Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for

Investigating the reactivity of a Lewis base supported terminal uranium imido metallocene

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1. Figures

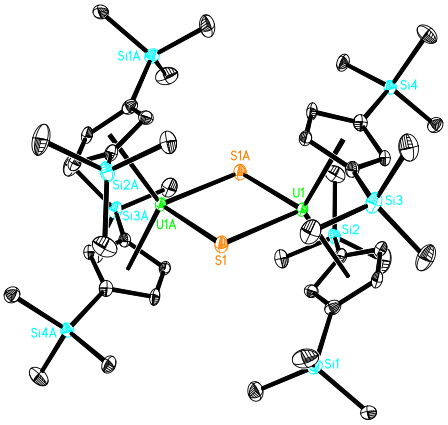

Figure S1. Molecular structure of **5** (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths (Å) and angles (º): U-C(Cp) (av.) 2.748(25), U-C(Cp) (range) 2.716(7) to 2.781(7), U-Cp (cent) 2.464(7) and 2.475(7), U-S(1) 2.592(2), U-S(1A) 2.600(2), Cp(cent)-U-Cp(cent) 123.8(2), S(1)-U-S(1A) 84.5(1).

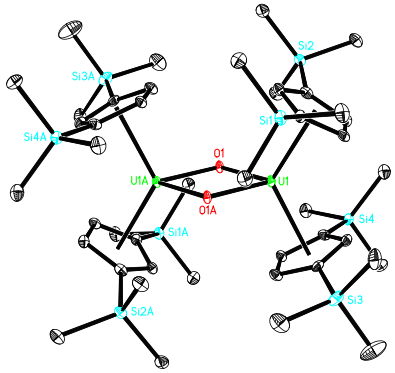

Figure S2. Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths (Å) and angles (º): U-C(Cp) (av.) 2.783(27), U-C(Cp) (range) 2.739(6) to 2.819(6), U-Cp (cent) 2.506(6) and 2.506(6), U-O(1) 2.115(3), U-O(1A) 2.124(4), Cp(cent)-U-Cp(cent) 123.4(2), O(1)-U-O(1A) 74.7(2).

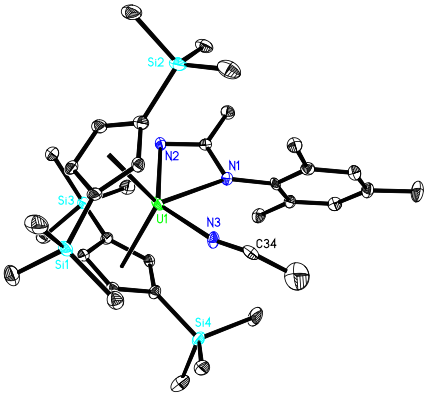

Figure S3. Molecular structure of **10** (thermal ellipsoids drawn at the 35% probability level).

2. Crystallographic details

Table S1. Crystal Data and Experimental Parameters for Compounds 2-6

Compound	**2**	**3**	**4**·C_6H_6	**5**	**6**
Formula	$C_{38}H_{63}N_3Si_4U$	$C_{47}H_{65}NSi_4U$	$C_{48}H_{68}N_2S_2Si_4U$	$C_{44}H_{84}S_2Si_8U_2$	$C_{44}H_{84}O_2Si_8U_2$
Fw	912.30	994.39	1087.55	1378.01	1345.89
crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$I2/a$	$P\bar{1}$	$P2_1/n$
a (Å)	10.135(1)	11.673(1)	21.876(1)	10.537(1)	11.985(1)
b (Å)	21.161(1)	39.848(1)	12.702(1)	11.547(1)	15.810(1)
c (Å)	20.430(1)	11.490(1)	38.216(1)	12.874(1)	15.473(1)
α (deg)	90	90	90	74.13(1)	90
β (deg)	100.05(1)	115.37(1)	105.03(1)	84.45(1)	100.52(1)
γ (deg)	90	90	90	76.59(1)	90
V (Å^3)	4314.25(7)	4829.2(4)	10256.0(4)	1464.62(7)	2882.44(9)
Z	4	4	8	1	2
D_{calc} (g/cm^3)	1.405	1.368	1.409	1.562	1.551
μ(Mo/Kα)$_{calc}$ (cm^{-1})	11.854	10.629	10.805	17.869	17.511
size (mm)	0.15 × 0.10 × 0.10	0.15 × 0.15 × 0.15	0.20 × 0.20 × 0.20	0.10 × 0.10 × 0.10	0.15 × 0.10 × 0.10
F(000)	1840	2008	4400	676	1320
2θ range (deg)	6.06 to 151.65	8.38 to 152.88	7.36 to 153.03	7.14 to 152.94	8.07 to 152.68
no. of reflns, collected	31986	34122	32730	17410	19746
no of obsd reflns	8628	9679	10246	5879	5758
no of variables	432	493	528	265	266
abscorr (T_{max}, T_{min})	1.00, 0.69	1.00, 0.63	1.00, 0.69	1.00, 0.51	1.00, 0.53
R	0.026	0.043	0.038	0.041	0.044
R_w	0.060	0.101	0.101	0.108	0.120
R_{all}	0.030	0.057	0.041	0.043	0.046
Gof	1.04	1.10	1.04	1.09	1.06
CCDC	2307461	2307462	2307467	2307458	2307459

Table S2. Crystal Data and Experimental Parameters for Compounds 7-9,11

Compound	**7**	**8**	**9**	**11**
Formula	$C_{50}H_{66}N_2O_2Si_4U$	$C_{43}H_{61}B_2NO_4Si_4U$	$C_{47}H_{67}N_3Si_4U$	$C_{44}H_{61}N_8Si_2U$
Fw	1077.43	1027.93	1024.42	996.21
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	$P2/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.121(1)	22.148(1)	19.529(1)	10.826(1)
b (Å)	10.631(1)	19.950(1)	19.612(1)	11.954(1)
c (Å)	19.805(1)	32.623(1)	27.013(2)	19.175(1)
α (deg)	90	90	76.69(1)	86.16(1)
β (deg)	97.79(1)	96.17(1)	88.48(1)	76.77(1)
γ (deg)	90	90	81.98(1)	87.17(1)
V (Å^3)	2528.47(3)	14331.5(3)	9969.32(17)	2408.66(7)
Z	2	12	8	2
D_{calc} (g/cm^3)	1.415	1.429	1.365	1.374
μ(Mo/Kα)$_{calc}$ (cm^{-1})	10.233	10.823	10.325	10.240
size (mm)	0.15 × 0.10 × 0.10	0.20 × 0.20 × 0.20	0.15 × 0.15 × 0.15	0.20 × 0. 20 × 0. 20
F(000)	1088	6192	4144	1002
2θ range (deg)	8.09 to 153.11	6.41 to 153.16	6.42 to 153.02	7.42 to 152.99
no. of reflns, collected	17995	107081	135102	33834
no of obsd reflns	5086	28921	40160	9634
no of variables	274	1531	2041	508
abscorr (T_{max}, T_{min})	1.00, 0.70	1.00, 0.14	1.00, 0.39	1.00, 0.78
R	0.031	0.061	0.057	0.037
R_w	0.078	0.169	0.135	0.094
R_{all}	0.033	0.099	0.076	0.040
Gof	1.05	1.05	1.06	1.07
CCDC	2307460	2307463	2307469	2307464

Table S3. Crystal Data and Experimental Parameters for Compounds 12-14,16

Compound	**12**	**13**	**14**	**16**
Formula	$C_{31}H_{53}INSi_4U$	$C_{37}H_{58}NSSi_4U$	$C_{37}H_{58}NSeSi_4U$	$C_{40}H_{64}N_2Si_4U$
Fw	917.03	899.29	946.19	923.32
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.743(1)	10.068(1)	10.068(1)	11.804(1)
b (Å)	11.412(1)	10.825(1)	10.840(1)	12.224(1)
c (Å)	16.434(1)	21.699(1)	21.791(1)	15.701(1)
α (deg)	77.71(1)	75.82(1)	79.67(1)	72.92(1)
β (deg)	72.61(1)	86.69(1)	78.95(1)	88.34(1)
γ (deg)	82.39(1)	64.54(1)	64.65(1)	84.16(1)
V (Å^3)	1873.45(12)	2067.35(9)	2096.62(15)	2154.34(5)
Z	2	2	2	2
D_{calc} (g/cm^3)	1.626	1.445	1.499	1.423
μ(Mo/Kα)$_{calc}$ (cm^{-1})	5.303	12.807	4.878	11.870
size (mm)	0.20 × 0.20 × 0.20	0.20 × 0.15 × 0.15	0.20 × 0. 20 × 0. 20	0.15 × 0.15 × 0.15
F(000)	894	902	938	932
2θ range (deg)	6.96 to 59.59	8.42 to 152.64	6.60 to 59.54	7.53 to 152.79
no. of reflns, collected	17108	26074	19698	28531
no of obsd reflns	8836	8249	9880	8670
no of variables	358	412	412	442
abscorr (T_{max}, T_{min})	1.00, 0.73	1.00, 0.62	1.00, 0.83	1.00, 0.67
R	0.047	0.043	0.046	0.042
R_w	0.088	0.117	0.080	0.111
R_{all}	0.059	0.045	0.059	0.044
Gof	0.94	1.07	0.92	1.07
CCDC	2307468	2307470	2307466	2307465

3. NMR spectra

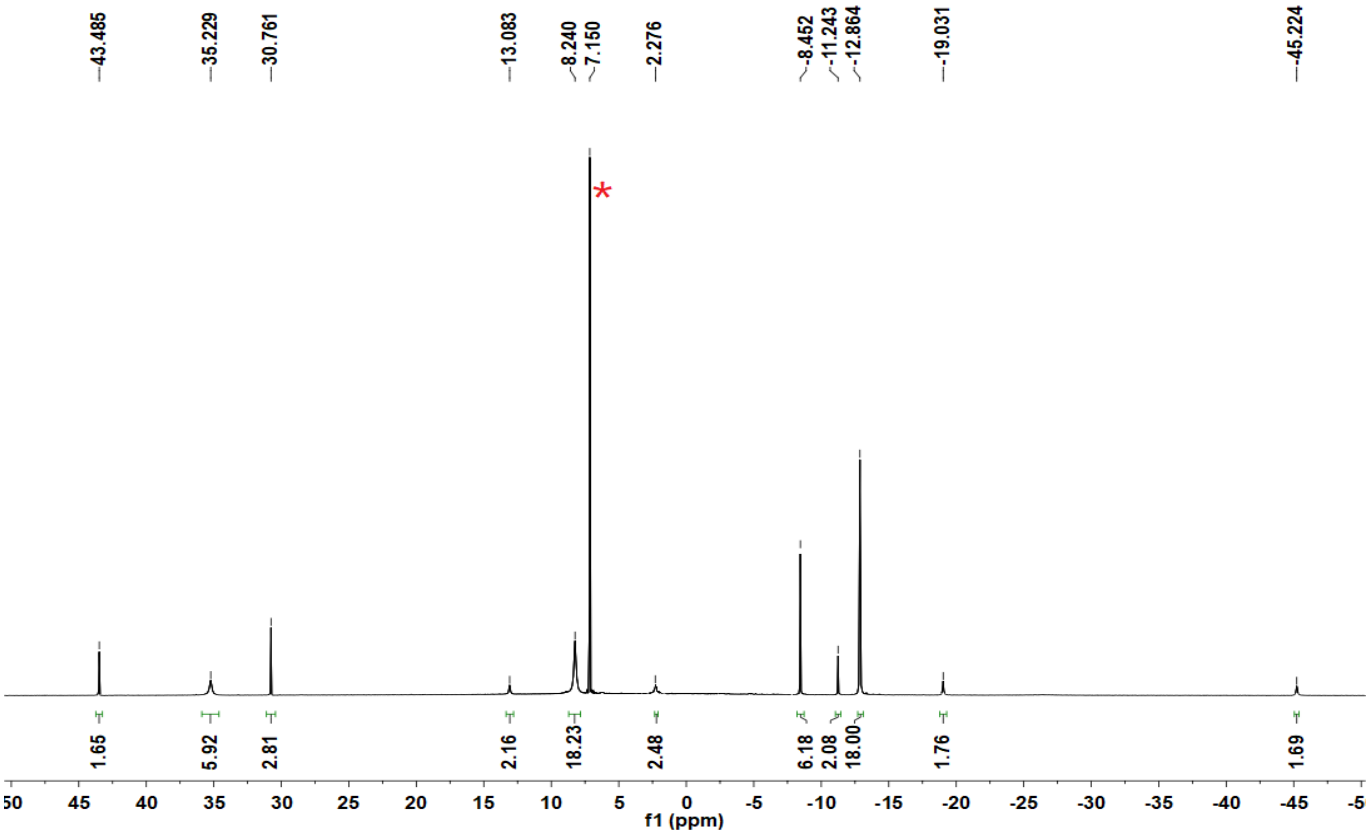

Figure S4. ^{1}H NMR spectrum for compound **2** (* solvent).

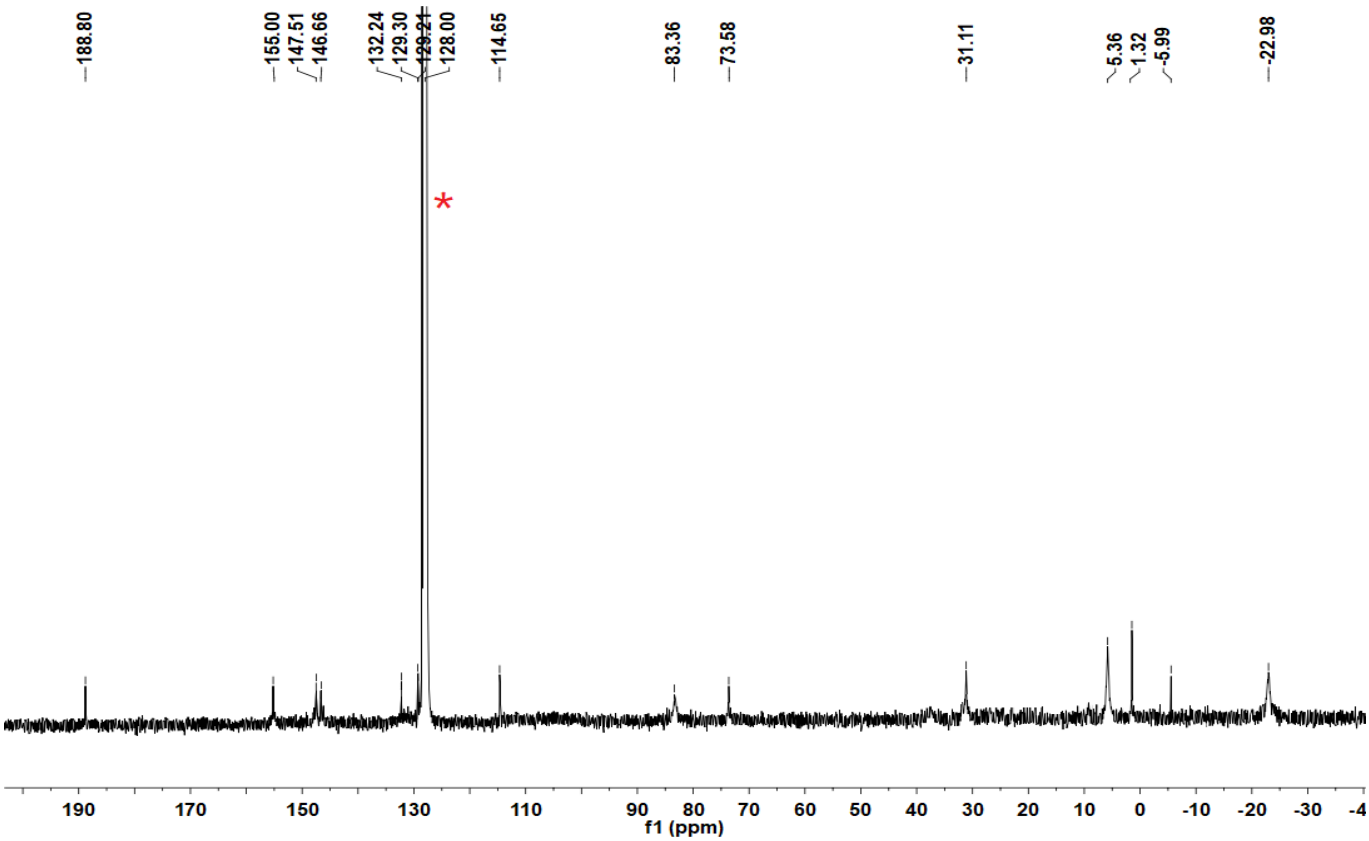

Figure S5. ^{13}C{^{1}H} NMR spectrum for compound **2** (* solvent).

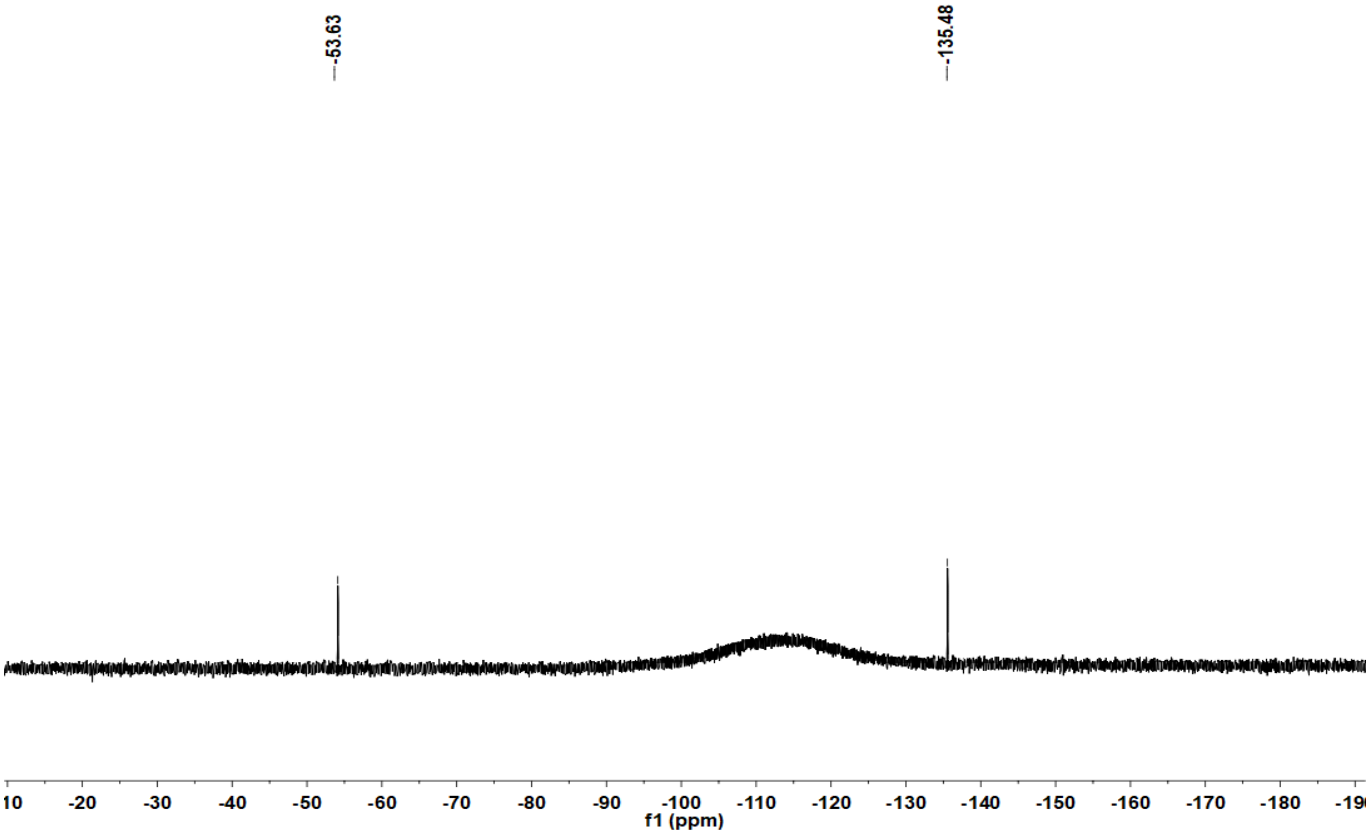

Figure S6. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **2** (* solvent).

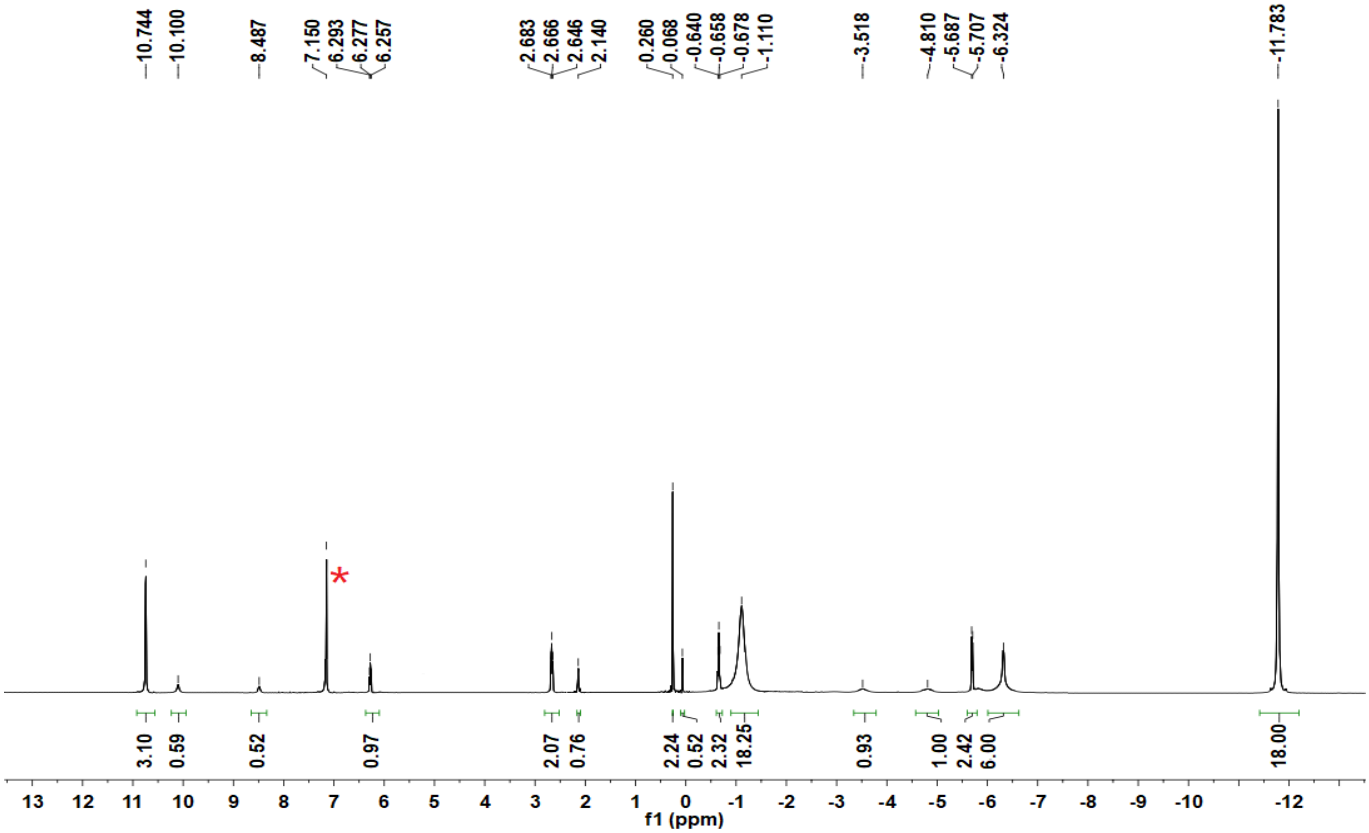

Figure S7. ^{1}H NMR spectrum for compound **3** (* solvent).

