Electronic Supplementary Material (ESI) for New Journal of Chemistry.


# The first azulenes with aryl substituents bearing pentafluorosulfanyl groups: Synthesis, spectroscopic and halochromic properties

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## ELECTRONIC SUPPORTING INFORMATION

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# Computational Supporting Information

## Computational Details / Methodology

DFT calculations were run with Gaussian 09 (Revision D.01),[2] all atoms were described with the 6-31G** basis set, with the exception of S where SDDALL was employed with an additional *d* function (0.503) (BS1).[3] Initial BP86[4] optimizations were performed using the 'grid = ultrafine' option, with all stationary points being fully characterized via analytical frequency calculations as minima (all positive eigenvalues). All energies were recomputed with a larger basis set; 6-311++G** (BS2). Corrections for the effect of DCM (ε = 8.93) solvent were run using the polarizable continuum model and BS1.[5] Single-point dispersion corrections to the BP86 results employed Grimme's D3 parameter set with Becke-Johnson damping as implemented in Gaussian.[6] Natural Bond Orbital (NBO) analysis calculations were viewed in GaussView (v5.0.8) to generate orbital pictures.

## Breakdown of Energy Contributions

The following tables detail the evolution of the relative energies as the successive corrections to the initial SCF energy are included. Terms used are:

**$\Delta E_{BS1}$** SCF energy computed with the BP86 functional with BS1

**$\Delta H_{BS1}$** Enthalpy at 0 K with BS1

**$\Delta G_{BS1}$** Free energy at 298.15 K and 1 atm with BS1

**$\Delta G_{BS1/DCM}$** Free energy corrected for DCM with BS1

**$\Delta G_{BS1/DCM+D3}$** Free energy corrected for DCM and dispersion effects with BS1

**$\Delta G_{DCM}$** Free energy corrected for basis set (BS2), dispersion effects and DCM solvent

In each case the final data used in the main article is highlighted in bold.

**Table S1** – Computed relative energies (kcal/mol) for $SF_5$ substituted azulene species **6**-**9**. Data in bold are those used in the main text. Energies are quoted relative to isomer **6** / **[7-H]$^+$** for neutral and cationic species respectively.

| | | $\Delta E_{BS1}$ | $\Delta H_{BS1}$ | $\Delta G_{BS1}$ | $\Delta G_{BS1/DCM}$ | $\Delta G_{BS1/DCM+D3}$ | $\Delta E_{BS2}$ | $\Delta G_{DCM}$ |
|---|---|---|---|---|---|---|---|---|
| *Neutral* | **6** | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | **0.0** |
| | **7** | 0.1 | 0.1 | 0.0 | 0.2 | -0.1 | 0.1 | **0.0** |
| | **8** | 1.4 | 1.5 | 1.8 | 1.5 | 0.9 | 1.5 | **1.0** |
| | **9** | 1.6 | 1.7 | 2.0 | 1.8 | 1.0 | 1.8 | **1.1** |
| *Protonated* | [**6**+H]$^+$ | 0.8 | 0.8 | 0.7 | 0.2 | 0.3 | 1.0 | **0.6** |
| | [**7**+H]$^+$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | **0.0** |
| | [**8**+H]$^+$ | 7.5 | 7.2 | 7.4 | 5.4 | 4.6 | 7.0 | **4.1** |
| | [**8**+H]$^+$ (iso) | 12.9 | 12.9 | 12.6 | 10.7 | 9.1 | 11.8 | **8.0** |
| | [**9**+H]$^+$ | 7.1 | 6.9 | 7.0 | 5.4 | 4.5 | 6.5 | **3.9** |
| | [**9**+H]$^+$ (iso) | 12.4 | 12.4 | 12.1 | 10.7 | 9.0 | 11.2 | **7.8** |

| | | | |
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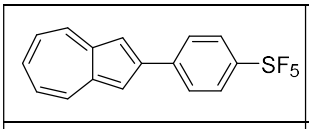
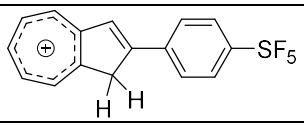
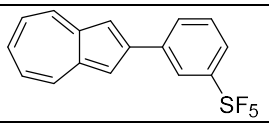
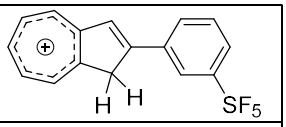
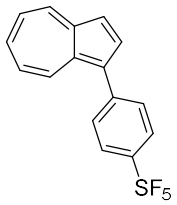
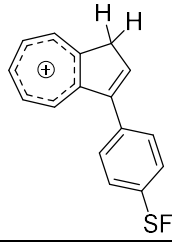
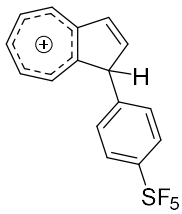
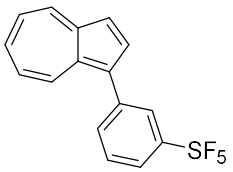
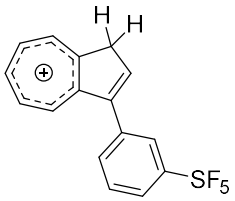
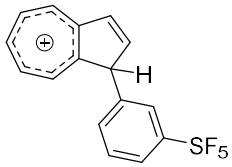
|  |  |  |  |
| **6** | [**6**+H]$^+$ | **7** | [**7**+H]$^+$ |
|  |  |  | |
| **8** | [**8**+H]$^+$ | [**8**+H]$^+$ (iso) | |
|  |  |  | |
| **9** | [**9**+H]$^+$ | [**9**+H]$^+$(iso) | |

**Table S2** – Computed HOMO and LUMO energies (eV) for $SF_5$ substituted azulene species **6**-**9**, and dipole magnitude (Debye, D).

| | | $E_{HOMO}$ [eV] | $E_{LUMO}$ [eV] | $\Delta E_{LUMO-HOMO}$ [eV] | Dipole [D] |
|---|---|---|---|---|---|
| *Neutral* | **6** | -5.093 | -3.157 | 1.936 | 6.30 |
| | **7** | -5.051 | -3.170 | 1.880 | 5.43 |
| | **8** | -5.016 | -3.087 | 1.929 | 6.39 |
| | **9** | -4.980 | -3.113 | 1.867 | 6.13 |
| *Protonated* | [**6**+H]$^+$ | -9.547 | -7.525 | 2.022 | 20.63 |
| | [**7**+H]$^+$ | -9.553 | -7.472 | 2.081 | 17.64 |
| | [**8**+H]$^+$ | -9.603 | -7.735 | 1.869 | 21.15 |
| | [**8**+H]$^+$ (iso) | -9.708 | -7.798 | 1.910 | 19.77 |
| | [**9**+H]$^+$ | -9.613 | -7.719 | 1.894 | 19.39 |
| | [**9**+H]$^+$ (iso) | -9.731 | -7.782 | 1.950 | 18.21 |

**Molecular Orbital Plots for 6-9 and their Protonated Forms**

| [**6**] | | [**6**+H]$^+$ | |
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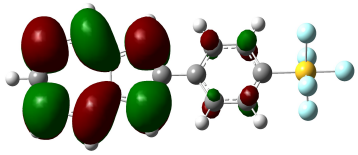
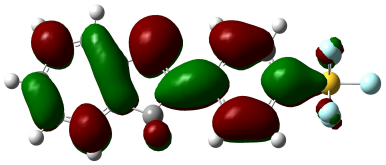
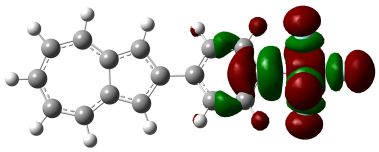
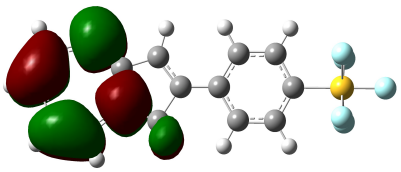
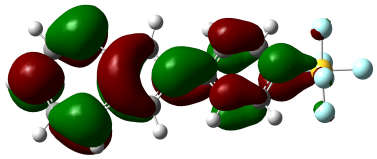
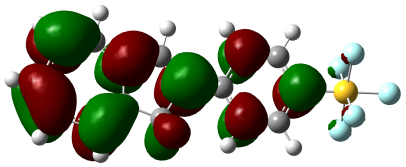
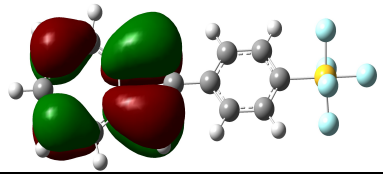
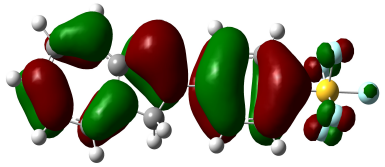
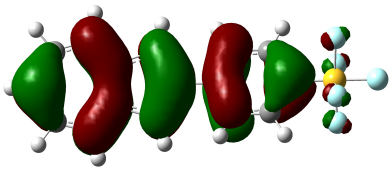
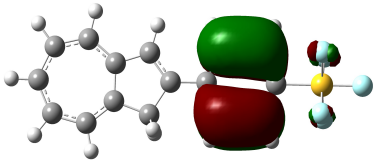
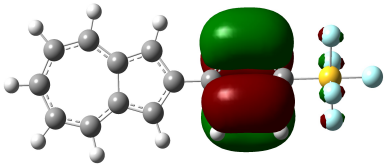
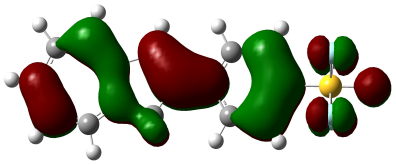
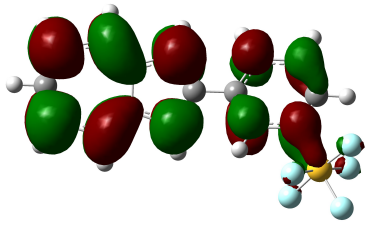
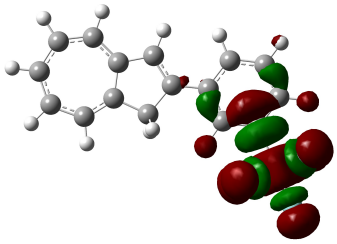
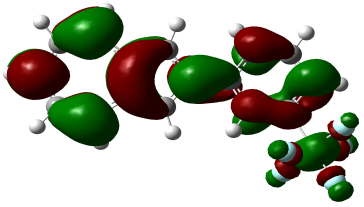
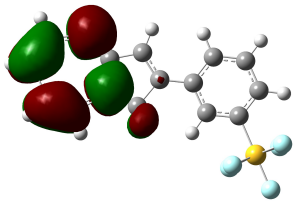
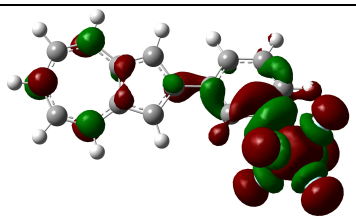
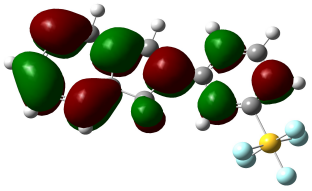
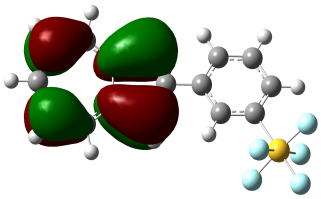
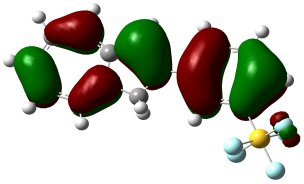
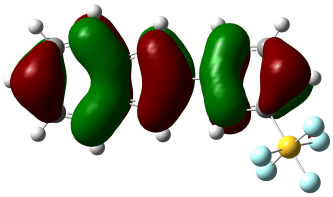
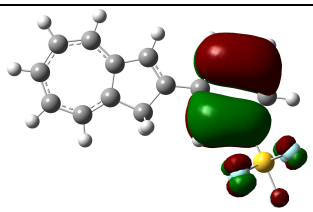
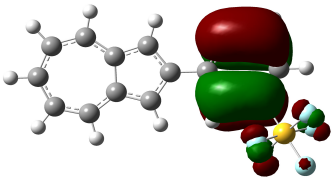
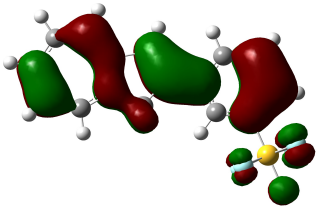
| LUMO + 2 |  | LUMO + 2 |  |
| LUMO + 1 |  | LUMO + 1 |  |
| LUMO |  | LUMO |  |
| HOMO |  | HOMO |  |
| HOMO - 1 |  | HOMO - 1 |  |
| HOMO - 2 |  | HOMO - 2 |  |

| [7] | | [7+H]$^+$ | |
|---|---|---|---|
| LUMO + 2 |  | LUMO + 2 |  |
| LUMO + 1 |  | LUMO + 1 |  |
| LUMO |  | LUMO |  |
| HOMO |  | HOMO |  |
| HOMO - 1 |  | HOMO - 1 |  |
| HOMO - 2 |  | HOMO - 2 |  |

| [**8**] | | [**8**+H]$^+$ | |
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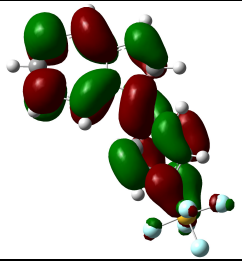
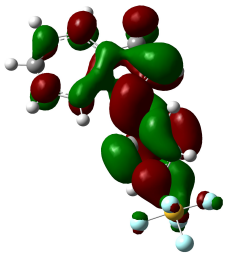
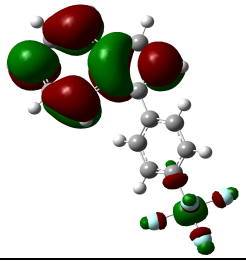
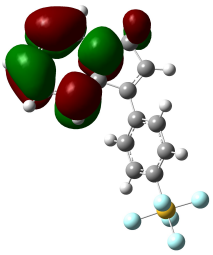
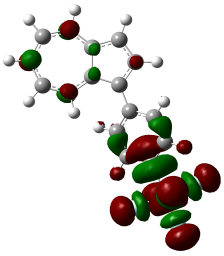
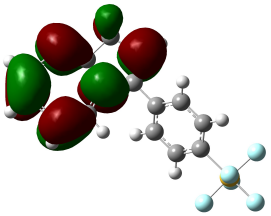
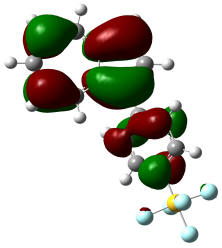
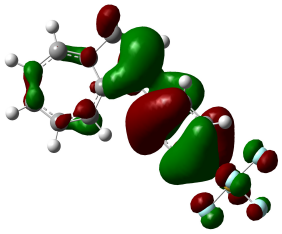
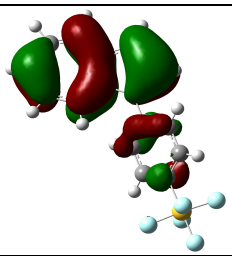
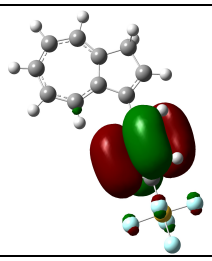
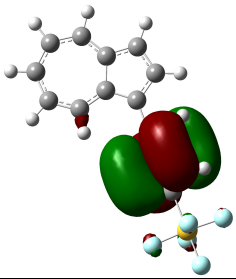
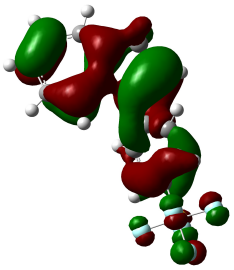
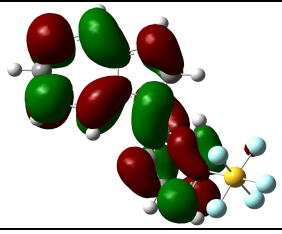
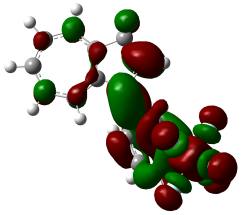
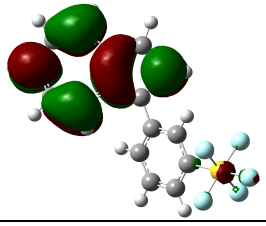
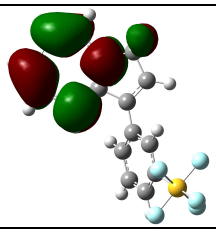
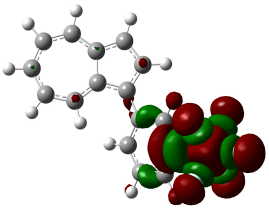
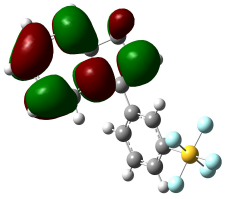
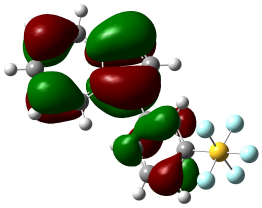
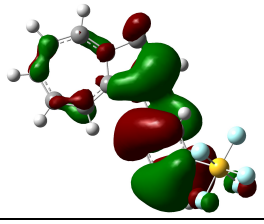
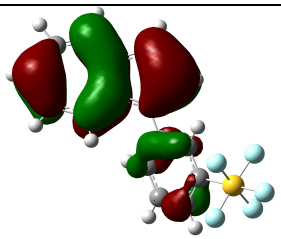
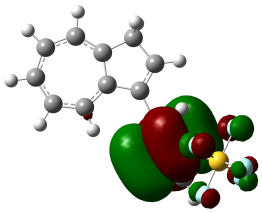
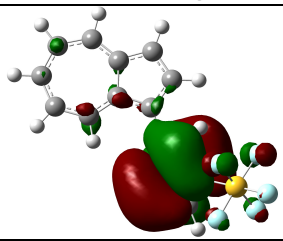
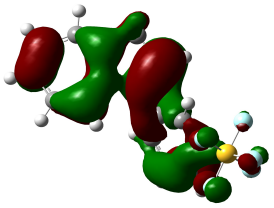
| LUMO + 2 |  | LUMO + 2 |  |
| LUMO + 1 |  | LUMO + 1 |  |
| LUMO |  | LUMO |  |
| HOMO |  | HOMO |  |
| HOMO - 1 |  | HOMO - 1 |  |
| HOMO - 2 |  | HOMO - 2 |  |

| [**9**] | | [**9**+H]$^+$ | |
|---|---|---|---|
| LUMO + 2 |  | LUMO + 2 |  |
| LUMO + 1 |  | LUMO + 1 |  |
| LUMO |  | LUMO |  |
| HOMO |  | HOMO |  |
| HOMO - 1 |  | HOMO - 1 |  |
| HOMO - 2 |  | HOMO - 2 |  |

**Cartesian Coordinates and Computed Energies (in Hartrees)**

**6**
SCF (BP86) Energy = -1125.60921202
Enthalpy 0K = -1125.382460
Enthalpy 298K = -1125.362983
Free Energy 298K = -1125.430038
Lowest Frequency = 25.4270 $cm^{-1}$
Second Frequency = 28.3561 $cm^{-1}$
SCF (DCM) Energy = -1125.61569159
SCF (BP86-D3) Energy = -1125.68091942
SCF (BS2) Energy = -1513.93882638

C -7.15544 0.00000 0.00000
C -6.55821 1.26263 0.16945
C -5.19273 1.59092 0.20798
C -6.55821 -1.26263 -0.16945
C -4.07947 0.74586 0.09082
C -5.19273 -1.59092 -0.20798
C -4.07947 -0.74586 -0.09082
H -8.25294 0.00000 0.00000
H -7.25177 2.10401 0.28318
H -4.96075 2.65598 0.34521
H -7.25177 -2.10401 -0.28318
H -4.96075 -2.65598 -0.34520
C -2.73002 1.14851 0.13268
H -2.39011 2.17359 0.29103
C -1.89887 0.00000 0.00000
C -2.73002 -1.14851 -0.13268
H -2.39011 -2.17359 -0.29103
C -0.42870 0.00000 0.00000
C 0.30129 -1.17372 0.30831
C 0.30129 1.17372 -0.30831
C 1.70039 -1.18520 0.31076
H -0.23521 -2.08929 0.57445
C 1.70039 1.18521 -0.31076
H -0.23521 2.08929 -0.57445
C 2.37914 0.00000 0.00000
H 2.24995 -2.09473 0.55681
H 2.24995 2.09473 -0.55681
S 4.21928 0.00000 0.00000
F 4.28793 -1.43838 -0.83869
F 5.87613 0.00000 0.00000
F 4.28780 -0.83719 1.43927
F 4.28780 0.83719 -1.43927
F 4.28793 1.43838 0.83869

**7**
SCF (BP86) Energy = -1125.60907440
Enthalpy 0K = -1125.382345
Enthalpy 298K = -1125.362864
Free Energy 298K = -1125.429969
Lowest Frequency = 23.9108 $cm^{-1}$
Second Frequency = 26.7256 $cm^{-1}$
SCF (DCM) Energy = -1125.61543348
SCF (BP86-D3) Energy = -1125.68106168
SCF (BS2) Energy = -1513.93863334

C -6.54208 -0.96399 0.08746
C -5.60682 -1.95695 -0.25714
C -4.21184 -1.84530 -0.38170
C -6.34076 0.39472 0.39243
C -3.39824 -0.71778 -0.19791
C -5.13743 1.11903 0.42627
C -3.83292 0.67315 0.16839
H -7.58626 -1.29997 0.12410
H -6.02202 -2.95290 -0.45097
H -3.68097 -2.76674 -0.65741
H -7.24511 0.96596 0.63285
H -5.22673 2.18250 0.68731
C -1.54119 0.64436 -0.08652
C -2.66650 1.46209 0.21665
H -2.63975 2.51855 0.48972
C -0.14186 1.09566 -0.13491
C 0.18724 2.46262 -0.30013
C 0.91688 0.16298 -0.01602
C 1.52042 2.88716 -0.34463
H -0.61674 3.19548 -0.41596
C 2.23565 0.61547 -0.06725
H 0.70206 -0.89501 0.13647
H 1.75225 3.94845 -0.47835
C 2.57300 1.96496 -0.22887
H 3.61467 2.28487 -0.26464
S 3.59668 -0.62194 0.09346
F 2.84624 -1.39019 1.36747
F 2.86217 -1.67222 -0.97190
F 4.82055 -1.72947 0.23513
F 4.43170 0.33703 1.17048
F 4.44780 0.05467 -1.16962
C -1.99647 -0.68123 -0.33501
H -1.37691 -1.53043 -0.62921

**8**
SCF (BP86) Energy = -1125.60701655
Enthalpy 0K = -1125.380013
Enthalpy 298K = -1125.360619
Free Energy 298K = -1125.427156
Lowest Frequency = 26.5867 $cm^{-1}$
Second Frequency = 34.5813 $cm^{-1}$
SCF (DCM) Energy = -1125.61325810
SCF (BP86-D3) Energy = -1125.68044617
SCF (BS2) Energy = -1513.93647875

C 5.57569 -2.06274 -0.24984
C 6.29740 -0.87445 -0.04122
C 5.80226 0.43344 0.10043
C 4.18820 -2.25795 -0.36029
C 4.47573 0.88243 0.11404
C 3.14944 -1.31499 -0.24597
C 3.22392 0.06018 0.00657
H 7.38803 -0.97772 -0.00374
H 6.55990 1.22036 0.21777
H 3.86854 -3.28744 -0.55959
H 2.13688 -1.71582 -0.38118
C 4.07052 2.23264 0.24311
H 4.74541 3.08278 0.35678
C 2.12385 0.96998 0.10020
H 6.18546 -2.96915 -0.35535
C 0.68690 0.66070 0.07098
C -0.21101 1.51076 -0.62295
C 0.14261 -0.45614 0.75432
C -1.58699 1.25940 -0.65077
H 0.18373 2.37238 -1.17066
C -1.23039 -0.73107 0.73110
H 0.79952 -1.09744 1.34917
C -2.07555 0.13321 0.02471
H -2.26277 1.91867 -1.19735
H -1.63453 -1.58953 1.26944

