

Supplementary material

For

Pyridine–Quinoline and Biquinoline–based Ruthenium *p*-cymene complexes as efficient catalysts for transfer hydrogenation studies: Synthesis and Structural Characterization

Nikolaos Zacharopoulos¹, Gregor Schnakenburg², Eleni I. Panagopoulou³, Nikolaos S. Thomaidis³ and Athanassios I. Philippopoulos^{1,*}

¹ Laboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou 15771, Athens, Greece.

² Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany.

³ Laboratory of Analytical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece.

Correspondence

Athanassios. I. Philippopoulos, Laboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou 15771, Athens, Greece. E-mail: atphilip@chem.uoa.gr

Table of Contents

Entry	
1) Figure S1	^1H NMR spectrum of 8-Mepq in CDCl_3
2) Figure S2	$^{13}\text{C}\{^1\text{H}\}$ -NMR of 8-Mepq in CDCl_3
3) Figure S3	^1H -NMR spectrum of 6'-Mepq in CDCl_3
4) Figure S4	$^{13}\text{C}\{^1\text{H}\}$ -NMR of 6'-Mepq in CDCl_3
5) Figure S5	^1H -NMR spectrum of 8,6'-Me₂pq in CDCl_3
6) Figure S6	$^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of 8,6'-Me₂pq in CDCl_3
7) Figure S7	^1H -NMR spectrum of 4,6'-Me₂pq in CDCl_3
8) Figure S8	^1H - ^1H COSY spectrum of 4,6'-Me₂pq in CDCl_3
9) Figure S9	$^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of 4,6'-Me₂pq in CDCl_3
10) Figure S10	HSQC spectrum of 4,6'-Me₂pq in CDCl_3
11) Figure S11	HMBC spectrum of 4,6'-Me₂pq in CDCl_3
12) Figure S12	^1H -NMR spectrum of pq in CDCl_3
13) Figure S13	ESI-HRMS of 8-Mepq in methanol
14) Figure S14	ESI-HRMS of 6'-Mepq in methanol
15) Figure S15	ESI-HRMS of 8,6'-Me₂pq in methanol
16) Figure S16	Intermolecular interactions in the unit cell of 8-Mepq
17) Figure S17	Intermolecular interactions in the unit cell of 4,6'-Me₂pq
18) Figure S18	Intermolecular interactions in the unit cell of 8,6'-Me₂pq
19) Figure S19	FT-IR spectrum of 1
20) Figure S20	FT-IR spectrum of 2
21) Figure S21	FT-IR spectrum of 3
22) Figure S22	FT-IR spectrum of 4
23) Figure S23	FT-IR spectrum of 5
24) Figure S24	FT-IR spectrum of 6

25) Figure S25	FT-IR spectrum of 8
26) Figure S26	^1H -NMR spectrum of 1 in $(\text{CD}_3)_2\text{CO}$
27) Figure S27	^1H - ^1H COSY spectrum of 1 in $(\text{CD}_3)_2\text{CO}$
28) Figure S28	$^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of 1 in $(\text{CD}_3)_2\text{CO}$
29) Figure S29	^1H - ^{13}C -HSQC spectrum of 1 in $(\text{CD}_3)_2\text{CO}$
30) Figure S30	^1H -NMR spectrum of 2 in $(\text{CD}_3)_2\text{CO}$
31) Figure S31	^1H - ^1H COSY spectrum of 2 in $(\text{CD}_3)_2\text{CO}$
32) Figure S32	$^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of 2 in $(\text{CD}_3)_2\text{CO}$
33) Figure S33	^1H - ^{13}C -HSQC spectrum of 2 in $(\text{CD}_3)_2\text{CO}$
34) Figure S34	^1H - ^1H COSY spectrum of 3 in $(\text{CD}_3)_2\text{CO}$
35) Figure S35	^1H - ^1H COSY spectrum of 4 in $(\text{CD}_3)_2\text{CO}$
36) Figure S36	$^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of 4 in $(\text{CD}_3)_2\text{CO}$
37) Figure S37	^1H - ^{13}C -HSQC spectrum of 4 in $(\text{CD}_3)_2\text{CO}$
38) Figure S38	^1H -NMR spectrum of 5 in $(\text{CD}_3)_2\text{CO}$
39) Figure S39	^1H - ^1H COSY spectrum of 5 in $(\text{CD}_3)_2\text{CO}$
40) Figure S40	$^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of 5 in $(\text{CD}_3)_2\text{CO}$
41) Figure S41	^1H - ^{13}C -HSQC spectrum of 5 in $(\text{CD}_3)_2\text{CO}$
42) Figure S42	^1H -NMR spectrum of Ru-pqcame in $(\text{CD}_3)_2\text{CO}$
43) Figure S43	^1H -NMR spectrum of 6 in $(\text{CD}_3)_2\text{CO}$
44) Figure S44	$^{13}\text{C}\{^1\text{H}\}$ -NMR of 6 in $(\text{CD}_3)_2\text{CO}$
45) Figure S45	^1H -NMR spectrum of 6-Cl in CDCl_3
46) Figure S46	^1H -NMR spectrum of 7-Cl in $(\text{CD}_3)_2\text{CO}$
47) Figure S47	^1H -NMR spectrum of 8 in $(\text{CD}_3)_2\text{CO}$
48) Figure S48	UV-vis spectrum of 1 in acetone
49) Figure S49	UV-vis spectrum of 2 in acetone
50) Figure S50	UV-vis spectrum of 3 in acetone
51) Figure S51	UV-vis spectrum of 4 in acetone
52) Figure S52	UV-vis spectrum of 5 in acetone
53) Figure S53	UV-vis spectrum of Ru-pqcame in acetone
54) Figure S54	UV-vis spectrum of 6 in acetone

55) Figure S55	UV-vis spectrum of 8 in acetone
56) Figure S56	Intermolecular interactions in the unit cell of 1
57) Figure S57	Intermolecular interactions in the unit cell of 4
58) Figure S58	Intermolecular interactions in the unit cell of 2
59) Figure S59	Intermolecular interactions in the unit cell of 6
60) Figure S60	Intermolecular interactions in the unit cell of 3
61) Figure S61	Molecular structure of the complex cation of 8 . Hydrogen atoms and the PF ₆ ⁻ anion are omitted for clarity. The ellipsoids were plotted at the 50% probability
62) Table S1	Selected improved crystallographic data for 8
63) Figure S62	Intermolecular interactions in the unit cell of 8
63) Figure S63	FT-IR spectrum of 9
64) Figure S64	FT-IR spectrum of 10
65) Figure S65	FT-IR spectrum of 11
66) Figure S66	¹ H-NMR spectrum of 9 in CDCl ₃
67) Figure S67	¹³ C{ ¹ H}-NMR spectrum of 9 in CDCl ₃
68) Figure S68	¹ H- ¹³ C-HSQC spectrum of 9 in CDCl ₃
69) Figure S69	¹ H- ¹ H COSY spectrum of 10 in CDCl ₃
70) Figure S70	¹³ C{ ¹ H}-NMR spectrum of 10 in CDCl ₃
71) Figure S71	¹ H- ¹³ C-HSQC spectrum of 10 in CDCl ₃
72) Figure S72	¹ H- ¹ H COSY spectrum of 11 in CDCl ₃
73) Figure S73	¹³ C{ ¹ H}-NMR spectrum of 11 in CDCl ₃
74) Figure S74	¹ H- ¹³ C-HSQC spectrum of 11 in CDCl ₃
75) Figure S75	UV-vis spectrum of 9 in CHCl ₃
76) Figure S76	UV-vis spectrum of 9 in H ₂ O
77) Figure S77	UV-vis spectrum of 10 in CHCl ₃
78) Figure S78	UV-vis spectrum of 10 in H ₂ O
79) Figure S79	UV-vis spectrum of 11 in CHCl ₃
80) Figure S80	Intermolecular interactions in the single crystal of 9
81) Figure S81	Conversion versus reaction time for acetophenone transfer hydrogenation by catalysts Ru-pqcame and 10 within 60 min
82) Figure S82	¹ H NMR spectrum (CH ₃ OD) of a sample of 4 showing the formation of Ru-H species

83) Table S2	Crystal and refinement data for 8-Mepq , 4,6'-Me₂pqca and 8,6'-Me₂pqca
84) Table S3	Crystal and refinement data for 1–4
85) Table S4	Crystal and refinement data for 7, 9 and 10