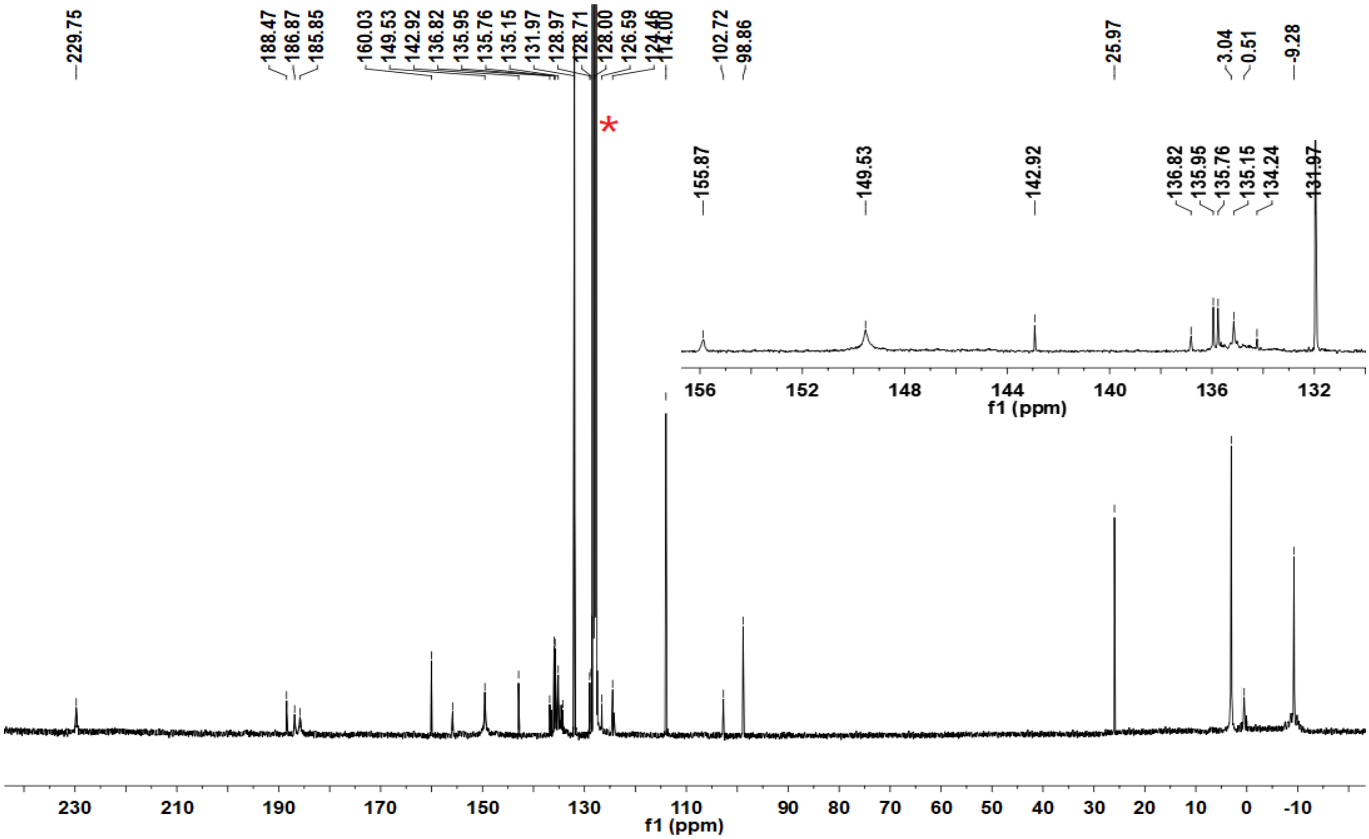

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum for compound **3** (* solvent).

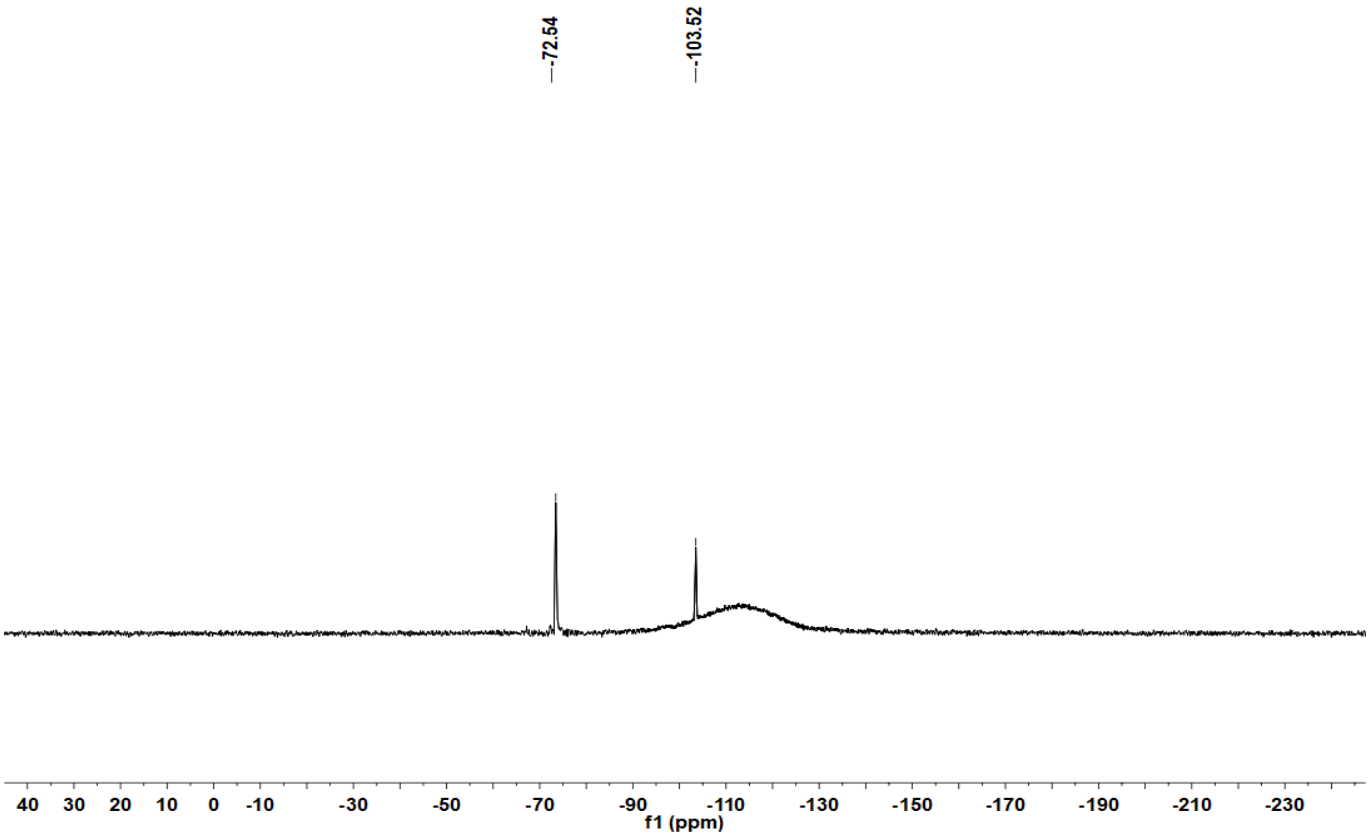

Figure S9. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **3** (* solvent).

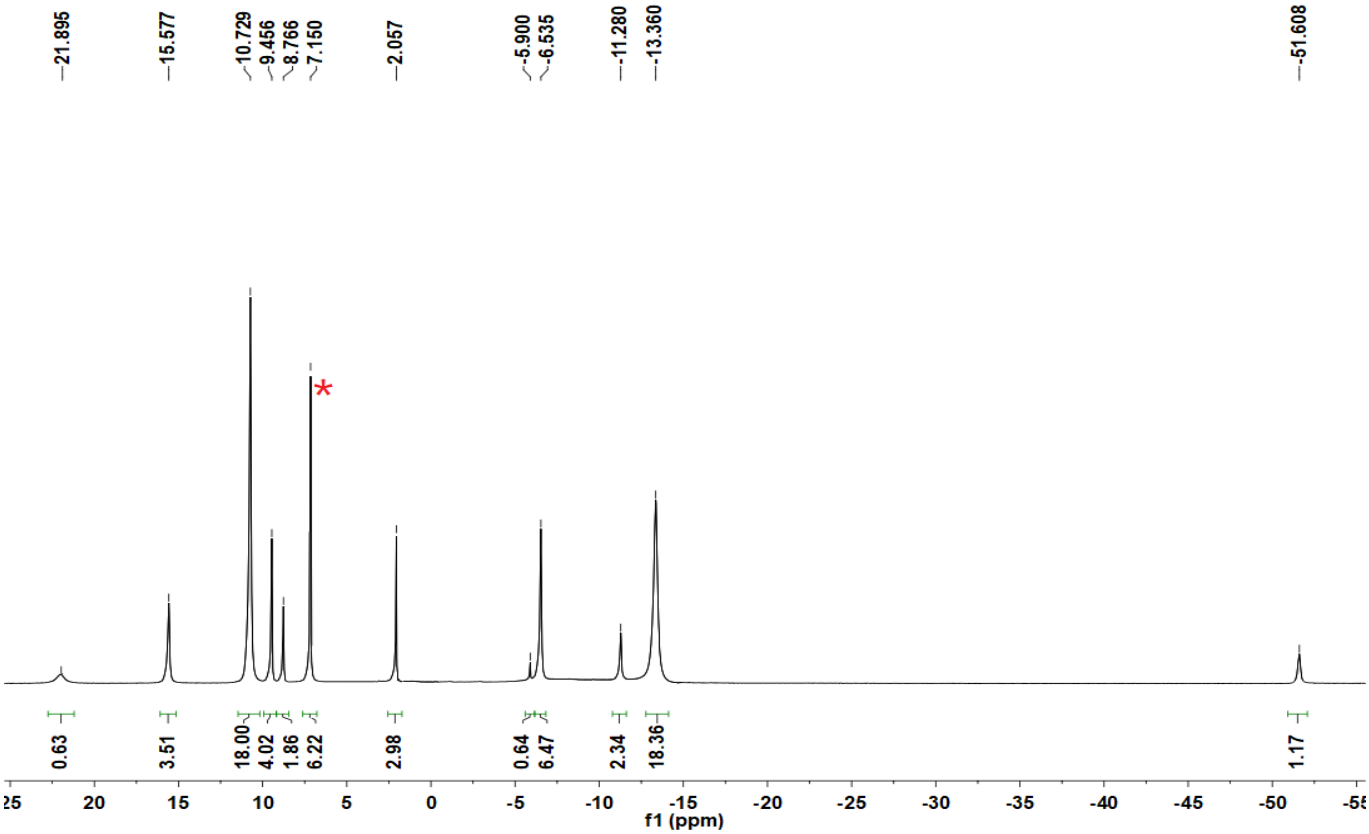

Figure S10. ^{1}H NMR spectrum for compound **4** (* solvent).

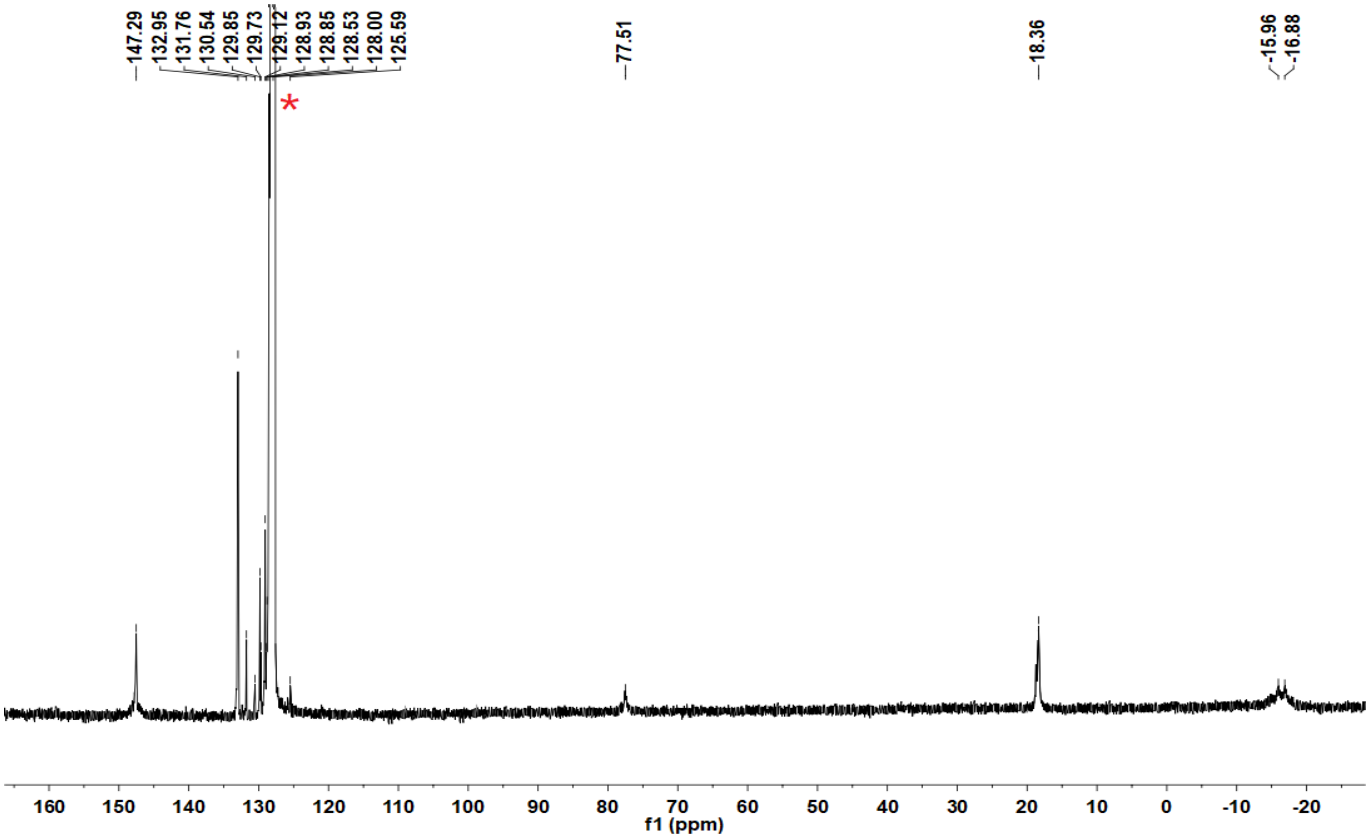

Figure S11. ^{13}C{^{1}H} NMR spectrum for compound **4** (* solvent).

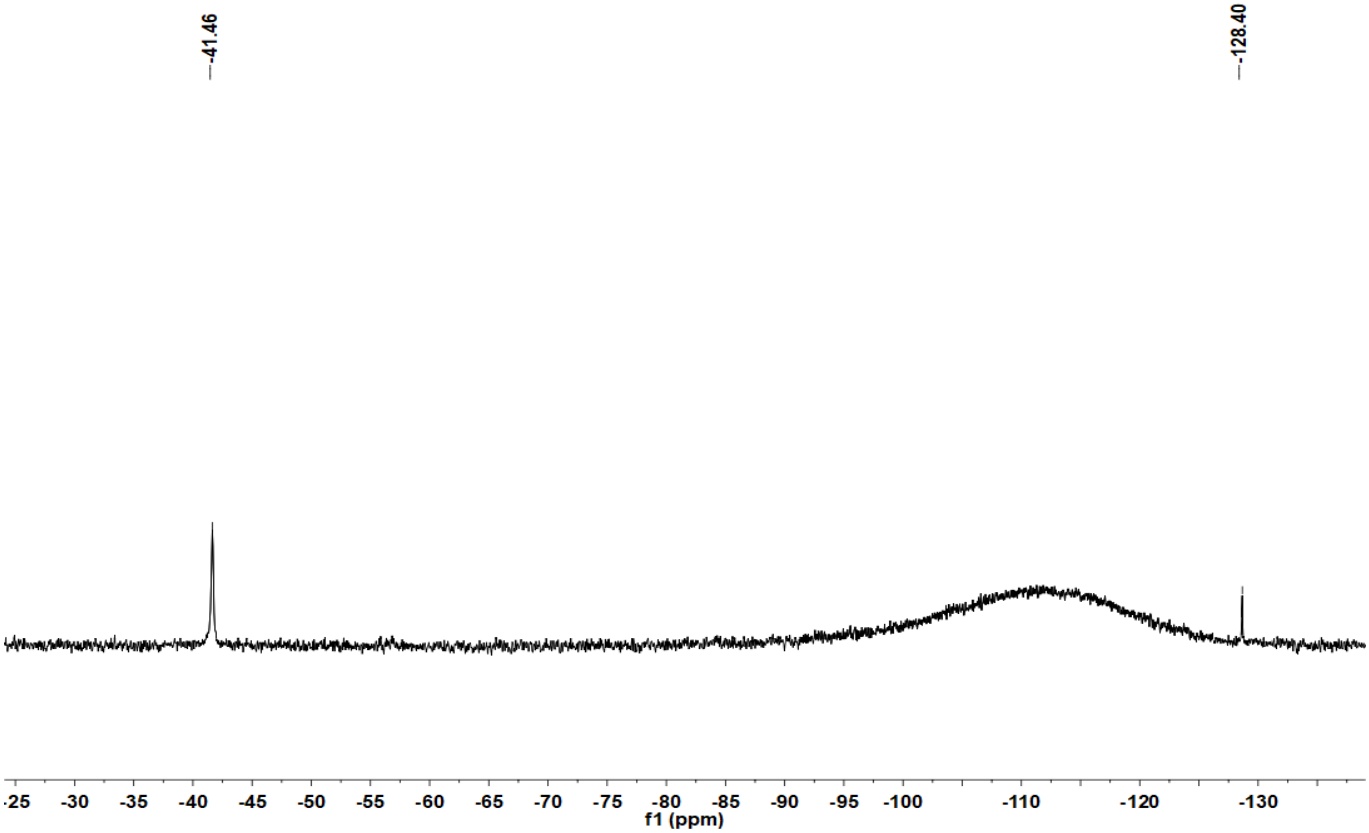

Figure S12. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **4** (* solvent).

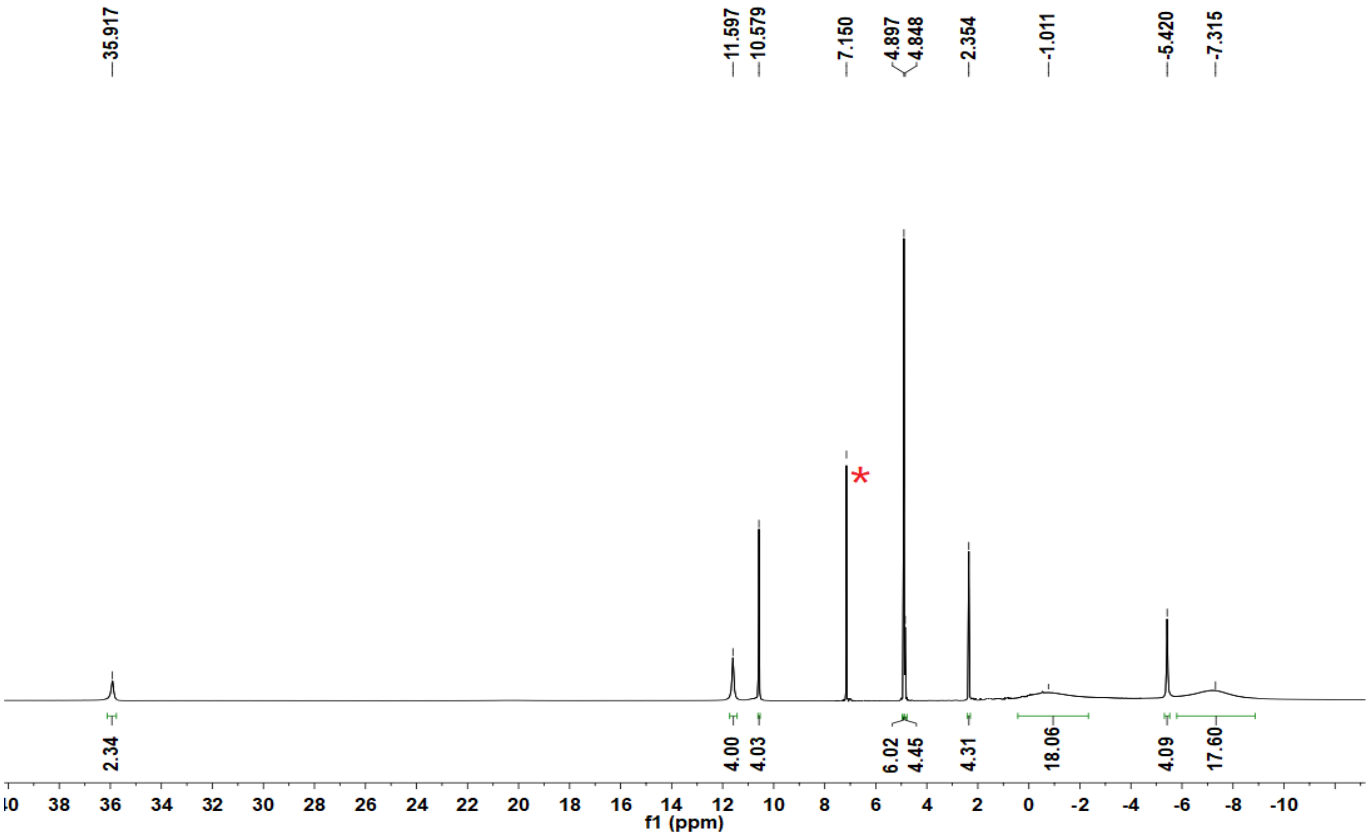

Figure S13. ^{1}H NMR spectrum for compound **7** (* solvent).

