Supporting Information

Synthesis of New Dirhodium(II) Complexes with Several Cyclometalated Thienylphosphines

Julio Lloret,[a] Francisco Estevan,[a] Pascual Lahuerta,[a] Pipsa Hirva,[b] Julia Pérez-Prieto,*[c] and Mercedes Sanaú[a]*

S4: Figure S1. Left: ORTEP for compound **5BB.CH_3CO_2H** with ellipsoids representing 30% of probability. Right: selected view of crystal packing for compound **5BB. CH_3CO_2H** (H atoms omitted for clarity). Selected bond distances (Å) and angles (º) are: Rh(1)-Rh(2), 2.4985(8); Rh(1)-P(1), 2.215(14); Rh(2)-C(1), 1.98(5); Rh(1)-O(1), 2.186(4); Rh(2)-O(2), 2.155(4); O(2)-O(4), 2.623(4); O(1)-O(5), 2.707(5); P(1)-Rh(1)-Rh(2), 90.11(4); Rh(1)-Rh(2)-C(1), 94.62(16).

S5: Figure S2. Left: ORTEP for compound **7A.CH_3CO_2H** with ellipsoids representing 30% of probability (H atoms omitted for clarity). Selected bond distances (Å) and angles (º): Rh(1)-Rh(2), 2.4361(12); Rh(1)-P(1), 2.212(3); Rh(2)-C(2), 1.988(9); Rh(1)-Oax, 2.396(8); Rh(2)-Oax, 2.2283(7); P(1)-Rh(1)-Rh(2), 91.60(8); Rh(1)-Rh(2)-C(2), 96.0(3).

Right: ORTEP for 2·CH_3COOH solvent molecules in the lattice of X-ray for compound **7A.CH_3CO_2H** with ellipsoids representing 30% of probability and H atoms omitted for clarity. Selected bond distances (Å) are: O(11)-O(13), 2.69(1); O(11)-C(27), 1.29(1); O(12)-C(27), 1.22(1).

S6: Figure S3. ORTEP for compound **10AA·$(py)_2$** with ellipsoids representing 30% of probability and H atoms omitted for clarity. Selected bond distances (Å) and angles (º) are: Rh(1)-Rh(2), 2.598(6); Rh(1)-P(1), 2.2151(16); Rh(2)-C(2), 1.980(6); Rh(2)-Nax, 2.268(5); P(1)-Rh(1)-Rh(2), 88.35(7); Rh(1)-Rh(2)-C(1), 95.1(3).

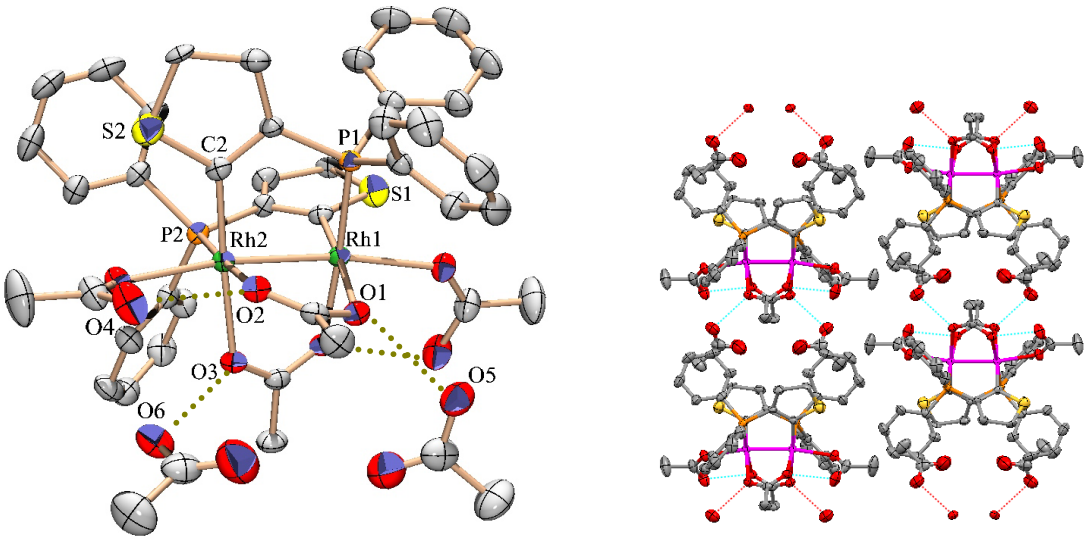
S7: Figure S4. Left: ORTEP for compound **11AA·py·$(H_2O)_{0.5}$** with ellipsoids representing 30% of probability. Right: bridging of two molecules of **11AA·py** by H_2O (H atoms omitted for clarity. Selected bond distances (Å) and angles (º) are: Rh(1)-Rh(2), 2.5268(7); Rh(1)-P(1), 2.2317(16); Rh(2)-C(1), 1.988(6); P(1)-Rh(1)-Rh(2), 88.44(7); Rh(1)-Rh(2)-C(1), 94.37(3).

