Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

for

Cobalt(I)-catalyzed CH-alkylation of terminal olefins, and beyond

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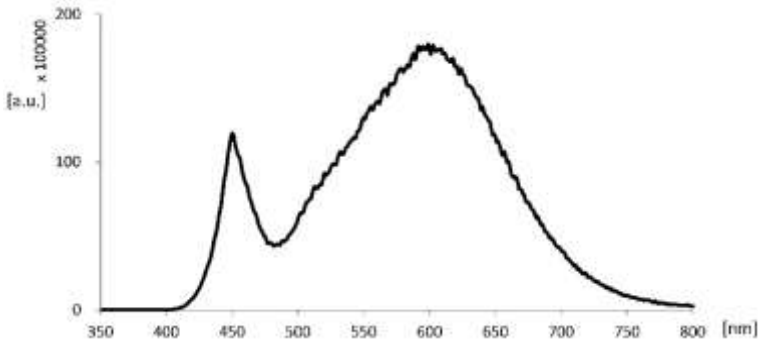
1. General Information

✓ All solvents and chemicals used in the syntheses were of reagent grade and were used without further purification. High resolution ESI mass spectra were recorded on a Mariner and SYNAPT spectrometer. ^{1}H and ^{13}CNMR spectra were recorded at rt on Bruker 400 and Varian 600 MHz instruments with TMS as an internal standard. EPR spectrum was recorded on Magnettech MS200 spectrometer. Thin layer chromatography (TLC) was performed using Merck Silica Gel GF254, 0.20 mm thickness.

✓ ND_4Cl used in deuterium experiment contained 98 atom% of deuterium.

✓ Photo-induced reactions were performed using a homemade photoreactor equipped with two LED light bulbs (300 Lm; warm light).

Emission spectrum of the LED light bulbs used:



✓ Cobalester (Cble **2**) was synthesized according to the reported procedure on 1 g scale.[1]

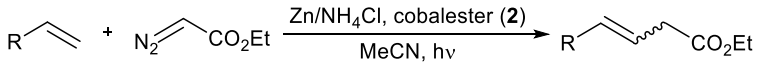
✓ -*O*TBDMS-Protected ketone **11** was synthesized according to the reported procedure.[2]

✓ Enamide **13** was synthesized according to the reported procedure.[3]

✓ In all reactions activated Zn powder was used. Activation process comprised: 1) washing with 10% HCl, 2) grinding, 3) washing with water, MeOH and Et_2O, 4) drying *in vacuo*.

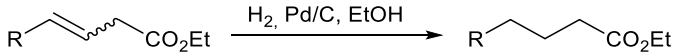
2. Description of general synthetic procedures

Representative procedure for C-H functionalization of olefins:



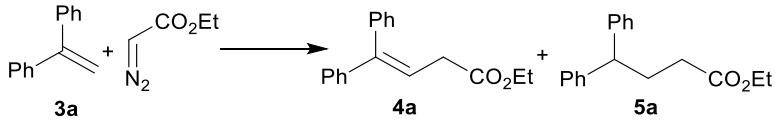
A reaction vessel equipped with a stirring bar was charged with cobalester (**2**) (14 mg, 2 mol%), Zn (196 mg, 3.0 mmol) and NH_4Cl (90 mg, 1.7 mmol). Degassed MeCN (5.0 mL) was added and then the reaction mixture was vigorously stirred in anaerobic conditions until cobalester (**2**) was fully reduced (color change was observed from red to green). Subsequently, an olefin (0.5 mmol) and ethyl diazoacetate (156 µl, 1.5 mmol) were added and the reaction was irradiated with visible light from LEDs (300 Lm; warm light). Progress of the reaction was monitored using thin layer chromatography (TLC). When the reaction was completed, it was diluted with Et_2O (20 mL), filtered through the cotton wool and concentrated in vacuo. The crude product was purified by flash chromatography (SiO_2).

Representative procedure for hydrogenation step:



Crude olefin was dissolved in EtOH (5.0 mL) and hydrogenated in a flow of hydrogen in the presence of Pd/C (30 mg) at room temperature for 2 h. The reaction mixture was filtered, washed with EtOH and concentrated in vacuo. The crude product was purified by flash chromatography (SiO_2).

3. Optimization studies



1. Background reactions

Entry	Light	Temperature [°C]	Conversion [%]	Yield [%]	4a:5a ratio
1	-	RT	63	34	1 : 1.4
2	LED	15	78	28	1 : 2.6
3	**LED**	**-**	**94**	**74**	**1 : 2.6**
4	-	42	94	65	1 : 1.3
5	-	60	86	68	1 : 1.5

Reaction conditions: Ph_2CCH_2 (0.5 mmol), EDA (3 equiv.), Zn (3 equiv.), NH_4Cl (3.4 equiv.), catalyst **2** (1 mol%), MeCN (2.5 mL), 18 h

2. Optimization of the solvent

Entry	Solvent	Additive	Conversion [%]	Yield [%]
1	**MeCN**	**-**	**n.d.**	**71**
2	Dry MeCN	-	85	63
3	Dry DMF	-	56	15
4	Dry MeOH	-	16	9
5	MeCN	H_2O (1 equiv.)	82	46
6	THF	H_2O (1 equiv.)	80	58
7	Acetone	H_2O (1 equiv.)	74	49

Reaction conditions: Ph_2CCH_2 (0.5 mmol), EDA (3 equiv.), Zn (3 equiv.), NH_4Cl (3.4 equiv.), catalyst **2** (1 mol%), 18 h, light: 2x300 Lm LED warm light

3. The influence of an amount of NH_4Cl

Entry	NH_4Cl [equiv.]	Conversion [%]	Yield [%]	4a:5a ratio
1	1.1	12	10	n.d.
2	2.2	90	48	n.d.
3	**3.4**	**94**	**74**	**2.7 : 1**
4	4.9	95	70	n.d.
5	5.6	85	63	n.d.

Reaction conditions: Ph_2CCH_2 (0.5 mmol), EDA (3 equiv.), Zn (3 equiv.), NH_4Cl, catalyst **2** (1 mol%), MeCN (2.5 mL), 18 h, light: 2x300 Lm LED warm light

4. Optimization of reaction time

Entry	Time [h]	Conversion [%]	Yield [%]
1	3	34	12
2	6	53	30
3	**18**	**94**	**74**

Reaction conditions: Ph_2CCH_2 (0.5 mmol), EDA (3 equiv.), Zn (3 equiv.), NH_4Cl (3.4 equiv.), catalyst **2** (1 mol%), MeCN (2.5 mL), light: 2x300 Lm LED warm light

5. Optimization of EDA equivalents

Entry	EDA [equiv.]	Conversion [%]	Yield [%]
1	2.0	95	34
2	**3**	**94**	**74**
3	4.0	93	48

Reaction conditions: Ph_2CCH_2 (0.5 mmol), EDA, Zn (3 equiv.), NH_4Cl (3.4 equiv.), catalyst **2** (1 mol%), MeCN (2.5 mL), 18 h light: 2x300 Lm LED warm light

6. Determination of the optimal concentration

Entry	Solvent [mL]	Conversion [%]	Yield [%]
1	1	98	56
2	**2.5**	**94**	**74**
3	5	82	42

Reaction conditions: Ph_2CCH_2 (0.5 mmol), EDA (3 equiv.), Zn (3 equiv.), NH_4Cl (3.4 equiv.), catalyst **2** (1 mol%), MeCN, 18 h light: 2x300 Lm LED warm light

7. The influence of a catalyst loading on the alkylation reaction

Entry	Catalyst 2 [% mol]	Conversion [%]	Yield [%]	4a:5a ratio
1[a]	0	33	3	n.d.
2	0.5	61	7	n.d.
3	1	94	74	2.7 : 1
4	2	97	80	3 : 1
5 [b]	**2**	**91**	**86**	**3.7 : 1**
6	3	99	76	4 : 1
7	5	100	91	6 : 1

Reaction conditions: Ph_2CCH_2 (0.5 mmol), EDA (3 equiv.), Zn (3 equiv.), NH_4Cl (3.4 equiv.), catalyst **2**, MeCN (2.5 mL), 18 h light: 2x300 Lm LED warm light; [a] 5.6 equiv of NH_4Cl was used; [b] 5 mL of MeCN was used

8. Determination of the optimal amount of Zn

Entry	Zn [equiv.]	NH_4Cl [equiv.]	Conversion [%]	Yield [%]	4a:5a ratio
1	0.9	3.4	50	38	2 : 1
2	1.8	3.4	93	85	2 : 1
3	3	3.4	91	86	3.7 : 1
4	**6**	**3.4**	**99**	**91**	**5 : 1**
5	6	2.2	91	80	8 : 1
6	6	1.1	90	79	13 : 1

Reaction conditions: Ph_2CCH_2 (0.5 mmol), EDA (3 equiv.), Zn, NH_4Cl, catalyst **2** (2 mol%), MeCN (5 mL), 18 h light: 2x300 Lm LED warm light

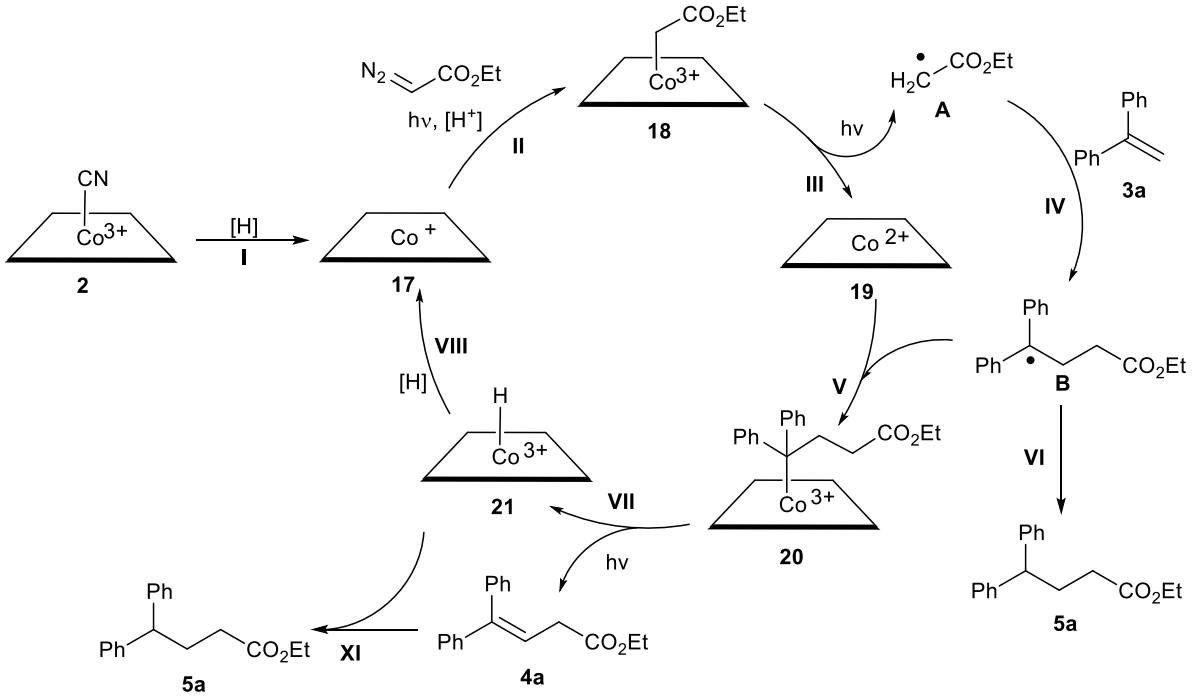
9. Thermally induced reactions

Entry	Light	Temperature [°C]	Conversion [%]	Yield [%]	4a:5a ratio
1	**LED**	**-**	**99**	**91**	**1 : 5.0**
2	-	42	80	76	1 : 1.8
3	-	60	90	62	1 : 2.5

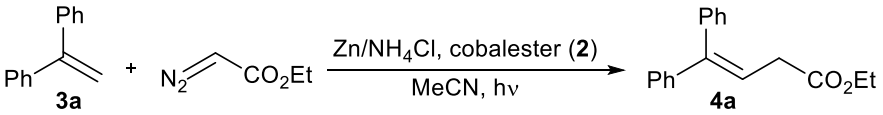
Reaction conditions: Ph_2CCH_2 (0.5 mmol), EDA (3 equiv.), Zn (6 equiv.), NH_4Cl (3.6 equiv.), catalyst **2** (2 mol%), MeCN (5 mL), 18 h light: 2x300 Lm LED warm light

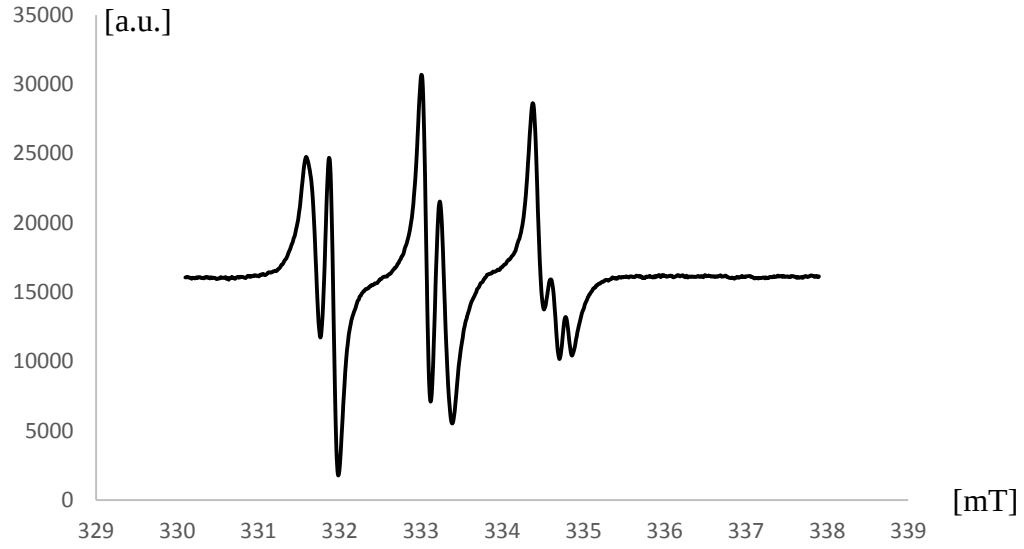
4. Mechanistic considerations

4a. Proposed Mechanism



4b. EPR spectroscopy



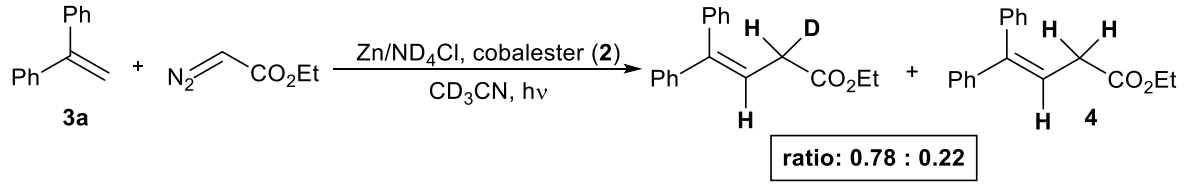


EPR spectra of the reaction mixture was recorded at 9,3 GHz, after 15 min of stirring;

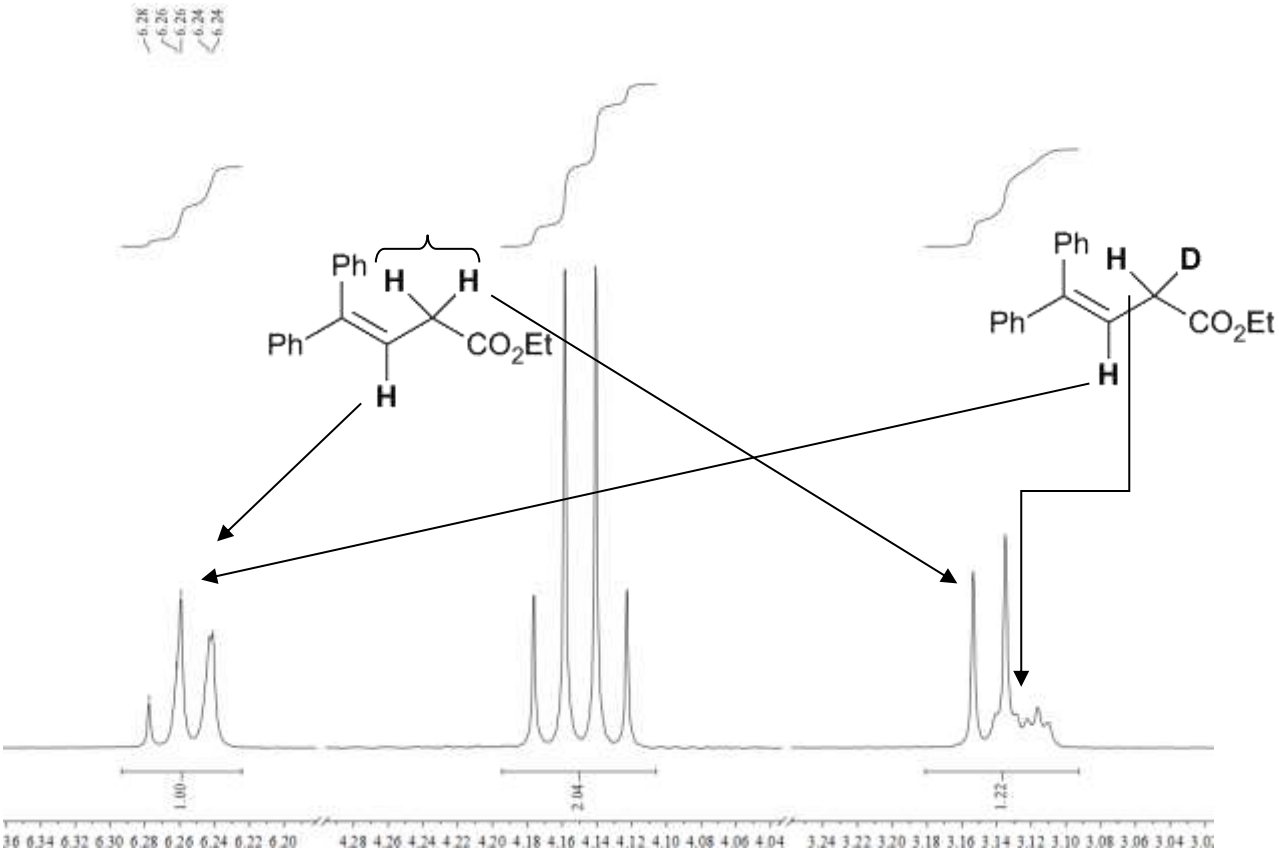
spin trap:	*N-tert*-Butyl-α-phenylnitrone;
central magnetic field:	333 mT;
sweep width:	7,9 mT;
modulation amplitude:	0,06 mT;
microwave strength:	6,3 mW;
sweep time:	30 s;
number of scans:	16

The experiment revealed the presence of radicals in the reaction mixture, suggesting radical mechanism of the reaction.

4c. Experiment with deuterated reagents

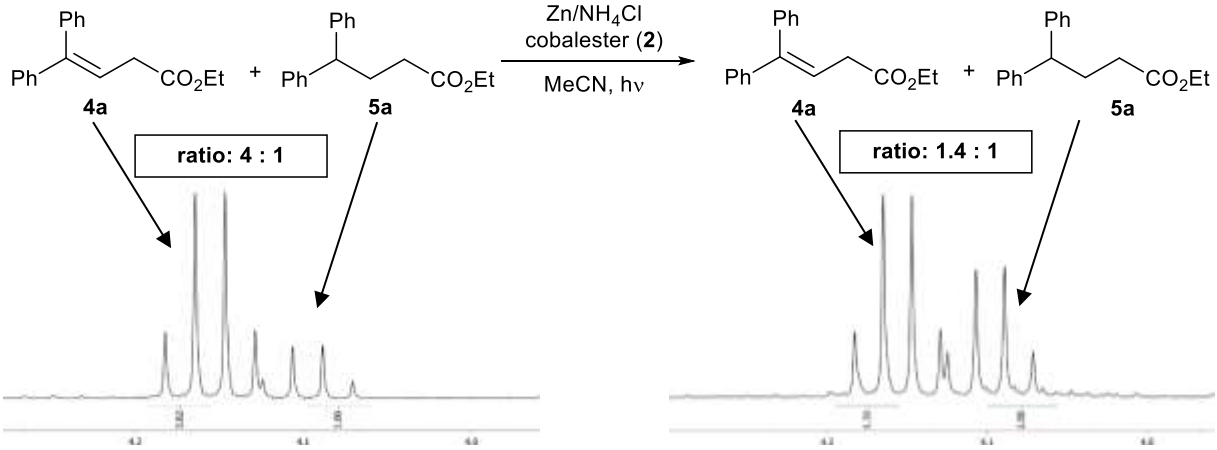


Conditions: substrate (0.5 mmol, 1.0 equiv.), EDA (1.5 mmol, 3 equiv.), cobalester **2** (2 mol%), Zn (6 equiv.), ND_4Cl (3.4 equiv.), CD_3CN (5 mL), light, 18 h



To prove the hypothesis of external proton incorporation at the α-position to the ester group, the experiment with ND_4Cl in CD_3CN was performed. The integration 1.22 for the signal at 3.14 ppm demonstrates that deuterated product is present, though in the mixture with protonated species (which can be explained by the presence of moisture), in 0.78 : 0.22 ratio. This result supports the proposed mechanism, in which alkylated cobalester **18** forms from the reaction of nucleophilic Co(I) species **17** with EDA.

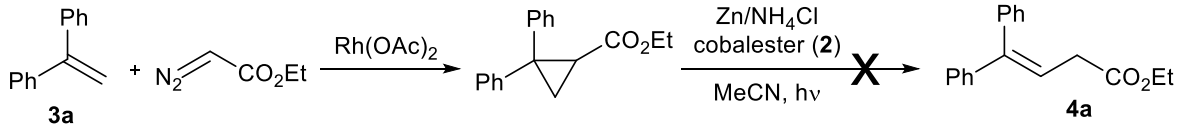
4d. Cobalester (**2**)-catalyzed saturation of double bonds



Conditions: cobalester **2** (2 mol%), Zn (6 equiv.), ND_4Cl (3.4 equiv.), MeCN (5 mL), light, 18 h

The mixture of unsaturated product **4a** and byproduct **5a** (ratio 4:1) was treated with cobalester (**2**) in reductive conditions and irradiated with light. After 18 h composition of the mixture changed to 1.4:1 showing that hydrogenation of olefin **4a** can occur after the desired C-H functionalization, during the reaction.

