

Phenylthiophene-dipicolinic acid-based emitters with strong solution blue and solid state green emission

Ana de Bettencourt-Dias, Andrei Poloukhine.*

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Crystal structure determinations

Crystal data, data collection and refinement details for compound **1** are given in the Supplementary information in Table S1 and selected bond lengths are given in Table S2. A suitable crystal was mounted on a glass fiber and placed in the low-temperature nitrogen stream. Data were collected on a Bruker SMART CCD area detector diffractometer equipped with a low-temperature device,⁵ using graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å). Data were measured using omega scans of 0.3° per frame and a full sphere of data was collected, for a total of 1850 frames. The first 50 frames were recollected at the end of data collection to monitor for decay. Multi-scan absorption corrections were applied using SADABS.⁶ Cell parameters were retrieved using SMART⁷ software and refined using SAINTPlus⁸ on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus⁸ software. The structures were solved by direct methods and refined by least square methods on F^2 using the SHELXTL⁹ program package. All non-hydrogen atoms were refined anisotropically. The majority of the hydrogen atoms were added geometrically and their parameters constrained to the parent site. The X-ray crystallographic information file CCDC 296287 can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Powder data were collected on a Bruker D8 Advance (Cu-K α radiation, $5-60^\circ$, 0.01° step, 0.5° s/step).

Calculations

DFT calculations were performed using the B3LYP method with the 6-31G(d) basis set. The geometries of the three compounds were optimized with **1** and **2** constrained to the C_i point group

and **3** without constraints. The initial geometries were derived from the conformation of **1** obtained by single crystal X-ray diffraction. Gaussian 03 was utilized for all calculations.¹⁰

Table S1. Crystallographic details for compound **1**.

Compound	1
CCDC number	296287
Formula	C ₄₄ H ₅₂ N ₆ O ₄ S ₂
M/g mol ⁻¹	793.04
Crystal system	Monoclinic
Space group	<i>P2₁/c</i>
<i>a</i> /Å	15.224(3)
<i>b</i> /Å	8.9383(18)
<i>c</i> /Å	17.234(3)
β ^o	114.36(3)
<i>V</i> / Å ³	2136.4(7)
<i>T</i> /K	100(2)
<i>Z</i>	2
<i>D_c</i> /g cm ⁻³	1.233
μ (Mo-K α)/mm ⁻¹	0.173
Independent reflections, <i>R</i> _{int} [<i>F</i> _o ≥4σ(<i>F</i> _o)]	5313, 0.0800
Reflections collected	21847
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> >2σ(<i>I</i>))	0.0575, 0.1231
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1055, 0.1436
Largest diff. peak and hole/Å ⁻³	0.969, -0.398

Table S2. Bond lengths [Å] and angles [°] for **1**.

C(1)-C(2)	1.357(3)	C(12)-H(12)	0.9500
C(1)-C(10)	1.466(3)	C(13)-O(1)	1.231(3)
C(1)-S(1)	1.727(2)	C(13)-N(2)	1.348(3)
C(2)-C(3)	1.402(3)	C(14)-O(2)	1.233(3)
C(2)-H(2)	0.9500	C(14)-N(3)	1.349(3)
C(3)-C(4)	1.362(3)	C(15)-N(2)	1.470(3)
C(3)-H(3)	0.9500	C(15)-C(16)	1.527(4)
C(4)-C(7)	1.459(3)	C(15)-H(15A)	0.9900
C(4)-S(1)	1.733(2)	C(15)-H(15B)	0.9900
C(5)-N(1)	1.344(3)	C(16)-H(16A)	0.9800
C(5)-C(6)	1.383(3)	C(16)-H(16B)	0.9800
C(5)-C(13)	1.512(3)	C(16)-H(16C)	0.9800
C(6)-C(7)	1.396(3)	C(17)-N(2)	1.461(3)
C(6)-H(6)	0.9500	C(17)-C(18)	1.515(4)
C(7)-C(8)	1.400(3)	C(17)-H(17A)	0.9900
C(8)-C(9)	1.383(3)	C(17)-H(17B)	0.9900
C(8)-H(8)	0.9500	C(18)-H(18A)	0.9800
C(9)-N(1)	1.341(3)	C(18)-H(18B)	0.9800
C(9)-C(14)	1.507(3)	C(18)-H(18C)	0.9800
C(10)-C(11)	1.399(3)	C(19)-N(3)	1.462(3)
C(10)-C(12)	1.400(3)	C(19)-C(20)	1.515(4)
C(11)-C(12)#1	1.383(3)	C(19)-H(19A)	0.9900
C(11)-H(11)	0.9500	C(19)-H(19B)	0.9900
C(12)-C(11)#1	1.383(3)	C(20)-H(20A)	0.9800

C(20)-H(20B)	0.9800	C(7)-C(6)-H(6)	120.1
C(20)-H(20C)	0.9800	C(6)-C(7)-C(8)	116.8(2)
C(21)-N(3)	1.469(3)	C(6)-C(7)-C(4)	121.0(2)
C(21)-C(22)	1.513(4)	C(8)-C(7)-C(4)	122.1(2)
C(21)-H(21A)	0.9900	C(9)-C(8)-C(7)	119.6(2)
C(21)-H(21B)	0.9900	C(9)-C(8)-H(8)	120.2
C(22)-H(22A)	0.9800	C(7)-C(8)-H(8)	120.2
C(22)-H(22B)	0.9800	N(1)-C(9)-C(8)	123.3(2)
C(22)-H(22C)	0.9800	N(1)-C(9)-C(14)	116.91(19)
		C(8)-C(9)-C(14)	119.2(2)
C(2)-C(1)-C(10)	127.7(2)	C(11)-C(10)-C(12)	119.0(2)
C(2)-C(1)-S(1)	110.42(18)	C(11)-C(10)-C(1)	119.6(2)
C(10)-C(1)-S(1)	121.92(18)	C(12)-C(10)-C(1)	121.4(2)
C(1)-C(2)-C(3)	113.6(2)	C(12)#1-C(11)-C(10)	120.5(2)
C(1)-C(2)-H(2)	123.2	C(12)#1-C(11)-H(11)	119.8
C(3)-C(2)-H(2)	123.2	C(10)-C(11)-H(11)	119.8
C(4)-C(3)-C(2)	113.7(2)	C(11)#1-C(12)-C(10)	120.5(2)
C(4)-C(3)-H(3)	123.1	C(11)#1-C(12)-H(12)	119.7
C(2)-C(3)-H(3)	123.1	C(10)-C(12)-H(12)	119.7
C(3)-C(4)-C(7)	128.3(2)	O(1)-C(13)-N(2)	123.2(2)
C(3)-C(4)-S(1)	109.96(18)	O(1)-C(13)-C(5)	117.5(2)
C(7)-C(4)-S(1)	121.70(17)	N(2)-C(13)-C(5)	119.3(2)
N(1)-C(5)-C(6)	123.2(2)	O(2)-C(14)-N(3)	122.9(2)
N(1)-C(5)-C(13)	118.17(19)	O(2)-C(14)-C(9)	118.0(2)
C(6)-C(5)-C(13)	118.5(2)	N(3)-C(14)-C(9)	118.9(2)
C(5)-C(6)-C(7)	119.7(2)	N(2)-C(15)-C(16)	112.6(2)
C(5)-C(6)-H(6)	120.1	N(2)-C(15)-H(15A)	109.1