S8: Figure S5. COSY NMR (400 MHz, CD_3CO_2D) of **7A**. Correlation between the protons within the thiophene ring (7.81(1H)-7.99(1H) ppm) and the protons within the phenyl rings (7.68(4H)-7.40(2H)-7.31(4H) ppm).

S9: Figure S6. HMBC ^{31}P-^{1}H NMR (400 MHz, CD_3CO_2D) of **7A**. Correlation between the phosphorous and the phenyl protons in *ortho*-position (at 7.68 ppm).

S10-S14: Evolution from 7A to 8 in CH_3CO_2H (CD_3CO_2D): Figure S7. Selected $^{31}P\{^{1}H\}$ NMR spectra of the evolution from **7A** to **8** in CH_3CO_2H. **Figure S8**. COSY NMR (400 MHz, CD_3CO_2D) spectrum from a 4:1 mixture of **7A**/**8.** The lines shows the ^{1}H-^{1}H correlation for compound **8**. **Figure S9.** Selected ^{1}H NMR spectra of the evolution

from **7A** to **8** in CD_3CO_2D at 70ºC. **Figure S10**. COSY NMR (400 MHz, CD_3CO_2D) spectrum from a mixture of **7A**/**8** after H/D interchange in CD_3CO_2D. The lines show ^1H-^1H correlations for compound **8**. The signal at 7.51 is missing due to a total H/D exchange. **Figure S11**. Evolution from **7A** to **8** at 70 ºC: a) in d4-acetic acid(◇), b) in acetic acid (○), c) in d4-acetic acid (△), but starting with a sample which had reached the equilibrium in acetic acid.



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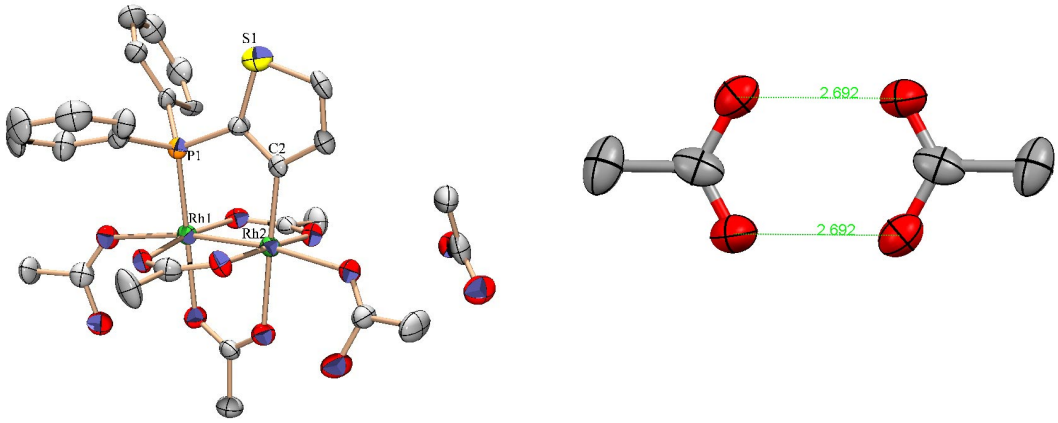

