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Supporting Information

Diolefins with an Ether/Thioether Functionality as Ligands in the Coordination Sphere of Ni and Rh.

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[Rh(trop$_2$S)(NCMe)$_2$][OTf] (6).

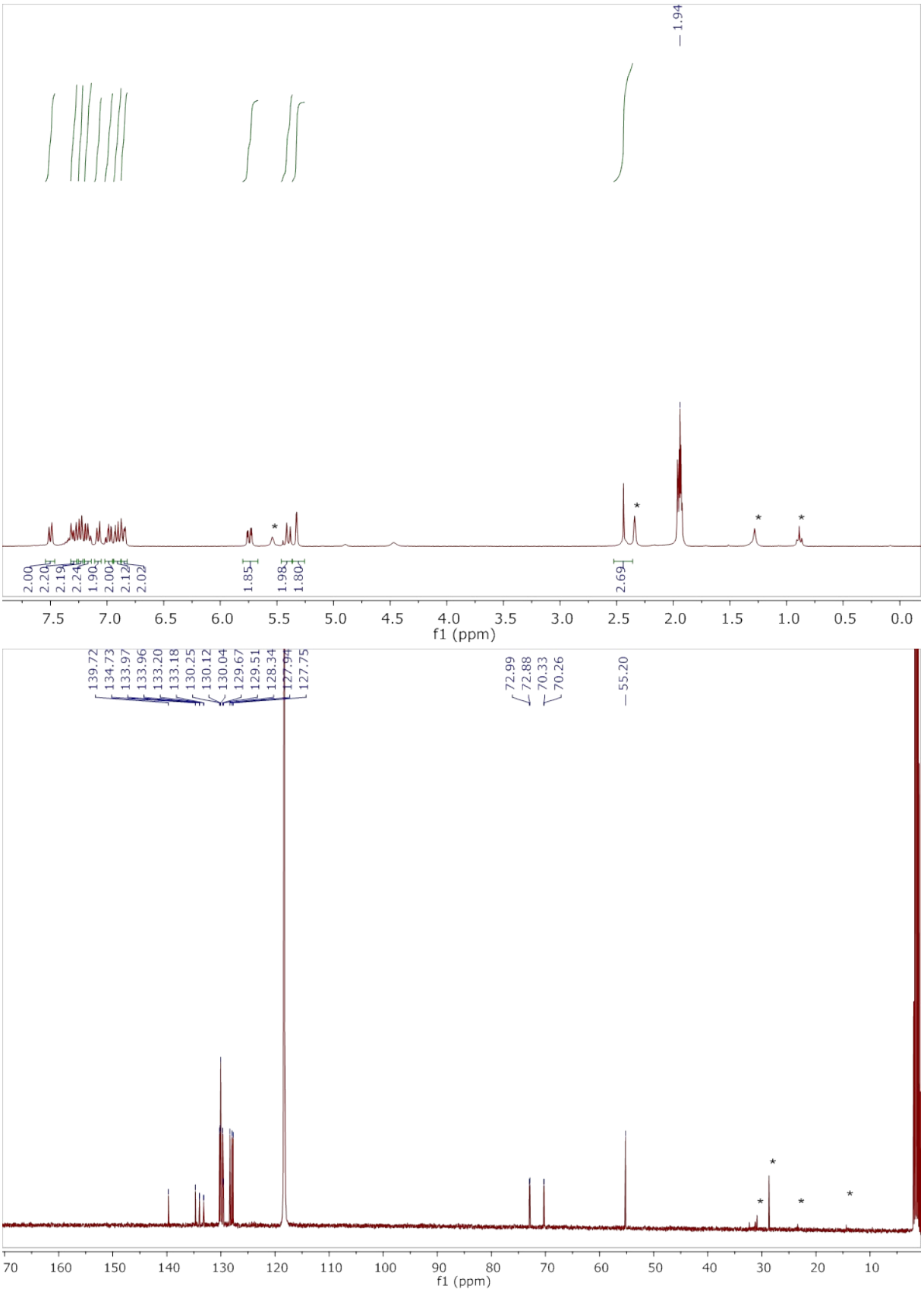

Figure S1. ^{1}H NMR (top) and ^{13}C NMR spectrum (bottom) of **6**; asterix denotes resonances ascribed to residual 1,5-cod and hexanes.

[Rh(trop$_2$S)(bipy)][OTf] (7).

