Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**Electronic Supplementary Information**

# 5-Thiocyanato-2′-Deoxyuridine as a Possible Radiosensitizer: Electron-Induced Formation of Uracil-C5-Thiyl Radical and Its Dimerization

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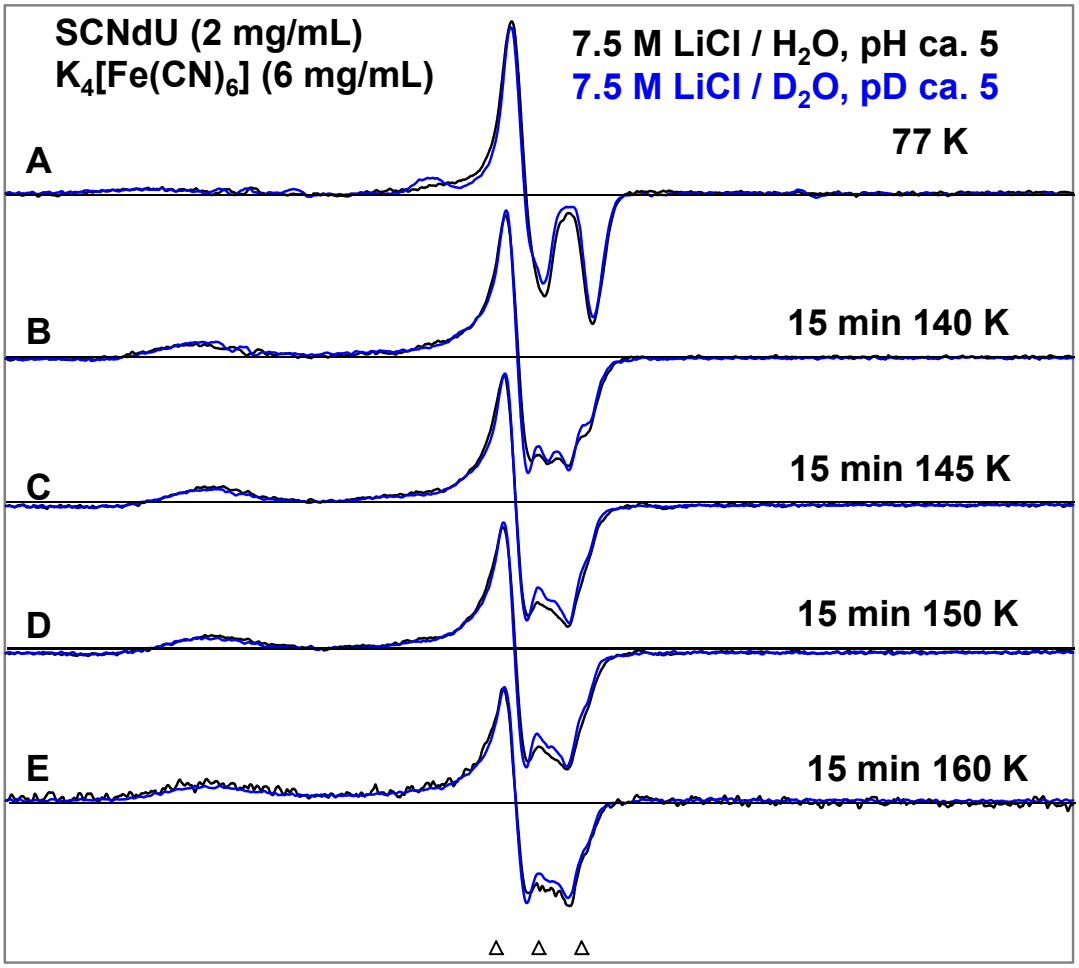


**Figure S1.** ESR spectra recorded at 77 K of matched γ-irradiated (77 K) $N_2$-saturated 7.5 M LiCl/$D_2O$ and 7.5 M LiCl/$H_2O$ solutions of SCNdU (2 mg/mL) with a hole scavenger $K_4[Fe(CN)_6]$ (6 mg/mL). (A) The π-anion radical of SCNdU upon $e_{pre}^-$ addition. Both spectra show the line components from U-5-S• as well (see Figure 1(A) in the main manuscript). Spectra (B) to (E) were obtained after at 140 to 160 K. Both spectra in Figure S1(E) are assigned to U-5-S• (see Figure 1 and its discussion in the main manuscript). The three reference markers (open triangles) in this Figure and in other Figures represent the position of Fremy's salt resonance with the central marker at g = 2.0056 and 13.09 G line spacing.

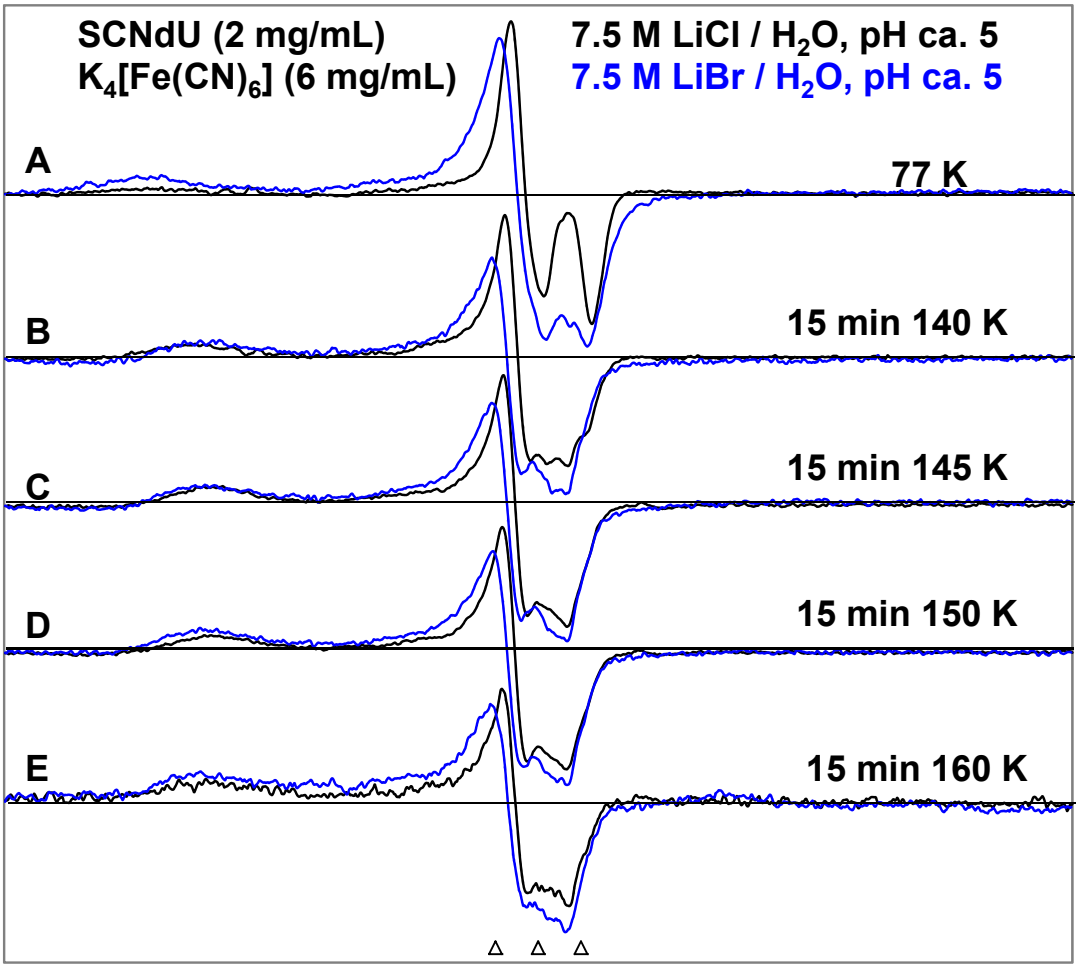


**Figure S2.** ESR spectra recorded at 77 K of matched γ-irradiated (77 K) $N_2$-saturated 7.5 M LiCl/$H_2O$ and 7.5 M LiBr/$H_2O$ solutions of SCNdU (2 mg/mL) with a hole scavenger $K_4[Fe(CN)_6]$ (6 mg/mL). (A) The π-anion radical of SCNdU upon $e_{pre}^-$ addition. Both spectra show the line components from U-5-S• as well (see Figure 1(A) in the main manuscript). Spectra (B) to (E) were obtained after at 140 to 160 K. Both spectra in Figure (E) are assigned to U-5-S• (see Figure 1 and its discussion in the main manuscript).

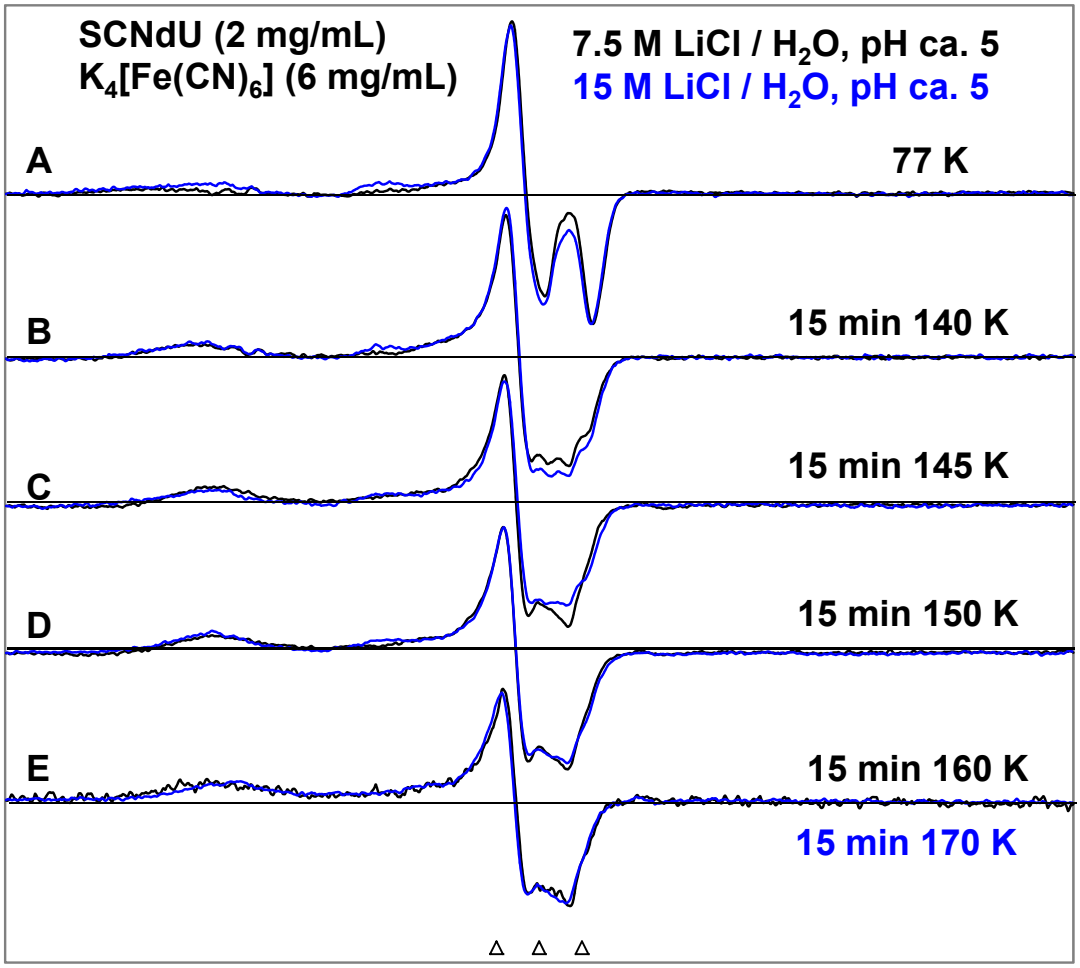


**Figure S3.** ESR spectra recorded at 77 K of matched γ-irradiated (77 K) $N_2$-saturated 7.5 M LiCl/$H_2O$ and 15 M LiCl/$H_2O$ solutions of SCNdU (2 mg/mL) with a hole scavenger $K_4[Fe(CN)_6]$ (6 mg/mL). (A) The π-anion radical of SCNdU upon $e_{pre}^-$ addition. Both spectra show the line components from U-5-S• as well (see Figure 1(A) in the main manuscript). Spectra (B) to (E) were obtained after at 140 to 170 K. Both spectra in Figure (E) are assigned to U-5-S• (see Figure 1 and its discussion in the main manuscript).

