

SUPPORTING INFORMATION

Catalytic Reduction of Carbon Dioxide by a Zinc Hydride Compound, [Tptm]ZnH, and Conversion to the Methanol Level

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Table S1: Cartesian Coordinates for Geometry Optimized Structures

[Tptm]Zn(O ₂ CH)				
atom	x	y	z	
Zn	-0.0910172961	-1.1040502130	-0.0023861772	
S	-0.3533810089	2.1473490132	-0.0606499548	
S	-1.0520155344	0.7636623420	2.4943547112	
S	-2.8518554105	0.4610109645	0.0885642910	
O	0.9864482540	-2.9762426897	-0.7238288537	
O	-1.1697300714	-2.5576785168	-1.0633527144	
N	1.2005219405	0.1715344347	-1.1369401977	
N	0.3678377520	-1.5310849472	2.0456632815	
N	-3.0517707141	2.8613923698	1.2956576581	
C	-1.1630224347	0.6824308229	0.6728646949	
C	-0.1436761503	-3.2928922069	-1.1894262047	
C	0.9576113718	1.4893581727	-1.0605041367	
C	1.7420340932	2.4123753570	-1.7797830897	
H	1.5245493285	3.4728438255	-1.7050291350	
C	2.7754825519	1.9431387567	-2.5715041107	
H	3.3886610795	2.6423841827	-3.1332071406	
C	3.0225230485	0.5641863300	-2.6445426940	
H	3.8226666044	0.1617847371	-3.2555013628	
C	2.2098633928	-0.2825171728	-1.9114340934	
H	2.3336099584	-1.3613593194	-1.9168887771	
C	-0.1069661928	-0.6673685104	2.9569611032	
C	0.1285171730	-0.8657466599	4.3318038371	
H	-0.2671180989	-0.1555493631	5.0505677843	
C	0.8610228426	-1.9680118159	4.7369249826	

H	1.0497709332	-2.1342676710	5.7938742817
C	1.3543012481	-2.8650525093	3.7775965807
H	1.9310855048	-3.7386584651	4.0590471307
C	1.0818550275	-2.6061574068	2.4454542814
H	1.4233920847	-3.2528477283	1.6427232304
C	-3.7210205569	1.9369262908	0.6079640342
C	-5.0783591930	2.0668426062	0.2656435515
H	-5.5805908564	1.2858215903	-0.2968665186
C	-5.7470128938	3.2155506378	0.6640618720
H	-6.7964650809	3.3502982429	0.4161257670
C	-5.0537153412	4.1945713549	1.3851779098
H	-5.5408553430	5.1069929495	1.7132260780
C	-3.7124380192	3.9665127672	1.6728398909
H	-3.1310287669	4.6978647221	2.2309306831
H	-0.2549731770	-4.2476605908	-1.7310879882

[Tptm]ZnH(CO ₂) (TS)			
atom	x	y	z
Zn	7.0202521610	4.4312491981	6.0158816755
H	6.5539146074	5.1269597177	7.5050011244
S	6.5572403454	4.7434576519	2.8277331798
S	6.3353887141	1.9937004396	3.9986418739
S	4.2193569089	4.0603493718	4.6110763808
N	8.1734820380	5.7601403181	4.7942160681
N	7.8544493356	2.4698979722	6.2298584241
N	4.0615368352	3.0281136056	2.1323614547
C	5.9582140708	3.7645517227	4.2493198859

C	7.8206422987	5.7972015008	3.4981665906
C	8.4467670042	6.6856005156	2.6021883344
H	8.1412988846	6.6987081491	1.5611210641
C	9.4384390324	7.5284734956	3.0720473779
H	9.9278409905	8.2217657673	2.3938589596
C	9.8031397544	7.4810836149	4.4251823425
H	10.5755924279	8.1254266707	4.8293633909
C	9.1449357567	6.5841265728	5.2470088399
H	9.3736532351	6.4940846456	6.3042702280
C	7.4287253809	1.5654878643	5.3316900734
C	7.8393486774	0.2202063257	5.4083138147
H	7.4770389300	-0.4920339677	4.6743149167
C	8.6941435547	-0.1664386710	6.4254580369
H	9.0161223639	-1.2013070846	6.4998278987
C	9.1361304564	0.7841983942	7.3566667652
H	9.8054503165	0.5187344424	8.1670531296
C	8.6908183379	2.0866131460	7.2203660616
H	8.9915123782	2.8743519854	7.9039047614
C	3.3461554389	3.5113309550	3.1464974974
C	1.9448408421	3.6108748716	3.1217976623
H	1.4055405398	4.0118383053	3.9744008647
C	1.2801698865	3.1833379843	1.9806878757
H	0.1967504803	3.2450894576	1.9246601307
C	2.0208770705	2.6738481620	0.9081161982
H	1.5376852367	2.3298198484	-0.0004189888
C	3.4044237711	2.6188245582	1.0366477330
H	4.0240187906	2.2309087995	0.2306159041
C	7.6681169468	5.5164082050	8.6250870558

O	7.0104890611	5.9698318987	9.5019098835
O	8.7370471306	5.2022088417	8.1542028508

[Tptm]ZnH			
atom	x	y	z
Zn	6.9810955023	4.4952423273	6.0854769244
H	6.7396294630	5.1734253021	7.5572571645
S	6.5882891511	4.7216683496	2.8207328421
S	6.3315736490	2.0024310313	4.0289659835
S	4.2375168357	4.0969212431	4.6067570838
N	8.2123267470	5.7363703498	4.7662931342
N	7.9033866354	2.5121092931	6.2020291446
N	4.0558647853	3.0303755618	2.1421126629
C	5.9760460402	3.7807936154	4.2646313430
C	7.8850053412	5.7449733187	3.4649508819
C	8.5575369675	6.5817036218	2.5508077554
H	8.2729104682	6.5694757259	1.5037779857
C	9.5675280567	7.4069857720	3.0120441131
H	10.0945342604	8.0587898776	2.3209170868
C	9.8998718729	7.3990469706	4.3749395229
H	10.6805468607	8.0366479892	4.7742249811
C	9.1911932148	6.5516261553	5.2083663784
H	9.3884576291	6.5109553243	6.2764401840
C	7.4897046156	1.5992763788	5.3095893861
C	7.9554600522	0.2692555730	5.3597661546
H	7.6050318087	-0.4492569069	4.6259803770
C	8.8504390595	-0.0929498136	6.3506981268

