Supporting Information for

Characterization and Dynamics of Substituted Ruthenacyclobutanes Relevant to the Olefin Cross-Metathesis Reaction

Anna G. Wenzel, Garrett Blake, David G. VanderVelde, and Robert H. Grubbs

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Dynamic NMR Behavior of Metallacycles in CD$_2$Cl$_2$ at –87 °C

I. Materials and Methods.

I.A. Materials. Unless otherwise indicated, all compounds were purchased from Aldrich and/or Fisher. Anhydrous pyridine (99.8%) was purchased from Aldrich and used as received. NMR solvents were purchased from Cambridge Isotope Laboratories, Inc., and distilled from calcium hydride (CaH_2) under an atmosphere of argon before use. Ethylene (99.999%) was purchased from Matheson Tri-Gas and dispensed utilizing a regulator equipped with a Matheson in-line gas purification system. Gas samples for NMR reactions were measured utilizing the Schlenk technique specified in: Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2005**, *127*, 5032-5033, and references therein. Anhydrous dichloromethane, benzene, diethyl ether, pentane, and tetrahydrofuran were obtained via elution through a solvent column drying system[1] and degassed with argon prior to use. The flash chromatography of organometallic compounds was performed utilizing silica gel 60 (230-400 mesh) purchased from TSI; the flash chromatography of all other compounds was performed utilizing silica gel 60 (32-63 micron) purchased from Bodman Industries. Stainless steel syringes or cannulae were used to transfer air or moisture-sensitive liquids. Slow additions of reagents were performed using a KD100 syringe pump purchased from KD Scientific, Inc. Catalyst $[(IMesH_2)Cl_2Ru{=}CH(PCy_3)](BF_4)$ was prepared according to literature procedures[2] with the following modification: the carbide precursor $(IMesH_2)(PCy_3)Cl_2Ru{\equiv}C$ was purified via flash chromatography on silica gel (40% dichloromethane in hexanes; TLC $R_f = 0.55$, using 50% dichloromethane in hexanes as the developing solvent; UV TLC visualization). The bispyridyl catalyst $(IMesH_2)(C_5H_5N)_2Cl_2Ru{=}CH(Ph)$ was prepared according to literature procedures.[3]

I.B. Instrumentation. Ambient nuclear magnetic resonance (NMR) spectra were obtained using a Bruker 300 MHz NMR Spectrometer. Variable-temperature (VT) NMR experiments were conducted using either a Varian Inova-500 or a Varian 400 MHz NMR spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CD_2Cl_2: δ 5.32). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CD_2Cl_2: δ 54.0). VT-NMR temperatures were obtained by digital thermometer analysis via a thermocouple cable threaded into an NMR tube filled with dichloromethane-d_2. The NMR tube and thermocouple were allowed to equilibrate until temperature readings stabilized (~5 min). Temperature readings were re-done prior to each NMR session, or subsequent to any changes to the instrument temperature. NMR spectral data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet), coupling constants in Hertz (Hz), and assignment. On metallacycle assignments, Latin letters (a, b, c, etc.) denote hydrogens; Greek letters (α, β, χ, etc.) designate carbons. All reactions were set up in triplicate to ensure thermal consistency in reaction comparison via VT-NMR.

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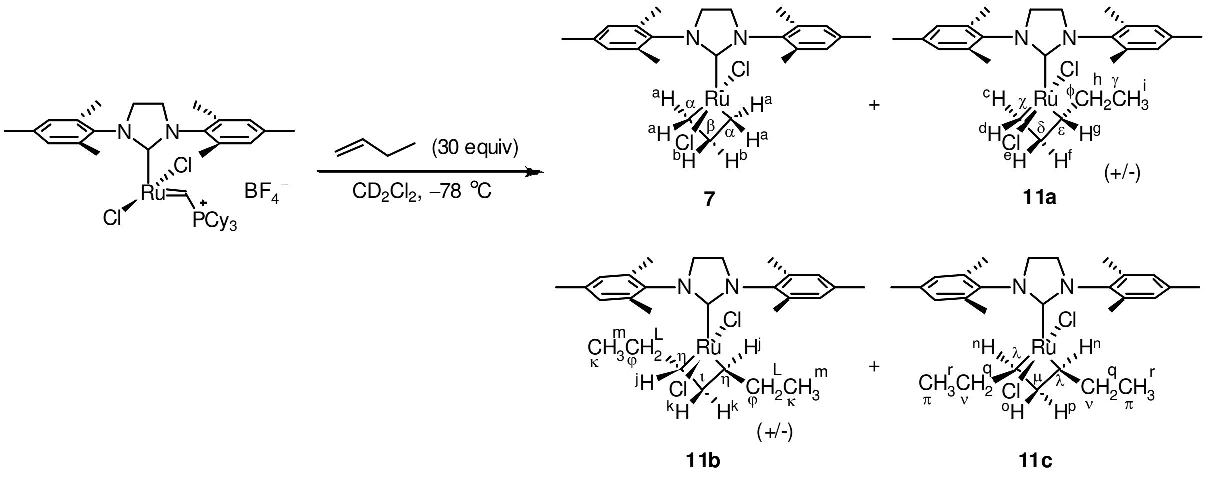
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

[2] Romero, P. E.; Piers, W. E.; McDonald, R. *Angew. Chem. Int. Ed.* **2004**, *43*, 6161-6165.

[3] Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001,** *123,* 6543-6554.

II. General Experimental Procedures.

II.A. Reaction of $[(IMesH_2)Cl_2Ru{=}CH(PCy_3)](BF_4)$ (5b) with 1-Butene.



$[(IMesH_2)Cl_2Ru{=}CH(PCy_3)](BF_4)$ (18.0 mg, 0.021 mmol, 1.0 equiv) was added to a J-Young tube in the glovebox. CD_2Cl_2 (600 μL) was then added, and the tube was sealed, shaken, and removed from the box. The NMR tube was attached via a ground glass joint to a calibrated gas bulb (43.48 cm^3) attached to a Schlenk line. The gas bulb was pressurized to 26.4 cm Hg at 21 °C with 1-butene (0.63 mmol, 30 equiv), which was then condensed into the NMR tube.[4,5] The tube was then sealed, shaken, and immersed in a –45 °C dry ice/acetonitrile cold bath. After 3 h at –45 °C, a brown to red-brown color change was observed. Analysis via VT-NMR (500 MHz, –86.6 °C) revealed complete conversion of the starting complex. Metallacycles **A**, **B**, and **C** were observed in 84% combined yield relative to anthracene (0.5 equiv) when it was added as an internal standard. Similar to the propene-derived metallacycles previously reported,[6] conversion to three metallacycles was observed: **7** (60%), **11a** (39%), **11b** (~1%), respectively. Only trace amounts of the *cis* metallacycle **11c** were visible at this time. The ratio of 1-butene:ethylene in solution was determined to be 86:14. Following analysis, the reaction was removed from the NMR and placed into a dry ice/isopropyl alcohol bath (–78 °C) for an additional 68 h (72 h total reaction time). The reddish color of reaction mixture was observed to diminish over this time period. Analysis via VT-NMR (500 MHz, –86.7 °C) revealed the equilibration of metallacycle species to **7** (~1%), **11a** (24%), **11b** (52%), and **11c** (24%), with minimal decomposition observed. The ratio of 1-butene:ethylene at this point was ~99:1. Metallacycle compositions, as well as 1-butene:ethylene ratios, from multiple trials are displayed on Table S1. ^1H NMR (500 MHz, CD_2Cl_2, –87 °C)[7] δ 7.75 (2H, br, $\mathbf{H^j}$ metallacycle **11b**), 7.74 (1H, br, $\mathbf{H^g}$ metallacycle **11a**), 7.08 (2H, br, $\mathbf{H^n}$ metallacycle **11c**), 6.64 (1H, br, $\mathbf{H^c}$ metallacycle **11a**), 6.60 (4H, br, $\mathbf{H^a}$

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[4] The addition of 30 equivalents of 1-butene serves to minimize the amount of starting catalyst that is converted to a bis-ruthenium sideproduct, in which only one of the rutheniums is metathesis-active. For a discussion on ruthenium catalyst decomposition, see: Hong, S. H.; Wenzel, A. G.; Salguero, T. T.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 7961-7968.

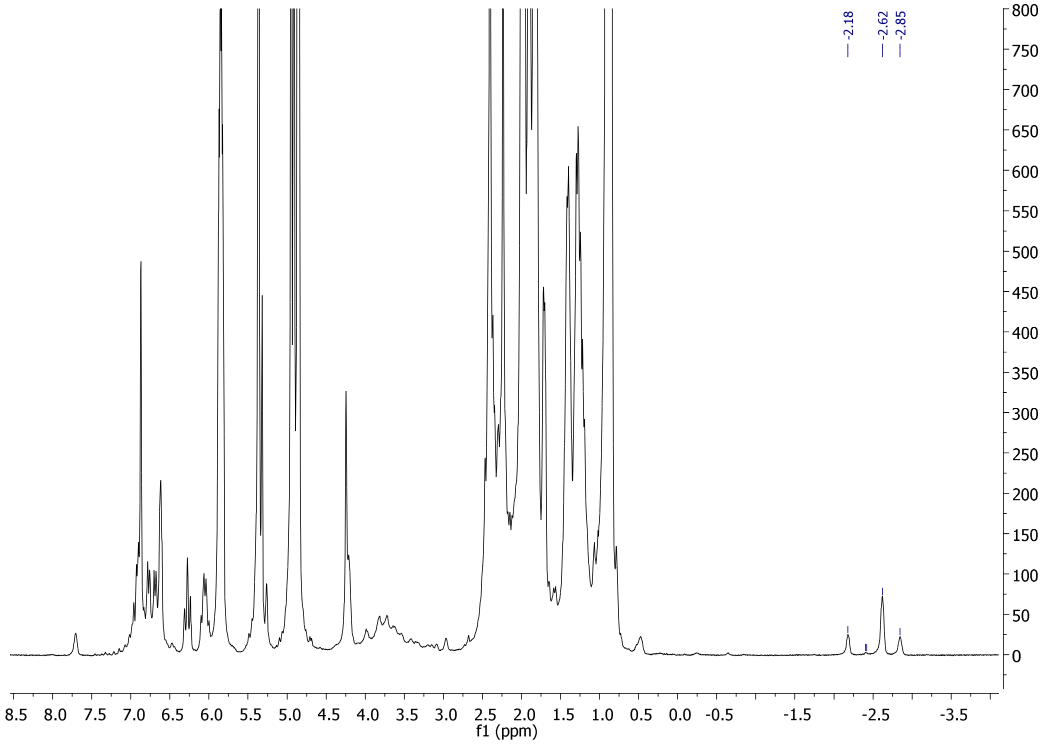
[5] For greater procedural detail on quantitated gas additions to NMR tubes, see: Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2005**, *127*, 5032-5033.

[6] Wenzel, A. G.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 16048–16049.

[7] Shifts corresponding to the NHC ligand of each species cannot be definitively assigned, as no 2D cross peaks were observed to enable identification. $\mathbf{H^r}$ of metallacycle **11c** could not be conclusively assigned due to peak overlap with 1-butene.

metallacycle **7**), 6.07 (1H, br, **H**$^{\mathbf{d}}$ metallacycle **11a**), 2.00 (4H, m, C**H**$_2$CH$_3$ **H**$^{\mathbf{q}}$ metallacycle **11c**), 1.83 (2H, m, C**H**$_2$CH$_3$ **H**$^{\mathbf{h}}$ metallacycle **11a**), 1.63 (4H, C**H**$_2$CH$_3$ **H**$^{\mathbf{L}}$ metallacycle **11b**), 0.50 (6H, m, CH$_2$C**H**$_3$ **H**$^{\mathbf{i}}$ metallacycle **11a**), 0.27 (6H, br t, CH$_2$C**H**$_3$ metallacycle **11b**), −1.72 (1H, br, **H**$^{\mathbf{o}}$ metallacycle **11c**), −2.18 (1H, br, **H**$^{\mathbf{f}}$ metallacycle **11a**), −2.41 (2H, d, *J* = 7.9 Hz, **H**$^{\mathbf{k}}$ metallacycle **11b**) −2.62 (2H, br, **H**$^{\mathbf{b}}$ metallacycle **7**), −2.85 (1H, br, **H**$^{\mathbf{e}}$ metallacycle **11a**), −3.20 (1H, t, *J* = 7.9 Hz, **H**$^{\mathbf{p}}$ metallacycle **11c**); ^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$, −95 °C)[8] δ 127.4 (**C**$^{\varepsilon}$ metallacycle **11a**), 123.0 (**C**$^{\eta}$ metallacycle **11b**), 121.1 (**C**$^{\lambda}$ metallacycle **11c**), 93.9 (**C**$^{\alpha}$ metallacycle **7**), 89.5 (**C**$^{\chi}$ metallacycle **11a**), 33.4 (**C**$^{\varphi}$ metallacycle **11b**), 14.0 (**C**$^{\iota}$ metallacycle **11b**), 12.6 (**C**$^{\mu}$ metallacycle **11c**), 1.7 (**C**$^{\beta}$ metallacycle **7**).

^{1}H-NMR spectrum (500 MHz, –87 °C) of metallacycles derived from 1-butene (3 h).



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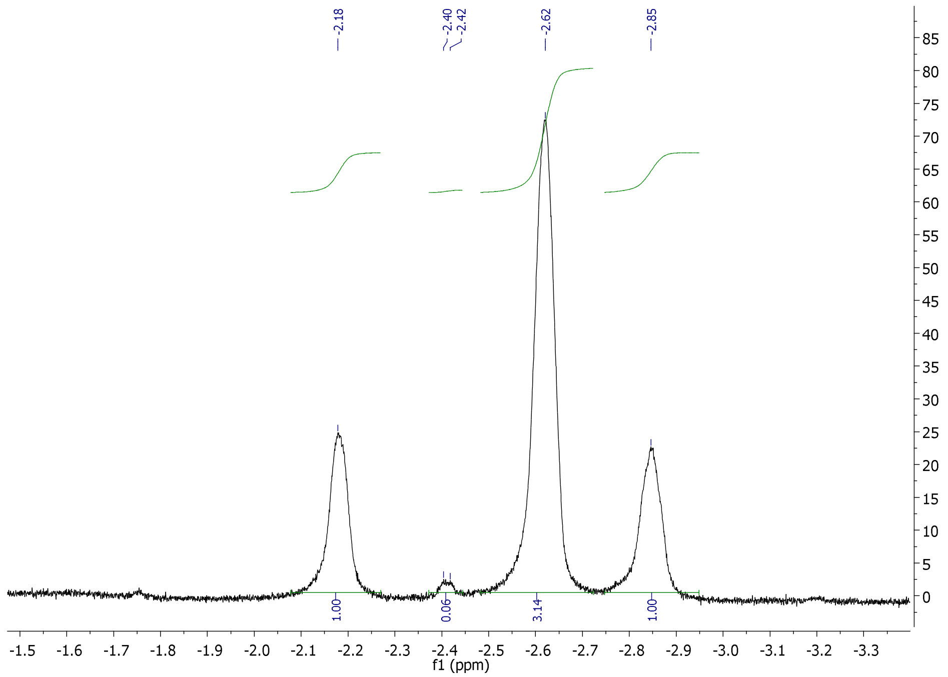
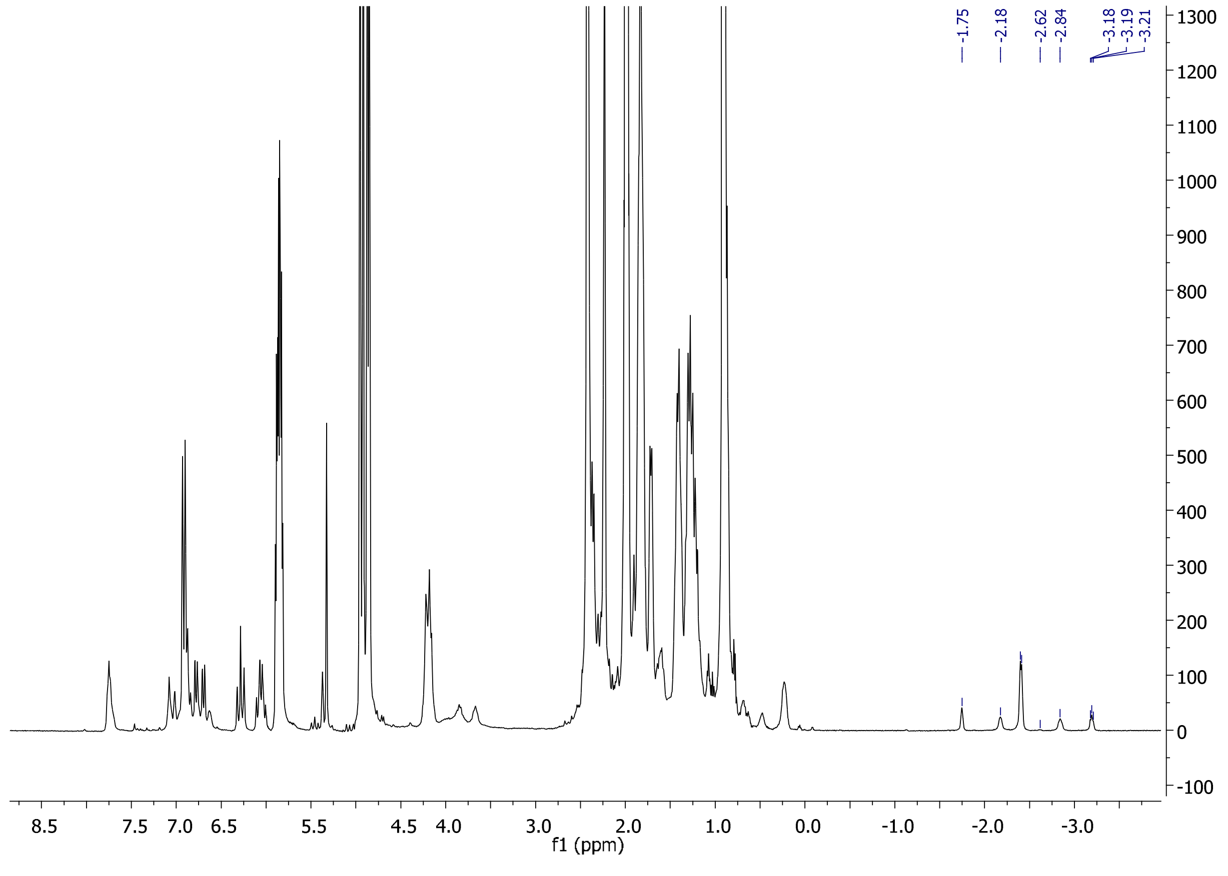
[8] Carbons δ, γ, κ, π, and ν could not be assigned due to peak interference from those of 1-butene.



^{1}H-NMR spectrum (500 MHz, –87 °C) of metallacycles derived from 1-butene (72 h).



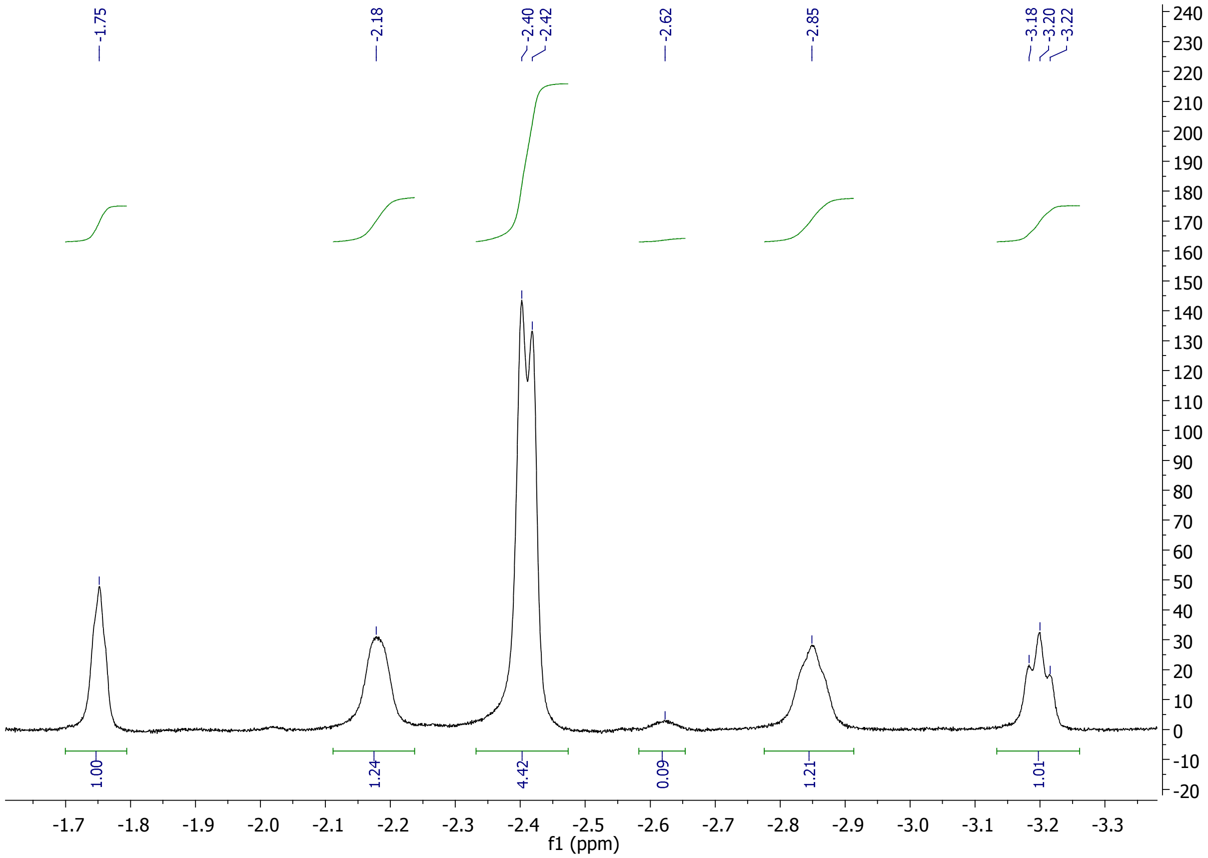


Table S1. Reaction compositions at 72 h for the reaction of with 1-butene with [(IMesH$_2$)Cl$_2$Ru=CH(PCy$_3$)](BF$_4$)

