Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information for

Alkyl Substituted [2.2]Paracyclophane-1,9-dienes

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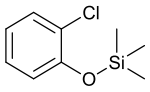
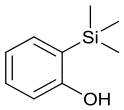
Table of Contents

1. Synthesis of 1-Chloro-2-[(trimethylsilyl)oxy]-benzene (S1)



2-Chlorophenol (50.00 g, 389 mmol) and trimethylsilyl chloride (TMSCl) (10.00 g, 92.1 mmol) were added to a flask under argon and heated at reflux. Additional TMSCl was added every ~ 12 hours (10.00 g, 92.1 mmol portions, final addition 5.00 g, 46.0 mmol and 55.00 g, 506 mol, 1.3 eq. in total) and the reaction was heated under reflux for a total of 72 hours. The reaction was cooled to RT and the excess TMSCl removed by distillation under argon and the product **S1** was isolated as a clear yellow liquid (76.8 g, 98%) and was used without further purification. **^{1}H NMR, ($CDCl_3$, 500 MHz), δ (ppm):** 7.35 (1H, dd, *J* = 7.9, 1.7 Hz), 7.13 (1H, td, *J* = 7.6, 1.7 Hz), 6.93-6.87 (2H, m), 0.29 (9H, s). **^{13}C NMR, ($CDCl_3$, 101 MHz), δ (ppm):** 151.31, 130.21, 127.52, 125.67, 122.31, 121.17, 0.26. **MS (EI, M^+):** calc. for $[C_9H_{13}ClOSi]^+$: *m*/*z* 200, found *m*/*z* 200; calc. for $[C_9H_{13}ClOSi\text{-}CH_3]^+$: *m*/*z* 185, found *m*/*z* 185.

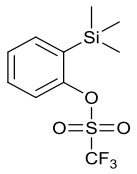
2. Synthesis of 2-(Trimethylsilyl)phenol (S2)[1]



Sodium (6.00 g, 261 mmol) was added to a 2-neck round bottom flask fitted with a condenser and a rubber septum. Under an argon atmosphere was added anhydrous toluene (125 mL) and the suspension heated to 110 °C with vigorous stirring. Once a fine dispersion of sodium had formed TMSCl (1.35 g, 12.4 mmol) was added in one portion followed by the dropwise addition of **S1** (24.95 g, 124.3 mmol), over 4 hours. The suspension was stirred for an additional 30 minutes and the bright purple suspension cooled to RT. The reaction was poured slowly into methanol (*caution: excess sodium*) and neutralised with aqueous ammonium chloride. The solvent was removed *in vacuo* and the residue dissolved in water (250 mL) and extracted with DCM (3 × 250 mL). The organic layers were combined, dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to reveal a pale yellow oil. Purification was achieved by distillation under reduced pressure (0.1 mbar, 70 °C) with

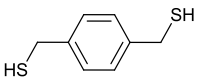
collection of the second fraction to reveal a clear oil (19.68 g, 95%). **^{1}H NMR, ($CDCl_3$, 500 MHz), δ (ppm):** 7.37 (1H, dd, *J* = 7.2, 1.7 Hz), 7.27-7.21 (1H, m), 6.93 (1H, td, *J* = 7.3, 0.5 Hz), 6.68 (1H, dd, *J* = 8.0, 0.5 Hz), 4.74 (1H, s), 0.32 (9H, s). ^{13}C NMR **($CDCl_3$, 101 MHz), δ (ppm):** 160.25, 135.18, 130.65, 125.34, 120.46, 114.42, -1.00. **MS (EI, M^+):** calc. for $[C_9H_{14}O]^+$: *m*/*z* 168, found *m*/*z* 168.

3. Synthesis of 2-(Trimethylsilyl)phenyl Trifluoromethanesulfonate (7)[2]



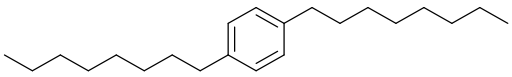
Compound **S2** (24.96 g, 150.1 mmol) and anhydrous pyridine (17.81 g, 225.1 mmol) were dissolved in anhydrous DCM (300 mL). The flask was cooled to 0 °C and trifluoromethanesulfonic anhydride (50.82 g, 180.1 mmol) was added dropwise over 2 hours. Once the addition was complete the reaction was warmed to RT and stirred for an additional 2 hours. The reaction was quenched slowly with water, the solvent removed *in vacuo* and diethyl ether (500 mL) added. The organic layer was washed with 1M aqueous HCl (3 × 250 mL), saturated $NaHCO_{3(aq)}$ (3 × 250 mL) and water (1 × 250 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*, resulting in a pale yellow oil. The residue was filtered through a short silica column (petroleum ether) to yield a clear oil (37.70 g, 84%). **^{1}H NMR, ($CDCl_3$, 500 MHz), δ (ppm):** 7.57-7.52 (1H, m), 7.47-7.42 (1H, m), 7.37-7.33 (2H, m), 0.38 (9H, s). **^{13}C NMR, ($CDCl_3$, 126 MHz), δ (ppm):** 155.12, 136.16, 132.55, 131.24, 127.64, 119.51, 118.53 (q, *J* = 320 Hz, S*C*F_3), -0.88. **MS (EI, M^+):** calc. for $[C_{10}H_{13}F_3OSSi]^+$: *m*/*z* 283, found *m*/*z* 283. **Elemental analysis:** found; C, 40.33; H, 4.38; S, 10.68. Calc.; $C_{10}H_{13}F_3O_3SSi$: C, 40.26; H, 4.39; S, 10.75%.

4. Synthesis of 1,4-Benzenedimethanethiol (11)



1,4-Bis(dichloromethyl)benzene (20.00 g, 114.3 mmol) and thiourea (20.87 g, 274.2 mmol) were dissolved in deoxygenated EtOH (200 mL) and heated under reflux. After 5 hours the suspension was cooled to RT and the solvent removed *in vacuo*. Sodium hydroxide (13.70 g, 342.7 mmol) and deoxygenated water (200 mL) were added to the residue followed by heating under reflux. After 5 hours the reaction was cooled to RT, neutralised with 50% aqueous H_2SO_4 (*v*/*v*) and extracted with DCM (3 × 100 mL). The organic layer was dried over MgSO4, filtered and the solvent removed *in vacuo*. The resulting solid was dissolved in DCM and MeOH and the product crystallised by the slow evaporation of DCM, yielding a white powder (16.29 g, 84%). **^{1}H NMR, ($CDCl_3$, 400 MHz), δ (ppm):** 7.28 (4H, s), 3.73 (4H, d, *J* = 7.5 Hz), 1.75 (2H, t, *J* = 7.5 Hz). **^{13}C NMR, ($CDCl_3$, 101 MHz), δ (ppm):** 139.96, 128.35, 28.60. **MS (EI, M^+):** calc. for $[C_8H_{10}]^+$: *m*/*z* 170, found *m*/*z* 170.

5. Synthesis of 1,4-Dioctylbenzene (8)



Magnesium (14.90 g, 613.0 mmol) was added to anhydrous THF (200 mL) and 1-bromooctane (118.0 g, 611.0 mmol) was added dropwise at a rate to keep the reaction refluxing, followed by heating at 50 °C for 2 hours. In a separate flask was added 1,4-dichlorobenzene (30.00 g, 204.1 mmol) and 1,2-bis(diphenylphosphino)propane nickel(II)chloride (560 mg, 1.03 mmol) in anhydrous THF (400 mL) and cooled to 0 °C. The octylmagnesium bromide solution was added by syringe to the 1,4-dichlorobenzene solution, stirred for 2 hours at 0 °C and warmed to RT. After 20 hours the reaction was cooled to 0 °C and quenched with saturated $NH_4Cl_{(aq)}$. The solvent was removed *in vacuo* and the residue dissolved in diethyl ether (500 mL), filtered and the organic layer washed with water (3 × 250 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to reveal a yellow oil. Purification was performed by high vacuum distillation, followed by

filtration of the residue through a short silica column (petroleum ether) to obtain a colourless oil (53.4 g, 87%). **^{1}H NMR, ($CDCl_3$, 400 MHz), δ (ppm):** 7.10 (4H, s), 2.57 (4H, t, *J* = 7.9 Hz), 1.67-1.52 (4H, m), 1.40-1.17 (20H, br m), 0.89 (6H, t, *J* = 7.1 Hz). **^{13}C NMR, ($CDCl_3$, 101 MHz), δ (ppm):** 140.07, 128.00, 35.56, 31.89, 31.65, 29.50, 29.40, 29.28, 22.63, 14.13. **MS (EI, M^+):** calc. for $[C_{22}H_{38}]^+$: *m*/*z* 302, found *m*/*z* 302.

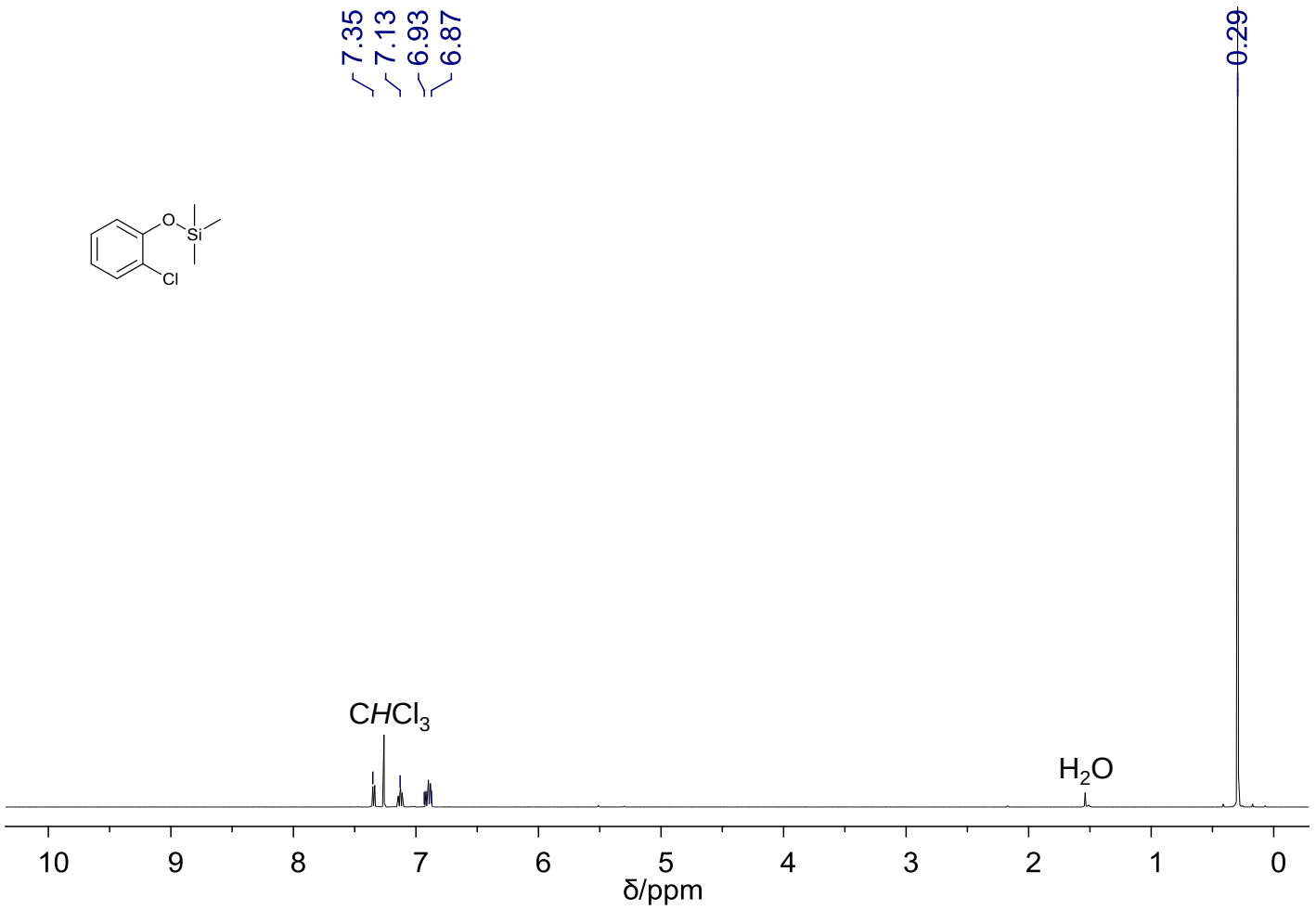
6. Benzyne Induced Stevens Rearrangement of Compound 12 with Isoamyl Nitrite and Anthranilic Acid (13)

To a refluxing solution of dithia[3.3]paracyclophane **12** (3.00 g, 6.03 mmol) and anthranilic acid (2.89 g, 21.1 mmol) in dry 1,2-dichloroethane (340 mL) under a nitrogen atmosphere, isoamyl nitrite (3.18 mL, 23.7 mmol) was added dropwise over 30 minutes. The resulting reaction mixture was refluxed for an additional 30 minutes. The solvent was removed *in vacuo* and the residue purified by column chromatography (DCM : petroleum ether, 10 : 90 (*v*/*v*)). The product was obtained as a yellowish oil (0.97 g, 25 %).

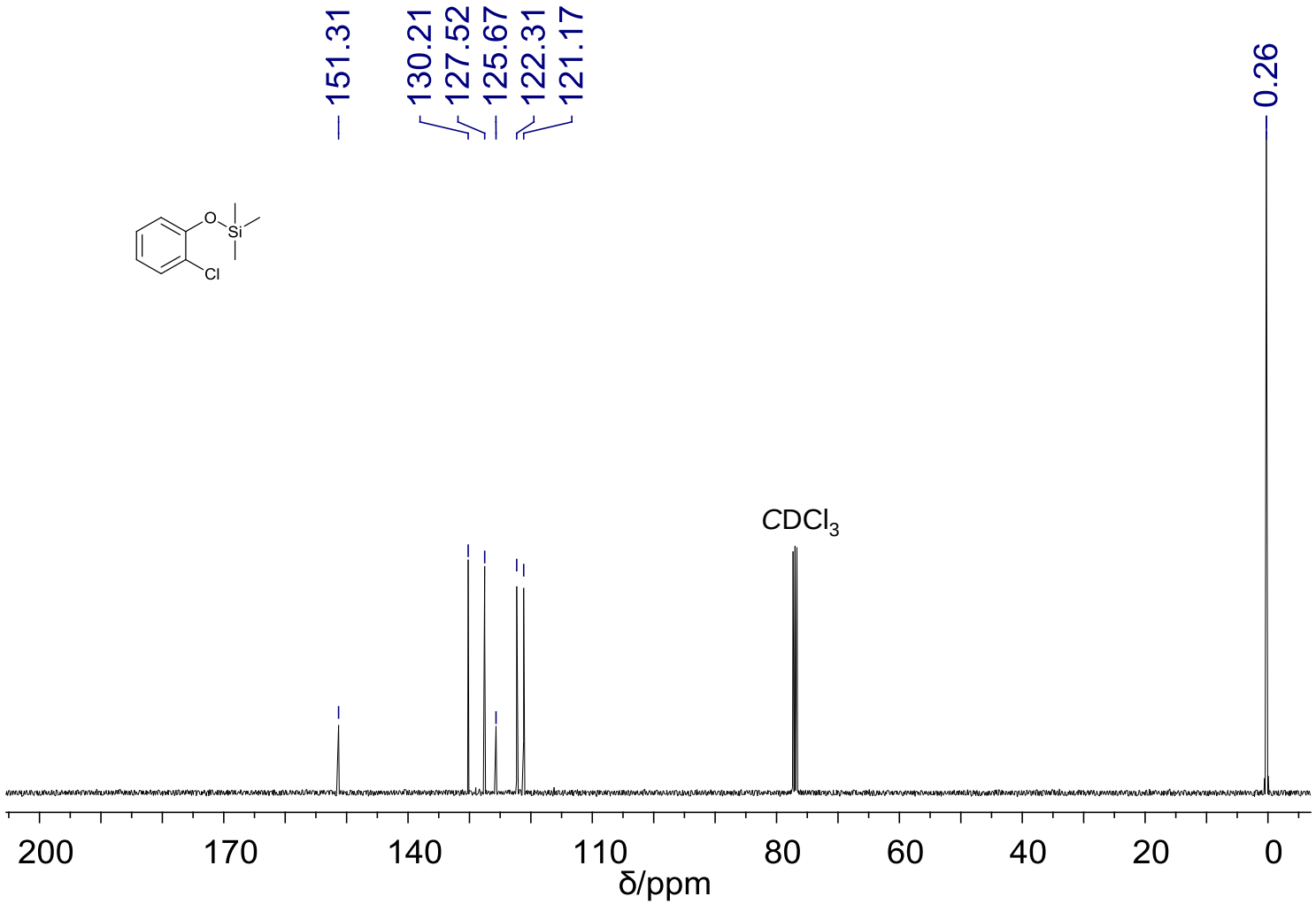
7. Benzyne Induced Stevens Rearrangement of Mixture of Isomers 16 and 17 with Isoamyl Nitrite and Anthranilic Acid (18)

To a refluxing solution of dithia[3.3]paracyclophanes **16** and **17** (2.88 g, 3.99 mmol) and anthranilic acid (1.92 g, 14.0 mmol) in dry 1,2-dichloroethane (120 mL) under a nitrogen atmosphere, isoamyl nitrite (2.19 mL, 16.3 mmol) was added dropwise over 30 minutes. The resulting reaction mixture was refluxed for an additional 30 minutes. The solvent was removed *in vacuo* and the residue purified by column chromatography (DCM : petroleum ether, 10 : 90 (*v*/*v*)). The product was obtained as a yellowish oil (1.12g, 32%).

