Electronic Supplementary Information

For

N-Heterocyclic Carbene Stabilized Parent Sulfenyl, Selenenyl, and Tellurenyl Cations (XH^+, X = S, Se, Te)

Liu Leo Liu,[a] Diya Zhu,[a] Levy L. Cao[a] and Douglas W. Stephan*[a]

[a]Department of Chemistry, University of Toronto, 80 St. George St, Toronto, Ontario, Canada M5S 3H6.

E-mail: dstephan@chem.utoronto.ca

Index

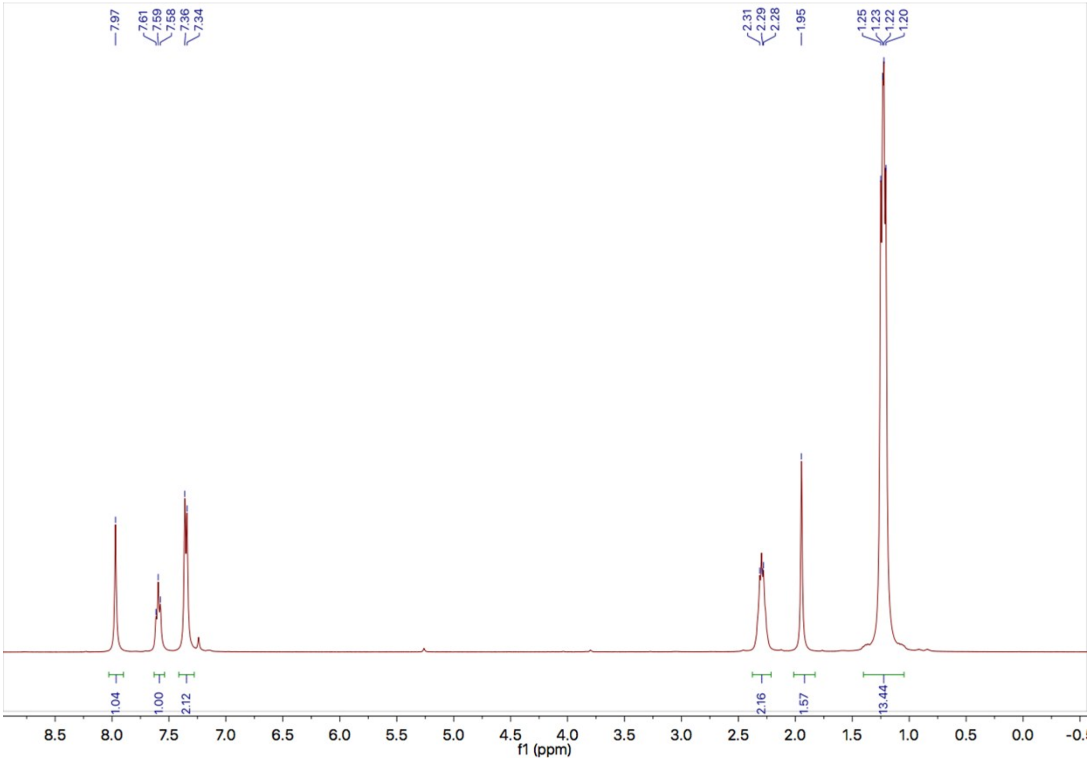
1. General

All manipulations were performed under an atmosphere of dry, oxygen-free N_2 by means of standard Schlenk or glovebox techniques (MBRAUN glovebox equipped with a -25 °C freezer). DCM and pentane were collected from a Grubbs-type column system manufactured by Innovative Technology. Pentane and DCM were stored over 4 Å molecular sieves. Molecular sieves, type 4 Å (pellets, 3.2 mm diameter) purchased from Sigma Aldrich were activated prior to usage by iteratively heating with 1050 W Haier microwave for 5 minutes and cooling under vacuum. The process was repeated until no further moisture was released upon heating. $CDCl_3$ purchased from Cambridge Isotope Laboratories was degassed and stored over 4 Å molecular sieves in the glovebox for at least 8 h prior to use. CD_2Cl_2 were purchased from Sigma Aldrich, and distilled over CaH_2. Unless otherwise mentioned, chemicals were purchased from Sigma Aldrich or TCI. NHC chalcogen adducts were prepared using literature methods.[S1] Spectra were recorded at room temperature (298K) unless otherwise mentioned either on a Bruker Avance III 400 MHz or an Agilent DD2 600 MHz spectrometer and spectra were referenced to residual solvents of $CDCl_3$ (^{1}H=7.26 ppm for the proton; ^{13}C=77.0 ppm for the carbon;) Other references: The ^{19}F, ^{77}Se and ^{125}Te NMR are referenced to the deuterium signal from the solvent with a ratio of gamma's to assign 0 ppm. Chemical shifts (δ) are reported in ppm and the absolute values of the coupling constants (*J*) are in Hz. High-resolution mass spectra (HRMS) were obtained on a JMS-T100LC JOEL DART.

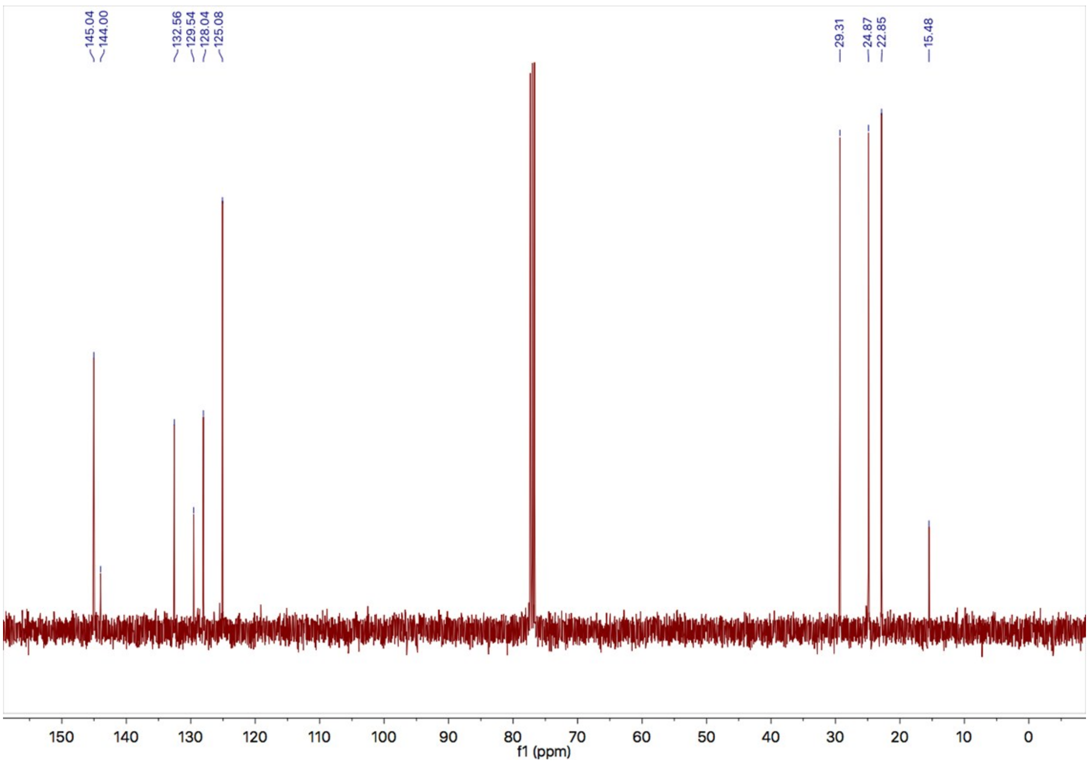
2. Synthesis and Characterization

2a: **1a** (50 mg, 0.12 mmol) was dissolved in 3 mL of DCM and two drops of MeOTf was added to the solution. After 5 minutes, 5 mL of pentane was added with rigorous stirring a precipitate appeared. The white solid was collected by filtration (61 mg; 88 %). Colourless crystals were grown by vapour diffusion of pentane into a saturated DCM solution. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2H, CH), 7.59 (t, 2H, $^3J_{HH}$ = 8.0 Hz, CH_{Dipp}), 7.35 (d, 4H, $^3J_{HH}$ = 8.0 Hz, CH_{Dipp}), 2.29 (m, 4H, $^3J_{HH}$ = 8.0 Hz, $C\underline{H}(CH_3)_2$), 1.95 (s, 3H, CH_3), 1.24 (d, 12H, $^3J_{HH}$ = 8.0 Hz, $CH(C\underline{H}_3)_2$), 1.21 (d, 12H, $^3J_{HH}$ = 8.0 Hz, $CH(C\underline{H}_3)_2$); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.0 (N-C_{Dipp}), 144.0 (s, CS), 132.6 (s, C_{Dipp}), 129.5 (s, C_{Dipp}), 128.0 (s, C_{Dipp}), 125.1 (s, CH), 29.3 (s, $\underline{C}H(CH_3)_2$), 24.9 (s, $CH(\underline{C}H_3)_2$), 22.9 (s, $CH(\underline{C}H_3)_2$), 15.5 (s, SCH_3); ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.3; elemental analysis for $C_{29}H_{39}F_3N_2O_3S_2$: calcd.: C 57.7, H 6.5, N 4.6, found: C 57.5, H 6.5, N 4.6; DART HRMS: m/z calculated for $[C_{28}H_{39}N_2S]^+$ (M^+) 435.28339, found 435.28457.

^{1}H NMR ($CDCl_3$)

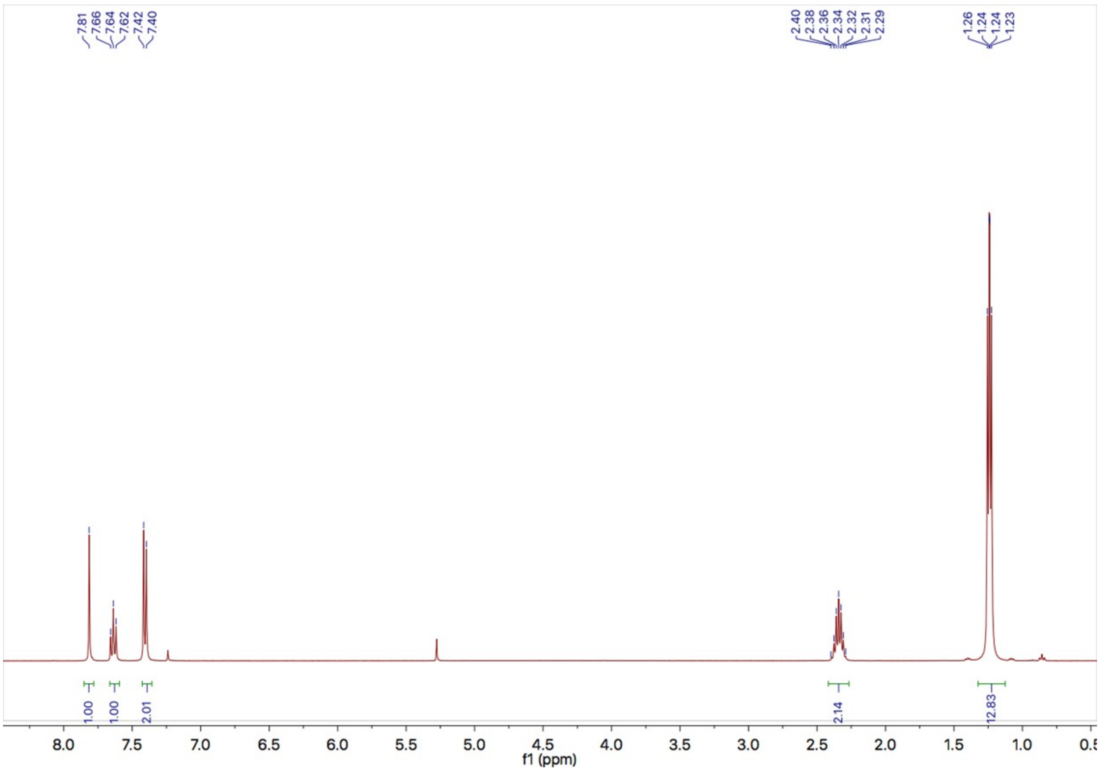


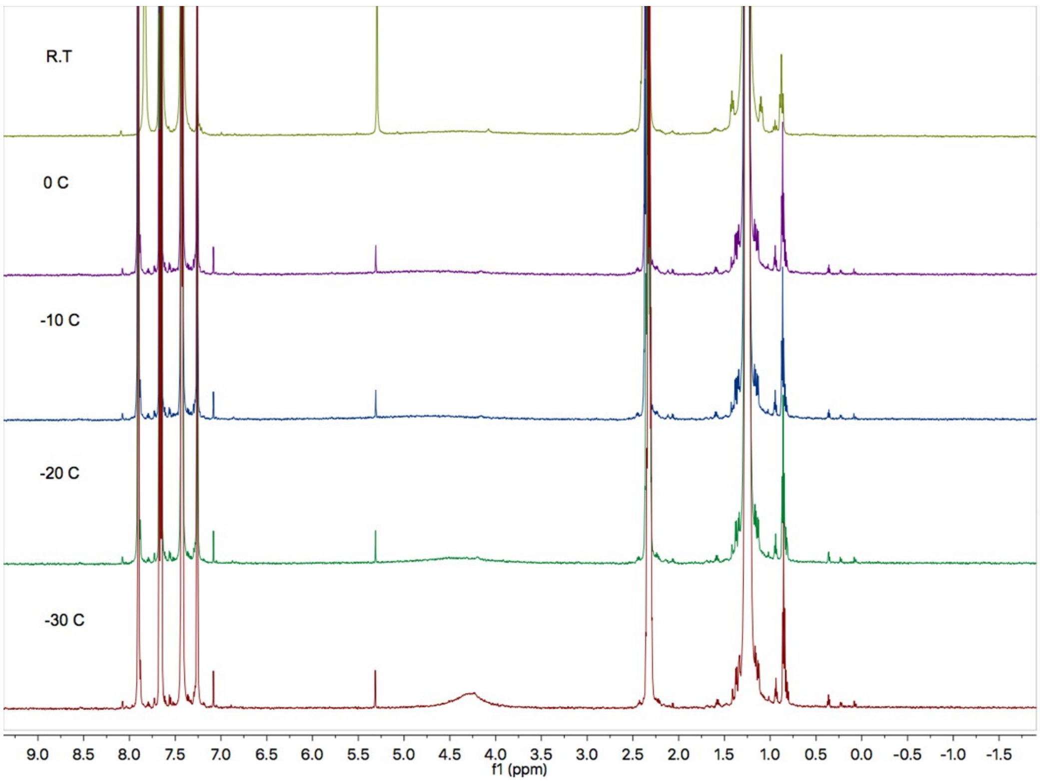
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$)



