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Supporting Information

for

1,4-Alkyl migration associated with simultaneous S-C bond cleavage and N-C bond formation in platinum complexes of 2-aminothioethers. Characterization of intramolecular interligand charge transfer phenomenon

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Table S1. The bond distances (in Å) obtained at the B3LYP/sdd level optimized geometry [**1**][OTf]

Bond	X-ray	Calculated
Pt(1)-S(1)	2.2783(7)	2.323
Pt(1)-N(1)	2.020(2)	2.056
Pt(1)-N(3)	1.9645(19)	2.028
N(2)-N(3)	1.292(3)	1.289
Pt(1)-N(4)	1.941(2)	1.981
S(1)-C(17)	1.771(2)	1.777
N(4)-C(12)	1.376(3)	1.375
S(1)-C(18)	**1.817(3)**	**1.831**
S(1)-Pt(1)-N(1)	175.47(6)	178.5
S(1)-Pt(1)-N(3)	99.56(6)	101.8
S(1)-Pt(1)-N(4)	84.34(8)	82.38
N(1)-Pt(1)-N(3)	77.70(8)	77.04
N(1)-Pt(1)-N(4)	98.68(9)	98.69
N(3)-Pt(1)-N(4)	174.15(10)	174.8
Pt(1)-S(1)-C(17)	99.49(9)	99.25
Pt(1)-N(1)-C(1)	129.29(16)	129.1
Pt(1)-N(1)-C(5)	112.33(17)	111.7
Pt(1)-N(3)-N(2)	120.52(16)	118.4
Pt(1)-N(3)-C(6)	125.37(15)	127.1
Pt(1)-N(4)-C(12)	122.24(18)	123.6

Table S2. The bond distances (in Å) obtained at the B3LYP/sdd level optimized geometry **2**

	X-ray	Calculated
Pt(1)-S(1)	2.2707(16)	2.329
Pt(1)-N(1)	2.045(5)	2.061
Pt(1)-N(3)	1.968(5)	2.004
Pt(1)-N(4)	1.988(5)	1.980
N(2)-N(3)	1.315(7)	1.313
S(1)-C(17)	1.738(7)	1.744
N(4)-C(12)	1.364(8)	1.366
S(1)-Pt(1)-N(1)	176.27(14)	175.7
S(1)-Pt(1)-N(3)	99.79(15)	100.9
S(1)-Pt(1)-N(4)	83.54(15)	82.63
N(1)-Pt(1)-N(3)	77.61(19)	77.07
N(1)-Pt(1)-N(4)	99.03(19)	99.17
N(3)-Pt(1)-N(4)	176.5(2)	176.3
Pt(1)-S(1)-C(17)	99.9(2)	99.47
Pt(1)-N(1)-C(1)	129.6(4)	129.5
Pt(1)-N(1)-C(5)	111.6(4)	111.6
Pt(1)-N(3)-N(2)	119.9(4)	119.0
Pt(1)-N(3)-C(6)	127.7(4)	127.5
Pt(1)-N(4)-C(12)	121.5(4)	123.6

Table S3. The bond distances (in Å) obtained at the B3LYP/sdd level optimized geometry **3**

	X-ray	Calculated
Pt(1)-S(1)	2.242(3)	2.313
Pt(1)-N(1)	2.055(8)	2.097
Pt(1)-N(2)	1.969(8)	2.009
Pt(1)-N(4)	1.981(8)	2.023
N(2)-N(3)	1.295(11)	1.308
S(1)-C(17)	1.721(11)	1.738
N(4)-C(12)	1.366(13)	1.383
S(1)-Pt(1)-N(1)	172.6(2)	173.3
S(1)-Pt(1)-N(3)	96.3(2)	97.1
S(1)-Pt(1)-N(4)	84.0(2)	83.4
N(1)-Pt(1)-N(3)	77.0(3)	76.2
N(1)-Pt(1)-N(4)	102.4(3)	103.1
N(3)-Pt(1)-N(4)	175.9(3)	174.5
Pt(1)-S(1)-C(17)	101.0(4)	99.7
Pt(1)-N(4)-C(12)	120.8(7)	120.6
Pt(1)-N(1)-C(5)	111.9(6)	110.6
Pt(1)-N(3)-N(2)	120.2(6)	119.4
Pt(1)-N(3)-C(6)	127.4(7)	127.0
Pt(1)-N(1)-C(1)	131.6(7)	131.4

Table S4. The bond distances (in Å) obtained at the B3LYP/sdd level optimized geometry [**5**][OTf]

	X-ray	Calculated
Pt(1)-S(1)	2.259(9)	2.316
Pt(1)-N(1)	2.036(3)	2.066
Pt(1)-N(2)	2.025(3)	2.050
Pt(1)-N(3)	1.981(3)	2.001
S(3)-C(17)	**1.814(4)**	**1.832**
S(3)-C(16)	1.774(4)	1.770
N(3)-C(11)	1.355(5)	1.372
S(1)-Pt(1)-N(1)	177.4(9)	177.7
S(1)-Pt(1)-N(2)	97.38(8)	99.54
S(1)-Pt(1)-N(3)	84.43(10)	82.18
N(1)-Pt(1)-N(2)	80.08(12)	78.99
N(1)-Pt(1)-N(3)	98.12(13)	99.32
N(2)-Pt(1)-N(3)	178.0(13)	177.7
Pt(1)-S(1)-C(16)	99.57(12)	99.46
Pt(1)-N(3)-C(11)	121.0(3)	121.8

Table S5. Some Selected Molecular Orbitals along with their energies and compositions of compound [**1**][OTf] in gas phase b3lyp/sdd level calculation

MO	Energy, eV	Composition		
		Pt	pap	(H_2N^SMe)
LUMO+5	-3.28	06	86	08
LUMO+4	-3.46	02	98	0
LUMO+3	-3.69	13	11	76
LUMO+2	-4.61	17	71	12
LUMO+1	-4.70	30	49	21
LUMO	**-6.48**	**10**	**79(N=N, 38)**	**11**
HOMO	**-8.23**	**08**	**14**	**78**
HOMO-1	-9.73	02	04	94
HOMO-2	-9.87	05	96	01
HOMO-3	-10.06	0	95	05
HOMO-4	-10.45	61	13	26
HOMO-5	-10.49	64	11	25
HOMO-6	-10.78	58	23	19
HOMO-7	-11.24	06	74(N=N, 36)	20
HOMO-8	-11.38	04	80(N=N, 39)	16
HOMO-9	-11.51	24	24	52
HOMO-10	-11.99	55	21	24
HOMO - LUMO = 1.75 eV				

Table S6. Some Selected Molecular Orbitals along with their energies and compositions of compound **2** in gas phase b3lyp/sdd level calculation

MO	Energy, eV	Composition		
		Pt	pap	(HN^S)
LUMO+5	-0.05	82	12	06
LUMO+4	-0.13	06	89	05
LUMO+3	-0.22	05	94	01
LUMO+2	-0.79	41	28	31(S,22)
LUMO+1	-1.35	02	98	0
LUMO	**-3.02**	**13**	**62(N=N, 29)**	**25**
HOMO	**-4.72**	**06**	**30**	**64(S,13)**
HOMO-1	-5.44	14	02	84(S,30)
HOMO-2	-6.60	08	85	07
HOMO-3	-6.82	73	12	15
HOMO-4	-6.92	09	88	03
HOMO-5	-7.04	31	17	52
HOMO-6	-7.10	41	23	36
HOMO-7	-7.48	30	16	54(S,42)
HOMO-8	-7.85	06	74(N=N, 56)	20
HOMO-9	-8.02	13	57	30(S,13)
HOMO-10	-8.15	14	52	34(S,13)

Table S7. Some Selected Molecular Orbitals along with their energies and compositions of compound **3** in gas phase b3lyp/sdd level calculation

MO	Energy, eV	Composition		
		Pt	pap	(BzN^S)
LUMO+5	-0.10	06	68	26
LUMO+4	-0.18	04	73	23
LUMO+3	-0.26	07	23	70
LUMO+2	-0.87	39	28	33(S,22)
LUMO+1	-1.28	04	94	02
LUMO	**-2.98**	**12**	**65(N=N, 31)**	**23**
HOMO	**-4.65**	**06**	**28**	**66(S,14)**
HOMO-1	-5.36	13	02	85(S,30)
HOMO-2	-6.53	10	45	45
HOMO-3	-6.65	01	43	56
HOMO-4	-6.74	74	08	18
HOMO-5	-6.85	03	10	87
HOMO-6	-6.91	11	81	08
HOMO-7	-6.99	30	13	57
HOMO-8	-7.05	30	21	49
HOMO-9	-7.54	19	36	45(S,34)
HOMO-10	-7.63	22	38	40(S,13)

Table S8. Some Selected Molecular Orbitals along with their energies and compositions of compound [**5**][OTf] in gas phase b3lyp/sdd level calculation.