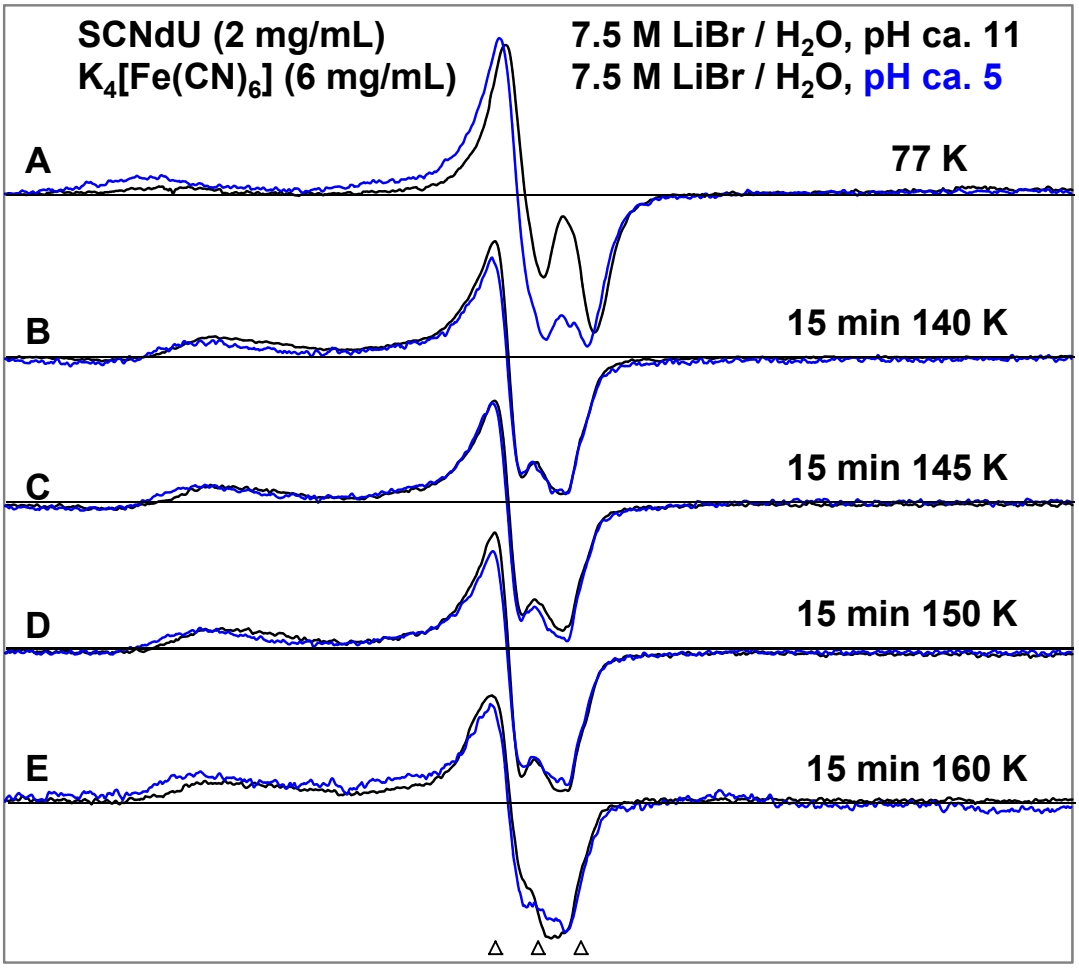


**Figure S4**. ESR spectra recorded at 77 K of matched γ-irradiated (77 K) $N_2$-saturated 7.5 M LiBr/$H_2O$ solutions with pHs ca. 5 and ca. 11 of SCNdU (2 mg/mL) with a hole scavenger $K_4[Fe(CN)_6]$ (6 mg/mL). (A) The π-anion radical of SCNdU upon $e_{pre}^-$ addition. Both spectra show the line components from U-5-S• as well (see Figure 1(A) in the main manuscript). Spectra (B) to (E) were obtained after at 140 to 160 K. Both spectra in Figure (E) are assigned to U-5-S• (see Figure 1 and its discussion in the main manuscript).

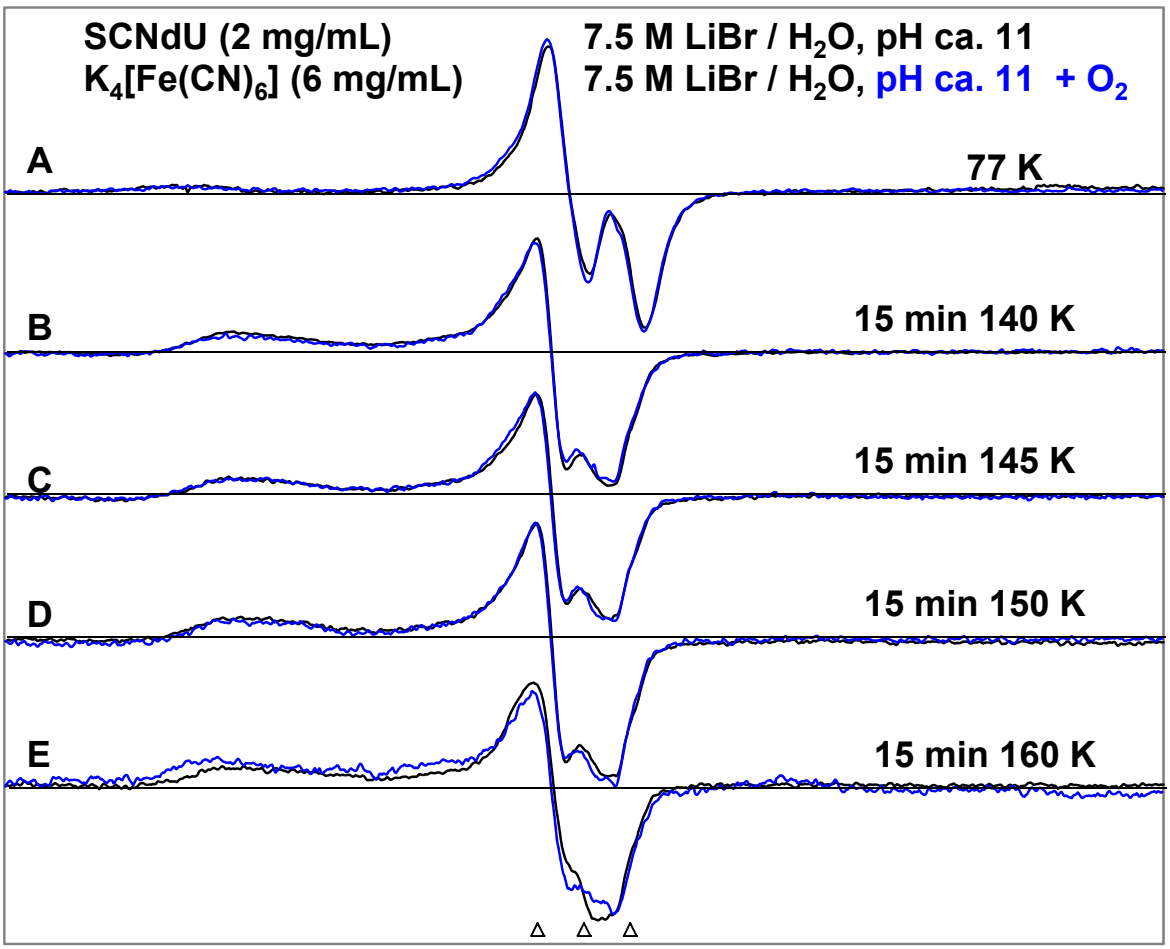


**Figure S5**. ESR spectra recorded at 77 K of matched γ-irradiated (77 K) $N_2$-saturated 7.5 M LiBr/$H_2O$ solutions with pH ca. 11 and in the presence and in absence of oxygen of SCNdU (2 mg/mL) with a hole scavenger $K_4[Fe(CN)_6]$ (6 mg/mL). Oxygen was bubbled for a minute into the solution. (A) The π-anion radical of SCNdU upon $e_{pre}^-$ addition. Both spectra show the line components from U-5-S• as well (see Figure 1(A) in the main manuscript). Spectra (B) to (E) were obtained after at 140 to 160 K. Both spectra in Figure (E) are assigned to U-5-S• (see Figure 1 and its discussion in the main manuscript).

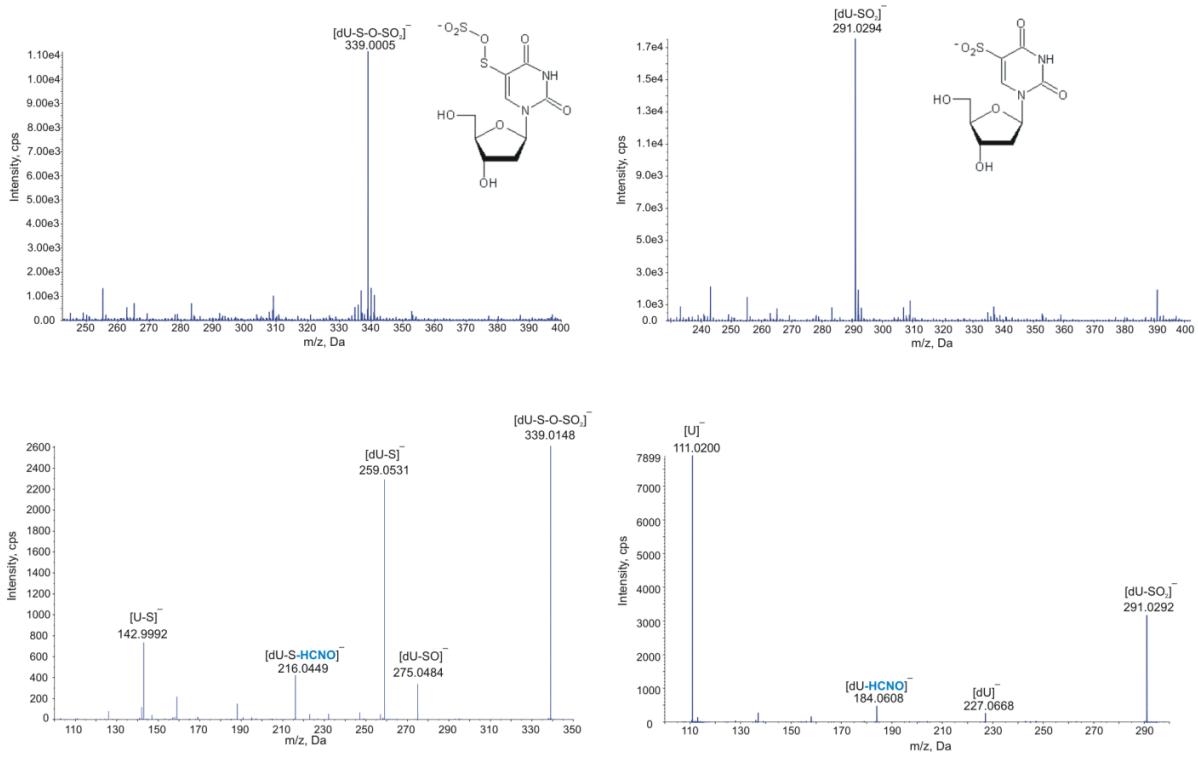


**Figure S6**. MS (upper panel) and MS/MS (lower panel) spectra (in negative ionization mode) of the additional products of the radiolysis (the dose of 50 Gy) and ion identities.

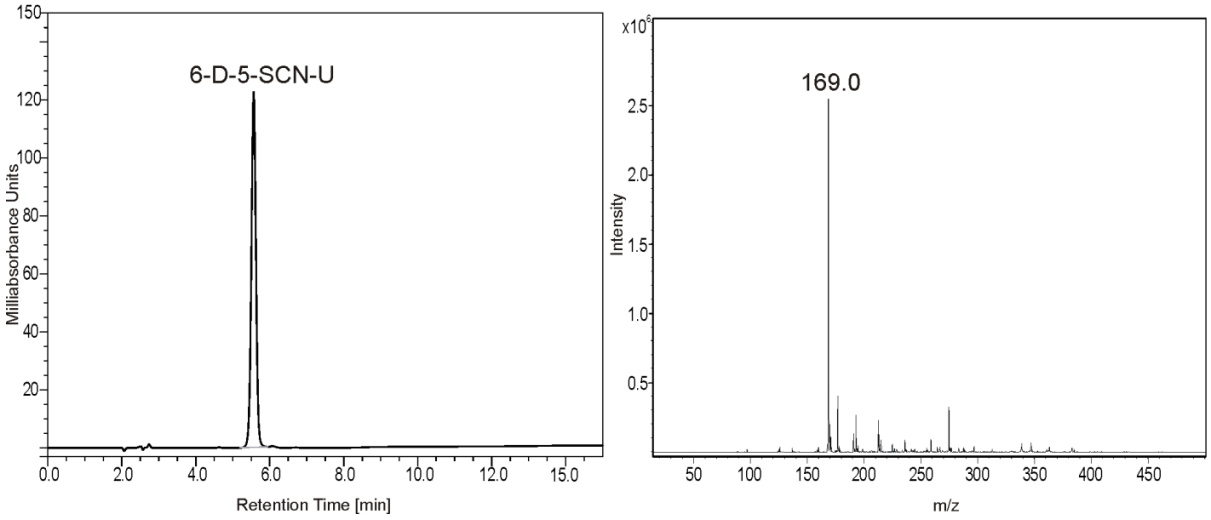


**Figure S7**. HPLC chromatogram and MS spectra (in negative ionization mode) of synthesized and purified 6-deutero-5-thiocyanatouracil (6-D-5-SCNU).

