Electronic Supplementary Material (ESI) for Catalysis Science & Technology

SUPPORTING INFORMATION

MOLECULAR RUTHENIUM COMPLEXES ANCHORED ON MAGNETIC NANOPARTICLES THAT ACT AS POWERFUL AND MAGNETICALLY RECYCLABLE STEREOSPECIFIC EPOXIDATION CATALYSTS

LYDIA VAQUER,[A] PAOLA RIENTE,[A] XAVIER SALA,[B] SUSANNA JANSAT[C], JORDI BENET-BUCHHOLZ,[A] ANTONI LLOBET,*[,A,B] MIQUEL A. PERICÀS.*[,A,C]

[a] Institute of Chemical Research of Catalonia, Av. Països Catalans, 16, 43007 Tarragona, Spain.
[b] Departament de Química, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, E-08193 Barcelona, Spain
[c] Departament de Química Orgànica, Universitat de Barcelona, c/ Martí I Franqués 1-11, 08080, Barcelona, Spain.

E-mail: *mapericas@iciq.es*, allobet@iciq.es

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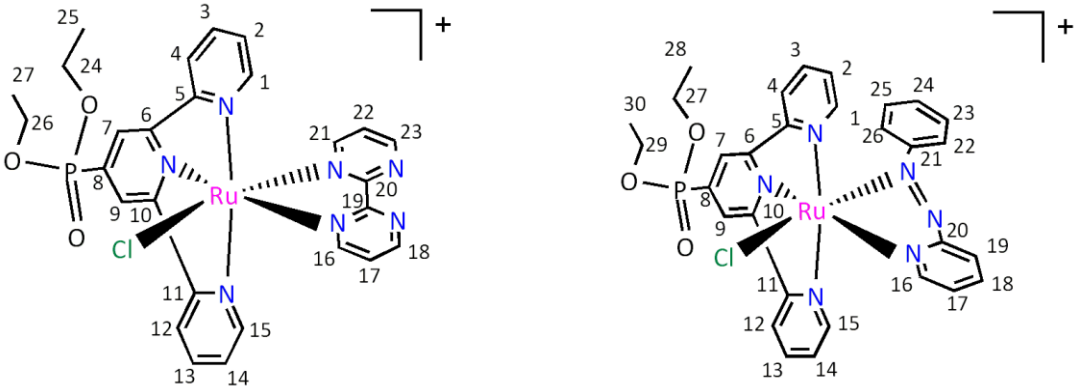

3a *trans*-**3b**

Figure S1

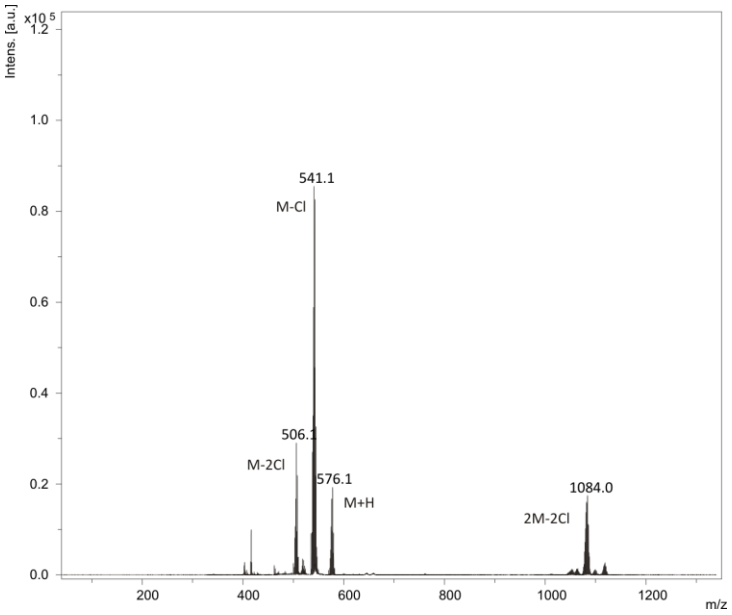

Figure S2. Maldi-TOF of **2**

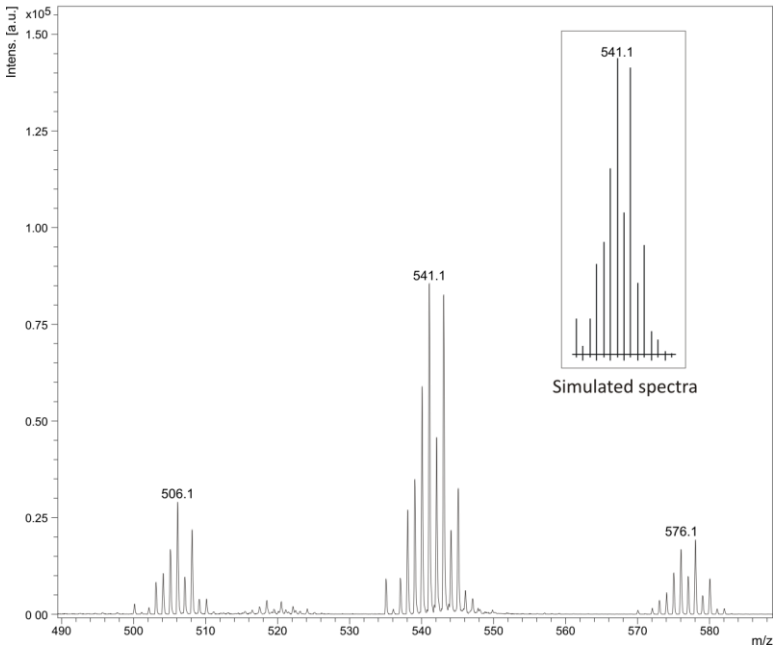

Figure S3. Zoom of Maldi-TOF of **2** and simulated spectra.