MO	Energy, eV	Composition		
		Pt	bpy	(H_2N^SMe)
LUMO+10	-1.75	64	06	30
LUMO+9	-1.82	26	01	73
LUMO+8	-2.08	82	08	10
LUMO+7	-2.53	39	01	60
LUMO+6	-2.75	87	03	10
LUMO+5	-3.21	02	93	05
LUMO+4	-3.38	21	07	72(S,23)
LUMO+3	-4.39	46	20	34(S,22)
LUMO+2	-4.58	02	97	01
LUMO+1	-4.73	02	98	0
LUMO	**-5.77**	**05**	**92**	**03**
HOMO	**-7.69**	**09**	**05**	**86**
HOMO-1	-9.38	01	0	99
HOMO-2	-9.92	84	02	14
HOMO-3	-9.96	51	09	40
HOMO-4	-10.36	54	32	04
HOMO-5	-10.57	15	80	05
HOMO-6	-11.08	44	09	47(S,24)
HOMO-7	-11.39	20	21	59
HOMO-8	-11.61	38	20	42(S,22)
HOMO-9	-11.83	19	14	67
HOMO-10	-12.02	01	99	0

Table S9. Selected list of vertical excitations computed at the TD-DFT/B3LYP/6-31+G**//B3LYP/6-31G* level of theory for [**1**][OTf]

Excited State	Wavelength (nm)	f	Energy (eV)	Transition	Character
1	**790.4**	**0.216**	**1.5685**	**(67%)HOMO → LUMO**	**H_2N^SMe(π)→pap($\pi^*_{N=N}$), ILCT**
5	425.2	0.174	2.9161	(63%)HOMO-2 → LUMO	pap(π) → pap($\pi^*_{N=N}$), ILCT
6	419.5	0.037	2.9555	(53%)HOMO → LUMO+1 (31%)HOMO → LUMO+2	H_2N^SMe(π)→pap(π^*), ILCT
8	382.9	0.063	3.2374	(40%)HOMO-6 → LUMO (23%)HOMO-5 → LUMO	Pt(dπ) → pap($\pi^*_{N=N}$), MLCT
10	351.1	0.038	3.5304	(37%)HOMO-6 → LUMO (33%)HOMO-4 → LUMO	Pt(dπ) → pap($\pi^*_{N=N}$), MLCT
14	281.1	0.061	4.4101	(53%)HOMO-8 → LUMO	pap(n, $_{N=N}$) → pap($\pi^*_{N=N}$), ILCT
18	268.5	0.068	4.6165	(53%)HOMO-1 → LUMO+1	H_2N^SMe(π)→pap(π^*), ILCT

Table S10. Selected list of vertical excitations computed at the TD-DFT/B3LYP/6-31+G**//B3LYP/6-31G* level of theory for **2**

Excited State	Wavelength (nm)	f	Energy (eV)	Transition	Character
1	**833.2**	**0.230**	**1.4880**	**(50%)HOMO → LUMO (25%)HOMO-1 → LUMO**	**HN^S(π)→pap($\pi^*_{N=N}$), ILCT**
3	722.3	0.103	1.7165	(34%)HOMO-1 → LUMO (33%)HOMO → LUMO	HN^S(π)→pap($\pi^*_{N=N}$),ILCT
5	413.2	0.111	3.0002	(59%)HOMO-2 → LUMO	pap(π) → pap($\pi^*_{N=N}$), ILCT
7	383.6	0.068	3.2322	(52%)HOMO-5 → LUMO	Pt(dπ)/HN^S (π) → pap($\pi^*_{N=N}$), MLCT
10	362.6	0.076	3.4186	(66%)HOMO-1 → LUMO+1	HN^S(π) → pap(π^*), ILCT
14	311.2	0.113	3.9834	(87%)HOMO → LUMO+3	HN^S(π) → pap(π^*), ILCT
19	283.7	0.063	4.3701	(79%)HOMO → LUMO+4	HN^S(π) → pap(π^*), ILCT

Table S11. Selected list of vertical excitations computed at the TD-DFT/B3LYP/6-31+G**//B3LYP/6-31G* level of theory for **3**

Excited State	Wavelength (nm)	f	Energy (eV)	Transition	Character
1	**839.4**	**0.192**	**1.4770**	**(36%)HOMO → LUMO** **(36%)HOMO-1 → LUMO**	**BzN^S(π)→pap($\pi^*_{N=N}$), ILCT**
2	717.3	0.134	1.7284	(48%)HOMO-1 → LUMO (25%)HOMO → LUMO	BzN^S(π)→pap($\pi^*_{N=N}$), ILCT
6	390.3	0.105	3.1767	(65%)HOMO-3 → LUMO	pap(π)/BzN^S(π)→ pap($\pi^*_{N=N}$), ILCT
8	367.3	0.046	3.3757	(69%)HOMO-6 → LUMO	pap(π) → pap($\pi^*_{N=N}$), ILCT
10	355.3	0.102	3.4894	(38%)HOMO-1 → LUMO+1 (27%)HOMO → LUMO+3	BzN^S(π) → pap(π^*), ILCT BzN^S(π) → L(π^*), ILCT
17	301.9	0.065	4.1060	(91%)HOMO → LUMO+4	BzN^S(π) → pap(π^*), ILCT
19	294.0	0.048	4.2162	(84%)HOMO → LUMO+5	BzN^S(π) → pap(π^*), ILCT
23	279.1	0.054	4.4422	(53%)HOMO-11 → LUMO	pap(π)/BzN^S(π)→ pap($\pi^*_{N=N}$), ILCT

Table S12. Selected list of vertical excitations computed at the TD-DFT/B3LYP/6-31+G**//B3LYP/6-31G* level of theory for [**5**][OTf]

Excited State	Wavelength (nm)	f	Energy (eV)	Transition	Character
1	**580.5**	**0.097**	**3.1356**	**(94%)HOMO → LUMO**	**H_2N^SMe(π)→bpy(π*), ILCT**
4	391.5	0.043	3.1667	(88%)HOMO → LUMO+3	H_2N^SMe(π)→Pt(d),LMCT H_2N^SMe(π)→ H_2N^SMe(π*),ILCT
6	349.7	0.021	3.5446	(65%)HOMO → LUMO+4	H_2N^SMe(π)→ H_2N^SMe(π*),ILCT
10	302.7	0.125	4.0961	(54%)HOMO-4 → LUMO (32%)HOMO-5 → LUMO	Pt(dπ) → bpy(π*), MLCT bpy(π) → bpy(π*), ILCT
11	293.0	0.298	4.2462	(49%)HOMO-5 → LUMO (29%)HOMO-4 → LUMO	bpy(π) → bpy(π*), ILCT Pt(dπ) → bpy(π*), MLCT
14	282.9	0.084	4.3824	(79%)HOMO → LUMO+7	H_2N^SMe(π)→H_2N^SMe (π*), ILCT
21	252.6	0.068	4.9077	(54%)HOMO-1 → LUMO+1	H_2N^SMe(π)→bpy(π*), ILCT
22	247.3	0.056	5.0127	(42%)HOMO-1 → LUMO+3	H_2N^SMe(π)→Pt(d),LMCT H_2N^SMe(π)→ H_2N^SMe(π*), ILCT

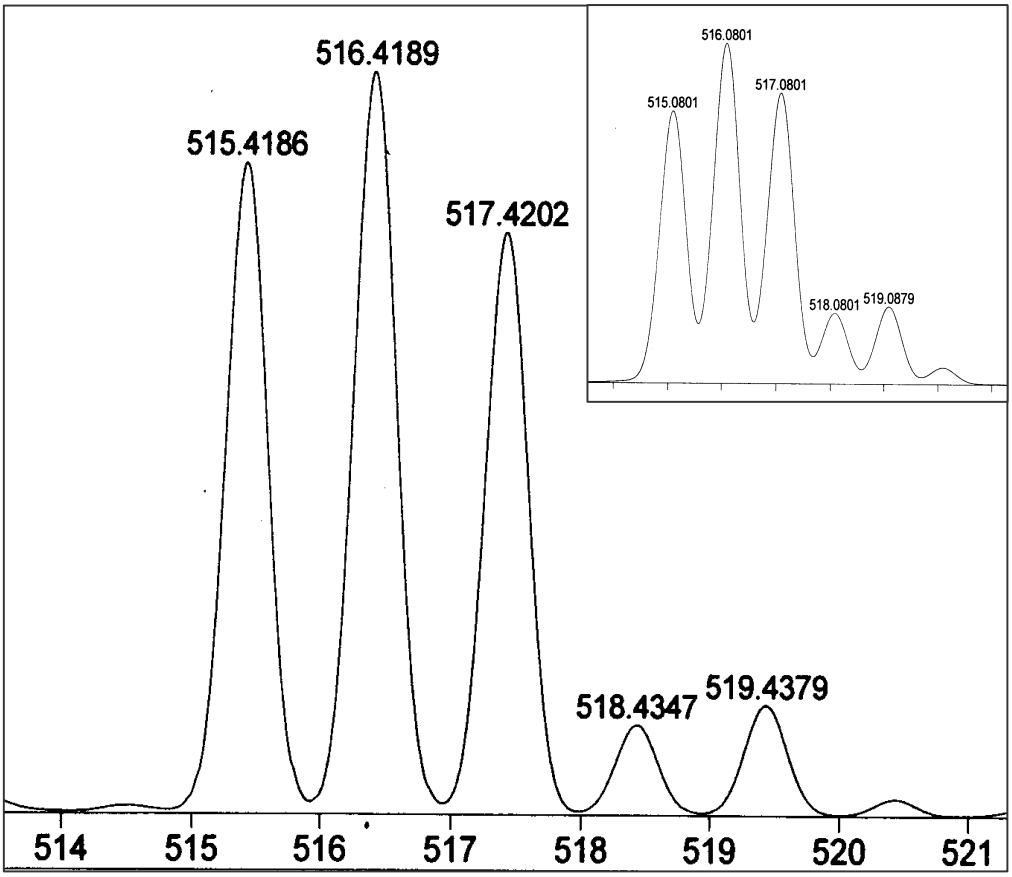


Figure S1. ESI-MS spectrum of the compound [**1**]Cl. Inset: simulated isotopic pattern.

