Supplementary Materials

Synthesis and Functionalization of a 1,2-Bis(trimethylsilyl)-1,2-disilacyclohexene That Can Serve as a Unit of *cis*-1,2-Dialkyldisilene

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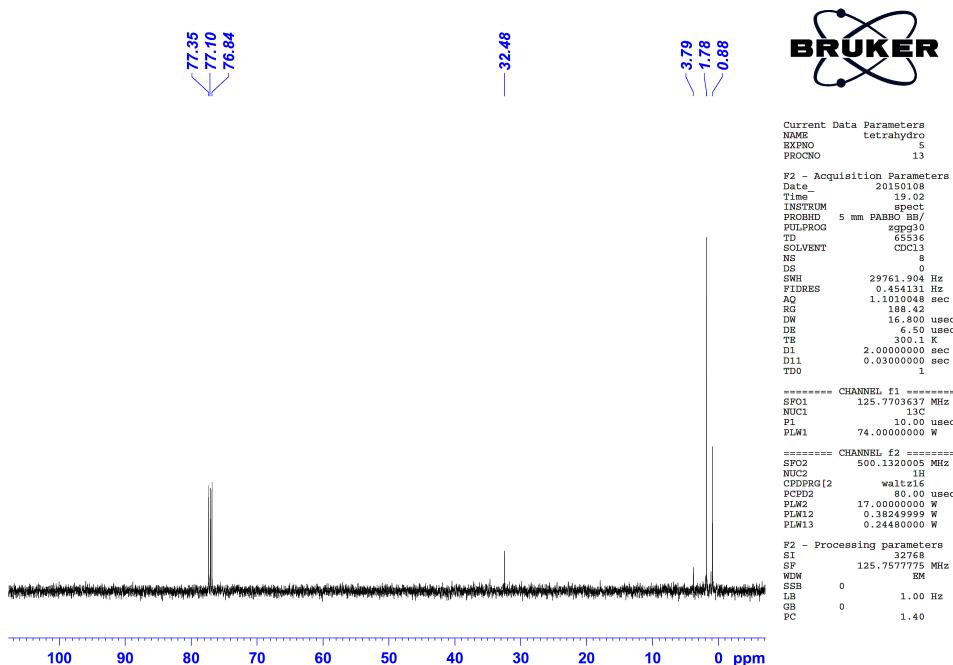
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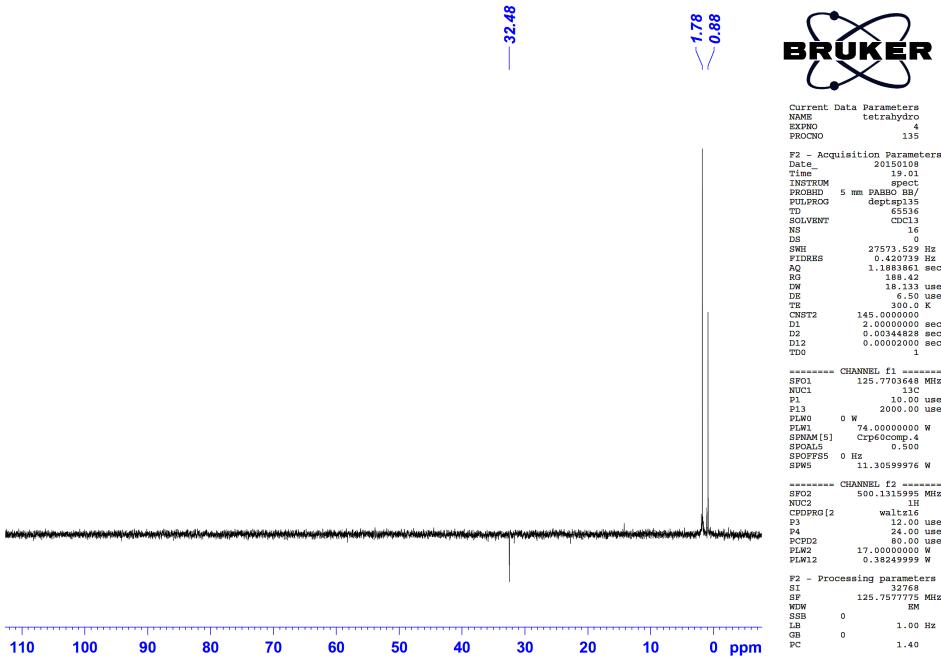
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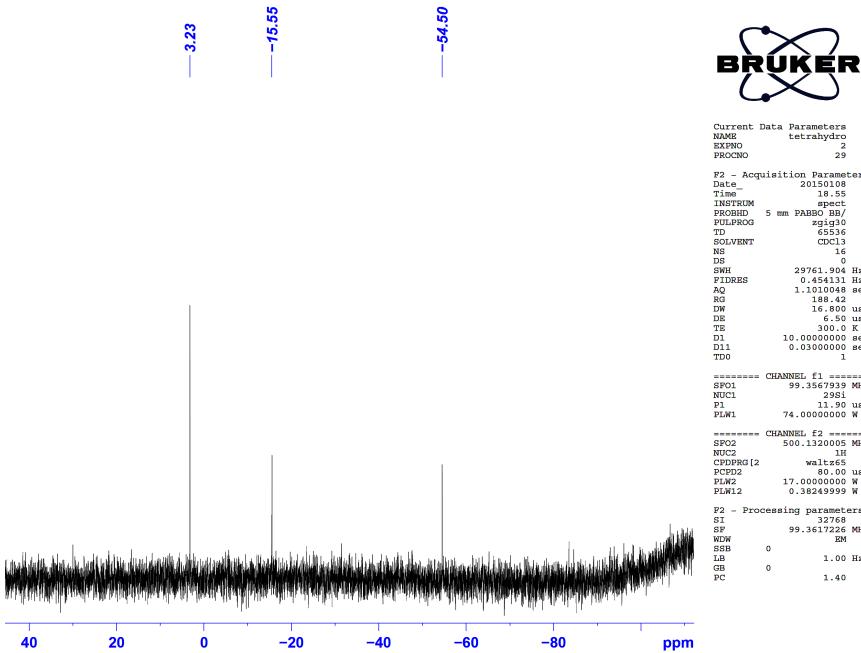
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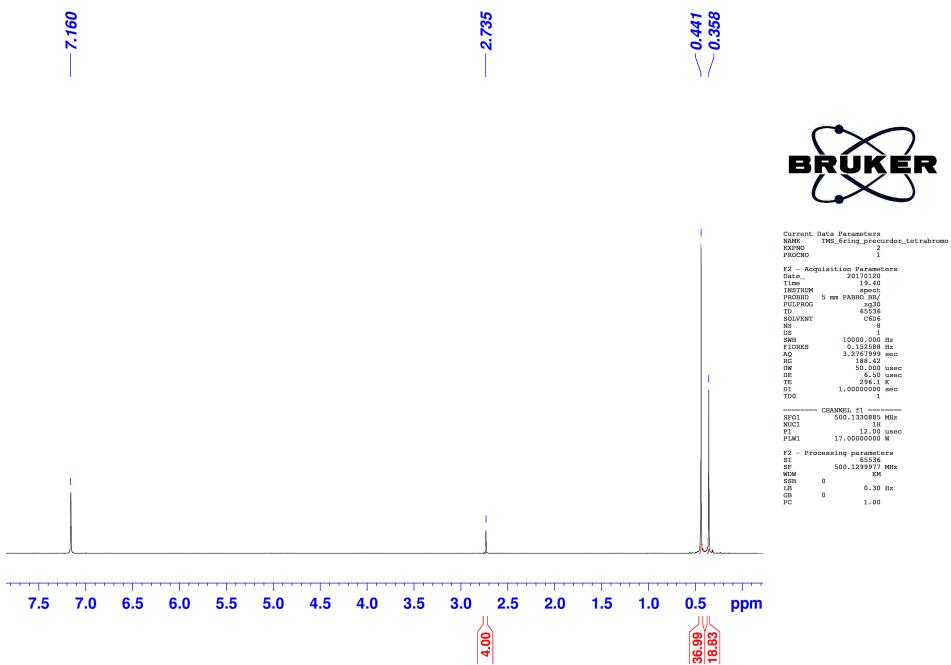
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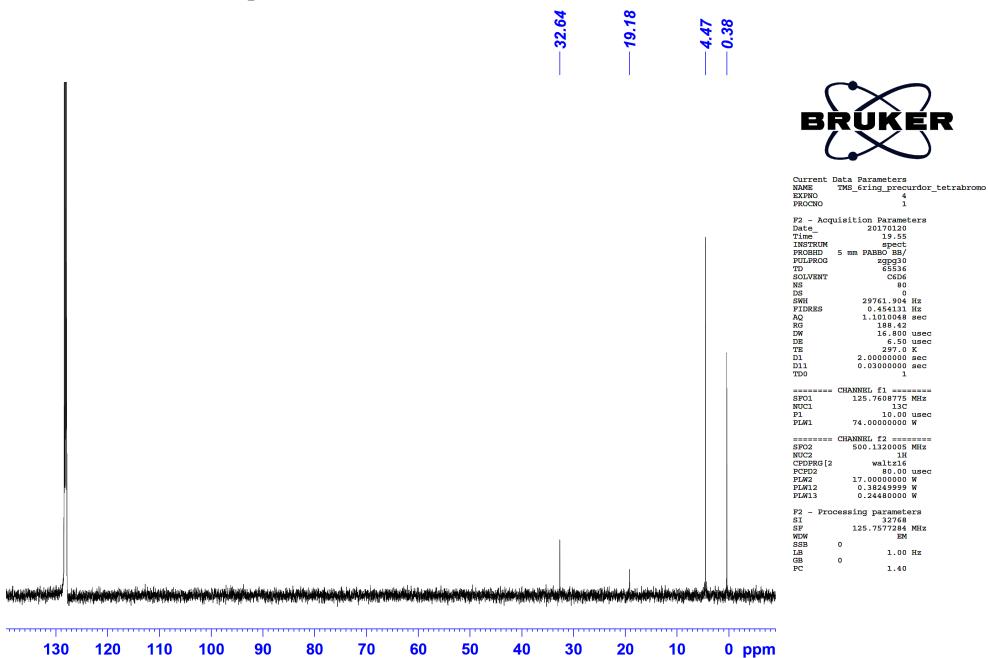
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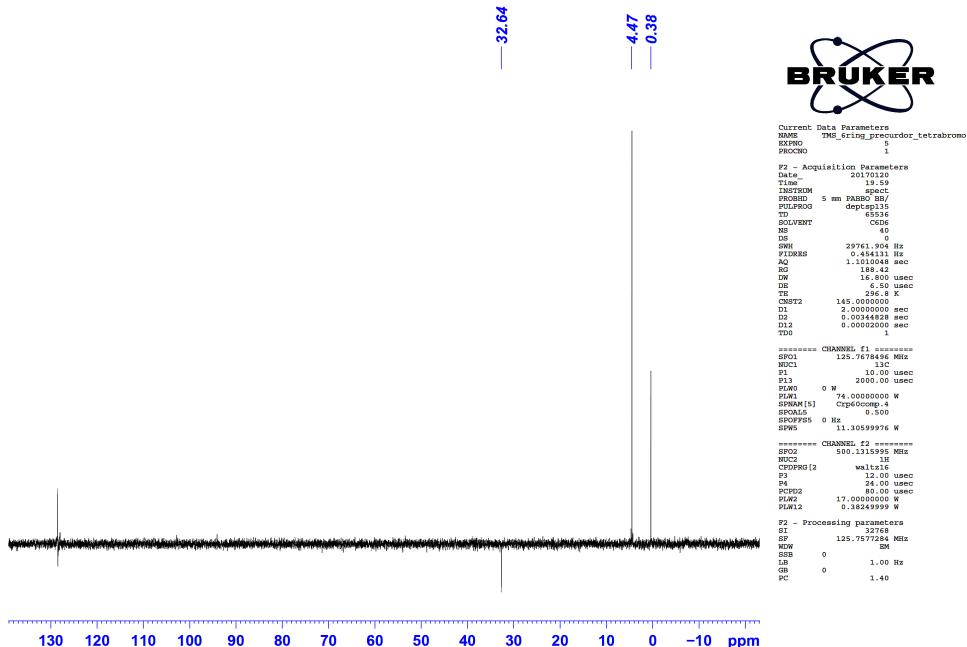
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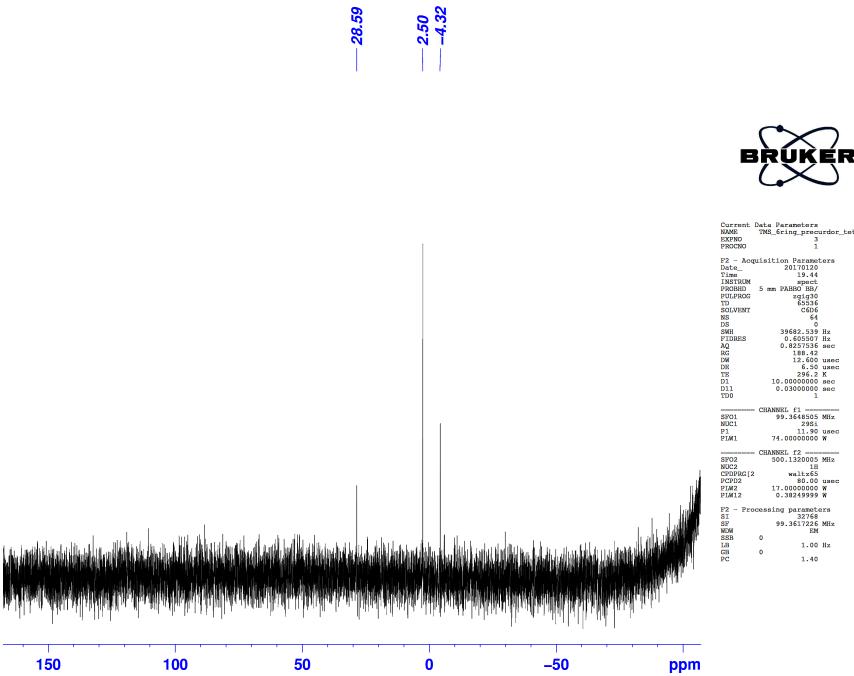
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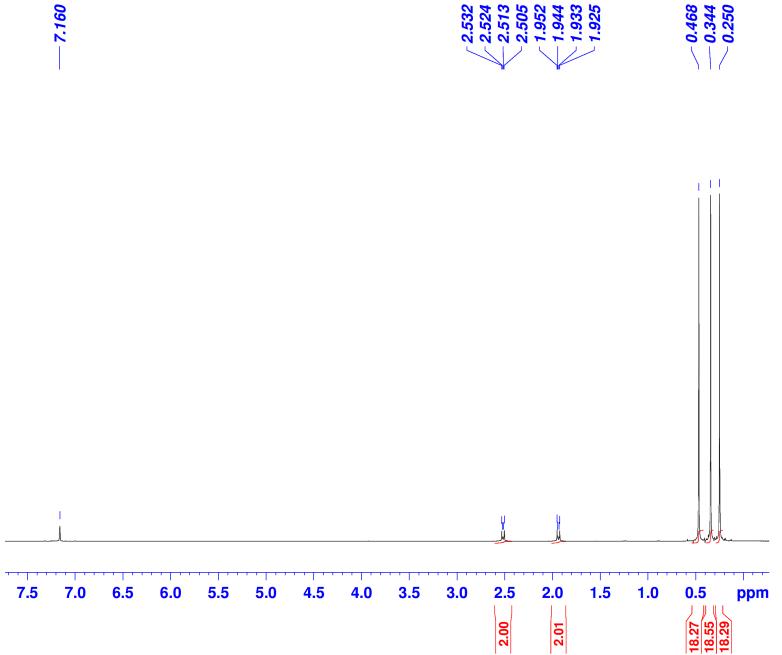
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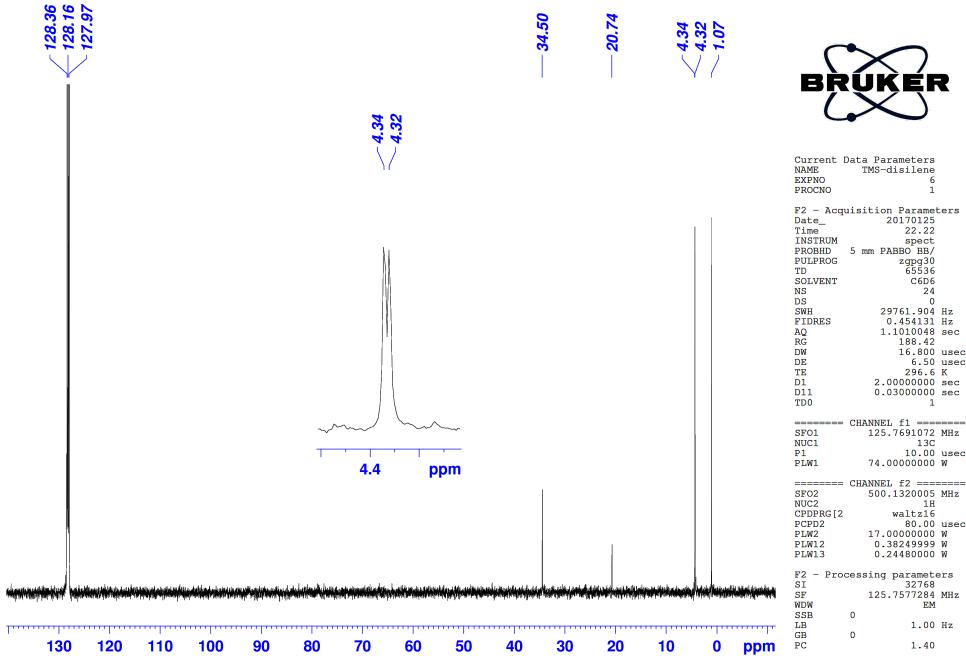
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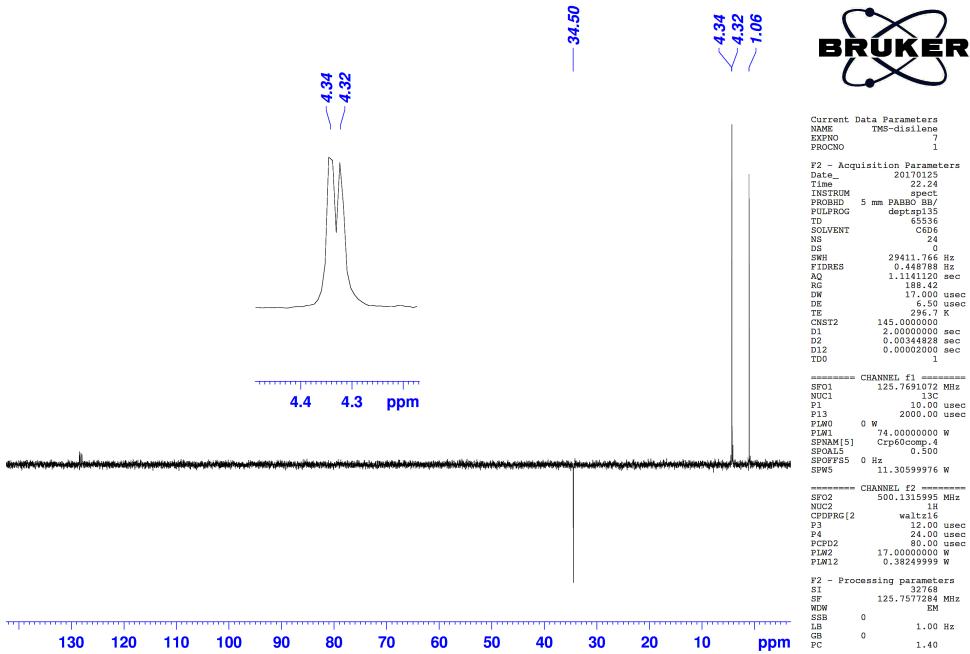
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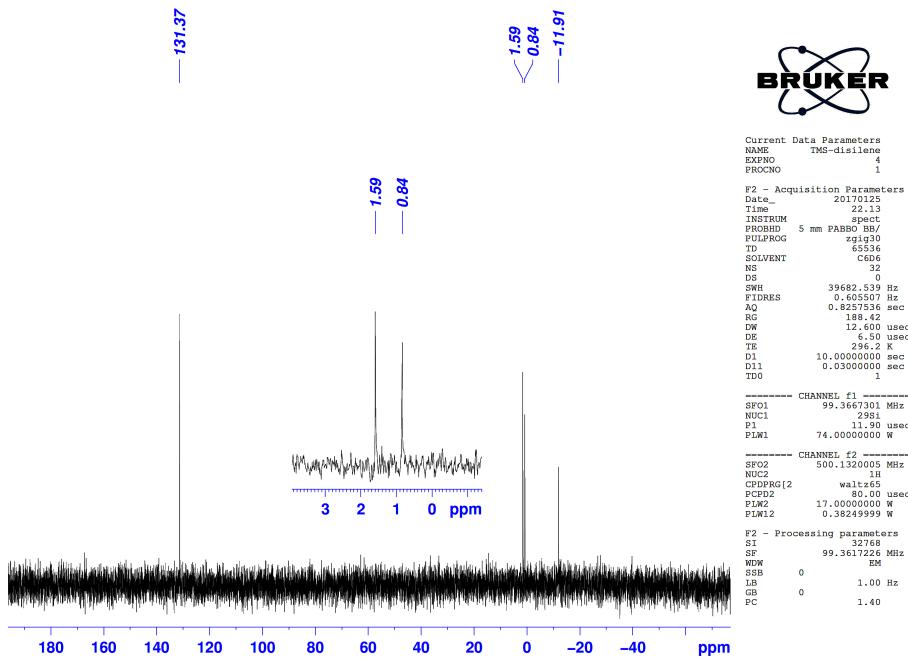
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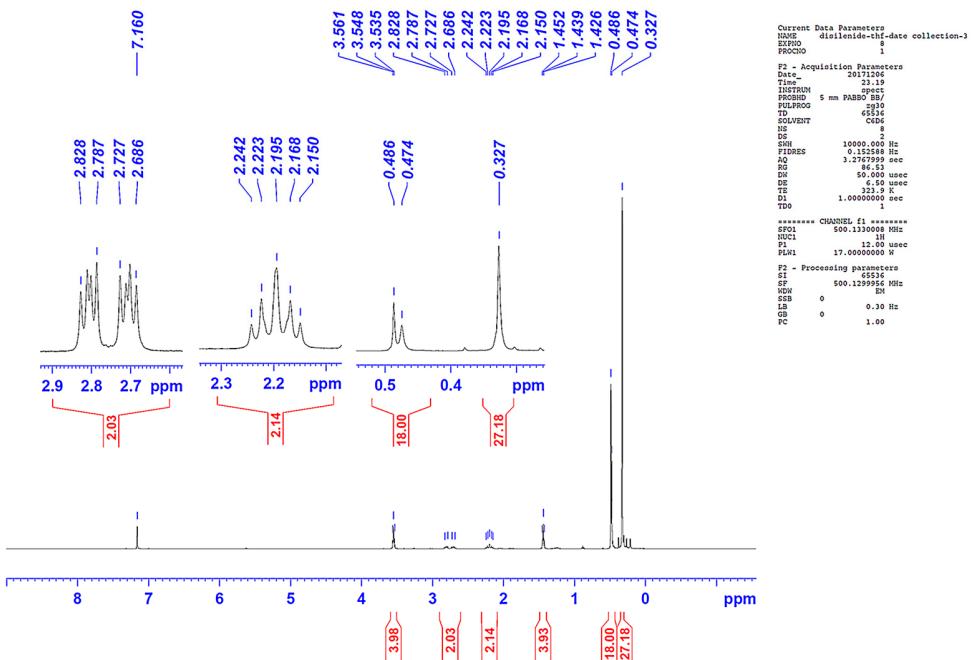
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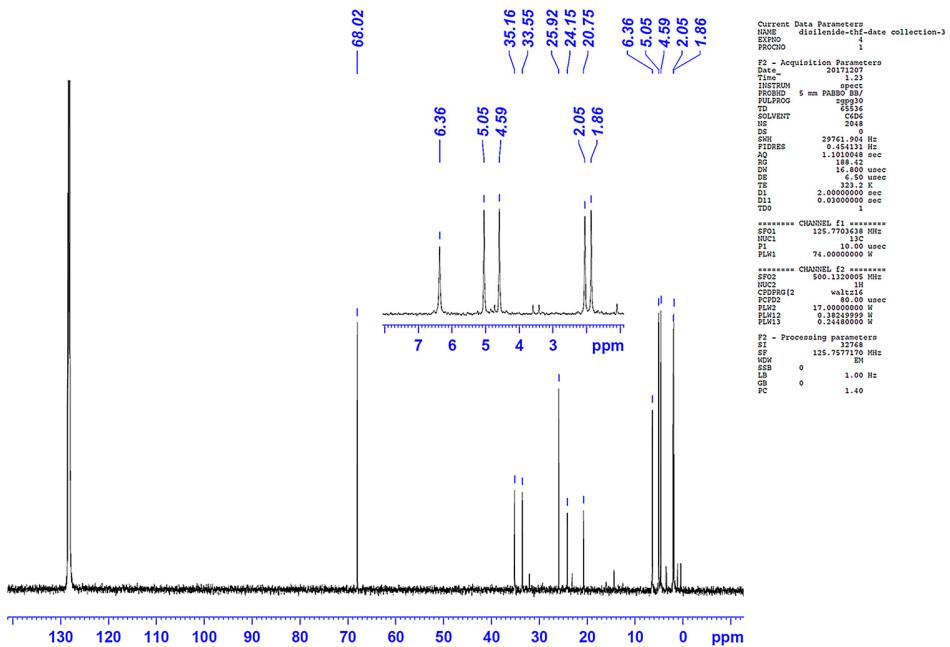
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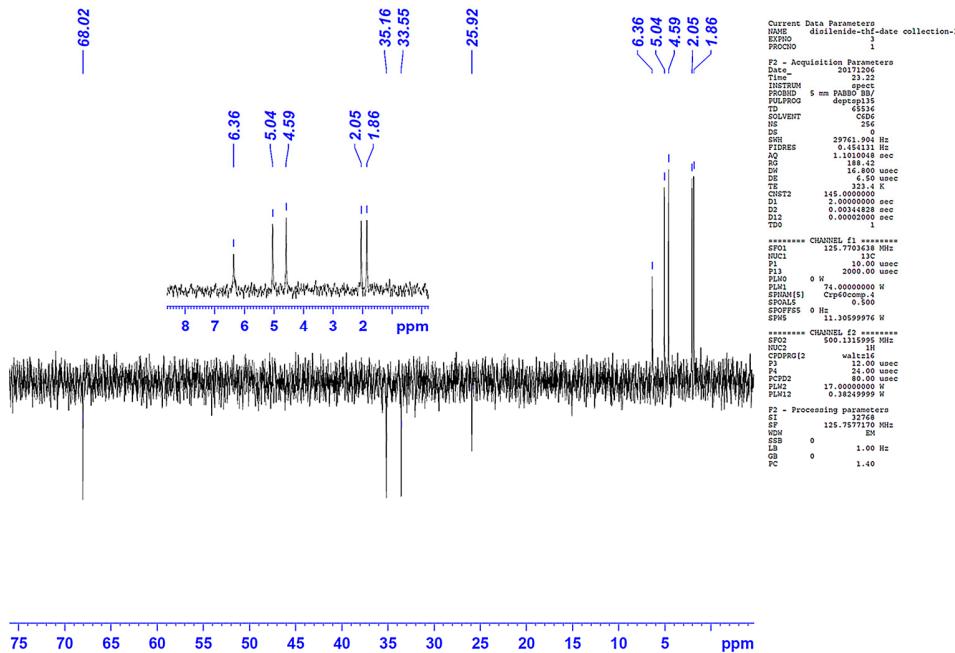
