Electronic Supplementary Material (ESI) for Faraday Discussions.

Mechanosynthesis and Photophysics of Colour-tunable Photoluminescent Group 13 Metal Complexes with Sterically Demanding Salen and Salophen Ligands

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A. General Information

All samples were prepared in HPLC grade solvent using crystals with varying concentrations on the order of μM.

Absorption spectra were recorded at room temperature using a Shimadzu UV3600 double beam spectrophotometer. Molar absorptivity was determined by linear fit of values obtained from five independent solutions at varying concentrations ranging from 10.0 to 40.0 μM. The sample solutions for the room temperature emission measurements were prepared in HPLC grade DMSO. Steady-state emission spectra were recorded at room temperature using a Cary Eclipse fluorescence spectrophotometer with excitation at 360 nm.

Excited state lifetimes were measured by time correlated single photon counting (TCSPC) using a pulsed diode laser (exciting at 400 nm) and PL emission was detected at the corresponding steady state emission maximum for each complex at each condition. The PL decays were fitted to a single exponential decay function.

Solution sample Φ_{PL} measurements were performed using an integrating sphere in an Otsuka Electronics quantum efficiency measurement system QE-2000. Samples were excited by an 150W Xenon Lamp coupled to a monochromator, which enabled selectivity of the excitation wavelength, chosen here to be 360 nm. The output was then fed into the ϕ 150mm Hemisphere HalfMoon integrating sphere via a fibre, exciting the sample. PL was collected with a multimode fibre and detected with an Electro-cooling CCD Image Sensor.

A-1. Compounds synthesis

Unless otherwise specified, all chemicals and solvents were purchased commercially, and used without further purification. All the synthesized compounds were characterized by ^{1}H, $^{13}C\{^{1}H$NMR, UV-VIS and FT-IR. Furthermore, complexes were characterized by mass spectroscopy. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker, AVANCE III HD (400 MHz), CD_2Cl_2 or $CDCl_3$ solution. Chemical shift values were recorded as parts per million relatives to tetramethylsilane as an internal standard, and coupling constants in Hertz. Mass spectra were recorded on an Agilent Q-TOF 6520 system using electrospray ionization in positive ion detection (ESI+) mode. Significant fragments are reported as *m*/*z* (relative intensity). The UV-Vis spectra were recorded on a spectrophotometer Biochrom Libra S50, toluene solution. The FT-IR were recorded on a Perkin Elmer Paragon 1000 spectrometer, KBr pressing rings. For mechanochemical. reactions, Retsch MM400 were used throughout the project.

*A-1-1. Synthesis of ligands **1** and **2***

Bis(3,5-di-tert-butyl) salen (1): 1,2-ethylenediamine (0.165 mL g, 2.5 mmol, 1eq.) and 3,5-di-tert-butyl salicyaldehyde (1.01 g, 5 mmol, 2 eq.) were placed in a 15 mL stainless steel jar together with one 10 mm stainless steel ball. The jar was closed and placed in the ball mill and grinded for 2 hours at 30 Hz. The yellow obtained solid was then placed in a 100°C for 36 hours to drive off the water by-product. The pure product was obtained as a yellow powder (1.14 g, 93% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 13.70 (s, 2H, −OH), 8.44 (s, 2H, −C*H*N-), 7.43 (d, *J* = 12.1 Hz, 4H, $C_6H_2(C(CH_3)_3)_2$), 7.12 (d, *J* = 8.6 Hz, 2H, $C_6H_2(C(CH_3)_3)$), 3.95 (s, 4H, $N(CH_2)_2N$), 1.50 (s, 18H, $C(CH_3)_3$); 1.34 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 167.64, 158.09 140.10, 136.65, 127.06, 126.11, 117.87, 59.64, 35.08, 34.16, 31.54, 29.50. IR (KBr)/cm^{-1} *v:* 2956, 2902, 2869, 2365, 1617, 1576, 1483, 1437, 1391, 1362, 1320, 1271, 1251, 1230, 1200, 1172, 1104, 1027, 974, 932, 877, 846, 756, 644.

Bis(3,5-di-tert-butyl) salophen (2): 1,2-phenylenediamine (0.27 g, 2.5 mmol, 1eq.) and 3,5-di-tert-butyl salicyaldehyde (1.01 g, 5 mmol, 2eq.) and acetic acid (70 μL.) were placed in a 15 mL stainless steel jar together with one 10 mm stainless steel ball. The jar was closed and placed in the ball mill and grinded for 2 hours at 30 Hz. The yellow obtained solid was then placed in a 100°C for 36 hours to drive off the water by-product. The pure product was obtained as a yellow powder (1.2 g, 90% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 13.64 (s, 2H, −OH), 8.73 (s, 2H, −C*H*N-), 7.49 (d, *J* = 2.5 Hz, 2H), 7.38-7.30 (m, 6H), 1.47 (s, 18H,−C$(CH_3)_3$), 1.36 (s, 18H, −C$(CH_3)_3$). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 164.83, 158.43, 142.71, 140.58, 136.98, 128.24, 127.45, 126.98, 119.64, 118.47, 35.06, 34.09, 31.21, 29.23. IR (KBr)/cm^{-1} *v:* 2963, 2902, 2869, 2365, 1628, 1595, 1465, 1439, 1393, 1360, 1320, 1294, 1271, 1253, 1235, 1212, 1173, 1132, 1041, 879, 839, 774, 780, 711, 645.

*A-1-2. Synthesis of complexes **3a-4b***

General procedure: An oven-dried stainless-steel grinder jar was charged with **1** or **2** (0.185 mmol), Aluminium or Indium Trichloride (0.277 mmol) and anhydrous $MgSO_4$ (300 mg). The jar was then grinded for 6 hours to give a yellow-orange powder. The reaction mixture was then suspended in chloroform, filtered, and the filtrate dried in vacuo to yield the pure product as a yellow powder.

tBu-Salen-Al (**3a**): Obtained as a white powder (112.8 mg, 88% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.43 (s, 2H), 7.60 (s, 2H), 7.13 (s, 2H), 4.12 (s, 2H), 3.80 (s, 2H), 1.54 (s, 18H), 1.33 (s, 18H).^{13}C NMR (100 MHz, CD_2Cl_2). δ 170.85, 162.93, 141.35, 139.55, 131.72, 127.83, 118.72, 55.17, 35.92, 34.36, 31.47, 29.88 IR (KBr)/cm^{-1} *v:* 2953, 2914, 2868, 2362, 1649, 1622, 1539, 1472, 1444, 1418, 1392, 1363, 1334, 1307, 1256, 1177, 1202, 1105, 1052, 983, 891, 847, 783, 759, 706, 637, 607, 500, 443. UV-VIS (DMSO)/nm $^{-1}$ wavelength: 280, 360 TOF-MS: calc for $C_{28}H_{39}CoN_3O_2$ ($[M + H]^+$) 517.3375; found 517.3385.
tBu-Salen-In (**3b**): Obtained as a yellowish powder (95.6 mg, 82% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.75 (s, 1H), 8.42 (s, 1H), 7.79 (s, 1H), 7.52 (s, 2H), 7.03 (s, 1H), 4.45 (s, 2H), 4.05 (s, 2H), 3.84 (s, 2H), 1.48 (s, 18 H), 1.,31 (s, 18H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 173.26, 172.13, 167.94, 142.75, 138.44, 130.98, 129.66, 118.10, 35.94, 34.30, 31.46, 31.21, 30.23, 29.67 IR (KBr)/cm^{-1} *v:*2961, 2906, 2869, 2345, 1653, 1623, 1534, 1477, 1465, 1440, 1412, 1392, 1363, 1334, 1261, 1201, 1170, 1100, 1026, 923, 910, 802, 745, 701, 640, 533. UV-VIS (DMSO)/nm $^{-1}$ wavelength: 331 TOF-MS: calc for $C_{28}H_{39}CoN_3O_2$ ($[M + H]^+$) 605.2598; found 605.2593.

tBu-Salophen-Al (**4a**): Obtained as a yellow powder. (96.2 mg, 80% yield). %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.03 (s, 2H), 7.82 – 7.72 (m, 4H), 7.49 (s, 2H), 7.33 (m, 2H), 1.60 (s, 18 H), 1.38 (s, 18 H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 164.40, 163.10, 141.72, 140.33, 138.09, 133.49, 128.85, 118.89, 115.90, 36.02, 34.48, 31.40, 30.01 IR (KBr)/cm^{-1} *v:* 2957, 2904, 2868, 1615, 1585, 1538, 1471, 1413, 1389, 1359, 1317, 1261, 1201, 1185, 1135, 1028, 872, 847, 817, 786, 745, 599, 568, 507, 446 UV-VIS (DMSO)/nm $^{-1}$ wavelength: 314, 330, 343, 409, 448 TOF-MS: calc for $C_{28}H_{39}CoN_3O_2$ ($[M + H]^+$) 565.3375; found 565.3370.
tBu-Salophen-In (**4b**): Obtained as a yellow powder. (96.5 mg, 70% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.85 (s, 2H), 7.75-7.62 (m, 4H), 7.48 (s, 2H), 7.18 (s, 2H), 1.51 (s, 18 H), 1.34 (s, 18 H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 169.51, 166.01, 143.10, 139.18, 137.25, 132.75, 130.54, 128.97, 116.79, 36.01, 34.41, 31.37, 29.71 IR (KBr)/cm^{-1} *v:* 2960, 2905, 2869, 1608, 1580, 1530, 1482, 1463, 1430, 1388, 1361, 1316, 1261, 1193, 1174, 1096, 1024, 871, 835, 803, 750, 668, 638, 533, 491, 443 UV-VIS (DMSO)/nm $^{-1}$ wavelength: 303, 338, 407 TOF-MS: calc for $C_{28}H_{39}CoN_3O_2$ ($[M + H]^+$) 653.2598; found 653.2599.

B. Green chemistry metrics (GCM) calculations

All convencional solution information have been obtained by [1]

*B-1. E-factor calculations**

**All quantities are expressed in grams. LAG was done by adding 1* $\frac{\mu L}{mmol}$ *of methanol*

Mechanosynthesis of t-Bu-Salen (**1**):

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - ethylenediamine + methanol - total\,product}{total\,product}$$

$$E = \frac{1.01 + 0.150 + 0.24 - 1.14}{1.14}$$

E = 0.4

Mechanosynthesis of t-Bu-Salophen (**2**):

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - phenylenediamine + acetic\,acid + methanol - total\,product}{total\,product}$$

$$E = \frac{1.01 + 0.27 + 0.0735 + 0.24 - 1.213}{1.213}$$

E = 0.314

Mechanosynthesis of t-Bu-Salen (Al)Cl (**3a**):

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - ethylenediamine + AlCl3 + methanol + MgSO4 - total\,product}{total\,product}$$

$$E = \frac{0.06 + 0.03 + 0.037 + 0.027 + 0.3 - 0.113}{0.113}$$

E = 3.02

Mechanosynthesis of t-Bu-Salen (In)Cl (**3b**):

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - ethylenedia\text{mine} + InCl3 + methanol + MgSO4 - total\,product}{total\,product}$$

$$E = \frac{0.06 + 0.03 + 0.061 + 0.027 + 0.3 - 0.097}{0.097}$$

E = 3.93

Mechanosynthesis of t-Bu-Salophen (Al)Cl (**4a**):

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - phenylenediamine + AlCl3 + methanol + MgSO4 - total\,product}{total\,product}$$

$$E = \frac{0.066 + 0.034 + 0.037 + 0.027 + 0.3 - 0.096}{0.096}$$

E = 3.83

Mechanosynthesis of t-Bu-Salophen (In)Cl (**4b**):

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - phenylenediamine + InCl3 + methanol + MgSO4 - total\,product}{total\,product}$$

$$E = \frac{0.066 + 0.034 + 0.061 + 0.027 + 0.3 - 0.097}{0.097}$$

E = 4.03

Conventional solution synthesis of Conventional solution synthesis of t-Bu-Salen **(1):**

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - ethylenediamine + ethanol\,(10\%) + Toluene\,(10\%) - total\,product}{total\,product}$$

$$E = \frac{1.01 + 0.150 + 1.184 + 0.701 - 0.96}{0.96}$$

E = 2.045

Conventional solution synthesis of t-Bu-Salophen **(2)**

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - phenylenediamine + ethanol\,(10\%) + Toluene\,(10\%) - total\,product}{total\,product}$$

$$E = \frac{1.01 + 0.27 + 1.184 + 0.701 - 0.96}{0.96}$$

E = 2.29

Conventional solution synthesis of t-Bu-Salen (Al)Cl **(3a)**:

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - ethylenediamine + AlCl3 + ethanol\,(10\%) + Toluene\,(10\%) - total\,product}{total\,product}$$

$$E = \frac{0.06 + 0.03 + 0.027 + 0.158 + 0.088 - 0.063}{0.063}$$

E = 4.76

Conventional solution synthesis of t-Bu-Salen (In)Cl (**3b**):

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - ethylenediamine + InCl3 + ethanol\,(10\%) + Toluene\,(10\%) - total\,product}{total\,product}$$

$$E = \frac{0.06 + 0.03 + 0.044 + 0.158 + 0.088 - 0.063}{0.063}$$

E = 5.03

Conventional solution synthesis of t-Bu-Salophen (Al)Cl **(4a)**:

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - phenylenediamine + AlCl3 + ethanol\,(10\%) + Toluene\,(10\%) - total\,product}{total\,product}$$

$$E = \frac{0.066 + 0.034 + 0.027 + 0.158 + 0.088 - 0.063}{0.063}$$

E = 4.92

Conventional solution synthesis of t-Bu-Salophen (In)Cl **(4b)**:

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - phenylenedia\text{mine} + InCl3 + ethanol\,(10\%) + Toluene\,(10\%) - total\,product}{total\,product}$$

$$E = \frac{0.066 + 0.034 + 0.044 + 0.158 + 0.088 - 0.063}{0.063}$$

E = 5.19

B-2. Energy usage calculations

Energy consumption and energy saved at each step (Ligand + Complex) of the mechanochemistry and conventional solution-based synthesis processes were calculated based on the following equation (1 kW = 3.6 MJ):

Energy consumption by unit operation/process (kWh) = Power rating of the instrument (kW) X Time of operation (h)

$$\%\ Energy\ saved = \frac{Energy\ used\ (Solution\ method\ -\ Mechanosynthesis)}{Energy\ used\ in\ Solution\ method}\ x\ 100$$

Power consumption of:

- Vibratory shaker mill (Retsch, MM400) = 150 W (2 station)
- Hot plate stirrer (Hei-standard), = 800 W

Larger scale projections were made using a conversion factor based on previously published data[1].

0.1 g;

Energy used for 0.1 g scale reaction:

Mechanosynthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

Energy used = (0.15 kW x 2 h) + (0.15 kW x 6 h) = 1.2 kwh/0.0001 kg = 12000 kwh/kg = 43200 MJ/kg (each complex)

Solution synthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

Energy used = (0.8 kW x 12 h) + (0.8 kW x 12 h) = 19.2 kwh/0.0001 kg = 192000 kwh/ kg = 691200 MJ/kg (each complex)

1.0 g;

Energy used for 1.0 g scale reaction:

Mechanosynthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

Energy used = (0.15 kW x 2 h) + (0.15 kW x 6 h) = 1.2 kwh/0.001 kg = 1200 kwh/ kg = 4320 MJ/kg (each complex)

Solution synthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

Energy used = (0.8 kW x 12 h) + (0.8 kW x 12 h) = 19.2 kwh/0.001 kg = 19200 kwh/ kg = 69120 MJ/kg (each complex)

30 g;

Energy used 30 g scale reaction:

Mechanosynthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

Energy used = (1.25 kW x 2 h) + (1.25 kW x 6 h) = 10 kwh/0.03 kg = 333.3 kwh/ kg = 1200 MJ/kg (each complex)

Solution synthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

Energy used = (0.8 kW x 12 h) + (0.8 kW x 12 h) = 19.2 kwh/0.03 kg = 640 kwh/ kg = 2304 MJ/kg (each complex)

60 g;

Energy used 60 g scale reaction:

Mechanosynthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

Energy used = (1.25 kW x 2 h) + (1.25 kW x 6 h) = 10 kwh/0.06 kg = 166.7 kwh/ kg = 600 MJ/kg (each complex)

Solution synthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

Energy used = (0.8 kW x 12 h) + (0.8 kW x 12 h) = 19.2 kwh/0.06 kg = 320 kwh/ kg = 1152 MJ/kg (each complex)

120 g;

Energy used 120 g scale reaction:

Mechanosynthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

Energy used = (1.6 kW x 2 h) + (1.6 kW x 6 h) = 12.8 kwh/0.120 kg = 106.7 kwh/ kg = 384 MJ/kg (each complex)

Solution synthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

Energy used = (0.8 kW x 12 h) + (0.8 kW x 12 h) = 19.2 kwh/0.120 kg = 160 kwh/ kg = 512 MJ/kg (each complex)

In order to make the energy calculations easier to read and compare between the mechanochemistry and solution-based methods, all the information has been summarised in Table S1:

Table S1. Energy consumption for the synthesis of complexes **3a** to **4b** at different scales

Scale (g)	Energy Consumption (kwh)	Energy Consumption ($kwh.kg^{-1}$)	Energy Consumption ($MJ.kg^{-1}$)
Mechanochemistry method			
0.1	1.2	12000	43200
1.0 (P)	1.2	1200	4320
30.0(P)	10	333.3	1200
60.0(P)	10	166.7	600
120.0(P)	12.8	106.7	384
Conventional solution-based method			
0.1	19.2	192000	691200
1.0(P)	19.2	19200	69120
30.0(P)	19.2	640	2304
60.0(P)	19.2	320	1152
120.0(P)	19.2	160	512

(P) Larger-scale projections based on literature values.[1]

Energy saved

0.1 g;

% Energy saved for the synthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

$$\%\, Energy\ saved\ = \frac{691200\ \frac{MJ}{Kg} - \ 43200\ \frac{MJ}{Kg}}{691200\ \frac{MJ}{Kg}}\ x\ 100$$

%Energy saved = 93.8 % (each complex)

1 g;

% Energy saved for the synthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

$$\%\, Energy\ saved\ = \frac{69120\ \frac{MJ}{Kg} - \ 4320\ \frac{MJ}{Kg}}{69120\ \frac{MJ}{Kg}}\ x\ 100$$

%Energy saved = 93.8 % (each complex)

30 g;

% Energy saved for the synthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

$$\%\, Energy\ saved\ = \frac{2304\ \frac{MJ}{Kg} -\ 1200\ \frac{MJ}{Kg}}{2304\ \frac{MJ}{Kg}}\ x\ 100$$

%Energy saved = 47.9 % (each complex)

60 g;

% Energy saved for the synthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

$$\%\, Energy\ saved\ = \frac{1152\ \frac{MJ}{Kg} -\ 600\ \frac{MJ}{Kg}}{1152\ \frac{MJ}{Kg}}\ x\ 100$$

%Energy saved = 47.9 % (each complex)

120 g;

% Energy saved for the synthesis of t-Bu-Salen (Al)Cl (**3a**), t-Bu-Salen (In)Cl (**3b**), t-Bu-Salophen (Al)Cl (**4a**), t-Bu-salophen (In)Cl (4**b**):

$$\%\, Energy\ saved\ = \frac{512\ \frac{MJ}{Kg} -\ 384\ \frac{MJ}{Kg}}{512\ \frac{MJ}{Kg}}\ x\ 100$$

%Energy saved = 25 % (each complex)

B-3. Process mass intensity (PMI) calculations

Mechanosynthesis of t-Bu-Salen (**1**):

Formula used:

$$PMI\ = \frac{Benzaldehyde\ +\ 1{,}2 - ethylenediamine}{total\ product}$$

$$PMI\ = \frac{1.01\ +\ 0.150}{1.14}$$

PMI = 1.02

Mechanosynthesis of t-Bu-Salophen (**2**):

Formula used:

$$PMI\ = \frac{Benzaldehyde\ + 1{,}2 - phenylenediamine}{total\ product}$$

$$PMI = \frac{1.01 + 0.27}{1.213}$$

PMI = 1.06

Mechanosynthesis of t-Bu-Salen (Al)Cl (**3a**):

Formula used:

$$PMI = \frac{Benzaldehyde + 1{,}2 - ethylenediamine + Ligand\,used + AlCl3 - Ligand\,total}{Complex\,total}$$

$$PMI = \frac{0.06 + 0.03 + 0.088 + 0.037 - 0.88}{0.113}$$

PMI = 1.13

Mechanosynthesis of t-Bu-Salen (In)Cl (**3b**):