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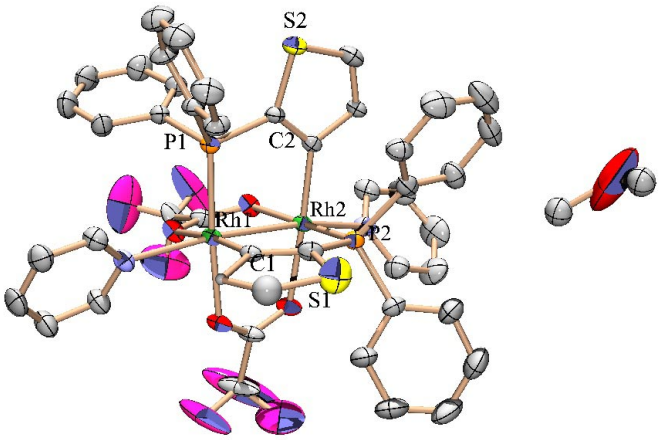

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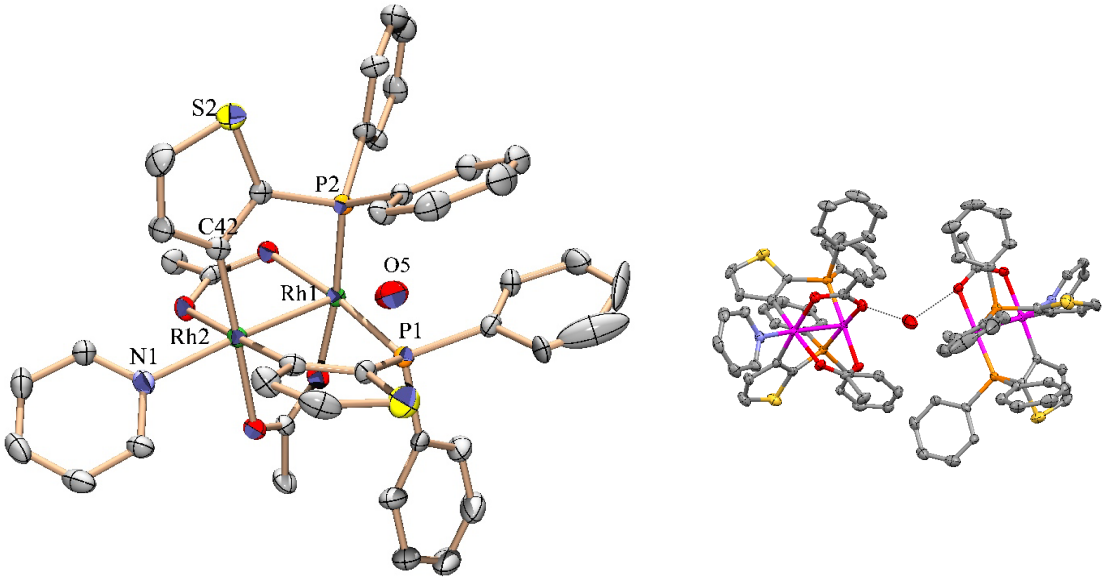