C(16)-C(15)-H(15A)	109.1	H(19A)-C(19)-H(19B)	107.9
N(2)-C(15)-H(15B)	109.1	C(19)-C(20)-H(20A)	109.5
C(16)-C(15)-H(15B)	109.1	C(19)-C(20)-H(20B)	109.5
H(15A)-C(15)-H(15B)	107.8	H(20A)-C(20)-H(20B)	109.5
C(15)-C(16)-H(16A)	109.5	C(19)-C(20)-H(20C)	109.5
C(15)-C(16)-H(16B)	109.5	H(20A)-C(20)-H(20C)	109.5
H(16A)-C(16)-H(16B)	109.5	H(20B)-C(20)-H(20C)	109.5
C(15)-C(16)-H(16C)	109.5	N(3)-C(21)-C(22)	109.9(2)
H(16A)-C(16)-H(16C)	109.5	N(3)-C(21)-H(21A)	109.7
H(16B)-C(16)-H(16C)	109.5	C(22)-C(21)-H(21A)	109.7
N(2)-C(17)-C(18)	113.3(2)	N(3)-C(21)-H(21B)	109.7
N(2)-C(17)-H(17A)	108.9	C(22)-C(21)-H(21B)	109.7
C(18)-C(17)-H(17A)	108.9	H(21A)-C(21)-H(21B)	108.2
N(2)-C(17)-H(17B)	108.9	C(21)-C(22)-H(22A)	109.5
C(18)-C(17)-H(17B)	108.9	C(21)-C(22)-H(22B)	109.5
H(17A)-C(17)-H(17B)	107.7	H(22A)-C(22)-H(22B)	109.5
C(17)-C(18)-H(18A)	109.5	C(21)-C(22)-H(22C)	109.5
C(17)-C(18)-H(18B)	109.5	H(22A)-C(22)-H(22C)	109.5
H(18A)-C(18)-H(18B)	109.5	H(22B)-C(22)-H(22C)	109.5
C(17)-C(18)-H(18C)	109.5	C(9)-N(1)-C(5)	117.19(19)
H(18A)-C(18)-H(18C)	109.5	C(13)-N(2)-C(17)	125.5(2)
H(18B)-C(18)-H(18C)	109.5	C(13)-N(2)-C(15)	117.9(2)
N(3)-C(19)-C(20)	111.7(2)	C(17)-N(2)-C(15)	116.2(2)
N(3)-C(19)-H(19A)	109.3	C(14)-N(3)-C(19)	124.8(2)
C(20)-C(19)-H(19A)	109.3	C(14)-N(3)-C(21)	118.1(2)
N(3)-C(19)-H(19B)	109.3	C(19)-N(3)-C(21)	116.8(2)
C(20)-C(19)-H(19B)	109.3	C(1)-S(1)-C(4)	92.26(11)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+2