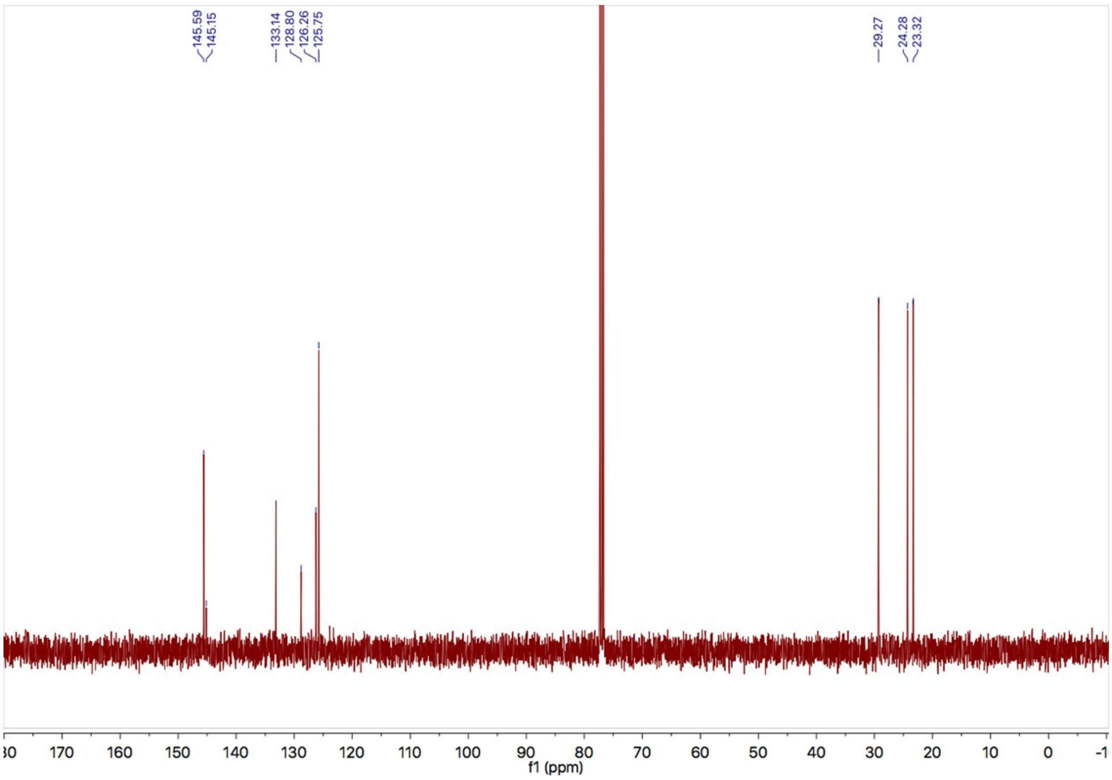
2b: **1a** (50 mg, 0.12 mmol) was dissolved in 3 mL of DCM and two drops of HOTf was added to the solution. After 5 minutes, 5 mL of pentane was added with rigorous stirring a precipitate appeared. The white solid was collected by filtration (53 mg; 77 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 2H, CH), 7.64 (t, 2H, $^3J_{HH}$ = 8.0 Hz, CH_{Dipp}), 7.41 (d, 4H, $^3J_{HH}$ = 8.0 Hz, CH_{Dipp}), 4.24 (br, 1H, SH), 2.34 (sept, 4H, $^3J_{HH}$ = 8.0 Hz, C<u>H</u>(CH_3)$_2$), 1.25 (d, 12H, $^3J_{HH}$ = 8.0 Hz, CH(C<u>H</u>$_3$)$_2$), 1.23 (d, 12H, $^3J_{HH}$ = 8.0 Hz, CH(C<u>H</u>$_3$)$_2$); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.6 (N-C_{Dipp}), 145.1 (s, CS), 133.1 (s, C_{Dipp}), 128.8 (s, C_{Dipp}), 126.3 (s, C_{Dipp}), 125.8 (s, CH), 29.3 (s, <u>C</u>H(CH_3)$_2$), 24.3 (s, CH(<u>C</u>H$_3$)$_2$), 23.3 (s, CH(<u>C</u>H$_3$)$_2$); ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.1; elemental analysis for $C_{28}H_{37}F_3N_2O_3S_2$: calcd.: C 49.5, H 5.6, N 3.8, found: C 47.8, H 4.8, N 4.8; DART HRMS: m/z calculated for $[C_{27}H_{37}N_2S]^+$ (M^+) 421.26774, found 421.26843.

^1H NMR ($CDCl_3$)



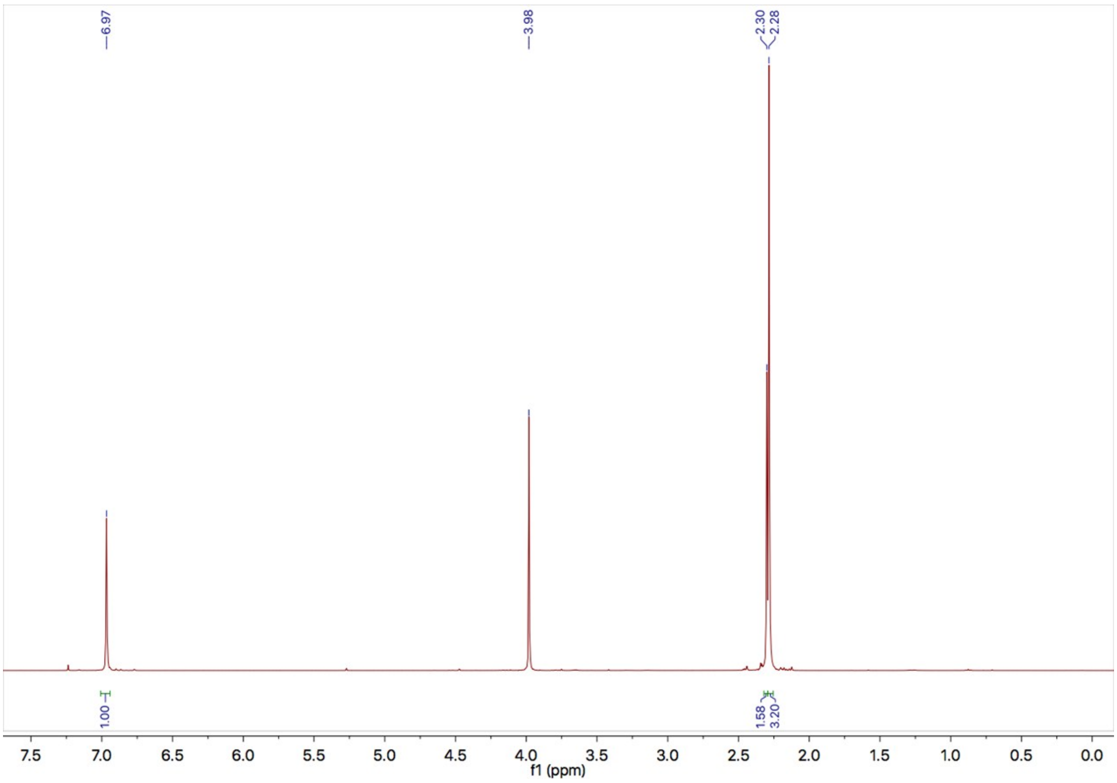


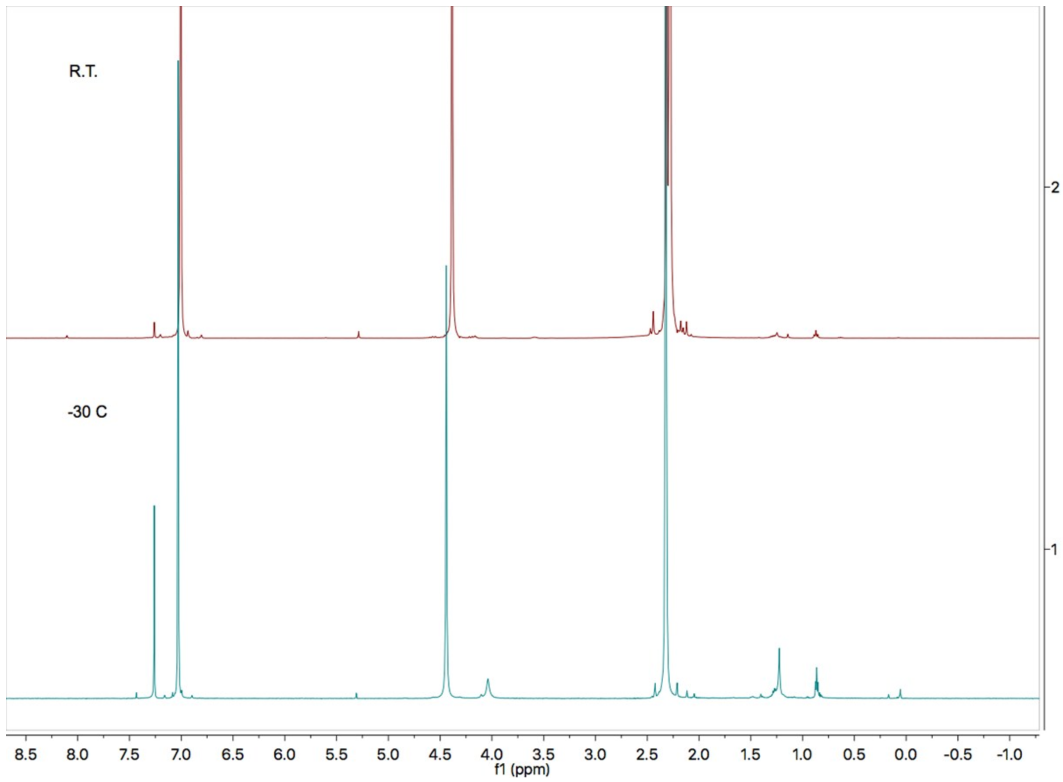
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$)



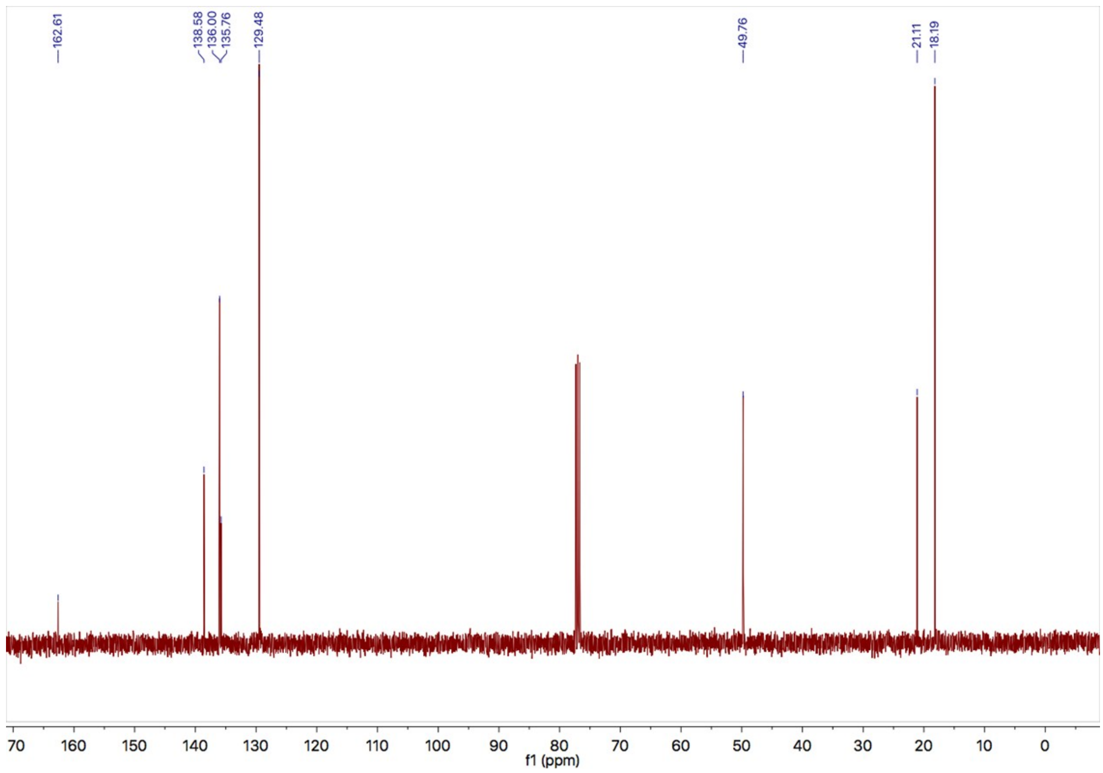
2c: **1b** (50 mg, 0.15 mmol) was dissolved in 3 mL of DCM and two drops of HOTf was added to the solution. After 5 minutes, 5 mL of pentane was added with rigorous stirring a precipitate appeared. The white solid was collected by filtration (59 mg; 81 %). Colourless crystals were grown by vapour diffusion of pentane into a saturated DCM solution. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 4 H, CH_{Mes}), 3.98 (s, 4 H, CH_2), 4.04 (br, 1H, SH), 2.30 (ov, s, 12 H, CH_3), 2.28 (ov, s, 6 H, CH_3); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 162.6 (s, CS), 138.6 (s, C_{Mes}), 136.0 (s, C_{Mes}), 135.8 (s, C_{Mes}), 129.5 (s, CH_{Mes}), 49.8 (s, CH_2), 21.1 (CH_3), 18.2 (CH_3); ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.8; elemental analysis for $C_{22}H_{27}F_3N_2O_3S_2$: calcd.: C 55.3, H 6.0, N 5.1, found: C 56.9, H 5.4, N 5.5; DART HRMS: m/z calculated for $[C_{21}H_{27}N_2S]^+$ (M^+) 339.18949, found 339.18906.

