Synthesis and Application of Methyl itaconate-Anthracene Adducts in Configuration Assignment of Chiral Secondary Alcohols by ^{1}H NMR

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I. ^{1}H, ^{13}C and 2D-NMR Spectra of MIA and Their Derivatives

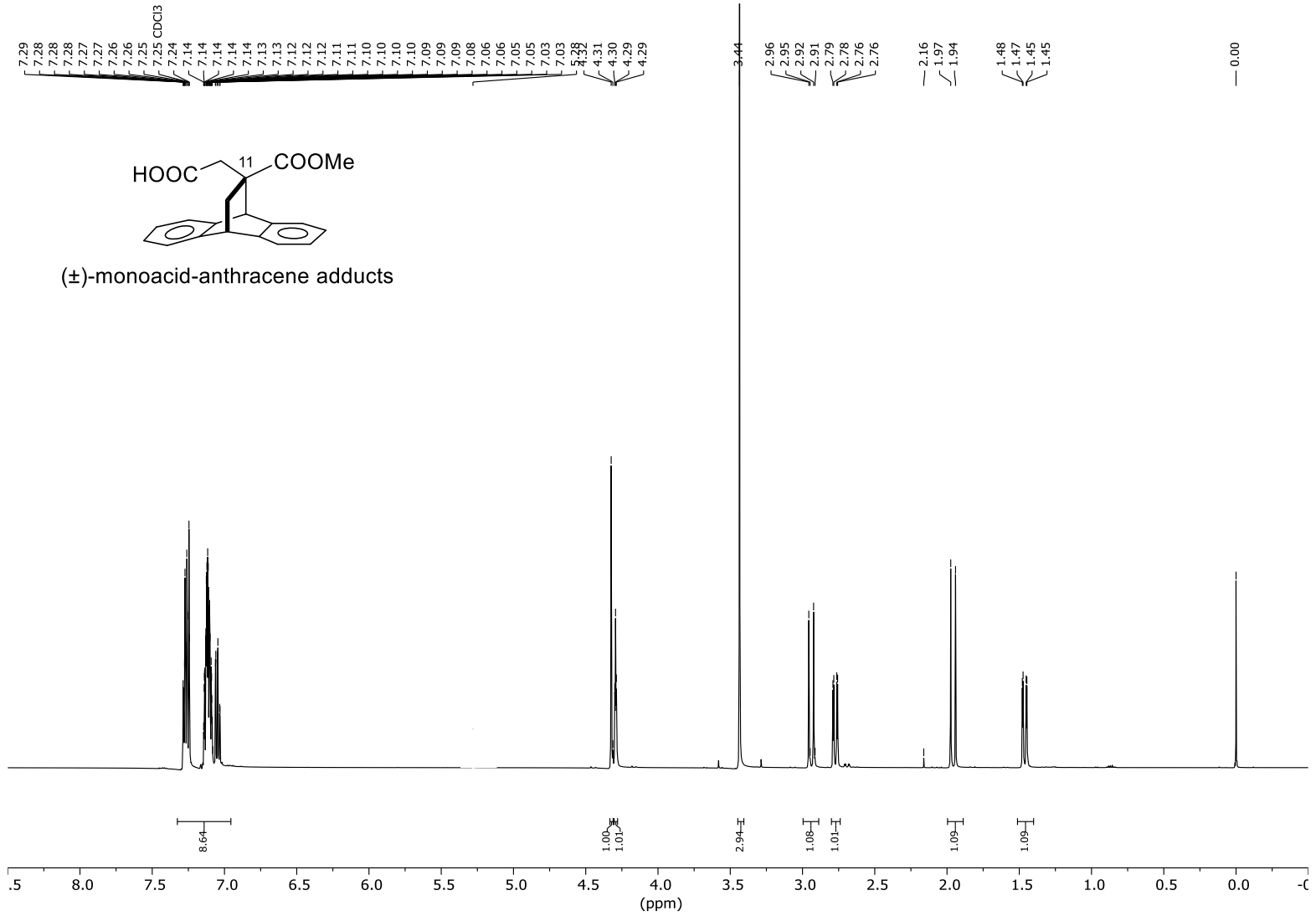

Figure S1 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (±)-monoacid-anthracene adducts

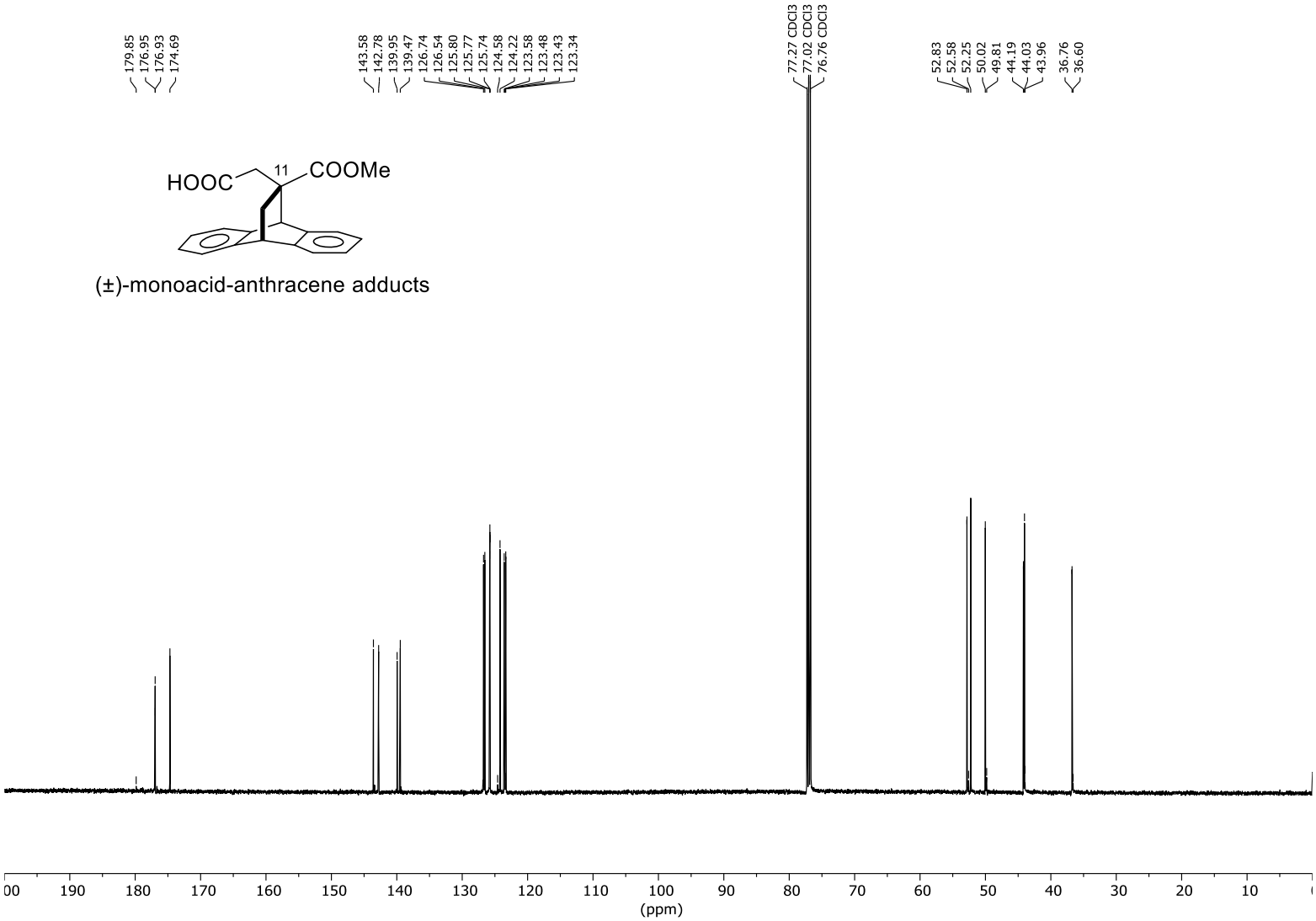

Figure S2 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (±)-monoacid-anthracene adducts

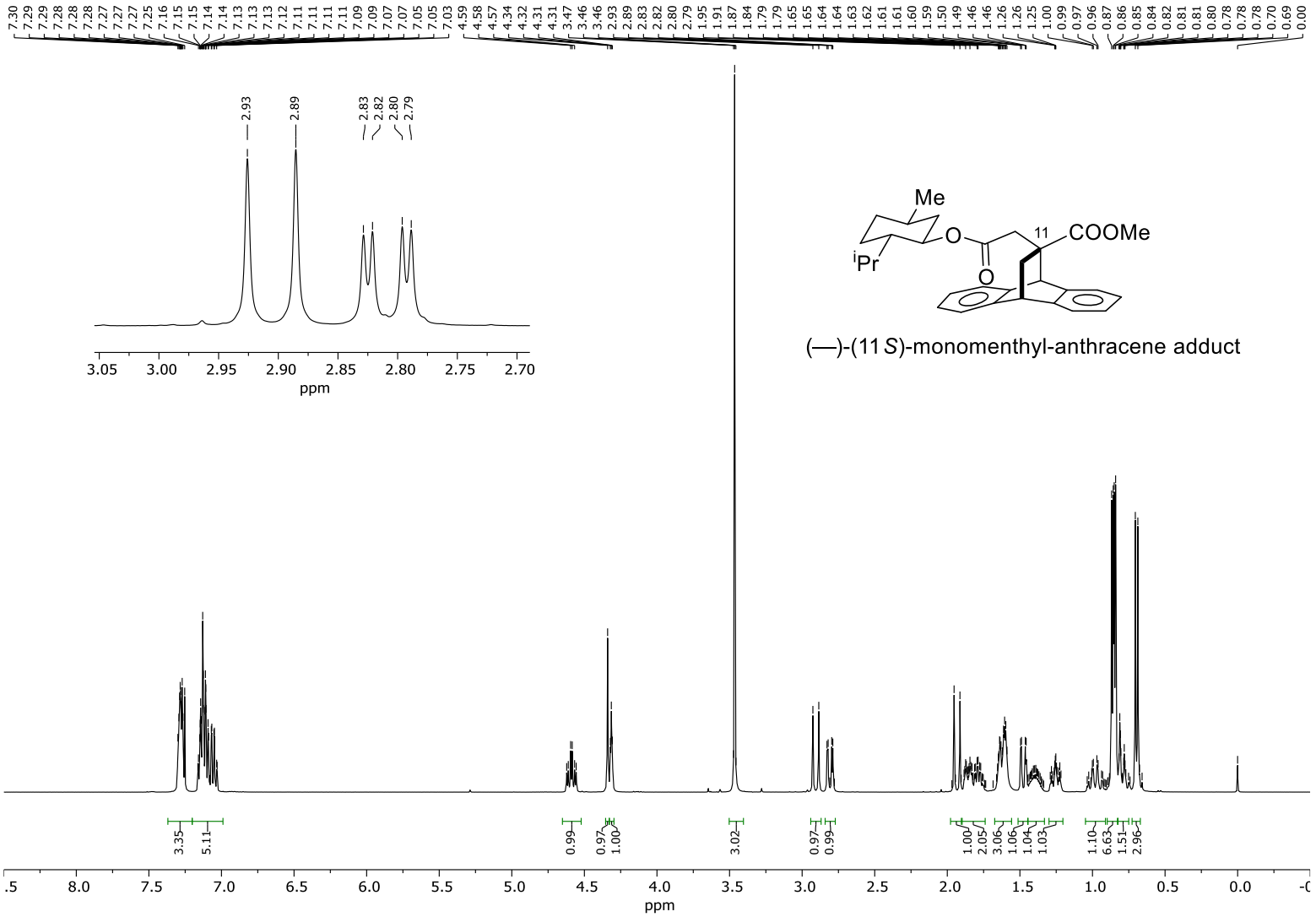

Figure S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (–)-(11*S*)-monomenthyl-anthracene adduct

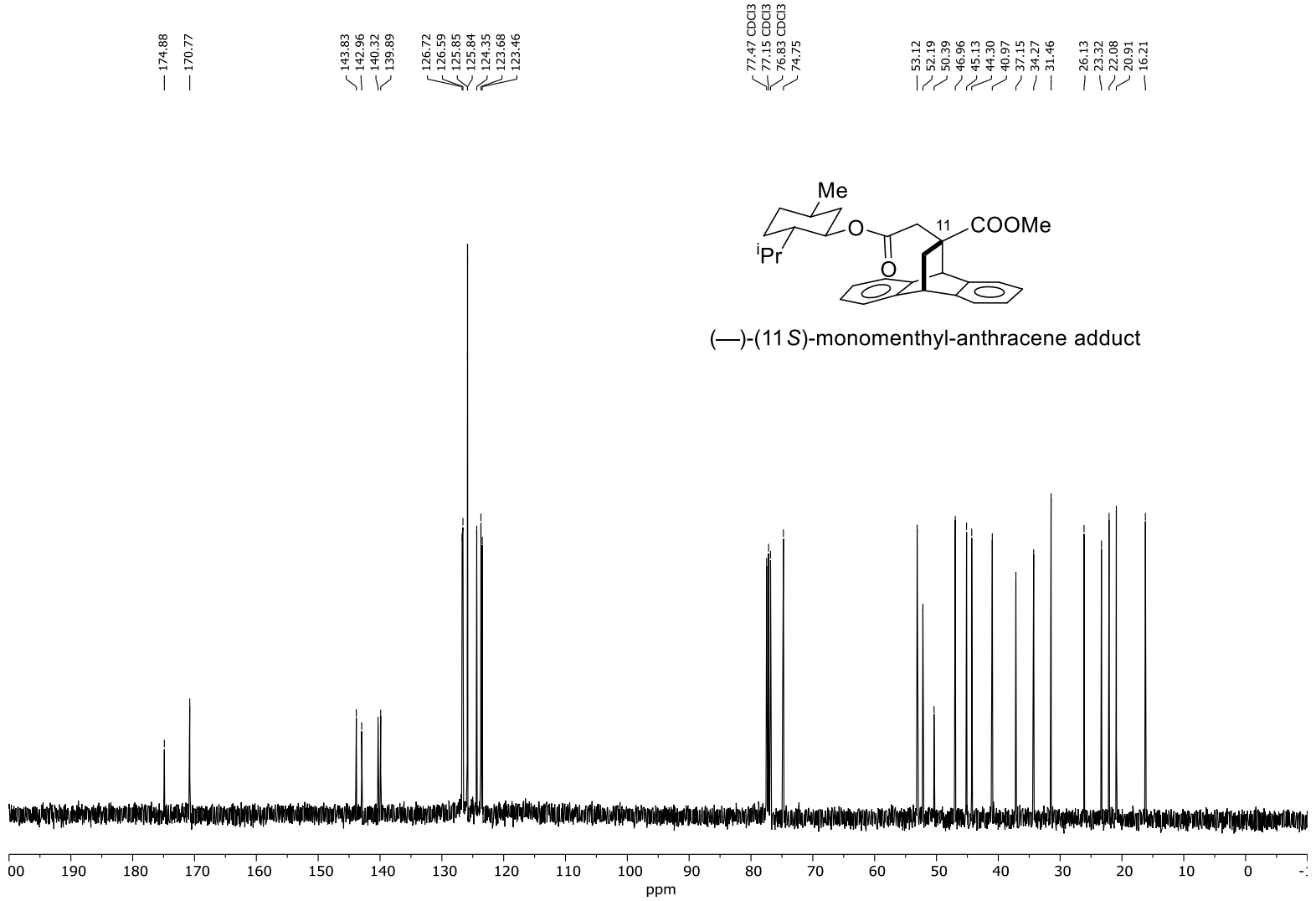

Figure S4 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (−)-(11*S*)-monomenthyl-anthracene adduct

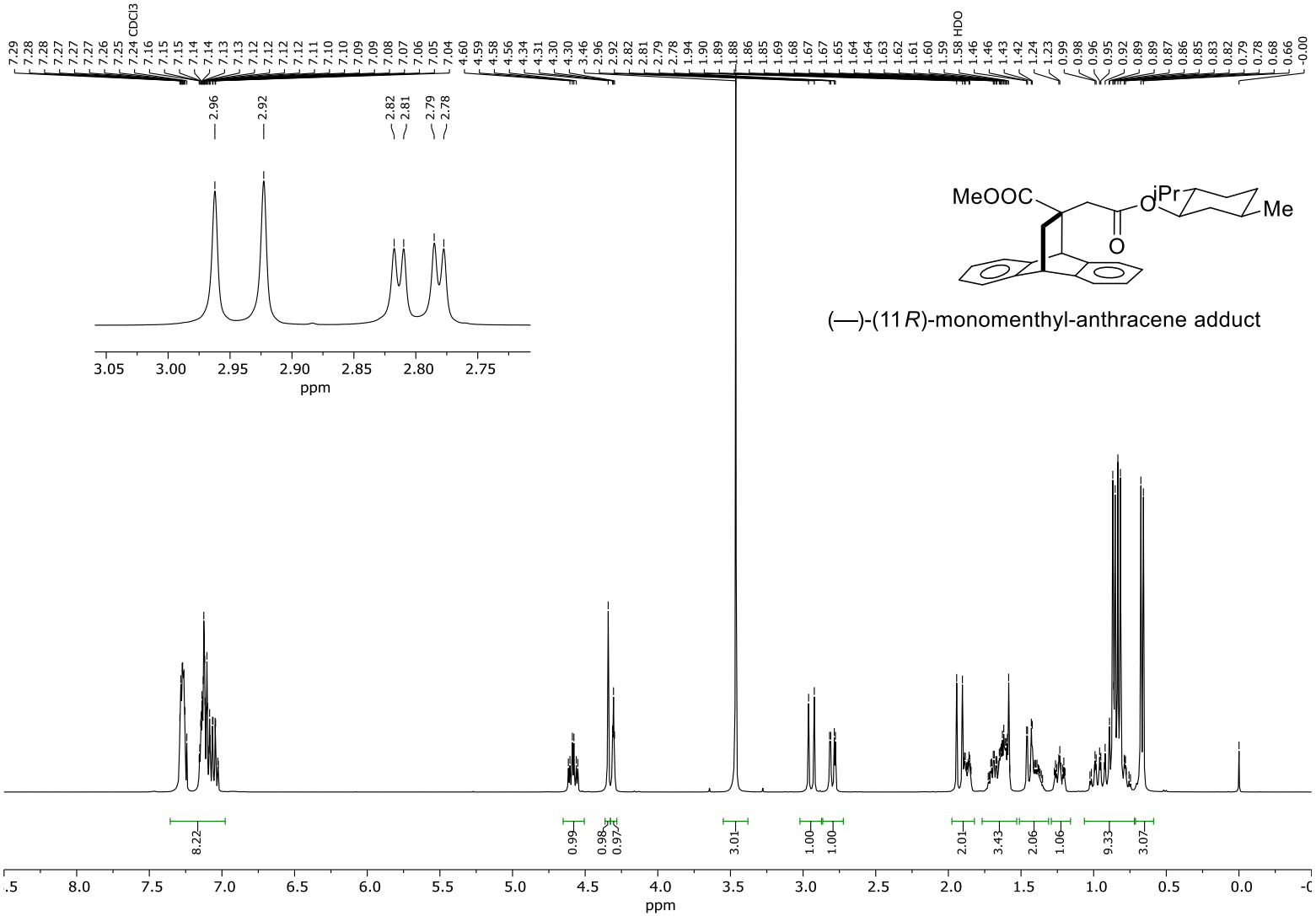

Figure S5 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (–)-(11*R*)-monomenthyl-anthracene adduct

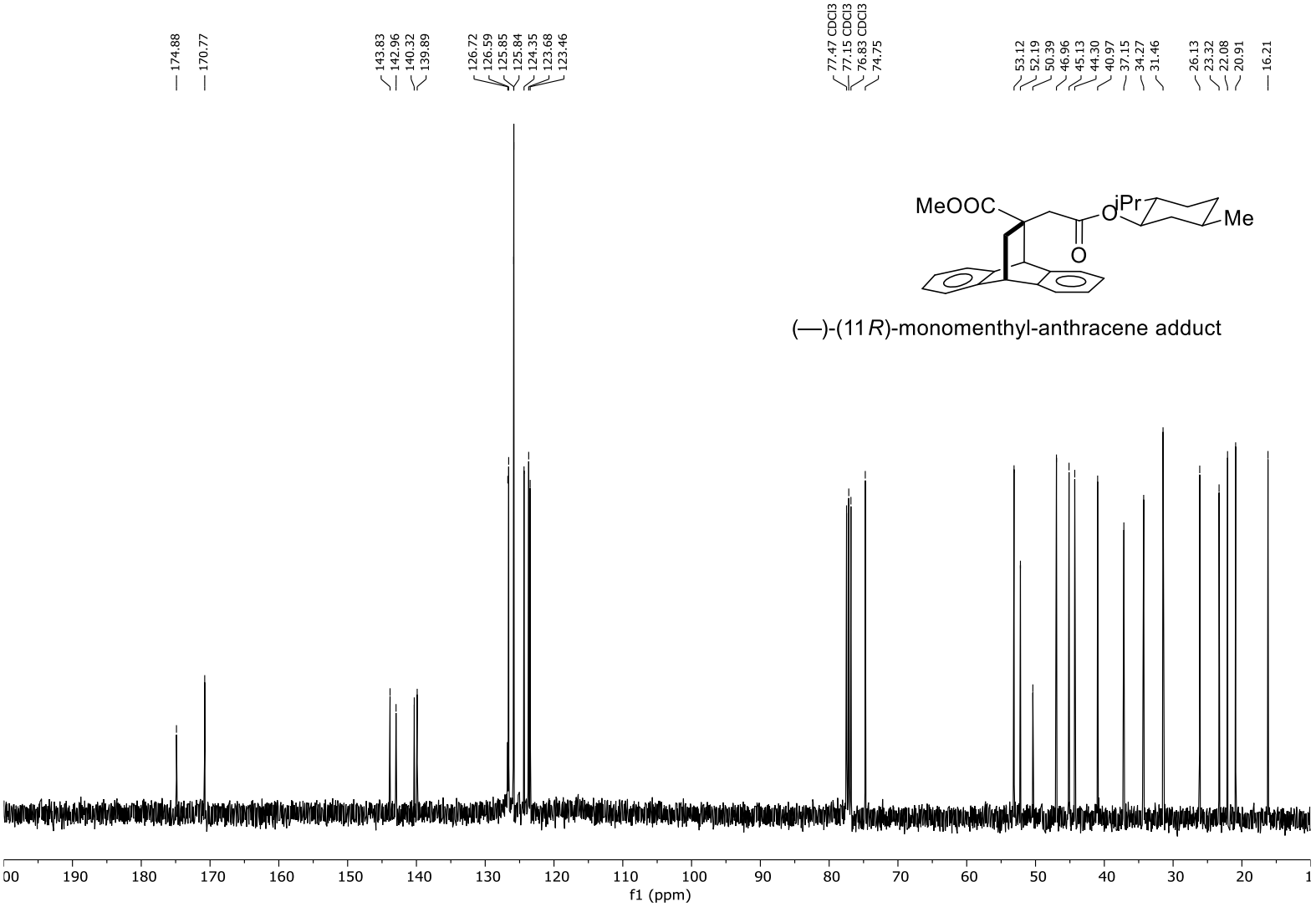

Figure S6 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (–)-(11*R*)-monomenthyl-anthracene adduct

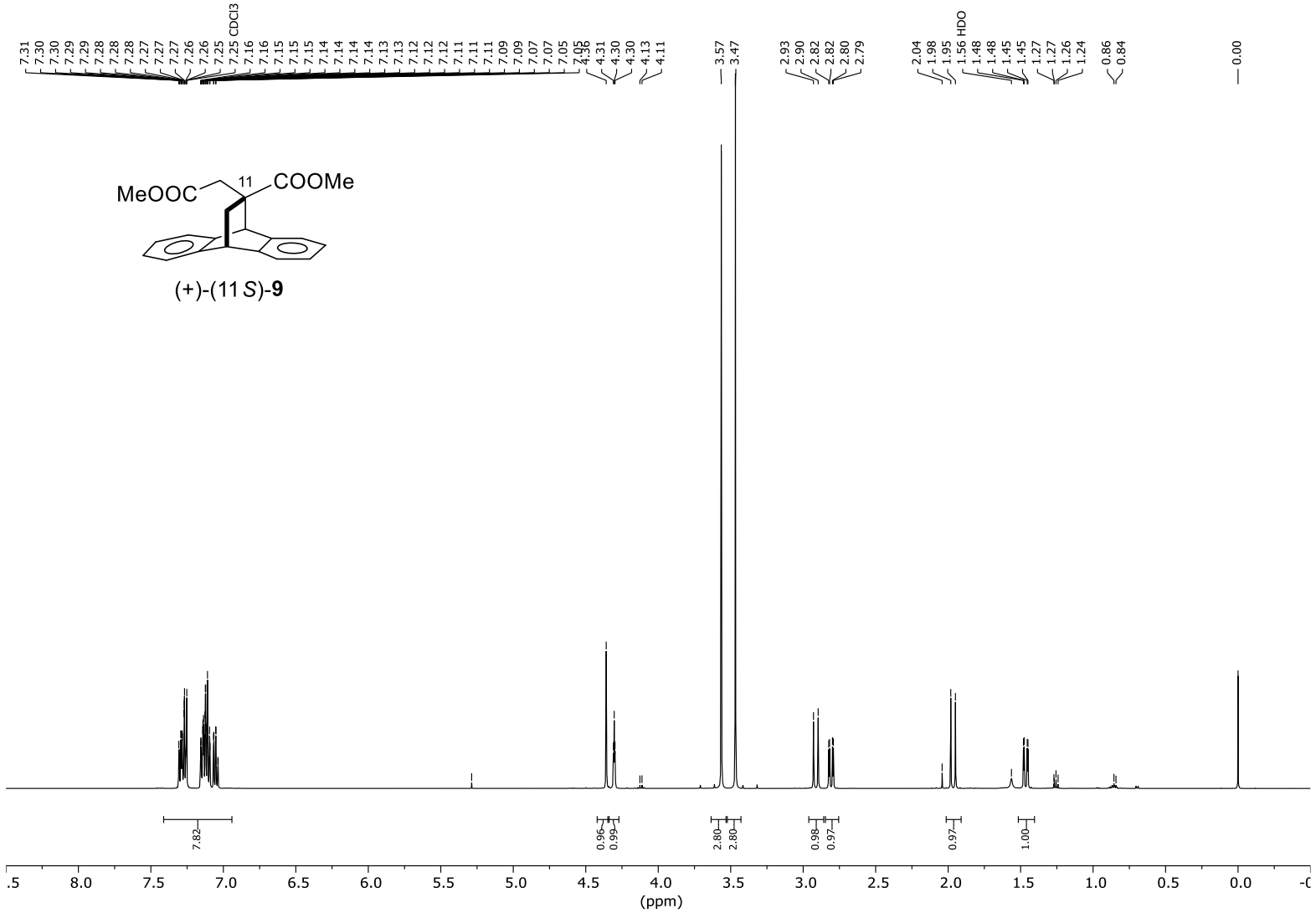

Figure S7 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (+)-(11*S*)-dimethyl itaconate-anthracene adduct, (+)-(11*S*)-**9**

