

Lipophilic $\text{Re}(\text{CO})_3\text{Pyca}$ Complexes for Mid-IR Imaging Applications

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Supplementary Information

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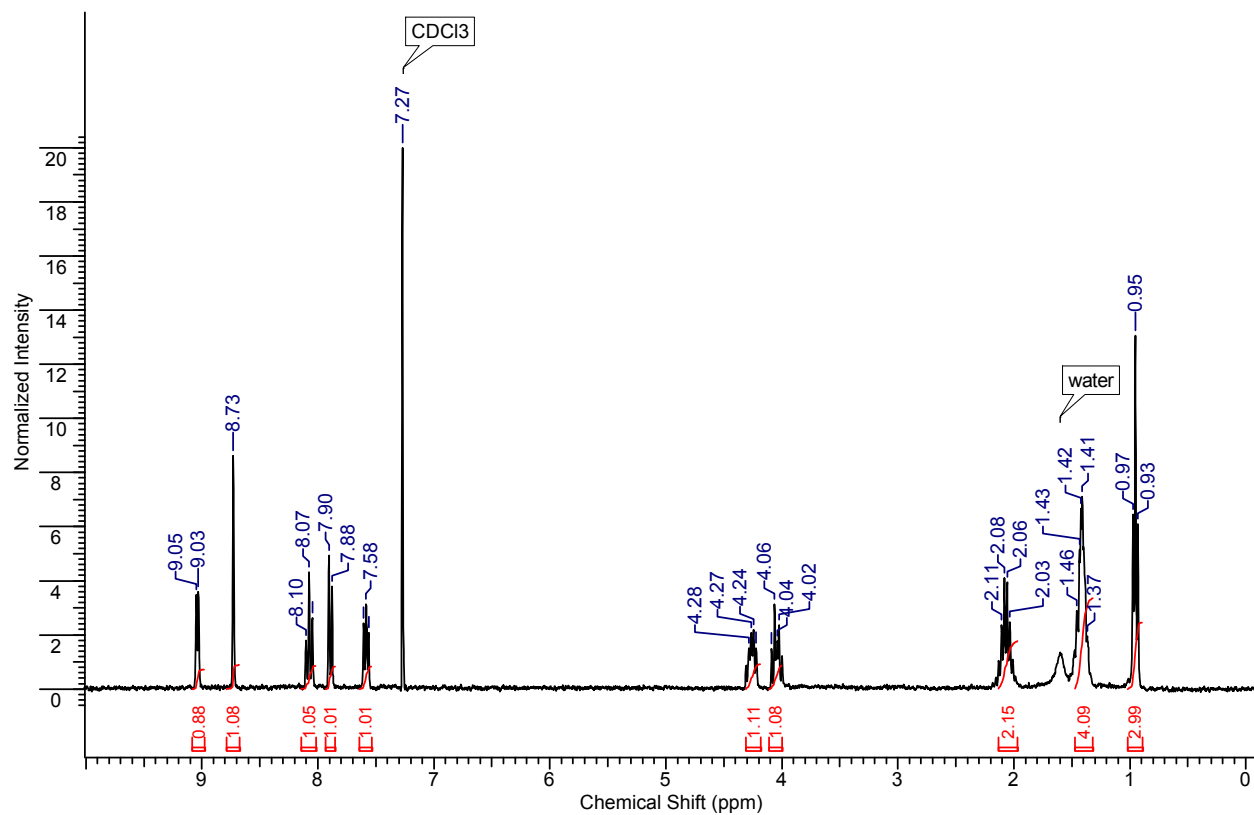


Figure S1: ^1H NMR (300 MHz) of **1a** in CDCl_3 .

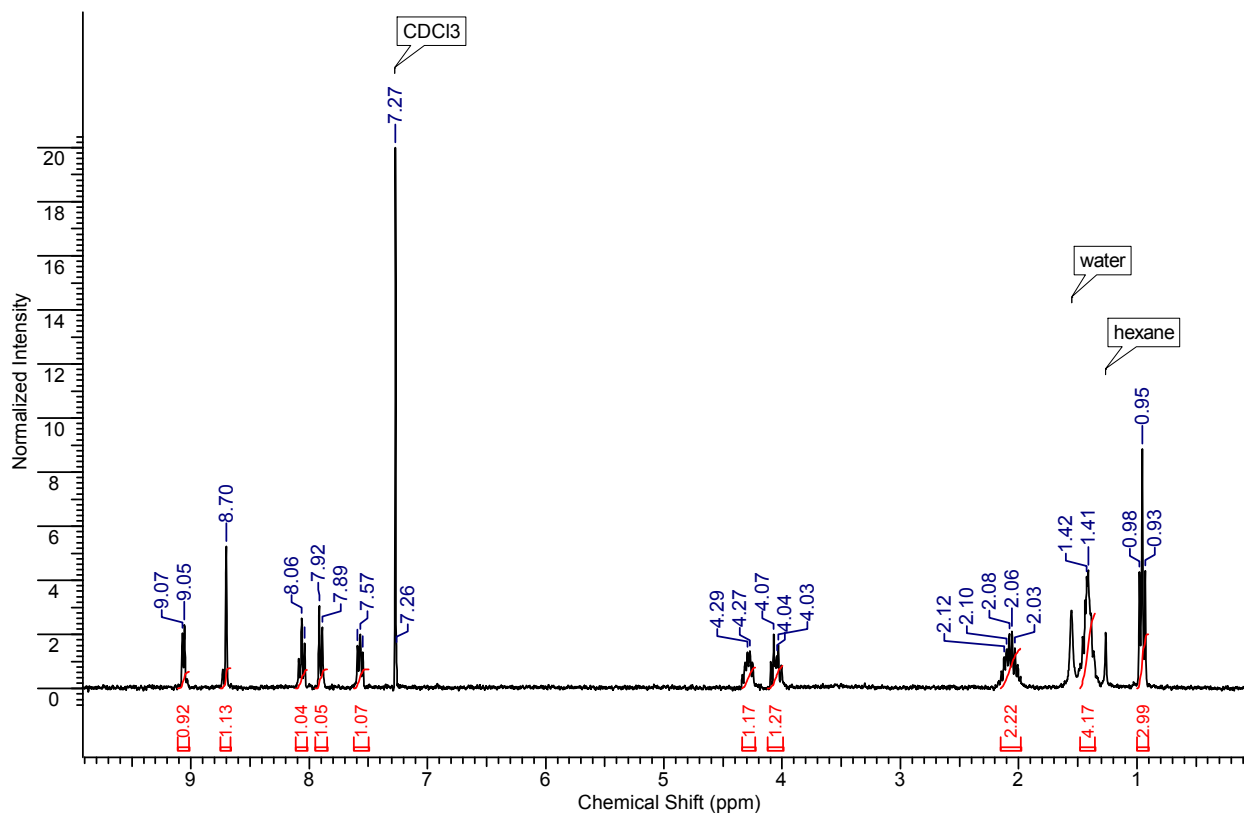


Figure S2: ^1H NMR (300 MHz) of **1b** in CDCl_3 .

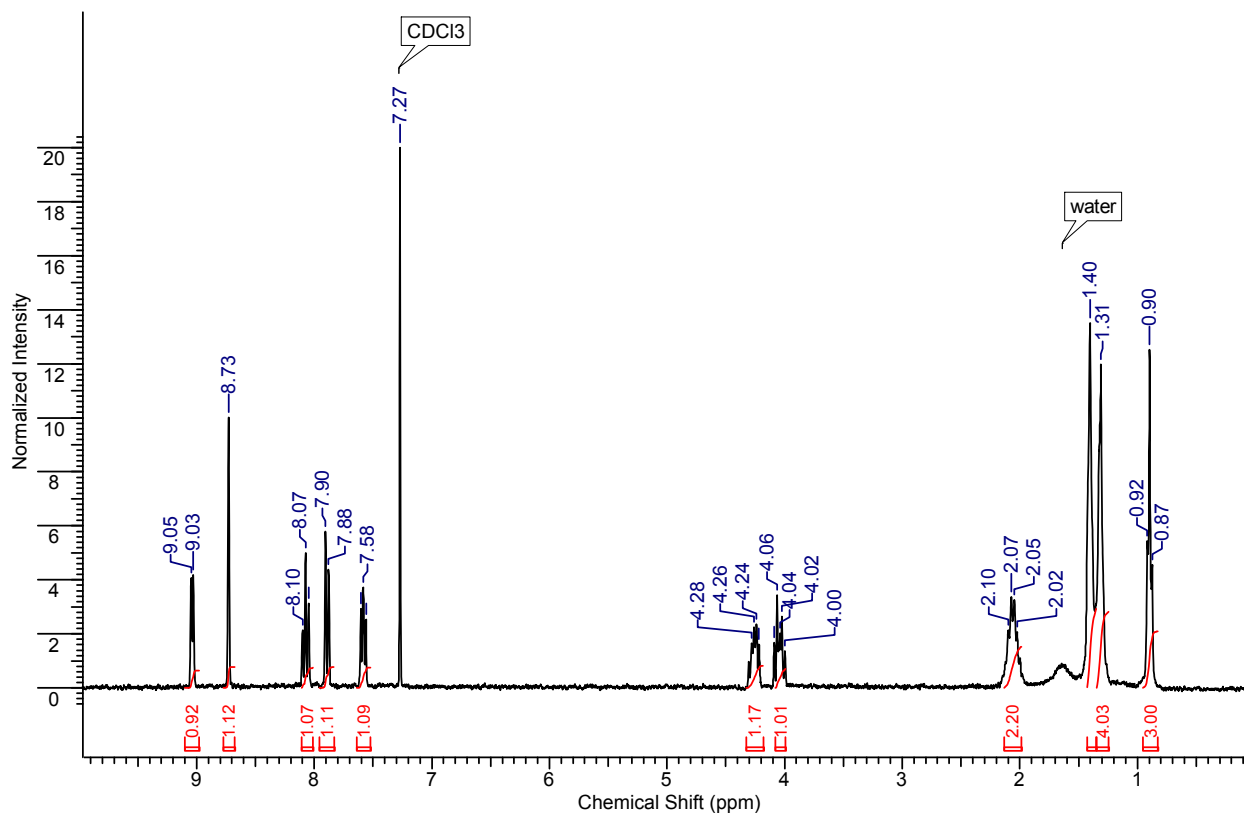


Figure S3: ^1H NMR (300 MHz) of **2a** in CDCl_3 .

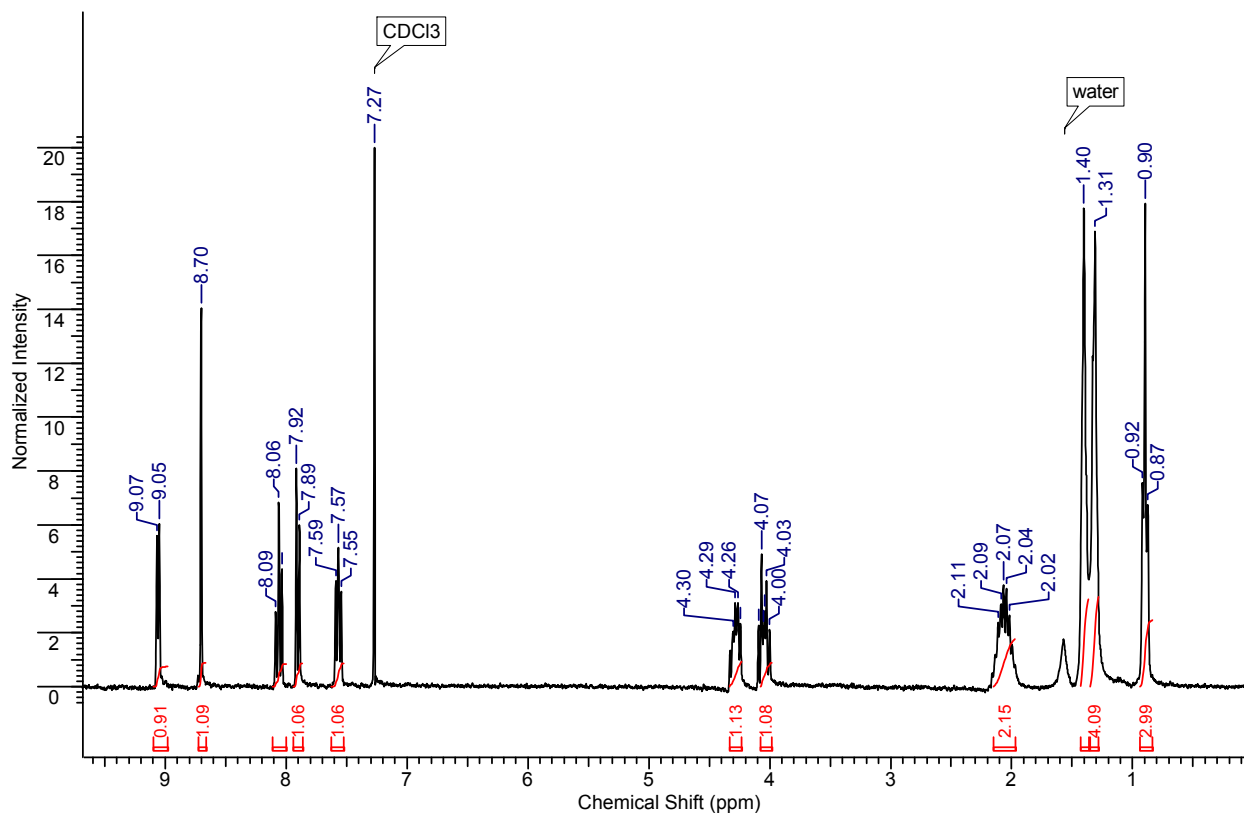


Figure S4: ^1H NMR (300 MHz) of **2b** in CDCl_3 .

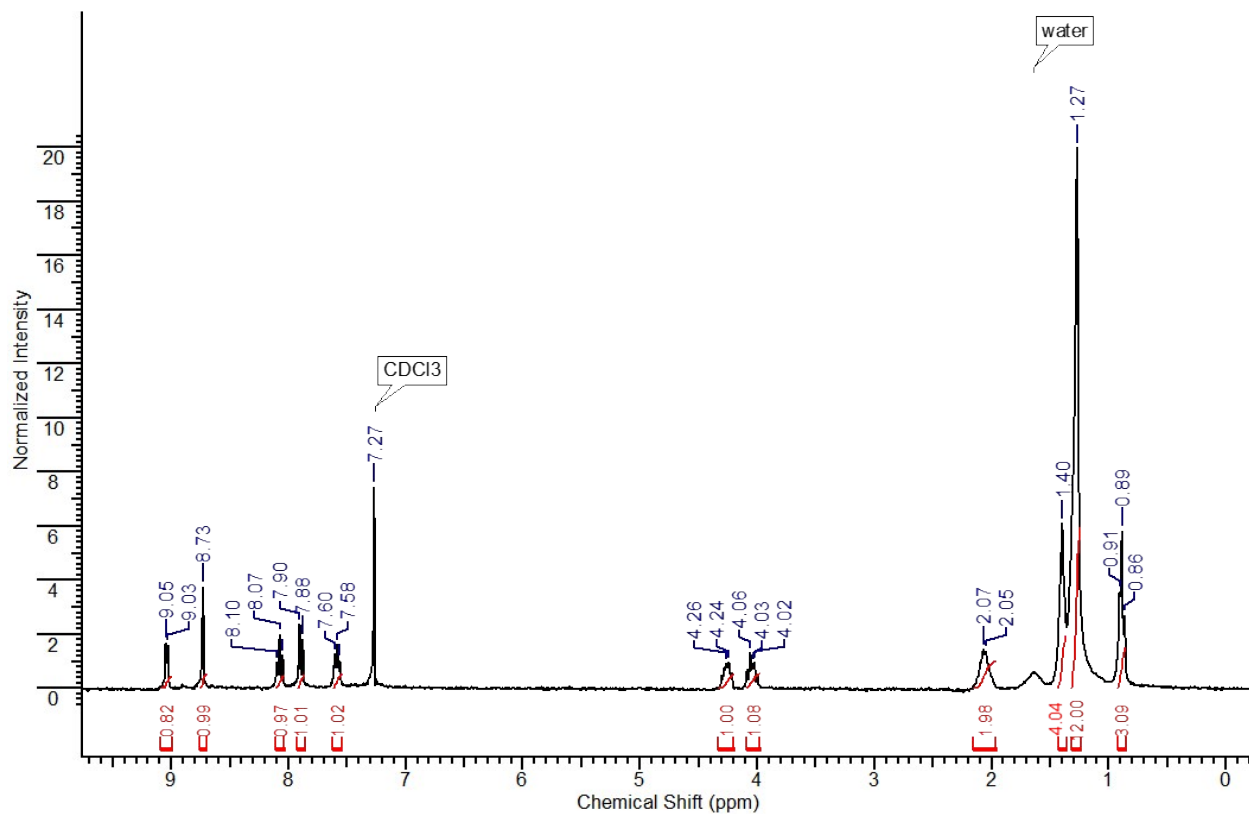


Figure S5: ^1H NMR (300 MHz) of **3a** in CDCl_3 .

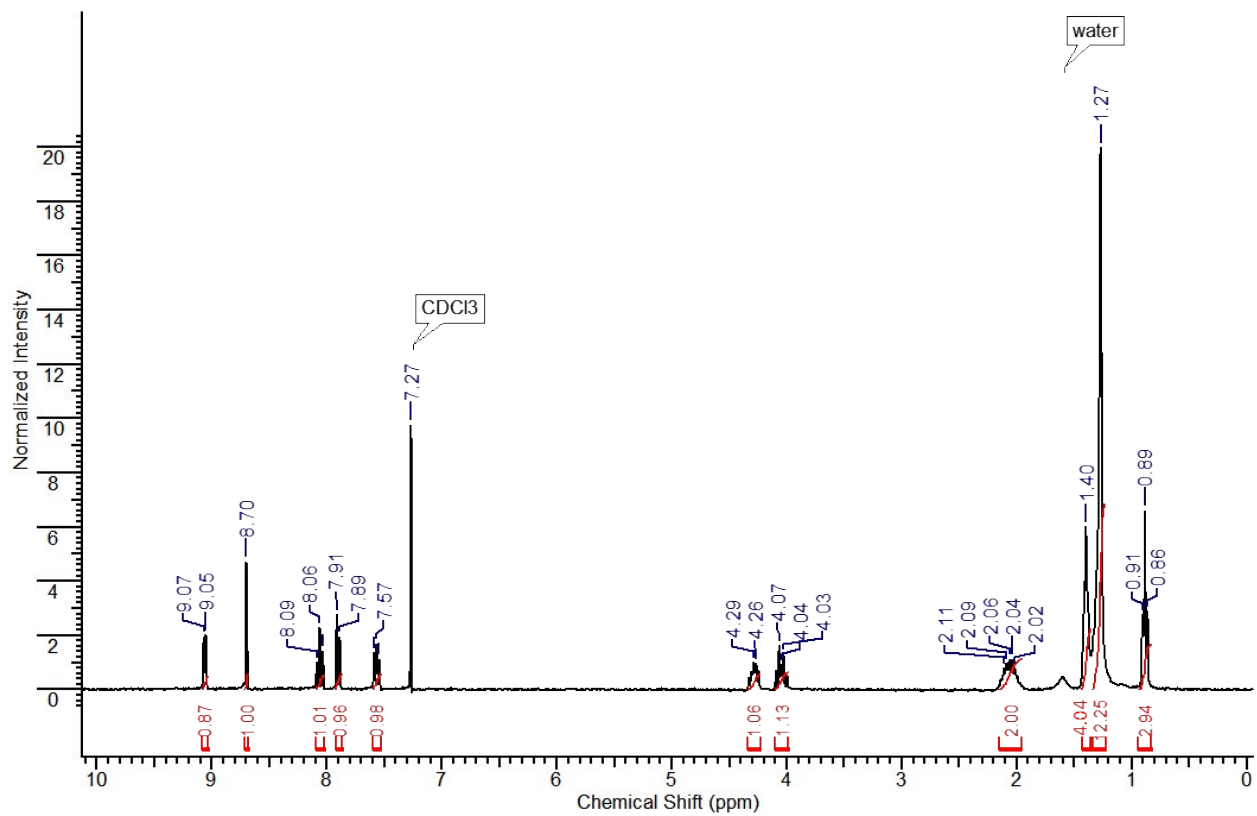


Figure S6: ^1H NMR (300 MHz) of **3b** in CDCl_3 .

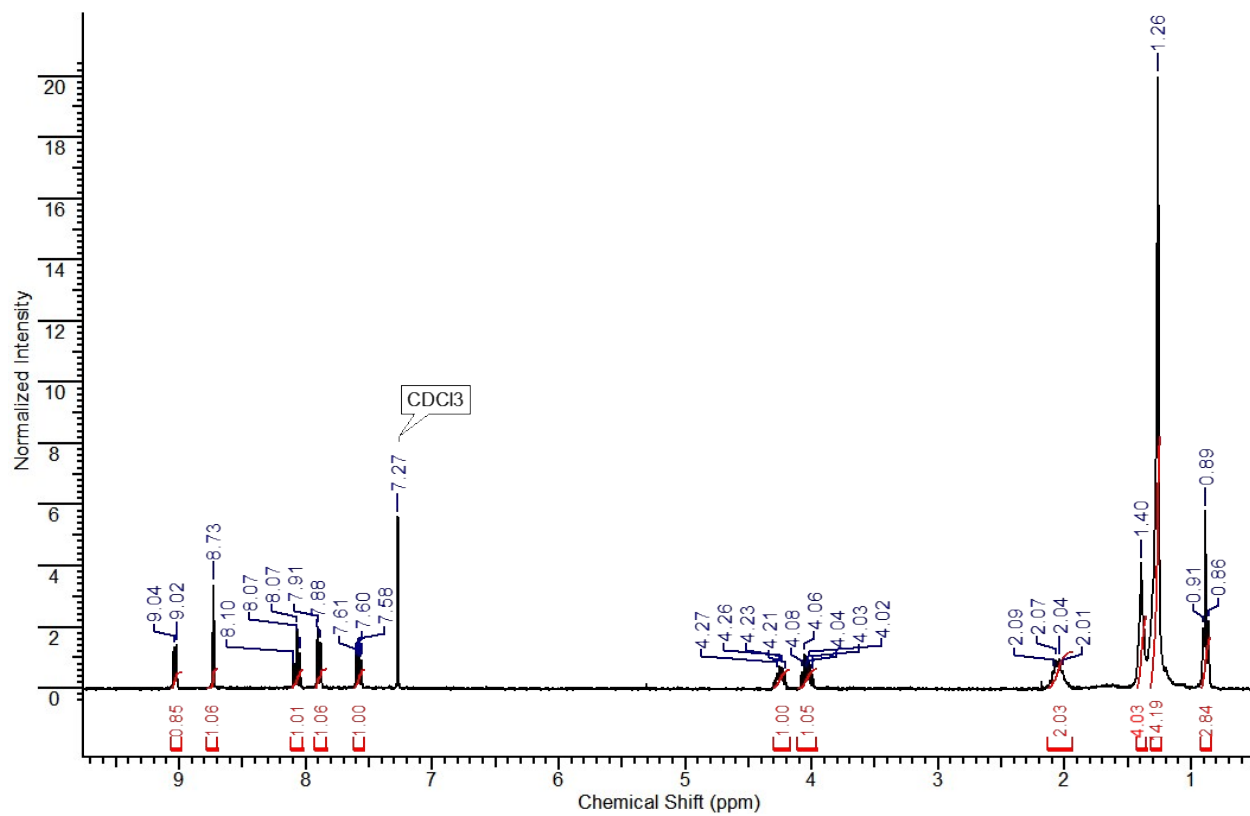


Figure S7: ^1H NMR (300 MHz) of **4a** in CDCl_3 .

