

Synthesis and Application of New Salan Titanium Complexes in the Catalytic Reduction of Aldehydes

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Single crystal X-ray diffraction analysis of compound 2

Crystals of compound **2** suitable for X-ray diffraction were obtained from a concentrated benzene solution at room temperature. The solid-state molecular structure of **2** is stabilized by the formation of intramolecular hydrogen bonds between the OH groups of the phenols and the N atoms of the amine moieties (see Figure S1). Such interactions show O(1)-H(1O)···N(1) and O(2)-H(2O)···N(2) bond lengths of 2.06 and 1.92 Å, respectively, and define two 6-member heterocycles.

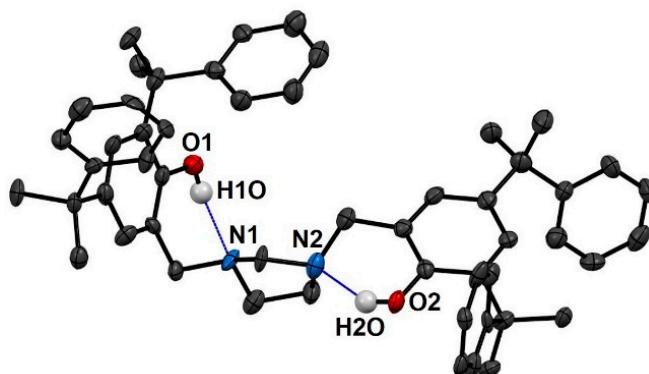


Figure S1. ORTEP diagram of **2** showing thermal ellipsoids at 40% probability level. Selected hydrogens atoms and co-crystallized solvent molecules were omitted for clarity.

Table S1 - Crystal data and structure refinement for compound **2**.

Compound	2 ·(C ₆ H ₆) _{1.5}
Empirical formula	C ₆₂ H ₆₉ N ₂ O ₂
Formula weight	874.19
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, P-1
<i>a</i> (Å)	10.802(7)
<i>b</i> (Å)	13.802(7)
<i>c</i> (Å)	17.804(9)
α(°)	72.03(3)
β(°)	89.71(4)
γ(°)	81.14(3)
Volume (Å ³)	2492(2)

Z	2
Calculated density (g m ⁻³)	1.165
Absorption coefficient (mm ⁻¹)	0.069
<i>F</i> (000)	942
Crystal size (mm)	0.10 x 0.20 x 0.20
θ range for data collection (°)	1.571 – 25.835
Limiting indices	-12 ≤ <i>h</i> ≤ 12, -15 ≤ <i>k</i> ≤ 16, -21 ≤ <i>l</i> ≤ 21
Reflections collected/unique	19307/7916 [<i>R</i> _{int} = 0.2103]
Completeness to θ = 25.242	86.0
Data/restraints/parameters	7916/0/605
Goodness-of-fit on <i>F</i> ²	0.863
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> ₁ = 0.1055, <i>wR</i> ₂ = 0.2183
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.3046, <i>wR</i> ₂ = 0.2781
Largest diff. peak/hole (e Å ⁻³)	0.307 and -0.379

^a *R*₁ = Σ ||*F*₀| - |*F*_c|| / Σ |*F*₀|; *wR*₂ = {Σ [*w*(*F*₀² - *F*_c²)²] / Σ [*w*(*F*₀²)²]}^{1/2}

NMR spectra of compounds 1-6

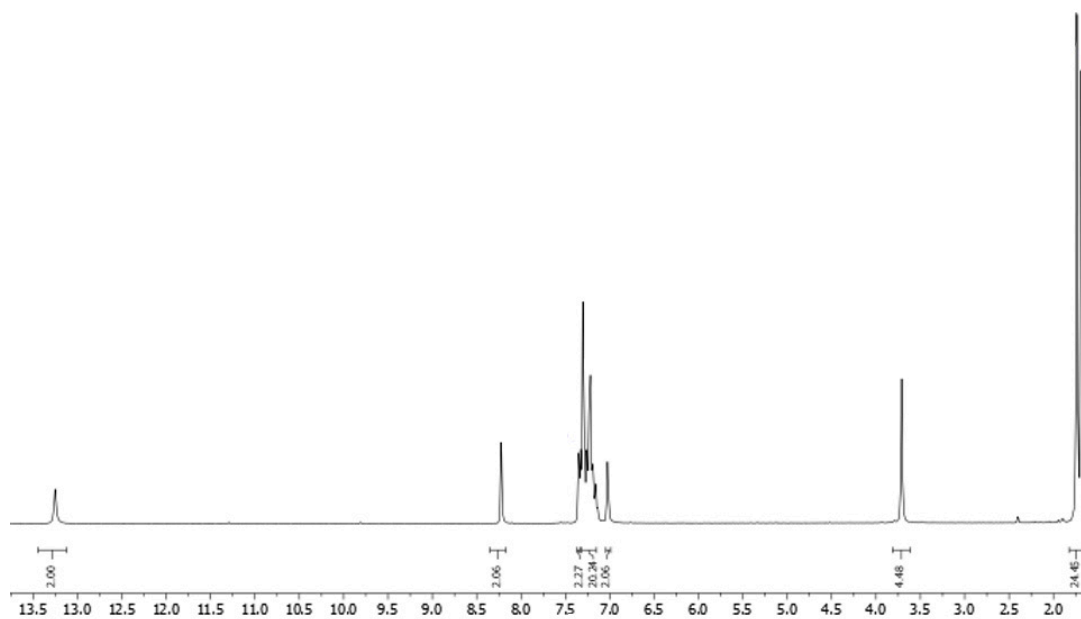


Figure S2A. ¹H NMR spectrum of **1** in CDCl₃.

