Chiral bidentate [*N*,*S*]-ferrocene ligands based on thiazoline framework. Synthesis and use in palladium-catalyzed asymmetric allylic alkylation.

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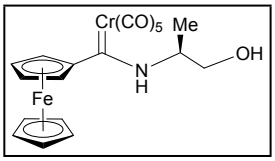
General considerations

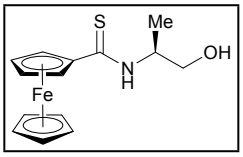
All operations were carried out under an inert atmosphere of nitrogen or argon gas using standard Schlenk techniques. Column chromatography was performed using 70–230 mesh silica gel. All reagents and solvents were obtained from commercial suppliers and used without further purification. All compounds were characterized by IR spectra, recorded on a Bruker Tensor 27 spectrophotometer, by means of film and KBr techniques, and all data are expressed in wave numbers (cm^{-1}). Optical rotation was measured with a Perkin-Elmer 241 polarimeter. Melting points were obtained on a Melt-Temp II apparatus and are uncorrected. NMR spectra were measured with a Bruker Avance III at 300 MHz for ^1H and 75 MHz for ^{13}C using $CDCl_3$ as a solvent. Chemical shifts are in ppm (δ), relative to TMS. The MS-FAB spectra were obtained on a JMS-SX102A using nitrobenzyl alcohol and polyethylene glycol matrices. MS-DART spectra were obtained on a AccuTOF JMS-T100LC; the values of the signals are expressed in mass/charge units (m/z).

Experimental details

[(Ferrocenyl)(*S*)-3-(hydroxypropan-2-amine)]-methylidene pentacarbonyl chromium (2)



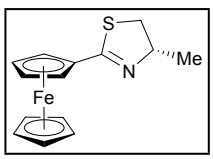
Red oil, 78%; $[\alpha]^{20}_D$ = –51.85 (c = 0.081 in $CHCl_3$); ^1H NMR ($CDCl_3$, ppm): δ 1.57 (d, 3H, $-CH_3$), 2.65 (br, s, 1H, -OH), 3.97 (d, *J* = 18.3 Hz, 2H, $-CH_2$), 4.23 (s, 5H, CHCp), 4.45 (d, *J* = 11 Hz, 2H, $CHCp_{subst}$), 4.47 (d, 2H, $CHCp_{subst}$), 4.73 (br, s, 1H, -CHN-), 9.87 (br, s, 1H, -NH-); ^{13}C NMR ($CDCl_3$, ppm): δ 17.9 ($-CH_3$), 59.1 ($-CH_2$-), 65.5 (-CHNH-), 68.7-68.8 ($CHCp_{subst}$), 69.7 (Cp), 70.2-70.3 ($CHCp_{subst}$), 98.9 (C_{ipso}, Fc), 223.7, 218.0 (CO), 267.2 ($C{=}Cr(CO)_5$); MS (FAB+): *m/z* (100%) 463; IR (KBr, cm^{-1}), 1887 (C=O); HRMS (FAB+): calcd for $C_{19}H_{17}NO_6CrFe$ [M+] 462.9810; found 462.9804.



(*S*)-*N*-(1-hydroxypropan-2-yl)ferrocenylthioamide (3).

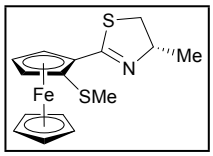
Orange solid, 91%; mp 140-141°C; $[\alpha]^{20}_D$ = –102 (*c* = 0.1 in $CHCl_3$); ^1H NMR ($CDCl_3$, ppm): δ 1.35 (d, *J* = 6.7 Hz, 3H, $-CH_3$), 2.53 (br,s, 1H, -OH), 3.72 (dd, *J* = 10.8, 4.5 Hz, 1H -C<u>H</u>$_2$OH), 3.89 (dd, *J* = 10.7, 3.4 Hz, 1H -C<u>H</u>$_2$OH), 4.18 (s, 5H, CHCp), 4.43 (s, 2H, $CHCp_{subst}$), 4.85-4.86 (m, 2H, $CHCp_{subst}$), 4.90-4.97 (m, 1H, -CHN-), 7.54 (d, *J* = 6.8 Hz, 1H, -C<u>H</u>NH-); ^{13}C NMR ($CDCl_3$, ppm): δ 16.4 ($-CH_3$), 51.9 ($-CH_2$-), 66.0 (-CHNH-), 68.9 ($CHCp_{subst}$), 70.9 (CHCp), 71.4 ($CHCp_{subst}$), 83.7 (C_{ipso}, Fc), 199.6 (C=S); MS-EI$^+$: m/z (100%) 303 [M^+], 269 [M^+–H_2S], 245 [M^+–$CH(CH_3)CH_2O$]; IR (KBr, cm^{-1}) 3348, 3332 (N-H), 1512 (C=S). HRMS (FAB$^+$): calcd for $C_{14}H_{17}FeNOS$ [M^+] 303.0380; found 303.0378.

(*S*)-4-methyl-2-ferrocenyl-2-thiazoline (4)



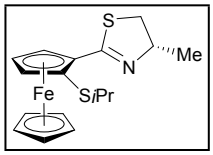
Orange solid, 90%; mp 101°C; $[\alpha]^{20}_D$ = –49 (*c* = 0.1 in $CHCl_3$); ^1H NMR ($CDCl_3$, ppm): δ 1.39 (d, *J* = 6.6 Hz, 3H, $-CH_3$), 2.94 (dd, *J* = 10.6, 7.2 Hz, 1H, -SCH_2-), 3.43 (dd, *J* = 10.6, 8.0 Hz, 1H -CH_2S), 4.18 (s, 5H, CHCp), 4.34 (s, 2H, $CHCp_{subst}$), 4.54 (dd, *J* = 14.7, 7.1 Hz, 1H, -CHN=), 4.70 (s, 2H, $CHCp_{subst}$); ^{13}C NMR ($CDCl_3$, ppm): δ 20.4 ($-CH_3$), 39.8 (-SCH_2-), 69.2, 69.5 ($CHCp_{subst}$), 70.1 (Cp), 70.4-70.5 ($CHCp_{subst}$), 72.4 (CHN=), 77.1 (C_{ipso}, Fc), 166.7 (C=N); IR (KBr, cm^{-1}) 1600 (C=N); MS (DART): m/z (100%): 286 [M^{+1}]; HRMS (ESI$^+$): calcd for $C_{14}H_{16}FeNS$ [M^+] 286.03529; found 286.03506.

(*S*,*S*$_P$)-4-methyl-2-[(2-methylthio)ferrocenyl]-2-thiazoline (5a)



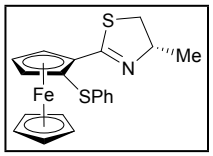
Orange oil, 89%; $[\alpha]^{20}_D$ = +26 (*c* = 0.158 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, ppm): δ 1.31 (d, *J* =6.6 Hz, 3H, -CH_3), 2.25 (s, 3H, -SCH_3), 2.89 (dd, *J* =10.7, 6.3 Hz, 1H, - SCH_2-), 3.36 (dd, *J* =10.7, 8.2 Hz, 1H, - SCH_2-), 4.12 (s, 5H, CHCp), 4.23-4.25 (m, 1H, $CHCp_{subst}$), 4.37-4.39 (m, 1H, $CHCp_{subst}$), 4.48-4.55 (m, 1H, -CHN=), 4.71 (dd, *J* = 2.5, 1.5 Hz, 1H, $CHCp_{subst}$); ^{13}C NMR ($CDCl_3$, ppm): δ 19.7 (-SCH_3), 20.0 (-CH_3), 39.5 (-SCH_2-), 68.8 ($CHCp_{subst}$), 70.5 ($CHCp_{subst}$), 71.1 (Cp), 71.3 (-CHN=), 72.7 ($CHCp_{subst}$), 78.3 (C_{ipso}, Fc), 84.9 (C_{ipso}, Fc), 165.0 (C=N); MS (DART): m/z (100%): 332 [M^{+1}]; IR (KBr, cm^{-1}) 1609 (C=N); HRMS (ESI^+): calcd for $C_{15}H_{18}FeNS_2$ [M^+] 332.02301; found 332.02383.

(*S*,*S*$_P$)-4-methyl-2-[(2-isopropylthio)ferrocenyl]-2-thiazoline (5b)



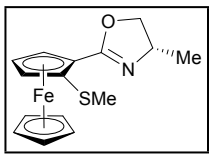
Orange oil, 81%. $[\alpha]^{20}_D$ = +28 (*c* = 1.53 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, ppm): δ 1.06 (dd, *J* = 12.7, 6.7 Hz, 6H, -$CH(C\underline{H}_3)_2$), 1.24 (d, *J* = 6.6 Hz, 3H, -CH_3), 2.76-2.88 (m, 2H,- $C\underline{H}(CH_3)_2$, -SCH_2-), 3.31 (dd, *J* = 10.5, 8.4 Hz, 1H, -SCH_2-), 4.08 (s, 5H, CHCp), 4.27 (s, 1H, -$CHCp_{subst}$), 4.35-4.42 (m, 2H, $CHCp_{subst}$,-CHN=), 4.80 (s, 1H, $CHCp_{subst}$); ^{13}C NMR ($CDCl_3$, ppm): δ 20.0 (-CH_3), 22.4, 22.9 (-$CH(\underline{C}H_3)_2$), 39.7 (-SCH_2-), 40.3 (-$\underline{C}H(CH_3)_2$), 69.8 ($CHCp_{subst}$), 70.4 ($CHCp_{subst}$), 70.4 (-CHN=), 71.2 (CHCp), 77.9 ($CHCp_{subst}$), 78.8 (C_{ipso}, Fc), 80.9 (C_{ipso}, Fc), 165.5 (C=N); MS (DART): m/z (100%): 360 [M^{+1}]; IR (KBr, cm^{-1}) 1612 (C=N); HRMS (ESI^+): calcd for $C_{17}H_{22}FeNS_2$ [M^+] 360.05431; found 360.05408.

(*S*,*S*$_P$)-4-methyl-2-[2-(phenylthio)ferrocenyl]-2-thiazoline (5c)



Orange solid, 79%; mp: 129°C, $[\alpha]^{20}_D$ = +159 (*c* = 0.124 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, ppm): δ 1.31 (dd, *J* = 6.7 Hz, 3H, -CH_3), 2.83 (dd, *J* = 10.7, 7.3 Hz, 1H, -SCH_2-), 3.40 (dd, *J* = 10.7, 8.3 Hz, 1H, -SCH_2-), 4.30 (s, 5H, CHCp), 4.45-4.51 (m, 2H, $CHCp_{subst}$,-CHN=), 4.54-4.55 (m, 1H, $CHCp_{sust}$), 5.04 (dd, *J* = 2.6, 1.6 Hz, 1H, $CHCp_{subst}$), 7.05-7.21 (m, 5H, CH_{Ph}); ^{13}C NMR ($CDCl_3$, ppm): δ 20.3 (-CH_3), 40.1 (-SCH_2-), 70.9 ($CHCp_{sust}$), 71.0 (-CHN=), 71.2 ($CHCp_{sust}$), 71.7 (CHCp), 77.8 (C_{ipso}, Fc), 78.0 ($CHCp_{sust}$), 81.0 (C_{ipso}, Fc), 125.3 (CH_{Ph}), 126.7 (CH_{Ph}), 128.7 (CH_{Ph}), 139.9 (C_{ipso}, Ph), 165.6 (C=N); MS (DART): m/z (100%): 394 [M^{+1}]; IR (KBr, cm^{-1}) 1608 (C=N); HRMS (ESI^+): calcd for $C_{20}H_{20}FeNS_2$ [M^+] 394.03866; found 394.03878.

