

SUPPORTING INFORMATION

Dehydrogenative alcohol coupling and one-pot cross metathesis/dehydrogenative coupling reactions of alcohols using Grubbs catalysts

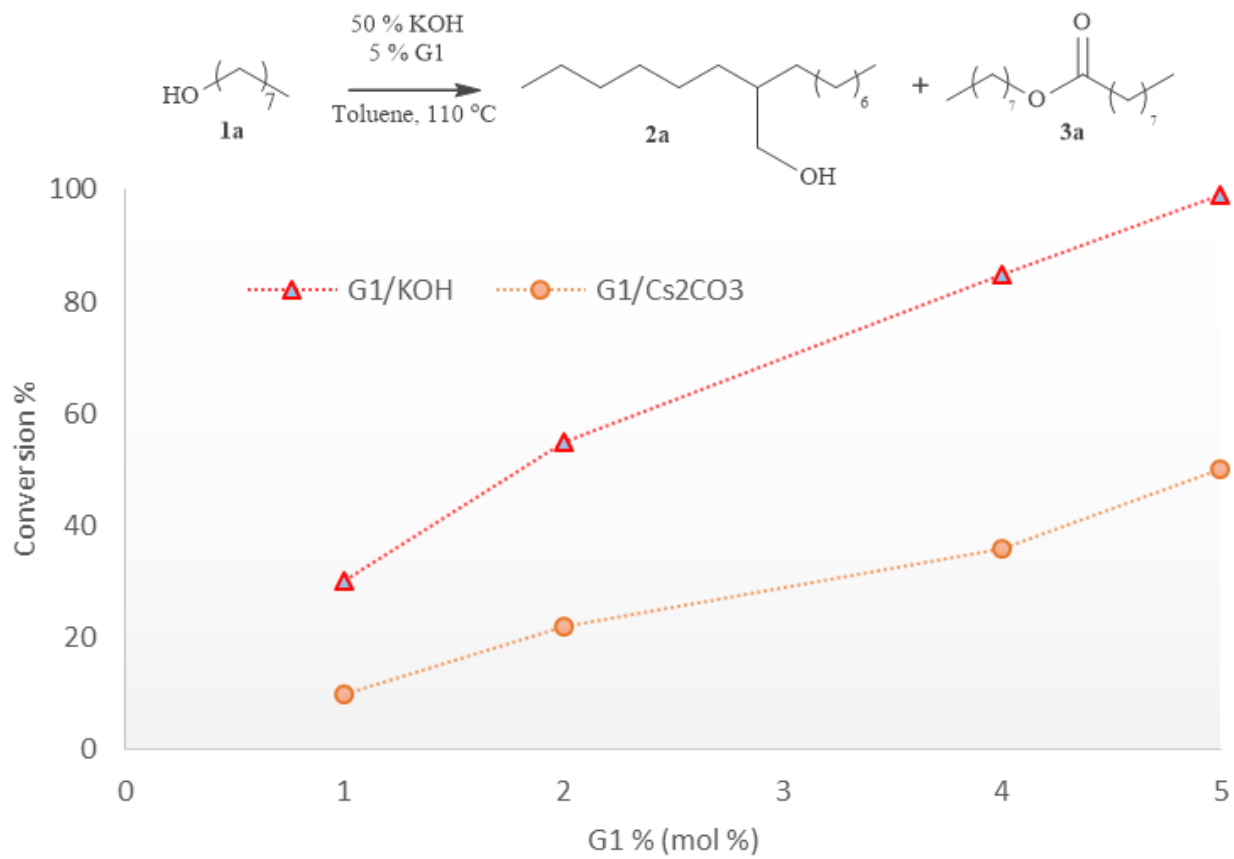
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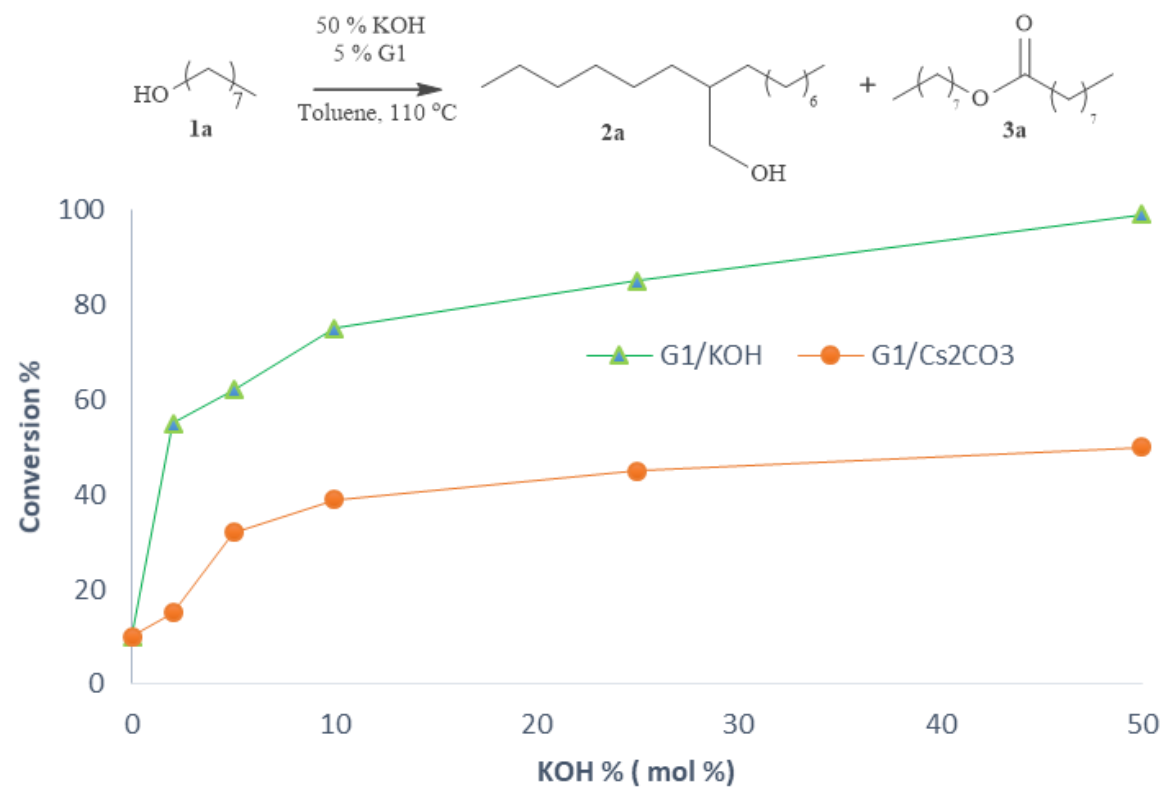
Table S1. The effect of KOH and PCy₃ on formation of benzoic acid/octanoic acid

Entry	KOH %	PCy ₃ %	Substrate	Time (h)	Conv. %	Yield % ^a	
						3a/3b	4a/4b
1		-	1a	48	65	55 (3a)	-
2	50	-	1b	48	99 ^b	13 (3b)	-
3		-	1a	48	90	-	4 (4a)
4	100	-	1b	48	80 ^b	-	8 (4b)
5		5	1a	24	84	78 (3a)	6 (4a)
6		15	1a	24	98	82 (3a)	16 (4a)
7	50	20	1a	24	65	44 (3a)	21 (4a)
8		20	1b	24	80	60 (3b)	20 (4b)
9		10	1a	12	90	70 (3a)	20 (4a)
10	100	10	1b	12	95	65 (3b)	30 (4b)

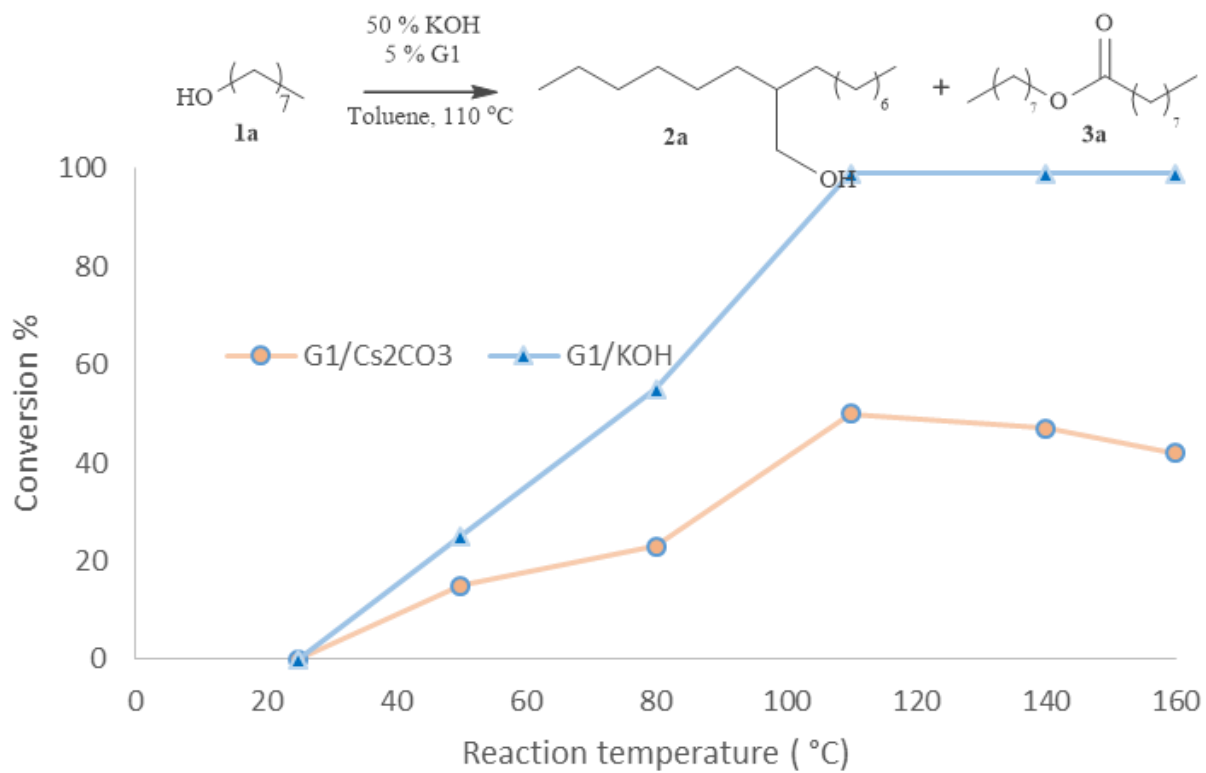
a: Determined by GC-MS. b: benzaldehyde was formed as the major product.



Graph S1. The effect of G1 % loading on conversion rate of dehydrogenative alcohol coupling of 1-octanol



Graph S2. The effect of KOH % loading on conversion rate of dehydrogenative alcohol coupling of 1-octanol



Graph S3. The effect of reaction temperature on conversion rate of dehydrogenative alcohol coupling of 1-octanol (p-xylene and mesitylene was used for experiments conducted at 140 and 160 °C, respectively.)

MECHANISTIC STUDIES

1. Representative procedure for 1-octanal coupling reactions

1.1. Mechanistic studies utilizing 1-octanal and Base

Base (KOH, Cs₂CO₃, NaOMe or KOtBu, 0.122 mmol) and 1-octanal (0.244 mmol) in dry toluene (1 mL) were added to a Schlenk reactor under nitrogen atmosphere. The reactor was heated to 110 °C in a preheated oil bath and magnetically stirred. Samples regularly were withdrawn from the reaction mixture, diluted with methanol and analyzed by GC/MS.

1.2. Mechanistic studies utilizing 1-octanal, Base and PCy₃

Base (KOH, Cs₂CO₃, NaOMe or KOtBu, 0.122 mmol), PCy₃ (0.0244 mmol) and 1-octanal (0.244 mmol) in dry toluene (1 mL) were added to a Schlenk reactor under nitrogen atmosphere. The reactor was heated to 110 °C in a preheated oil bath and magnetically stirred. Samples regularly were withdrawn from the reaction mixture, diluted with methanol and analyzed by GC/MS.