C 2.66682 2.28116 0.22526
H 2.06432 3.18700 0.33276
S -3.88024 -0.21601 -0.01155
F -3.63226 -1.83604 -0.31757
F -3.92408 -0.53364 1.62433
F -5.50731 -0.53132 -0.04493
F -4.26692 1.37678 0.29168
F -3.97466 0.07453 -1.65033

**9**
SCF (BP86) Energy = -1125.60662573
Enthalpy 0K = -1125.379693
Enthalpy 298K = -1125.360275
Free Energy 298K = -1125.426893
Lowest Frequency = 25.9372 $cm^{-1}$
Second Frequency = 28.4744 $cm^{-1}$
SCF (DCM) Energy = -1125.61277993
SCF (BP86-D3) Energy = -1125.68029203
SCF (BS2) Energy = -1513.93602210

C 5.80433 1.04459 0.90033
C 6.12417 -0.26921 0.51567
C 5.26481 -1.26984 0.02935
C 4.56157 1.70122 0.89182
C 3.89100 -1.20681 -0.23477
C 3.31200 1.22517 0.45255
C 2.97879 -0.02252 -0.08797
H 7.17585 -0.55740 0.62735
H 5.73243 -2.24299 -0.17398
H 4.56475 2.72735 1.27768
H 2.47888 1.93223 0.55550
C 1.68013 -0.44944 -0.50716
H 6.64599 1.64130 1.27467
C 0.44372 0.34636 -0.56917
C -0.78340 -0.23318 -0.15954
C 0.42036 1.67538 -1.06028
C -1.95783 0.51558 -0.24635
H -0.79913 -1.24831 0.23925
C -0.77388 2.40598 -1.12089
H 1.34702 2.12262 -1.43188
H -0.76792 3.42962 -1.50882
S -3.54132 -0.26724 0.29343
C -1.98991 1.83528 -0.71403
H -2.92555 2.39220 -0.76737
F -4.00110 1.08989 1.14553
F -4.35406 0.29922 -1.04759
F -4.96444 -0.96714 0.77445
F -3.20031 -1.68270 -0.51851
F -2.84761 -0.89209 1.67397
C 3.09818 -2.27954 -0.70785
H 3.46644 -3.28249 -0.93048
C 1.77731 -1.82551 -0.86075
H 0.94184 -2.42415 -1.23343

[**6**+H]$^+$
SCF (BP86) Energy = -1125.98217350
Enthalpy 0K = -1125.742957
Enthalpy 298K = -1125.723181
Free Energy 298K = -1125.791165
Lowest Frequency = 20.5404 $cm^{-1}$
Second Frequency = 27.2957 $cm^{-1}$
SCF (DCM) Energy = -1126.04607059
SCF (BP86-D3) Energy = -1126.05530917
SCF (BS2) Energy = -1514.29983115

C 7.17478 0.04411 -0.00013
C 6.59670 -1.22526 -0.00014
C 5.22161 -1.57484 -0.00006
C 6.53506 1.31197 -0.00004
C 4.12004 -0.72832 0.00004
C 5.17611 1.61311 0.00004
C 4.07493 0.71264 0.00006
H 8.27020 0.07071 -0.00019
H 7.29507 -2.06986 -0.00021
H 5.00664 -2.65068 -0.00008
H 7.20992 2.17571 -0.00005
H 4.91713 2.67869 0.00009
C 1.84912 0.03201 0.00009
C 2.69998 1.12792 0.00009
H 2.39785 2.17692 0.00011
C 0.39434 0.03153 0.00007
C -0.34168 1.24755 0.00002
C -0.32533 -1.19270 0.00010
C -1.73720 1.24458 -0.00001
H 0.17799 2.20964 -0.00000
C -1.72250 -1.21008 0.00007
H 0.20741 -2.14818 0.00014
C -2.40837 0.01225 0.00002
H -2.29583 2.18135 -0.00006
H -2.26830 -2.15436 0.00010
S -4.25813 0.00064 -0.00003
F -4.30377 1.17204 -1.17499
F -5.89926 -0.00943 -0.00007
F -4.30383 1.17211 1.17486
F -4.28958 -1.17169 -1.17481
F -4.28964 -1.17162 1.17481
C 2.69215 -1.22587 0.00012
H 2.49418 -1.86335 -0.88391
H 2.49429 -1.86308 0.88439

[**7**+H]$^+$
SCF (BP86) Energy = -1125.98343580
Enthalpy 0K = -1125.744201
Enthalpy 298K = -1125.724428
Free Energy 298K = -1125.792327
Lowest Frequency = 21.3981 $cm^{-1}$
Second Frequency = 26.2716 $cm^{-1}$
SCF (DCM) Energy = -1126.04637204
SCF (BP86-D3) Energy = -1126.05689531
SCF (BS2) Energy = -1514.30143885

C -6.55951 -0.94823 0.00007
C -5.61530 -1.97493 0.00014
C -4.19981 -1.87932 0.00010
C -6.34582 0.45558 -0.00005
C -3.41638 -0.73189 -0.00001
C -5.14802 1.16478 -0.00012
C -3.82147 0.65173 -0.00008
H -7.60889 -1.26359 0.00010
H -6.01621 -2.99489 0.00022
H -3.66050 -2.83471 0.00016
H -7.25591 1.06651 -0.00009
H -5.23365 2.25803 -0.00020
C -1.49497 0.69619 -0.00004
C -2.64344 1.47405 -0.00010
H -2.68172 2.56506 -0.00015
C -0.11109 1.14571 0.00001
C 0.22417 2.52715 0.00008
C 0.93914 0.19136 -0.00002
C 1.55886 2.93599 0.00013
H -0.56493 3.28413 0.00010
C 2.26216 0.62753 0.00003
H 0.72722 -0.87836 -0.00008

H 1.80530 4.00144 0.00019
C -1.90489 -0.76139 -0.00005
H -1.51859 -1.30619 0.88388
H -1.51873 -1.30601 -0.88415
C 2.59900 1.98794 0.00011
H 3.64356 2.30337 0.00015
S 3.61016 -0.63828 -0.00001
F 2.83462 -1.52677 1.17461
F 2.83464 -1.52666 -1.17474
F 4.80401 -1.76582 -0.00006
F 4.44029 0.18425 1.17589
F 4.44031 0.18436 -1.17583

[**8**+H]$^+$
SCF (BP86) Energy = -1125.97156840
Enthalpy 0K = -1125.732657
Enthalpy 298K = -1125.712923
Free Energy 298K = -1125.780585
Lowest Frequency = 21.8696 cm$^{-1}$
Second Frequency = 31.8750 cm$^{-1}$
SCF (DCM) Energy = -1126.03771501
SCF (BP86-D3) Energy = -1126.04623660
SCF (BS2) Energy = -1514.29034319

C 5.40247 -2.19925 -0.27015
C 6.18215 -1.05114 -0.09231
C 5.75649 0.28858 0.05607
C 3.99418 -2.30793 -0.34632
C 4.45364 0.78341 0.09855
C 3.02232 -1.31128 -0.22350
C 3.20580 0.07397 0.00447
H 7.26700 -1.20605 -0.07802
H 6.55652 1.03301 0.15473
H 3.61083 -3.31941 -0.52421
H 1.98007 -1.63806 -0.31992
C 2.10380 1.04007 0.12113
H 5.95513 -3.13953 -0.37777
C 0.65957 0.71361 0.08384
C -0.19779 1.42129 -0.78759
C 0.11303 -0.27493 0.93440
C -1.57103 1.14539 -0.82105
H 0.21353 2.18039 -1.46042
C -1.25952 -0.55717 0.91349
H 0.75094 -0.80180 1.65194
C -2.07812 0.15597 0.02970
H -2.23010 1.68714 -1.50079
H -1.68285 -1.30981 1.57995
C 2.64718 2.29635 0.25320
H 2.07111 3.21729 0.37089
S -3.88702 -0.22313 -0.01520
F -3.58712 -1.85835 -0.00817
F -3.97242 -0.23034 1.64340
F -5.49394 -0.56328 -0.05637
F -4.27200 1.39168 -0.02507
F -3.88643 -0.23646 -1.67636
C 4.13977 2.25251 0.25281
H 4.57669 2.67464 1.18121
H 4.58694 2.84651 -0.57152

[**8**+H]$^+$ (iso)
SCF (BP86) Energy = -1125.96289986
Enthalpy 0K = -1125.723724
Enthalpy 298K = -1125.704045
Free Energy 298K = -1125.772223
Lowest Frequency = 17.3883 cm$^{-1}$
Second Frequency = 27.3577 cm$^{-1}$
SCF (DCM) Energy = -1126.02934737
SCF (BP86-D3) Energy = -1126.03842609
SCF (BS2) Energy = -1514.28265358

C -5.10317 -2.26921 0.15919
C -5.72527 -1.19548 0.83757
C -5.32214 0.13957 0.93358
C -3.92514 -2.26383 -0.59792
C -4.17810 0.75061 0.36655
C -3.06114 -1.18214 -0.88085
C -3.17404 0.14280 -0.46432
H -6.65257 -1.44734 1.36507
H -5.97159 0.79819 1.52283
H -3.63285 -3.22662 -1.03260
H -2.18385 -1.41586 -1.49731
H -5.61364 -3.23571 0.23864
C -0.70368 0.86930 -0.59975
C 0.17535 0.64148 -1.67454
C -0.22858 0.75947 0.72314
C 1.51682 0.30116 -1.43968
H -0.17558 0.74011 -2.70777
C 1.10791 0.42197 0.97309
H -0.89917 0.94444 1.56927
C 1.95835 0.19439 -0.11675
H 2.20056 0.12953 -2.27220
H 1.47934 0.33946 1.99545
C -2.69293 2.43989 -0.14612
H -2.19859 3.41267 -0.20014
S 3.72079 -0.26096 0.20463
F 3.86443 0.92435 1.35859
F 3.26880 -1.35002 1.37681
F 5.28595 -0.67038 0.49173
F 3.65995 -1.47112 -0.93296
F 4.25608 0.80288 -0.95171
C -3.83825 2.15537 0.53881
H -4.43327 2.85771 1.12678
C -2.17041 1.22259 -0.86309
H -2.28153 1.38963 -1.95768

[**9**+H]$^+$
SCF (BP86) Energy = -1125.97219361
Enthalpy 0K = -1125.733261
Enthalpy 298K = -1125.713520
Free Energy 298K = -1125.781177
Lowest Frequency = 21.1950 cm$^{-1}$
Second Frequency = 26.9162 cm$^{-1}$
SCF (DCM) Energy = -1126.03771323
SCF (BP86-D3) Energy = -1126.04707125
SCF (BS2) Energy = -1514.29114348

C 5.59620 1.20564 1.10624
C 6.01132 -0.07926 0.73994
C 5.24738 -1.12267 0.16915
C 4.30947 1.78325 0.99761
C 3.90323 -1.10884 -0.20091
C 3.13835 1.23959 0.46325
C 2.94221 -0.04267 -0.10400
H 7.06426 -0.31544 0.93129
H 5.78463 -2.06288 -0.00778
H 4.21965 2.80431 1.38624
H 2.25086 1.88308 0.48894
C 1.65854 -0.51484 -0.64152
H 6.36620 1.84791 1.54862
C 0.41016 0.27859 -0.72722
C -0.78501 -0.26369 -0.20734
C 0.38255 1.54696 -1.35199
C -1.96707 0.47278 -0.31958
H -0.78354 -1.23459 0.29063

C -0.81977 2.26047 -1.45305
H 1.29413 1.95914 -1.79758
H -0.83736 3.23463 -1.95021
C 1.81107 -1.82556 -1.02855
H 1.02595 -2.44128 -1.47413
C 3.20401 -2.30899 -0.79344
H 3.69534 -2.65837 -1.72482
H 3.24530 -3.17747 -0.10317
S -3.52225 -0.24720 0.37519
C -2.01151 1.73022 -0.93291
H -2.94979 2.28179 -1.00698
F -3.93412 1.19912 1.07661
F -4.37433 0.16187 -0.98771
F -4.90162 -0.89166 0.99383
F -3.18224 -1.73531 -0.28848
F -2.74173 -0.69752 1.77484

[**9**+H]$^+$ (iso)
SCF (BP86) Energy = -1125.96366960
Enthalpy 0K = -1125.724474
Enthalpy 298K = -1125.704787
Free Energy 298K = -1125.773016
Lowest Frequency = 13.4931 cm$^{-1}$
Second Frequency = 26.4208 cm$^{-1}$
SCF (DCM) Energy = -1126.02926070
SCF (BP86-D3) Energy = -1126.03947120
SCF (BS2) Energy = -1514.28360379

C 4.79481 -2.28460 -0.58370
C 5.63828 -1.16526 -0.39484
C 5.31070 0.12405 0.03471
C 3.41312 -2.38639 -0.37972
C 4.03762 0.62994 0.39088
C 2.51112 -1.39698 0.07214
C 2.78467 -0.07489 0.41720
H 6.69800 -1.33246 -0.61982
H 6.14290 0.83489 0.10504
H 2.96932 -3.36498 -0.59593
H 1.46077 -1.70489 0.15263
H 5.29207 -3.19474 -0.93782
C 0.46044 0.97545 0.03578
C -0.73378 0.36686 0.46072
C 0.50487 1.63990 -1.20723
C -1.85740 0.43103 -0.37223
H -0.79699 -0.13773 1.42725
C -0.63805 1.69749 -2.01596
H 1.43109 2.12085 -1.53963
H -0.60313 2.22107 -2.97581
C 2.47696 2.16908 1.11116
H 2.00568 3.09139 1.45888
C 3.79880 2.00104 0.81759
H 4.58111 2.75951 0.89356
C 1.70950 0.88818 0.91775
H 1.38523 0.52599 1.91896
S -3.41651 -0.38775 0.19057
C -1.83624 1.08800 -1.60651
H -2.72865 1.12874 -2.23261
F -2.57726 -1.75035 0.66112
F -3.24894 0.23825 1.72233
F -4.79588 -1.12522 0.69403
F -4.32602 0.92671 -0.24701
F -3.65476 -1.06283 -1.30716

## Cyclic Voltammetry – General experimental details

Cyclic voltammagrams (CVs) were taken using a Metrohm Autolab Potentiostat/Galvanostat connected to a three-electrode cell. Boron doped diamond working-, platinum foil counter- and platinum wire pseudo reference electrodes were used. All CVs were referenced to the ferrocene/ferrocenium ($Fc/Fc^+$) redox couple as an internal reference.

All CVs were taken in dry acetonitrile which was degassed by sparging with argon for one hour to remove dissolved oxygen prior to making up solutions. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ($Bu_4NPF_6$) which was used as received from the vendor (Sigma-Aldrich) without further purification.

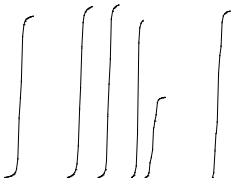
*A typical procedure was as follows:*

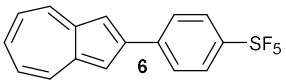
A four-necked heart-shaped glass flask ("electrochemical cell" or "cell") was sequentially cleaned with acetonitrile and acetone then dried using a heat gun. The working electrode was cleaned in acetonitrile and acetone then polished with fine alumina paste, rinsed with deionised water and acetone and air dried. The platinum counter- and reference electrodes were cleaned with acetonitrile and acetone, dried and then heated to glowing in a Bunsen burner flame to remove any residual organic material. The working and counter electrodes were inserted through holes drilled into rubber septa which in turn were inserted into the cell with one electrode/septum in each of two necks. The platinum wire reference electrode was inserted into a third neck and held in place with a stopper. The fourth neck was stoppered after purging the cell with argon, and used to add/remove solutions to/from the cell with a syringe.

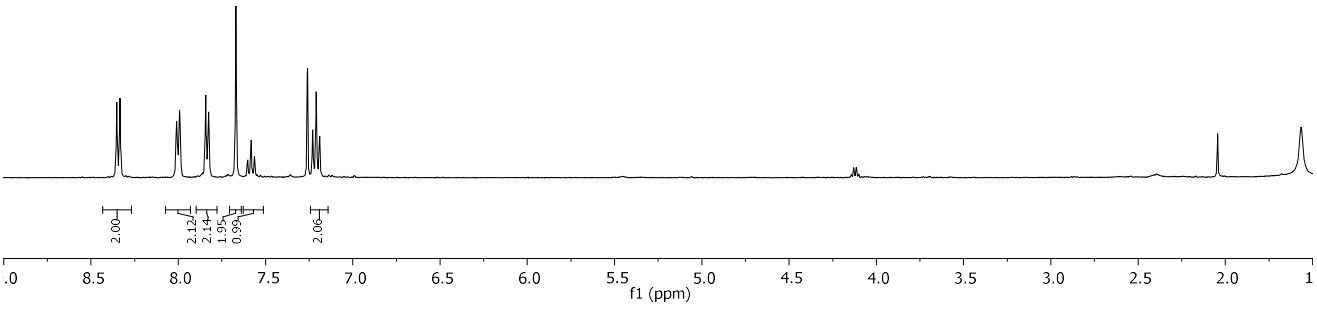
A 0.1 M solution of $Bu_4NPF_6$ in dry, degassed acetonitrile was prepared ("stock solution"). Some of the stock solution was then used to prepare a 5 mM solution of the substrate to be analysed ("substrate solution"). A 25 mM solution of ferrocene in dry acetonitrile was prepared for the internal reference ("reference solution").

The cell was charged with 5 mL of stock solution which was enough to ensure that the electrodes were sufficiently covered. The solution in the cell was sparged with argon for 20 min. Background CVs were taken at a scan rate of 100 mV $s^{-1}$ and a variety of potential ranges. 0.5 mL (0.1 mL for **6** and **8**) of solution was then removed from the cell and replaced with 0.5 mL (0.1 mL for **6** and **8**) of substrate solution, resulting in 5 mL of 0.5 mM (0.1 mM for **6** and **8**) substrate in stock solution. After sparging briefly with argon, CVs were taken at a variety of potential ranges. Finally, 0.1 mL of reference solution was added to the cell, resulting in 0.5 mM ferrocene solution, and a CV taken for the internal reference.