^{1}H NMR ($CDCl_3$)



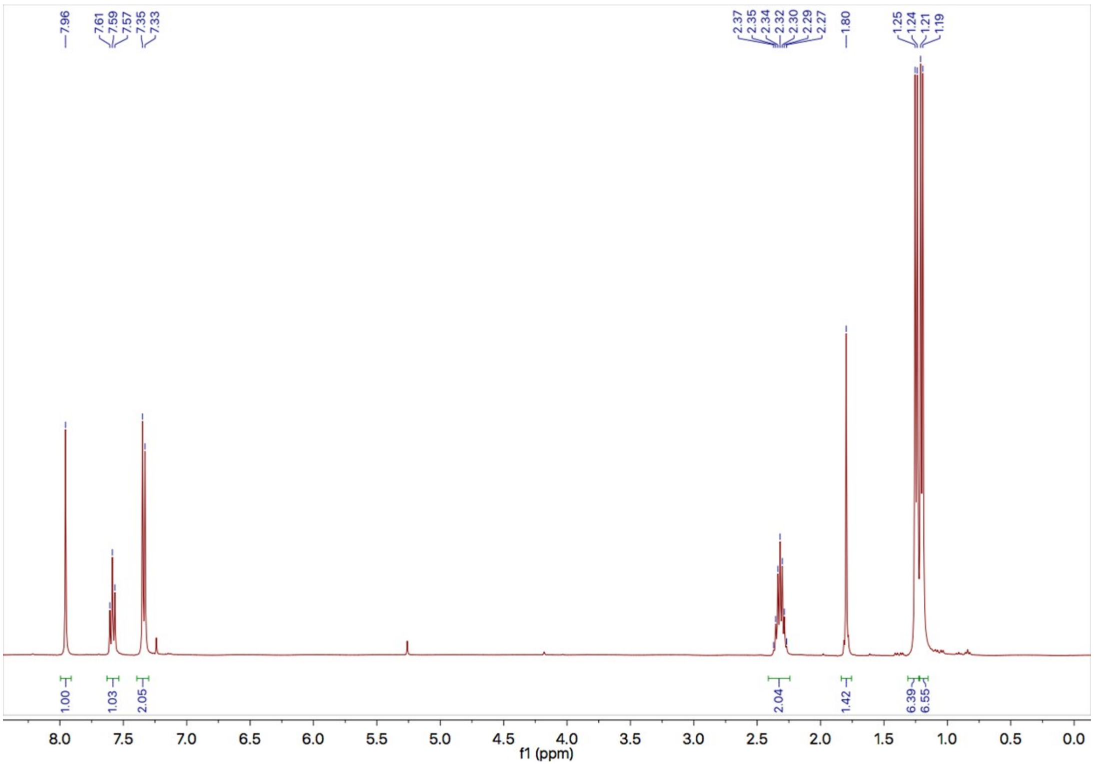


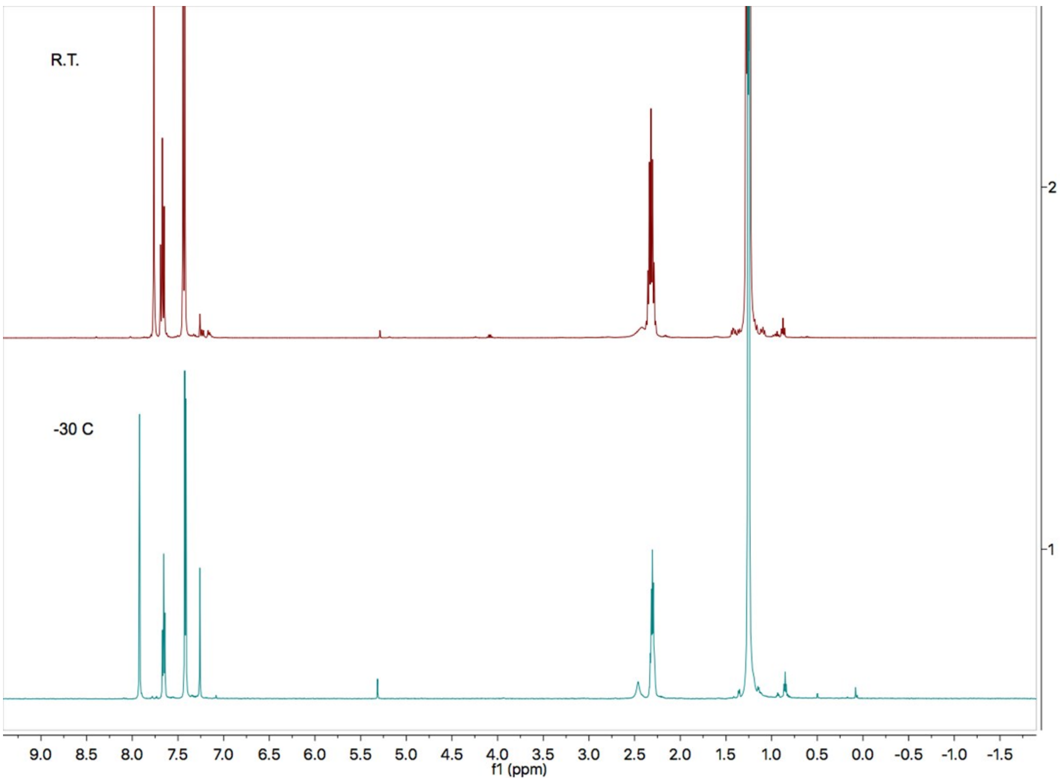
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$)



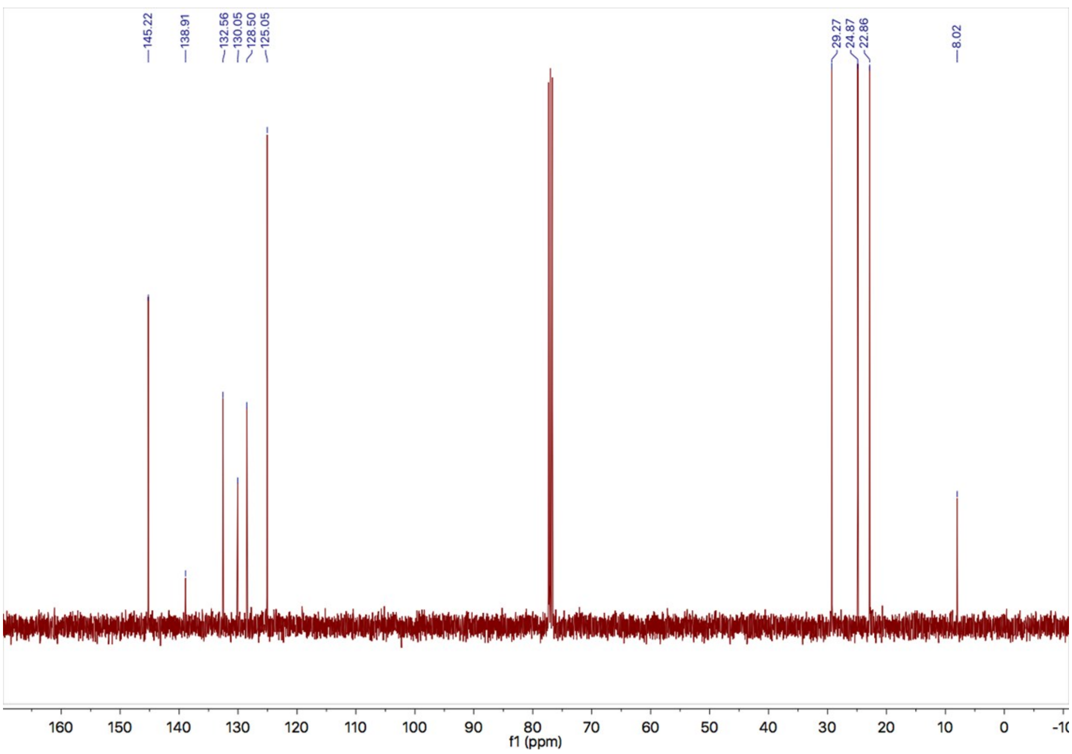
2d: **1c** (50 mg, 0.11 mmol) was dissolved in 3 mL of DCM and two drops of MeOTf was added to the solution. After 5 minutes, 5 mL of pentane was added with rigorous stirring a precipitate appeared. The white solid was collected by filtration (54 mg; 80 %). Colourless crystals were grown by vapour diffusion of pentane into a saturated DCM solution. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H, CH), 7.59 (t, 2H, $^3J_{HH}$ = 8.0 Hz, CH_{Dipp}), 7.34 (d, 4H, $^3J_{HH}$ = 8.0 Hz, CH_{Dipp}), 2.46 (br, 1H, SeH), 2.32 (sept, 4H, $^3J_{HH}$ = 8.0 Hz, $C\underline{H}(CH_3)_2$), 1.80 (s, 3H, CH_3), 1.24 (d, 12H, $^3J_{HH}$ = 8.0 Hz, $CH(C\underline{H}_3)_2$), 1.19 (d, 12H, $^3J_{HH}$ = 8.0 Hz, $CH(C\underline{H}_3)_2$); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.2 (NC_{Dipp}), 138.9 (s, CSe), 132.6 (s, C_{Dipp}), 130.0 (s, C_{Dipp}), 128.5 (s, C_{Dipp}), 125.0 (s, CH), 29.3 (s, $\underline{C}H(CH_3)_2$), 24.9 (s, $CH(\underline{C}H_3)_2$), 22.9 (s, $CH(\underline{C}H_3)_2$), 8.0 (s, $SeCH_3$); ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.3; ^{77}Se NMR (114 MHz, CD_2Cl_2) δ 222.7 (q J_{SeH} = 13.7 Hz); elemental analysis for $C_{29}H_{39}F_3N_2O_3SSe$: calcd.: C 54.6, H 6.2, N 4.4, found: C 54.7, H 6.1, N 4.3; DART HRMS: m/z calculated for $[C_{28}H_{39}N_2Se]^+$ (M^+) 483.22730, found 483.22799.

^{1}H NMR ($CDCl_3$)

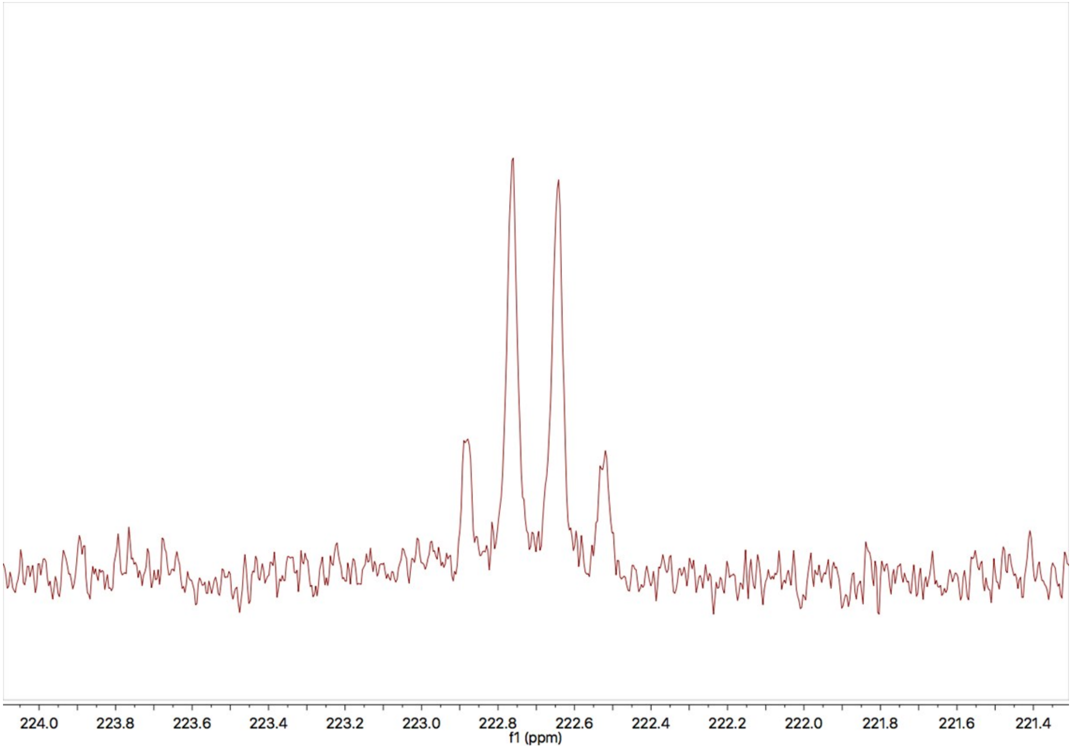




$^{13}C\{^{1}H\}$ NMR ($CDCl_3$)

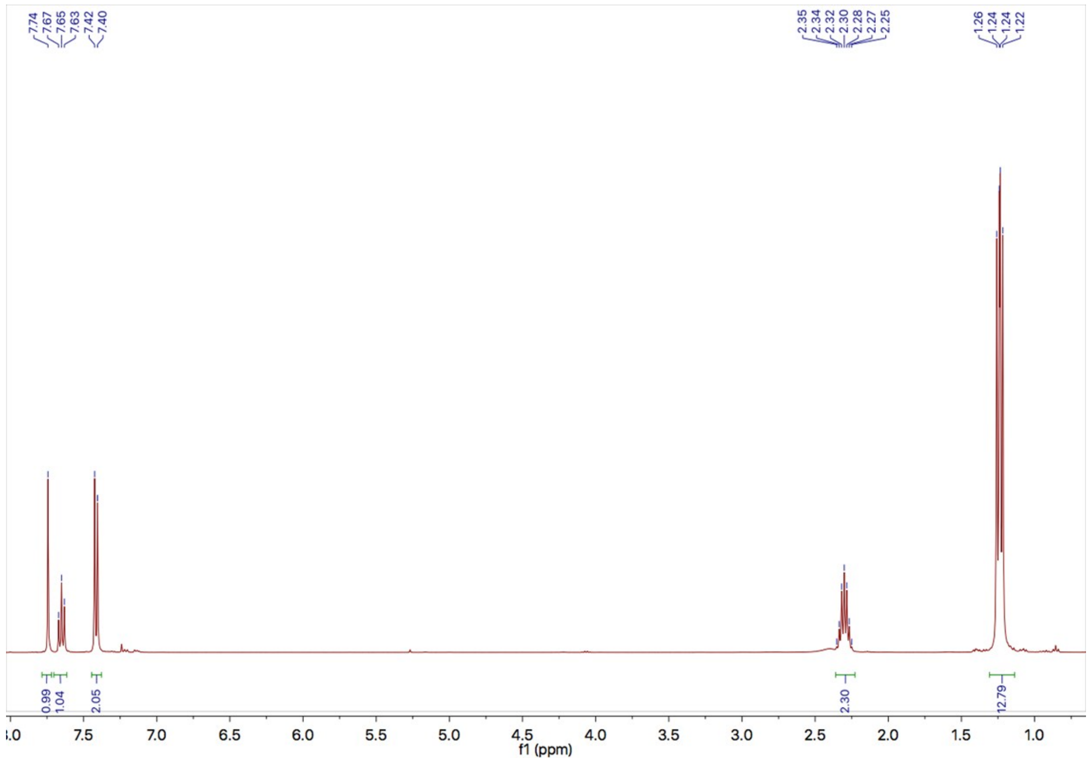


^{77}Se NMR (CD_2Cl_2)

