Electronic Supplementary Material (ESI) for Dalton Transactions.

Lipophilic $Re(CO)_3$Pyca Complexes for Mid-IR Imaging Applications

Briana R. Schrage,[a] Baylee R. Frisinger,[a] Sarah J. Schmidtke Sobeck [b] and Christopher J. Ziegler [*a]

a Department of Chemistry, University of Akron, Akron, Ohio 44312-3601, United States
b Department of Chemistry, College of Wooster, Wooster, Ohio 44691, United States

Supplementary Information

Table of Contents

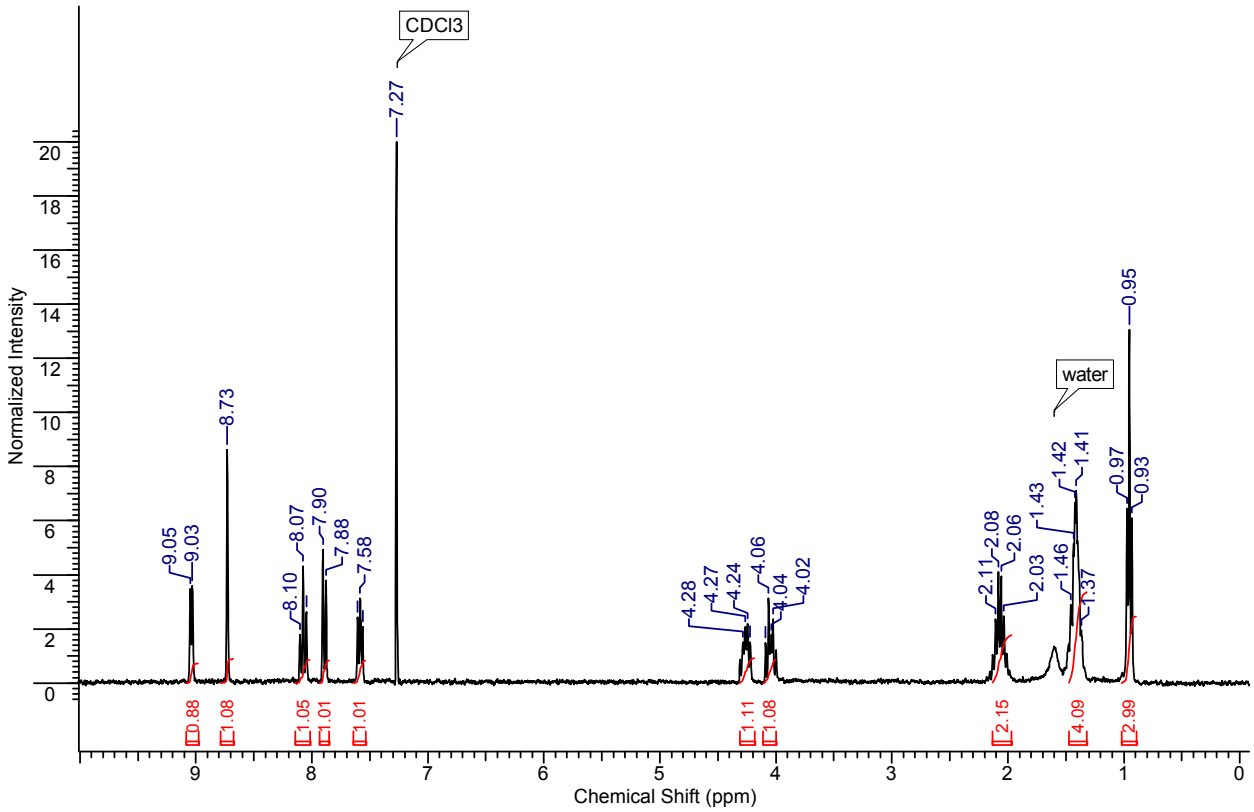


Figure S1: ^{1}H NMR (300 MHz) of **1a** in $CDCl_3$.

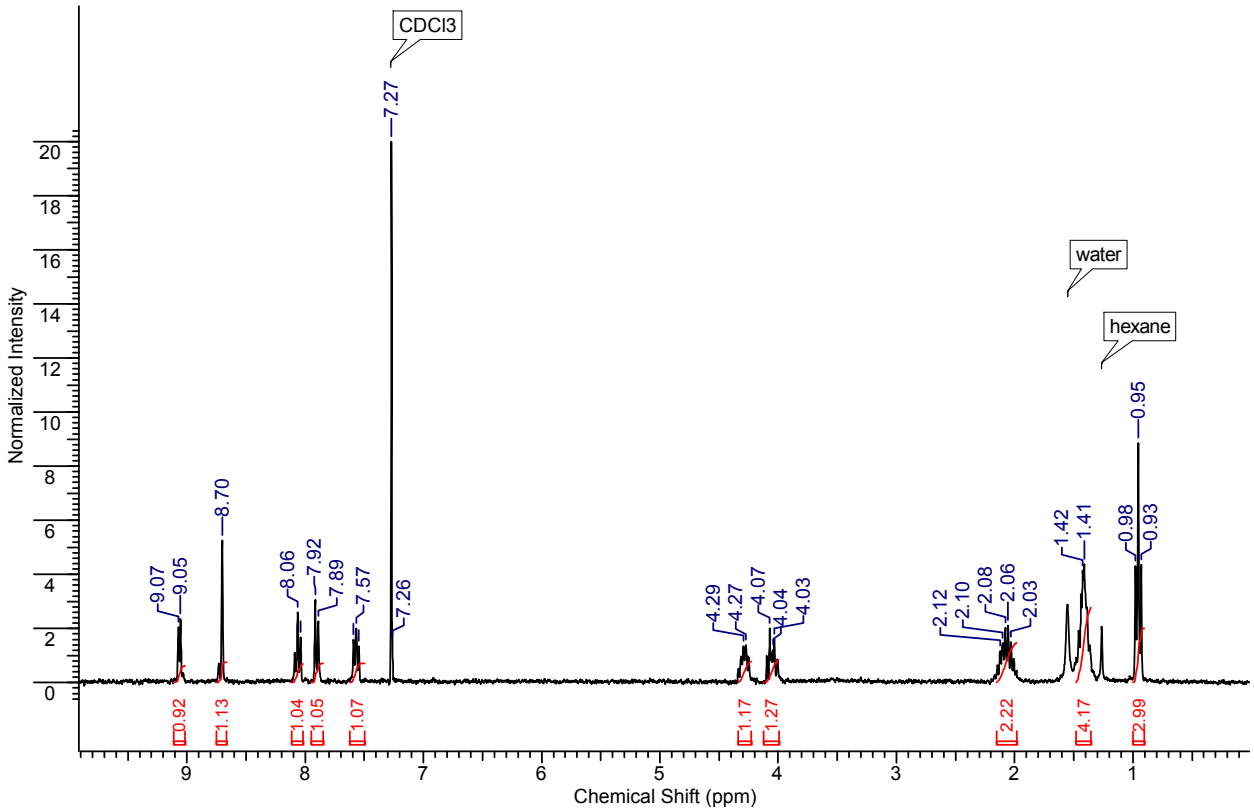


Figure S2: ^{1}H NMR (300 MHz) of **1b** in $CDCl_3$.

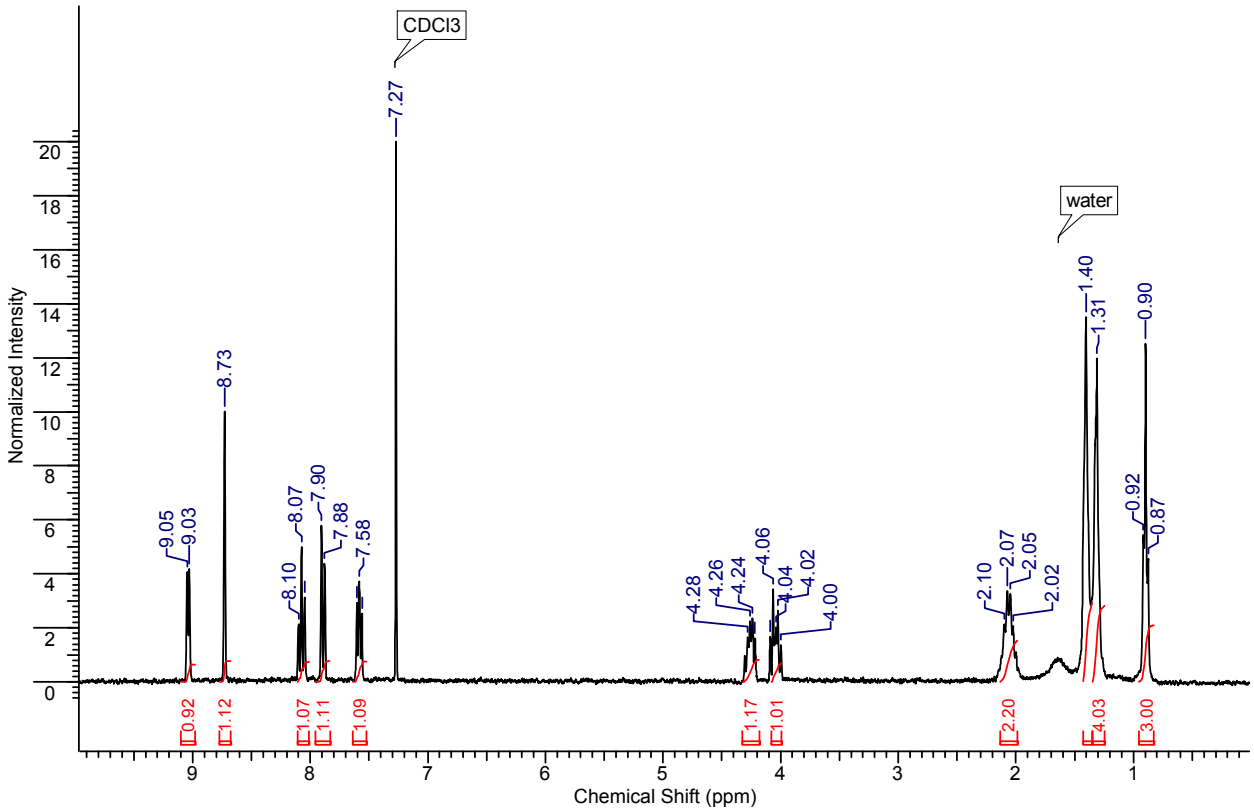


Figure S3: ^{1}H NMR (300 MHz) of **2a** in $CDCl_3$.

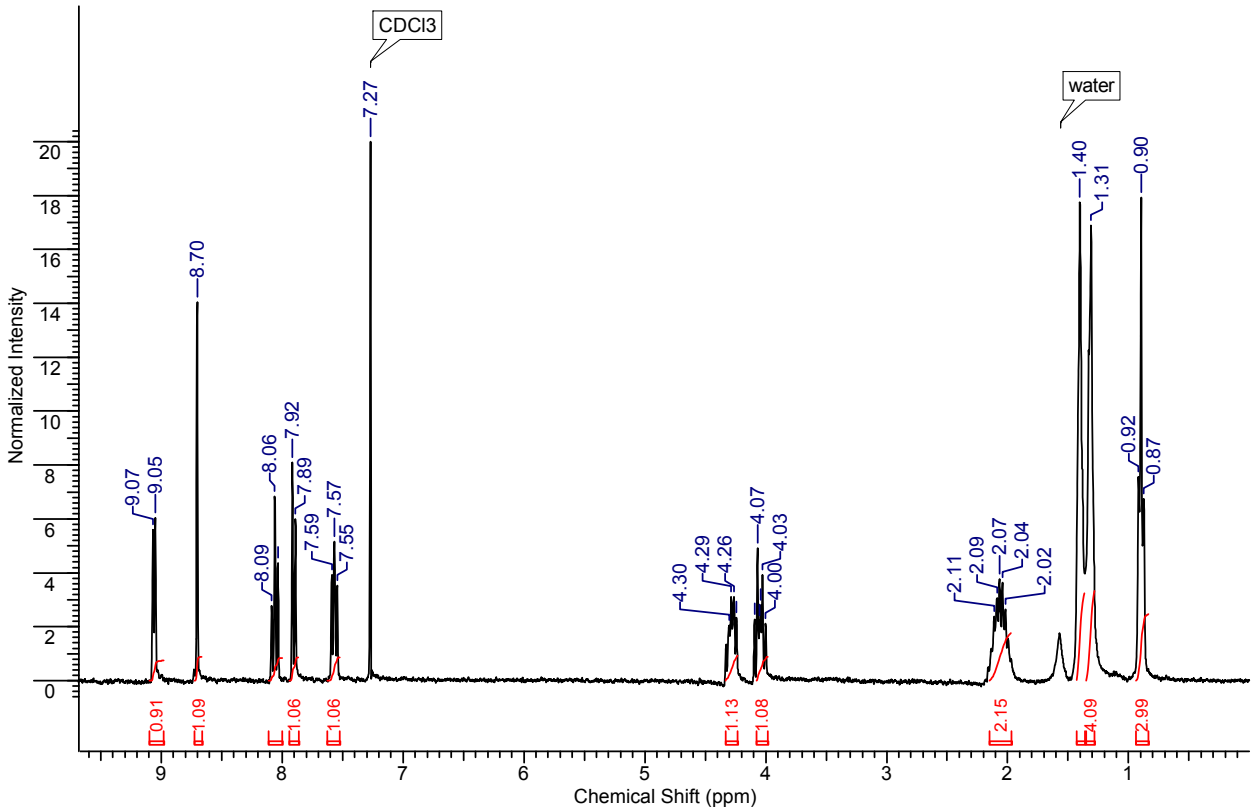


Figure S4: ^{1}H NMR (300 MHz) of **2b** in $CDCl_3$.

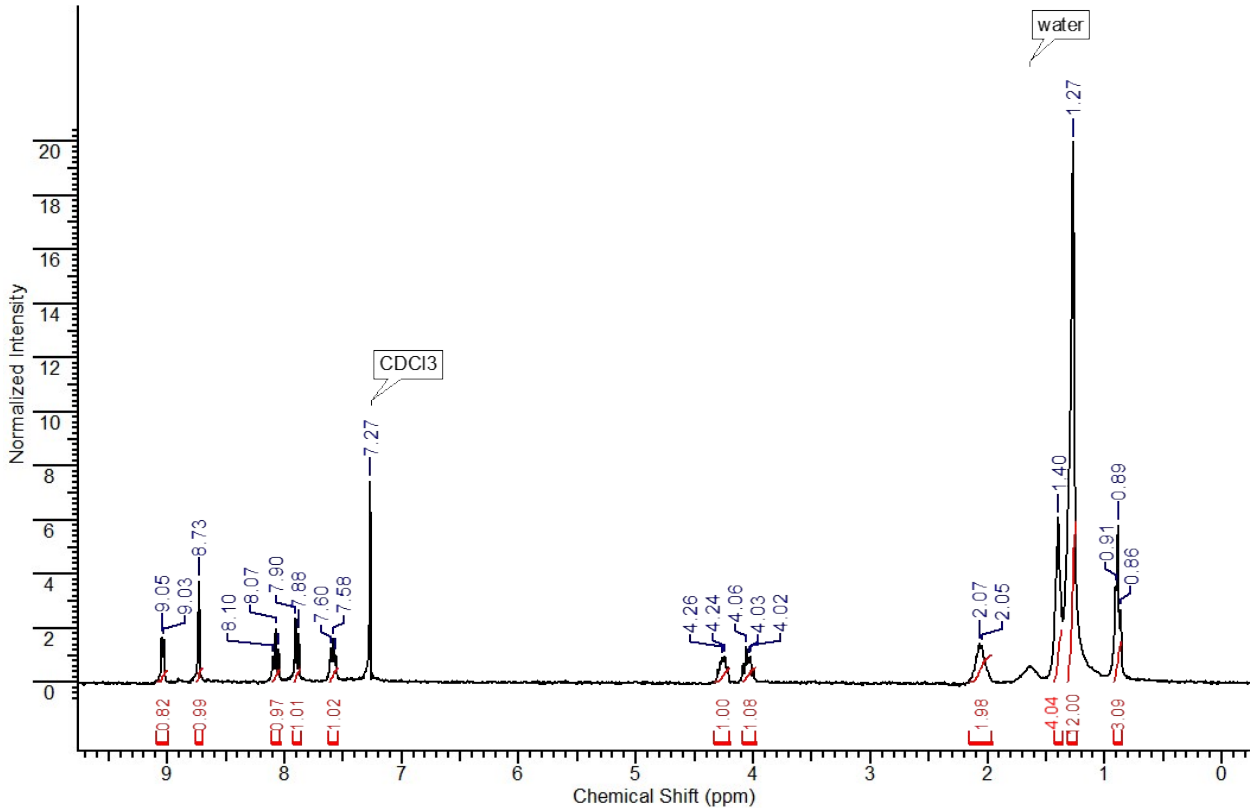


Figure S5: ^{1}H NMR (300 MHz) of **3a** in $CDCl_3$.

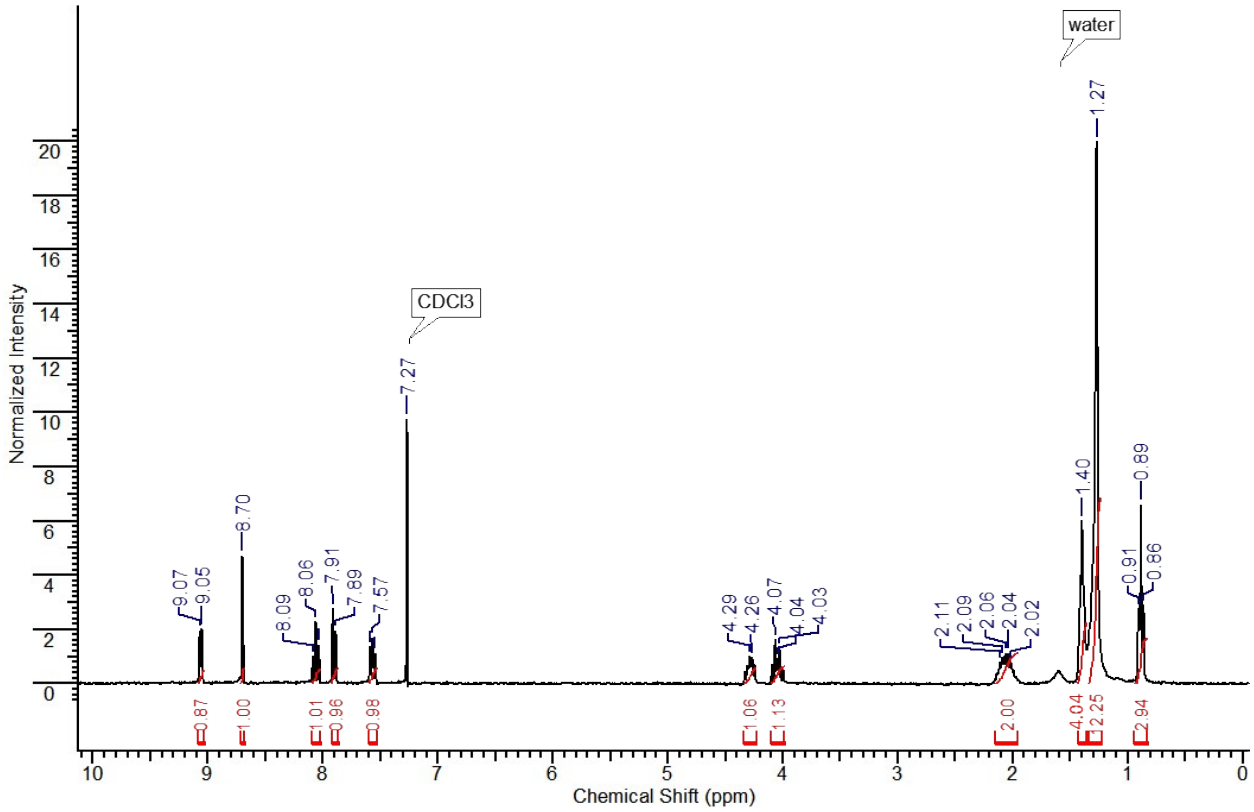


Figure S6: ^{1}H NMR (300 MHz) of **3b** in $CDCl_3$.

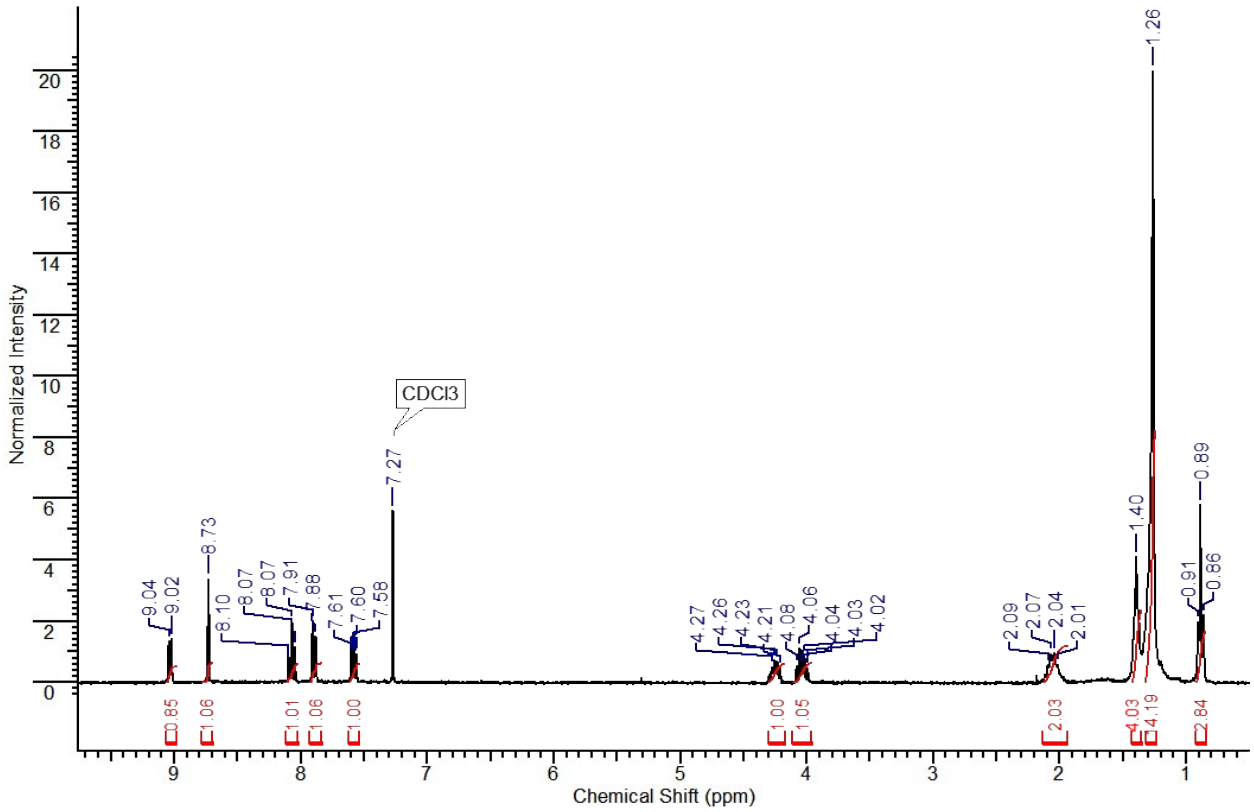


Figure S7: ^{1}H NMR (300 MHz) of **4a** in $CDCl_3$.

