Supporting Information for:

# An Isolable Boron-Centered Radical Aion Stabilized by Carbazole Moiety

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## Experimental Procedures

1. Materials and instruments

All experiments were carried out under a nitrogen or argon atmosphere by using standard Schlenk techniques and a glovebox. Solvents were dried prior to use. $Mes_2BF$, 3,6-di-tert-butylcarbazole, n-BuLi and 15-Crown-5 were purchased and used upon arrival. Cyclic voltammetry was performed on a CHI660E electrochemical workstation with platinum as the working and a saturated calomel electrode as reference. Freshly distilled THF was used as a solvent and n-$Bu_4NPF_6$ ($10^{-1}$M) was used as electrolyte. EPR spectra were obtained using CIQTEK EPR 200-Plus with continues-wave X band frequency. UV-Vis spectra were recorded on Lambda 750 spectrometer. X-ray crystal structures were obtained by using Agilent SuperNova CCD detectors. $^1$H-NMR spectra were recorded on a Bruker DPX 400. Infrared spectra were collected on a VECTOR22 FT-IR spectrometer.

2. Synthesis and preparations

2.1 3,6-Di-tert-butyl-N-(dimesitylboryl)carbazole was synthesized using a procedure shown in previous article.[23]

A solution of 3,6-di-tert-butylcarbazole (1.12 g, 4.0 mmol) in n-pentane (50 mL) was combined at room temperature with an equimolar amount of an n-butyllithium solution in n-hexane (1.6 m, 2.63 mL, 4.2 mmol). After stirring the mixture for 1 h, an n-pentane solution (10 mL) of fluorodimesitylborane (1.08 g, 4.0 mmol) was added. The slurry was stirred overnight, filtered, and the solvent and volatile components were removed from the filtrate. Purification of the residue was effected by column chromatography on silica with n-pentane. Product **1** was crystallized from n-pentane to give 1.41 g (67%) of pure **1** as a colorless solid. $^{1}$H-NMR ($CDCl_3$): δ = 1.39 (s, 18 H), 2.03 (s, 12 H), 2.32 (s, 6 H), 6.8 (m, 6 H), 7.09 (dd, 2 H), 7.94 (d, 2 H) ppm. $^{13}$C-NMR ($CDCl_3$ ): δ = 21.3 (s, p-$CH_3$ ), 22.0 (s, o-$CH_3$ ), 31.8 [s, C-$(CH_3)_3$], 34.7 [s, $C(CH_3)_3$], 115.0 (s, tBuCCHCH), 115.4 (s, tBuCCHC), 123.9 (s, tBuCCHCH), 128.6 [s, BCCCHC($CH_3$)], 128.2, 141.0, 141.7 (3s, tBuCCHCC), 138.8, 145.5 [2s, BCC($CH_3$)-CHC($CH_3$)] ppm. $^{11}$B-NMR($CDCl_3$): δ = 51.7 ppm. MS/EI: m/z (%)= 527.4 (100) $[M]^+$ , 512.4 (41) $[M-CH_3]^+$, 249.2 (68) $[B-Mes_2]^+$. $C_{38}H_{46}BN$ (527.60): calcd. C 86.51, H 8.79, N 2.65; found C 86.52, H 8.89, N 2.43.

2.2. Synthesis of $\mathbf{1}^{\bullet-}$

Under anaerobic and anhydrous conditions, a mixture of 1 (0.21 g, 0.398 mmol), 15-Crown-5 (0.092g, 0.418 mmol) and Na (0.011 g, 0.478 mmol) in THF (≈ 30 mL) was stirred at room temperature for 1 day. The resultant blue solution was filtered and then the filtrate was vaporated to remove the solvent THF. The resultant blue solid is dissolved in toluene to give a blue toluene solution, which is stored at around -30 °C for 1 day to afford blue X-ray-quality crystals of $\mathbf{1}^{\bullet-}$. Yield: 0.112 g, 26.0 %. Elemental analysis (%) Calcd: C 72.07; H 8.75; N 1.29; Found: C 72.04, H 8.74, N 1.31.