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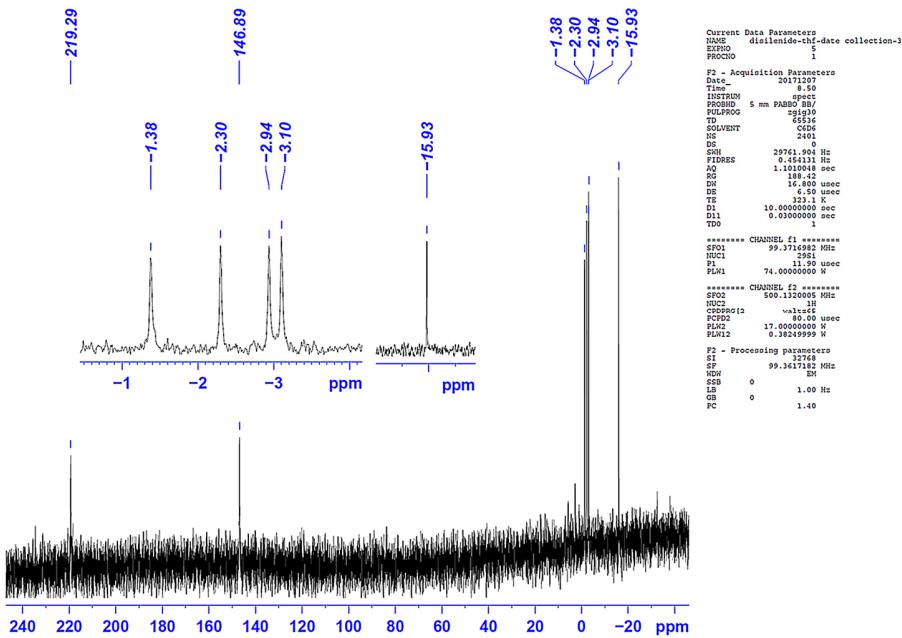
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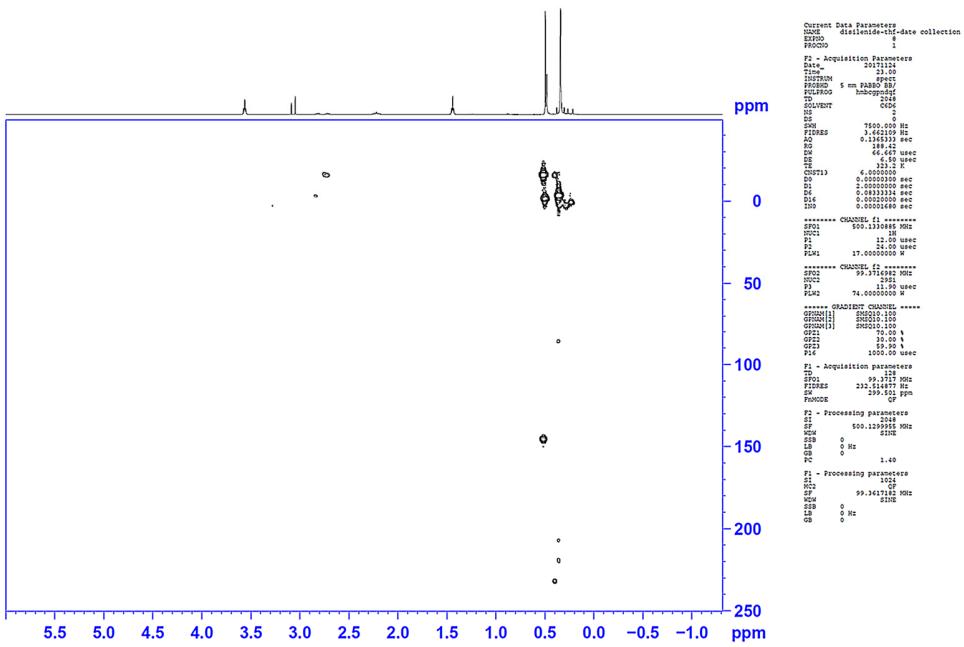
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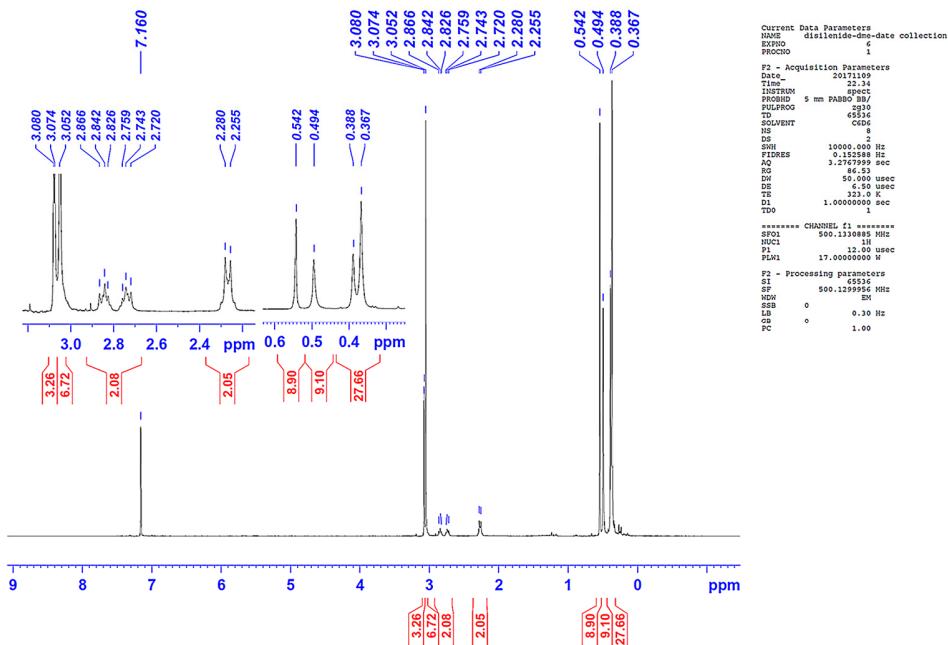
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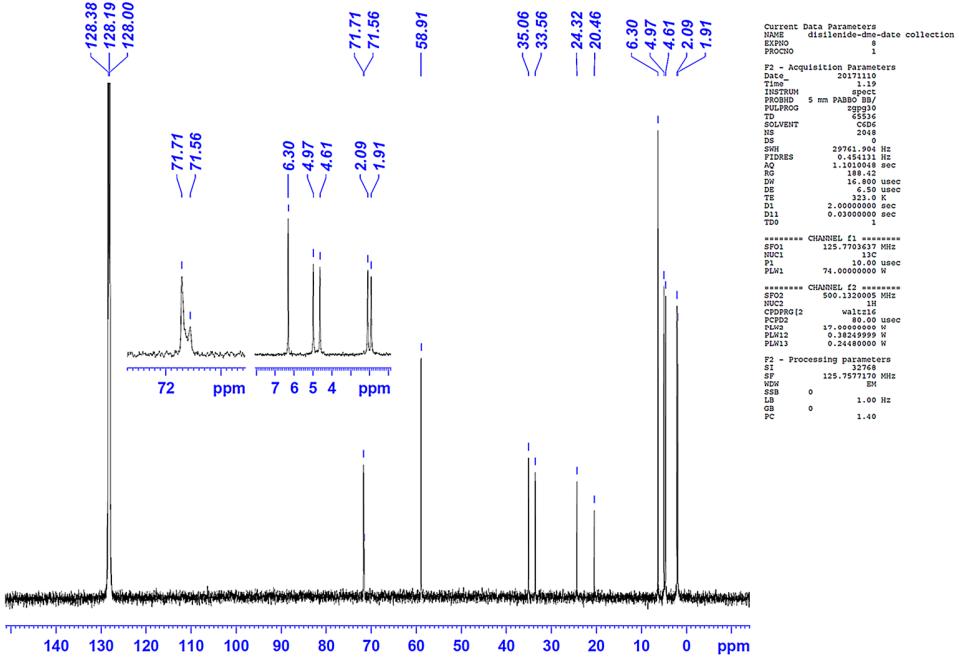
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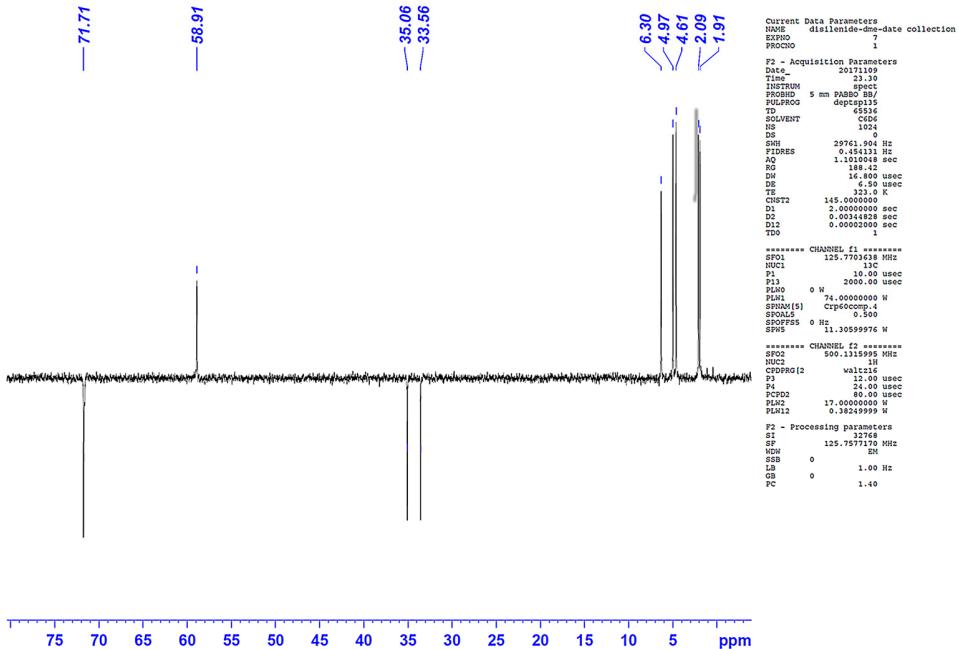
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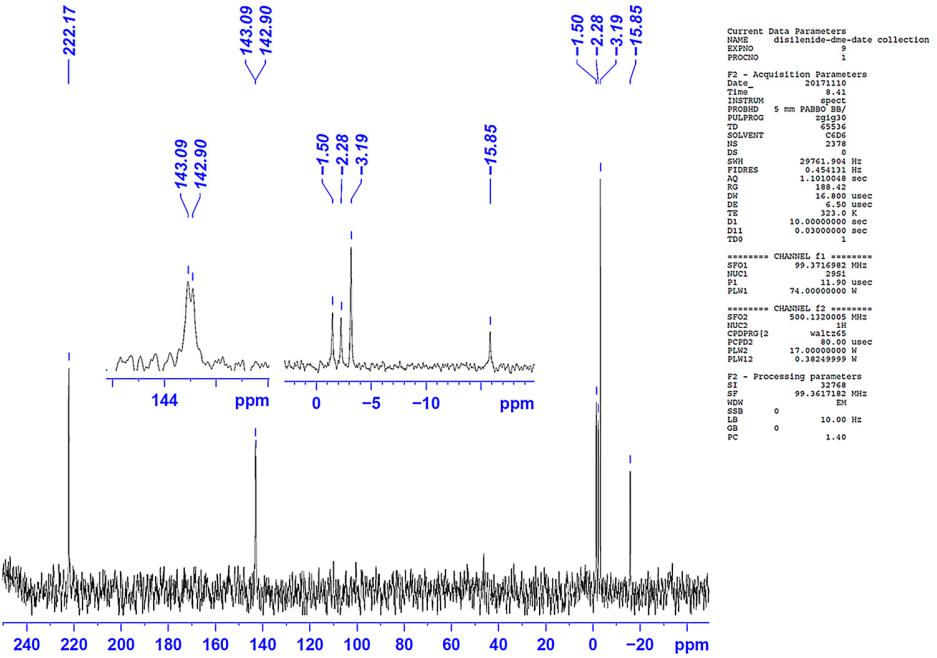
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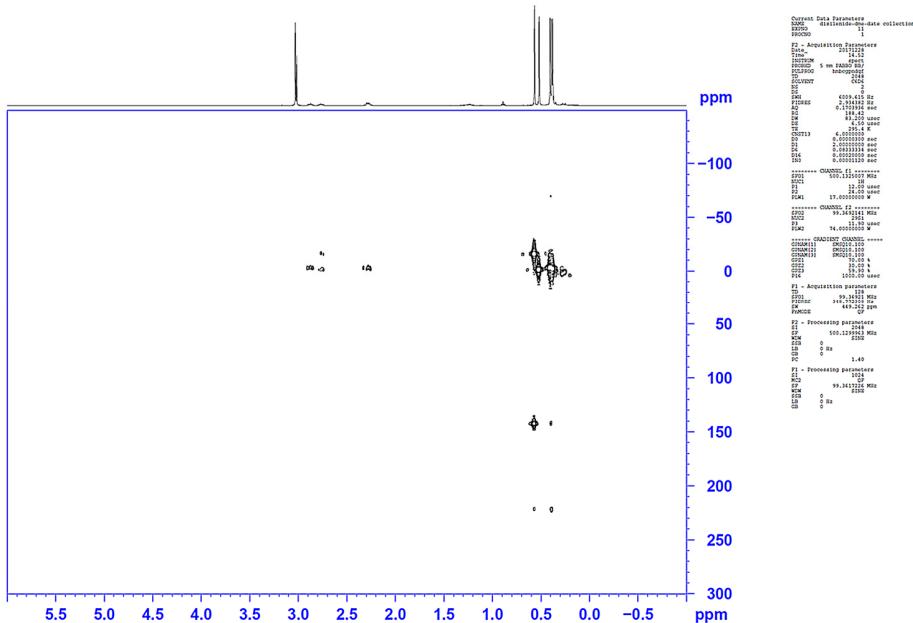
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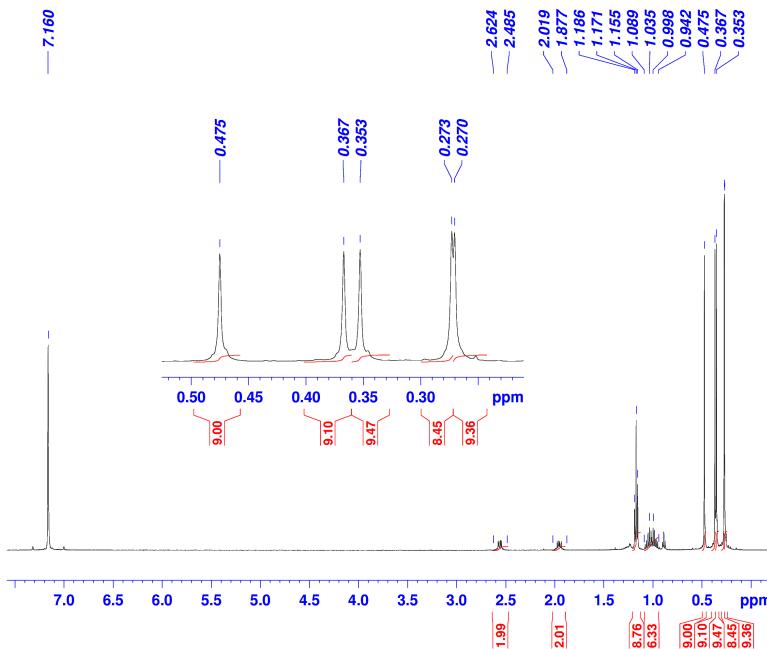
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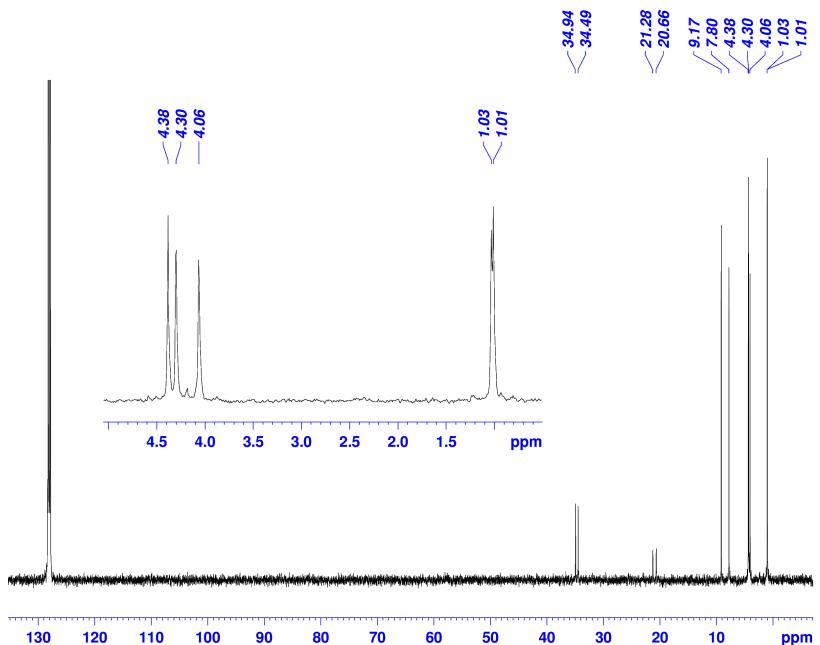
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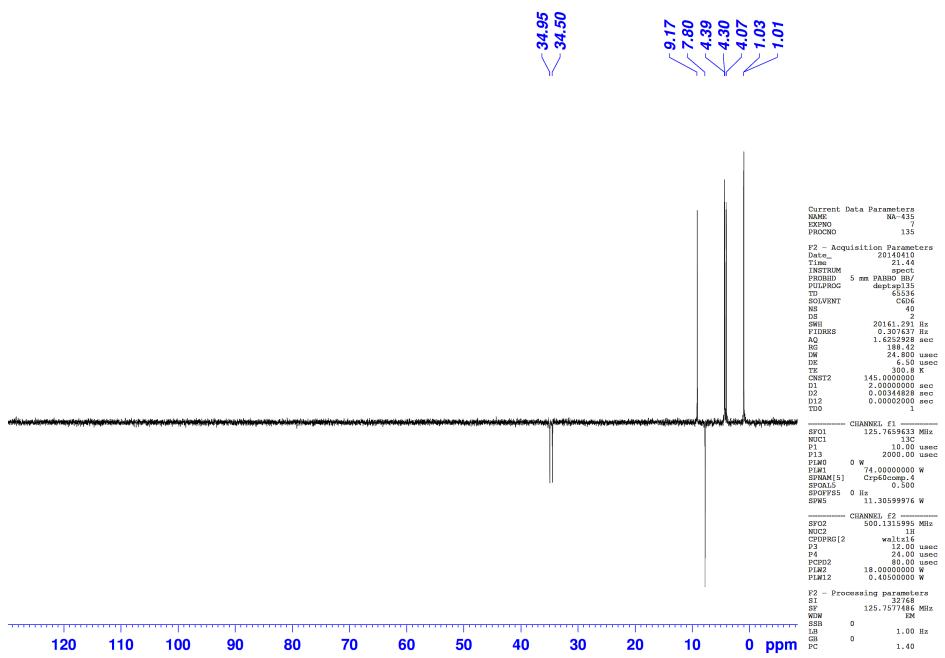
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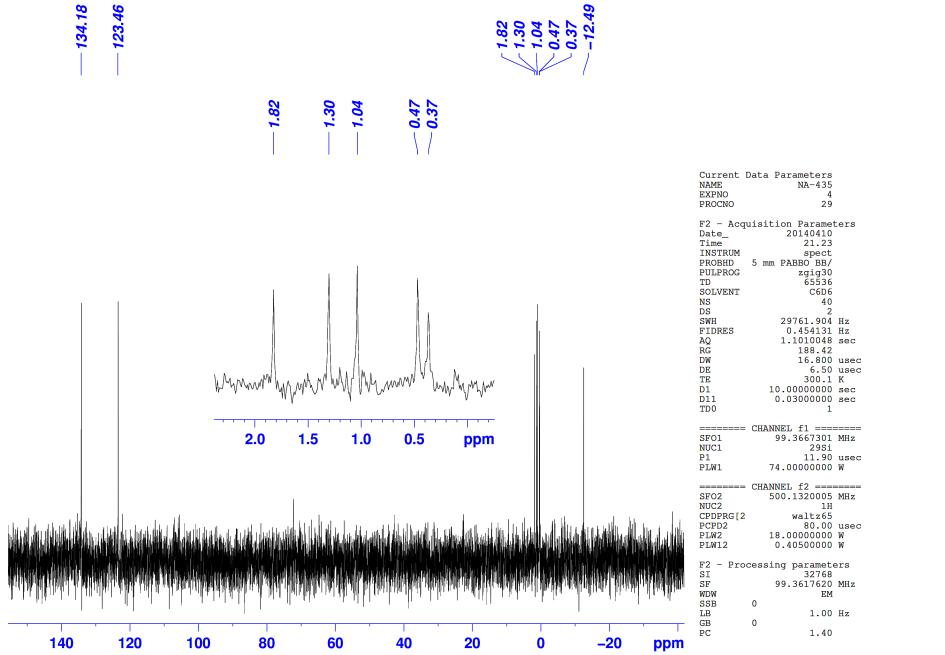
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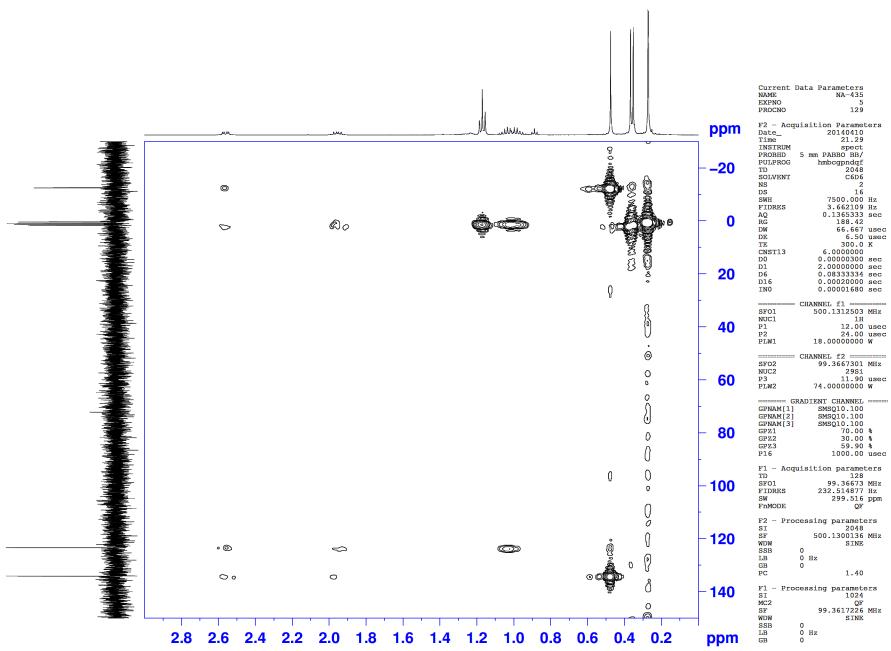
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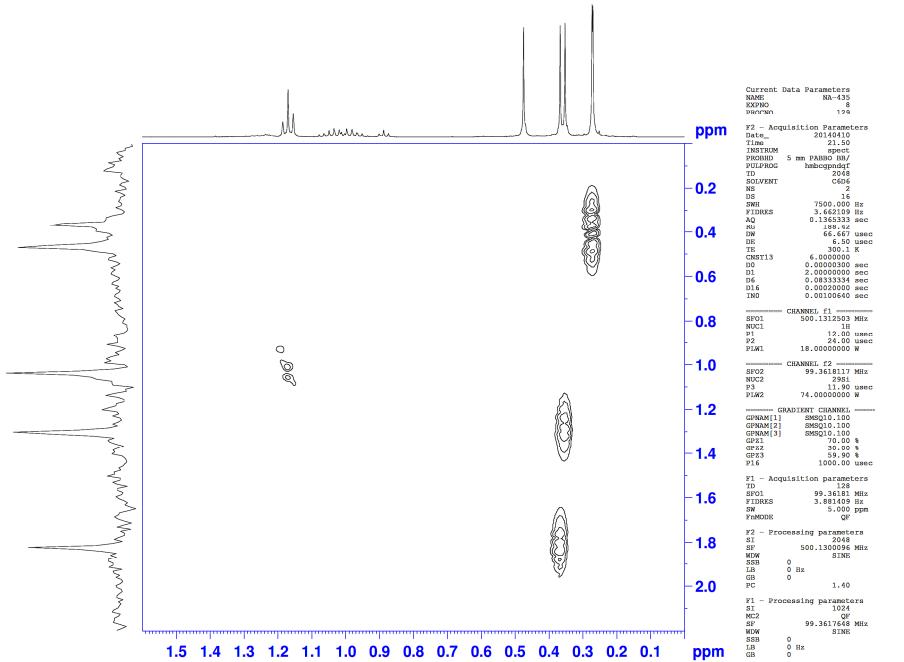
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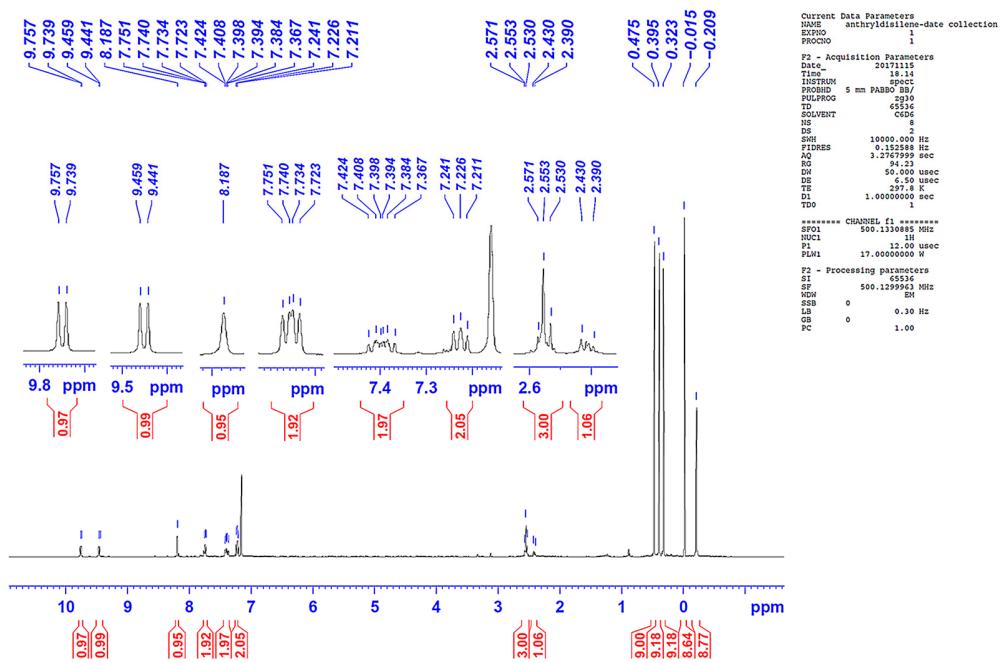
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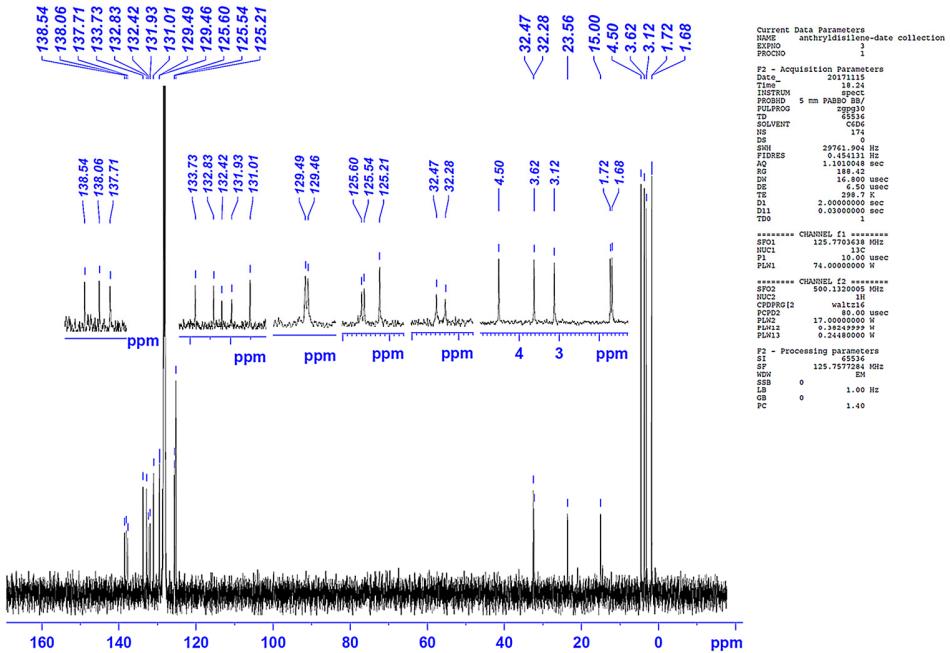
