Supporting Information

Synthesis of 3,5-Disubstituted BODIPYs Bearing N-Containing Five-membered Heteroaryl Groups via Nucleophilic C–N Bond Formation

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Complete list of ref 20: SI-1

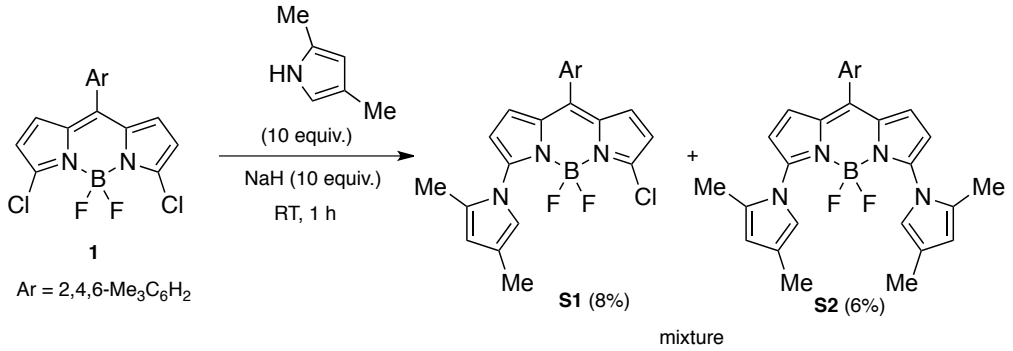
Reaction of 1 with 2,4-dimethylpyrrole SI-2

Tables S1: SI-3

Figures S1–S36: SI-6

Complete list of ref 20. *Gaussian 09, Revision D.01*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; 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.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc., Wallingford CT, 2009.

Reaction of 1 with 2,4-dimethylpyrrole



A mixture of **1** (50.7 mg, 0.134 mmol), 2,4-dimetylpyrrole (140 μl, 1.35 mmol), prewashed NaH (55.1 mg, 60% in paraffin liquid, 1.37 mmol), and THF (10 mL) was stirred for 1 h at room temperature. After a similar work-up described in the synthesis of **5**, the residue was subjected to silica-gel column chromatography (hexane/AcOEt = 5/1). The fraction of R_f = 0.57 (hexane/AcOEt = 5/1) was collected and evaporated to give a mixture of 3-[1-(2,4-dimethyl)pyrrolyl]-BODIPY and 3,5-[1-(2,4-dimethyl)pyrrolyl]-BODIPY [8.8 mg, mono : di = 4 (8%) : 3 (6%)] as a red oil. As the amounts of these products were low, we did not measure their optical properties. The ^{1}H NMR spectra of **S1** and **S2** are shown in Figure S36.

S1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12–2.13 (m, 3H, pyrrole-Me), 2.14 (s, 6H, *ortho*-Me), 2.23–2.24 (m, 3H, pyrrole-Me), 2.36 (s, 3H, *para*-Me), 5.96 (s, 1H, pyrrole), 6.31 (d, 2H, J = 4.0 Hz, BODIPY-pyrrole), 6.54 (d, 1H, J = 3.6 Hz, BODOPY-pyrrole), 6.68 (d, 1H, J = 3.6 Hz, BODIPY-pyrrole), 6.96 (s, 2H, *meta*-Mes), 7.14 (s, pyrrole); HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{24}H_{24}BClF_2N_3$, 438.1714; found, 438.1725.

S2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07–2.08 (m, 6H, pyrrole-Me), 2.18 (s, 6H, *ortho*-Me), 2.20–2.21 (m, 6H, pyrrole-Me), 2.38 (s, 3H, *para*-Me), 5.90 (s, 2H, pyrrole), 6.25 (d, 2H, J = 4.2 Hz, BODIPY-pyrrole), 6.62 (d, 2H, J = 4.2 Hz, BODOPY-pyrrole), 6.98 (s, 2H, *meta*-Mes), 7.00 (s, 2H, pyrrole); HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{30}H_{32}BF_2N_4$, 497.2684; found, 497.2693.

Table S1. Cartesian coordinates (Å) and energies of the optimized structures of **2, 4**, and **9**: calculated at the level of B3LYP/6-31G(d).

Compound **2** (E = –1441.10067884 a.u.)

C	-0.935981	-1.210975	-0.074827
N	0.463387	-1.263299	-0.097623
C	-0.936060	1.211058	0.074560
C	-1.439827	2.533846	0.082324
N	0.463295	1.263446	0.097106
B	1.397756	0.000140	-0.000505
F	2.173955	0.131770	-1.143973
F	2.174659	-0.131279	1.142507
H	-2.488085	2.797734	0.081875
C	-0.353595	3.388080	0.101097
H	-0.358457	4.467241	0.147929
C	-1.630842	0.000020	-0.000133
C	-1.439698	-2.533778	-0.082333
H	-2.487946	-2.797708	-0.081707
C	-0.353438	-3.387968	-0.100908
H	-0.358268	-4.467145	-0.147398
C	-3.128959	-0.000037	0.000015
C	-3.823674	-0.018976	1.228920
C	-3.823925	0.018846	-1.228750
C	-5.223151	-0.019795	1.205629
C	-5.223398	0.019554	-1.205173
C	-5.920539	-0.000148	0.000299
H	-5.766709	-0.036440	2.146870
H	-5.767149	0.036156	-2.146303
H	-7.007231	-0.000191	0.000410
C	-3.089478	-0.042570	2.551229
H	-2.424908	-0.910756	2.629619
H	-2.464549	0.848141	2.683867
H	-3.795487	-0.083840	3.385627
C	-3.090005	0.042497	-2.551210
H	-2.425518	0.910734	-2.629738
H	-2.465035	-0.848166	-2.683979
H	-3.796190	0.083713	-3.385462
C	0.805948	2.574244	0.101917
C	0.806087	-2.574105	-0.102008
C	2.451519	4.294929	-0.480091
H	1.725767	4.895344	-1.010208
C	4.239665	3.494708	0.372606
H	5.284551	3.463213	0.649087
C	4.239723	-3.495122	-0.372193
H	5.284625	-3.463903	-0.648647
N	2.105741	-3.070406	-0.083015
N	2.105636	3.070443	0.083159
N	3.716441	-4.569673	0.328754
N	3.716567	4.569636	-0.327906
C	2.451425	-4.294720	0.480738
H	1.725556	-4.894813	1.011061
C	3.281510	2.558923	0.634228
H	3.295382	1.611089	1.143326
C	3.281716	-2.559315	-0.634276
H	3.295761	-1.611721	-1.143800

Compound **4** (E = –1441.07665043 a.u.)

C	0.923400	-1.212985	0.034636
N	-0.477718	-1.265738	0.072480
C	0.923396	1.212981	-0.034646
C	1.424732	2.536406	0.008461
N	-0.477723	1.265732	-0.072500
B	-1.400393	-0.000006	-0.000017
F	-2.192902	0.106410	1.141989
F	-2.192880	-0.106430	-1.142036
H	2.473071	2.798776	0.037975
C	0.341623	3.393310	0.008097
H	0.324743	4.471077	0.035437
C	1.616248	-0.000001	-0.000005
C	1.424738	-2.536411	-0.008462
H	2.473076	-2.798779	-0.037970
C	0.341629	-3.393316	-0.008093
H	0.324751	-4.471083	-0.035422
C	3.114743	0.000001	0.000001
C	3.810230	0.018556	-1.228308
C	3.810220	-0.018551	1.228315
C	5.209748	0.016783	-1.205317
C	5.209738	-0.016774	1.205336
C	5.907195	0.000005	0.000012
H	5.753277	0.028888	-2.146735
H	5.753260	-0.028878	2.146759
H	6.993980	0.000007	0.000017
C	3.075777	0.036317	-2.550473
H	2.410346	-0.828401	-2.654867
H	2.451607	0.931374	-2.654128
H	3.781579	0.020456	-3.386087
C	3.075756	-0.036315	2.550475
H	2.410324	0.828402	2.654864
H	2.451586	-0.931372	2.654123
H	3.781551	-0.020454	3.386094
C	-0.814112	2.579739	-0.043120
C	-0.814107	-2.579745	0.043114
C	-4.256867	3.510691	-0.298891
H	-5.310810	3.426670	-0.519998
C	-4.256863	-3.510677	0.298918
H	-5.310803	-3.426649	0.520037
N	-2.107765	-3.091618	0.056208
N	-2.107769	3.091617	-0.056206
C	-3.302460	2.537812	-0.455764
H	-3.352932	1.530568	-0.832646
C	-3.302447	-2.537805	0.455780
H	-3.352907	-1.530560	0.832662
C	-3.552523	-4.637796	-0.198481
H	-3.941178	-5.614232	-0.458043
C	-3.552514	4.637806	0.198498
H	-3.941159	5.614245	0.458063
N	-2.260448	-4.398086	-0.342401
N	-2.260439	4.398087	0.342404

Compound **9** (E = – 1409.00599345 a.u.)

C	-0.937387	-1.211253	-0.070485
N	0.462673	-1.267045	-0.098195
C	-0.937402	1.211266	0.070445
C	-1.444901	2.532278	0.059502
N	0.462656	1.267070	0.098118
B	1.394055	0.000024	-0.000077
F	2.170769	0.138817	-1.143608
F	2.170882	-0.138733	1.143380
H	-2.494131	2.792598	0.052951
C	-0.361908	3.389129	0.067986
H	-0.370375	4.468536	0.102121
C	-1.630691	0.000002	-0.000022
C	-1.444876	-2.532268	-0.059497
H	-2.494103	-2.792596	-0.052916
C	-0.361876	-3.389110	-0.067950
H	-0.370336	-4.468518	-0.102030
C	-3.129289	-0.000008	0.000001
C	-3.825279	-0.011284	1.228206
C	-3.825318	0.011258	-1.228182
C	-5.224854	-0.012290	1.205364
C	-5.224891	0.012244	-1.205296
C	-5.922442	-0.000028	0.000045
H	-5.768362	-0.023118	2.146850
H	-5.768429	0.023065	-2.146765
H	-7.009251	-0.000036	0.000062
C	-3.090882	-0.026260	2.550481
H	-2.422751	-0.891365	2.631404
H	-2.468733	0.867115	2.677651
H	-3.796510	-0.066204	3.385479
C	-3.090963	0.026244	-2.550480
H	-2.422846	0.891358	-2.631424
H	-2.468805	-0.867122	-2.677671
H	-3.796618	0.066179	-3.385456
C	0.803603	2.581181	0.084692
C	0.803630	-2.581156	-0.084703
C	4.267103	3.458599	0.448259
H	5.286096	3.333206	0.788249
C	4.267118	-3.458668	-0.448207
H	5.286115	-3.333324	-0.788204
N	2.096283	-3.087027	-0.069149
N	2.096261	3.087038	0.069171
C	3.253030	2.561392	0.644326
H	3.225571	1.609638	1.145746
C	3.253066	-2.561452	-0.644341
H	3.225633	-1.609736	-1.145831
C	3.735569	-4.575653	0.273016
H	4.276433	-5.450688	0.607236
C	3.735582	4.575647	-0.272887
H	4.276467	5.450692	-0.607045
C	2.407724	4.331615	-0.486377
H	1.658803	4.891514	-1.024309
C	2.407717	-4.331575	0.486483
H	1.658781	-4.891420	1.024451

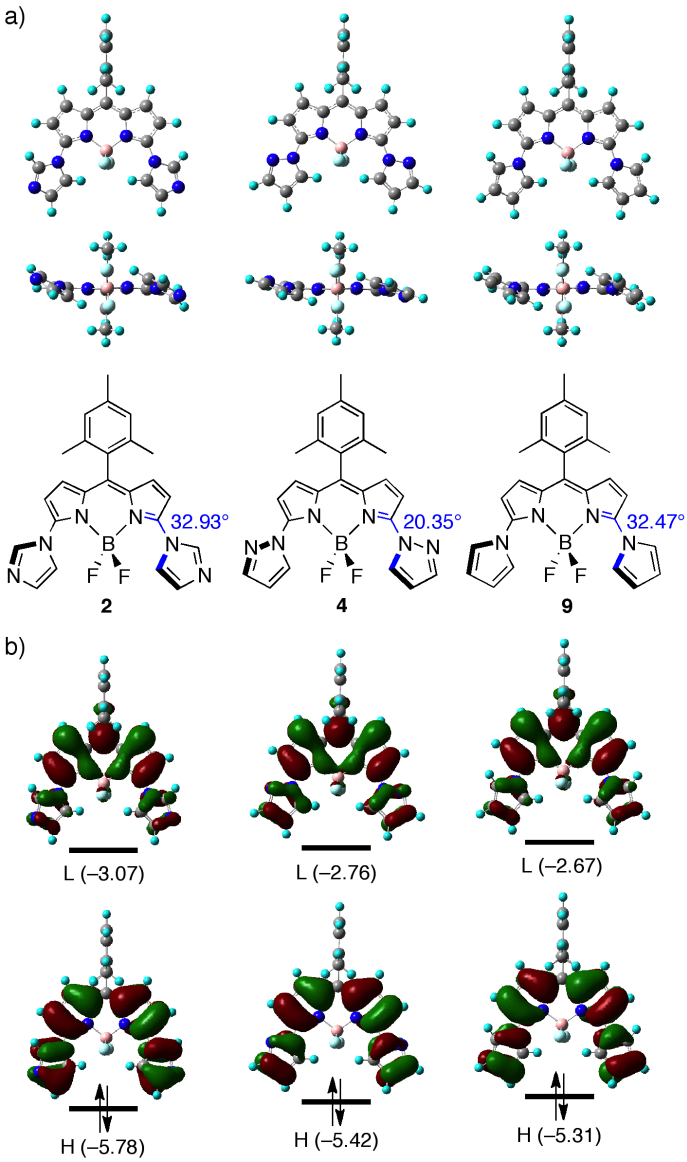


Figure S1. a) Top and side views and b) selected Kohn–Sham orbitals and their energies (in eV) of the optimized structures of **2**, **4**, and **9** calculated by the DFT method. H = HOMO. L = LUMO. The C–N–C–N torsion angles are indicated in blue.

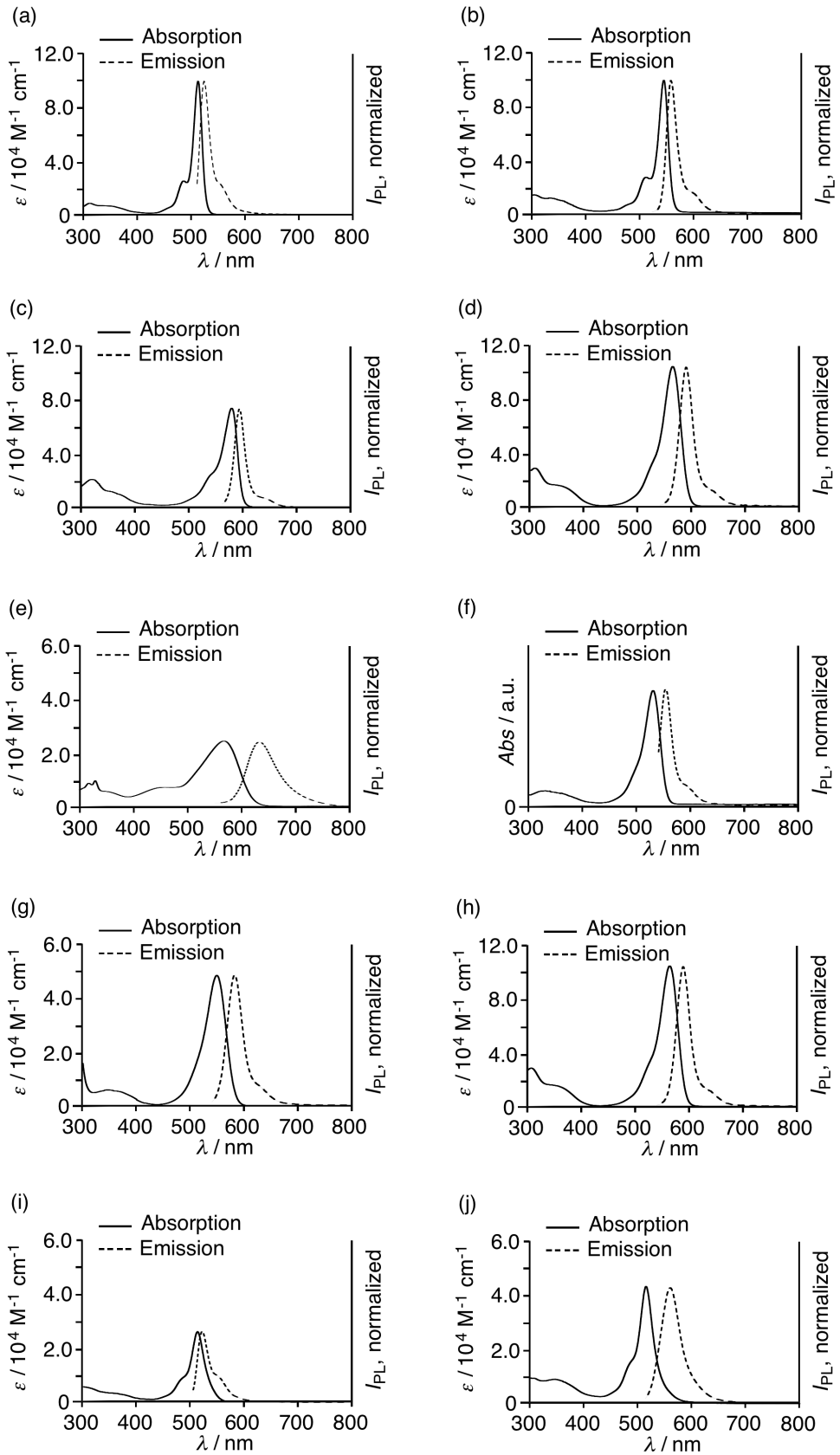


Figure S2. UV/Vis absorption spectra (solid line) and fluorescence spectra (dashed line; excited at the absorption maxima) of (a) **3**, (b) **5**, (c) **6**, (d) **7**, (e) **10**, (f) **11**, (g) **12**, (h) **16**, (i) **17**, and (j) **18** in CH_2Cl_2.