H	9.2178669072	-1.1139531870	6.4040384912
C	9.2729866759	0.8640976366	7.2853094059
H	9.9677487619	0.6159312323	8.0797425704
C	8.7678892321	2.1472109897	7.1702998623
H	9.0425369083	2.9298070883	7.8727405069
C	3.3528488753	3.5391251364	3.1526440132
C	1.9525944139	3.6593125337	3.1312445884
H	1.4233043657	4.0806443828	3.9803290636
C	1.2763275850	3.2261390986	1.9993640093
H	0.1936416362	3.3036645700	1.9470704607
C	2.0045170631	2.6903956147	0.9308461786
H	1.5122682064	2.3412782129	0.0290675027
C	3.3876646313	2.6161406107	1.0552074535
H	3.9977012404	2.2074203027	0.2520122381

[Tptm]ZnH[HCO ₂ Si(OCH ₃) ₃] (TS)			
atom	x	y	z
Zn	7.1950949237	3.8287700823	6.1164551866
H	6.3391169530	4.1463777917	7.6265833572
S	6.5710749859	4.9355671092	3.1182235848
S	6.5508475752	1.9686106782	3.5187979704
S	4.3709521150	3.6613280357	4.7451559972
N	8.1229349054	5.5629692526	5.2876489949
N	8.0786982541	1.9087592613	5.7930320657
N	4.0843842709	3.3337791084	2.0870603481
C	6.0950752600	3.5787635418	4.2360235328
C	7.7358768061	5.9050858932	4.0486031238

C	8.2415192471	7.0629050146	3.4264052454
H	7.9103973803	7.3206375712	2.4256882771
C	9.1496554223	7.8520410648	4.1106254309
H	9.5468091476	8.7498403468	3.6449433696
C	9.5497143640	7.4849140738	5.4033616085
H	10.2611579912	8.0775790738	5.9675904417
C	9.0129182711	6.3332814992	5.9527166489
H	9.2663891062	5.9744544398	6.9457731200
C	7.7078838829	1.2672740873	4.6733757518
C	8.2267149261	-0.0046176799	4.3637622805
H	7.9106843557	-0.5039241555	3.4536362004
C	9.1319845799	-0.5922893842	5.2307221371
H	9.5397086864	-1.5737463398	5.0048443928
C	9.5172133232	0.0868495864	6.3955014169
H	10.2256116959	-0.3408429270	7.0958964974
C	8.9666818427	1.3341711508	6.6350870018
C	3.4256102565	3.4870914666	3.2347963135
C	2.0229609451	3.5235226959	3.3179439652
H	1.5320135476	3.6503598055	4.2780384003
C	1.2941144990	3.3946990714	2.1441706779
H	0.2079515384	3.4189498098	2.1701379318
C	1.9748882600	3.2345430413	0.9318678083
H	1.4413346891	3.1314884295	-0.0073006402
C	3.3650649679	3.2107539043	0.9613221290
H	3.9387264568	3.0882498001	0.0446776778
H	9.2125965524	1.9336915674	7.5065255418
O	8.6493995244	4.0581049003	8.0268437951
C	7.5907145837	4.2821871348	8.6688911978

O	7.3832293348	5.5646935096	9.1329760477
H	7.1398206467	3.5190527807	9.3191930653
Si	6.3144928833	6.0221470948	10.3420894535
O	5.7998940072	7.5258798400	9.9377862091
O	7.0753375312	5.9423198217	11.7917233223
O	5.0439656033	5.0126760314	10.4972019422
C	3.8895543025	5.0153131900	9.6575836993
C	6.4375389930	8.4729861400	9.0915908933
H	3.1198058347	4.4164933173	10.1521057402
H	4.1175444856	4.5704266157	8.6825194488
H	3.5101066334	6.0321581010	9.5094440651
H	5.6670425226	9.1157791692	8.6553669001
H	6.9940055547	7.9851527254	8.2844540848
H	7.1263712728	9.1031988053	9.6681546591
C	8.3827071959	6.4347527779	12.0517843985
H	8.7187359439	6.0155184851	13.0044831520
H	8.3829561176	7.5291121731	12.1371702508
H	9.0907052826	6.1391765660	11.2680754250



atom	x	y	z
Zn	4.0685928807	2.9610302926	6.2910673809
S	5.2749036347	3.3380761535	3.3162793129
S	7.1642279490	2.4604614818	5.4669830571
O	3.0050589711	3.4505615053	7.7961036576
N	3.0139564493	2.3727861142	4.5277962945
N	5.2704493681	1.3788455463	7.1162776858

C	5.7496921257	3.5531310934	5.0673816532
C	3.6592740089	2.5941823497	3.3707999656
C	3.0761185915	2.2554602386	2.1365719171
H	3.6203104567	2.4429644195	1.2166135785
C	1.8131008289	1.6867720351	2.1256724540
H	1.3478518697	1.4184220435	1.1810667187
C	1.1434653912	1.4660452679	3.3357511313
H	0.1497878118	1.0339663243	3.3660246220
C	1.7765399073	1.8283016310	4.5130664661
H	1.2940582476	1.7113925177	5.4788233409
C	6.5439321344	1.3371903584	6.6959022815
C	7.4516200222	0.3980125678	7.2243150290
H	8.4767953547	0.3843781697	6.8688864769
C	7.0152766930	-0.4847111880	8.1970100780
H	7.7038678095	-1.2132983351	8.6157688116
C	5.6863895746	-0.4253923939	8.6427273708
H	5.3132304459	-1.0932346243	9.4107271741
C	4.8556822390	0.5260706120	8.0763479163
H	3.8216486103	0.6410335633	8.3866861831
S	6.0553489558	5.2725628220	5.5030395564
N	7.9583510384	4.8947841943	3.6391434204
C	7.4351011377	5.7839847539	4.4807952496
C	7.9124941362	7.0994423029	4.6069564395
H	7.4527358511	7.7878569912	5.3093440091
C	8.9823028212	7.4847049531	3.8109592174
H	9.3788820510	8.4940393475	3.8805274932
C	9.5407944831	6.5596267341	2.9218271186
H	10.3775332060	6.8230539374	2.2832113304