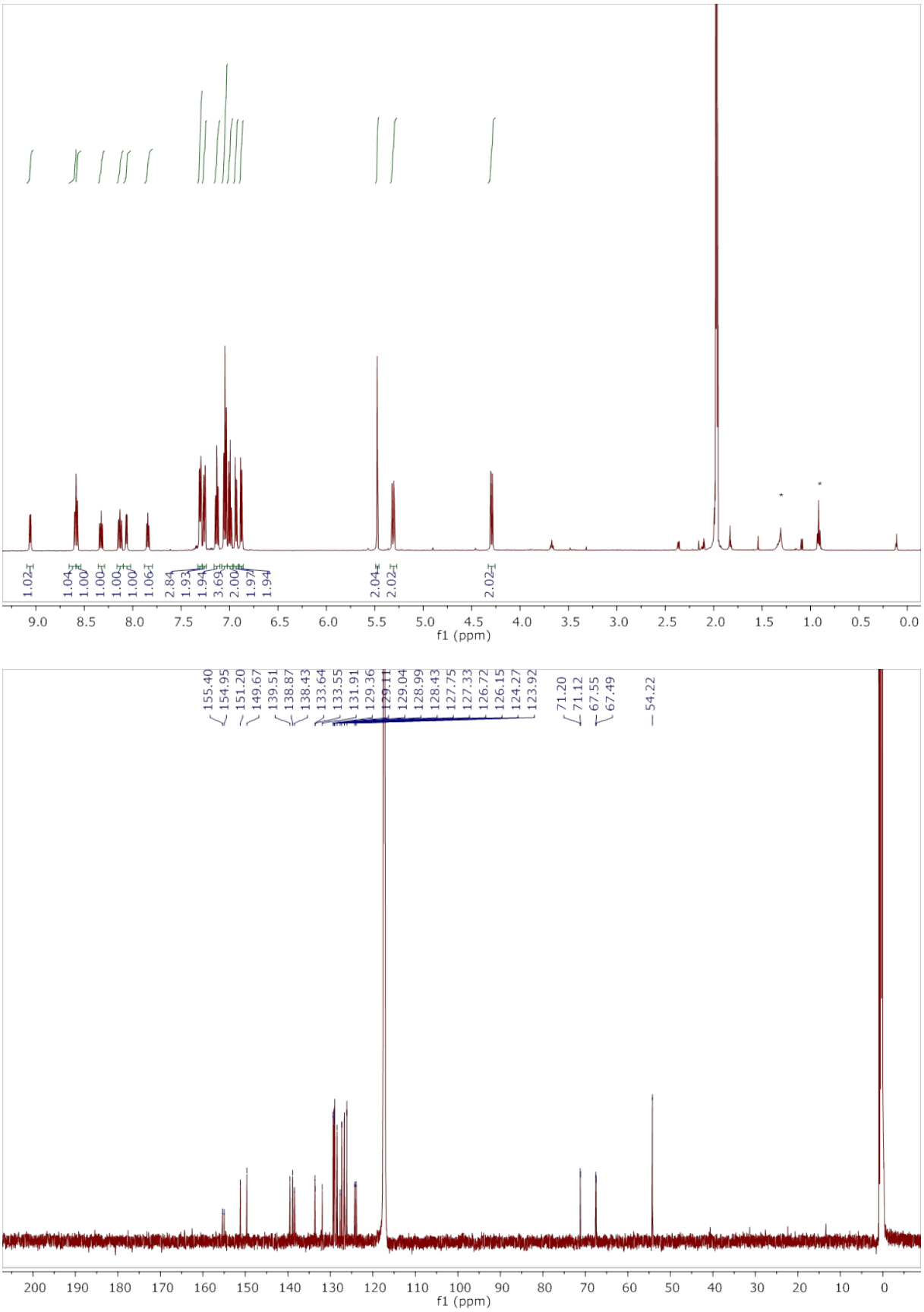

Figure S2. ^{1}H NMR (top) and ^{13}C NMR spectrum (bottom) of **7**; asterix denotes resonances ascribed to residual hexanes.

[Rh(trop$_2$S)(NCMe)$_2$][OTf] (6) and [Rh(trop$_2$S)(bipy)][OTf] (7).

