

Supporting Information

Redox Properties of Ferrocenyl Ene-diynyl Bridged $\text{Cp}^*(\text{dppe})\text{M}-\text{C}\equiv\text{C}-1,4-(\text{C}_6\text{H}_4)$ (M = Fe, Ru) Complexes

Rim Makhoul,^{||} Josef B. G. Gluyas,[§] Kevin B. Vincent,[†] Hiba Sahnoune^{‡,||} Jean-François Halet,^{*,||} Paul J. Low,^{*,§} Jean-René Hamon,^{||} and Claude Lapinte^{*,||}

^{||} Université Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France.

[§]School of Molecular Sciences, University of Western Australia, 35 Stirling Highway, Crawley, Perth 6009, Australia

[†]Department of Chemistry, Durham University, South Rd, Durham, DH1 3LE, UK

[‡]Département de Chimie, Faculté des Sciences, Université M'Hamed Bougara, Boumerdès, Algeria

Contents

UV-vis spectra	S3
NIR Spectra of 1 ⁿ⁺ Collected Spectroelectrochemically	S4
4-(Trimethylsilylethynyl)bromo benzene.....	S5
NMR spectra of 1 and 2	S6
Supplementary references.....	S13

UV-vis spectra

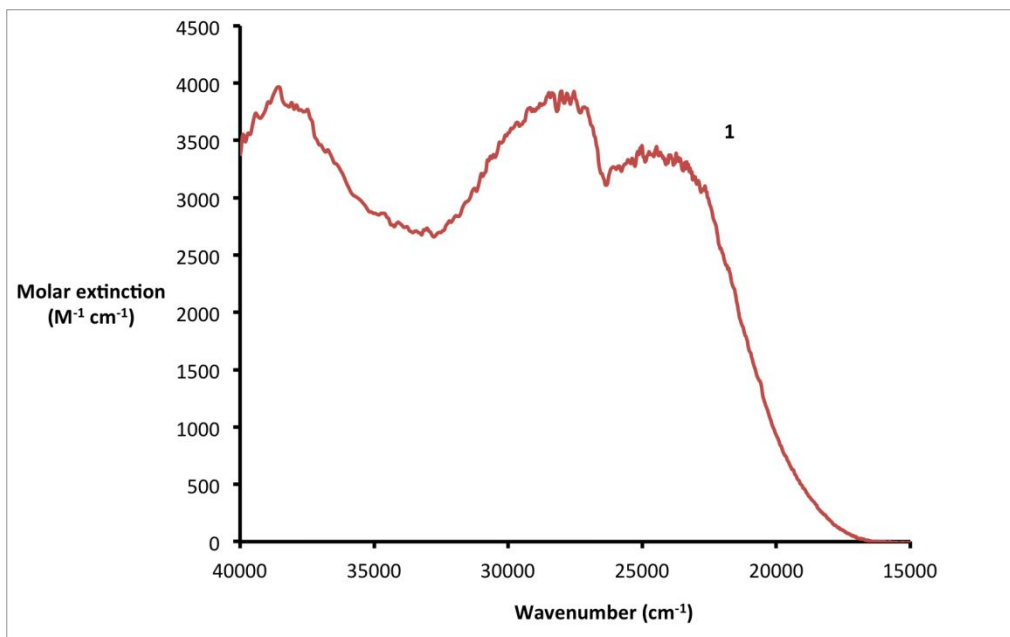


Figure S1. UV-vis spectrum of **1** in 0.1 M CH₂Cl₂/NBu₄PF₆.