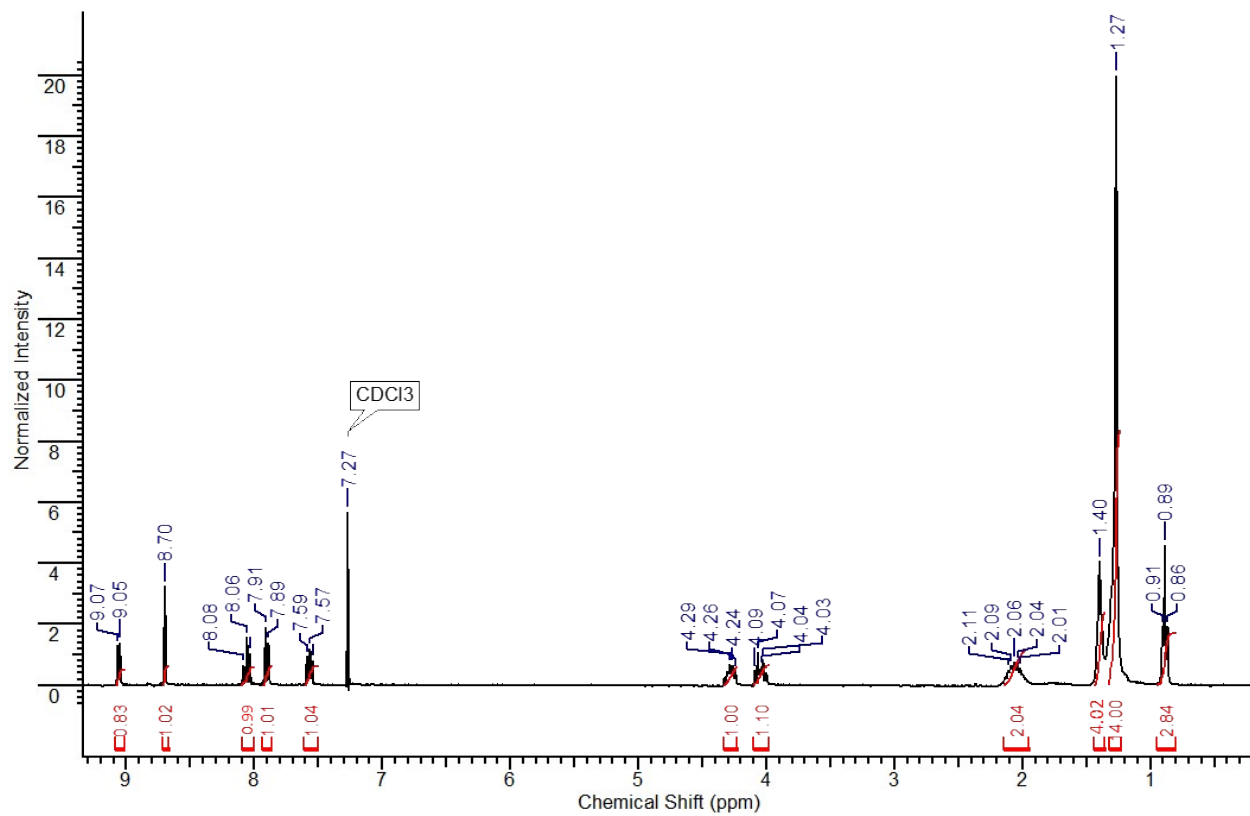


Figure S8: ¹H NMR (300 MHz) of **4b** in CDCl₃.

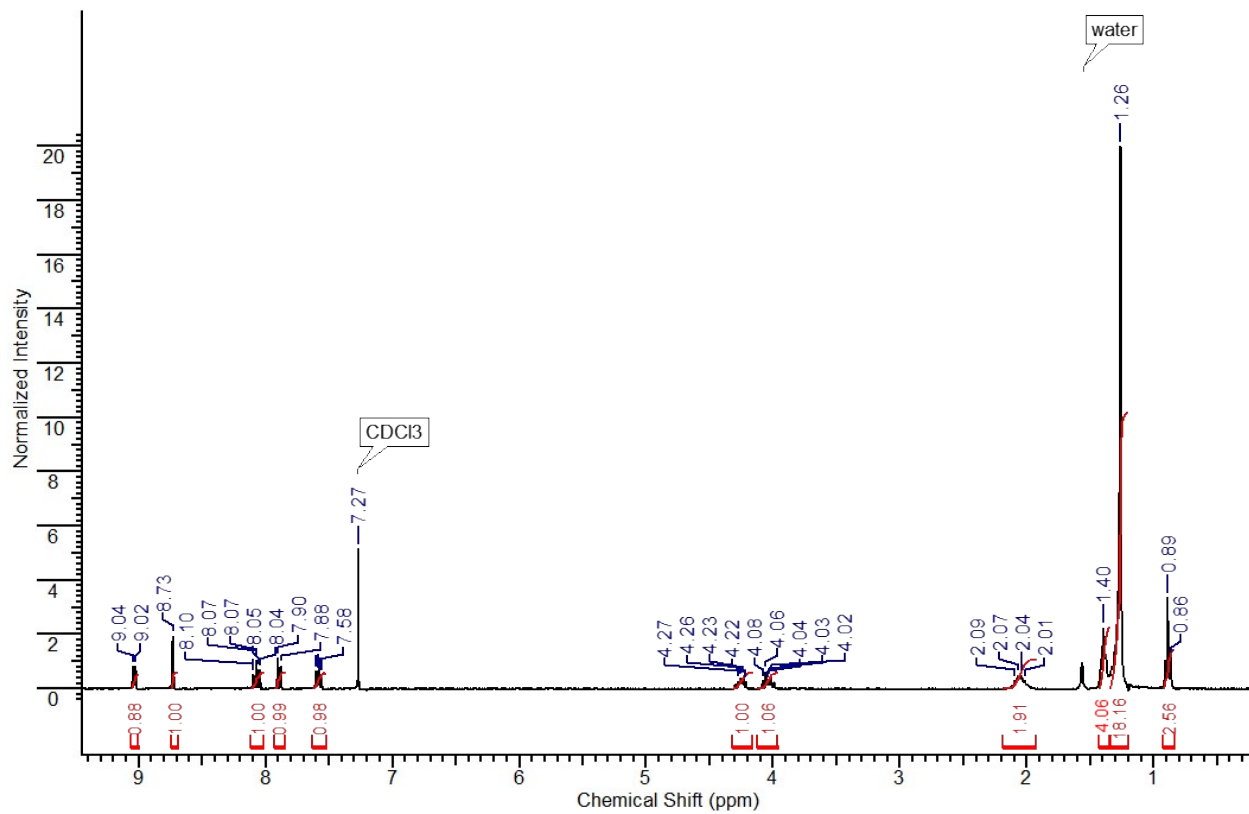


Figure S9: ^1H NMR (300 MHz) of **5a** in CDCl_3 .

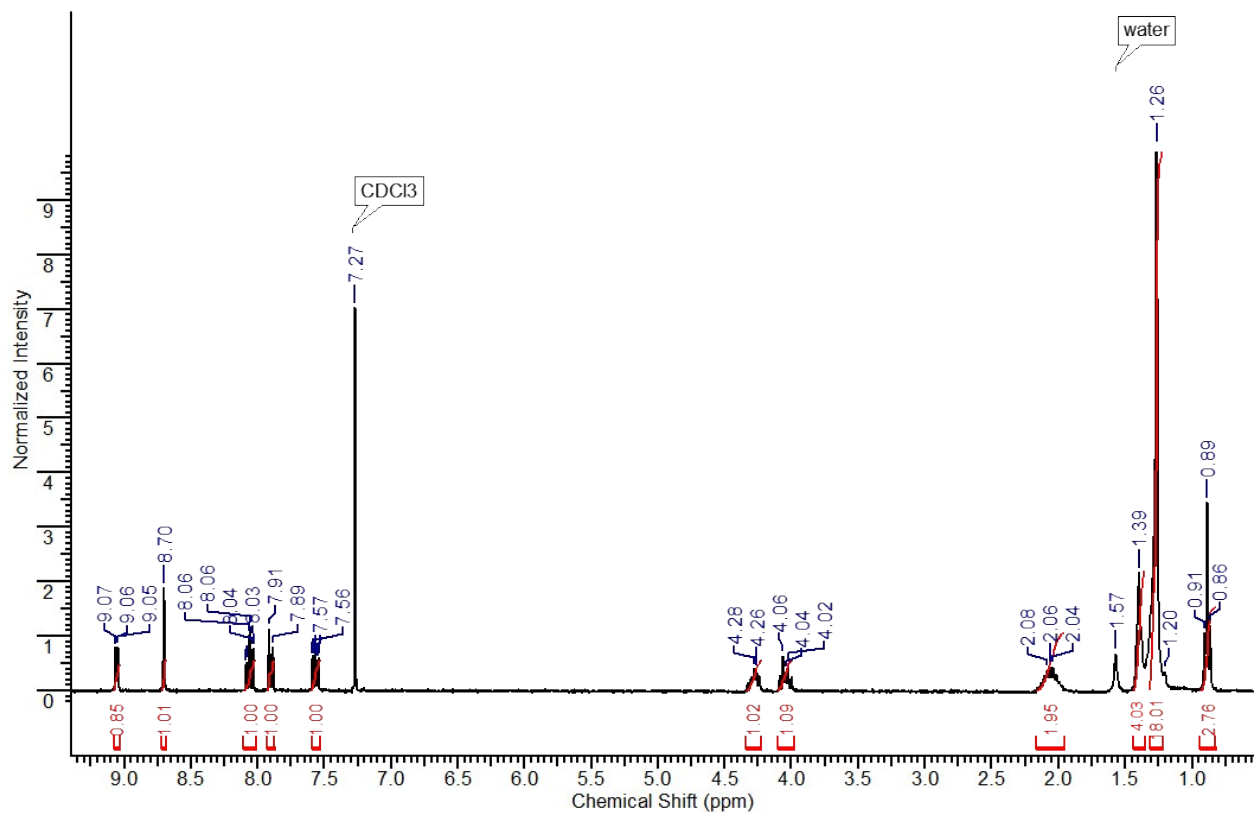


Figure S10: ^1H NMR (300 MHz) of **5b** in CDCl_3 .

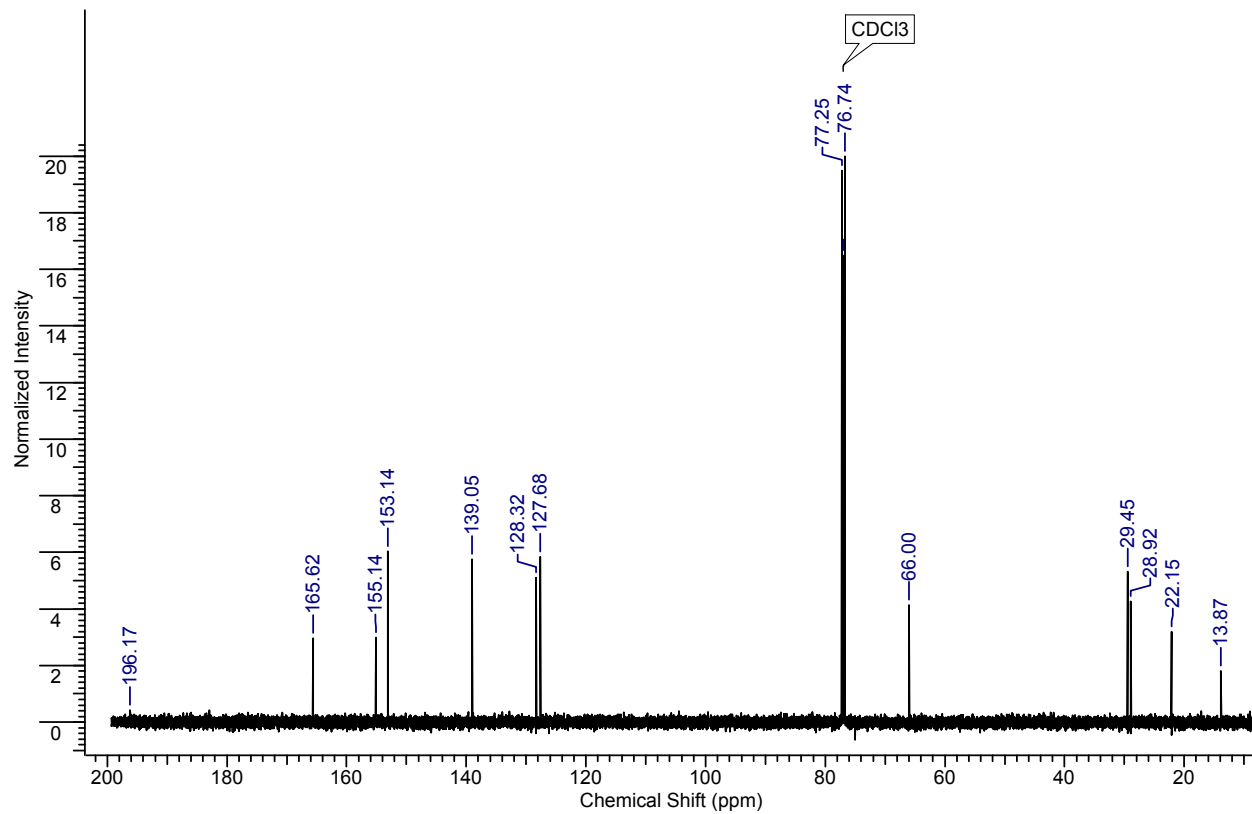


Figure S11: $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) of **1a** in CDCl_3 .

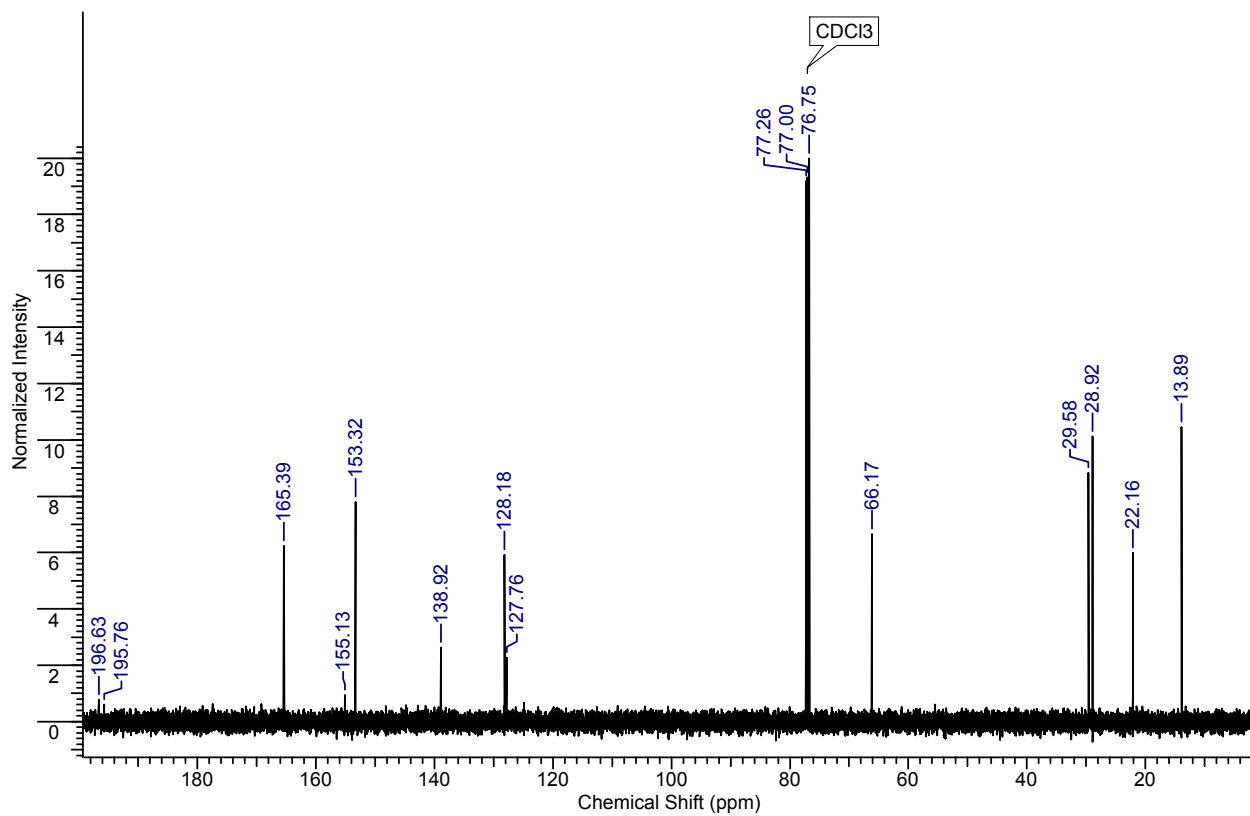


Figure S12: $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) of **1b** in CDCl_3 .

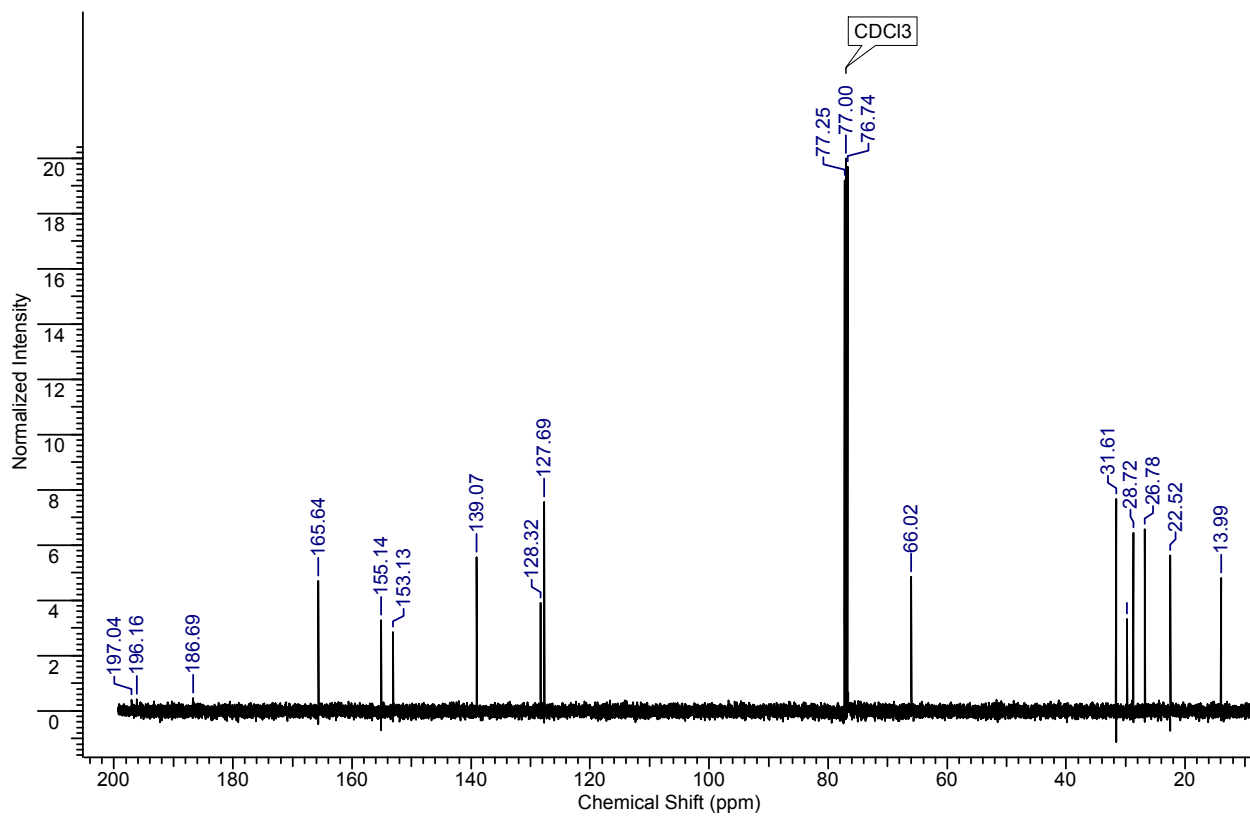


Figure S13: $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) of **2a** in CDCl_3 .