1.3. G1 (HG2) catalyzed coupling reactions utilizing 1-octanal and Cs₂CO₃ (KOH)/PCy₃

G1 or HG2 (0.0122 mmol), Base (KOH, Cs₂CO₃, NaOMe or KOtBu, 0.122 mmol), PCy₃ (0.0244 mmol) and 1-octanal (0.244 mmol) in dry toluene (1 mL) were added to a Schlenk reactor under nitrogen atmosphere. The reactor was heated to 110 °C in a preheated oil bath and magnetically stirred. Samples regularly were withdrawn from the reaction mixture, diluted with methanol and analyzed by GC/MS.

2. Representative procedure for 1-octanal and 1-octanol coupling reactions

2.1. Mechanistic studies utilizing 1-octanal/1-octanol and Cs₂CO₃ and KOH

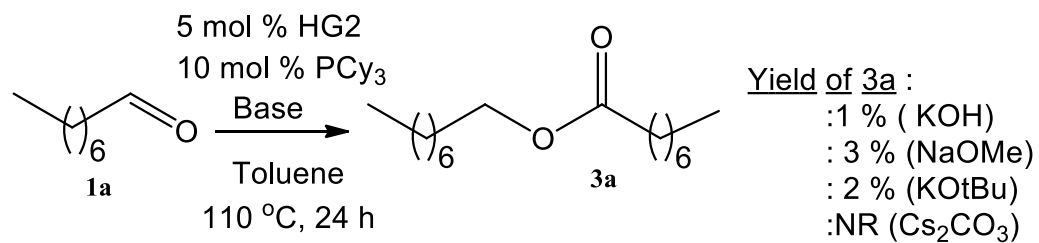
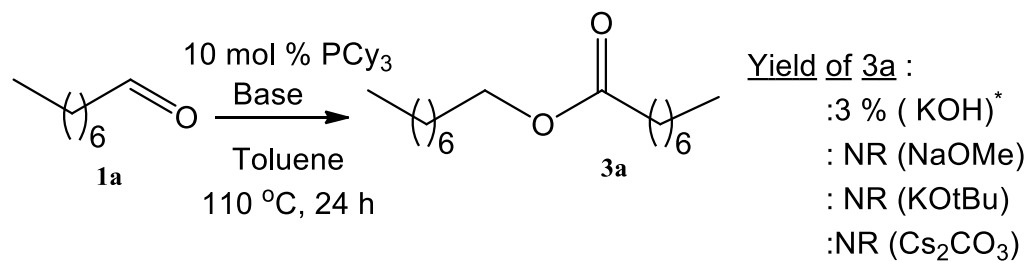
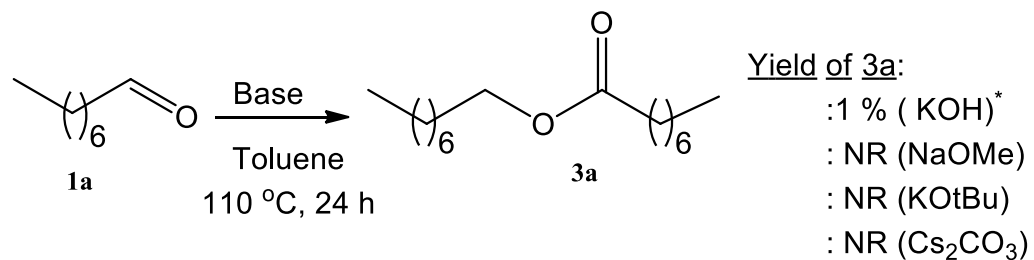
Base (KOH, Cs₂CO₃, NaOMe or KOtBu, 0.122 mmol) and 1-octanal (0.244 mmol) and 1-octanol (0.244 mmol) in dry toluene (1 mL) were added to a Schlenk reactor under nitrogen atmosphere. The reactor was heated to 110 °C in a preheated oil bath and magnetically stirred. Samples regularly were withdrawn from the reaction mixture, diluted with methanol and analyzed by GC/MS.

2.2. Mechanistic studies utilizing 1-octanal and Cs₂CO₃ (KOH)/PCy₃

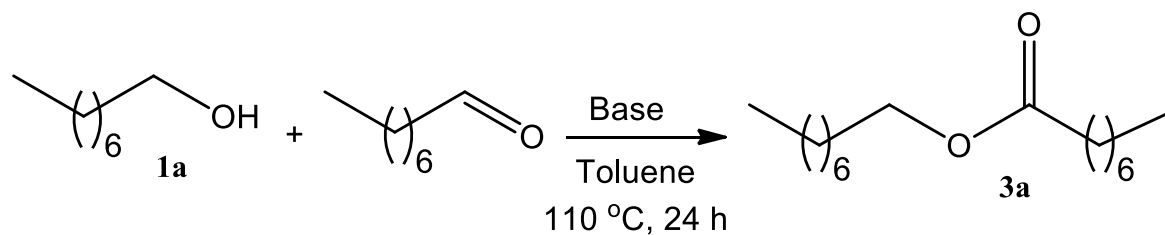
Base (KOH, Cs₂CO₃, NaOMe or KOtBu, 0.122 mmol), PCy₃ (0.0244 mmol), 1-octanal (0.244 mmol) and 1-octanol (0.244 mmol) in dry toluene (1 mL) were added to a Schlenk reactor under nitrogen atmosphere. The reactor was heated to 110 °C in a preheated oil bath and magnetically stirred. Samples regularly were withdrawn from the reaction mixture, diluted with methanol and analyzed by GC/MS.

2.3. G1 (HG2) catalyzed coupling reactions utilizing 1-octanal and Cs₂CO₃ (KOH)/PCy₃

G1 or HG2 (0.0122 mmol), Base (KOH, Cs₂CO₃, NaOMe or KOtBu, 0.122 mmol), PCy₃ (0.0244 mmol) and 1-octanal (0.244 mmol) in dry toluene (1 mL) were added to a Schlenk reactor under nitrogen atmosphere. The reactor was heated to 110 °C in a preheated oil bath and magnetically stirred. Samples regularly were withdrawn from the reaction mixture, diluted with methanol and analyzed by GC/MS.

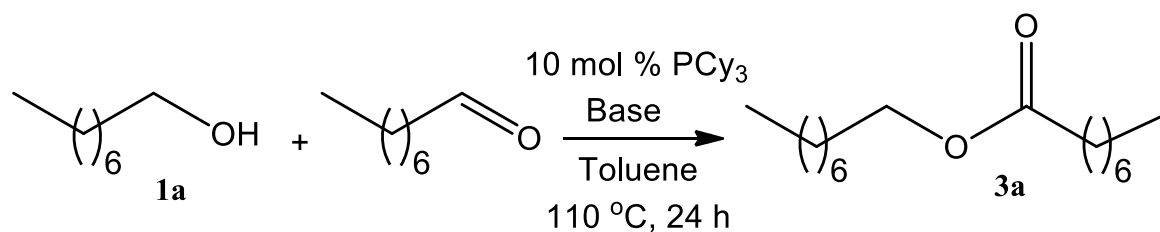


Scheme S1. The reaction of 1-octanal in the absence and presence of HG2



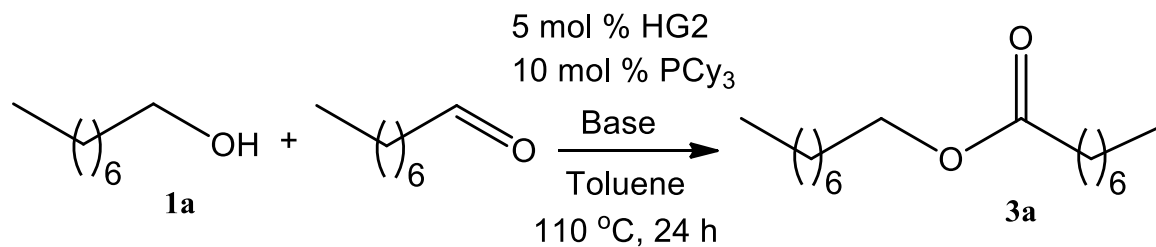
Yield of 3a : 38 % (KOH)*
 : 32 % (NaOMe)
 : 34 % (KOtBu)
 : 36 % (Cs₂CO₃)

* octanoic acid is formed in 8 % yield



Yield of 3a: 38 % (KOH)*
 : 33 % (NaOMe)
 : 34 % (KOtBu)
 : 35 % (Cs₂CO₃)

* octanoic acid is formed in 10 % yield



Yield of 3a : 80% (KOH)*
 : 82 % (NaOMe)
 : 60 % (KOtBu)
 : 82 (Cs₂CO₃)

* octanoic acid is formed in 12 % yield

Scheme S2. The reaction of 1-octanal/1-octanol mixture in the absence and presence of HG2

Spectroscopic datas for the selected compounds:

2-hexyyl-1-decanol (2a)

^1H NMR (400 MHz, CDCl_3) δ 3.48 (d, $J = 5.1$ Hz, 2H), 1.20 (m, 26H), 0.81 (t, 6H)

^{13}C NMR (100 MHz, CDCl_3) δ 65.85, 40.16, 31.89, 30.85, 29.94, 29.35, 22.34, 14.13

MS (EI, m/z) $[\text{M}]^+$: 242

Octyl octanoate (3a)

^1H NMR (400 MHz, CDCl_3) δ 3.99 (t, $J = 6.4$ Hz, 2H), 2.22 (t, $J = 7.5$ Hz, 2H), 1.55 (m, 4H), 1.22 (s, 18H), 0.81 (t, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 173.80, 63.91, 34.08, 31.90, 29.34, 25.80, 25.21, 22.61, 13.86

MS (EI, m/z) $[\text{M}]^+$: 256

Octanoic acid (4a)

^1H NMR (400 MHz, CDCl_3) δ 12.00 (s, 1H), 2.35 (t, $J = 7.5$ Hz, 2H), 1.71 – 1.57 (m, 2H), 1.53 – 1.12 (m, 9H), 0.89 (t, $J = 9.9$, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 180.81, 33.47, 31.63, 28.91, 24.65, 22.59, 14.00

MS (EI, m/z) $[\text{M}]^+$: 158 (methyl ester derivative)

Benzyl benzoate (3b)

^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 7.9$ Hz, 2H), 7.70 – 7.15 (m, 8H), 5.36 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 166.92, 136.01, 133.11, 130.18, 129.77, 128.67, 128.45, 128.32, 128.24, 67.12

MS (EI, m/z) $[\text{M}]^+$: 212

Benzoic acid (4b)

^1H NMR (400 MHz, CDCl_3) δ 13.00-12.00 (s, 1H), 8.13 (d, $J = 8.4$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.7$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 172.59, 133.88, 130.49, 129.07, 128.21

MS (EI, m/z) $[\text{M}]^+$: 136 (methyl ester derivative)

Cinnamyl Cinnamate (2g)

^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 16.0$ Hz, 2H), 7.26 (m, 10H), 6.56 (d, $J = 15.9$ Hz, 1H), 6.36 (d, $J = 17.1$ Hz, 1H), 6.22 (ddd, $J = 13.7$, 6.3, 4.9 Hz, 1H), 4.73 (d, $J = 6.3$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 166.69, 145.33, 136.22, 134.29, 130.47, 129.02, 128.69, 128.21, 126.79, 123.43, 118.02, 65.24.

MS (EI, m/z) $[\text{M}]^+$: 264

10-undecen-1-yl-10-undecenoate (2e)

^1H NMR (400 MHz, CDCl_3) δ 5.85 (m, 2H), 5.05 (m, 4 H), 4.10 (t, $J = 6.7$ Hz, 2H), 2.33 (t, $J = 7.5$ Hz, 2H), 2.07 (t, $J = 10.4$ Hz, 4H), 1.85 – 1.59 (m, 4H), 1.56 – 1.19 (m, 24H).