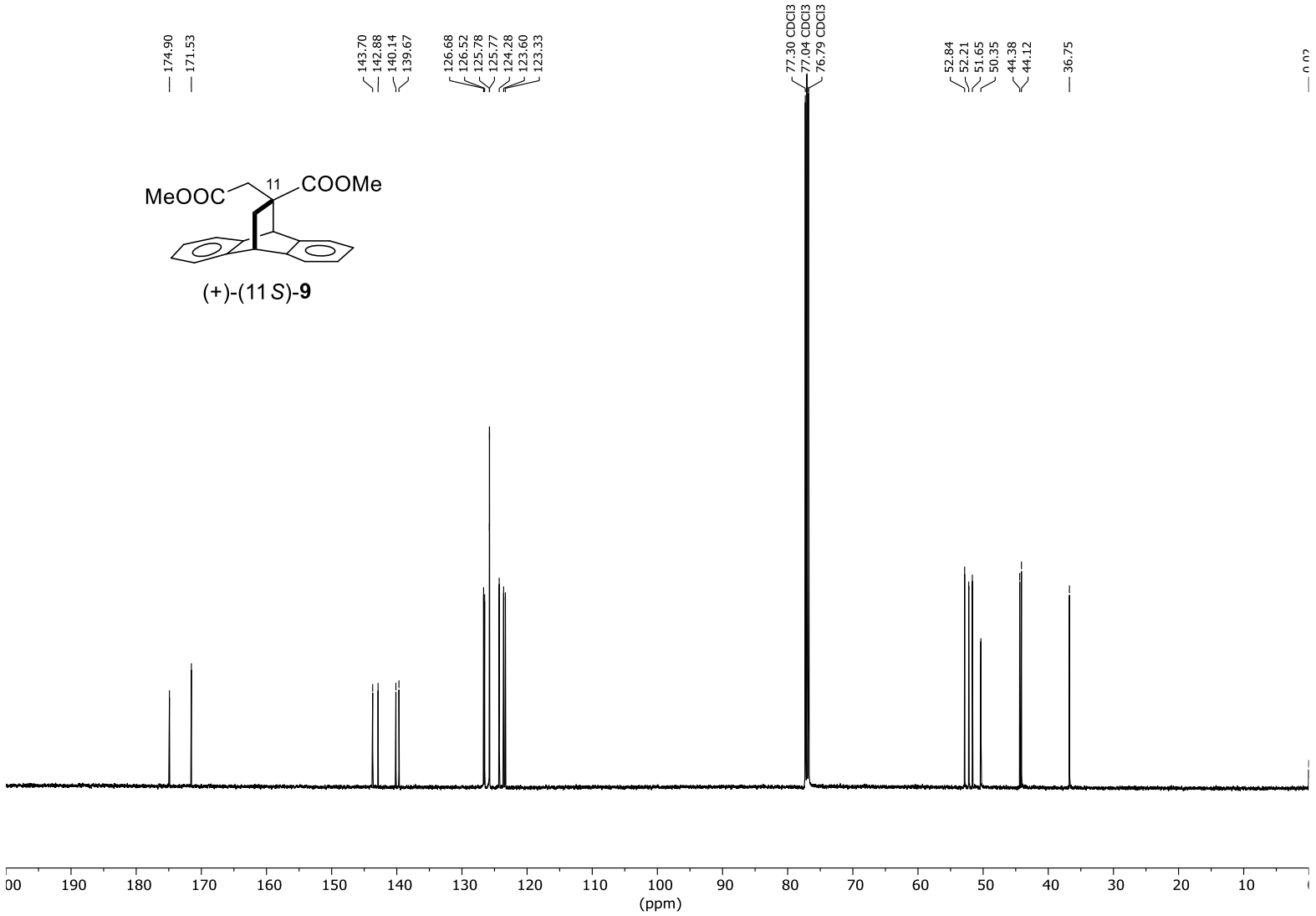

Figure S8 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (+)-(11*S*)-dimethyl itaconate-anthracene adduct, (+)-(11*S*)-**9**

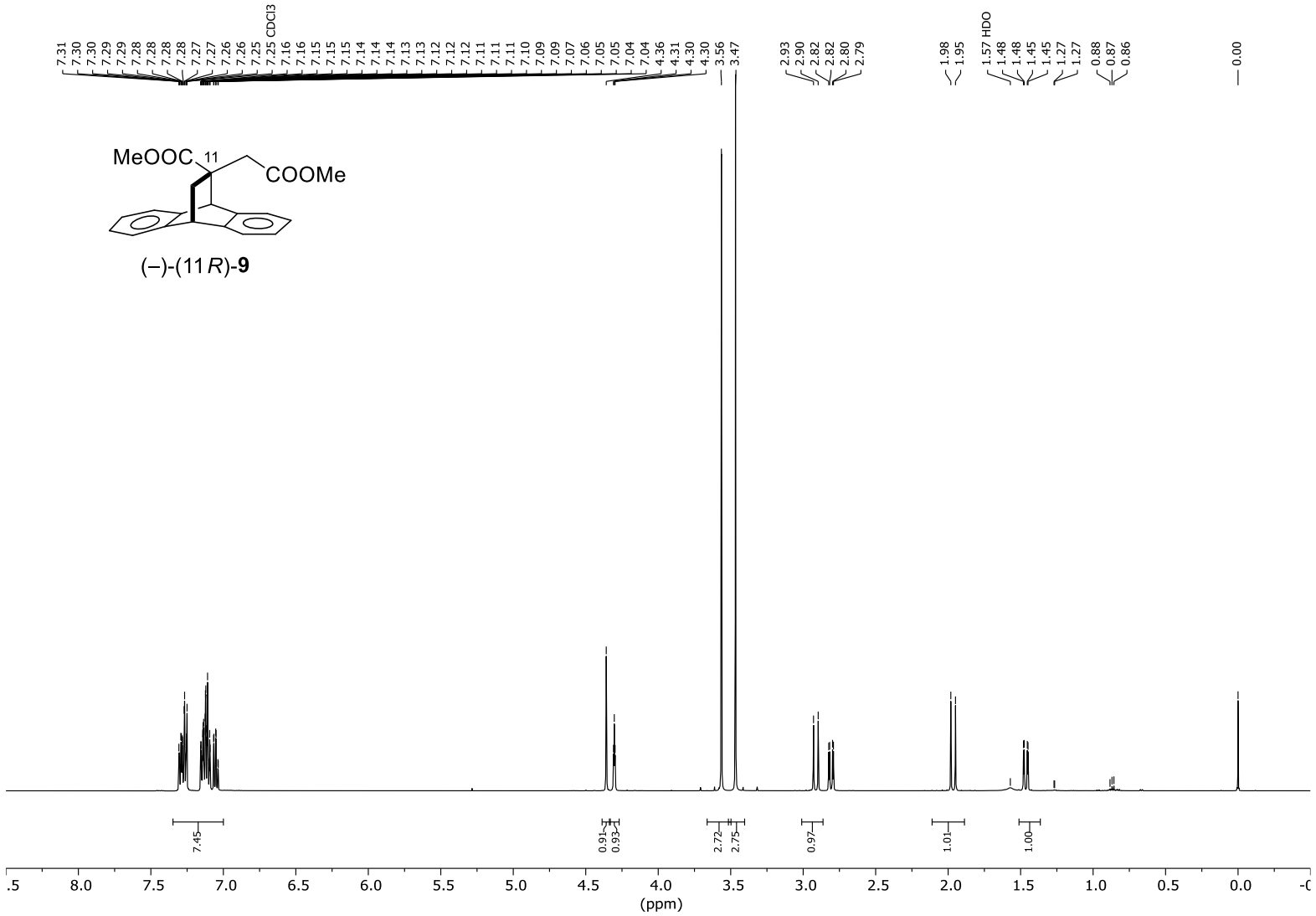

Figure S9 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (–)-(11*R*)-dimethyl itaconate-anthracene adduct, (–)-(11*R*)-**9**

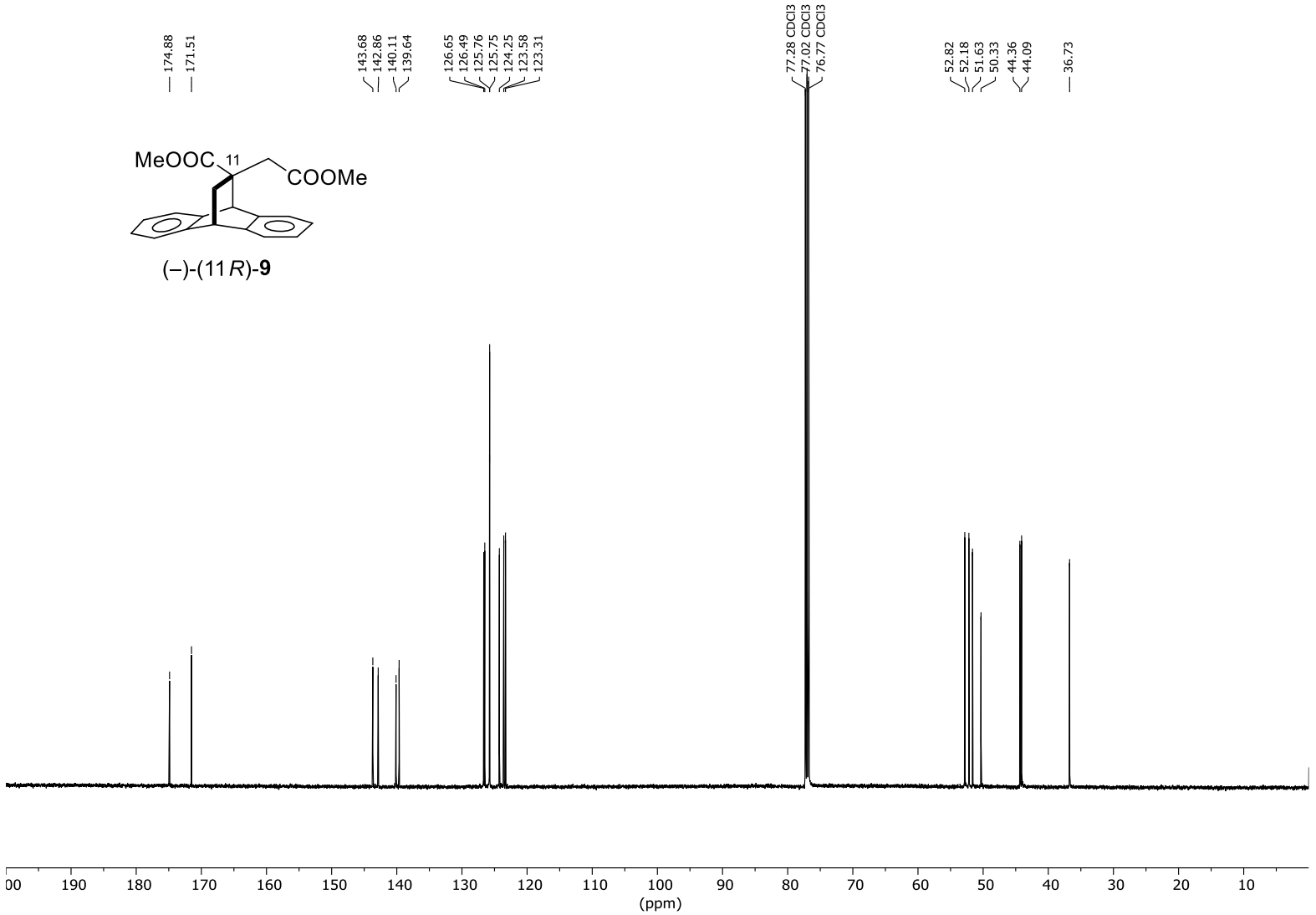

Figure S10 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (–)-(11*R*)-dimethyl itaconate-anthracene adduct, (–)-(11*R*)-**9**

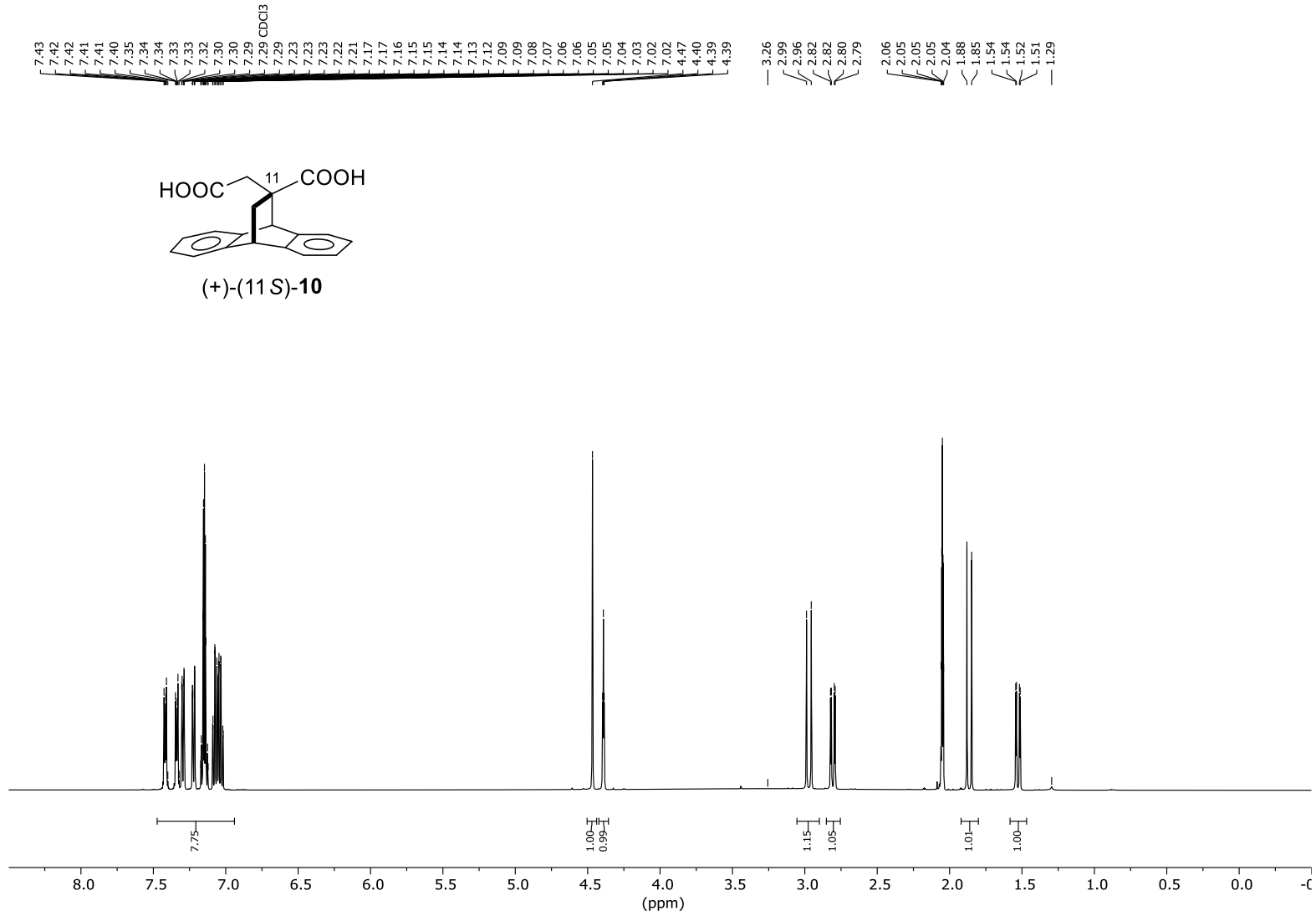

Figure S11 ^{1}H NMR (500 MHz, Acetone-d_6) spectrum of (+)-(11*S*)-itaconic acid-anthracene adduct, (+)-(11*S*)-**10**

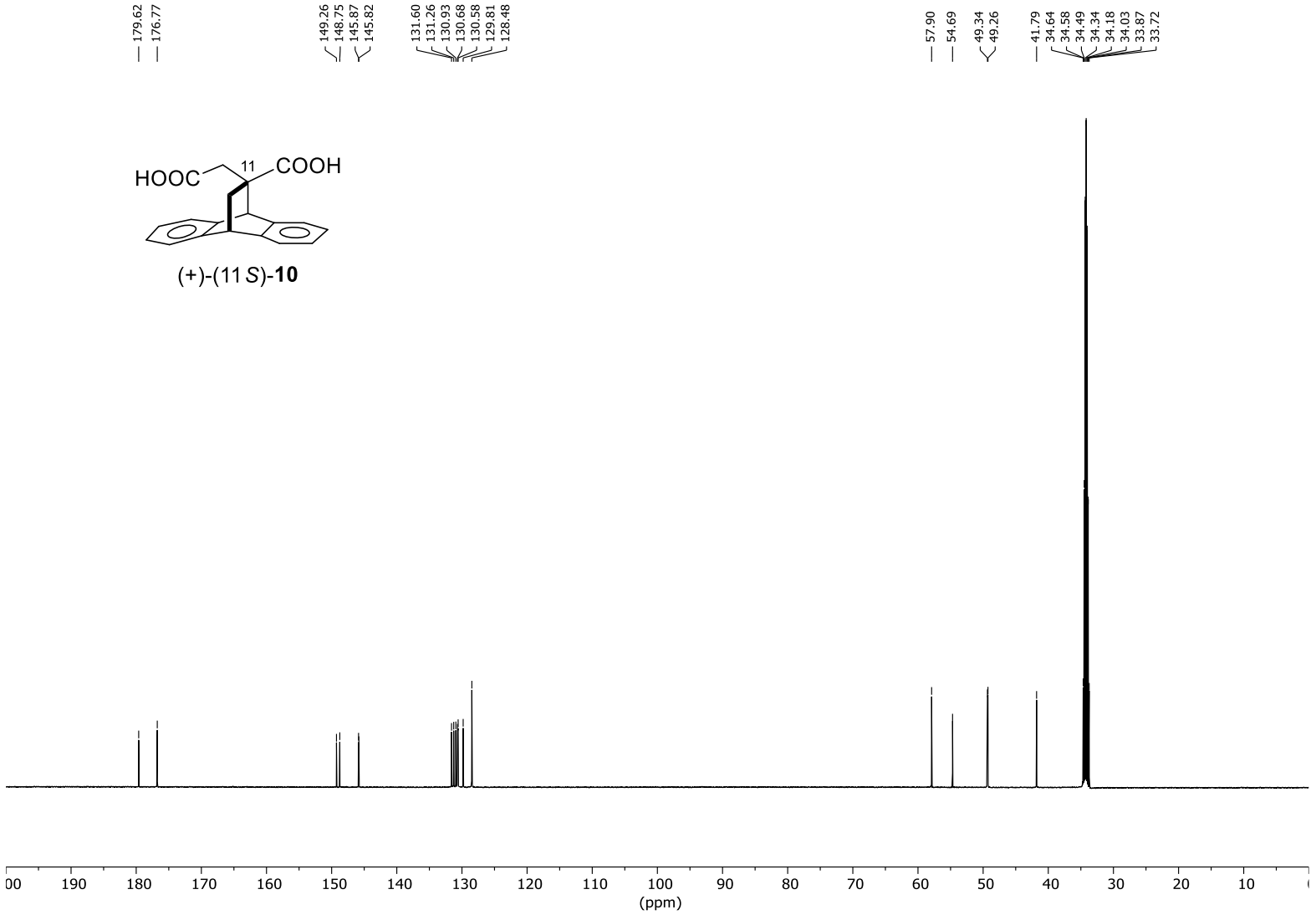

Figure S12 ^{13}C NMR (126 MHz, Acetone-d_6) spectra of (+)-(11*S*)-itaconic acid-anthracene adduct, (+)-(11*S*)-**10**

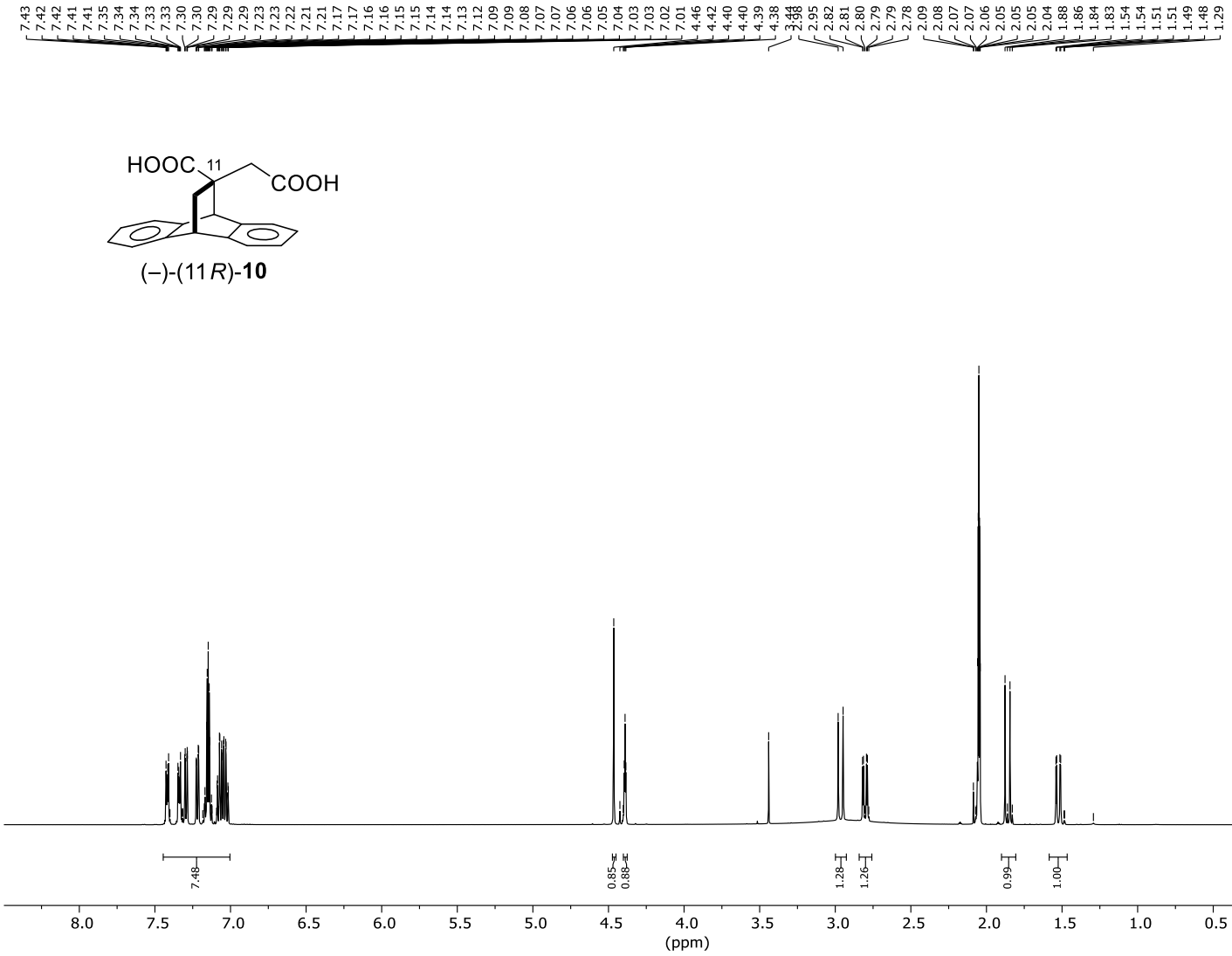

Figure S13 ^{1}H NMR (500 MHz, Acetone-d_6) spectrum of (–)-(11*S*)-itaconic acid-anthracene adduct, (–)-(11*S*)-**10**

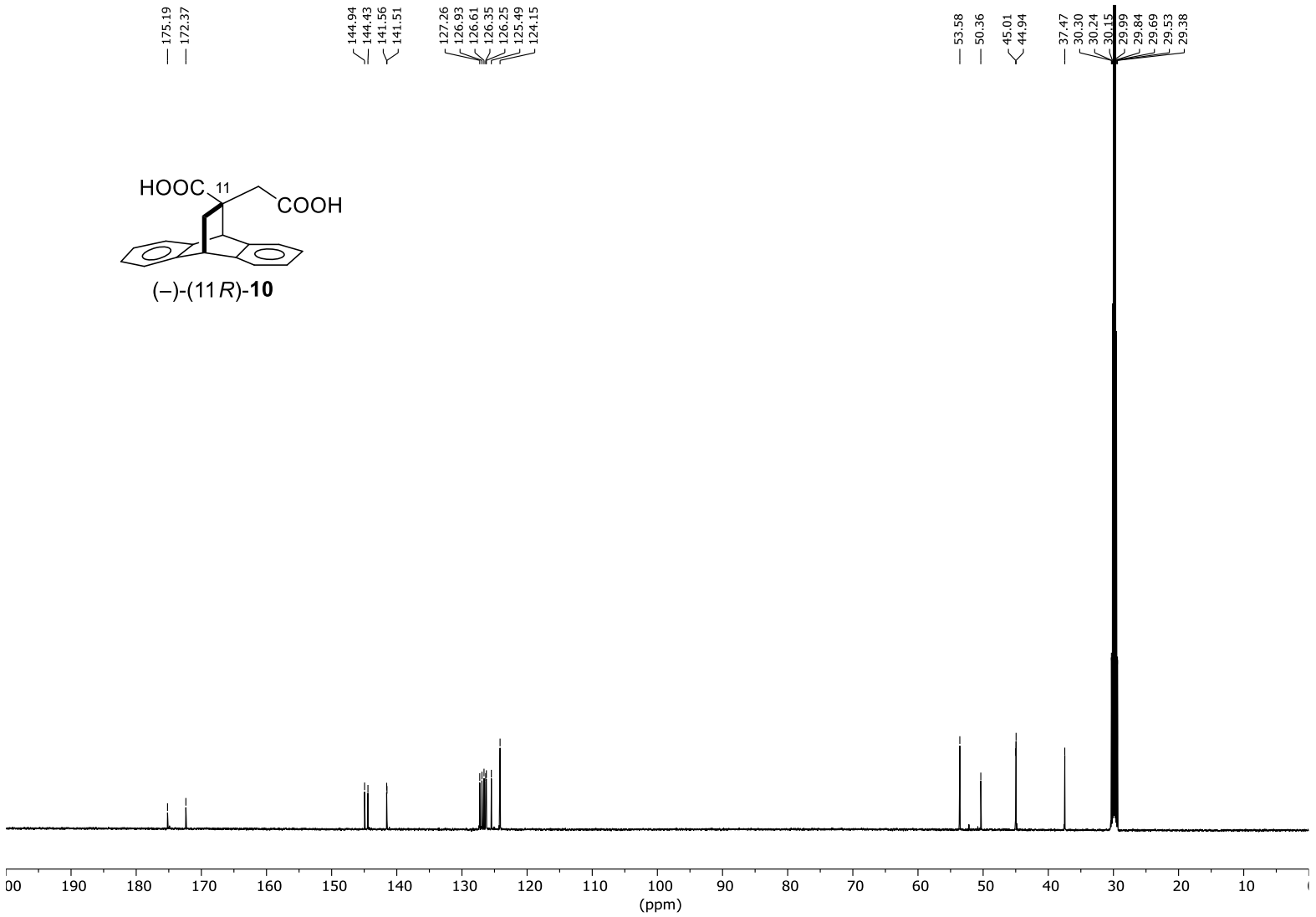

Figure S14 ^{13}C NMR (126 MHz, Acetone-d_6) spectra of(–)-(11*S*)-itaconic acid-anthracene adduct, (–)-(11*S*)-**10**

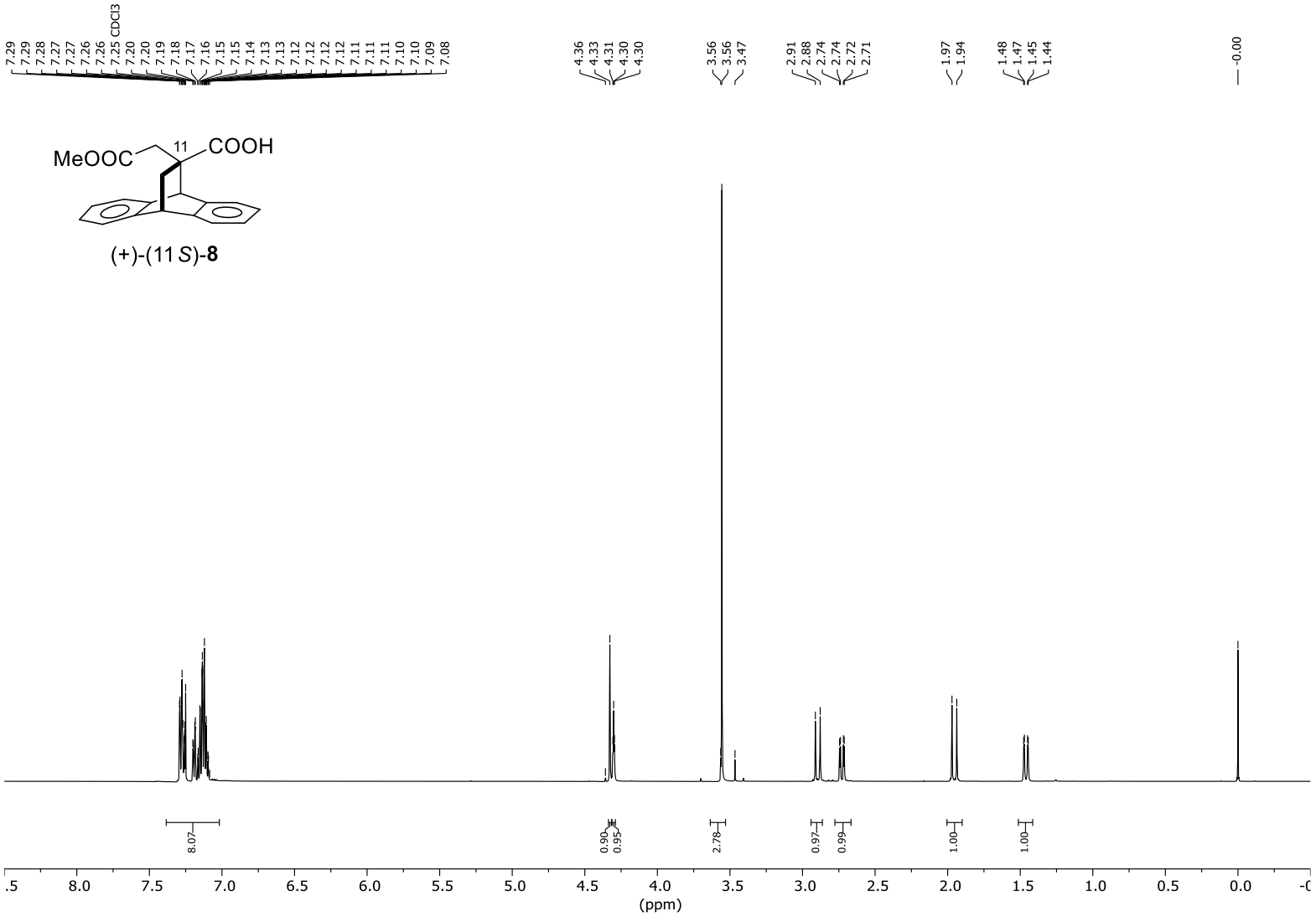

Figure S15 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (+)-(11*S*)-methyl itaconate-anthracene adduct, (+)-(11*S*)-**8**