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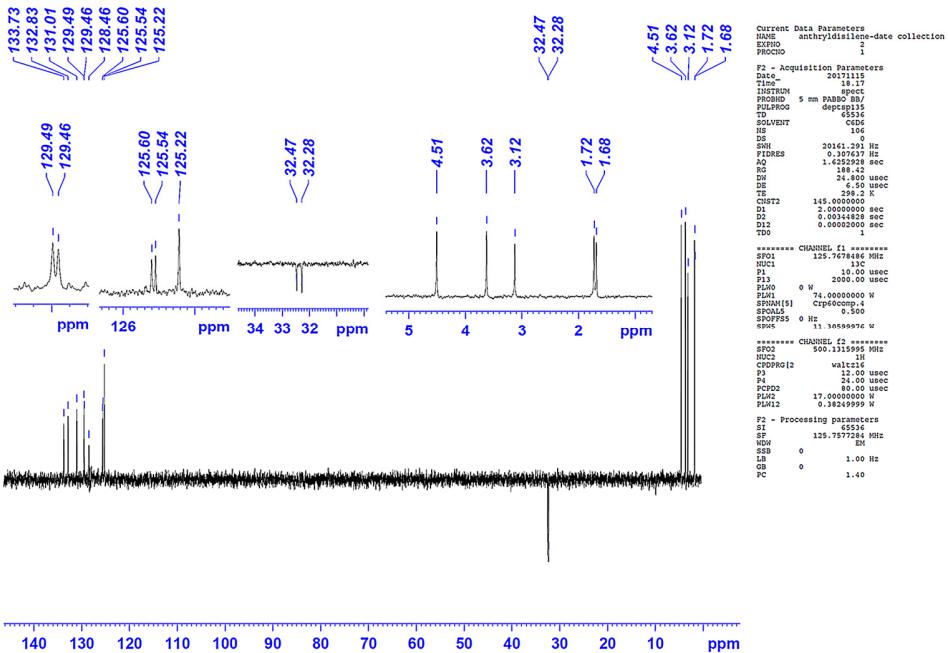
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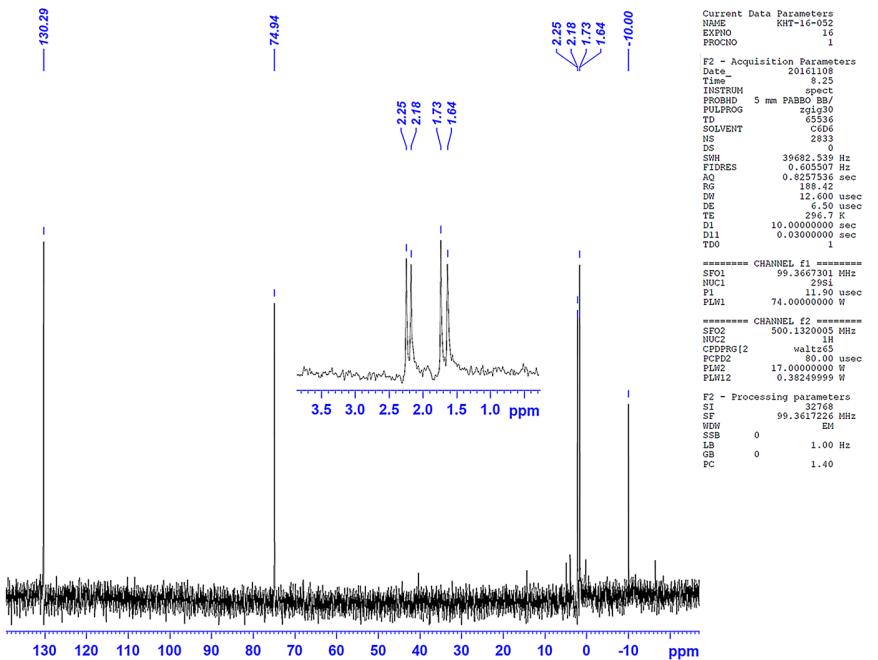
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–S17–
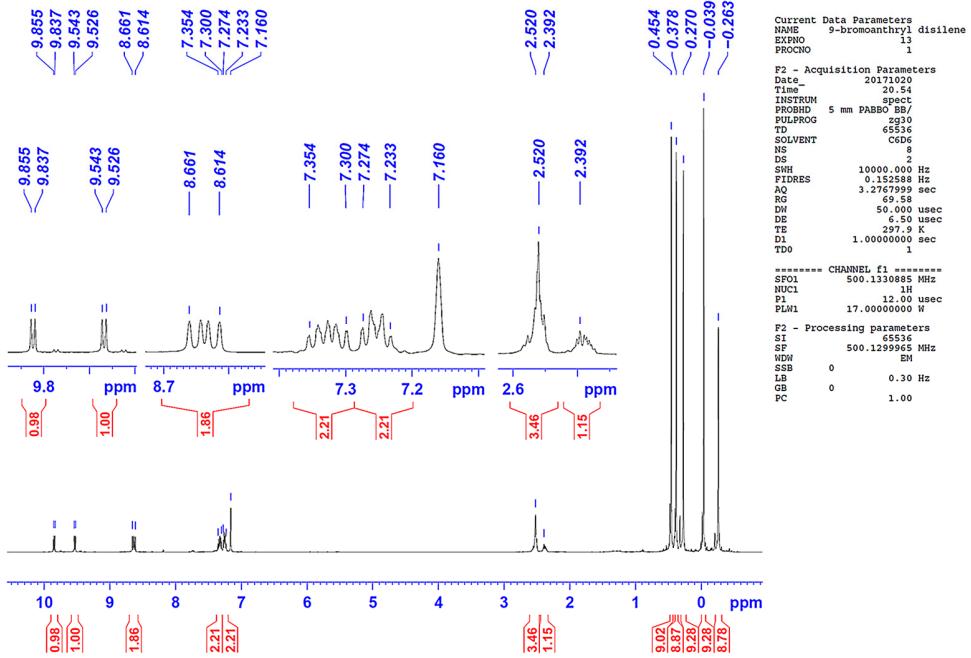
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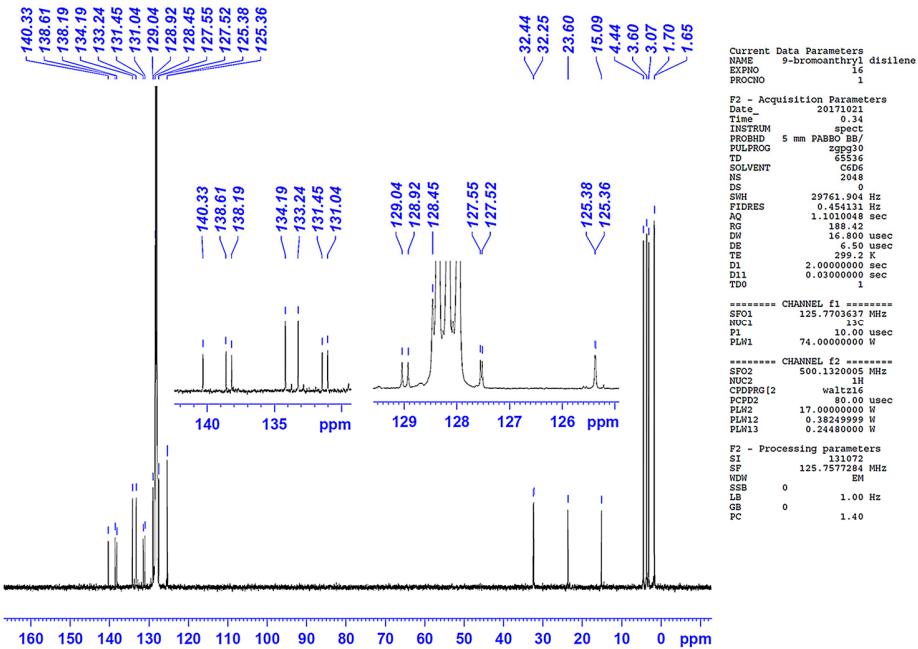
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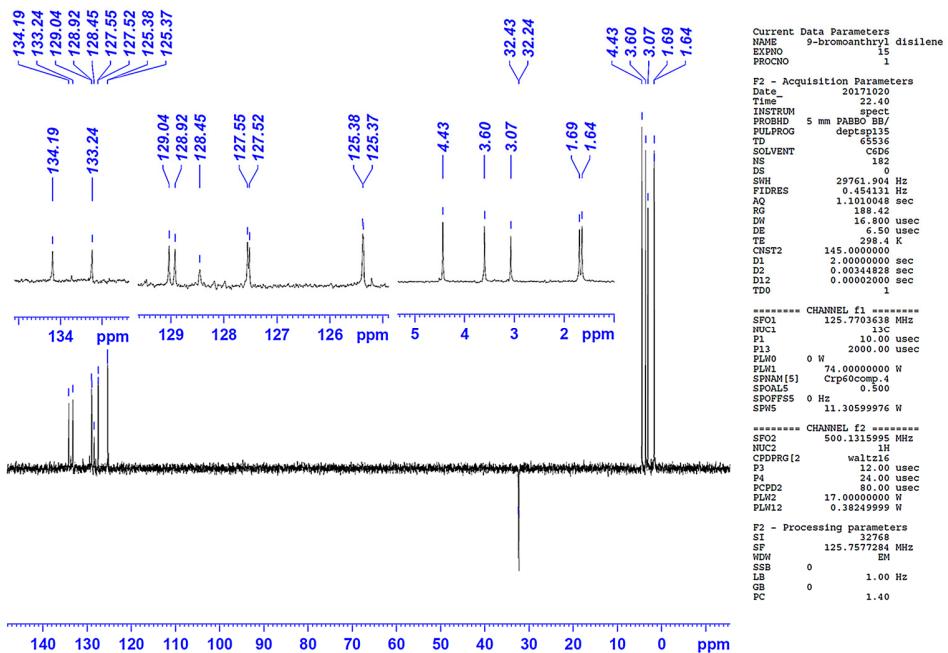
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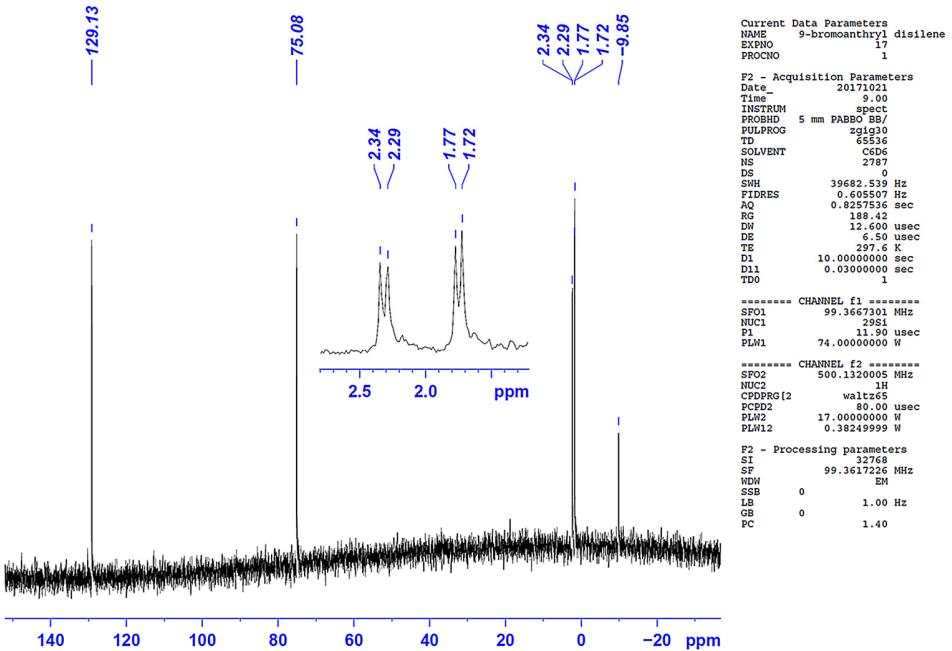
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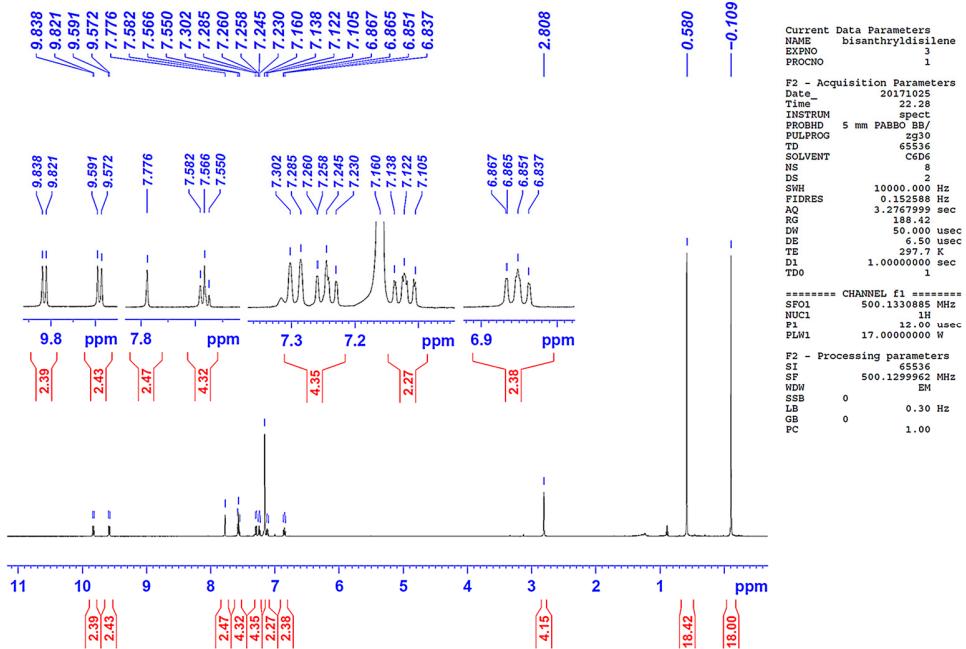
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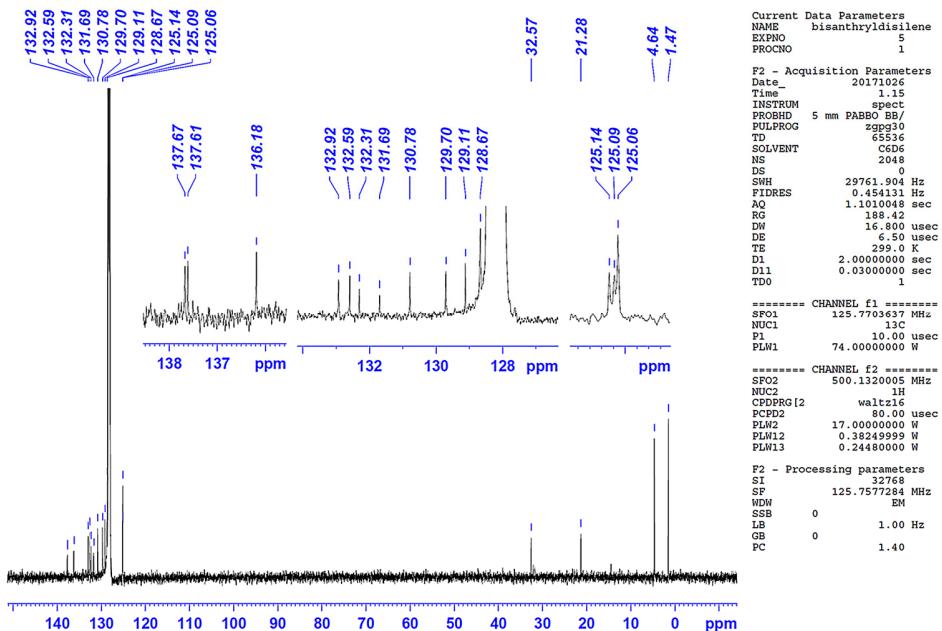
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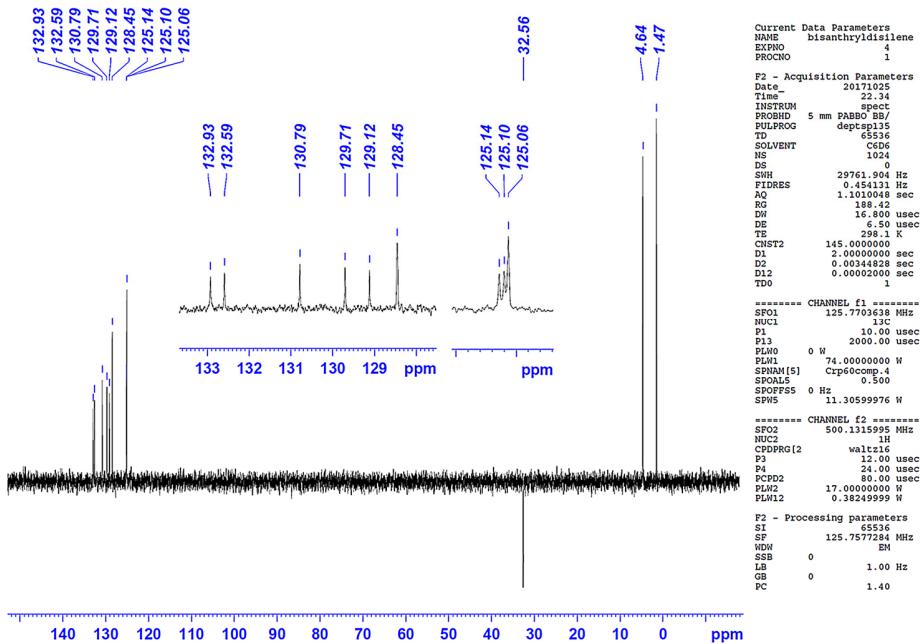
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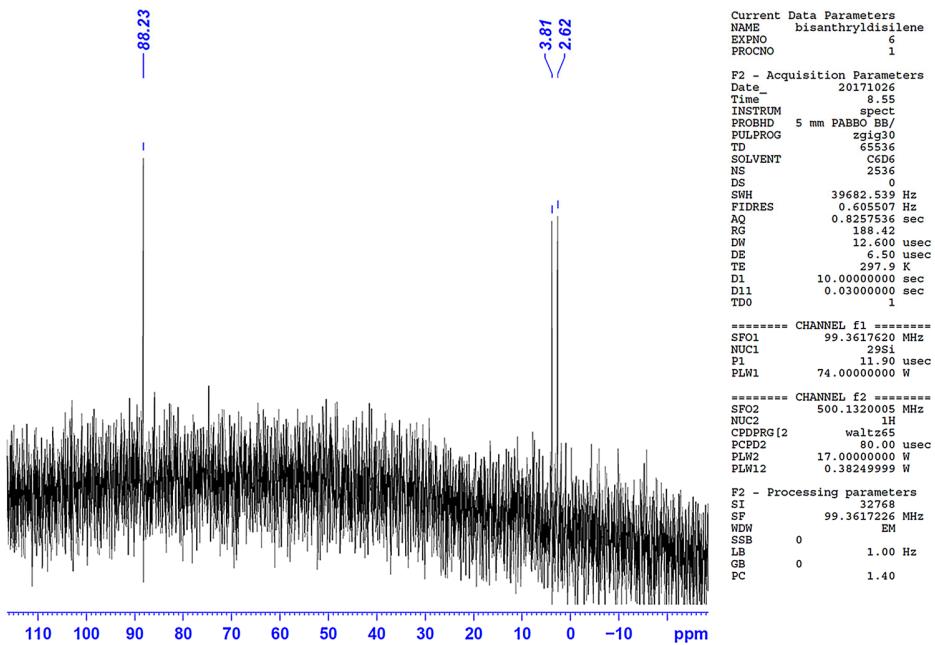
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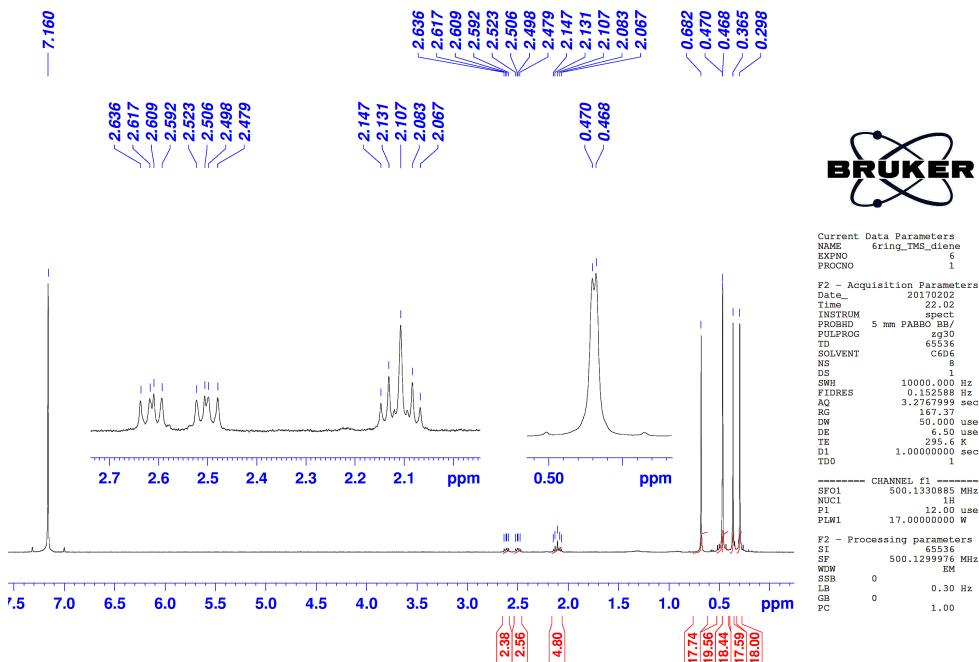
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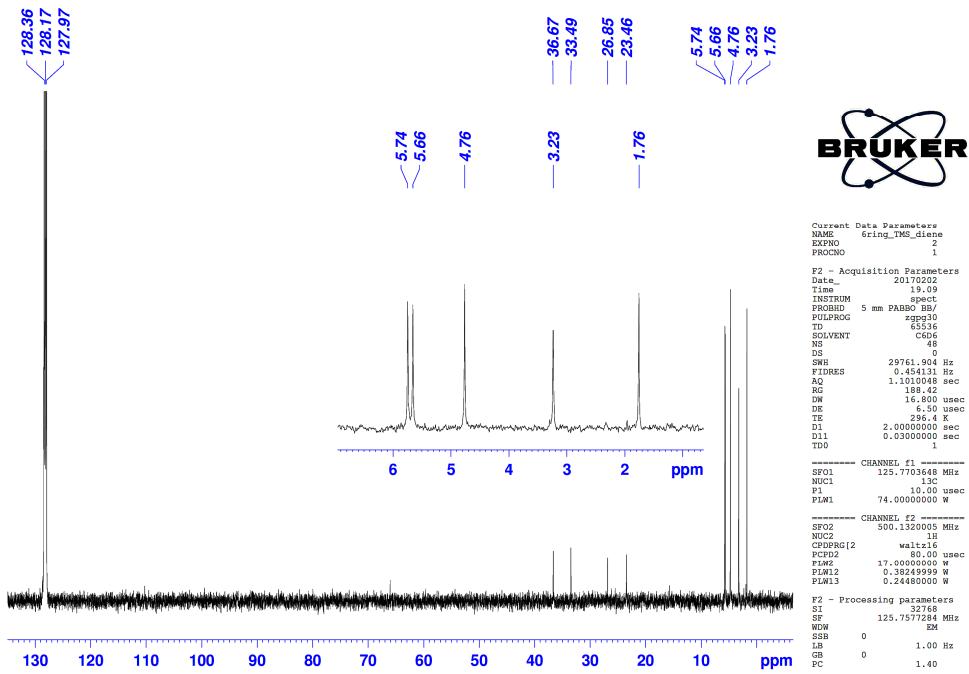
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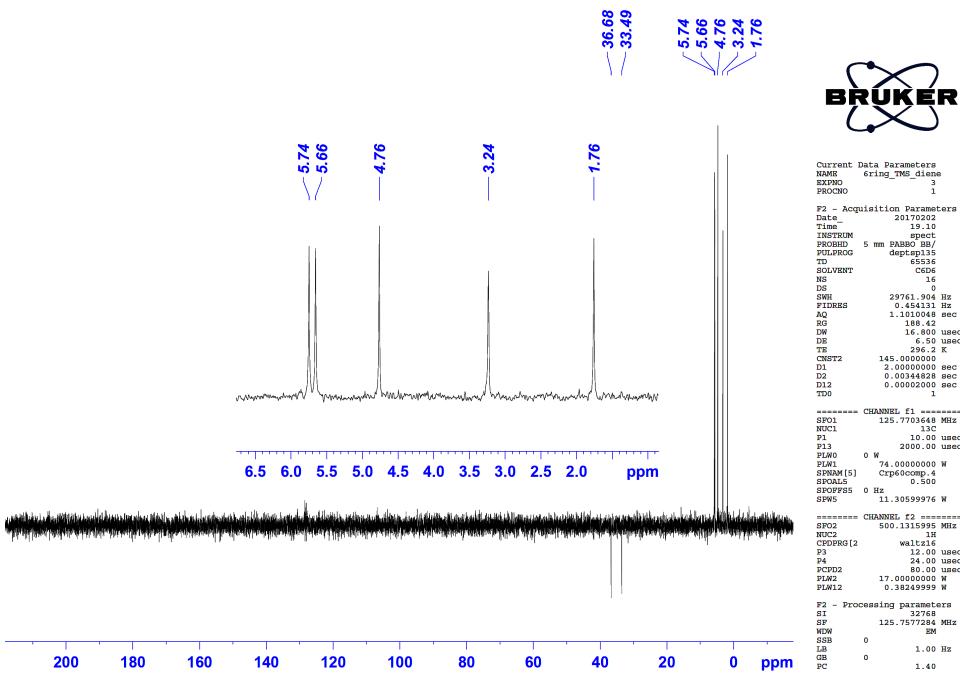
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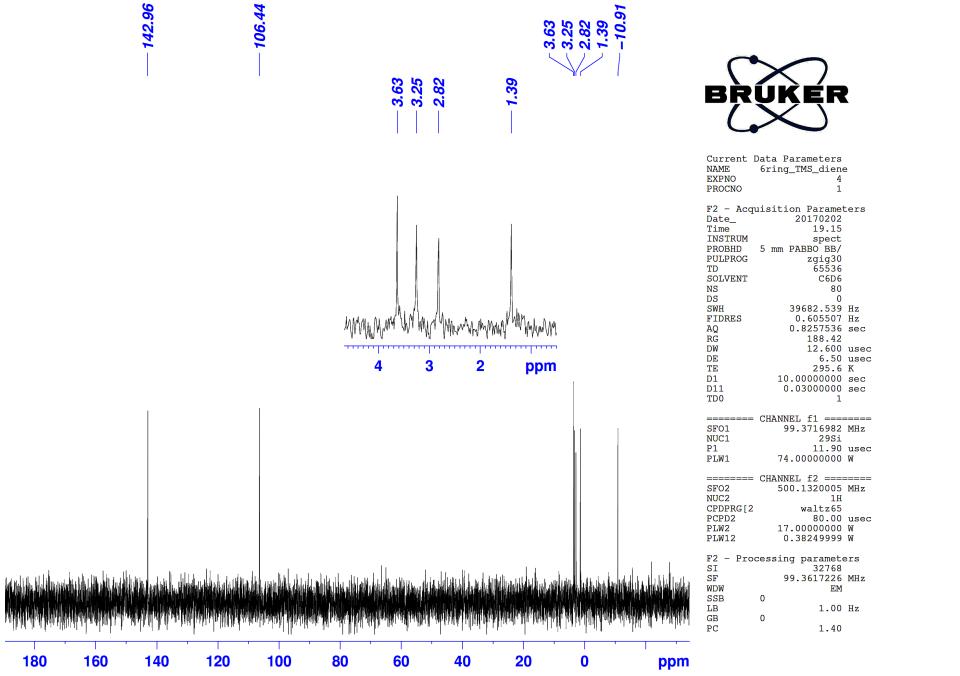
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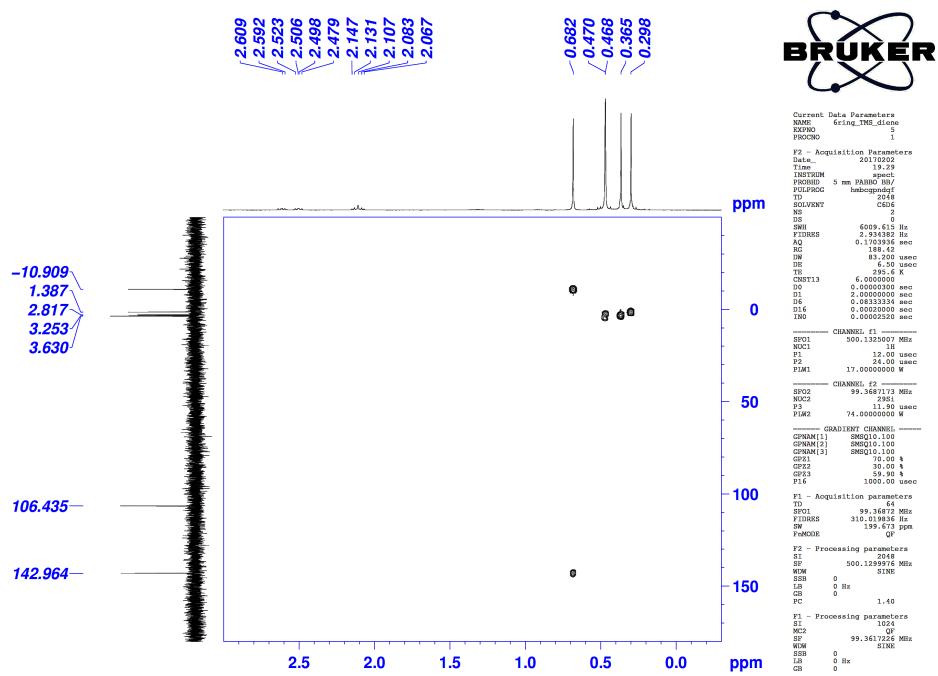
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2. UV-vis Spectra