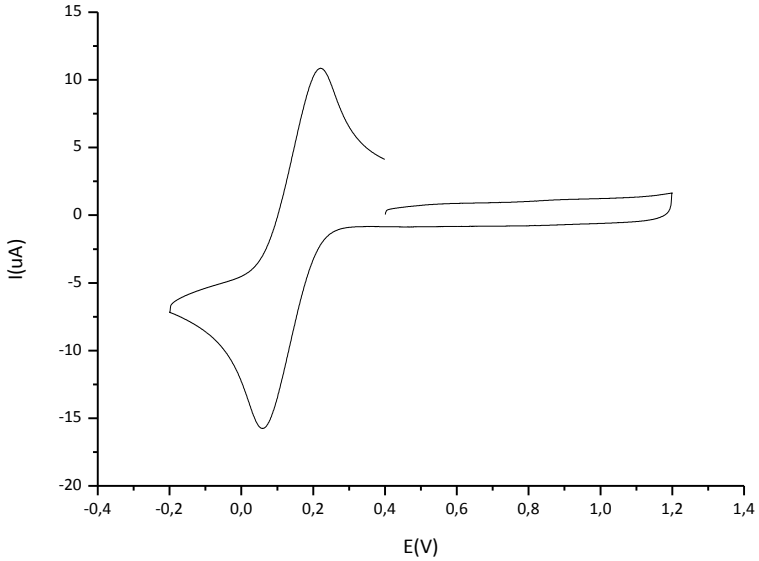

Figure S4. CV of **2** in CH_2Cl_2 (TBAH).

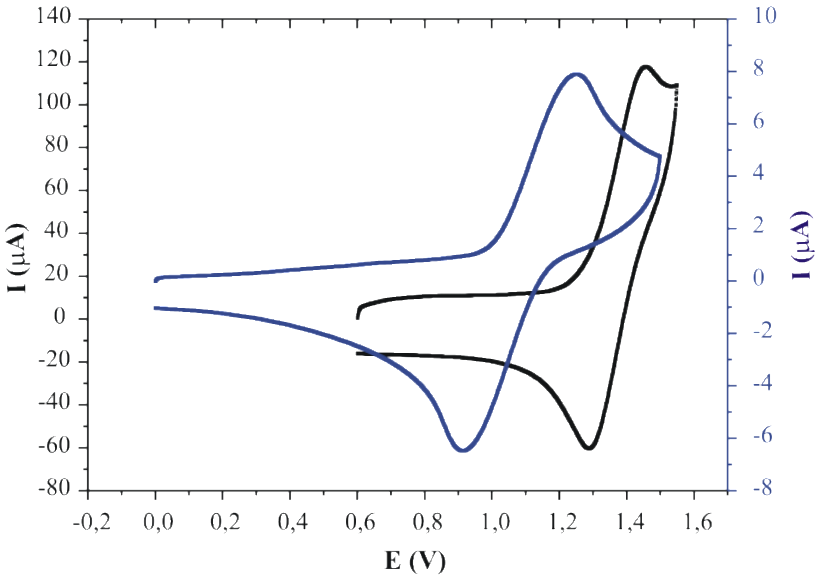

Figure S5. CV of **3a** (blue) and *trans*-**3b** (black) in CH_2Cl_2 (TBAH).

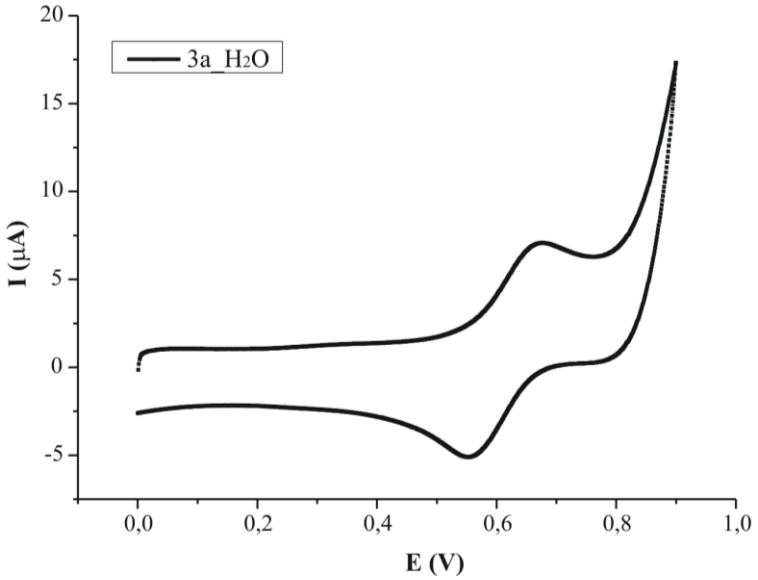

Figure S6. CV of **3a** in H_2O (pH 7).

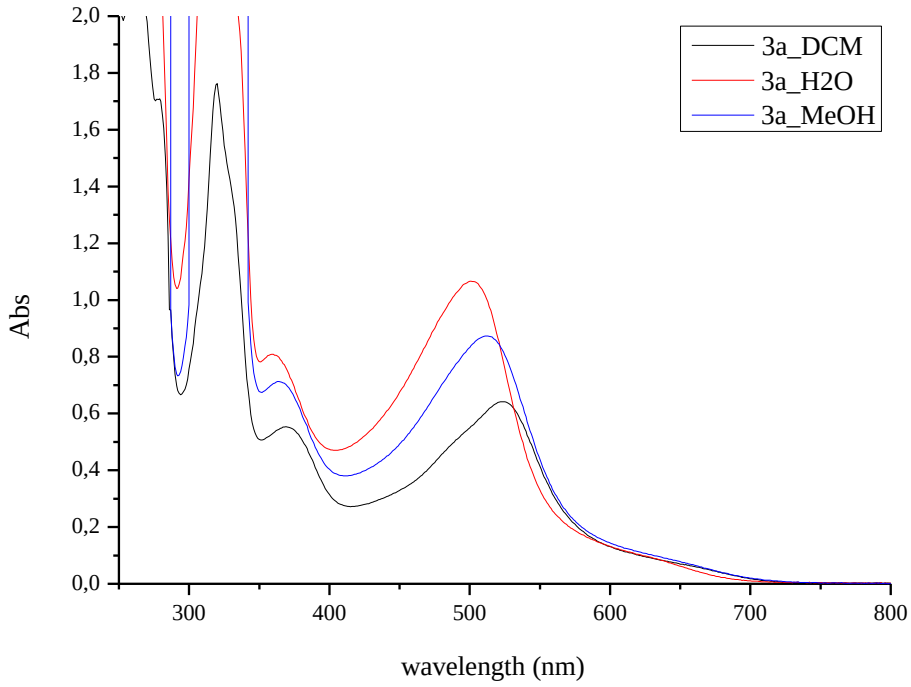

Figure S7. UV-Vis spectra of **3a** in H_2O (red), MeOH (blue) and DCM (black).