**Computational details**

All calculations have been performed by using the Gaussian 09 programs. Geometrical structures were optimized using the DFT method with the hybrid functional B3LYP[24, 25]and 6-31G(d,p) basis set, which has been applied in previous studies.[26, 27]Vibrational frequencies were calculated at the same level to characterize the stationary point as minima points. The vertical transition energies were calculated using the TDDFT method with B3LYP/6-31+G(d,p). Solvent effects were simulated using the polarizable continuum model (PCM).[28, 29]

**Table S1.** Experimental and Calculated Structural Parameters (avg.) for $\mathbf{1}^{\bullet-}$

| $\mathbf{1}^{\bullet-}$ | |
|---|---|
| Formula | $C_{65}H_{94}BNNaO_{10}$ |
| Formula weigh | 1083.21 |
| Temp. (K) | 170 K |
| Crystal system | Monoclinic |
| Space group | P1 21/n1 |
| a (Å) | 13.6926 (6) |
| b (Å) | 20.8222 (9) |
| c(Å) | 22.0394 (9) |
| α(° ) | 90 |
| β(° ) | 96.374 (4) |
| γ(° ) | 90 |
| V [Å3] | 6244.8 (5) |
| Z | 4 |
| R indexes (all data) | $R_1$(reflections)= 0.1081<br>$wR_2$(reflections)= 0.3747 |
| Completeness | 0.999 |