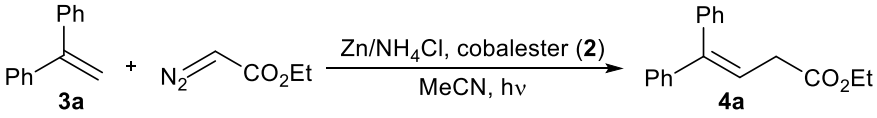
4e. Verification of cyclopropane-intermediate mechanism

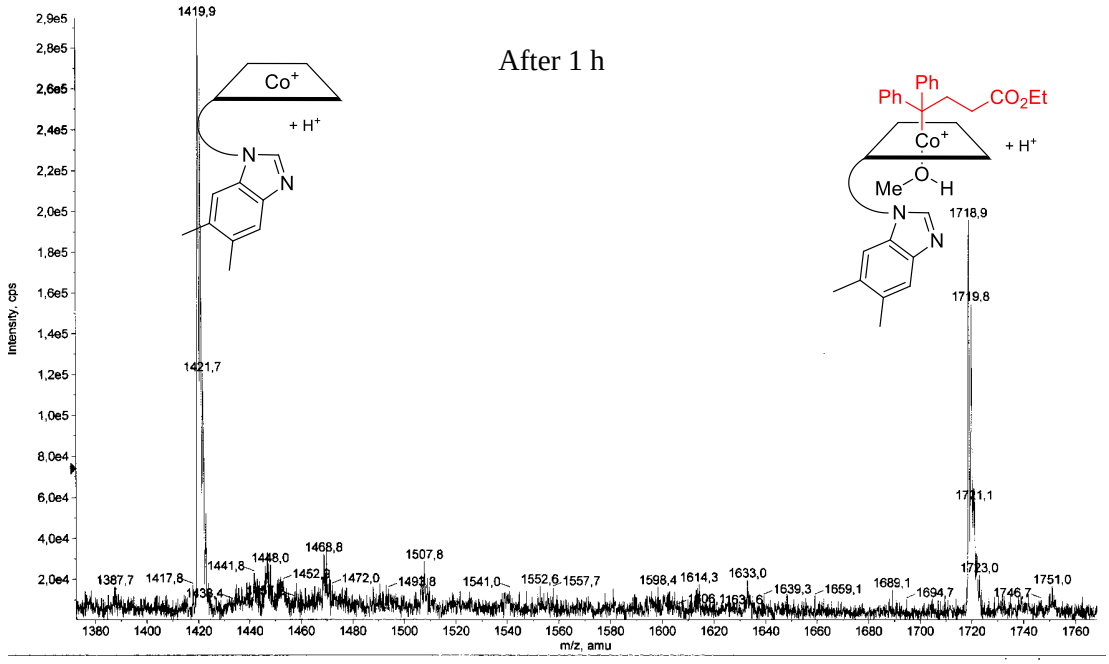


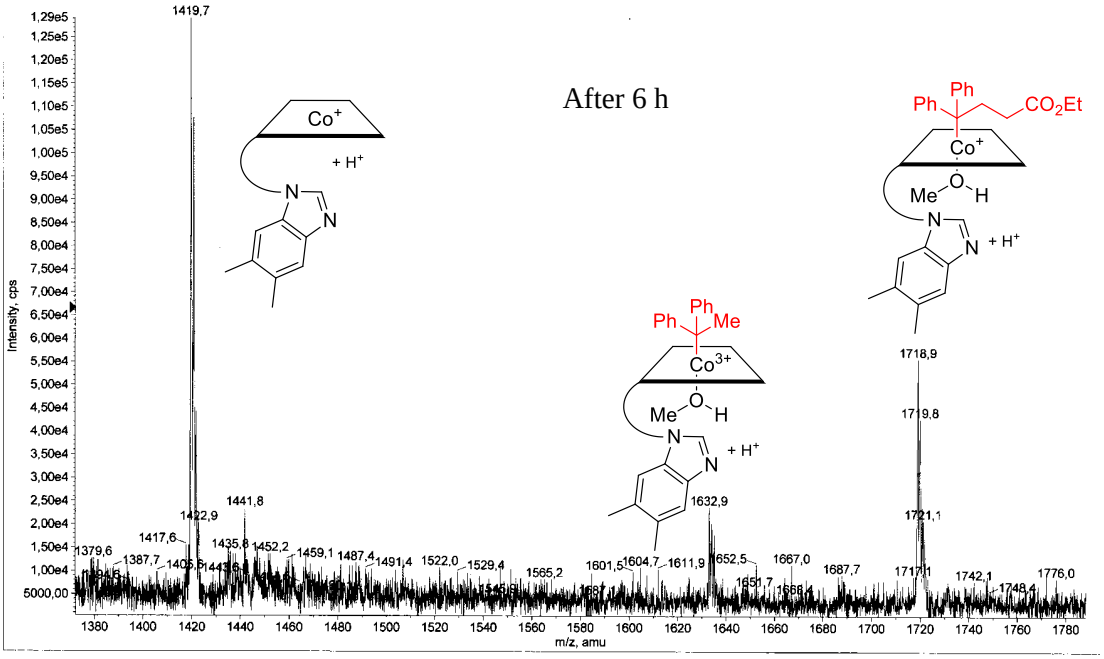
Substituted cyclopropane was synthesized using standard rhodium-catalyzed approach.[4] It was subsequently subjected to our model, cobalt-catalyzed reaction conditions. No conversion was observed (cyclopropane species was recovered), thus excluding cyclopropane-intermediate pathway from the considered reaction mechanism.

4f. Mass spectrometry studies

1) Composition of reaction mixtures were studied using LR mass spectrometry

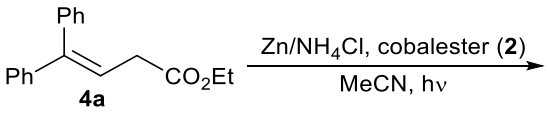


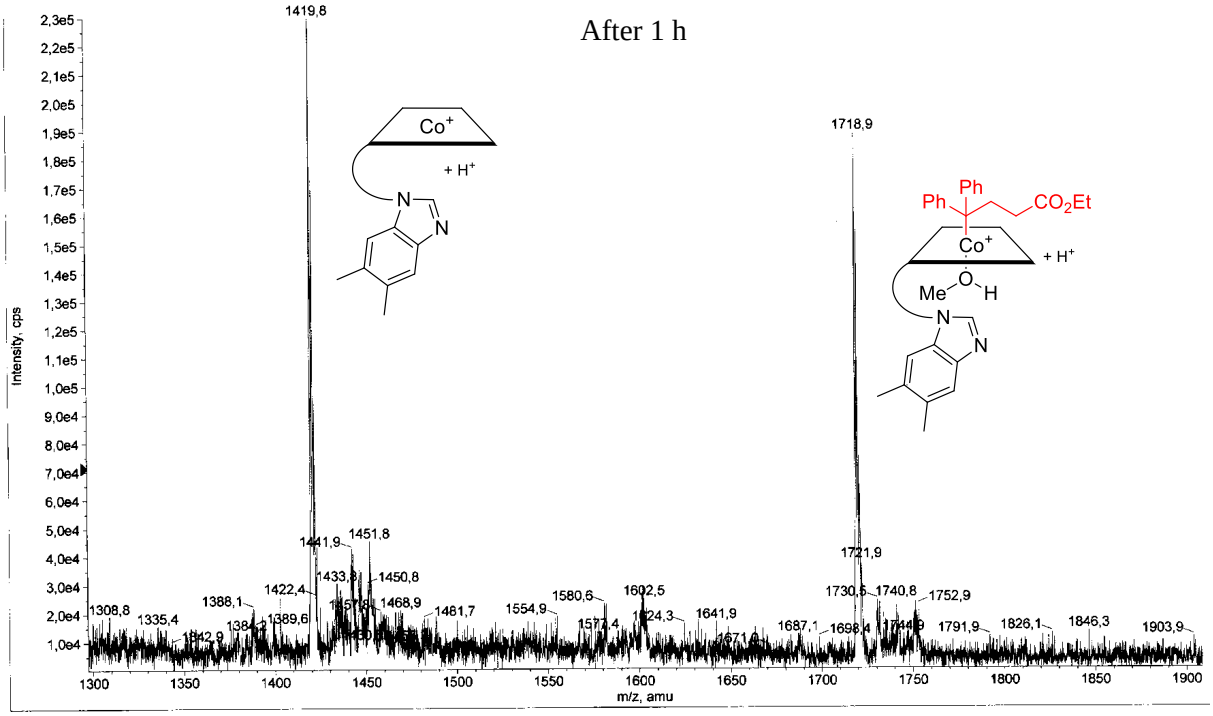




Initially, only the catalyst and the catalyst-product complex was observed suggesting high reaction rate for the alkylation of the catalyst with EDA and subsequent reaction with olefin. Presumably hydrocobaltation is the slowest step and after 6 h , when the concentration of EDA decreases, the interaction between the catalyst and olefin **5** becomes competitive.

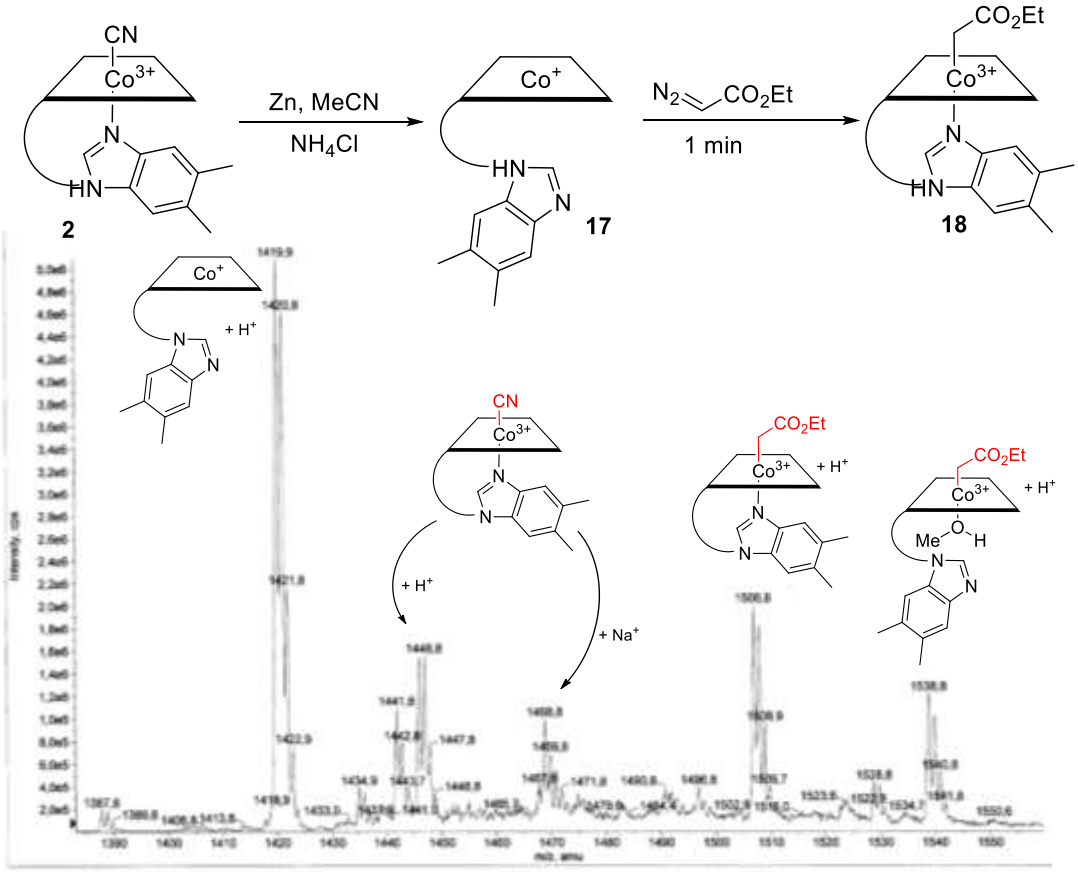
2)

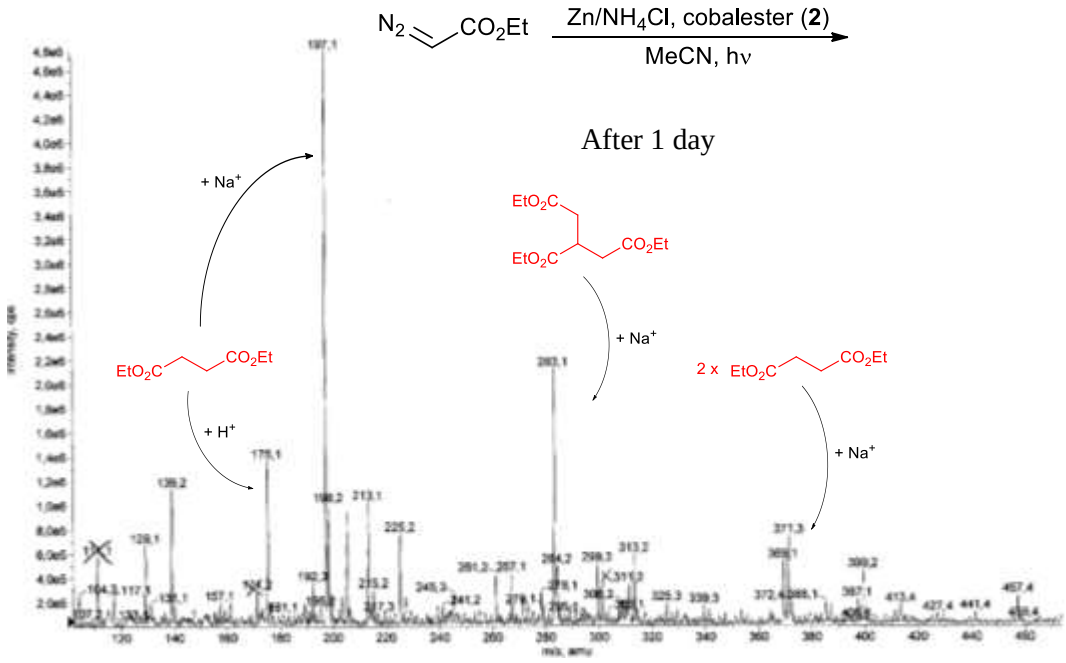




LR ESI spectrum shows peak at 1718.9 corresponding to the catalyst alkylated with product **4a**. We assume that initially formed unsaturated product can undergo hydrogenation catalyzed by cobalester (**2**).

3)

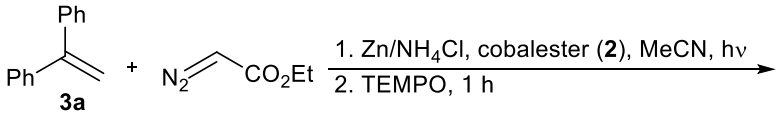


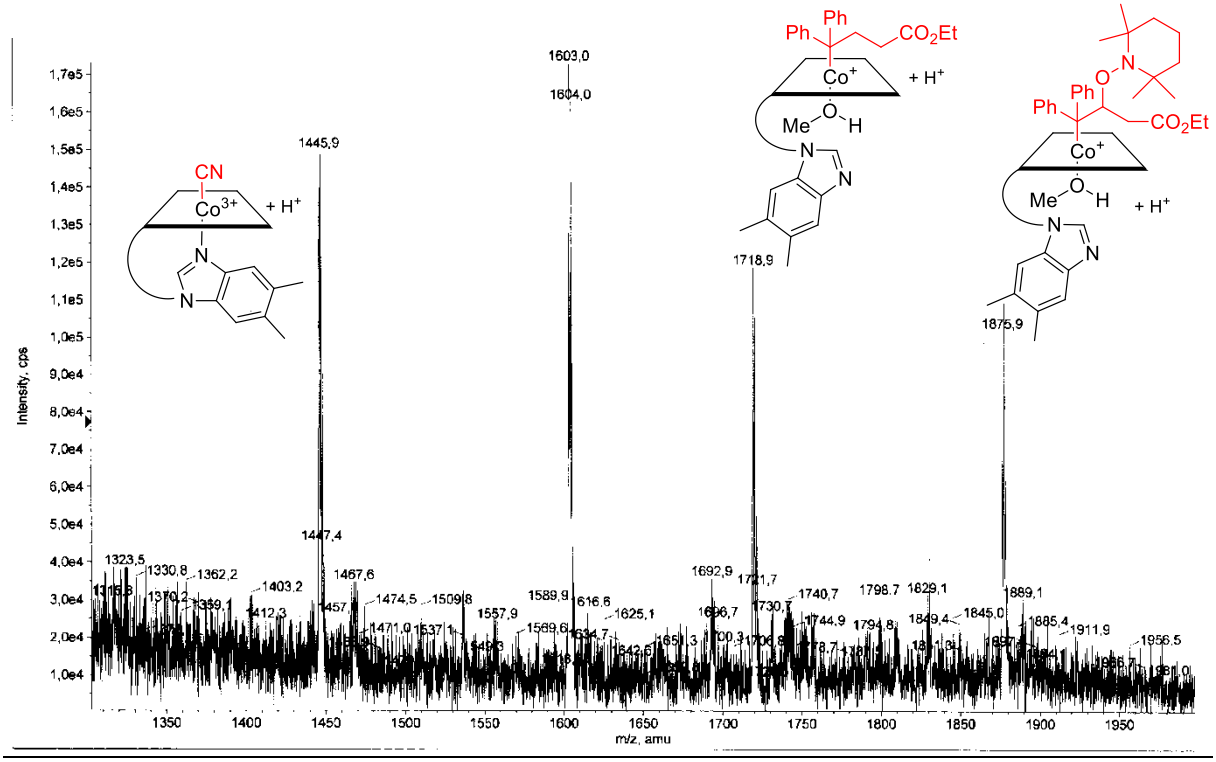


LR ESI experiment revealed that upon treatment of the reduced catalyst **17** with only EDA, alkylated cobalester **18** is formed (peaks at 1506.8 and 1538.8). Hence, vitamin B_{12}

derivatives can be alkylated with diazocompounds. Subjecting EDA to standard reaction conditions results in dimers, trimers etc. formation.

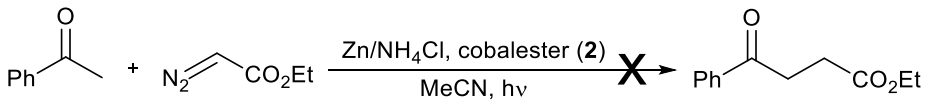
4)





When TEMPO was used as a radical scavenger, a cobalester-product-TEMPO adduct was observed, which further supports the radical mechanism.

4g. Background experiment for reactions of OTMS- and OTBDMS-protected ketones **9** and **11**

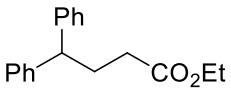


Standard conditions: substrate (0.5 mmol, 1.0 equiv.), EDA (1.5 mmol, 3 equiv.), cobalester **2** (2 mol%), Zn (6 equiv.), NH_4Cl (3.4 equiv.), MeCN (5 mL), light, 18 h

In order to prove that the presence of double bond is necessary for C-H functionalization at the α-position, the reaction of acetophenone with EDA was performed. The reaction led only to the recovery of ketone, thus excluding the mechanism proposed by Gutsche and Hillman.[5]

5. Scope and analytical data for newly synthesized compounds

Ethyl 4,4-diphenylbutanoate (5a)[6]



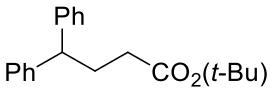
Anal. calcd for $C_{18}H_{20}O_2$: C 80.56, H. 7.51, found: C 80.66, H 7.59

HRMS ESI calcd for $C_{18}H_{20}O_2$ $[M+H]^+$ 268.1463, found: 268.1461

^{1}H (400 MHz, $CDCl_3$): δ = 7.31-7.23 (m, 8H), 7.20-6.97 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.94 (t, *J* = 8.2 Hz, 1H), 2.43-2.35 (m, 2H), 2.30-2.24 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H) ppm.[6]

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.4, 144.2, 128.5, 127.9, 126.3, 60.3, 50.6, 32.8, 30.6, 14.2 ppm.

t-Butyl 4,4-diphenylbutanoate (5b)



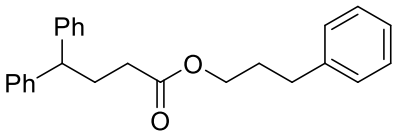
Anal. calcd for $C_{20}H_{24}O_2$: C 81.04, H. 8.16, found: C 80.91, H 8.15

HRMS ESI calcd for $C_{20}H_{24}O_2Na$ $[M+Na]^+$ 319.1667, found: 319.1674

^{1}H (400 MHz, $CDCl_3$): δ = 7.29-7.22 (m, 8H), 7.19-7.15 (m, 2H), 3.92 (t, *J* = 7.9 Hz, 1H), 2.36-2.31 (m, 2H), 2.19-2.15 (m, 2H), 1.43 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8, 144.3, 128.5, 127.9, 126.3, 80.15, 50.5, 34.0, 30.8, 28.1 ppm.

3-Phenyl-*n*-propyl 4,4-diphenylbutanoate (5c)



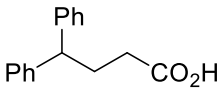
Anal. calcd for $C_{25}H_{26}O_2$: C 83.76, H. 7.31, found: C 83.85, H 7.26

HRMS ESI calcd for $C_{25}H_{26}O_2Na$ $[M+Na]^+$ 381.1830, found: 381.1832

^{1}H (400 MHz, $CDCl_3$): δ = 7.28-7.22 (m, 10H), 7.18-7.13 (m, 5H), 4.05 (t, *J* = 6.5 Hz, 2H), 3.93 (t, *J* = 7.8 Hz, 1H), 2.64 (t, *J*=7.7 Hz, 2H), 2.38 (q, *J*=7.6 Hz, 2H), 2.26 (t, *J* = 7.5 Hz, 2H), 1.92 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.4, 144.2, 141.2, 128.6, 128.5, 128.4, 127.9, 126.4, 126.1, 63.8, 50.6, 32.8, 32.3, 30.7, 30.3 ppm.

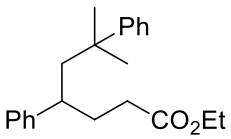
4,4-Diphenylbutanoic acid (5d)[6]



^{1}H (400 MHz, $CDCl_3$): δ = 11.25 (s(br), 1H), 7.29-7.22 (m, 8H), 7.19-7.15 (m, 2H), 3.94 (t, *J* = 7.6 Hz, 1H), 2.42-2.36 (m, 2H), 2.33-2.29 (m, 2H) ppm.[6]

^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.7, 143.9, 128.6, 127.8, 126.4, 50.4, 32.5, 30.3 ppm.

Ethyl 4,6-diphenyl-6-methylheptanate (5e)



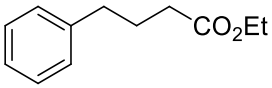
Anal. calcd for $C_{22}H_{28}O_2$: C 81.44, H. 8.70, found: C 81.34, H 8.82

HRMS ESI calcd for $C_{22}H_{28}O_2$ $[M+H]^+$ 324.2089, found: 324.2095

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.09 (m, 8.9H, overlapping with $CHCl_3$), 6.97-6.94 (m, 2H), 4.04-3.96 (m, 2H), 2.38-2.30 (m, 1H), 2.12-1.97 (m, 2H), 1.95-1.82 (m, 2H), 1.91-1.65 (m, 2H), 1.24 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.11 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.5, 149.1, 145.9, 128.2, 127.9, 127.8, 125.9, 125.8, 125.4, 60.1, 51.3, 42.2, 38.4, 34.0, 32.4, 30.7, 28.3, 14.2 ppm.

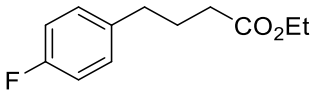
Ethyl 4-phenylbutanoate (5f)[7]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.25 (m, 2H), 7.21-7.16 (m, 3H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 2.32 (t, *J* = 7.6 Hz, 2H), 1.96 (quin, *J* = 7.6 Hz, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm.[7]

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.5, 141.4, 128.5, 128.4, 125.9, 60.2, 35.1, 33.7, 26.5, 14.2 ppm.