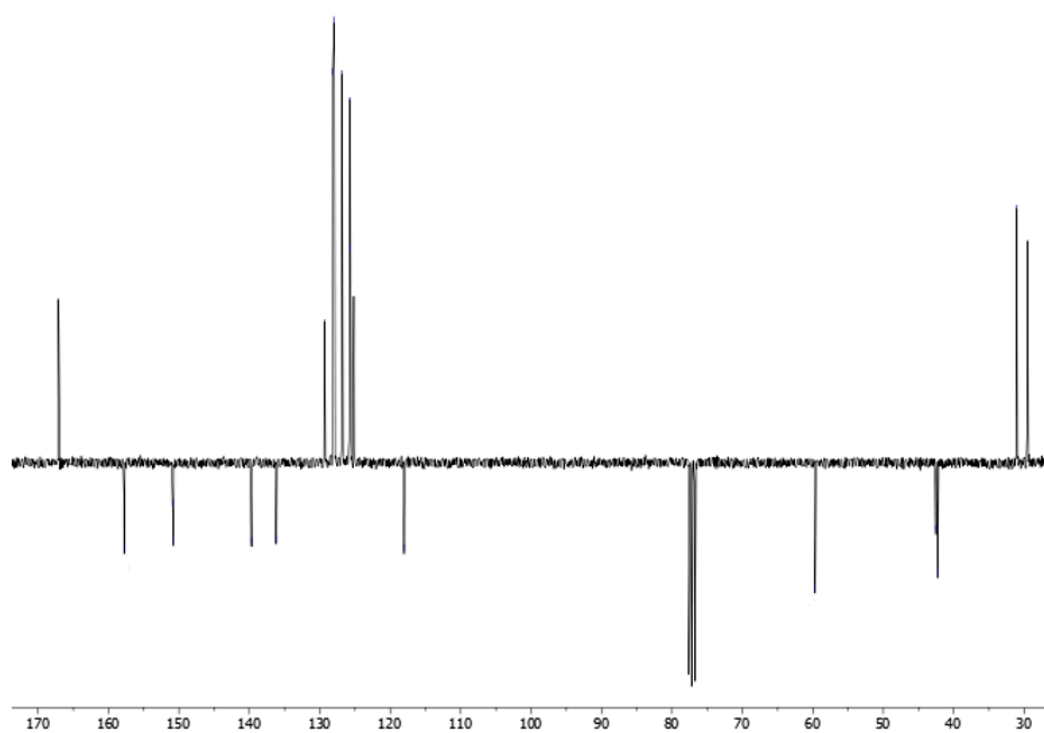


Figure S2B. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** in CDCl_3 .