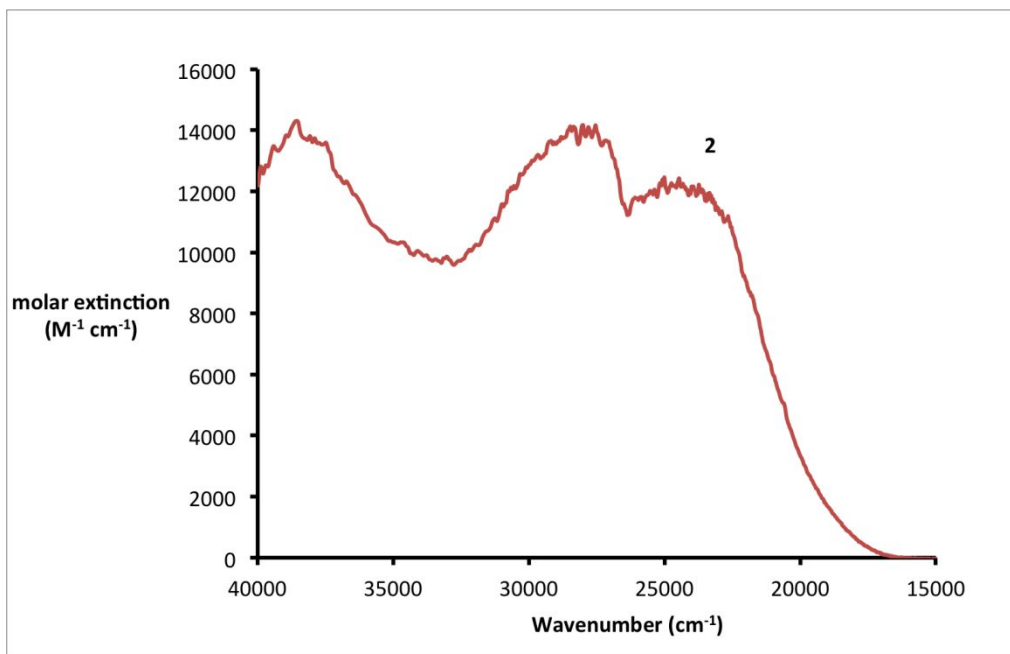


Figure S2. UV-vis spectrum of **2** in 0.1 M CH₂Cl₂/NBu₄PF₆.

NIR Spectra of $[1]^{n+}$ Collected Spectroelectrochemically

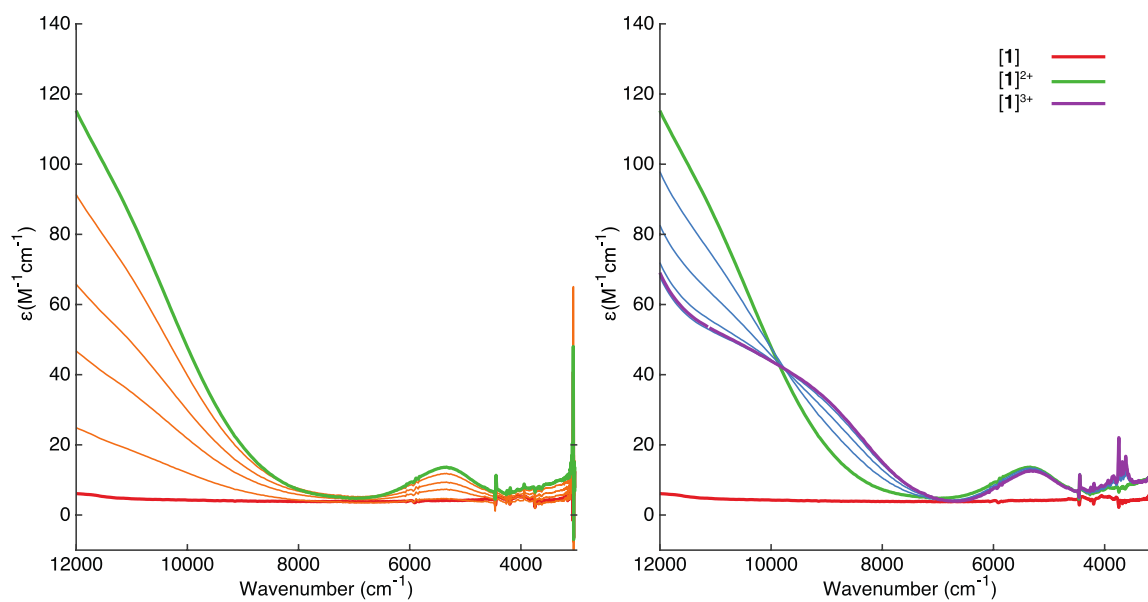


Figure S3. NIR spectra of **1**ⁿ⁺ collected spectroelectrochemically in 0.1 M CH_2Cl_2/NBu_4PF_6 . The changes observed upon oxidation from **1** to **1**²⁺ are shown to the left and the changes observed upon oxidation from **1**²⁺ to **1**³⁺ on the right.

4-(Trimethylsilylethynyl)bromo benzene. Ethynyltrimethylsilane (955 mg, 9.72 mmol) was added to a mixture of 4-bromo-iodobenzene (2.50 g, 8.84 mmol),¹ PdCl₂(PPh₃)₂ (62.0 mg, 88.4 μmol)²⁻³ and copper(I) iodide (17.0 mg, 88.4 μmol) in degassed triethylamine (50 mL) under a N₂ atmosphere. The resulting mixture was stirred for 1.5 h at ambient temperature, after which time the volatiles were removed under reduced pressure. The resulting residue was suspended in hexanes and passed through a short silica column (eluent: hexanes). Concentration of the combined filtrates gave a colourless oil which solidified on drying in vacuum to afford the product as a white solid (2.20 g, 8.70 mmol, 98%). ¹H NMR (400 MHz CDCl₃): δ = 0.24 (s, 9H, Si(CH₃)₃), 7.32, 7.43 (AA'BB' system, 4H, ³J_{H-H} = 8.8 Hz, ⁴J_{H-H} = 2.1 Hz, C₆H₄). ¹³C NMR (100 MHz, CDCl₃): δ = 0.0 (Si(CH₃)₃), 95.7 (C≡C-Si), 105.0 (C≡C-C₆H₄), 122.3 (C_q, C₆H₄), 122.8 (C_q, C₆H₄), 131.6 (C-H, C₆H₄), 133.5 (C-H, C₆H₄), C-Br not observed. FT-IR (CH₂Cl₂) ν 2157 cm⁻¹ (C≡C). EI-MS: *m/z* (%) 252 (66) [M]⁺, 237 (100) [M - CH₃]⁺. Anal. Calcd For C₁₁H₁₃SiBr: C, 52.18; H, 5.18. Found: C, 52.30; H, 5.26.