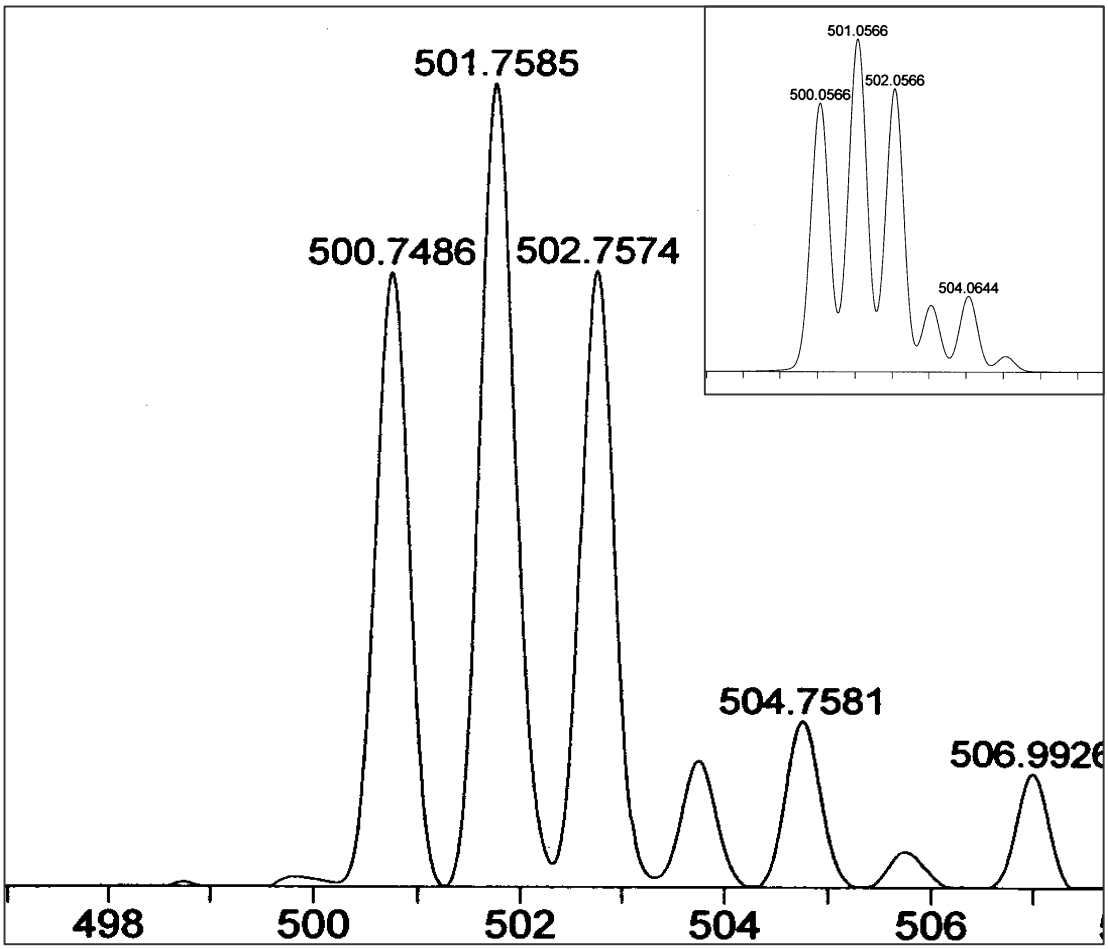


Figure S2. ESI-MS spectrum of the compound **2**. Inset: simulated isotopic pattern.

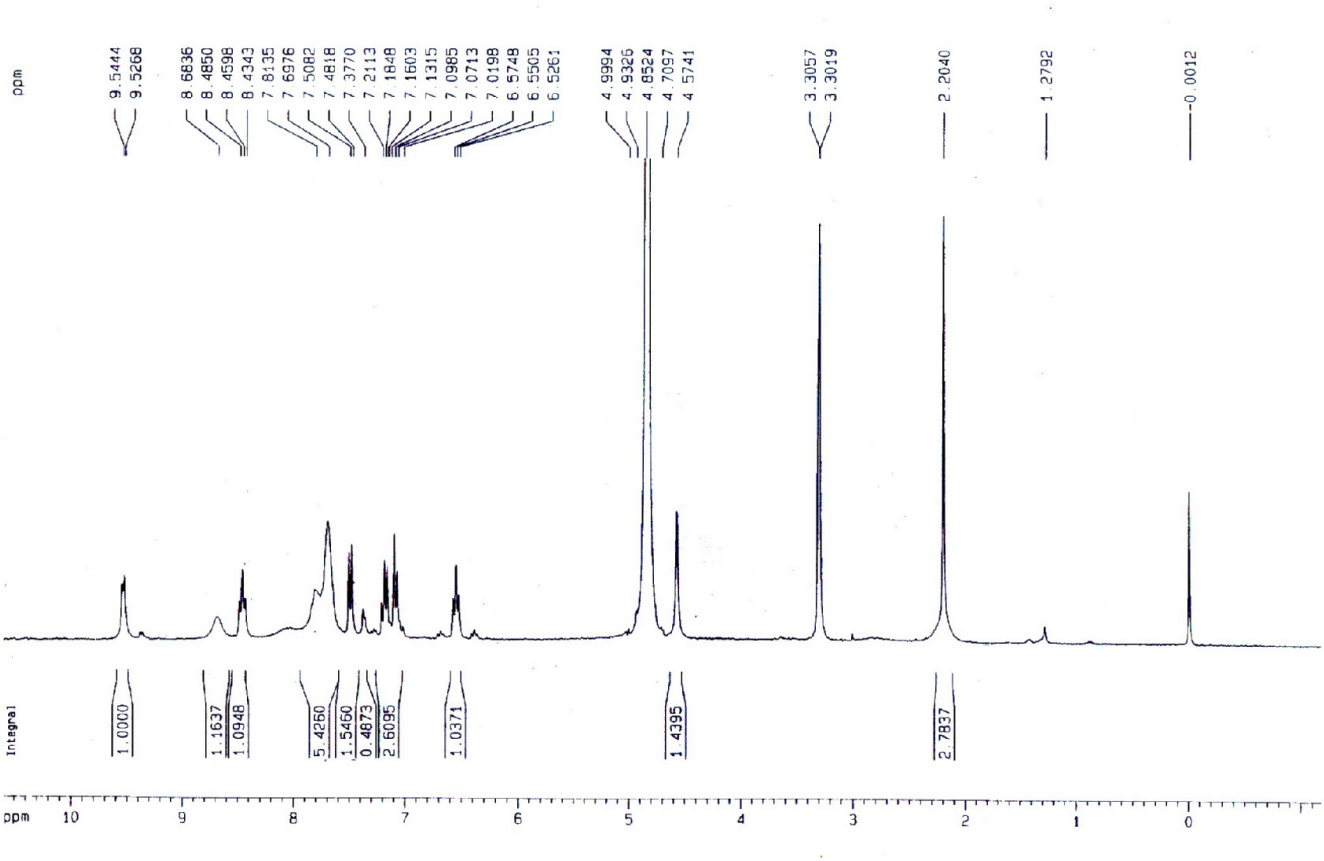


Figure S3. ^{1}H NMR spectrum of the compound [**1**]Cl.