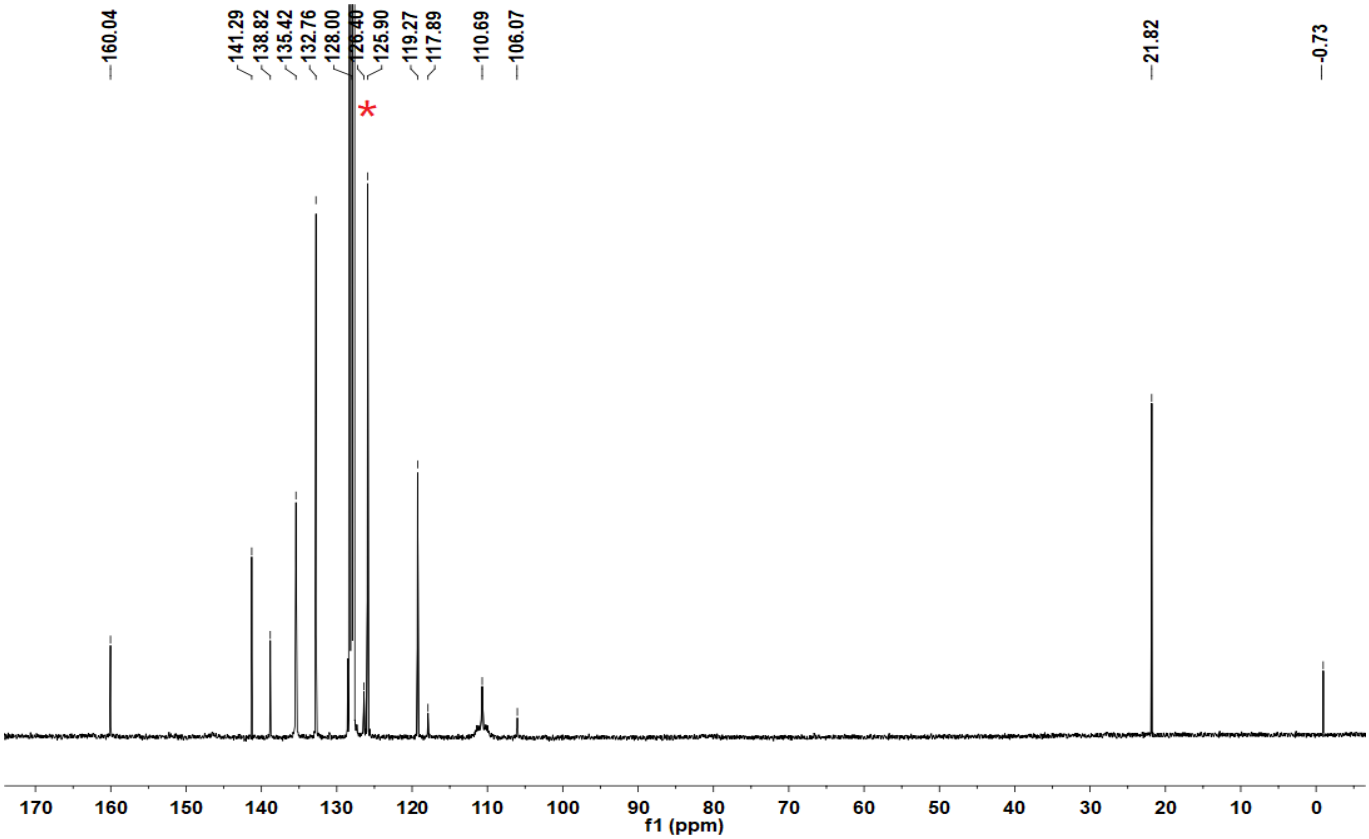

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum for compound **7** (* solvent).

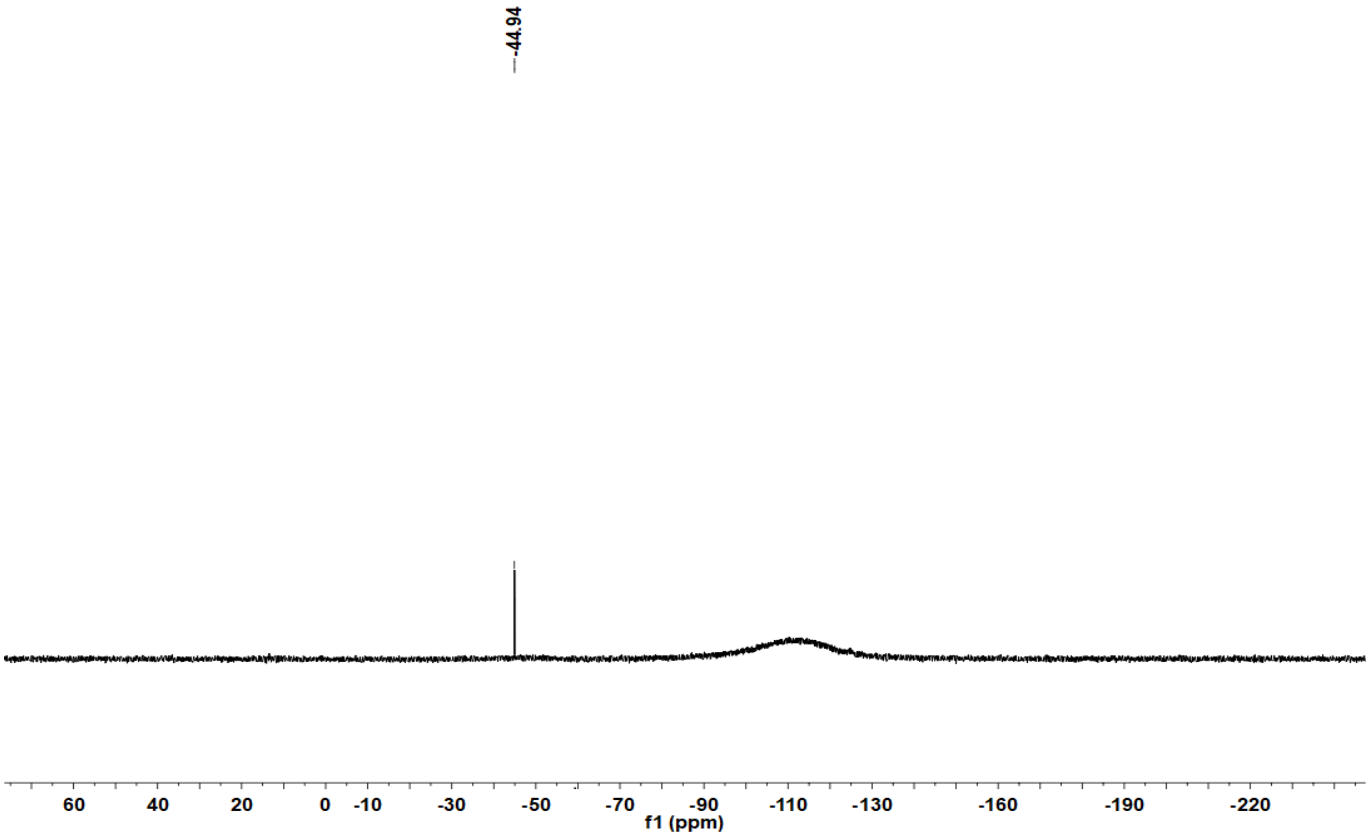

Figure S15. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **7** (* solvent).

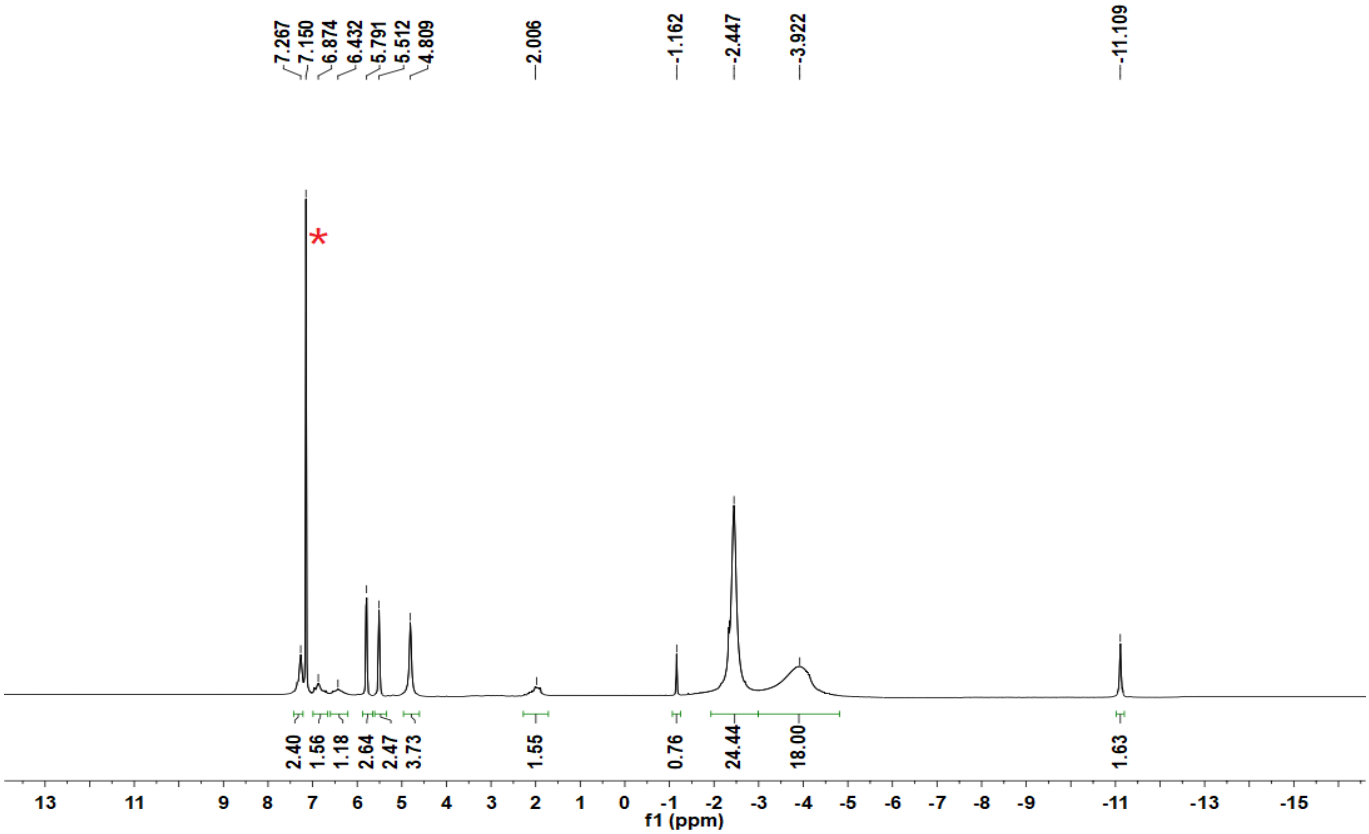

Figure S16. ^{1}H NMR spectrum for compound **8** (* solvent).

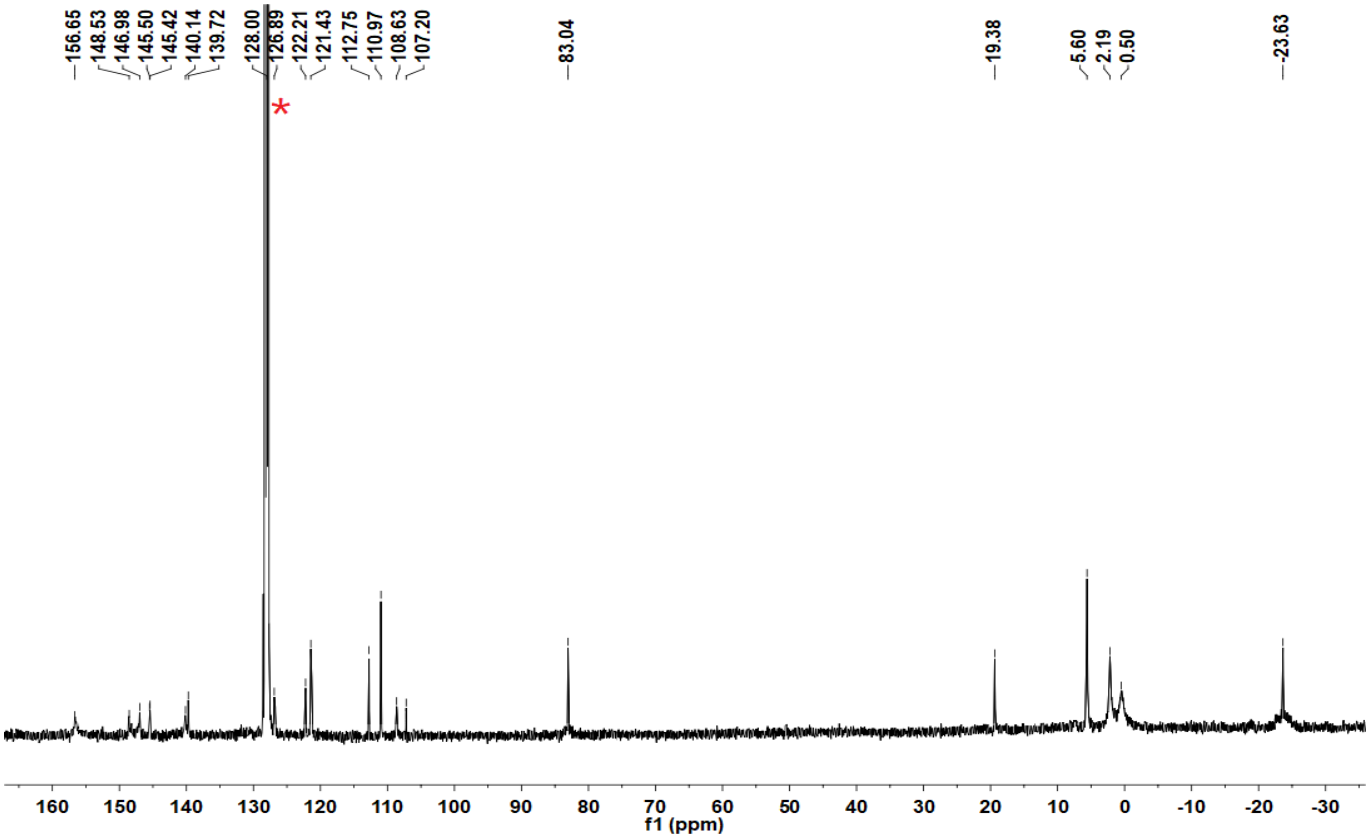

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum for compound **8** (* solvent).

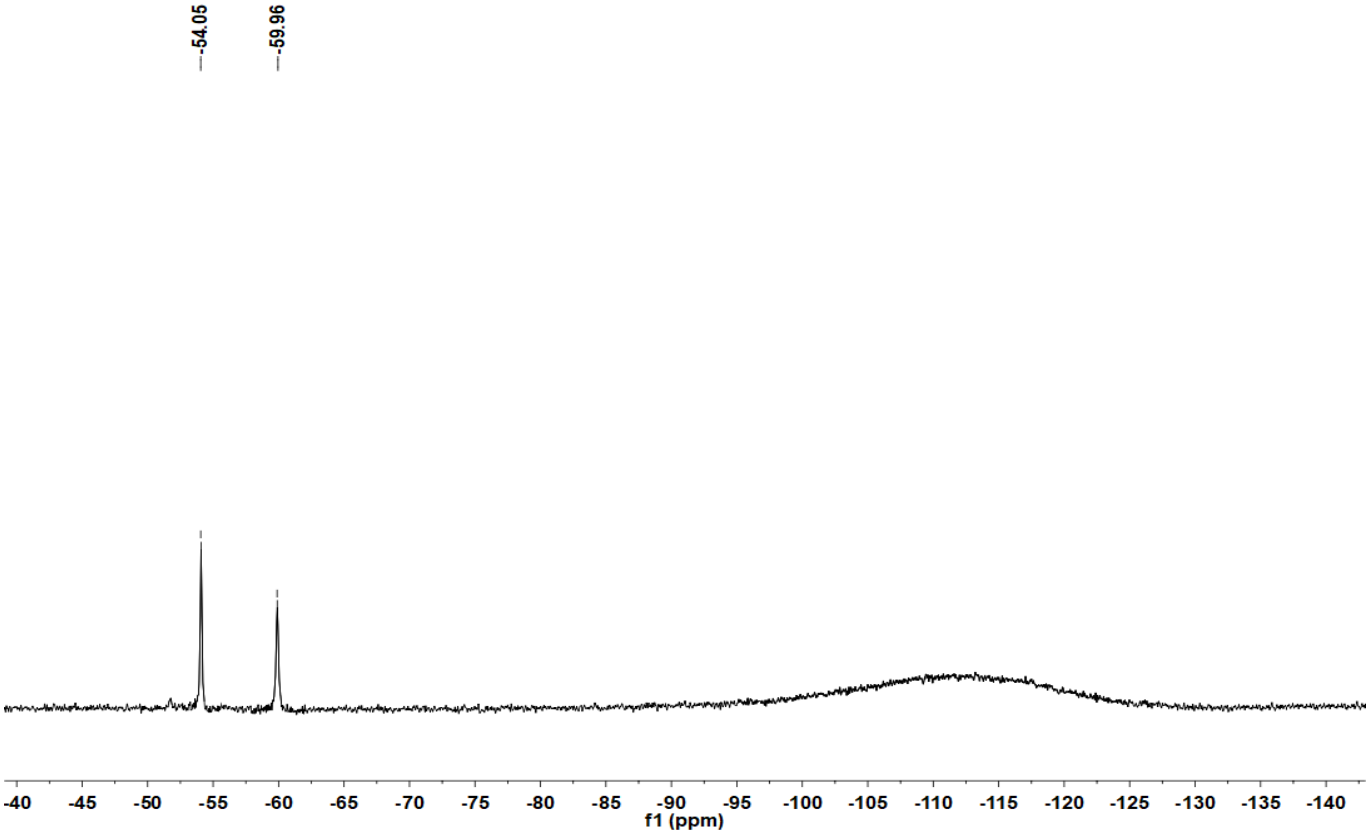

Figure S18. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **8** (* solvent).

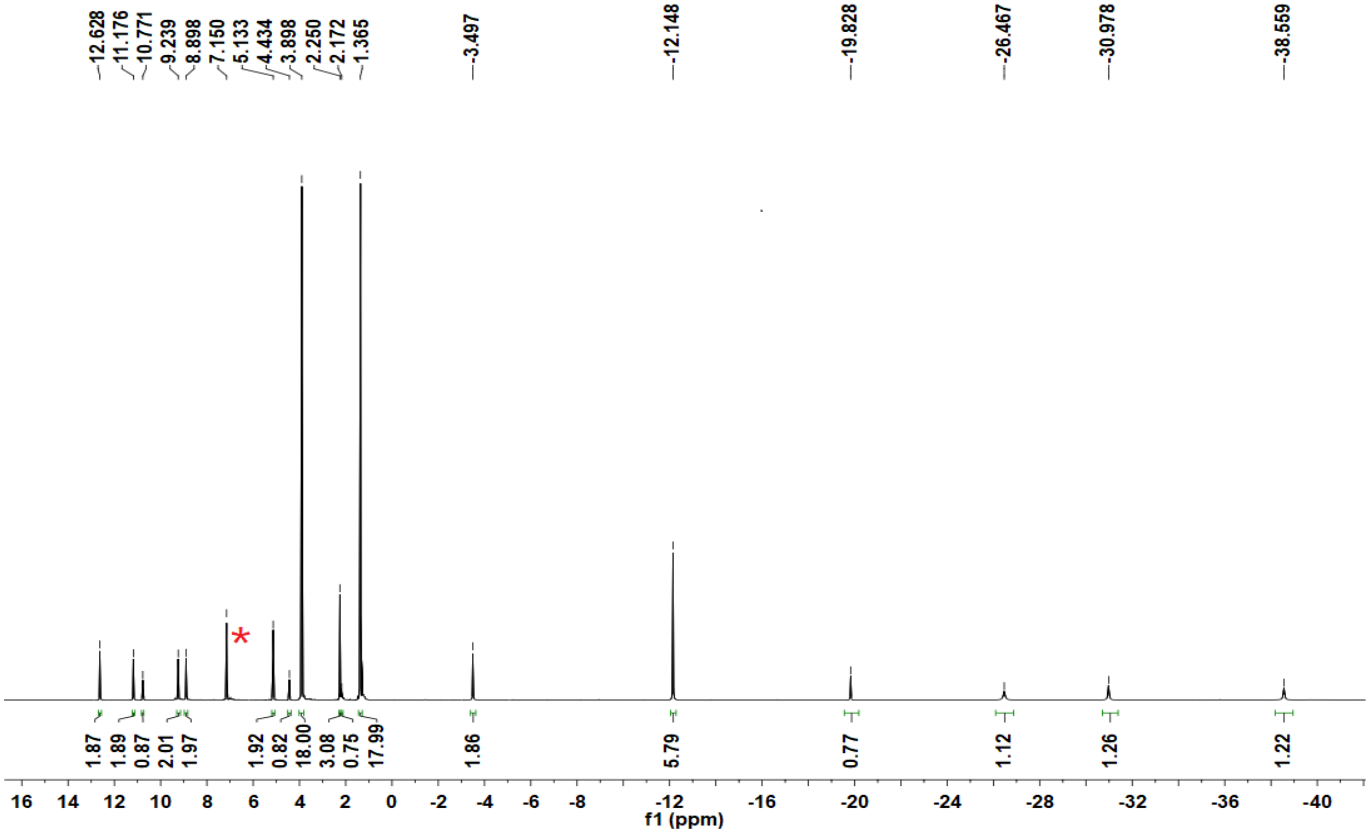

Figure S19. ^{1}H NMR spectrum for compound **9** (* solvent).

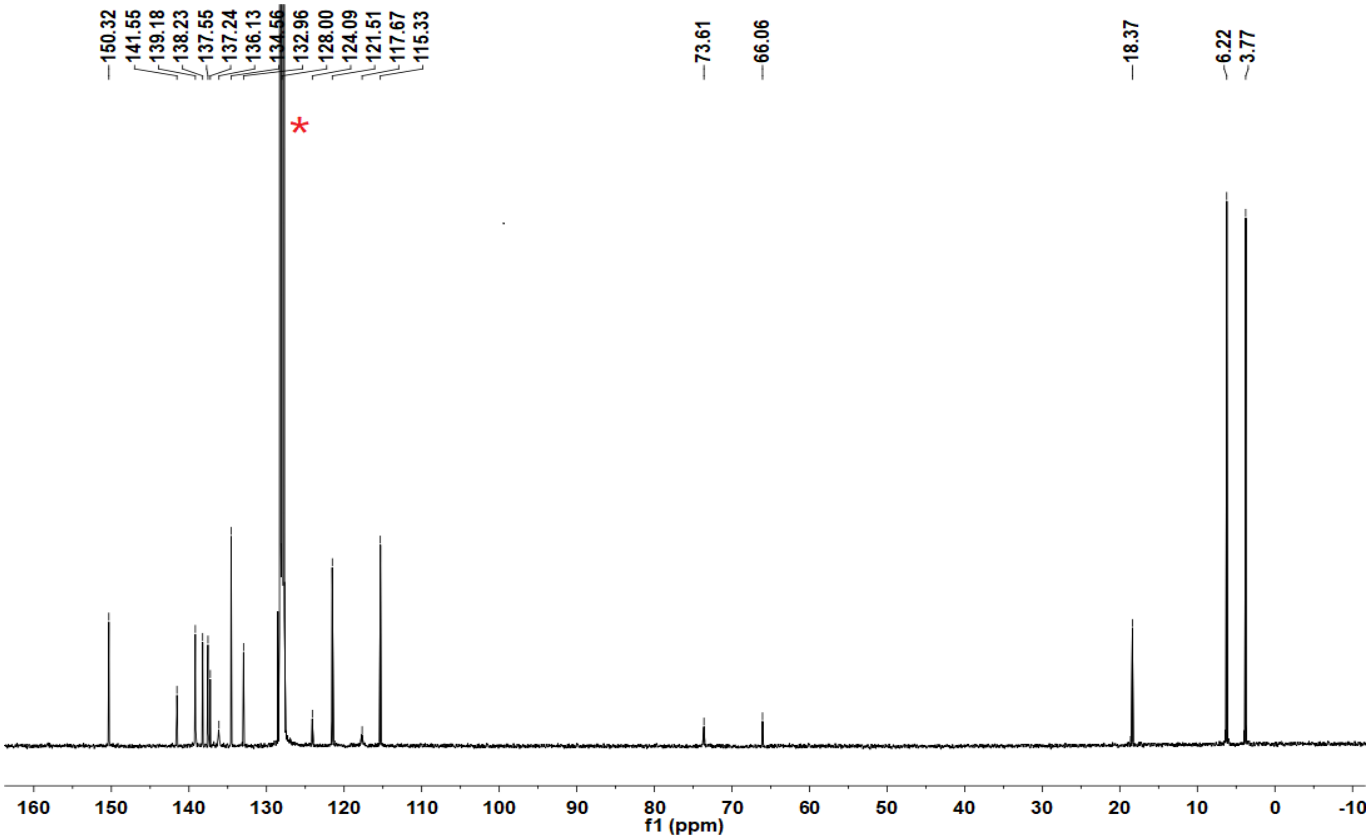

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum for compound **9** (* solvent).