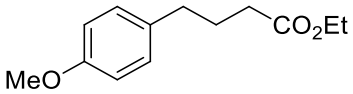
Ethyl 4-(4-fluorophenyl)butanoate (5g)[8]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.01 – 6.92 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.94 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ppm.[8]

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.3, 162.5, 160.1, 137.03, 137.00 129.8, 129.7, 115.2, 115.0, 60.3, 34.3, 33.5, 26.6, 14.2 ppm.

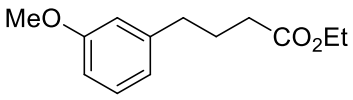
Ethyl 4-(4-methoxyphenyl)butanoate (5j)[8]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11-7.07 (m, 2H), 6.85-6.80 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 2.59 (t, *J* = 7.6 Hz, 2H), 2.30 (t, *J* = 7.7 Hz, 2H), 1.92 (quin, *J* = 7.6 Hz, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm.[8]

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.5, 157.9, 133.5, 129.4, 113.8, 60.2, 55.2, 34.2, 33.6, 26.8, 14.2 ppm.

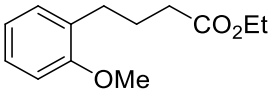
Ethyl 4-(3-methoxyphenyl)butanoate (5k)[8]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21-7.16 (m, 1H), 6.79-6.72 (m, 3H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 2.63 (t, *J* = 7.8 Hz, 2H), 2.32 (t, *J* = 7.3 Hz, 2H), 1.95 (quin, *J* = 7.6 Hz, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm.[8]

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.4, 159.7, 143.1, 129.3, 120.9, 114.2, 111.3, 60.2, 55.1, 35.2, 33.7, 26.4, 14.2 ppm.

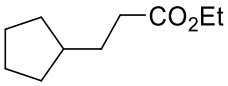
Ethyl 4-(2-methoxyphenyl)butanoate (5l)[8]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.09 (m, 2H), 6.90-6.81 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.32 (t, *J* = 7.8 Hz, 2H), 1.92 (quin, *J* = 7.6 Hz, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm.[8]

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.7, 157.5, 130.0, 127.2, 120.4, 110.2, 60.1, 55.2, 34.0, 29.5, 25.1, 14.2 ppm.

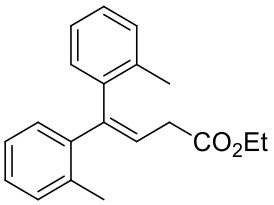
Ethyl 3-(cyclopentyl)propionate (5n)[9]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.11 (q, *J* = 7.2 Hz, 2H), 2.30 (t, *J* = 7.8 Hz, 2H), 1.81-1.44 (m, 9H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.15-1.02 (m, 2H) ppm.[9]

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.0, 60.1, 39.7, 33.7, 32.4, 31.2, 25.1, 14.2 ppm.

Ethyl 4,4-di(2-methylphenyl)but-3-enoate (5o)



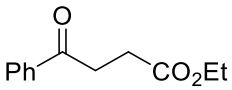
Anal. calcd for $C_{20}H_{22}O_2$: C 81.60, H 7.53, found: C 81.53, H 7.43

HRMS ESI calcd for $C_{20}H_{22}O_2Na$ $[M+Na]^+$ 317.1517, found: 317.1513

^{1}H NMR (400 MHz, $CDCl_3$): δ = δ 7.22-7.06 (m, 8H), 5.96 (t, 7.2 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.08 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 2.09 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.8, 143.6, 141.7, 139.2, 136.3, 135.6, 130.9, 130.5, 130.4, 129.8, 127.4, 127.0, 125.5, 124.7, 60.6, 35.3, 21.0, 19.9, 14.2 ppm.

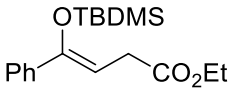
Ethyl 4-oxo-4-phenylbutanoate (10)[10]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00-7.94 (m, 2H), 7.58-7.52 (m, 3H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.30 (t, *J* = 7.1 Hz, 2H), 2.74 (t, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm.[10]

^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.1, 172.8, 136.6, 133.1, 128.6, 128.0, 60.6, 33.4, 28.3, 14.2 ppm.

Ethyl 4-phenyl-4-(*tert*-butyldimethylsiloxyl)but-3-enoate (12)



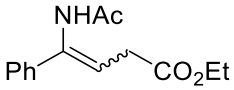
Anal. calcd for $C_{18}H_{28}O_3Si$: C 67.46, H. 8.81, found: C 67.48, H 8.73

HRMS ESI calcd for $C_{18}H_{28}O_3NaSi$ $[M+Na]^+$ 343.1705, found: 343.1707

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.43 (m, 2H), 7.31-7.25 (m, 3H, overlapping with $CHCl_3$), 5.29 (t, *J* = 7.0 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.25 (d, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.98 (s, 9H), -0.06 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.1, 151.6, 139.0, 127.92, 127.90, 126.2, 103.0, 60.5, 31.9, 25.8, 18.3, 14.3, -4.1 ppm

Ethyl 4-phenyl-4-(*N*-acetylamine)but-3-enoate (14a)



as a mixture of E/Z stereoisomers with restricted rotation of the C-N amide bond

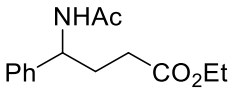
Anal. calcd for $C_{14}H_{17}NO_3$: C 68.00, H 6.93, N 5.66, found: C 68.14, H 6.98, N 5.43

HRMS ESI calcd for $C_{14}H_{17}NO_3Na$ $[M+Na]^+$ 270.1106, found: 270.1111

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.22 (m, 5H), 7.24 (br s, 0.4H), 6.93 (br s, 0.1H), 6.64 (br s, 0.5H), 6.52 (t, *J* = 8.0 Hz, 0.5H), 6.02 (t, *J* = 7.4 Hz, 0.1H), 5.94 (t, *J* = 7.2 Hz, 0.4H), 4.21-4.08 (m, 2H), 3.28 (d, *J* = 7.4 Hz, 0.2H), 3.20 (d, *J* = 7.1 Hz, 0.8H), 3.04 (d, *J* = 7.8 Hz, 1H), 2.16 (s, 1.2H), 2.04 (s, 1.5H) 1.73 (s, 0.3H), 1.30-1,23 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.0, 171.9, 168.2, 137.3, 136.7, 136.5, 128.9, 128.7, 128.5, 128.4, 125.9, 116.0, 110.0, 61.0, 60.7, 34.2, 34.0, 24.5, 23.5, 14.2 ppm

Ethyl 4-phenyl-4-(*N*-acetylamine)butanoate (14b)



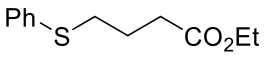
Anal. calcd for $C_{14}H_{19}NO_3$: C 67.45, H 7.68, N 5.62, found: C 67.33, H 7.48, N 5.50

HRMS ESI calcd for $C_{14}H_{19}NO_3Na$ $[M+Na]^+$ 272.1263, found: 272.1265

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.23 (m, 5H, overlapping with $CHCl_3$), 6.01 (d, *J* = 4.2 Hz, 1H), 4.98 (q, *J* = 8.3 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.41-2.26 (m, 2H), 2.21-2.03 (m, 2H), 1.97 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.6, 169.3, 141.5, 128.8, 127.6, 126.5, 60.6, 53.2, 31.3, 30.8, 23.4, 14.2 ppm

Ethyl 4-(phenylthio)butanoate (16)[11]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.25 (m, 4H), 7.20-7.15 (m, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.96 (t, *J* = 7.0 Hz, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 1.96 (quin, *J* = 7.4 Hz, *J* = 7.3 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm.[11]

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 136.1, 129.4, 128.9, 126.0, 60.4, 33.0, 32.9, 24.4, 14.2 ppm.

6. References

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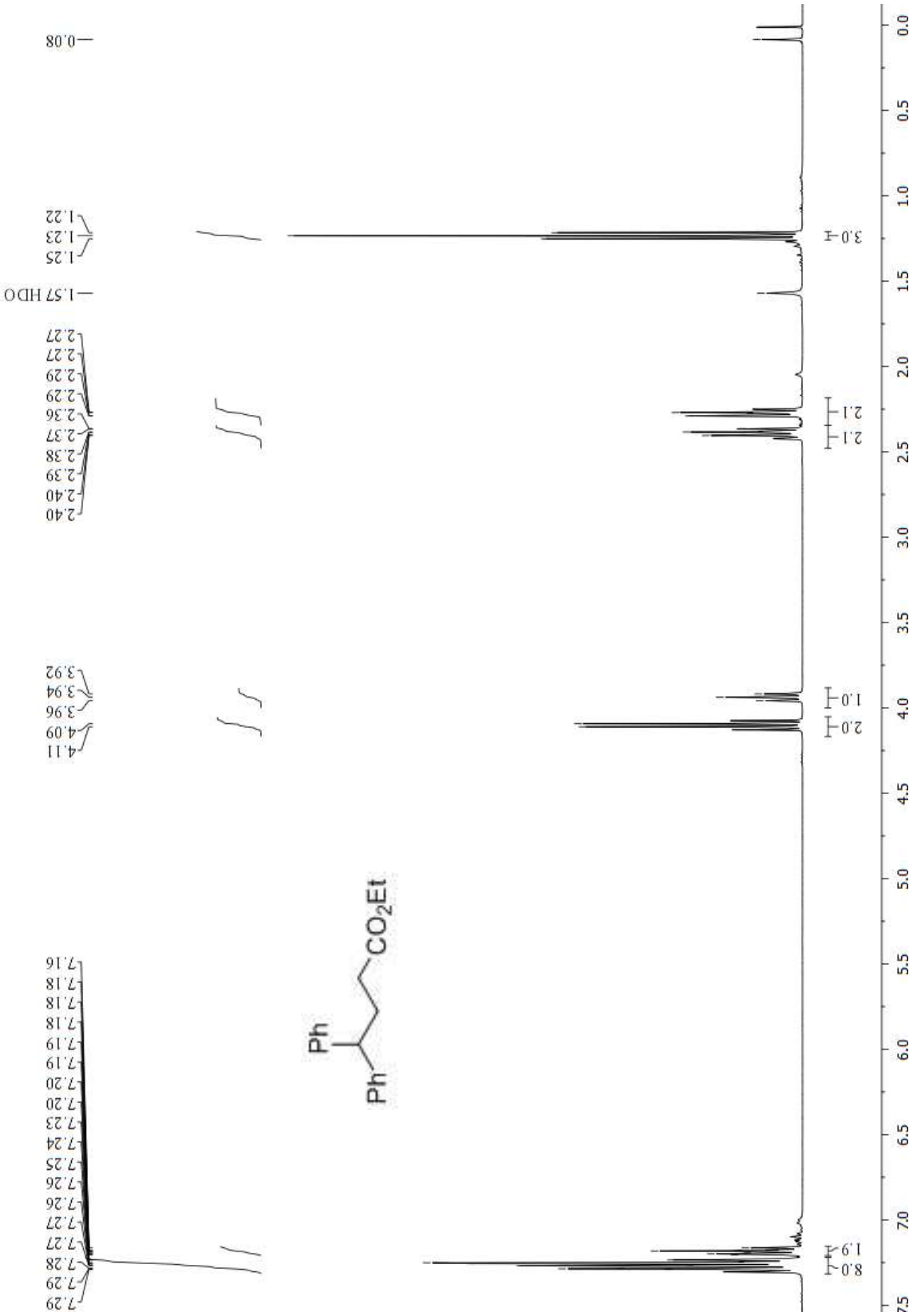
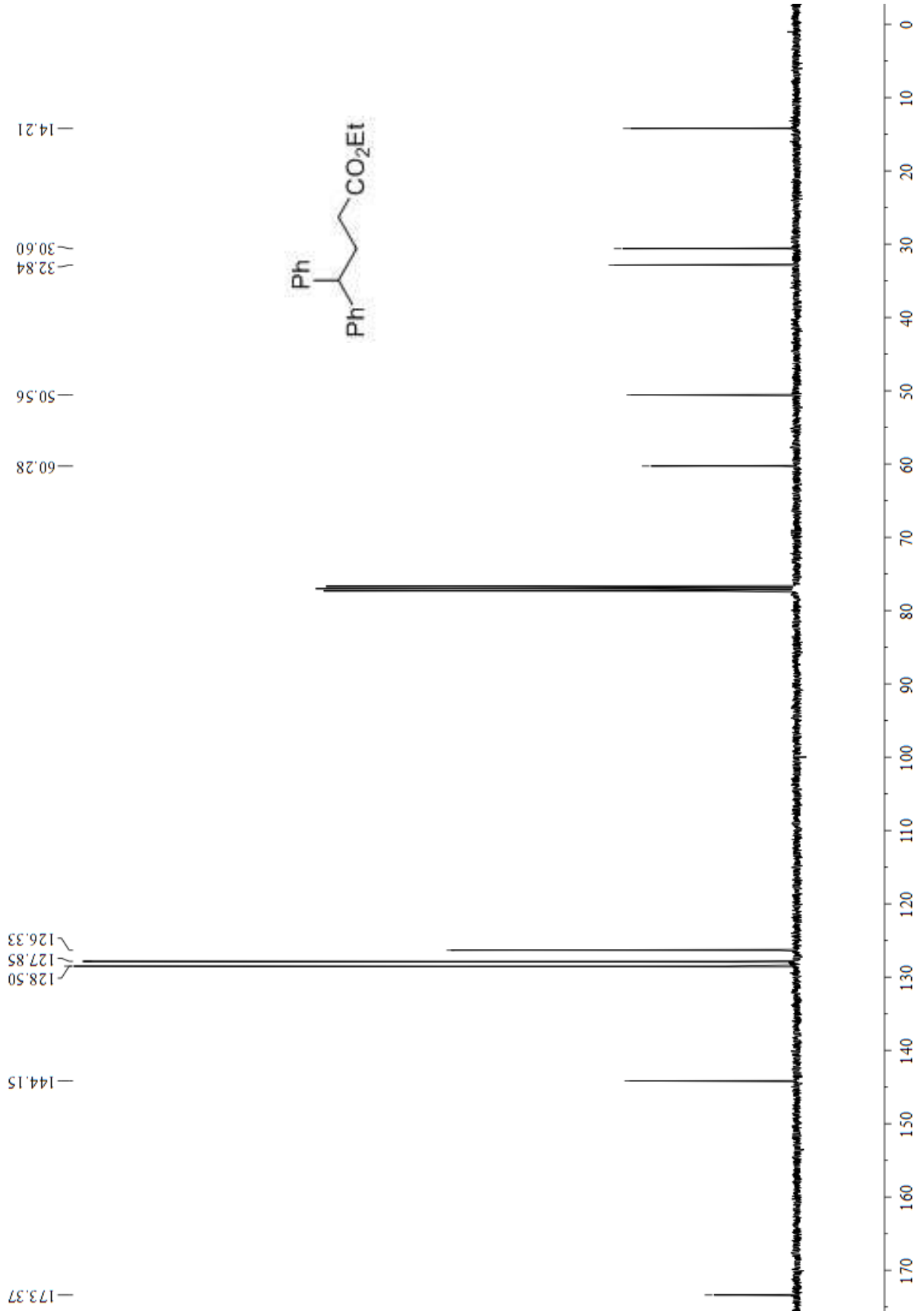
7. ^{1}H and ^{13}C NMR spectra

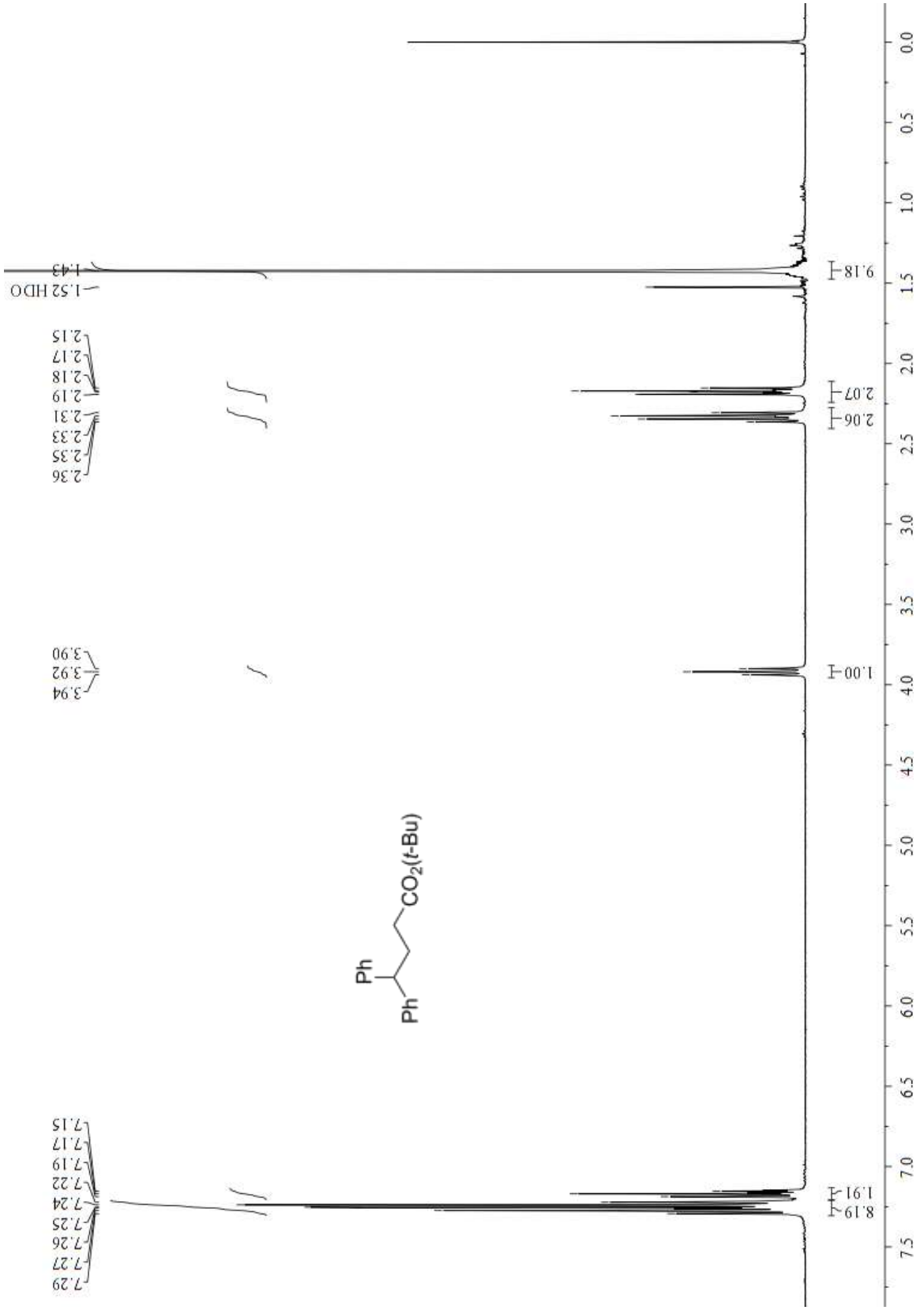
Ethyl 4,4-diphenylbutanoate (5a) - ^{1}H NMR



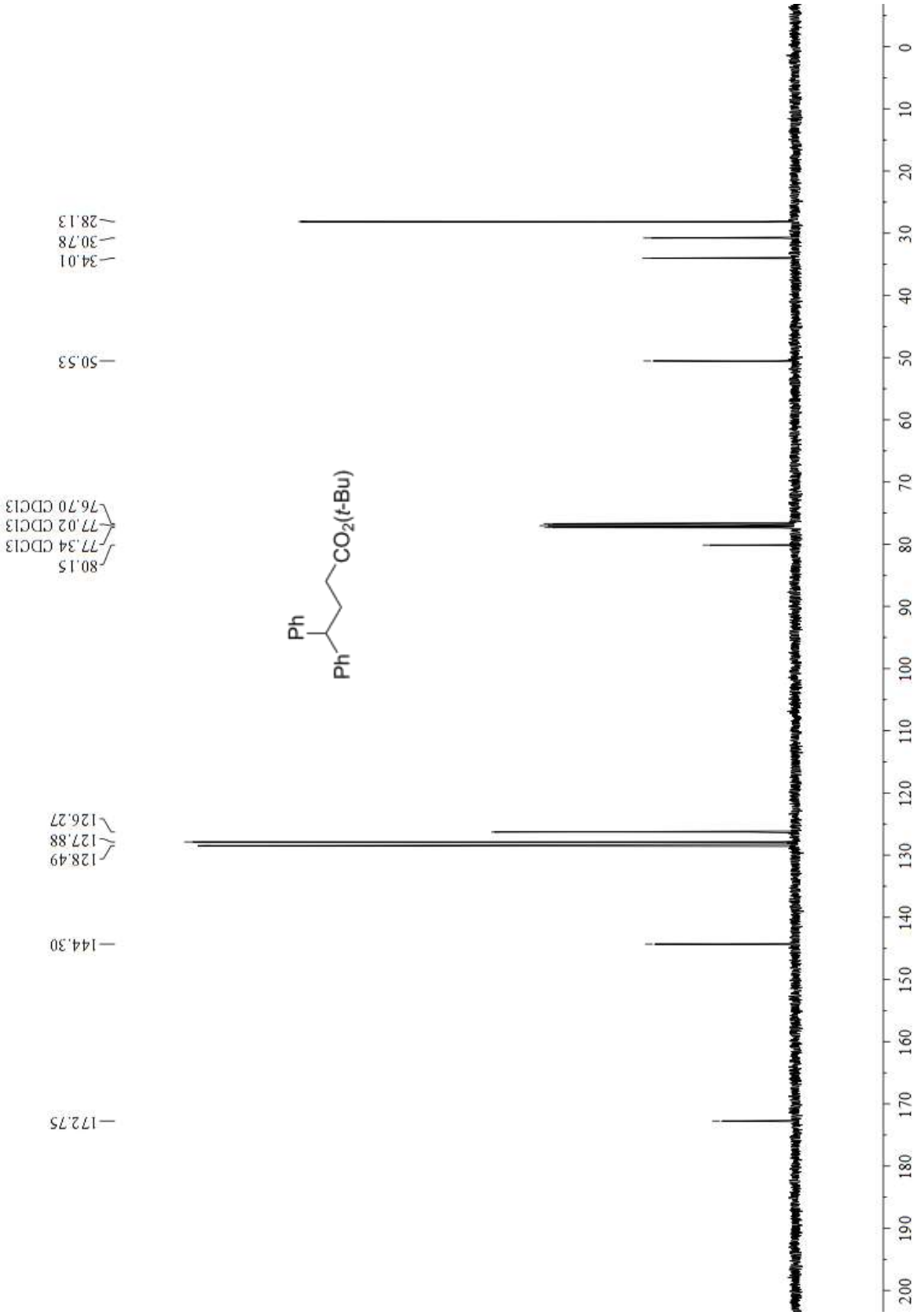
Ethyl 4,4-diphenylbutanoate (5a) – ^{13}C NMR