Reaction 1

	7	11a	11b	11c
Integral	0.01	0.32	0.71	0.33
% composition	0.7%	24%	52%	24%

(1-butene + 3-hexene):ethylene

99:1

Reaction 2

	7	11a	11b	11c
Integral	0.02	2.13	4.21	1.78
% composition	0.2%	26%	52%	22%

(1-butene + 3-hexene):ethylene

99:1

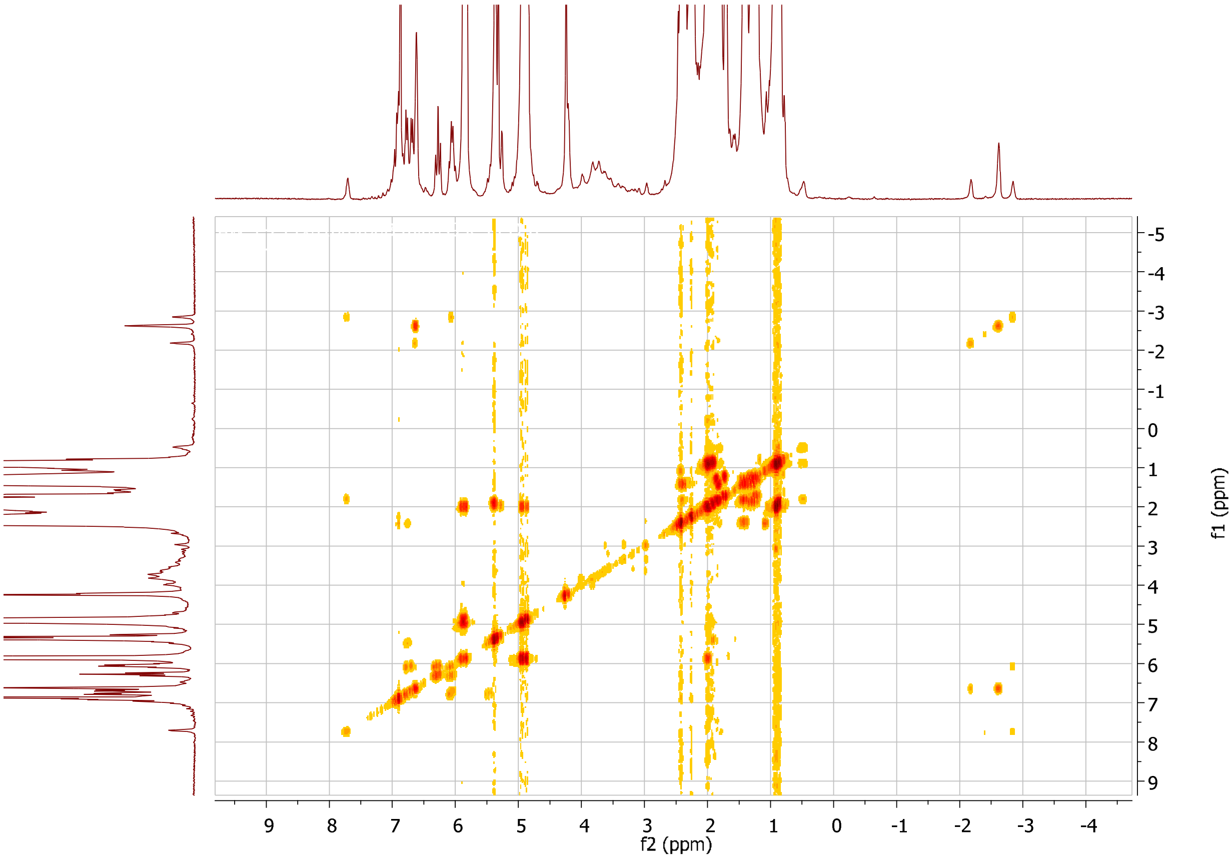
Reaction 3

	7	11a	11b	11c
Integral	0.18	2.01	4.21	2.0
% composition	2%	24%	50%	24%

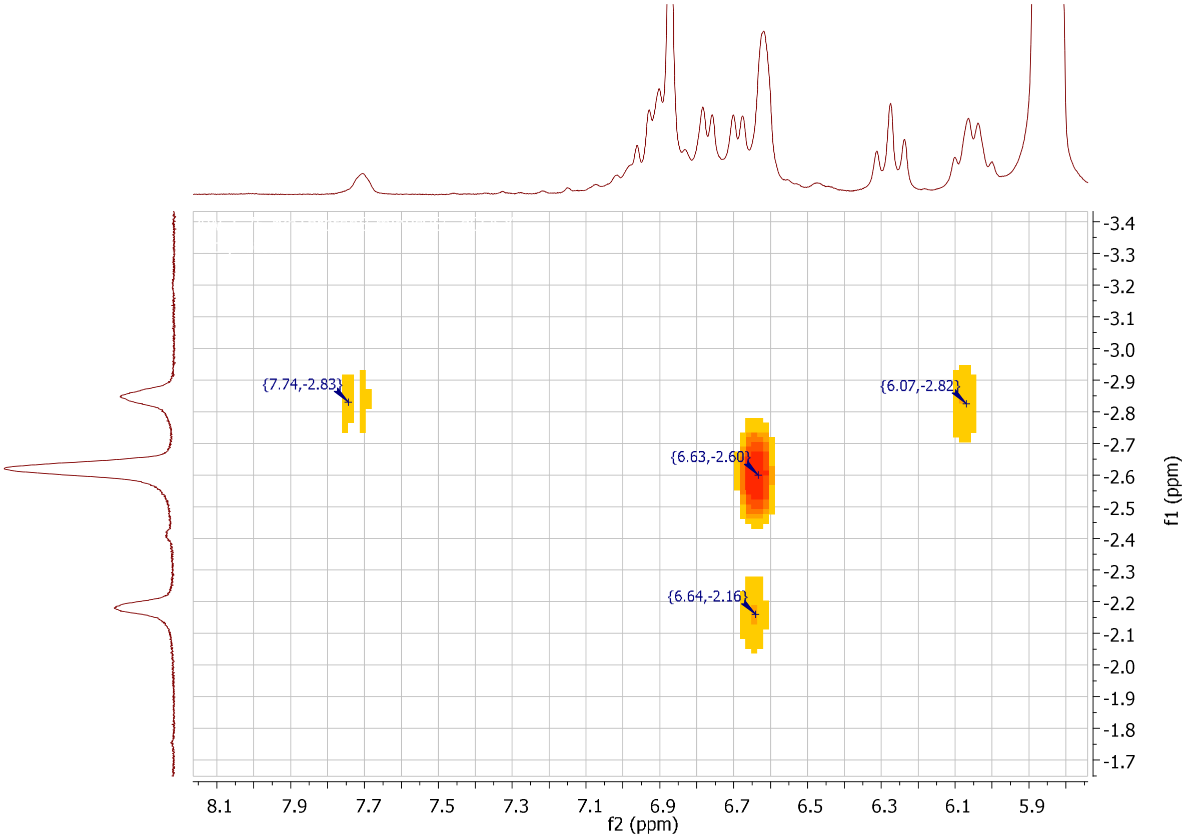
(1-butene + 3-hexene):ethylene

98:2

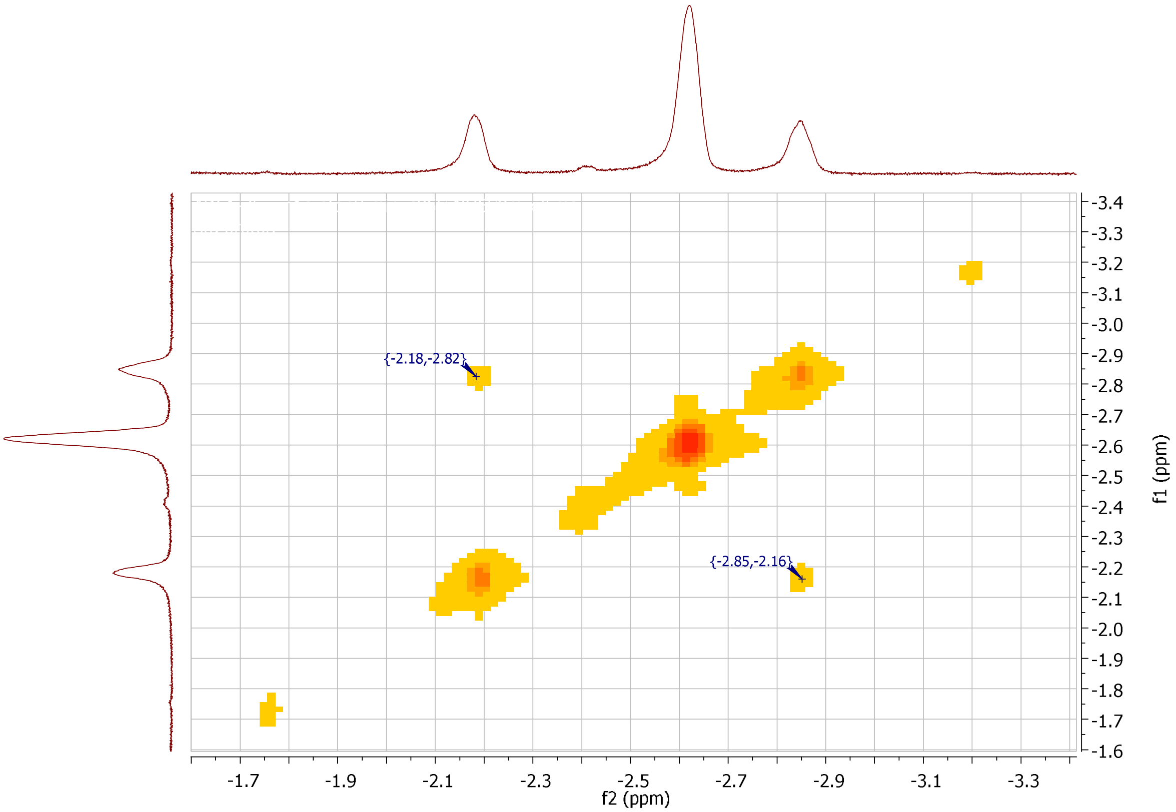
gCOSY (500 MHz, CD_2Cl_2, –87 ˚C) (3 h)**.**



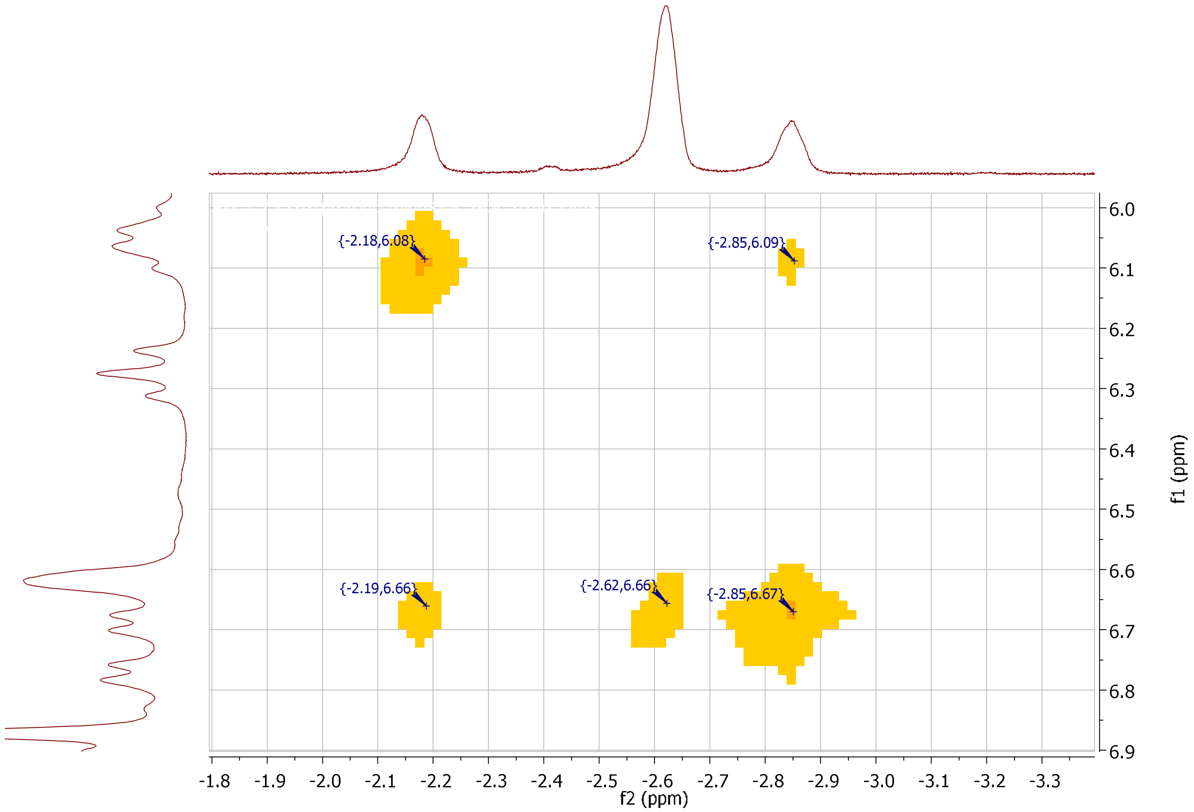
gCOSY (500 MHz, CD_2Cl_2, –87 ˚C) (3 h; f1 = δ –1.7 → –3.4 ppm, f2 = δ 5.9 → 8.1 ppm,).



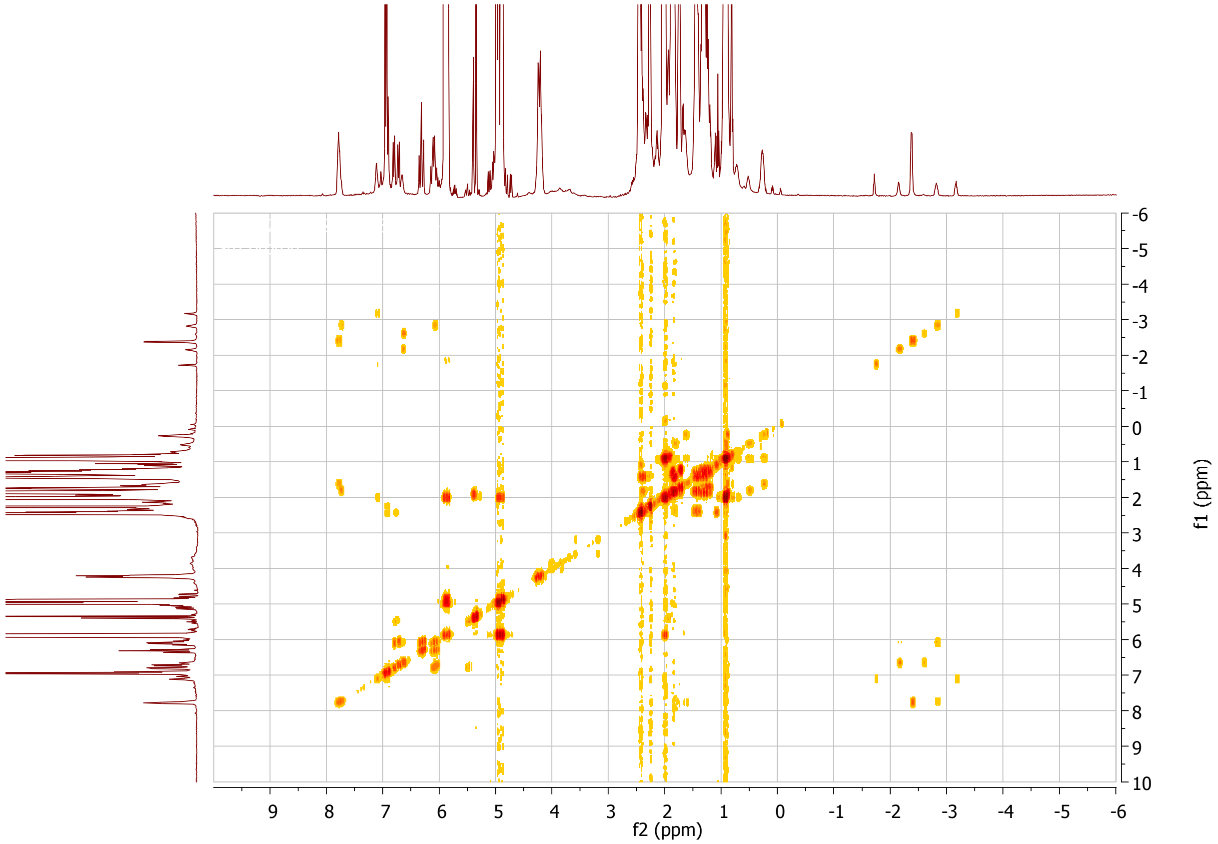
NOESY-2D (500 MHz, CD_2Cl_2, –87 ˚C; mix = 35 ms) (3 h; f1,f2 = δ –1.6 → –3.4 ppm).



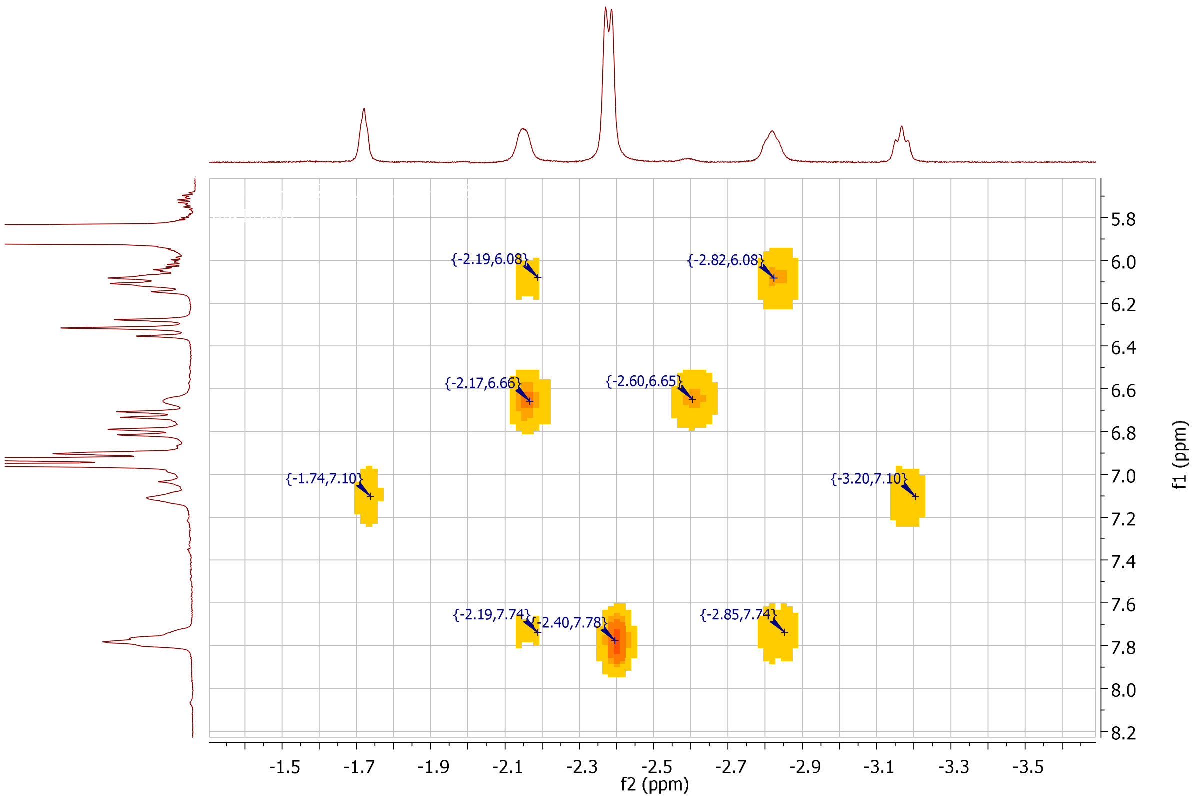
NOESY-2D (500 MHz, CD_2Cl_2, –87 ˚C; mix = 35 ms) (3 h; f1 = 6.0 → 6.9, f2 = δ –1.8 → –3.4 ppm).



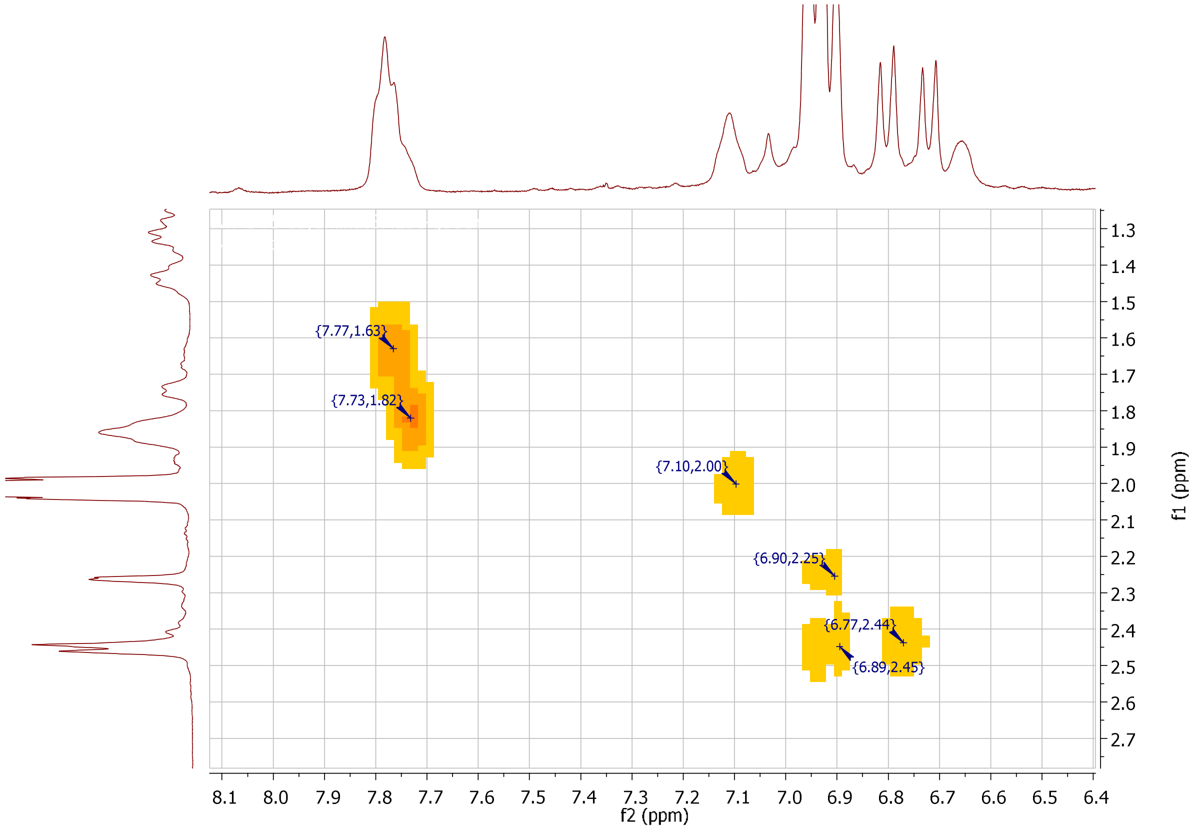
gCOSY (500 MHz, CD_2Cl_2, –87 ˚C) (72 h reaction time)**.**



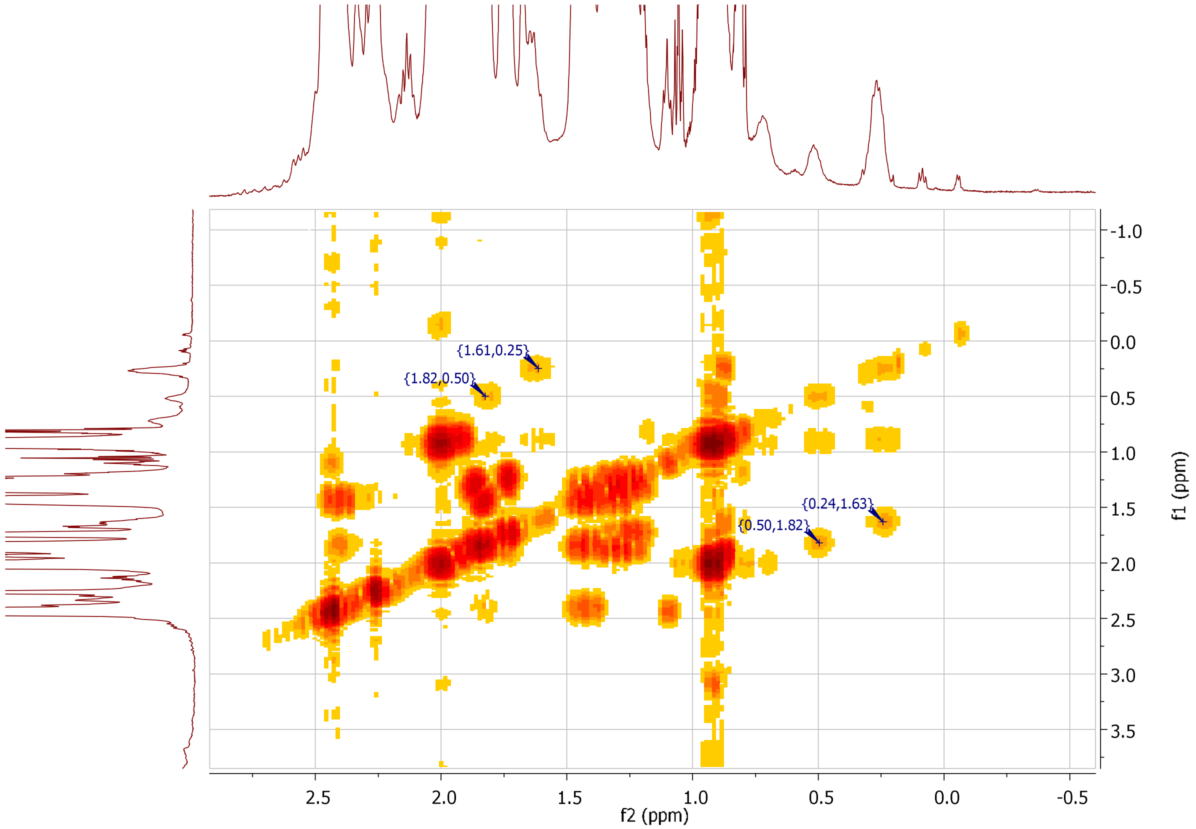
gCOSY (500 MHz, CD$_2$Cl$_2$, –87 ˚C) (72 h; f1 = δ 5.7 → 8.2 ppm, f2 = δ –1.3 → –3.7 ppm).



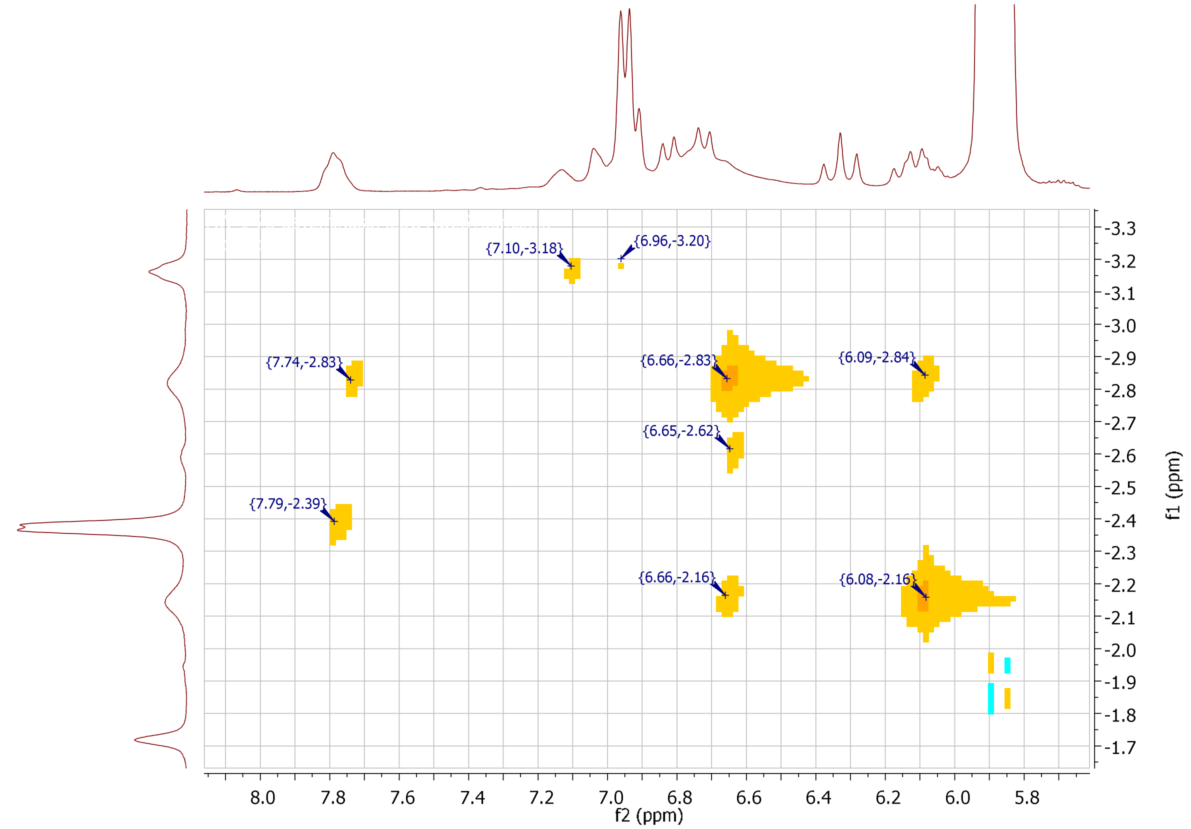
gCOSY (500 MHz, CD$_2$Cl$_2$, –87 ˚C) (72 h; f1 = δ 6.4 → 8.1 ppm, f2 = δ 1.3 → 2.7 ppm).