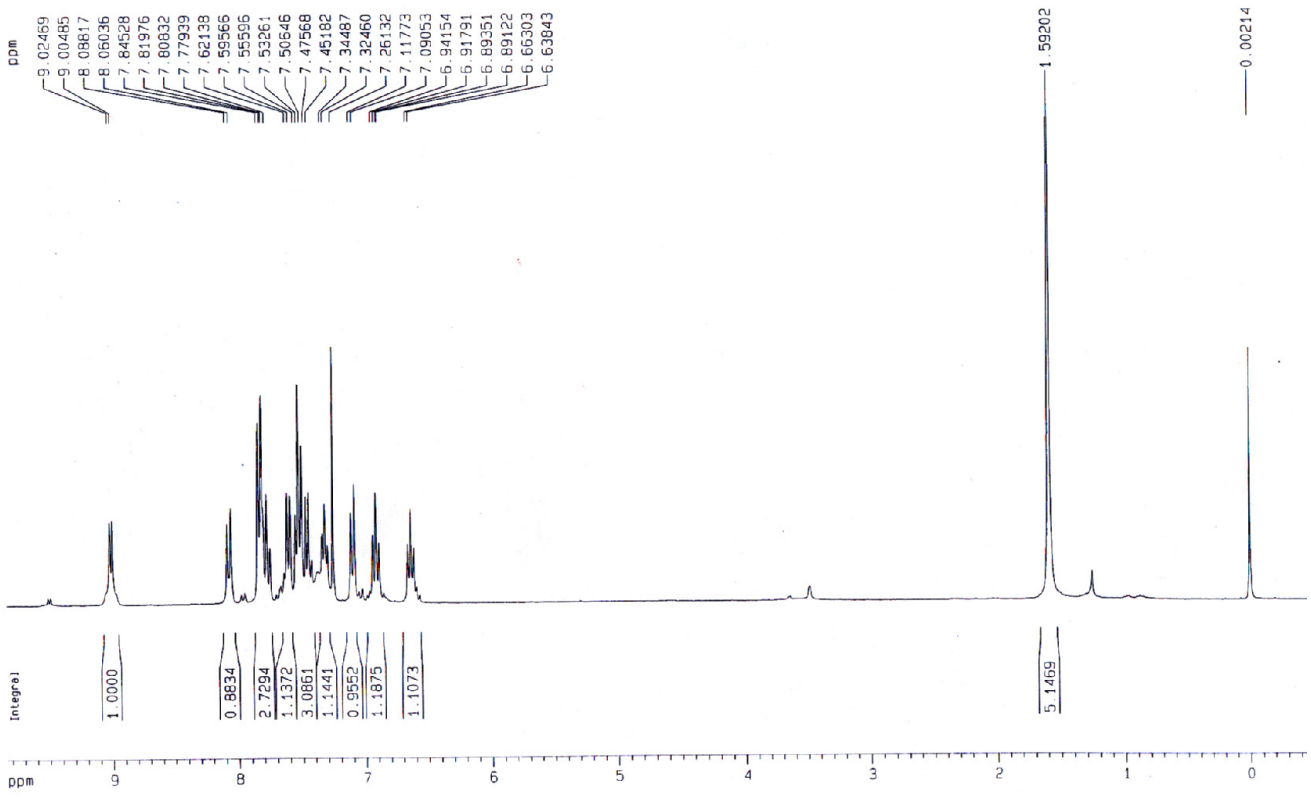


Figure S4. ^{1}H NMR spectrum of the compound **2**

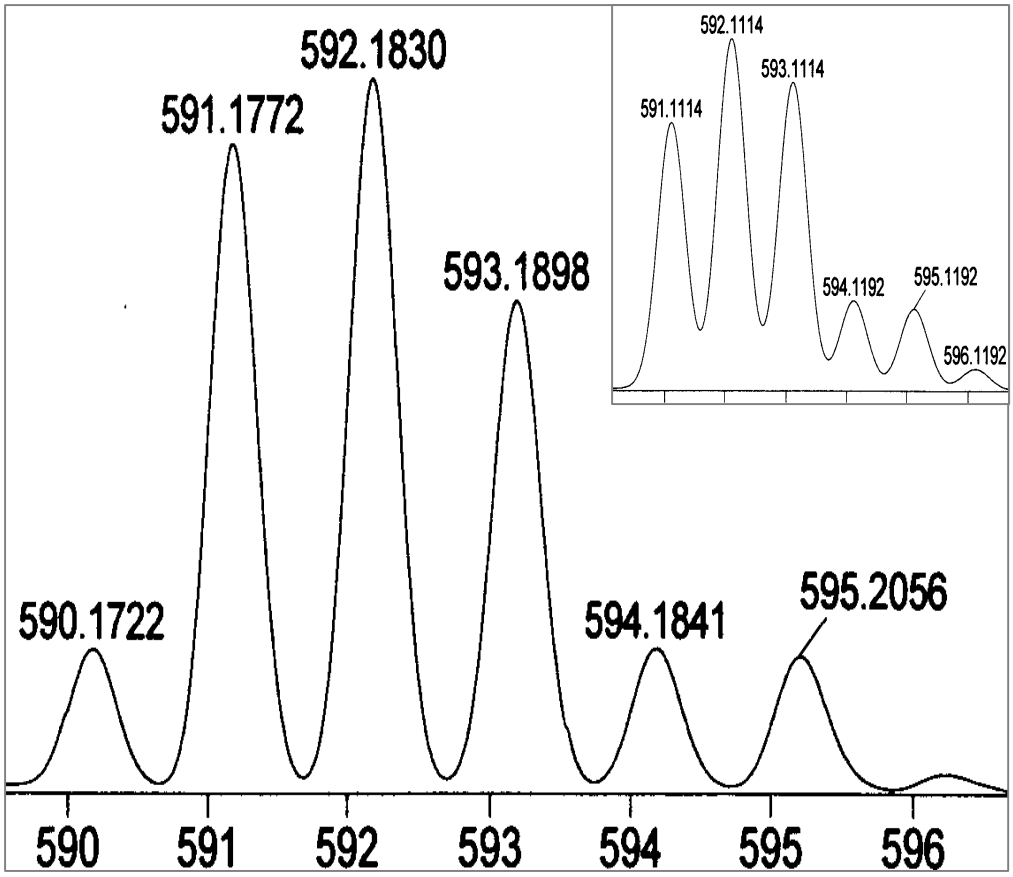


Figure S5. ESI-MS spectrum of the compound **3**. Inset: simulated isotopic pattern.

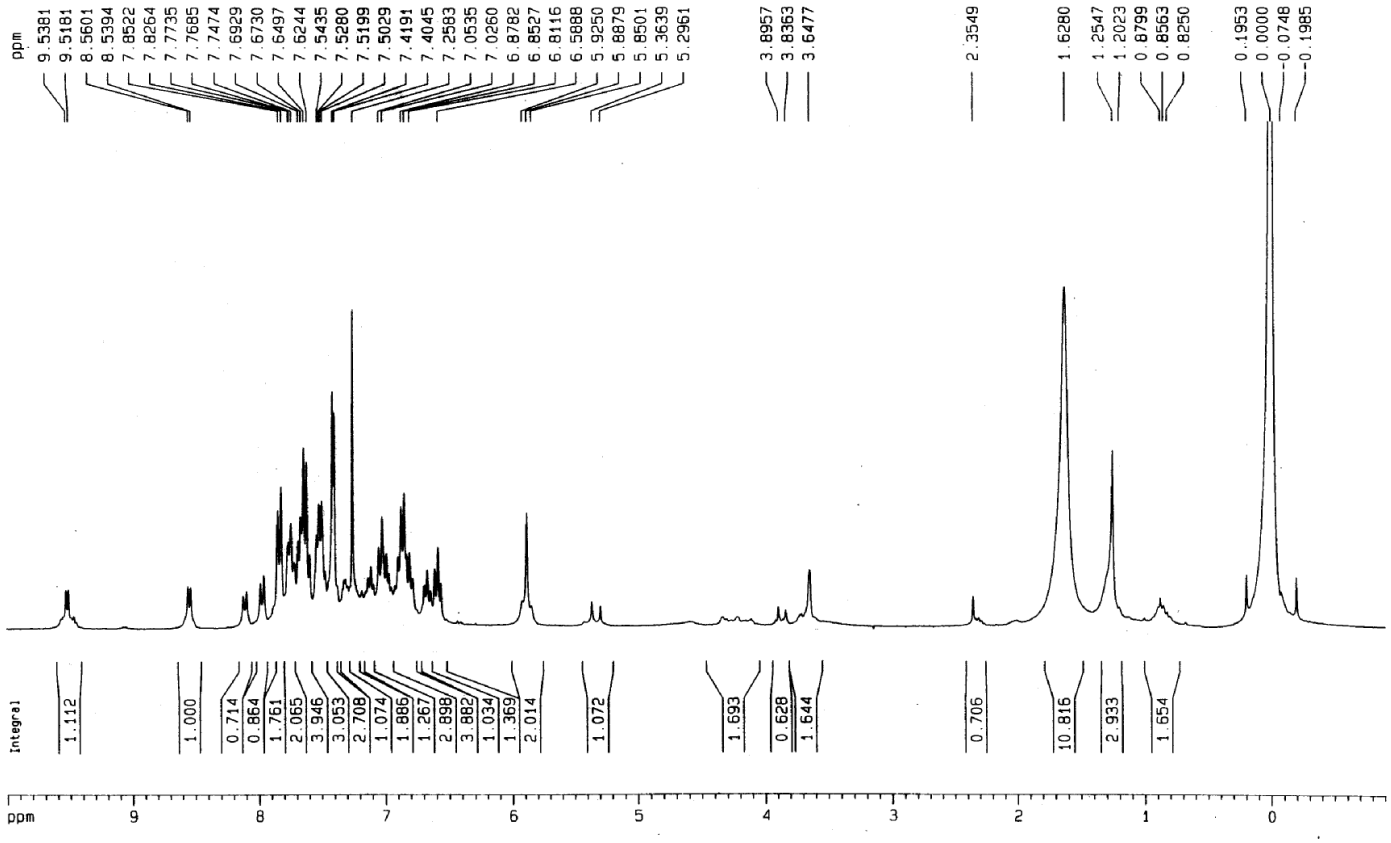


Figure S6. ^{1}H NMR spectrum of the compound **3**

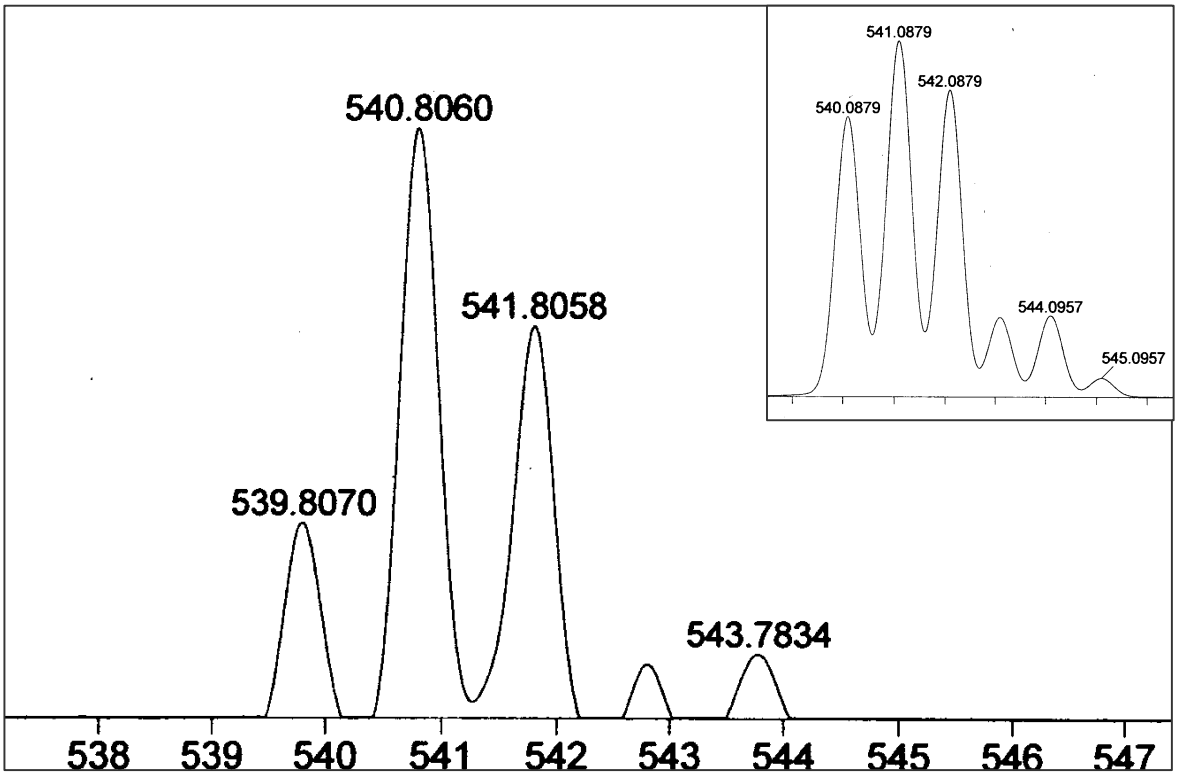


Figure S7. ESI-MS spectrum of the compound **4**. Inset: simulated isotopic pattern