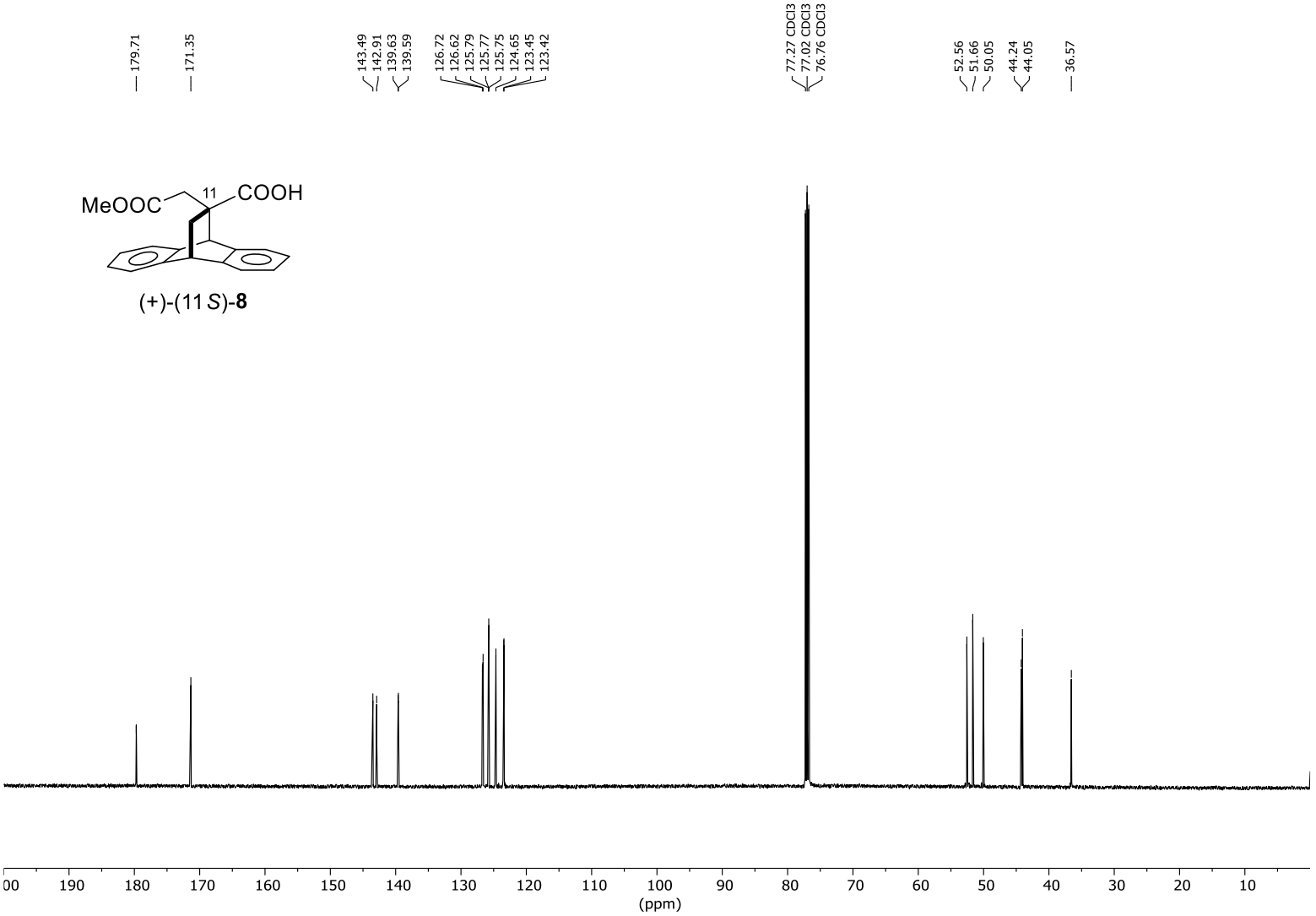

Figure S16 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (+)-(11*S*)-methyl itaconate-anthracene adduct, (+)-(11*S*)-**8**

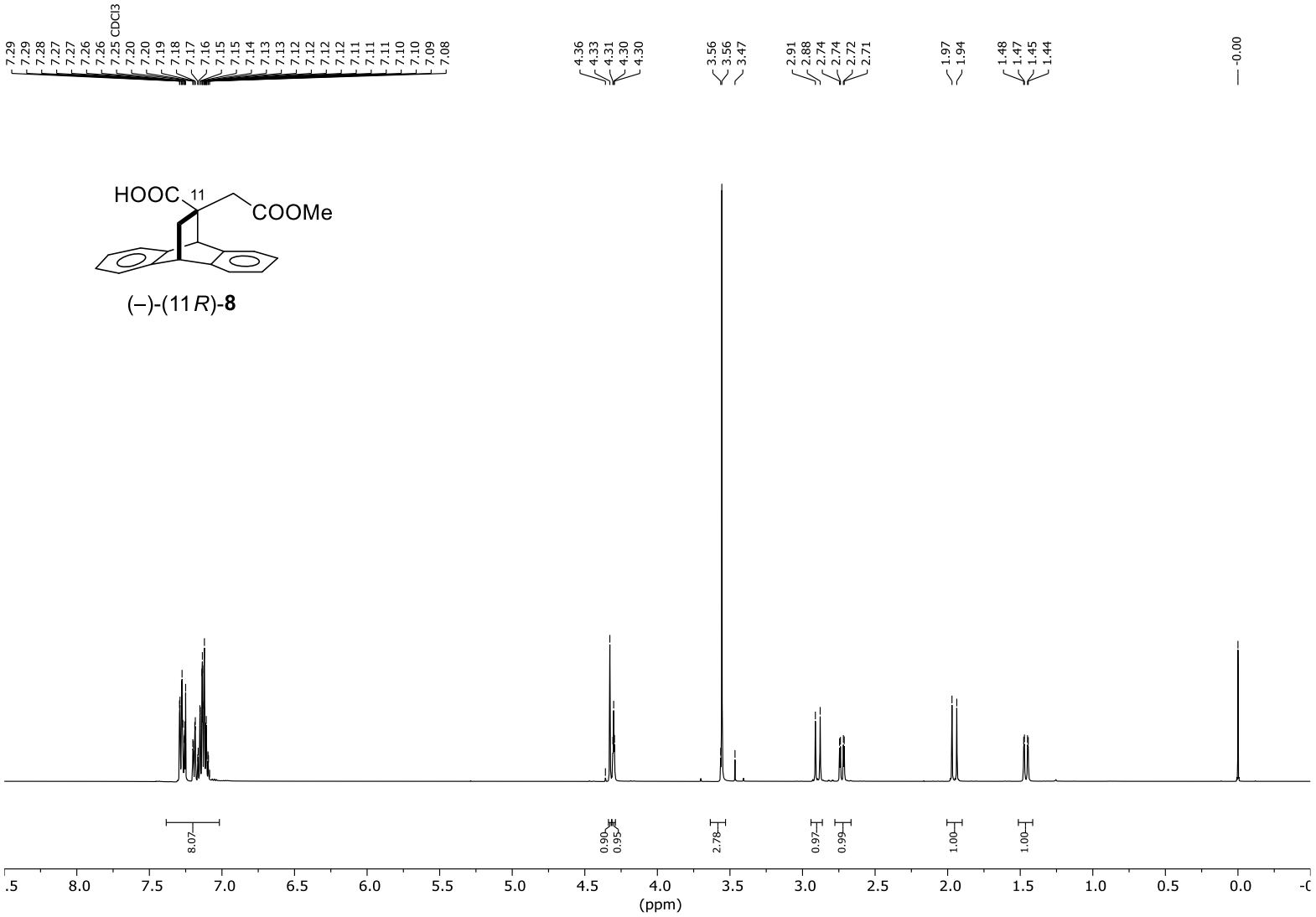

Figure S17 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (–)-(11*R*)-methyl itaconate-anthracene adduct, (–)-(11*R*)-**8**

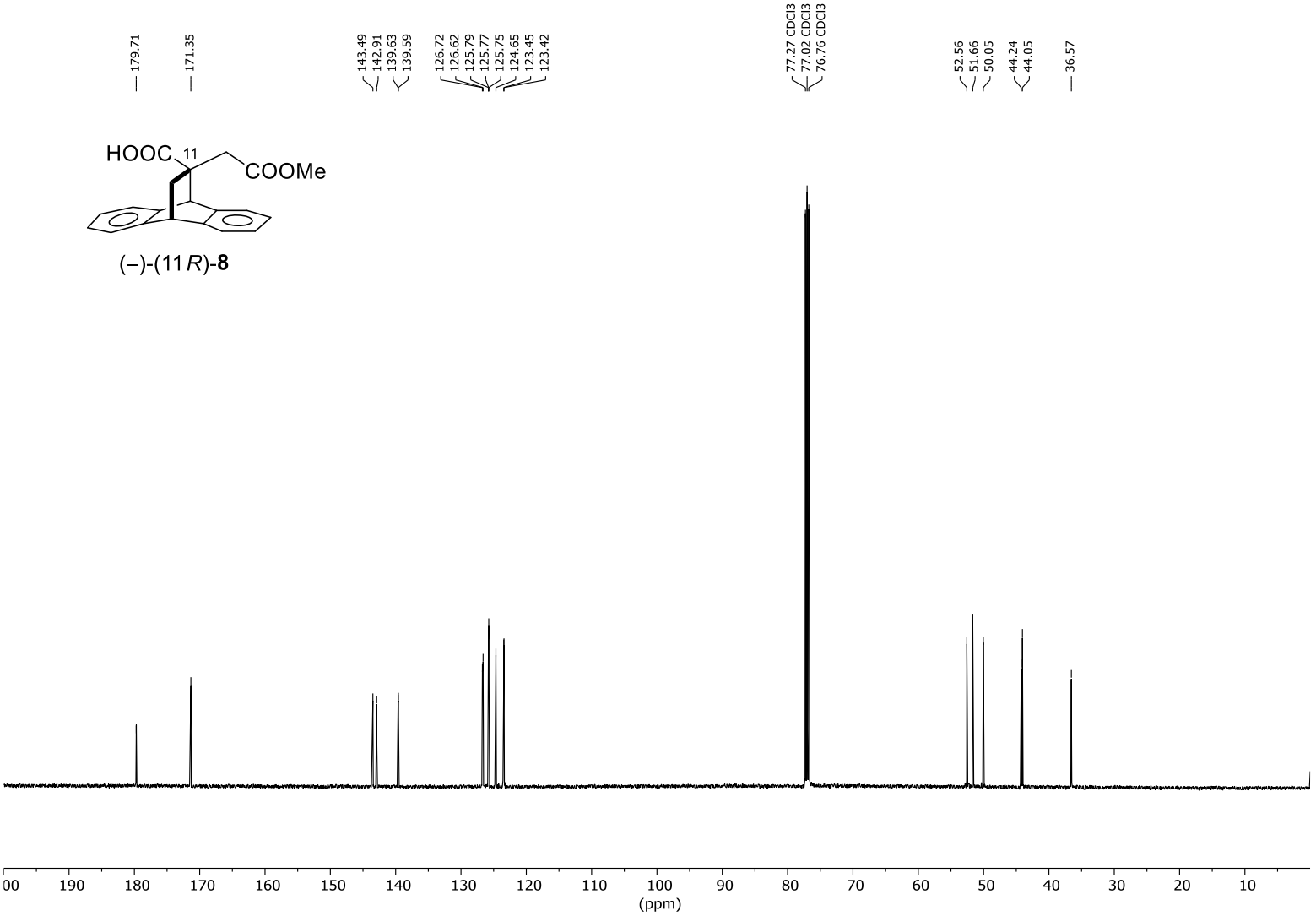

Figure S18 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (–)-(11*R*)-methyl itaconate-anthracene adduct, (–)-(11*R*)-**8**

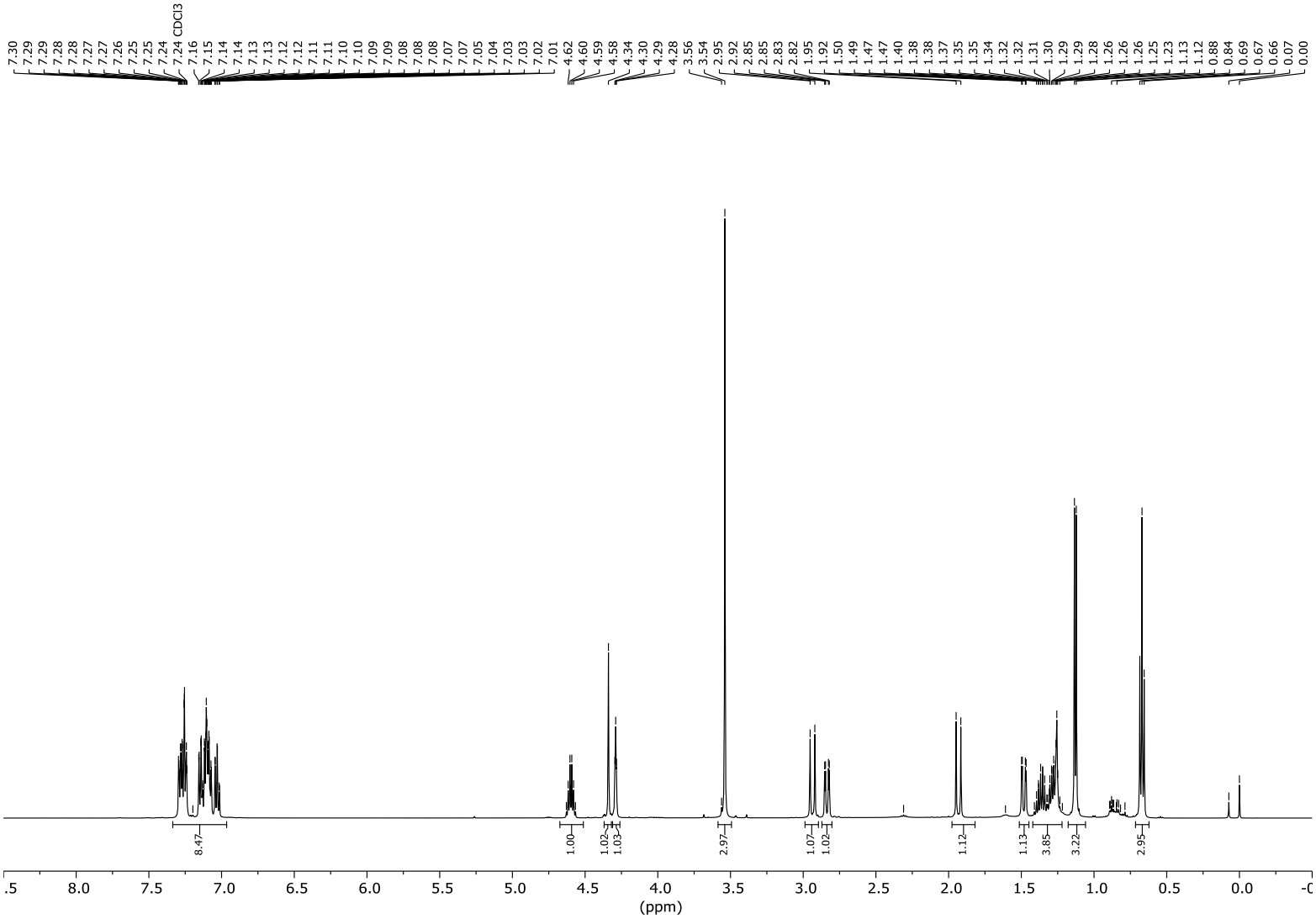

Figure S19 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*S*)-**11**

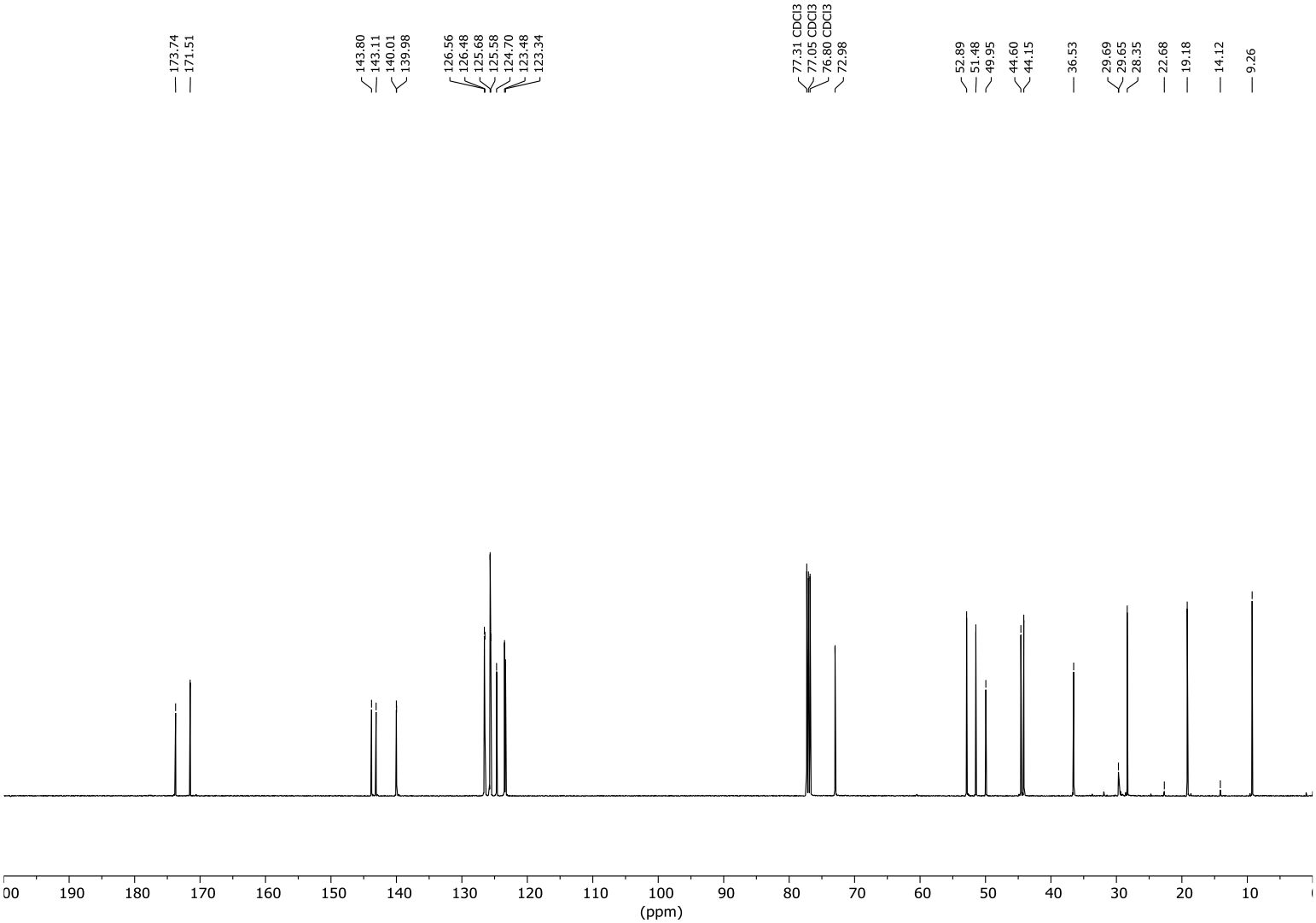

Figure 20 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*S*)-**11**

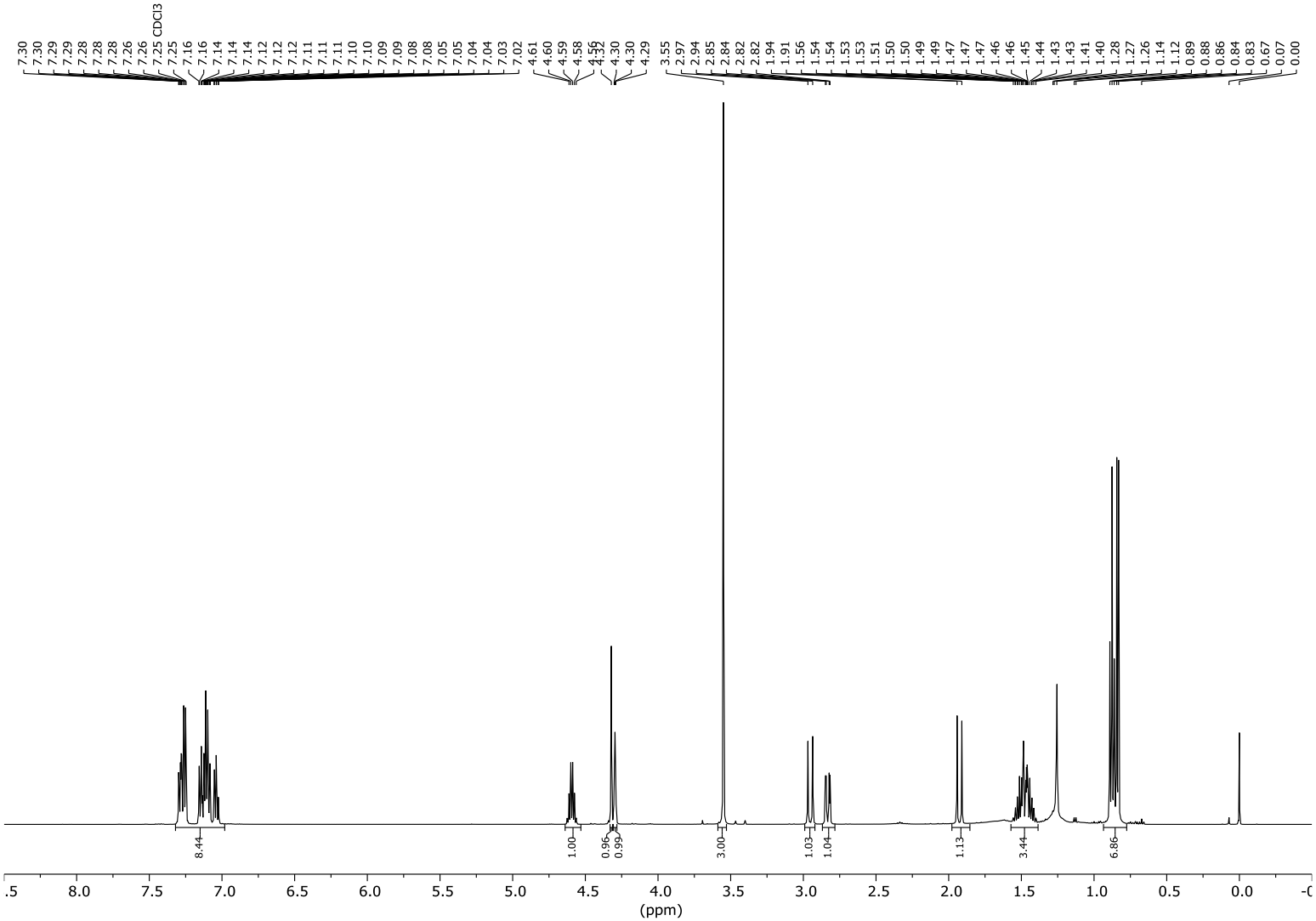

Figure S21 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (−)-(11*R*,1′*S*)-**12**

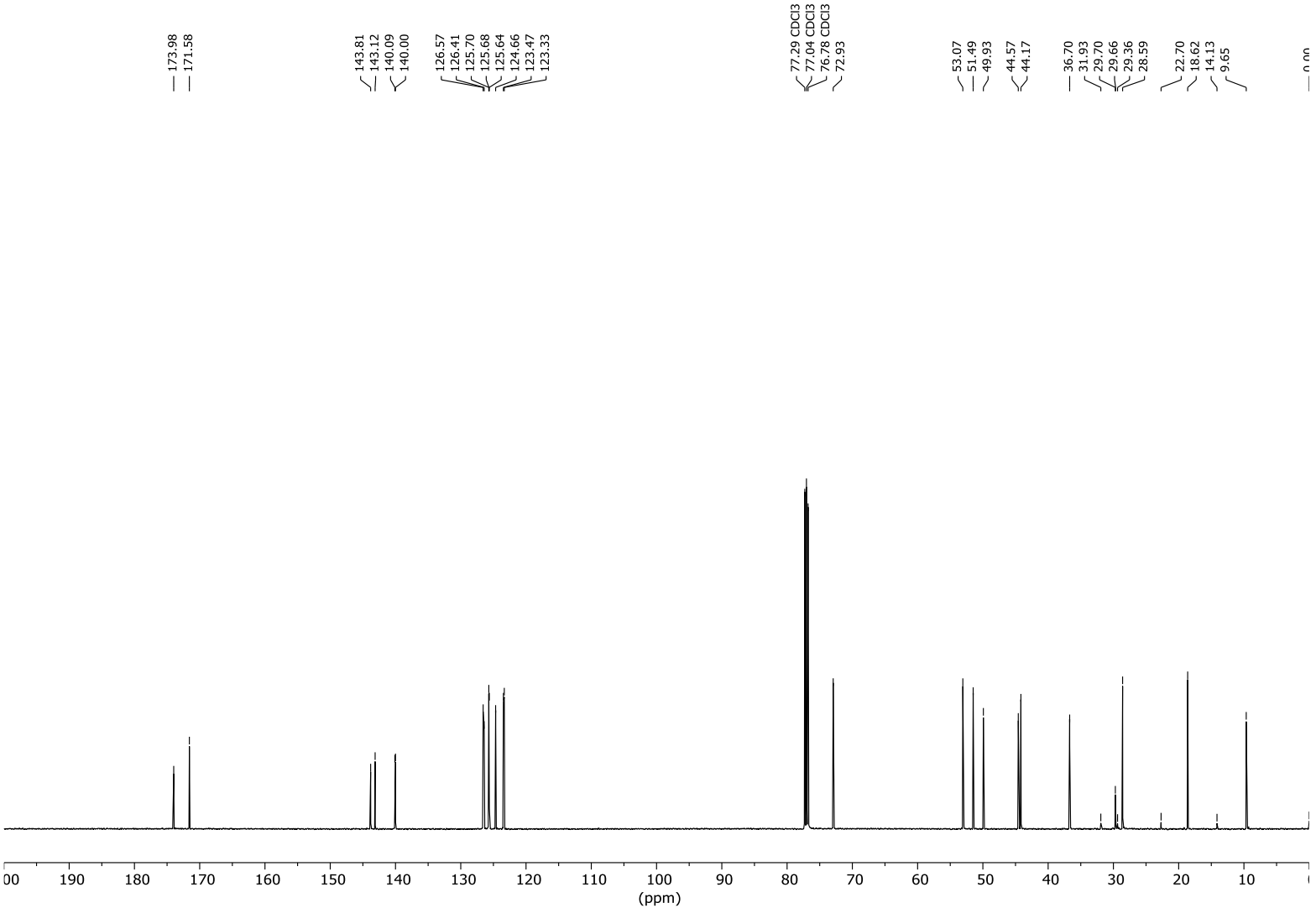

Figure S22 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (–)-(11*R*,1′*S*)-**12**

