

- Supporting Information -

Francisco Castillo^{1,2}, Rodrigo Faúndez³, Jorge Tapia^{3,4}, Camilo Verdugo¹, Marcelo Preite¹, Ivonne Chávez³, Juan Manuel-Manriquez³, Pedro D. Ortiz⁵, Ximena Zarate⁵ and Eduardo Schott^{3,6*}

¹*Departamento de Química Orgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Avenida Vicuña Mackenna 4860, 7820244, Macul, Santiago, Chile.*

²*Instituto de Ingeniería Biológica y Médica, IIMB, Pontificia Universidad Católica de Chile, Avenida Vicuña Mackenna 4860, 7820244, Macul, Santiago, Chile.*

³ *Departamento de Química Inorgánica, Facultad de Química y Farmacia, Centro de Energía UC, Centro de Investigación en Nanotecnología y Materiales Avanzados CIEN-UC, Pontificia Universidad Católica de Chile, Avenida Vicuña Mackenna, 4860, 7820244, Macul, Santiago, Chile.*

⁴*Departamento de Ciencias Químicas y Biológicas, Universidad Bernardo O'Higgins, Facultad de Salud, General Gana, 1702, Santiago, Chile*

⁵*Instituto de Ciencias Químicas Aplicadas, Theoretical and Computational Chemistry Center, Facultad de Ingeniería, Universidad Autónoma de Chile, 8910060, San Miguel, Santiago, Chile.*

⁶*Millennium Nuclei on Catalytic Processes towards Sustainable Chemistry (CSC), Santiago, Chile*

Atom N°	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Aromatic distances	1,414	1,413	1,405	1,405	1,402	1,403	1,401	1,404	1,401	1,403	1,410	1,404	1,408	1,404	1,404	Ar ₁ -Ar ₂
	1,394	1,390	1,395	1,396	1,397	1,394	1,398	1,396	1,399	1,398	1,398	1,396	1,391	1,398	1,397	Ar ₂ -Ar ₃
	1,414	1,413	1,406	1,405	1,401	1,404	1,401	1,404	1,401	1,403	1,408	1,404	1,407	1,403	1,403	Ar ₃ -Ar ₄
	1,414	1,403	1,405	1,405	1,406	1,403	1,406	1,404	1,405	1,404	1,404	1,403	1,399	1,405	1,404	Ar ₄ -Ar ₅
	1,394	1,399	1,395	1,396	1,395	1,398	1,396	1,399	1,394	1,396	1,402	1,398	1,402	1,397	1,397	Ar ₅ -Ar ₆
	1,414	1,403	1,406	1,405	1,406	1,403	1,406	1,404	1,406	1,404	1,404	1,403	1,400	1,405	1,403	Ar ₆ -Ar ₁
	1,523	1,511	1,510	1,512	1,511	1,515	1,515	1,519	1,518	1,516	1,521	1,517	1,522	1,517	1,521	Ar ₁ -Ch ₁
Aliphatic distances	1,607	1,593	1,584	1,576	1,568	1,560	1,558	1,553	1,553	1,554	1,563	1,551	1,541	1,556	1,546	Ch ₁ -Ch ₂
	1,584	1,583	1,570	1,562	1,558	1,552	1,554	1,544	1,544	1,540	1,547	1,539	1,553	1,541	1,537	Ch ₂ -Ch ₃
	1,607	1,583	1,576	1,557	1,552	1,549	1,543	1,547	1,545	1,544	1,548	1,546	1,548	1,547	1,541	Ch ₃ -Ch ₄
	1,523	1,593	1,570	1,557	1,551	1,549	1,545	1,547	1,546	1,545	1,544	1,545	1,544	1,546	1,544	Ch ₄ -Ch ₅
	-	1,511	1,584	1,562	1,552	1,541	1,548	1,545	1,548	1,541	1,547	1,540	1,545	1,542	1,539	Ch ₅ -Ch ₆
	-	-	1,510	1,576	1,561	1,550	1,539	1,546	1,549	1,545	1,546	1,542	1,544	1,543	1,539	Ch ₆ -Ch ₇
	-	-	-	1,512	1,570	1,554	1,545	1,540	1,544	1,545	1,543	1,543	1,541	1,551	1,540	Ch ₇ -Ch ₈
	-	-	-	-	1,511	1,564	1,551	1,547	1,539	1,544	1,546	1,539	1,546	1,549	1,542	Ch ₈ -Ch ₉
	-	-	-	-	-	1,512	1,559	1,549	1,542	1,542	1,546	1,540	1,547	1,548	1,547	Ch ₉ -Ch ₁₀
	-	-	-	-	-	-	1,514	1,557	1,544	1,547	1,546	1,542	1,541	1,544	1,542	Ch ₁₀ -Ch ₁₁
	-	-	-	-	-	-	-	1,518	1,552	1,552	1,545	1,539	1,542	1,542	1,540	Ch ₁₁ -Ch ₁₂
	-	-	-	-	-	-	-	-	1,517	1,557	1,549	1,546	1,538	1,539	1,539	Ch ₁₂ -Ch ₁₃
	-	-	-	-	-	-	-	-	-	1,516	1,554	1,547	1,549	1,540	1,539	Ch ₁₃ -Ch ₁₄
	-	-	-	-	-	-	-	-	-	-	1,517	1,554	1,557	1,545	1,544	Ch ₁₄ -Ch ₁₅
	-	-	-	-	-	-	-	-	-	-	-	1,521	1,554	1,549	1,541	Ch ₁₅ -Ch ₁₆
	-	-	-	-	-	-	-	-	-	-	-	-	1,516	1,555	1,537	Ch ₁₆ -Ch ₁₇
	-	-	-	-	-	-	-	-	-	-	-	-	-	1,517	1,546	Ch ₁₇ -Ch ₁₈
	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1,521	Ch ₁₈ -Ch ₁₉
TAC	Ch ₅ = Ar ₁	Ch ₆ = Ar ₁	Ch ₇ = Ar ₁	Ch ₈ = Ar ₁	Ch ₉ = Ar ₁	Ch ₁₀ = Ar ₁	Ch ₁₁ = Ar ₁	Ch ₁₂ = Ar ₁	Ch ₁₃ = Ar ₁	Ch ₁₄ = Ar ₁	Ch ₁₅ = Ar ₁	Ch ₁₆ = Ar ₁	Ch ₁₇ = Ar ₁	Ch ₁₈ = Ar ₁	Ch ₁₉ = Ar ₁	

Table S1. Bond Distances for the cyclophanes family, in Angstrom.

Atom N°	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Aromatic angles	150,11	156,58	161,79	164,37	168,94	172,71	175,41	178,04	177,64	177,24	178,39	179,85	178,05	178,22	179,53	D ₁₀ -D ₁₁ -Ar ₁
	150,11	156,58	161,79	164,37	167,97	172,47	175,17	177,70	177,37	177,21	178,28	179,80	177,75	178,24	179,53	D ₁₁ -D ₁₂ -Ar ₁
	141,42	150,59	158,50	161,17	166,91	171,87	174,41	178,43	178,96	177,10	178,78	178,99	176,55	178,60	178,01	D ₁₂ -Ar ₁ -Ch ₁₁
	141,42	150,59	158,50	161,17	167,97	171,84	175,08	178,54	178,18	176,21	179,31	176,42	178,17	177,85	178,01	D ₁₀ -Ar ₁ -Ch ₁₀
Aliphatic angles	1,539	106,35	107,37	107,03	108,64	110,19	111,69	113,09	115,68	112,71	115,52	114,92	117,85	114,01	115,92	Ar ₁ -Ch ₁₁ -Ch ₂
	106,90	106,35	107,37	107,03	110,50	112,23	113,52	115,62	115,19	112,06	115,50	117,93	114,79	112,90	115,92	Ar ₁ -Ch ₁₀ -Ch ₁₁
	122,67	121,15	117,40	116,33	115,73	114,54	114,49	113,73	116,36	113,88	116,52	114,20	112,35	114,08	114,43	Ch ₁₁ -Ch ₂ -Ch ₃
	122,67	119,38	117,01	116,28	114,97	115,08	113,34	114,55	118,16	114,40	117,16	113,48	114,07	113,69	113,02	Ch ₂ -Ch ₃ -Ch ₄
	-	121,15	117,01	117,81	115,94	115,95	115,12	114,13	114,71	115,20	116,03	114,79	116,18	114,01	114,14	Ch ₃ -Ch ₄ -Ch ₅
	-	-	117,40	116,28	115,89	114,43	115,79	113,61	114,05	114,09	113,52	113,19	115,51	112,65	113,45	Ch ₄ -Ch ₅ -Ch ₆
	-	-	-	116,33	113,64	114,68	114,46	114,72	117,51	114,59	115,73	114,75	113,27	116,36	114,60	Ch ₅ -Ch ₆ -Ch ₇
	-	-	-	-	116,40	113,87	114,03	112,13	116,56	115,37	113,70	115,73	114,83	116,03	111,88	Ch ₆ -Ch ₇ -Ch ₈
	-	-	-	-	-	115,52	113,85	115,24	115,38	115,28	114,28	114,23	114,36	117,51	115,90	Ch ₇ -Ch ₈ -Ch ₉
	-	-	-	-	-	-	115,21	112,92	112,92	114,77	115,54	113,12	115,57	115,45	115,62	Ch ₈ -Ch ₉ -Ch ₁₀
	-	-	-	-	-	-	-	114,83	116,00	112,54	115,44	114,33	114,54	116,83	115,62	Ch ₉ -Ch ₁₀ -Ch ₁₁
	-	-	-	-	-	-	-	-	116,52	114,60	113,95	114,16	114,50	113,51	115,90	Ch ₁₀ -Ch ₁₁ -Ch ₁₂
	-	-	-	-	-	-	-	-	-	114,88	114,87	115,73	115,68	115,03	111,88	Ch ₁₁ -Ch ₁₂ -Ch ₁₃
	-	-	-	-	-	-	-	-	-	-	115,76	117,91	113,86	115,72	114,60	Ch ₁₂ -Ch ₁₃ -Ch ₁₄
	-	-	-	-	-	-	-	-	-	-	-	117,68	116,05	112,17	113,45	Ch ₁₃ -Ch ₁₄ -Ch ₁₅
	-	-	-	-	-	-	-	-	-	-	-	-	116,48	114,36	114,14	Ch ₁₄ -Ch ₁₅ -Ch ₁₆
	-	-	-	-	-	-	-	-	-	-	-	-	-	114,33	113,02	Ch ₁₅ -Ch ₁₆ -Ch ₁₇
	-	-	-	-	-	-	-	-	-	-	-	-	-	-	114,43	Ch ₁₆ -Ch ₁₇ -Ch ₁₈
TAC	Ch ₁₀ = Ch ₄ Ch ₁₀₋₁ = Ch ₃	Ch ₁₁ = Ch ₅ Ch ₁₁₋₁ = Ch ₂	Ch ₁₂ = Ch ₆ Ch ₁₂₋₁ = Ch ₁	Ch ₁₃ = Ch ₇ Ch ₁₃₋₁ = Ch ₁	Ch ₁₄ = Ch ₈ Ch ₁₄₋₁ = Ch ₁	Ch ₁₅ = Ch ₉ Ch ₁₅₋₁ = Ch ₁	Ch ₁₆ = Ch ₁₀ Ch ₁₆₋₁ = Ch ₁	Ch ₁₇ = Ch ₁₁ Ch ₁₇₋₁ = Ch ₁	Ch ₁₈ = Ch ₁₂ Ch ₁₈₋₁ = Ch ₁	Ch ₁₉ = Ch ₁₃ Ch ₁₉₋₁ = Ch ₁	Ch ₂₀ = Ch ₁₄ Ch ₂₀₋₁ = Ch ₁	Ch ₂₁ = Ch ₁₅ Ch ₂₁₋₁ = Ch ₁	Ch ₂₂ = Ch ₁₆ Ch ₂₂₋₁ = Ch ₁	Ch ₂₃ = Ch ₁₇ Ch ₂₃₋₁ = Ch ₁	Ch ₂₄ = Ch ₁₈ Ch ₂₄₋₁ = Ch ₁	Ch ₂₅ = Ch ₁₉ Ch ₂₅₋₁ = Ch ₁

Table S2. Bond Angles for the cyclophane family, in degree.

