Supporting Information for:

Triphenylene-Imidazolium Salts and Their NHC Metal Complexes, Materials with Segregated Multicolumnar Mesophases.

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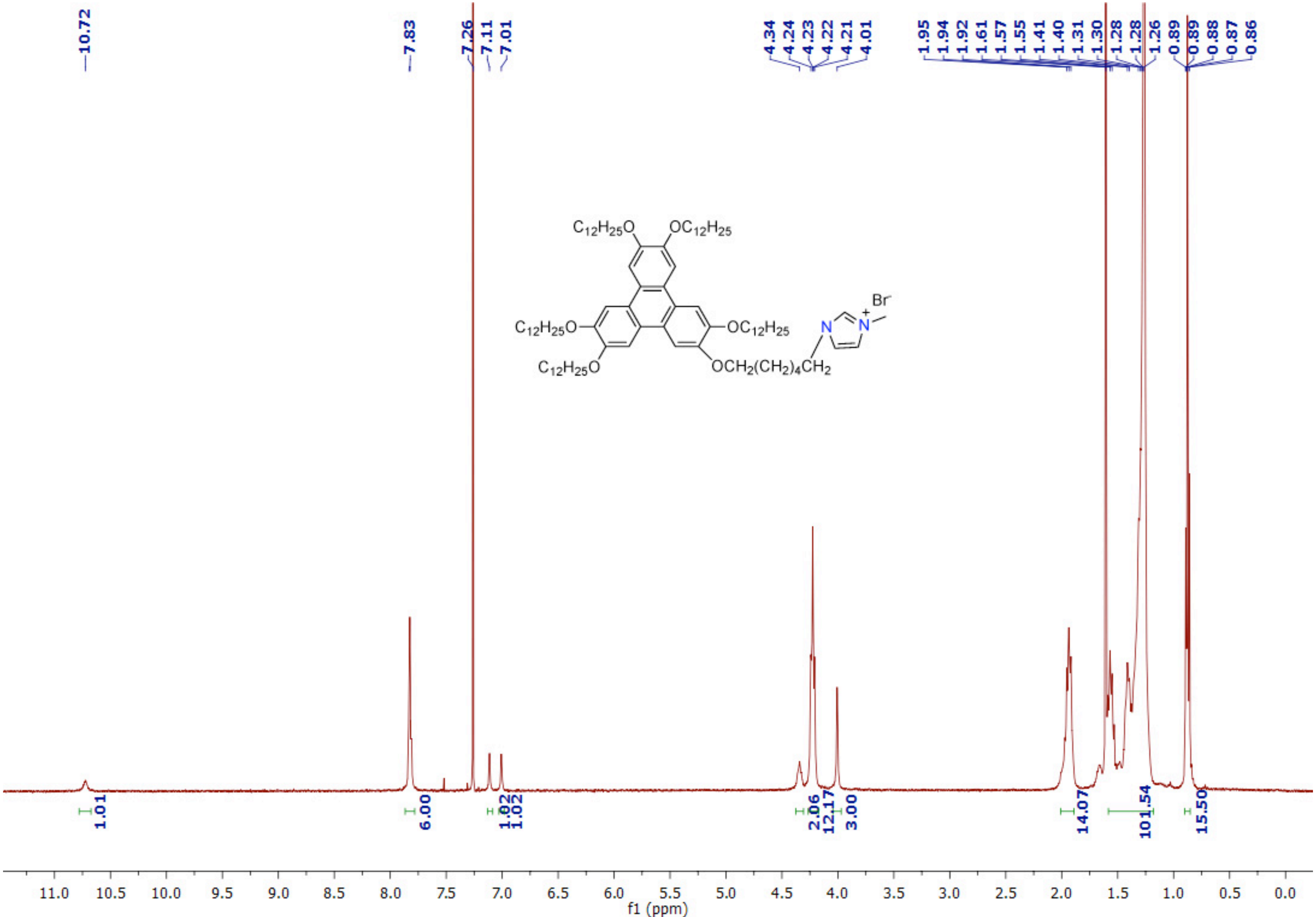

Figure S1. ^{1}H NMR (400.14 MHz) spectrum of **1** in $CDCl_3$.

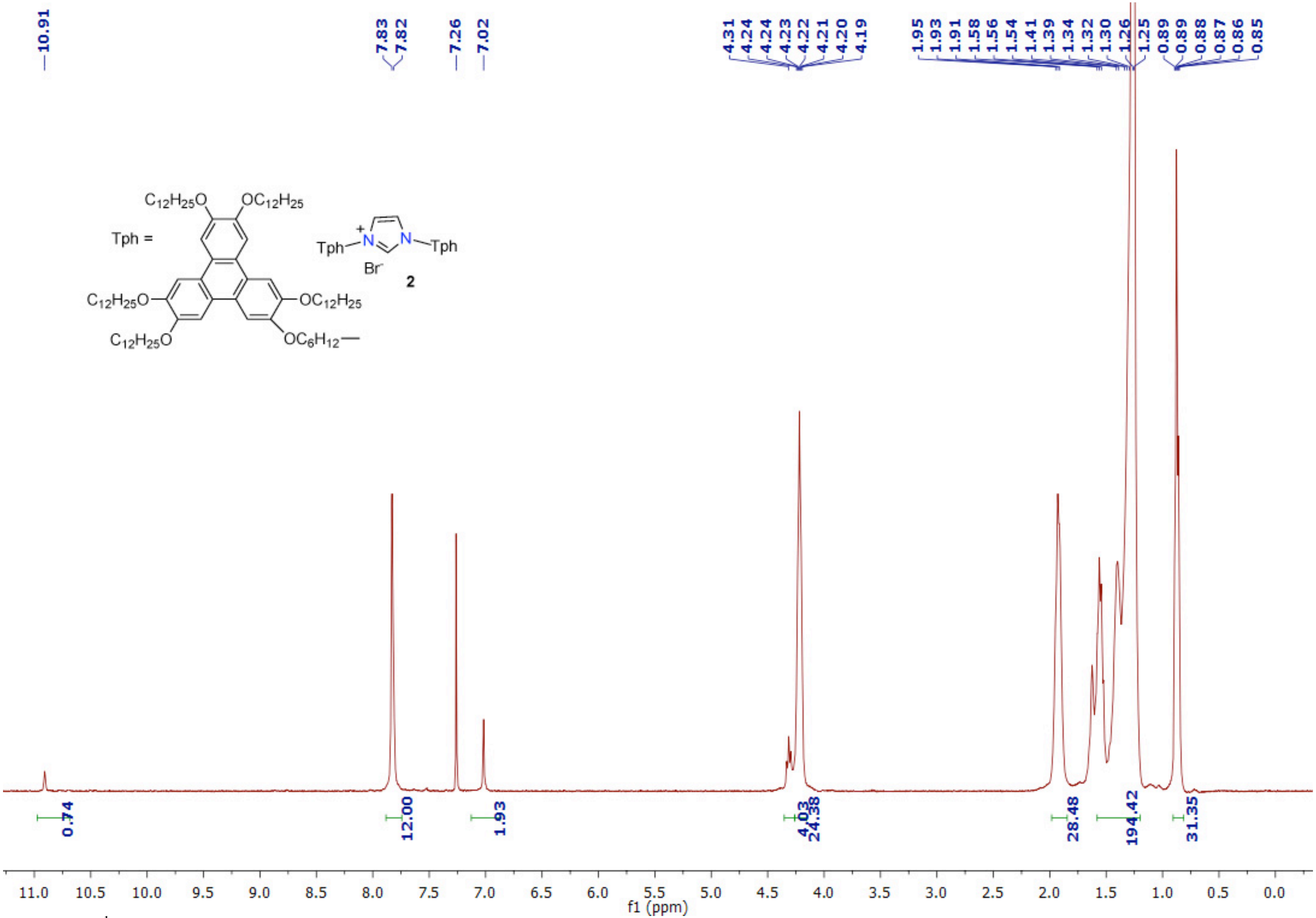

Figure S2. [1]H NMR (400.14 MHz) spectrum of **2** in $CDCl_3$.

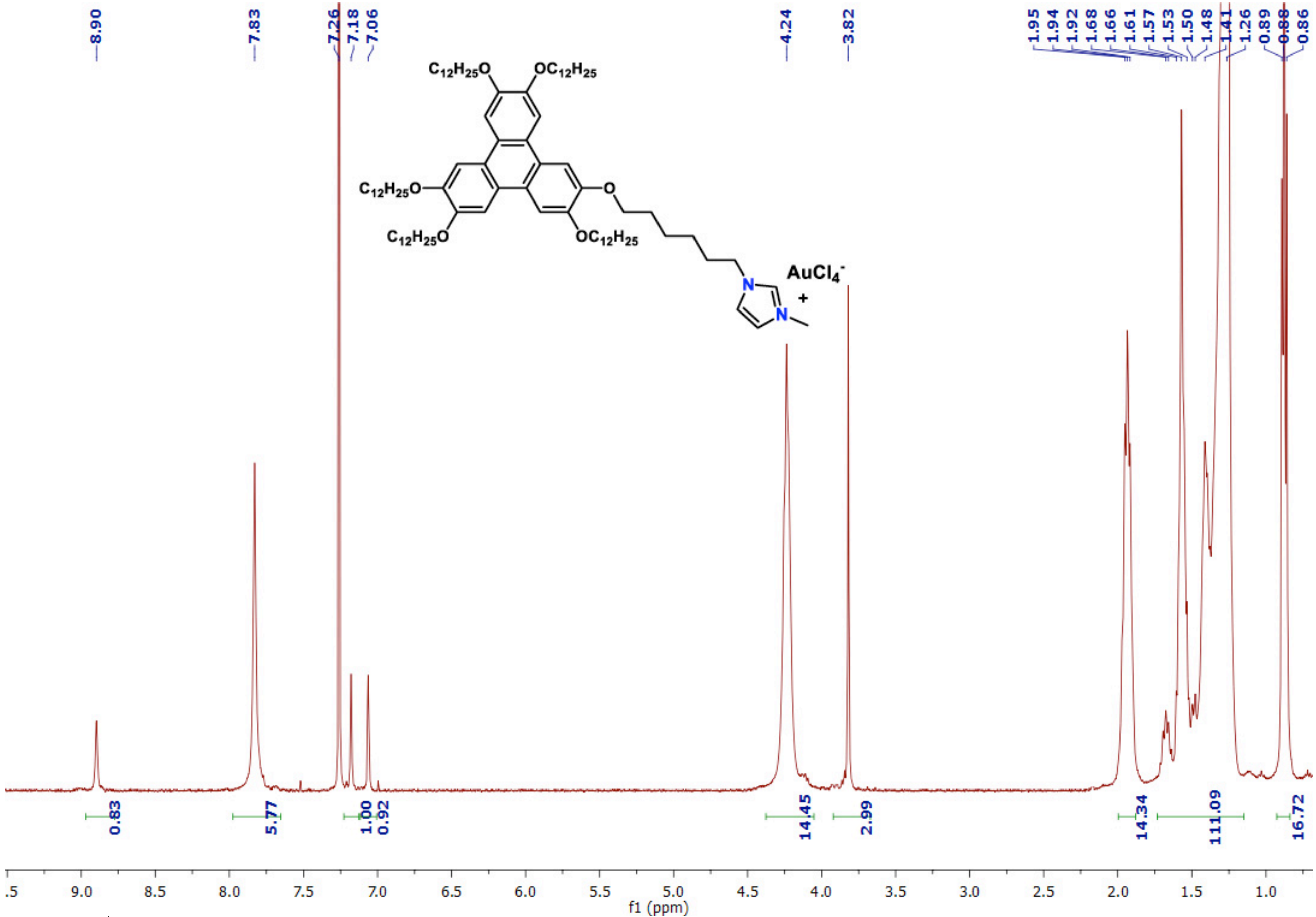

Figure S3. ^{1}H NMR (400.14 MHz) spectrum of **3** in $CDCl_3$.

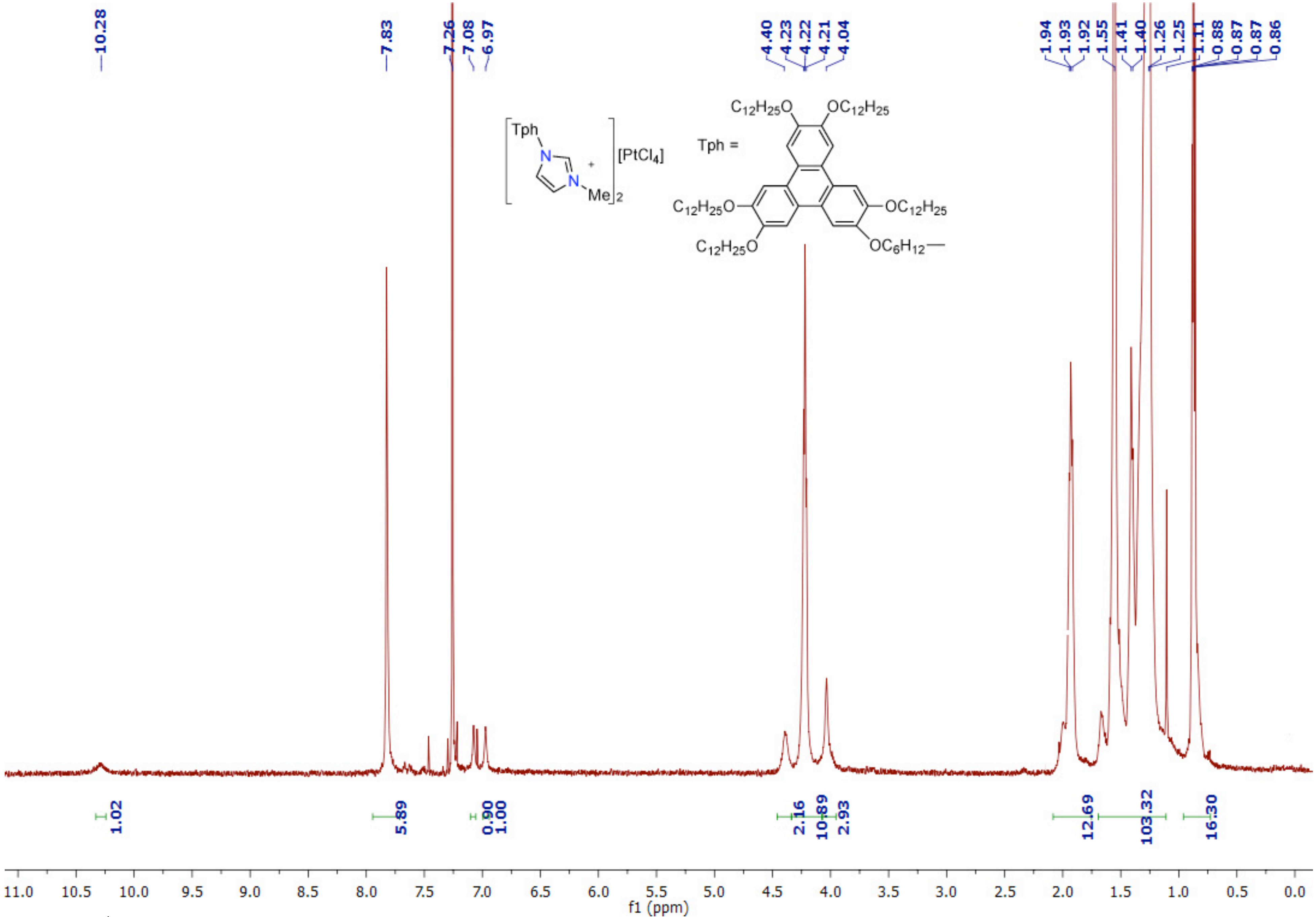

Figure S4. ^{1}H NMR (400.14 MHz) spectrum of **4** in $CDCl_3$.

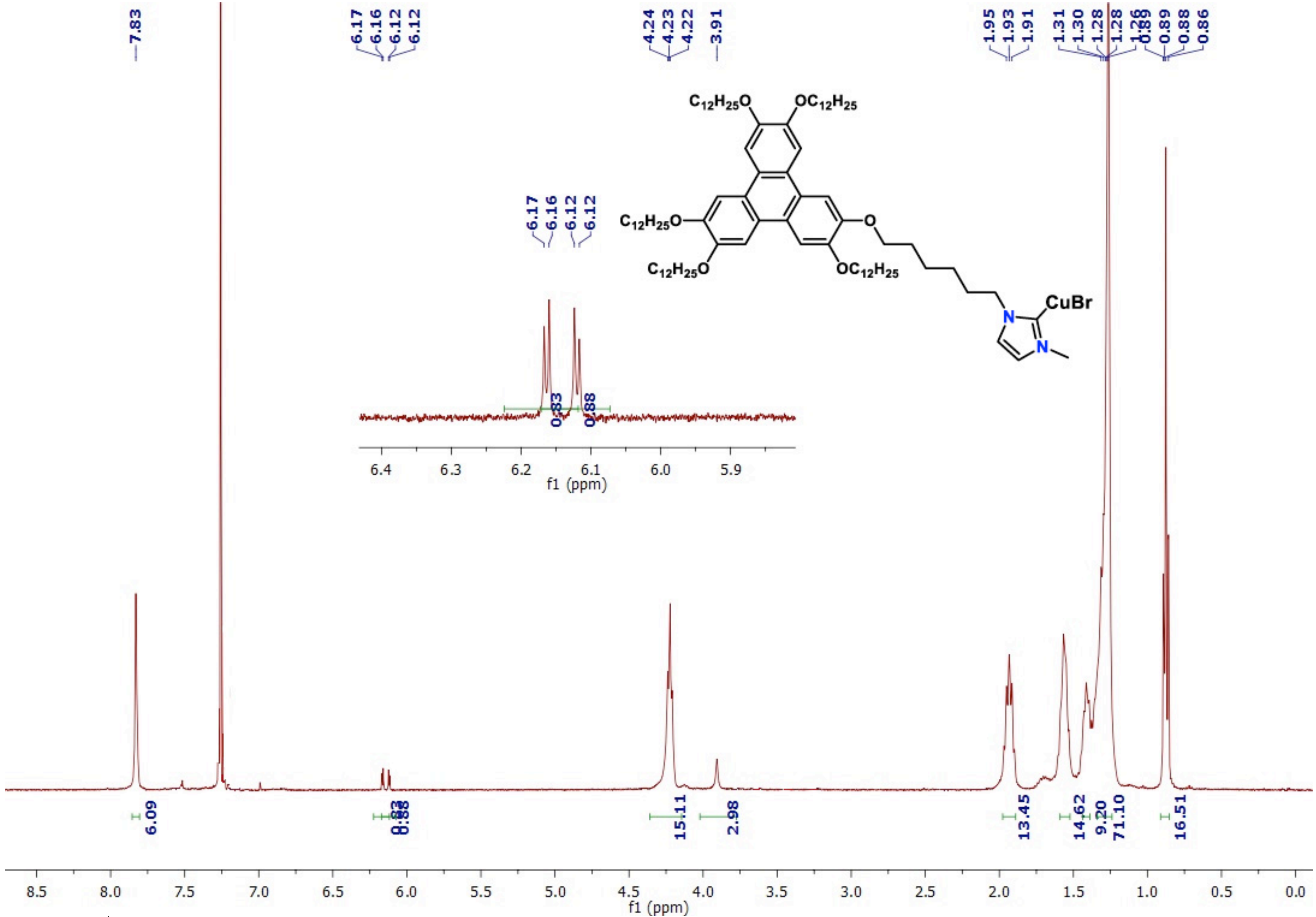

Figure S5. ^{1}H NMR (400.14 MHz) spectrum of **5** in $CDCl_3$.