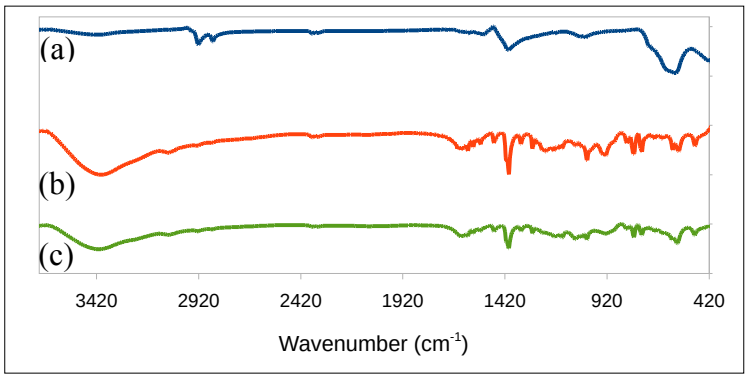

Figure S8. IR spectrum of (a) MNPs, (b) **4a** and (c) **6a**.

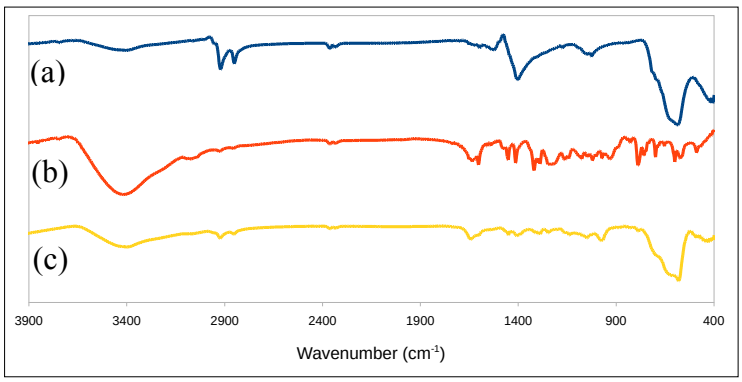

Figure S9. IR spectrum of (a) MNPs, (b) *trans*-**4b** and (c) *trans*-**6b**.

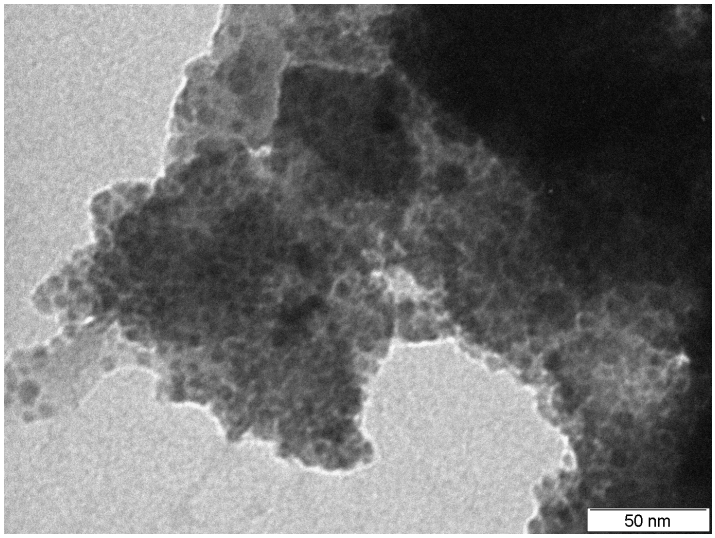

Figure S10. TEM micrograph of **7a** after second catalytic run.

X-Ray Crystal Structure Determination

Crystals of *cis*-**3b** and *trans*-**3b** were obtained by slow diffusion of diethyl ether over a solution of complex in dichloromethane. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data collection: Crystal structure determinations were carried out using a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoK_α radiation, Montel mirrors as monochromator and a Oxford Cryosystem plus low temperature device (T = -173 °C). Full-sphere data collection was used with ω and φ scans. Programs used: Data collection APEX-2[1], data reduction Bruker Saint[2] V/.60A and absorption correction SADABS[3].

Structure Solution and Refinement: Crystal structure solution was achieved using direct methods as implemented in SHELXTL[4] and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program SHELXTL. All non-hydrogen atoms were refined including anisotropic displacement parameters.

Compound *cis*-**3b**: The asymmetric unit is made up by one molecule of the complex, one PF_6 anion and a half molecule of dichloromethane. The dichloromethane molecule is disordered in two + two positions located around a C2 rotation axes (25:25:25:25). The dichloromethane molecule is shared with the neighboring asymmetric unit. The phosphorous rest of the main molecule is disordered in two orientations (ratio 92:08).
Compound *trans*-**3b**: The asymmetric unit is made up by one molecule of the complex, one PF_6 anion, a half dichloromethane molecule and a quarter of water molecule. The phosphorous rest of the main molecule is disordered in two orientations (ratio 52:48). Also the PF_6 anion is disordered in two orientations (ratio 77:33). The dichloromethane molecule is disordered over an inversion center. In the region of the water molecule only the electron density corresponding to a quarter of water could be localized.

Crystal data for *cis*-3b at 100 K: $C_{30}H_{29}Cl_1N_6O_3P_1Ru_1 + 1/2\ CH_2Cl_2 + PF_6^-$, 876.52 gmol^{-1}, Monoclinic, C2/c, a = 29.0844(10) Å, b = 15.0420(5) Å, c = 16.3344(6) Å, α = 90°, β = 108.315(2)°, γ = 90°, V = 6784.1(4) Å^3, Z = 8, ρ_{calcd} = 1.716 Mg/m^3, R_{1obs}= 0.0349 (R_{1ref} = 0.0471), $wR2_{obs}$ = 0.798 ($wR2_{ref}$ = 0.0858), for 8505 reflections with I>2σ(I) (for 10257 reflections [R_{int}: 0.0533] with a total of 45833 reflections measured), diffracting 2theta range: 1.54º to 30.78º, goodness-of-fit on F^2 = 1.026, largest diff. peak (hole) = 1.024 (-0.724) e Å^{-3}.
Crystal data for *trans*-3b at 100 K: $C_{30}H_{29}Cl_1N_6O_3P_1Ru_1 + 1/2\ CH_2Cl_2 + PF_6^- + 1/4\ H_2O$, 881.02 gmol^{-1}, Triclinic, P-1, a = 10.9643(7) Å, b = 11.9921(8) Å, c = 15.4910(15) Å, α = 110.491(5)°, β = 99.026(4)°, γ = 107.666(3)°, V = 1737.2(2) Å^3, Z = 2, ρ_{calcd} = 1.684 Mg/m^3, R_{1obs}= 0.0502 (R_{1ref} = 0.0622), $wR2_{obs}$ = 0.1284 ($wR2_{ref}$ = 0.1367), for 8446 reflections with I>2σ(I) (for 10105 reflections [R_{int}: 0.0543] with a total measured of 29332 reflections), diffracting 2theta range: 1.47º to 30.78º, goodness-of-fit on F^2 = 1.028, largest diff. peak (hole) = 2.090 (-1.373) e Å^{-3}.