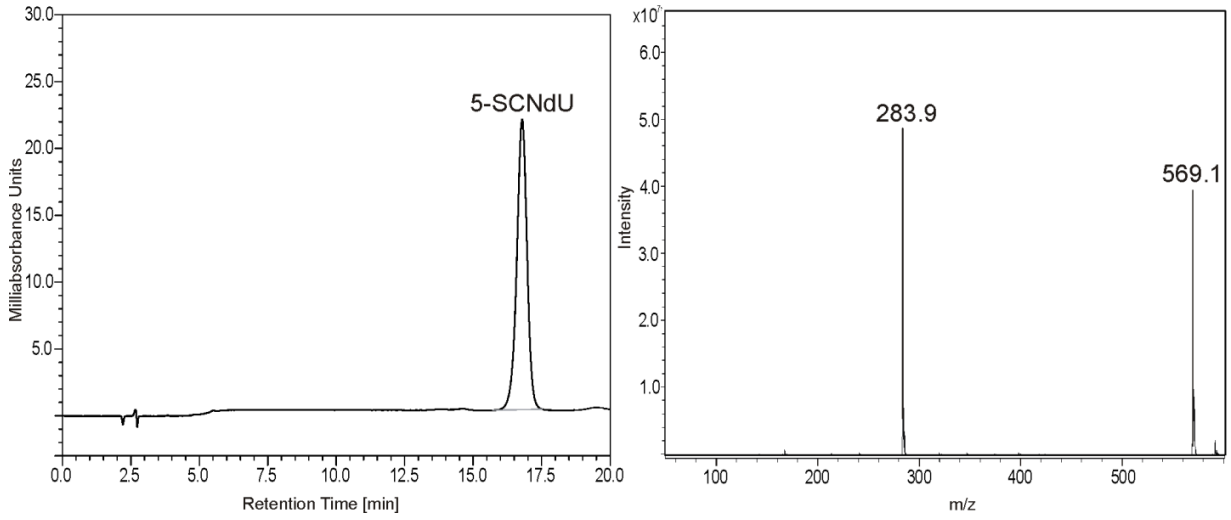


**Figure S8.** HPLC chromatogram and MS spectra (in negative ionization mode) of synthesized and purified 5-thiocyanato-2′-deoxyuridine (SCNdU).

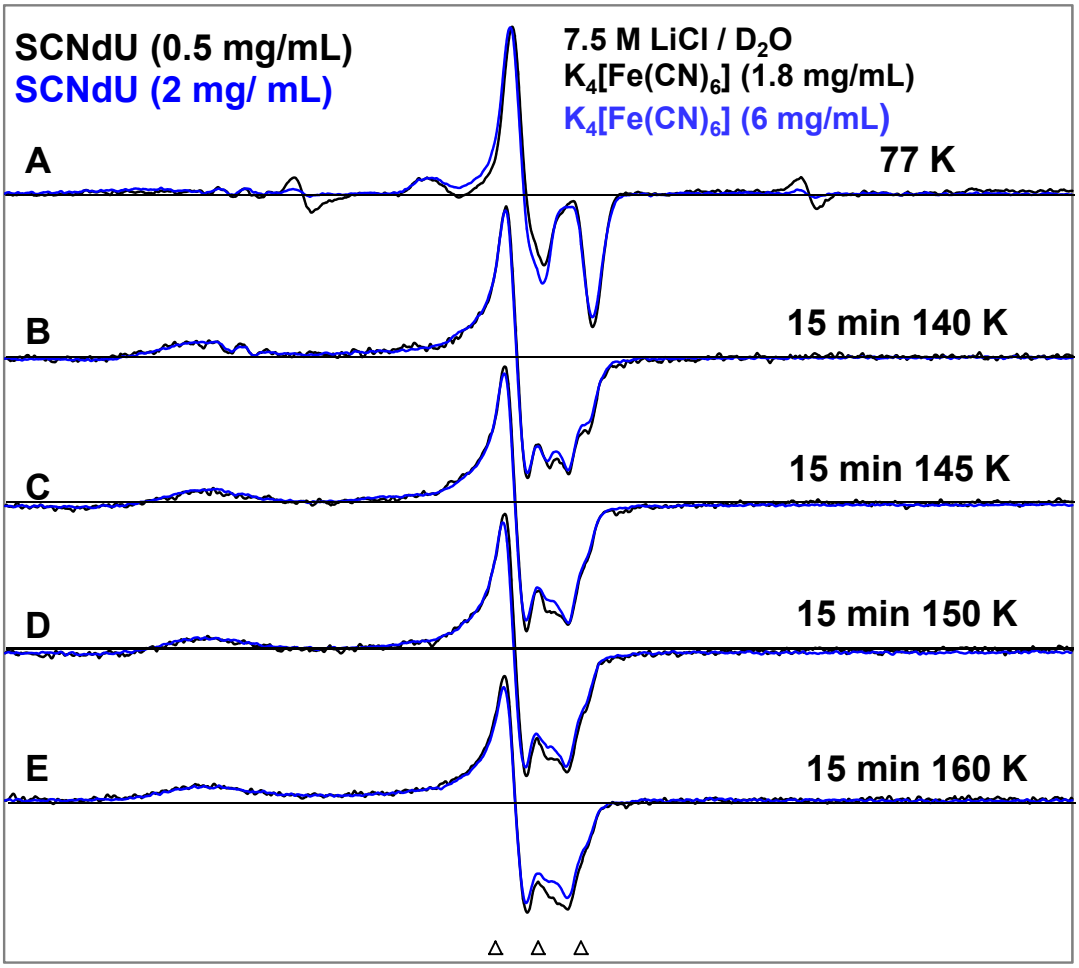


**Figure S9**. ESR spectra recorded at 77 K of matched γ-irradiated (77 K) $N_2$-saturated 7.5 M LiCl/$D_2O$ solutions with two different concentrations of SCNdU (0.5 and 2 mg/mL) with hole scavenger $K_4[Fe(CN)_6]$ (1.8 and 6 mg/mL). (A) The π-anion radical of SCNdU upon $e_{pre}^-$ addition. Both spectra show the line components from U-5-S• as well (see Figure 1(A) in the main manuscript). Spectra (B) to (E) were obtained after at 140 to 160 K. Both spectra in Figure (E) are assigned to U-5-S• (see Figure 1 and its discussion in the main manuscript).

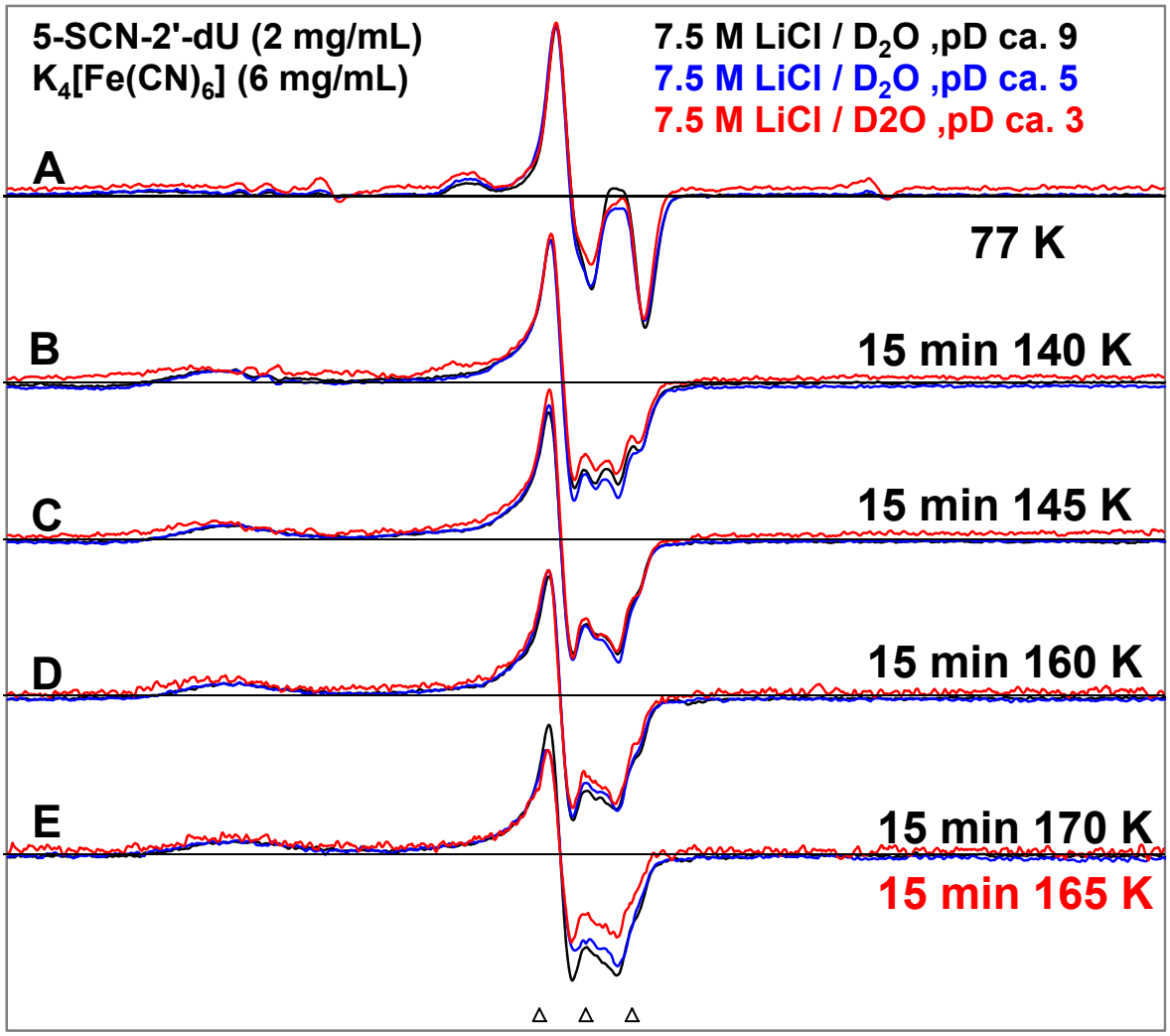


**Figure S10**. ESR spectra recorded at 77 K of matched γ-irradiated (77 K) $N_2$-saturated 7.5 M LiCl/$D_2O$ solutions with pHs ca. 3, 5, and ca. 9 of SCNdU (2 mg/mL) with a hole scavenger $K_4[Fe(CN)_6]$ (6 mg/mL). (A) The π-anion radical of SCNdU upon $e_{pre}^-$ addition. Both spectra show the line components from U-5-S• as well (see Figure 1(A) in the main manuscript). Spectra (B) to (E) were obtained after at 140 to 160 K. Both spectra in Figure (E) are assigned to U-5-S• (see Figure 1 and its discussion in the main manuscript).

**Stationary points geometries, calculated at M06-2x/6-31++G(d,p) level, PCM model of water solution. No imaginary frequencies found, with the exception of transition states (p. E and F).**

**A. Neutral forms of SCNdU**

**a) C3'-exo-front neutral SCNdU E= -1325.92322588 G= -1325.745605**

| | | | |
|---|---|---|---|
| O | 0.243092473 | 0.199494015 | -0.2445158654 |
| C | -0.1007823416 | 0.215456957 | 1.1088273932 |
| C | 1.1648474031 | 0.5800863382 | 1.9040135063 |
| C | 2.1206999572 | 1.095641215 | 0.8224001503 |
| C | 1.6687032898 | 0.3131607391 | -0.4046150151 |
| N | -0.6313446271 | -1.1325279433 | 1.4881343255 |
| C | -1.1797910597 | -1.228459273 | 2.7606695182 |
| N | -1.6624987512 | -2.4752434339 | 3.0900849918 |
| C | -1.6595244894 | -3.6253623847 | 2.304562451 |
| C | -1.0772070223 | -3.4134564648 | 0.9857431708 |
| C | -0.5914992107 | -2.1922771239 | 0.6396506243 |
| O | -1.2215726435 | -0.275518006 | 3.5195048516 |
| S | -1.0972804208 | -4.7280598039 | -0.1957039967 |
| C | 0.081696338 | -5.7466394846 | 0.5101599383 |
| N | 0.8679088212 | -6.4725272791 | 0.9588310256 |
| O | -2.1033830514 | -4.6780012587 | 2.7338066778 |
| O | 1.9097066555 | 2.4679968766 | 0.5355382367 |
| C | 2.3233846666 | -1.053529547 | -0.5098255066 |

| | | | |
|---|---|---|---|
| O | 1.6855342716 | -1.7497408119 | -1.5678074226 |
| H | -2.0545668013 | -2.5608481621 | 4.0229372807 |
| H | -0.1462400767 | -1.9990301378 | -0.33389205 |
| H | 1.8291126337 | 0.8764611782 | -1.3271034136 |
| H | 3.1704679143 | 0.9031700798 | 1.0710810211 |
| H | 0.9606628403 | 1.3305451553 | 2.6685890582 |
| H | 1.5766275563 | -0.3042997919 | 2.3981533948 |
| H | -0.923570479 | 0.9153572809 | 1.2665892476 |
| H | 3.392675446 | -0.9154898056 | -0.7086424497 |
| H | 2.2194939403 | -1.6064224156 | 0.4361774646 |
| H | 2.1372029438 | -2.5905577731 | -1.7096646383 |
| H | 2.1440939129 | 2.9911167777 | 1.3123389313 |