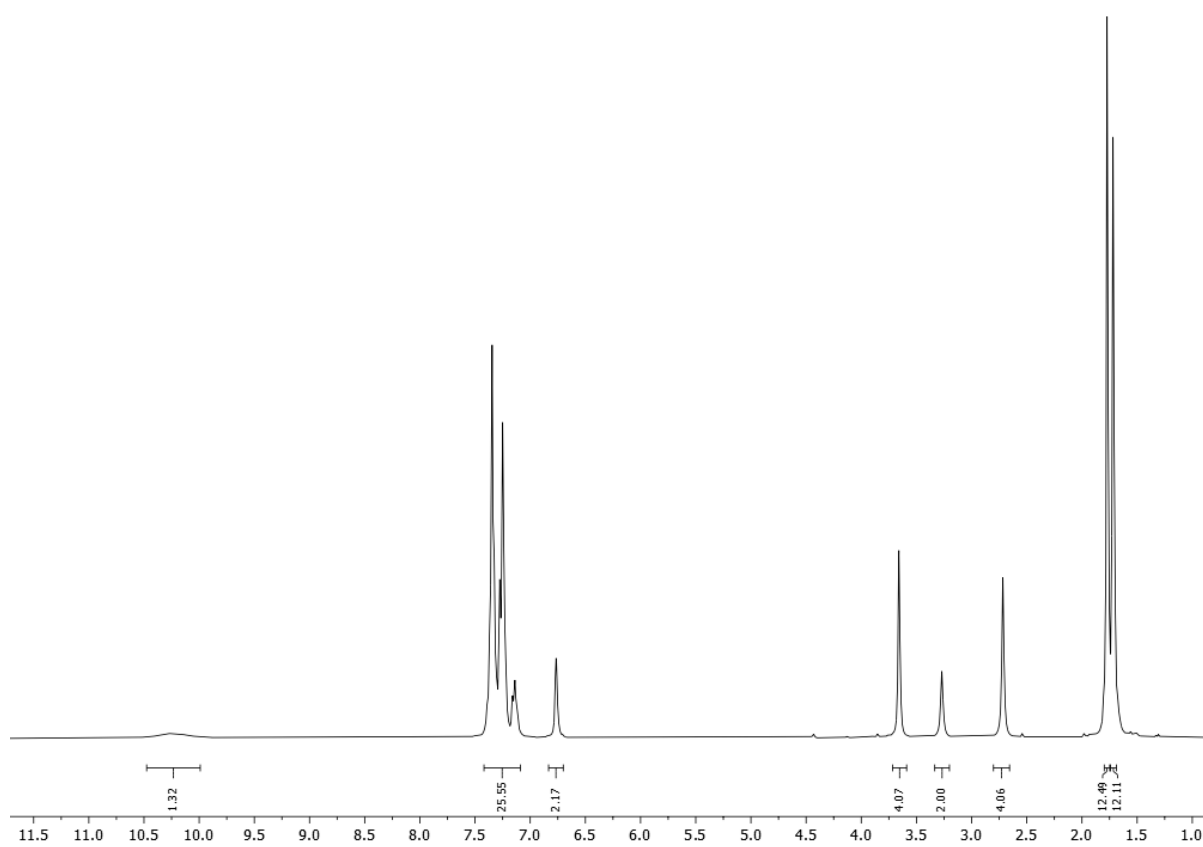


Figure S3A. ^1H NMR spectrum of **2** in CDCl_3 .

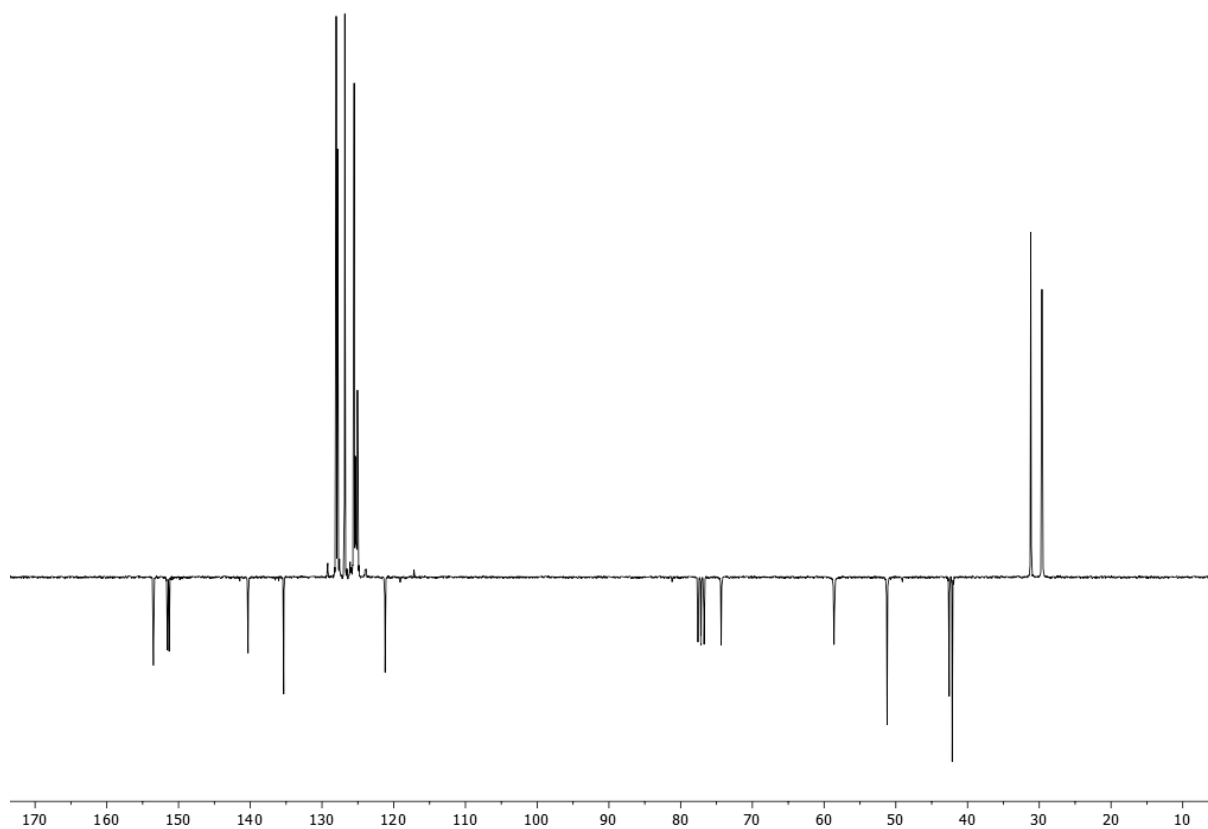


Figure S3B. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** in CDCl_3 .