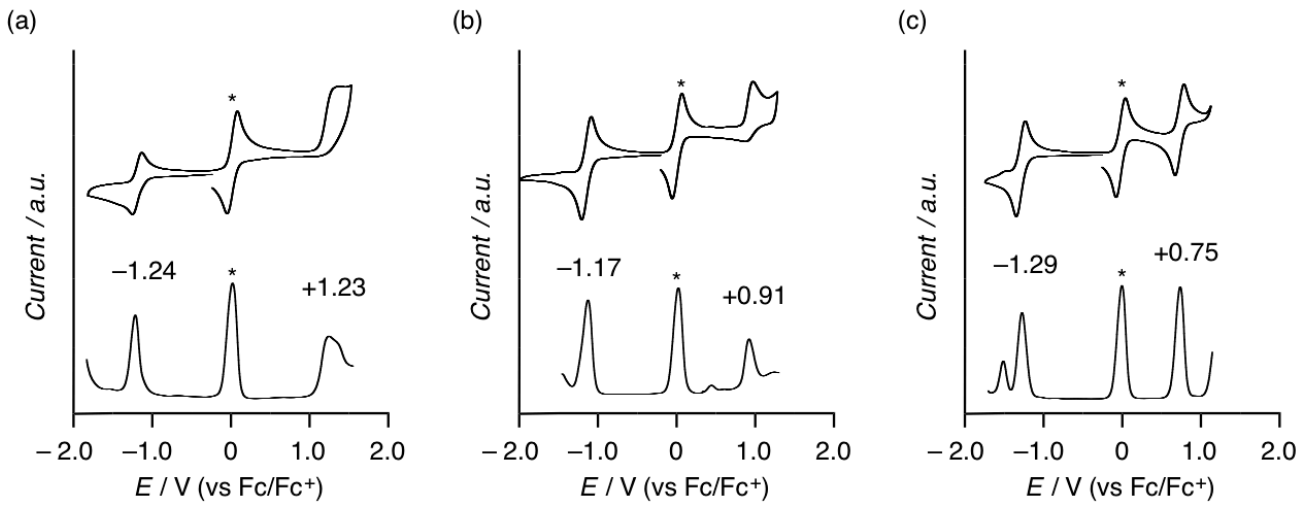


Figure S3. Cyclic voltammograms (upper) and differential pulse voltammograms (lower) of (a) **1**, (b) **2**, and (c) **4**. Measured in CH_2Cl_2 with 0.1 M nBu$_4$NPF$_6$ as a supporting electrolyte; Ag/Ag$^+$ [$AgNO_3$ (MeCN)] as a reference electrode; scan rate 60 mV s^{-1}. Asterisk (*) indicates Fc/Fc$^+$.

^{1}H and ^{13}C{^{1}H} NMR Charts (Figures S4–S36) Asterisks (*) indicate the residual solvents.

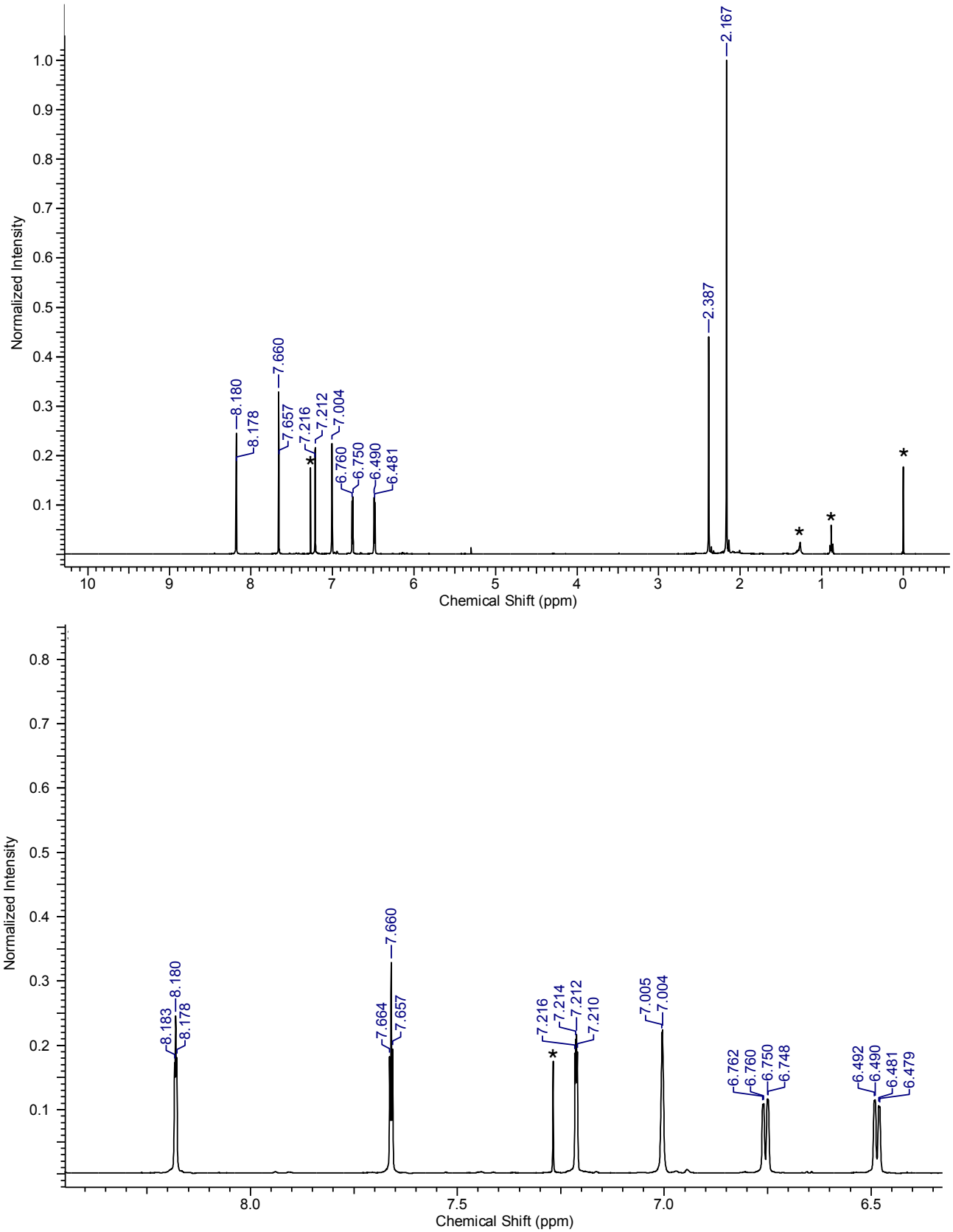


Figure S4. ^{1}H NMR spectra of **2** in $CDCl_3$.

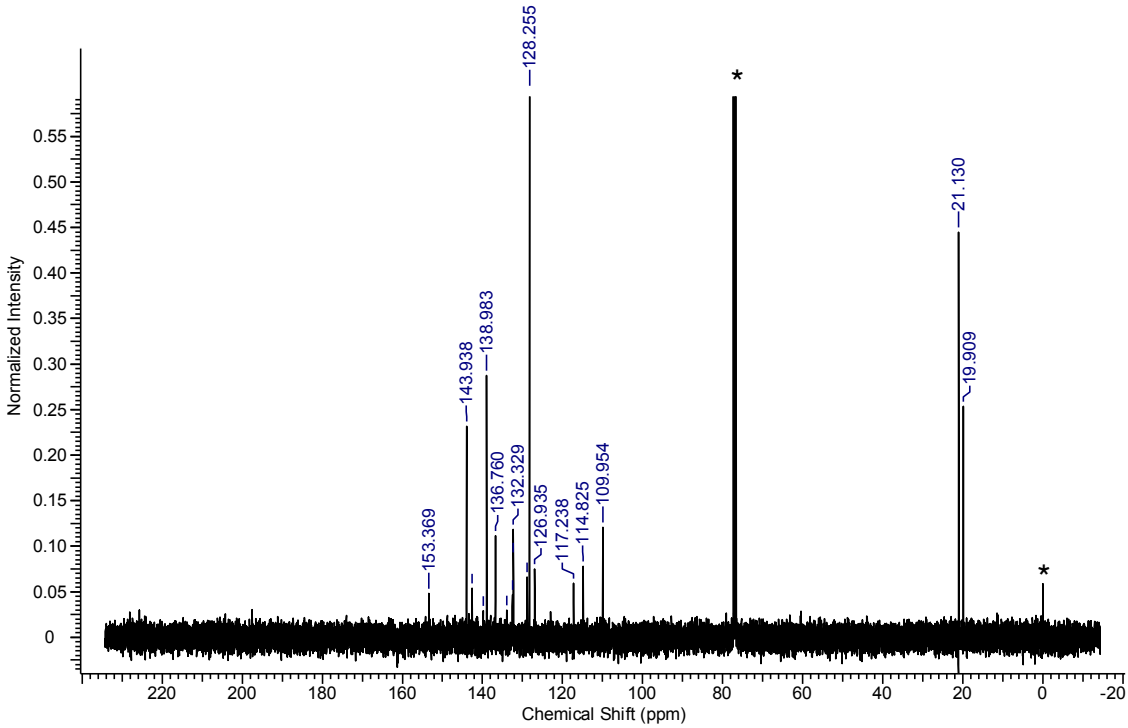


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

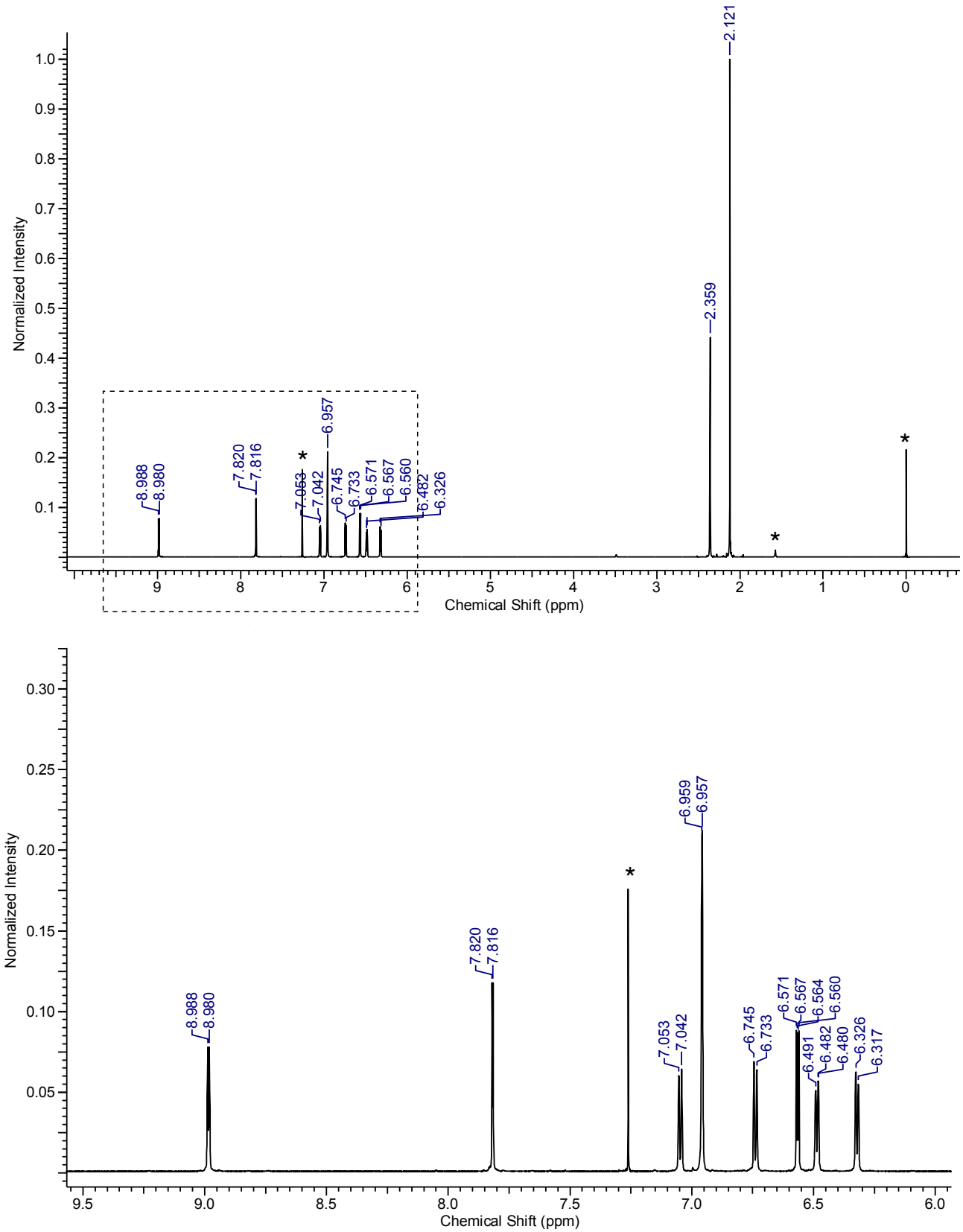


Figure S6. ^{1}H NMR spectra of **3** in $CDCl_3$.

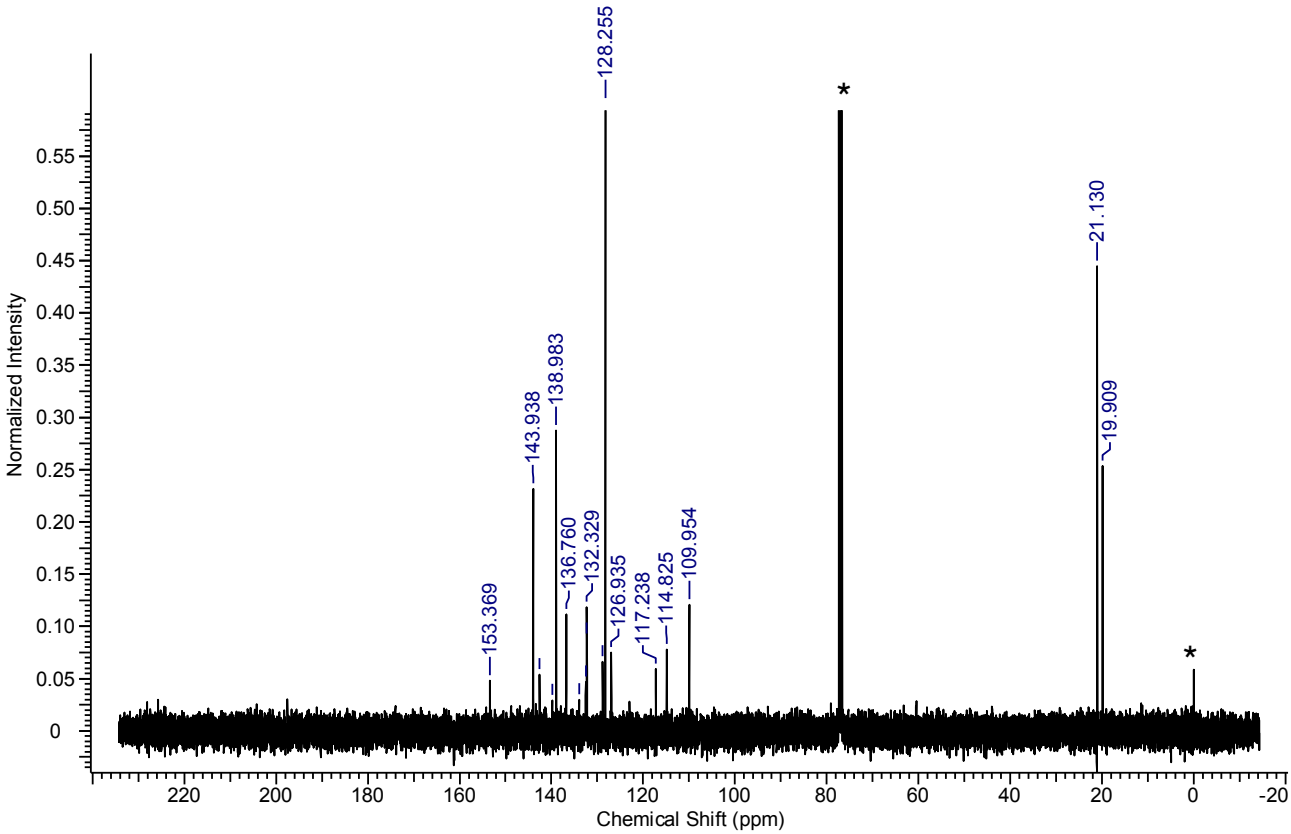


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

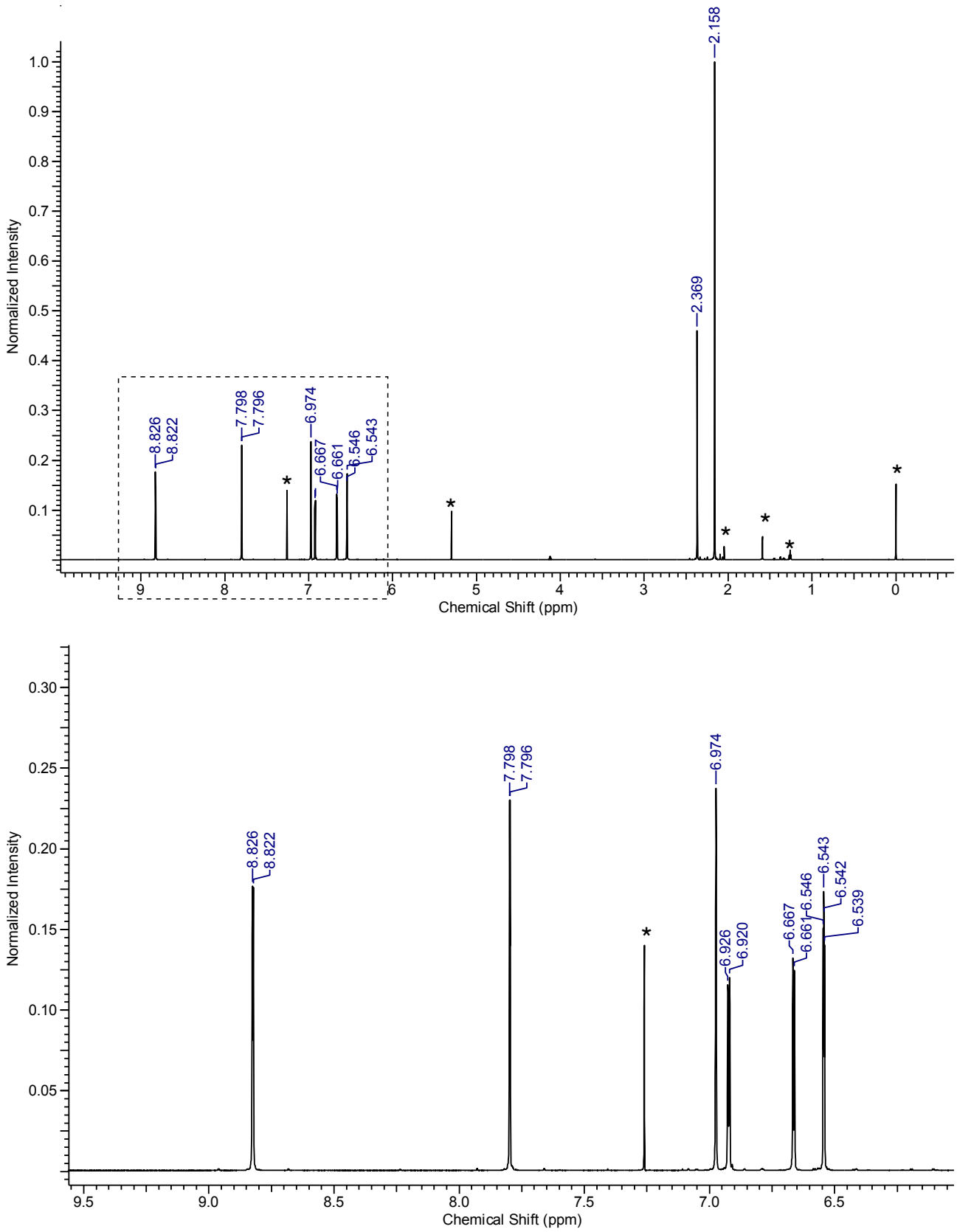


Figure S8. ^{1}H NMR spectrum of **4** in $CDCl_3$.