## NMR Spectra




SF5
6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0.99
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8.0
7.5
7.0
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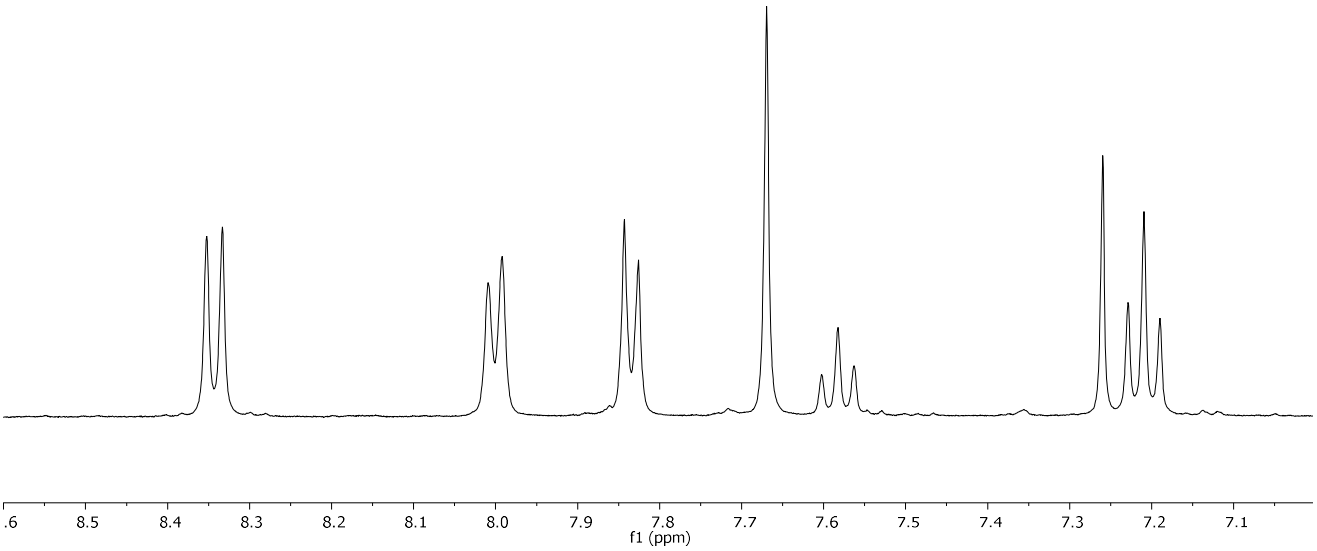
3.5
3.0
2.5
2.0
f1 (ppm)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8.4
8.3
8.2
8.1
8.0
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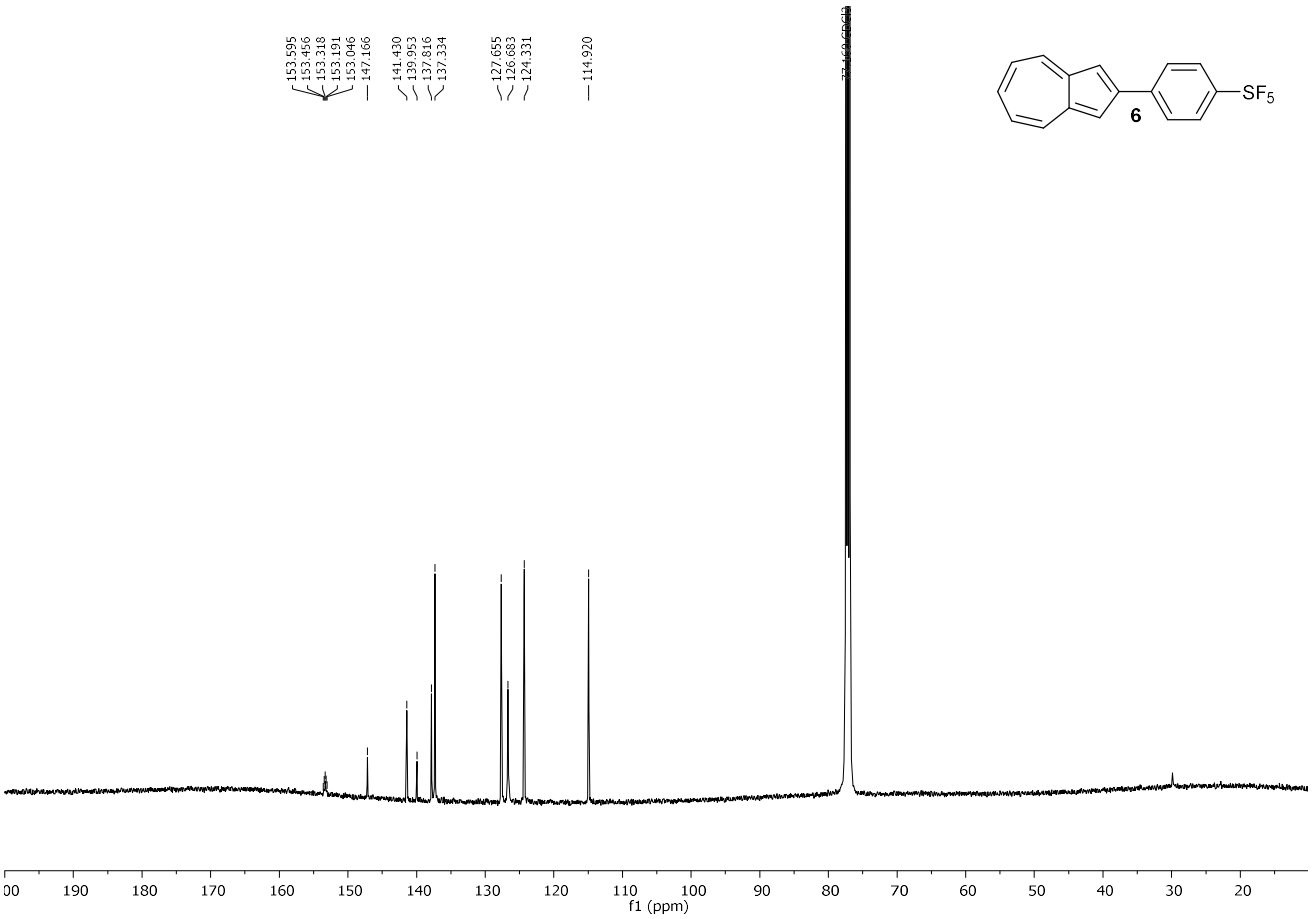
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)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153.456
153.318
153.191
153.046
147.166
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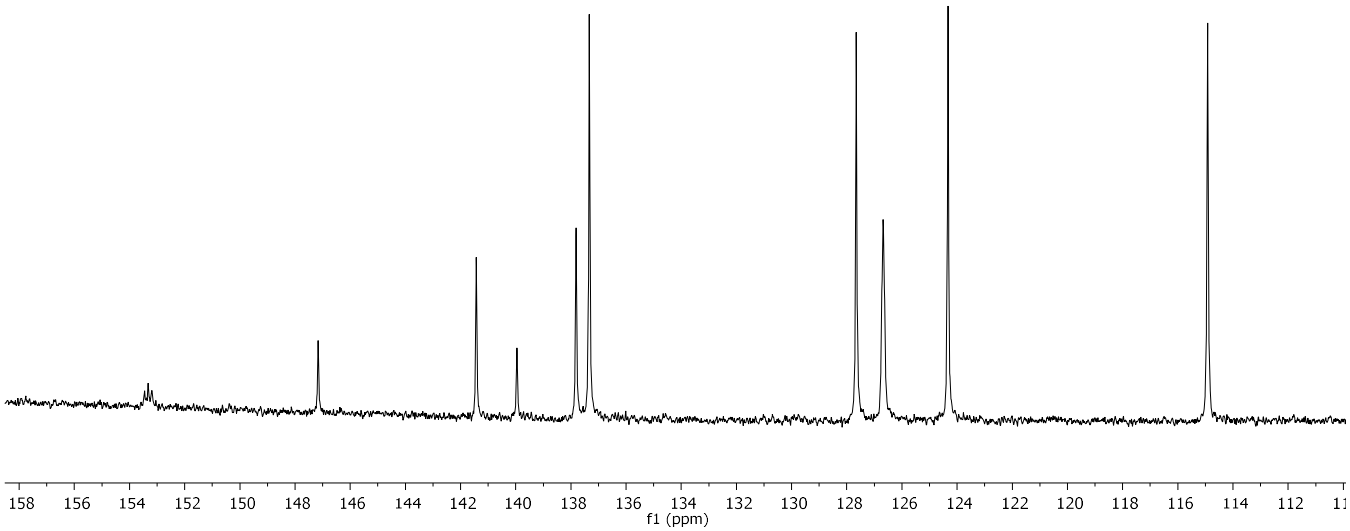
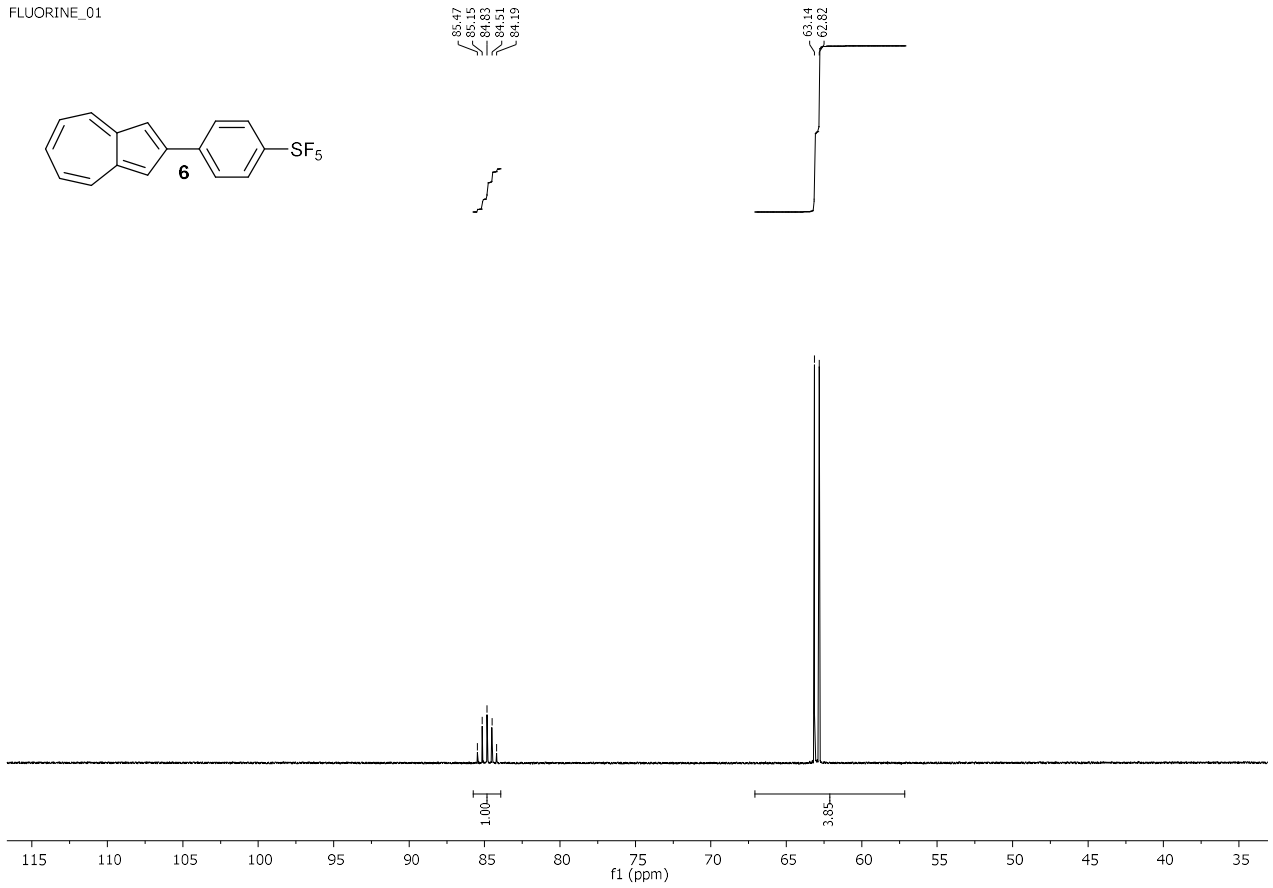
139.953
137.816
137.334
127.655
126.683
124.331
114.920
SF5
6
f1 (ppm)


f1 (ppm)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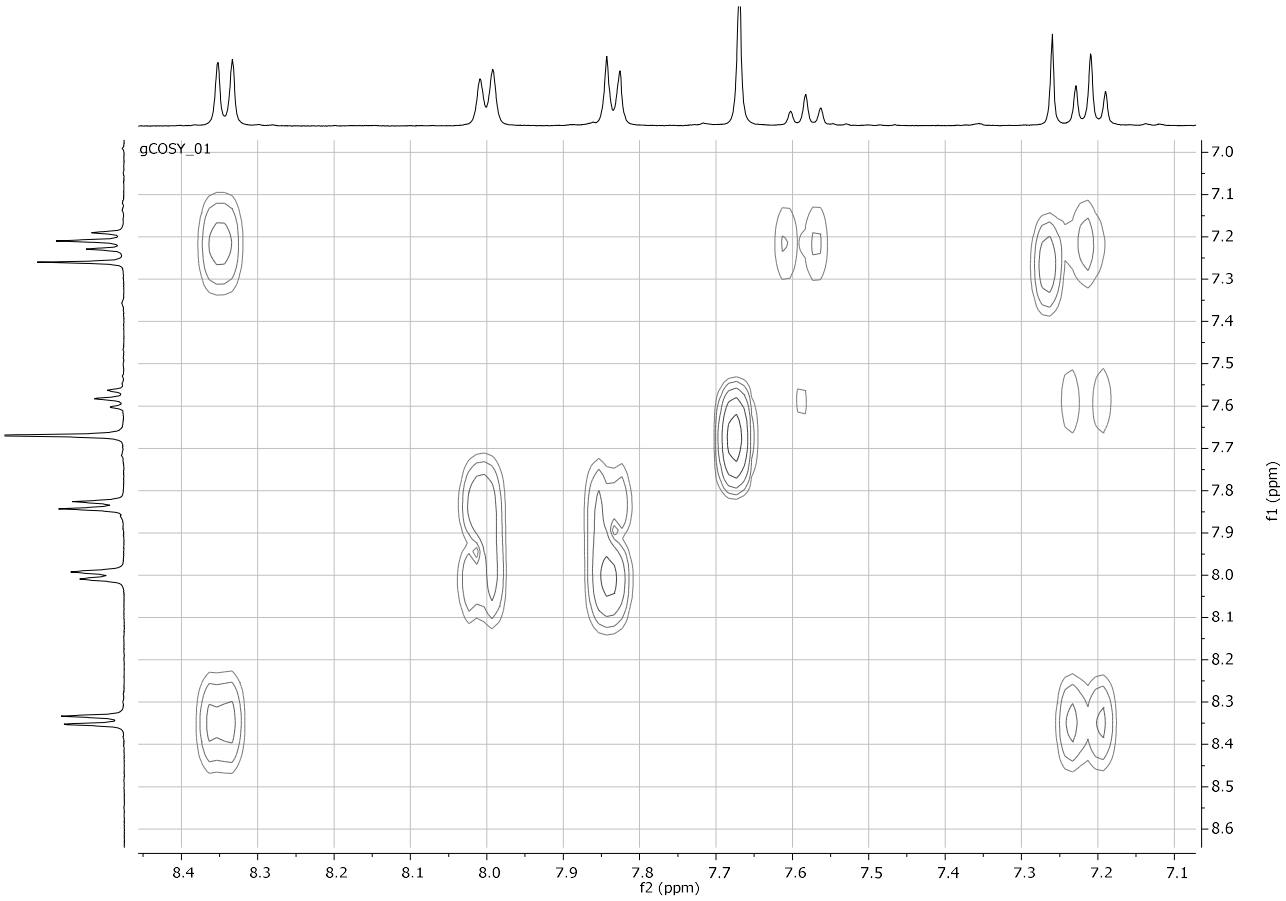
84.51
84.19
63.14
62.82
SF5
6
1.00
3.85
f1 (ppm)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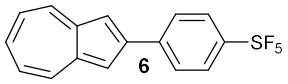
f2 (ppm)
f1 (ppm)

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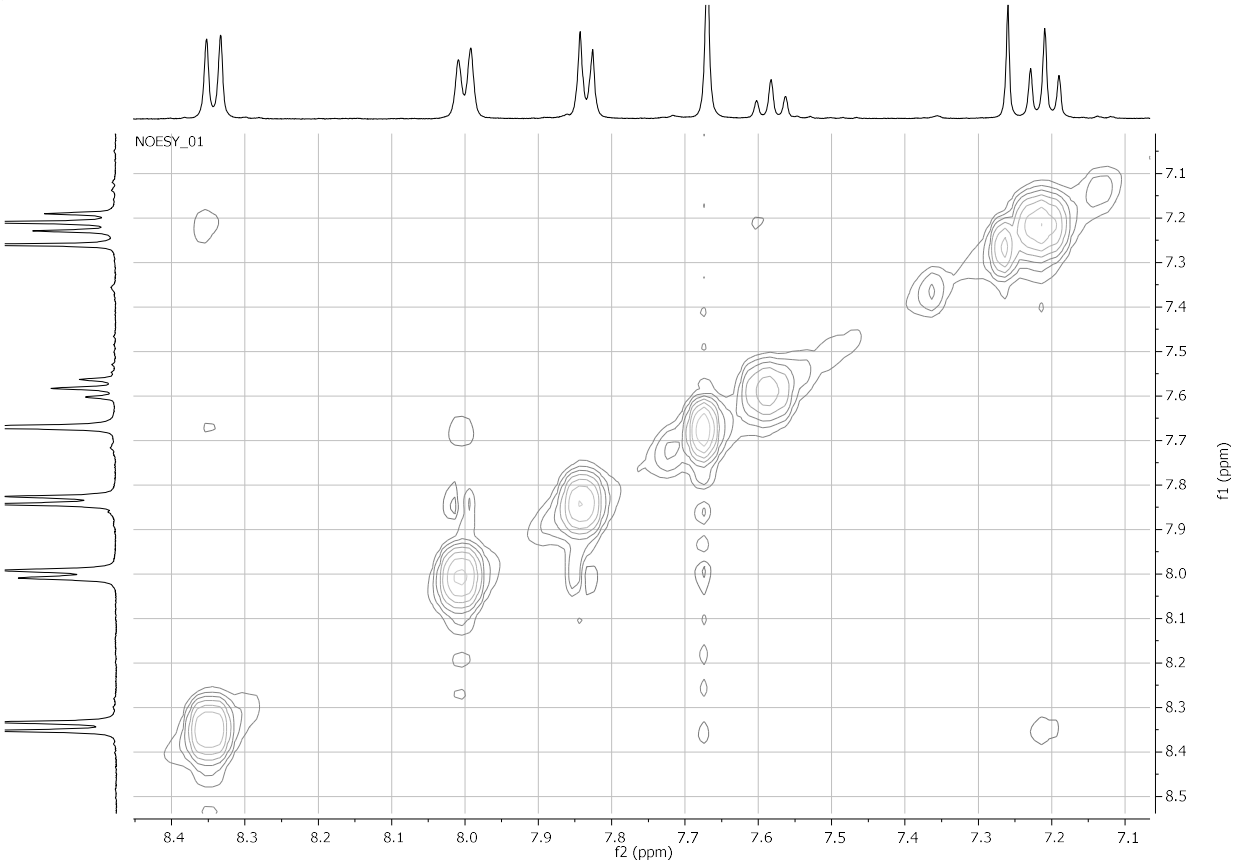
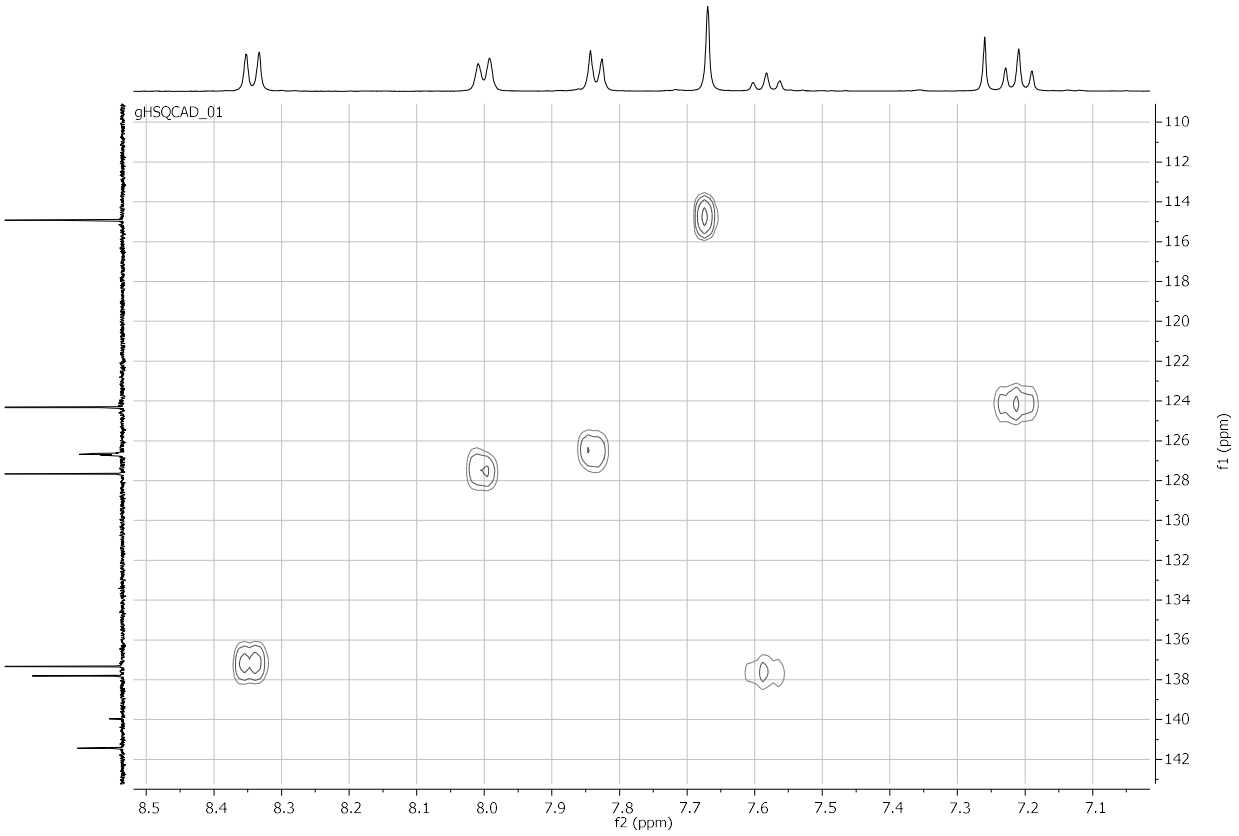
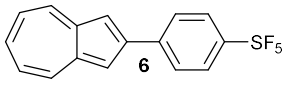
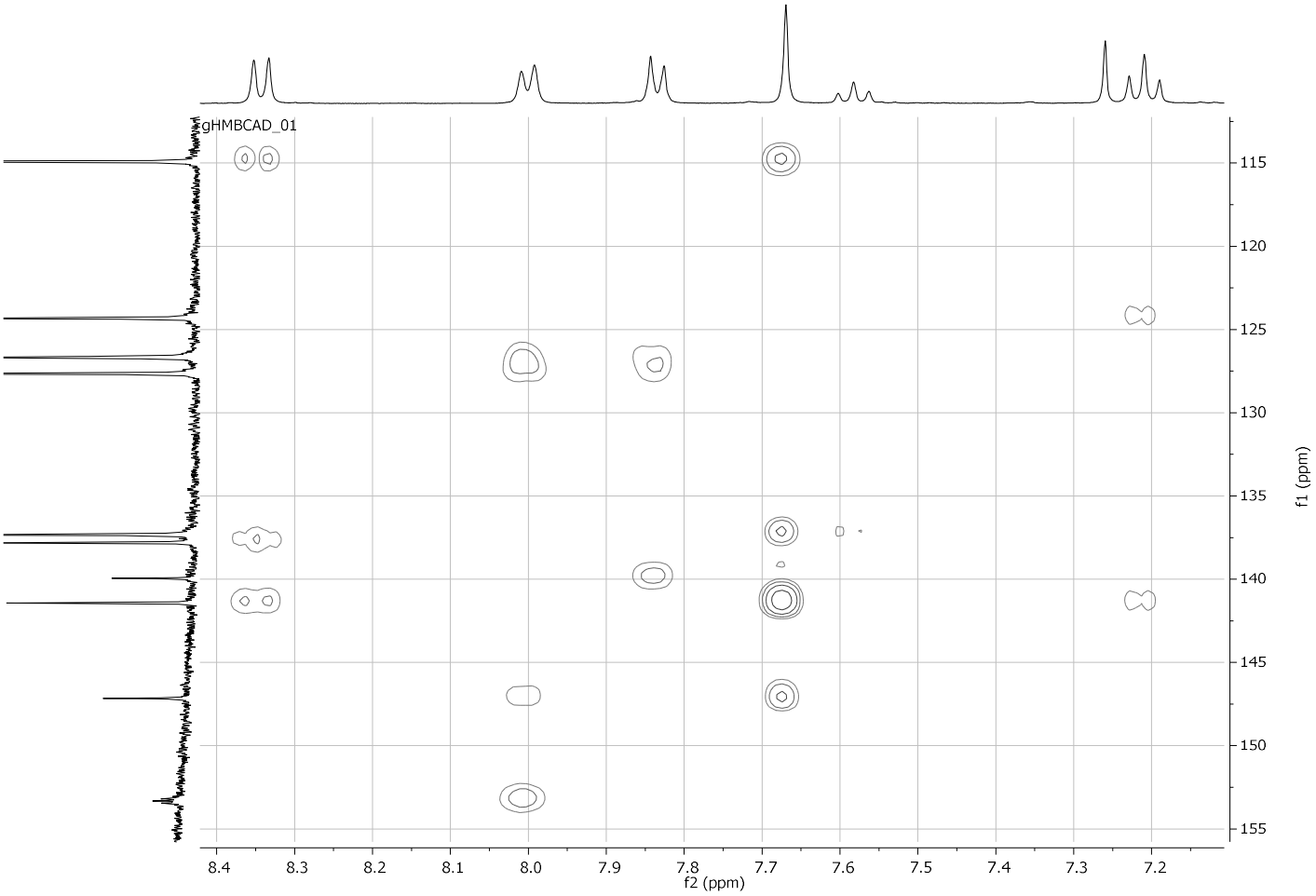



SF5

**6**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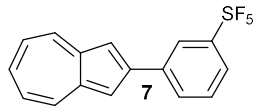
120
125
130
135
140
145
150
155
f1 (ppm)
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f2 (ppm)