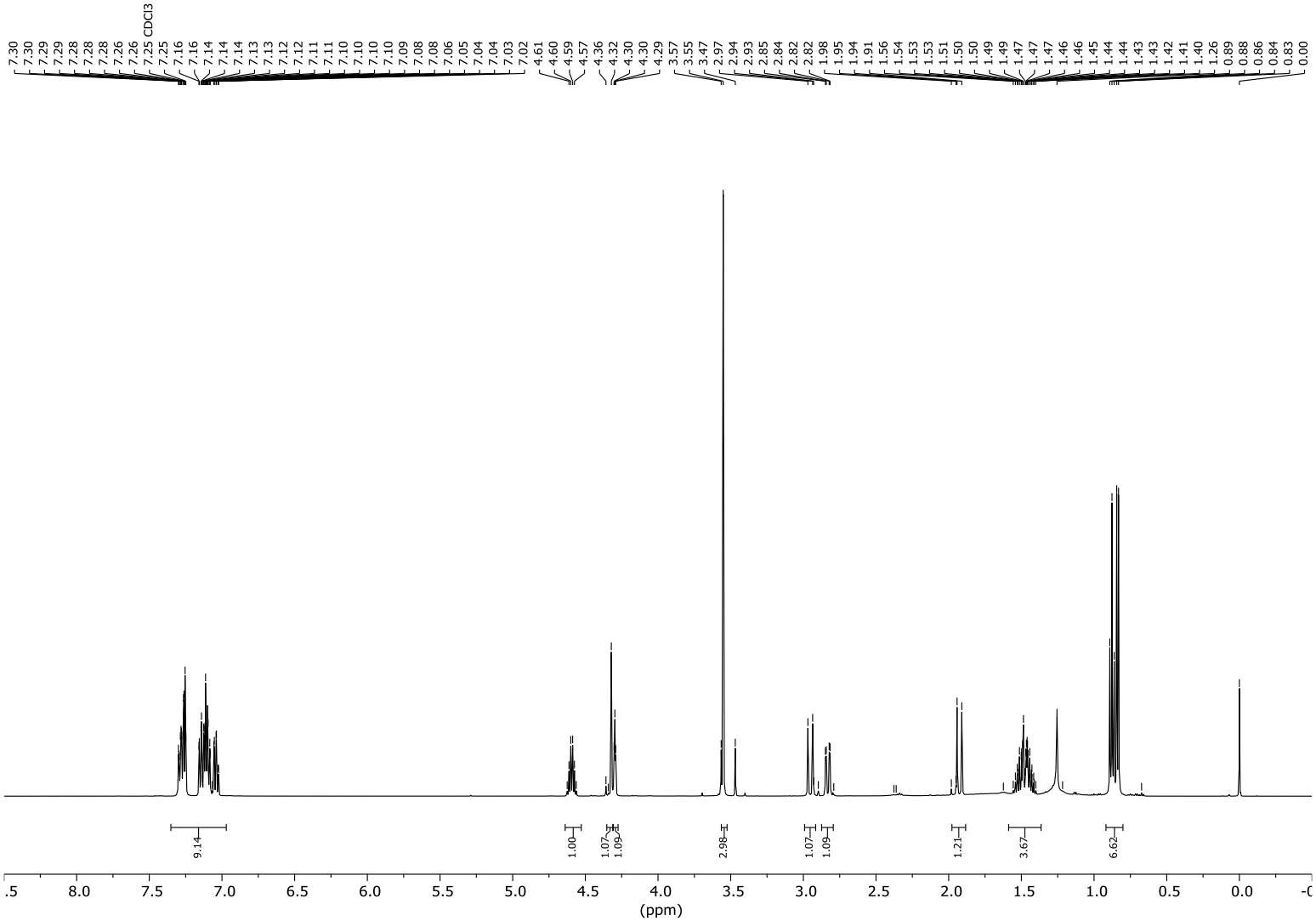

Figure S23 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*R*)-**13**

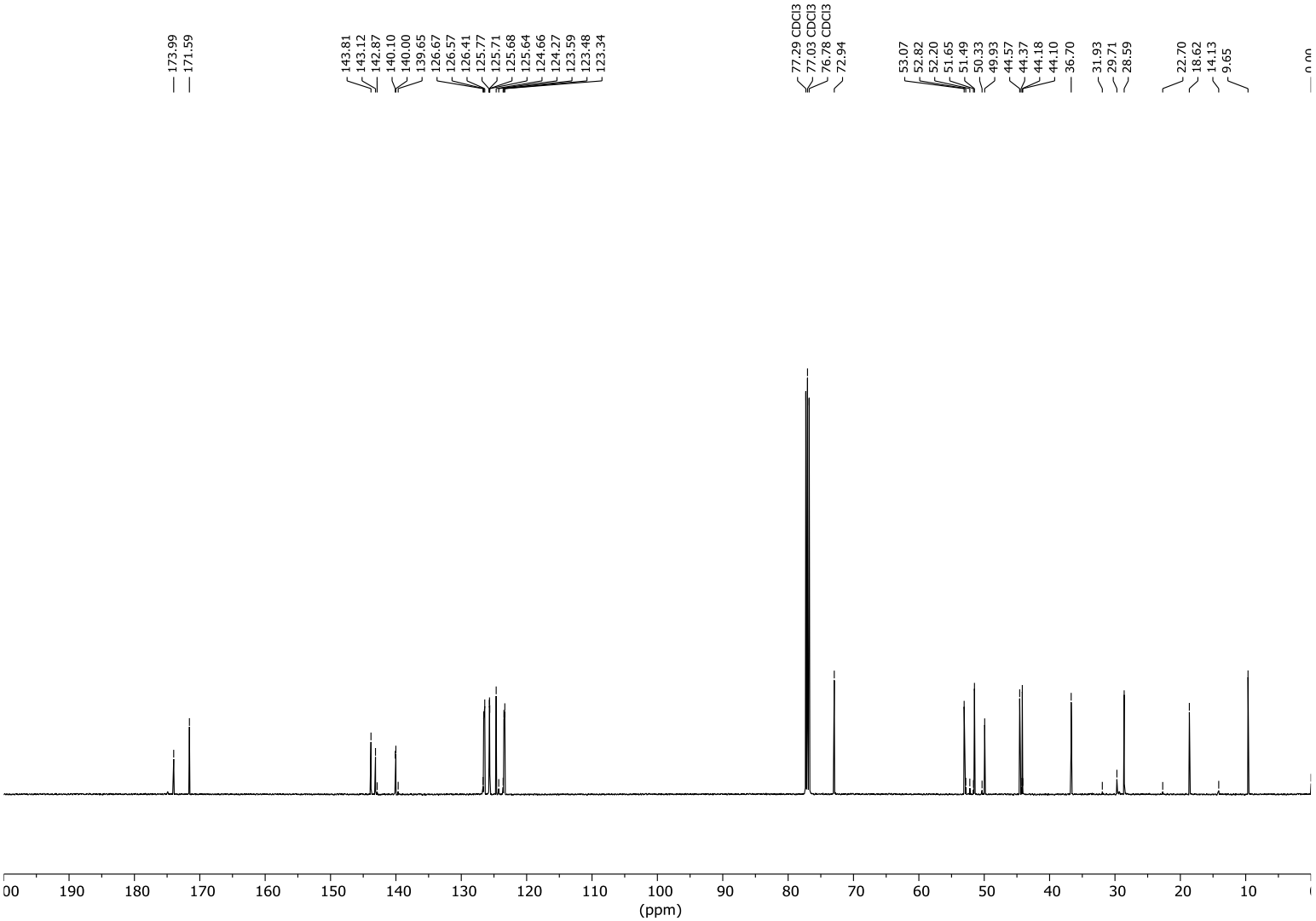

Figure S24 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*R*)-**13**

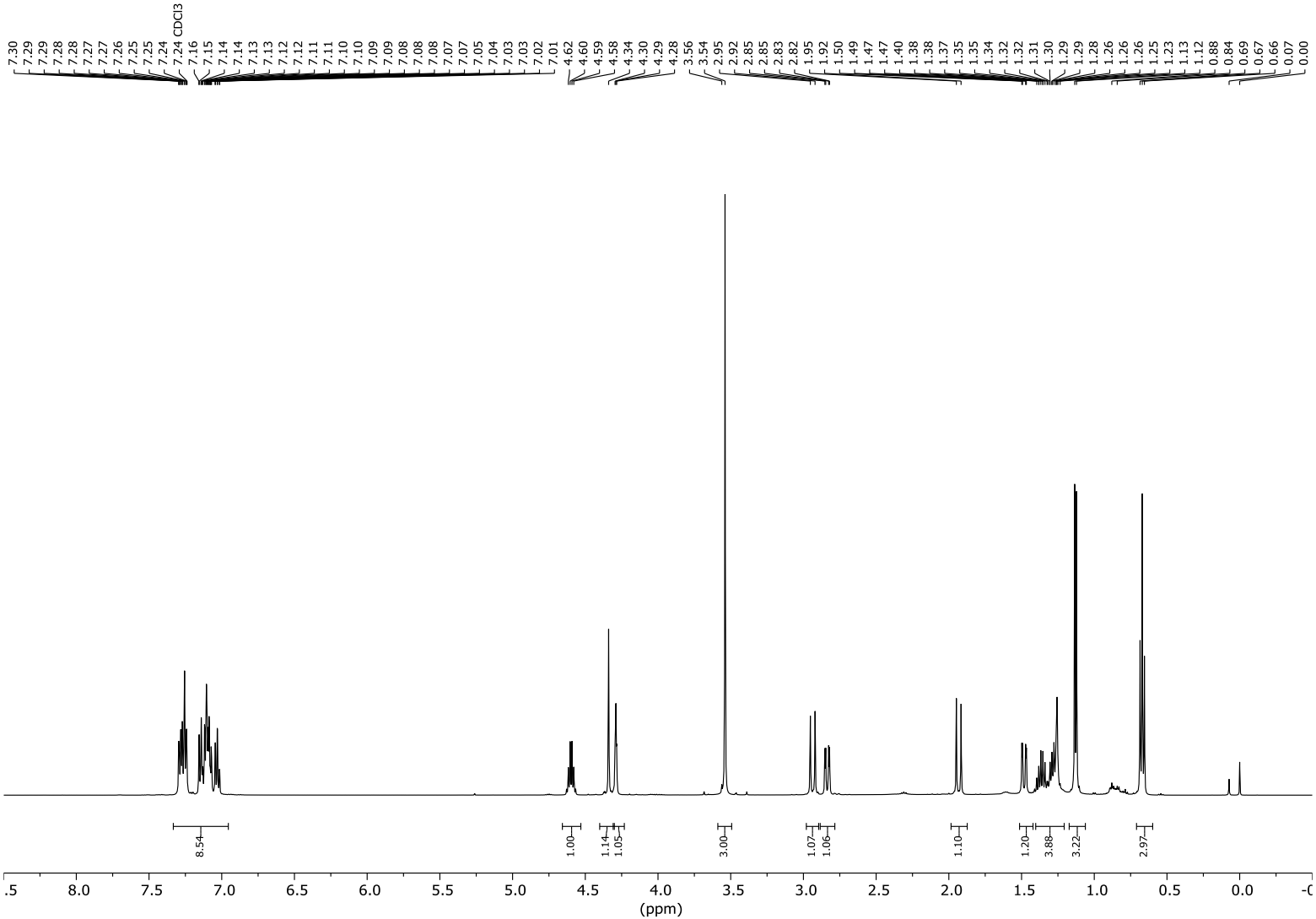

Figure S25 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (−)-(11*R*,1′*R*)-**14**

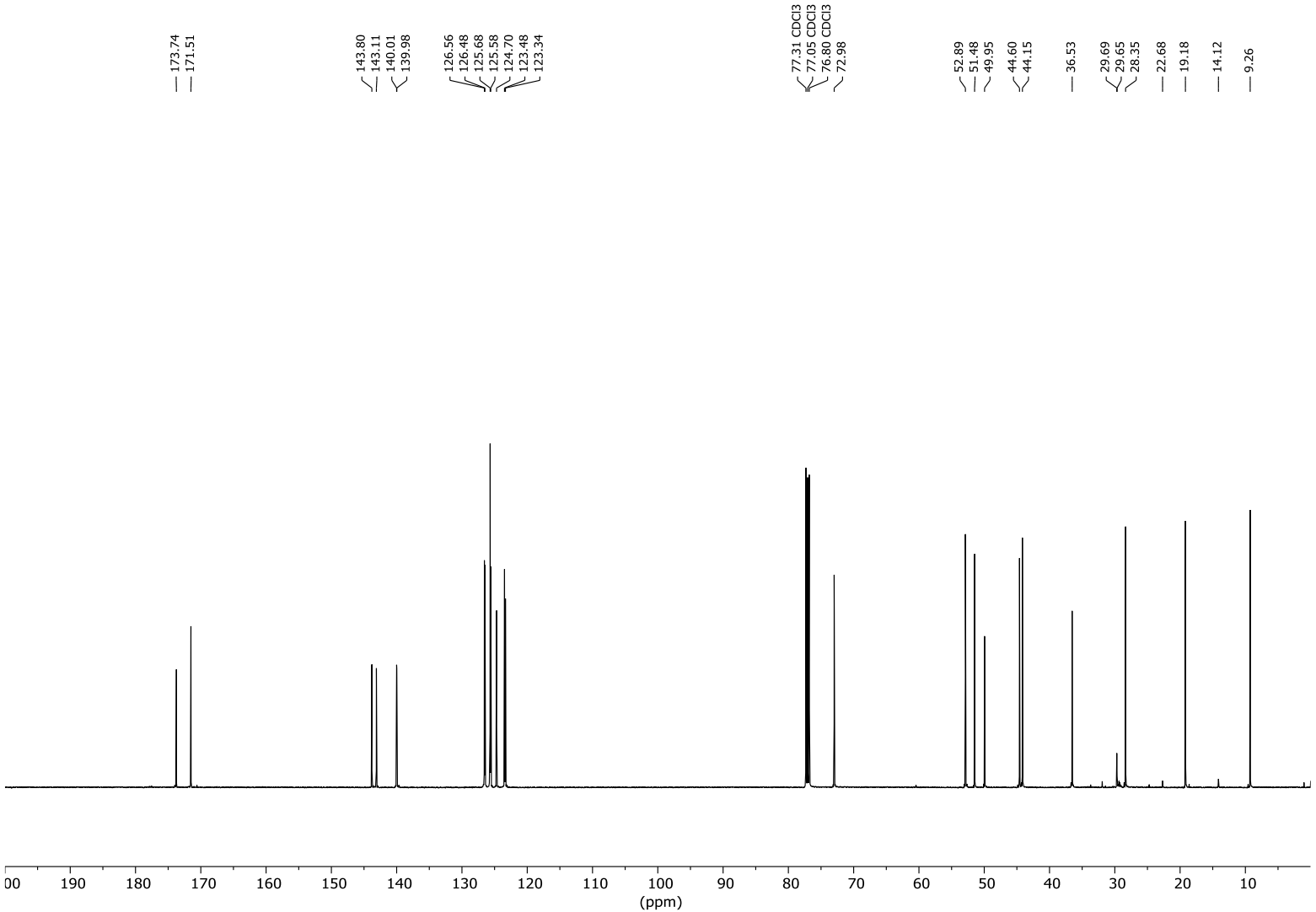

Figure S26 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (–)-(11*R*,1′*R*)-**14**

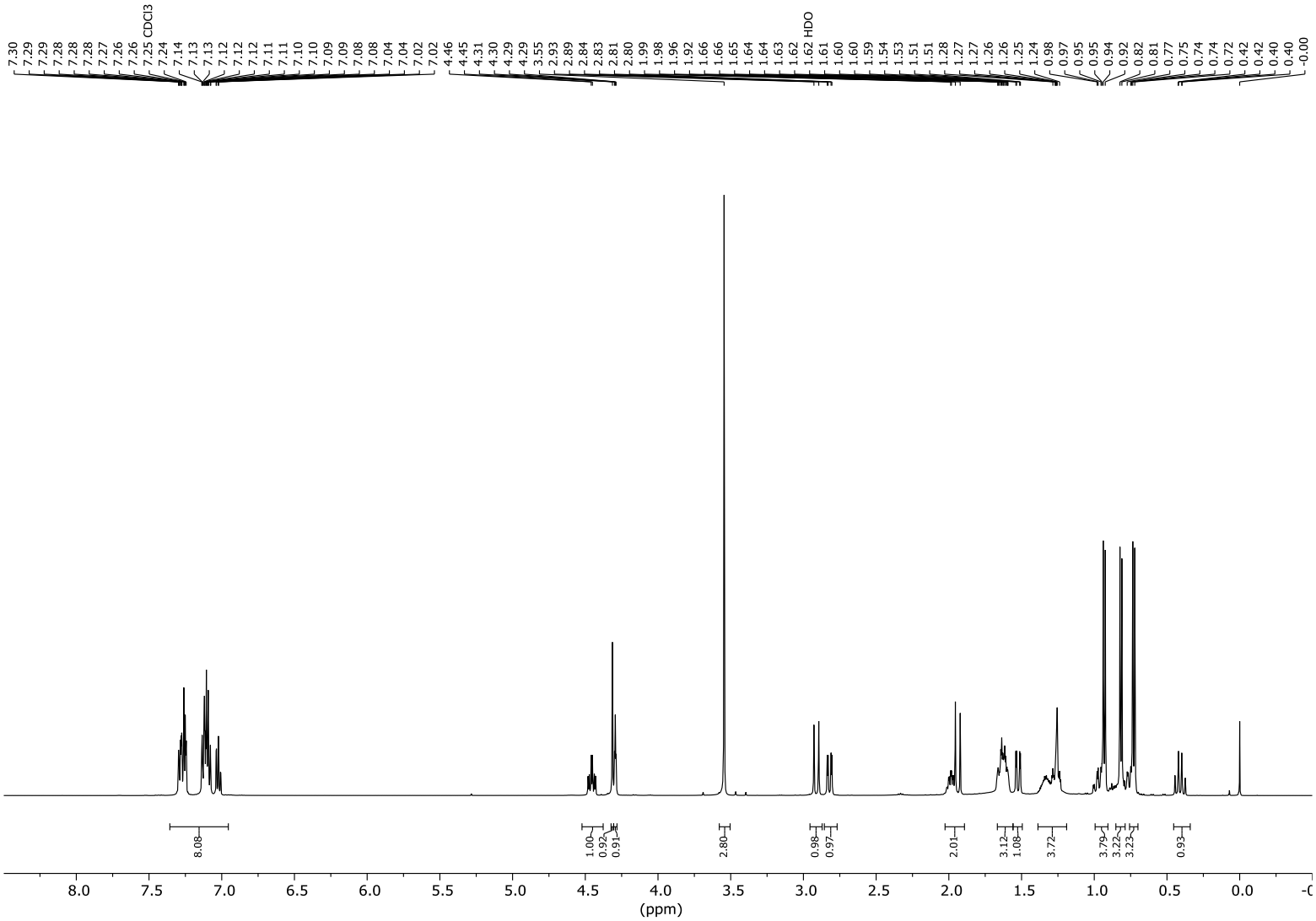

Figure S27 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (–)-(11*S*,1′*S*)-**15**

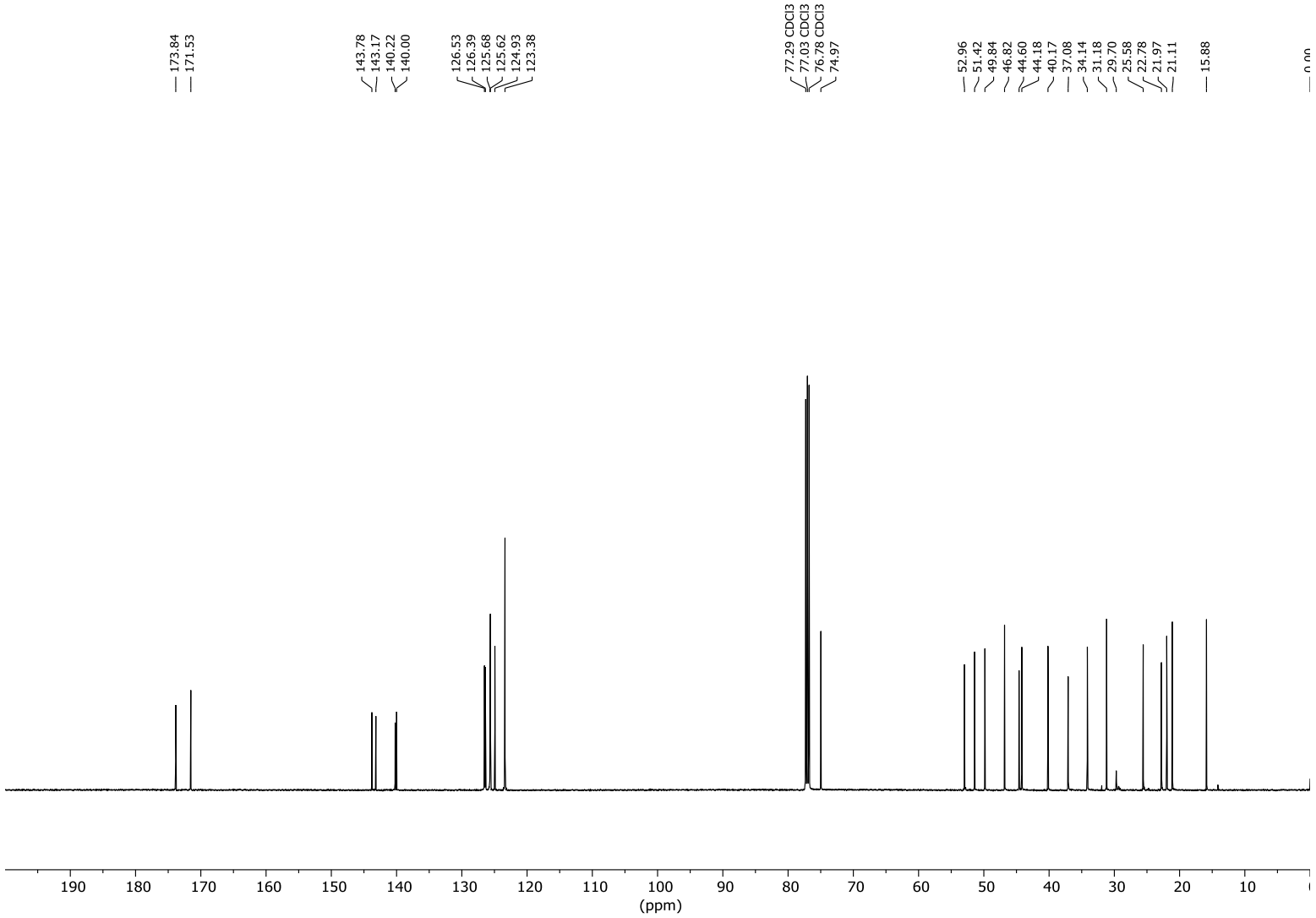

Figure S28 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (–)-(11*S*,1′*S*)-**15**

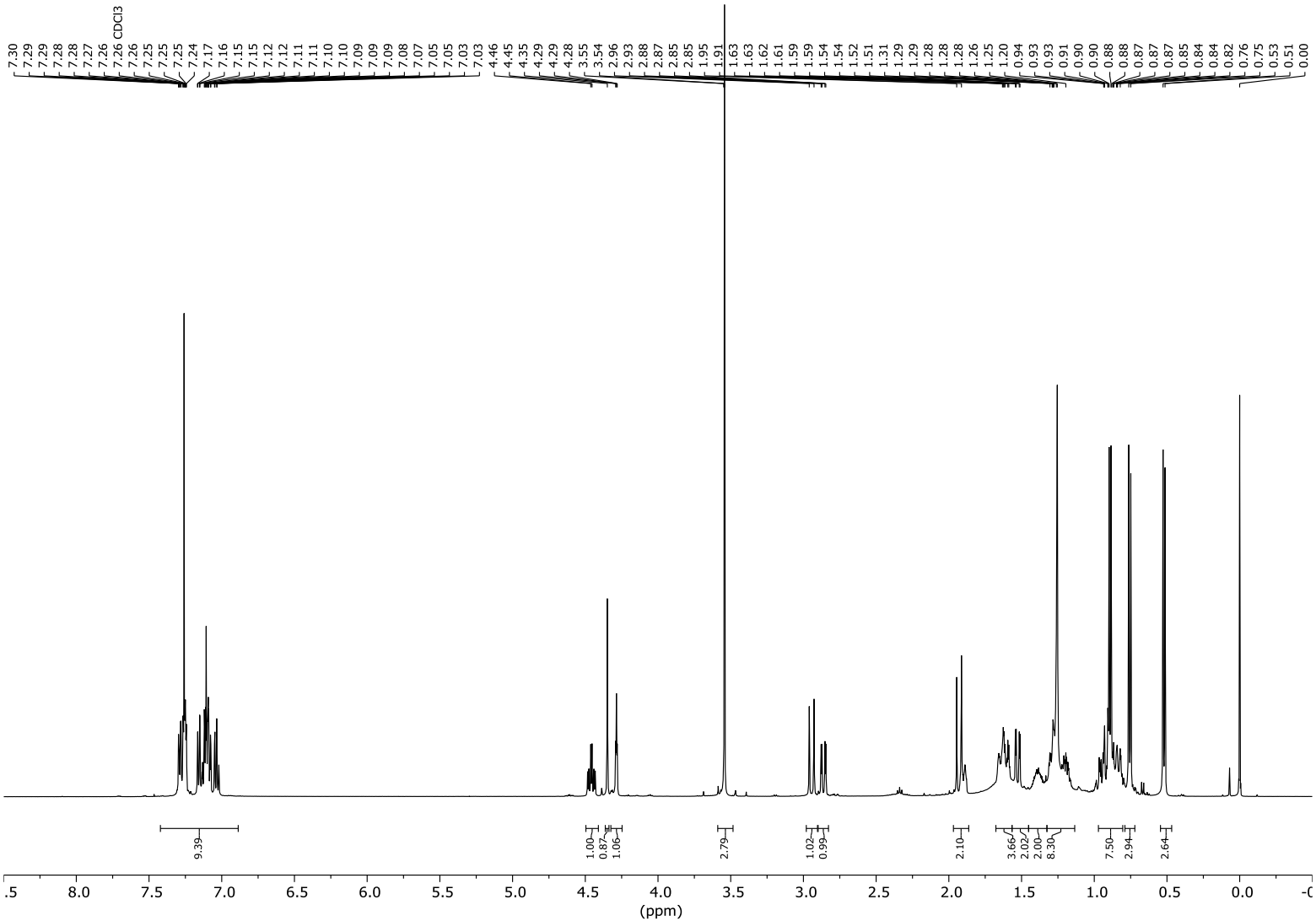

Figure S29 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (−)-(11*R*,1′*S*)-**16**

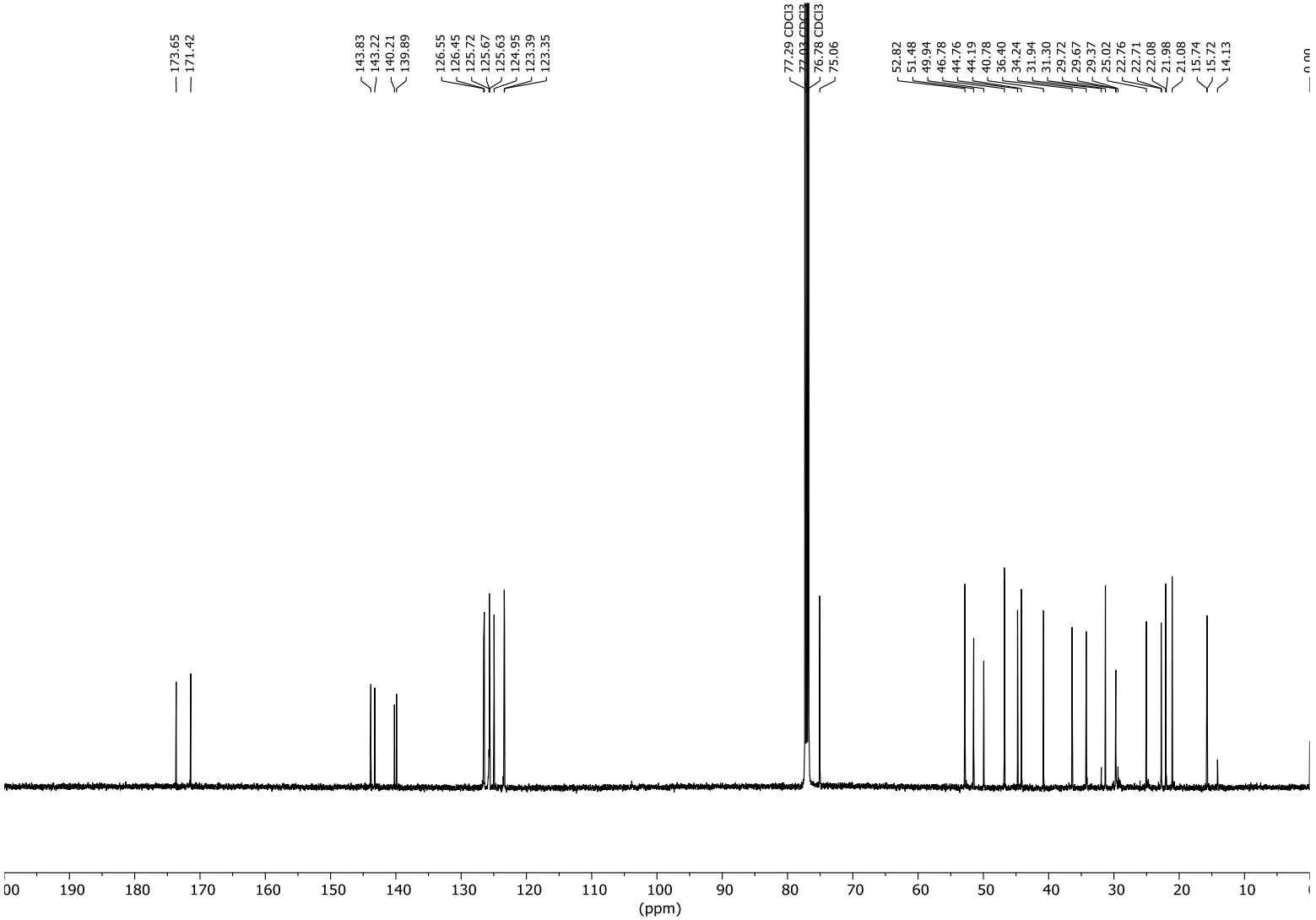

Figure S30 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (–)-(11*R*,1′*S*)-**16**