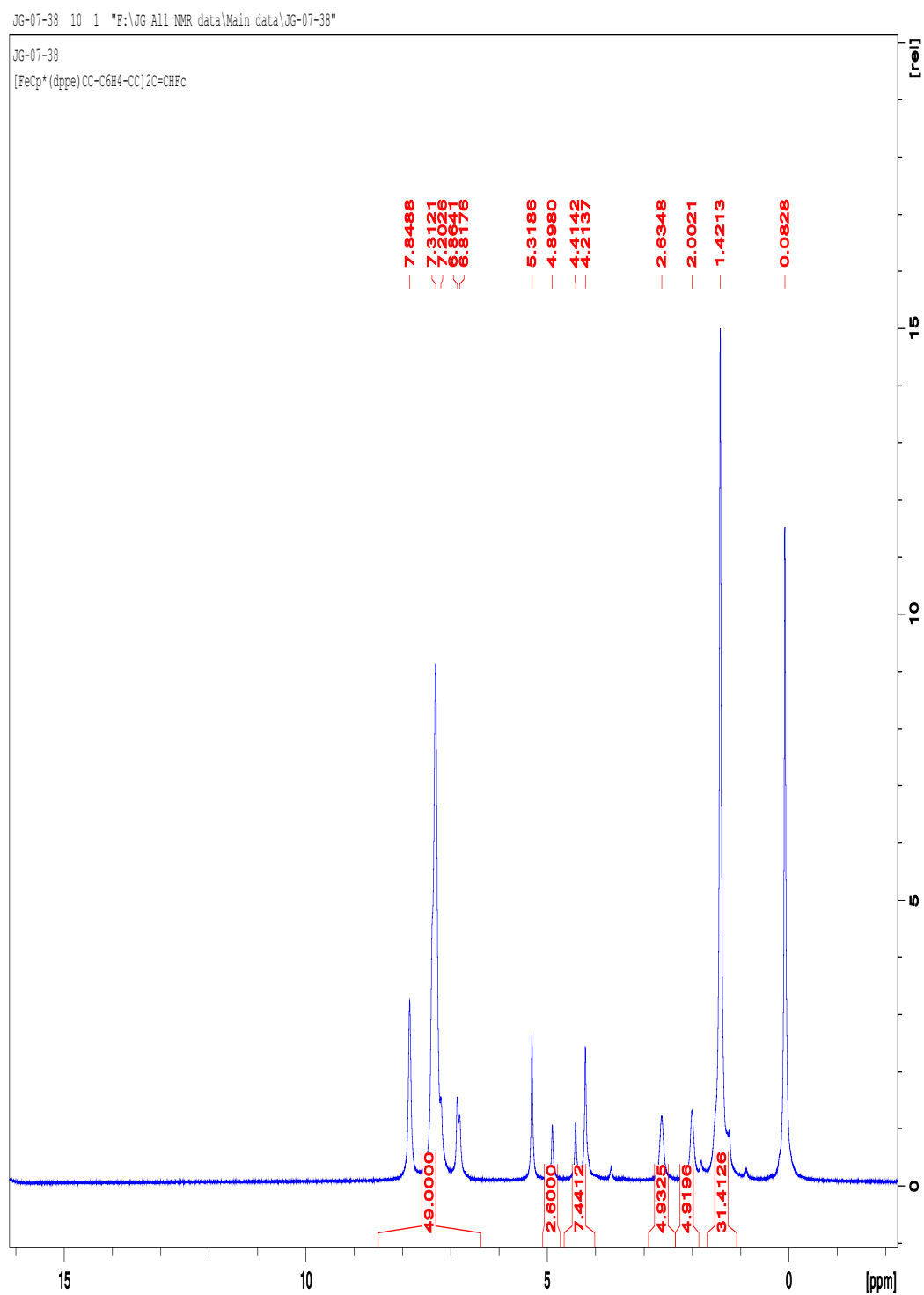


Figure S4. ^1H NMR spectrum of **1** (CDCl_3).