**b) C3'-exo-back neutral SCNdU E= -1325.92309668 G= -1325.745356**

| | | | |
|---|---|---|---|
| O | 0.2772805227 | 0.3407795499 | -0.2533600208 |
| C | -0.037209587 | 0.170519519 | 1.0968313358 |
| C | 1.2163746267 | 0.5267248699 | 1.913458905 |
| C | 2.1018997698 | 1.2479286825 | 0.8912166484 |
| C | 1.6860128386 | 0.5848607102 | -0.4159510135 |
| N | -0.4647933103 | -1.2472012811 | 1.3179655611 |
| C | -0.9971953251 | -1.5273341053 | 2.5700270586 |
| N | -1.3983770787 | -2.8321045128 | 2.7491173835 |
| C | -1.317477487 | -3.8817003483 | 1.8371994012 |
| C | -0.7473884701 | -3.4821074077 | 0.5570530102 |

| | | | |
|---|---|---|---|
| C | -0.3660746432 | -2.1940143753 | 0.3490037244 |
| O | -1.0965121124 | -0.674908445 | 3.4355631518 |
| S | -0.4744512167 | -4.7039728498 | -0.6910189473 |
| C | -2.0991600674 | -5.0189511826 | -1.1219455576 |
| N | -3.186790118 | -5.2736379544 | -1.4356086467 |
| O | -1.7151224663 | -4.9977366069 | 2.1301838168 |
| O | 1.7690395966 | 2.6213660461 | 0.7774651356 |
| C | 2.4393396883 | -0.7043955877 | -0.695578128 |
| O | 1.8296544005 | -1.3138506708 | -1.8214776091 |
| H | -1.7915077385 | -3.0484608913 | 3.6601450252 |
| H | 0.0513673813 | -1.8566287851 | -0.5972816067 |
| H | 1.7835164538 | 1.2665387313 | -1.2645684903 |
| H | 3.1696789806 | 1.1178715554 | 1.100497996 |
| H | 0.9764406737 | 1.1559446511 | 2.7712146158 |
| H | 1.7050162131 | -0.3797845955 | 2.2816781879 |
| H | -0.9034137688 | 0.7852488364 | 1.3488304911 |
| H | 3.4905576515 | -0.4627970273 | -0.8914402664 |
| H | 2.3988943623 | -1.3741742179 | 0.1771589571 |
| H | 2.3422769829 | -2.0905401526 | -2.0767195477 |
| H | 1.9926377074 | 3.0683943038 | 1.603443932 |

**c) C3'-endo-front neutral SCNdU E= -1325.91984651 G= -1325.744085**

| | | | |
|---|---|---|---|
| C | 0.1321707828 | -0.602177815 | 0.1151669269 |
| N | -0.011052971 | -0.1708340732 | 1.3942139939 |

| | | | |
|---|---|---|---|
| C | 0.9842689438 | 0.5605314355 | 2.0345244962 |
| N | 2.0915813753 | 0.8303476934 | 1.2619604087 |
| C | 2.3274284255 | 0.4482898241 | -0.056054772 |
| C | 1.2382328834 | -0.3353274235 | -0.6262843344 |
| C | -1.2305377227 | -0.4693187113 | 2.2152138841 |
| O | -1.9979205297 | -1.4210715031 | 1.531632597 |
| C | -3.2814886516 | -0.8802032091 | 1.1711600951 |
| C | -3.0973424984 | 0.6331875531 | 1.2345001893 |
| C | -2.1072447937 | 0.7696754508 | 2.3918358468 |
| O | -4.352827096 | 1.235562851 | 1.4513604247 |
| C | -3.7104019711 | -1.3988879643 | -0.1781734074 |
| O | -3.9477281074 | -2.7910524696 | -0.0682932392 |
| O | 0.8726094277 | 0.934188455 | 3.1887283998 |
| O | 3.3552167455 | 0.770173869 | -0.6285818716 |
| S | 1.4169435855 | -1.0243697706 | -2.2436424659 |
| C | 1.2862005047 | 0.4113826081 | -3.1634058488 |
| N | 1.2124497413 | 1.3622681087 | -3.8240877426 |
| H | 2.8192487764 | 1.3737695751 | 1.7166509428 |
| H | -0.6910591815 | -1.194741975 | -0.2672948112 |
| H | -4.0164338494 | -1.1824300627 | 1.9297766271 |
| H | -2.6510026906 | 0.9958083894 | 0.2966913723 |
| H | -2.6565714826 | 0.689969098 | 3.3351797398 |
| H | -1.533634122 | 1.696769903 | 2.3915030897 |
| H | -0.8597726129 | -0.8812100738 | 3.1545846347 |

| | | | |
|---|---|---|---|
| H | -4.621815811 | -0.8587649571 | -0.467282935 |
| H | -2.9316984348 | -1.1875851865 | -0.9238572742 |
| H | -4.2318314917 | -3.1296536589 | -0.9255258868 |
| H | -4.2723891839 | 2.1901302208 | 1.3353260485 |

**d) C3'-endo-back neutral SCNdU E= -1325.91984651 G= -1325.744085**

| | | | |
|---|---|---|---|
| C | 0.1416336663 | -0.5226471753 | 0.3039194551 |
| N | 0.0319630709 | 0.0957111404 | 1.5454362251 |
| C | 1.1237185783 | 0.5427582281 | 2.2172905485 |
| C | 2.3888338883 | 0.3589992989 | 1.7579610059 |
| C | 2.6130241114 | -0.3085844948 | 0.4812538496 |
| N | 1.4315005592 | -0.6941294529 | -0.1462118512 |
| C | -1.3672340431 | 0.2989649297 | 2.048091815 |
| C | -2.0029617727 | -1.0156262898 | 2.4961672969 |
| C | -1.7025674852 | -1.0310982393 | 3.9955171302 |
| C | -1.8016667569 | 0.4516991848 | 4.3399817516 |
| O | -1.3126553153 | 1.1343728432 | 3.1712732807 |
| C | -1.0101271239 | 0.8616945786 | 5.5561126002 |
| O | -1.28067164 | 2.2257902469 | 5.8260103558 |
| O | -2.6343261492 | -1.7424160516 | 4.7785575481 |
| S | 3.7771630167 | 0.85841838 | 2.7313545063 |
| C | 4.3306221491 | 2.1565459 | 1.7651877408 |
| N | 4.7487874254 | 3.0354342721 | 1.1337823984 |
| O | 3.6966307382 | -0.516975615 | -0.0387901451 |

| | | | |
|---|---|---|---|
| O | -0.8350665913 | -0.8836140434 | -0.3286657783 |
| H | 1.521511302 | -1.1488048441 | -1.0499518521 |
| H | 0.9147450182 | 1.0604982644 | 3.1467251713 |
| H | -2.85853631 | 0.7148915159 | 4.4853089752 |
| H | -0.6813391522 | -1.3927910316 | 4.1856913203 |
| H | -3.0867987776 | -0.9561613882 | 2.3567593685 |
| H | -1.6223239228 | -1.8774830524 | 1.9481198447 |
| H | -1.9044087247 | 0.7884438916 | 1.2340919213 |
| H | -1.3236949735 | 0.2191492564 | 6.3893611131 |
| H | 0.0609081465 | 0.6974560422 | 5.3753186455 |
| H | -0.7940512444 | 2.492106068 | 6.6149280061 |
| H | -2.4464249747 | -2.6868948148 | 4.7184202685 |

**B. Anionradical forms of SCNdU**

**a) C3'-exo-front anionradical SCNdU E= -1326.01357383 G= -1325.842517**

| | | | |
|---|---|---|---|
| O | 0.2053110817 | 0.2404859482 | -0.159513996 |
| C | -0.0117946307 | 0.1208185376 | 1.2375154308 |
| C | 1.3775912632 | 0.0977130393 | 1.8879170433 |
| C | 2.2475163182 | 0.8115325526 | 0.8559433599 |
| C | 1.6001403407 | 0.3676667538 | -0.4538280977 |
| N | -0.7972256709 | -1.0847054125 | 1.4976449806 |
| C | -1.6478809036 | -1.0636918626 | 2.5654402431 |
| N | -2.2669512298 | -2.2618440896 | 2.859221149 |
| C | -1.9285217662 | -3.5453262376 | 2.3479548661 |

| | | | |
|---|---|---|---|
| C | -1.057841362 | -3.4900491821 | 1.2435798577 |
| C | -0.4604079621 | -2.2729426834 | 0.8064281545 |
| O | -1.8704415884 | -0.0527875817 | 3.2416869629 |
| S | -0.6226168511 | -4.9797847813 | 0.4310861794 |
| C | 0.8975058125 | -5.3417703806 | 1.1608842172 |
| N | 1.9274152465 | -5.5787285118 | 1.6458595903 |
| O | -2.4382873588 | -4.5359325697 | 2.9124974155 |
| O | 2.1124543504 | 2.2238380894 | 0.9315828157 |
| C | 2.1890475017 | -0.9373797332 | -0.965123338 |
| O | 1.4153853447 | -1.3613920059 | -2.0751953383 |
| H | -2.8416857238 | -2.2542568601 | 3.6921235262 |
| H | -0.1198302327 | -2.1284719494 | -0.2125897207 |
| H | 1.697600193 | 1.1411359535 | -1.2225906164 |
| H | 3.3024831812 | 0.5184836915 | 0.9127518347 |
| H | 1.3837120451 | 0.5928020073 | 2.8616601847 |
| H | 1.7057576127 | -0.9391340598 | 2.017149887 |
| H | -0.6118403212 | 0.9639310015 | 1.5814315822 |
| H | 3.2317358535 | -0.7547919846 | -1.2563228859 |
| H | 2.1739956171 | -1.6962596899 | -0.1702913636 |
| H | 1.7845884907 | -2.1850193611 | -2.4147963146 |
| H | 2.4697354373 | 2.5263570746 | 1.7759152924 |

**b) C3’-exo-back anionradical SCNdU E= -1326.01269553 G= -1325.842836**

| | | | |
|---|---|---|---|
| O | 0.1947594 | 0.3513036891 | -0.1371862629 |

| | | | |
|---|---|---|---|
| C | 0.0429761868 | 0.11004238 | 1.2532448754 |
| C | 1.4519965704 | 0.1766179789 | 1.8557230939 |
| C | 2.2061642426 | 1.0549390287 | 0.8606386547 |
| C | 1.5543665305 | 0.6569303676 | -0.4621766416 |
| N | -0.6117361076 | -1.1819852042 | 1.4445231197 |
| C | -1.4517494536 | -1.3136755933 | 2.5137349431 |
| N | -1.9423936634 | -2.5832508172 | 2.7343679577 |
| C | -1.5361938103 | -3.7873558567 | 2.0969566193 |
| C | -0.6320631523 | -3.580787349 | 1.0395558534 |
| C | -0.1620966857 | -2.283645049 | 0.6762687042 |
| O | -1.7704651641 | -0.3744063157 | 3.2521004638 |
| S | -0.0485721533 | -4.9700047533 | 0.1427755947 |
| C | -1.2366852308 | -5.1033065259 | -1.0956707505 |
| N | -2.0348633604 | -5.2144994938 | -1.9335614032 |
| O | -2.0228979169 | -4.8532648606 | 2.5312963215 |
| O | 1.9361918892 | 2.4360418193 | 1.0598920953 |
| C | 2.255856009 | -0.5264569857 | -1.1086170984 |
| O | 1.4927873117 | -0.9261015889 | -2.2348558259 |
| H | -2.5355450407 | -2.68423413 | 3.5477032701 |
| H | 0.1383730276 | -2.0395836822 | -0.3365727128 |
| H | 1.5373700021 | 1.5001749196 | -1.1601867814 |
| H | 3.2865694971 | 0.8673376746 | 0.8602617434 |
| H | 1.4485549865 | 0.5907566183 | 2.8665697126 |
| H | 1.8856194827 | -0.8283104637 | 1.8872846712 |

| | | | |
|---|---|---|---|
| H | -0.6218699991 | 0.8622405876 | 1.6788395304 |
| H | 3.2642276577 | -0.2097815621 | -1.4060485271 |
| H | 2.3450369128 | -1.3522106321 | -0.3891987396 |
| H | 1.9358943294 | -1.6673539454 | -2.6643196395 |
| H | 2.2649021623 | 2.6957062033 | 1.9297616618 |