Formula used:

$$PMI = \frac{Benzaldehyde + 1{,}2 - ethylenediamine + Ligand\,used + InCl3 - Ligand\,total}{Complex\,total}$$

$$PMI = \frac{0.06 + 0.03 + 0.088 + 0.061 - 0.088}{0.097}$$

PMI = 1.55

Mechanosynthesis of t-Bu-Salophen (Al)Cl (**4a**):

Formula used:

$$PMI = \frac{Benzaldehyde + 1{,}2 - phenylenediamine + Ligand\,used + AlCl3 - Ligand\,total}{Complex\,total}$$

$$PMI = \frac{0.066 + 0.034 + +0.087 + 0.037 - 0.087}{0.096}$$

PMI = 1.42

Mechanosynthesis of t-Bu-Salophen (In)Cl (**4b**):

Formula used:

$$PMI = \frac{Benzaldehyde + 1{,}2 - phenylenediamine + Ligand\,used + InCl3 - Ligand\,total}{Complex\,total}$$

$$E = \frac{0.066 + 0.034 + 0.087 + 0.061 - 0.087}{0.097}$$

PMI = 1.66

Conventional solution synthesis of Conventional solution synthesis of t-Bu-Salen **(1):**

Formula used:

$$PMI = \frac{Benzaldehyde + 1{,}2 - ethylenediamine + ethanol\,(10\%) + Toluene\,(10\%)}{total\,product}$$

$$PMI = \frac{1.01 + 0.150 + 1.184 + 0.701}{0.96}$$

PMI = 3.17

Conventional solution synthesis of t-Bu-Salophen **(2)**

Formula used:

$$PMI = \frac{Benzaldehyde + 1{,}2 - phenylenediamine + ethanol\,(10\%) + Toluene\,(10\%)}{total\ product}$$

$$PMI = \frac{1.01 + 0.27 + 1.184 + 0.701}{0.96}$$

PMI = 3.30

Conventional solution synthesis of t-Bu-Salen (Al)Cl **(3a)**:

Formula used:

$$E = \frac{Benzaldehyde + 1{,}2 - ethylenediamine + Ligand\ used + AlCl3 + EtOH + Toluene - Ligand\ total}{Complex\ total}$$

$$\text{PMI} = \frac{0.06 + 0.03 + 0.088 + 0.027 + 1.578 - 0.077}{0.063}$$

PMI = 39.7

Conventional solution synthesis of t-Bu-Salen (In)Cl (**3b**):

Formula used:

$$PMI = \frac{Benzaldehyde + 1{,}2 - ethylenediamine + Ligand\ used + InCl3 + EtOH + Toluene - Ligand\ total}{Complex\ total}$$

$$PMI = \frac{0.06 + 0.03 + 0.088 + 0.044 + 1.58 + 0.088 - 0.077}{0.063}$$

PMI = 28.8

Conventional solution synthesis of t-Bu-Salophen (In)Cl **(4b)**:

Formula used:

$$PMI = \frac{Benzaldehyde + 1{,}2 - phenylenediamine + Ligand\ used + AlCl3 + EtOH + Toluene - Ligand\ total}{Complex\ total}$$

$$PMI = \frac{0.066 + 0.034 + 0.087 + 0.027 + 1.58 + 0.088 - 0.076}{0.063}$$

PMI = 28.7

Conventional solution synthesis of t-Bu-Salophen (Al)Cl **(4a)**:

Formula used:

$$PMI = \frac{Benzaldehyde + 1{,}2 - phenylenediamine + Ligand\ used + InCl3 + EtOH + Toluene - Ligand\ total}{Complex\ total}$$

$$PMI = \frac{0.066 + 0.034 + 0.087 + 0.044 + 1.58 + 0.088 - 0.076}{0.063}$$

PMI = 28.9

B-4. Generalized reaction mass efficiency (RME)

Mechanosynthesis of t-Bu-Salen (**1**):

Formula used:

$$RME = \frac{Ligand\ total}{Benzaldehyde + 1{,}2 - ethylenediamine}$$

RME = 0.98

Mechanosynthesis of t-Bu-Salophen (**2**):

Formula used:

$$RME = \frac{Ligand\ total}{Benzaldehyde + 1{,}2 - phenylenediamine}$$

$$RME = \frac{1.21}{1.01 + 0.27}$$

RME = 0.95

Mechanosynthesis of t-Bu-Salen (Al)Cl (**3a**):

Formula used:

$$RME = \frac{Complex\ total}{Benzaldehyde + 1{,}2 - ethylenedia\text{mine} + AlCl3}$$

$$RME = \frac{0.113}{0.06 + 0.03 + 0.037}$$

RME = 0.89

Mechanosynthesis of t-Bu-Salen (In)Cl (**3b**):

Formula used:

$$RME = \frac{Complex\ total}{Benzaldehyde + 1{,}2 - ethylenediamine + InCl3}$$

$$RME = \frac{0.097}{0.06 + 0.03 + 0.061}$$

RME = 0.64

Mechanosynthesis of t-Bu-Salophen (Al)Cl (**4a**):

Formula used:

$$RME = \frac{Benzaldehyde + 1{,}2 - phenylenediamine + Ligand\ used + AlCl3 - Ligand\ total}{Complex\ total}$$

$$RME = \frac{0.096}{0.066 + 0.034 + 0.037}$$

RME = 0.70

Mechanosynthesis of t-Bu-Salophen (In)Cl (**4b**):

Formula used:

$$RME = \frac{Complex\ total}{Benzaldehyde + 1{,}2 - phenylenediamine + InCl3}$$

$$RME = \frac{0.097}{0.066 + 0.034 + 0.061}$$

RME = 0.60

Conventional solution synthesis of t-Bu-Salen **(1):**

Formula used:

$$RME = \frac{Ligand\ total}{Benzaldehyde + 1{,}2 - ethylenediamine}$$

$$RME = \frac{0.96}{1.01 + 0.150}$$

RME = 0.82

Conventional solution synthesis of t-Bu-Salophen **(2)**

Formula used:

$$RME = \frac{Ligand\ total}{Benzaldehyde + 1{,}2 - phenylenediamine}$$

$$RME = \frac{0.96}{1.01 + 0.27}$$

RME = 0.75

Conventional solution synthesis of t-Bu-Salen (Al)Cl **(3a)**:

Formula used:

$$RME = \frac{Complex\ total}{Benzaldehyde + 1{,}2 - ethylenediamine + AlCl3}$$

$$RME = \frac{0.063}{0.06 + 0.03 + 0.027}$$

RME = 0.53

Conventional solution synthesis of t-Bu-Salen (In)Cl (**3b**):

Formula used:

$$RME = \frac{Complex\ total}{Benzaldehyde + 1{,}2 - ethylenediamine + InCl3}$$

$$RME = \frac{0.063}{0.06 + 0.03 + 0.044}$$

RME = 0.47

Conventional solution synthesis of t-Bu-Salophen (Al)Cl **(4a)**:

Formula used:

$$RME = \frac{Complex\ total}{Benzaldehyde\ + 1{,}2 - phenylenediamine\ +\ InCl3}$$

$$RME = \frac{0.063}{0.066 + 0.034 + 0.044}$$

RME = 0.43

Conventional solution synthesis of t-Bu-Salophen (In)Cl **(4b)**:

Formula used:

$$RME\ = \frac{Complex\ total}{Benzaldehyde\ + 1{,}2 - phenylenedia\text{mine}\ +\ InCl3}$$