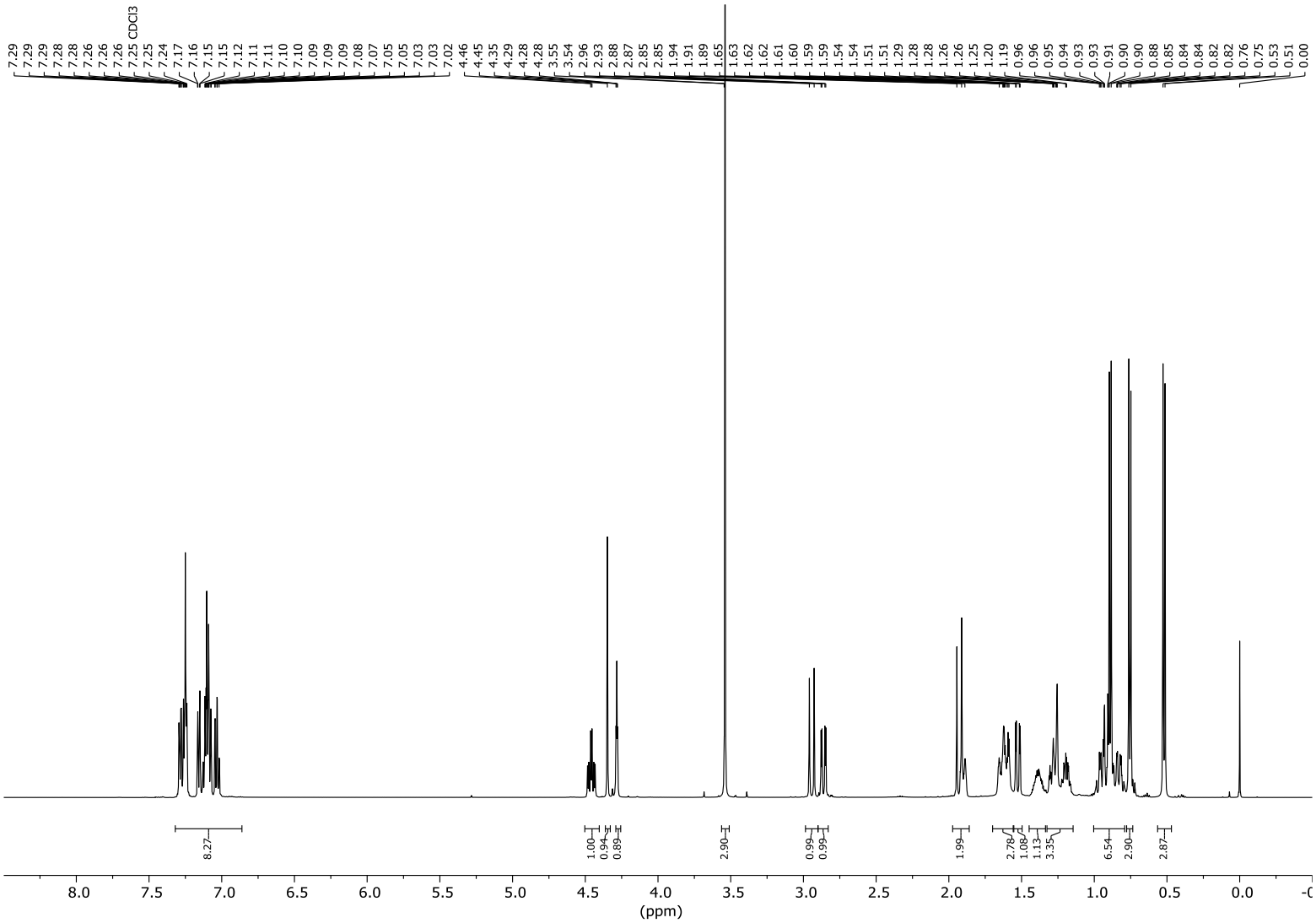

Figure S31 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*R*)-**17**

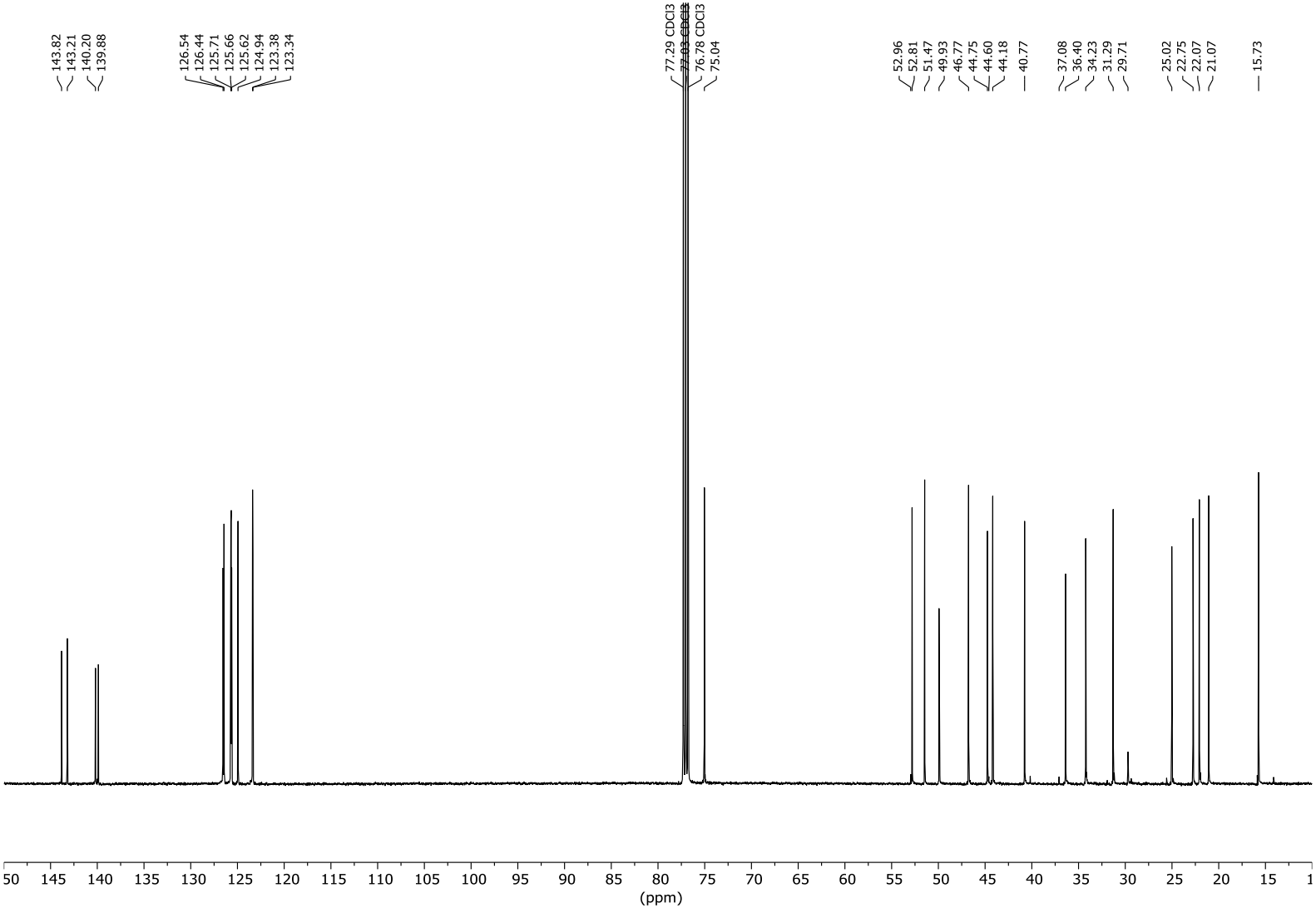

Figure S32 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*R*)-**17**

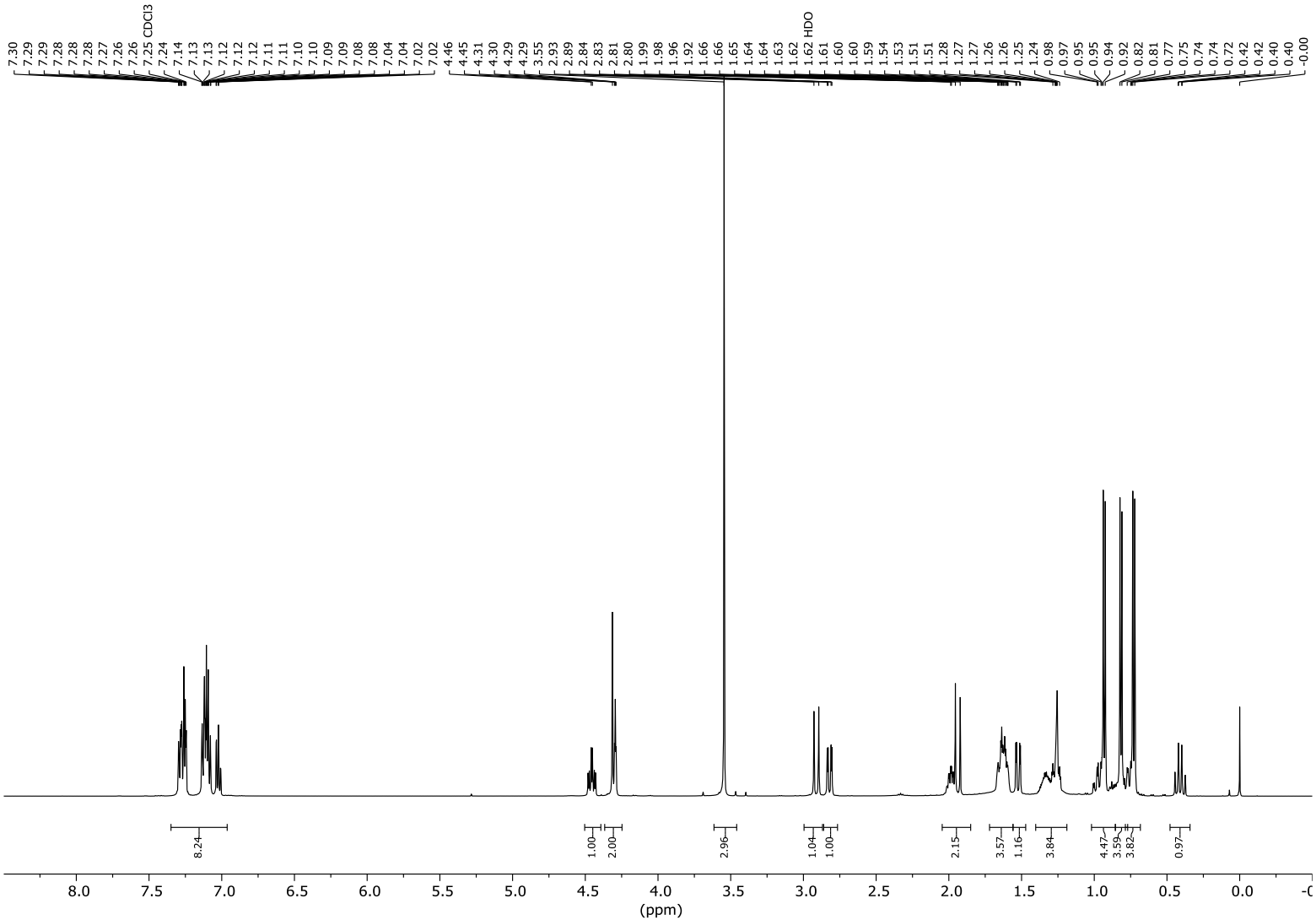

Figure S33 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (+)-(11*R*,1′*R*)-**18**

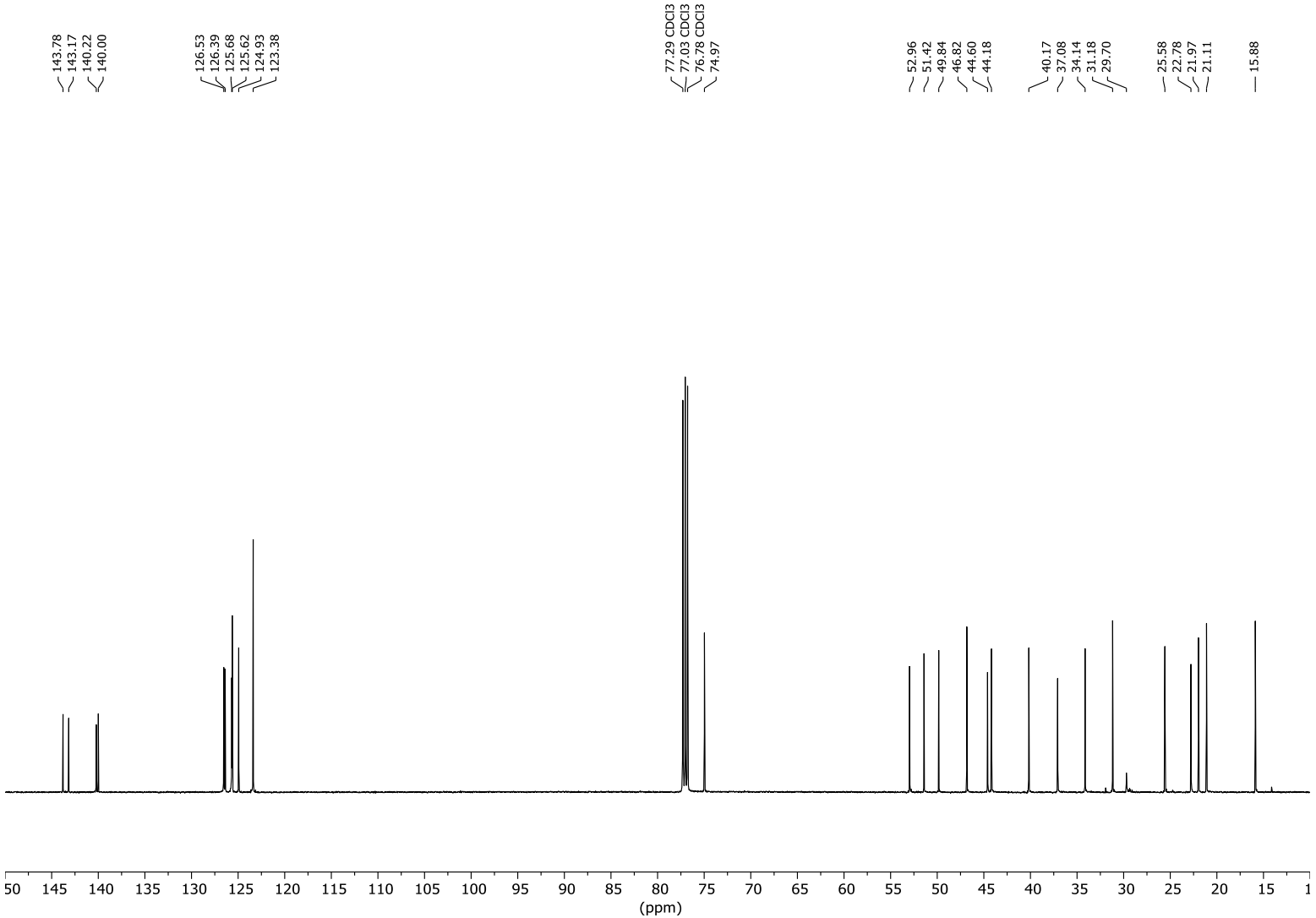

Figure S34 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (+)-(11*R*,1′*R*)-**18**

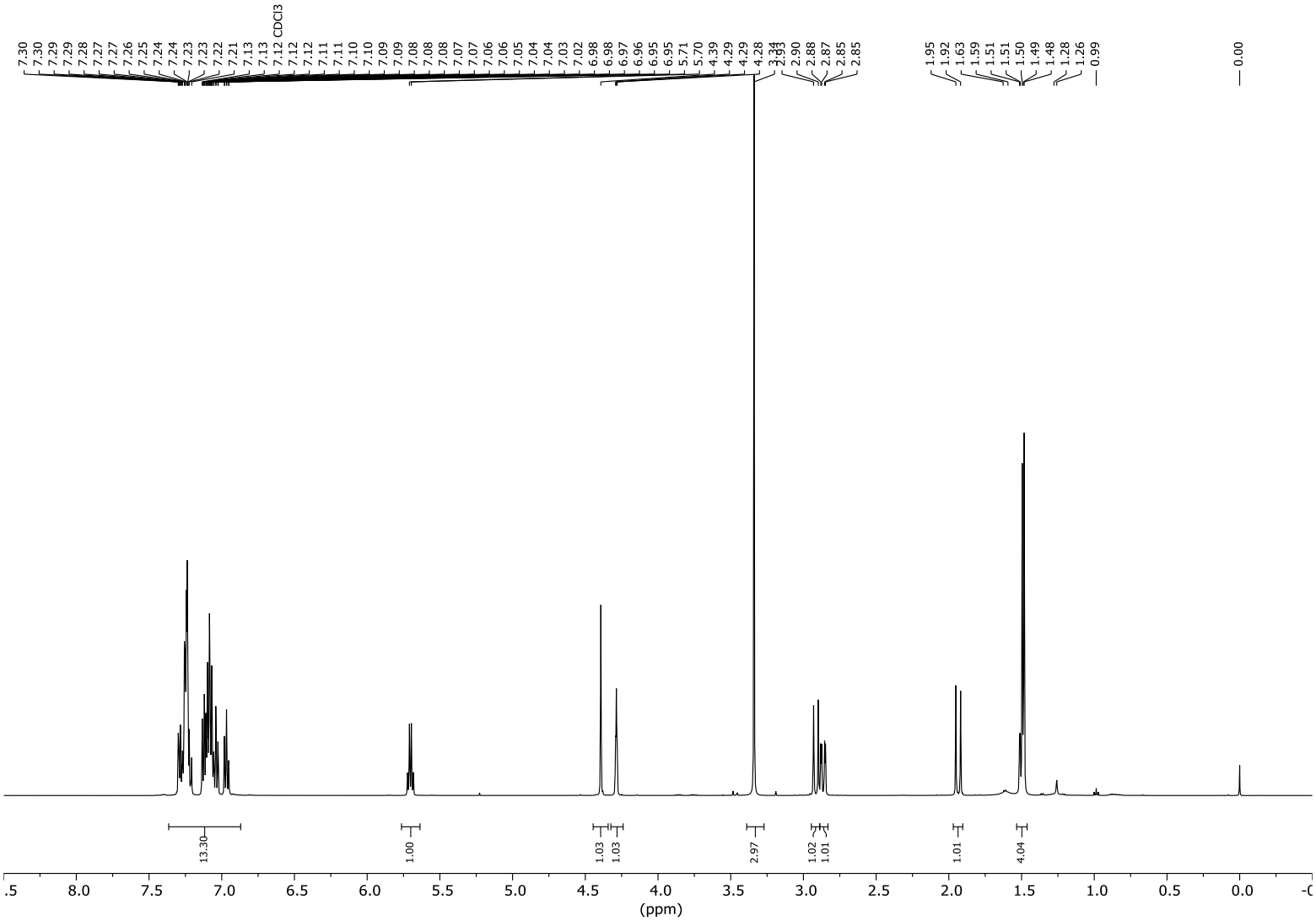

Figure S35 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*S*)-**19**

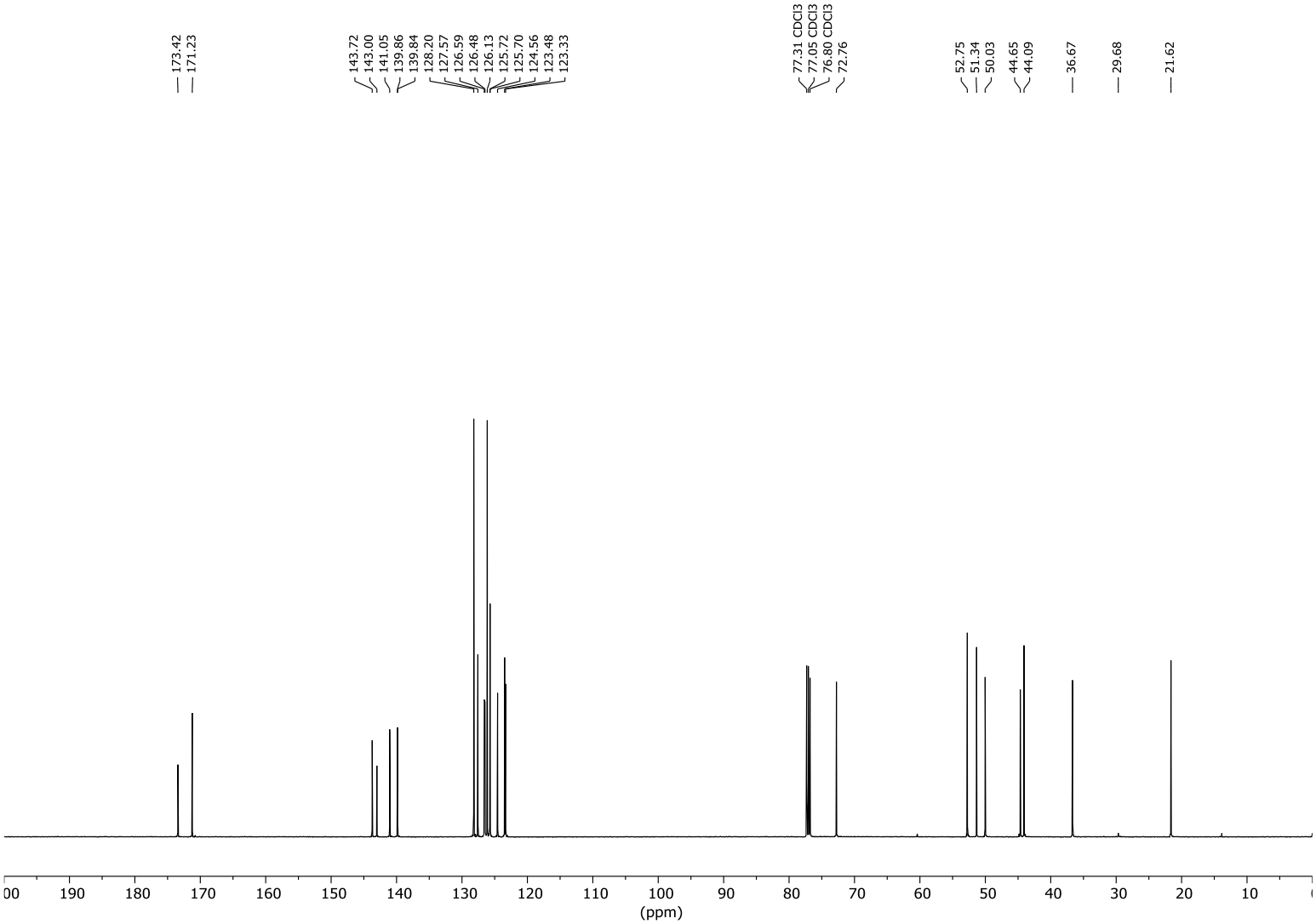

Figure S36 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*S*)-**19**

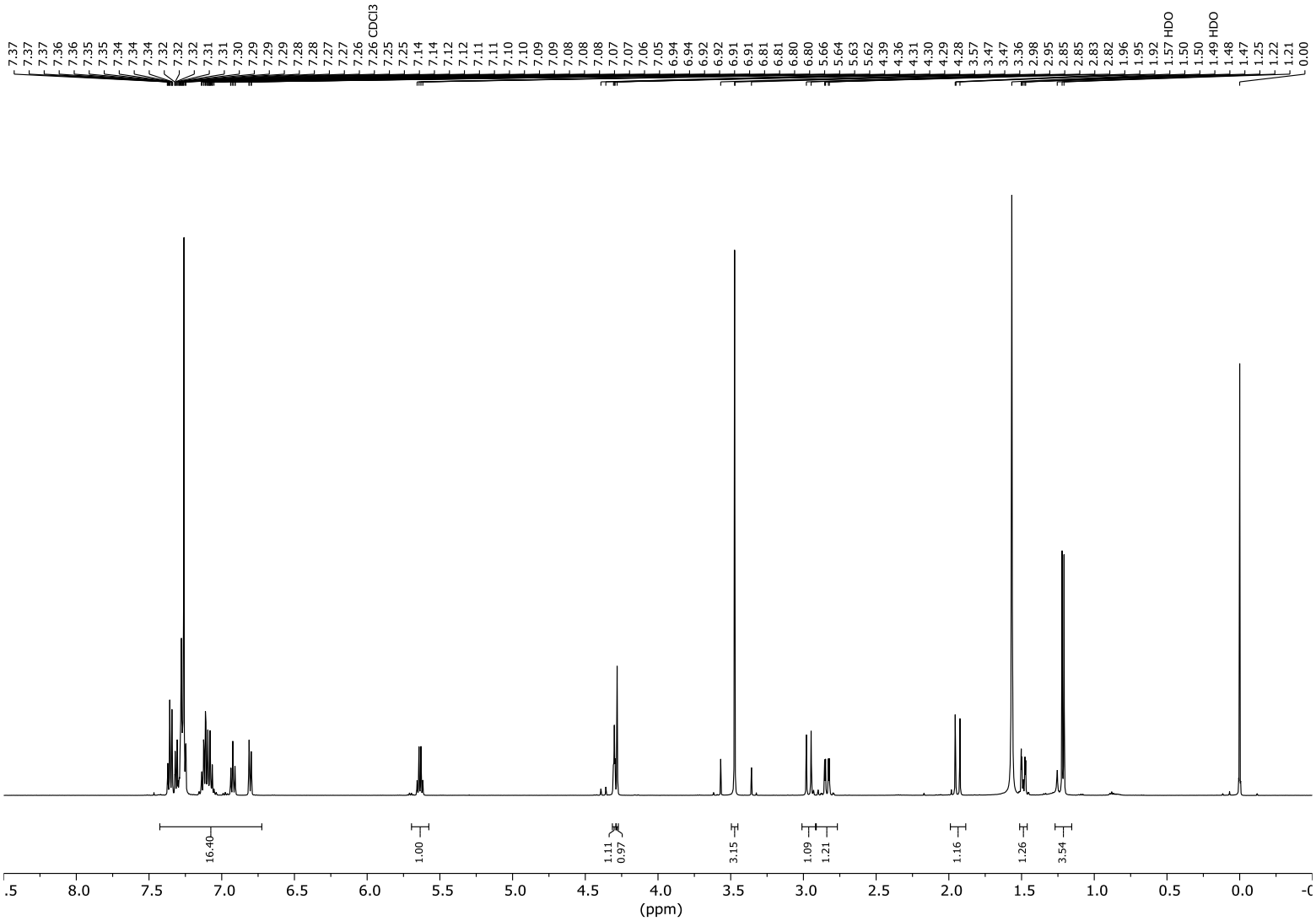

Figure S37 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (−)-(11*R*,1′*S*)-**20**

