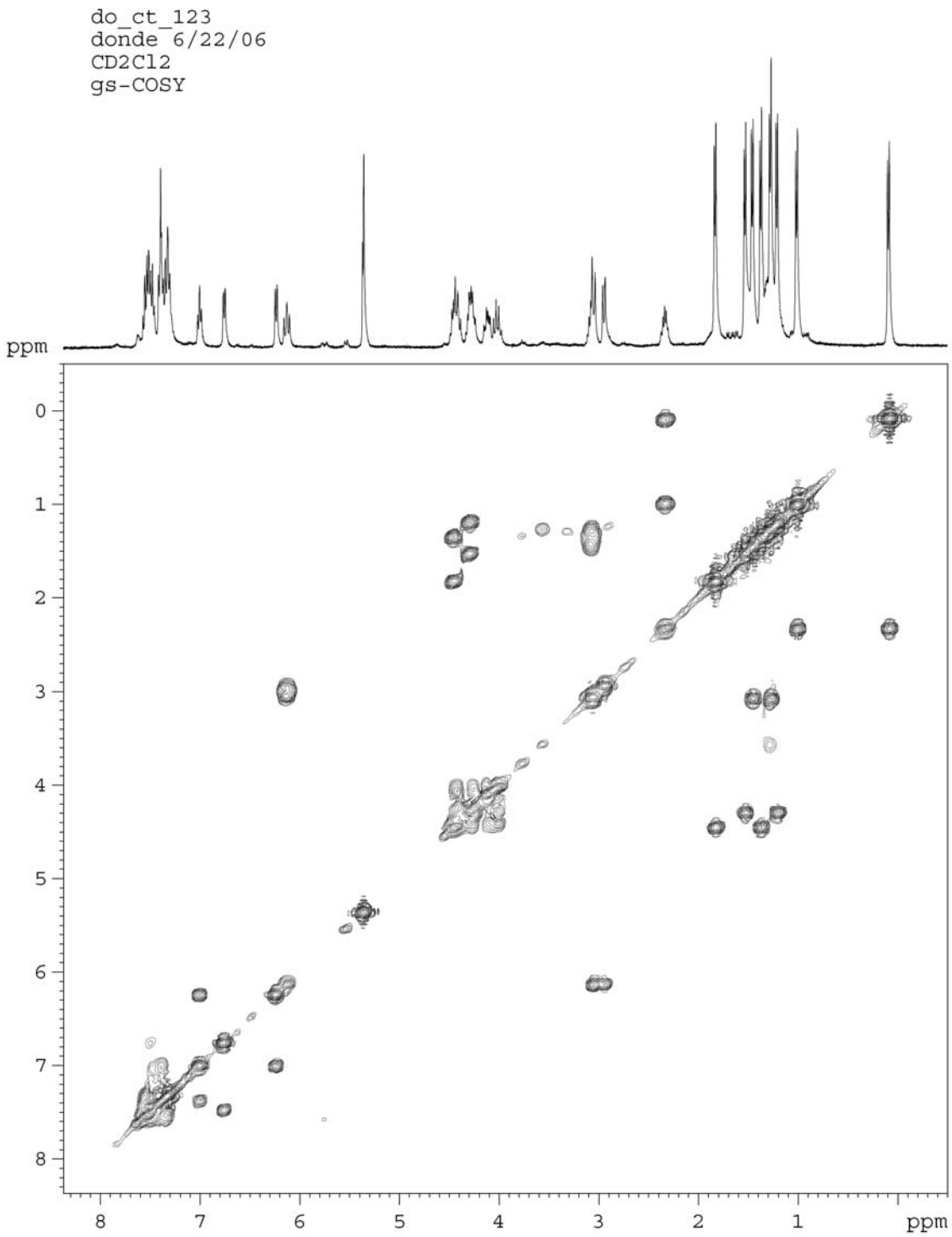

Figure A10. COSYLR spectrum of **12** in CD_2Cl_2 at 22 °C.

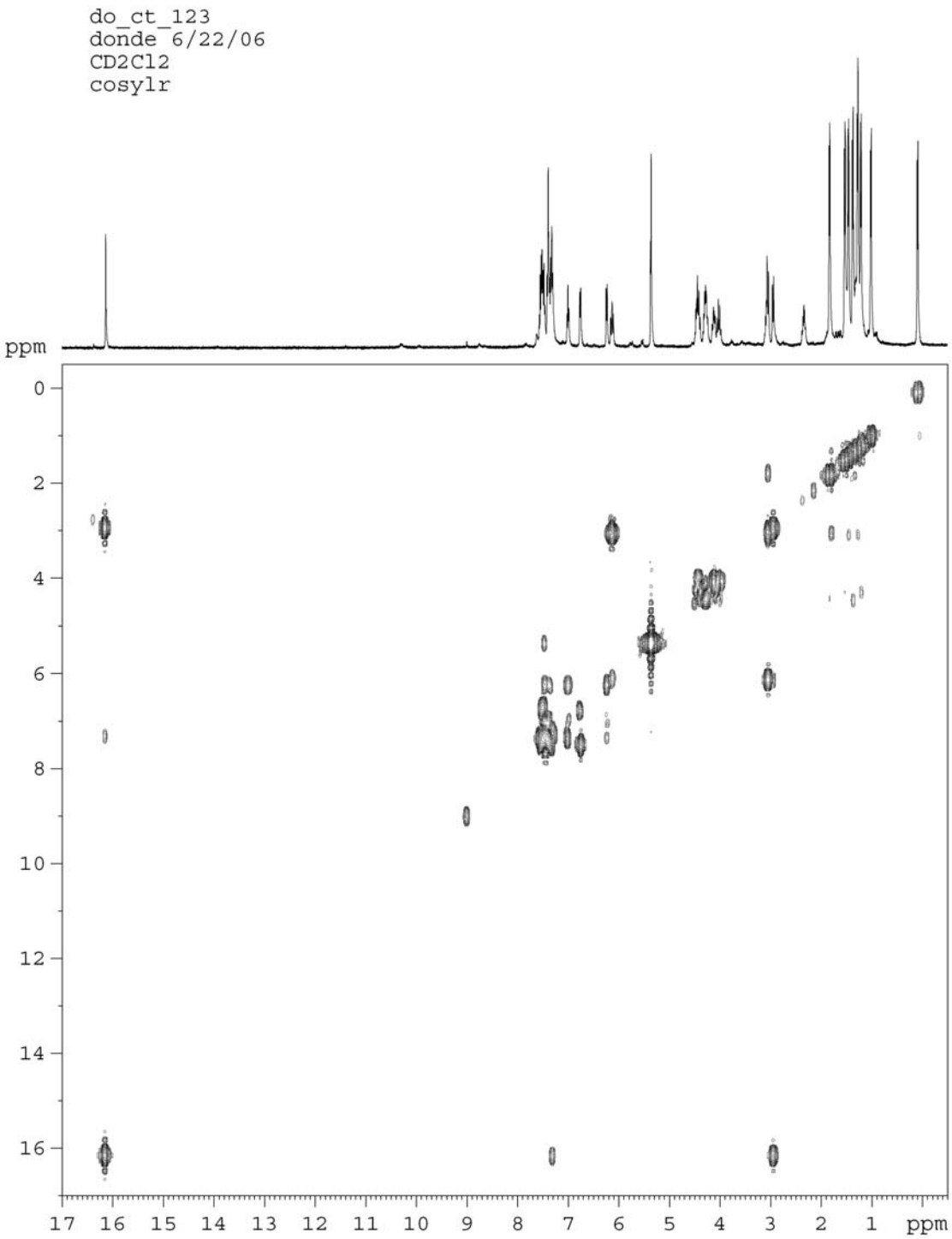

Figure A11. COSYLR spectrum of **12** in CD_2Cl_2 at 22 °C.

