Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supporting Information

Selenium Containing Imidazolium Salt In Designing Single Source Precursors for Silver Bromide and Selenide Nano-Particles

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1. Experimental Section

Genral

^{1}H, $^{13}C\{^{1}H\}$ and $^{77}Se\{^{1}H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX 300 NMR spectrometer at 300.13, 75.47 and 57.24 MHz respectively. The chemical shifts are reported in ppm relative to the residual deuterated solvent or the internal standard (tetramethylsilane in case of ^{1}H, $^{13}C\{^{1}H\}$ NMR and Me_2Se for $^{77}Se\{^{1}H\}$ NMR). All reactions were carried out in glassware dried in an oven and under N_2 atmosphere at room temperature.

X-ray diffraction data for crystals of **1** was collected on a BRUKER AXS SMART−APEX CCD diffractometer using Mo-Kα = 0.71073 Å; radiations monochromator, graphite). Frames were collected at $T = 298$ K by ω, φ, and 2θ-rotations with full quadrant data collection strategy (four domains each with 600 frames) at 10s per frame with SMART. The measured intensities were reduced to F^2 and corrected for absorption with SADABS.[1] Structure solution, refinement, and data output were carried out with the SHELXTL package by direct methods.[2] Non-hydrogen atoms were refined anisotropically.

Elemental composition of these phases has been obtained by a Carl ZEISS EVO5O scanning electron microscope (SEM). Sample was mounted on a circular metallic sample holder with a sticky carbon tape, associated EDX system Model QuanTax 200, which is based on the SDD technology and provides an energy resolution of 127 eV at Mn K alpha.

Powder X-ray diffraction (PXRD) studies were carried out on a Bruker D8 Advance diffractometer using Ni-filtered Cu*Kα* radiation, scan speed of 1 s and scan step of 0.05°. Transmission electron microscopic (TEM) studies were carried out using a JEOL JEM 200CX TEM instrument operated at 200 kV. The specimens for these studies were prepared by dispersing the powdered sample in ethanol by ultrasonic treatment. Few drops of resulting solution were put on a porous carbon film supported on a copper grid and dried in air. High Resolution Mass Spectral (HR-MS) measurements were performed with electron spray ionization (10 *eV*, 180 °C source temperature) and using sodium formate as calibrant on a Bruker MIcroTOF-Q II, taking sample in CH_3CN.

Chemicals

Oleic acid (OA), octadecylamine (ODA), oleylamine (OM), 1-octadecene (ODE), trioctylphosphine (TOP), Ag_2O, $AgBF_4$, benzyl bromide procured from Sigma-Aldrich (USA) were used as received. All the solvents of AR grade i.e. 1,2-dichloroethane, dichloromethane, acetonitrile and ethanol were dried and distilled before use by known standard procedures.[3] The 1−(2−chloroethyl)−1*H*−imidazole was synthesized by reported procedure.[4]

1−(2−(Phenylseleno)ethyl)−1*H*−imidazole (A)

Diphenyldiselenide (0.624 g, 2.0 mmol) dissolved in 30 mL of EtOH was stirred under N_2 atmosphere at room temperature. Sodium borohydride (0.151 g, 4.0 mmol) was added to it as solid and the mixture further stirred for 15 min. When it became colorless due to the formation of PhSeNa, 1−(2−chloroethyl)−1*H*−imidazole (0.522g, 4.0 mmol) dissolved in 10 cm^3 of ethanol was added with constant stirring and the mixture stirred further for 3h. It was extracted with chloroform (4 × 25 mL). The extract was washed with water (3 × 40 mL) and dried over anhydrous sodium sulphate. The solvent was evaporated off under reduced pressure on a rotary evaporator to get 1−(2−(phenylseleno)ethyl)−1*H*−imidazole (**A**) as yellow oil.

Yield 0.909 g, 90%. ^{1}H NMR ($CDCl_3$, 25 ºC, vs Me_4Si): δ (ppm): 3.07 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, H-$_5$), 4.06 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, H_6), 6.84 (s, 1H, H_7), 6.99 (s, 1H, H_8), 7.17−7.24 (m, 3H, H_1& H_2), 7.38 (s, 1H, H_9), 7.41−7.45 (m, 2H, H_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC, vs Me_4Si): δ (ppm): 27.4 (C_5), 46.2 (C_6), 127.1 (C_1) 127.1 (C_7), 128.6 (C_8), 128.8 (C_2), 130.8 (C_9), 132.6 (C_3), 136.4 (C_4); ^{77}Se{^{1}H} NMR ($CDCl_3$, 25 ºC, vs Me_2Se); (δ, ppm): 282.60.

3-Benzyl-1-(2-phenylselanyl-ethyl)-3*H*-imidazolium bromide (L)

A (0.502 g, 2.0 mmol) was placed in a Schlenk tube equipped with a magnetic stirrer and benzyl bromide (0.342 g, 2.0 mmol) was added. The mixture was heated for 8 h at 85°C under N_2 atm and thereafter allowed to cool to room temperature. The dark red oil obtained was washed with dry CH_3CN (2 × 40 mL) and dried in vacuo.

Yield 0.802 g, 95%. ^{1}H NMR ($CDCl_3$, 25 ºC, TMS); (δ, ppm): 3.40 (t, $^3J_{H\text{-}H}$ = 6.3 Hz, 2H, H_5), 4.55 (t, $^3J_{H\text{-}H}$ = 6.0 Hz, 2H, H_6), 5.51(s, 2H, H_{10}), 7.20 - 7.46 (m, 11H, H_1,H_2,H_3,H_7,H_{12},H_{13}&H_{14}), 7.58 (s, 1H, H_8), 10.09 (s, 1H, H_9). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC, TMS); (δ, ppm): 26.9 (C_5), 49.6 (C_6), 52.8 (C_{10}), 121.5 (C_7), 122.6 (C_8), 127.4 (C_1), 128.7 (C_2), 128.9 (C_4), 129.0 (C_{13}&C_{14}), 129.2 (C_{12}), 131.1 (C_{11}), 132.8 (C_3), 136.1 (C_9). ^{77}Se {^{1}H} NMR ($CDCl_3$, 25 ºC, Me_2Se); (δ, ppm): 277.83. HRMS: M-Br (m/z) 343.0723.

Complex 1

L (0.211 g, 0.5 mmol) was dissolved in dry CH_2Cl_2 (20 mL) and solid Ag_2O (0.058 g, 0.25 mmol) was added under N_2 atm. The reaction mixture was stirred overnight in the dark at room temperature. Then the suspension was filtered through a celite pad and the solvent was evaporated under reduced pressure to give a light sensitive white solid **1**.

Yield 0.026 g, 43%. ^{1}H NMR (DMSO, 25 ºC, TMS); (δ, ppm): 3.28 (t, $^3J_{H-H}$ = 6.3 Hz, 4H, H_5), 4.38 (t, $^3J_{H-H}$ = 6.3 Hz, 4H, H_6), 5.24 (s, 4H, H_{10}), 7.09 (s, 2H, H_7), 7.21–7.27 (m, 12H, H_1,H_2,H_{13}&H_{14}), 7.36–7.39 (m, 10H, H_3, H_8 &H_{11}), 8.80 (s, 2H, H_9) . ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC, TMS); (δ, ppm): 27.5 (C_5), 51.0 (C_6), 54.1 (C_{10}), 121.9 (C_7), 122.3 (C_8), 126.7 (C_1), 127.5 (C_2), 127.9 (C_4), 128.7 (C_{14}), 129.0 (C_{13}), 129.3 (C_{12}), 131.2 (C_3), 137.1 (C_{11}), 179.2 (C_9). ^{77}Se{^{1}H} NMR (DMSO, 25 ºC, Me_2Se); (δ, ppm): 264.70. HR-MS: 343.0729 [$PhCH_2$-Imi-2CSePh]$^+$, and 451.0856 [{Ag($PhCH_2$-Imi-2CSePh) }+H]$^+$.

Complex 2

Solid $AgBF_4$ (0.097 g, 0.5 mmol) was added to **L (**0.211 g, 0.5 mmol, dissolved in 20 mL of CH_2Cl_2). The reaction mixture was stirred for 4h at room temperature. In the resulting mixture, AgBr appeared as white precipitate was filtered off through celite. Solid Ag_2O (0.116 g, 0.5 mmol) was added to colorless filtrate under N_2 atm. in the dark. The reaction mixture was further stirred overnight at room temperature. It was filtered through a celite pad and solvent from filtrate was evaporated under reduced pressure to give a light sensitive white solid **2**.

Yield 0.33 g, 75%. ^{1}H NMR (DMSO, 25 ºC, TMS); (δ, ppm): 3.36 (t, $^3J_{H-H}$ = 6.0 Hz, 4H, H_5), 4.35 (t, $^3J_{H-H}$ = 6.0 Hz, 4H, H_6), 5.24(s, 4H, H_{10}), 7.19–7.35 (m, 20H, H_1,H_2,H_3,H_{12},H_{13}&H_{14}), 7.49 (d, 4H, H_7&H_8)., ^{13}C{^{1}H} NMR (DMSO, 25 ºC, TMS); (δ, ppm): 28.0 (C_5), 51.9 (C_6), 54.9 (C_{10}), 122.4 (C_7), 122.8 (C_8), 128.7 (C_1), 128.8 (C_2), 129.0 (C_4), 129.4 (C_{14}), 131.3(C_{13}), 131.9 (C_{12}), 134.7 (C_{11}), 137.1 (C_3) 179.6 (C_9). ^{77}Se{^{1}H} NMR (DMSO, 25 ºC, Me_2Se); (δ, ppm): 262.07. HRMS: M-BF_4^- (m/z) 791.0313.

Synthesis of Silver Bromide Nano-Particles

A slurry containing 0.1 mmol of complex **1**, 10 mmol of octadecylamine (ODA), 10 mmol of 1-octadecane (ODE) and 20 mmol of oleic acid (OA), prepared in a three necked flask (100 mL) was heated to 100 °C to remove water and oxygen, The resulting homogeneous brown solution was heated to 200 °C under N_2 and kept at the same temperature for 30 min, affording a dark colloidal solution. The solution was air-cooled and NPs of AgBr were precipitated with excess ethanol. They were washed with ethanol and dried in air at 60 °C.