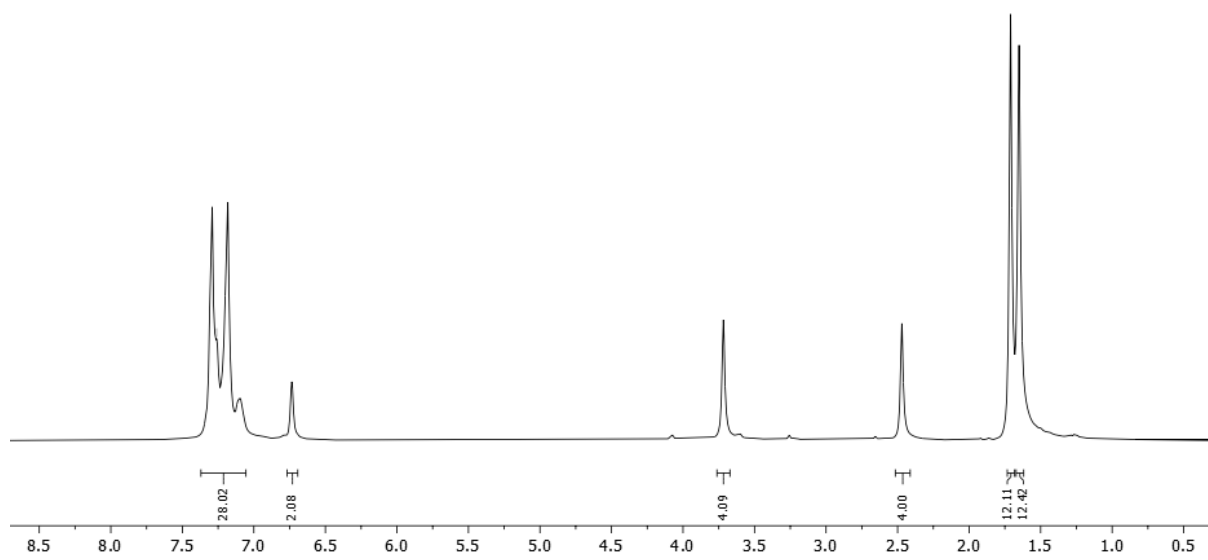


Figure S4A. ^1H NMR spectrum of **3** in CDCl_3 .

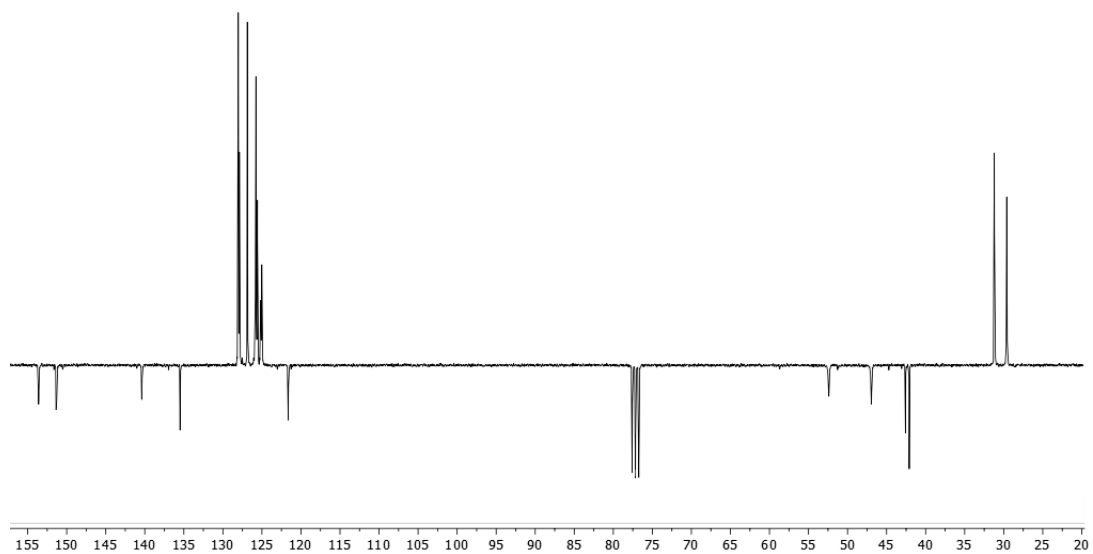


Figure S4B. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in CDCl_3 .

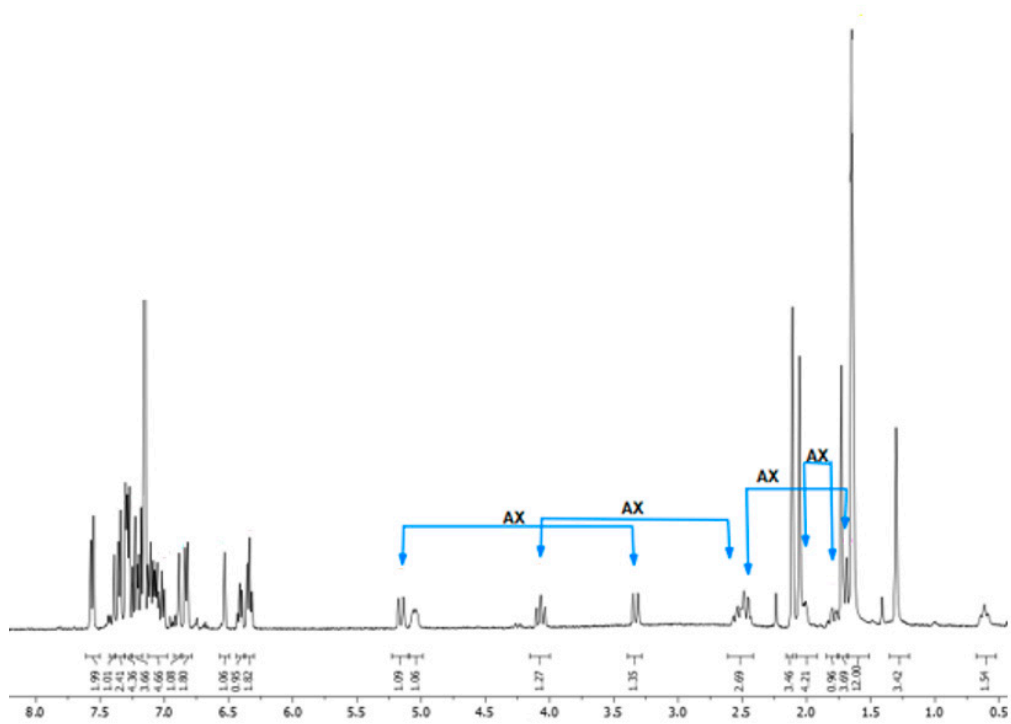


Figure S5A. ^1H NMR spectrum of **4** in C_6D_6 .