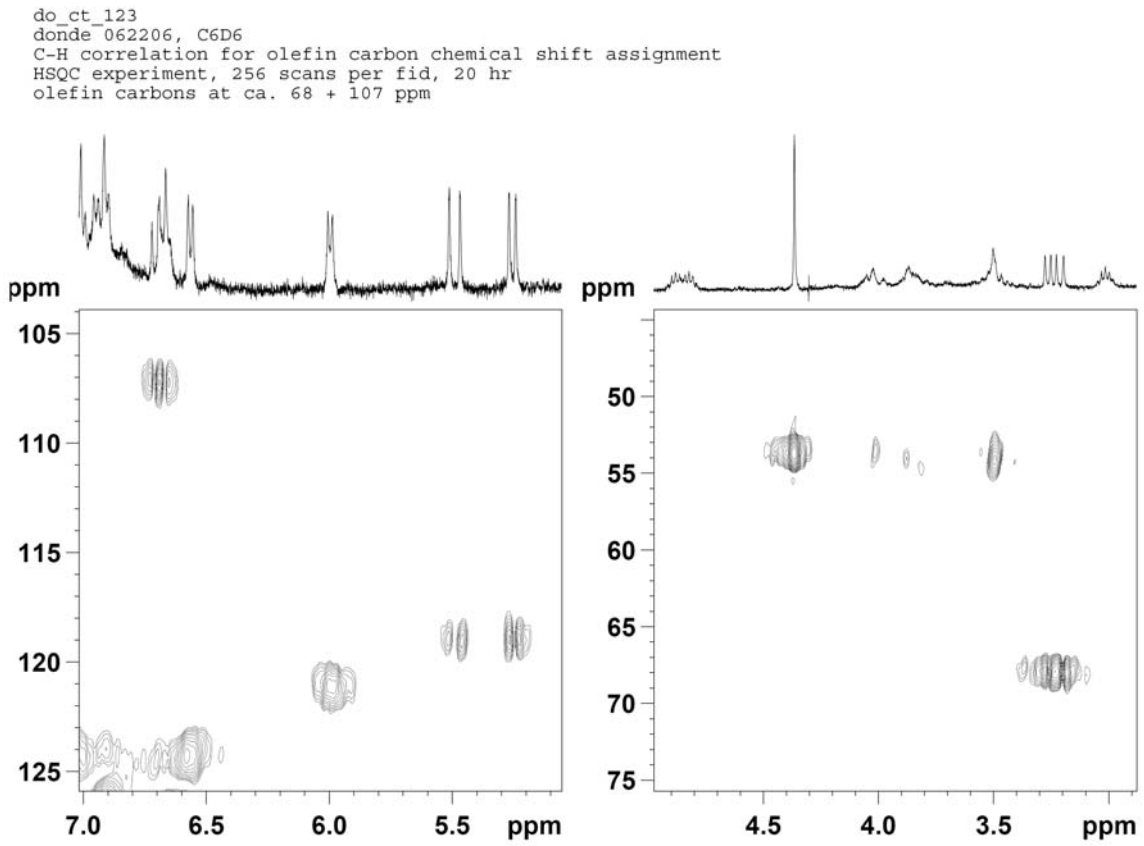

Figure A12. Selected regions of HSQC spectrum of **12** in C_6D_6 at 22 °C.

Interestingly, upon addition of **9** to complex **11**, a benzylidene resonance at 16.49 ppm is initially observed in the ^{1}H NMR spectrum of the crude reaction, but disappears after a few hours at room temperature (Figure 10). Unlike other observed intermediates, a relatively high conversion (25%) is initially observed. However, attempts to isolate or further characterize this intermediate by VT NMR spectroscopy were unsuccessful.

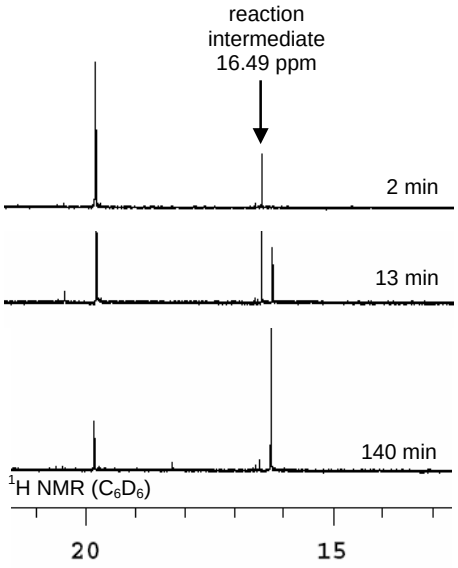

Figure A12a. Benzylidene region (H_α) of ^{1}H NMR spectra of the reaction between **11** and **9** at different time points.

Complex **15**: To a 4-mL vial in the glovebox was added **14** (12 mg, 0.012 mmol) and pentane (ca. 0.5 mL). Vial capped with a screwcap containing a PTFE septum and removed from the glovebox. Divinylbenzene (1.8 μL, 0.012 mmol) added via syringe. Vial taken into the glovebox. The reaction stirred at 22 °C overnight, filtered through a pipette column and washed with pentane (4 x 2 mL). Solid eluted with CH_2Cl_2 and concentrated to green solid (8 mg, 89%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 16.25 ppm (s, Ru=C*H*Ar of **15b**), 15.57 (s, Ru=C*H*Ar of **15a**), 15.37 (s, minor isomer C). Olefin resonances for isomer **15a**: 2.93 (d, 1H, *J* = 12.4 Hz, H_c), 3.05 (br d, 1H, *J* = 9.6 Hz, H_b), 5.93 (dd, 1H, *J* = 9.6, 12.4 Hz, H_a). Olefin resonances for isomer **15b**: 3.25 (dd, 1H, *J* = 1.3, 12.2 Hz, H_c), 2.23 (dt, 1H, *J* = 9.4, 1.2 Hz, H_b), 5.41 (overlapping with other peaks, shift determined by COSY, H_a). Olefin resonances for isomer C: 2.78 (d, 1H, *J* = 12.5 Hz, H_c), 2.88 (br d, 1H, *J* = 10.0 Hz, H_b), 5.81 (overlapping with other peaks, shift determined by COSY, H_a)

Select ^{13}C shifts from HMQC experiments (CD_2Cl_2) for olefin carbons:

Isomer A: CH_2: 84.34 ppm, CH: 101.20 ppm.
Isomer B: CH_2: 64.91 ppm, CH: 92.80 ppm.
Isomer C: can not be determined due to S/N issues.

The proton resonance at 3.05 ppm (H_b of isomer **15a**) has an unambiguous NOE to a methyl group (1.48 ppm) and to an isopropyl methine (3.36 ppm) [and to 5.93 ppm, which is the cis-disposed H_a]. This NOE might be expected if this conformer is identical to the X-ray structure. H_c would be expected to have an NOE to an aromatic proton, as it is facing a region where the *i*-Pr group is facing away. H_c does in fact have an NOE to a proton at 5.69, which is an aromatic doublet and thus consistent with an H ortho to N(2) [see X-ray structure].

The proton resonance at 2.23 ppm (H_b of isomer **15b**) has an ambiguous NOE to the methyl region (ambiguous because this proton sits on top of a methine associated with the minor component, note that a methine would be expected to have a strong NOE to a methyl group). This is most likely an olefin-methyl NOE however, because methine-methyl NOEs typically come in pairs (provided there is a chemical shift difference between the methyl groups). The assignment of isomer **15b** to the side-bound, "CH_2 down" conformation is based upon the absence of NOEs involving H_c and the methyl/methine region and one NOE involving H_a (5.41 ppm) and the methyl region is detected (NOE to 1.67 ppm), in addition to the expected NOE to H_b at 2.22 ppm.

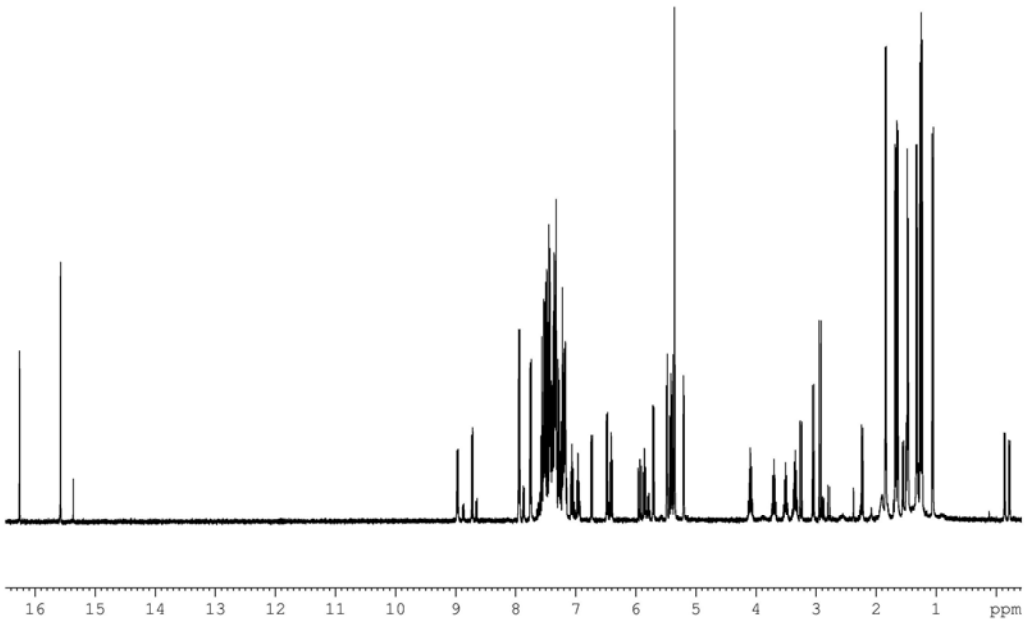

Figure A13. ^{1}H NMR spectrum of **15** in CD_2Cl_2 at 22 °C.