Synthesis of Silver Selenide Nano-Particles

A slurry containing 0.1 mmol of complex **2**, 10 mmol of trioctyphosphine (TOP) and 20 mmol of oleic acid (OA) was prepared and treated by a procedure described above to get the NPs of Ag_2Se.

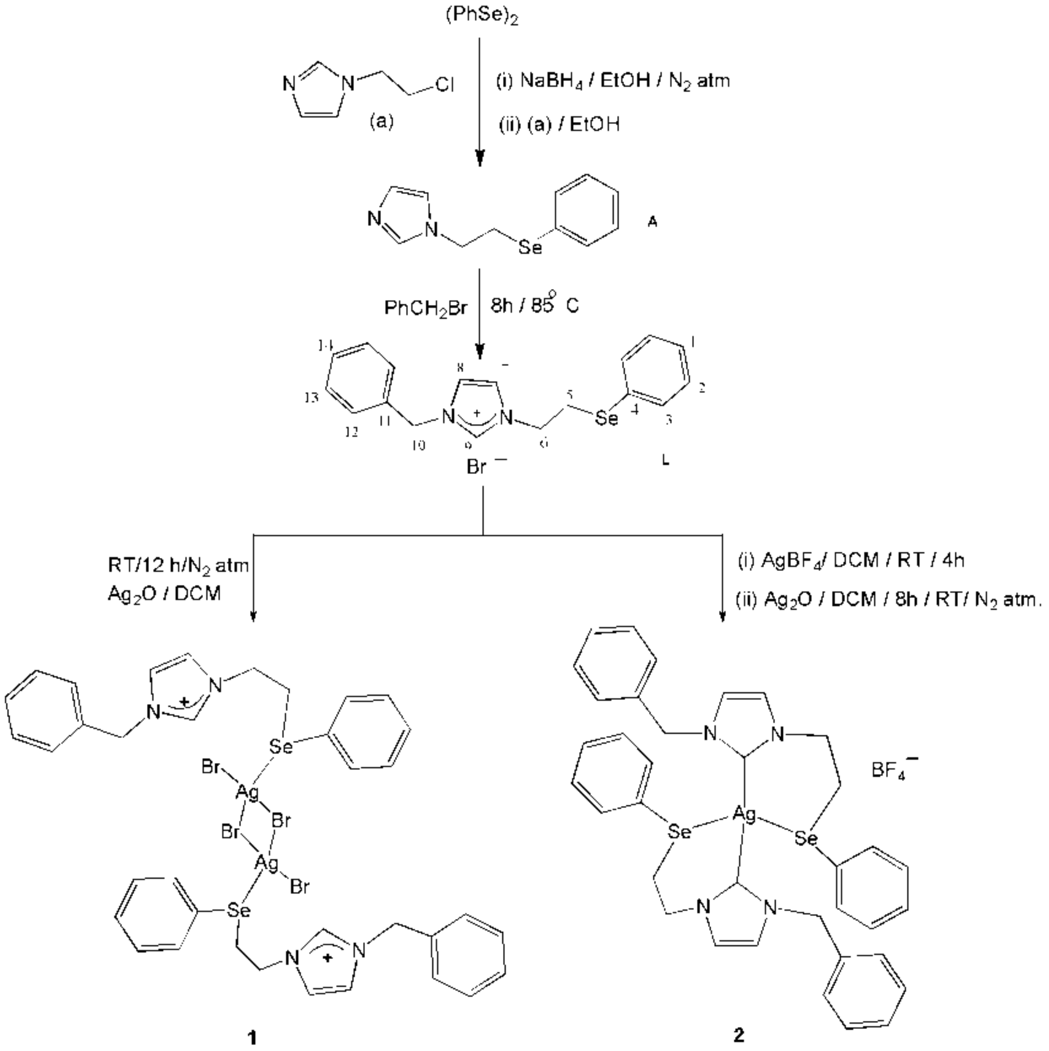
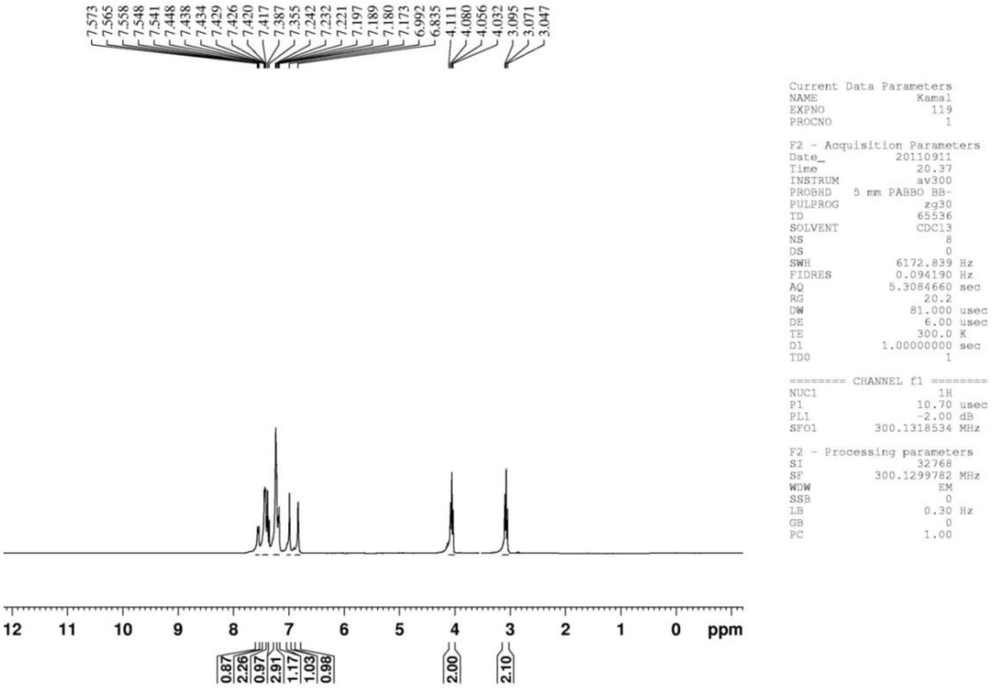


Figure S1. Synthesis of **L**, complexes **1** and **2**

2. NMR Spectra



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FIDRES            0.094190 Hz
AQ               5.3084660 sec
RG                    20.2
DW                  81.000 usec
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TE                   300.0 K
D1              1.00000000 sec
TD0                      1

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PL1                  -2.00 dB
SFO1           300.1318534 MHz

F2 - Processing parameters
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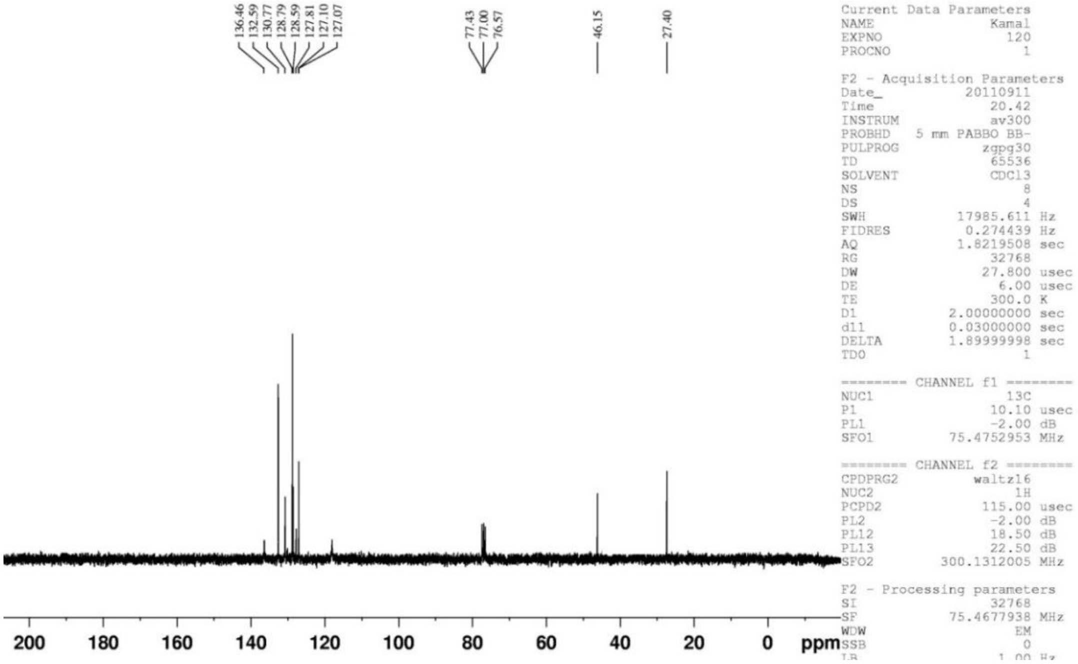
Figure S2. ^{1}H NMR of (**A**).