SF5

7


2.09
1.06
1.00
1.00
2.10
2.11
2.07
8.5
8.0
7.5
7.0
6.5
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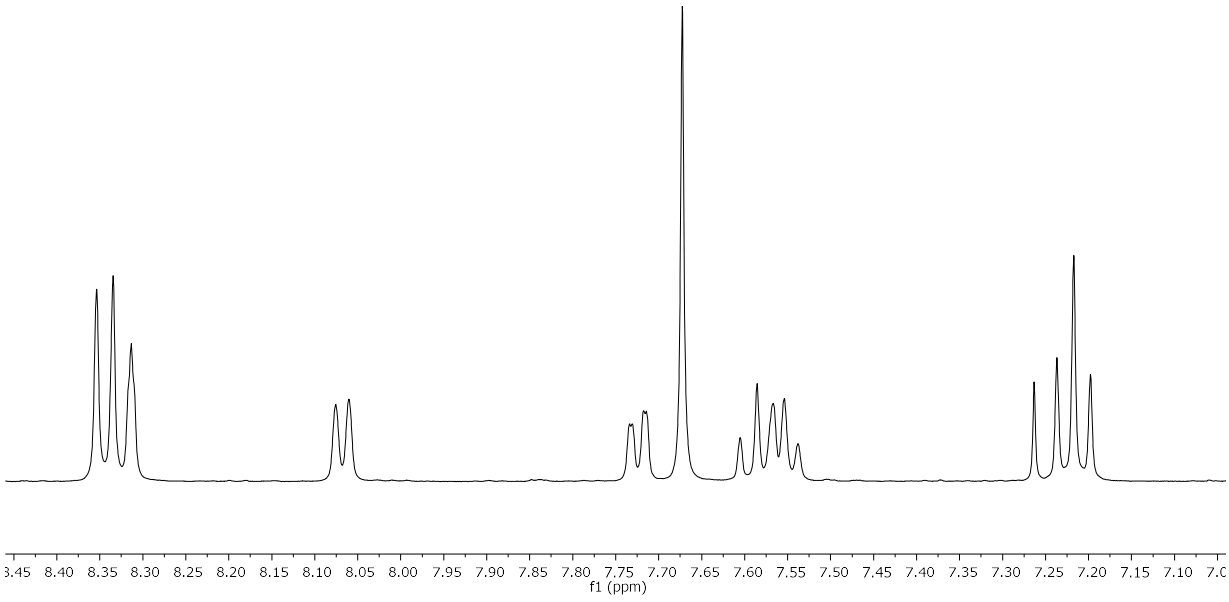
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)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7.80
7.75
7.70
7.65
7.60
7.55
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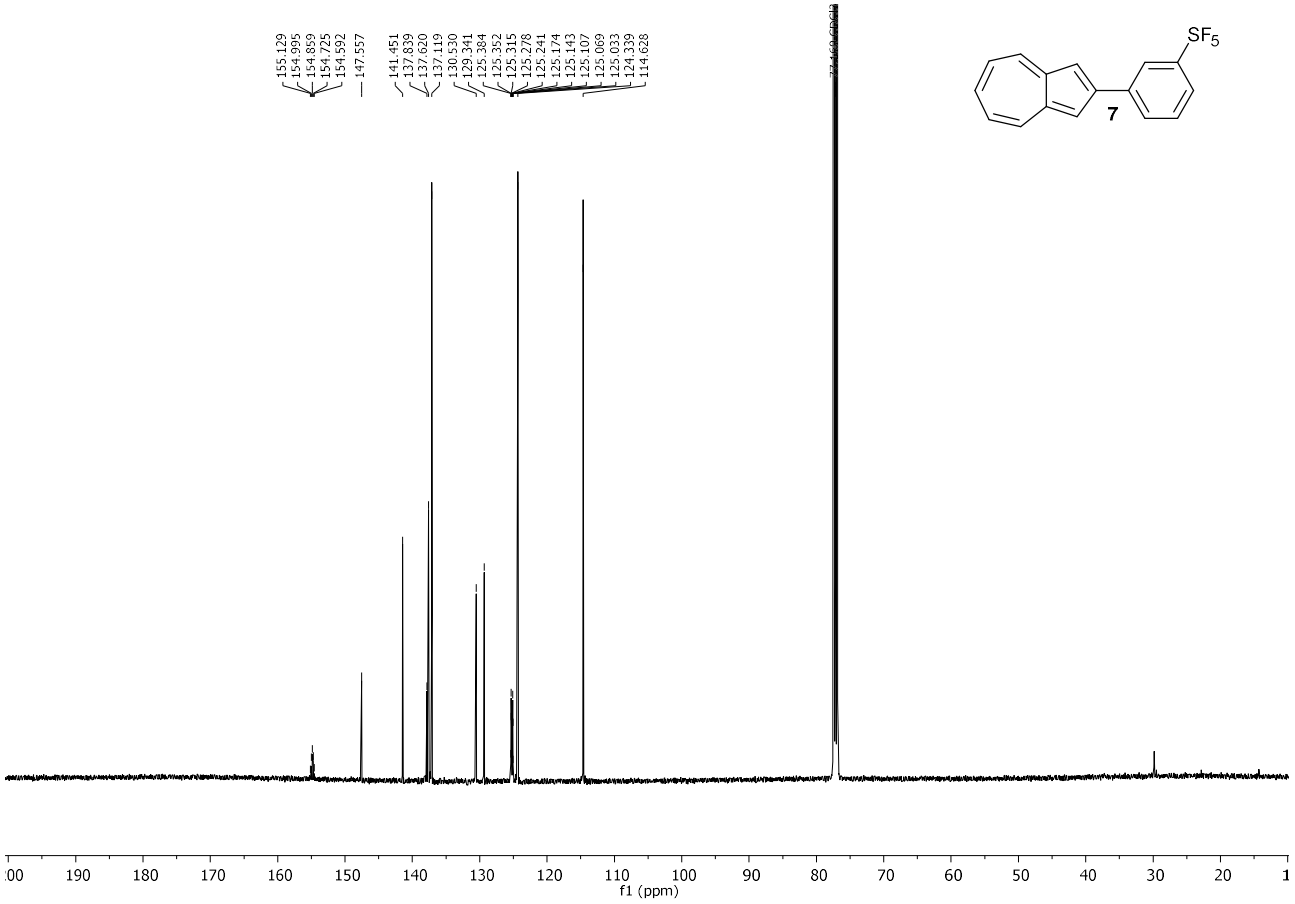
7.35
7.30
7.25
7.20
7.15
7.10
f1 (ppm)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130.530
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125.352
125.315
125.278
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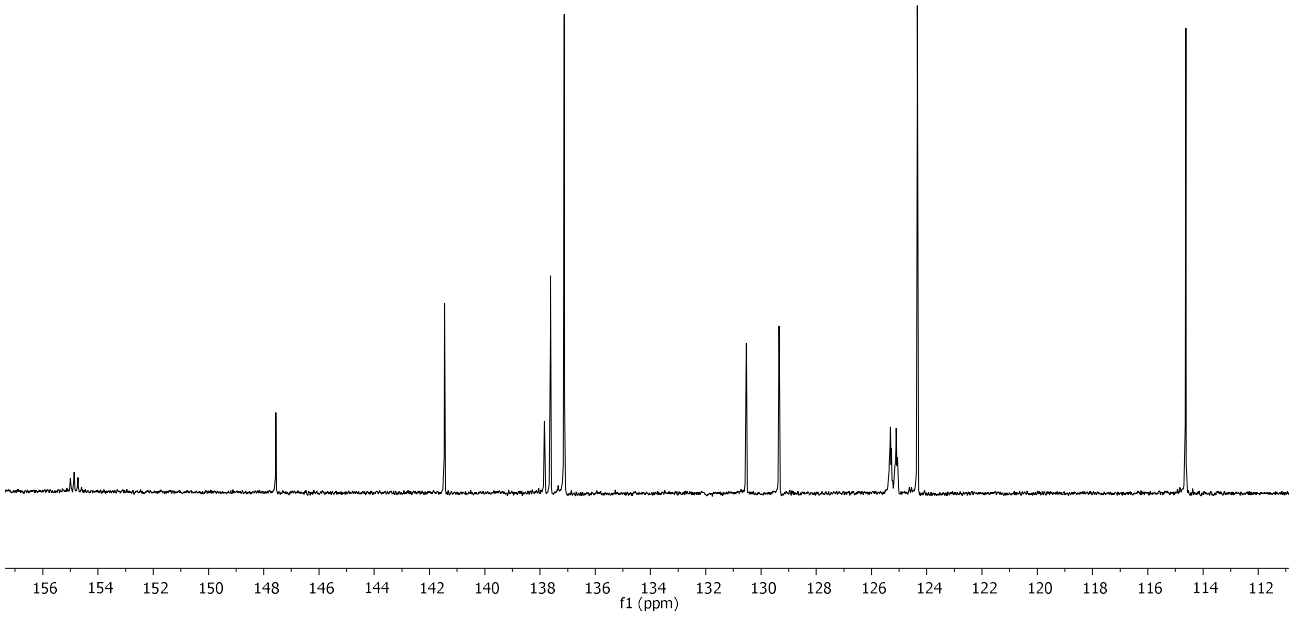
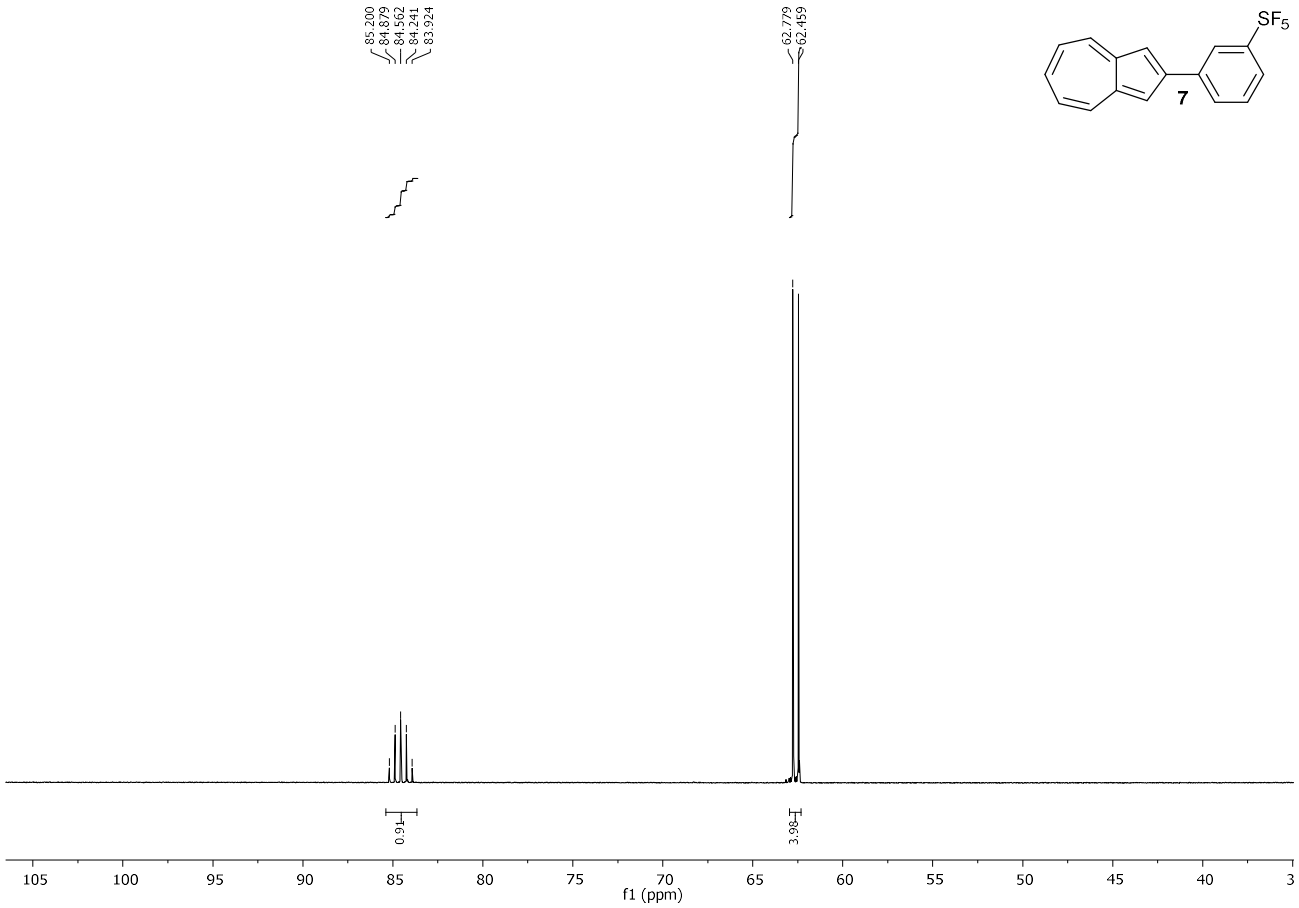
125.107
125.069
125.033
124.339
114.628
77.469 77.213
SF5
7
f1 (ppm)


f1 (ppm)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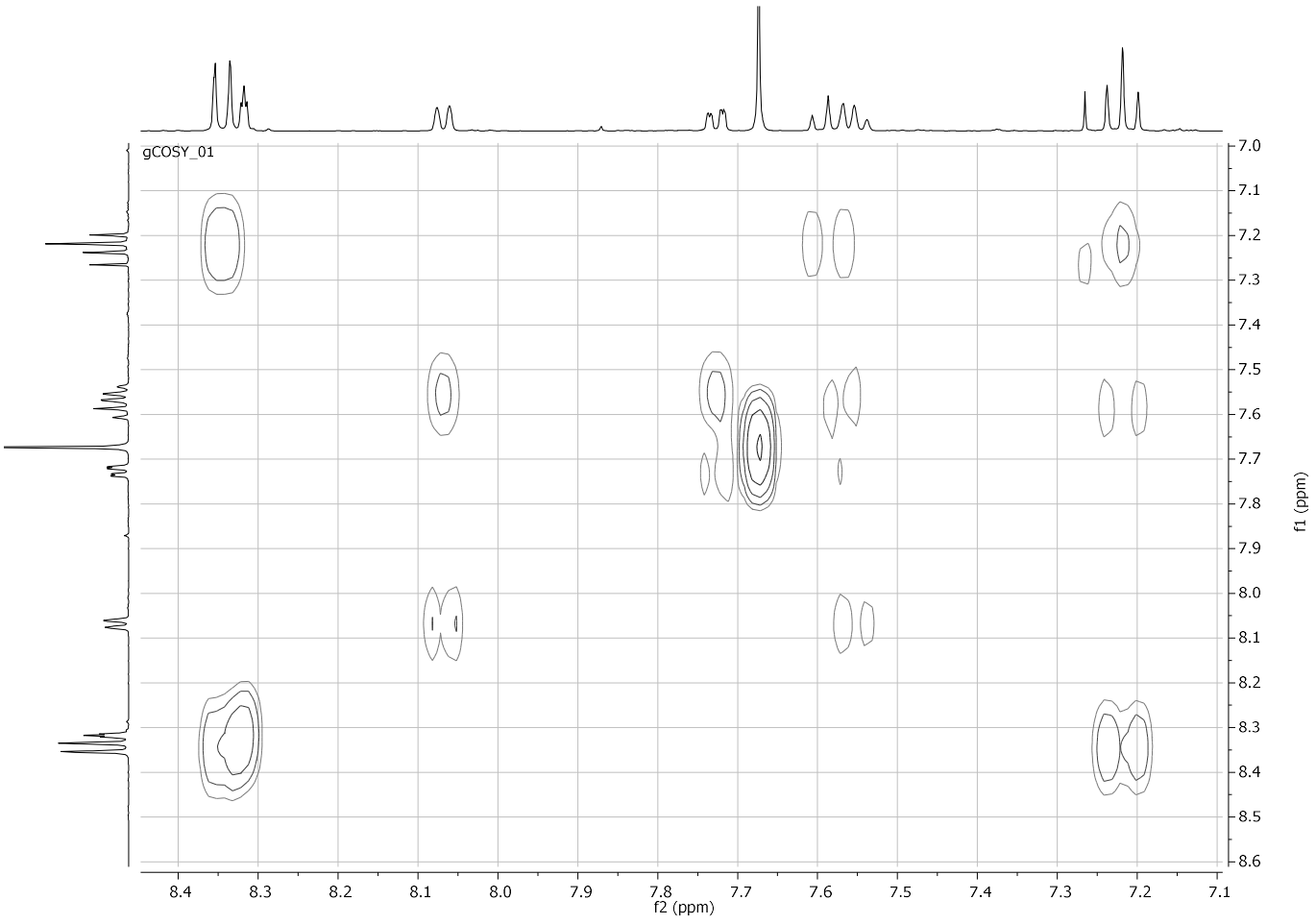
84.562
84.241
83.924
62.779
62.459
SF5
7
0.91
3.98
105
100
95
90
85
80
75
70
65
60
55
50
45
40
3
f1 (ppm)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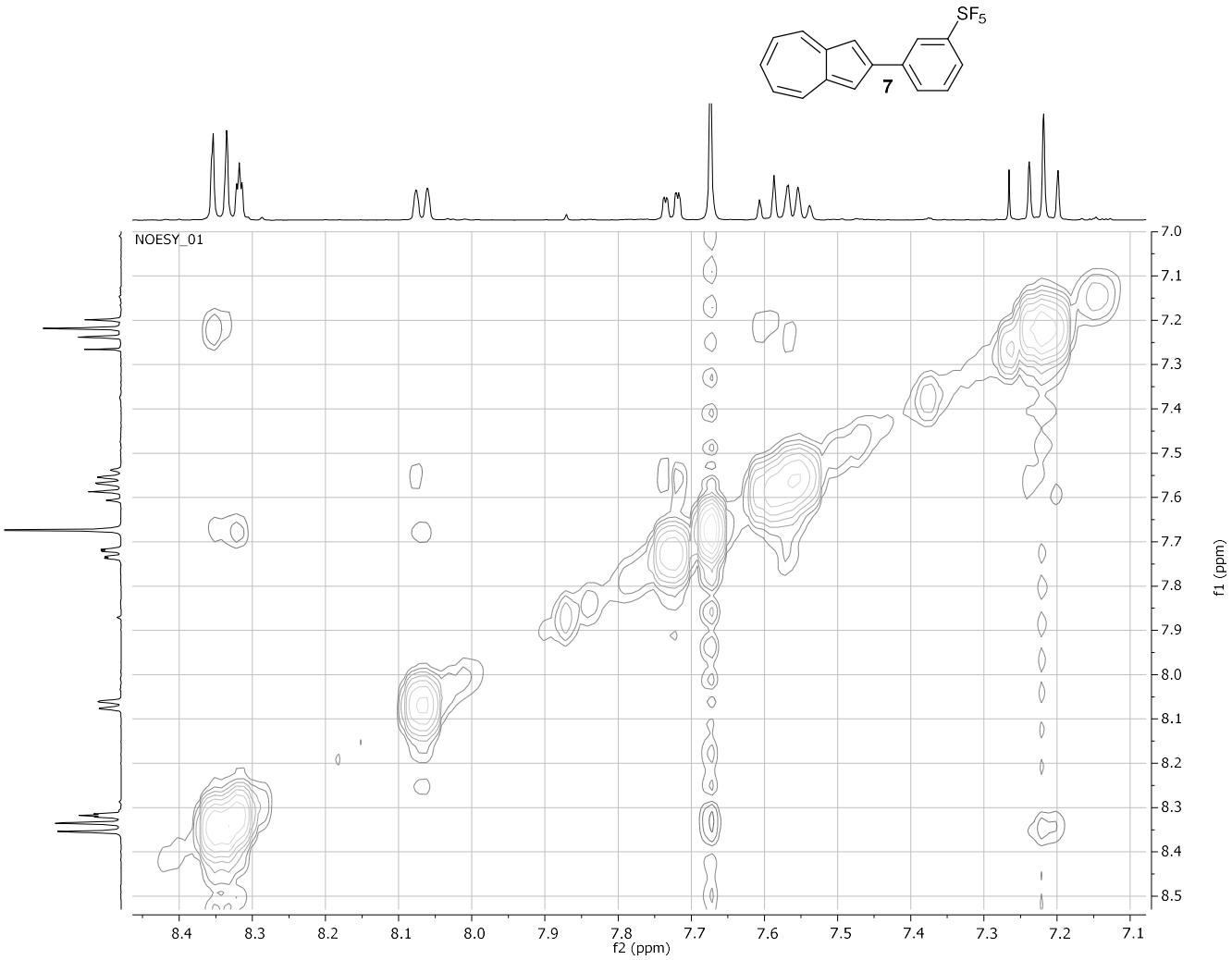
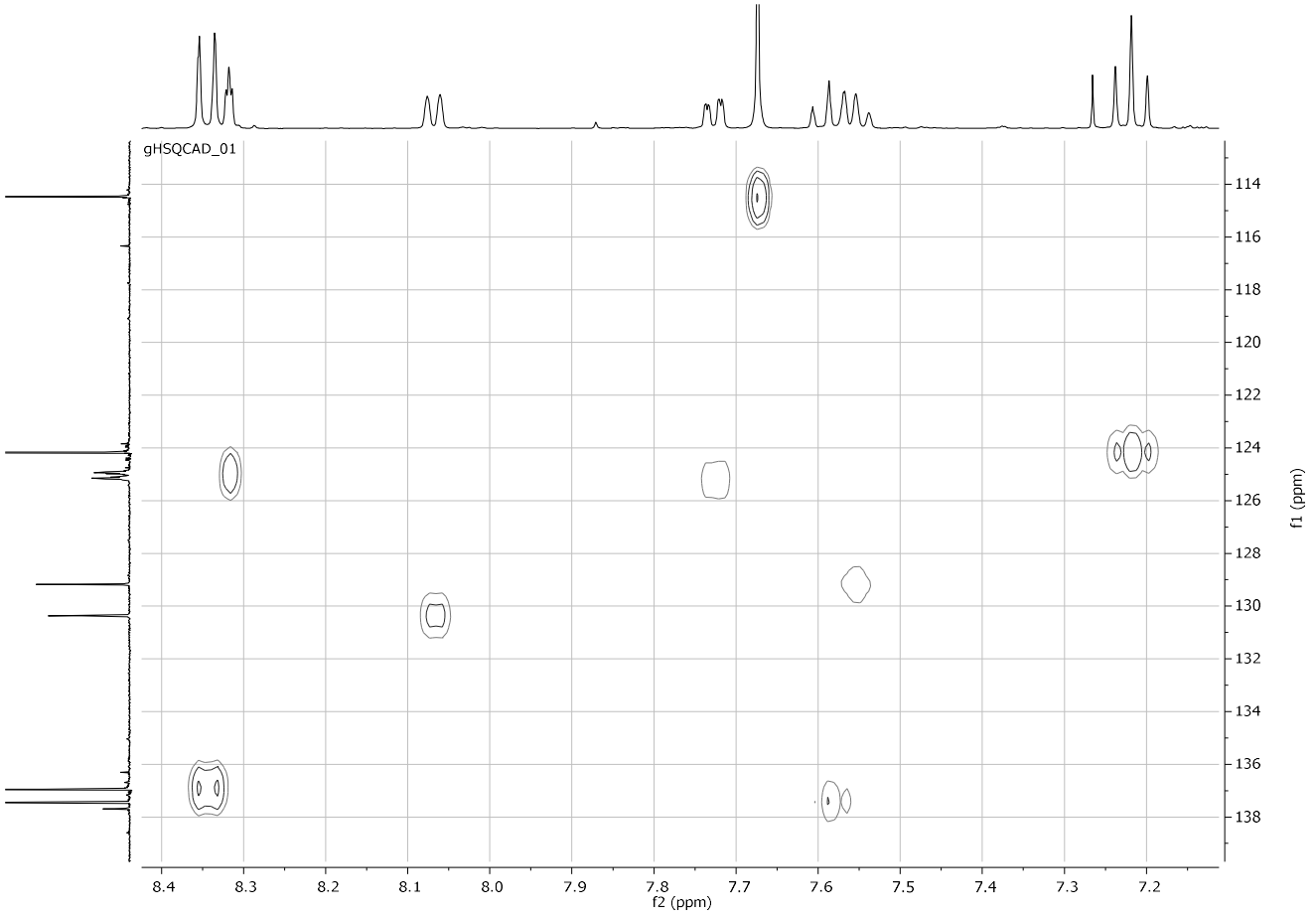
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.2
8.3
8.4
8.5
8.6
f1 (ppm)
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f2 (ppm)