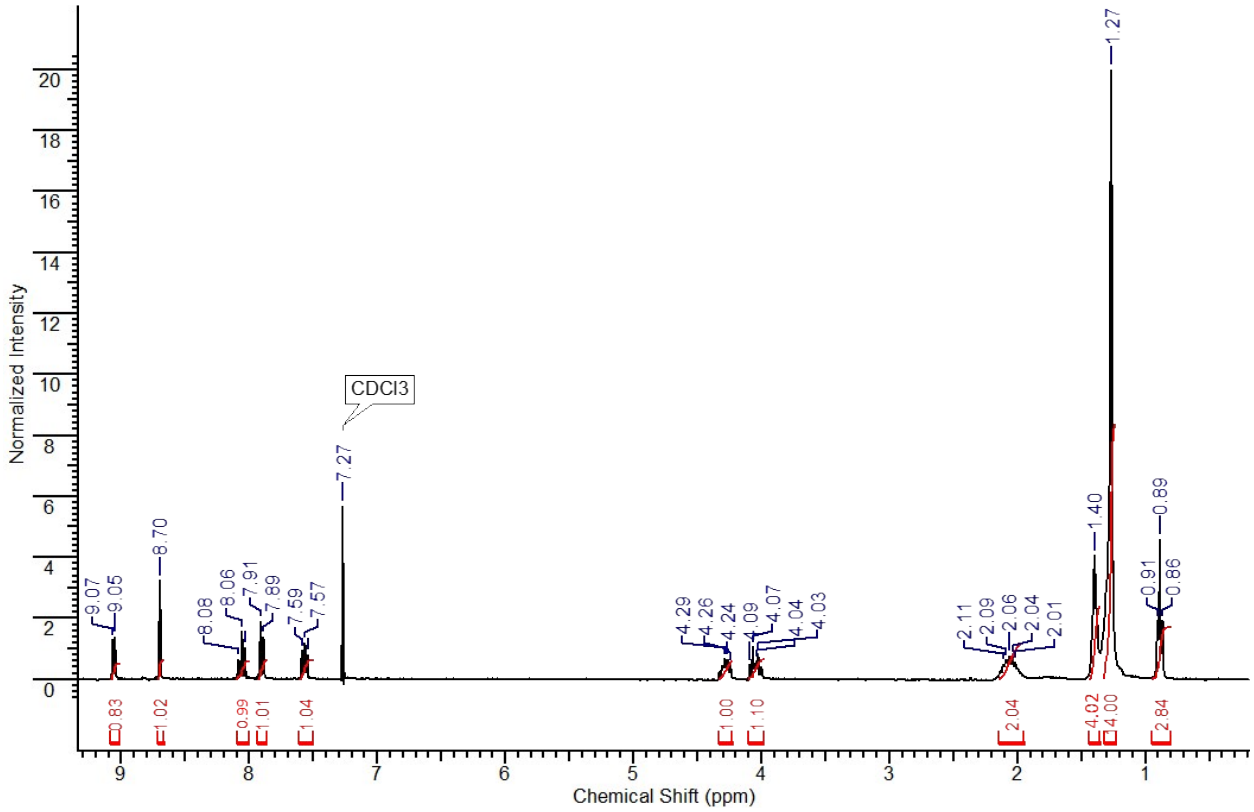


Figure S8: ^{1}H NMR (300 MHz) of **4b** in $CDCl_3$.

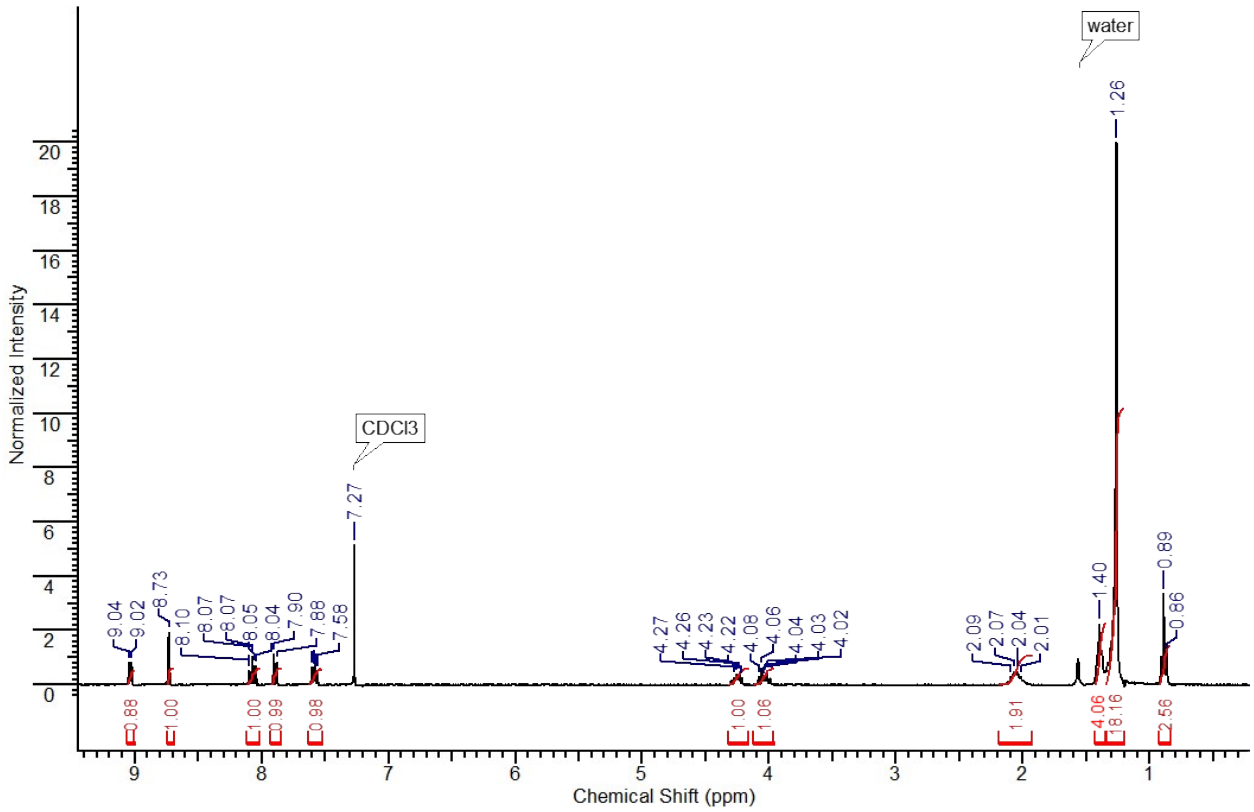


Figure S9: ^{1}H NMR (300 MHz) of **5a** in $CDCl_3$.

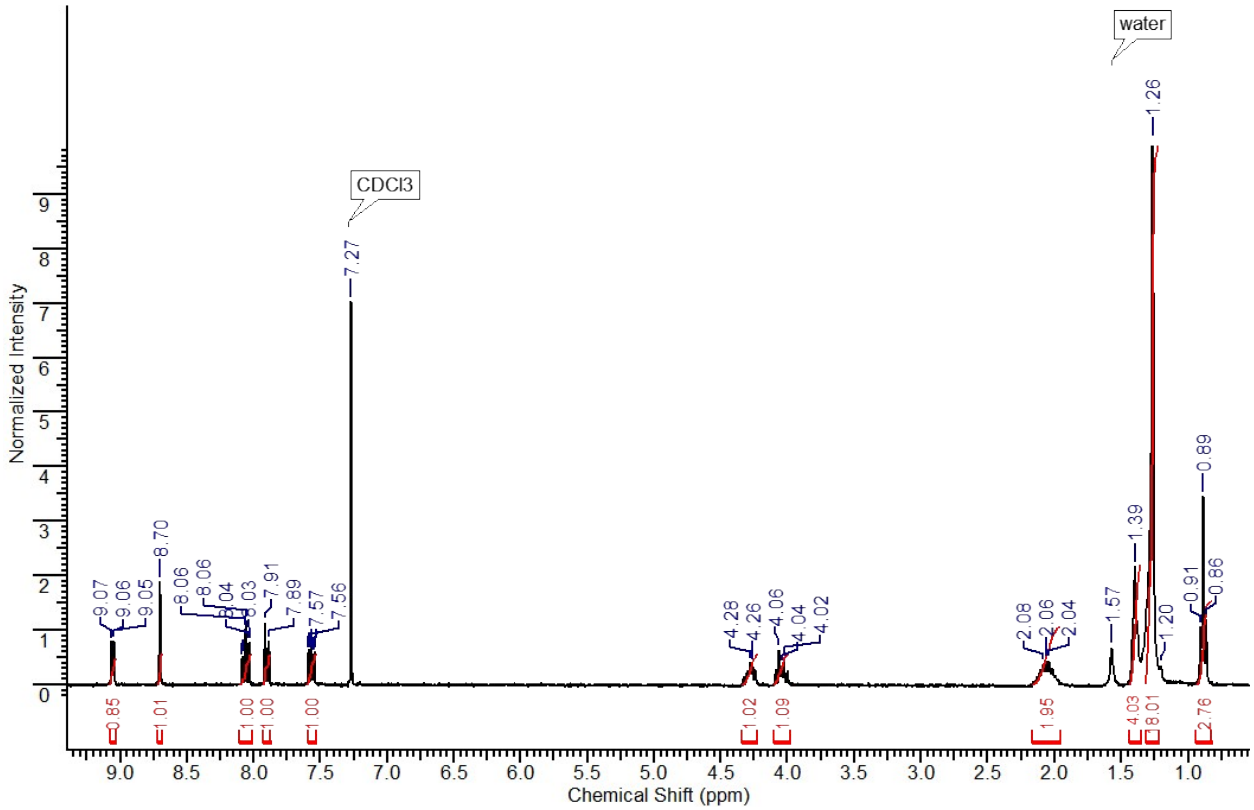


Figure S10: ^{1}H NMR (300 MHz) of **5b** in $CDCl_3$.

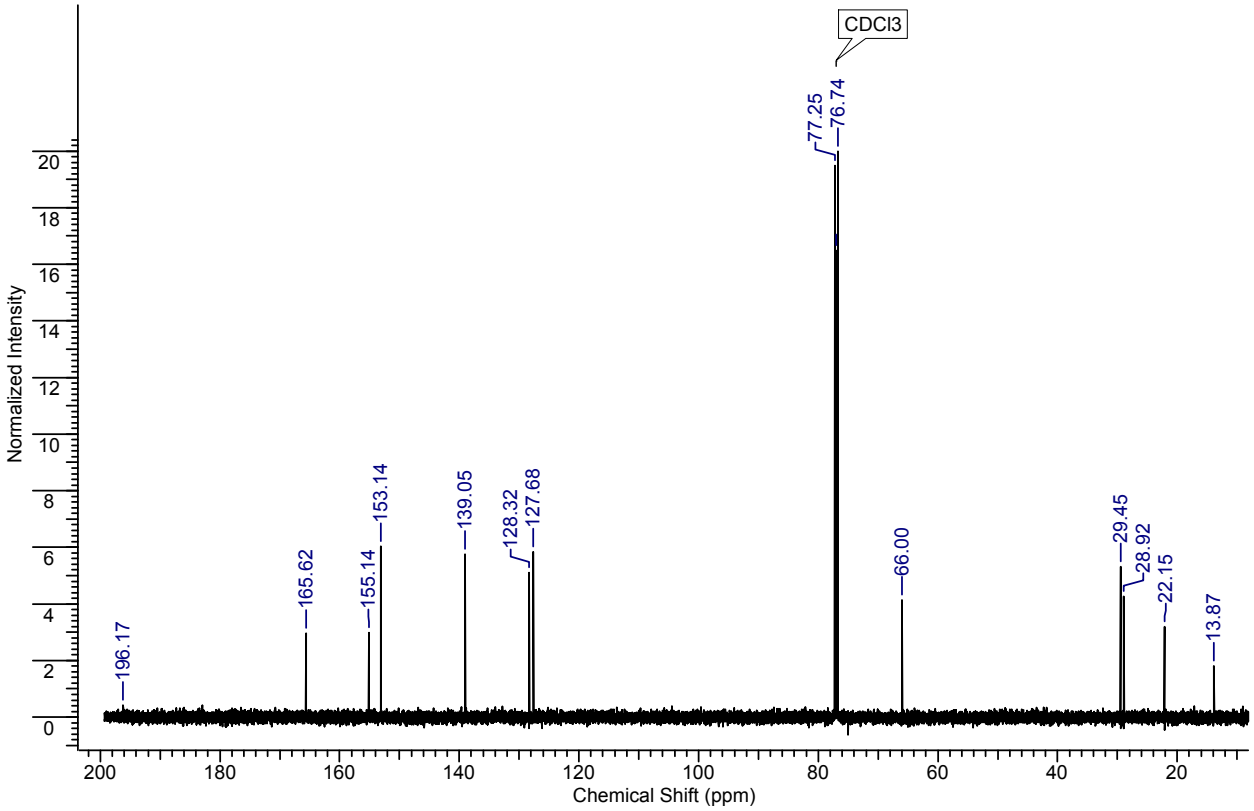


Figure S11: $^{13}C\{^{1}H\}$ NMR (125 MHz) of **1a** in $CDCl_3$.

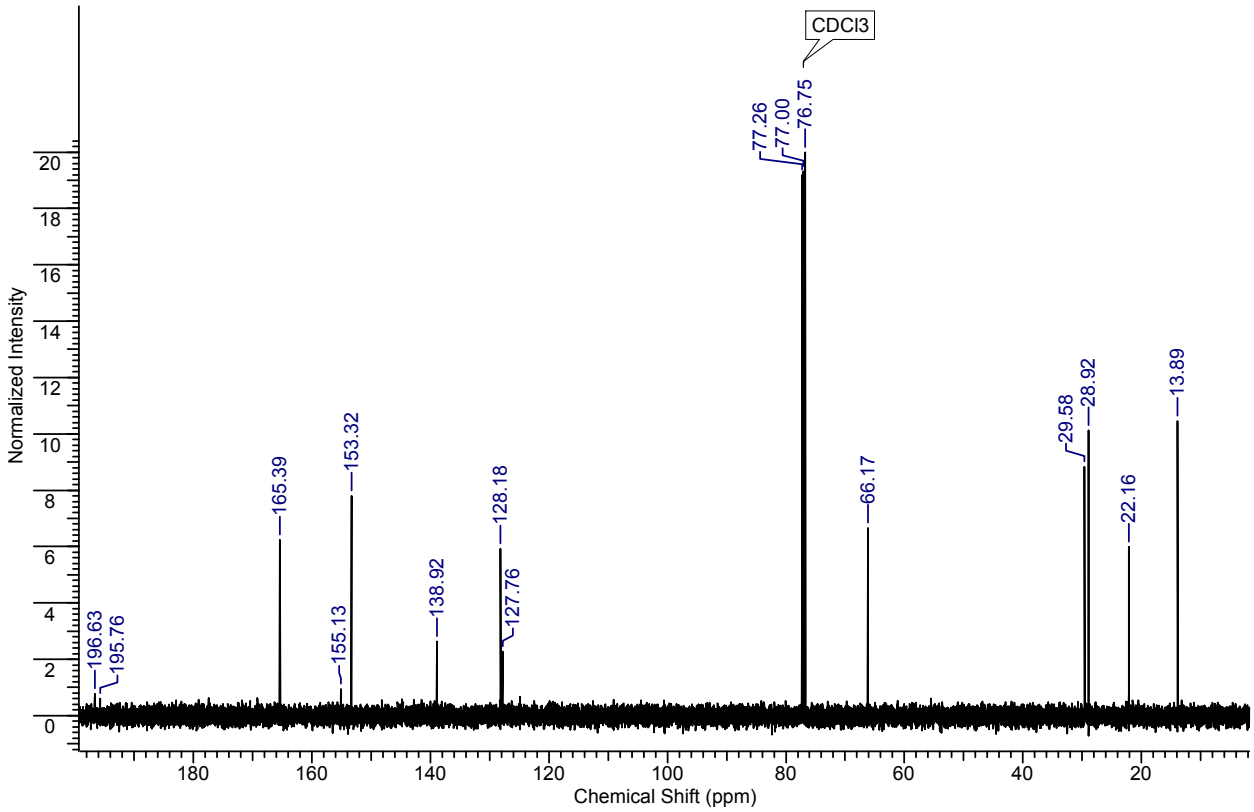


Figure S12: $^{13}C\{^{1}H\}$ NMR (125 MHz) of **1b** in $CDCl_3$.

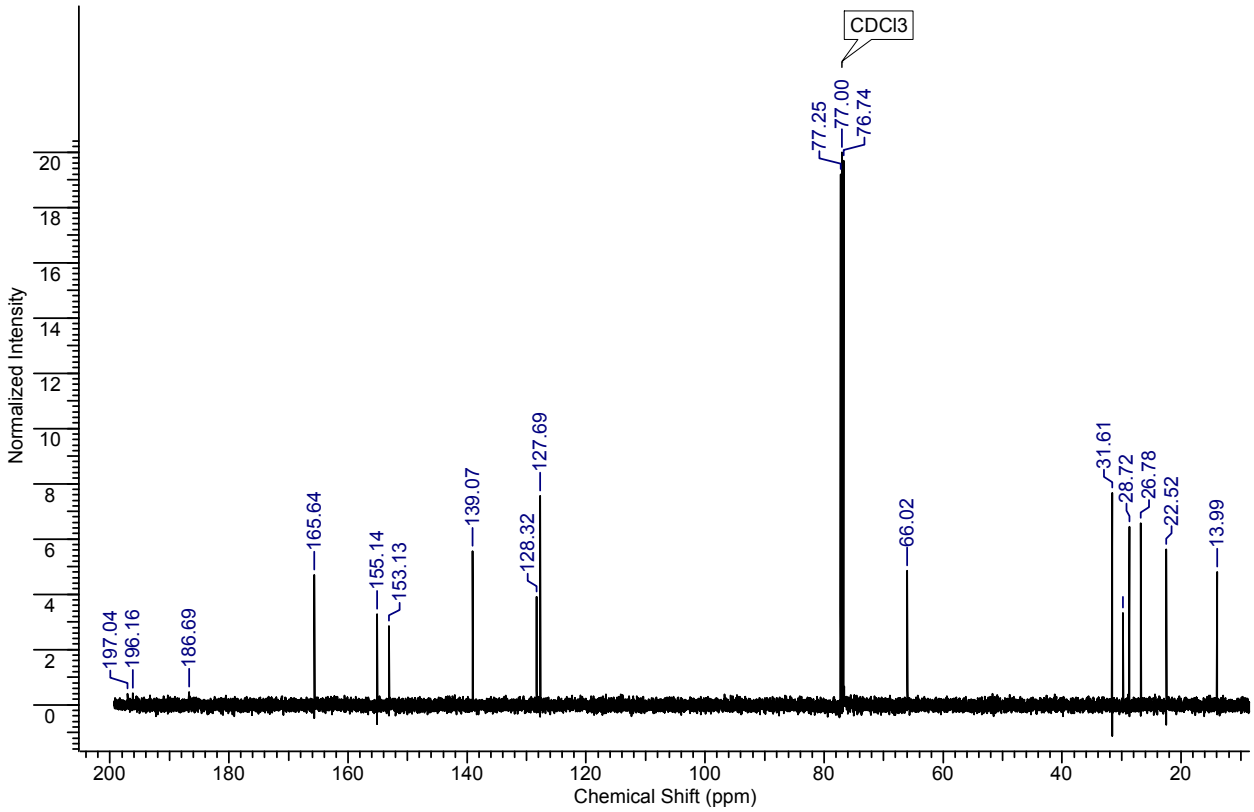


Figure S13: $^{13}C\{^{1}H\}$ NMR (125 MHz) of **2a** in $CDCl_3$.