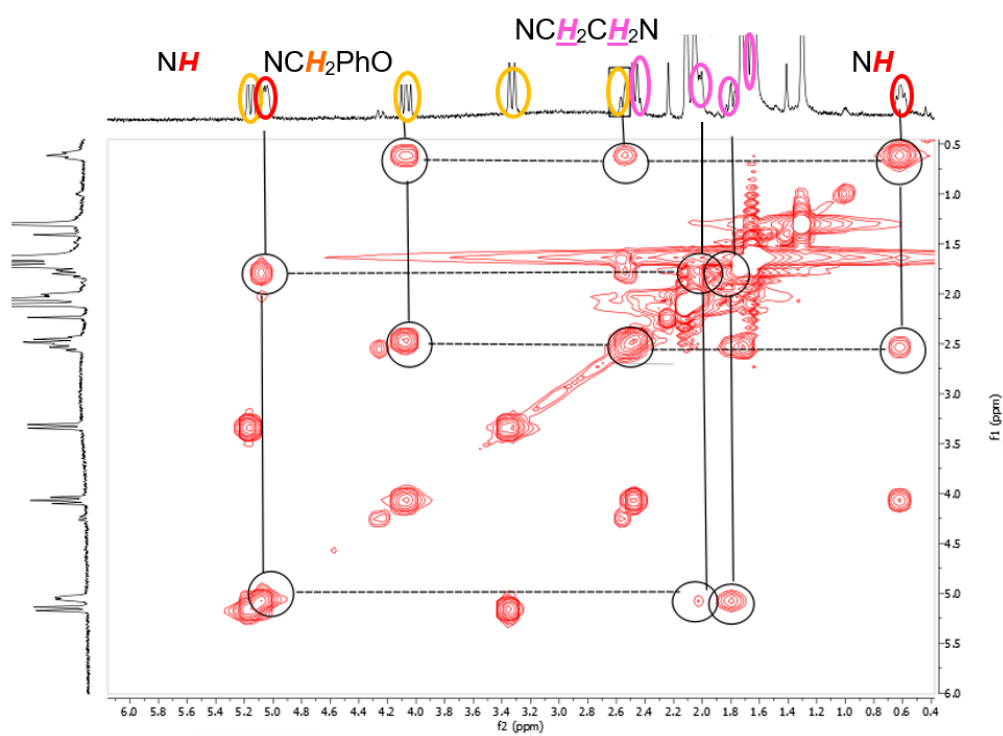


Figure S5B. ^1H - ^1H COSY NMR spectrum of **4** in C_6D_6

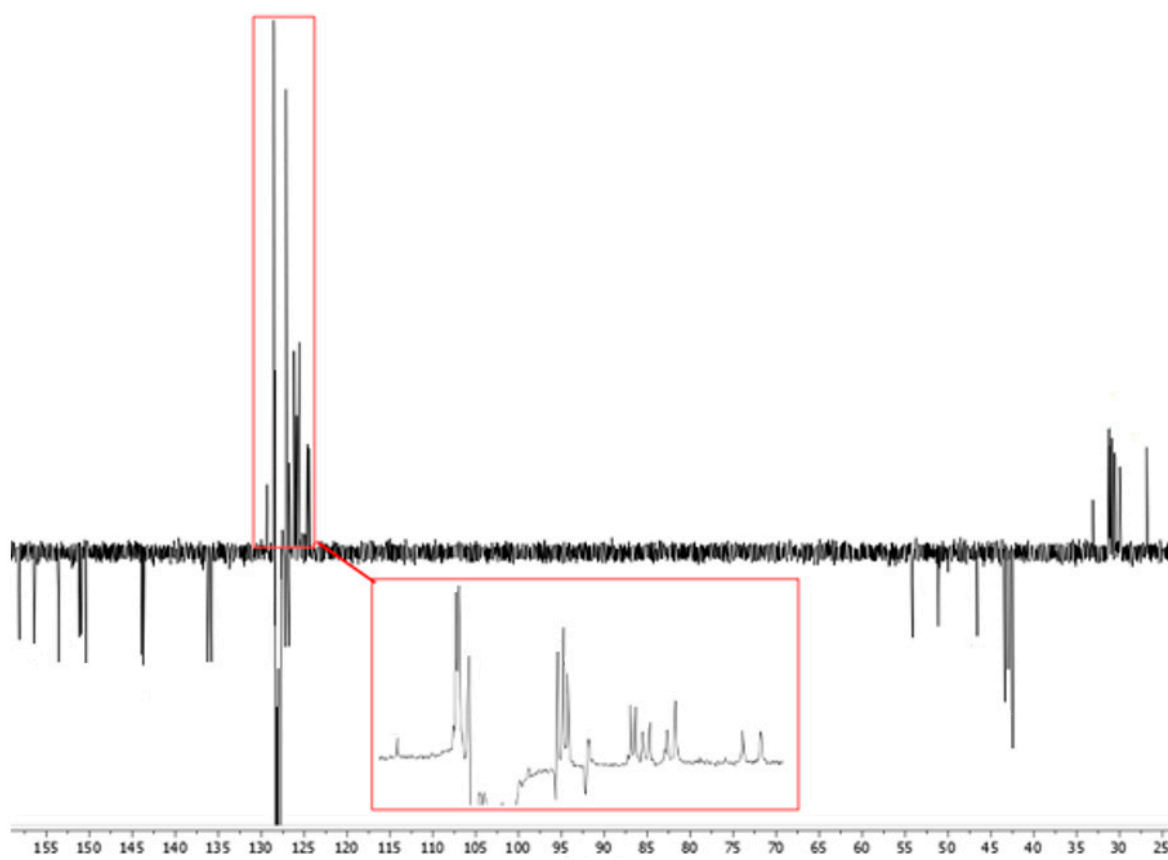