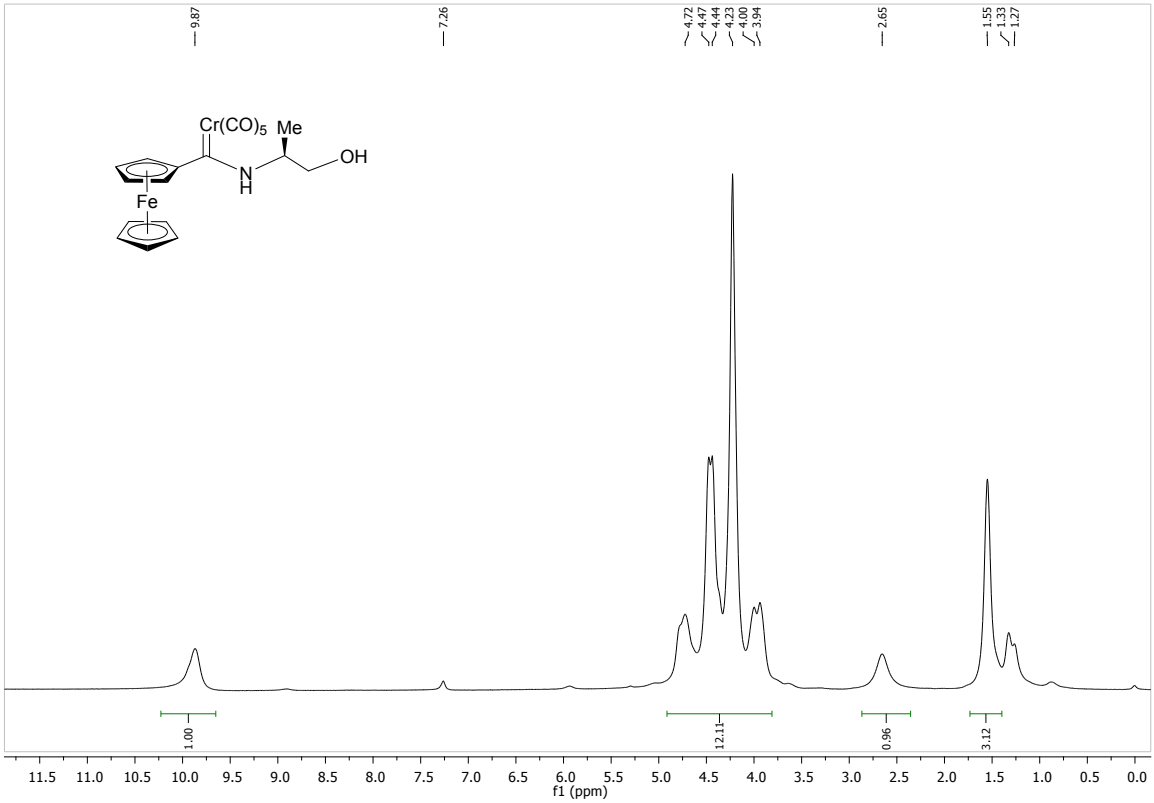
(*S*,*S*$_P$)-4-methyl-2-[(2-methylthio)ferrocenyl]-2-oxazoline (6)

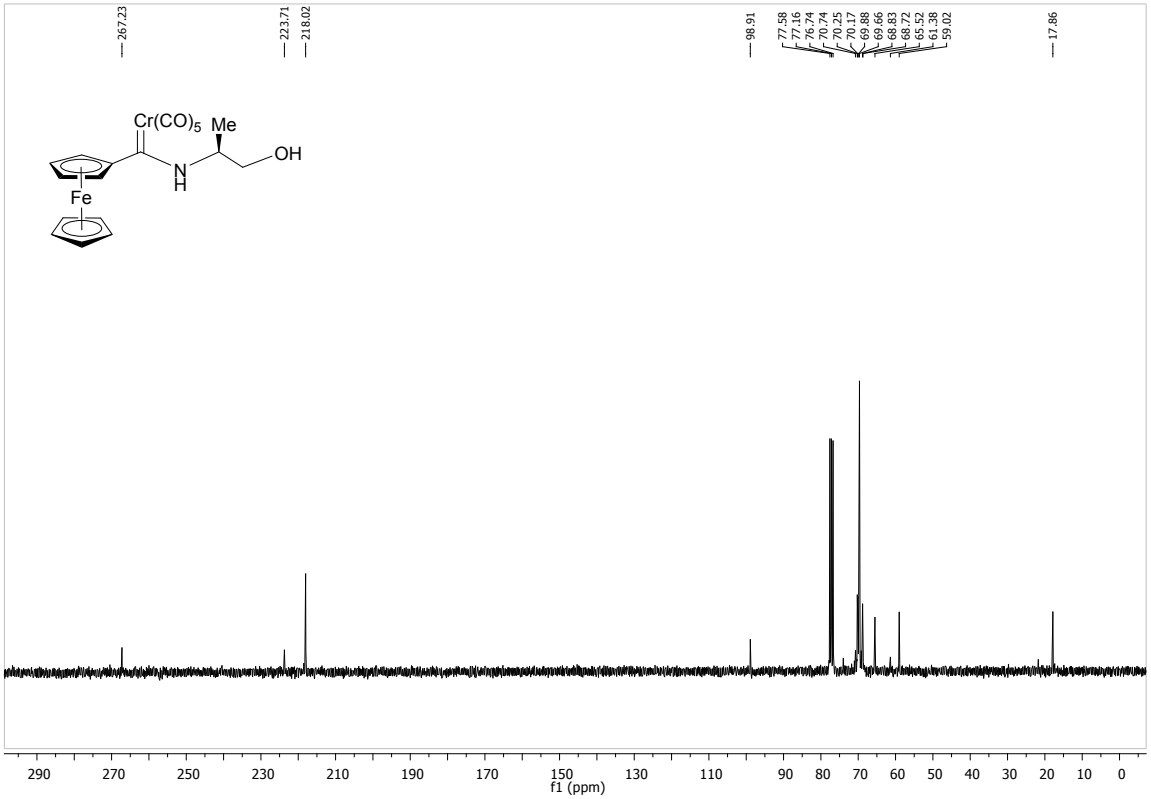


Orange oil, 95%; $[\alpha]^{20}_D$ = –176 (*c* = 0.142 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, ppm): δ 1.32 (d, *J* = 6.5 Hz, 3H, -CH_3), 2.36 (s, 3H, -SCH_3), 3.88 (dd, *J* = 7.7, 7.2 Hz, 1H, -CHN-), 4.17 (s, 5H, Cp), 4.21-4.29 (m, 2H, -OCH_2-, $CHCp_{subst}$), 4.37-4.46 (m, 2H, -OCH_2-, $CHCp_{subst}$), 4.73 (s, 1H, $CHCp_{subst}$); ^{13}C NMR ($CDCl_3$, ppm): δ 18.3 (-CH_3), 21.8 (-SCH_3), 62.1 (-CHN-), 68.6 ($CHCp_{subst}$), 70.2 ($CHCp_{subst}$), 70.4 (C_{ipso}, Fc), 70.6 ($CHCp_{subst}$), 71.1 (Cp), 73.7 (-OCH_2-), 87.3 (C_{ipso}, Fc), 165.1 (C=N); matching known analytical data[18]; IR (KBr, cm^{-1}) 1648 (C=N); HRMS (ESI^+): calcd for $C_{15}H_{18}FeNOS$ [M^+] 316.04585; found 316.04587.

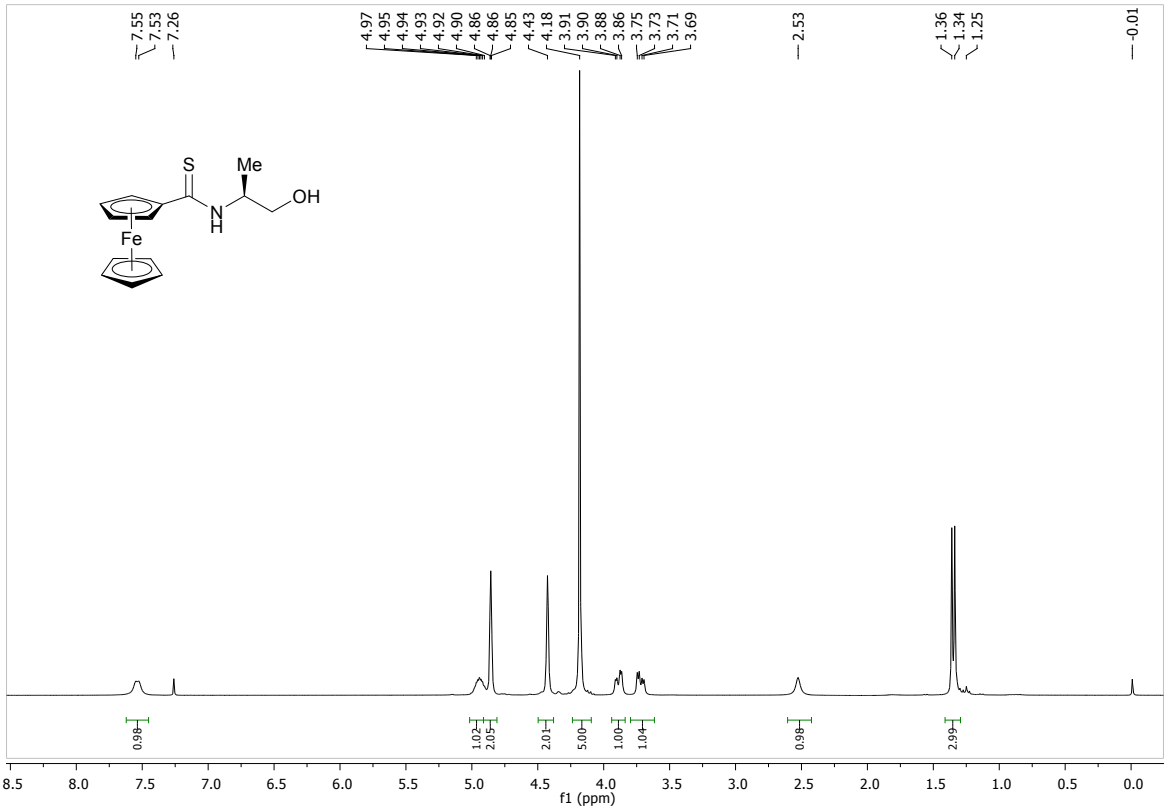
NMR Spectra

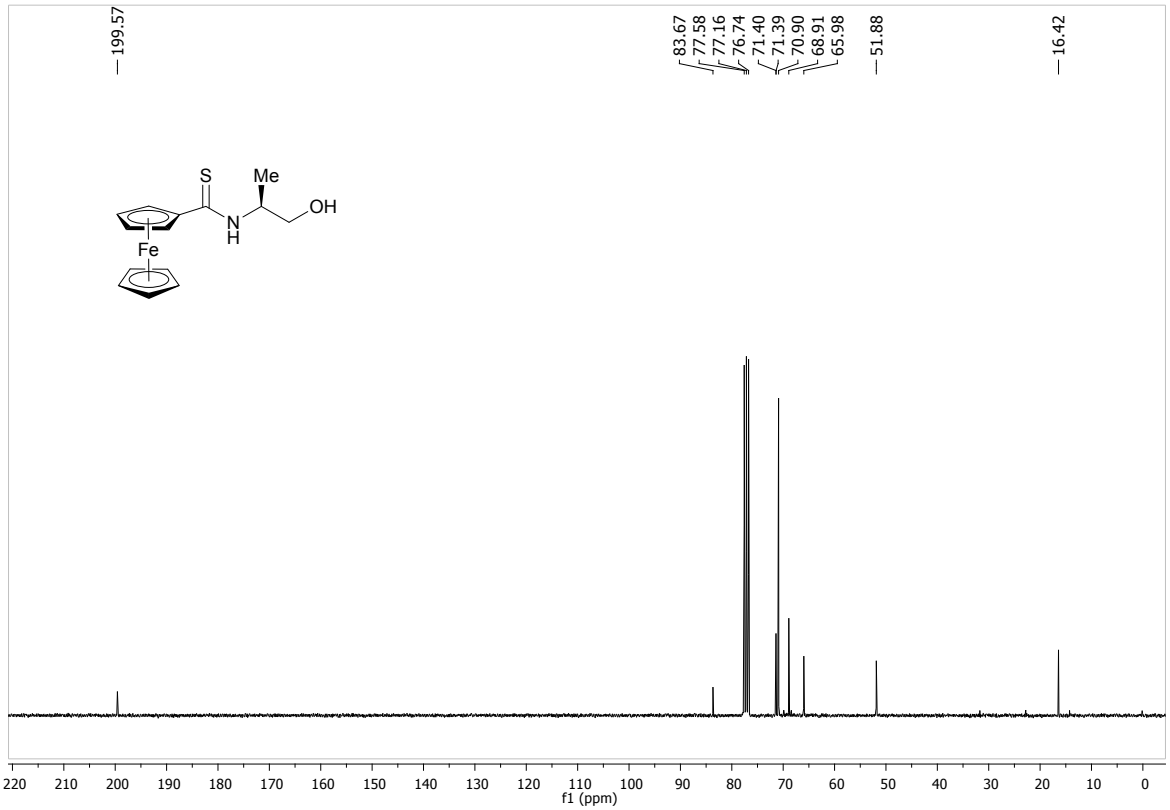
[(Ferrocenyl)(*S*)-3-(hydroxypropan-2-amine)]-methylidene pentacarbonyl chromium (2)