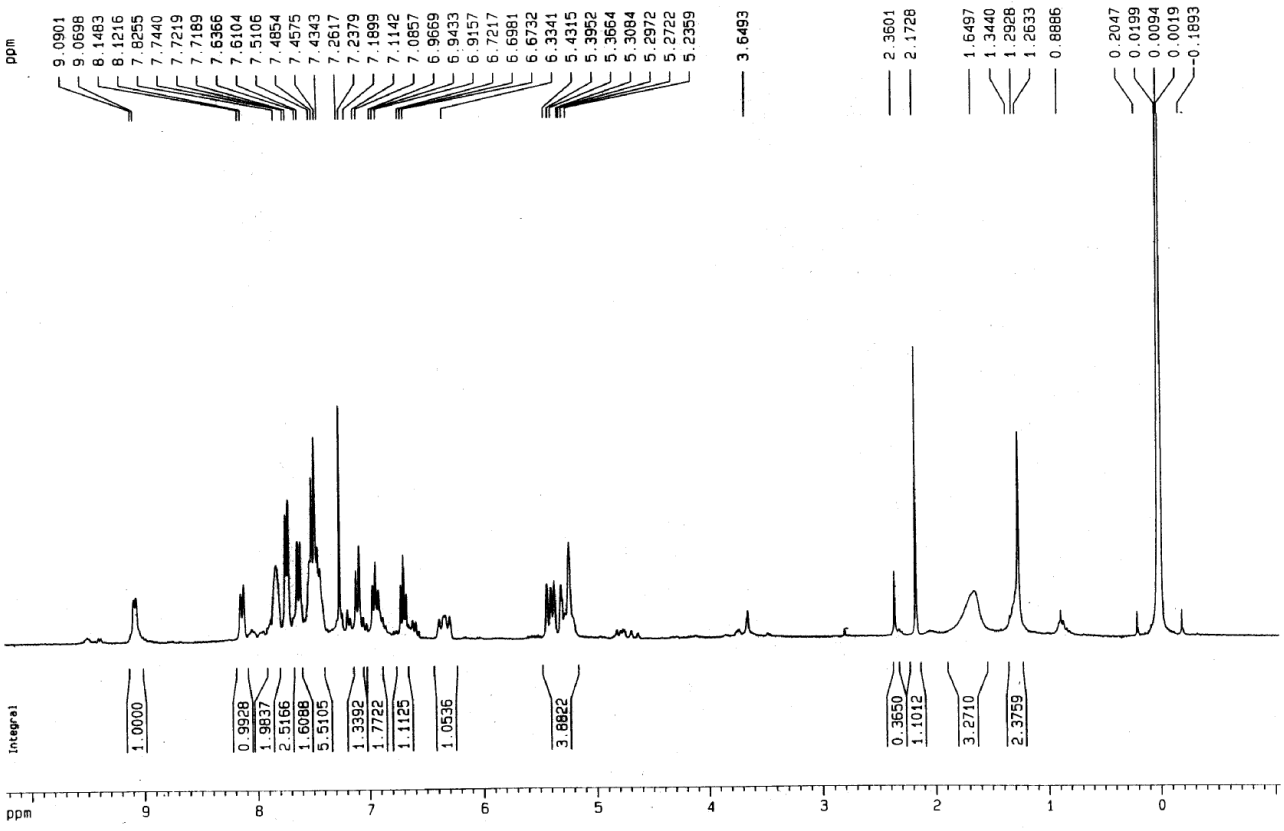


Figure S8. ^{1}H NMR spectrum of the compound **4**

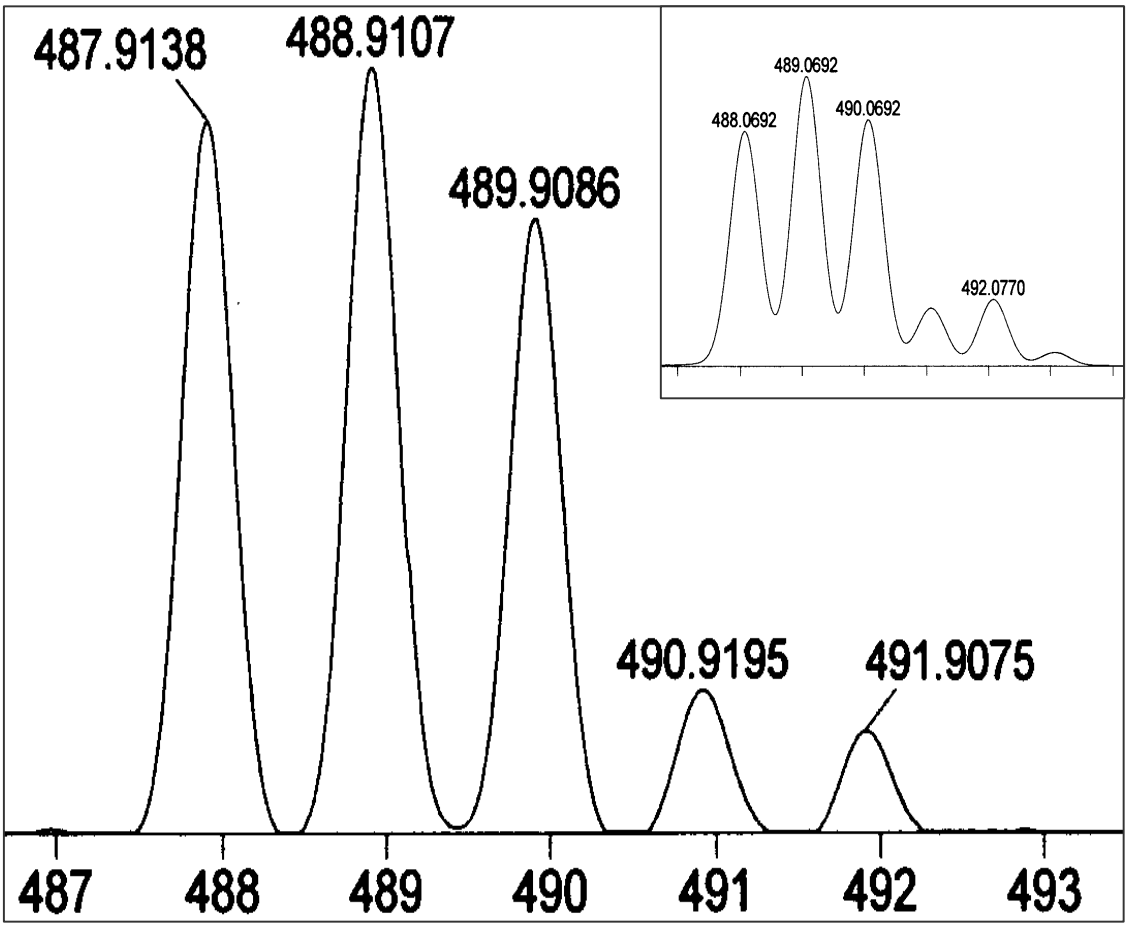


Figure S9. ESI-MS spectrum of the compound [**5**]Cl. Inset: simulated isotopic pattern.