^{13}C NMR (100 MHz, CDCl_3) δ 174.08, 139.15, 114.14, 64.39, 51.28, 34.09, 33.24, 31.75, 29.47, 29.21, 28.89, 26.03, 24.61, 22.05

MS (EI, m/z) $[\text{M}]^+$: 336

Undecyl undecanoate

^1H NMR (400 MHz, CDCl_3) δ 4.09 (t, $J = 6.4$ Hz, 2H), 2.29 (t, $J = 7.6$ Hz, 2H), 1.62 (m, 4H), 1.29 (m, 30H), 0.88 (t, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 178.76, 64.38, 34.31, 31.40, 31.05, 25.73, 25.10, 24.90, 24.34, 23.10, 22.21

MS (EI, m/z) $[\text{M}]^+$: 340

γ -Butyrolactone

^1H NMR (400 MHz, CDCl_3) δ 4.35 (t, $J = 7.1$ Hz, 2H), 2.49 (t, $J = 6.9$ Hz, 2H), 2.23 (m, 2H)

^{13}C NMR (100 MHz, CDCl_3) δ 173.48, 66.79, 22.88, 22.58

MS (EI, m/z) $[\text{M}]^+$: 86

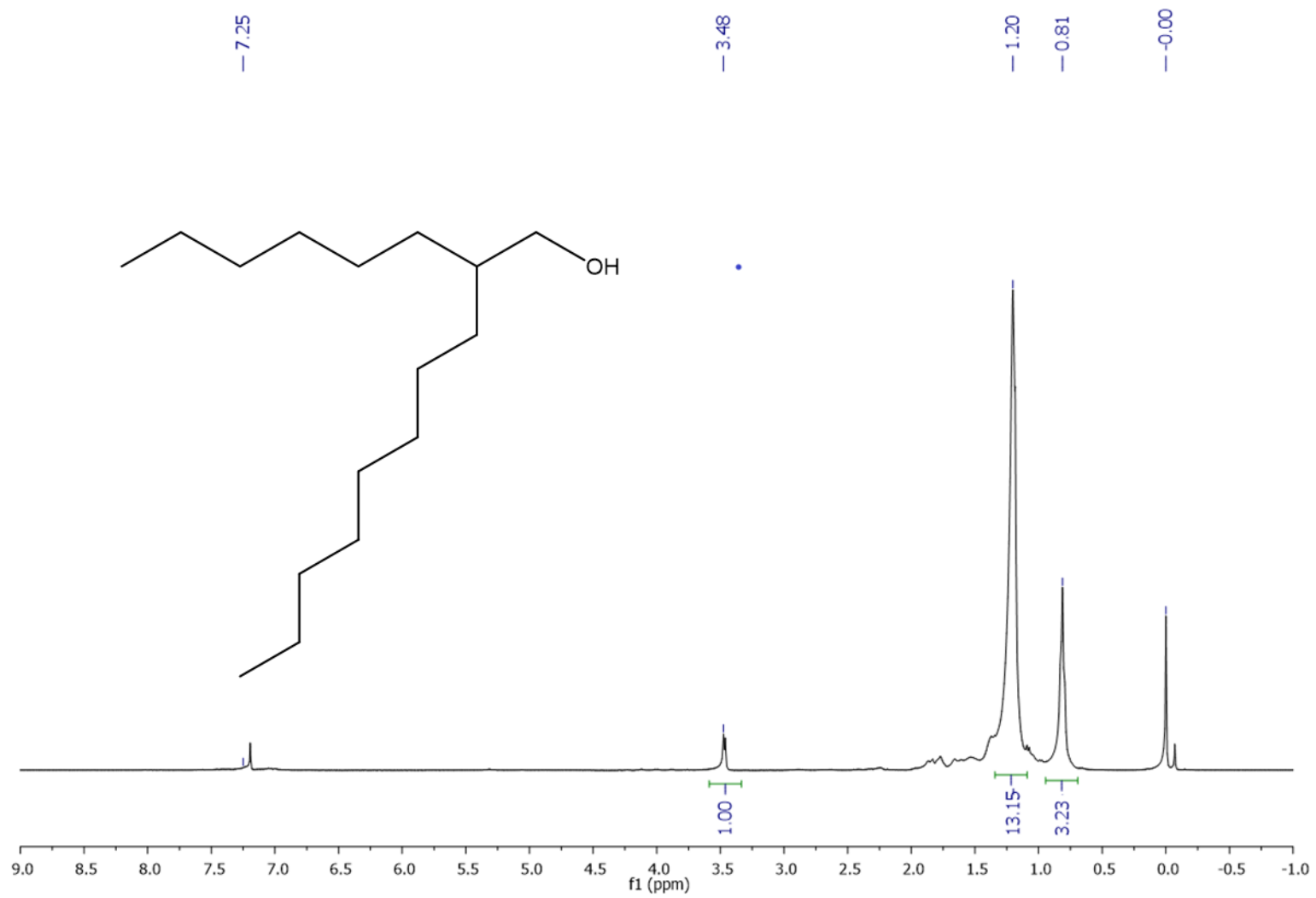


Figure S1. ^1H NMR spectrum of 2-hexyl-1-decanol (400 MHz, CDCl_3)

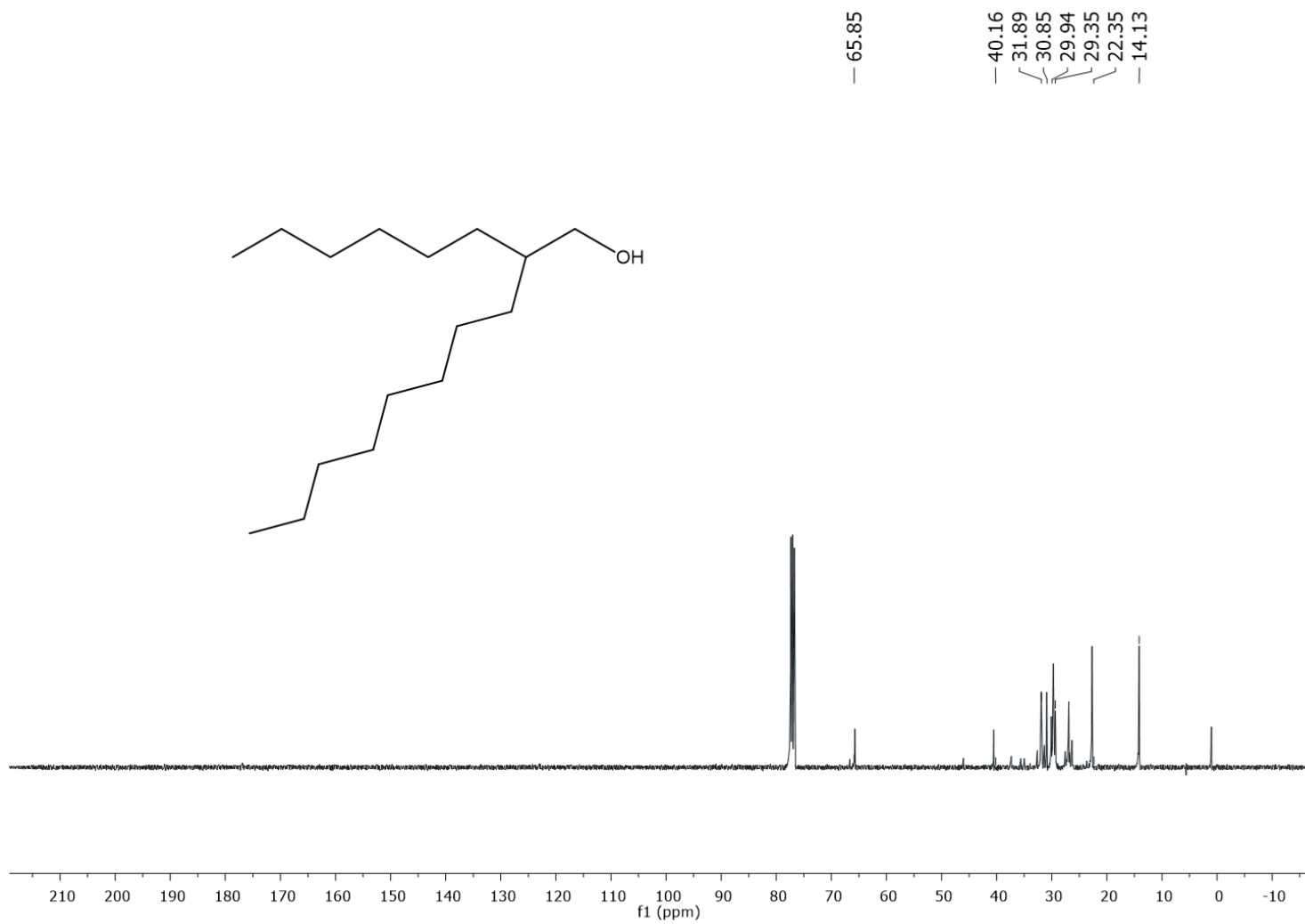


Figure S2. ^{13}C NMR spectrum of 2-hexyl-1-decanol (100 MHz, CDCl_3)

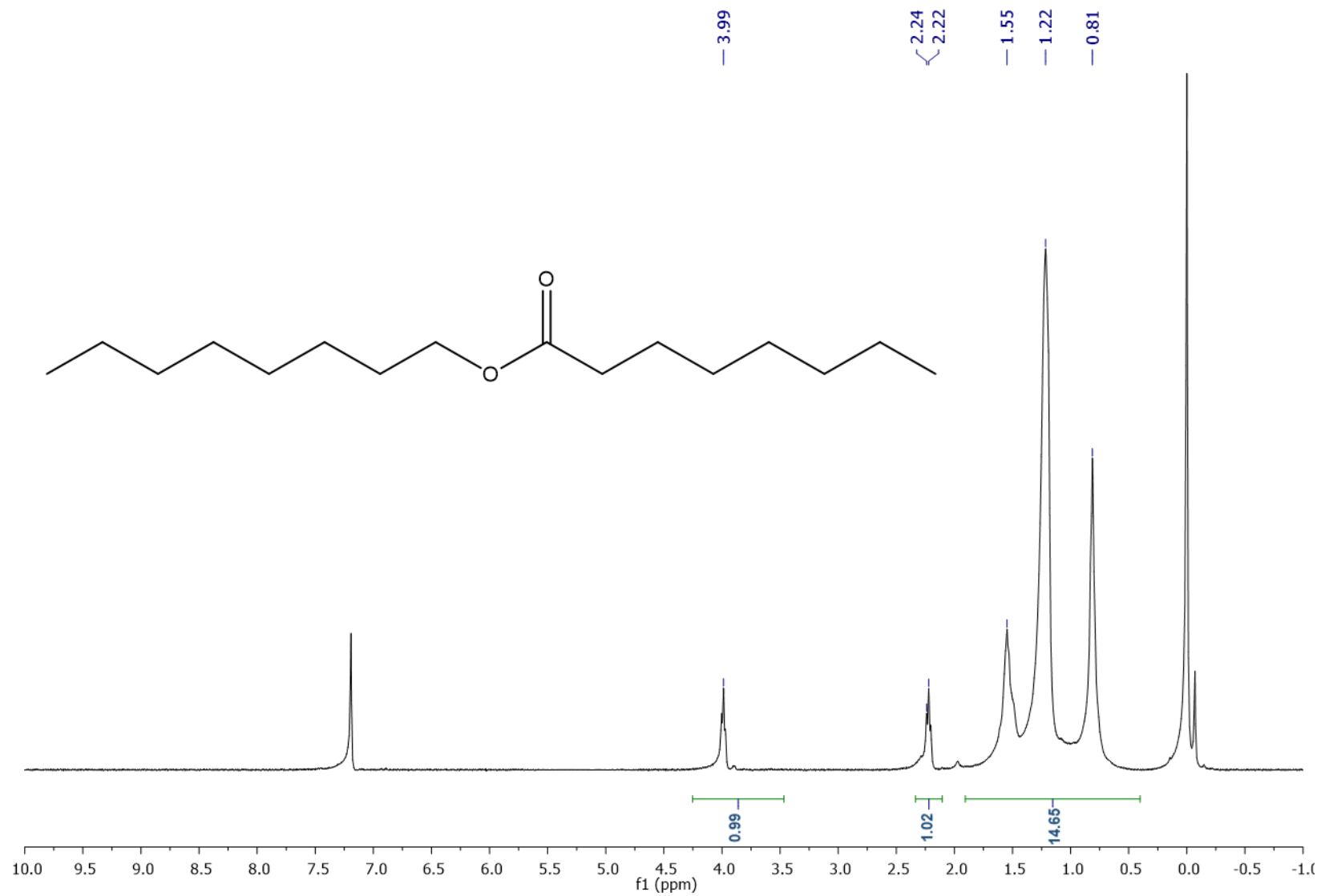


Figure S3. ^1H NMR spectrum of octyl octanoate (400 MHz, CDCl_3)