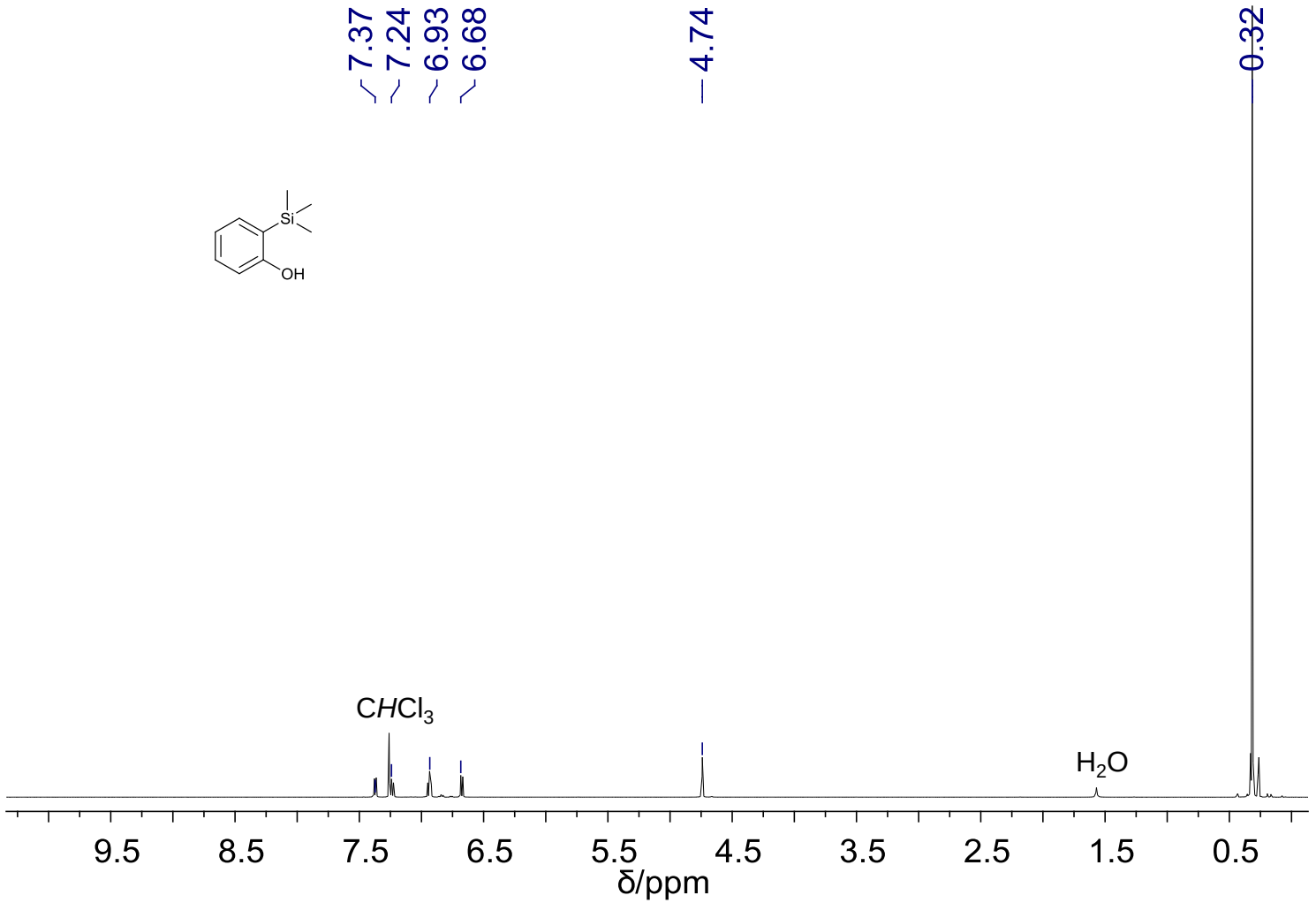
8. ^{1}H NMR ($CDCl_3$, 500 MHz) Spectrum of 1-Chloro-2-[(trimethylsilyl)oxy]-benzene (S1)



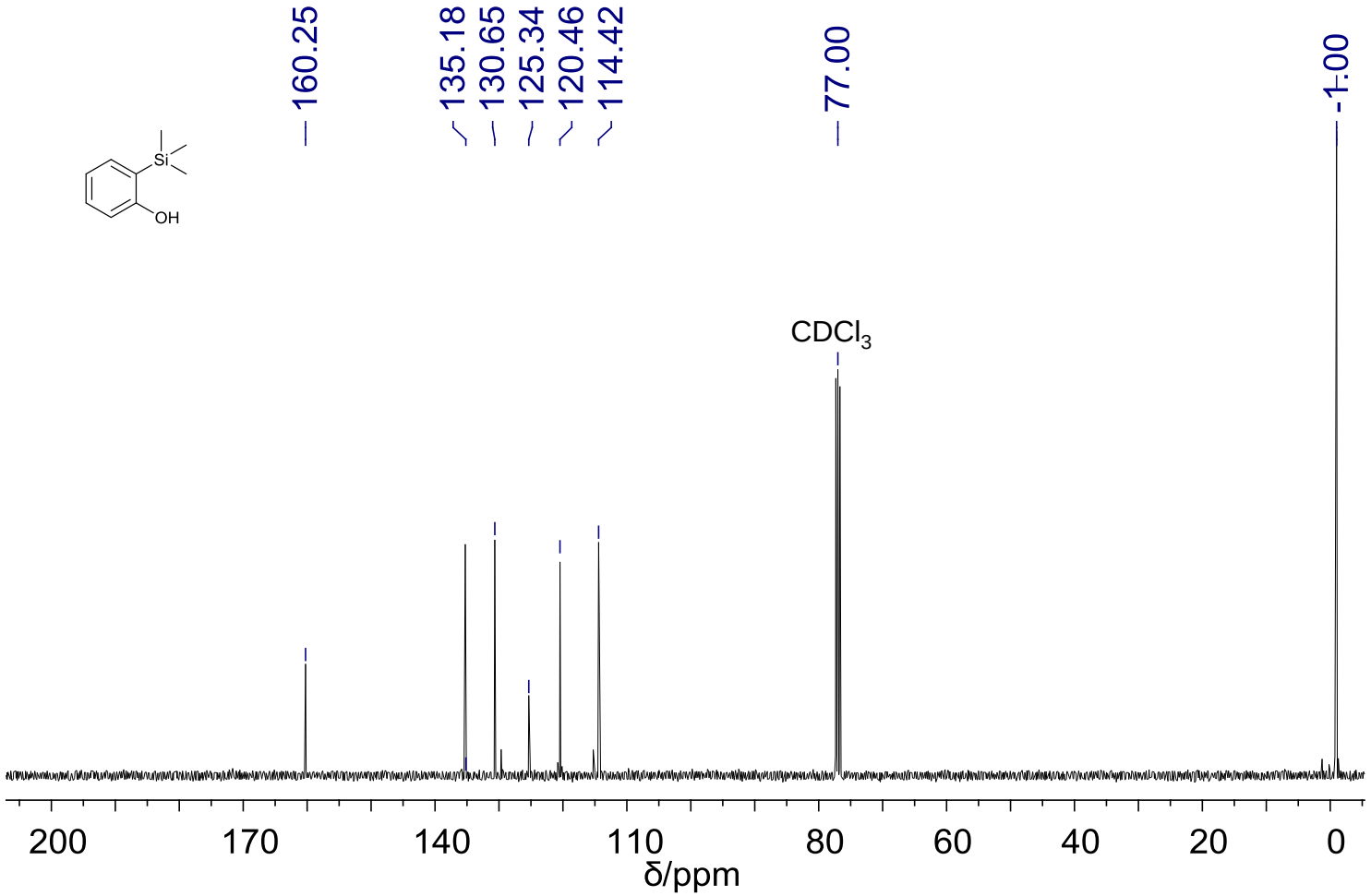
9. ^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1-Chloro-2-[(trimethylsilyl)oxy]-benzene (S1)



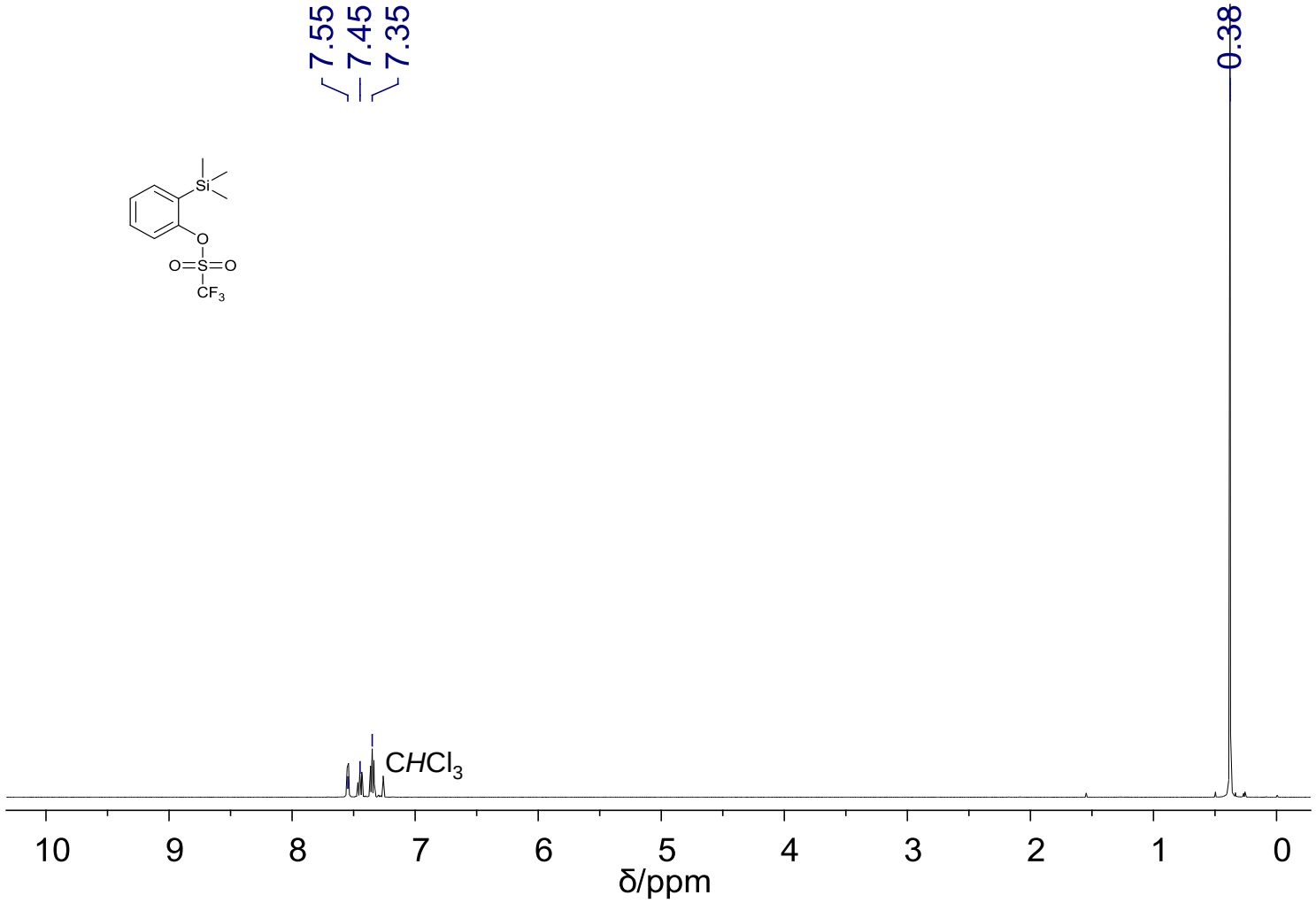
10. ^{1}H NMR ($CDCl_3$, 500 MHz) Spectrum of 2-(Trimethylsilyl)phenol (S2)



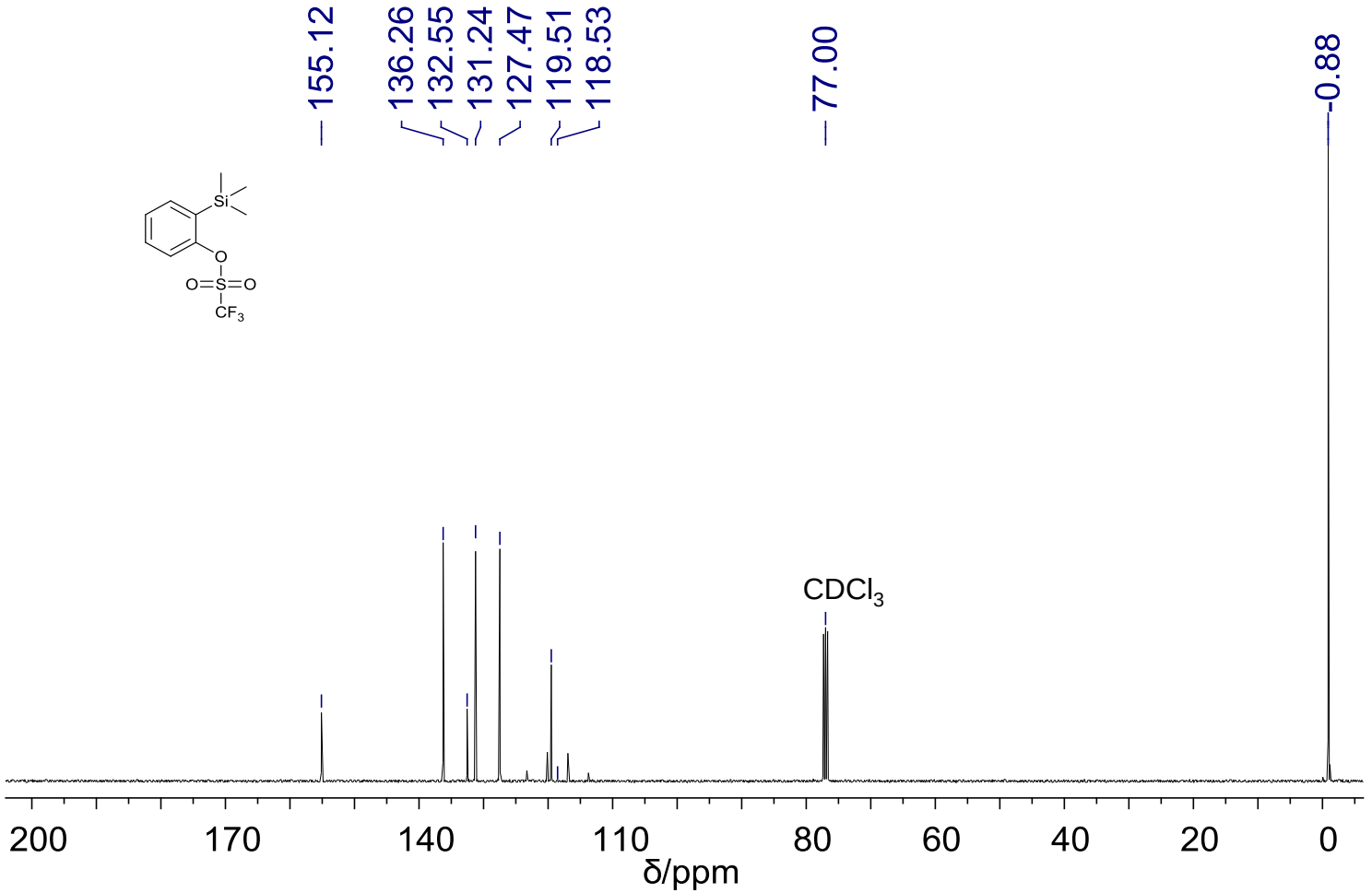
11. ^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 2-(Trimethylsilyl)phenol (S2)