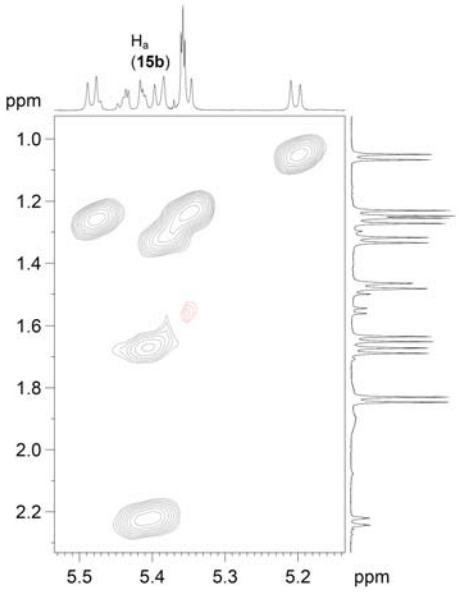

Figure A14. 2D-NOESY/EXSY spectrum of **15** in CD_2Cl_2 at 22 °C.

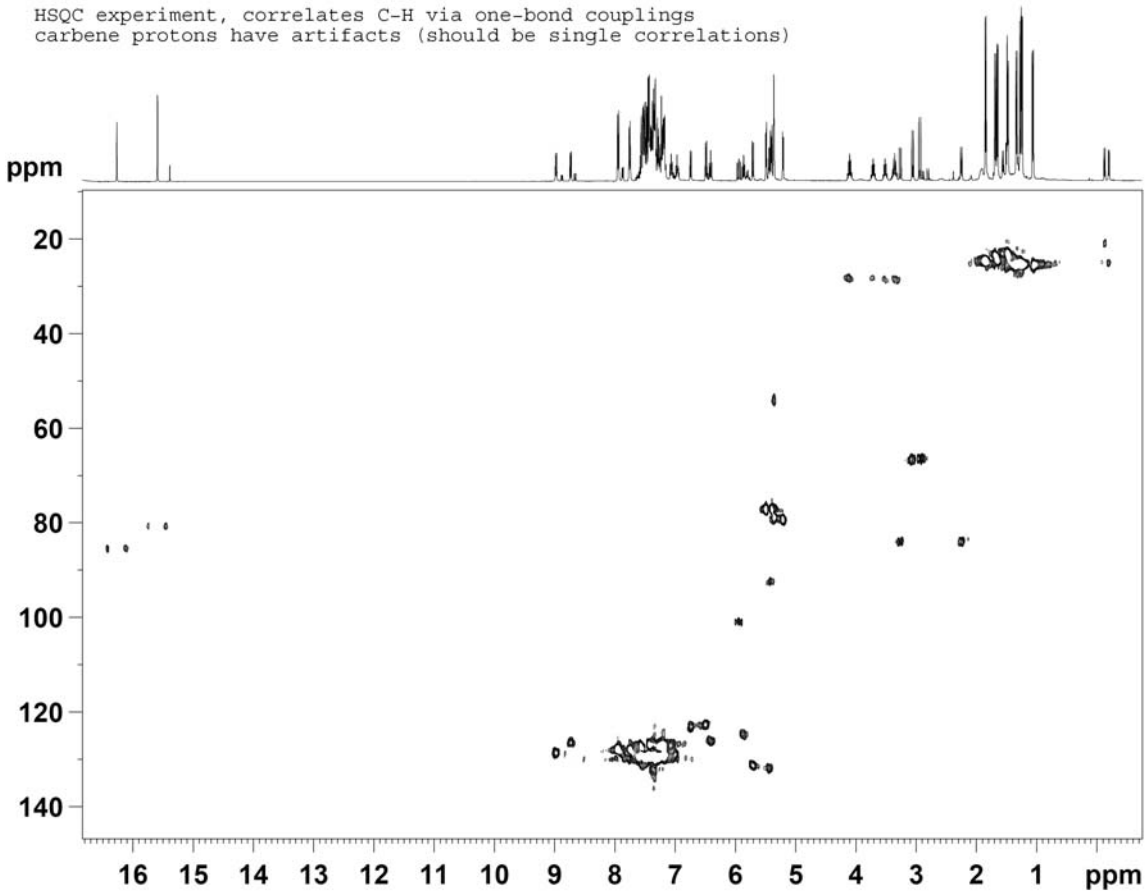

Figure A15. HSQC spectrum of **15** in CD_2Cl_2 at 22 °C.

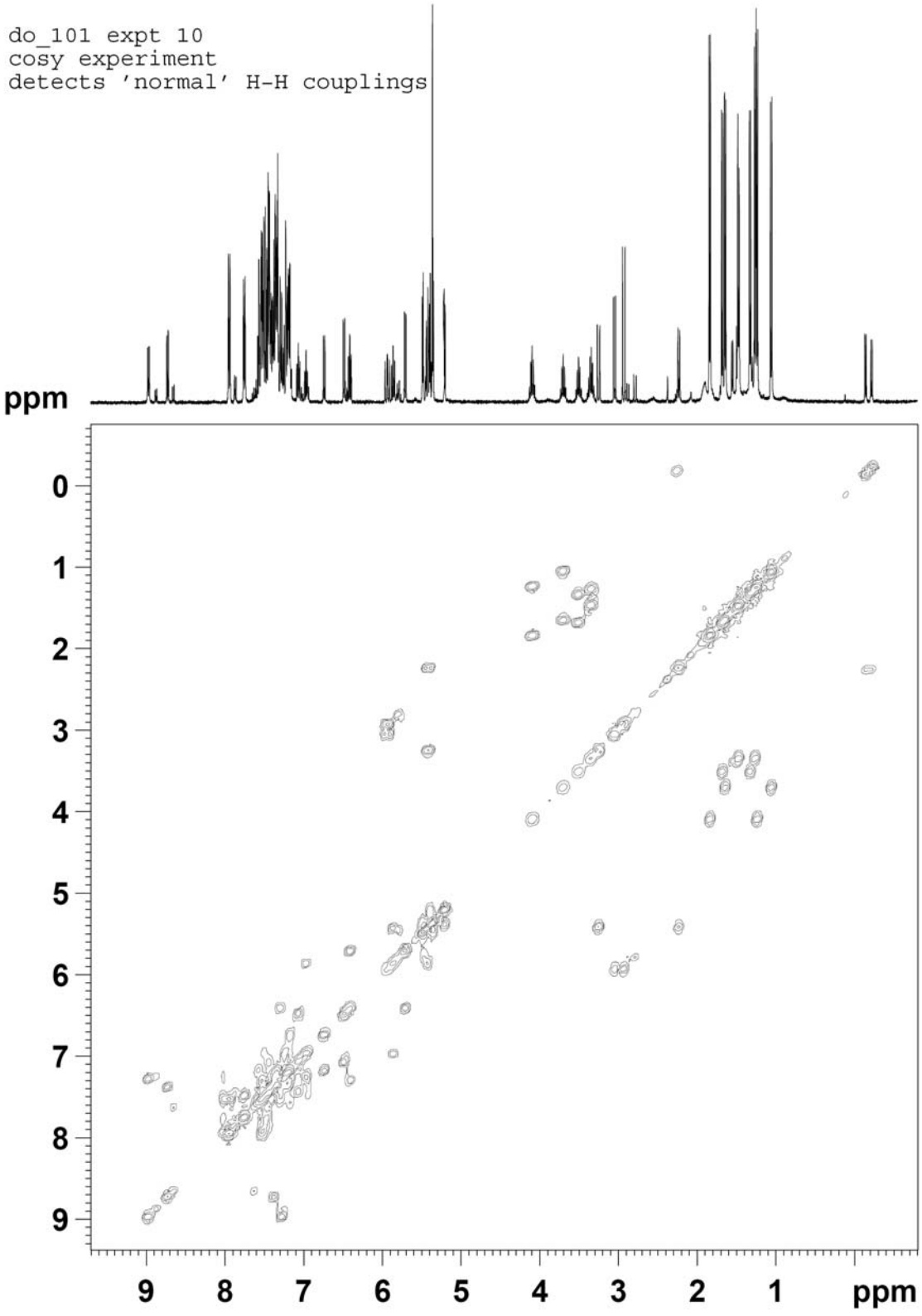

Figure A16. Selected region of a COSY spectrum of **15** in CD_2Cl_2 at 22 °C.