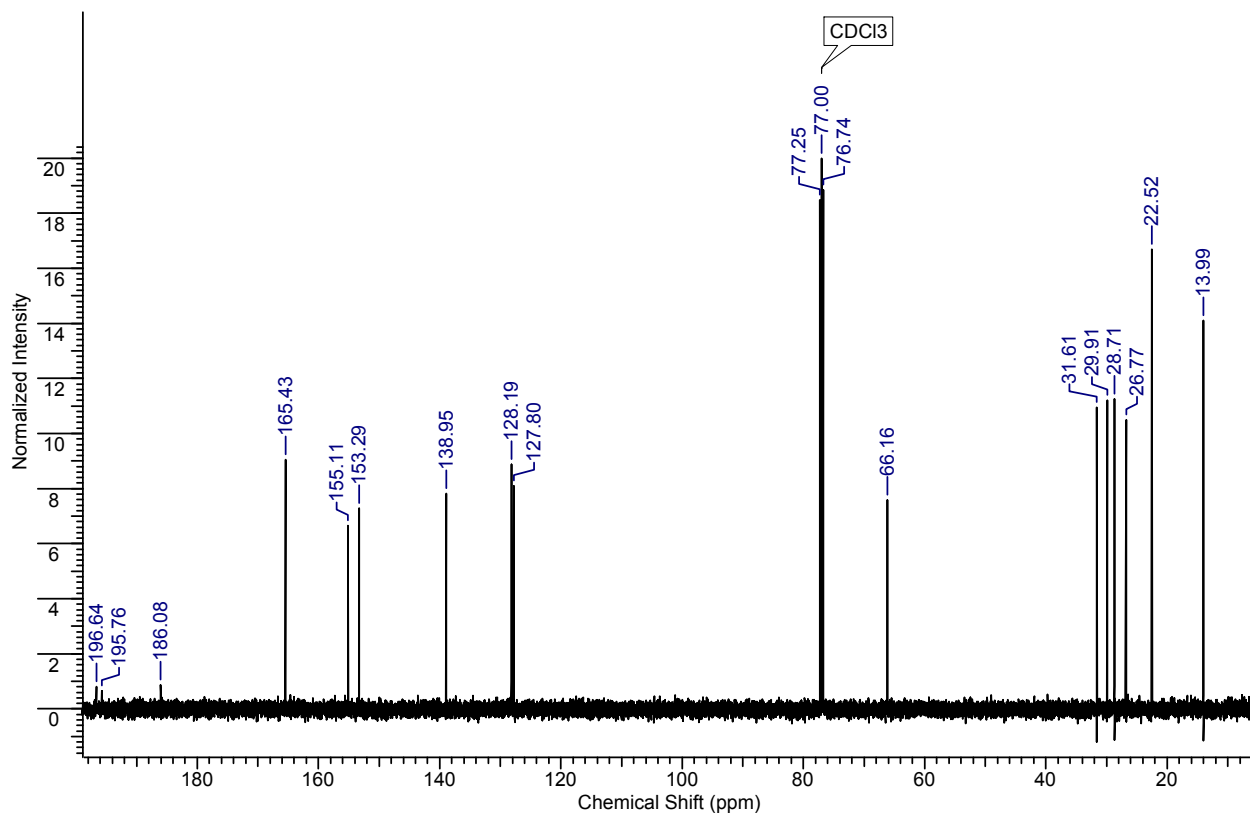


Figure S14: $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) of **2b** in CDCl_3 .

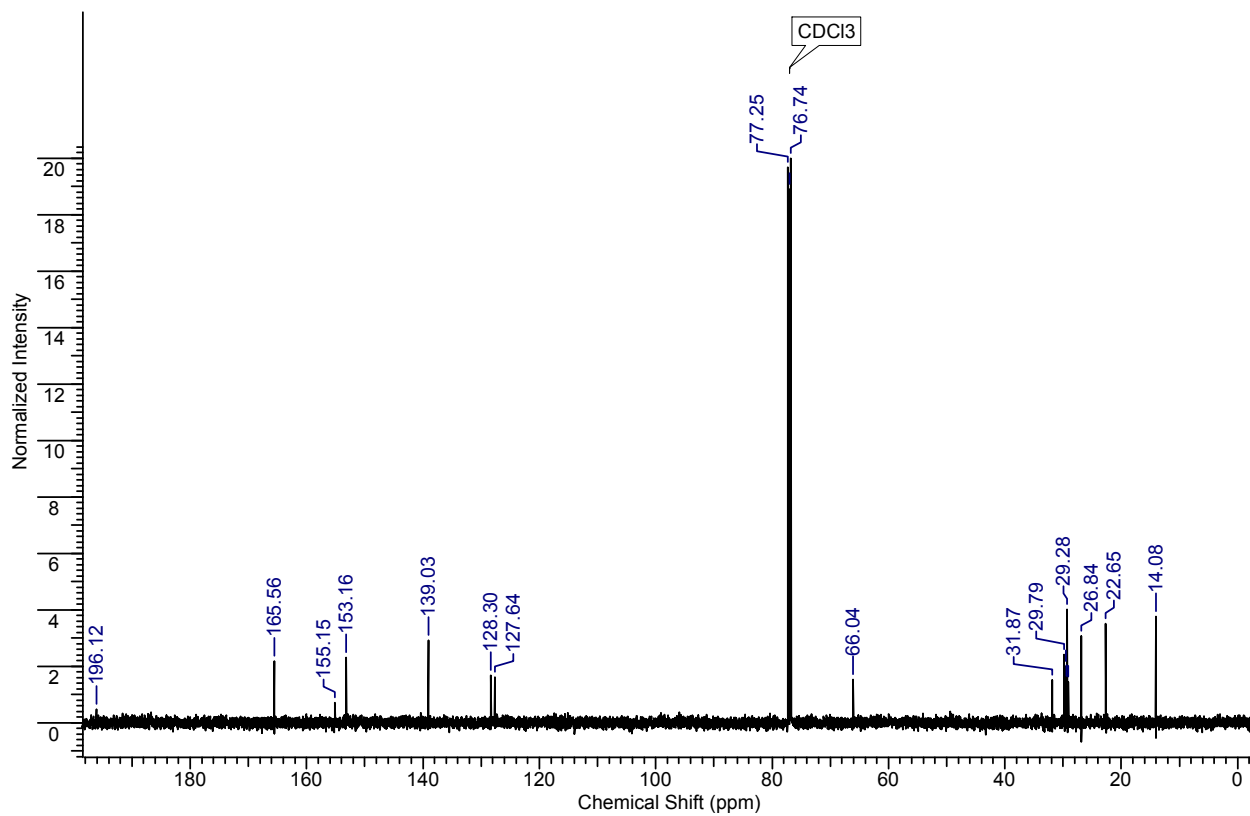


Figure S15: $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) of **3a** in CDCl_3 .

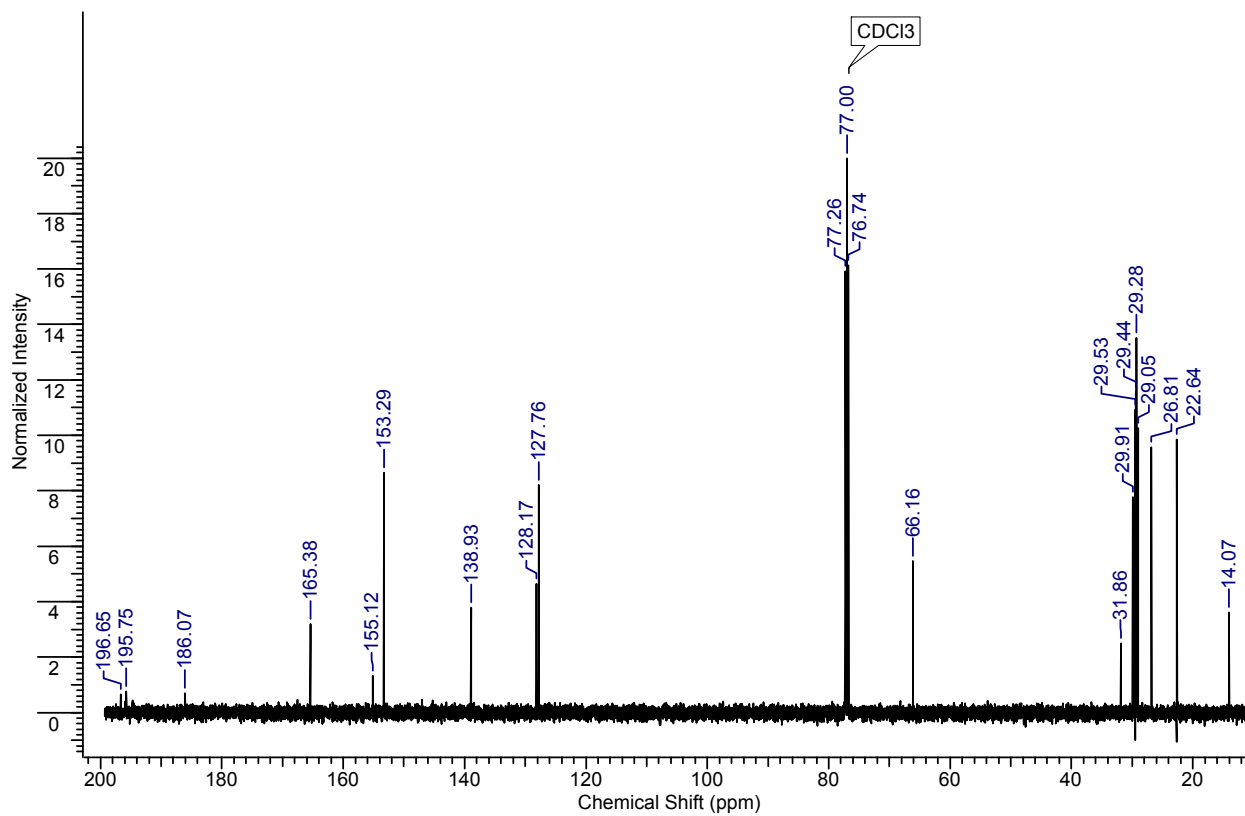


Figure S16: $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) of **3b** in CDCl_3 .

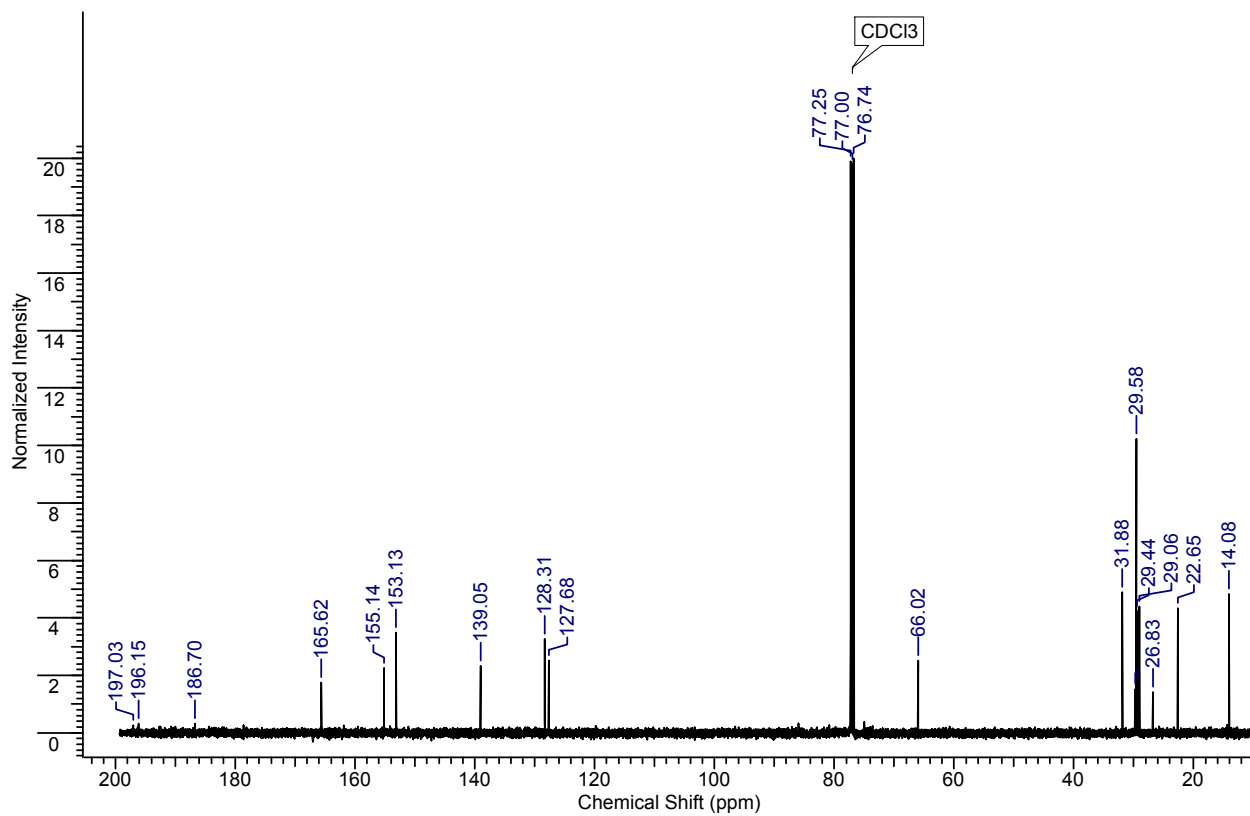


Figure S17: $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) of **4a** in CDCl_3 .

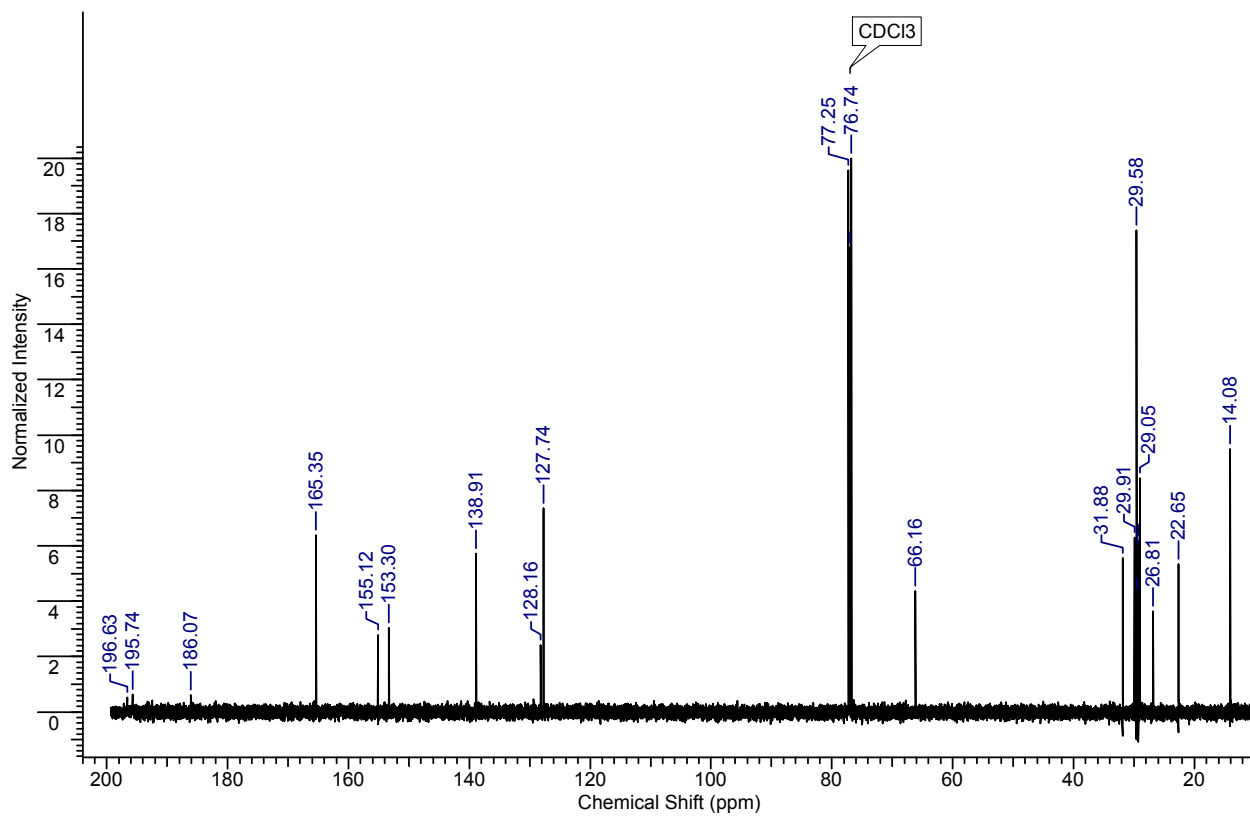


Figure S18: $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) of **4b** in CDCl_3 .

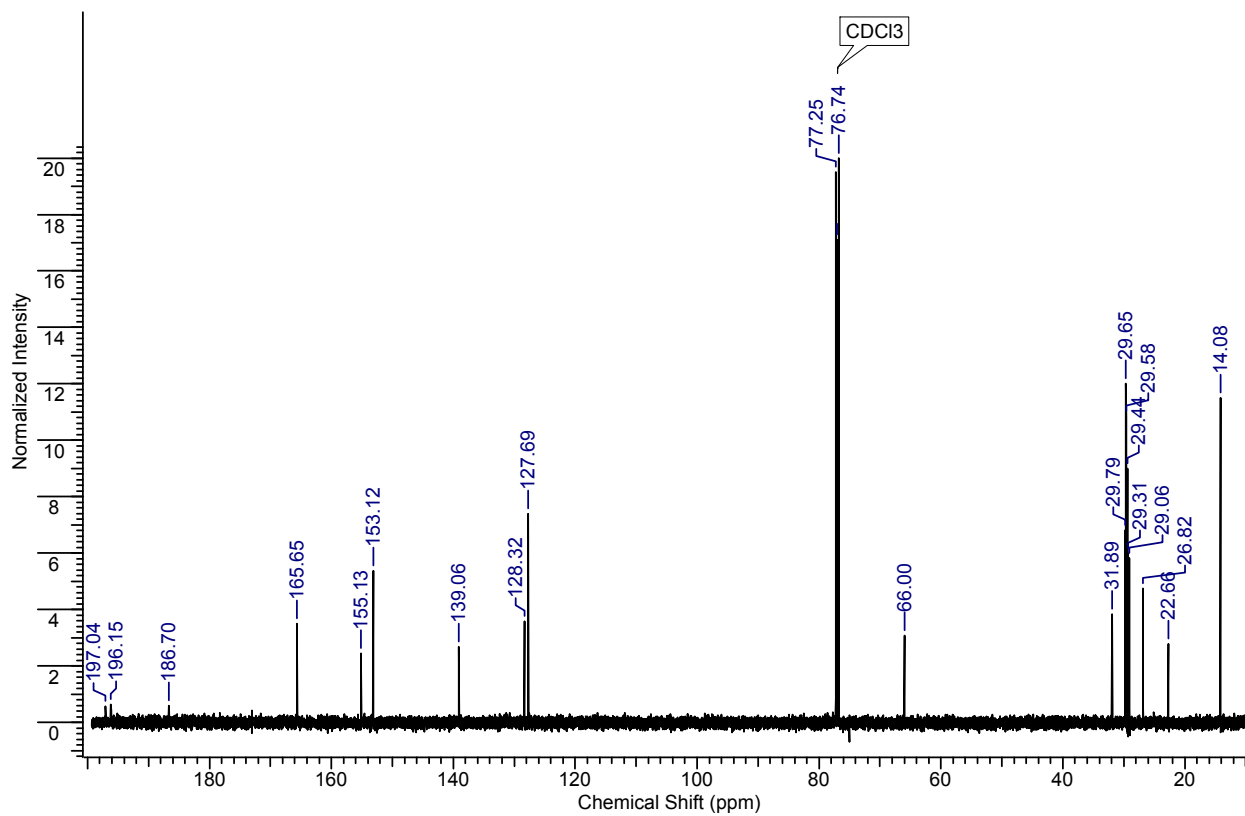


Figure S19: $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) of **5a** in CDCl_3 .

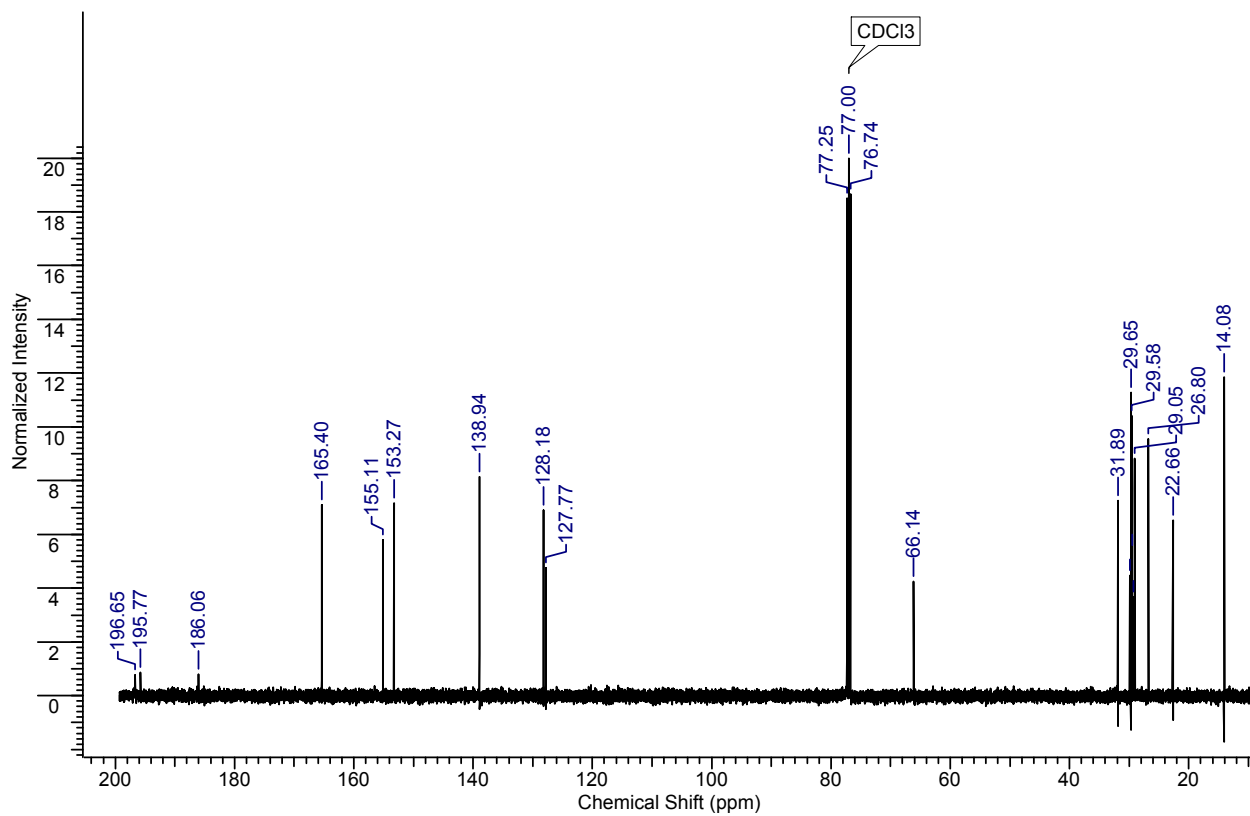


Figure S20: $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz) of **5b** in CDCl_3 .