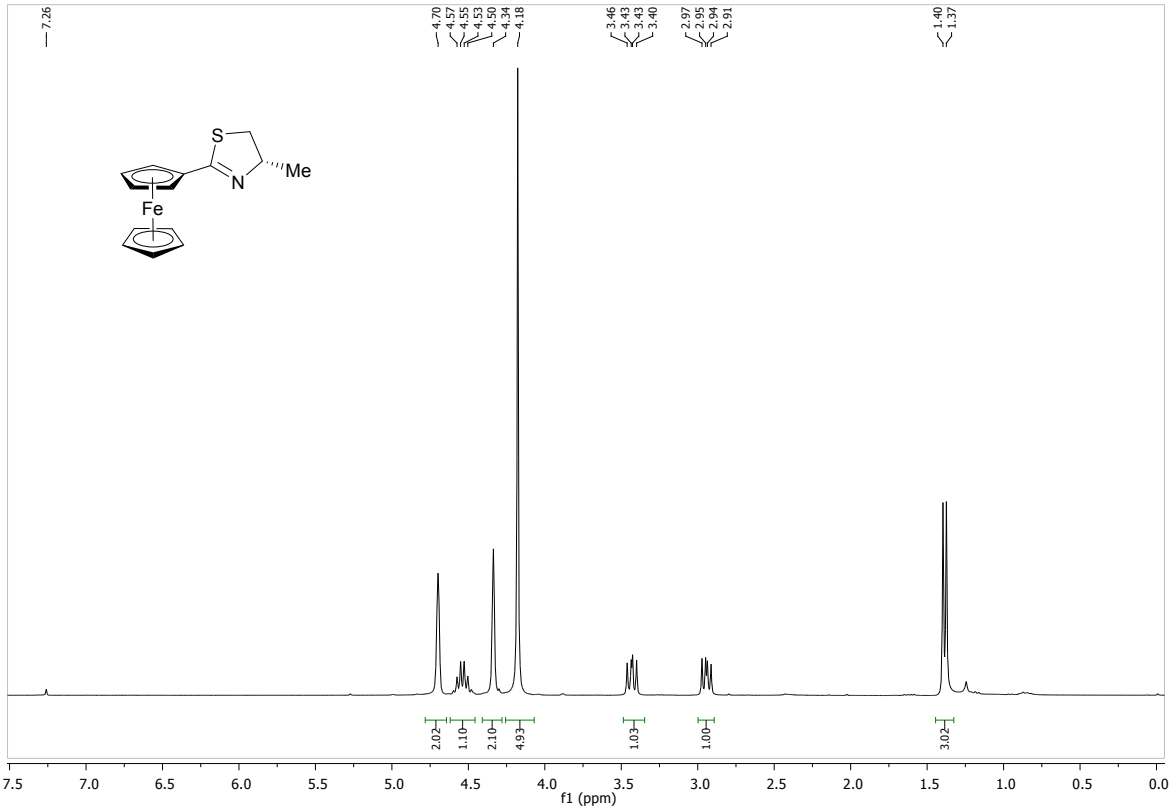


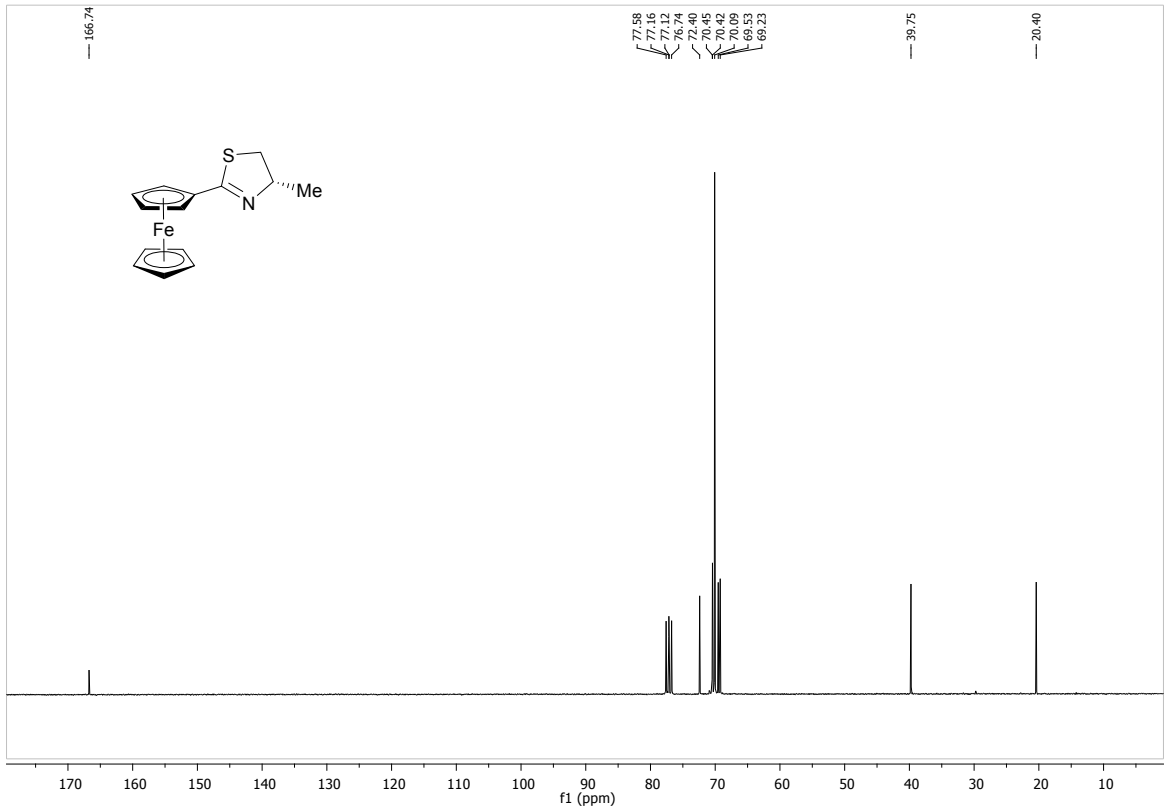
(*S*)-*N*-(1-hydroxypropan-2-yl)ferrocenylthioamide (3)



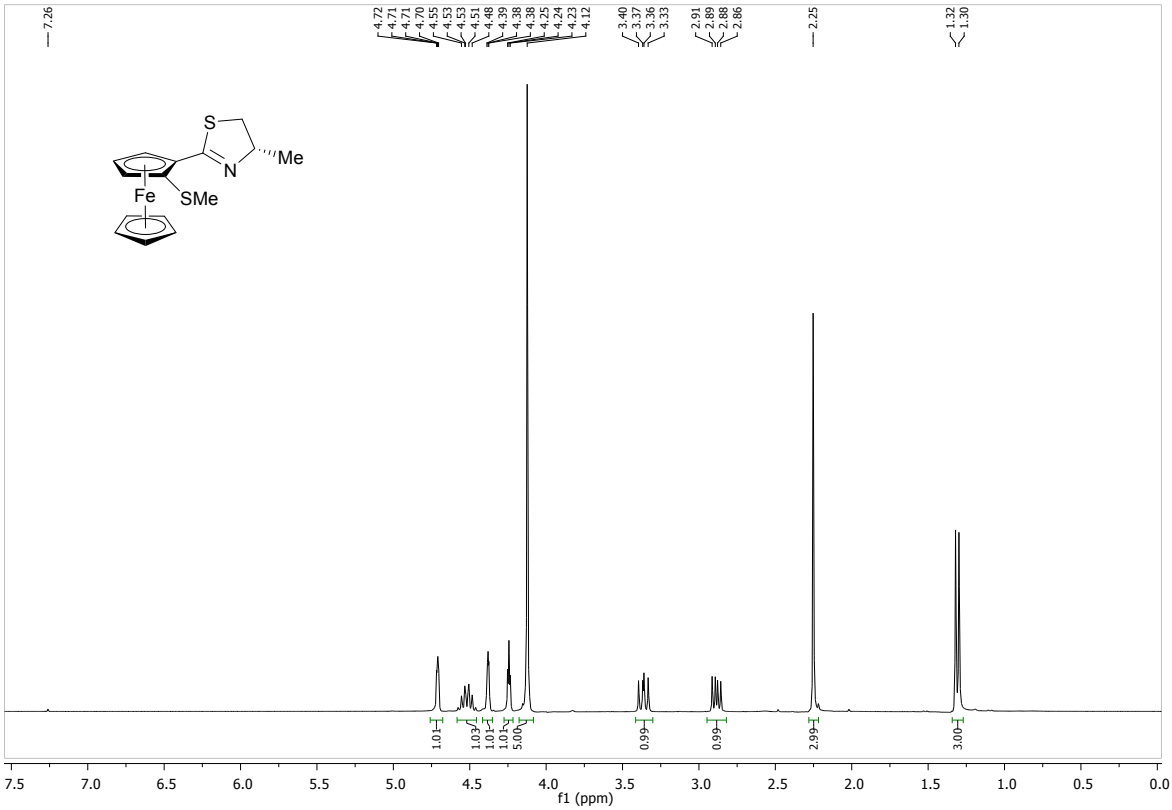


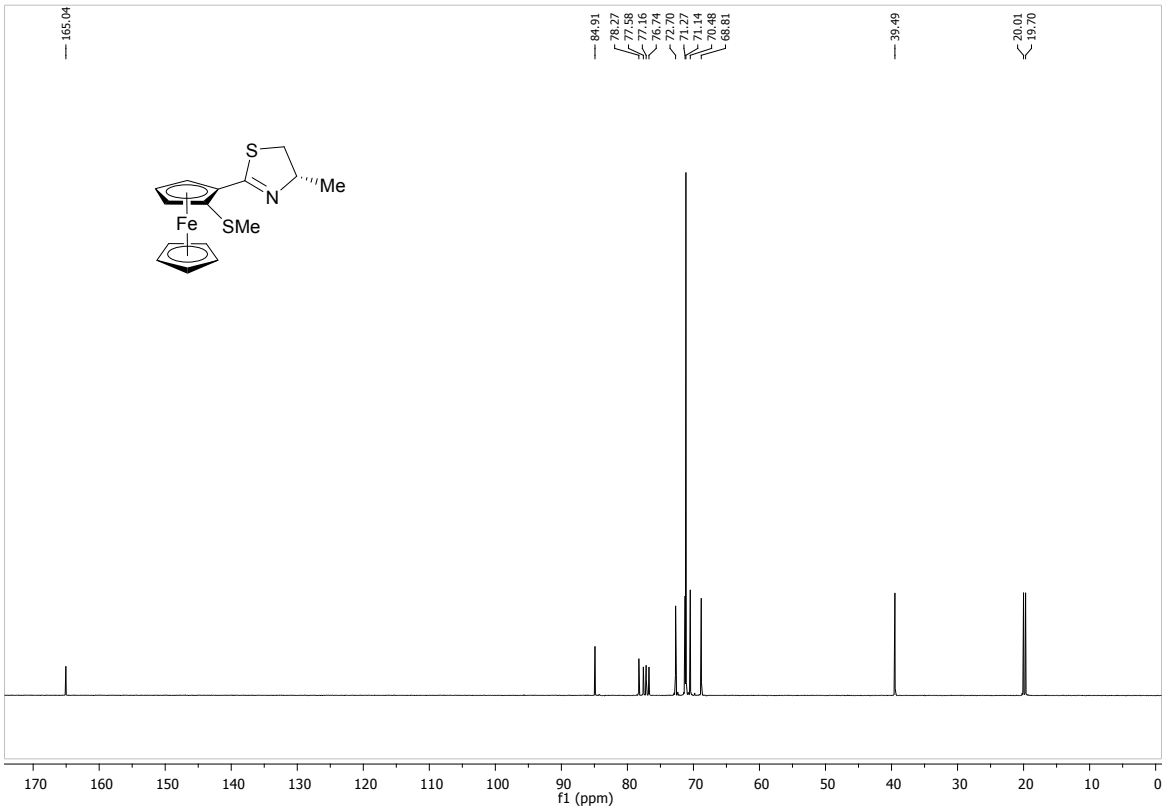
(*S*)-4-methyl-2-ferrocenyl-2-thiazoline (4)