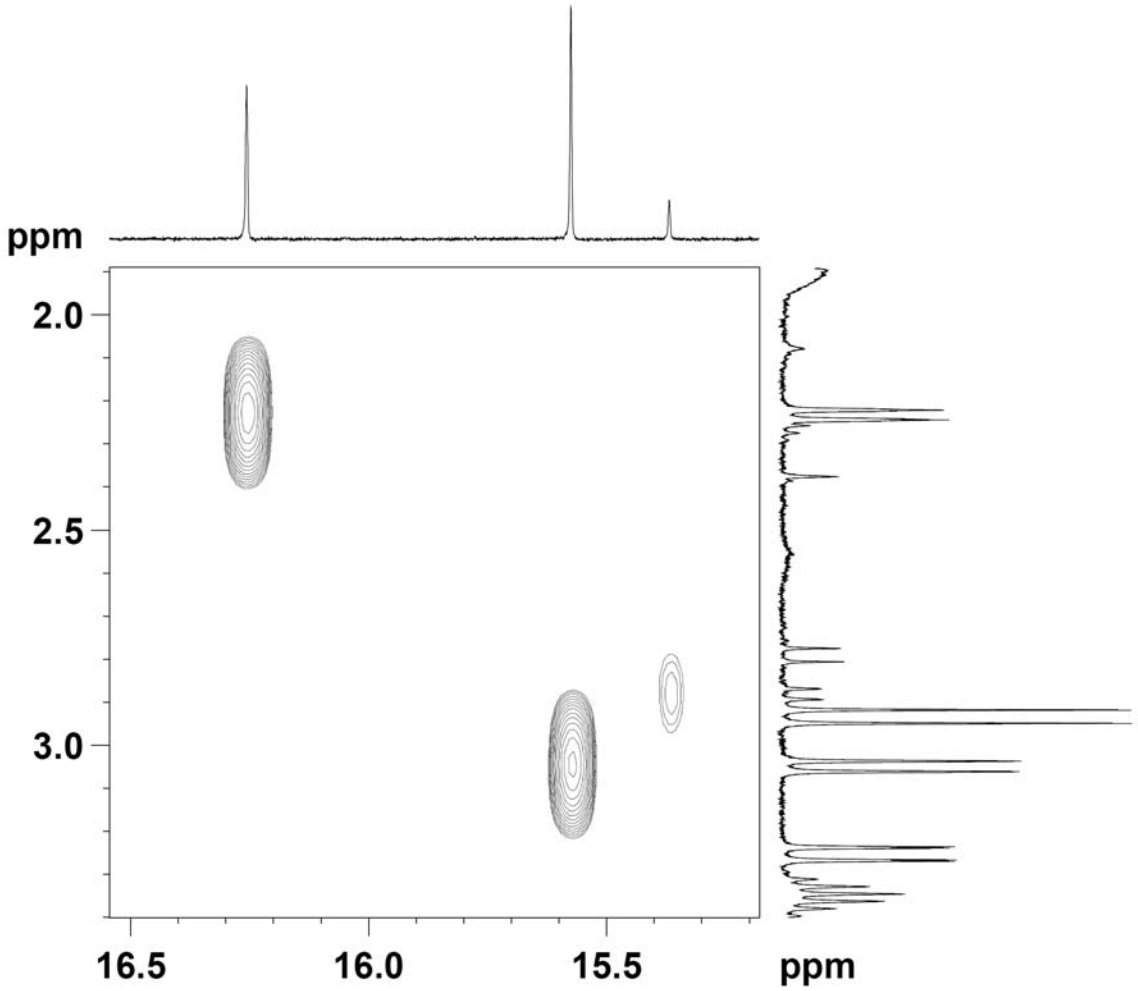

Figure A17. Selected region of a COSYLR spectrum of **15** in CD_2Cl_2 at 22 °C.

Complex **17**: To a 4-mL vial in the glovebox was added **16** (99 mg, 0.143 mmol) and toluene (ca. 2 mL). Vial capped with a screwcap containing a PTFE septum and removed from the glovebox. Divinylbenzene (**9**) (19 μL, 0.14 mmol) added via syringe. Vial taken into the glovebox. The reaction stirred at 22 °C overnight, filtered through a pipette column and washed with toluene (ca. 1 mL) and pentane (3 mL). Solid eluted with CH_2Cl_2 and concentrated to yellow-green solid (32 mg, 40%). HRMS (FAB) *m*/*z* (%): 568.1392 $[M-H]^+$ (11). Calcd: 568.1366.

The broad peak at 5.52 is assigned as H_a because it has COSY crosspeaks to signals at 3.59 ppm and to 2.68 ppm. Note that 3.59 and 2.68 do not have COSY crosspeaks to each other, which might be

expected if they are geminal olefin resonances. A complication is that 2.68 is a region that likely contains Cy resonances as well. Note that 5.52 has an NOE to 3.59 (cis-disposed H_b) and 3.59 has a strong NOE into the 2.68 region (geminal disposed H_a).

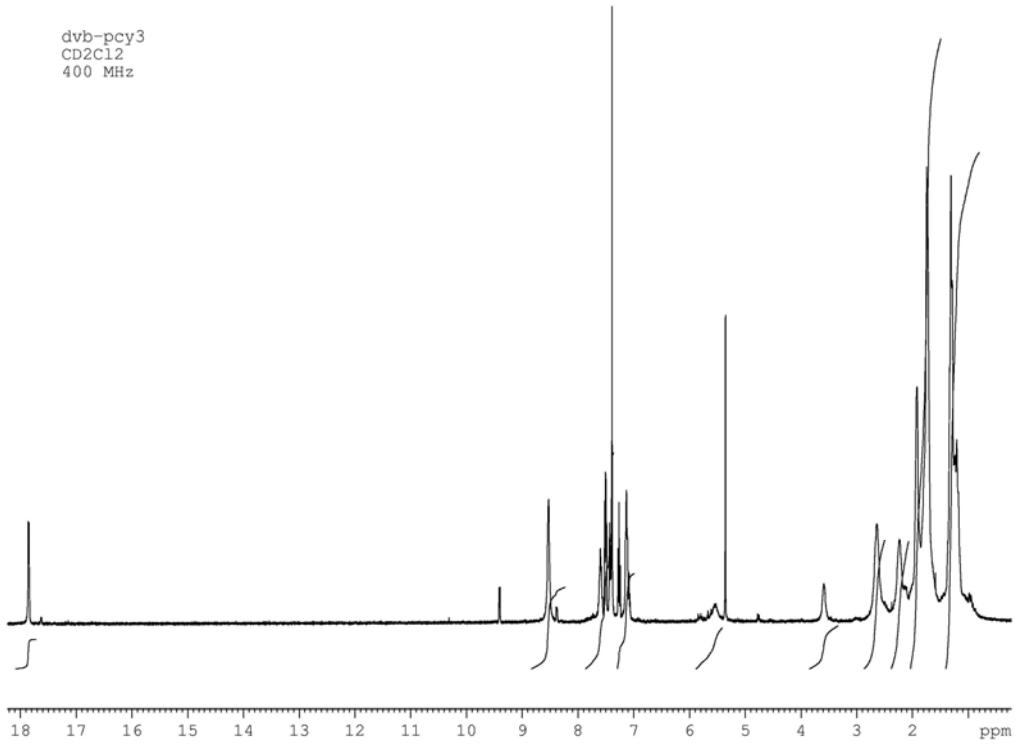

Figure A18. ^{1}H NMR spectrum of **17** in CD_2Cl_2 at 22 °C.

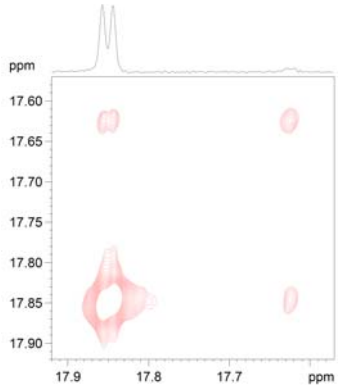

Figure A19. 2D-EXSYspectrum of **17** in CD_2Cl_2 at 22 °C.