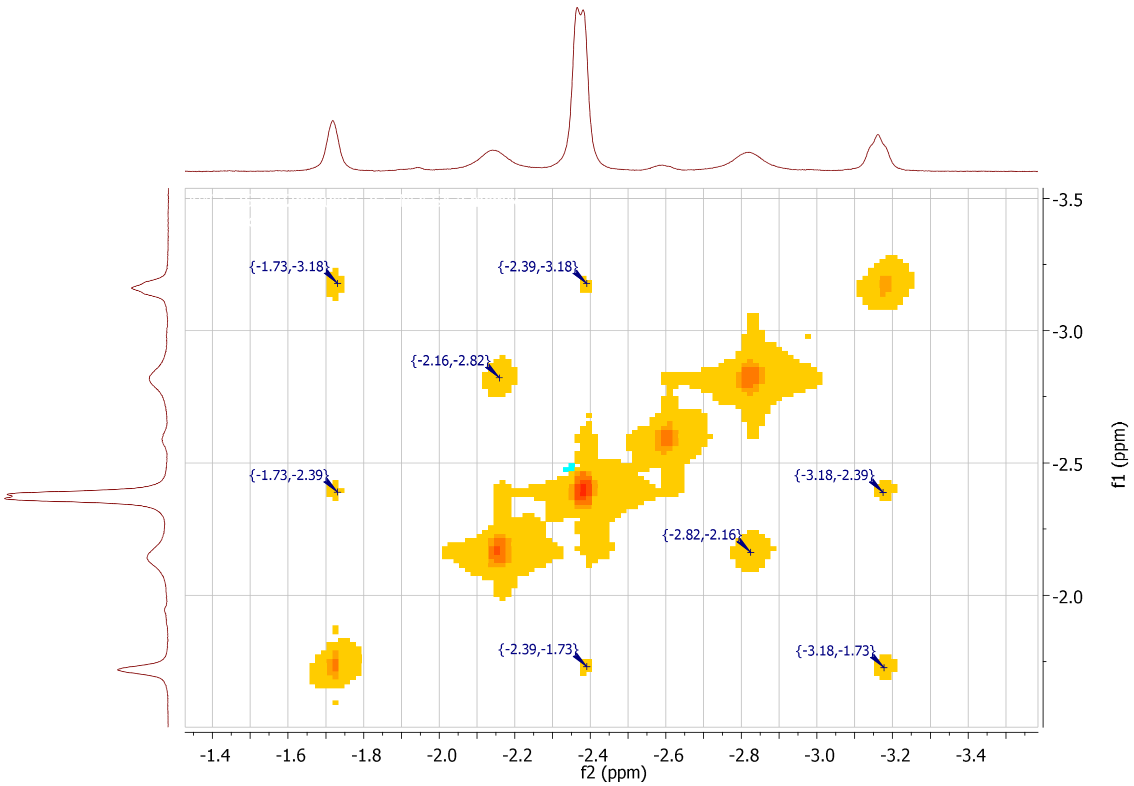
gCOSY (500 MHz, CD$_2$Cl$_2$, –87 ˚C) (72 h; f1 = δ –0.50 → 3.0 ppm, f2 = δ –1.0 → –4.0 ppm).



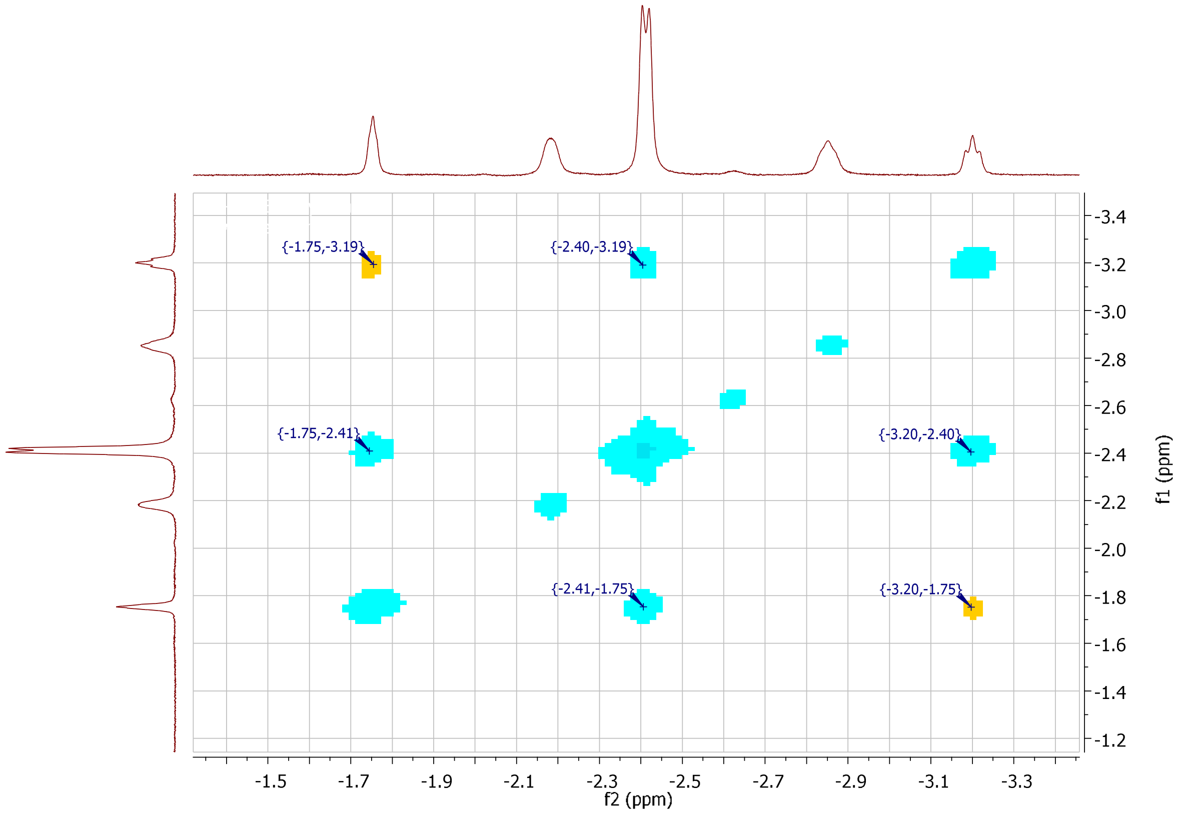
NOESY-2D (500 MHz, CD$_2$Cl$_2$, –87 ˚C; mix = 35 ms) (72 h; f1 = 5.6 → 8.15, f2 = –1.6 → –3.4 ppm).



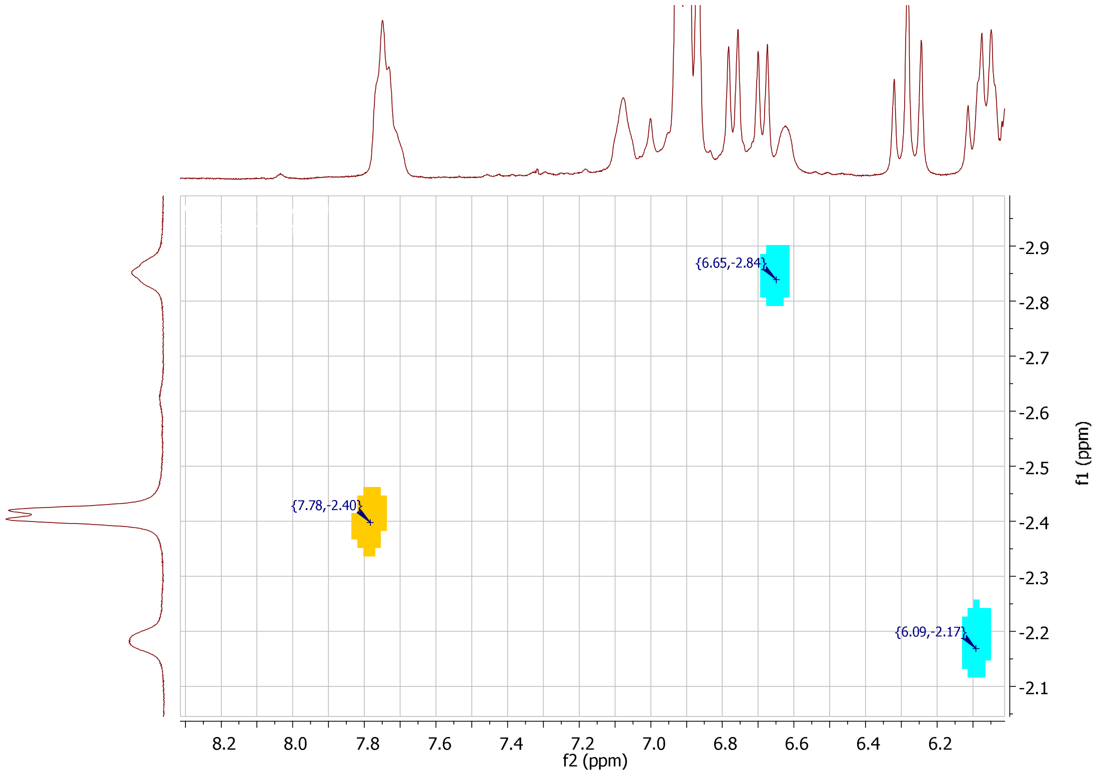
NOESY-2D (500 MHz, CD_2Cl_2, –87 ˚C; mix = 35 ms) (72 h; f1,f2 = δ –1.5 → –3.5 ppm).



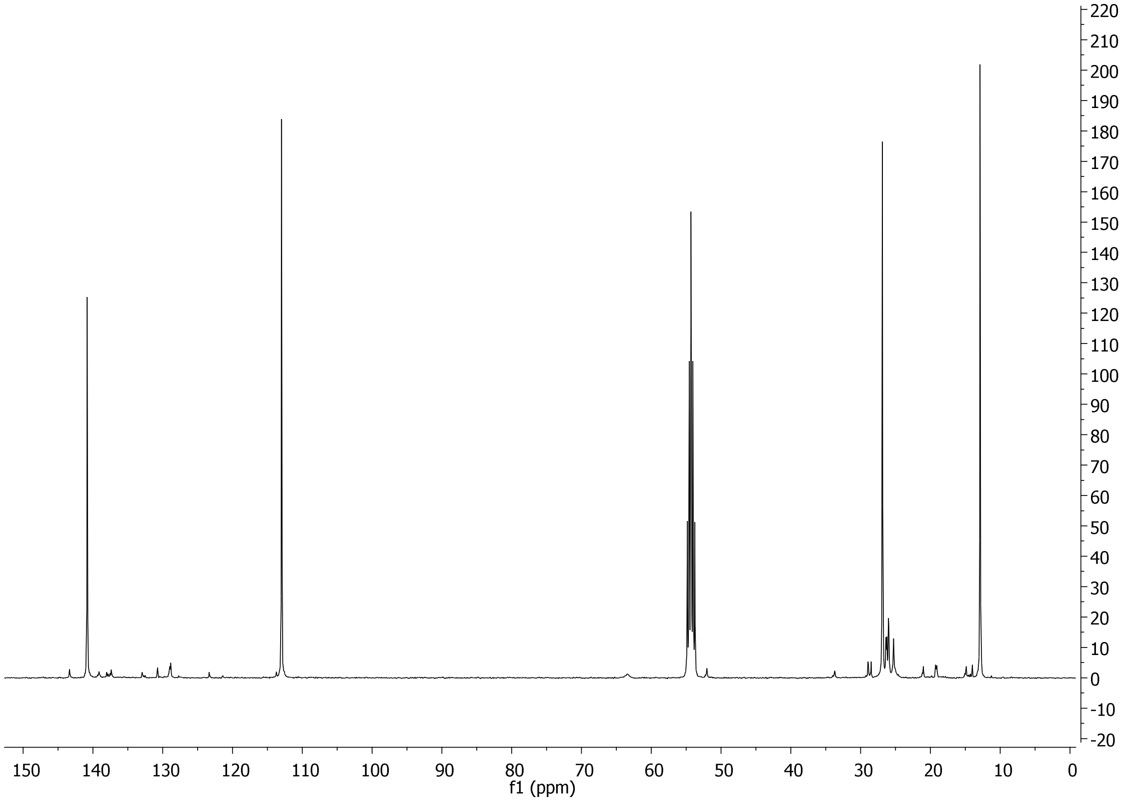
ROESY-2D (400 MHz, CD_2Cl_2, –80 ˚C; mix = 0.15 s) (72 h; f1,f2 = –1.2 → –3.4 ppm).



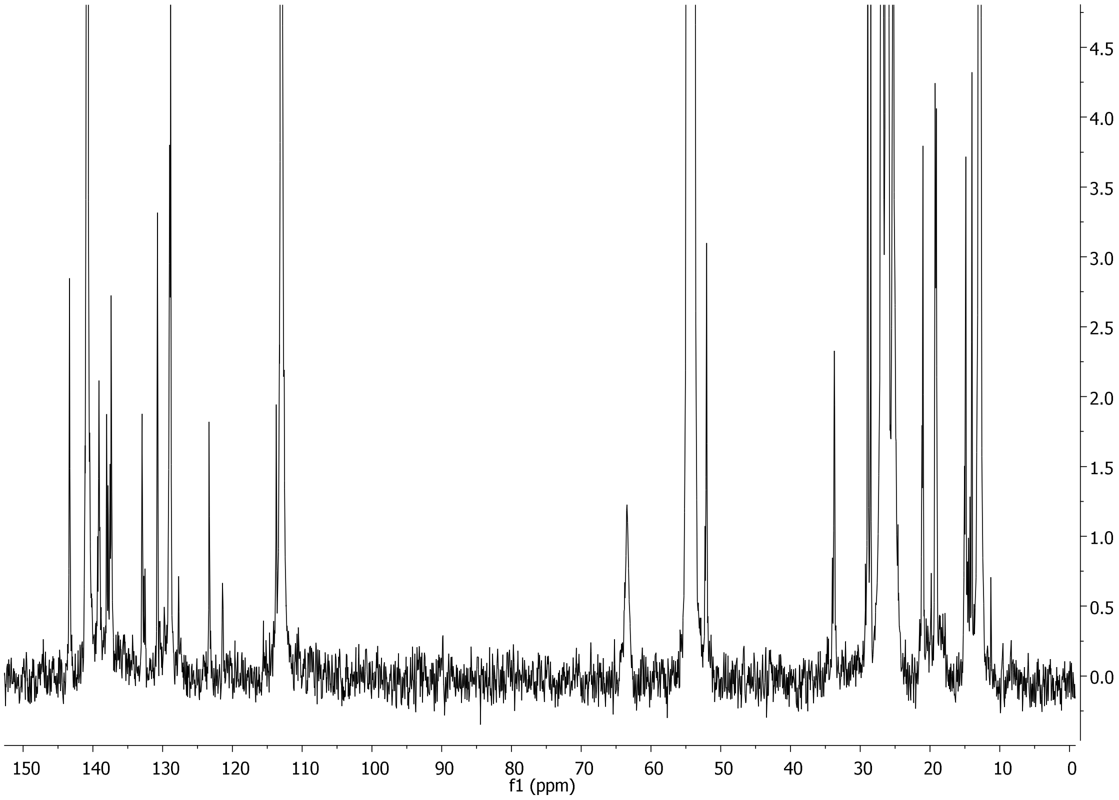
ROESY-2D (400 MHz, CD_2Cl_2, –80 ˚C; mix = 0.15 s) (72 h; f1 = –2.05 → 3.0, f2 = 8.3 → 6.1 ppm).



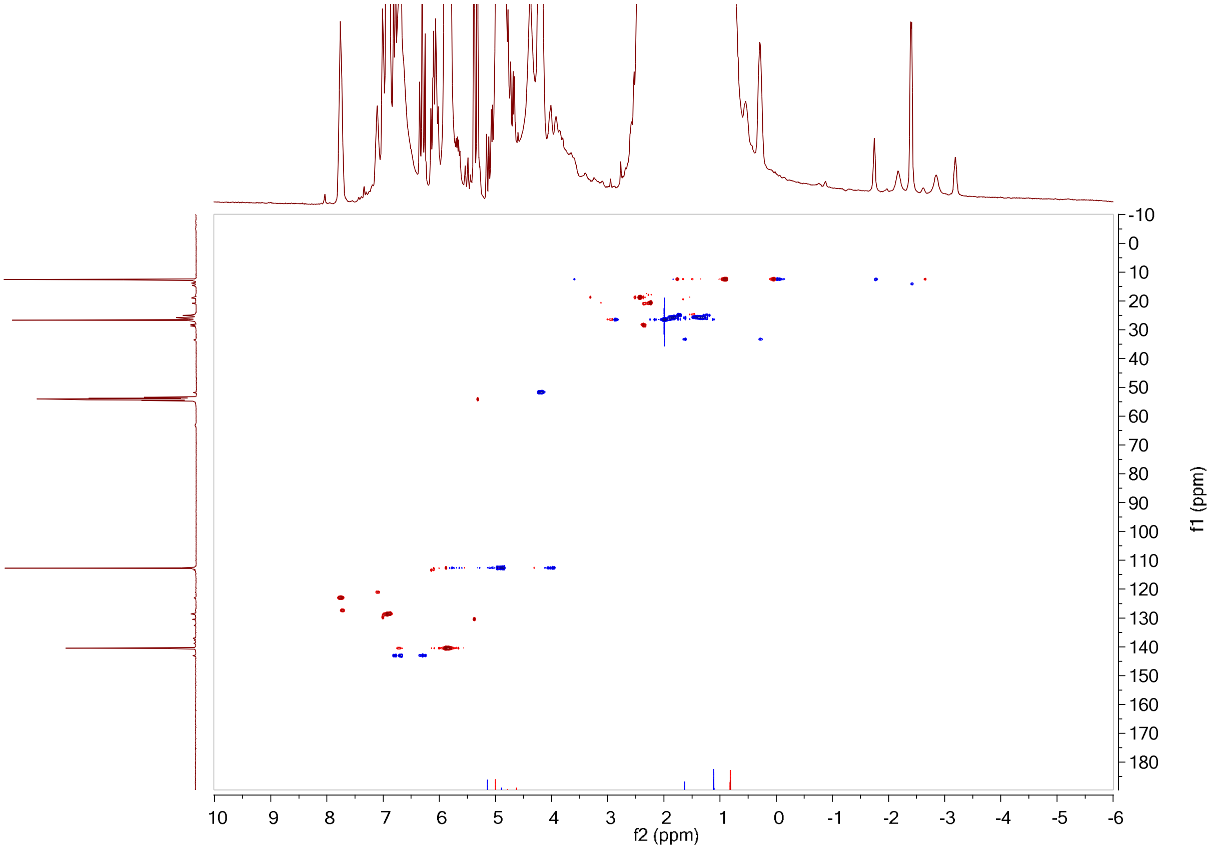
^{13}C NMR (100 MHz, CD_2Cl_2, –80 ˚C) (72 h; spectrum fit to height).



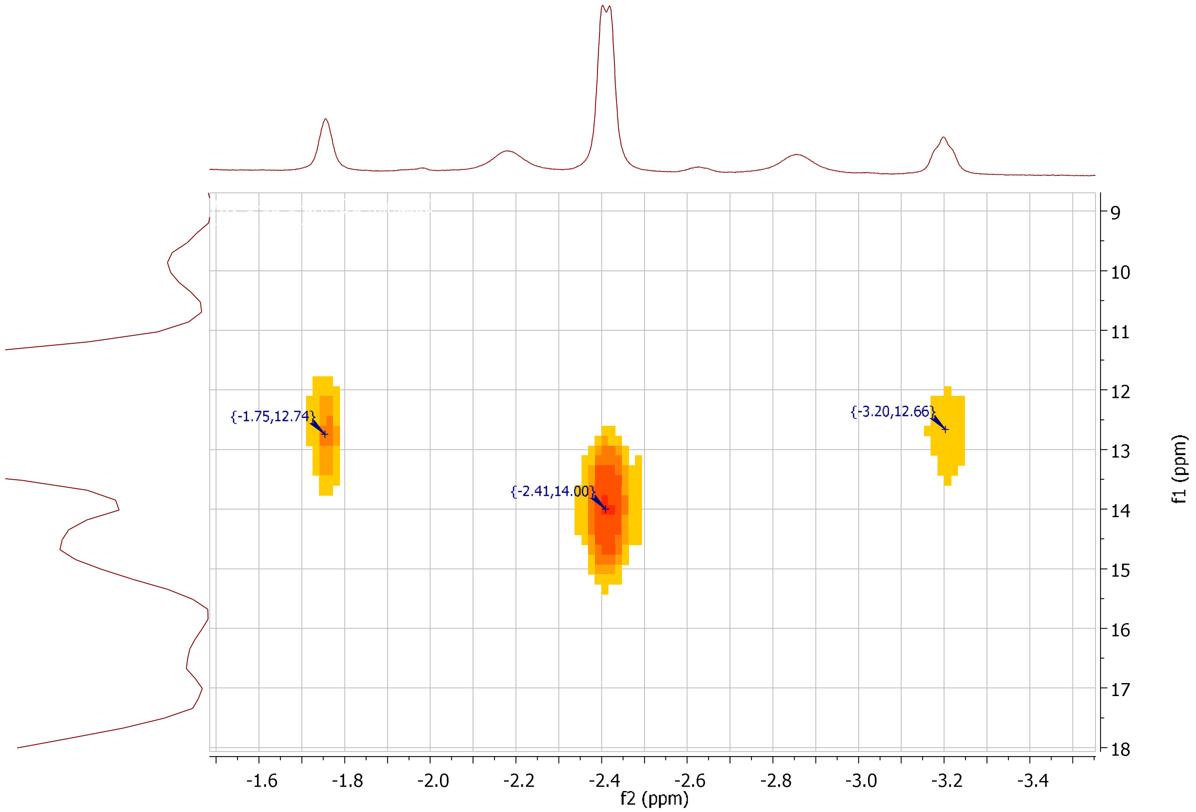
^{13}C NMR (100 MHz, CD$_2$Cl$_2$, –80 ˚C) (after 72 h; magnified view).



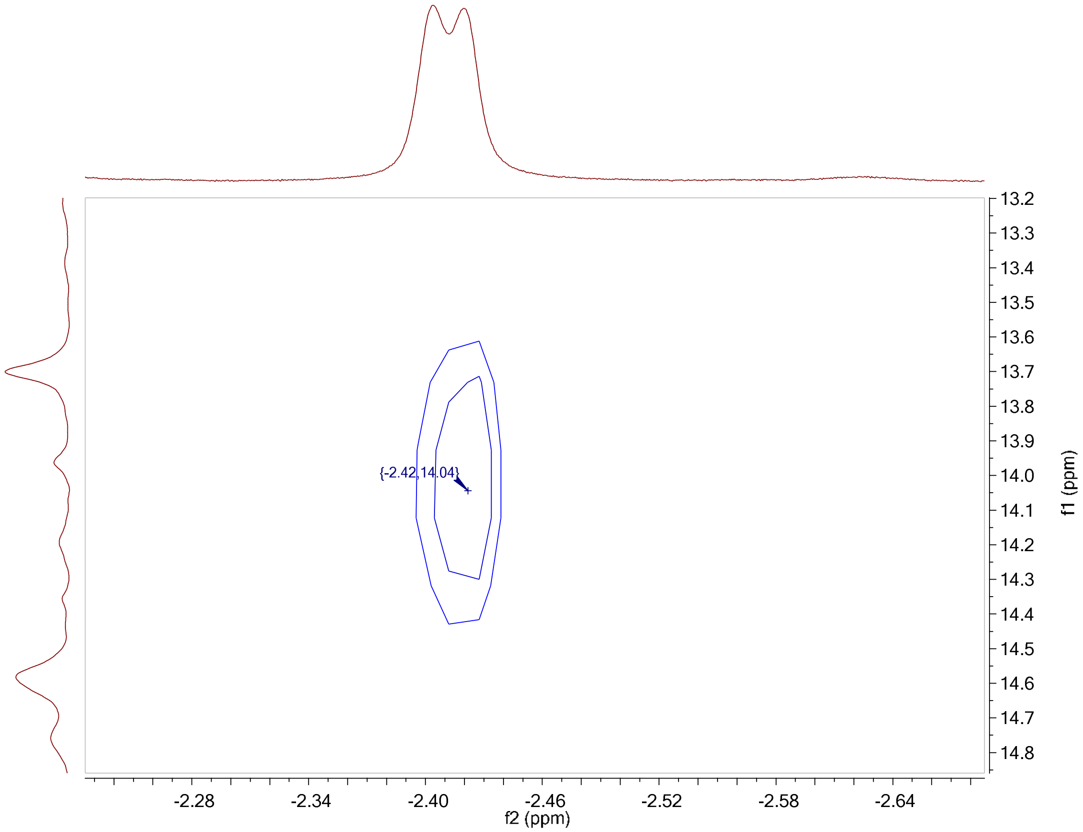
gHSQC (400 MHz, CD$_2$Cl$_2$, –80 ˚C) (after 72 h; full spectrum).