$$PMI = \frac{0.063}{0.066 + 0.034 + 0.027}$$

RME = 0.49

C. NMR, FT-IR and UV-vis spectra, TOF-MS analysis, spectra photophysical measurements and X-ray structure.

C-1-1. NMR spectra

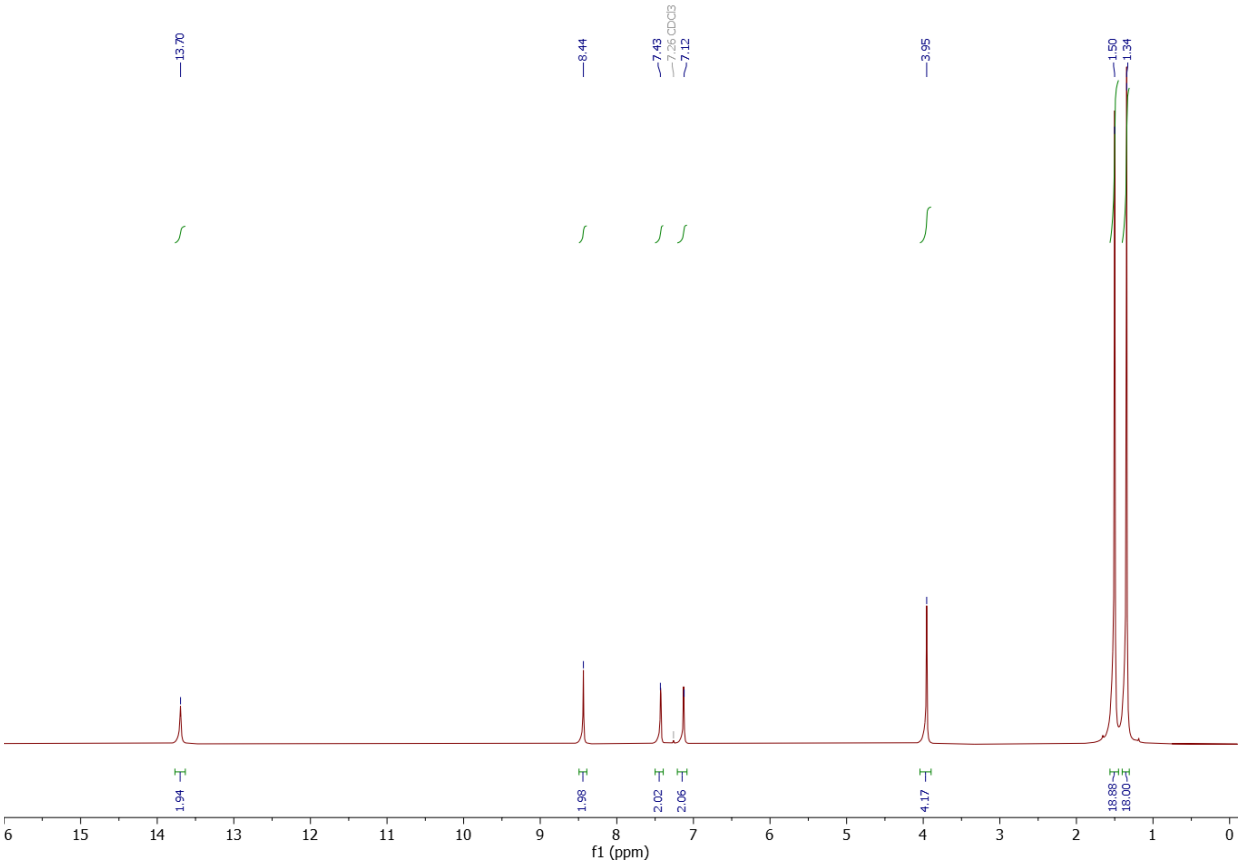


Figure S1. ^{1}H NMR spectrum of **1** in CD_2Cl_2

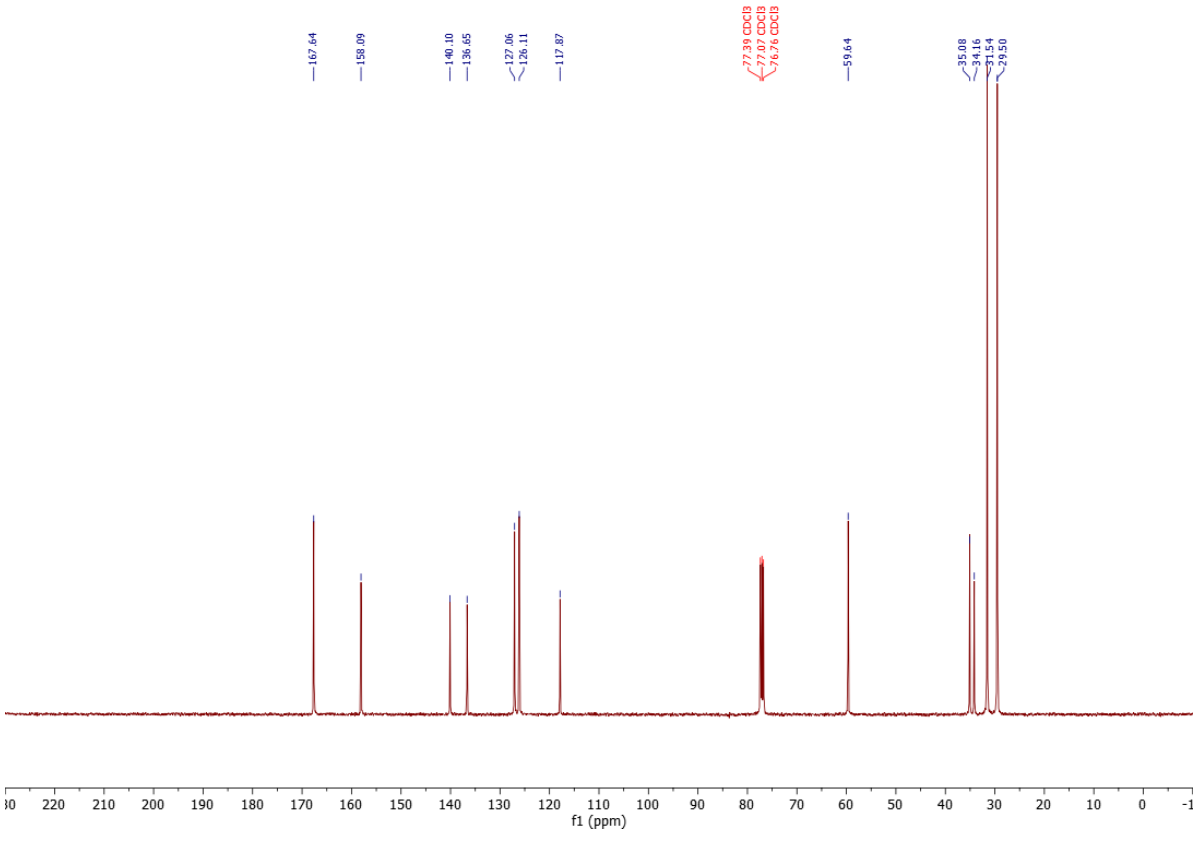


Figure S2. $^{13}C\{^{1}H\}$ spectrum of **1** in CD_2Cl_2

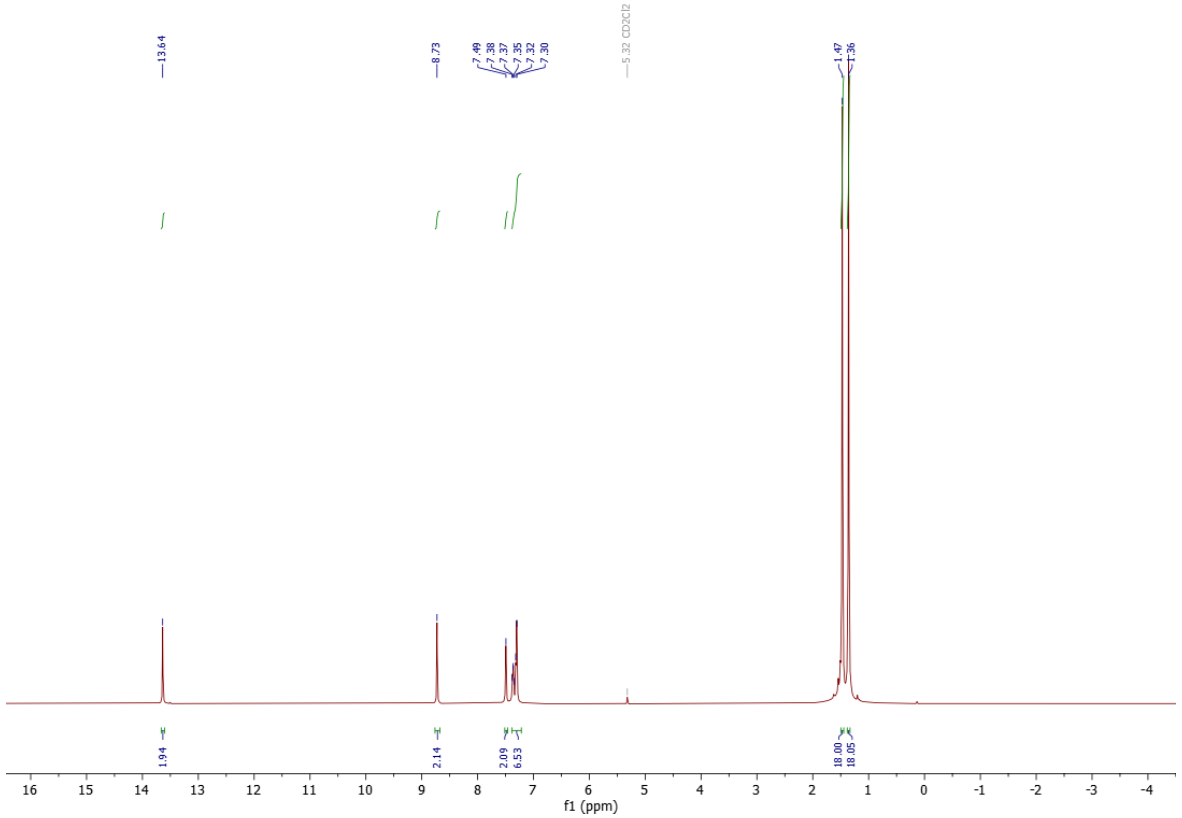


Figure S3. ^{1}H NMR spectrum of **2** in CD_2Cl_2

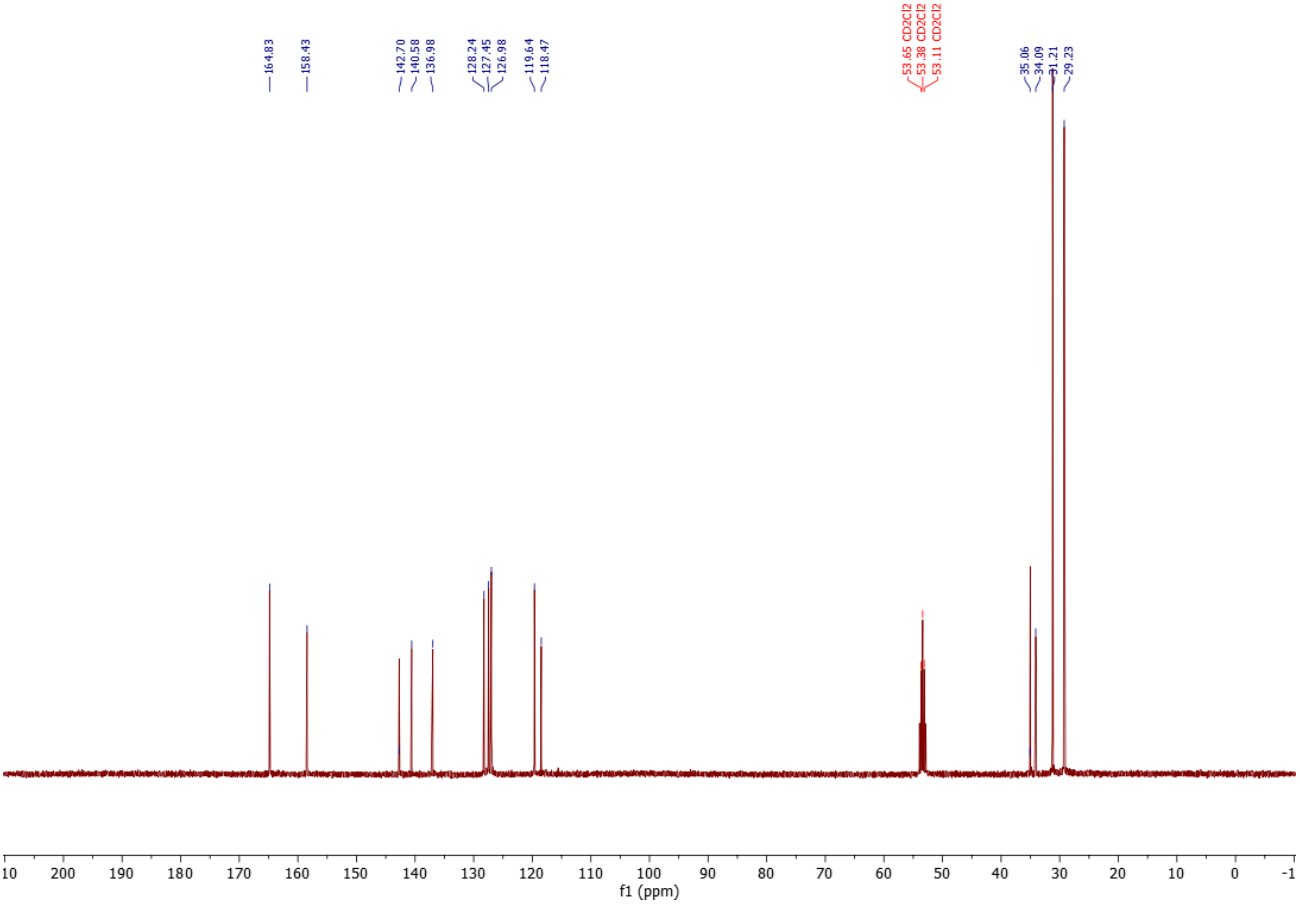


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in CD_2Cl_2

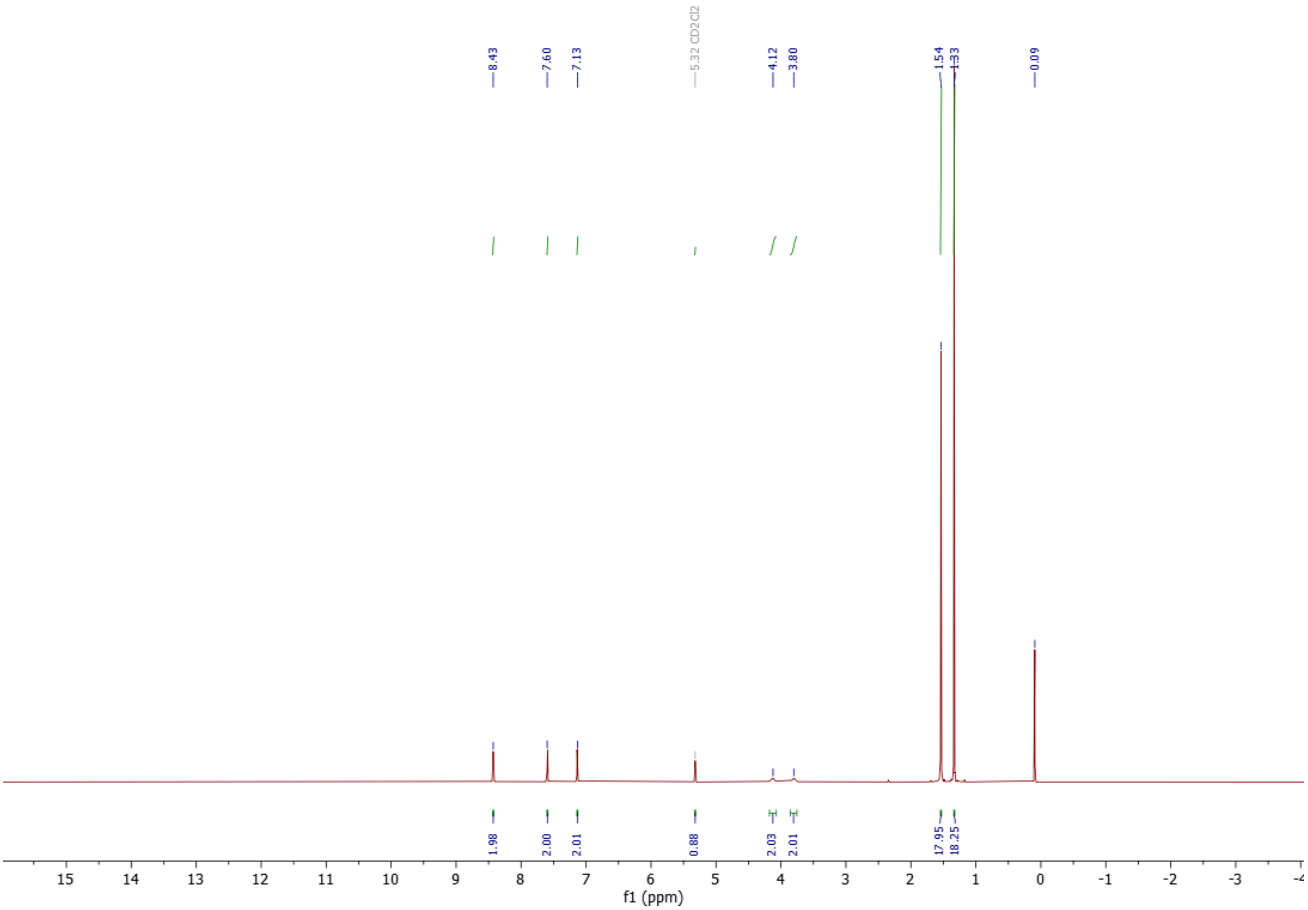


Figure S5. ^{1}H NMR spectrum of **3a** in CD_2Cl_2

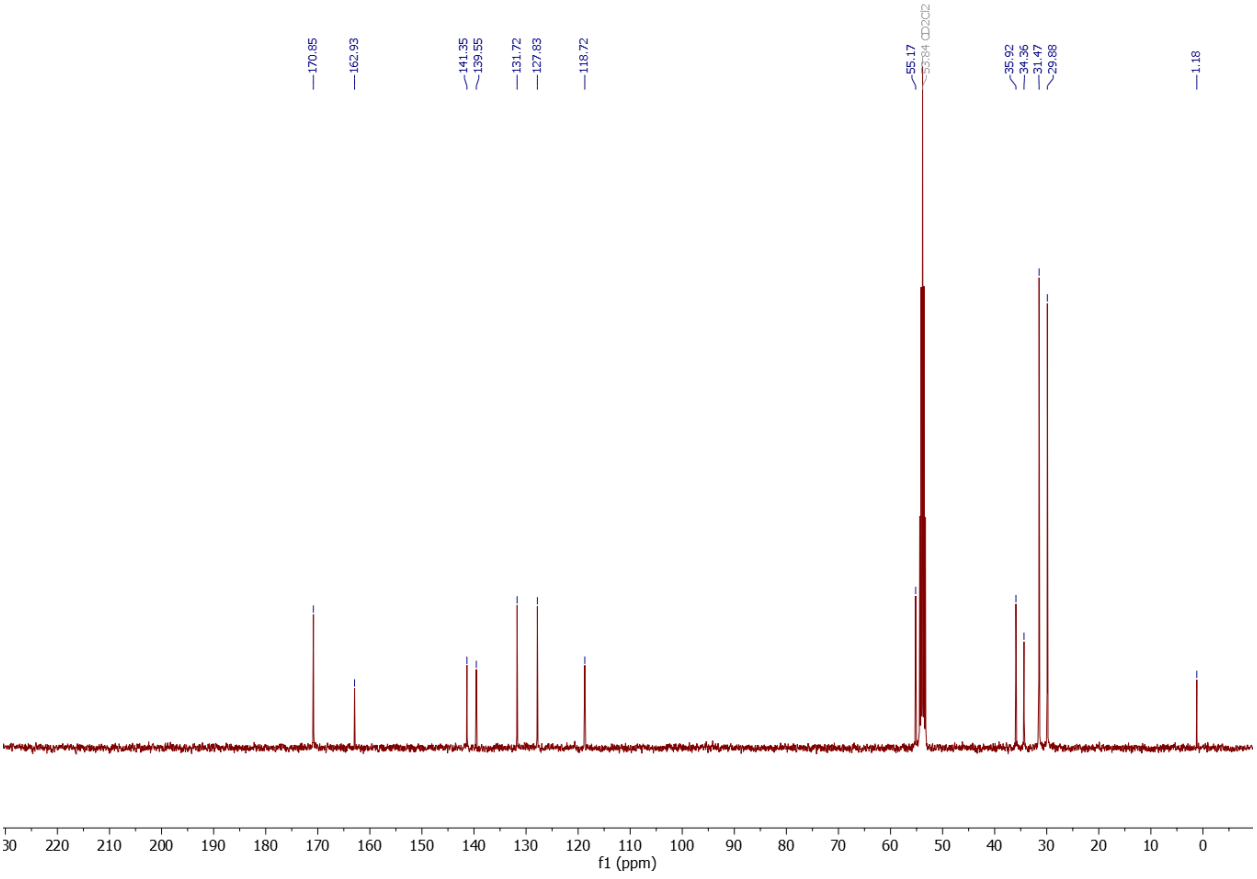


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in CD_2Cl_2

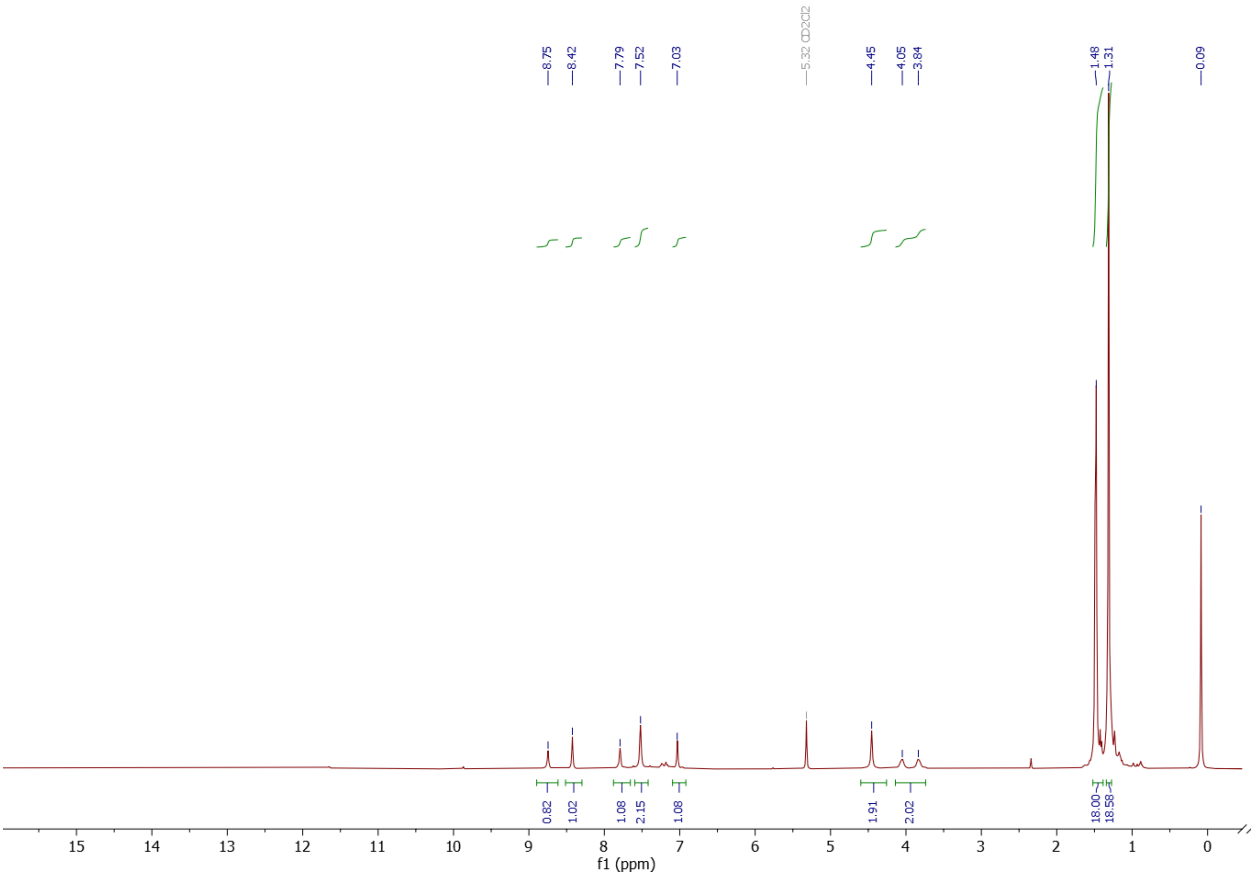


Figure S7. ^{1}H NMR spectrum of **3b** in CD_2Cl_2

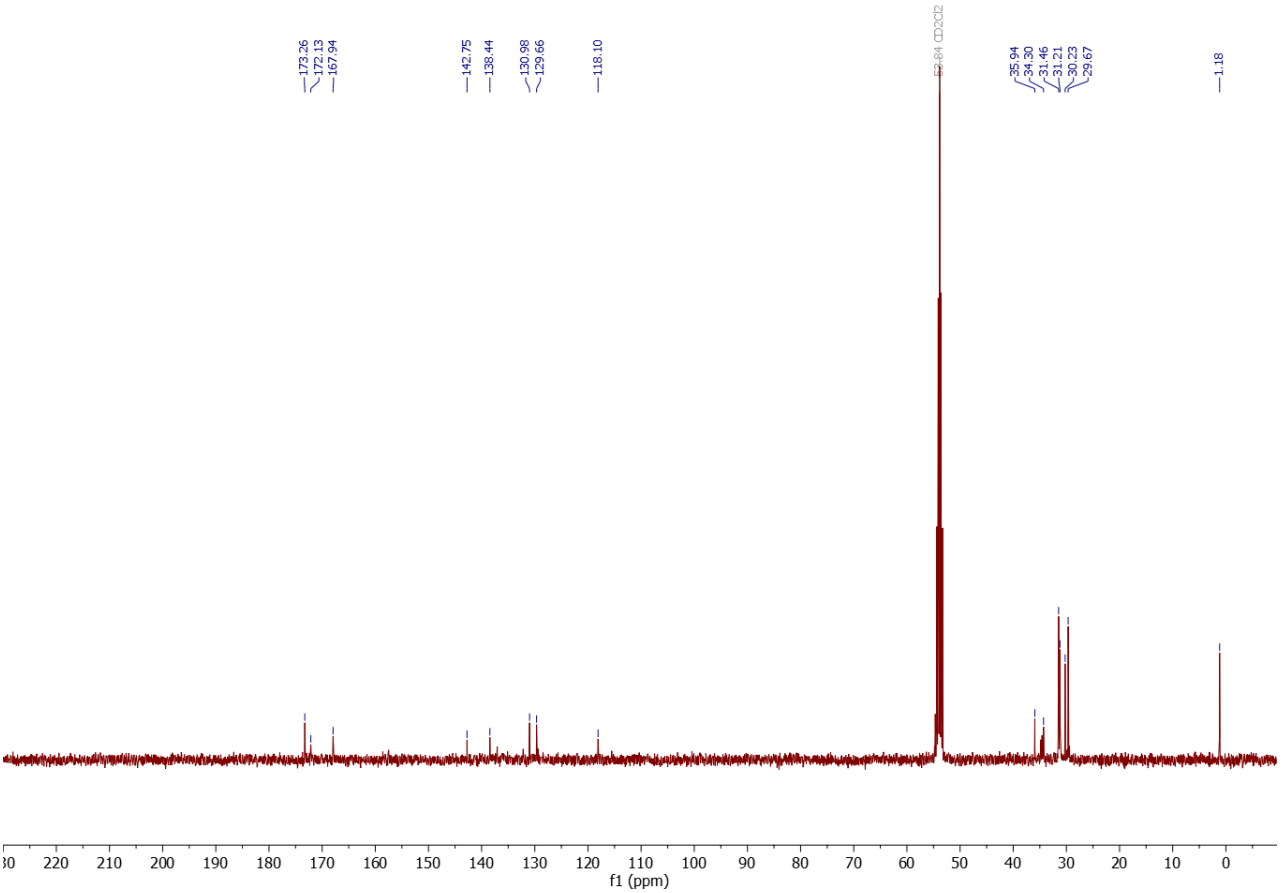


Figure S8. ^{13}C{^{1}H} NMR spectrum of **3b** in CD_2Cl_2

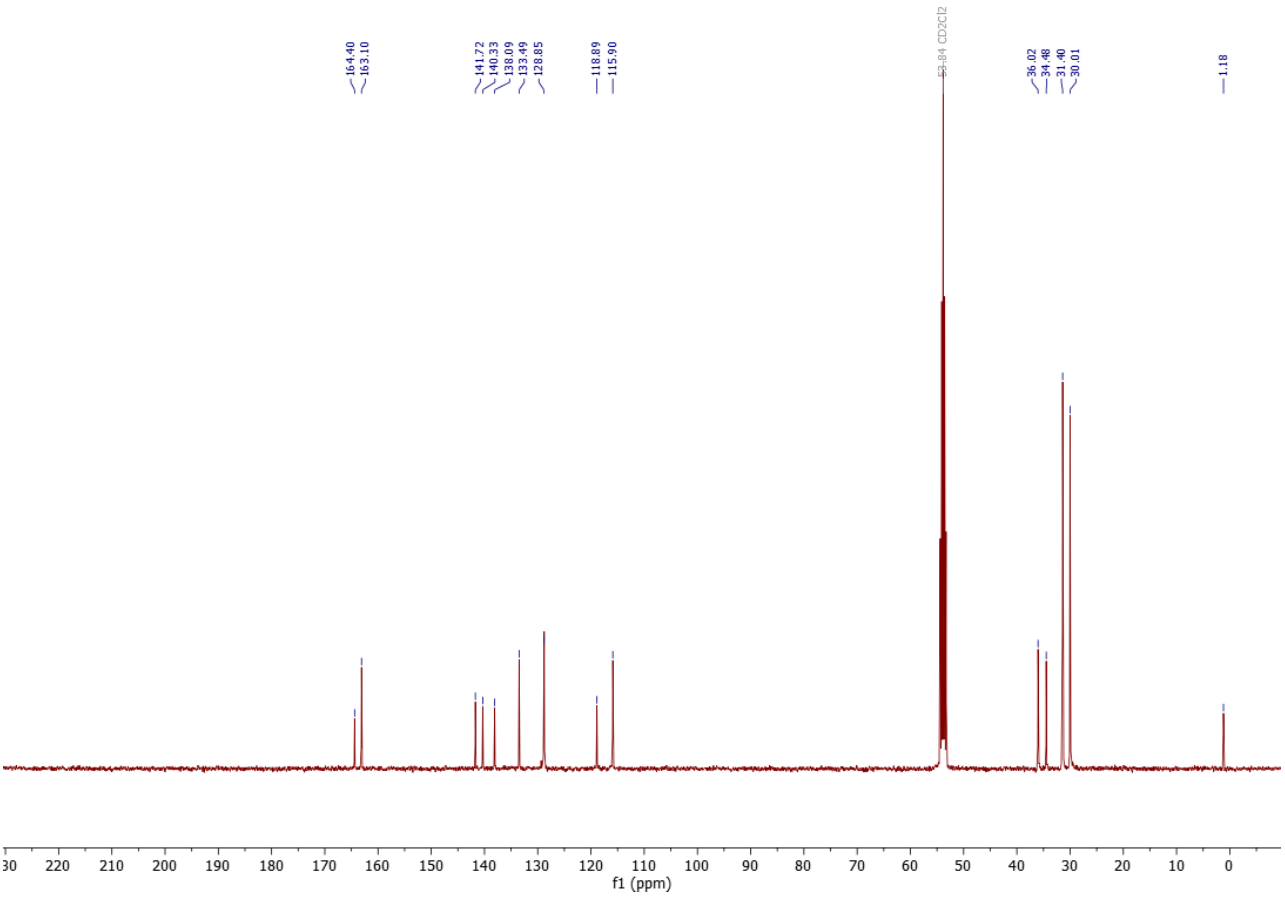


Figure S9. ^{1}H NMR spectrum of **4a** in CD_2Cl_2

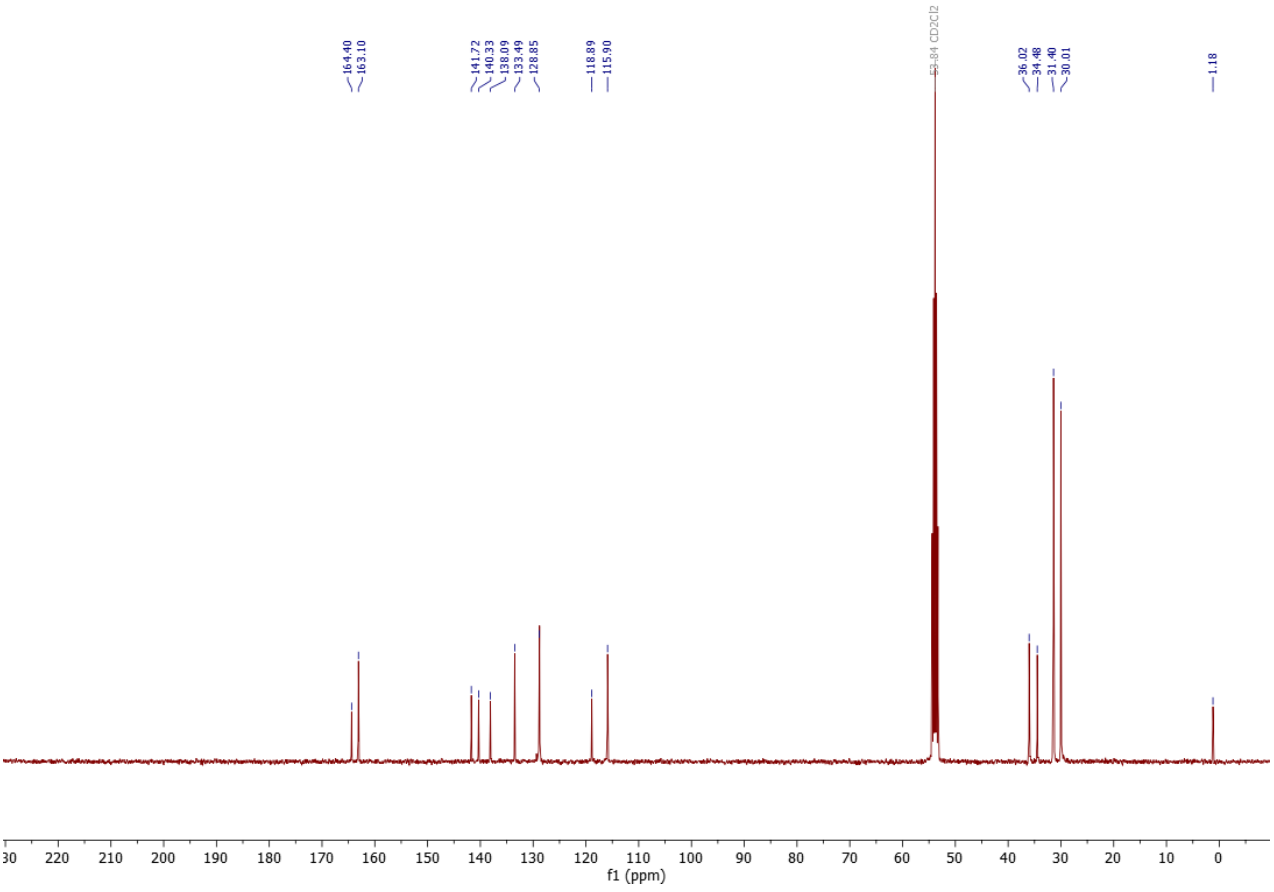


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **4a** in CD_2Cl_2

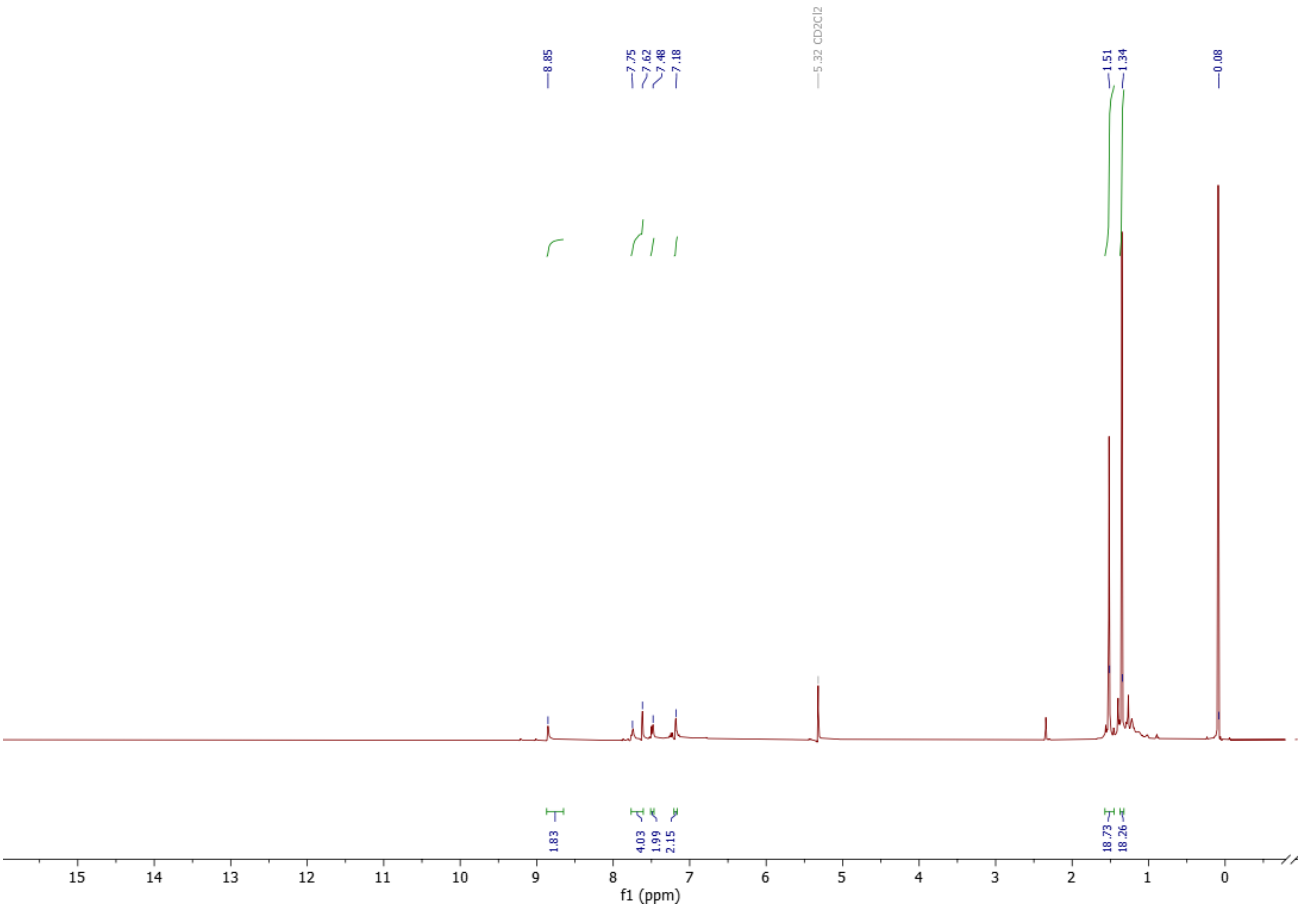