SF5
7
NOESY_01
f2 (ppm)
f1 (ppm)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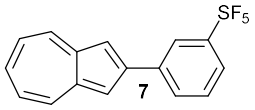
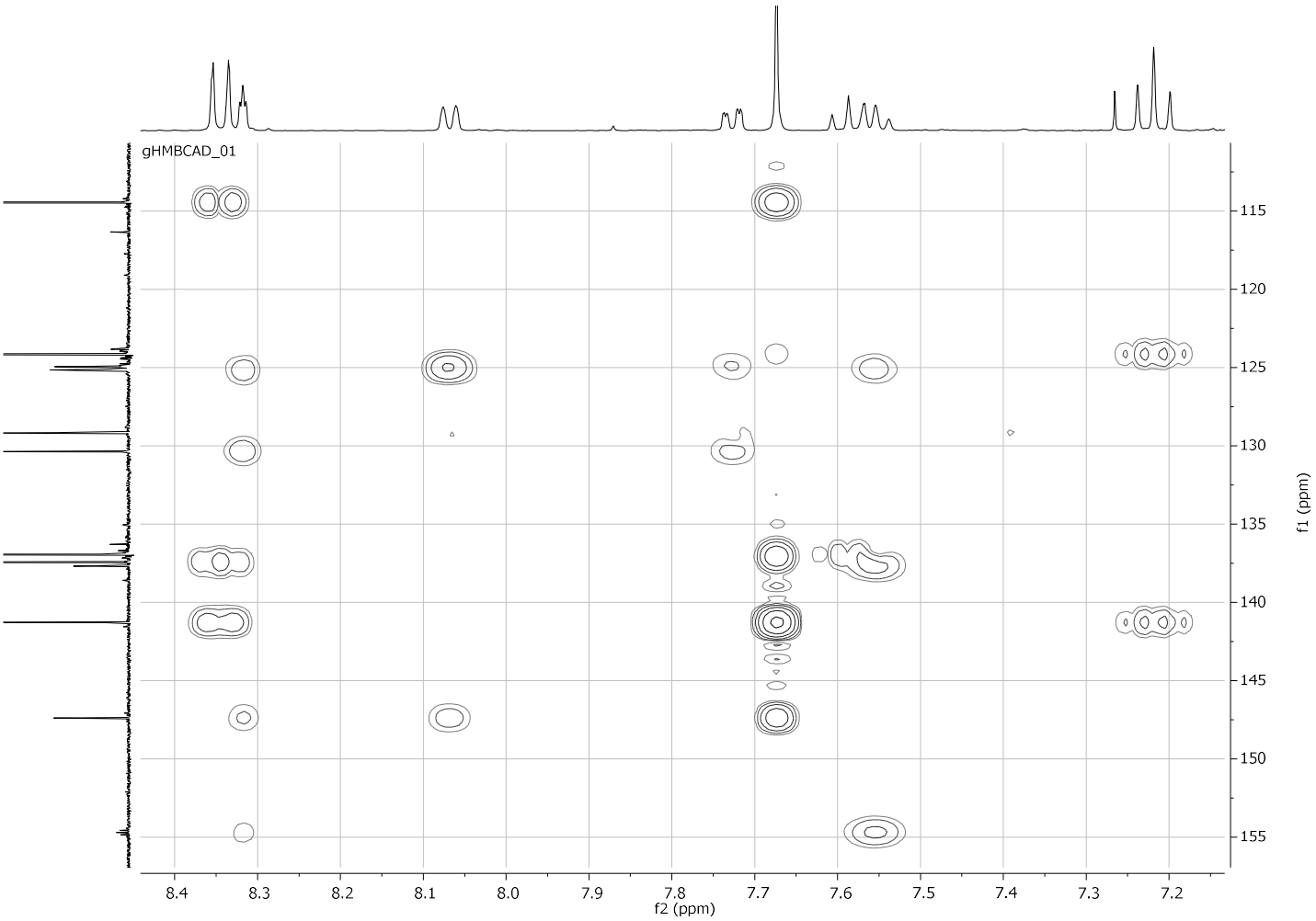
f2 (ppm)
f1 (ppm)


SF5

**7**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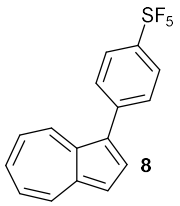
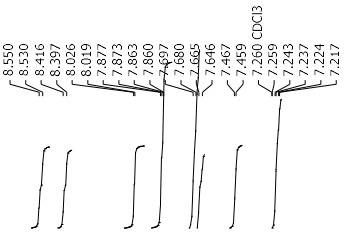
115
120
125
130
135
140
145
150
155
f1 (ppm)
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f2 (ppm)


SF5
8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8.019
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7.863
7.860
7.697
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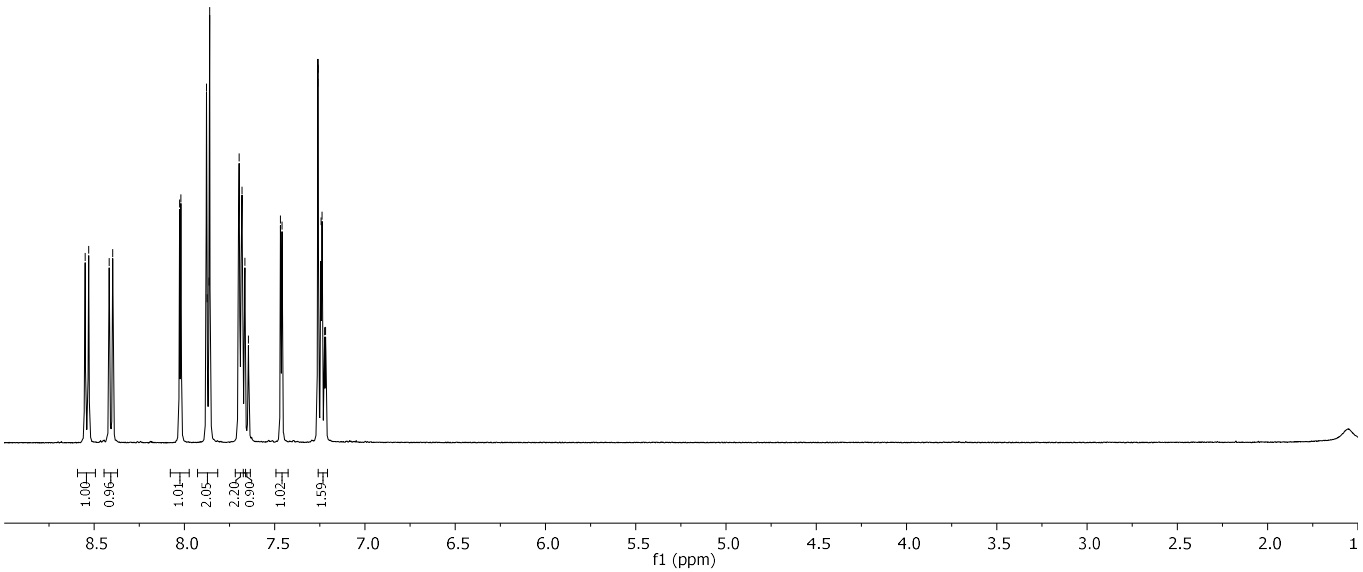
7.259
7.243
7.237
7.224
7.217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2.05
2.20
0.90
1.02
1.59
8.5
8.0
7.5
7.0
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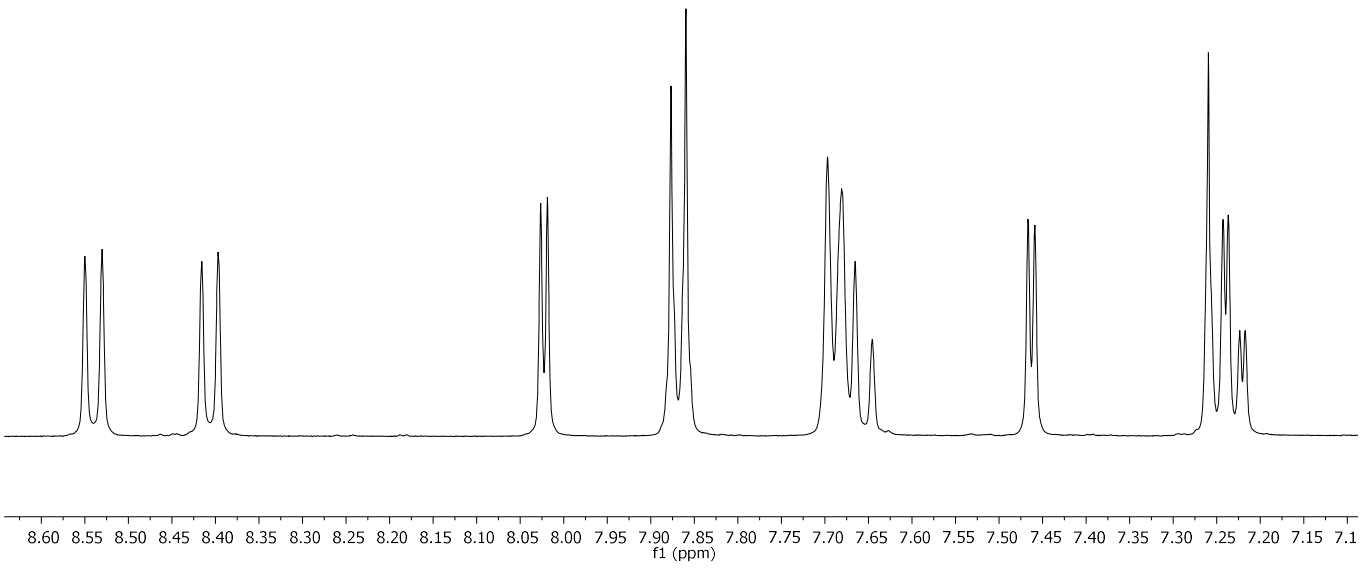
3.5
3.0
2.5
2.0
1
f1 (ppm)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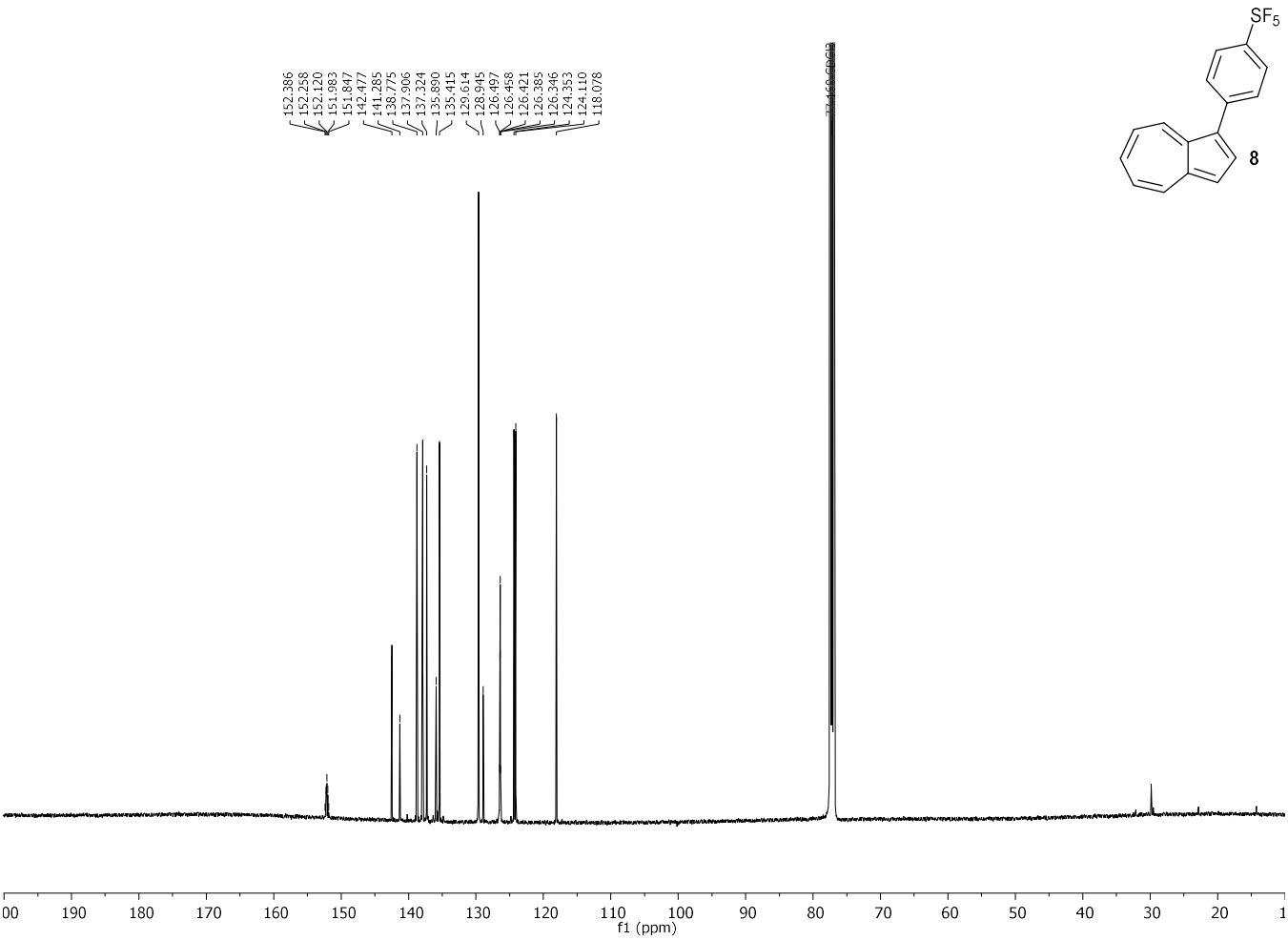
f1 (ppm)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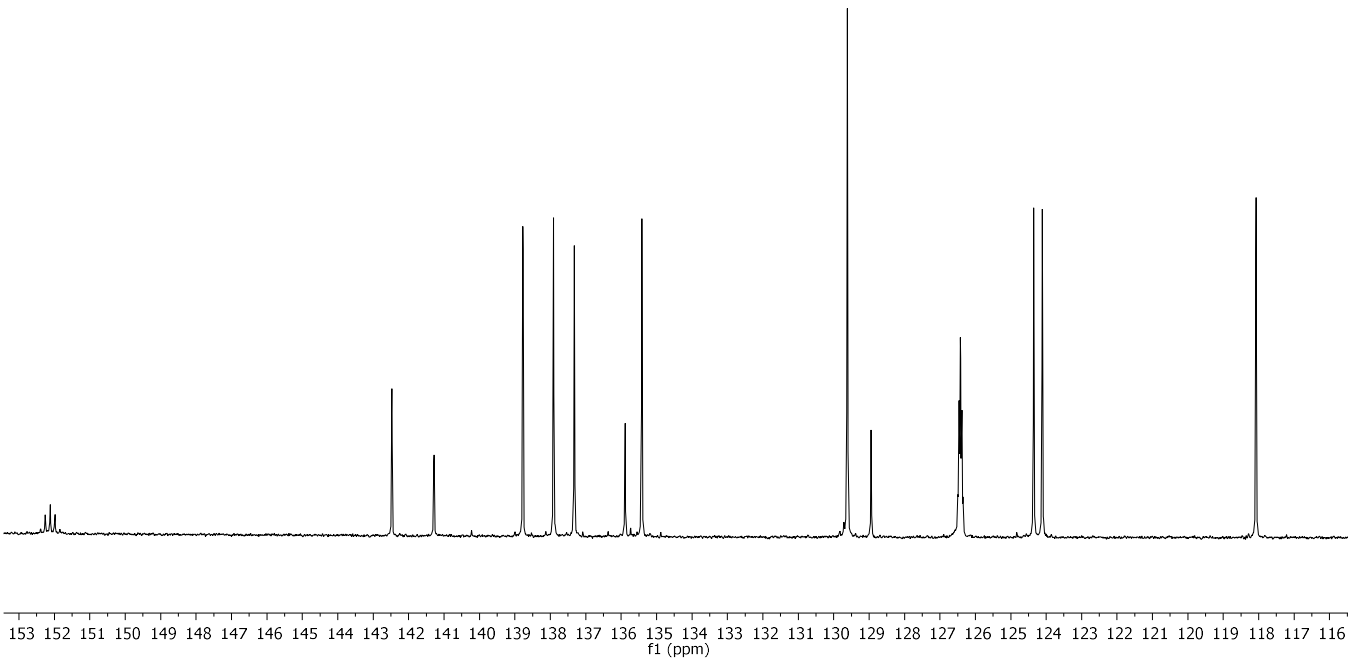
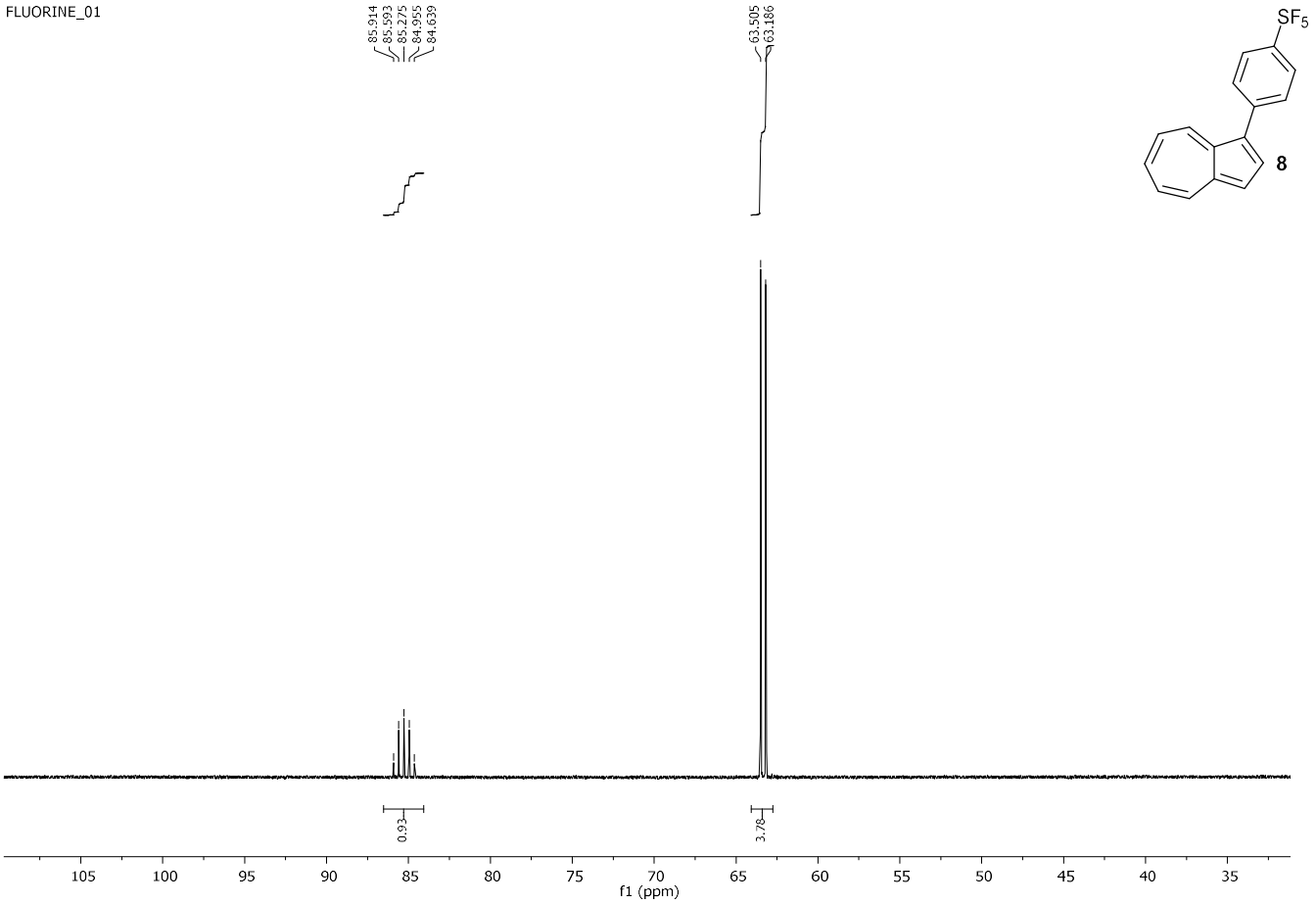
137.324
135.890
135.415
129.614
128.945
126.497
126.458
126.421
126.385
126.346
124.353
124.110
118.078
SF5
8
f1 (ppm)


f1 (ppm)