**c) C3'-endo-front anionradical SCNdU E= -1326.01289481 G= -1325.843165**

| | | | |
|---|---|---|---|
| C | 0.0538234146 | -0.1801393355 | 0.0224169614 |
| N | 0.049235532 | -0.1797083674 | 1.4387566062 |
| C | 1.1851318554 | -0.0095324881 | 2.1843574802 |
| N | 2.3563387966 | 0.0931005216 | 1.4651816177 |
| C | 2.5046204183 | 0.1839868541 | 0.055273373 |
| C | 1.304614548 | -0.0400683007 | -0.6457622118 |
| C | -1.2376567647 | -0.16159513 | 2.1161790666 |
| O | -1.9866261369 | -1.2964187974 | 1.6834854332 |
| C | -3.280475873 | -0.9084855898 | 1.2310475942 |
| C | -3.144428899 | 0.5535536277 | 0.8061146228 |
| C | -2.0952232862 | 1.0732012289 | 1.7887353534 |
| O | -4.4137189119 | 1.1694802984 | 0.9100503101 |
| C | -3.7315181197 | -1.8178366541 | 0.1147034756 |
| O | -3.9898183923 | -3.1054237893 | 0.6514411123 |
| O | 1.1953949843 | 0.0571188095 | 3.4174303975 |
| O | 3.6463094354 | 0.4336792353 | -0.3830680302 |
| S | 1.3356380458 | -0.0630695293 | -2.3958030567 |

| | | | |
|---|---|---|---|
| C | 0.9044304161 | 1.5623949298 | -2.7780659567 |
| N | 0.6136997487 | 2.6576744674 | -3.0383031569 |
| H | 3.1881618266 | 0.2646775764 | 2.0151610903 |
| H | -0.7666339097 | -0.724768009 | -0.4323986397 |
| H | -4.0014283573 | -0.9639064908 | 2.0616434904 |
| H | -2.7754991735 | 0.6131821003 | -0.2272779415 |
| H | -2.6105589567 | 1.4134357554 | 2.6920829705 |
| H | -1.487703003 | 1.8889823342 | 1.3919216254 |
| H | -1.0231859167 | -0.2456832314 | 3.1807094435 |
| H | -4.6373883991 | -1.3868782512 | -0.3320640405 |
| H | -2.9450123893 | -1.8610061309 | -0.651510524 |
| H | -4.2983419616 | -3.6833617043 | -0.0562698306 |
| H | -4.3785825813 | 2.0378402415 | 0.4913564921 |

**d) C3'-endo-back anionradical SCNdU E= -1326.01214721 G= -1325.843283**

| | | | |
|---|---|---|---|
| C | -0.028389197 | 0.0251410293 | -0.0089172158 |
| N | -0.0681710134 | 0.0347604708 | 1.3602528128 |
| C | 1.094447834 | -0.0612866542 | 2.1645733856 |
| C | 2.3544914496 | -0.1845750448 | 1.5079073242 |
| C | 2.4730944297 | -0.1906013735 | 0.106632462 |
| N | 1.2309900853 | -0.0296367779 | -0.5646125554 |
| C | -1.3606301295 | -0.0337252451 | 2.0209496673 |
| C | -1.5933651724 | -1.3399629489 | 2.8006602755 |
| C | -1.404657691 | -0.9426085033 | 4.2645717785 |

| | | | |
|---|---|---|---|
| C | -1.8327299688 | 0.5242983225 | 4.2499577804 |
| O | -1.427940184 | 1.0228310739 | 2.9794841111 |
| C | -1.204193496 | 1.3442053727 | 5.3492958554 |
| O | -1.782094406 | 2.6400282027 | 5.3398025622 |
| O | -2.2232846682 | -1.6427841857 | 5.1817360229 |
| S | 3.7991288349 | -0.3799773524 | 2.4813160253 |
| C | 4.3244879368 | 1.2494703812 | 2.6529611504 |
| N | 4.7051082678 | 2.3414630313 | 2.7715434303 |
| O | 3.4938985512 | -0.3048120707 | -0.6043347678 |
| O | -1.0324409917 | 0.0573036321 | -0.7273464034 |
| H | 1.2588530614 | -0.062647698 | -1.5753795144 |
| H | 1.0087676746 | 0.3979244607 | 3.144091174 |
| H | -2.9295154129 | 0.5684857068 | 4.3415785134 |
| H | -0.3487890024 | -1.0221565577 | 4.5578671818 |
| H | -2.6279563285 | -1.6702089832 | 2.6667329733 |
| H | -0.9174671221 | -2.1304473286 | 2.4686015276 |
| H | -2.1099781264 | 0.124077569 | 1.246307892 |
| H | -1.3905737545 | 0.8351145875 | 6.3042745873 |
| H | -0.1195751062 | 1.3956021273 | 5.180499245 |
| H | -1.3797709501 | 3.1670541335 | 6.0399610955 |
| H | -1.8455586912 | -2.5166218291 | 5.3380341393 |

**C. Anionradical complex-1 forms of SCNdU**

**a) C3'-exo-front complex-1 E= -1326.01603195 G= -1325.845063**

| | | | |
|---|---|---|---|
| C | 0.1411231721 | -0.1178424904 | 0.0221257944 |
| N | 0.0195638986 | 0.0737294576 | 1.3846189033 |
| C | 1.1270279475 | 0.2455517804 | 2.1898419399 |
| N | 2.3454606941 | 0.1581822031 | 1.5446582367 |
| C | 2.5845749438 | -0.0308558153 | 0.177153103 |
| C | 1.3495374191 | -0.1672155664 | -0.5484582165 |
| C | -1.3038532888 | 0.1923122129 | 2.0496918544 |
| O | -2.2813771637 | -0.3689667608 | 1.2159792704 |
| C | -3.2917618067 | 0.6006190414 | 0.8853100534 |
| C | -3.2044572514 | 1.6428638575 | 1.9944926587 |
| C | -1.7072947398 | 1.6514273026 | 2.3050233129 |
| O | -3.9673834907 | 1.1523464667 | 3.0866381399 |
| C | -3.0655153816 | 1.1755352423 | -0.5046558877 |
| O | -3.0746261428 | 0.1226262858 | -1.4414335133 |
| O | 1.0390959391 | 0.4608678256 | 3.3920529888 |
| O | 3.7278313292 | -0.0657448066 | -0.2551762053 |
| S | 1.798716488 | 0.7399227824 | -3.8364991662 |
| C | 0.2068720484 | 0.7295013303 | -3.3764258692 |
| N | -0.9197311407 | 0.7232449662 | -3.0452273383 |
| H | 3.1595995798 | 0.2817546758 | 2.139185363 |
| H | -0.790840607 | -0.2385190845 | -0.523424654 |
| H | -4.2503068651 | 0.0741622896 | 0.9132442923 |
| H | -3.5711531775 | 2.6231762658 | 1.6696278382 |
| H | -1.4894036555 | 1.96462341 | 3.3273824371 |

| | | | |
|---|---|---|---|
| H | -1.1746026482 | 2.317315745 | 1.6188871107 |
| H | -1.2271129731 | -0.3878797099 | 2.9713976217 |
| H | -3.8654262705 | 1.8997340774 | -0.714010327 |
| H | -2.1082838752 | 1.7187504574 | -0.540013034 |
| H | -2.3947108645 | 0.3139217214 | -2.122726643 |
| H | -3.9000295743 | 1.7756392733 | 3.8209029519 |

**b) C3'-exo-back complex-1 E= -1326.00632630 G= -1325.835951**

| | | | |
|---|---|---|---|
| C | -0.0701245998 | -0.3072207166 | -0.0810082313 |
| N | -0.0732943566 | 0.0323406603 | 1.267376211 |
| C | 1.0853872926 | 0.3724799397 | 1.9208521131 |
| N | 2.224279414 | 0.3440781887 | 1.1450074527 |
| C | 2.3207512566 | 0.0387050622 | -0.2222537658 |
| C | 1.053118446 | -0.3123371263 | -0.8171731727 |
| C | -1.3148216534 | 0.0842576773 | 2.0820357212 |
| O | -2.3671308414 | -0.5035419523 | 1.3637875537 |
| C | -3.3600087819 | 0.4776185339 | 1.0278935671 |
| C | -3.2425254047 | 1.5270051356 | 2.1272606053 |
| C | -1.7382183541 | 1.5274309127 | 2.4095457481 |
| O | -3.9943245056 | 1.0496220232 | 3.232657146 |
| C | -3.1330185867 | 1.0493785286 | -0.3611863581 |
| O | -3.1444954593 | -0.0348016581 | -1.2742915483 |
| O | 1.1077053536 | 0.6830589521 | 3.10995694 |
| O | 3.4202162061 | 0.0900947414 | -0.7675363227 |

| | | | |
|---|---|---|---|
| S | 0.6747255723 | -0.8226600509 | -3.3431621316 |
| C | 1.4451237091 | -2.2989906394 | -3.2255271337 |
| N | 1.988970918 | -3.3327684253 | -3.1323464653 |
| H | 3.0823639298 | 0.5978686766 | 1.6245876887 |
| H | -1.0463595841 | -0.569780537 | -0.4799638279 |
| H | -4.3263015179 | -0.033137397 | 1.0625588261 |
| H | -3.6073071032 | 2.5082385501 | 1.8026990896 |
| H | -1.5076706833 | 1.7953105797 | 3.4415541692 |
| H | -1.2219153001 | 2.2330145604 | 1.751783126 |
| H | -1.1207777758 | -0.5089056282 | 2.9781868542 |
| H | -3.9350343853 | 1.7642131601 | -0.5818646957 |
| H | -2.172598463 | 1.5845584817 | -0.4052448775 |
| H | -3.0246746129 | 0.305052495 | -2.1692343718 |
| H | -3.8851225026 | 1.6589551026 | 3.9736120503 |

**c) C3'-endo-front complex-1 E= -1326.00683113 G= -1325.839459**

| | | | |
|---|---|---|---|
| C | -0.1427217279 | -0.0174207041 | -0.0146301288 |
| C | -0.0829292365 | 0.0371997942 | 1.5189294998 |
| O | 1.2842396785 | 0.1671035989 | 1.8673860402 |
| C | 2.1168393622 | 0.1275514674 | 0.705673132 |
| C | 1.2143538699 | 0.5365445738 | -0.4581158857 |
| N | -0.8070554656 | 1.176898608 | 2.0964526046 |
| C | -0.3433188263 | 2.470690474 | 1.8778340377 |
| C | -0.9693638818 | 3.5602081191 | 2.3365246925 |

| | | | |
|---|---|---|---|
| C | -2.1842732501 | 3.4269691484 | 3.1080183138 |
| N | -2.571130857 | 2.091543618 | 3.2967941335 |
| C | -1.9571856425 | 0.9495606498 | 2.8202434006 |
| O | -2.4214826734 | -0.1656618912 | 3.0339866306 |
| O | -2.8684396115 | 4.3242807903 | 3.5883384917 |
| S | 0.1625839445 | 5.8487445869 | 1.5439090213 |
| C | 1.1036182724 | 4.914636781 | 0.5352658867 |
| N | 1.7509027724 | 4.2241688043 | -0.1580938481 |
| C | 3.3028083273 | 1.0411427508 | 0.8915536055 |
| O | 4.1583324618 | 0.4785684657 | 1.8734083726 |
| O | 1.7211293341 | -0.0394207701 | -1.6452515924 |
| H | -3.4210644659 | 1.9298759249 | 3.828270853 |
| H | 0.5828304415 | 2.5279661473 | 1.3120478325 |
| H | 2.4651081509 | -0.902311965 | 0.5368280242 |
| H | 1.195490218 | 1.6316953275 | -0.5506925264 |
| H | -0.2051947316 | -1.0602160296 | -0.3397100959 |
| H | -1.0006727892 | 0.5284371801 | -0.411526862 |
| H | -0.5119292448 | -0.8483302373 | 1.9865889756 |
| H | 3.8154383681 | 1.1326142602 | -0.0758737378 |
| H | 2.946390058 | 2.035565182 | 1.1932295809 |
| H | 4.9007466255 | 1.0761412641 | 2.0206599852 |
| H | 1.3098327367 | 0.3894544805 | -2.4050831214 |

**d) C3’-endo-front complex-1 E= -1326.00433386 G= -1325.835415**

| | | | |
|---|---|---|---|
| O | -0.0058031361 | -0.0576061519 | -0.0344879399 |
| C | -0.0250034565 | -0.035308514 | 1.3722739209 |
| C | 1.4329387203 | -0.027124303 | 1.8323210274 |
| C | 2.1487346665 | -0.6901092607 | 0.6554156474 |
| C | 1.3387152714 | -0.1610696265 | -0.5255014361 |
| N | -0.7593995894 | -1.2324047737 | 1.8593323901 |
| C | -1.1732621266 | -1.1893363323 | 3.1696442971 |
| N | -1.8423072299 | -2.311427073 | 3.6082051967 |
| C | -2.1202495169 | -3.4817668717 | 2.8846551751 |
| C | -1.6447387722 | -3.4370944187 | 1.5212239053 |
| C | -1.0064694185 | -2.3473898568 | 1.0664420118 |
| O | -0.9615027683 | -0.2254524589 | 3.9017350798 |
| S | -1.9111196349 | -5.3327691392 | -0.2125130093 |
| C | -3.5580293882 | -5.0853550035 | -0.3282047903 |
| N | -4.713459556 | -4.905049177 | -0.4019257678 |
| O | -2.7189773501 | -4.3974499667 | 3.4421895673 |
| O | 3.4979932154 | -0.3137937318 | 0.4891637529 |
| C | 1.3889528597 | -1.0404519013 | -1.7501370472 |
| O | 0.7089553545 | -0.3817034521 | -2.8049380656 |
| H | -2.150975672 | -2.2799537622 | 4.5748882527 |
| H | -0.657337858 | -2.2492946872 | 0.0442632844 |
| H | 1.7037434934 | 0.8433059113 | -0.7840176753 |
| H | 2.0573064897 | -1.7852655785 | 0.7092960947 |
| H | 1.785368488 | 1.0057002534 | 1.9176874643 |

| | | | |
|---|---|---|---|
| H | 1.5719881084 | -0.5324578719 | 2.788882927 |
| H | -0.5889198137 | 0.8292333644 | 1.7258948809 |
| H | 2.4456248751 | -1.2058659569 | -1.9996968265 |
| H | 0.9286349829 | -2.0128068832 | -1.5279764585 |
| H | 0.7313759166 | -0.9416977495 | -3.5898840365 |
| H | 4.0406284023 | -0.7797602037 | 1.1368920462 |