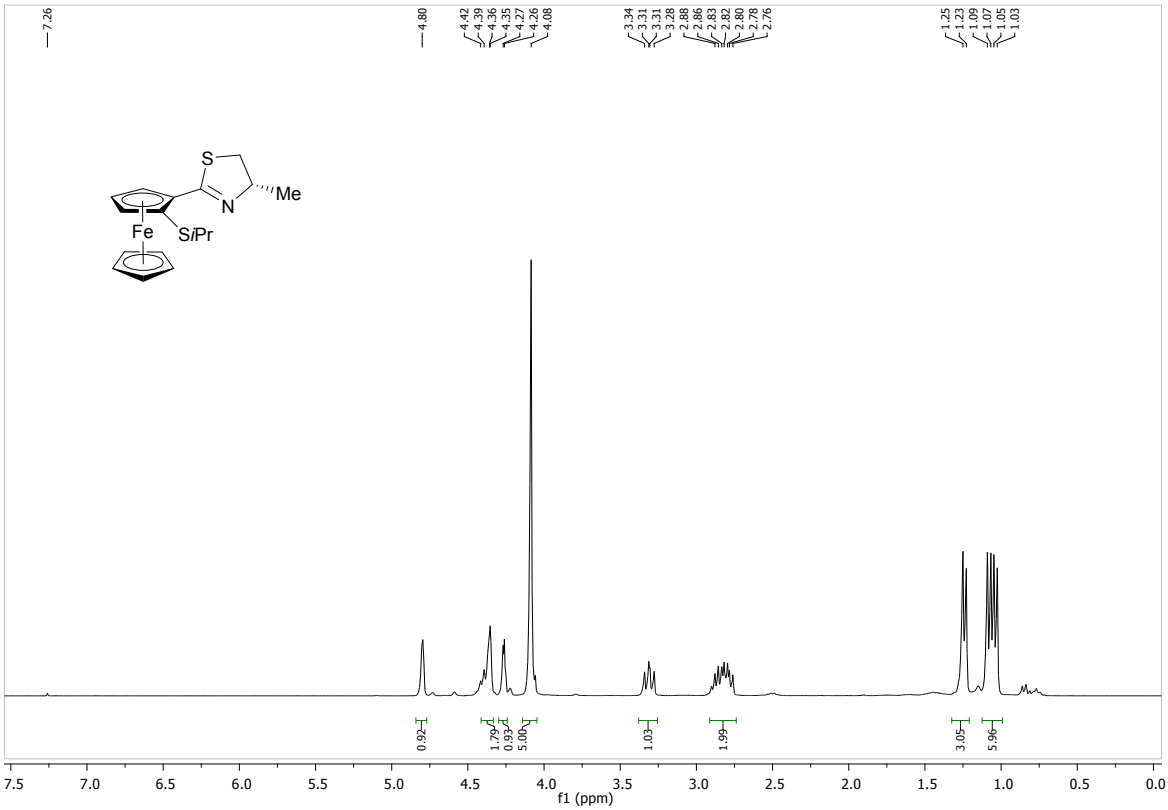


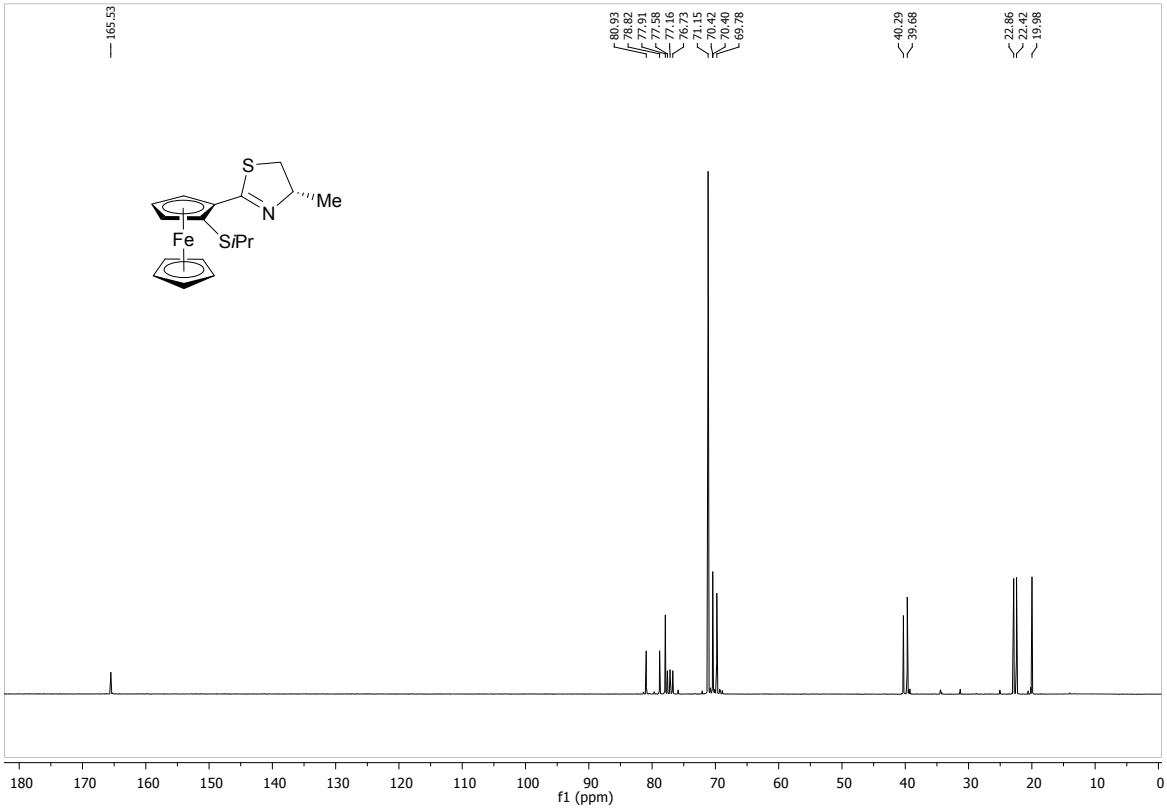
(*S*,*S*$_P$)-4-methyl-2-[(2-methylthio)ferrocenyl]-2-thiazoline (5a)



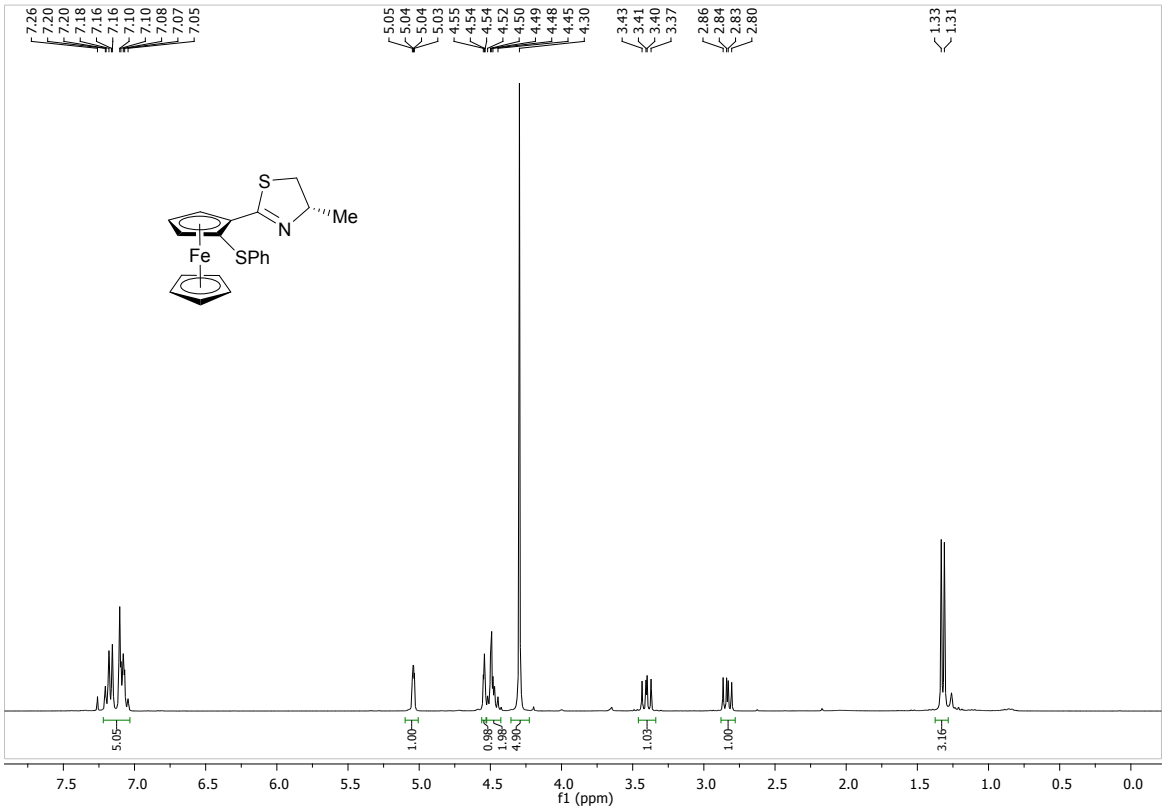


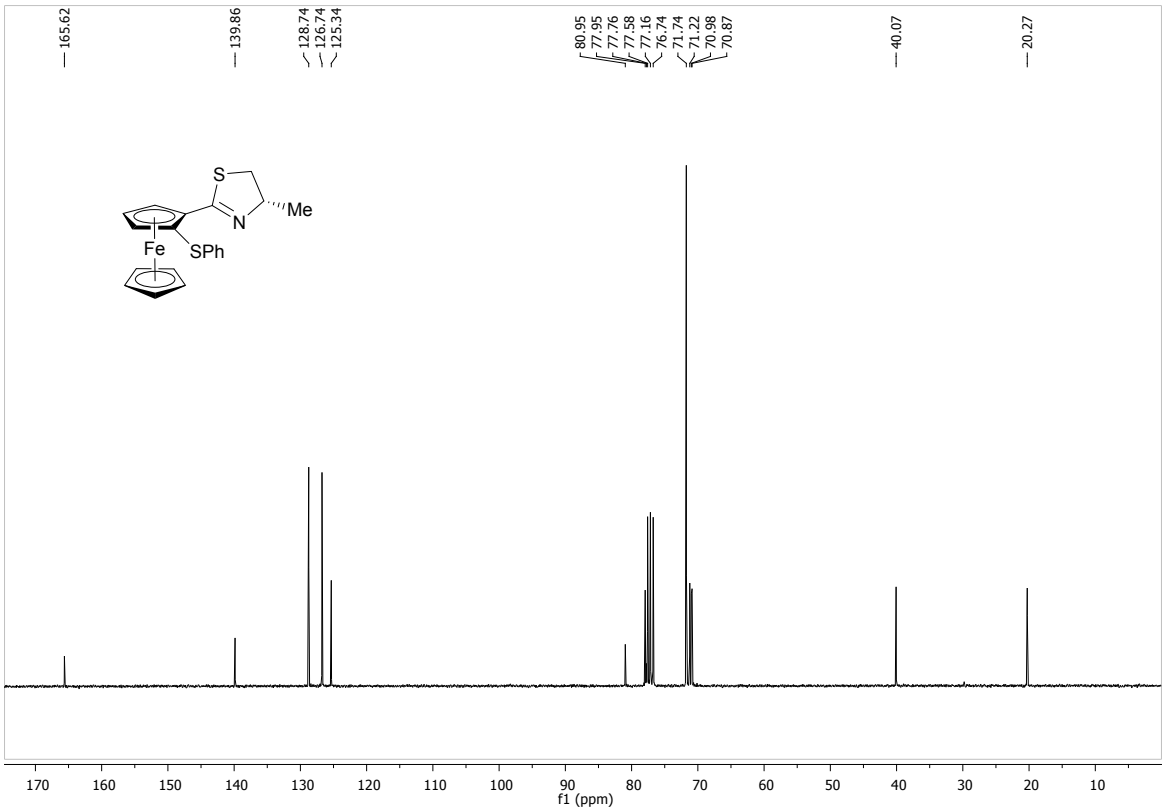
(*S*,*S*$_P$)-4-methyl-2-[(2-isopropylthio)ferrocenyl]-2-thiazoline (5b)



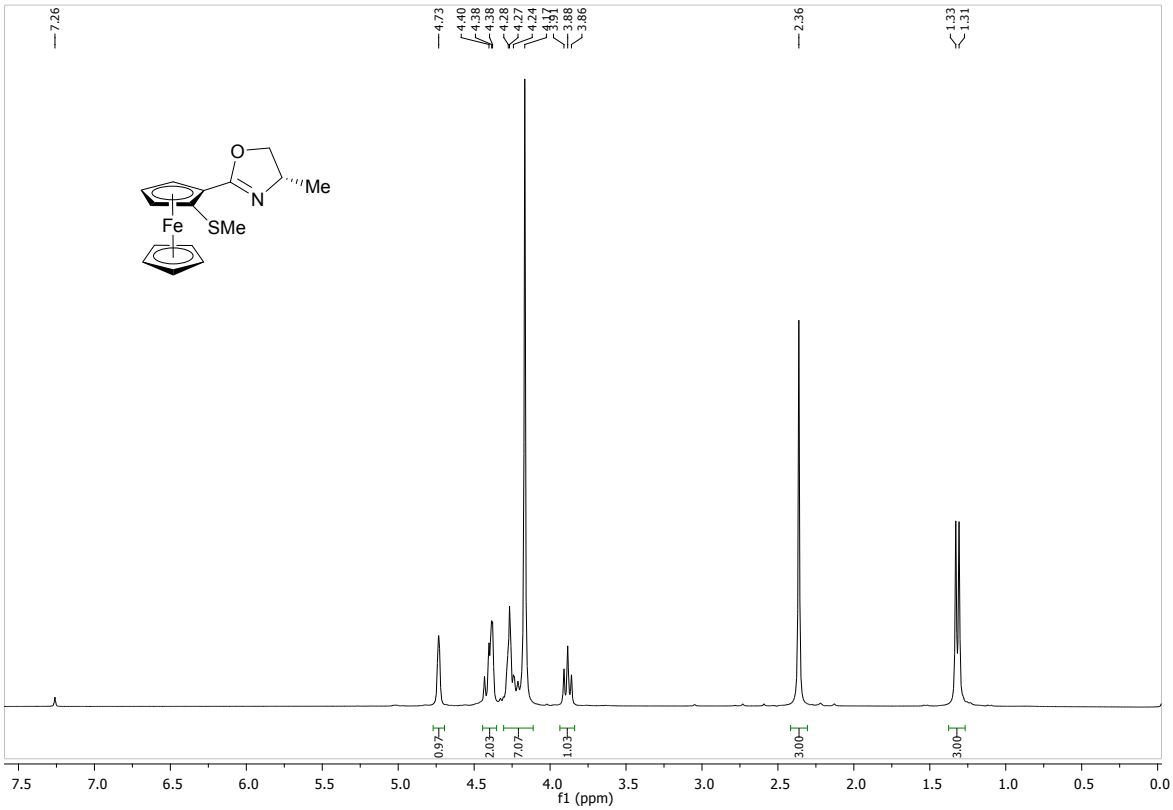


(*S*,*S*$_P$)-4-methyl-2-[2-(phenylthio)ferrocenyl]-2-thiazoline (5c)