(a)

(b)
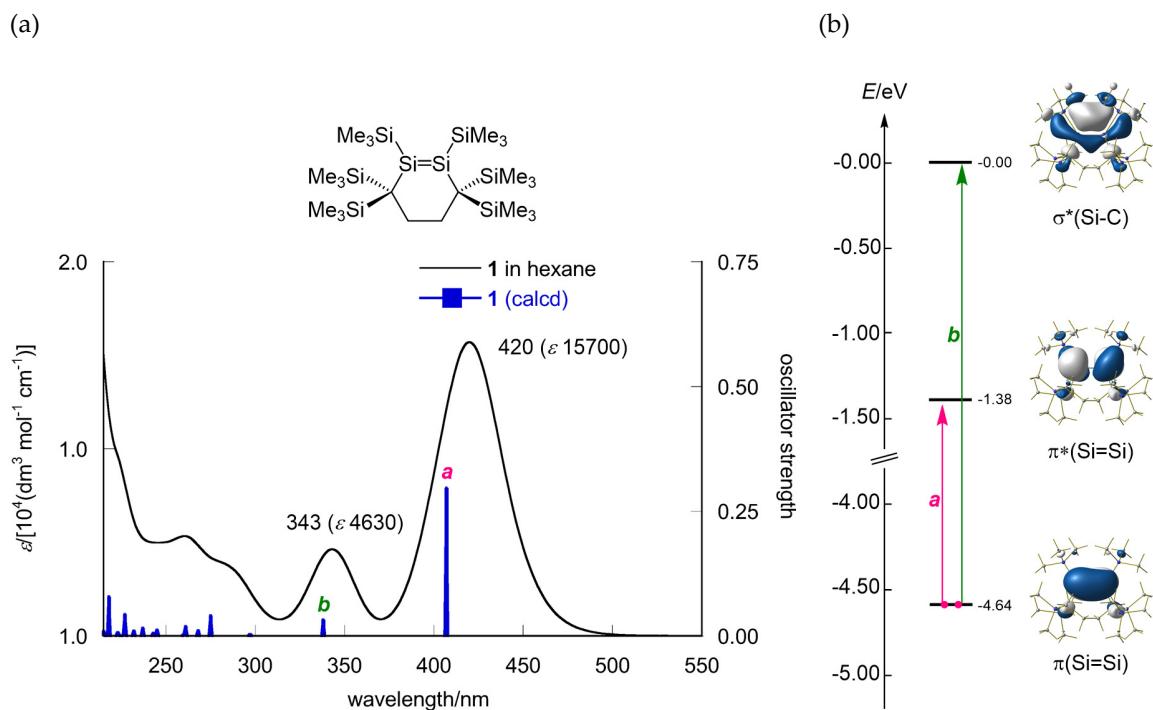
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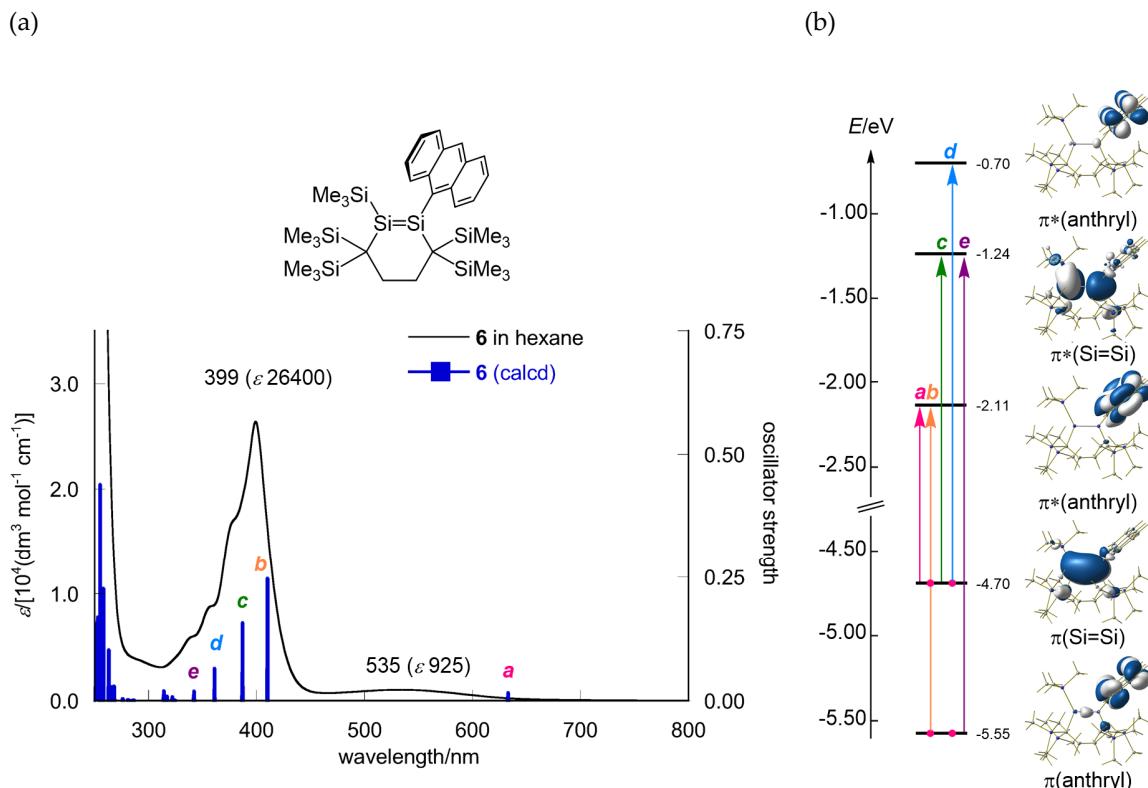
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(a)