Figure S5C. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** in C_6D_6 .

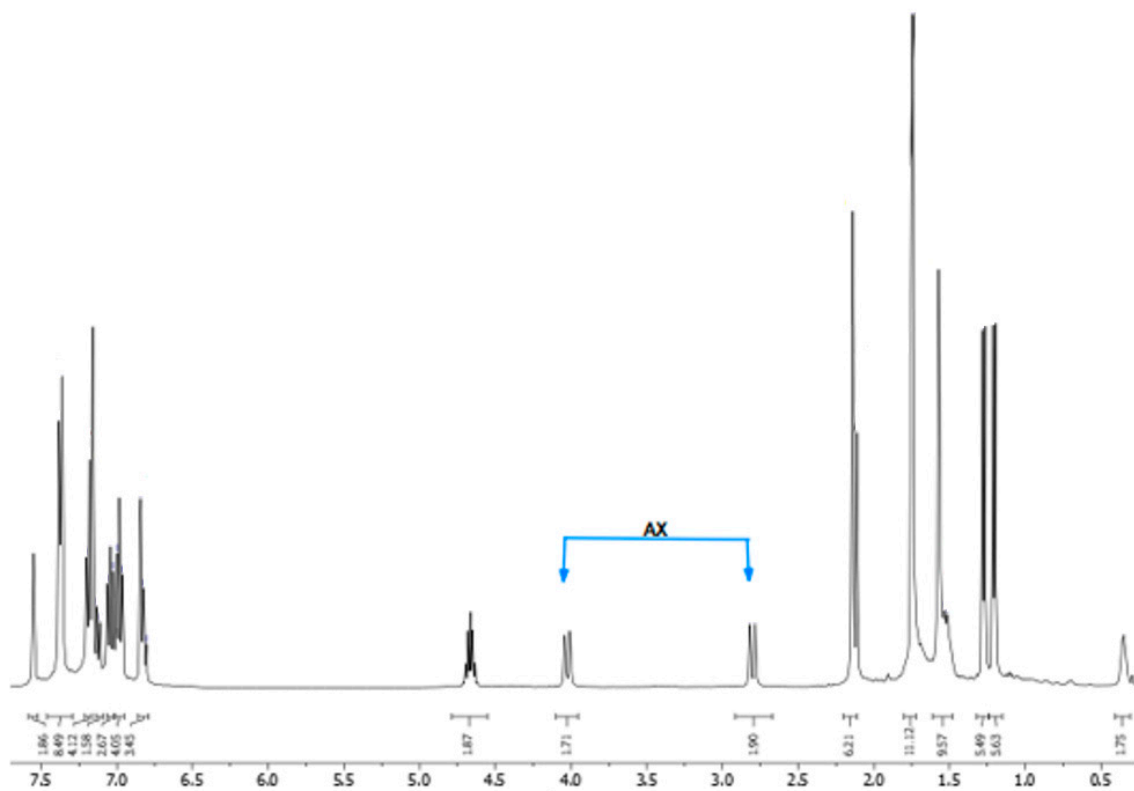


Figure S6A. ¹H NMR spectrum of 5 in C₆D₆.