(S,S_P)-4-methyl-2-[(2-methylthio)ferrocenyl]-2-oxazoline (6)



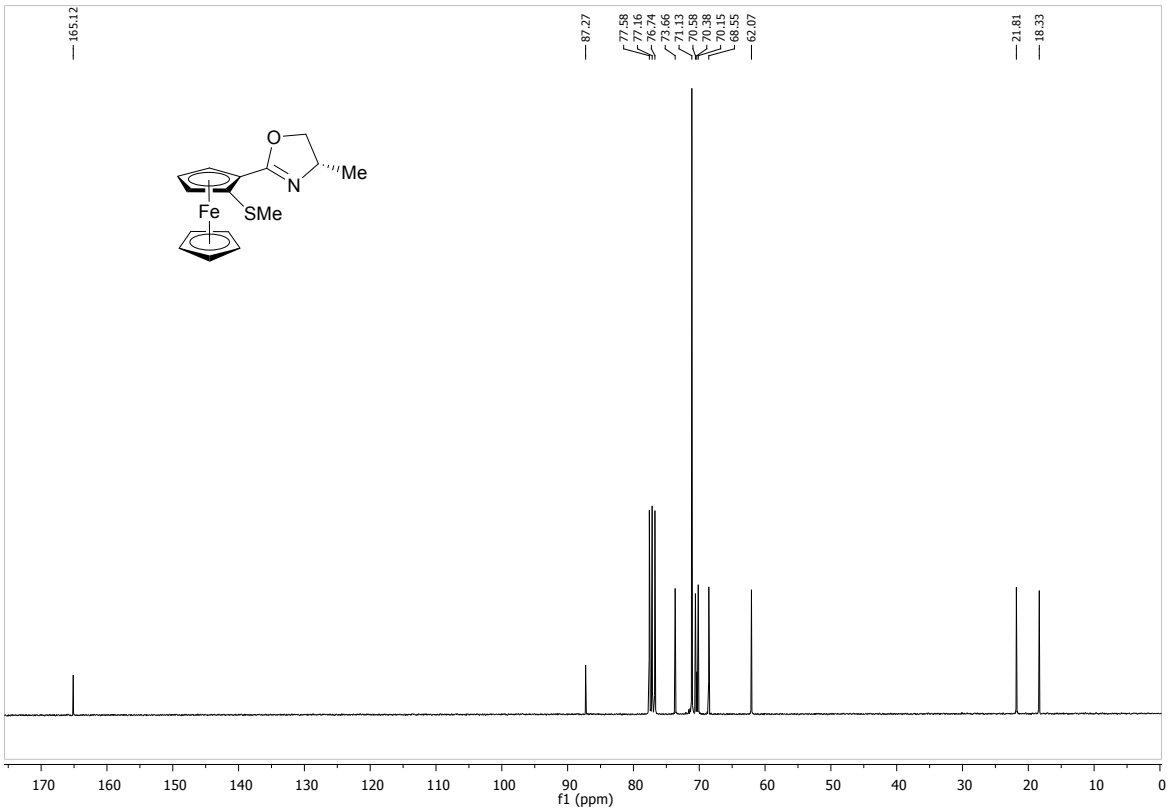


Table 1. Cartesian coordinates (Å) of optimized geometries at M06/6-311+G(d,p) level of theory

***Endo* (*S*)-4-(*t*-BuLi)$_2$**

Fe	-2.31801	-0.82264	-0.32859
N	0.81373	1.54294	0.30752
S	-1.25866	2.94622	-0.47181
H	-0.20369	4.67705	0.85527
C	-3.47568	-2.1092	0.75992
H	-3.47976	-3.18405	0.63881
C	-2.61894	-1.36941	1.62064
H	-1.84766	-1.77728	2.2608
C	-2.9059	0.00976	1.44124
H	-2.38984	0.83296	1.91925
C	-3.94025	0.12584	0.47132
H	-4.35792	1.05099	0.09684
C	-4.29325	-1.18626	0.05128
H	-5.0289	-1.437	-0.70097
C	-1.08175	-1.96396	-1.50618
H	-1.031	-3.04414	-1.47894
C	-1.96062	-1.19512	-2.319
H	-2.68091	-1.58787	-3.02344
C	-1.75973	0.17347	-2.01828
H	-2.27966	1.0128	-2.46128
C	-0.74438	0.25531	-1.01224
C	-0.3304	-1.0786	-0.69513
H	0.39266	-1.35265	0.06917
C	0.16037	3.87341	0.21116
H	0.72634	4.30253	-0.62027
C	0.97289	2.83287	0.98304
C	0.53609	2.69992	2.43278
H	2.03648	3.10767	0.94945
C	-0.2727	1.46505	-0.36219
H	0.72039	3.62972	2.98011
H	1.08155	1.89292	2.92989
H	-0.5346	2.47226	2.48927
Li	2.26955	0.12969	0.23263
C	3.39349	-0.31822	-1.5924
C	3.89801	1.10473	-1.37766
C	2.55967	-0.33086	-2.8641
C	4.62605	-1.18835	-1.83074
H	4.52982	1.20505	-0.47917
H	3.07406	1.8324	-1.28432
H	4.51576	1.46378	-2.22955
H	2.20686	-1.33988	-3.12858
H	3.12925	0.04247	-3.74409
H	1.66067	0.29814	-2.77884
H	5.32634	-1.17593	-0.97861
H	5.21451	-0.86269	-2.7152
H	4.38221	-2.24985	-2.03735

H	2.91218	0.62849	2.29537
H	0.63103	-0.69505	2.4998
Li	3.01432	-1.92338	-0.29393
C	3.38802	-0.36978	2.32306
C	1.25932	-1.59984	2.54463
H	4.36227	-0.27023	1.81788
H	3.61006	-0.55123	3.39653
C	2.5237	-1.47106	1.71344
H	1.47805	-1.78127	3.61996
C	3.31058	-2.77127	1.86079
H	4.27186	-2.76717	1.30942
H	3.59507	-2.98481	2.91322
H	2.73973	-3.65157	1.52162
H	0.62858	-2.43756	2.20924

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***Endo*(*S*)-4-(*t*-BuLi)-TMEDA**

Fe	2.80749	-0.53215	-0.26791
N	-0.50462	1.38488	0.25593
S	1.2654	3.0899	-0.67792
H	-0.92187	4.10511	-0.63779
C	4.64719	-1.1089	0.4193
H	5.35593	-1.70238	-0.14235
C	4.54985	0.30997	0.40739
H	5.17009	0.98728	-0.16408
C	3.46264	0.67982	1.24381
H	3.10388	1.6895	1.40081
C	2.88444	-0.50686	1.77236
H	2.0049	-0.56428	2.40249
C	3.6192	-1.61246	1.26311
H	3.39692	-2.65528	1.44704
C	2.64001	-1.02531	-2.25626
H	3.45198	-1.35898	-2.88804
C	1.79759	-1.85802	-1.46433
H	1.86321	-2.93507	-1.37592
C	0.89644	-1.03235	-0.75013
H	0.16066	-1.35552	-0.0171
C	1.17429	0.32462	-1.10676
C	2.26214	0.32444	-2.03878
H	2.72077	1.19877	-2.48257
C	-0.21583	3.78427	0.13533
H	0.06984	4.64458	0.74495
C	-0.77024	2.63269	0.97325
C	-0.15635	2.55568	2.36143
H	-1.85567	2.75163	1.07868
C	0.5367	1.46793	-0.48052
H	-0.38682	3.45875	2.93637
H	0.93337	2.45544	2.29591
H	-0.54589	1.68834	2.90065
Li	-1.81952	-0.30995	0.30593
C	-1.57482	-1.87983	1.78141
C	-1.33154	-1.03156	3.0212

C	-0.46368	-2.91822	1.74039
C	-2.86027	-2.6561	2.02021
H	-2.10975	-0.26323	3.17523
H	-0.36566	-0.5026	2.97209
H	-1.30912	-1.63773	3.95907
H	-0.54179	-3.59407	0.87189
H	-0.4745	-3.57367	2.64273
H	0.54188	-2.46908	1.70774
H	-3.74599	-2.01253	2.14275
H	-2.8092	-3.27307	2.94883
H	-3.09002	-3.36475	1.20778
H	-2.78734	-2.80339	-0.78055
H	-2.62546	-3.01435	-2.55324
C	-2.24435	-2.47068	-1.66846
H	-4.35203	-1.43344	-2.51844
H	-1.1921	-2.7308	-1.5233
C	-3.79051	-0.65893	-1.9644
N	-2.37995	-1.02774	-1.84179
H	-4.42005	-1.33535	-0.01407
H	-3.86083	0.25001	-2.57248
C	-4.45946	-0.42479	-0.62578
H	-5.53017	-0.19657	-0.79988
C	-1.64215	-0.60713	-3.02421
H	-2.06656	-1.04126	-3.94867
H	-0.59826	-0.92379	-2.94557
N	-3.83005	0.65438	0.14
H	-4.45813	-0.15267	1.97359
H	-1.65959	0.48488	-3.11365
C	-4.49489	0.7939	1.42859
H	-5.55248	1.09523	1.313
H	-3.20779	1.92623	-1.43331
C	-3.89558	1.91646	-0.5819
H	-4.91778	2.12639	-0.94885
H	-3.98396	1.55058	2.03336
H	-3.60969	2.73594	0.08306

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Endo (*S*)-4-(*t*-BuLi)

Fe	1.66279	-0.74696	-0.02206
N	-1.38393	1.65605	-0.70431
S	0.73017	3.06503	-0.06148
H	-0.96967	4.54965	-0.90116
C	3.11594	-1.21247	1.33719
H	4.17221	-1.26551	1.11004
C	2.40633	-0.05044	1.74733
H	2.8244	0.93748	1.88901
C	1.03616	-0.4065	1.89389
H	0.22618	0.26309	2.15583
C	0.89883	-1.78277	1.5754
H	-0.03094	-2.33688	1.55001
C	2.18368	-2.28081	1.22806
H	2.40537	-3.28773	0.90125

C	2.51397	-0.7161	-1.89225
H	3.52547	-1.01975	-2.1248
C	1.36846	-1.55957	-1.88551
H	1.35489	-2.61999	-2.09889
C	0.24846	-0.79184	-1.4865
H	-0.75047	-1.18682	-1.32031
C	0.70045	0.54762	-1.24642
C	2.11168	0.5826	-1.4978
H	2.7515	1.44953	-1.39581
C	-0.87842	3.92592	-0.00801
H	-0.92334	4.55994	0.88035
C	-1.92165	2.80846	0.02818
C	-2.27761	2.38057	1.44253
H	-2.82985	3.15057	-0.48491
C	-0.1021	1.6425	-0.73348
H	-2.77804	3.19229	1.97972
H	-1.37236	2.10676	1.99621
H	-2.94131	1.51018	1.43522
Li	-2.53883	0.04808	-1.05276
C	-3.17448	-1.72506	-0.23164
C	-3.0654	-1.48993	1.27038
C	-2.41704	-3.00649	-0.54369
C	-4.64136	-1.98903	-0.54236
H	-3.70487	-0.66059	1.61341
H	-2.03802	-1.25454	1.59634
H	-3.38557	-2.382	1.85829
H	-2.46588	-3.27674	-1.60924
H	-2.83162	-3.87414	0.01963
H	-1.34919	-2.95562	-0.27449
H	-5.28947	-1.13336	-0.29841
H	-5.03805	-2.85365	0.03913
H	-4.80818	-2.2283	-1.60251