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SOLVENT              CDCl3
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DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                   32768
DW                  27.800 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
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P1                   10.10 usec
PL1                  -2.00 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
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NUC2                    1H
PCPD2               115.00 usec
PL2                  -2.00 dB
PL12                 18.50 dB
PL13                 22.50 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
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SSB                      0
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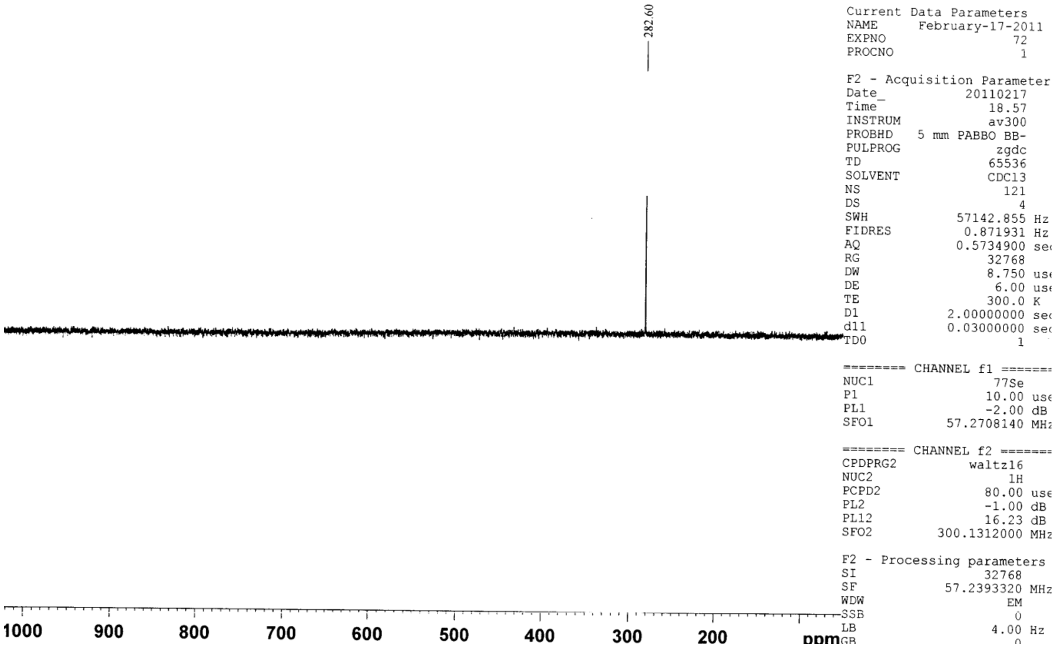
Figure S3. ^{13}C{^{1}H} NMR of (**A**).



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NS                     121
DS                       4
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FIDRES           0.871931 Hz
AQ              0.5734900 se
RG                   32768
DW                   8.750 us
DE                    6.00 us
TE                   300.0 K
D1             2.00000000 se
d11            0.03000000 se
TD0                      1

======== CHANNEL f1 ======
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P1                   10.00 use
PL1                  -2.00 dB
SFO1            57.2708140 MHz

======== CHANNEL f2 ======
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 use
PL2                  -1.00 dB
PL12                 16.23 dB
SFO2           300.1312000 MHz

F2 - Processing parameters
SI                   32768
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WDW                     EM
SSB                      0
LB                    4.00 Hz
GB                       0
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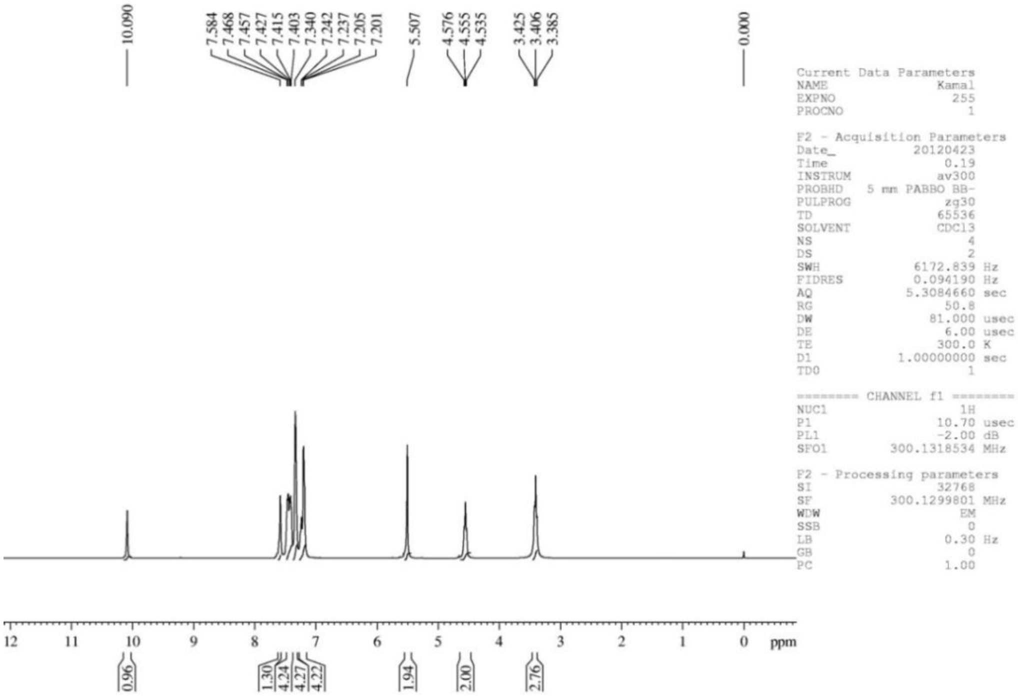
Figure S4. $^{77}Se\{^{1}H\}$ NMR of (**A**).



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PROCNO                   1

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PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       4
DS                       2
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ               5.3084660 sec
RG                    50.8
DW                  81.000 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.70 usec
PL1                  -2.00 dB
SFO1           300.1318534 MHz

F2 - Processing parameters
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WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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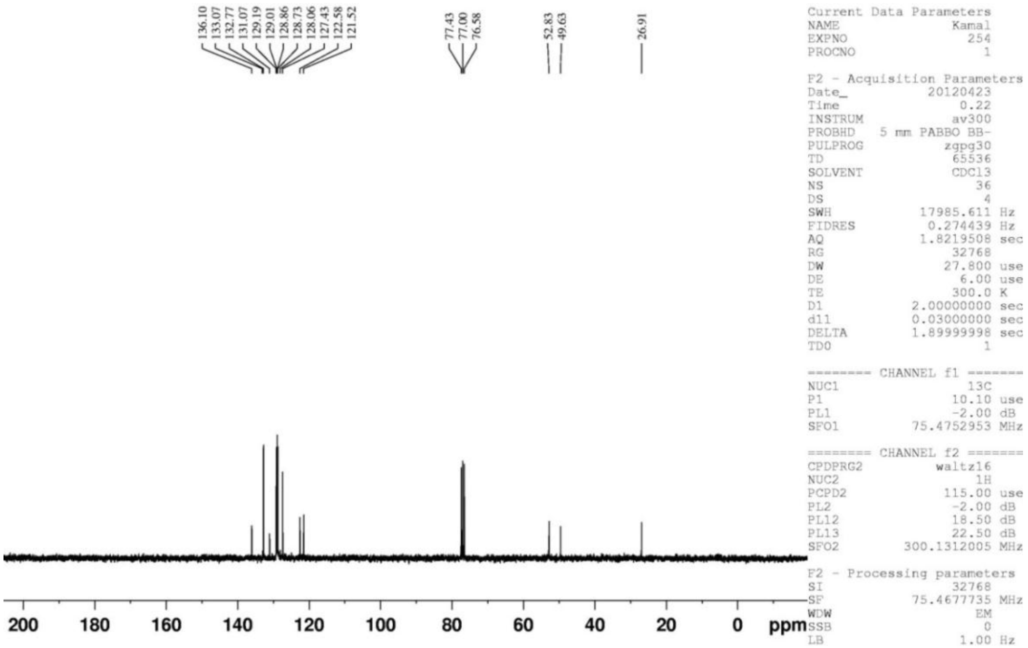
Figure S5. ^{1}H NMR of (**L**).



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PROCNO                   1

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PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      36
DS                       4
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                   32768
DW                  27.800 use
DE                    6.00 use
TE                   300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                      1

======== CHANNEL f1 =======
NUC1                   13C
P1                   10.10 use
PL1                  -2.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 =======
CPDPRG2            waltz16
NUC2                    1H
PCPD2               115.00 use
PL2                  -2.00 dB
PL12                 18.50 dB
PL13                 22.50 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
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SF             75.4677735 MHz
WDW                     EM
SSB                      0
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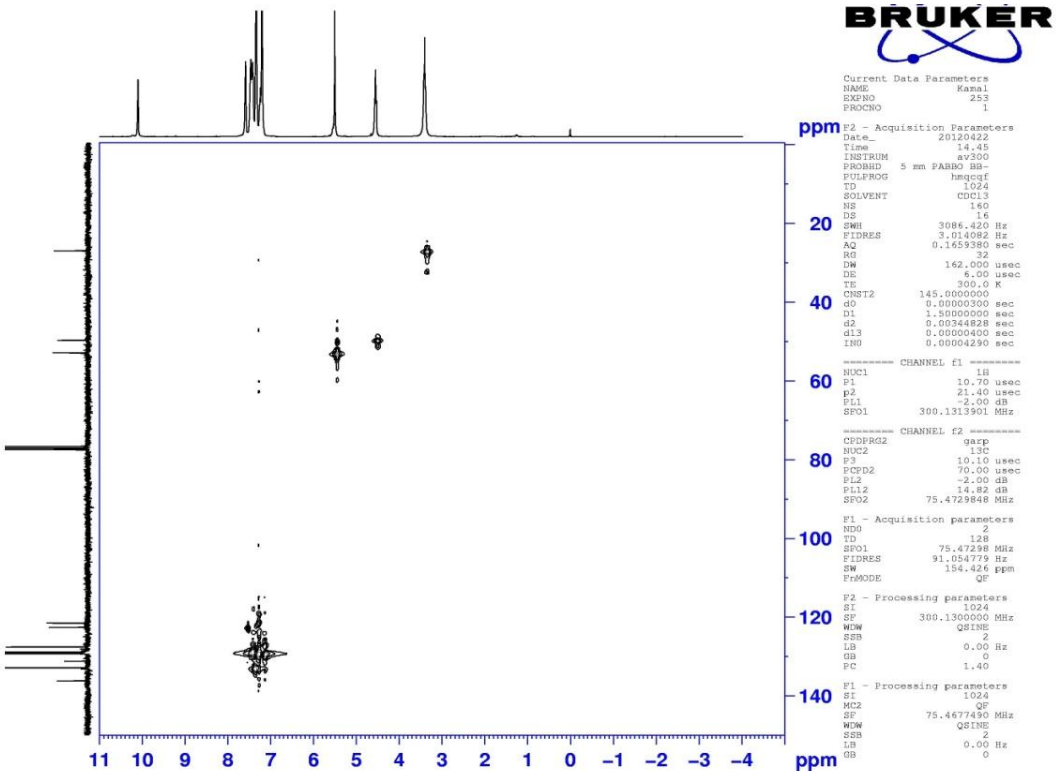
Figure S6. ^{13}C{^{1}H} NMR of (**L**).