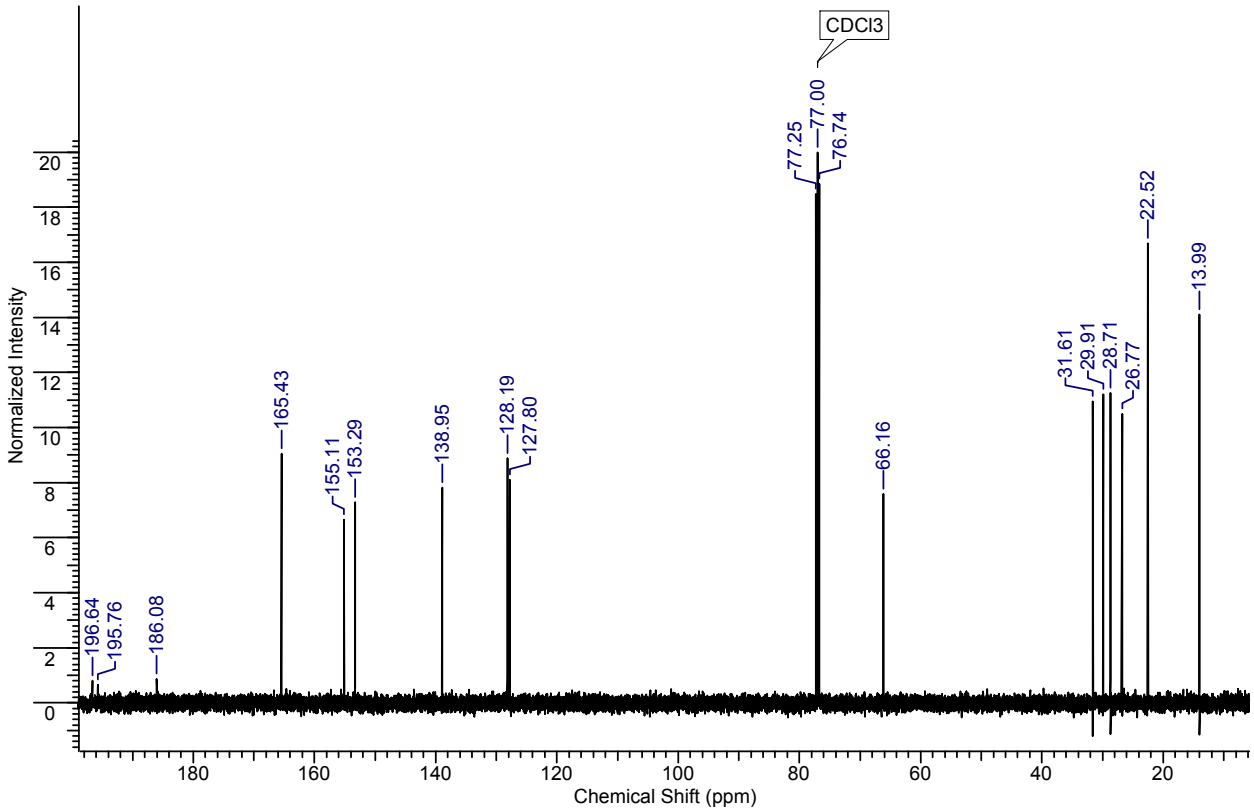


Figure S14: $^{13}C\{^{1}H\}$ NMR (125 MHz) of **2b** in $CDCl_3$.

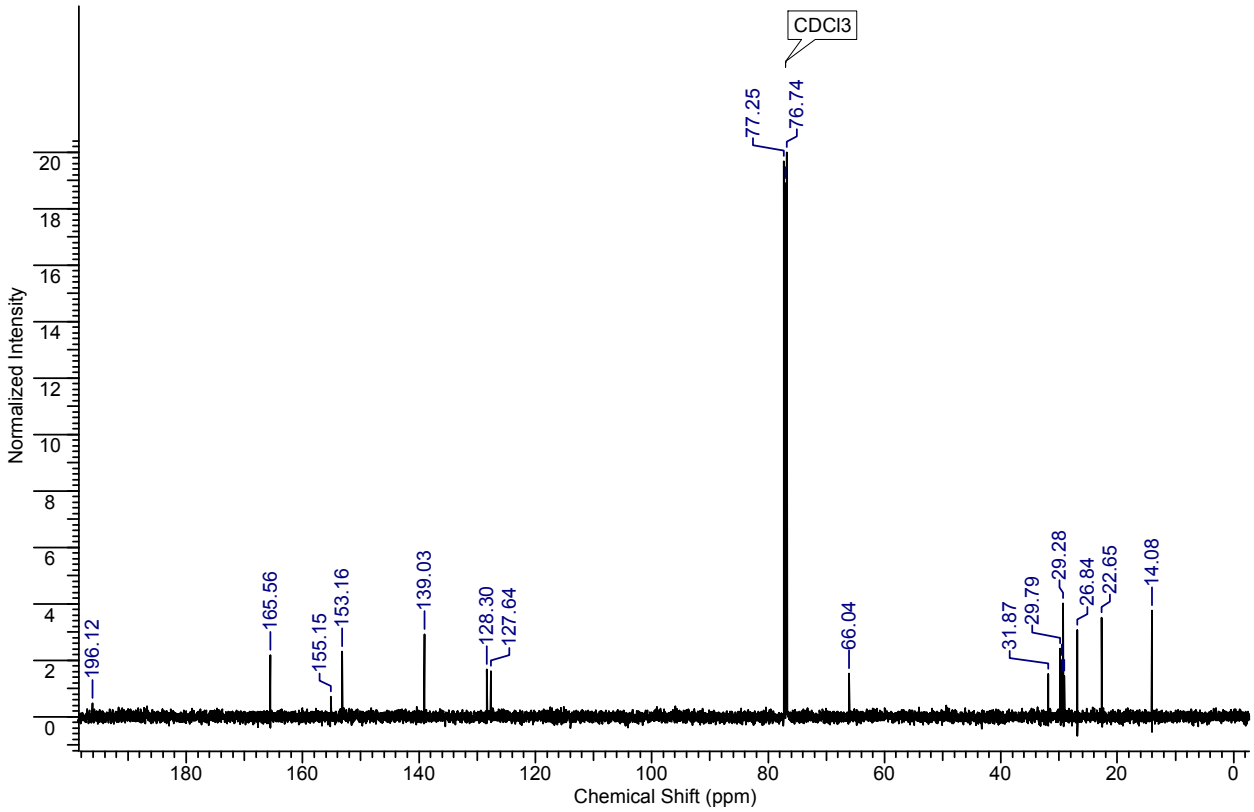


Figure S15: $^{13}C\{^{1}H\}$ NMR (125 MHz) of **3a** in $CDCl_3$.

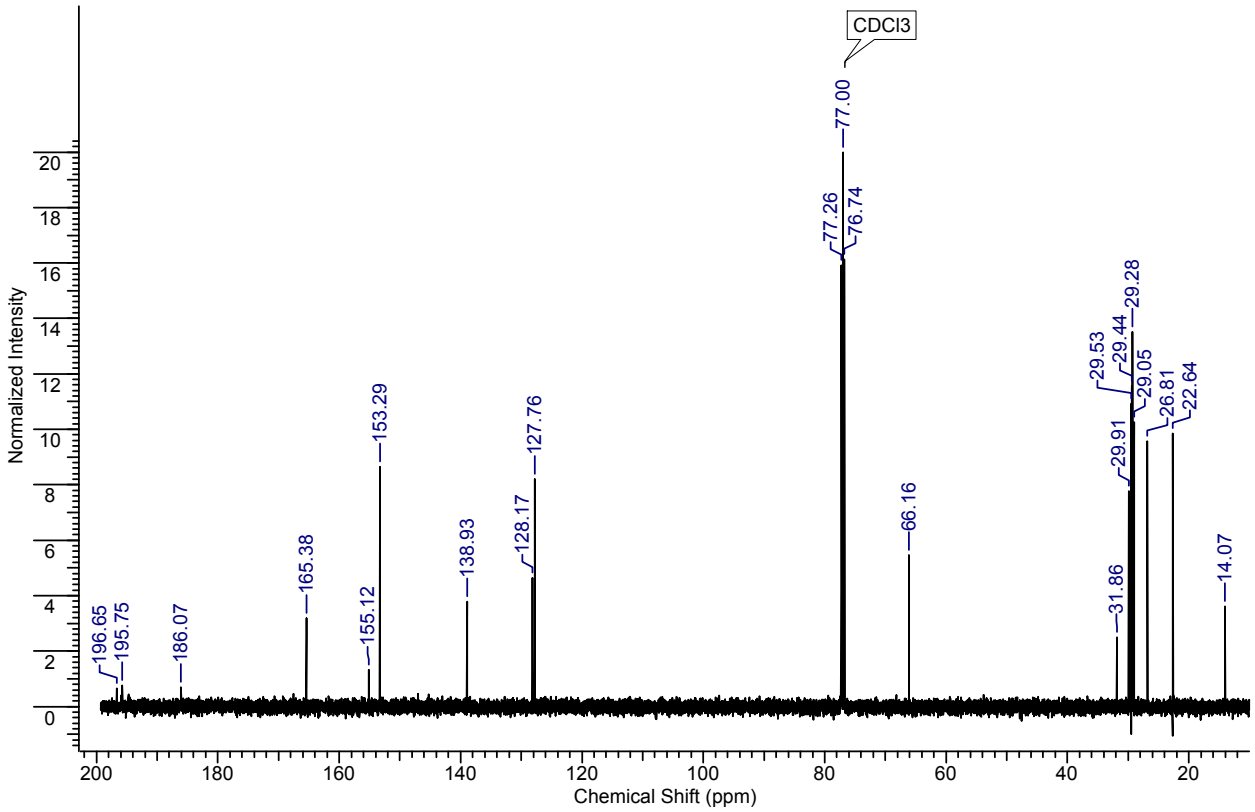


Figure S16: $^{13}C\{^{1}H\}$ NMR (125 MHz) of **3b** in $CDCl_3$.

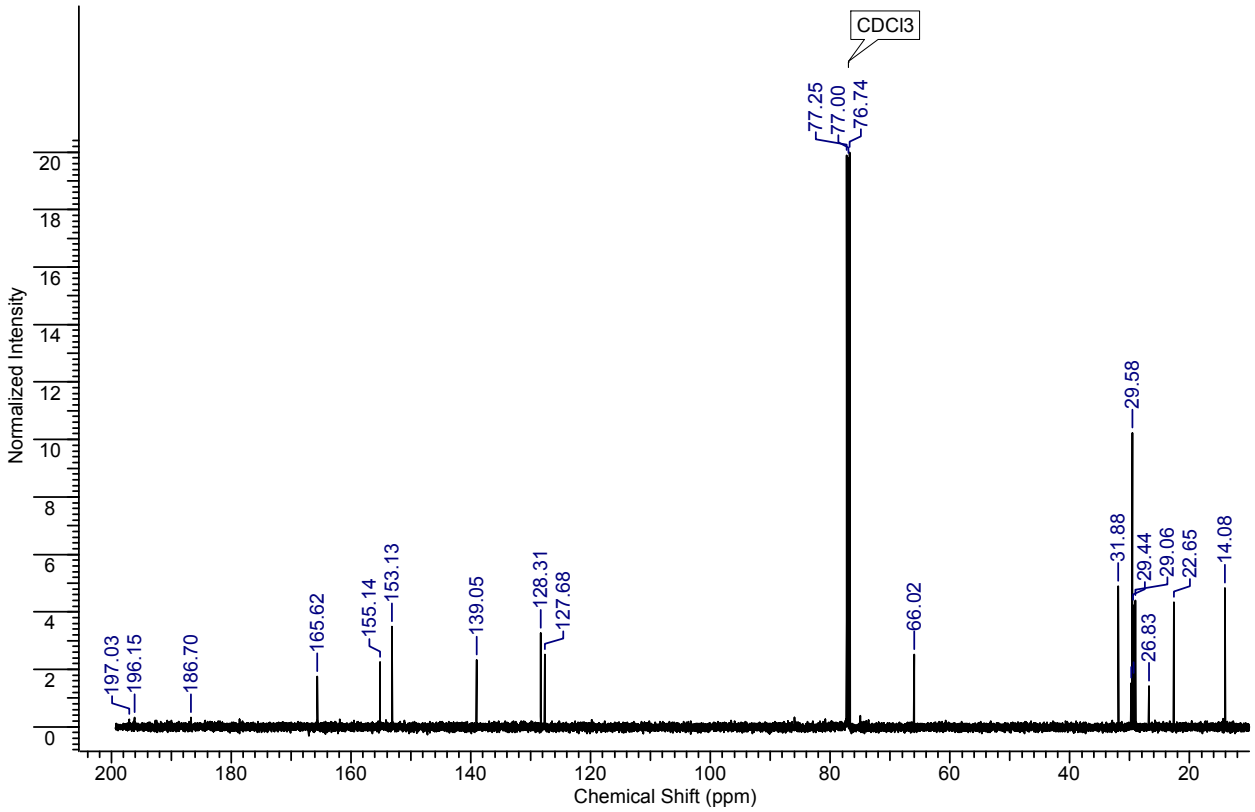


Figure S17: $^{13}C\{^{1}H\}$ NMR (125 MHz) of **4a** in $CDCl_3$.

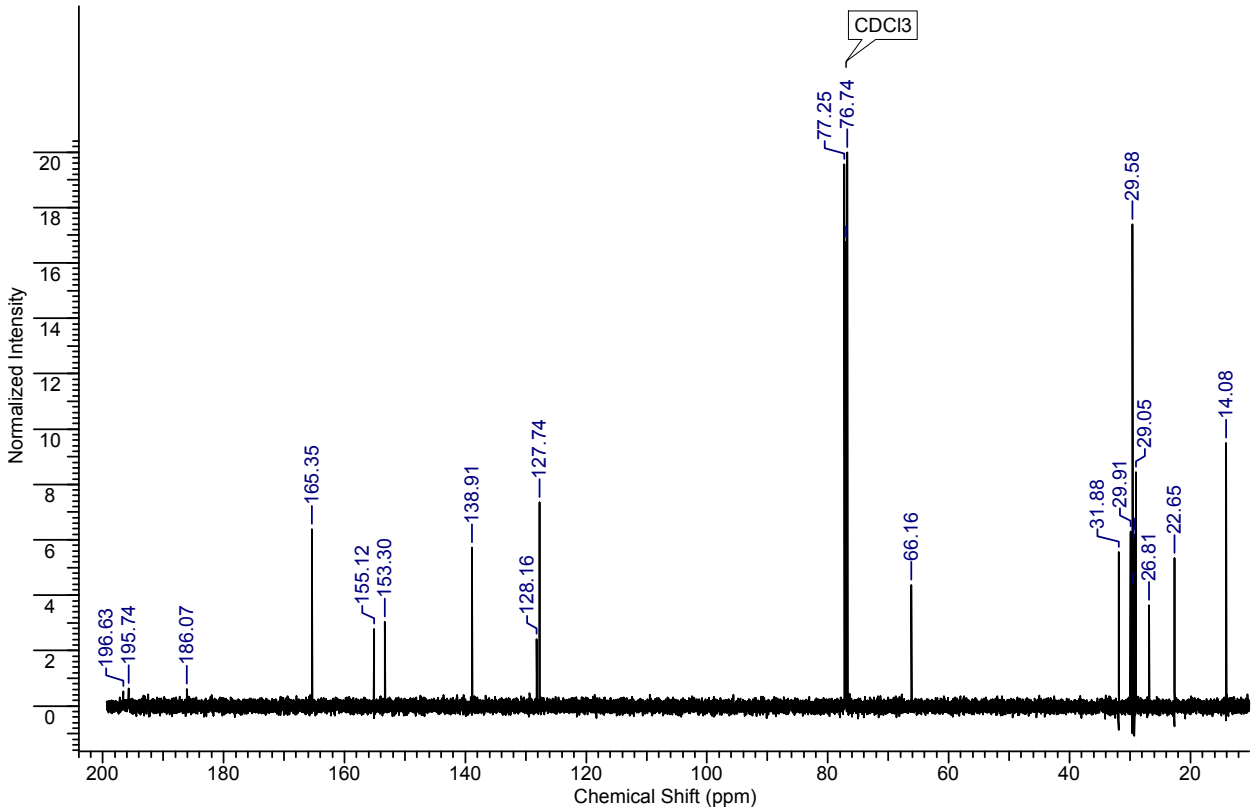


Figure S18: $^{13}C\{^{1}H\}$ NMR (125 MHz) of **4b** in $CDCl_3$.

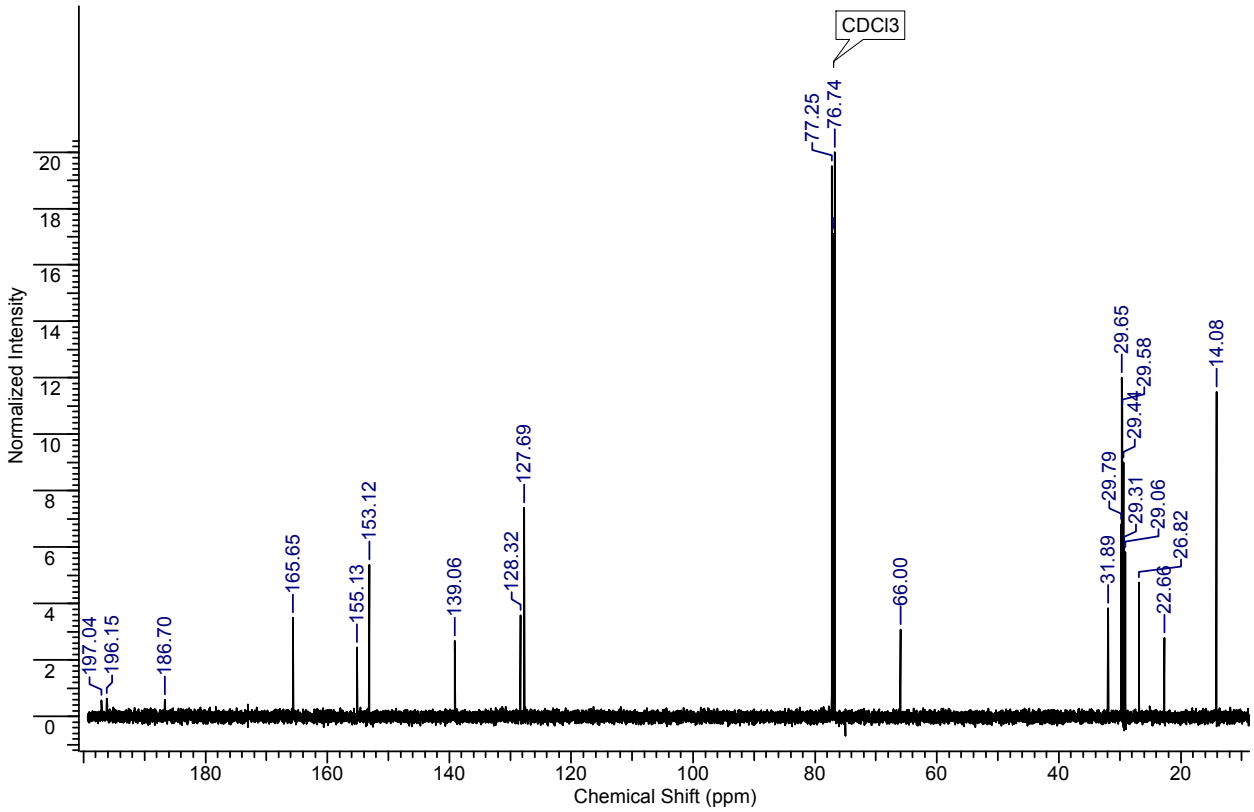


Figure S19: $^{13}C\{^{1}H\}$ NMR (125 MHz) of **5a** in $CDCl_3$.

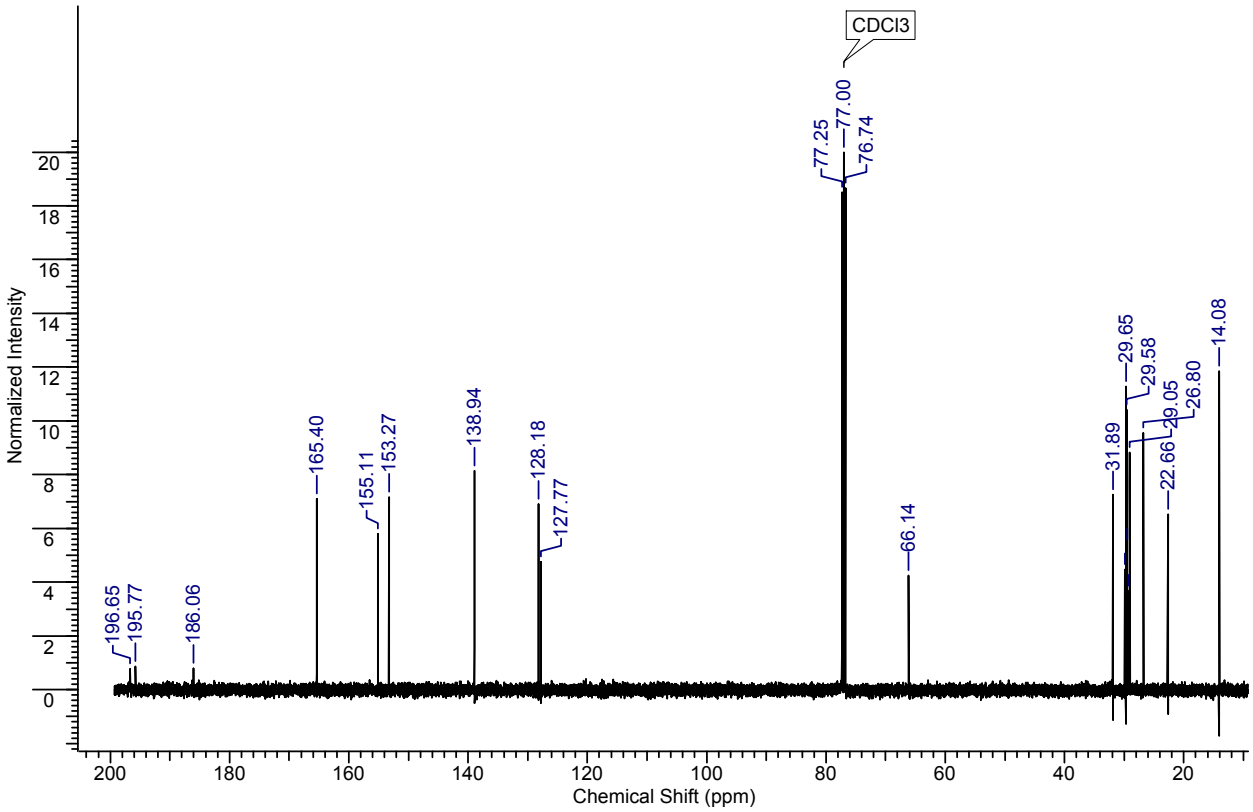


Figure S20: $^{13}C\{^{1}H\}$ NMR (125 MHz) of **5b** in $CDCl_3$.