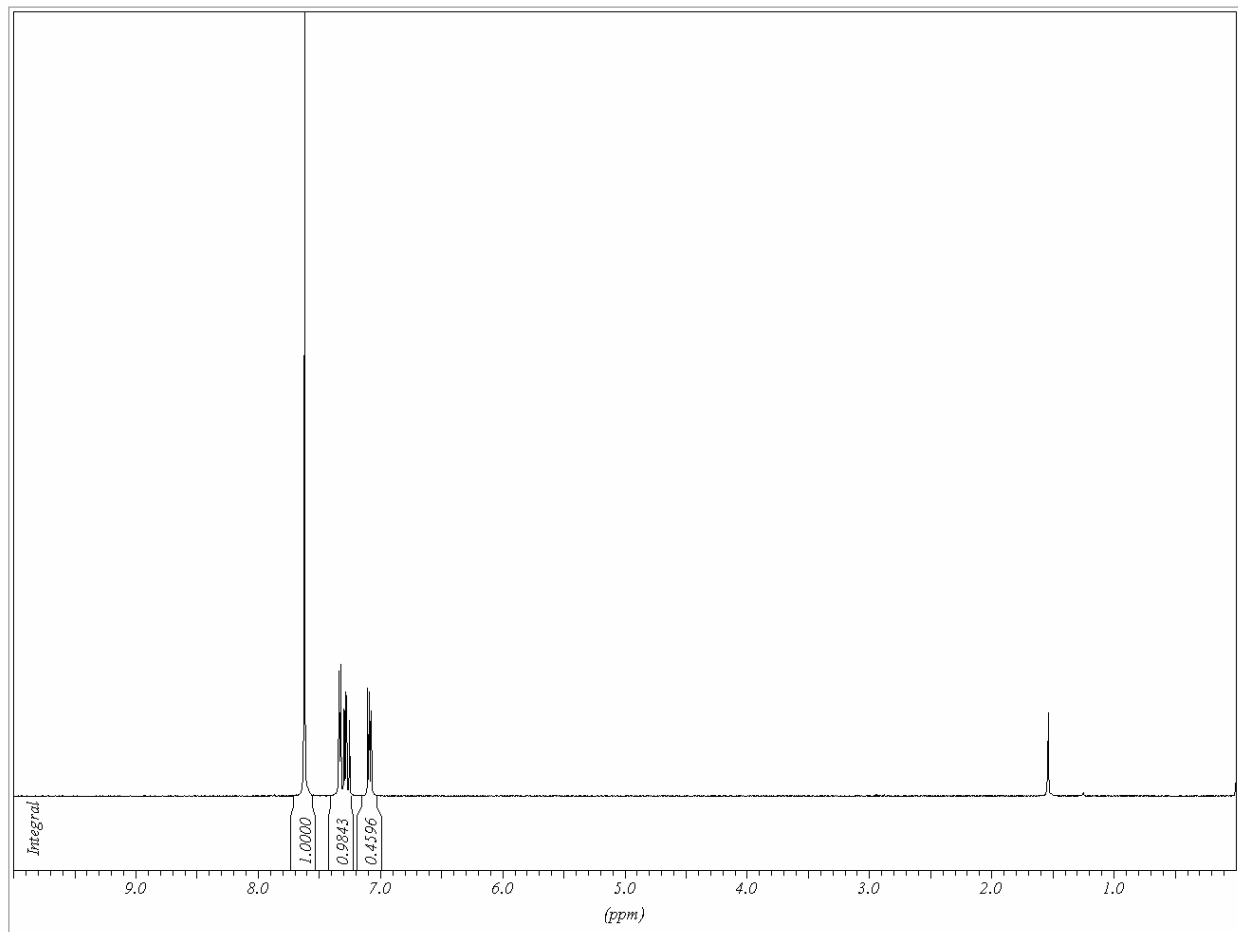


Figure S1. ¹H-NMR spectrum of compound **a** in CDCl₃. Peak at 1.535 ppm is water.

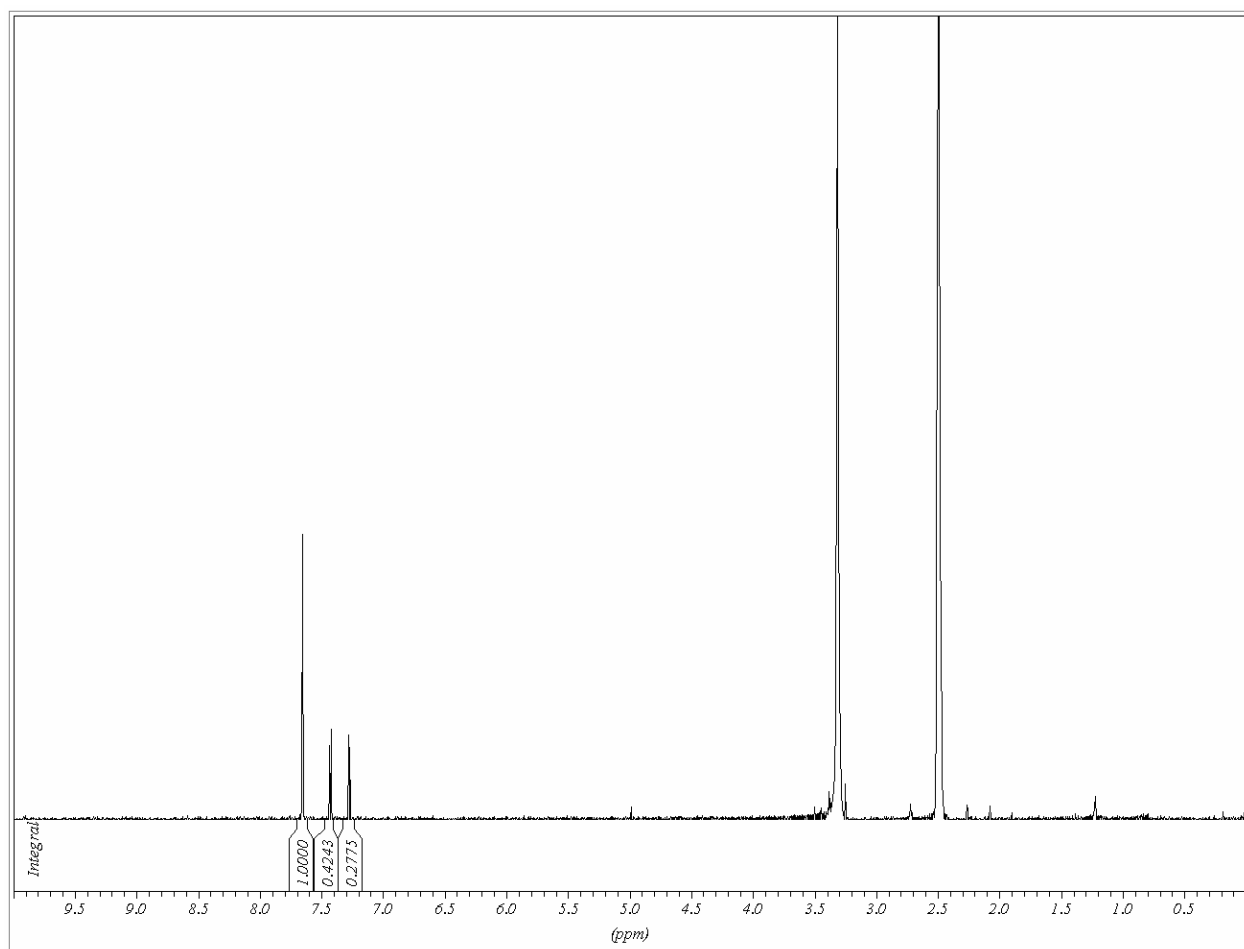


Figure S2. ¹H-NMR spectrum of compound **a** in *d*⁶-DMSO. Peak at 3.248 ppm is water.