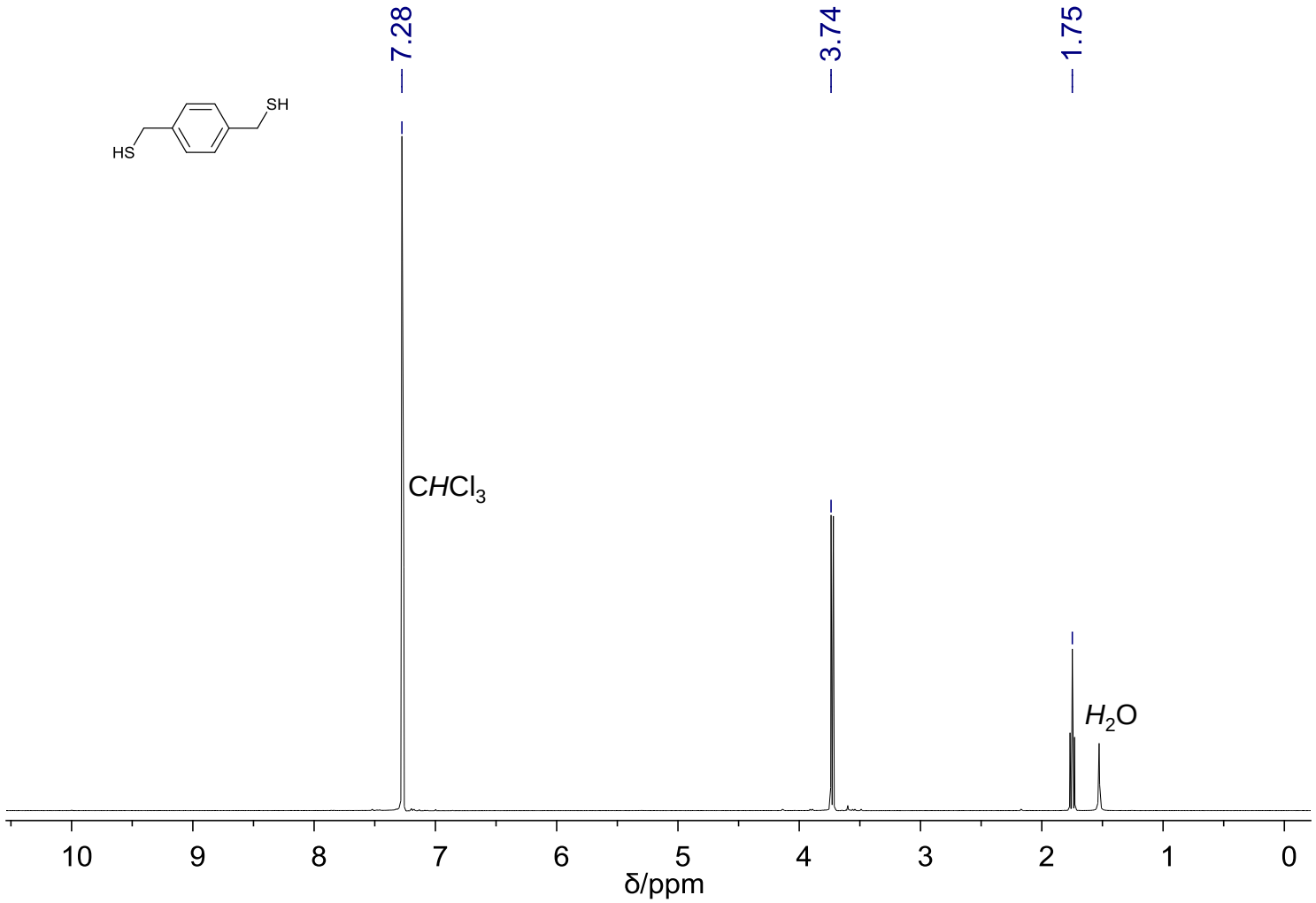
12. ^{1}H NMR ($CDCl_3$, 500 MHz) Spectrum of 2-(Trimethylsilyl)phenyl Trifluoromethanesulfonate (7)



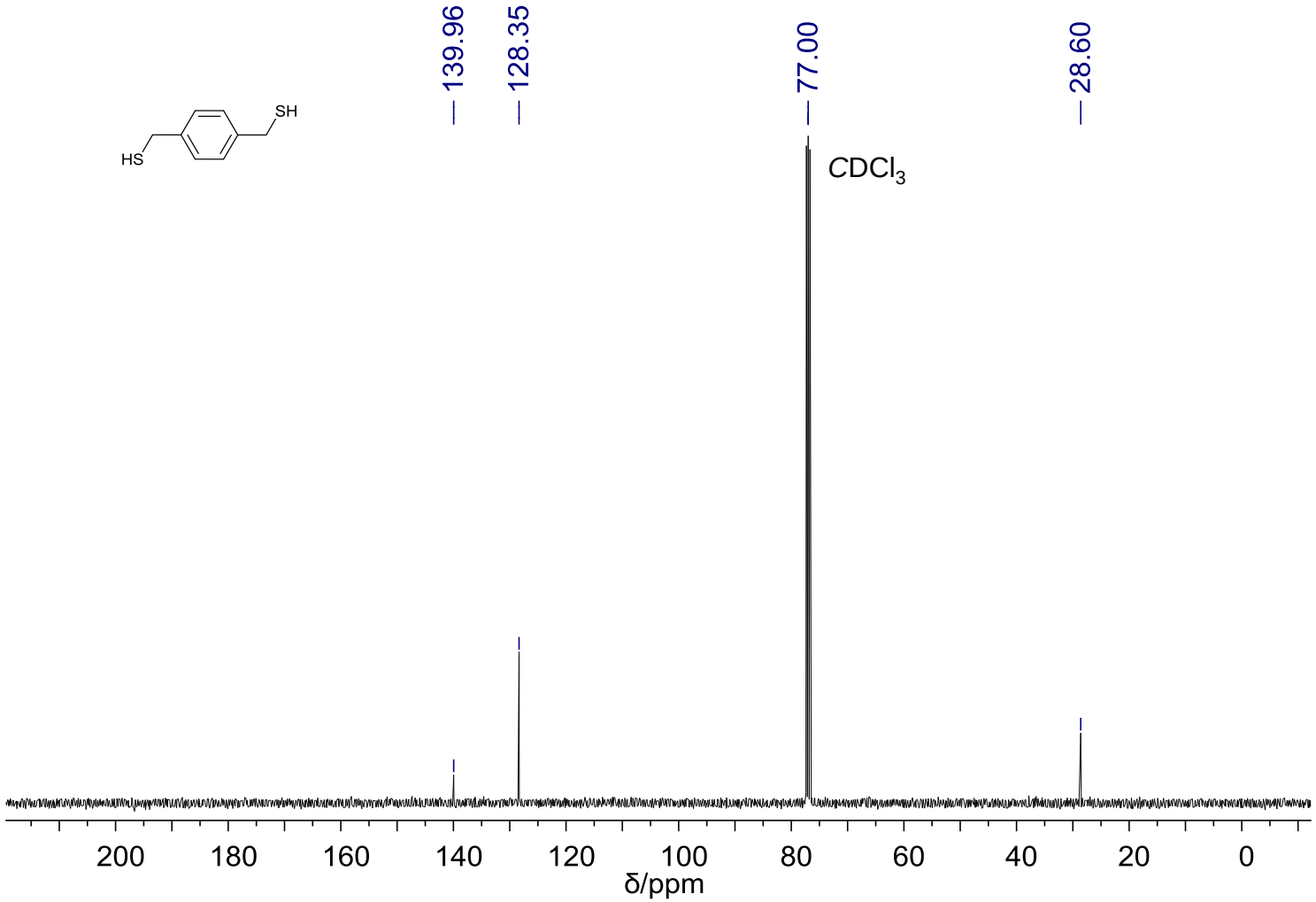
13. ^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 2-(Trimethylsilyl)phenyl Trifluoromethanesulfonate (7)



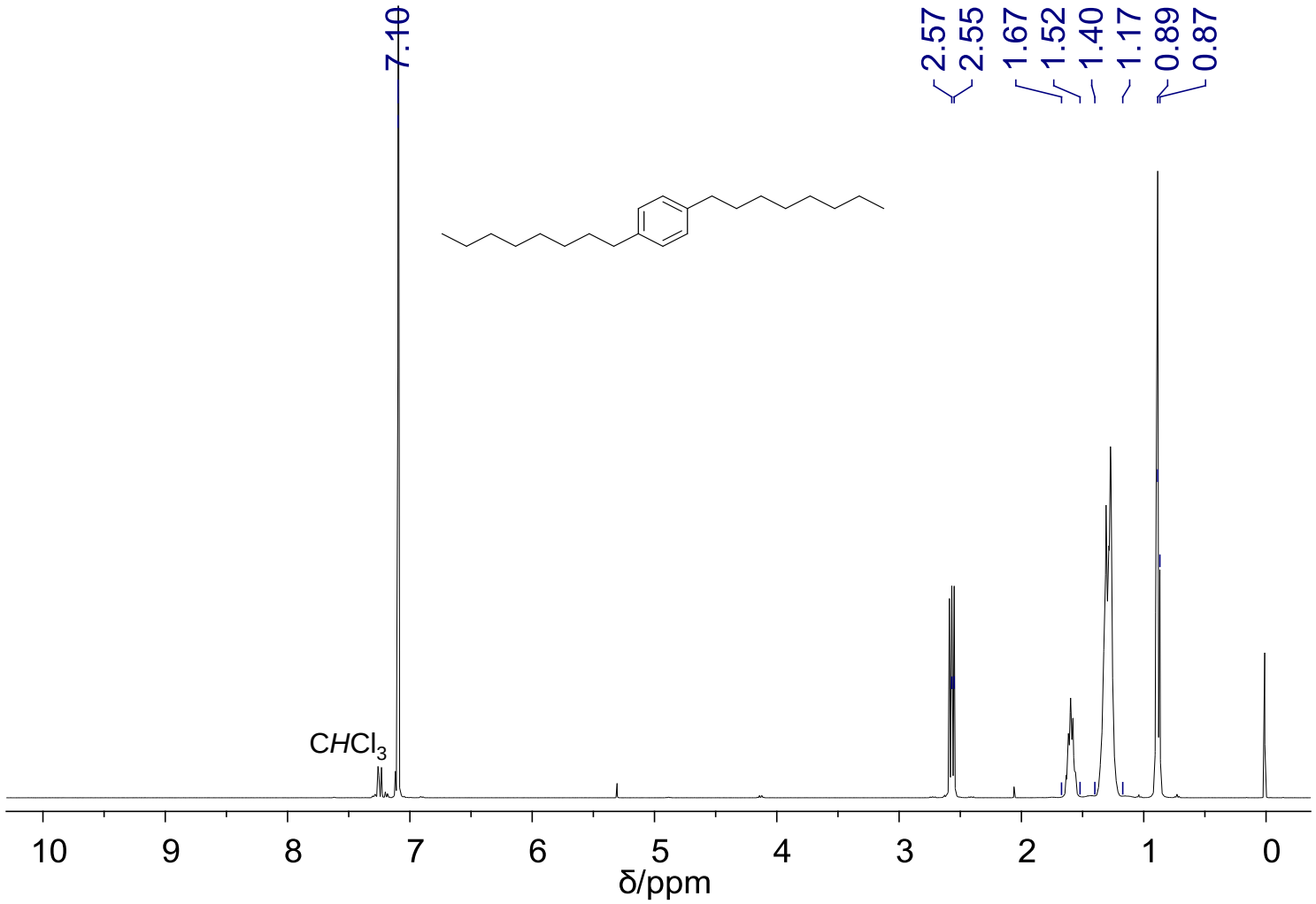
14. ^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1,4-Benzenedimethanethiol (11)



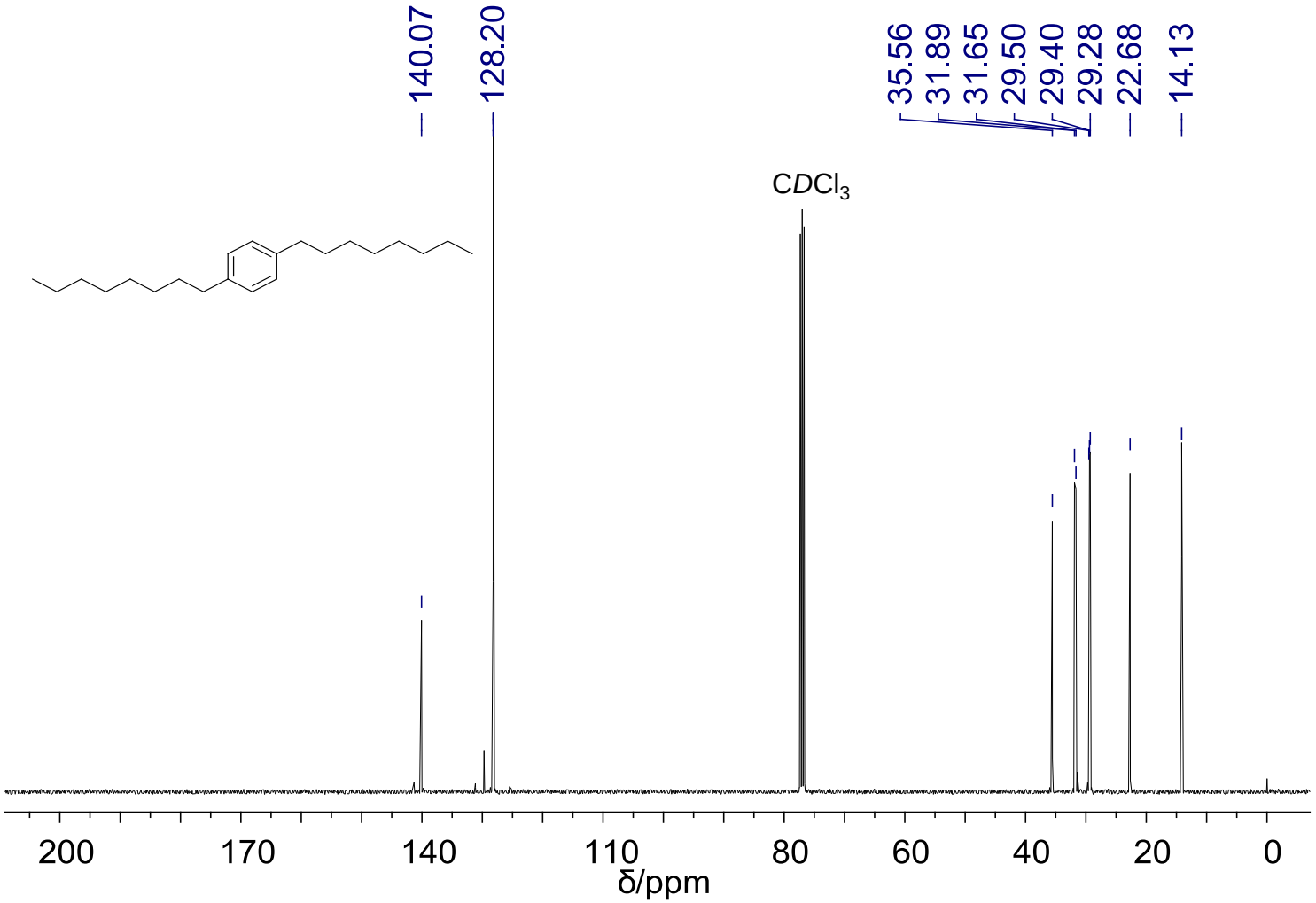
15. ^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1,4-Benzenedimethanethiol (11)