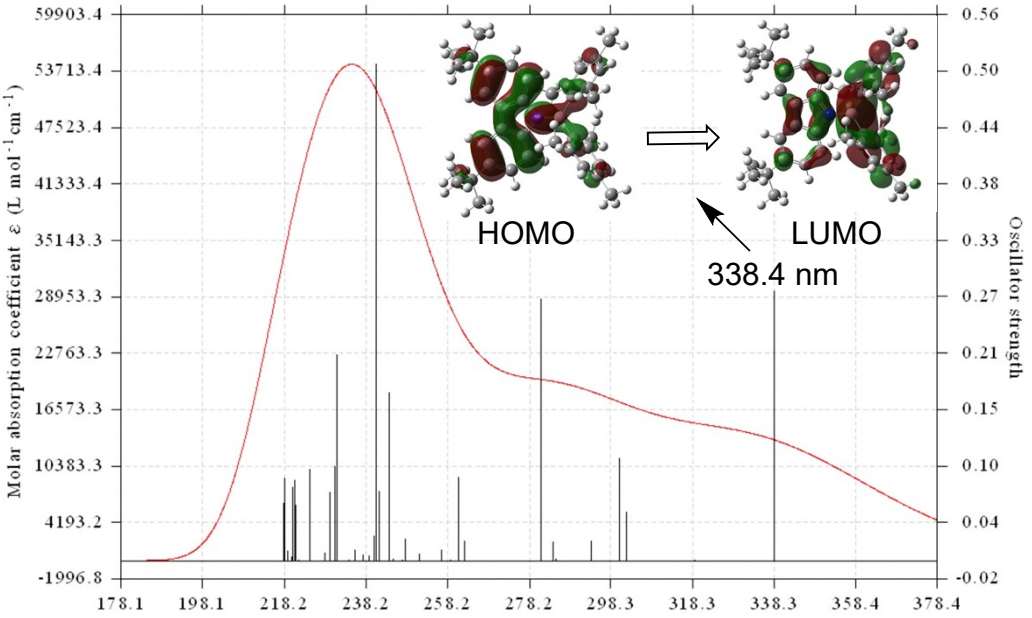



**Fig. S1** (a) Calculated absorption spectrum of **1** and (b) related molecular obtials

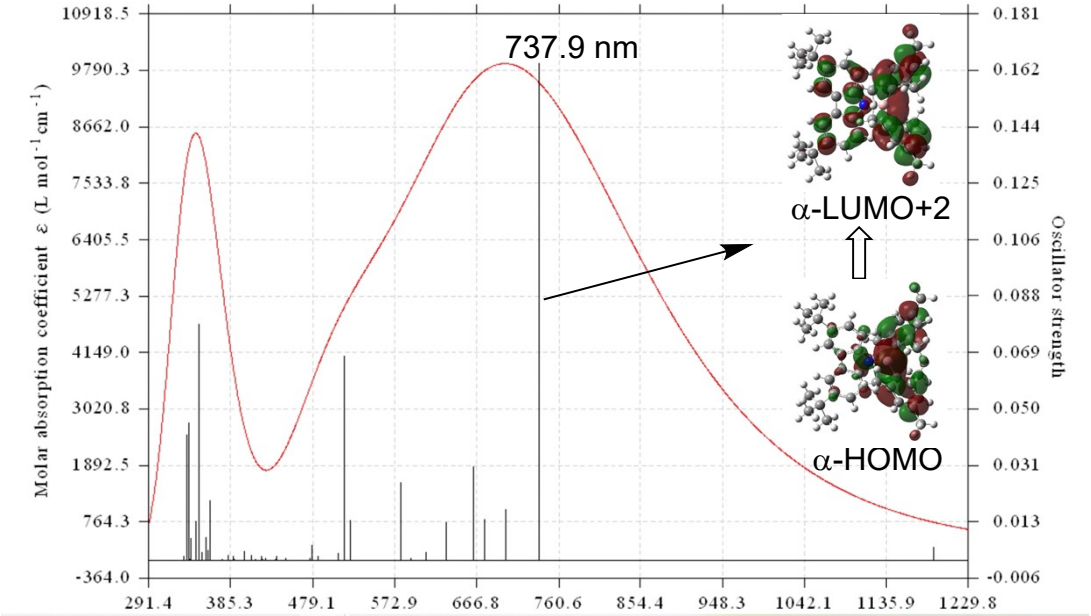



**Fig. S2 (a)** Calculated absorption spectrum of $\mathbf{1}^{\bullet-}$ and (b) related molecular obtials

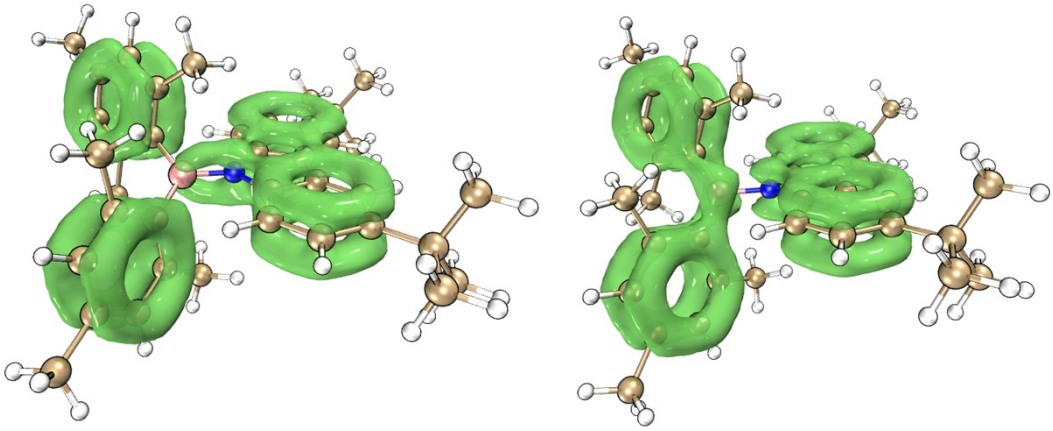
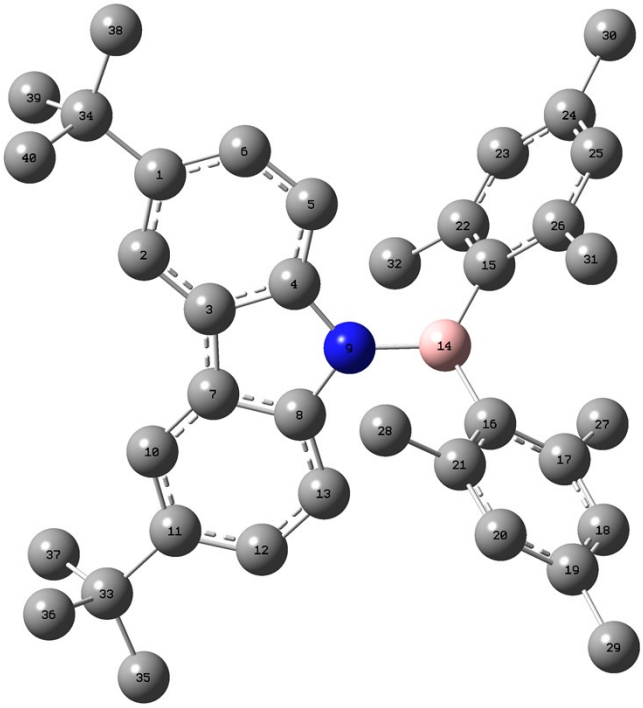