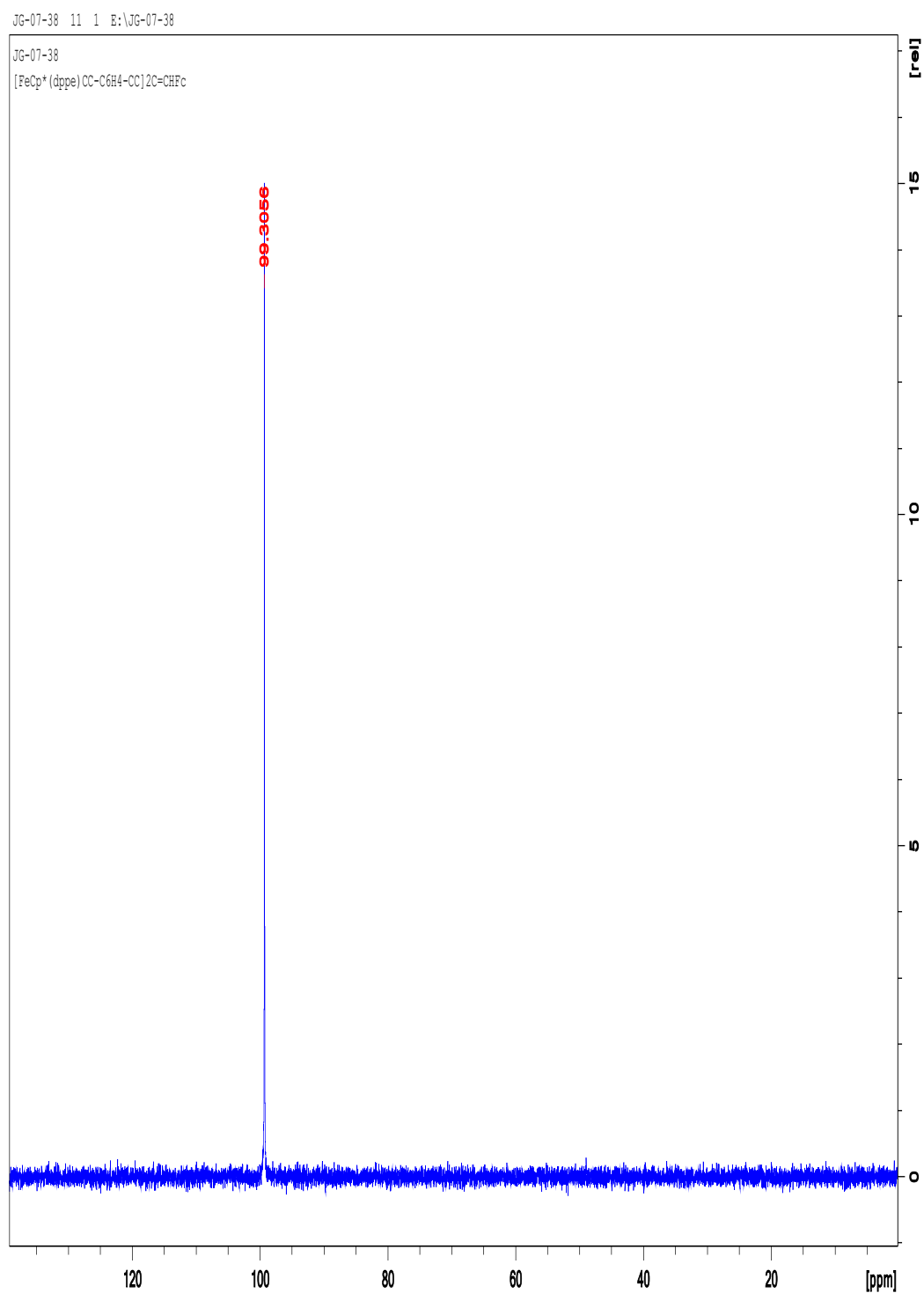