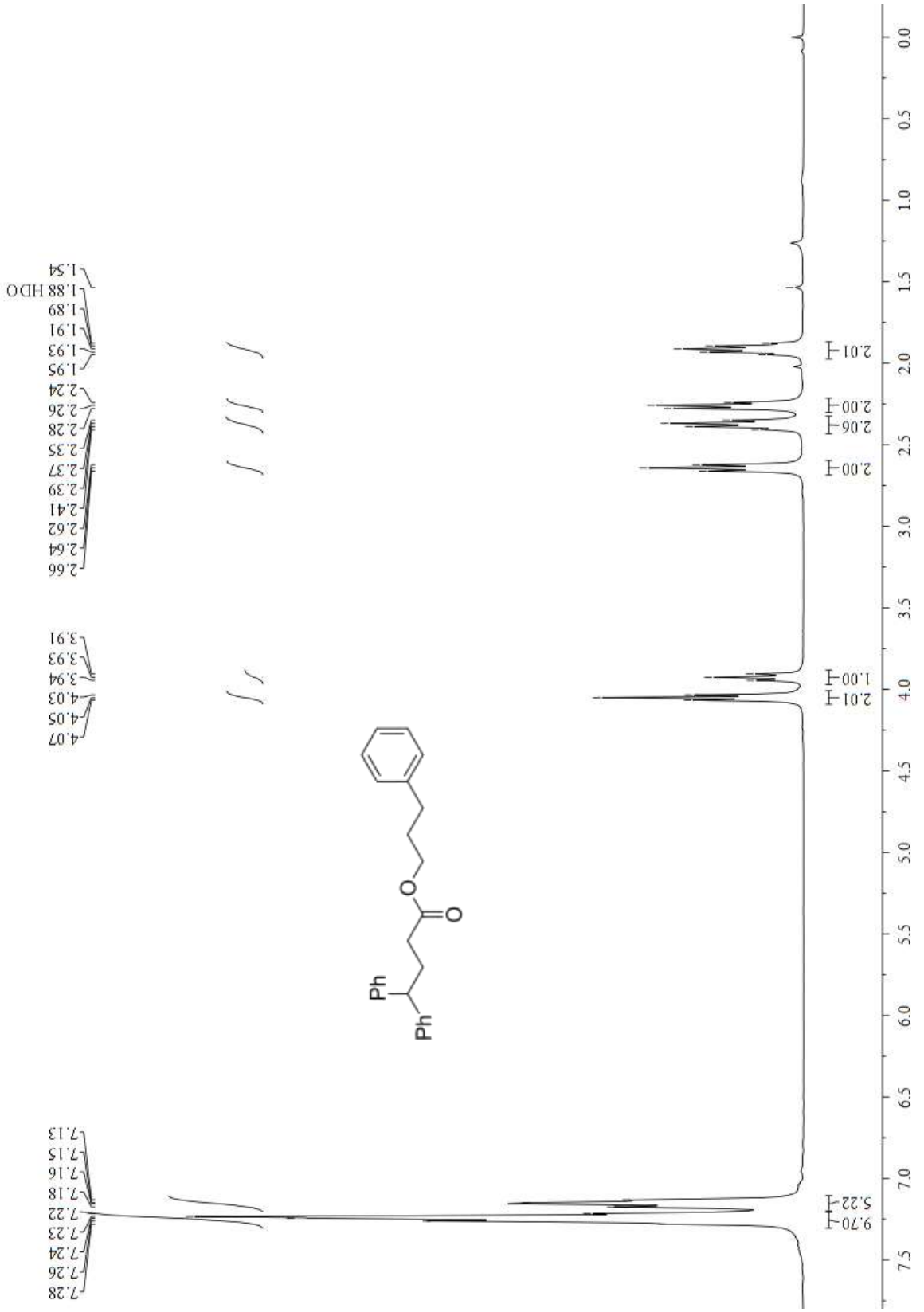
***t*-Butyl 4,4-diphenylbutanoate (5b) - ^{1}H NMR**



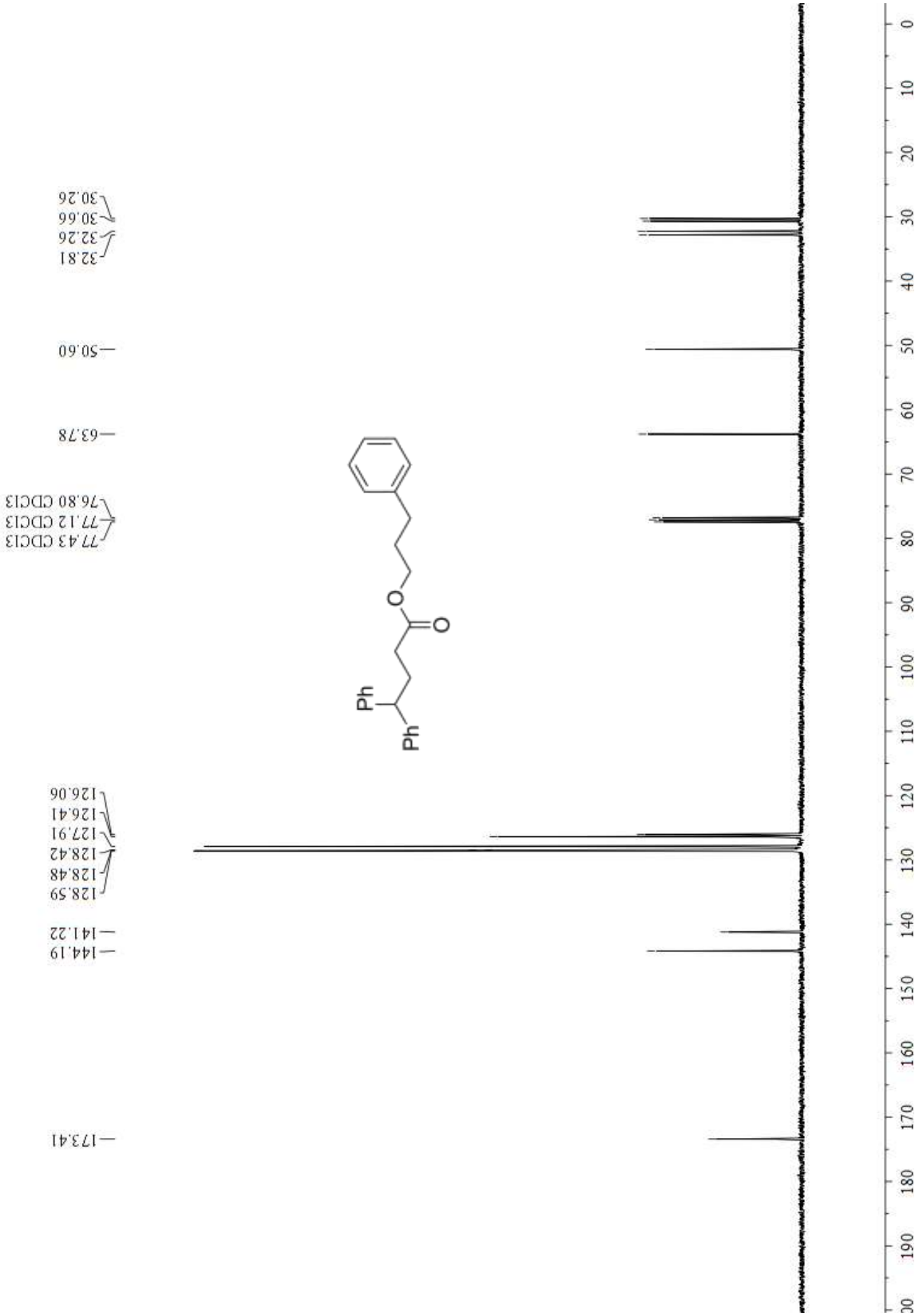
_t_-Butyl 4,4-diphenylbutanoate (5b) – ^{13}C NMR



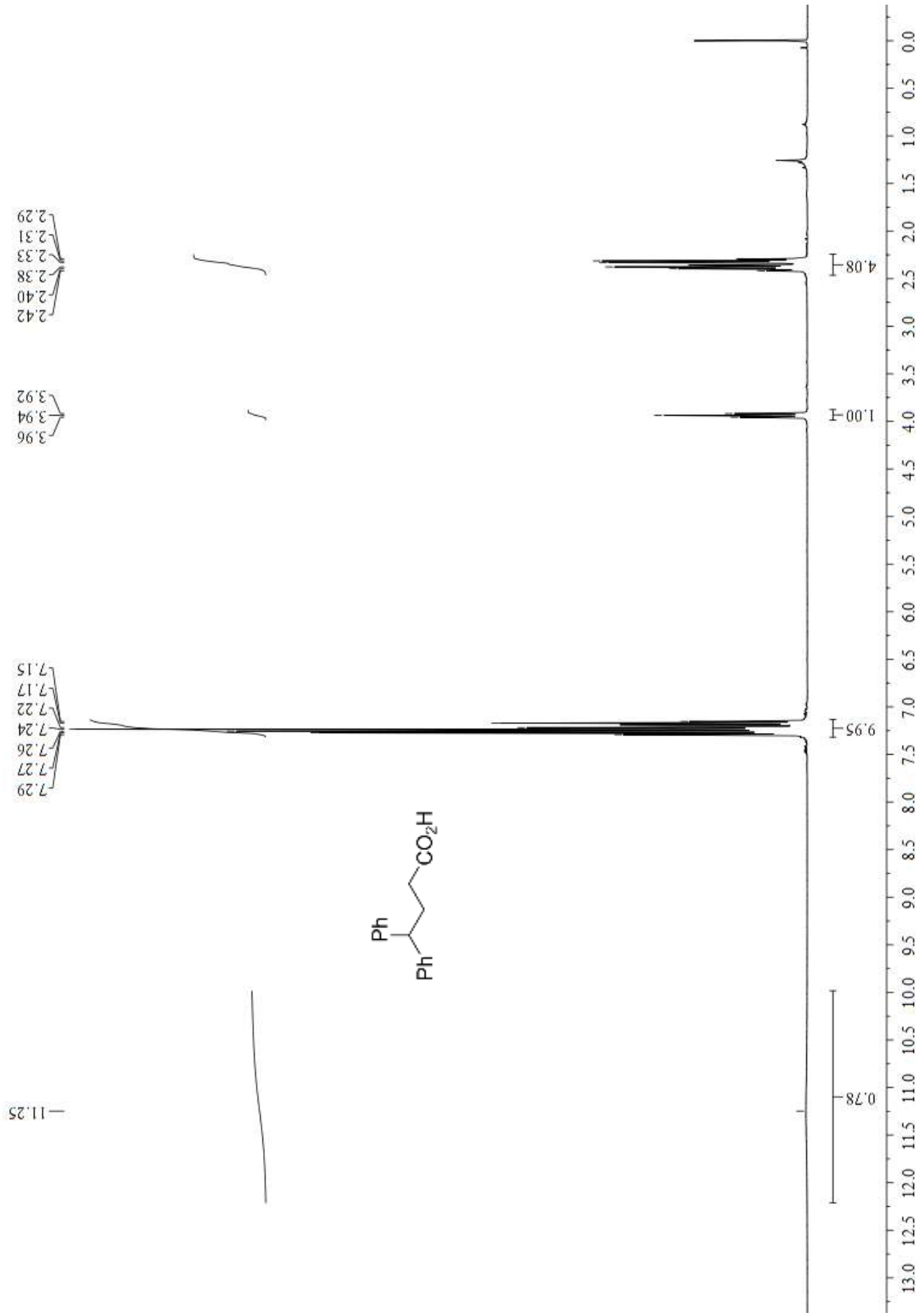
3-Phenyl-*n*-propyl 4,4-diphenylbutanoate (5c) - ^{1}H NMR



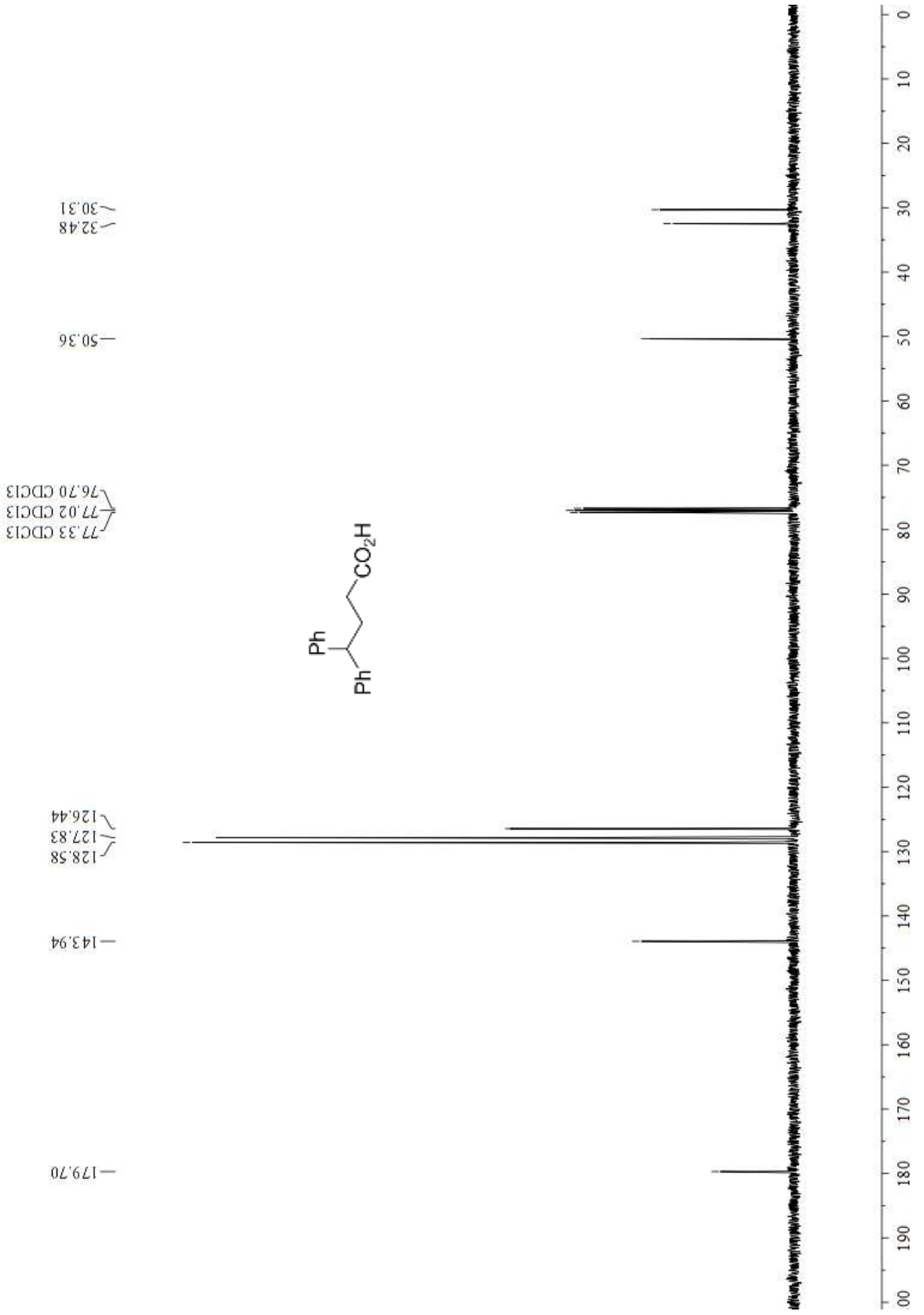
3-Phenyl-*n*-propyl 4,4-diphenylbutanoate (5c) – ^{13}C NMR



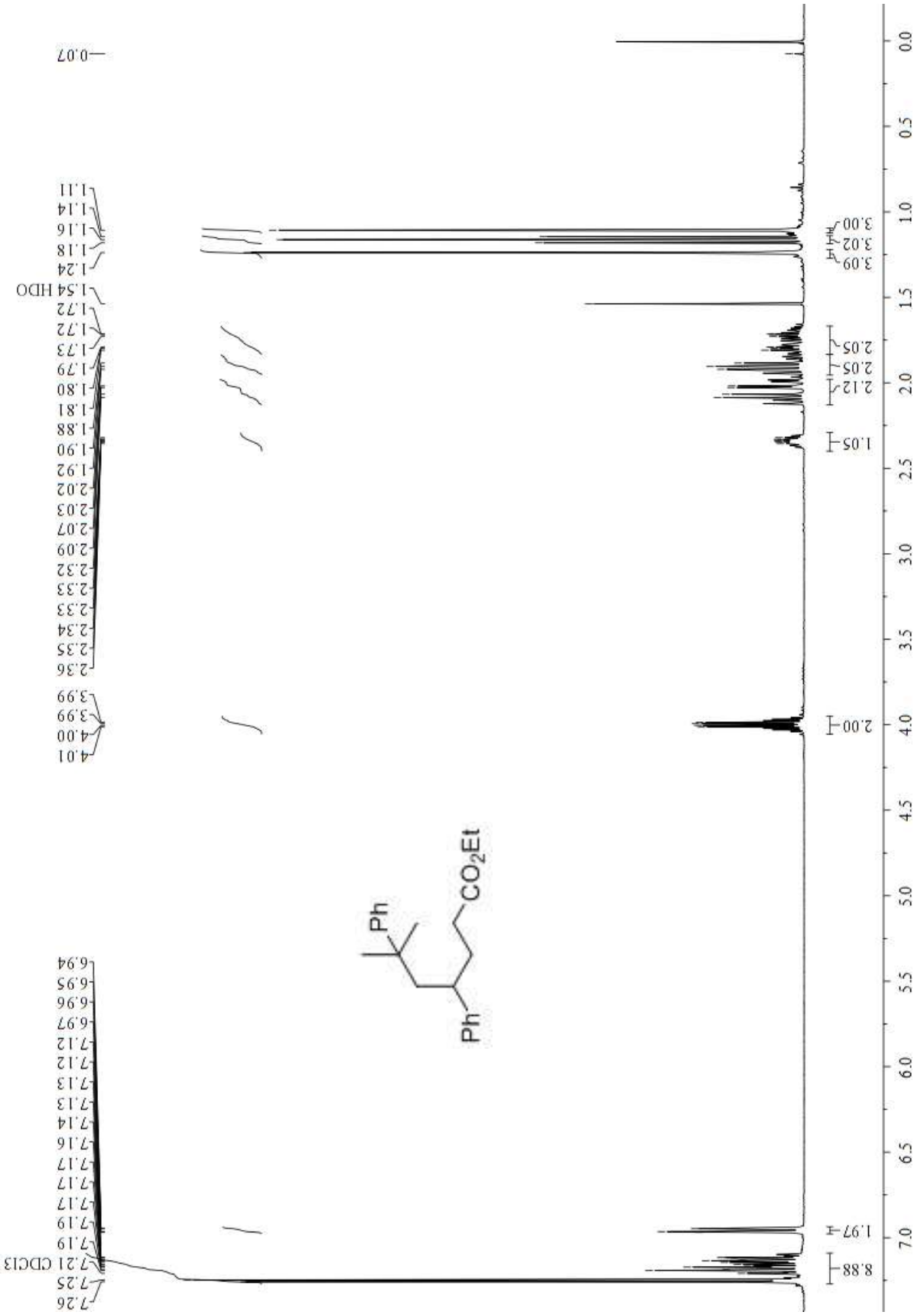
4,4-Diphenylbutanoic acid (5d) - ^{1}H NMR



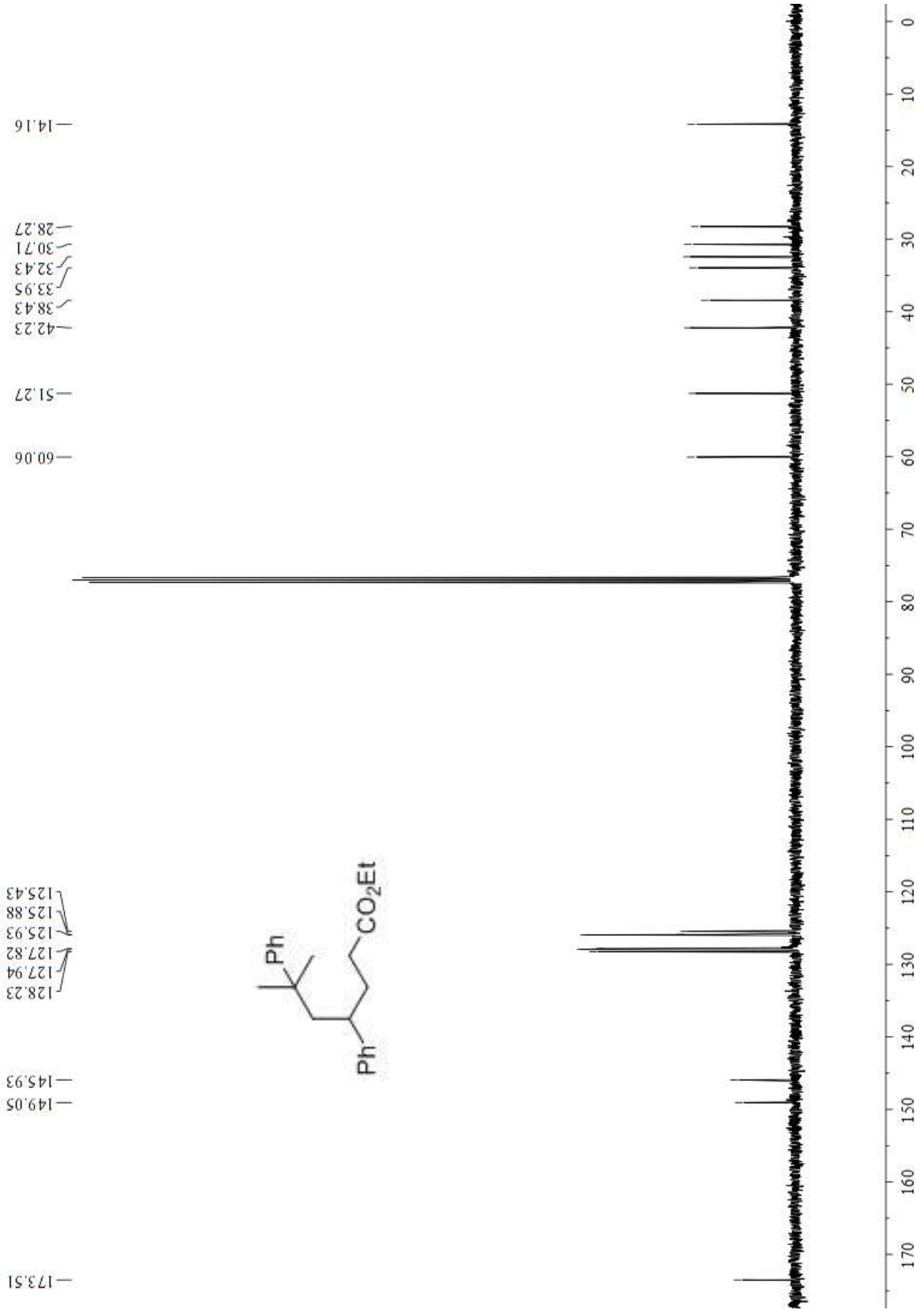
4,4-Diphenylbutanoic acid (5d) – ^{13}C NMR