FLUORINE_01
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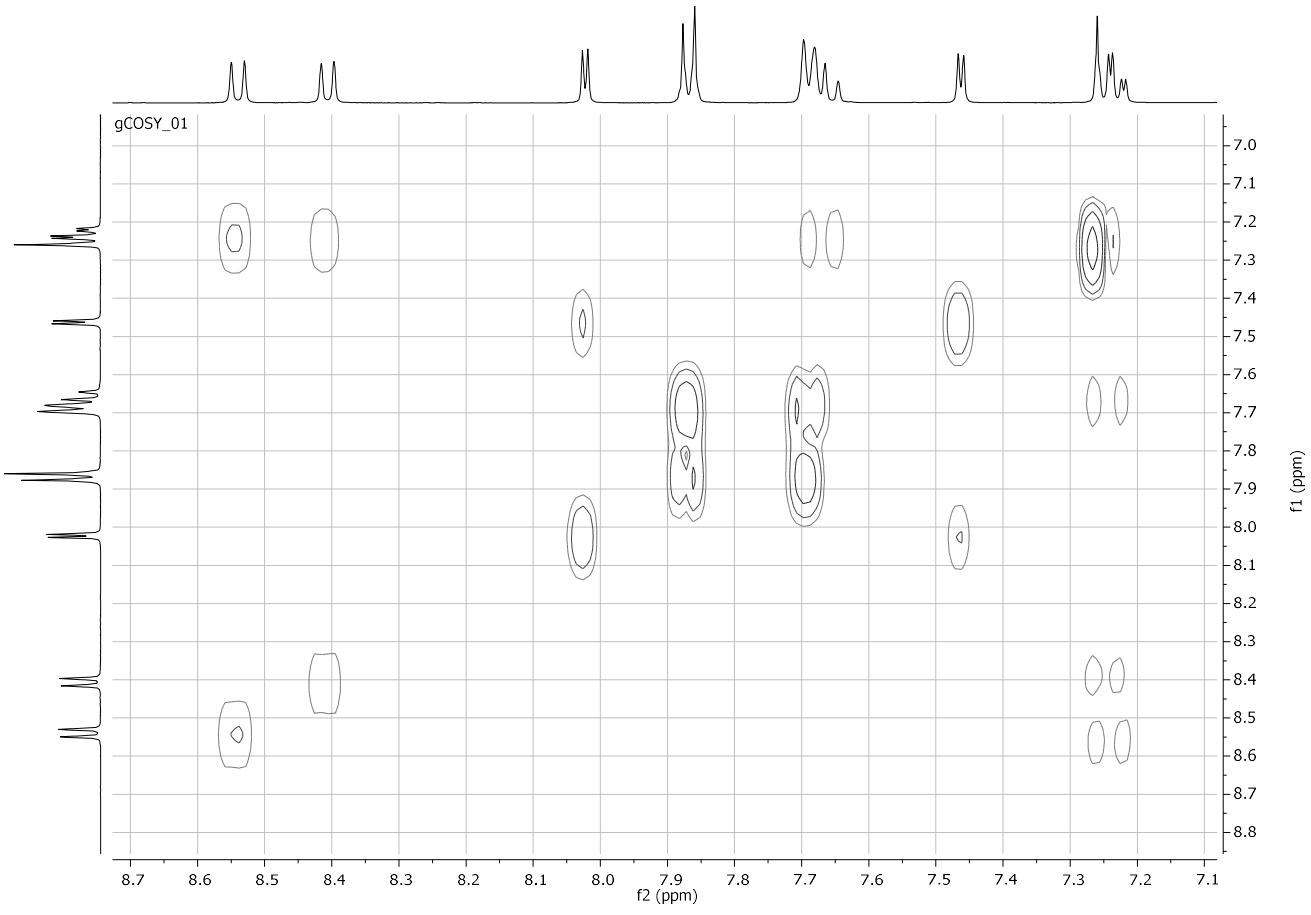
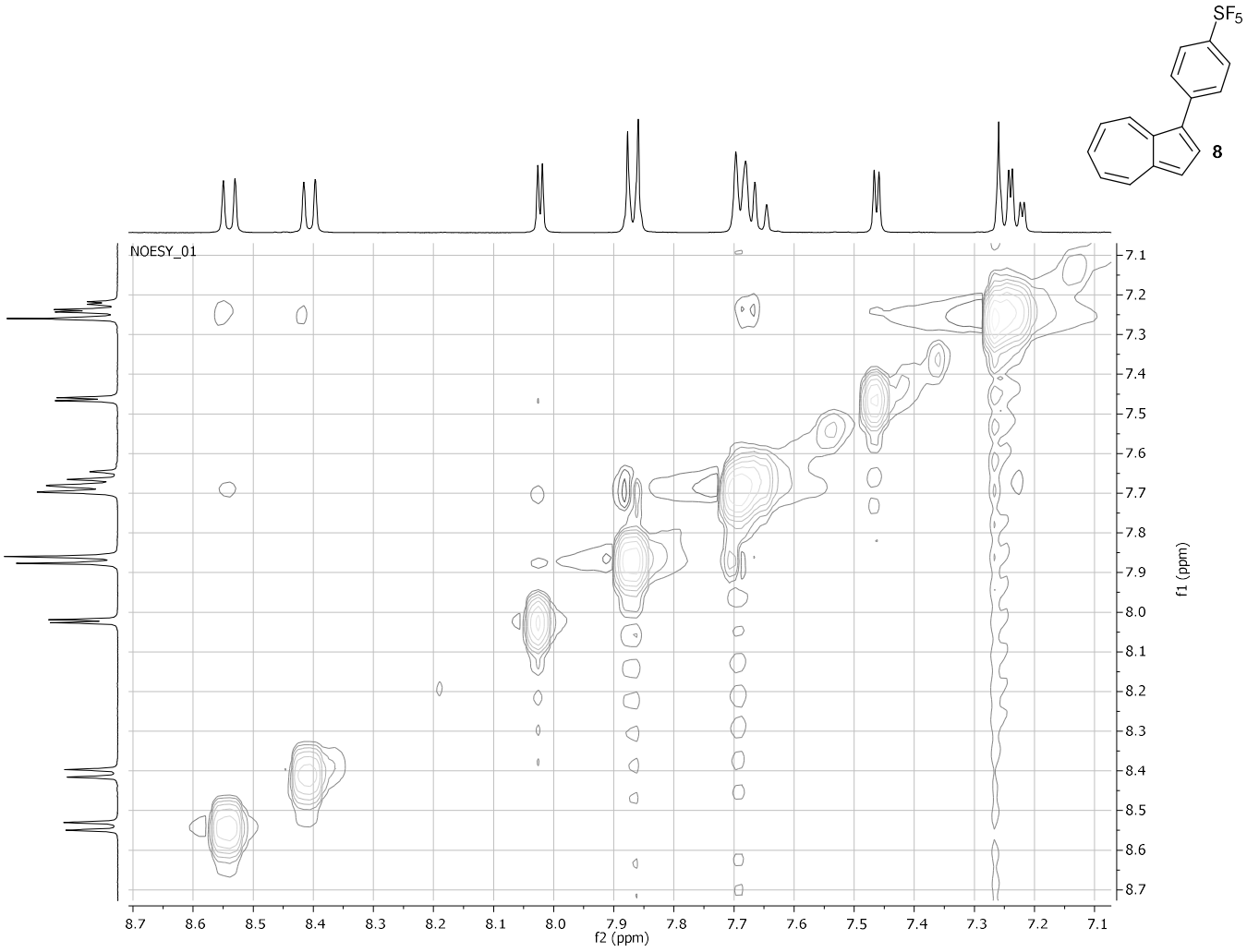
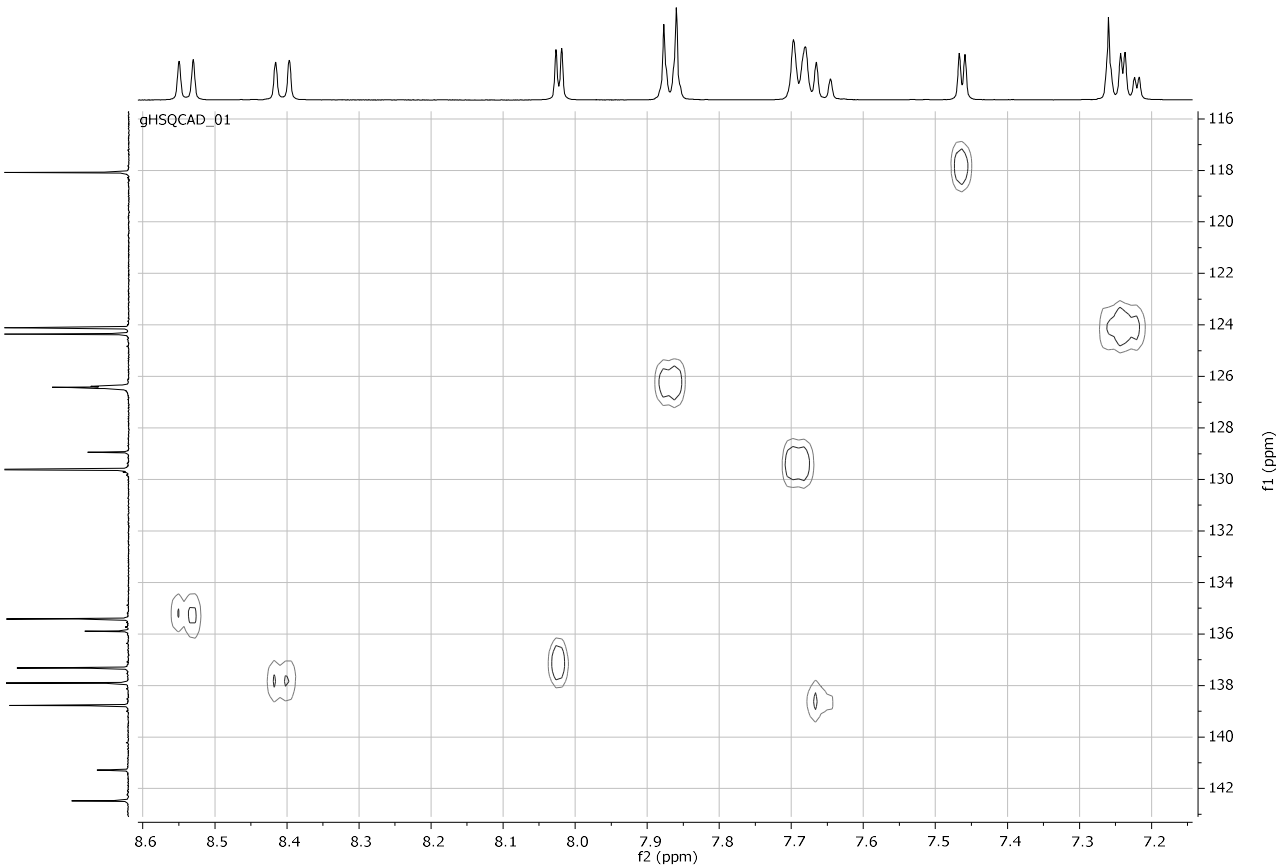
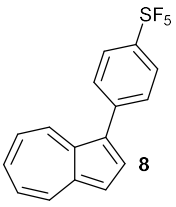
85.593
85.275
84.955
84.639
63.505
63.186
SF5
8
0.93
3.78
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
f1 (ppm)

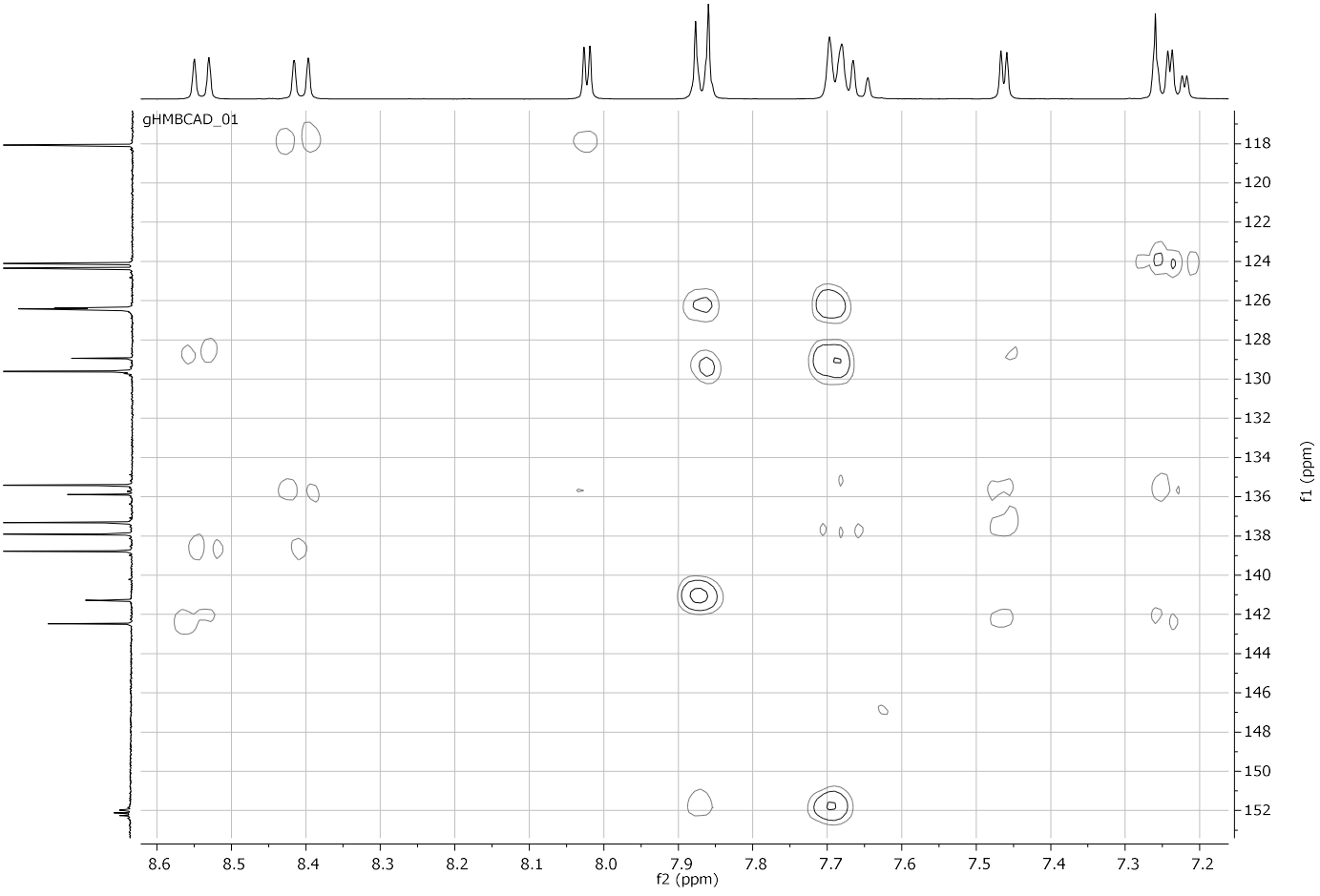

gCOSY_01
7.0
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.2
8.3
8.4
8.5
8.6
8.7
8.8
f1 (ppm)
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f2 (ppm)

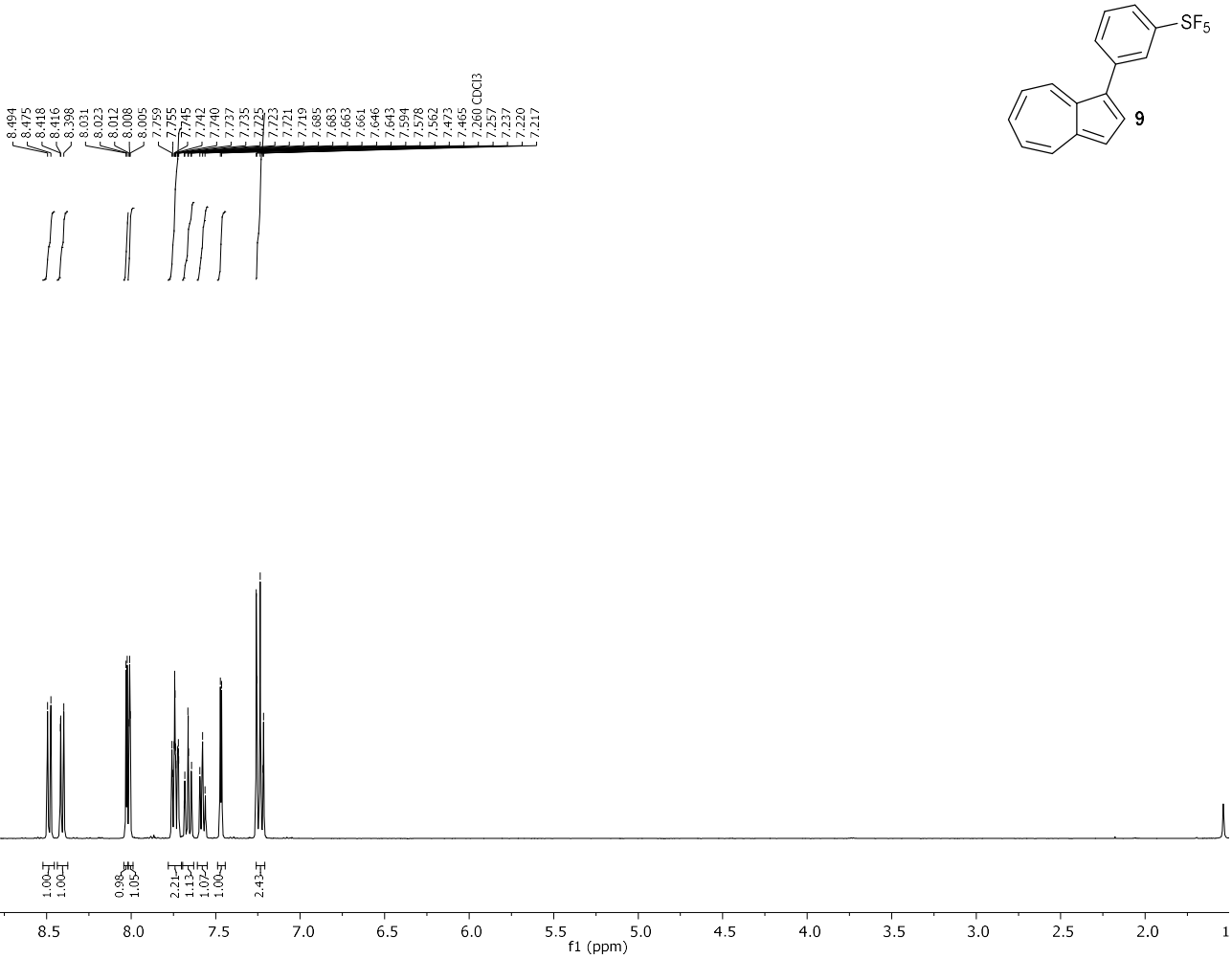

SF5
8
NOESY_01
f1 (ppm)
f2 (ppm)

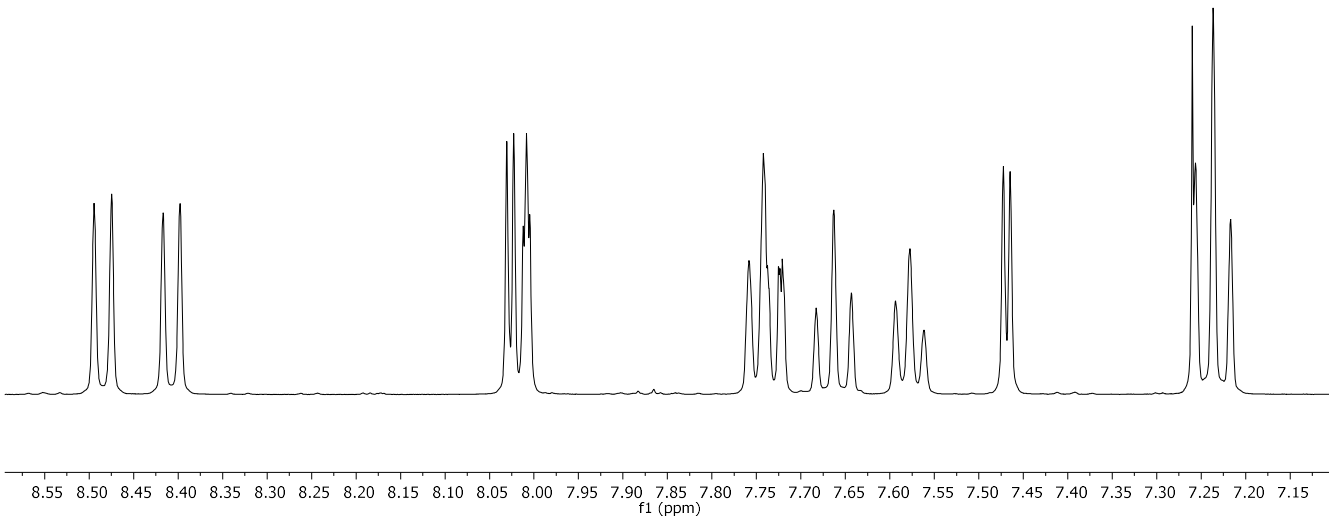

gHSQCAD_01
f1 (ppm)
f2 (ppm)

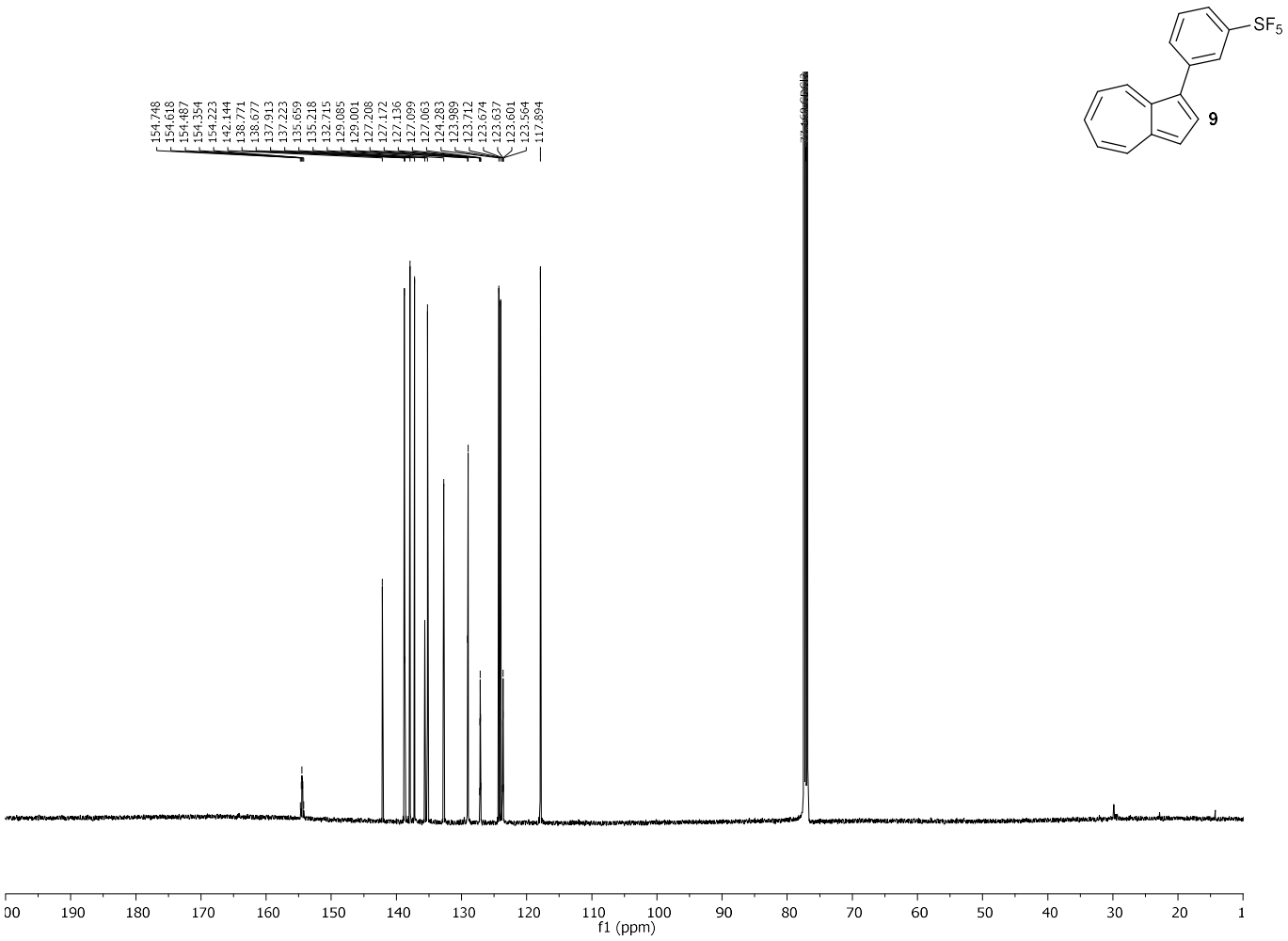

SF5

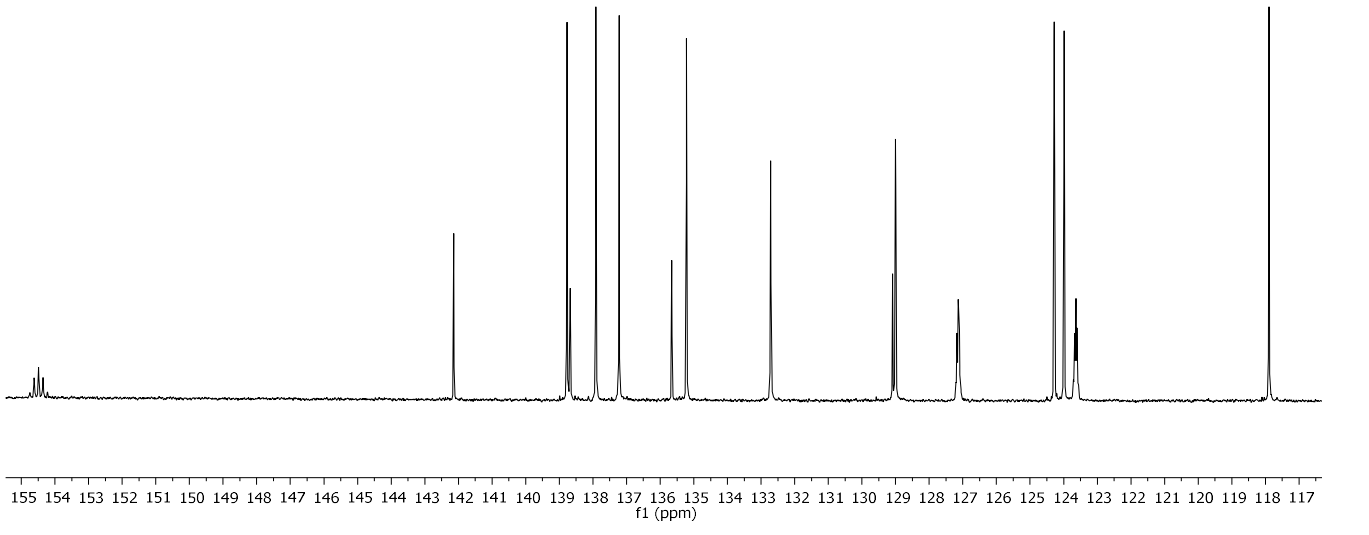
**8**

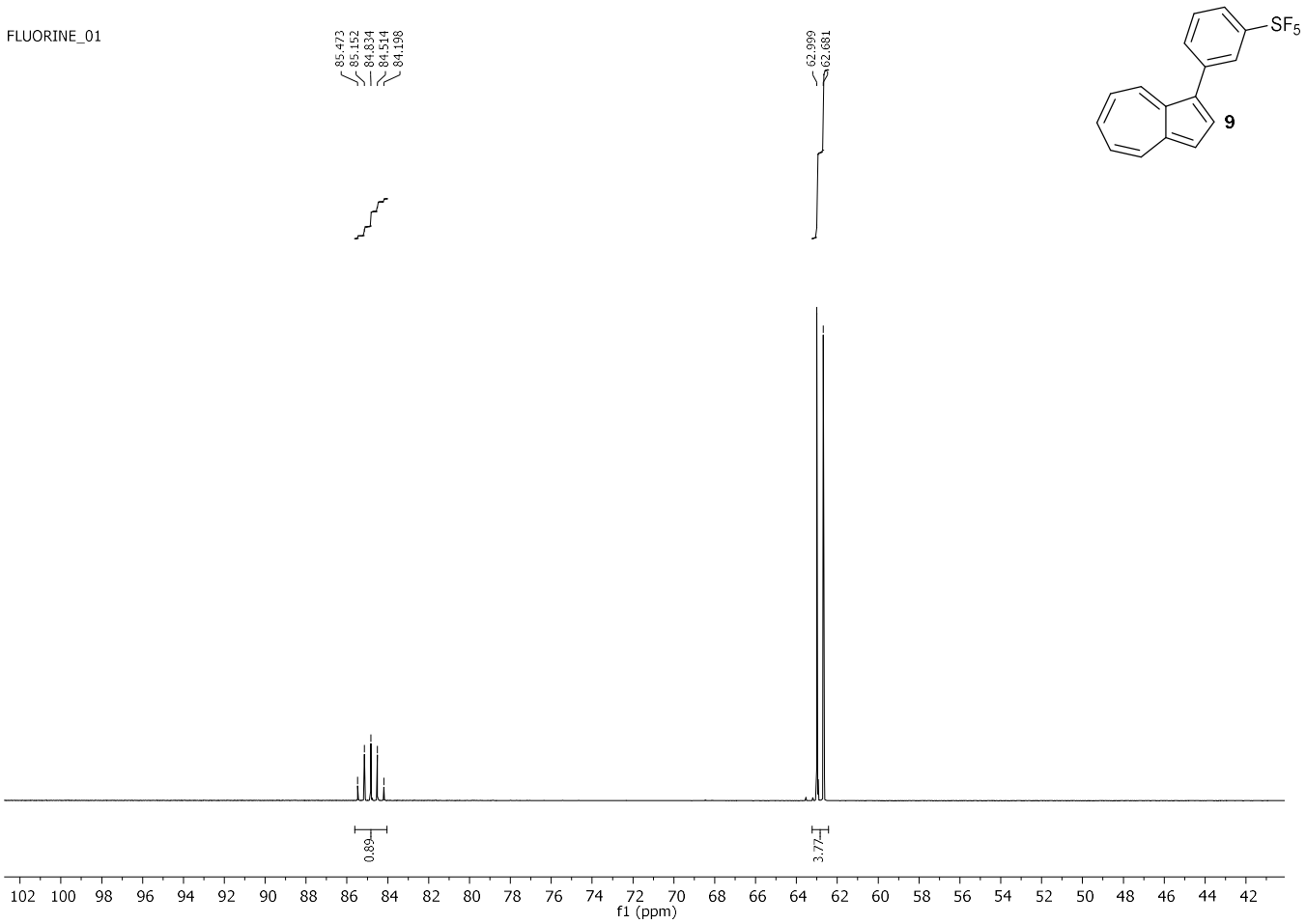

gHMBCAD_01
118
120
122
124
126
128
130
132
134
136
138
140
142
144
146
148
150
152
f1 (ppm)
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f2 (ppm)