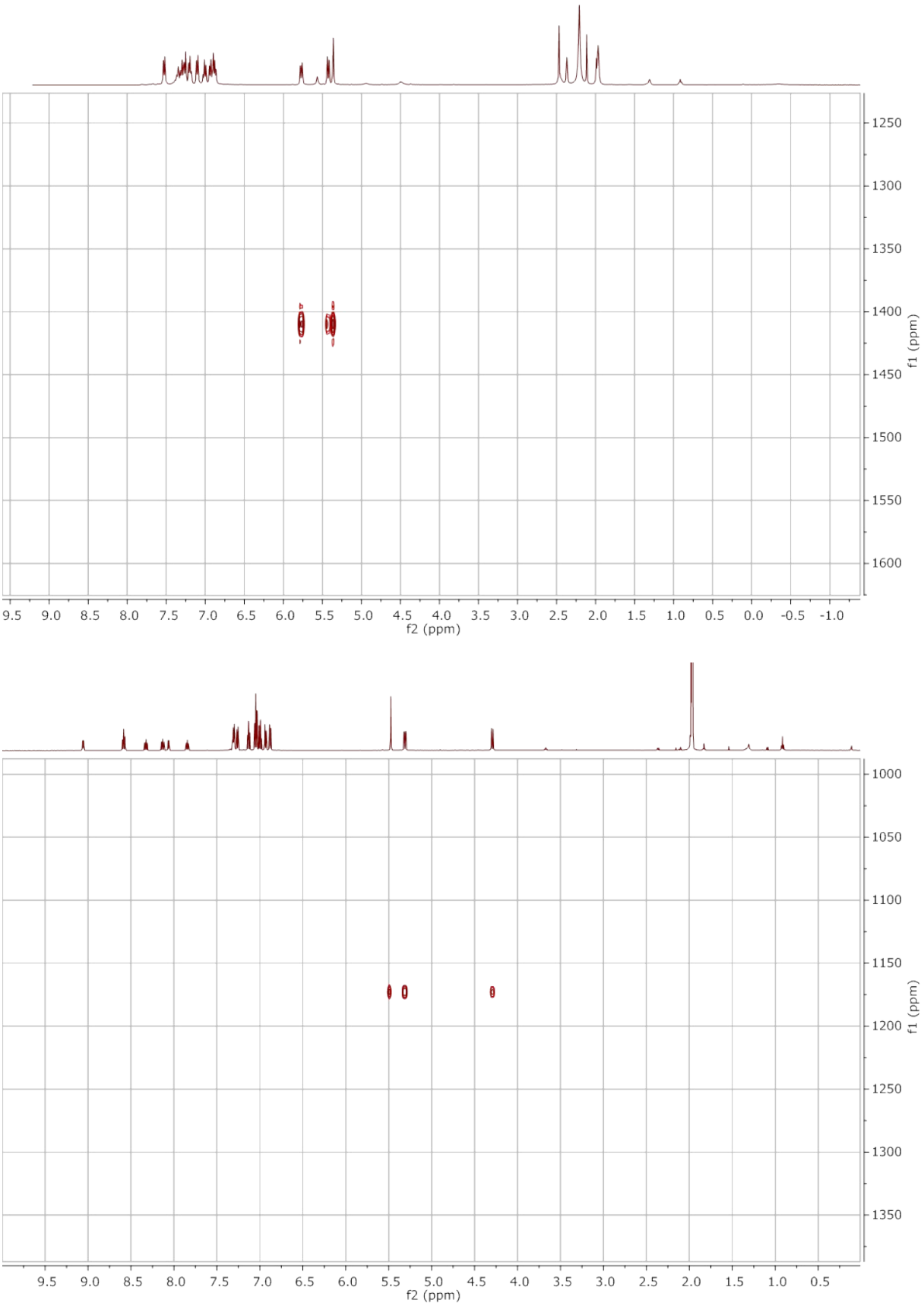

Figure S3. $^{1}H^{103}Rh$ correlated NMR spectra of **6** (top) and **7** (bottom).