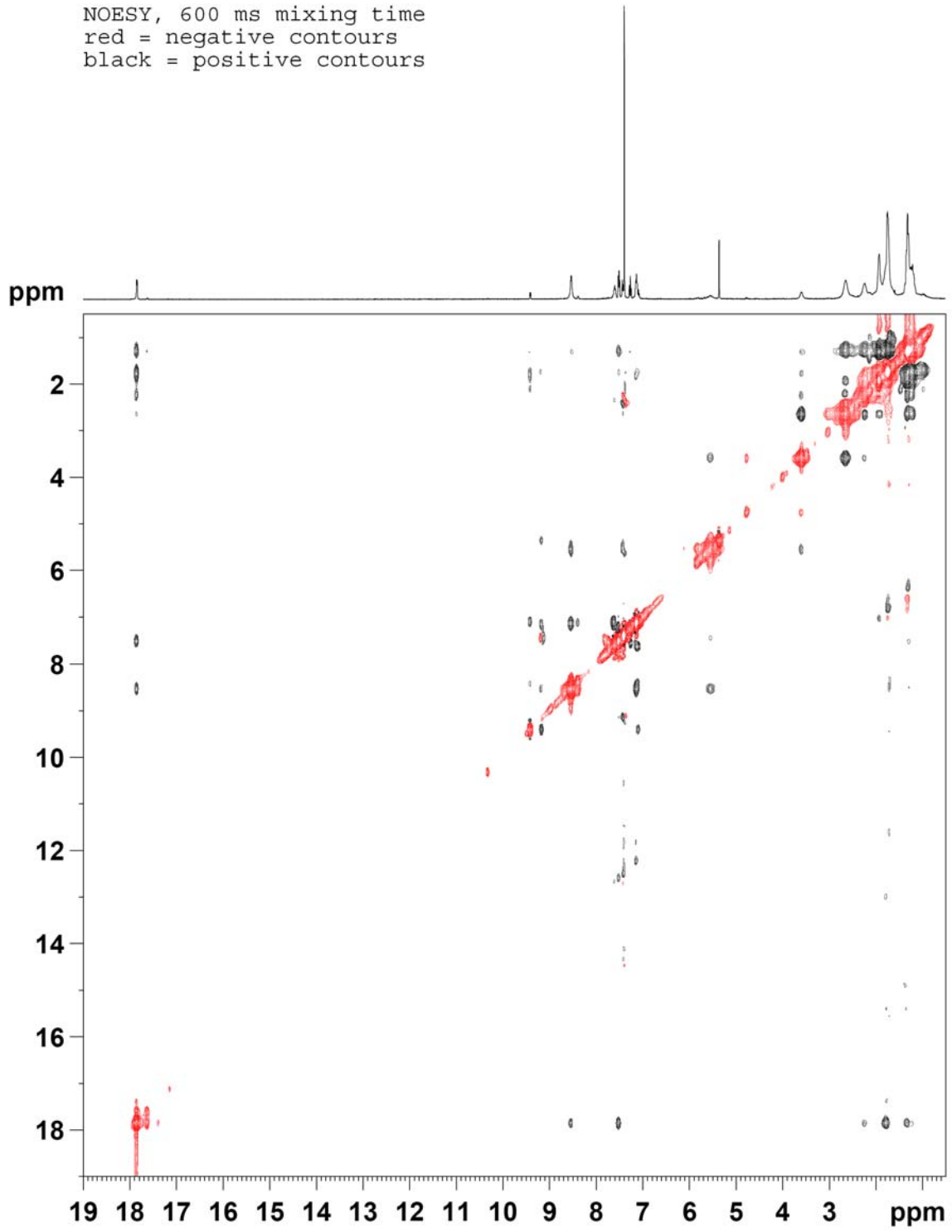

Figure A20. 2D-NOESY/EXSYspectrum of **17** in CD_2Cl_2 at 22 °C.

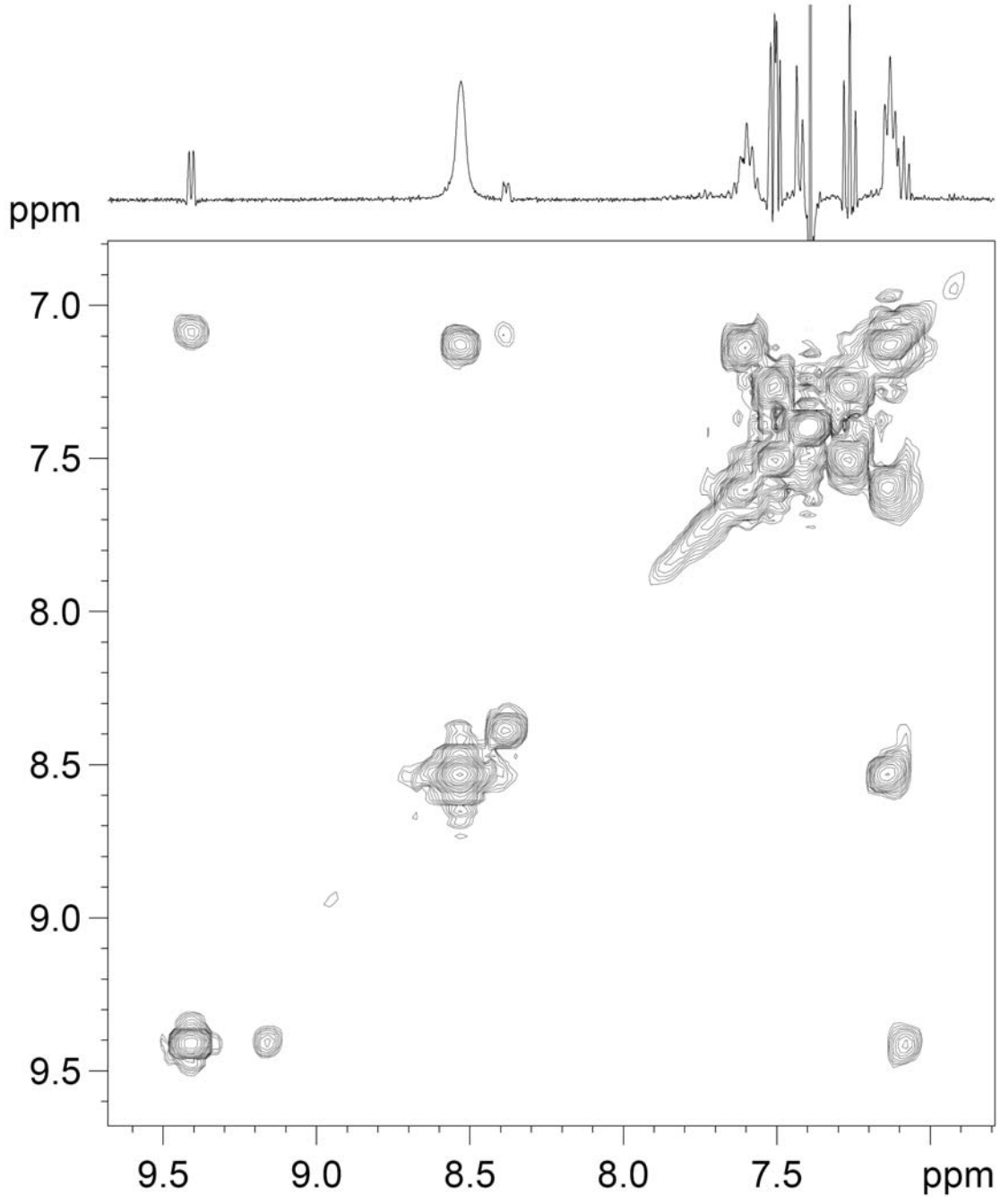

Figure A21. COSY spectrum of **17** in CD_2Cl_2 at 22 °C.

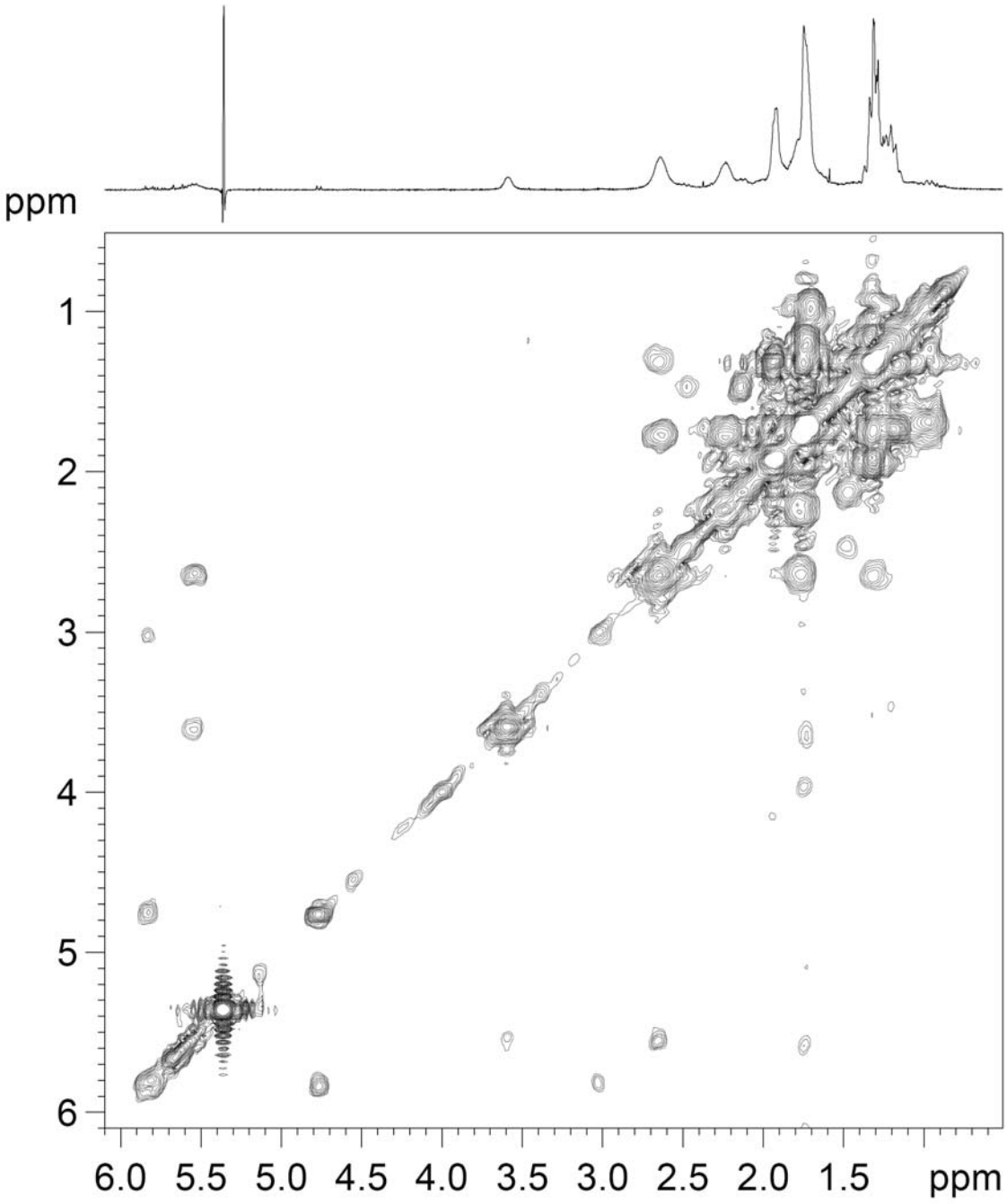

Figure A22. COSY spectrum of **17** in CD_2Cl_2 at 22 °C.