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PROCNO                   1

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TD                    1024
SOLVENT              CDCl3
NS                     160
DS                      16
SWH               3086.420 Hz
FIDRES            3.014082 Hz
AQ               0.1659380 sec
RG                      32
DW                 162.000 usec
DE                    6.00 usec
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D1              1.50000000 sec
d2              0.00344828 sec
d13             0.00000400 sec
IN0             0.00004290 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.70 usec
p2                   21.40 usec
PL1                  -2.00 dB
SFO1           300.1313901 MHz

======== CHANNEL f2 ========
CPDPRG2               garp
NUC2                   13C
P3                   10.10 usec
PCPD2                70.00 usec
PL2                  -2.00 dB
PL12                 14.82 dB
SFO2            75.4729848 MHz

F1 - Acquisition parameters
ND0                      2
TD                     128
SFO1              75.47298 MHz
FIDRES           91.054779 Hz
SW                 154.426 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    1024
SF             300.1300000 MHz
WDW                  QSINE
SSB                      2
LB                    0.00 Hz
GB                       0
PC                    1.40

F1 - Processing parameters
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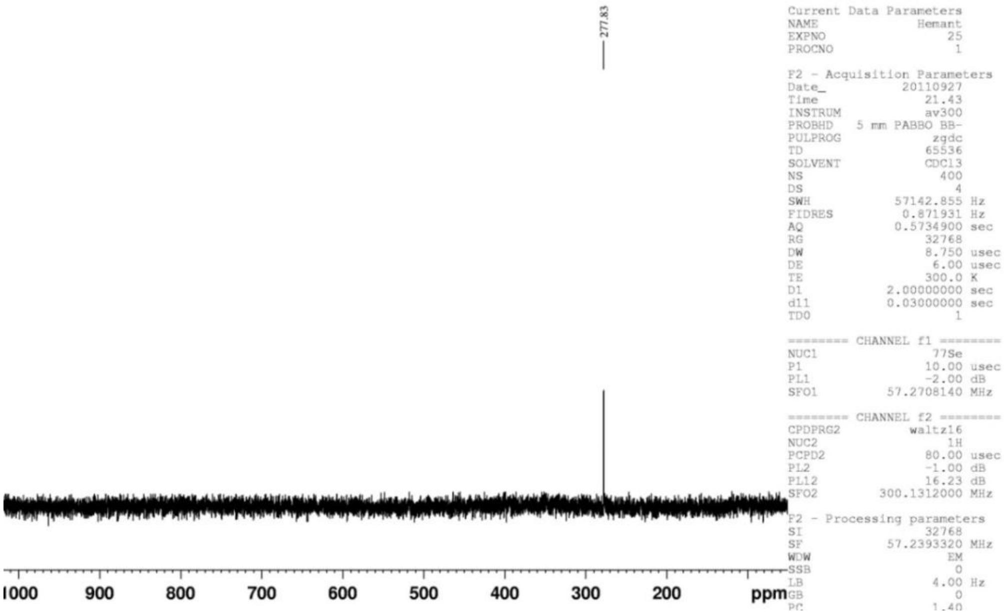
Figure S7. HMQC NMR of (**L**).



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FIDRES          0.871931 Hz
AQ             0.5734900 sec
RG                 32768
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DE                  6.00 usec
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PL1                -2.00 dB
SFO1          57.2708140 MHz

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NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               16.23 dB
SFO2         300.1312000 MHz

F2 - Processing parameters
SI                 32768
SF            57.2393320 MHz
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SSB                    0
LB                  4.00 Hz
GB                     0
PC                  1.40
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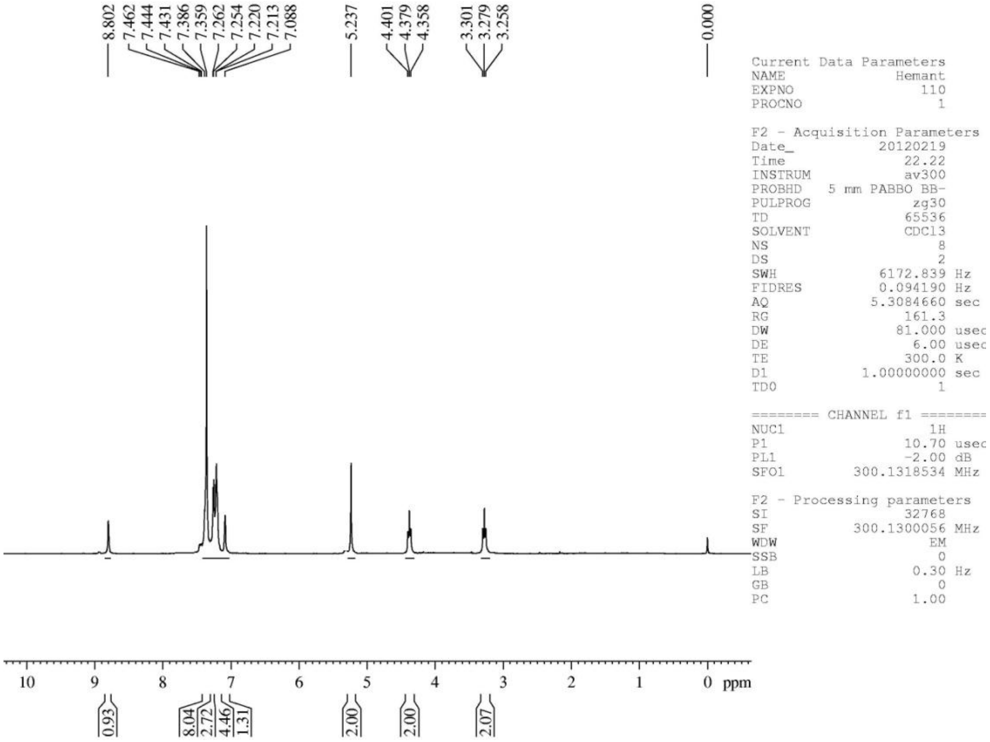
Figure S8.^{77}Se{^{1}H} NMR of (**L**).



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PROCNO                 1

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SOLVENT            CDCl3
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DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                 161.3
DW                81.000 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec
TD0                    1

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P1                 10.70 usec
PL1                -2.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
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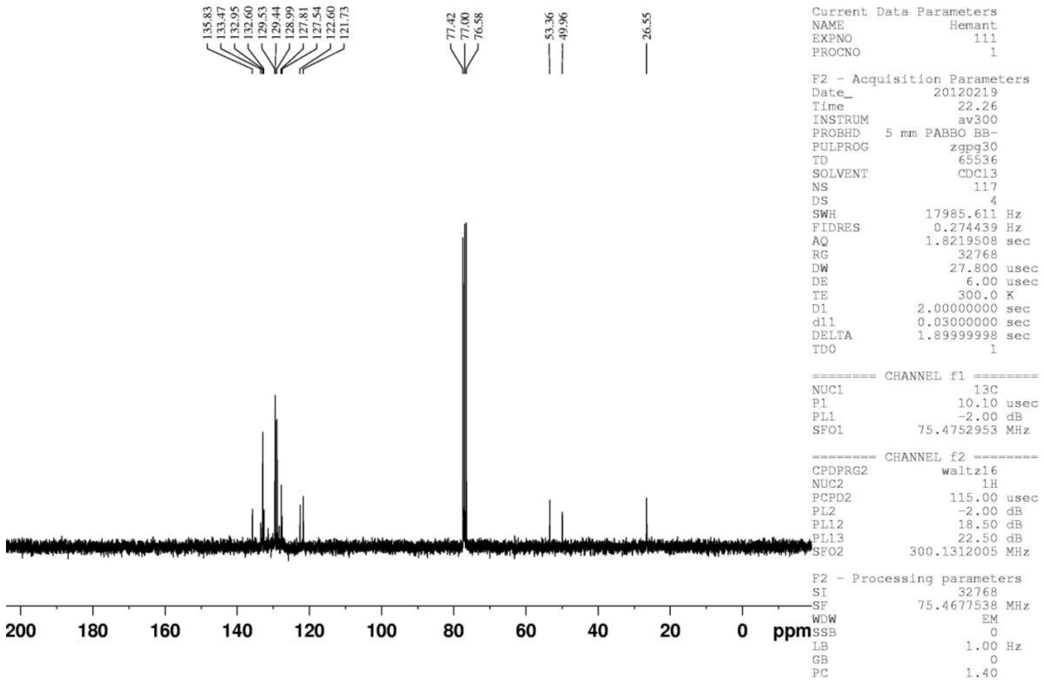
Figure S9. ^{1}H NMR of **1**.



