Electronic Supplementary Material (ESI) for RSC Advances.

A new intermediate in spontaneous styrene polymerisation inhibited by 2-nitrophenol

Electronic Supplementary Information

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Contents

1 NMR data for compound 1

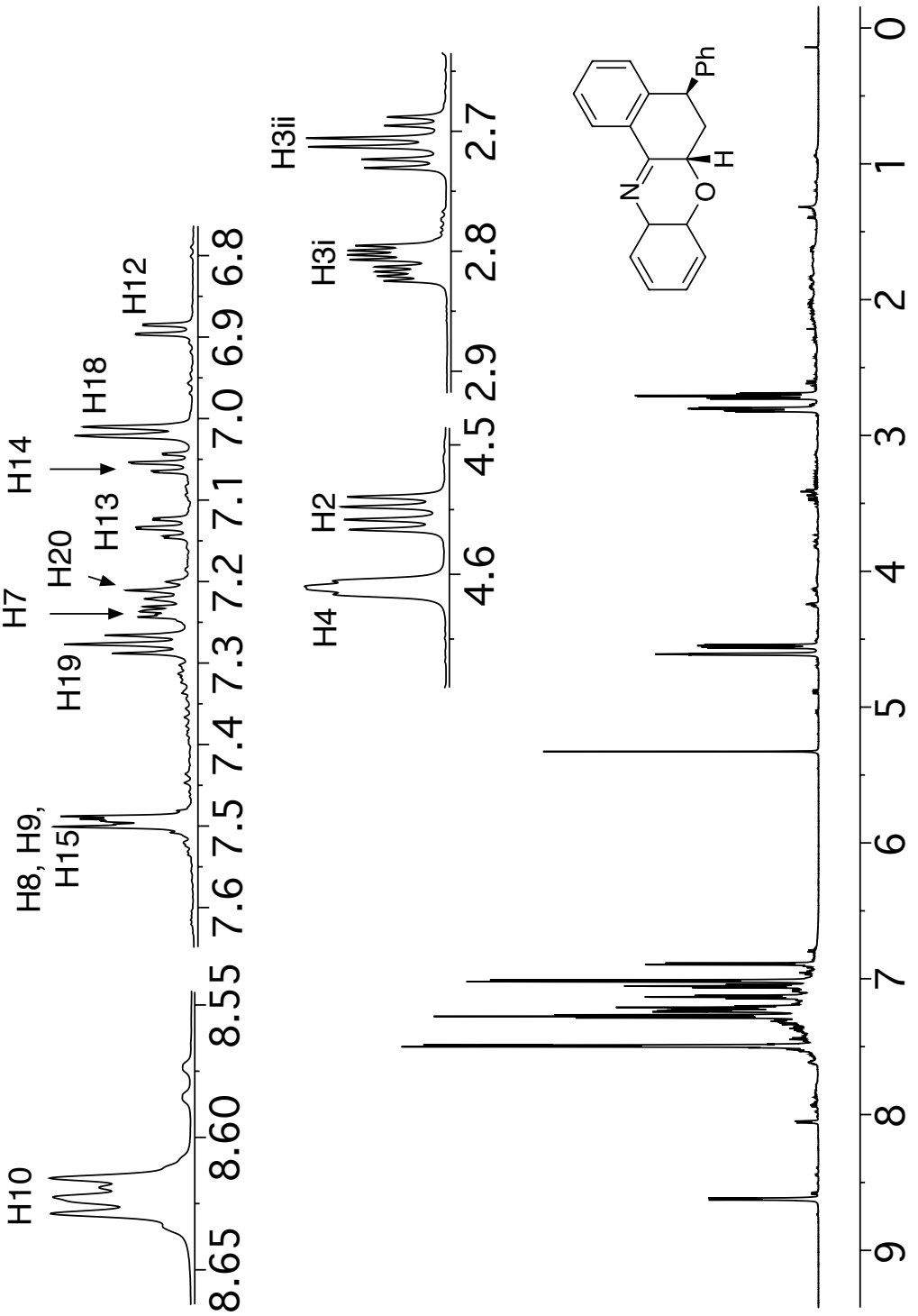

Figure 1.1 ^{1}H-NMR of **1** (700 MHz, $CDCl_3$)

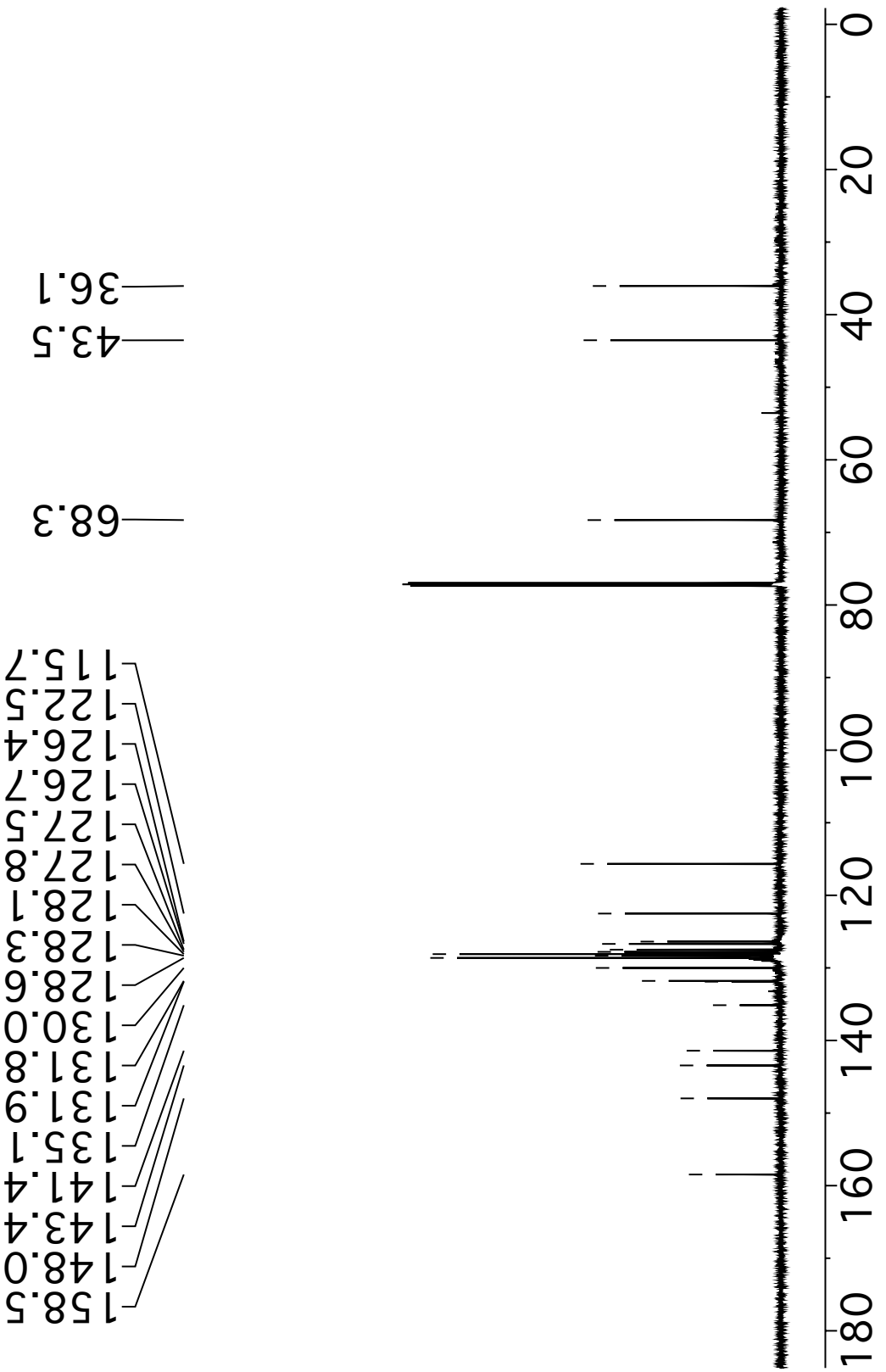

Figure 1.2 ^{13}C-NMR of **1** (700 MHz, $CDCl_3$)