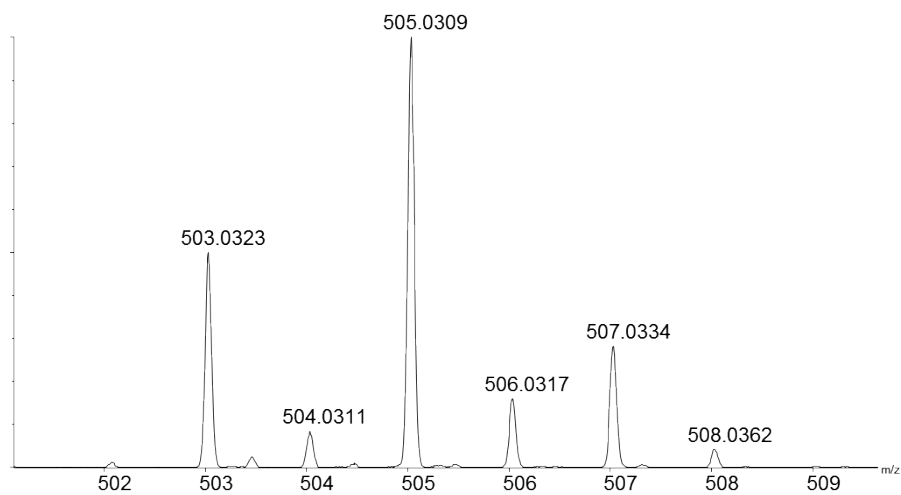
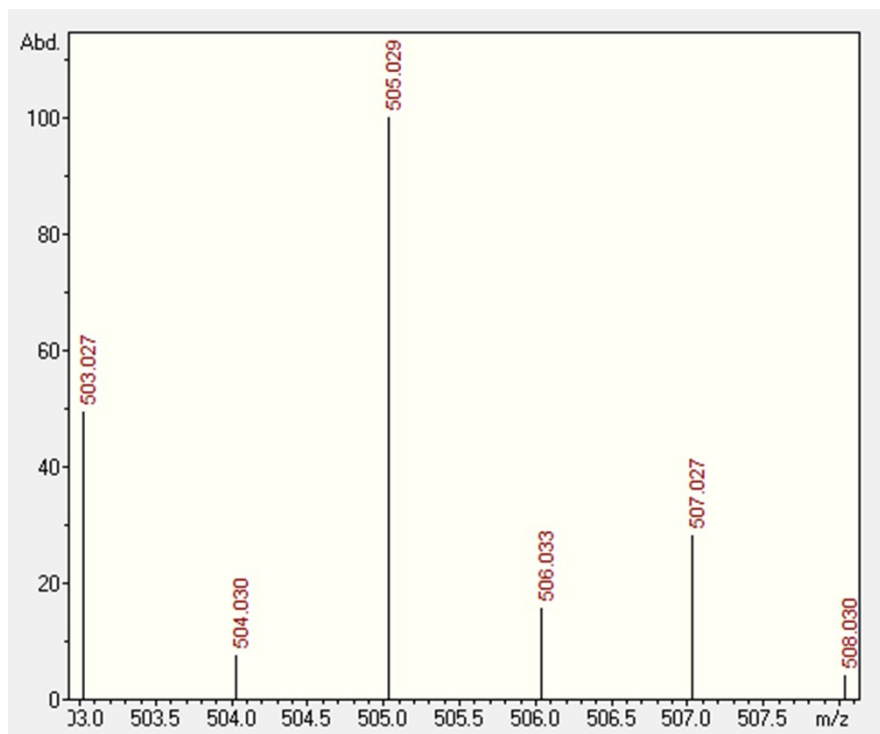


Figure S21: High-resolution ESI mass spectra of **1a**. Top: calculated spectrum. Bottom: experimental spectrum.

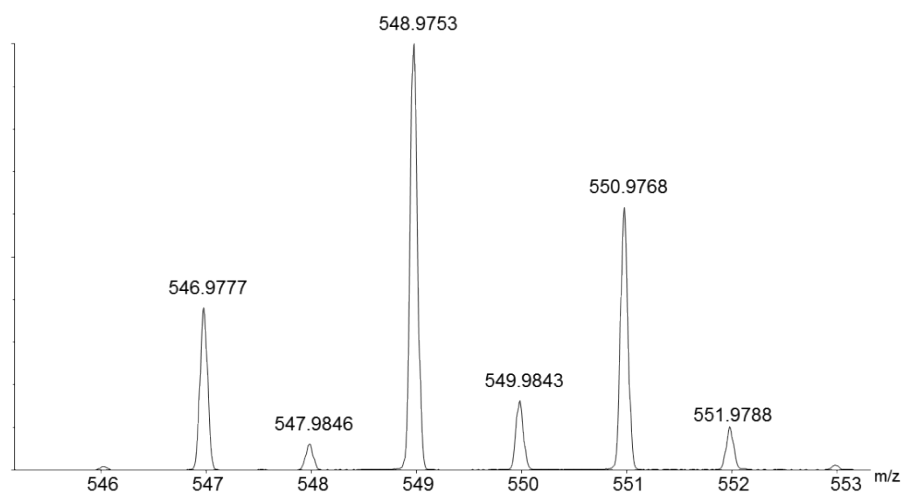
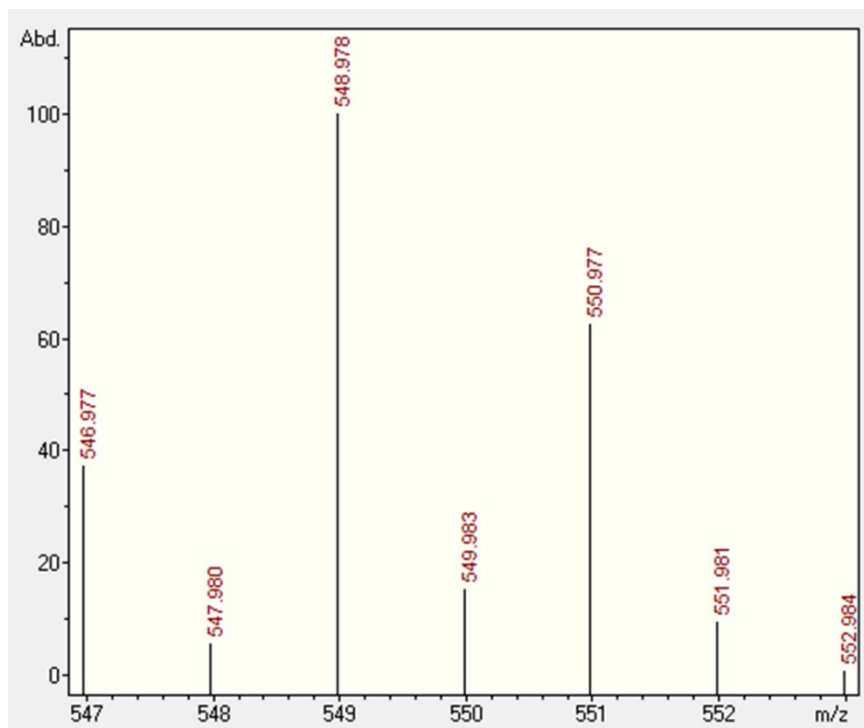


Figure S22: High-resolution ESI mass spectra of **1b**. Top: calculated spectrum. Bottom: experimental spectrum.

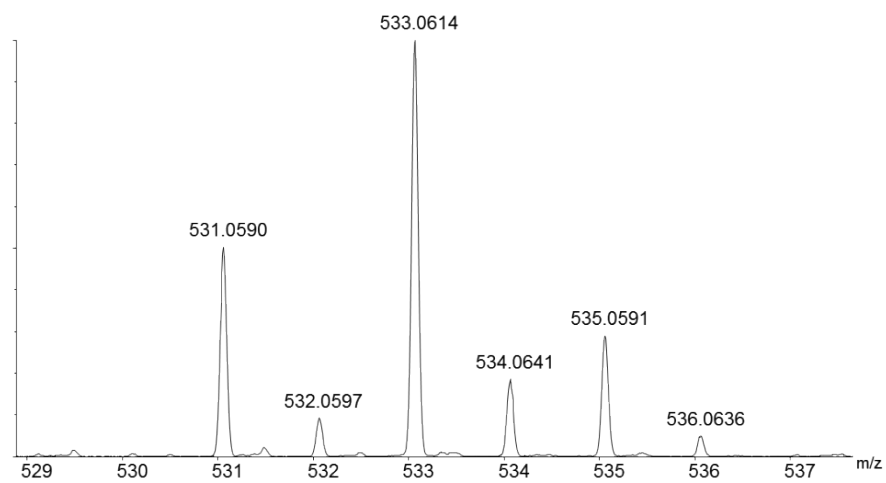
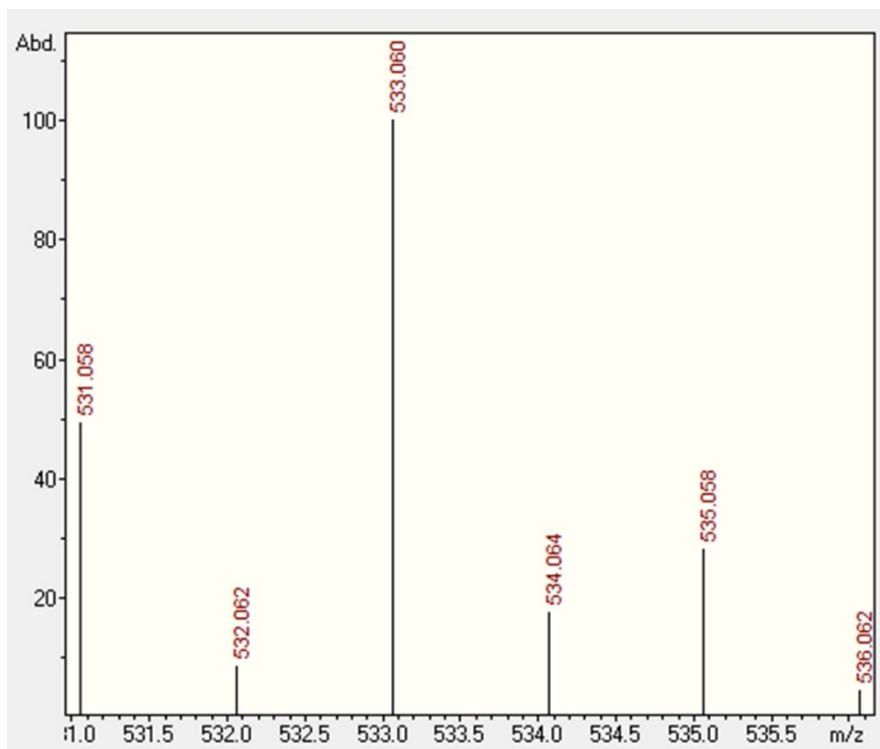


Figure S23: High-resolution ESI mass spectra of **2a**. Top: calculated spectrum. Bottom: experimental spectrum.

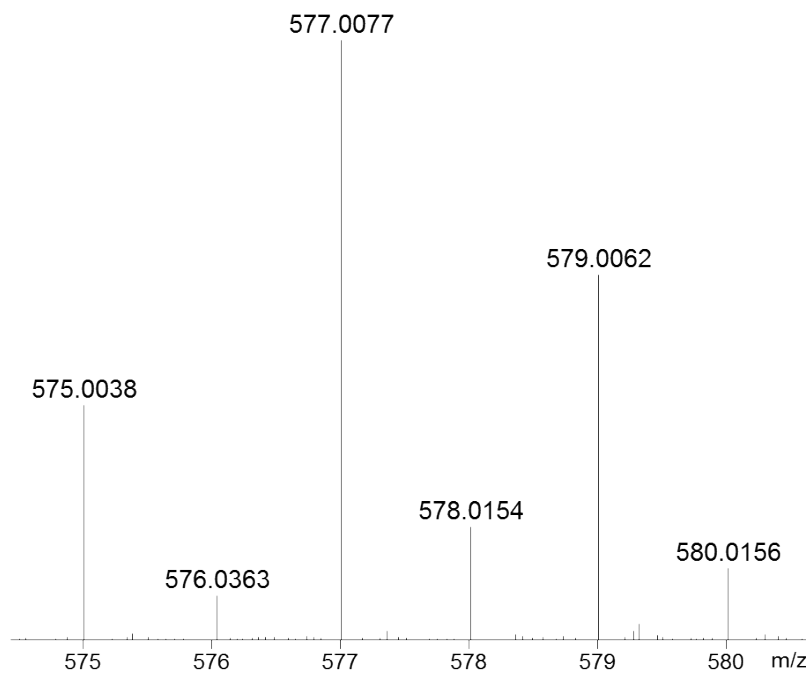
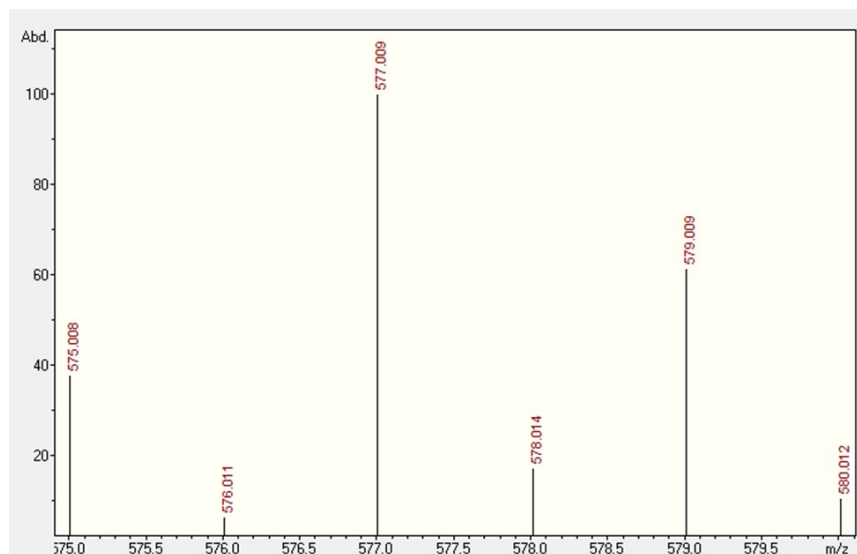


Figure S24: High-resolution ESI mass spectra of **2b**. Top: calculated spectrum. Bottom: experimental spectrum.

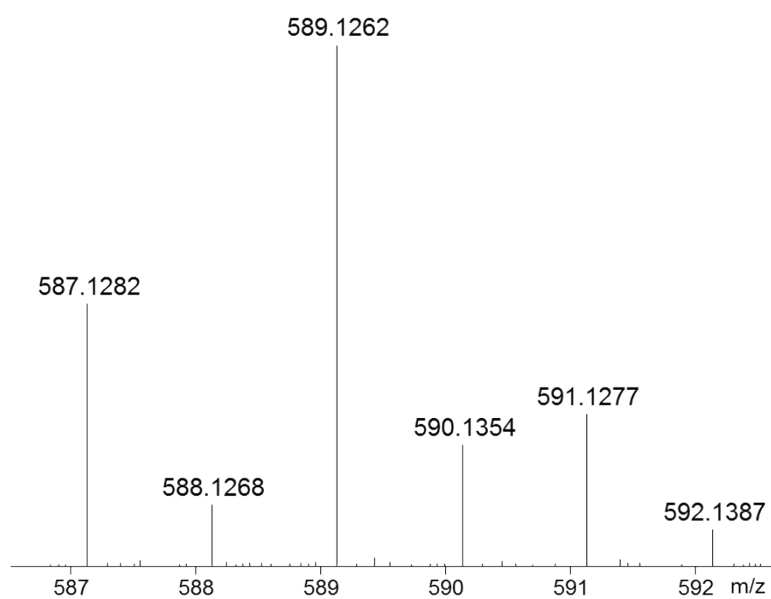
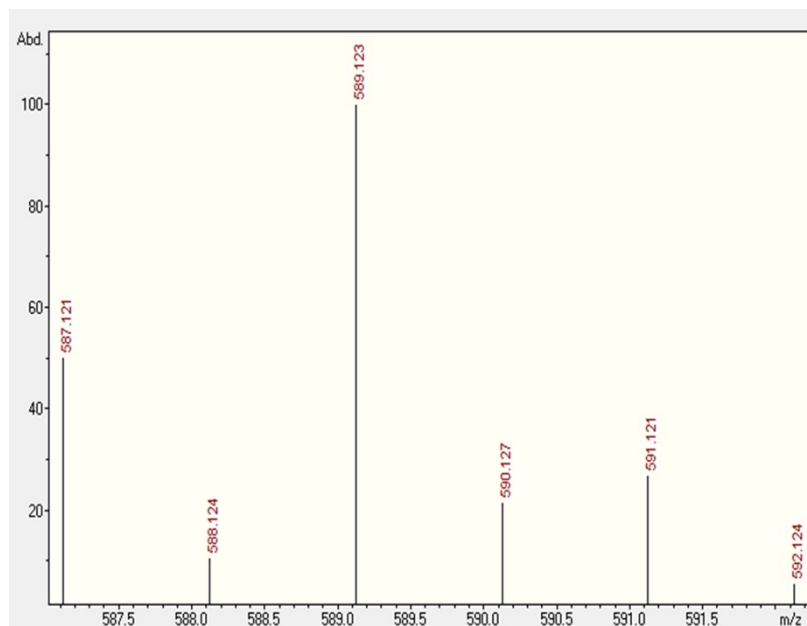


Figure S25: High-resolution ESI mass spectra of **3a**. Top: calculated spectrum. Bottom: experimental spectrum.

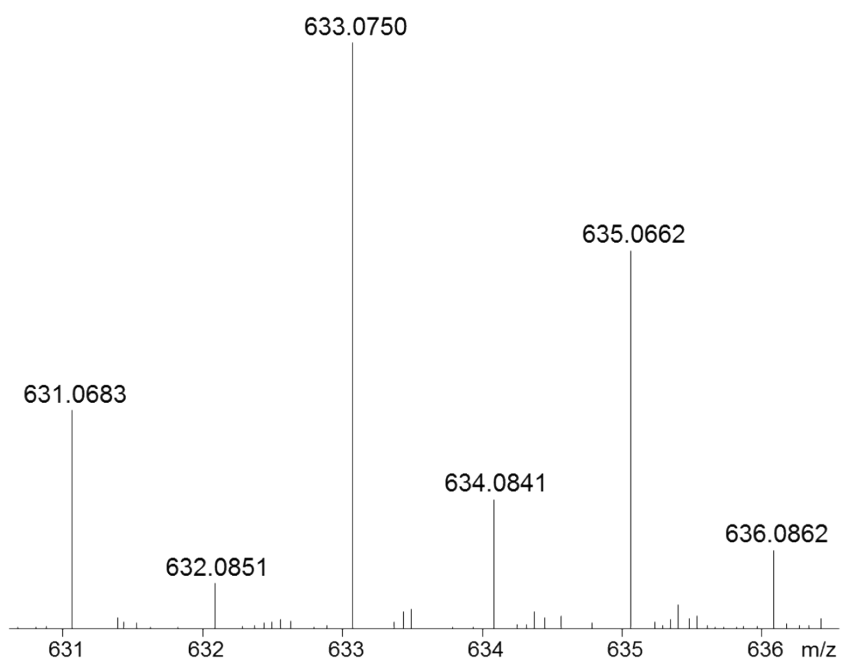
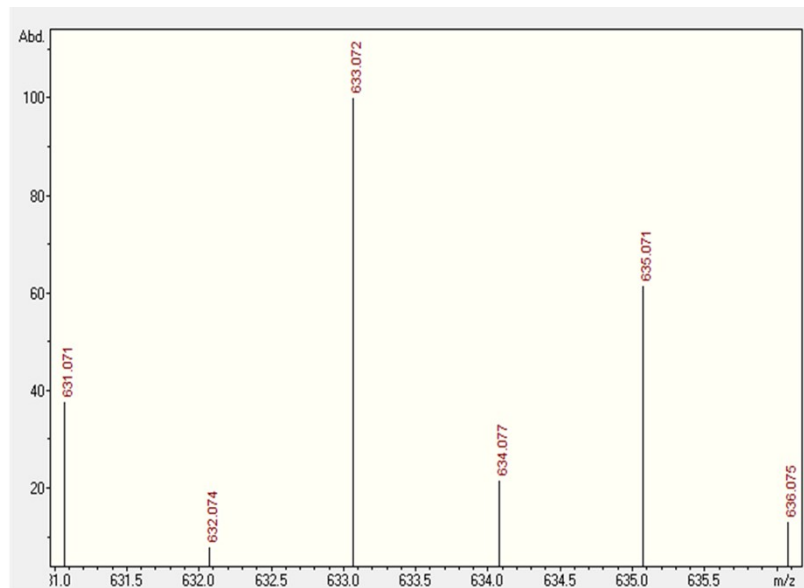


Figure S26: High-resolution ESI mass spectra of **3b**. Top: calculated spectrum. Bottom: experimental spectrum.

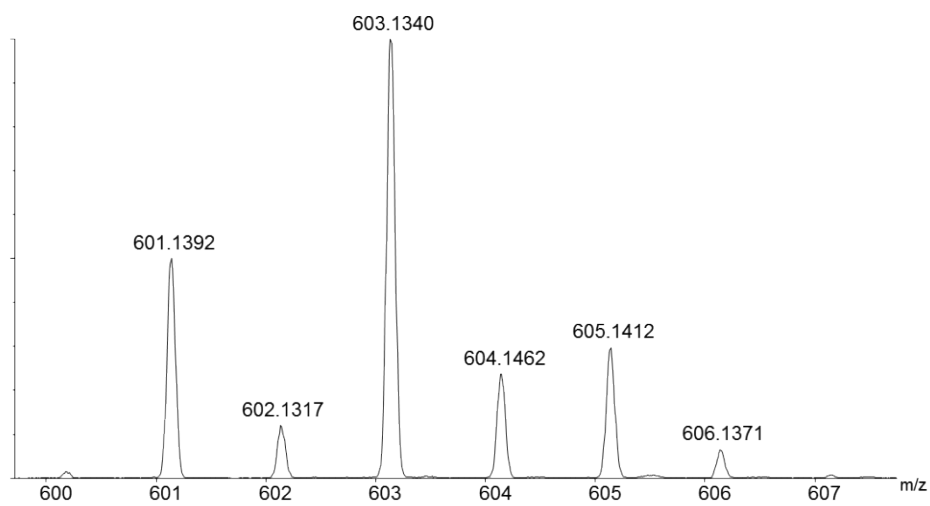
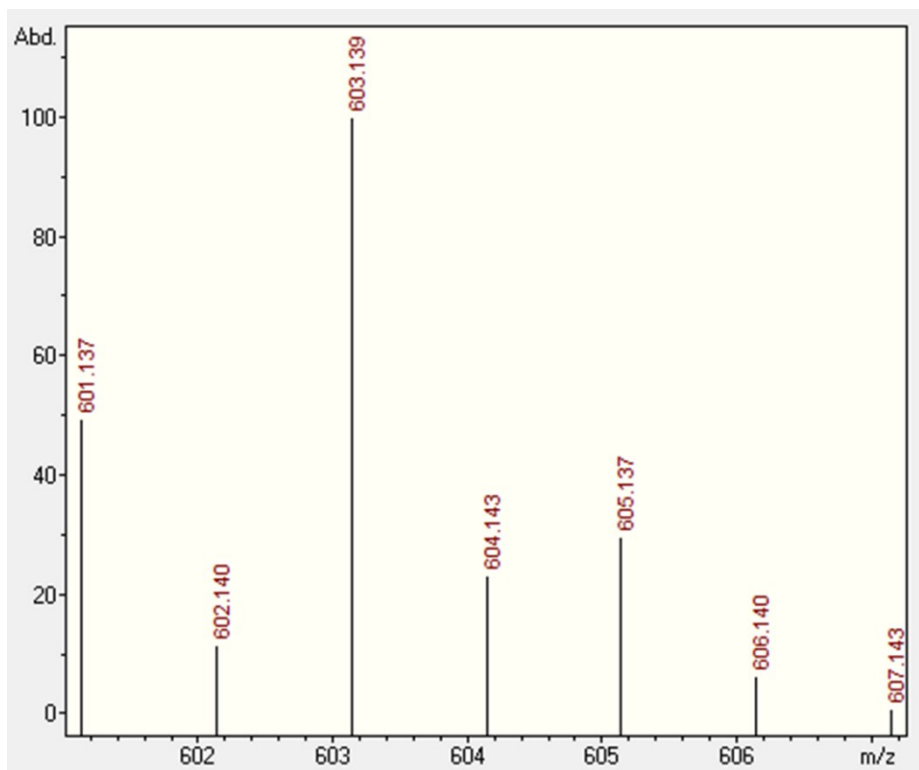


Figure S27: High-resolution ESI mass spectra of **4a**. Top: calculated spectrum. Bottom: experimental spectrum.