(b)
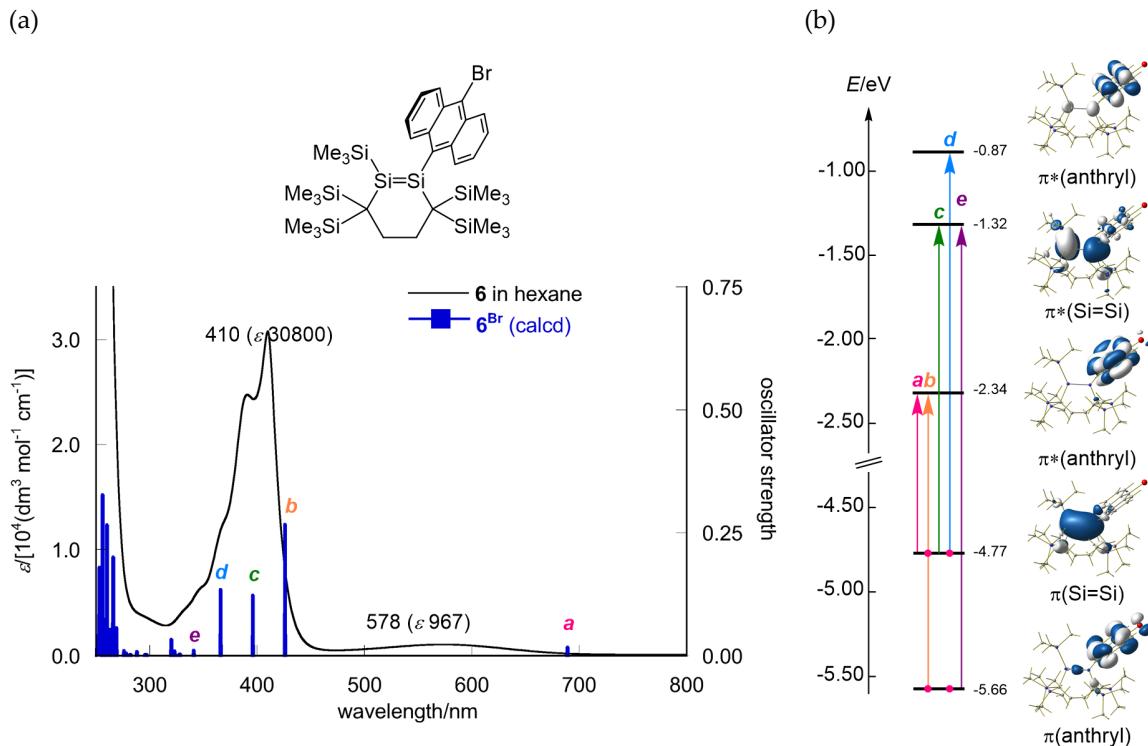
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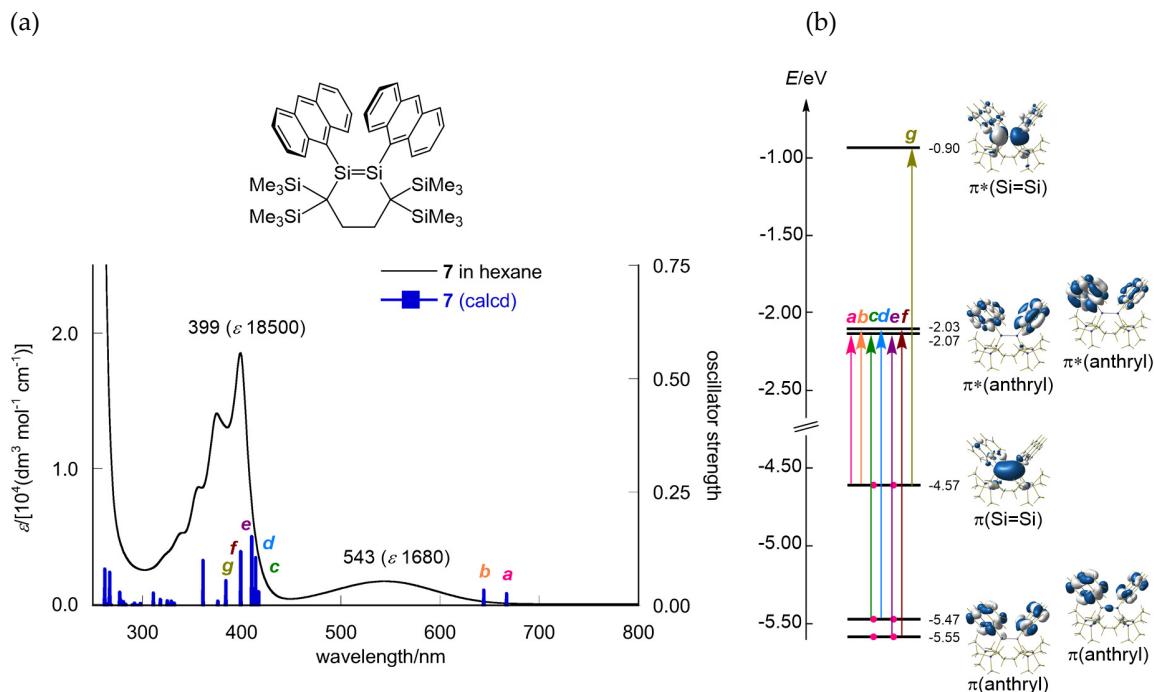
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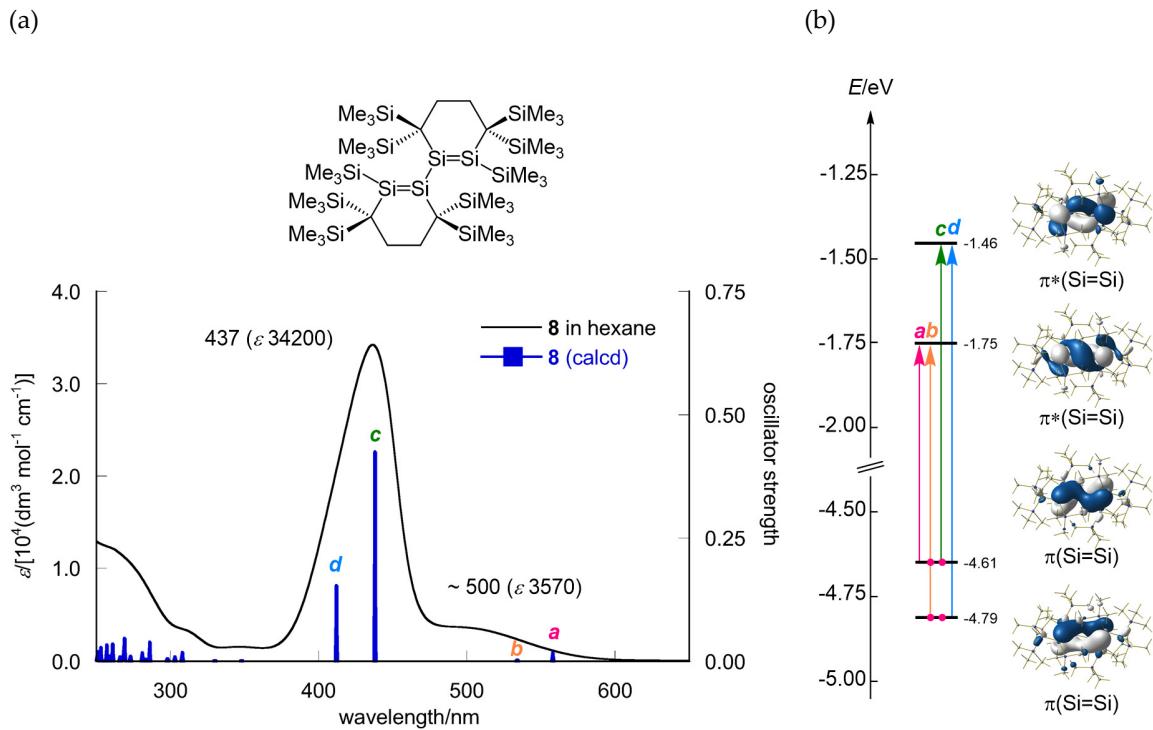
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3. DFT Calculations