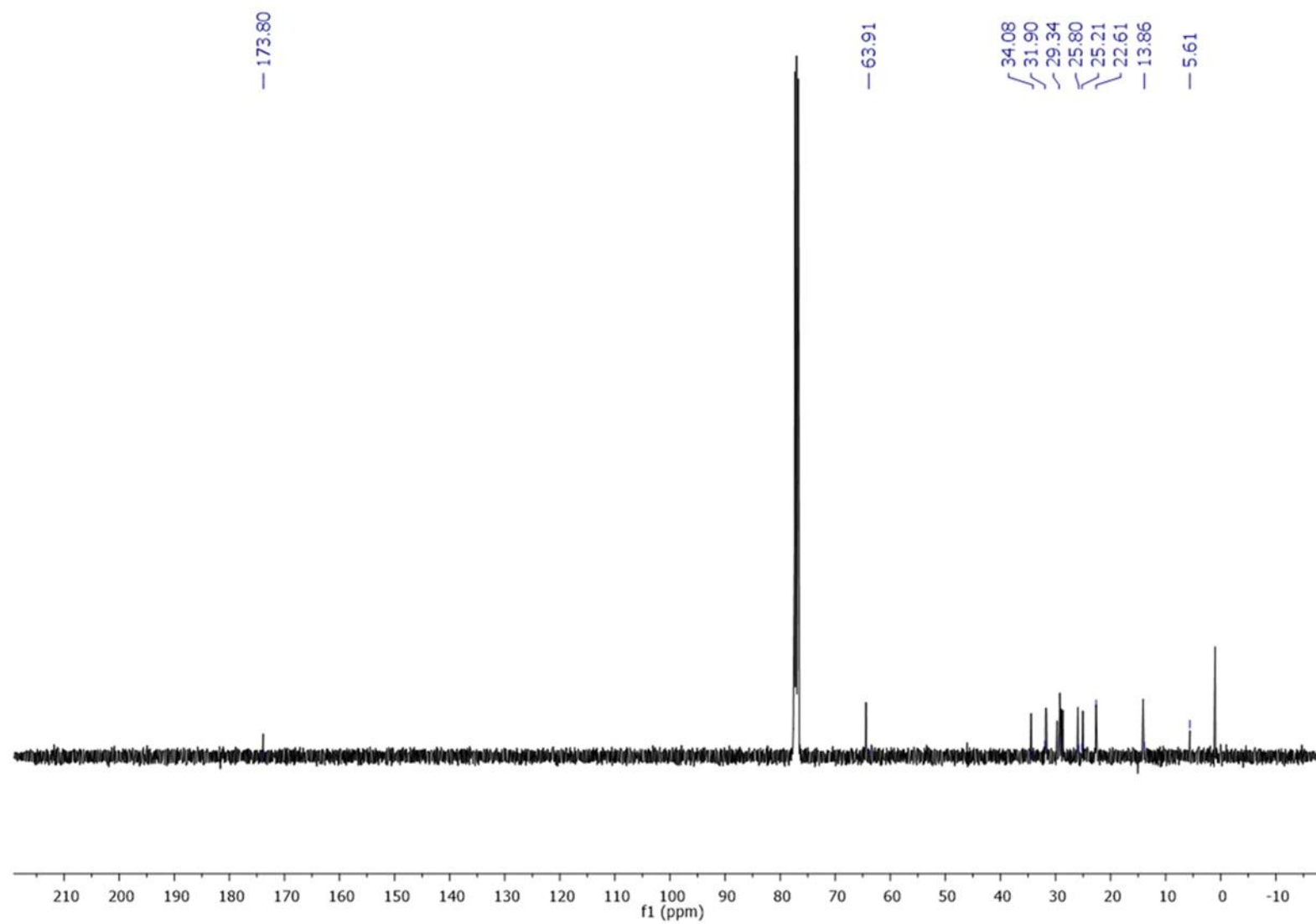


Figure S4. ^{13}C NMR spectrum of octyl octanoate (100 MHz, CDCl_3)

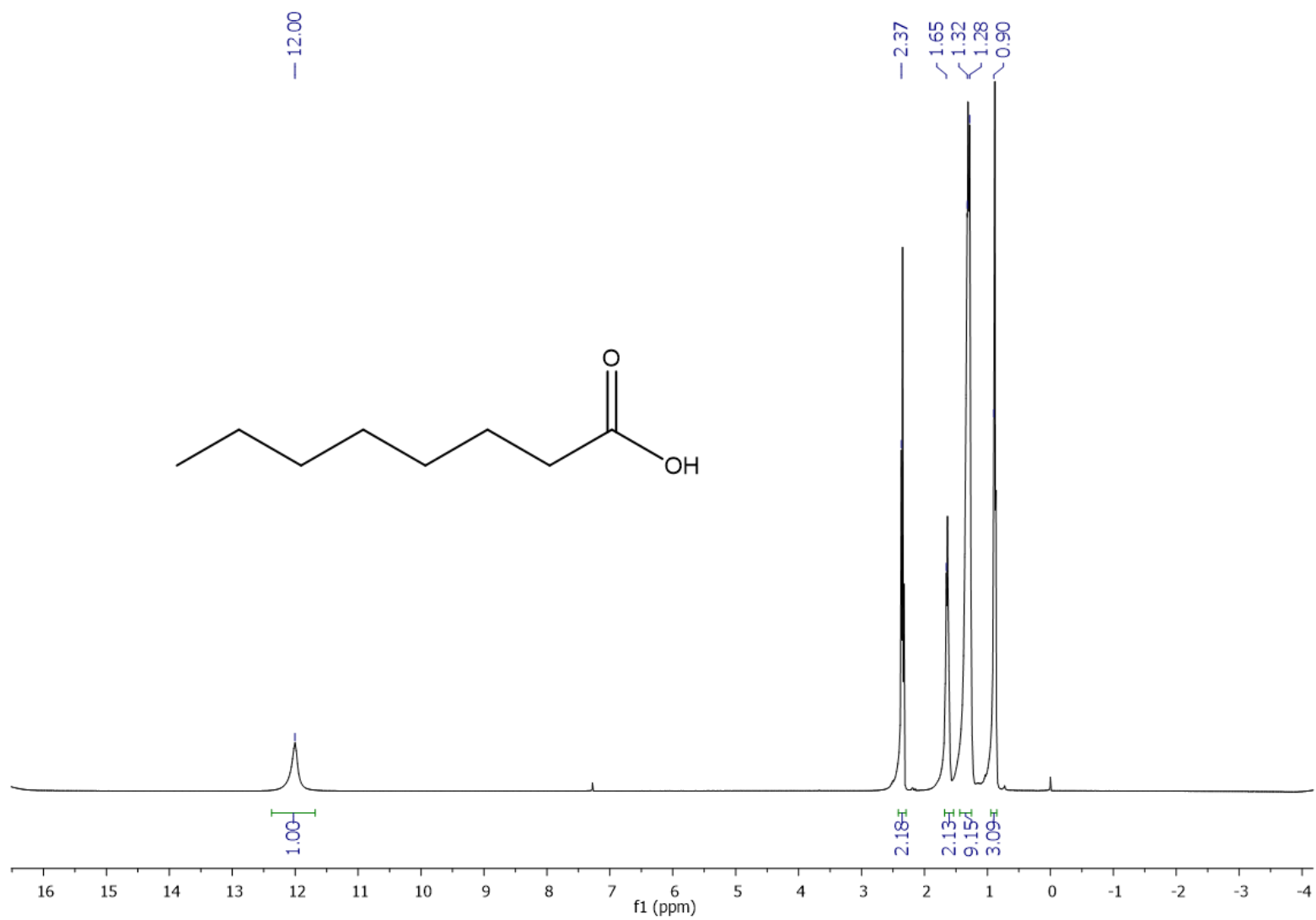


Figure S5. ^1H NMR spectrum of octanoic acid (400 MHz, CDCl_3)

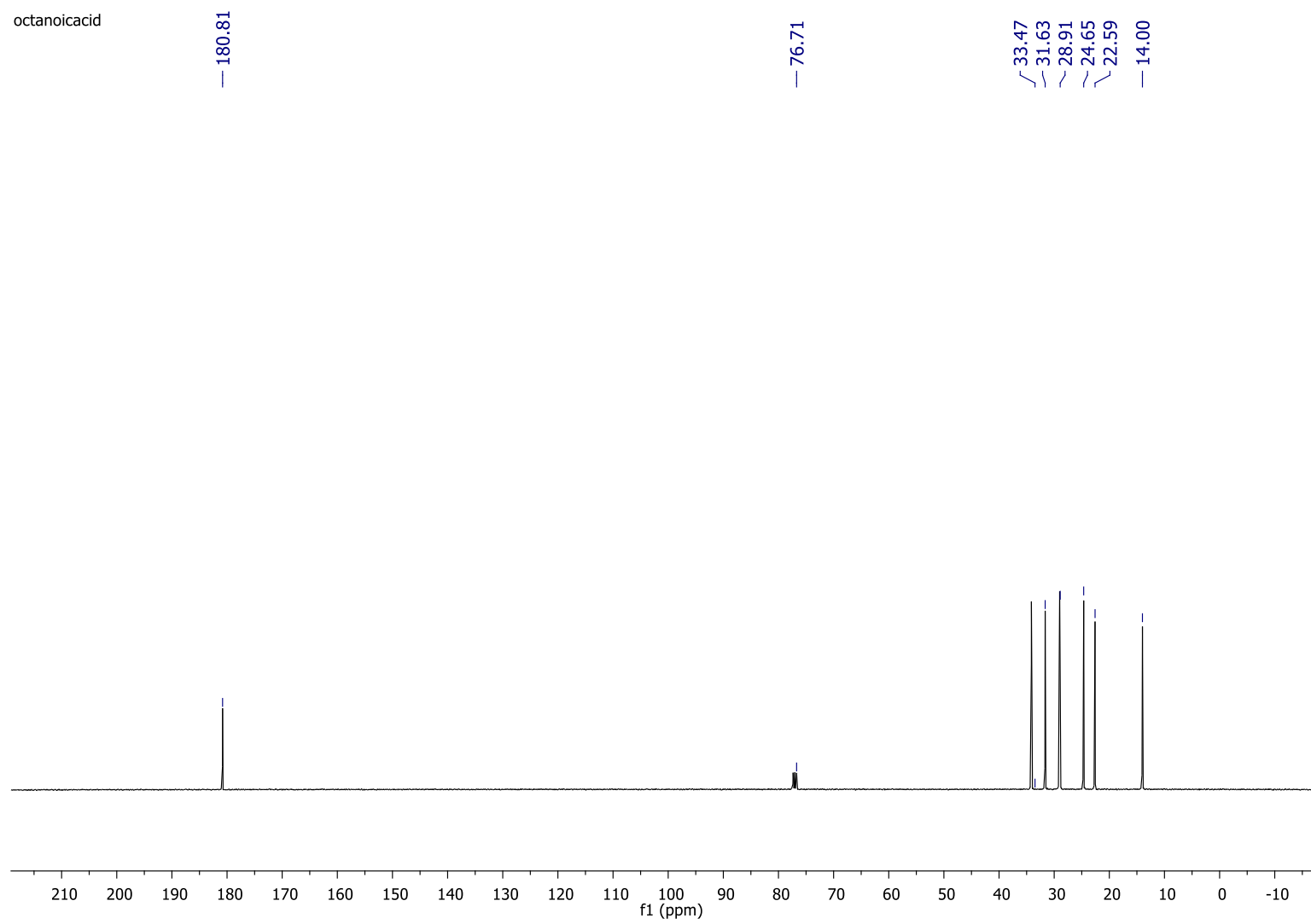


Figure S6. ^{13}C NMR spectrum of octanoic acid (100 MHz, CDCl_3)