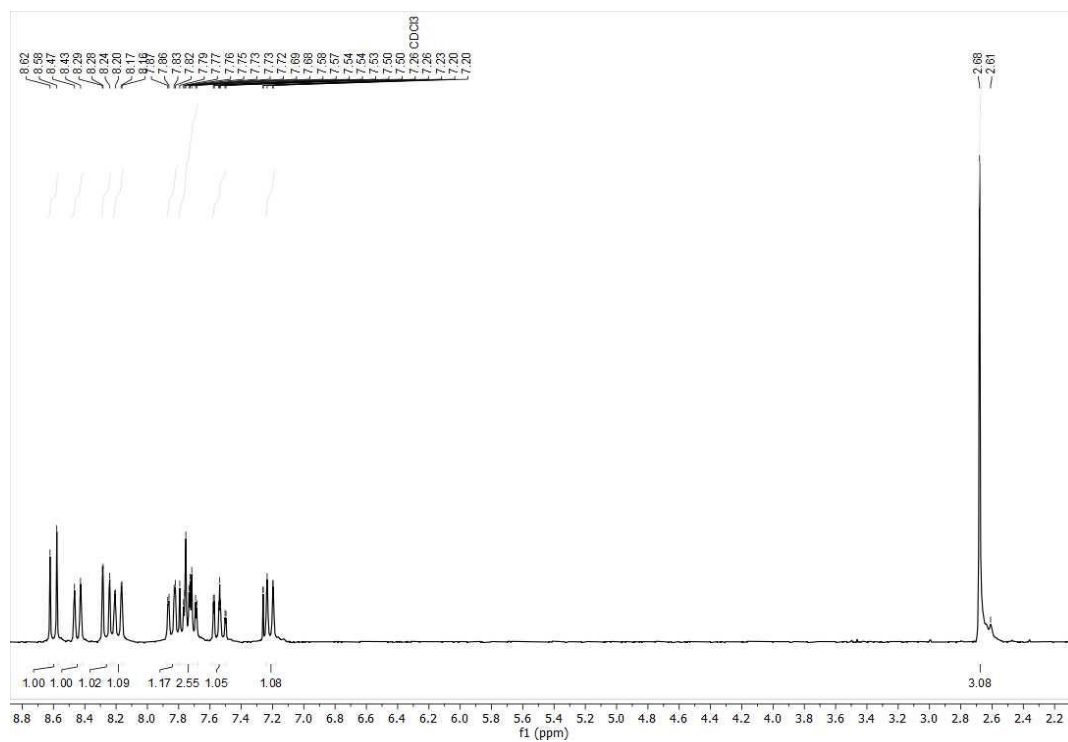


Figure S1. ¹H-NMR of 8-Mepq in CDCl₃

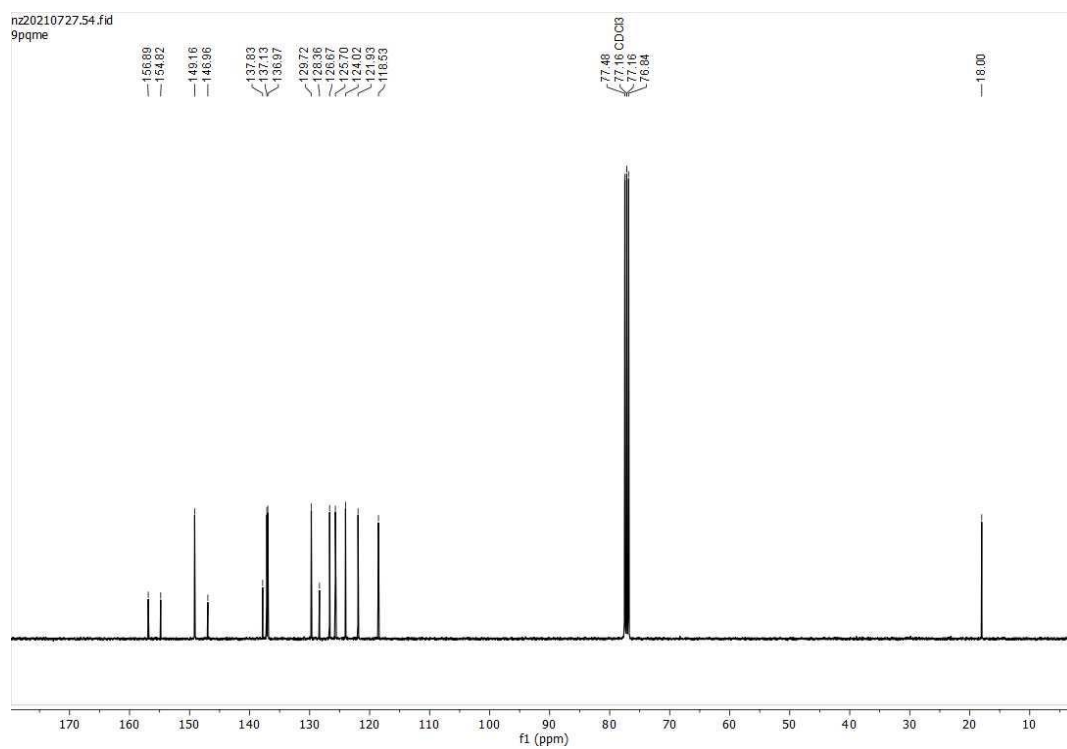


Figure S2. ¹³C{¹H}-NMR of 8-Mepq in CDCl₃

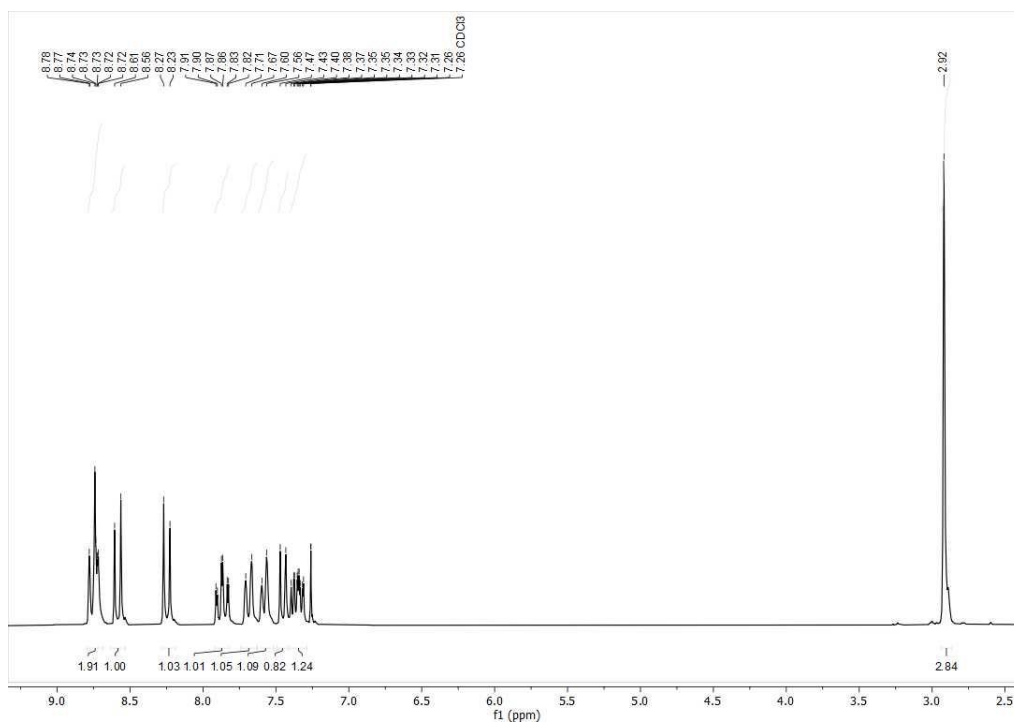


Figure S3. ¹H-NMR spectrum of 6'-Mepq in CDCl₃

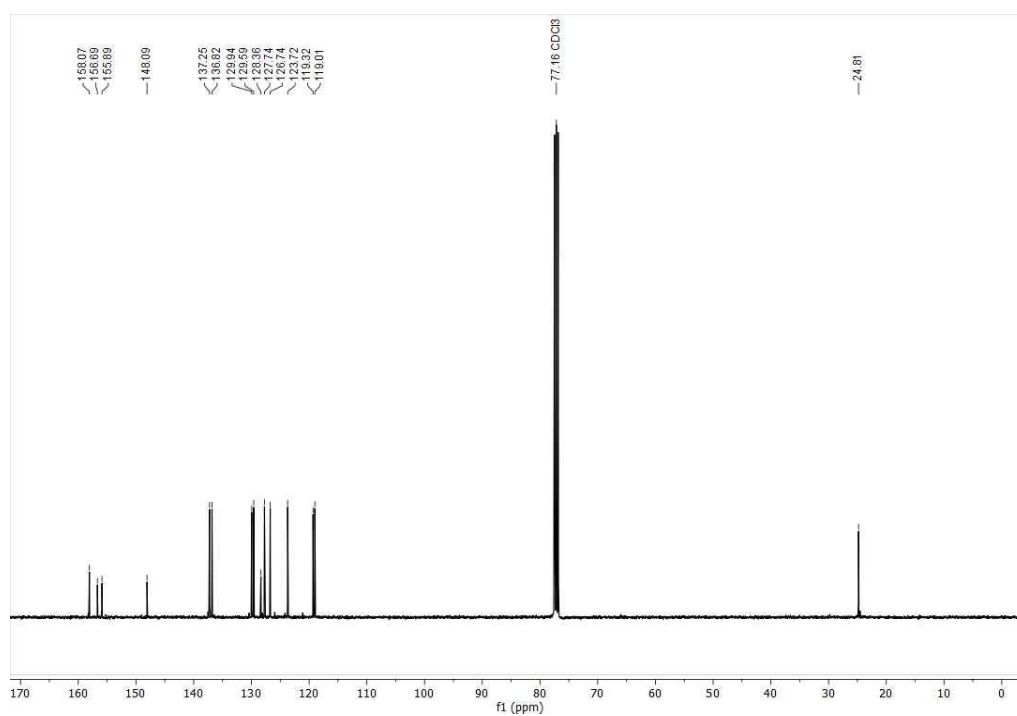


Figure S4. ¹³C{¹H}-NMR of 6'-Mepq in CDCl₃

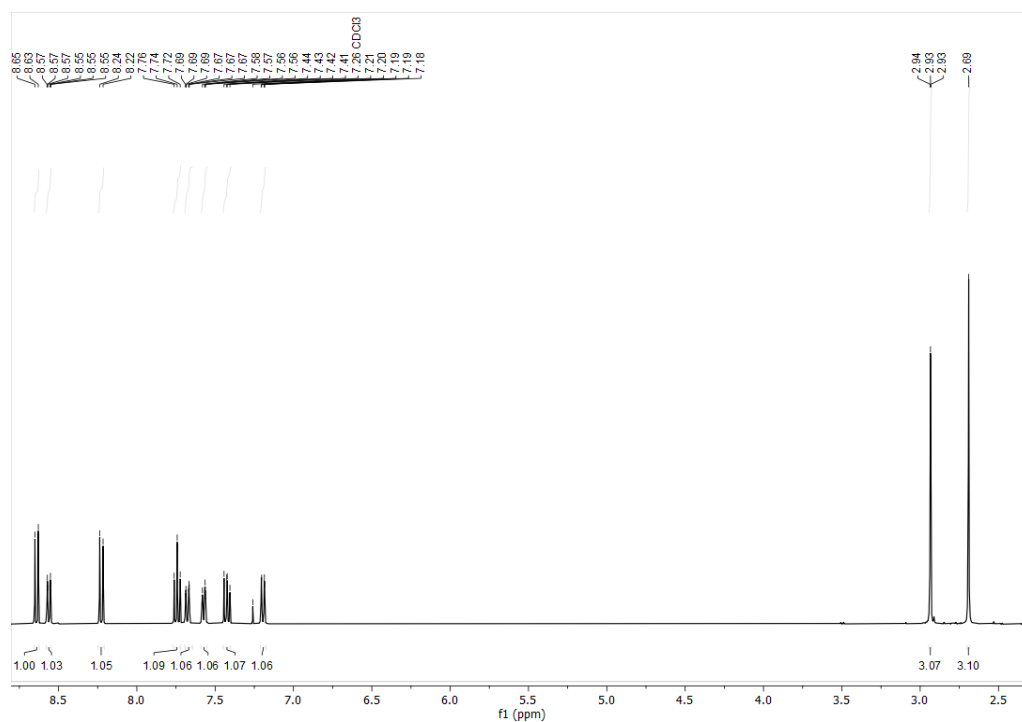


Figure S5. ¹H-NMR spectrum of 8,6'-Me₂pq in CDCl₃

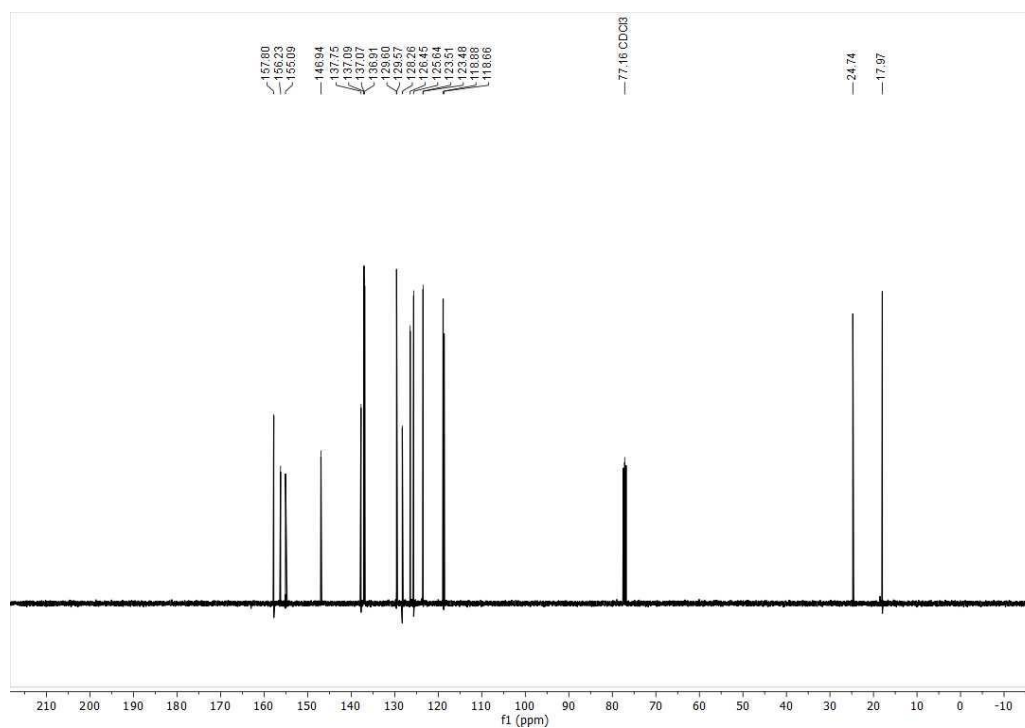


Figure S6. ¹³C{¹H}-NMR spectrum of 8,6'-Me₂pq in CDCl₃

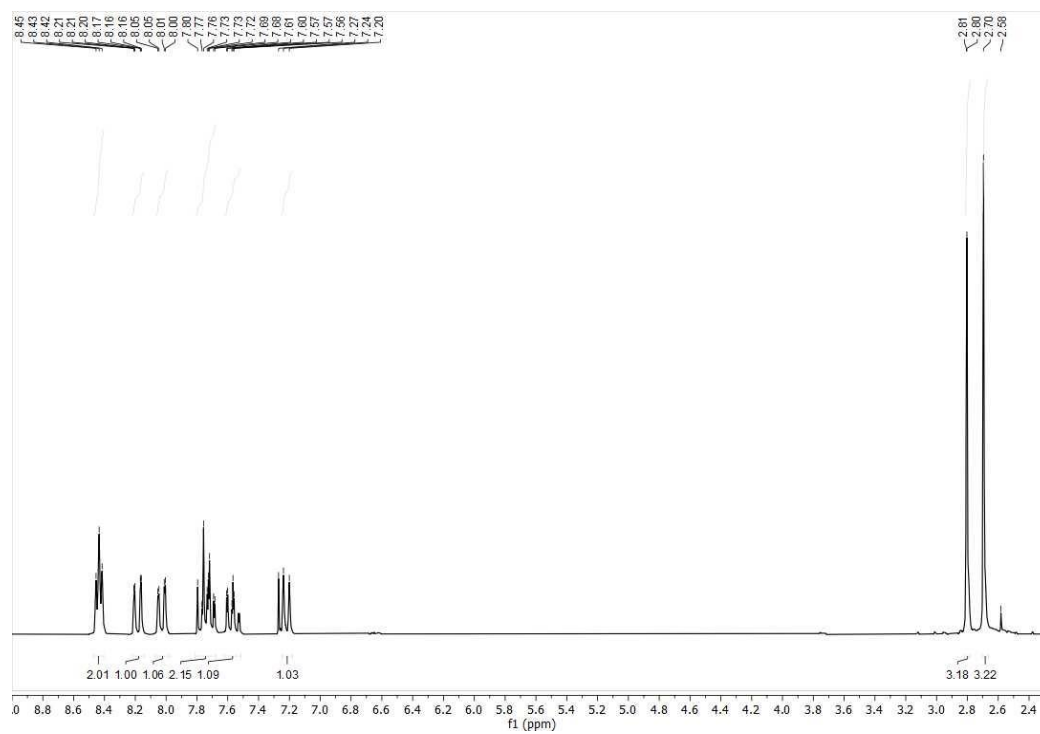


Figure S7. ¹H-NMR spectrum of 4,6'-Me₂pq in CDCl₃

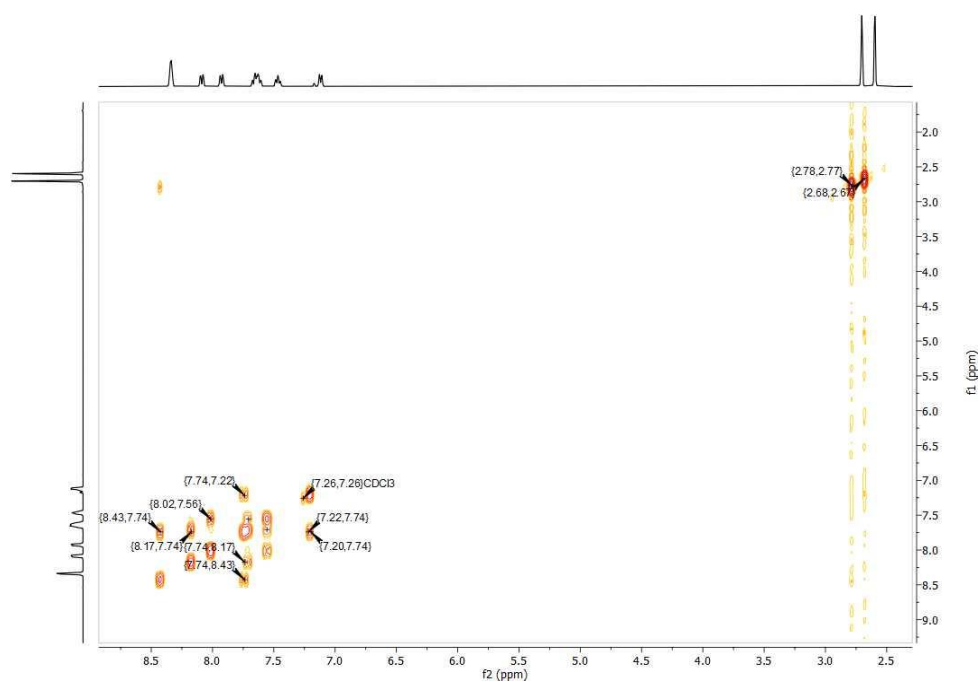


Figure S8. ^1H - ^1H COSY spectrum of 4,6'-Me₂pq in CDCl₃

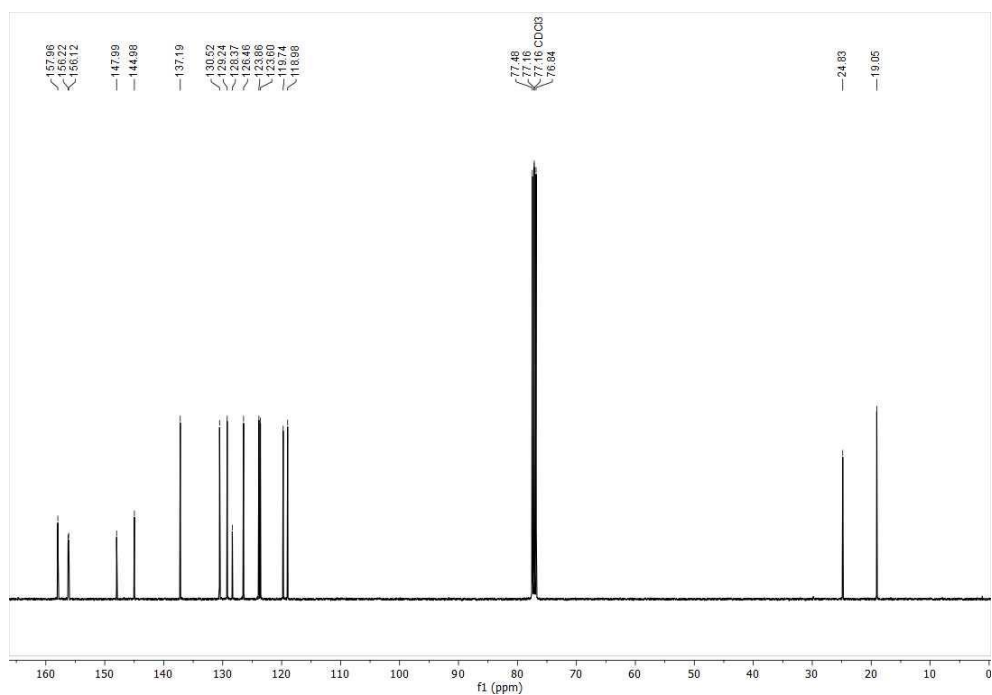


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of 4,6'-Me₂pq in CDCl₃

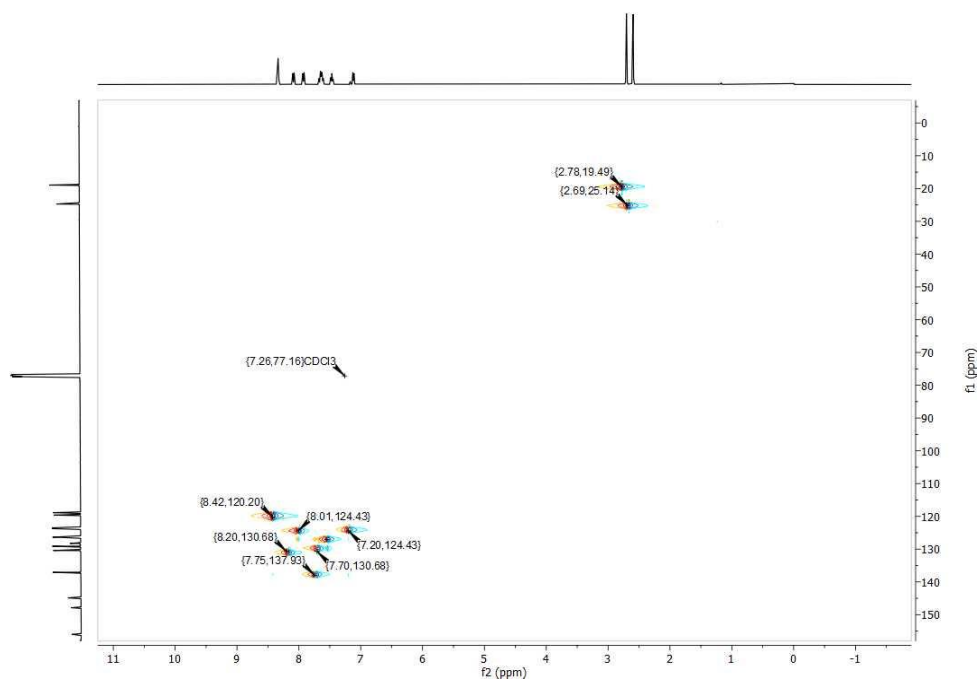


Figure S10. ¹H-¹³C-HSQC of 4,6'-Me₂pq in CDCl₃

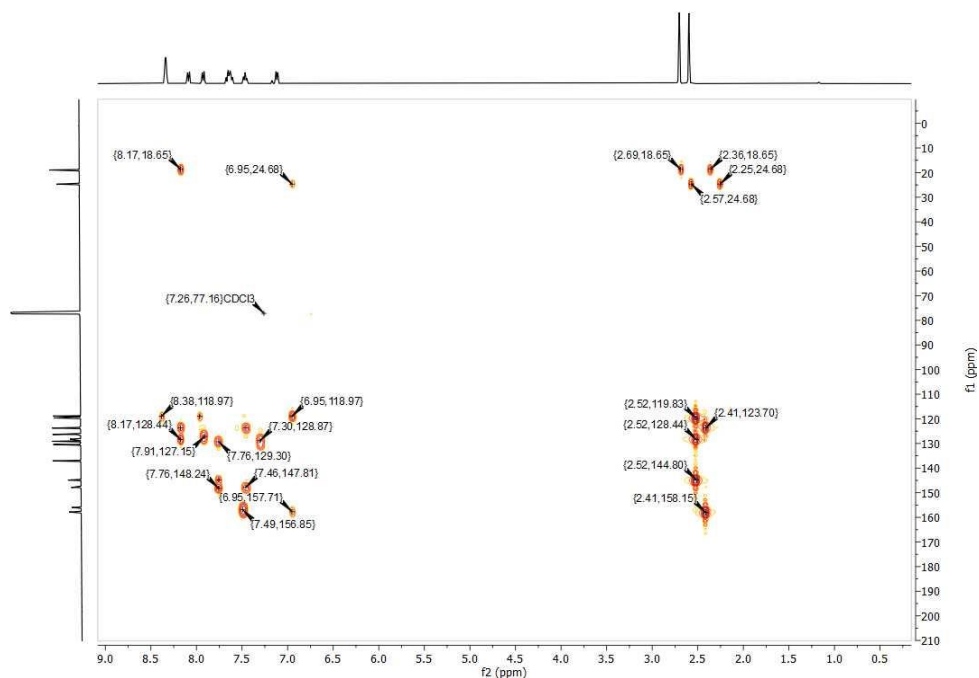


Figure S11. ¹H-¹³C-HMBC spectrum of 4,6'-Me₂pq in CDCl₃

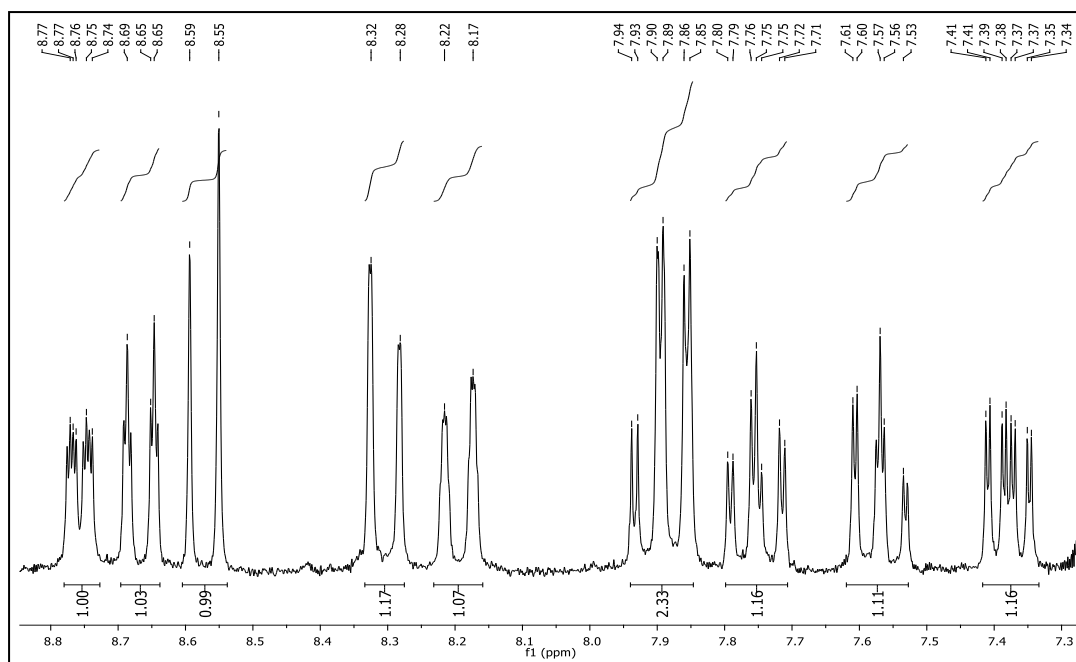


Figure S12. ¹H NMR spectrum of **pq** in CDCl₃

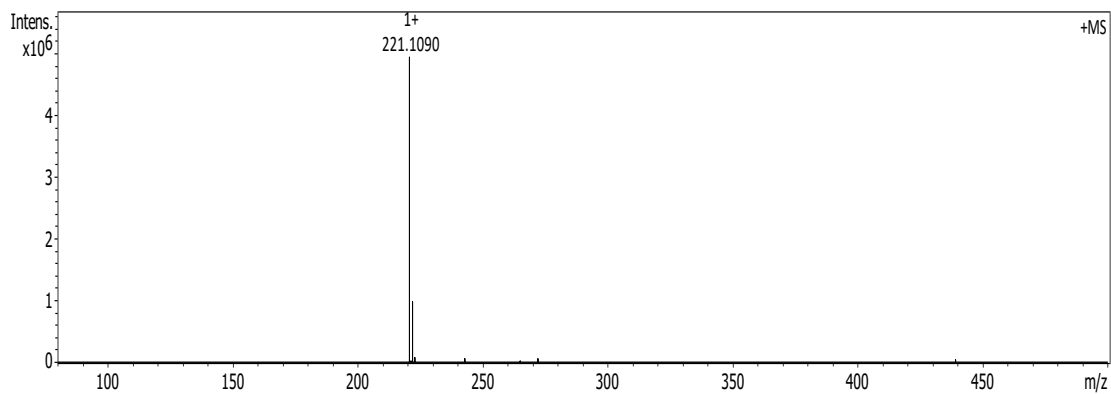


Figure S13. ESI-HRMS of **8-Mepq** in methanol

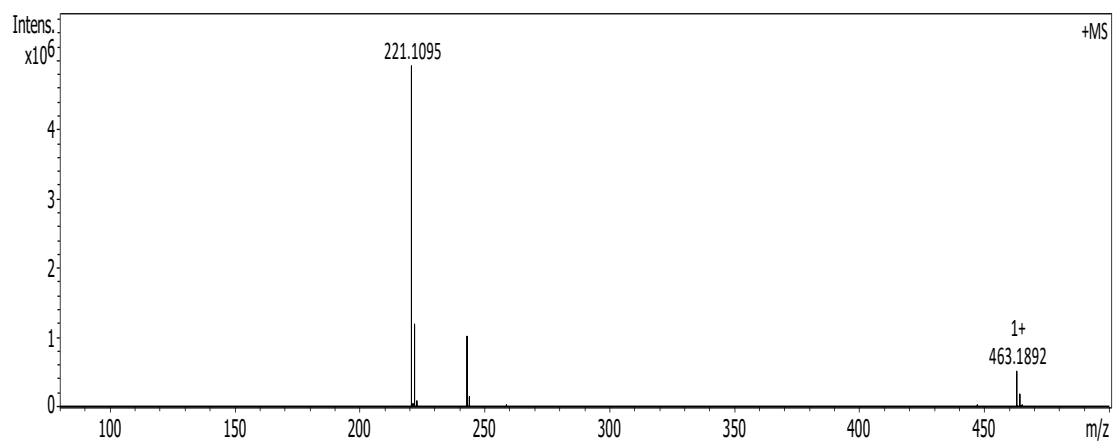
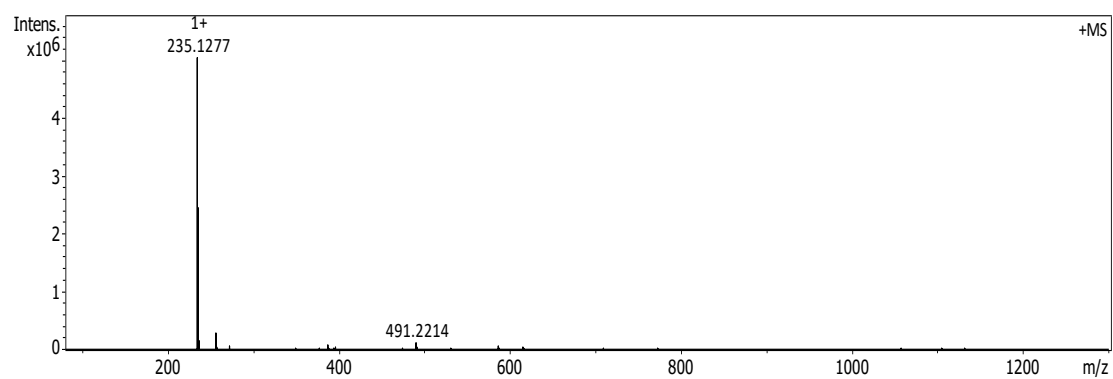
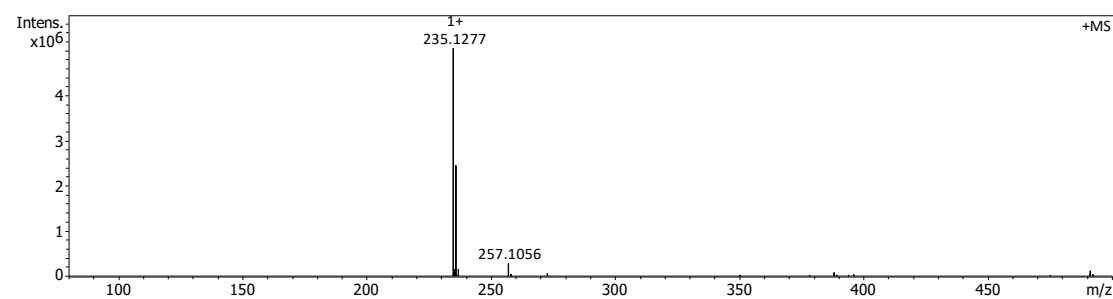


Figure S14. ESI-HRMS of 6'-Mepq in methanol



(a)



(b)