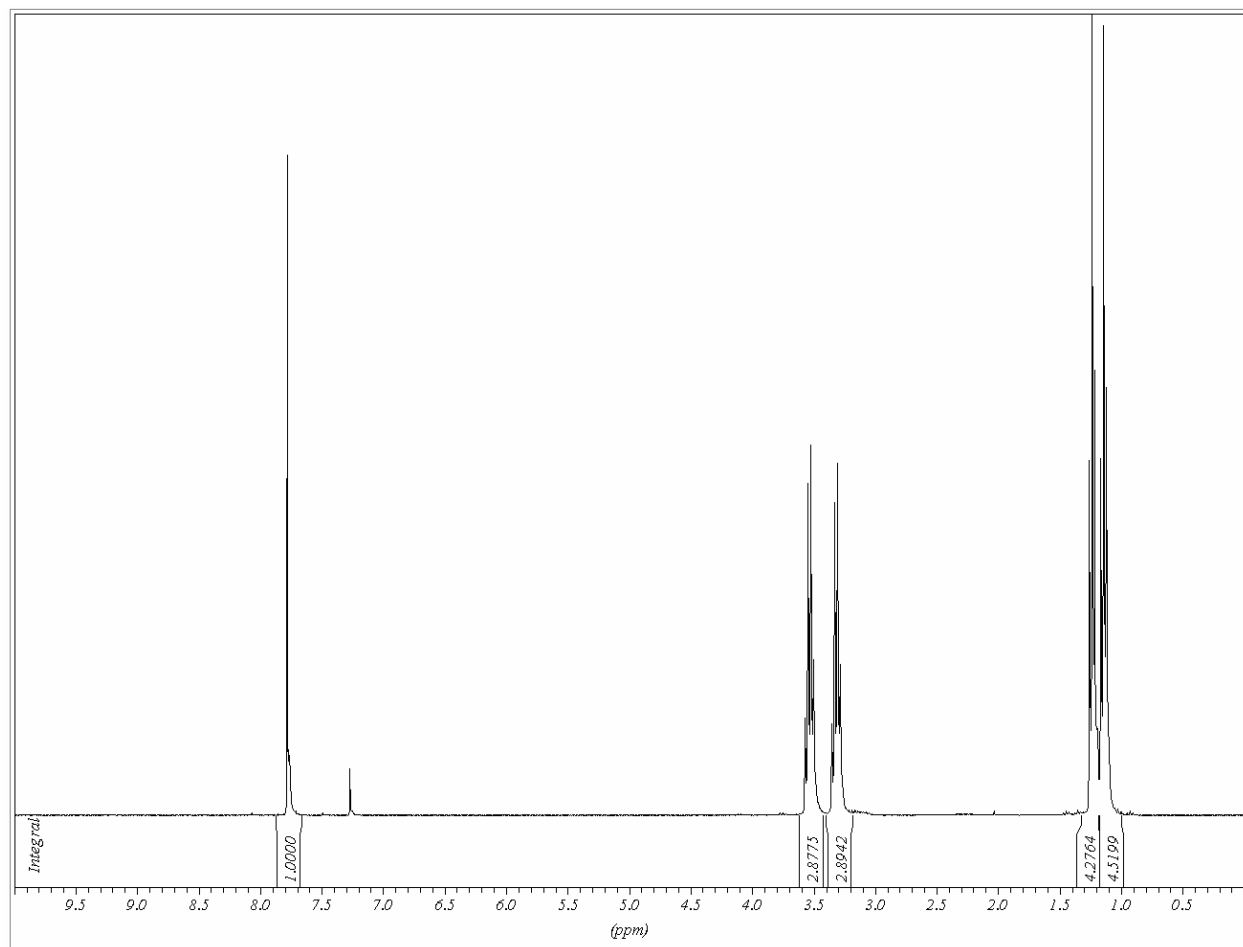


Figure S3. $^1\text{H-NMR}$ spectrum of compound **d** in CDCl_3 .