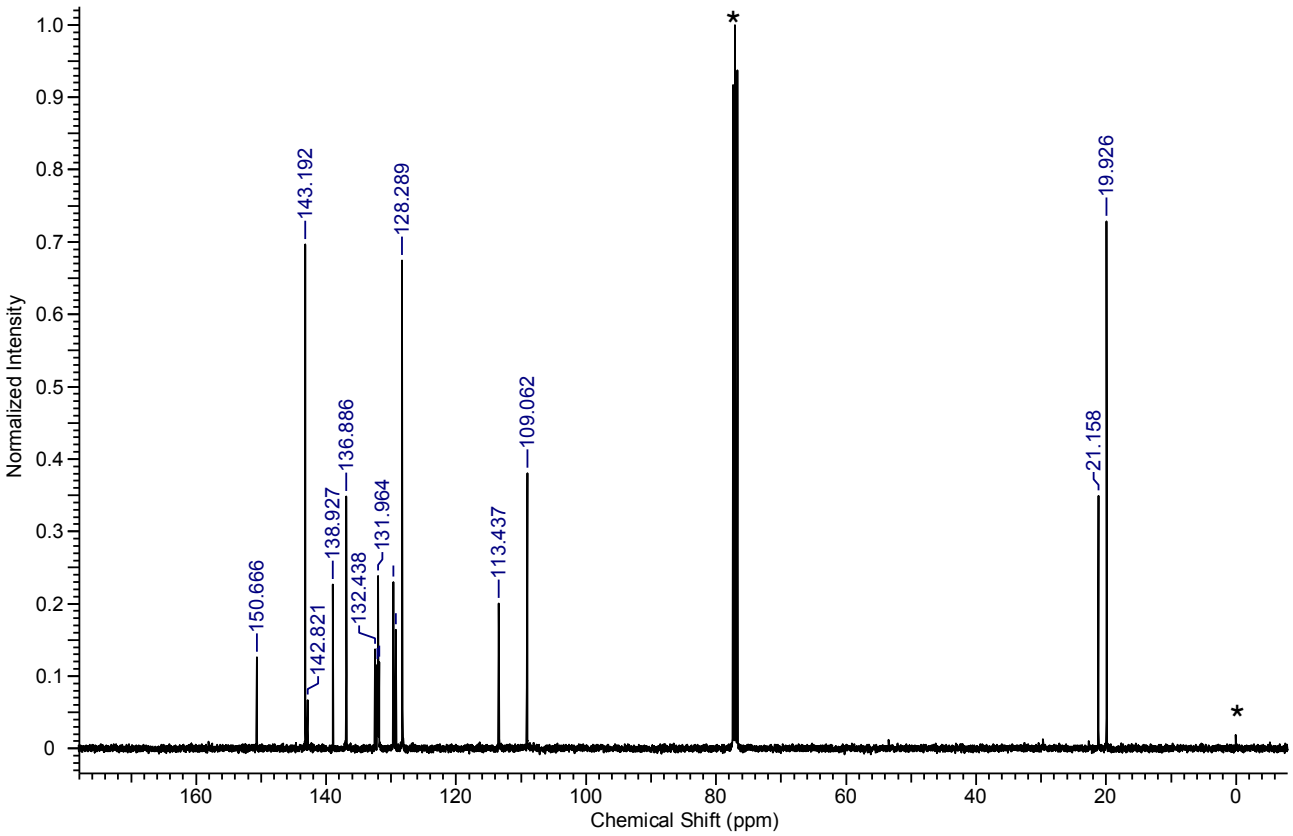


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

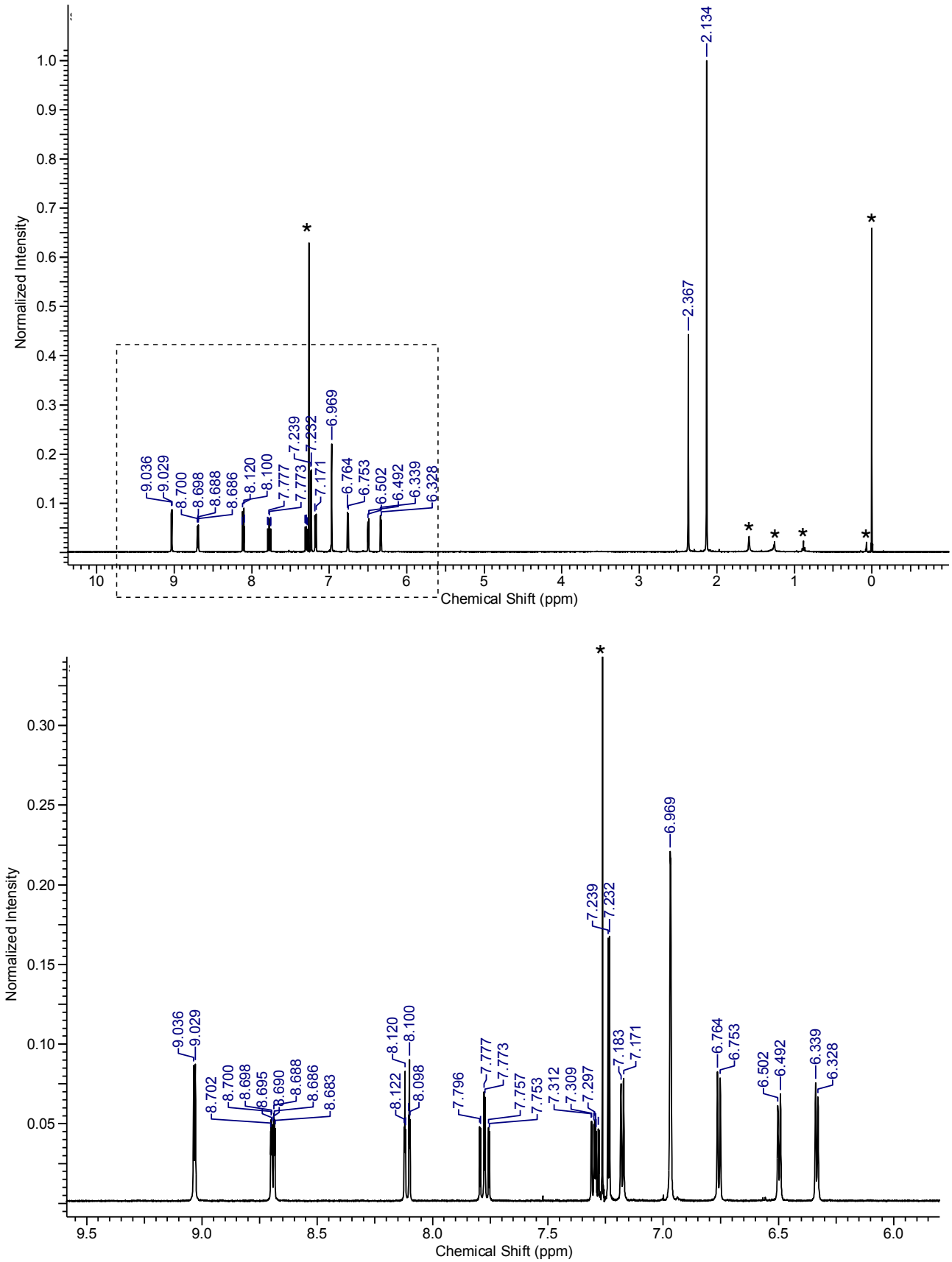


Figure S10. ^{1}H NMR spectra of **5** in $CDCl_3$.

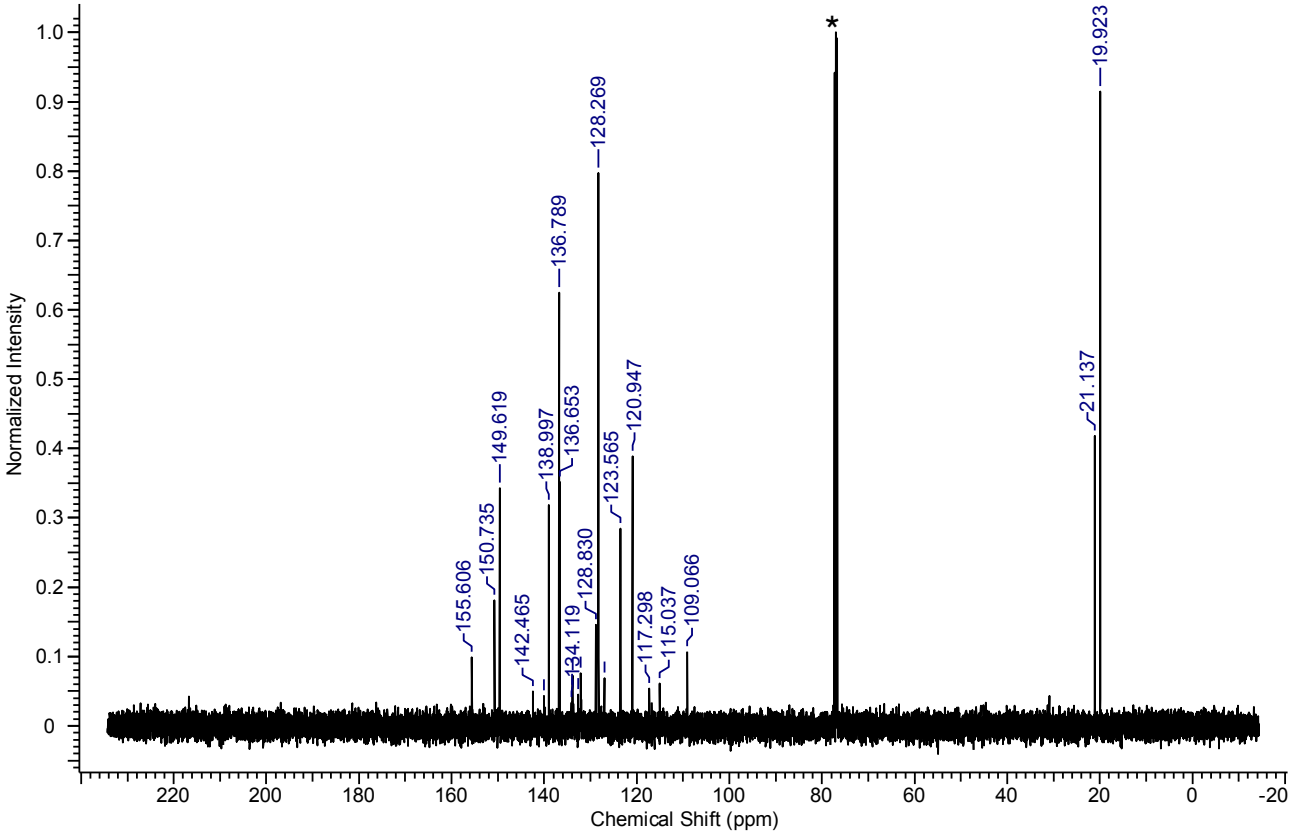


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

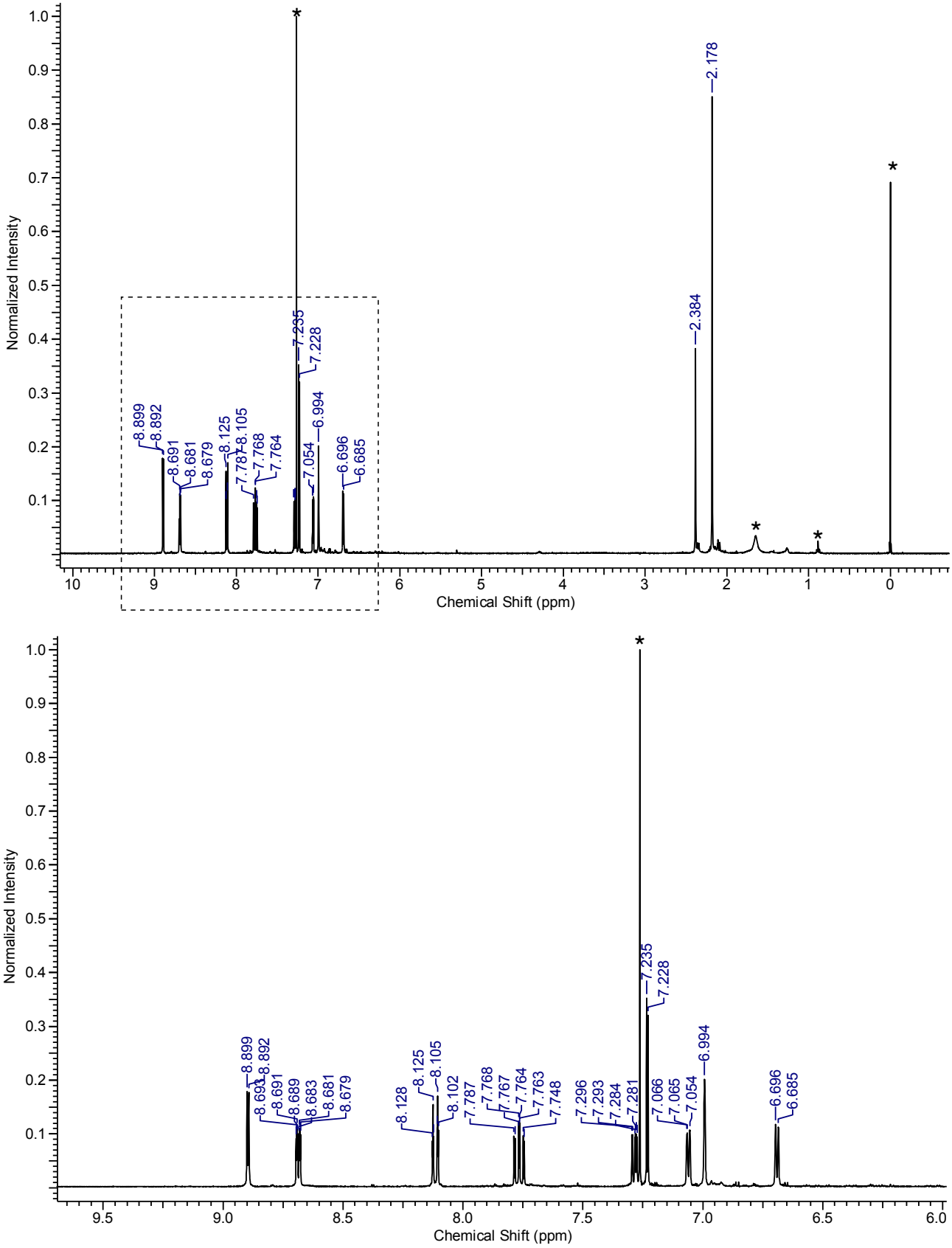


Figure S12. ^{1}H NMR spectra of **6** in $CDCl_3$.