Figure S15. ESI-HRMS of 8,6'-Me₂pq in methanol

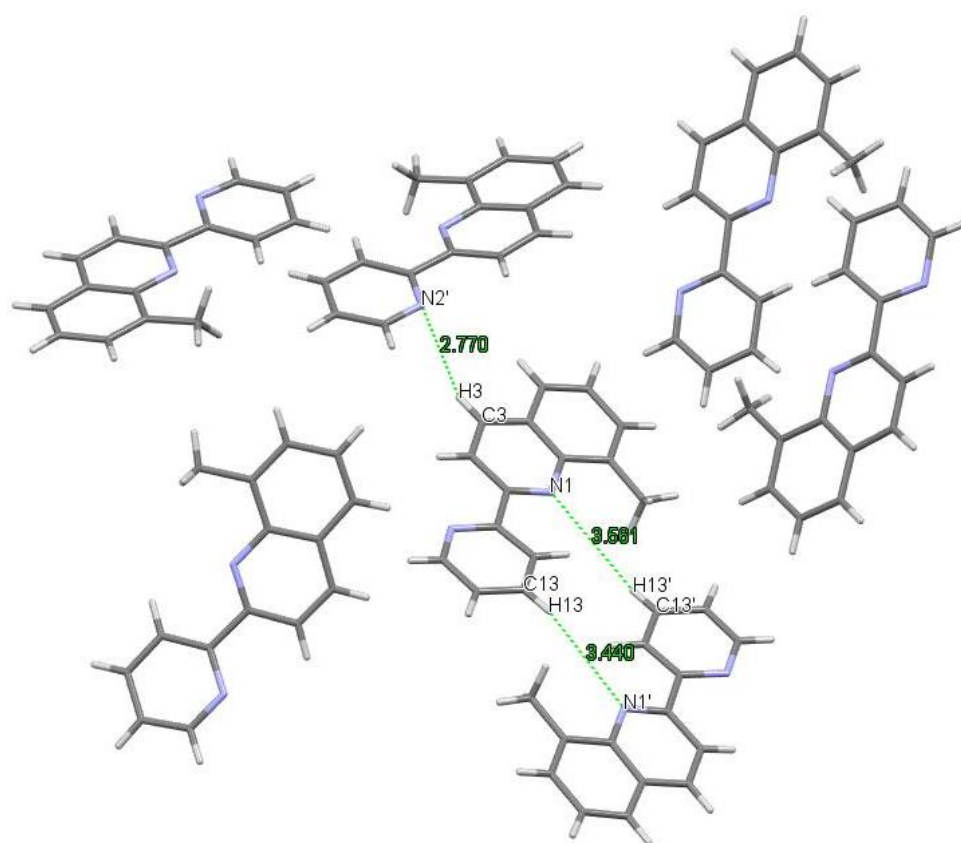


Figure S16. Intermolecular interactions in the single crystal of **8-Mepq**

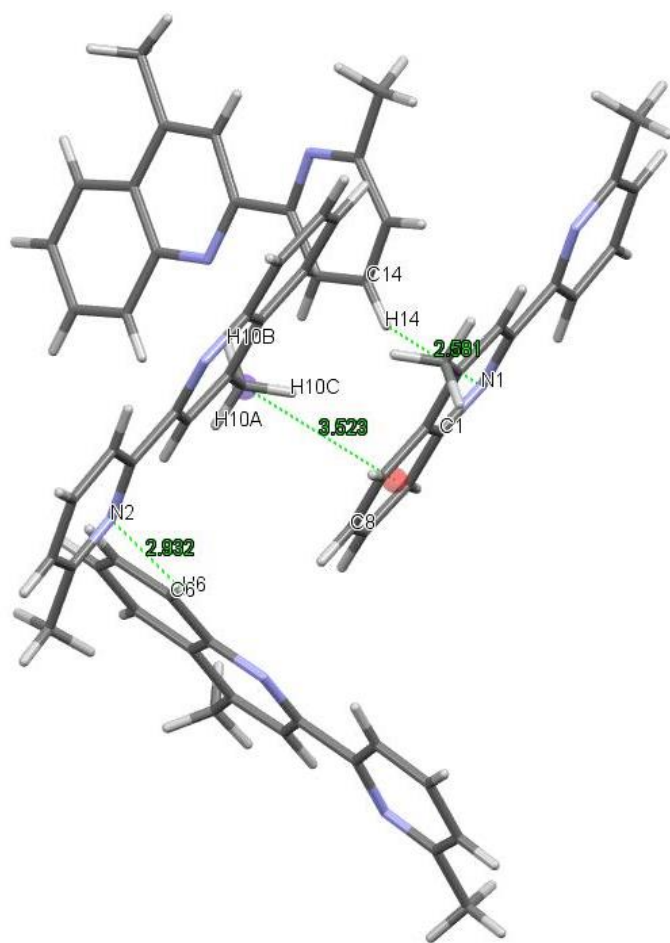


Figure S17. Intermolecular interactions in the single crystal of 4,6'-Me₂pq

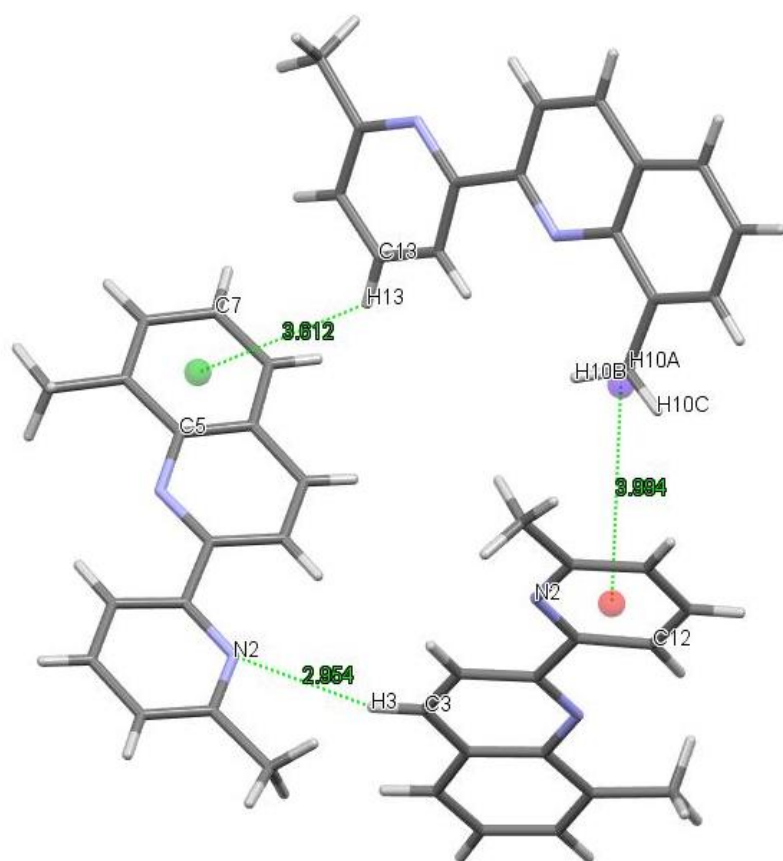


Figure S18. Intermolecular interactions in the single crystal of 8,6'-Me₂pq

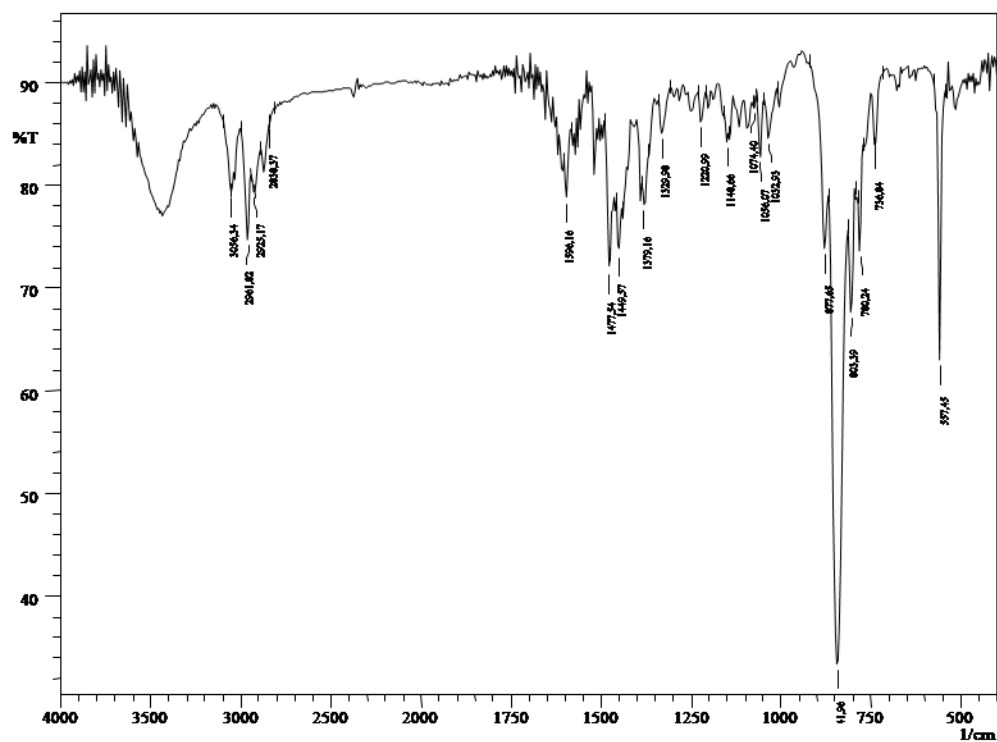


Figure S19. FT-IR spectrum of 1

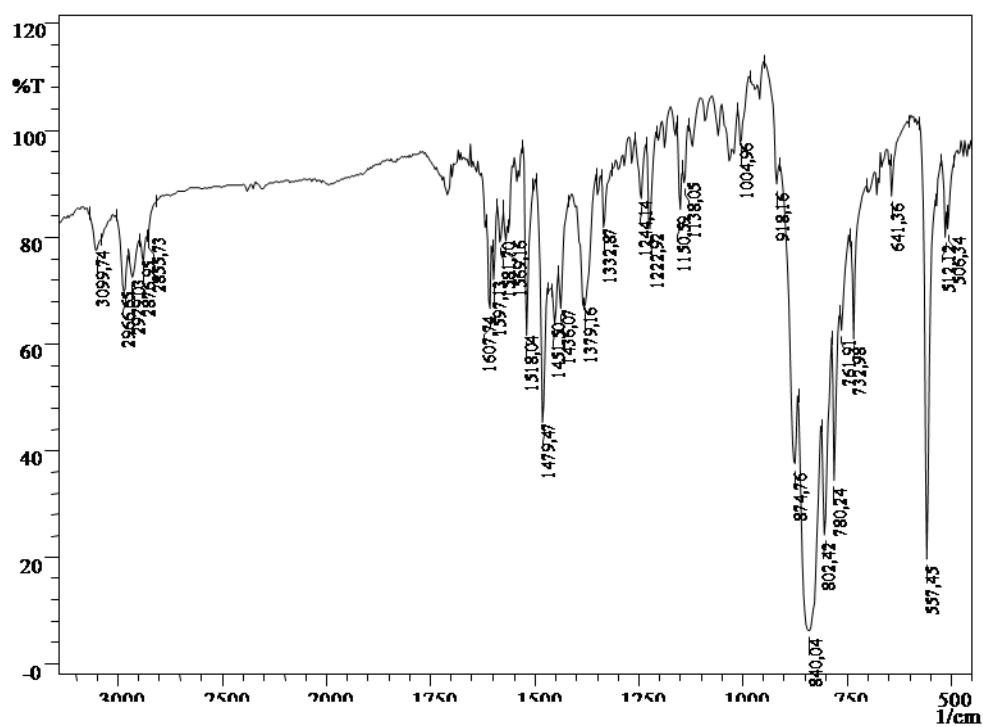


Figure S20. FT-IR spectrum of 2

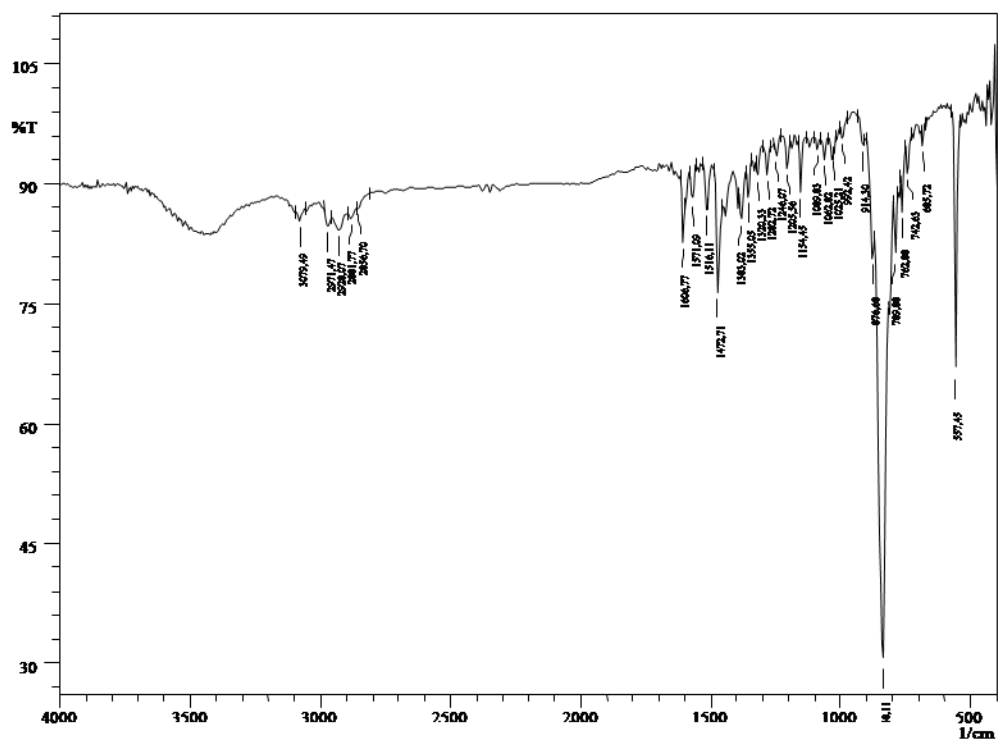


Figure S21. FT-IR spectrum of 3

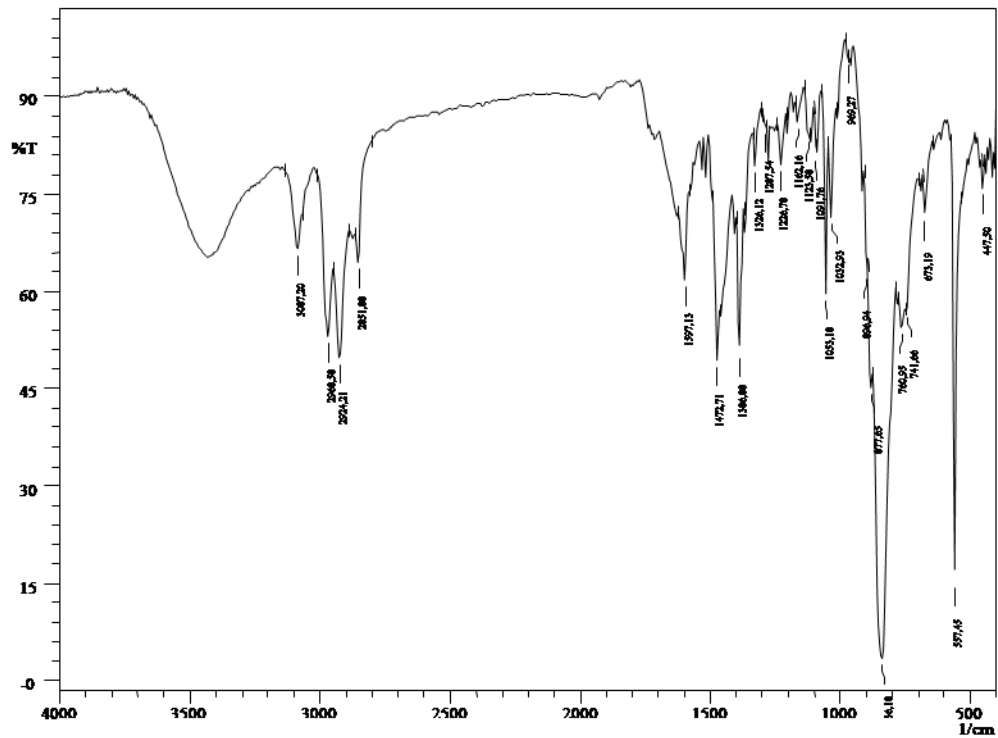


Figure S22. FT-IR spectrum of 4

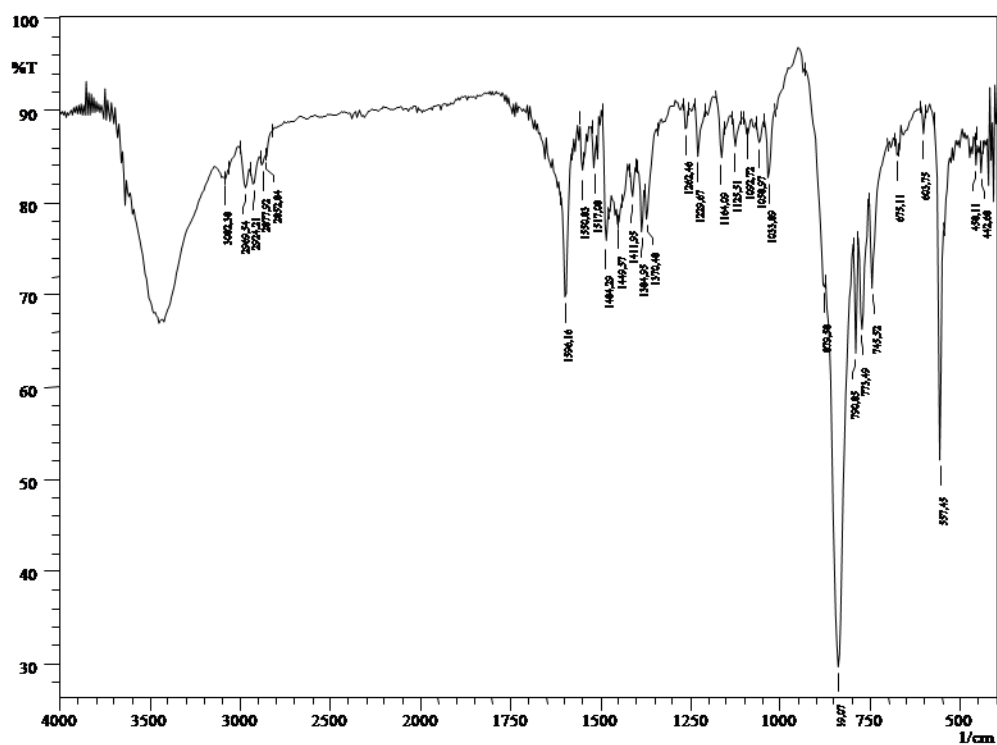


Figure S23. FT-IR spectrum of 5

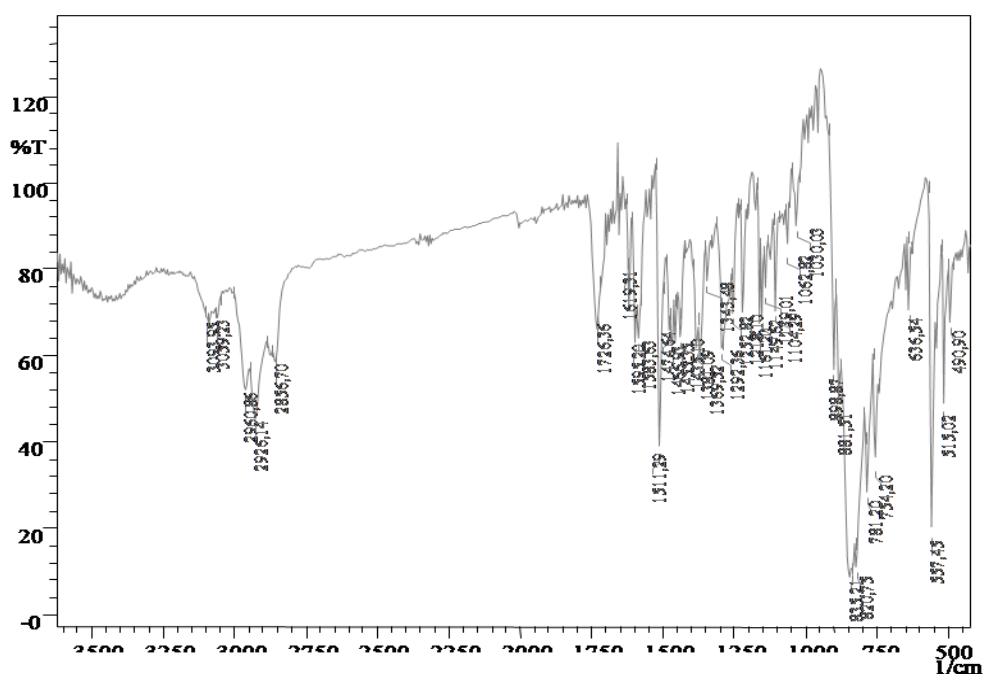


Figure S24. FT-IR spectrum of 6

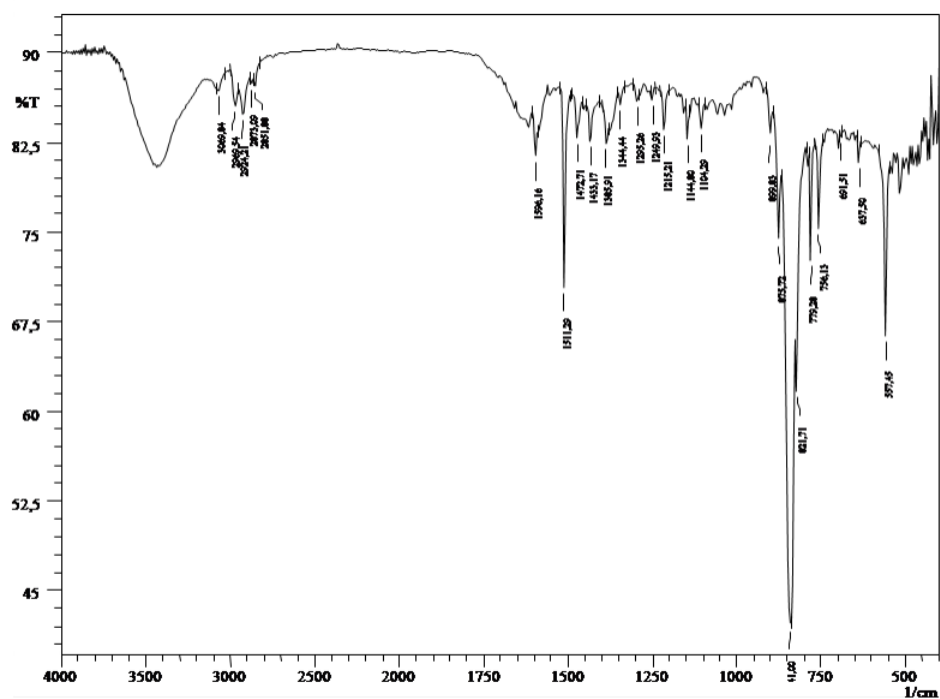


Figure S25. FT-IR spectrum of 8

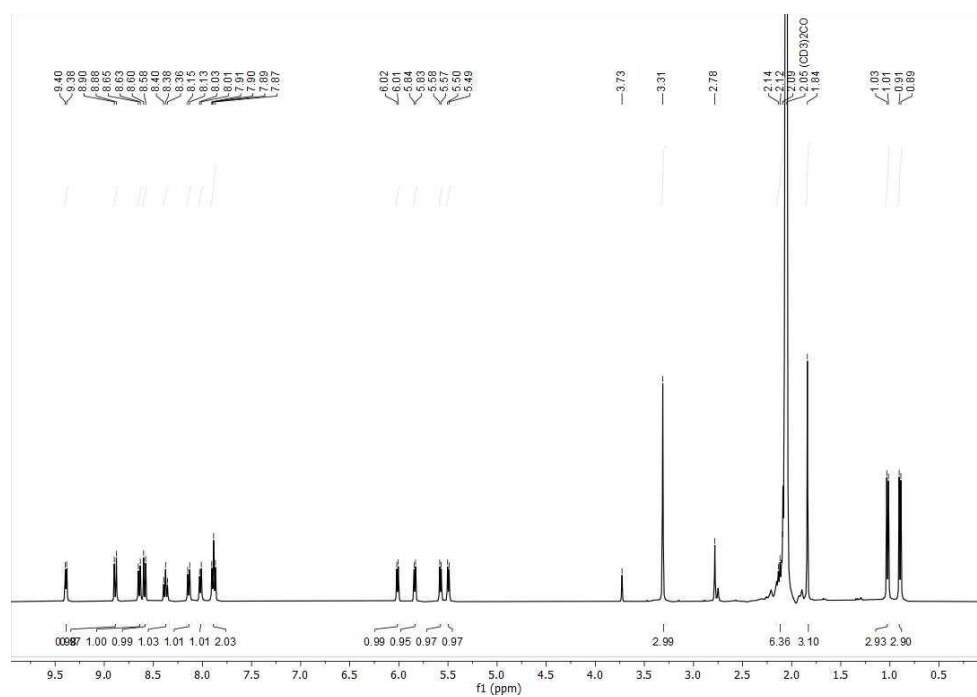


Figure S26. ^1H -NMR spectrum of 1 in $(\text{CD}_3)_2\text{CO}$

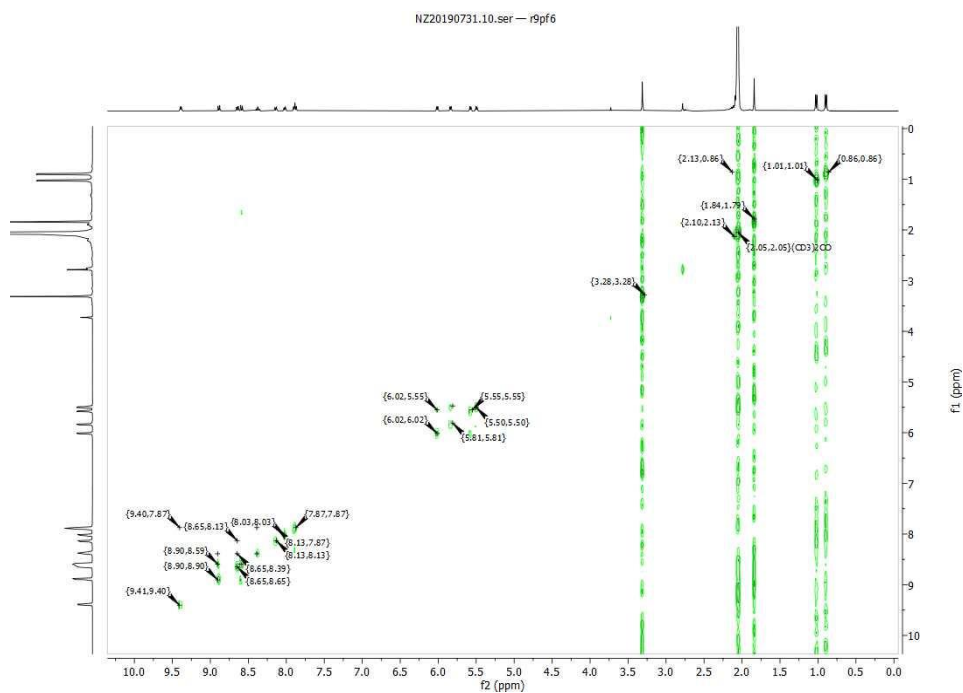


Figure S27. ^1H - ^1H COSY spectrum of **1** in $(\text{CD}_3)_2\text{CO}$

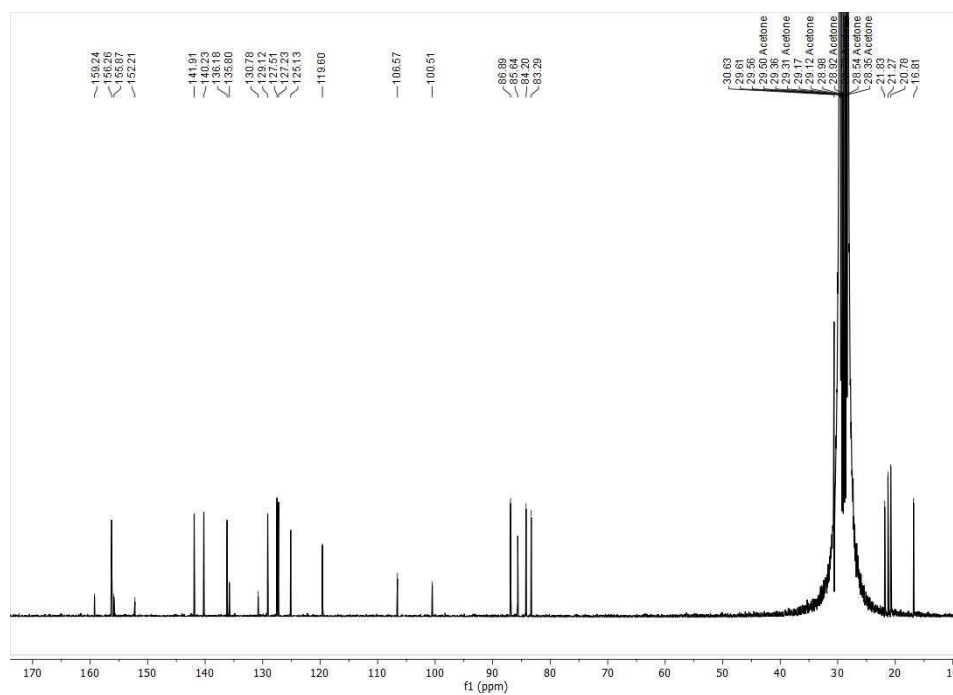


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **1** in $(\text{CD}_3)_2\text{CO}$

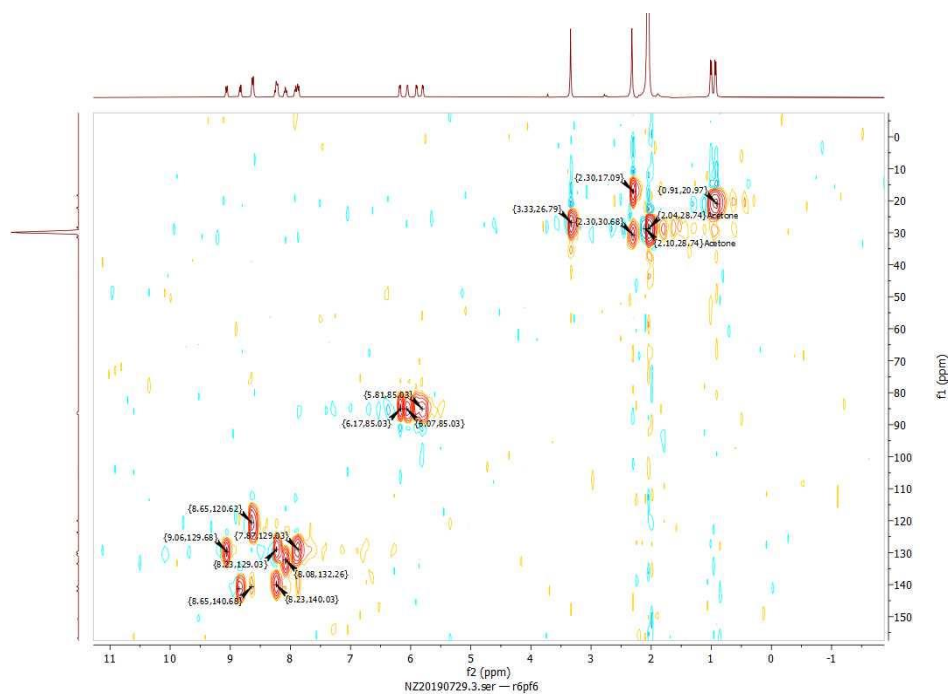


Figure S29. ^1H - ^{13}C -HSQC spectrum of **1** in $(\text{CD}_3)_2\text{CO}$

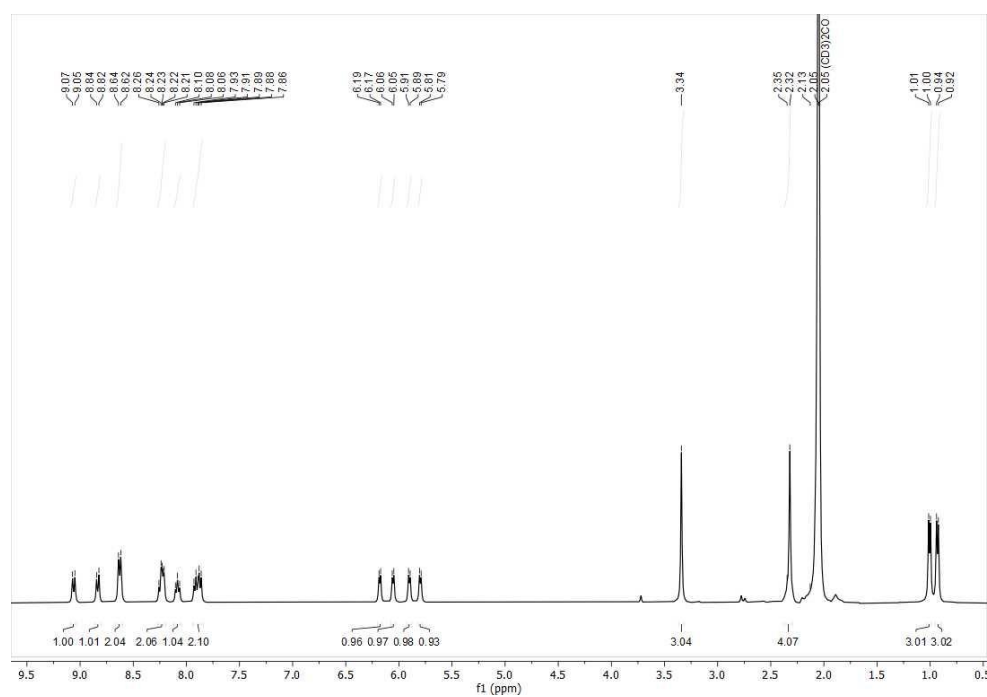


Figure S30. ^1H -NMR spectrum of **2** in $(\text{CD}_3)_2\text{CO}$

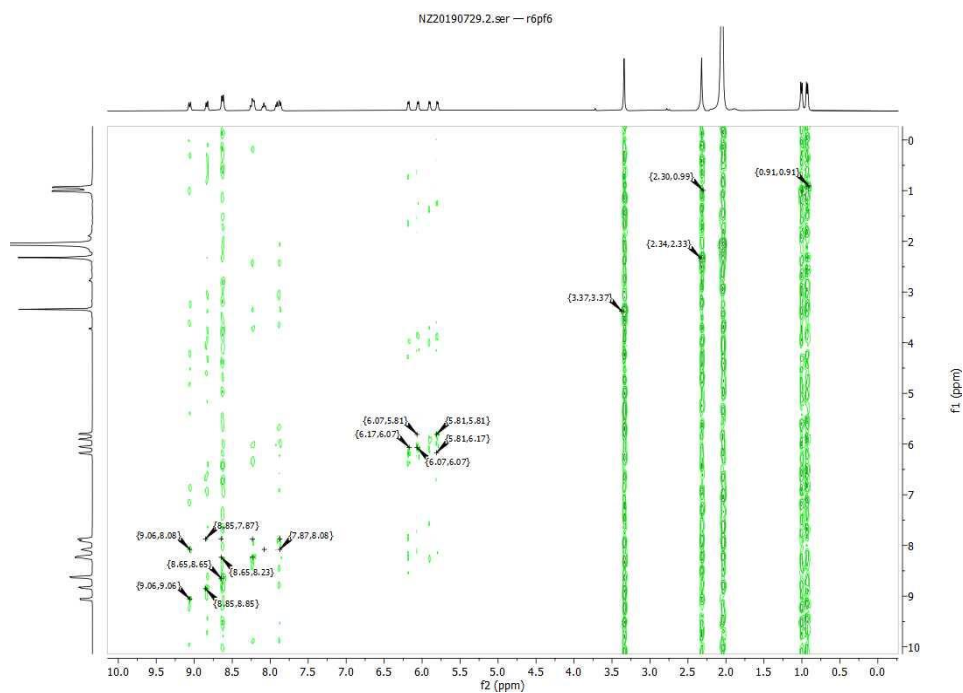


Figure S31. ^1H - ^1H COSY spectrum of **2** in $(\text{CD}_3)_2\text{CO}$

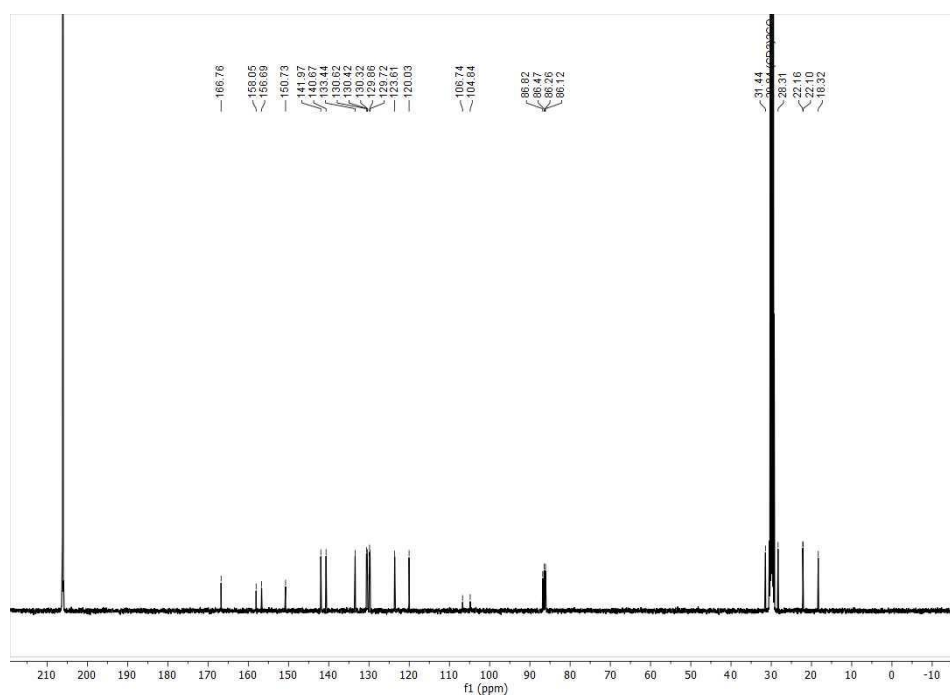


Figure S32. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2** in $(\text{CD}_3)_2\text{CO}$