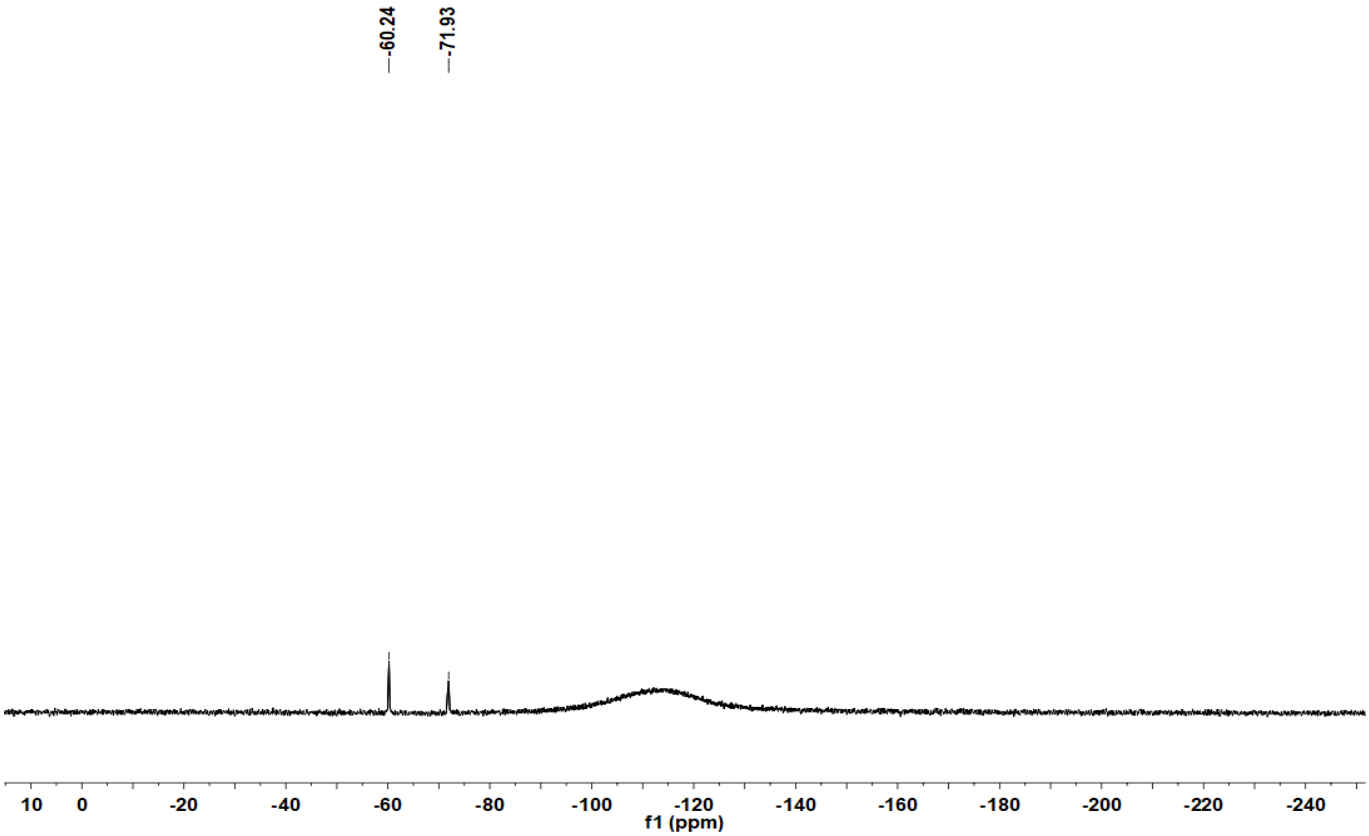

Figure S21. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **9** (* solvent).

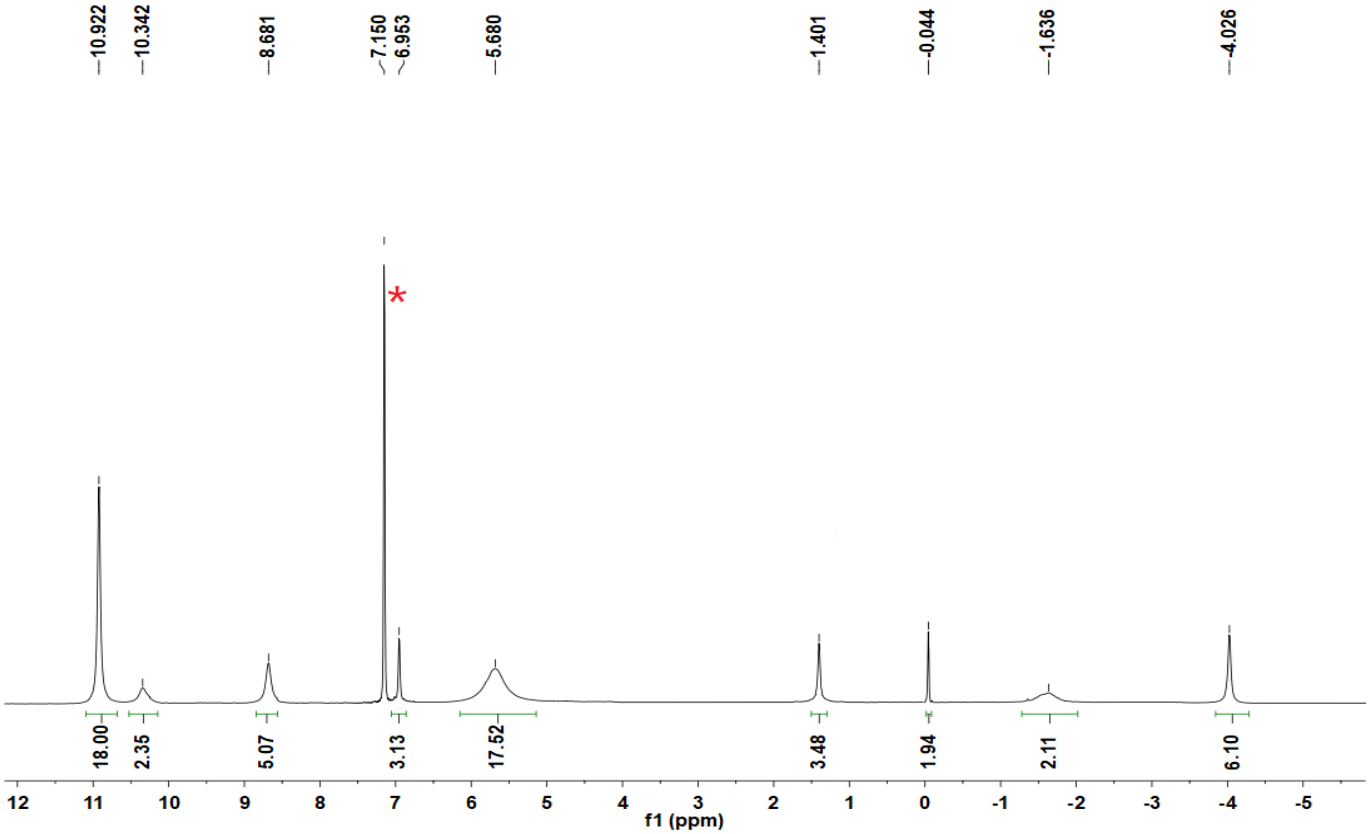

Figure S22. ^{1}H NMR spectrum for compound **10** (* solvent).

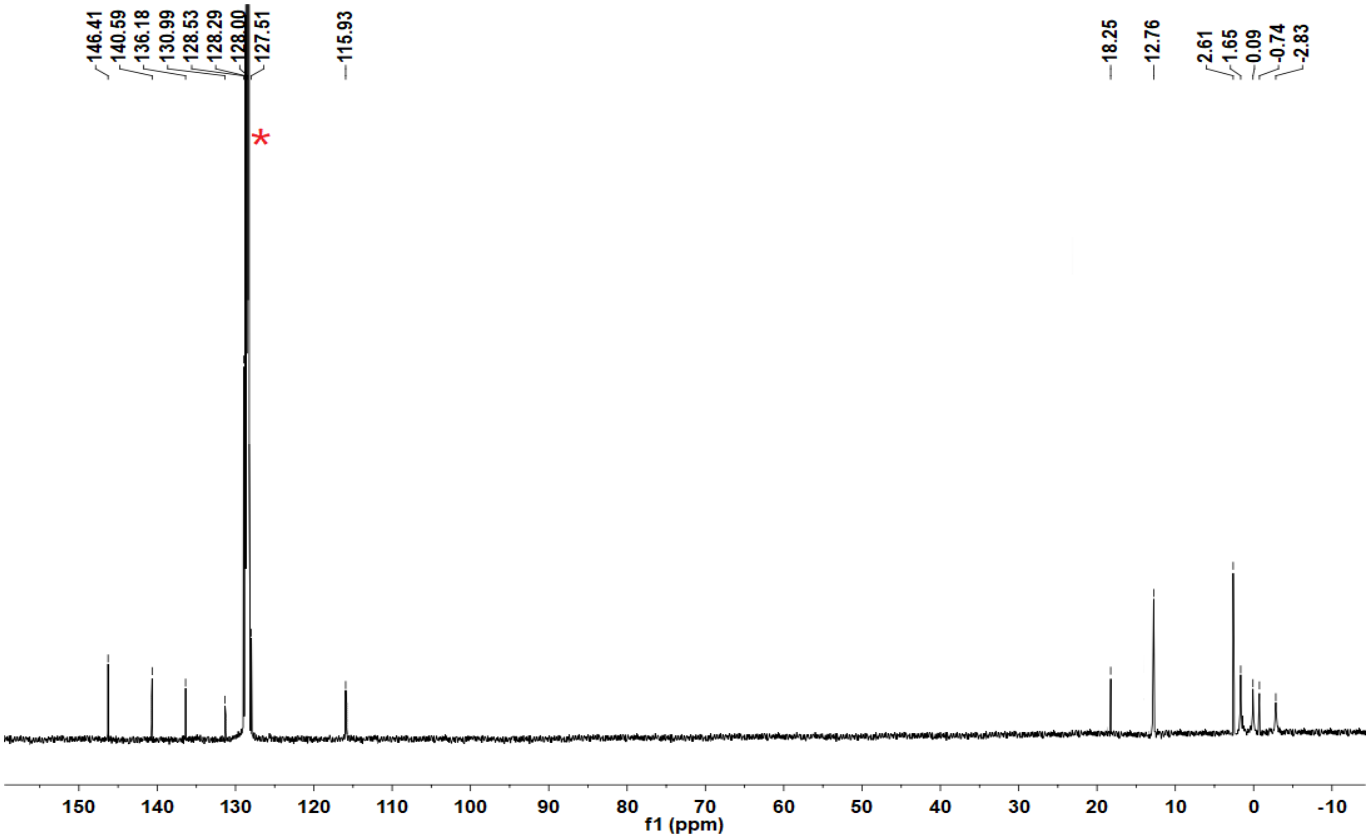

Figure S23. ^{13}C{^{1}H} NMR spectrum for compound **10** (* solvent).

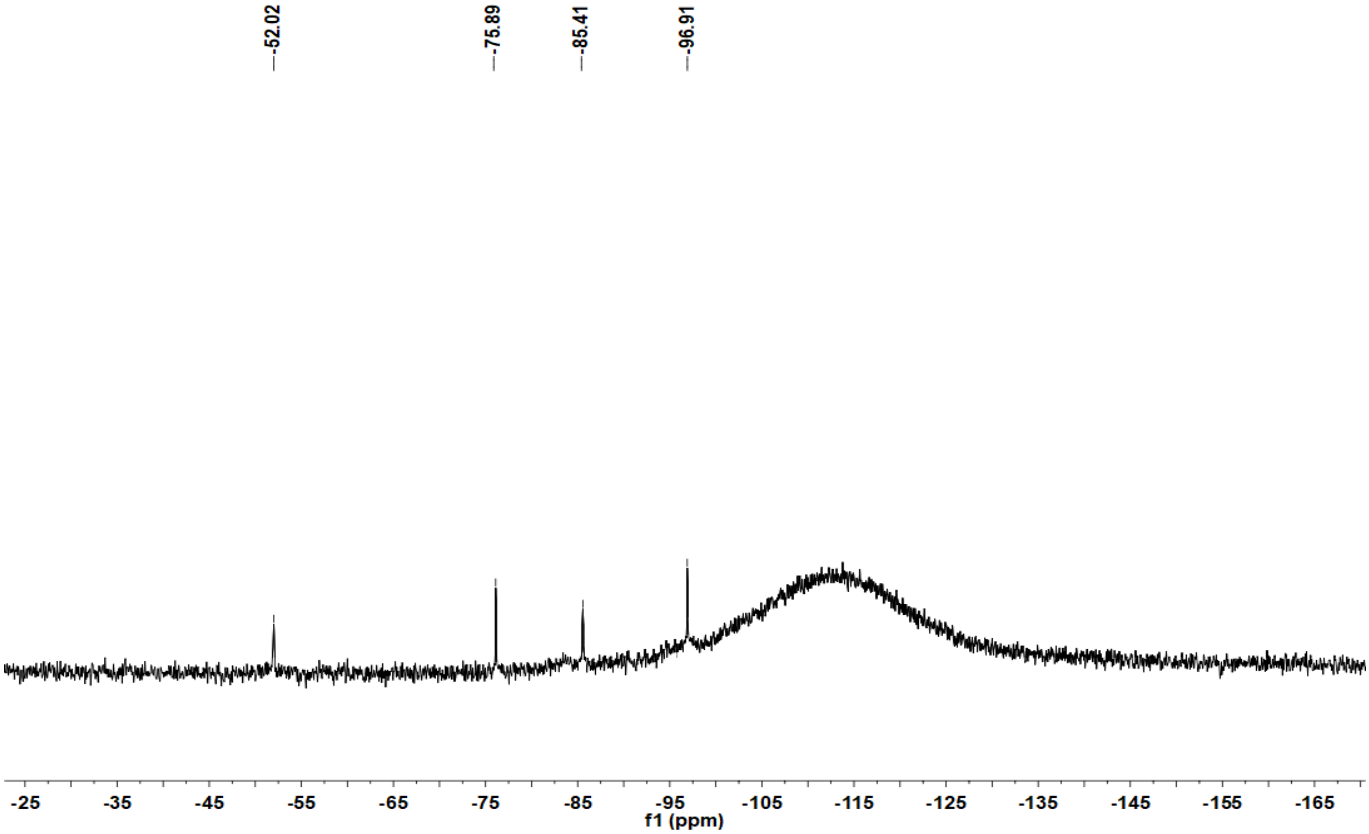

Figure S24. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **10** (* solvent).

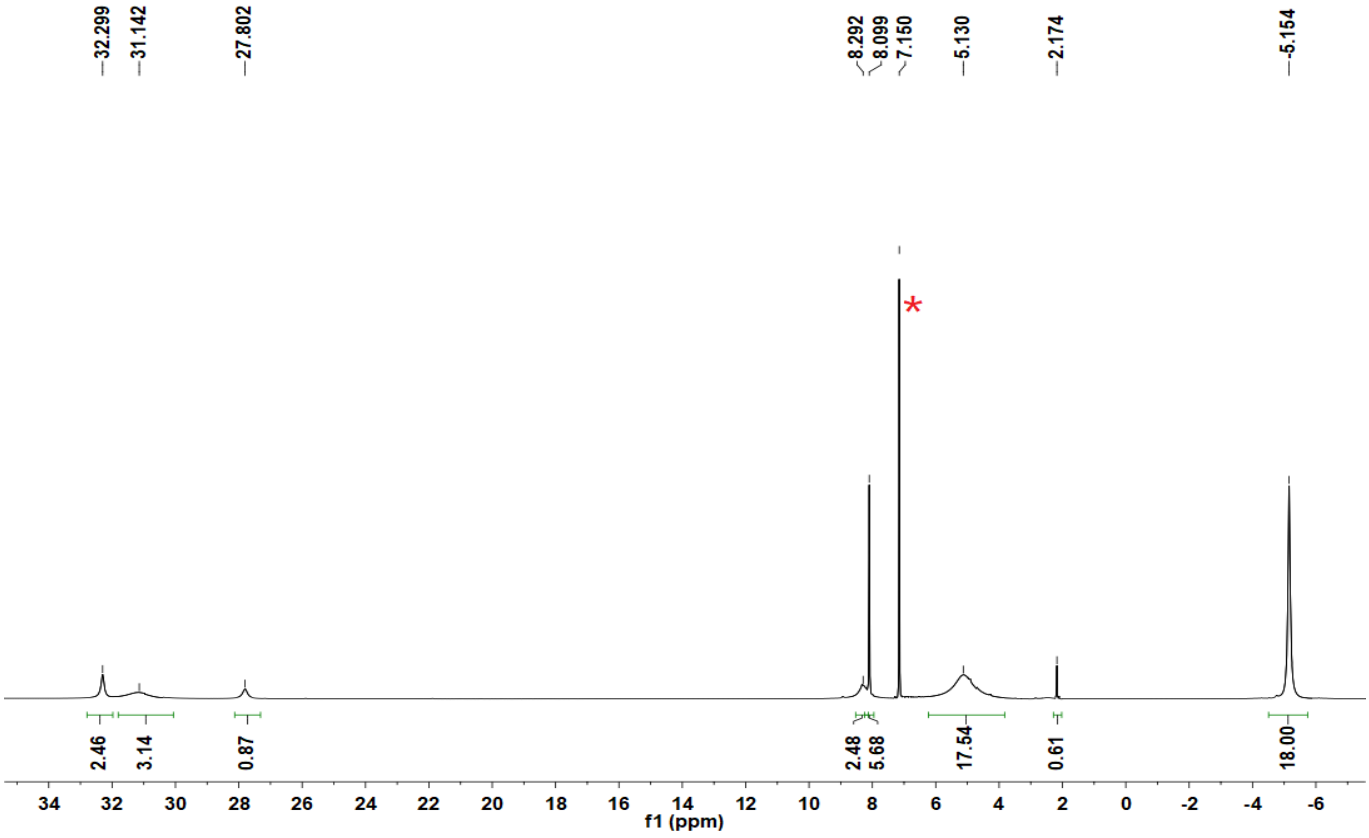

Figure S25. ^{1}H NMR spectrum for compound **12** (* solvent).

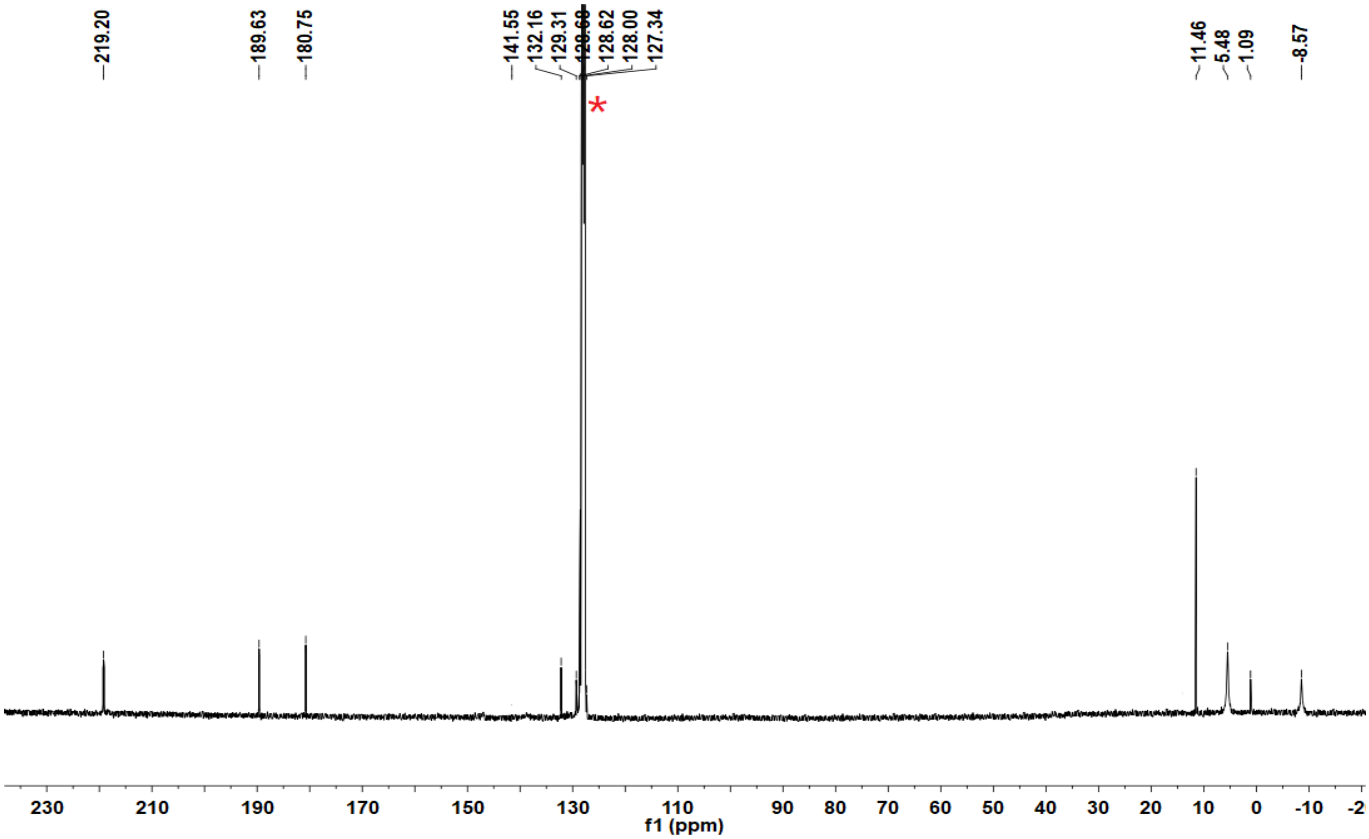

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum for compound **12** (* solvent).