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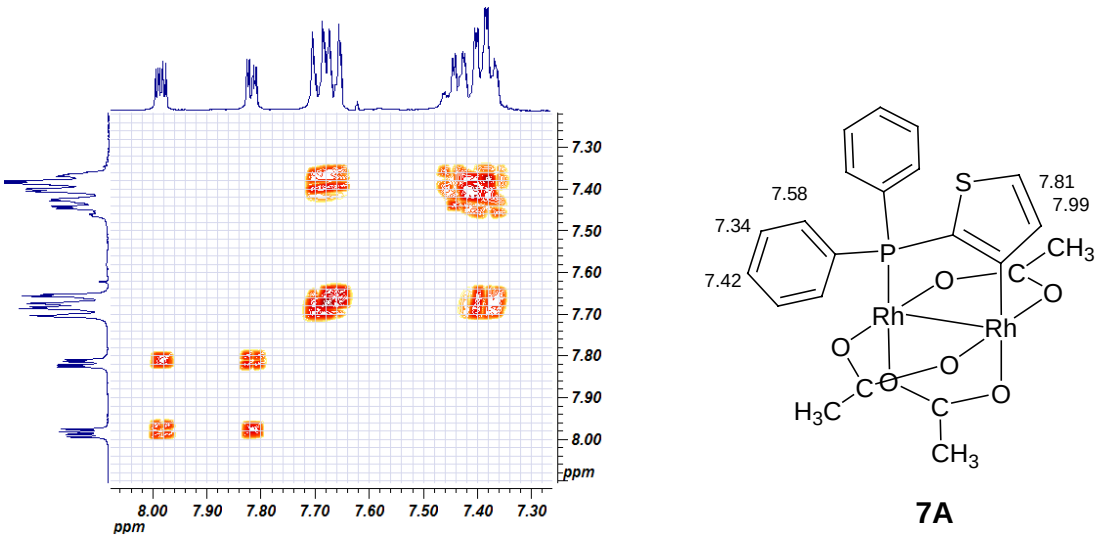
Characterization of the mono-cyclometalated compound 7A.

2D NMR, COSY and HMBC ^{31}P-^{1}H for compound **7A**.



7A

Figure S5. COSY NMR (400 MHz, CD_3CO_2D) of **7A**. Correlation between the protons within the thiophene ring (7.81(1H)-7.99(1H) ppm) and the protons within the phenyl rings (7.68(4H)-7.40(2H)-7.31(4H) ppm).