Cyclic Voltammogram of 5

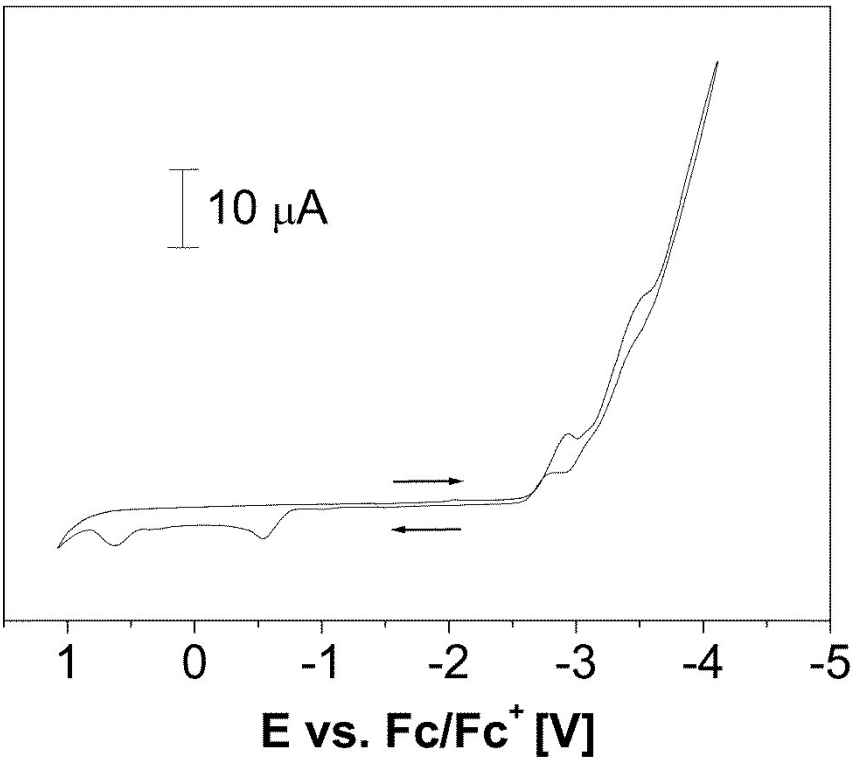

Figure S4. Cyclic voltammogram of **5** at 23 °C in THF / 0.1 M $[(n\text{Bu})_4\text{N}][PF_6]$ with a scan rate of 50 mV/s referenced vs. ferrocene/ferrocenium (Fc/Fc^+).

Cyclic Voltammograms of 7

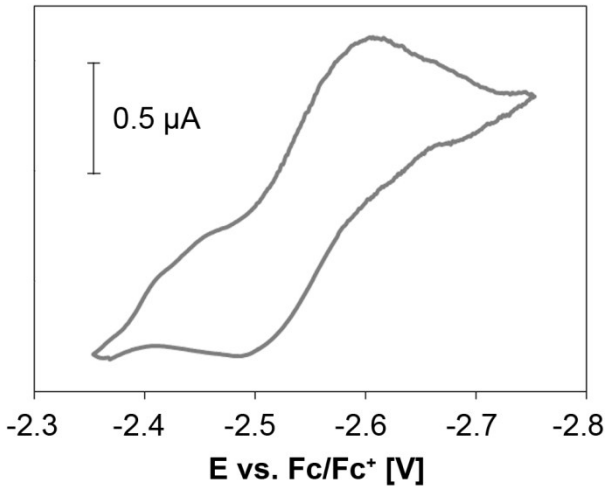

Figure S5. Cyclic voltammogram of **7** at 23 °C in THF / 0.1 M $[(n\text{Bu})_4\text{N}][PF_6]$ with a scan rate of 25 mV/s referenced vs. ferrocene/ferrocenium (Fc/Fc^+); $E_1/E_1' = -2.55$ V.

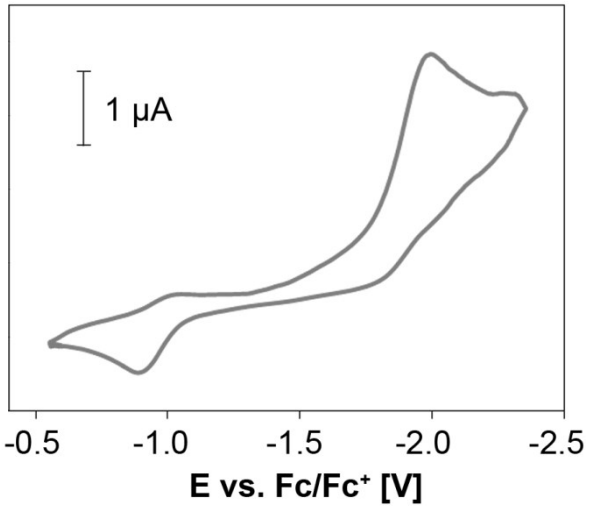

Figure S6. Cyclic voltammogram of **7** at 23 °C in THF / 0.1 M $[(n\text{Bu})_4\text{N}][PF_6]$ with a scan rate of 100 mV/s referenced vs. ferrocene/ferrocenium (Fc/Fc^+); $E^{red} = -1.99$ V, $E^{ox} = -0.89$ V.