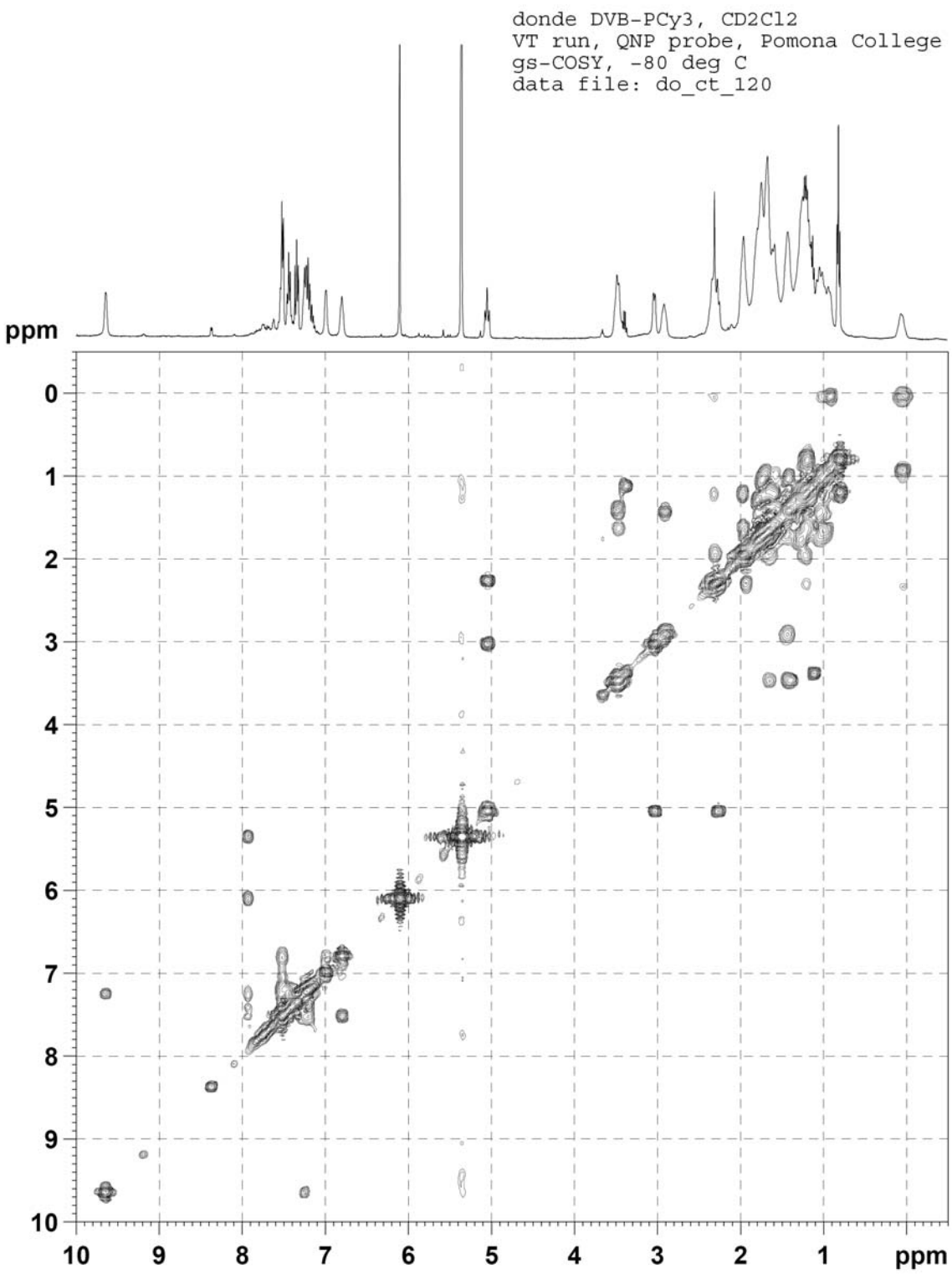

Figure A23. COSY spectrum of **17** in CD_2Cl_2 at –80 °C.

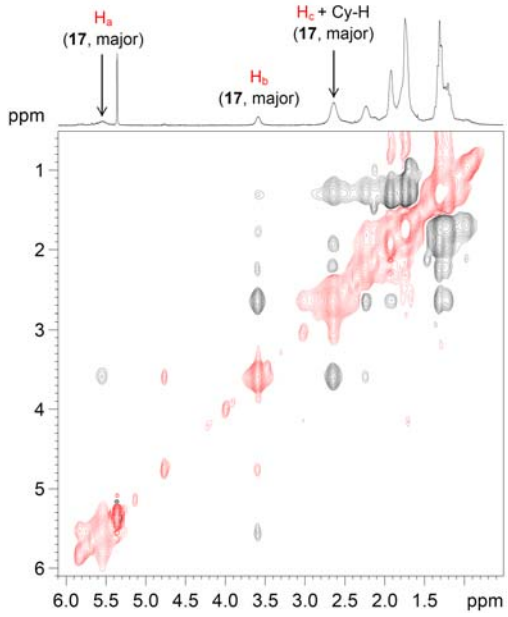

Figure A23a. Olefin and alkyl-region of a 2D-NOESY/EXSY spectrum of **17**.

2D-EXSY experiments conducted in CD_2Cl_2 at room temperature demonstrated exchange between all olefinic protons of the major and minor isomers (Figure A23a). The benzylidene resonances also undergo exchange (Figure A23b).

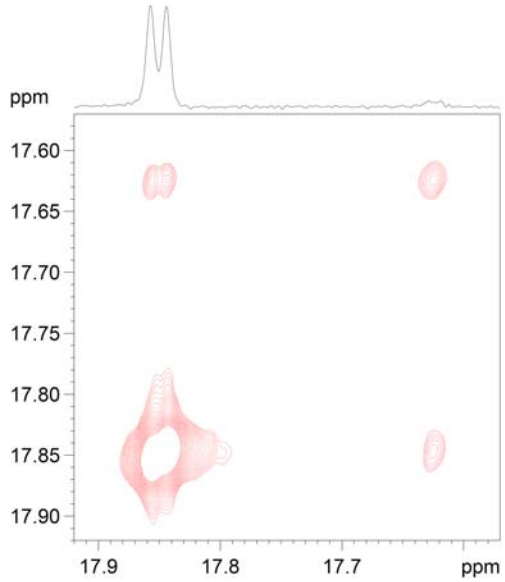

Figure A23b. Benzylidene-containing region of a 2D-EXSY spectrum of the benzylidene region of **17**.

Complex **20**: Synthesized utilizing procedure analogous to the synthesis of **17** MS (FAB): 608.2 $[M]^+$. Calcd: 608.1377. (due to sample stability issues, only low-res MS data could be obtained for this compound). The synthesis of the 1-ethenyl-2-(1-methylethenyl)-benzene is reported elsewhere.[12]

Select data for major isomer: ^{1}H NMR (CD_2Cl, 400 MHz): 15.86 ppm (br s, 1H, Ru=C*H*Ar), 15.50 (s, 0.26H, minor Ru=C*H*Ar)], 7.45 ppm (t, 1H, J = 7.4 Hz, H meta to benzylidene moiety), 7.35 ppm (d, 1H, J = 7.4 Hz, H ortho to benzylidene moiety), 7.06 ppm (splitting obscured by overlap, 1H, H para to benzylidene moiety), 6.45 ppm (d, 1H, J = 7.6 Hz, H ortho to alpha olefin), 4.6-3.8 (m, 4H, NHC backbone protons, exchange cross peaks observed between these backbone resonances), 3.2 ppm (br s, H_c), 2.94 (1H, H_b, overlapping with other resonances), 2.92 ppm (s, 3H, *ortho*-Me grp), 2.73 (s, 3H, *ortho*-Me grp), 2.37 (6H, overlapping *para*-Me grps), 2.35 (s, 3H, *ortho*-Me grp), 2.10 (s, C*H*$_3$C(Ar)=CH_2), 1.44 (s, 3H, *ortho*-Me grp).

Select $^{13}C\{^1H\}$ NMR data (CD_2Cl_2, 100 MHz) for the major isomer: benzylidene carbon: 295.33 ppm, CH_2 carbon of olefin: 67.7 ppm, quaternary carbon of olefin: 117.4 ppm (assignment is tentative), alpha Me group carbon: 26.47 ppm. For the minor isomer: olefin protons at 2.96 and 2.16 ppm and olefinic CH_2 carbon at 62.96 ppm.