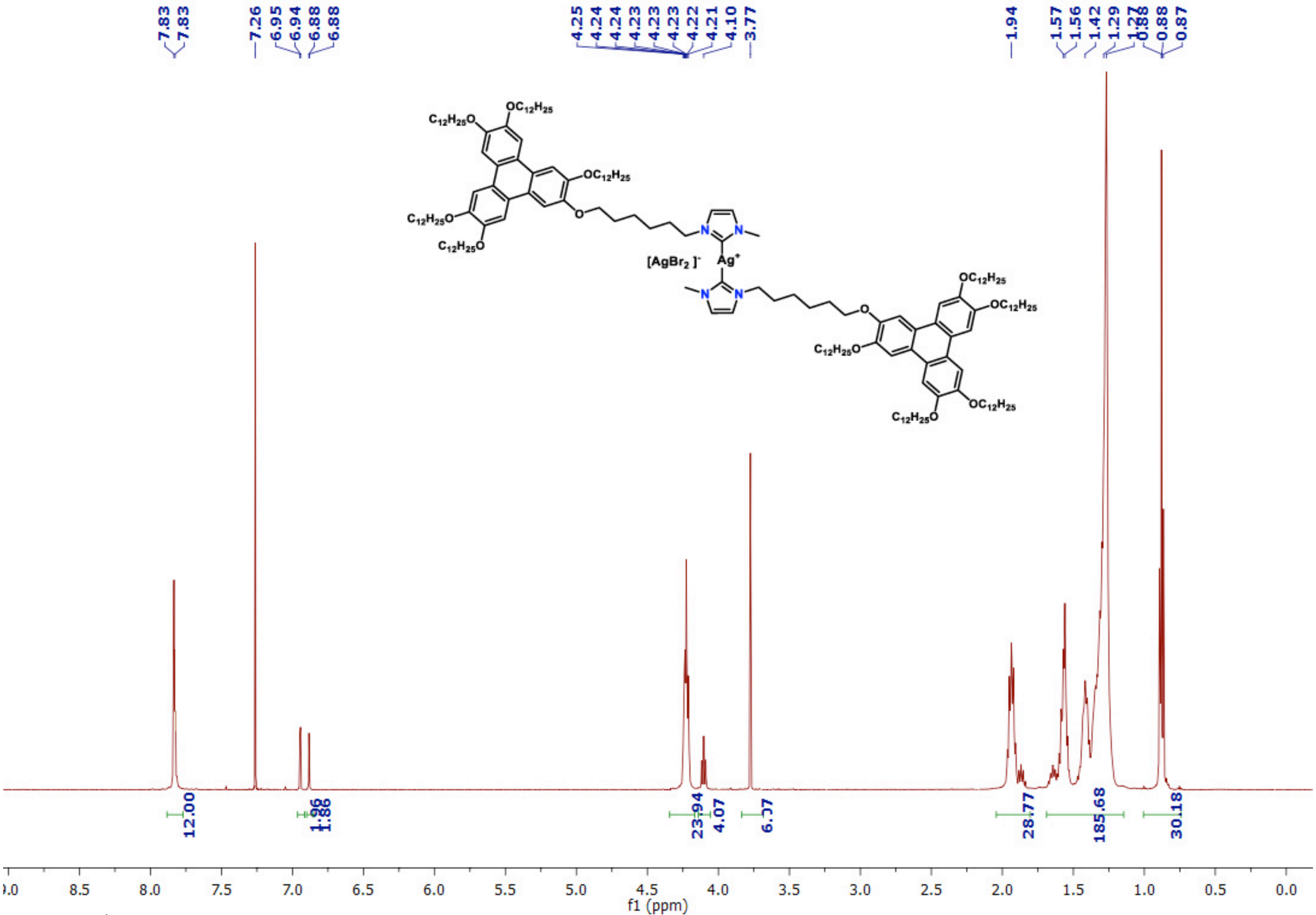

Figure S6. ^{1}H NMR (499.73 MHz) spectrum of **6** in $CDCl_3$.

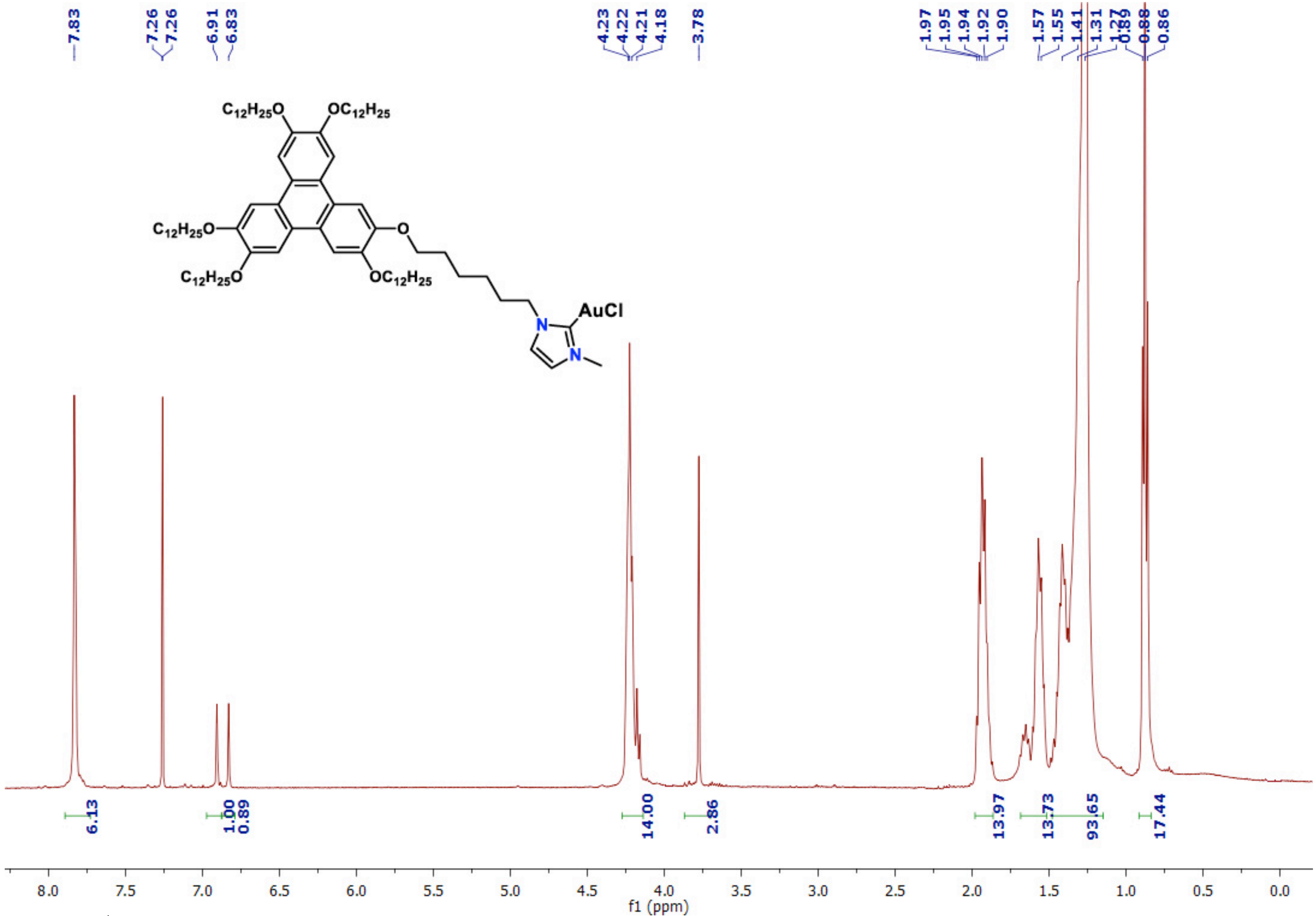

Figure S7. ^{1}H NMR (400.14 MHz) spectrum of **7** in $CDCl_3$.

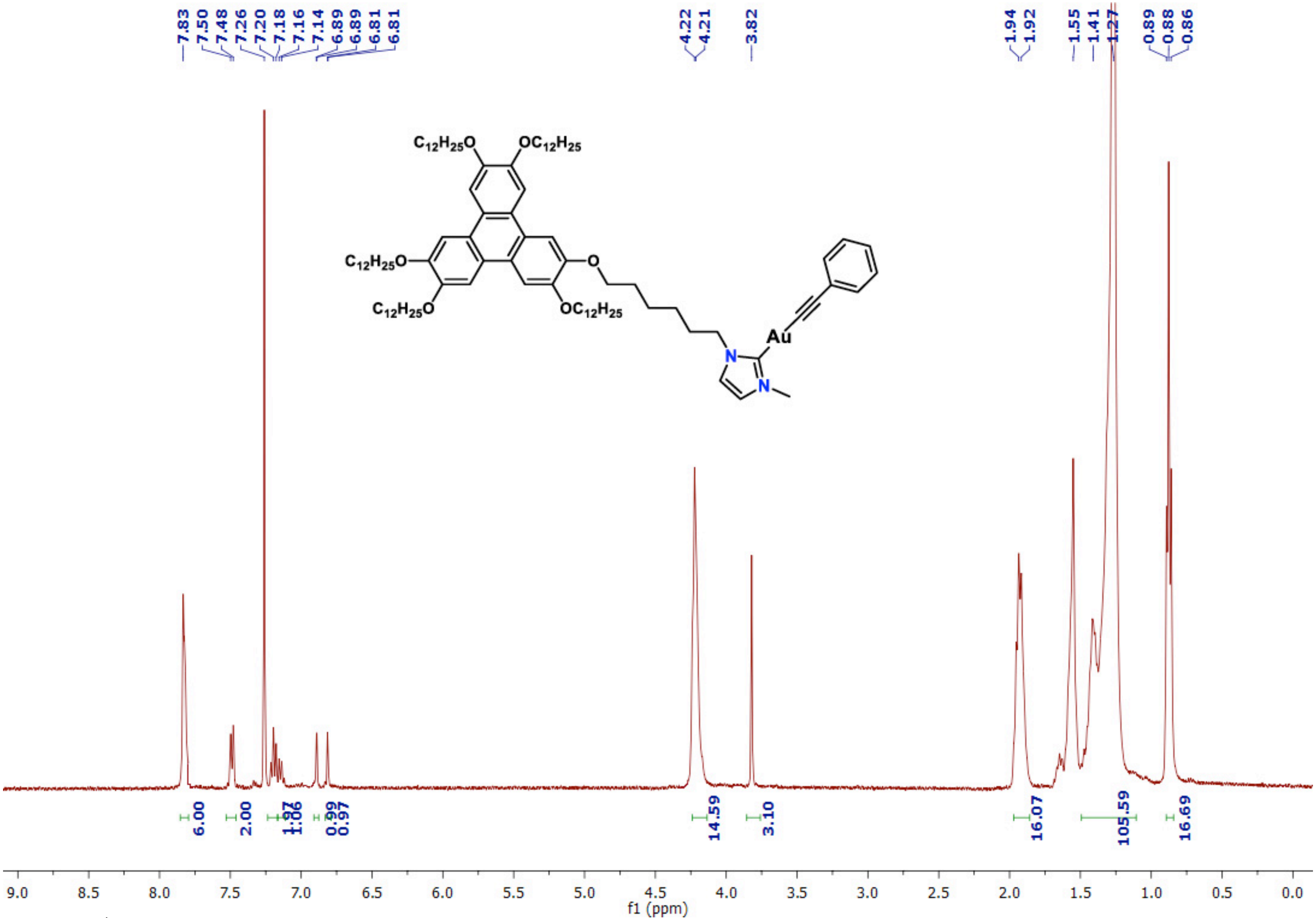

Figure S8. ^{1}H NMR (400.14 MHz) spectrum of **8** in $CDCl_3$.

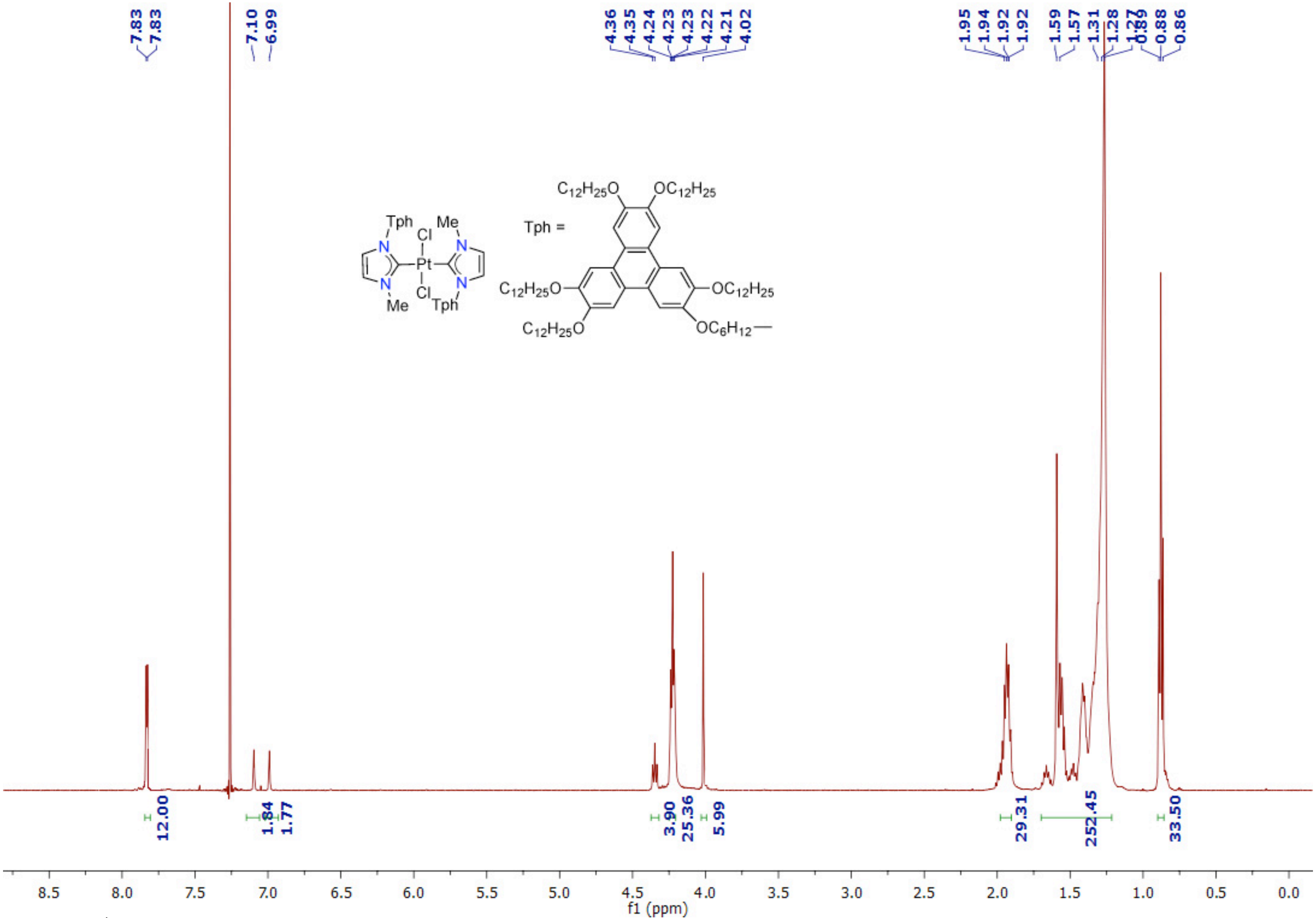

Figure S9. ^{1}H NMR (400.14 MHz) spectrum of **9** in $CDCl_3$.

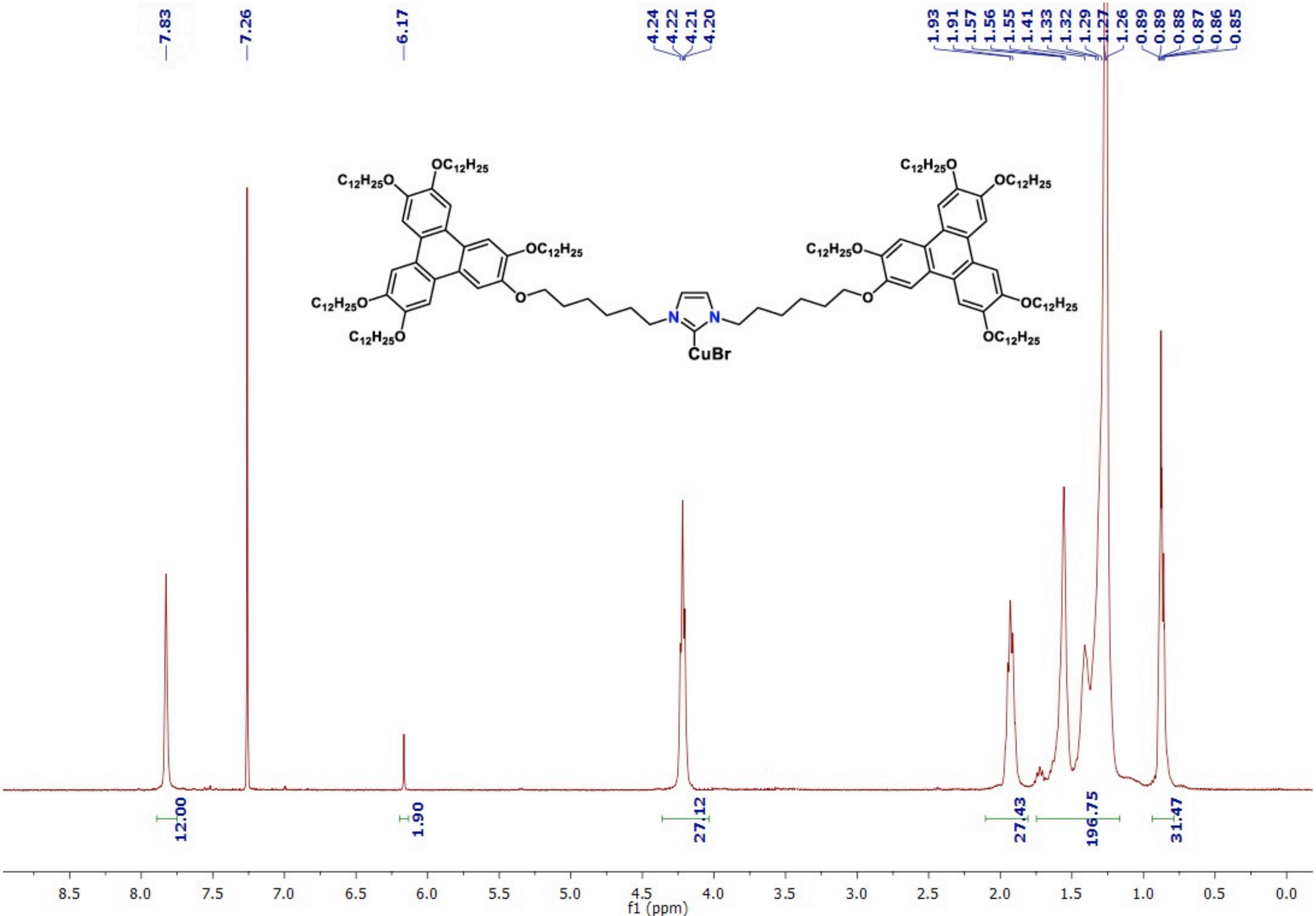

Figure S10. ^{1}H NMR (400.14 MHz) spectrum of **10** in $CDCl_3$.