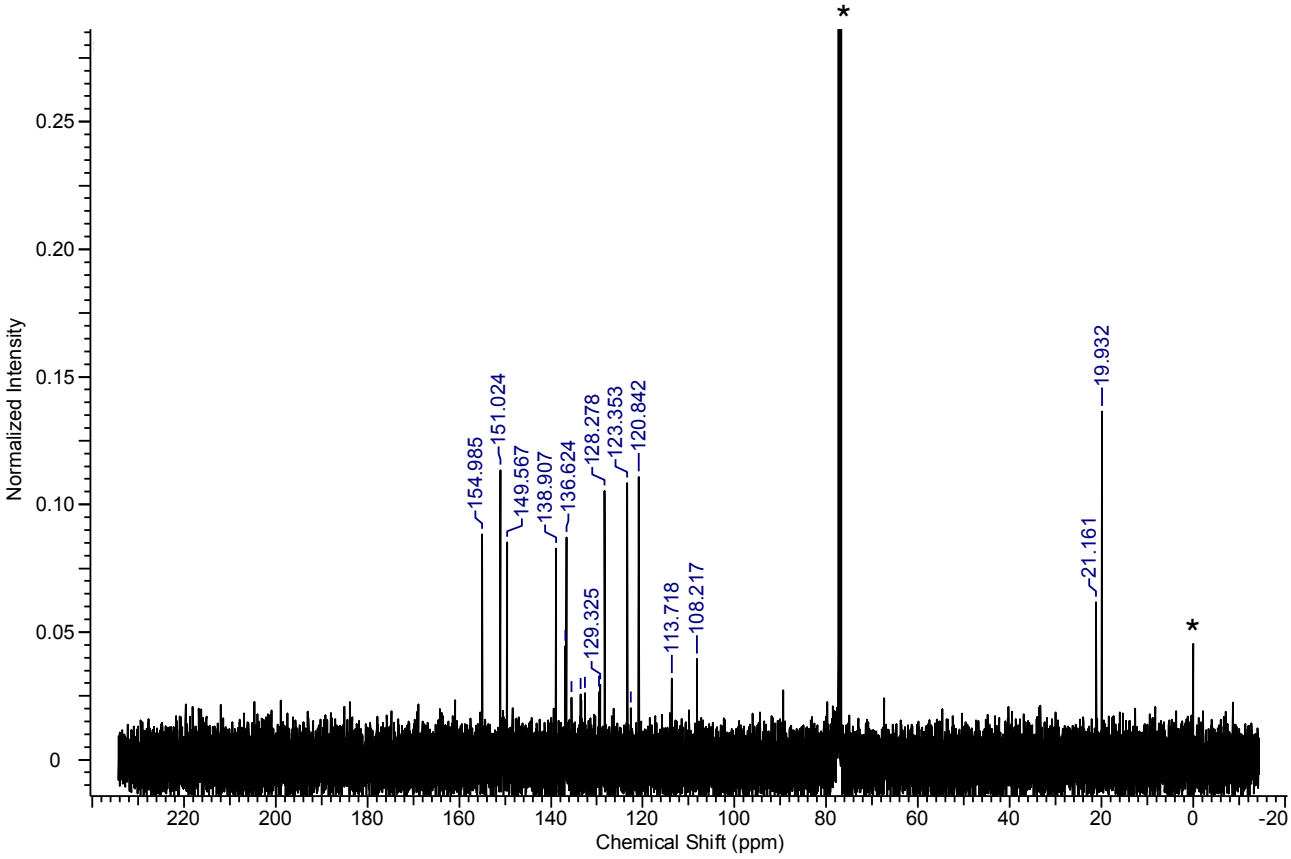


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

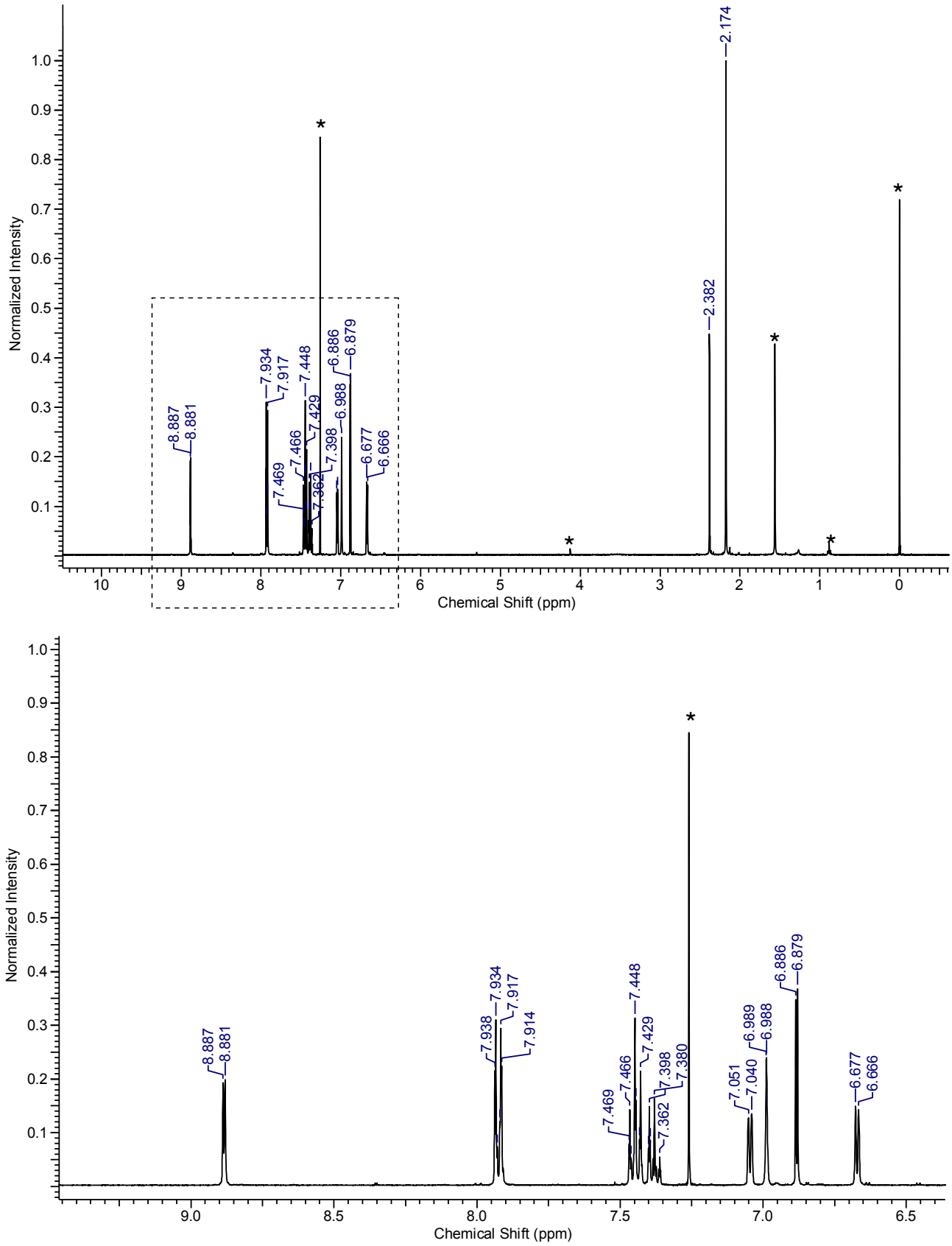


Figure S14. ^{1}H NMR spectra of **7** in $CDCl_3$.

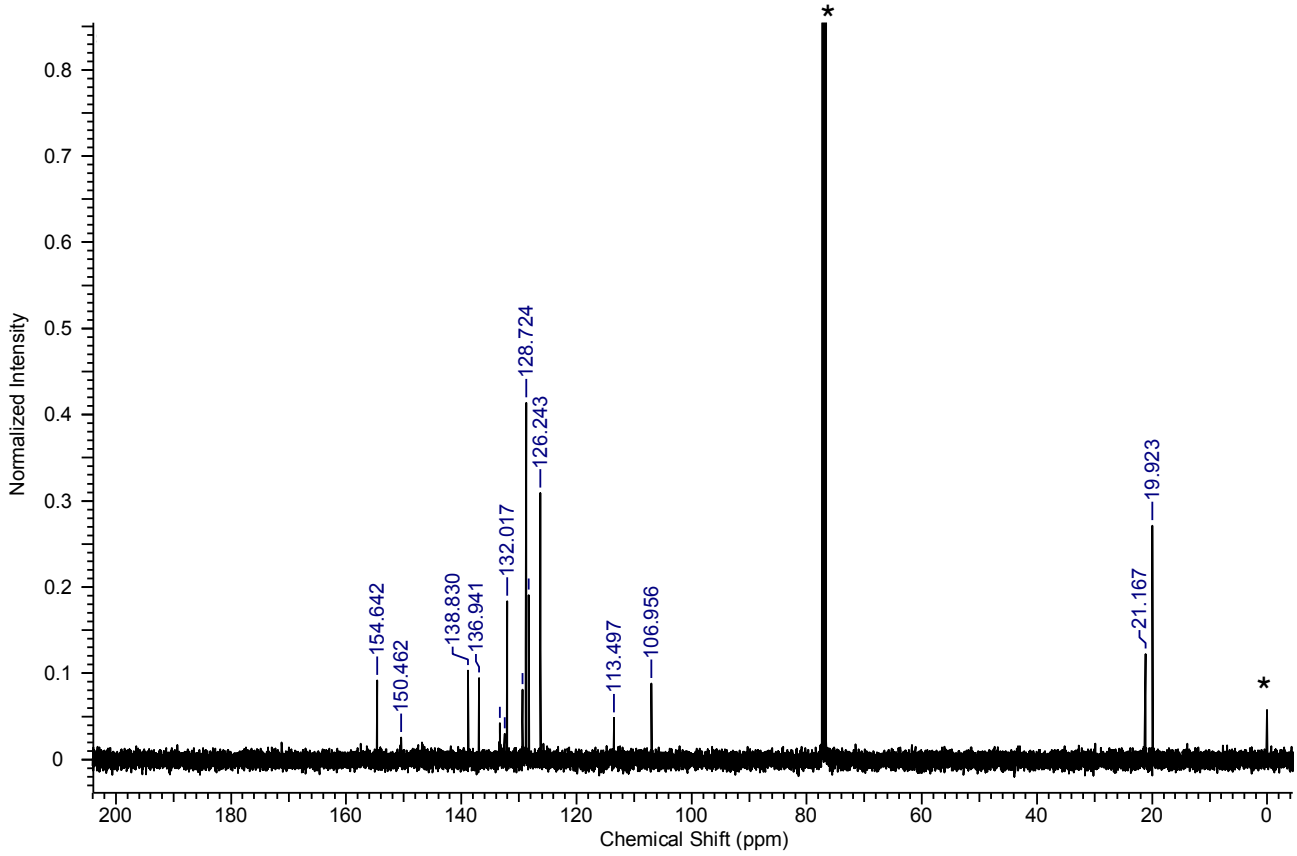


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

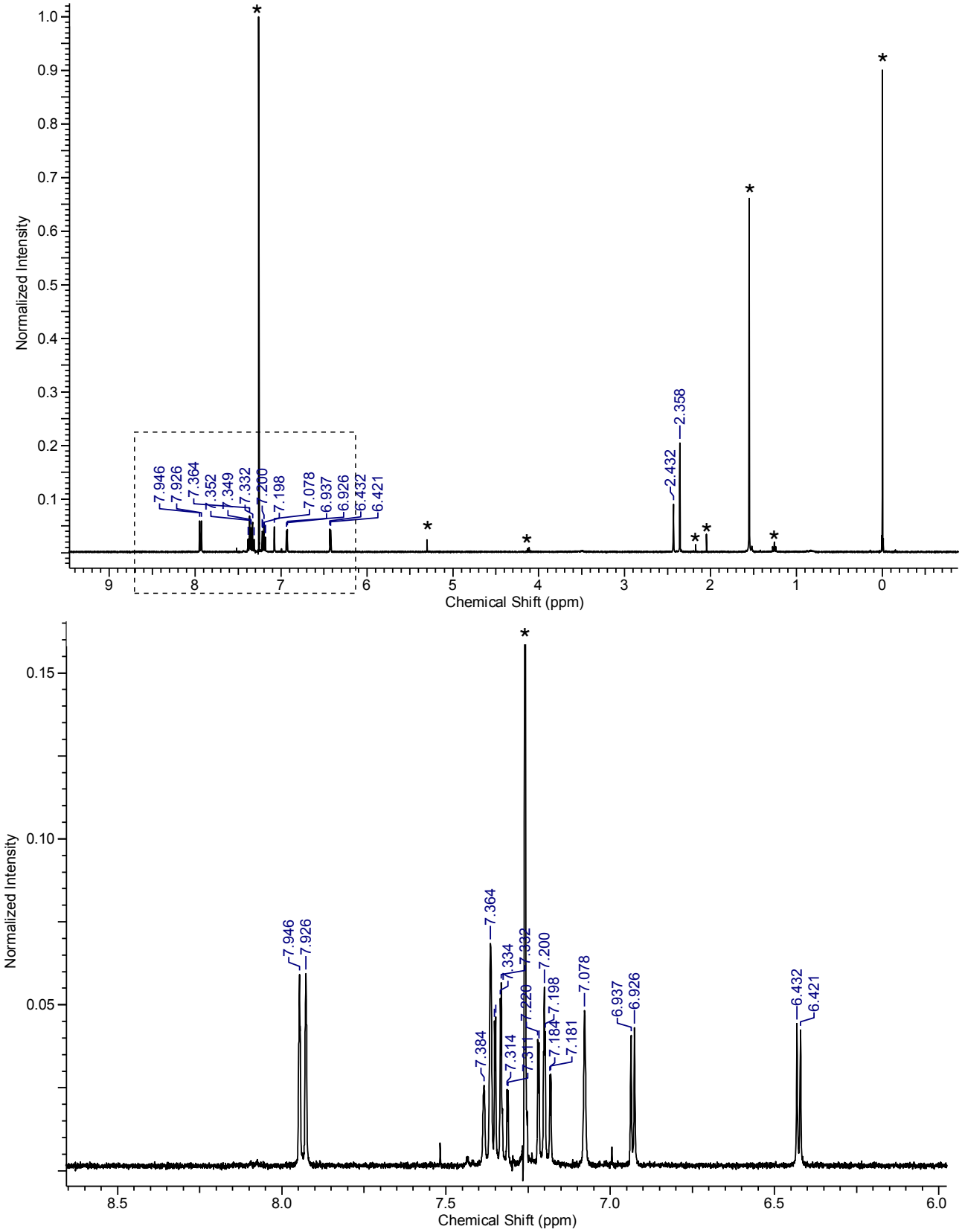


Figure S16. ^{1}H NMR spectra of **10** in $CDCl_3$.

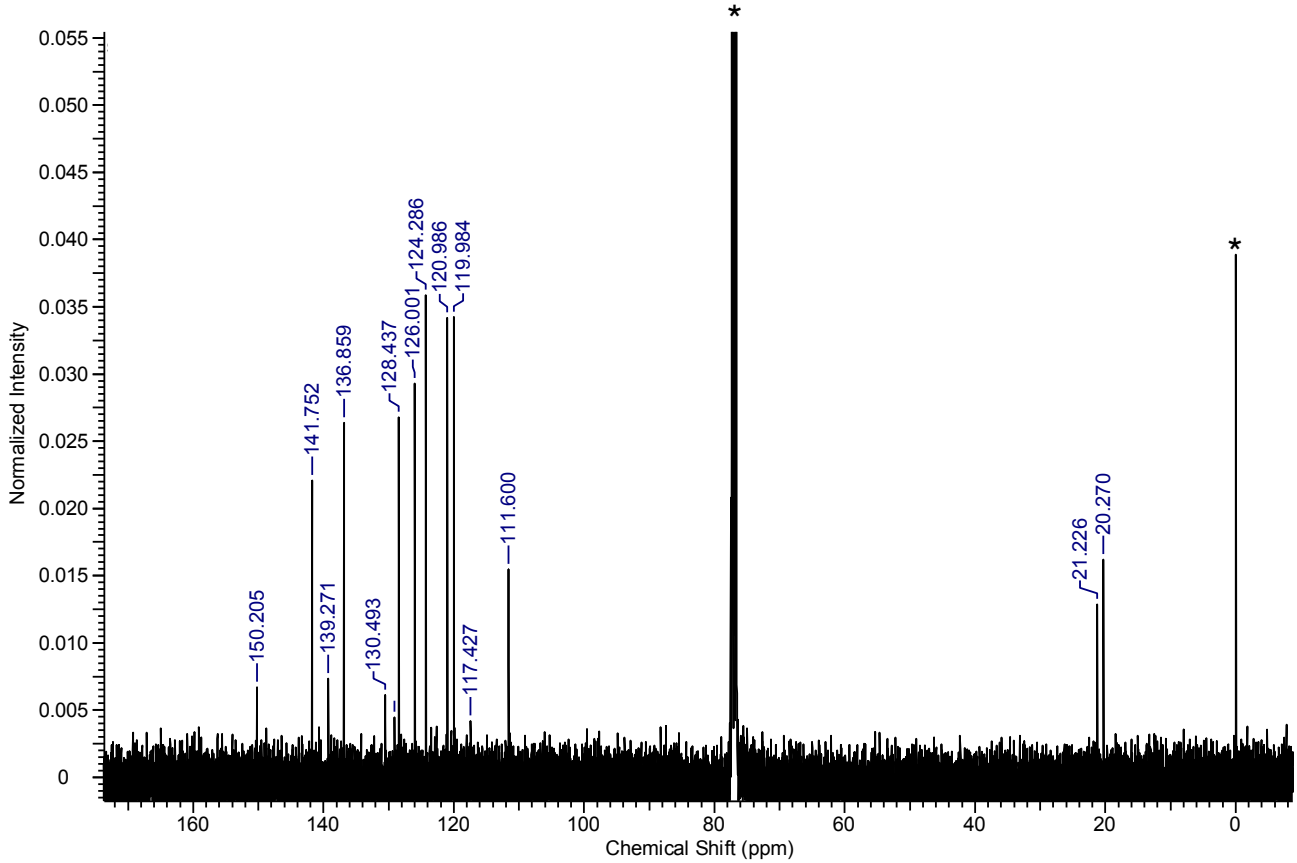


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **10** in $CDCl_3$.