CCDC numbers for *cis*-**3b** and *trans*-**3b** are 896921 & 896922 respectively

[1] Data collection with APEX II versions v1.0-22, v2009.1-0 and v2009.1-02. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.
[2] Data reduction with Bruker SAINT versions V.2.10(2003), V/.60A and V7.60A. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.
[3] SADABS: V.2.10(2003); V2008 and V2008/1 Bruker (2001). Bruker AXS Inc., Madison, Wisconsin, USA. Blessing, Acta Cryst. (1995) A51 33-38.
[4] Sheldrick, G.M. *Acta Cryst.* **2008** A64, 112-122. SHELXTL versions V6.12 and 6.14.

NMR CHARACTERIZATION

3a

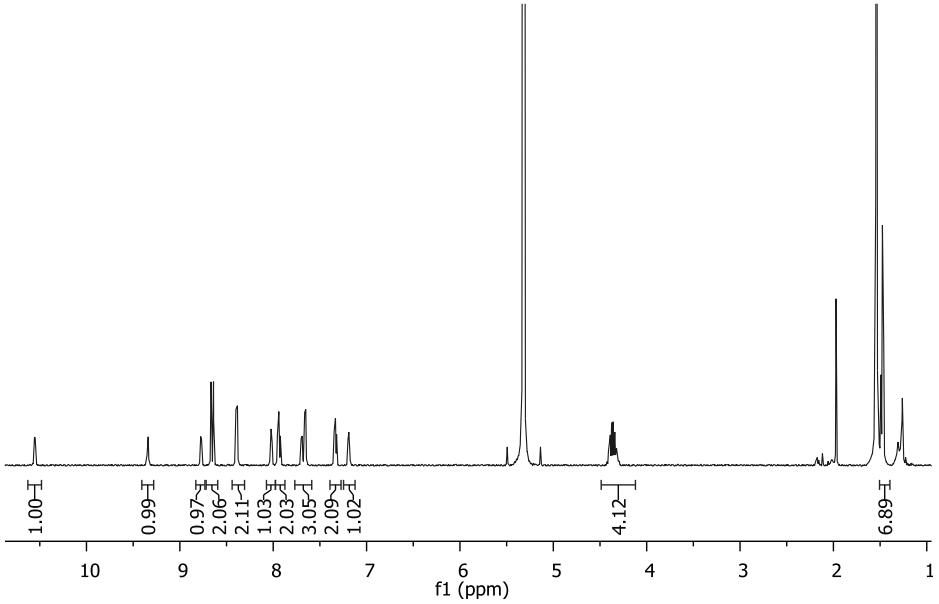

Figure S11. ^{1}H-NMR of **3a**.

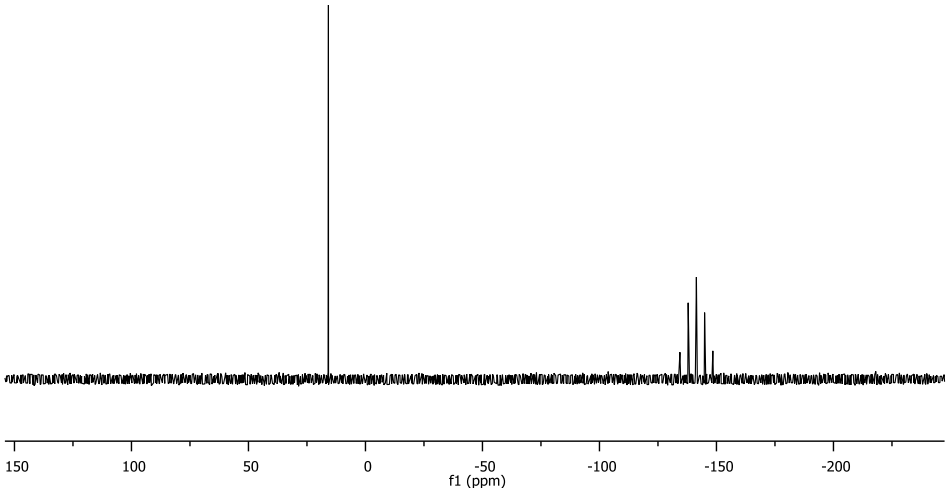

Figure S12. ^{31}P-NMR of **3a**.

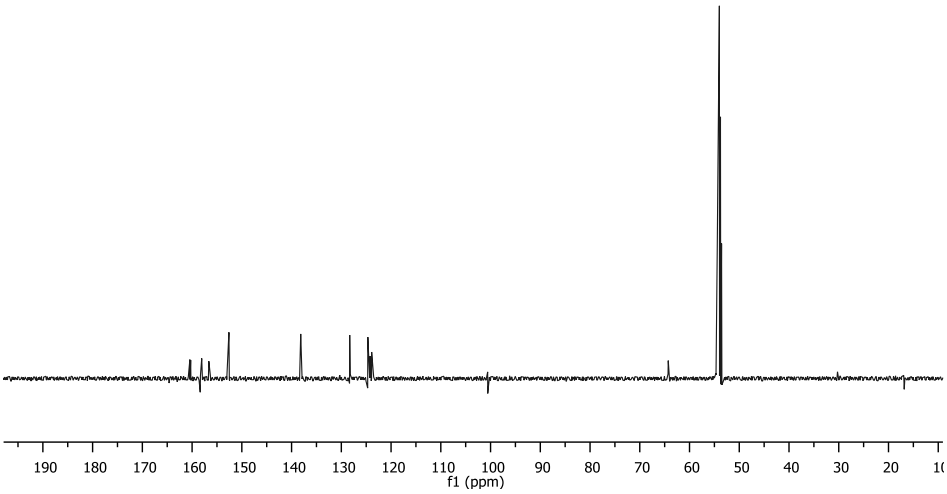

Figure S13. ^{13}C-NMR of **3a**.