**D. Anionradical complex-2 forms of SCNdU**

**a) C3'-exo-front complex-2 E= -1326.04018073 G= -1325.868348**

| | | | |
|---|---|---|---|
| C | 0.1271178858 | -0.3047745752 | 0.1390288942 |
| N | 0.0115475111 | 0.0165220909 | 1.4408447292 |
| C | 1.1235181806 | 0.2791865147 | 2.2448035419 |
| N | 2.3313028375 | 0.2077855213 | 1.5969784202 |
| C | 2.5705301671 | -0.0943294661 | 0.2563923289 |
| C | 1.3461352502 | -0.3773138101 | -0.524858326 |
| C | -1.3184150099 | 0.0796188881 | 2.1367063636 |
| O | -2.3061807559 | -0.3766028573 | 1.2676045064 |
| C | -3.1553645115 | 0.7147569156 | 0.8595864405 |
| C | -3.12704836 | 1.6634284206 | 2.0509699687 |
| C | -1.682040261 | 1.519760774 | 2.542827784 |
| O | -4.0619652132 | 1.1711215975 | 2.997139765 |
| C | -2.6558965575 | 1.355299266 | -0.4248974702 |
| O | -2.5527230673 | 0.361851009 | -1.4152373597 |
| O | 1.0087836387 | 0.5499965387 | 3.4257169859 |

| | | | |
|---|---|---|---|
| O | 3.7115769212 | -0.1109648573 | -0.1655808487 |
| S | 1.4231603221 | -0.7878925784 | -2.1674949619 |
| C | -1.1725932411 | 2.3828549566 | -4.4223859478 |
| N | -1.6304905452 | 1.7435767326 | -3.5503682124 |
| H | 3.1462041751 | 0.4021407449 | 2.1711782997 |
| H | -0.8058294816 | -0.4972645048 | -0.3872702589 |
| H | -4.1485338207 | 0.2856114595 | 0.7042767496 |
| H | -3.3662517956 | 2.69315519 | 1.7622908368 |
| H | -1.5924311893 | 1.6698022713 | 3.6193141928 |
| H | -1.0281880847 | 2.2397957236 | 2.0427638732 |
| H | -1.2363266714 | -0.6002895497 | 2.986641941 |
| H | -3.36454388 | 2.1450709353 | -0.7122049403 |
| H | -1.6800747874 | 1.8405056251 | -0.2489948255 |
| H | -2.225190039 | 0.8075859304 | -2.2417221239 |
| H | -4.0402393327 | 1.7333371459 | 3.7816313091 |

**b) C3'-exo-back complex-2 E= -1326.03362814 G= -1325.862149**

| | | | |
|---|---|---|---|
| C | -0.099053839 | -0.0269901893 | -0.5631964096 |
| N | -0.0689207284 | 0.0134809179 | 0.7761765381 |
| C | 1.1273526685 | 0.1357781597 | 1.4873343809 |
| N | 2.2443491454 | 0.312955647 | 0.7111312295 |
| C | 2.3352303306 | 0.2518822234 | -0.6762731208 |
| C | 1.0325722808 | 0.1083343339 | -1.361063072 |
| C | -1.2762302983 | -0.2762037344 | 1.614369252 |

| | | | |
|---|---|---|---|
| O | -2.3475490999 | -0.5955037186 | 0.7772567426 |
| C | -3.3289059462 | 0.4551892589 | 0.7980586781 |
| C | -3.1985886399 | 1.0578076339 | 2.1915308721 |
| C | -1.6928441916 | 0.9435480923 | 2.4548808985 |
| O | -3.9572629994 | 0.2384011001 | 3.0658335107 |
| C | -3.0828230565 | 1.4629158055 | -0.3116513561 |
| O | -3.0743264671 | 0.7488473211 | -1.5366265689 |
| O | 1.1519247475 | 0.1195981157 | 2.7041362477 |
| O | 3.4236682814 | 0.332006107 | -1.2178420282 |
| S | 0.9207361185 | 0.0651458035 | -3.0497383331 |
| C | 1.5366129609 | -2.9410345858 | 0.2388769025 |
| N | 0.6932042363 | -2.8899877438 | 1.0575221885 |
| H | 3.1201206653 | 0.3828627239 | 1.2200052654 |
| H | -1.0789902572 | -0.1715022588 | -1.0101928229 |
| H | -4.2993824149 | -0.0266683394 | 0.6556604088 |
| H | -3.5482454048 | 2.0959021177 | 2.2268012862 |
| H | -1.4682939646 | 0.7991601722 | 3.512408717 |
| H | -1.1702470249 | 1.8427597266 | 2.1174605064 |
| H | -1.0027669031 | -1.1547385197 | 2.2013859496 |
| H | -3.8831210687 | 2.2120507177 | -0.2915925196 |
| H | -2.1240852117 | 1.9811834052 | -0.1571267629 |
| H | -2.9682095366 | 1.3725544432 | -2.2651892573 |
| H | -3.8509182701 | 0.5624659432 | 3.9689830523 |

**c) C3'-endo-front complex-2 E= -1326.03839646 G= -1325.868186**

| | | | |
|---|---|---|---|
| C | -0.2190803881 | -0.1901883707 | 0.2966910792 |
| C | 0.0613312461 | -0.0093589878 | 1.7865009711 |
| O | 1.4165613418 | 0.3089328323 | 1.9181643576 |
| C | 2.0356836661 | 0.427290297 | 0.6201701104 |
| C | 0.8724064285 | 0.6574884811 | -0.3509278827 |
| N | -0.7471303574 | 1.1245552607 | 2.3584428137 |
| C | -0.201480637 | 2.3083125185 | 2.6867071368 |
| C | -0.9229769576 | 3.376556286 | 3.2036623943 |
| C | -2.3750785729 | 3.1791232751 | 3.410940951 |
| N | -2.8312180003 | 1.9089684346 | 3.0605863513 |
| C | -2.1077757038 | 0.8591781588 | 2.551003712 |
| O | -2.5943213466 | -0.2221170941 | 2.2805716403 |
| O | -3.1537282883 | 4.0047609086 | 3.8484124131 |
| S | -0.1683401658 | 4.8426593181 | 3.5902220706 |
| C | 2.4512719999 | 3.5811030605 | -3.1003613695 |
| N | 2.0768080251 | 2.5280724651 | -2.7402891337 |
| C | 3.0619983542 | 1.5297174507 | 0.6247316873 |
| O | 4.1333572474 | 1.1526365302 | 1.4738685039 |
| O | 1.1529700421 | 0.253006573 | -1.6586919675 |
| H | -3.8215520035 | 1.7295896121 | 3.1980389993 |
| H | 0.8686541166 | 2.3844814552 | 2.5342082006 |
| H | 2.5203228649 | -0.5279738688 | 0.3760959467 |
| H | 0.5920558606 | 1.7242022177 | -0.3295895938 |

| | | | |
|---|---|---|---|
| H | -0.0555960198 | -1.2383923079 | 0.0263007596 |
| H | -1.2338654589 | 0.0920000445 | 0.0159438176 |
| H | -0.1896273803 | -0.8788228735 | 2.3954902614 |
| H | 3.3992658328 | 1.6734713276 | -0.4107452897 |
| H | 2.5979985487 | 2.4666316208 | 0.9650970547 |
| H | 4.809677708 | 1.8395641532 | 1.4487316037 |
| H | 1.5152663638 | 1.0469274244 | -2.1397557664 |

**d) C3'-endo-back complex-2 E= -1326.02910139 G= -1325.861071**

| | | | |
|---|---|---|---|
| C | 0.0477848922 | -0.4496999985 | 1.0592397565 |
| C | 0.3924698738 | 0.5078921869 | 2.197041139 |
| O | 1.7555095219 | 0.8032599253 | 2.0823431952 |
| C | 2.3103581299 | 0.2240131944 | 0.8878752707 |
| C | 1.1044232877 | -0.0999043162 | 0.0105398364 |
| N | -0.3846564021 | 1.7871323063 | 2.0983535284 |
| C | 0.2074034328 | 2.9750445388 | 1.9174160969 |
| C | -0.4623385639 | 4.1922023084 | 1.9697265378 |
| C | -1.9054263579 | 4.1587963208 | 2.2913057927 |
| N | -2.4162790926 | 2.877970094 | 2.4730611606 |
| C | -1.7306517228 | 1.6894705891 | 2.4686198068 |
| O | -2.2492959721 | 0.6194531527 | 2.7248842197 |
| O | -2.6366915378 | 5.1273367534 | 2.3970433239 |
| S | 0.3507221449 | 5.6537892513 | 1.7040318152 |
| C | -0.4050379003 | 2.2749633569 | 5.1977603989 |

| | | | |
|---|---|---|---|
| N | -0.3485579689 | 2.214245807 | 6.37086505 |
| C | 3.298212106 | 1.1722427551 | 0.255830582 |
| O | 4.4162269742 | 1.2942039424 | 1.1174249775 |
| O | 1.4469359377 | -1.1533431139 | -0.8619986654 |
| H | -3.3951273453 | 2.8128440443 | 2.735221176 |
| H | 1.2741602871 | 2.9427297222 | 1.730620296 |
| H | 2.8195250096 | -0.7118659399 | 1.155472685 |
| H | 0.8048424916 | 0.7921008288 | -0.5594546213 |
| H | 0.212239628 | -1.4782735884 | 1.39529852 |
| H | -0.981133342 | -0.3479060434 | 0.7149515751 |
| H | 0.169139591 | 0.122668463 | 3.1942573705 |
| H | 3.5874730783 | 0.7540527136 | -0.7176426556 |
| H | 2.8186332514 | 2.1461802082 | 0.0868142886 |
| H | 5.0578801557 | 1.892200565 | 0.7164926914 |
| H | 0.7545106624 | -1.2546951881 | -1.5264650818 |

**E. Transition state between anionradical and complex-1 forms of SCNdU (TS-1); one imaginary frequency found, abstracting $SCN^-$**

**a) C3'-exo-front TS-1 E= -1326.00014741 G= -1325.828665**

| | | | |
|---|---|---|---|
| C | 0.0544798946 | -0.3753804289 | 0.0299829978 |
| N | 0.033296293 | -0.0900503456 | 1.4052474131 |
| C | 1.1862514404 | -0.0167739807 | 2.1313058065 |
| N | 2.3430942181 | -0.222084205 | 1.398020566 |
| C | 2.4610726554 | -0.1363747672 | -0.0001535518 |

| | | | |
|---|---|---|---|
| C | 1.2165578845 | -0.375853934 | -0.6949505641 |
| C | -1.2173574587 | 0.3018525764 | 2.0702292688 |
| O | -2.2951604439 | -0.3986834555 | 1.4829424009 |
| C | -3.2952468775 | 0.5087095503 | 1.0008527377 |
| C | -3.0502579212 | 1.8082801432 | 1.7628922842 |
| C | -1.5298949436 | 1.795613144 | 1.9104993473 |
| O | -3.7098910289 | 1.6890924123 | 3.0149962781 |
| C | -3.1993146605 | 0.7045730967 | -0.5038755551 |
| O | -3.2417966065 | -0.5759371507 | -1.1138223189 |
| O | 1.226164989 | 0.2171802715 | 3.3417841501 |
| O | 3.5760551876 | 0.0672431334 | -0.4835764603 |
| S | 1.1583450042 | 0.506468857 | -2.561208116 |
| C | 0.3013711164 | 1.8985640585 | -2.184755112 |
| N | -0.3344322772 | 2.7942155606 | -1.7762346224 |
| H | 3.2024787228 | -0.1357486435 | 1.9300994917 |
| H | -0.9166513539 | -0.6277899942 | -0.3838502512 |
| H | -4.2665552168 | 0.0756660657 | 1.2588549653 |
| H | -3.4138558487 | 2.6833266501 | 1.2114140378 |
| H | -1.1803302831 | 2.3841596694 | 2.7613932844 |
| H | -1.056119544 | 2.178179722 | 0.9993145284 |
| H | -1.1169923387 | 0.0062736245 | 3.1156590118 |
| H | -4.0482247035 | 1.3226970927 | -0.8239321015 |
| H | -2.2704541341 | 1.2301399589 | -0.7678814456 |
| H | -3.1911648009 | -0.4665693333 | -2.0708879398 |