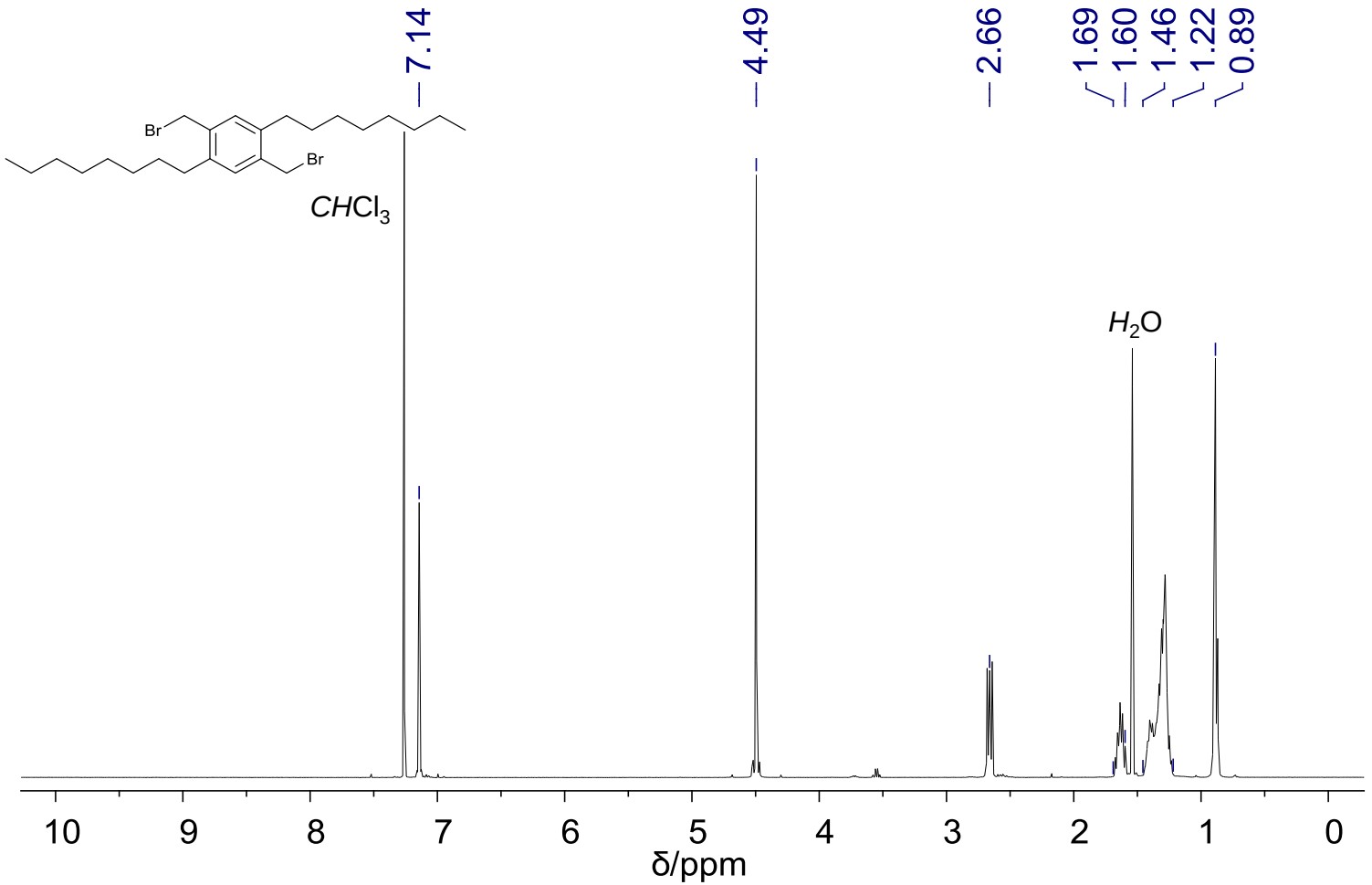
16. ^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1,4-Dioctylbenzene (8)



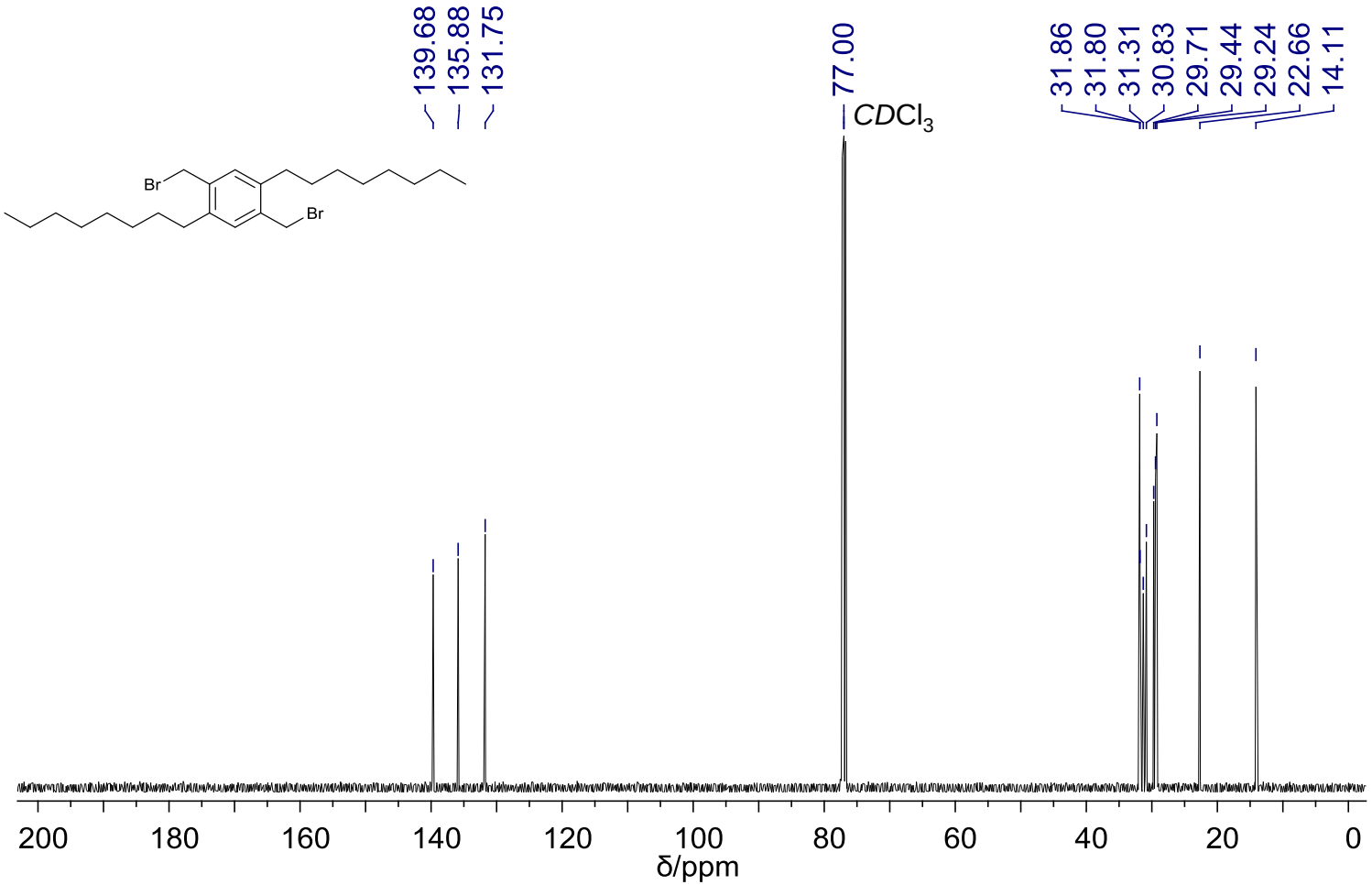
17. ^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 1,4-Dioctylbenzene (8)



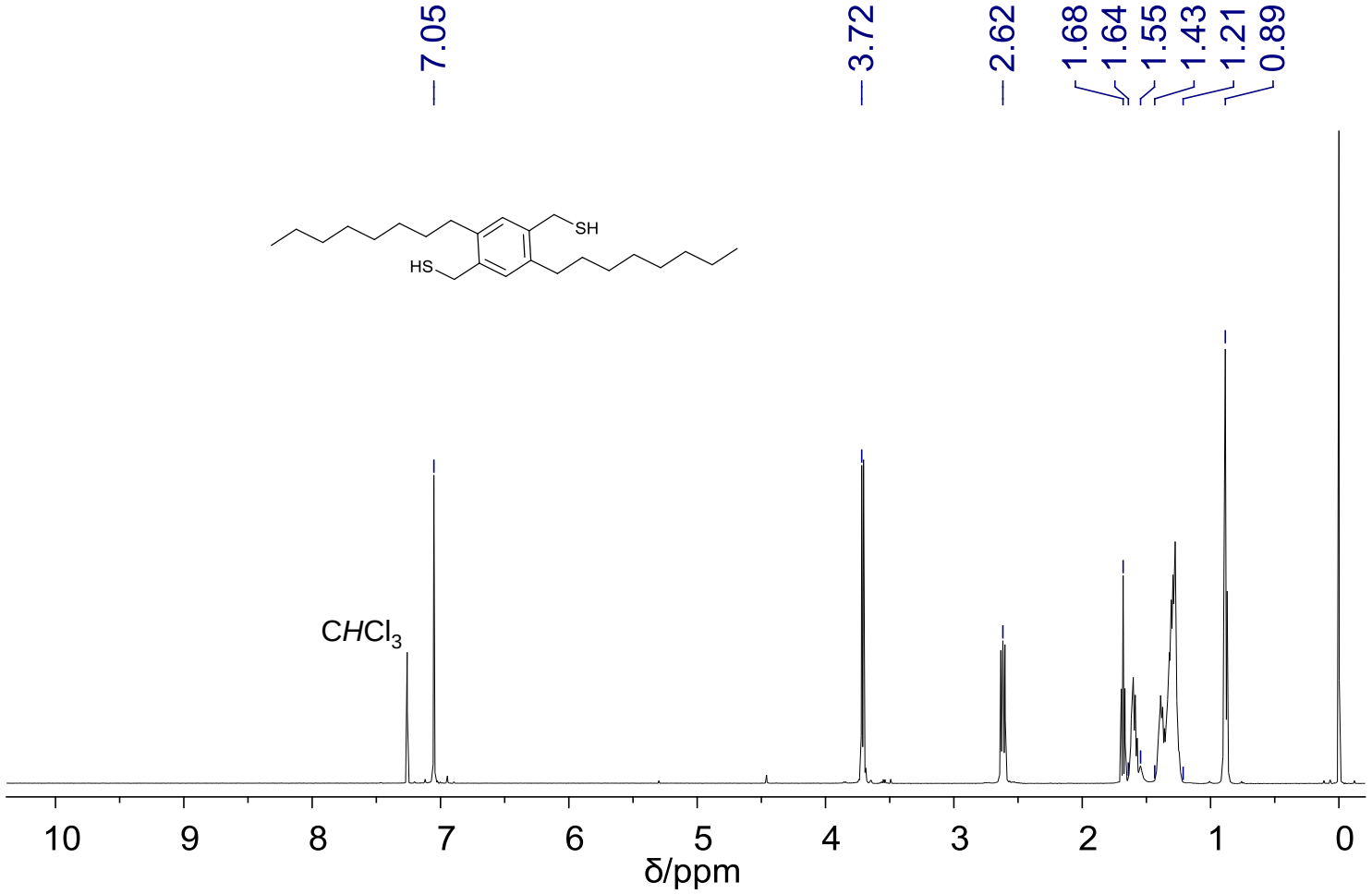
18. ^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of 1,4-Bis(bromomethyl)-2,5-bis(octyl)benzene (9)



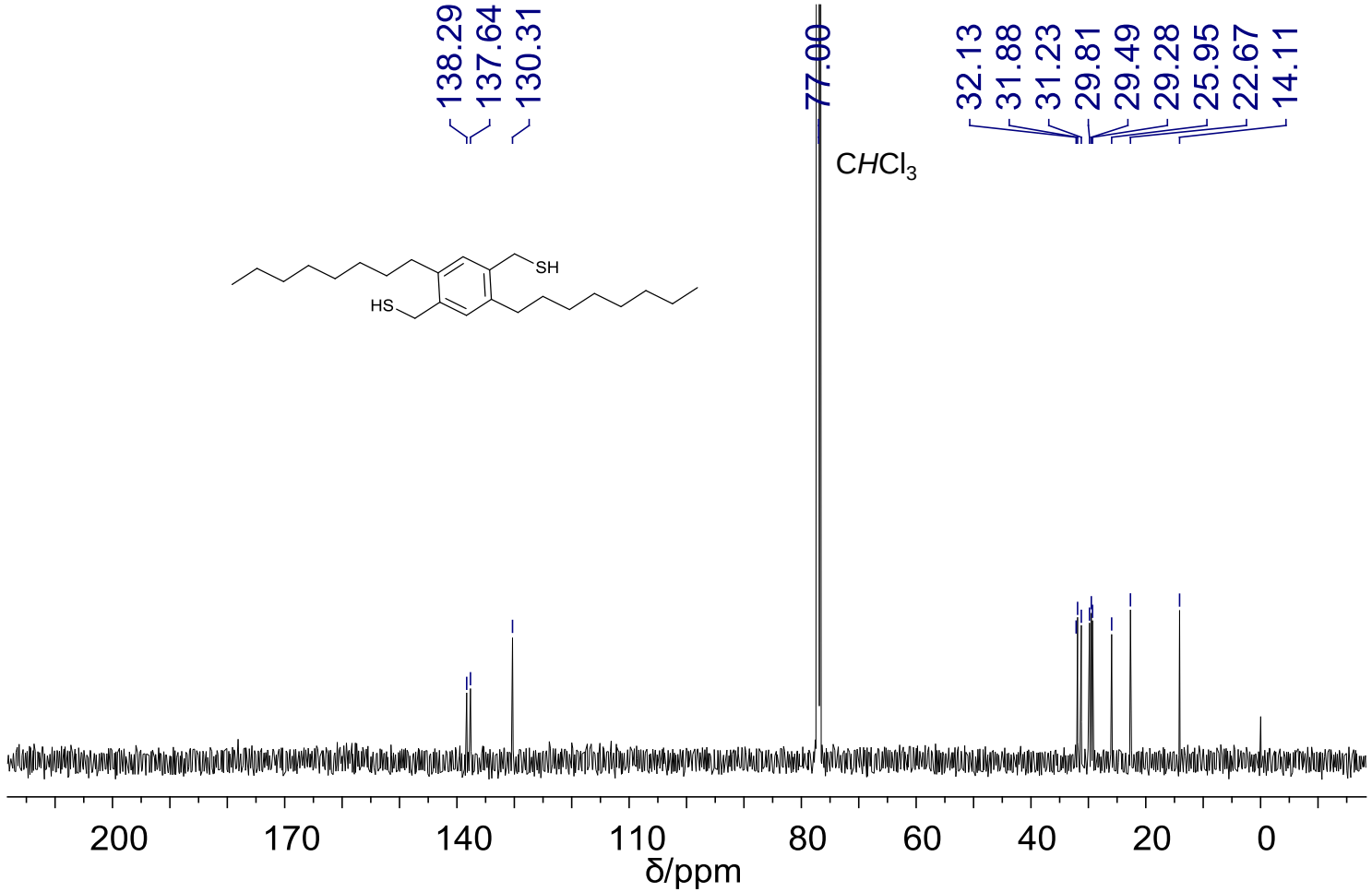
19. ^{13}C NMR ($CDCl_3$, 126 MHz) Spectrum of 1,4-Bis(bromomethyl)-2,5-bis(octyl)benzene (9)