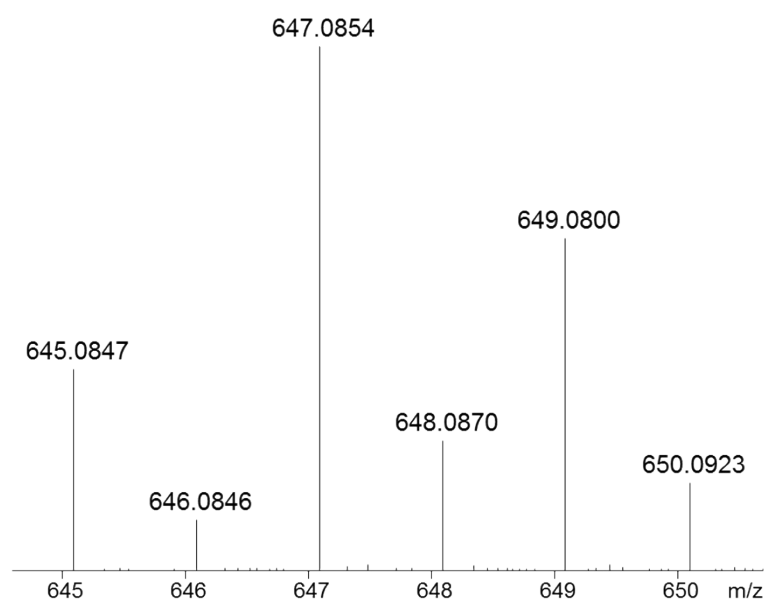
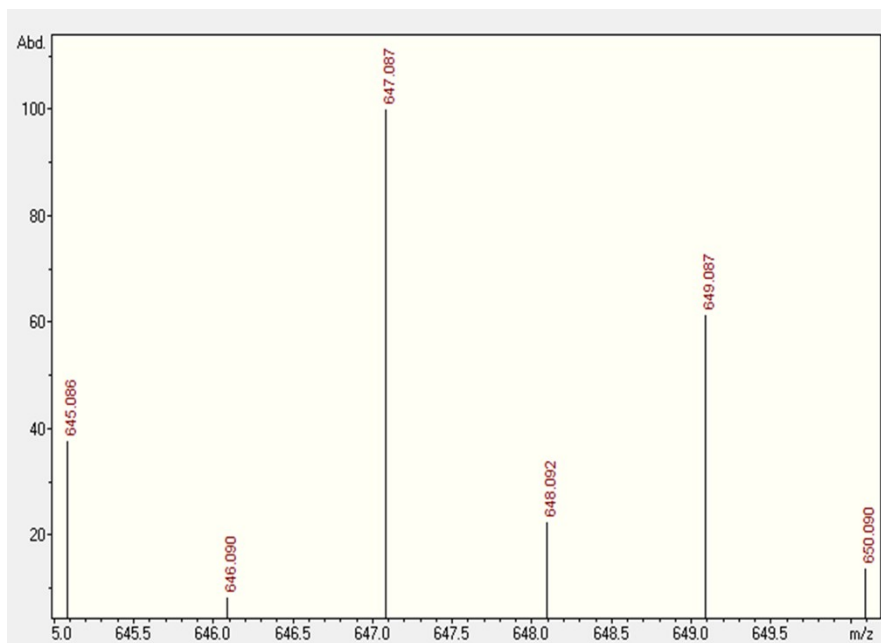


Figure S28: High-resolution ESI mass spectra of **4b**. Top: calculated spectrum. Bottom: experimental spectrum.

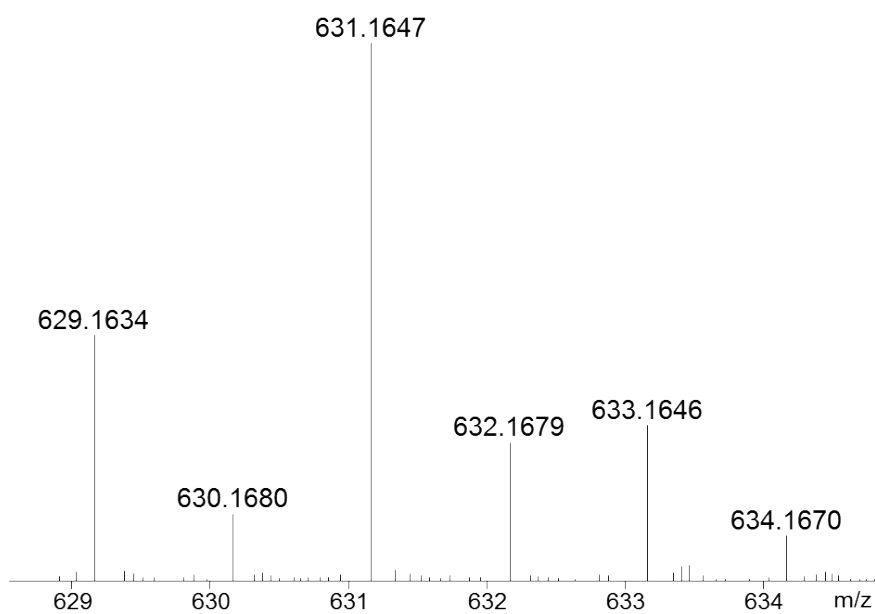
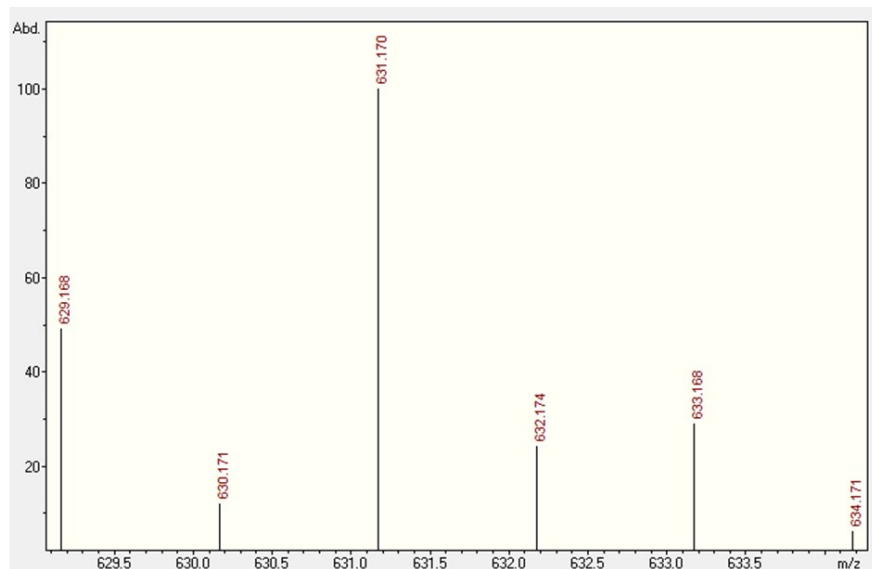


Figure S29: High-resolution ESI mass spectra of **5a**. Top: calculated spectrum. Bottom: experimental spectrum.

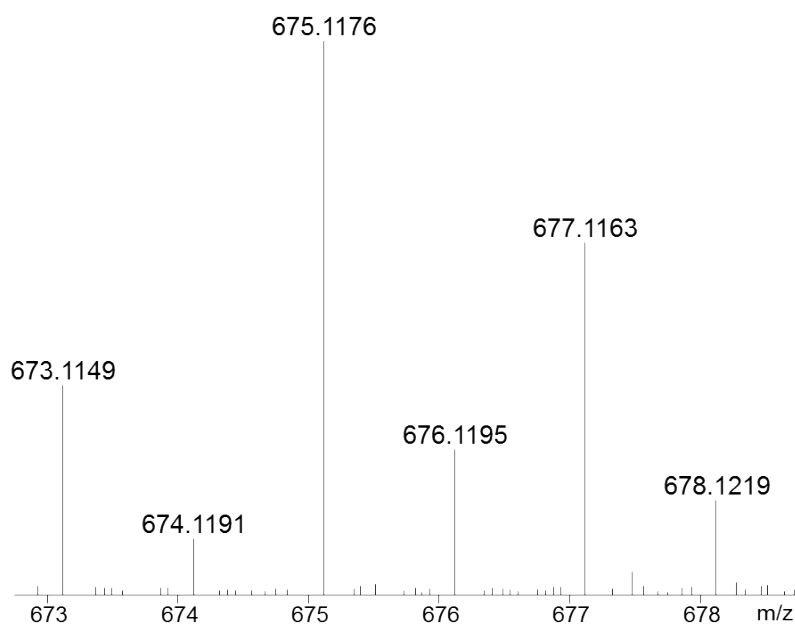
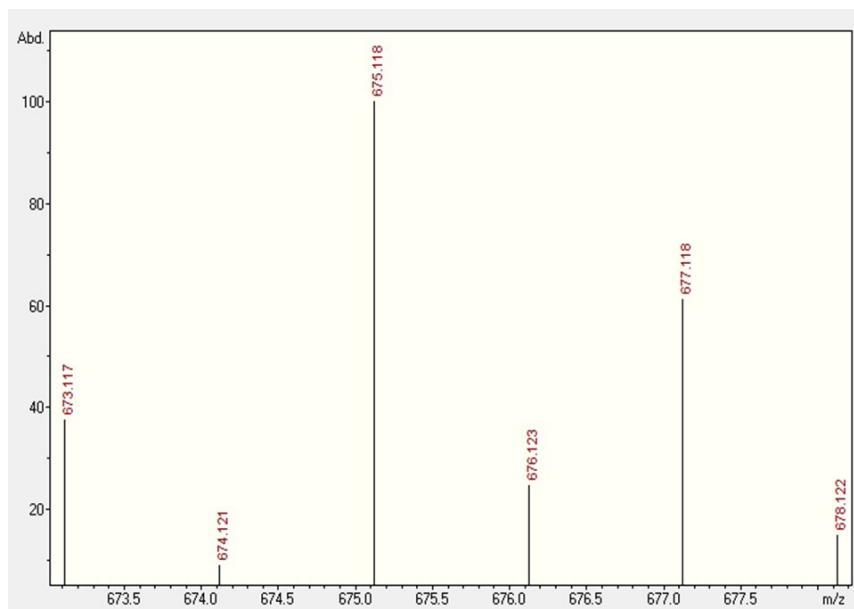


Figure S30: High-resolution ESI mass spectra of **5b**. Top: calculated spectrum. Bottom: experimental spectrum.

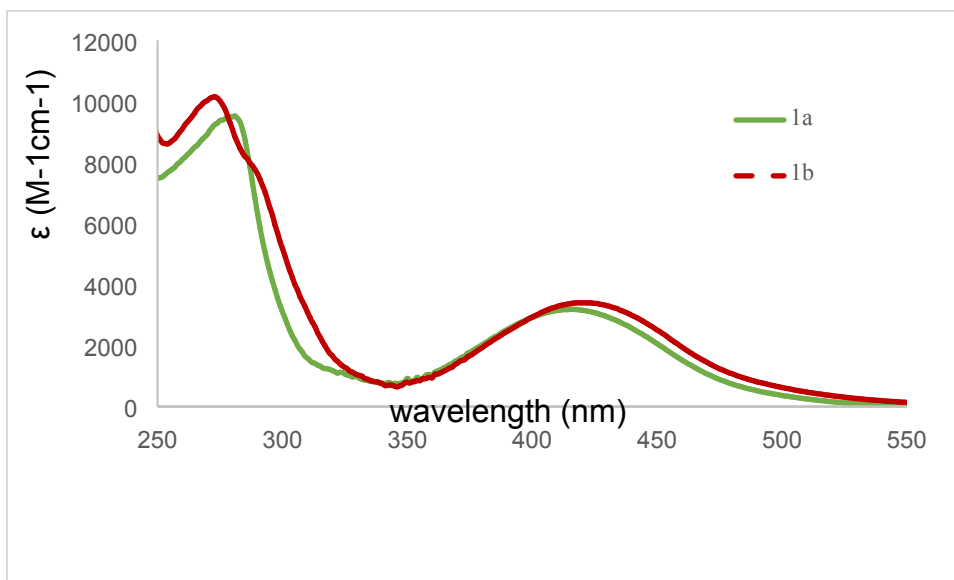


Figure S31: UV-visible spectra for compounds **1a** and **1b** in DCM.

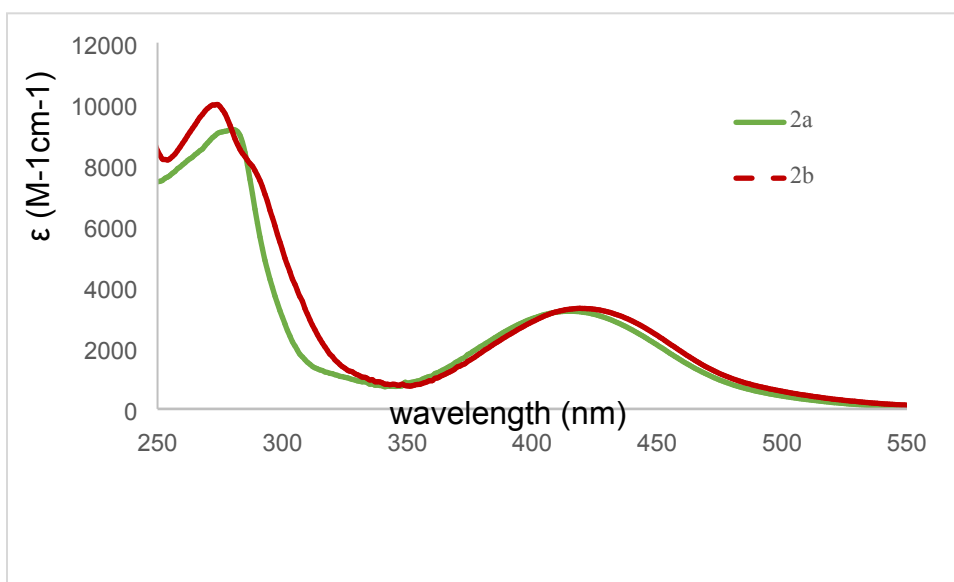


Figure S32: UV-visible spectra for compounds **2a** and **2b** in DCM.

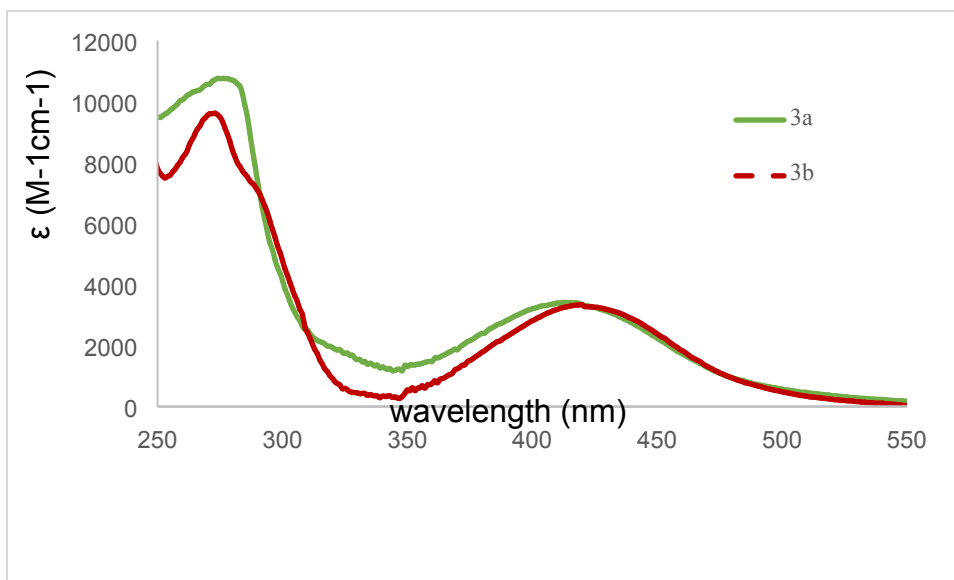


Figure S33: UV-visible spectra for compounds **3a** and **3b** in DCM.

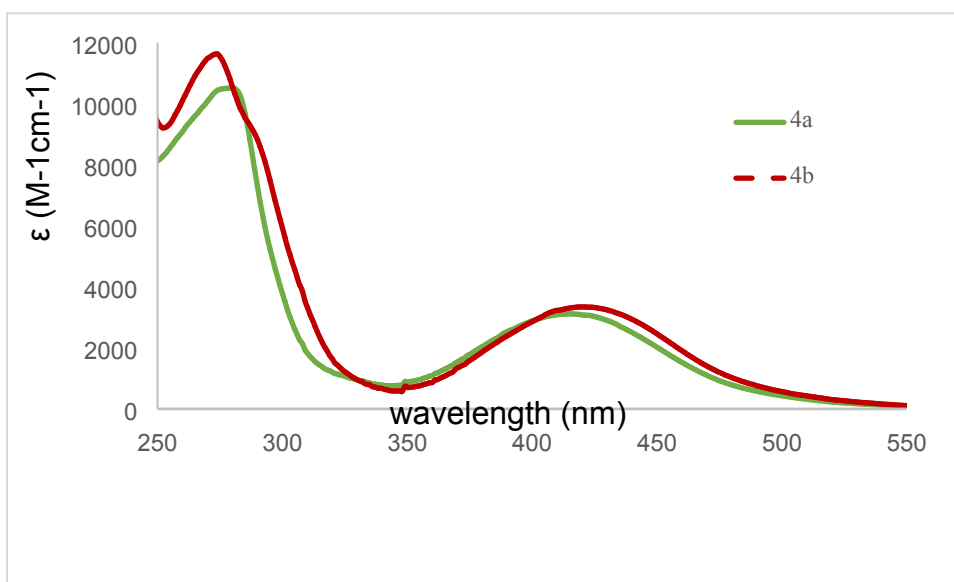


Figure S34: UV-visible spectra for compounds **4a** and **4b** in DCM.

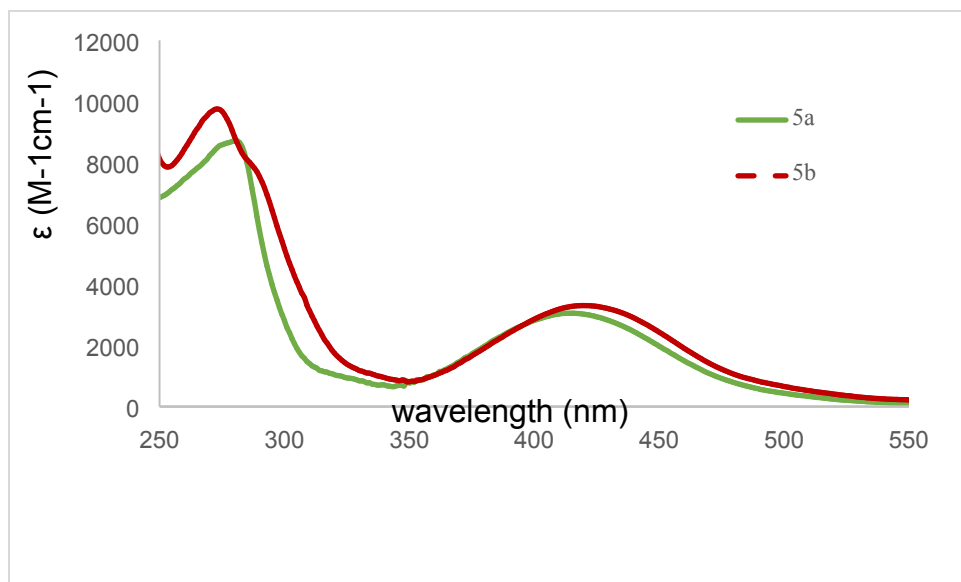


Figure S35: UV-visible spectra for compounds **5a** and **5b** in DCM.

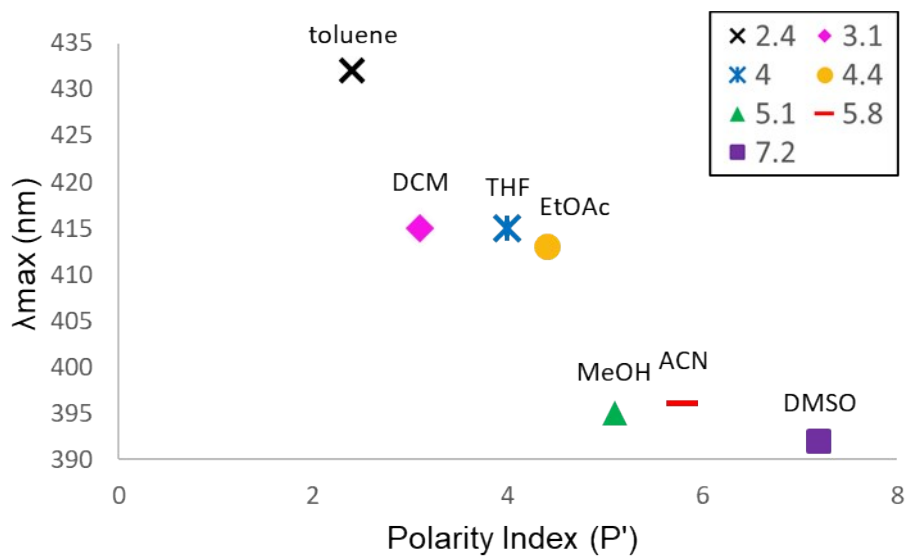


Figure S36: Solvent polarity index (P') versus λ_{\max} for **1a**.