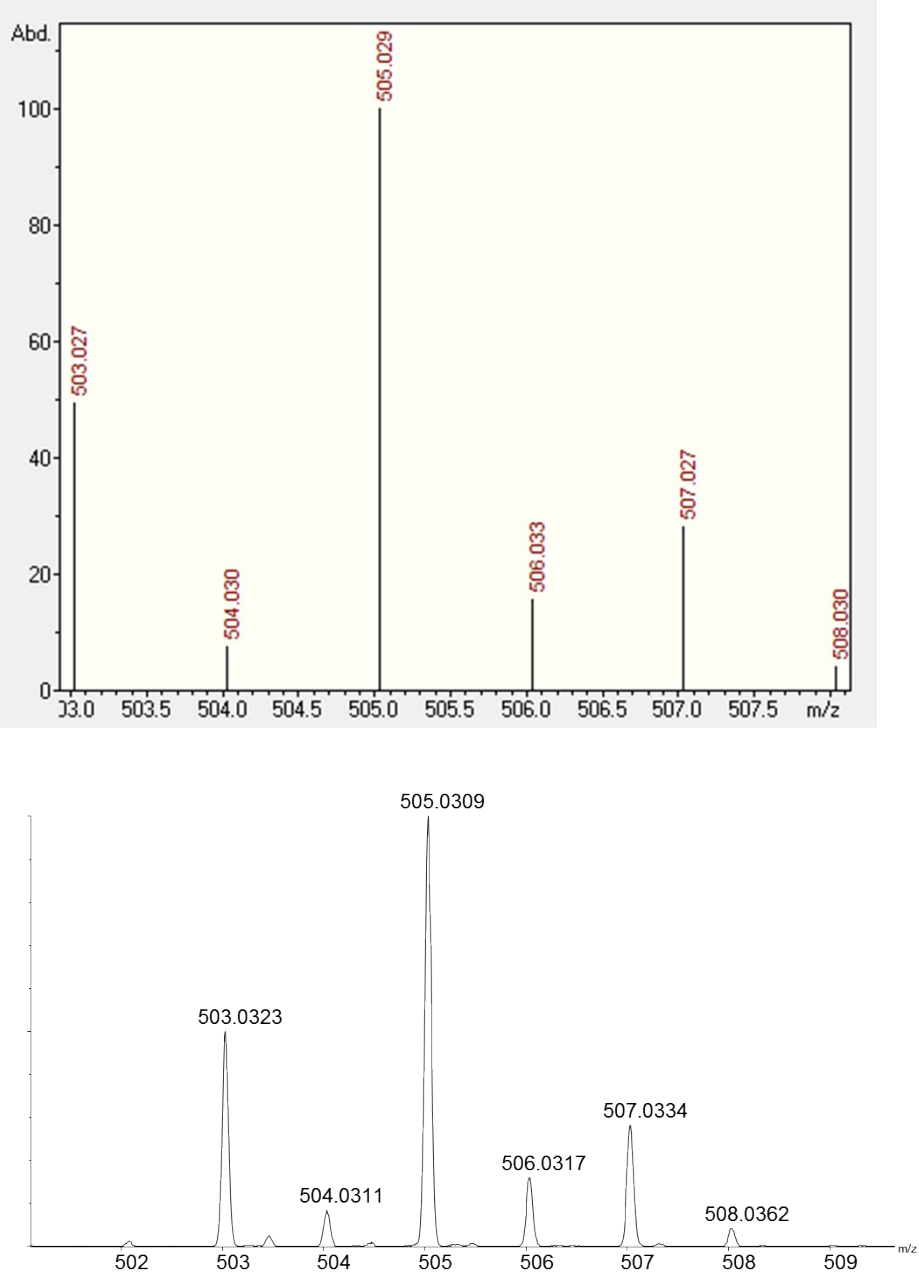


Figure S21: High-resolution ESI mass spectra of **1a**. Top: calculated spectrum. Bottom: experimental spectrum.

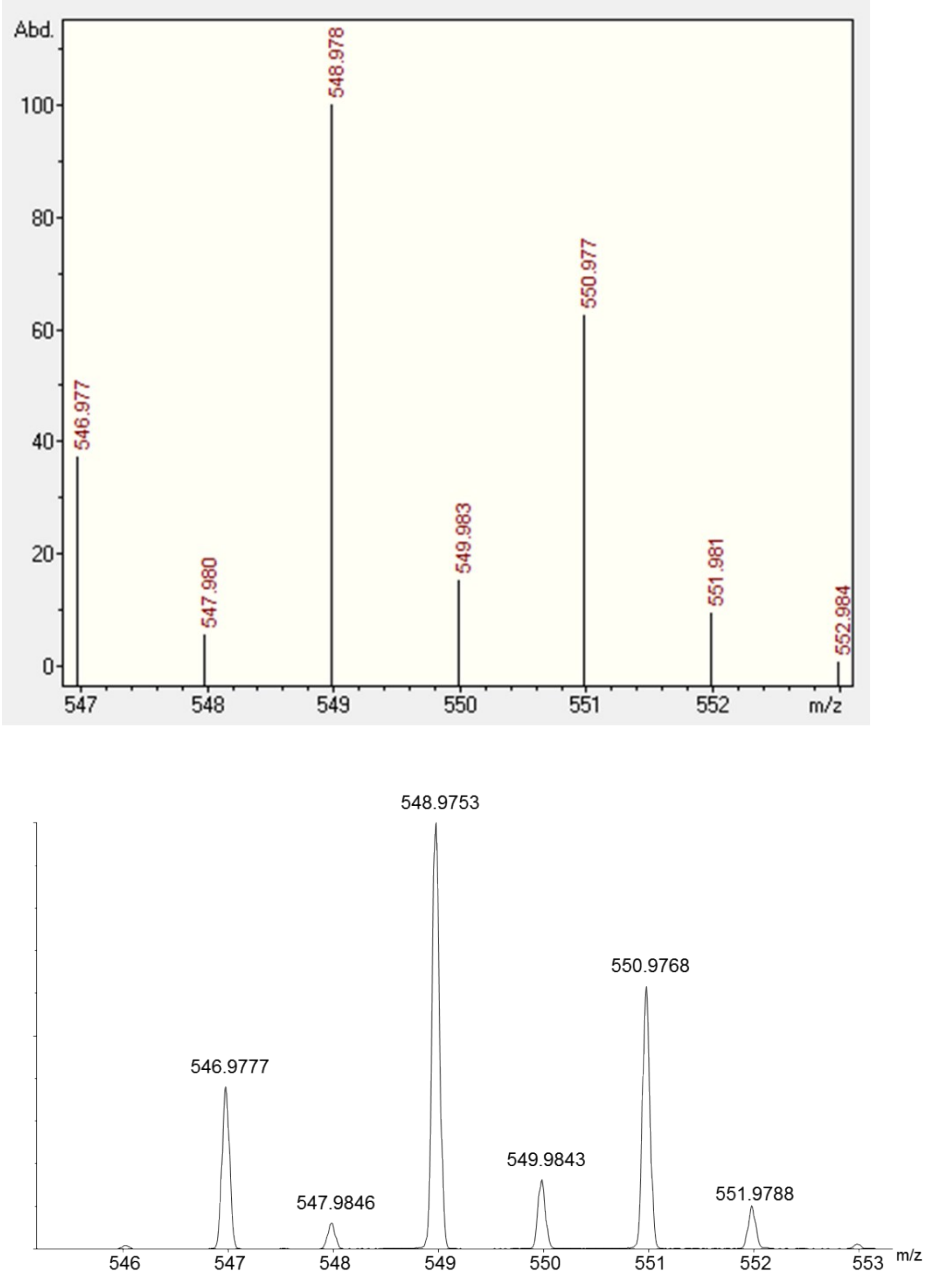


Figure S22: High-resolution ESI mass spectra of **1b**. Top: calculated spectrum. Bottom: experimental spectrum.

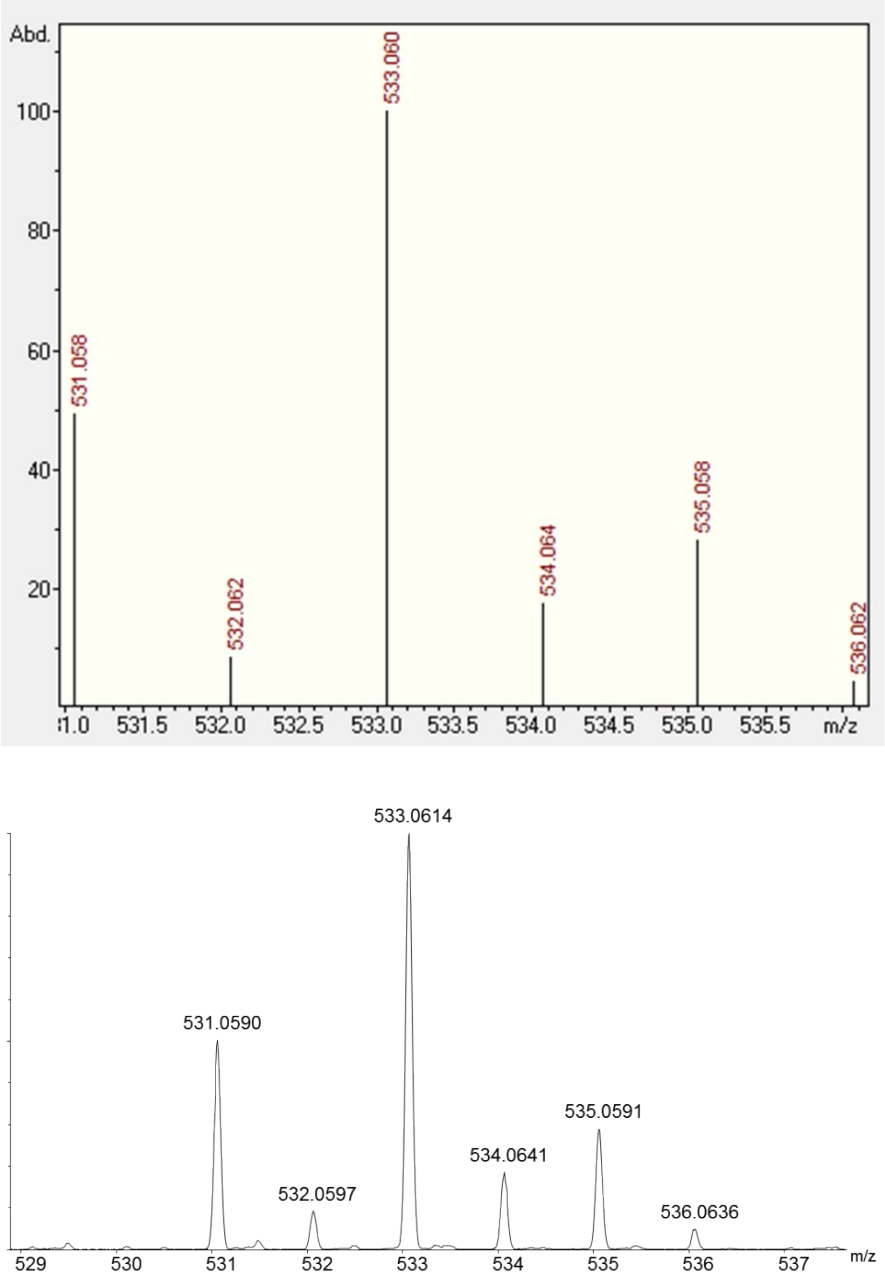


Figure S23: High-resolution ESI mass spectra of **2a**. Top: calculated spectrum. Bottom: experimental spectrum.

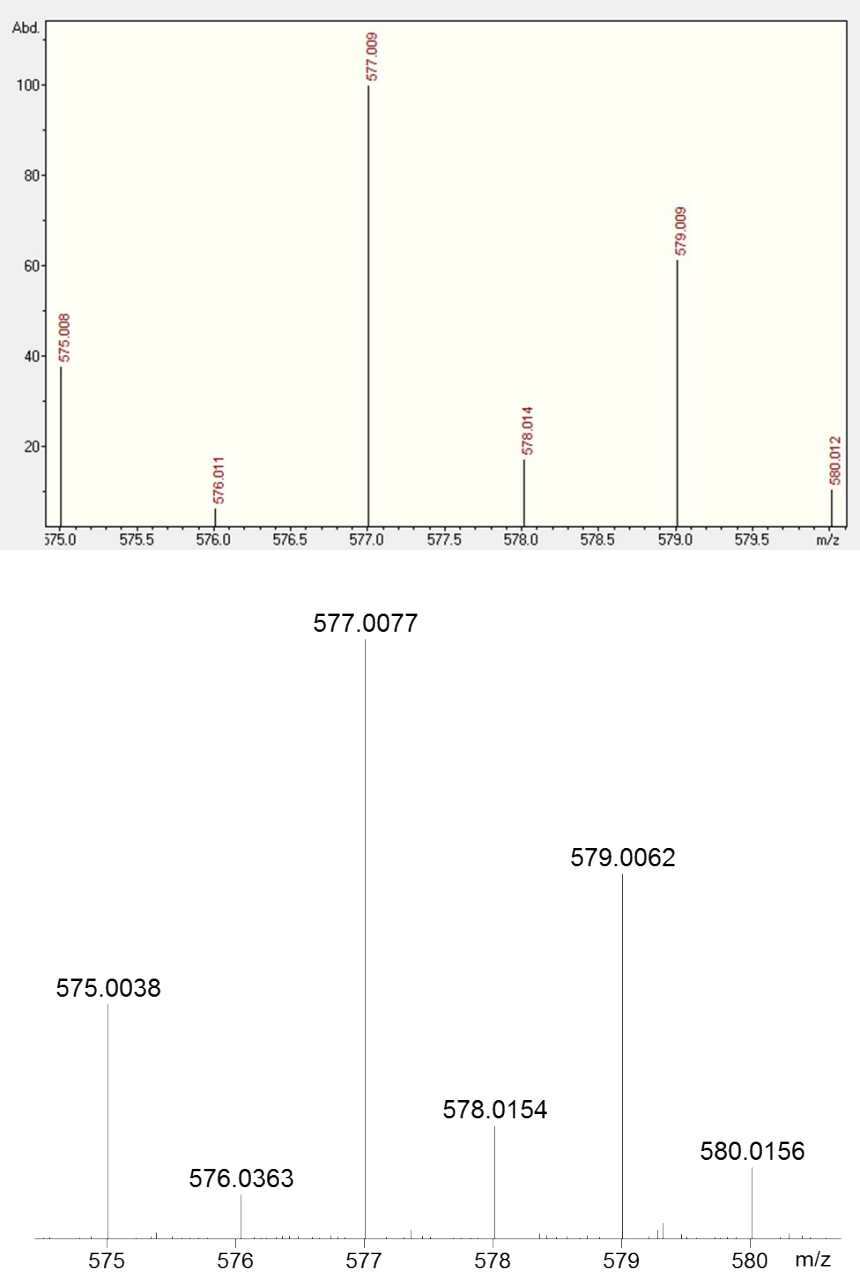


Figure S24: High-resolution ESI mass spectra of **2b**. Top: calculated spectrum. Bottom: experimental spectrum.

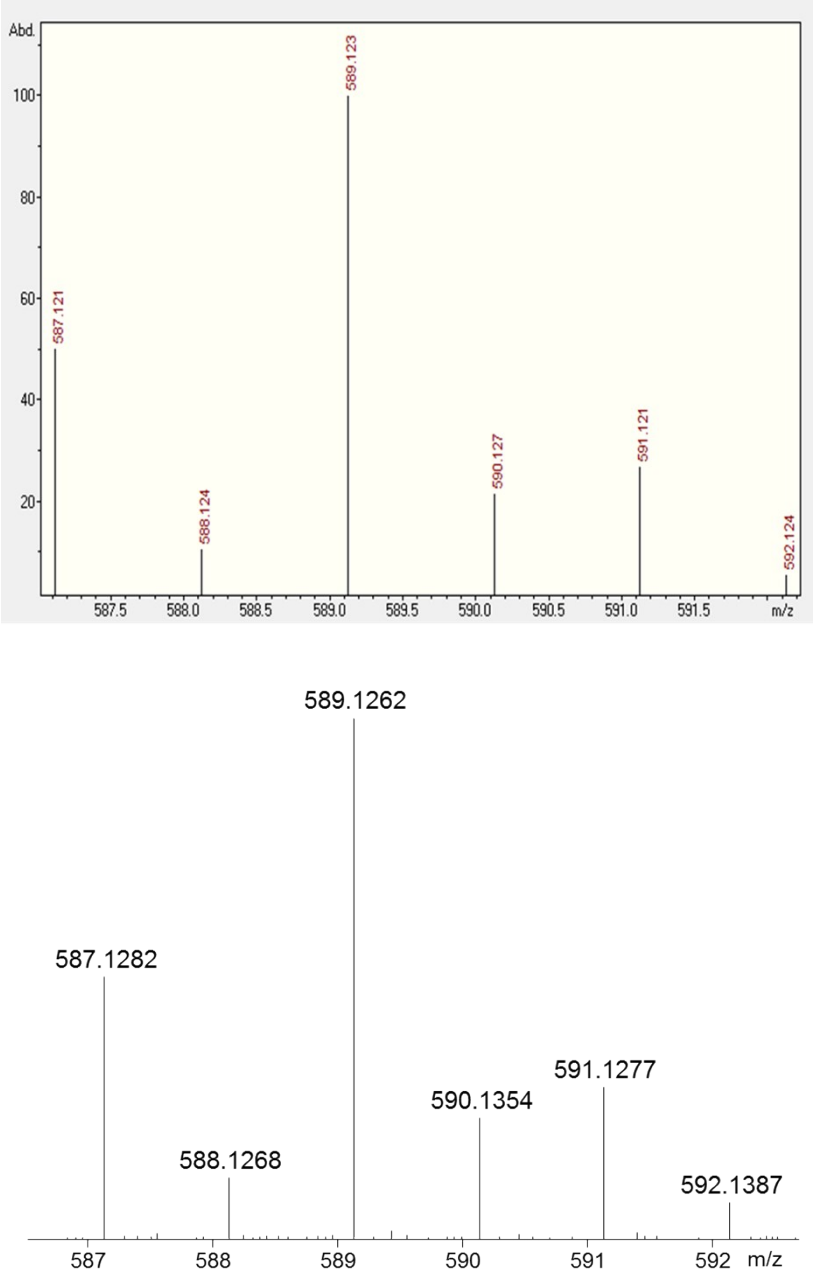


Figure S25: High-resolution ESI mass spectra of **3a**. Top: calculated spectrum. Bottom: experimental spectrum.

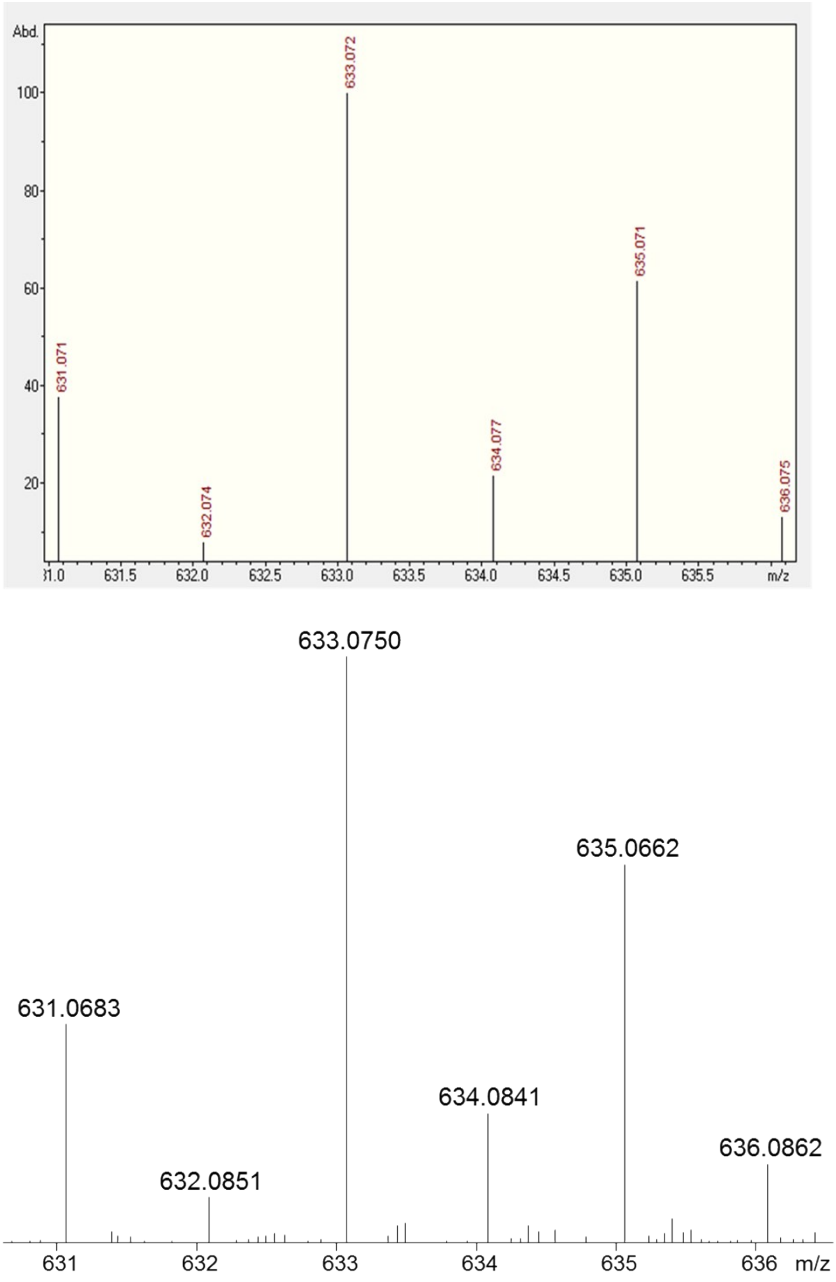


Figure S26: High-resolution ESI mass spectra of **3b**. Top: calculated spectrum. Bottom: experimental spectrum.