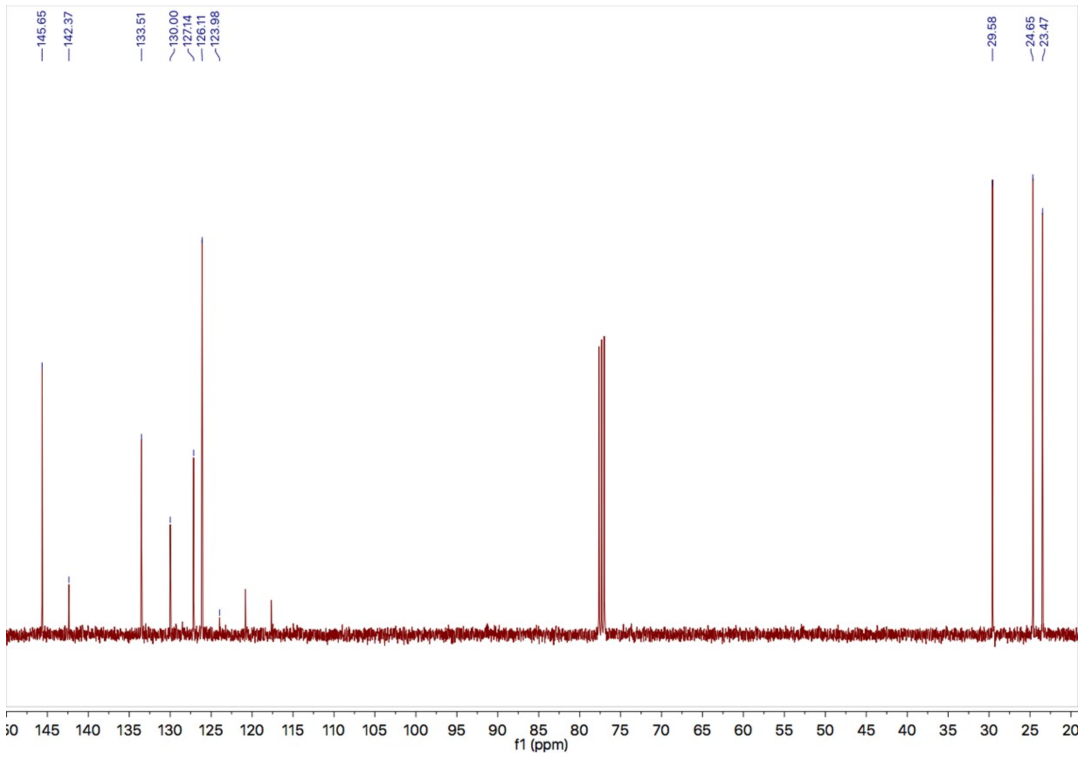


2e: **1c** (50 mg, 0.11 mmol) was dissolved in 3 mL of DCM and two drops of HOTf was added to the solution. After 5 minutes, 5 mL of pentane was added with rigorous stirring a precipitate appeared. The white solid was collected by filtration (54 mg; 82 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 2H, CH), 7.65 (t, 2H, $^{3}J_{HH}$ = 8.0 Hz, CH_{Dipp}), 7.41 (d, 4H, $^{3}J_{HH}$ = 8.0 Hz, CH_{Dipp}), 2.30 (sept, 4H, $^{3}J_{HH}$ = 8.0 Hz, C$\underline{H}$(CH_3)$_2$), 1.25 (d, 12H, $^{3}J_{HH}$ = 8.0 Hz, CH(C$\underline{H}_3$)$_2$), 1.23 (d, 12H, $^{3}J_{HH}$ = 8.0 Hz, CH(C$\underline{H}_3$)$_2$); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.3 (NC_{Dipp}), 142.0 (s, CSe), 133.2 (s, C_{Dipp}), 129.7 (s, C_{Dipp}), 126.8 (s, C_{Dipp}), 125.8 (s, CH), 29.3 (s, $\underline{C}$H(CH_3)$_2$), 24.3 (s, CH($\underline{C}H_3$)$_2$), 23.2 (s, CH($\underline{C}H_3$)$_2$); ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.8; ^{77}Se NMR (114 MHz, (CD_2Cl_2)) δ 135.3 (d, J_{SeH} = 75.2 Hz); elemental analysis for $C_{28}H_{37}F_3N_2O_3SSe$: calcd.: C 48.7, H 5.5, N 3.9, found: C 46.8, H 4.9, N 3.6; DART HRMS: m/z calculated for $[C_{27}H_{37}N_2Se]^+$ (M^+) 469.21220, found 469.21282.

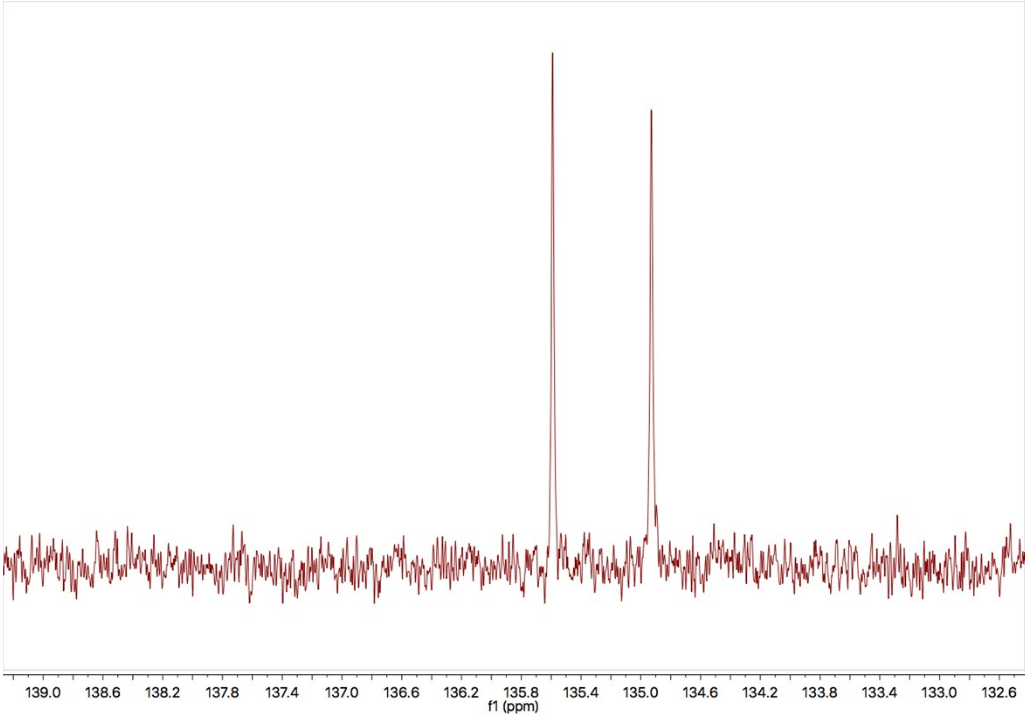
^{1}H NMR ($CDCl_3$)



$^{13}C\{^1H\}$ NMR ($CDCl_3$)

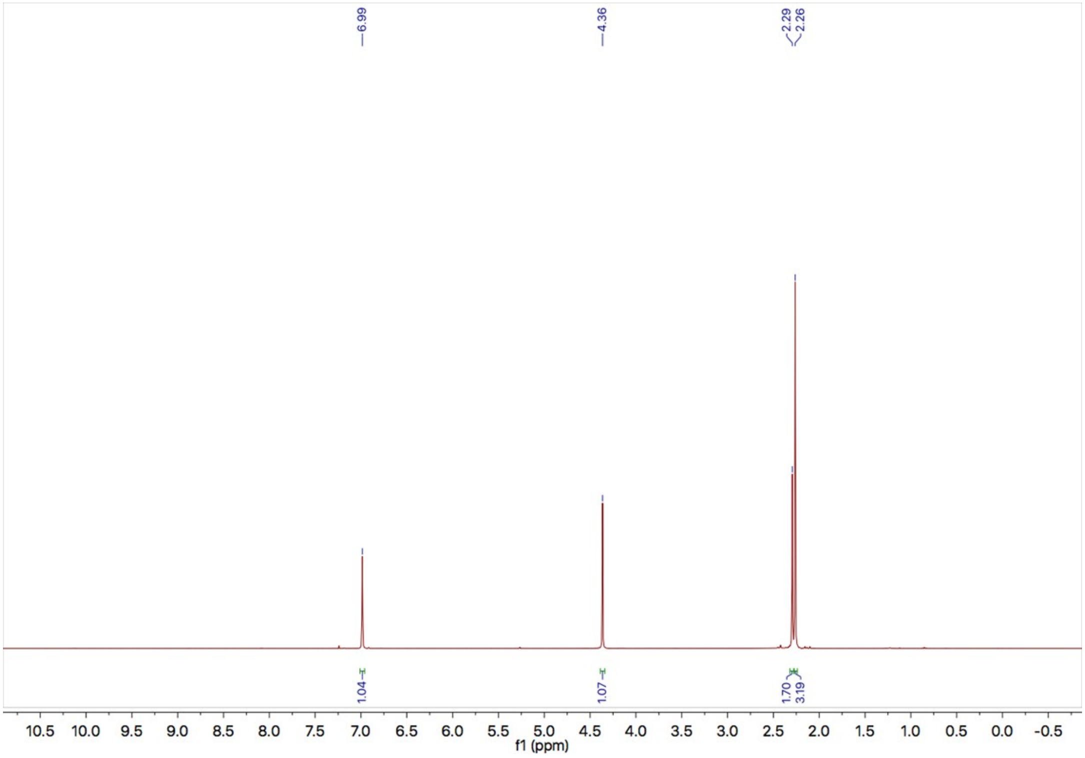


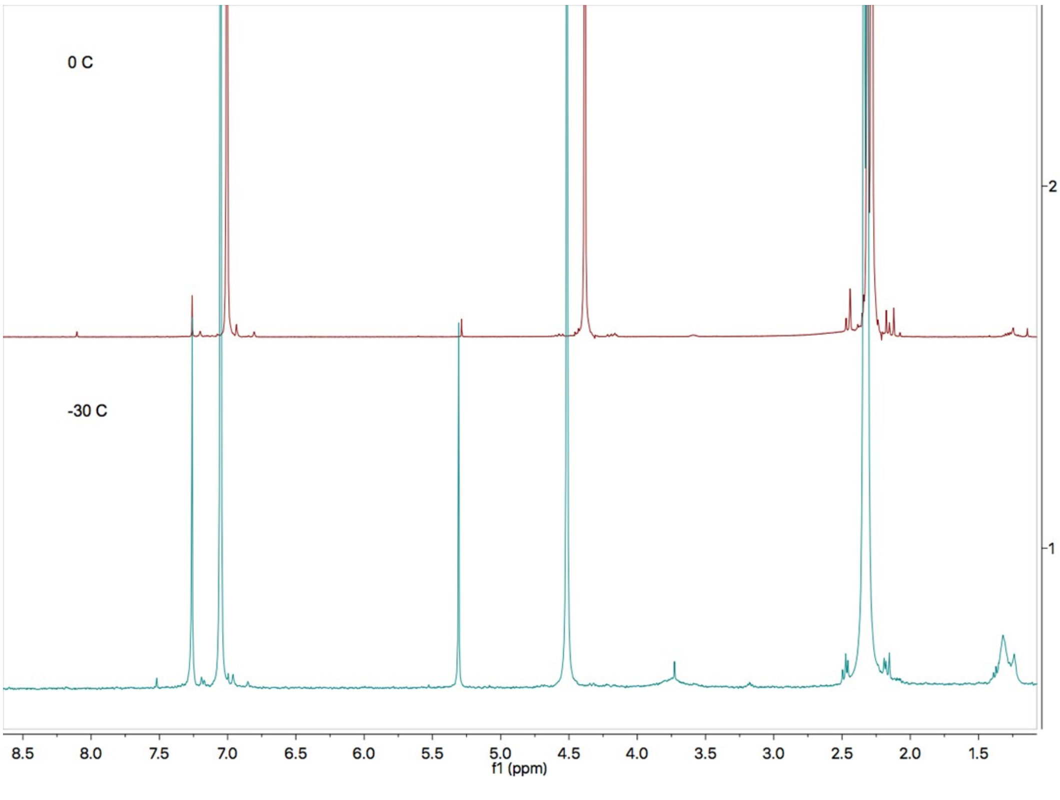
^{77}Se NMR (CD_2Cl_2)



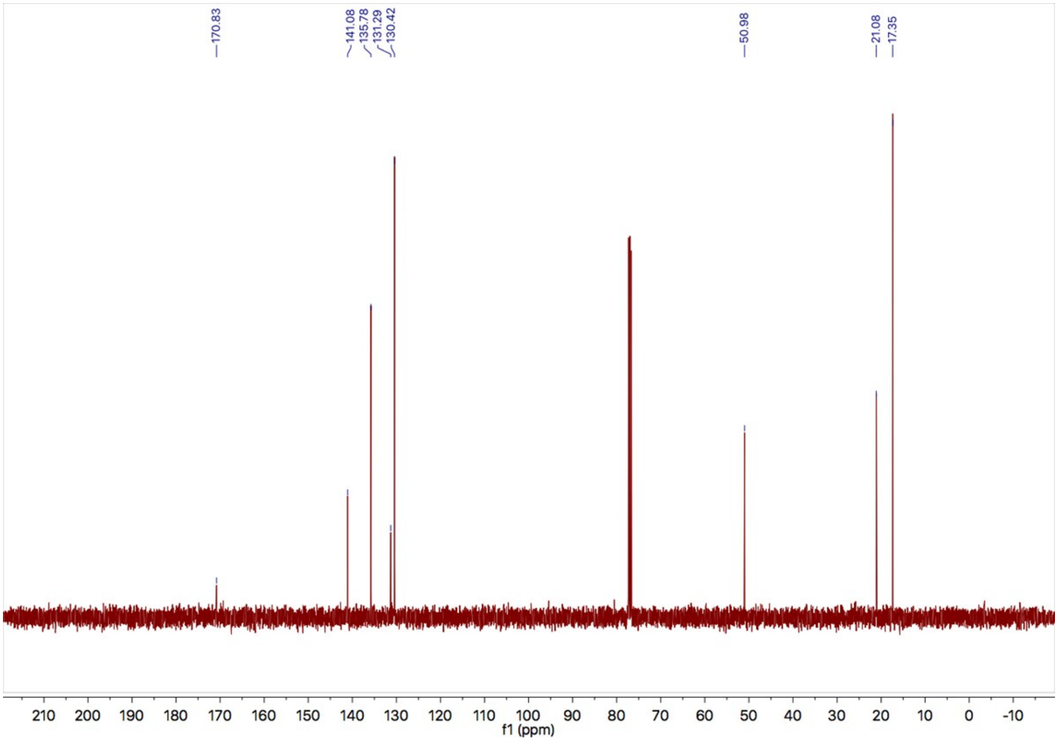
2f: **1d** (50 mg, 0.13 mmol) was dissolved in 3 mL of DCM and two drops of HOTf was added to the solution. After 5 minutes, 5 mL of pentane was added with rigorous stirring a precipitate appeared. The white solid was collected by filtration (63 mg; 90 %). Colourless crystals were grown by vapour diffusion of pentane into a saturated DCM solution. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 4 H, CH_{Mes}), 4.36 (s, 4 H, CH_2), 3.59 (br, 1H, SeH), 2.29 (s, 6 H, CH_3), 2.26 (s, 12 H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.8 (s, CSe), 141.1 (s, C_{Mes}), 135.8 (s, C_{Mes}), 131.3 (s, C_{Mes}), 130.4 (s, CH_{Mes}), 51.0 (s, CH_2), 21.1 (CH_3), 17.4 (CH_3); ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.8; ^{77}Se NMR (114 MHz, CD_2Cl_2) δ 133.4 (d, J_{SeH} = 65.0 Hz); elemental analysis for $C_{22}H_{27}F_3N_2O_3SSe$: calcd.: C 41.9, H 4.5, N 4.1, found: C 41.8, H 4.3, N 4.0; DART HRMS: m/z calculated for $[C_{21}H_{27}N_2Se]^+$ (M^+) 387.13395, found 387.13410.