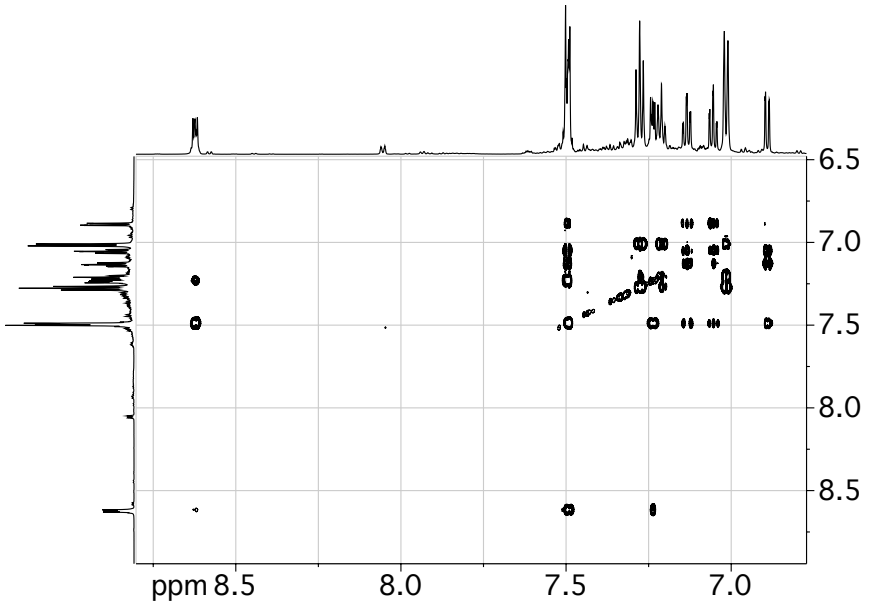

Figure 1.3 ^{1}H-^{1}H COSY NMR of **1** (700 MHz, $CDCl_3$)