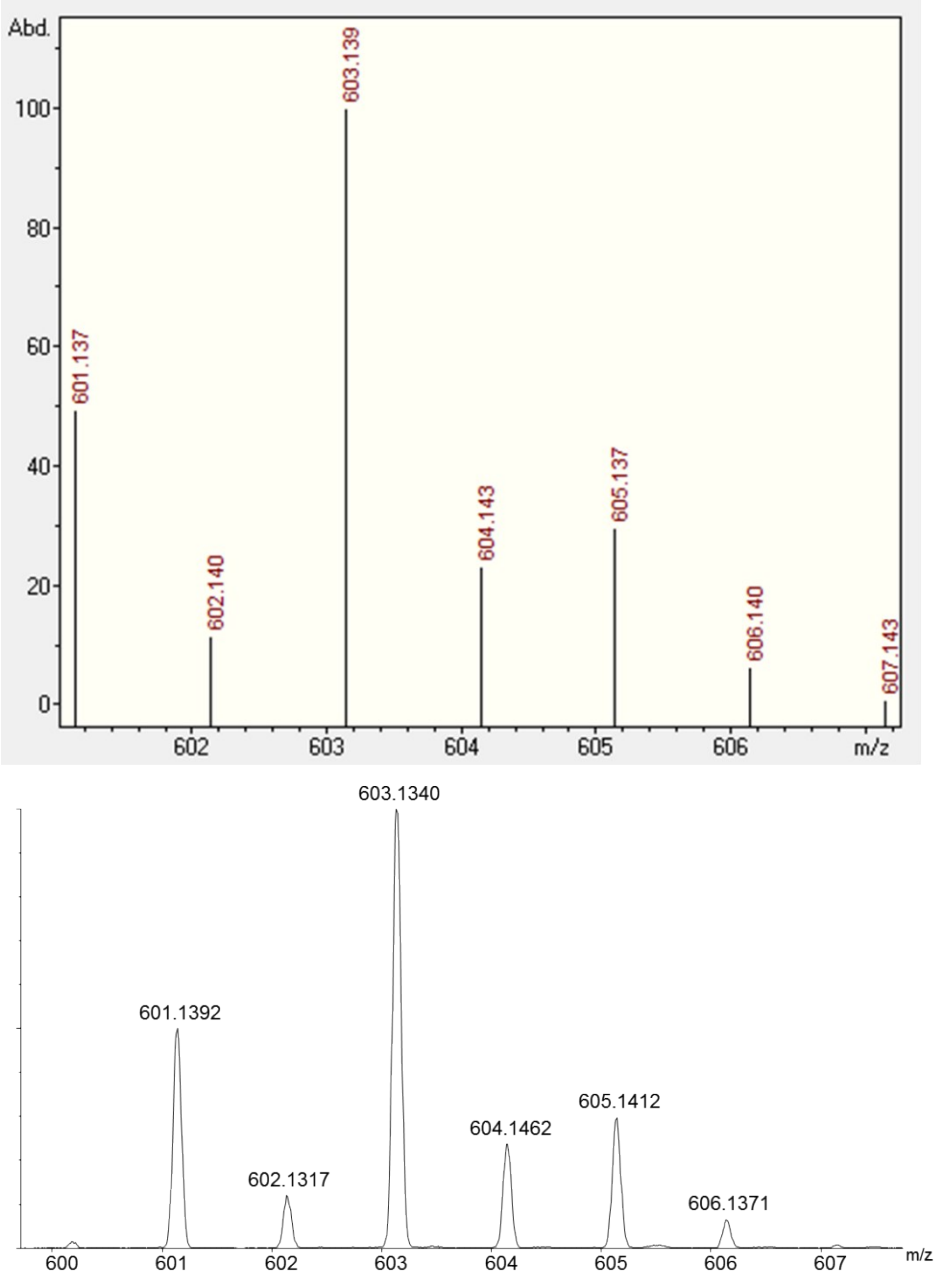


Figure S27: High-resolution ESI mass spectra of **4a**. Top: calculated spectrum. Bottom: experimental spectrum.

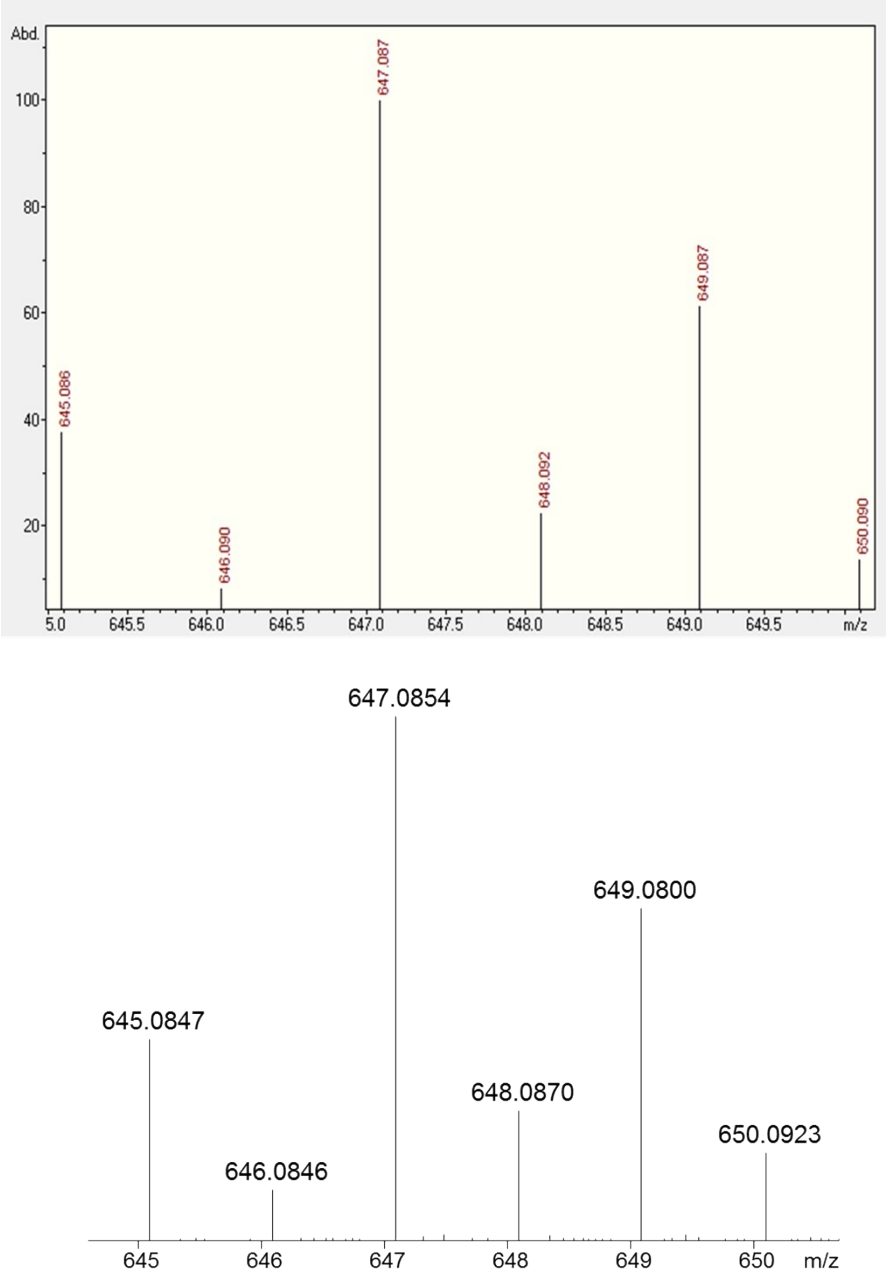
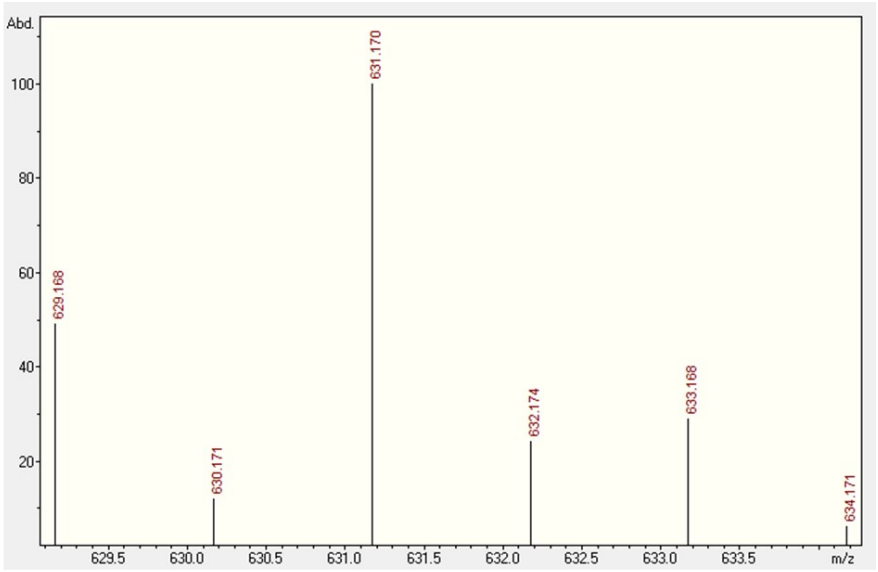


Figure S28: High-resolution ESI mass spectra of **4b**. Top: calculated spectrum. Bottom: experimental spectrum.



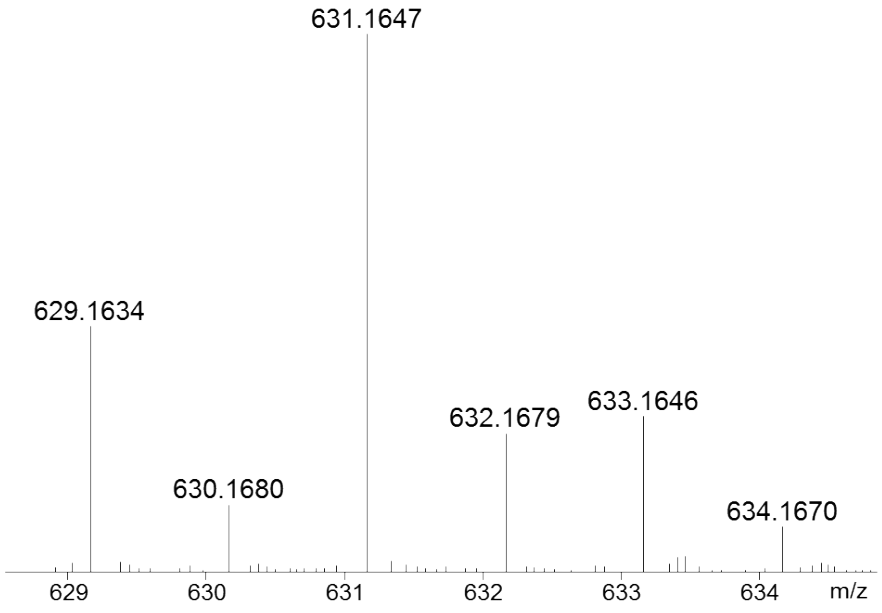


Figure S29: High-resolution ESI mass spectra of **5a**. Top: calculated spectrum. Bottom: experimental spectrum.

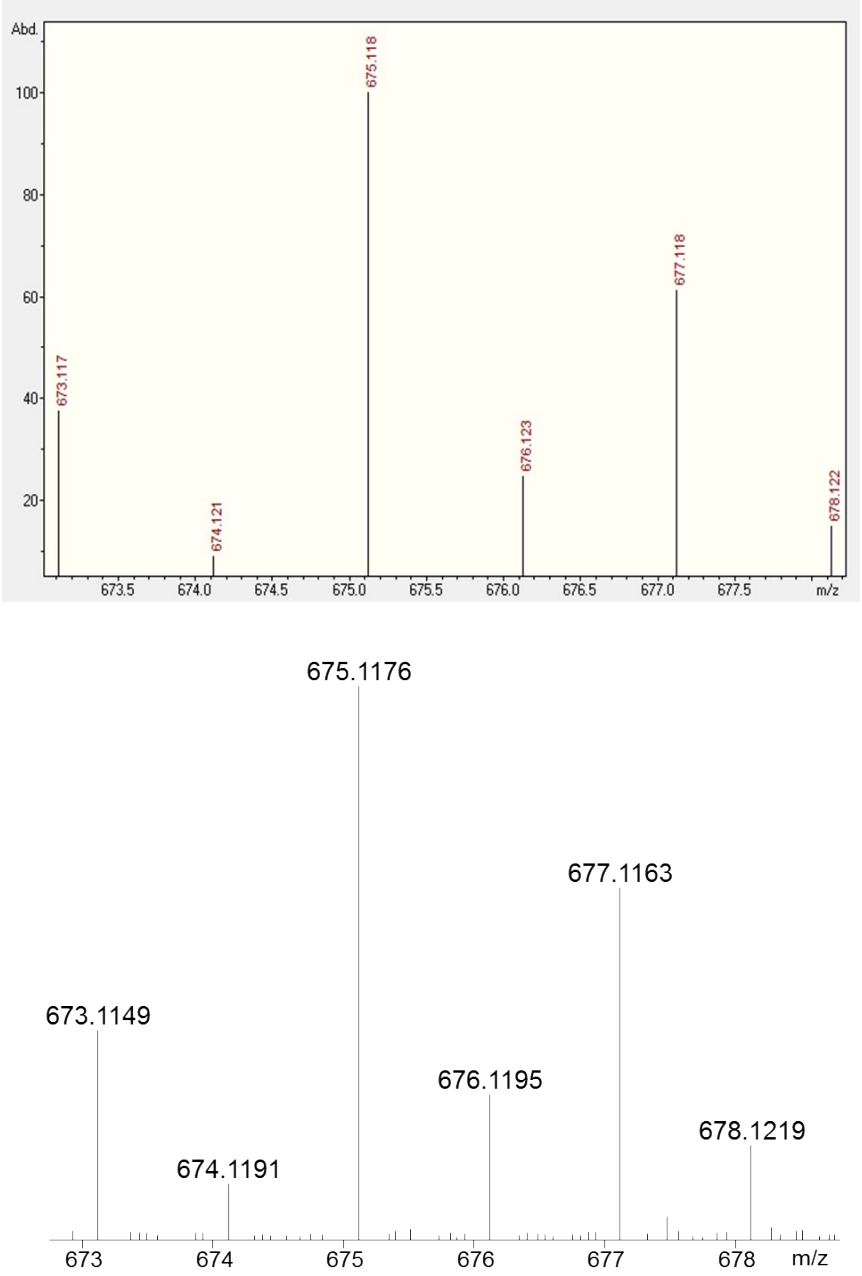


Figure S30: High-resolution ESI mass spectra of **5b**. Top: calculated spectrum. Bottom: experimental spectrum.

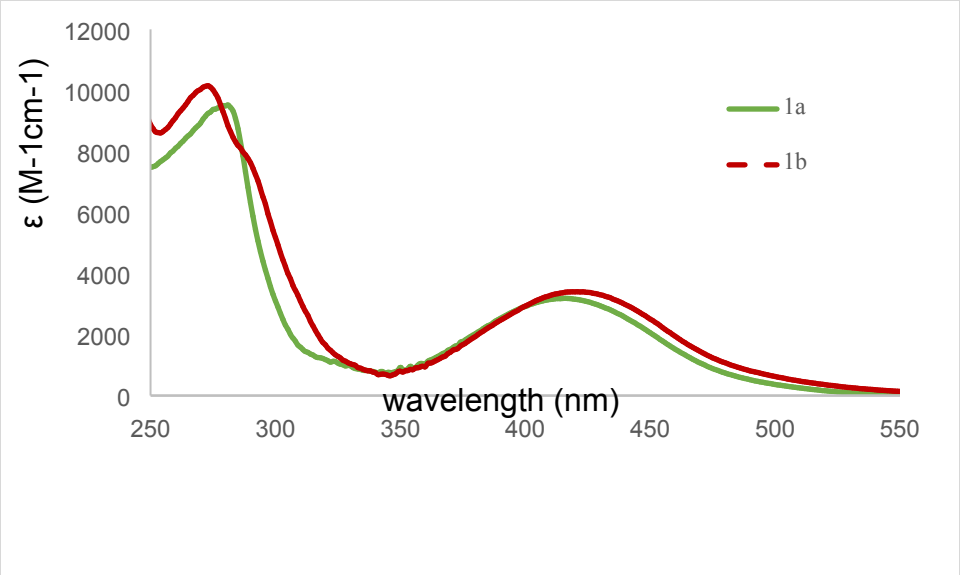


Figure S31: UV-visible spectra for compounds **1a** and **1b** in DCM.

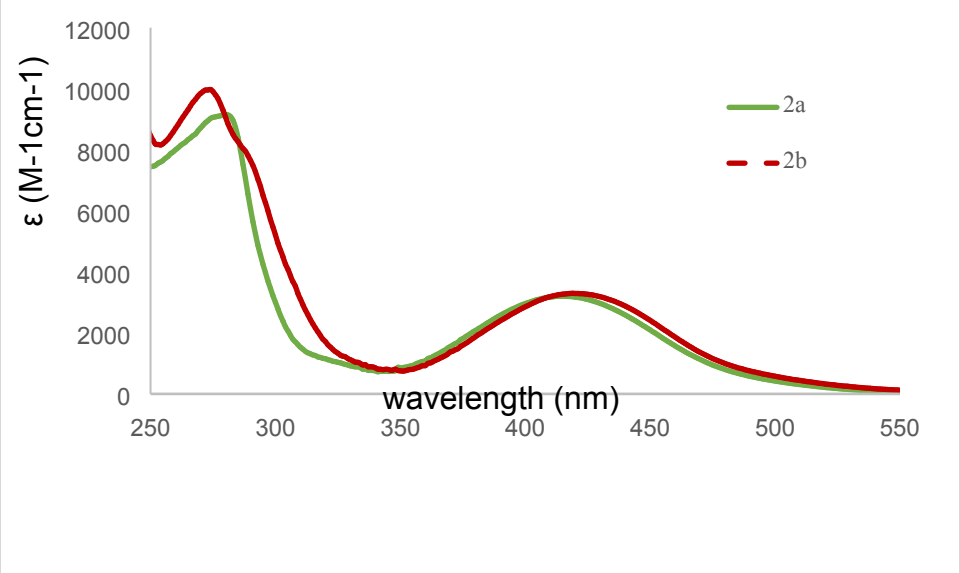


Figure S32: UV-visible spectra for compounds **2a** and **2b** in DCM.

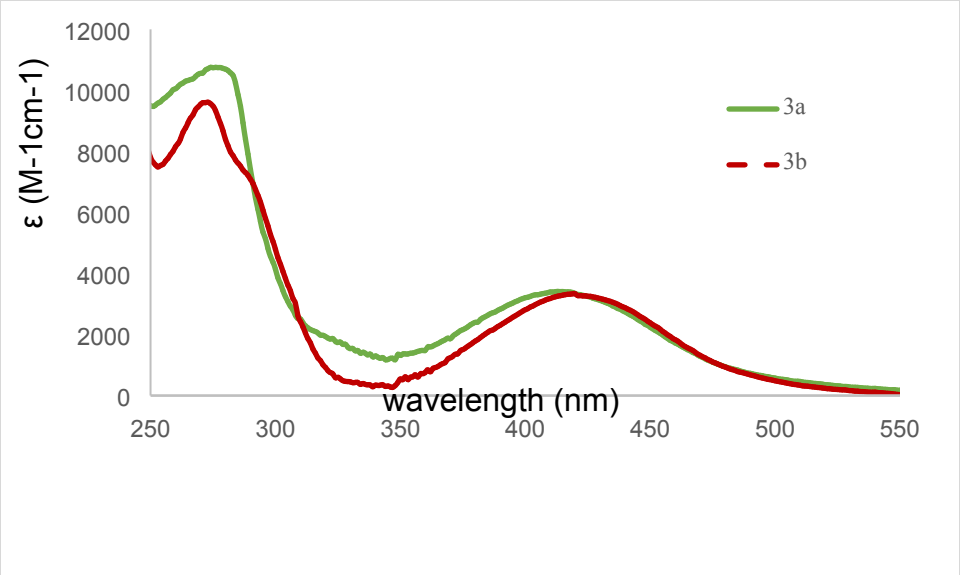


Figure S33: UV-visible spectra for compounds **3a** and **3b** in DCM.

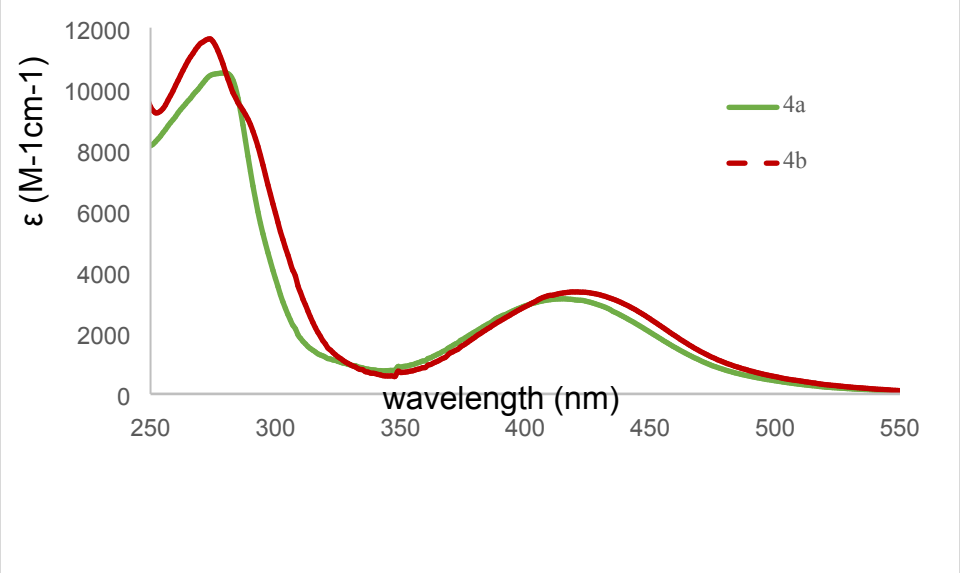


Figure S34: UV-visible spectra for compounds **4a** and **4b** in DCM.

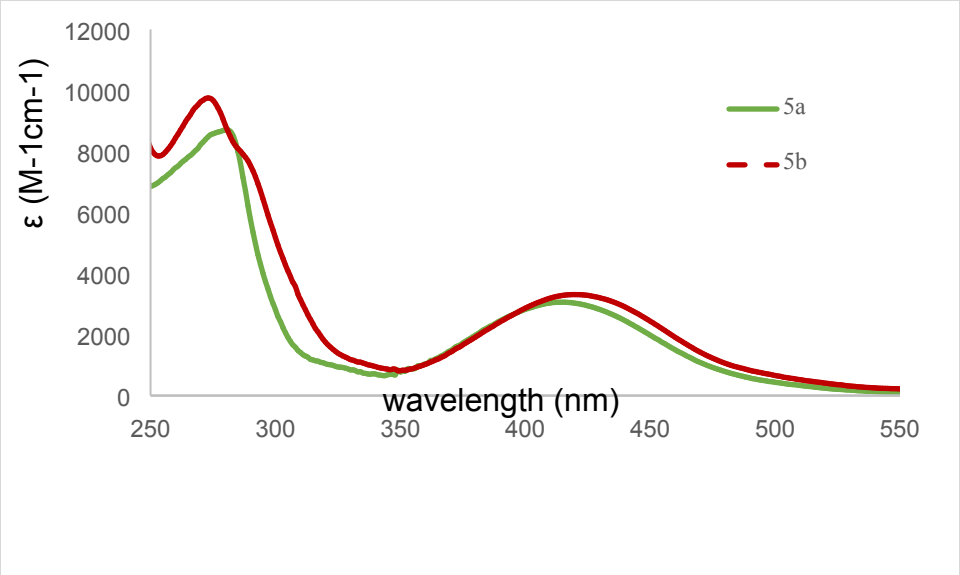


Figure S35: UV-visible spectra for compounds **5a** and **5b** in DCM.