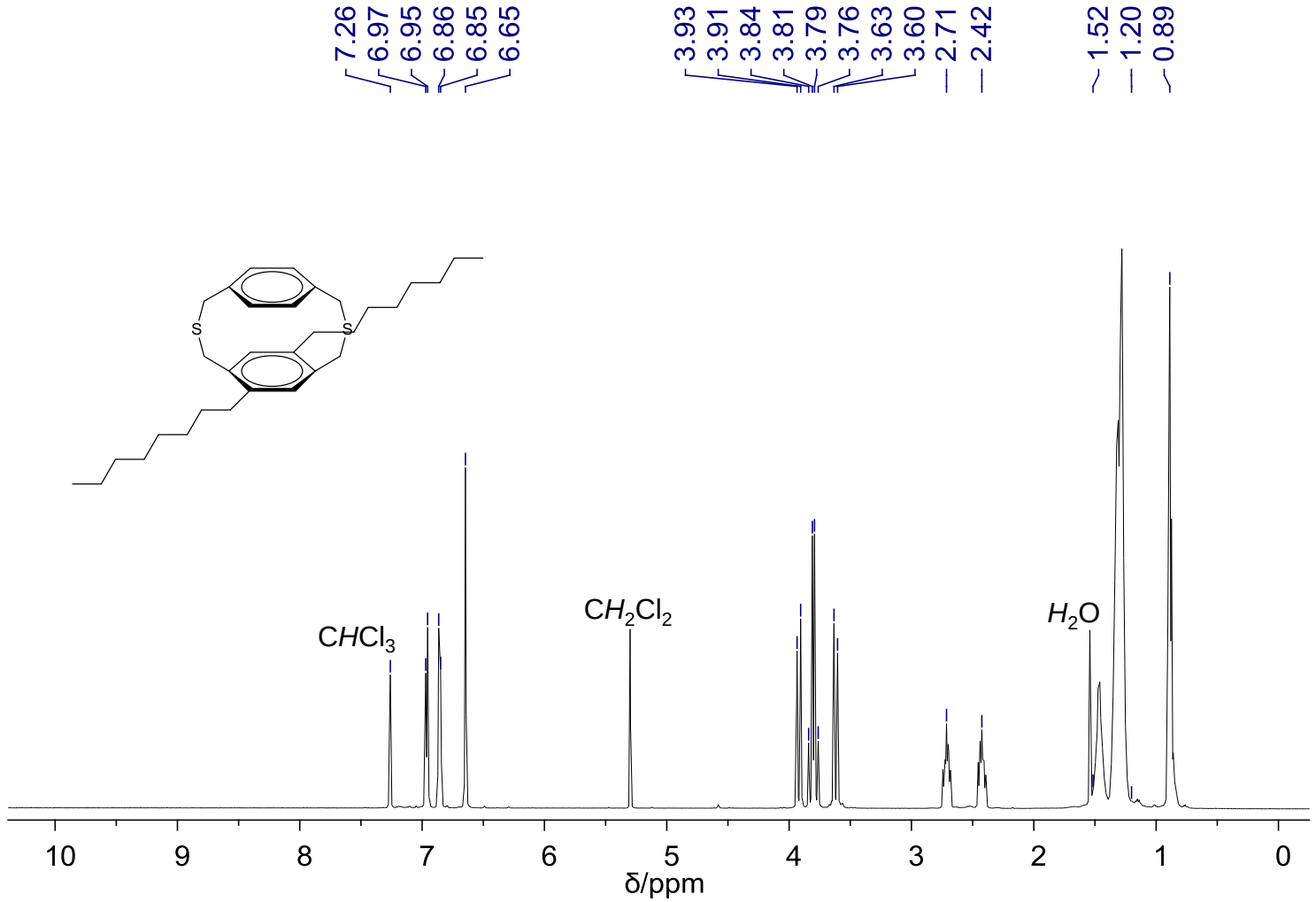
20. ^{1}H NMR ($CDCl_3$, 500 MHz) Spectrum of 1,4-Bis(thiolatomethyl)-2,5-bis(octyl)benzene (10)



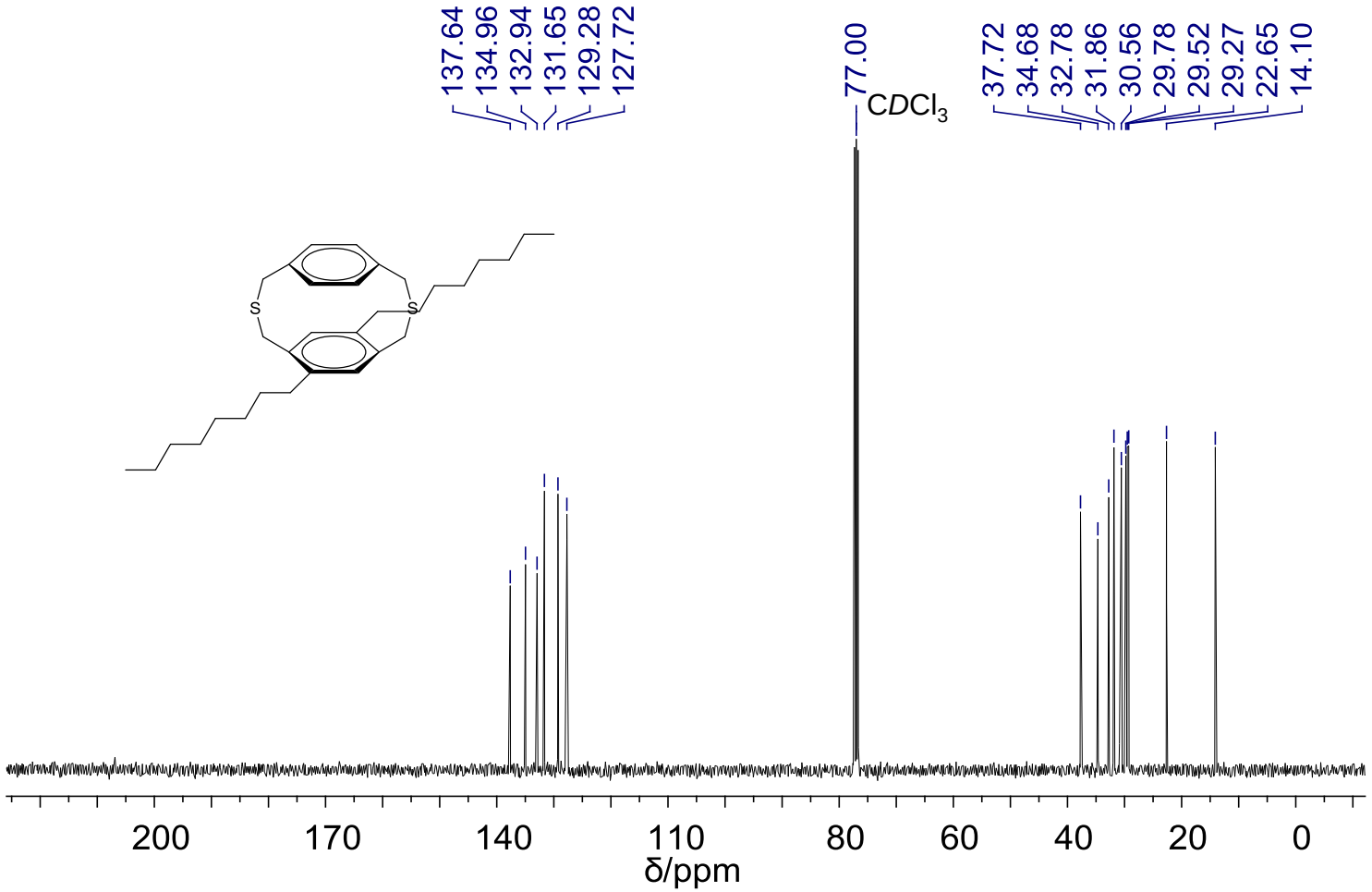
21. ^{13}C NMR ($CDCl_3$, 126 MHz) Spectrum of 1,4-Bis(thiolatomethyl)-2,5-bis(octyl)benzene (10)



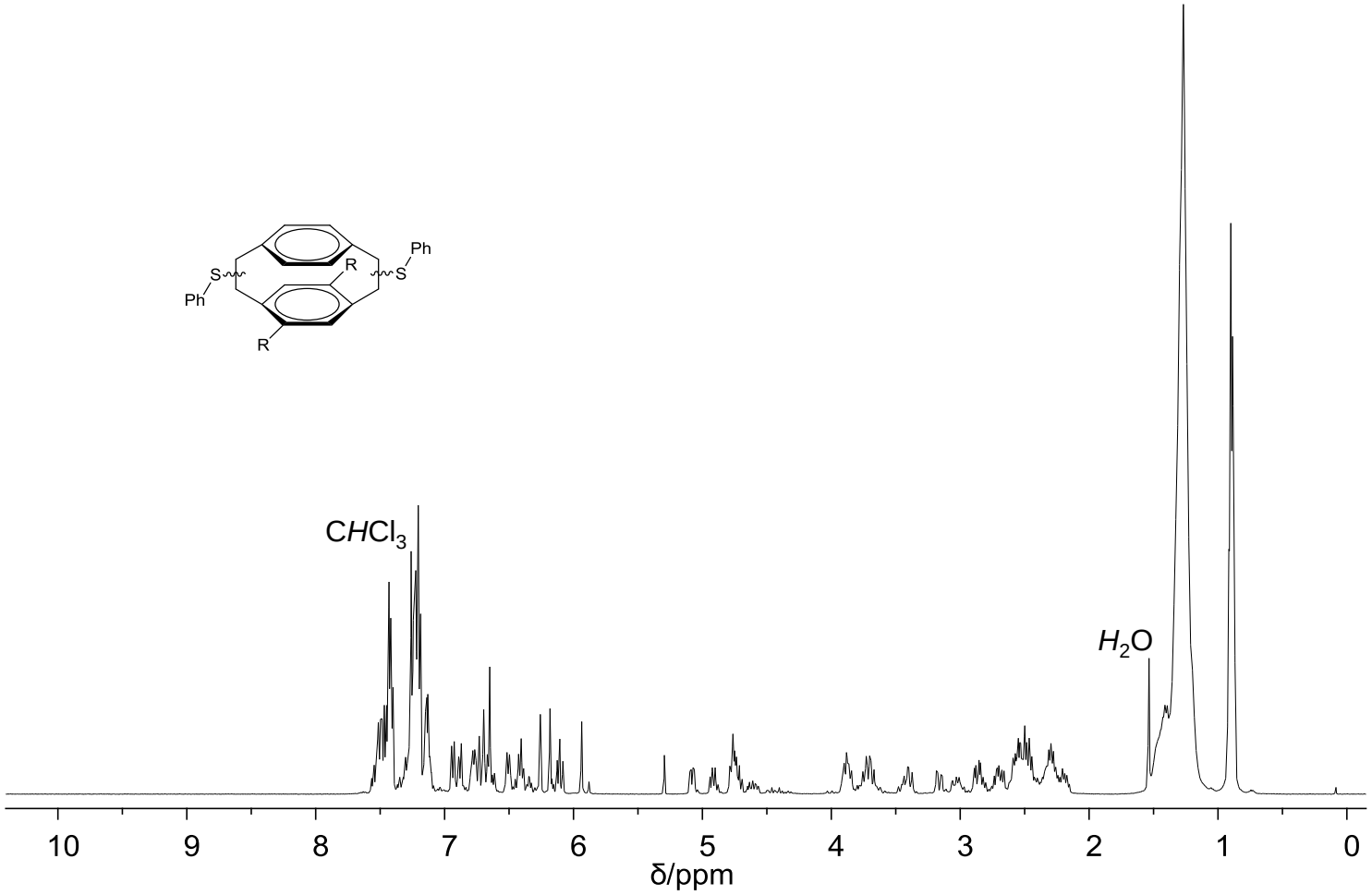
22. ^{1}H NMR ($CDCl_3$, 500 MHz) Spectrum of 5,8-Dioctyl-2,11-dithia[3.3]paracyclophane (12)



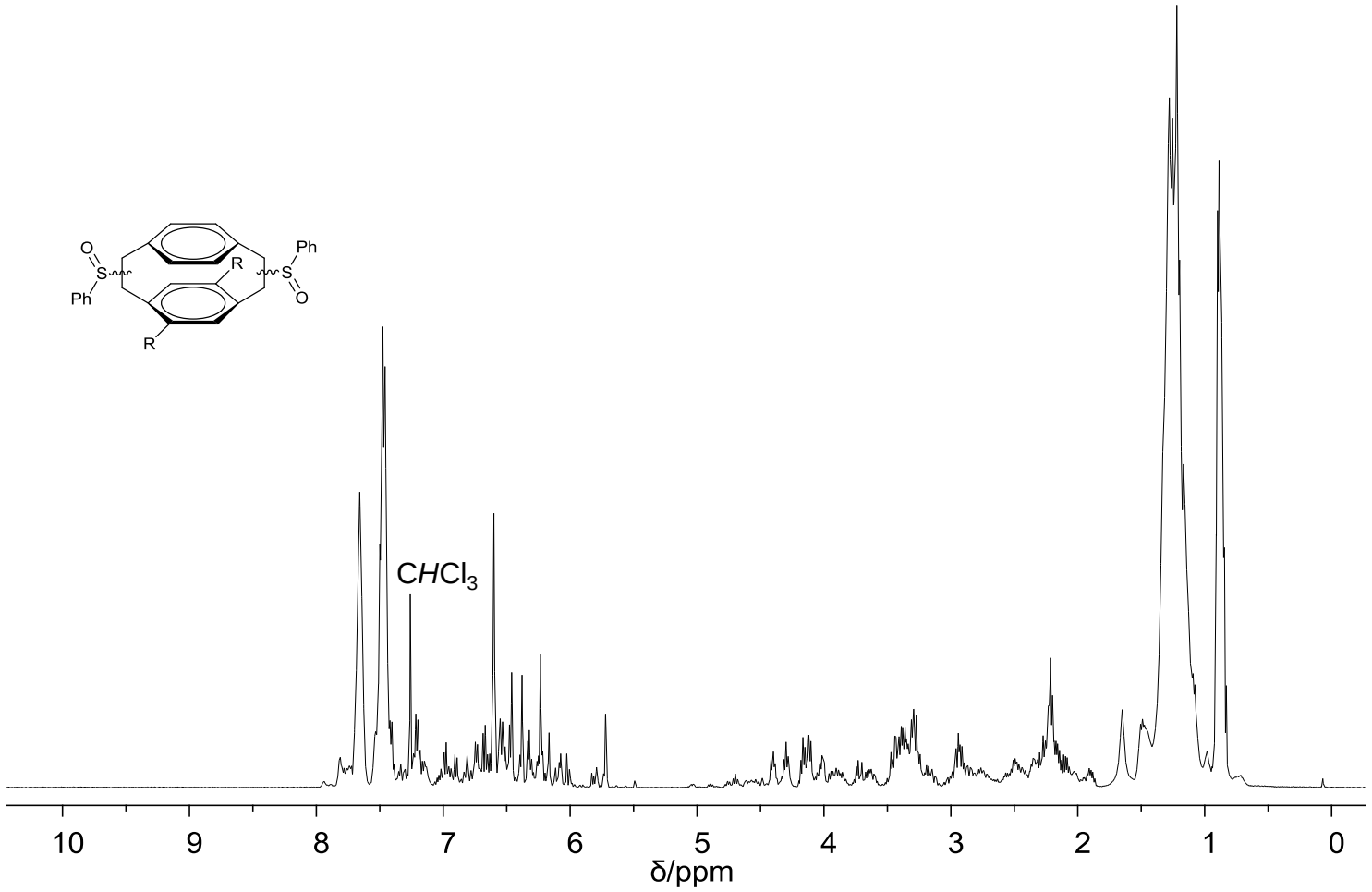
23. ^{13}C NMR ($CDCl_3$, 101 MHz) Spectrum of 5,8-Dioctyl-2,11-dithia[3.3]paracyclophane (12)