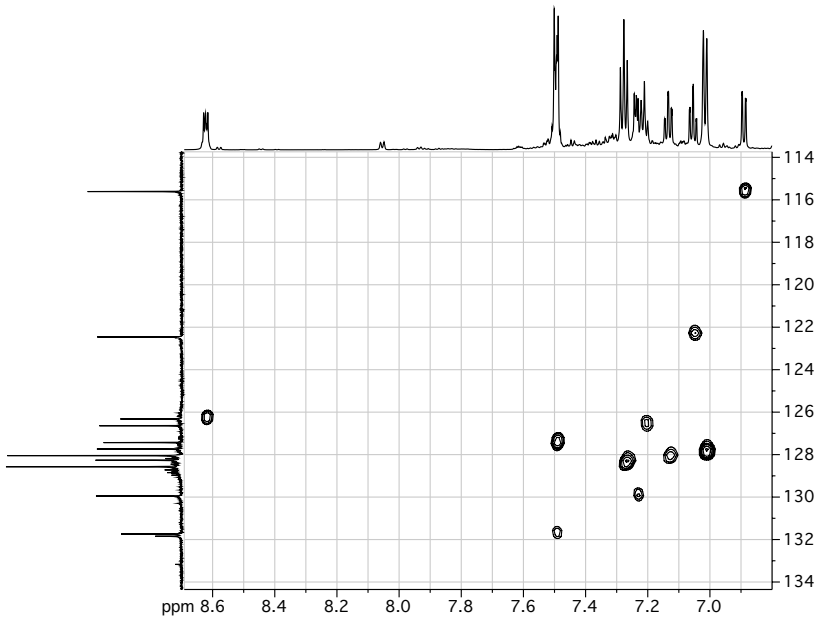

Figure 1.4 HSQC NMR of low field region

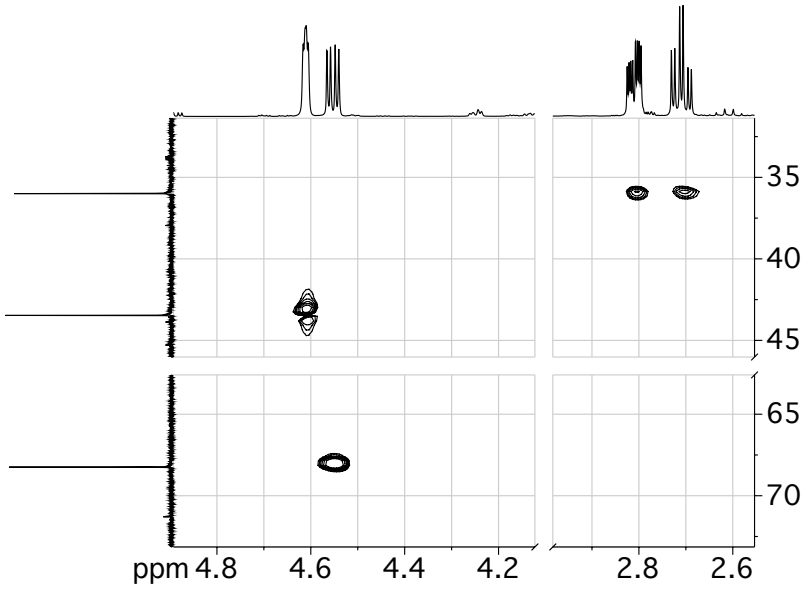

Figure 1.5 HSQC NMR of high field region

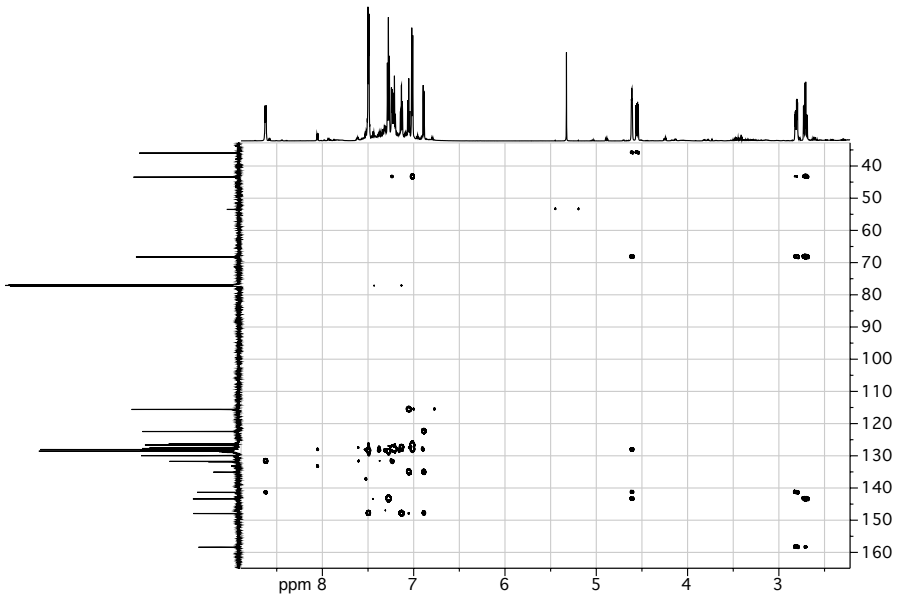

Figure 1.6 HMBC full spectrum

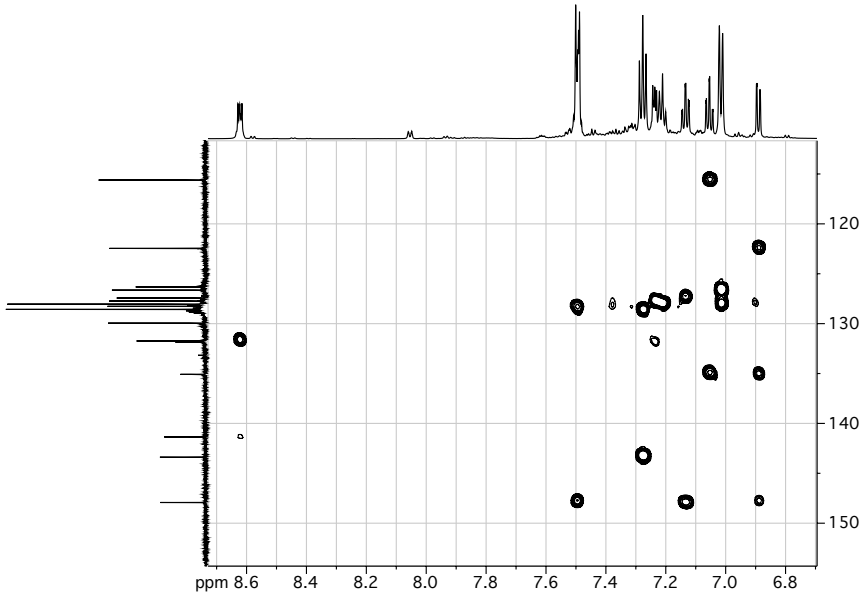

Figure 1.7 HMBC low field region

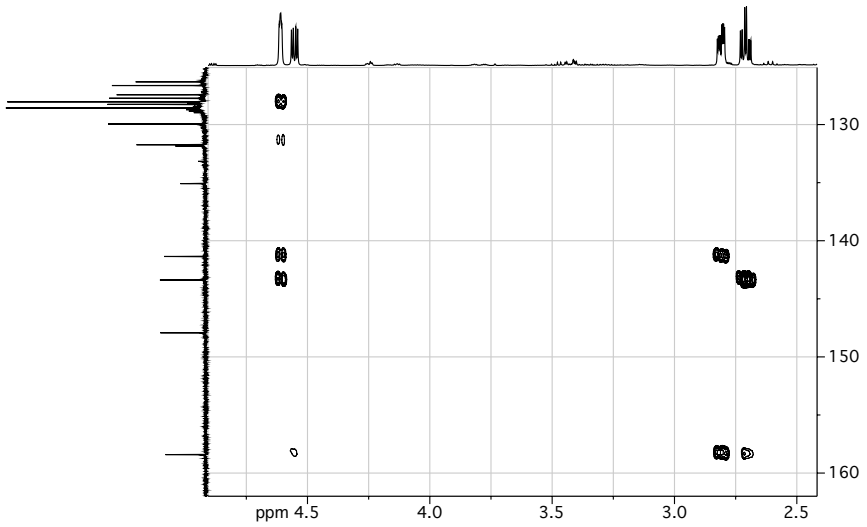

Figure 1.8 HMBC insert 3

Table 1 ^{1}H-NMR data and 2D correlations, compound **1**

δ (ppm)	Splitting Pattern	J_{H-H} (Hz)	Integration	COSY	HSQC	HMBC	Assignment
8.59-8.62	m	-	1	H7, H8, H9	C10	C1, C5(w), C8/9	H10
7.46-7.50	m	-	3	H9, H13(w), H14	C8, C9, C15	C12(w), C14, C16	H8, H9 & H15
7.26	t	8	2	H20, H18, H22	C19	C17, C18, C20	H19
7.21-7.23	m	-	1	H10	C7	C4(w), C6(w)	H7
7.19	t	7	1	H18, H19, H21, H22	C20	C17(w), C18	H20
7.12	td	8, 1.5	1	H12, H14, H15	C13	C11, C12, C15(w), C16(w)	H13
7.04	td	8, 1.5	1	H12(w), H13, H15	C14	C11, C12, C15(w), C16	H14
7.00	d	8	2	H19,H20(w) ,H21	C18	C4, C18, C20	H18
6.87	dd	8, 1	1	H13, H14(w)	C12	C11, C14, C16	H12
4.59	dd	4, 3	1	H3b	C4	C2(w), C3, C5, C6, C7, C8/9, C17, C18	H4
4.54	dd	12, 5	1	H3a	C2	C1, C3	H2
2.79	dddd	12, 5, 3	1	H2, H3a	C3	C1, C2, C4, C5	H3i
2.69	td	12, 5	1	H4, H3a, H3b	C3	C1, C2, C4, C17	H3ii

Table 2 ^{13}C NMR data and 2D correlations, compound **1**

δ (ppm)	HSQC	HMBC	Assignment
36.1	H3i & H3ii	H2, H4	C3
43.5	H4	H3i, H3ii, H7(w), H18	C4
68.3	H2	H3i, H3ii, H4	C2
115.7	H12	H13(w), H14, H15(w)	C12
122.5	H14	H12	C14
126.4	H10	-	C10
126.7	H20	H18	C20
127.5	H15	H13, H16	C15
127.8	H8 or H9	-	C8 or C9
128.1	H18	H4	C18
128.3	H13	-	C13
128.6	H19	H18	C19
130.0	H7	-	C7
131.8	H8 or H9	H10	C8 or C9
131.9	-	H7(w)	C6
135.1	-	H12, H14	C16
141.4	-	H3i, H4, H10(w)	C5
143.4	-	H3ii, H4, H19	C17
148.0	-	H13, H15	C11
158.5	-	H2, H3i, H3ii, H10	C1