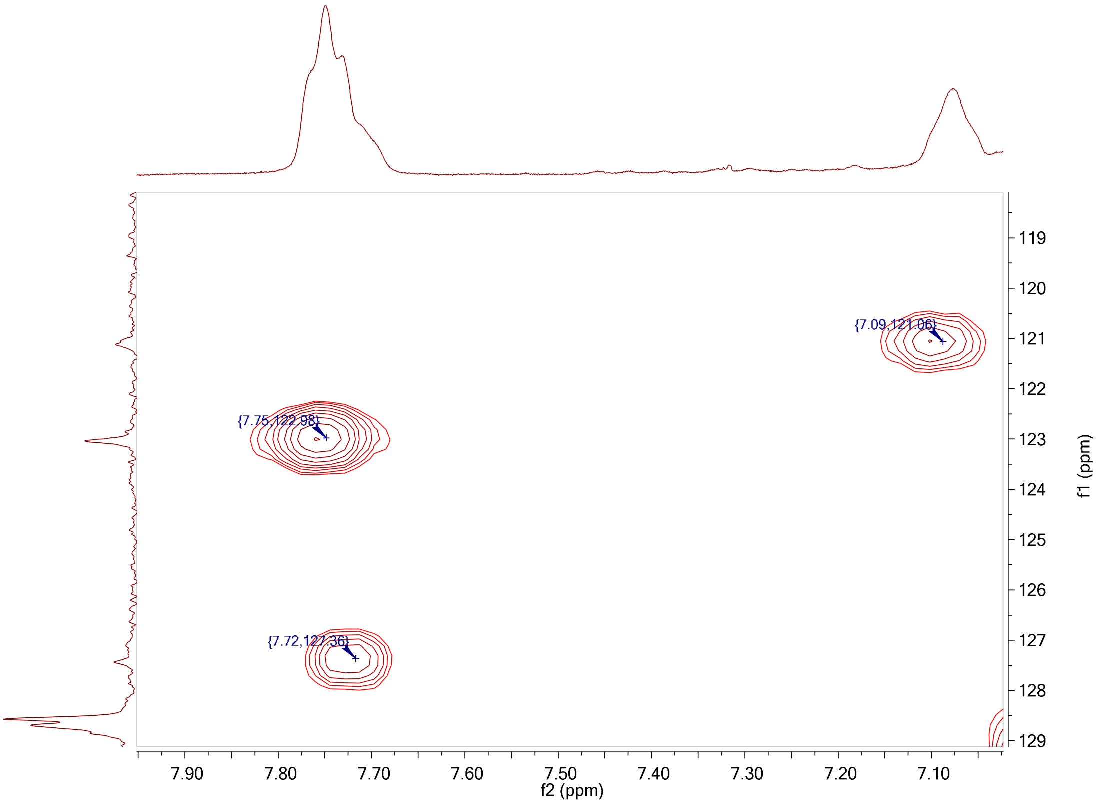
gHMQC (400 MHz, CD$_2$Cl$_2$, –80 ˚C) (after 72 h; zoomed f1 = 9 → 18, f2 = –2.23 → –2.68 ppm).



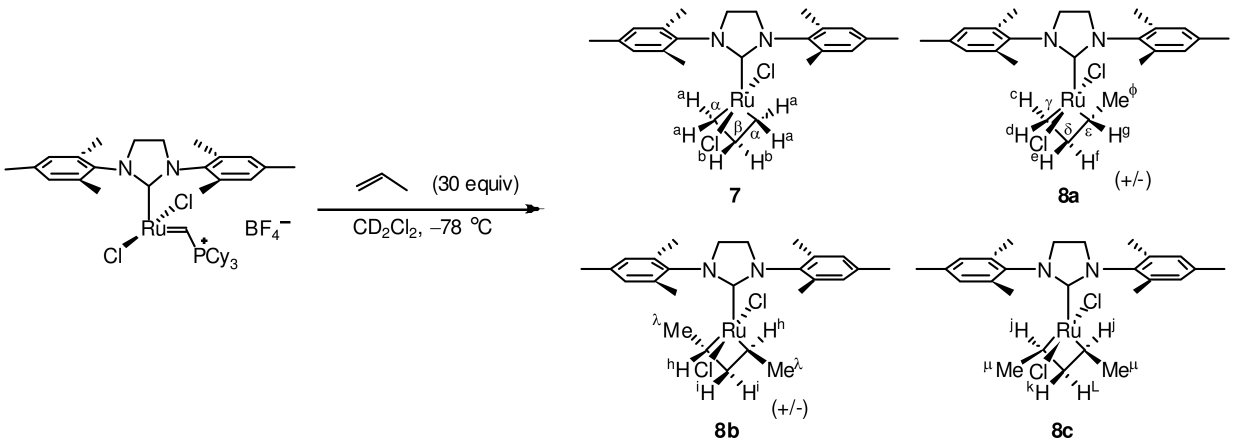
gHSQC (400 MHz, CD$_2$Cl$_2$, –80 ˚C) (after 72 h; zoomed f1 = 13.2 → 14.8, f2 = –2.23 → –2.68 ppm).



gHSQC (400 MHz, CD_2Cl_2, –80 ˚C) (after 72 h; zoomed f1 = 118 → 129, f2 = 7.0 → 8.0 ppm).



II.B. Reaction of $[(IMesH_2)Cl_2Ru{=}CH(PCy_3)](BF_4)$ (5b) with Propene.



This reaction was set up on a 0.021-mmol scale according to the same general procedure as that used for the 1-butene reaction. In this case, propene (0.63 mmol, 30 equiv), was condensed into the NMR tube. After 3 h at −78 °C, complete conversion of the starting catalyst was observed. Metallacycles **A**, **E**, and **F** were observed in 76% combined yield relative to anthracene (0.5 equiv) when it was added as an internal standard. Spectral characterization information was found to match literature values:[6] **7** (59%), **8a** (38%), **8b** (3%). The ratio of propene:ethylene was determined to be 95:5. The reaction was allowed to stand at −78 °C. Analysis after 69 h (72 h time point) at −78 °C found the metallacycle ratios to have equlibrated. Some decomposition was observed, as the combined yield of metallacycle species had decreased to 64% yield. The *cis*-substituted metallaycle **8c** is now clearly visible, with an overall metallacycle distribution of: **7** (38%), **8a** (50%), **8b** (9%), and **8c** (3%). The ratio of propene:ethylene in solution at this point was determined to be 96:4. ^{1}H NMR (500 MHz, CD_2Cl_2, −87 ˚C)[9] δ 7.85 (2H, br, $\mathbf{H}^{h}$ metallacycle **8b**), 7.76 (1H, br, $\mathbf{H}^{g}$ metallacycle **8a**), 7.09 (2H, br, $\mathbf{H}^{j}$ metallacycle **8c**), 6.65 (1H, br, $\mathbf{H}^{c}$ metallacycle **8a**), 6.60 (4H, br, $\mathbf{H}^{a}$ metallacycle **7**), 6.05 (1H, br, $\mathbf{H}^{d}$ metallacycle **8a**), 0.97 (3H, br, RuCH(C**H**$_3$) metallacycle **8c**), 0.89 (3H, d, J = 5.4 Hz, RuCH(C**H**$_3$) metallacycle **8a**), 0.72 (6H, d, J = 5.6 Hz, RuCH(C**H**$_3$) metallacycle **8b**), −1.66 (1H, br, $\mathbf{H}^{k}$ metallacycle **8c**), −2.12 (1H, br, $\mathbf{H}^{f}$ metallacycle **8a**), −2.35 (2H, br, $\mathbf{H}^{i}$ metallacycle **8b**), −2.62 (2H, br, $\mathbf{H}^{b}$ metallacycle **7**), −2.85 (1H, br, $\mathbf{H}^{e}$ metallacycle **8a**), −3.21 (1H, $\mathbf{H}^{L}$ metallacycle **8c**); ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, −80 ˚C)[10] δ 120.2 ($\mathbf{C}^{\varepsilon}$ metallacycle **8a**), 93.9 ($\mathbf{C}^{\alpha}$ metallacycle **7**), 89.3 ($\mathbf{C}^{\gamma}$ metallacycle **8a**), 25.8 (RuCH(**C**H$_3^{\phi}$) metallacycle **8a**) 9.0 ($\mathbf{C}^{\delta}$ metallacycle **8a**), 6.6 (RuCH(**C**H$_3^{\lambda}$ metallacycle **8b**), 1.7 ($\mathbf{C}^{\beta}$ metallacycle **7**).

Note:* in a separate experiment conducted under the same conditions, the propene:ethylene ratio was observed via ^{1}H NMR to be 97:3 at 72 h (500 MHz, −87.3 °C). In this case, the metallacycle ratio observed was: **7 (23%), **8a** (63%), **8b** (9%), **8c** (4%).

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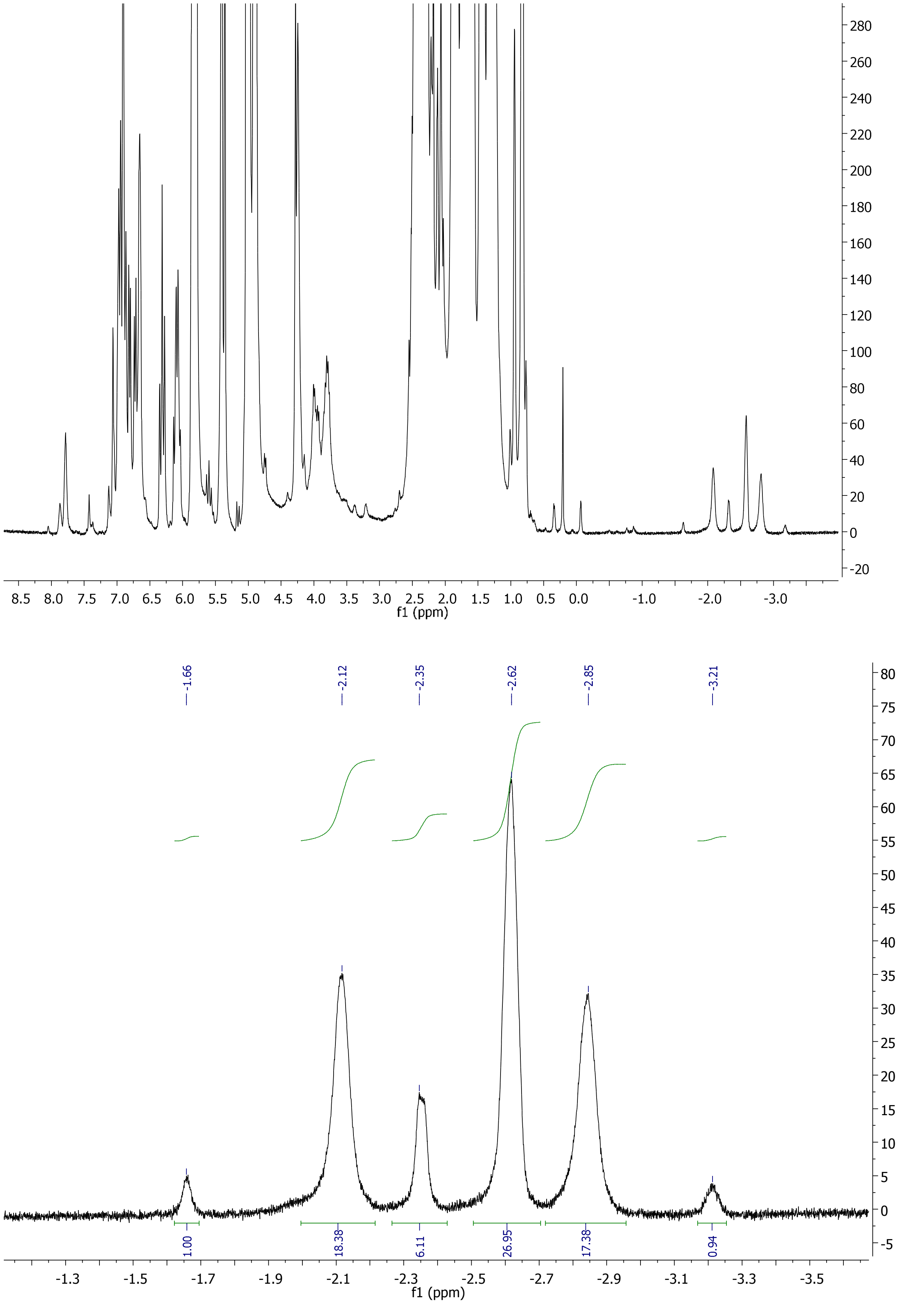
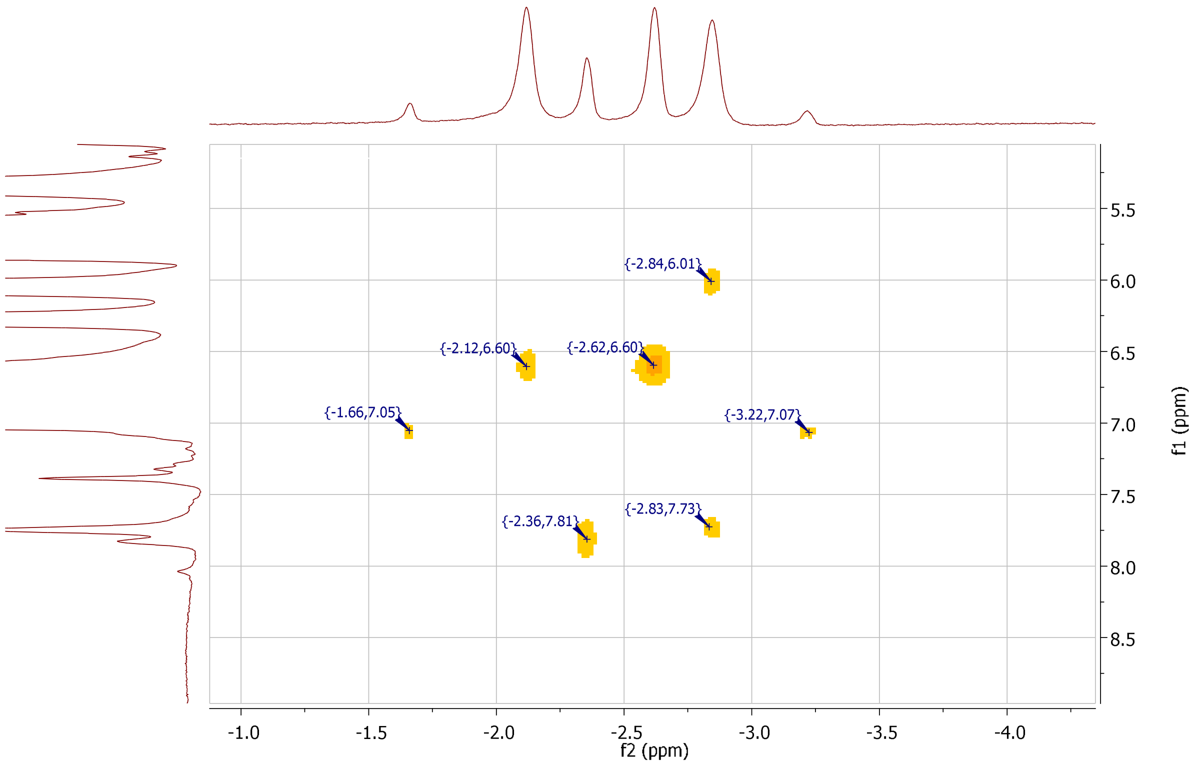
[9] Shifts corresponding to the NHC ligand of each species cannot be definitively assigned, as no 2D crosspeaks were observed to enable identification.

[10] The ^{13}C chemical shifts for the α- and β-carbons of metallacycles **8b** and **8c** could not be conclusively assigned due to their low yields and peak overlap in the NMR spectra.

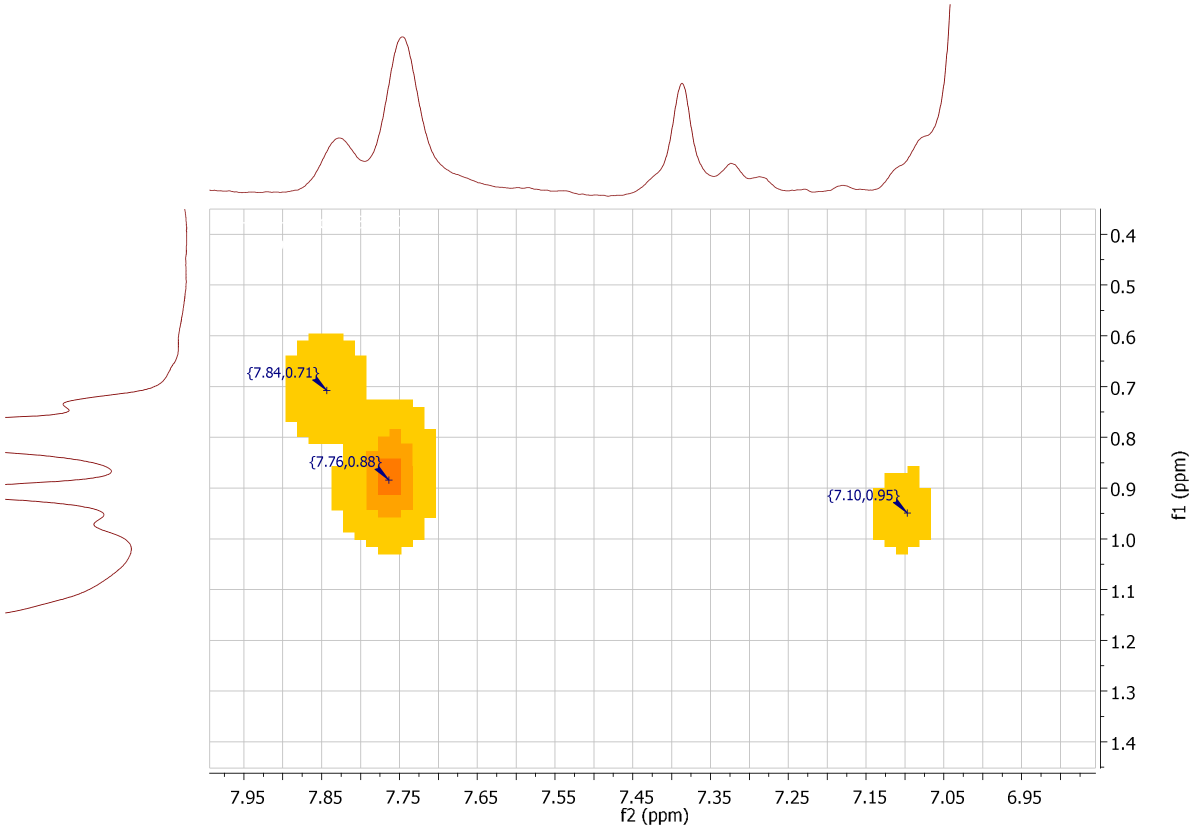
^{1}H-NMR spectrum (500 MHz, –87 °C) of metallacycles derived from propene (72 h).



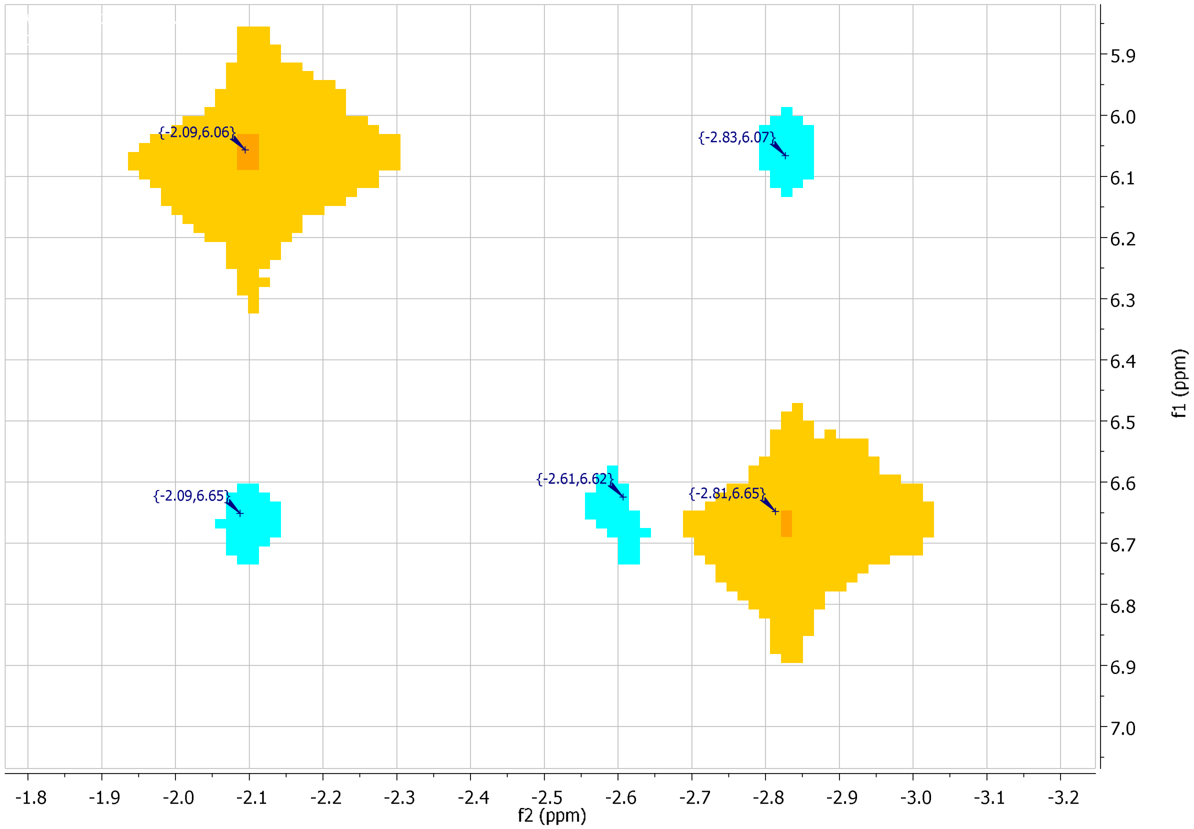
gCOSY (500 MHz, CD_2Cl_2, –87 ˚C) (72 h; f1 = δ 5.0 → 9.0 ppm, f2 = δ –1.0 → –4.0 ppm).



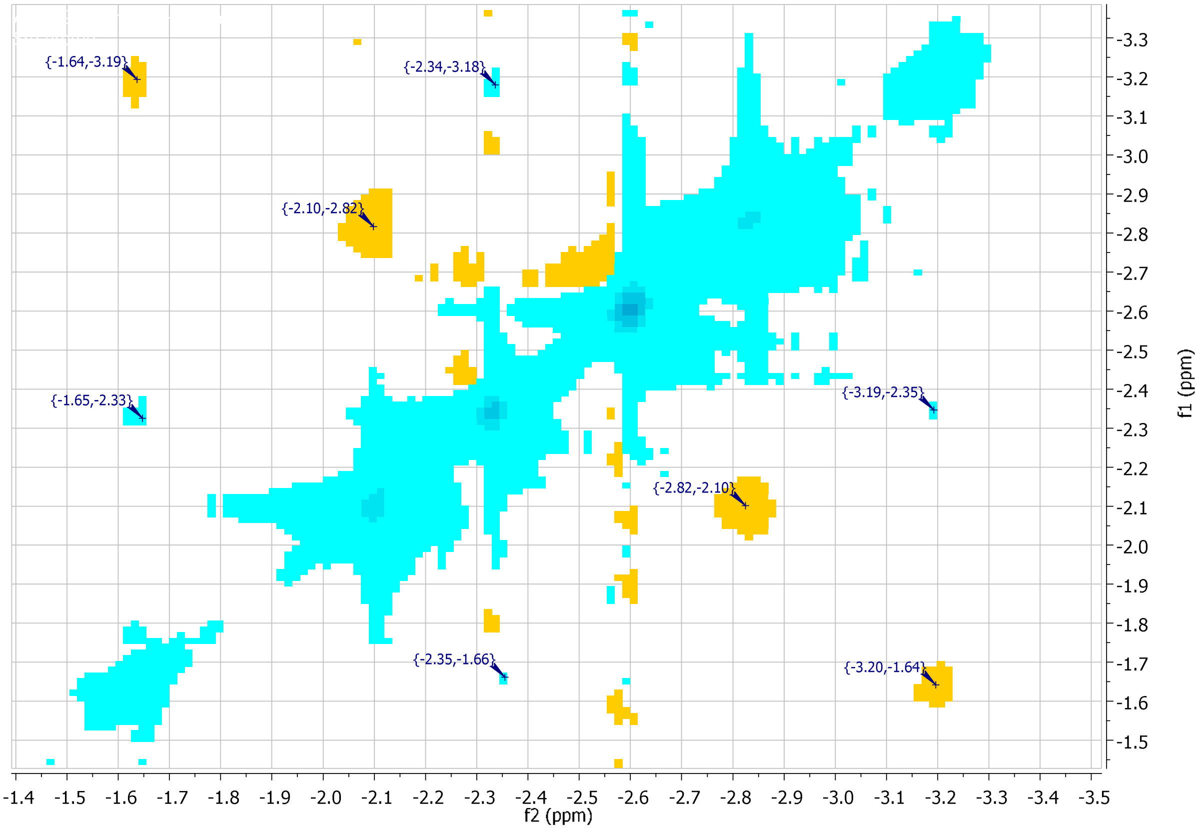
gCOSY (500 MHz, CD_2Cl_2, –87 ˚C) (72 h; f1 = δ 0.4 → 1.4 ppm, f2 = δ 7.95 → 6.95 ppm).