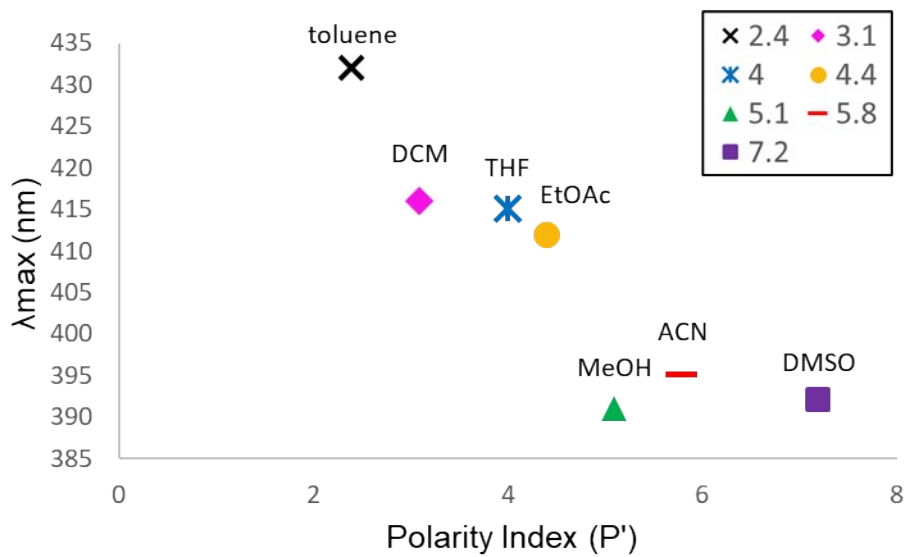


Figure S37: Solvent polarity index (P') versus λ_{\max} for **2a**.

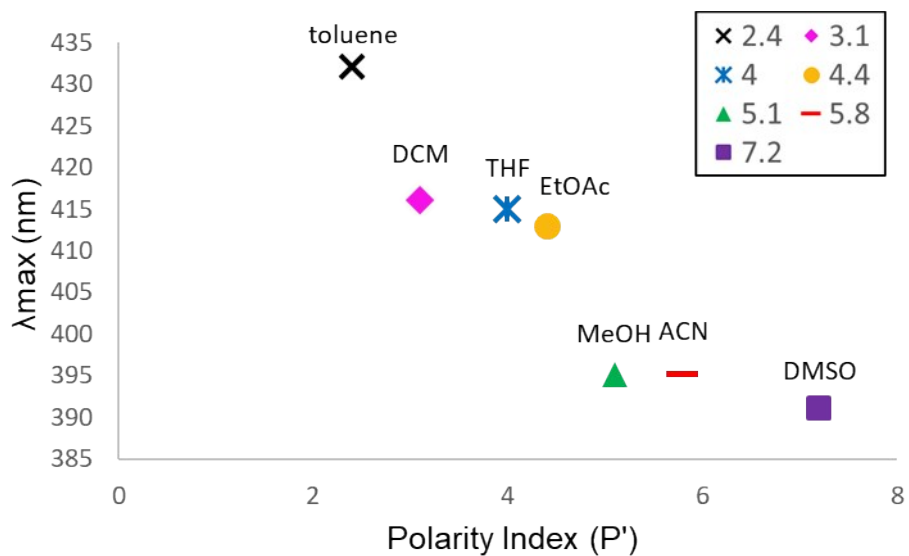


Figure S38: Solvent polarity index (P') versus λ_{\max} for **3a**.

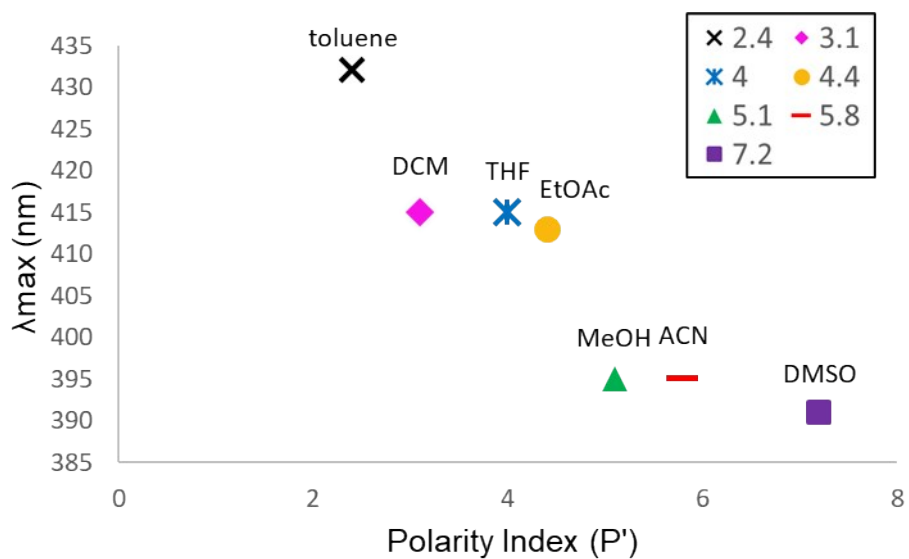


Figure S39: Solvent polarity index (P') versus λ_{\max} for **4a**.

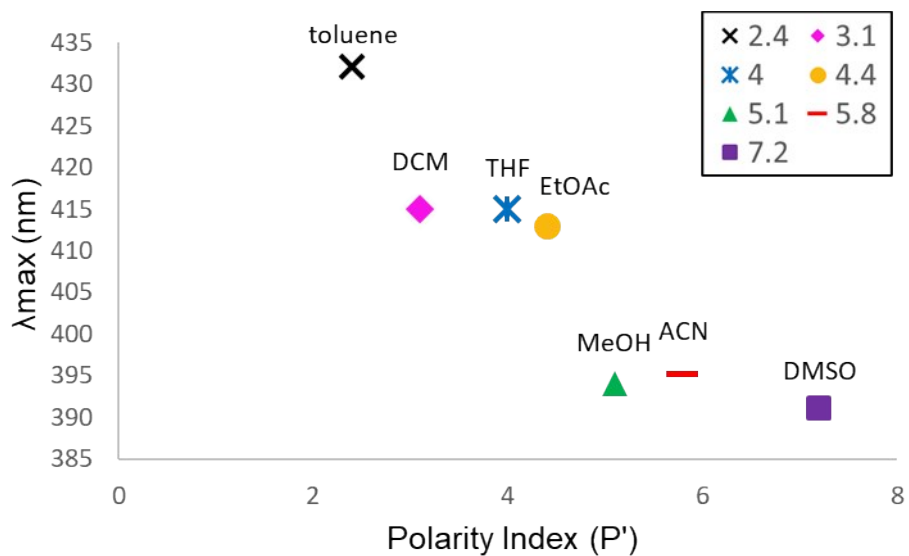


Figure S40: Solvent polarity index (P') versus λ_{\max} for **5a**.

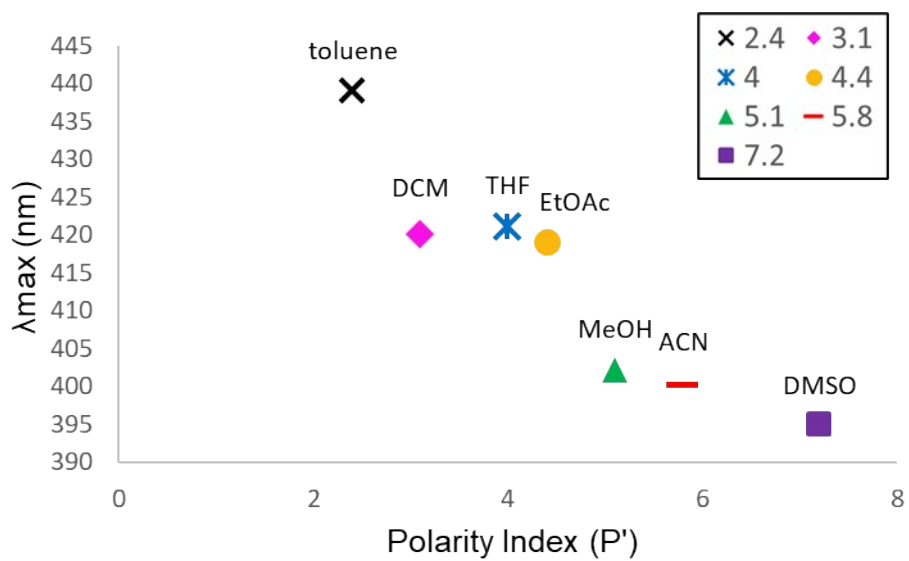


Figure S41: Solvent polarity index (P') versus λ_{\max} for **1b**.

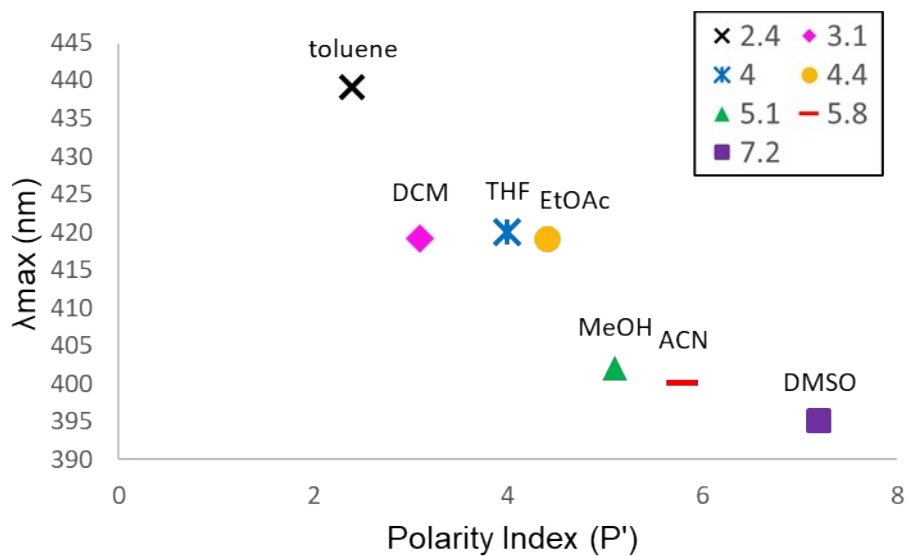


Figure S42: Solvent polarity index (P') versus λ_{\max} for **2b**.

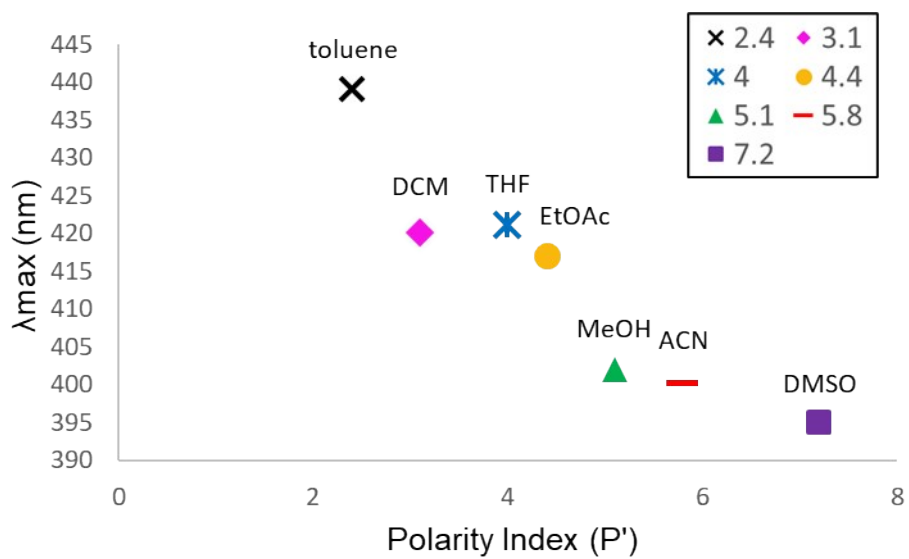


Figure S43: Solvent polarity index (P') versus λ_{\max} for **3b**.

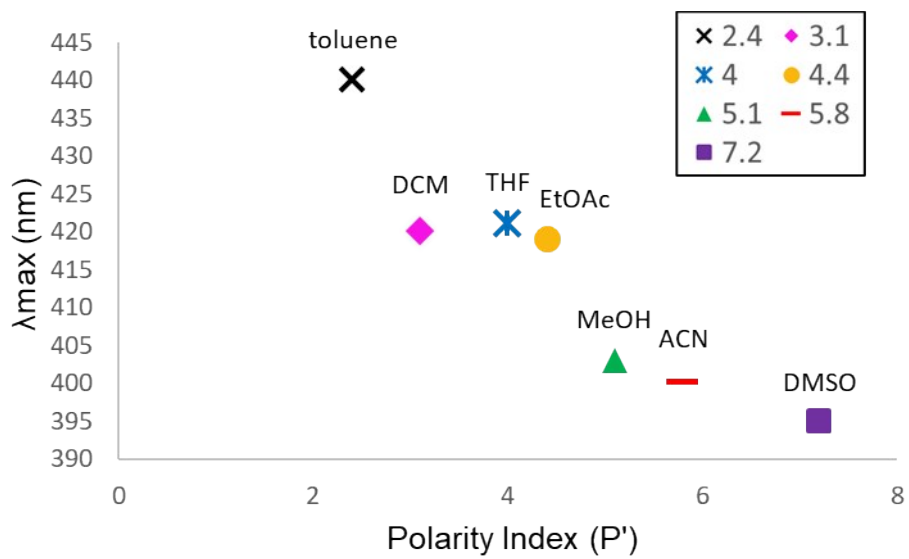


Figure S44: Solvent polarity index (P') versus λ_{\max} for **4b**.

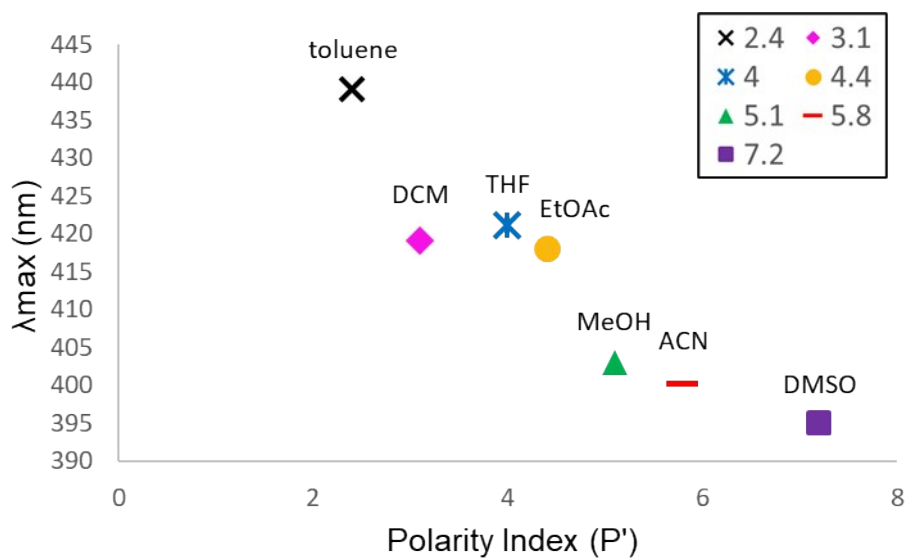


Figure S45: Solvent polarity index (P') versus λ_{\max} for **5b**.

Sample: 5Cl
Size: 2.8400 mg
Method: Heat/Cool/Heat
Comment: 5Cl

DSC

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Operator: BS
Run Date: 16-Jul-2020 09:19
Instrument: DSC Q200 V24.11 Build 124

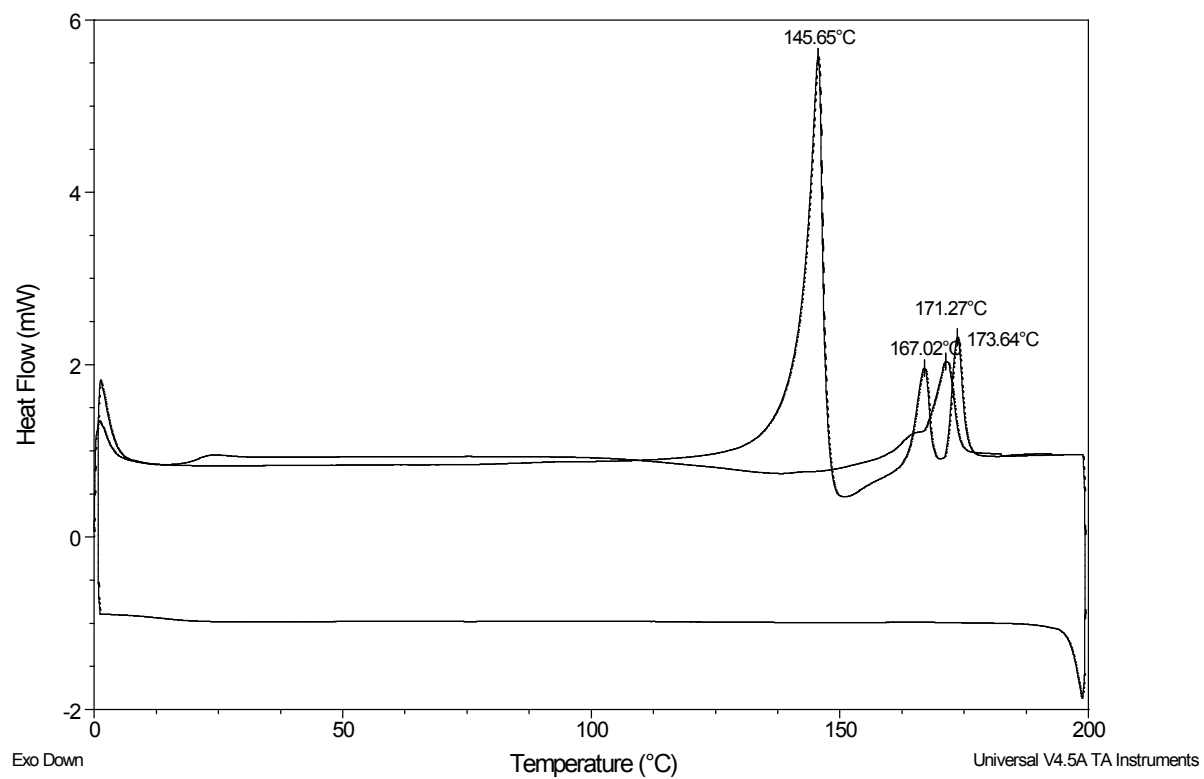


Figure S46: DSC thermogram for **1a**.

Sample: 5Br
Size: 3.7900 mg
Method: Heat/Cool/Heat
Comment: 5Br

DSC

File: E:\New folder (2)\5Br.001
Operator: BS
Run Date: 16-Jul-2020 10:25
Instrument: DSC Q200 V24.11 Build 124

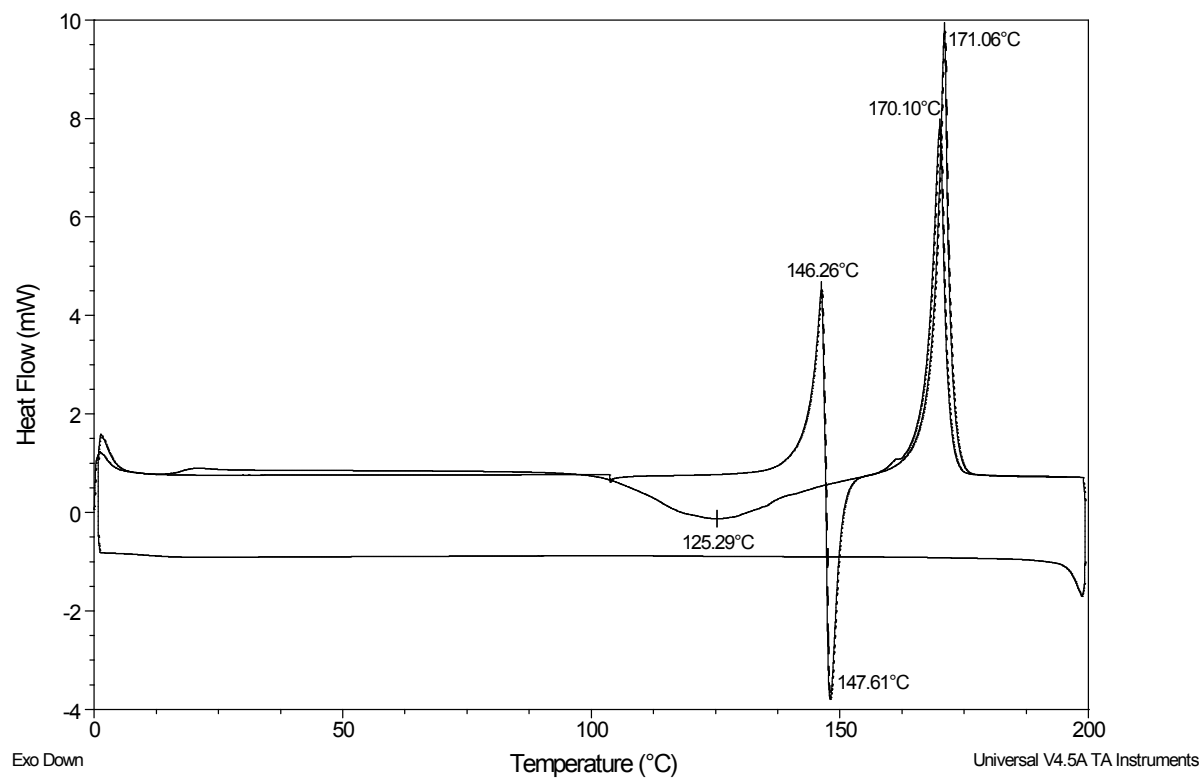


Figure S47: DSC thermogram of 1b.