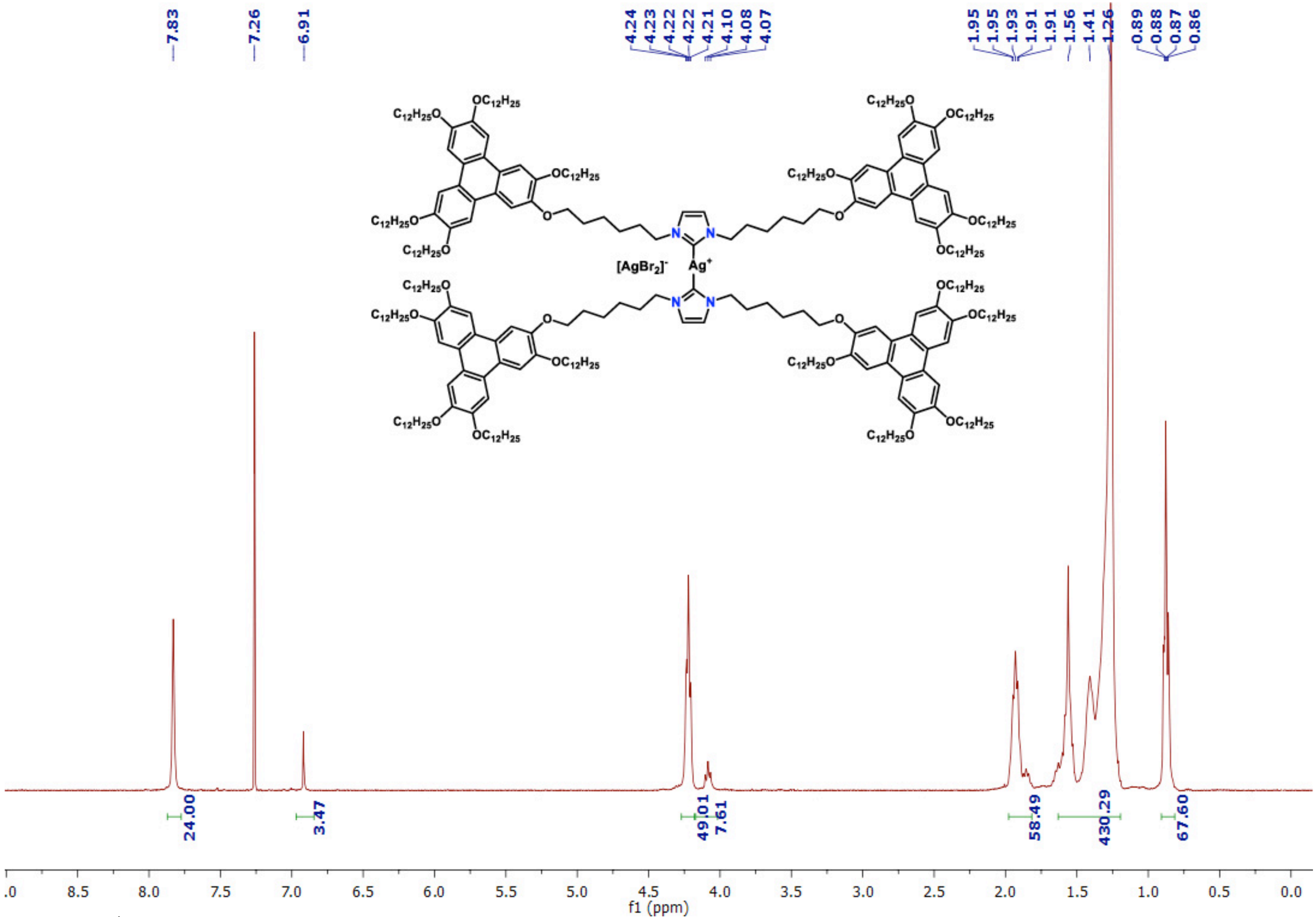

Figure S11. ^{1}H NMR (400.14 MHz) spectrum of **11** in $CDCl_3$.

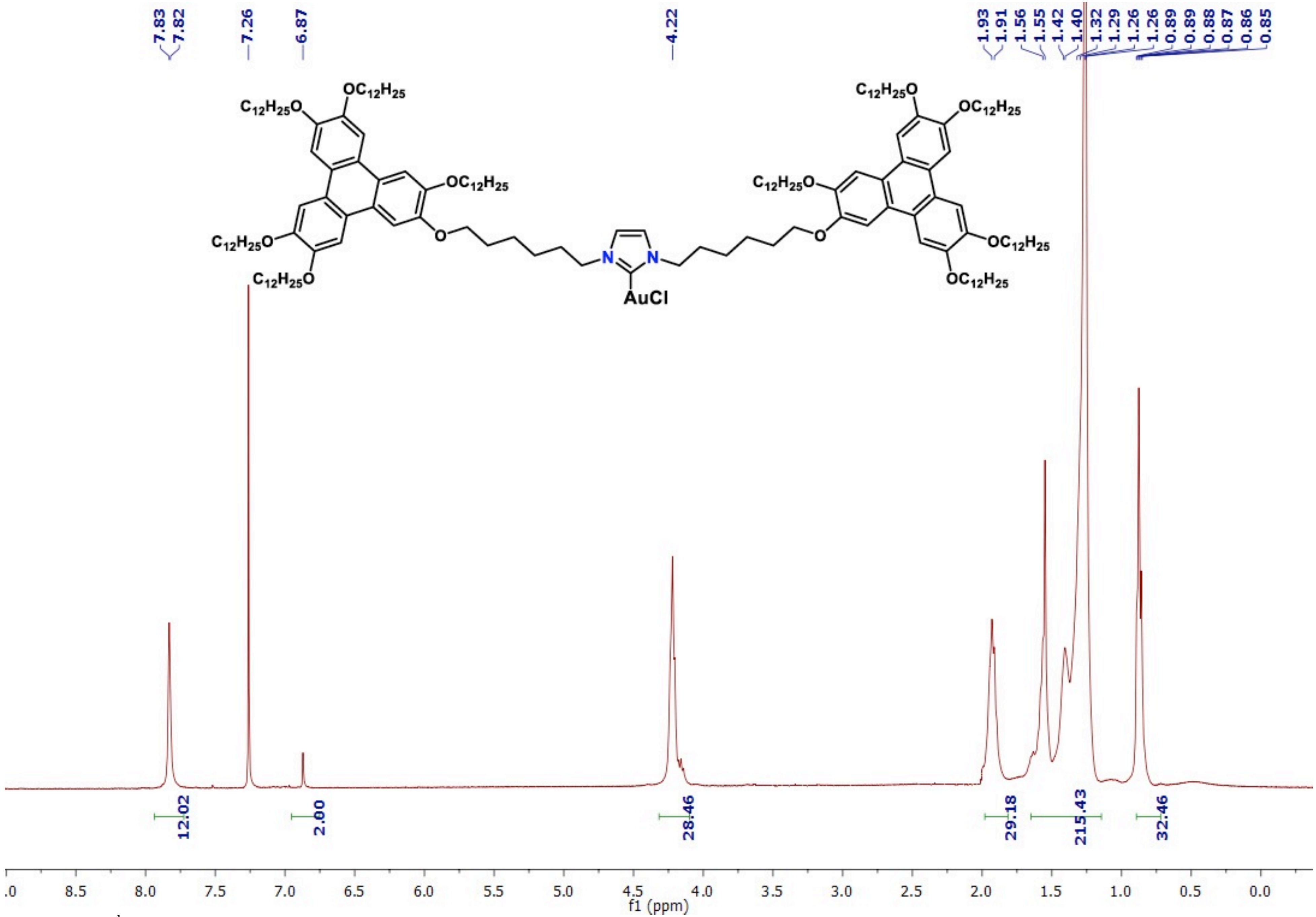

Figure S12. ^{1}H NMR (400.14 MHz) spectrum of **12** in $CDCl_3$.

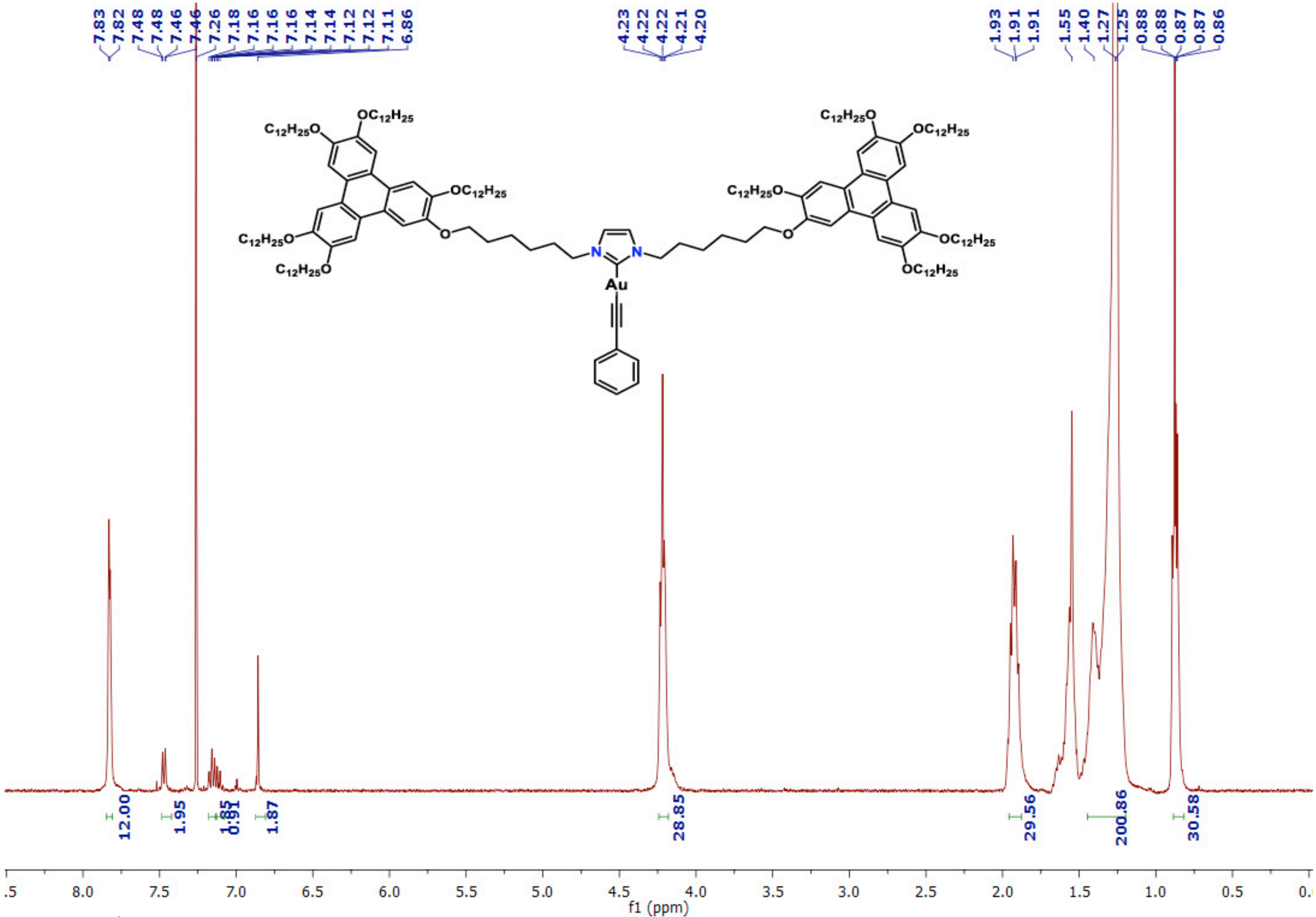

Figure S13. ^{1}H NMR (400.14 MHz) spectrum of **13** in $CDCl_3$.

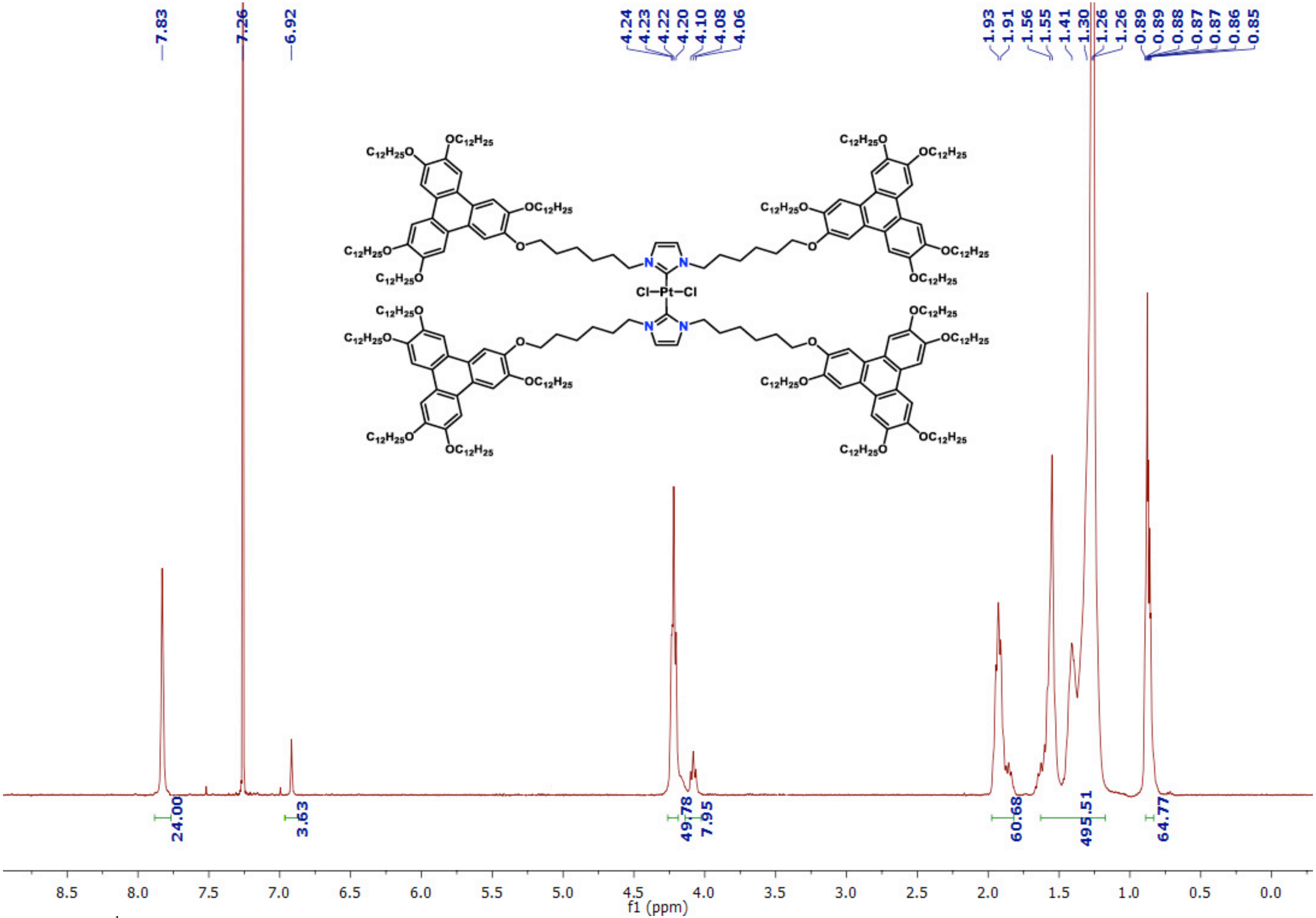

Figure S14. ^{1}H NMR (400.14 MHz) spectrum of **14** in $CDCl_3$.

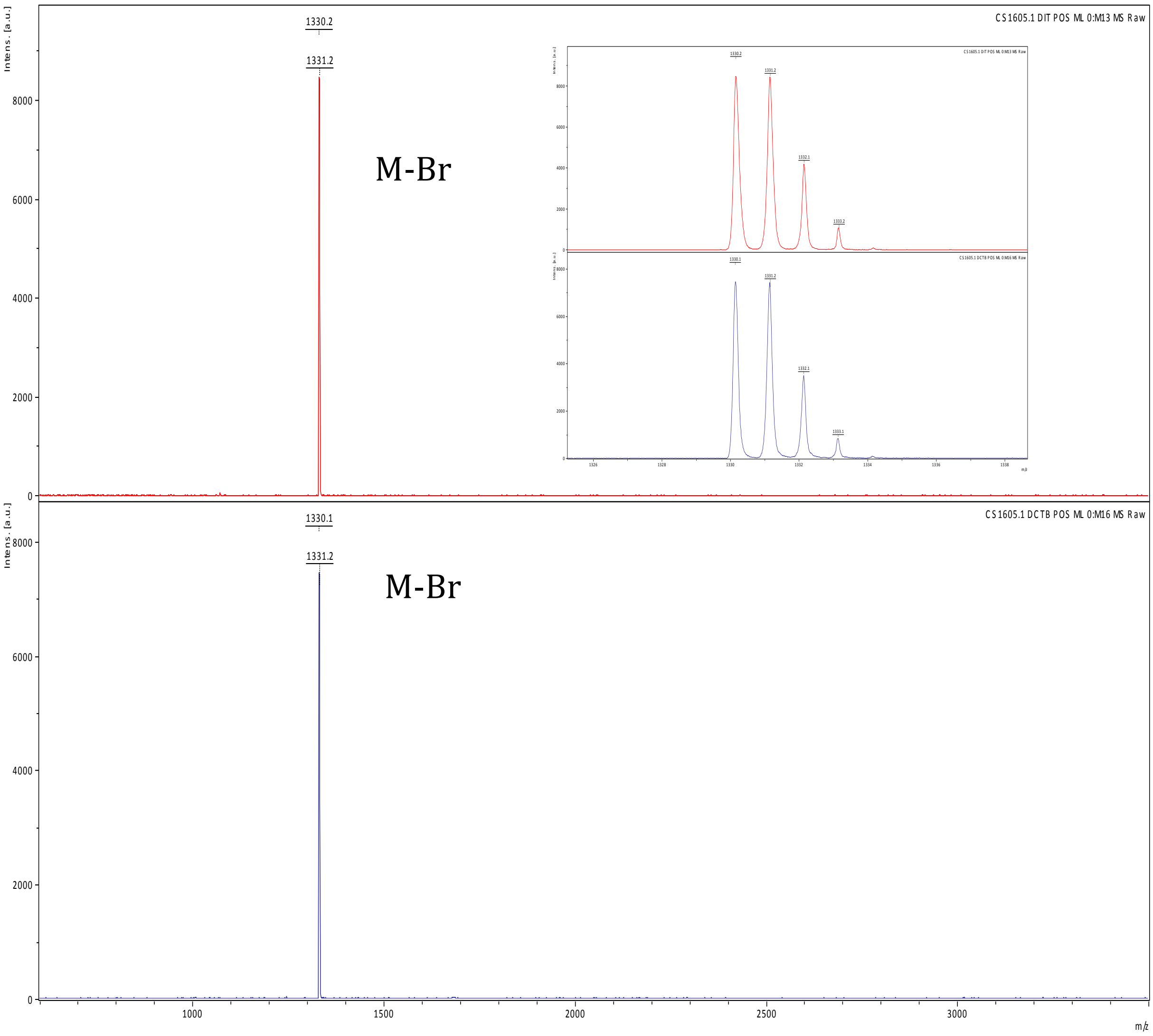

Figure S15. MALDI-TOF mass spectrum of compound **1**. Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