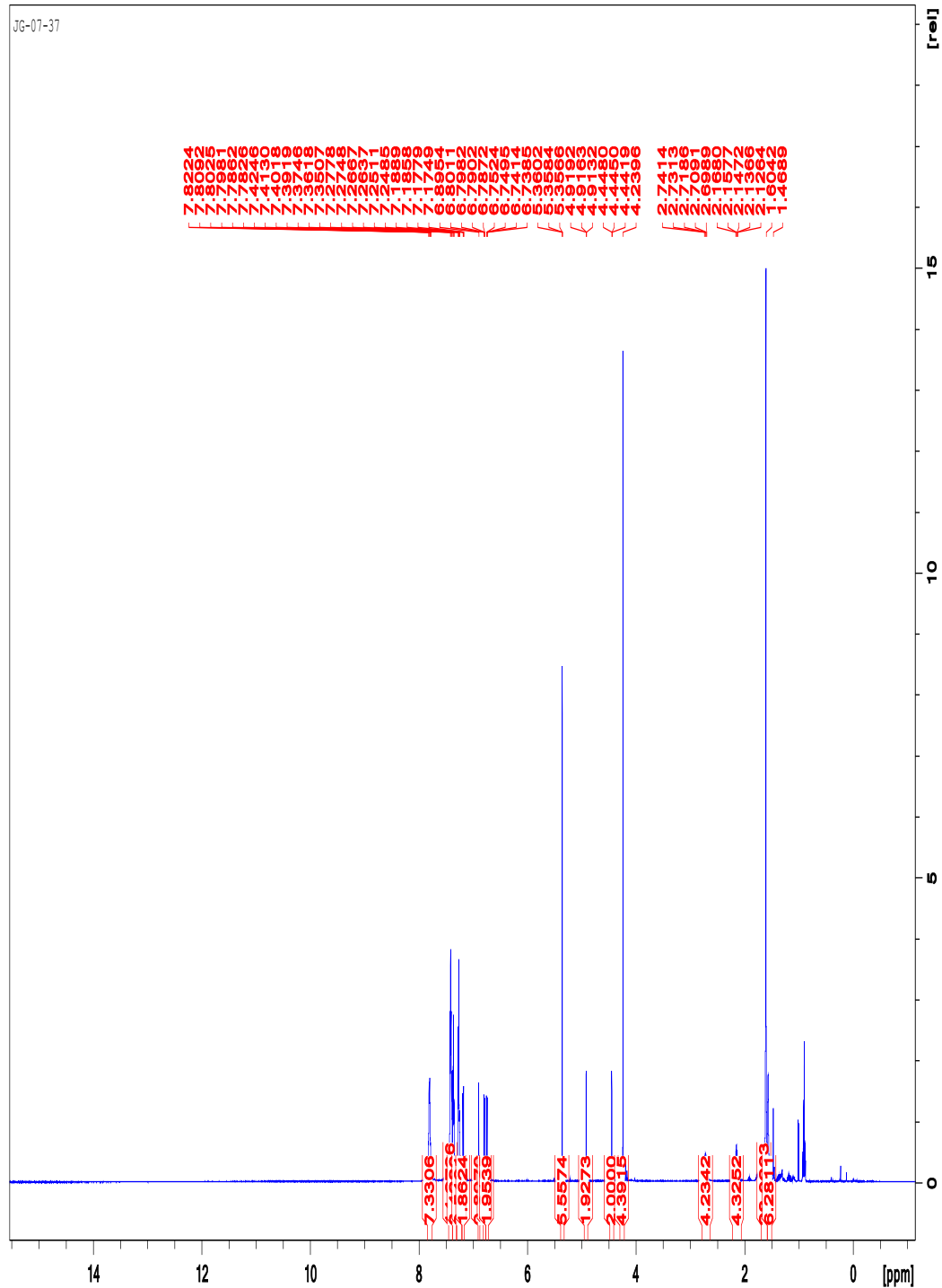
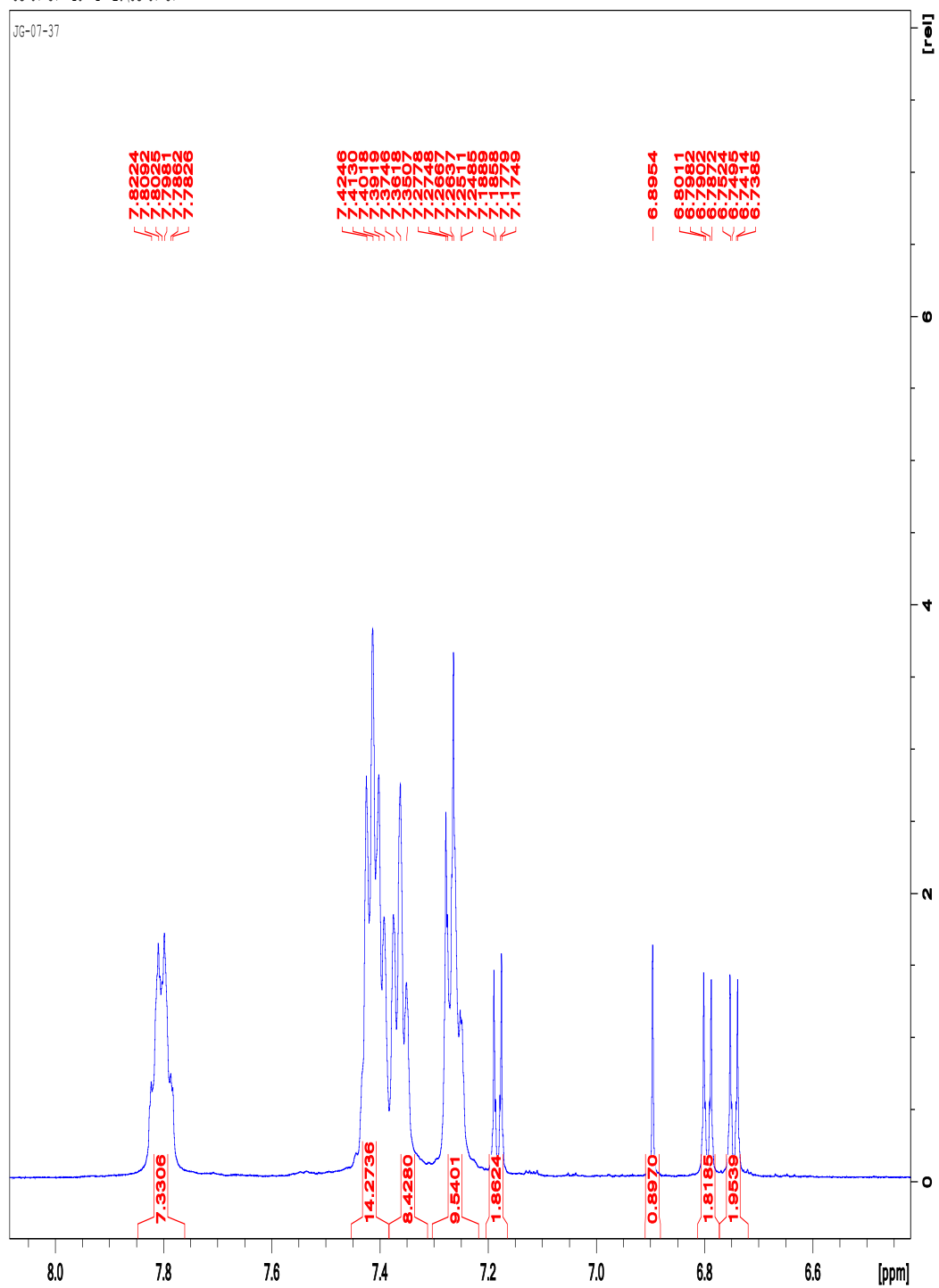