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***Endo*(*S*)-4**

Fe	-1.50906	-0.03439	-0.045
N	2.22197	-0.43922	-1.1783
S	2.15393	-0.39683	1.45866
H	4.35441	-1.08417	0.76301
C	-2.88474	1.08498	0.96994
H	-3.68908	0.67866	1.56822
C	-1.57022	1.38081	1.42561
H	-1.19249	1.23606	2.42913
C	-0.81784	1.85245	0.31519
H	0.23247	2.11363	0.32914
C	-1.66382	1.84765	-0.82609
H	-1.37319	2.1183	-1.83213
C	-2.94234	1.37206	-0.42185
H	-3.79815	1.22319	-1.06641
C	-1.97563	-2.01102	0.22306
H	-2.82847	-2.3812	0.77564
C	-1.9512	-1.69526	-1.16479

H	-2.7859	-1.77977	-1.84751
C	-0.66115	-1.20523	-1.48635
H	-0.31287	-0.84836	-2.44563
C	0.12202	-1.2176	-0.29206
C	-0.69877	-1.71812	0.76597
H	-0.39784	-1.83383	1.79922
C	3.78306	-0.15616	0.67274
H	4.32189	0.64604	1.18324
C	3.47725	0.1909	-0.79234
C	3.36852	1.68967	-1.02244
H	4.27505	-0.21075	-1.43028
C	1.48208	-0.70916	-0.18485
H	4.32894	2.1845	-0.84487
H	2.62665	2.12503	-0.34286
H	3.0542	1.895	-2.04879

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***Exo* (*S*)-4-(*t*-BuLi)$_2$**

Fe	-2.40219	-0.5366	0.4665
N	0.88852	1.4461	-0.44259
S	-1.14207	3.10443	-0.29854
H	0.20412	4.41187	-1.83342
C	-4.32006	-1.02845	-0.03133
H	-5.1343	-1.10661	0.67652
C	-3.91711	0.15238	-0.71484
H	-4.36541	1.13233	-0.61781
C	-2.78287	-0.17	-1.50955
H	-2.21272	0.52489	-2.11435
C	-2.48556	-1.54541	-1.32069
H	-1.65881	-2.08372	-1.76564
C	-3.43277	-2.07603	-0.40363
H	-3.45155	-3.09095	-0.02946
C	-2.35099	-0.29864	2.50323
H	-3.19002	-0.44606	3.16938
C	-1.41549	-1.29261	2.10278
H	-1.42563	-2.33253	2.40113
C	-0.49836	-0.70549	1.19752
H	0.29957	-1.23077	0.6775
C	-0.86857	0.66691	1.02927
C	-2.02477	0.90996	1.83984
H	-2.56008	1.84751	1.91858
C	0.02882	3.34502	-1.67848
H	-0.41293	2.91496	-2.58279
C	1.29448	2.6042	-1.24926
C	2.2325	3.49145	-0.44514
H	1.81728	2.23393	-2.14204
C	-0.25123	1.61142	0.11296
H	2.58076	4.32968	-1.05695
H	3.10636	2.93571	-0.09665
H	1.7155	3.89381	0.43321
Li	2.11672	-0.22596	-0.23256
C	1.81099	-2.31545	-1.10858

C	1.26341	-1.452	-2.23767
C	0.81902	-3.43838	-0.84225
C	3.09218	-2.96188	-1.64001
H	1.97409	-0.66865	-2.55914
H	0.32555	-0.94047	-1.97214
H	1.0495	-2.04859	-3.15192
H	1.20939	-4.18288	-0.1299
H	0.57132	-4.00596	-1.76747
H	-0.13547	-3.08361	-0.42724
H	3.85581	-2.22013	-1.92187
H	2.91164	-3.58514	-2.54098
H	3.57075	-3.65641	-0.91988
H	3.91293	1.04619	-0.73841
H	2.68039	1.429	1.7017
Li	3.05925	-2.14961	0.55729
C	4.58295	0.42404	-0.11639
C	3.45378	0.73834	2.07061
H	5.06838	-0.2812	-0.80711
H	5.37777	1.11825	0.23663
C	3.88402	-0.2907	1.03637
H	4.3046	1.37231	2.40771
C	4.92923	-1.18823	1.69205
H	5.329	-1.96317	1.01071
H	5.82247	-0.62292	2.03519
H	4.54288	-1.70227	2.58756
H	3.0378	0.26345	2.96998

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***Exo* (*S*)-4-(*t*-BuLi)-TMEDA**

Fe	-2.56016	-0.77042	0.03127
N	0.23244	1.72985	-0.45781
S	-1.98895	3.06611	-0.90797
H	-0.7281	4.90248	0.0404
C	-2.71402	-2.01739	1.64289
H	-2.49122	-3.07612	1.62616
C	-1.78791	-0.97278	1.91664
H	-0.73219	-1.08006	2.13834
C	-2.47769	0.26203	1.79618
H	-2.03258	1.24415	1.90058
C	-3.82704	-0.01302	1.44578
H	-4.5937	0.72461	1.24874
C	-3.97459	-1.42518	1.35216
H	-4.87714	-1.95406	1.07696
C	-1.99634	-1.88996	-1.59533
H	-1.87867	-2.96603	-1.60162
C	-3.19983	-1.1868	-1.87838
H	-4.15043	-1.63152	-2.13895
C	-2.94816	0.19707	-1.72065
H	-3.6696	0.9945	-1.84379
C	-1.57773	0.35628	-1.33088
C	-0.99288	-0.94833	-1.25369
H	0.02403	-1.19112	-0.9644

C	-0.48917	4.04459	-0.59083
H	-0.08415	4.39924	-1.54658
C	0.4638	3.07303	0.09155
C	1.90423	3.50916	-0.04207
H	0.20443	3.01009	1.16222
C	-0.96178	1.59945	-0.89842
H	2.0454	4.50505	0.39017
H	2.19087	3.55222	-1.09998
H	2.57925	2.82374	0.4815
Li	1.71066	0.32946	0.27454
C	2.20355	0.25645	2.3519
C	2.04437	-0.98883	3.20871
C	1.44997	1.365	3.07341
C	3.68093	0.62731	2.39193
H	0.99428	-1.30463	3.31471
H	2.41367	-0.82136	4.24737
H	2.60475	-1.85866	2.83122
H	1.61397	2.35574	2.62151
H	1.77202	1.4647	4.13667
H	0.36157	1.19126	3.09584
H	3.90072	1.57041	1.86338
H	4.32862	-0.14663	1.94684
H	4.05066	0.77104	3.43453
H	3.73495	2.06403	-1.58656
H	4.96831	0.91705	-2.15373
C	4.22461	1.11325	-1.36053
H	3.07864	-0.12504	-3.40068
C	2.44186	0.04284	-2.5126
N	3.23015	0.04798	-1.28238
H	1.93129	1.00519	-2.62365
H	4.18571	-1.68402	-2.04462
H	1.67967	-0.73826	-2.4739
C	3.91215	-1.24002	-1.0705
H	4.85882	-1.04273	-0.55421
C	3.1498	-2.20959	-0.18962
H	3.76111	-3.12796	-0.06359
H	3.04703	-1.7459	0.79988
N	1.81048	-2.53581	-0.65278
C	1.06109	-3.20411	0.39736
H	2.39629	-2.88433	-2.64844
C	1.82306	-3.35772	-1.84637
H	1.51698	-4.17341	0.67534
H	0.03556	-3.39368	0.05964
H	2.26449	-4.3546	-1.65514
H	0.79873	-3.5004	-2.20938
H	4.74547	1.21199	-0.40283
H	1.02041	-2.57282	1.28998

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***Exo* (*S*)-4-(*t*-BuLi)**

Fe	1.0541	1.41529	0.06394
N	-1.80003	-0.88643	-0.25488

S	-3.29327	1.23324	0.11026
H	-3.7566	0.32882	-2.07281
C	2.86297	1.10568	-0.83281
H	3.74175	0.74488	-0.31523
C	1.87177	0.28818	-1.44172
H	1.88217	-0.79874	-1.45581
C	0.85946	1.1446	-1.95628
H	-0.05496	0.82954	-2.44423
C	1.22463	2.48789	-1.66942
H	0.64408	3.36928	-1.90623
C	2.46597	2.46309	-0.97594
H	2.99461	3.32414	-0.5897
C	1.33413	1.08173	2.06963
H	2.2814	0.83857	2.53167
C	0.81242	2.3878	1.85559
H	1.29689	3.3162	2.1253
C	-0.42704	2.26725	1.18092
H	-1.05685	3.07987	0.84258
C	-0.67751	0.87286	0.9725
C	0.42437	0.1427	1.52907
H	0.55865	-0.93486	1.53737
C	-3.92433	-0.02696	-1.05259
H	-4.99577	-0.16697	-0.89266
C	-3.12252	-1.29277	-0.73924
C	-3.7872	-2.16865	0.30908
H	-2.99299	-1.87161	-1.66263
C	-1.80093	0.28882	0.25835
H	-4.7437	-2.55486	-0.05679
H	-3.97039	-1.59545	1.22465
H	-3.14671	-3.0178	0.56281
Li	-0.05574	-1.89074	-0.39896
C	1.5107	-3.15109	0.01736
C	2.78337	-2.55464	0.59532
C	1.91744	-4.01678	-1.166
C	0.92422	-4.07568	1.07868
H	3.32108	-1.92037	-0.12692
H	3.50425	-3.34592	0.90426
H	2.60585	-1.93901	1.49241
H	1.06529	-4.54777	-1.61637
H	2.6522	-4.8022	-0.87204
H	2.39515	-3.43492	-1.96932
H	0.02832	-4.61102	0.72646
H	0.63921	-3.54269	2.00064
H	1.64865	-4.86346	1.39207

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***Exo* (*S*)-4**

Fe	1.56903	0.11174	0.0394
N	-2.09738	0.27288	1.07739
S	-2.18254	-0.38082	-1.47707
H	-2.95633	-2.25029	-0.17378
C	3.10437	-0.88471	0.94869

H	3.90078	-0.41445	1.50953
C	1.85326	-1.31442	1.47296
H	1.5248	-1.22054	2.4992
C	1.08459	-1.83608	0.39778
H	0.06355	-2.19147	0.46194
C	1.8574	-1.73077	-0.79094
H	1.53045	-2.00819	-1.78434
C	3.10718	-1.14293	-0.44997
H	3.90571	-0.902	-1.13866
C	1.78328	2.11854	0.41453
H	2.58331	2.56299	0.99102
C	1.80454	1.87118	-0.98702
H	2.6199	2.0975	-1.66052
C	0.588	1.23482	-1.3427
H	0.31283	0.88784	-2.33043
C	-0.19369	1.0894	-0.15388
C	0.55392	1.64009	0.93174
H	0.22803	1.64222	1.96261
C	-3.34239	-1.24401	-0.36381
H	-4.3227	-1.32237	-0.84044
C	-3.38189	-0.39559	0.91539
C	-4.48275	0.65223	0.8838
H	-3.54025	-1.05512	1.7785
C	-1.46438	0.39095	-0.015
H	-5.47095	0.18152	0.85656
H	-4.37559	1.28773	-0.00256
H	-4.42453	1.29033	1.76899

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***Endo* (*S*)-4-(*t*-BuLi)-ether**

Fe	2.61003	-0.47412	-0.20858
N	-0.841	1.36588	-0.10954
S	1.07351	3.15869	-0.19545
H	-1.03086	4.26885	-0.56892
C	4.42279	-0.57027	0.73026
H	5.37741	-0.47657	0.23011
C	3.64612	0.49856	1.25656
H	3.90221	1.54952	1.22856
C	2.44505	-0.05457	1.78377
H	1.61938	0.49988	2.21296
C	2.47956	-1.45947	1.58532
H	1.68875	-2.15417	1.83824
C	3.7	-1.77865	0.93062
H	4.0065	-2.76453	0.60804
C	2.9113	-0.50903	-2.23909
H	3.85835	-0.69537	-2.72712
C	1.95263	-1.49393	-1.86669
H	2.04761	-2.5626	-2.00763
C	0.8746	-0.84775	-1.21632
H	0.01779	-1.32632	-0.74643
C	1.1639	0.55342	-1.18571
C	2.4329	0.7571	-1.82011

H	2.93595	1.70741	-1.94495
C	-0.58448	3.75201	0.28481
H	-0.4949	4.45028	1.12036
C	-1.3621	2.49014	0.66794
C	-1.25831	2.16303	2.14898
H	-2.41853	2.62432	0.3976
C	0.35655	1.55553	-0.51613
H	-1.76251	2.9239	2.75409
H	-0.20678	2.11911	2.45524
H	-1.71038	1.18994	2.36828
Li	-1.98881	-0.35766	-0.07143
C	-1.79553	-2.25033	0.79941
C	-1.44706	-1.9546	2.25085
C	-0.88136	-3.36704	0.32662
C	-3.21032	-2.81165	0.77758
H	-2.14135	-1.23171	2.71422
H	-0.43496	-1.53259	2.36503
H	-1.48674	-2.8649	2.89624
H	-1.0771	-3.65867	-0.71859
H	-1.00652	-4.29204	0.93648
H	0.18693	-3.10642	0.3881
H	-3.95761	-2.10912	1.18139
H	-3.30538	-3.73883	1.39099
H	-3.5388	-3.08413	-0.23904
H	-5.59314	0.83357	1.90778
C	-4.68145	0.7713	1.30761
H	-4.24552	1.77379	1.24939
H	-3.98154	0.11071	1.83311
C	-4.99329	0.23158	-0.06132
H	-5.45073	-0.76779	0.01134
H	-5.70087	0.88408	-0.59784
O	-3.7939	0.13501	-0.81003
C	-3.99407	-0.42922	-2.09823
H	-4.58342	-1.35393	-1.99545
H	-4.57907	0.2741	-2.71166
C	-2.65114	-0.72277	-2.71322
H	-2.03193	0.18033	-2.75508
H	-2.12278	-1.49106	-2.13211
H	-2.76959	-1.09953	-3.73216