Atom N°	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Aromatic distances	1,408	1,397	1,393	1,397	1,397	1,397	1,396	1,398	1,398	1,398	1,400	1,401	1,401	1,401	1,401	Ar1-Ar2
	1,399	1,400	1,402	1,398	1,397	1,395	1,398	1,397	1,398	1,399	1,393	1,395	1,393	1,393	1,394	Ar2-Ar3
	1,406	1,397	1,397	1,397	1,396	1,396	1,396	1,397	1,394	1,395	1,401	1,397	1,399	1,398	1,399	Ar3-Ar4
	1,408	1,402	1,400	1,397	1,397	1,397	1,398	1,398	1,399	1,399	1,399	1,400	1,399	1,400	1,400	Ar4-Ar5
	1,399	1,396	1,394	1,398	1,397	1,398	1,396	1,397	1,395	1,394	1,399	1,398	1,400	1,399	1,399	Ar5-Ar6
	1,406	1,402	1,402	1,397	1,396	1,397	1,398	1,397	1,401	1,400	1,394	1,397	1,395	1,396	1,395	Ar6-Ar1
Aliphatic distances	1,446	1,425	1,419	1,416	1,409	1,410	1,413	1,407	1,402	1,403	1,405	1,404	1,407	1,403	1,403	Ar1-Ch1
	1,539	1,529	1,507	1,515	1,497	1,494	1,501	1,483	1,472	1,472	1,473	1,470	1,472	1,470	1,468	Ch1-Ch2
	1,567	1,575	1,557	1,555	1,544	1,545	1,532	1,536	1,530	1,530	1,532	1,535	1,529	1,546	1,530	Ch2-Ch3
	1,539	1,575	1,580	1,561	1,563	1,551	1,544	1,545	1,540	1,538	1,541	1,539	1,541	1,541	1,544	Ch3-Ch4
	1,446	1,529	1,558	1,561	1,552	1,549	1,552	1,538	1,538	1,540	1,539	1,545	1,543	1,541	1,546	Ch4-Ch5
	-	1,425	1,530	1,555	1,563	1,543	1,548	1,546	1,545	1,545	1,544	1,545	1,546	1,545	1,549	Ch5-Ch6
	-	-	1,421	1,515	1,544	1,554	1,545	1,546	1,552	1,550	1,544	1,540	1,552	1,544	1,549	Ch6-Ch7
	-	-	-	1,416	1,497	1,541	1,563	1,538	1,544	1,545	1,539	1,544	1,551	1,540	1,546	Ch7-Ch8
	-	-	-	-	1,409	1,496	1,541	1,545	1,538	1,539	1,543	1,547	1,545	1,548	1,542	Ch8-Ch9
	-	-	-	-	-	1,409	1,536	1,547	1,538	1,542	1,544	1,541	1,550	1,545	1,545	Ch9-Ch10
	-	-	-	-	-	-	1,408	1,483	1,536	1,545	1,540	1,542	1,544	1,552	1,547	Ch10-Ch11
	-	-	-	-	-	-	-	1,407	1,484	1,543	1,542	1,539	1,542	1,543	1,539	Ch11-Ch12
	-	-	-	-	-	-	-	-	1,409	1,480	1,532	1,544	1,538	1,540	1,542	Ch12-Ch13
	-	-	-	-	-	-	-	-	-	1,409	1,469	1,533	1,544	1,540	1,543	Ch13-Ch14
	-	-	-	-	-	-	-	-	-	-	1,397	1,472	1,531	1,542	1,550	Ch14-Ch15
	-	-	-	-	-	-	-	-	-	-	-	1,399	1,471	1,529	1,546	Ch15-Ch16
	-	-	-	-	-	-	-	-	-	-	-	-	1,398	1,464	1,527	Ch16-Ch17
	-	-	-	-	-	-	-	-	-	-	-	-	-	1,397	1,464	Ch17-Ch18
	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1,398	Ch18-Ch19
TAC	Ch5 = Ar4	Ch6 = Ar5	Ch7 = Ar6	Ch8 = Ar7	Ch9 = Ar8	Ch10 = Ar9	Ch11 = Ar10	Ch12 = Ar11	Ch13 = Ar12	Ch14 = Ar13	Ch15 = Ar14	Ch16 = Ar15	Ch17 = Ar16	Ch18 = Ar17	Ch19 = Ar18	

Table S3. Bond Distances for the dioxacyclophane family, in Angstrom.

Atom N°	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Aromatic angles	148,75	154,91	157,74	162,36	168,62	170,91	171,29	175,56	176,57	177,17	176,92	177,98	177,81	178,12	177,59	D10-D17-Ar1
	148,75	154,91	157,83	162,36	168,62	170,57	171,27	175,56	176,66	177,34	177,08	177,47	177,58	177,88	177,44	D10-D17-Ar4
	142,63	153,52	161,62	165,30	174,25	175,76	174,25	178,03	175,62	175,49	176,18	176,27	176,45	175,79	176,14	D10-Ar1-Ch1
	148,75	153,52	158,95	165,30	174,25	175,41	177,65	178,03	177,65	177,53	174,60	175,56	175,31	174,99	175,02	D10-Ar4-Ch10
Aliphatic angles	107,54	106,95	107,89	108,29	113,54	112,45	111,64	117,45	120,84	120,71	120,21	118,44	118,17	119,58	119,42	Ar1-Ch1-Ch2
	107,54	106,95	106,58	108,29	113,54	114,02	114,96	117,45	117,78	116,63	122,90	121,43	121,50	120,99	120,57	Ar4-Ch10-Ch10-1
	122,13	121,27	120,37	115,20	115,24	113,44	111,51	113,45	112,54	112,30	113,47	112,29	112,17	113,34	112,69	Ch1-Ch2-Ch3
	122,13	122,40	130,00	117,52	116,21	115,25	117,54	115,19	115,35	114,45	115,67	112,71	112,42	114,04	112,35	Ch2-Ch3-Ch4
	-	121,27	124,21	121,03	114,91	116,86	118,13	113,05	113,16	114,43	113,17	114,62	114,30	114,87	115,81	Ch3-Ch4-Ch5
	-	-	115,12	117,52	114,91	114,86	119,60	114,96	114,70	112,22	114,17	115,72	117,13	116,04	116,84	Ch4-Ch5-Ch6
	-	-	-	115,20	116,21	114,10	118,63	116,17	114,27	113,88	116,09	114,75	115,14	116,52	118,55	Ch5-Ch6-Ch7
	-	-	-	-	115,24	115,60	112,29	114,96	114,50	114,58	114,41	114,69	116,40	114,85	116,90	Ch6-Ch7-Ch8
	-	-	-	-	-	114,76	117,41	113,05	113,09	112,71	114,49	114,04	115,61	115,69	115,95	Ch7-Ch8-Ch9
	-	-	-	-	-	-	114,35	115,19	114,04	114,71	114,49	114,94	115,49	115,82	114,84	Ch8-Ch9-Ch10
	-	-	-	-	-	-	-	113,45	114,61	112,97	112,59	112,98	114,44	117,44	115,65	Ch9-Ch10-Ch11
	-	-	-	-	-	-	-	-	113,54	114,11	115,89	113,72	113,10	115,52	113,79	Ch10-Ch11-Ch12
	-	-	-	-	-	-	-	-	-	112,99	115,44	115,19	113,75	115,50	115,27	Ch11-Ch12-Ch13
	-	-	-	-	-	-	-	-	-	-	109,34	115,09	115,04	112,37	114,73	Ch12-Ch13-Ch14
	-	-	-	-	-	-	-	-	-	-	-	109,31	114,93	115,67	113,78	Ch13-Ch14-Ch15
	-	-	-	-	-	-	-	-	-	-	-	-	108,90	114,53	116,56	Ch14-Ch15-Ch16
	-	-	-	-	-	-	-	-	-	-	-	-	-	107,40	116,97	Ch15-Ch16-Ch17
	-	-	-	-	-	-	-	-	-	-	-	-	-	-	107,78	Ch16-Ch17-Ch18
TAC	Ch10 = Ch1 = Ch3	Ch5 = Ch6-1 = Ch4	Ch6 = Ch7-1 = Ch5	Ch7 = Ch8-1 = Ch6	Ch8 = Ch9-1 = Ch7	Ch9 = Ch10-1 = Ch8	Ch10 = Ch11-1 = Ch9	Ch11 = Ch12-1 = Ch10	Ch12 = Ch13-1 = Ch11	Ch13 = Ch14-1 = Ch12	Ch14 = Ch15-1 = Ch13	Ch15 = Ch16-1 = Ch14	Ch16 = Ch17-1 = Ch15	Ch17 = Ch18-1 = Ch16	Ch18 = Ch19-1 = Ch17	

Table S4. Bond Angles for the dioxacyclophane family, in degree.

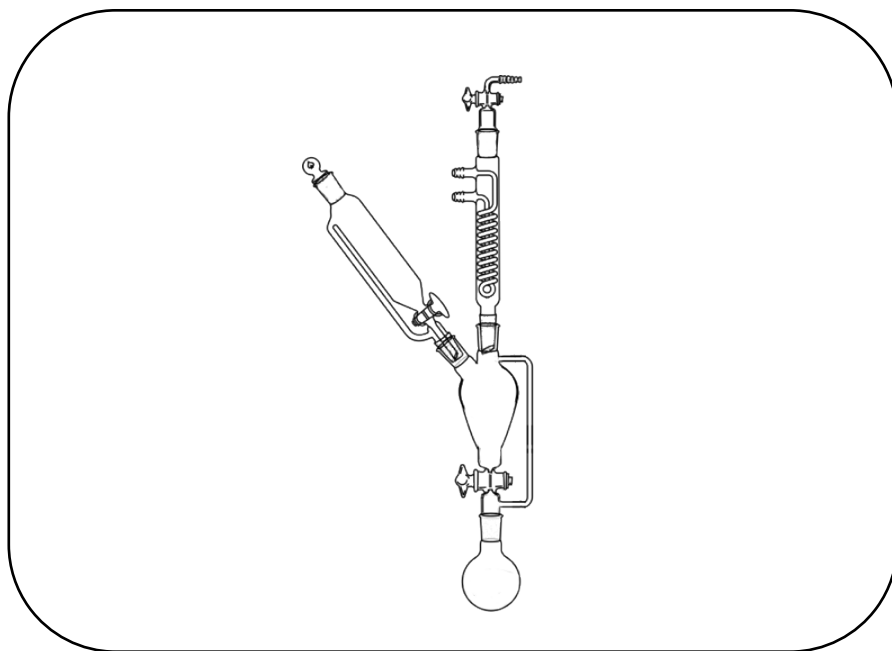
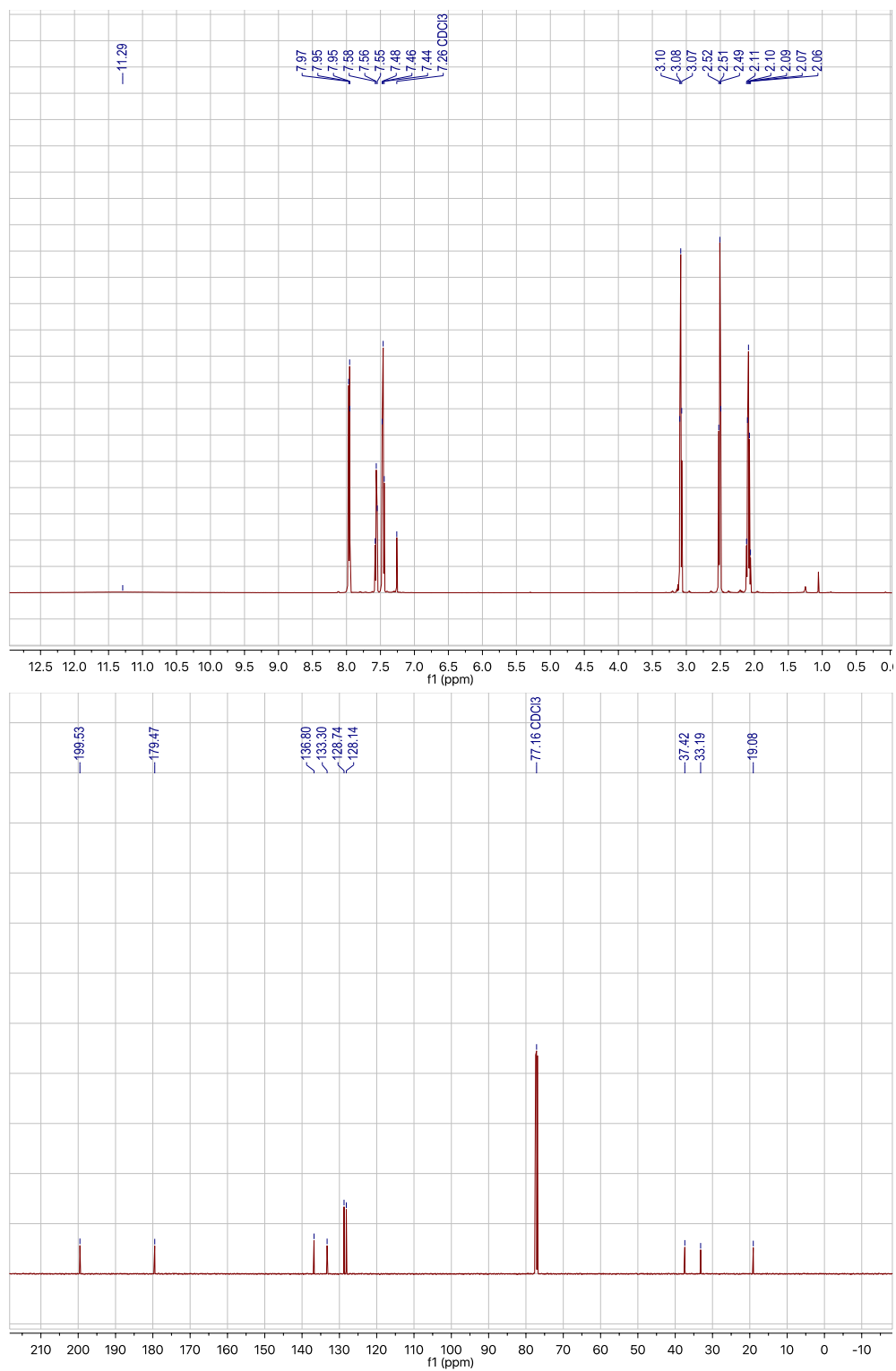
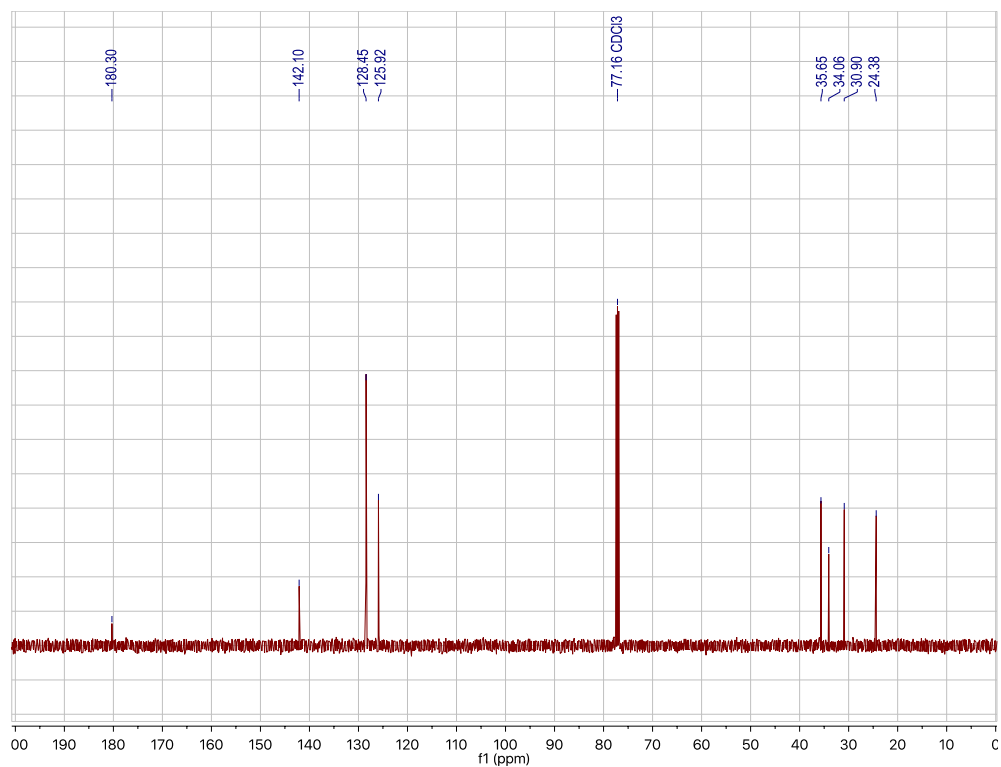
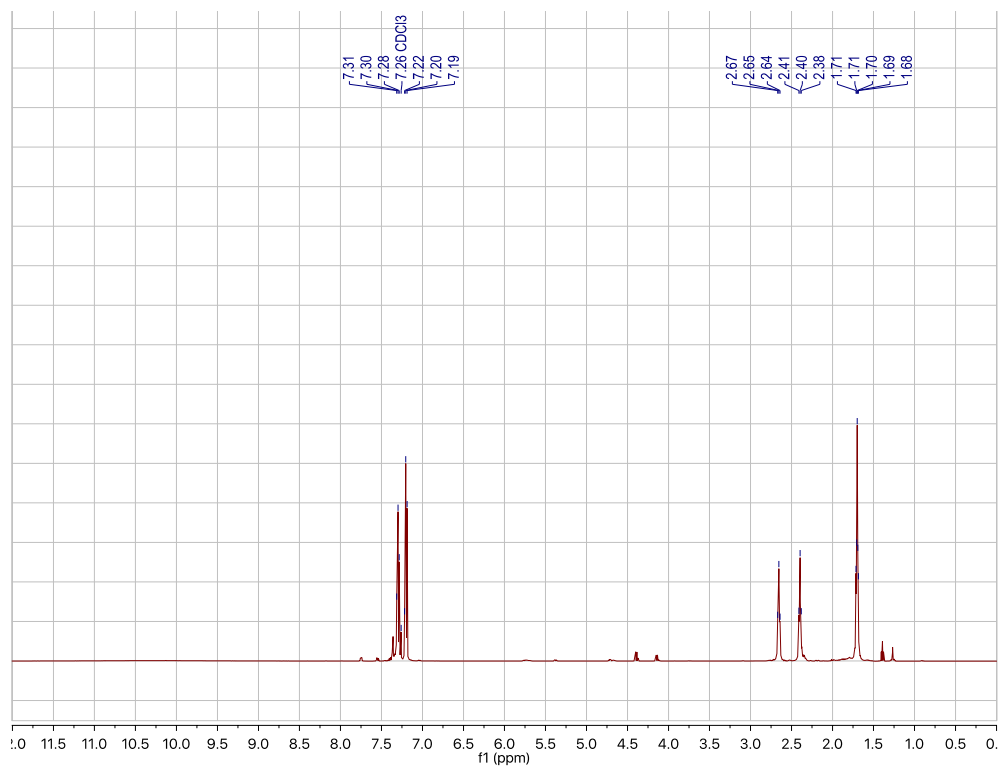