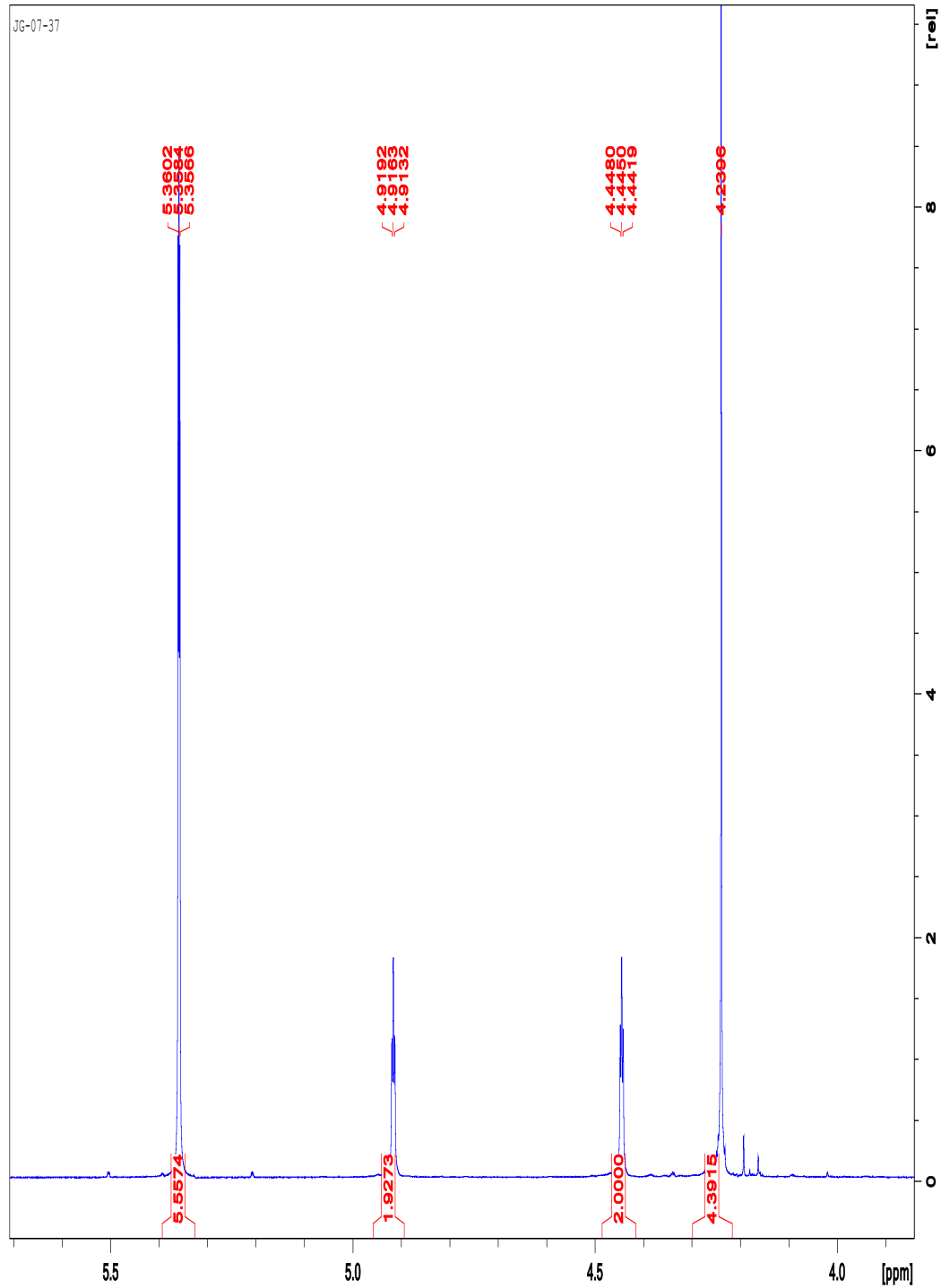