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***Exo* (*S*)-4-(*t*-BuLi)-ether**

Fe	2.60378	-0.40033	0.17955
N	-0.77625	1.32599	-0.24926
S	0.98147	3.2715	-0.07151
H	0.10792	3.19456	-2.31222
C	3.29437	-1.94818	-0.95919
H	3.30303	-2.98136	-0.63819
C	2.21579	-1.29368	-1.6155
H	1.26034	-1.73781	-1.86702
C	2.58519	0.06482	-1.80799
H	1.9582	0.83742	-2.23587

C	3.88766	0.25394	-1.27049
H	4.42936	1.1898	-1.23388
C	4.32719	-0.99364	-0.74592
H	5.26677	-1.17582	-0.24194
C	2.02011	-1.1936	1.98205
H	2.13222	-2.23289	2.26129
C	2.97651	-0.1591	2.18601
H	3.94089	-0.26898	2.66301
C	2.47025	1.0333	1.61236
H	2.97432	1.99069	1.57992
C	1.18189	0.73565	1.054
C	0.9131	-0.65127	1.28733
H	0.05981	-1.21166	0.91287
C	-0.31914	3.44936	-1.33769
H	-0.6742	4.48222	-1.35977
C	-1.4129	2.46797	-0.91475
C	-2.43293	3.10416	0.01761
H	-1.92597	2.09984	-1.81384
C	0.36246	1.62723	0.25404
H	-2.96169	3.91896	-0.48834
H	-1.93327	3.51442	0.90286
H	-3.16422	2.3606	0.34702
Li	-1.822	-0.51918	-0.18853
C	-1.63634	-2.60598	-0.47015
C	-0.55868	-3.46925	0.16422
C	-1.60404	-2.88044	-1.96747
C	-2.97046	-3.13188	0.0447
H	0.45548	-3.20838	-0.17794
H	-0.69993	-4.54889	-0.07315
H	-0.55315	-3.39793	1.26491
H	-2.40014	-2.35346	-2.51902
H	-1.74202	-3.96363	-2.1977
H	-0.65176	-2.58791	-2.43546
H	-3.8365	-2.61872	-0.40457
H	-3.07029	-3.03638	1.13823
H	-3.10733	-4.21497	-0.18292
H	-2.76645	-0.27258	3.63993
C	-2.6003	-0.19591	2.56249
H	-1.97136	0.68171	2.3749
H	-2.05765	-1.09393	2.24036
C	-3.91192	-0.08299	1.83282
H	-4.53493	-0.97571	1.99953
H	-4.48741	0.79576	2.17026
O	-3.65132	0.04546	0.44449
C	-4.82418	0.04549	-0.34702
H	-5.37672	-0.8917	-0.17459
H	-5.47308	0.87891	-0.02798
C	-4.42964	0.18314	-1.79221
H	-3.92814	1.14044	-1.96948
H	-3.75716	-0.63087	-2.08831
H	-5.31035	0.14	-2.43816

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***Endo* (*S*)-4-(*t*-BuLi)2TS**

Fe	-2.05246	-0.84448	-0.36689
N	0.94691	1.81294	0.18236
S	-1.21835	2.92448	-0.78529
H	-0.37496	4.87174	0.38098
C	-3.60538	-1.9968	0.31146
H	-3.80885	-3.00662	-0.01866
C	-2.75925	-1.62598	1.39123
H	-2.20149	-2.30773	2.01996
C	-2.72371	-0.2076	1.4571
H	-2.12689	0.38222	2.14191
C	-3.55488	0.29983	0.41944
H	-3.70901	1.34523	0.18599
C	-4.09856	-0.80582	-0.28754
H	-4.73933	-0.75077	-1.15746
C	-0.60497	-2.01478	-1.22063
H	-0.52797	-3.08401	-1.04281
C	-1.43154	-1.43223	-2.22939
H	-2.04832	-1.96395	-2.94283
C	-1.34998	-0.02744	-2.09327
H	-1.87305	0.70856	-2.69143
C	-0.45643	0.2406	-1.00311
C	0.01963	-0.99335	-0.43717
H	0.87303	-1.00811	0.68443
C	0.08314	4.05047	-0.17501
H	0.6262	4.45507	-1.03333
C	0.97418	3.17692	0.71081
C	0.52443	3.15975	2.16263
H	2.00725	3.54693	0.65718
C	-0.11439	1.55661	-0.49024
H	0.5894	4.15922	2.60443
H	1.14874	2.48164	2.75232
H	-0.51341	2.81286	2.23414
Li	2.31371	0.35014	0.34491
C	3.423	-0.60978	-1.23031
C	4.38425	0.54038	-0.96531
C	2.79545	-0.39724	-2.60195
C	4.24647	-1.89184	-1.29455
H	4.94297	0.42065	-0.02401
H	3.87524	1.52077	-0.92249
H	5.14728	0.64623	-1.76499
H	2.0909	-1.19986	-2.87928
H	3.55714	-0.36202	-3.41055
H	2.22579	0.54112	-2.65913
H	4.81384	-2.08007	-0.37109
H	4.98252	-1.88315	-2.12568
H	3.63866	-2.80234	-1.48759
H	2.94903	0.48623	2.4638
H	0.4415	0.17847	2.95114
Li	2.03492	-1.88079	-0.38716

C	3.01199	-0.61601	2.40115
C	0.61143	-0.90642	2.89687
H	3.87583	-0.86537	1.76797
H	3.26848	-0.94187	3.42647
C	1.71389	-1.24925	1.91216
H	0.84681	-1.25452	3.91958
C	1.87657	-2.76174	1.87554
H	2.76376	-3.09066	1.30452
H	2.00695	-3.20244	2.87988
H	0.98507	-3.2518	1.44423
H	-0.34173	-1.36524	2.60686

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***Endo*(*S*)-4-(*t*-BuLi)-etherTS**

Fe	2.30572	-0.61741	-0.31215
N	-0.94101	1.66428	0.03882
S	1.12597	3.05954	-0.78177
H	-0.87325	4.37331	-1.07211
C	4.29738	-0.88614	0.04508
H	5.01556	-1.18873	-0.70532
C	3.9171	0.45128	0.34716
H	4.29547	1.34634	-0.12902
C	2.91496	0.40186	1.35586
H	2.3903	1.25374	1.7707
C	2.67876	-0.96012	1.67844
H	1.94802	-1.32886	2.38543
C	3.52835	-1.75772	0.86503
H	3.5552	-2.83934	0.8479
C	1.97149	-1.21265	-2.24055
H	2.72143	-1.6586	-2.88214
C	1.08942	-1.904	-1.35551
H	1.07987	-2.98046	-1.21771
C	0.27913	-0.98366	-0.63526
H	-0.6008	-1.34654	0.3774
C	0.69495	0.31397	-1.10751
C	1.73737	0.17502	-2.08813
H	2.24937	0.97735	-2.60586
C	-0.32689	3.99983	-0.20138
H	0.0026	4.8467	0.40522
C	-1.15025	2.99487	0.60866
C	-0.77536	2.98395	2.08114
H	-2.21407	3.25168	0.51645
C	0.1766	1.56308	-0.5853
H	-0.98544	3.95382	2.54397
H	0.29167	2.76462	2.20131
H	-1.33676	2.21376	2.61699
Li	-1.84334	-0.193	0.05965
C	-1.4102	-1.7805	1.58191
C	-1.05741	-0.83917	2.72126
C	-0.60489	-3.06088	1.71863
C	-2.88484	-2.1444	1.68913
H	-1.74425	0.02162	2.7688

H	-0.04208	-0.42621	2.62074
H	-1.11497	-1.33292	3.71234
H	-0.87205	-3.78944	0.93831
H	-0.77392	-3.55674	2.69388
H	0.47553	-2.88022	1.62644
H	-3.55045	-1.26636	1.65153
H	-3.11186	-2.65259	2.64921
H	-3.20594	-2.83193	0.89252
H	-5.35157	1.86003	0.62671
C	-4.43135	1.38682	0.27432
H	-3.88615	2.10518	-0.34514
H	-3.81962	1.15315	1.15504
C	-4.75093	0.14673	-0.51449
H	-5.29669	-0.58649	0.10162
H	-5.38562	0.38621	-1.38204
O	-3.54601	-0.44145	-0.97322
C	-3.7833	-1.60235	-1.76137
H	-4.38233	-2.31385	-1.17041
H	-4.38305	-1.31187	-2.63815
C	-2.47159	-2.21004	-2.17074
H	-1.86177	-1.4945	-2.73171
H	-1.89675	-2.533	-1.29605
H	-2.64568	-3.08291	-2.80588

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***Endo*(*S*)-4-(*t*-BuLi)-TMEDA-TS**

Fe	-2.6911	-0.5376	0.32257
N	0.60865	1.52946	-0.33792
S	-1.35497	3.10176	0.42872
H	0.70366	4.35531	0.4135
C	-4.53525	-1.25455	-0.21014
H	-5.14665	-1.89704	0.40919
C	-4.5426	0.16799	-0.20241
H	-5.15857	0.79866	0.42479
C	-3.56108	0.6154	-1.12643
H	-3.29201	1.64738	-1.31475
C	-2.94403	-0.52834	-1.70493
H	-2.12167	-0.5187	-2.40941
C	-3.54807	-1.68374	-1.13843
H	-3.26422	-2.70826	-1.33936
C	-2.37917	-0.94647	2.30559
H	-3.14605	-1.28651	2.99074
C	-1.53321	-1.76841	1.49738
H	-1.58078	-2.85244	1.47061
C	-0.68291	-0.96941	0.68466
H	0.11705	-1.41002	-0.34248
C	-1.03735	0.38808	1.01422
C	-2.08024	0.40523	2.00738
H	-2.55377	1.27999	2.43749
C	0.07977	3.90059	-0.36201
H	-0.26378	4.67955	-1.04698
C	0.80658	2.76868	-1.09095

C	0.31586	2.56583	-2.51498
H	1.87782	3.00298	-1.11631
C	-0.47934	1.54439	0.34378
H	0.49404	3.45877	-3.12361
H	-0.75925	2.34915	-2.51897
H	0.83118	1.71846	-2.97767
Li	1.64107	-0.33324	-0.19279
C	0.90623	-2.05141	-1.49393
C	1.34183	-1.24231	-2.70326
C	-0.22965	-2.96143	-1.91832
C	2.03335	-2.94744	-1.0113
H	2.14296	-0.51538	-2.48906
H	0.50074	-0.66656	-3.11642
H	1.72661	-1.88413	-3.52574
H	-0.63733	-3.52535	-1.0655
H	0.09578	-3.7051	-2.673
H	-1.0625	-2.40108	-2.36129
H	2.91114	-2.39635	-0.6433
H	2.40556	-3.62104	-1.81294
H	1.69463	-3.59491	-0.18847
H	2.92458	-2.46347	1.66989
H	2.70015	-1.99457	3.37746
C	2.33356	-1.84106	2.34602
H	4.32734	-0.30705	2.86718
H	1.29423	-2.17762	2.28396
C	3.79703	0.02848	1.95484
N	2.41162	-0.4341	1.96312
H	4.63934	-1.52295	0.72172
H	3.78791	1.12415	1.9993
C	4.5787	-0.42774	0.74183
H	5.62038	-0.0605	0.83474
C	1.642	0.35802	2.91607
H	2.08494	0.31092	3.92768
H	0.61571	-0.01358	2.96587
N	3.99721	0.00697	-0.52772
H	4.67352	-1.69501	-1.56852
H	1.6102	1.4052	2.59517
C	4.73725	-0.605	-1.62512
H	5.80271	-0.31162	-1.60403
H	3.44444	1.94971	0.0855
C	4.0606	1.4534	-0.66999
H	5.09749	1.82988	-0.58567
H	4.31318	-0.29523	-2.5842
H	3.67284	1.73448	-1.65504

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***Endo*(*S*)-4-(*t*-BuLi)TS**

Fe	-1.03617	-1.29063	-0.0361
N	1.96293	1.10237	-0.50411
S	2.90105	-1.33968	-0.35371
H	4.68354	0.15043	-0.99473
C	-2.2385	-2.41962	1.17639