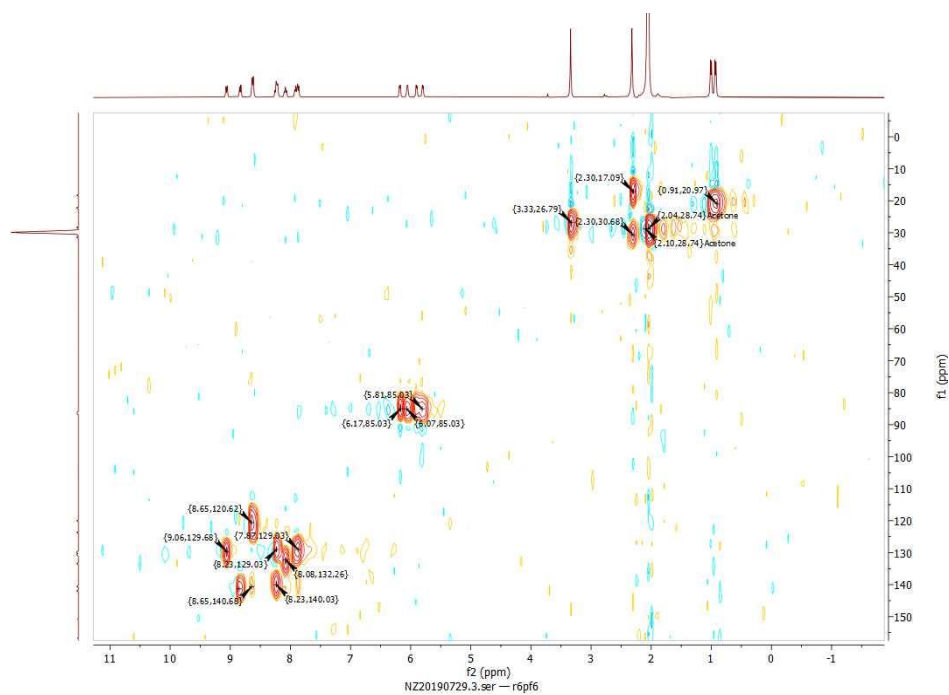


Figure S33. ^1H - ^{13}C -HSQC spectrum of **2** in $(\text{CD}_3)_2\text{CO}$

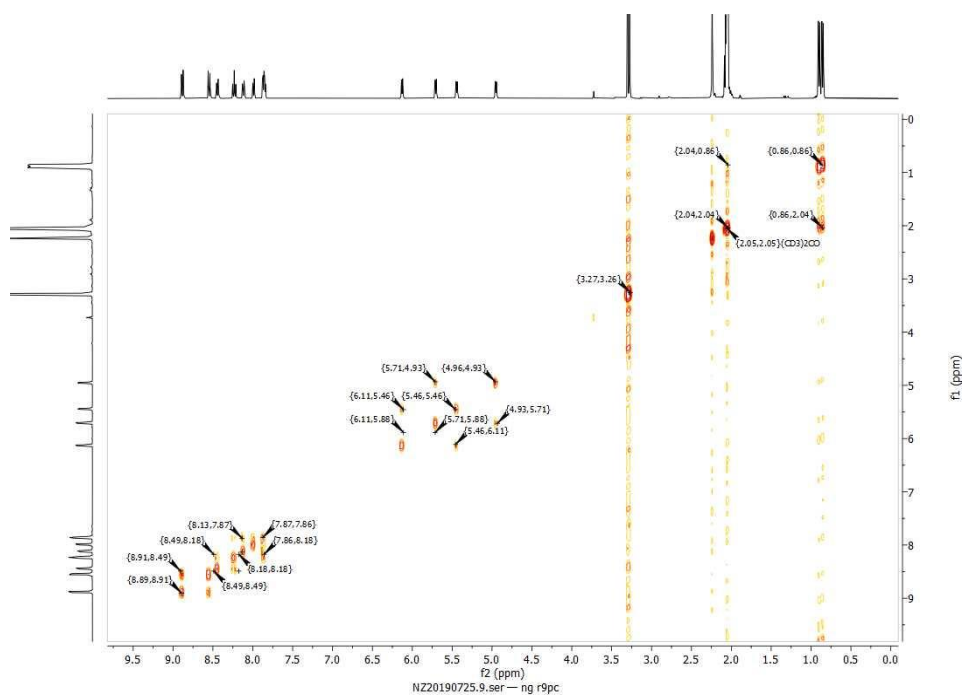


Figure S34. ^1H - ^1H COSY spectrum of **3** in $(\text{CD}_3)_2\text{CO}$

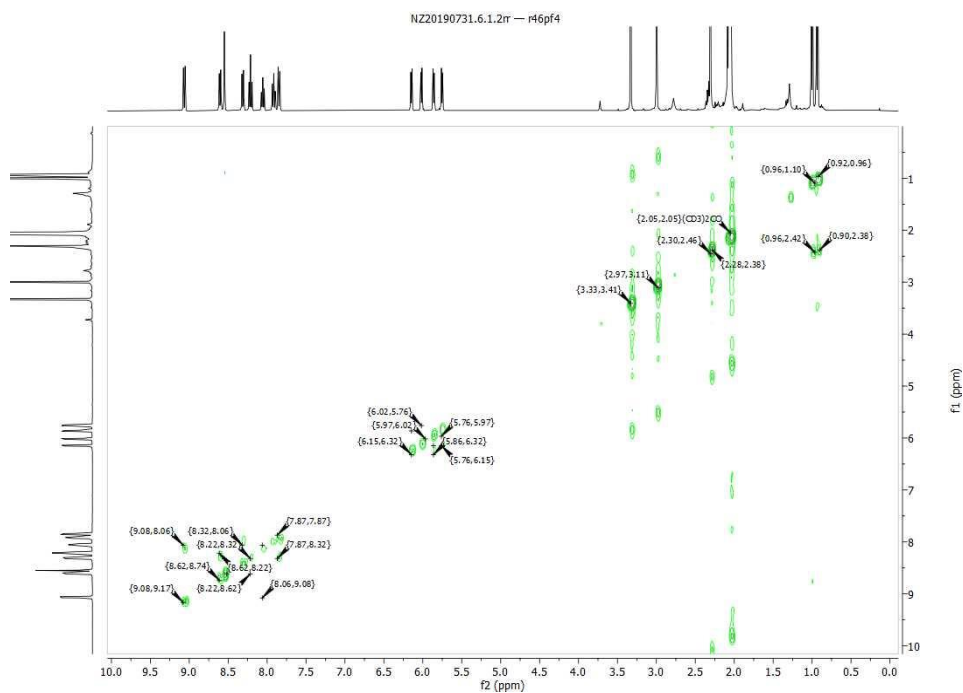


Figure S35. ^1H - ^1H COSY spectrum of **4** in $(\text{CD}_3)_2\text{CO}$

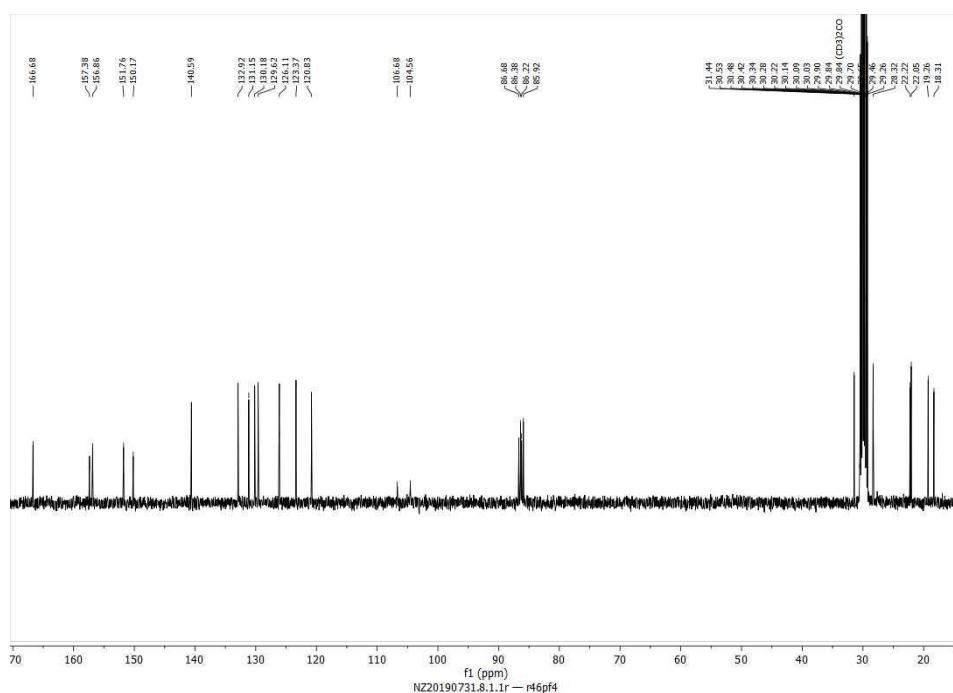


Figure S36. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **4** in $(\text{CD}_3)_2\text{CO}$



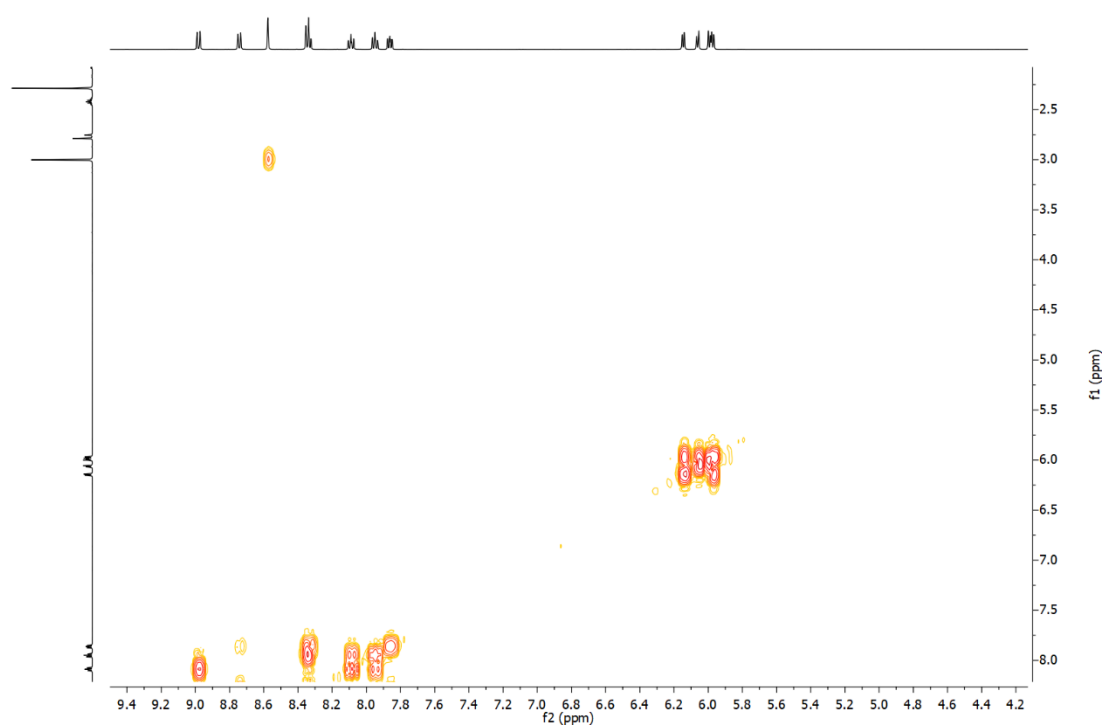


Figure S39. ^1H - ^1H COSY spectrum of **5** in $(\text{CD}_3)_2\text{CO}$

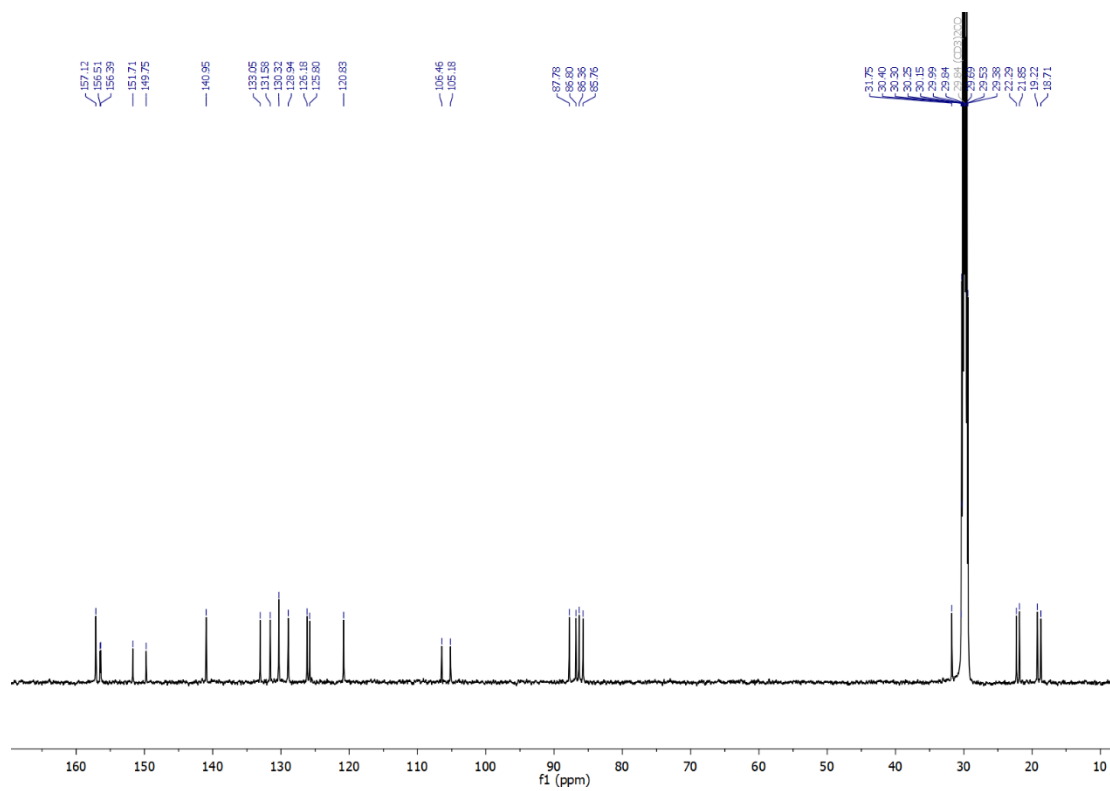


Figure S40. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **5** in $(\text{CD}_3)_2\text{CO}$