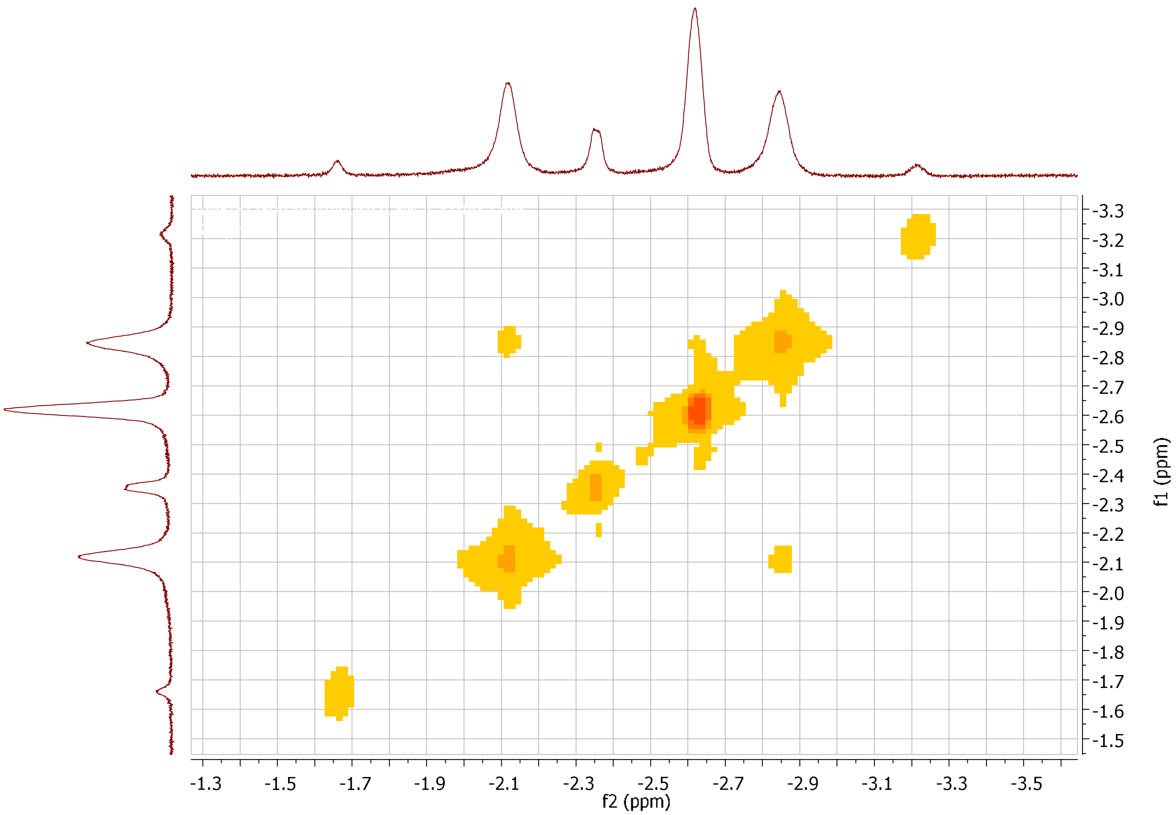
ROESY-2D (500 MHz, CD$_2$Cl$_2$, –87 ˚C; mix = 0.050 s) (72 h; f1 = –1.5 → –3.3, f2 = –1.4 → –3.5 ppm).



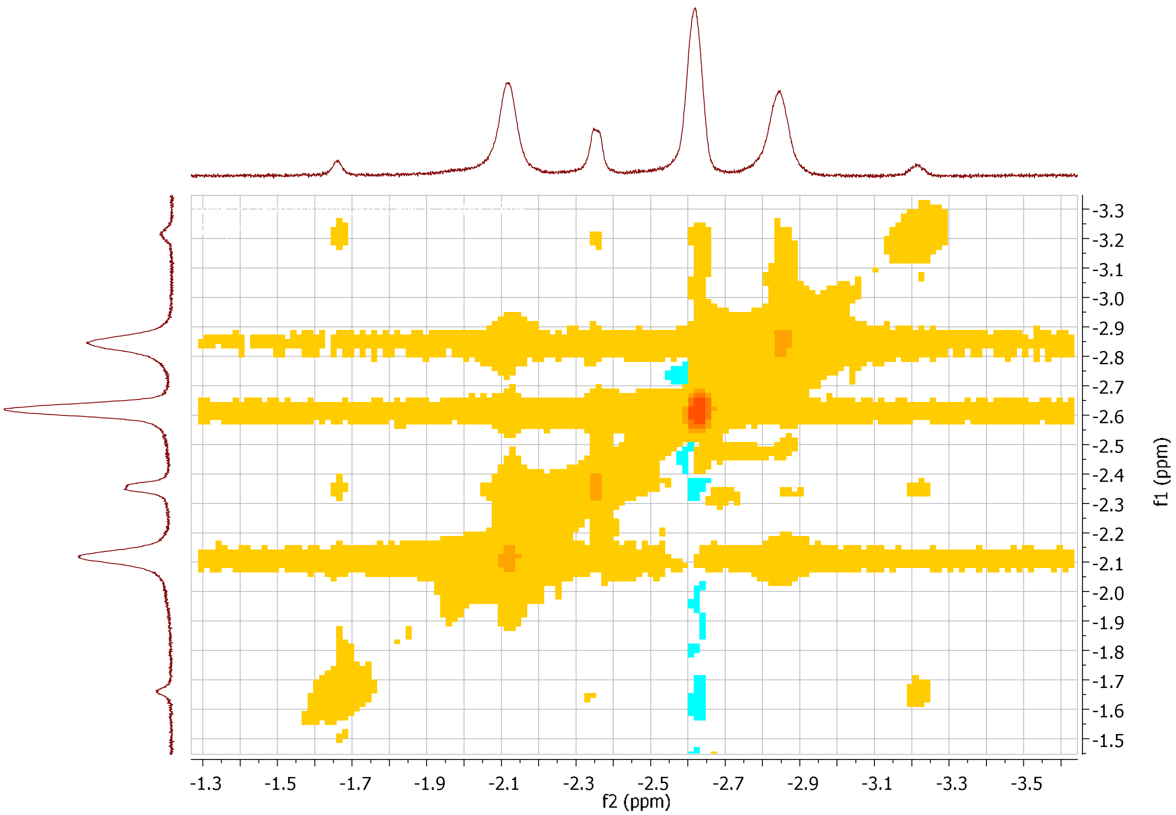
ROESY-2D (500 MHz, CD$_2$Cl$_2$, –87 ˚C; mix = 0.050 s) (72 h; f1 = –1.5 → –3.3, f2 = –1.4 → –3.5 ppm).



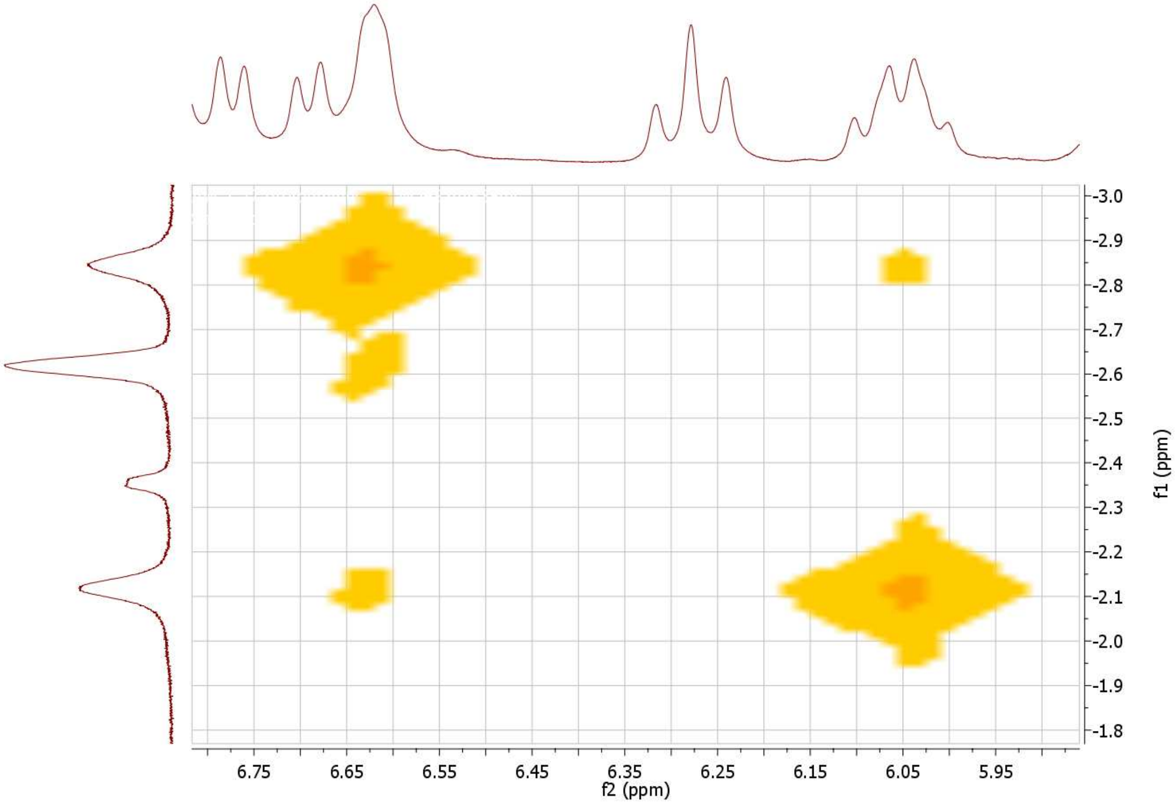
NOESY-2D (500 MHz, CD_2Cl_2, –87 ˚C; mix = 35 ms) (72 h; f1 = –1.3 → –3.6, f2 = –1.5 → –3.3 ppm).



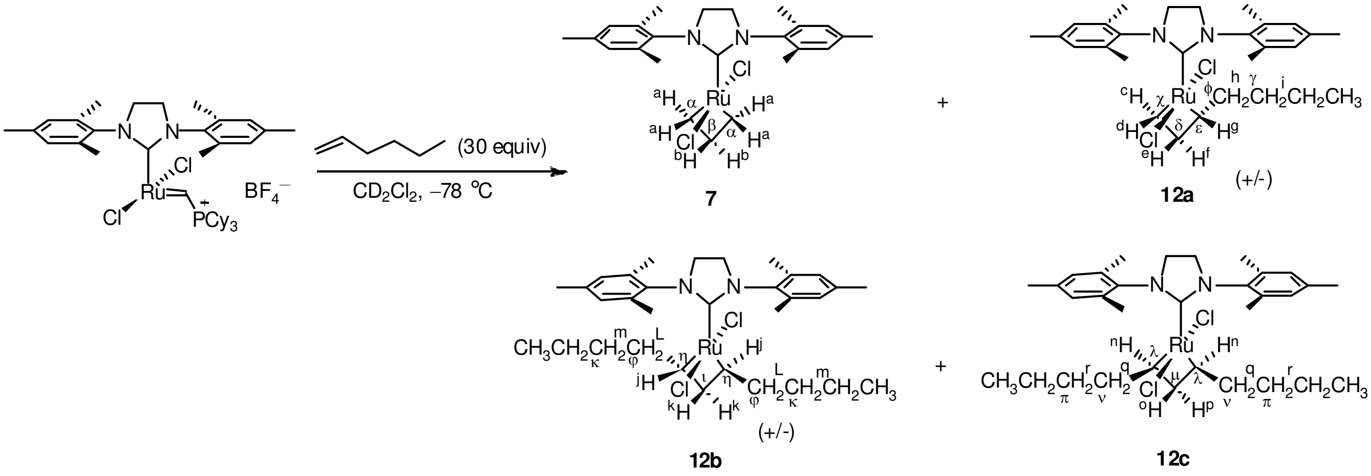
NOESY-2D (500 MHz, CD_2Cl_2, –87 ˚C; mix = 35 ms) (72 h; f1 = –1.3 → –3.6, f2 = –1.5 → –3.3 ppm).



NOESY-2D (500 MHz, CD_2Cl_2, –87 ˚C; mix = 35 ms) (72 h; f1 = −1.8 → –3.0, f2 = 5.9 → 6.8 ppm).

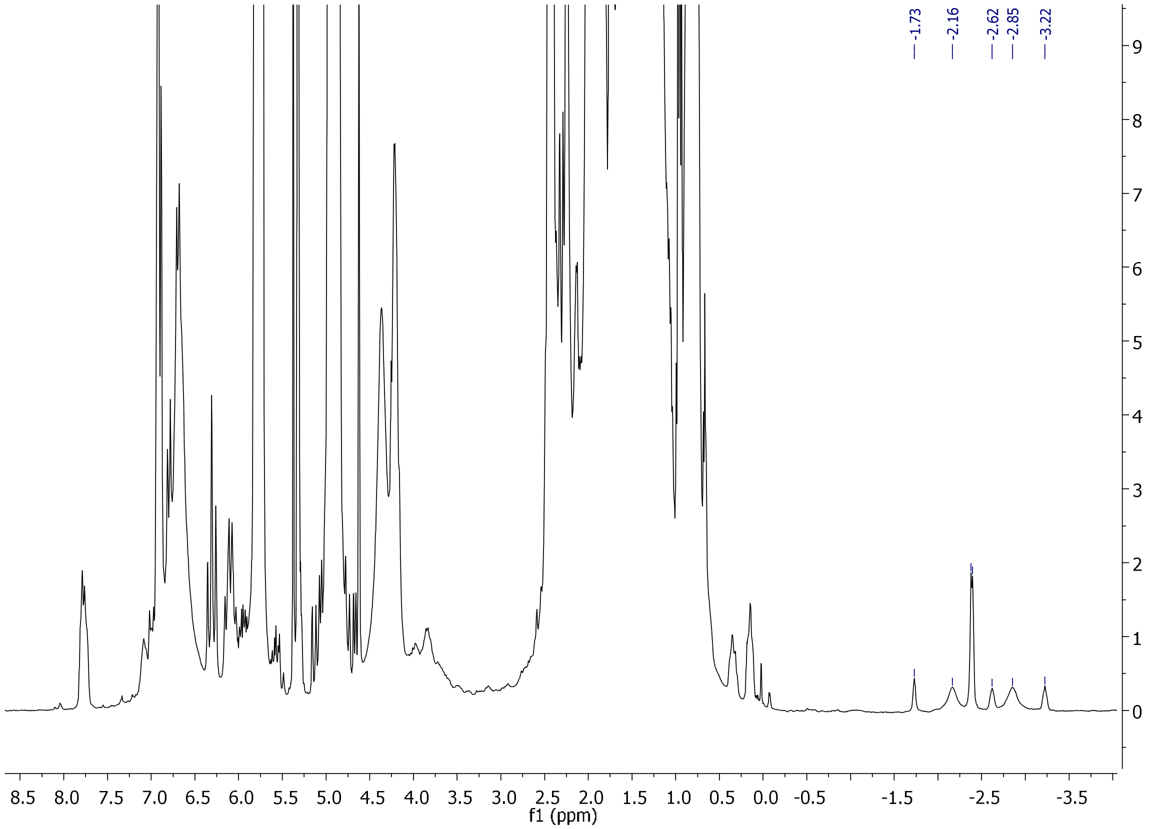


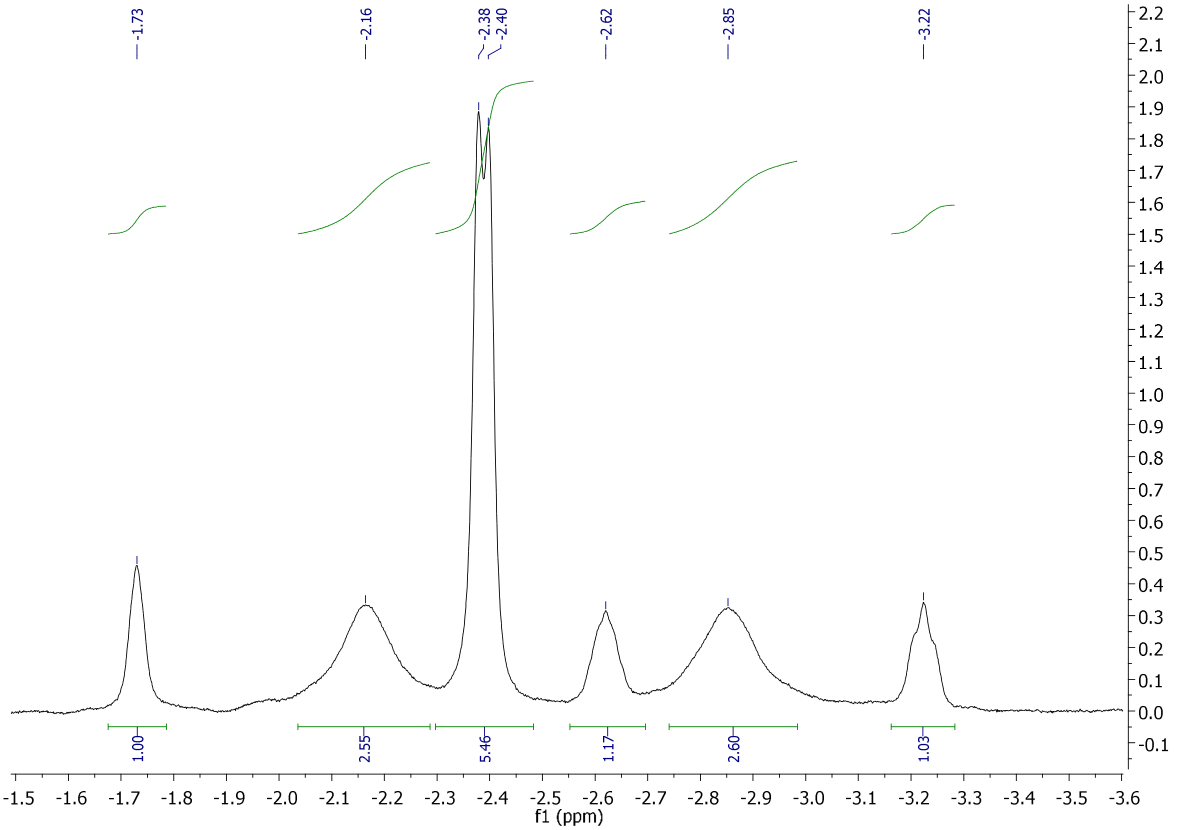
II.C. Reaction of [(IMesH$_2$)Cl$_2$Ru=CH(PCy$_3$)](BF$_4$) (5b) with 1-Hexene.



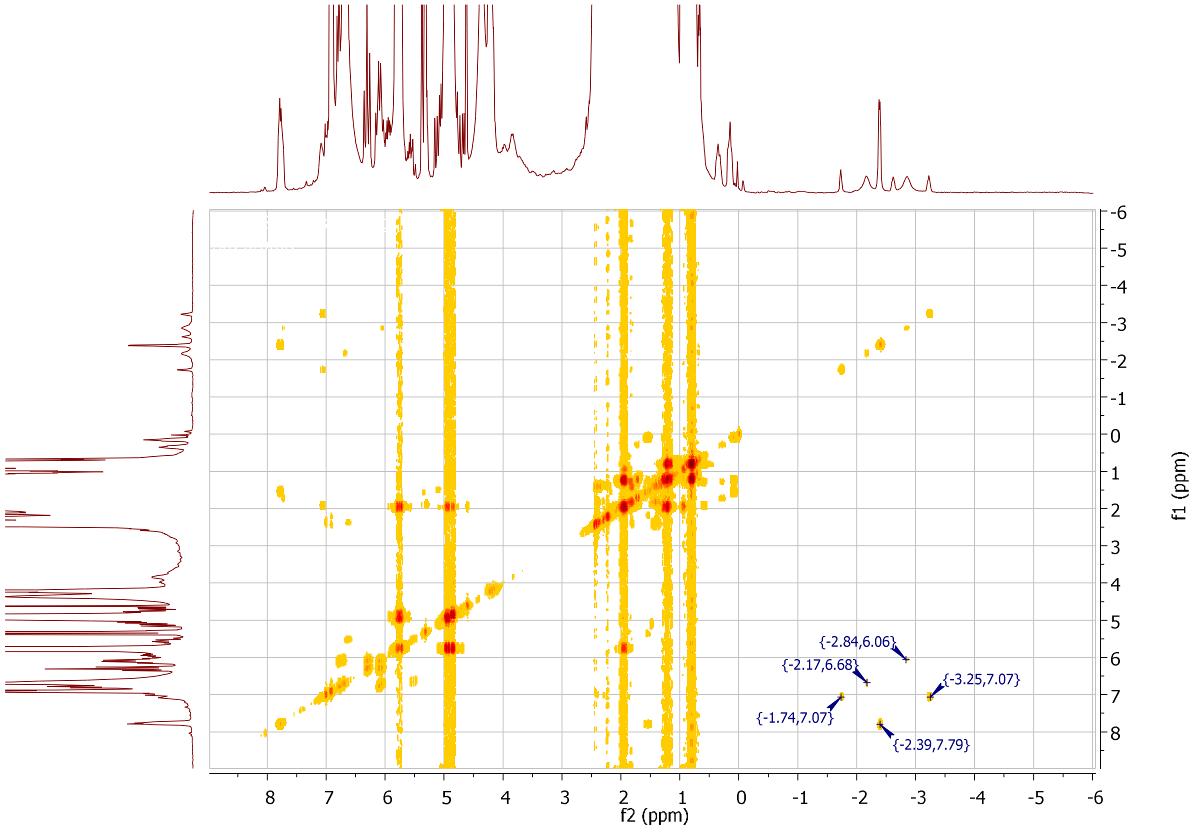
To a screw-top NMR tube in the glovebox, [(IMesH$_2$)Cl$_2$Ru=CH(PCy$_3$)](BF$_4$) (18.0 mg, 0.021 mmol, 1.0 equiv) and CD$_2$Cl$_2$ (600 μL) were added. The tube was sealed, shaken to mix the contents, and removed from the glovebox. The NMR tube was attached to an argon line via a needle inlet and placed in a cold bath chilled to −78 °C (dry ice/isopropyl alcohol). After 5 minutes, 1-hexene (79 μL, 0.63 mmol, 30 equiv) was added in one portion via syringe. The argon line was removed from the NMR tube, and the tube's cap and septum were wrapped with Teflon tape. The NMR tube was shaken to mix the contents. Reaction progress was monitored by VT-NMR at −80 °C. After 3 h, complete conversion of the starting catalyst was observed. Metallacycles **A**, **B**, and **C** were observed in 86% combined yield relative to anthracene (0.4 equiv) when it was added as an internal standard. ^{1}H-NMR analysis at −80 °C revealed four metallacycles: **7** (8%), **12a** (40%), **12b** (37%), and **12c** (15%). The ratio of 1-hexene:ethylene was determined to be > 99:1. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, −80 °C) δ 7.79 (2H, br, **H**^{j} metallacycle **12b**), 7.76 (**H**^{g} metallacycle **12a**), 7.07 (**H**^{n} metallacycle **12c**), 6.71 (1H, br, **H**^{c} metallacycle **12a**), 6.60 (4H, br, **H**^{a} metallacycle **7**), 6.09 (1H, br, **H**^{d} metallacycle **12a**), 1.88 (2H, m, **H**^{q} metallacycle **12c**), 1.73 (2H, m, **H**^{h} metallacycle **12a**), 1.58 (2H, br, **H**^{L} metallacycle **12b**), −1.73 (1H, br, **H**^{o} metallacycle **12c**), −2.16 (1H, br, **H**^{f} metallacycle **12a**), **H**^{k} metallacycle **12b**), −2.62 (2H, br, **H**^{b} metallacycle **7**), −2.85 (1H, br, **H**^{e} metallacycle **12a**), −3.22 (1H, br, **H**^{p} metallacycle **12c**); ^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$, −80 °C) δ 127.4 (**C**$^{\varepsilon}$ metallacycle **12a**), 123.0 (**C**$^{\eta}$ metallacycle **12b**), 121.1 (**C**$^{\lambda}$ metallacycle **12c**), 93.9 (**C**$^{\alpha}$ metallacycle **7**), 90.0 (**C**$^{\chi}$ metallacycle **12a**), 14.2 (**C**$^{\iota}$ metallacycle **12b**), 1.7 (**C**$^{\beta}$ metallacycle **7**).

^{1}H-NMR spectrum (400 MHz, –80 °C) of metallacycles derived from 1-hexene (3 h).