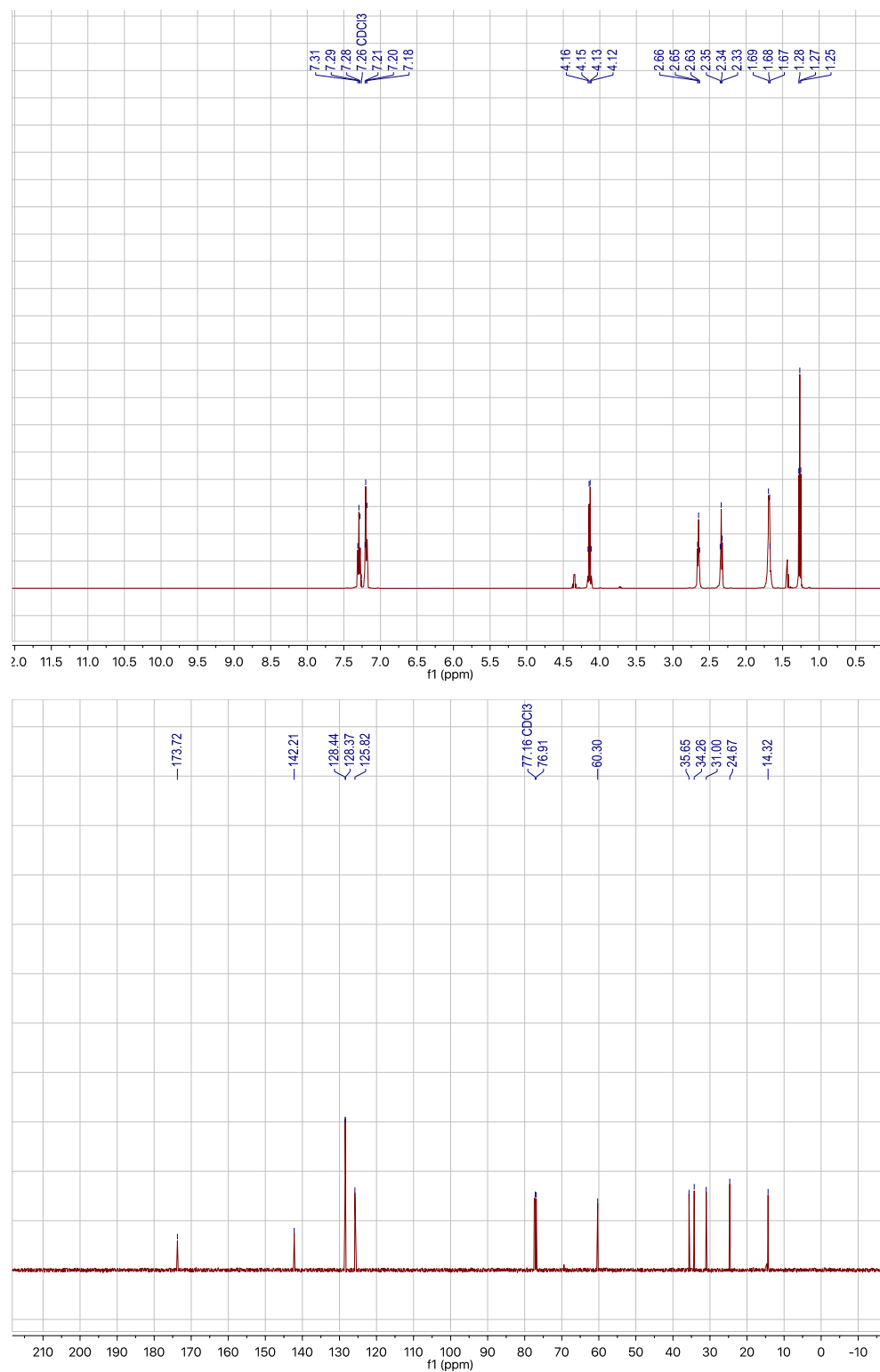
Figure S01. High dilution system used in the acyloin condensation.



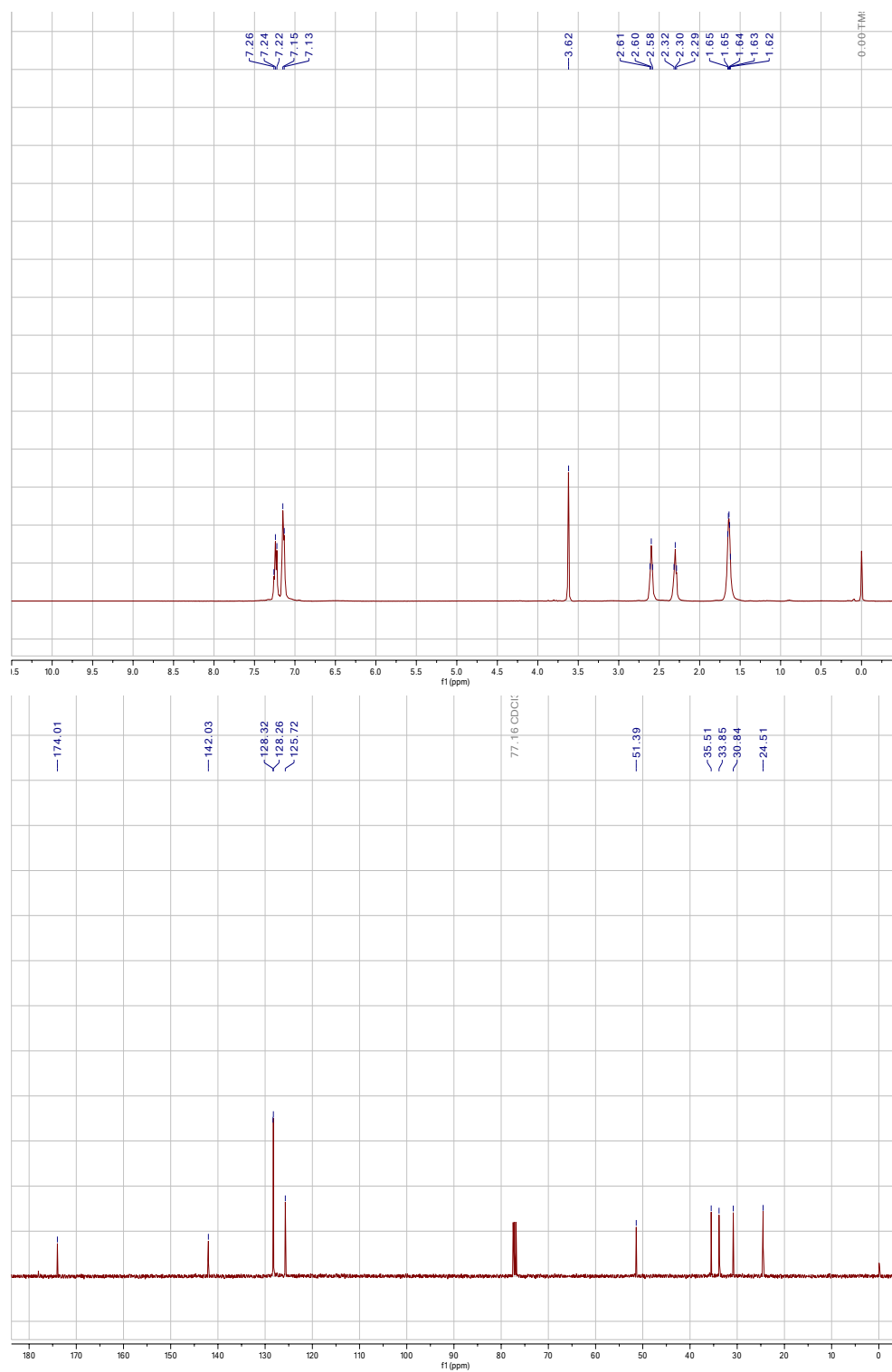
^1H and ^{13}C NMR spectra for 5-oxo-5-phenyl pentanoic acid (**P1**).