C	8.9919282251	5.2826311581	2.8767423057
H	9.3914594254	4.5282351011	2.2019168375
C	2.4563127882	4.6370766657	8.1807003937
O	1.0429685127	4.5130482261	8.4832376492
H	2.5477602024	5.4345450210	7.4192107936
H	2.8923769896	5.0100019124	9.1215921015
Si	-0.0027374559	3.6738869766	7.5485664810
O	0.0609302753	4.0737798530	5.9428577166
O	-1.4782138656	4.0374823911	8.1979373067
O	0.2126030356	2.0312794634	7.5063024463
C	0.6966169695	1.3112728343	8.6369188028
H	1.6485502817	1.7310847318	8.9766245014
H	0.8390147123	0.2678061518	8.3352455223
H	-0.0249557506	1.3323925195	9.4639071298
C	-2.6613753204	3.3439504523	7.8304975738
H	-2.5009816847	2.2594471239	7.7868854290
H	-3.0329618549	3.6769565889	6.8520830391
H	-3.4293608354	3.5550444592	8.5810198980
C	-0.2346847706	5.3901111524	5.4911584594
H	-1.2736515817	5.6676012369	5.7103746714
H	-0.0857658046	5.4187644534	4.4075743067
H	0.4256802225	6.1346466857	5.9534379932

[Tptm]ZnOCH ₂ OSi(OMe) ₃ (TS)			
atom	x	y	z
Zn	3.9870006301	3.2646340346	6.2822766650
S	5.1418117072	3.4429620691	3.2193056105
S	7.0119859898	2.4328468316	5.3100047058

O	3.7741081566	5.1540607138	7.2641874081
N	2.9275742397	2.5168080225	4.5449079458
N	5.2544442032	1.8572705759	7.3196756921
C	5.6989242032	3.6560395597	4.9387186097
C	3.5187311693	2.7419318988	3.3582448275
C	2.8796138364	2.4063840512	2.1485944942
H	3.3821013556	2.6080214102	1.2080114211
C	1.6277321611	1.8198710272	2.1860770454
H	1.1214039416	1.5575461482	1.2611780384
C	1.0288081990	1.5589575198	3.4261341997
H	0.0552511858	1.0884970075	3.5032595751
C	1.7114188876	1.9238469727	4.5728243159
H	1.2880999480	1.7332028635	5.5522188183
C	6.4532249219	1.6025850501	6.7714918010
C	7.3267063347	0.6566477575	7.3460712483
H	8.2915526892	0.4714538167	6.8851951688
C	6.9363037728	-0.0109981089	8.4928942439
H	7.5994645690	-0.7415159605	8.9480646187
C	5.6856735826	0.2677600496	9.0645173739
H	5.3499049323	-0.2298208113	9.9674950350
C	4.8816347173	1.2068265154	8.4430222710
H	3.9012226742	1.4819779179	8.8192285498
S	6.2266870354	5.3456969148	5.2765918702
N	7.9772003240	4.6577581132	3.3396552092
C	7.6193582496	5.6216871895	4.1886934274
C	8.2906929613	6.8550257129	4.2728217347
H	7.9652378317	7.6092678426	4.9827431398
C	9.3711938029	7.0737226165	3.4309559017

H	9.9121991420	8.0154617540	3.4700256353
C	9.7553098031	6.0678197381	2.5366464525
H	10.5958163391	6.1997975922	1.8631701917
C	9.0256606131	4.8844189006	2.5338644085
H	9.2854421399	4.0726124245	1.8570049610
C	3.2526950311	4.7892035982	8.3480747292
O	2.4669801839	3.0859971041	7.7906422191
H	2.3404089053	5.2774068113	8.7231465237
H	3.8431453829	4.2881832002	9.1293761889
Si	0.8676475772	2.8960769496	7.9943589433
O	-0.0689076155	3.7376379991	6.9240622502
O	0.5238917470	3.3376744422	9.5576047553
O	0.3625248228	1.3405965580	7.7051305996
C	0.8461052804	0.2373627956	8.4559877545
H	1.8622679244	-0.0426276330	8.1481075006
H	0.1848203081	-0.6163689513	8.2765476197
H	0.8552363169	0.4478151290	9.5337170154
C	-0.8114337621	3.3665084361	10.0481821350
H	-1.2704864134	2.3697664423	10.0250371361
H	-1.4420707145	4.0463929722	9.4617720073
H	-0.7875721830	3.7156446714	11.0849565749
C	0.1238774349	5.1110510134	6.6109630247
H	-0.2577633139	5.7586004638	7.4121550554
H	-0.4356336774	5.3342820391	5.6973174063
H	1.1803508851	5.3517803412	6.4396245856

[Tptm]ZnOSi(OCH ₃) ₃			
atom	x	y	z
Zn	3.6640169504	3.4907744447	5.8317839117
S	6.1800958537	3.3586592260	3.7821271768
S	5.9684156522	1.3571298599	6.0470750859
O	1.9025026000	2.8957360991	6.2526469743
N	3.4905326138	3.7972127191	3.7146101536
N	8.5012772779	1.9666326274	5.3682768858
C	5.7670945454	3.0754490228	5.5481578271
C	4.6249633028	3.7234314092	3.0051282623
C	4.6195799485	3.9160134711	1.6099987271
H	5.5493253912	3.8520828277	1.0542143065
C	3.4164294224	4.1734859193	0.9745059003
H	3.3944061426	4.3237051896	-0.1013589470
C	2.2302596846	4.2253933980	1.7220475659
H	1.2701046463	4.4078830696	1.2531031351
C	2.3176251223	4.0259912212	3.0896030171
H	1.4453507546	4.0267268124	3.7369216413
C	7.7025629247	0.9888059094	5.7922696762
C	8.1522294114	-0.3177906976	6.0471454479
H	7.4602154260	-1.0816743189	6.3880707181
C	9.4968670986	-0.5965474743	5.8457667614
H	9.8808737154	-1.5961105779	6.0309317040
C	10.3466816126	0.4221154193	5.3999867237
H	11.4031119485	0.2427263457	5.2289313884
C	9.7982210084	1.6805749558	5.1774069846
H	10.4180765902	2.5043525940	4.8291153851