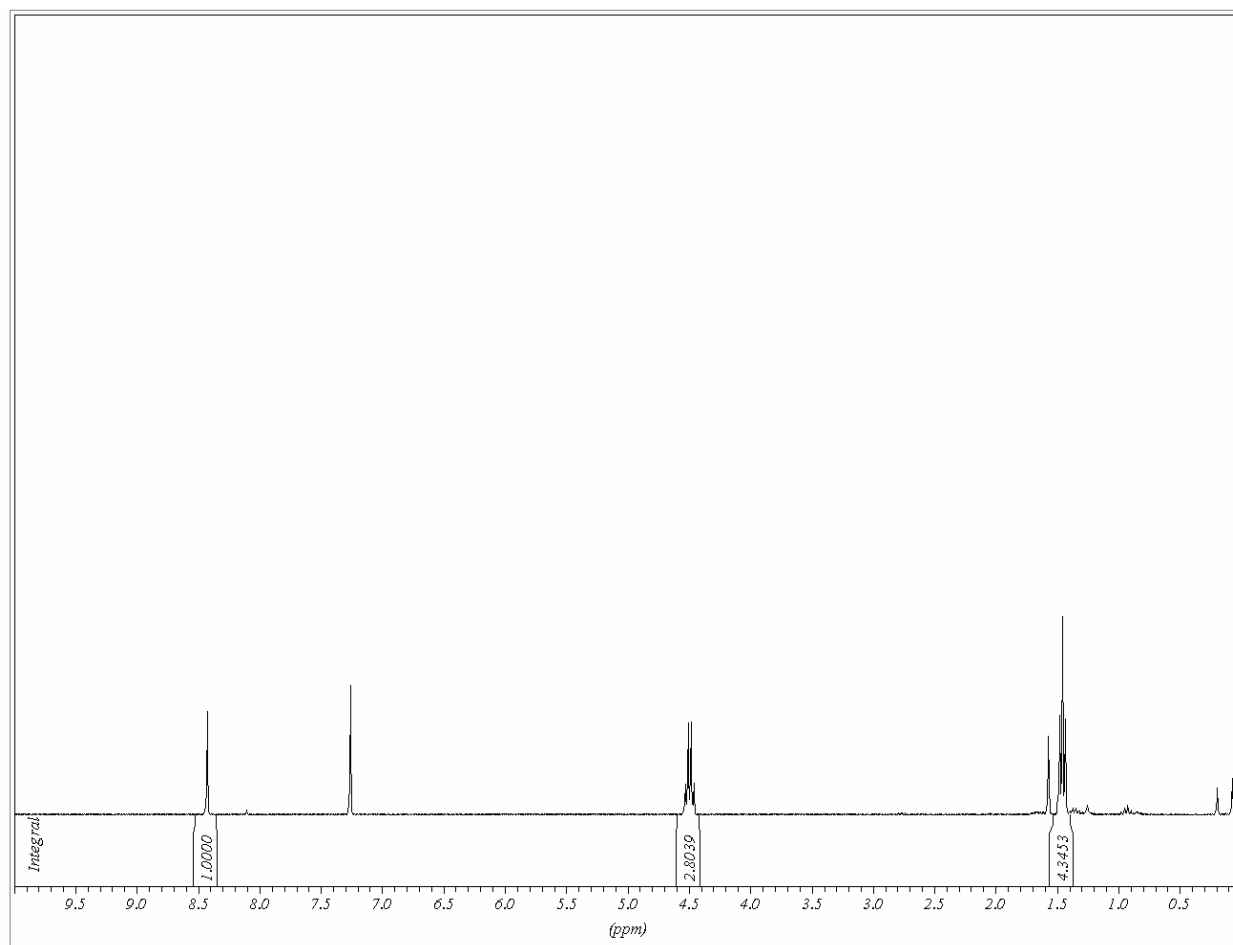


Figure S4. $^1\text{H-NMR}$ spectrum of compound **e** in CDCl_3 .

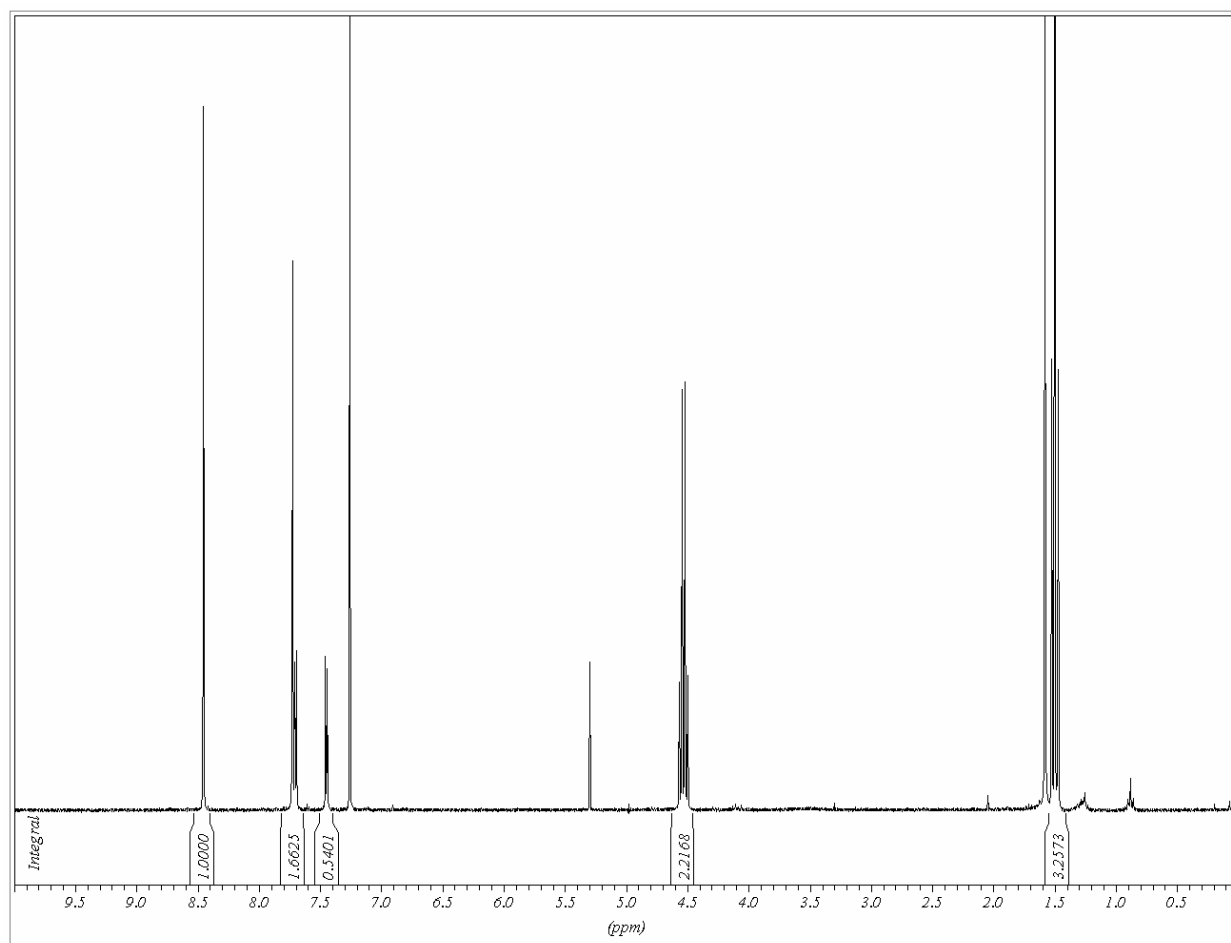


Figure S5. ¹H-NMR of compound **1** in CDCl₃. Peaks not integrated correspond to water at 1.579 ppm and 5.2995 ppm for CH₂Cl₂.