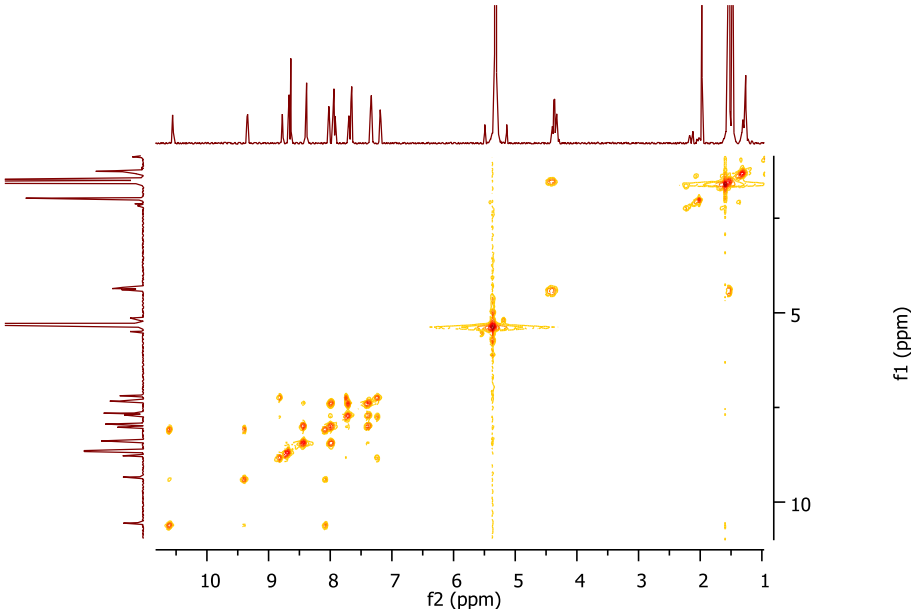

Figure S14. COSY of **3a**.

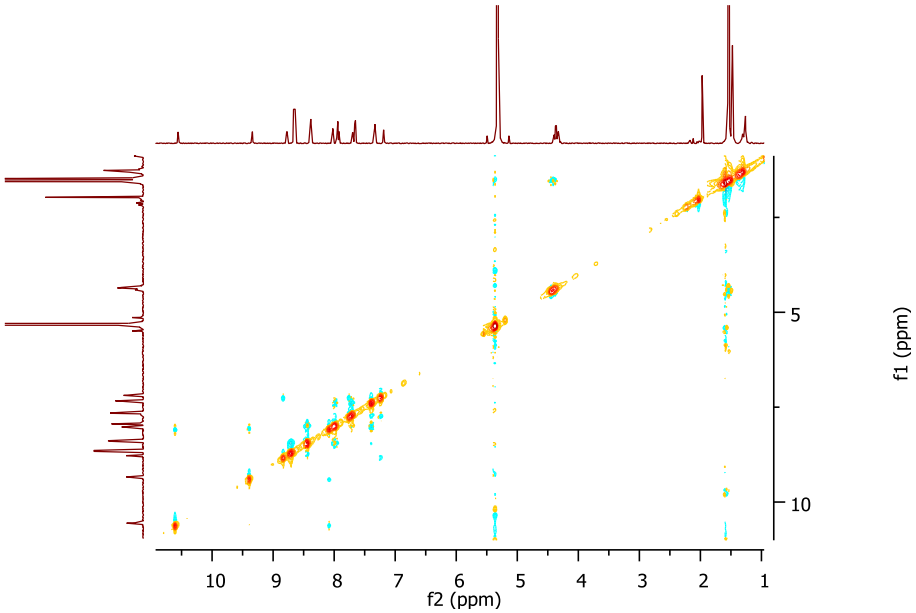

Figure S15. NOESY of **3a**.

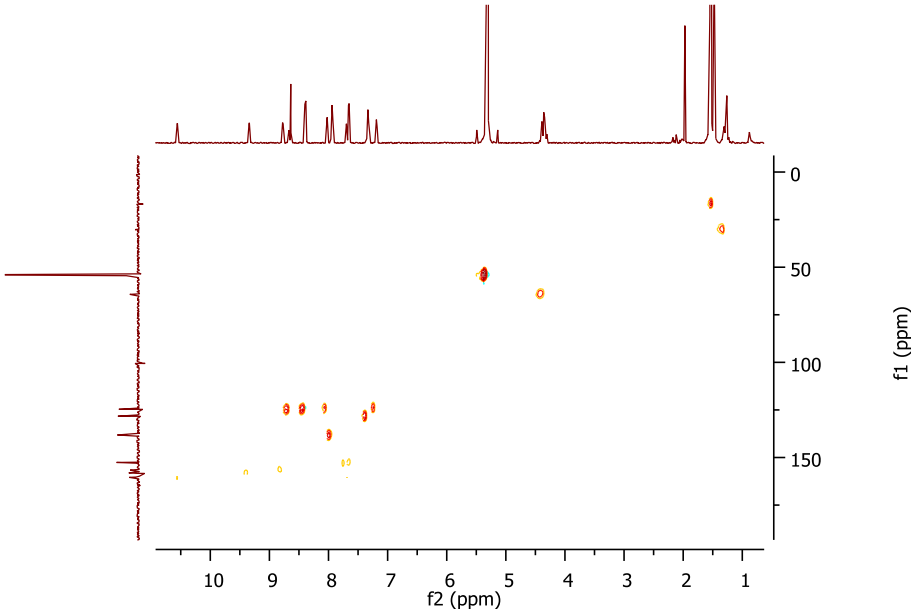

Figure S16. HMQC of **3a**.