S	6.7278697817	4.2341910773	6.5848704702
N	4.2007901575	5.1695528312	7.0681978348
C	5.5138325047	5.3184103877	7.3007903922
C	5.9913994440	6.3432624574	8.1402232052
H	7.0584158900	6.4424191045	8.3114611640
C	5.0831652422	7.2018758251	8.7351168355
H	5.4357887017	7.9968775358	9.3863782663
C	3.7117094488	7.0331942008	8.4967379738
H	2.9711908500	7.6806450793	8.9522680776
C	3.3164607970	6.0018092899	7.6617247754
H	2.2667688862	5.8006661208	7.4635263824
Si	0.9397322769	3.0712543947	7.5126672503
O	1.7807690315	3.0356736911	8.9433286427
O	-0.2374615113	1.9012576564	7.4719156735
O	0.1789532139	4.5710414518	7.5576911757
C	-0.7801283440	4.9424071198	6.5820480555
H	-0.3036937841	5.1868197732	5.6215198068
H	-1.3130512805	5.8326455900	6.9342416750
H	-1.5118364136	4.1434908274	6.4070226375
C	-1.0380006898	1.5770808081	8.5932782933
H	-1.8135795198	0.8735059987	8.2725259211
H	-1.5361989907	2.4604712815	9.0191789596
H	-0.4461147510	1.0985829686	9.3848996790
C	1.4055103186	3.6637449189	10.1556577406
H	0.6721696942	3.0619110910	10.7102205427
H	0.9755107660	4.6576490261	9.9841942877
H	2.2982845686	3.7682158676	10.7818925549

CO ₂			
atom	x	y	z
O	-0.0153867266	1.1695331574	0.0000000000
C	-0.0001351702	-0.0000080196	0.0000000000
O	0.0154881365	-1.1695271408	0.0000000000

H ₂ CO			
atom	x	y	z
O	0.0000000000	0.0000000000	-0.6034832953
C	0.0000000000	0.0000000000	0.6031349701
H	0.0000000000	0.9379638015	1.1981465361
H	0.0000000000	-0.9379638015	1.1981465361

HCO ₂ Si(OMe) ₃			
atom	x	y	z
O	0.0888369737	0.1820106340	-1.5982504207
C	-0.1663903780	0.0978262404	-0.4290374685
O	0.3325647888	0.9549604964	0.4975060380
H	-0.8316983319	-0.6689156808	0.0033215976
Si	0.0829083122	0.8706388959	2.1666195675
O	0.0528380668	2.4192709151	2.6851772284
O	1.2457625203	-0.0553310024	2.8403578929
O	-1.3182900423	0.1113196207	2.5127634719
C	-2.6021576797	0.7304901721	2.5436171939
C	0.5632039098	3.5896788235	2.0523425333

C	2.6460296894	0.1765833858	2.7212111395
H	-3.2831399296	0.0587046624	3.0717441410
H	-2.9857123341	0.8900904633	1.5281583611
H	-2.5682971524	1.6918710843	3.0658146158
H	3.1640165352	-0.6712035428	3.1758919599
H	2.9401770159	1.0908702097	3.2505633795
H	2.9535930785	0.2549085468	1.6716987150
H	-0.0904610210	4.4284713845	2.3076334746
H	0.5971600975	3.4782238472	0.9643607914
H	1.5710261845	3.8087750138	2.4222652170

Table S2. Comparison of Calculated {[Tptm]Zn} Bond Lengths with Experimentally Determined values in [Tptm]ZnX and Related Compounds in the Literature.

Compound	$d(\text{Zn-C})/\text{\AA}$	$d(\text{Zn-N})/\text{\AA}$	$d(\text{Zn-N})/\text{\AA}$	Ref
Calculated				
[Tptm]ZnO ₂ CH	2.190	2.142	2.141	
[[Tptm]ZnH(OCO)] [‡]	2.166	2.142	2.142	
[Tptm]ZnH	2.199	2.190	2.190	
[[Tptm]ZnH{OCHOSi(OMe) ₃ }] [‡]	2.193	2.134	2.138	
[Tptm]ZnOCH ₂ OSi(OMe) ₃	2.162	2.137	2.151	
[[Tptm]Zn{OCH ₂ OSi(OMe) ₃ }] [‡]	2.211	2.160	2.168	
[Tptm]ZnOSi(OMe) ₃	2.162	2.146	2.153	
Experimental				
[Tptm]ZnH	2.105	2.076	2.078	1
[Tptm]ZnMe #1	2.095	2.097	2.103	1
[Tptm]ZnMe #2	2.098	2.077	2.101	1
[Bptm ^{STol}]ZnCl	2.059	2.024	2.035	1
[Bptm ^{STol}]ZnBr	2.078	2.035	2.045	2
[Bptm ^{STol}]ZnI	2.075	2.037	2.046	2
[Bptm ^{STol}]ZnO ₂ CH	2.076	2.017	2.029	2
[Bptm ^{STol}]ZnN(SiMe ₃) ₂	2.100	2.069	2.079	2
	2.078	2.061	2.081	2

Table S3: Thermodynamic Data for Geometry Optimized Structures

Compound	G_{298K} (kcal mol ⁻¹)	H (kcal mol ⁻¹)
[Tptm]ZnH	-1281211.578	-1281164.369
[Tptm]ZnO ₂ CH	-1399573.517	-1399522.073
[[Tptm]ZnH(OCO)] [‡]	-1399536.987	-1399484.844
[[Tptm]ZnH{OCHOSi(OMe) ₃ }] [‡]	-1798319.852	-1798252.691
[Tptm]ZnOCH ₂ OSi(OMe) ₃	-1798351.418	-1798282.775
[[Tptm]Zn{OCH ₂ OSi(OMe) ₃ }] [‡]	-1798348.456	-1798278.779
[Tptm]ZnOSi(OMe) ₃	-1726513.455	-1726446.196
CO ₂	-118339.832	-118324.580
HCO ₂ Si(OMe) ₃	-517129.649	-517093.636
CH ₂ O	-71846.746	-71831.170

Table S4: ΔG and ΔH Data for Transformations

Transformation	ΔG_{298K} (kcal mol ⁻¹)	ΔH (kcal mol ⁻¹)
[Tptm]ZnH + CO ₂ → [[Tptm]ZnH(OCO)] [‡]	14.423	4.105
[Tptm]ZnH + CO ₂ → [Tptm]ZnO ₂ CH	-22.107	-33.124
[Tptm]ZnH + HCO ₂ Si(OMe) ₃ → [[Tptm]ZnH{OCHOSi(OMe) ₃ }] [‡]	21.374	5.315
[Tptm]ZnH + HCO ₂ Si(OMe) ₃ → [Tptm]ZnOCH ₂ OSi(OMe) ₃	-10.191	-24.770
[Tptm]ZnOCH ₂ OSi(OMe) ₃ → [[Tptm]Zn{OCH ₂ OSi(OMe) ₃ }] [‡]	2.962	3.996
[Tptm]ZnOCH ₂ OSi(OMe) ₃ → [Tptm]ZnOSi(OMe) ₃ + CH ₂ O	-8.783	5.409