All theoretical calculations were performed using the Gaussian 09[S1] and GRRM14[S2] programs. Geometry optimizations and frequency analyses of **1**, **6**, **6**[Br], **7**, and **8** were carried out at the B3PW91-D3/6-31G(d) level of theory for all compounds. Imaginary frequencies were not found in any of the optimized structures. Atomic coordinates for these compounds are summarized in a .xyz file (optimized_structure_na04.xyz). The transition energies and oscillator strengths of the electron transitions of **1**, **6**, **6**[Br], **7**, and **8** were calculated using a time-dependent hybrid DFT method (TD DFT) at the B3LYP/6-311G(d) level of theory (Tables S1-S5). Selected Kohn-Sham orbitals of **1**, **6**, **6**[Br], **7**, and **8** are shown in Figures S46-S50, respectively. Selected structural parameters and spectral data were summarized in Table S6.

Calculated Transition Energies and Oscillator Strengths of the Electron Transitions

Table S1. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of **1**

```
-------------------------------------------------------------------
Excited State   1:      Singlet-A    3.0400 eV  407.84 nm  f=0.2970  <S**2>=0.000
    151 ->152          0.69541
    151 ->153          0.11294
Excited State   2:      Singlet-A    3.6708 eV  337.76 nm  f=0.0325  <S**2>=0.000
    151 ->152         -0.11132
    151 ->153          0.69259

Excited State   3:      Singlet-A    4.1756 eV  296.93 nm  f=0.0033  <S**2>=0.000
    150 ->152          0.69227
    151 ->155          0.10556

Excited State   4:      Singlet-A    4.3616 eV  284.27 nm  f=0.0003  <S**2>=0.000
    151 ->155          0.68344
    151 ->159          0.11496

Excited State   5:      Singlet-A    4.5099 eV  274.92 nm  f=0.0410  <S**2>=0.000
    149 ->152         -0.18045
    151 ->154          0.67327

Excited State   6:      Singlet-A    4.6192 eV  268.41 nm  f=0.0108  <S**2>=0.000
    149 ->152          0.63398
    151 ->154          0.20058
    151 ->156         -0.21182

Excited State   7:      Singlet-A    4.7439 eV  261.35 nm  f=0.0194  <S**2>=0.000
    149 ->152          0.24149
    151 ->156          0.64524

Excited State   8:      Singlet-A    4.7761 eV  259.60 nm  f=0.0030  <S**2>=0.000
    151 ->157          0.64430
    151 ->159         -0.24075

Excited State   9:      Singlet-A    5.0575 eV  245.15 nm  f=0.0121  <S**2>=0.000
    147 ->152         -0.20212
    148 ->152          0.56935
    151 ->158         -0.34352

Excited State  10:      Singlet-A    5.1125 eV  242.51 nm  f=0.0058  <S**2>=0.000
    147 ->152         -0.17502
    148 ->152          0.30887
    151 ->158          0.58868
    151 ->159         -0.13291

Excited State  11:      Singlet-A    5.1435 eV  241.05 nm  f=0.0000  <S**2>=0.000
    151 ->157          0.25934
    151 ->158          0.14198
    151 ->159          0.62935

Excited State  12:      Singlet-A    5.2392 eV  236.65 nm  f=0.0053  <S**2>=0.000
    151 ->156          0.12813
    151 ->160          0.68417

Excited State  13:      Singlet-A    5.2421 eV  236.51 nm  f=0.0160  <S**2>=0.000
    147 ->152          0.64637
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      148 ->152         0.26122

Excited State  14:      Singlet-A     5.3532 eV 231.61 nm  f=0.0103  <S**2>=0.000
      151 ->161         0.67455

Excited State  15:      Singlet-A     5.4548 eV 227.29 nm  f=0.0434  <S**2>=0.000
      150 ->153        -0.21307
      151 ->162         0.58727
      151 ->163        -0.30095

Excited State  16:      Singlet-A     5.4765 eV 226.39 nm  f=0.0008  <S**2>=0.000
      146 ->152         0.70082

Excited State  17:      Singlet-A     5.5720 eV 222.51 nm  f=0.0071  <S**2>=0.000
      151 ->162         0.31612
      151 ->163         0.61477

Excited State  18:      Singlet-A     5.6991 eV 217.55 nm  f=0.0789  <S**2>=0.000
      150 ->153         0.63864
      151 ->162         0.19558
      151 ->163        -0.10860
      151 ->165         0.10638

Excited State  19:      Singlet-A     5.7695 eV 214.90 nm  f=0.0099  <S**2>=0.000
      151 ->161        -0.10744
      151 ->164         0.66255
      151 ->167         0.18075

Excited State  20:      Singlet-A     5.8205 eV 213.01 nm  f=0.0125  <S**2>=0.000
      150 ->153        -0.11215
      151 ->165         0.67262
      151 ->169        -0.11097

Excited State  21:      Singlet-A     5.8938 eV 210.36 nm  f=0.0009  <S**2>=0.000
      143 ->152        -0.12073
      145 ->152         0.68561

Excited State  22:      Singlet-A     5.9183 eV 209.49 nm  f=0.0010  <S**2>=0.000
      142 ->152        -0.13001
      144 ->152         0.65459
      151 ->167        -0.15955
      151 ->168        -0.14458

Excited State  23:      Singlet-A     5.9274 eV 209.17 nm  f=0.0097  <S**2>=0.000
      144 ->152         0.12320
      151 ->164        -0.20175
      151 ->167         0.61530
      151 ->168        -0.13112
      151 ->171         0.11668

Excited State  24:      Singlet-A     5.9320 eV 209.01 nm  f=0.0004  <S**2>=0.000
      151 ->166         0.65925
      151 ->169         0.16228

Excited State  25:      Singlet-A     5.9655 eV 207.84 nm  f=0.0045  <S**2>=0.000
      144 ->152         0.18394
      151 ->167         0.14167
      151 ->168         0.62601
      151 ->171        -0.16672

Excited State  26:      Singlet-A     6.0047 eV 206.48 nm  f=0.0018  <S**2>=0.000
      141 ->152         0.10446
      143 ->152         0.67519
      145 ->152         0.11491
      151 ->169        -0.11576

Excited State  27:      Singlet-A     6.0214 eV 205.91 nm  f=0.0061  <S**2>=0.000
```

```
     143 ->152        0.11546
     151 ->165        0.12130
     151 ->166       -0.15733
     151 ->169        0.64851

 Excited State  28:      Singlet-A      6.0637 eV 204.47 nm  f=0.0147  <S**2>=0.000
     136 ->152        0.16657
     139 ->152       -0.13126
     140 ->152       -0.38745
     142 ->152        0.40989
     149 ->153        0.34779

 Excited State  29:      Singlet-A      6.0873 eV 203.68 nm  f=0.0631  <S**2>=0.000
     139 ->152        0.14445
     140 ->152        0.20109
     142 ->152       -0.22046
     149 ->153        0.57382
     151 ->171        0.16947

 Excited State  30:      Singlet-A      6.0894 eV 203.61 nm  f=0.0111  <S**2>=0.000
     142 ->152        0.13117
     149 ->153       -0.13712
     151 ->168        0.19133
     151 ->171        0.61928

 Excited State  31:      Singlet-A      6.1198 eV 202.60 nm  f=0.0016  <S**2>=0.000
     136 ->152       -0.15829
     140 ->152        0.45031
     142 ->152        0.48896
     144 ->152        0.11550

 Excited State  32:      Singlet-A      6.1257 eV 202.40 nm  f=0.0576  <S**2>=0.000
     138 ->152        0.26970
     141 ->152        0.60533
     151 ->170       -0.19014
---------------------------------------------------------------------------
JOB name: ti552Si2TD
Method/Basis: TD-B3LYP-D3/6-311G(d) [hexane]
```