**Fig. S3** LOL-π isosurface of **1** (left) and **1**$^{\bullet-}$ (right) with isovalue of 0.35.

**Mulliken charges and spin densities for all atoms in free 1$^{\bullet-}$**

**spin density：**




**1 C 0.011083**

**2 C -0.001813**

**3 C 0.002061**

**4 C 0.018097**

**5 C 0.012346**

**6 C -0.004266**

**7 C 0.002062**

**8 C 0.018096**

**9 N -0.040116**

**10 C -0.001813**

**11 C 0.011083**

**12 C -0.004267**

**13 C 0.012347**

**14 B 0.627243**

**15 C -0.065859**

**16 C -0.065854**

**17 C 0.094503**

**18 C -0.050654**

**19 C 0.12508**

**20 C -0.044568**

**21 C 0.086101**

**22 C 0.086117**

**23 C -0.044575**

**24 C 0.12509**

**25 C -0.050656**

**26 C 0.0945**

**27 C 0.012802**

**28 C 0.009586**

**29 C 0.001722**

**30 C 0.001722**

**31 C 0.012801**

**32 C 0.009586**

**33 C -0.000595**

**34 C -0.000595**

**35 C 0.000037**

**36 C 0.000453**

**37 C 0.000312**

**38 C 0.000037**

**39 C 0.000453**

**40 C 0.000312**

**Coordinates for optimized geometries of 1 and $1^{\bullet-}$**

Neutral **1**

| | | | |
|---|---|---|---|
| C | -2.80995200 | 2.97076100 | 0.61249000 |
| C | -3.09122300 | 1.62720300 | 0.33456600 |
| C | -2.05749100 | 0.71250800 | 0.13452900 |
| C | -0.70741900 | 1.12035800 | 0.20159300 |
| C | -0.40475400 | 2.44785000 | 0.50379400 |
| C | -1.45606400 | 3.34713700 | 0.69480900 |
| C | -2.05751100 | -0.71248400 | -0.13446100 |
| C | -0.70745300 | -1.12036000 | -0.20160300 |
| N | 0.15353100 | -0.00001300 | -0.00001800 |
| C | -3.09127800 | -1.62715100 | -0.33446800 |

| | | | |
|---|---|---|---|
| C | -2.81005400 | -2.97070500 | -0.61244700 |
| C | -1.45617600 | -3.34711100 | -0.69483900 |
| C | -0.40483700 | -2.44785600 | -0.50385100 |
| B | 1.60058600 | -0.00002700 | -0.00001500 |
| C | 2.39022600 | 1.32511900 | -0.37487700 |
| C | 2.39021800 | -1.32517500 | 0.37486200 |
| C | 3.34600500 | -1.90993400 | -0.49677100 |
| C | 4.06820300 | -3.03740100 | -0.09284200 |
| C | 3.90359600 | -3.60960400 | 1.17050600 |
| C | 2.96560300 | -3.03085700 | 2.02693700 |
| C | 2.20363400 | -1.91889500 | 1.65235600 |
| C | 2.20366000 | 1.91885600 | -1.65237100 |
| C | 2.96566200 | 3.03079200 | -2.02694600 |
| C | 3.90366100 | 3.60951900 | -1.17049800 |
| C | 4.06823300 | 3.03731900 | 0.09284700 |
| C | 3.34601100 | 1.90985600 | 0.49676900 |
| C | 3.58447600 | -1.38018100 | -1.89552500 |
| C | 1.18355200 | -1.40454800 | 2.64942500 |
| C | 4.73235800 | -4.79424500 | 1.60537300 |
| C | 4.73244100 | 4.79415500 | -1.60535100 |
| C | 3.58447800 | 1.38010300 | 1.89552200 |

| | | | |
|---|---|---|---|
| C | 1.18355500 | 1.40454600 | -2.64943900 |
| C | -3.96669300 | -3.96699400 | -0.82364300 |
| C | -3.96657100 | 3.96708500 | 0.82364900 |
| C | -3.46716900 | -5.39521700 | -1.11288100 |
| C | -4.84451500 | -4.01519400 | 0.44942900 |
| C | -4.83148900 | -3.50917400 | -2.02204500 |
| C | -3.46703000 | 5.39529600 | 1.11292900 |
| C | -4.84431800 | 4.01530900 | -0.44947400 |
| C | -4.83144900 | 3.50928800 | 2.02199400 |
| H | -4.11947200 | 1.28210300 | 0.27852200 |
| H | 0.61704500 | 2.79166500 | 0.58715900 |
| H | -1.19671200 | 4.37464900 | 0.92027300 |
| H | -4.11951400 | -1.28202600 | -0.27835800 |
| H | -1.19686400 | -4.37463000 | -0.92031900 |
| H | 0.61694700 | -2.79170000 | -0.58725900 |
| H | 4.78385600 | -3.47744200 | -0.78425700 |
| H | 2.81633000 | -3.45938800 | 3.01605900 |
| H | 2.81642400 | 3.45932300 | -3.01607200 |
| H | 4.78387400 | 3.47735200 | 0.78428000 |
| H | 2.68097100 | -1.44846300 | -2.51265400 |
| H | 3.89024800 | -0.33067900 | -1.88829000 |