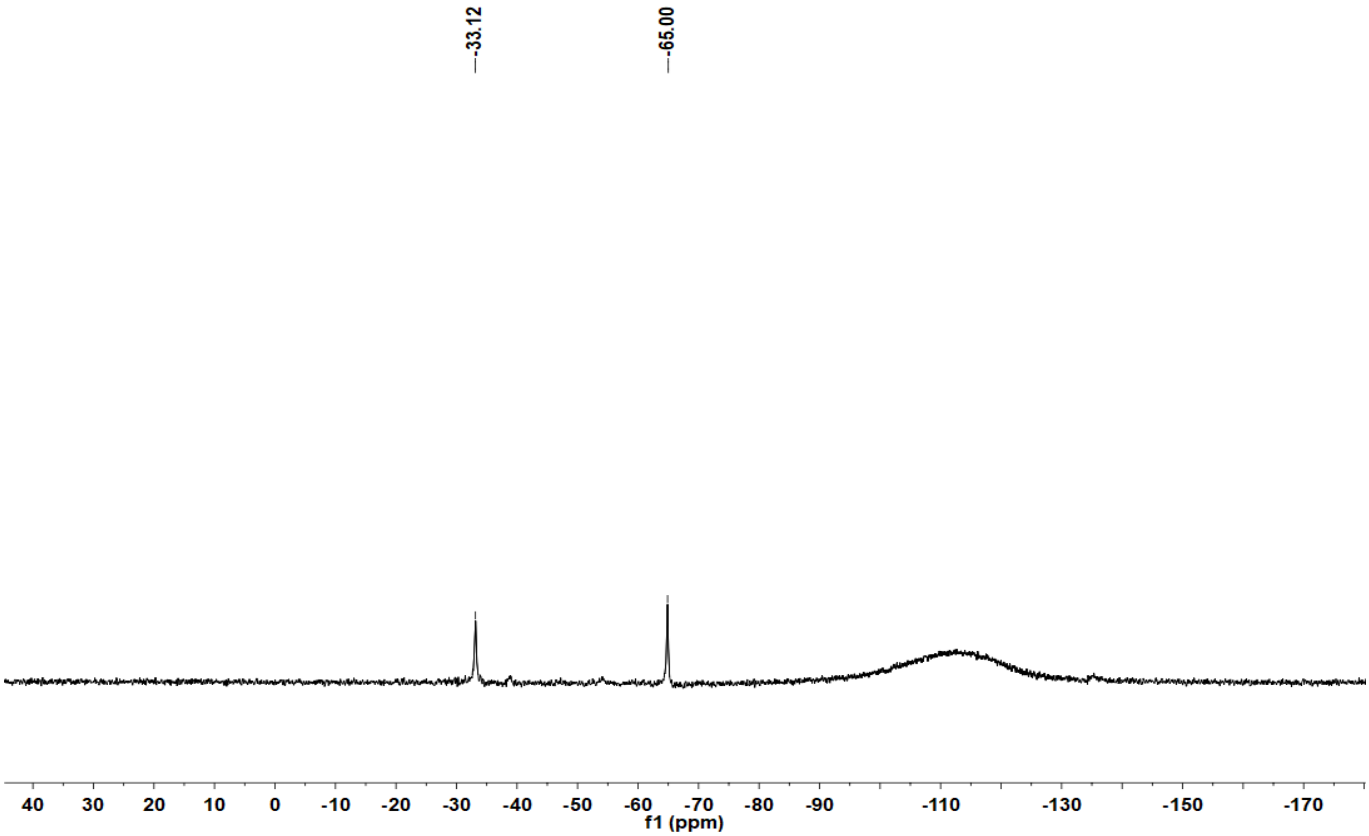

Figure S27. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **12** (* solvent).

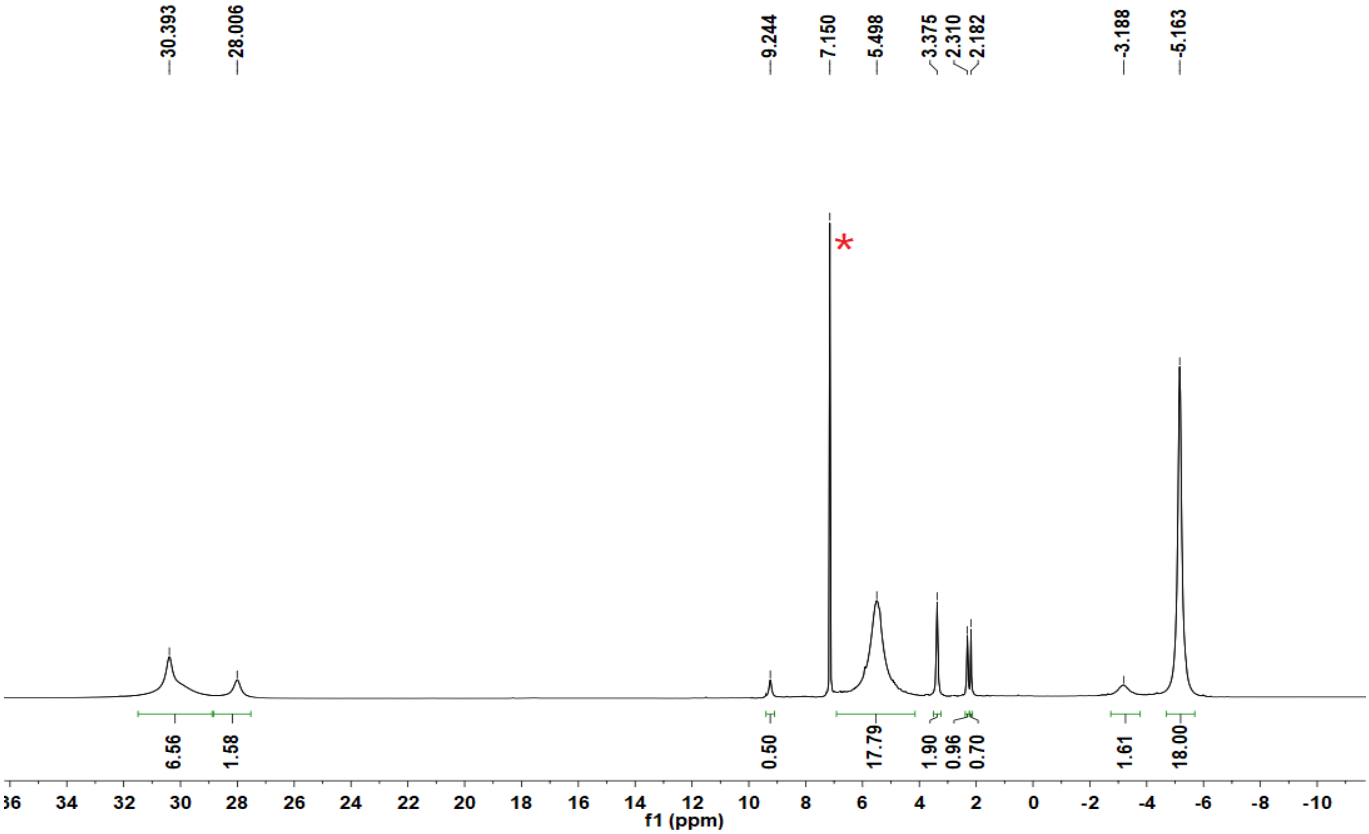

Figure S28. ^{1}H NMR spectrum for compound **13** (* solvent).

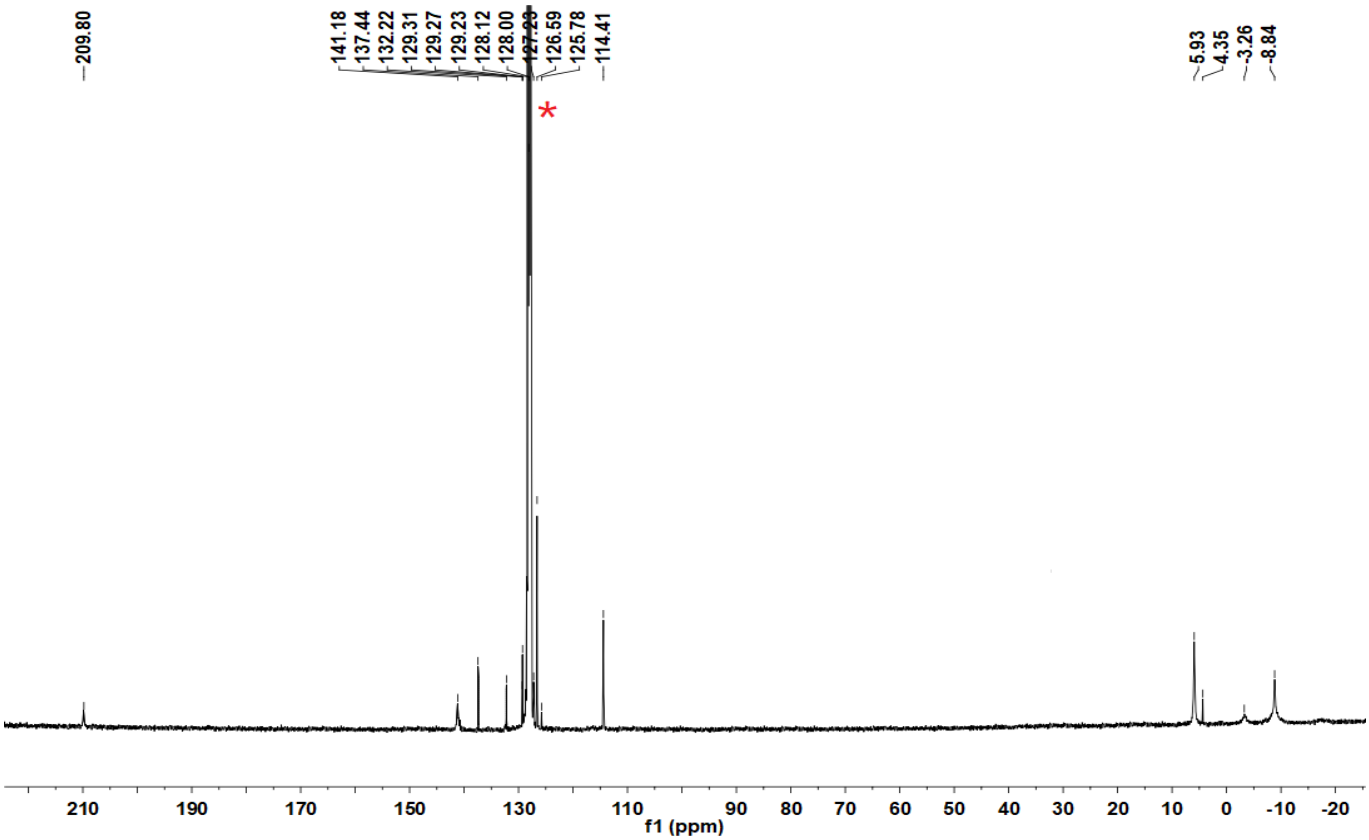

Figure S29. ^{13}C{^{1}H} NMR spectrum for compound **13** (* solvent).

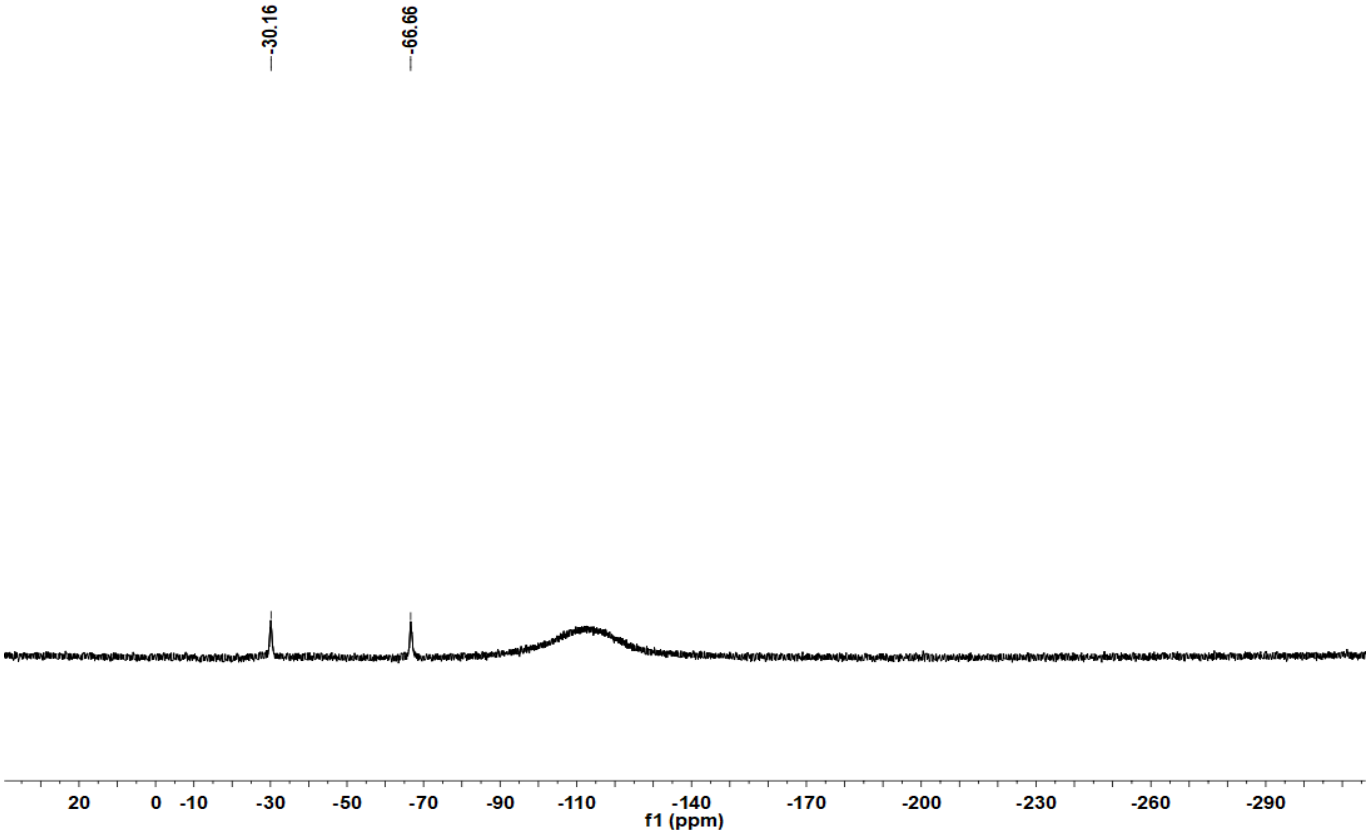

Figure S30. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **13** (* solvent).

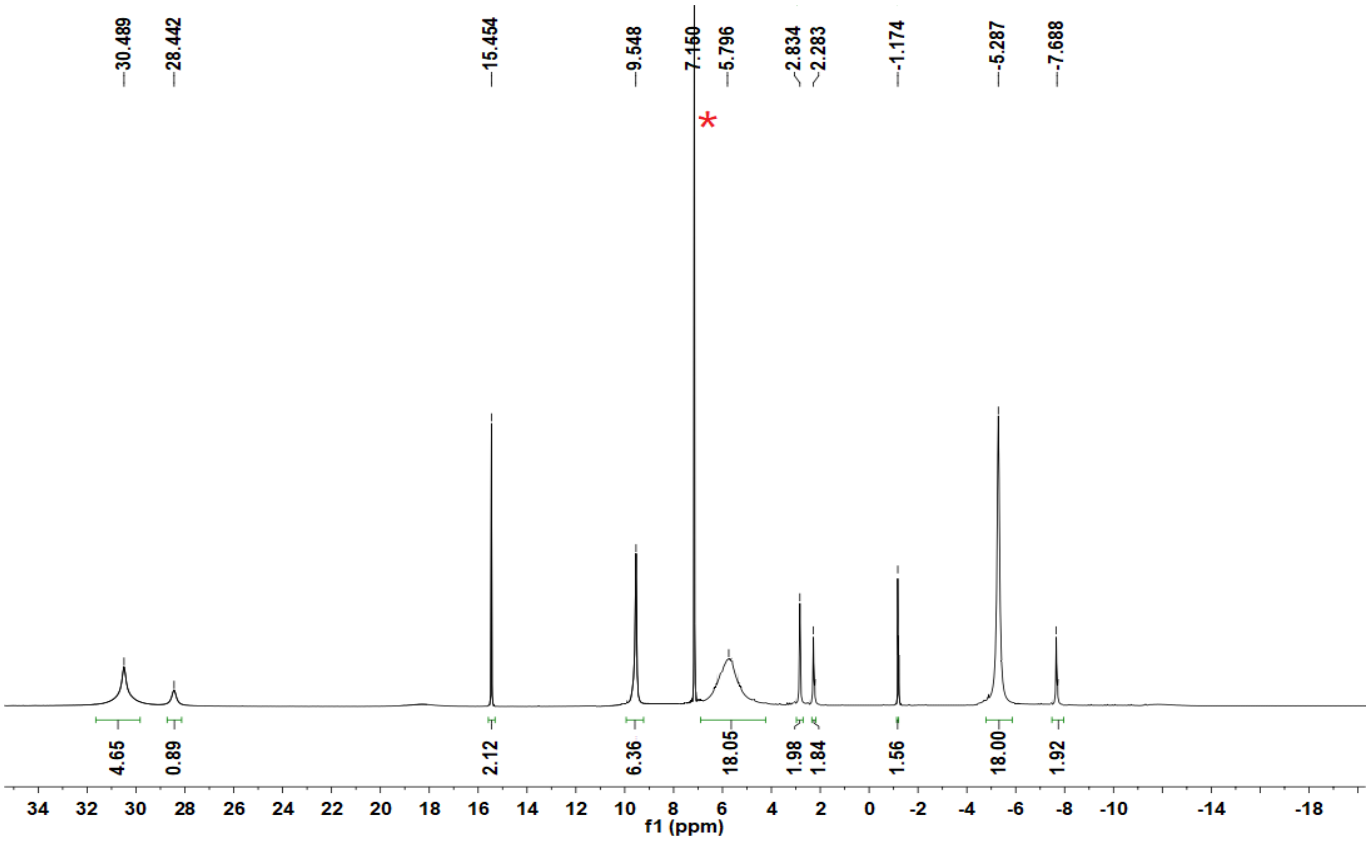

Figure S31. ^{1}H NMR spectrum for compound **14** (* solvent).

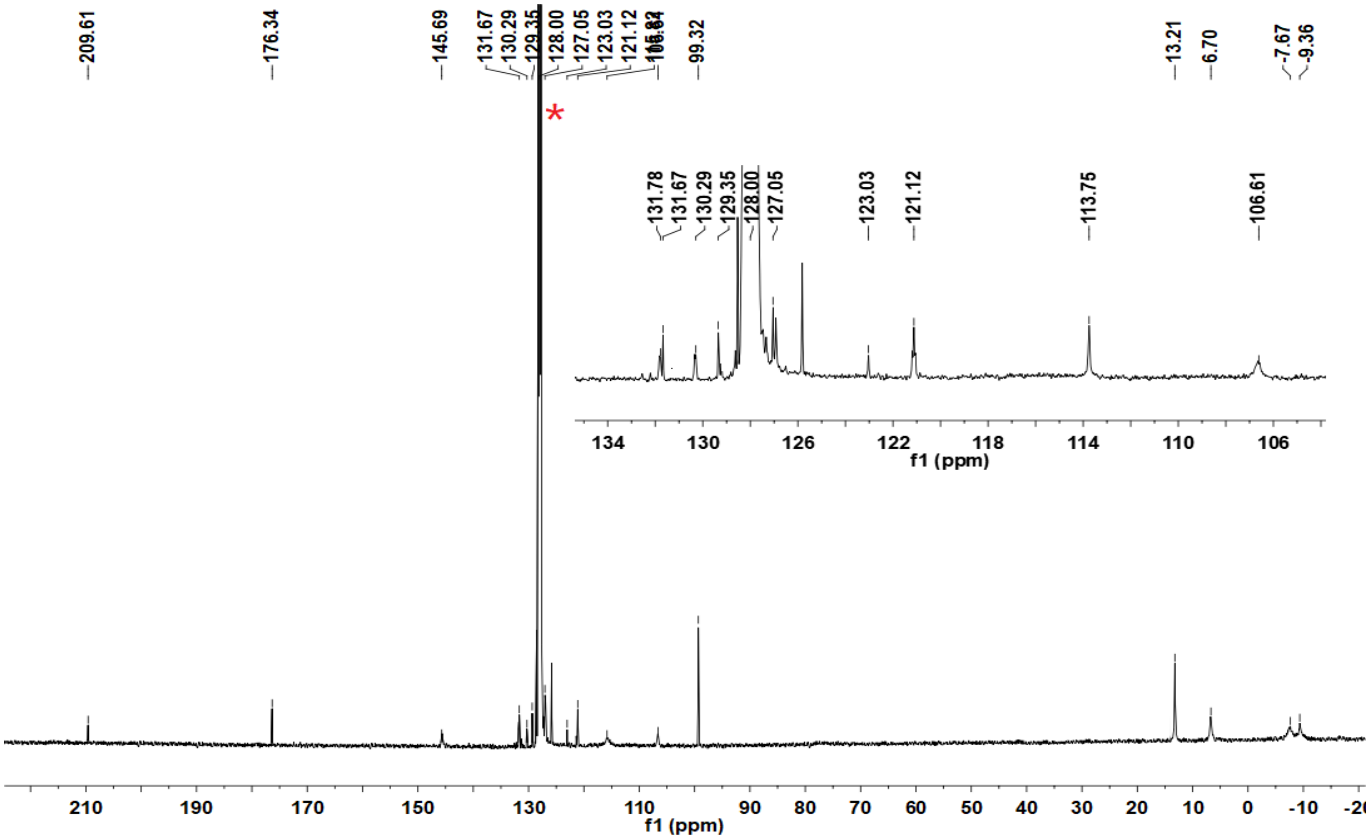

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum for compound **14** (* solvent).