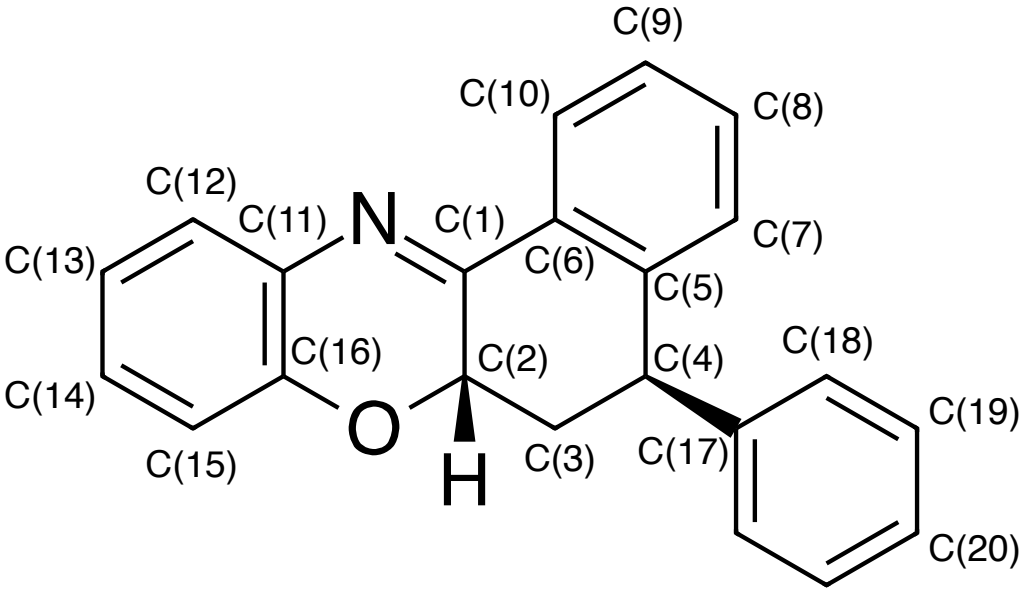

Figure 1.9 Labelling scheme **1**. H-atom labelling follows that of parent carbon.

2 NMR data for compound 2

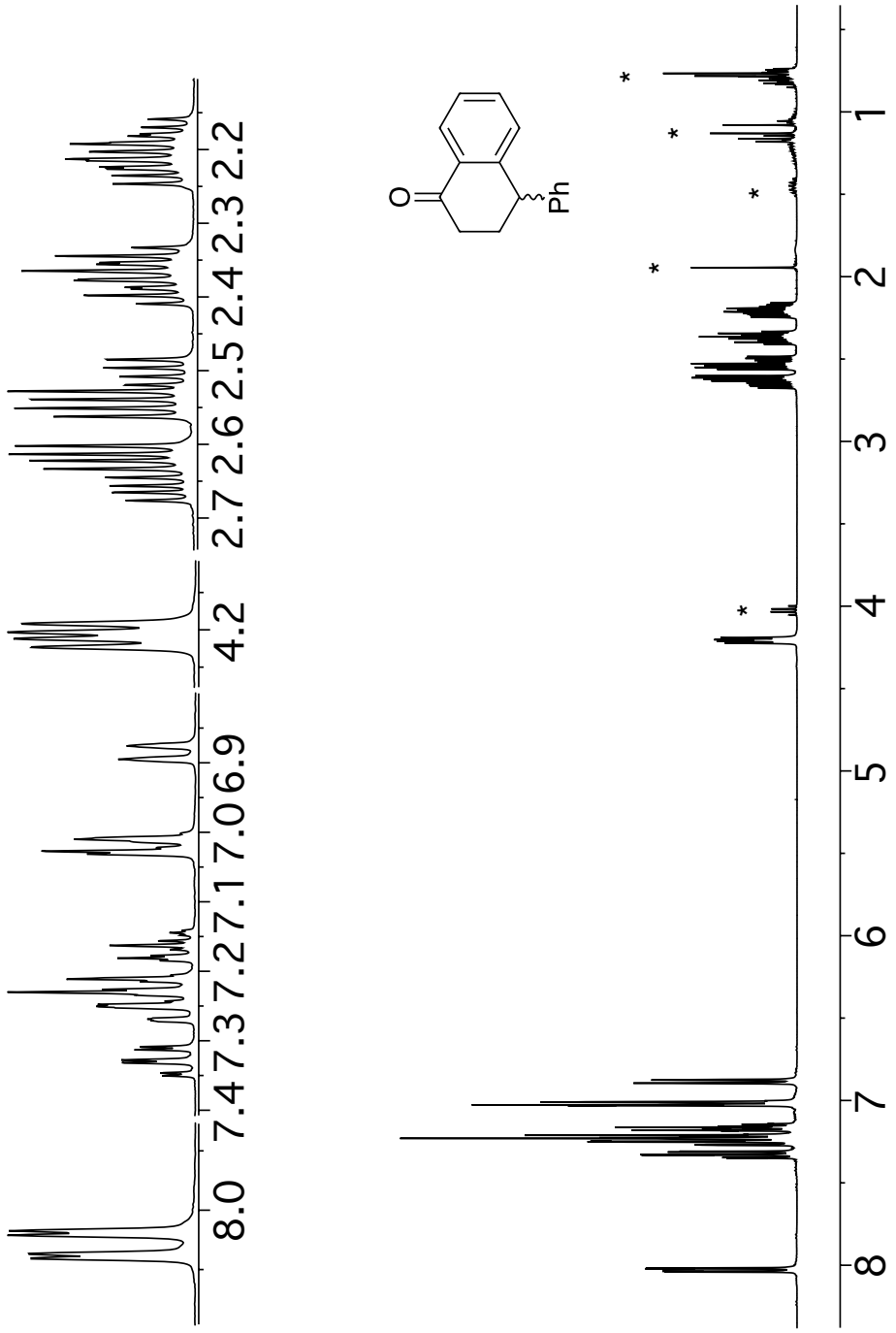

Figure 2.1 ^{1}H-NMR of **2** (400 MHz, $CDCl_3$). ∗ Indicate EtOAc and Pet. Ether impurities.