| | | | |
|---|---|---|---|
| H | 4.36462100 | -1.95610500 | -2.40072600 |
| H | 1.42818400 | -1.74389100 | 3.66000600 |
| H | 1.12050300 | -0.31400600 | 2.67089500 |
| H | 0.18032900 | -1.77639000 | 2.41191600 |
| H | 5.01180200 | -5.42194800 | 0.75380500 |
| H | 5.66294000 | -4.47027600 | 2.08846800 |
| H | 4.19383200 | -5.41744000 | 2.32574600 |
| H | 4.19412100 | 5.41708200 | -2.32610800 |
| H | 5.01144800 | 5.42213000 | -0.75383700 |
| H | 5.66326700 | 4.47017700 | -2.08796500 |
| H | 4.36457300 | 1.95607300 | 2.40074600 |
| H | 2.68095500 | 1.44831600 | 2.51263400 |
| H | 3.89032000 | 0.33062100 | 1.88828700 |
| H | 1.12047300 | 0.31400600 | -2.67092100 |
| H | 0.18034600 | 1.77641700 | -2.41191600 |
| H | 1.42819000 | 1.74389600 | -3.66001600 |
| H | -4.32345500 | -6.06399400 | -1.24800600 |
| H | -2.86647300 | -5.44073200 | -2.02711500 |
| H | -2.86597400 | -5.79182100 | -0.28828400 |
| H | -5.67865000 | -4.71290000 | 0.31269000 |
| H | -5.26676000 | -3.03505400 | 0.68982700 |

| | | | |
|---|---|---|---|
| H | -4.26126700 | -4.34764200 | 1.31431100 |
| H | -4.23778700 | -3.47143600 | -2.94113500 |
| H | -5.66248900 | -4.20562900 | -2.18163400 |
| H | -5.25743000 | -2.51464600 | -1.86003000 |
| H | -4.32330700 | 6.06409100 | 1.24801800 |
| H | -2.86638000 | 5.44078400 | 2.02719400 |
| H | -2.86578500 | 5.79190000 | 0.28836900 |
| H | -5.67844200 | 4.71303700 | -0.31278600 |
| H | -5.26657000 | 3.03517400 | -0.68988800 |
| H | -4.26100900 | 4.34773500 | -1.31432300 |
| H | -4.23781000 | 3.47155200 | 2.94112500 |
| H | -5.66245000 | 4.20575600 | 2.18152000 |
| H | -5.25740100 | 2.51476600 | 1.85996800 |

Anionic radical **1**$^{\bullet-}$

| | | | |
|---|---|---|---|
| C | -2.74057900 | 2.89172100 | 0.97375100 |
| C | -3.05392500 | 1.59779500 | 0.53748400 |
| C | -2.04258100 | 0.68719900 | 0.22316200 |
| C | -0.67345100 | 1.05997800 | 0.34098400 |
| C | -0.34383600 | 2.34661700 | 0.78450600 |
| C | -1.37444600 | 3.23338300 | 1.08810600 |
| C | -2.04227000 | -0.68769100 | -0.22316800 |

| | | | |
|---|---|---|---|
| C | -0.67297300 | -1.05994700 | -0.34069000 |
| N | 0.16319200 | 0.00017600 | 0.00022900 |
| C | -3.05319600 | -1.59867900 | -0.53769900 |
| C | -2.73925800 | -2.89249300 | -0.97387700 |
| C | -1.37296900 | -3.23363500 | -1.08792400 |
| C | -0.34276600 | -2.34646700 | -0.78411500 |
| B | 1.68760500 | 0.00045000 | 0.00039500 |
| C | 2.40223600 | 1.22075600 | -0.68309600 |
| C | 2.40250800 | -1.21987600 | 0.68356300 |
| C | 3.54785200 | -1.85137700 | 0.09372100 |
| C | 4.16162600 | -2.95010000 | 0.70312000 |
| C | 3.70198100 | -3.49445000 | 1.90534600 |
| C | 2.59383100 | -2.87865400 | 2.49901000 |
| C | 1.95257500 | -1.77919500 | 1.92695800 |
| C | 1.95236700 | 1.77939200 | -1.92682100 |
| C | 2.59334800 | 2.87883900 | -2.49920600 |
| C | 3.70115600 | 3.49527800 | -1.90557800 |
| C | 4.16075500 | 2.95159100 | -0.70303300 |
| C | 3.54725500 | 1.85290400 | -0.09329400 |
| C | 4.11339500 | -1.38685600 | -1.23169500 |
| C | 0.81134000 | -1.16136000 | 2.70692900 |