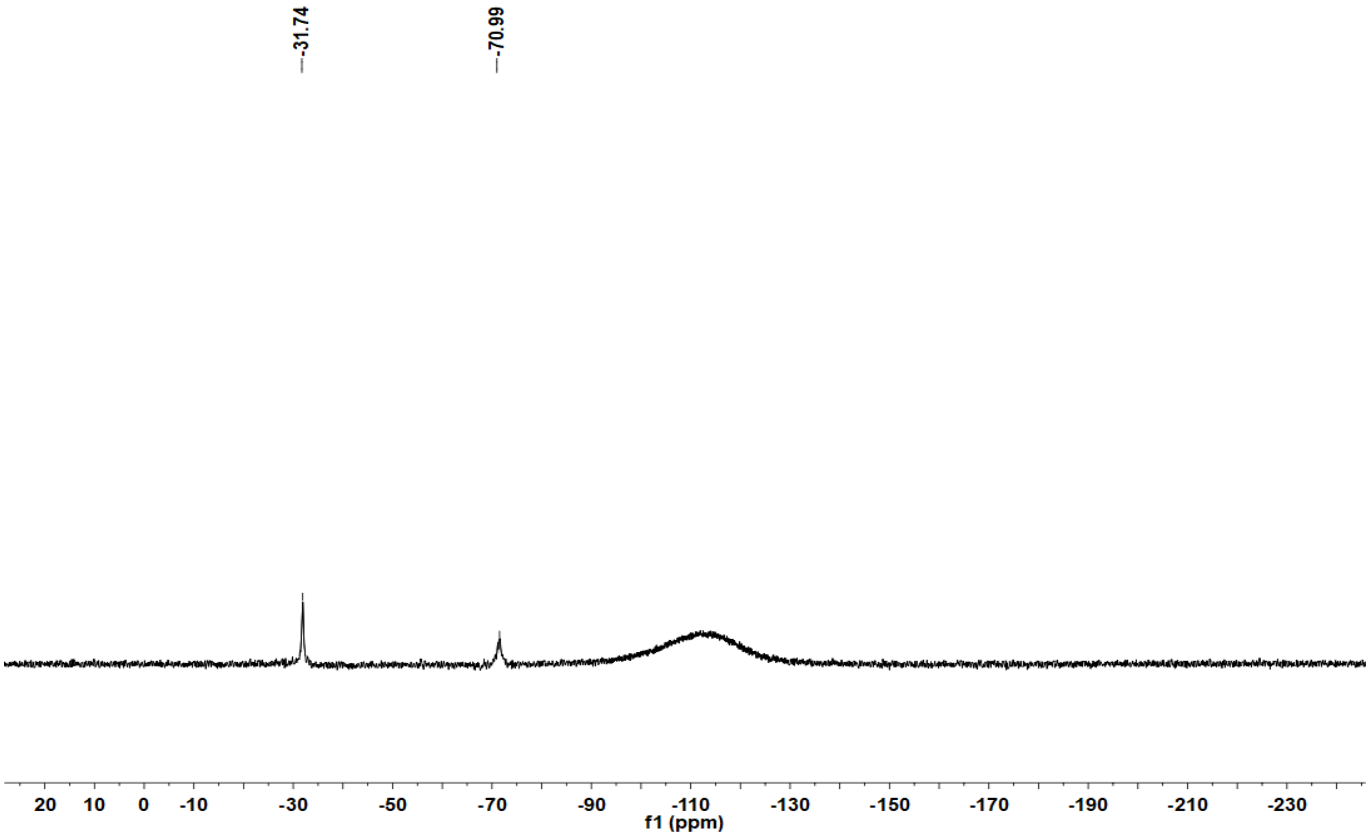

Figure S33. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **14** (* solvent).

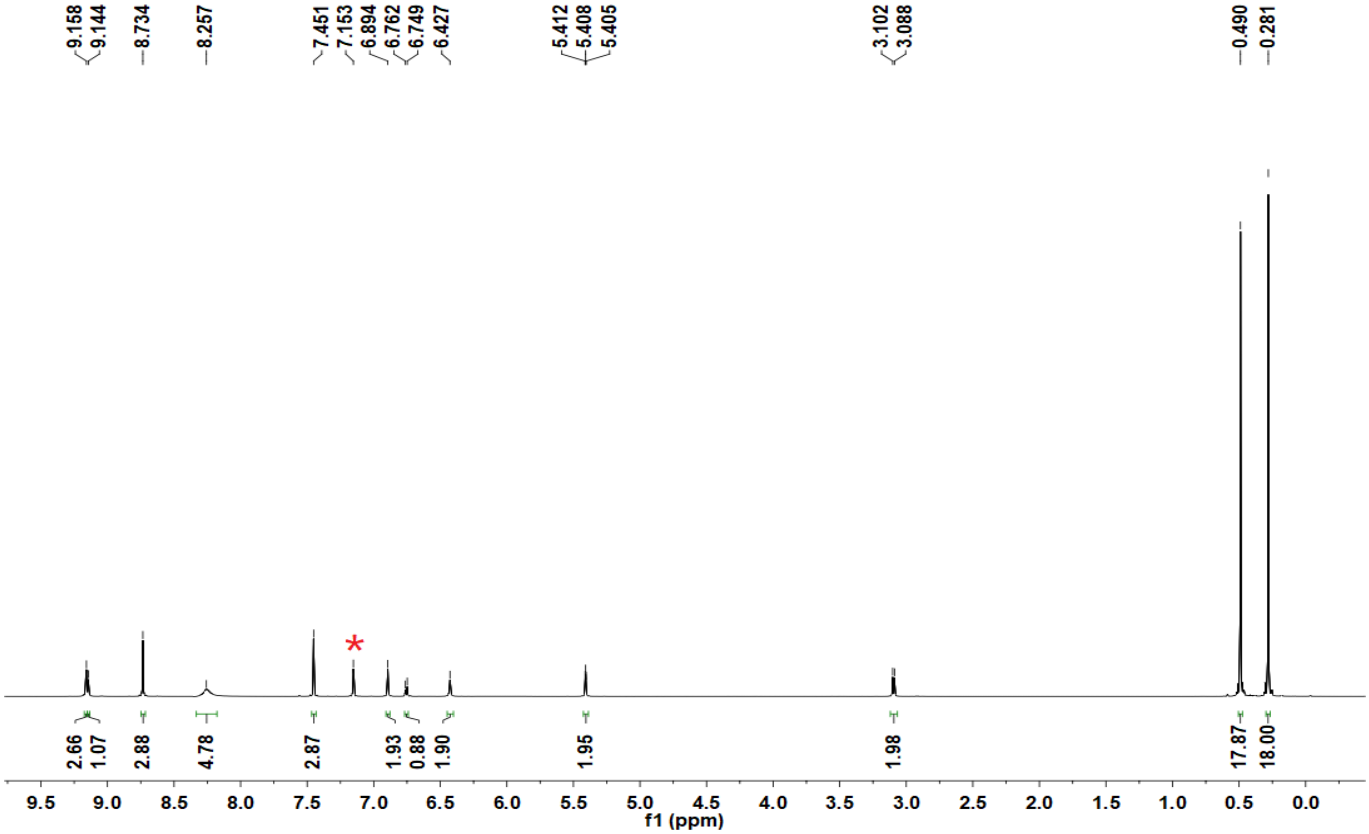

Figure S34. ^{1}H NMR spectrum for compound **15** (* solvent).

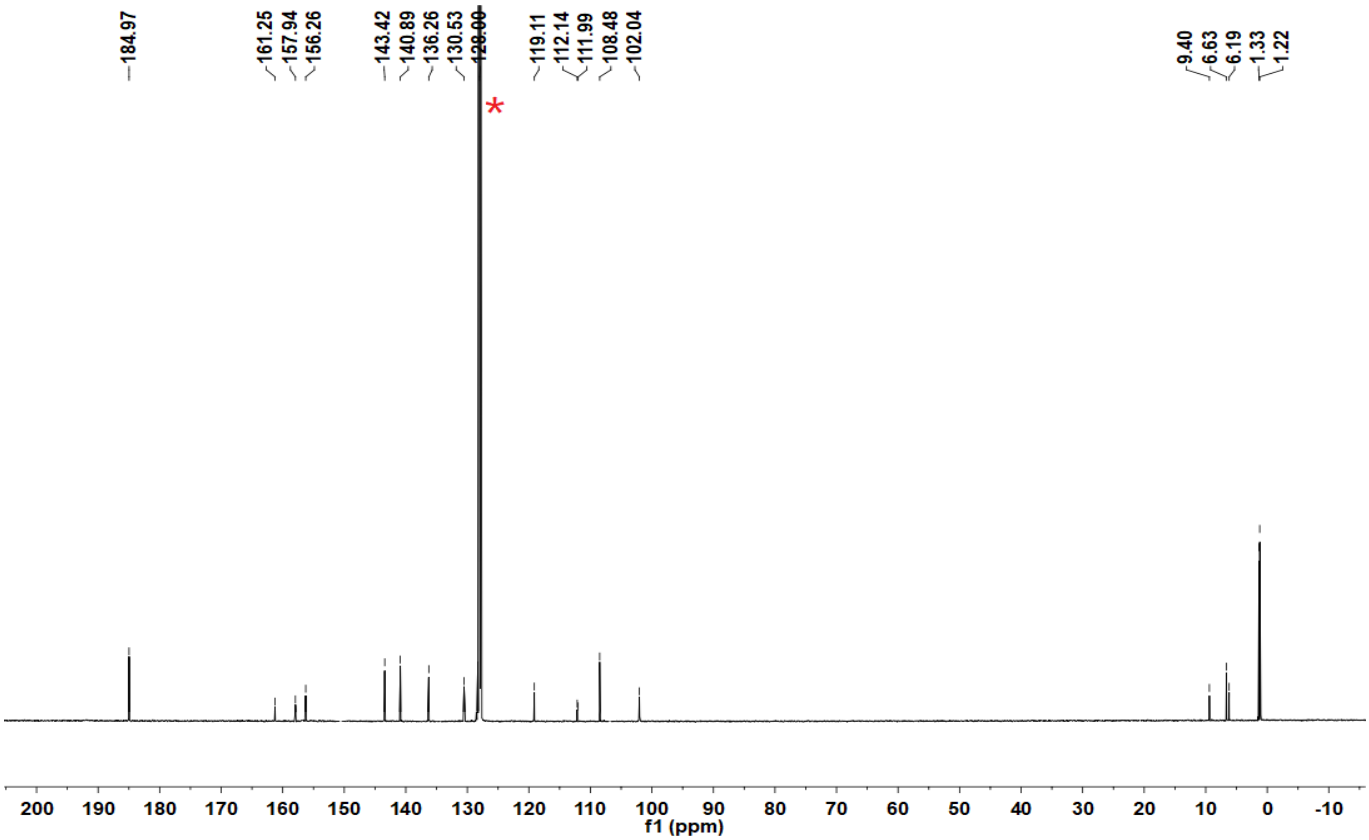

Figure S35. ^{13}C{^{1}H} NMR spectrum for compound **15** (* solvent).

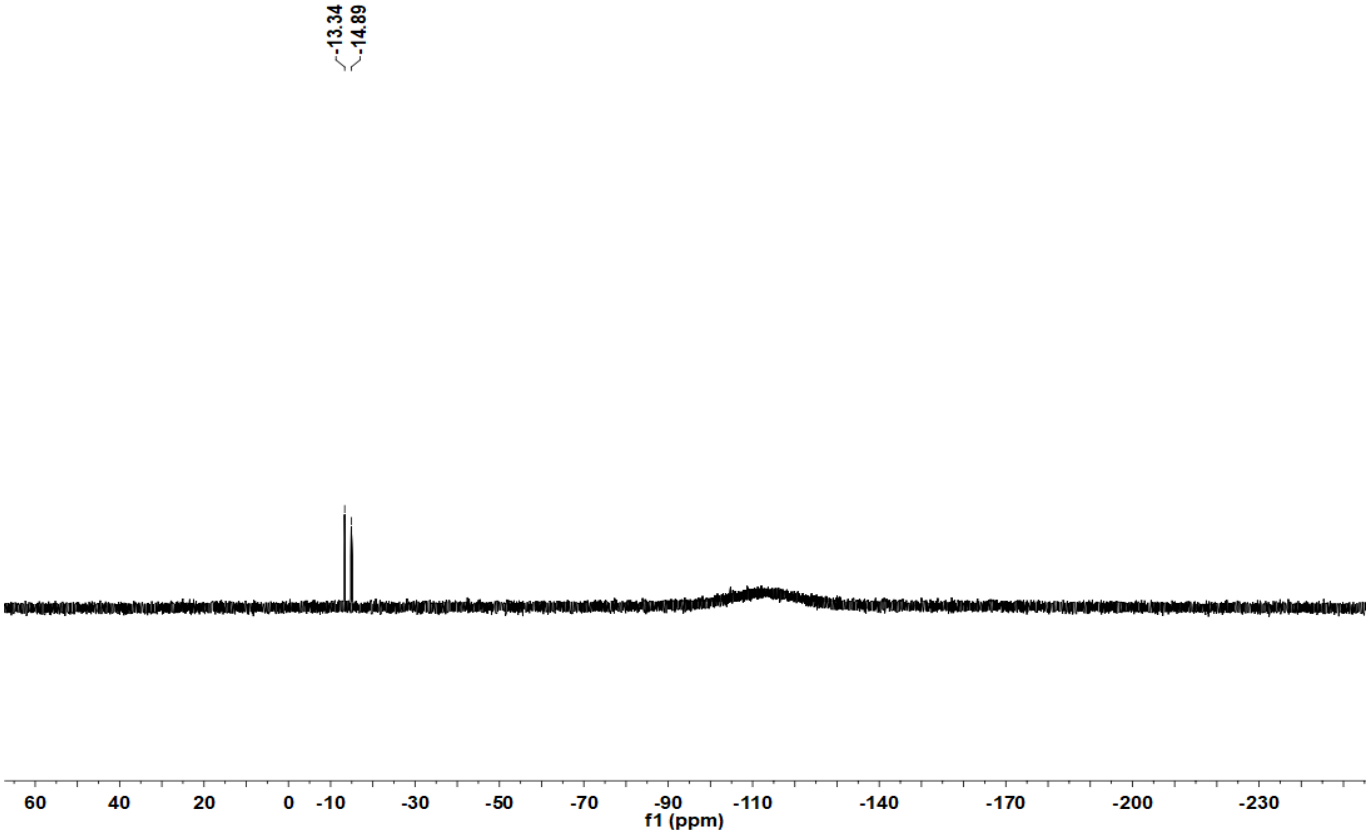

Figure S36. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **15** (* solvent).

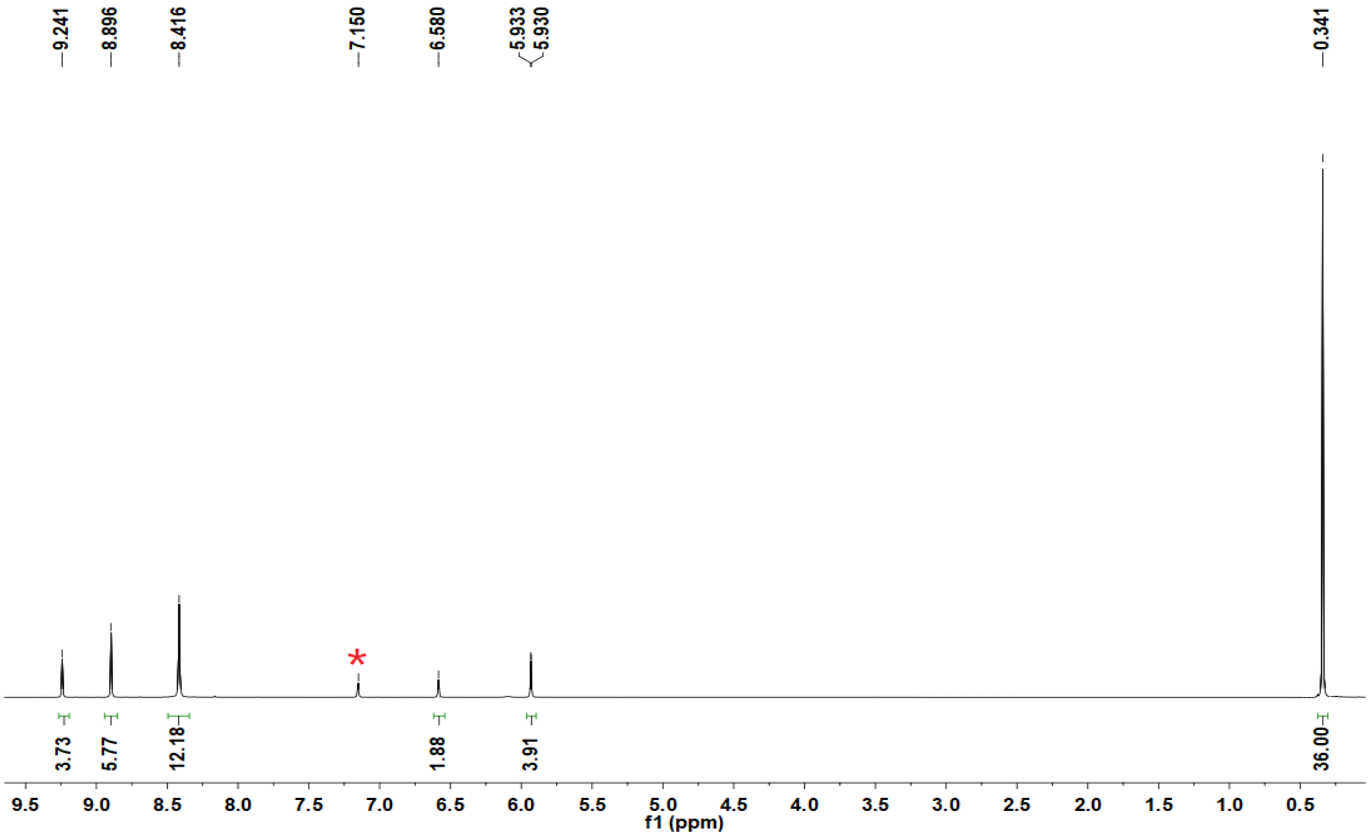

Figure S37. ^{1}H NMR spectrum for compound **16** (* solvent).

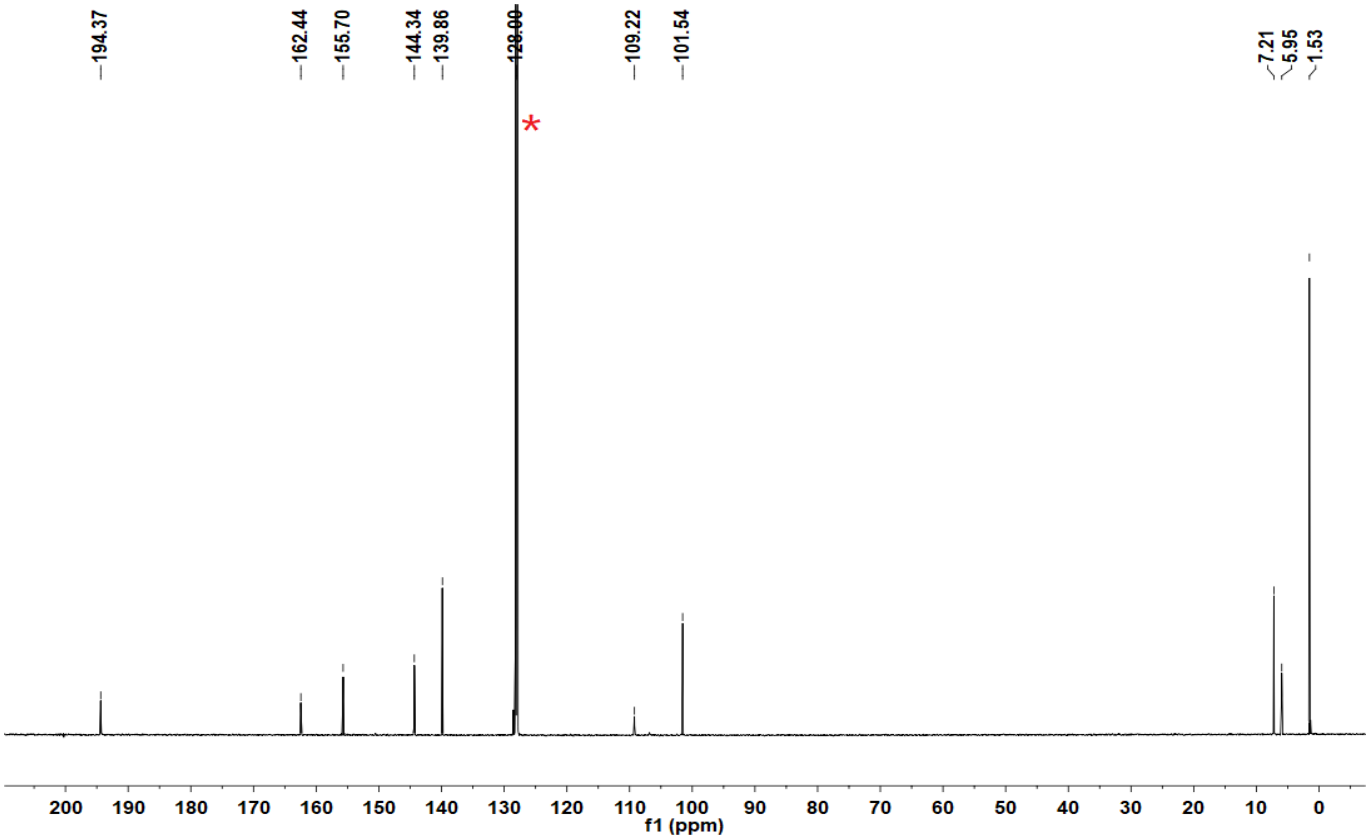

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum for compound **16** (* solvent).

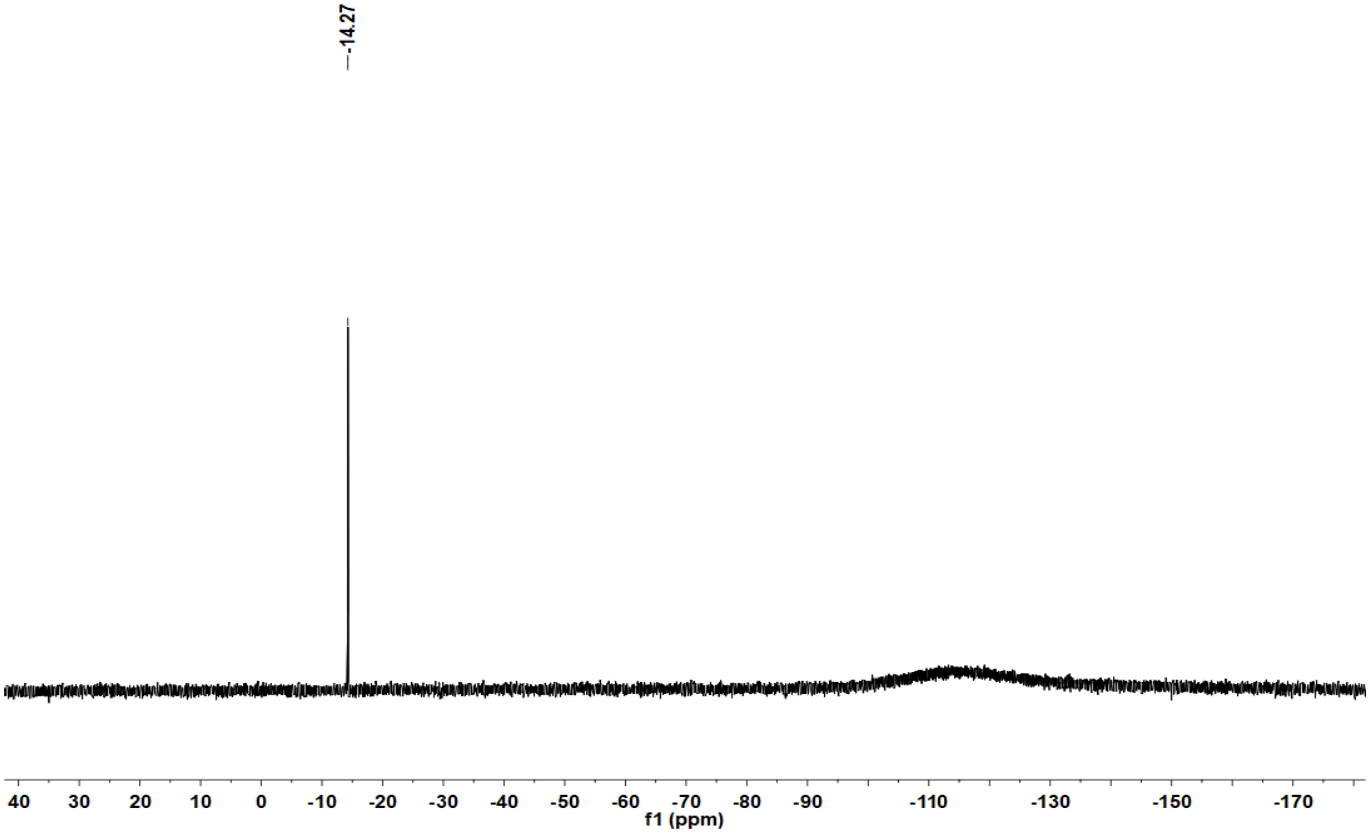

Figure S39. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **16** (* solvent).