Table S2. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of **6**

```
---------------------------------------------------------------------------
 Excited State   1:      Singlet-A      1.9565 eV 633.71 nm  f=0.0166  <S**2>=0.000
     177 ->178        0.70501

 Excited State   2:      Singlet-A      3.0231 eV 410.13 nm  f=0.2474  <S**2>=0.000
     176 ->178        0.66314
     177 ->179       -0.22931

 Excited State   3:      Singlet-A      3.2023 eV 387.17 nm  f=0.1577  <S**2>=0.000
     176 ->178        0.21627
     177 ->179        0.61532
     177 ->180        0.24484

 Excited State   4:      Singlet-A      3.4339 eV 361.06 nm  f=0.0655  <S**2>=0.000
     177 ->179       -0.22178
     177 ->180        0.65704

 Excited State   5:      Singlet-A      3.6297 eV 341.58 nm  f=0.0202  <S**2>=0.000
     174 ->178        0.18245
     176 ->179        0.66889
```

```
Excited State   6:      Singlet-A    3.8250 eV 324.14 nm  f=0.0017  <S**2>=0.000
    177 ->182         0.68259
    177 ->183         0.10647
    177 ->184         0.11108

Excited State   7:      Singlet-A    3.8451 eV 322.45 nm  f=0.0085  <S**2>=0.000
    174 ->178         0.47359
    175 ->178        -0.12519
    176 ->179        -0.17249
    176 ->180         0.46745

Excited State   8:      Singlet-A    3.9064 eV 317.39 nm  f=0.0094  <S**2>=0.000
    175 ->178         0.27917
    177 ->181         0.63857

Excited State   9:      Singlet-A    3.9495 eV 313.92 nm  f=0.0203  <S**2>=0.000
    175 ->178         0.62923
    177 ->181        -0.28391

Excited State  10:      Singlet-A    4.3424 eV 285.52 nm  f=0.0021  <S**2>=0.000
    173 ->178         0.69215

Excited State  11:      Singlet-A    4.3895 eV 282.45 nm  f=0.0009  <S**2>=0.000
    172 ->178         0.23107
    177 ->182        -0.14114
    177 ->183         0.55755
    177 ->184         0.30019

Excited State  12:      Singlet-A    4.4155 eV 280.79 nm  f=0.0024  <S**2>=0.000
    171 ->178        -0.15425
    172 ->178         0.58017
    176 ->181         0.24536
    177 ->183        -0.22592
    177 ->184        -0.10468

Excited State  13:      Singlet-A    4.4853 eV 276.42 nm  f=0.0047  <S**2>=0.000
    175 ->179         0.67047

Excited State  14:      Singlet-A    4.6350 eV 267.50 nm  f=0.0299  <S**2>=0.000
    170 ->178        -0.13086
    171 ->178         0.57194
    172 ->178         0.20292
    174 ->178         0.12394
    176 ->180        -0.12260
    176 ->181        -0.16400
    177 ->184         0.15656

Excited State  15:      Singlet-A    4.6617 eV 265.96 nm  f=0.0288  <S**2>=0.000
    171 ->178        -0.27025
    174 ->178         0.11485
    176 ->180        -0.13206
    176 ->181        -0.12995
    177 ->183        -0.29062
    177 ->184         0.51164

Excited State  16:      Singlet-A    4.7166 eV 262.87 nm  f=0.1032  <S**2>=0.000
    171 ->178        -0.17003
    174 ->178         0.16091
    176 ->180        -0.18119
    176 ->181        -0.26459
    177 ->184        -0.22489
    177 ->185         0.50165

Excited State  17:      Singlet-A    4.8010 eV 258.25 nm  f=0.2271  <S**2>=0.000
    172 ->178        -0.18268
    174 ->178         0.20127
    176 ->180        -0.21204
```

```
                176 ->181           0.50189
                176 ->182          -0.24105
                177 ->185           0.17826

Excited State  18:      Singlet-A      4.8538 eV  255.44 nm  f=0.0154  <S**2>=0.000
                172 ->178          -0.10986
                176 ->181           0.21104
                176 ->182           0.59909
                177 ->185           0.11718
                177 ->186           0.13187

Excited State  19:      Singlet-A      4.8544 eV  255.41 nm  f=0.4240  <S**2>=0.000
                173 ->179          -0.28558
                174 ->178          -0.23010
                174 ->179          -0.11967
                176 ->180           0.25067
                176 ->182          -0.17684
                177 ->184           0.13152
                177 ->185           0.30505
                177 ->186           0.31989

Excited State  20:      Singlet-A      4.8972 eV  253.17 nm  f=0.1697  <S**2>=0.000
                169 ->178          -0.28092
                170 ->178           0.43492
                171 ->178           0.10637
                173 ->179           0.19644
                174 ->178          -0.14883
                176 ->180           0.15845
                176 ->182           0.11061
                177 ->185           0.16126
                177 ->186          -0.22930

Excited State  21:      Singlet-A      4.9224 eV  251.88 nm  f=0.1542  <S**2>=0.000
                169 ->178          -0.18758
                170 ->178           0.29463
                174 ->178           0.14431
                174 ->179           0.17878
                176 ->180          -0.15481
                177 ->185          -0.13998
                177 ->186           0.47307
                177 ->188           0.11539

Excited State  22:      Singlet-A      4.9365 eV  251.16 nm  f=0.0832  <S**2>=0.000
                169 ->178           0.10053
                170 ->178          -0.21964
                173 ->179           0.58801
                174 ->178          -0.10106
                176 ->180           0.11071
                177 ->185           0.10790
                177 ->186           0.18098

Excited State  23:      Singlet-A      4.9847 eV  248.73 nm  f=0.1471  <S**2>=0.000
                174 ->178          -0.10697
                174 ->179           0.65726
                176 ->180           0.13630

Excited State  24:      Singlet-A      5.0405 eV  245.97 nm  f=0.0035  <S**2>=0.000
                167 ->178          -0.13156
                169 ->178           0.55224
                170 ->178           0.36976
                171 ->178           0.11133

Excited State  25:      Singlet-A      5.1943 eV  238.69 nm  f=0.0173  <S**2>=0.000
                168 ->178          -0.20468
                177 ->187           0.65144

Excited State  26:      Singlet-A      5.2074 eV  238.09 nm  f=0.0059  <S**2>=0.000
```

```
   165 ->178        -0.10564
   166 ->178        -0.12427
   168 ->178         0.63185
   177 ->187         0.20514

Excited State  27:      Singlet-A      5.2377 eV  236.71 nm  f=0.0229  <S**2>=0.000
   177 ->186        -0.15360
   177 ->188         0.64506
   177 ->189         0.18551

Excited State  28:      Singlet-A      5.2828 eV  234.69 nm  f=0.0218  <S**2>=0.000
   171 ->179         0.47403
   172 ->179         0.49218

Excited State  29:      Singlet-A      5.3326 eV  232.50 nm  f=0.0030  <S**2>=0.000
   162 ->178        -0.10286
   163 ->178        -0.10796
   165 ->178         0.18812
   166 ->178         0.44992
   167 ->178        -0.37685
   168 ->178         0.15857
   171 ->179         0.13863
   172 ->179        -0.11789

Excited State  30:      Singlet-A      5.3520 eV  231.66 nm  f=0.0033  <S**2>=0.000
   167 ->178         0.18670
   171 ->179         0.46074
   172 ->179        -0.41742
   174 ->181         0.12188

Excited State  31:      Singlet-A      5.3727 eV  230.77 nm  f=0.1079  <S**2>=0.000
   175 ->180         0.67105

Excited State  32:      Singlet-A      5.3933 eV  229.88 nm  f=0.0025  <S**2>=0.000
   158 ->178         0.11214
   160 ->178         0.10381
   163 ->178         0.22042
   166 ->178         0.43094
   167 ->178         0.35261
   169 ->178         0.16244
   176 ->183        -0.16746
------------------------------------------------------------------------
JOB name: ti552SiAntTD
Method/Basis: TD-B3LYP-D3/6-311G(d) [hexane]
```

Table S3. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of **6**[Br]

```
------------------------------------------------------------------------
Excited State   1:      Singlet-A      1.7996 eV  688.97 nm  f=0.0177  <S**2>=0.000
   194 ->195         0.70538

Excited State   2:      Singlet-A      2.9114 eV  425.86 nm  f=0.2676  <S**2>=0.000
   193 ->195         0.68615
   194 ->196         0.15154

Excited State   3:      Singlet-A      3.1308 eV  396.02 nm  f=0.1236  <S**2>=0.000
   193 ->195        -0.12562
   194 ->196         0.59830
   194 ->197         0.34249
```

```
Excited State   4:      Singlet-A    3.3836 eV  366.42 nm  f=0.1352  <S**2>=0.000
   194 ->196       -0.31852
   194 ->197        0.61195

Excited State   5:      Singlet-A    3.6388 eV  340.73 nm  f=0.0115  <S**2>=0.000
   191 ->195        0.27888
   193 ->196        0.62476
   193 ->197        0.13825

Excited State   6:      Singlet-A    3.7775 eV  328.21 nm  f=0.0039  <S**2>=0.000
   191 ->195        0.10305
   192 ->195        0.66044
   193 ->197        0.12545
   194 ->198        0.14762

Excited State   7:      Singlet-A    3.8154 eV  324.96 nm  f=0.0012  <S**2>=0.000
   194 ->198        0.13665
   194 ->199       -0.41200
   194 ->200        0.52334
   194 ->201       -0.11232

Excited State   8:      Singlet-A    3.8355 eV  323.26 nm  f=0.0106  <S**2>=0.000
   191 ->195        0.40365
   192 ->195       -0.15267
   193 ->196       -0.27829
   193 ->197        0.45480
   194 ->198       -0.12099

Excited State   9:      Singlet-A    3.8720 eV  320.21 nm  f=0.0339  <S**2>=0.000
   192 ->195       -0.14925
   194 ->198        0.65772
   194 ->199        0.10227

Excited State  10:      Singlet-A    4.1814 eV  296.51 nm  f=0.0021  <S**2>=0.000
   190 ->195        0.68459
   191 ->195       -0.12979

Excited State  11:      Singlet-A    4.1938 eV  295.64 nm  f=0.0035  <S**2>=0.000
   194 ->199        0.55278
   194 ->200        0.41903

Excited State  12:      Singlet-A    4.3096 eV  287.69 nm  f=0.0009  <S**2>=0.000
   188 ->195        0.47037
   189 ->195        0.46733
   193 ->198        0.18694

Excited State  13:      Singlet-A    4.3897 eV  282.44 nm  f=0.0032  <S**2>=0.000
   194 ->200        0.16879
   194 ->201        0.61074
   194 ->202        0.27660

Excited State  14:      Singlet-A    4.4656 eV  277.64 nm  f=0.0059  <S**2>=0.000
   187 ->195        0.15563
   188 ->195       -0.46440
   189 ->195        0.48681

Excited State  15:      Singlet-A    4.4850 eV  276.44 nm  f=0.0109  <S**2>=0.000
   192 ->196        0.66513
   193 ->197       -0.10895
```

```
Excited State  16:      Singlet-A    4.6141 eV  268.71 nm  f=0.0574  <S**2>=0.000
      186 ->195        -0.29108
      191 ->195         0.14619
      193 ->197        -0.15321
      193 ->198        -0.30360
      193 ->199         0.42310
      194 ->201         0.10261
      194 ->202        -0.14912
      194 ->203        -0.13315

Excited State  17:      Singlet-A    4.6565 eV  266.26 nm  f=0.2016  <S**2>=0.000
      186 ->195         0.41888
      187 ->195        -0.10662
      191 ->195         0.24267
      193 ->197        -0.25105
      193 ->199        -0.16420
      193 ->200         0.10821
      194 ->201         0.12089
      194 ->202        -0.24690
      194 ->203        -0.18467

Excited State  18:      Singlet-A    4.6840 eV  264.70 nm  f=0.0374  <S**2>=0.000
      186 ->195         0.33232
      187 ->195        -0.15425
      193 ->199         0.41629
      193 ->200         0.33371
      194 ->202         0.12708

Excited State  19:      Singlet-A    4.7138 eV  263.02 nm  f=0.0538  <S**2>=0.000
      193 ->198        -0.11088
      194 ->201        -0.20724
      194 ->202         0.48250
      194 ->203        -0.40719

Excited State  20:      Singlet-A    4.7589 eV  260.53 nm  f=0.0555  <S**2>=0.000
      185 ->195        -0.26408
      186 ->195         0.12378
      187 ->195         0.55551
      189 ->195        -0.11206
      193 ->198         0.20379

Excited State  21:      Singlet-A    4.7740 eV  259.70 nm  f=0.2667  <S**2>=0.000
      185 ->195         0.10229
      186 ->195        -0.17695
      187 ->195        -0.18572
      188 ->195        -0.16427
      191 ->195         0.20136
      193 ->197        -0.22378
      193 ->198         0.50029
      193 ->199         0.12316

Excited State  22:      Singlet-A    4.8363 eV  256.36 nm  f=0.3279  <S**2>=0.000
      190 ->196        -0.19562
      191 ->195         0.18601
      193 ->197        -0.19628
      193 ->198        -0.17735
      194 ->202         0.22006
      194 ->203         0.43261
      194 ->204         0.22653
```

```
Excited State  23:      Singlet-A     4.8784 eV  254.15 nm  f=0.0025  <S**2>=0.000
   182 ->195        0.47576
   183 ->195        0.11262
   185 ->195       -0.37544
   187 ->195       -0.19130
   190 ->196        0.18364
   194 ->204       -0.13890

Excited State  24:      Singlet-A     4.8890 eV  253.60 nm  f=0.0127  <S**2>=0.000
   182 ->195        0.47029
   185 ->195        0.43001
   187 ->195        0.20983

Excited State  25:      Singlet-A     4.9011 eV  252.97 nm  f=0.1804  <S**2>=0.000
   182 ->195       -0.16967
   185 ->195        0.13415
   190 ->196        0.38611
   191 ->195        0.15447
   193 ->197       -0.15705
   194 ->203        0.22289
   194 ->204       -0.38490

Excited State  26:      Singlet-A     4.9298 eV  251.50 nm  f=0.0133  <S**2>=0.000
   190 ->196        0.47877
   191 ->196       -0.10557
   193 ->200        0.10400
   194 ->204        0.45026

Excited State  27:      Singlet-A     4.9444 eV  250.76 nm  f=0.0408  <S**2>=0.000
   186 ->195       -0.22665
   193 ->199       -0.27234
   193 ->200        0.55908
   194 ->204       -0.13428

Excited State  28:      Singlet-A     5.0342 eV  246.28 nm  f=0.0057  <S**2>=0.000
   179 ->195        0.17358
   181 ->195       -0.10104
   184 ->195        0.65680

Excited State  29:      Singlet-A     5.0804 eV  244.04 nm  f=0.0296  <S**2>=0.000
   190 ->196        0.14662
   191 ->196        0.66492

Excited State  30:      Singlet-A     5.1645 eV  240.07 nm  f=0.0010  <S**2>=0.000
   177 ->195        0.11600
   178 ->195       -0.14048
   179 ->195       -0.16235
   180 ->195        0.14241
   181 ->195        0.49584
   183 ->195       -0.36126
   184 ->195        0.16846

Excited State  31:      Singlet-A     5.2196 eV  237.53 nm  f=0.0032  <S**2>=0.000
   174 ->195        0.11680
   178 ->195        0.14165
   179 ->195       -0.19923
   180 ->195        0.17284
   181 ->195        0.28490
   183 ->195        0.46685
   185 ->195        0.17380
```

```
    194 ->205        0.16393
    194 ->206        0.10927


 Excited State  32:      Singlet-A      5.2274 eV  237.18 nm  f=0.0239  <S**2>=0.000
    179 ->195        0.12910
    180 ->195       -0.10591
    183 ->195       -0.13134
    189 ->196        0.15291
    194 ->205        0.58957
    194 ->206        0.23163
 ----------------------------------------------------------------------
JOB name: ti552SiAntBrTD
Method/Basis: TD-B3LYP-D3/6-311G(d) [hexane]
```