^{1}H NMR ($CDCl_3$)

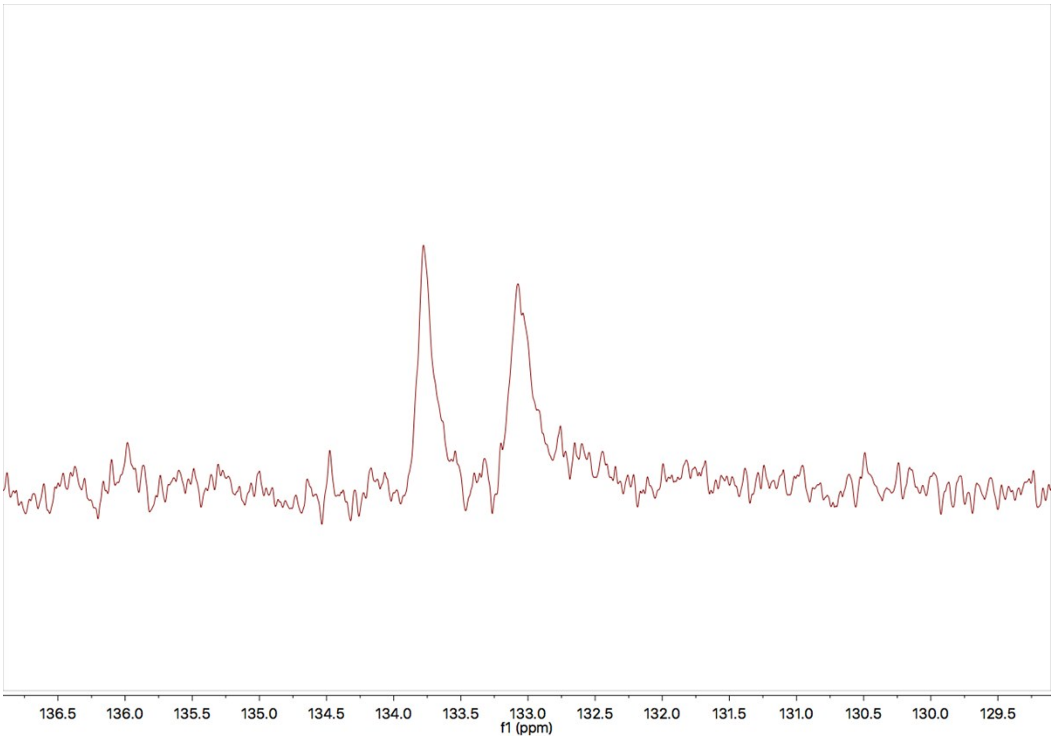




$^{13}C\{^1H\}$ NMR ($CDCl_3$)



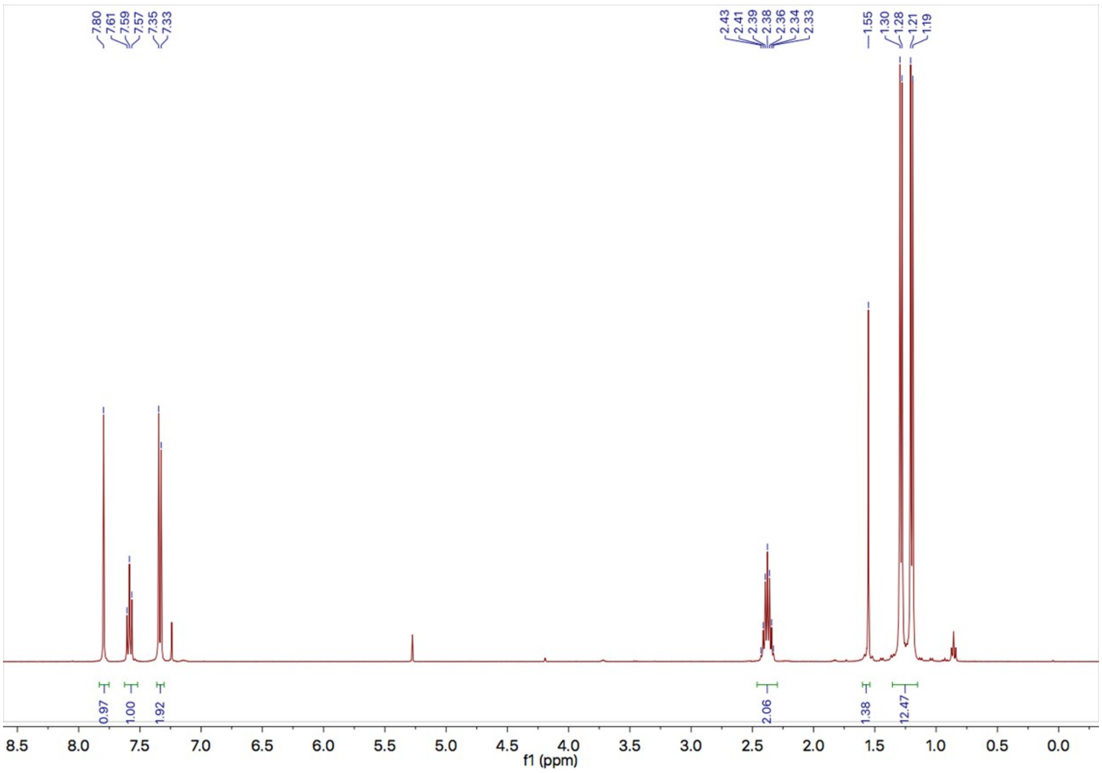
^{77}Se NMR (CD_2Cl_2)



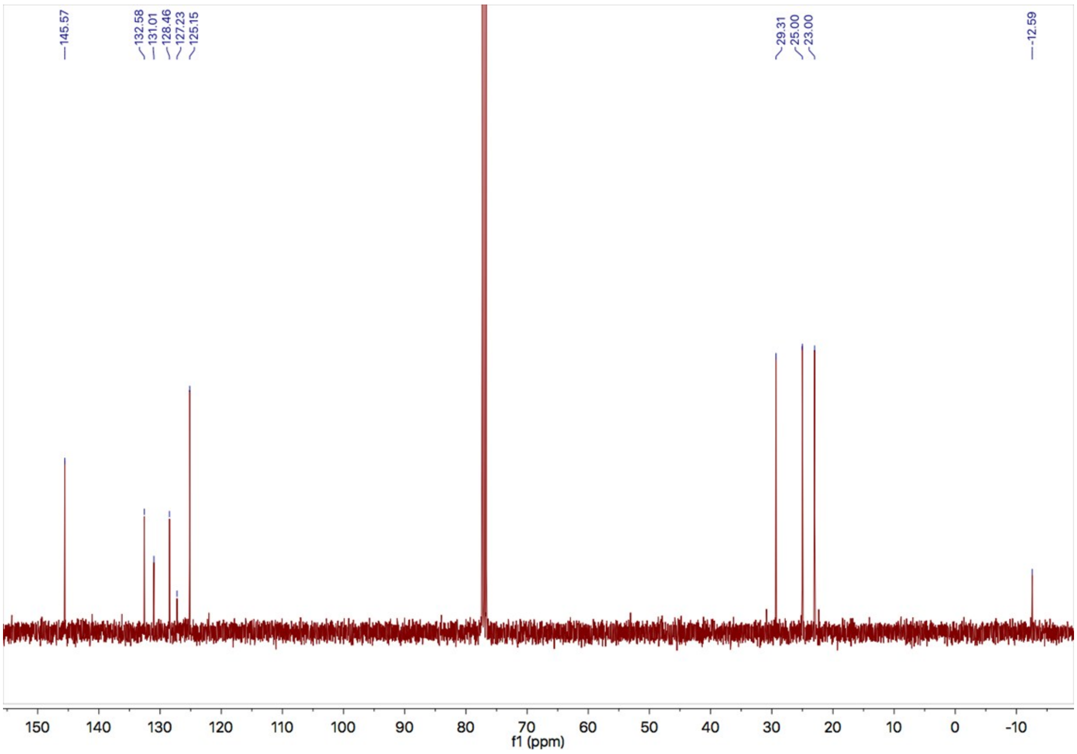
2g: **1e** (50 mg, 0.097 mmol) was dissolved in 3 mL of DCM and two drops of MeOTf was added to the solution. After 5 minutes, 5 mL of pentane was added with rigorous stirring a precipitate appeared. The white solid was collected by filtration (47 mg; 72 %). Colourless crystals were grown by vapour diffusion of pentane into a saturated DCM solution. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 2H, CH), 7.59 (t, 2H, $^{3}J_{HH}$ = 8.0 Hz, CH_{Dipp}), 7.34 (d, 4H, $^{3}J_{HH}$ = 8.0 Hz, CH_{Dipp}), 2.38 (sept, 4H, $^{3}J_{HH}$ =

8.0 Hz, C$\underline{H}$(CH_3)$_2$), 1.55 (s, 3H, CH_3), 1.29 (d, 12H, $^3J_{HH}$ = 8.0 Hz, CH(C$\underline{H}_3$)$_2$), 1.20 (d, 12H, $^3J_{HH}$ = 8.0 Hz, CH(C$\underline{H}_3$)$_2$); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.6 (N-C_{Dipp}), 132.6 (s, C_{Dipp}), 131.0 (s, C_{Dipp}), 128.5 (s, C_{Dipp}), 127.2 (s, CTe), 125.1 (s, CH), 29.3 (s, $\underline{C}$H(CH_3)$_2$), 25.0 (s, CH($\underline{C}H_3$)$_2$), 23.0 (s, CH($\underline{C}H_3$)$_2$), -12.6 ($TeCH_3$); ^{19}F NMR (377 MHz, $CDCl_3$) δ -78.2; ^{125}Te NMR (189 MHz, $CDCl_3$) δ 478.0 (q J_{TeH} = 22.7 Hz); elemental analysis for $C_{29}H_{39}F_3N_2O_3STe$: calcd.: C 51.2, H 5.8, N 4.1, found: C 50.5, H 5.8, N 4.1; DART HRMS: m/z calculated for $[C_{28}H_{39}N_2Te]^+$ (M^+) 533.21755, found 533.21683.

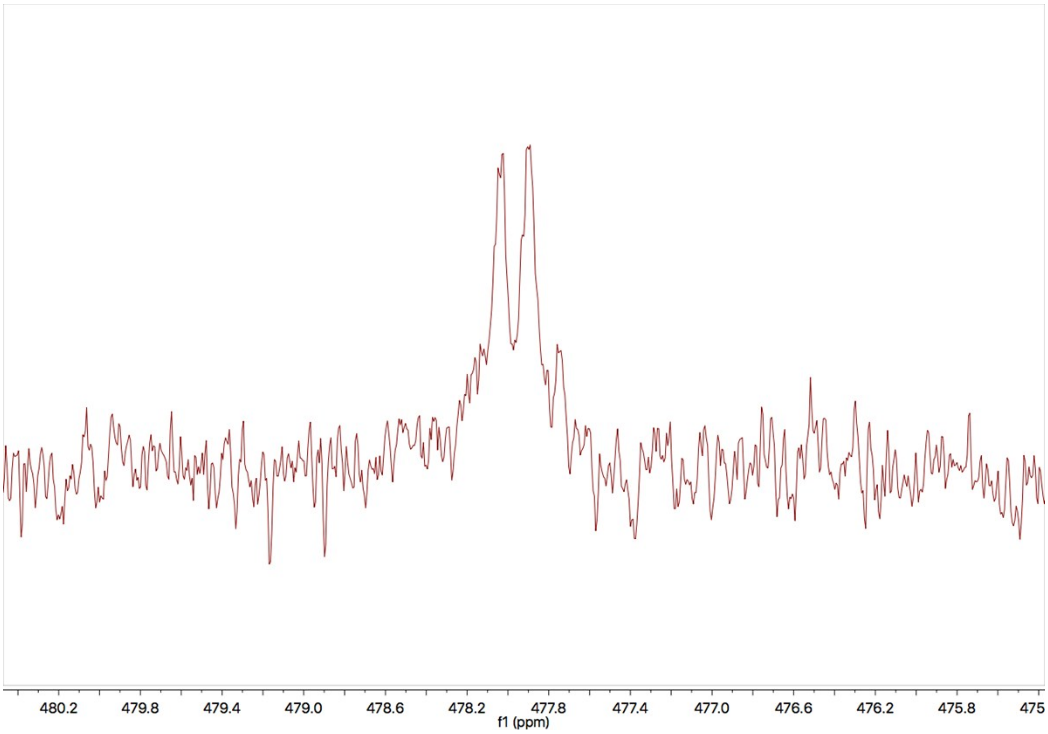
^1H NMR ($CDCl_3$)



$^{13}C\{^1H\}$ NMR ($CDCl_3$)

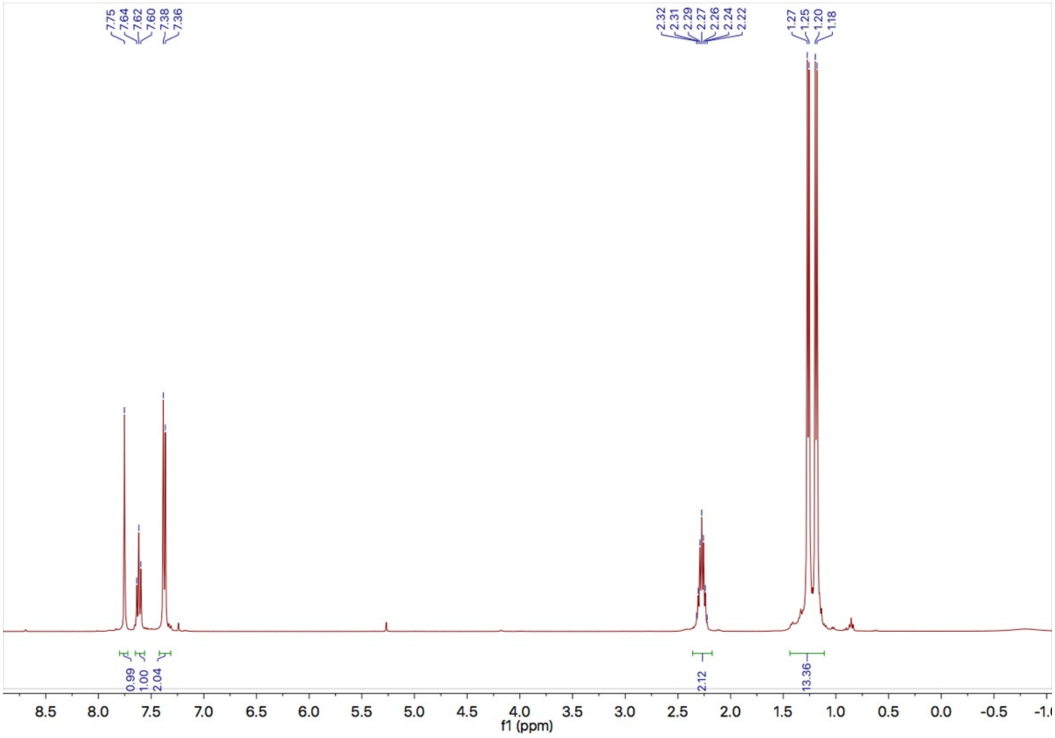


^{125}Te NMR ($CDCl_3$)