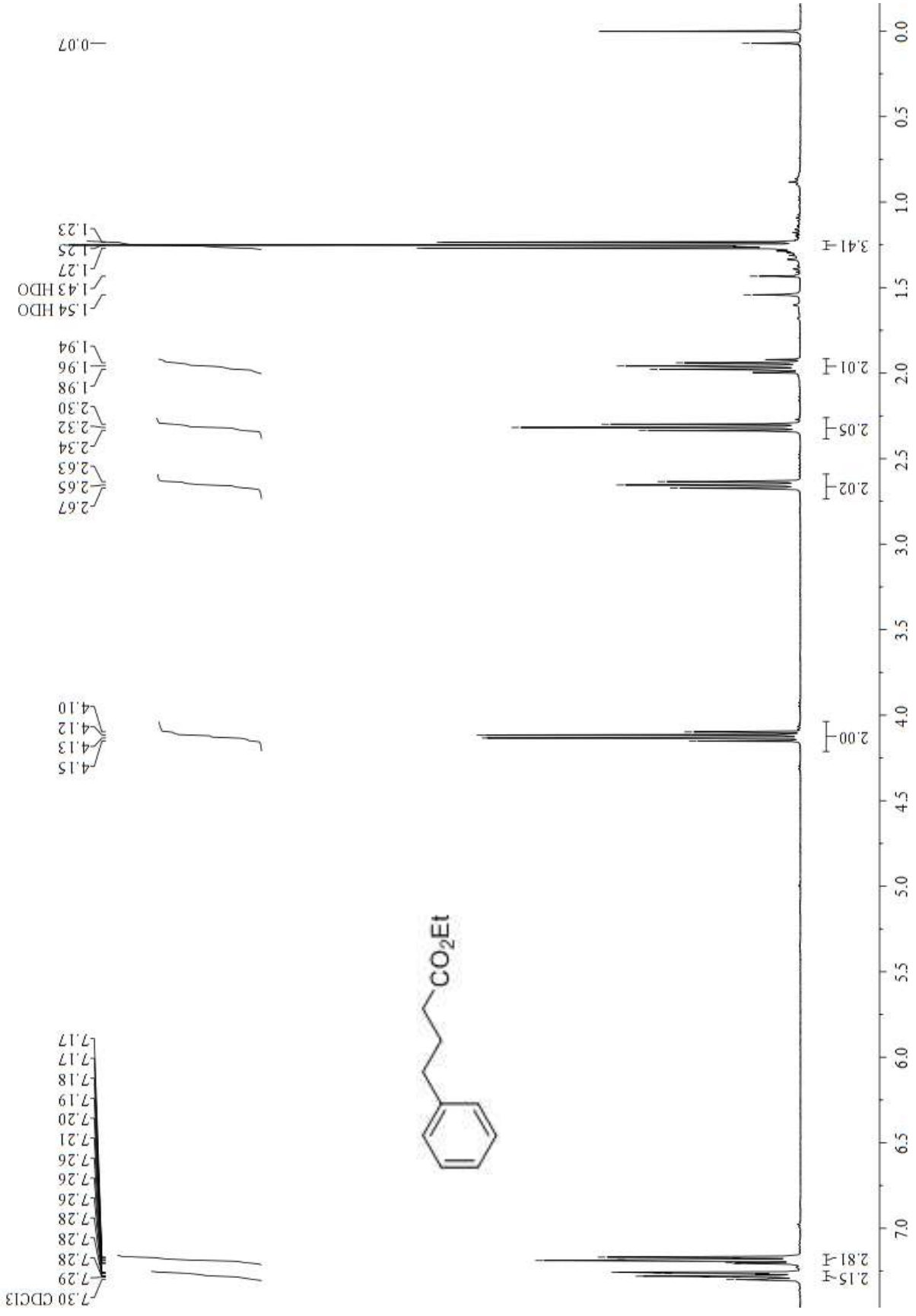
Ethyl 4,6-diphenyl-6-methylheptanate (5e) – ^{1}H NMR



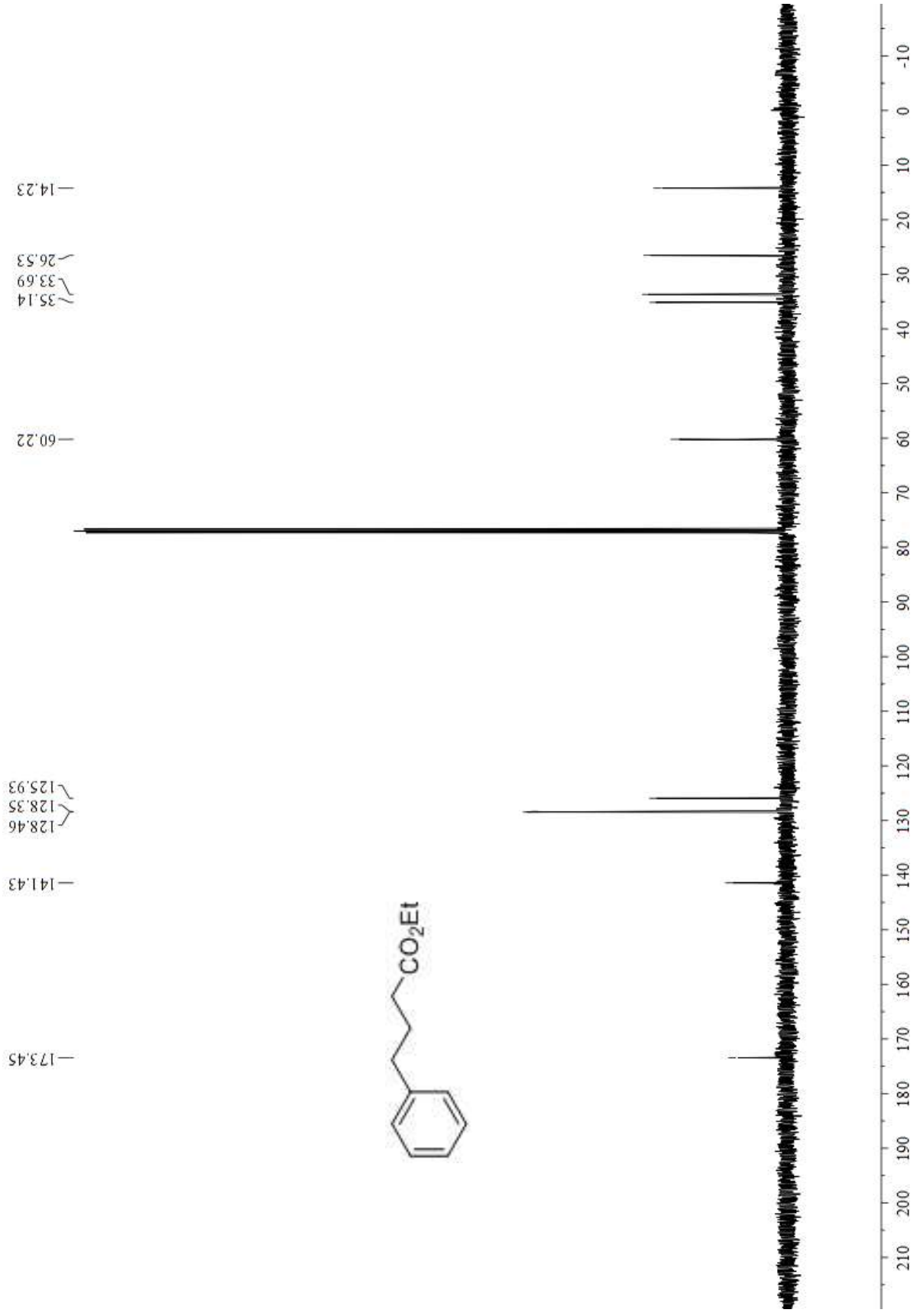
Ethyl 4,6-diphenyl-6-methylheptanate (5e) – ^{13}C NMR



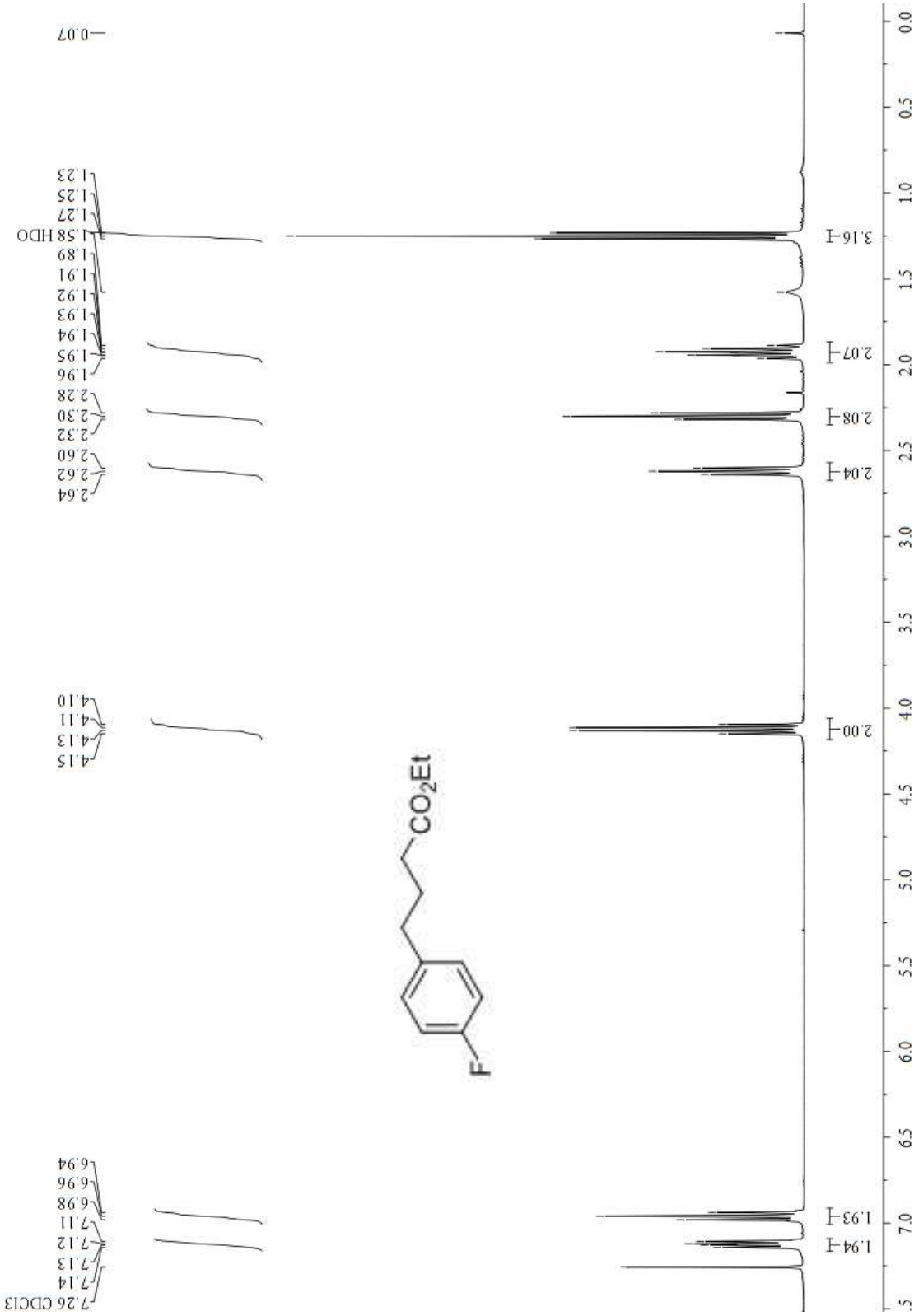
Ethyl 4-phenylbutanoate (5f) – ^{1}H NMR



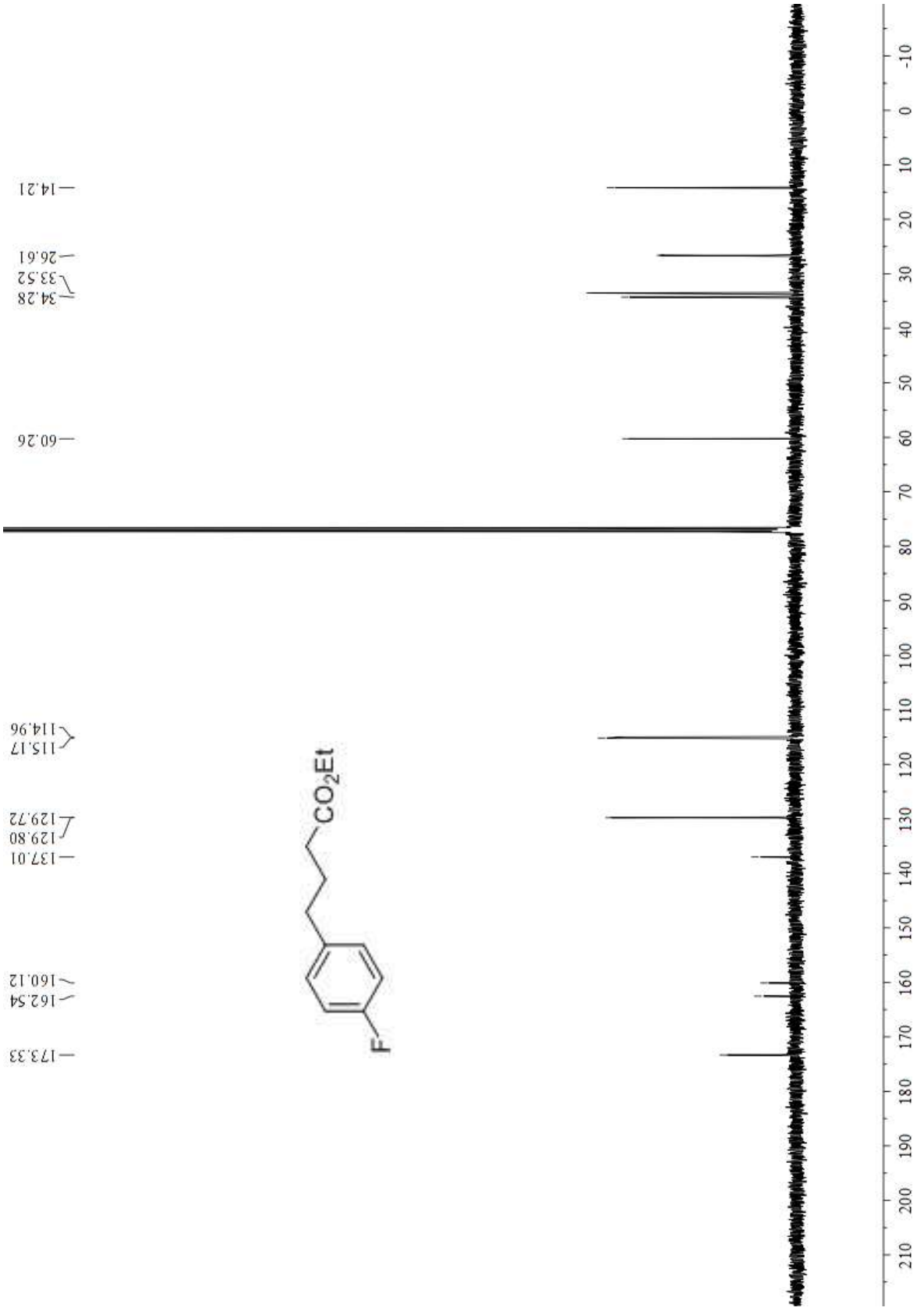
Ethyl 4-phenylbutanoate (5f) – ^{13}C NMR



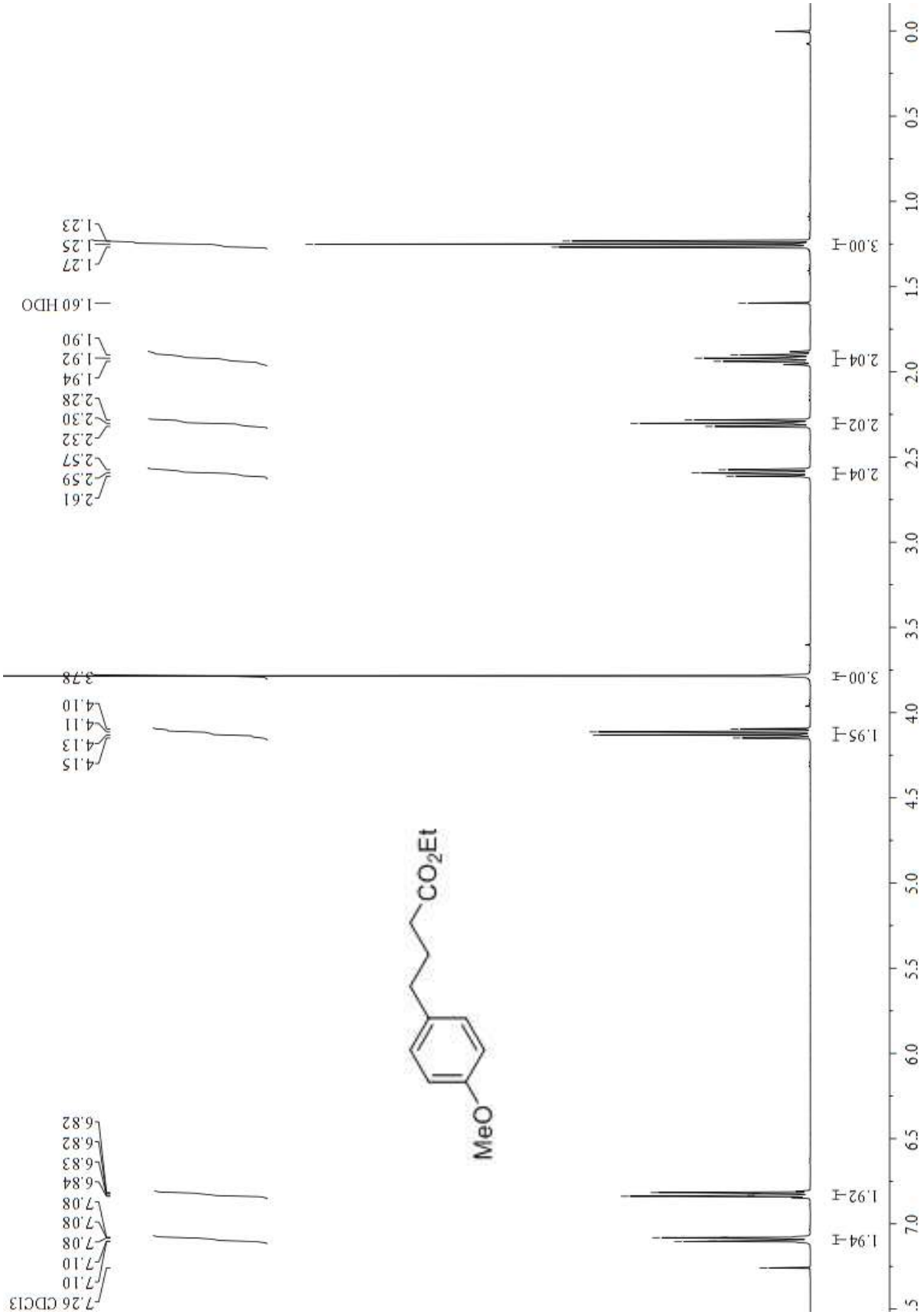
Ethyl 4-(4-fluorophenyl)butanoate (5g) – ^{1}H NMR



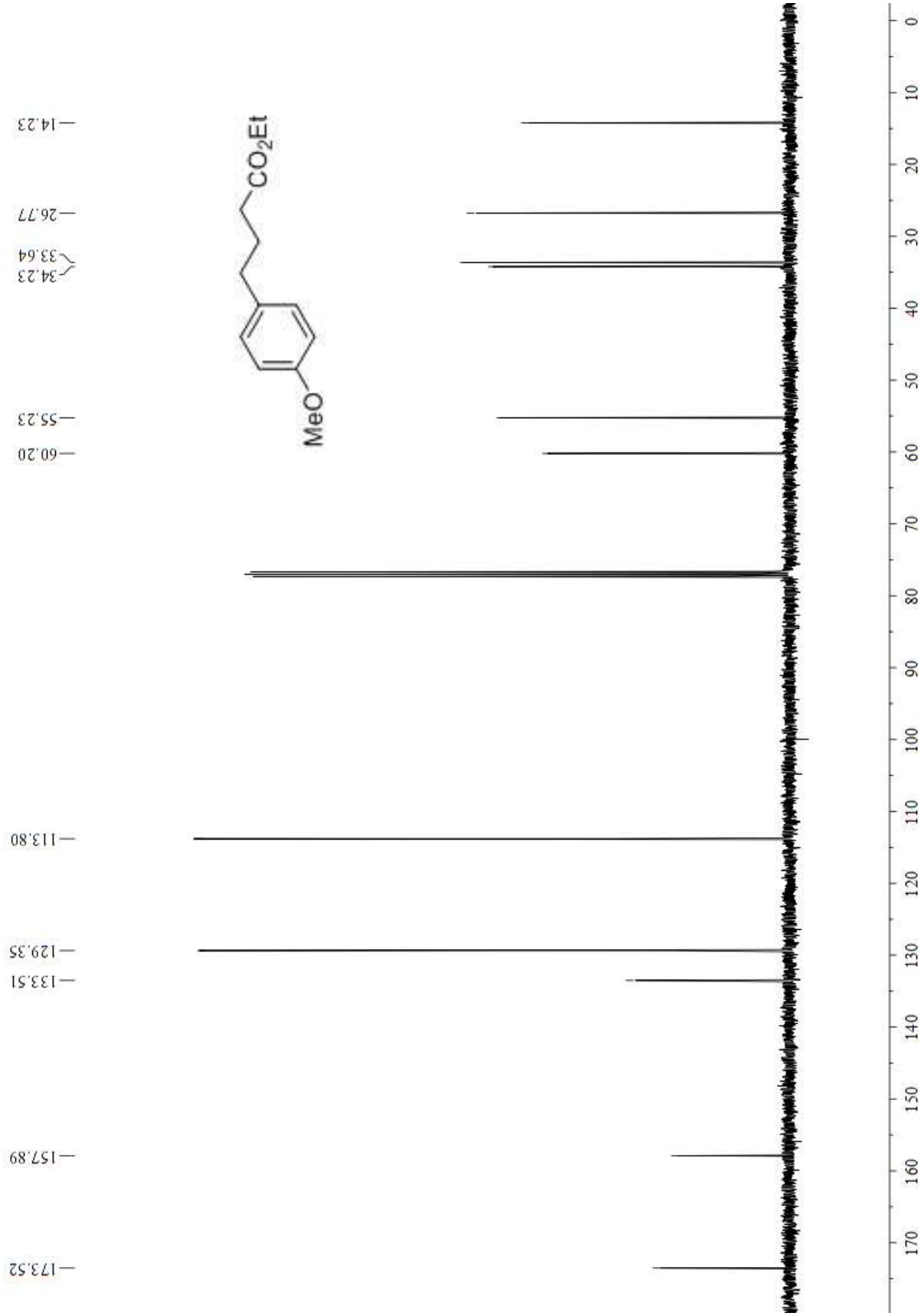
Ethyl 4-(4-fluorophenyl)butanoate (5g) – ^{13}C NMR