H	-2.99521	-3.10808	0.82512
C	-0.8705	-2.73	1.41328
H	-0.40194	-3.69514	1.27474
C	-0.21618	-1.53651	1.82071
H	0.84191	-1.43837	2.03008
C	-1.17545	-0.48636	1.8345
H	-0.97903	0.55637	2.05228
C	-2.42629	-1.03437	1.43647
H	-3.3456	-0.4787	1.30517
C	-1.36872	-1.84387	-1.98387
H	-1.96226	-2.69393	-2.2955
C	-1.84262	-0.51643	-1.76003
H	-2.87752	-0.20942	-1.86292
C	-0.78599	0.32139	-1.31133
H	-1.0332	1.46759	-0.62469
C	0.37419	-0.54257	-1.26368
C	0.01185	-1.87097	-1.67634
H	0.66639	-2.73258	-1.73046
C	4.08959	0.02166	-0.0858
H	4.75365	-0.23149	0.744
C	3.22552	1.24767	0.21728
C	2.93448	1.40908	1.70088
H	3.73817	2.14678	-0.14886
C	1.6596	-0.12566	-0.74208
H	3.85433	1.59717	2.26402
H	2.46408	0.50163	2.09693
H	2.24913	2.24488	1.86961
Li	0.40074	2.25366	-0.90895
C	-1.37086	2.86526	-0.04548
C	-0.57981	3.64831	0.98827
C	-2.74378	2.5334	0.48918
C	-1.51015	3.68331	-1.31727
H	0.43514	3.92895	0.64503
H	-0.45057	3.08324	1.92155
H	-1.06713	4.60746	1.25882
H	-3.31892	1.92733	-0.22656
H	-3.34444	3.4393	0.70069
H	-2.68861	1.96164	1.42581
H	-0.53973	3.96092	-1.7816
H	-2.02323	4.64954	-1.15651
H	-2.07616	3.13574	-2.085

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***Exo*(*S*)-4-(*t*-BuLi)$_2$TS**

Fe	-2.14887	-0.52083	-0.14877
N	1.28852	1.56351	-0.18624
S	-0.72063	3.24073	-0.35506
H	0.4542	3.66075	1.70065
C	-3.19227	-1.8576	1.00215
H	-3.33593	-2.90355	0.76694
C	-2.11598	-1.30711	1.75211
H	-1.32354	-1.86785	2.23476

C	-2.28577	0.10483	1.79686
H	-1.60801	0.8129	2.25654
C	-3.47183	0.4254	1.08487
H	-3.85306	1.42267	0.90932
C	-4.03178	-0.78646	0.59397
H	-4.9183	-0.87474	-0.01966
C	-1.38411	-1.51302	-1.78048
H	-1.44066	-2.58506	-1.93418
C	-2.39163	-0.59064	-2.17884
H	-3.32559	-0.82968	-2.67111
C	-1.98441	0.69872	-1.7611
H	-2.54151	1.61839	-1.89324
C	-0.71162	0.55712	-1.118
C	-0.32728	-0.83025	-1.10493
H	0.94418	-1.15941	-1.09532
C	0.70993	3.77483	0.64328
H	0.93266	4.82461	0.438
C	1.85484	2.84742	0.23127
C	2.69293	3.40633	-0.90607
H	2.50012	2.67284	1.10392
C	0.06259	1.64695	-0.54665
H	3.20338	4.32567	-0.6023
H	2.05895	3.62728	-1.77202
H	3.44997	2.67966	-1.21775
Li	2.32408	-0.16116	0.05641
C	2.31927	-1.76757	-1.53508
C	3.78405	-1.48309	-1.22916
C	2.08125	-1.47378	-3.00582
C	2.02292	-3.22776	-1.24876
H	4.07222	-1.77924	-0.21123
H	4.05067	-0.41784	-1.36224
H	4.45953	-2.03242	-1.91208
H	1.04986	-1.69243	-3.3117
H	2.74621	-2.07065	-3.65805
H	2.2645	-0.41385	-3.23691
H	2.31676	-3.5227	-0.22732
H	2.55709	-3.91944	-1.92643
H	0.95028	-3.45991	-1.37713
H	3.56772	0.60178	1.7494
H	1.04939	0.9599	2.56693
Li	0.73144	-1.83745	0.60065
C	3.4333	-0.40582	2.19011
C	1.13342	-0.0721	2.94216
H	4.18875	-1.0581	1.73181
H	3.72909	-0.28864	3.25311
C	2.01174	-0.94435	2.05301
H	1.53175	-0.00662	3.97763
C	2.01399	-2.35116	2.64506
H	2.72905	-3.01731	2.13971
H	2.27926	-2.36239	3.72311
H	1.02471	-2.85239	2.60065

H	0.1094	-0.45663	3.0379

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Exo (*S*)-4-(*t*-BuLi)-etherTS

Fe	2.50881	-0.27446	0.23416
N	-0.99187	1.30412	-0.42715
S	0.66078	3.26747	0.11331
H	-0.0651	3.43709	-2.17558
C	3.79874	-1.49769	-0.77862
H	4.03707	-2.51218	-0.48729
C	2.72964	-1.1067	-1.63004
H	2.01666	-1.7727	-2.09659
C	2.72974	0.31057	-1.71251
H	2.00456	0.91454	-2.24536
C	3.80488	0.80042	-0.91934
H	4.04717	1.84173	-0.75194
C	4.46674	-0.31988	-0.34325
H	5.30525	-0.28051	0.33924
C	1.6449	-1.35977	1.75696
H	1.81218	-2.41897	1.91988
C	2.48029	-0.32594	2.27981
H	3.35649	-0.45684	2.90266
C	1.99588	0.90879	1.78814
H	2.42232	1.88715	1.97767
C	0.85045	0.60839	0.96952
C	0.61602	-0.81532	0.93954
H	-0.2844	-1.64049	0.24963
C	-0.56461	3.5555	-1.20939
H	-0.96288	4.57005	-1.13157
C	-1.63745	2.48927	-0.98581
C	-2.73129	2.96041	-0.03757
H	-2.0854	2.22204	-1.9535
C	0.09565	1.57501	0.19909
H	-3.3061	3.78228	-0.47741
H	-2.2885	3.31191	0.90172
H	-3.41239	2.13718	0.19911
Li	-1.6823	-0.59406	-0.16435
C	-1.03256	-2.63101	-0.60963
C	-2.35279	-3.30369	-0.26294
C	0.06682	-3.66802	-0.47219
C	-1.06337	-2.14109	-2.04998
H	-2.36736	-3.65251	0.77986
H	-2.53831	-4.19593	-0.89597
H	-3.22643	-2.64776	-0.39371
H	1.06237	-3.24295	-0.6596
H	-0.07152	-4.51249	-1.17418
H	0.08653	-4.09311	0.54124
H	-0.13412	-1.61905	-2.32262
H	-1.88664	-1.43271	-2.25647
H	-1.19914	-2.96608	-2.77758
H	-2.56629	-0.62451	3.65794
C	-2.44288	-0.48762	2.58069

H	-1.96508	0.48429	2.41443
H	-1.76435	-1.27178	2.22355
C	-3.77714	-0.55397	1.89035
H	-4.2594	-1.53345	2.04112
H	-4.46255	0.21938	2.2741
O	-3.59204	-0.34309	0.49692
C	-4.81737	-0.33132	-0.21431
H	-5.34301	-1.28542	-0.04532
H	-5.4548	0.47038	0.19434
C	-4.54834	-0.11466	-1.67813
H	-3.97882	0.8077	-1.83651
H	-3.98549	-0.95128	-2.10308
H	-5.48935	-0.03038	-2.22811

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***Exo* (*S*)-4-(*t*-BuLi)-TMEDA-TS**

Fe	2.78927	-0.41003	0.30436
N	-0.61996	1.46476	-0.4781
S	1.32421	3.17571	-0.01604
H	0.72736	3.20045	-2.34547
C	3.65	-1.69832	-1.03092
H	3.40163	-2.74921	-1.09558
C	2.98523	-0.64461	-1.71573
H	2.14089	-0.75114	-2.38512
C	3.5733	0.58264	-1.30381
H	3.25827	1.57318	-1.60674
C	4.59641	0.2902	-0.36344
H	5.20403	1.01608	0.16043
C	4.64468	-1.12186	-0.19509
H	5.29803	-1.66	0.47853
C	1.70542	-1.52439	1.64761
H	1.79084	-2.60169	1.74853
C	2.53735	-0.58263	2.32894
H	3.32984	-0.81052	3.03112
C	2.18706	0.71266	1.87434
H	2.64661	1.64629	2.17766
C	1.11871	0.54116	0.92339
C	0.80724	-0.85691	0.7694
H	0.06114	-1.43864	-0.21582
C	0.22435	3.52598	-1.42947
H	0.01894	4.59741	-1.48925
C	-1.0298	2.70361	-1.14469
C	-2.00257	3.47899	-0.26766
H	-1.51747	2.44069	-2.09372
C	0.50013	1.58959	0.13647
H	-2.3996	4.34853	-0.80186
H	-1.49772	3.83105	0.63898
H	-2.84634	2.85519	0.03824
Li	-1.53834	-0.4563	-0.18674
C	-0.69854	-2.2755	-1.26798
C	0.46371	-3.16866	-1.6512
C	-1.30608	-1.71	-2.53967

C	-1.69528	-3.15149	-0.52969
H	1.19814	-2.65112	-2.28083
H	0.12771	-4.05842	-2.22147
H	0.99824	-3.54035	-0.76381
H	-2.15232	-1.02701	-2.36215
H	-1.69369	-2.50615	-3.21353
H	-0.56219	-1.14204	-3.11676
H	-2.57283	-2.60896	-0.14922
H	-1.21708	-3.62818	0.33988
H	-2.09105	-3.97152	-1.16626
N	-2.44077	-0.491	1.87428
N	-3.99725	-0.19078	-0.70527
C	-3.89746	-0.5594	1.74802
C	-4.44461	0.27413	0.60686
H	-4.12647	1.31676	0.72707
H	-5.55109	0.28309	0.66265
H	-4.38298	-0.24524	2.69185
H	-4.17324	-1.61009	1.60086
C	-1.96598	-1.6026	2.69482
H	-0.87652	-1.55682	2.77799
H	-2.23232	-2.55463	2.22794
H	-2.40437	-1.56815	3.70864
C	-2.03289	0.75885	2.51026
H	-2.47582	0.85537	3.51816
H	-0.94279	0.78149	2.60463
H	-2.33295	1.62288	1.912
C	-4.71348	-1.39959	-1.09766
H	-4.30533	-1.78904	-2.03511
H	-5.79072	-1.19353	-1.23808
H	-4.61011	-2.18556	-0.34737
C	-4.24269	0.82666	-1.71623
H	-3.89576	0.47216	-2.69194
H	-3.70483	1.74671	-1.47557
H	-5.31888	1.06694	-1.80353

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***Exo*(*S*)-4-(*t*-BuLi)TS**

Fe	-1.46913	-0.89773	0.07028
N	2.15983	0.32341	0.16973
S	2.24337	-2.29381	0.16541
H	4.326	-1.92131	-1.02115
C	-2.8784	-0.28804	-1.27321
H	-3.62504	0.46712	-1.06501
C	-1.57245	-0.04575	-1.78274
H	-1.15091	0.92312	-2.01817
C	-0.89327	-1.29214	-1.85219
H	0.13627	-1.43916	-2.1555
C	-1.77447	-2.30509	-1.38546
H	-1.53822	-3.35644	-1.28828
C	-3.00415	-1.68365	-1.02896
H	-3.87029	-2.18009	-0.61263
C	-1.83554	0.11996	1.81723

H	-2.69543	0.75946	1.98212
C	-1.82042	-1.28702	2.05513
H	-2.63947	-1.88254	2.43778
C	-0.55769	-1.78252	1.65521
H	-0.23014	-2.81444	1.69405
C	0.19775	-0.65998	1.16908
C	-0.59758	0.54708	1.26464
H	-0.51079	1.70946	0.56981
C	3.7918	-1.40705	-0.22015
H	4.42123	-1.38145	0.67761
C	3.3425	-0.00699	-0.62004
C	4.43234	1.02795	-0.44917
H	3.02305	-0.03029	-1.67749
C	1.49574	-0.7186	0.5315
H	5.314	0.77332	-1.04547
H	4.73487	1.09137	0.60221
H	4.08525	2.01616	-0.7673
Li	1.13184	1.94807	0.64566
C	-0.40817	3.14174	-0.02117
C	-1.86797	3.32185	-0.3641
C	0.46804	3.59409	-1.17687
C	-0.08128	3.95159	1.22124
H	-2.14548	2.77529	-1.27574
H	-2.1339	4.38331	-0.53399
H	-2.51898	2.95375	0.44274
H	1.55175	3.49439	-0.97094
H	0.32085	4.66437	-1.42879
H	0.27128	3.02172	-2.09327
H	0.97733	3.86636	1.54852
H	-0.69706	3.63826	2.07692
H	-0.2376	5.03759	1.08344