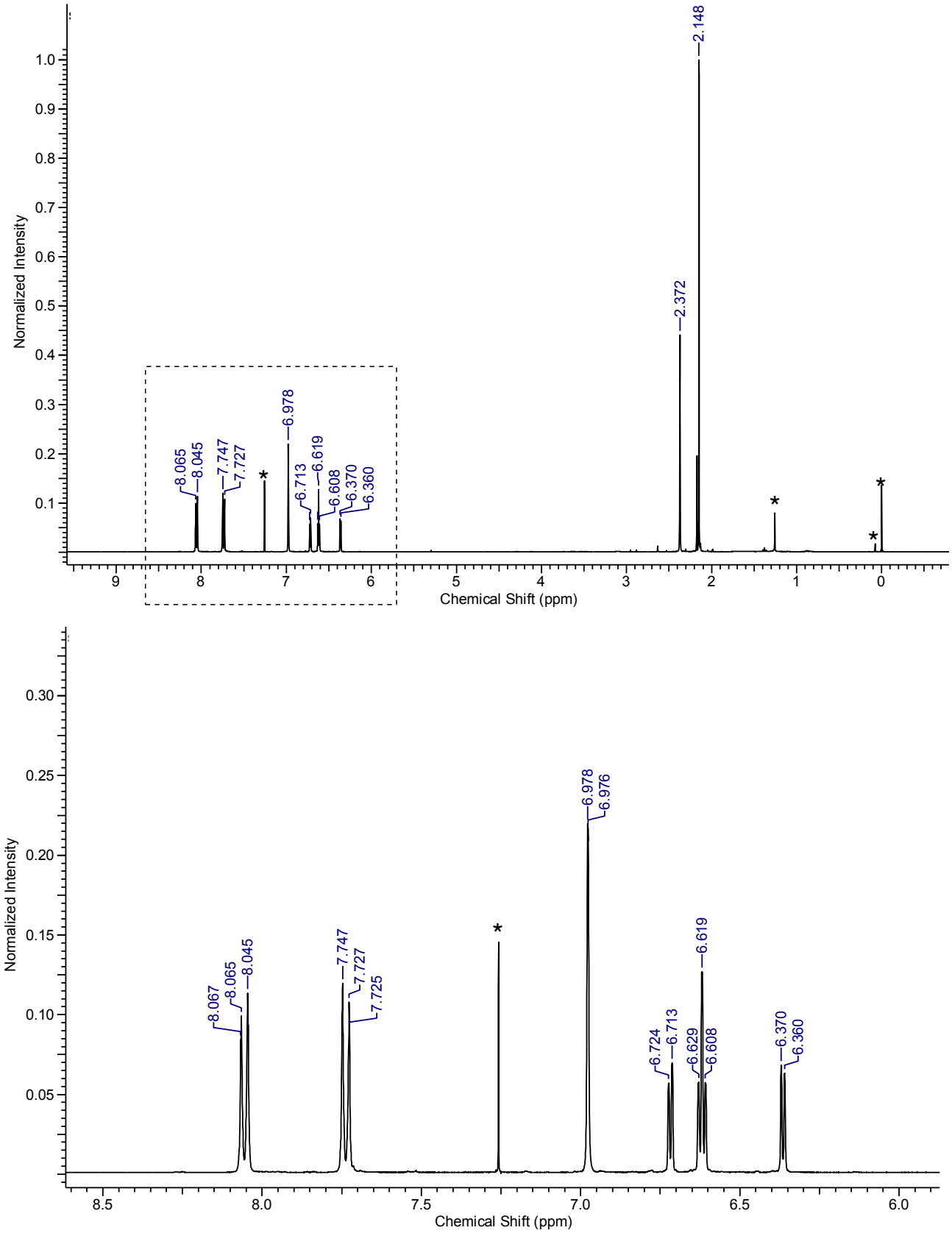


Figure S18. ^{1}H NMR spectra of **11** in $CDCl_3$.

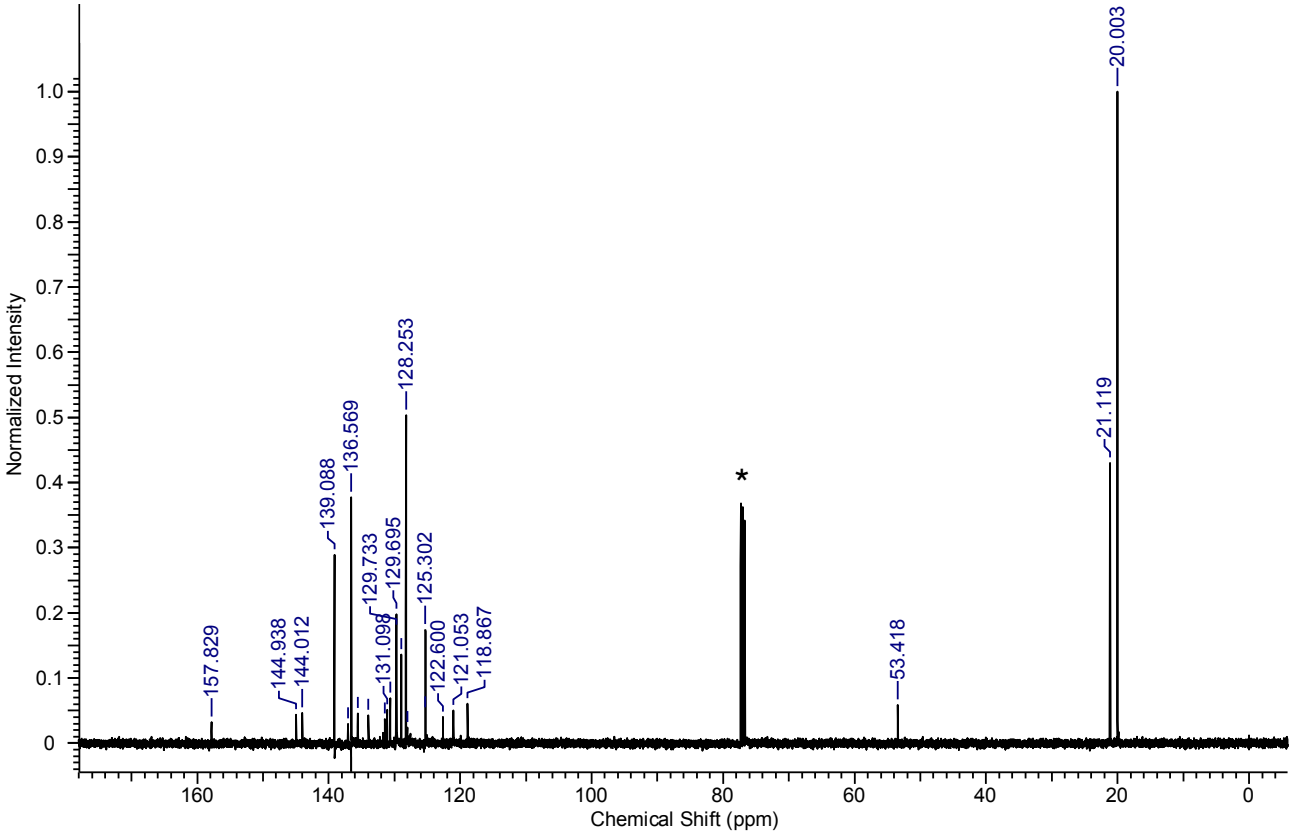


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **11** in $CDCl_3$.

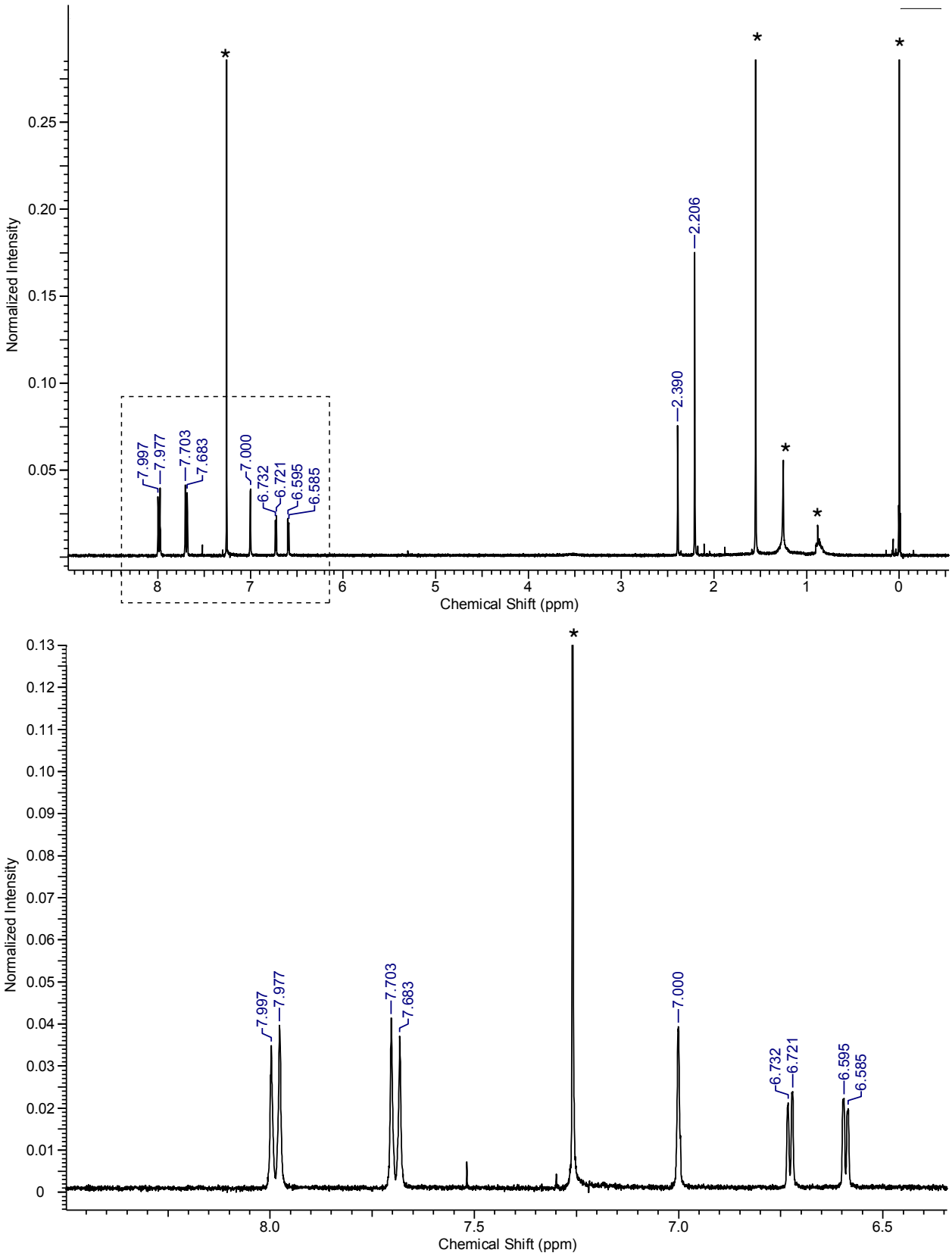


Figure S20. ^{1}H NMR spectra of **12** in $CDCl_3$.

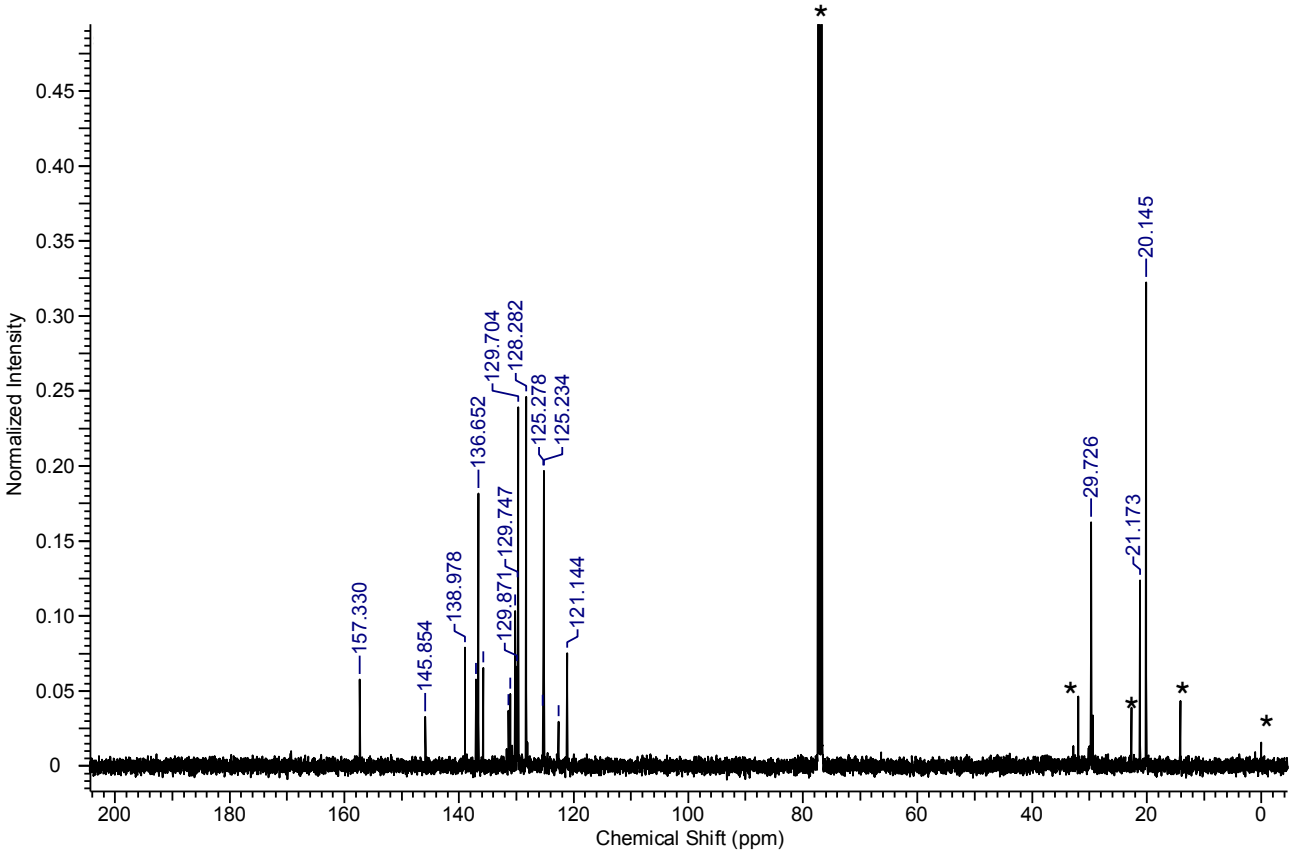


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **12** in $CDCl_3$.

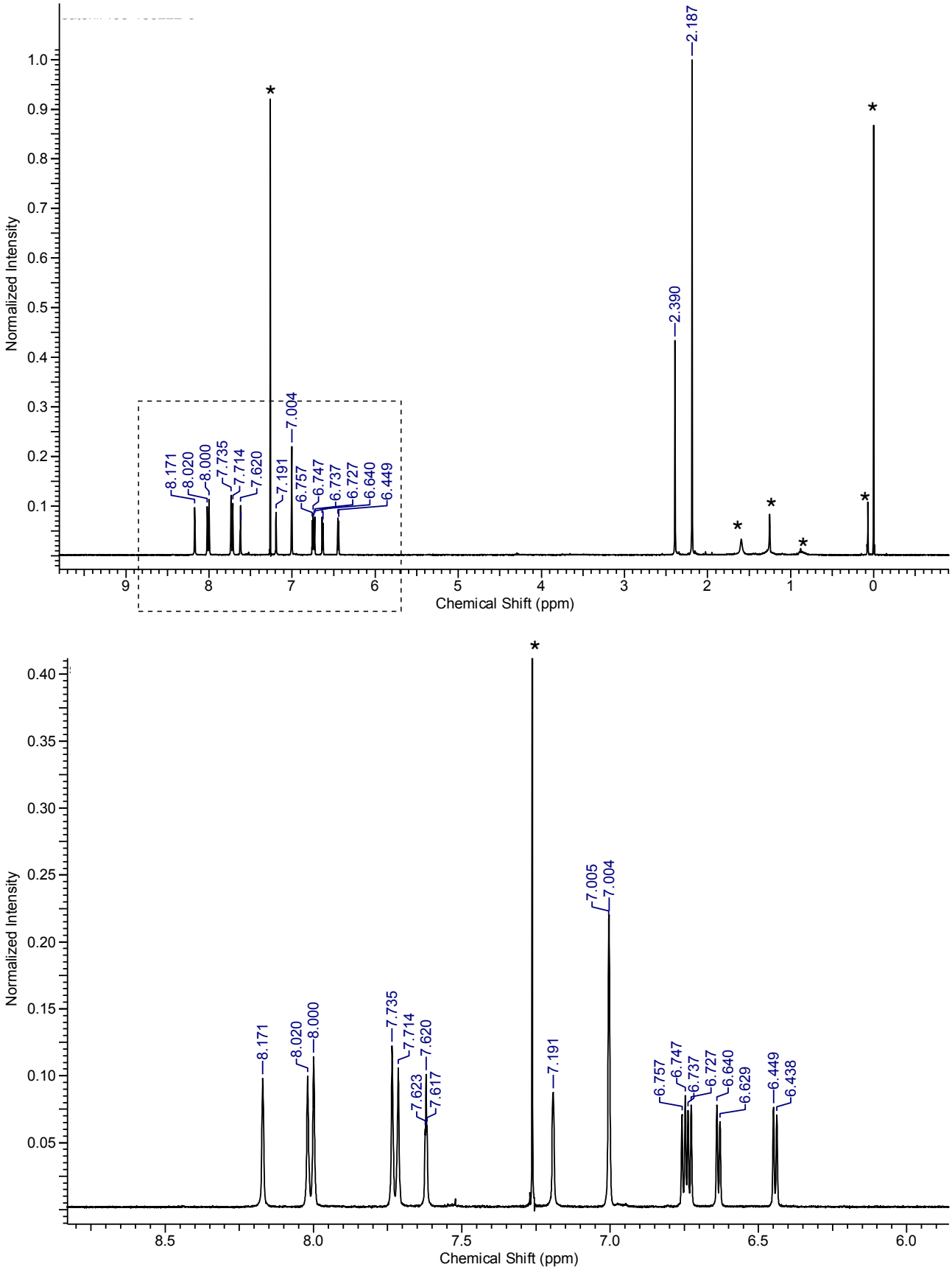


Figure S22. ^{1}H NMR spectra of **13** in $CDCl_3$.