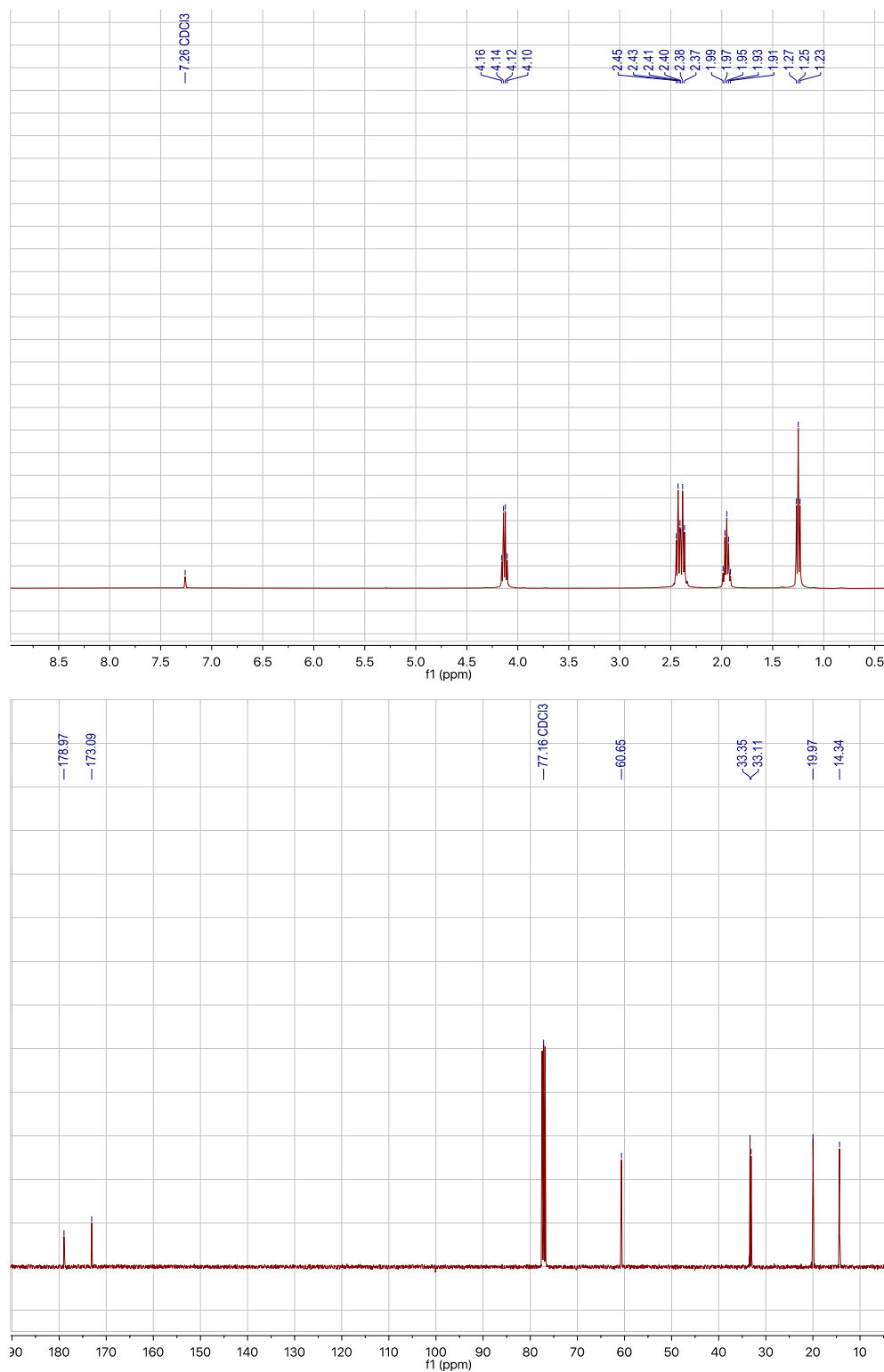
¹H and ¹³C NMR spectra for 5-phenyl pentanoic acid (P2).



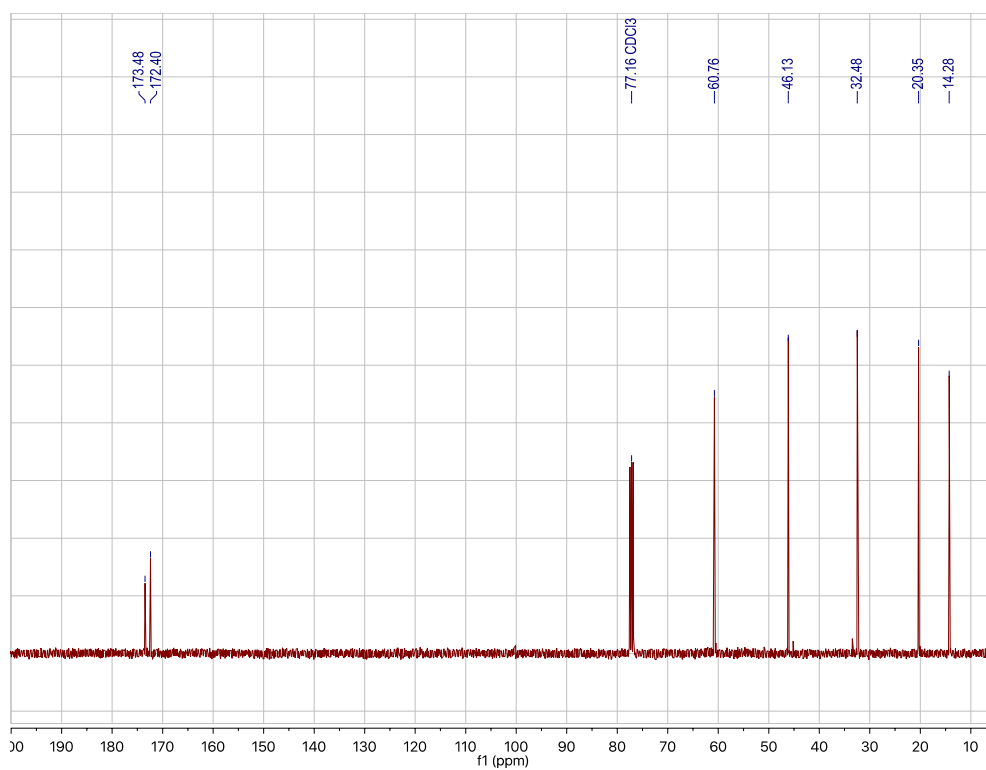
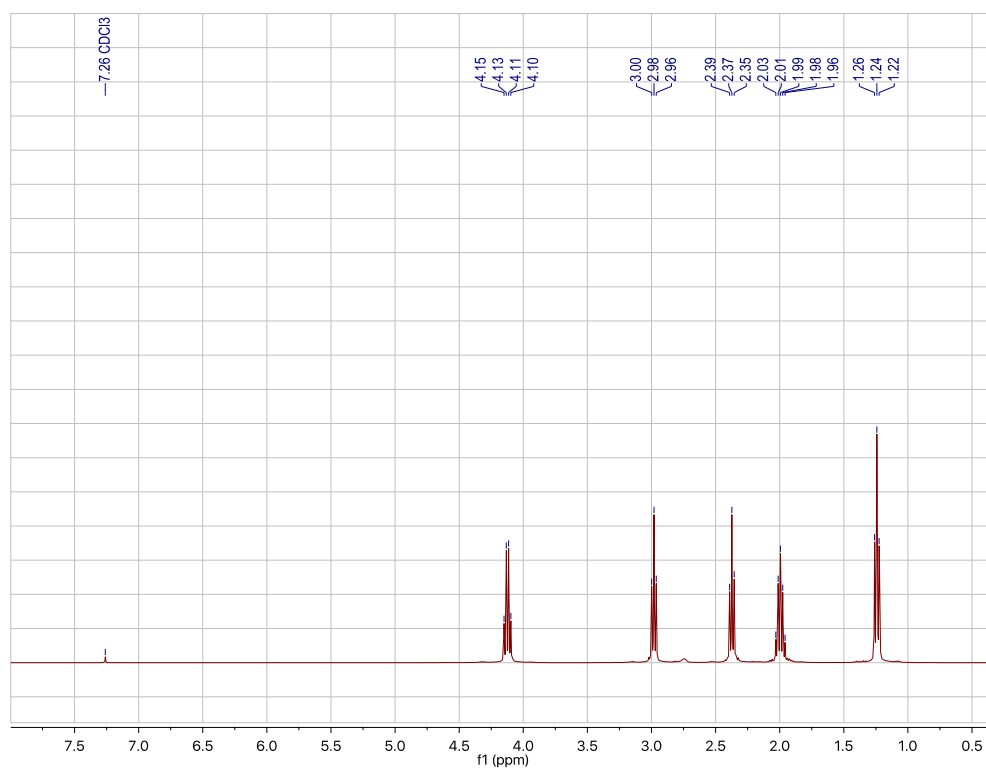
^1H and ^{13}C NMR spectra for ethyl 5-phenyl pentanoate (**P3a**).



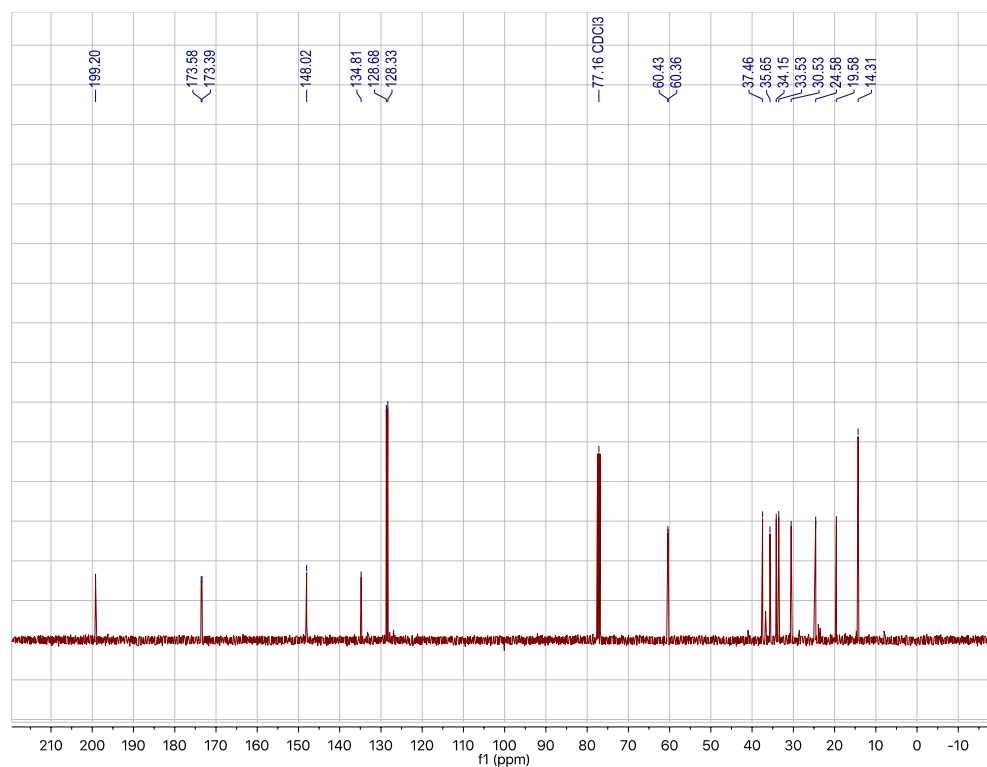
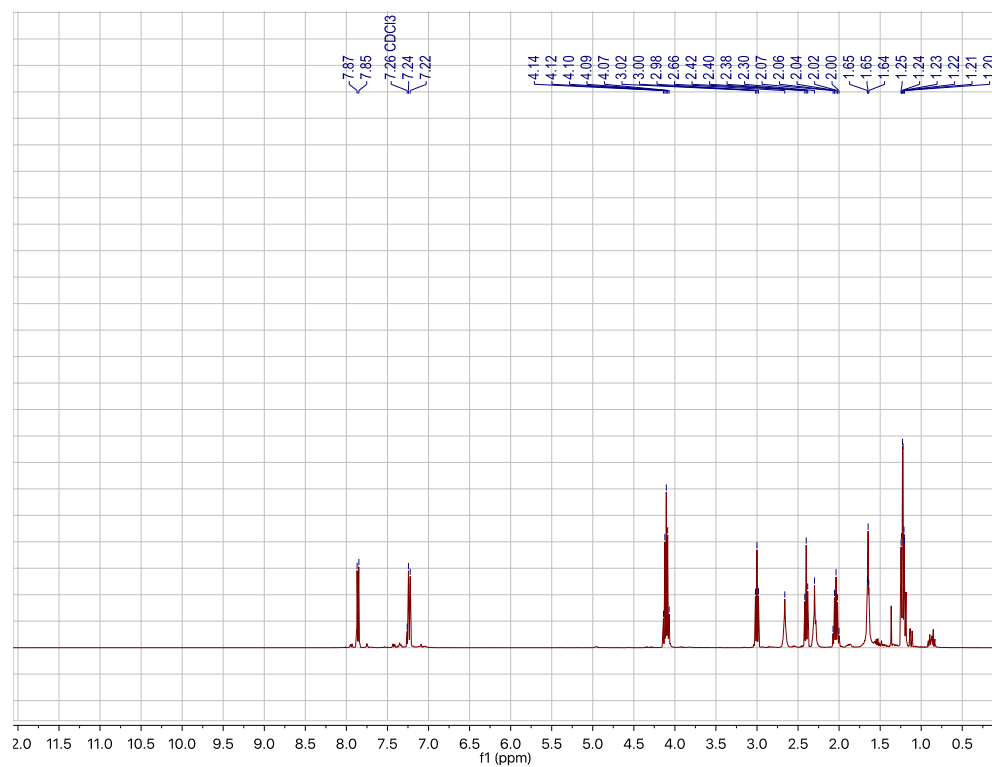
¹H and ¹³C NMR spectra for methyl 5-phenyl pentanoate (**P3b**).