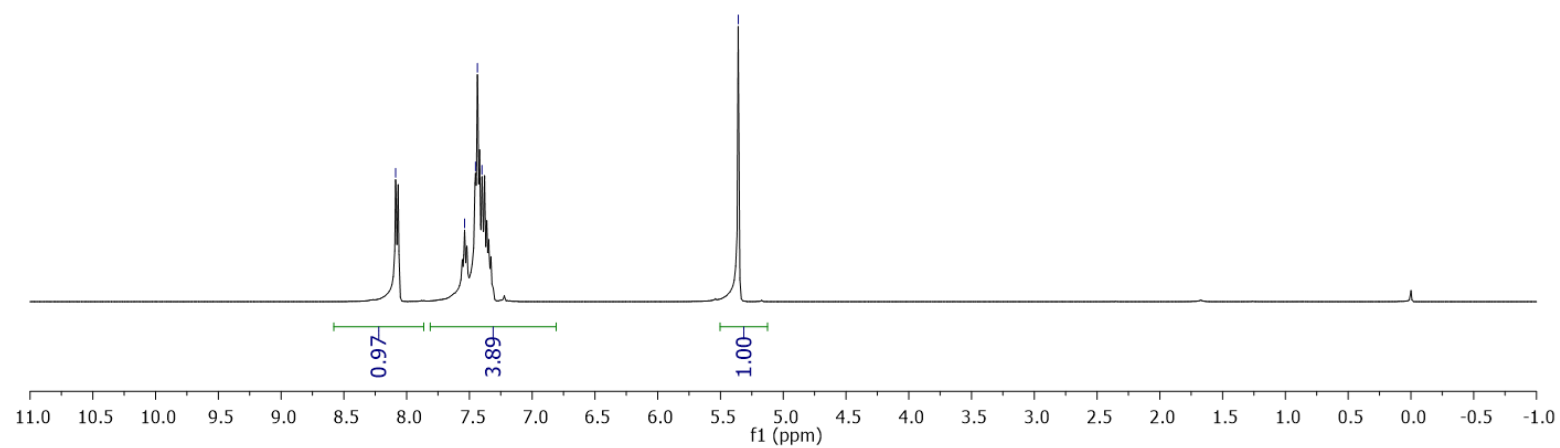
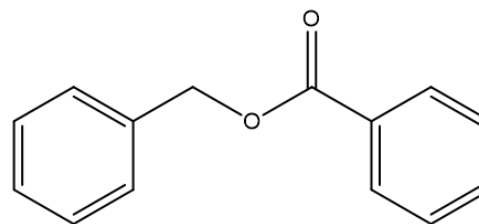
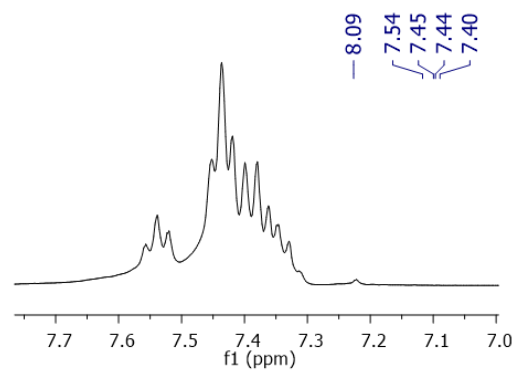


Figure S7. ^1H NMR spectrum of benzyl benzoate (400 MHz, CDCl_3)

benzylbenzoate

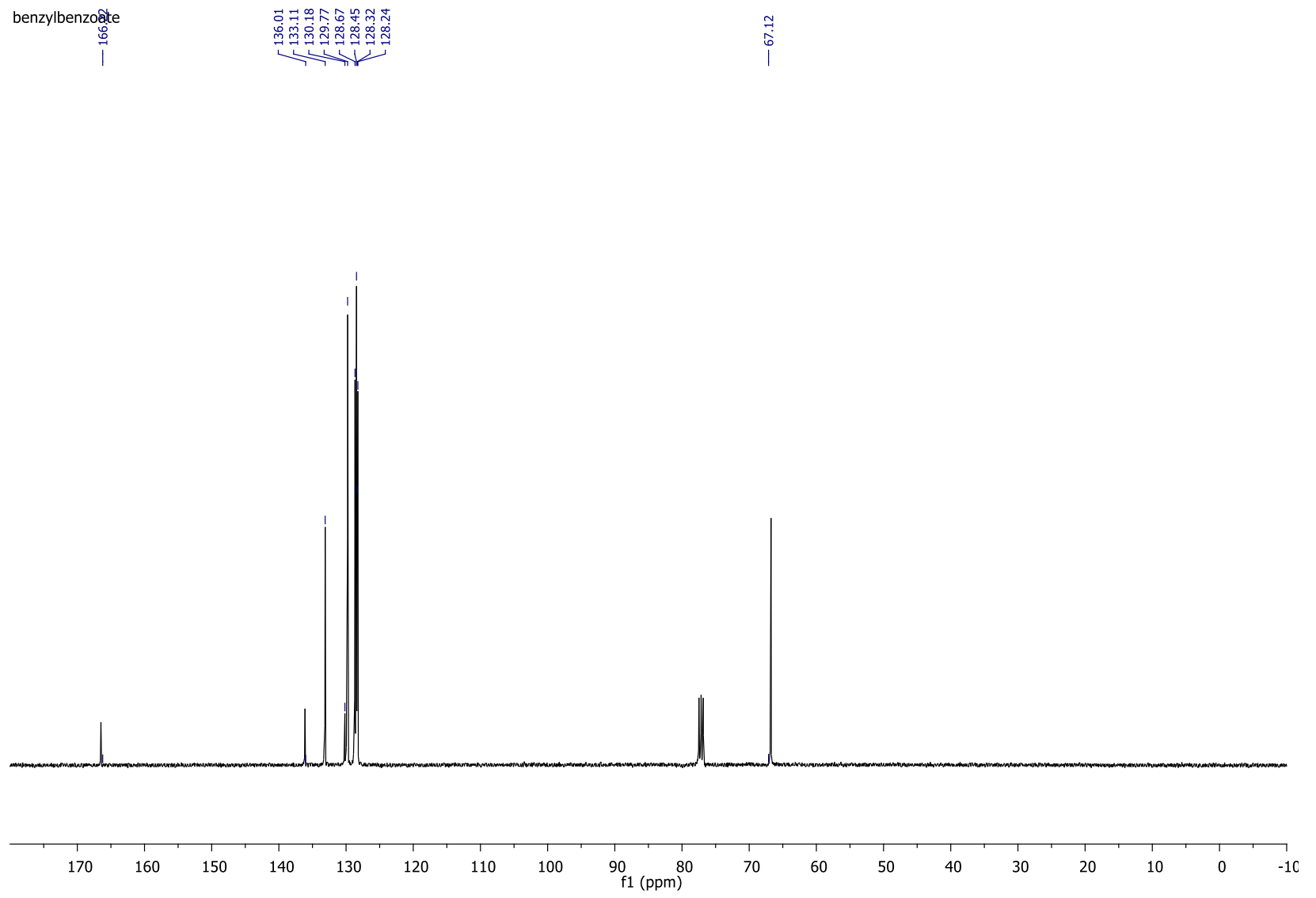
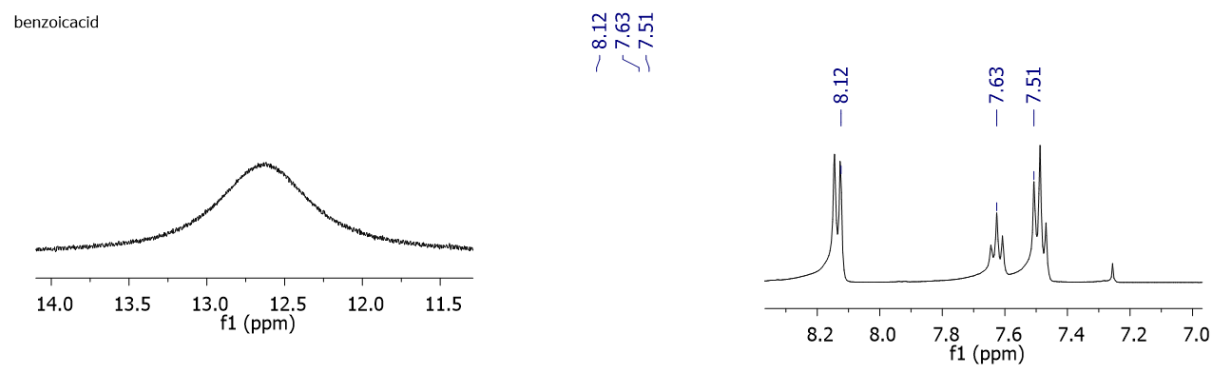


Figure S8. ^{13}C NMR spectrum of benzyl benzoate (100 MHz, CDCl_3)



8.12
7.63
7.51

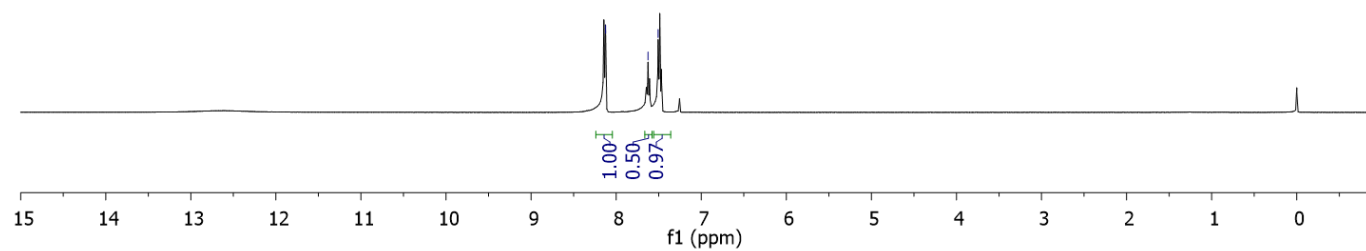
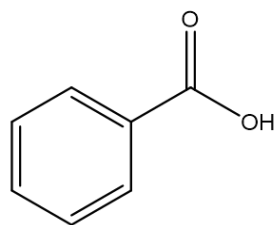
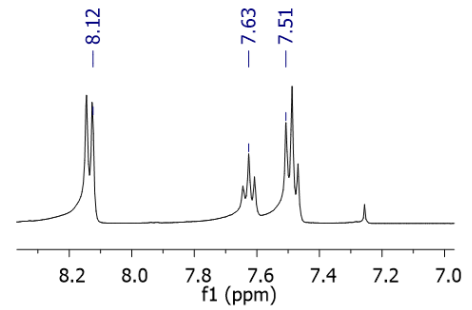