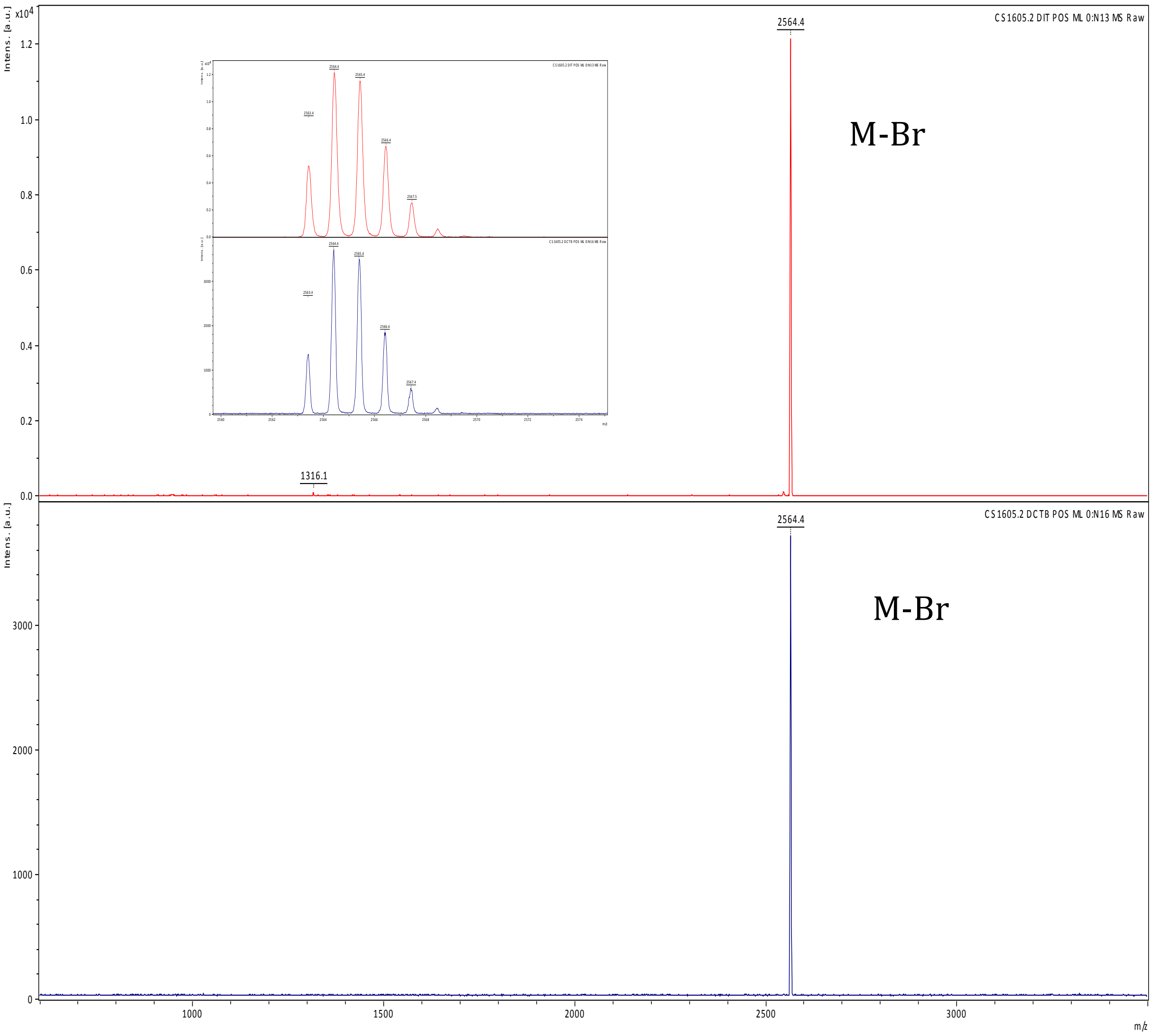

Figure S16. MALDI-TOF mass spectrum of compound **2**. Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

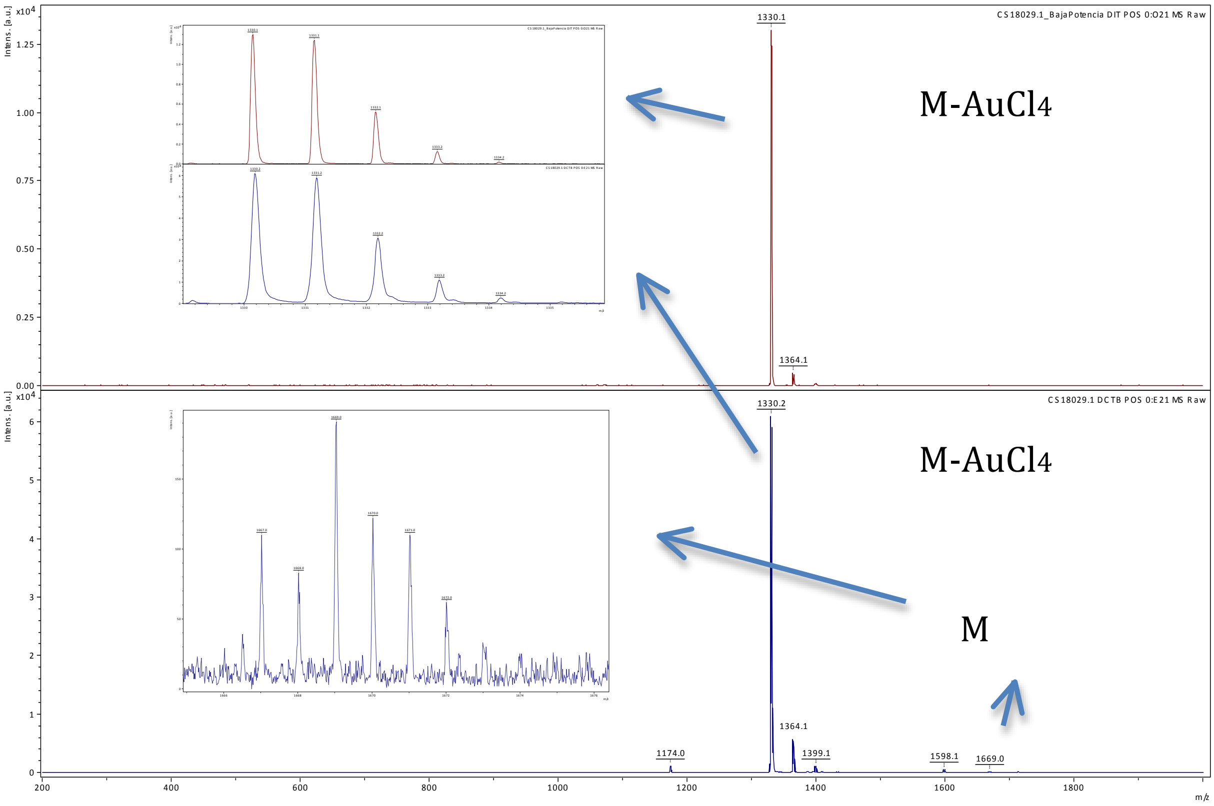

Figure S17. MALDI-TOF mass spectrum of compound **3** (positive m/z). Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

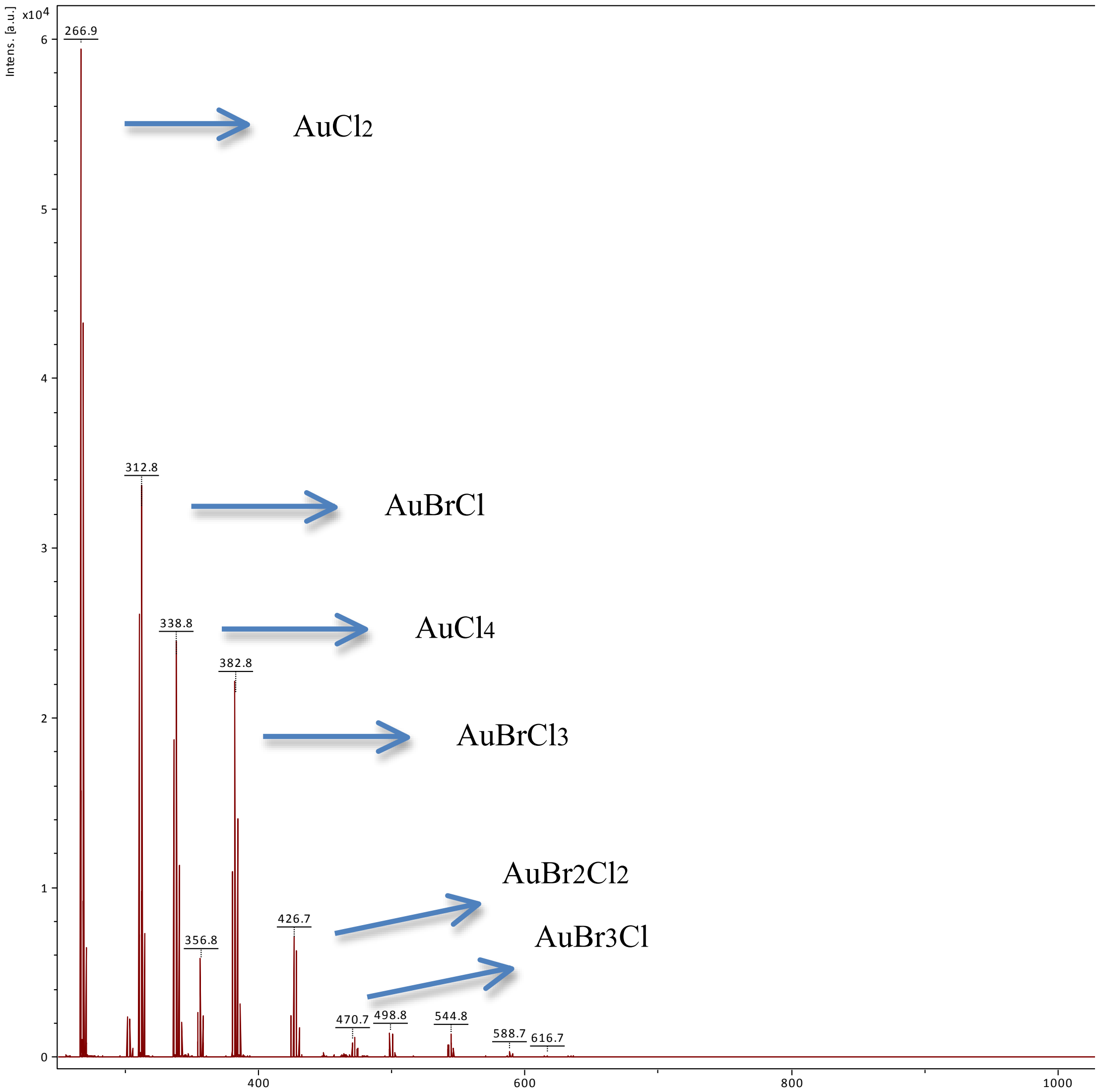

Figure S18. MALDI-TOF mass spectrum of compound **3** (negative m/z). Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

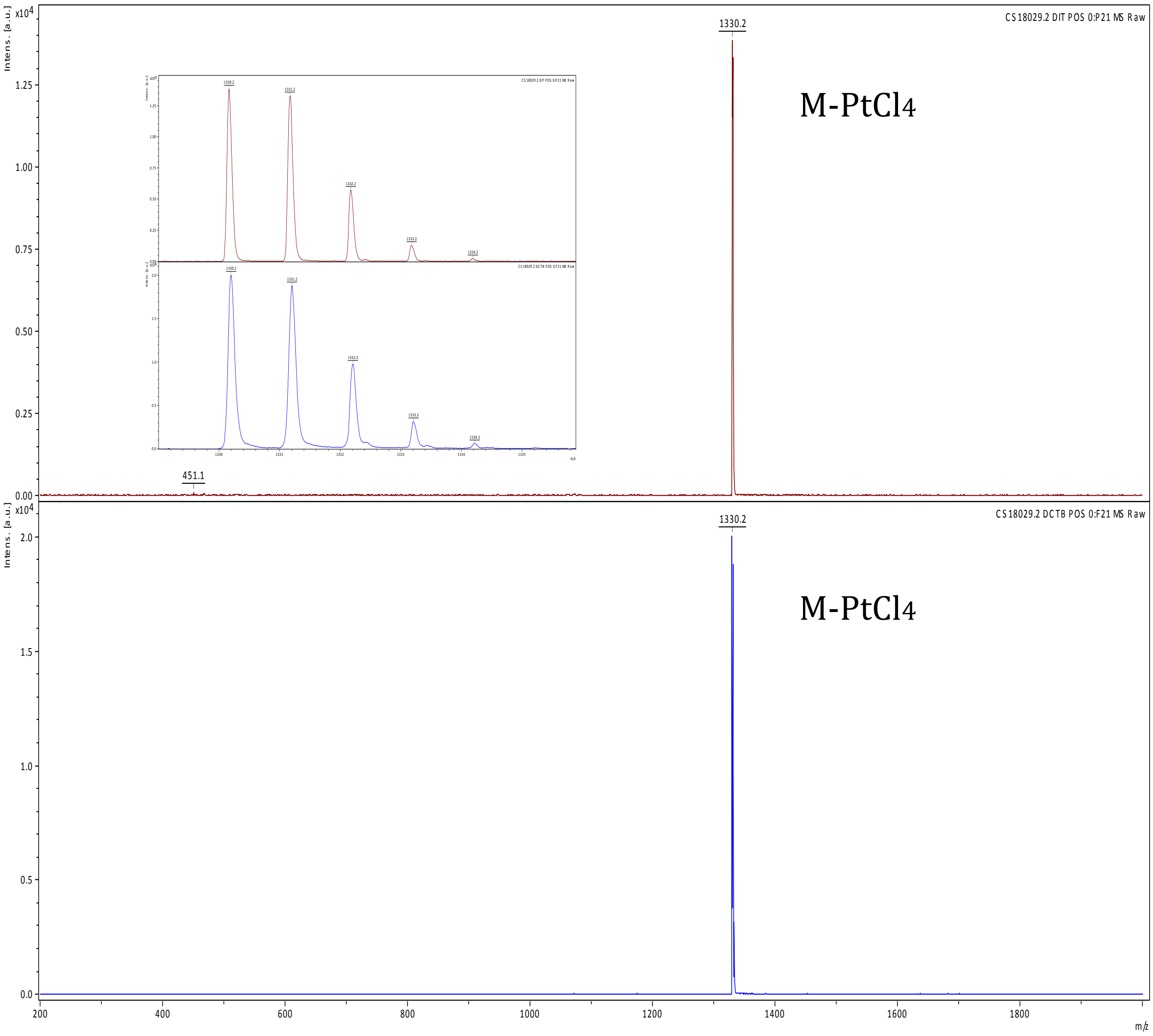

Figure S19. MALDI-TOF mass spectrum of compound **4**. Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

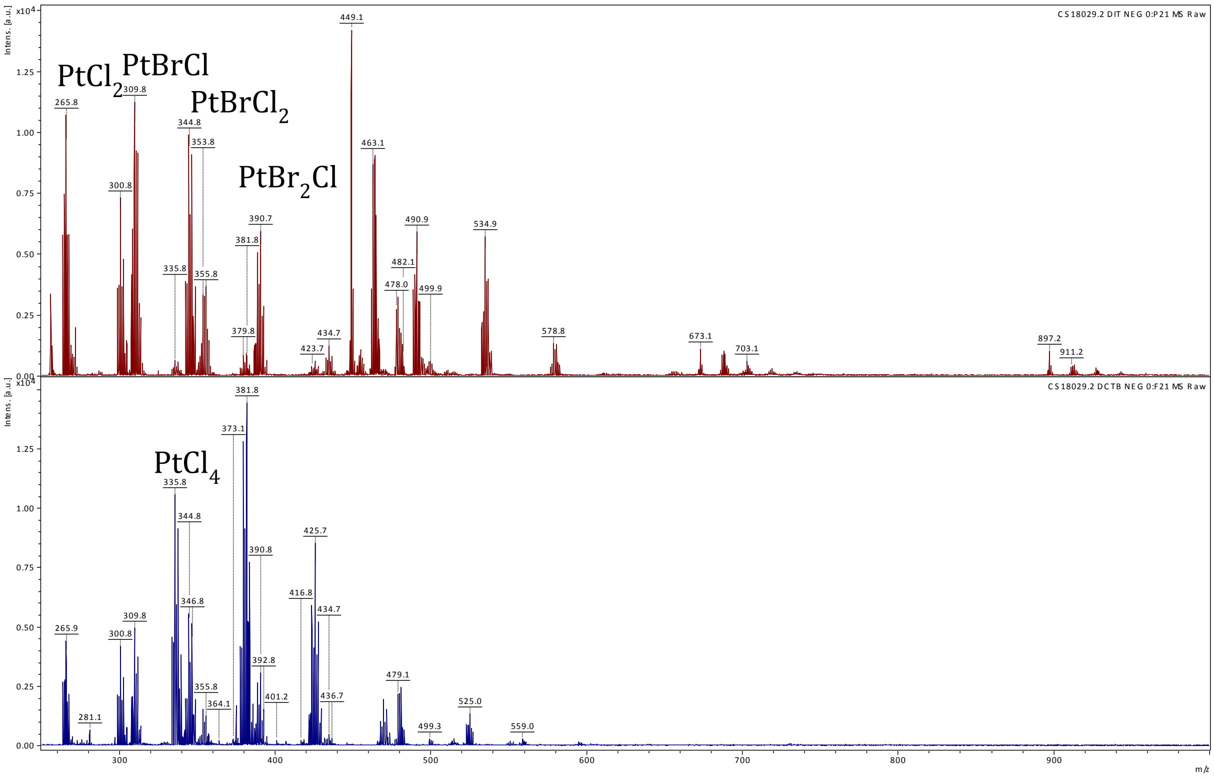

Figure S20. MALDI-TOF mass spectrum of compound **4** (m/z negative). Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