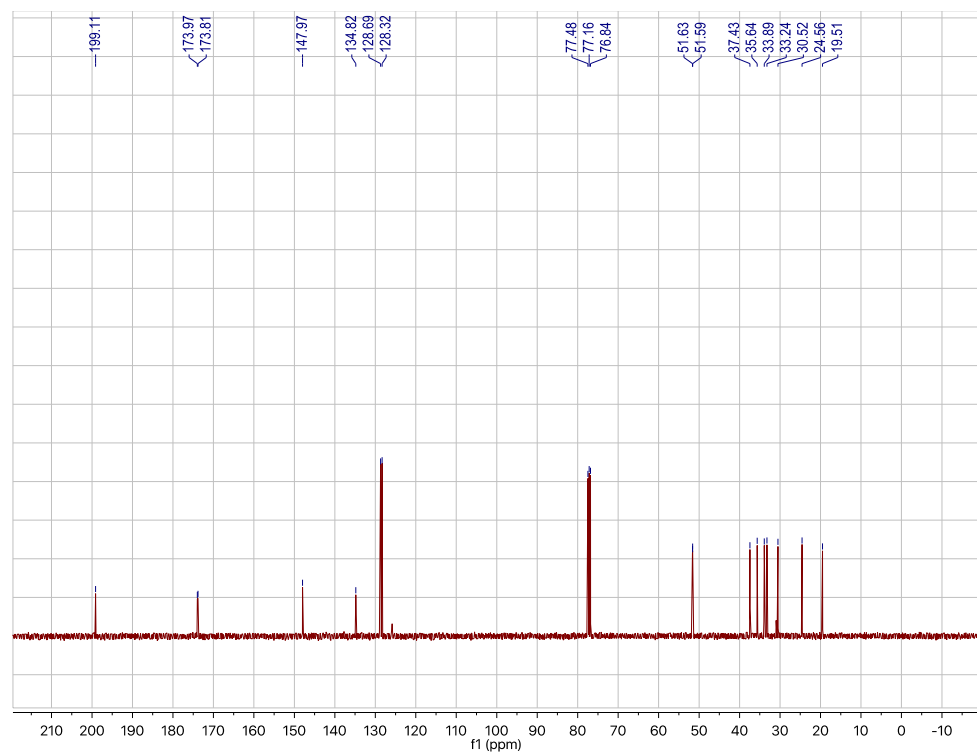
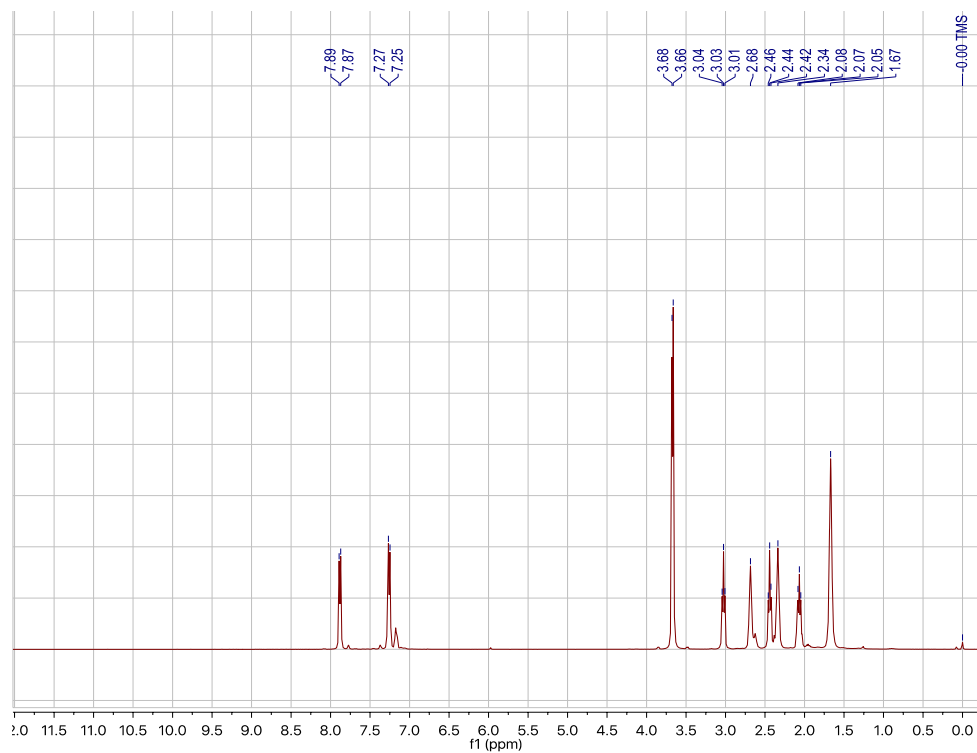
¹H and ¹³C NMR spectra for 5-ethoxycarbonyl pentanoic acid (**P4a**).



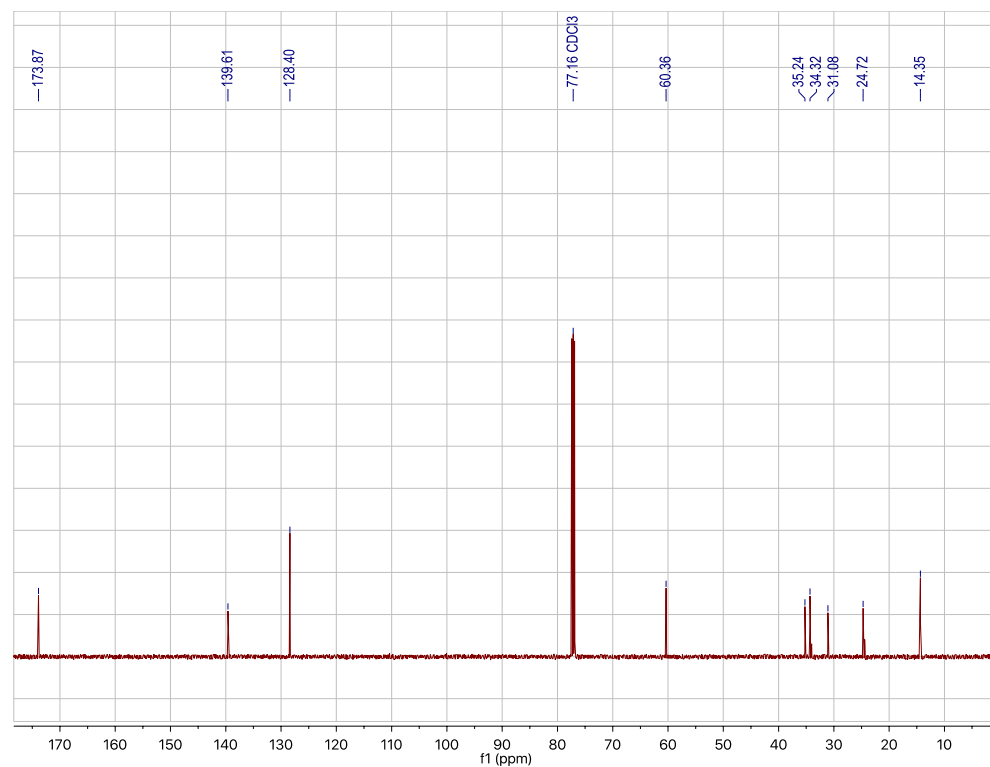
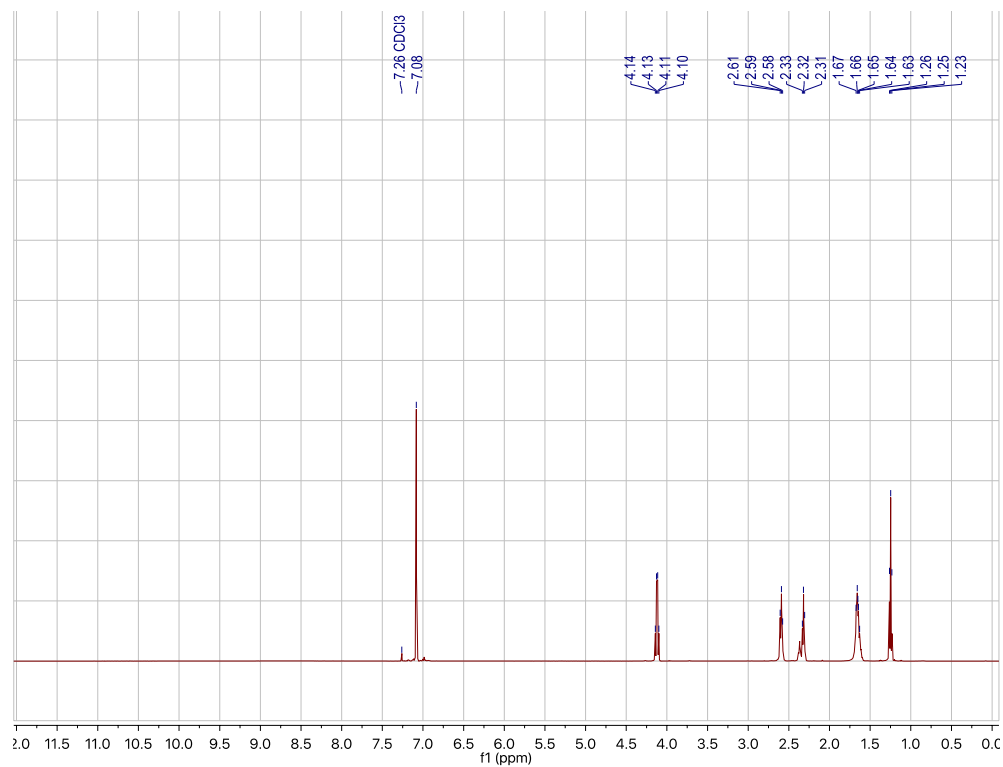
¹H and ¹³C NMR spectra for 5-ethoxycarbonyl pentanoyl chloride (**P5a**).



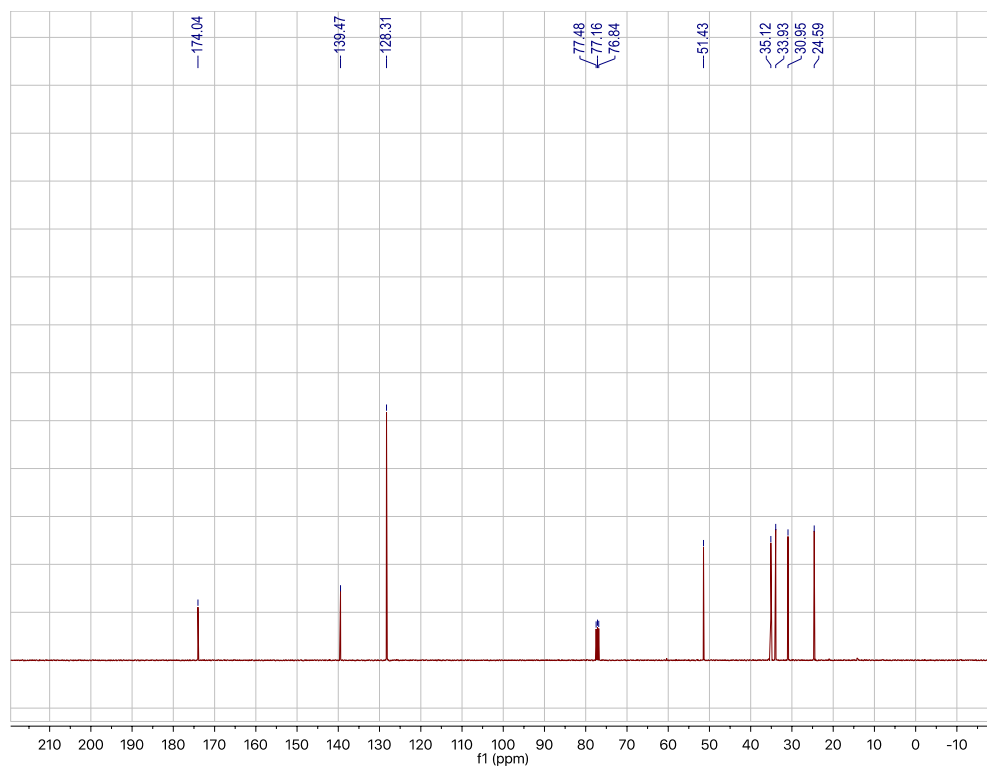
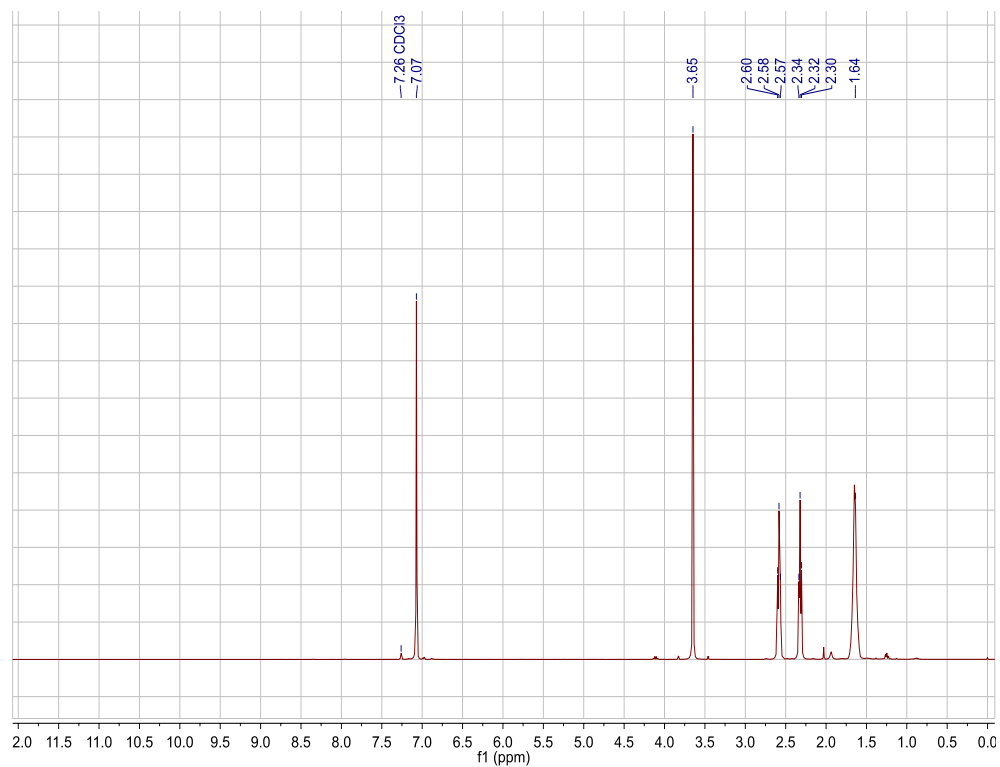
¹H and ¹³C NMR spectra for ethyl 5-(4-(4-ethoxycarbonyl)phenyl)-5-oxo-pentanoate (**P6a**).