Solvent-Corrected Free Energies (*G°*, Hartree), Solvent-Corrected Enthalpies (*H°*, Hartree), and Cartesian Coordinates (Å) of Optimized Structures

***Endo*/*endo*-2**

$G° = -1231.342084$

$H° = -1231.264902$

C	-2.57884900	-0.72304600	-1.61999800
C	-1.97556800	-1.29257100	-0.47229800
C	-1.12622700	-0.46886600	0.47132500
C	-1.87069100	0.67450100	1.13942200
C	-2.43320800	1.73758400	0.38999200
C	-2.53204900	1.75363700	-1.06723800
C	-2.59657900	0.70673100	-1.92004600
C	-1.93046500	0.71958900	2.53867300
C	-2.50459200	1.79729200	3.21176900
C	-3.01679000	2.87031000	2.47838000
C	-2.97367200	2.83697700	1.08893100
C	-3.23220900	-1.58301500	-2.52748900
C	-3.33974900	-2.94864700	-2.29113700
C	-2.77688900	-3.49694400	-1.13578800
C	-2.09451600	-2.66918600	-0.24630900
O	0.00004200	-0.00032100	-0.29485400
C	2.57832400	0.72376800	-1.62028200
C	1.97515400	1.29264700	-0.47219100
C	1.12631600	0.46829200	0.47131200
C	1.87120300	-0.67513900	1.13879900
C	2.43386100	-1.73774900	0.38882600
C	2.53251100	-1.75314900	-1.06841400
C	2.59665800	-0.70587500	-1.92081100
C	1.93124100	-0.72080100	2.53802900
C	2.50578700	-1.79862600	3.21056000
C	3.01816300	-2.87119300	2.47662400
C	2.97478200	-2.83728800	1.08720500
C	3.23103100	1.58434800	-2.52767500
C	3.33805600	2.94994200	-2.29088200
C	2.77534500	3.49759100	-1.13515400
C	2.09359600	2.66922600	-0.24575400
H	-0.76903900	-1.13738000	1.26387800
H	-2.67349500	2.74222700	-1.50029500
H	-2.78440500	0.94475700	-2.96553000
H	-1.50394300	-0.10271800	3.10783000
H	-2.53237300	1.80915400	4.29751200
H	-3.45074000	3.72640900	2.98698000
H	-3.38847000	3.66339200	0.51747700
H	-3.67843500	-1.15377100	-3.42083600
H	-3.85961600	-3.58326500	-3.00317800
H	-2.84949600	-4.56284000	-0.94031400
H	-1.62302700	-3.09842400	0.63387600
H	0.76906800	1.13639800	1.26416900
H	2.67431000	-2.74149900	-1.50190300
H	2.78459600	-0.94344600	-2.96637800
H	1.50459600	0.10114600	3.10761500
H	2.53372800	-1.81096200	4.29629400
H	3.45247200	-3.72736800	2.98479000
H	3.38972500	-3.66333200	0.51532000
H	3.67717500	1.15560800	-3.42130500
H	3.85740900	3.58503100	-3.00287700
H	2.84755500	4.56344600	-0.93931700
H	1.62222200	3.09795600	0.63474100