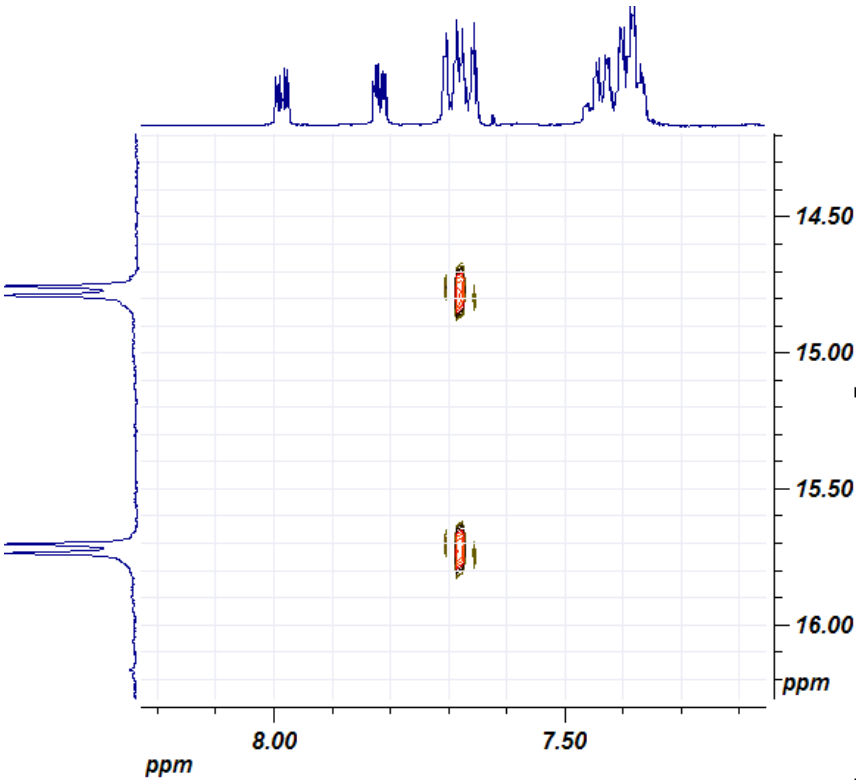


Figure S6. HMBC ^{31}P-^{1}H NMR (400 MHz, CD_3CO_2D) of **7A**. Correlation between the phosphorous and the phenyl protons