Figure S11. ^{1}H NMR spectrum of **4b** in CD_2Cl_2

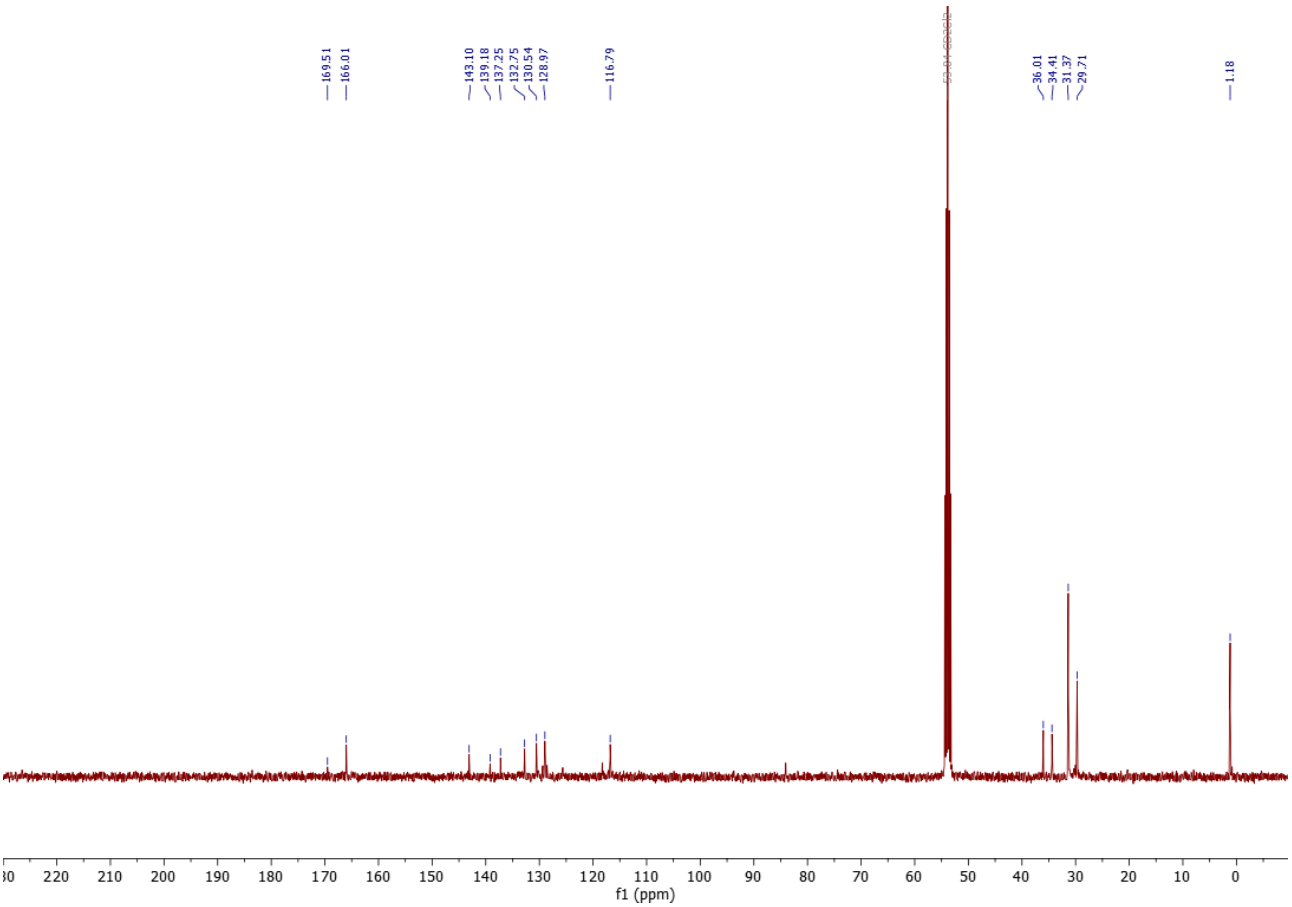


Figure S12. ^{13}C{^{1}H} NMR spectrum of **4b** in CD_2Cl_2

C-1-2. FT-IR spectra

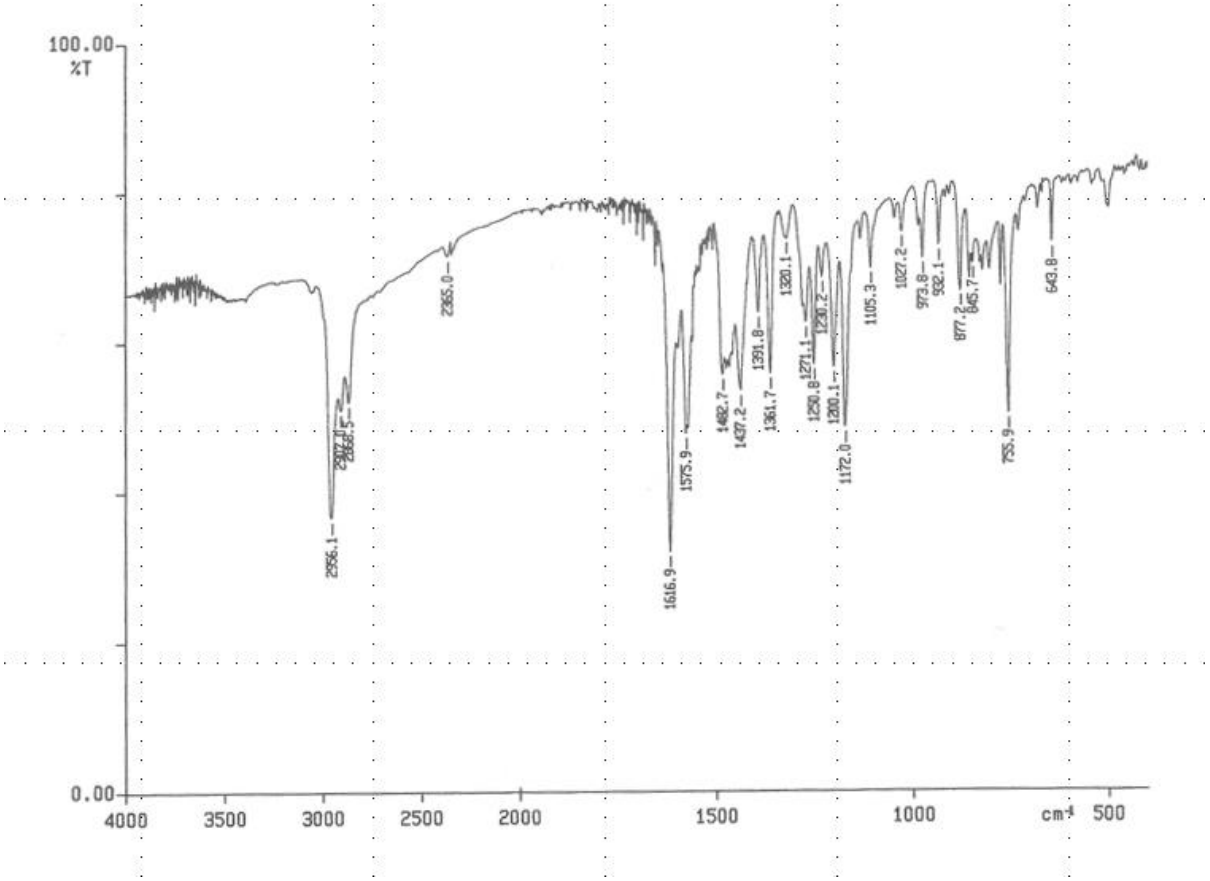


Figure S13. FT-IR spectrum of **1** in KBr

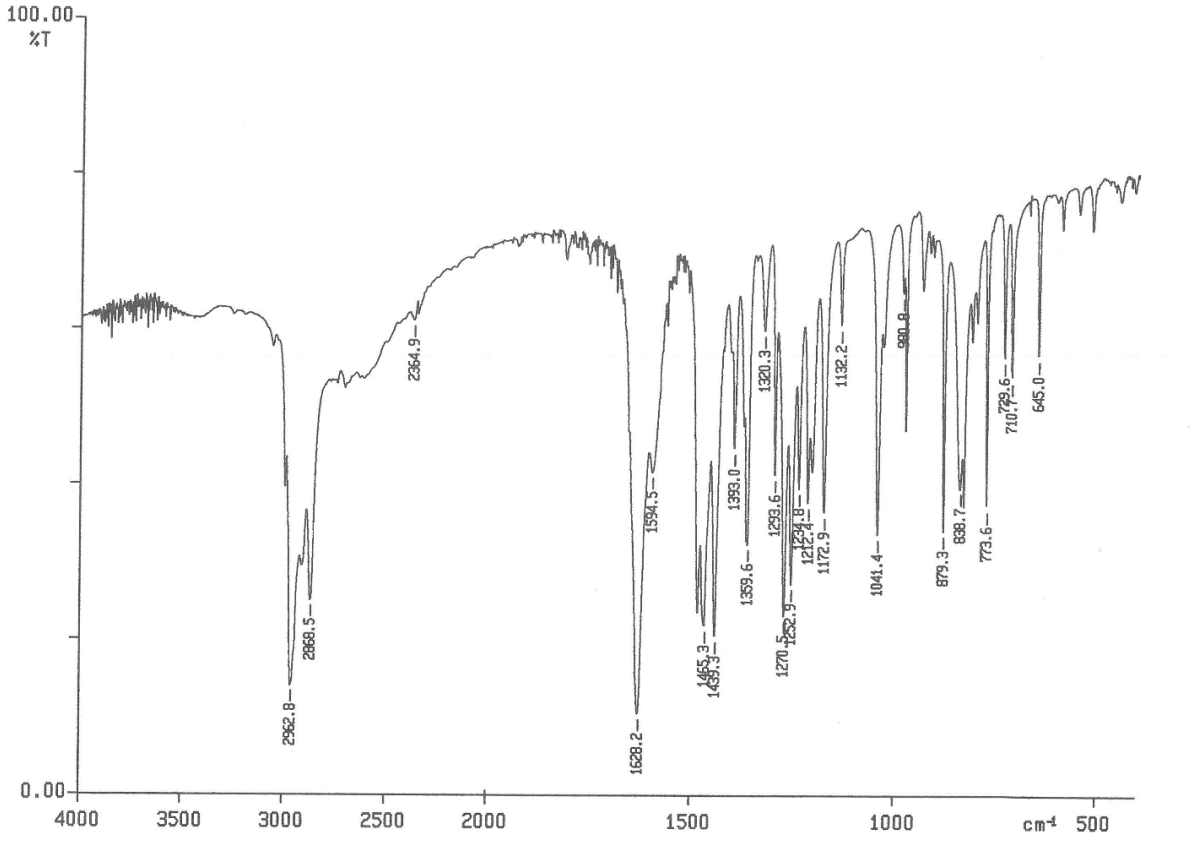


Figure S14. FT-IR spectrum of **2** in KBr

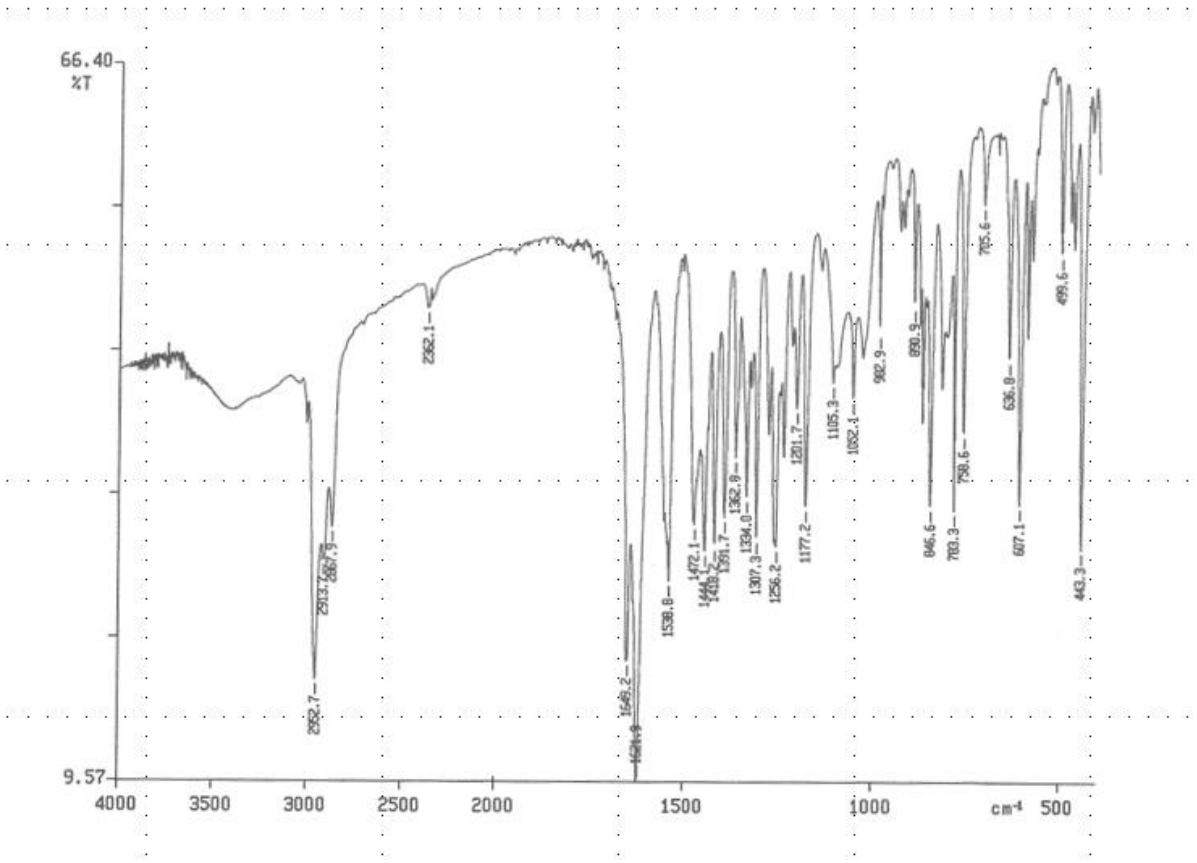


Figure S15. FT-IR spectrum of **3a** in KBr

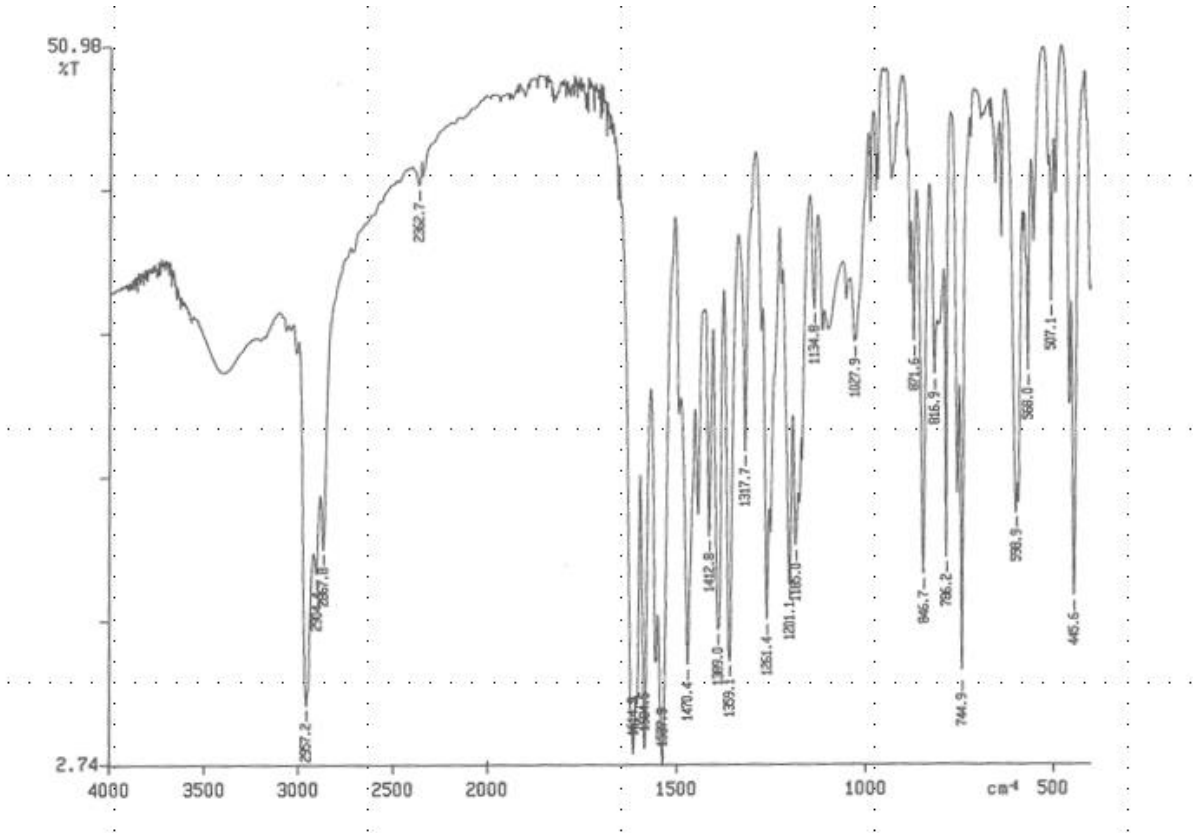


Figure S16. FT-IR spectrum of **3b** in KBr

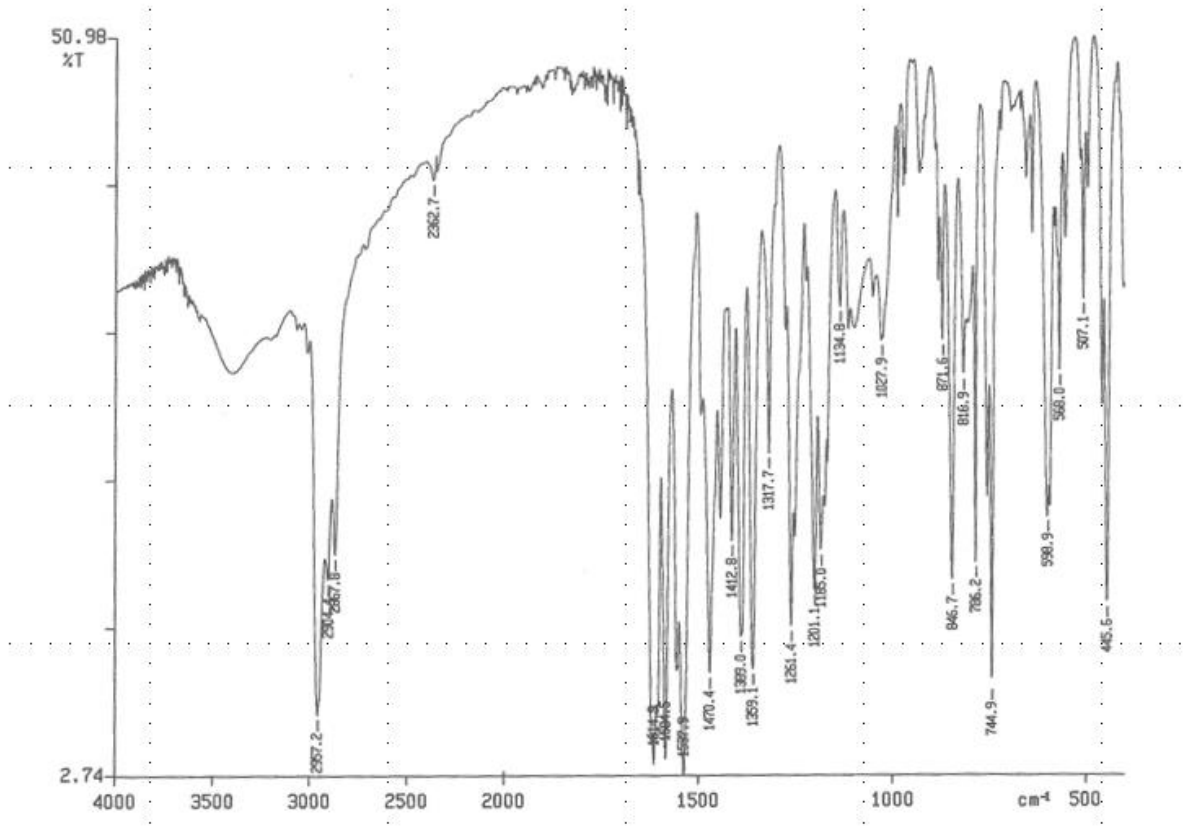


Figure S17. FT-IR spectrum of **4a** in KBr

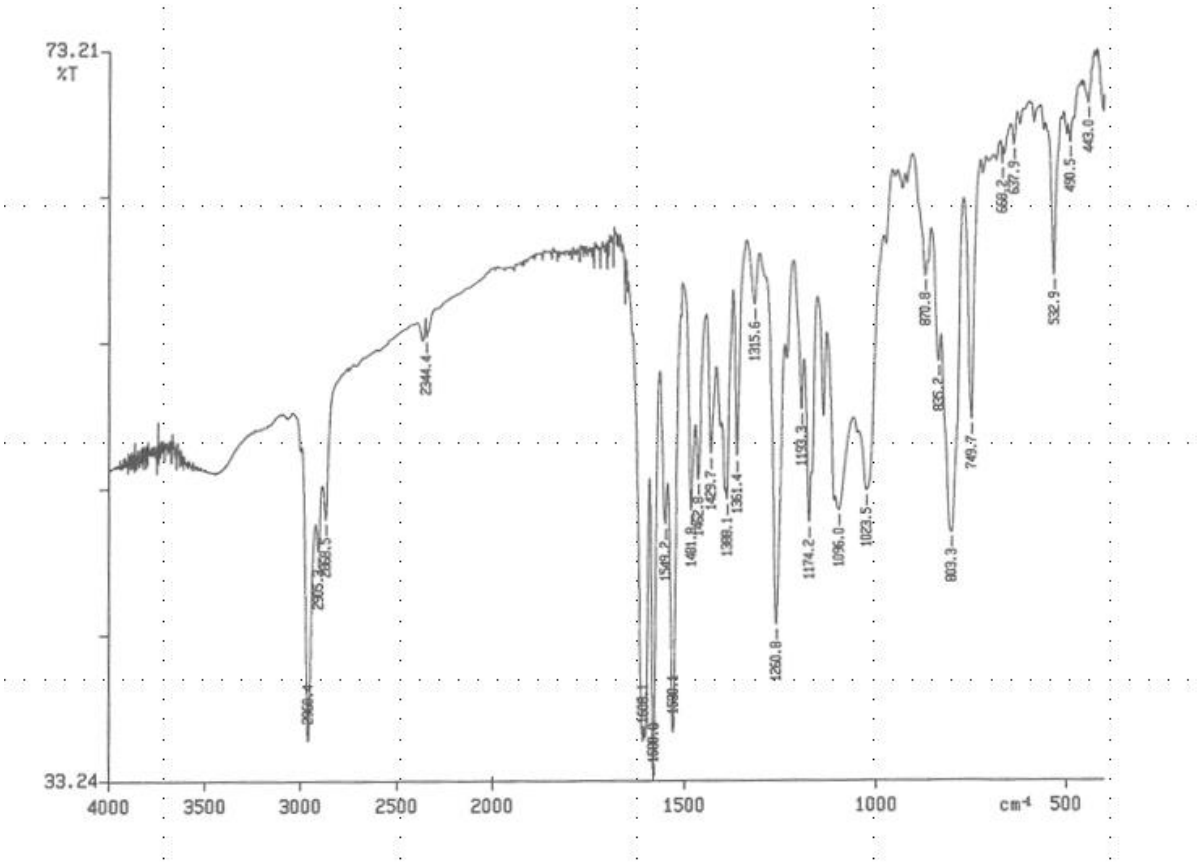


Figure S18. FT-IR spectrum of **4b** in KBr

C-1-3. UV-Vis spectra

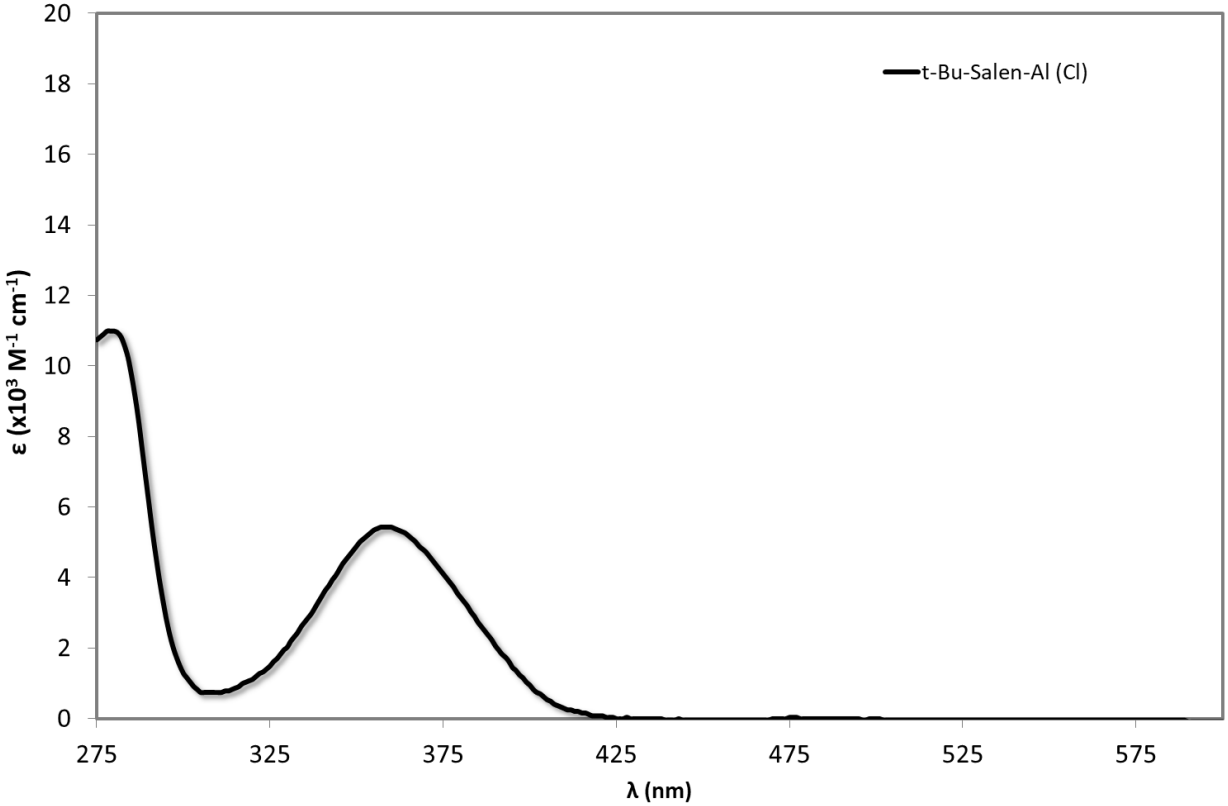


Figure S19. UV-VIS spectrum of **3a** in DMSO

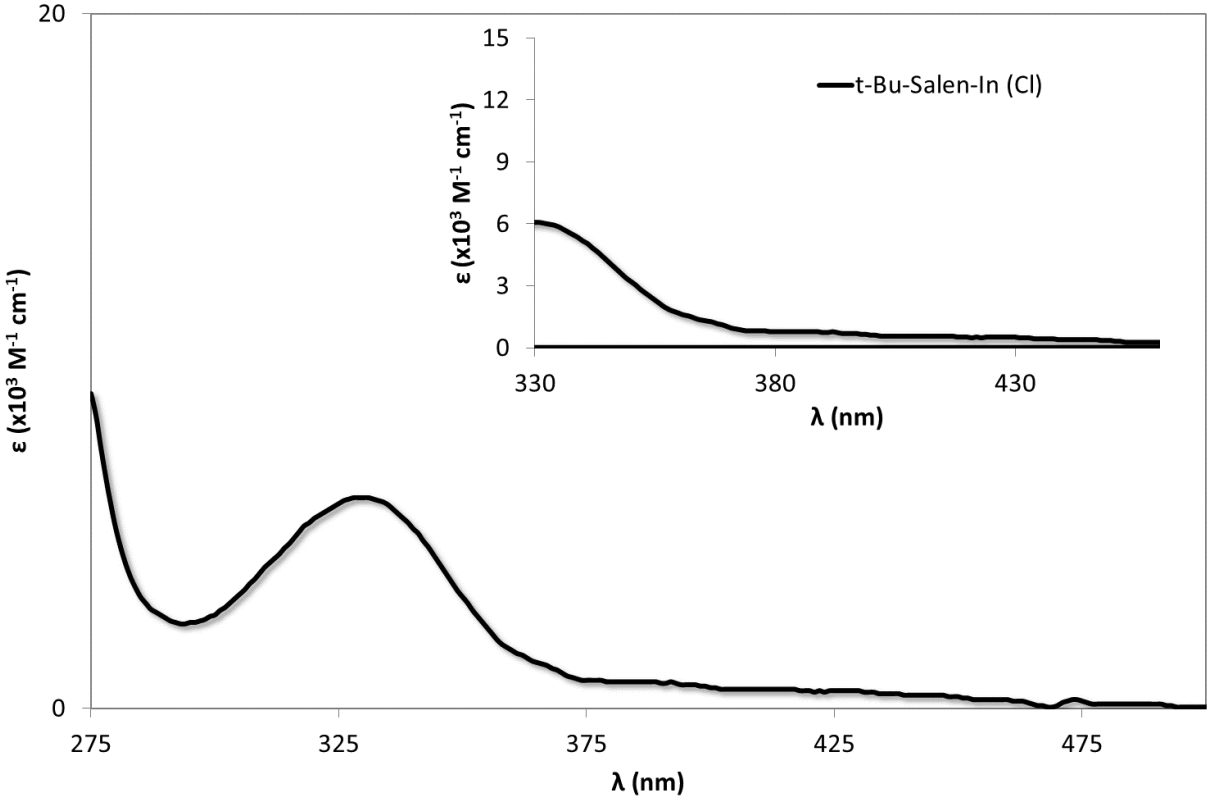


Figure S20. UV-VIS spectrum of **3b** in DMSO

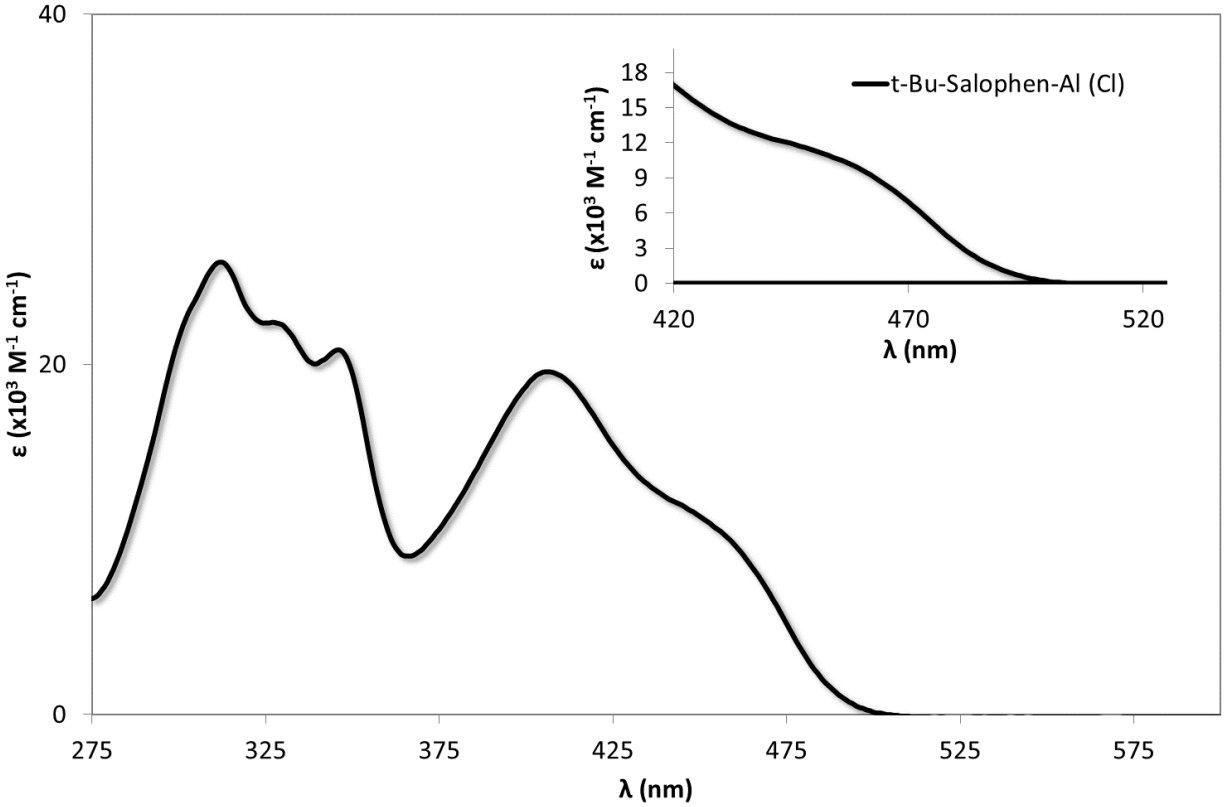


Figure S21. UV-VIS spectrum of **4a** in DMSO

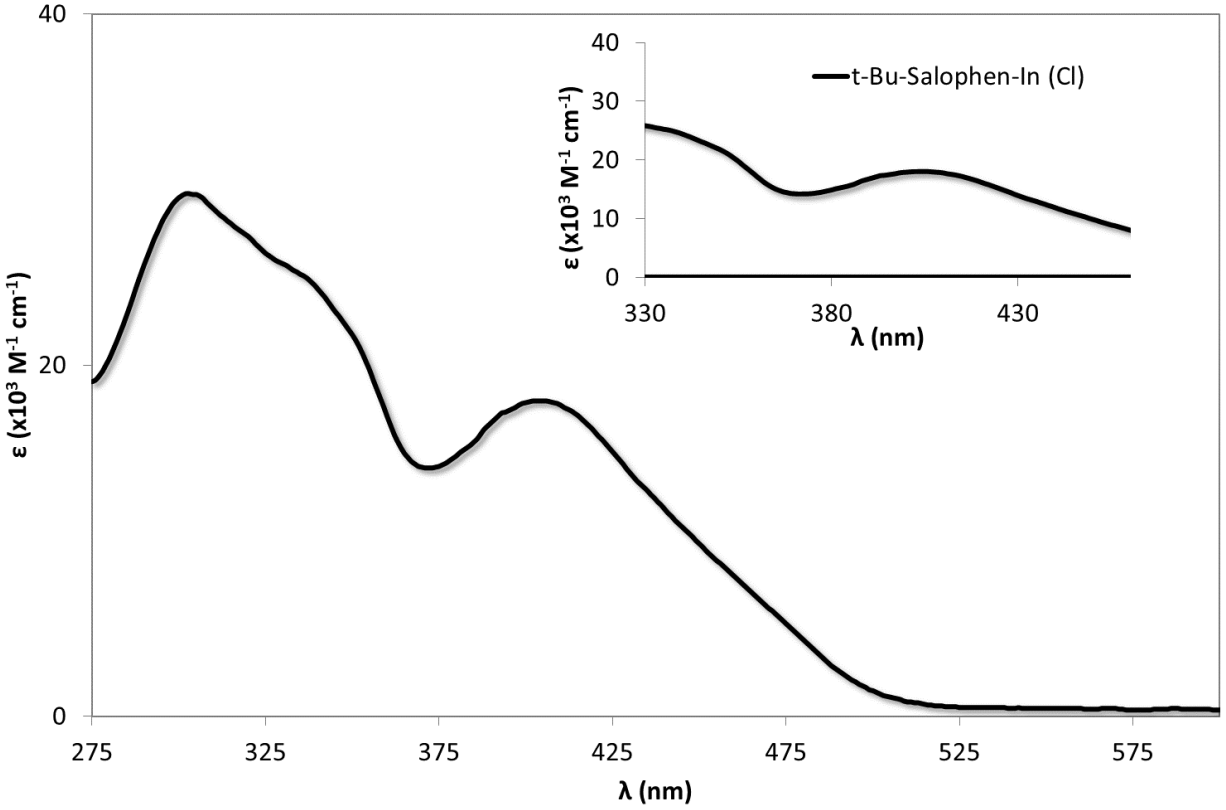
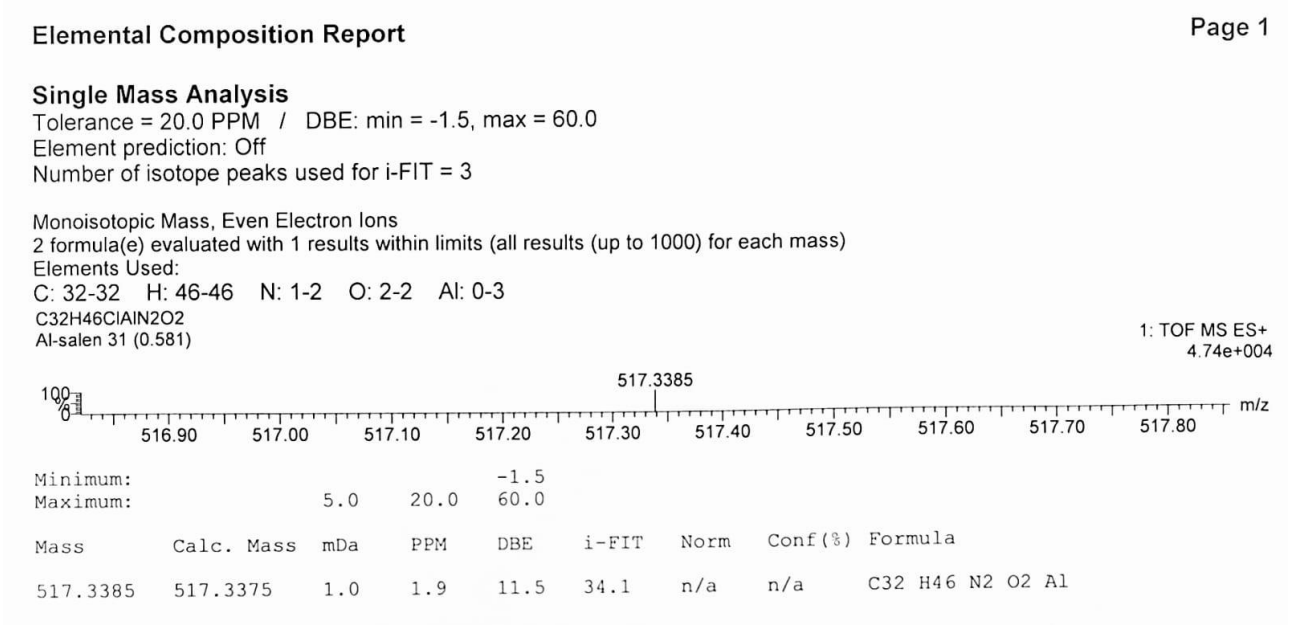


Figure S22. UV-VIS spectrum of **4b** in DMSO

C-1-4. TOF-MS analysis



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 60.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

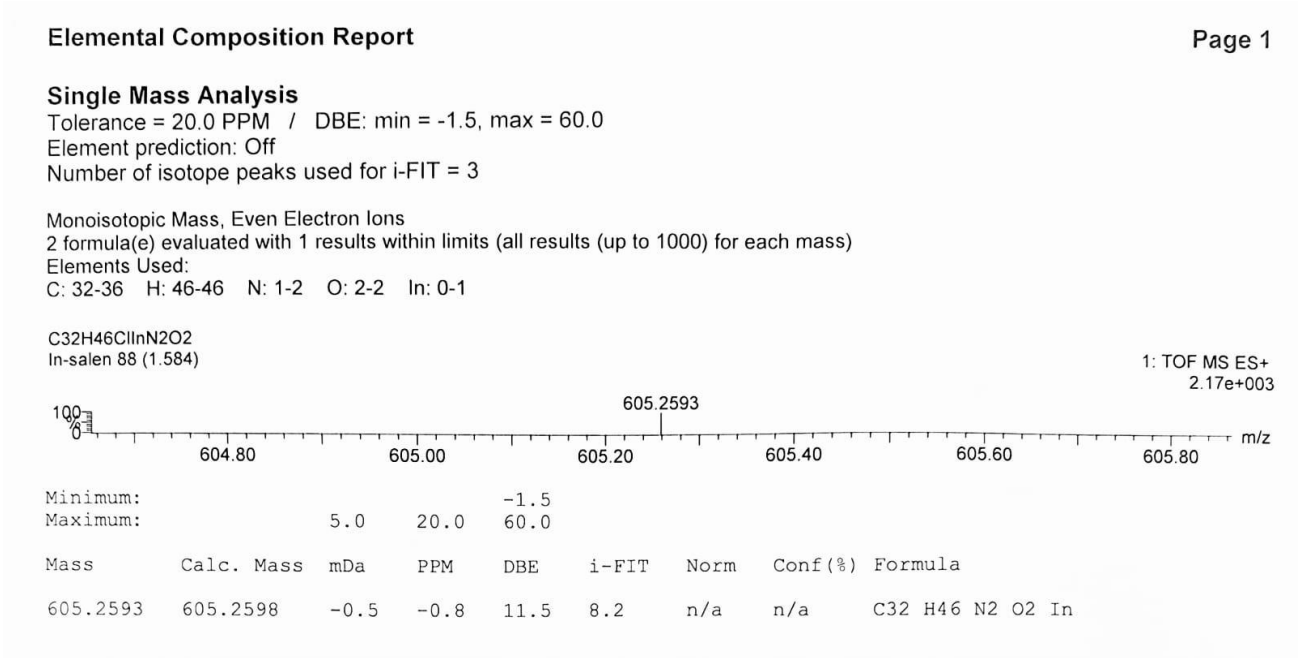
Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 32-32 H: 46-46 N: 1-2 O: 2-2 Al: 0-3

C32H46ClAlN2O2
Al-salen 31 (0.581)

1: TOF MS ES+
4.74e+004

Minimum:				-1.5				
Maximum:		5.0	20.0	60.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
517.3385	517.3375	1.0	1.9	11.5	34.1	n/a	n/a	C32 H46 N2 O2 Al

Figure S23. Single mass analysis report of 3**a** done by WATERS XEVO G2-X2 ESI-TOF.



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 60.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 32-36 H: 46-46 N: 1-2 O: 2-2 In: 0-1

C32H46ClInN2O2
In-salen 88 (1.584)

1: TOF MS ES+
2.17e+003

Minimum:				-1.5				
Maximum:		5.0	20.0	60.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
605.2593	605.2598	-0.5	-0.8	11.5	8.2	n/a	n/a	C32 H46 N2 O2 In

Figure S24. Single mass analysis report of **3b** done by WATERS XEVO G2-X2 ESI-TOF.

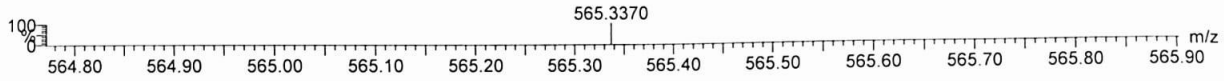
Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 60.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 36-36 H: 46-46 N: 1-2 O: 2-2 Al: 0-3

C36H46ClAlN2O2
Al-salophen 44 (0.801)

1: TOF MS ES+
1.60e+002



Minimum:				-1.5				
Maximum:		5.0	20.0	60.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
565.3370	565.3375	-0.5	-0.9	15.5	20.0	n/a	n/a	C36 H46 N2 O2 Al