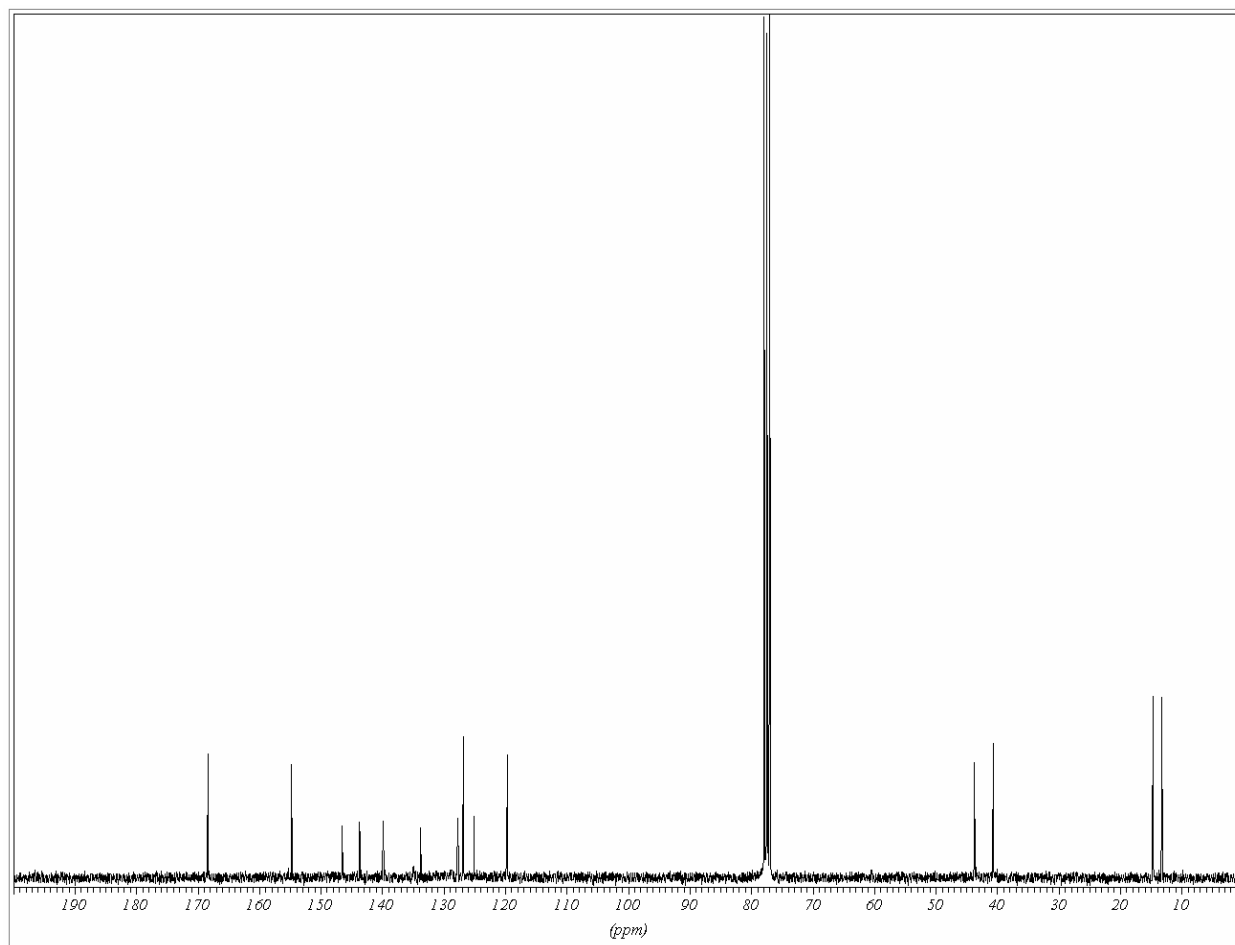


Figure S6. ^{13}C -NMR of compound **1** in CDCl_3 .

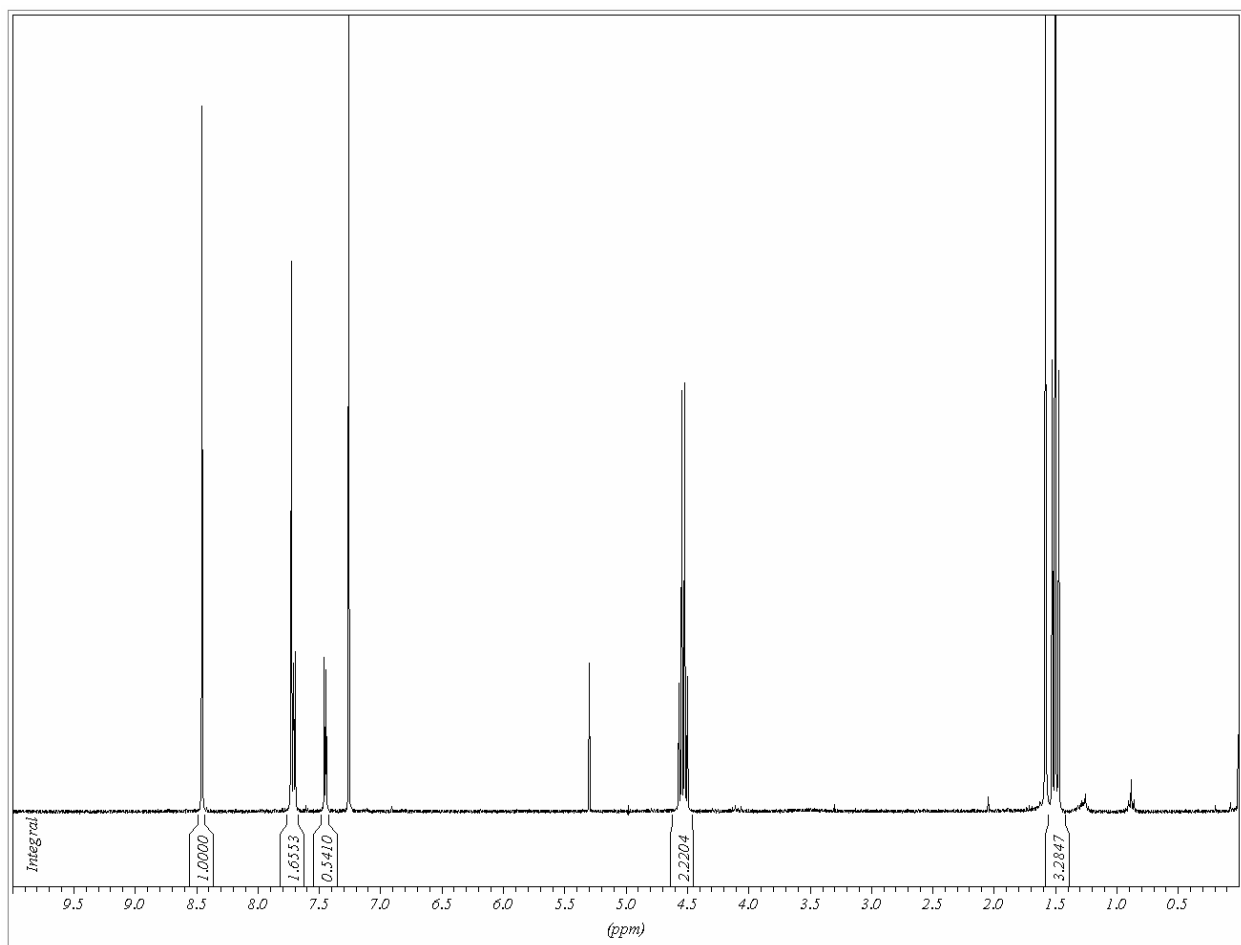


Figure S7. ¹H-NMR of compound **2** in CDCl₃. Peaks not integrated correspond to water at 1.579 ppm and 5.2995 ppm for CH₂Cl₂.