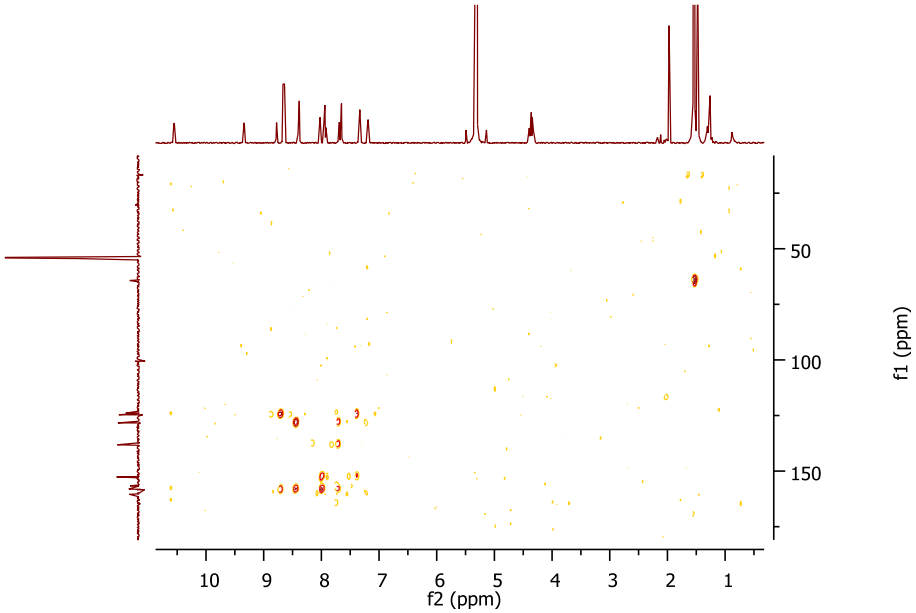

Figure S17. HMBC of **3a**.

Trans-**3b**

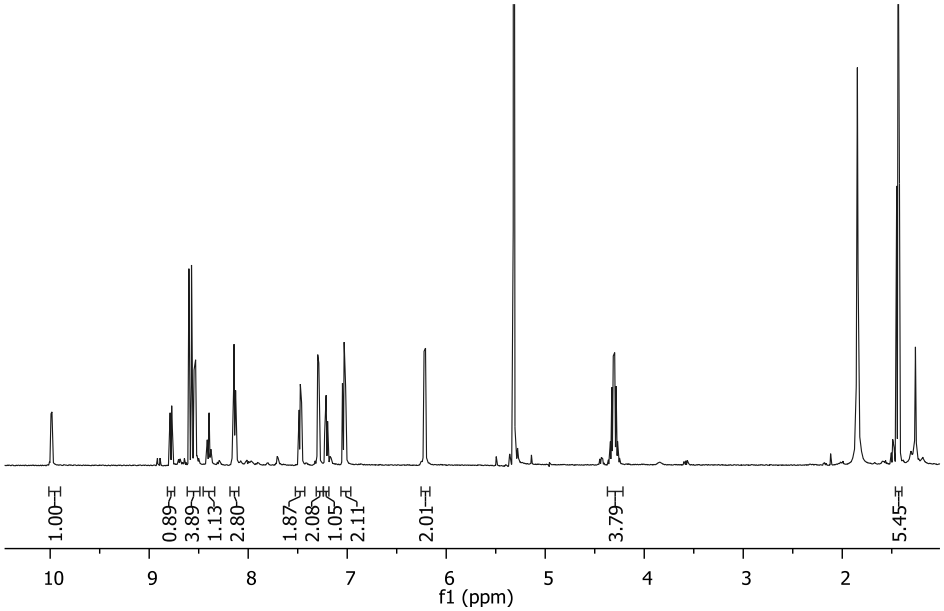

Figure S18. ^{1}H-NMR of *trans*-**3b**.

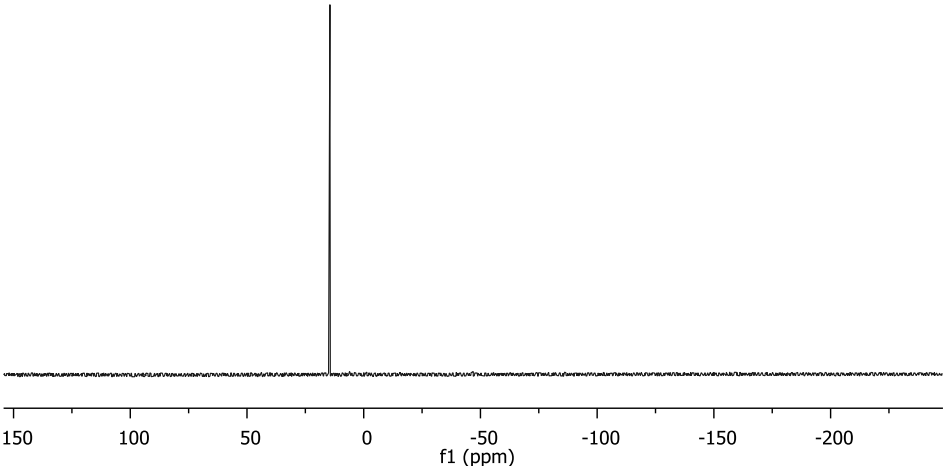

Figure S19. ^{31}P-NMR of *trans*-3b

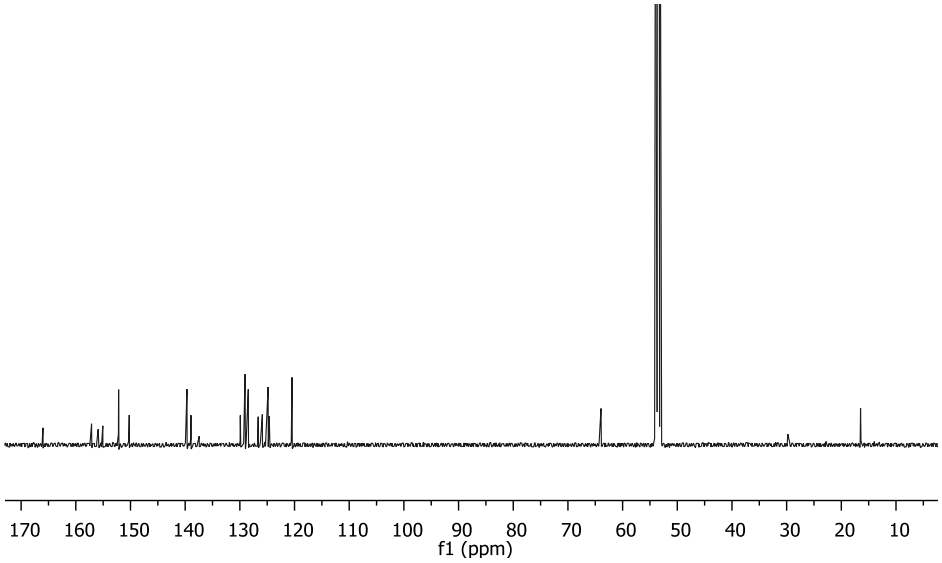

Figure S20. ^{13}C-NMR of *trans*-**3b**.