Table S5: Transition State Imaginary Frequencies

Transition state	Imaginary frequency (cm ⁻¹)	Description of motion
[[Tptm]ZnH(OCO)] [‡]	-386.55	Zn–H–C motion
[[Tptm]ZnH{OCHOSi(OMe) ₃ }] [‡]	-653.95	Zn–H–C motion
[[Tptm]Zn{OCH ₂ OSi(OMe) ₃ }] [‡]	-146.45	H ₂ C–O _{ax} Zn & H ₂ CO–Zn motion

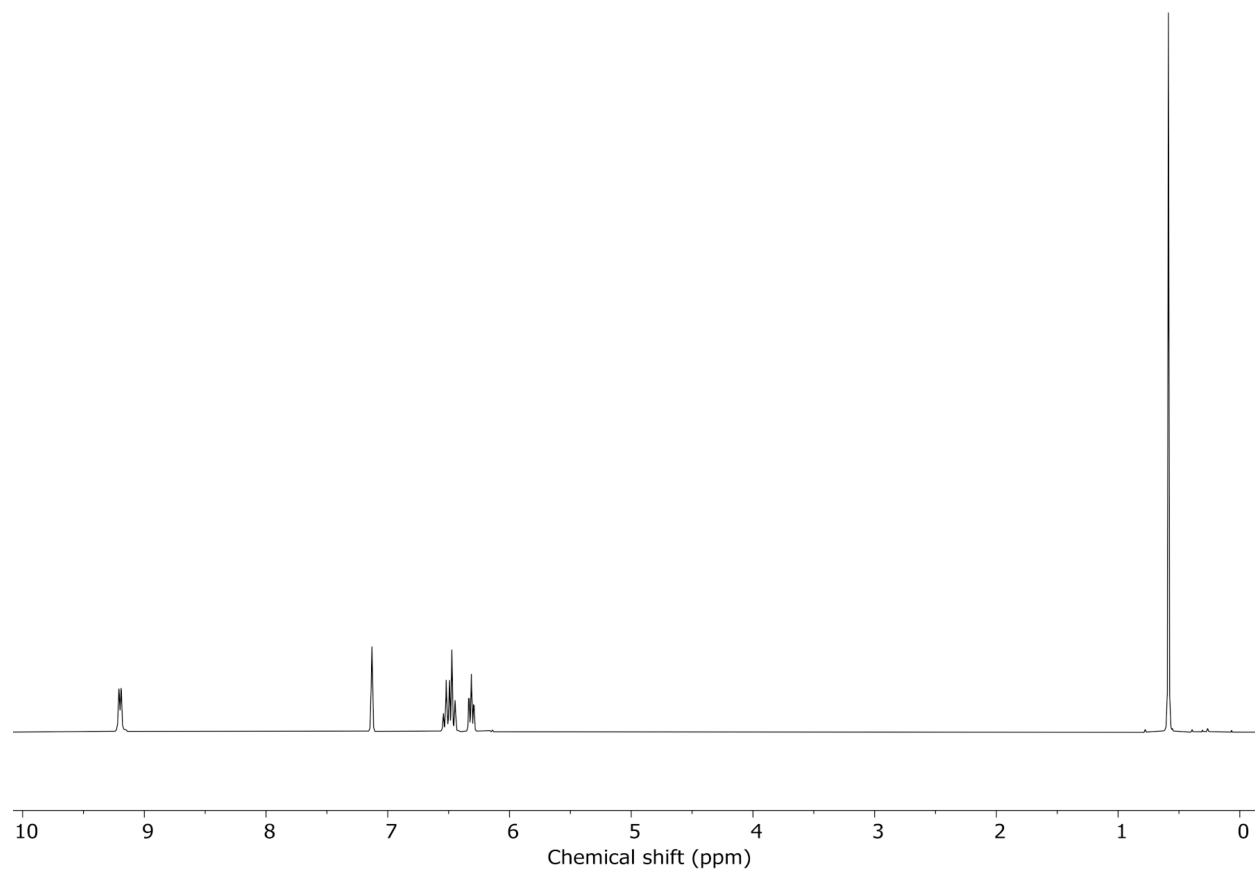


Figure S1. ^1H NMR spectrum of $[\text{Tptm}]\text{ZnOSiMe}_3$ (C_6D_6).