in *ortho*-position (at 7.68 ppm).

Evolution from 7A to 8 in CH_3CO_2H (CD_3CO_2D)

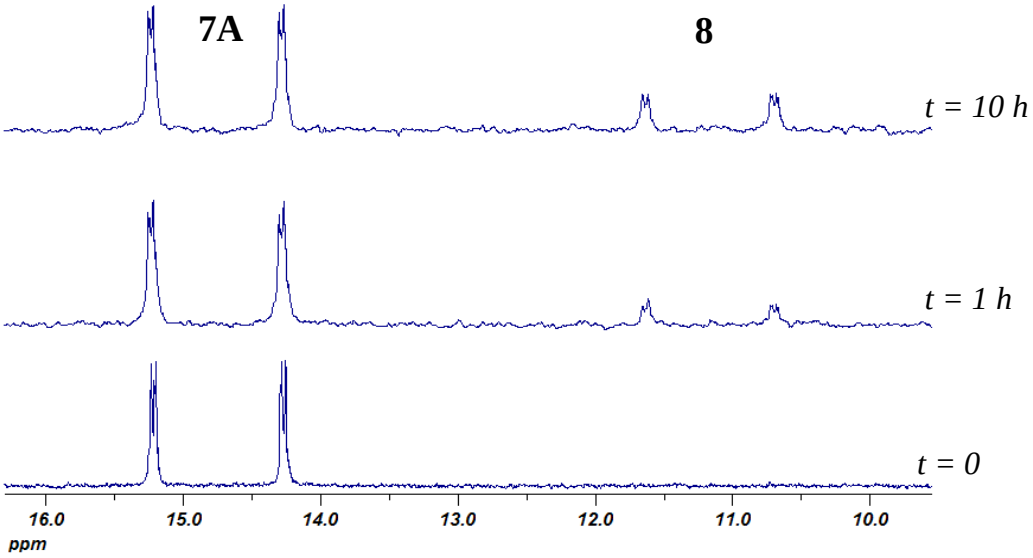
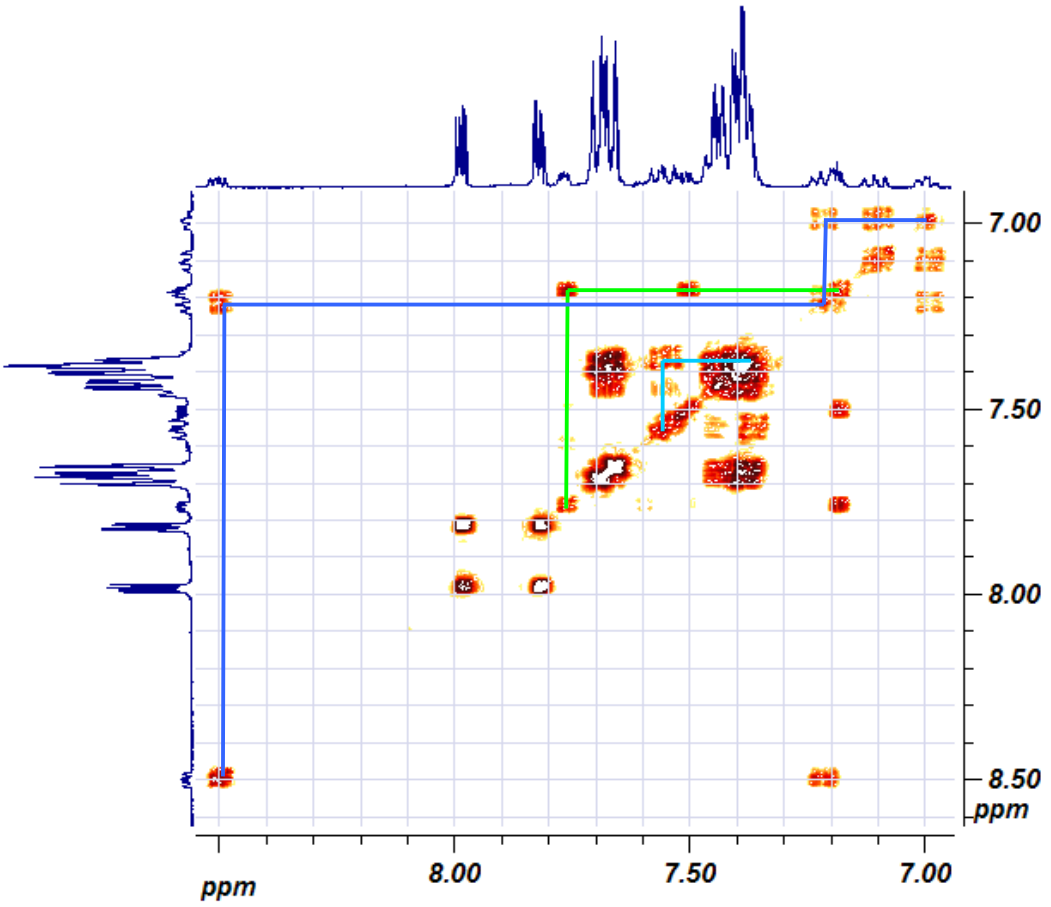