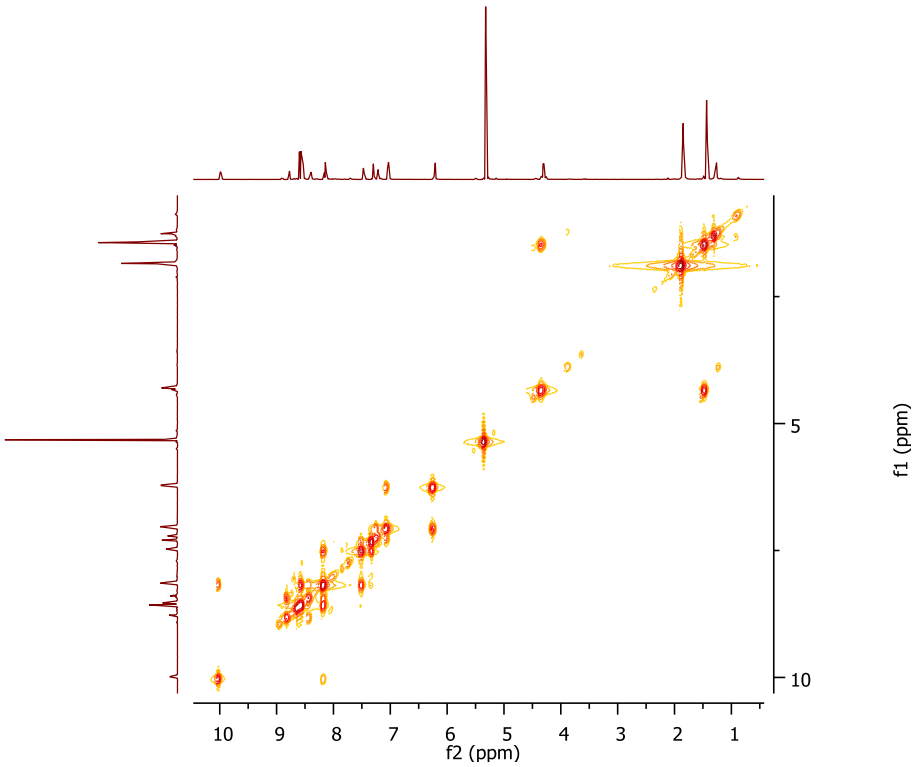

Figure S21. COSY of *trans*-**3b**.

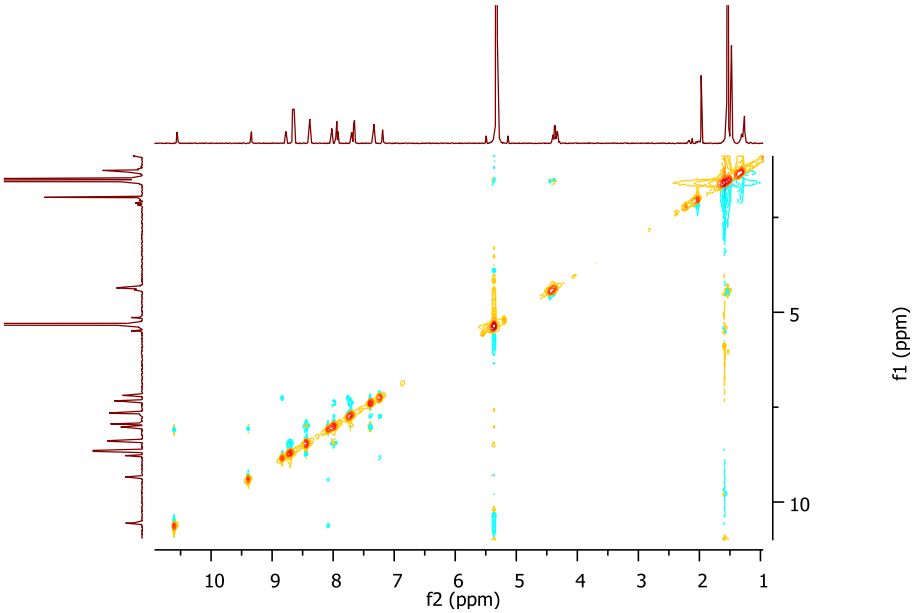

Figure S22. NOESY of *trans*-**3b**.

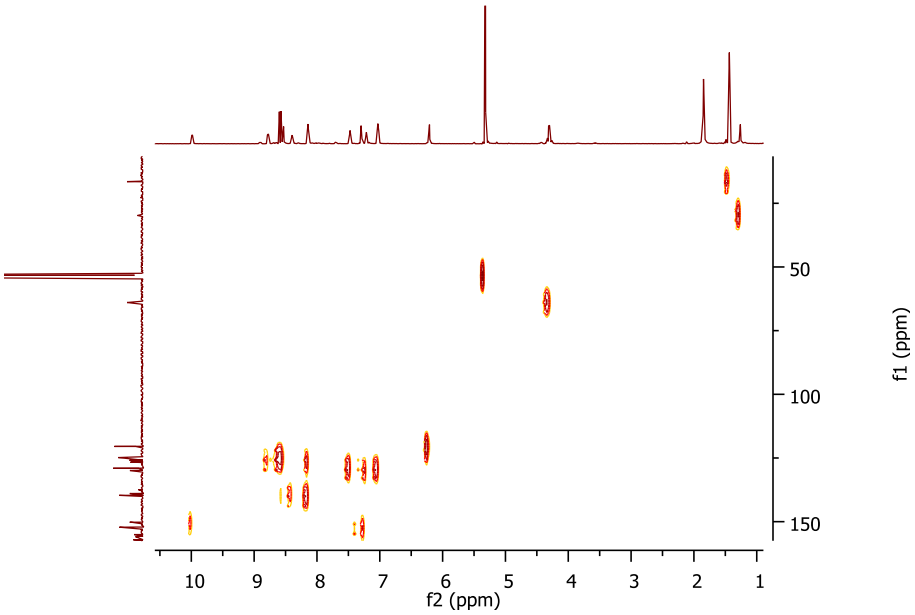

Figure S23. HMQC of *trans*-**3b**.