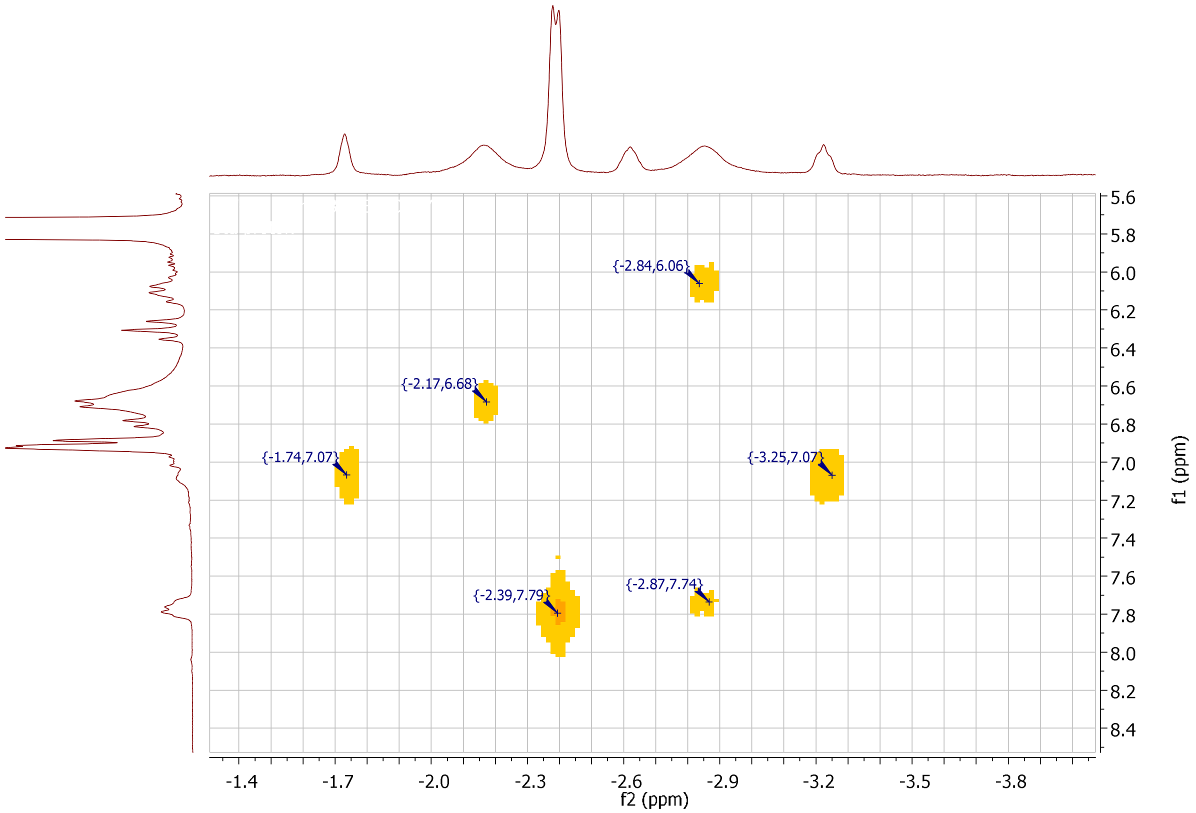




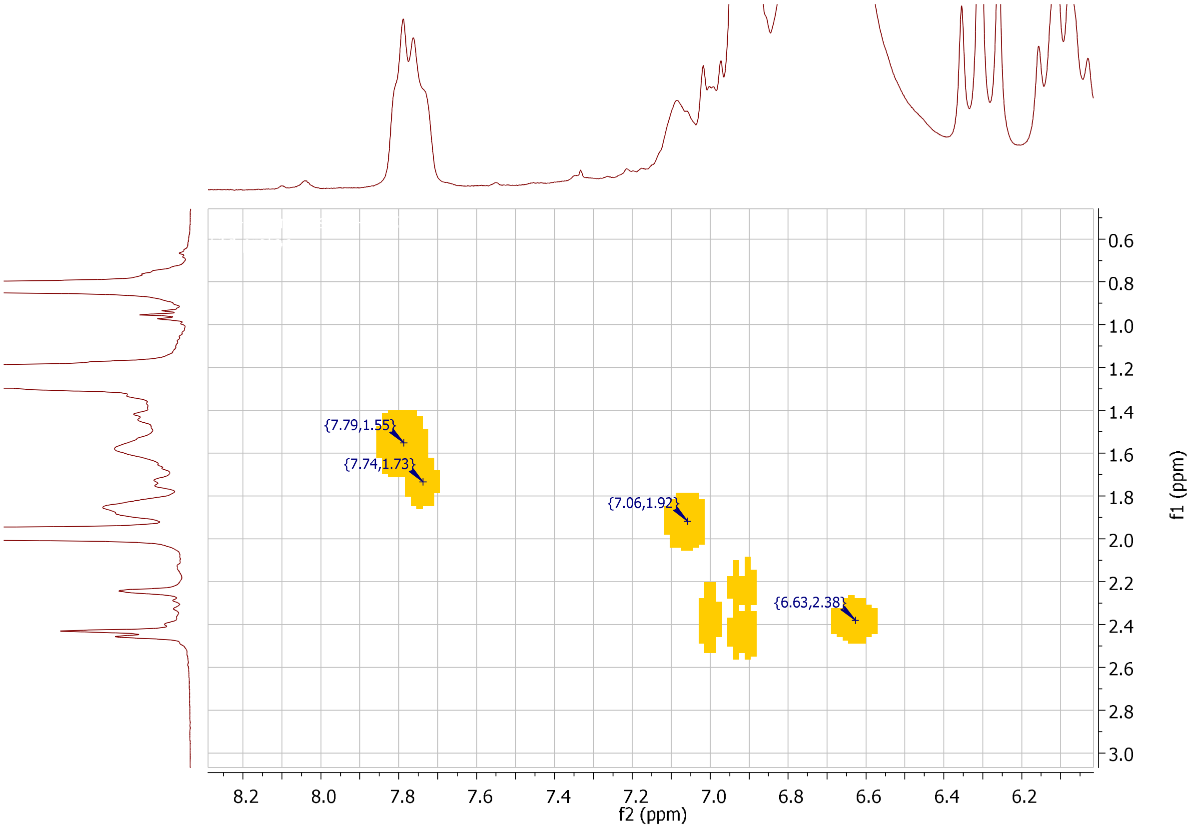
gCOSY (500 MHz, CD$_2$Cl$_2$, –87 ˚C) (after 3 h, full spectrum).



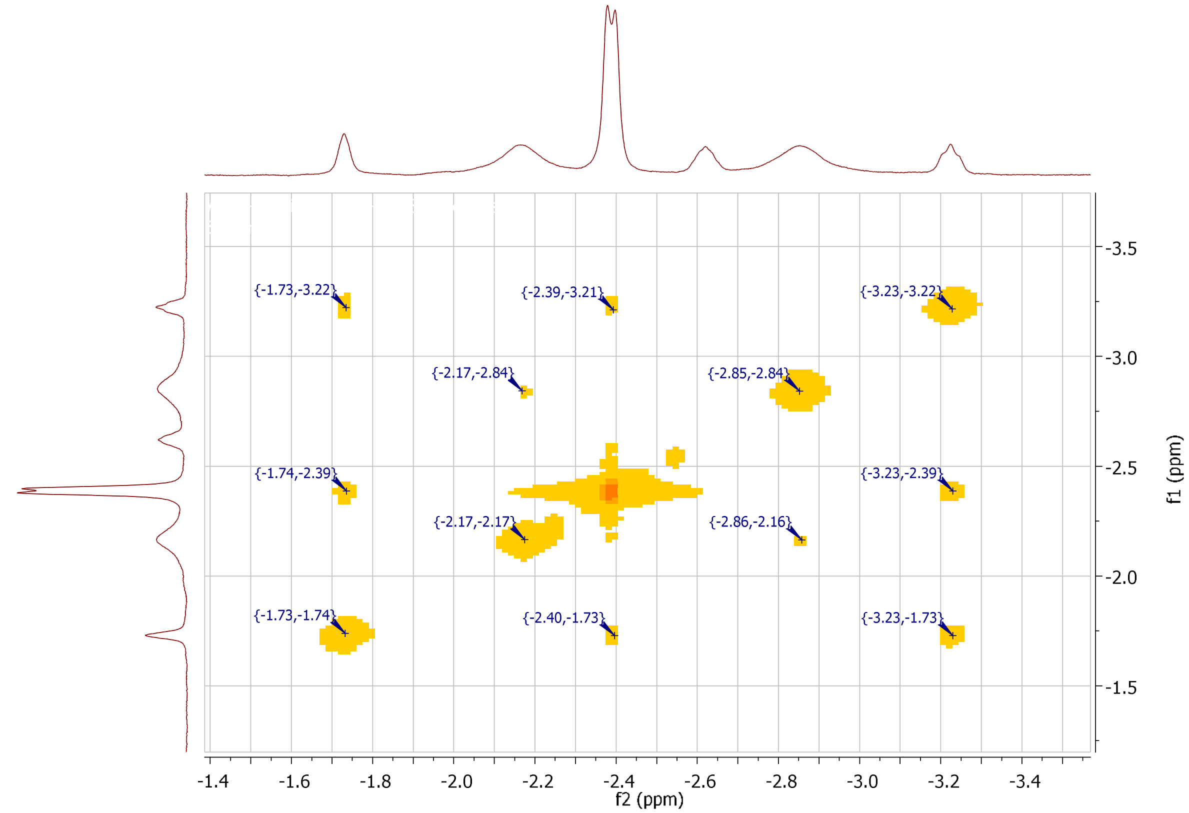
gCOSY (500 MHz, CD$_2$Cl$_2$, –87 ˚C) (after 3 h; f1 = δ 5.6 → 8.4 ppm, f2 = δ –1.4 → –4.1 ppm).



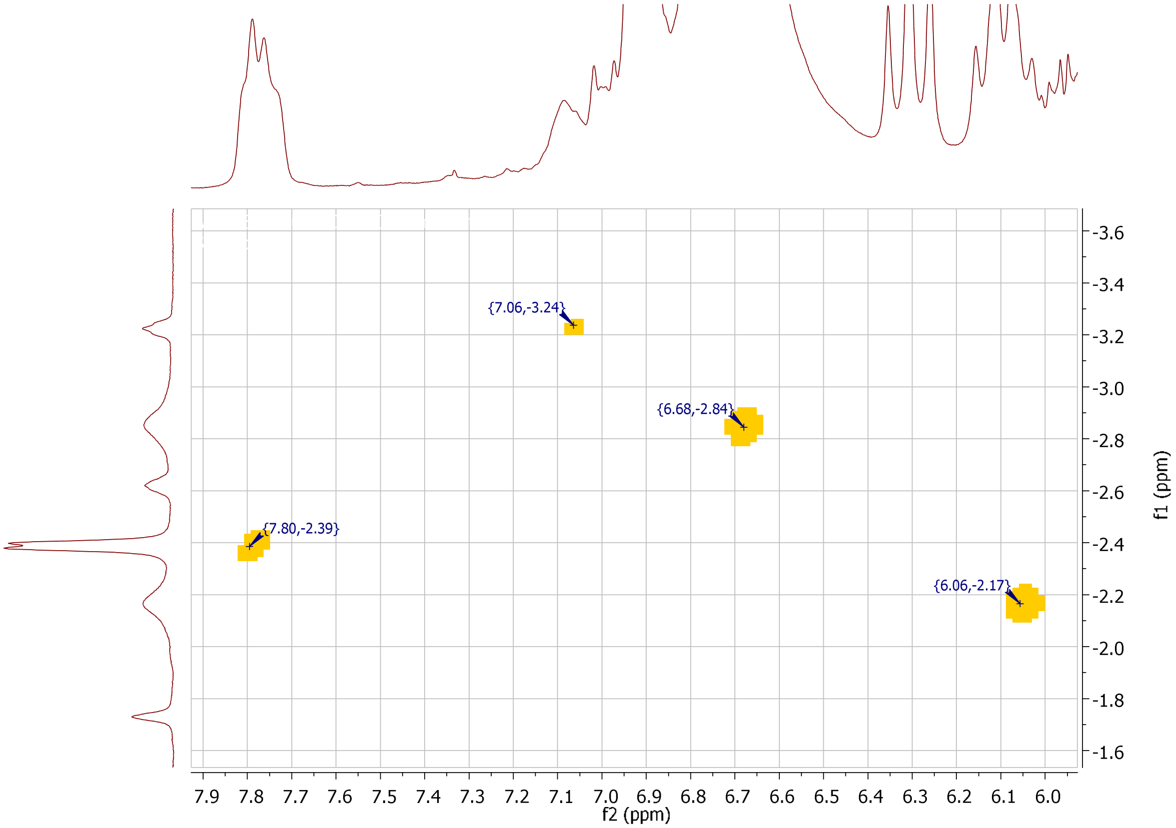
gCOSY (500 MHz, CD_2Cl_2, –87 ˚C) (after 3 h; f1 = δ 6.1 → 8.3 ppm, f2 = δ 0.6 → 3.0 ppm).



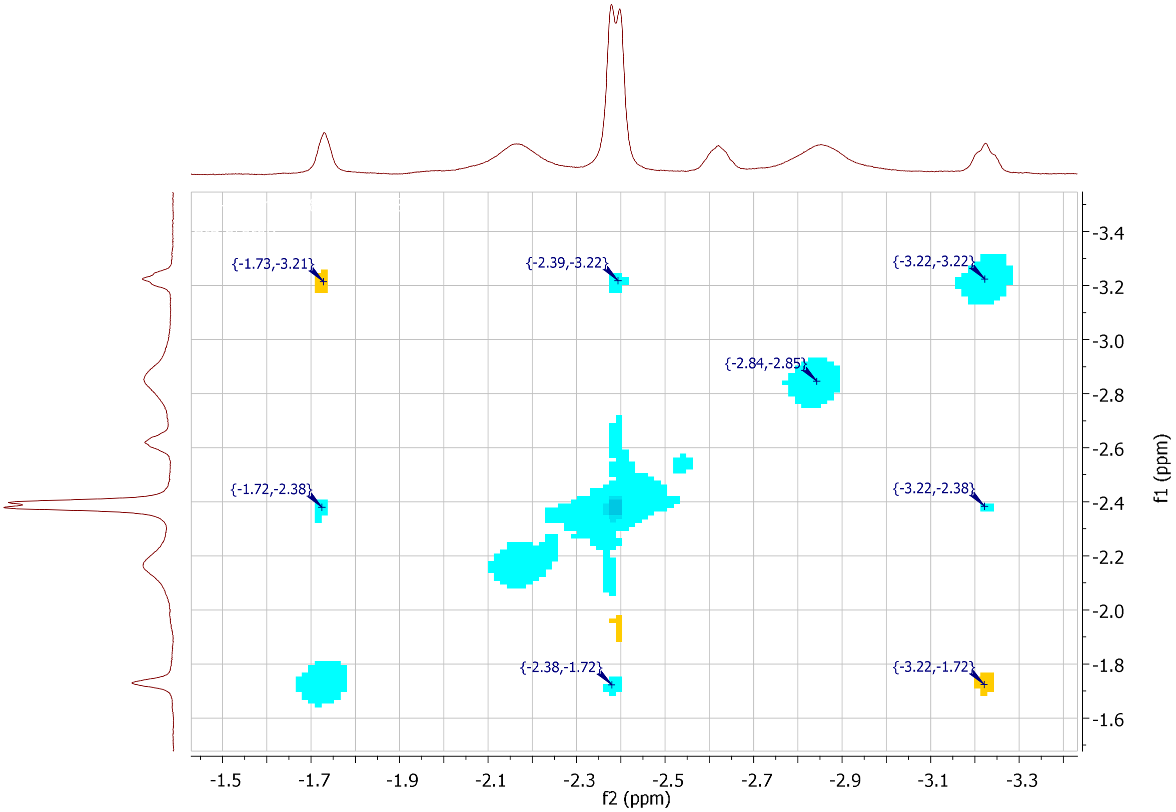
NOESY-2D (500 MHz, CD_2Cl_2, –87 ˚C; mix = 35 ms) (after 3 h; f1 = δ –1.25 → –3.75 ppm, f2 = –1.4 → –3.5).



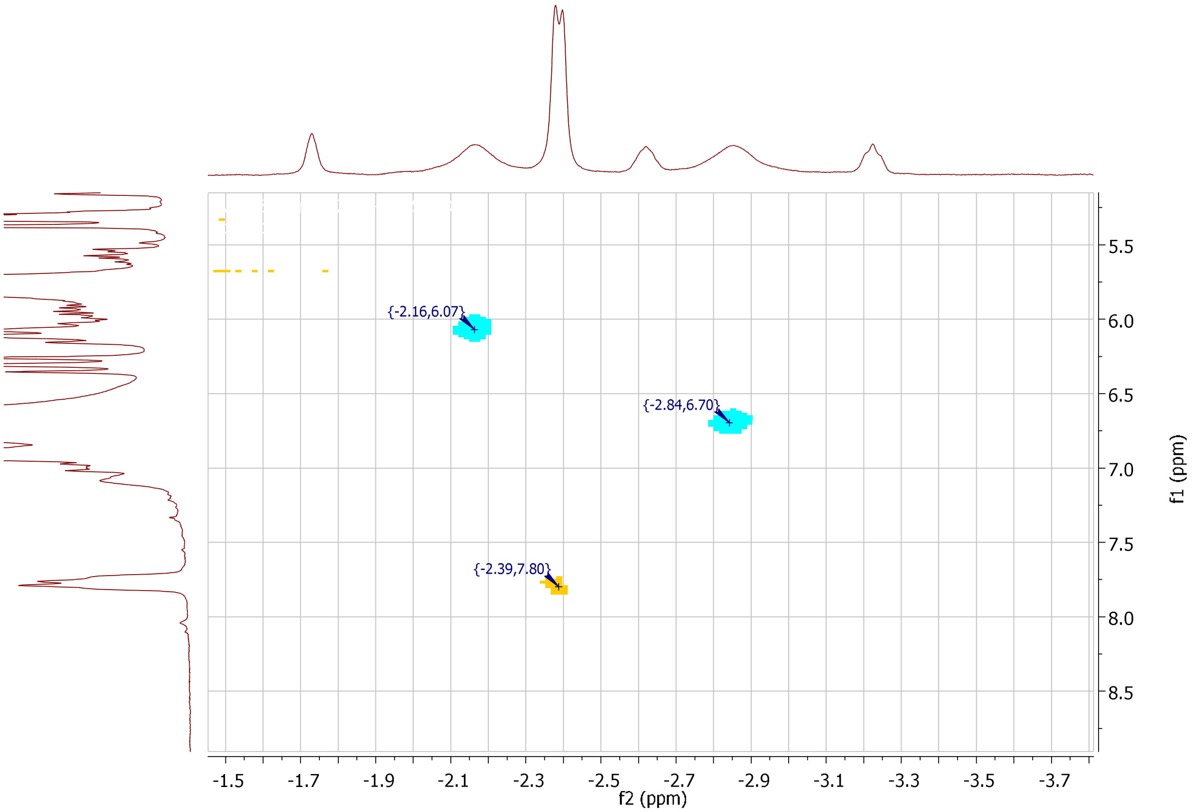
NOESY-2D (500 MHz, CD_2Cl_2, –87 ˚C; mix = 35 ms) (after 3 h; f1 = δ –1.6 → –3.75 ppm, f2 = –1.4 → –3.5).



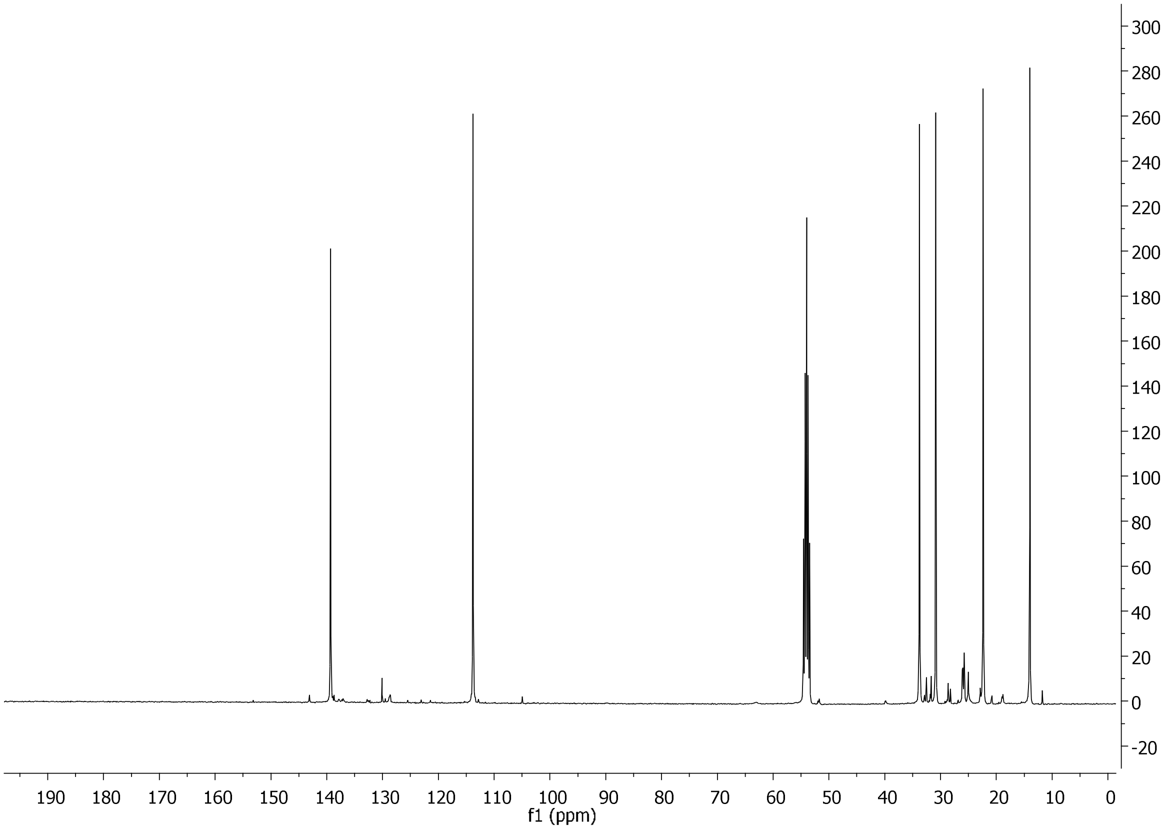
ROESY-2D (500 MHz, CD_2Cl_2, –87 ˚C; mix = 0.035 s) (after 3 h; f1 = –1.5 → –3.5, f2 = –1.45 → –3.4 ppm).



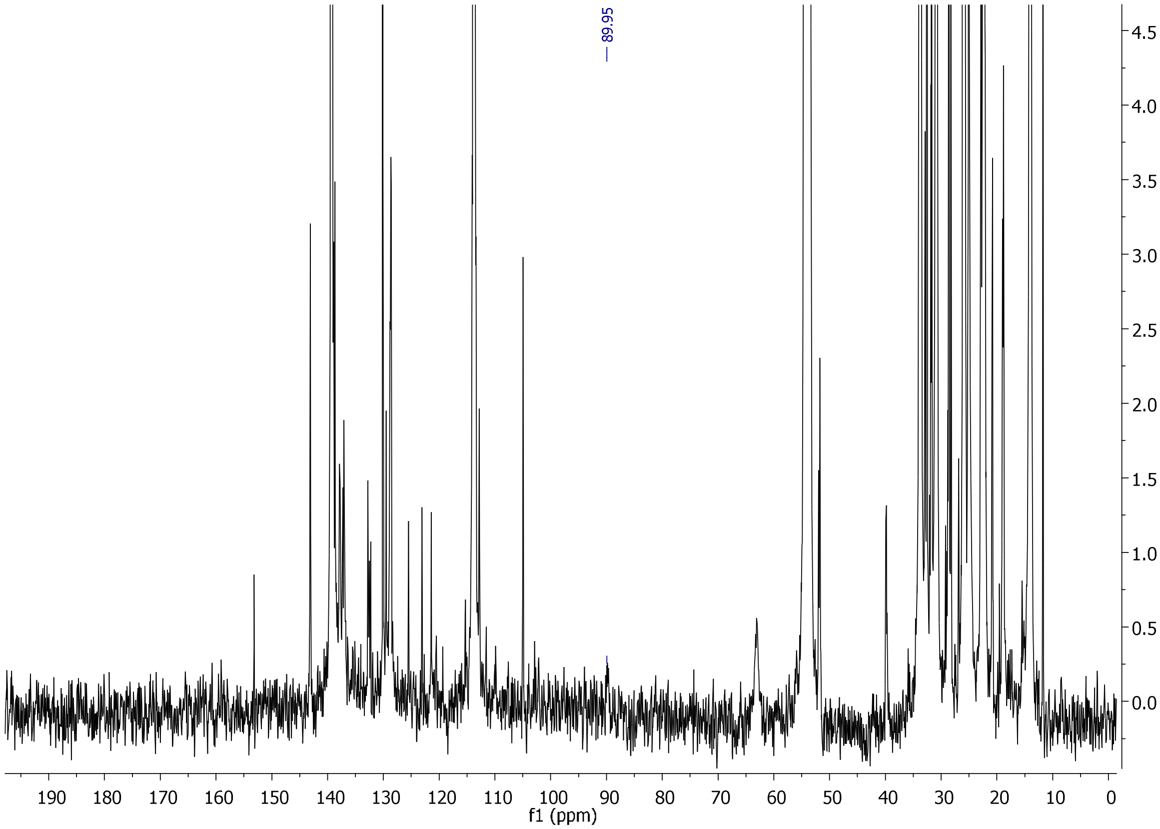
ROESY-2D (500 MHz, CD_2Cl_2, –87 ˚C; mix = 0.035 s) (after 3 h; f1 = 5.0 → 9.0, f2 = –1.5 → –3.8 ppm).