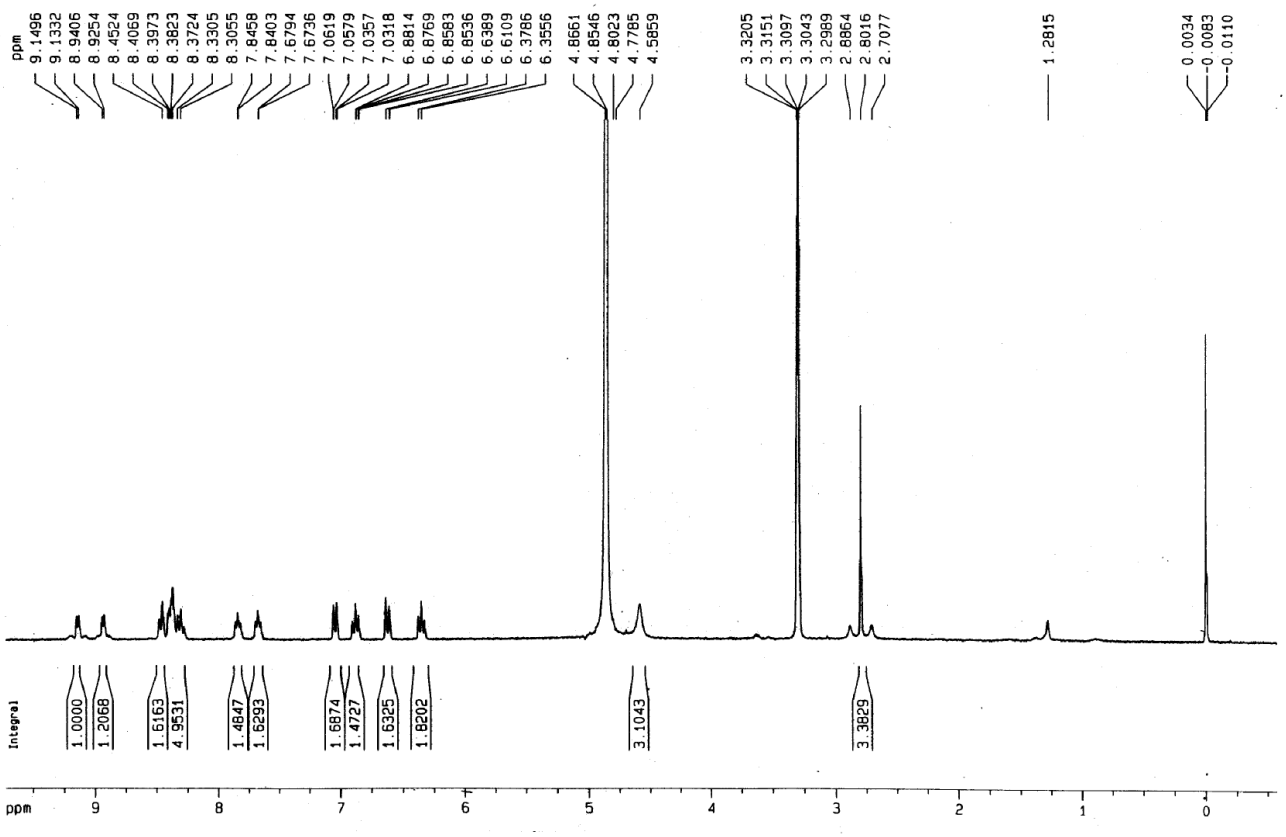


Figure S10. ^{1}H NMR spectrum of the compound [**5**]Cl

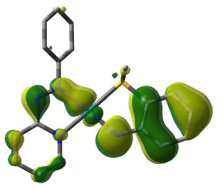
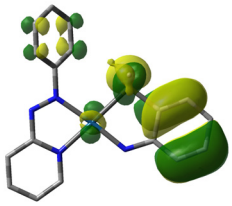
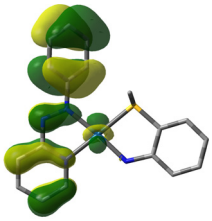
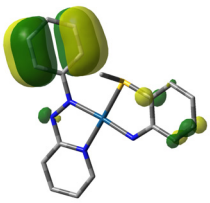
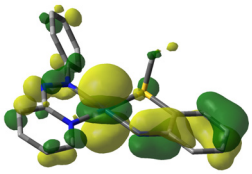
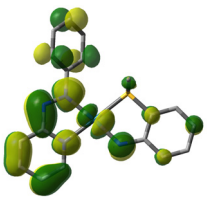
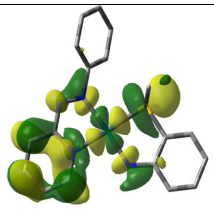
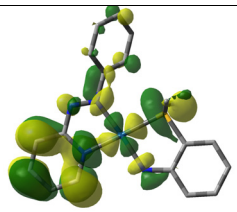
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
HOMO-4	LUMO	LUMO+1	LUMO+2

Figure S11. DFT calculated frontier orbitals for the compound [**1**][OTf]

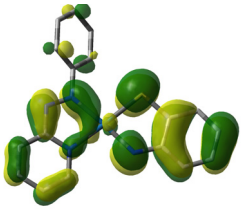
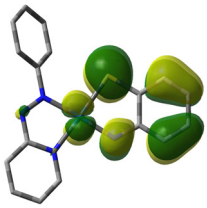
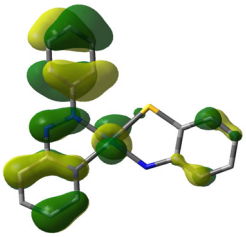
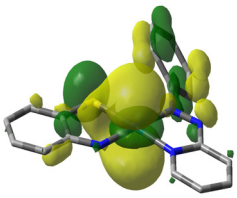
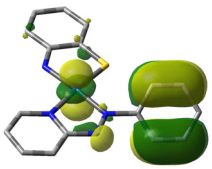
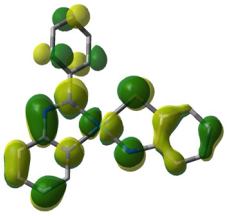
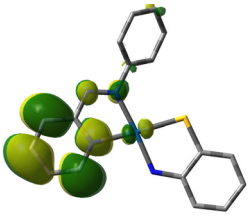
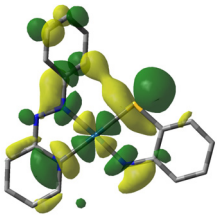
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
HOMO-4	LUMO	LUMO+1	LUMO+2

Figure S12. DFT calculated frontier orbitals for the compound **2**

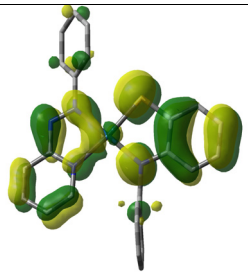
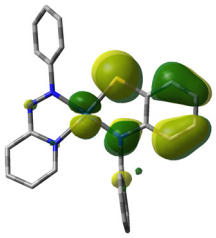
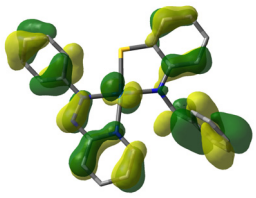
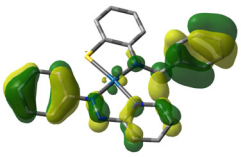
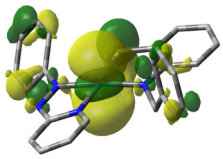
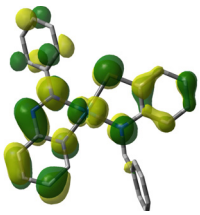
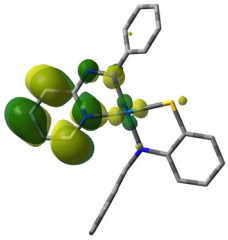
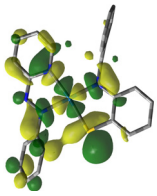
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
HOMO-4	LUMO	LUMO+1	LUMO+2

Figure S13. DFT calculated frontier orbitals for the compound **3**

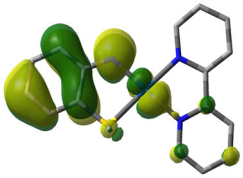
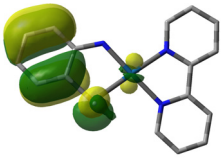
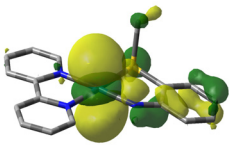
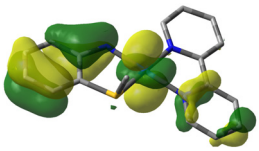
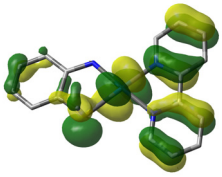
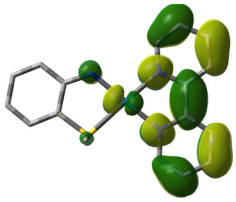
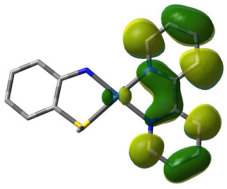
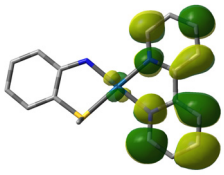
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
HOMO-4	LUMO	LUMO+1	LUMO+2

Figure S14. DFT calculated frontier orbitals for the compound [**5**][OTf]

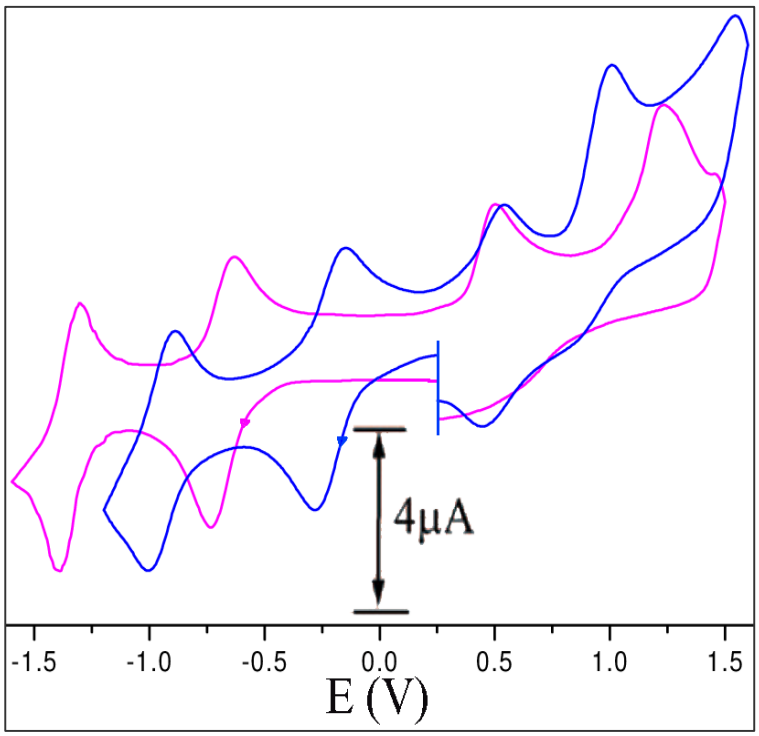


Figure S15. Cyclic voltammograms of the compound [**1**][OTf] (blue) and **2** (pink) in CH_3CN / 0.1 M Et_4NClO_4.