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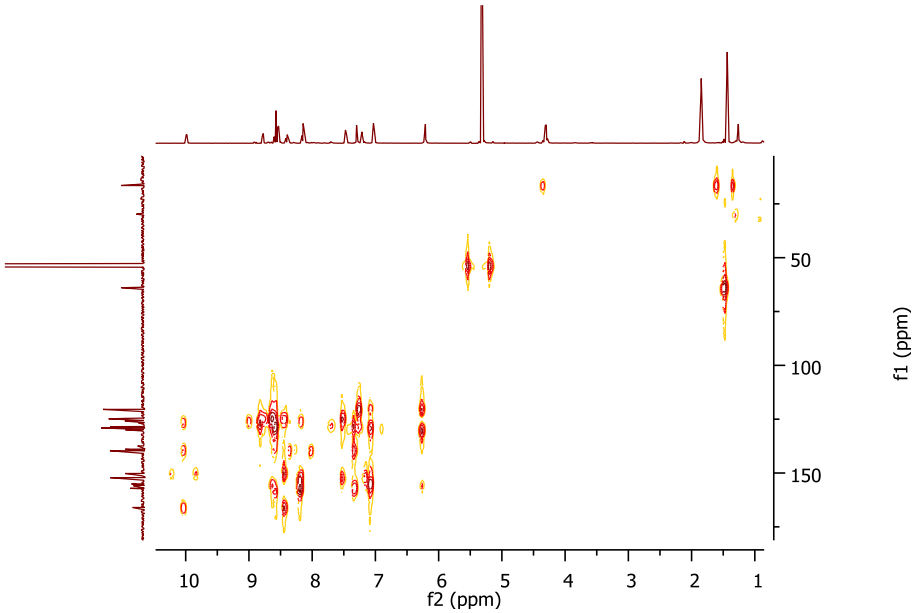

Figure S24. HMBC of *trans*-**3b**.

3b-mixture of isomers

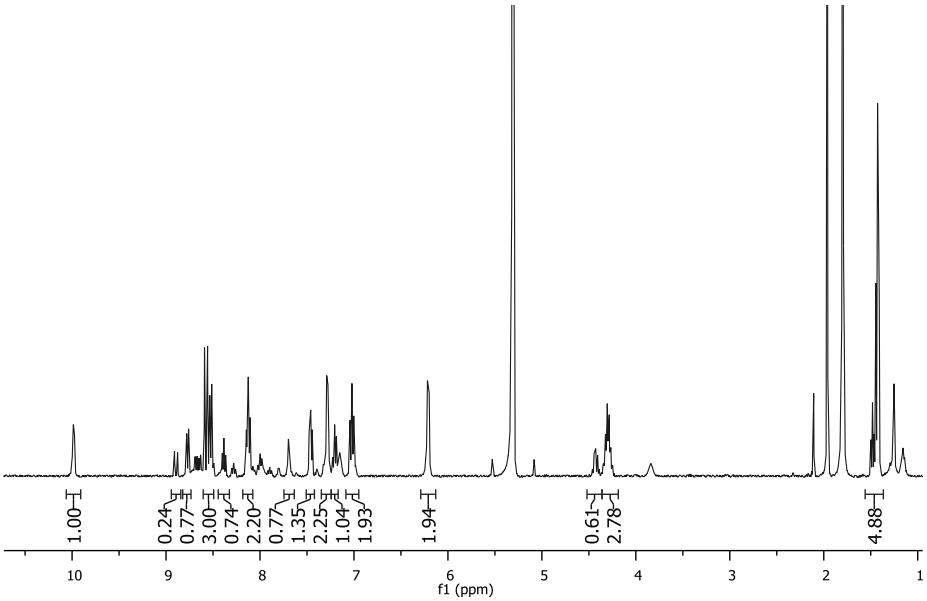

Figure S25. ^{1}H-NMR of the mixture of isomers of **3b**.

4a

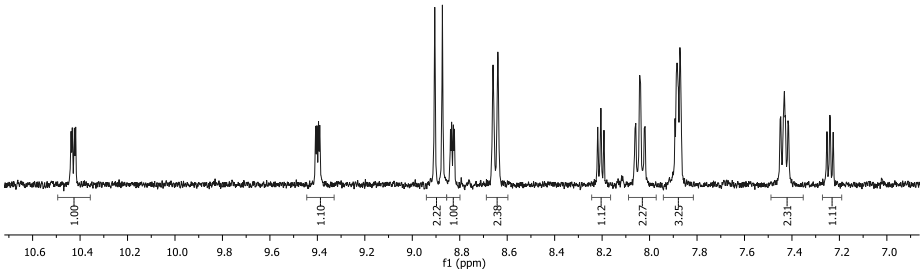

Figure S26. ^{1}H-NMR of **4a**.

Trans-**4b**

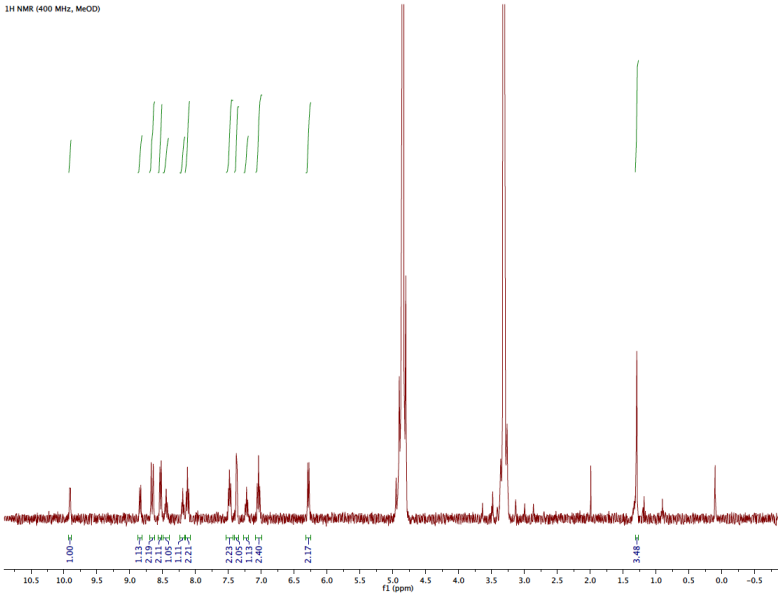

Figure S27. ^{1}H-NMR of *trans*-**4b**.