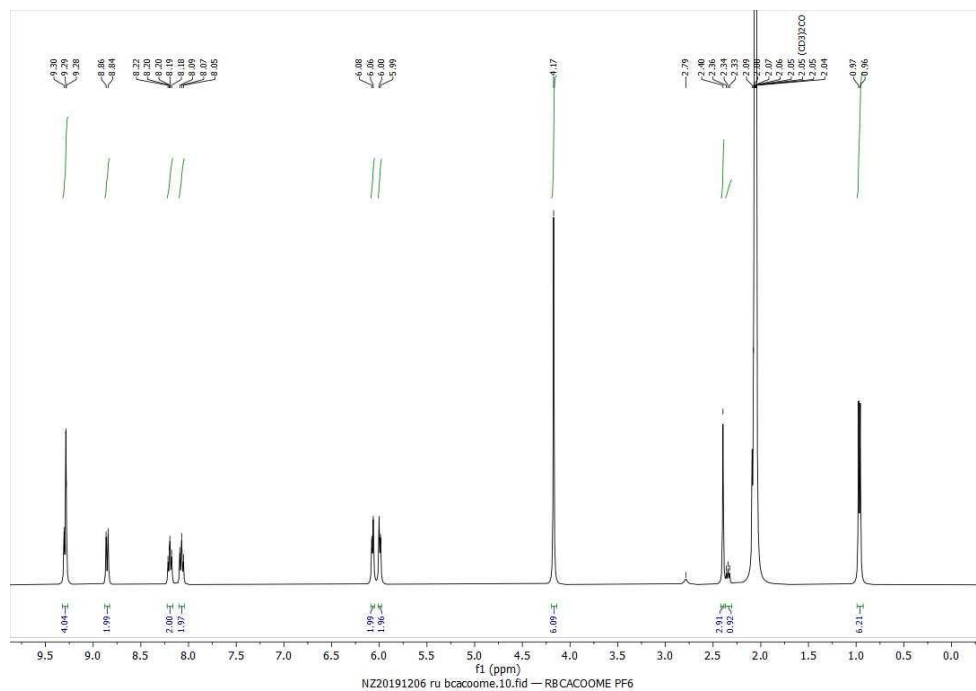


Figure S43. ¹H-NMR spectrum of **6** in (CD₃)₂CO

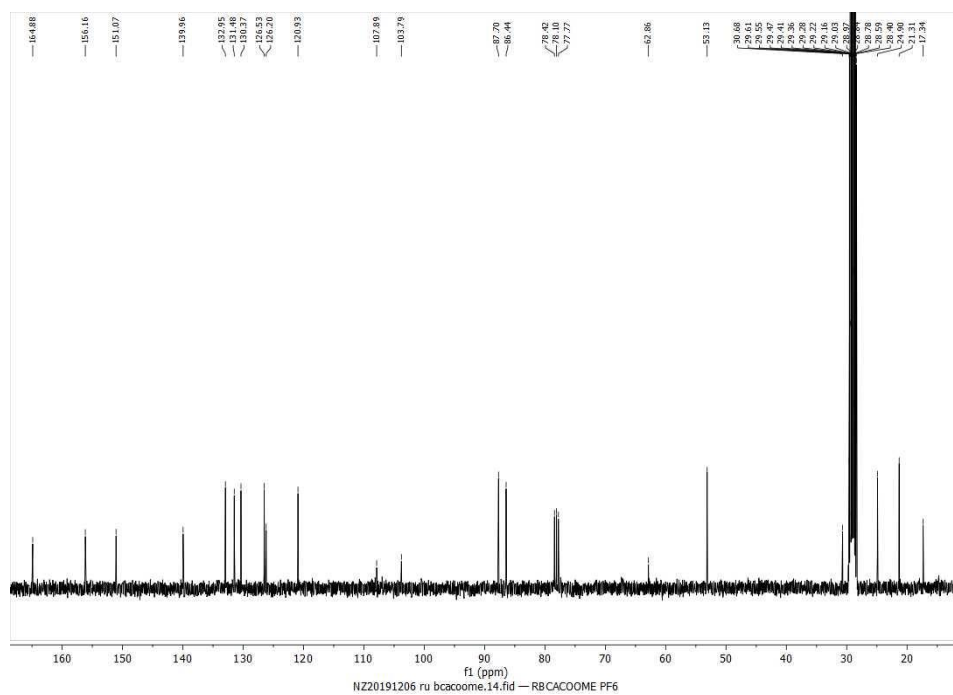


Figure S44. ¹³C{¹H}-NMR of **6** in (CD₃)₂CO

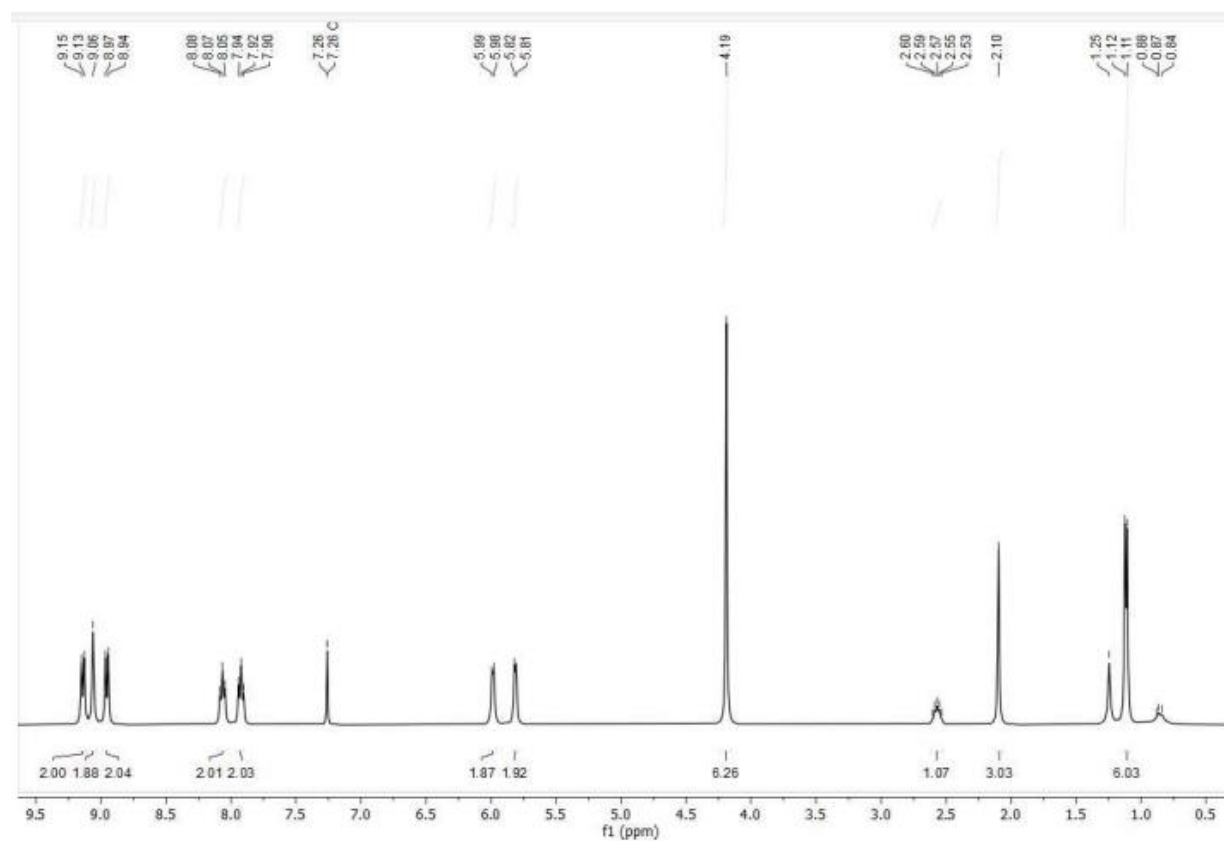


Figure S45. ¹H-NMR spectrum of 6-Cl in CDCl₃

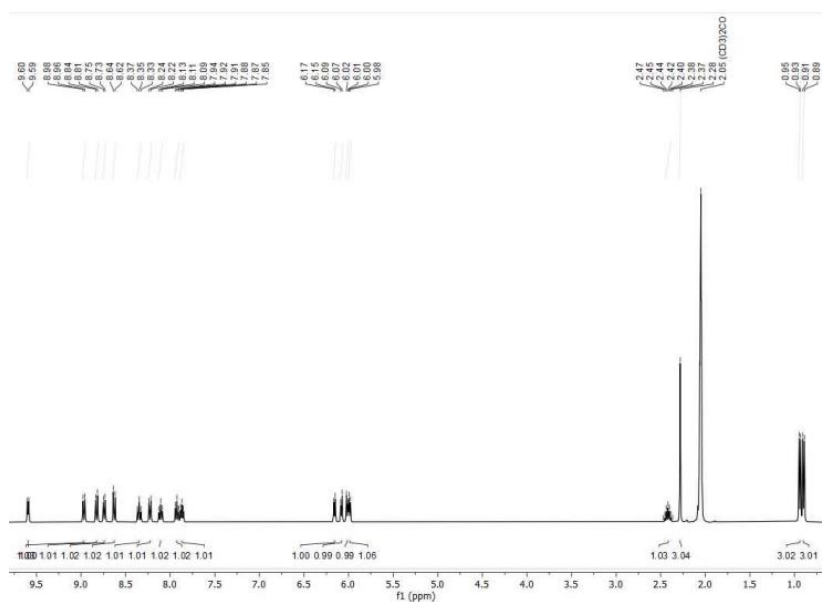


Figure S46. ¹H-NMR spectrum of 7-Cl in (CD₃)₂CO

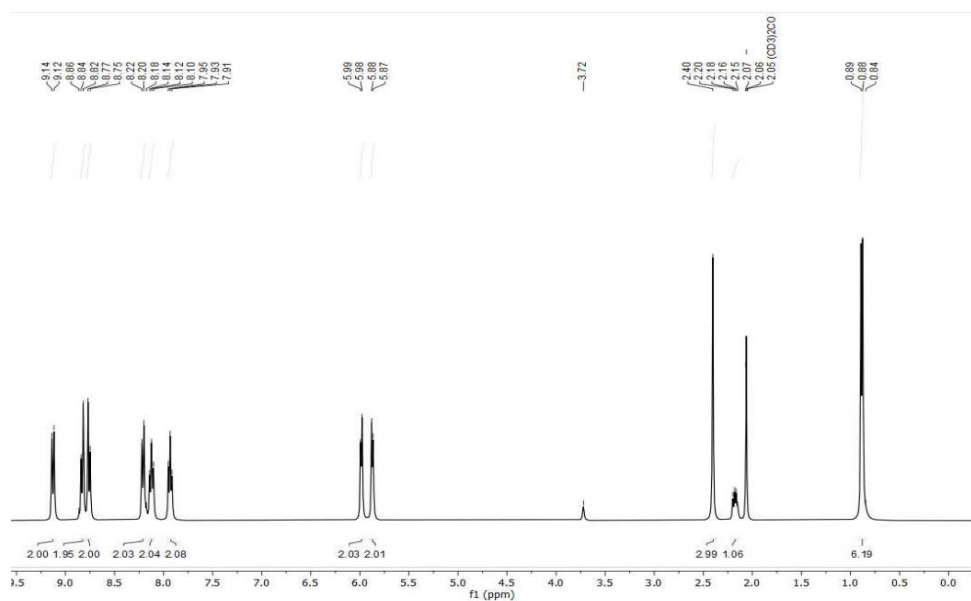


Figure S47. ¹H-NMR spectrum of 8 in (CD₃)₂CO

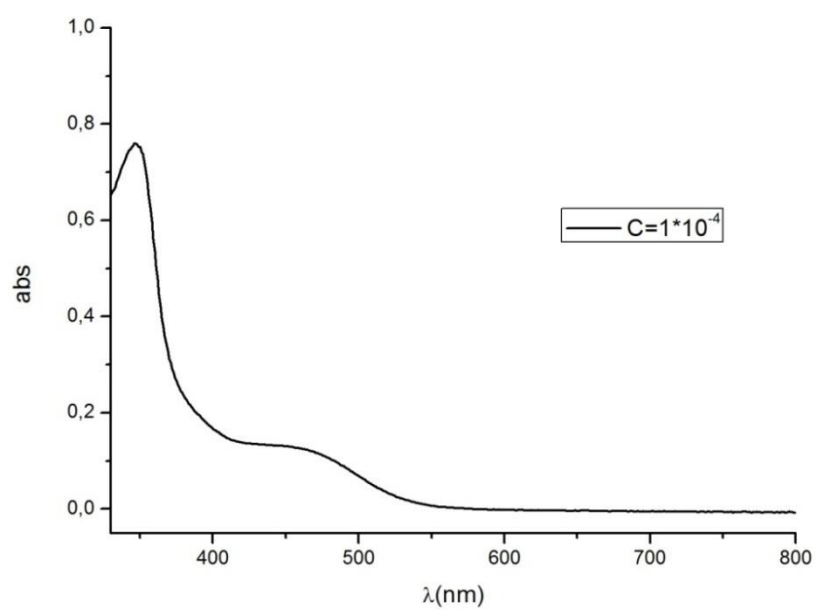


Figure S48. UV-vis spectrum of **1** in acetone

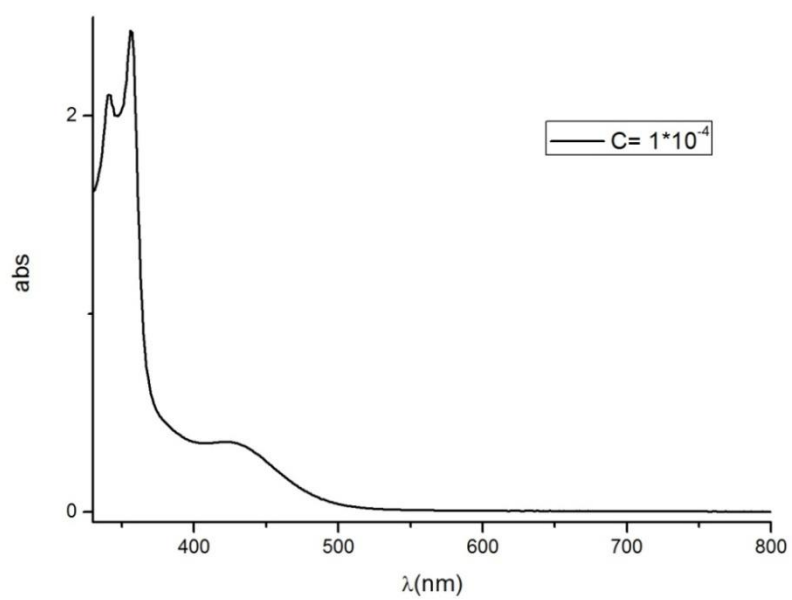


Figure S49. UV-vis spectrum of **2** in acetone

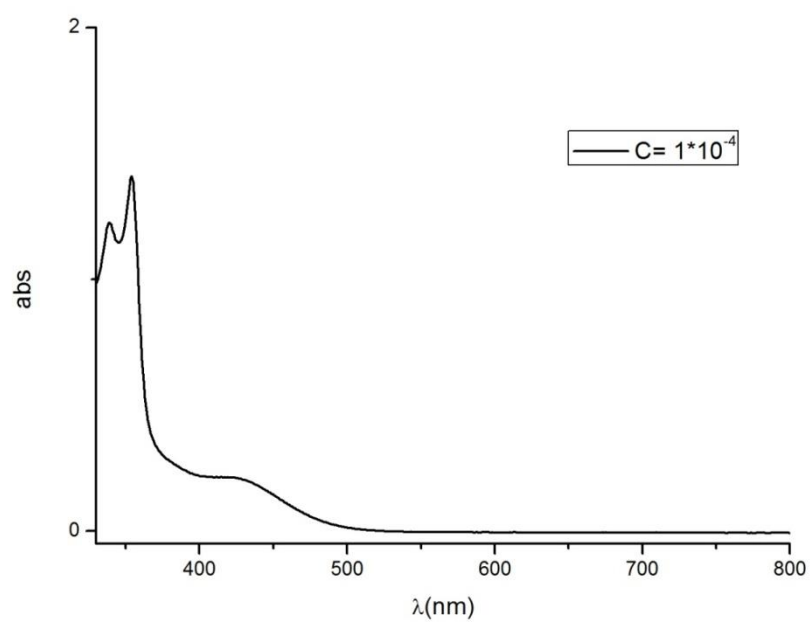


Figure S50. UV-vis spectrum of **3** in acetone

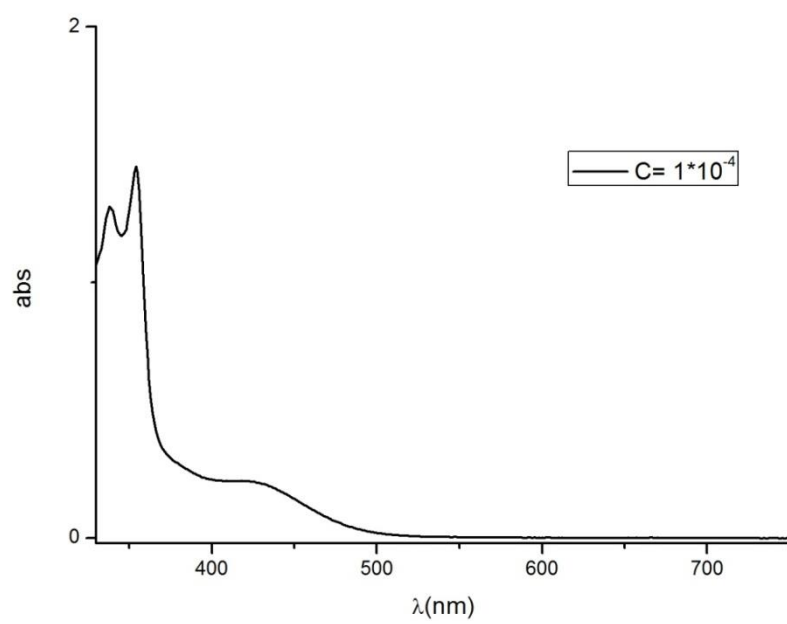


Figure S51. UV-vis spectrum of **4** in acetone

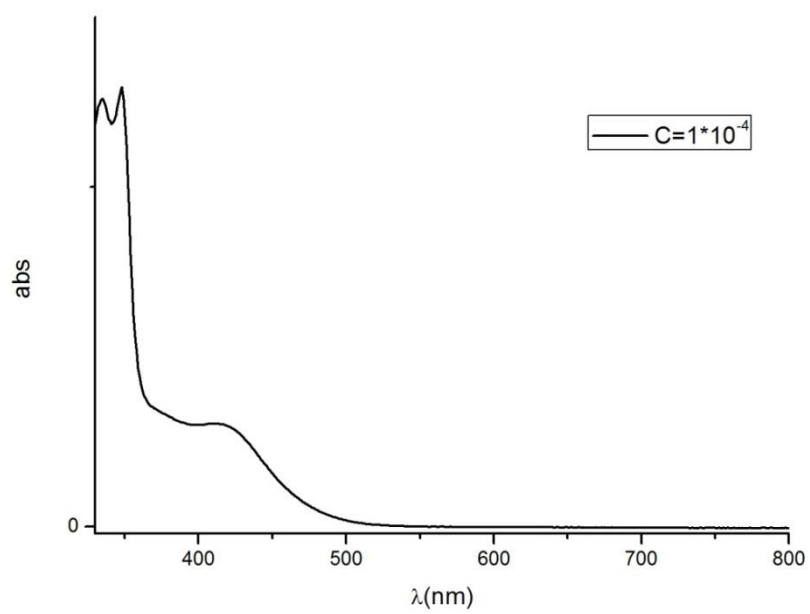


Figure S52. UV-vis spectrum of **5** in acetone

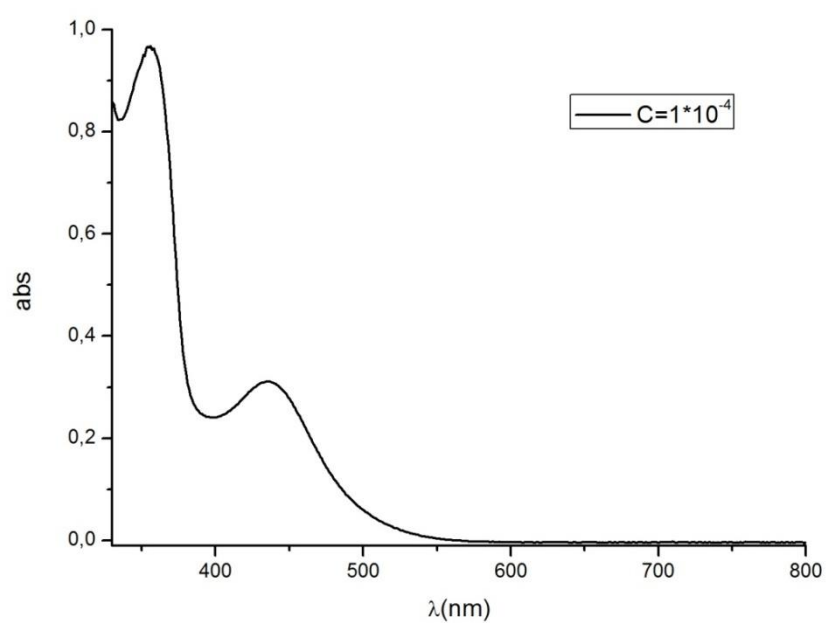


Figure S53. UV-vis spectrum of **Ru-pqcame** in acetone

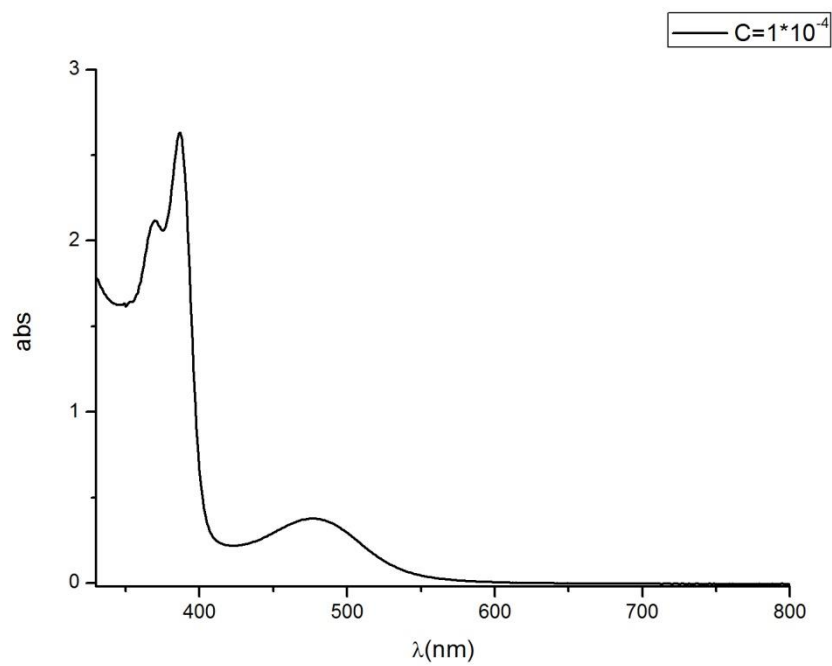


Figure S54. UV-vis spectrum of **6** in acetone

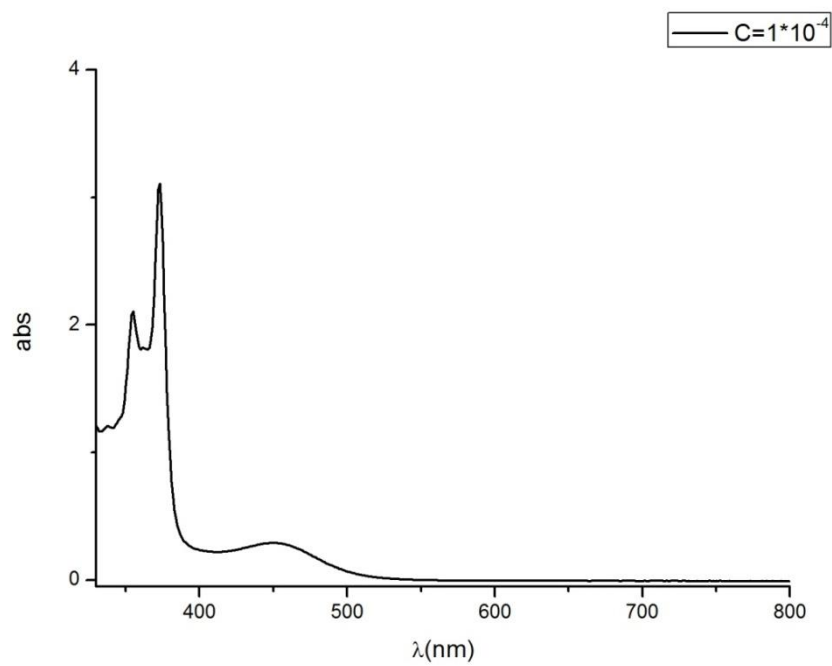


Figure S55. UV-vis spectrum of **8** in acetone

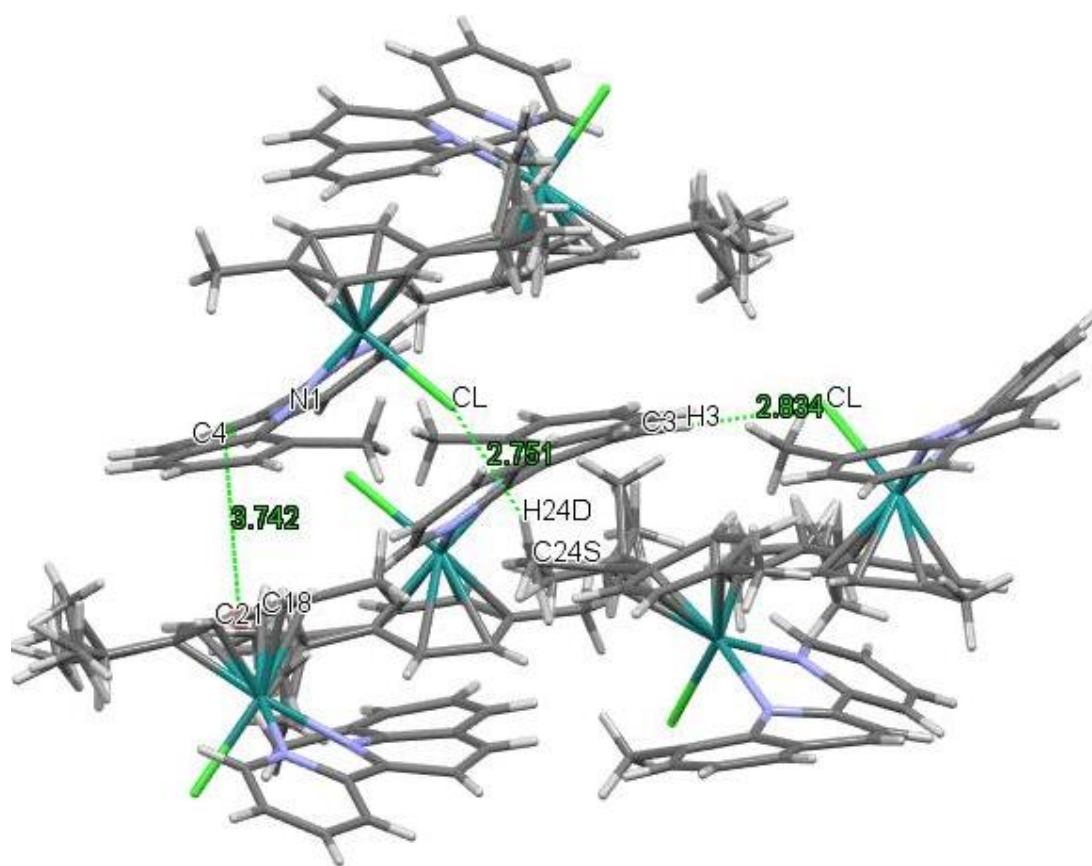


Figure S56. Intermolecular interactions in the unit cell of **1**

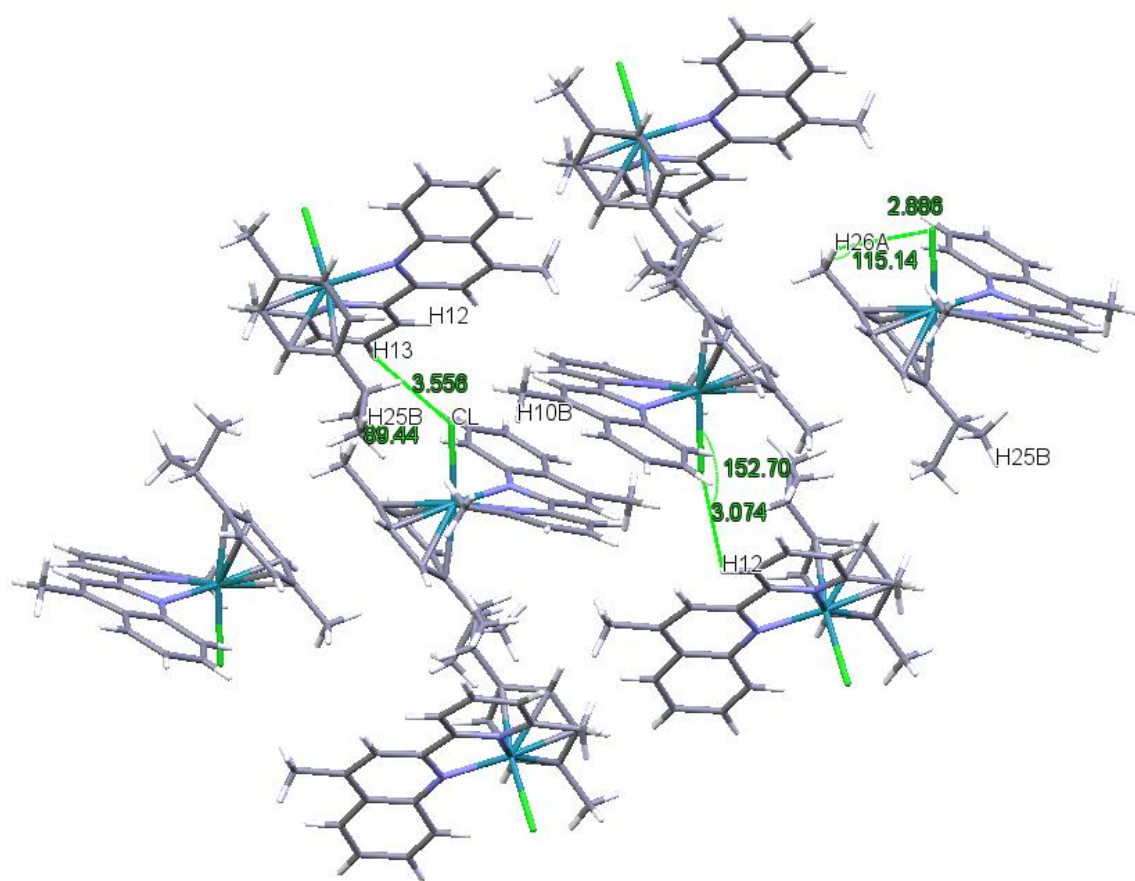


Figure S57. Intermolecular interactions in the unit cell of **4**

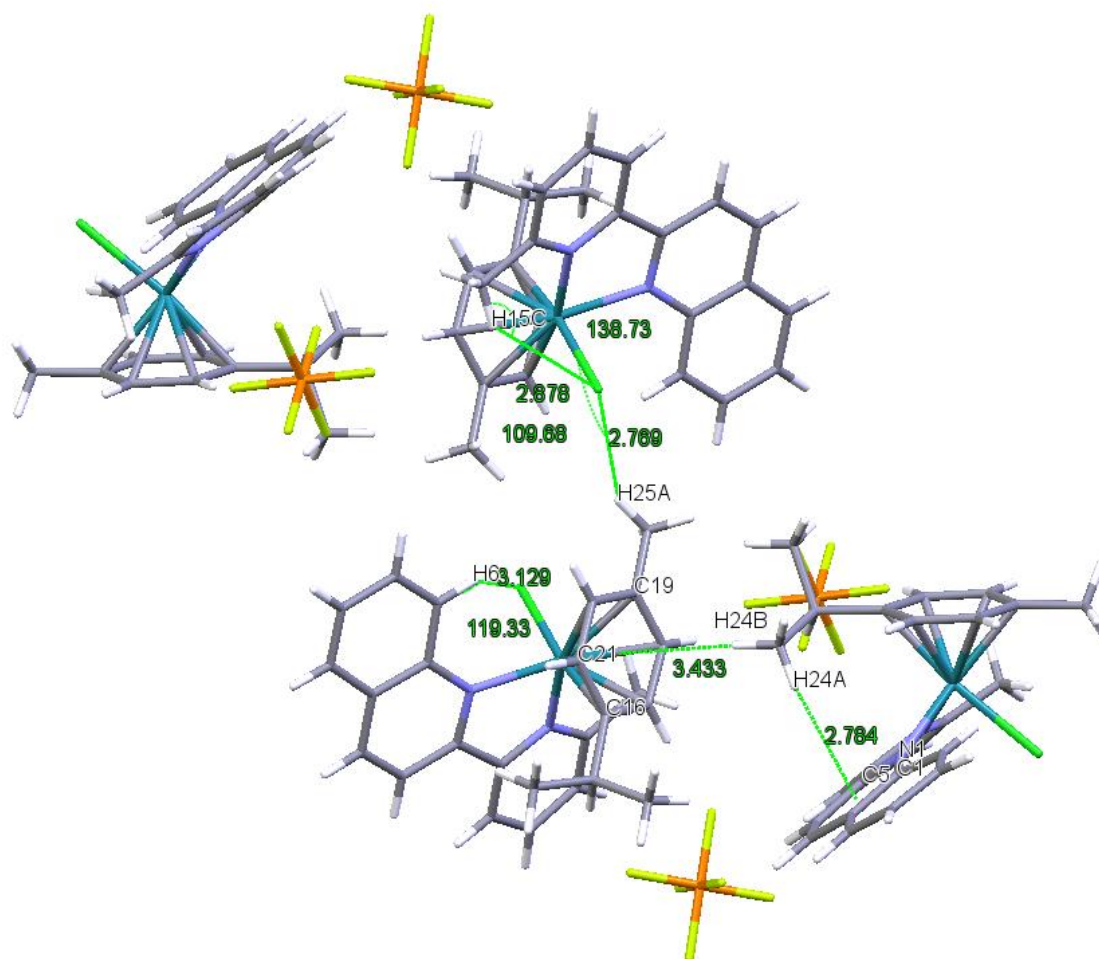


Figure S58. Intermolecular interactions in the unit cell of **2**

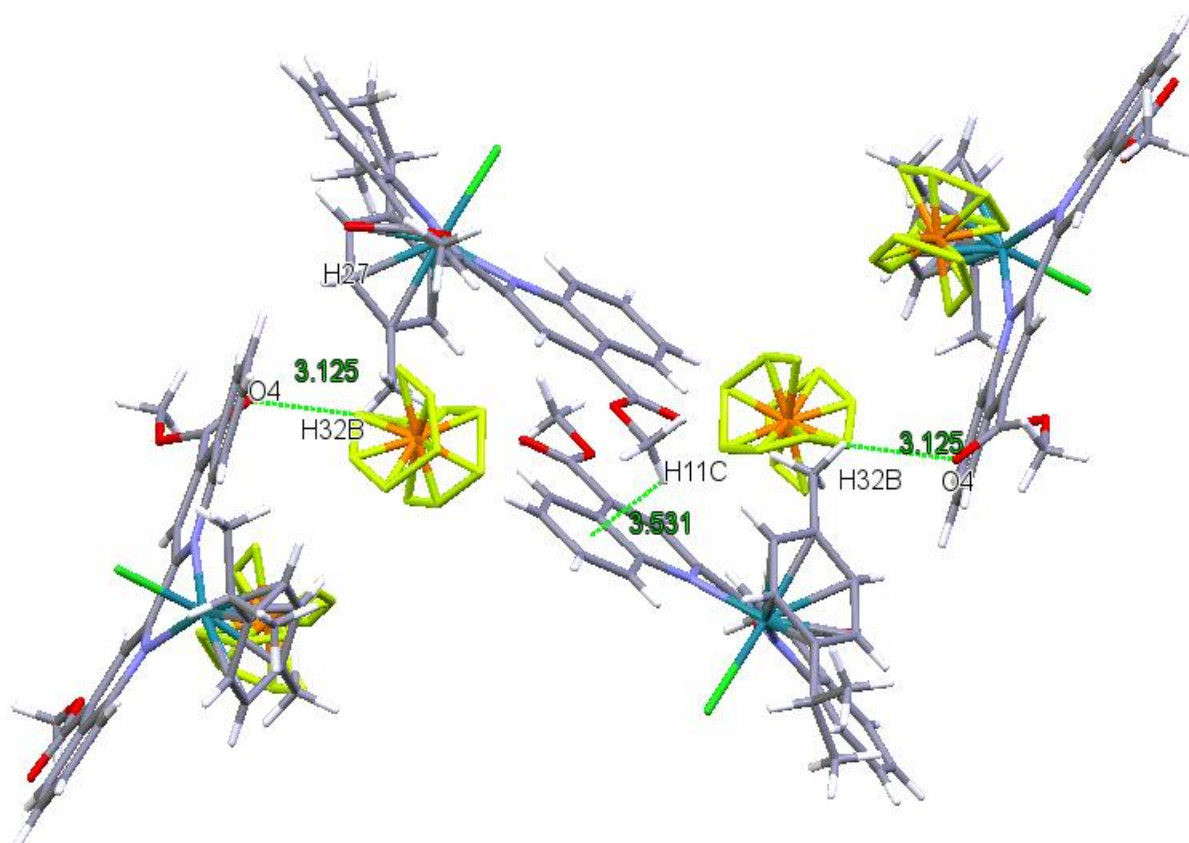


Figure S59. Intermolecular interactions in the unit cell of **6**

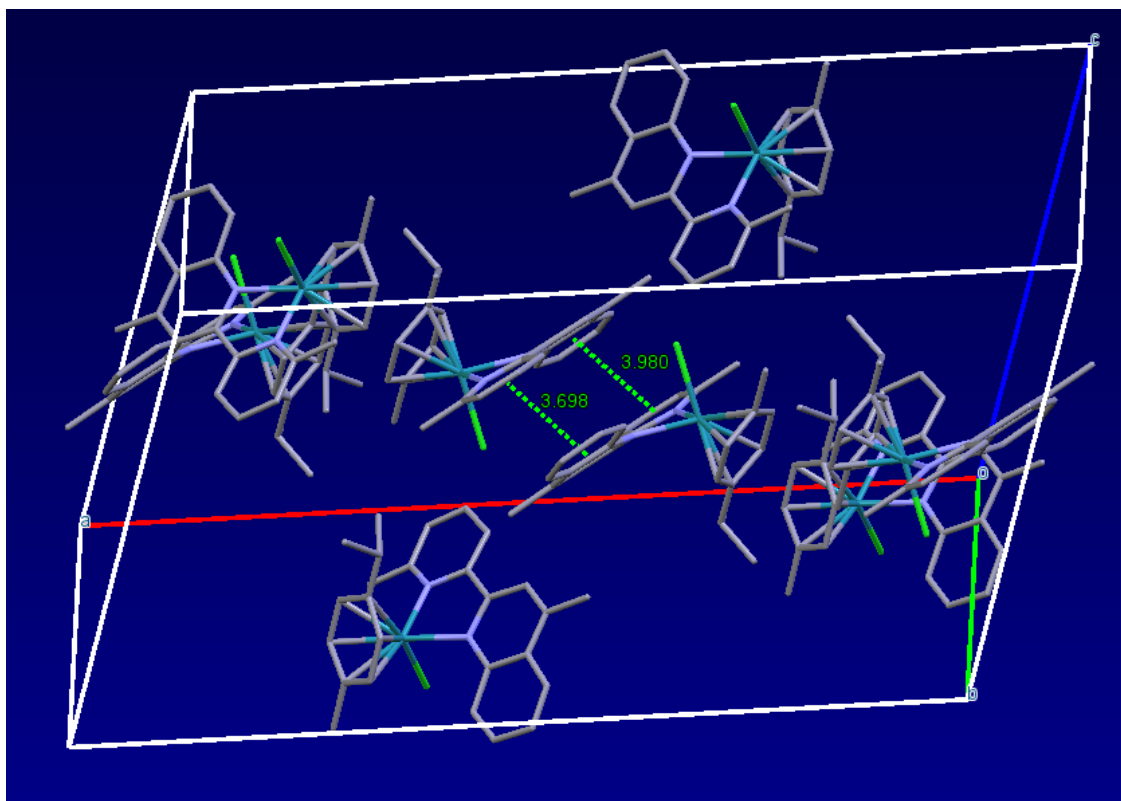


Figure S60. Intermolecular interactions in the unit cell of **3**

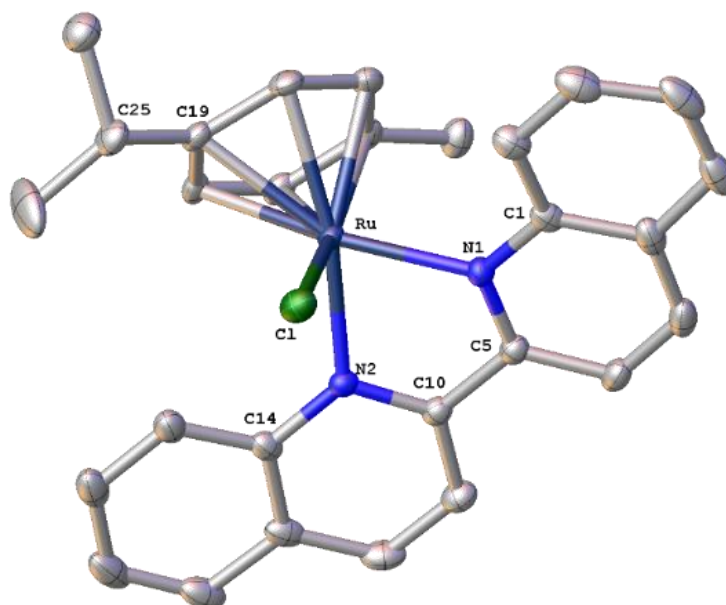


Figure S61. Molecular structure of cation of **8**. Hydrogen atoms and the PF_6^- anion are omitted for clarity. The ellipsoids were plotted at the 50% probability.

Table S1 Improved crystallographic data for **8**