Figure S5. ^{31}P NMR spectrum of **1** (CDCl_3).







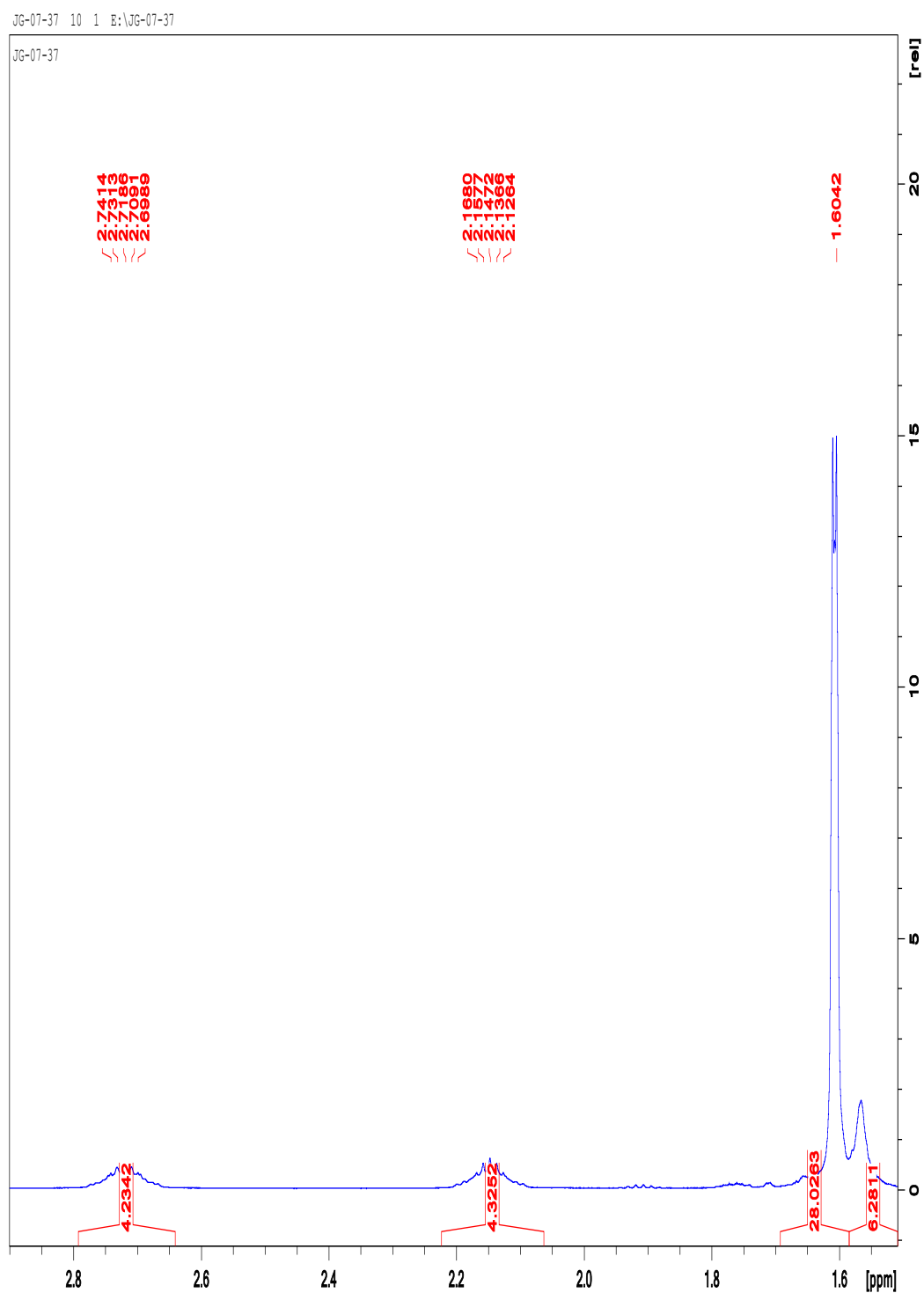


Figure S6. ^1H NMR spectrum of **2** (CDCl_3) and expansions of key regions

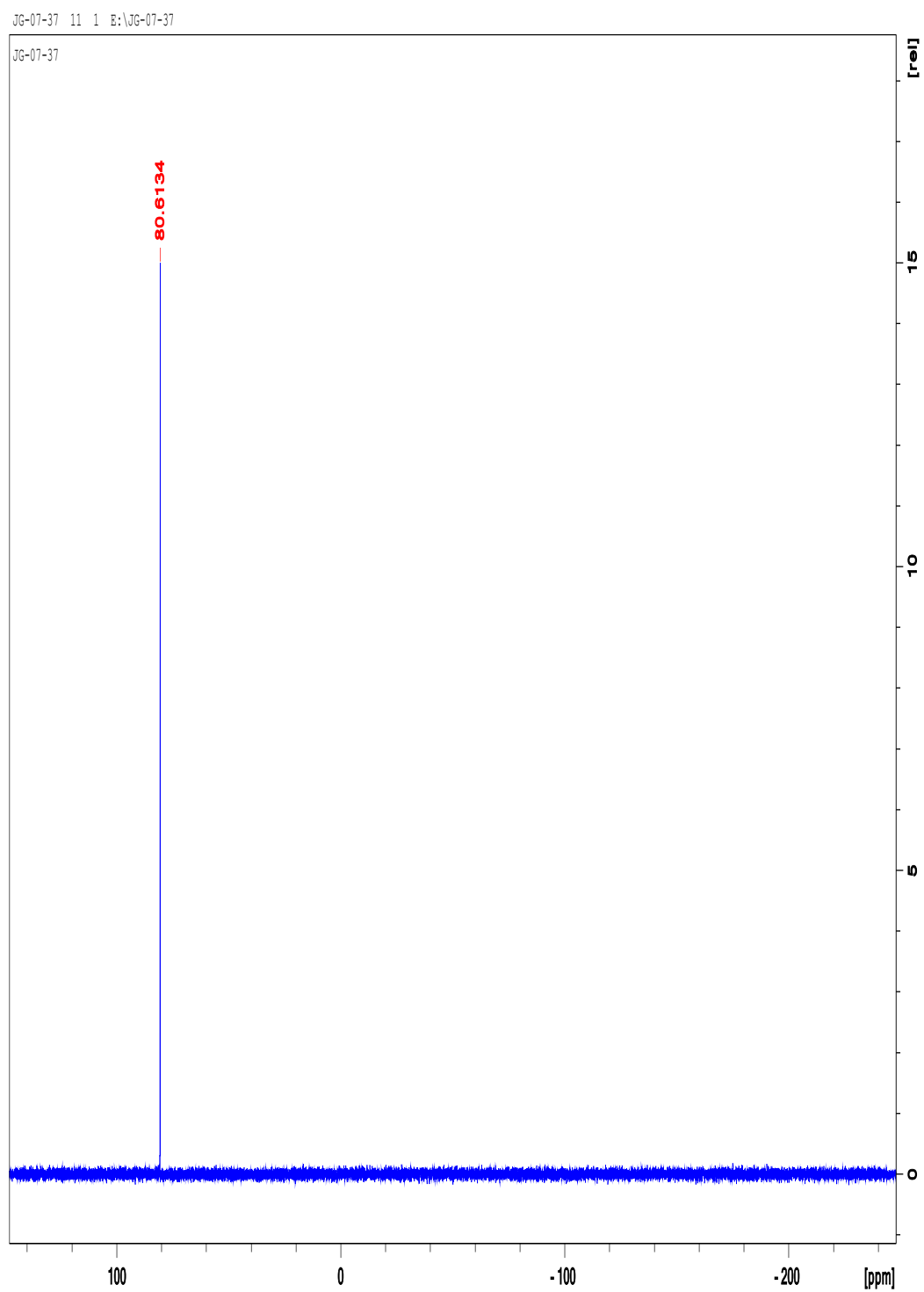


Figure S7. ^{31}P NMR spectrum of **2** (CDCl_3)

References

- S1. Cross, T. A.; Davis, M. C., Synthesis of hydroxyalkyl-substituted, push-pull chromophores based on diphenylacetylenes and 1,4-bis(phenylethynyl)benzenes. *Synth Commun* **2008**, *38* (4), 499-516.
- S2. Miyaura, N.; Suzuki, A., Palladium-Catalyzed Reaction of 1-Alkenylboronates with Vinylic Halides - (1z,3e)-1-Phenyl-1,3-Octadiene - (Benzene, 1,3-Octadienyl, (Z,E)). *Org Synth* **1990**, *68*, 130-137.
- S3. Gluyas, J. B. G.; Burschka, C.; Dorrich, S.; Vallet, J.; Gronemeyer, H.; Tacke, R., Disila-analogues of the synthetic retinoids EC23 and TTNN: synthesis, structure and biological evaluation. *Org Biomol Chem* **2012**, *10* (34), 6914-6929.