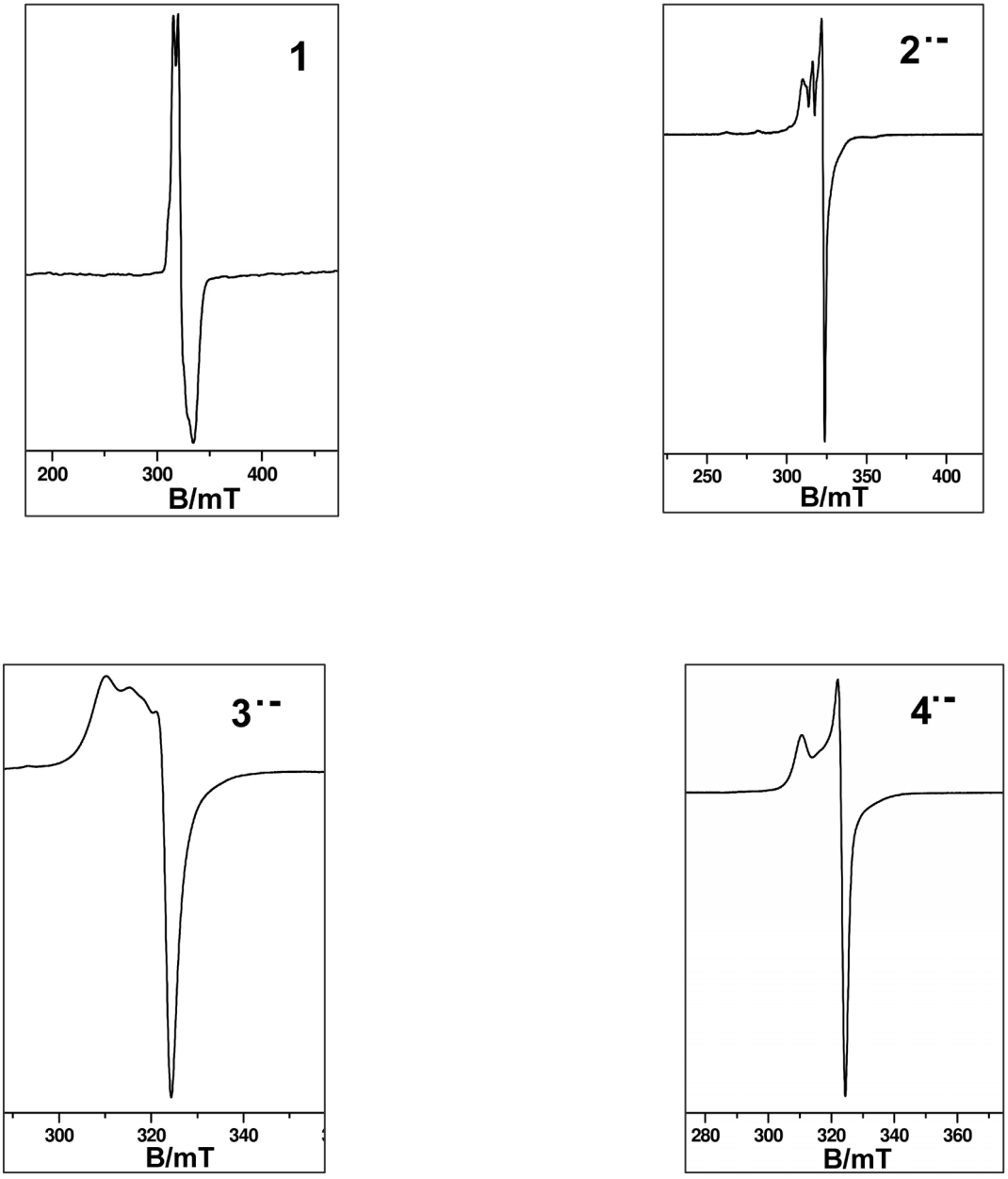


Figure S16. X-band EPR spectrum of compound **1**, $\mathbf{2}^{\cdot-}$, $\mathbf{3}^{\cdot-}$, $\mathbf{4}^{\cdot-}$ in CH_3CN/0.1 M Et_4NClO_4 at 120K.

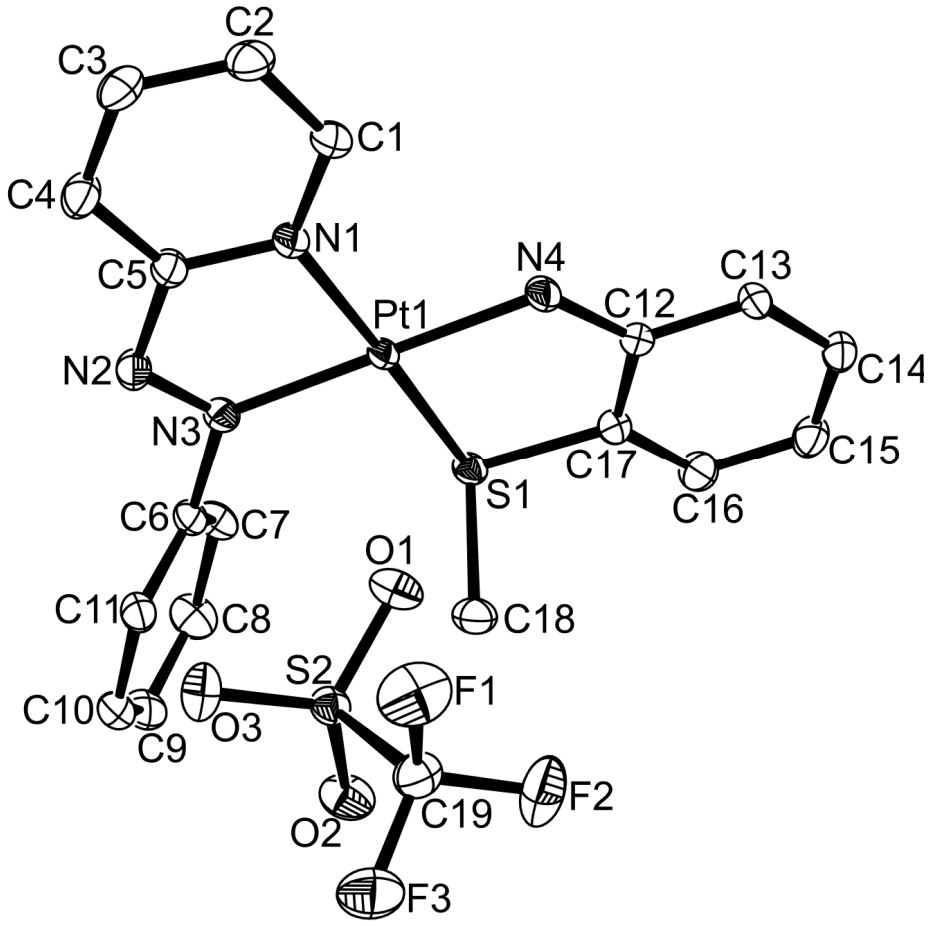


Figure S17. ORTEP and atom numbering scheme of the compound [**1**][OTf]