***Endo*/*exo*-2**

$G° = -1231.344089$

$H° = -1231.267262$

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C	-1.75325500	1.42812300	0.24222600
C	-1.06984200	0.08182800	0.02084300
C	-1.86150300	-0.78085700	-0.94766300
C	-3.11050700	-1.29515000	-0.52859000
C	-3.74784600	-0.92306100	0.73673700
C	-3.68289400	0.26366700	1.38680800
C	-1.35702600	-1.12104300	-2.20612900
C	-2.05960300	-1.98587200	-3.04488500
C	-3.27355100	-2.53541000	-2.62312700
C	-3.78460000	-2.19782700	-1.37470600
C	-3.52120300	2.72592500	1.28181800
C	-2.94178100	3.90478300	0.82397500
C	-1.77794700	3.84926400	0.05183900
C	-1.18851600	2.61681700	-0.22952200
O	0.26117800	0.23252400	-0.45689600
C	3.19965600	0.31318200	-1.09803900
C	2.48546600	0.98790900	-0.07797000
C	1.26281100	0.38291900	0.57579000
C	1.52001900	-0.92644400	1.29813000
C	1.98532100	-2.07814200	0.61652400
C	2.43747000	-2.08573100	-0.77201200
C	2.95533900	-1.07019200	-1.49957900
C	1.20918300	-1.01678700	2.66121000
C	1.32127500	-2.21946200	3.35720200
C	1.73351100	-3.36883900	2.67881100
C	2.05363600	-3.29399200	1.32774600
C	4.23893600	1.00484100	-1.75494000
C	4.60503800	2.29419200	-1.38672400
C	3.92449900	2.93714700	-0.34966800
C	2.86916100	2.28507000	0.28533900
H	-1.06333300	-0.44719000	0.98577400
H	-4.44108300	-1.66174800	1.13572500
H	-4.32845800	0.38336100	2.25541100
H	-0.39303200	-0.72808400	-2.50661500
H	-1.64983800	-2.24725400	-4.01650900
H	-3.81647400	-3.22420100	-3.26409500
H	-4.73193000	-2.61646000	-1.04476300
H	-4.43722400	2.76321200	1.86598500
H	-3.39702300	4.86168300	1.06286100
H	-1.32118300	4.76367900	-0.31612300
H	-0.26907700	2.56493100	-0.80213800
H	0.89462500	1.10276800	1.31636700
H	2.44623800	-3.06908300	-1.23849200
H	3.33602900	-1.32667600	-2.48668200
H	0.85601000	-0.12788200	3.17799000
H	1.06691800	-2.26378600	4.41211100
H	1.80713000	-4.31814300	3.20154900
H	2.38871000	-4.18489000	0.80296600
H	4.77646500	0.49952200	-2.55307600
H	5.41821700	2.79565900	-1.90356300
H	4.19932500	3.94491800	-0.05249500
H	2.31586300	2.79569900	1.06909900

***Exo*/*exo*-2**

$G^\circ = -1231.344461$

$H^\circ = -1231.268256$

C	3.51203500	0.96558800	0.10617100
C	2.33021000	0.59495800	0.78930400
C	1.19752400	-0.01539300	-0.01585600
C	1.56478300	-1.41644600	-0.49270300
C	2.53370500	-1.54939400	-1.51437300
C	3.32585100	-0.42077000	-2.00688900
C	3.74911200	0.65917200	-1.30671300
C	0.94087600	-2.55556600	0.02374900
C	1.22755700	-3.82022000	-0.48981400
C	2.13990100	-3.95613600	-1.53992200
C	2.78013900	-2.83004700	-2.04690000
C	4.51751700	1.64449600	0.82230900
C	4.38881900	1.89740800	2.18376700
C	3.23629200	1.48522100	2.85805400
C	2.21295200	0.84393700	2.16017900
O	0.00000000	0.00000000	0.75760000
C	-3.51203500	-0.96558800	0.10617100
C	-2.33021000	-0.59495700	0.78930500
C	-1.19752400	0.01539400	-0.01585500
C	-1.56478300	1.41644600	-0.49270300
C	-2.53370500	1.54939400	-1.51437300
C	-3.32585100	0.42076900	-2.00688900
C	-3.74911200	-0.65917200	-1.30671200
C	-0.94087600	2.55556700	0.02374900
C	-1.22755800	3.82022100	-0.48981400
C	-2.13990200	3.95613600	-1.53992100
C	-2.78014000	2.83004700	-2.04689900
C	-4.51751600	-1.64449700	0.82230900
C	-4.38881800	-1.89740900	2.18376800
C	-3.23629200	-1.48522200	2.85805400
C	-2.21295100	-0.84393700	2.16018000
H	1.06370000	0.61326400	-0.90850300
H	3.70956300	-0.52998500	-3.01976500
H	4.43929300	1.33170400	-1.81338200
H	0.20820000	-2.44052300	0.81491200
H	0.72602800	-4.69413200	-0.08398900
H	2.35339500	-4.93585500	-1.95756200
H	3.50544200	-2.93326800	-2.85002000
H	5.41619900	1.95484100	0.29551500
H	5.18201600	2.41286100	2.71750400
H	3.12540400	1.67994600	3.92094200
H	1.30215500	0.55578800	2.67174100
H	-1.06370000	-0.61326400	-0.90850200
H	-3.70956300	0.52998500	-3.01976500
H	-4.43929300	-1.33170400	-1.81338200
H	-0.20820000	2.44052300	0.81491200
H	-0.72602900	4.69413300	-0.08398900
H	-2.35339700	4.93585500	-1.95756100
H	-3.50544300	2.93326800	-2.85002000
H	-5.41619900	-1.95484100	0.29551500
H	-5.18201500	-2.41286200	2.71750400
H	-3.12540300	-1.67994600	3.92094200
H	-1.30215400	-0.55578800	2.67174200