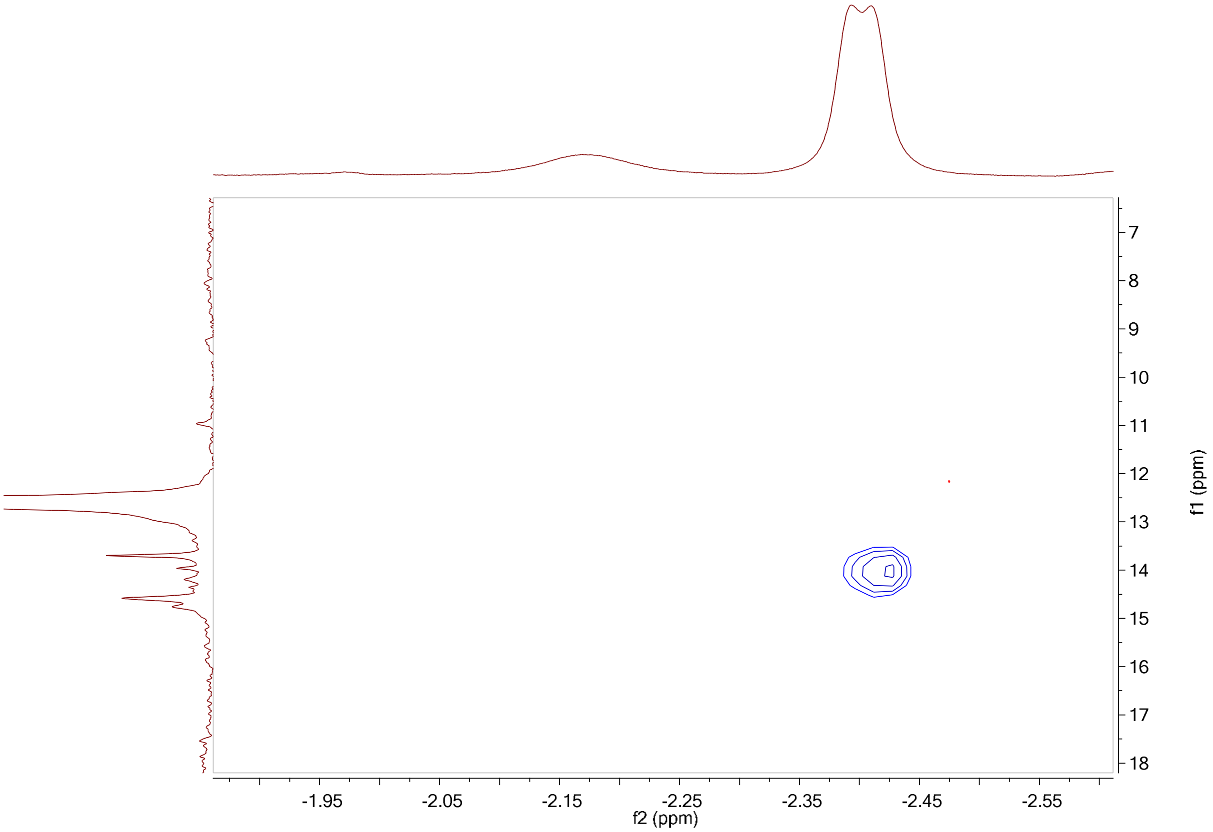
^{13}C NMR (100 MHz, CD_2Cl_2, –80 ˚C) (after 3 h; spectrum fit to height).



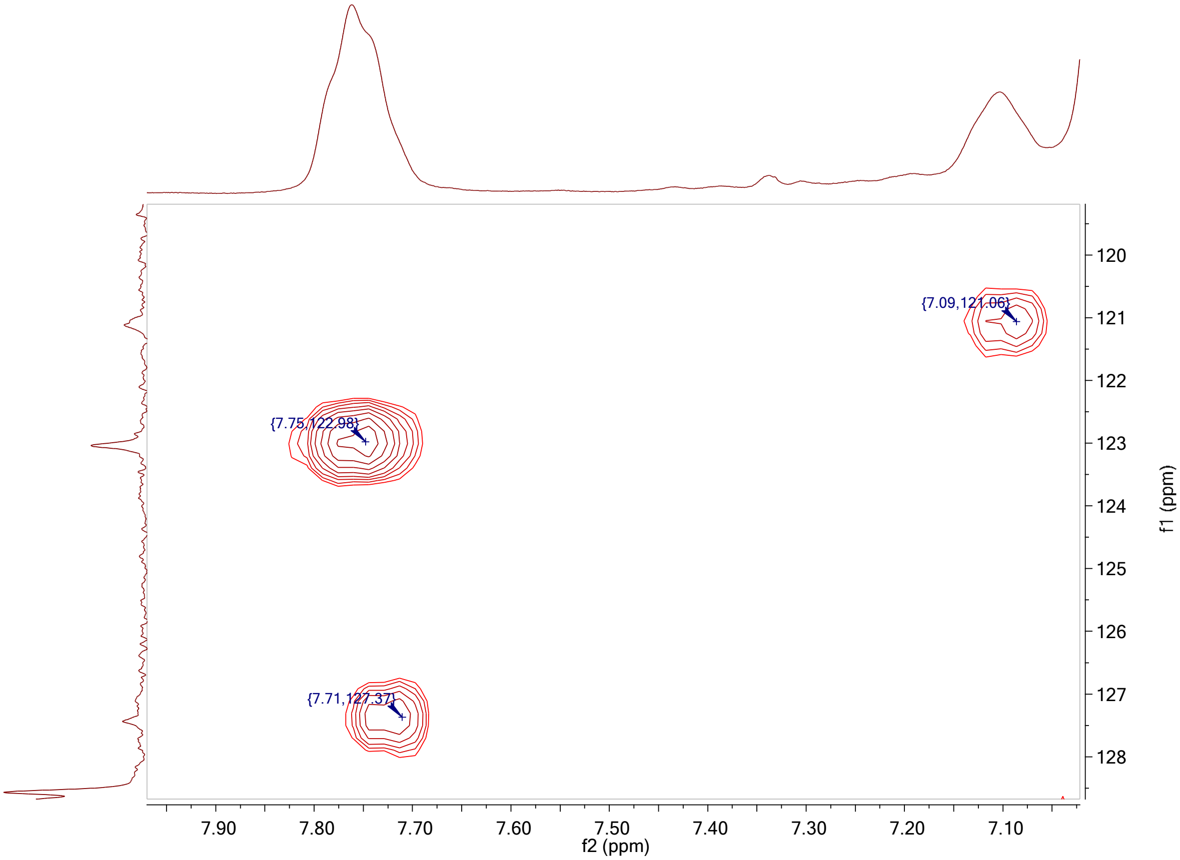
^{13}C NMR (100 MHz, CD_2Cl_2, –80 ˚C) (after 3 h; magnified view).



gHSQC (400 MHz, CD_2Cl_2, –80 ˚C) (after 3 h; zoomed f1 = 6.5→ 18.0, f2 = δ –1.9 → –2.60 ppm).

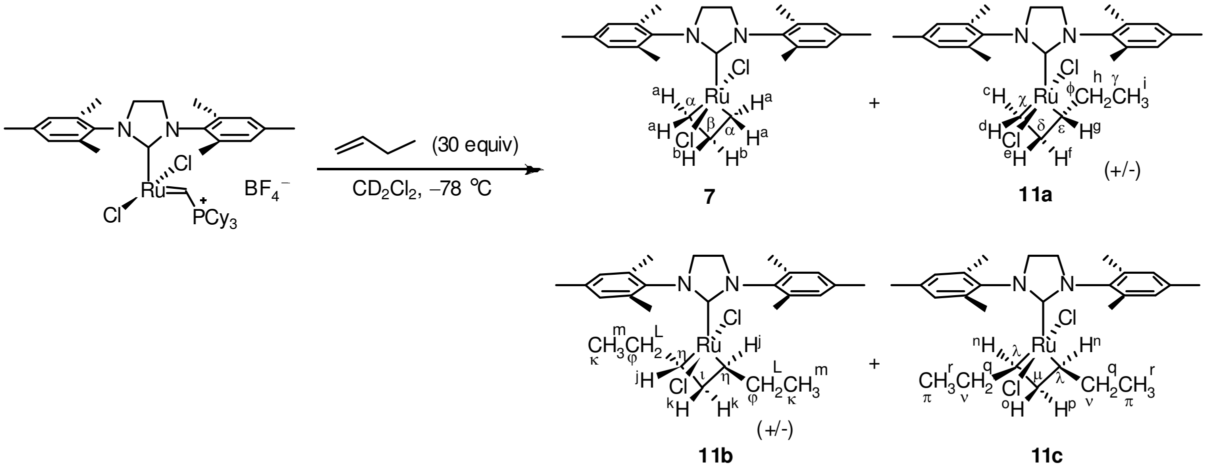


gHSQC (400 MHz, CD_2Cl_2, –80 ˚C) (after 3 h; zoomed f1 = 119→ 128.5, f2 = δ 7.95 → 7.05 ppm).



II.D. Dynamic NMR Behavior of Metallacycles in CD_2Cl_2 at –87 °C.

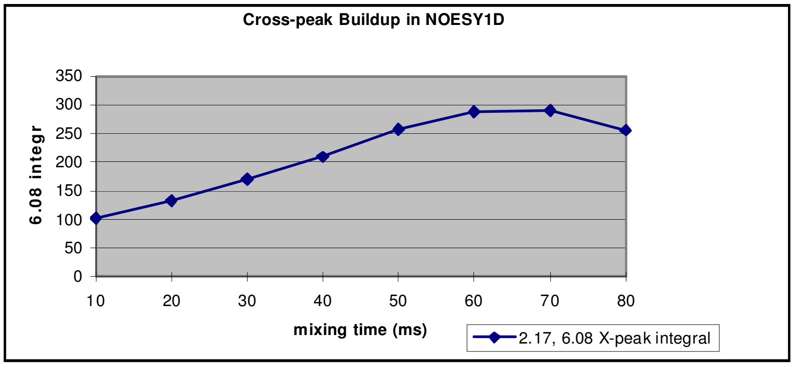
II.D.1. NOE Buildup Curves for Optimal Mixing Time Selection.



A plot of the peak volume at (–2.63 **H^a**, 6.60 **H^b**) relative to mixing time for ethylene-derived metallacycle **7** has previously been reported.[6] In this, the linear region of NOE buildup was found to lie in the region below 50 ms.[11] Additional NOE buildup curves were obtained to investigate methylene exchange in the monosubtituted metallacycle (e.g. **11a**) and *cis*/*trans* exchange (e.g. **11b** ⇆ **11c**) in the case of the disubstituted metallacycles. Representative plots are shown below:

Figure 1. NOE Buildup Curve for 2.17(H^f),6.08(H^d) Interaction in Metallacycle 11a.

Integral	mix time (ms)
102.505	10
132.682	20
170.154	30
209.164	40
258.248	50
287.895	60
289.706	70
255.995	80



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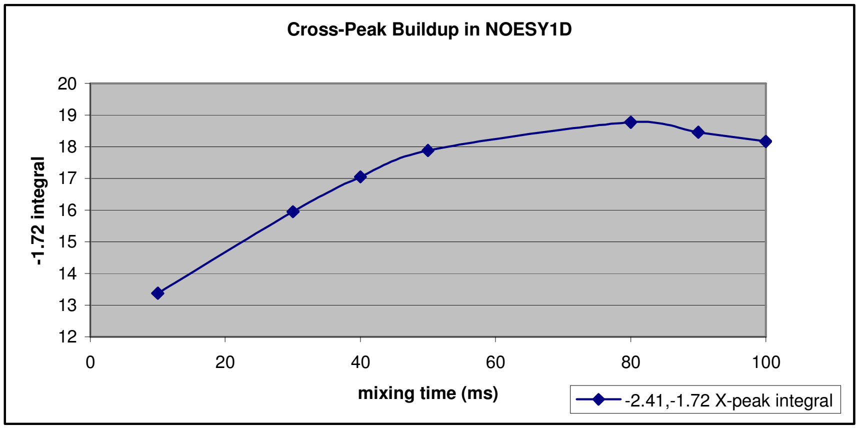
[11] Linear regions in plots of peak intensity vs. time are generally attributed to mixing times where spin diffusion is minimal. See: Neuhaus, D.; Williamson, M. P. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*, 2nd Ed.; Wiley-VCH: New York, 2000; Chapter 4.

Figure 2. NOE Buildup Curve for –2.41(H^k *trans*-Substituted Metallacycle C), –1.72(H^o, *cis*-Substituted Metallacycle 11c) Interaction.

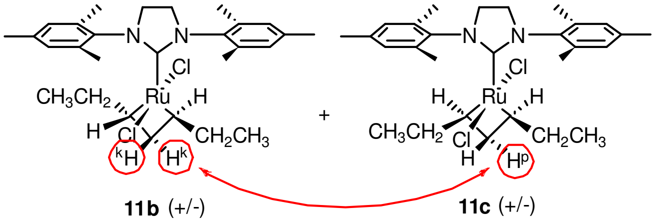
Integral	mix time (ms)
13.4	10
16.0	30
17.1	40
17.9	50
18.8	80
18.5	90
18.2	100



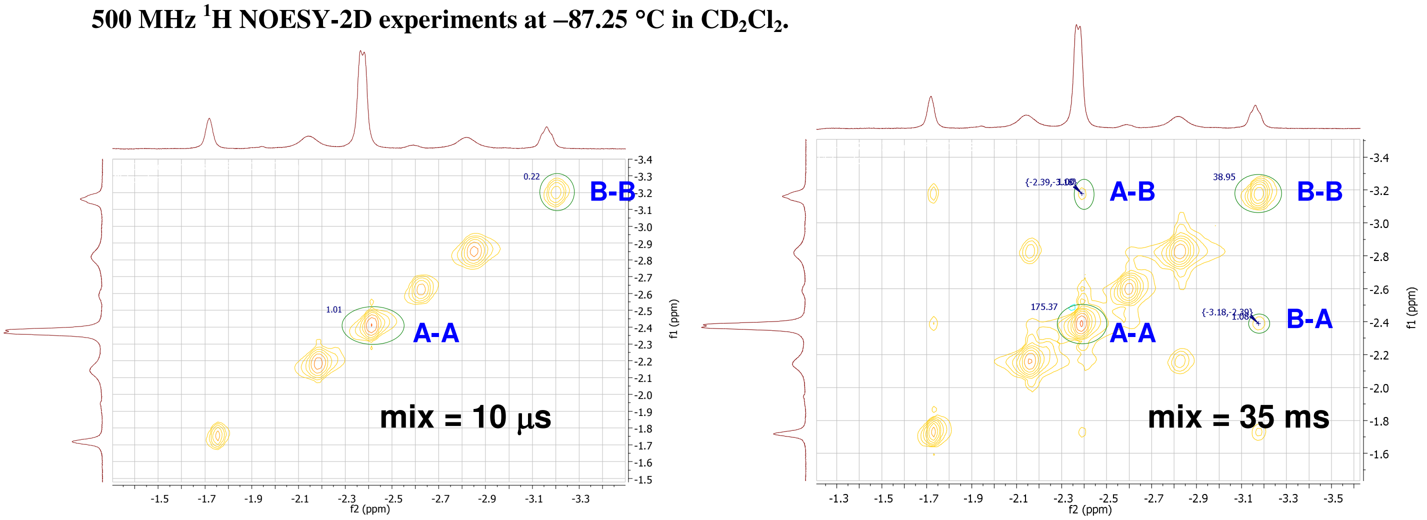
II.D.2. *EXSYCALC* Analysis of Exchange Cross-Peaks *(See ROESY-2D for Exchange Data)*. The dynamics of interconversion between the α- and β-positions of metallacycle **11a**, and the *cis*- and *trans*-stereoisomers **8**, **11**, and **12** were determined by quantifying the off-diagonal NOESY-2D exchange peaks in the region of minimal spin diffusion (20-50 ms). This technique is commonly referred to as EXSY, and is well-known.[12] Analysis of exchange experiments are reported below.

II.D.2.A. Exchange within 1-Butene-Derived Metallacycles.

II.D.2.A.1 Exchange Between the –2.41(H^k *trans*-Substituted Metallacycle 11b), –3.20(H^p, *cis*-Substituted Metallacycle 11c) Interaction.



500 MHz ^{1}H NOESY-2D experiments at –87.25 °C in CD$_2$Cl$_2$.



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[12] The *EXSYCALC* software package and instructions for crosspeak analysis can be obtained at: http://www.mestrelab.com.

mix = 10 □s

f2	f1	identity	volume
-2.41	-2.41	**A-A**	1.01
-3.20	-3.20	**B-B**	0.22

mix = 35 ms

f2	f1	identity	volume
-2.41	-2.41	**A-A**	175.37
-2.41	-3.20	**A-B**	1.00
-3.20	-3.20	**B-B**	38.95
-3.20	-2.40	**B-A**	1.08

Peak volumes were entered into *EXSYCALC* to afford the following rate constants:

temp	mixing time	$k_{trans \rightarrow cis}$ (s^{-1})	$k_{cis \rightarrow trans}$ (s^{-1})
187.24 K	35 ms	0.17 ± 0.01	0.74 ± 0.06

The constants were then input into the following expression to provide an estimate of the Gibbs free energy of activation ($\Delta G^{\neq}$) at –87.25 °C (185.75 K):

$$\Delta G^{\neq} = RT[\ln(k_B/h) - \ln(k/T)]$$

$h = 6.626075 \times 10^{-34}$ J·s

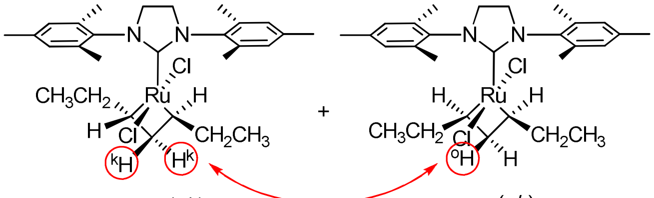
$k_B = 1.380658 \times 10^{-23}$ J/K

$R = 1.987 \times 10^{-3}$ kcal·K^{-1}·mol^{-1}

T = 185.75 K

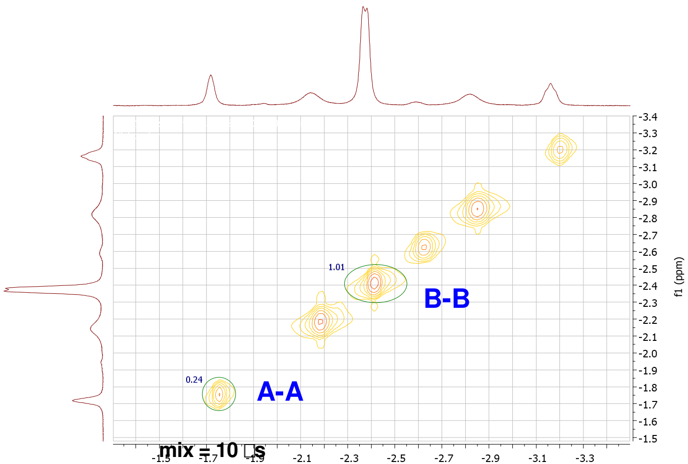
	kcal mol^{-1}
$\Delta G^{\neq}_{trans \rightarrow cis}$	11.35 ± 0.03
$\Delta G^{\neq}_{cis \rightarrow trans}$	10.81 ± 0.03

II.D.2.A.2 Exchange Between the –2.41(H^k *trans*-Substituted Metallacycle 11b), –1.72 (H^o, *cis*-Substituted Metallacycle 11c) Interaction.



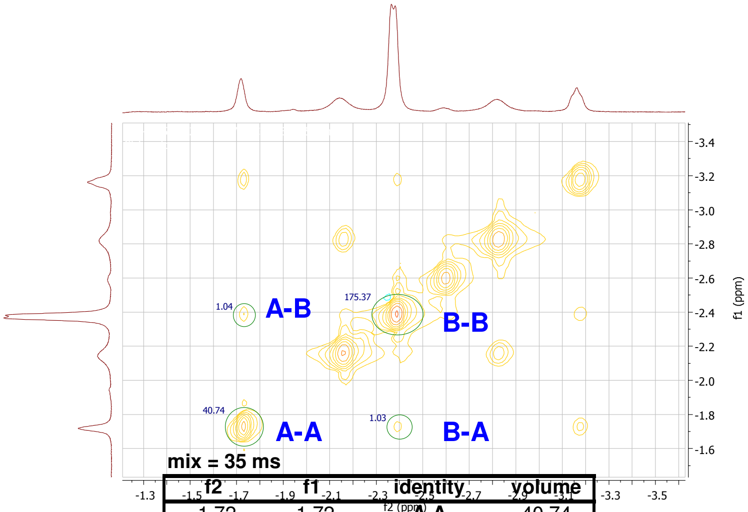
11b (+/-) **11c** (+/-)

500 MHz ^{1}H NOESY-2D experiments at –87.25 °C in CD_2Cl_2.



mix = 10 □s

f2	f1	identity	volume
-1.72	-1.72	A-A	0.24
-2.41	-2.41	B-B	1.01



mix = 35 ms

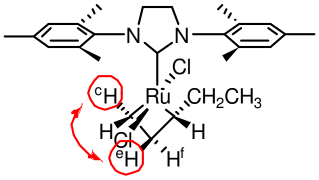
f2	f1	identity	volume
-1.72	-1.72	A-A	40.74
-1.72	-2.41	A-B	1.04
-2.41	-2.41	B-B	175.37
-2.41	-1.72	B-A	1.03

Peak volumes were entered into *EXSYCALC* to afford the following values:

temp	mixing time	$k_{cis\rightarrow trans}$	$k_{trans\rightarrow cis}$
185.75 K	35 ms	0.71 ± 0.06 s^{-1}	0.17 ± 0.01 s^{-1}

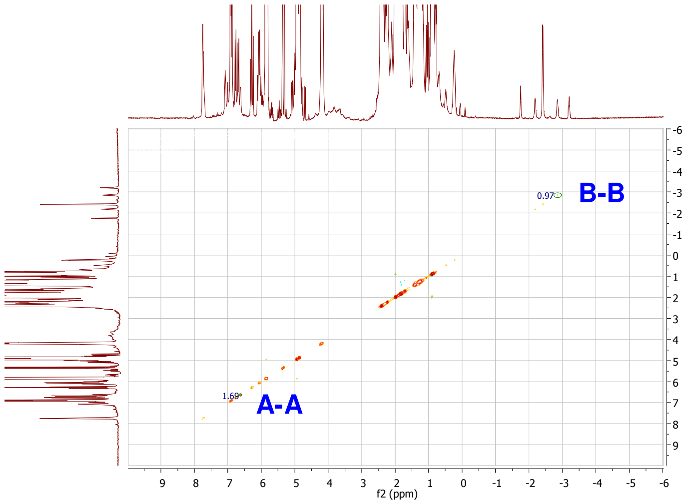
	kcal mol^{-1}
$\Delta G^{\neq}_{cis\rightarrow trans}$	10.82 ± 0.02
$\Delta G^{\neq}_{trans\rightarrow cis}$	11.35 ± 0.02

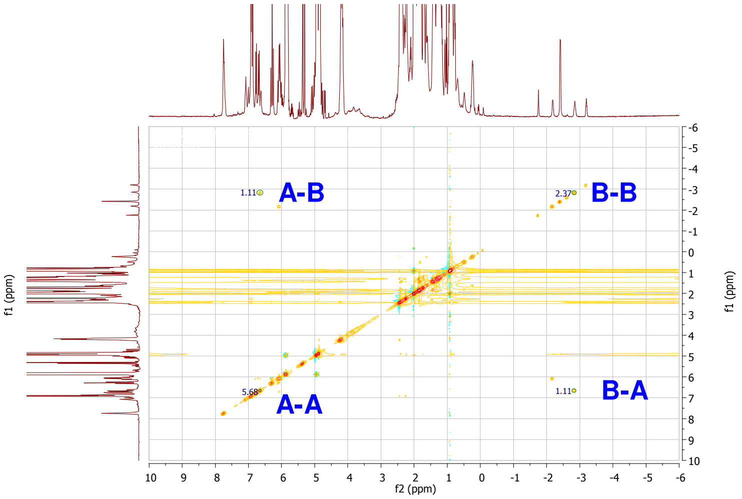
II.D.2.A.3 Exchange Between the –2.85 (H^e Metallacycle 11a), 6.64 (H^c Metallacycle 11a) Interaction.



11a

500 MHz ^1H NOESY-2D experiments at –87.25 °C in CD_2Cl_2





mix = 10 □s

f2	f1	identity	volume
6.64	6.64	**A-A**	1.69
-2.84	-2.84	**B-B**	0.97

mix = 35 ms

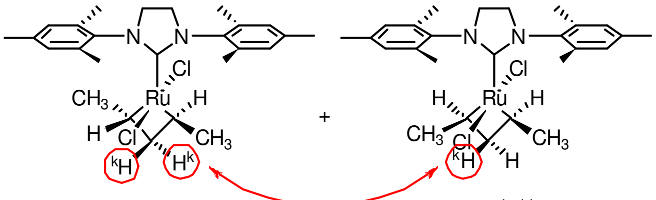
f2	f1	identity	volume
6.64	6.64	**A-A**	5.68
6.64	-2.85	**A-B**	1.11
-2.85	-2.85	**B-B**	2.37
-2.85	6.64	**B-A**	1.11

Peak volumes were entered into *EXSYCALC* to afford the following values:

temp	mixing time	$k_{\alpha\rightarrow\beta}$	$\Delta G^{\neq}_{\alpha\rightarrow\beta}$
185.75 K	35 ms	**6.7 ± 0.5 s^{-1}**	**9.99 ± 0.03 kcal mol^{-1}**

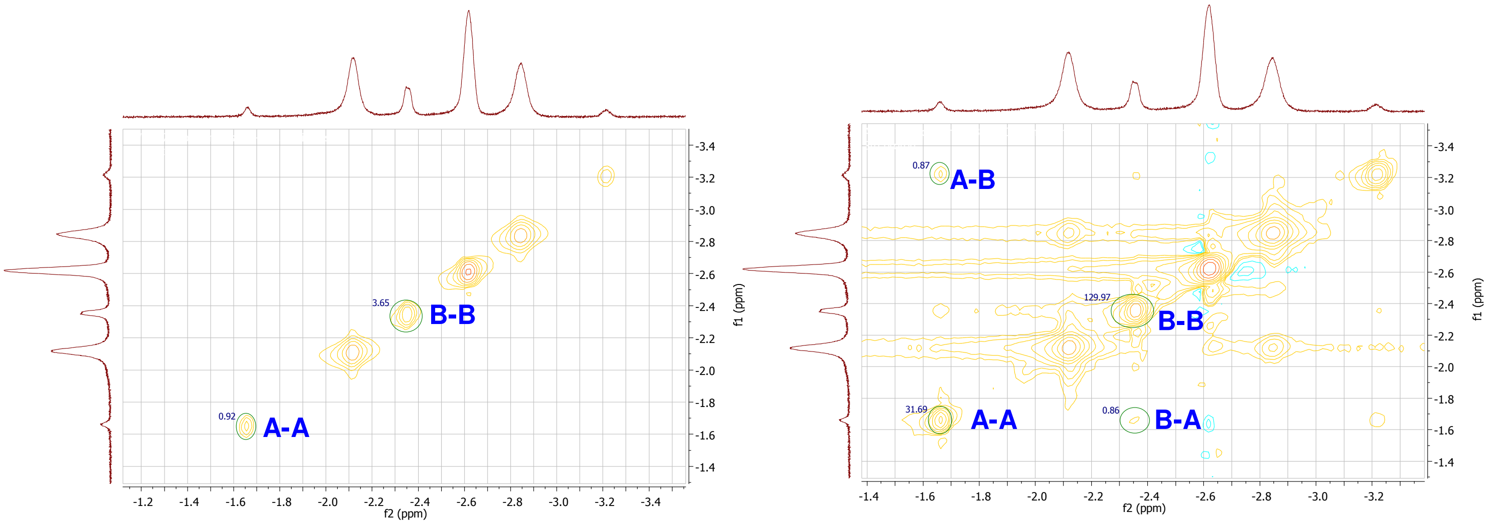
II.D.2.B. Exchange within Propene-Derived Metallacycles.