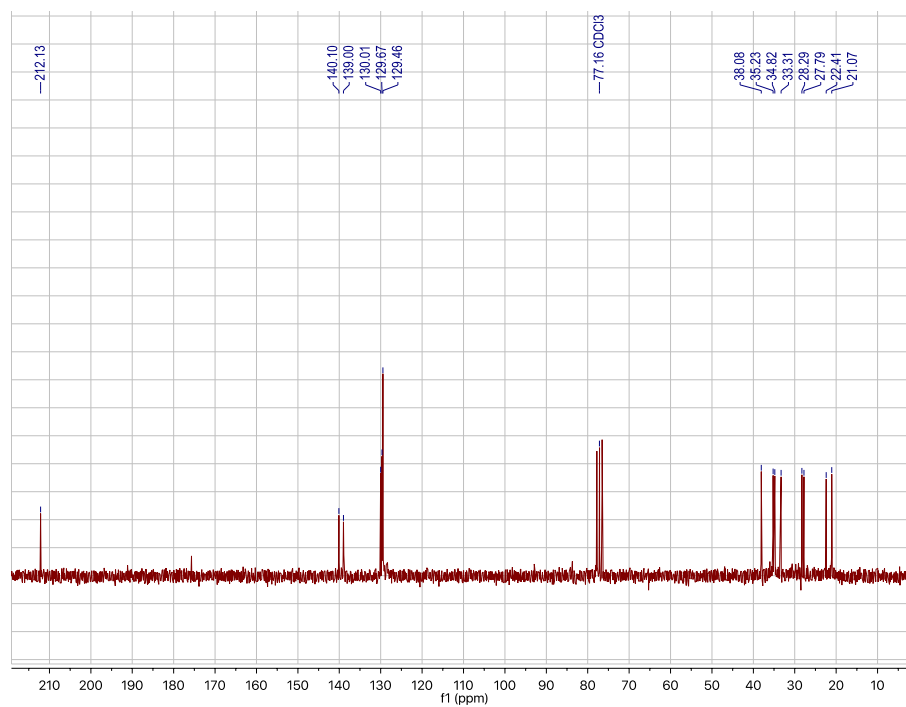
¹H and ¹³C NMR spectra for methyl 5-(4-(4-methoxycarbonyl)phenyl)-5-oxo-pentanoate (P6b).



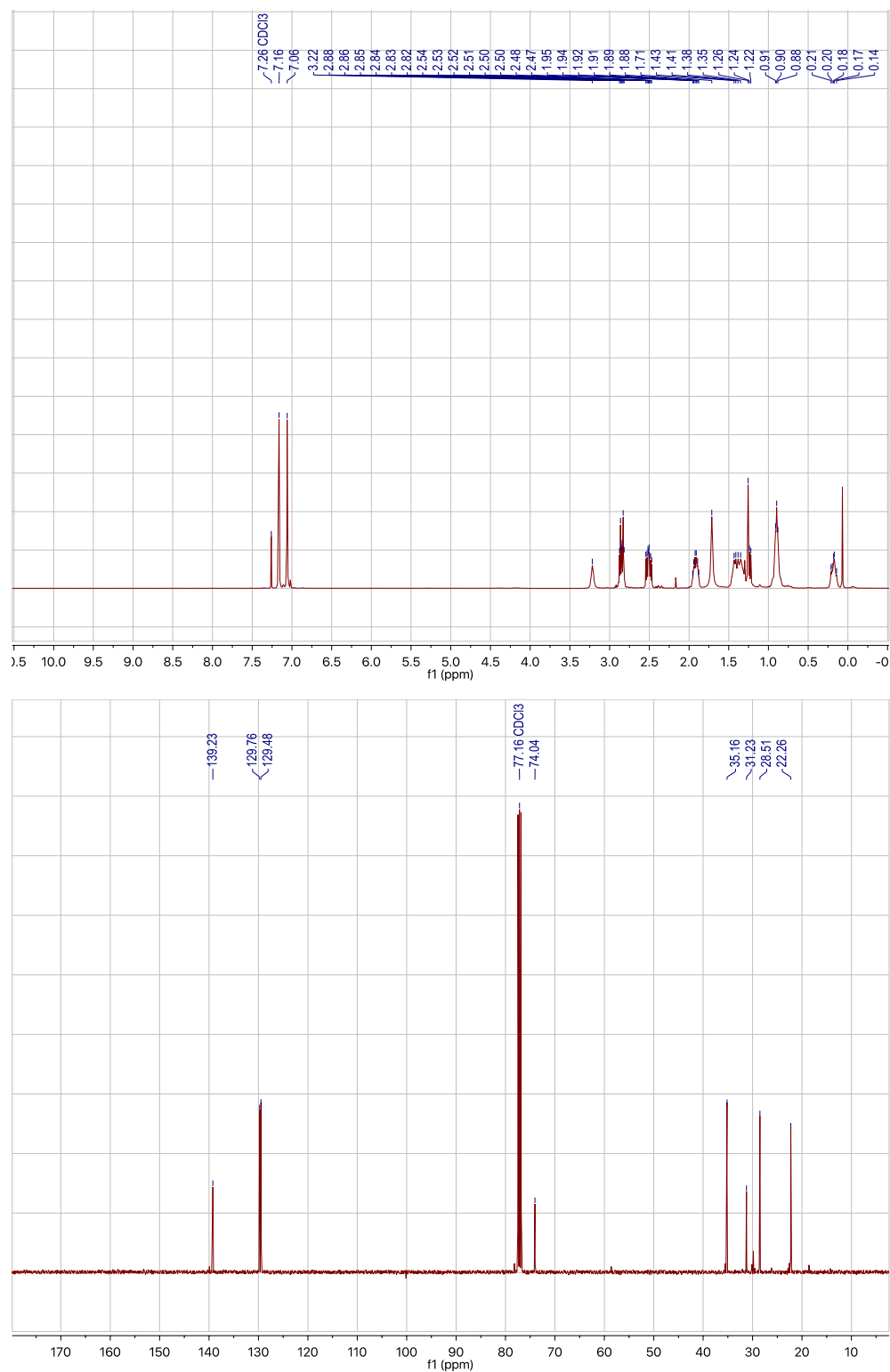
¹H and ¹³C NMR spectra for diethyl 5,5'-(1,4-phenylene)dipentanoate (**P7a**).



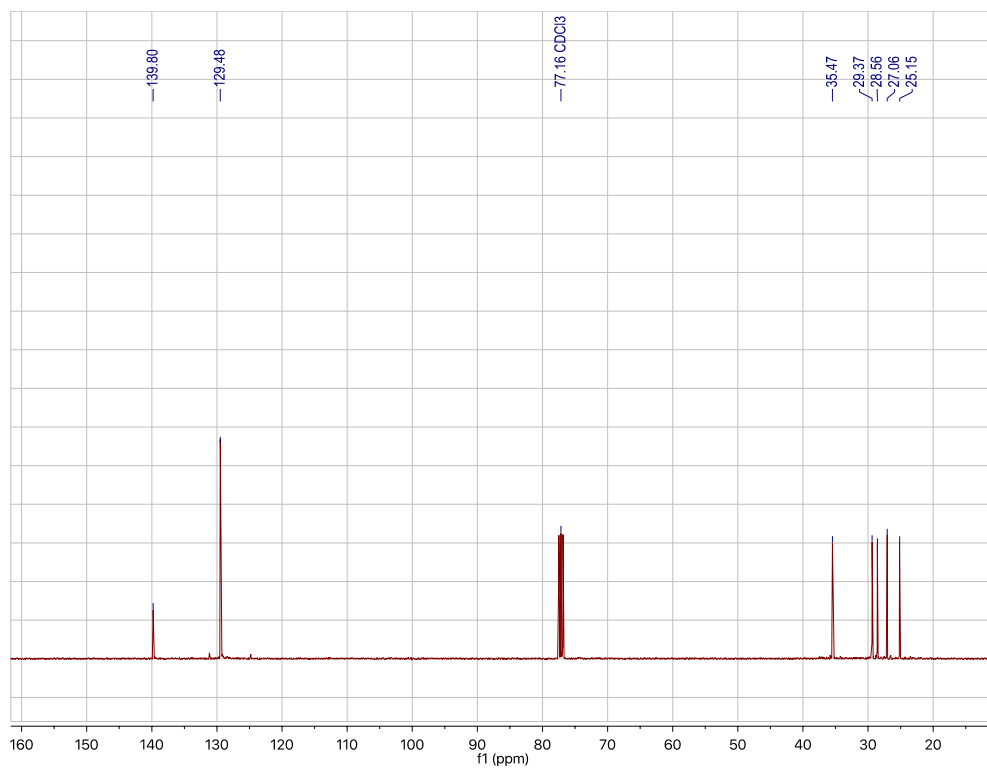
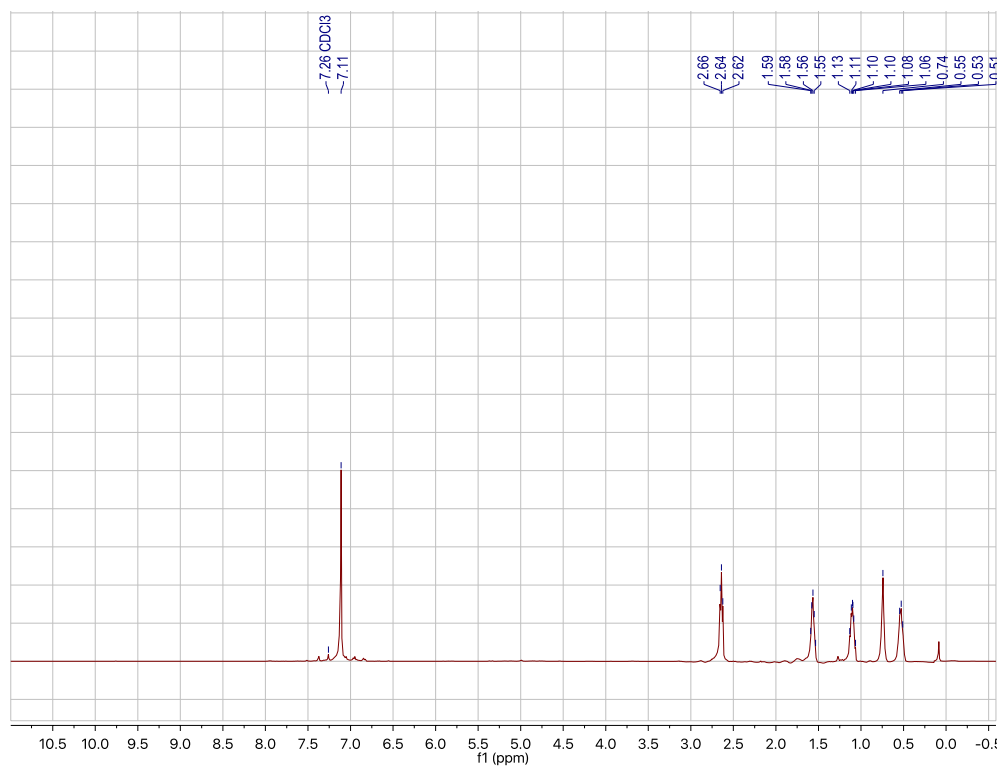
¹H and ¹³C NMR spectra for dimethyl 5,5'-(1,4-phenylene)dipentanoate (**P7b**).



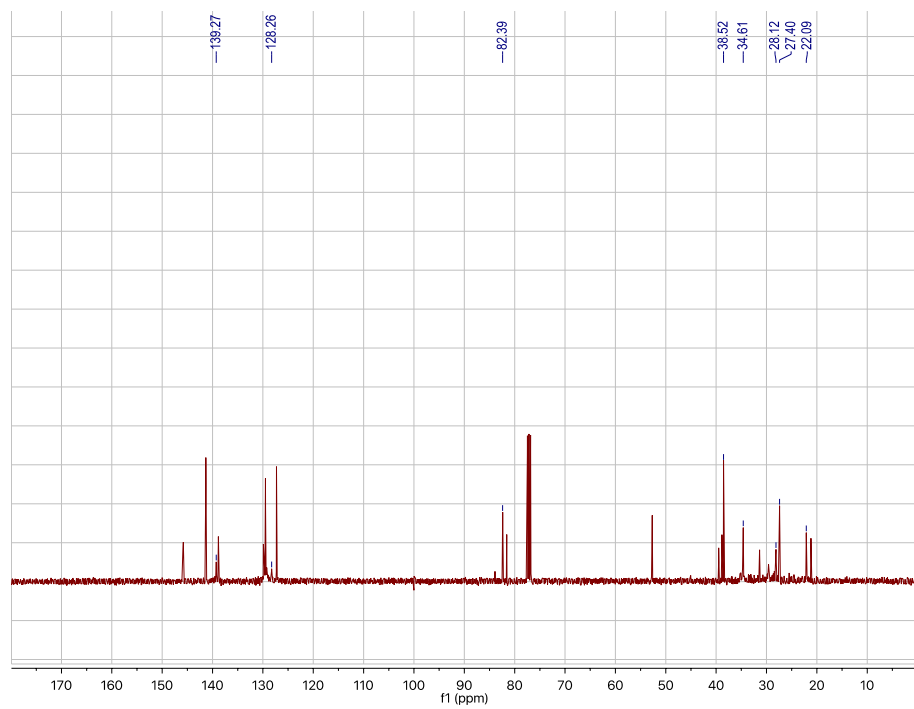
¹³C NMR spectra for 7-hydroxy-1(1,4)-benzenecycloundecaphan-6-one (**P8**) and 1(1,4)-benzeneocycloundecaphan-6,7-diol (**P9**) mixture.