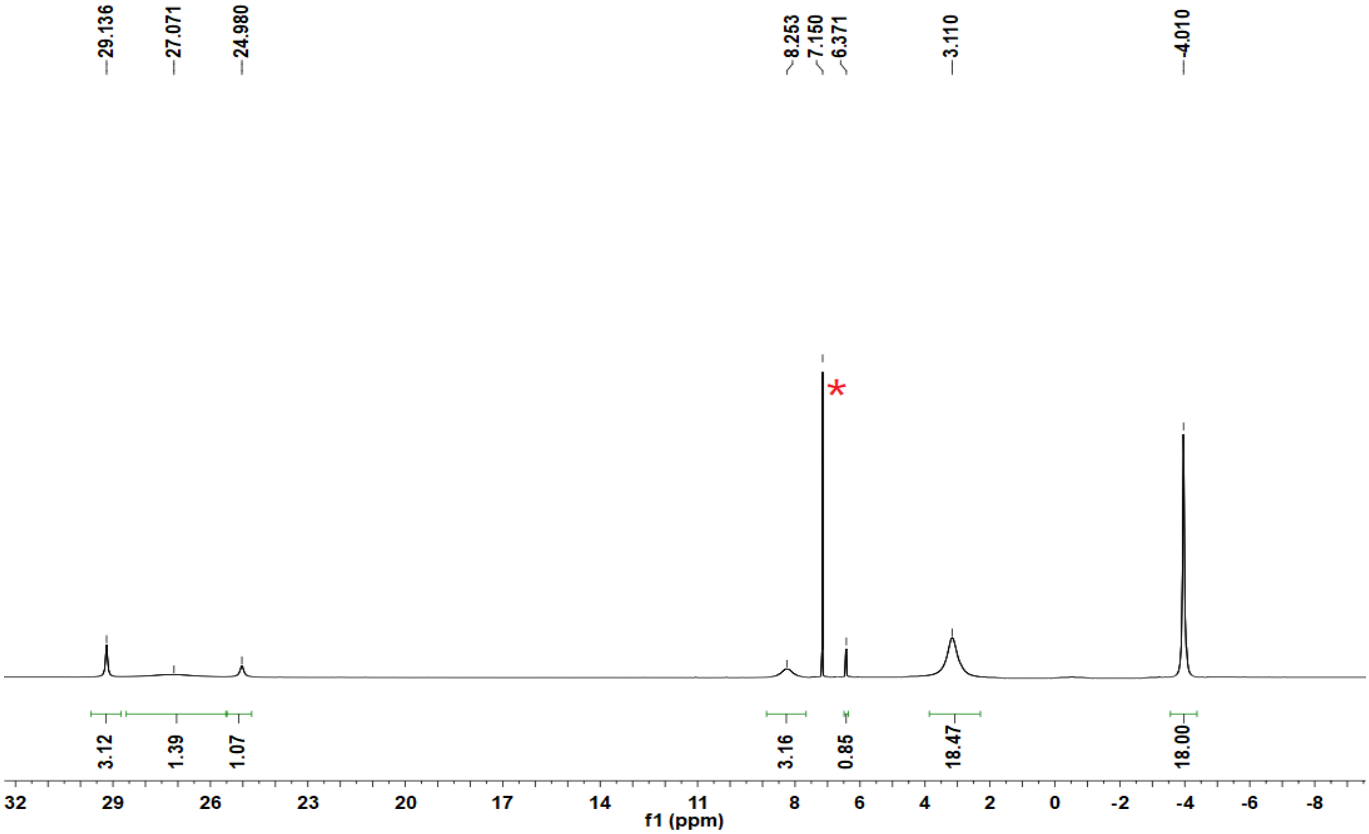

Figure S40. ^{1}H NMR spectrum for compound **17** (* solvent).

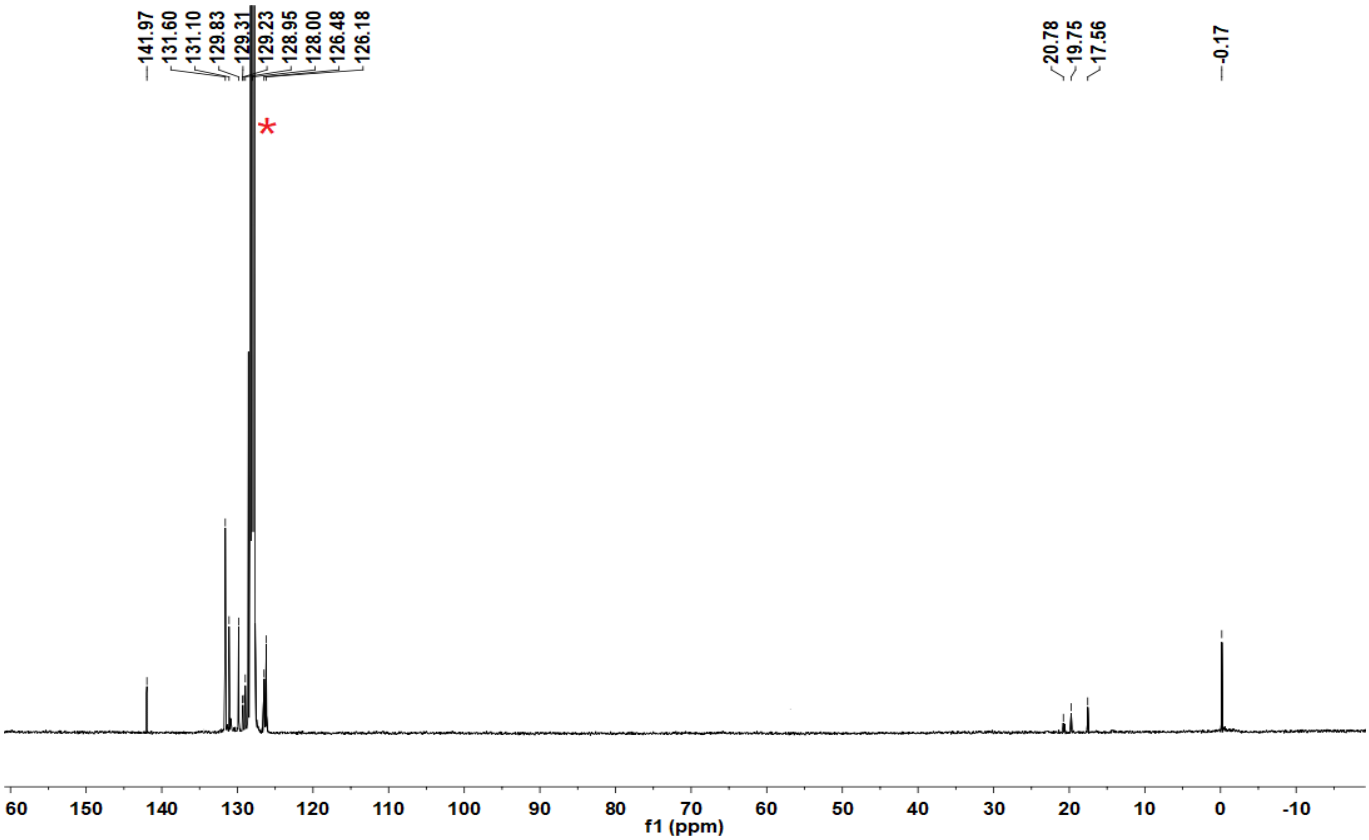

Figure S41. ^{13}C{^{1}H} NMR spectrum for compound **17** (* solvent).

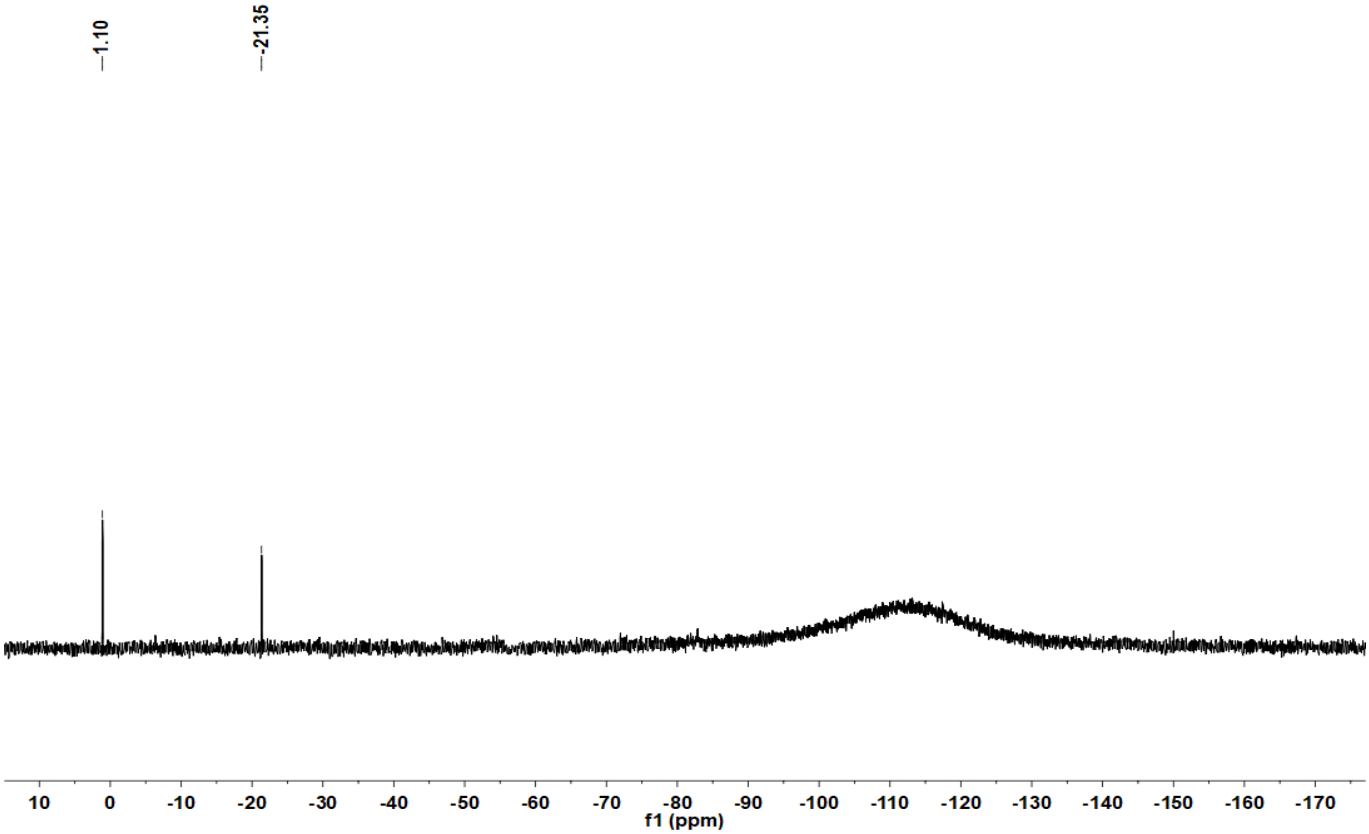

Figure S42. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **17** (* solvent).

4. UV-vis-NIR spectra

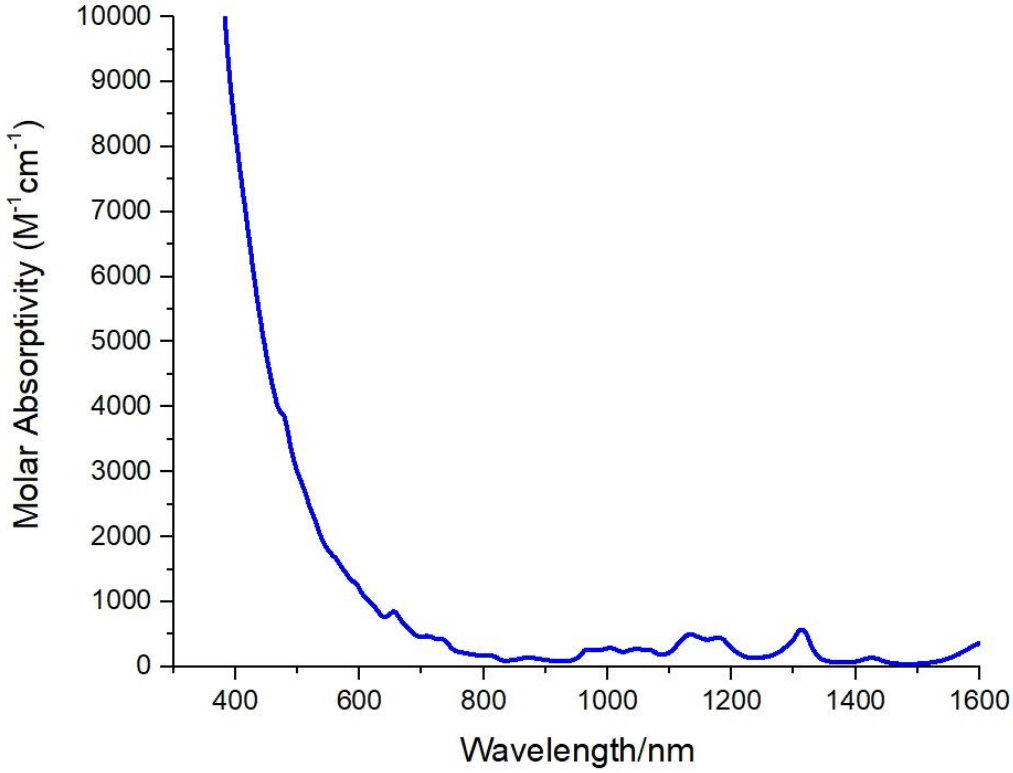

Fig. S43. UV-Vis spectrum of **2**.

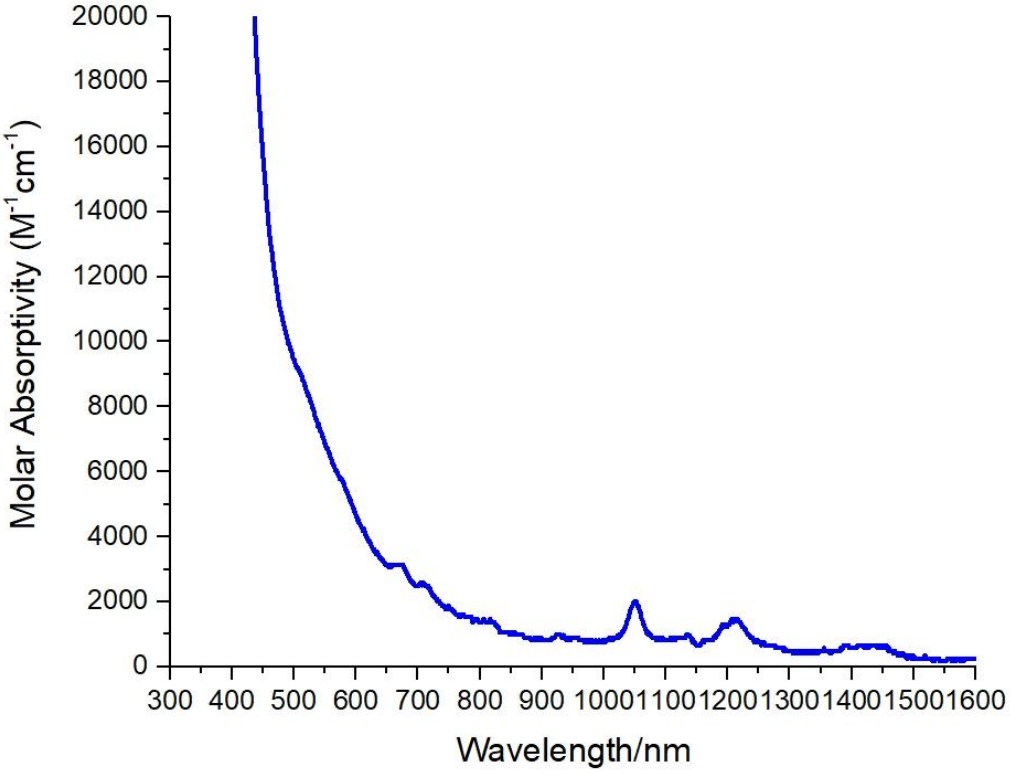

Fig. S44. UV-Vis spectrum of **3**.

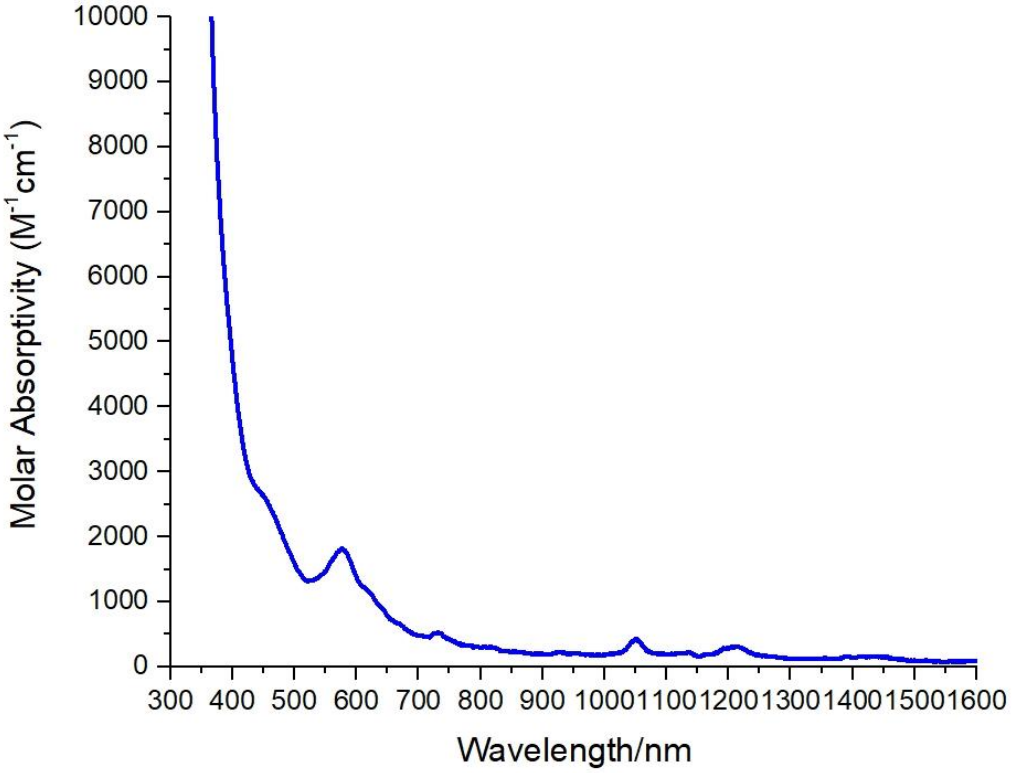

Fig. S45. UV-Vis spectrum of **4**.

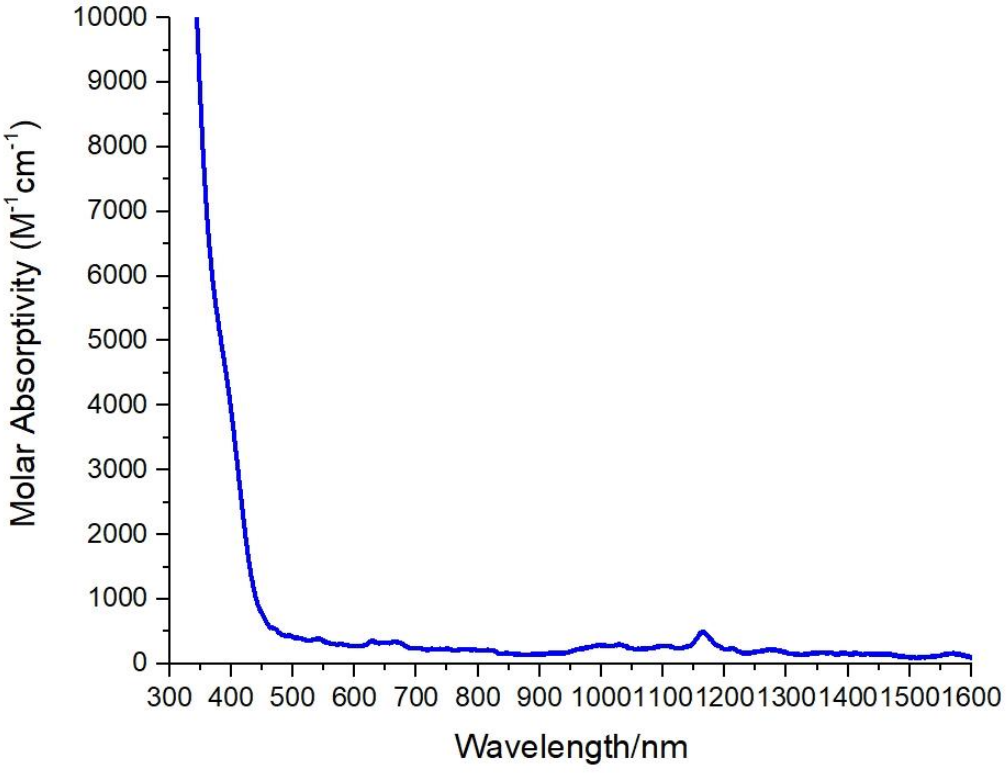

Fig. S46. UV-Vis spectrum of **7**.