II.D.2.B.1. Exchange Between the –2.35 (H^i *trans*-Substituted Metallacycle 8b), –1.66 (H^k, *cis*-Substituted Metallacycle 8c) Interaction.



8b (+/-) **8c** (+/-)

500 MHz ^1H NOESY-2D experiments at –87.25 °C in CD_2Cl_2



mix = 10 μs

f2	f1	identity	volume
-1.66	-1.66	A-A	0.92
-2.35	-2.35	B-B	3.65

mix = 35 ms

f2	f1	identity	volume
-2.35	-2.35	A-A	31.69
-2.35	-3.21	A-B	0.87
-3.21	-3.21	B-B	129.97
-3.21	-2.35	B-A	0.86

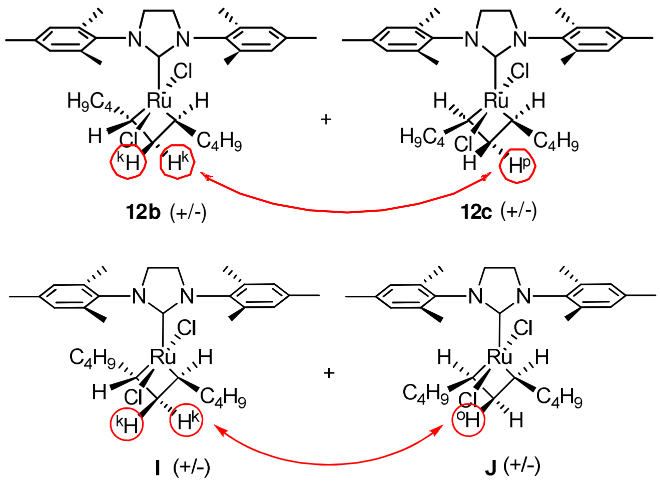
Peak volumes were entered into *EXSYCALC* to afford the following values:

temp	mixing time	$k_{cis \rightarrow trans}$ (s^{-1})	$k_{trans \rightarrow cis}$ (s^{-1})
185.75 K	35 ms	0.76 ± 0.06	0.19 ± 0.02

	kcal mol^{-1}
$\Delta G^{\neq}_{cis \rightarrow trans}$	10.80 ± 0.03
$\Delta G^{\neq}_{trans \rightarrow cis}$	11.31 ± 0.04

II.D.2.C. Exchange within 1-Hexene-Derived Metallacycles.

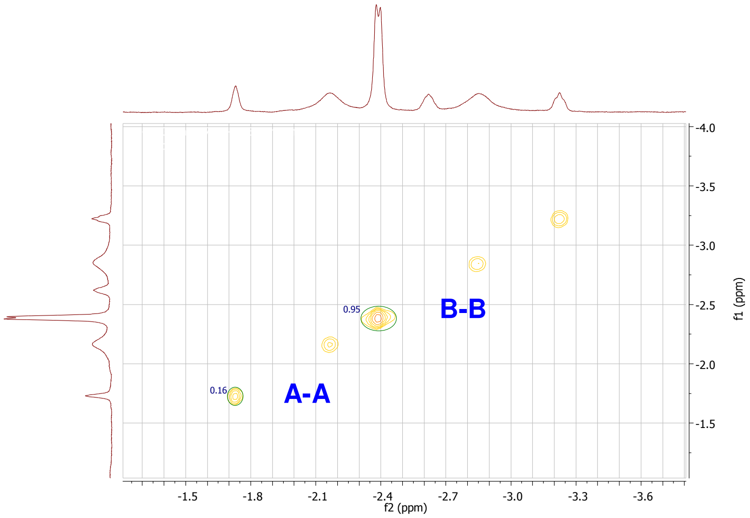
II.D.2.C.1 Exchange Between the –2.41 (H^k *trans*-Substituted Metallacycle 12b), –1.73 (H^o, *cis*-Substituted Metallacycle 12c) Interaction.



12b (+/-) **12c** (+/-)

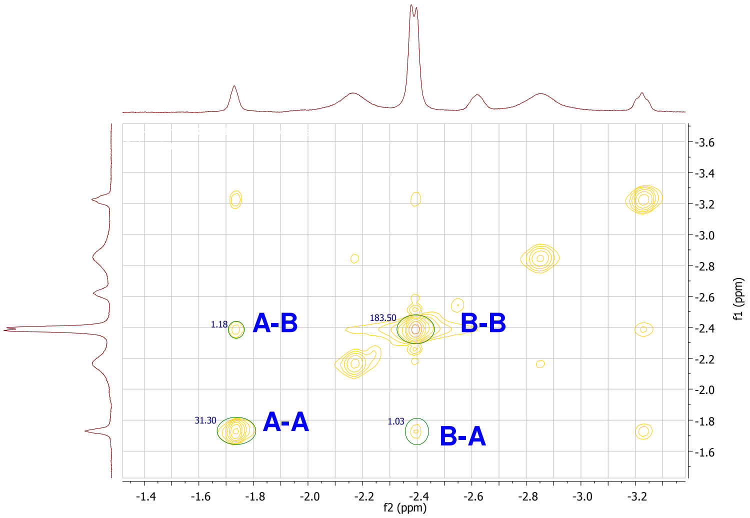
I (+/-) **J** (+/-)

500 MHz ^{1}H NOESY-2D experiments at –87.25 °C in CD_2Cl_2.



mix = 10 s

f2	f1	identity	volume
-1.73	-1.73	A-A	0.16
-2.39	-2.39	B-B	0.95



mix = 35 ms

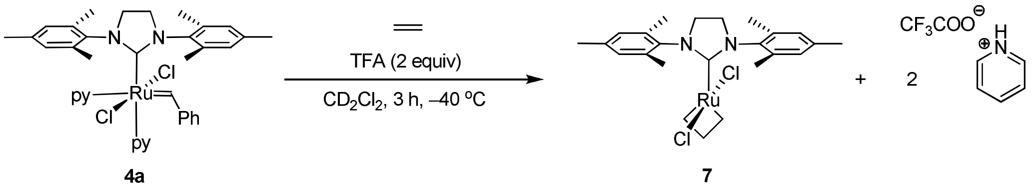
f2	f1	identity	volume
-1.73	-1.73	A-A	31.30
-1.73	-2.39	A-B	1.18
-2.39	-2.39	B-B	183.50
-1.73	-1.73	B-A	1.03

Peak volumes were entered into *EXSYCALC* to afford the following values:

temp	mixing time	$k_{cis\rightarrow trans}$ (s^{-1})	$k_{trans\rightarrow cis}$ (s^{-1})
185.75 K	35 ms	0.9 ± 0.1	0.18 ± 0.02

	kcal mol^{-1}
$\Delta G^{\neq}_{cis\rightarrow trans}$	10.7 ± 0.1
$\Delta G^{\neq}_{trans\rightarrow cis}$	11.33 ± 0.08

II.E. Reaction of $(IMesH_2)(C_5H_5N)_2Cl_2Ru{=}CH(Ph)$ (4a) with Trifluoroacetic Acid and Ethylene.

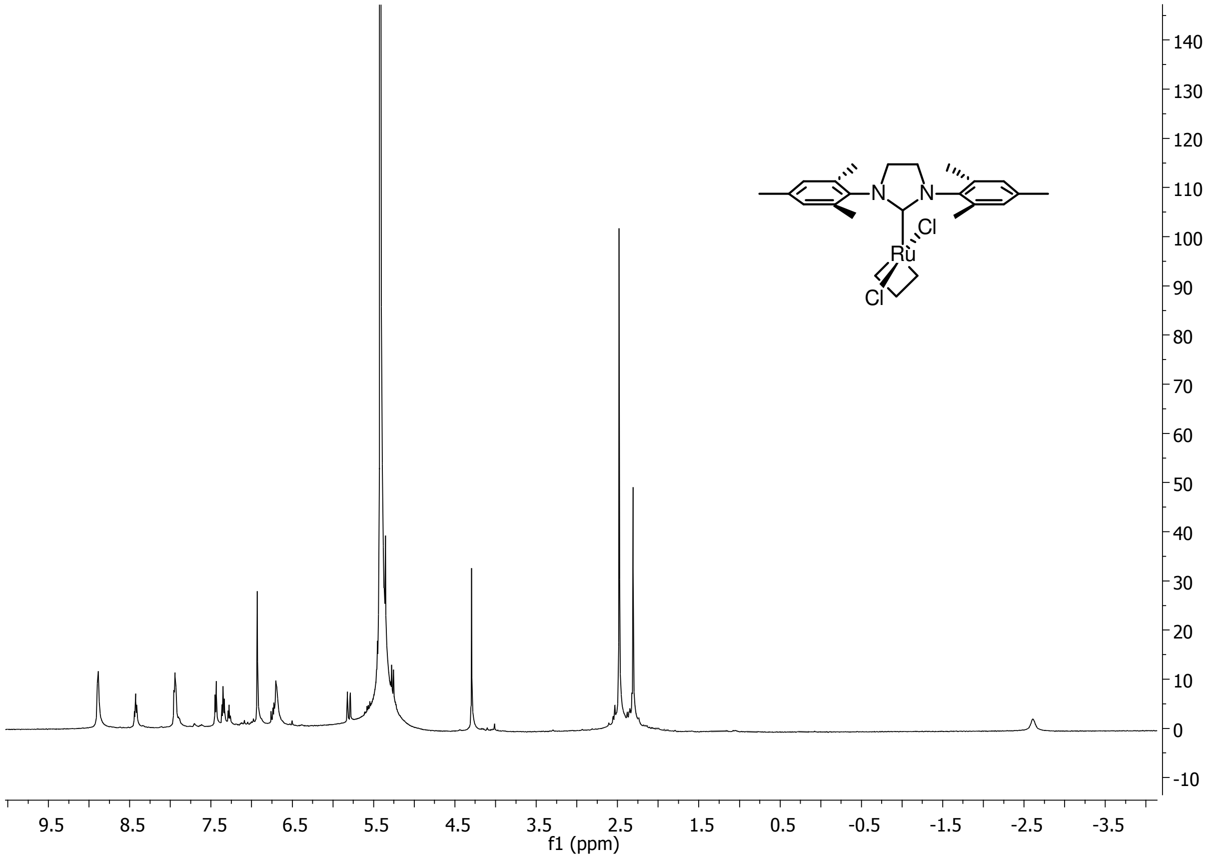


4a **7**

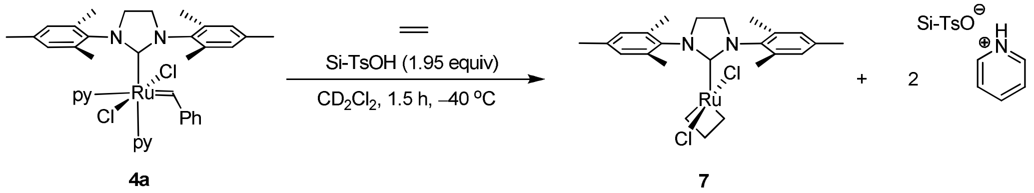
In the glovebox under an atmosphere of nitrogen: $(IMesH_2)(C_5H_5N)_2Cl_2Ru{=}CH(Ph)$ (30.1 mg, 0.042 mmol) and anthracene (internal standard; 5.0 mg, 0.028 mmol, 0.67 equiv) were dissolved in anhydrous CD_2Cl_2 (1.5 mL). A 500-µL portion of this solution, corresponding to 0.014 mmol of $(IMesH_2)(C_5H_5N)_2Cl_2Ru{=}CH(Ph)$ and 0.009 mmol of anthracene, was placed into a 5-mL conical flask equipped with a stirbar. The flask was capped with a rubber septum, and the contents were mixed. An additional 500-µL portion of the aforementioned solution was added to a NMR tube to serve as a t_0 timepoint. Both the flask and the NMR tube were removed from the glovebox. The flask was initially connected to a Schlenk line equipped with argon and cooled, with stirring, to –78 °C using a dry ice/isopropyl alcohol cold bath. After 5 minutes, the flask was evacuated under high-vacuum (50 mTorr) and backfilled with an atmosphere of ethylene. The dry ice/isopropyl alcohol cold bath was then exchanged for a dry ice/acetonitrile bath chilled to –40 °C. A positive pressure of ethylene was maintained throughout the experiment via tubing connections to an ethylene tank equipped with a mineral oil-filled bubbler.

To a separate, flame-dried, 5-mL flask under an atmosphere of argon, trifluoroacetic acid (TFA; 4.2 µL, 0.057 mmol) was dissolved in anhydrous CD_2Cl_2 (1.0 mL). A 500-µL portion of this solution, corresponding to 0.028 mmol trifluoroacetic acid (2.0 equiv relative to $(IMesH_2)(C_5H_5N)_2Cl_2Ru{=}CH(Ph)$) was placed into a 1-mL syringe equipped with a needle and attached to a syringe pump. This TFA solution was then slowly added (0.17 mL/h) to the $(IMesH_2)(C_5H_5N)_2Cl_2Ru{=}CH(Ph)$ solution at –40 °C. During this time, a green to purple-red color change was observed. Upon complete addition, an aliquot of the reaction solution (~700 µL) was rapidly transferred via a small-gauge cannula to a Teflon-capped, screw-top NMR tube at –78 °C under an atmosphere of argon. The reaction sample was then analyzed via VT-NMR at –40 °C. The desired ethylene-derived metallacycle **7** was observed in 83% yield. No visible decomposition was observed over an additional 3-hour time period at this temperature. NMR analytical data for the ruthenium metallacycle was found to match that reported in the literature.[5,6] The proton spectrum shown below corresponds to the above reaction conducted in the absence of the anthracene internal standard. Excess ethylene (~17 equiv), styrene from the $(IMesH_2)(C_5H_5N)_2Cl_2Ru{=}CH(Ph)$, and pyridinium trifluoroacetate were additionally present.
Note: the commercially-available Dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine)ruthenium(II) **4b**, when substituted for **4a**, afforded equivalent results in this reaction.

^{1}H-NMR spectrum (500 MHz, –40 °C) of metallacycle derived from ethylene, TFA, and bispyridyl catalyst.



II.F. Reaction of (IMesH$_2$)(C$_5$H$_5$N)$_2$Cl$_2$Ru=CH(Ph) (4a) with Si-Toluenesulfonic Acid and Ethylene.



In the glovebox under an atmosphere of nitrogen: (IMesH$_2$)(C$_5$H$_5$N)$_2$Cl$_2$Ru=CH(Ph) (15.5 mg, 0.021 mmol, 1.0 equiv) was added to a 10-mL conical vial equipped with a stirbar and dissolved in anhydrous CD$_2$Cl$_2$ (1.5 mL). The flask was capped with a rubber septum and removed from the glovebox. The flask was connected to a Schlenk line equipped with argon and cooled, with stirring, to −78 °C using a dry ice/isopropyl alcohol cold bath. After 5 minutes, the flask was evacuated under high-vacuum (50 mTorr) and backfilled with an atmosphere of ethylene. SiliaBond® toluenesulfonic acid[13] (Si-TsOH; 62 mg, 0.67 mmol/g, 0.042 mmol) was then added in one portion under a positive pressure of ethylene. The flask was re-sealed and transferred to a dry ice/acetonitrile bath chilled to –40 °C. The reaction was stirred at –40 °C for 1.5 h; a positive pressure of ethylene was maintained throughout the experiment via a tubing connection to an

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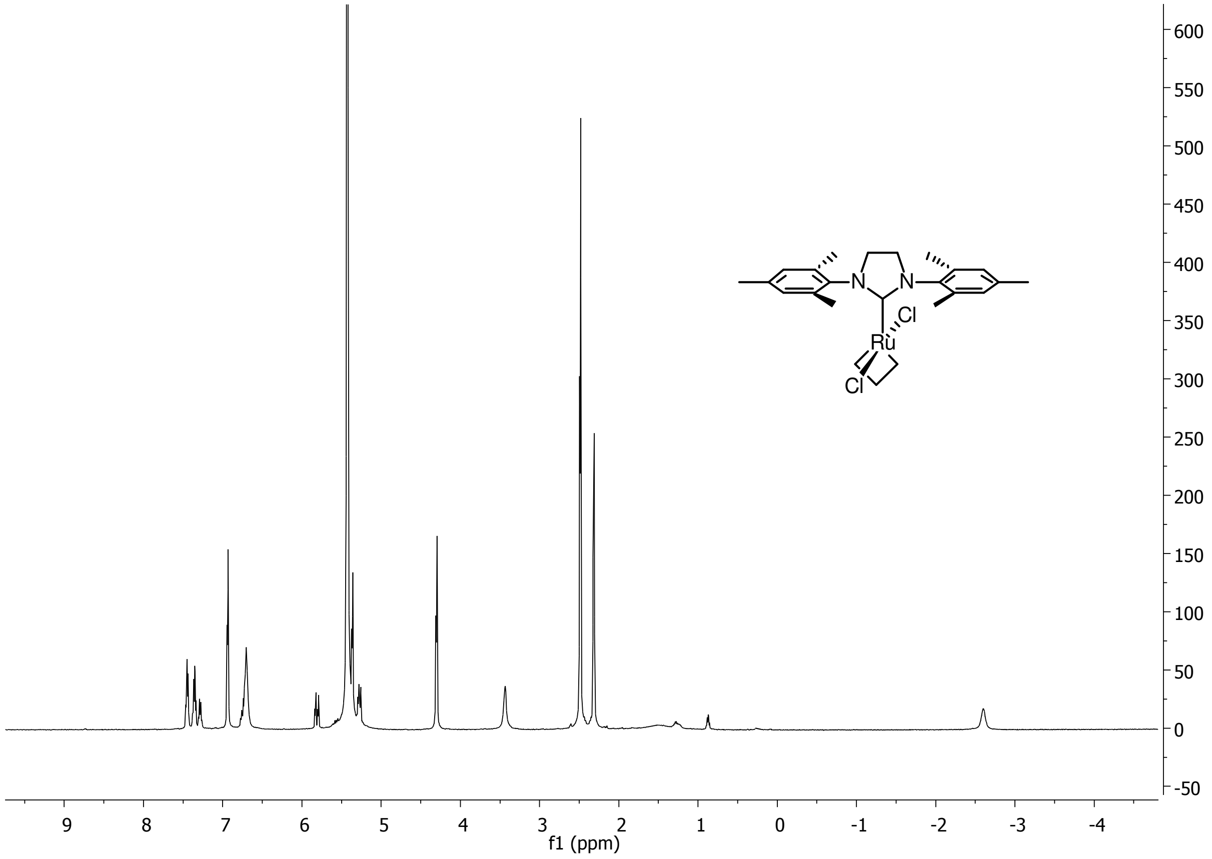
[13] The SiliaBond® toluenesulfonic acid used in this experiment was purchased from Silicycle: www.silicycle.com; item R60530B-10G. This material was generously donated from Norac Pharma, Azusa, California, USA.

ethylene tank equipped with a mineral oil-filled bubbler. During this time period, a green to purple-red color change was observed. Upon reaction completion, the stirring was stopped, and the solids present were allowed to settle. An aliquot of the reaction solution (~700 µL) was then rapidly transferred via a small-gauge cannula to a Teflon-capped, screw-top NMR tube at –78 °C under an atmosphere of argon. The reaction sample was then analyzed via VT-NMR at –40 °C. Complete conversion to the desired ethylene-derived metallacycle **7** was observed. No visible decomposition was observed over an additional 8-hour time period at this temperature. NMR analytical data for the ruthenium metallacycle was found to match that reported in the literature.[4] A ^{1}H-NMR spectrum (500 MHz, –40 °C) of this reaction is shown below. Excess ethylene (~16 equiv) and styrene from the (IMesH$_2$)(C$_5$H$_5$N)$_2$Cl$_2$Ru=CH(Ph) are additionally present. The broad singlet at δ 3.43 ppm corresponds to residual SiliaBond® silica (Si-O**H**) present in the reaction mixture.

Note: the commercially-available Dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine)ruthenium(II) **4b**, when substituted for **4a**, afforded equivalent results in this reaction.

^{1}H-NMR spectrum (500 MHz, –40 °C) of metallacycle derived from ethylene, Si-TsOH, and bispyridyl catalyst.

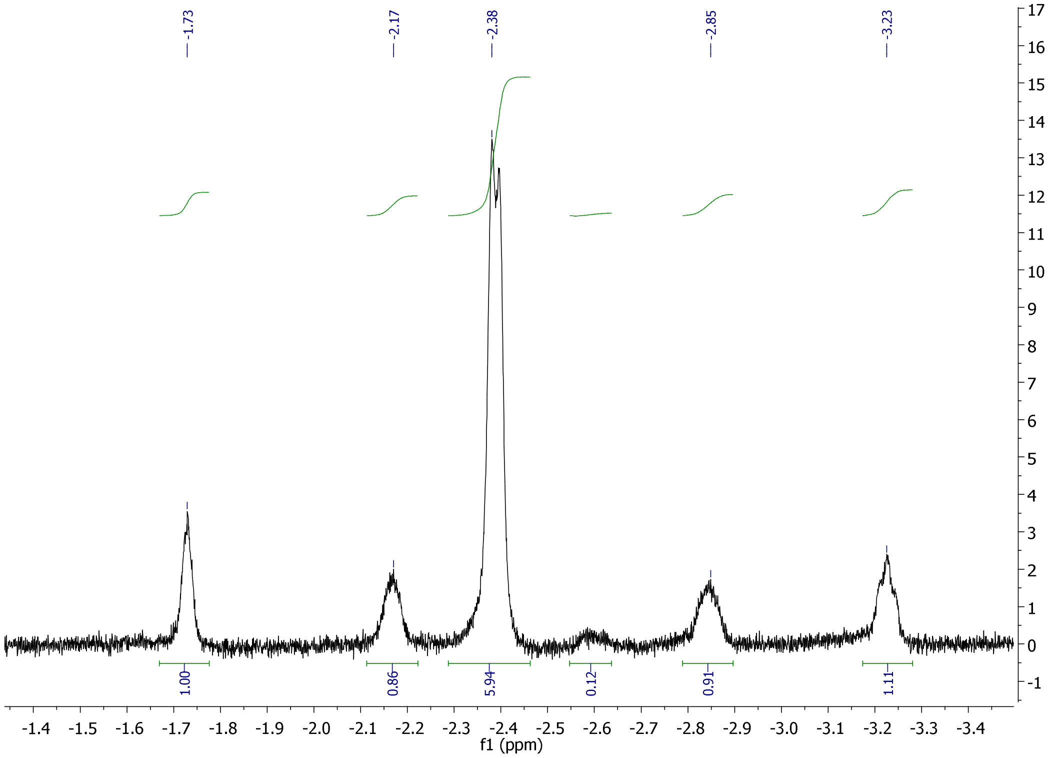


II.G. Reaction of (IMesH$_2$)(C$_5$H$_5$N)$_2$Cl$_2$Ru=CH(Ph) (4a) with TFA and 1-Hexene.

To a screw-top NMR tube in the glovebox, (IMesH$_2$)(C$_5$H$_5$N)$_2$Cl$_2$Ru=CH(Ph) (15.2 mg, 0.021 mmol, 1.0 equiv) and CD$_2$Cl$_2$ (600 μL) were added. The tube was sealed, shaken to mix the contents, and removed from the glovebox. The NMR tube was attached to an argon line via a needle inlet and placed in a cold bath chilled to −78 °C (dry ice/isopropyl alcohol). After 5 minutes, 1-hexene (79 μL, 0.63 mmol, 30 equiv) was added in one portion via syringe. The argon inlet was removed, and the NMR tube was shaken to mix the contents. The argon inlet was re-inserted, and trifluoroacetic acid (3.0 μL, 0.040 mmol, 1.9 equiv) was added in one portion via syringe. The argon line was again removed from the NMR tube, and the tube's cap and septum were wrapped with Teflon tape. The NMR tube was shaken to mix the contents. Reaction progress was monitored by VT-NMR at −80 °C. After 1 h, maximal yield of metallacycles (19%) was observed. ^{1}H-NMR analysis at −87 °C revealed four metallacycles: **7** (1%), **12a** (18%), **12b** (60%), and **12c** (21%). The ratio of 1-hexene:ethylene was determined to be > 99:1. NMR spectral data for metallacycles **7** and **12a-c** are reported above.

Note: the commercially-available Dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine)ruthenium(II) **4b**, when substituted for **4a**, afforded equivalent results in this reaction.

^{1}H-NMR spectrum (500 MHz, –87 °C) of metallacycles derived from the reaction of (IMesH$_2$)(C$_5$H$_5$N)$_2$Cl$_2$Ru=CH(Ph) with 1-hexene and TFA. (1 h, upfield region)



^{1}H-NMR spectrum (500 MHz, –87 °C) of metallacycles derived from the reaction of (IMesH$_2$)(C$_5$H$_5$N)$_2$Cl$_2$Ru=CH(Ph) with 1-hexene and TFA. (1 h, full spectrum)