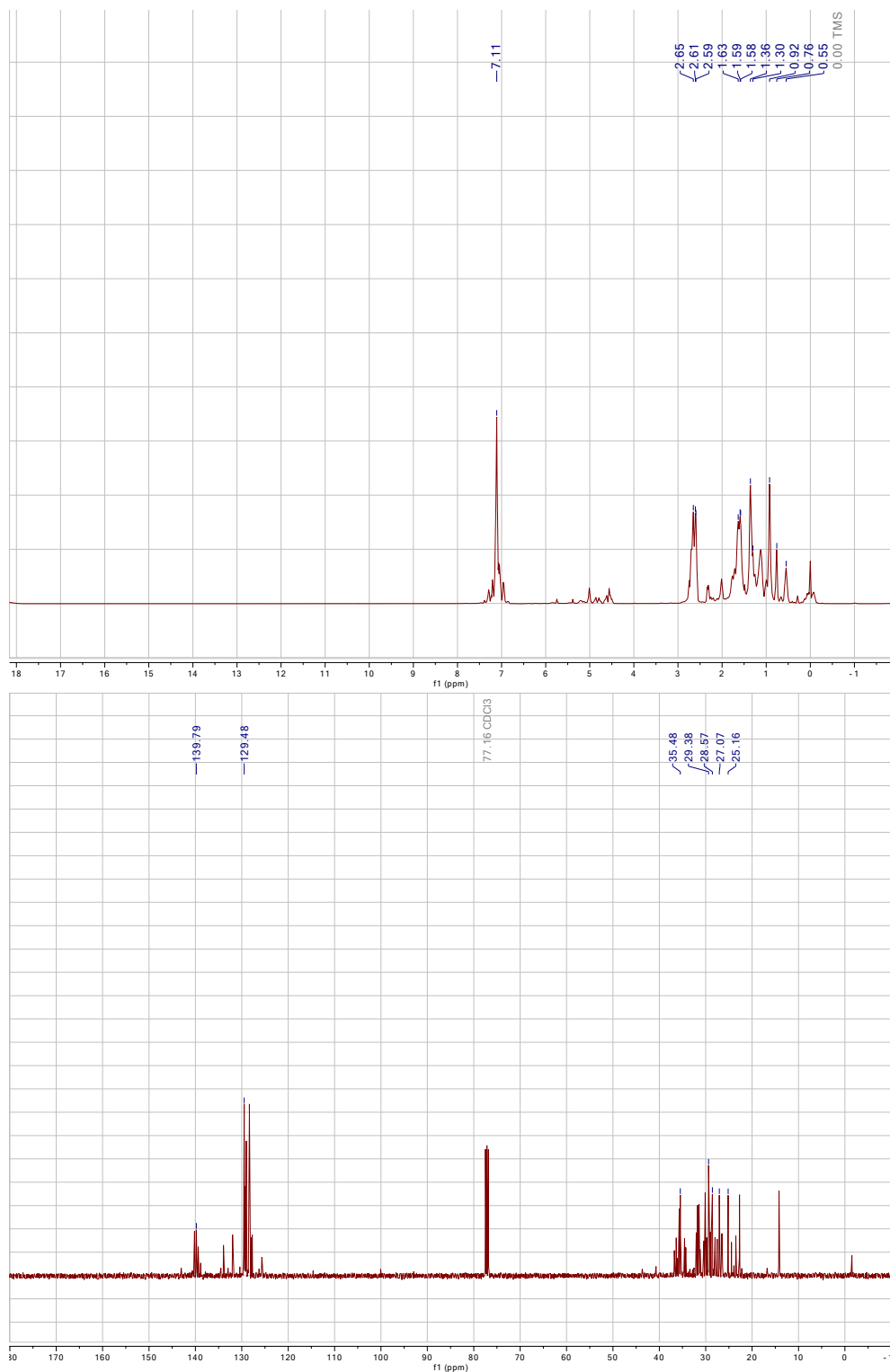
¹H and ¹³C NMR spectra for 1(1,4)-benzenecycloundecaphan-6,7-diol (**P9**).



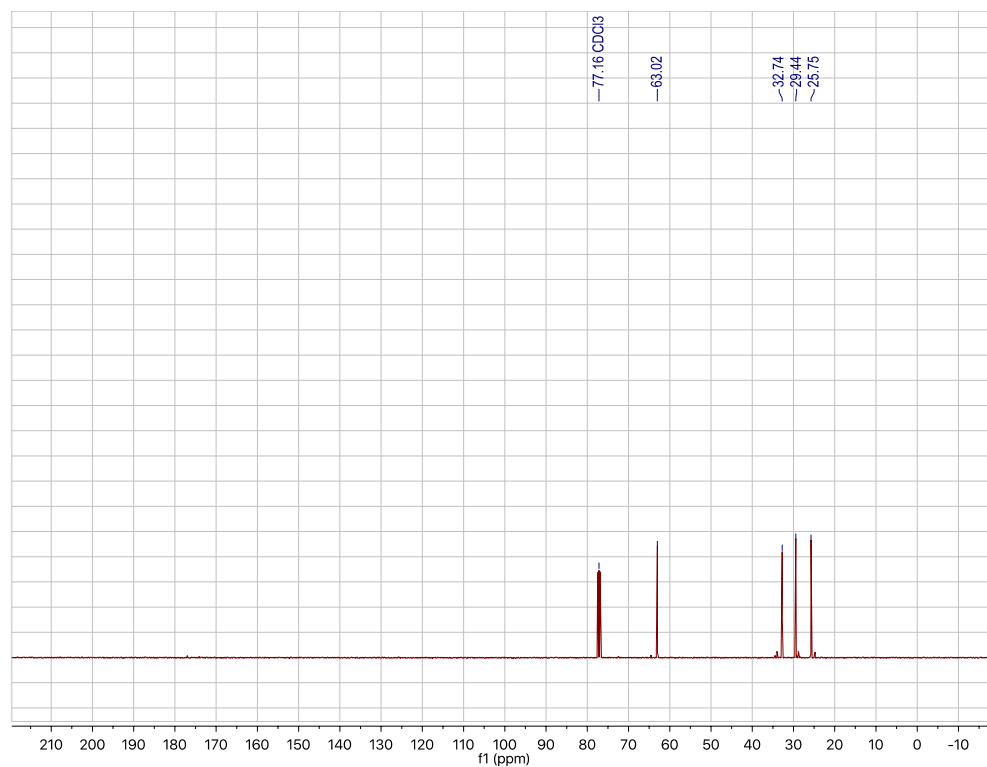
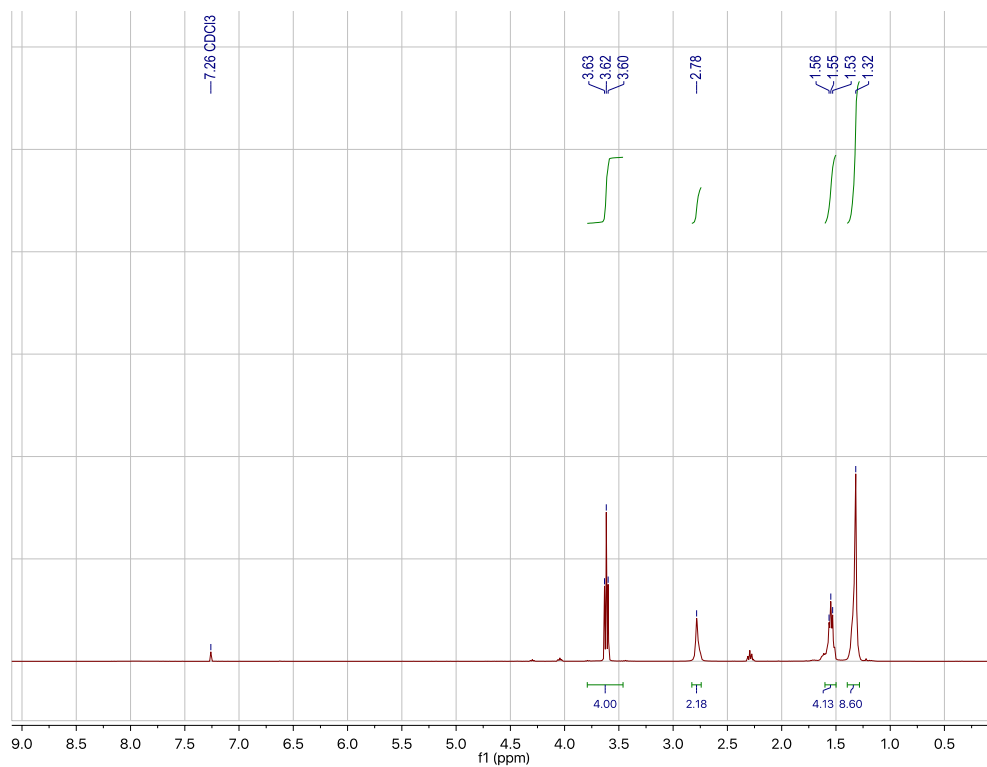
¹H and ¹³C NMR spectra for 1(1,4)-benzenecycloundecaphane (**P10**).



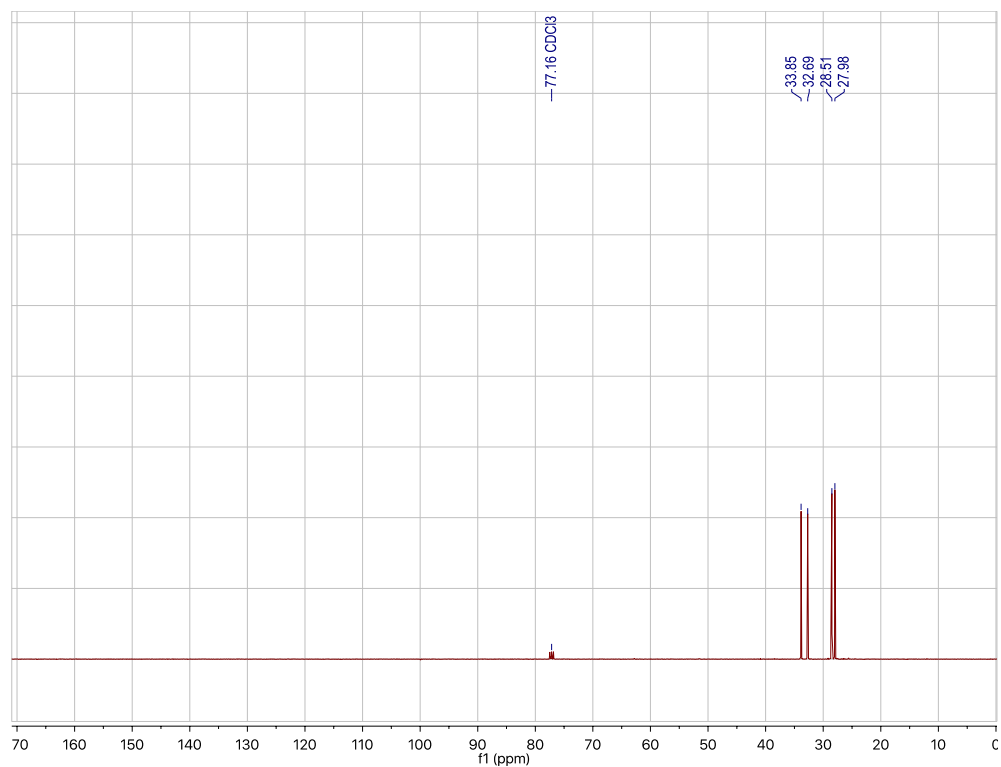
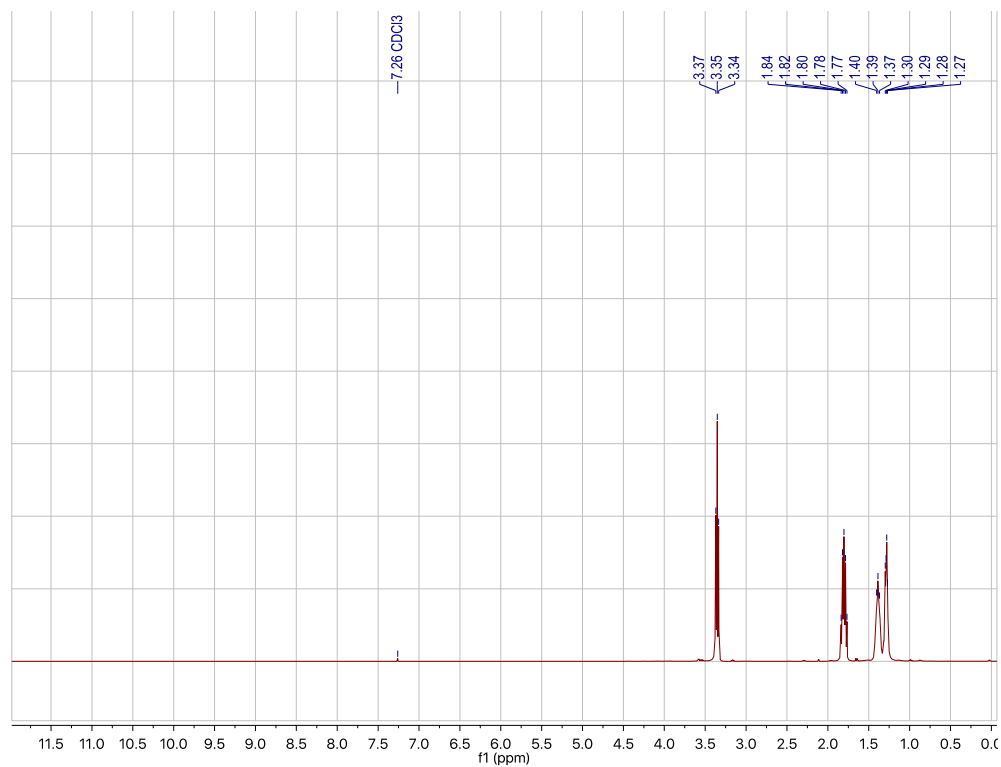
^{13}C NMR spectra for 1(1,4)-benzenecycloundecaphan-6,7-diyl dimethanesulfonate (**P11**).