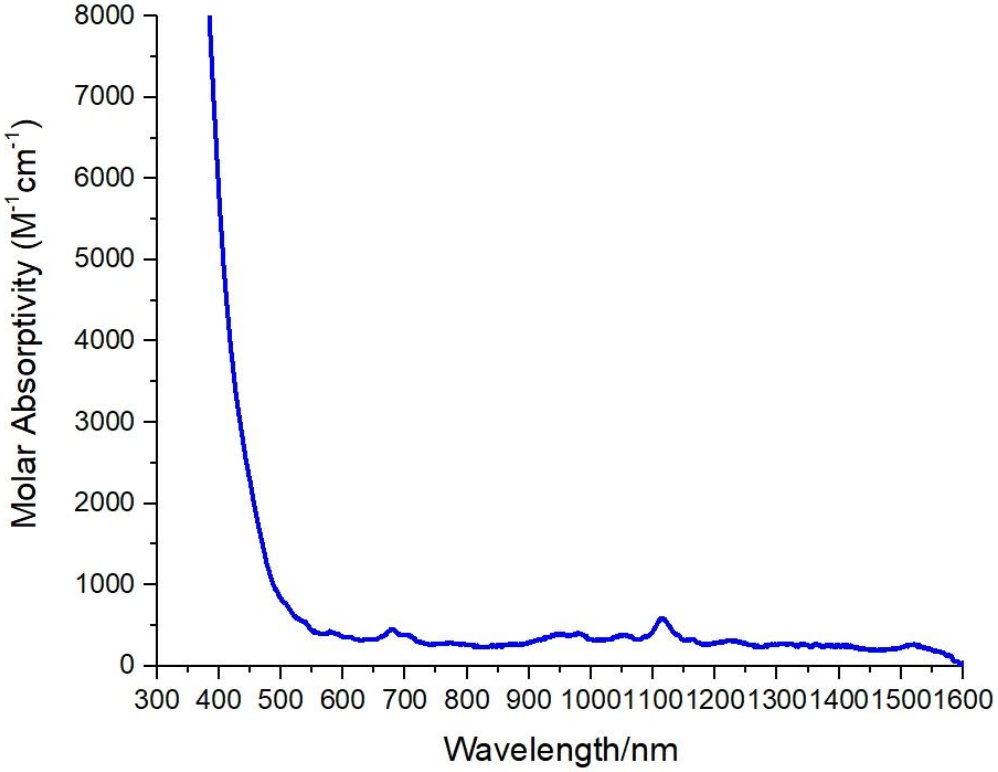

Fig. S47. UV-Vis spectrum of **8**.

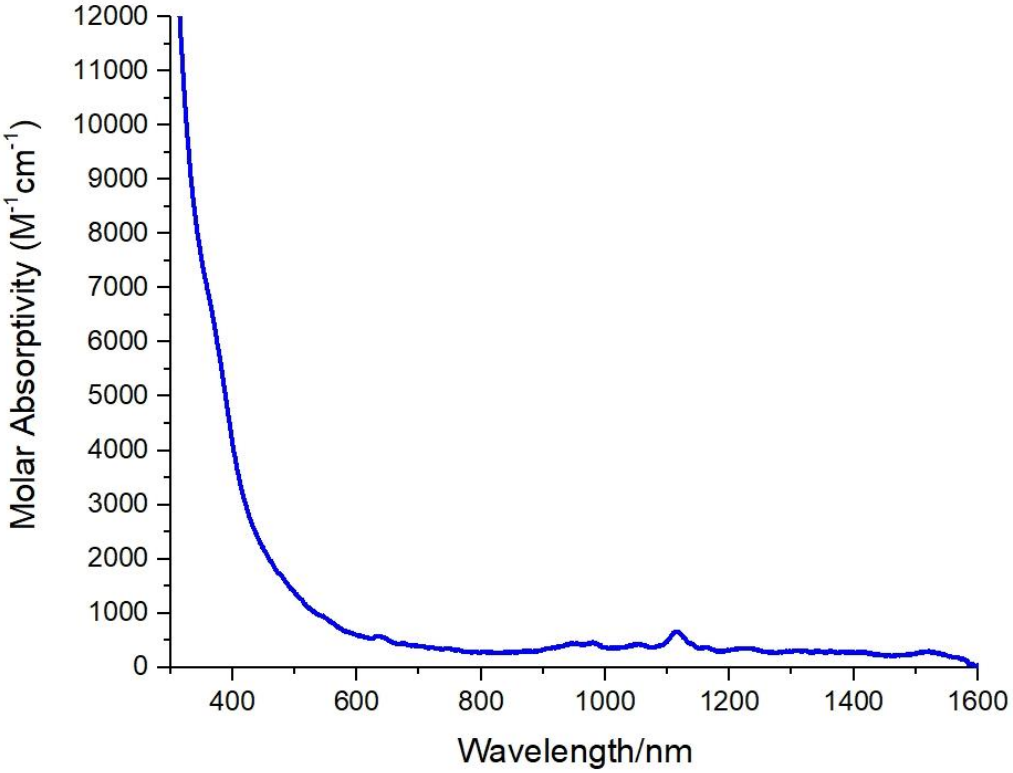

Fig. S48. UV-Vis spectrum of **9**.

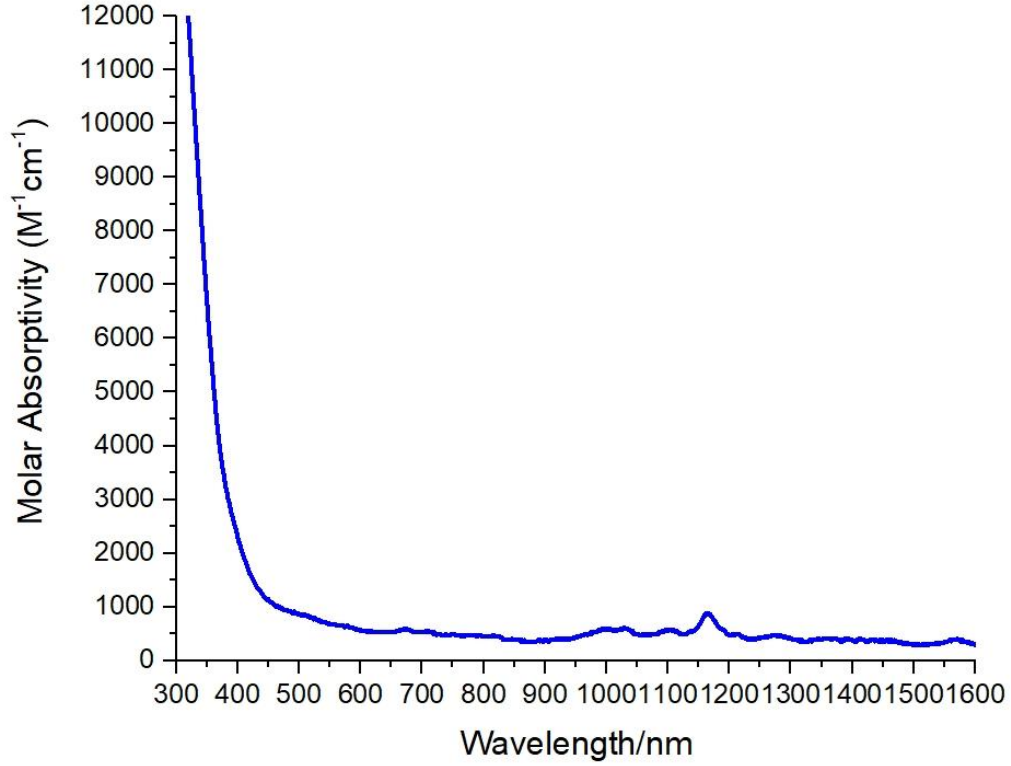

Fig. S49. UV-Vis spectrum of **10**.

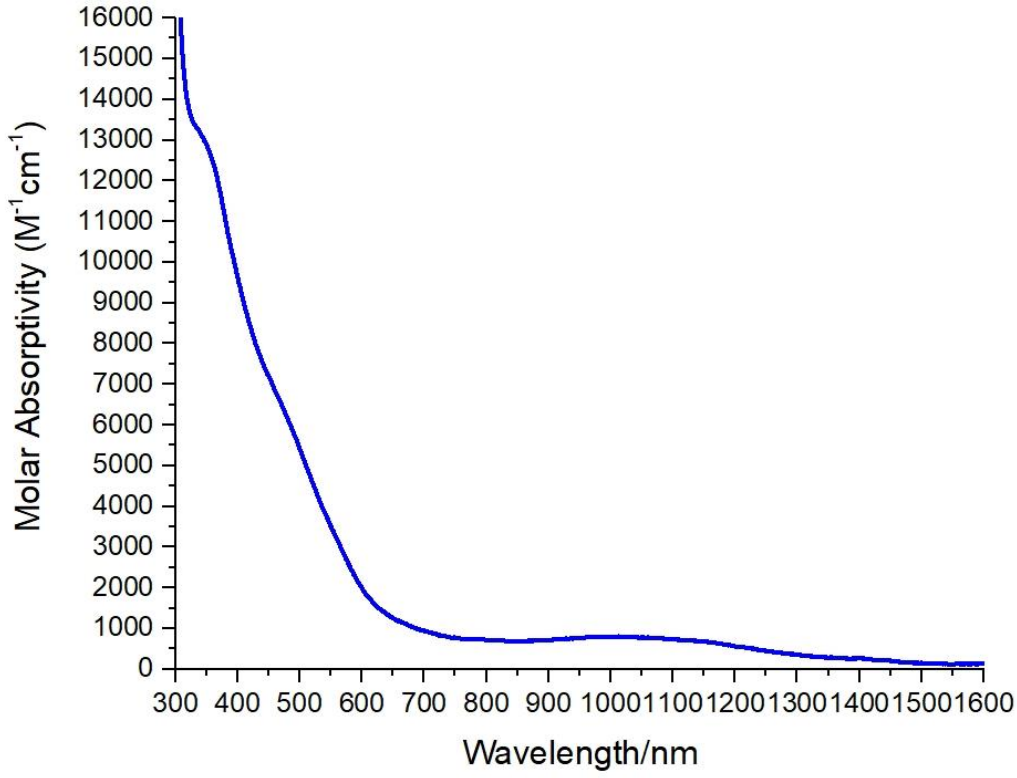

Fig. S50. UV-Vis spectrum of **12**.

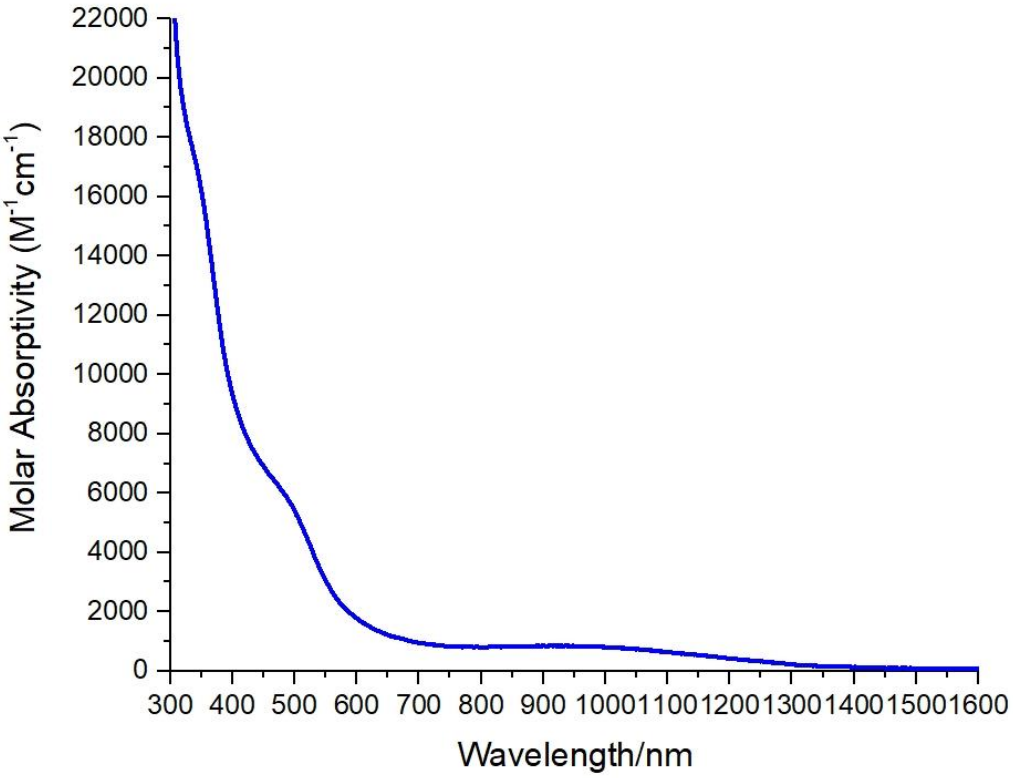

Fig. S51. UV-Vis spectrum of **13**.

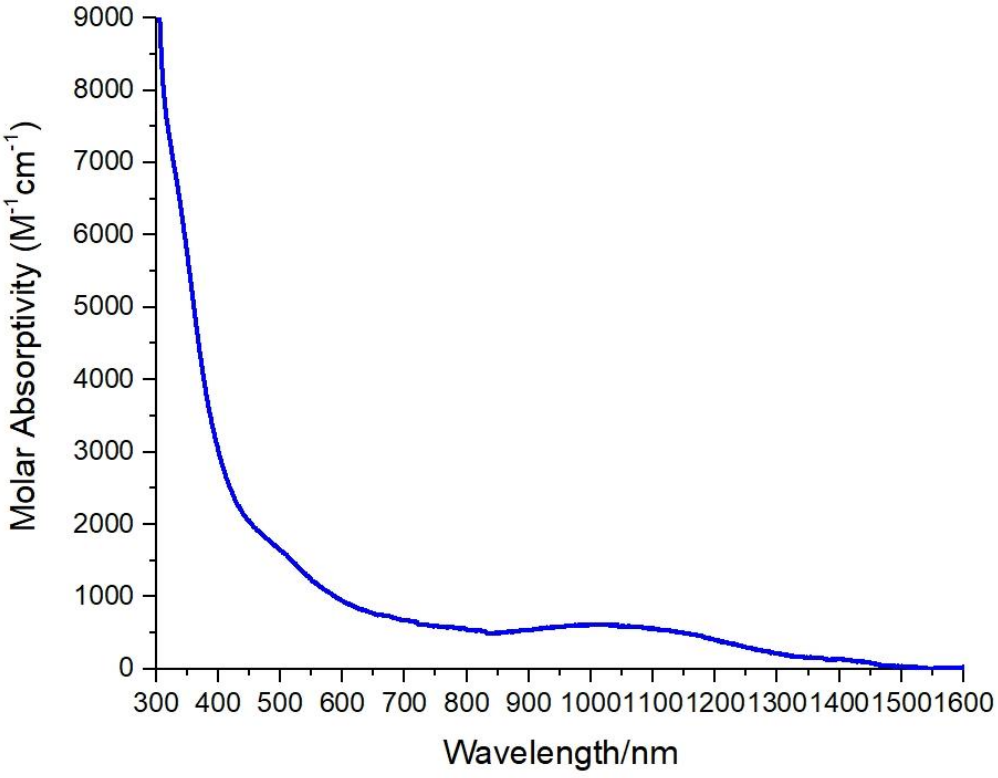

Fig. S52. UV-Vis spectrum of **14**.

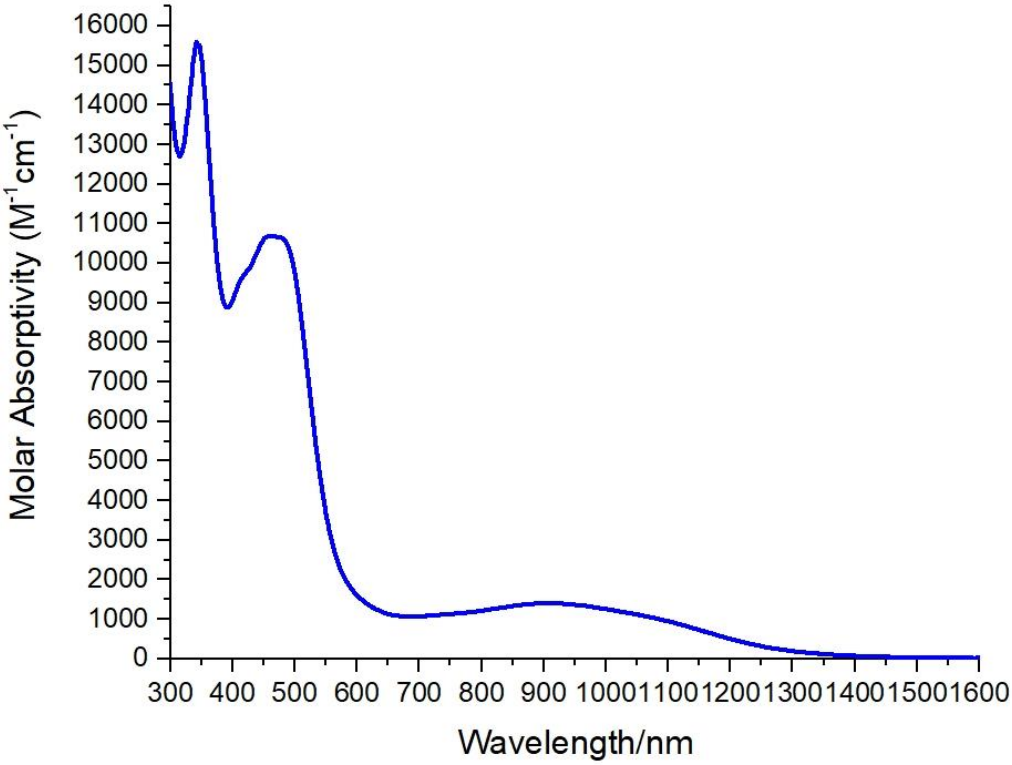

Fig. S53. UV-Vis spectrum of **15**. λ_{max} = 342 nm (ε = 1.56 × 10^4 $M^{-1}cm^{-1}$), 460 nm (ε = 1.06 × 10^4 $M^{-1}cm^{-1}$).

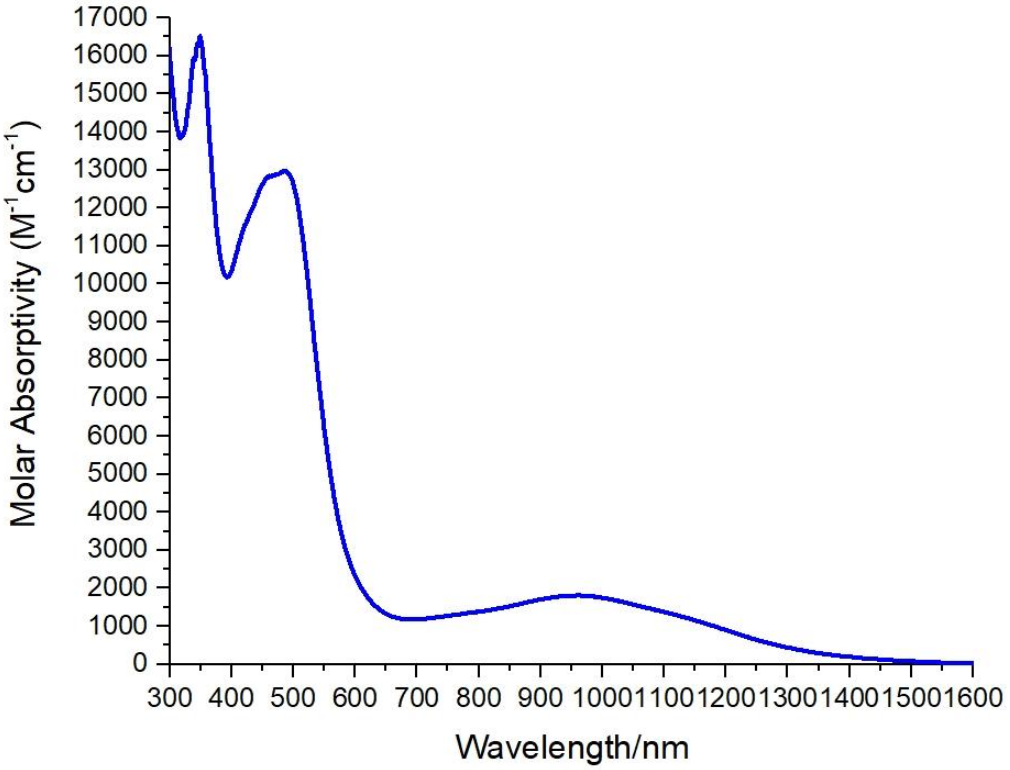

Fig. S54. UV-Vis spectrum of **16**. λ_{max} = 349 nm (ε = 1.65 × 10^4 $M^{-1}cm^{-1}$), 487nm (ε = 1.30 × 10^4 $M^{-1}cm^{-1}$).

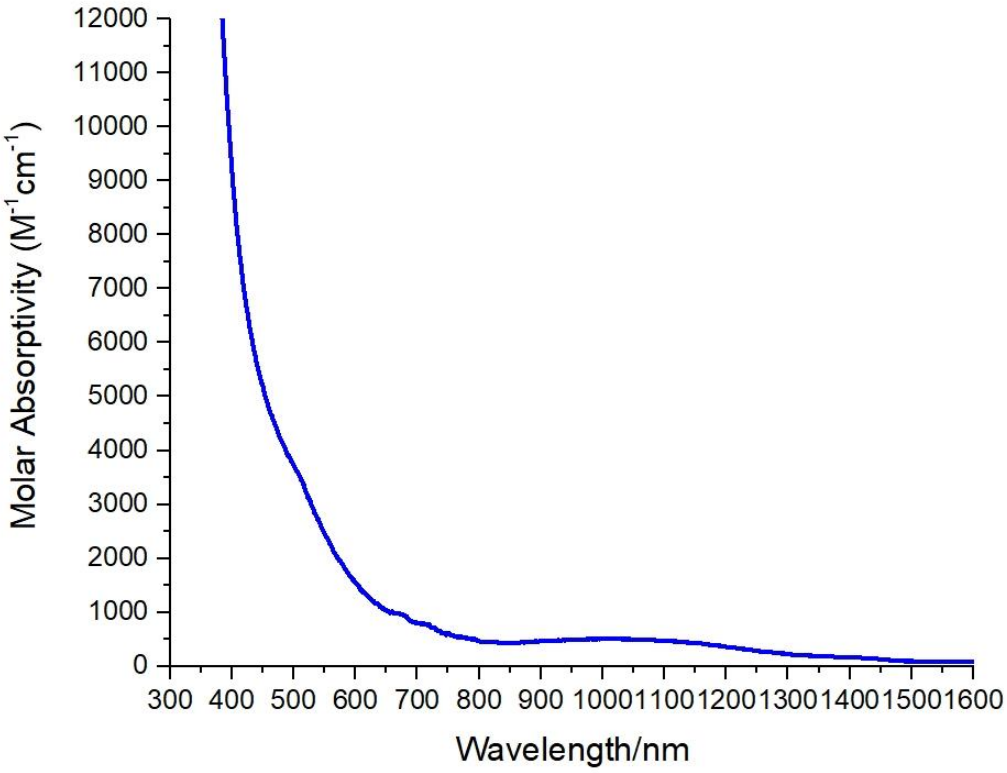

Fig. S55. UV-Vis spectrum of **17**.