Figure S25. Single mass analysis report of **4a** done by WATERS XEVO G2-X2 ESI-TOF.

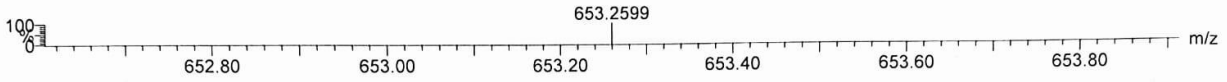
Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 60.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 32-36 H: 46-46 N: 1-2 O: 2-2 In: 0-1

C36H46ClInN2O2
In-salophen 195 (3.454)

1: TOF MS ES+
9.83e+002



Minimum:				-1.5				
Maximum:		5.0	20.0	60.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
653.2599	653.2598	0.1	0.2	15.5	8.3	n/a	n/a	C36 H46 N2 O2 In

Figure S26. Single mass analysis report of 4**b** done by WATERS XEVO G2-X2 ESI-TOF.

C-1-5. Lifetime and CIE

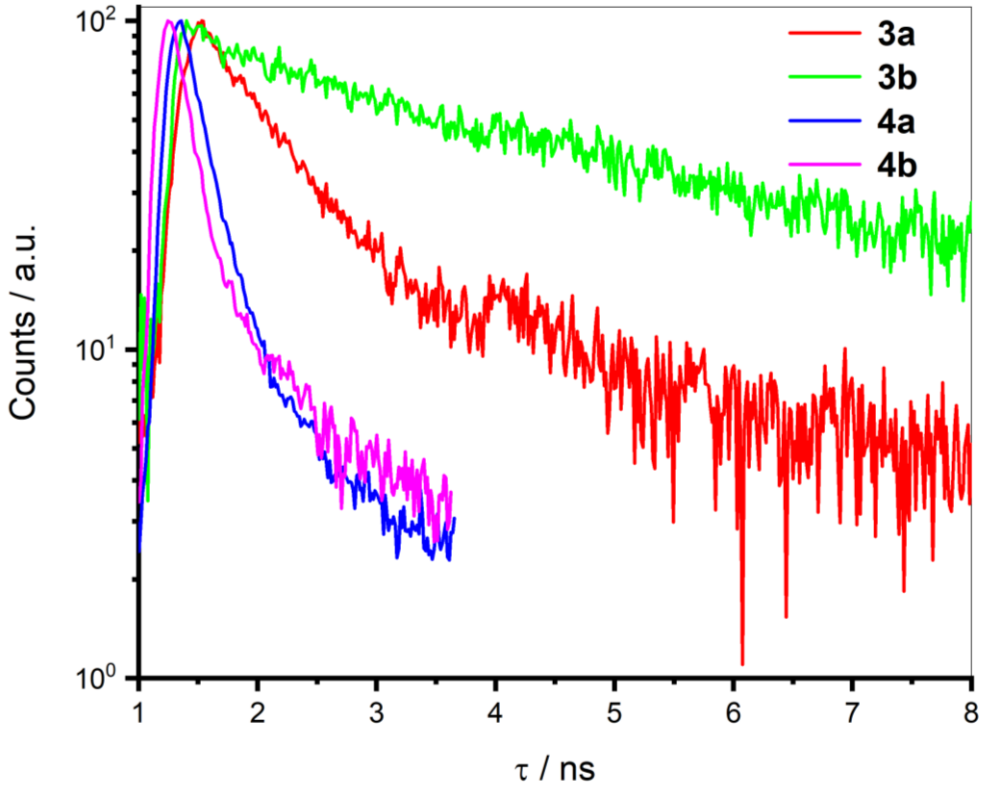


Figure S27. Lifetime of complexes **3a-4b** excited at 400 nm.

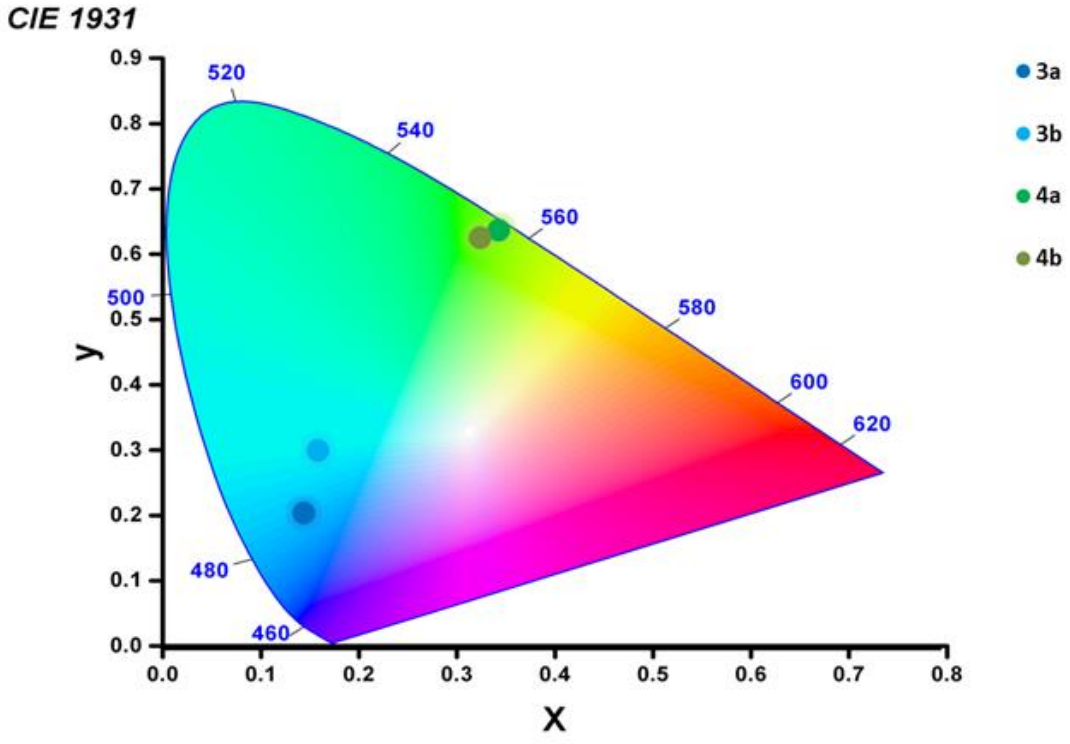


Figure S28. CIE1931 of complexes **3a-4b** excited at 360 nm.

C-1-6. X-Ray structure

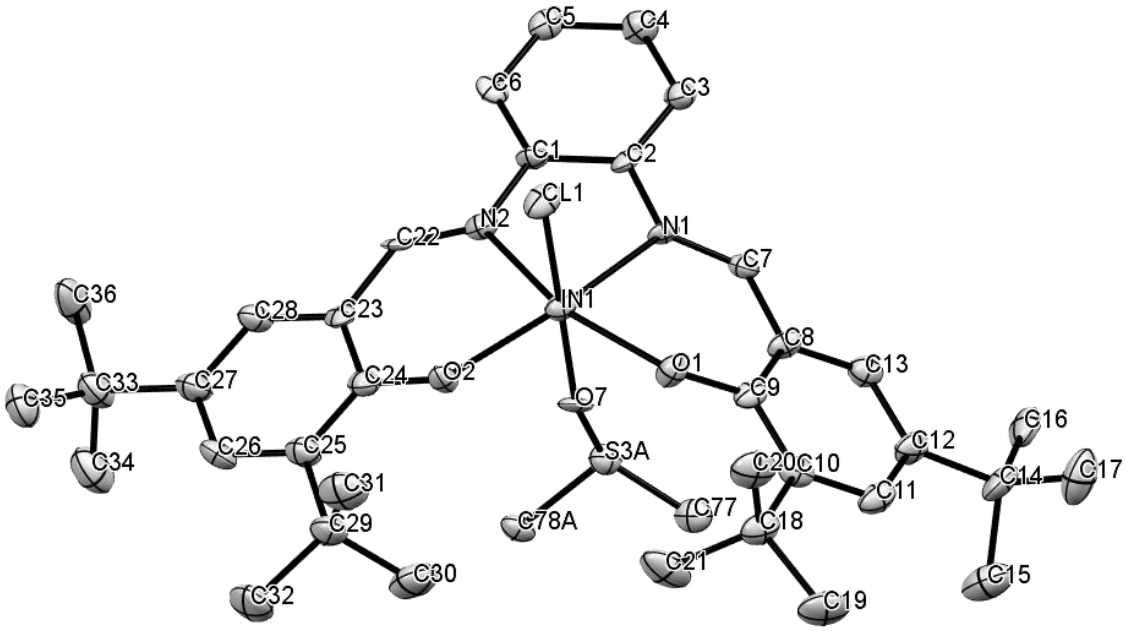


Figure S29. ORTEP structure of **4b** (drawn with 50% probability, top). H-atoms are removed for clarity, selected Bond Lengths [Å] and Angles [deg]: In(1)–Cl(1) 2.458, In(1)–O(7) 2.309, In(1)–O(1) 2.073, In(1)–O(2) 2.068, In(1)–N(1) 2.225, In(1)–N(2) 2.192; Cl(1)-In(1)-O(7) 178.47, O(2)-In(1)-N(1) 159.34, O(1)-In(1)-N(2) 159.19, C(27)-In(1)-C(12) 137.80.