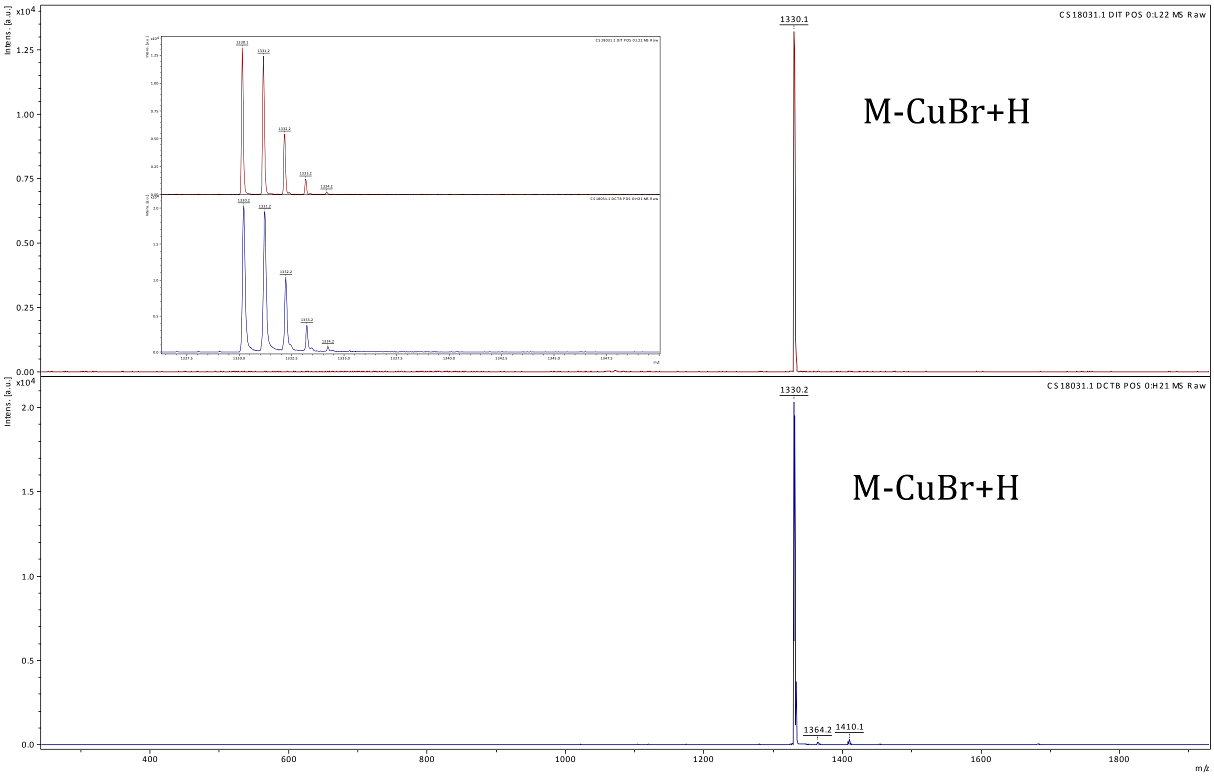

Figure S21. MALDI-TOF mass spectrum of compound **5**. Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

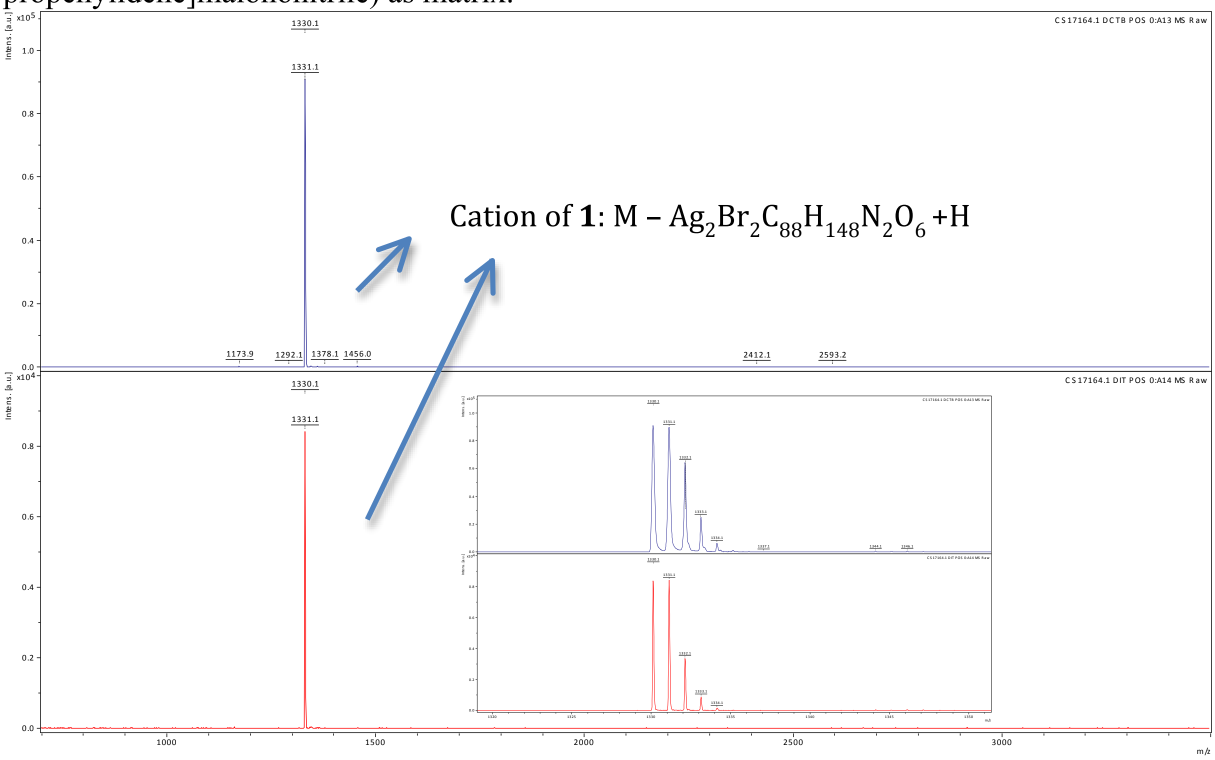

Figure S22. MALDI-TOF mass spectrum of compound **6**. Up (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix; down (red) with DIT (dithranol) as matrix.

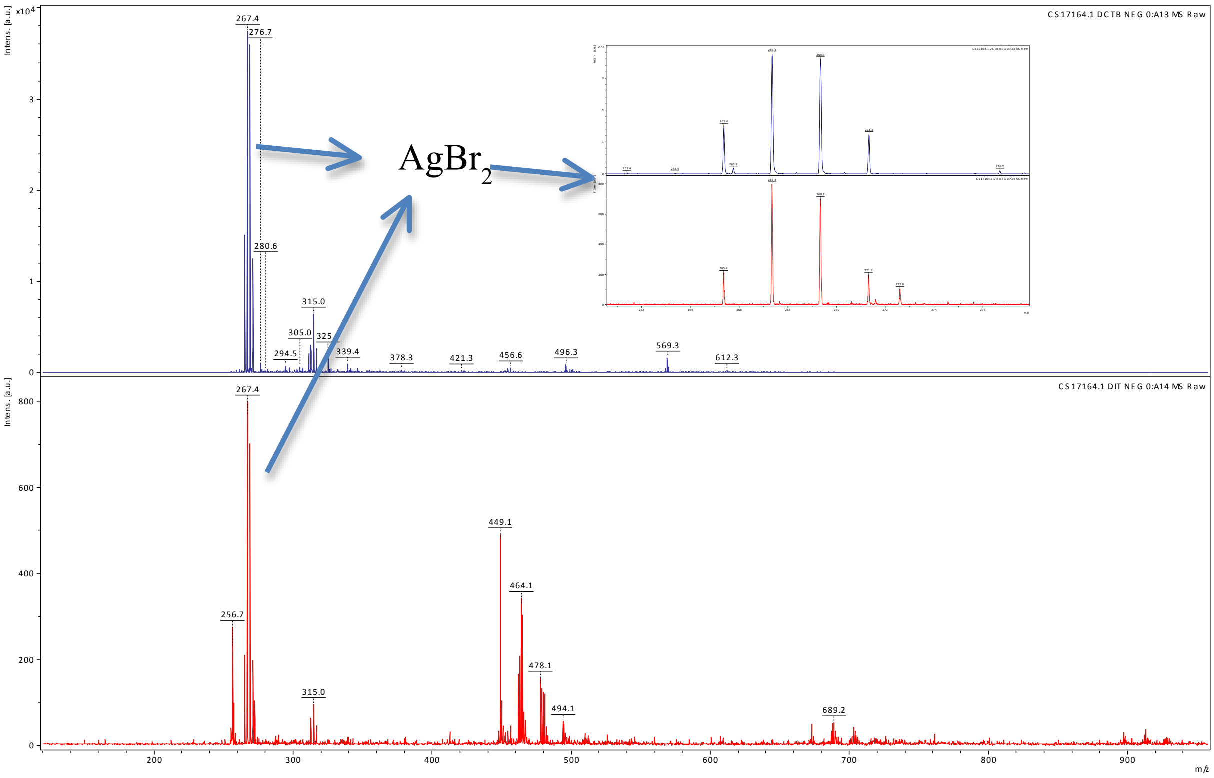

Figure S23. MALDI-TOF mass spectrum of compound **6** (m/z negative). Up (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix; down (red) with DIT (dithranol) as matrix.

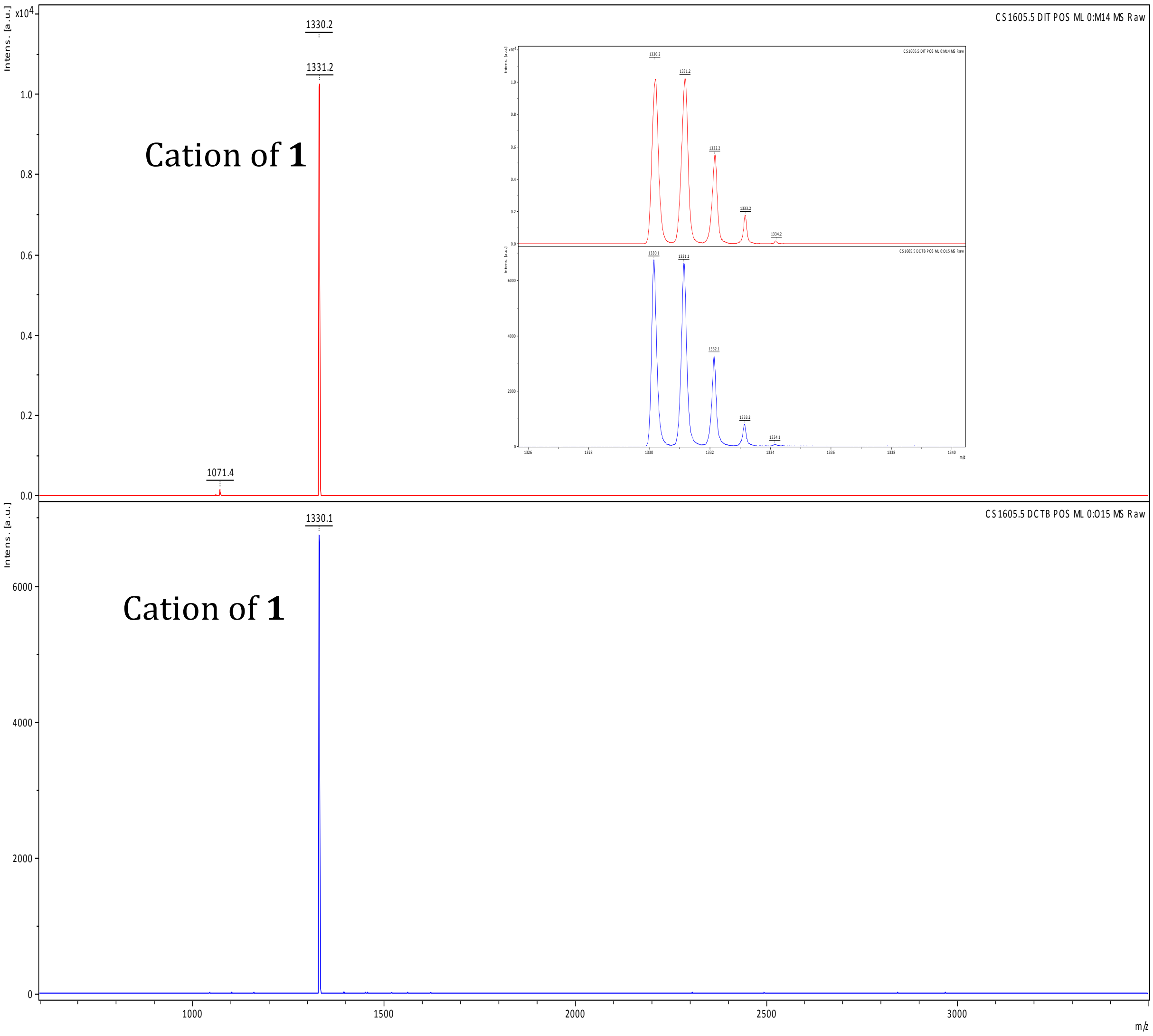

Figure S24. MALDI-TOF mass spectrum of compound **7**. Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

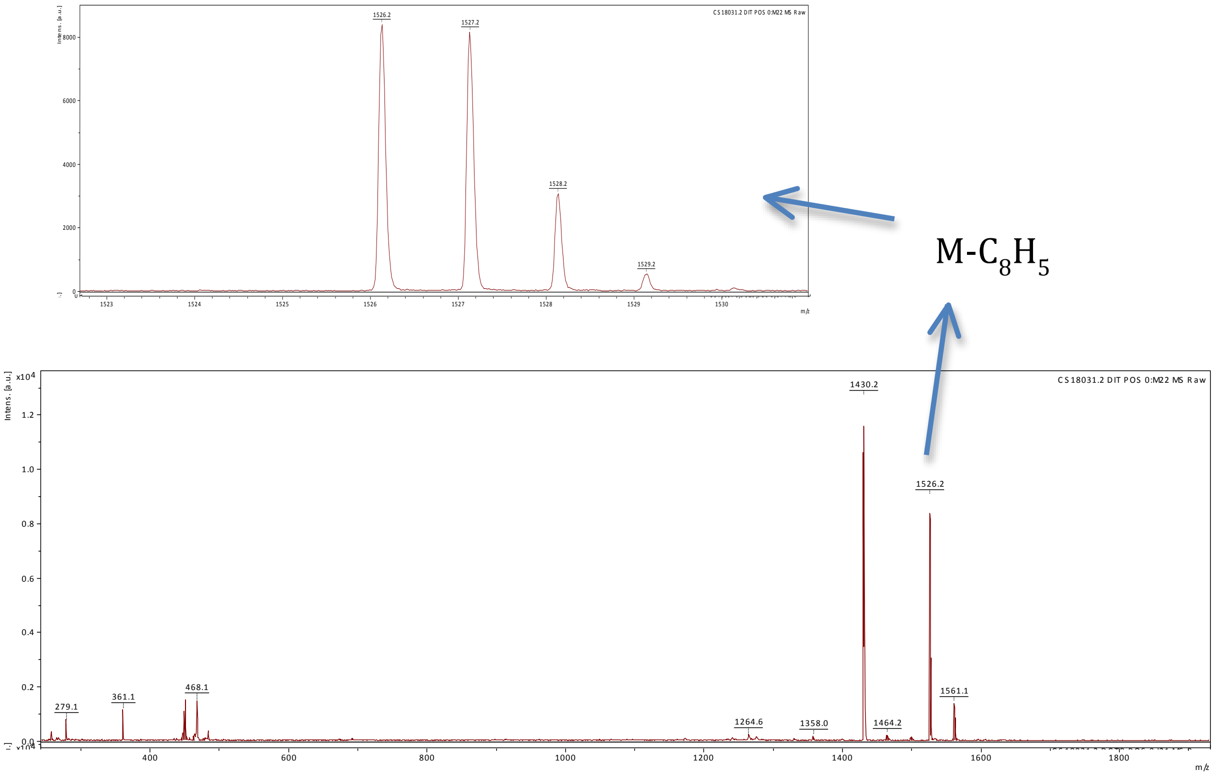

Figure S25. MALDI-TOF mass spectrum of compound **8** (DIT (dithranol) as matrix).

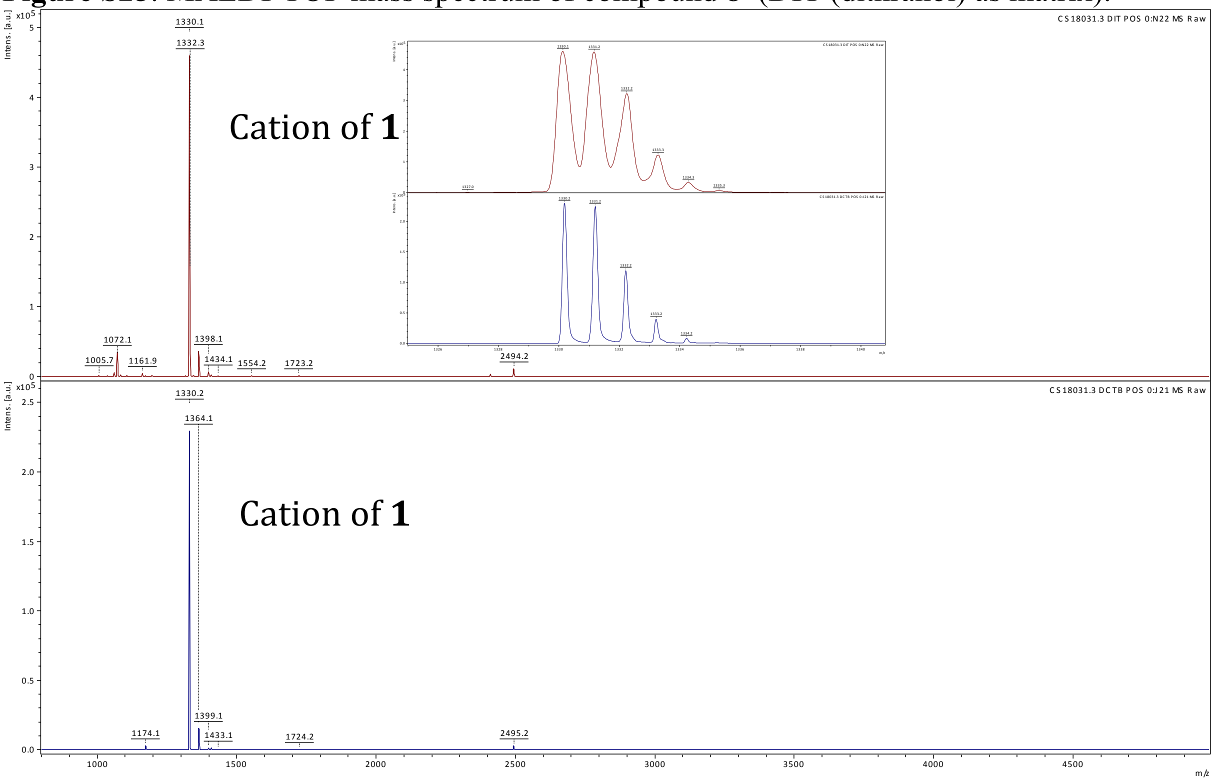

Figure S26. MALDI-TOF mass spectrum of compound **9**. Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