Major benzylidene NOEs to two methyl groups at 2.35 and 2.89. Note these methyls are in exchange with one another, so the benzylidene likely has an NOE to one site. A strong NOE between the benzylidene resonance is observed to 6.45 ppm (likely the ortho aromatic H). The general identity of H_b, H_c, and the alpha-Me group were preliminarily established with COSYLR and HSQC data (below). An NOE between 2.94 and 2.10 ppm establishes the former as H_b. A strong NOE is observed between 2.94 and 3.2 ppm, as expected. EXSY crosspeaks are not observed for the benzylidene nor olefin

resonances. EXSY crosspeaks are observed for aromatic singlets and mesityl methyl groups, indicating NHC ligand dynamics at work.

COSYLR data: major benzylidene has a COSYLR interaction to shifts at 2.94 and 7.35 ppm. If this compound is like the others, this implies one olefin resides at 2.94. There is a proton at 2.94 that is attached to a carbon at 68 ppm (HSQC data) bearing an additional attached proton at 3.2 ppm. Both the 3.2 and 2.94 peak have a COSYLR interaction with a resonance at 2.102, which identifies this resonance as that of the alpha methyl group. Further evidence for this assignment is that the 2.10 peak connects to a ^{13}C resonance at 26.47 ppm, which is a unique resonance relative to the mesityl methyl resonances (all at 20 ppm).

Identity of major isomer's conformation: olefin at 3.2 shows a strong NOE to Mes Me groups at 1.44 ppm and 2.73 ppm (these Me groups are also in exchange with one another). The benzylidene NOEs to two methyl groups at 2.35 and 2.92 ppm—again these two Me groups are in exchange with one another.

These data are consistent with a solution conformation similar to the X-ray crystal structure. Further, they suggest that the slow dynamics involve rotation about the Ru-C1 bond, as the benzylidene and olefin to Me NOEs are unique (they would have NOE'd to the same set of methyl groups if there was slow rotation about the N2-Mes bond). The NHC backbone EXSY behavior is additional evidence for this slow motion—slow rotation about the N2-Mes bond would not exchange the backbone resonances.

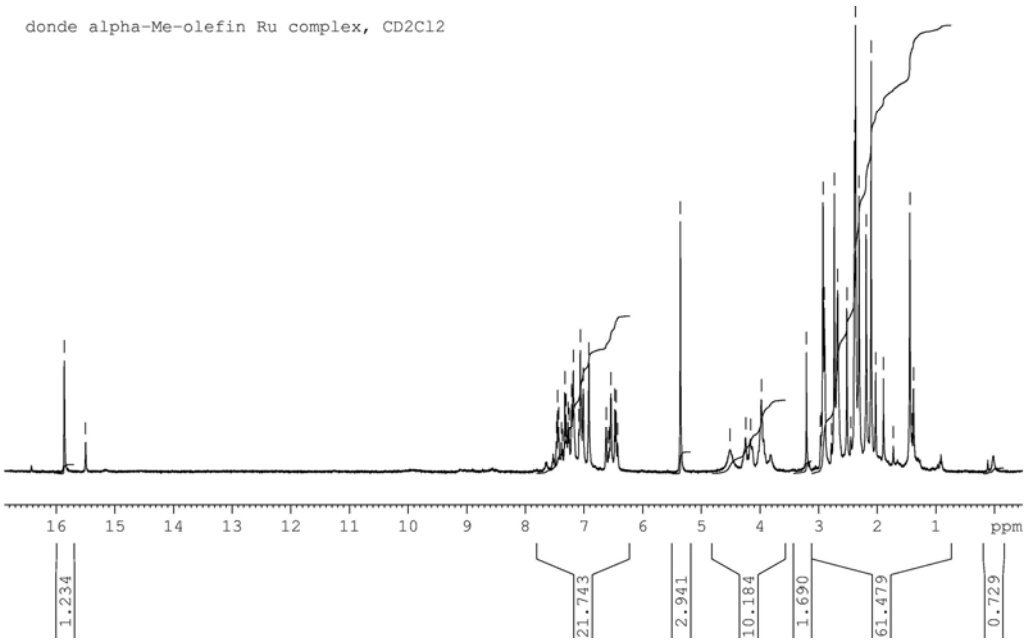

Figure A24. ^{1}H NMR spectrum of **20** in CD_2Cl_2 at 22 °C.

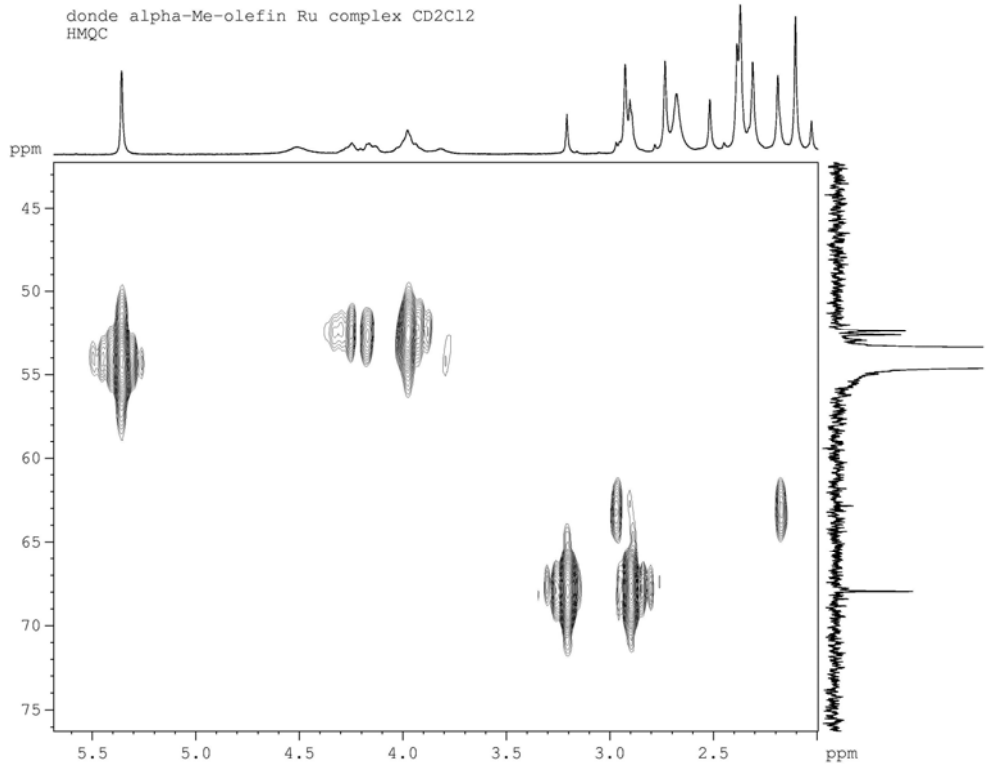

Figure A25. HSQC spectrum of **20** in CD_2Cl_2 at 22 °C.