***Endo*/*endo*-3**

$G^\circ = -1554.327239$

$H^\circ = -1554.248637$

C	3.30018200	0.48962300	-1.42947200
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C	1.42587900	0.25610300	0.31291700
C	1.87454100	-1.02410100	0.98193000
C	2.50455200	-2.08202200	0.27940000
C	2.91950200	-2.00372600	-1.11859300
C	3.25481000	-0.91245400	-1.84335700
C	1.60177800	-1.18661900	2.34871600
C	1.90169100	-2.37115500	3.02143300
C	2.48140700	-3.43137400	2.32134700
C	2.77258000	-3.28196700	0.96908300
C	4.20427300	1.33452100	-2.10770300
C	4.36722700	2.66771900	-1.75020700
C	3.61124000	3.19721400	-0.70069200
C	2.69159900	2.38677900	-0.03880200
C	-3.30007600	-0.49046400	-1.42938000
C	-2.51190000	-1.04099400	-0.38968600
C	-1.42590500	-0.25556600	0.31298000
C	-1.87487700	1.02476200	0.98150800
C	-2.50527000	2.08220800	0.27861600
C	-2.92055600	2.00318600	-1.11922100
C	-3.25549400	0.91151800	-1.84358000
C	-1.60191900	1.18793800	2.34817300
C	-1.90198800	2.37270100	3.02041600
C	-2.48203800	3.43249300	2.31995000
C	-2.77342500	3.28241700	0.96781400
C	-4.20362100	-1.33603800	-2.10751800
C	-4.36590500	-2.66922000	-1.74967900
C	-3.60980800	-3.19800400	-0.69987300
C	-2.69069100	-2.38690500	-0.03808500
H	1.00874200	0.90625000	1.08478000
H	3.05839400	-2.96820500	-1.60387300
H	3.63399800	-1.09632900	-2.84703800
H	1.13789300	-0.36613900	2.88986800
H	1.67160200	-2.46823400	4.07862700
H	2.70834000	-4.36583000	2.82660200
H	3.23859000	-4.09962000	0.42488500
H	4.79619000	0.91669100	-2.91804300
H	5.07772600	3.29125100	-2.28535600
H	3.72354900	4.23825900	-0.41167700
H	2.08071200	2.80740100	0.75578100
H	-1.00856800	-0.90528800	1.08508600
H	-3.06016500	2.96742800	-1.60476500
H	-3.63508500	1.09495900	-2.84718800
H	-1.13776400	0.36780400	2.88961700
H	-1.67174300	2.47030700	4.07752800
H	-2.70905700	4.36713000	2.82483200
H	-3.23972700	4.09971400	0.42333600
H	-4.79564000	-0.91872800	-2.91805300
H	-5.07596200	-3.29331000	-2.28476600
H	-3.72162900	-4.23902200	-0.41057000
H	-2.07968200	-2.80698400	0.75669300
S	-0.00003200	0.00024600	-0.88980000