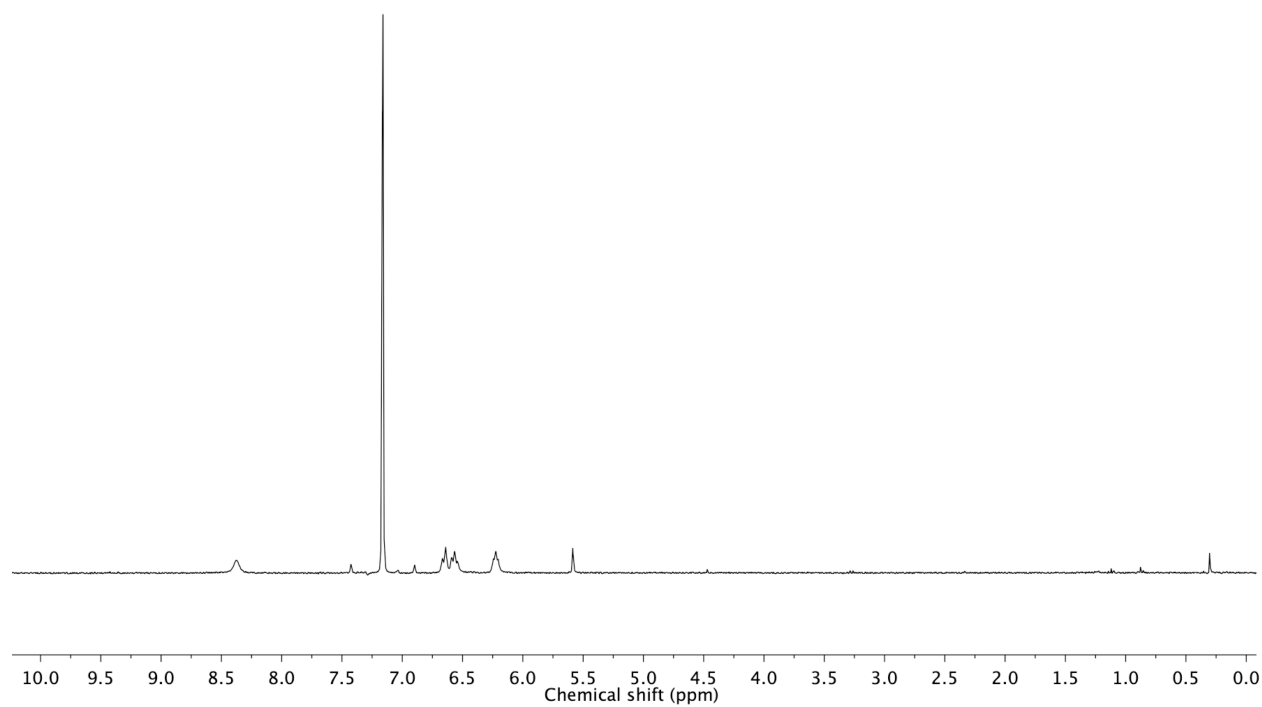


Figure S2. ^1H NMR spectrum of $[\text{Tptm}]\text{ZnH}$ (C_6D_6)

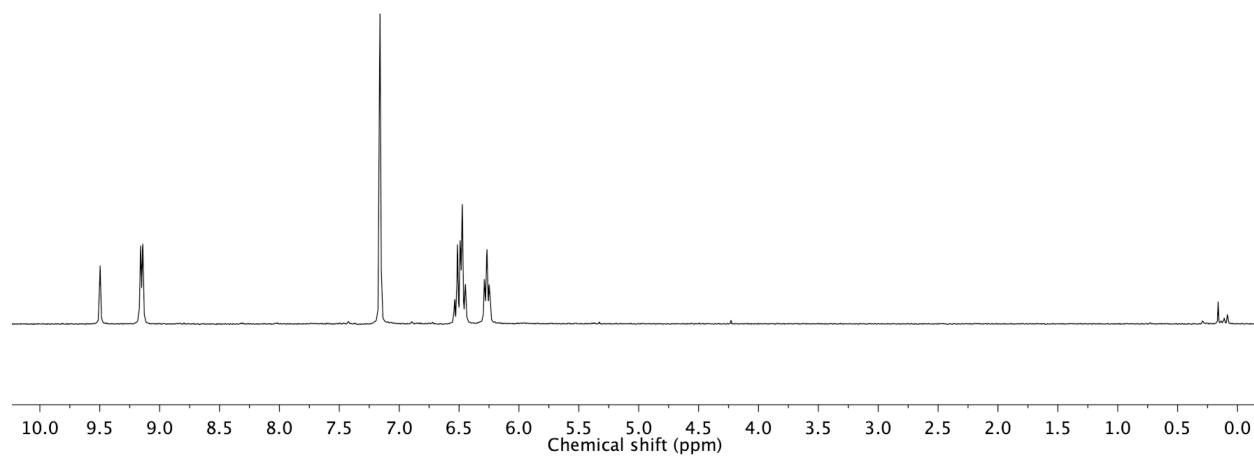


Figure S3. ^1H NMR spectrum of $[\text{Tptm}]\text{ZnO}_2\text{CH}$ (C_6D_6)