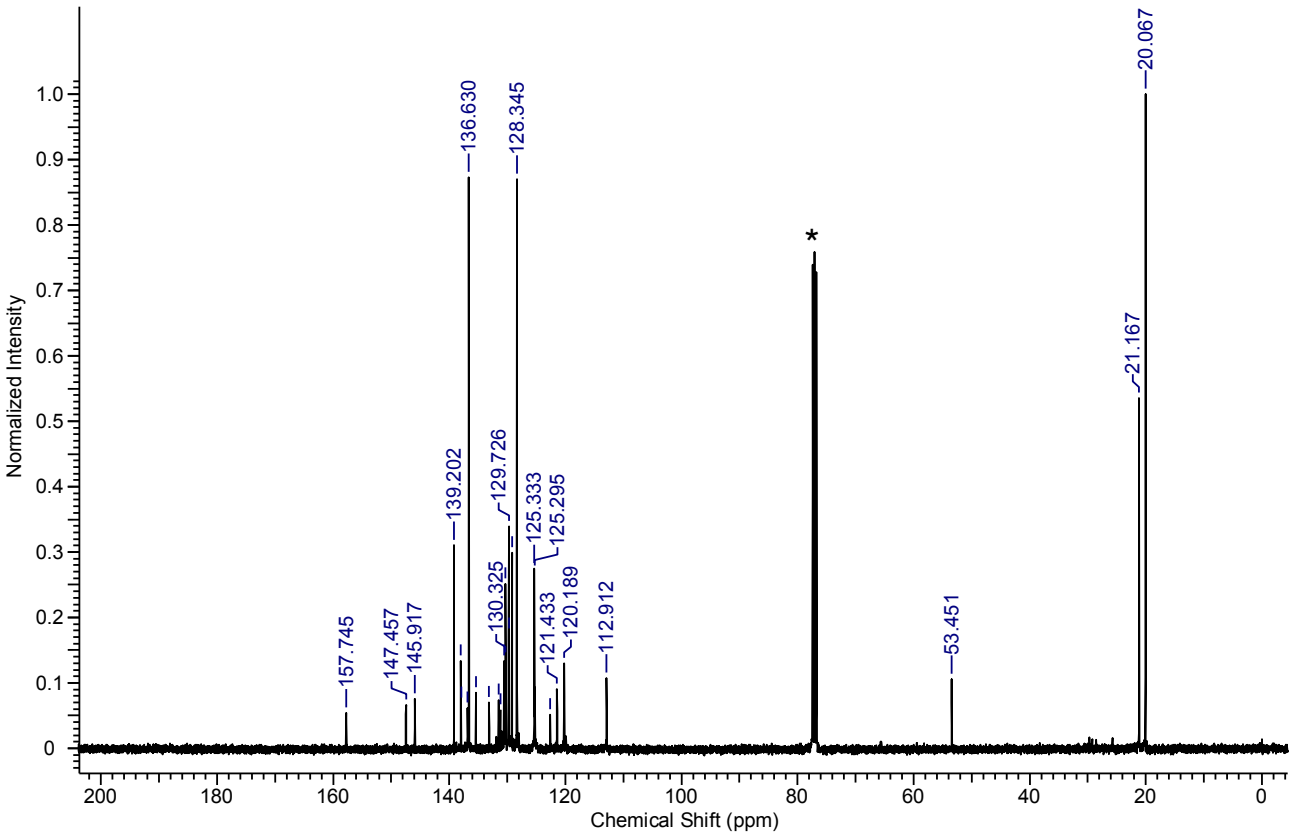


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **13** in $CDCl_3$.

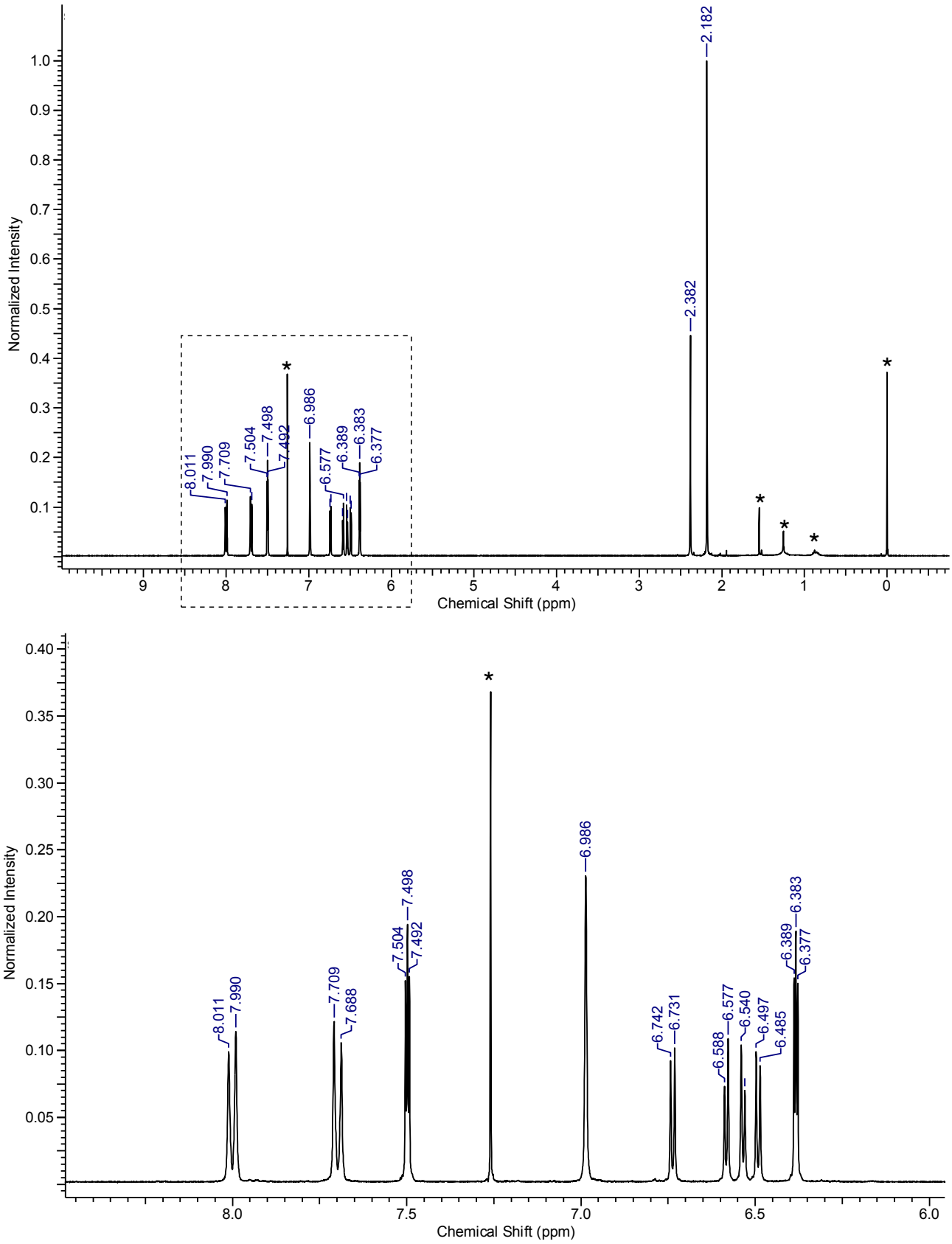


Figure S24. ^{1}H NMR spectra of **14** in $CDCl_3$.

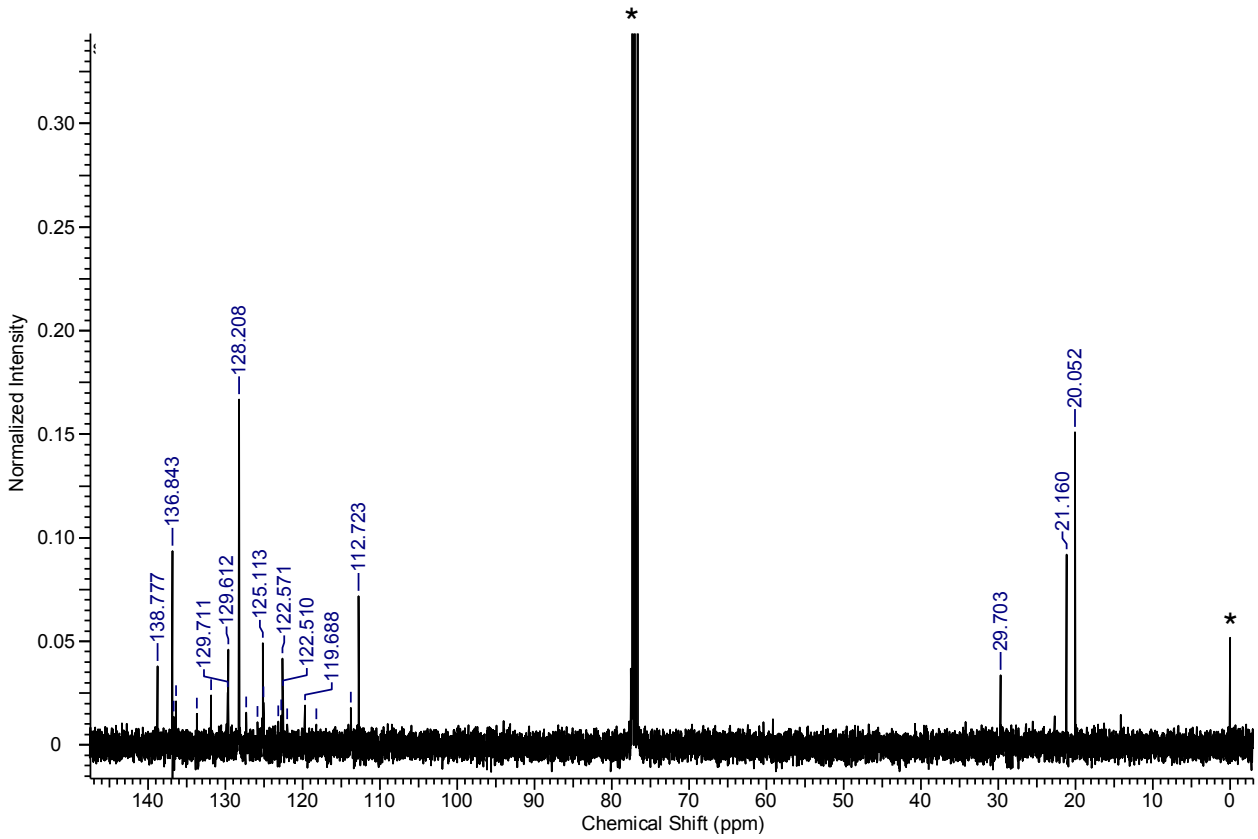


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **14** in $CDCl_3$.

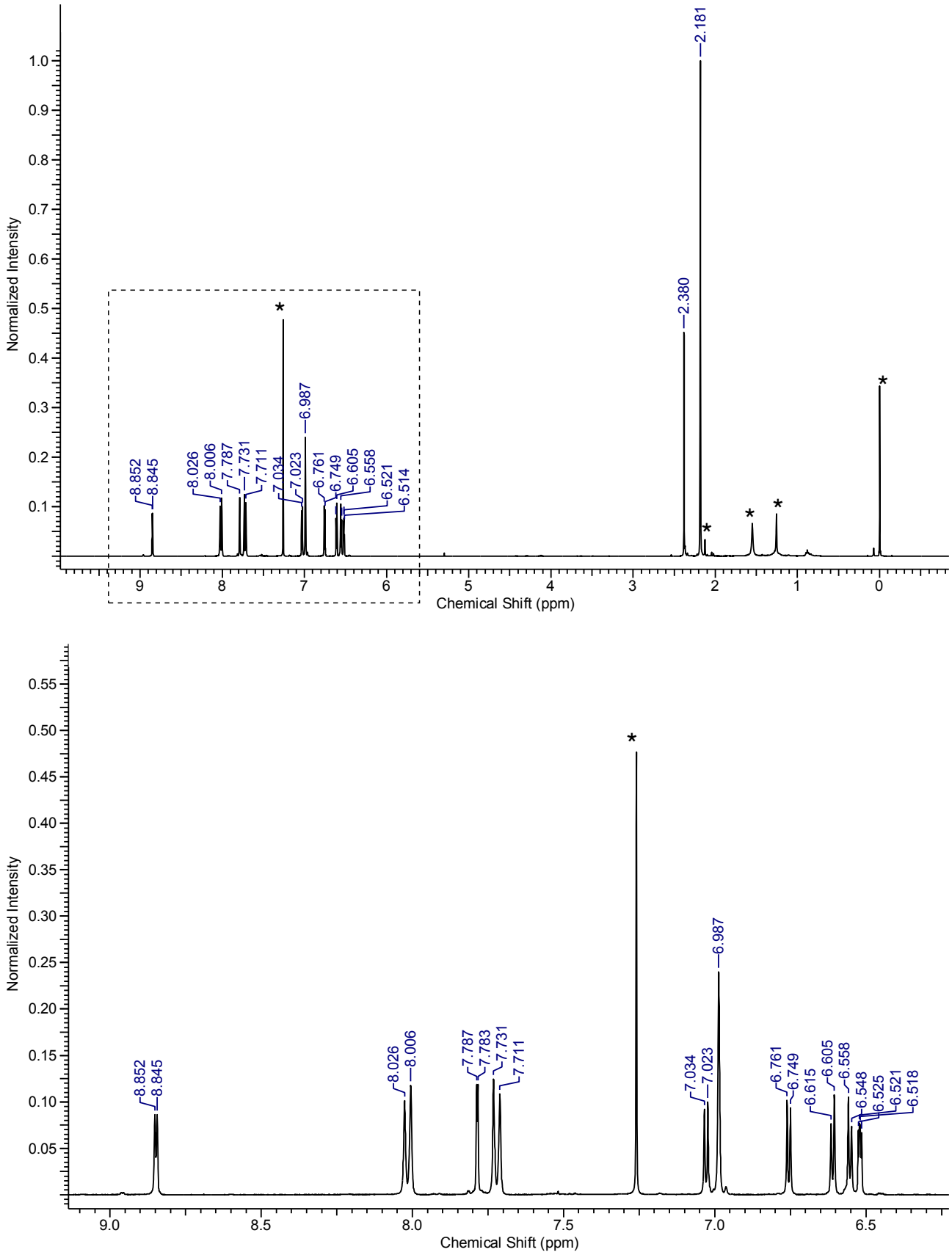


Figure S26. ^{1}H NMR spectra of **15** in $CDCl_3$.

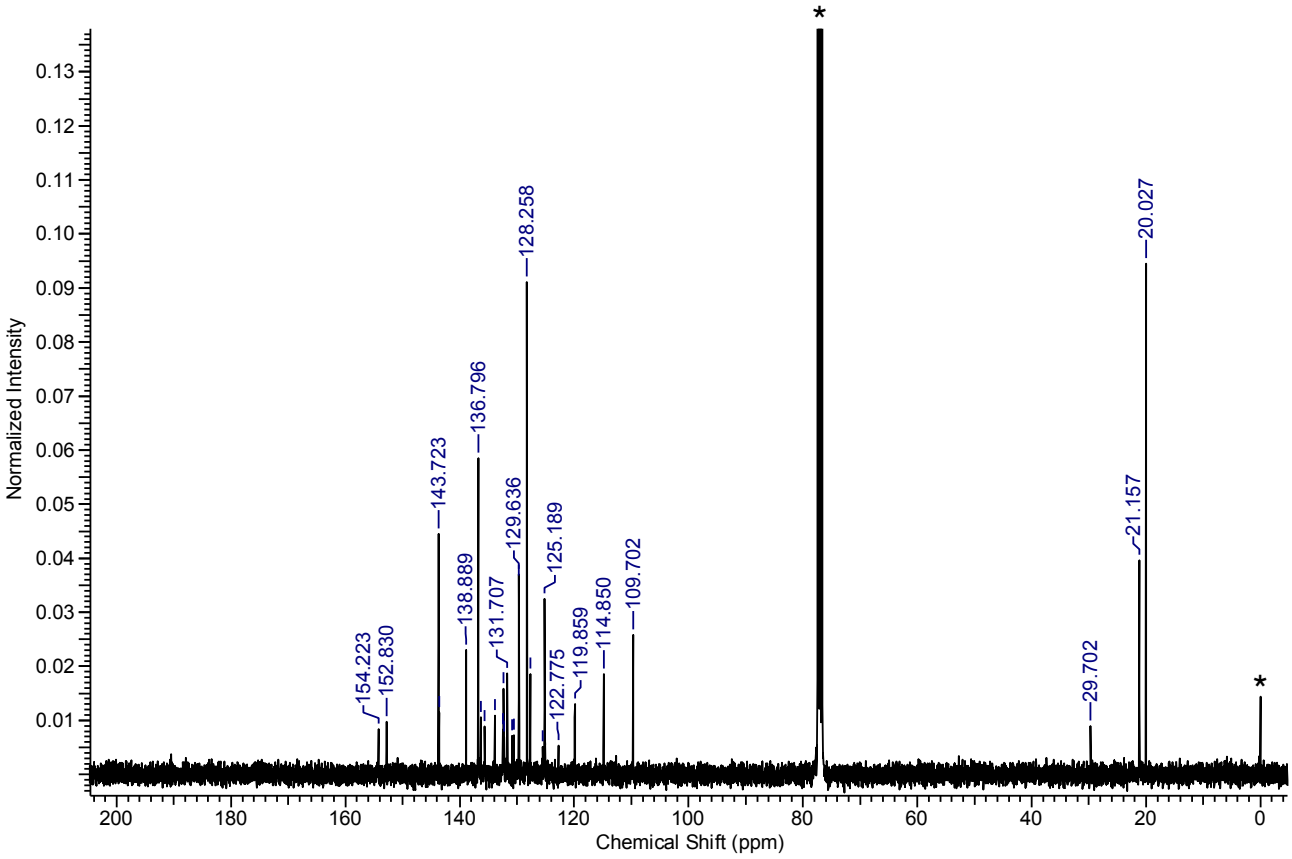


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **15** in $CDCl_3$.