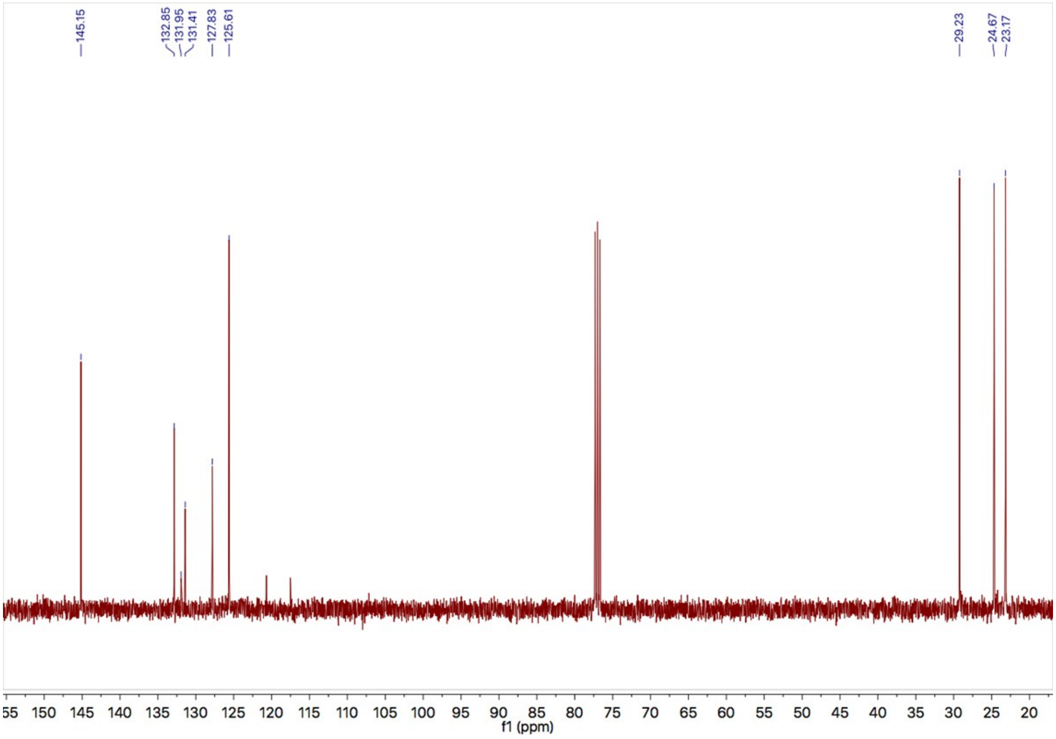


2h: **1e** (50 mg, 0.097 mmol) was dissolved in 3 mL of DCM at -25 ^{o}C and two drops of HOTf was added to the solution. After 2 minutes, 5 mL of cold pentane was added with rigorous stirring a precipitate appeared. The white solid was collected by filtration (40 mg; 62 %). This compound decomposes at -25 ^{o}C in solid state or solution. NMR data were collected at -40 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 2H, CH), 7.62 (t, 2H, $^{3}J_{HH}$ = 8.0 Hz, CH_{Dipp}), 7.37 (d, 4H, $^{3}J_{HH}$ = 8.0 Hz, CH_{Dipp}), 2.27 (sept, 4H, $^3J_{HH}$ = 8.0 Hz, C$\underline{H}$(CH_3)$_2$), 1.26 (d, 12H, $^3J_{HH}$ = 8.0 Hz, CH(C$\underline{H}_3$)$_2$), 1.19 (d, 12H, $^3J_{HH}$ = 8.0 Hz, CH(C$\underline{H}_3$)$_2$); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 132.9 (N-C$_{Dipp}$), 130.6 (s, C$_{Dipp}$), 130.1 (s, CTe), 127.4 (s, C$_{Dipp}$), 125.6 (s, C$_{Dipp}$), 125.1 (s, CH), 29.0 (s, $\underline{C}$H(CH_3)$_2$), 24.5 (s, CH($\underline{C}H_3$)$_2$), 23.2 (s, CH($\underline{C}H_3$)$_2$); ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.9; ^{125}Te NMR (189 MHz, CD_2Cl_2) δ 234.1 (br); DART HRMS: m/z calculated for $[C_{27}H_{37}N_2Te]^+$ (M^+) 519.20190, found 519.20165.

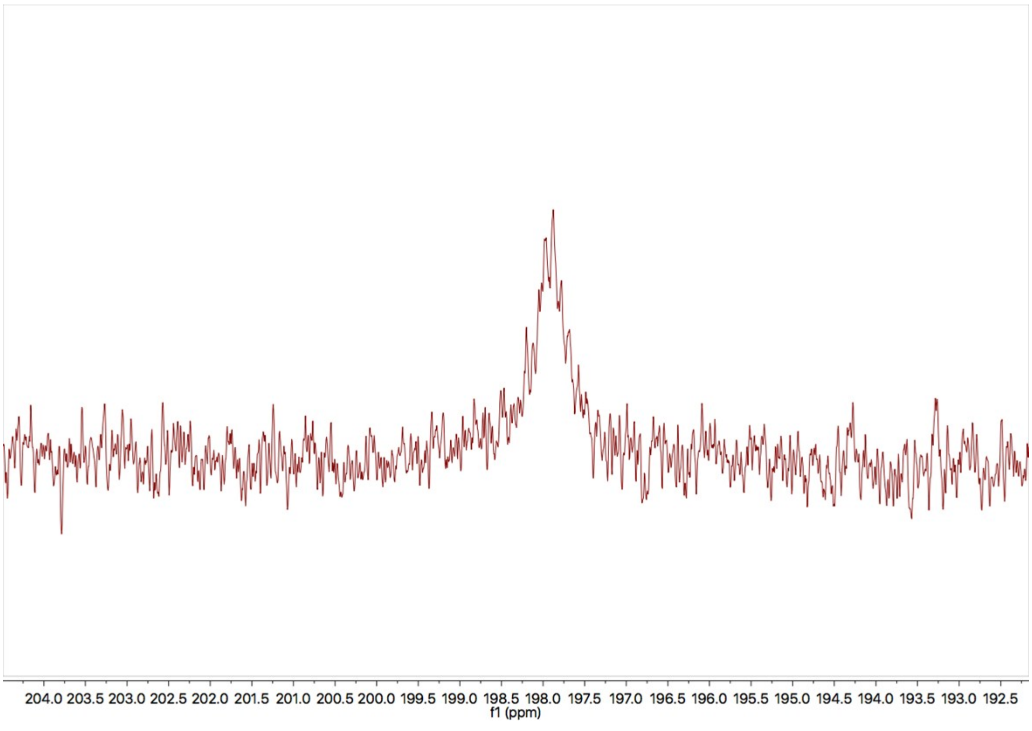
^{1}H NMR ($CDCl_3$)



^{13}C{^{1}H} NMR ($CDCl_3$)



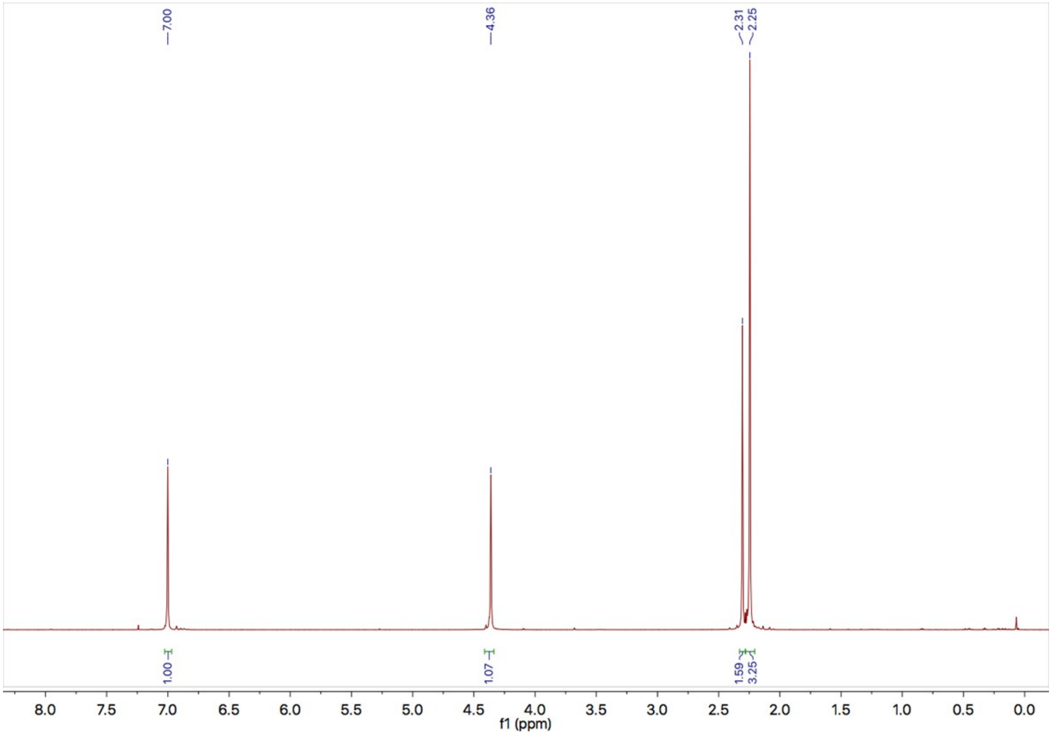
^{125}Te NMR (CD_2Cl_2)



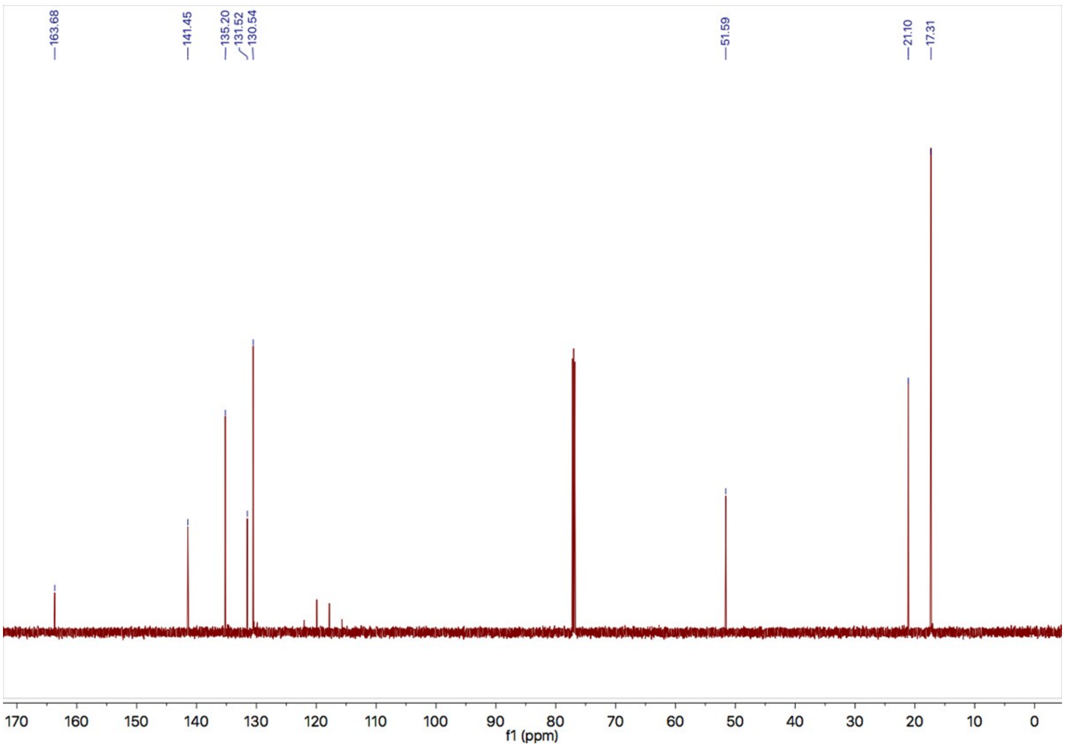
2i: **1f** (50 mg, 0.12 mmol) was dissolved in 3 mL of DCM at -25 ^oC and two drops of HOTf was added to the solution. After 2 minutes, 5 mL of cold pentane was added with rigorous stirring a precipitate appeared. The white solid was collected by filtration (34 mg; 50 %). This compound decomposes at -25 ^oC in solid state or solution. NMR data were collected at -20 ^oC. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.00 (s, 4 H, CH_{Mes}), 4.36 (s, 4 H, CH_2), 2.30 (s, 6 H, CH_3), 2.24 (s, 12 H, CH_3); $^{13}C\{^1H\}$ NMR (101

MHz, CD_2Cl_2) δ 163.7 (s, CTe), 141.5 (s, C_{Mes}), 135.2 (s, C_{Mes}), 131.5 (s, C_{Mes}), 130.5 (s, CH_{Mes}), 51.6 (s, CH_2), 21.1 (CH_3), 17.3 (CH_3); ^{19}F NMR (377 MHz, CD_2Cl_2) δ -78.1; ^{125}Te NMR (189 MHz, CD_2Cl_2) δ 197.8 (br); DART HRMS: m/z calculated for $[C_{21}H_{27}N_2Te]^+$ (M^+) 437.12365, found 437.12350.