D. DFT calculations

D-1-1. Computational details

Calculations were performed with Gaussian 16(C01) package (DFT),[2] using the Becke Three-Parameter functional with the non-local correlation by Perdew and Wang (B3PW91)[3] and the D3 version of Grimme's dispersion with Becke-Johnson damping (GD3BJ).[4] Whereas H, C, O, Cl, S and N atoms were represented with the 6-31G(d,p)++ basis set,[5] In and Al atoms were described by the Stuttgart/Dresden Effective Core Potential and the associated basis set,[6] as implemented in Gaussian 16(C01). Molecular geometries were optimized without any geometric constraints using the SMD continuum solvent model (DMSO).[7] To calculate free energy (G) corrections, frequency calculations were performed at the same level of theory. TD-DFT studies were carried out using the same level of theory that ground state optimizations as implemented in Gaussian 16(C01). UV-Vis data was plotted using Gaussum[8] and the Mulliken population of the orbitals was calculated using Chemissian package.[9]

D-1-2. Computed structures

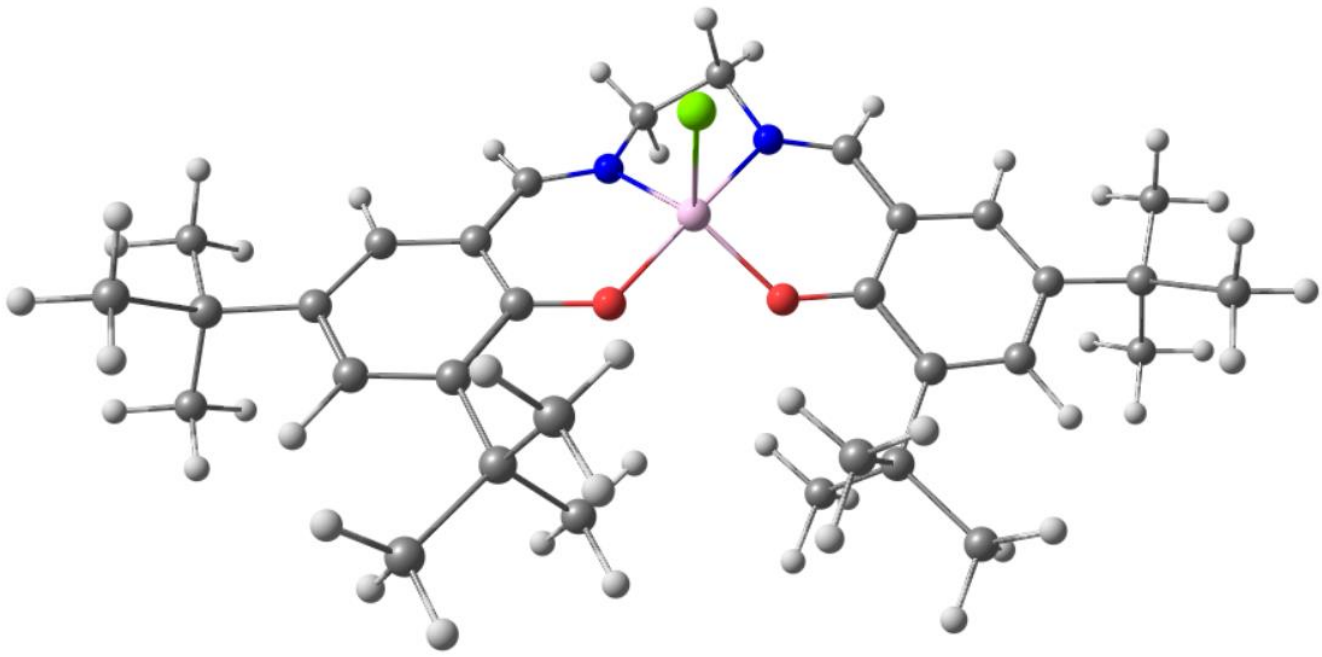


Figure S30. Optimised structure of **3a**

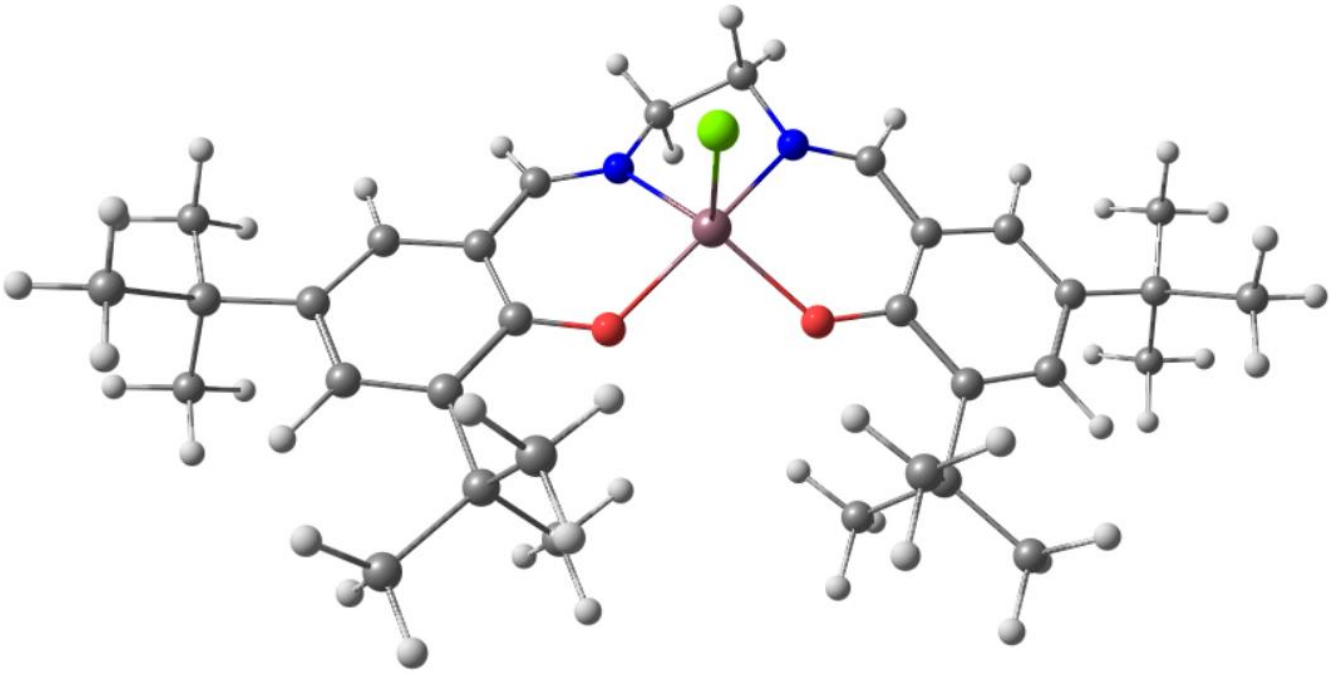


Figure S31. Optimised structure of **3b**

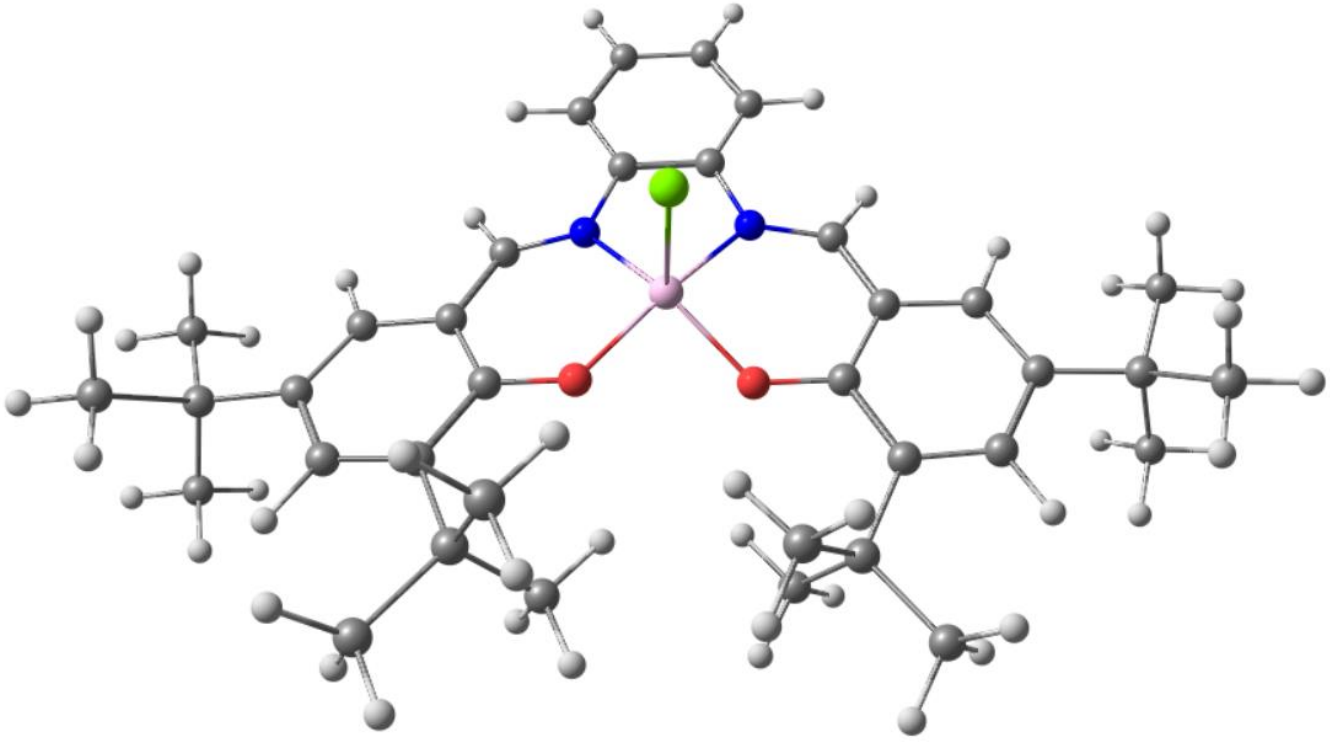


Figure S32. Optimised structure of **4a**

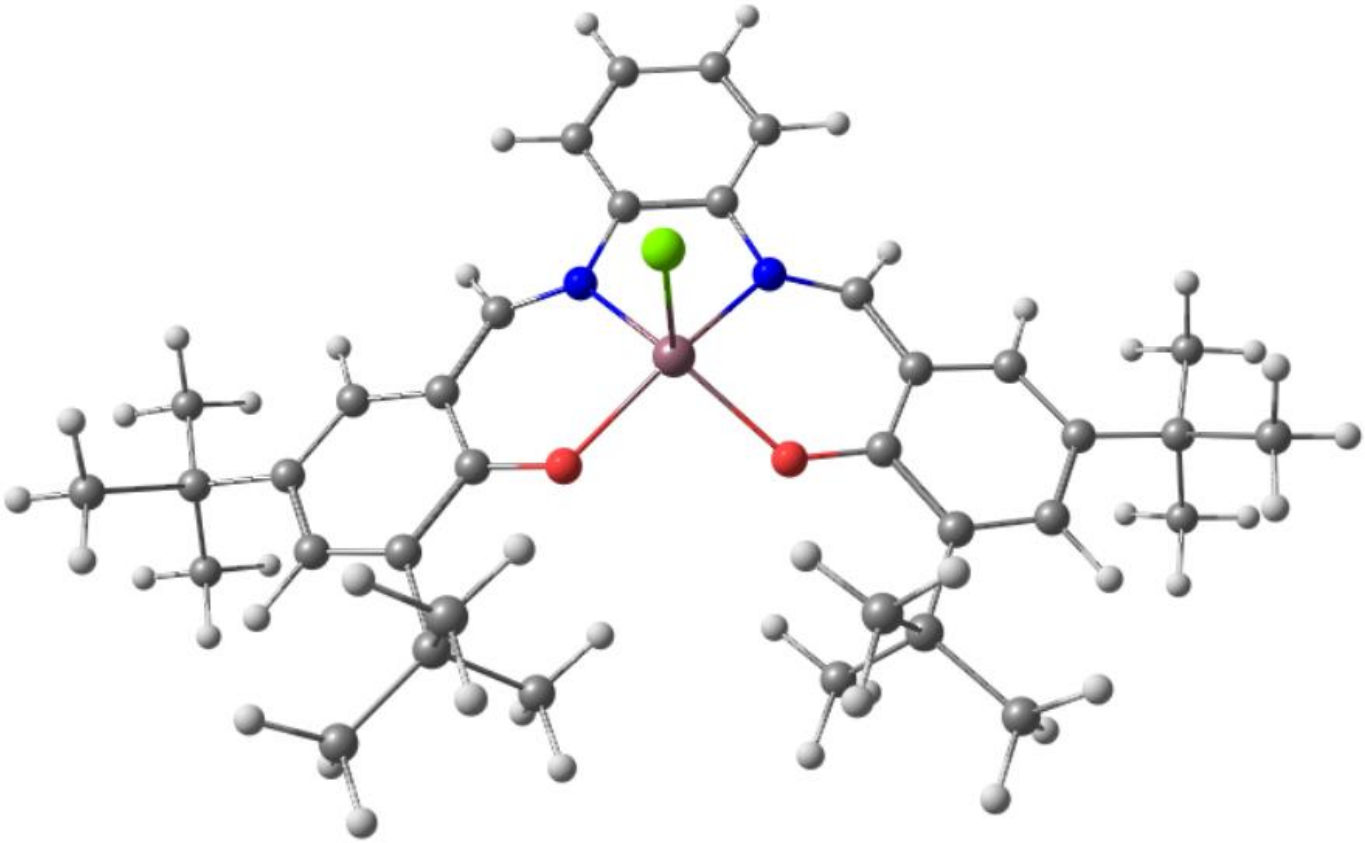


Figure S33. Optimised structure of **4b**

D-1-3. Mulliken analysis

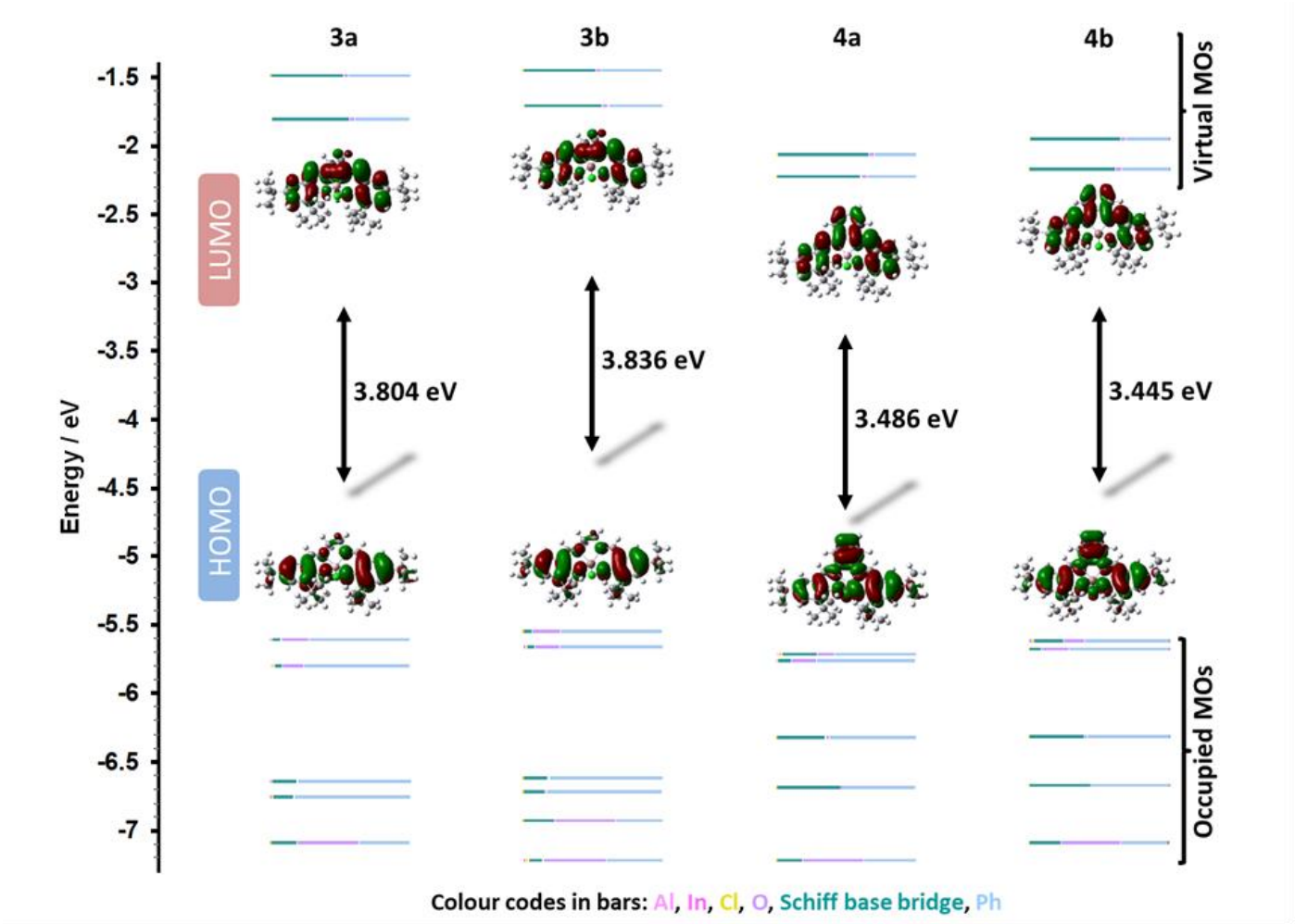


Figure S34. Mulliken orbital analysis of **3a-4b**

D-1-4. Atomic coordinates

3a

13	-0.011604000	-1.173378000	0.334471000
17	0.141518000	-1.344298000	2.570362000
8	1.271648000	0.093971000	0.041504000
8	-1.285868000	0.006722000	-0.175384000
7	1.170302000	-2.544420000	-0.466405000
7	-1.326447000	-2.653973000	0.114075000
6	2.453700000	-2.417811000	-0.627852000
1	3.014640000	-3.287457000	-0.980357000
6	3.207615000	-1.228635000	-0.388798000
6	2.574212000	0.004555000	-0.063507000
6	3.392846000	1.159756000	0.122317000
6	4.764599000	1.009250000	-0.018709000
1	5.388398000	1.883075000	0.131564000
6	5.414085000	-0.204487000	-0.343950000
6	4.612508000	-1.310345000	-0.529884000
1	5.036088000	-2.276537000	-0.786386000
6	6.936409000	-0.231612000	-0.471447000
6	7.374264000	0.756096000	-1.565643000
1	7.067251000	1.780872000	-1.333527000
1	6.939510000	0.484482000	-2.533866000
1	8.465436000	0.750701000	-1.668601000
6	7.453296000	-1.624346000	-0.840151000
1	8.544948000	-1.601621000	-0.922997000
1	7.053973000	-1.964191000	-1.801971000
1	7.193559000	-2.368429000	-0.079355000
6	7.565534000	0.183073000	0.869000000
1	8.659090000	0.176024000	0.795031000
1	7.273668000	-0.507837000	1.667536000
1	7.258280000	1.190835000	1.166317000
6	2.764703000	2.509181000	0.481370000
6	3.817742000	3.611890000	0.631622000
1	4.378519000	3.775114000	-0.295363000
1	4.533244000	3.393824000	1.432127000
1	3.316546000	4.552192000	0.884655000
6	2.016087000	2.388956000	1.820655000
1	2.710153000	2.126816000	2.627422000
1	1.239482000	1.624629000	1.773703000
1	1.547874000	3.346564000	2.076592000
6	1.789726000	2.937241000	-0.628917000
1	1.337078000	3.903380000	-0.378063000
1	0.996457000	2.201006000	-0.755167000
1	2.317015000	3.050814000	-1.583210000
6	-2.606669000	-2.534315000	-0.017579000
1	-3.212111000	-3.441629000	-0.095974000
6	-3.301536000	-1.281396000	-0.079383000
6	-2.603021000	-0.046607000	-0.169193000
6	-3.358836000	1.156367000	-0.281506000
6	-4.743947000	1.053365000	-0.277435000
1	-5.321359000	1.967960000	-0.349565000
6	-5.458518000	-0.161254000	-0.188971000
6	-4.712695000	-1.319490000	-0.101128000
1	-5.190399000	-2.292429000	-0.039435000
6	-2.654824000	2.510995000	-0.407410000
6	-1.744923000	2.749363000	0.810881000
1	-1.259716000	3.728499000	0.728035000
1	-0.973015000	1.983534000	0.883195000
1	-2.331096000	2.742466000	1.737059000
6	-1.822447000	2.529122000	-1.701724000
1	-1.297501000	3.486357000	-1.799617000
1	-2.471545000	2.410085000	-2.576873000
1	-1.083954000	1.726026000	-1.705617000
6	-3.651821000	3.672623000	-0.476569000
1	-3.098053000	4.613362000	-0.564080000
1	-4.272475000	3.736804000	0.424069000
1	-4.314241000	3.598590000	-1.346038000

6	-6.986441000	-0.139028000	-0.200108000
6	-7.477570000	0.509691000	-1.504964000
1	-8.573040000	0.537602000	-1.527192000
1	-7.133749000	-0.057811000	-2.376721000
1	-8.587007000	0.712328000	1.004149000
1	-7.116314000	1.537850000	-1.608323000
6	-7.491363000	0.682356000	0.997875000
1	-7.130092000	1.715154000	0.962592000
1	-7.157306000	0.240304000	1.942957000
6	-7.578203000	-1.547601000	-0.106395000
1	-7.271113000	-2.174253000	-0.950806000
1	-8.671592000	-1.488550000	-0.117216000
1	-7.282003000	-2.051954000	0.819774000
6	-0.687226000	-3.959737000	0.103421000
1	-0.364899000	-4.197970000	1.124173000
1	-1.362612000	-4.744471000	-0.248219000
6	0.530887000	-3.817144000	-0.801721000
1	0.203413000	-3.777341000	-1.847403000
1	1.223351000	-4.654986000	-0.681116000