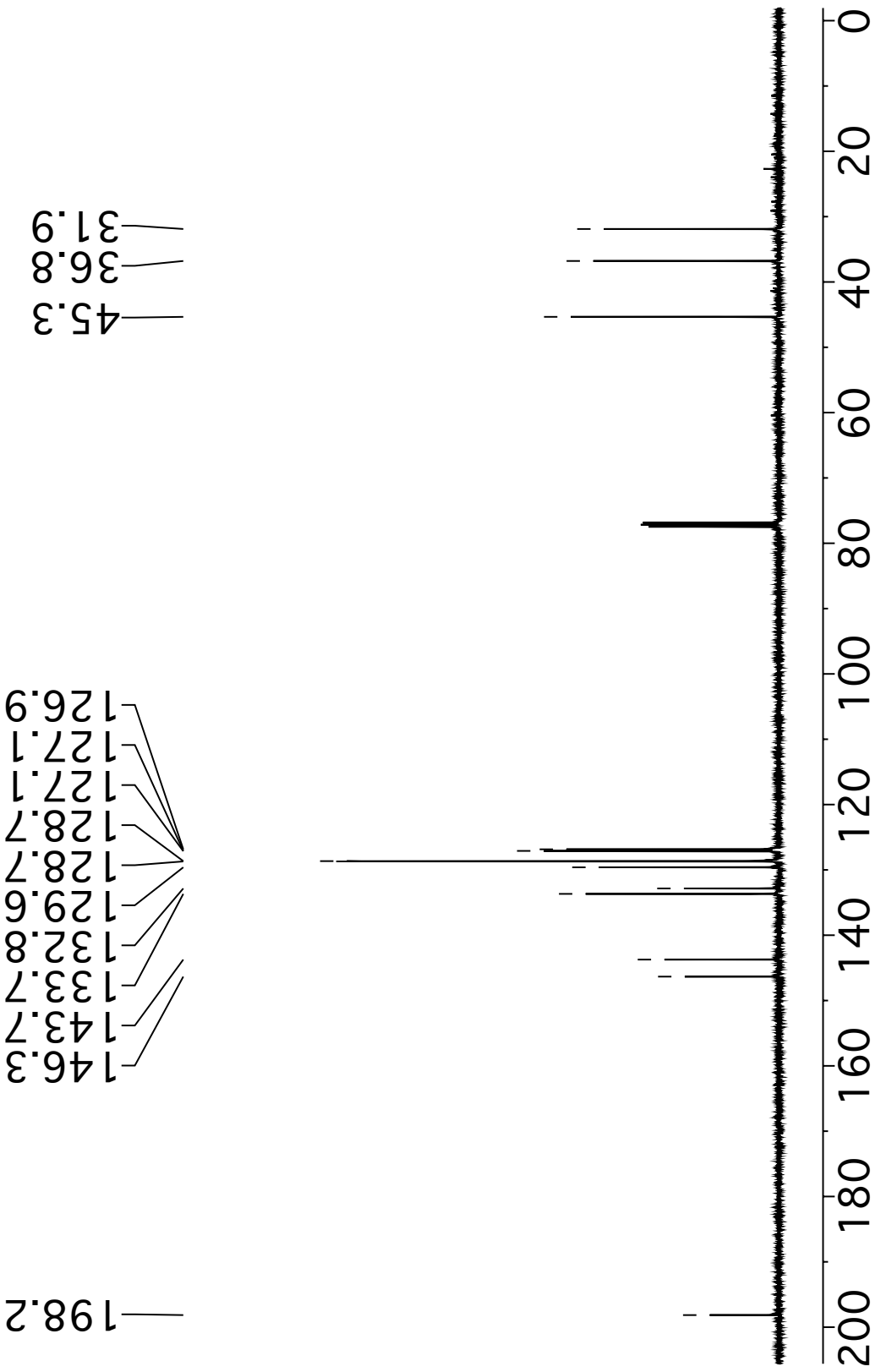

Figure 2.2 ^{13}C-NMR of **2** (400 MHz, $CDCl_3$)

3 NMR data for compound 3

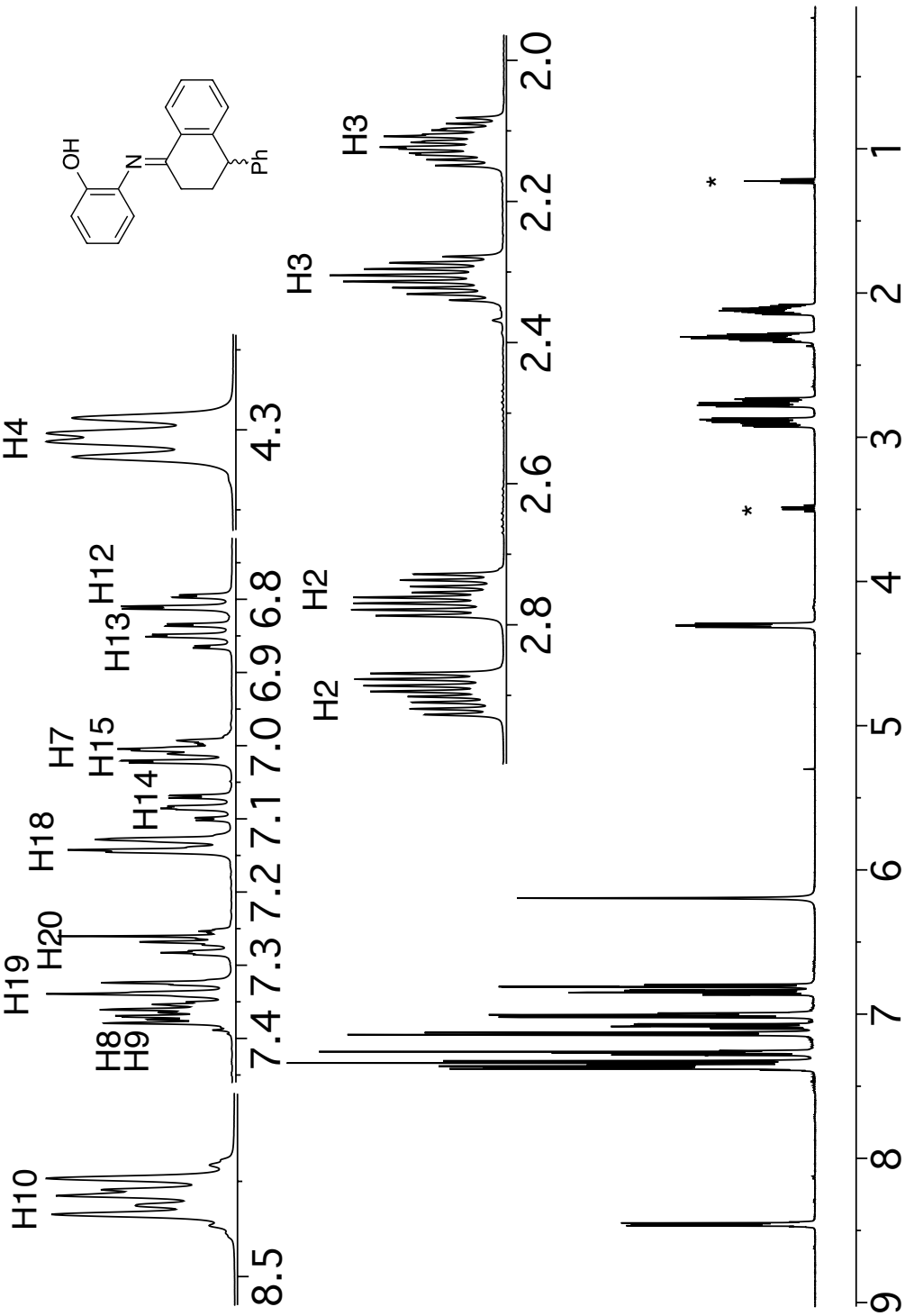

Figure 3.1 ^{1}H-NMR of **3** (500 MHz, $CDCl_3$) $*$ indicate diethyl ether impurity