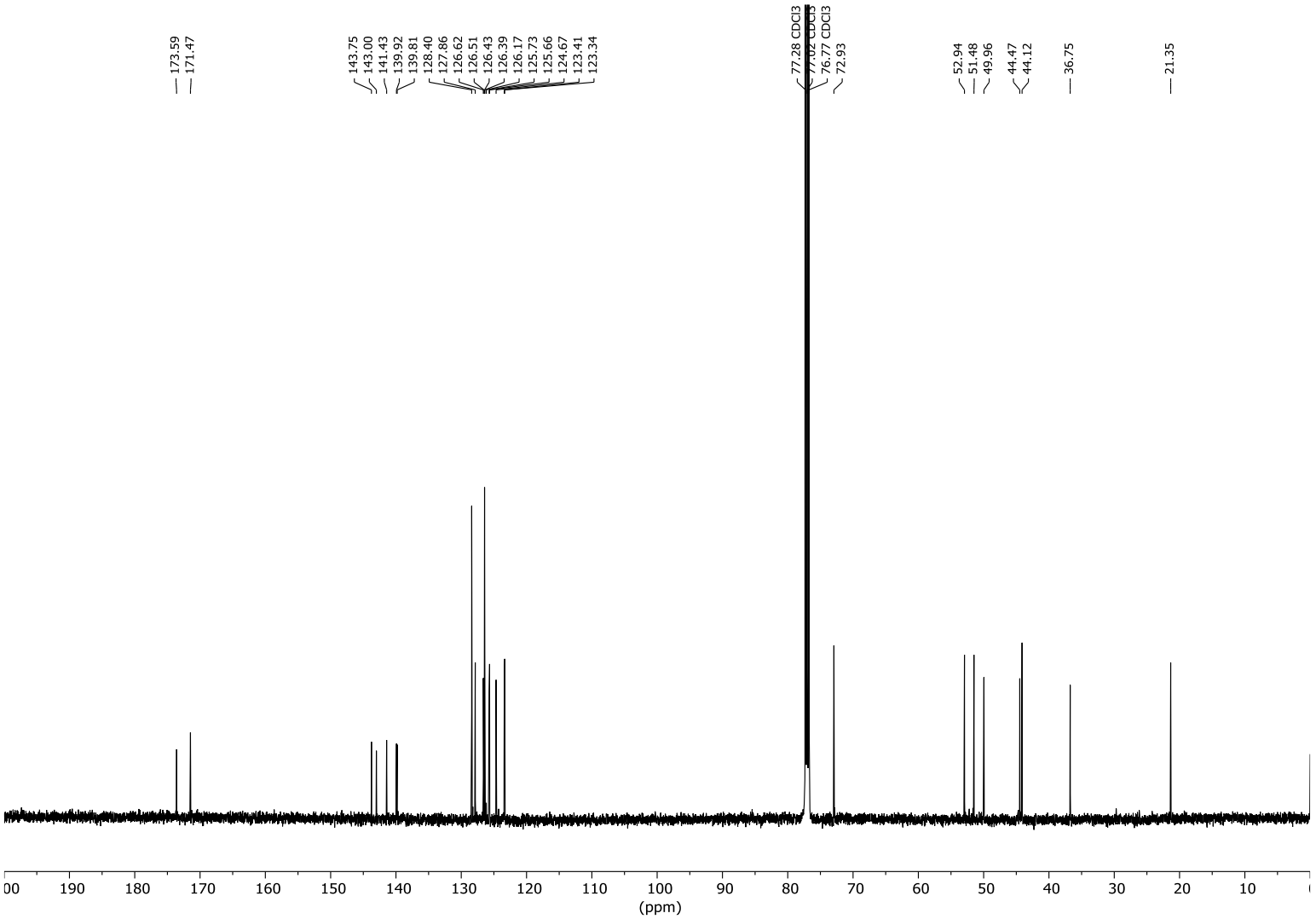

Figure S38 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (–)-(11*R*,1′*S*)-**20**

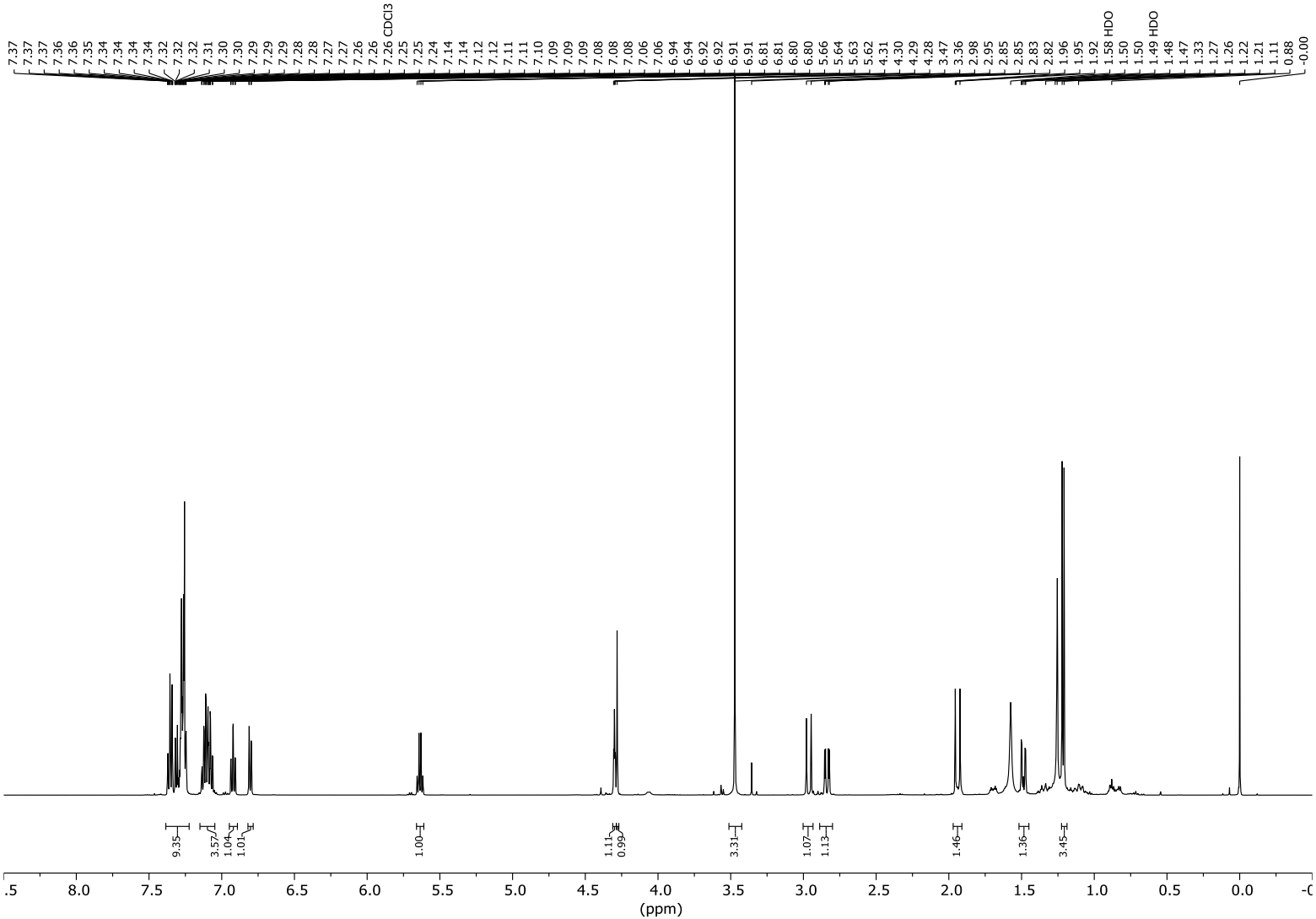

Figure S39 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (–)-(11*S*,1′*R*)-**21**

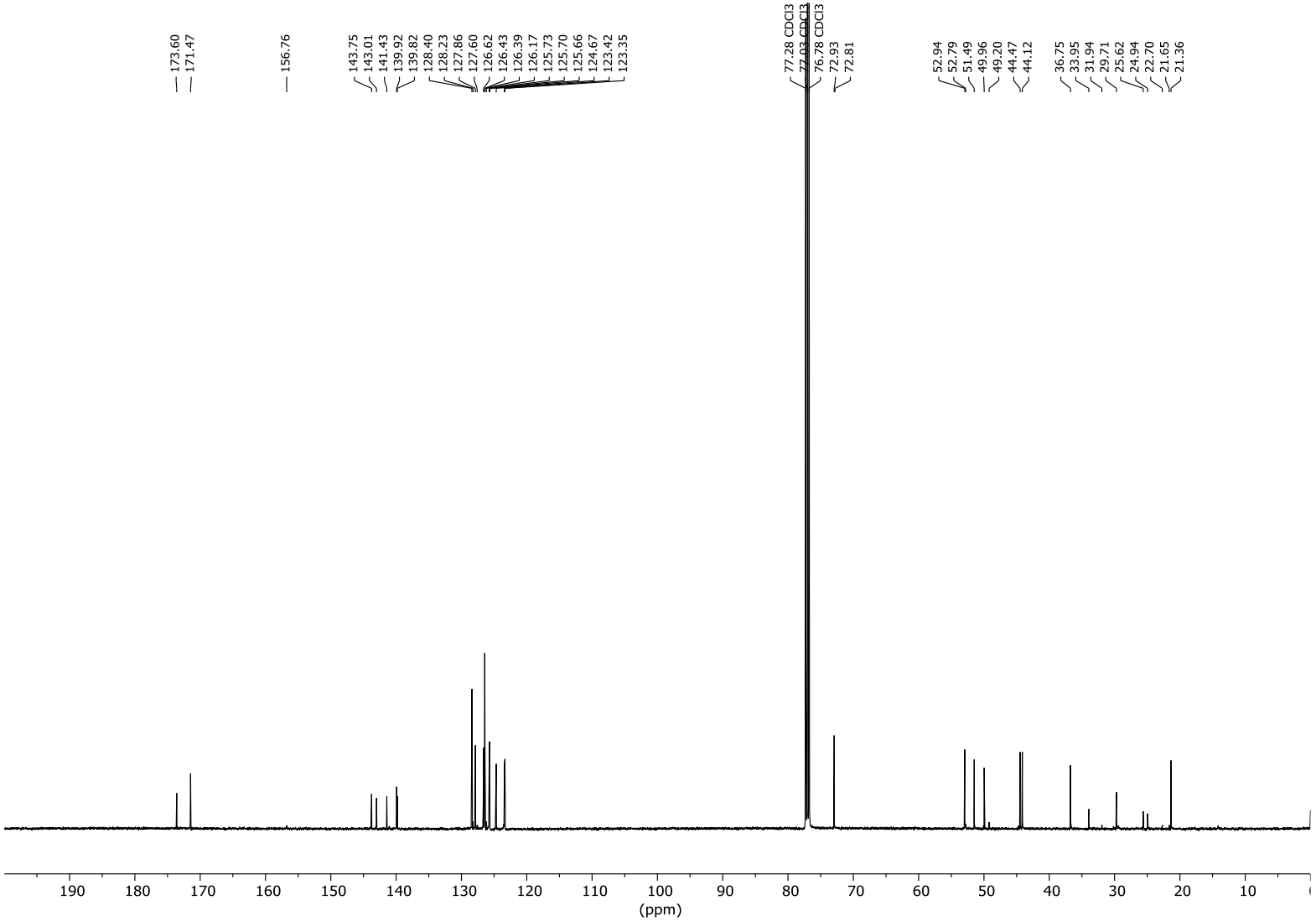

Figure S40 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (–)-(11*S*,1′*R*)-**21**

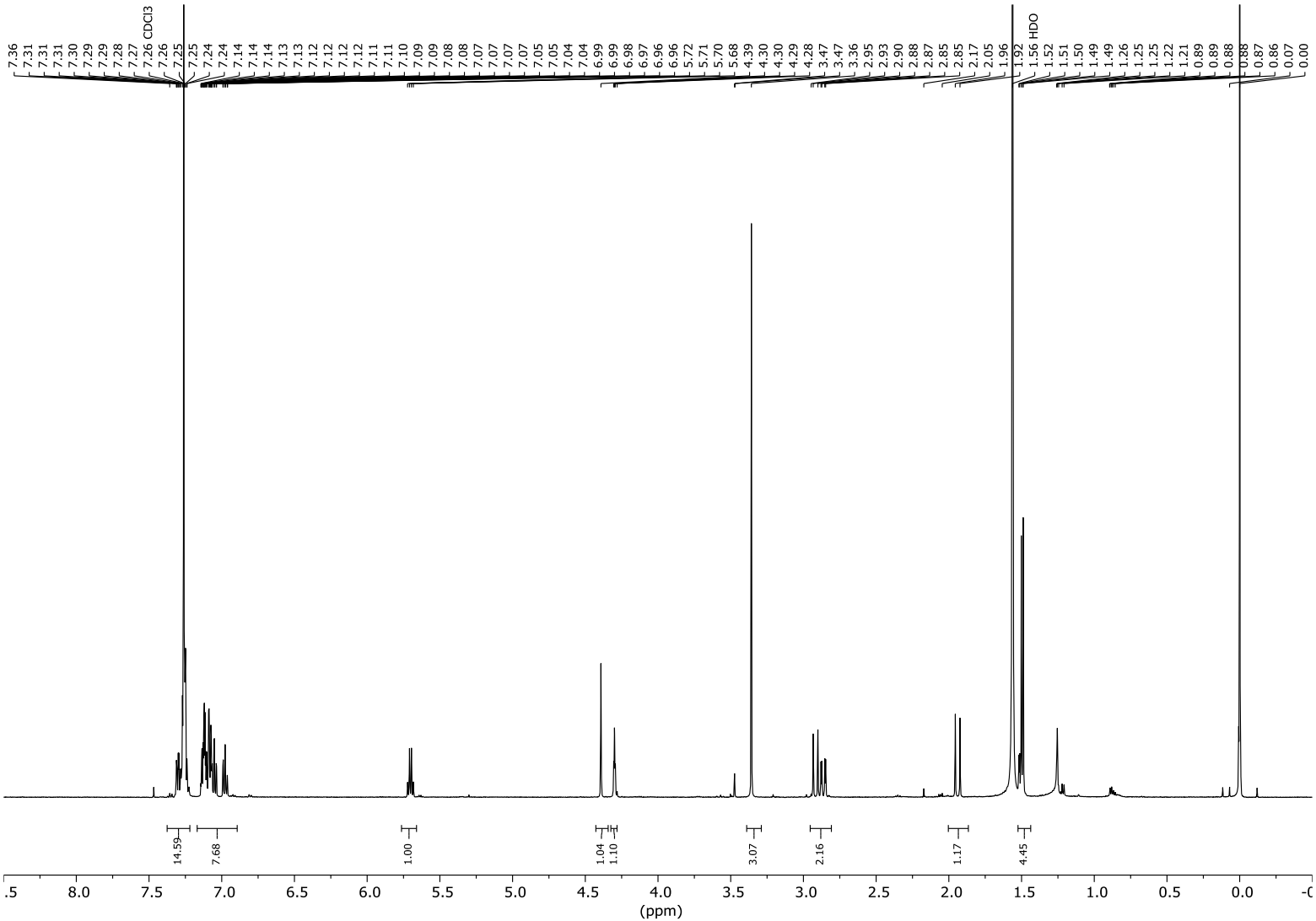

Figure S41 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (−)-(11*R*,1′*R*)-**22**

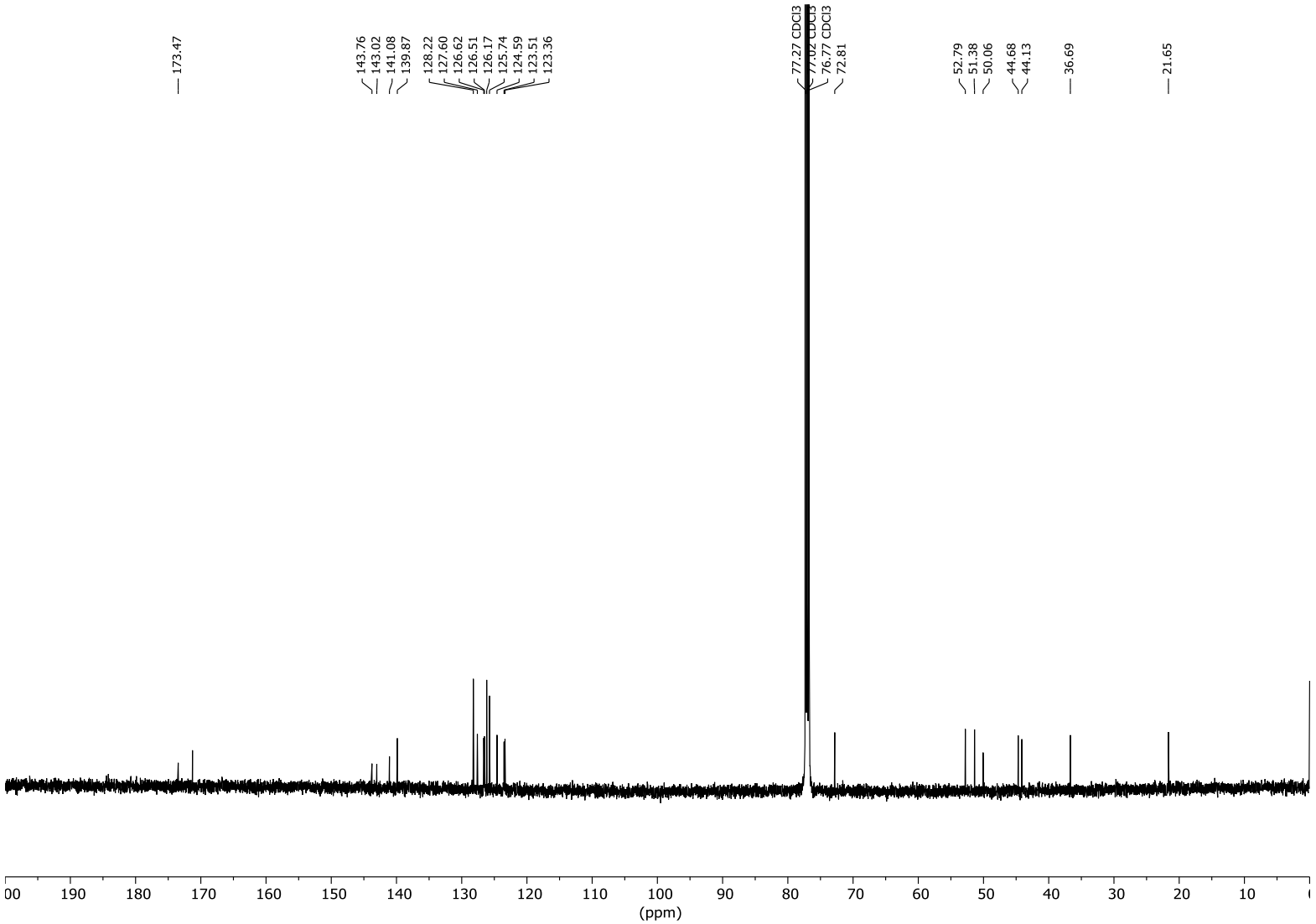

Figure S42 ^{13}C NMR (126 MHz, $CDCl_3$) spectra of (−)-(11*R*,1′*R*)-**22**

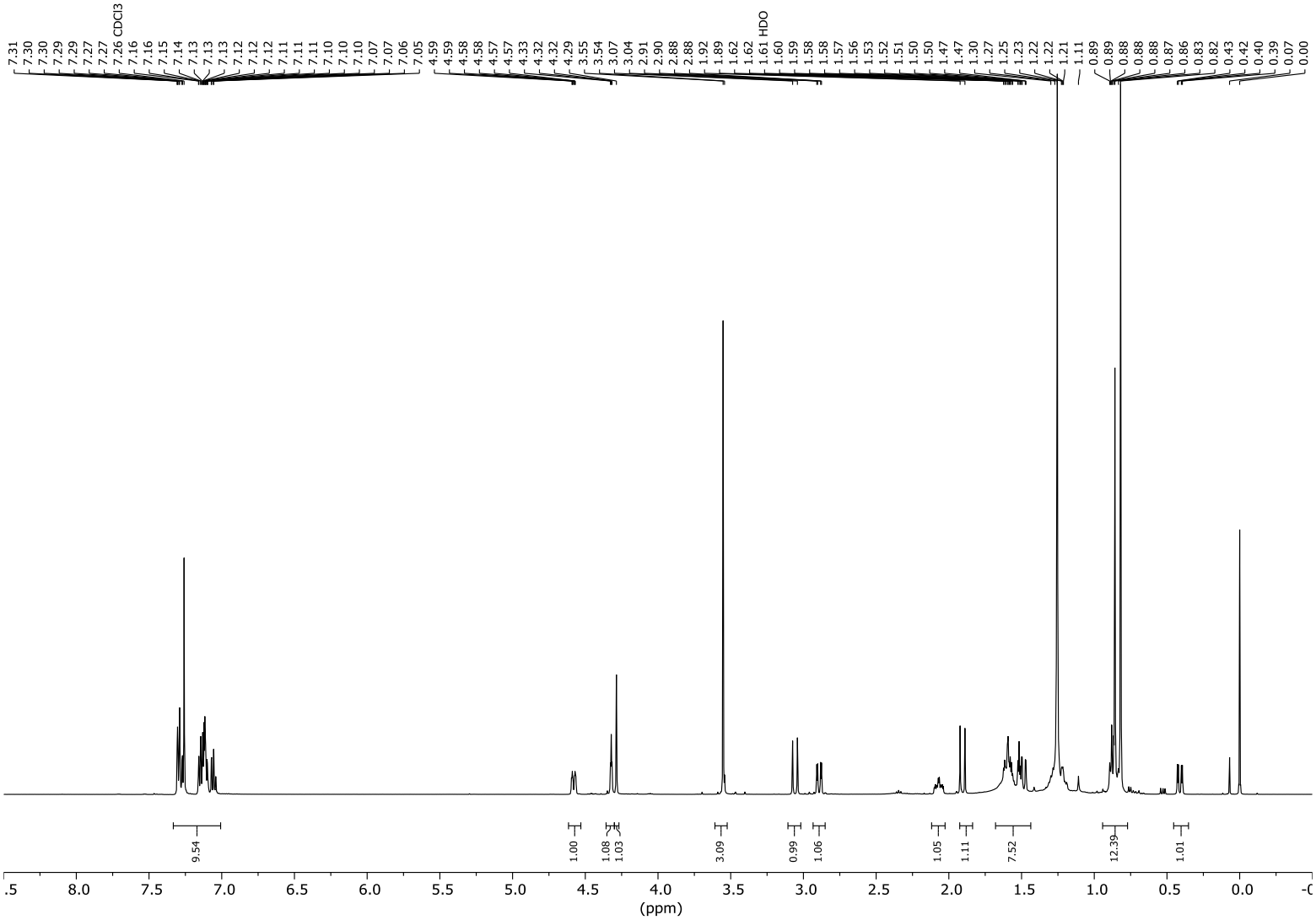

Figure S43 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*S*)-**23**

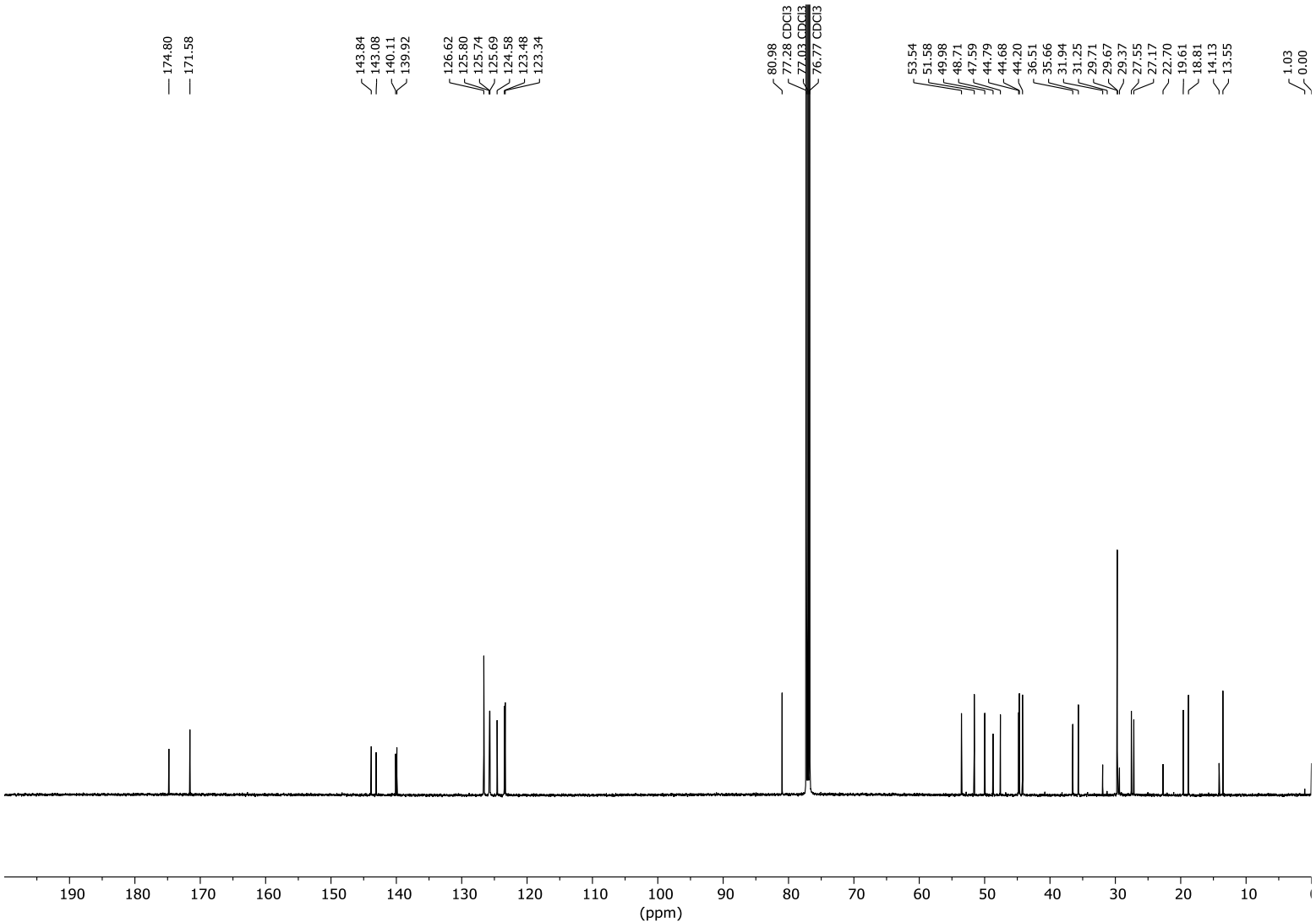

Figure S44 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*S*)-**23**

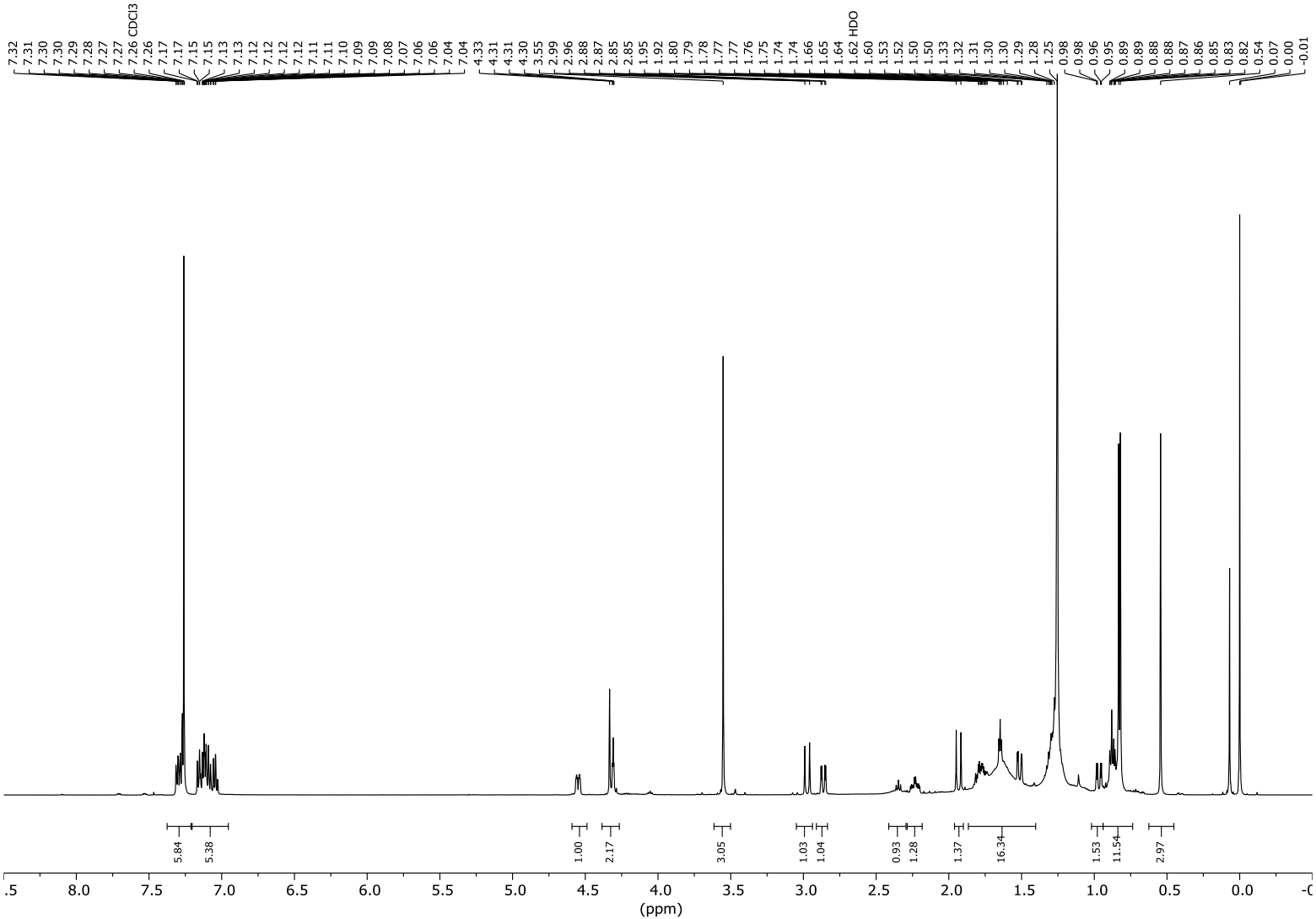

Figure S45 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (–)-(11*R*,1′*S*)-**24**