3b

49	0.010361000	-0.867422000	0.513902000
17	0.214879000	-0.847275000	2.895075000
8	1.479205000	0.416055000	-0.078280000
8	-1.508061000	0.359881000	-0.037934000
7	1.242873000	-2.416463000	-0.396823000
7	-1.386696000	-2.495708000	0.168594000
6	2.511825000	-2.296223000	-0.625572000
1	3.050663000	-3.174313000	-0.996556000
6	3.306250000	-1.109776000	-0.451500000
6	2.766647000	0.188888000	-0.188419000
6	3.676174000	1.287913000	-0.079476000
6	5.031779000	1.037194000	-0.230828000
1	5.718005000	1.871348000	-0.139078000
6	5.586153000	-0.234073000	-0.498231000
6	4.702041000	-1.285564000	-0.610858000
1	5.056673000	-2.289790000	-0.822206000
6	7.099638000	-0.379944000	-0.649010000
6	7.583465000	0.504043000	-1.810519000
1	7.352730000	1.560402000	-1.639421000
1	7.111377000	0.203946000	-2.752520000
1	8.669374000	0.415338000	-1.930404000
6	7.508581000	-1.826547000	-0.937320000
1	8.597273000	-1.887985000	-1.037860000
1	7.067626000	-2.195271000	-1.869841000
1	7.211146000	-2.501646000	-0.127501000
6	7.785689000	0.070021000	0.651582000
1	8.874041000	-0.022697000	0.560209000
1	7.461355000	-0.546080000	1.497451000
1	7.559272000	1.114407000	0.888897000
6	3.153166000	2.699281000	0.214156000
6	4.290249000	3.723444000	0.303217000
1	4.852501000	3.798210000	-0.634134000
1	4.994986000	3.488988000	1.108619000
1	3.866108000	4.711007000	0.513170000
6	2.411620000	2.711606000	1.562932000
1	3.082884000	2.413099000	2.376183000
1	1.558534000	2.031976000	1.553671000
1	2.047312000	3.722414000	1.780711000
6	2.204282000	3.155046000	-0.908722000
1	1.838927000	4.167770000	-0.701490000
1	1.346131000	2.487422000	-0.995011000
1	2.727395000	3.176867000	-1.871656000
6	-2.649489000	-2.377268000	-0.077515000
1	-3.225749000	-3.292076000	-0.250693000
6	-3.392379000	-1.145678000	-0.150316000
6	-2.802132000	0.156602000	-0.125493000
6	-3.666420000	1.291760000	-0.231471000

6	-5.030441000	1.071386000	-0.353381000
1	-5.682397000	1.934143000	-0.428135000
6	-5.634382000	-0.204161000	-0.389591000
6	-4.792971000	-1.292178000	-0.292763000
1	-5.187887000	-2.303336000	-0.317895000
6	-3.086279000	2.711488000	-0.204248000
6	-2.338439000	2.950134000	1.119952000
1	-1.940246000	3.971232000	1.145275000
1	-1.508063000	2.253243000	1.239518000
1	-3.016089000	2.832064000	1.973197000
6	-2.126620000	2.908723000	-1.391490000
1	-1.709415000	3.922397000	-1.371457000
1	-2.657688000	2.782436000	-2.341971000
1	-1.303949000	2.193400000	-1.356475000
6	-4.180613000	3.779651000	-0.312418000
1	-3.715781000	4.770850000	-0.285310000
1	-4.893229000	3.726569000	0.518157000
1	-4.740501000	3.704068000	-1.251072000
6	-7.151617000	-0.316160000	-0.531704000
6	-7.592702000	0.362538000	-1.839122000
1	-8.680579000	0.295510000	-1.955107000
1	-7.127606000	-0.119938000	-2.705851000
1	-8.917184000	0.322873000	0.569982000
1	-7.321051000	1.422806000	-1.857493000
6	-7.826471000	0.386599000	0.658021000
1	-7.557717000	1.446676000	0.707943000
1	-7.533343000	-0.080407000	1.604722000
6	-7.616970000	-1.774043000	-0.561556000
1	-7.184010000	-2.321070000	-1.406152000
1	-8.706451000	-1.810410000	-0.665704000
1	-7.353656000	-2.303590000	0.360511000
6	-0.709648000	-3.782334000	0.150301000
1	-0.409930000	-4.026401000	1.177052000
1	-1.359081000	-4.579396000	-0.225384000
6	0.538532000	-3.652555000	-0.729035000
1	0.226670000	-3.594160000	-1.778981000
1	1.186465000	-4.526737000	-0.607712000

4a

13	0.023742000	0.771972000	0.412360000
17	0.159154000	0.929091000	2.636528000
8	-1.278500000	-0.476633000	0.155139000
8	1.249106000	-0.443705000	-0.157479000
7	-1.255902000	2.214726000	-0.099075000
7	1.314023000	2.241712000	-0.052318000
6	0.726129000	3.518160000	-0.096010000
6	-0.683956000	3.502408000	-0.126091000
6	-1.391778000	4.708468000	-0.144864000
1	-2.476066000	4.717160000	-0.129050000
6	-0.702521000	5.914803000	-0.155818000
1	-1.258206000	6.847329000	-0.165923000
6	0.694609000	5.930087000	-0.131507000
1	1.229818000	6.874547000	-0.125516000
6	1.408523000	4.738882000	-0.094544000
1	2.491449000	4.770511000	-0.049374000
6	-2.533448000	2.040264000	-0.336790000
1	-3.131562000	2.908753000	-0.611292000
6	-3.236283000	0.811541000	-0.260206000
6	-2.578911000	-0.420544000	0.022426000
6	-3.371404000	-1.602776000	0.137201000
6	-4.737885000	-1.484208000	-0.064424000
1	-5.341539000	-2.380177000	0.024141000
6	-5.409145000	-0.277442000	-0.377555000
6	-4.638025000	0.858216000	-0.469250000
1	-5.081215000	1.823415000	-0.693458000
6	-6.922266000	-0.292238000	-0.585127000
6	-7.265762000	-1.238913000	-1.747152000
1	-6.933728000	-2.262891000	-1.548472000
1	-6.791799000	-0.904582000	-2.676522000

1	-8.349587000	-1.265254000	-1.907644000
6	-7.465675000	1.099920000	-0.915494000
1	-8.549669000	1.046315000	-1.060387000
1	-7.026552000	1.499198000	-1.836224000
1	-7.273512000	1.813291000	-0.106751000
6	-7.606417000	-0.791813000	0.698058000
1	-8.694002000	-0.813785000	0.564609000
1	-7.379978000	-0.132749000	1.543327000
1	-7.283028000	-1.803461000	0.963019000
6	-2.726609000	-2.946969000	0.482018000
6	-3.760138000	-4.073715000	0.579002000
1	-4.287081000	-4.232628000	-0.368270000
1	-4.505175000	-3.885410000	1.359894000
1	-3.246187000	-5.007245000	0.831181000
6	-2.017717000	-2.842878000	1.844065000
1	-2.738773000	-2.609704000	2.635823000
1	-1.251596000	-2.066463000	1.837029000
1	-1.541428000	-3.798117000	2.092864000
6	-1.716793000	-3.325606000	-0.613294000
1	-1.247102000	-4.286413000	-0.374794000
1	-0.938871000	-2.568474000	-0.702557000
1	-2.218633000	-3.427558000	-1.582418000
6	2.603701000	2.072960000	-0.184839000
1	3.237364000	2.947453000	-0.330736000
6	3.273264000	0.819494000	-0.174812000
6	2.562440000	-0.414259000	-0.187179000
6	3.308712000	-1.627195000	-0.266741000
6	4.692803000	-1.533289000	-0.288803000
1	5.262213000	-2.454635000	-0.331290000
6	5.421024000	-0.320754000	-0.264572000
6	4.688773000	0.844491000	-0.223103000
1	5.175000000	1.814911000	-0.218736000
6	2.597732000	-2.980366000	-0.342011000
6	1.686670000	-3.170834000	0.882982000
1	1.197271000	-4.149926000	0.834501000
1	0.919058000	-2.399324000	0.930062000
1	2.273946000	-3.134597000	1.807741000
6	1.773950000	-3.031573000	-1.640713000
1	1.232146000	-3.981598000	-1.709554000
1	2.433053000	-2.955485000	-2.513054000
1	1.050453000	-2.215904000	-1.682511000
6	3.586606000	-4.150599000	-0.369974000
1	3.025187000	-5.089396000	-0.421676000
1	4.208191000	-4.185879000	0.531626000
1	4.247510000	-4.114509000	-1.242844000
6	6.947751000	-0.359133000	-0.297969000
6	7.411057000	-1.060051000	-1.585864000
1	8.505655000	-1.100231000	-1.623444000
1	7.059435000	-0.520645000	-2.472182000
1	8.558247000	-1.180198000	0.912236000
1	7.038044000	-2.087408000	-1.646208000
6	7.463003000	-1.141261000	0.921592000
1	7.093543000	-2.171667000	0.929280000
1	7.147118000	-0.662201000	1.854769000
6	7.553522000	1.046109000	-0.264949000
1	7.242076000	1.643309000	-1.128831000
1	8.646014000	0.975758000	-0.286730000
1	7.273325000	1.587701000	0.645042000

4b

49	0.010709000	0.559157000	0.747461000
17	0.068229000	0.711253000	3.121998000
8	-1.488270000	-0.735745000	0.308812000
8	1.453370000	-0.739391000	0.160715000
7	-1.320330000	2.137168000	0.031969000
7	1.343161000	2.139318000	0.018974000
6	0.721015000	3.401660000	-0.015832000

6	-0.697996000	3.399473000	-0.009995000
6	-1.389062000	4.615256000	0.005250000
1	-2.472876000	4.622913000	0.059140000
6	-0.691907000	5.817701000	-0.013341000
1	-1.239994000	6.754664000	0.003769000
6	0.704598000	5.820208000	-0.020149000
1	1.249343000	6.759208000	-0.008991000
6	1.406766000	4.620598000	-0.007856000
1	2.490977000	4.634421000	0.033219000
6	-2.557333000	1.950873000	-0.344791000
1	-3.108324000	2.810850000	-0.730245000
6	-3.292573000	0.726297000	-0.328060000
6	-2.746894000	-0.556064000	0.003544000
6	-3.615968000	-1.692712000	-0.030224000
6	-4.939006000	-1.495332000	-0.390651000
1	-5.595475000	-2.357533000	-0.411797000
6	-5.499094000	-0.243599000	-0.737262000
6	-4.657425000	0.843912000	-0.702804000
1	-5.019427000	1.835429000	-0.956009000
6	-6.974660000	-0.161358000	-1.123486000
6	-7.227941000	-1.050692000	-2.352036000
1	-6.979123000	-2.097914000	-2.152670000
1	-6.627745000	-0.717604000	-3.205851000
1	-8.284370000	-1.008446000	-2.640886000
6	-7.396742000	1.269881000	-1.463936000
1	-8.457537000	1.285754000	-1.734926000
1	-6.830919000	1.669138000	-2.312746000
1	-7.260987000	1.946393000	-0.613151000
6	-7.835235000	-0.658204000	0.050035000
1	-8.898567000	-0.611220000	-0.211434000
1	-7.675690000	-0.040148000	0.940387000
1	-7.602785000	-1.695101000	0.313150000
6	-3.084744000	-3.085051000	0.330487000
6	-4.179262000	-4.154391000	0.242164000
1	-4.590414000	-4.241165000	-0.769594000
1	-5.005967000	-3.957438000	0.933602000
1	-3.750663000	-5.126241000	0.508470000
6	-2.552071000	-3.084480000	1.774687000
1	-3.347815000	-2.819984000	2.480260000
1	-1.732135000	-2.375373000	1.897230000
1	-2.186994000	-4.083995000	2.038070000
6	-1.960818000	-3.486404000	-0.641240000
1	-1.584883000	-4.484059000	-0.386342000
1	-1.131488000	-2.780695000	-0.594300000
1	-2.333010000	-3.519643000	-1.671568000
6	2.586671000	1.952753000	-0.332568000
1	3.156407000	2.815017000	-0.684045000
6	3.307132000	0.718339000	-0.329761000
6	2.727629000	-0.568546000	-0.086214000
6	3.575917000	-1.718488000	-0.155546000
6	4.918140000	-1.526631000	-0.441643000
1	5.559899000	-2.399142000	-0.482736000
6	5.514122000	-0.268711000	-0.690837000
6	4.688084000	0.830555000	-0.639722000
1	5.076149000	1.826754000	-0.827914000
6	2.999528000	-3.121541000	0.068300000
6	2.353474000	-3.221322000	1.461780000
1	1.974199000	-4.237012000	1.623263000
1	1.523106000	-2.522695000	1.568876000
1	3.089221000	-3.008530000	2.245698000
6	1.953610000	-3.423378000	-1.019831000
1	1.516144000	-4.415155000	-0.856801000
1	2.418459000	-3.418884000	-2.012336000
1	1.151113000	-2.684976000	-1.010214000
6	4.082033000	-4.203609000	-0.014529000
1	3.620626000	-5.183079000	0.149379000
1	4.856659000	-4.070671000	0.748874000
1	4.567540000	-4.228656000	-0.996154000
6	7.007052000	-0.192913000	-1.005327000

6	7.301087000	-1.013491000	-2.272158000
1	8.370426000	-0.976498000	-2.509646000
1	6.747503000	-0.617979000	-3.130833000
1	8.879374000	-0.732960000	-0.036826000
1	7.023911000	-2.065170000	-2.147611000
6	7.804581000	-0.774446000	0.173699000
1	7.542915000	-1.820306000	0.363637000
1	7.614903000	-0.206995000	1.091408000
6	7.468554000	1.247244000	-1.240982000
1	6.951456000	1.705810000	-2.090875000
1	8.541378000	1.258377000	-1.459914000
1	7.302651000	1.875903000	-0.359377000

E- Cost calculation

Table S2. Average Price of Electricity to household and non-household medium size consumer, by European Country, 2020 and 2021 (euro per Kilowatthour) reproduced from (https://ec.europa.eu/eurostat/databrowser/bookmark/16fed460-2ba9-4e42-8f41-1258ca339ca2?lang=en) accessed in May 2022. Note that United Kingdom 2021 values have been reproduced from (https://www.ukpower.co.uk/home_energy/tariffs-per-unit-kwh) and (https://www.gov.uk/government/statistical-data-sets/gas-and-electricity-prices-in-the-non-domestic-sector) to household and non-household respectively. Data use for calculation in Table S3 and S4are highlighted in yellow.

Energy indicator	Medium size household		Non-household, medium size consumers	
TIME	2020	2021	2020	2021
GEO (Labels)				
European Union - 27 countries (from 2020)	0,2134	0,2203	0,0818	0,0859
European Union - 28 countries (2013-2020)	:	:	:	:
Euro area (EA11-1999, EA12-2001, EA13-2007, EA15-2008, EA16-2009,	0,2263	0,2322	0,0835	0,0888
Euro area - 19 countries (from 2015)	:	:	:	:
Belgium	0,2792	0,2702	0,0795	0,0810
Bulgaria	0,0997	0,1024	0,0805	0,0842
Czechia	0,1841	0,1802	0,0716	0,0739
Denmark	0,2833	0,2900	0,0540	0,0725
Germany (until 1990 former territory of the FRG)	0,3043	0,3193	0,0849	0,0908
Estonia	0,1236	0,1324	0,0675	0,0834
Ireland	0,2413	0,2555	0,1265	0,1378
Greece	0,1674	0,1680	0,0823	0,0890
Spain	0,2239	0,2323	0,0786	0,0931
France	0,1893	0,1946	0,0847	0,0850
Croatia	0,1301	0,1291	0,0898	0,0881
Italy	0,2226	0,2259	0,0856	0,0939
Cyprus	0,2133	0,1976	0,1178	0,1091
Latvia	0,1420	0,1403	0,0813	0,0849
Lithuania	0,1426	0,1348	0,0871	0,0932
Luxembourg	0,1986	0,1988	0,0824	0,0836
Hungary	0,1031	0,1003	0,0849	0,0818
Malta	0,1284	0,1285	0,1328	0,1330
Netherlands	0,1427	0,1281	0,0680	0,0721
Austria	0,2111	0,2216	0,0877	0,0884
Poland	0,1475	0,1548	0,0800	0,0731
Portugal	0,2120	0,2089	0,0794	0,0755
Romania	0,1459	0,1536	0,0890	0,0824
Slovenia	0,1448	0,1662	0,0811	0,0757
Slovakia	0,1686	0,1668	0,0977	0,0929
Finland	0,1740	0,1767	0,0625	0,0669
Sweden	0,1826 e	0,2114	0,0641	0,0705
Iceland	0,1341	0,1355	0,0713	0,0449
Liechtenstein	0,2115	0,2071	0,0880	0,0863
Norway	0,1355	0,1826	0,0417	0,0715
Switzerland	:	:	:	:
United Kingdom	0,2203	0.2407*	0,1065	0.1546**
Montenegro	0,0988	0,0980	0,0766	0,0773
North Macedonia	0,0782	0,0841	0,0778	0,0752
Albania	0,0922 e	:	0,1037	:
Serbia	0,0738	0,0791	0,0748	0,0702
Turkey	0,0995	0,0834	0,0774	0,0648
Bosnia and Herzegovina	0,0870	0,0875	0,0708	0,0719
Kosovo (under United Nations Security Council Resolution 1244/99)	0,0605	0,0605	0,0638	0,0635
Moldova	0,1068	0,0851	0,0795	0,0633
Ukraine	0,0466	0,0485	0,0595	0,0595
Georgia	0,0663	0,0631	0,0505	0,0713

Special value	
:	not available
Available flags:	
e	estimated
p	provisional

Table S3. Average costs calculation to medium size household consumers in euro for the mechanochemical synthesis of 1 kg of the ligands **1** and **2** and complexes **3a**, **3b**, **4a** and **4b**

Year	**2020**	**2021**	**2020**	**2021**	**2020**	**2021**	**2020**	**2021**	**2020**	**2021**	**2020**	**2021**
	1		**2**		**3a**		**3b**		**4a**		**4b**	
Spain	671.7	696.9	671.7	696.9	2686.8	2787.6	2686.8	2787.6	2686.8	2787.6	2686.8	2787.6
Germany	912.9	957.9	912.9	957.9	3651.6	3831.6	3651.6	3831.6	3651.6	3831.6	3651.6	3831.6
France	567.9	583.6	567.9	583.6	2271.6	2335.2	2271.6	2335.2	2271.6	2335.2	2271.6	2335.2
UK	660.9	722.1	660.9	722.1	2643.6	2888.4	2643.6	2888.4	2643.6	2888.4	2643.6	2888.4

Table S4. Average costs calculation to non-household, medium size consumers in euro for the mechanochemical synthesis of 1 kg of the ligands **1** and **2** and complexes **3a**, **3b**, **4a** and **4b**

Year	**2020**	**2021**	**2020**	**2021**	**2020**	**2021**	**2020**	**2021**	**2020**	**2021**	**2020**	**2021**
	1		**2**		**3a**		**3b**		**4a**		**4b**	
Spain	235.8	279.3	235.8	279.3	943.2	1117.2	943.2	1117.2	943.2	1117.2	943.2	1117.2
Germany	254.7	272.4	254.7	272.4	1018.8	1089.6	1018.8	1089.6	1018.8	1089.6	1018.8	1089.6
France	254.1	255	254.1	255	1016.4	1020	1016.4	1020	1016.4	1020	1016.4	1020
UK	319.5	463.8	319.5	463.8	1278	1855.2	1278	1855.2	1278	1855.2	1278	1855.2

F. REFERENCES

1. F. Garcia, H. C. Ong and V. K. Singh, *Inorg. Chem. Commun.*, 2020.
2. M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, G. Petersson and H. J. G. I. W. C. Nakatsuji, *Comp. Chem.*, 2016, **1**.
3. A. D. J. J. C. P. Becke, *Proc. Nat. Ac. Sc.*, 1993, **98**, 5648-5652.
4. S. Grimme, S. Ehrlich and L. J. J. o. c. c. Goerigk, *J. Comput. Chem*, 2011, **32**, 1456-1465.
5. a. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley and J. J. T. J. o. c. p. Mantzaris, *J. Chem. Phys.*, 1988, **89**, 2193-2218.
6. T. Dunning and P. Hay, *J. Chem. Phys.*, 1977.
7. A. V. Marenich, C. J. Cramer and D. G. J. T. J. o. P. C. B. Truhlar, *J. Chem. Phys.*, 2009, **113**, 6378-6396.
8. A. R. J. J. o. c. c. Allouche, *J. Comput. Chem*, 2011, **32**, 174-182.
9. S.Leonid, *Chemissian*, n.d.