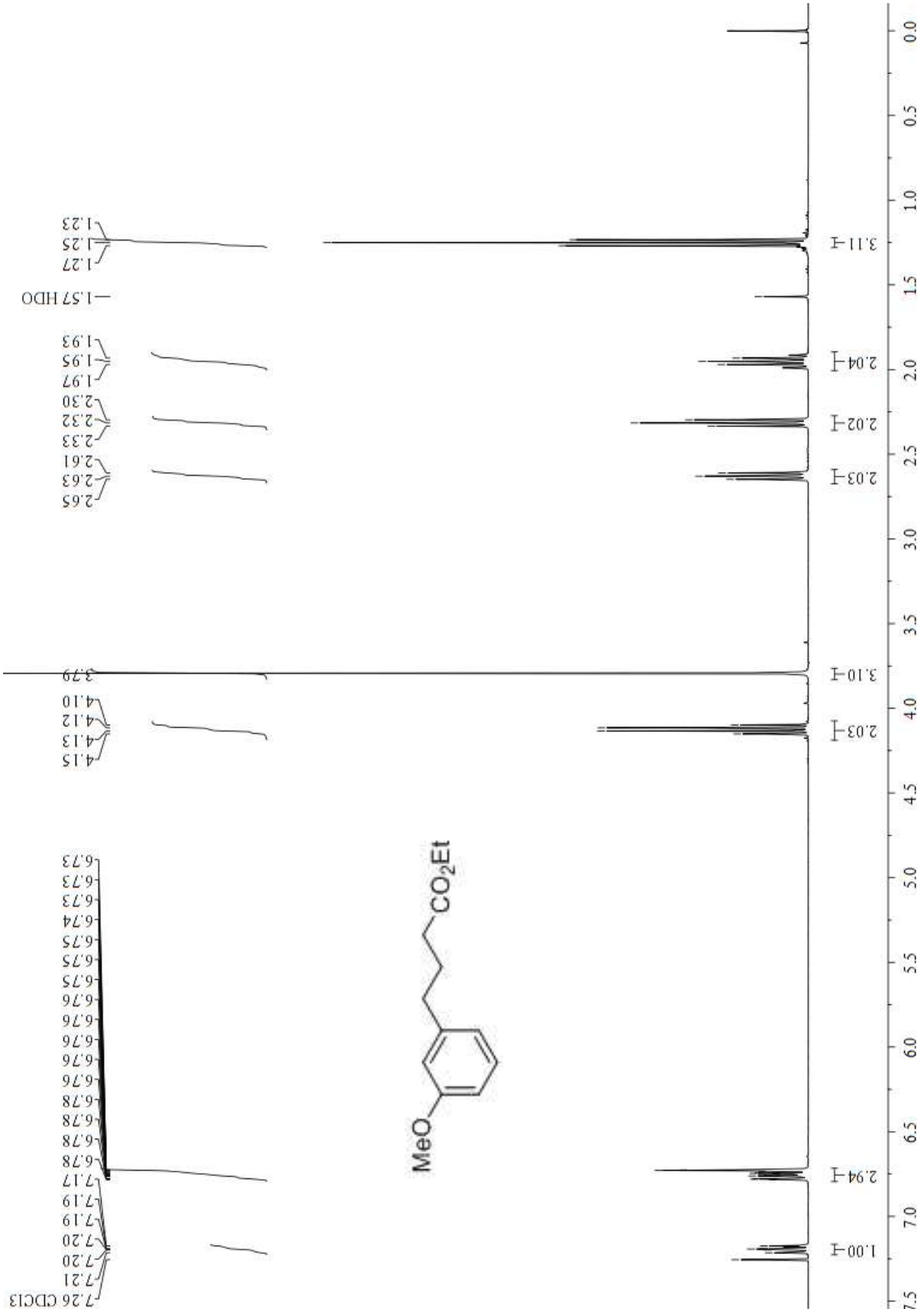
Ethyl 4-(4-methoxyphenyl)butanoate (5j) – ^{1}H NMR



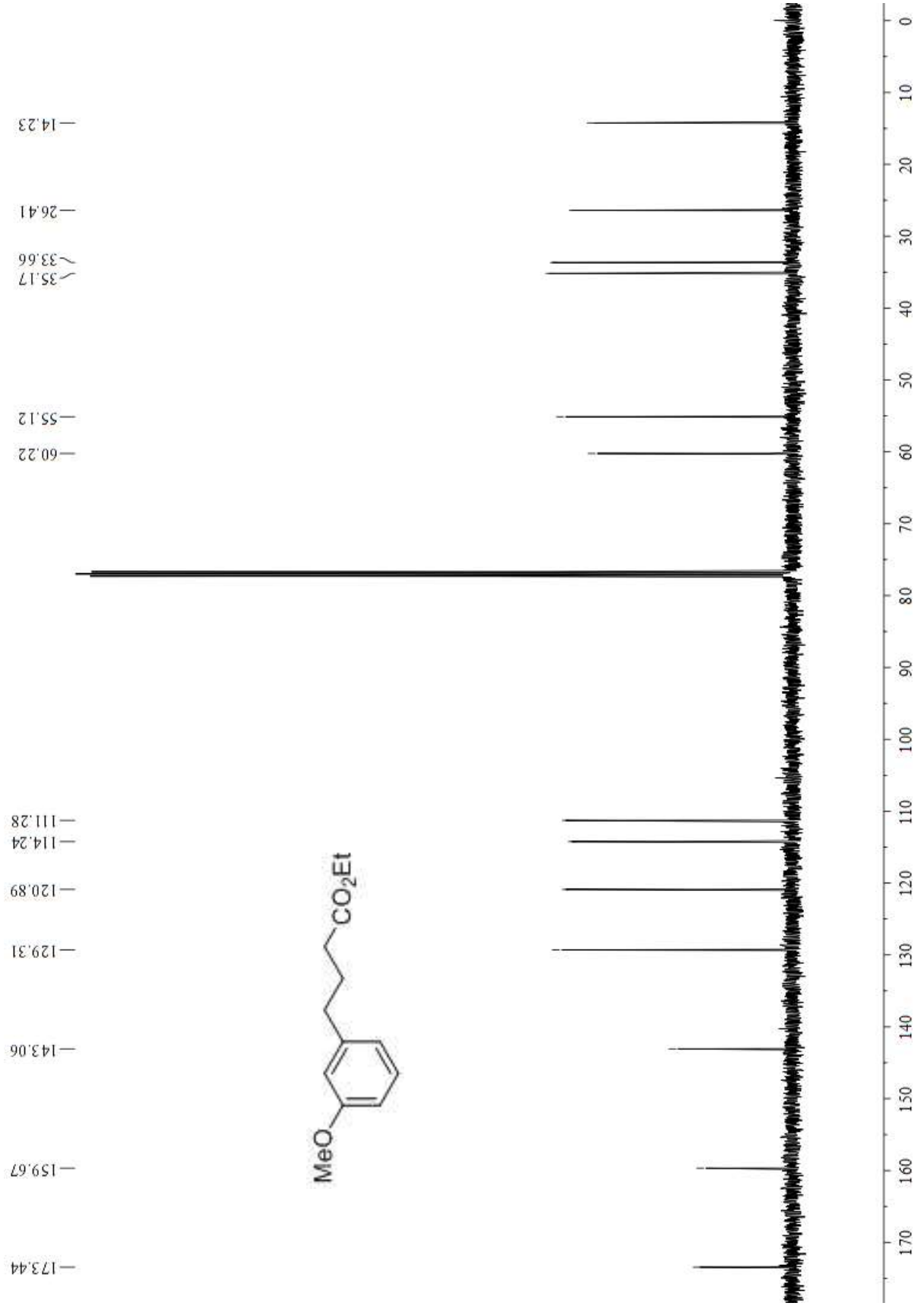
Ethyl 4-(4-methoxyphenyl)butanoate (5j) – ^{13}C NMR



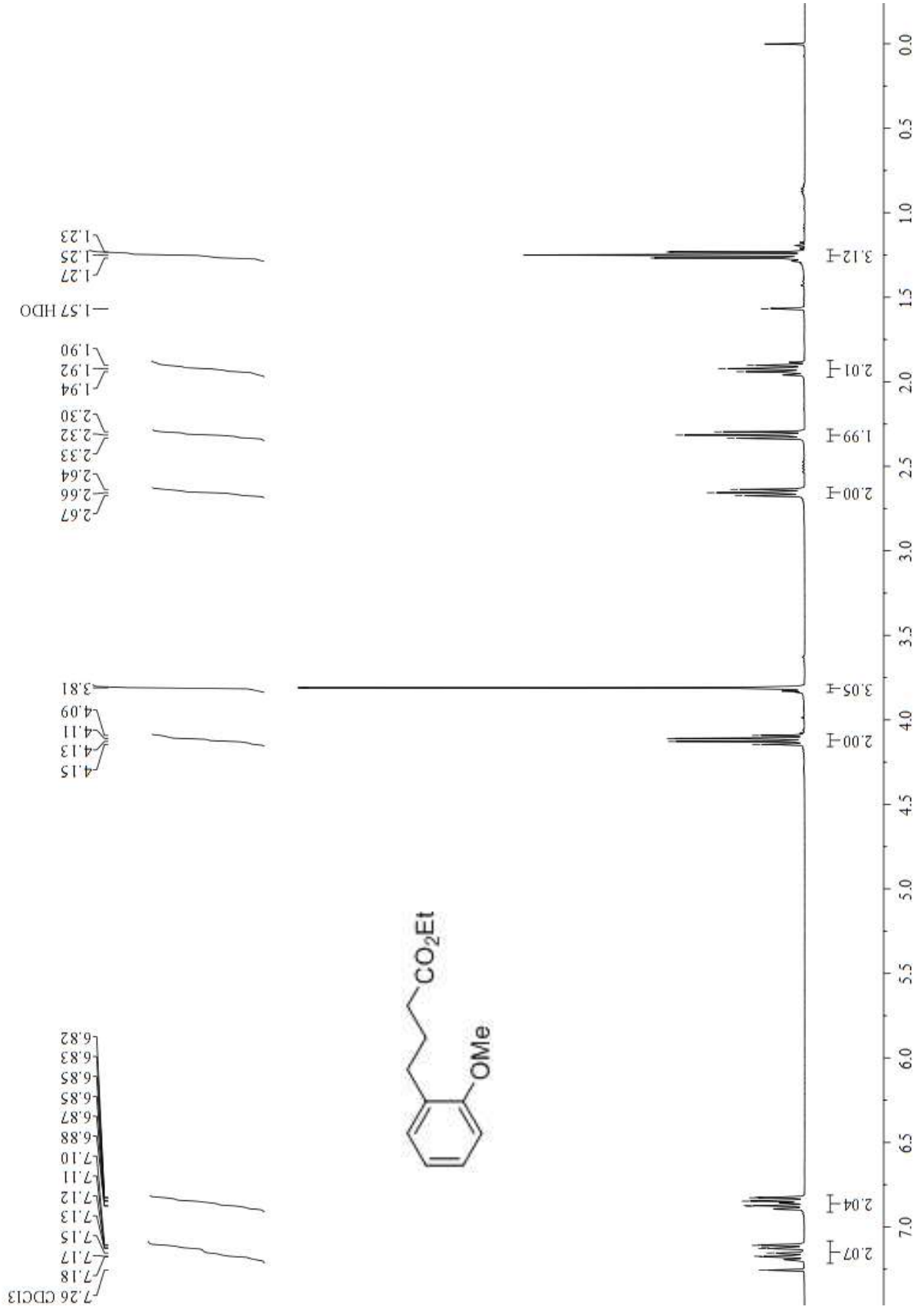
Ethyl 4-(3-methoxyphenyl)butanoate (5k) – ^{1}H NMR



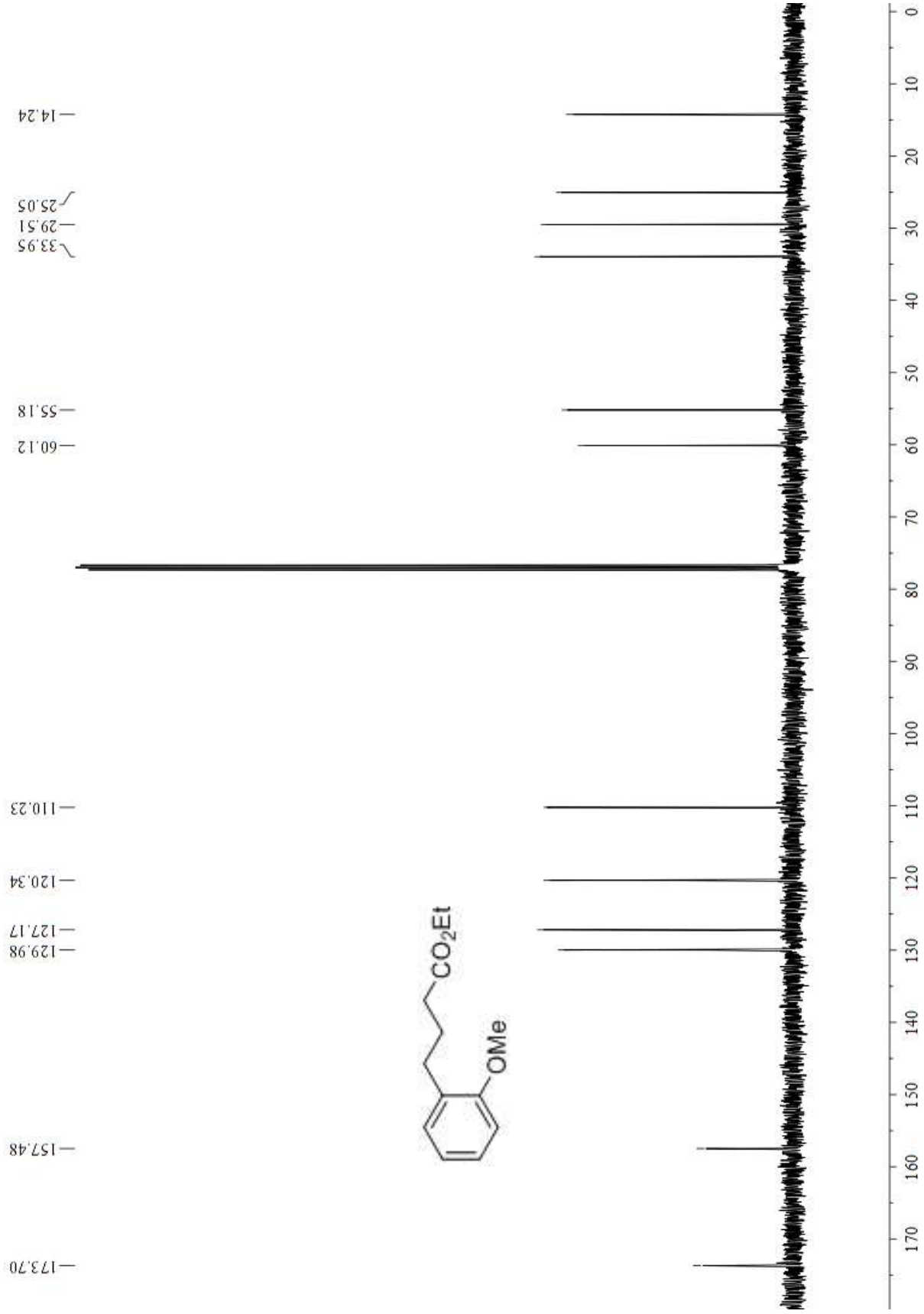
Ethyl 4-(3-methoxyphenyl)butanoate (5k) – ^{13}C NMR



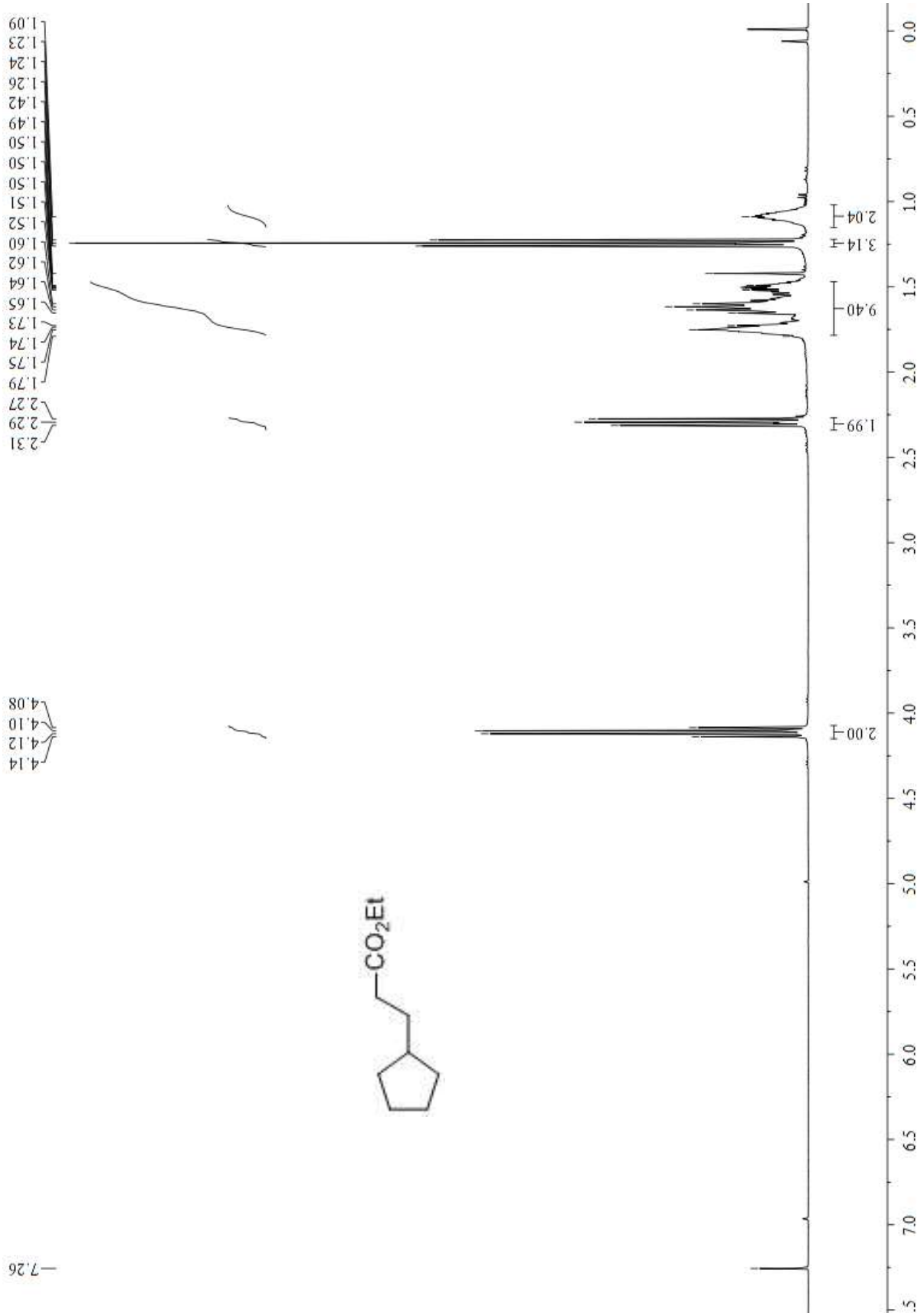
Ethyl 4-(2-methoxyphenyl)butanoate (5l) – ^{1}H NMR



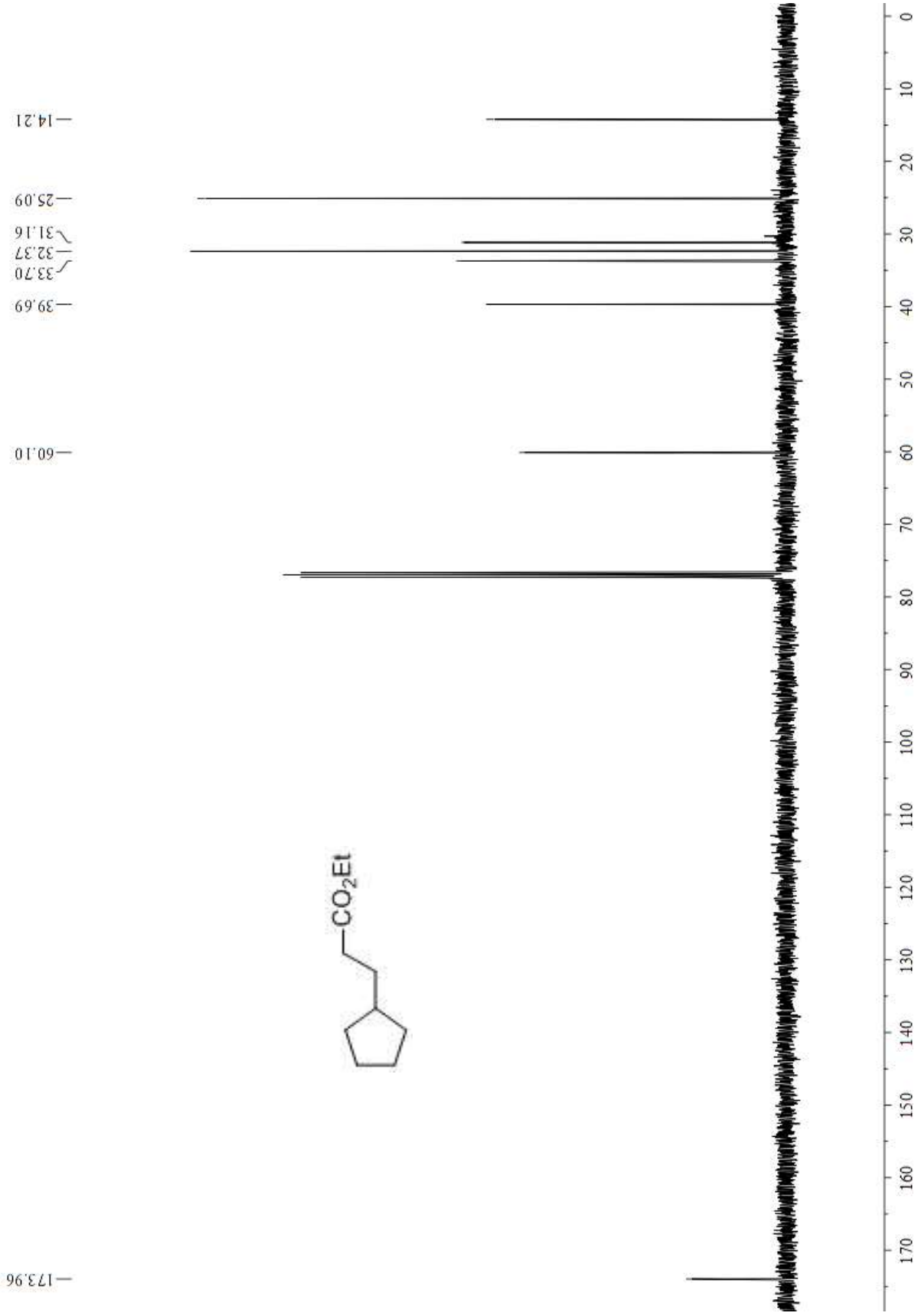
Ethyl 4-(2-methoxyphenyl)butanoate (5l) – ^{13}C NMR