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PROCNO                  1

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TD                  65536
SOLVENT             CDCl3
NS                    117
DS                      4
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                  32768
DW                 27.800 usec
DE                   6.00 usec
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P1                  10.10 usec
PL1                 -2.00 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2              115.00 usec
PL2                 -2.00 dB
PL12                18.50 dB
PL13                22.50 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
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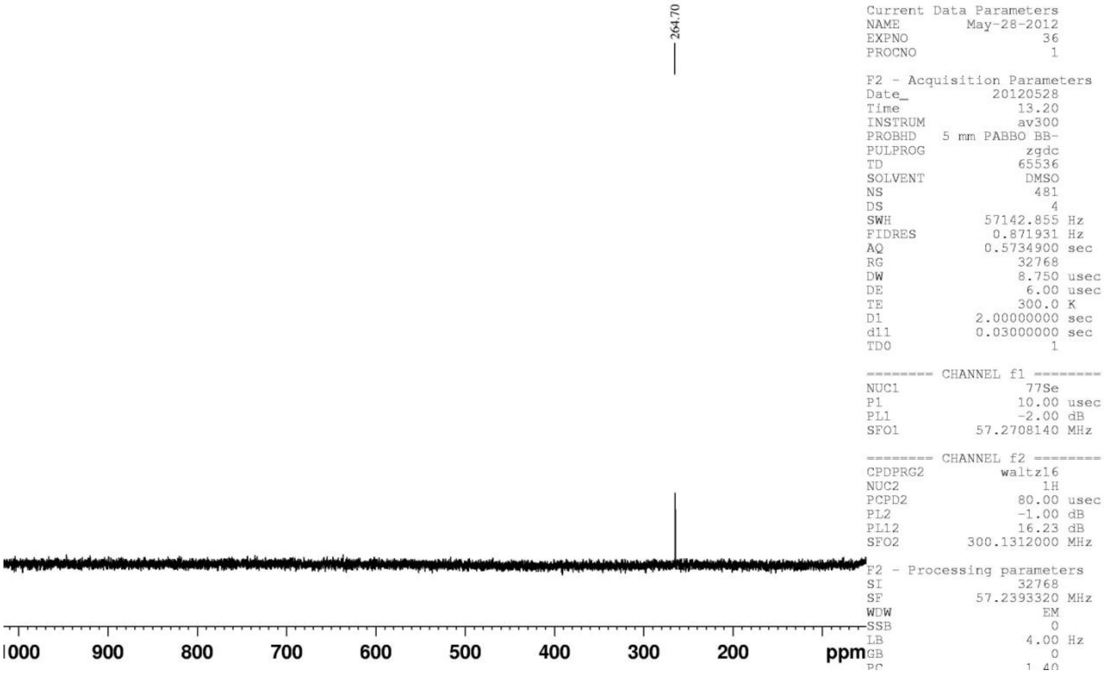
Figure S10. $^{13}C\{^1H\}$ NMR of **1**.



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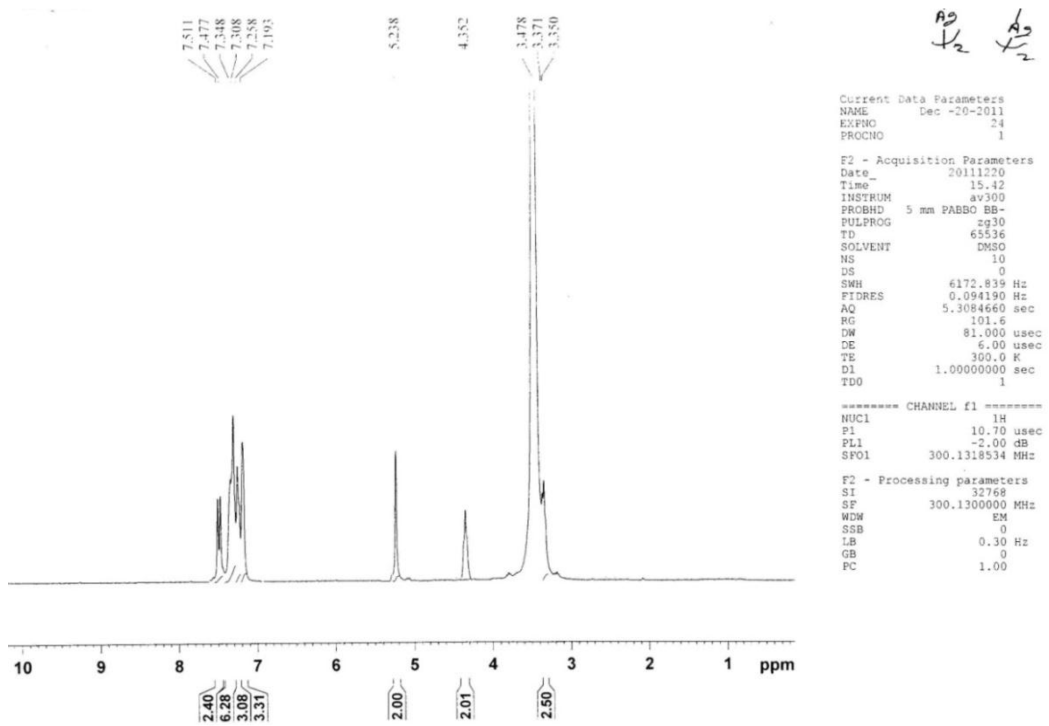
FIDRES           0.871931 Hz
AQ              0.5734900 sec
RG                  32768
DW                  8.750 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                 77Se
P1                  10.00 usec
PL1                 -2.00 dB
SFO1           57.2708140 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -1.00 dB
PL12                16.23 dB
SFO2          300.1312000 MHz

F2 - Processing parameters
SI                  32768
SF             57.2393320 MHz
WDW                    EM
SSB                     0
LB                   4.00 Hz
GB                      0
PC                   1.40
```

Figure S11. $^{77}Se\{^1H\}$ NMR of **1**.



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Current Data Parameters
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EXPNO                   24
PROCNO                   1

F2 - Acquisition Parameters
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PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      10
DS                       0
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                   101.6
DW                  81.000 usec
DE                    6.00 usec
TE                   300.0 K
D1             1.00000000 sec
TD0                      1

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NUC1                    1H
P1                   10.70 usec
PL1                  -2.00 dB
SFO1           300.1318534 MHz

F2 - Processing parameters
SI                   32768
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WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```
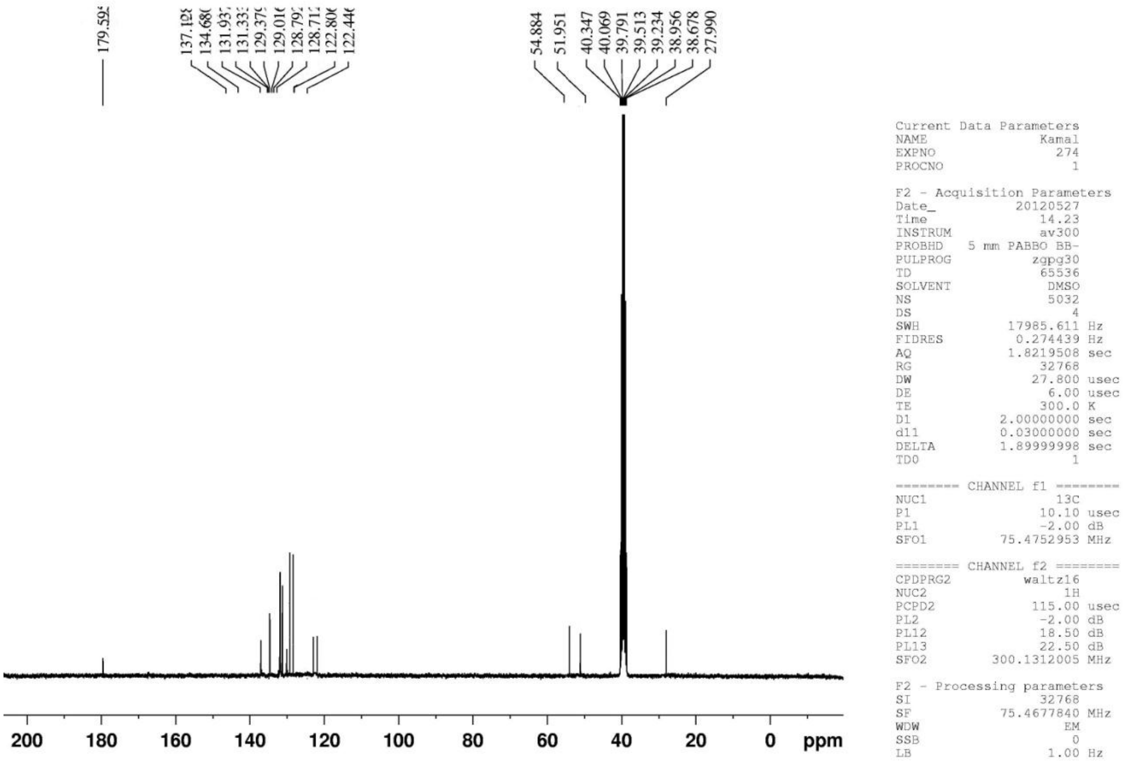

Figure S12. ^{1}H NMR of **2**.



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Current Data Parameters
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EXPNO                  274
PROCNO                   1

F2 - Acquisition Parameters
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Time                 14.23
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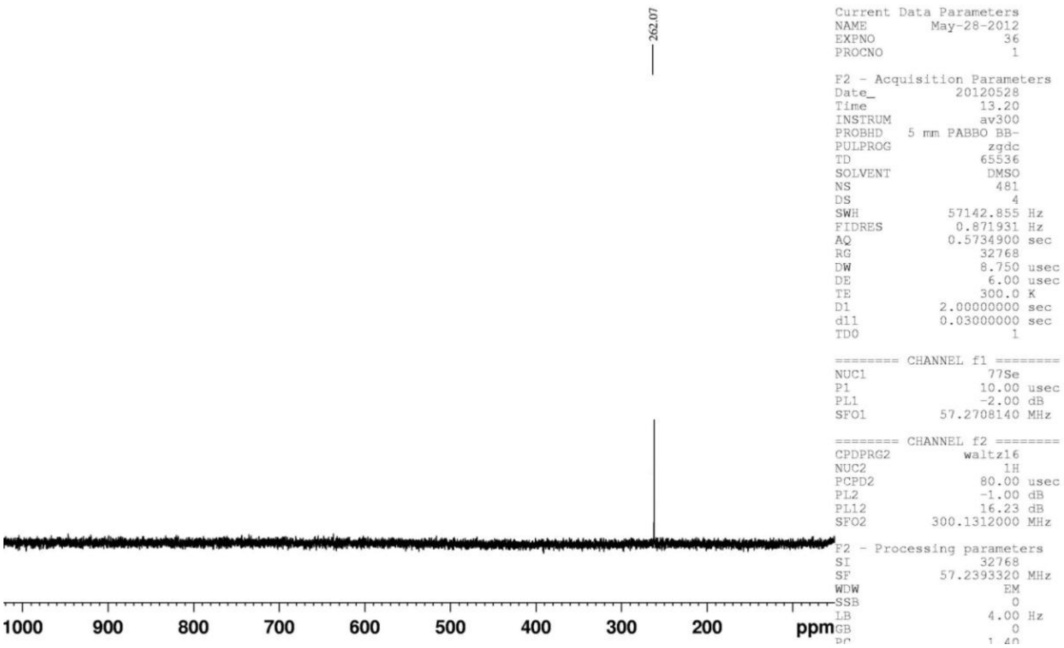
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT               DMSO
NS                    5032
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                   32768
DW                  27.800 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.10 usec
PL1                  -2.00 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               115.00 usec
PL2                  -2.00 dB
PL12                 18.50 dB
PL13                 22.50 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF              75.4677840 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
```