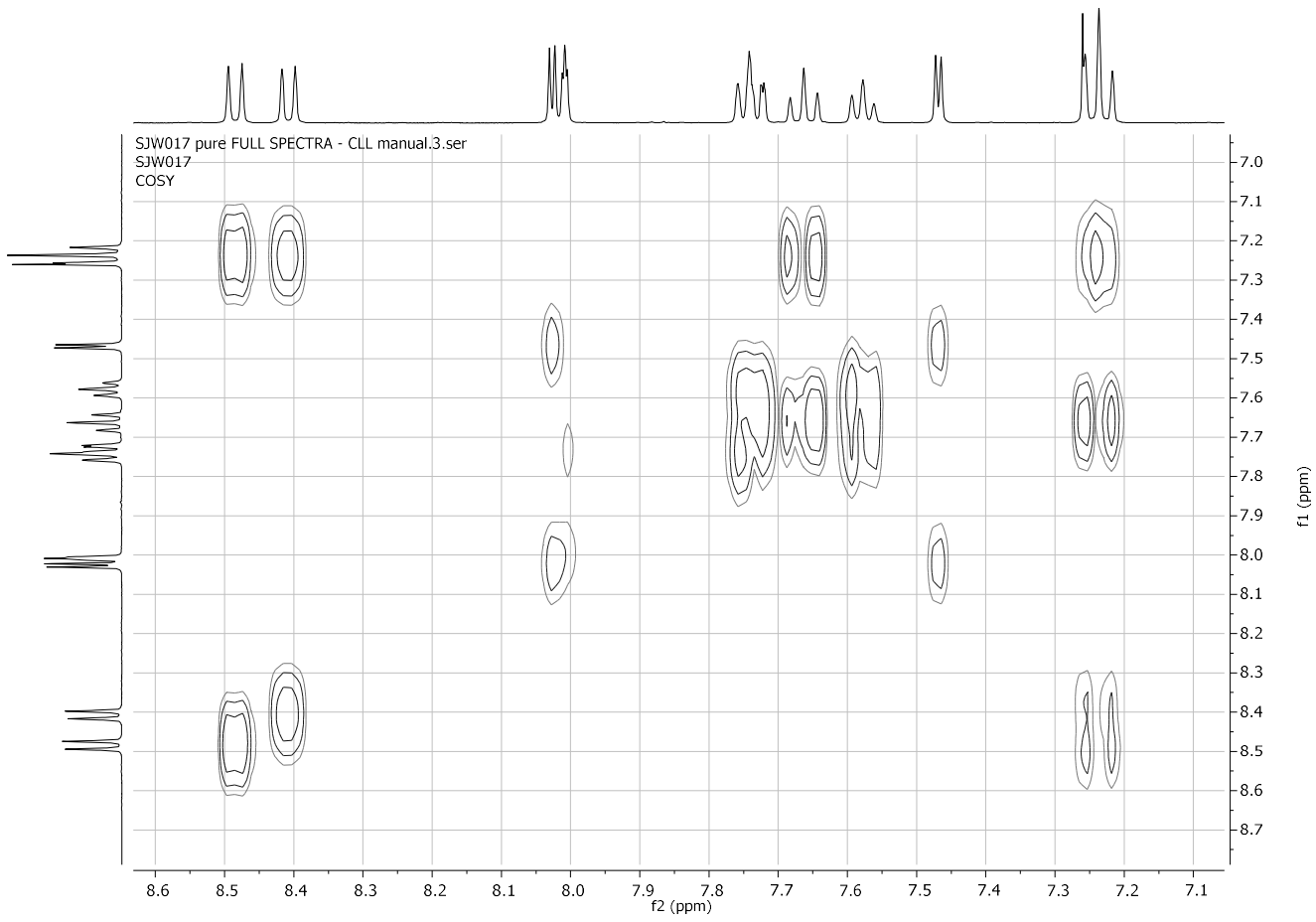

8.494
8.475
8.418
8.416
8.398
8.031
8.023
8.012
8.008
8.005
7.759
7.755
7.745
7.742
7.740
7.737
7.735
7.725
7.723
7.721
7.719
7.685
7.683
7.663
7.661
7.646
7.643
7.594
7.578
7.562
7.473
7.465
7.260 CDCl3
7.257
7.237
7.220
7.217
SF5
9
1.00
1.00
0.98
1.05
2.21
1.13
1.07
1.00
2.43
f1 (ppm)

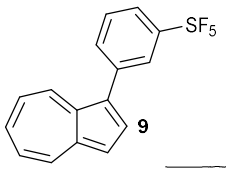

f1 (ppm)


SF5
9
154.748
154.618
154.487
154.354
154.223
142.144
138.771
138.677
137.913
137.223
135.659
135.218
132.715
129.085
129.001
127.208
127.172
127.136
127.099
127.063
124.283
123.989
123.712
123.674
123.637
123.601
123.564
117.894
f1 (ppm)


f1 (ppm)

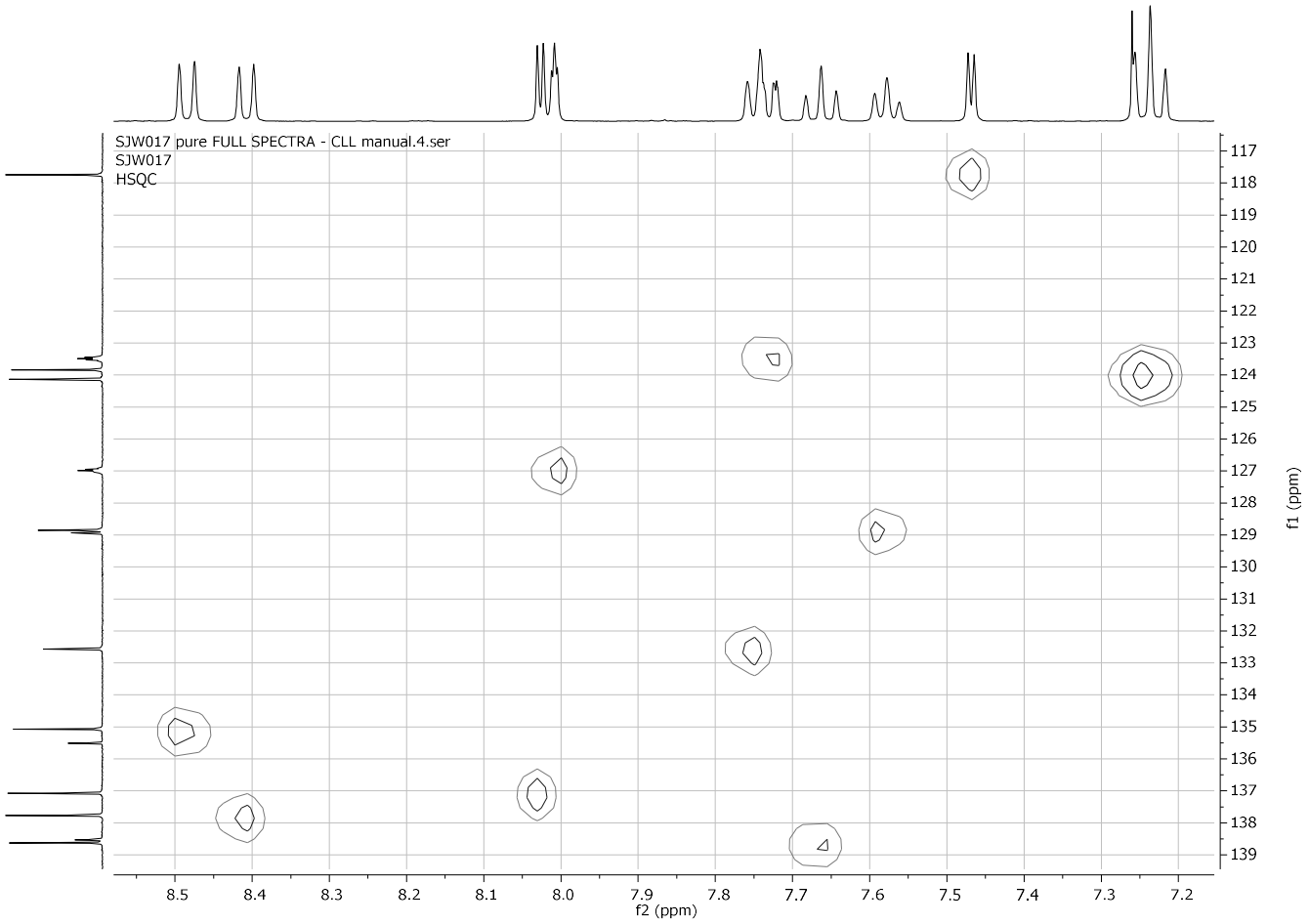

FLUORINE_01
85.473
85.152
84.834
84.514
84.198
62.999
62.681
SF5
9
0.89
3.77
f1 (ppm)

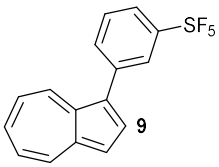

SJW017 pure FULL SPECTRA - CLL manual.3.ser
SJW017
COSY
f2 (ppm)
f1 (ppm)


SF5

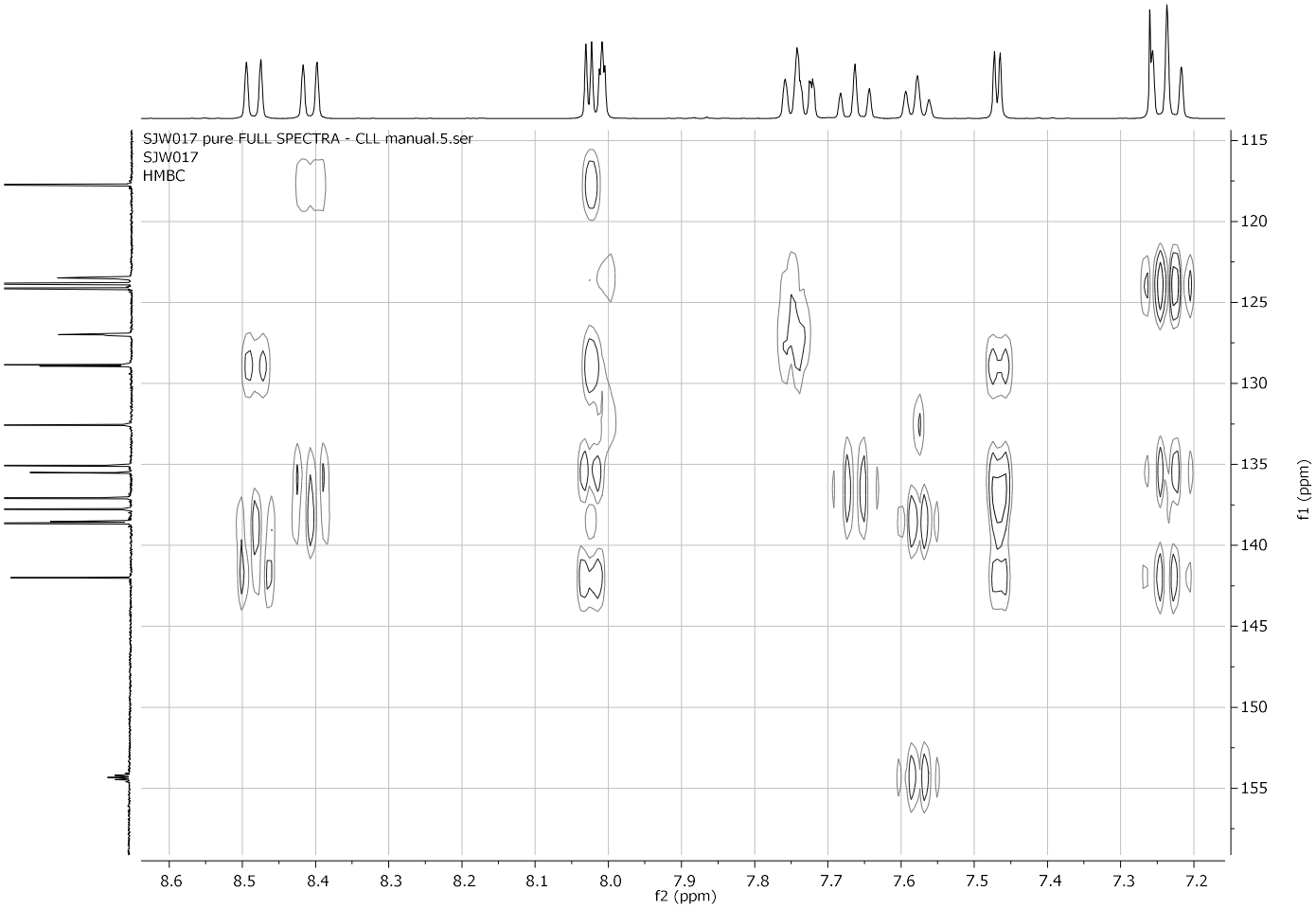
**9**


SJW017 pure FULL SPECTRA - CLL manual.6.ser
SJW017
NOESY
f2 (ppm)
f1 (ppm)

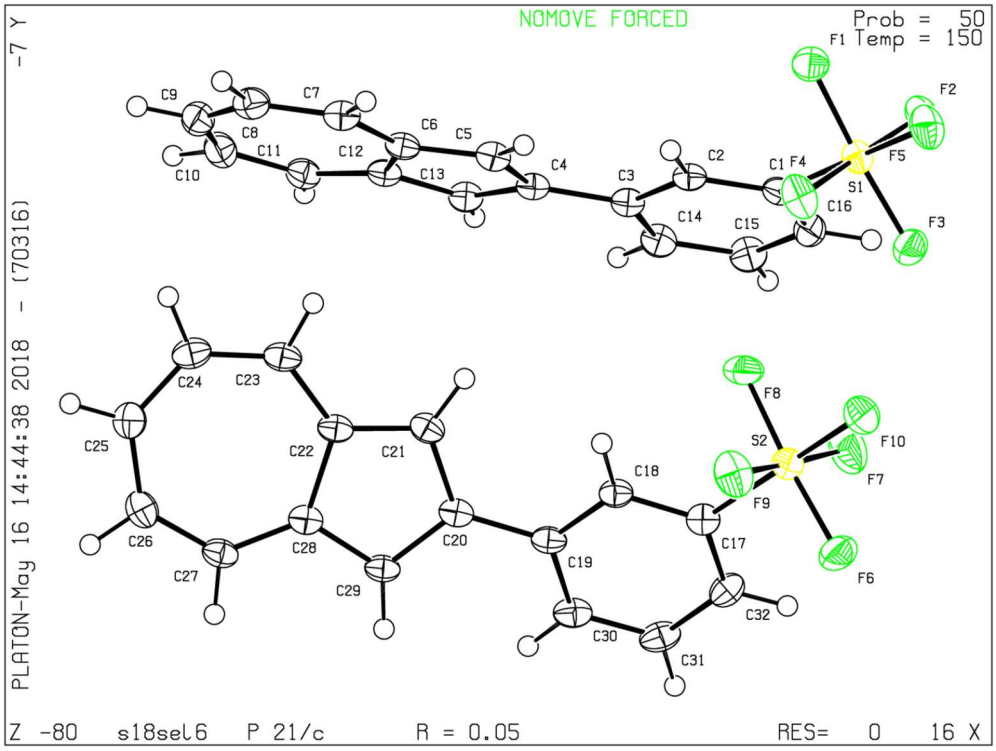

SJW017 pure FULL SPECTRA - CLL manual.4.ser
SJW017
HSQC
f2 (ppm)
f1 (ppm)


SF5

**9**


SJW017 pure FULL SPECTRA - CLL manual.5.ser
SJW017
HMBC
f2 (ppm)
f1 (ppm)

**Crystallographic supporting Information for 7**



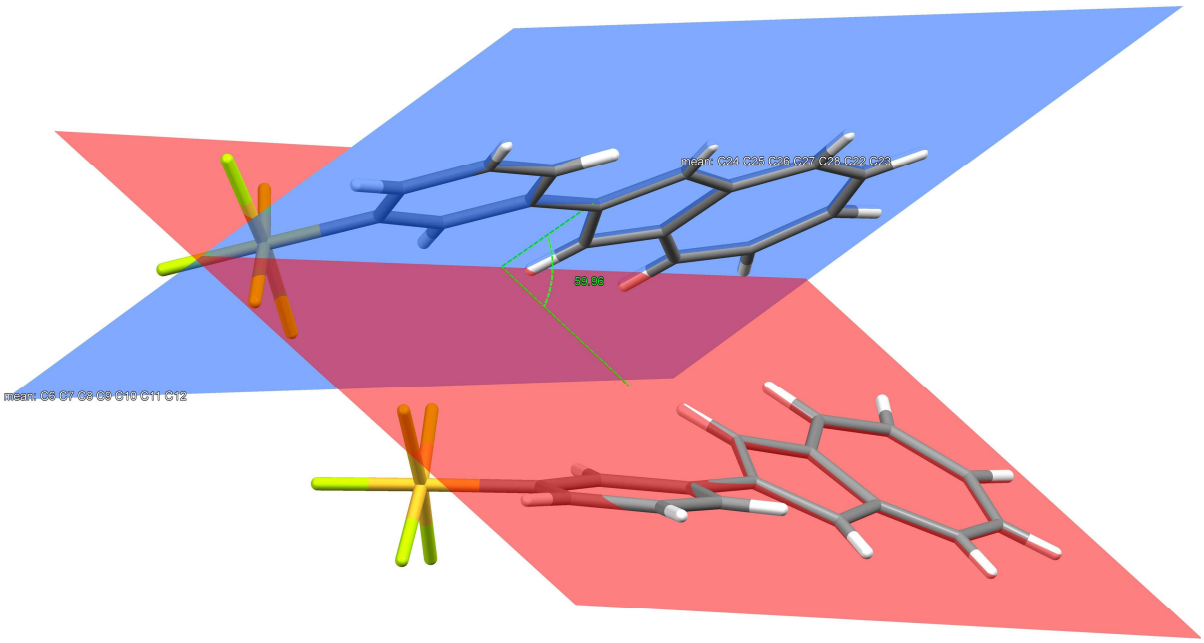



**Table S3**. Crystal data and structure refinement for **7**.

| | | |
|---|---|---|
| CCDC Identification code | 1850019 | |
| Empirical formula | $C_{16}H_{11}F_5S$ | |
| Formula weight | 330.31 | |
| Temperature | 150.0(3) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 9.8076(2) Å | α= 90°. |
| | b = 27.7775(5) Å | β= 103.526(2)°. |
| | c = 10.2800(2) Å | γ = 90°. |
| Volume | 2722.91(9) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.611 $Mg/m^3$ | |
| Absorption coefficient | 2.616 $mm^{-1}$ | |
| F(000) | 1344 | |
| Crystal size | 0.287 x 0.203 x 0.041 $mm^3$ | |
| Theta range for data collection | 3.182 to 73.202°. | |
| Index ranges | -12<=h<=12, -32<=k<=34, -11<=l<=12 | |
| Reflections collected | 25699 | |
| Independent reflections | 5428 [R(int) = 0.0495] | |
| Completeness to theta = 67.684° | 99.9 % | |
| Absorption correction | Gaussian | |
| Max. and min. transmission | 1.000 and 0.435 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5428 / 0 / 397 | |
| Goodness-of-fit on $F^2$ | 1.106 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0537, wR2 = 0.1215 | |
| R indices (all data) | R1 = 0.0608, wR2 = 0.1249 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.422 and -0.543 $e.Å^{-3}$ | |

**Table S4**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **7**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 8600(1) | 2769(1) | 7378(1) | 23(1) |
| F(1) | 10002(2) | 3058(1) | 7981(2) | 31(1) |
| F(2) | 9254(2) | 2574(1) | 6208(2) | 29(1) |
| F(3) | 7266(2) | 2440(1) | 6859(2) | 32(1) |
| F(4) | 8012(2) | 2921(1) | 8636(2) | 32(1) |
| F(5) | 9308(2) | 2320(1) | 8239(2) | 35(1) |
| C(1) | 7794(3) | 3278(1) | 6406(3) | 21(1) |
| C(2) | 7889(3) | 3726(1) | 7002(3) | 20(1) |
| C(3) | 7280(3) | 4126(1) | 6254(3) | 21(1) |
| C(4) | 7393(3) | 4608(1) | 6868(3) | 21(1) |
| C(5) | 7929(3) | 4714(1) | 8236(3) | 21(1) |
| C(6) | 7916(3) | 5211(1) | 8421(3) | 21(1) |
| C(7) | 8395(3) | 5453(1) | 9634(3) | 24(1) |
| C(8) | 8419(3) | 5944(1) | 9882(3) | 28(1) |
| C(9) | 7963(3) | 6321(1) | 8990(3) | 29(1) |
| C(10) | 7375(3) | 6309(1) | 7623(3) | 29(1) |
| C(11) | 7088(3) | 5912(1) | 6778(3) | 25(1) |
| C(12) | 7309(3) | 5427(1) | 7082(3) | 21(1) |
| C(13) | 7009(3) | 5045(1) | 6178(3) | 22(1) |
| C(14) | 6603(3) | 4057(1) | 4909(3) | 26(1) |
| C(15) | 6516(3) | 3604(1) | 4334(3) | 28(1) |
| C(16) | 7109(3) | 3206(1) | 5082(3) | 25(1) |
| S(2) | 3707(1) | 2878(1) | 7185(1) | 27(1) |
| F(6) | 2425(2) | 2522(1) | 7069(2) | 43(1) |
| F(7) | 3898(2) | 2706(1) | 5774(2) | 48(1) |
| F(8) | 5074(2) | 3197(1) | 7373(2) | 38(1) |
| F(9) | 3601(2) | 3017(1) | 8656(2) | 37(1) |
| F(10) | 4688(2) | 2445(1) | 7826(2) | 42(1) |
| C(17) | 2585(3) | 3372(1) | 6472(3) | 23(1) |
| C(18) | 2864(3) | 3827(1) | 7004(3) | 22(1) |
| C(19) | 1944(3) | 4208(1) | 6524(3) | 21(1) |
| C(20) | 2234(3) | 4690(1) | 7109(3) | 20(1) |
| C(21) | 3554(3) | 4863(1) | 7795(3) | 23(1) |
| C(22) | 3405(3) | 5327(1) | 8254(3) | 22(1) |
| C(23) | 4475(3) | 5617(1) | 8968(3) | 24(1) |
| C(24) | 4394(3) | 6078(1) | 9459(3) | 27(1) |
| C(25) | 3220(3) | 6364(1) | 9409(3) | 27(1) |
| C(26) | 1812(3) | 6268(1) | 8828(3) | 28(1) |
| C(27) | 1223(3) | 5863(1) | 8125(3) | 24(1) |
| C(28) | 1887(3) | 5448(1) | 7834(3) | 21(1) |
| C(29) | 1219(3) | 5047(1) | 7123(3) | 22(1) |
| C(30) | 757(3) | 4111(1) | 5501(3) | 25(1) |
| C(31) | 513(3) | 3656(1) | 4960(3) | 28(1) |
| C(32) | 1429(3) | 3279(1) | 5427(3) | 27(1) |