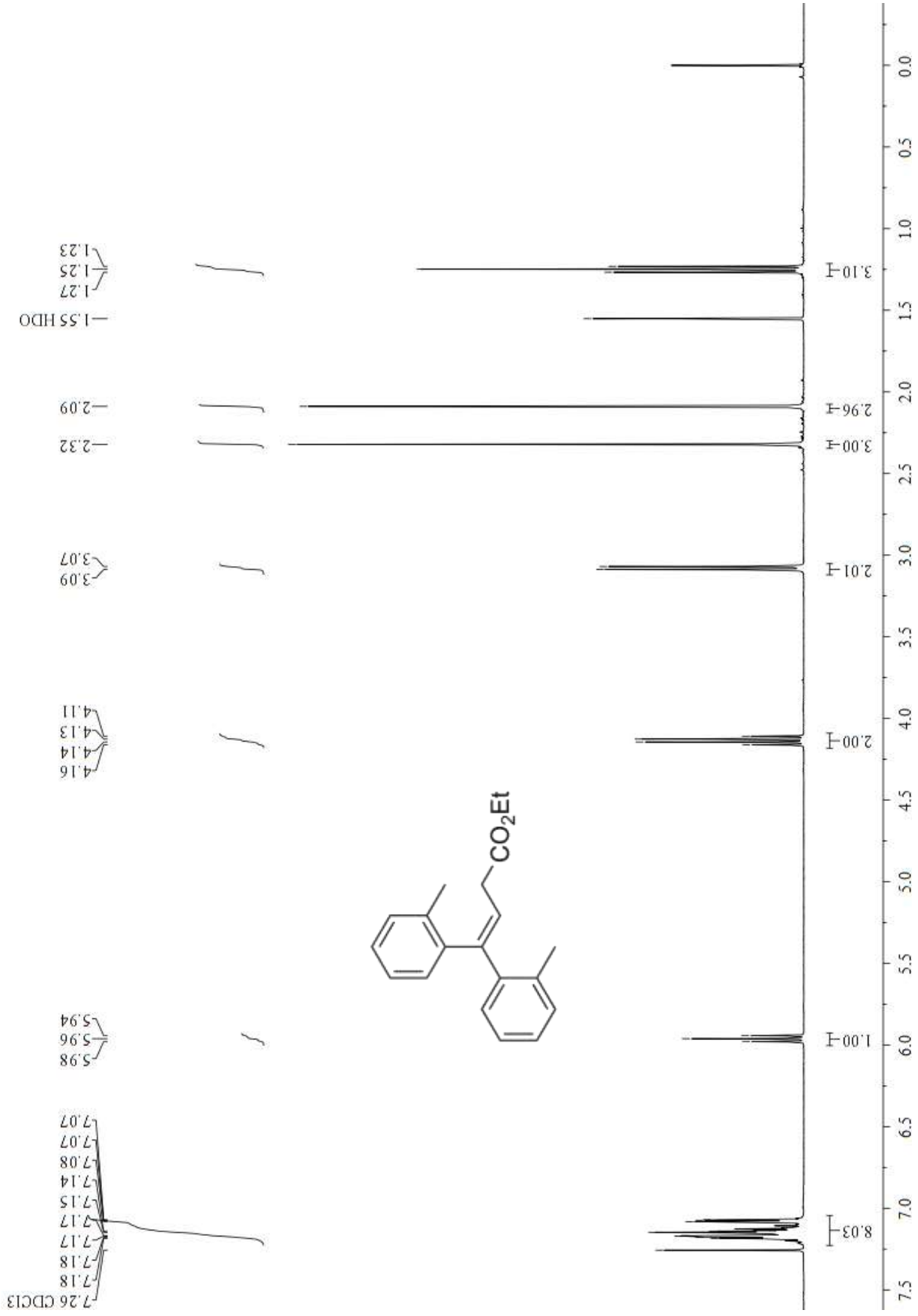
Ethyl 3-(cyclopentyl)propionate (5n) – ^{1}H NMR



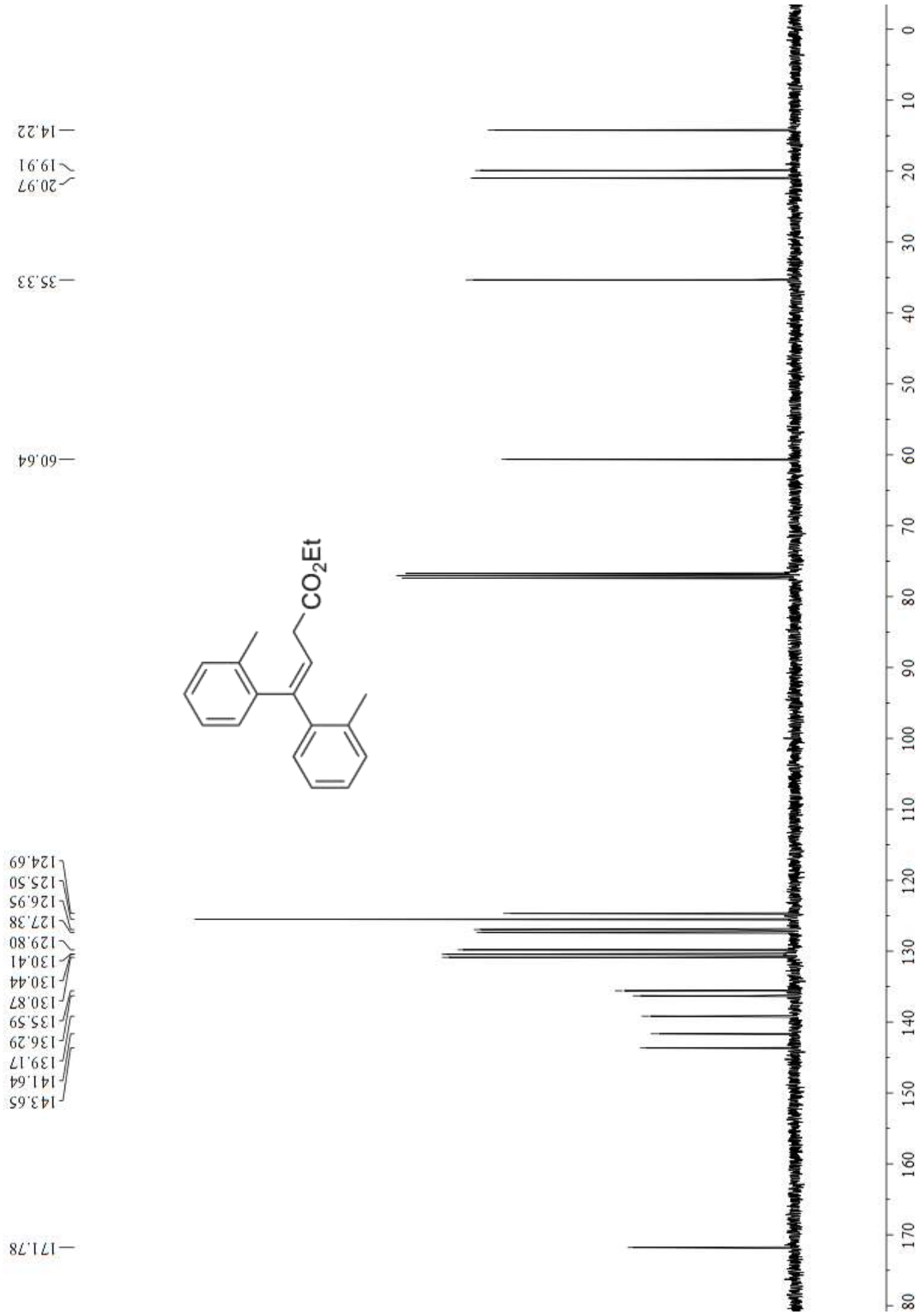
Ethyl 3-(cyclopentyl)propionate (5n) – ^{13}C NMR



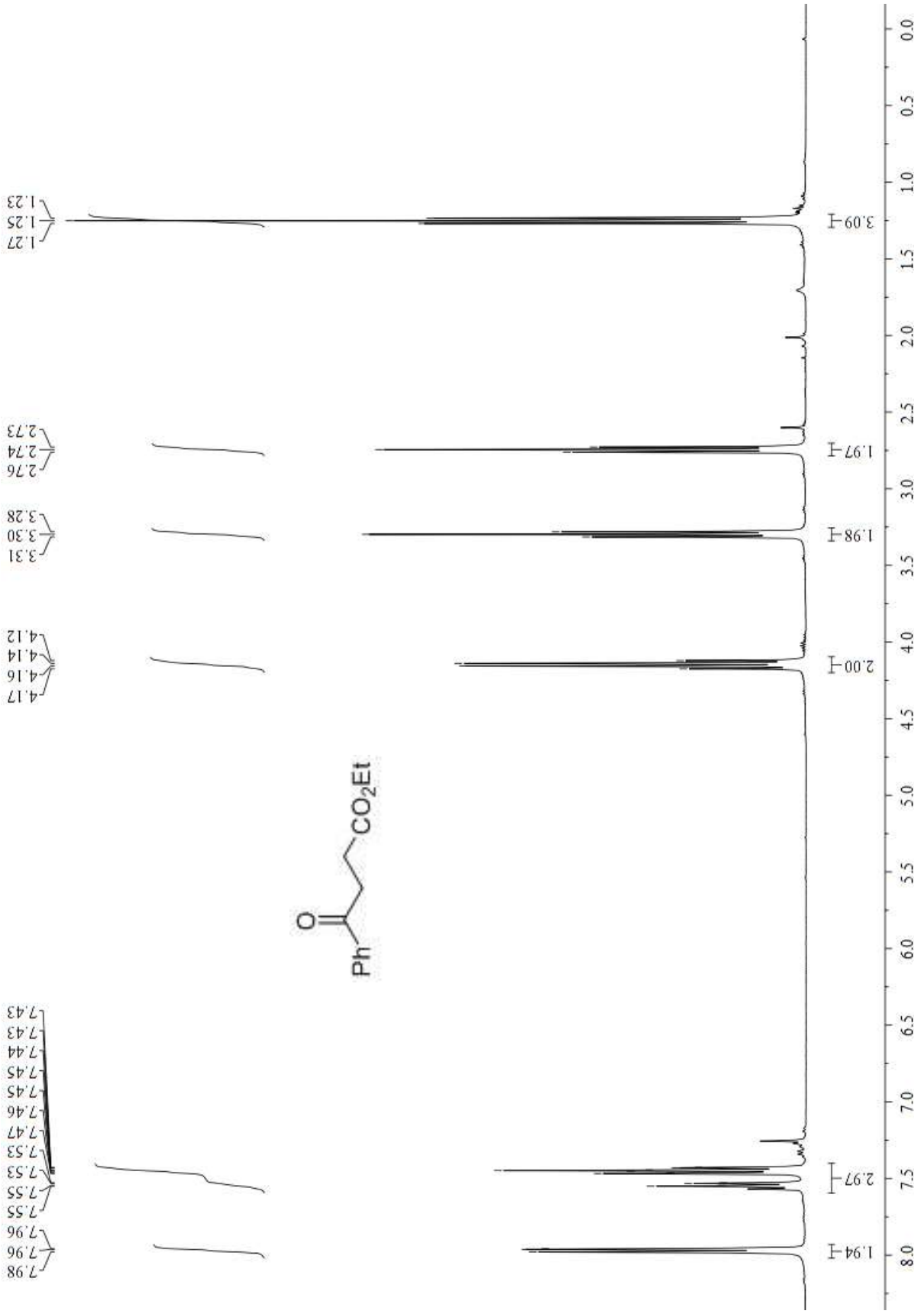
Ethyl 4,4-di(2-methylphenyl)but-3-enoate (5o) – ^{1}H NMR



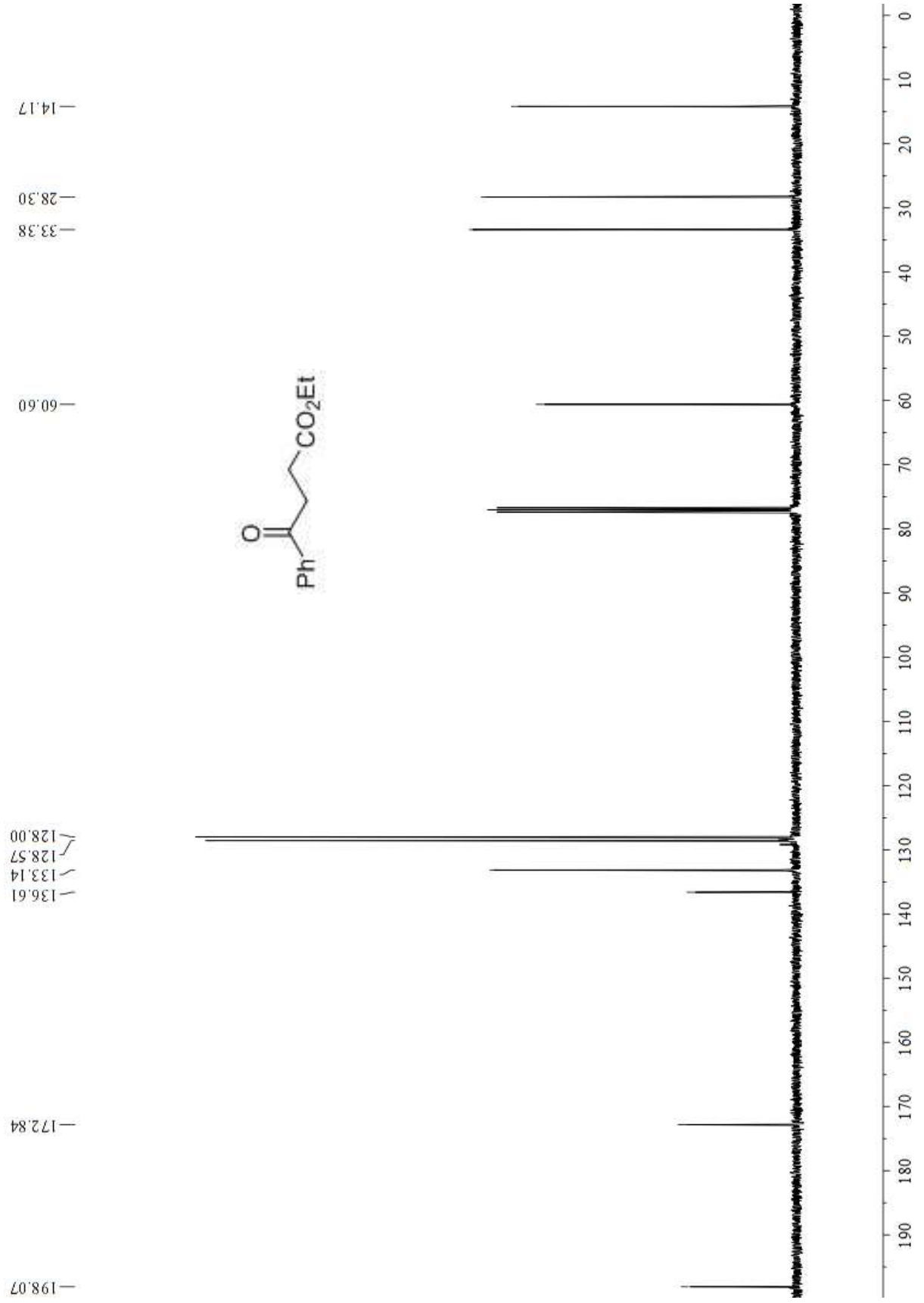
Ethyl 4,4-di(2-methylphenyl)but-3-enoate (5o) – ^{13}C NMR



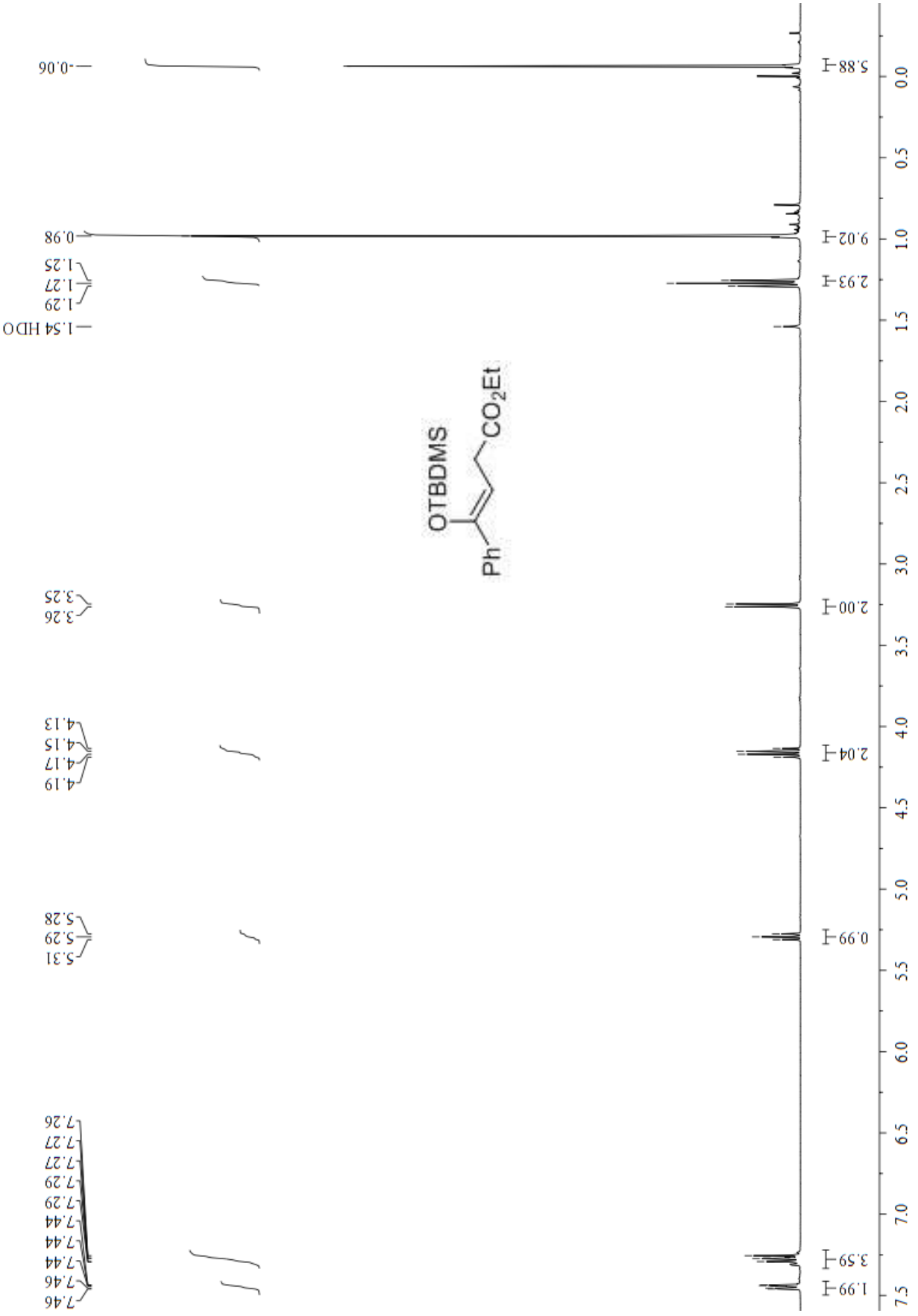
Ethyl 4-oxo-4-phenylbutanoate (10) – ^{1}H NMR