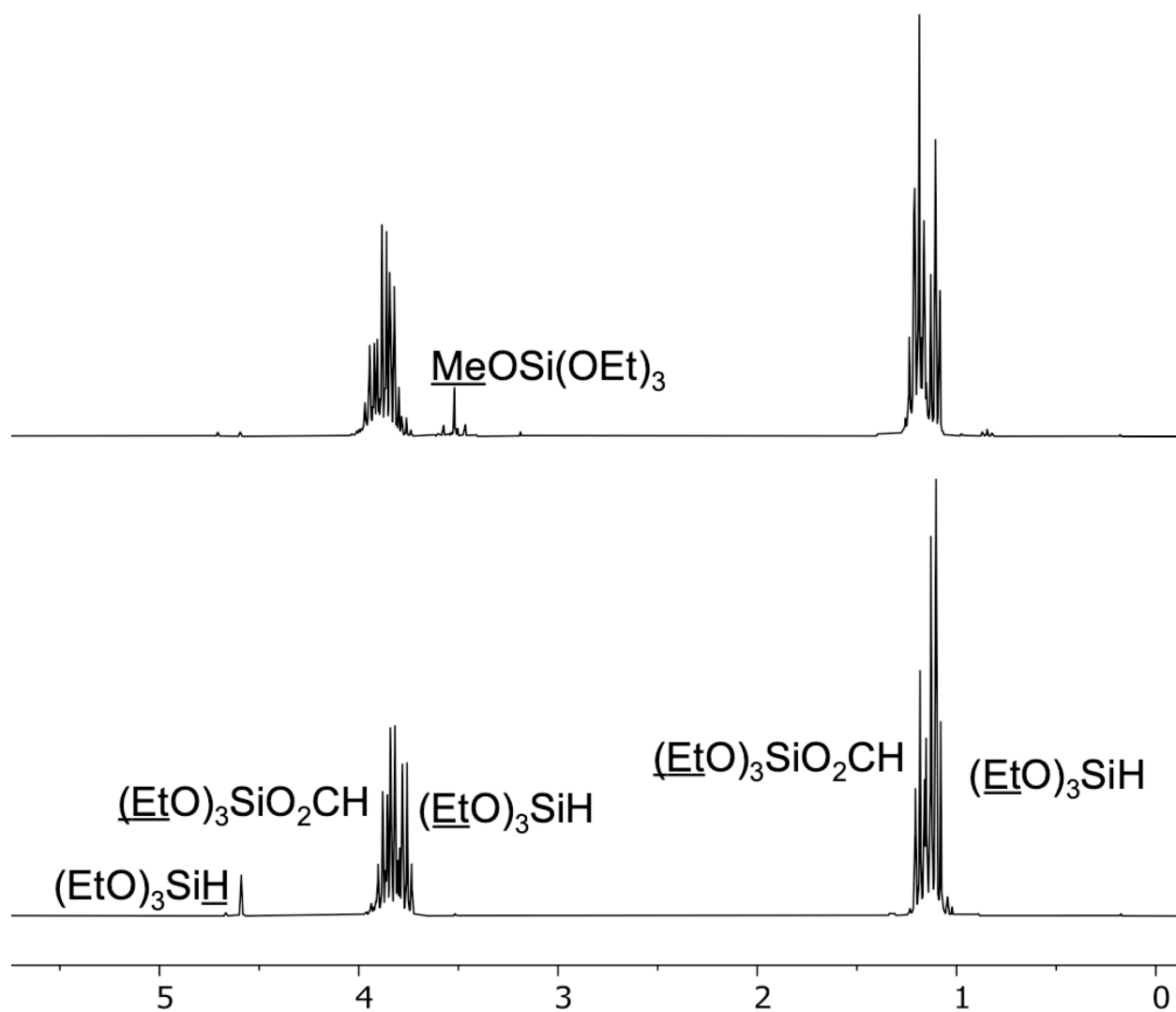


Figure S4. Conversion of $\text{HCO}_2\text{Si}(\text{OEt})_3$ to $\text{MeOSi}(\text{OEt})_3$ by $(\text{EtO})_3\text{SiH}$ catalyzed by $[\text{Tptm}]\text{ZnH}$ (C_6D_6).

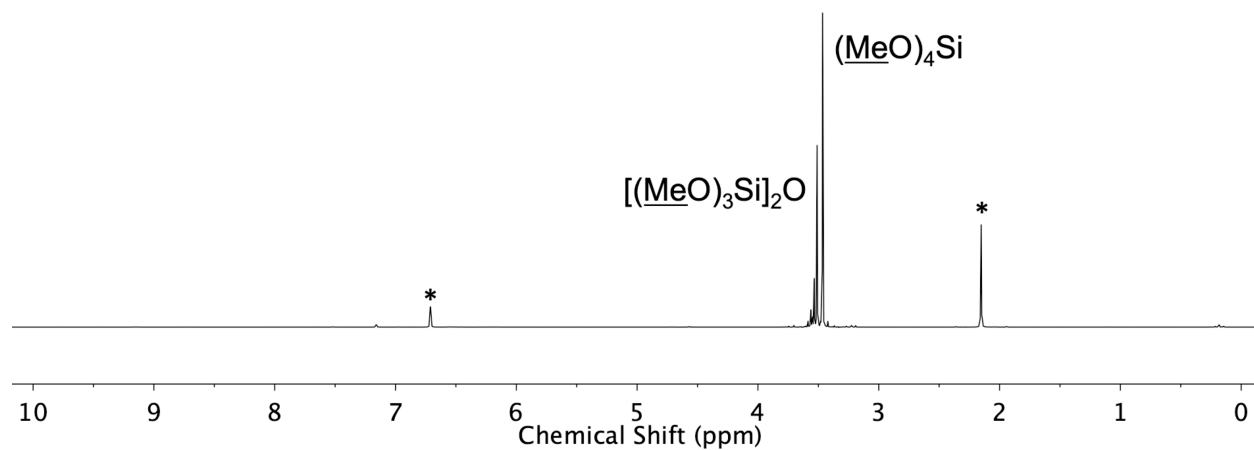


Figure S5. Formation of $\text{Si}(\text{OMe})_4$ from $\text{HCO}_2\text{Si}(\text{OMe})_3$ by $(\text{MeO})_3\text{SiH}$ catalyzed by $[\text{Tptm}]\text{ZnH}$ (C_6D_6 ; * = mesitylene).

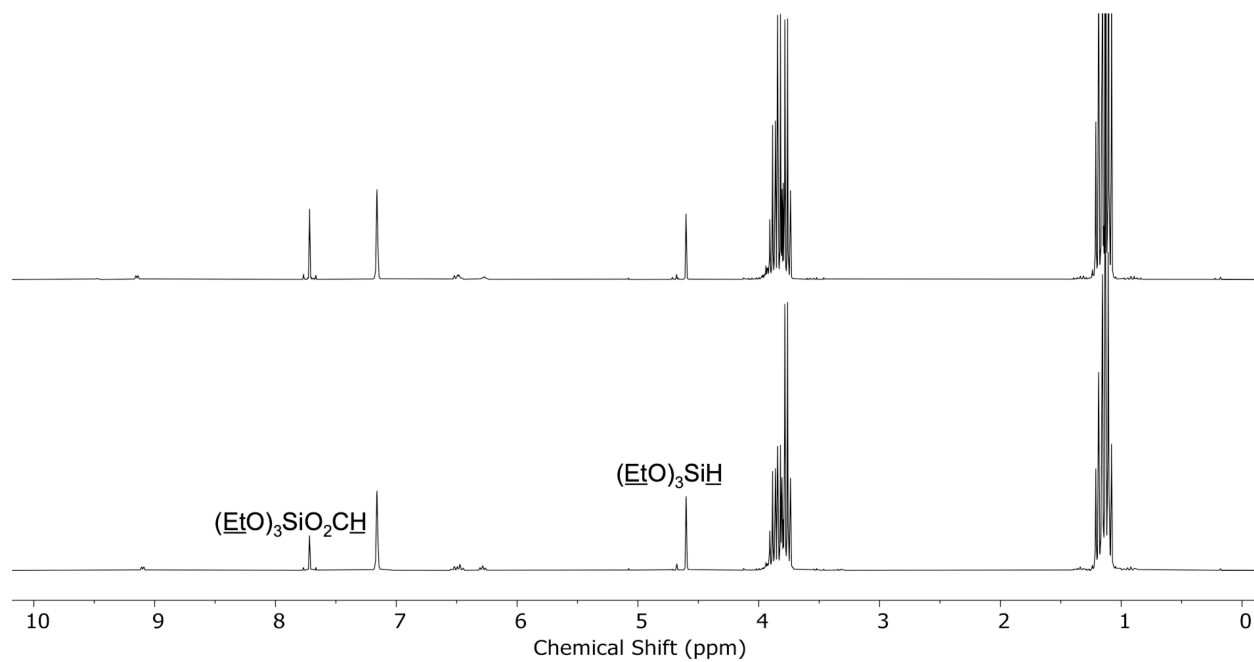


Figure S6. Reaction of $(\text{EtO})_3\text{SiO}_2\text{CH}$ with $(\text{EtO})_3\text{SiH}$ in the presence of CO_2 and zinc catalyst demonstrating that methoxy species are not formed.