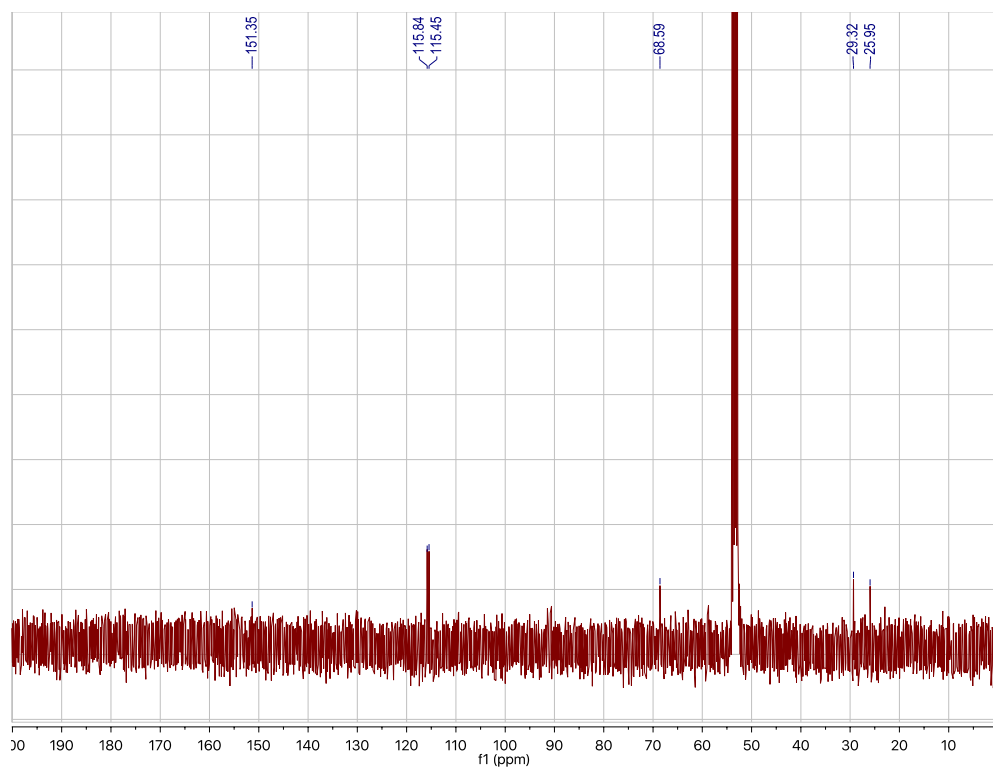
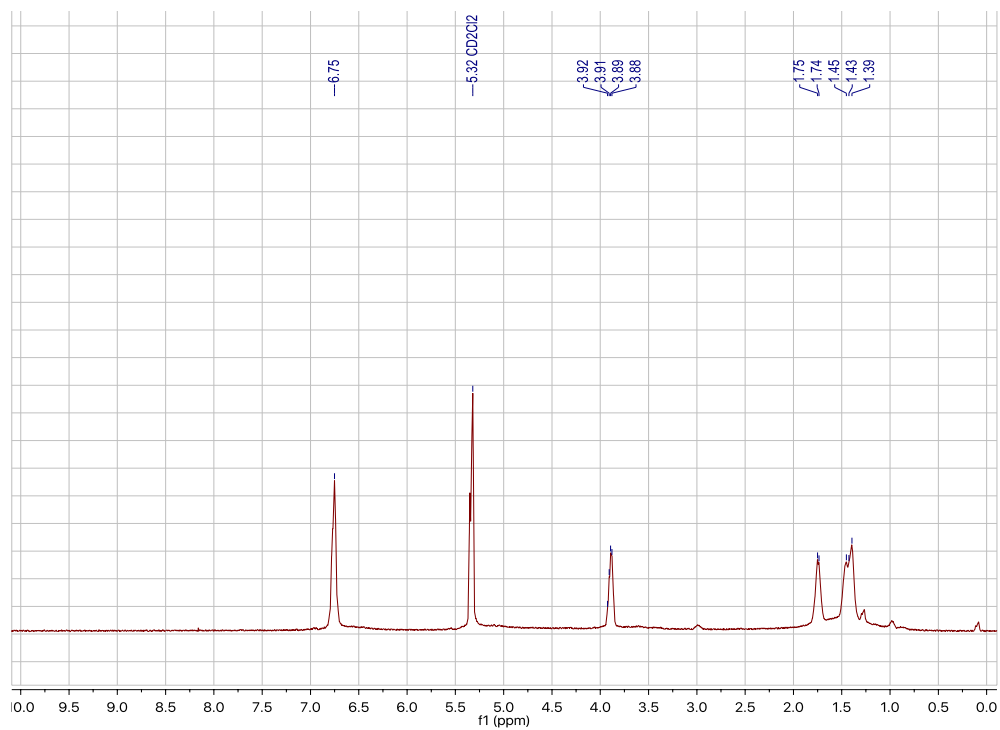
^1H and ^{13}C NMR spectra for 1(1,4)-benzenecycloundecaphane (**P10**) starting from (**P11**).



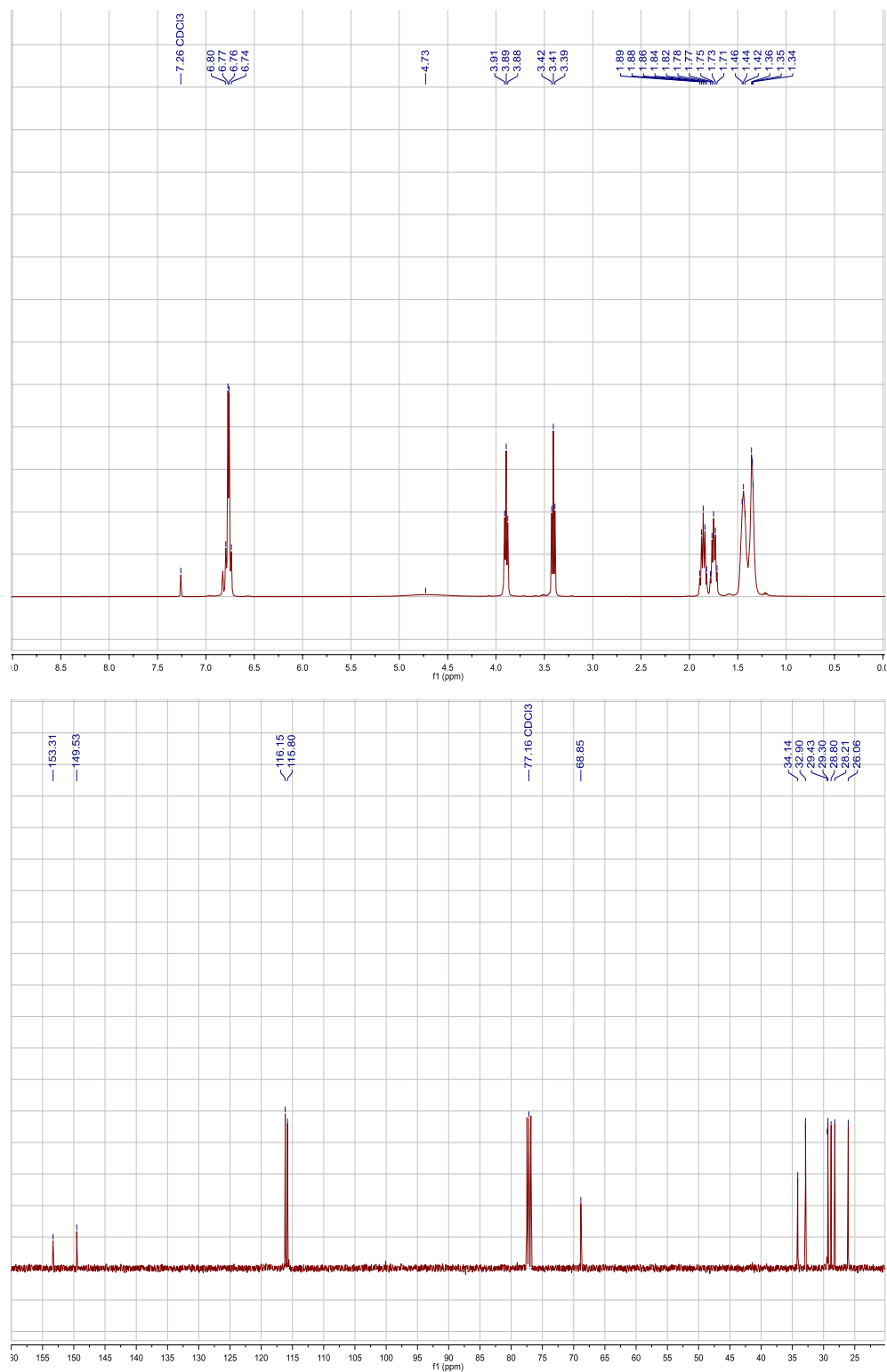
¹H and ¹³C NMR spectra for 1,8-octanediol (P12).



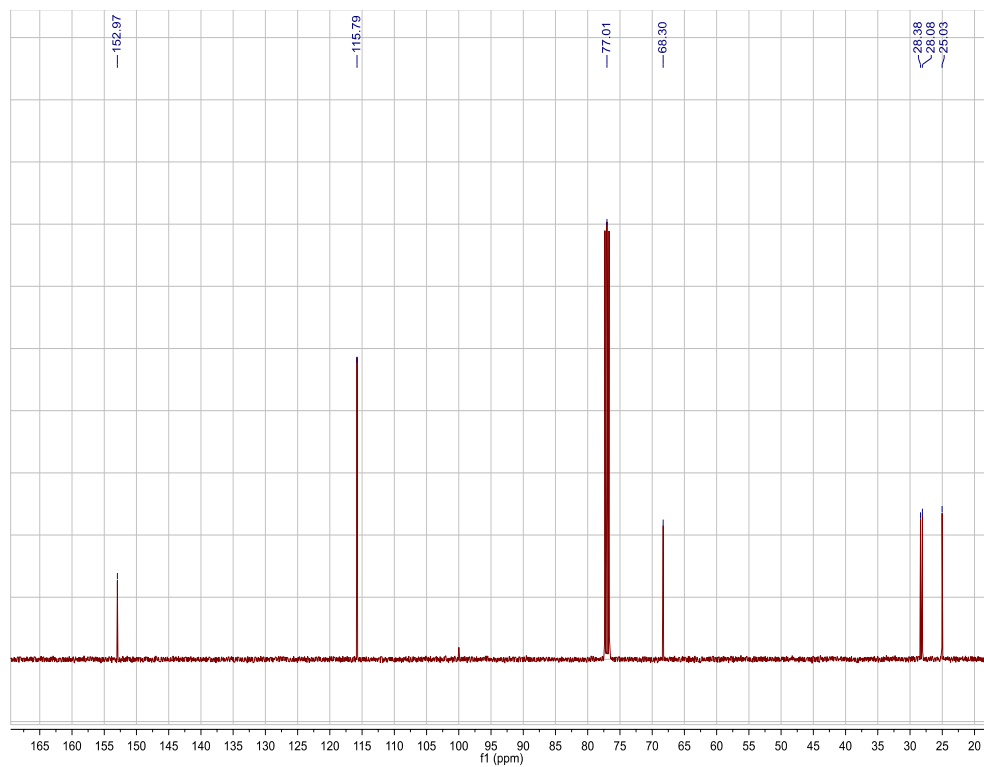
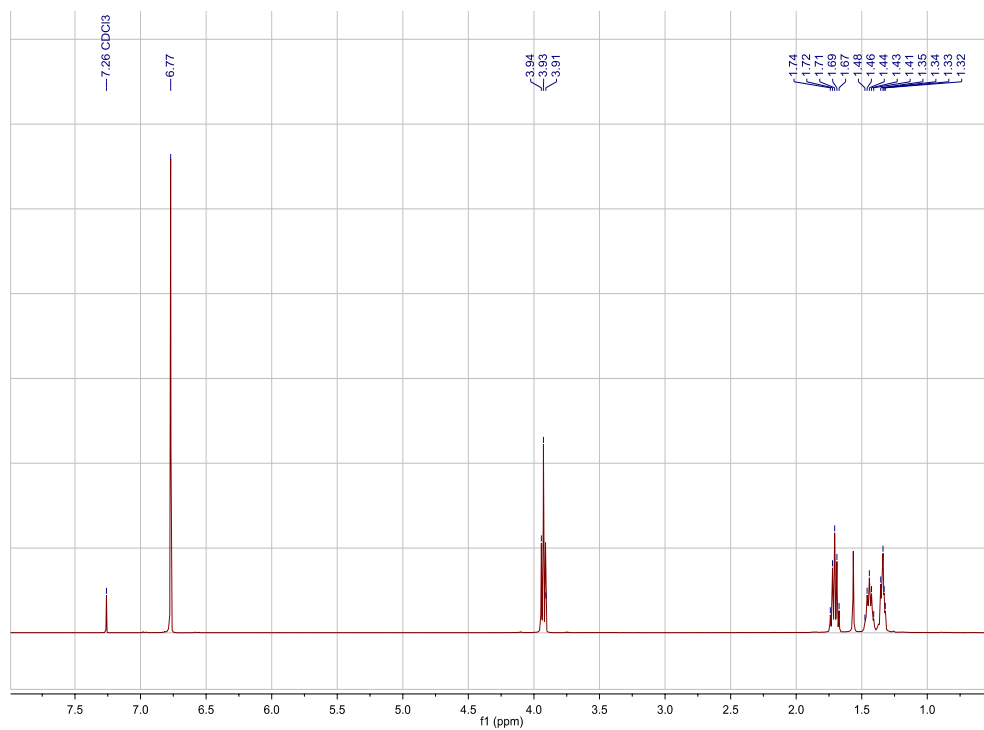
^1H and ^{13}C NMR spectra for 1,8-dibromooctane (P13).



¹H and ¹³C NMR spectra for 2,11-dioxa-1(1,4)-benzenecycloundecaphane (**P15**) in one step.



¹H and ¹³C NMR spectra for *p*-hydroxyphenyl-8-bromooctyl ether (**P14**).



¹H and ¹³C NMR spectra for 2,11-dioxa-1(1,4)-benzenecycloundecaphane (**P15**) in two steps.