Figure S13. ^{13}C{^{1}H} NMR of **2**



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Current Data Parameters
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EXPNO                  36
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120528
Time                13.20
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PROBHD   5 mm PABBO BB-
PULPROG              zgdc
TD                  65536
SOLVENT              DMSO
NS                    481
DS                      4
SWH             57142.855 Hz
FIDRES           0.871931 Hz
AQ              0.5734900 sec
RG                  32768
DW                  8.750 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                 77Se
P1                  10.00 usec
PL1                 -2.00 dB
SFO1           57.2708140 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -1.00 dB
PL12                16.23 dB
SFO2          300.1312000 MHz

F2 - Processing parameters
SI                  32768
SF             57.2393320 MHz
WDW                    EM
SSB                     0
LB                   4.00 Hz
GB                      0
PC                   1.40
```
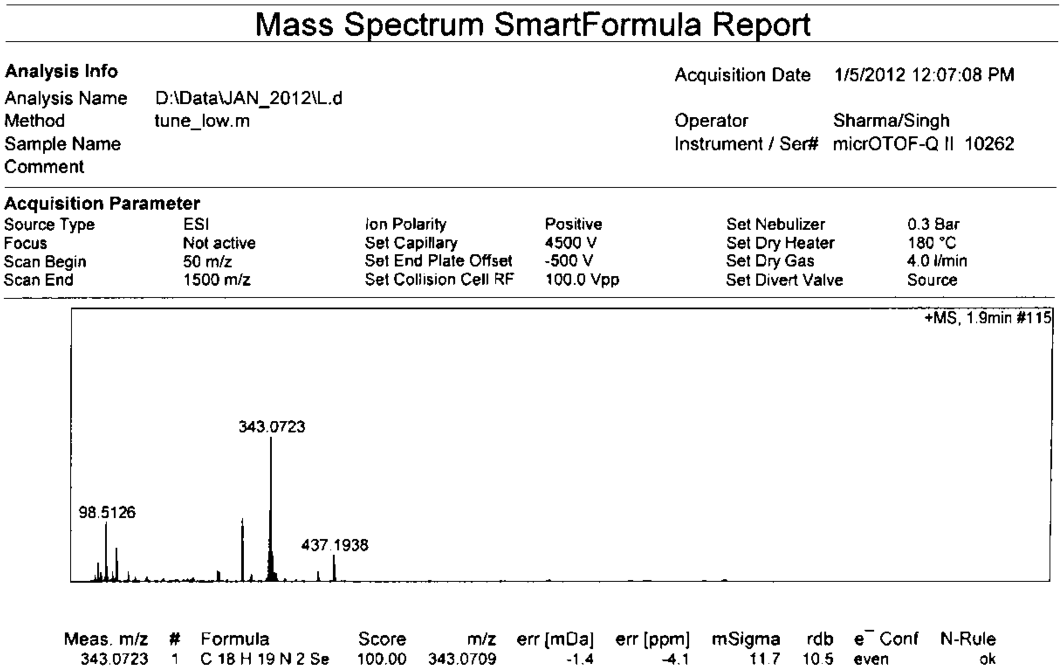

Figure S14. ^{77}Se{^{1}H} NMR of **2**

3. Mass Spectra

In mass spectrum of ligand **L** the peak appearing at 343.0723 corresponds to **[L**-Br]$^+$ cation. The mass spectrum of complex **1** shows two characteristic peaks at 343.0729 and 451.0856 which correspond to [L-Br]$^+$ and [Ag{L-Br}+H]$^+$ cationic fragments respectively. In mass spectrum of complex **2,** peak of **[2**-BF$_4$]$^+$ cation appears at 791.0313.



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\JAN_2012\L.d
Method tune_low.m
Sample Name
Comment

Acquisition Date 1/5/2012 12:07:08 PM

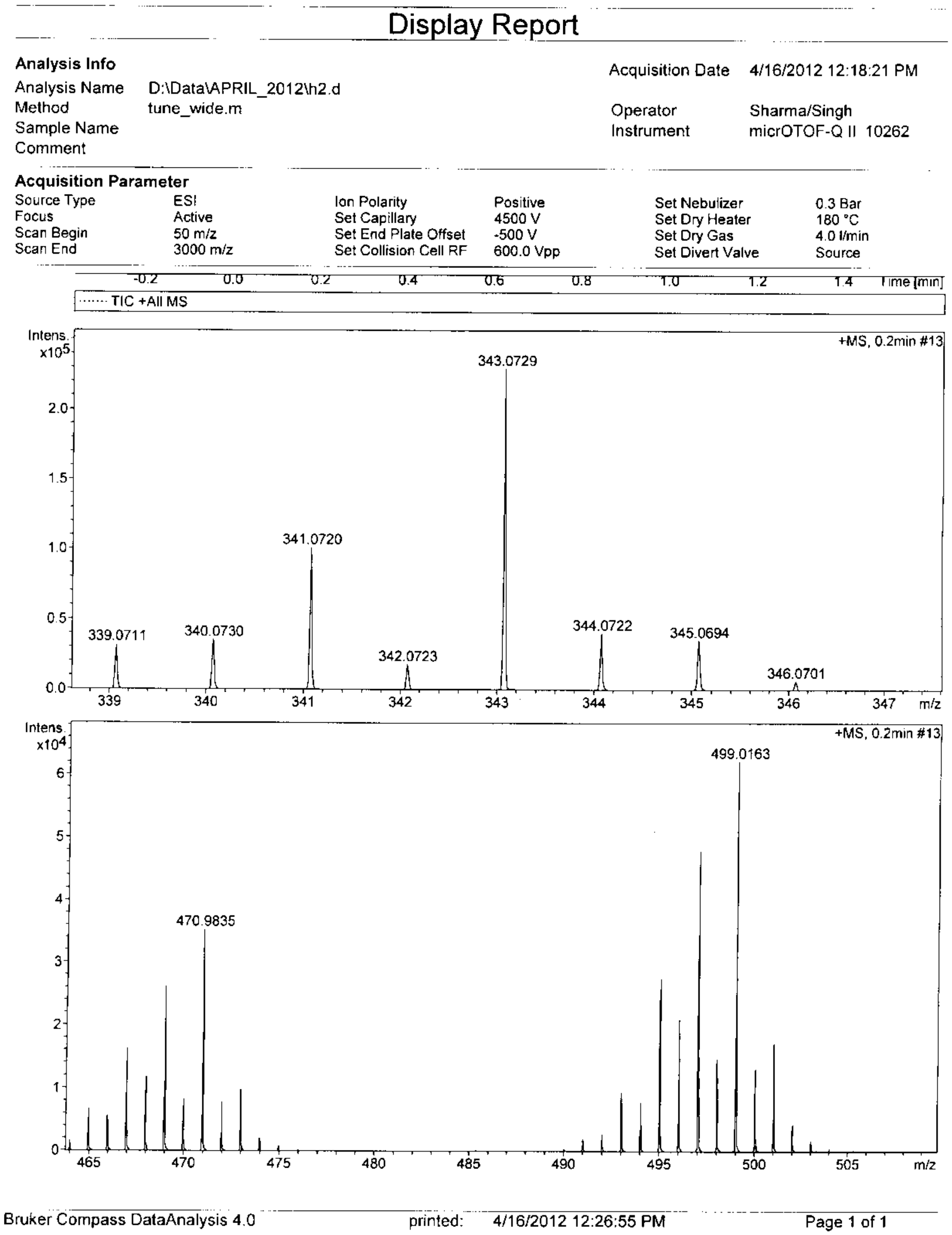
Operator Sharma/Singh
Instrument / Ser# micrOTOF-Q II 10262

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e^- Conf	N-Rule
343.0723	1	C 18 H 19 N 2 Se	100.00	343.0709	-1.4	-4.1	11.7	10.5	even	ok

Figure S15. Mass spectra of (**L**)



Display Report

Analysis Info

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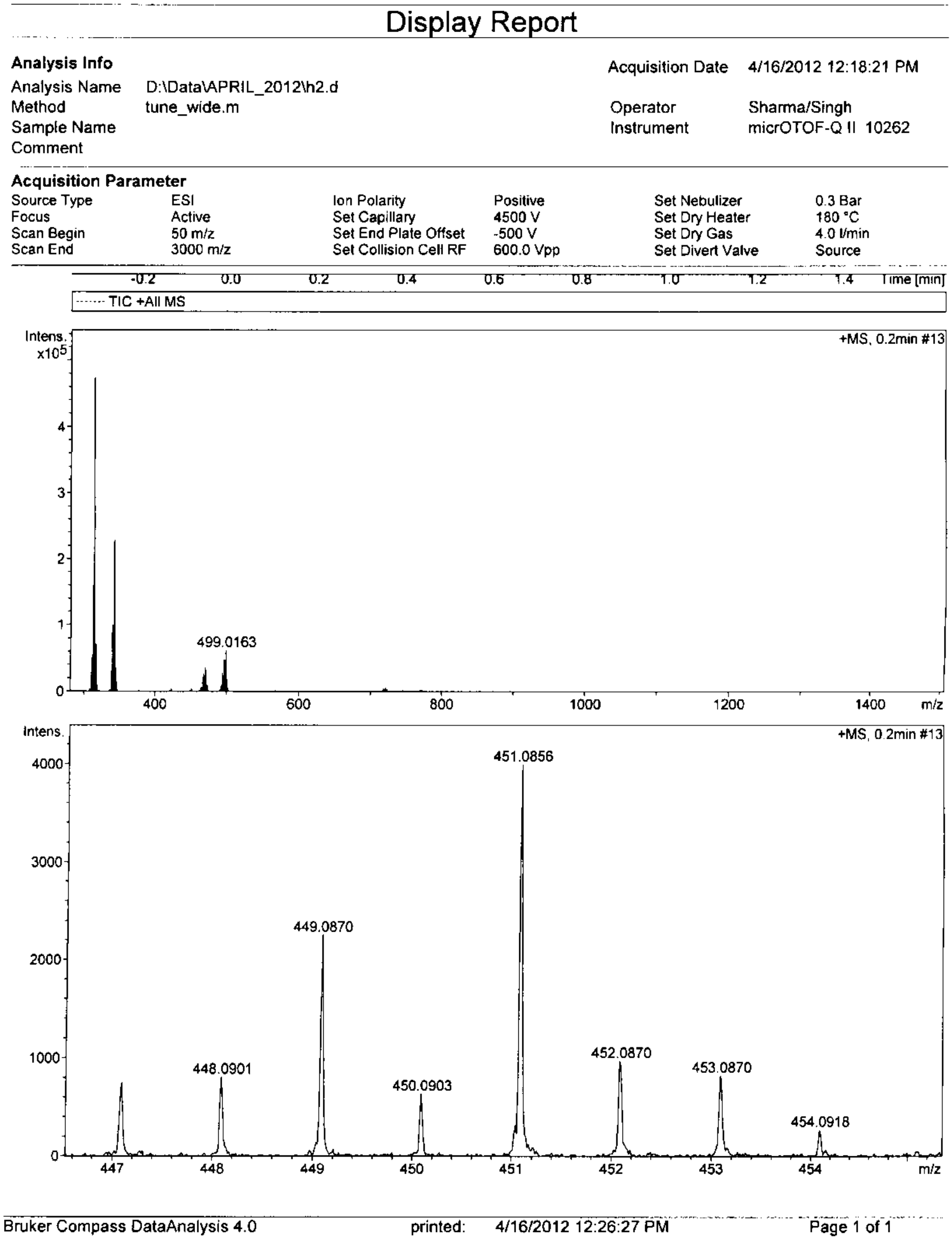
Method	tune_wide.m	Operator	Sharma/Singh
Sample Name		Instrument	micrOTOF-Q II 10262
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

Bruker Compass DataAnalysis 4.0 printed: 4/16/2012 12:26:55 PM Page 1 of 1

Figure S16. Mass spectra of **1.**



Display Report

Analysis Info