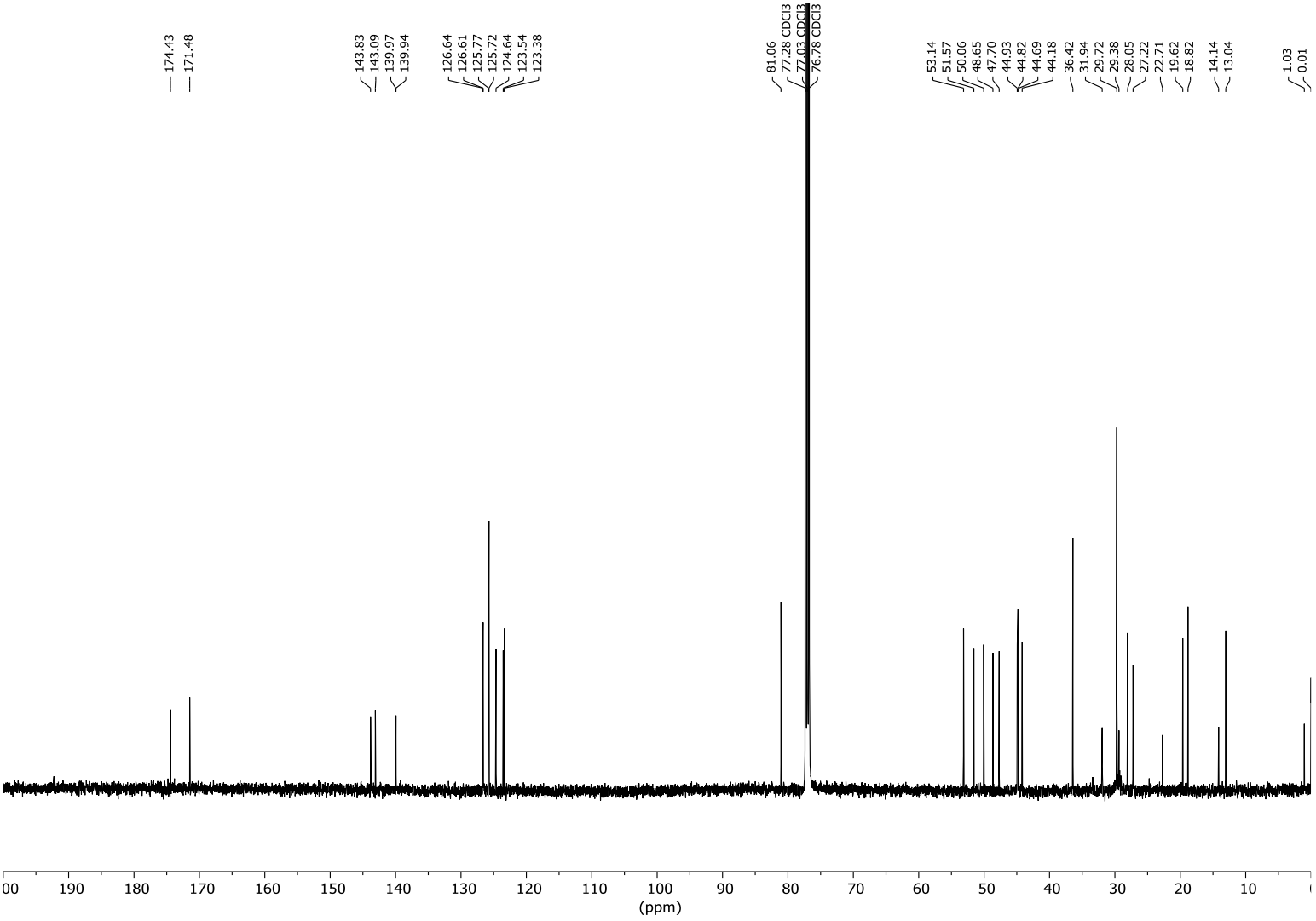

Figure S46 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (−)-(11*R*,1′*S*)-**24**

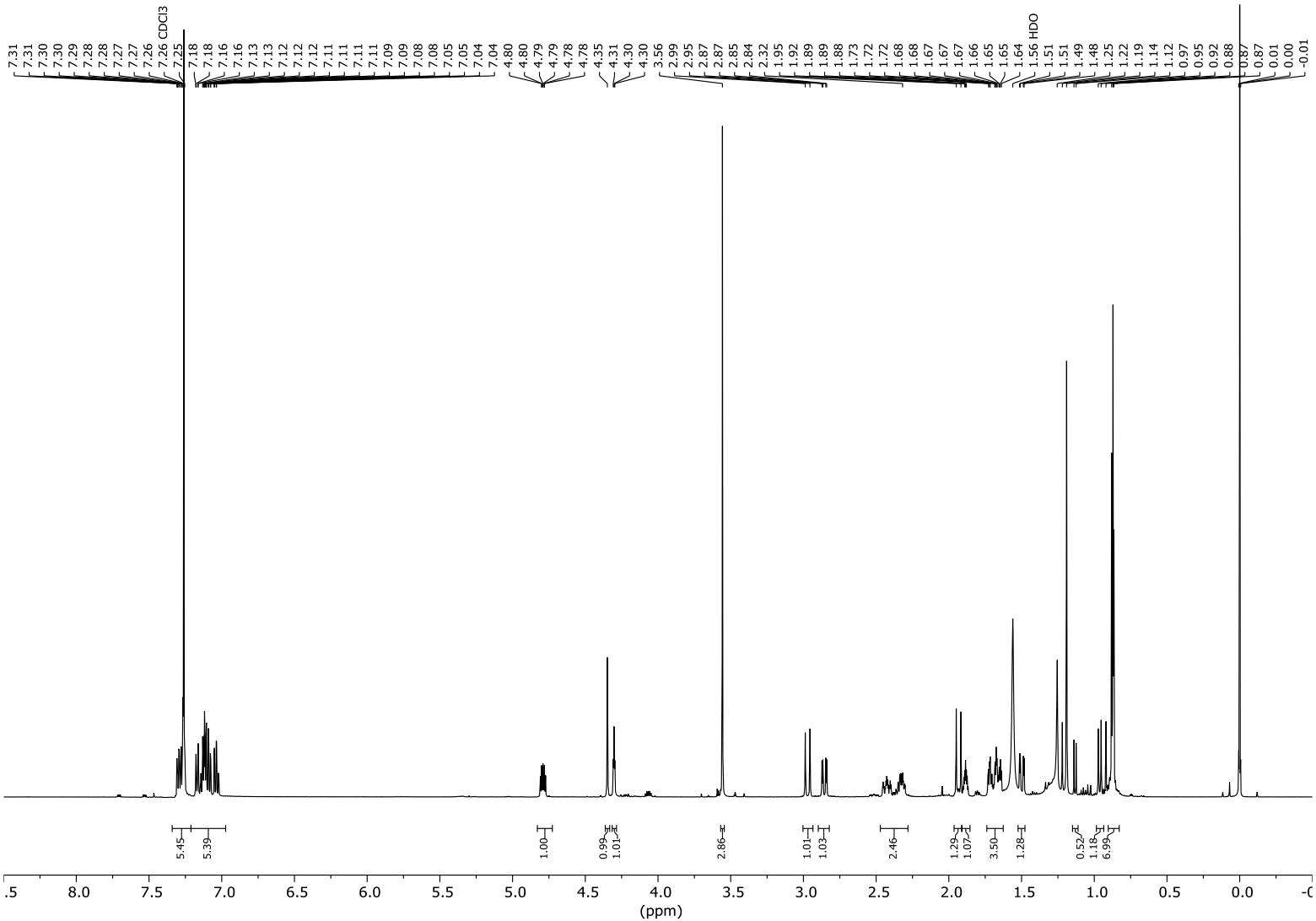

Figure S47 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*S*)-**25**

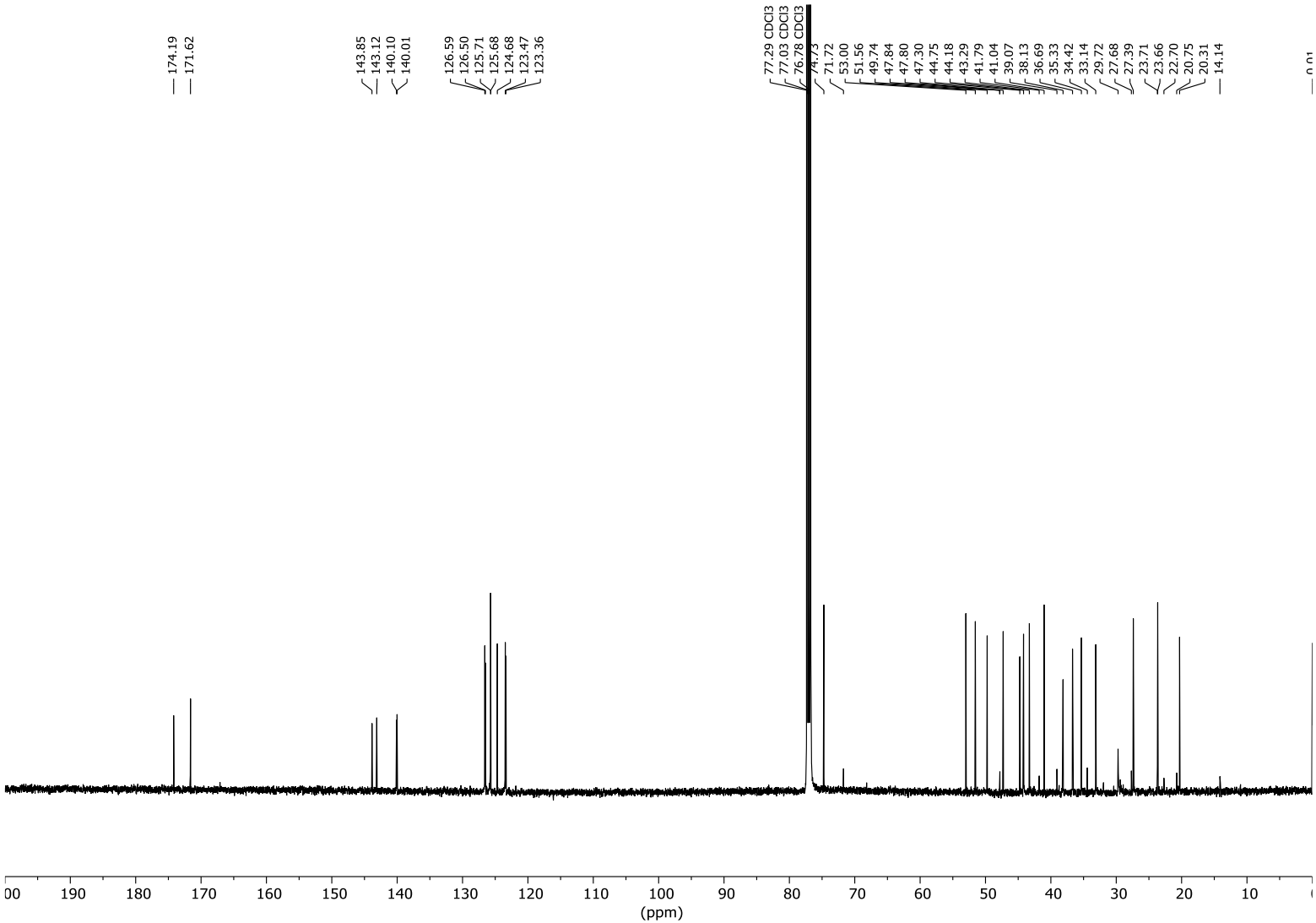

Figure S48 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*S*)-**25**

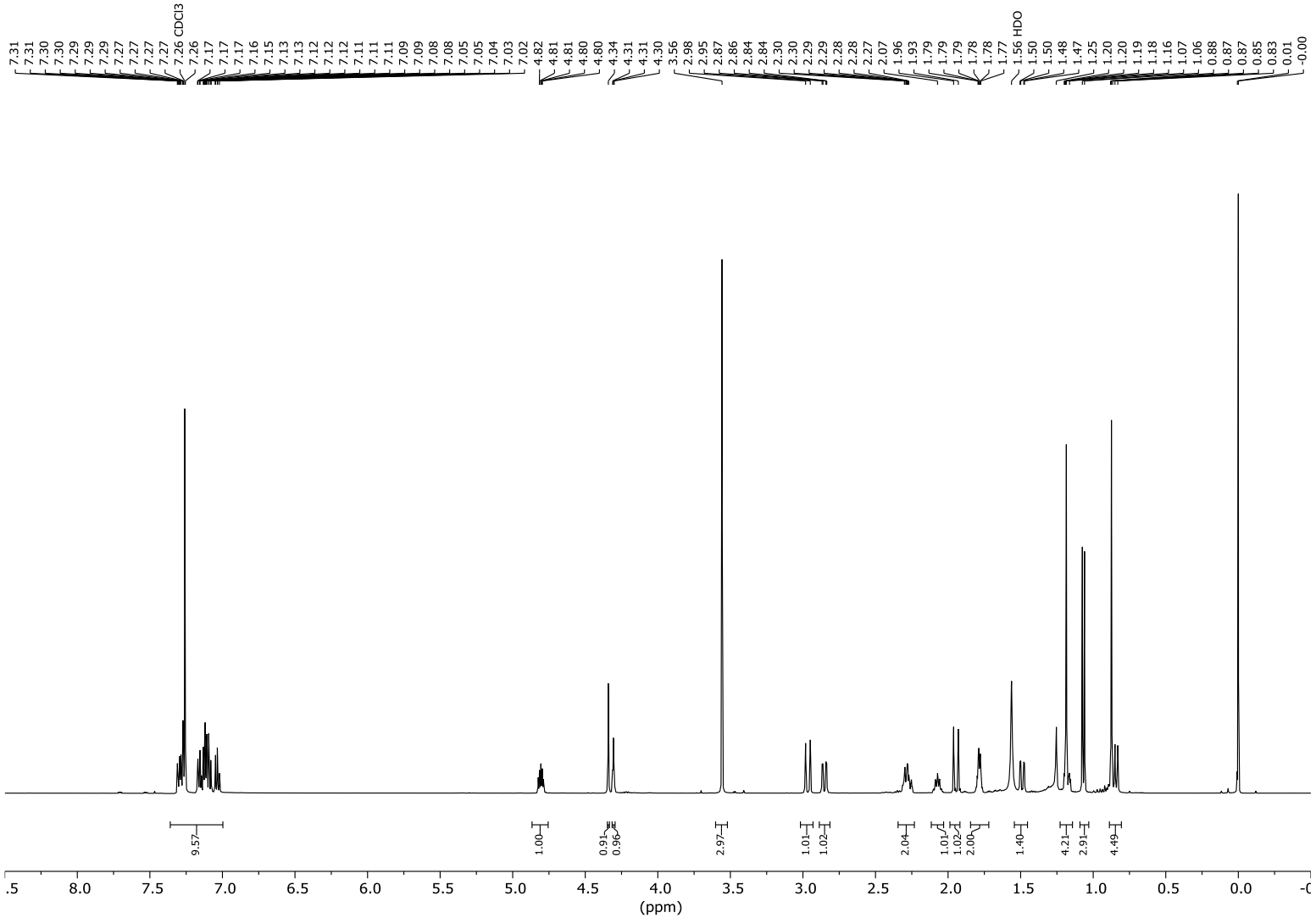

Figure S49 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (−)-(11*R*,1′*S*)-**26**

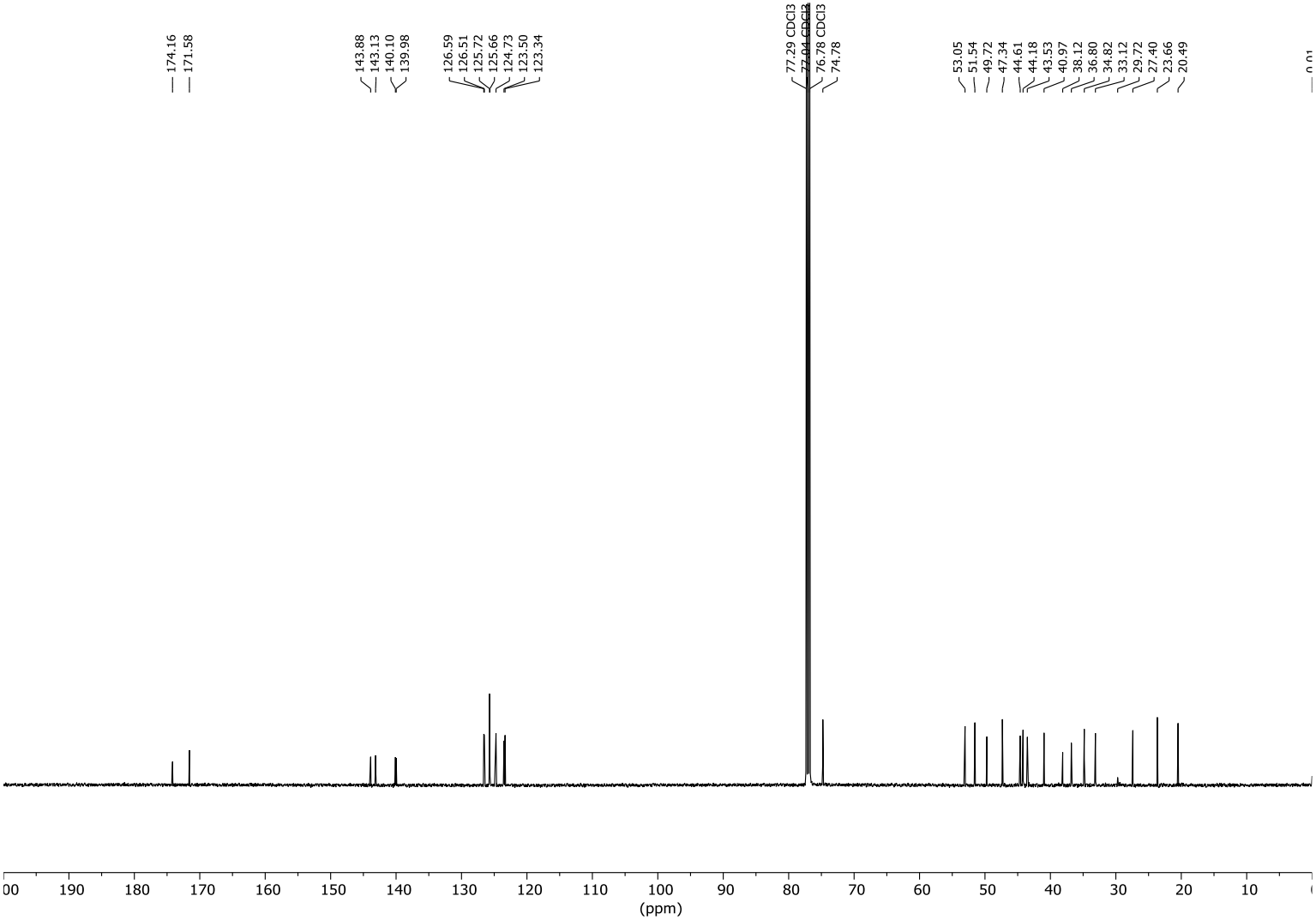

Figure S50 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (–)-(11*R*,1′*S*)-**26**

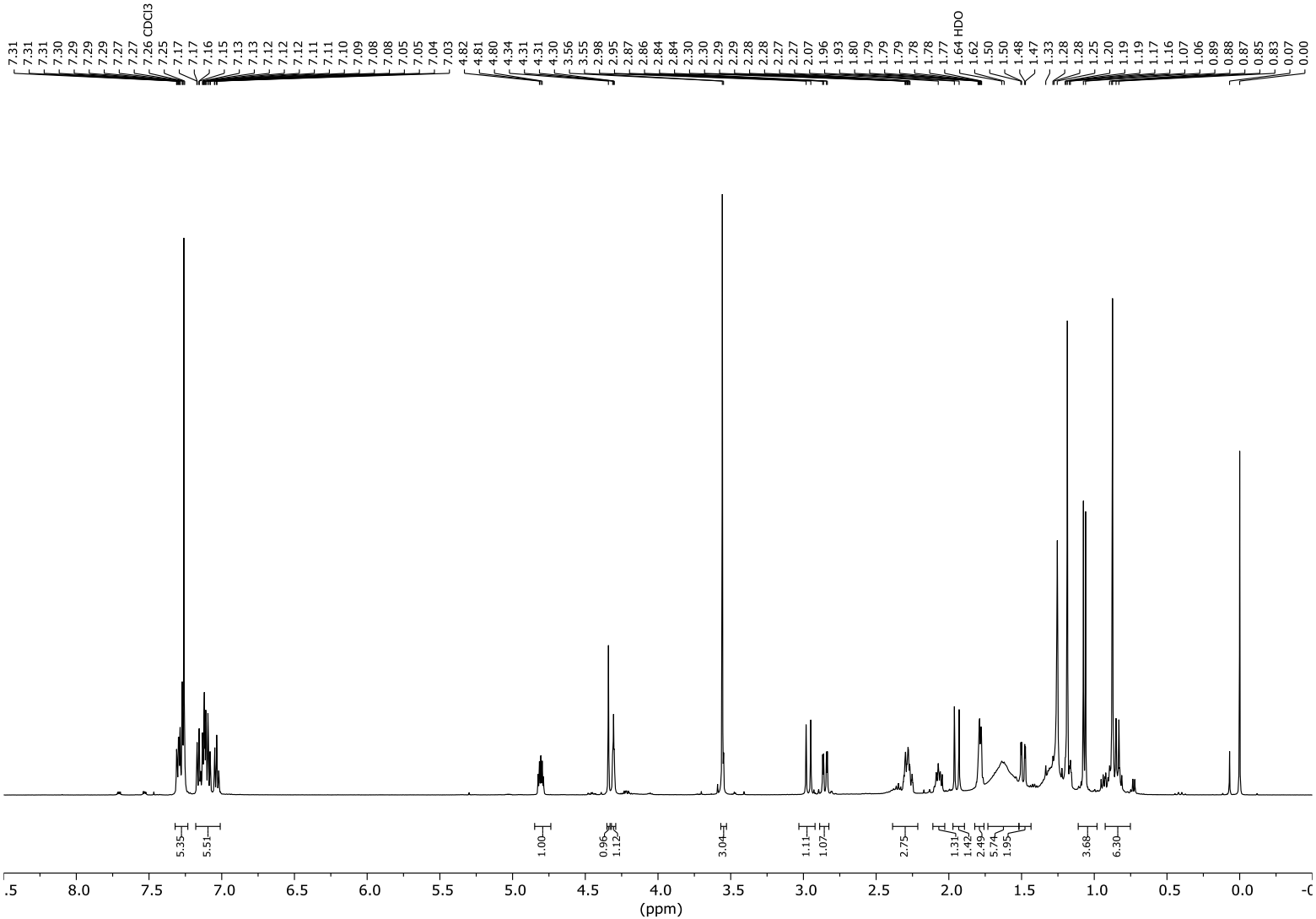

Figure S51 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*R*)-**27**

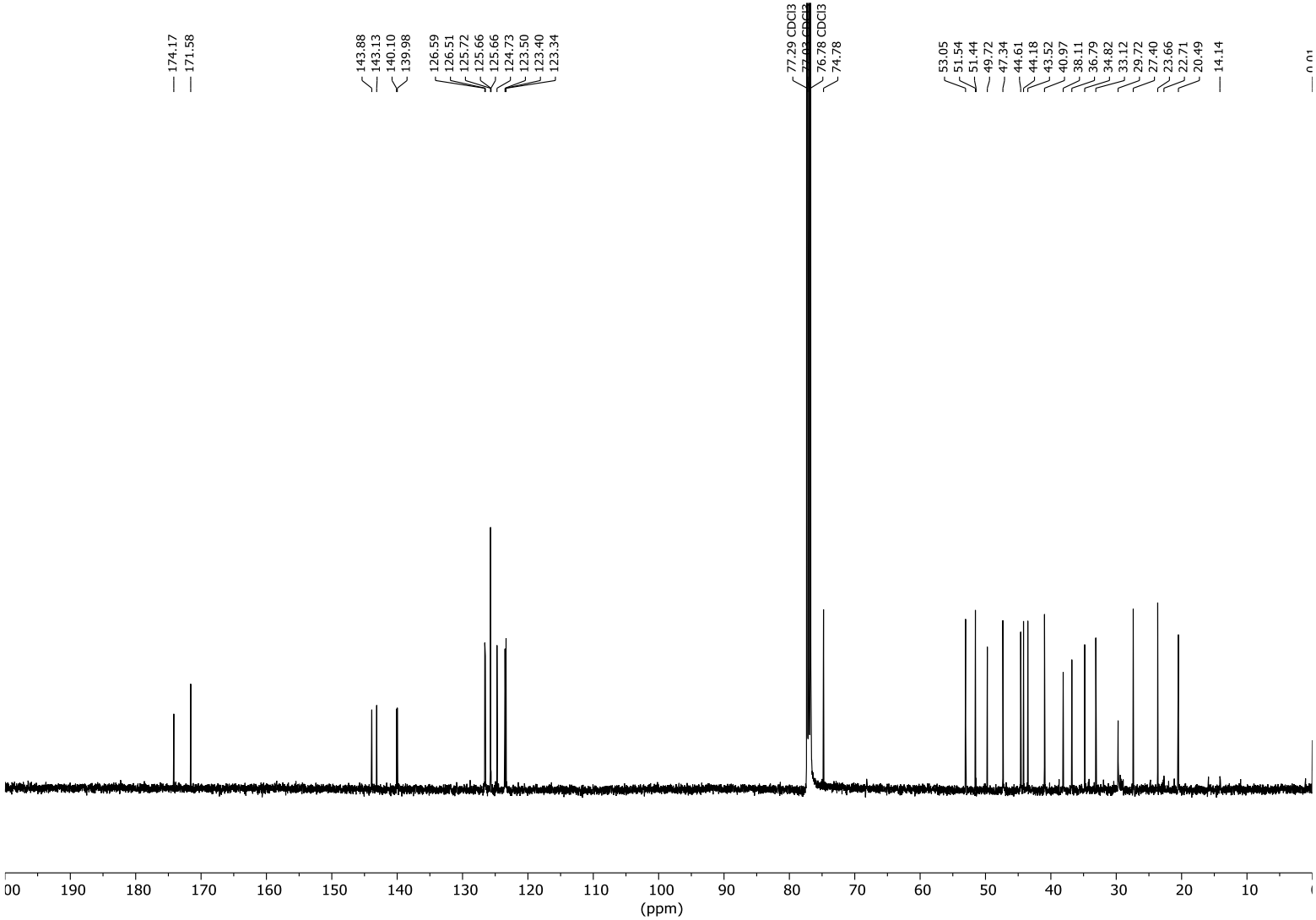

Figure S52 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (+)-(11*S*,1′*R*)-**27**