Bond Lengths for 8							
Atom	Atom	Length/Å	Atom	Atom	Length/Å		
Ru	Cl	2.3859(6)	C14	C18	1.409(3)		
Ru	N1	2.0931(18)	C15	C16	1.354(4)		
Ru	N2	2.1010(18)	C16	C17	1.408(4)		
Ru	C19	2.250(2)	C17	C18	1.371(3)		
Ru	C20	2.201(2)	C19	C20	1.435(3)		
Ru	C21	2.186(2)	C19	C24	1.412(3)		
Ru	C22	2.203(2)	C19	C25	1.518(3)		
Ru	C23	2.179(2)	C20	C21	1.402(3)		
Ru	C24	2.227(2)	C21	C22	1.431(3)		
N1	C1	1.388(3)	C22	C23	1.413(3)		
N1	C5	1.340(3)	C22	C28	1.501(3)		
N2	C10	1.335(3)	C23	C24	1.424(3)		
N2	C14	1.379(3)	C25	C26	1.525(6)		
Bond Angles for 8							
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Ru	Cl	86.52(5)	N2	C14	C18	119.8(2)
N1	Ru	N2	76.49(7)	C18	C14	C13	119.8(2)
N1	Ru	C19	153.20(8)	C16	C15	C13	120.3(3)
N1	Ru	C20	116.03(8)	C15	C16	C17	120.8(2)
N1	Ru	C21	91.84(8)	C18	C17	C16	120.5(3)
N1	Ru	C22	93.16(8)	C17	C18	C14	119.8(2)
N1	Ru	C23	121.35(8)	C20	C19	Ru	69.34(12)
N1	Ru	C24	159.04(8)	C20	C19	C25	118.8(2)
N2	Ru	Cl	87.59(5)	C24	C19	Ru	70.75(13)
N2	Ru	C19	130.22(8)	C24	C19	C20	117.7(2)
N2	Ru	C20	166.78(8)	C24	C19	C25	123.5(2)
N2	Ru	C21	144.40(8)	C25	C19	Ru	129.35(16)
N2	Ru	C22	108.14(8)	C19	C20	Ru	73.05(13)
N2	Ru	C23	89.89(8)	C21	C20	Ru	70.81(13)
N2	Ru	C24	100.04(8)	C21	C20	C19	120.7(2)
C19	Ru	Cl	91.91(6)	C20	C21	Ru	71.92(13)
C20	Ru	Cl	97.05(6)	C20	C21	C22	122.0(2)
C20	Ru	C19	37.61(8)	C22	C21	Ru	71.58(13)
C20	Ru	C22	68.51(9)	C21	C22	Ru	70.35(13)
C20	Ru	C24	66.77(9)	C21	C22	C28	121.4(2)
C21	Ru	Cl	125.69(7)	C23	C22	Ru	70.27(13)
C21	Ru	C19	67.52(8)	C23	C22	C21	116.8(2)
C21	Ru	C20	37.27(9)	C23	C22	C28	121.6(2)
C21	Ru	C22	38.07(9)	C28	C22	Ru	126.85(16)
C21	Ru	C24	78.99(9)	C22	C23	Ru	72.10(13)

C22	Ru	Cl	163.76(7)	C22	C23	C24	121.6(2)
C22	Ru	C19	81.08(8)	C24	C23	Ru	72.99(13)
C22	Ru	C24	68.00(8)	C19	C24	Ru	72.49(13)
C23	Ru	Cl	150.52(6)	C19	C24	C23	121.1(2)
C23	Ru	C19	67.74(8)	C23	C24	Ru	69.31(12)
C23	Ru	C20	79.97(9)	C19	C25	C26	111.3(3)
C23	Ru	C21	67.45(9)	C19	C25	C26S	106.6(3)
C23	Ru	C22	37.63(9)	C27	C25	C19	115.5(2)
C23	Ru	C24	37.70(8)	C27	C25	C26	116.3(4)
C24	Ru	Cl	114.17(6)	C27	C25	C26S	99.7(5)