Figure S7. Selected $^{31}P\{^1H\}$ NMR spectra of the evolution from **7A** to **8** in CH_3CO_2H.



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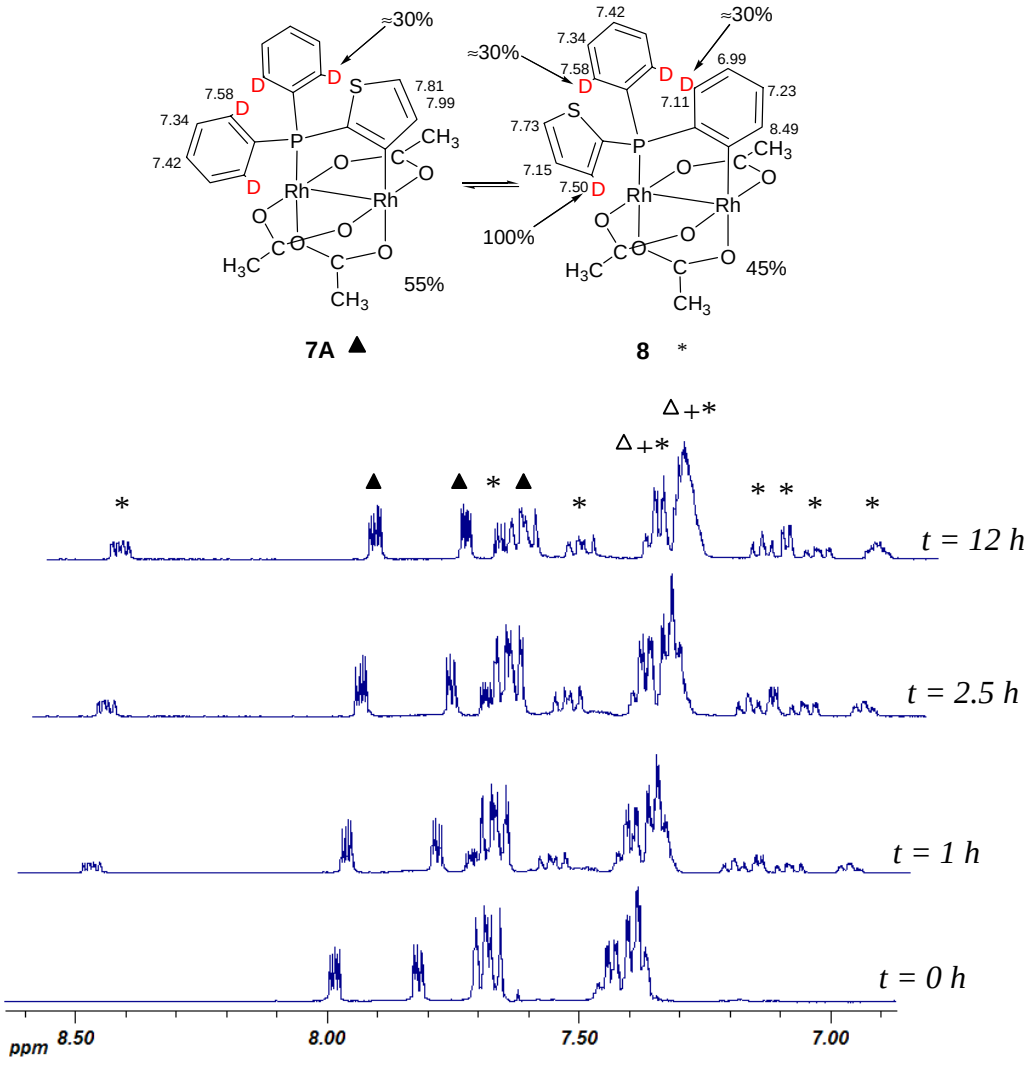
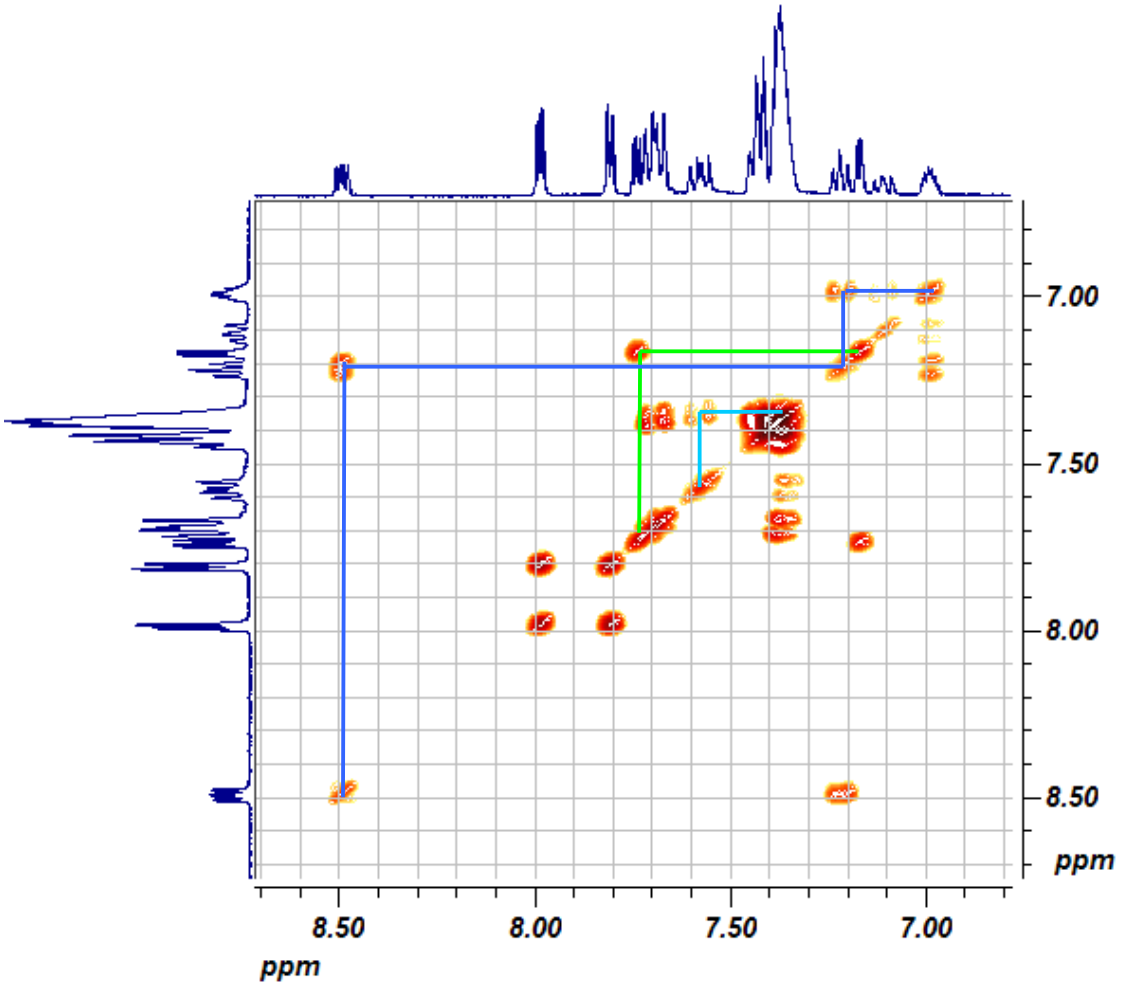