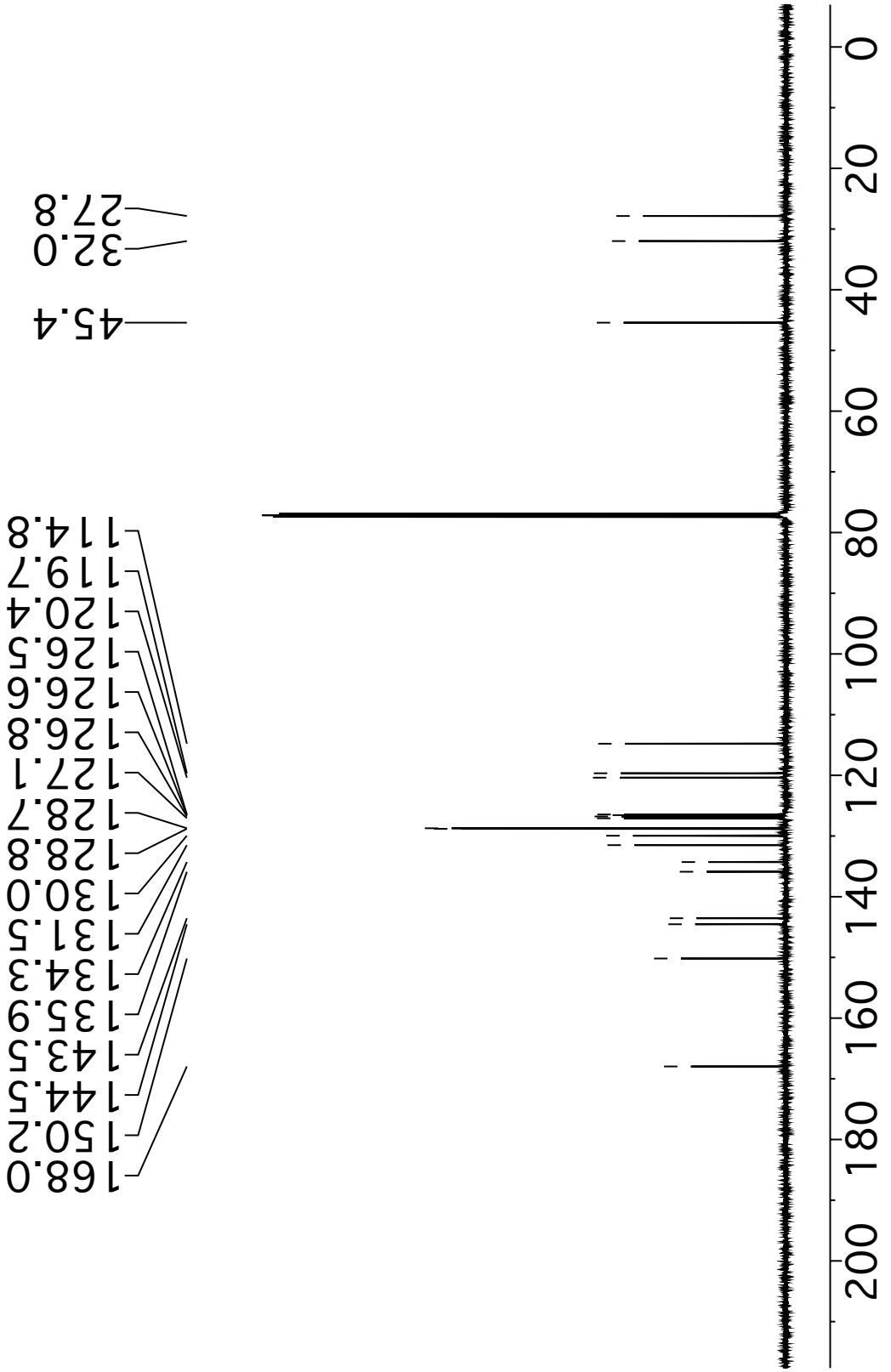

Figure 3.2 ^{13}C-NMR of **3** (500 MHz, $CDCl_3$)