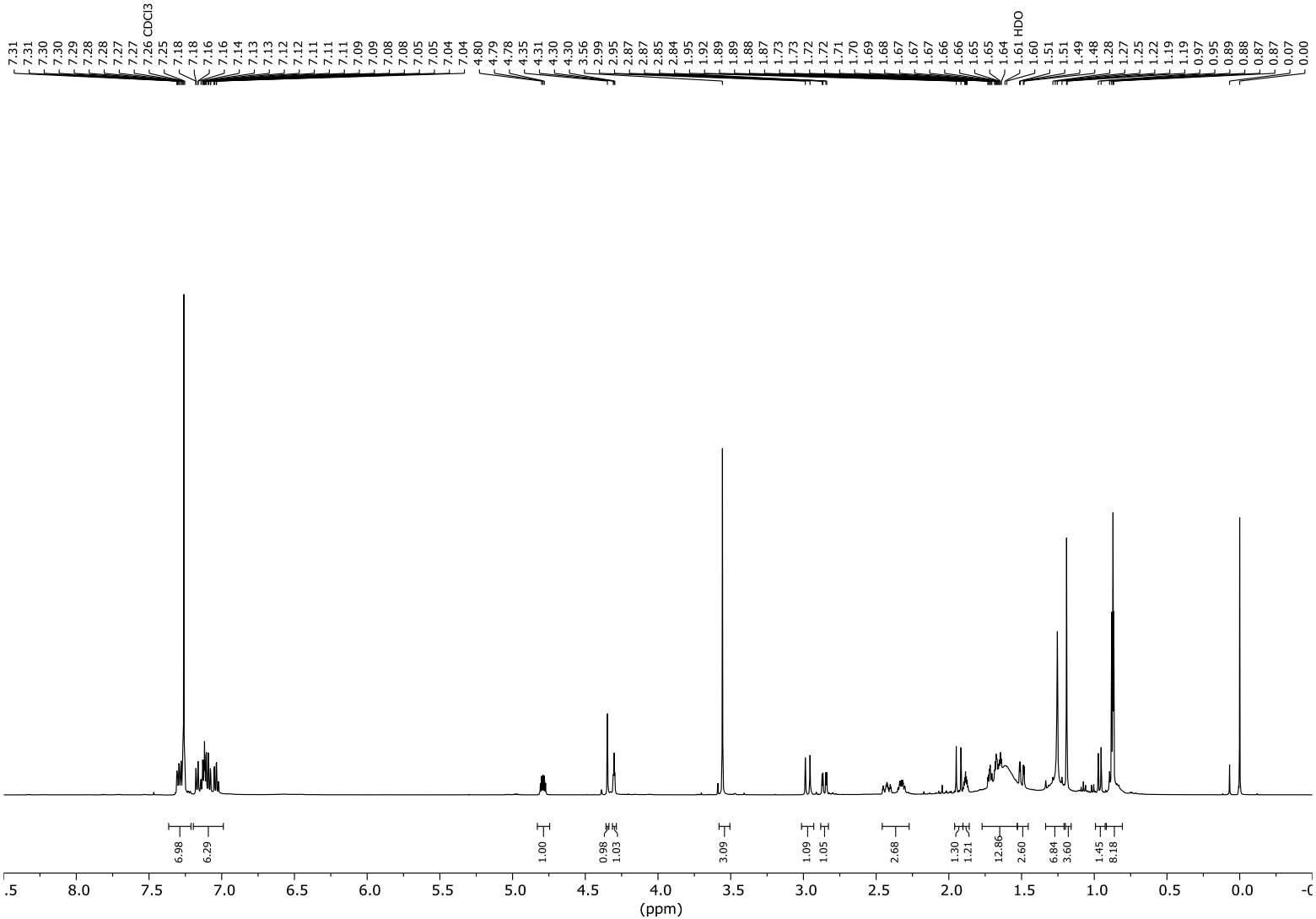

Figure S53 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (–)-(11*R*,1′*R*)-**28**

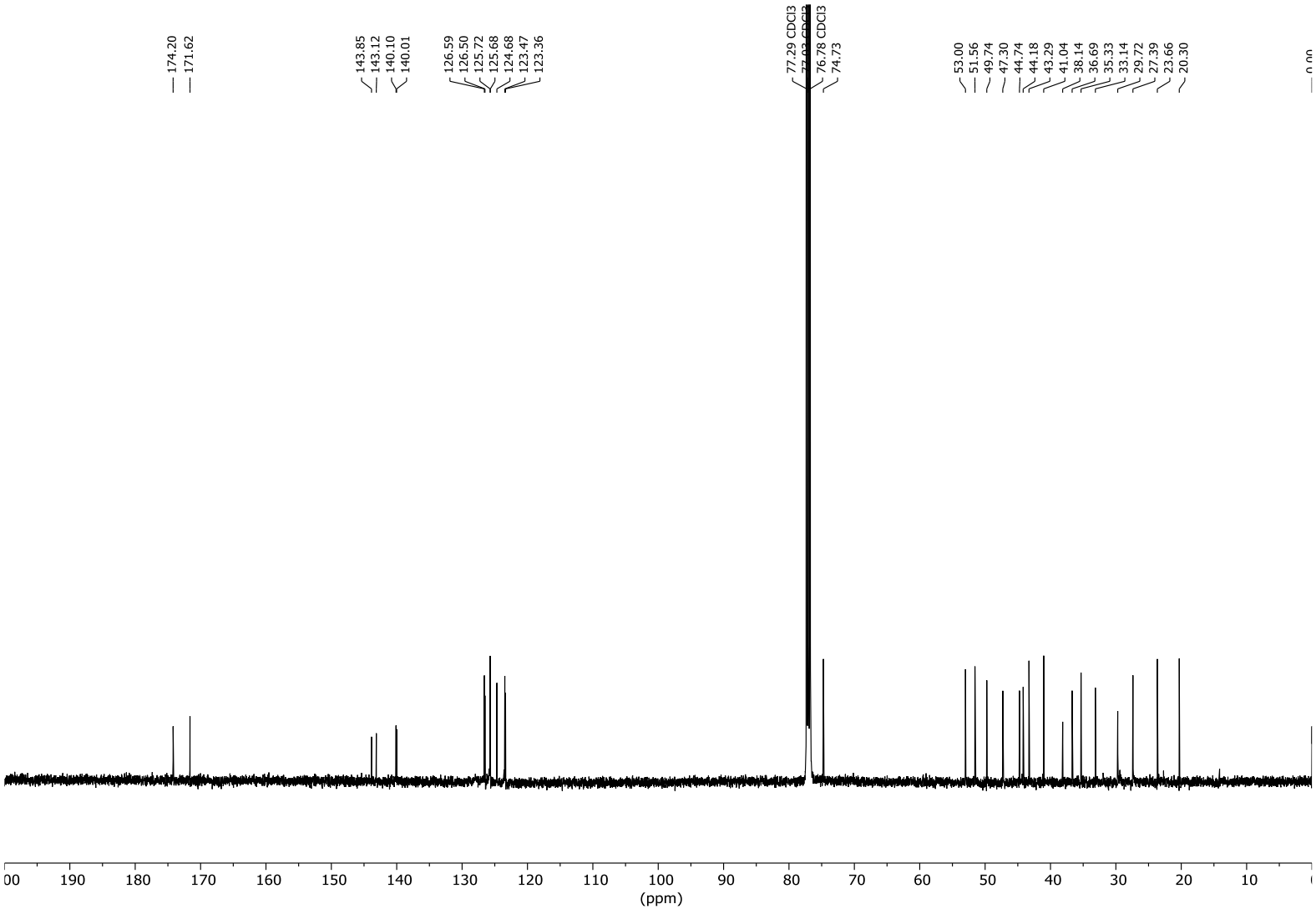

Figure S54 ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of (–)-(11*R*,1′*R*)-**28**

II. Density Function Theory Calculations

The structures of selected chiral secondary alcohol which were bonded to the chiral derivatizing agents, methyl itaconate-anthracene adducts (**8**) were undergone the conformer distributions using Spartan14 with the Molecular Mechanic Force Field (MMFF) and further geometrical optimization with the Gaussian 09 program using the Density Functional Theory together with the 6-311++G(d,p), followed by frequency calculations at the same level of theory. Including the gas-pahse single point energy calculations at these optimized structures were performed with the same level basis set.

The structures with the minimized energy were applied to identify and describe the influence of the anisotropic magnetic field from the aromatic part of anthracene to the different substituents of the selected alcohols. With the distance between the chiral alcohol substituents to the aromatic part of anthracene as well as the difference of chemical shift values described the shielding effect to the substituents which located close to the aromatic part.

References

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L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(11*S*,1′*S*)-**11**

Geometry with 54 atoms:

C	-0.0222905852	-0.0540091412	0.0309051326
C	-0.0171836542	-0.1579912357	2.8111899238
C	1.1869753575	-0.1121617053	2.1112161902
C	1.1878138836	-0.0561642519	0.7139770941
C	-2.8902596448	-3.2246967288	-2.3649096304
C	-1.68477634	-3.1733108397	-3.0618197864
C	-2.3876388337	1.2405677299	-1.0071642614
C	-3.1962867274	-2.248140318	-1.4117207599
C	-2.286910221	-1.2277755576	-1.1603596029
C	-1.075583288	-1.1730513934	-1.8662486218
C	-0.7730868807	-2.1418809407	-2.8162874622
C	-2.4470288821	-0.084436839	-0.1764019393
C	-1.0394866055	1.3354150119	-1.7888571488
C	-0.2088653101	0.0079392736	-1.4734462641
C	-1.2344796304	-0.1504378787	2.1228903426
C	-1.2347034173	-0.1025124778	0.7344514772
C	-0.1260565145	2.5078316541	-1.3800814721
C	-1.2513586832	1.4268952662	-3.3127700371
O	0.8687969954	2.7888631375	-2.0133159455

O	-0.4978093295	3.1271058138	-0.2564553782
C	0.3370863378	4.2271145646	0.2328834673
C	-0.1045917836	5.5166599243	-0.4460411292
C	-1.9604501341	2.684153763	-3.7662237593
O	-2.2385410169	3.6339740694	-3.0739166257
O	-2.2424025161	2.620842118	-5.084752237
C	-2.8808632108	3.7801711559	-5.6523136809
C	1.1113150984	5.195391882	2.4697920917
C	0.1786177294	4.2143992976	1.7517699843
H	-0.0112355432	-0.2039890618	3.8946571576
H	2.1274608289	-0.1227399987	2.6508893472
H	2.1246439484	-0.0153592955	0.1678624014
H	-3.5930122258	-4.0273979687	-2.5588545062
H	-1.4514201142	-3.9355694872	-3.7967394244
H	-2.5046332468	2.0946217539	-0.3449467306
H	-3.2254470701	1.2511132942	-1.7073475312
H	-4.1346680066	-2.2915831301	-0.8678985832
H	0.1648188368	-2.1007143275	-3.3609670462
H	-3.3835106771	-0.1473945333	0.3807423175
H	0.7402478701	0.0302947939	-2.0096382288
H	-2.1711213881	-0.1865255865	2.6701878058
H	-1.8174651991	0.5641526874	-3.6698097531
H	-0.2858258254	1.4033986556	-3.826152279
H	1.3684445965	3.9952419908	-0.0425142858
H	-0.0174311991	5.4292482168	-1.5295083375
H	0.5230856229	6.3499324698	-0.1206249232
H	-1.1444753792	5.7452732525	-0.197694096
H	-3.0237417825	3.5458331264	-6.7048441787
H	-3.8398249288	3.9645736295	-5.1661582566
H	-2.2452805609	4.6592609151	-5.5374844923
H	1.0073656556	5.0972689983	3.5532457481

H	2.1595663463	5.0029139678	2.2201500584
H	0.8921471483	6.2349529453	2.2131594565
H	-0.865094009	4.4357915789	2.0013312374
H	0.3763696861	3.1965995036	2.1003516

(11*R*,1′*S*)-**12**

Geometry with 54 atoms:

C	-0.0024886758	-0.0116290942	-0.0090797527
C	0.0441254478	-0.1063688837	2.773511827
C	1.2353884378	-0.1451952607	2.0510424125
C	1.217078453	-0.0920632216	0.6539605947
C	-3.1641998975	-2.9643192527	-2.32601721
C	-1.9714707252	-3.0140341718	-3.045934224
C	-2.2635470919	1.453201633	-1.0041988305
C	-3.3729732616	-1.9587485333	-1.3776909058
C	-2.3782781848	-1.0133879145	-1.1549595221
C	-1.1788531513	-1.0624468035	-1.8799277545
C	-0.9748268859	-2.058593042	-2.8279907869
C	-2.42407062	0.1409234142	-0.1724470014
C	-0.9374646145	1.411158445	-1.8380958591
C	-0.2056414155	0.0460521535	-1.5127787009
C	-1.1816076175	-0.0140607104	2.1069666146
C	-1.2010612345	0.0291840119	0.7178284233
C	-0.0574680698	2.6454705494	-1.4568774109
C	-1.1521632659	1.488672592	-3.3613932621
O	-0.351774917	1.0651833386	-4.1628069872
O	-2.2772513127	2.1388157349	-3.703776376
C	-2.5524083007	2.3318319849	-5.1309931785
C	-2.7082376751	4.8701711473	-4.7821491285
C	-3.4093504142	3.5890116893	-5.2395671834
C	-3.2326855256	1.0857108194	-5.6825453214

C	1.2642500601	2.7385081751	-2.1947439715
O	2.2368410606	2.0586529267	-1.9705296246
O	1.2335192608	3.7007834618	-3.1403548499
C	2.4239927313	3.8325140793	-3.9409381004
H	0.066632438	-0.1491817031	3.8568960779
H	2.1826265029	-0.2146505091	2.5742568962
H	2.1423902755	-0.1004053535	0.089166861
H	-3.9322817296	-3.7100283484	-2.4993118457
H	-1.8151005572	-3.7975950517	-3.7790952697
H	-2.2495732145	2.3072748557	-0.3227365374
H	-3.1218102534	1.5765667576	-1.6617461422
H	-4.3007763806	-1.9215594249	-0.8153756236
H	-0.0511133356	-2.0887507404	-3.395343341
H	-3.3533891075	0.161345936	0.4000618196
H	0.7295689543	-0.0245083321	-2.0618702093
H	-2.1091516975	0.0170830878	2.670125777
H	0.1698621614	2.5750319069	-0.3914521034
H	-0.6318290945	3.556404348	-1.6316912082
H	-1.5890601653	2.4805228203	-5.6242535878
H	-3.363536271	5.7363868887	-4.9048713853
H	-2.4237112419	4.8114989118	-3.7296050958
H	-1.7999666998	5.0537360749	-5.3640424528
H	-3.7092811596	3.6862066044	-6.2888706722
H	-4.3307813007	3.4357268571	-4.6665196249
H	-2.5967740661	0.2083129472	-5.558730733
H	-3.4322339061	1.2143915532	-6.7499704414
H	-4.1838561652	0.9070960869	-5.1738063115
H	2.6101585565	2.9087156352	-4.4897804529
H	2.223557564	4.653161258	-4.6262376373
H	3.284392885	4.0589494614	-3.3100314053

(11*S*,1′*R*)-**13**

Geometry with 54 atoms:

C	1.7309185272	-0.1931297983	-1.265378206
C	2.5019835751	-2.6205396488	-2.3856056454
C	3.4010171097	-1.8918174872	-1.6095187067
C	3.0154236725	-0.673615669	-1.0420207397
C	-0.4714550846	3.0472233404	-4.2059687058
C	0.426298818	3.7677767275	-3.4209352554
C	-1.1105415859	-0.071834091	-0.7548957252
C	-0.8187083551	1.737625108	-3.8589738205
C	-0.2580383775	1.1574207754	-2.7275088932
C	0.6416301412	1.8851928165	-1.9339201274
C	0.9839586546	3.1881461413	-2.2770516853
C	-0.5183907197	-0.2384192615	-2.1932231864
C	-0.1216924209	0.7235103804	0.1545647273
C	1.1476146888	1.1037095416	-0.7361240053
C	1.2085787589	-2.1375816407	-2.6079514702
C	0.8275898011	-0.9225189912	-2.0523941168
C	0.4239215894	-0.05272654	1.3711142426
C	-0.7416904212	2.029379328	0.6928085403
O	1.0919962922	0.4936678109	2.22267719
O	0.1234408716	-1.353953667	1.3778920839
C	0.5818543182	-2.1663582281	2.5094444969
C	-1.830384737	-2.762736607	3.1391499878
C	-0.4568506365	-3.2688411911	2.6910509381
C	1.9814701299	-2.6892768031	2.2169315712
C	-1.9212051144	1.8281754003	1.618597053
O	-2.341079102	0.7691481028	2.0204097772
O	-2.4615591027	3.0162944533	1.9615174312
C	-3.5747291177	2.9664411109	2.873912614
H	2.8076855875	-3.563898899	-2.8245289305

H	4.4042629327	-2.2693034213	-1.445832571
H	3.7133928398	-0.1071715512	-0.4341247984
H	-0.8999988246	3.5015312878	-5.0924028586
H	0.694766354	4.7812393242	-3.6973847561
H	-1.3165372371	-1.0504784515	-0.3292010439
H	-2.0611518044	0.4602874725	-0.8268998733
H	-1.5159730908	1.1769579951	-4.4735194129
H	1.6812396752	3.7506007489	-1.6642892284
H	-1.2040970813	-0.8021698513	-2.8283433899
H	1.8632192948	1.667719616	-0.1373682605
H	0.5111881804	-2.7046766579	-3.2164043828
H	-1.0629968046	2.6640171858	-0.1359627649
H	0.0088553272	2.5975259733	1.2493256139
H	0.6028203254	-1.511367948	3.3831541998
H	-2.235352723	-2.0326713381	2.4362368881
H	-2.5402442898	-3.5901919514	3.22260018
H	-1.769104796	-2.2768645361	4.1178432977
H	-0.5418354209	-3.8235186524	1.7496605589
H	-0.0600990249	-3.9727927924	3.4312406699
H	2.6831574095	-1.8652316661	2.0820040601
H	2.3296103861	-3.3000152905	3.0546788856
H	1.9851884964	-3.3039272511	1.3132363295
H	-3.8649550612	4.0025570665	3.0331691229
H	-4.3991806381	2.3990550866	2.4399465287
H	-3.2752321853	2.5024271081	3.8145655721

(11*R*,1′*R*)-**14**

Geometry with 54 atoms:

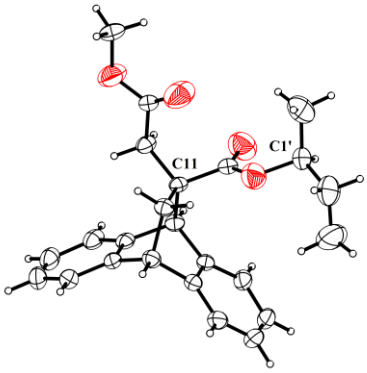
C	2.1097053804	-1.2528453972	-1.1750597704
C	-4.8595414754	-1.5738183775	-0.8792166659
C	-4.1052526372	-2.5585019353	-1.5138506331

C	-2.723365636	-2.4018842303	-1.6603299717
C	-0.5606528483	3.0169531196	-2.954541874
C	0.1970733695	2.0274198119	-3.577388975
C	-0.9717199091	0.3611026334	0.9283905576
C	-1.29893669	2.7214411263	-1.8041992247
C	-1.279174165	1.429786949	-1.2922636541
C	-0.5158290153	0.4341401742	-1.9198894417
C	0.2259820903	0.7298873902	-3.0573206456
C	-2.0313401175	0.9184865109	-0.0785985112
C	-0.1126336318	-0.7548876093	0.2550886879
C	-0.6307213613	-0.9195738118	-1.2444660795
C	-4.2419722114	-0.4188297794	-0.3885306968
C	-2.8702613327	-0.2579398597	-0.5420868658
C	-0.2658756267	-2.1183691445	0.9639310374
C	1.400094483	-0.4632347552	0.1636254884
O	2.1738934721	-1.289339618	-0.271188033
O	1.7626758634	0.7550665174	0.5739198448
C	3.1953420545	1.0726897413	0.5972179039
C	0.243751974	-2.1536868676	2.3876273486
O	0.8820051698	-1.2897014354	2.9395783413
O	-0.0988368402	-3.3158540493	2.9834527548
C	0.3680695344	-3.4972723787	4.3335678259
C	3.8214640597	0.4769540662	1.8517270325
C	2.816595388	3.2102171089	-0.7742251416
C	3.3018640006	2.5929027505	0.5383346973
H	-5.9308188912	-1.7004190218	-0.7690529012
H	-4.5903796853	-3.4495340363	-1.8963681848
H	-2.1355760931	-3.1707134413	-2.151676014
H	-0.5800281021	4.0209114985	-3.3639169415
H	0.766117253	2.2631719932	-4.4697310962
H	-1.4927534163	-0.0420268754	1.7992211848

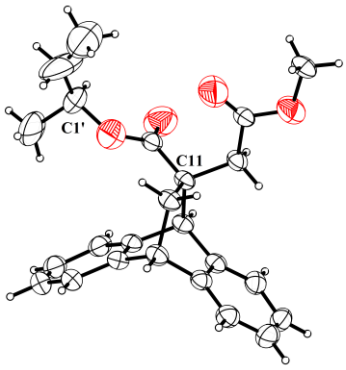
H	-0.3364969524	1.1718576651	1.2765206762
H	-1.8899178318	3.493340204	-1.3214180524
H	0.8176744385	-0.0409493034	-3.5401037313
H	-2.6357466012	1.6967135817	0.3909355273
H	-0.0489153774	-1.6882024961	-1.7532272452
H	-4.8319667258	0.3490372091	0.1018688231
H	0.2832995409	-2.8861993778	0.4107588661
H	-1.3133150193	-2.4257766992	0.9679029791
H	3.6379281114	0.6211575533	-0.2938883682
H	-0.0012852107	-4.4737445017	4.6388745687
H	1.4581623507	-3.4718274215	4.3663438996
H	-0.028816303	-2.7160396075	4.9832313731
H	3.7000674207	-0.6058663327	1.8732373604
H	4.8911896269	0.7039957198	1.8694552002
H	3.3602918796	0.8959219214	2.7493168152
H	2.9233296336	4.2982679168	-0.75380329
H	3.3963918127	2.8358022913	-1.6235858601
H	1.7667362606	2.9788240019	-0.9604015612
H	2.7469870813	3.0123930796	1.3851538328
H	4.3548482085	2.8485958684	0.7010468029

III. Crystallographic Data

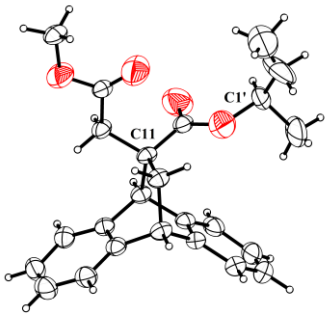
Single crystals of **11** - **14** were crystallized in CH_2Cl_2/hexane. A suitable crystal was selected and collected on a SuperNova, Single source at offset/far, HyPix3000 diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimization. ORTEP diagrams of the asymmetric units and crystallographic data are shown below.



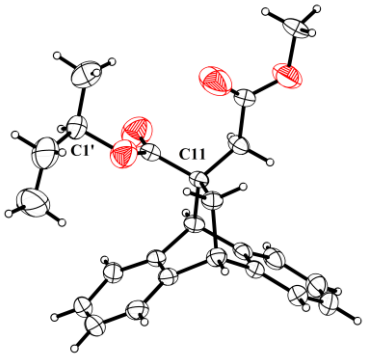
(11*S*,1′*S*)-**11**



(11*R*,1′*S*)-**12**



(11*S*,1′*R*)-**13**



(11*R*,1′*R*)-**14**

Figure S55 ORTEP diagram of the X-ray crystal structure of **11**-**14**

Crystal data and structure refinement for **11** – **14**.

Identification Code	(11*S*,1′*S*)-**11**	(11*R*,1′*S*)-**12**	(11*S*,1′*R*)-**13**	(11*R*,1′*R*)-**14**
CCDC No.	2094178	2094086	1873119	2094087
Empirical formula	$C_{24}H_{26}O_4$	$C_{24}H_{26}O_4$	$C_{24}H_{26}O_4$	$C_{24}H_{26}O_4$
Formula weight	378.45	378.45	378.45	378.45
Temperature/K	293(2)	293(2)	293(2)	293(2)
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	10.0659(2)	10.1047(2)	10.1003(3)	10.0685(3)
b/Å	10.1740(3)	10.1997(3)	10.1984(3)	10.1743(3)
c/Å	20.3251(5)	20.2588(5)	20.2551(5)	20.3368(6)
Volume/Å^3	2081.50(9)	2087.9(9)	2086.4(1)	2083.3(1)
Z	4	4	4	4
Crystal size/mm^3	0.5 × 0.4 × 0.3	0.4 × 0.35 × 0.3	0.4 × 0.3 × 0.3	0.4 × 0.4 × 0.3
Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.478 to 54.886	4.02 to 54.914	4.022 to 54.816	4.476 to 54.852
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-25 \le l \le 26$	$-13 \le h \le 12$, $-13 \le k \le 12$, $-24 \le l \le 25$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-25 \le l \le 25$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-25 \le l \le 25$
Reflections collected	23193	26461	23812	16394
Independent reflections	4427 [*R*int = 0.0391, *R*sigma = 0.0354]	4494 [*R*int = 0.0506, *R*sigma = 0.0302]	4493 [*R*int = 0.0443, *R*sigma = 0.0297]	4382 [*R*int = 0.0466, *R*sigma = 0.0411]
Data/restraints/parameters	4427/0/257	4494/0/257	4493/0/257	4382/0/257
Goodness-of-fit on F^2	1.059	1.079	1.063	1.029
Final R indexes [I>=2σ (I)]	*R*1 = 0.0506, *wR*2 = 0.1279	*R*1 = 0.0604, *wR*2 = 0.1758	*R*1 = 0.0591, *wR*2 = 0.1691	*R*1 = 0.0523, *wR*2 = 0.1299
Final R indexes [all data]	*R*1 = 0.0720, *wR*2 = 0.1412	*R*1 = 0.0837, *wR*2 = 0.1937	*R*1 = 0.0796, *wR*2 = 0.1850	*R*1 = 0.0760, *wR*2 = 0.1456
Largest diff. peak/hole / e Å^{-3}	0.30/-0.19	0.42/-0.20	0.39/-0.21	0.27/-0.18
Flack parameter	0.3(5)	-0.2(4)	0.3(4)	0.3(6)

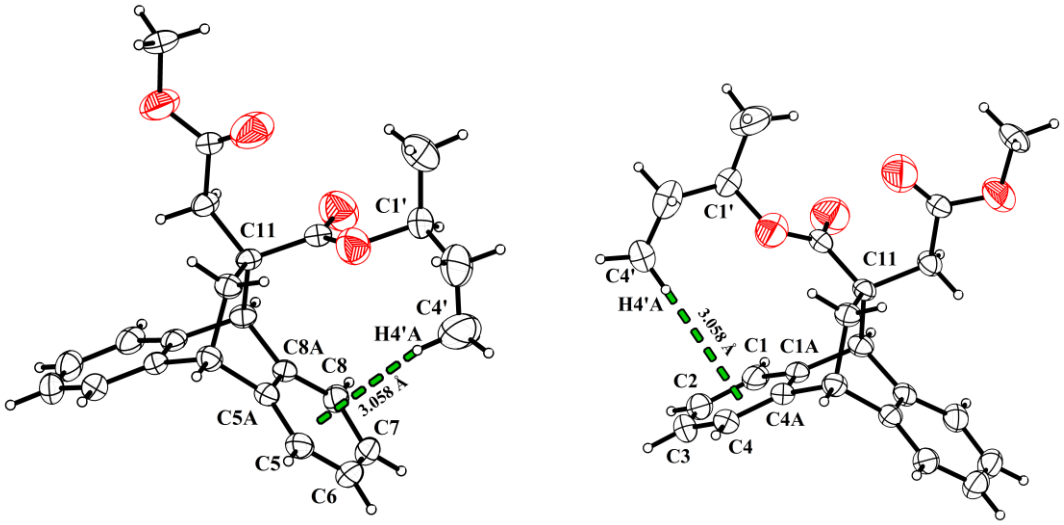


Figure S56 C – H …π interaction in **11** and **14**

The C – H …π interaction parameters

Compound	H-bond	D-H/Å	D…A/Å	H…A/Å	D-H…A/°
11	C4'-H4'A… π	0.96(7)	3.847(6)	3.0577(1)	140.5(4)
14	C4'-H4'A… π	0.96(6)	3.844(6)	3.0576(1)	140.1(3)

[1] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

[2] Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.

[3] Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.