| | | | |
|---|---|---|---|
| H | -3.531511346 | 2.480000282 | 3.5392758961 |

**b) C3'-exo-back TS-1 E= -1325.99735881 G= -1325.825794**

| | | | |
|---|---|---|---|
| C | -0.5246572235 | 0.0656456779 | -0.3681543784 |
| N | 0.4395590511 | 1.0871355059 | -0.4855631778 |
| C | 0.0682058407 | 2.3962772064 | -0.6034068521 |
| N | -1.2979880536 | 2.6158764835 | -0.5329097208 |
| C | -2.2481037532 | 1.7230291161 | -0.0020828464 |
| C | -1.8352091732 | 0.3442255844 | -0.0866034935 |
| C | 1.8668186254 | 0.7701244739 | -0.4149468495 |
| O | 2.1102638796 | -0.4313648572 | -1.1259205831 |
| C | 2.8056148509 | -1.3809214569 | -0.3094786696 |
| C | 3.4106573105 | -0.564902048 | 0.8304163581 |
| C | 2.3615508327 | 0.529562655 | 1.016371743 |
| O | 4.6454438757 | -0.0426592904 | 0.3622101259 |
| C | 1.8725412489 | -2.4668985086 | 0.2030209878 |
| O | 1.1939178894 | -3.0220118188 | -0.9099047442 |
| O | 0.8582361084 | 3.3309557709 | -0.7549650394 |
| O | -3.3173579212 | 2.1776735015 | 0.4104136063 |
| S | -2.7763618571 | -0.8433409781 | 1.3275561764 |
| C | -4.2257664809 | -1.1366170718 | 0.531351663 |
| N | -5.2278774054 | -1.3349999776 | -0.0346475433 |
| H | -1.5707074263 | 3.5917654237 | -0.5775858375 |
| H | -0.1458921111 | -0.9281916197 | -0.5841429925 |

| | | | |
|---|---|---|---|
| H | 3.5867078891 | -1.8281656637 | -0.9317278724 |
| H | 3.5596924873 | -1.1684707402 | 1.7334801297 |
| H | 2.7682276891 | 1.4356808915 | 1.4704325971 |
| H | 1.5363557377 | 0.1689369903 | 1.6393526666 |
| H | 2.3906303531 | 1.5939669313 | -0.901773027 |
| H | 2.4759180781 | -3.2238426799 | 0.7202350681 |
| H | 1.155486232 | -2.0474642044 | 0.9238155832 |
| H | 0.6487354923 | -3.7580486049 | -0.6076882159 |
| H | 5.0356642312 | 0.5058400013 | 1.0544252759 |

**c) C3'-endo-front TS-1 E=-1325.99797433 G=-1325.829065**

| | | | |
|---|---|---|---|
| C | 0.0164057638 | 0.2614552252 | -0.015442552 |
| N | -0.0068679727 | 0.1258270934 | 1.3837965194 |
| C | 1.1366773205 | -0.1605114929 | 2.0794410604 |
| N | 2.2820884989 | -0.2083848854 | 1.3018601506 |
| C | 2.4277801662 | 0.3070527645 | 0.0015340348 |
| C | 1.1798592916 | 0.3882069961 | -0.7206715013 |
| C | -1.2433615522 | 0.3892415918 | 2.1155236807 |
| O | -2.2761471005 | -0.4109944013 | 1.5506218365 |
| C | -3.4086723405 | 0.3932123893 | 1.2185542584 |
| C | -2.844426124 | 1.8008113784 | 0.9869817247 |
| C | -1.7110142389 | 1.8479515174 | 2.0041459639 |
| O | -3.7843362578 | 2.8251474539 | 1.2472260168 |
| C | -4.1107694247 | -0.1947882956 | 0.0196230871 |

| | | | |
|---|---|---|---|
| O | -4.699702428 | -1.4279747942 | 0.3978680551 |
| O | 1.1839133995 | -0.358169173 | 3.2940677941 |
| O | 3.560445457 | 0.5697504288 | -0.4050344447 |
| S | 1.2241951732 | 1.7747666532 | -2.2601837441 |
| C | 0.2727311402 | 2.9722179126 | -1.5727164887 |
| N | -0.4377167988 | 3.6956579347 | -0.9868074467 |
| H | 3.1371974581 | -0.3791868849 | 1.820216147 |
| H | -0.962217308 | 0.2126518134 | -0.4818957198 |
| H | -4.1036649838 | 0.4311831574 | 2.0711713174 |
| H | -2.4521110699 | 1.8963960674 | -0.0346681024 |
| H | -2.1251828815 | 2.1788017825 | 2.9617250288 |
| H | -0.8994587569 | 2.5177361013 | 1.712796036 |
| H | -1.0557893089 | 0.08528319 | 3.145172479 |
| H | -4.8756886907 | 0.5166046269 | -0.3214021914 |
| H | -3.3803250278 | -0.3381513427 | -0.788821174 |
| H | -5.1419653397 | -1.8118557571 | -0.3682957304 |
| H | -4.266812383 | 3.0333515464 | 0.438782984 |

**d) C3'-endo-back TS-1 E= -1325.99662644 G= -1325.828214**

| | | | |
|---|---|---|---|
| O | -0.1520886275 | -1.8761535477 | 1.282273338 |
| C | 0.9295414637 | -1.901103161 | 2.216181865 |
| C | 1.9773575221 | -0.8996746375 | 1.6940153919 |
| C | 1.4643640388 | -0.4973834737 | 0.307753149 |
| C | -0.0388110149 | -0.7337949283 | 0.4425566831 |

| | | | |
|---|---|---|---|
| N | 1.4162119386 | -3.2636145297 | 2.3124418572 |
| C | 1.1251474032 | -4.0015185104 | 3.4316464041 |
| N | 1.6256940592 | -5.2913998045 | 3.4120189175 |
| C | 2.5914483019 | -5.799773442 | 2.5230365121 |
| C | 2.6400713466 | -5.0862698449 | 1.2693441804 |
| C | 2.0147255008 | -3.872984941 | 1.1892477504 |
| O | 0.4856632056 | -3.5821283678 | 4.3961336267 |
| S | 4.4747056057 | -5.2901362266 | 0.3313954074 |
| C | 4.2169989551 | -6.7583597141 | -0.4442595668 |
| N | 4.0242925727 | -7.7779488695 | -0.9797276236 |
| O | 3.2344489154 | -6.7950823756 | 2.8601516212 |
| O | 1.6835968991 | 0.8560455615 | -0.0333707234 |
| C | -0.7289068844 | -0.9962288994 | -0.8724177481 |
| O | -2.130005224 | -1.0272753612 | -0.6509957767 |
| H | 1.4661220263 | -5.8211976378 | 4.2618957182 |
| H | 1.903235652 | -3.3149578593 | 0.2646475319 |
| H | -0.4907523139 | 0.1457648217 | 0.9281115153 |
| H | 1.8717717441 | -1.1547927788 | -0.4734749264 |
| H | 1.9844001391 | -0.008622487 | 2.3276795399 |
| H | 2.9807840701 | -1.330265474 | 1.6835680593 |
| H | 0.5646415497 | -1.6363055284 | 3.2087696149 |
| H | -0.4568996202 | -0.192507353 | -1.5693829195 |
| H | -0.3702523366 | -1.9534521675 | -1.274607064 |
| H | -2.5747571666 | -1.2148479577 | -1.4857044317 |

| | | | |
|---|---|---|---|
| H | 2.6103118967 | 0.9768453878 | -0.2727660354 |

**F. Transition state between anionradical and complex-2 forms of SCNdU (TS-2); one imaginary frequency found, abstracting $CN^-$**

**a) C3'-exo-front TS-2 E= -1326.00740459 G= -1325.836037**

| | | | |
|---|---|---|---|
| C | 0.0380384969 | -0.128631945 | 0.0110077836 |
| N | 0.015469533 | -0.0210199959 | 1.4063634146 |
| C | 1.1518129253 | 0.0789694795 | 2.1509986616 |
| N | 2.3328503866 | -0.0047902647 | 1.4323201756 |
| C | 2.4897283294 | 0.0152370602 | 0.0396183561 |
| C | 1.2545852818 | -0.1682502592 | -0.6882802321 |
| C | -1.2570081727 | 0.2358121044 | 2.0986008748 |
| O | -2.3003555127 | -0.4294610408 | 1.4185059471 |
| C | -3.3341991764 | 0.4881173344 | 1.0382469137 |
| C | -3.1484618708 | 1.6950097756 | 1.954269027 |
| C | -1.6304411716 | 1.724333169 | 2.125720266 |
| O | -3.8149134587 | 1.4011548555 | 3.1734395754 |
| C | -3.2379688784 | 0.8687918008 | -0.4308865299 |
| O | -3.209111015 | -0.3270353387 | -1.1923168867 |
| O | 1.1610154977 | 0.2421867984 | 3.3740091177 |
| O | 3.6257208226 | 0.148447621 | -0.4188295346 |
| S | 1.2805455619 | -0.1034748553 | -2.4099629395 |
| C | 0.7009595471 | 1.6282385246 | -2.744033921 |
| N | 0.1863149074 | 2.6315885673 | -2.4241480877 |

H 3.1780508289 0.0985102767 1.9815120085

H -0.9092937303 -0.3741585405 -0.4505226142

H -4.2881330803 -0.0123046028 1.2298371382

H -3.5419701177 2.6152217674 1.506758862

H -1.3187296747 2.2098205041 3.0527287037

H -1.1571963285 2.2408870295 1.2838678128

H -1.1512976897 -0.1828762222 3.100187155

H -4.112713965 1.4807657036 -0.6858505431

H -2.3314782765 1.4631005635 -0.6139182205

H -3.1703017278 -0.0986147231 -2.1287609575

H -3.674694504 2.1305915808 3.790372859

**b) C3'-exo-back TS-2 E= -1326.00527568 G= -1325.835408**

C 0.0393413874 -0.0939128699 -0.0825500623

N 0.0236857798 0.0011766651 1.3139641783

C 1.1535564616 0.1838851136 2.0482798318

N 2.334827192 0.1606660234 1.324816121

C 2.4948218458 0.0285721159 -0.0598472568

C 1.2501240553 -0.007540422 -0.7976028609

C -1.2540098876 0.1380579777 2.0337158731

O -2.2702612077 -0.5230888596 1.3125584101

C -3.3500797315 0.3707976102 1.0103991887

C -3.2158061928 1.5083768367 2.0187790421

C -1.6990151072 1.599157553 2.1820912414

| | | | |
|---|---|---|---|
| O | -3.8558628289 | 1.0845446986 | 3.2131970386 |
| C | -3.2832715148 | 0.8696288915 | -0.4245432643 |
| O | -3.2037591734 | -0.2602332437 | -1.2765500551 |
| O | 1.1571003531 | 0.3601295721 | 3.2708489271 |
| O | 3.6397887696 | -0.029910982 | -0.5117800976 |
| S | 1.2996306939 | -0.3272995703 | -2.483535928 |
| C | 1.0316629064 | -2.1779273115 | -2.5391250093 |
| N | 0.7493033898 | -3.2232705771 | -2.0945592073 |
| H | 3.1807546811 | 0.2711198775 | 1.8711129103 |
| H | -0.9180863642 | -0.2579975971 | -0.555820533 |
| H | -4.2769741899 | -0.1899346985 | 1.1641193602 |
| H | -3.6579959852 | 2.4407694394 | 1.6485142957 |
| H | -1.3992377637 | 2.0255552058 | 3.1412399502 |
| H | -1.2627391947 | 2.2039940401 | 1.3804788815 |
| H | -1.1166092734 | -0.3510191153 | 2.9996045099 |
| H | -4.1864806871 | 1.4590079246 | -0.6274957312 |
| H | -2.4072564843 | 1.5192253008 | -0.5633122433 |
| H | -3.1964843131 | 0.0393583469 | -2.1935226272 |
| H | -3.728264115 | 1.7577331969 | 3.8934688715 |