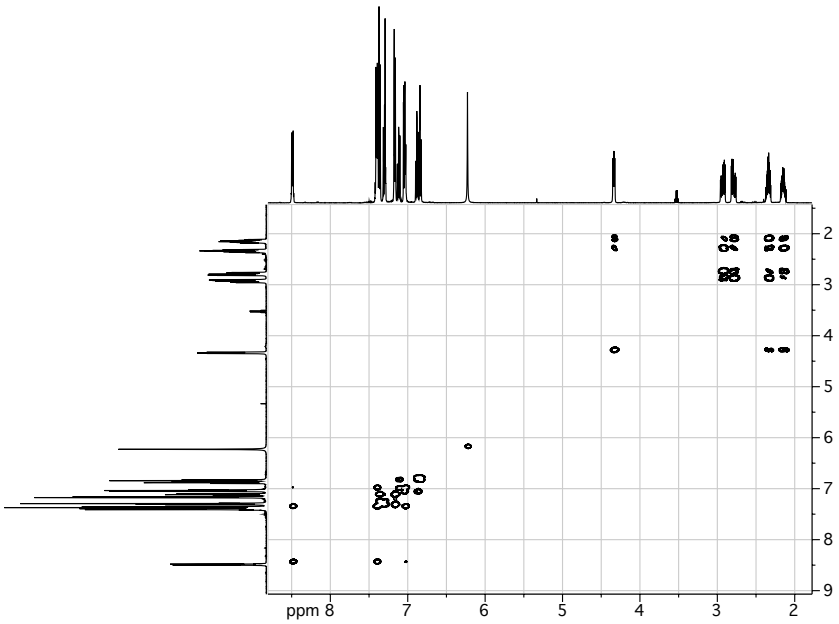

Figure 3.3 COSY NMR of **3**

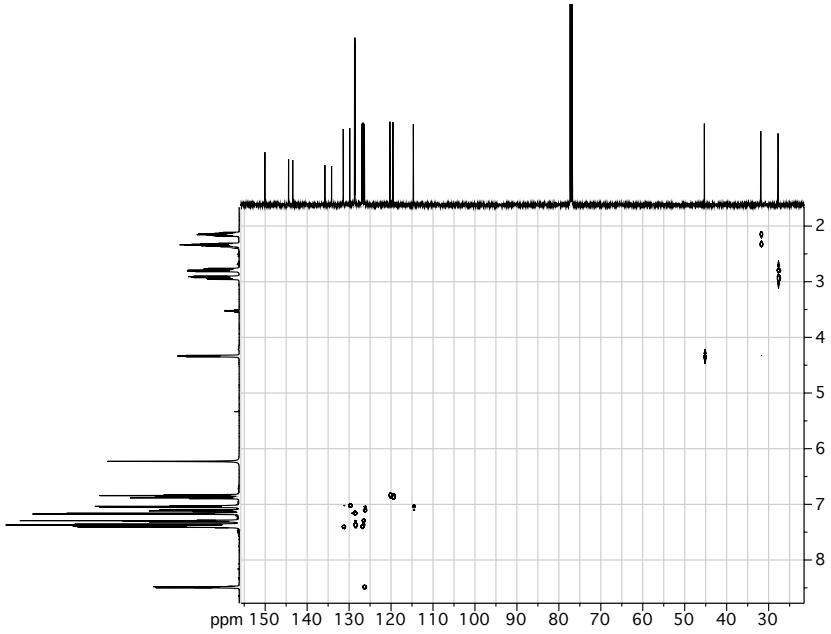

Figure 3.4 HSQC NMR of **3**

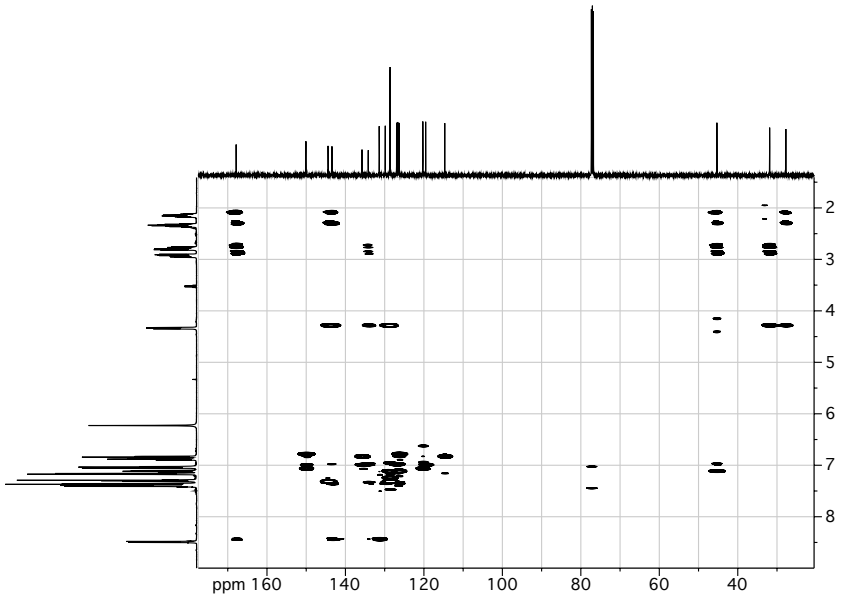

Figure 3.5 HMBC NMR of **3**

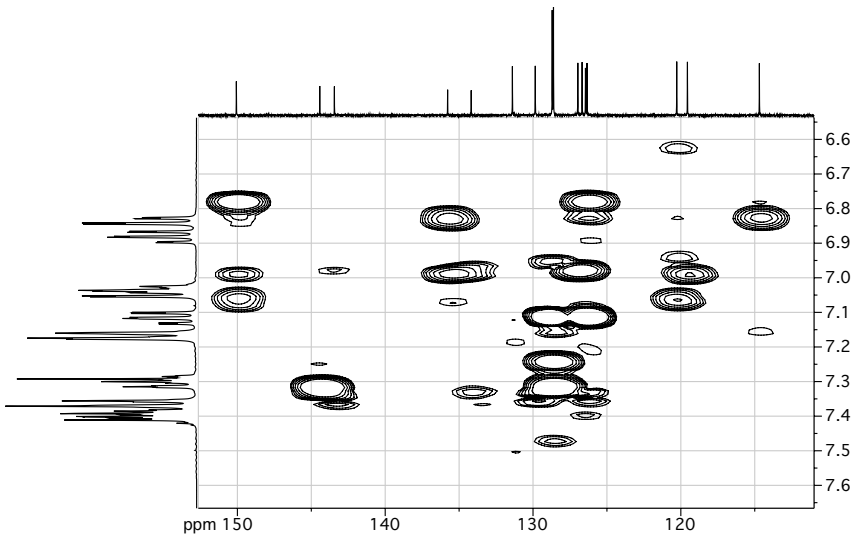

Figure 3.6 HMBC NMR of **3**

Table 3 ^{1}H-NMR data and 2D correlations, compound **3**

δ (ppm)	Integration (H)	Splitting Pattern	J_{H-H} (Hz)	COSY	HSQC	HMBC	Assignment
8.44-8.47	1	m	-	H8, H9	C10	C1, C5(w)	H10
7.35-7.39	2	m	-	H10, H7	C8, C9	-	H8 & H9
7.33	2	t	7.5	H18, H20	C19	C17, C18	H19
7.27	1	tt	7, 1	H19	C20	C17(w), C18, C19	H20
7.13	2	d	7	H19	C18	C19, C20	H18
7.09	1	ddd	8, 7, 1.5	H13, H15	C14	C12, C16	H14
6.99-7.02	2	m	-	H8, H14	C7, C15	C4, C9, C11, C16	H7 & H15
6.85	1	td	7.5, 1.5	H12, H14	C13	C11, C15	H13
6.80	1	dd	8, 1.5	-	C12	C14, C16	H12
6.20	1	s	s	-	-	-	-OH
4.31	1	dd	7.5, 5	H3	C4	C2, C4, C5	H4
2.90	1	ddd	16.5, 9, 4	H2, H3	C2	C1, C3, C4, C6	H2
2.76	1	ddd	16.5, 9, 4	H2, H3	C2	C1, C3, C4, C6	H2
2.31	1	ddt	13, 9, 4	H2, H3	C3	C1, C2, C4, C5	H3
2.12	1	dddd	13, 9, 7.5, 4	H2, H3	C3	C1, C2, C4, C5	H3

Table 4 ^{13}C-NMR data and 2D correlations, compound **3**

δ (ppm)	HSQC	HMBC	Assignment
27.8	H2a + H2b	H3a, H3b, H4	C2
32.0	H3a + H3b	H2a, H2b, H4	C3
45.4	H4	H2a, H2b, H3a, H3b, H7(w) ,H18	C4
114.8	H15	H5	C15
119.7	H13	H4	C13
120.4	H12	H7	C12
126.4	H14	-	C14
126.6	H10	-	C10
126.8	H20	-	C20
127.1	H9	H7	C9
128.7	H19	H18, H20	C19
128.8	H18	H4, H19	C18
129.9	H7	-	C7
131.5	H8	H10	C8
134.3	-	H2a, H2b	C6
135.9	-	H13, H15	C11
143.5	-	H3a, H3b, H4, H7(w), H10(w)	C5
144.5	-	H19, H20(w)	C17
150.2	-	H12, H15, H17	C16
168.0	-	H10, H2a, H2b, H3a, H3b	C1

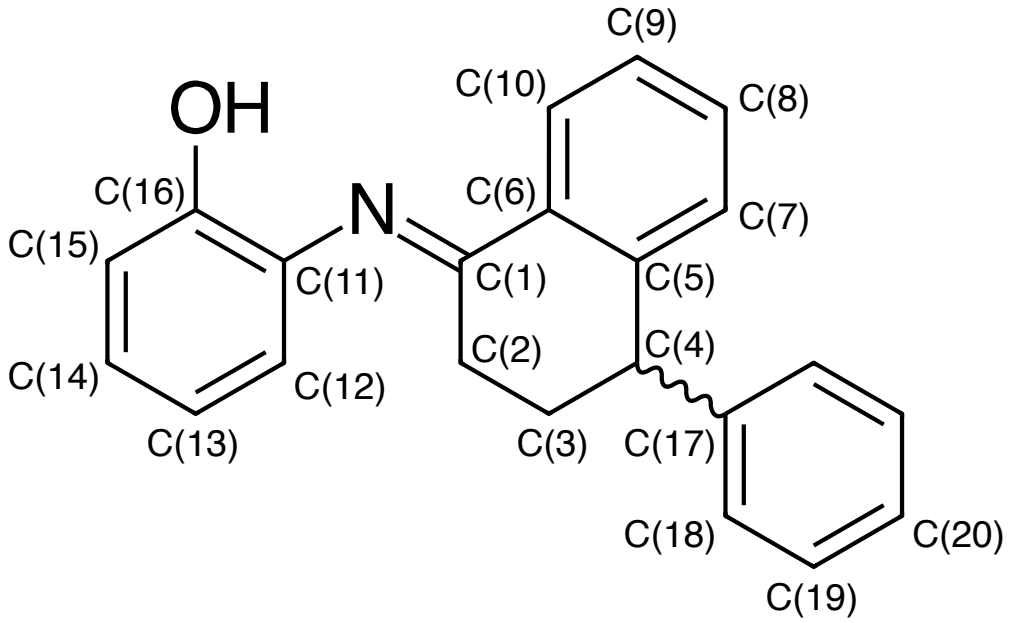

Figure 3.7 Labelling scheme **3**. H-atom labelling follows that of parent carbon.