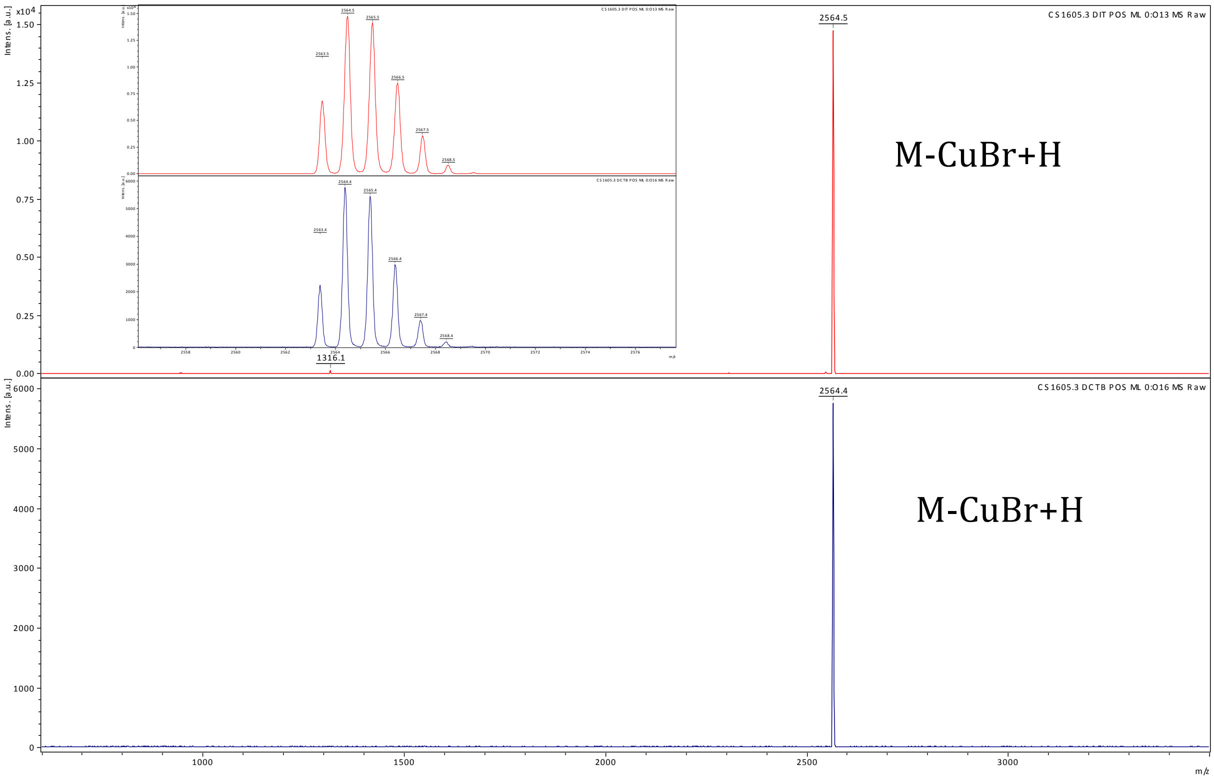

Figure S27. MALDI-TOF mass spectrum of compound **10**. Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

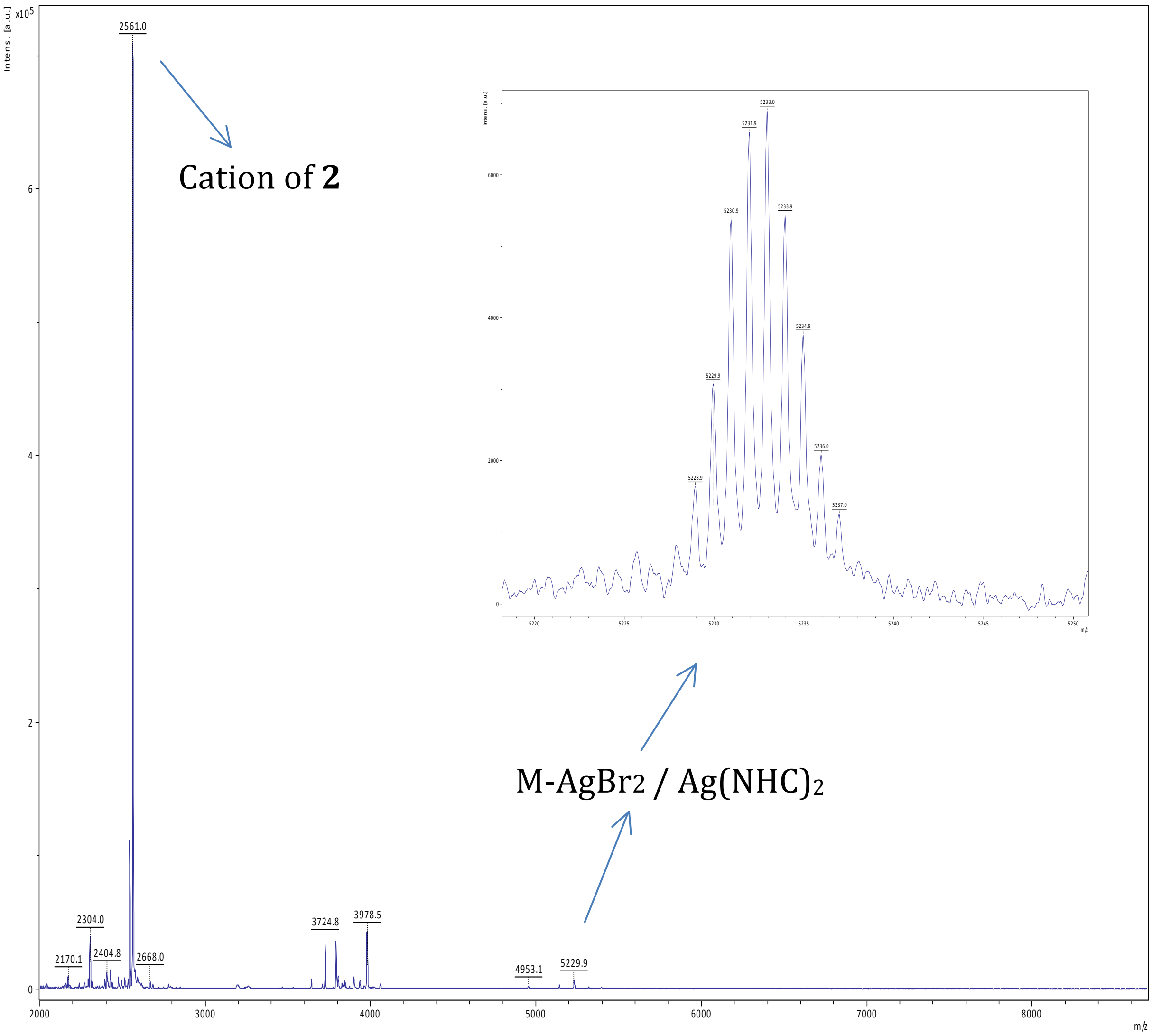

Figure S28. MALDI-TOF mass spectrum of compound **11**. DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

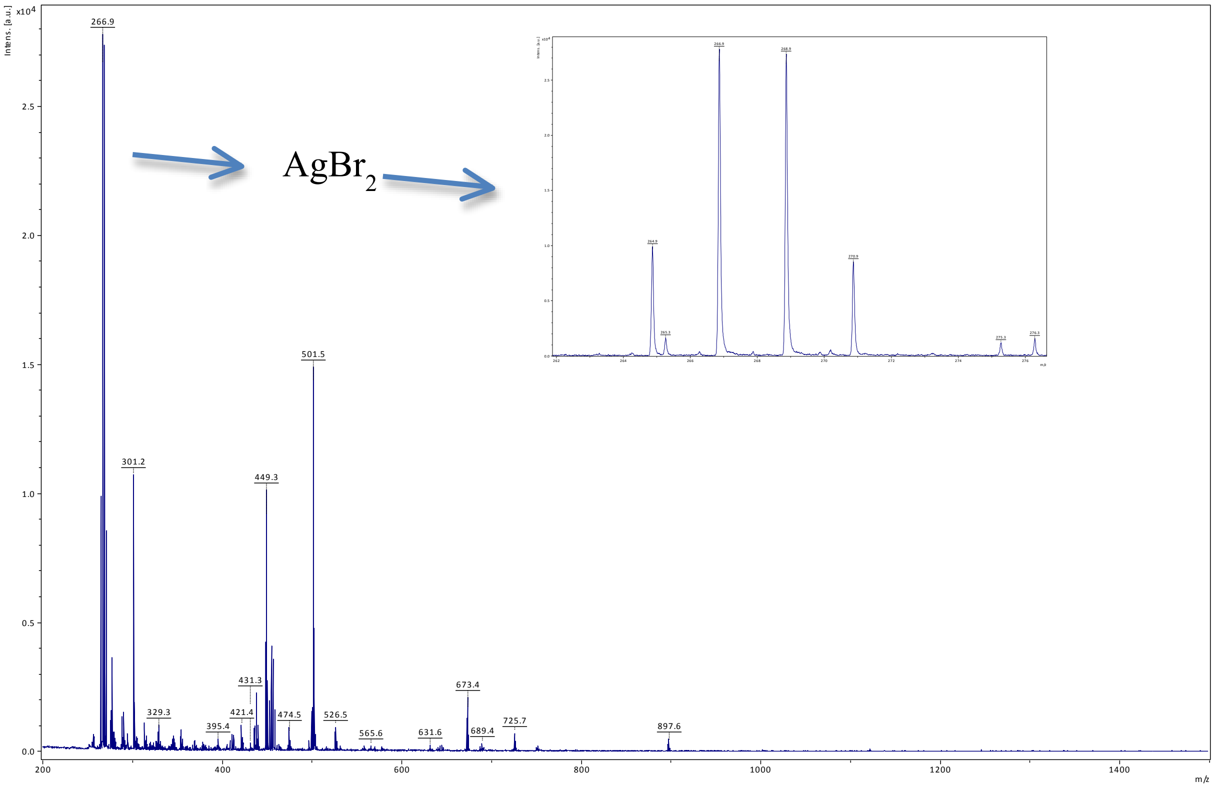

Figure S29. MALDI-TOF mass spectrum of compound **11** (m/z negative). DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

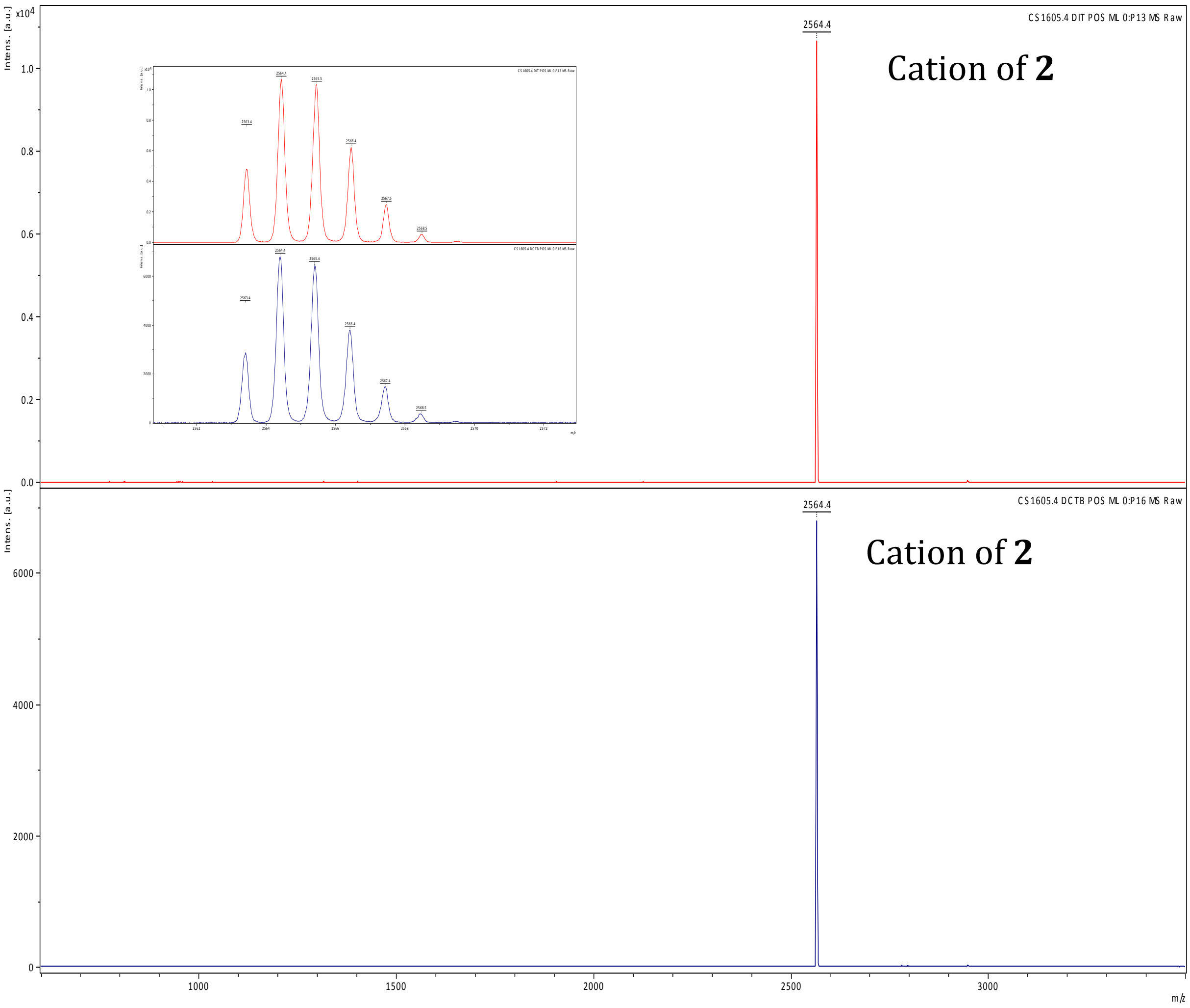

Figure S30. MALDI-TOF mass spectrum of compound **12**. Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

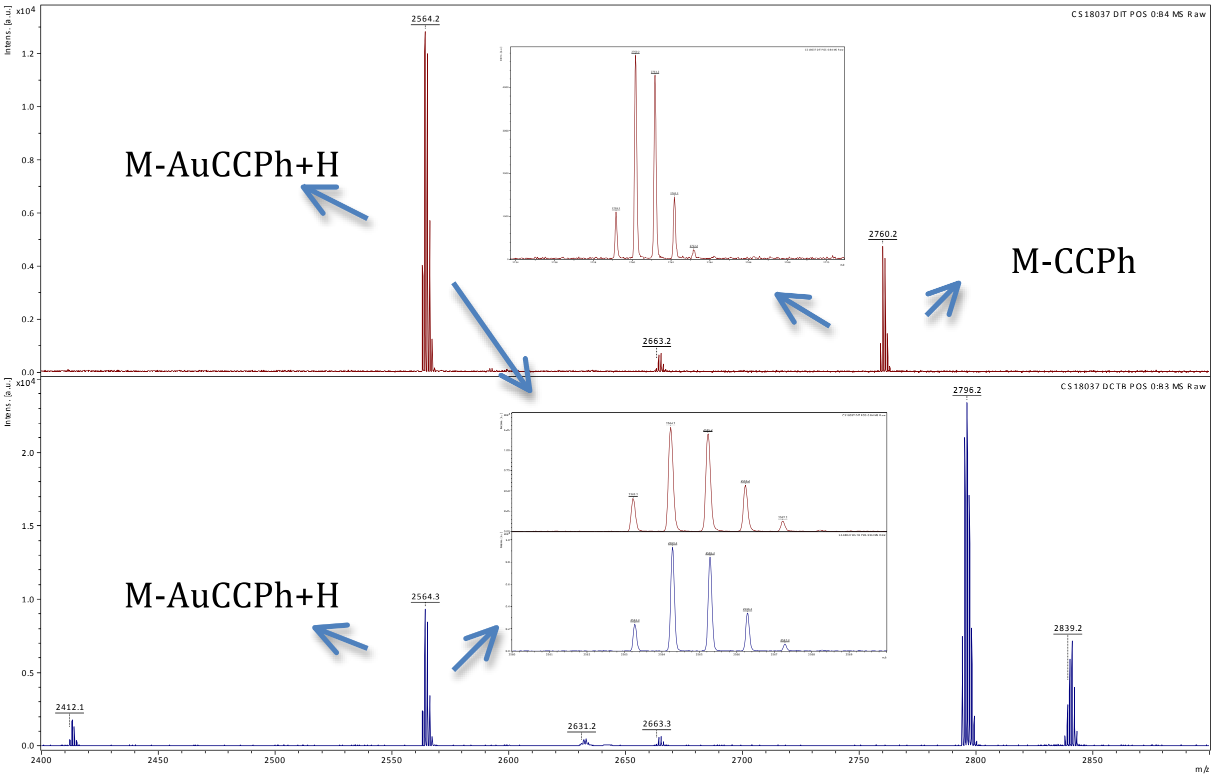

Figure S31. MALDI-TOF mass spectrum of compound **13**. Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

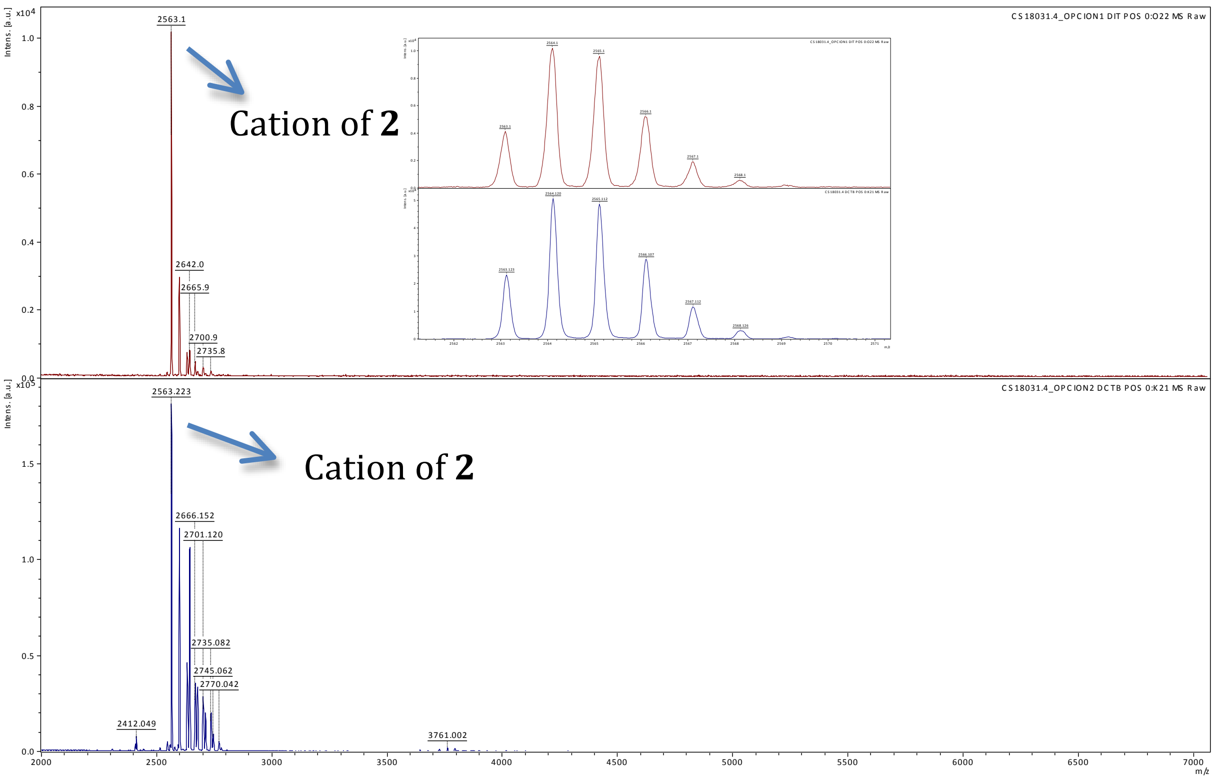

Figure S32. MALDI-TOF mass spectrum of compound **14**. Up (red) with DIT (dithranol) as matrix; down (blue) with DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.