Figure S9. ^1H NMR spectrum of benzoic acid (400 MHz, CDCl_3)

benzoic acid

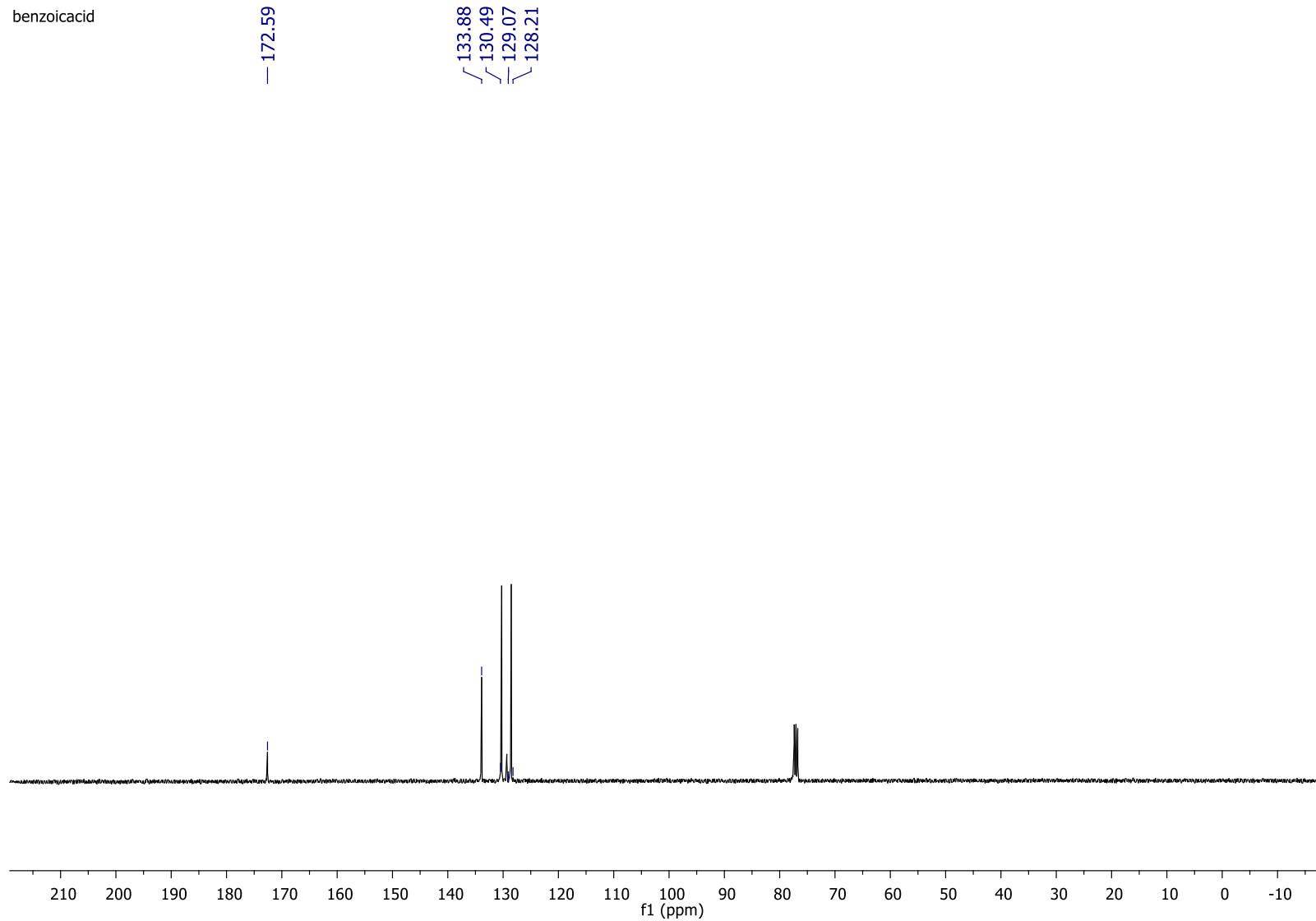


Figure S10. ^{13}C NMR spectrum of benzoic acid (100 MHz, CDCl_3)

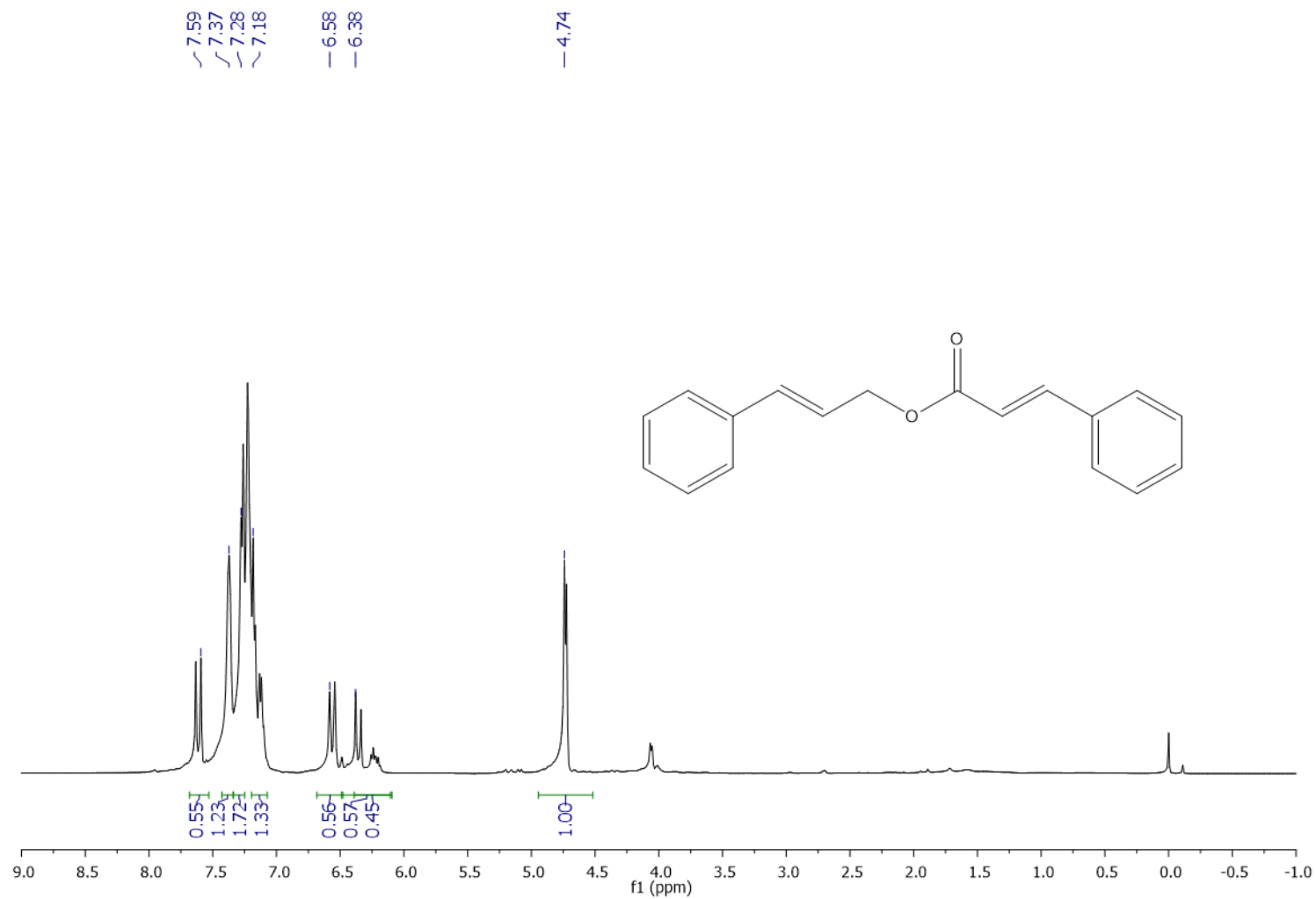


Figure S11. ¹H NMR spectrum of cinnamyl cinnamate (400 MHz, CDCl₃)

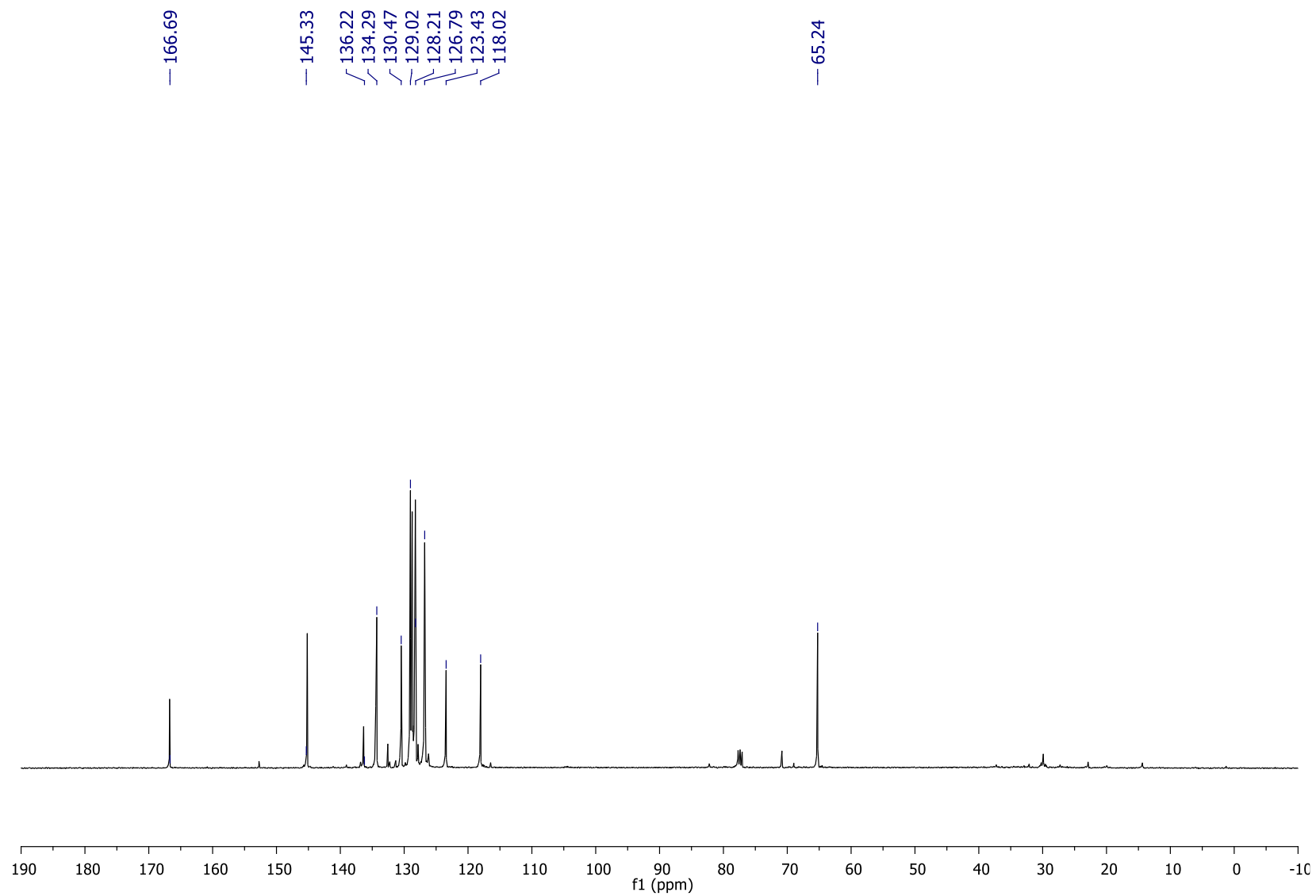


Figure S12. ^{13}C NMR spectrum of cinnamyl cinnamate (100 MHz, CDCl_3)