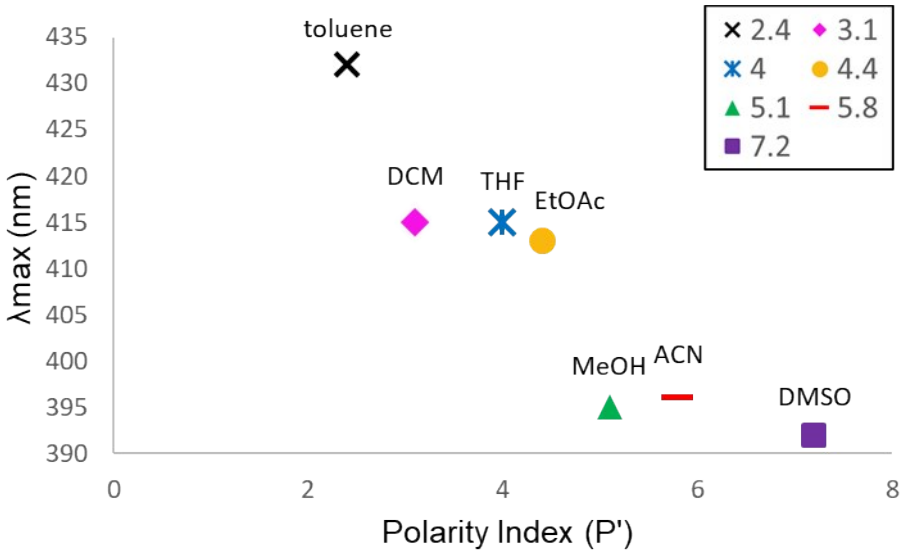


Figure S36: Solvent polarity index (*P'*) versus λ_{max} for **1a**.

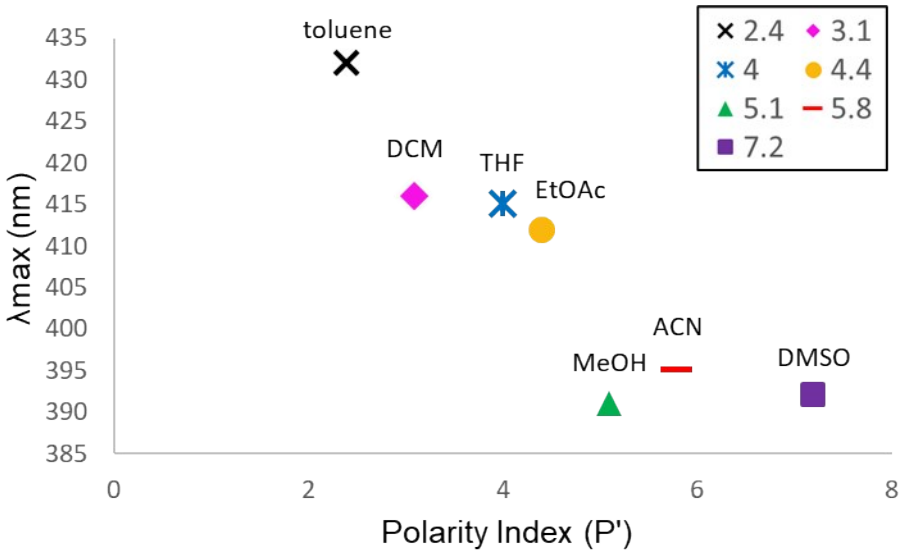


Figure S37: Solvent polarity index (*P'*) versus λ_{max} for **2a**.

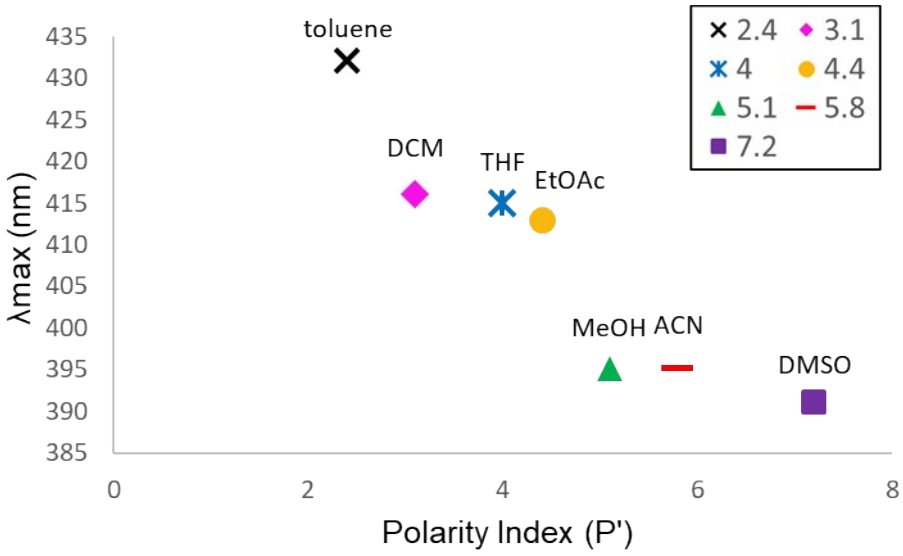


Figure S38: Solvent polarity index (*P'*) versus λ_{max} for **3a**.

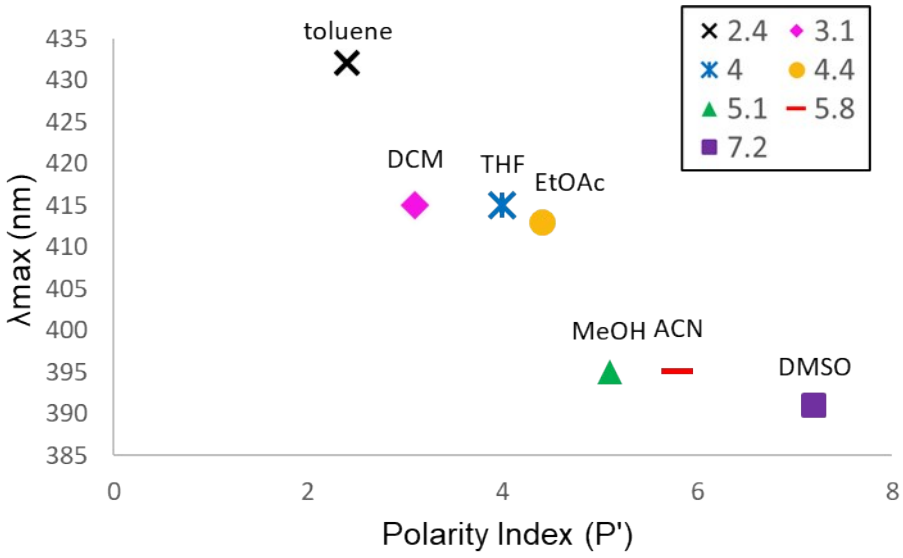


Figure S39: Solvent polarity index (*P'*) versus λ_{max} for **4a**.

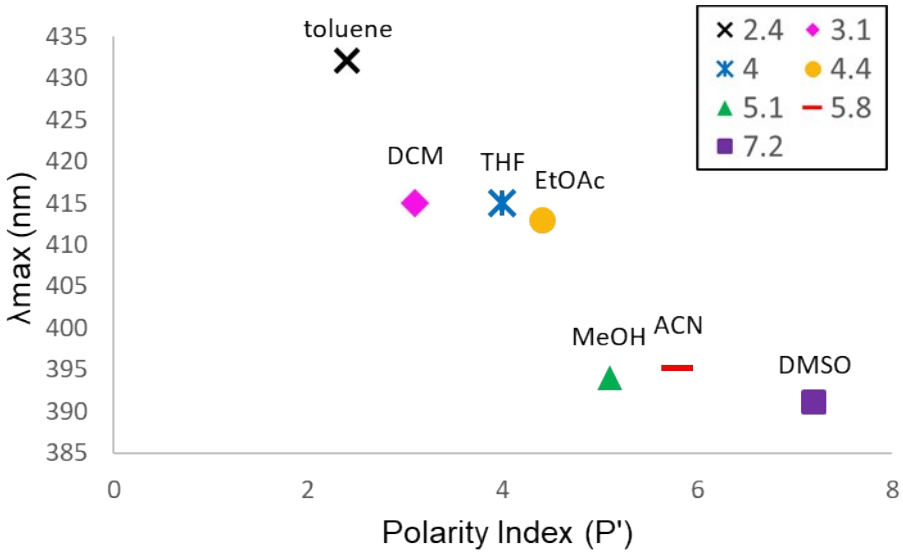


Figure S40: Solvent polarity index (*P'*) versus λ_{max} for **5a**.

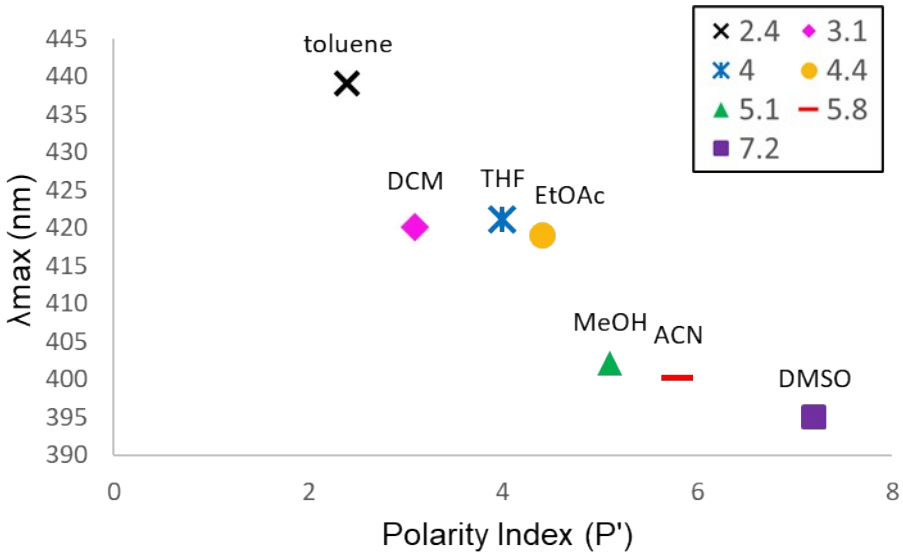


Figure S41: Solvent polarity index (*P'*) versus λ_{max} for **1b**.

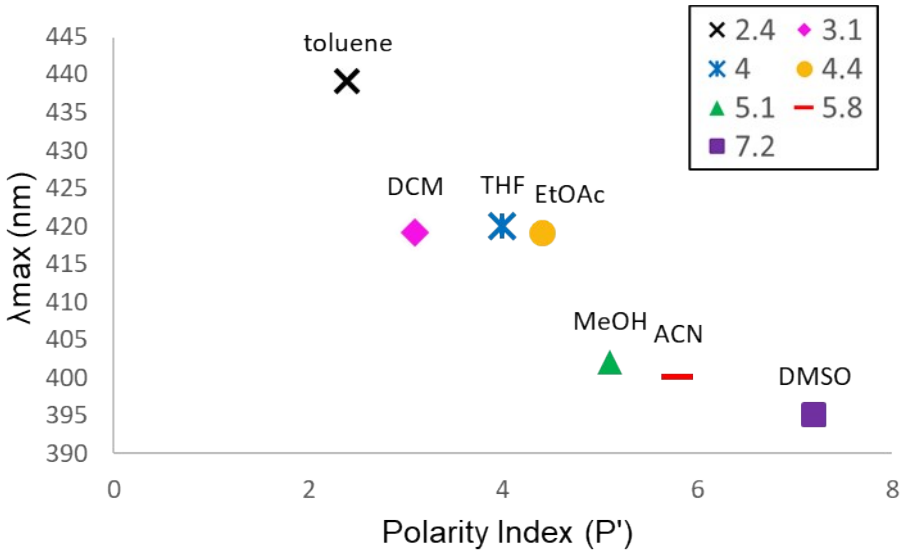


Figure S42: Solvent polarity index (*P'*) versus λ_{max} for **2b**.

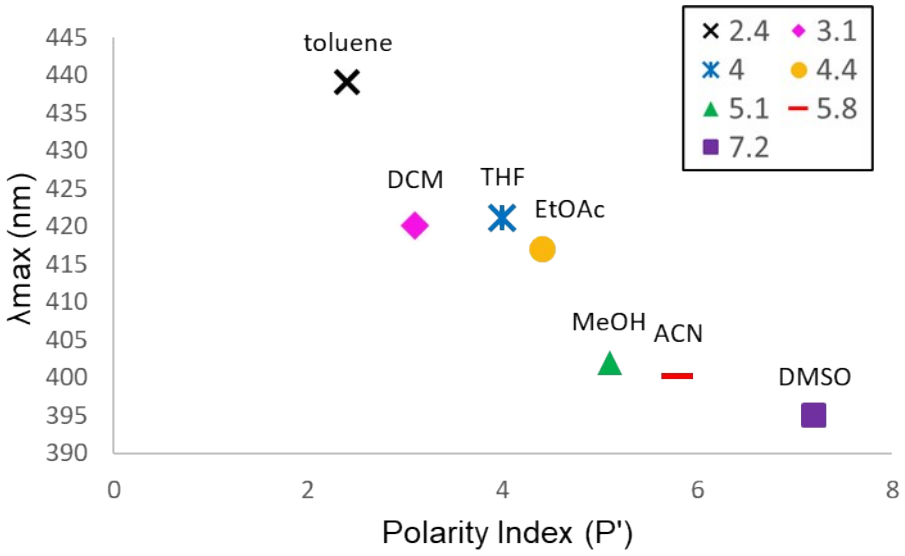


Figure S43: Solvent polarity index (*P'*) versus λ_{max} for **3b**.

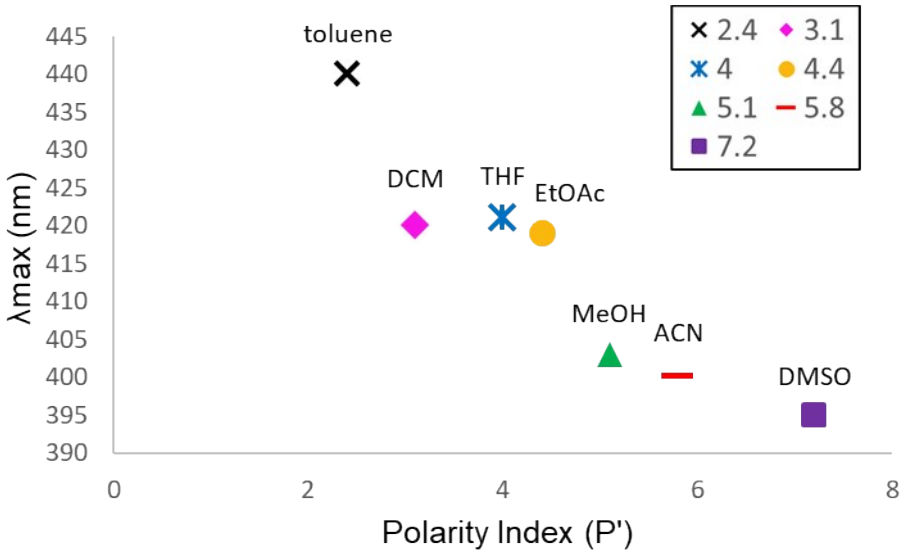


Figure S44: Solvent polarity index (*P'*) versus λ_{max} for **4b**.

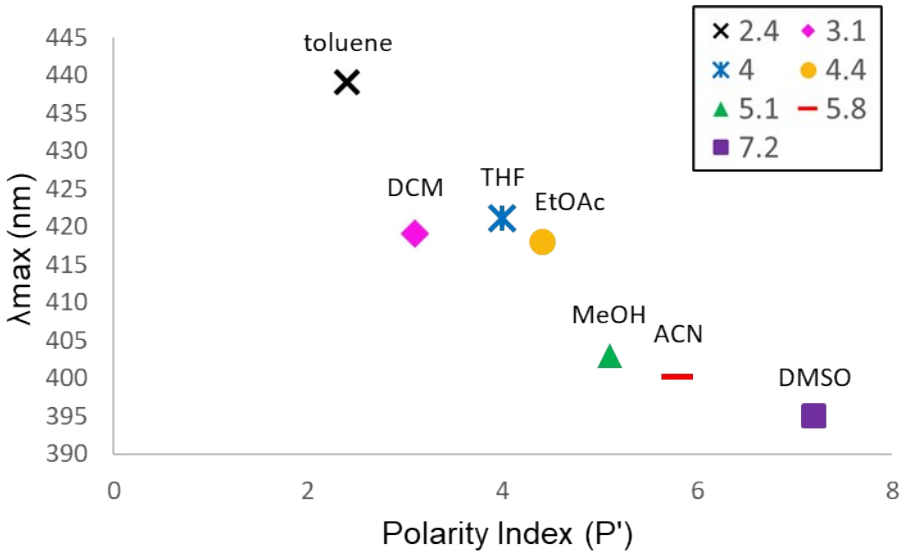


Figure S45: Solvent polarity index (*P'*) versus λ_{max} for **5b**.

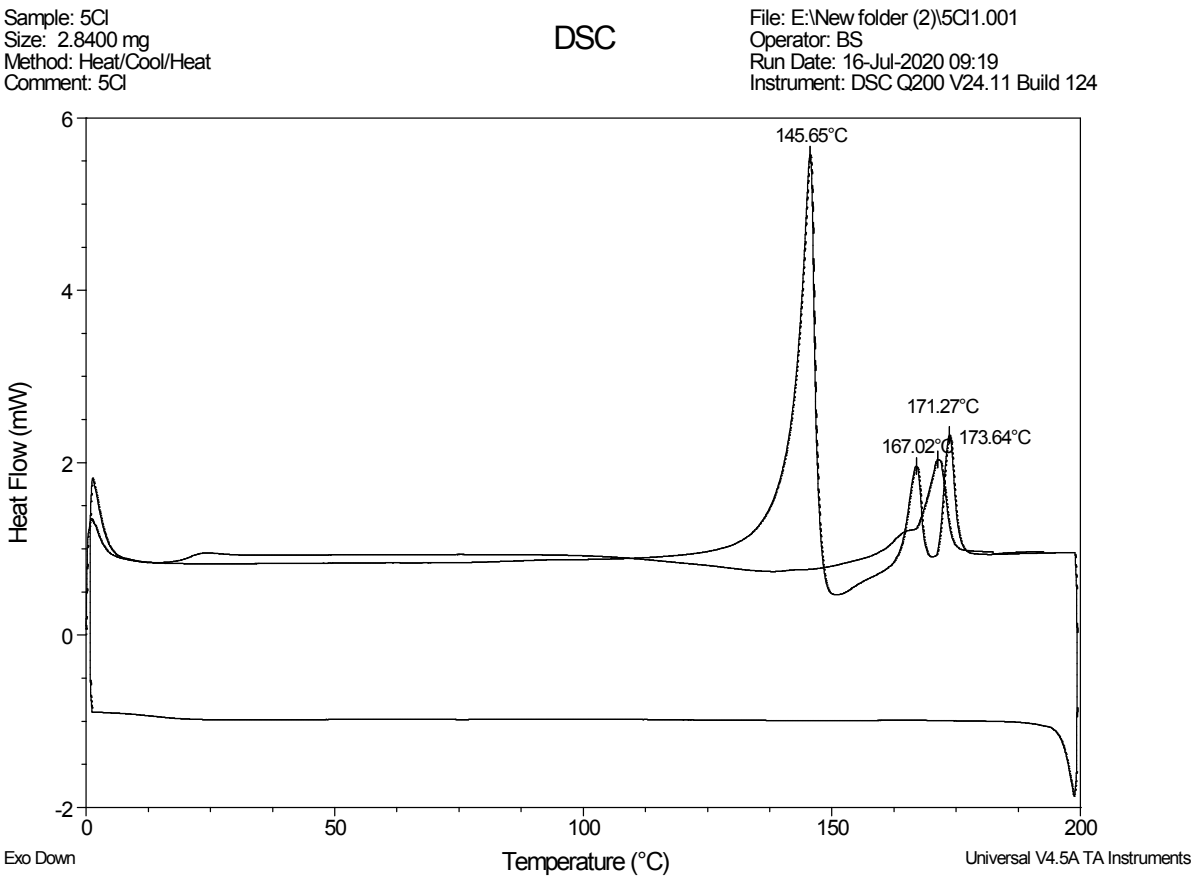


Figure S46: DSC thermogram for **1a**.