Sample: 7Cl
Size: 4.3000 mg
Method: Heat/Cool/Heat
Comment: 7Cl

DSC

File: E:\New folder (2)\7Cl.001
Operator: BS
Run Date: 17-Jul-2020 08:41
Instrument: DSC Q200 V24.11 Build 124

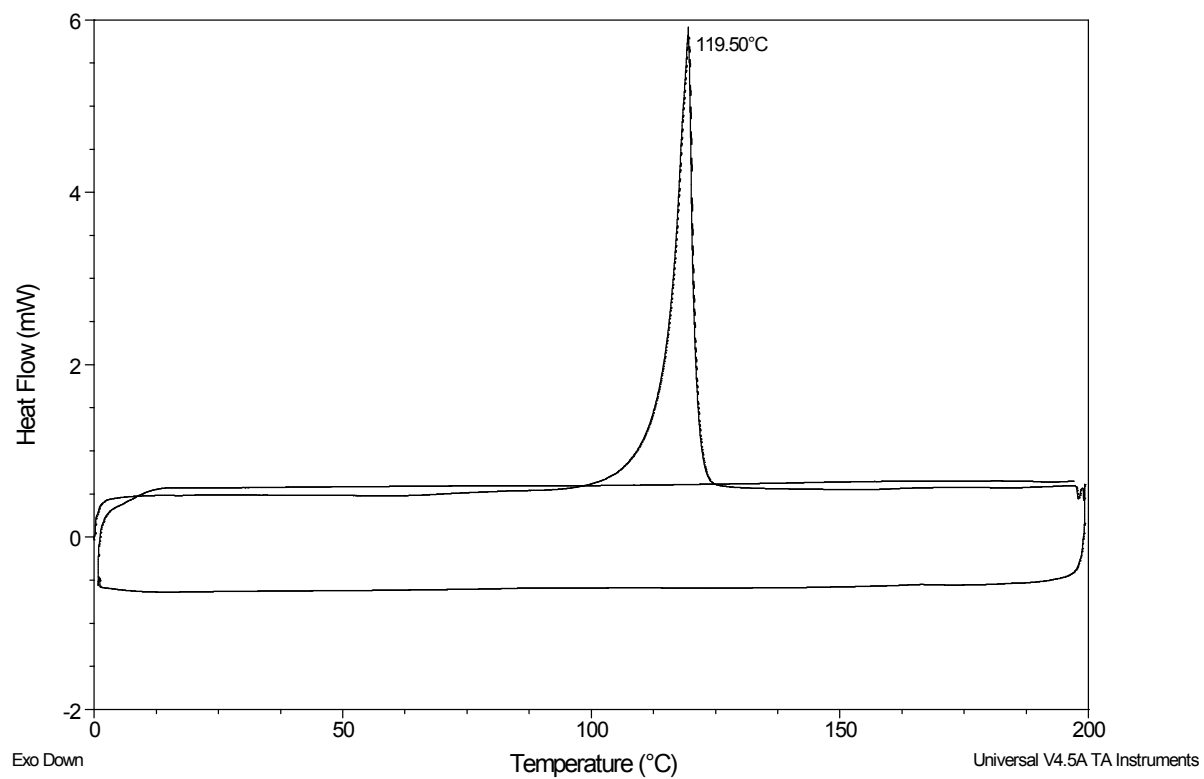


Figure S48: DSC thermogram of **2a**.

Sample: 7Br
Size: 4.5400 mg
Method: Heat/Cool/Heat
Comment: 7Br

DSC

File: E:\New folder (2)\7Br.001
Operator: BS
Run Date: 17-Jul-2020 09:53
Instrument: DSC Q200 V24.11 Build 124

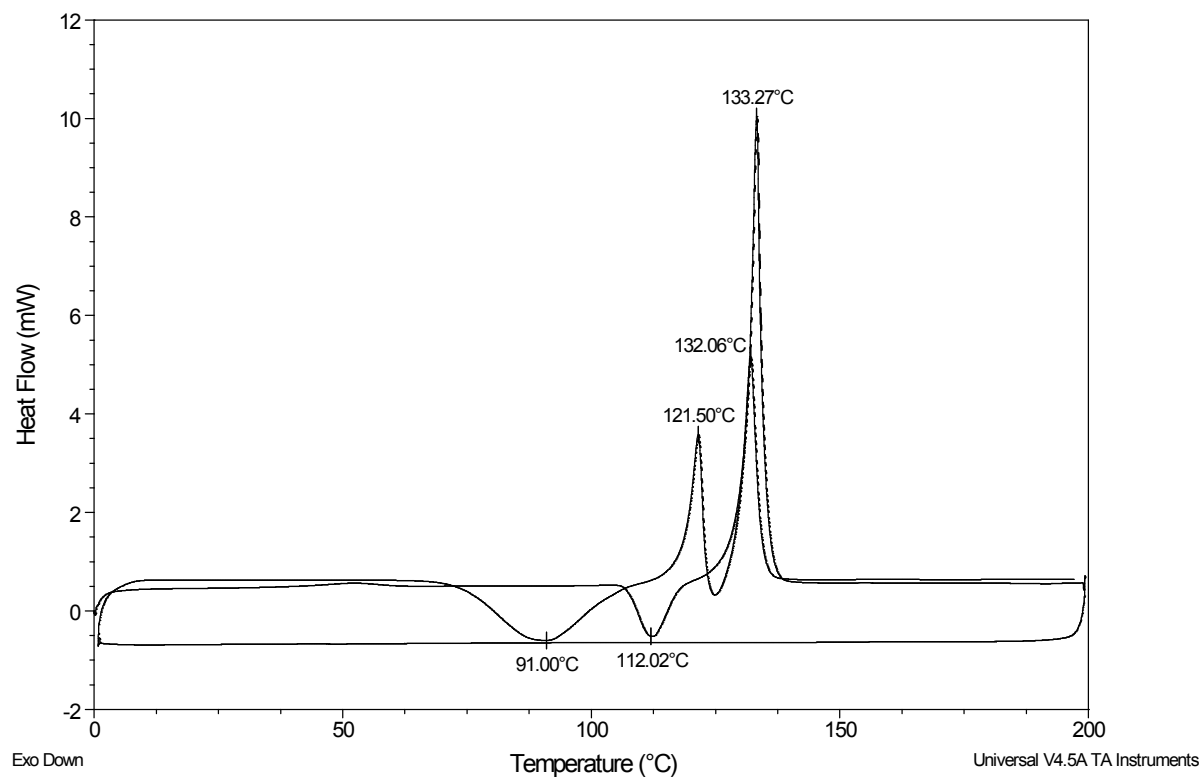


Figure S49: DSC thermogram of **2b**.

Sample: 11Cl
Size: 3.9200 mg
Method: Heat/Cool/Heat
Comment: 11Cl

DSC

File: E:\New folder (2)\11d.001
Operator: BS
Run Date: 14-Jul-2020 15:30
Instrument: DSC Q200 V24.11 Build 124

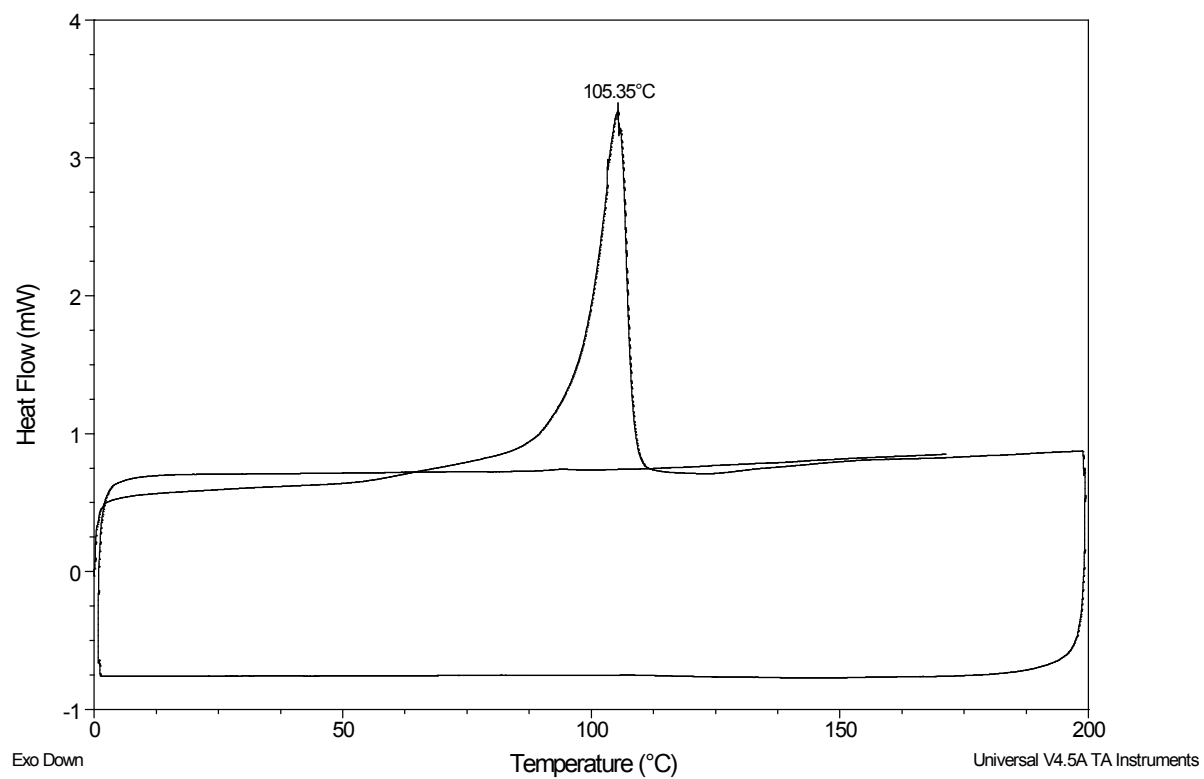


Figure S50: DSC thermogram of **3a**.

Sample: 11Br
Size: 4.0300 mg
Method: Heat/Cool/Heat
Comment: 11Br

DSC

File: E:\New folder (2)\11Br.001
Operator: BS
Run Date: 14-Jul-2020 16:34
Instrument: DSC Q200 V24.11 Build 124

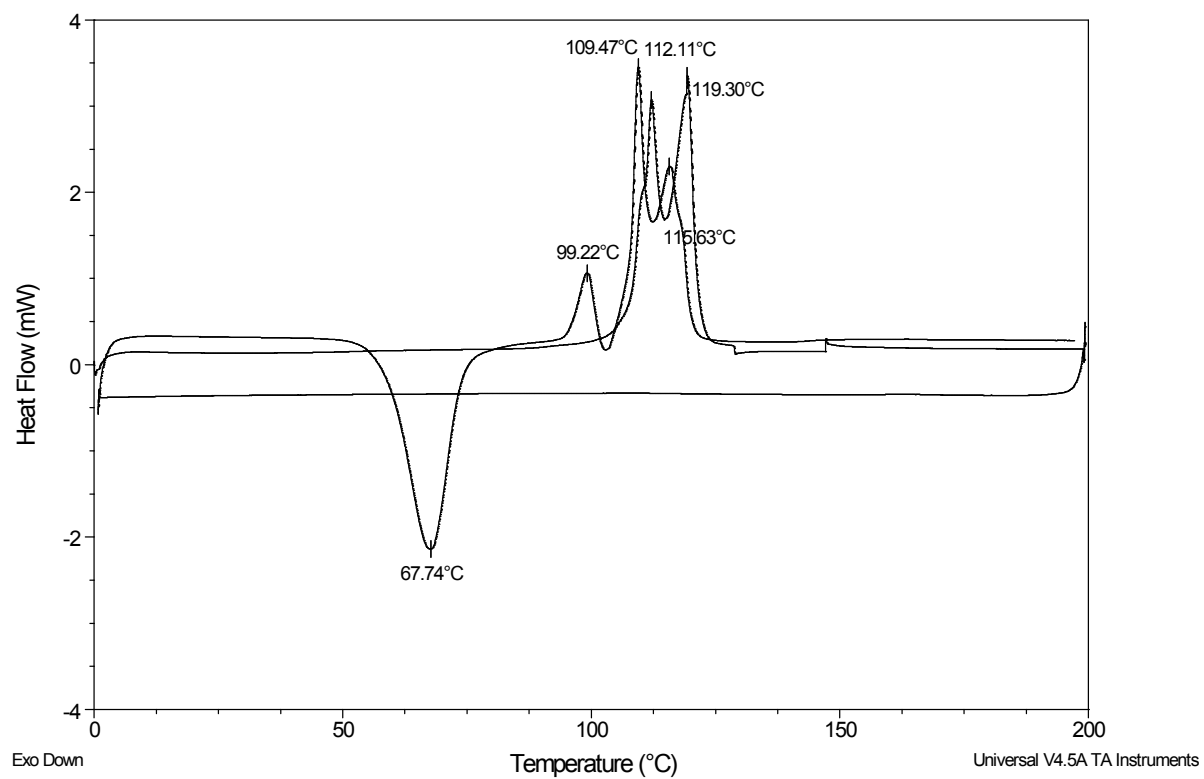


Figure S51: DSC thermogram of 3b.

Sample: 12Cl
Size: 4.2600 mg
Method: Heat/Cool/Heat
Comment: 12Cl

DSC

File: E:\New folder (2)\12d1.001
Operator: BS
Run Date: 14-Jul-2020 14:21
Instrument: DSC Q200 V24.11 Build 124

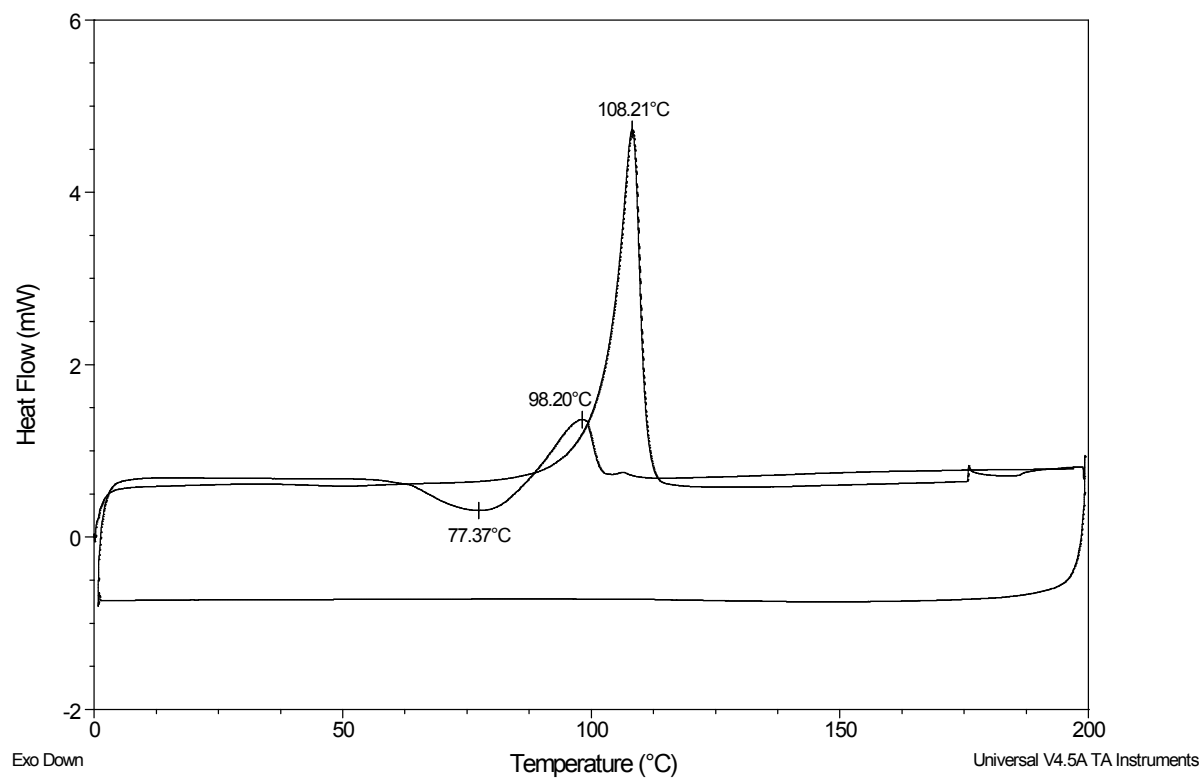


Figure S52: DSC thermogram of **4a**.

Sample: 12Br
Size: 2.9600 mg
Method: Heat/Cool/Heat
Comment: 12Br

DSC

File: E:\New folder (2)\12Br1.001
Operator: BS
Run Date: 14-Jul-2020 13:15
Instrument: DSC Q200 V24.11 Build 124

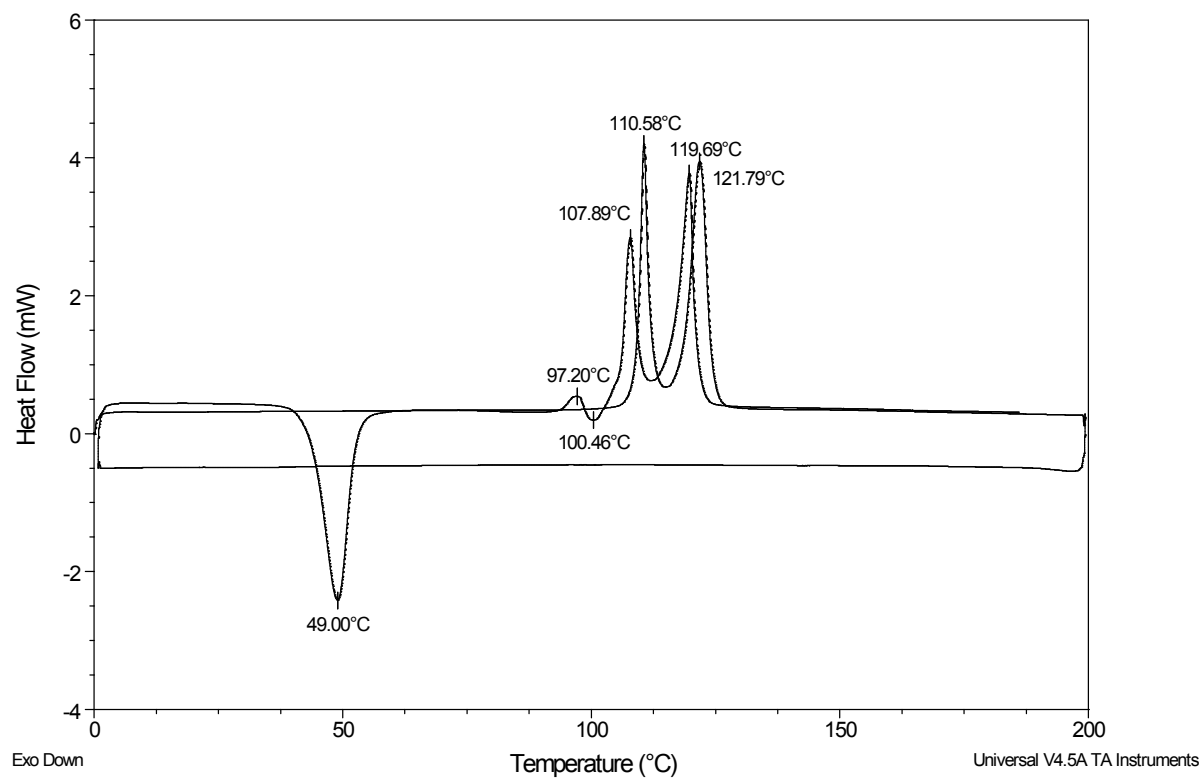


Figure S53: DSC thermogram of 4b.

Sample: 14Cl
Size: 3.6700 mg
Method: Heat/Cool/Heat
Comment: 14Cl

DSC

File: E:\14Cl.001
Operator: BS
Run Date: 29-Jun-2020 14:31
Instrument: DSC Q200 V24.11 Build 124

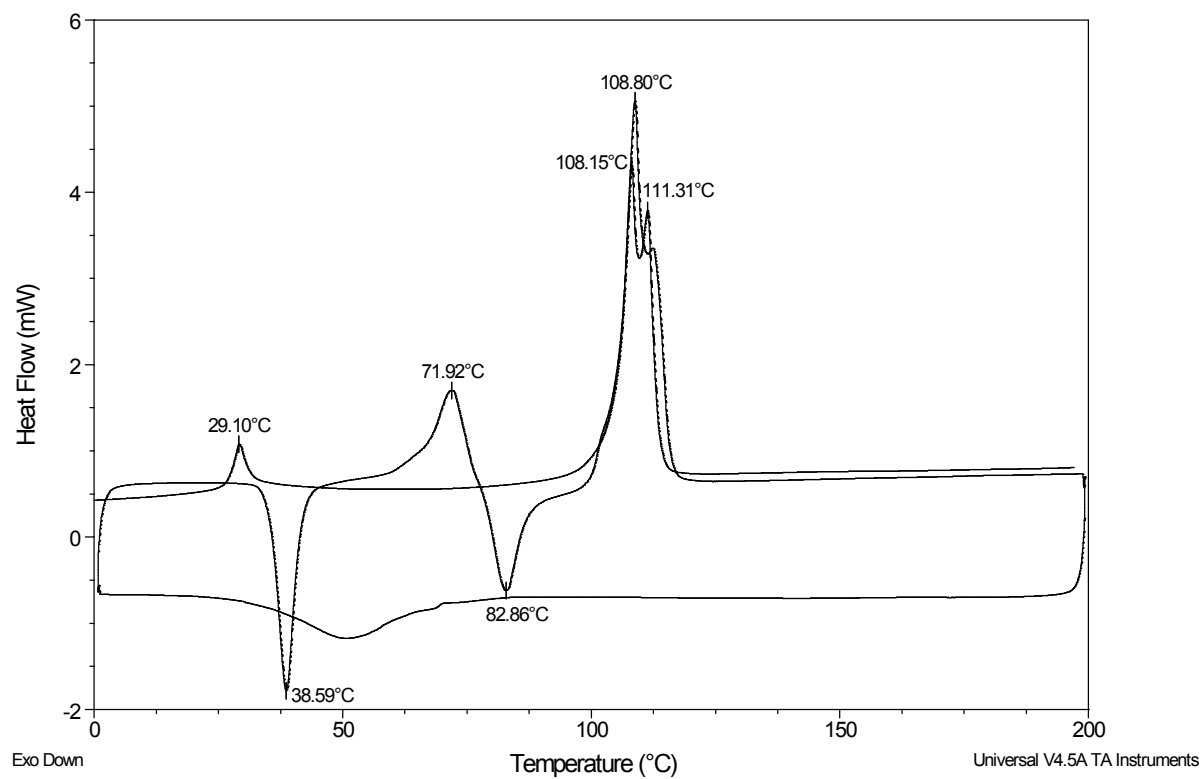


Figure S54: DSC thermogram of 5a.