Ethyl 4-oxo-4-phenylbutanoate (10) – ^{13}C NMR

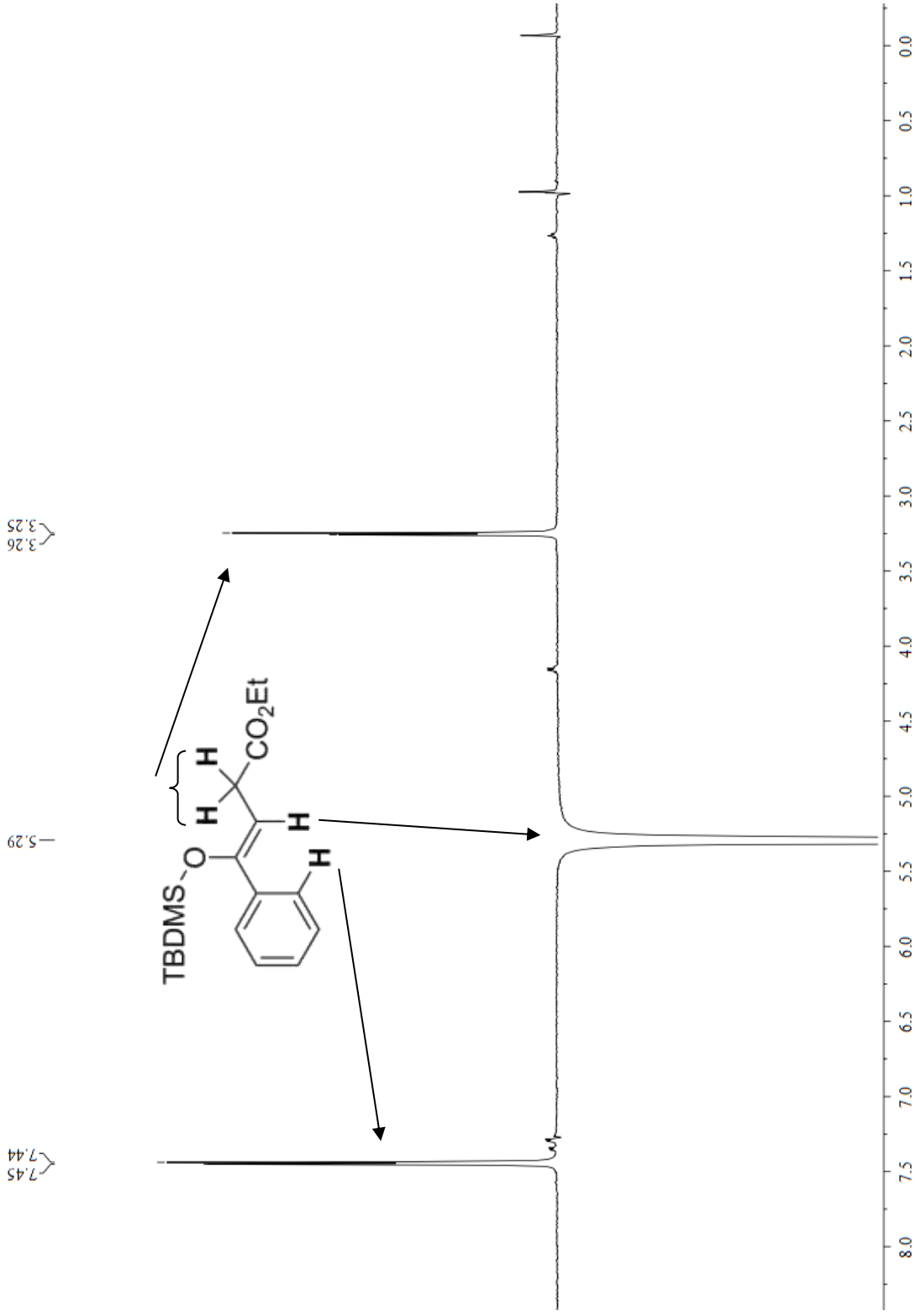


Ethyl 4-phenyl-4-(tert-butyldimethylsiloxyl)but-3-enoate (12) – ^{1}H NMR

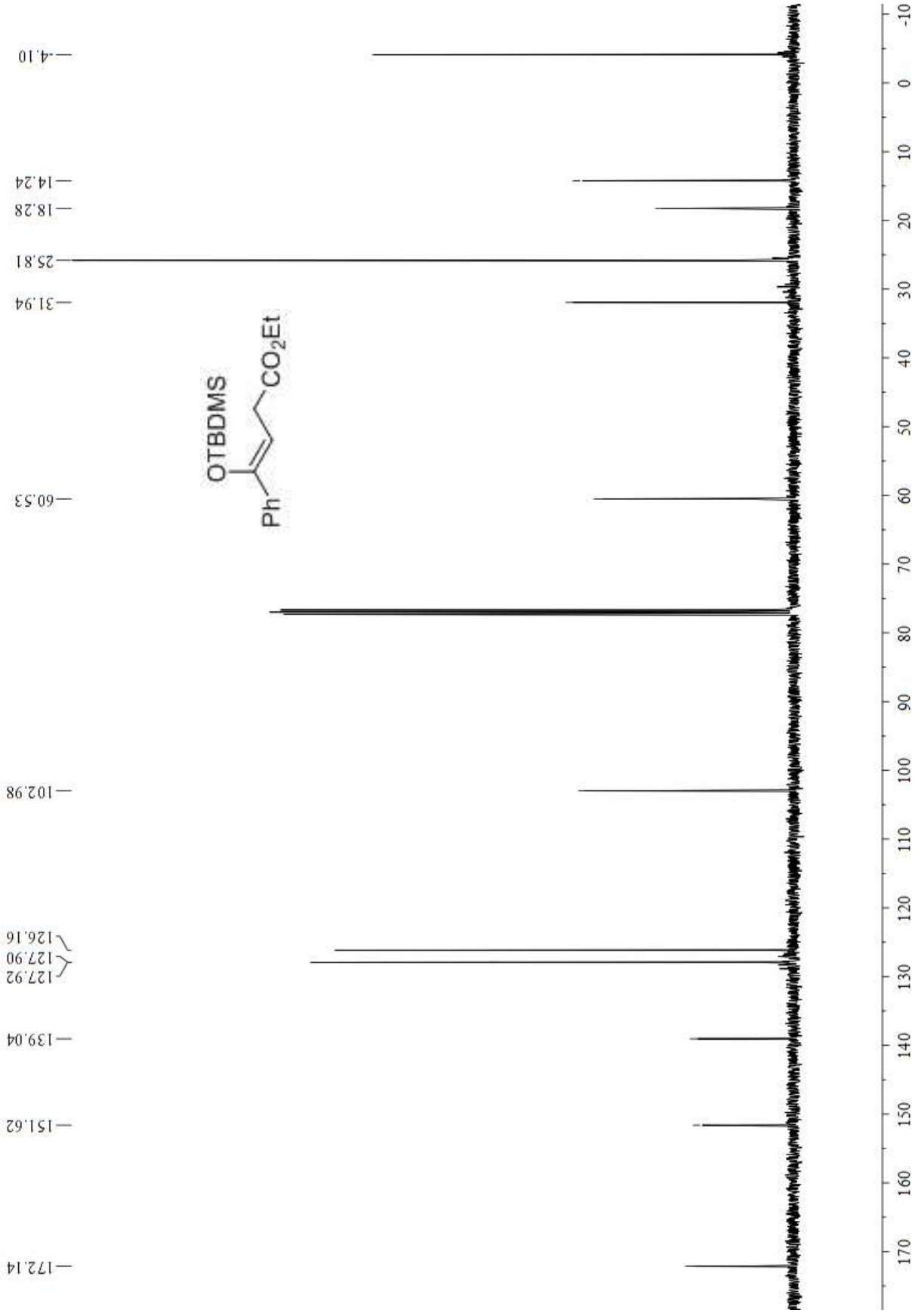


Ethyl 4-phenyl-4-(tert-butyldimethylsiloxyl)but-3-enoate (12) – 1D NOESY

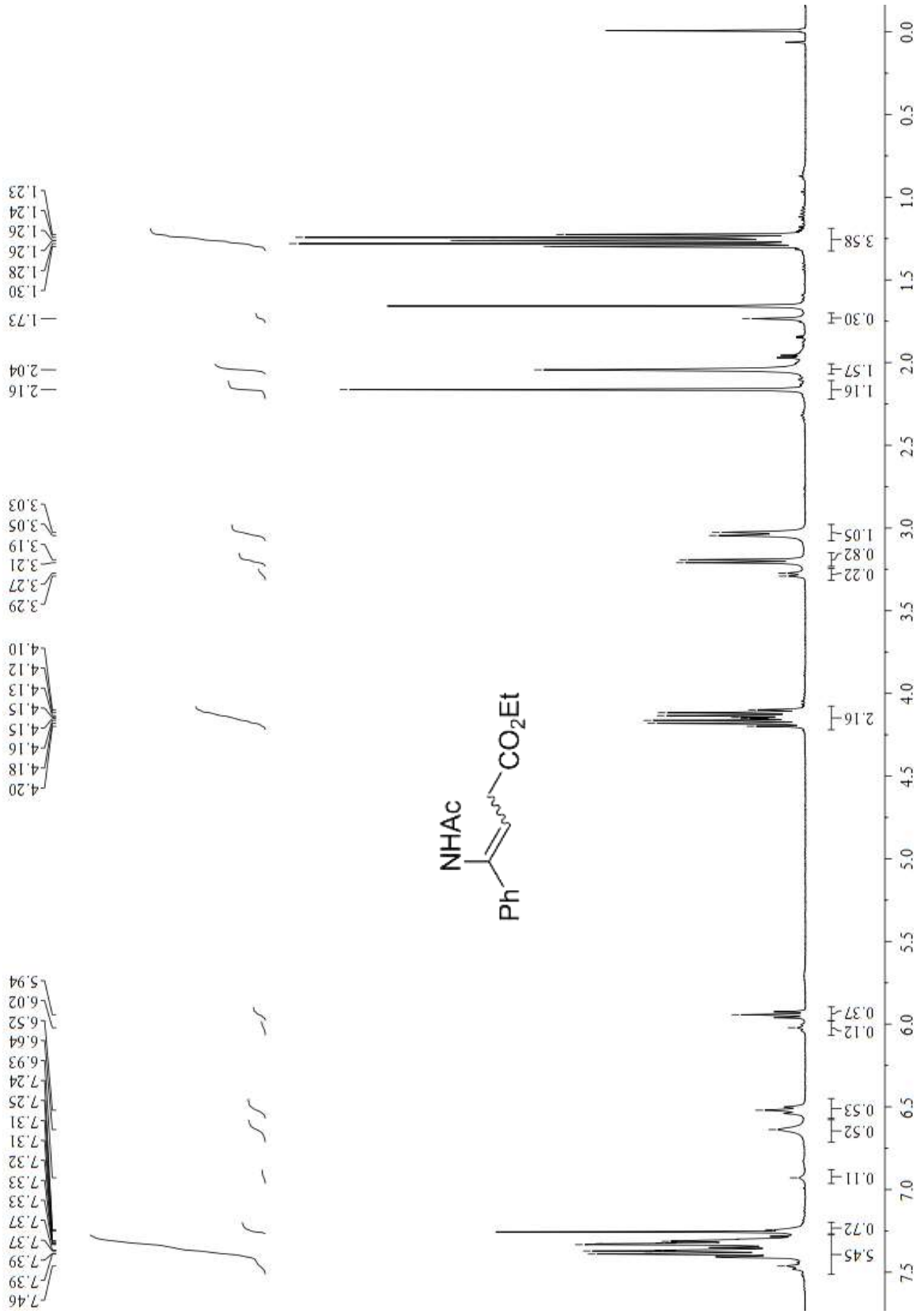
Upon irradiation of the vinyl proton, the interaction with aromatic proton in *-orto* position was observed, thus proving the *Z* configuration of the compound.



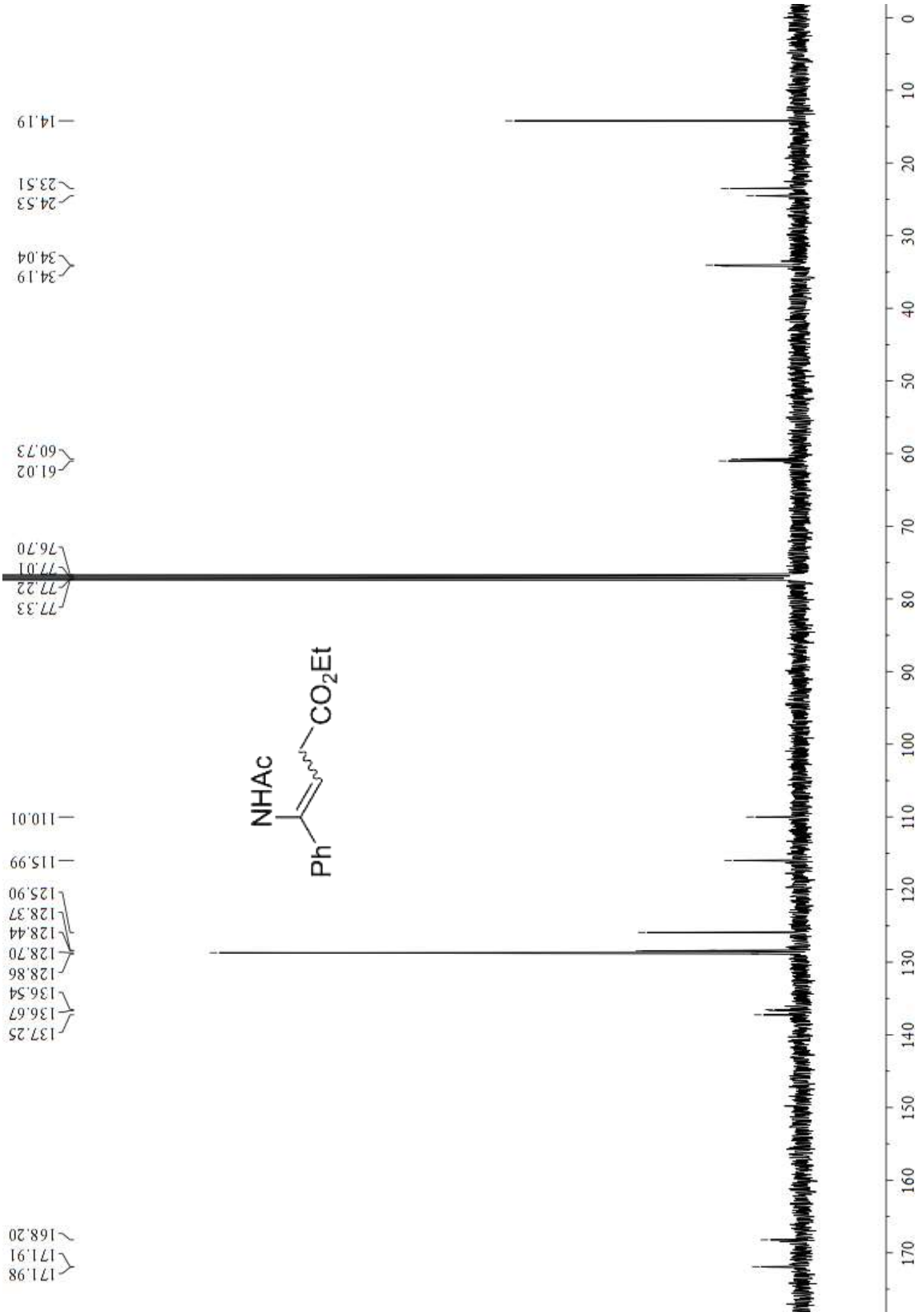
Ethyl 4-phenyl-4-(tert-butyldimethylsiloxyl)but-3-enoate (12) – ^{13}C NMR



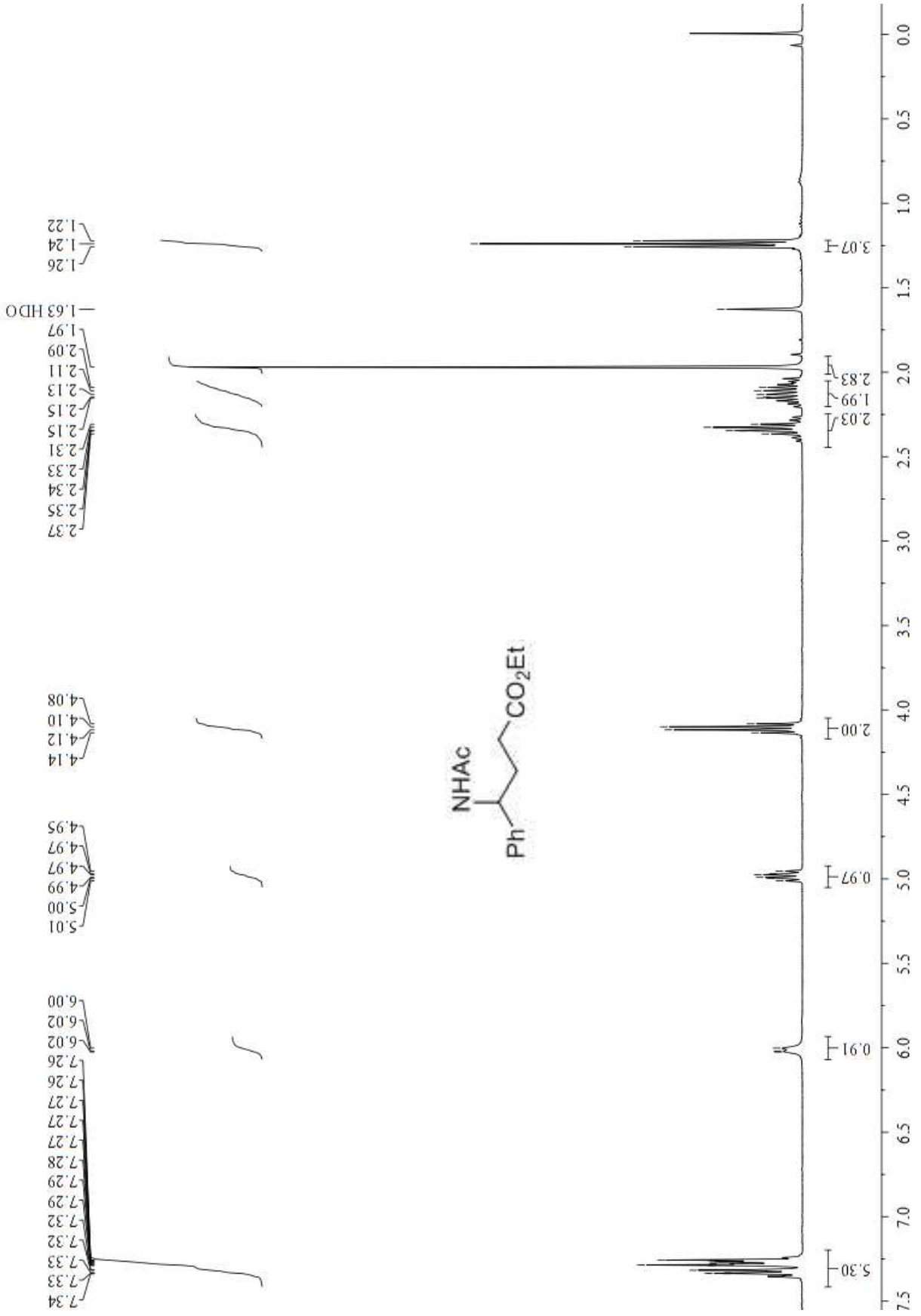
E- and *Z*- Ethyl 4-phenyl-4-(*N*-acetylamine)but-3-enoate (14a) – ^{1}H NMR



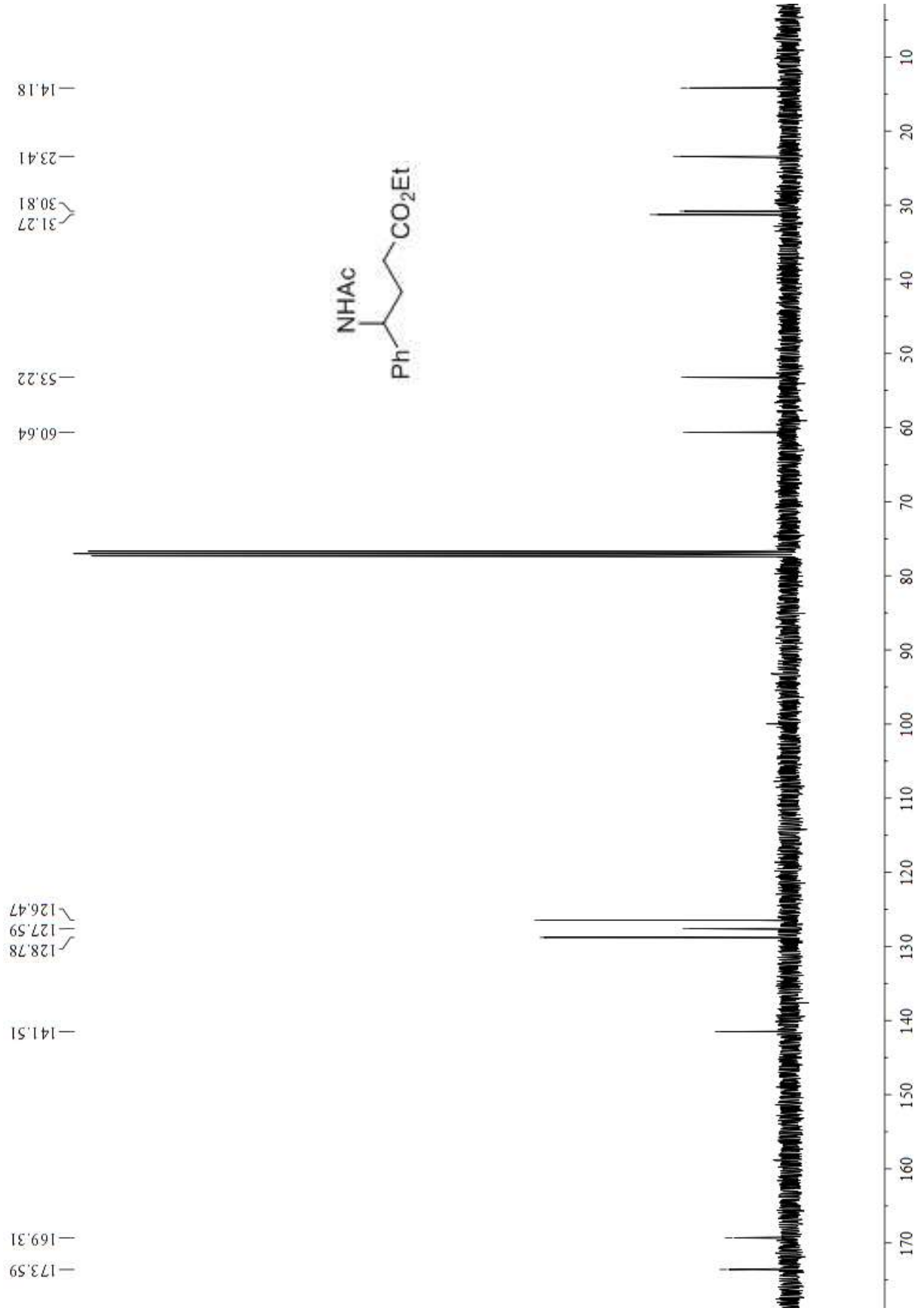
E- and *Z*- Ethyl 4-phenyl-4-(*N*-acetylamine)but-3-enoate (14a) – ^{13}C NMR



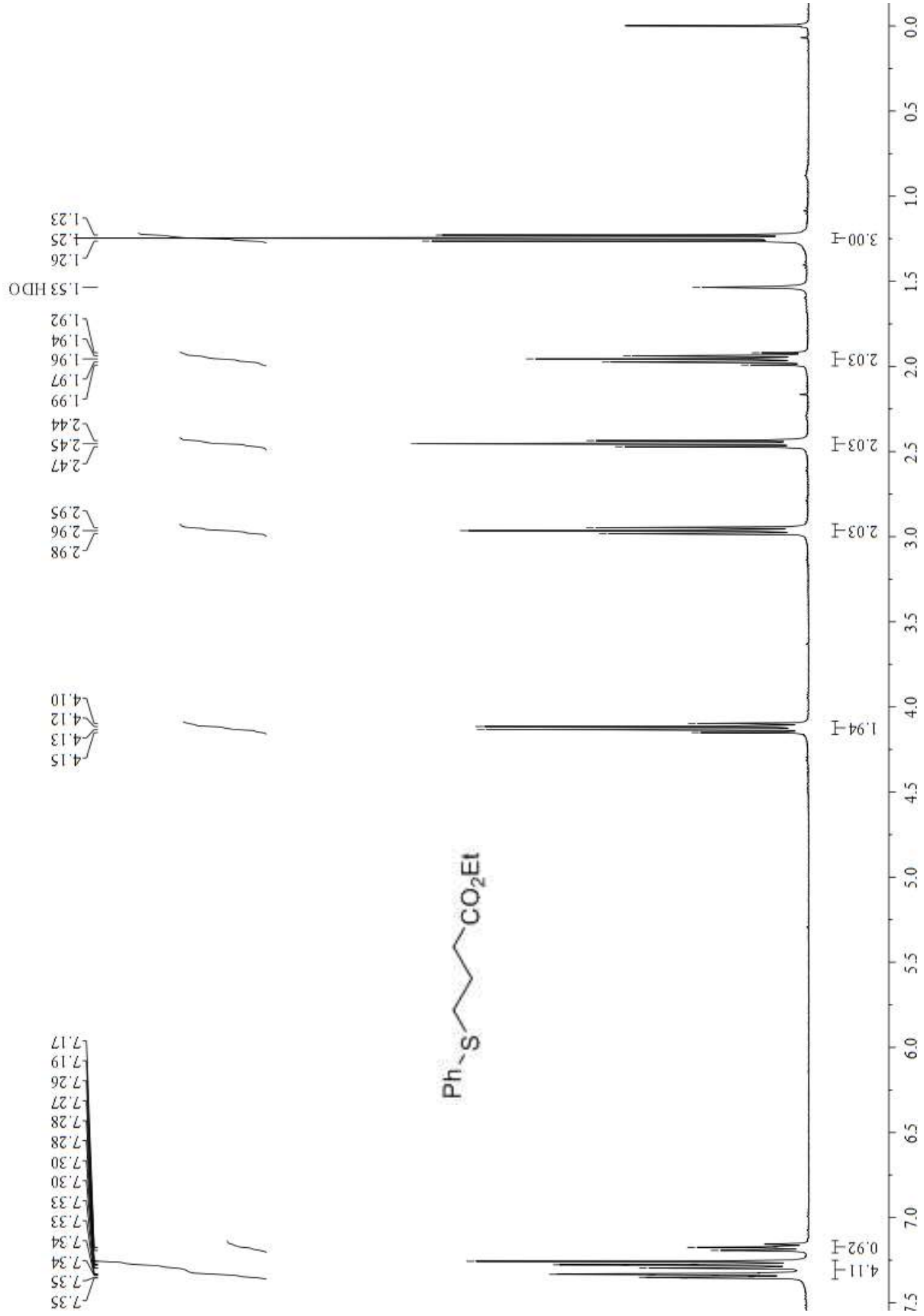
Ethyl 4-phenyl-4-(*N*-acetylamine)butanoate (14b) – ^{1}H NMR



Ethyl 4-phenyl-4-(*N*-acetylamine)butanoate (14b) – ^{13}C NMR



Ethyl 4-(phenylthio)butanoate (16) – ^{1}H NMR



Ethyl 4-(phenylthio)butanoate (16) – ^{13}C NMR