Table S4.   Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of **7**

```
 ----------------------------------------------------------------------
 Excited State   1:      Singlet-A      1.8590 eV  666.96 nm  f=0.0265  <S**2>=0.000
    203 -> 204       0.69351
    203 -> 205       0.12643


 Excited State   2:      Singlet-A      1.9249 eV  644.11 nm  f=0.0341  <S**2>=0.000
    203 -> 204      -0.12550
    203 -> 205       0.69249


 Excited State   3:      Singlet-A      2.9730 eV  417.04 nm  f=0.0314  <S**2>=0.000
    201 -> 204       0.17773
    201 -> 205       0.16081
    202 -> 204       0.63948
    202 -> 205       0.17678


 Excited State   4:      Singlet-A      2.9943 eV  414.07 nm  f=0.1066  <S**2>=0.000
    201 -> 205      -0.12173
    202 -> 204      -0.15748
    202 -> 205       0.66662
    203 -> 206       0.10845


 Excited State   5:      Singlet-A      3.0222 eV  410.24 nm  f=0.1526  <S**2>=0.000
    201 -> 204       0.62294
    201 -> 205      -0.20393
    202 -> 204      -0.11030
    203 -> 206      -0.22618


 Excited State   6:      Singlet-A      3.1096 eV  398.71 nm  f=0.1194  <S**2>=0.000
    201 -> 204       0.18147
    201 -> 205       0.63643
    202 -> 204      -0.22047


 Excited State   7:      Singlet-A      3.2302 eV  383.82 nm  f=0.0550  <S**2>=0.000
    201 -> 204       0.16927
    203 -> 206       0.52433
    203 -> 207       0.26201
    203 -> 208      -0.31701


 Excited State   8:      Singlet-A      3.2989 eV  375.84 nm  f=0.0106  <S**2>=0.000
    203 -> 206      -0.12843
    203 -> 207       0.63353
    203 -> 208       0.26479


 Excited State   9:      Singlet-A      3.4323 eV  361.23 nm  f=0.1003  <S**2>=0.000
```

```
  203 -> 206      0.34031
  203 -> 207     -0.15024
  203 -> 208      0.55972
  203 -> 211      0.11072

Excited State  10:      Singlet-A      3.7293 eV  332.46 nm  f=0.0058  <S**2>=0.000
  203 -> 209      0.39671
  203 -> 211      0.55731

Excited State  11:      Singlet-A      3.7683 eV  329.02 nm  f=0.0104  <S**2>=0.000
  203 -> 209      0.55209
  203 -> 211     -0.37677

Excited State  12:      Singlet-A      3.7810 eV  327.91 nm  f=0.0002  <S**2>=0.000
  199 -> 204     -0.25706
  199 -> 205     -0.15717
  200 -> 204     -0.11607
  200 -> 205      0.16173
  201 -> 207     -0.20508
  202 -> 206      0.51315
  202 -> 208     -0.11817
  203 -> 209     -0.17281

Excited State  13:      Singlet-A      3.8140 eV  325.08 nm  f=0.0107  <S**2>=0.000
  199 -> 204     -0.26752
  199 -> 205     -0.15337
  200 -> 204      0.19757
  200 -> 205     -0.29106
  201 -> 206     -0.29708
  201 -> 208      0.21342
  202 -> 206     -0.11632
  202 -> 207      0.30109
  202 -> 208      0.10768
  203 -> 210      0.10804

Excited State  14:      Singlet-A      3.8930 eV  318.48 nm  f=0.0117  <S**2>=0.000
  200 -> 204     -0.12992
  200 -> 205      0.17305
  202 -> 206     -0.19273
  202 -> 208     -0.18882
  203 -> 210      0.58094

Excited State  15:      Singlet-A      3.8958 eV  318.25 nm  f=0.0023  <S**2>=0.000
  199 -> 204      0.20170
  199 -> 205      0.11824
  200 -> 204      0.12018
  200 -> 205     -0.17198
  201 -> 207      0.21319
  202 -> 206      0.39401
  202 -> 208      0.25484
  203 -> 210      0.33124

Excited State  16:      Singlet-A      3.9852 eV  311.11 nm  f=0.0280  <S**2>=0.000
  199 -> 204     -0.10670
  200 -> 205     -0.10260
  201 -> 206      0.60803
  201 -> 208      0.17071
  202 -> 207      0.15429
  203 -> 210      0.13444

Excited State  17:      Singlet-A      4.1568 eV  298.27 nm  f=0.0053  <S**2>=0.000
  198 -> 204      0.65630
  198 -> 205     -0.20020
  200 -> 204     -0.10508

Excited State  18:      Singlet-A      4.2069 eV  294.72 nm  f=0.0134  <S**2>=0.000
  198 -> 204      0.17093
```

```
          198 -> 205      0.63294
          200 -> 204     -0.16935
          200 -> 205     -0.15221

Excited State  19:      Singlet-A      4.2299 eV 293.12 nm  f=0.0008  <S**2>=0.000
          198 -> 204      0.14189
          198 -> 205      0.19507
          200 -> 204      0.55635
          200 -> 205      0.35192

Excited State  20:      Singlet-A      4.2424 eV 292.25 nm  f=0.0057  <S**2>=0.000
          203 -> 212      0.68839

Excited State  21:      Singlet-A      4.2786 eV 289.77 nm  f=0.0018  <S**2>=0.000
          199 -> 204     -0.37809
          199 -> 205      0.59402

Excited State  22:      Singlet-A      4.3854 eV 282.72 nm  f=0.0029  <S**2>=0.000
          196 -> 205     -0.15760
          197 -> 204      0.26505
          197 -> 205     -0.32181
          201 -> 207      0.28564
          201 -> 208     -0.14442
          202 -> 207      0.33646
          202 -> 208     -0.19079
          202 -> 209     -0.10101

Excited State  23:      Singlet-A      4.4093 eV 281.19 nm  f=0.0059  <S**2>=0.000
          196 -> 204     -0.16649
          196 -> 205     -0.24338
          197 -> 204      0.42282
          197 -> 205     -0.13415
          201 -> 207     -0.18068
          201 -> 208      0.17530
          201 -> 209     -0.12945
          202 -> 207     -0.30441
          202 -> 208      0.11798
          202 -> 210      0.12711

Excited State  24:      Singlet-A      4.4166 eV 280.72 nm  f=0.0029  <S**2>=0.000
          196 -> 204      0.40522
          197 -> 205     -0.37402
          201 -> 207     -0.22544
          201 -> 210      0.12274
          202 -> 207     -0.11546
          202 -> 208      0.19007
          202 -> 209     -0.17620

Excited State  25:      Singlet-A      4.4566 eV 278.21 nm  f=0.0135  <S**2>=0.000
          196 -> 204      0.12342
          201 -> 207      0.22735
          201 -> 208      0.45688
          202 -> 207     -0.22894
          202 -> 208     -0.38355

Excited State  26:      Singlet-A      4.4835 eV 276.53 nm  f=0.0297  <S**2>=0.000
          203 -> 213      0.55213
          203 -> 214      0.35257
          203 -> 215      0.10451
          203 -> 218      0.13086

Excited State  27:      Singlet-A      4.6207 eV 268.32 nm  f=0.0027  <S**2>=0.000
          196 -> 204      0.36673
          196 -> 205      0.19626
          197 -> 204      0.43002
          197 -> 205      0.33959
          201 -> 209      0.10066
```

```
Excited State  28:      Singlet-A     4.6398 eV  267.22 nm  f=0.0510  <S**2>=0.000
      194 -> 204         0.14240
      194 -> 205         0.13396
      195 -> 204         0.39066
      195 -> 205        -0.14986
      196 -> 204        -0.11225
      202 -> 209        -0.18022
      203 -> 213         0.25487
      203 -> 214        -0.34317

Excited State  29:      Singlet-A     4.6521 eV  266.51 nm  f=0.0231  <S**2>=0.000
      194 -> 204         0.10743
      195 -> 204         0.45217
      195 -> 205        -0.17778
      202 -> 209         0.10571
      203 -> 213        -0.27089
      203 -> 214         0.33914

Excited State  30:      Singlet-A     4.6676 eV  265.63 nm  f=0.0062  <S**2>=0.000
      194 -> 204         0.37538
      195 -> 205         0.48126
      196 -> 204        -0.18555
      196 -> 205         0.17133
      197 -> 205        -0.12971
      201 -> 209         0.10080
      202 -> 211        -0.11074

Excited State  31:      Singlet-A     4.6746 eV  265.23 nm  f=0.0003  <S**2>=0.000
      194 -> 204        -0.14701
      195 -> 205        -0.23815
      196 -> 204        -0.23918
      196 -> 205         0.51752
      197 -> 204         0.14919
      197 -> 205        -0.19953

Excited State  32:      Singlet-A     4.7238 eV  262.47 nm  f=0.0808  <S**2>=0.000
      194 -> 204         0.13006
      194 -> 205        -0.14419
      195 -> 205        -0.14156
      196 -> 205        -0.11613
      199 -> 204        -0.15048
      199 -> 205        -0.10999
      200 -> 204        -0.12242
      200 -> 205         0.20198
      201 -> 207         0.24035
      201 -> 209         0.15940
      202 -> 208         0.22759
      202 -> 210        -0.16576
      203 -> 215         0.32085
      203 -> 216         0.14044
--------------------------------------------------------------------------
JOB name: ti552Ant2TD
Method/Basis: TD-B3LYP-D3/6-311G(d) [hexane]
```

Table S5. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of **8**

```
--------------------------------------------------------------------------
Excited State   1:      Singlet-A     2.2210 eV  558.24 nm  f=0.0181  <S**2>=0.000
      260 -> 263        -0.27062
      261 -> 262         0.65165
```

```
Excited State   2:      Singlet-A      2.3184 eV  534.78 nm  f=0.0034  <S**2>=0.000
      260 -> 262         0.58675
      261 -> 263        -0.39196

Excited State   3:      Singlet-A      2.8261 eV  438.71 nm  f=0.4257  <S**2>=0.000
      260 -> 262         0.39217
      261 -> 263         0.58535

Excited State   4:      Singlet-A      3.0058 eV  412.48 nm  f=0.1538  <S**2>=0.000
      260 -> 263         0.64538
      261 -> 262         0.26327

Excited State   5:      Singlet-A      3.5651 eV  347.77 nm  f=0.0020  <S**2>=0.000
      261 -> 264         0.69620

Excited State   6:      Singlet-A      3.7556 eV  330.13 nm  f=0.0022  <S**2>=0.000
      260 -> 264         0.68038
      261 -> 265         0.16167

Excited State   7:      Singlet-A      3.9780 eV  311.68 nm  f=0.0003  <S**2>=0.000
      259 -> 262         0.22513
      260 -> 264        -0.14284
      260 -> 266         0.26120
      261 -> 265         0.58813

Excited State   8:      Singlet-A      4.0275 eV  307.84 nm  f=0.0187  <S**2>=0.000
      260 -> 265         0.41005
      261 -> 266         0.54771

Excited State   9:      Singlet-A      4.0979 eV  302.55 nm  f=0.0094  <S**2>=0.000
      258 -> 263         0.21916
      259 -> 262         0.60887
      260 -> 264         0.10946
      261 -> 265        -0.21528

Excited State  10:      Singlet-A      4.1588 eV  298.13 nm  f=0.0061  <S**2>=0.000
      257 -> 263         0.10577
      258 -> 262         0.60406
      259 -> 263         0.31955

Excited State  11:      Singlet-A      4.3403 eV  285.66 nm  f=0.0294  <S**2>=0.000
      259 -> 263         0.18493
      260 -> 265         0.52452
      261 -> 266        -0.40439

Excited State  12:      Singlet-A      4.3427 eV  285.50 nm  f=0.0104  <S**2>=0.000
      260 -> 266         0.62606
      261 -> 265        -0.25567
      261 -> 267        -0.10144

Excited State  13:      Singlet-A      4.3837 eV  282.83 nm  f=0.0051  <S**2>=0.000
      256 -> 263         0.10980
      257 -> 262         0.65098
      258 -> 263         0.18694
      259 -> 262        -0.11519

Excited State  14:      Singlet-A      4.4168 eV  280.71 nm  f=0.0182  <S**2>=0.000
      256 -> 262        -0.13986
      257 -> 263        -0.11815
```

```
    258 -> 262       -0.31047
    259 -> 263        0.57226
    260 -> 265       -0.16077

Excited State  15:      Singlet-A      4.5385 eV 273.18 nm  f=0.0107  <S**2>=0.000
    260 -> 268       -0.12687
    261 -> 267        0.66650
    261 -> 269        0.10850

Excited State  16:      Singlet-A      4.6088 eV 269.01 nm  f=0.0471  <S**2>=0.000
    256 -> 262        0.44374
    257 -> 263        0.33222
    258 -> 262       -0.14895
    259 -> 263        0.10428
    260 -> 267        0.13862
    260 -> 270        0.10429
    261 -> 268       -0.30249

Excited State  17:      Singlet-A      4.6213 eV 268.29 nm  f=0.0112  <S**2>=0.000
    257 -> 262       -0.21873
    258 -> 263        0.60799
    259 -> 262       -0.18392
    261 -> 269        0.11247

Excited State  18:      Singlet-A      4.6609 eV 266.01 nm  f=0.0094  <S**2>=0.000
    256 -> 262        0.30261
    257 -> 263        0.18351
    260 -> 267       -0.34830
    260 -> 270       -0.12522
    261 -> 268        0.45250

Excited State  19:      Singlet-A      4.7137 eV 263.03 nm  f=0.0000  <S**2>=0.000
    258 -> 263       -0.16327
    260 -> 268       -0.20607
    260 -> 271       -0.11621
    261 -> 267       -0.16546
    261 -> 269        0.51387
    261 -> 270        0.32268

Excited State  20:      Singlet-A      4.7540 eV 260.80 nm  f=0.0359  <S**2>=0.000
    256 -> 262        0.19620
    257 -> 263       -0.12549
    260 -> 267        0.53042
    261 -> 268        0.27408
    261 -> 271        0.24895

Excited State  21:      Singlet-A      4.7814 eV 259.31 nm  f=0.0115  <S**2>=0.000
    254 -> 262       -0.11504
    256 -> 262       -0.36017
    257 -> 263        0.53598
    260 -> 267        0.15726
    261 -> 268        0.14410

Excited State  22:      Singlet-A      4.8180 eV 257.34 nm  f=0.0335  <S**2>=0.000
    255 -> 262       -0.12380
    260 -> 268        0.32251
    260 -> 271        0.10155
    261 -> 269        0.41725
    261 -> 270       -0.37664
    261 -> 276        0.12597
```

```
Excited State  23:      Singlet-A      4.8680 eV  254.69 nm  f=0.0012  <S**2>=0.000
    255 -> 262         0.62836
    256 -> 263         0.20553
    261 -> 269         0.10406

Excited State  24:      Singlet-A      4.8934 eV  253.37 nm  f=0.0282  <S**2>=0.000
    254 -> 262         0.58914
    255 -> 263         0.16304
    257 -> 263         0.13258
    260 -> 269        -0.26805

Excited State  25:      Singlet-A      4.9039 eV  252.83 nm  f=0.0002  <S**2>=0.000
    253 -> 262         0.45003
    254 -> 263        -0.12750
    255 -> 262        -0.21694
    256 -> 263         0.44865

Excited State  26:      Singlet-A      4.9333 eV  251.32 nm  f=0.0205  <S**2>=0.000
    254 -> 262         0.28893
    260 -> 269         0.55122
    260 -> 270         0.21557
    261 -> 268         0.15520
    261 -> 271        -0.11988

Excited State  27:      Singlet-A      4.9577 eV  250.08 nm  f=0.0004  <S**2>=0.000
    260 -> 267        -0.18024
    260 -> 269         0.16770
    261 -> 266        -0.10810
    261 -> 268        -0.23193
    261 -> 271         0.56650

Excited State  28:      Singlet-A      4.9598 eV  249.98 nm  f=0.0044  <S**2>=0.000
    260 -> 268         0.51424
    260 -> 271         0.10416
    261 -> 270         0.43774

Excited State  29:      Singlet-A      5.0580 eV  245.12 nm  f=0.0016  <S**2>=0.000
    260 -> 269        -0.17809
    260 -> 270         0.56016
    261 -> 271         0.11448
    261 -> 272         0.28494
    261 -> 274         0.14955

Excited State  30:      Singlet-A      5.0696 eV  244.56 nm  f=0.0008  <S**2>=0.000
    251 -> 262        -0.13771
    253 -> 262        -0.46213
    256 -> 263         0.47186

Excited State  31:      Singlet-A      5.0975 eV  243.23 nm  f=0.0027  <S**2>=0.000
    260 -> 270        -0.22995
    260 -> 275         0.10281
    261 -> 271        -0.19883
    261 -> 272         0.60748

Excited State  32:      Singlet-A      5.1147 eV  242.41 nm  f=0.0013  <S**2>=0.000
    260 -> 266        -0.10534
    260 -> 268        -0.16651
    260 -> 271         0.55044
    260 -> 272         0.12605
```

```
   261 -> 273      0.30040
   261 -> 276      0.16433
```

```
JOB name: ti552butadieneTD
Method/Basis: TD-B3LYP-D3/6-311G(d) [hexane]
```

Table S6. Selected Parameters

Cpd	d/Å	angle sum at Si/°	β/°	τ/°
1 (XRD)	2.1762(5)	358.52(3) (*Si1*–SiMe₃), 359.61(3) (*Si2*–SiMe₃)	12.9 (*Si1*–SiMe₃), 6.5 (*Si2*–SiMe₃)	17.7
1 (calcd)[a]	2.17640	358.58, 358.58	12.6 (*Si1*), 12.6 (*Si1*)	12.9
4 (XRD)	2.2035(5)	358.04(3) (=*Si*···K), 359.94(3) (=*Si*–SiMe₃)	3.7 (=*Si*···K), 1.5 (=*Si*–SiMe₃)	2.5
5 (XRD)	2.1860(19)	358.8(1) (=*Si*–SiEt₃), 358.6(1) (=*Si*–SiMe₃)	11.2 (=*Si*–SiEt₃), 12.1 (=*Si*–SiMe₃)	17.6
6 (XRD)	2.1598(6)	360.00(5) (=*Si*–Ant), 355.98(3) (=*Si*–SiMe₃)	0.1 (=*Si*–Ant), 22.5 (=*Si*–SiMe₃)	0.1
6 (calcd)[a]	2.15862	358.25 (=Si–Ant), 354.93 (=*Si*–SiMe₃)	12.9 (=Si–Ant), 25.3 (=*Si*–SiMe₃)	3.7
6[Br] (XRD)	2.1711(7)	359.76(6) (=*Si*–Ant[Br]), 356.04(5) (=*Si*–SiMe₃)	4.7 (=*Si*–Ant[Br]), 22.4 (=*Si*–SiMe₃)	8.5
6[Br] (calcd)[a]	2.1574	358.25 (=*Si*–Ant[Br]), 354.93 (=*Si*–SiMe₃)	12.1 (=*Si*–Ant[Br]), 25.3 (=*Si*–SiMe₃)	3.7
7 (XRD)	2.1525(7)	357.10(6) (*Si1*–Ant), 355.71(6) (*Si2*–Ant)	17.4 (=*Si1*–Ant), 21.0 (=*Si2*–Ant)	3.3
7 (calcd)[a]	2.1440	356.42 (*Si1*–Ant), 358.43 (*Si2*–Ant)	19.1 (=*Si1*–Ant), 12.8 (=*Si2*–Ant)	2.8
8 (XRD)	2.1850(4) (Si1=Si2) 2.1915(5) (Si3=Si4)	359.99(4) (Si1), 359.99(3) (Si2), 359.98(3) (Si3), 359.94(4) (Si4)	0.3 (Si1), 1.2 (Si2), 1.0 (Si3), 2.4 (Si4)	0.7 (Si1=Si2), 1.8 (Si3=Si4) [-88.36(2)° (Si1–Si2–Si3–Si4)]
8 (calcd)[a]	2.1907, 2.1904	359.33 (Si1), 359.04 (Si2), 359.10 (Si3), 358.39 (Si4)	13.6 (Si1), 10.5 (Si2), 10.3 (Si3), 13.3 (Si4)	3.9 (Si1=Si2), 3.9 (Si3=Si4), [-71.4° (Si1–Si2–Si3–Si4)]

a. The geometry was optimized at the B3PW91-D3/6-31G(d) level of theory.

4. References

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