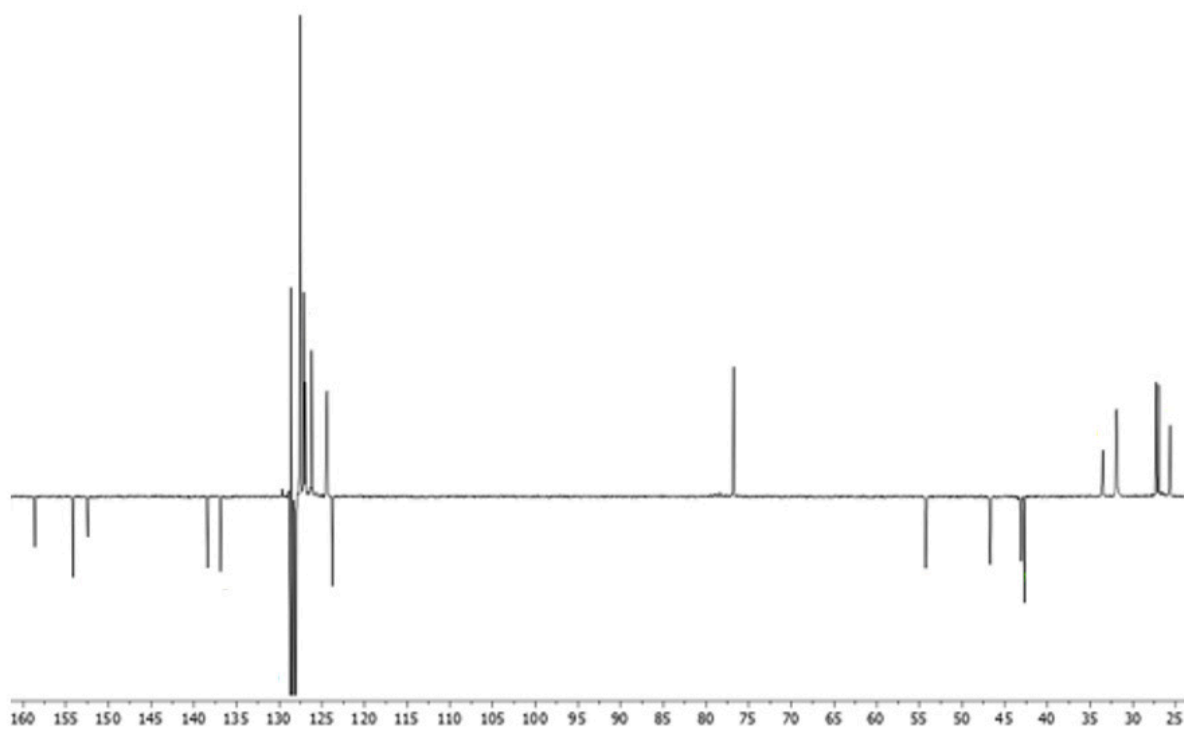


Figure S6B. ¹³C{¹H} NMR spectrum of 5 in C₆D₆.

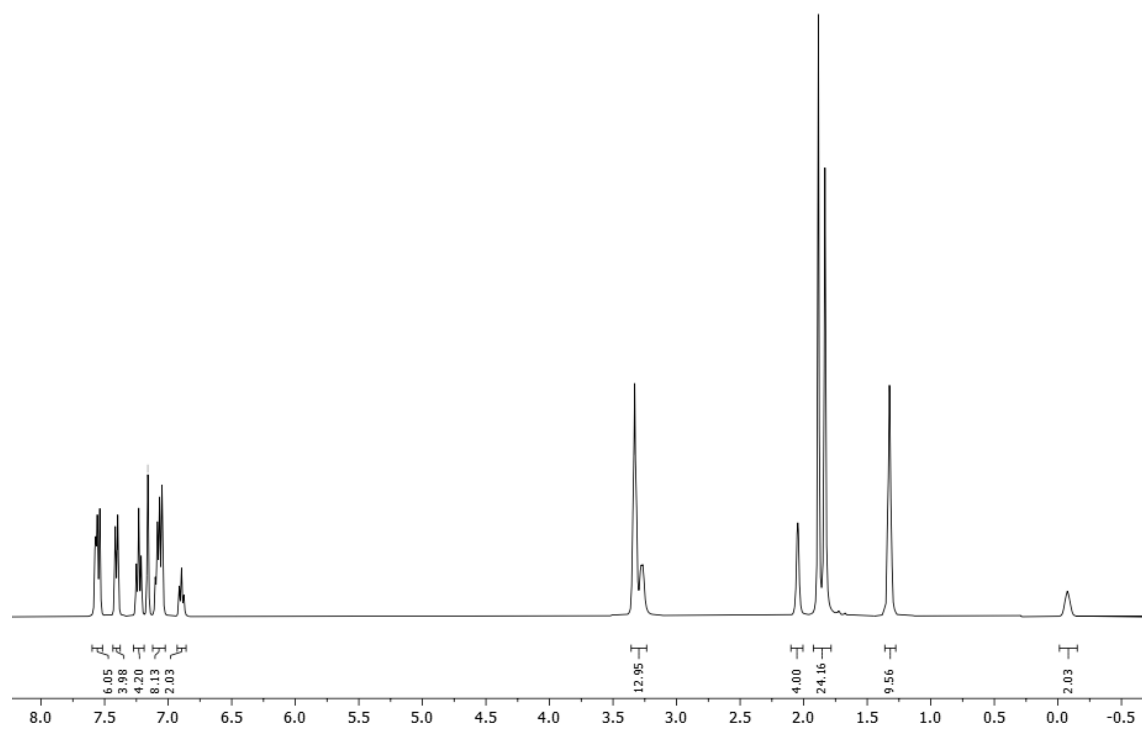


Figure S7A. ^1H NMR spectrum of **6** in C_6D_6 .