| | | | |
|---|---|---|---|
| C | 4.35302800 | -4.70769000 | 2.52534200 |
| C | 4.35188900 | 4.70850000 | -2.52593800 |
| C | 4.11270400 | 1.38918400 | 1.23244300 |
| C | 0.81153100 | 1.16080600 | -2.70678100 |
| C | -3.87362500 | -3.88125700 | -1.30847000 |
| C | -3.87539900 | 3.88004000 | 1.30812700 |
| C | -3.34495900 | -5.25275900 | -1.77080700 |
| C | -4.75341900 | -4.11048800 | -0.05645400 |
| C | -4.75221800 | -3.30526400 | -2.44466000 |
| C | -3.34735700 | 5.25172200 | 1.77064500 |
| C | -4.75499400 | 4.10899200 | 0.05592100 |
| C | -4.75403200 | 3.30366300 | 2.44409100 |
| H | -4.09229500 | 1.28734600 | 0.44386200 |
| H | 0.69281600 | 2.64763000 | 0.87573800 |
| H | -1.09631500 | 4.22621300 | 1.42445900 |
| H | -4.09170500 | -1.28863000 | -0.44430100 |
| H | -1.09438300 | -4.22636500 | -1.42419500 |
| H | 0.69402300 | -2.64708200 | -0.87511200 |
| H | 5.02165500 | -3.40675700 | 0.21245600 |
| H | 2.22995200 | -3.25755800 | 3.45469800 |
| H | 2.22953000 | 3.25721100 | -3.45512700 |

| | | | |
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| H | 5.02052200 | 3.40875900 | -0.21238600 |
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| H | 4.61365500 | -0.41481000 | -1.15959000 |
| H | 4.83976000 | -2.11101000 | -1.61863000 |
| H | 0.80473600 | -1.52991600 | 3.73894800 |
| H | 0.89291700 | -0.06888500 | 2.73288000 |
| H | -0.16678000 | -1.38893900 | 2.26923300 |
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| H | 4.36144700 | -4.64593000 | 3.62045200 |
| H | 3.82851500 | -5.63933200 | 2.26617000 |
| H | 4.36025000 | 4.64644500 | -3.62103000 |
| H | 3.82718300 | 5.64009400 | -2.26698000 |
| H | 5.38907500 | 4.82264300 | -2.19102200 |
| H | 4.83874300 | 2.11377200 | 1.61917800 |
| H | 3.31856300 | 1.26012200 | 1.97638900 |
| H | 4.61331800 | 0.41728200 | 1.16088400 |
| H | 0.89350600 | 0.06835000 | -2.73223000 |
| H | -0.16677100 | 1.38822900 | -2.26940900 |
| H | 0.80503100 | 1.52890500 | -3.73896300 |
| H | -4.18562800 | -5.91884200 | -1.99701000 |
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| | | | |
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| H | -5.57429300 | -4.80528000 | -0.27693200 |
| H | -5.19354900 | -3.17560800 | 0.30266700 |
| H | -4.15989900 | -4.53148300 | 0.76180200 |
| H | -4.15779600 | -3.14622300 | -3.35047600 |
| H | -5.57316400 | -3.99149600 | -2.68970600 |
| H | -5.19173900 | -2.34322600 | -2.16542300 |
| H | -4.18833000 | 5.91747900 | 1.99668300 |
| H | -2.73796800 | 5.16683900 | 2.67628600 |
| H | -2.73988500 | 5.73351300 | 0.99776300 |
| H | -5.57618100 | 4.80346400 | 0.27624300 |
| H | -5.19468900 | 3.17396200 | -0.30334100 |
| H | -4.16144800 | 4.53024800 | -0.76218200 |
| H | -4.15975700 | 3.14481400 | 3.35003800 |
| H | -5.57529800 | 3.98956900 | 2.68897500 |
| H | -5.19311700 | 2.34146600 | 2.16471400 |