Figure S9. Selected ^{1}H NMR spectra of the evolution from **7A** to **8** in CD_3CO_2D at 70 ^{o}C.



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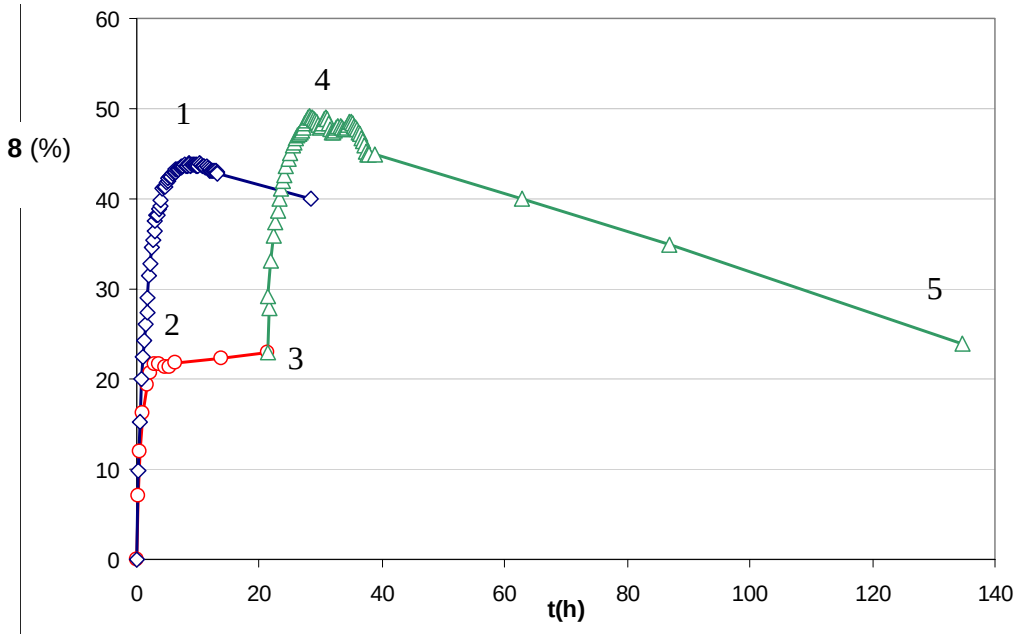

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