4 Comparison of NMR data for compound 1

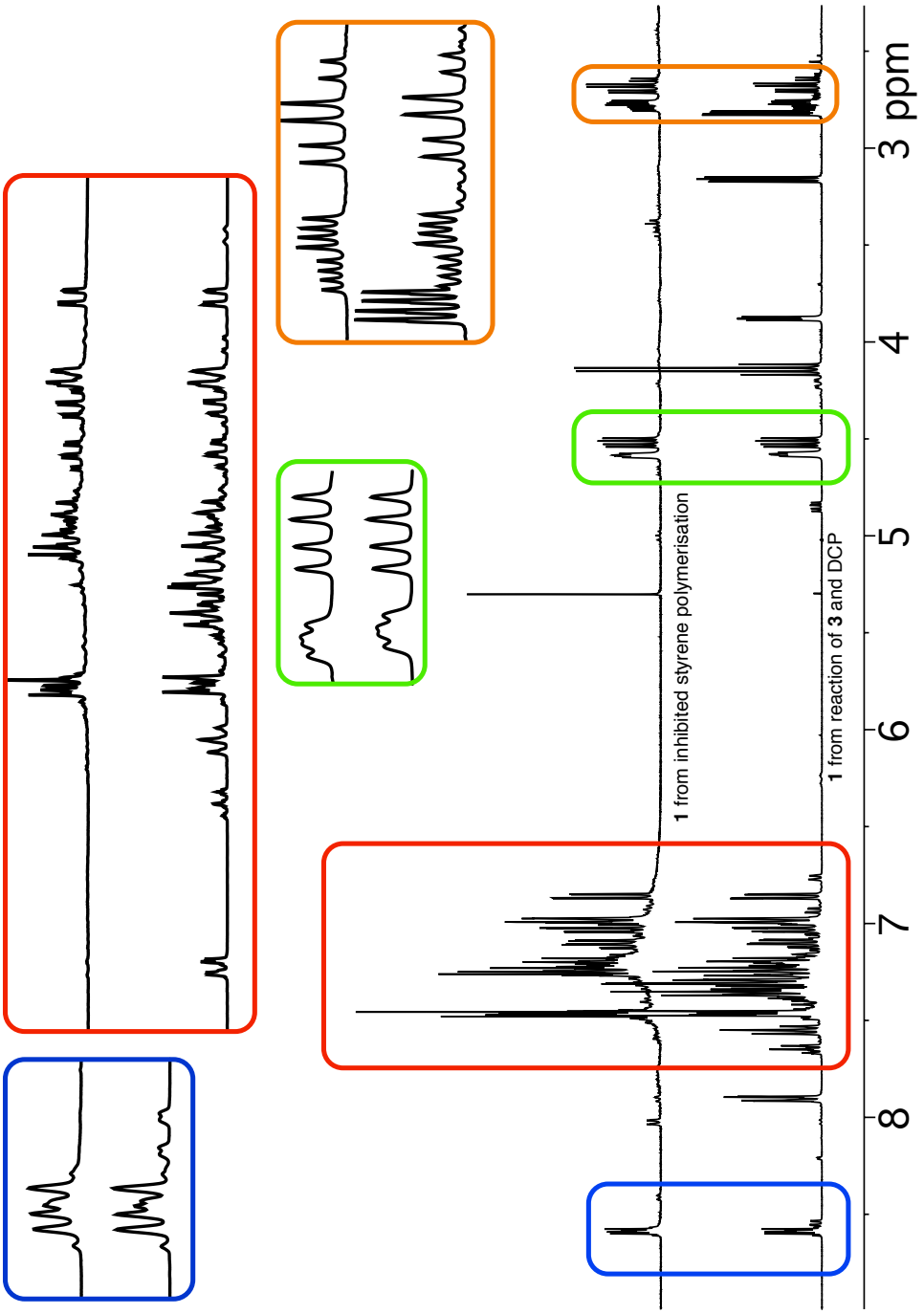

Figure 4.1 Comparison of ^{1}H-NMR for **1** Top Spectrum crude product from reaction of **3** with DCP , Bottom spectrum purified **1** from 2-nitrophenol inhibited styrene polymerisation reaction (400 MHz, $CDCl_3$)

5 Diagrams of disorder for crystal structure of compound 3

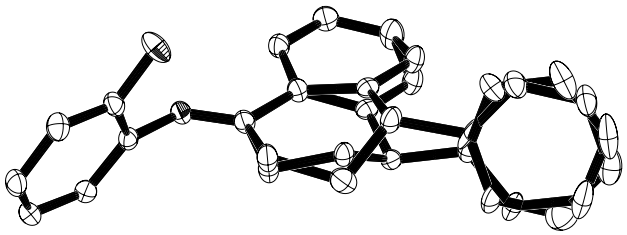

Figure 5.1 Superimposition of disordered components in asymetric unit of compound **3**

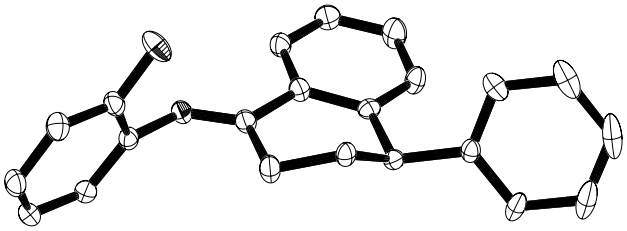

Figure 5.2 Component 1 of disorder in asymmetric unit of compound **3** (79% occupancy)

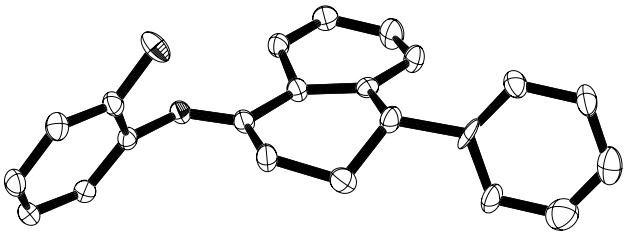

Figure 5.3 Component 2 of disorder in asymmetric unit of compound **3** (21% occupancy)