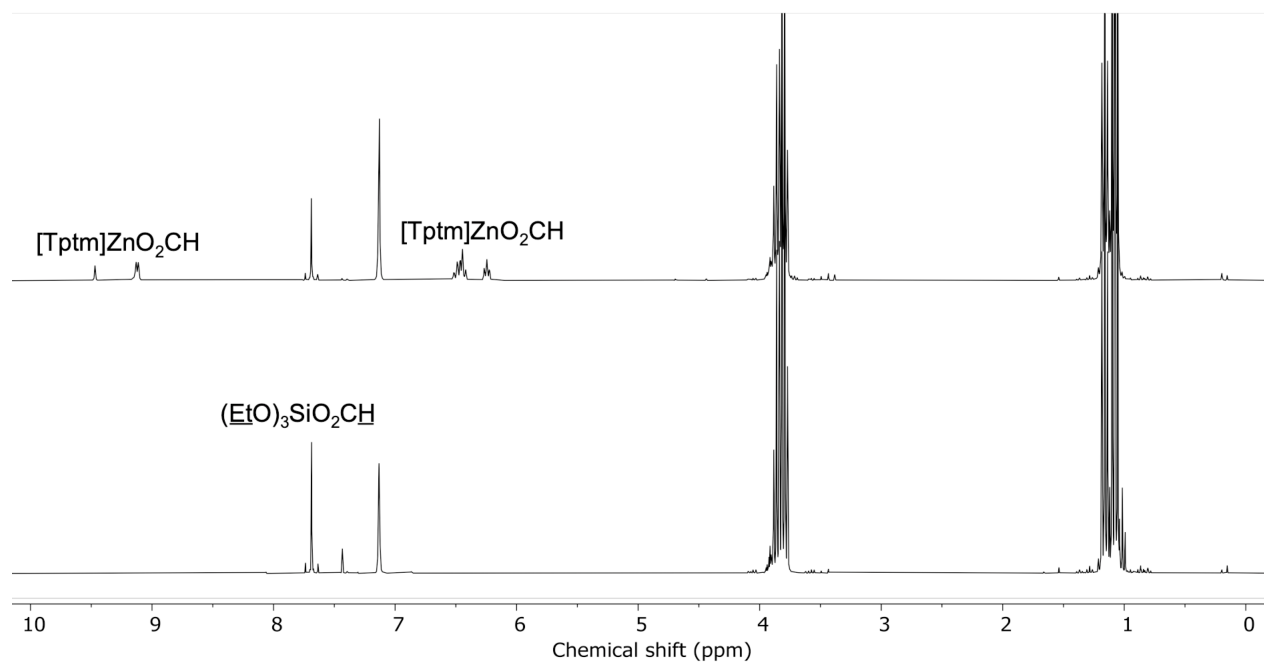


Figure S7. Formation of $[\text{Tptm}]\text{ZnO}_2\text{CH}$ upon reaction of $[\text{Tptm}]\text{ZnH}$ with $(\text{EtO})_3\text{SiO}_2\text{CH}$ (C_6D_6).

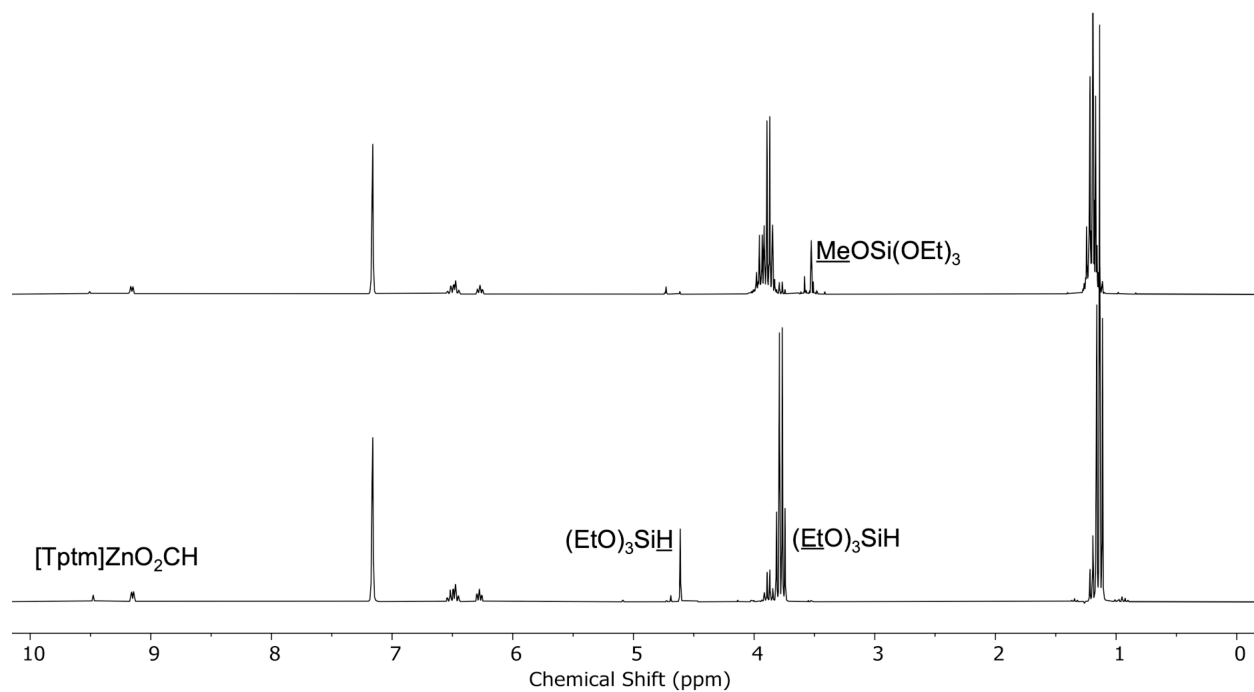


Figure S8. Reaction of $[\text{Tptm}]\text{ZnO}_2\text{CH}$ with $(\text{EtO})_3\text{SiH}$: Formation of methoxy species (C_6D_6)

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