**c) C3’-endo-front TS-2 E= -1326.00583869 G= -1325.836719**

| | | | |
|---|---|---|---|
| C | 0.0307905299 | 0.2136613648 | 0.0459309567 |
| N | -0.0290343535 | -0.2729018403 | 1.322168263 |
| C | 1.1130322454 | -0.4122691495 | 2.120021766 |

| | | | |
|---|---|---|---|
| C | 2.3858916036 | -0.07682718 | 1.6434075844 |
| C | 2.521817577 | 0.341475501 | 0.2646028016 |
| N | 1.2980244441 | 0.5771065298 | -0.37675697 |
| C | -1.2868096304 | -0.8529001159 | 1.7888549698 |
| C | -1.2518800446 | -2.3881566701 | 1.8921916637 |
| C | -1.1536700879 | -2.6599195869 | 3.3946223985 |
| C | -1.8534192103 | -1.4356647409 | 3.98372046 |
| O | -1.5399562594 | -0.3625418696 | 3.0986015368 |
| C | -1.4004071369 | -1.096075139 | 5.3817244221 |
| O | -2.2241445497 | -0.0584213457 | 5.888393322 |
| O | -1.8316186469 | -3.8205328599 | 3.8312896508 |
| S | 3.8009868558 | -0.4628100209 | 2.5476620674 |
| C | 3.7899428619 | -2.3248022929 | 2.4999397353 |
| N | 3.2327884698 | -3.343717295 | 2.336392286 |
| O | 3.560346379 | 0.5398317978 | -0.3657505266 |
| O | -0.9407775051 | 0.3284969999 | -0.7021788581 |
| H | 1.3505100904 | 0.9080578768 | -1.3331217823 |
| H | 0.9241666925 | -0.6167016853 | 3.1650238431 |
| H | -2.9388330756 | -1.6189554144 | 3.9831891391 |
| H | -0.1041935967 | -2.6866322523 | 3.7215045106 |
| H | -2.1963349728 | -2.8039102331 | 1.529400144 |
| H | -0.4280919657 | -2.8126246953 | 1.3138689382 |
| H | -2.0537792384 | -0.5006294023 | 1.1000537113 |
| H | -1.4825062017 | -2.0023131879 | 5.9963458018 |

| | | | |
|---|---|---|---|
| H | -0.3472636978 | -0.7836774001 | 5.3507737322 |
| H | -1.9383377372 | 0.158375461 | 6.7834835016 |
| H | -1.3087038146 | -4.5975723579 | 3.6000288508 |

**d) C3'-endo-back TS-2 E= -1326.00482254 G= -1325.834167**

| | | | |
|---|---|---|---|
| C | 0.0975665012 | 0.3498862468 | 0.0942187404 |
| N | 0.1147522901 | 0.1741816606 | 1.4852888857 |
| C | 1.2569463534 | 0.3796493979 | 2.2180817952 |
| N | 2.3406840228 | 0.8460711289 | 1.4960511801 |
| C | 2.4740150738 | 0.9419069486 | 0.1044843273 |
| C | 1.2271583226 | 0.7816398606 | -0.6111420819 |
| C | -0.976309258 | -0.5337440538 | 2.1469129462 |
| O | -0.8049970562 | -1.9346846068 | 1.9423956251 |
| C | -1.9697338461 | -2.51922265 | 1.3605896889 |
| C | -2.7378922378 | -1.3590557735 | 0.7106978355 |
| C | -2.371531505 | -0.1893616855 | 1.6190050044 |
| O | -4.1392971648 | -1.5456771393 | 0.7116002315 |
| C | -1.5605064346 | -3.5933122738 | 0.381695255 |
| O | -0.9972140528 | -4.6757602865 | 1.1060474542 |
| O | 1.346846046 | 0.1813600229 | 3.4288122402 |
| O | 3.5881910967 | 1.1770164329 | -0.3619154897 |
| S | 1.2399987686 | 0.8014610689 | -2.3328416281 |
| C | 1.1737735626 | -1.0188690887 | -2.7374680354 |
| N | 0.9599314371 | -2.1305906701 | -2.4318363625 |

| | | | |
|---|---|---|---|
| H | 3.1865531813 | 0.9840527279 | 2.0368806825 |
| H | -0.8711320644 | 0.2998601629 | -0.3809890057 |
| H | -2.5997350662 | -2.9559931345 | 2.1499947658 |
| H | -2.3802233783 | -1.2043535812 | -0.3166025852 |
| H | -3.0762032405 | -0.1900366232 | 2.456032393 |
| H | -2.4182125832 | 0.7869392223 | 1.1339965832 |
| H | -0.8693247754 | -0.31375678 | 3.2079206639 |
| H | -2.450605615 | -3.9207174537 | -0.1744542293 |
| H | -0.8361291034 | -3.1677483864 | -0.3270937691 |
| H | -0.6674158554 | -5.3314981298 | 0.4807087142 |
| H | -4.3928770521 | -2.0918943467 | -0.0420861128 |

**G. Radical rad-dU, formed via abstracting $SCN^-$ from anionradical SCNdU**

**a) C3'-exo rad-dU E= -834.866664494 G= -834.696449**

| | | | |
|---|---|---|---|
| C | -0.0555613029 | -0.247065744 | 0.0768000205 |
| C | 0.038873771 | -0.0824906199 | 1.6026956464 |
| O | 1.3975980861 | -0.0573972263 | 1.9388200732 |
| C | 2.2106797067 | -0.0134418593 | 0.753845053 |
| C | 1.3583326139 | -0.6873006692 | -0.3145190076 |
| N | -0.5987756554 | 1.1798979373 | 2.0752165991 |
| C | 0.1335517471 | 2.2464930991 | 2.5549013375 |
| C | -0.4928686854 | 3.3533328509 | 2.9675198173 |
| C | -1.9206579721 | 3.5281731055 | 2.9664249293 |
| N | -2.5602326825 | 2.3830414401 | 2.4760962499 |

| | | | |
|---|---|---|---|
| C | -1.9781464272 | 1.2145547594 | 2.0234026105 |
| O | -2.6386236172 | 0.2739203467 | 1.6030572245 |
| O | -2.5665062442 | 4.501821336 | 3.3255468183 |
| C | 2.5872903377 | 1.4141234678 | 0.3969314816 |
| O | 3.2099473035 | 1.9862379883 | 1.535092085 |
| O | 1.5412969575 | -2.0858866127 | -0.1646475284 |
| H | -3.5748924123 | 2.4071312218 | 2.432552469 |
| H | 1.2132492687 | 2.1130293784 | 2.5659957078 |
| H | 3.1110918495 | -0.5921845976 | 0.9749098926 |
| H | 1.630816417 | -0.3628210805 | -1.325167167 |
| H | -0.8117914487 | -0.9800131007 | -0.2068084705 |
| H | -0.3105834438 | 0.7062676514 | -0.3950202525 |
| H | -0.4534530238 | -0.8902918184 | 2.148062306 |
| H | 3.2674669369 | 1.3929430312 | -0.4625857936 |
| H | 1.6936946749 | 1.9906955961 | 0.1136715326 |
| H | 3.5520394637 | 2.8577326796 | 1.3018477315 |
| H | 0.9880423963 | -2.5460569592 | -0.8083430525 |

**b) C3'-endo rad-dU E= -834.863865038 G= -834.695870**

| | | | |
|---|---|---|---|
| C | 0.1151921923 | -0.5063800275 | 0.1738276203 |
| N | -0.0171834827 | 0.0886630451 | 1.4149115796 |
| C | 1.0423805806 | 0.7353790156 | 2.0147892279 |
| C | 2.2342813271 | 0.7796253562 | 1.4133242167 |
| C | 2.5118487618 | 0.2044782232 | 0.1232733403 |

| | | | |
|---|---|---|---|
| N | 1.3674230998 | -0.4067362401 | -0.4023365971 |
| C | -1.3626031007 | -0.0199175433 | 2.0512383237 |
| C | -1.6076018855 | -1.4077322882 | 2.6450258524 |
| C | -1.1958403174 | -1.2183012965 | 4.1056762804 |
| C | -1.6385586682 | 0.2197374145 | 4.3603863744 |
| O | -1.4206668387 | 0.8971464063 | 3.1126069889 |
| C | -0.8860249627 | 0.9109454092 | 5.4693512332 |
| O | -1.4665729704 | 2.1860921013 | 5.678734373 |
| O | -1.8517637375 | -2.0664013886 | 5.0212579591 |
| O | 3.564295711 | 0.207851921 | -0.4966350258 |
| O | -0.8118224045 | -1.0852428185 | -0.3750448934 |
| H | 1.4590604141 | -0.8423095207 | -1.315540372 |
| H | 0.825351583 | 1.2011975528 | 2.9693680648 |
| H | -2.7138041721 | 0.2268170135 | 4.5878520668 |
| H | -0.1044434471 | -1.298405333 | 4.2181871544 |
| H | -2.6777364142 | -1.6342487318 | 2.6102196269 |
| H | -1.0612854737 | -2.1909015651 | 2.1180790094 |
| H | -2.0810973675 | 0.2494616326 | 1.2755320464 |
| H | -0.96301643 | 0.2840146095 | 6.3673886162 |
| H | 0.1747902748 | 0.9983747719 | 5.1971893685 |
| H | -1.0092698998 | 2.6237223054 | 6.4064613072 |
| H | -1.4519634436 | -2.9437093957 | 4.9836393506 |

**H. Radical rad-S-dU formed via abstracting $CN^-$ from anionradical SCNdU**

**a) C3'-exo rad-S-dU E= -1233.09375526 G= -1232.922596**

| | | | |
|---|---|---|---|
| C | -0.0532578282 | -0.4065215421 | 0.0772541843 |
| N | -0.0551628007 | 0.0568021352 | 1.3402580199 |
| C | 1.1164956198 | 0.4599824077 | 1.9877273562 |
| N | 2.2572276575 | 0.3498168094 | 1.2325942948 |
| C | 2.3764225062 | -0.0962889891 | -0.0836305365 |
| C | 1.0940660957 | -0.5035789966 | -0.7004022518 |
| C | -1.3114890963 | 0.1672786524 | 2.1525795184 |
| O | -2.3507105031 | -0.4568211777 | 1.4632507413 |
| C | -3.3273576069 | 0.5111816463 | 1.0372996623 |
| C | -3.2178449566 | 1.6285692232 | 2.0679318643 |
| C | -1.7172612801 | 1.6345983723 | 2.3782345814 |
| O | -3.9901087278 | 1.2295416539 | 3.1875772289 |
| C | -3.0554166278 | 0.9807550982 | -0.3816295294 |
| O | -3.0029308449 | -0.1717979245 | -1.2050446069 |
| O | 1.1020766541 | 0.8741313484 | 3.1314725776 |
| O | 3.4689619619 | -0.1258010133 | -0.617470703 |
| S | 1.0213470665 | -1.068187839 | -2.2966021751 |
| H | 3.1148747507 | 0.6387518795 | 1.6936956056 |
| H | -1.0201988131 | -0.7052542414 | -0.3196608425 |
| H | -4.2975636943 | 0.0104784839 | 1.0855956211 |
| H | -3.5638300505 | 2.5904883939 | 1.6732036106 |
| H | -1.5043384671 | 1.9612858194 | 3.3965455605 |
| H | -1.1805568785 | 2.2935740481 | 1.6897397106 |

| | | | |
|---|---|---|---|
| H | -1.1109713473 | -0.3721395641 | 3.0797775773 |
| H | -3.8620403139 | 1.6567625827 | -0.6886380399 |
| H | -2.1068297924 | 1.5371761441 | -0.4313664429 |
| H | -2.9105912001 | 0.1010601468 | -2.1260617135 |
| H | -3.9115064145 | 1.8980457912 | 3.8796666979 |

**b) C3'-endo rad-S-dU E= -1233.09032133 G= -1232.921436**

| | | | |
|---|---|---|---|
| C | -0.0388237896 | -0.3703762332 | 0.2538035321 |
| C | 0.1094865939 | -0.0798623637 | 1.7470922781 |
| O | 1.4762219496 | 0.0562475358 | 2.0087676916 |
| C | 2.2450335698 | -0.0573690965 | 0.7979943319 |
| C | 1.2498371103 | 0.2171239417 | -0.3260670192 |
| N | -0.5731456875 | 1.2032966446 | 2.1304569222 |
| C | 0.1056747082 | 2.3199284225 | 2.4480053056 |
| C | -0.4996962722 | 3.5168805129 | 2.8064821047 |
| C | -1.9793429764 | 3.5446722885 | 2.8509440195 |
| N | -2.5801991652 | 2.3286301463 | 2.5268408443 |
| C | -1.9711962036 | 1.1493262865 | 2.1778371973 |
| O | -2.5806218503 | 0.1282227488 | 1.922940605 |
| O | -2.6676161541 | 4.5039193633 | 3.141311868 |
| S | 0.4185840672 | 4.8872921735 | 3.1916618806 |
| C | 3.41742592 | 0.8904017626 | 0.8316298067 |
| O | 4.321229193 | 0.449285218 | 1.8290515616 |
| O | 1.7083592255 | -0.4132699778 | -1.5003914827 |

H -3.5950673641 2.3010132531 2.5609491623

H 1.1853641647 2.2311889078 2.4223114148

H 2.610051463 -1.0896479787 0.7076232372

H 1.1504687424 1.3010149637 -0.4830456572

H -0.0319412297 -1.4533341562 0.09779019

H -0.95458133 0.0422877445 -0.1699989323

H -0.3306074339 -0.8449834713 2.3878770488

H 3.883349093 0.8797336036 -0.1626738555

H 3.0643312514 1.9100446756 1.0384561906

H 5.0823145606 1.041335421 1.8462937957

H 1.2107861504 -0.0803529124 -2.2569701916

**I. Anion $SCN^-$ E= -491.135262236 G= -491.144665**

C 0.1692315331 0.0000000082 -0.0172374042

N -0.0885615562 0. 1.1284008604

S 0.5349662812 0. -1.6446101736

**J. Anion $CN^-$ E= -92.9322830053 G= -92.946331**

C 0. 0. -0.0091755211

N 0. 0. 1.1671755211