**Table S5**. Bond lengths [Å] for **7**.

| | | | |
|---|---|---|---|
| S(1)-F(3) | 1.5823(19) | S(2)-F(7) | 1.580(2) |
| S(1)-F(2) | 1.5853(18) | S(2)-F(8) | 1.581(2) |
| S(1)-F(1) | 1.5882(19) | S(2)-F(6) | 1.582(2) |
| S(1)-F(4) | 1.5906(18) | S(2)-F(10) | 1.585(2) |
| S(1)-F(5) | 1.5919(18) | S(2)-F(9) | 1.587(2) |
| S(1)-C(1) | 1.804(3) | S(2)-C(17) | 1.802(3) |
| C(1)-C(2) | 1.381(4) | C(17)-C(18) | 1.381(4) |
| C(1)-C(16) | 1.384(4) | C(17)-C(32) | 1.392(4) |
| C(2)-C(3) | 1.403(4) | C(18)-C(19) | 1.402(4) |
| C(2)-H(2) | 0.9500 | C(18)-H(18) | 0.9500 |
| C(3)-C(14) | 1.400(4) | C(19)-C(30) | 1.399(4) |
| C(3)-C(4) | 1.471(4) | C(19)-C(20) | 1.469(4) |
| C(4)-C(13) | 1.412(4) | C(20)-C(21) | 1.406(4) |
| C(4)-C(5) | 1.413(4) | C(20)-C(29) | 1.408(4) |
| C(5)-C(6) | 1.394(4) | C(21)-C(22) | 1.393(4) |
| C(5)-H(5) | 0.9500 | C(21)-H(21) | 0.9500 |
| C(6)-C(7) | 1.397(4) | C(22)-C(23) | 1.390(4) |
| C(6)-C(12) | 1.492(4) | C(22)-C(28) | 1.488(4) |
| C(7)-C(8) | 1.388(4) | C(23)-C(24) | 1.385(4) |
| C(7)-H(7) | 0.9500 | C(23)-H(23) | 0.9500 |
| C(8)-C(9) | 1.395(5) | C(24)-C(25) | 1.390(4) |
| C(8)-H(8) | 0.9500 | C(24)-H(24) | 0.9500 |
| C(9)-C(10) | 1.390(5) | C(25)-C(26) | 1.396(4) |
| C(9)-H(9) | 0.9500 | C(25)-H(25) | 0.9500 |
| C(10)-C(11) | 1.390(4) | C(26)-C(27) | 1.388(4) |
| C(10)-H(10) | 0.9500 | C(26)-H(26) | 0.9500 |
| C(11)-C(12) | 1.387(4) | C(27)-C(28) | 1.390(4) |
| C(11)-H(11) | 0.9500 | C(27)-H(27) | 0.9500 |
| C(12)-C(13) | 1.398(4) | C(28)-C(29) | 1.408(4) |
| C(13)-H(13) | 0.9500 | C(29)-H(29) | 0.9500 |
| C(14)-C(15) | 1.385(4) | C(30)-C(31) | 1.378(5) |
| C(14)-H(14) | 0.9500 | C(30)-H(30) | 0.9500 |
| C(15)-C(16) | 1.394(4) | C(31)-C(32) | 1.391(4) |
| C(15)-H(15) | 0.9500 | C(31)-H(31) | 0.9500 |
| C(16)-H(16) | 0.9500 | C(32)-H(32) | 0.9500 |

**Table S6**. Bond angles [°] for **7**.

| | | | |
|---|---|---|---|
| F(3)-S(1)-F(2) | 89.79(10) | C(14)-C(15)-H(15) | 119.7 |
| F(3)-S(1)-F(1) | 174.80(11) | C(16)-C(15)-H(15) | 119.7 |
| F(2)-S(1)-F(1) | 90.13(10) | C(1)-C(16)-C(15) | 118.1(3) |
| F(3)-S(1)-F(4) | 89.96(11) | C(1)-C(16)-H(16) | 120.9 |
| F(2)-S(1)-F(4) | 174.47(10) | C(15)-C(16)-H(16) | 120.9 |
| F(1)-S(1)-F(4) | 89.62(11) | F(7)-S(2)-F(8) | 90.14(13) |
| F(3)-S(1)-F(5) | 87.39(11) | F(7)-S(2)-F(6) | 90.22(14) |
| F(2)-S(1)-F(5) | 87.31(10) | F(8)-S(2)-F(6) | 174.84(11) |
| F(1)-S(1)-F(5) | 87.42(10) | F(7)-S(2)-F(10) | 87.70(12) |
| F(4)-S(1)-F(5) | 87.16(10) | F(8)-S(2)-F(10) | 87.67(11) |
| F(3)-S(1)-C(1) | 92.55(12) | F(6)-S(2)-F(10) | 87.20(11) |
| F(2)-S(1)-C(1) | 92.85(12) | F(7)-S(2)-F(9) | 175.22(12) |
| F(1)-S(1)-C(1) | 92.65(12) | F(8)-S(2)-F(9) | 89.46(12) |
| F(4)-S(1)-C(1) | 92.67(12) | F(6)-S(2)-F(9) | 89.75(13) |
| F(5)-S(1)-C(1) | 179.82(14) | F(10)-S(2)-F(9) | 87.52(12) |
| C(2)-C(1)-C(16) | 122.3(3) | F(7)-S(2)-C(17) | 92.87(13) |
| C(2)-C(1)-S(1) | 119.0(2) | F(8)-S(2)-C(17) | 92.48(12) |
| C(16)-C(1)-S(1) | 118.7(2) | F(6)-S(2)-C(17) | 92.64(12) |
| C(1)-C(2)-C(3) | 119.7(3) | F(10)-S(2)-C(17) | 179.41(14) |
| C(1)-C(2)-H(2) | 120.2 | F(9)-S(2)-C(17) | 91.91(12) |
| C(3)-C(2)-H(2) | 120.2 | C(18)-C(17)-C(32) | 121.7(3) |
| C(14)-C(3)-C(2) | 118.4(3) | C(18)-C(17)-S(2) | 119.4(2) |
| C(14)-C(3)-C(4) | 121.3(3) | C(32)-C(17)-S(2) | 118.9(2) |
| C(2)-C(3)-C(4) | 120.3(3) | C(17)-C(18)-C(19) | 120.0(3) |
| C(13)-C(4)-C(5) | 108.3(3) | C(17)-C(18)-H(18) | 120.0 |
| C(13)-C(4)-C(3) | 125.6(3) | C(19)-C(18)-H(18) | 120.0 |
| C(5)-C(4)-C(3) | 126.2(3) | C(30)-C(19)-C(18) | 118.3(3) |
| C(6)-C(5)-C(4) | 109.3(2) | C(30)-C(19)-C(20) | 122.0(3) |
| C(6)-C(5)-H(5) | 125.4 | C(18)-C(19)-C(20) | 119.7(3) |
| C(4)-C(5)-H(5) | 125.4 | C(21)-C(20)-C(29) | 109.0(3) |
| C(5)-C(6)-C(7) | 125.8(3) | C(21)-C(20)-C(19) | 125.7(3) |
| C(5)-C(6)-C(12) | 106.7(2) | C(29)-C(20)-C(19) | 125.2(3) |
| C(7)-C(6)-C(12) | 127.5(3) | C(22)-C(21)-C(20) | 109.1(3) |
| C(8)-C(7)-C(6) | 128.6(3) | C(22)-C(21)-H(21) | 125.4 |
| C(8)-C(7)-H(7) | 115.7 | C(20)-C(21)-H(21) | 125.4 |
| C(6)-C(7)-H(7) | 115.7 | C(23)-C(22)-C(21) | 126.1(3) |
| C(7)-C(8)-C(9) | 129.0(3) | C(23)-C(22)-C(28) | 127.1(3) |
| C(7)-C(8)-H(8) | 115.5 | C(21)-C(22)-C(28) | 106.8(2) |
| C(9)-C(8)-H(8) | 115.5 | C(24)-C(23)-C(22) | 128.9(3) |
| C(10)-C(9)-C(8) | 129.8(3) | C(24)-C(23)-H(23) | 115.5 |
| C(10)-C(9)-H(9) | 115.1 | C(22)-C(23)-H(23) | 115.5 |
| C(8)-C(9)-H(9) | 115.1 | C(23)-C(24)-C(25) | 129.2(3) |
| C(9)-C(10)-C(11) | 128.8(3) | C(23)-C(24)-H(24) | 115.4 |
| C(9)-C(10)-H(10) | 115.6 | C(25)-C(24)-H(24) | 115.4 |
| C(11)-C(10)-H(10) | 115.6 | C(24)-C(25)-C(26) | 129.4(3) |
| C(12)-C(11)-C(10) | 129.1(3) | C(24)-C(25)-H(25) | 115.3 |
| C(12)-C(11)-H(11) | 115.5 | C(26)-C(25)-H(25) | 115.3 |
| C(10)-C(11)-H(11) | 115.5 | C(27)-C(26)-C(25) | 128.8(3) |
| C(11)-C(12)-C(13) | 126.2(3) | C(27)-C(26)-H(26) | 115.6 |
| C(11)-C(12)-C(6) | 127.3(3) | C(25)-C(26)-H(26) | 115.6 |
| C(13)-C(12)-C(6) | 106.5(2) | C(26)-C(27)-C(28) | 128.7(3) |
| C(12)-C(13)-C(4) | 109.3(2) | C(26)-C(27)-H(27) | 115.6 |
| C(12)-C(13)-H(13) | 125.4 | C(28)-C(27)-H(27) | 115.6 |
| C(4)-C(13)-H(13) | 125.4 | C(27)-C(28)-C(29) | 125.7(3) |
| C(15)-C(14)-C(3) | 120.9(3) | C(27)-C(28)-C(22) | 127.8(3) |
| C(15)-C(14)-H(14) | 119.5 | C(29)-C(28)-C(22) | 106.5(2) |
| C(3)-C(14)-H(14) | 119.5 | C(20)-C(29)-C(28) | 108.6(2) |
| C(14)-C(15)-C(16) | 120.6(3) | C(20)-C(29)-H(29) | 125.7 |

| | | | |
|---|---|---|---|
| C(28)-C(29)-H(29) | 125.7 | C(30)-C(31)-H(31) | 119.5 |
| C(31)-C(30)-C(19) | 121.0(3) | C(32)-C(31)-H(31) | 119.5 |
| C(31)-C(30)-H(30) | 119.5 | C(31)-C(32)-C(17) | 118.1(3) |
| C(19)-C(30)-H(30) | 119.5 | C(31)-C(32)-H(32) | 121.0 |
| C(30)-C(31)-C(32) | 120.9(3) | C(17)-C(32)-H(32) | 121.0 |

**Table S7**. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 25(1) | 23(1) | 19(1) | 1(1) | 3(1) | 3(1) |
| F(1) | 26(1) | 33(1) | 30(1) | -1(1) | -6(1) | 2(1) |
| F(2) | 32(1) | 32(1) | 24(1) | -3(1) | 8(1) | 8(1) |
| F(3) | 32(1) | 25(1) | 39(1) | 1(1) | 6(1) | -3(1) |
| F(4) | 44(1) | 32(1) | 22(1) | 5(1) | 12(1) | 11(1) |
| F(5) | 43(1) | 27(1) | 30(1) | 7(1) | 2(1) | 11(1) |
| C(1) | 18(1) | 24(1) | 22(1) | 4(1) | 5(1) | 2(1) |
| C(2) | 17(1) | 27(1) | 15(1) | 2(1) | 3(1) | -1(1) |
| C(3) | 19(1) | 26(1) | 18(1) | 3(1) | 5(1) | 0(1) |
| C(4) | 17(1) | 25(1) | 21(1) | 3(1) | 4(1) | 0(1) |
| C(5) | 20(1) | 27(1) | 17(1) | 6(1) | 5(1) | 2(1) |
| C(6) | 17(1) | 28(2) | 19(1) | 3(1) | 5(1) | 1(1) |
| C(7) | 21(1) | 32(2) | 18(1) | 2(1) | 4(1) | -1(1) |
| C(8) | 25(2) | 36(2) | 24(2) | -4(1) | 8(1) | -3(1) |
| C(9) | 29(2) | 28(2) | 33(2) | -4(1) | 14(1) | -1(1) |
| C(10) | 30(2) | 25(2) | 34(2) | 3(1) | 12(1) | 4(1) |
| C(11) | 22(1) | 28(2) | 25(2) | 4(1) | 5(1) | 2(1) |
| C(12) | 17(1) | 27(1) | 20(1) | 3(1) | 3(1) | 1(1) |
| C(13) | 21(1) | 28(2) | 17(1) | 3(1) | 2(1) | 1(1) |
| C(14) | 25(2) | 30(2) | 21(1) | 4(1) | 1(1) | 3(1) |
| C(15) | 28(2) | 34(2) | 18(1) | 0(1) | -4(1) | 2(1) |
| C(16) | 26(2) | 26(2) | 22(2) | -3(1) | 4(1) | 0(1) |
| S(2) | 23(1) | 25(1) | 31(1) | -2(1) | 4(1) | 1(1) |
| F(6) | 28(1) | 25(1) | 69(2) | 6(1) | -1(1) | -4(1) |
| F(7) | 55(1) | 48(1) | 39(1) | -14(1) | 12(1) | 13(1) |
| F(8) | 19(1) | 36(1) | 58(1) | 3(1) | 4(1) | 0(1) |
| F(9) | 48(1) | 36(1) | 26(1) | 7(1) | 6(1) | 10(1) |
| F(10) | 32(1) | 29(1) | 60(1) | 3(1) | 0(1) | 8(1) |
| C(17) | 24(1) | 27(2) | 20(1) | 2(1) | 5(1) | 0(1) |
| C(18) | 19(1) | 28(2) | 17(1) | 1(1) | 1(1) | -1(1) |
| C(19) | 18(1) | 30(2) | 17(1) | 3(1) | 6(1) | -1(1) |
| C(20) | 18(1) | 28(1) | 14(1) | 5(1) | 3(1) | 1(1) |
| C(21) | 20(1) | 29(2) | 18(1) | 3(1) | 2(1) | 4(1) |
| C(22) | 17(1) | 29(2) | 17(1) | 6(1) | 1(1) | 2(1) |
| C(23) | 18(1) | 35(2) | 19(1) | 3(1) | 1(1) | 2(1) |
| C(24) | 23(1) | 36(2) | 21(1) | 0(1) | 0(1) | -4(1) |
| C(25) | 31(2) | 28(2) | 21(1) | -2(1) | 6(1) | 0(1) |
| C(26) | 31(2) | 26(2) | 26(2) | 2(1) | 7(1) | 6(1) |
| C(27) | 19(1) | 29(2) | 23(1) | 6(1) | 4(1) | 3(1) |
| C(28) | 20(1) | 26(1) | 16(1) | 6(1) | 4(1) | 1(1) |
| C(29) | 16(1) | 29(2) | 19(1) | 4(1) | 2(1) | 1(1) |
| C(30) | 20(1) | 32(2) | 22(1) | 9(1) | 2(1) | 0(1) |
| C(31) | 22(1) | 37(2) | 21(1) | 4(1) | -3(1) | -6(1) |
| C(32) | 28(2) | 28(2) | 21(1) | -2(1) | 2(1) | -6(1) |

**Table S8**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^{-3}$) for **7**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 8365 | 3763 | 7914 | 24 |
| H(5) | 8248 | 4483 | 8922 | 26 |
| H(7) | 8752 | 5254 | 10390 | 29 |
| H(8) | 8799 | 6036 | 10784 | 33 |
| H(9) | 8070 | 6633 | 9377 | 35 |
| H(10) | 7137 | 6613 | 7209 | 35 |
| H(11) | 6684 | 5983 | 5865 | 30 |
| H(13) | 6609 | 5074 | 5246 | 27 |
| H(14) | 6197 | 4325 | 4384 | 31 |
| H(15) | 6049 | 3564 | 3421 | 34 |
| H(16) | 7044 | 2894 | 4694 | 30 |
| H(18) | 3680 | 3883 | 7694 | 26 |
| H(21) | 4412 | 4690 | 7926 | 27 |
| H(23) | 5389 | 5481 | 9142 | 29 |
| H(24) | 5265 | 6219 | 9892 | 33 |
| H(25) | 3402 | 6669 | 9831 | 32 |
| H(26) | 1169 | 6514 | 8927 | 33 |
| H(27) | 234 | 5870 | 7800 | 29 |
| H(29) | 246 | 5022 | 6719 | 26 |
| H(30) | 111 | 4362 | 5175 | 30 |
| H(31) | -293 | 3600 | 4258 | 34 |
| H(32) | 1270 | 2967 | 5043 | 32 |

**Table S9**. Torsion angles [°] for **7**.

| | | | |
|---|---|---|---|
| F(3)-S(1)-C(1)-C(2) | 134.6(2) | F(7)-S(2)-C(17)-C(18) | -130.2(2) |
| F(2)-S(1)-C(1)-C(2) | -135.5(2) | F(8)-S(2)-C(17)-C(18) | -39.9(3) |
| F(1)-S(1)-C(1)-C(2) | -45.3(2) | F(6)-S(2)-C(17)-C(18) | 139.5(2) |
| F(4)-S(1)-C(1)-C(2) | 44.5(2) | F(9)-S(2)-C(17)-C(18) | 49.6(3) |
| F(3)-S(1)-C(1)-C(16) | -45.9(2) | F(7)-S(2)-C(17)-C(32) | 51.9(3) |
| F(2)-S(1)-C(1)-C(16) | 44.0(2) | F(8)-S(2)-C(17)-C(32) | 142.2(3) |
| F(1)-S(1)-C(1)-C(16) | 134.3(2) | F(6)-S(2)-C(17)-C(32) | -38.4(3) |
| F(4)-S(1)-C(1)-C(16) | -136.0(2) | F(9)-S(2)-C(17)-C(32) | -128.3(3) |
| C(16)-C(1)-C(2)-C(3) | -0.1(4) | C(32)-C(17)-C(18)-C(19) | 2.5(4) |
| S(1)-C(1)-C(2)-C(3) | 179.4(2) | S(2)-C(17)-C(18)-C(19) | -175.4(2) |
| C(1)-C(2)-C(3)-C(14) | -0.8(4) | C(17)-C(18)-C(19)-C(30) | -0.4(4) |
| C(1)-C(2)-C(3)-C(4) | -178.9(3) | C(17)-C(18)-C(19)-C(20) | 178.9(3) |
| C(14)-C(3)-C(4)-C(13) | -7.8(4) | C(30)-C(19)-C(20)-C(21) | -158.2(3) |
| C(2)-C(3)-C(4)-C(13) | 170.2(3) | C(18)-C(19)-C(20)-C(21) | 22.6(4) |
| C(14)-C(3)-C(4)-C(5) | 173.5(3) | C(30)-C(19)-C(20)-C(29) | 24.8(4) |
| C(2)-C(3)-C(4)-C(5) | -8.4(4) | C(18)-C(19)-C(20)-C(29) | -154.5(3) |
| C(13)-C(4)-C(5)-C(6) | -1.1(3) | C(29)-C(20)-C(21)-C(22) | 0.1(3) |
| C(3)-C(4)-C(5)-C(6) | 177.7(3) | C(19)-C(20)-C(21)-C(22) | -177.4(3) |
| C(4)-C(5)-C(6)-C(7) | -178.5(3) | C(20)-C(21)-C(22)-C(23) | -179.6(3) |
| C(4)-C(5)-C(6)-C(12) | 1.0(3) | C(20)-C(21)-C(22)-C(28) | 0.6(3) |
| C(5)-C(6)-C(7)-C(8) | 179.6(3) | C(21)-C(22)-C(23)-C(24) | -179.4(3) |
| C(12)-C(6)-C(7)-C(8) | 0.1(5) | C(28)-C(22)-C(23)-C(24) | 0.5(5) |
| C(6)-C(7)-C(8)-C(9) | 0.6(5) | C(22)-C(23)-C(24)-C(25) | 2.5(6) |
| C(7)-C(8)-C(9)-C(10) | -0.5(6) | C(23)-C(24)-C(25)-C(26) | -1.4(6) |
| C(8)-C(9)-C(10)-C(11) | -0.1(6) | C(24)-C(25)-C(26)-C(27) | -1.3(6) |
| C(9)-C(10)-C(11)-C(12) | 0.2(6) | C(25)-C(26)-C(27)-C(28) | 0.7(6) |
| C(10)-C(11)-C(12)-C(13) | -179.3(3) | C(26)-C(27)-C(28)-C(29) | 179.4(3) |
| C(10)-C(11)-C(12)-C(6) | 0.3(5) | C(26)-C(27)-C(28)-C(22) | 2.6(5) |
| C(5)-C(6)-C(12)-C(11) | 179.8(3) | C(23)-C(22)-C(28)-C(27) | -3.6(5) |
| C(7)-C(6)-C(12)-C(11) | -0.7(5) | C(21)-C(22)-C(28)-C(27) | 176.3(3) |
| C(5)-C(6)-C(12)-C(13) | -0.5(3) | C(23)-C(22)-C(28)-C(29) | 179.2(3) |
| C(7)-C(6)-C(12)-C(13) | 179.0(3) | C(21)-C(22)-C(28)-C(29) | -1.0(3) |
| C(11)-C(12)-C(13)-C(4) | 179.5(3) | C(21)-C(20)-C(29)-C(28) | -0.7(3) |
| C(6)-C(12)-C(13)-C(4) | -0.2(3) | C(19)-C(20)-C(29)-C(28) | 176.8(3) |
| C(5)-C(4)-C(13)-C(12) | 0.8(3) | C(27)-C(28)-C(29)-C(20) | -176.3(3) |
| C(3)-C(4)-C(13)-C(12) | -178.0(3) | C(22)-C(28)-C(29)-C(20) | 1.0(3) |
| C(2)-C(3)-C(14)-C(15) | 1.0(4) | C(18)-C(19)-C(30)-C(31) | -1.3(4) |
| C(4)-C(3)-C(14)-C(15) | 179.1(3) | C(20)-C(19)-C(30)-C(31) | 179.5(3) |
| C(3)-C(14)-C(15)-C(16) | -0.3(5) | C(19)-C(30)-C(31)-C(32) | 0.9(5) |
| C(2)-C(1)-C(16)-C(15) | 0.9(5) | C(30)-C(31)-C(32)-C(17) | 1.2(5) |
| S(1)-C(1)-C(16)-C(15) | -178.7(2) | C(18)-C(17)-C(32)-C(31) | -2.8(5) |
| C(14)-C(15)-C(16)-C(1) | -0.6(5) | S(2)-C(17)-C(32)-C(31) | 175.0(2) |

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