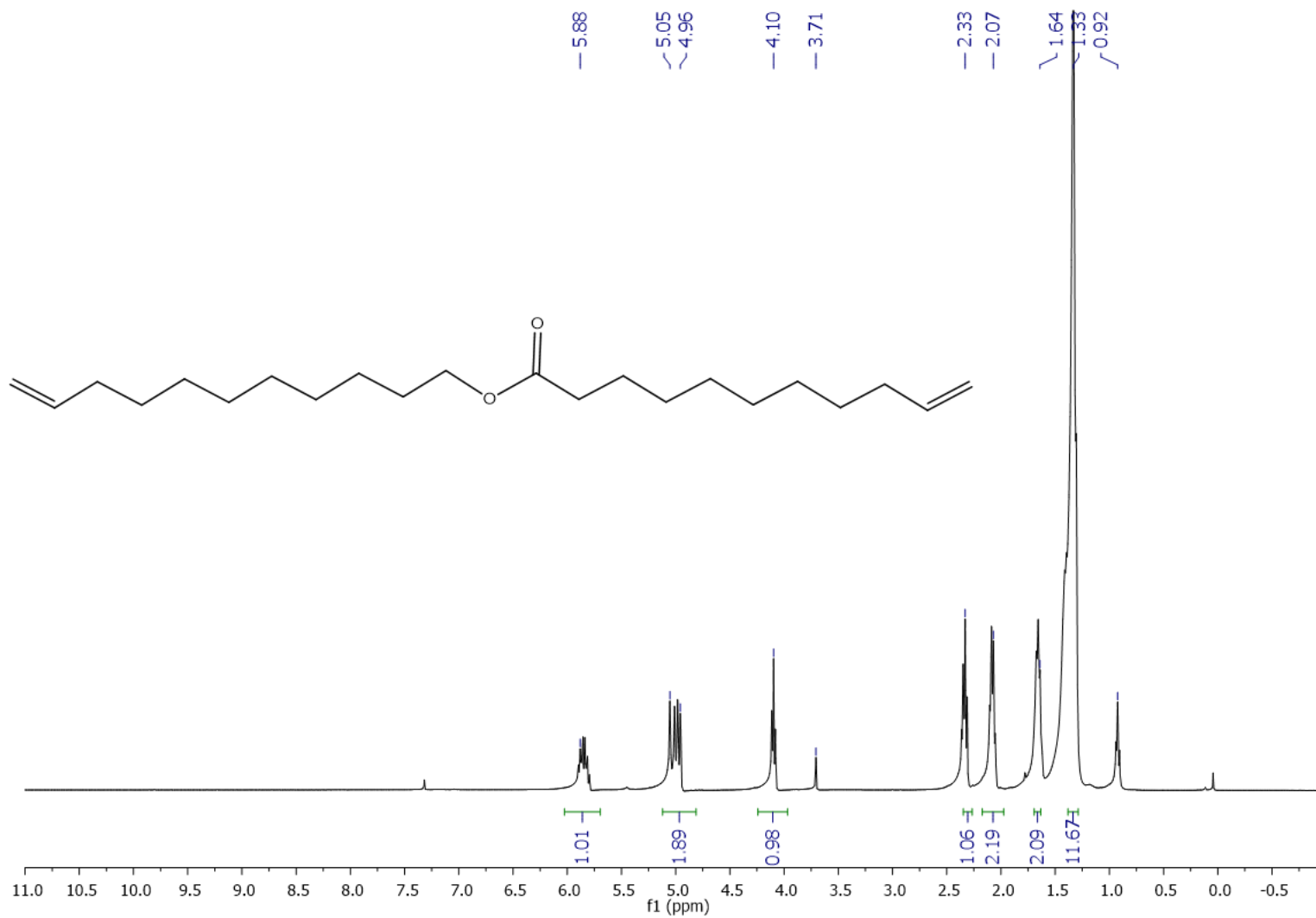


Figure S13. ¹H NMR spectrum of 10-undecen-1-yl-10-undecenoate (400 MHz, CDCl₃)

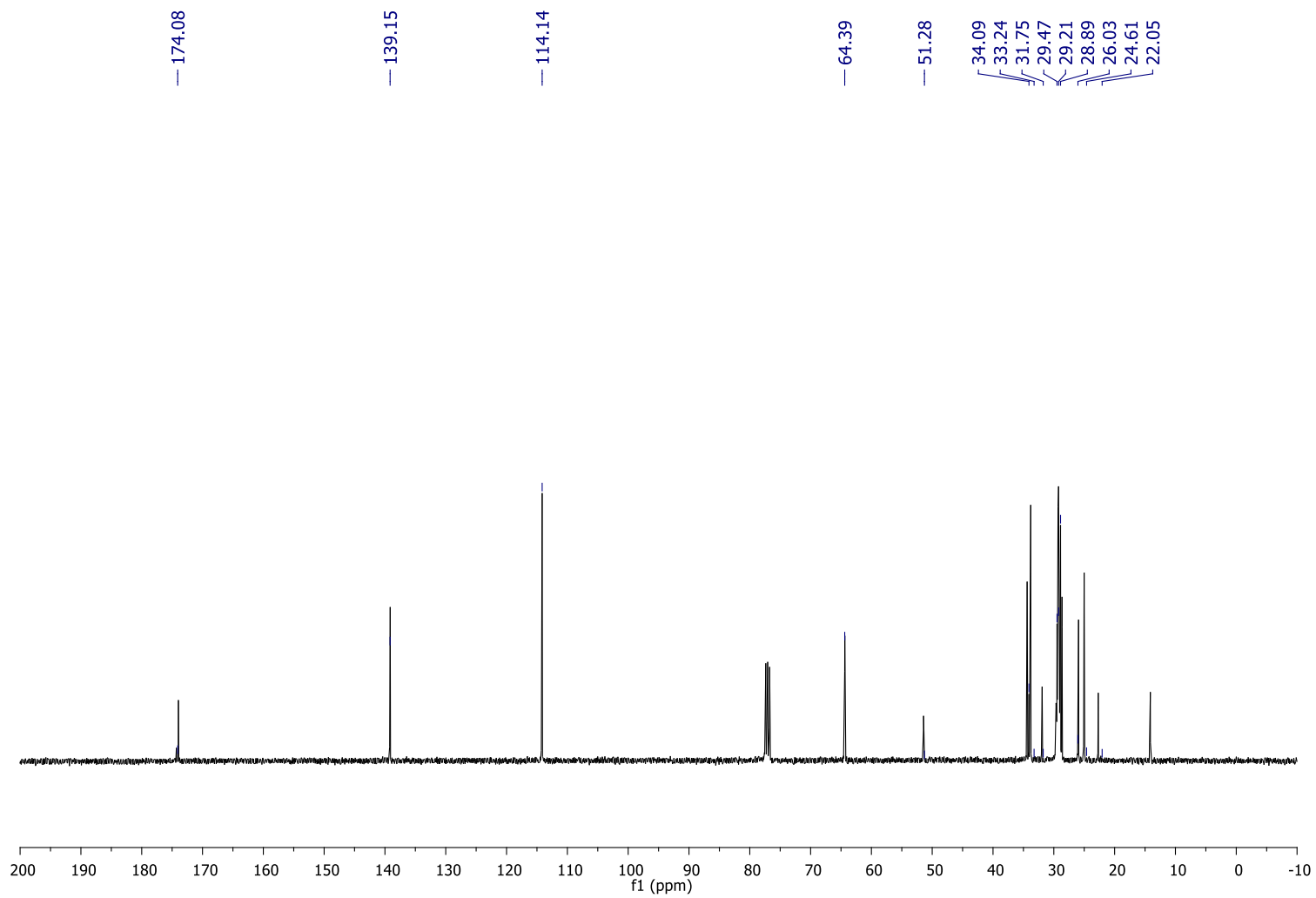


Figure S14. ^{13}C NMR spectrum of 10-undecen-1-yl-10-undecenoate (100 MHz, CDCl_3)

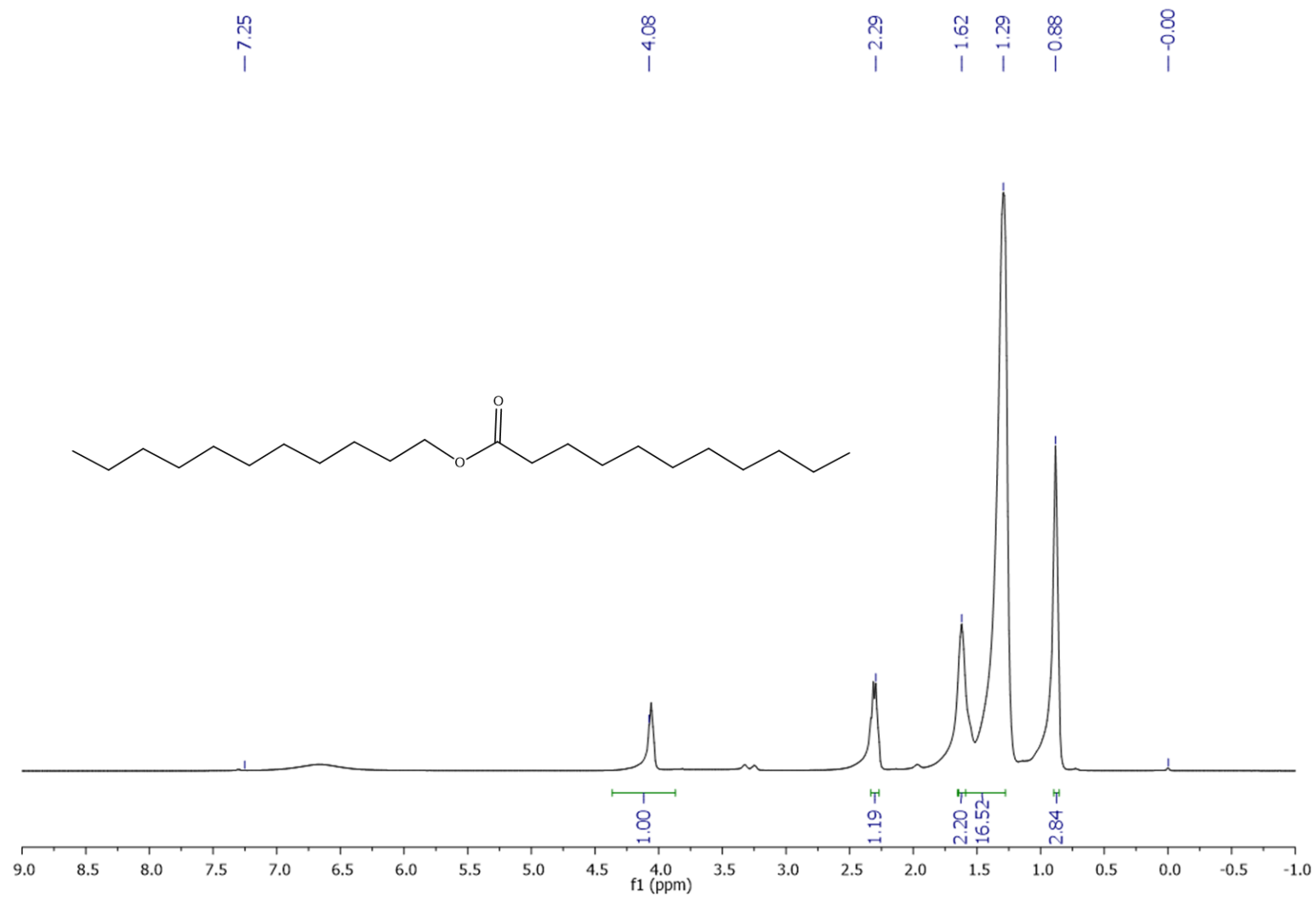


Figure S15. ¹H NMR spectrum of undecyl undecanoate (400 MHz, CDCl₃)