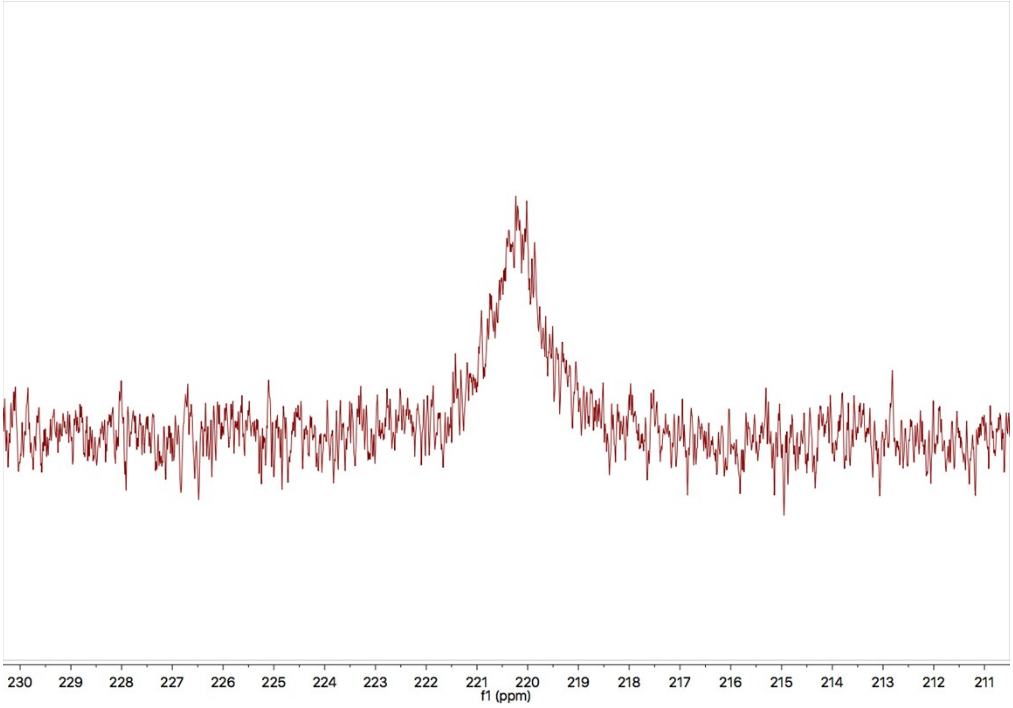
^1H NMR (CD_2Cl_2)



$^{13}C\{^1H\}$ NMR (CD_2Cl_2)



^{125}Te NMR (CD_2Cl_2)



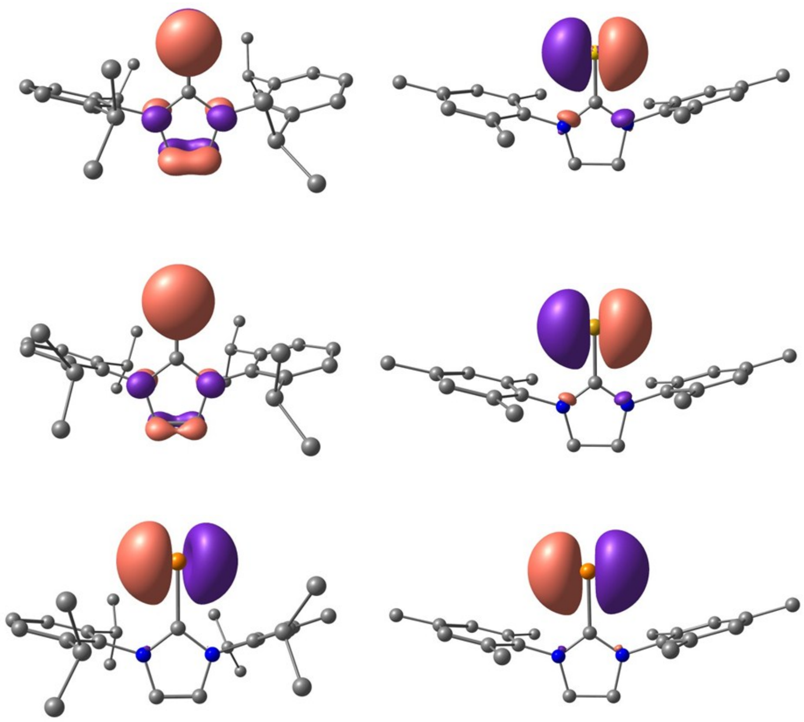
3. Computational details and the HOMOs of compounds **1**:

Calculations were carried out with the Gaussian 09 package.[S2] Geometry optimizations were performed with the M06-2X functional because this method was recently established as an excellent functional for describing main group systems.[S3] The 6-311G(d) basis set was used for C, H and N atoms. The SDD basis set was applied for S, Se and Te. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum) and provide frontier molecular orbitals (HOMO). Natural bond orbital (NBO) calculations were carried out using NBO 5.9 program[S4] at the same level of theory.

X = S

X = Se

X = Te



HOMOs of compounds **1**

Cartesian coordinates:

1a:

6	-0.005327	-0.128994	-0.166873
7	1.067569	-0.156984	0.678994
7	-1.096398	-0.093494	0.656796
6	0.646885	-0.141968	2.001370
6	-0.699726	-0.091492	1.987820
6	-2.451706	0.077070	0.219203
6	-3.307098	-1.032210	0.239508
6	-2.859241	1.351562	-0.186186
6	-4.626548	-0.829123	-0.158863
6	-4.188871	1.501852	-0.580405
6	-5.062678	0.425765	-0.565862
1	-5.323306	-1.658892	-0.156157
1	-4.542525	2.475720	-0.901930
1	-6.092857	0.562985	-0.875493
6	2.438153	-0.119444	0.260821
6	3.096384	1.117375	0.270547
6	3.052997	-1.310387	-0.133307
6	4.435110	1.131555	-0.115868
6	4.394458	-1.244575	-0.509774
6	5.078570	-0.038380	-0.498659
1	4.981353	2.067680	-0.126758
1	4.906445	-2.149465	-0.820331
1	6.120734	-0.006461	-0.797357
6	2.365893	2.406083	0.609265
6	2.312665	-2.634353	-0.161484
6	-1.925169	2.548720	-0.190836
1	-0.920750	2.212273	0.078201
6	-2.792384	-2.411877	0.613055
1	1.487971	2.156589	1.212061
1	1.268273	-2.450596	0.102242
1	-1.992768	-2.288713	1.349563
1	-1.421564	-0.058762	2.786192
1	1.353285	-0.163790	2.813773
6	1.866889	3.076353	-0.678474
1	1.285246	3.971790	-0.438926
1	2.714052	3.378795	-1.301000
1	1.244213	2.399606	-1.268349
6	3.218183	3.376334	1.430172
1	3.635467	2.897056	2.318582
1	4.046277	3.782839	0.844617
1	2.609115	4.223617	1.753261
6	2.324687	-3.241157	-1.567584
1	3.338897	-3.508457	-1.877122

1	1.720063	-4.151404	-1.589205
1	1.912189	-2.535849	-2.289998
6	2.895193	-3.605486	0.871043
1	3.938798	-3.841355	0.645297
1	2.858416	-3.184670	1.878813
1	2.333938	-4.543108	0.871899
6	-3.862355	-3.302413	1.246638
1	-4.371140	-2.802054	2.073913
1	-4.617361	-3.606906	0.517536
1	-3.403803	-4.215997	1.630946
6	-2.186581	-3.092726	-0.622246
1	-1.768574	-4.066901	-0.353371
1	-2.959681	-3.251619	-1.379518
1	-1.401250	-2.485651	-1.077470
6	-1.831338	3.173525	-1.585580
1	-2.794016	3.580130	-1.907543
1	-1.109815	3.994502	-1.582623
1	-1.503670	2.429942	-2.313388
6	-2.362455	3.580061	0.855122
1	-1.661979	4.418956	0.878374
1	-3.354056	3.980053	0.626064
1	-2.402644	3.141073	1.855078
16	0.018830	-0.137476	-1.864112

1b:

6	0.034123	0.072343	0.098194
7	-1.060826	0.323594	0.865900
7	1.126174	0.118786	0.905179
6	-0.729288	0.386215	2.288056
6	0.794797	0.554562	2.259089
6	2.480423	0.021911	0.466979
6	3.124005	1.143609	-0.055609
6	3.129120	-1.208348	0.594757
6	4.464283	1.020736	-0.415932
6	4.466891	-1.288607	0.224585
6	5.152234	-0.180860	-0.272727
1	4.978452	1.883501	-0.830127
1	4.984436	-2.240251	0.312233
6	-2.414353	0.173804	0.439342
6	-2.975185	-1.103244	0.337415
6	-3.152411	1.325004	0.167759
6	-4.317156	-1.200312	-0.014016
6	-4.493672	1.183175	-0.181205
6	-5.092405	-0.069687	-0.269317
1	-4.769220	-2.184978	-0.102388
1	-5.078724	2.071607	-0.401667
6	-2.130513	-2.332422	0.535670
6	-2.482214	2.671873	0.203506
6	2.359860	-2.414427	1.061462
1	1.529088	-2.610864	0.377805
6	2.362191	2.420690	-0.283926
1	-1.504030	-2.266940	1.428797
1	-1.655301	2.696397	-0.511153
1	1.614290	2.265669	-1.066669
1	1.096538	1.597065	2.410299
1	-1.032408	-0.539501	2.790726
1	-1.241908	1.220158	2.770137
1	1.306705	-0.061040	3.000676
1	1.933677	-2.267395	2.057754
1	2.998007	-3.297881	1.093287
1	-2.752287	-3.224083	0.621131
1	-1.459429	-2.455076	-0.319028
1	3.029556	3.225020	-0.594127
1	1.830911	2.748819	0.612942
1	-3.184486	3.465745	-0.051954
1	-2.065302	2.893742	1.189720
6	-6.542402	-0.216809	-0.652043
1	-7.096605	-0.765762	0.113044
1	-7.020574	0.754709	-0.782360
1	-6.643748	-0.769255	-1.589417
6	6.609579	-0.289470	-0.639334
1	6.923168	0.539529	-1.275023
1	7.236751	-0.277872	0.256465
1	6.814860	-1.220818	-1.170664
16	0.038916	-0.237029	-1.558460

1c:

6	0.002166	-0.185063	-0.077819
7	1.074310	-0.252819	0.763632
7	-1.081125	-0.089612	0.743738
6	0.657562	-0.220211	2.086209
6	-0.687394	-0.125372	2.074118
6	-2.443449	0.050221	0.312952
6	-3.258894	-1.081893	0.305252
6	-2.887770	1.324299	-0.069903
6	-4.594495	-0.906469	-0.062088
6	-4.226650	1.446870	-0.428640
6	-5.074377	0.344105	-0.415304

1	-5.258909	-1.763797	-0.085769
1	-4.614084	2.410250	-0.737677
1	-6.113813	0.462329	-0.700813
6	2.436197	-0.070275	0.348326
6	2.929173	1.237700	0.314371
6	3.192424	-1.189236	-0.011233
6	4.260802	1.406370	-0.064821
6	4.518002	-0.970603	-0.377841
6	5.047956	0.313995	-0.398654
1	4.680789	2.405709	-0.113210
1	5.141557	-1.809040	-0.665581
1	6.080681	0.464867	-0.693103
6	2.054084	2.443277	0.614893
6	2.583417	-2.578313	0.017245
6	-1.938208	2.511129	-0.091017
1	-0.955801	2.136138	-0.387911
6	-2.719474	-2.469217	0.600009
1	1.082399	2.093224	0.974000
1	1.509374	-2.467636	-0.155450
1	-1.697079	-2.372784	0.974740
1	-1.410004	-0.084028	2.871593
1	1.364502	-0.254323	2.897757
6	1.798898	3.251996	-0.662415
1	1.117447	4.082480	-0.453996
1	2.730322	3.672286	-1.052189
1	1.356720	2.624814	-1.439390
6	2.653199	3.320812	1.717468
1	2.837154	2.747153	2.628915
1	3.601565	3.765126	1.404421
1	1.971438	4.139358	1.961159
6	3.123834	-3.482371	-1.090417
1	4.170434	-3.751233	-0.924367
1	2.552064	-4.412347	-1.119771
1	3.037993	-2.999819	-2.065729
6	2.790580	-3.219812	1.394779
1	3.857339	-3.323666	1.612888
1	2.342124	-2.619103	2.189852
1	2.339019	-4.214533	1.429164
6	-3.540193	-3.191010	1.671922
1	-3.590682	-2.610143	2.595931
1	-4.563684	-3.376200	1.336587
1	-3.091173	-4.160044	1.902006
6	-2.654680	-3.283406	-0.698001
1	-2.218248	-4.267907	-0.510273
1	-3.655132	-3.431169	-1.114696
1	-2.046646	-2.769141	-1.444682
6	-2.326065	3.564017	-1.128354
1	-3.236393	4.101696	-0.849109
1	-1.527587	4.304300	-1.215941
1	-2.475190	3.111788	-2.110890
6	-1.812798	3.147598	1.298855
1	-1.105150	3.981569	1.271280
1	-2.778630	3.535310	1.635249
1	-1.456636	2.433986	2.045130
34	0.022545	-0.227155	-1.927090

1d:

6	0.030234	0.062686	0.099274
7	-1.063230	0.245140	0.873868
7	1.126626	0.170257	0.882602
6	-0.727131	0.377017	2.292023
6	0.798077	0.550674	2.256479
6	2.482318	0.062233	0.449728
6	3.151822	1.197648	-0.005473
6	3.104484	-1.185686	0.521267
6	4.490133	1.066086	-0.367702
6	4.441358	-1.273979	0.148999
6	5.151039	-0.156914	-0.289163
1	5.024899	1.938594	-0.732529
1	4.939352	-2.238992	0.190064
6	-2.420586	0.120835	0.450028
6	-3.017337	-1.142225	0.417891
6	-3.120225	1.278091	0.112859
6	-4.357978	-1.220685	0.058959
6	-4.462276	1.155318	-0.240356
6	-5.096225	-0.082927	-0.267312
1	-4.838534	-2.194777	0.020249
1	-5.020555	2.046913	-0.511493
6	-2.204530	-2.375881	0.703038
6	-2.409147	2.603706	0.083533
6	2.313388	-2.397296	0.933569
1	1.498821	-2.567900	0.223975
6	2.417740	2.502373	-0.156489
1	-1.703071	-2.323936	1.673072
1	-1.583546	2.567599	-0.632744
1	1.584941	2.381993	-0.854789
1	1.102444	1.584833	2.446812
1	-1.030647	-0.521829	2.838482

34	0.028158	-0.266073	-1.713908
1	-1.242991	1.232811	2.730979
1	1.317597	-0.094663	2.967203
1	1.863956	-2.273568	1.922956
1	2.943244	-3.286836	0.956583
1	-2.832863	-3.266812	0.697164
1	-1.430207	-2.493014	-0.060319
1	3.079778	3.278732	-0.540364
1	2.005599	2.853702	0.793277
1	-3.086787	3.405519	-0.210220
1	-1.984537	2.859971	1.058318
6	-6.543522	-0.208909	-0.666930
1	-7.108982	-0.778598	0.073950
1	-7.014465	0.769099	-0.772900
1	-6.637615	-0.730587	-1.622767
6	6.607054	-0.275097	-0.657748
1	6.924626	0.551583	-1.294568
1	7.235251	-0.265416	0.237463
1	6.806198	-1.208077	-1.188090

1e:

6	-0.007686	-0.142919	0.097429
7	1.071641	-0.022526	0.916120
7	-1.081302	-0.129801	0.936988
6	0.678092	0.055783	2.241710
6	-0.670086	-0.013364	2.254753
6	-2.451260	-0.019772	0.515535
6	-3.158190	-1.185364	0.203400
6	-3.001205	1.263091	0.431805
6	-4.484918	-1.036707	-0.192514
6	-4.331828	1.359011	0.023622
6	-5.065429	0.222506	-0.281110
1	-5.070277	-1.911853	-0.449359
1	-4.793921	2.335997	-0.069059
1	-6.097186	0.317239	-0.601116
6	2.434304	0.103523	0.481533
6	2.892211	1.375233	0.118707
6	3.236291	-1.039327	0.455515
6	4.236066	1.490805	-0.229058
6	4.574392	-0.871764	0.100481
6	5.071230	0.380779	-0.229001
1	4.633842	2.459304	-0.511634
1	5.231830	-1.734419	0.073259
1	6.114460	0.492109	-0.503065
6	1.978489	2.588082	0.103087
6	2.687736	-2.417215	0.775041
6	-2.193059	2.518809	0.714469
1	-1.250327	2.230204	1.186872
6	-2.508406	-2.550890	0.327624
1	0.944436	2.240330	0.165742
1	1.605077	-2.333017	0.904040
1	-1.432871	-2.421961	0.181084
1	-1.380796	0.027149	3.062849
1	1.399474	0.150715	3.035553
6	2.096863	3.368713	-1.207970
1	1.351322	4.167207	-1.236035
1	3.080004	3.833878	-1.318067
1	1.924153	2.710832	-2.061585
6	2.249204	3.486046	1.314889
1	2.107363	2.944566	2.253708
1	3.275780	3.862933	1.297934
1	1.574271	4.346232	1.313772
6	2.930195	-3.388282	-0.384467
1	3.997224	-3.572241	-0.535762
1	2.455602	-4.350043	-0.175096
1	2.513108	-2.993536	-1.312343
6	3.282642	-2.953572	2.081363
1	4.367818	-3.062286	2.000677
1	3.077031	-2.283732	2.919887
1	2.864633	-3.934829	2.318833
6	-2.740673	-3.115428	1.734944
1	-2.337044	-2.452954	2.504829
1	-3.810104	-3.240415	1.927220
1	-2.260409	-4.091214	1.843521
6	-2.987016	-3.532305	-0.741695
1	-2.390085	-4.445886	-0.698851
1	-4.031283	-3.820699	-0.594851
1	-2.878754	-3.103146	-1.739504
6	-1.846280	3.242881	-0.591851
1	-2.754091	3.562247	-1.111464
1	-1.246337	4.133394	-0.381308
1	-1.282589	2.593724	-1.265826
6	-2.914494	3.453592	1.689819
1	-2.272432	4.300129	1.944402
1	-3.831966	3.859217	1.256616
1	-3.181121	2.937051	2.614835
52	-0.001372	-0.356492	-1.962708

1f:

6	0.029533	0.058054	0.086254
7	-1.060715	0.214898	0.862904
7	1.124978	0.182506	0.860874
6	-0.729228	0.402771	2.278129
6	0.803996	0.497428	2.255595
6	2.485042	0.073186	0.437292
6	3.162987	1.218009	0.018346
6	3.101810	-1.178597	0.488037
6	4.502525	1.088978	-0.339063
6	4.440185	-1.262836	0.120252
6	5.156677	-0.139137	-0.288476
1	5.044115	1.967800	-0.677710
1	4.934159	-2.230423	0.141863
6	-2.423375	0.103647	0.447794
6	-3.036497	-1.151917	0.457542
6	-3.109280	1.261139	0.082667
6	-4.378168	-1.224133	0.101686
6	-4.452874	1.143445	-0.265740
6	-5.101670	-0.087449	-0.258739
1	-4.871347	-2.192509	0.093669
1	-5.001163	2.033889	-0.559928
6	-2.240357	-2.386615	0.783299
6	-2.386142	2.578725	0.013747
6	2.308266	-2.398530	0.870383
1	1.510656	-2.567525	0.141187
6	2.436044	2.529585	-0.104891
1	-1.746091	-2.313672	1.755774
1	-1.584031	2.524643	-0.728149
1	1.638434	2.444250	-0.848647
1	1.167726	1.497176	2.509126
1	-1.089647	-0.446774	2.865370
1	-1.205607	1.306650	2.663265
1	1.284657	-0.217937	2.926441
1	1.837307	-2.289496	1.851362
1	2.942965	-3.284446	0.897150
1	-2.879466	-3.269672	0.796610
1	-1.461713	-2.536525	0.029852
1	3.114370	3.323324	-0.418240
1	1.974856	2.834163	0.838396
1	-3.064864	3.382659	-0.271379
1	-1.929540	2.845835	0.970825
6	-6.549073	-0.206883	-0.659488
1	-7.115696	-0.784557	0.074077
1	-7.018631	0.772852	-0.755127
1	-6.642686	-0.717188	-1.621583
6	6.613888	-0.254603	-0.652867
1	6.931516	0.572805	-1.288730
1	7.239404	-0.243418	0.244239
1	6.816273	-1.187078	-1.182652
52	0.022893	-0.299312	-1.949594

2c:

6	0.003598	0.094695	0.059113
7	-1.104511	0.259018	0.766568
7	1.102001	0.217018	0.776417
6	-0.767744	0.457551	2.192749
6	0.768236	0.584286	2.166061
6	2.447468	0.077284	0.292204
6	3.161106	1.220923	-0.071220
6	2.992435	-1.209754	0.231476
6	4.472591	1.045474	-0.504939
6	4.304750	-1.330239	-0.208546
6	5.061255	-0.215219	-0.573620
1	5.048068	1.918225	-0.798804
1	4.751062	-2.318153	-0.269962
6	-2.449623	0.095238	0.293339
6	-2.988846	-1.196663	0.233974
6	-3.172617	1.234085	-0.069464
6	-4.304425	-1.322105	-0.194991
6	-4.487784	1.053801	-0.491213
6	-5.070328	-0.210188	-0.553821
1	-4.748590	-2.311652	-0.250747
1	-5.070850	1.923490	-0.777437
6	-2.157412	-2.402158	0.589031
6	-2.538547	2.599222	-0.023430
6	2.172985	-2.417165	0.605296
1	1.383291	-2.599610	-0.129859
6	2.549222	2.594978	0.005940
1	-1.687811	-2.303795	1.570686
1	-1.624403	2.635005	-0.622921
1	1.478433	2.582728	-0.210331
1	1.112241	1.601813	2.360085
1	-1.113403	-0.403420	2.767915
1	-1.292106	-0.238580	-1.805632
1	-1.263880	1.351474	2.568065
1	1.268754	-0.095692	2.854989
1	1.695080	-2.300112	1.581688

1	2.796289	-3.309329	0.645742
1	-2.769927	-3.302398	0.604899
1	-1.357538	-2.562291	-0.140909
1	3.023093	3.267000	-0.708911
1	2.686480	3.031737	0.999560
1	-3.219869	3.355264	-0.410682
1	-2.273024	2.887316	0.997149
6	-6.493014	-0.391480	-1.007800
1	-7.074792	-0.923718	-0.252504
1	-6.978762	0.564926	-1.198276
1	-6.532965	-0.981090	-1.926557
6	6.492334	-0.373681	-1.009524
1	6.803779	0.442447	-1.661675
1	7.154276	-0.374175	-0.139396
1	6.644828	-1.314490	-1.539307
16	0.075374	-0.218029	-1.666966

2f:

6	0.037973	0.100369	0.237157
7	-1.072815	0.281694	0.934102
7	1.130719	0.226485	0.965377
6	-0.744652	0.495779	2.361686
6	0.789404	0.634285	2.342138
6	2.474963	0.086288	0.479776
6	3.167887	1.221361	0.052739
6	3.039021	-1.194550	0.472588
6	4.473837	1.042692	-0.397203
6	4.344732	-1.318303	0.014640
6	5.077984	-0.212240	-0.419269
1	5.032642	1.908689	-0.739128
1	4.804879	-2.301562	-0.005501
6	-2.419719	0.127996	0.462314
6	-2.977288	-1.156142	0.425889
6	-3.126824	1.270528	0.082300
6	-4.292975	-1.270929	-0.006146
6	-4.442920	1.101484	-0.341638
6	-5.041952	-0.155275	-0.387769
1	-4.750776	-2.255045	-0.045542
1	-5.013769	1.974633	-0.641752
6	-2.166746	-2.367062	0.809299
6	-2.476964	2.628693	0.112636
6	2.247134	-2.391602	0.929187
1	1.413380	-2.597373	0.251509
6	2.542518	2.591128	0.087904
1	-1.716314	-2.264118	1.799500
1	-1.562105	2.647837	-0.486399
1	1.471081	2.562781	-0.123232
1	1.123665	1.660908	2.504549
1	-1.086189	-0.363837	2.941545
34	0.158325	-0.259193	-1.623977
1	-1.329116	-0.271638	-1.737098
1	-1.251102	1.388204	2.726515
1	1.290726	-0.018706	3.055905
1	1.829334	-2.245869	1.928877
1	2.874650	-3.281205	0.958536
1	-2.789827	-3.260120	0.822111
1	-1.354090	-2.543198	0.097697
1	3.007931	3.245760	-0.648249
1	2.678784	3.057938	1.067920
1	-3.149814	3.387889	-0.283259
1	-2.208738	2.925773	1.130016
6	-6.464423	-0.324501	-0.847536
1	-7.052390	-0.860082	-0.099583
1	-6.943746	0.636492	-1.031466
1	-6.504530	-0.905263	-1.772010
6	6.502498	-0.374387	-0.874789
1	6.801898	0.430349	-1.546279
1	7.177857	-0.358235	-0.015213
1	6.648998	-1.324500	-1.389672

2i:

6	0.054403	0.052392	0.442215
7	-1.064488	0.284831	1.109950
7	1.132732	0.241244	1.185697
6	-0.759366	0.568848	2.530344
6	0.763271	0.783654	2.507981
6	2.481133	0.118027	0.708883
6	3.110860	-1.126724	0.827559
6	3.111605	1.233834	0.148489
6	4.413694	-1.236320	0.355836
6	4.415493	1.069342	-0.311199
6	5.080171	-0.152150	-0.216984
1	4.923971	-2.191134	0.437968
1	4.926146	1.919794	-0.753063
6	-2.404420	0.129905	0.620552
6	-3.048114	-1.099703	0.775489
6	-3.012973	1.230628	0.006785
6	-4.347527	-1.210088	0.285020

6	-4.309977	1.068933	-0.465085	1	-2.540963	-2.247740	2.527255
6	-4.993892	-0.141089	-0.331471	1	-2.785840	-3.210550	1.077908
1	-4.866322	-2.158667	0.386684	1	2.853891	3.174174	-0.737201
1	-4.802679	1.906188	-0.950380	1	2.558474	3.134266	0.995437
6	-2.376743	-2.270001	1.446014	1	3.070728	-3.145027	1.562239
6	-2.268764	2.529427	-0.158972	1	1.569787	-2.638078	0.790635
6	2.427109	2.573545	0.065355	1	-2.925908	3.304445	-0.550641
1	1.354145	2.483429	-0.120939	1	-1.860087	2.886247	0.790015
6	2.391413	-2.303962	1.431501	6	-6.409193	-0.274572	-0.823846
1	-1.297954	-2.285394	1.272912	1	-7.107707	0.121283	-0.081986
1	-1.431285	2.421630	-0.855299	1	-6.562229	0.283036	-1.748694
1	1.967640	-2.061737	2.409351	1	-6.672681	-1.316720	-1.004781
1	1.288143	0.243613	3.294820	6	6.479529	-0.305925	-0.747472
1	-1.055056	-0.290666	3.136630	1	6.456172	-0.590858	-1.802824
52	0.253706	-0.536455	-1.561919	1	7.039027	0.626612	-0.669753
1	-1.400282	-0.647330	-1.677125	1	7.026209	-1.080442	-0.209013
1	-1.316889	1.444813	2.859251				
1	1.042528	1.839244	2.552901				

4. Tables of Crystallographic Data:

X-ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in an N_2 filled glovebox, mounted on a MiTegen Micromount, and placed under a N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). The data were collected at 150(2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS).

Structure Solution and Refinement. The structures were solved by direct methods using XS or the intrinsic phasing methods using XT and subjected to full-matrix least-squares refinement on F^2 using XL as implemented in the SHELXTL suite of programs. All non-hydrogen atoms were refined with anisotropically thermal parameters. Carbon bound hydrogen atoms were placed in geometrically calculated positions and refined using an appropriate riding model and coupled isotropic thermal parameters, and the X (X = S, Se) bound hydrogen atom was located in difference Fourier maps and the hydrogen atom for the X = S was refined in an unrestrained manner, whereas Se – H bond length was restrained based on the literature known value (0.989 Å).

Summary of crystallographic data for compound **2a, 2c, 2d, 2f, 2g**

	2a	**2c**	**2d**	**2f**	**2g**
empirical formula	C29 H39 F3 N2 O3 S2	C22 H27 F3 N2 O3 S2	C29 H39 F3 N2 O3 S Se	C22 H27 F3 N2 O3 S Se	C29 H39 F3 N2 O3 S Te
formula weight	584.74	488.57	631.64	535.47	680.28
crystal system	Orthorhombic	Triclinic	Orthorhombic	Monoclinic	Orthorhombic

space group	*P*bca	$P\bar{1}$	*P*bca	*C*2/c	*P*bca
a (Å)	15.9377(14)	8.783(13)	16.1430(16)	33.690(4)	16.234(2)
b (Å)	17.3130(13)	16.48(2)	17.3306(17)	8.5921(9)	17.579(3)
c (Å)	21.9697(18)	17.56(2)	21.714(2)	18.017(2)	21.880(3)
α (deg.)		73.04(6)			
β (deg.)		89.36(5)		110.240(7)	
γ (deg.)		78.37(4)			
vol (Å^3)	6062.1(9)	2378(6)	6075.0(10)	4893.2(10)	6244.1(16)
Z	8	4	8	8	8
ρ (calcd) (Mg·cm^3)	1.281	1.365	1.381	1.454	1.447
μ (mm^{-1})	0.226	0.273	1.355	1.668	1.069
F(000)	2480	1024	2624	2192	2768
Theta range (°)	1.854 to 28.738	1.214 to 27.796	1.963 to 27.614	2.306 to 27.482	1.945 to 25.590
T(K)	150(2)	150(2)	150(2)	150(2)	150(2)
reflections collected	92925	34133	53460	40631	121842
unique reflections	7765	10900	7045	5615	5806
R_{int}	0.1115	0.0479	0.0538	0.0437	0.1423
GOF (F^2)	0.971	1.058	1.023	1.199	1.056
R1 indices [$I>2\sigma(I)$]	0.0537	0.0639	0.0412	0.0382	0.0511
wR2 indices (all data)	0.1767	0.1885	0.1057	0.1117	0.1037
Largest diff. peak and hole (e. Å^{-3})	0.478 & -0.626	0.538 & -0.554	1.623 & -0.553	1.856 & -1.507	1.460 & -1.003
CCDC No.	1515486	1515485	1515487	1515484	1515488

5. References:

S1. K. Srinivas, P. Suresh, C. N. Babu, A. Sathyanarayana and G. Prabusankar, *RSC Adv.*, 2015, **5**, 15579-15590.

S2. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

S3. Y. Zhao and D. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.

S4. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, and F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2009); http://www.chem.wisc.edu/~nbo5