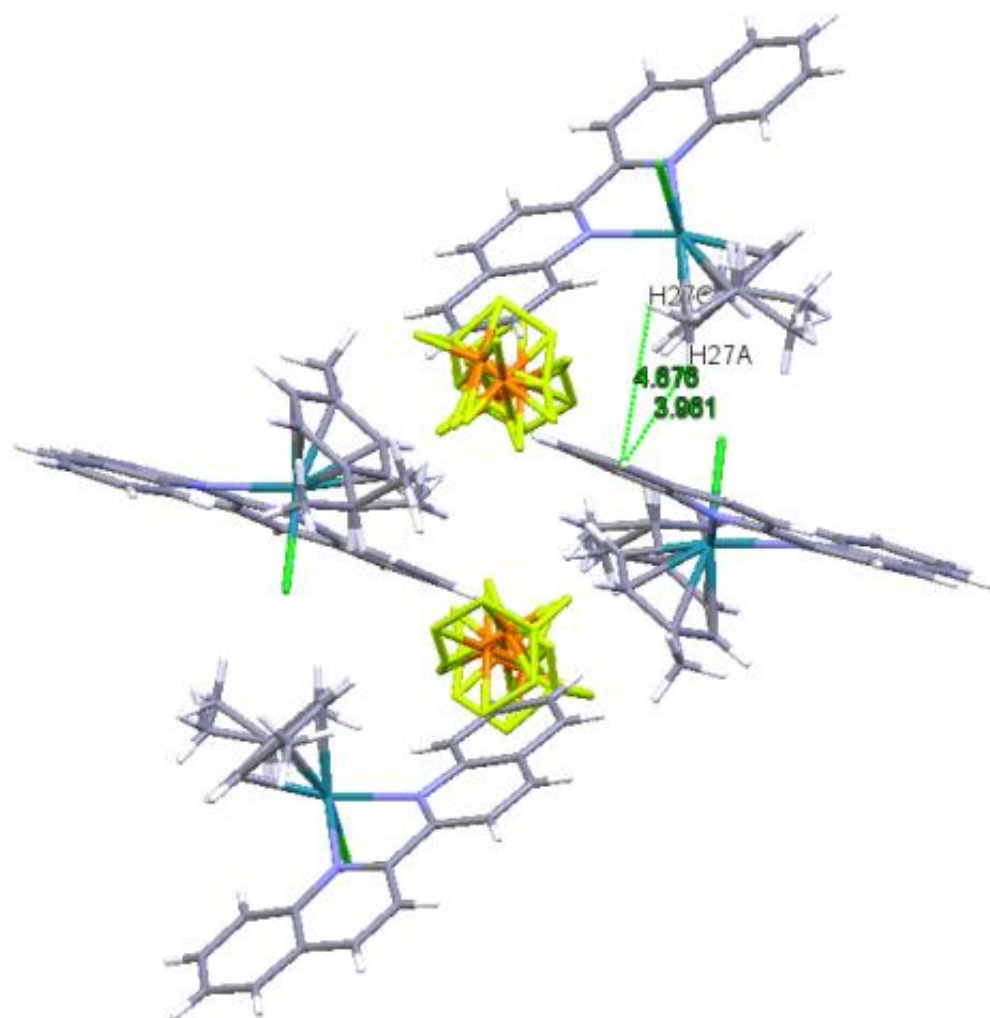


Figure S62. Intermolecular interactions in the unit cell of **8**

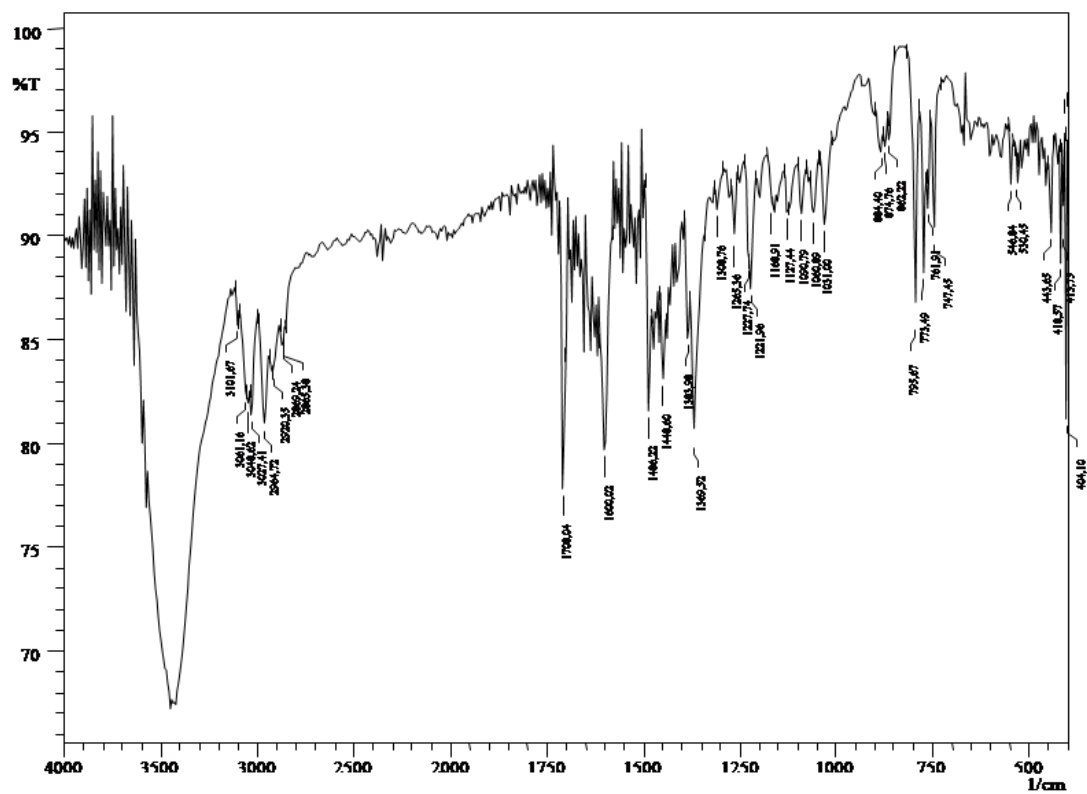


Figure S63. FT-IR spectrum of 9

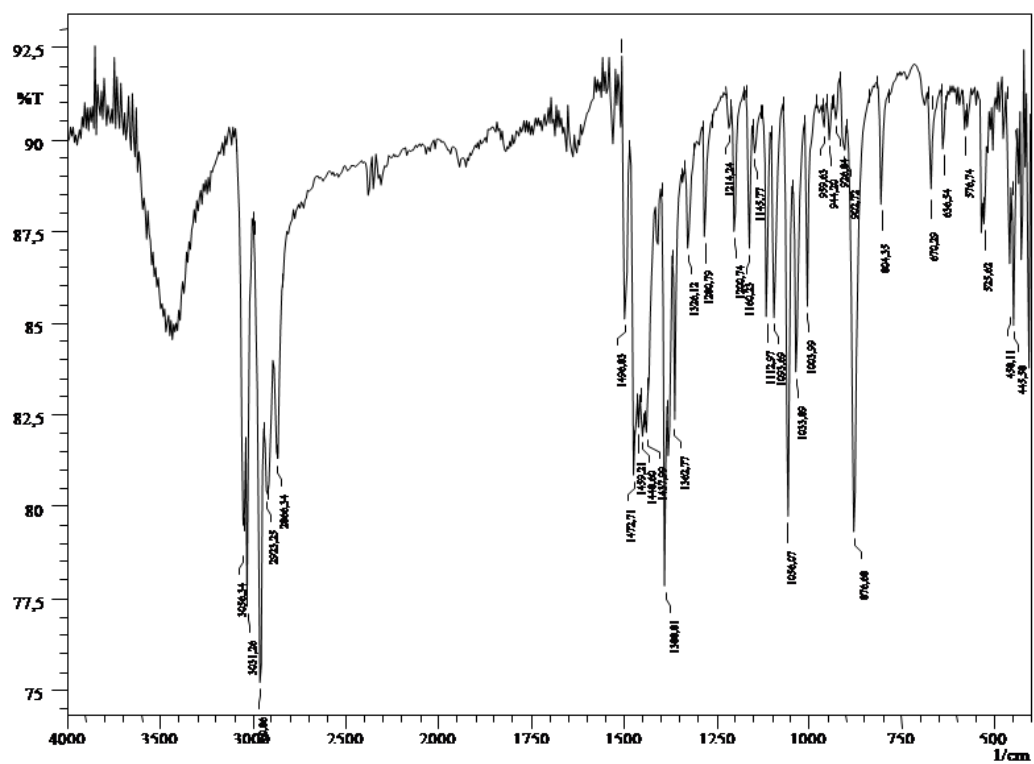


Figure S64. FT-IR spectrum of 10

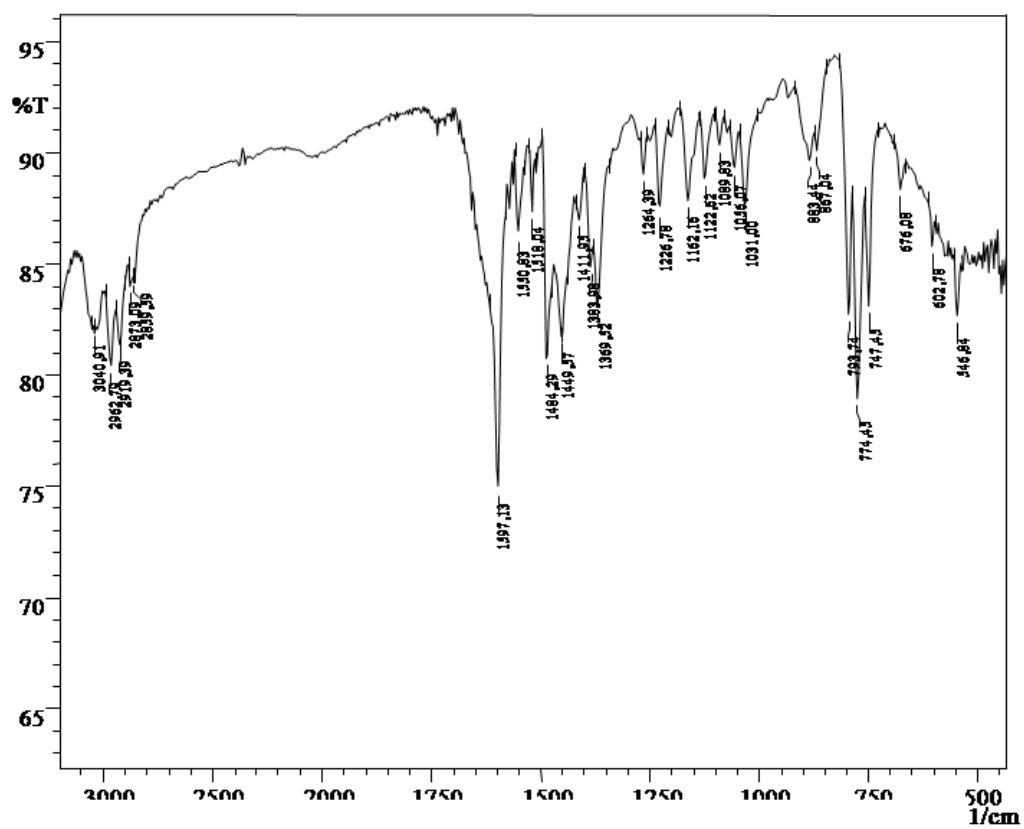


Figure S65. FT-IR spectrum of 11

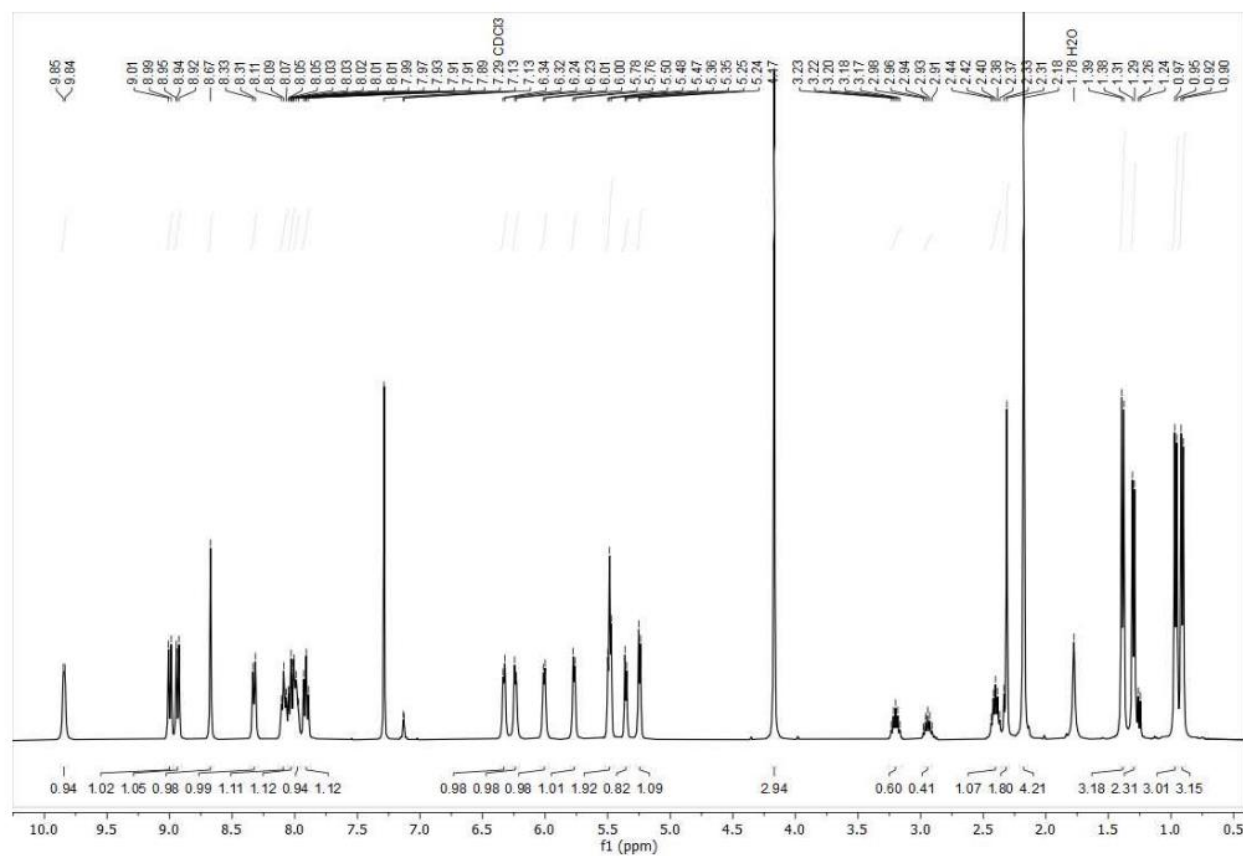


Figure S66. ¹H-NMR spectrum of **9** in CDCl₃

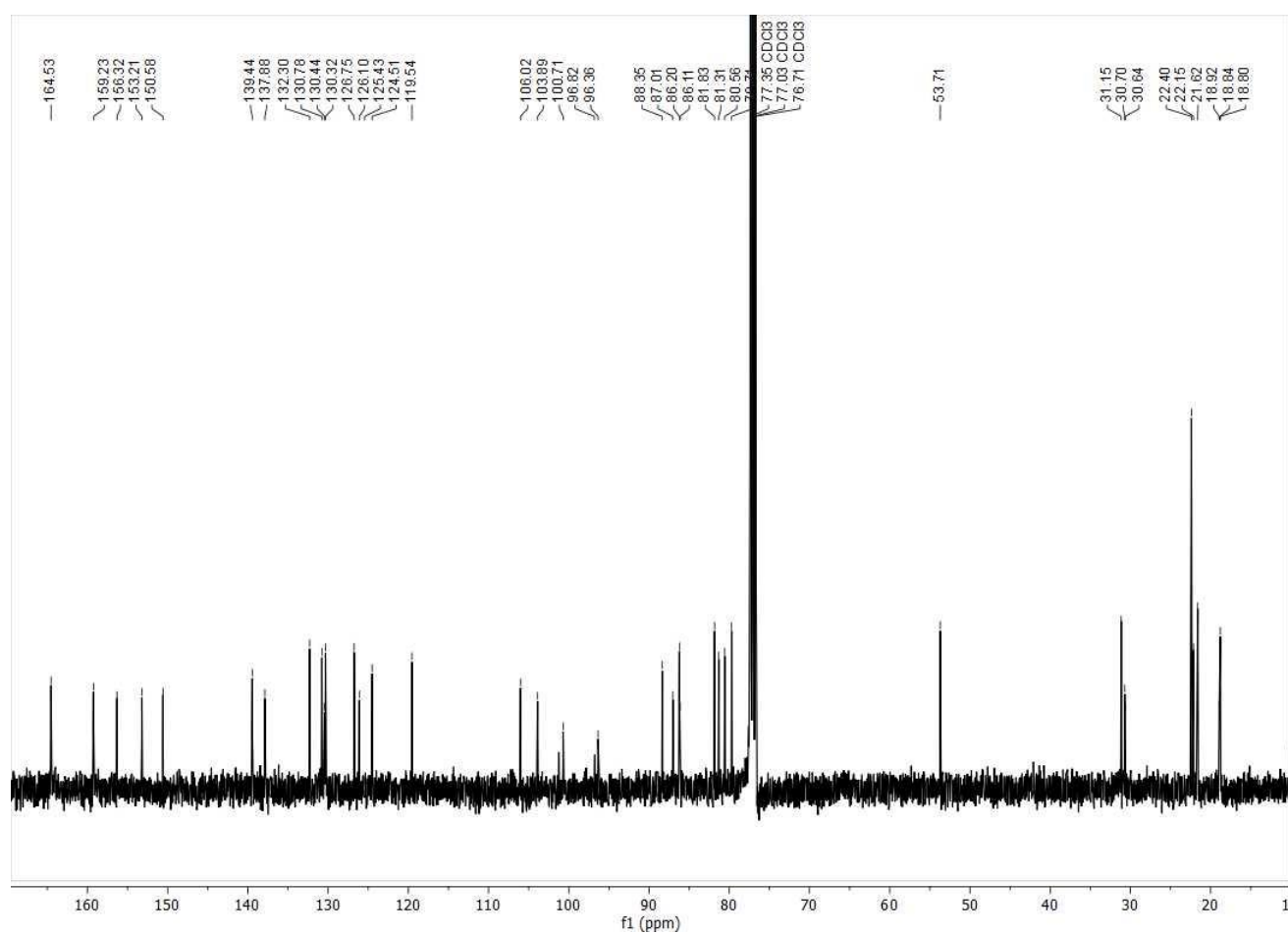


Figure S67. ¹³C{¹H}-NMR spectrum of **9** in CDCl₃

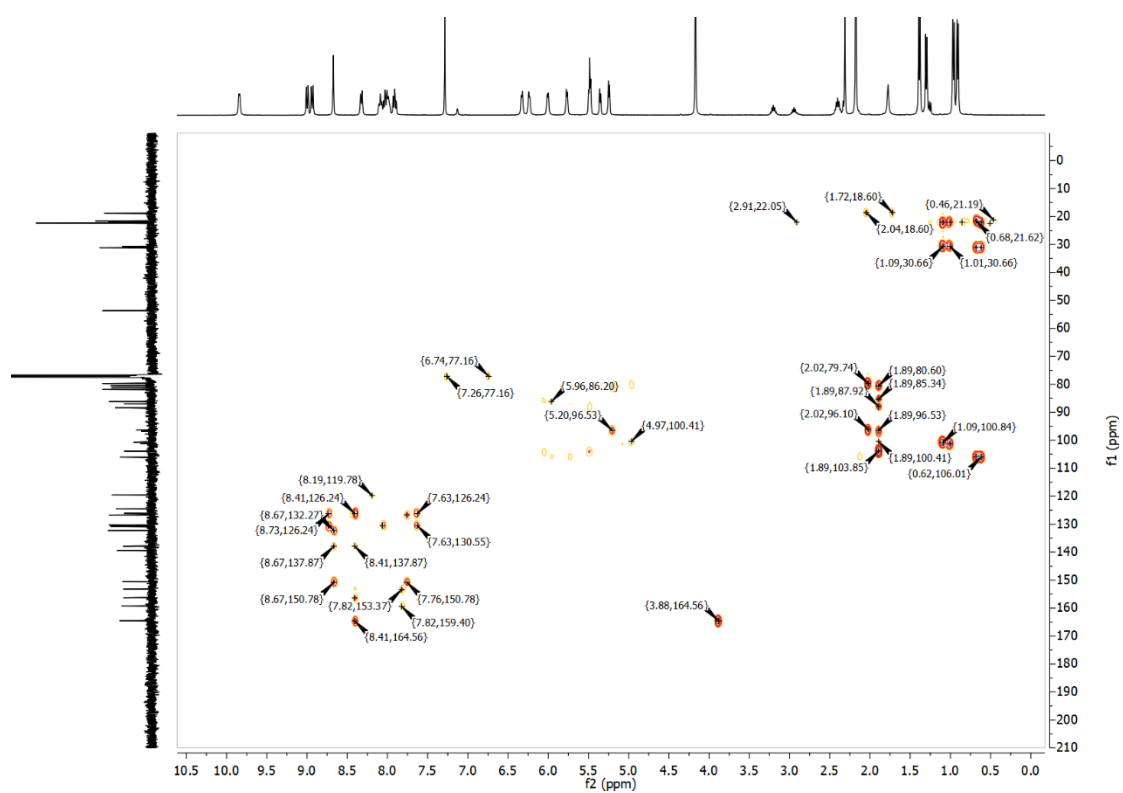


Figure S68. ^1H - ^{13}C -HSQC spectrum of **9** in CDCl_3

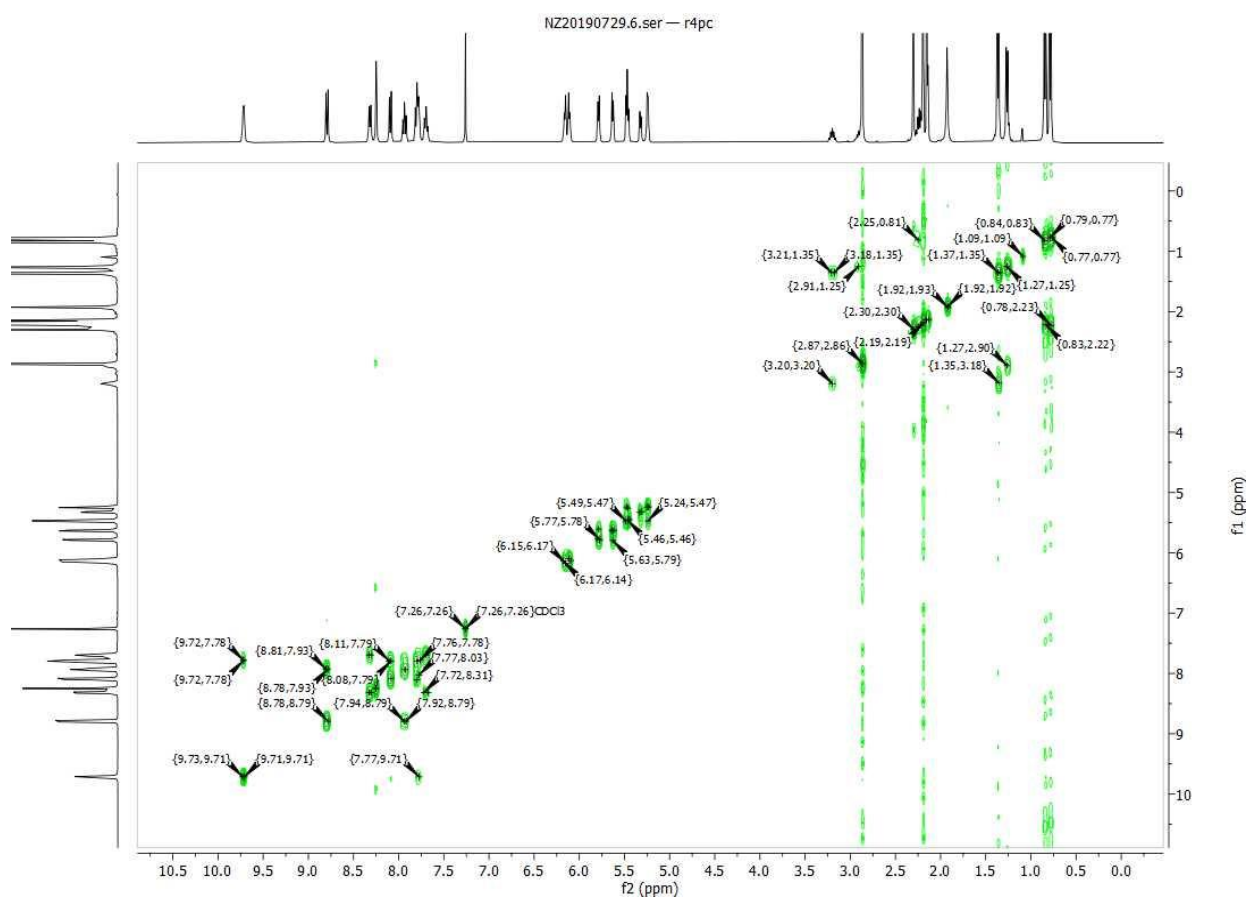


Figure S69. ^1H - ^1H COSY spectrum of **10** in CDCl_3

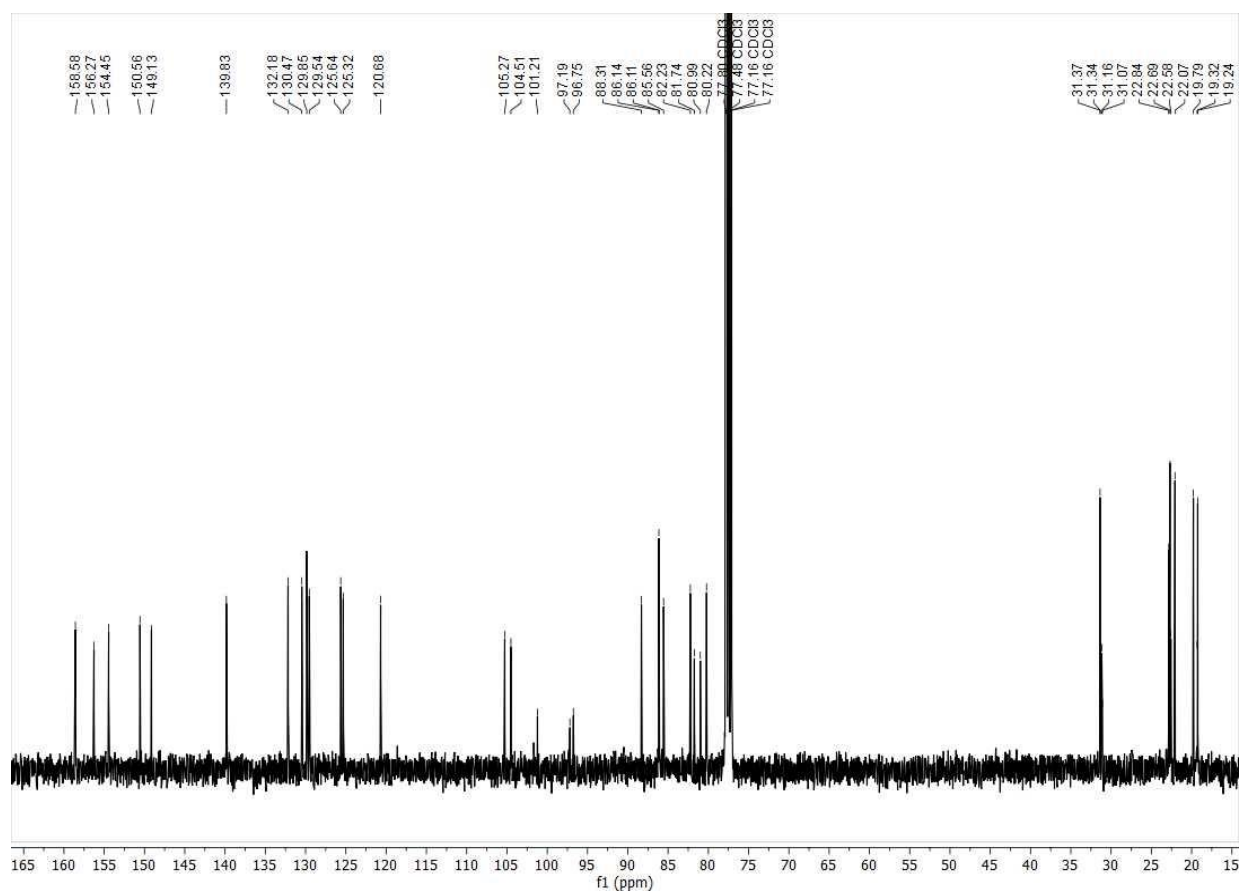


Figure S70. ¹³C{¹H}-NMR spectrum of **10** in CDCl₃

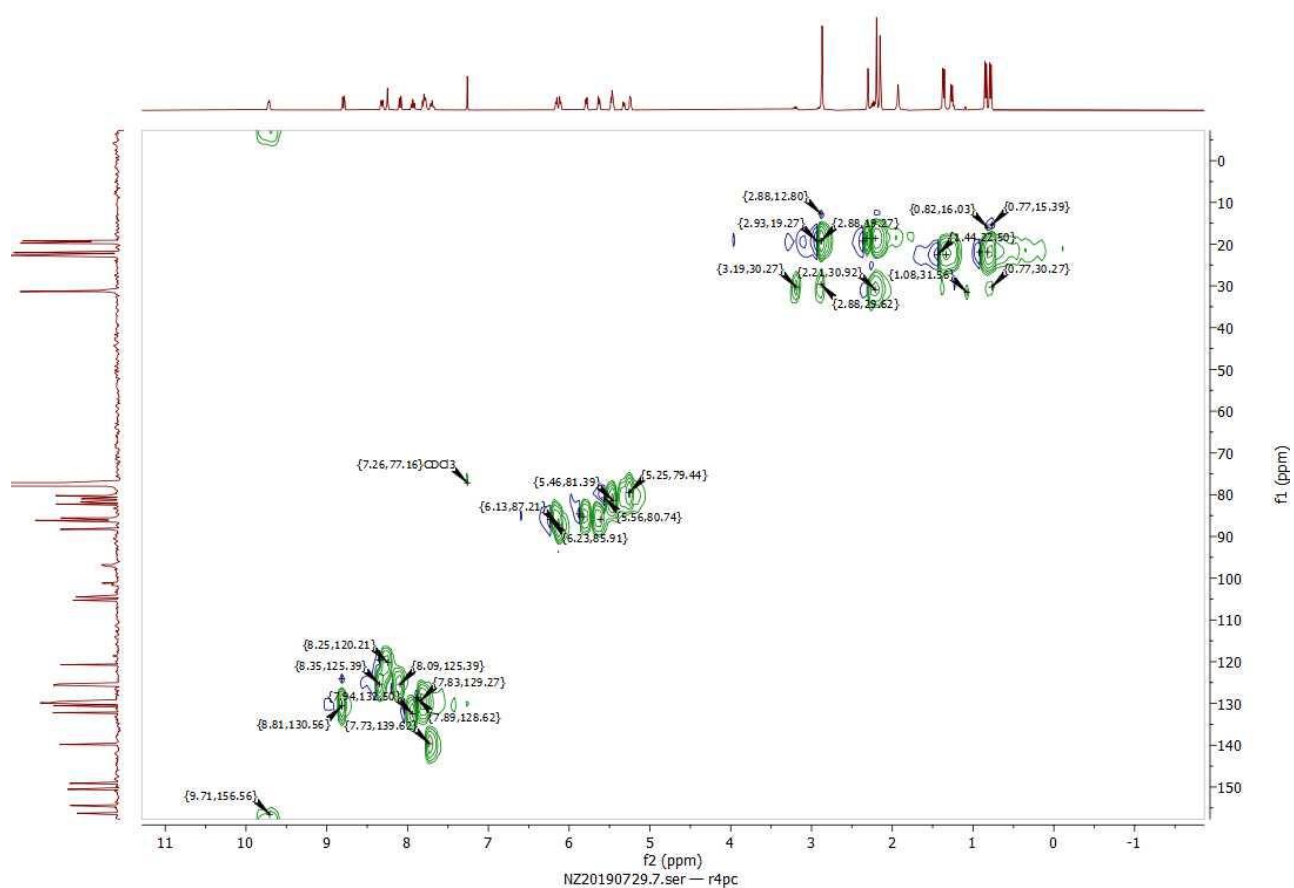


Figure S71. ^1H - ^{13}C -HSQC spectrum of **10** in CDCl_3

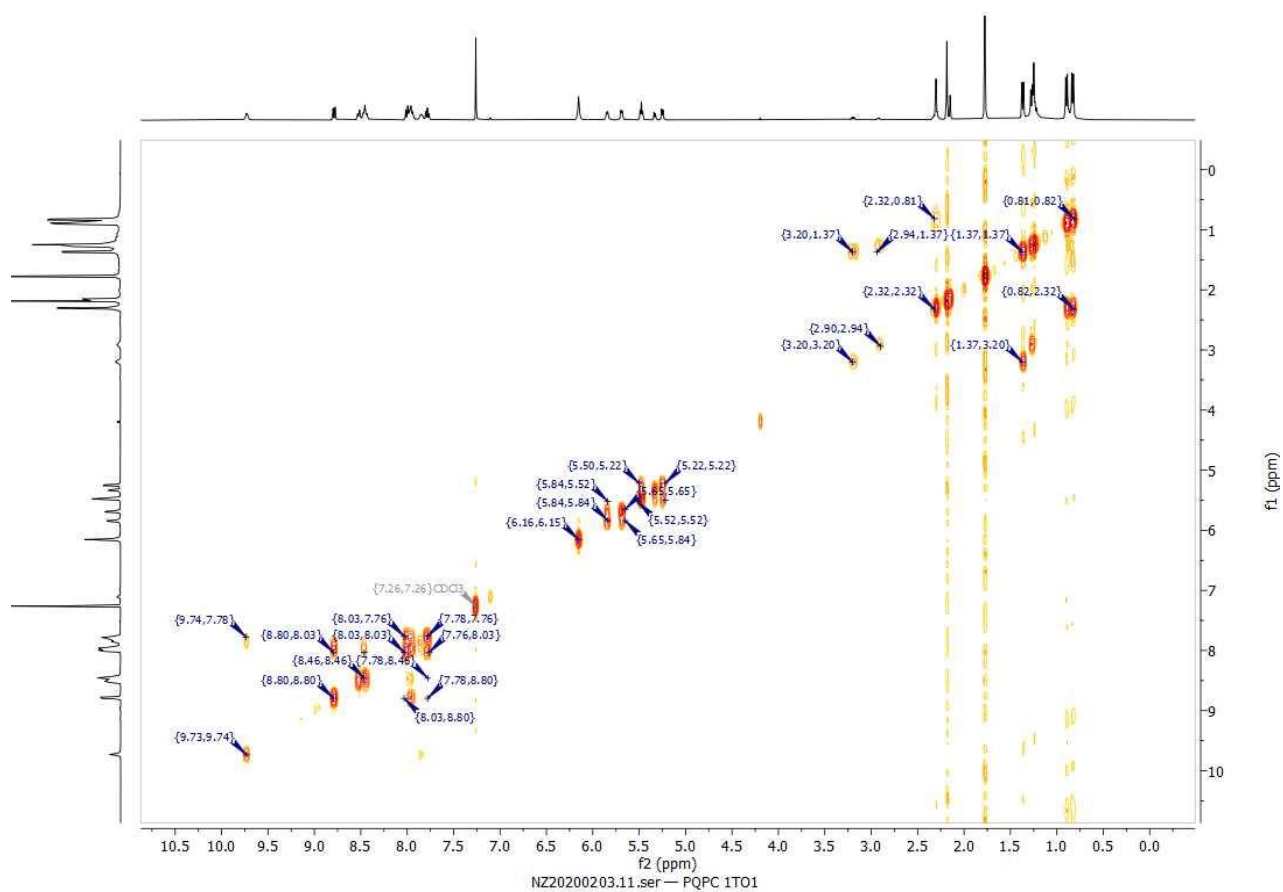


Figure S72. ^1H - ^1H COSY spectrum of **11** in CDCl_3

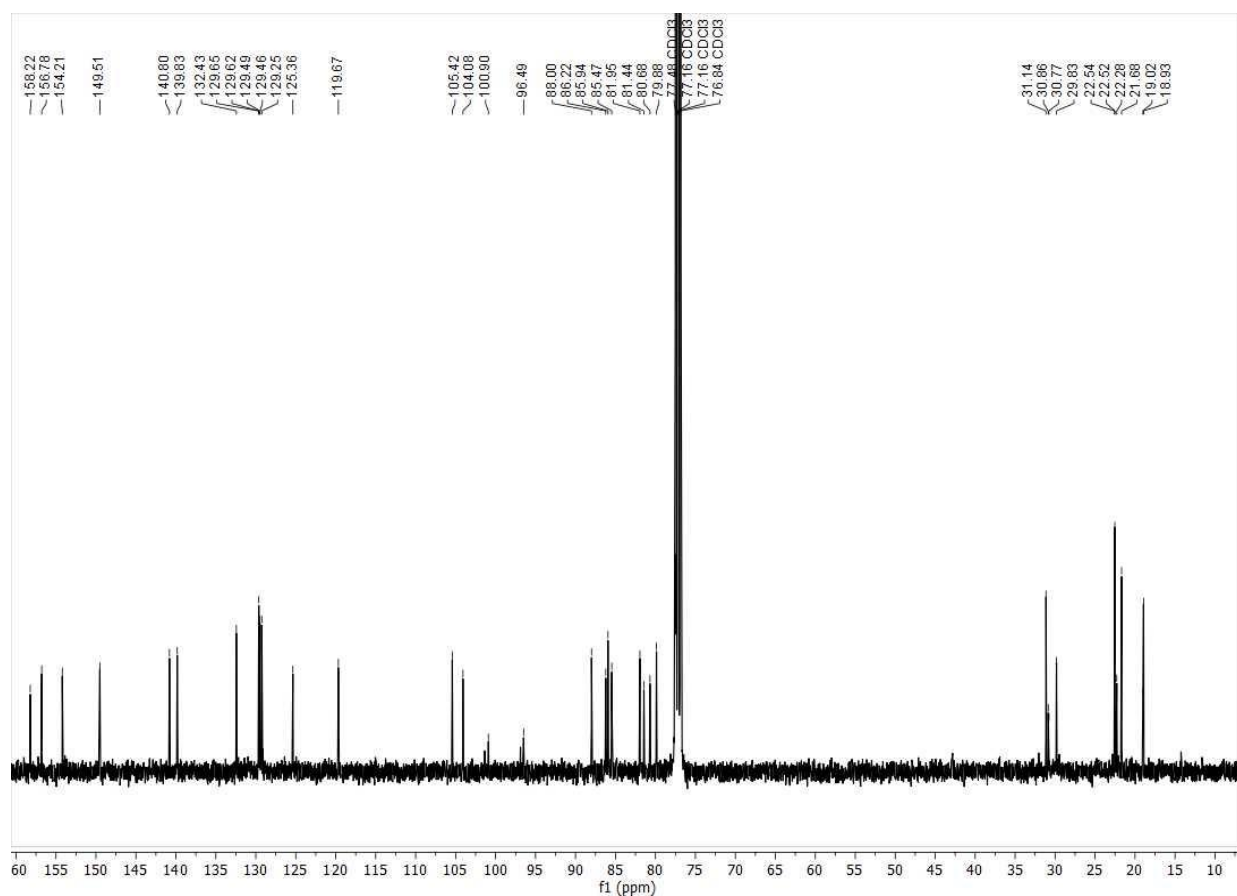


Figure S73. ¹³C{¹H}-NMR spectrum of **11** in CDCl₃

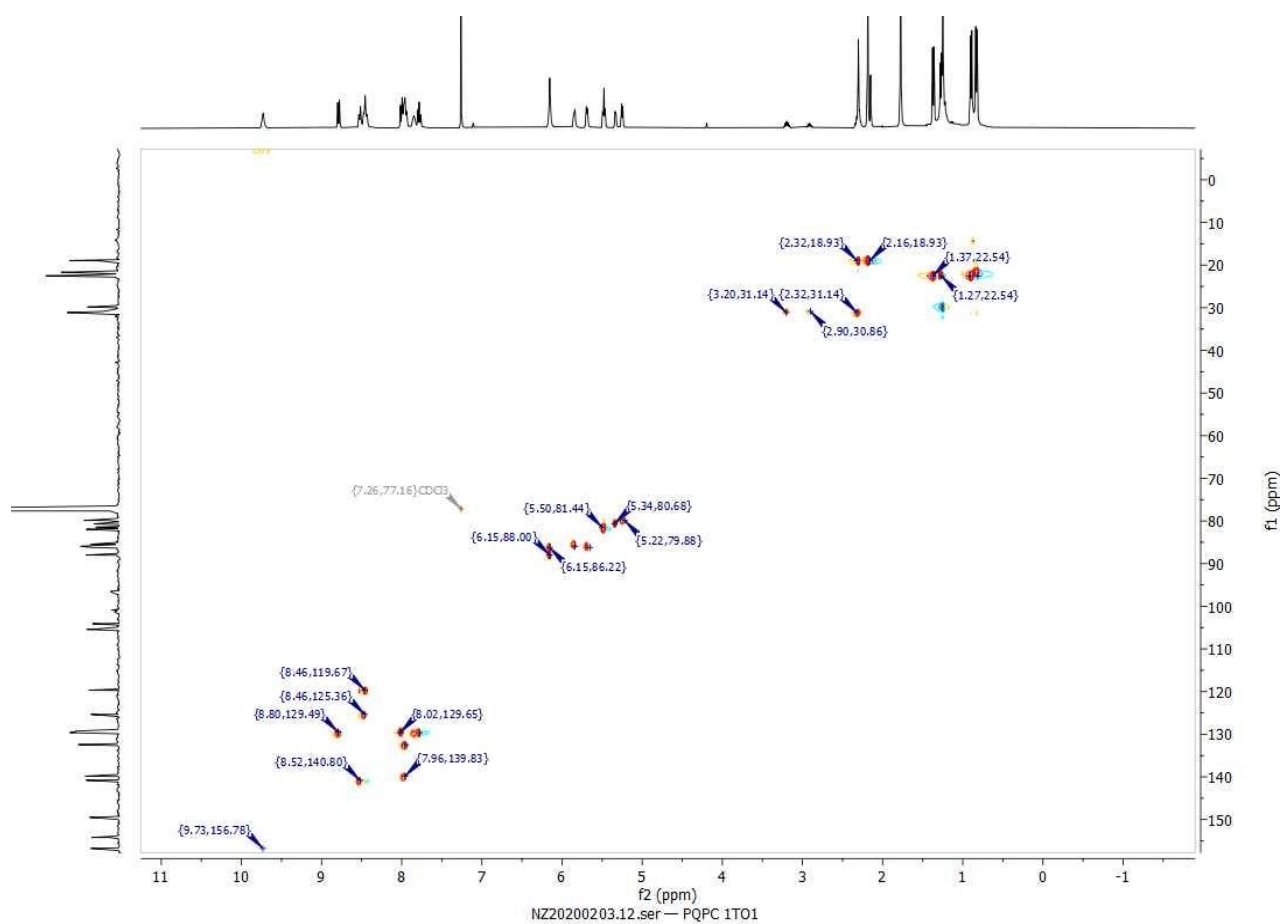


Figure S74. ^1H - ^{13}C -HSQC spectrum of **11** in CDCl_3

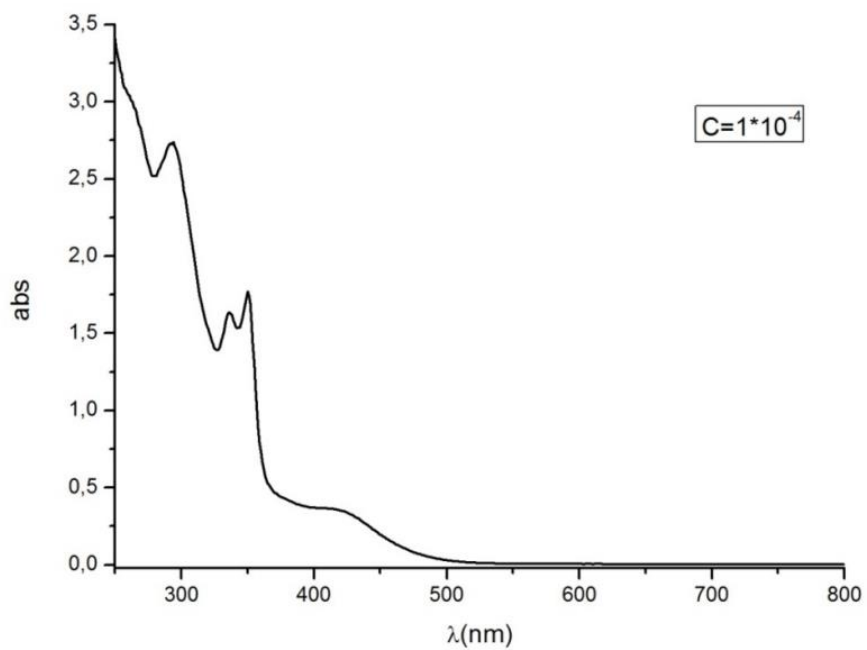


Figure S75. UV-vis spectrum of **9** in CHCl_3

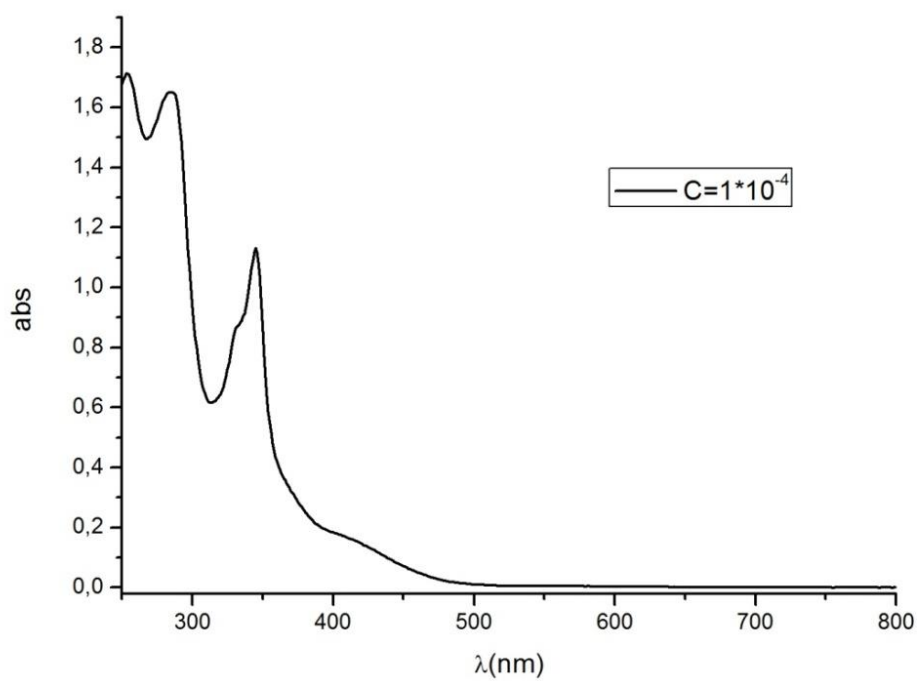


Figure S76. UV-vis spectrum of **9** in H_2O

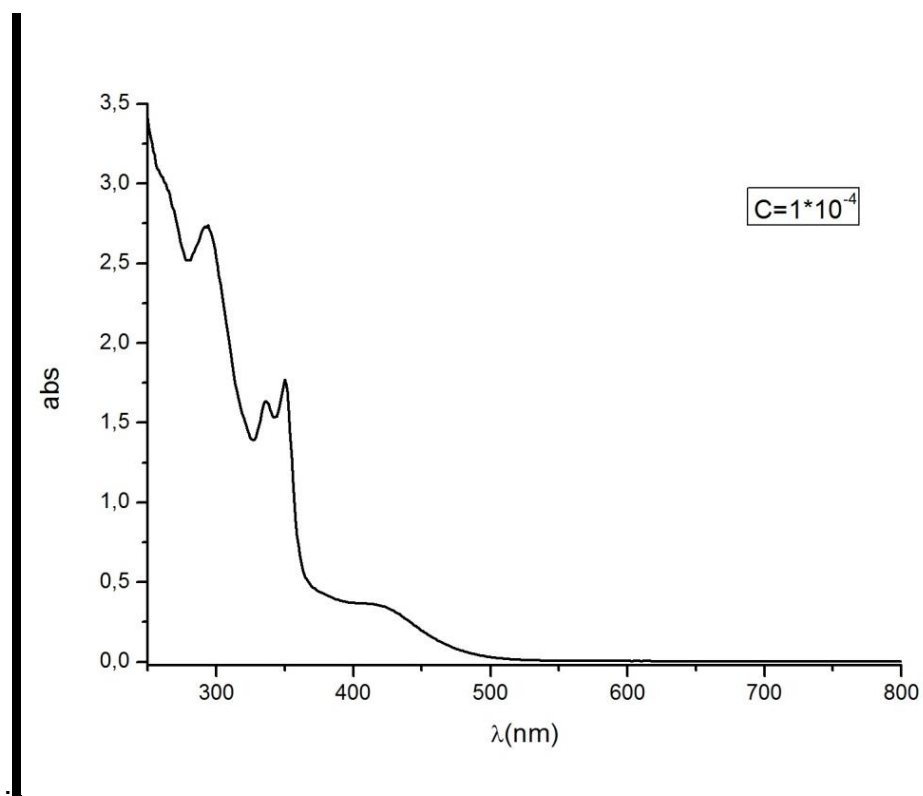


Figure S77. UV-vis spectrum of **10** in CHCl_3

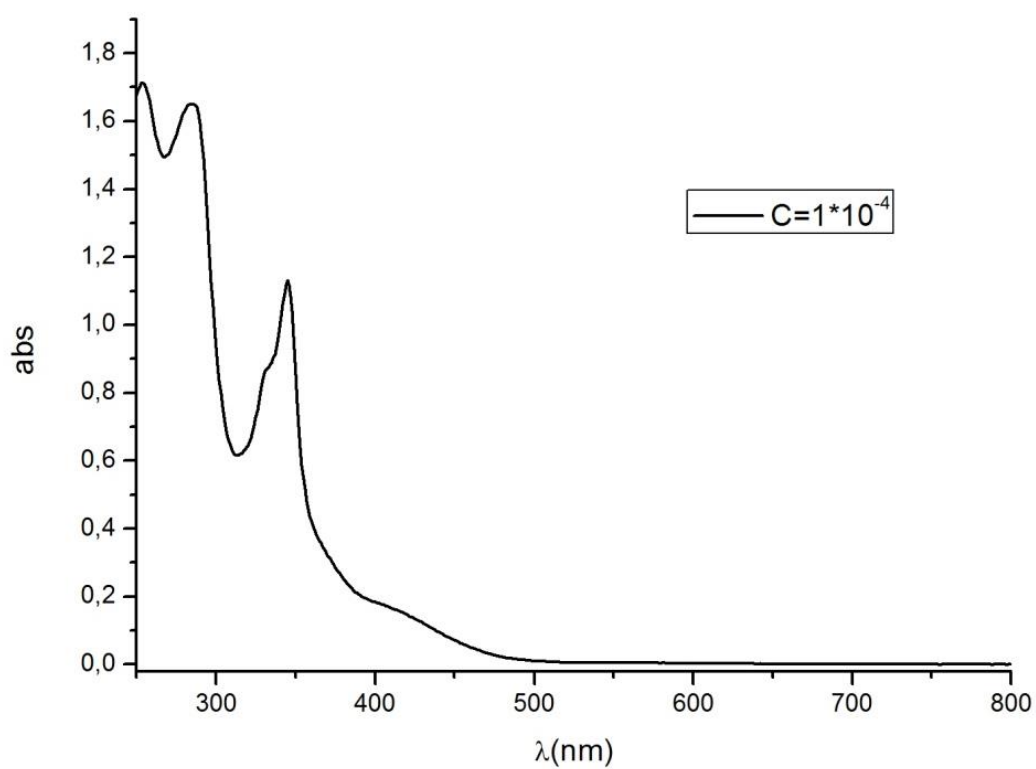


Figure S78. UV-vis spectrum of **10** in H_2O

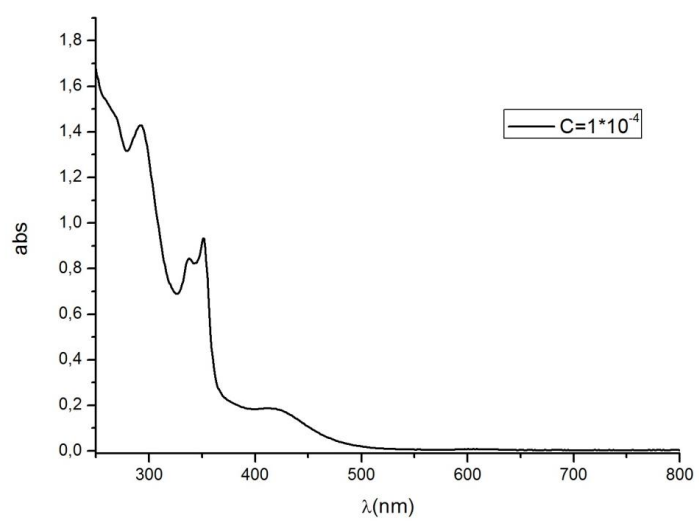


Figure S79. UV-vis spectrum of **11** in CHCl_3

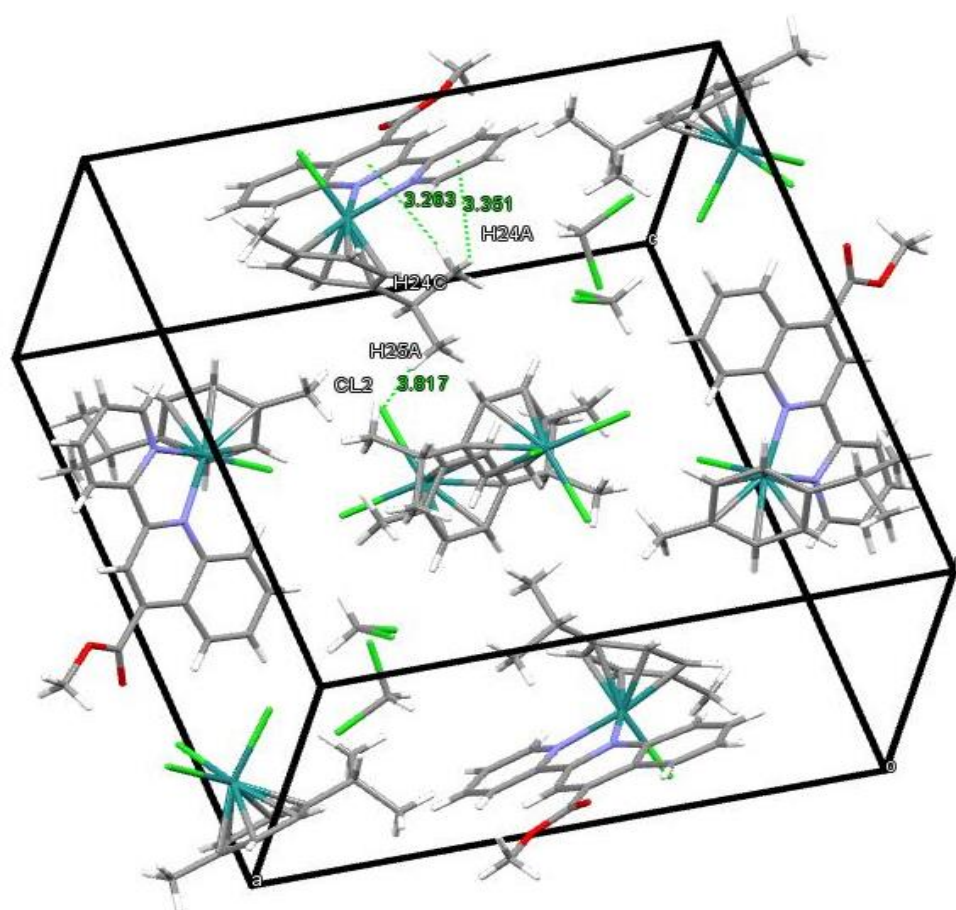


Figure S80. Intermolecular interactions in the single crystal of **9**

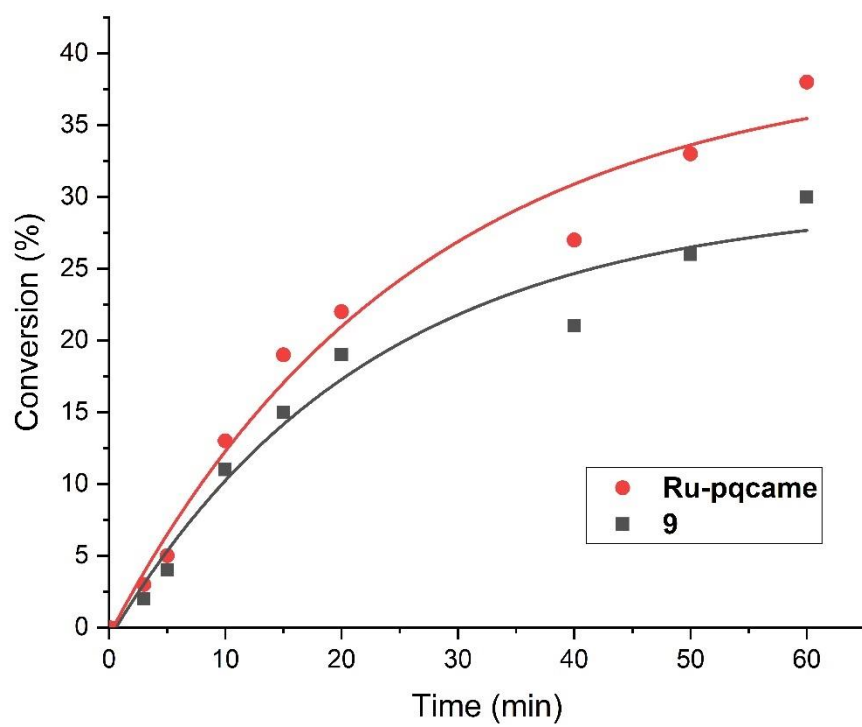


Figure S81. Conversion versus reaction time for acetophenone transfer hydrogenation by catalysts **Ru-pqcame** and **9** within 60 min

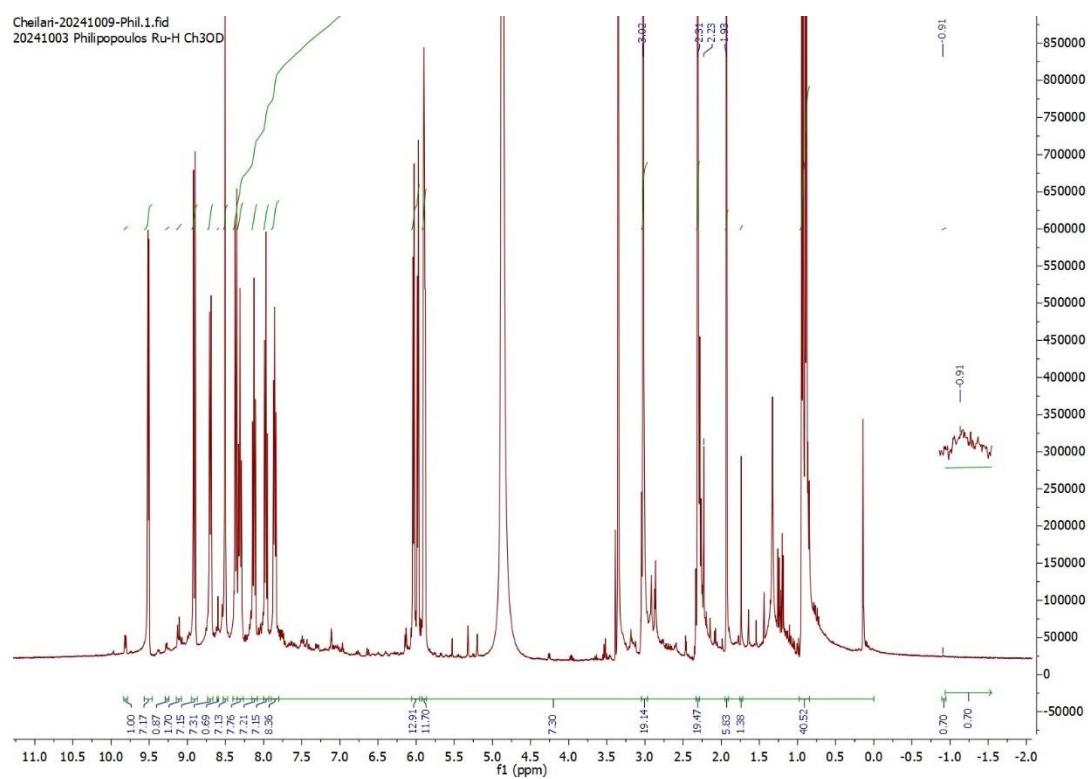


Figure S82. ^1H NMR spectrum (CH_3OD) of a sample of **4** showing the formation of Ru-H species

TABLE S2 Crystal and refinement data for **8-Mepq**, **4,6'-Me₂pqca** and **8,6'- Me₂pqca**.

	8-Mepq	4,6'-Me₂pq	8,6'-Me₂pq
Empirical formula	C ₁₅ H ₁₂ N ₂	C ₁₆ H ₁₄ N ₂	C ₁₆ H ₁₄ N ₂
Molecular weight	220.27	234.29	234.29
Crystal color	colourless plate	colourless block	yellow plank
Crystal size (mm ³)	0.32 × 0.16 × 0.06	0.32 × 0.24 × 0.2	0.21 × 0.05 × 0.04
Temperature (K)	100.01	100	100
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	<i>Pn</i> 2 ₁ <i>a</i>	<i>Pbca</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>Unit cell dimensions</i>			
<i>a</i> (Å)	22.2546(8)	9.6069(2)	4.7706(7)
<i>b</i> (Å)	24.9016(9)	14.6504(3)	14.830(3)
<i>c</i> (Å)	3.92100(10)	17.8853(4)	17.148(4)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
<i>V</i> (Å ³)	2172.92(12)	2517.27(9)	1213.2(4)
<i>Z</i>	8	8	4
ρ_{calc} (g cm ⁻³)	1.347	2517.27(9)	1.283
μ (mm ⁻¹)	0.627	8	0.076
2 θ range (°)	7.1 to 135.498°	12.076 to 135.488°	5.986 to 55.998°
Index ranges	-26 ≤ <i>h</i> ≤ 26, -29 ≤ <i>k</i> ≤ 29, -4 ≤ <i>l</i> ≤ 4	-11 ≤ <i>h</i> ≤ 11, -17 ≤ <i>k</i> ≤ 17, -19 ≤ <i>l</i> ≤ 21	-6 ≤ <i>h</i> ≤ 4, -19 ≤ <i>k</i> ≤ 19, -22 ≤ <i>l</i> ≤ 22
Reflections collected	64914	32014	9291
Independent reflections	3949	2261	2932
Data/restraints/parameters	3949/1/309	2261/0/165	2932/0/165
Goodness-of-fit on <i>F</i> ²	1.126	1.084	1.012
Final <i>R</i> indexes [<i>I</i> > 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0533, <i>wR</i> ₂ = 0.1379	<i>R</i> ₁ = 0.0404, <i>wR</i> ₂ = 0.1001	<i>R</i> ₁ = 0.0621, <i>wR</i> ₂ = 0.1470
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0545, <i>wR</i> ₂ = 0.1388	<i>R</i> ₁ = 0.0424, <i>wR</i> ₂ = 0.1019	<i>R</i> ₁ = 0.1117, <i>wR</i> ₂ = 0.1794
Largest diff. peak/hole/e Å ⁻³	0.40/-0.27	0.18/-0.25	0.27/-0.31

TABLE S3 Crystal and refinement data for **1–4**

	1	2	3	4
Crystal Habitus	clear orange block	clear orange block	clear orange plate	clear orange plank
Device Type	Bruker X8-KappaApexII	Bruker X8-KappaApexII	Bruker X8-KappaApexII	Bruker X8-KappaApexII