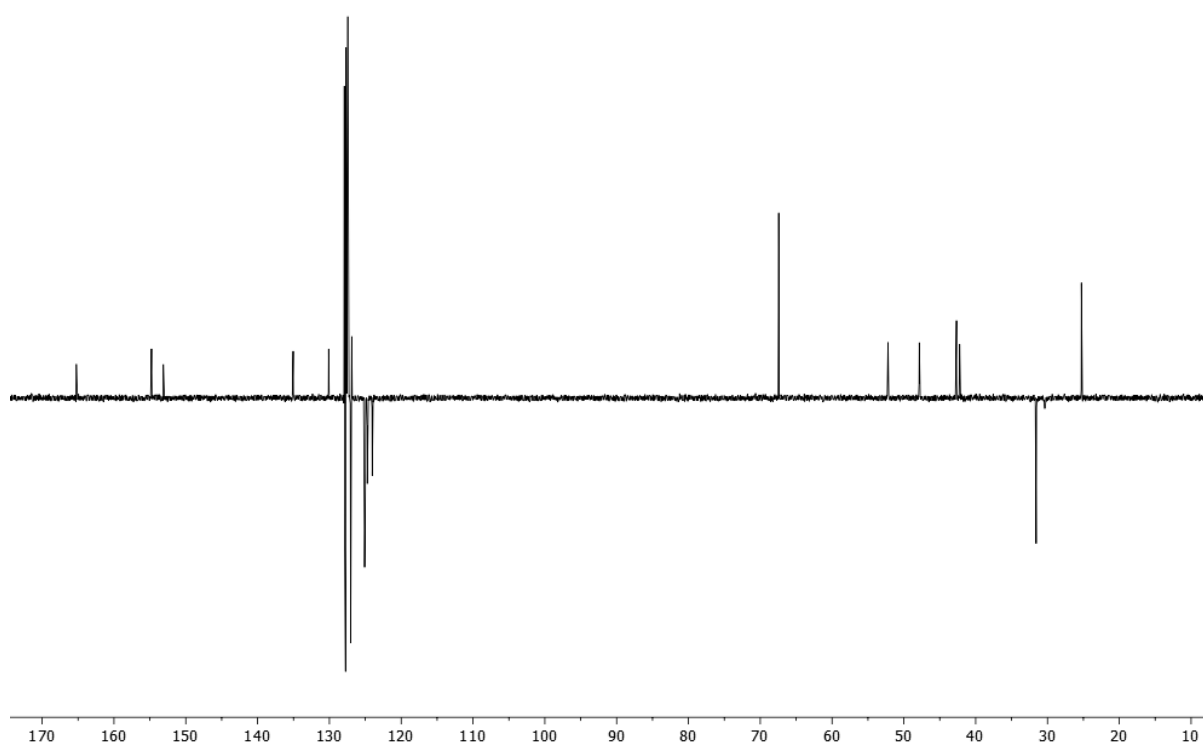


Figure S7B. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** in C_6D_6 .

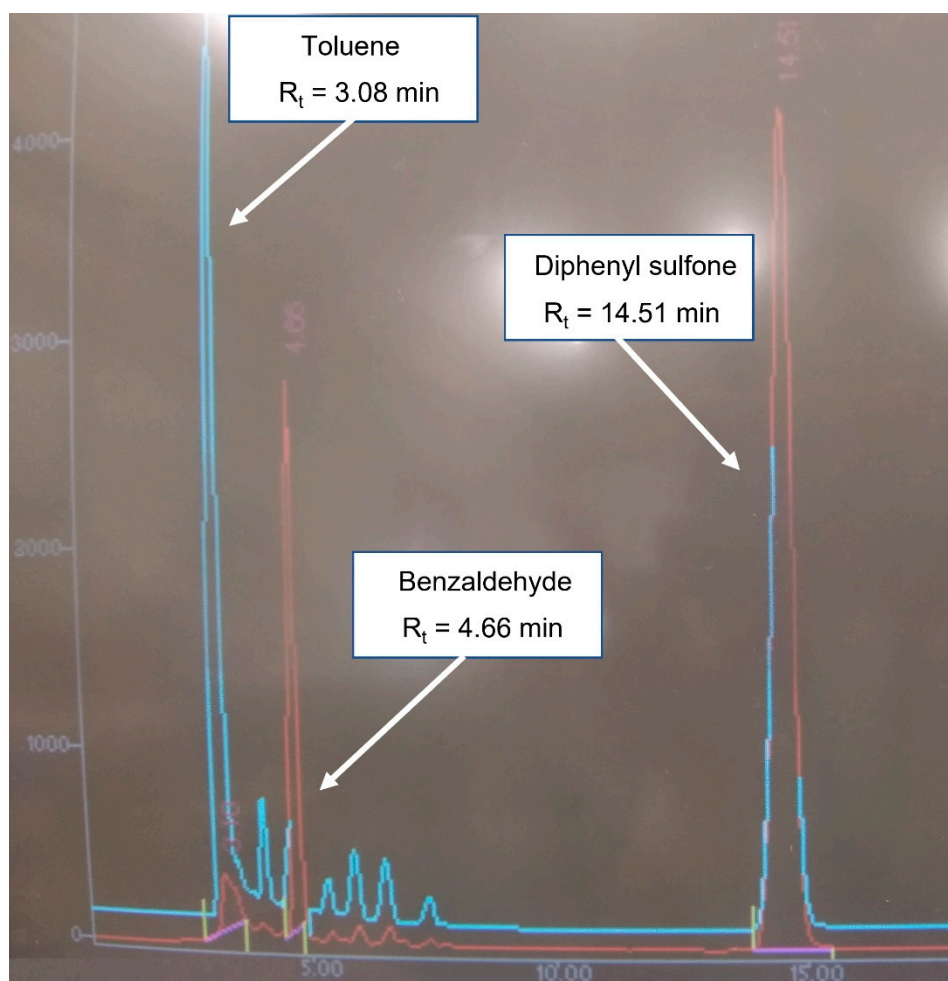


Figure S8. HPLC spectra of the products obtained after 4 h at 55 °C in the absence (blue) and in the presence (red) of TEMPO (Table 1, entries 2 and 3, respectively).