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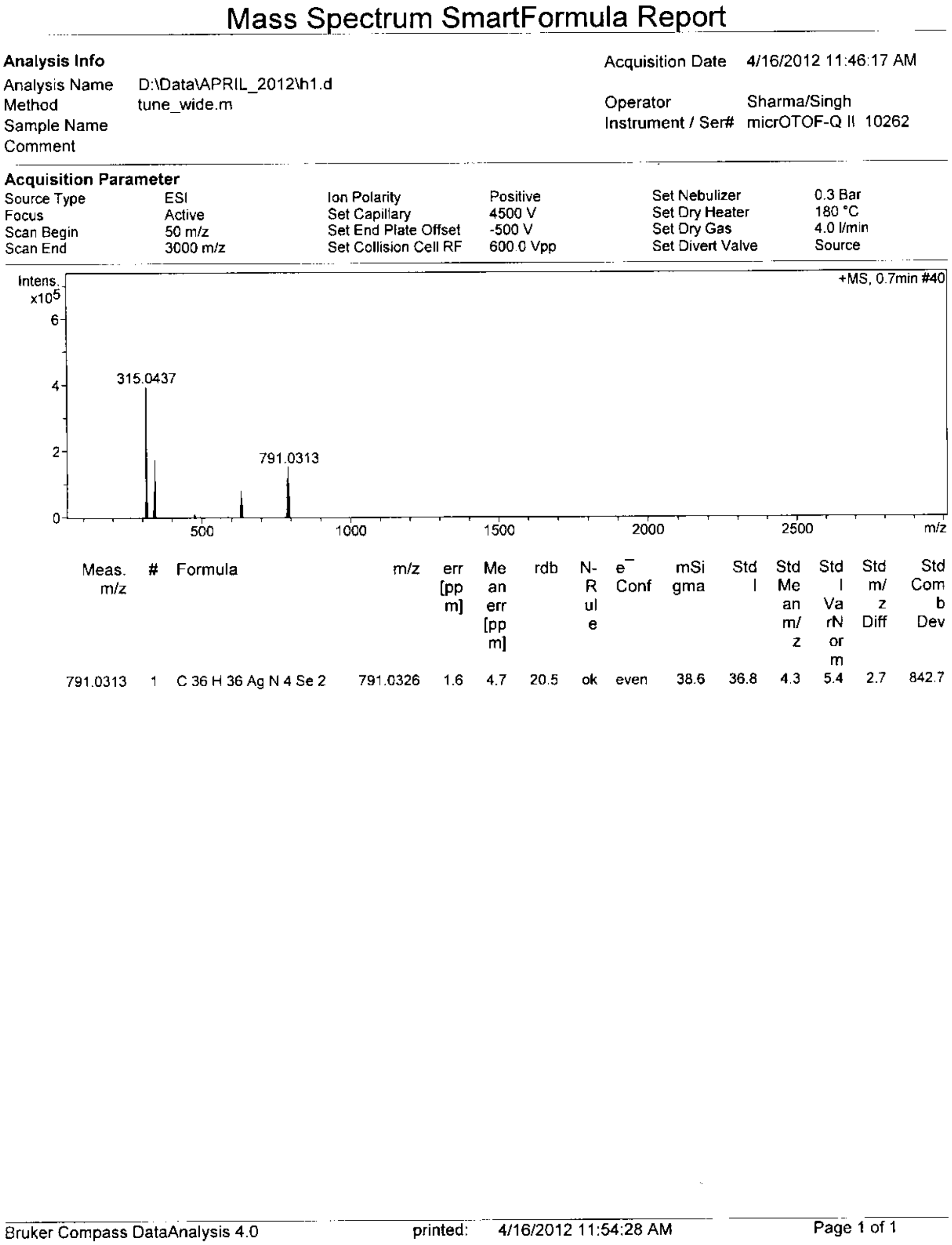
Sample Name		Instrument	micrOTOF-Q II 10262
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

Bruker Compass DataAnalysis 4.0 printed: 4/16/2012 12:26:27 PM Page 1 of 1

Figure S17. Mass spectra of **1.**



Mass Spectrum SmartFormula Report

Analysis Info

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Method	tune_wide.m	Operator	Sharma/Singh
Sample Name		Instrument / Ser#	micrOTOF-Q II 10262
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
791.0313	1	C 36 H 36 Ag N 4 Se 2	791.0326	1.6	4.7	20.5	ok	even	38.6	36.8	4.3	5.4	2.7	842.7

Bruker Compass DataAnalysis 4.0 printed: 4/16/2012 11:54:28 AM Page 1 of 1

Figure S18. Mass spectra of **2.**

4. Crystal data

Table T1. Structural refinement parameters of **1.**

Compounds	**1**
Empirical formula	$C_{36}H_{38}Ag_2Br_4N_4Se_2$
Formula wt.	1219.96
Crystal size [mm]	0.29×0.25×0.21
Crystal system	Monoclinic
Space group	*P 21/c*
Unit Cell dimension	a = 11.534(2)Å b = 13.521(2)Å c = 12.778(2)Å α = 90.00° β = 97.081(3)° γ = 90.00°
Volume [$Å^3$]	1977.6(5)
Z	2
Density (Calc.) [$Mg \cdot m^{-3}$]	2.049
Absorption coeff. [mm^{-1}]	6.903
F(000)	1168.0
θ range [°]	2.20–26.97

Index ranges	$-13 \leq h \leq 13$ $-16 \leq k \leq 16$ $-15 \leq l \leq 15$
Reflections collected	18117
Independent reflections (R_{int}.)	3476 (0.0430)
Max./min. Transmission	0.025/0.004
Data/restraints/parameters	3476/0/217
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0271$, $wR_2 = 0.0652$
R indices (all data)	$R_1 = 0.0354$, $wR_2 = 0.0683$
Largest diff. peak/hole [e.Å^{-3}]	0.526/–0.625

Table T2. Selected bond lengths [Å] and bond angles [^{o}] of complex **1**

Bond length [Å]	Bond angle [^{o}]
Se(1)—C(6) 1.925(4)	Br(1)–Ag(1)–Se(1) 124.65(18)
Se(1)—C(7) 1.952(4)	Br(1)–Ag(1)–Br(2) 111.91(2)
N(1)—C(8) 1.464(4)	Se(1)–Ag(1)–Br(2) 104.86(17)
N(1)—C(9) 1.325(5)	C(8)–N(1)–C(9) 124.3(3)
N(1)—C(10) 1.371(5)	C(9)–N(1)–C(10) 108.8(3)
N(2)—C(9) 1.323(5)	C(8)–N(1)–C(10) 126.9(3)
N(2)—C(11) 1.364(5)	C(9)–N(2)–C(11) 108.3(3)
N(2)—C(12) 1.480(5)	C(9)–N(2)–C(12) 122.8(4)
Se(1)—Ag(1) 2.6633(6)	C(11)–N(2)–C(12) 128.7(4)
Br(1)—Ag(1) 2.6618(6)	C(6)–Se(1)–C(7) 100.17(15)
Br(2)—Ag(1) 2.6501(6)	C(6)–Se(1)–Ag(1) 111.36(11)
Ag(1)—Ag(1) 3.1172(8)	C(7)–Se(1)–Ag(1) 109.69(12)

5. SEM−EDX data

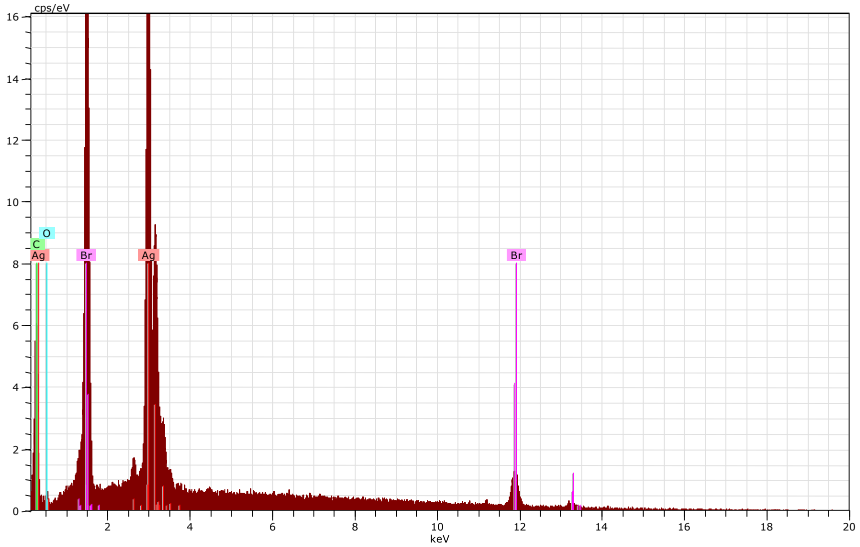

Figure S19. SEM - EDX of AgBr NPs.

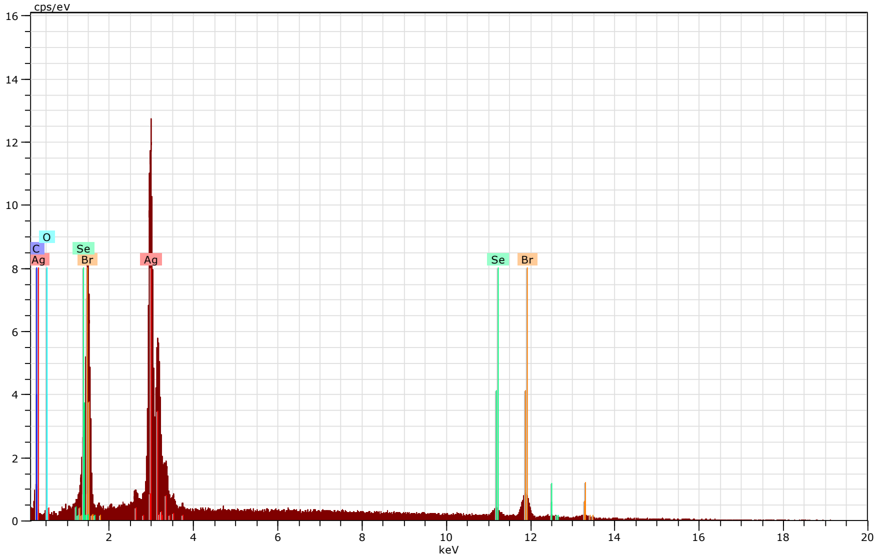