Empirical formula	C ₂₅ H ₂₆ ClN ₂ Ru	C ₂₅ H ₂₆ ClF ₆ N ₂ PRu	C ₂₆ H ₂₈ ClF ₆ N ₂ PRu	C ₂₆ H ₂₈ ClN ₂ Ru
Moiety formula	C ₂₅ H ₂₆ Cl N ₂ Ru	C ₂₅ H ₂₆ Cl N ₂ Ru, F ₆ P	C ₂₆ H ₂₈ Cl N ₂ Ru, F ₆ P	C ₂₆ H ₂₈ Cl N ₂ Ru
Formula weight	491.00	635.97	649.99	505.02
Temperature/K	100	100	100	100
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic
Space group	Pbca	P2 ₁ /c	P-1	C2/c
a/Å	17.8445(13)	9.2097(3)	14.0446(19)	27.203(9)
b/Å	13.6553(9)	23.6119(7)	14.7713(18)	13.222(5)
c/Å	19.6773(16)	12.1242(4)	15.238(2)	15.605(6)
α/°	90	90	111.169(3)	90
β/°	90	108.8567(9)	116.028(4)	106.946(10)
γ/°	90	90	92.252(4)	90
Volume/Å ³	4794.8(6)	2495.01(14)	2574.2(6)	5369(3)
Z	8	4	4	8
ρ _{calc} /cm ³	1.360	1.693	1.677	1.250
μ/mm ⁻¹	0.778	0.863	0.838	0.696
F(000)	2008.0	1280.0	1312.0	2072.0
Crystal size/mm ³	0.24 × 0.19 × 0.08	0.15 × 0.12 × 0.08	0.09 × 0.05 × 0.03	0.12 × 0.07 × 0.04
Absorption correction	empirical	empirical	empirical	empirical
Tmin; Tmax	0.5664; 0.7460	0.6552; 0.7462	0.5675; 0.7460	0.5227; 0.7459
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.288 to 56°	6.278 to 55.992°	3.042 to 55.998°	3.13 to 55.998°
Completeness to theta	0.997	0.998	0.998	0.990
Index ranges	-23 ≤ h ≤ 23, -11 ≤ k ≤ 18, -20 ≤ l ≤ 25	-12 ≤ h ≤ 12, -31 ≤ k ≤ 31, -15 ≤ l ≤ 16	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20	-35 ≤ h ≤ 32, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20
Reflections collected	40510	51000	84607	18166
Independent reflections	5771 [R _{int} = 0.1442, R _{sigma} = 0.0874]	6012 [R _{int} = 0.0250, R _{sigma} = 0.0127]	12426 [R _{int} = 0.1599, R _{sigma} = 0.1130]	6392 [R _{int} = 0.1673, R _{sigma} = 0.2225]
Data/restraints/parameters	5771/288/296	6012/0/329	12426/0/677	6392/108/276
Goodness-of-fit on F ²	1.177	1.056	1.055	1.033
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.1716, wR ₂ = 0.3795	R ₁ = 0.0245, wR ₂ = 0.0631	R ₁ = 0.0785, wR ₂ = 0.2067	R ₁ = 0.1313, wR ₂ = 0.3085
Final R indexes [all data]	R ₁ = 0.1862, wR ₂ = 0.3872	R ₁ = 0.0271, wR ₂ = 0.0650	R ₁ = 0.1498, wR ₂ = 0.2512	R ₁ = 0.2182, wR ₂ = 0.3561
Largest diff. peak/hole / e Å ⁻³	2.62/-2.37	2.25/-0.44	1.66/-1.95	1.58/-1.61

TABLE S4 Crystal and refinement data for **6**, **8** and **9**

	6	8	9
Crystal Habitus	clear red plate	clear red plank	clear red plank
Device Type	Bruker X8-KappaApexII	Bruker X8-KappaApexII	Bruker X8-KappaApexII
Empirical formula	C ₃₂ H ₃₀ N ₂ O ₄ F ₆ PClRu	C ₂₈ H ₂₆ N ₂ F ₆ PClRu	C ₃₇ H ₄₂ Cl ₆ N ₂ O ₂ Ru ₂
Moiety formula	C ₃₂ H ₃₀ Cl N ₂ O ₄ Ru, F ₆ P	C ₂₈ H ₂₆ Cl N ₂ Ru, F ₆ P	C ₂₆ H ₂₆ Cl N ₂ O ₂ Ru, C ₁₀ H ₁₄ Cl ₃ Ru, C H ₂ Cl ₂
Formula weight	788.07	672.00	961.56
Temperature/K	100	100	100
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n
a/Å	12.3138(9)	12.3889(6)	18.1466(18)
b/Å	10.7950(9)	15.0047(8)	10.6868(11)
c/Å	23.521(2)	13.8402(7)	19.736(2)
α /°	90	90	90
β /°	98.205(3)	94.5731(17)	91.465(3)
γ /°	90	90	90
Volume/Å ³	3094.6(4)	2564.6(2)	3826.1(7)
Z	4	4	4
ρ_{calc} /g/cm ³	1.691	1.740	1.669
μ /mm ⁻¹	0.723	0.844	1.244
F(000)	1592.0	1352.0	1936.0
Crystal size/mm ³	0.09 × 0.09 × 0.02	0.19 × 0.11 × 0.1	0.12 × 0.04 × 0.02
Absorption correction	empirical	empirical	empirical
Tmin; Tmax	0.6335; 0.7459	0.6632; 0.7461	0.6136; 0.7462
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	5.49 to 55.996°	4.01 to 55.988°	4.334 to 56°
Completeness to theta	0.998	0.999	0.998
Index ranges	-15 ≤ h ≤ 16, -14 ≤ k ≤ 14, -31 ≤ l ≤ 31	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -18 ≤ l ≤ 18	-23 ≤ h ≤ 23, -14 ≤ k ≤ 14, -26 ≤ l ≤ 25
Reflections collected	40166	94212	71161
Independent reflections	7465 [R _{int} = 0.1238, R _{sigma} = 0.1000]	6192 [R _{int} = 0.0494, R _{sigma} = 0.0184]	9211 [R _{int} = 0.1116, R _{sigma} = 0.0660]
Data/restraints/parameters	7465/42/484	6192/36/421	9211/0/449
Goodness-of-fit on F ²	0.975	1.081	1.074
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0571, wR ₂ = 0.1445	R ₁ = 0.0299, wR ₂ = 0.0668	R ₁ = 0.0494, wR ₂ = 0.1211
Final R indexes [all data]	R ₁ = 0.1071, wR ₂ = 0.1741	R ₁ = 0.0389, wR ₂ = 0.0732	R ₁ = 0.0879, wR ₂ = 0.1487
Largest diff. peak/hole / e Å ⁻³	1.13/-1.34	0.88/-0.68	1.39/-1.90