Sample: 14Br
Size: 4.7500 mg
Method: Heat/Cool/Heat
Comment: 14Br

DSC

File: E:\New folder (2)\14Br1.001
Operator: BS
Run Date: 14-Jul-2020 12:08
Instrument: DSC Q200 V24.11 Build 124

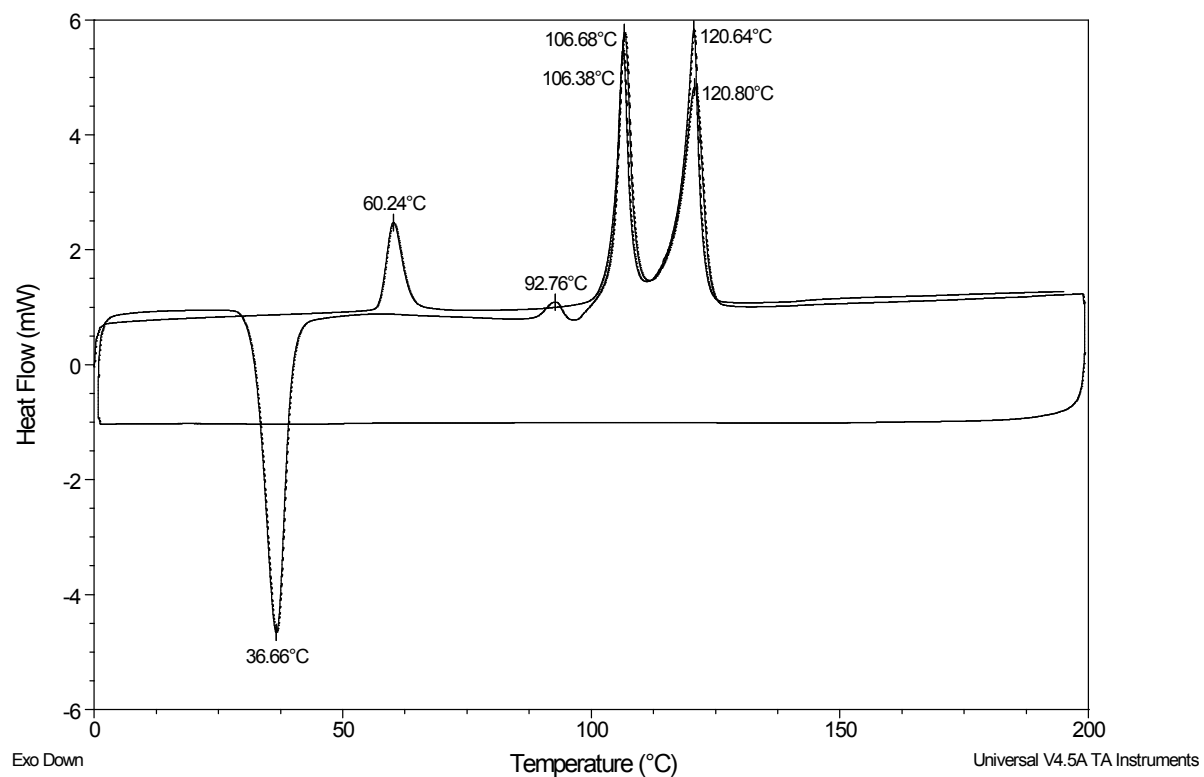


Figure S55: DSC thermogram of 5b.

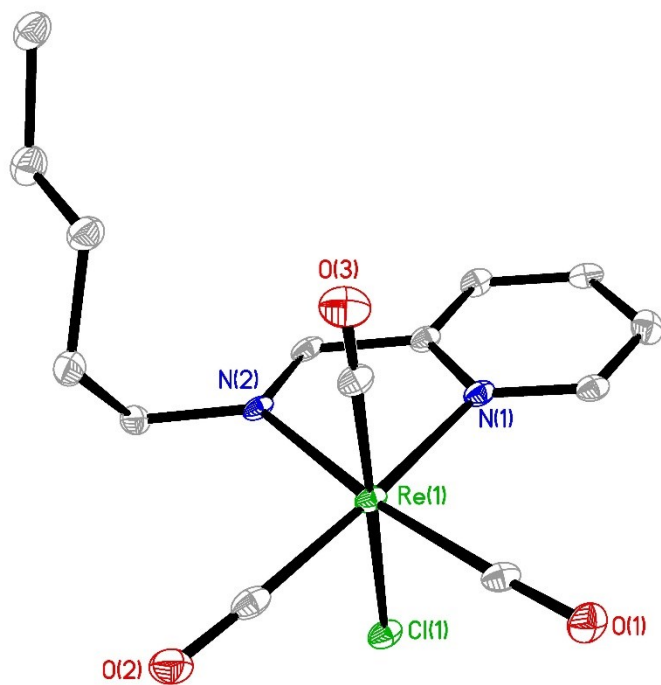


Figure S56: The structures of compound **1a** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

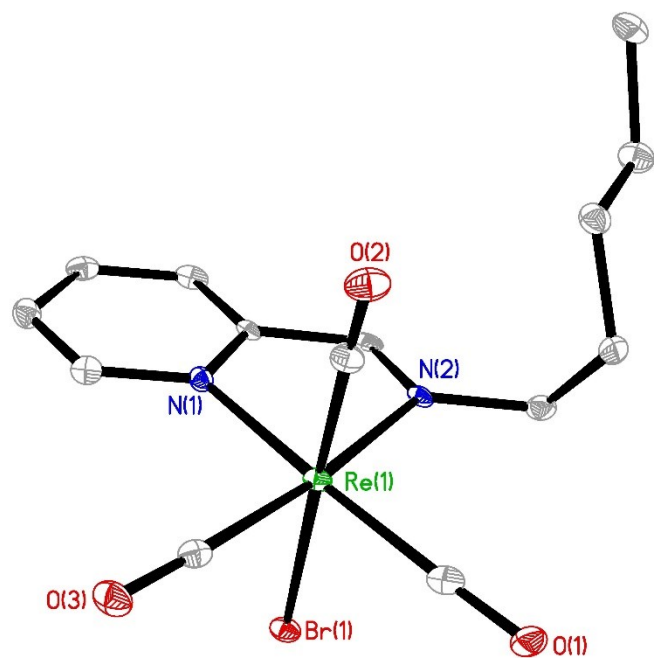


Figure S57: The structures of compound **1b** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

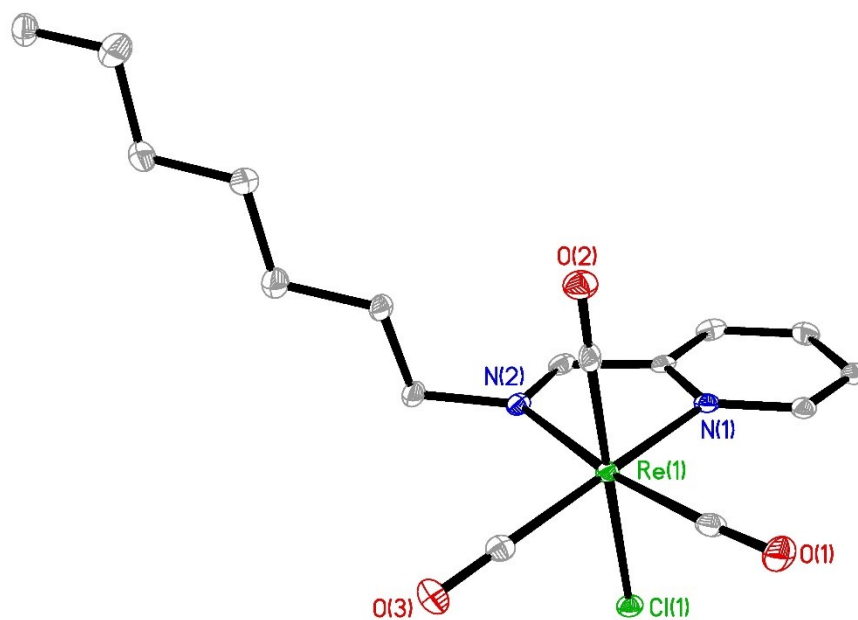


Figure S58: The structures of compound **2a** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

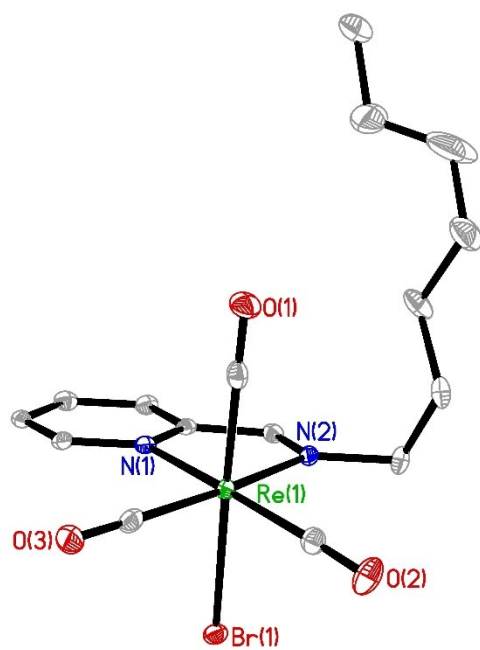


Figure S59: The structures of compound **2b** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

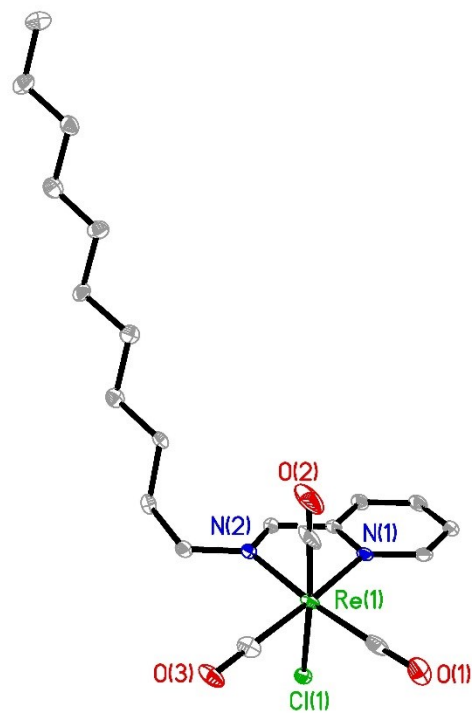


Figure S60: The structures of compound **3a** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

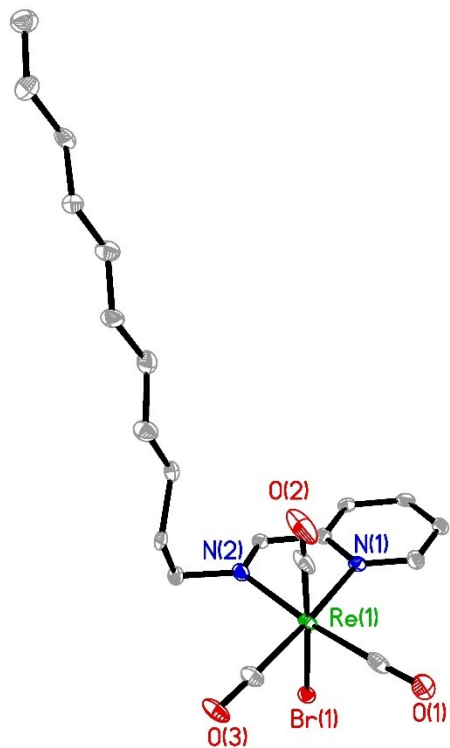


Figure S61: The structures of compound **3b** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

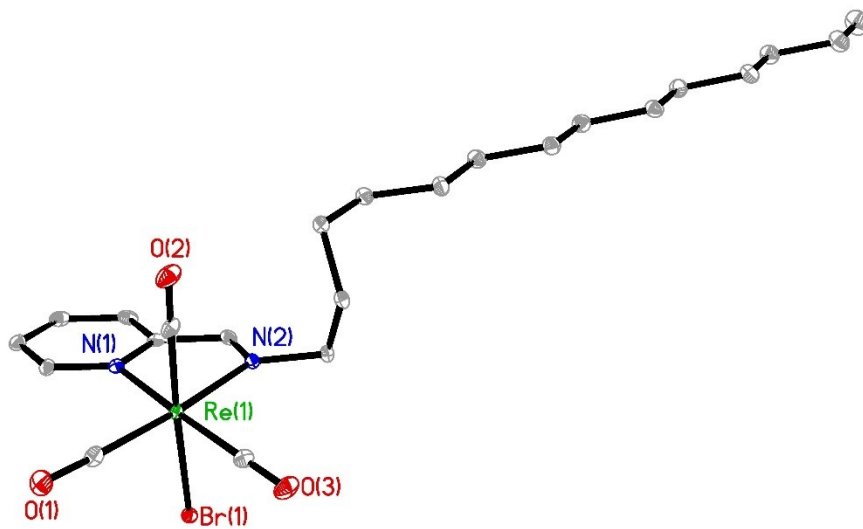


Figure S62: The structures of compound **5b** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

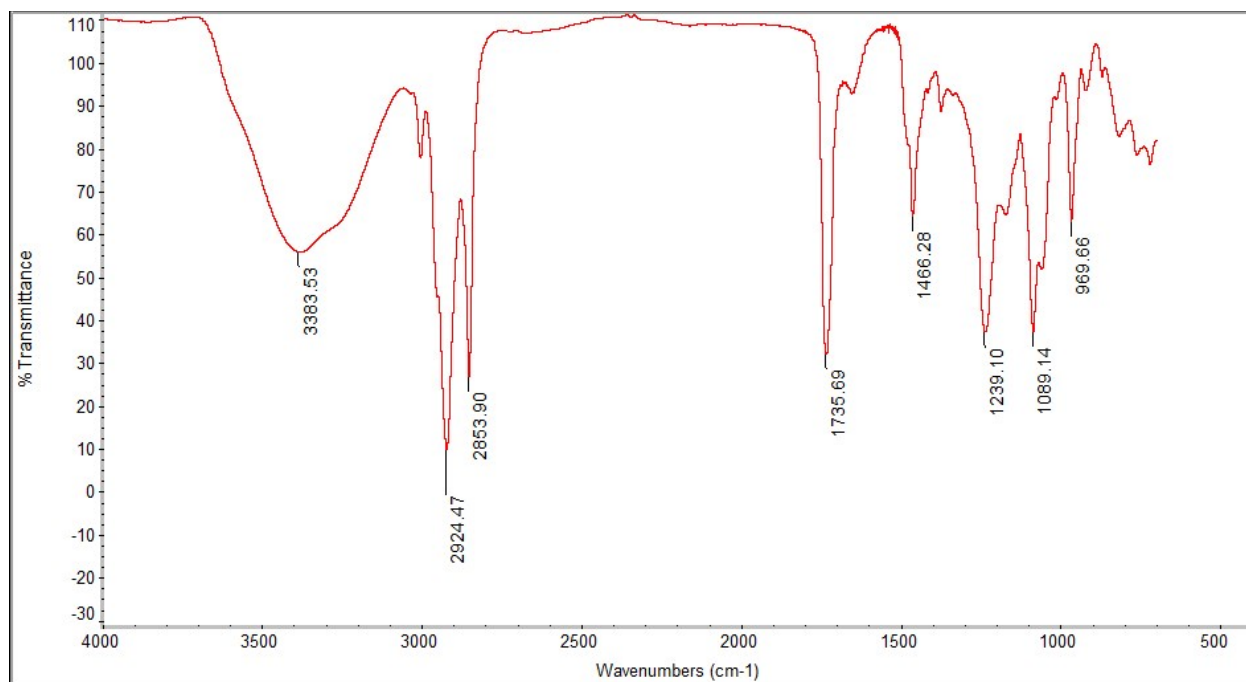


Figure S63: FTIR spectrum of 100 mol % DOPC vesicles.

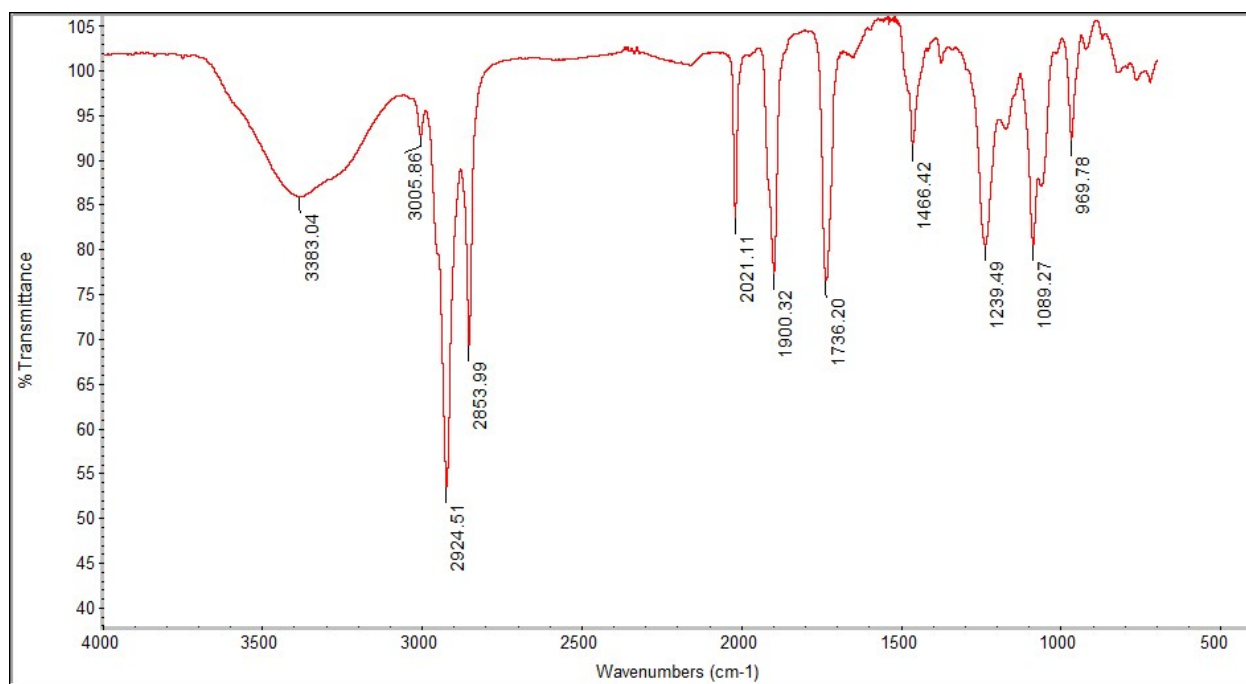


Figure S64: FTIR spectrum of 95 mol % DOPC, and 5 mol % by Re(I) content of compound 5a vesicles.

Table S1: X-ray crystal data and structure parameters for compounds **1a,b** and **2a,b**.

Compound	1a	1b	2a	2b
CCDC	2040147	2040148	2040149	2040150
Empirical formula	C ₁₄ H ₁₆ ClN ₂ O ₃ Re	C ₁₄ H ₁₆ BrN ₂ O ₃ Re	C ₁₆ H ₂₀ ClN ₂ O ₃ Re	C ₁₆ H ₂₀ BrN ₂ O ₃ Re
Formula weight	481.94	526.40	509.99	554.45
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	C2/c
a/ Å	12.987(15)	13.0993(5)	14.1835(10)	37.124(10)
b/ Å	9.232(11)	9.2231(4)	9.7002(7)	8.127(2)
c/ Å	13.131(16)	13.0735(5)	12.7862(9)	12.214(4)
α(°)	90	90	90	90
β(°)	92.96(2)	92.466(2)	91.480(3)	95.870(10)
γ(°)	90	90	90	90
Volume (Å ³)	1572(3)	1578.03(11)	1758.6(2)	3665.5(18)
Z	4	4	4	8
Dc (Mg/m ³)	2.036	2.216	1.926	2.009
μ (mm ⁻¹)	7.909	10.243	7.076	8.825
F(000)	920	992	984	2112
reflns collected	14201	14638	16206	34493
indep. reflns	3877	3876	4374	4544
GOF on F ²	1.036	1.011	1.071	1.041
R1 (on F _o ² , I > 2σ(I))	0.0322	0.0323	0.0275	0.0215
wR2 (on F _o ² , I > 2σ(I))	0.0752	0.0615	0.0619	0.0539
R1 (all data)	0.0426	0.0452	0.0397	0.0260
wR2 (all data)	0.0797	0.0665	0.0810	0.0550

Table S2: X-ray crystal data and structure parameters for compounds **3a,b** and **5b**.

Compound	3a	3b	5b
CCDC	2040151	2040152	2040153
Empirical formula	C ₄₀ H ₅₆ Cl ₂ N ₄ O ₆ Re ₂	C ₄₀ H ₅₆ Br ₂ N ₄ O ₆ Re ₂	C ₂₃ H ₃₄ BrN ₂ O ₃ Re
Formula weight	1132.18	1221.10	652.63
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a/ Å	6.460(4)	6.499(3)	6.5604(5)
b/ Å	8.018(4)	8.104(4)	8.0273(5)
c/ Å	22.053(13)	22.210(11)	24.7618(19)
α(°)	84.53(3)	87.49(4)	96.463(3)
β(°)	85.03(3)	82.67(3)	94.773(3)
γ(°)	75.25(3)	74.59(3)	103.929(2)
Volume (Å ³)	1097.2(10)	1118.4(9)	1249.37(16)
Z	1	1	2
Dc (Mg/m ³)	1.714	1.813	1.735
μ (mm ⁻¹)	5.680	7.240	6.487
F(000)	556	592	640
reflns collected	48124	42444	61344
indep. reflns	5473	5549	6226
GOF on F ²	1.060	1.068	1.020
R1 (on F _o ² , I > 2σ(I))	0.0349	0.0381	0.0155
wR2 (on F _o ² , I > 2σ(I))	0.0807	0.0665	0.0373
R1 (all data)	0.0446	0.0536	0.0170
wR2 (all data)	0.0828	0.0695	0.0377

	1a	1b	2a	2b
Re-N _(imine) (Å)	2.184(5)	2.171(4)	2.172(3)	2.167(3)
Re-N _(py) (Å)	2.166(5)	2.161(4)	2.175(4)	2.174(3)
Re-C (Å)	1.917(6) 1.930(6) 1.930(6)	1.927(5) 1.908(5) 1.914(5)	1.922(5) 1.899(5) 1.936(5)	1.919(4) 1.928(3) 1.920(3)
C-O _(c≡o) (Å)	1.161(6) 1.167(6) 1.159(7)	1.147(6) 1.152(6) 1.158(5)	1.151(6) 1.161(6) 1.146(5)	1.137(4) 1.141(4) 1.148(4)
Re-X _(Cl,Br) (Å)	2.513(3)	2.6196(5)	2.4997(12)	2.6264(7)
N-Re-N (°)	74.65(15)	74.68(14)	74.72(14)	74.85(10)

Table S3: Selected bond lengths and angles for compounds **1a,b** and **2a,b**.

Table S4: Selected bond lengths and angles for compounds **3a**, **b**, and **5b**.

	3a	3b	5b
Re-N _(imine) (Å)	2.161(4)	2.152(5)	2.1609(16)
Re-N _(py) (Å)	2.181(4)	2.180(4)	2.1726(16)
Re-C (Å)	1.930(6) 1.914(6) 1.932(5)	1.908(7) 1.900(6) 1.917(6)	1.920(2) 1.910(2) 1.926(2)
C-O _(c≡o) (Å)	1.148(7) 1.142(7) 1.136(6)	1.162(7) 1.169(7) 1.151(6)	1.150(3) 1.146(3) 1.148(3)
Re-X _(Cl,Br) (Å)	2.4713(17)	2.6174(13)	2.6226(3)
N-Re-N (°)	74.67(15)	74.90(16)	74.80(6)