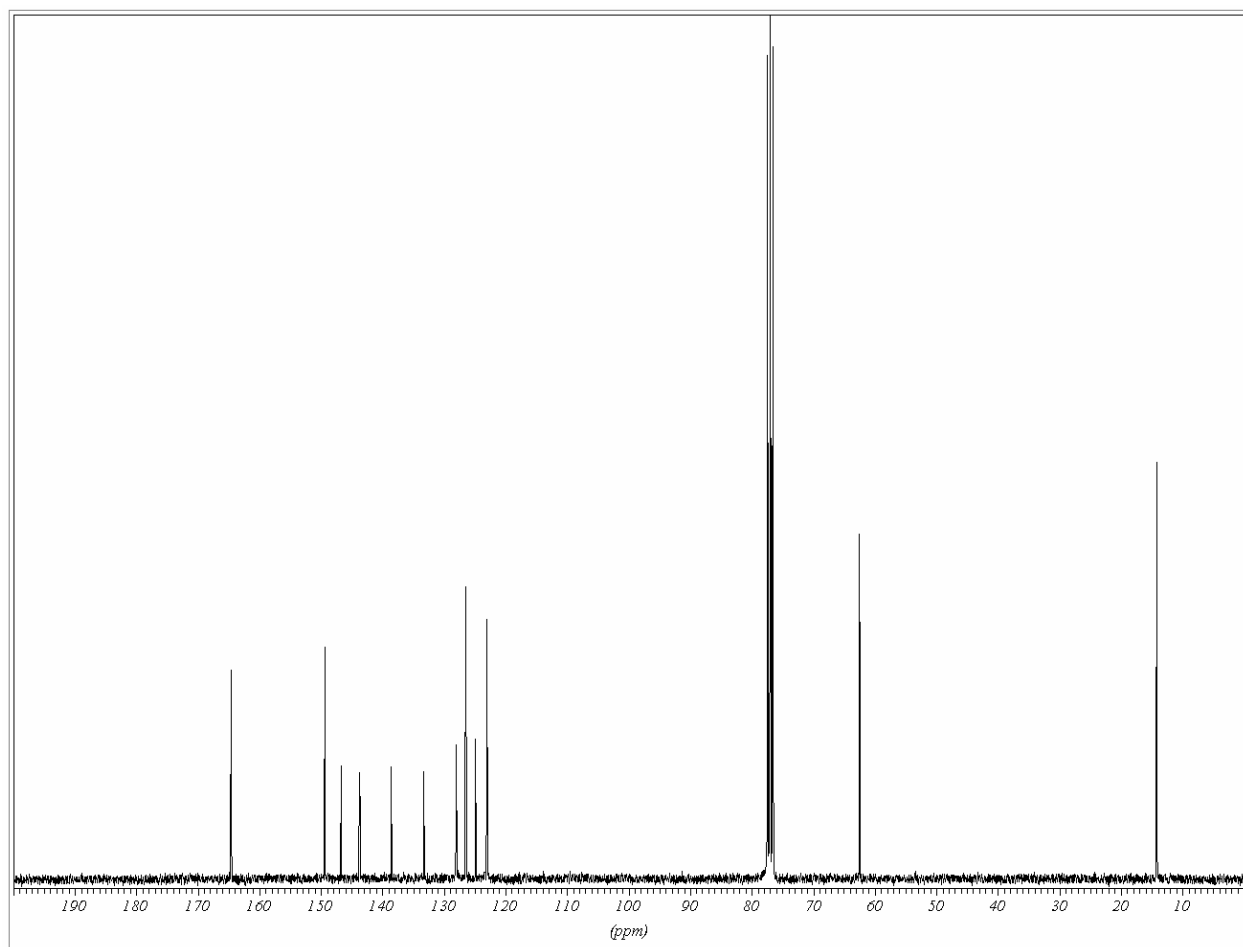


Figure S8. ^{13}C -NMR of compound 2 in CDCl_3 .