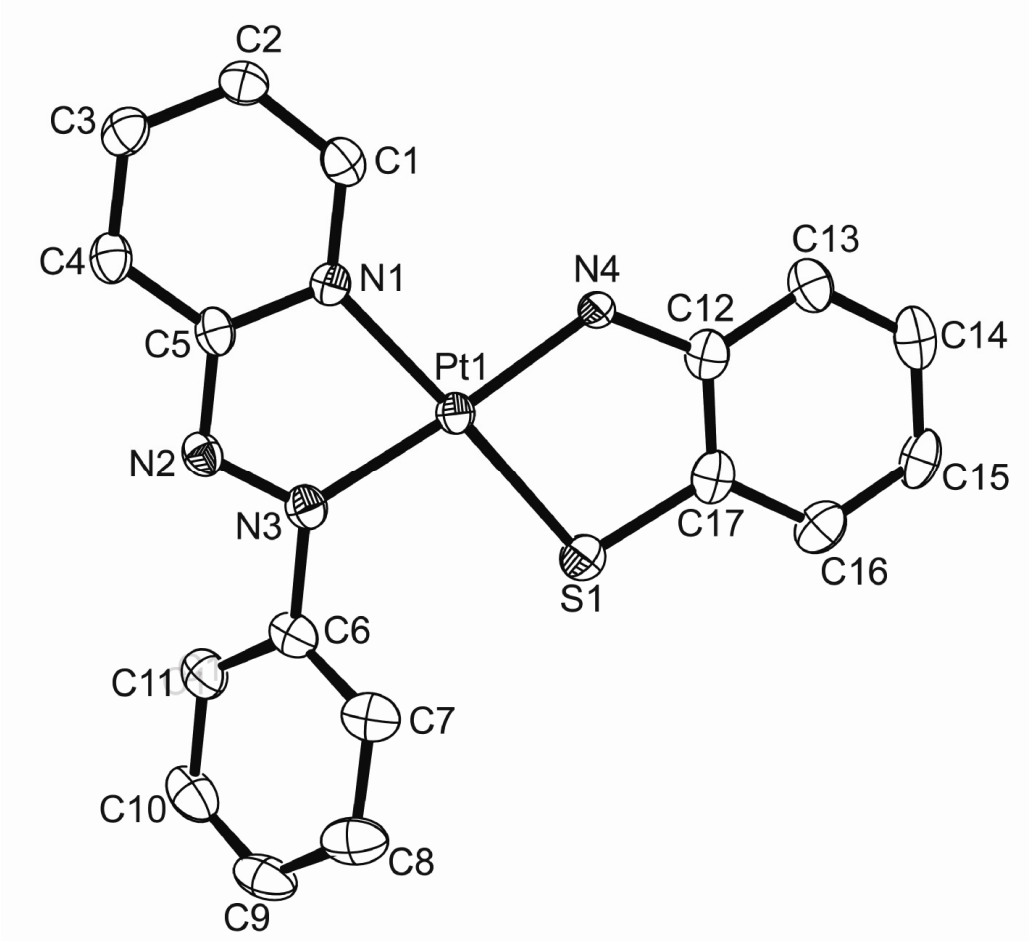


Figure S18. ORTEP atom numbering scheme of the compound **2**

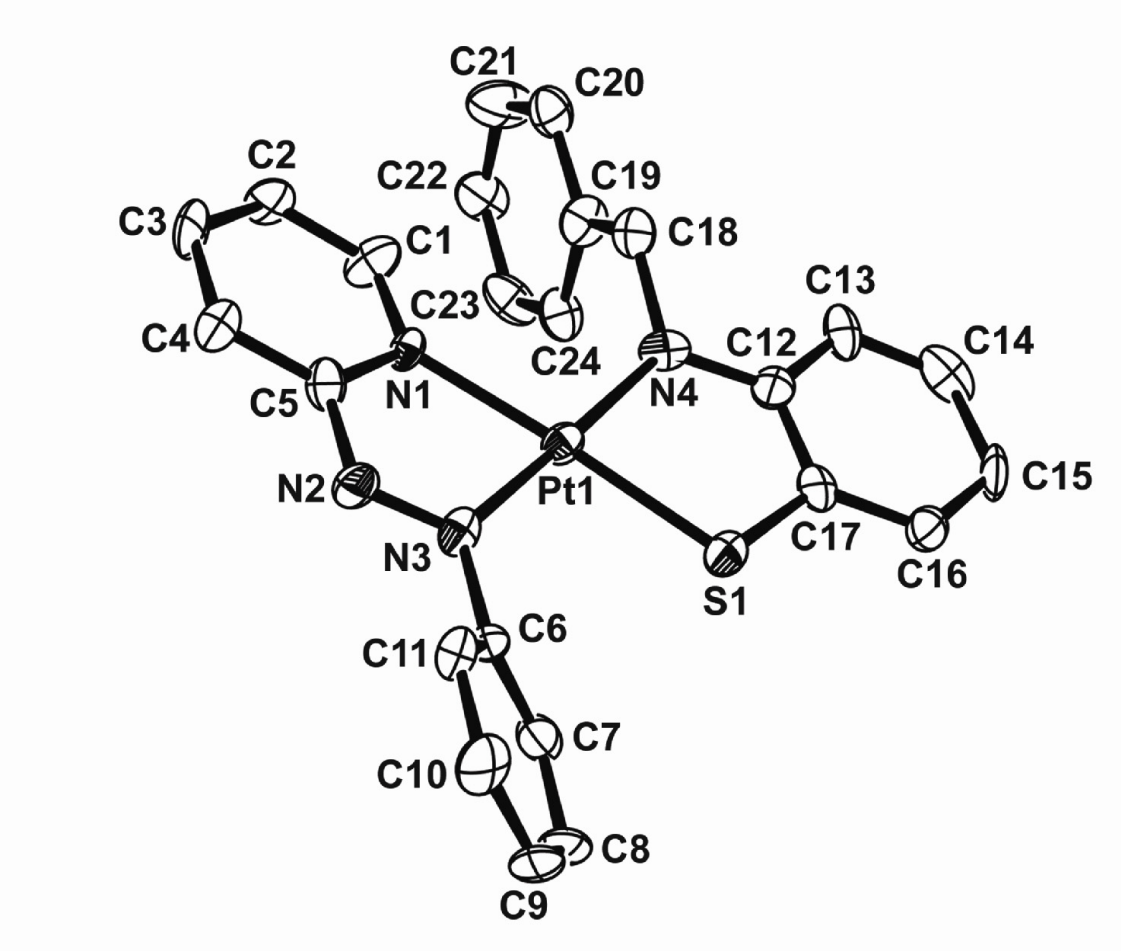


Figure S19. ORTEP atom numbering scheme of the compound **3**

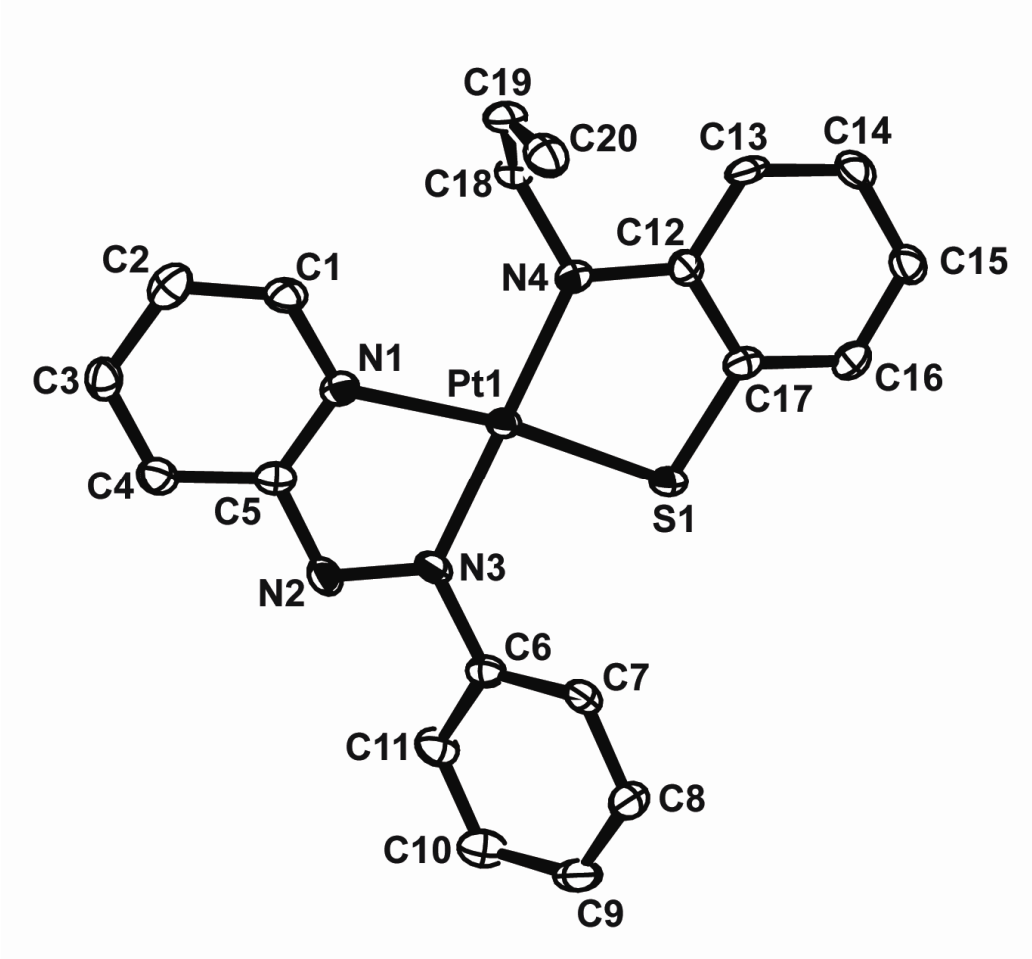


Figure S20. ORTEP atom numbering scheme of the compound **4**

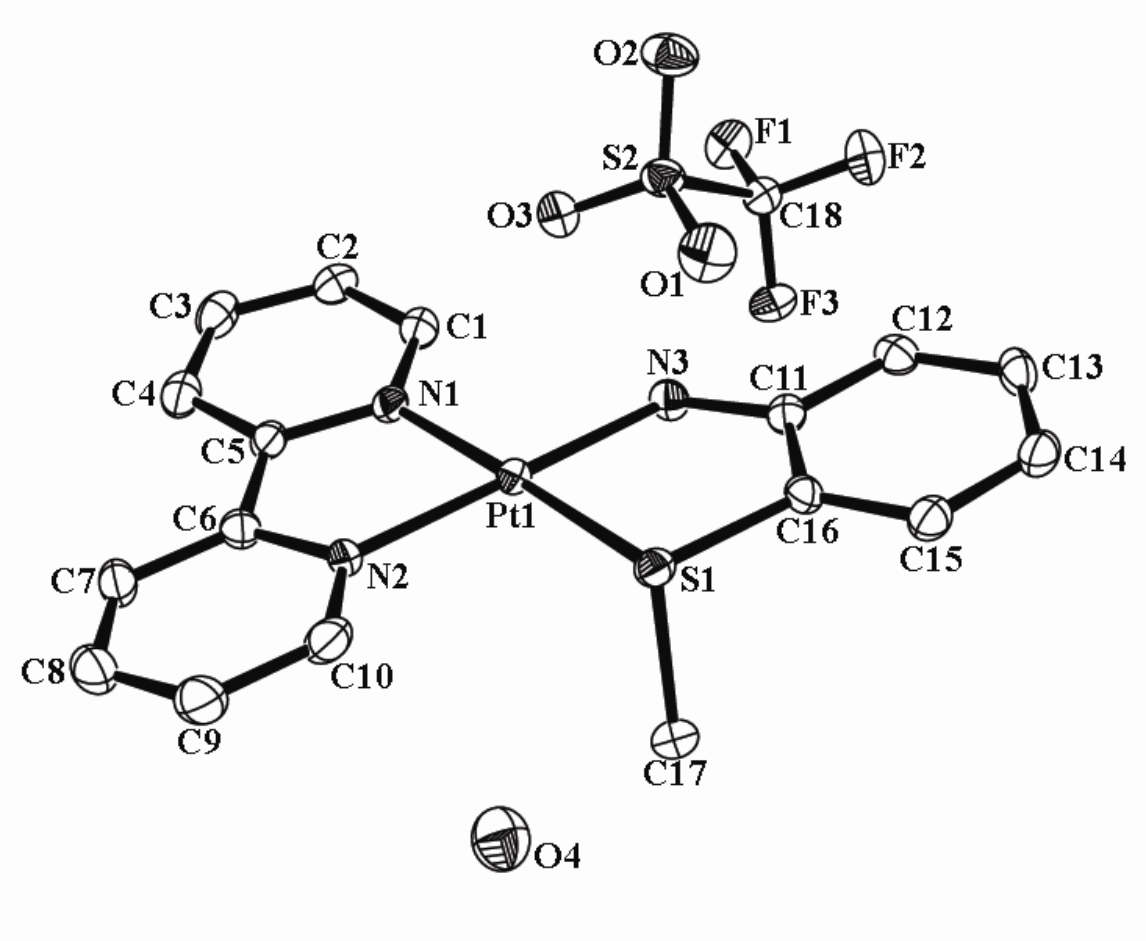


Figure S21. ORTEP atom numbering scheme of the compound [**5**][OTf]