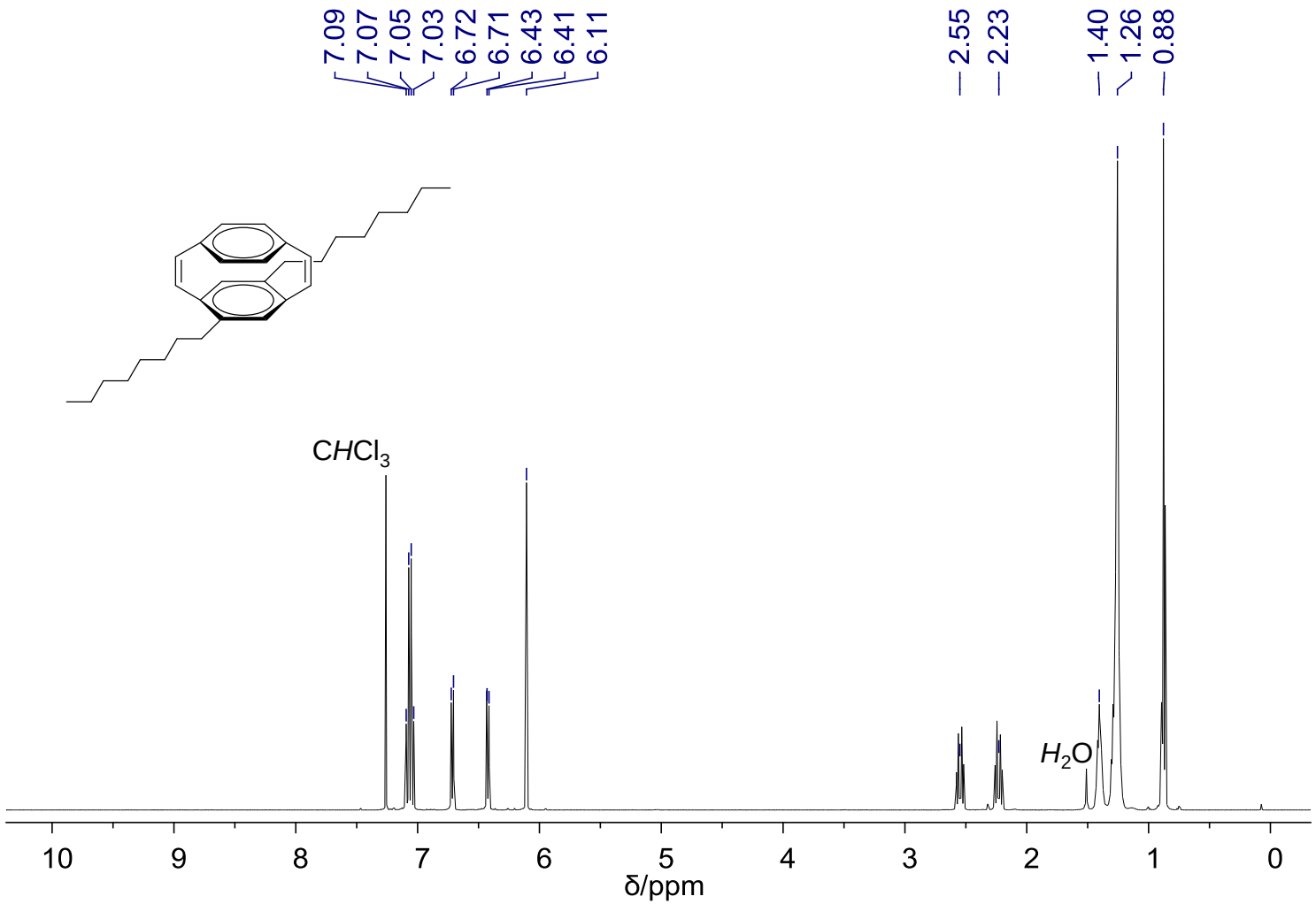
24. ^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of Benzyne Induced Stevens Rearrangement of Compound 12 (13)



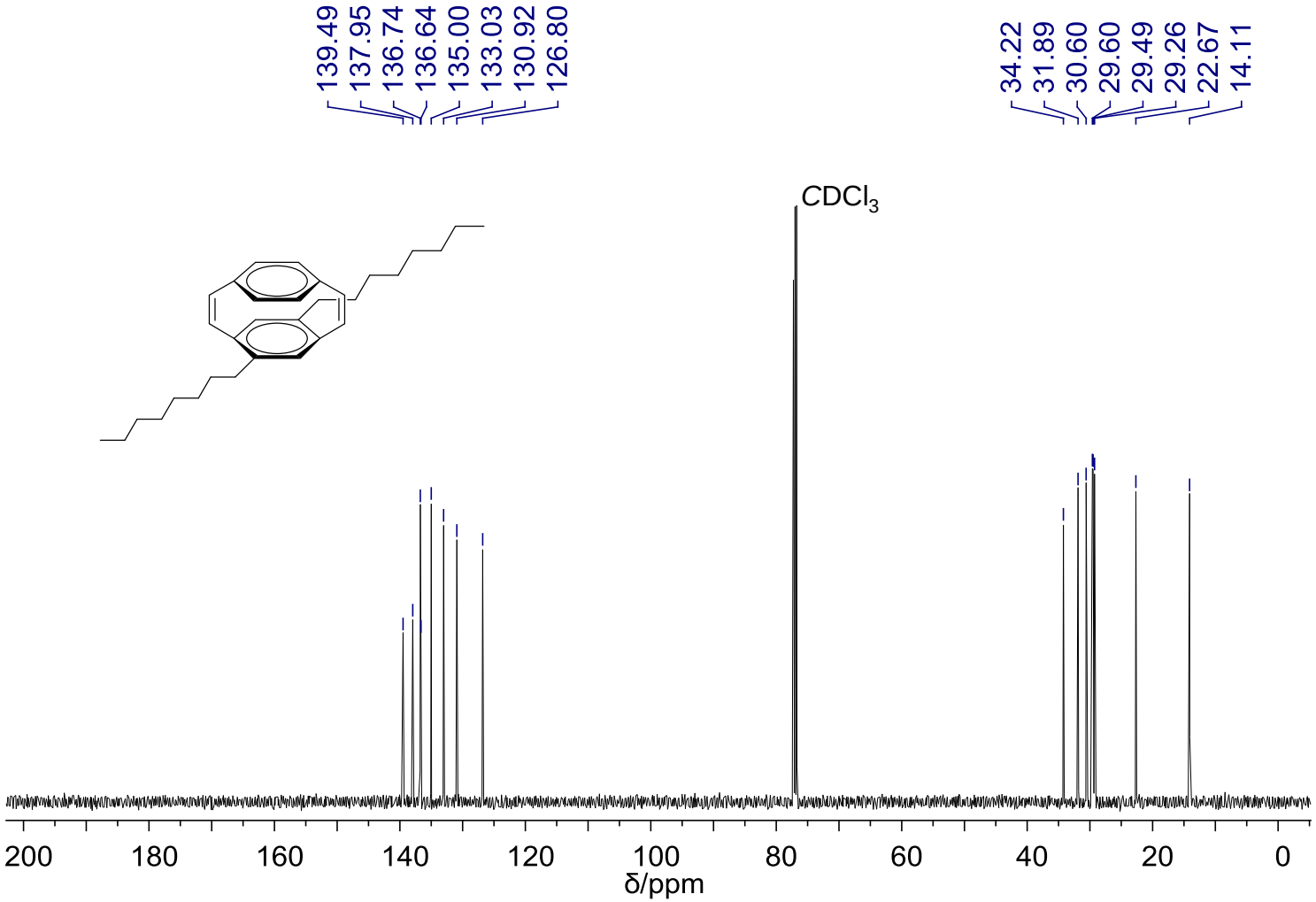
25. ^{1}H NMR ($CDCl_3$, 500 MHz) Spectrum of Oxidation of Phenyl Sulfides of Compound 13 (14)



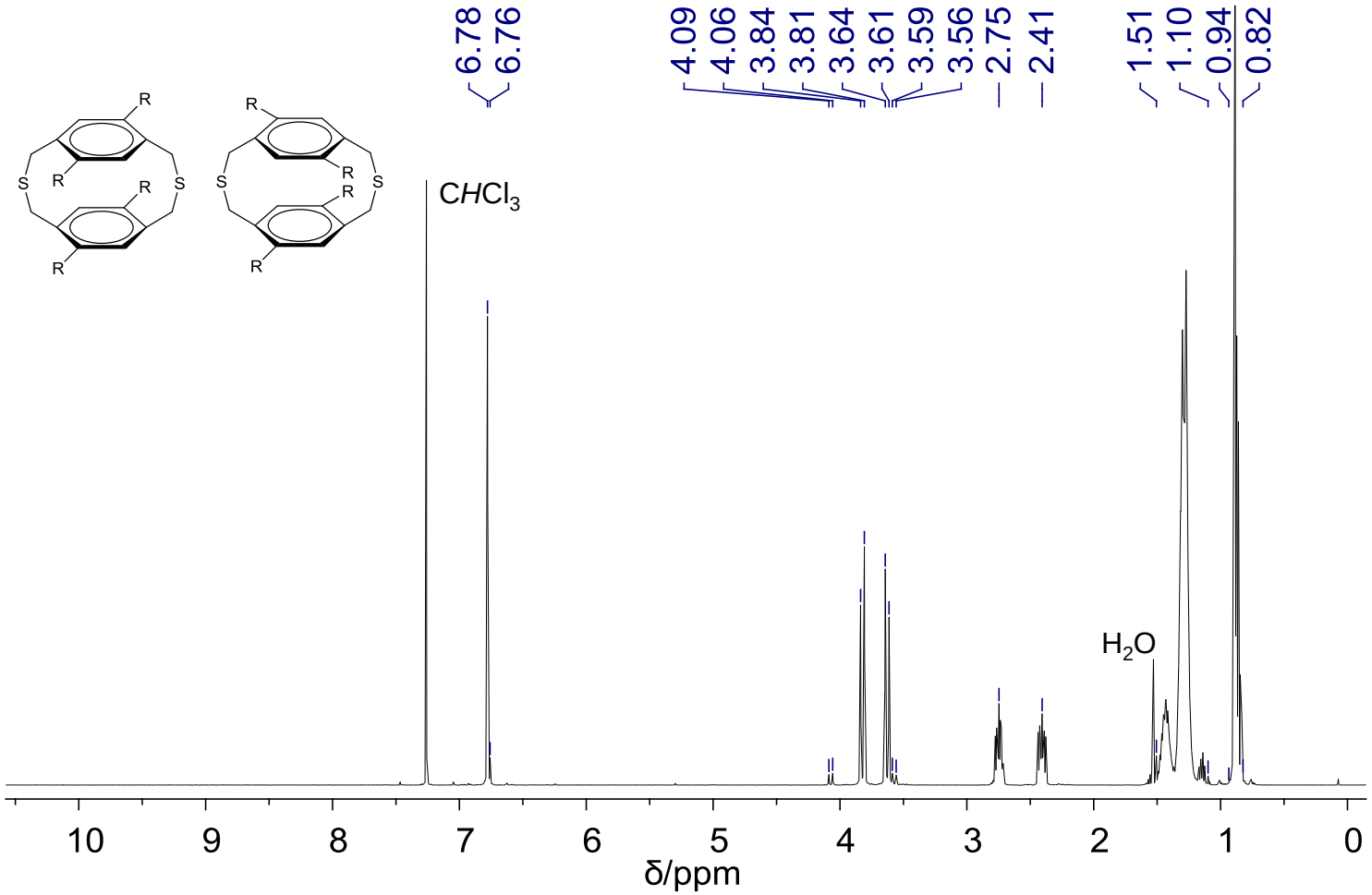
26. ^{1}H NMR ($CDCl_3$, 500 MHz) Spectrum of 4,7-Dioctyl-[2.2]paracyclophane-1,9-diene (15)



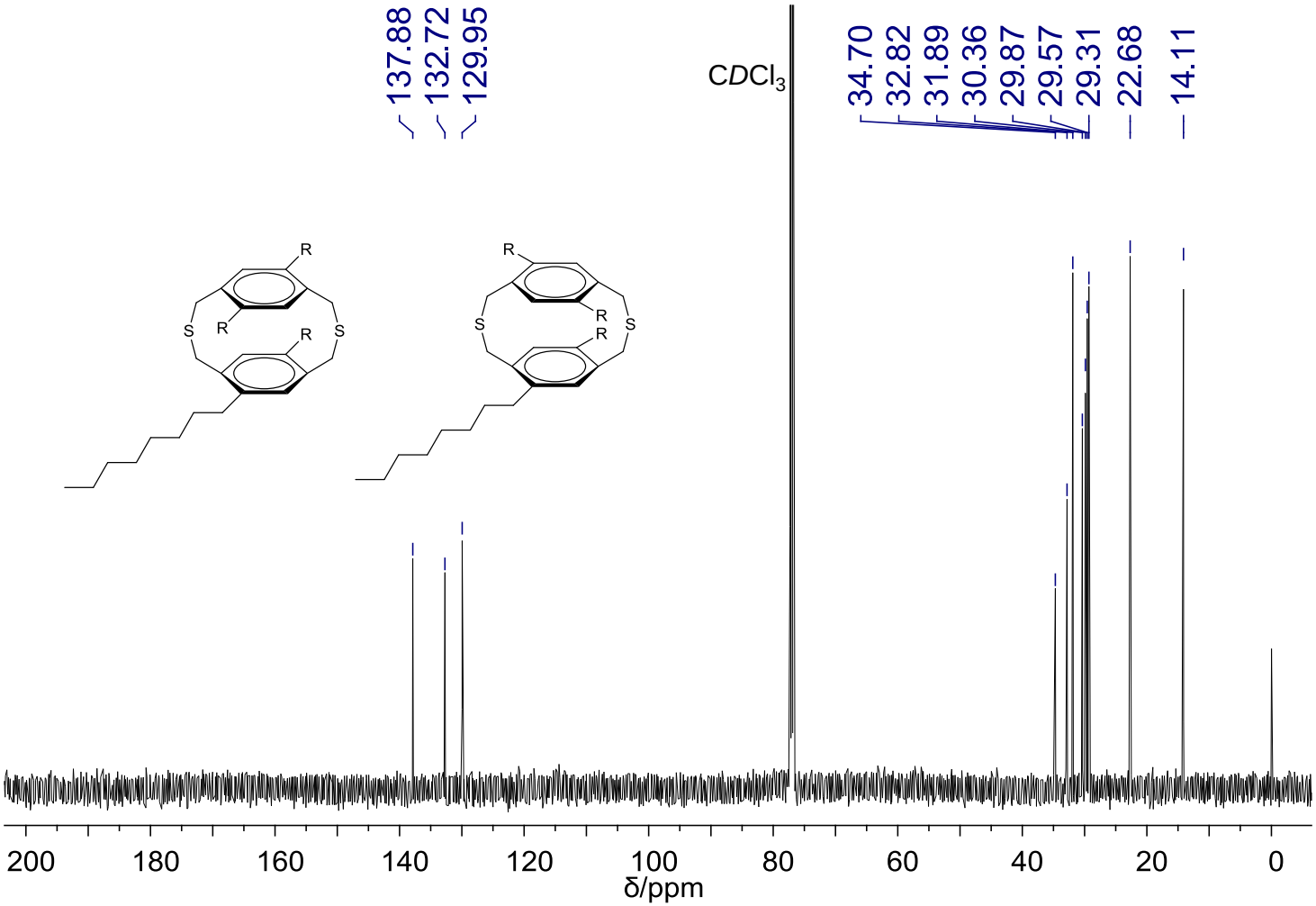
27. ^{13}C NMR ($CDCl_3$, 126 MHz) Spectrum of 4,7-Dioctyl-[2.2]paracyclophane-1,9-diene (15)