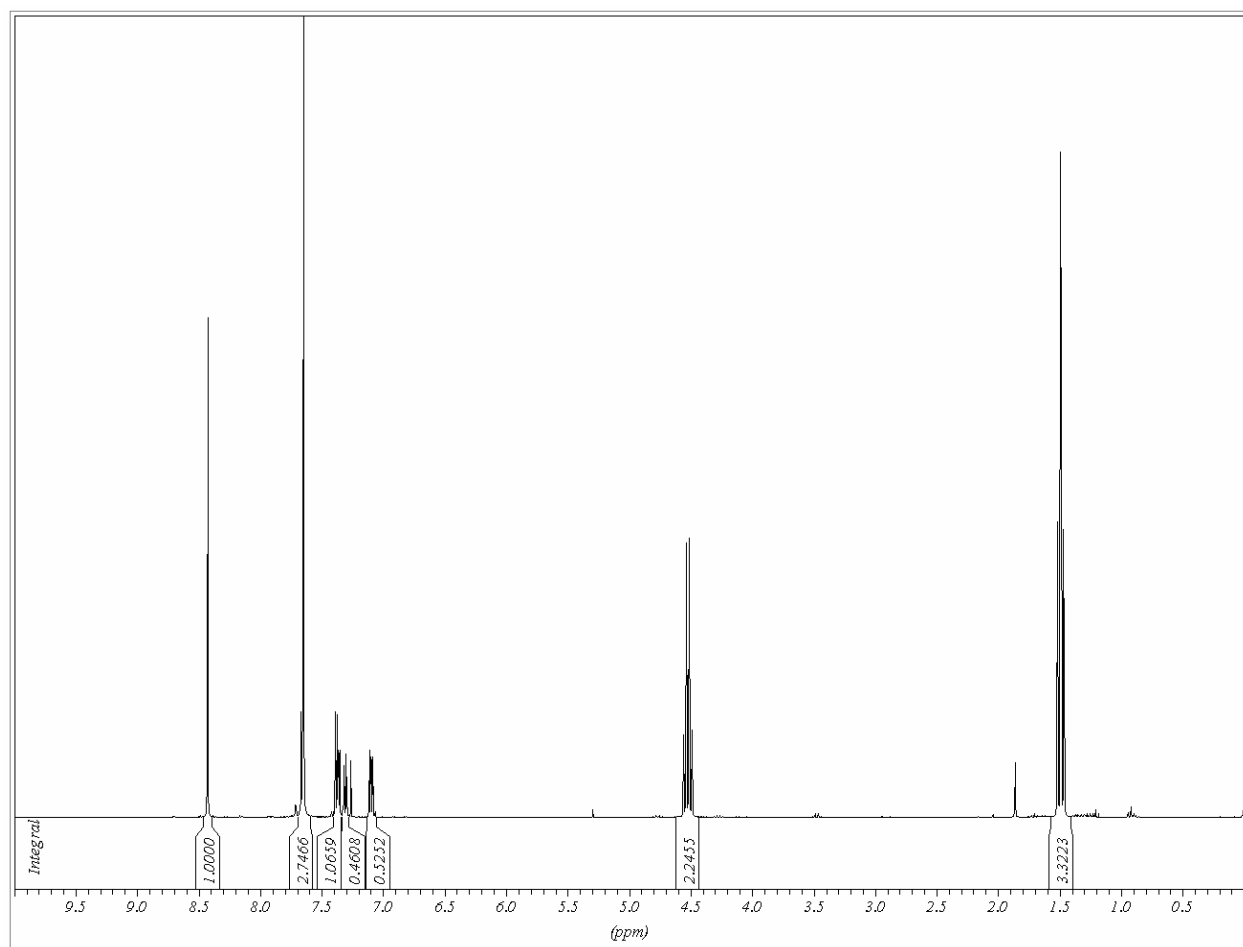


Figure S9. ¹H-NMR of compound **3** in CDCl₃.

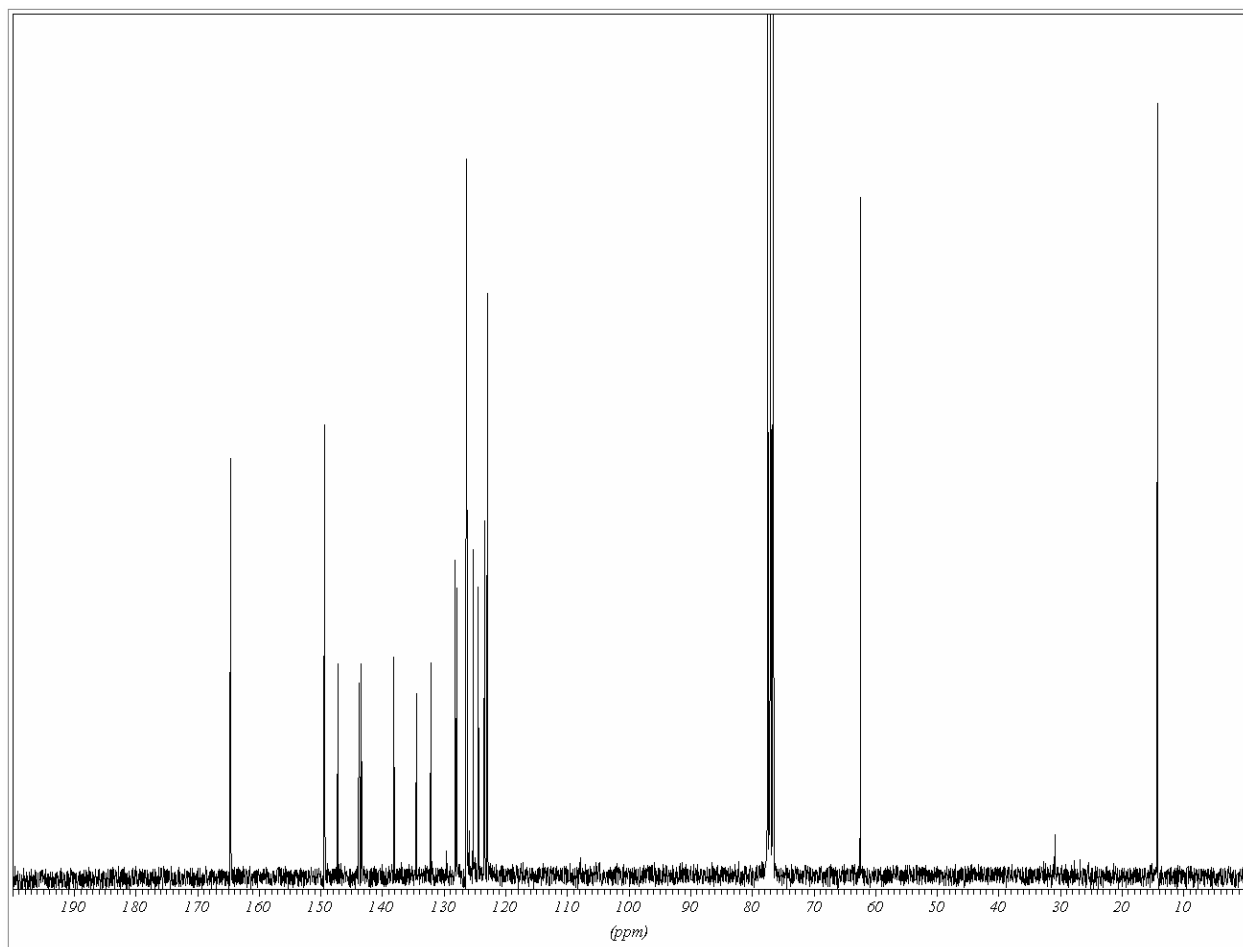


Figure S10. ^{13}C -NMR of compound **3** in CDCl_3 .

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