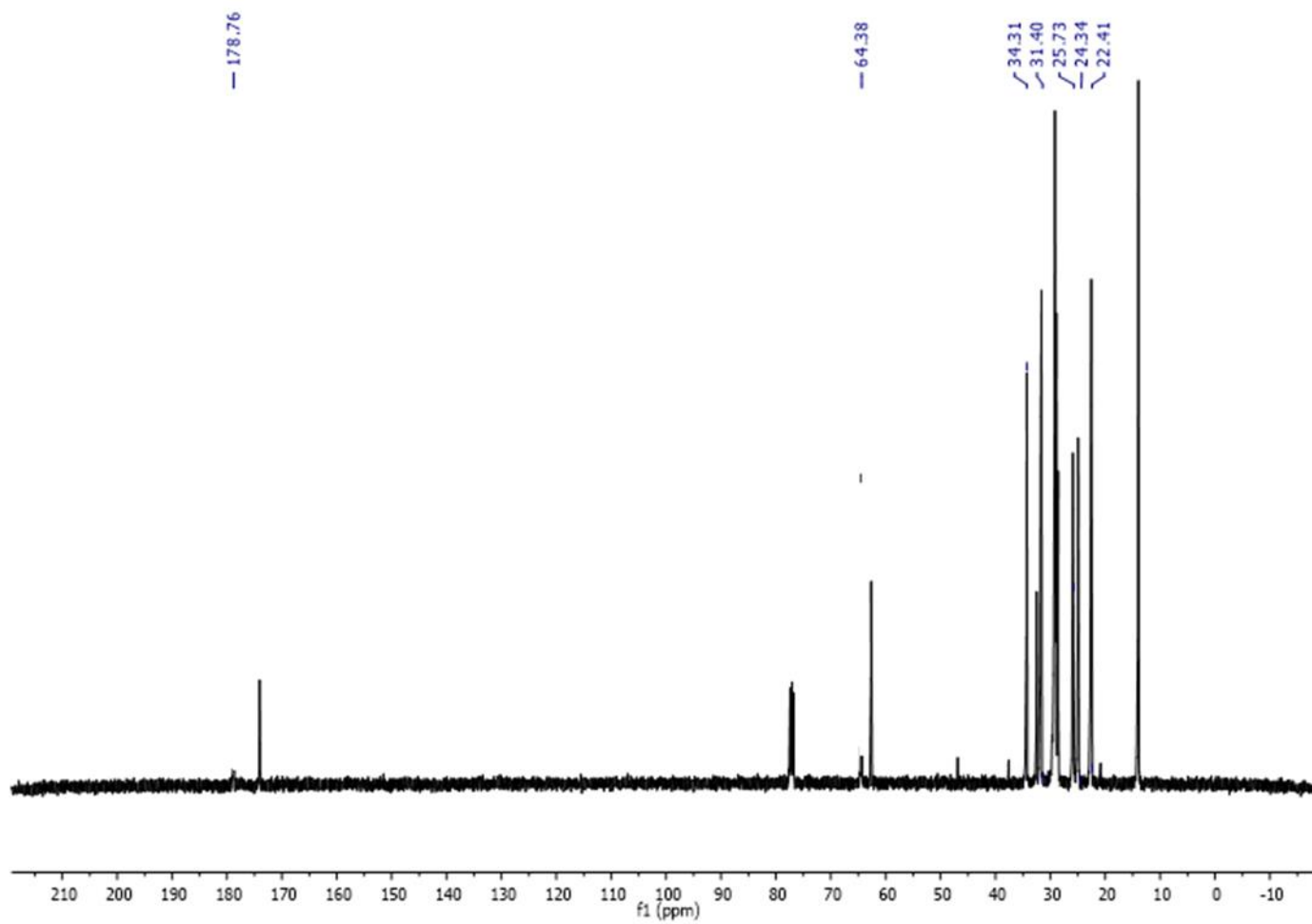


Figure S16. ^{13}C NMR spectrum of undecyl undecanoate (100 MHz, CDCl_3)

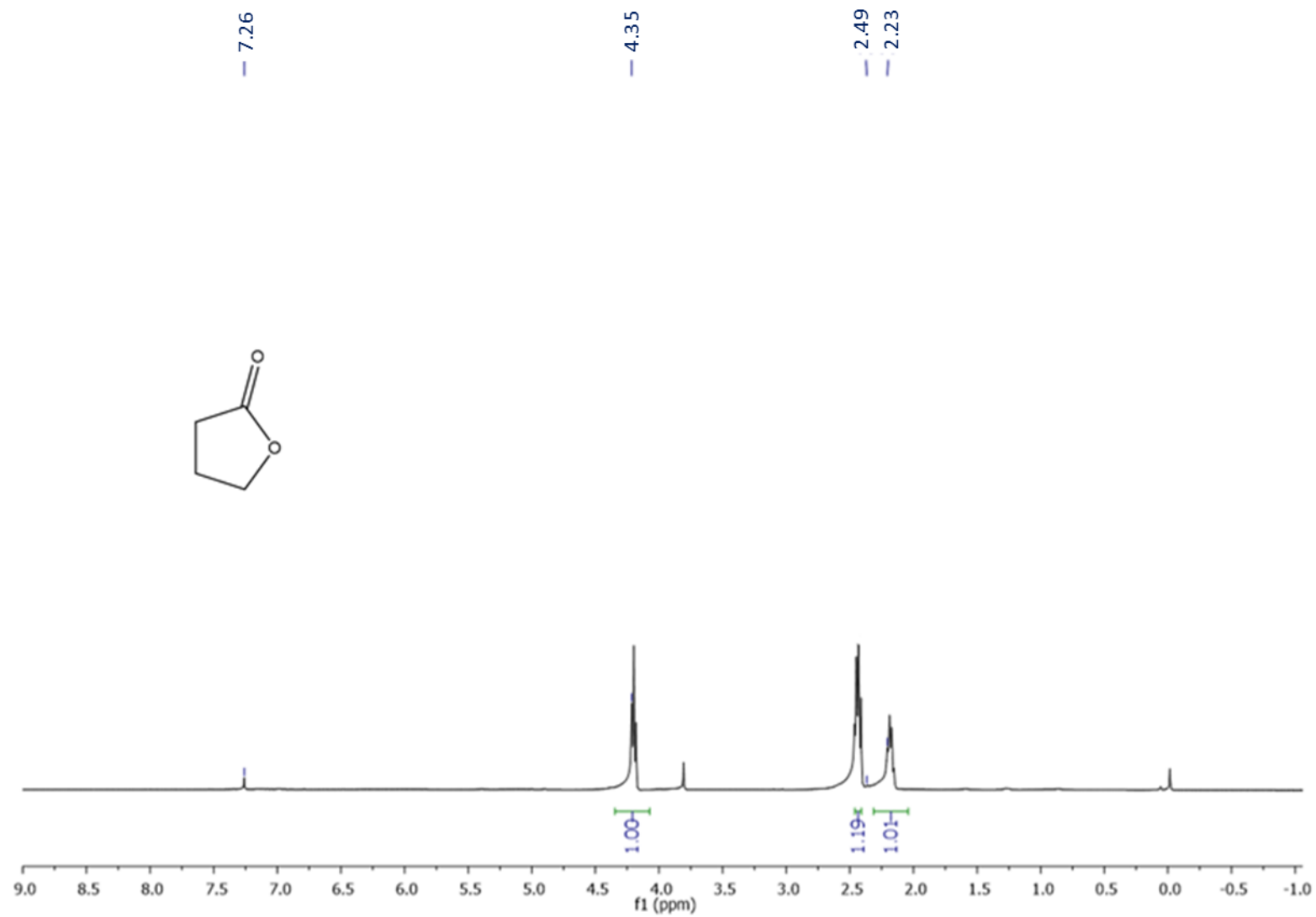


Figure S17. ^1H NMR spectrum of γ -butyrolactone (400 MHz, CDCl_3)

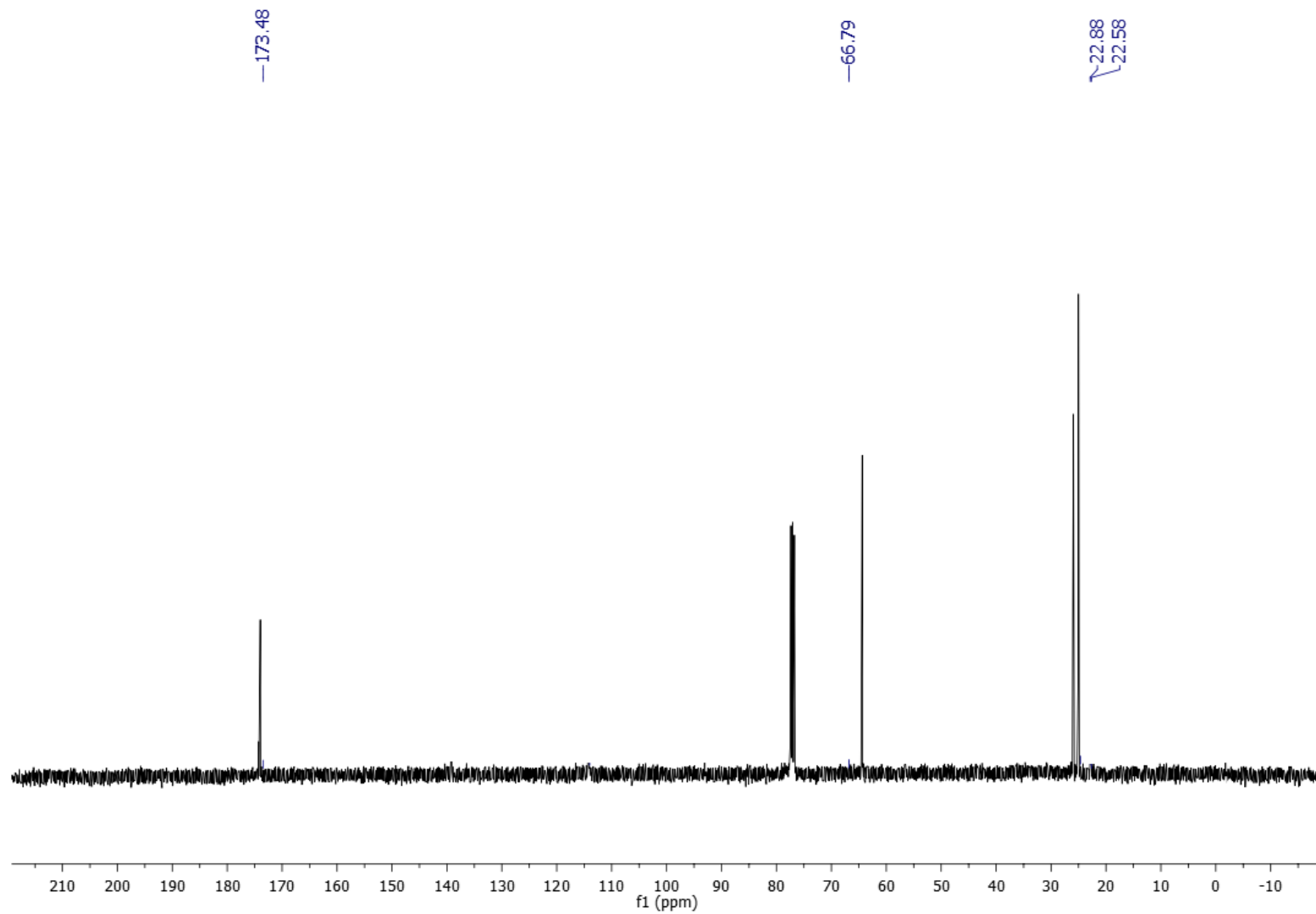


Figure S18. ^{13}C NMR spectrum of γ -butyrolactone (100 MHz, CDCl_3)