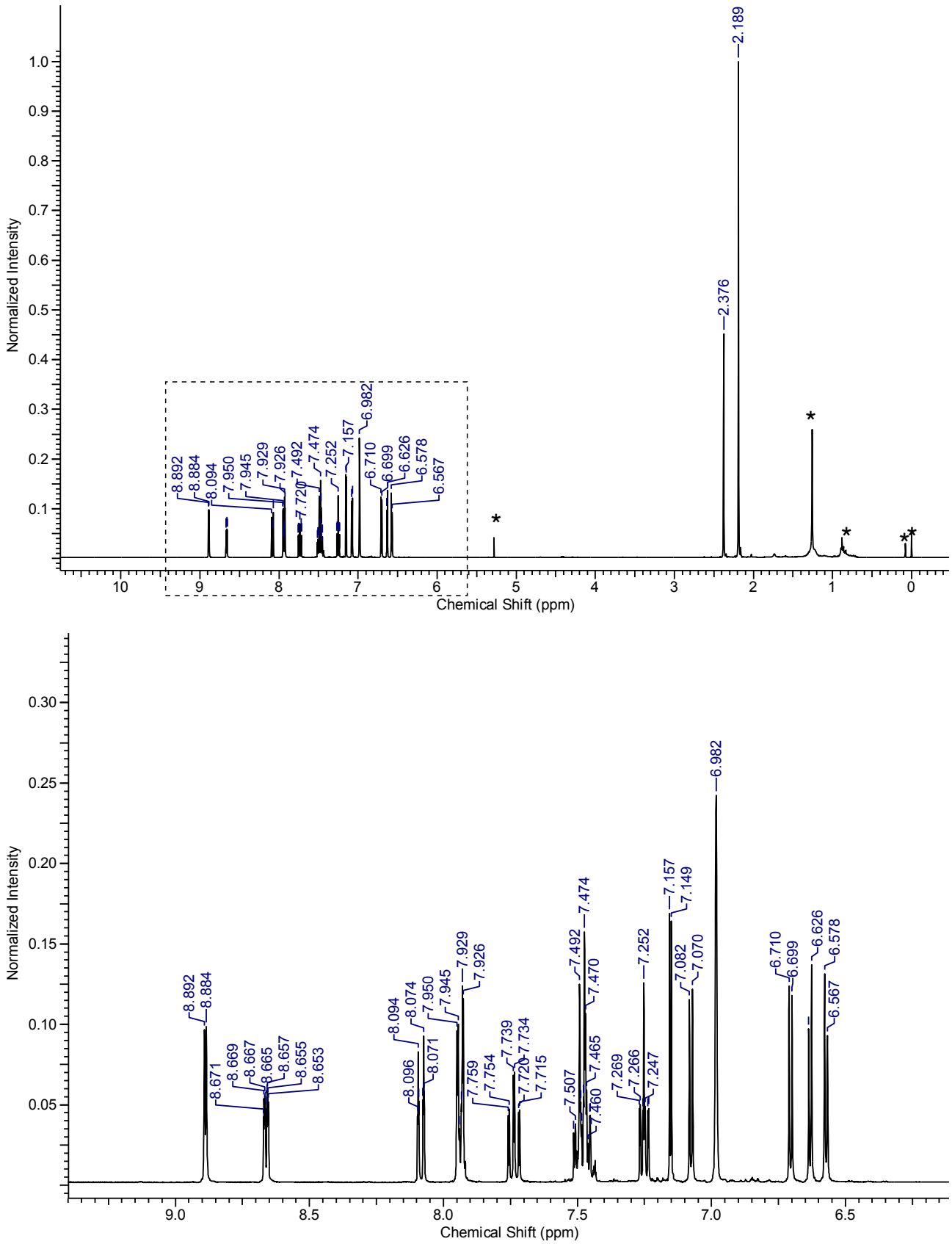


Figure S28. ^{1}H NMR spectra of **16** in $CDCl_3$.

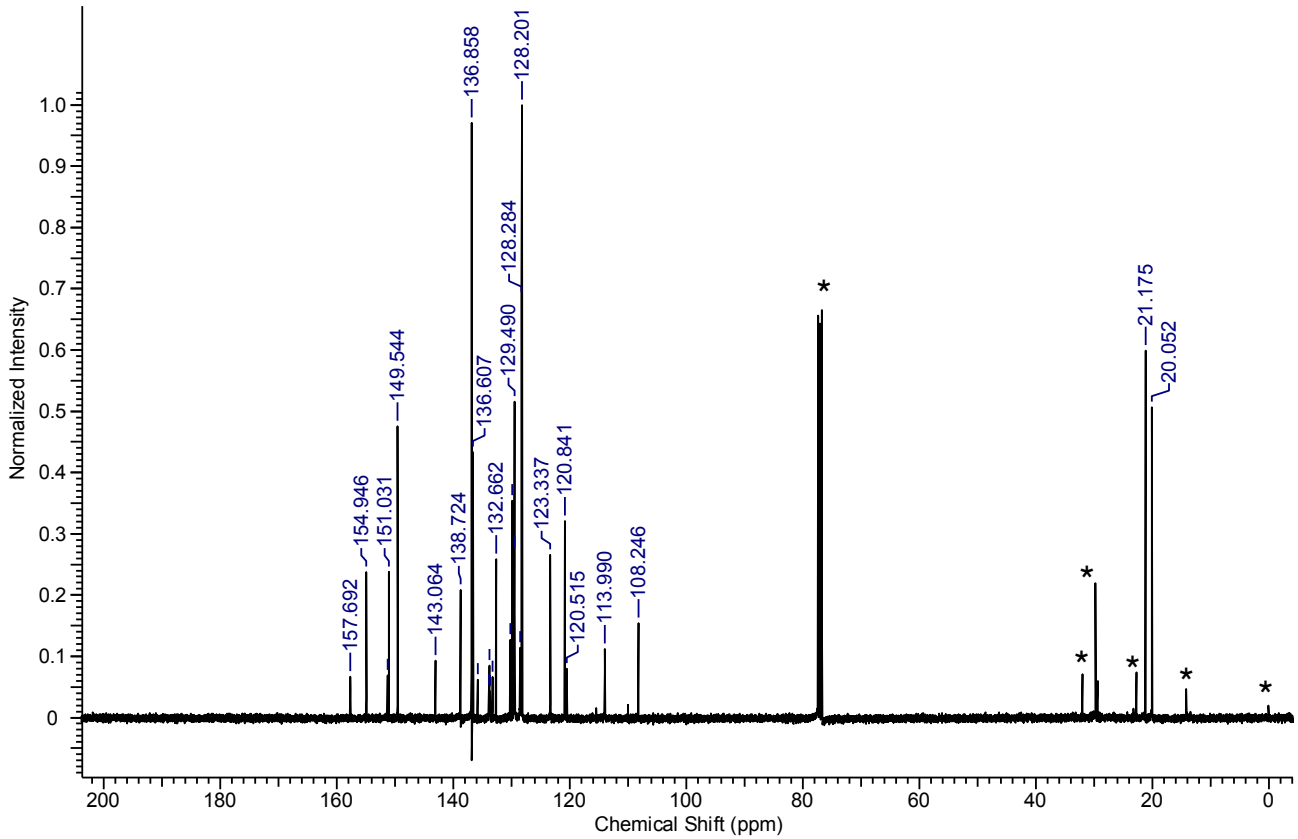


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **16** in $CDCl_3$.

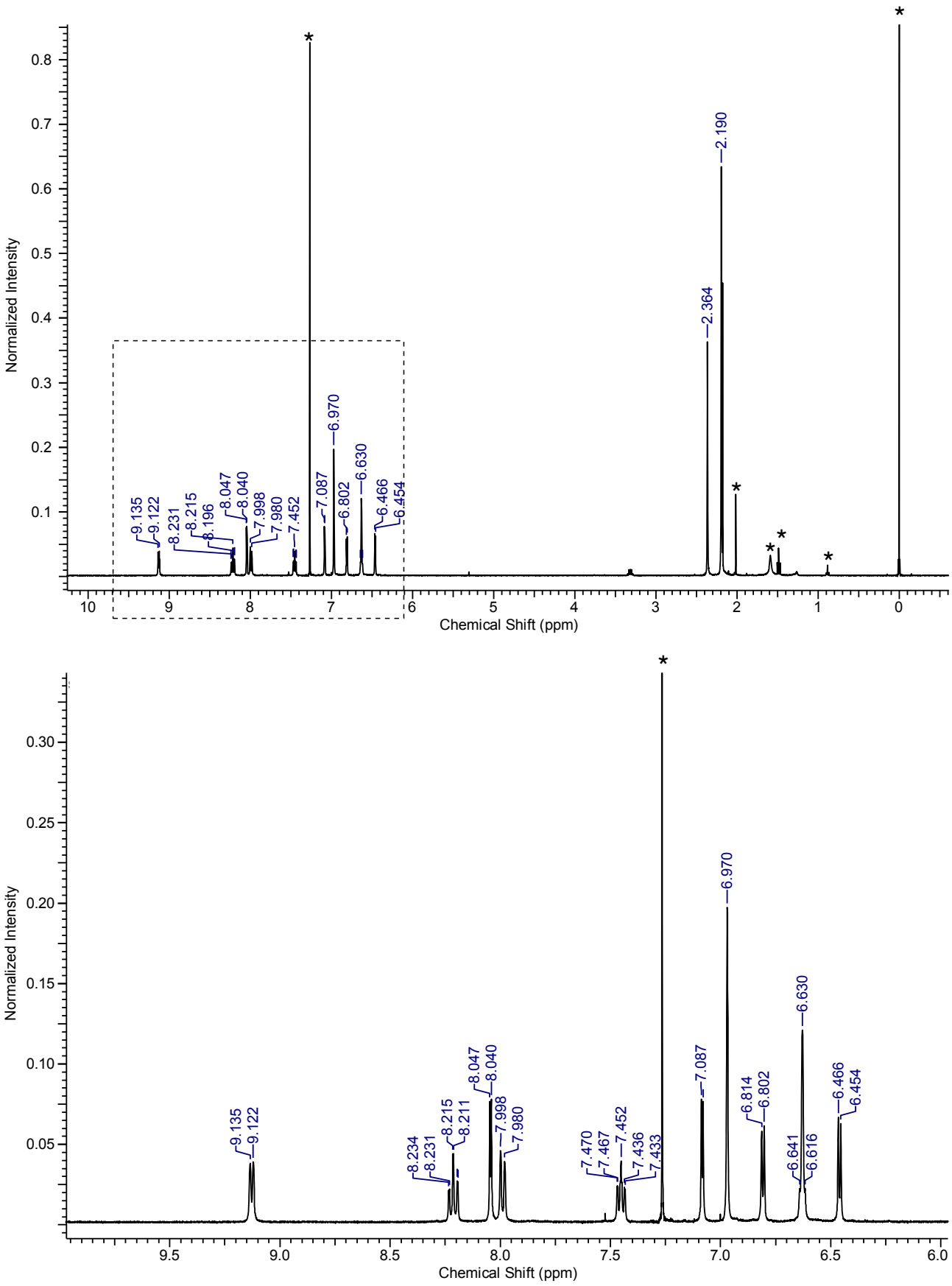


Figure S30. ^{1}H NMR spectra of **17** in $CDCl_3$.

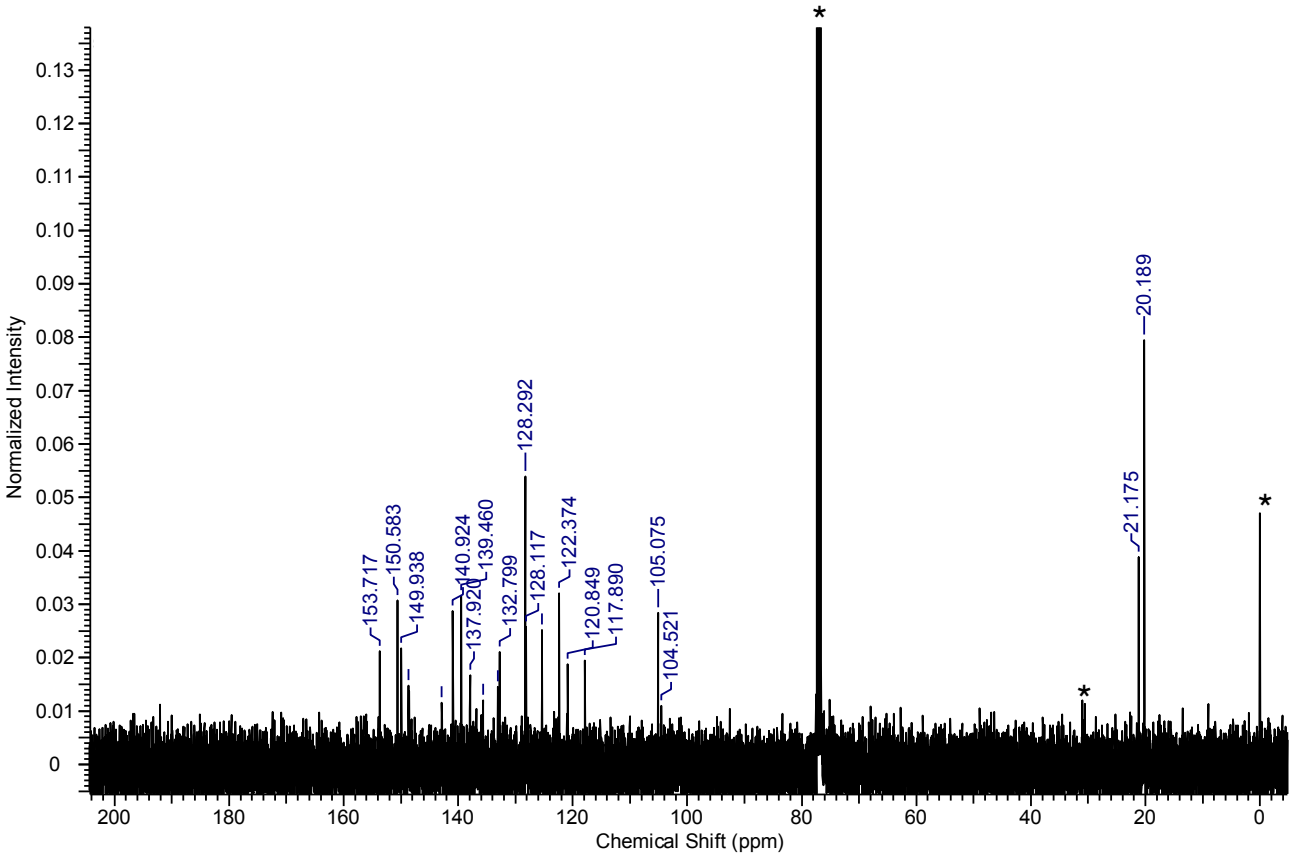


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **17** in $CDCl_3$.

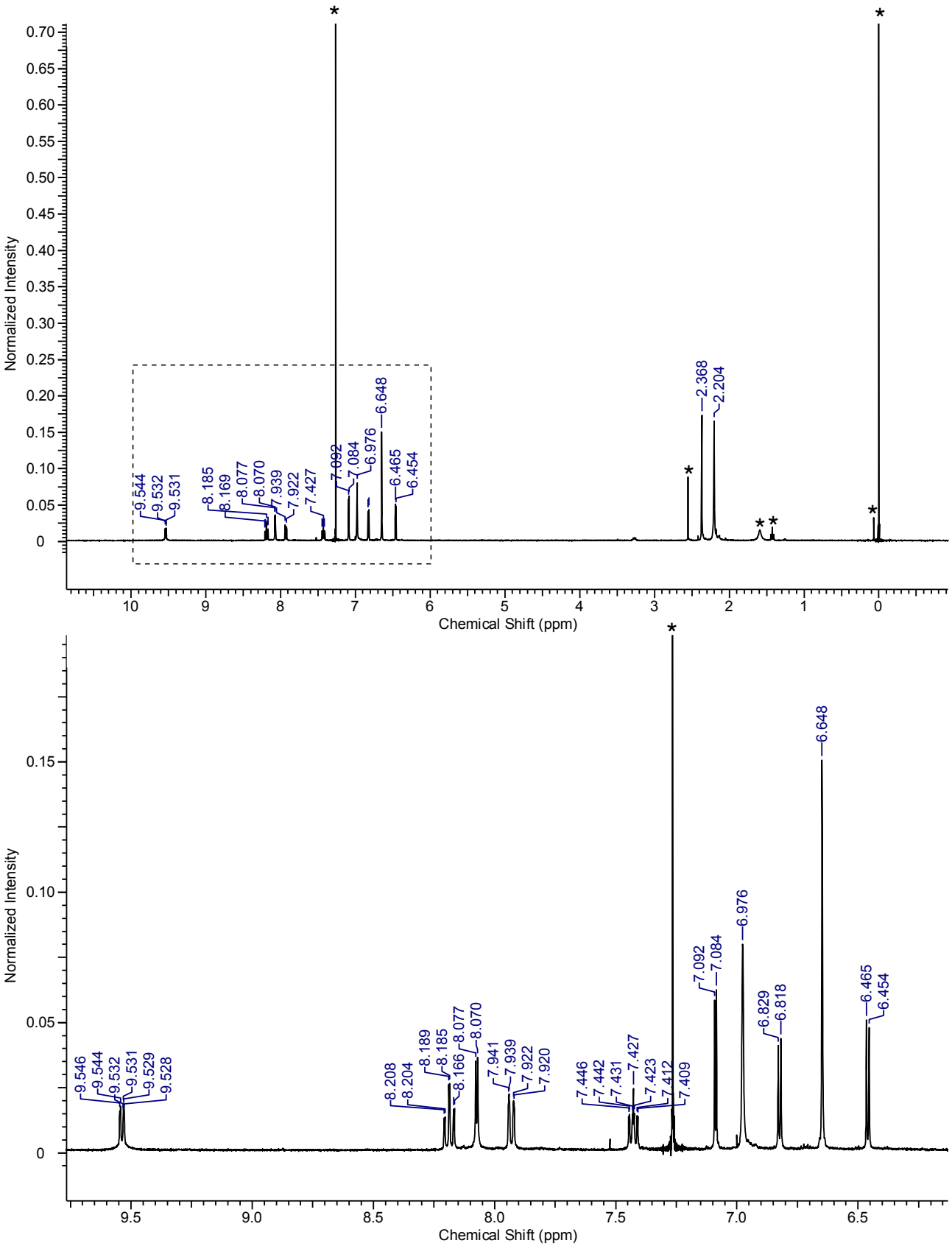


Figure S32. ^{1}H NMR spectra of **18** in $CDCl_3$.