DSC thermograms not included in the text.

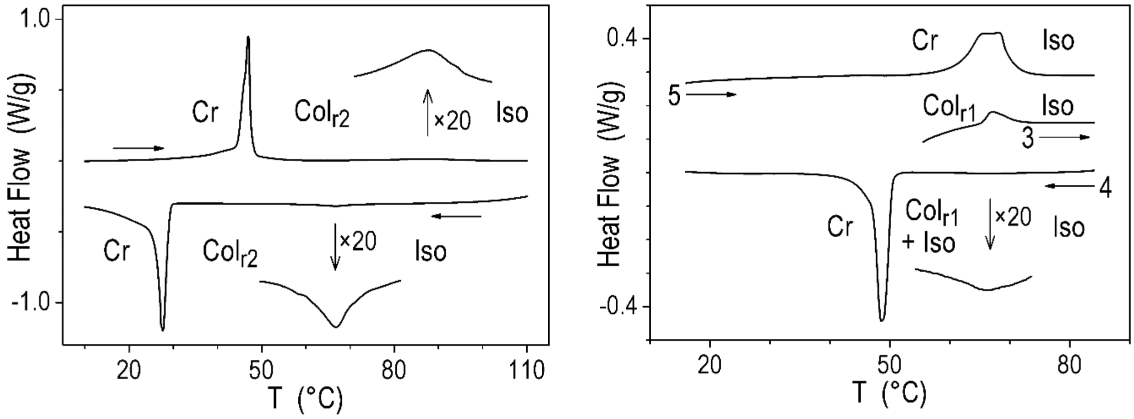

Fig. S33. DSC thermograms of imidazolium salts **2** (left) and **3** (right). It should be noted that to observe the mesophase-isotropic liquid transition for **3**, the DSC scans were adapted to the slow-developing and small range of the mesophase as follows: (1) first heating from 25 to 85 °C (10 °C/min); (2) first cooling from 85 to 62 °C (10 °C/min) holding for 3 minutes at 62 °C and then, cooling to 54 °C; (3) second heating from 54 to 85 °C (10 °C/min); (4) second cooling from 85 to 15 °C (10 °C/min); (5) final heating from 15 to 85 °C (2 °C/min). The three last scans are collected in Figure.

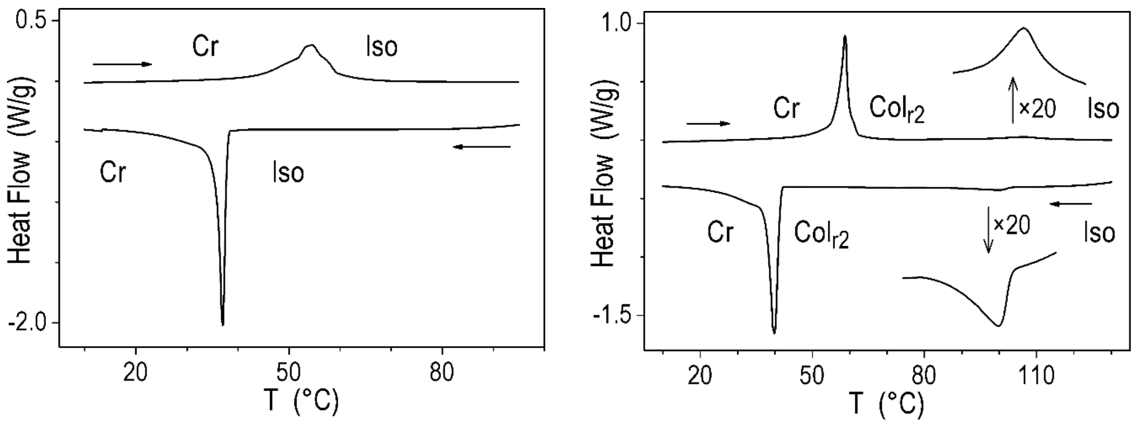

Fig. S34. DSC thermograms of copper carbene **5** (left) and silver carbene **6** (right).

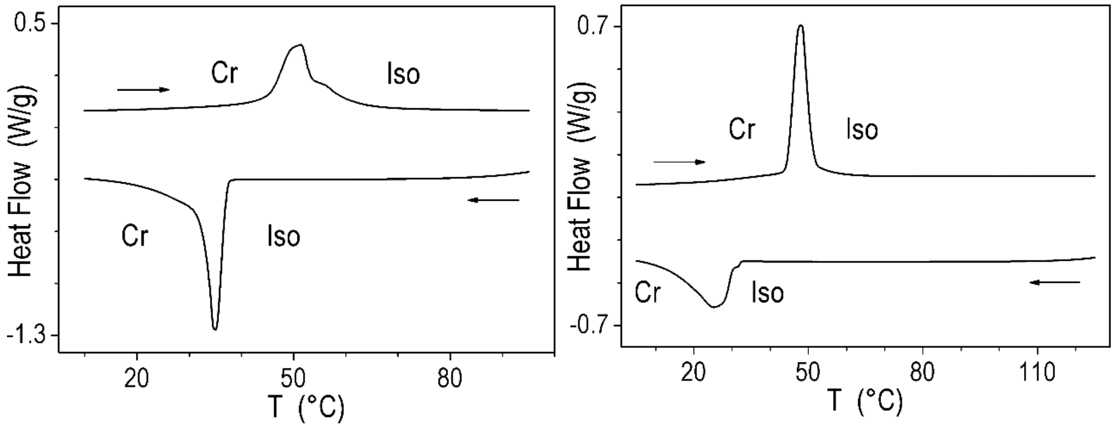

Fig. S35. DSC thermograms of gold carbenes **7** (left) and **8** (right).

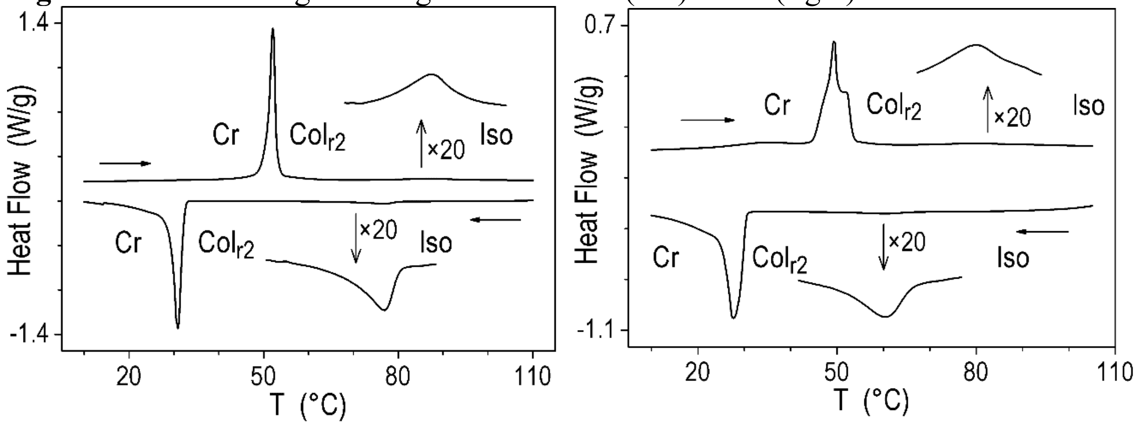

Fig. S36. DSC thermograms of platinum carbene **9** (left) and copper carbene **10** (right).

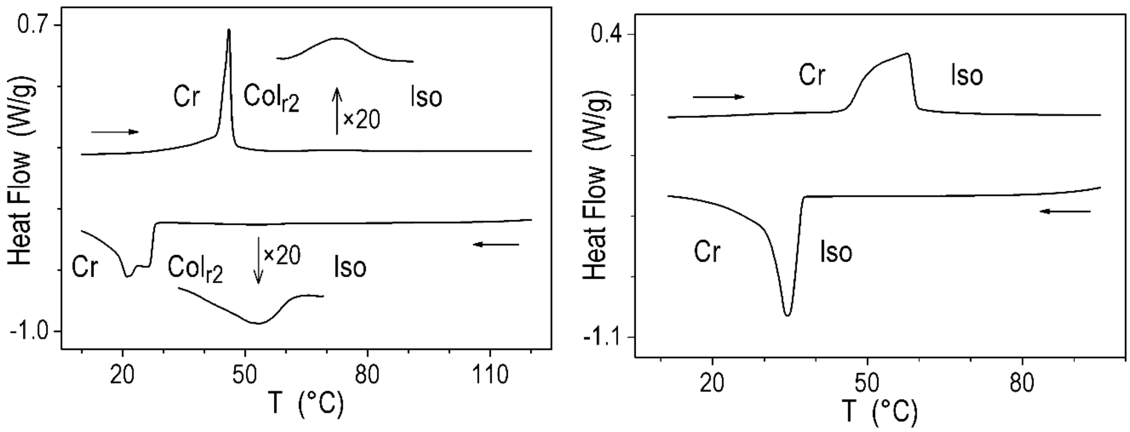

Fig. S37. DSC thermograms of silver carbene **11** (left) and gold carbene **12** (right).

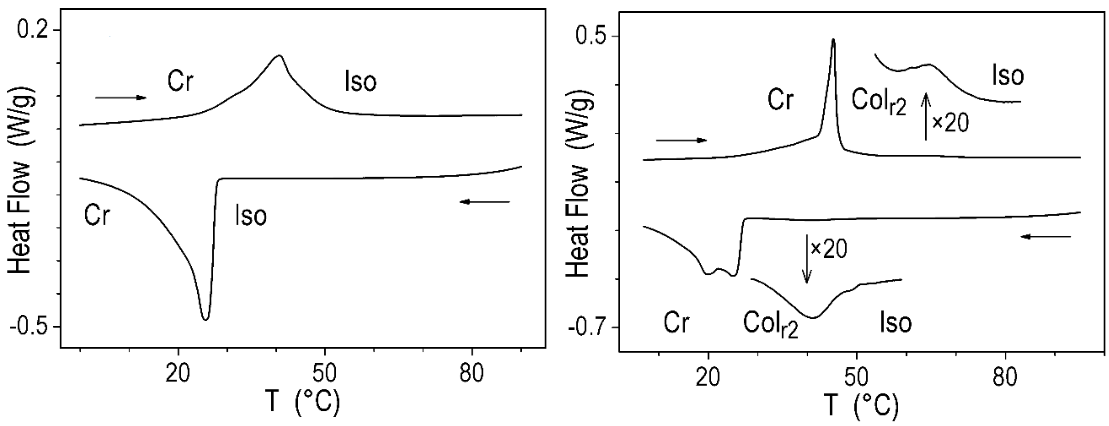

Fig. S38. DSC thermograms of gold carbene **13** (left) and platinum carbene **14** (right).

Table S1. Indexation tables for imidazolium ligands and carbenes.

[a,b]: measured Bragg angles and spacings; [c]: intensity (VS: very strong, S: strong, M: medium, W: weak, VW: very weak); [d]: Miller indices; [e,f]: calculated Bragg angles and spacings

I. Col$_{r1}$ phase

1; T = 70°C

N°	2θ$_{meas}$[°][a]	d$_{meas}$[Å][b]	Intens[c]	*hk*[d]	2θ$_{calc}$[°][e]	d$_{calc}$[Å][f]
1	1.76	50.1	VS	11	1.766	49.97
2	2.07	42.7	S	20	2.069	42.66
3	2.86	30.9	M	02	2.863	30.83
4	3.44	25.7	VW	31	3.419	25.82
5	3.53	25.0	S	22	3.533	24.99
6	4.14	21.31	M	40	4.139	21.327
7	4.43	19.93	M	13	4.418	19.982
8	5.37	16.44	W	51	5.370	16.444
9	5.72	15.43	VW	04	5.728	15.415

a = 85.3(1) Å; b = 61.6(6) Å; A = 5260 Å^2

3; T = 60°C

N°	2θ$_{meas}$ [°]	d$_{meas}$ [Å]	Intens	*hk*	2θ$_{calc}$ [°]	d$_{calc}$ [Å]
1	1.77	49.9	VS	11	1.775	49.73
2	2.07	42.5	S	20	2.073	42.57
3	2.86	30.9	M	02	2.881	30.64
4	3.59	24.6	M	22	3.550	24.87
5	4.14	21.3	W	40	4.147	21.29
6	4.43	19.9	VW	13	4.445	19.86

a = 85.1(5) Å; b = 61.2(7) Å; A = 5217 Å^2

4; T = 60°C

N°	2θ$_{meas}$ [°]	d$_{meas}$ [Å]	Intens	*hk*	2θ$_{calc}$ [°]	d$_{calc}$ [Å]
1	1.76	50.1	VS	11	1.774	49.76
2	2.07	42.5	S	20	2.081	42.42
3	2.87	30.8	M	02	2.874	30.72
4	3.44	25.6	VW	31	3.436	25.69
5	3.56	24.8	M	22	3.548	24.88
6	4.16	21.21	M	40	4.162	21.210
7	4.44	19.90	M	13	4.435	19.905
8	5.40	16.34	W	51	5.399	16.355
9	5.76	15.34	VW	04	5.750	15.357

a = 84.8(4) Å; b = 61.4(3) Å; A = 5212 Å^2

II. Col$_h$ phase

4; T = 110°C

N°	2θ$_{meas}$ [°]	d$_{meas}$ [Å]	Intens	*hk*	2θ$_{calc}$ [°]	d$_{calc}$ [Å]
1	2.04	43.2	VS	10	2.041	43.24
2	3.55	24.9	VW	11	3.535	24.97

$a = b$ = 49.9(3) Å; γ = 120°; A = 2159 Å^2

Rectangular coordinates: $a_r = a\sqrt{3}$ = 86.4(9) Å; $b_r = a$ = 49.9(3) Å; A = 4319 Å^2

III. Col$_{r2}$ phase

2; T = 70°C

N°	2θ$_{meas}$ [°]	d$_{meas}$ [Å]	Intens	*hk*	2θ$_{calc}$ [°]	d$_{calc}$ [Å]
1	1.87	47.1	S	01	1.876	47.04
2	2.17	40.7	VS	11/20	2.170/2.181	40.67/40.48
3	2.88	30.7	S	21	2.877	30.68
4	3.76	23.50	VS	02/31	3.753/3.771	23.520/23.408
5	4.75	18.59	M	41	4.749	18.592
6	5.75	15.3	VW	13/42/51	5.736/5.756/5.767	15.394/15.342/15.310
7	6.04	14.63	W	23	6.039	14.621
8	6.53	13.52	W	33/60	6.514/6.545	13.558/13.493

a = 80.9(6) Å; b = 47.0(4) Å; A = 3808 Å^2

6; T = 70°C

N°	2θ$_{meas}$ [°]	d$_{meas}$ [Å]	Intens	*hk*	2θ$_{calc}$ [°]	d$_{calc}$ [Å]
1	1.80	49.0	S	01	1.801	49.02
2	2.09	42.1	VS	11/20	2.086/2.106	42.31/41.91
3	2.77	31.9	S	21	2.771	31.85
4	3.63	24.32	S	02/31	3.602/3.637	24.510/24.274
5	4.20	21.0	VW	22/40	4.172/4.213	21.1575/20.955
6	4.58	19.26	M	41	4.582	19.268
7	4.80	18.4	VW	32	4.792	18.425
8	5.55	15.9	VW	13/42/51	5.506/5.544/5.567	16.038/15.927/15.862
9	5.85	15.1	VW	23	5.800	15.224
10	6.32	13.96	W	33/60	6.261/6.321	14.105/13.970

a = 83.8(2) Å; b = 49.0(2) Å; A = 4109 Å^2

10; T = 50°C

N°	2θ$_{meas}$ [°]	d$_{meas}$ [Å]	Intens	*hk*	2θ$_{calc}$ [°]	d$_{calc}$ [Å]
1	1.87	47.3	S	01	1.867	47.29
2	2.16	40.8	VS	11/20	2.161/2.179	40.84/40.51
3	2.87	30.8	S	21	2.869	30.77
4	3.76	23.46	VS	02/31	3.734/3.764	23.64/23.45
5	4.74	18.61	M	41	4.742	18.62
6	6.02	14.7	VW	23	6.011	14.69
7	6.52	13.54	W	33/60	6.487/6.540	13.61/13.50
8	7.1	12.4	VW	43	7.100	12.44

a = 81.0(2) Å; *b* = 47.2(9) Å; *A* = 3831 Å^2

11; T = 50°C

N°	2θ$_{meas}$ [°]	d$_{meas}$ [Å]	Intens	*hk*	2θ$_{calc}$ [°]	d$_{calc}$ [Å]
1	1.87	47.3	S	01	1.865	47.33
2	2.16	40.8	VS	11/20	2.159/2.176	40.88/40.56
3	2.86	30.8	S	21	2.867	30.80
4	3.76	23.50	S	02/31	3.730/3.760	23.66/23.48
5	4.36	20.26	VW	22/40	4.319/4.354	20.44/20.28
6	4.74	18.61	M	41	4.737	18.639
7	4.97	17.76	VW	32	4.958	17.807
8	5.69	15.51	VW	13/42/51	5.702/5.735/5.754	15.486/15.398/15.346
9	6.03	14.66	VW	23	6.006	14.703
10	6.53	13.52	W	33/60	6.481/6.533	13.626/13.518

a = 81.1(1) Å; *b* = 47.3(3) Å; *A* = 3839 Å^2

9; T = 70°C

N°	2θ$_{meas}$ [°]	d$_{meas}$ [Å]	Intens	*hk*	2θ$_{calc}$ [°]	d$_{calc}$ [Å]
1	1.81	48.6	S	01	1.817	48.57
2	2.10	42.0	VS	11/20	2.100/2.106	42.03/41.92
3	2.78	31.7	S	21	2.782	31.73
4	3.64	24.28	S	02/31	3.635/3.645	24.28/24.22
5	4.22	20.94	W	22/40	4.201/4.213	21.01/20.96
6	4.59	19.22	M	41	4.588	19.242
7	4.82	18.3	VW	32	4.817	18.330
8	5.55	15.9	VW	13/42/51	5.555/5.565/5.571	15.896/15.866/15.848
9	5.82	15.2	VW	23	5.847	15.103
10	6.34	13.93	W	33/60	6.304/6.321	14.009/13.972
11	7.31	12.1	VW	04/62	7.274/7.293	12.142/12.110

a = 83.8(3) Å; *b* = 48.5(7) Å; *A* = 4072 Å^2

14; T = 55°C

N°	$2\theta_{meas}$ [°]	d_{meas} [Å]	Intens	*hk*	$2\theta_{calc}$ [°]	d_{calc} [Å]
1	1.87	47.1	S	01	1.880	46.96
2	2.17	40.7	VS	11/20	2.173/2.181	40.62/40.48
3	2.87	30.8	S	21	2.879	30.66
4	3.76	23.5	S	02/31	3.760/3.773	23.48/23.40
5	4.75	18.58	M	41	4.751	18.585
6	5.00	17.65	VW	32	4.985	17.713
7	6.04	14.62	VW	23	6.048	14.600
8	6.54	13.50	W	33/60	6.522/6.546	13.540/13.492

a = 80.9(5) Å; *b* = 46.9(6) Å; *A* = 3801 Å^2

X–ray diffraction patterns not included in the text.