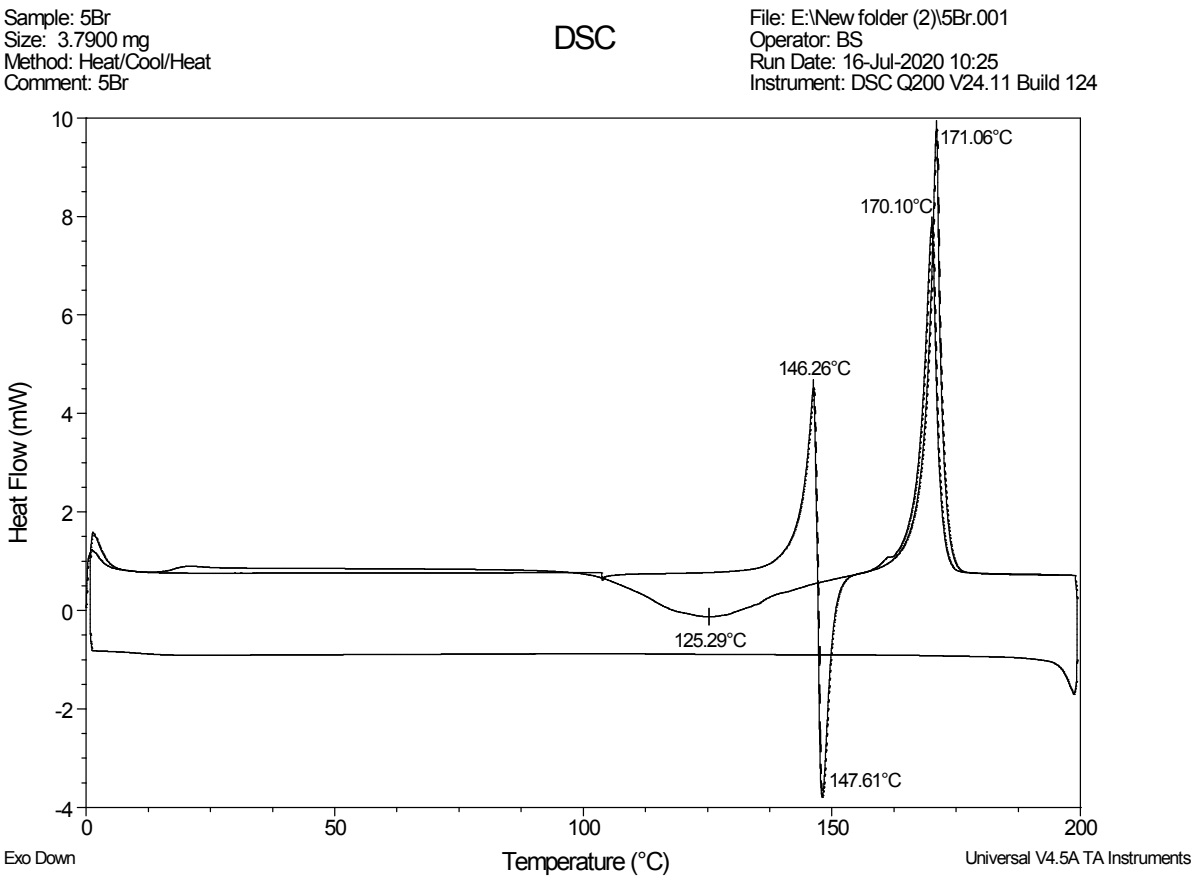


Figure S47: DSC thermogram of **1b**.

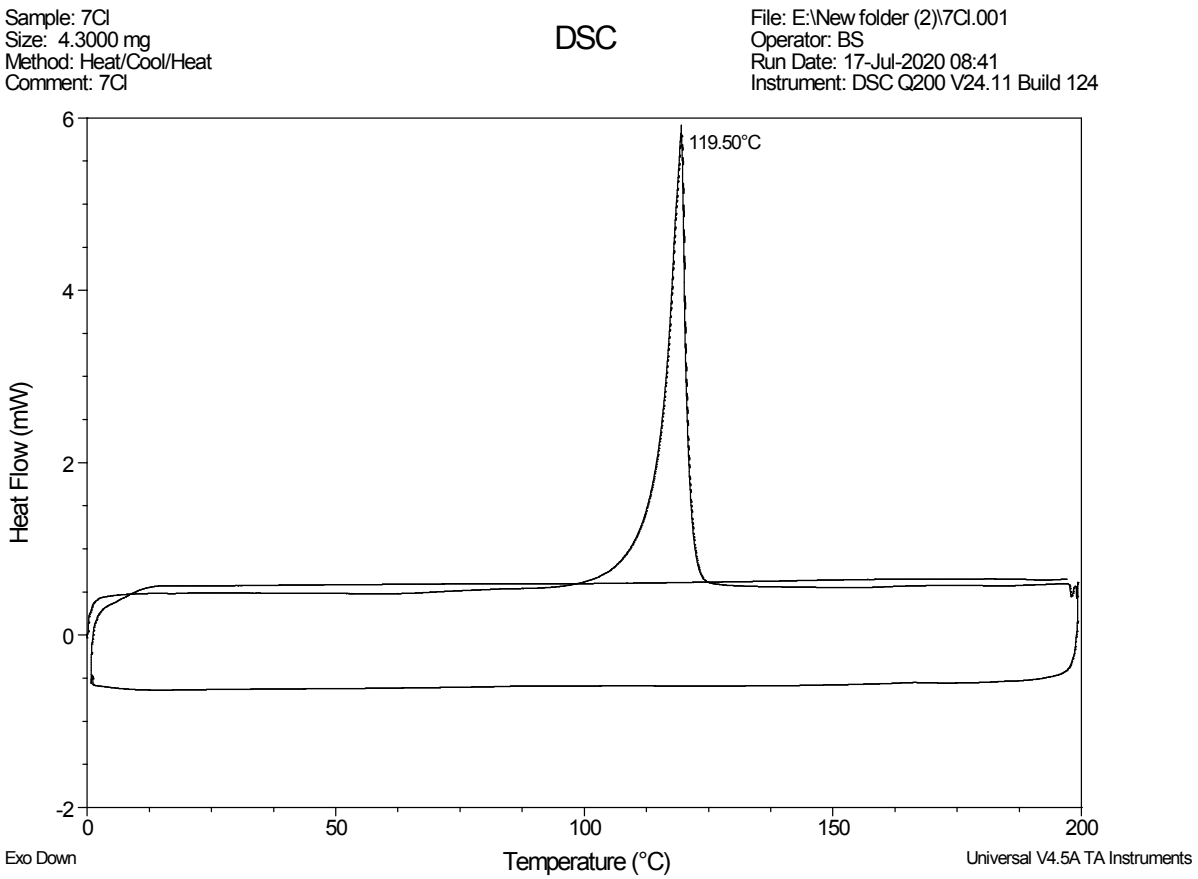


Figure S48: DSC thermogram of **2a**.

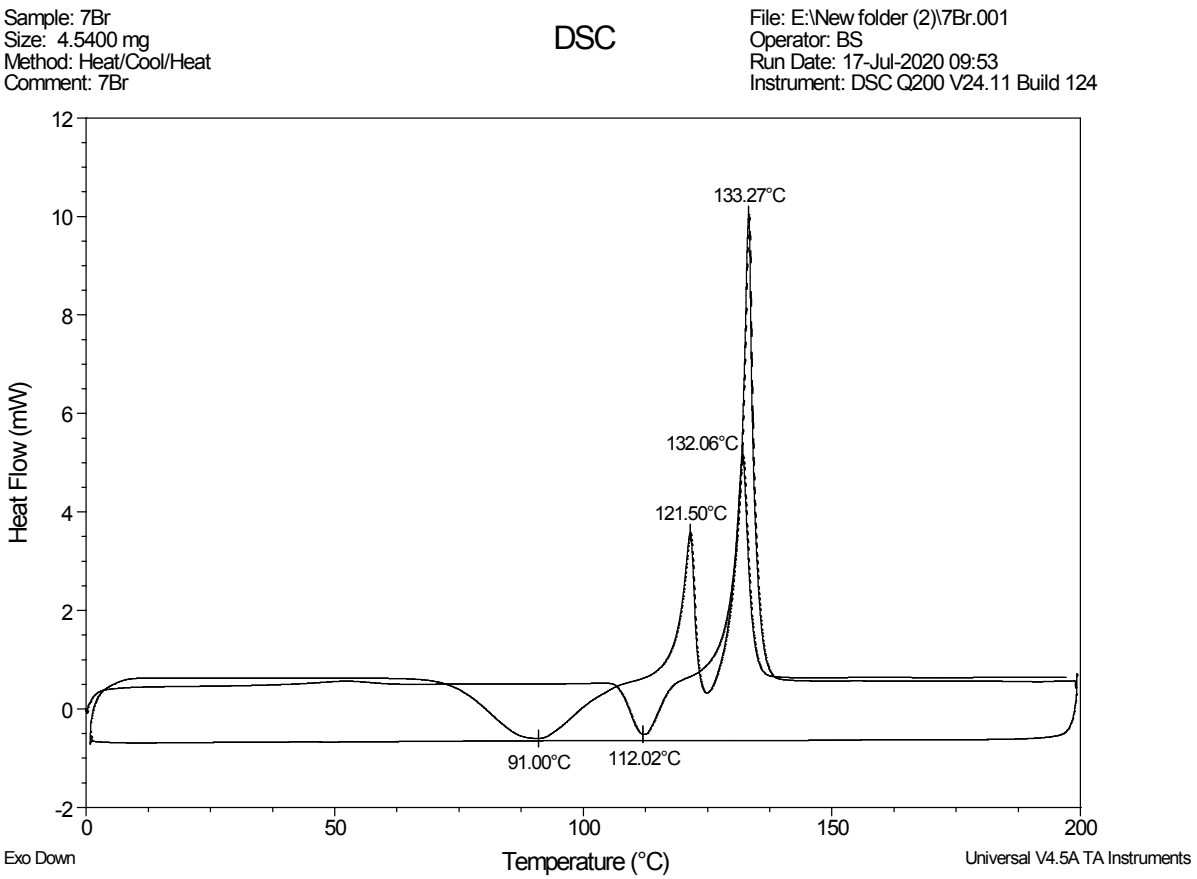


Figure S49: DSC thermogram of **2b**.

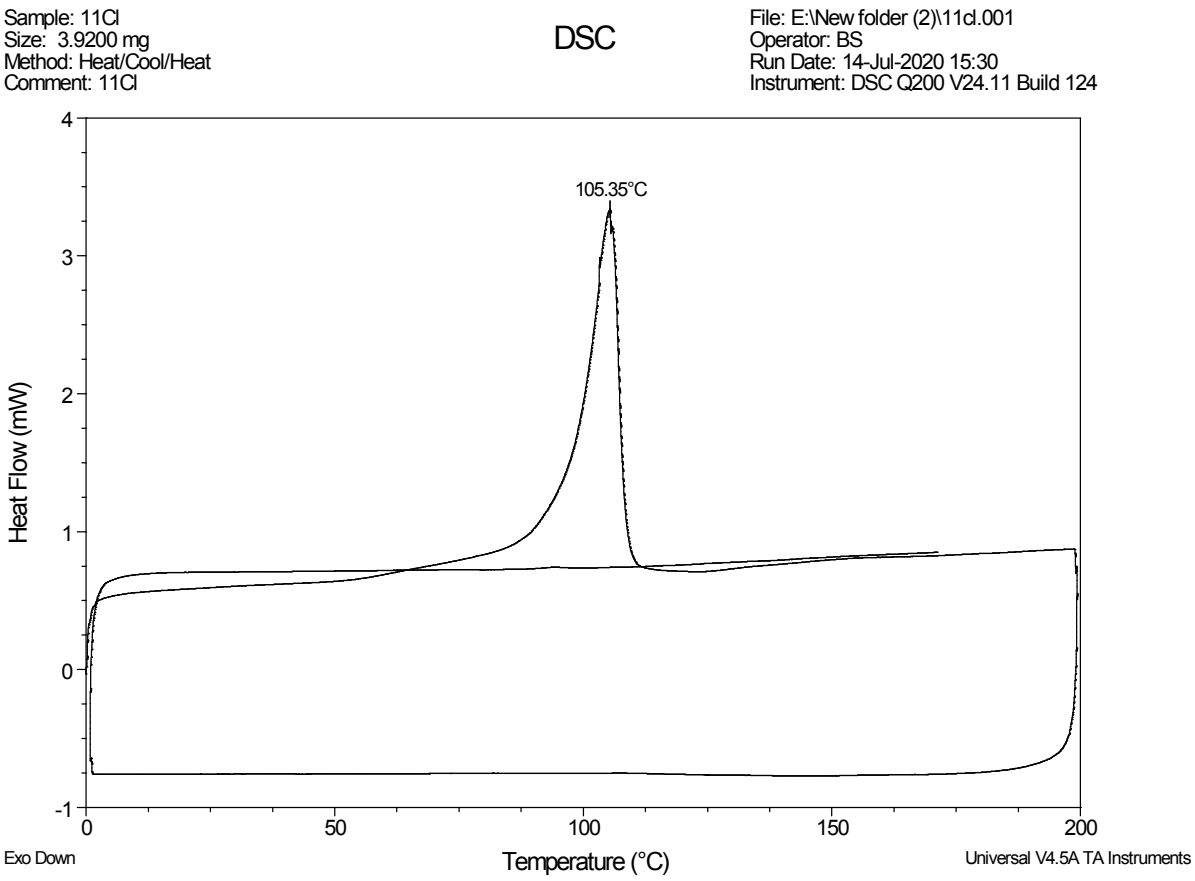


Figure S50: DSC thermogram of **3a**.

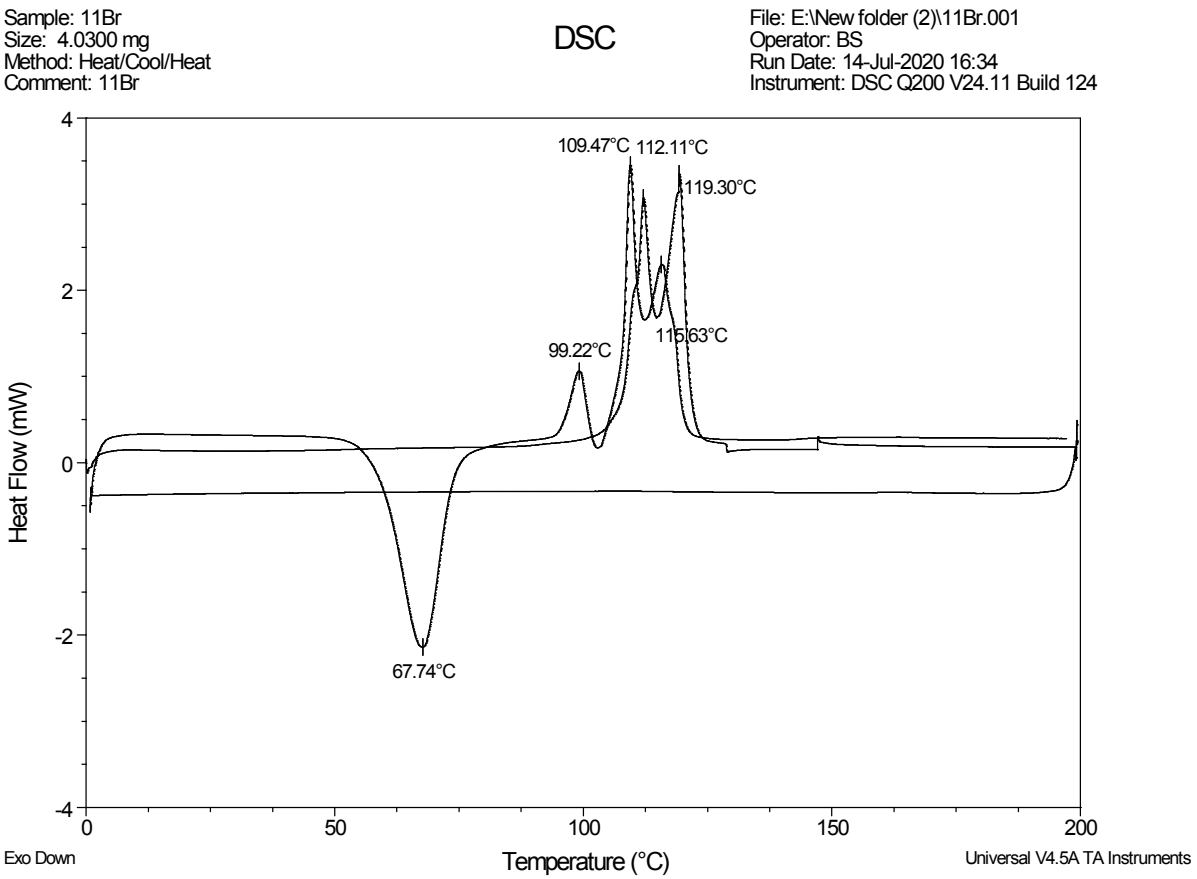


Figure S51: DSC thermogram of **3b**.