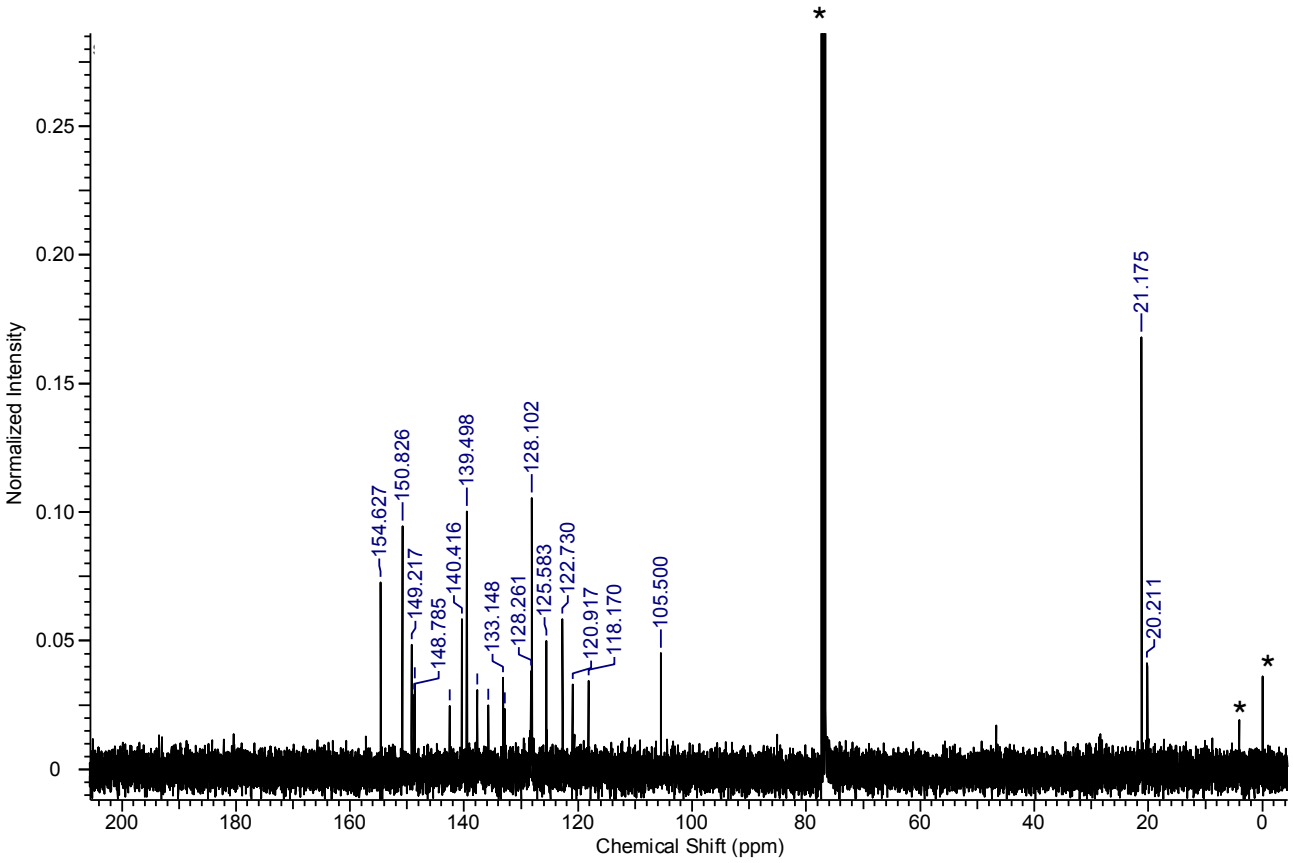
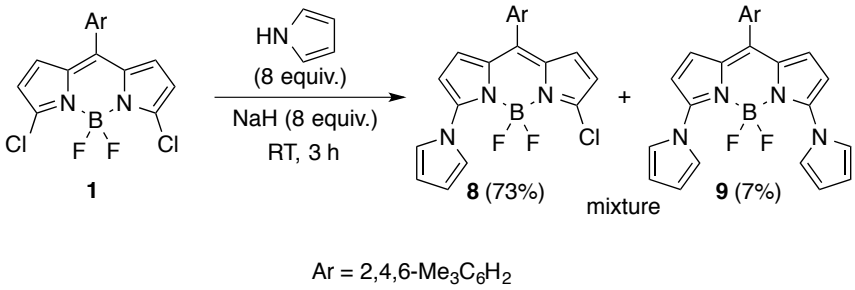
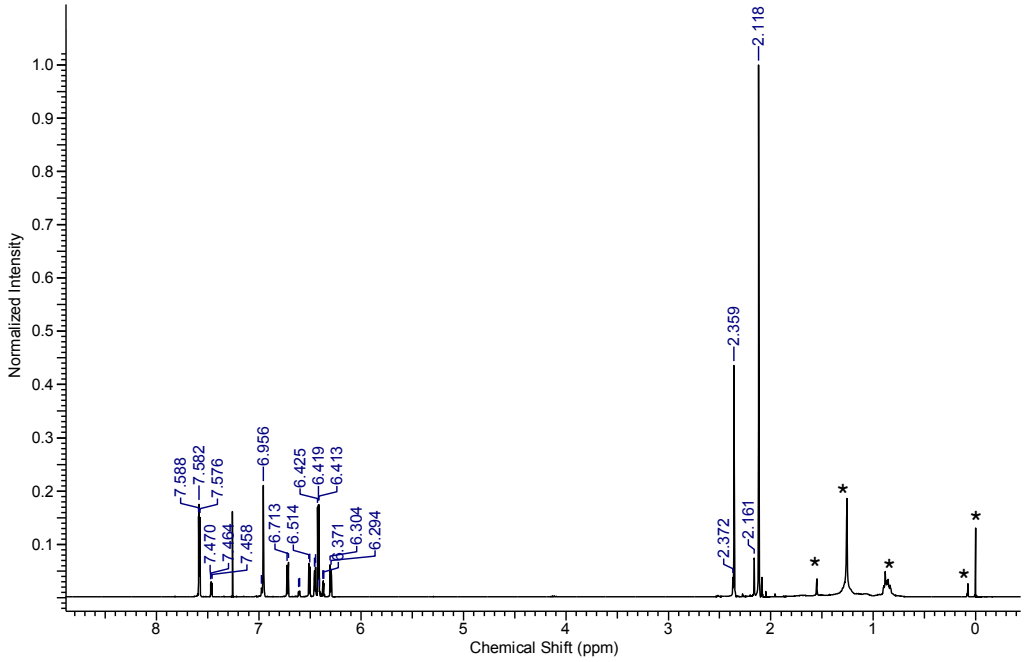


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of **18** in $CDCl_3$.





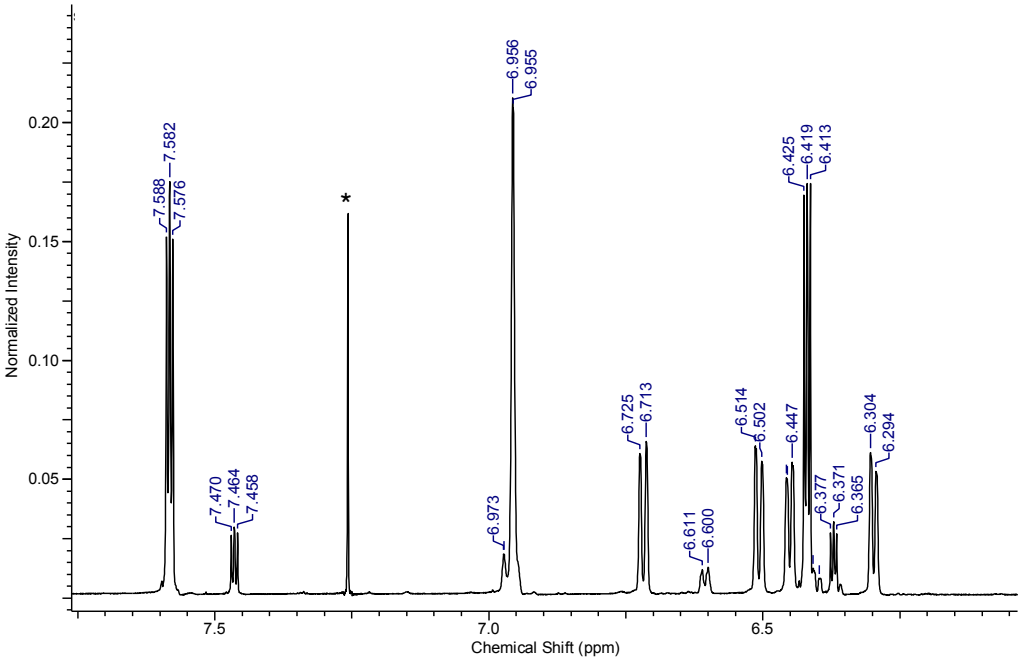
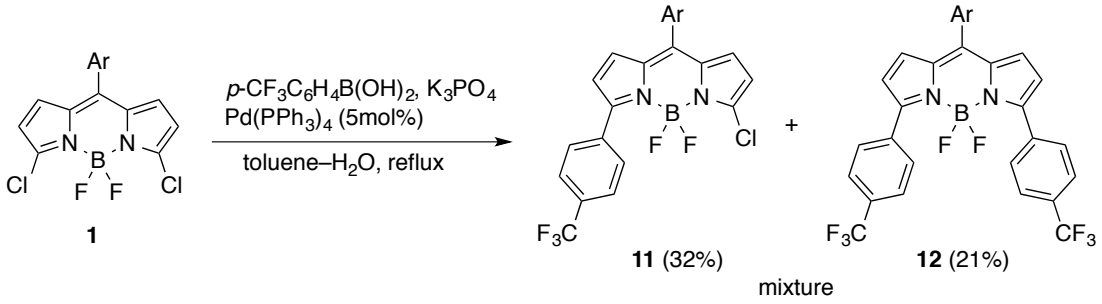
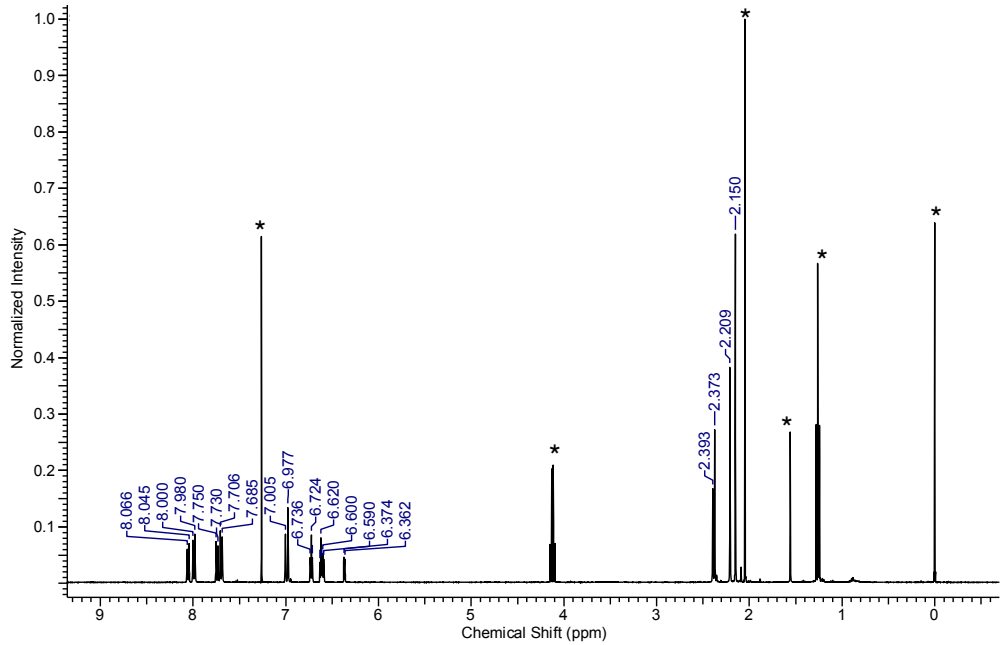


Figure S34. ^{1}H NMR spectra of a mixture of **8** and **9** in $CDCl_3$.



Ar = 2,4,6-$Me_3C_6H_2$



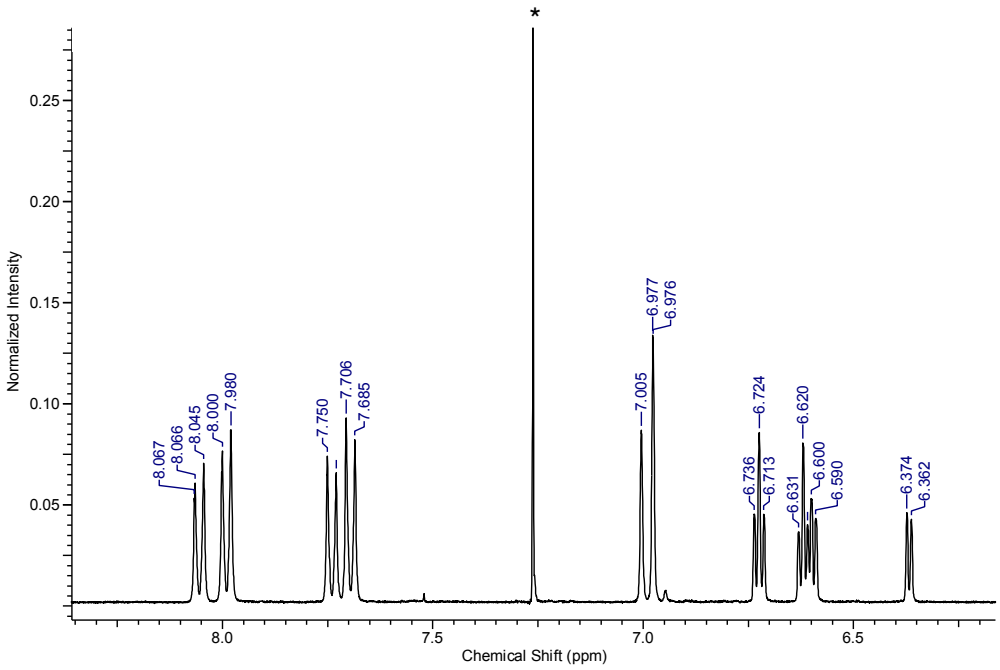


Figure S35. ^{1}H NMR spectra of a mixture of **11** and **12** in $CDCl_3$.

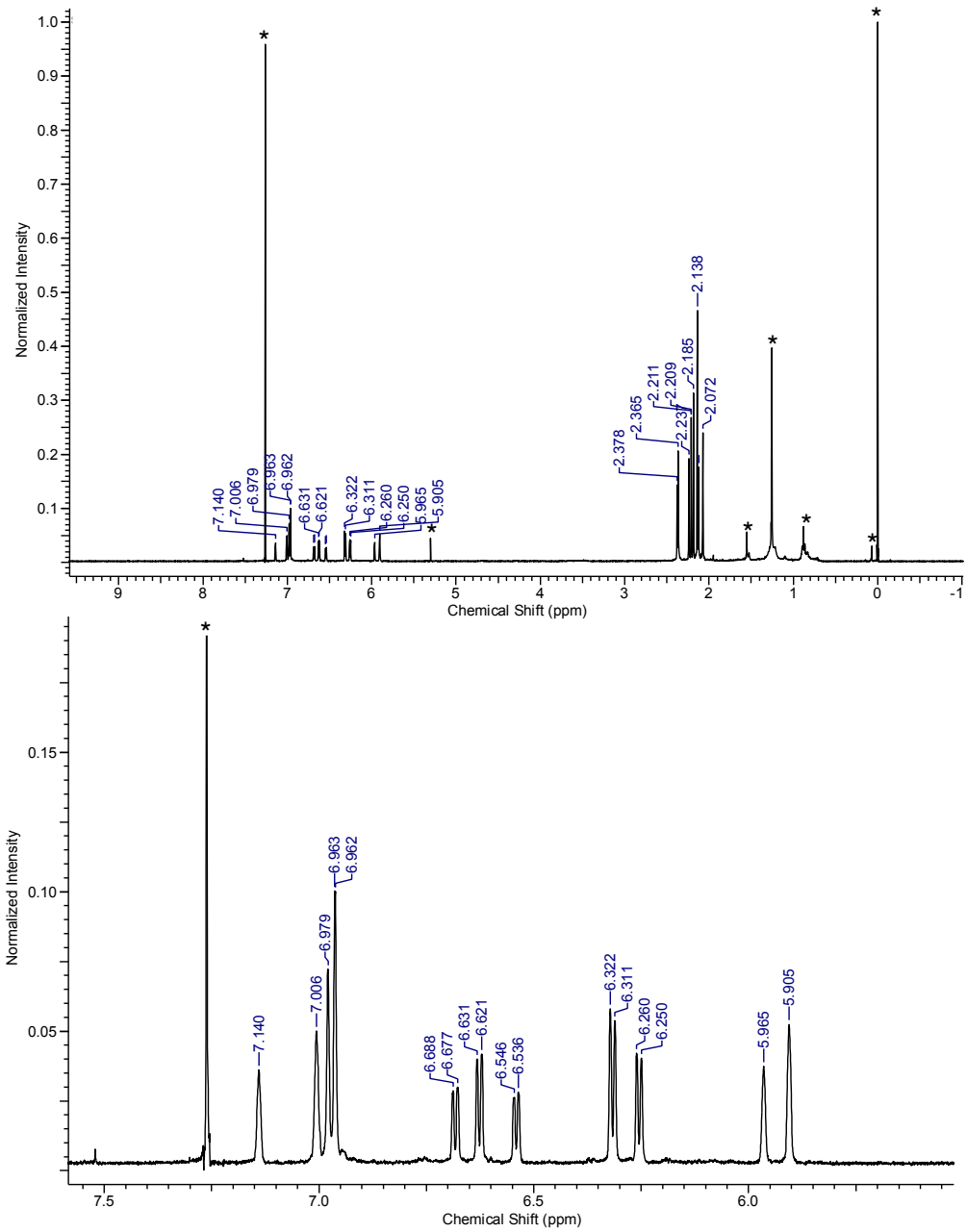


Figure S36. ^{1}H NMR spectra of a mixture of **S1** and **S2**.