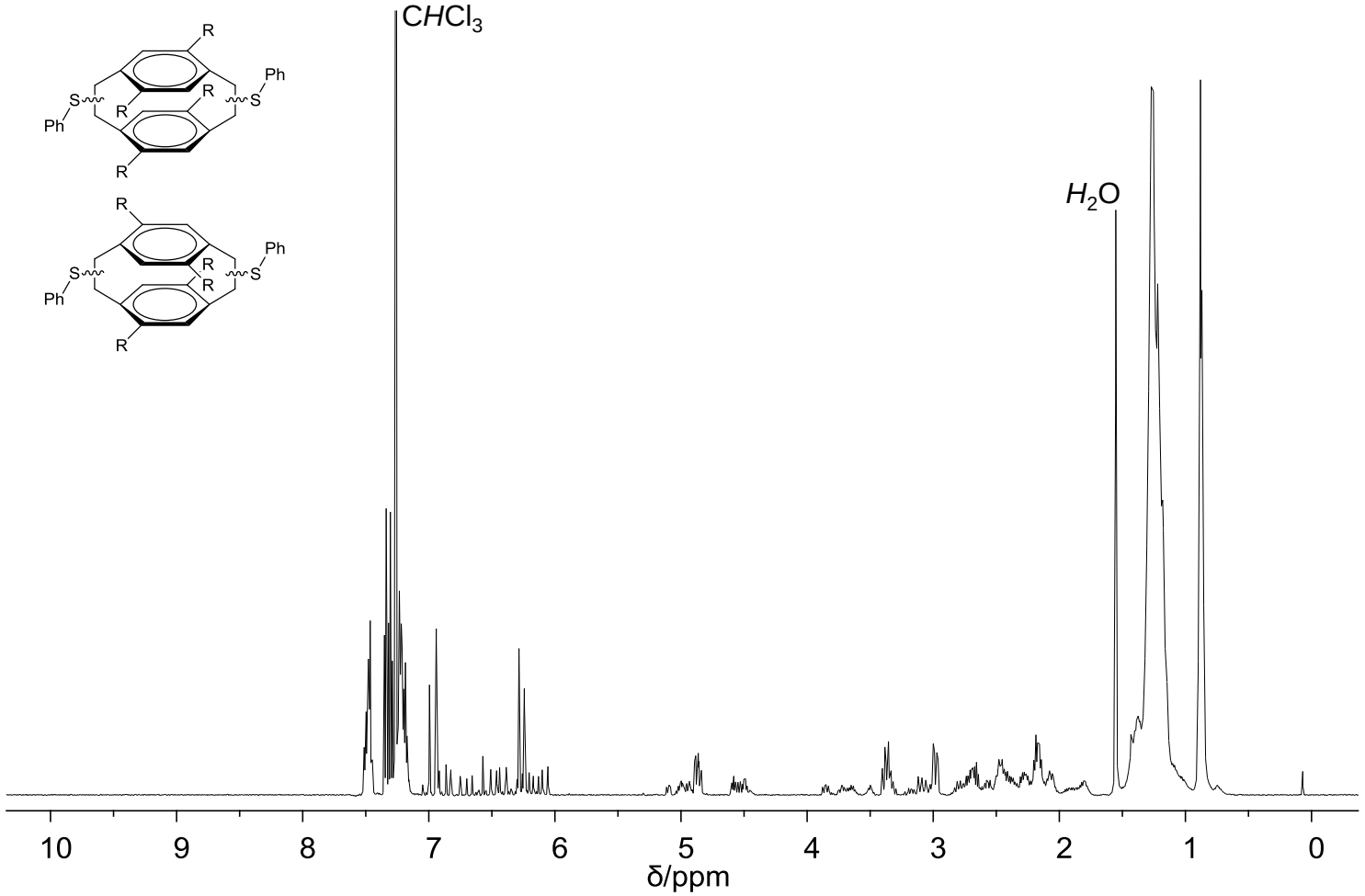
28. ^{1}H NMR ($CDCl_3$, 500 MHz) Spectrum of 5,8,14,17-Tetraoctyl-2,11-dithia[3.3]paracyclophane (16) and 6,9,14,17-Tetraoctyl-2,11-dithia[3.3]paracyclophane (17)



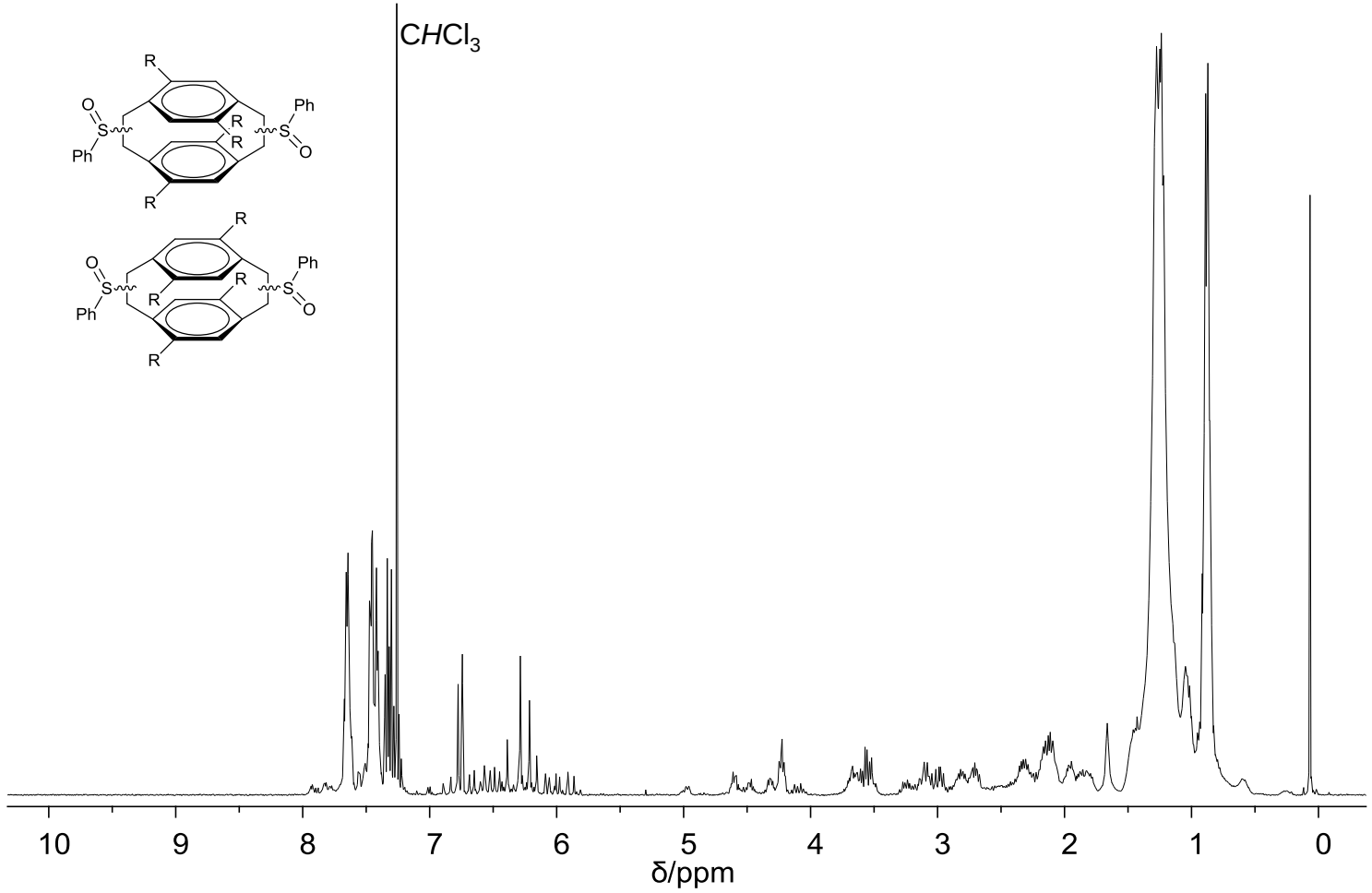
29. ^{13}C NMR ($CDCl_3$, 126 MHz) Spectrum of 5,8,14,17-Tetraoctyl-2,11-dithia[3.3]paracyclophane (16) and 6,9,14,17-Tetraoctyl-2,11-dithia[3.3]paracyclophane (17)



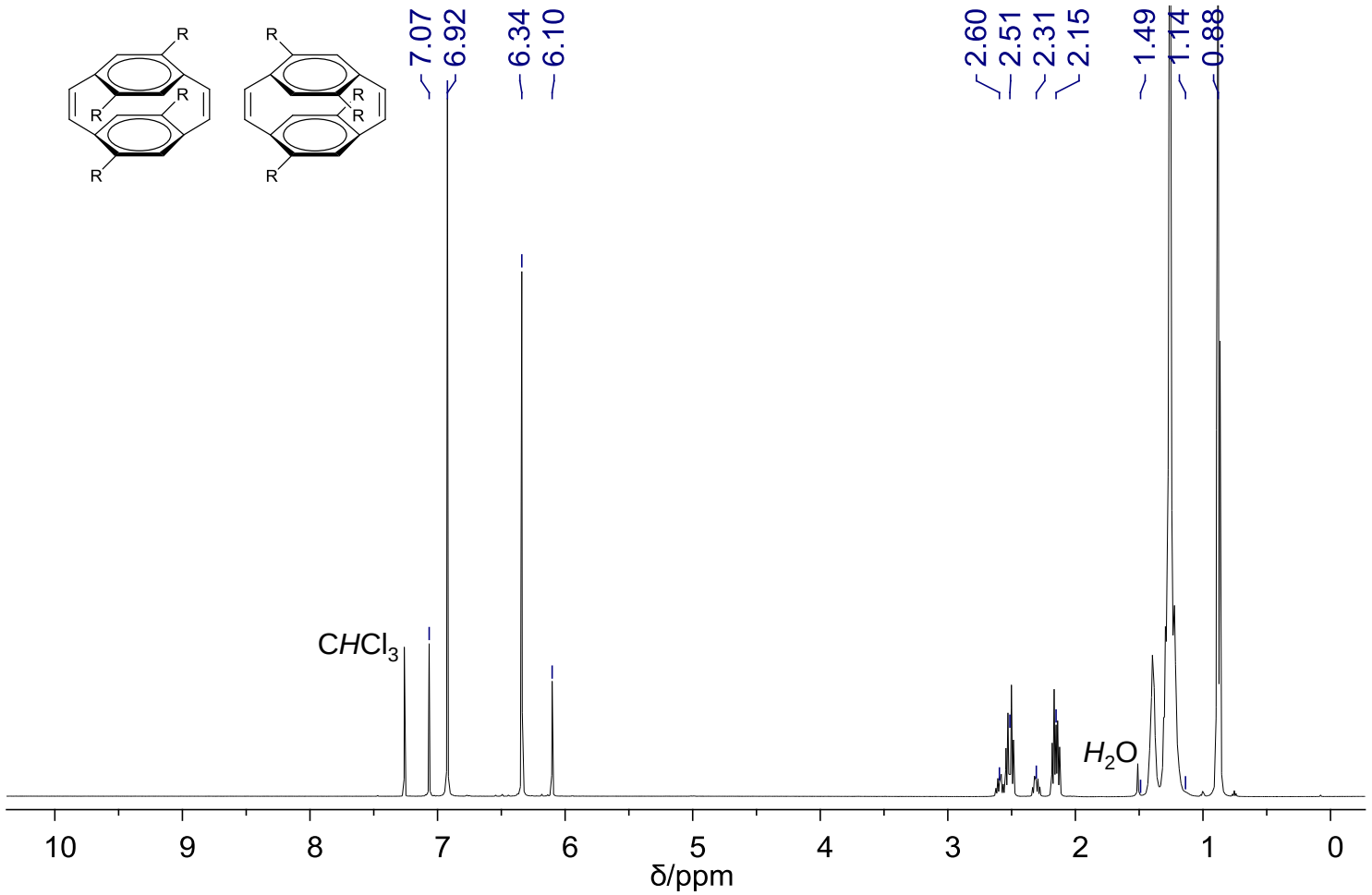
30. ^{1}H NMR ($CDCl_3$, 500 MHz) Spectrum of Benzyne Induced Stevens Rearrangement of Mixture of Isomers 16 and 17 (18)



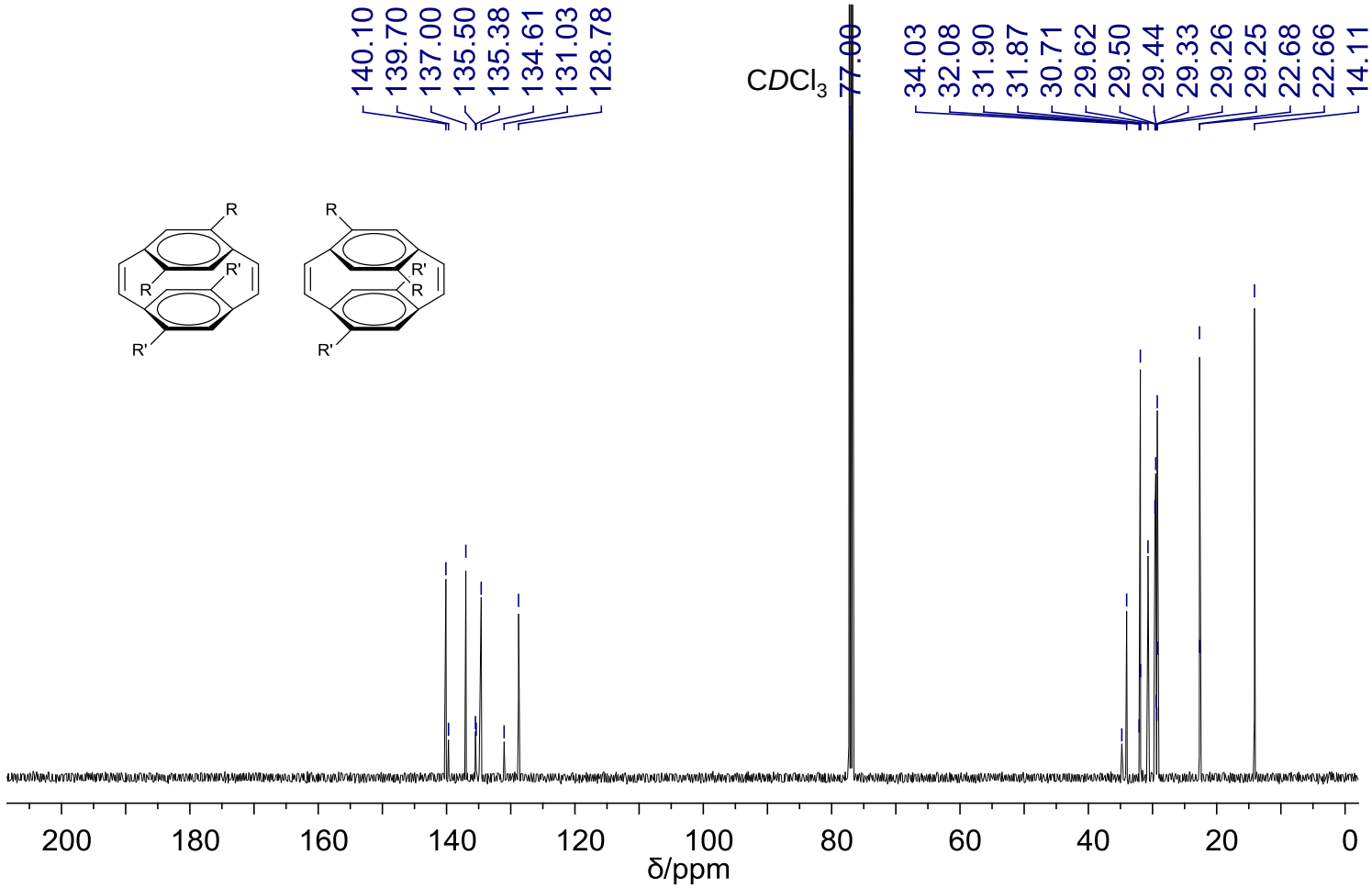
31. ^{1}H NMR ($CDCl_3$, 400 MHz) Spectrum of Oxidation of Phenyl Sulfides of Compound 18 (19)



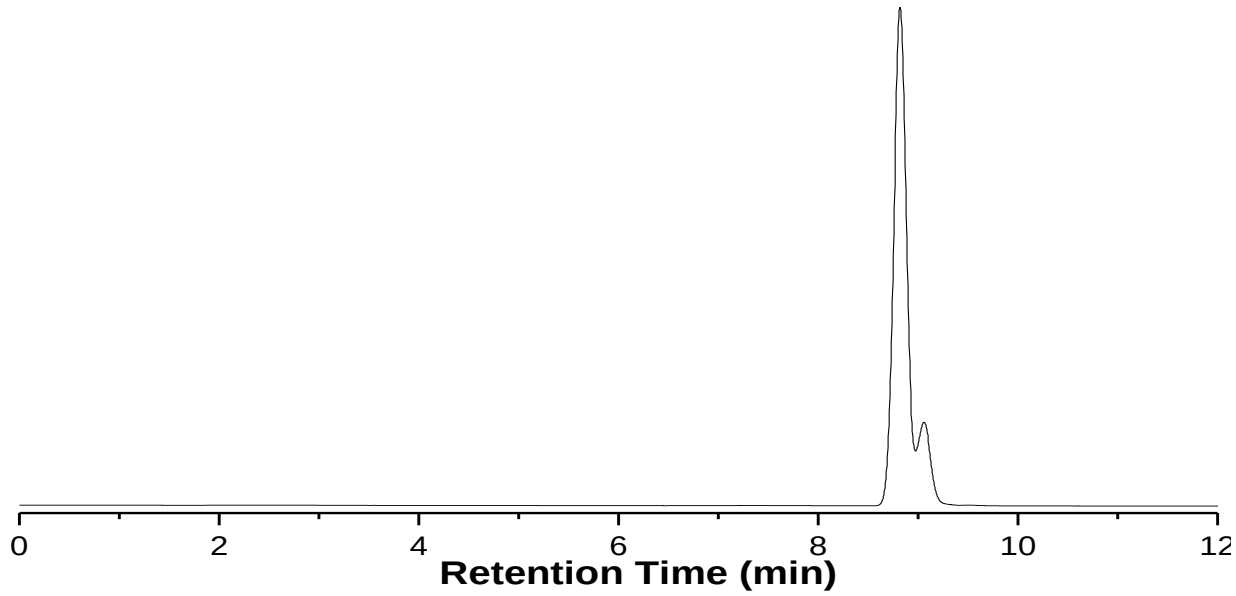
32. ^{1}H NMR ($CDCl_3$, 500 MHz) Spectrum of 4,7,12,15-Tetraoctyl-[2.2]paracyclophane-1,9-diene (20) and 5,8,12,15-Tetraoctyl-[2.2]paracyclophane-1,9-diene (21)