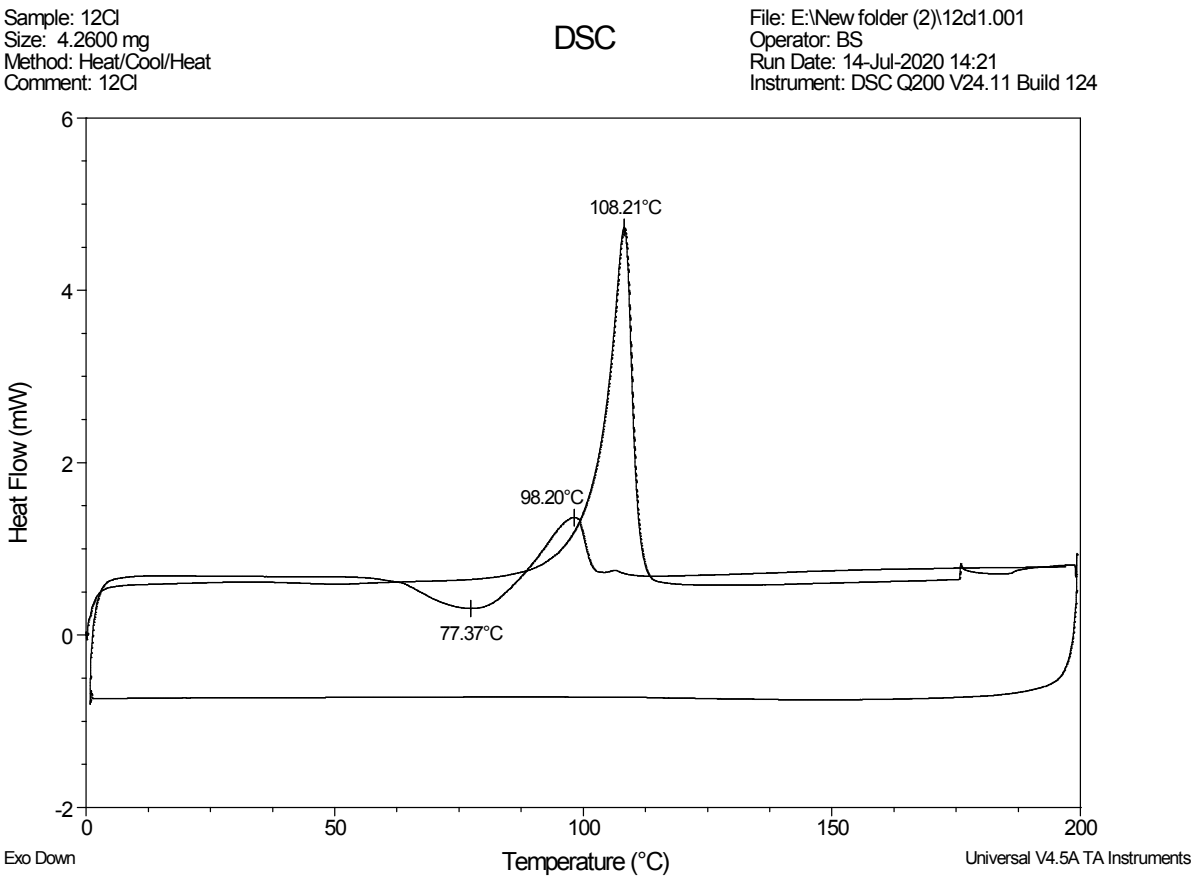


Figure S52: DSC thermogram of **4a.**

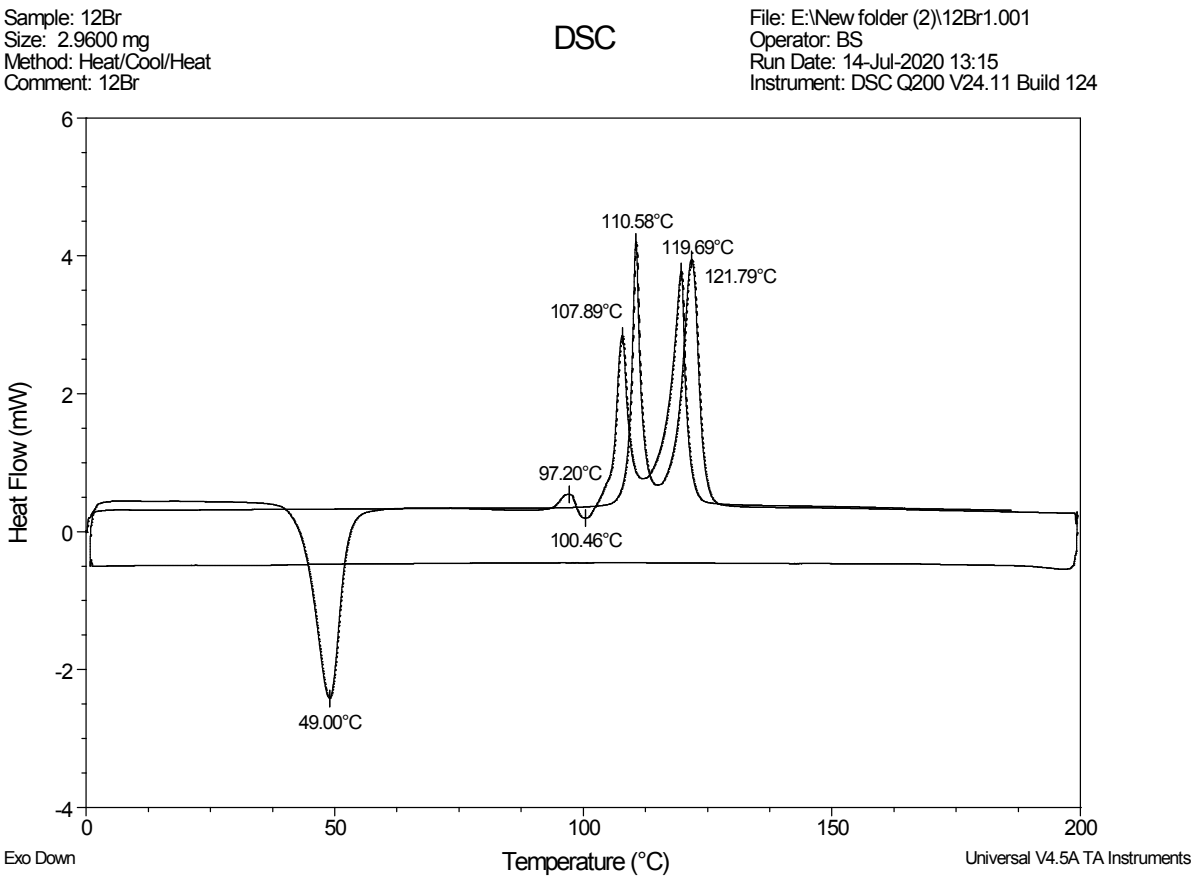


Figure S53: DSC thermogram of **4b.**

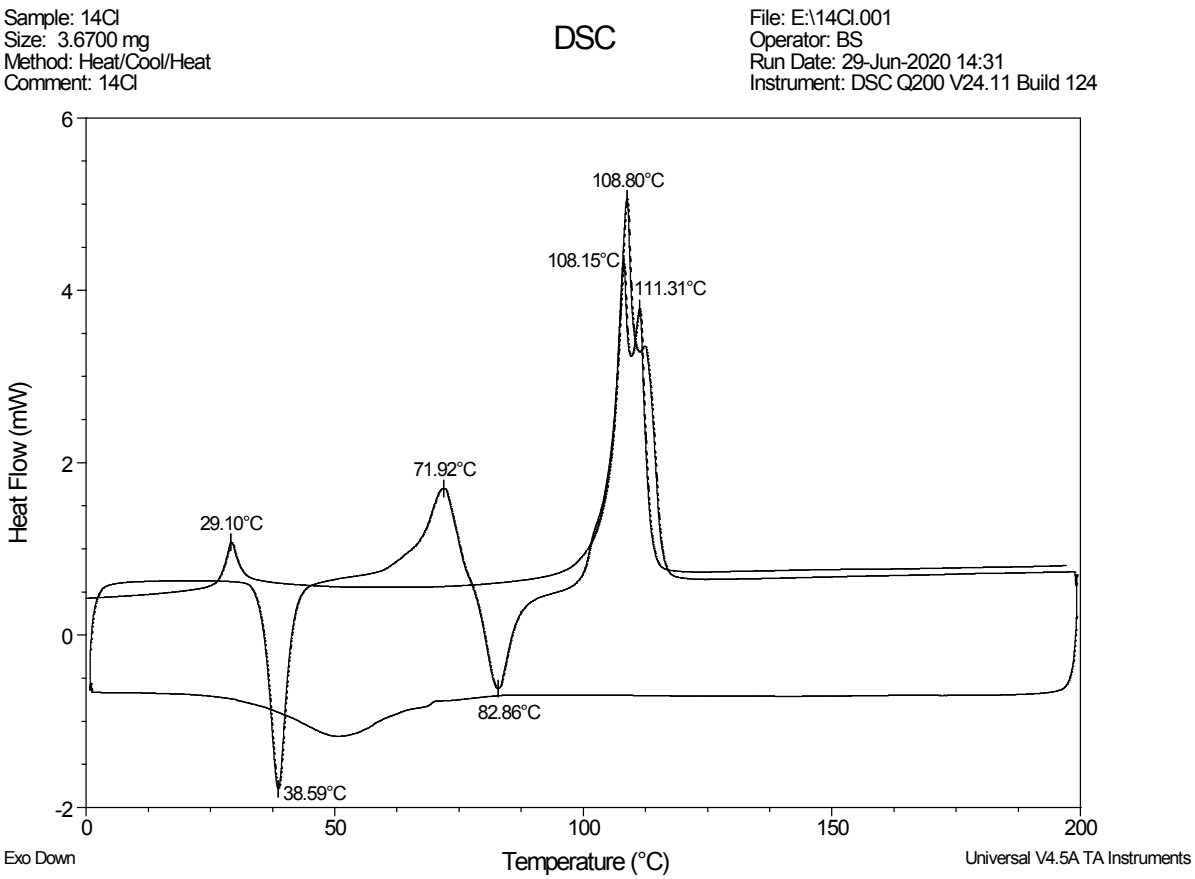


Figure S54: DSC thermogram of **5a.**

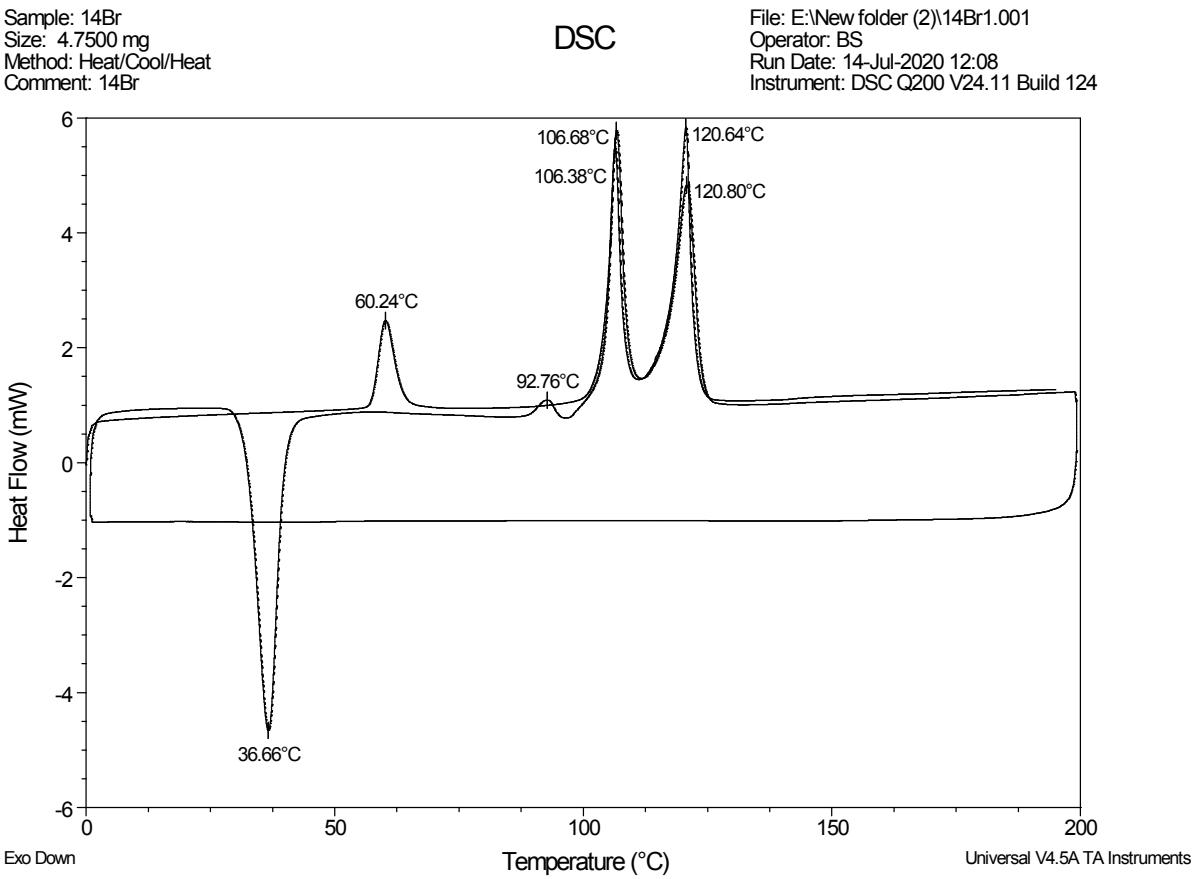


Figure S55: DSC thermogram of **5b.**

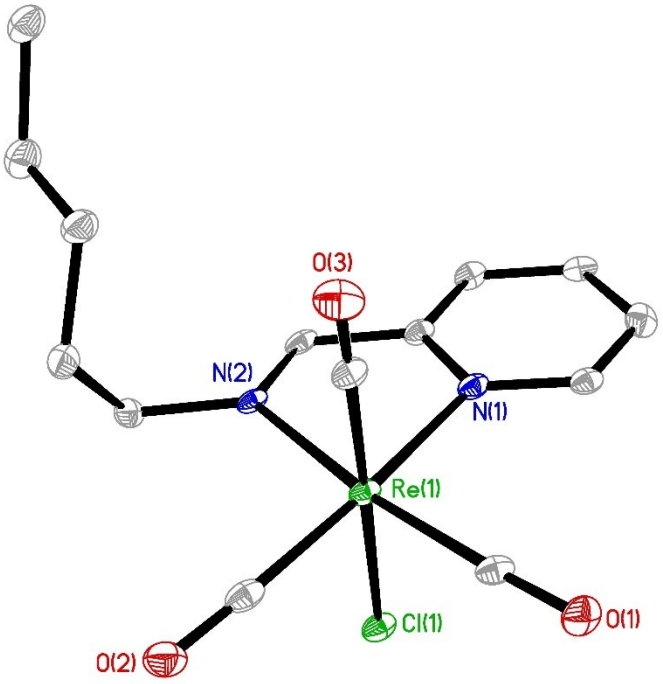


Figure S56: The structures of compound **1a** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

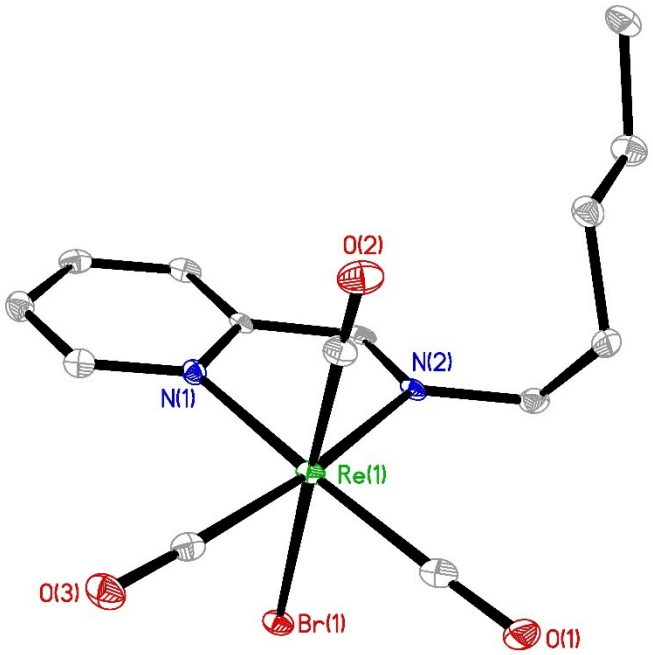


Figure S57: The structures of compound **1b** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

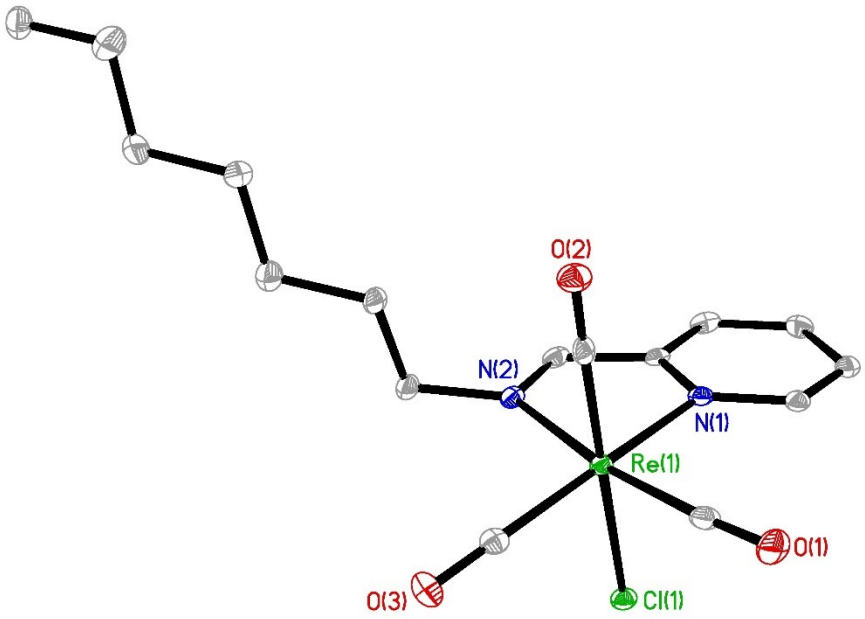


Figure S58: The structures of compound **2a** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

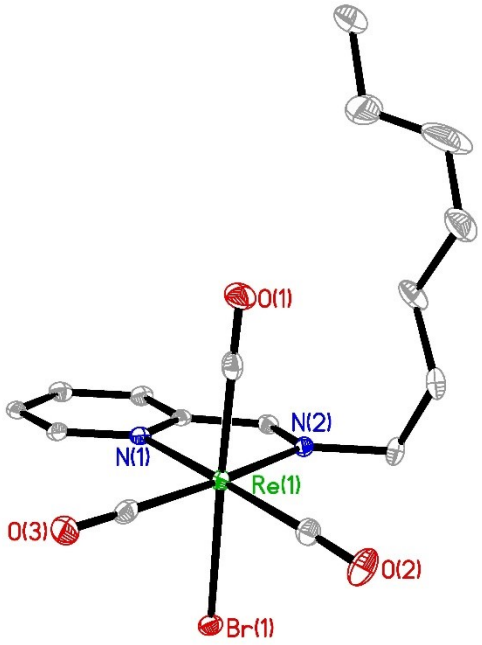


Figure S59: The structures of compound **2b** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

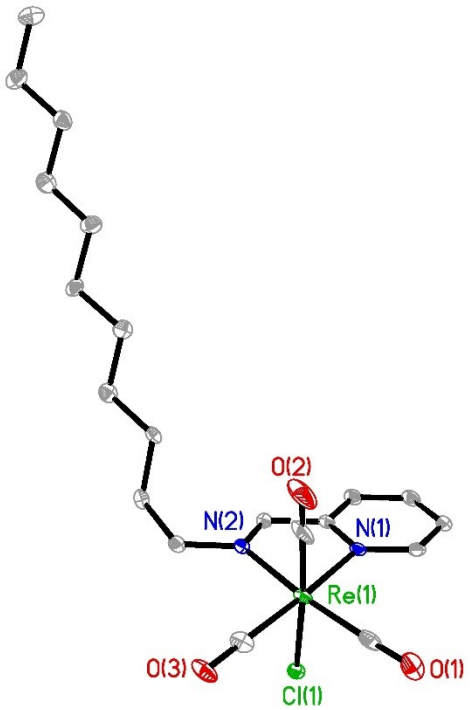


Figure S60: The structures of compound **3a** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

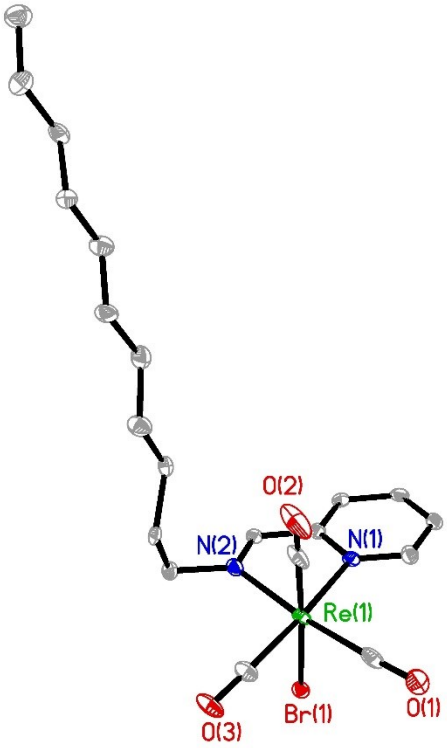


Figure S61: The structures of compound **3b** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

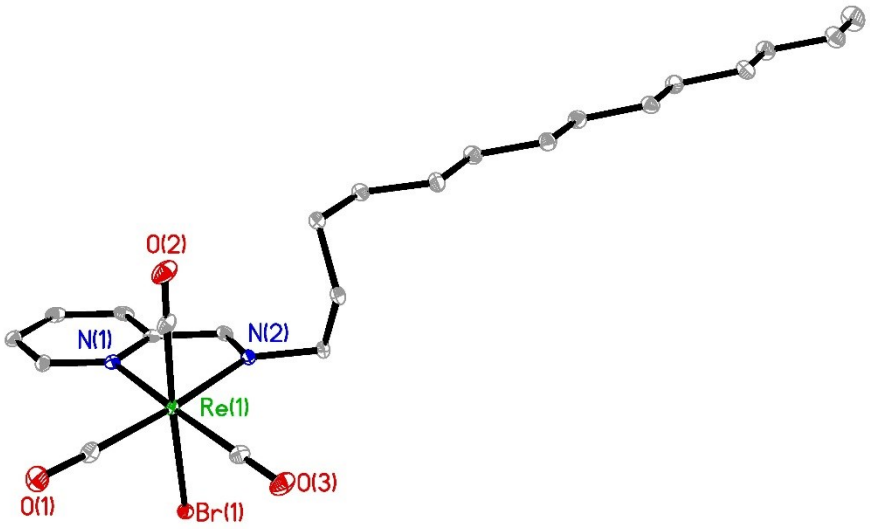


Figure S62: The structures of compound **5b** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

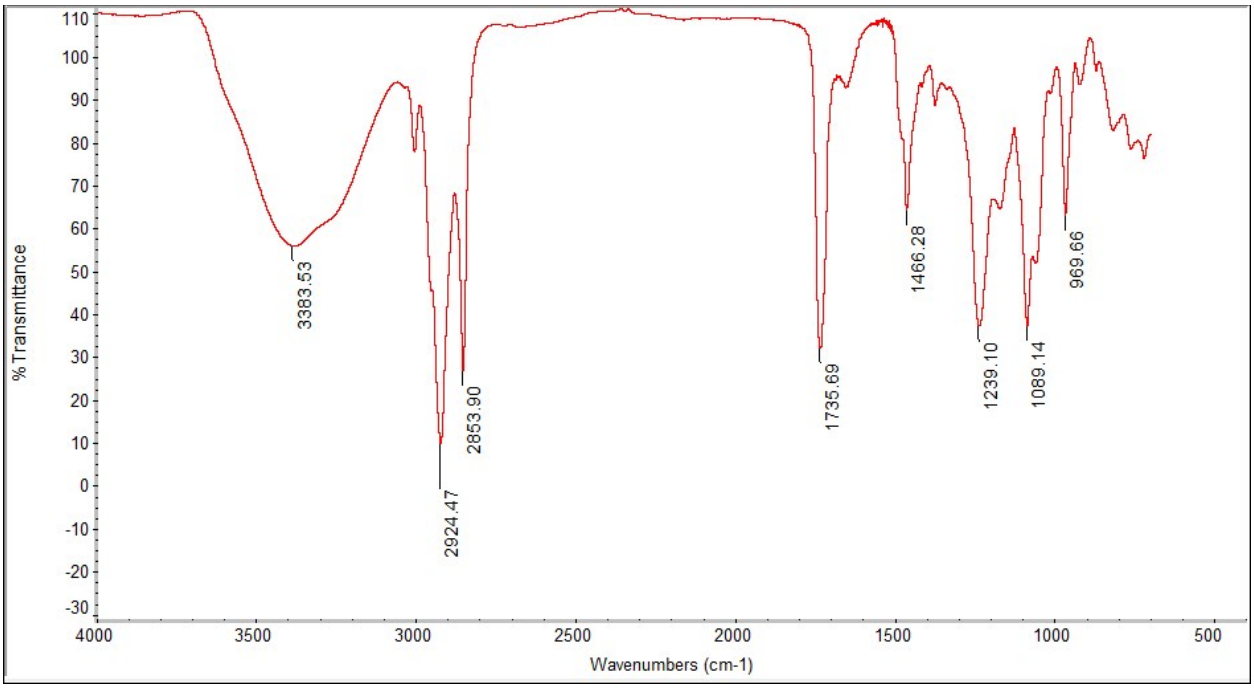


Figure S63: FTIR spectrum of 100 mol % DOPC vesicles.

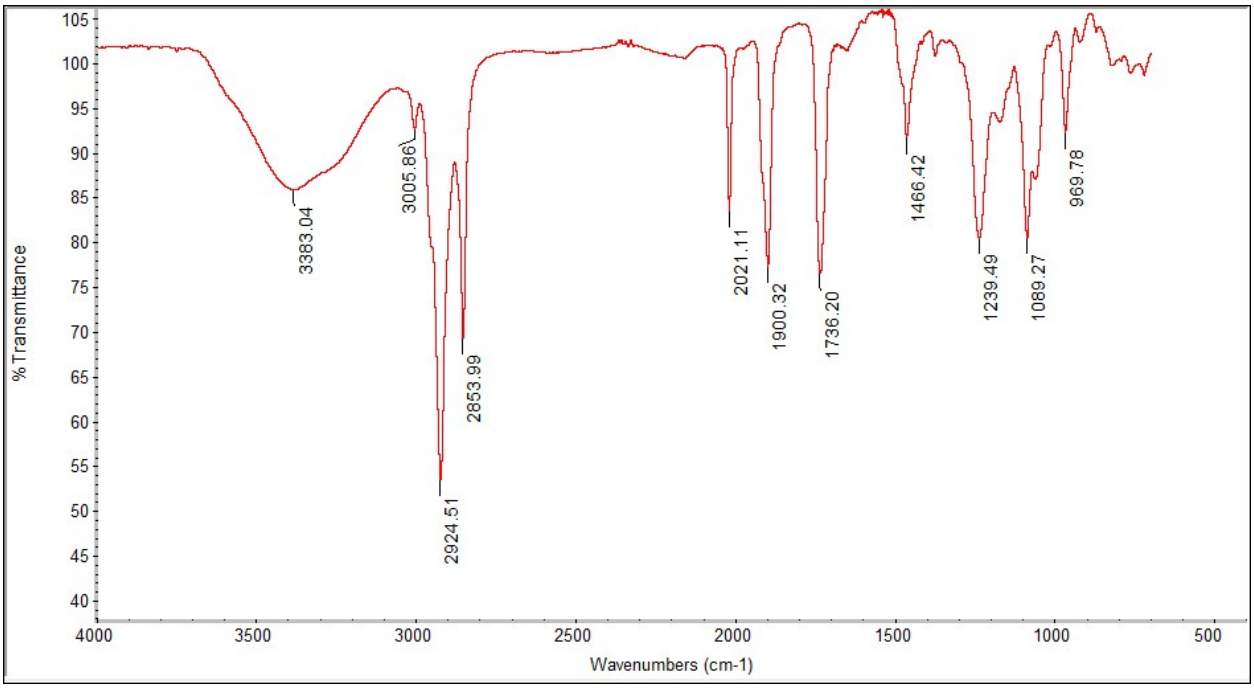


Figure S64: FTIR spectrum of 95 mol % DOPC, and 5 mol % by Re(I) content of compound **5a** vesicles.

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	$C_{14}H_{16}ClN_2O_3Re$	$C_{14}H_{16}BrN_2O_3Re$	$C_{16}H_{20}ClN_2O_3Re$	$C_{16}H_{20}BrN_2O_3Re$
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	$C_{40}H_{56}Cl_2N_4O_6Re_2$	$C_{40}H_{56}Br_2N_4O_6Re_2$	$C_{23}H_{34}BrN_2O_3Re$
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-$O_{(c\equiv o)}$ (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-$O_{(c\equiv o)}$ (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)