***Endo*/*exo*-3**

$G^{\circ} = -1554.323018$

$H^{\circ} = -1554.244998$

C	-2.65428400	1.38083200	1.33671700
C	-1.71619400	1.39380000	0.27364800
C	-1.29743100	0.04201300	-0.29669400
C	-2.42143600	-0.54962700	-1.13414100
C	-3.54769200	-1.05623200	-0.43972800
C	-3.73906500	-0.88184400	1.00171000
C	-3.35383900	0.16819000	1.76766500
C	-2.38068300	-0.64246500	-2.53019900
C	-3.40282000	-1.27278800	-3.23939200
C	-4.48561900	-1.83123700	-2.55469100
C	-4.55106200	-1.72407400	-1.16979900
C	-2.96513800	2.59449000	1.98270800
C	-2.42638000	3.80117700	1.54936200
C	-1.55115800	3.81379800	0.45943700
C	-1.19671400	2.61706800	-0.16379200
C	3.69681400	-0.04901500	-1.03689800
C	2.81627600	0.76496100	-0.28404800
C	1.49616900	0.25886300	0.25502400
C	1.57563800	-0.94567800	1.16579600
C	2.15028600	-2.17800100	0.76517600
C	2.85165900	-2.38365000	-0.49914800
C	3.50436900	-1.48059100	-1.26519100
C	0.99795500	-0.84850300	2.44070900
C	0.95075000	-1.93965400	3.30816300
C	1.47846500	-3.16658200	2.90029400
C	2.06560400	-3.27689700	1.64404100
C	4.85099400	0.54430100	-1.59109600
C	5.15909900	1.88272700	-1.37802000
C	4.30296500	2.67313700	-0.60618300
C	3.14318600	2.11291700	-0.07535100
H	-1.16404300	-0.63271400	0.55647900
H	-4.36588500	-1.63334300	1.47889600
H	-3.70250800	0.17739700	2.79916300
H	-1.53416900	-0.23463600	-3.07447200
H	-3.34275700	-1.34335800	-4.32166500
H	-5.27536900	-2.34118000	-3.09896200
H	-5.40053100	-2.13868700	-0.63284200
H	-3.66298400	2.57923400	2.81624700
H	-2.68821100	4.72670300	2.05436000
H	-1.12917900	4.75069400	0.10660100
H	-0.48565300	2.62361900	-0.98357500
H	1.04625900	1.07542100	0.82227600
H	2.92643500	-3.42446200	-0.80917500
H	4.04677700	-1.87556300	-2.12234900
H	0.56787100	0.10009400	2.75130700
H	0.48994900	-1.83553800	4.28624400
H	1.43547500	-4.03009300	3.55792100
H	2.48857700	-4.22698100	1.32776500
H	5.51932100	-0.07559600	-2.18325700
H	6.06052200	2.30846500	-1.80960900
H	4.52865700	3.72123000	-0.43186700
H	2.46291300	2.73361200	0.50202900
S	0.31713900	0.00419200	-1.19424900

***Exo*/*exo*-3**

$G^{\circ} = -1554.318146$

$H^{\circ} = -1554.240399$

C	3.77843200	0.22187400	-0.76758900
C	2.73216300	1.02802100	-0.25478200
C	1.41033100	0.33708300	0.04227400
C	1.52658300	-0.52120100	1.29692100
C	2.26074400	-1.72817600	1.17793300
C	3.03159000	-2.07713800	-0.01809100
C	3.68589900	-1.23720200	-0.85722200
C	0.91978000	-0.20689000	2.51760500
C	0.99254300	-1.08096600	3.60244400
C	1.66701800	-2.29844800	3.47473000
C	2.29029500	-2.61504700	2.27246600
C	4.97635100	0.84324800	-1.17250700
C	5.16882200	2.21146200	-1.01444000
C	4.15590400	2.99063900	-0.44876900
C	2.94830200	2.39960500	-0.07772800
C	-3.77838200	0.22192700	0.76761300
C	-2.73212300	1.02805500	0.25475300
C	-1.41030800	0.33709700	-0.04232000
C	-1.52661500	-0.52122500	-1.29693700
C	-2.26076700	-1.72820000	-1.17788600
C	-3.03157600	-2.07711800	0.01817500
C	-3.68585000	-1.23714700	0.85729800
C	-0.91987900	-0.20693500	-2.51765700
C	-0.99266900	-1.08104600	-3.60246700
C	-1.66711500	-2.29853500	-3.47468600
C	-2.29034000	-2.61510900	-2.27238600
C	-4.97628800	0.84331300	1.17254800
C	-5.16875900	2.21152300	1.01444600
C	-4.15585400	2.99068200	0.44872800
C	-2.94826400	2.39963600	0.07766500
H	1.22733700	-0.34936100	-0.79112000
H	3.18630800	-3.14362300	-0.17350300
H	4.31407600	-1.69551900	-1.61931700
H	0.36338600	0.72060000	2.60852100
H	0.50408700	-0.82052200	4.53719300
H	1.70886100	-2.99350000	4.30857500
H	2.83196100	-3.55220400	2.17199300
H	5.76819400	0.22879300	-1.59342800
H	6.10432600	2.66848400	-1.32412000
H	4.29653200	4.05915600	-0.31343600
H	2.16213300	3.02187100	0.33956200
H	-1.22729400	-0.34932700	0.79108400
H	-3.18629700	-3.14359800	0.17362500
H	-4.31400100	-1.69543200	1.61943500
H	-0.36351200	0.72056700	-2.60861500
H	-0.50427100	-0.82061400	-4.53724800
H	-1.70897800	-2.99361300	-4.30850800
H	-2.83199300	-3.55227000	-2.17186500
H	-5.76812400	0.22886800	1.59349800
H	-6.10425400	2.66855600	1.32413900
H	-4.29648400	4.05919700	0.31337900
H	-2.16210400	3.02188800	-0.33966300
S	0.00001900	1.53180600	-0.00006000

Full Gaussian 09 Reference:

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