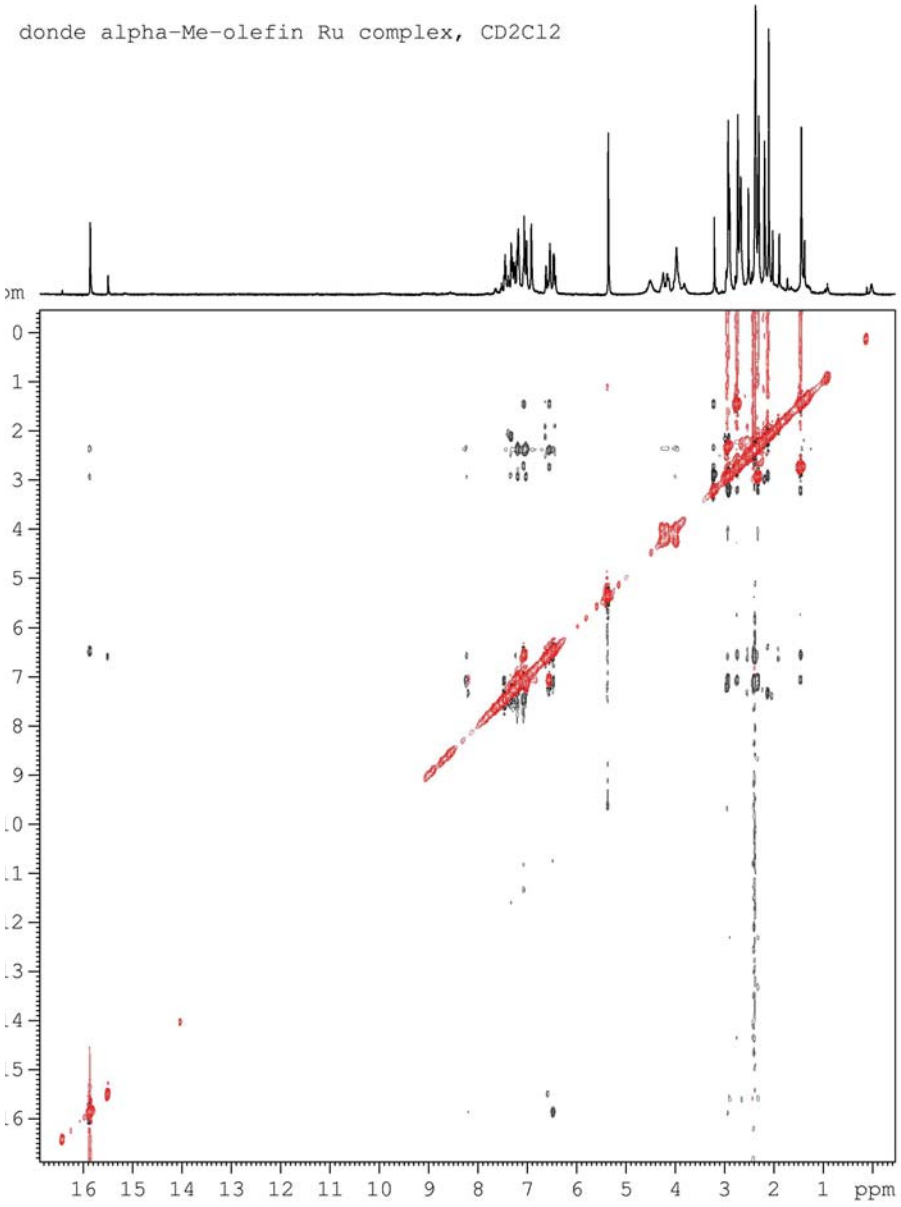

Figure A26. 2D-NOESY/EXSY spectrum of **20** in CD_2Cl_2 at 22 °C.

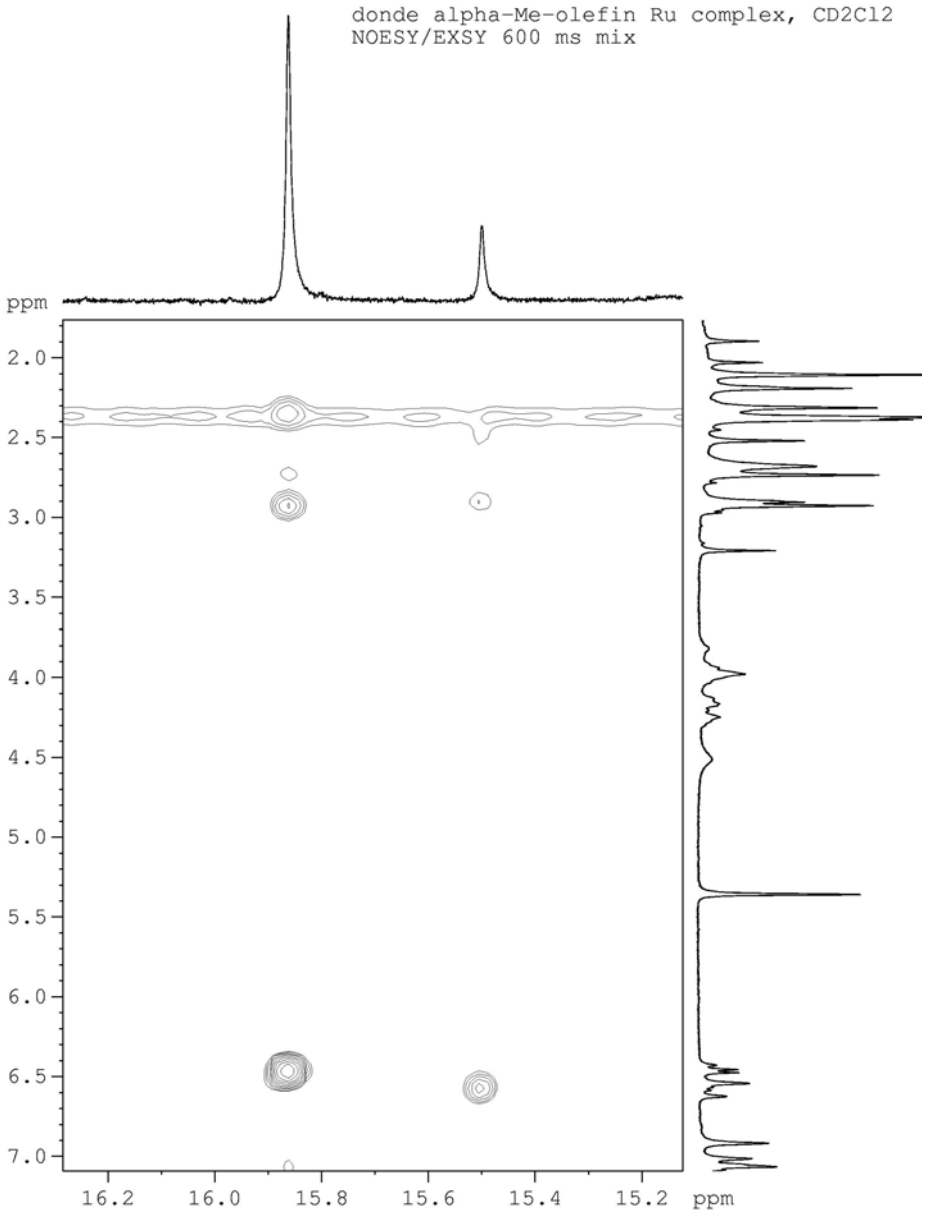

Figure A27. 2D-NOESY/EXSY spectrum of **20** in CD_2Cl_2 at 22 °C.

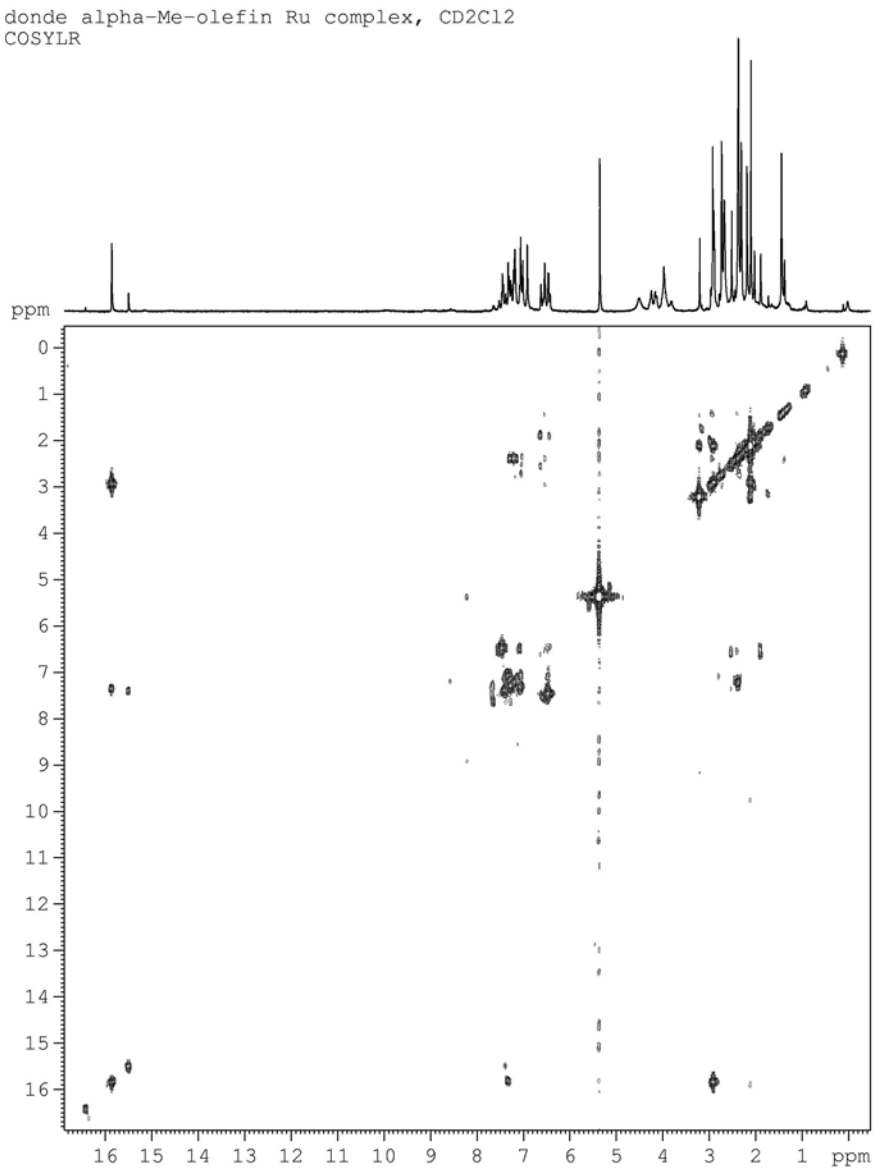

Figure A28. COSYLR spectrum of **20** in CD_2Cl_2 at 22 °C.

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