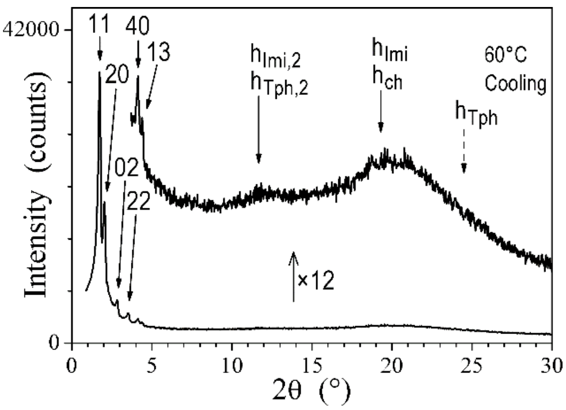

Fig. S39. X–ray diffraction pattern of imidazolium salt **3**.

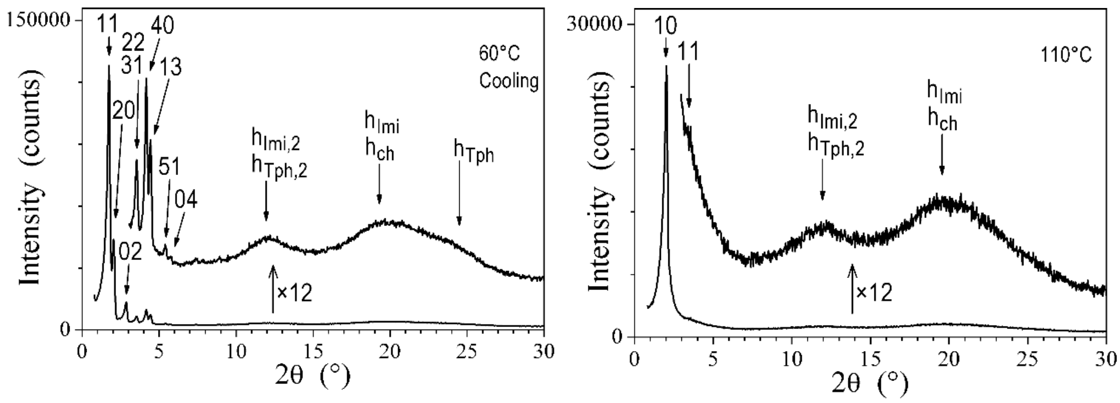

Fig. S40. X–ray diffraction patterns of imidazolium salt **4** at 60ºC cooling (left: $Colr_1$) and 110ºC heating (right: Col_h).

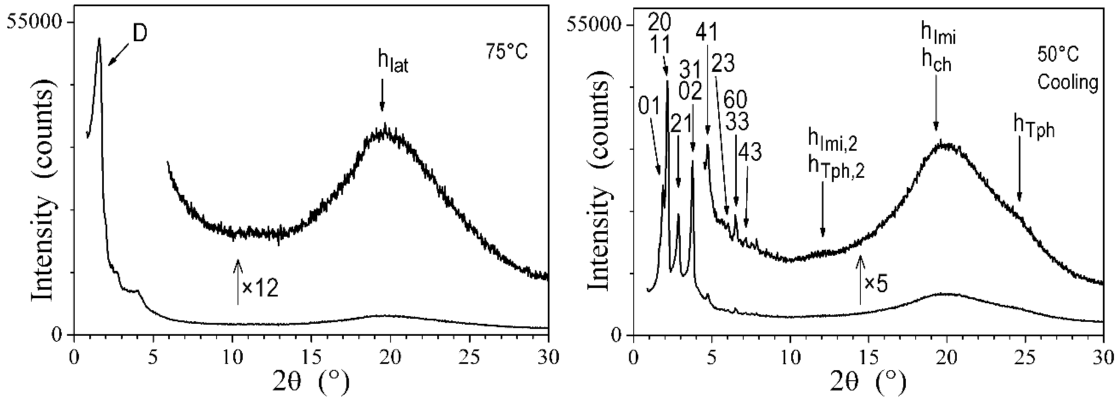

Fig. S41. X–ray diffraction patterns of copper carbenes **5** (left) and **10** (right).

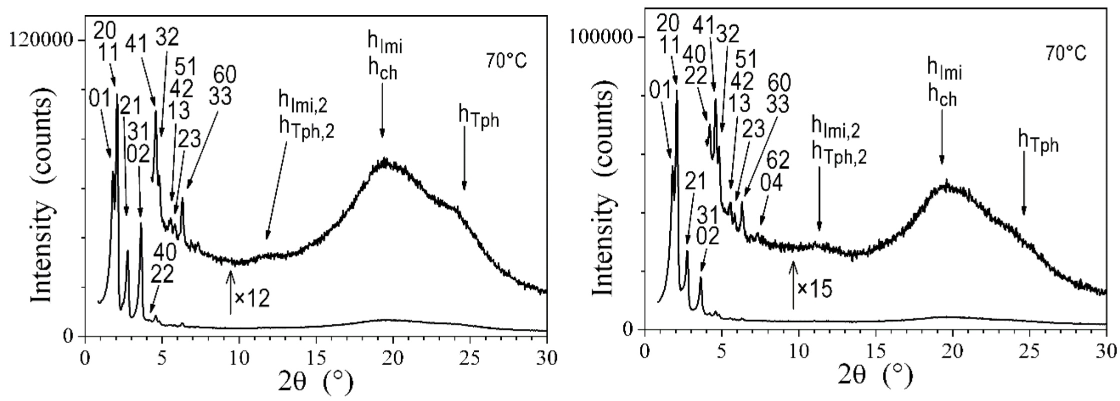

Fig. S42. X–ray diffraction patterns of silver carbene **6** (left), and platinum carbene **9** (right).

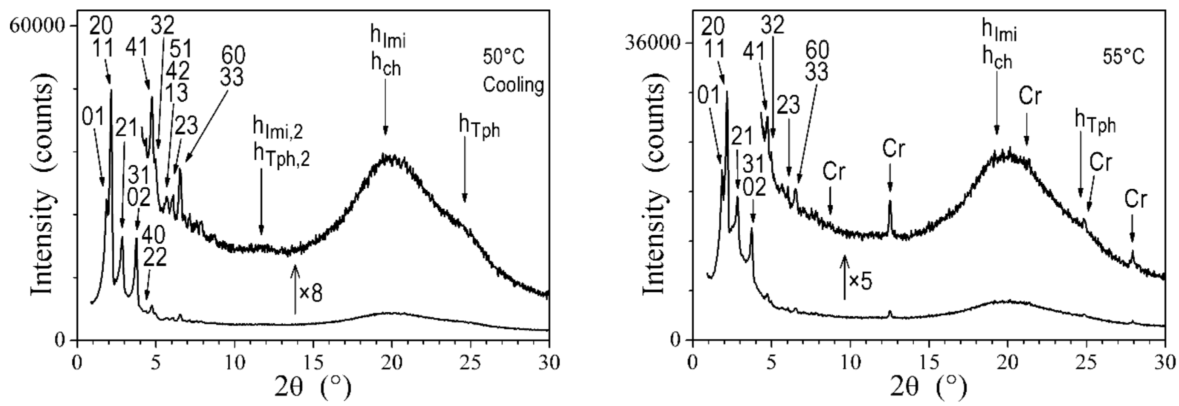

Fig. S43. X–ray diffraction patterns of silver carbene **11** (left) and platinum carbene **14** (right).

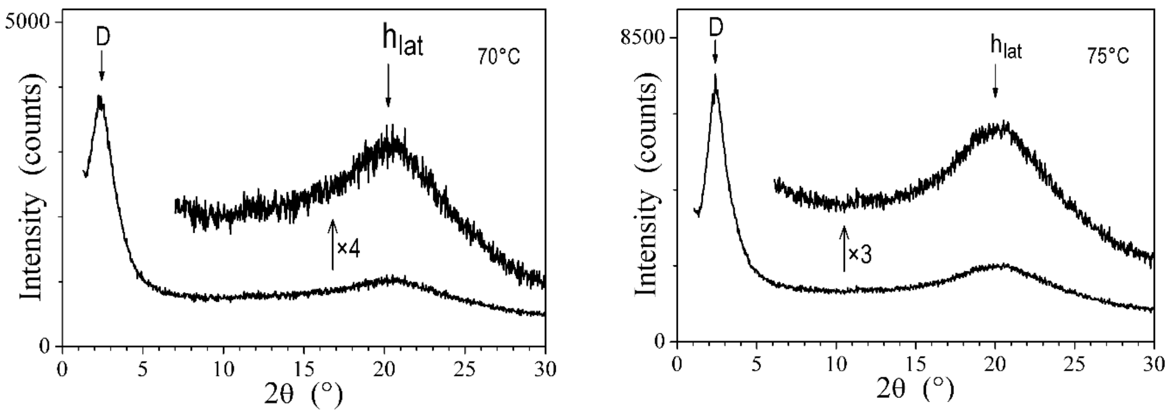

Fig. S44. X–ray diffraction patterns of chloro gold carbenes **7** (left) and **12** (right).

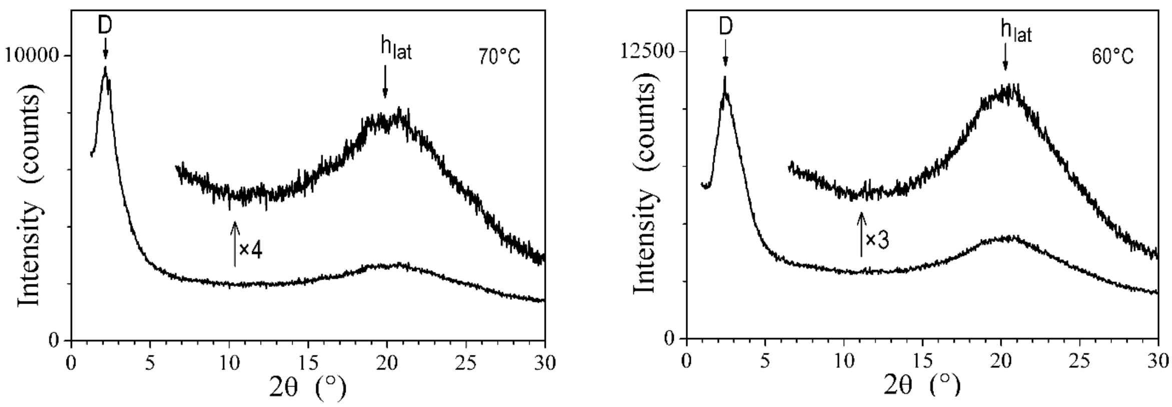

Fig. S45. X–ray diffraction patterns of acetylide gold carbenes **8** (left) and **13** (right).

Table S2. UV–visible data for compounds in dichloromethane solution at 298K.

Comp.	λ/nm (ε x10^{-3}/$M^{-1}cm^{-1}$)
1	346 (3.4), 308 (25.1), 279 (93.6)
2	346 (8.7), 308 (53.4), 279 (206.3)
3	346 (3.3), 308 (24.3), 279 (90.9)
4	346 (7.5), 308 (52.8), 279 (211.1)
5	346 (3.7), 308 (26.1), 279 (97.1)
6	346 (8.2), 308 (55.3), 279 (221.3)
7	346 (4.1), 308 (27.6), 279 (100.6)
8	346 (6.3), 308 (27.7), 279 (90.8)
9	346 (8.1), 308 (54.8), 279 (217.1)
10	346 (9.7), 308 (56.1), 279 (216.1)
11	346 (25.6), 308 (121.4), 279 (454.2)
12	346 (10.5), 308 (58.6), 279 (226.2)
13	346 (10.8), 308 (61.1), 279 (205.1)
14	346 (24.5), 308 (119.5), 279 (452.1)

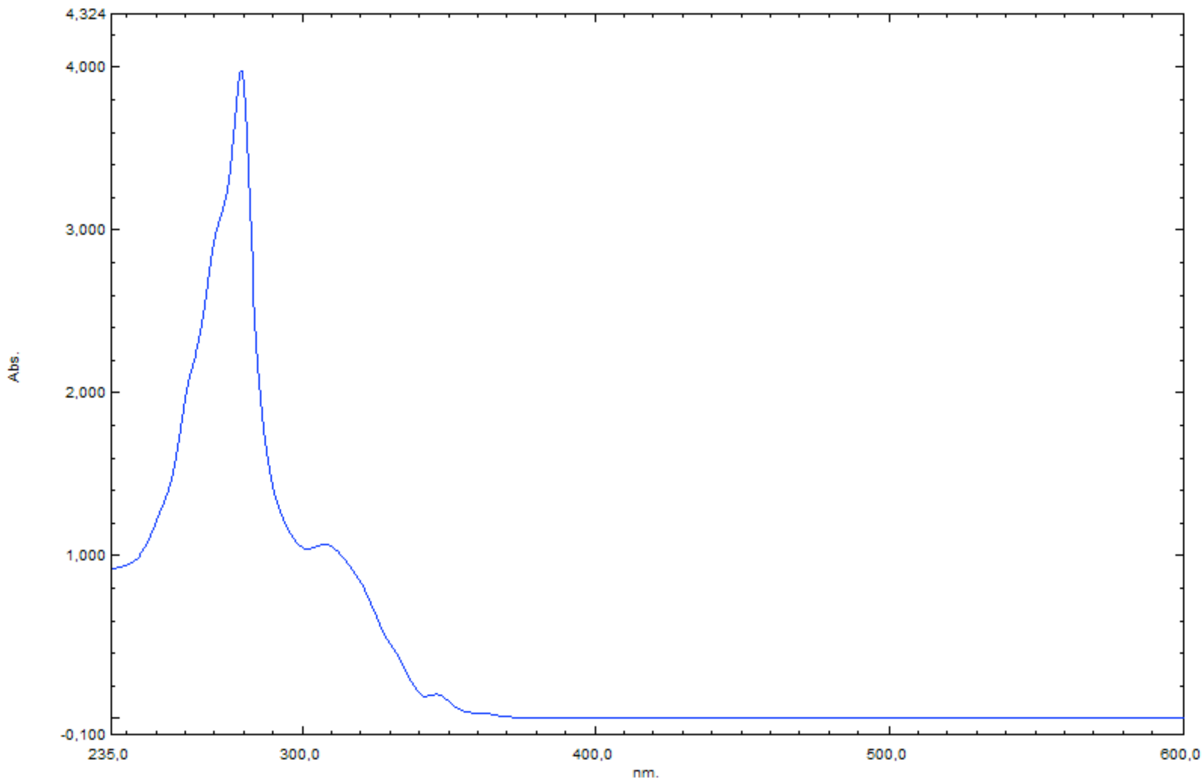

Fig. S46. Representative absorption spectrum. Absorption spectrum of compound **1**, recorded in dichloromethane solution (4.25x10^{-5}M) at room temperature.

Table S3. Excitation and emission data (nm) in KBr dispersion for prepared compounds.[a]

Comp.	**KBr 298 K**	
	λ_{exc}	λ_{emis}
1	292, 342	388, 405sh,
2	292, 342	388, 405sh,
3	270-360	387
4	270-360	387
5	278, 321, 345	369, 387
6	280, 291, 330, 341	387, 404sh
7	282, 291, 332, 341	388, 405sh, 466, 497
8	335	387, 408, 467
9	281, 292, 330sh, 340	389, 405sh, 464
10	277	388, 406sh
11	282, 291sh, 330, 341	391, 403sh, 435, 466
12	280, 290sh, 328, 341sh	388, 404sh, 467
13	335	387, 407, 467
14	282, 291, 330, 340	389, 405sh, 465

[a] Most intense peaks underlined.

Table S4. Excitation and emission data (nm) in dichloromethane solution for prepared compounds.[a]

Compound	**CH_2Cl_2 298 K**	
	λ_{exc}	λ_{emis}
1	285, 310sh 270-360	384
2	293, 323 270-360	385
3	287, 318sh 270-360	385
4	294, 328 270-360	385
5	280, 328	384
6	295, 326	385
7	281, 292, 342	384
8	279, 321, 345	372sh, 385, 403sh
9	294, 340	385
10	282, 293, 341	384
11	282, 313sh	385
12	295, 326	385
13	308sh, 329, 346	373sh, 385, 404
14	295, 330	384

[a] Most intense peaks underlined.

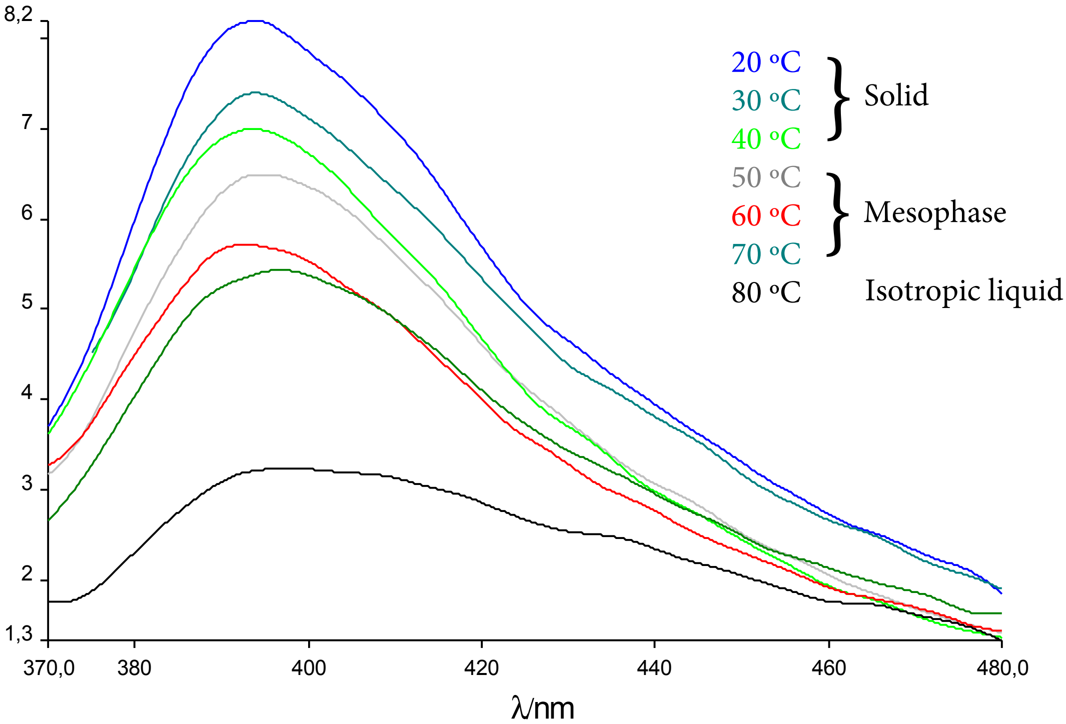

Figure S43. Emission spectrum of compound **2** on heating. Emission intensity in arbitrary units.