Figure S20. SEM - EDX of (Ag + AgBr + Ag_2Se) NPs.

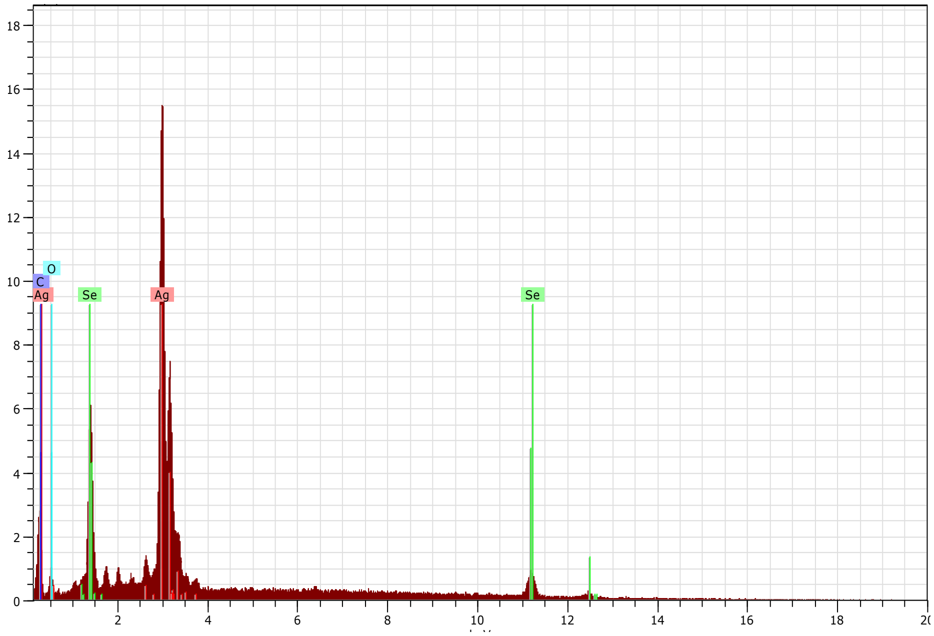

Figure S21. SEM - EDX of Ag_2Se NPs.

6. Powder XRD Data

Each of the powder XRD patterns of both types of NPs was found matching with that of the corresponding known standard phase of the same composition. The powder X-ray diffraction pattern of AgBr NPs was indexes on the basis of a cubic unit cell (JCPDS #79−0149) with the d values (*hkl*): 3.33 (111), 2.88 (200), 2.04 (220), 1.74 (311), 1.66 (222), 1.44 (400), 1.32 (331), 1.29 (420), 1.17 (422), 1.11 (511)

For (Ag + AgBr + Ag_2Se) NPs a cubic unit cell (JCPDS #04−0783) with the d values (*hkl*): 2.35 (111), 2.04 (200), 1.44 (220), 1.23 (311) for Ag NP**s,** a cubic unit cell (JCPDS #06−0438) with the d values (*hkl*): 3.33 (111), 2.88 (200), 2.04 (220), 1.74 (311), 1.60 (222), 1.44 (400), 1.32 (331), 1.29 (420), 1.29 (420), 1.77 (422) for AgBr NP**s,** a orthorombic unit cell (JCPDS #24−1041) with the d values (*hkl*): 3.33 (111), 2.89 (102), 2.73 (120), 2.67 (112), 2.58 (121), 2.42 (013), 2.25 (031), 2.23 (122), 2.16 (200), 2.11 (113), 2.08 (201), 2.06 (130), 2.01 (032), 2.00 (211), 1.94 (004), 1.88 (123), 1.87 (014), 1.84 (220), 1.82 (212), 1.76 (221), 1.76 (104), 1.71 (114), 1.66 (222), 1.63 (140), 1.61 (213), 1.60 (230), 1.59 (230), 1.56 (231), 1.50 (223), 1.47 (232), 1.45 (043), 1.44 (204) for Ag_2Se NP**s,** For Ag_2Se NPs orthorhombic unit cell (JCPDS # 24−1041) with d values (*hkl*): 3.88 (002), 3.77 (101), 3.69 (110), 3.52 (020), 3.33 (111), 2.89 (102), 2.73 (120), 2.67 (112), 2.58 (121), 2.42 (013), 2.25 (031), 2.23 (122), 2.16 (200), 2.11 (113), 2.08 (201), 2.06 (130), 2.01 (032), 2.00 (211), 1.94 (004), 1.88 (123), 1.87 (014), 1.84 (220), 1.82 (212), 1.79 (221), 1.76 (104), 1.71 (114), 1.66 (222), 1.61 (213), 1.56 (231), 1.50 (223), 1.44 (204), 1.42 (301), 1.41 (214) .

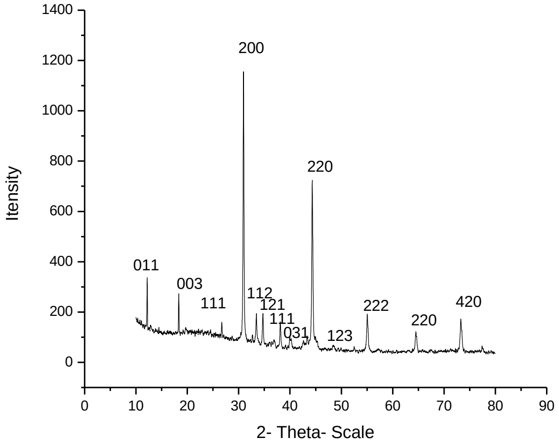

Figure S22. PXRD of (Ag + AgBr + Ag_2Se) NPs.

7. TEM images

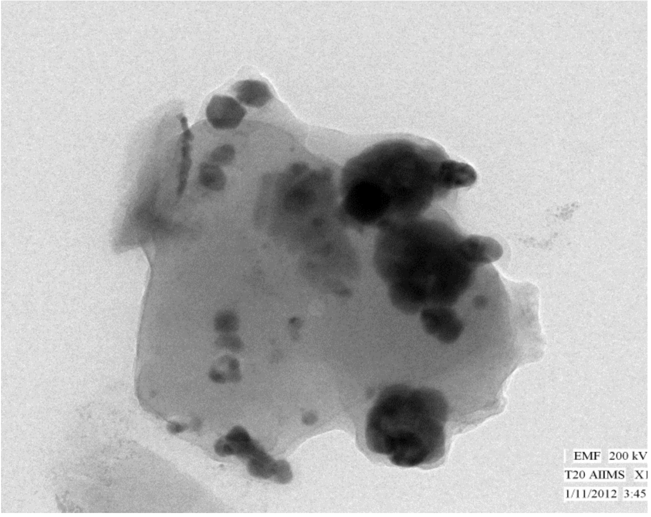

Figure S23. TEM image of (Ag + AgBr + Ag_2Se) NPs.

References

1 SADABS V2.10 (Sheldrick, G. M. **2003**).

2 (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.*, **1990**, 46, 467; (b) Sheldrick, G. M. *SHELXL-NT Version 6.12*, University of Gottingen, Germany, **2000**.

3 Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th Eds. ELBS, Longman Group U K Ltd., **1989**.

4 Lee, H. M.; Zeng, J. Y.; Hee, C. H.; Lee, M. T. *Inorg. Chem.*, **2004**, 43, 6822–6829.