33. ^{13}C NMR ($CDCl_3$, 126 MHz) Spectrum of 4,7,12,15-Tetraoctyl-[2.2]paracyclophane-1,9-diene (20) and 5,8,12,15-Tetraoctyl-[2.2]paracyclophane-1,9-diene (21)



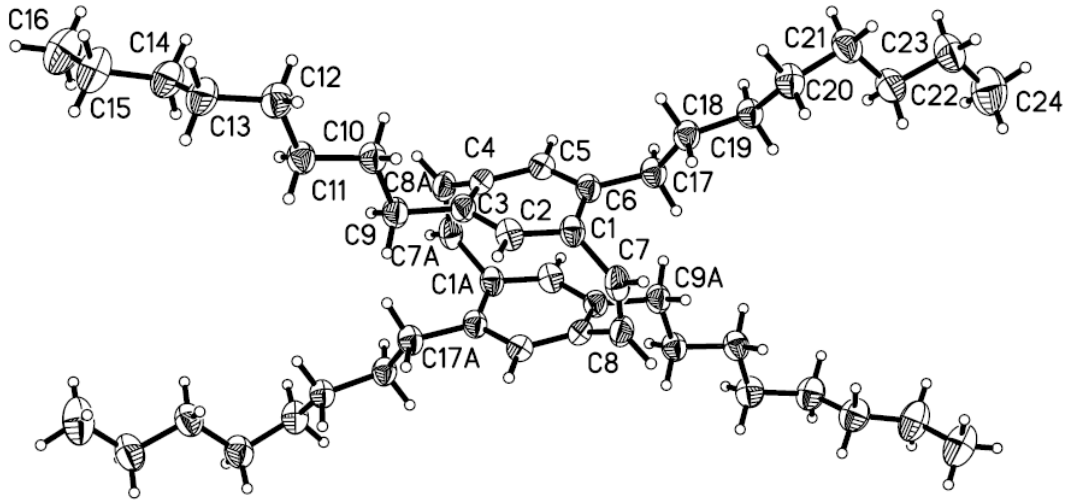
34. HPLC trace of Mixture of 4,7,12,15-Tetraoctyl-[2.2]paracyclophane-1,9-diene (20) and 5,8,12,15-Tetraoctyl-[2.2]paracyclophane-1,9-diene (21)



Flow rate: 0.5 ml min^{-1}

Wavelength = 254 nm
100% Hexane

35. Crystal data and Structure Refinement for 4,7,12,15-Tetraoctyl-[2.2]paracyclophane-1,9-diene (20)



Identification code	z:\s2318b\work\twin5
Empirical formula	C_{48} H_{76}
Formula weight	653.09
Temperature	230(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 17.926(12) A alpha = 90 deg. b = 14.393(10) A beta = 93.891(14) deg. c = 8.191(6) A gamma = 90 deg.
Volume	2109(3) A^3
Z, Calculated density	2, 1.029 Mg/m^3
Absorption coefficient	0.057 mm^-1
F(000)	728

Crystal size	0.60 x 0.60 x 0.60 mm
Theta range for data collection	1.82 to 25.03 deg.
Limiting indices	0<=h<=21, -17<=k<=0, -9<=l<=9
Reflections collected / unique	6592 / 6592 [R(int) = 0.0000]
Completeness to theta = 25.03	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9667 and 0.9667
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6592 / 0 / 220
Goodness-of-fit on F^2	0.958
Final R indices [I>2sigma(I)]	R1 = 0.0538, wR2 = 0.1449
R indices (all data)	R1 = 0.0719, wR2 = 0.1546
Largest diff. peak and hole	0.231 and -0.161 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s2318btw. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	4875(1)	3649(1)	5123(2)	37(1)
C(2)	5561(1)	3763(1)	4445(2)	40(1)
C(3)	5662(1)	4367(1)	3147(2)	38(1)
C(4)	5051(1)	4909(1)	2584(1)	37(1)
C(5)	4348(1)	4621(1)	2987(1)	39(1)
C(6)	4240(1)	3978(1)	4218(1)	36(1)
C(7)	4835(1)	3422(1)	6908(2)	43(1)
C(8)	4852(1)	4114(1)	8000(2)	44(1)
C(9)	6414(1)	4468(1)	2455(2)	43(1)
C(10)	6530(1)	3767(1)	1100(2)	40(1)
C(11)	7259(1)	3884(1)	289(2)	43(1)
C(12)	7368(1)	3181(1)	-1055(2)	49(1)
C(13)	8075(1)	3312(1)	-1960(2)	53(1)
C(14)	8069(1)	4155(1)	-3080(2)	55(1)
C(15)	8744(1)	4237(1)	-4072(2)	70(1)
C(16)	8724(1)	5055(1)	-5236(2)	81(1)
C(17)	3465(1)	3730(1)	4662(2)	39(1)
C(18)	3267(1)	2714(1)	4373(2)	39(1)
C(19)	2456(1)	2507(1)	4629(2)	38(1)
C(20)	2268(1)	1480(1)	4545(2)	47(1)

C(21)	1441(1)	1254(1)	4426(2)	52(1)
C(22)	1011(1)	1631(1)	5797(2)	52(1)
C(23)	207(1)	1310(1)	5775(2)	65(1)
C(24)	-223(1)	1719(2)	7102(3)	89(1)

Table 3. Bond lengths [A] and angles [deg] for s2318btw.

C(1)-C(2)	1.3921(18)
C(1)-C(6)	1.3981(18)
C(1)-C(7)	1.505(2)
C(2)-C(3)	1.3951(18)
C(2)-H(2)	0.9500
C(3)-C(4)	1.3970(18)
C(3)-C(9)	1.5043(18)
C(4)-C(5)	1.3876(18)
C(4)-C(8)#1	1.500(2)
C(5)-C(6)	1.3925(18)
C(5)-H(5)	0.9500
C(6)-C(17)	1.5033(18)
C(7)-C(8)	1.338(2)
C(7)-H(7)	0.9500
C(8)-C(4)#1	1.500(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.5246(18)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.5156(18)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.5179(19)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.523(2)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.521(2)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.507(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.513(2)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(18)	1.5194(19)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.5136(18)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.5163(19)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(21)	1.514(2)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900

C(21)-C(22)	1.506(2)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.512(2)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.496(2)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800

C(2)-C(1)-C(6)	117.27(12)
C(2)-C(1)-C(7)	120.97(11)
C(6)-C(1)-C(7)	119.86(11)
C(1)-C(2)-C(3)	122.77(12)
C(1)-C(2)-H(2)	118.6
C(3)-C(2)-H(2)	118.6
C(2)-C(3)-C(4)	117.39(11)
C(2)-C(3)-C(9)	120.92(11)
C(4)-C(3)-C(9)	121.59(12)
C(5)-C(4)-C(3)	117.32(12)
C(5)-C(4)-C(8)#1	118.87(11)
C(3)-C(4)-C(8)#1	121.59(11)
C(4)-C(5)-C(6)	122.97(11)
C(4)-C(5)-H(5)	118.5
C(6)-C(5)-H(5)	118.5
C(5)-C(6)-C(1)	117.41(11)
C(5)-C(6)-C(17)	120.63(11)
C(1)-C(6)-C(17)	121.64(12)
C(8)-C(7)-C(1)	119.18(12)
C(8)-C(7)-H(7)	120.4
C(1)-C(7)-H(7)	120.4
C(7)-C(8)-C(4)#1	118.87(12)
C(7)-C(8)-H(8)	120.6
C(4)#1-C(8)-H(8)	120.6
C(3)-C(9)-C(10)	112.35(10)
C(3)-C(9)-H(9A)	109.1
C(10)-C(9)-H(9A)	109.1
C(3)-C(9)-H(9B)	109.1
C(10)-C(9)-H(9B)	109.1
H(9A)-C(9)-H(9B)	107.9
C(11)-C(10)-C(9)	114.20(10)
C(11)-C(10)-H(10A)	108.7
C(9)-C(10)-H(10A)	108.7
C(11)-C(10)-H(10B)	108.7
C(9)-C(10)-H(10B)	108.7
H(10A)-C(10)-H(10B)	107.6
C(10)-C(11)-C(12)	113.67(11)
C(10)-C(11)-H(11A)	108.8
C(12)-C(11)-H(11A)	108.8
C(10)-C(11)-H(11B)	108.8
C(12)-C(11)-H(11B)	108.8
H(11A)-C(11)-H(11B)	107.7
C(11)-C(12)-C(13)	115.03(11)
C(11)-C(12)-H(12A)	108.5
C(13)-C(12)-H(12A)	108.5
C(11)-C(12)-H(12B)	108.5
C(13)-C(12)-H(12B)	108.5
H(12A)-C(12)-H(12B)	107.5

C(14)-C(13)-C(12)	114.87(12)
C(14)-C(13)-H(13A)	108.5
C(12)-C(13)-H(13A)	108.5
C(14)-C(13)-H(13B)	108.5
C(12)-C(13)-H(13B)	108.5
H(13A)-C(13)-H(13B)	107.5
C(15)-C(14)-C(13)	114.49(12)
C(15)-C(14)-H(14A)	108.6
C(13)-C(14)-H(14A)	108.6
C(15)-C(14)-H(14B)	108.6
C(13)-C(14)-H(14B)	108.6
H(14A)-C(14)-H(14B)	107.6
C(14)-C(15)-C(16)	114.53(14)
C(14)-C(15)-H(15A)	108.6
C(16)-C(15)-H(15A)	108.6
C(14)-C(15)-H(15B)	108.6
C(16)-C(15)-H(15B)	108.6
H(15A)-C(15)-H(15B)	107.6
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(6)-C(17)-C(18)	113.55(10)
C(6)-C(17)-H(17A)	108.9
C(18)-C(17)-H(17A)	108.9
C(6)-C(17)-H(17B)	108.9
C(18)-C(17)-H(17B)	108.9
H(17A)-C(17)-H(17B)	107.7
C(19)-C(18)-C(17)	112.59(10)
C(19)-C(18)-H(18A)	109.1
C(17)-C(18)-H(18A)	109.1
C(19)-C(18)-H(18B)	109.1
C(17)-C(18)-H(18B)	109.1
H(18A)-C(18)-H(18B)	107.8
C(18)-C(19)-C(20)	113.47(10)
C(18)-C(19)-H(19A)	108.9
C(20)-C(19)-H(19A)	108.9
C(18)-C(19)-H(19B)	108.9
C(20)-C(19)-H(19B)	108.9
H(19A)-C(19)-H(19B)	107.7
C(21)-C(20)-C(19)	115.19(11)
C(21)-C(20)-H(20A)	108.5
C(19)-C(20)-H(20A)	108.5
C(21)-C(20)-H(20B)	108.5
C(19)-C(20)-H(20B)	108.5
H(20A)-C(20)-H(20B)	107.5
C(22)-C(21)-C(20)	115.04(12)
C(22)-C(21)-H(21A)	108.5
C(20)-C(21)-H(21A)	108.5
C(22)-C(21)-H(21B)	108.5
C(20)-C(21)-H(21B)	108.5
H(21A)-C(21)-H(21B)	107.5
C(21)-C(22)-C(23)	114.63(12)
C(21)-C(22)-H(22A)	108.6
C(23)-C(22)-H(22A)	108.6
C(21)-C(22)-H(22B)	108.6
C(23)-C(22)-H(22B)	108.6
H(22A)-C(22)-H(22B)	107.6
C(24)-C(23)-C(22)	114.19(14)

C(24)-C(23)-H(23A)	108.7
C(22)-C(23)-H(23A)	108.7
C(24)-C(23)-H(23B)	108.7
C(22)-C(23)-H(23B)	108.7
H(23A)-C(23)-H(23B)	107.6
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for s2318btw. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	37(1)	29(1)	46(1)	0(1)	11(1)	-2(1)
C(2)	36(1)	32(1)	51(1)	-1(1)	8(1)	2(1)
C(3)	37(1)	39(1)	39(1)	-8(1)	11(1)	-6(1)
C(4)	39(1)	46(1)	28(1)	-1(1)	7(1)	-5(1)
C(5)	37(1)	46(1)	36(1)	-1(1)	3(1)	-3(1)
C(6)	35(1)	33(1)	41(1)	-4(1)	9(1)	-3(1)
C(7)	36(1)	41(1)	54(1)	16(1)	8(1)	-1(1)
C(8)	37(1)	58(1)	38(1)	14(1)	6(1)	-5(1)
C(9)	39(1)	45(1)	46(1)	-8(1)	13(1)	-6(1)
C(10)	37(1)	39(1)	46(1)	-3(1)	8(1)	-1(1)
C(11)	40(1)	40(1)	51(1)	-6(1)	11(1)	-1(1)
C(12)	52(1)	41(1)	55(1)	-8(1)	14(1)	2(1)
C(13)	54(1)	50(1)	55(1)	-5(1)	19(1)	9(1)
C(14)	59(1)	52(1)	54(1)	-4(1)	16(1)	8(1)
C(15)	79(1)	68(1)	67(1)	7(1)	32(1)	12(1)
C(16)	101(1)	76(1)	70(1)	12(1)	32(1)	5(1)
C(17)	36(1)	35(1)	47(1)	-2(1)	9(1)	-1(1)
C(18)	37(1)	38(1)	42(1)	-4(1)	11(1)	0(1)
C(19)	36(1)	35(1)	43(1)	-2(1)	8(1)	-1(1)
C(20)	48(1)	35(1)	59(1)	-5(1)	16(1)	-2(1)
C(21)	53(1)	42(1)	63(1)	-9(1)	11(1)	-12(1)
C(22)	46(1)	48(1)	63(1)	-6(1)	9(1)	-7(1)
C(23)	48(1)	66(1)	81(1)	-2(1)	11(1)	-12(1)
C(24)	63(1)	95(2)	112(2)	1(1)	32(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s2318btw.

	x	y	z	U(eq)
H(2)	5977	3414	4886	47
H(5)	3921	4875	2396	47
H(7)	4798	2794	7255	52
H(8)	4803	3988	9126	53
H(9A)	6810	4383	3344	51

H(9B)	6461	5104	2015	51
H(10A)	6513	3133	1565	48
H(10B)	6111	3823	255	48
H(11A)	7679	3828	1133	52
H(11B)	7276	4517	-181	52
H(12A)	6931	3211	-1859	59
H(12B)	7378	2551	-567	59
H(13A)	8507	3366	-1144	63
H(13B)	8153	2749	-2623	63
H(14A)	7616	4129	-3838	66
H(14B)	8035	4722	-2405	66
H(15A)	8791	3659	-4712	84
H(15B)	9196	4290	-3313	84
H(16A)	8284	5004	-6011	122
H(16B)	9178	5056	-5838	122
H(16C)	8696	5634	-4614	122
H(17A)	3100	4120	4011	47
H(17B)	3418	3877	5832	47
H(18A)	3372	2544	3240	46
H(18B)	3589	2325	5128	46
H(19A)	2136	2839	3785	45
H(19B)	2336	2749	5711	45
H(20A)	2494	1210	3583	56
H(20B)	2503	1173	5532	56
H(21A)	1216	1501	3378	63
H(21B)	1382	570	4398	63
H(22A)	1018	2318	5743	62
H(22B)	1271	1446	6852	62
H(23A)	-48	1473	4703	78
H(23B)	200	625	5876	78
H(24A)	17	1549	8170	133
H(24B)	-736	1479	7011	133
H(24C)	-233	2397	6994	133

36. References

1. D. J. Atkinson, J. Sperry and M. A. Brimble, *Synthesis*, 2010, **6**, 911-913.
2. S. M. Bronner and N. K. Garg, *J. Org. Chem.*, 2009, **74**, 8842-8843.