

Ruthenium-catalysed oxidative coupling of vinyl derivatives and application in tandem hydrogenation

Naba Abuhafez,[§] Hervé Ruffin,[§] Raghu Kamaraj, Christian Bruneau and Rafael Gramage-Doria*

e-mail: rafael.gramage-doria@univ-rennes1.fr

Univ Rennes, CNRS, ISCR-UMR 6226, F-35000 Rennes, France

[§]These authors contributed equally to this work.

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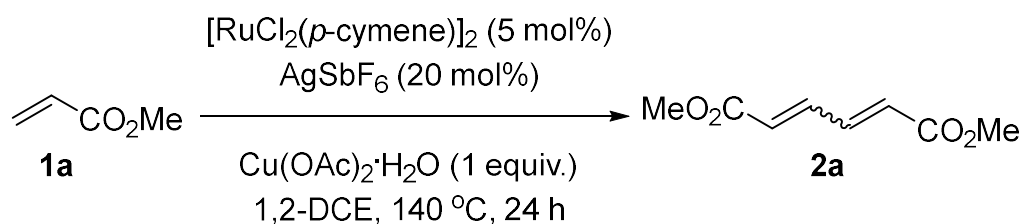
1. General methods.

Solvents were purified with an MB SPS-800 purification system or dried with CaH₂ and distilled prior to use. CDCl₃ was filtered through alumina and stored under argon over molecular sieves. All chemicals were purchased from commercial sources and used as received. Unless otherwise specified, reactions were carried out under argon atmosphere by employing standard Schlenk and vacuum-line techniques. ¹H and ¹³C NMR spectra were recorded with a Bruker GPX (400 MHz) spectrometer. ¹H NMR spectra were referenced to residual protiated solvent (δ = 7.26 ppm for CDCl₃). ¹³C NMR spectra were referenced to CDCl₃ (δ = 77.00 ppm). Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; q, quadruplet; p, pentuplet; hept, heptuplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; tdd, doublet of doublet of triplets. Coupling constants, *J*, were reported in hertz unit (Hz). The reactions were monitored by using a Shimadzu 2014 gas chromatograph equipped with an EquityTM-1 Fused Silica capillary column (30 m x 0.25 mm x 0.25 μ m) and an FID detector; conversion and selectivity were determined by using dodecane as internal standard. Ethyl (*Z*)-but-2-enoate was synthesized according to a literature procedure.^[1]

2. Catalytic experiments.

General procedure: In a dry Schlenk tube under argon atmosphere, the vinyl derivative **1** (1 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (0.05 mmol, 31 mg), AgSbF_6 (0.2 mmol, 69 mg), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (1 mmol, 200 mg) and dry 1,2-dichloroethane (3 mL) were added and the reaction mixture was placed in a preheated oil bath at 140 °C and stirred for 24 h. Then, the reaction mixture was cooled down to room temperature and further diluted with ethyl acetate 10 mL prior filtration over a pad of celite. NEt_3 (5 mL) were added to the solution and then evaporated to dryness. The crude residue was purified by column chromatography with a mixture of heptane and ethyl acetate as the eluent affording the corresponding product **2**.

Reaction optimization:



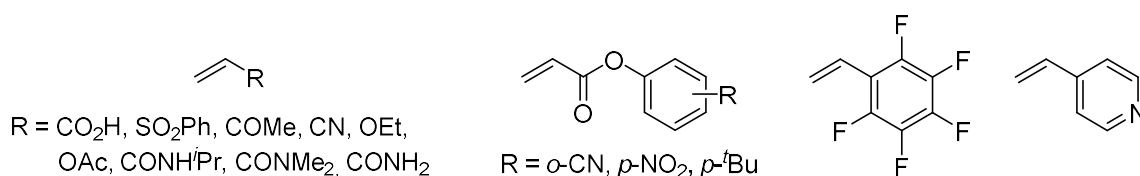
Entry	Deviation from standard conditions	Conversion ^a	Yield (%) ^b
1	None	>99	96 (90:10)
2	w/o $[\text{RuCl}_2(p\text{-cymene})]_2$	0	-
3	w/o AgSbF_6	<5	-
4	w/o $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	0	-
5	60 °C instead of 140 °C	<5	-
6	80 °C instead of 140 °C	28	n.d.
7	100 °C instead of 140 °C	67	55 (85:15)
8	120 °C instead of 140 °C	79	68 (84:16)
9	1,4-dioxane instead of 1,2-DCE	50	27
10	toluene instead of 1,2-DCE	0	-
11	DEC instead of 1,2-DCE	85	n.d.
12	diethyl ether instead of 1,2-DCE	65	n.d.
13	DMF instead of 1,2-DCE	0	-
14	EtOH instead of 1,2-DCE	0	-
15	water instead of 1,2-DCE	0	-
16	acetone instead of 1,2-DCE	0	-
17	acetic acid instead of 1,2-DCE	<5	-
18	w/o solvent	0	-
19	air instead of argon	<5	-
20	with $[\text{RuCl}_3 \cdot \text{H}_2\text{O}]$ (10 mol%)	0	-
21	with $[\text{Ru}(\text{NC}^t\text{Bu})_6(\text{BF}_4)_2]$ (10 mol%)	0	-
22	with $[\text{Ru}(\text{MesCO}_2)_2(p\text{-cymene})]$ (10 mol%)	>99	96 (90:10)
23	with $[\text{RuCl}_2(p\text{-cymene})]_2$ (2.5 mol%)	47	n.d.
24	5 hours instead of 24 hours	35	26 (82:18)
25	10 hours instead of 24 hours	40	35 (84:16)

^aConversion estimated by GC, TLC and ¹H NMR.

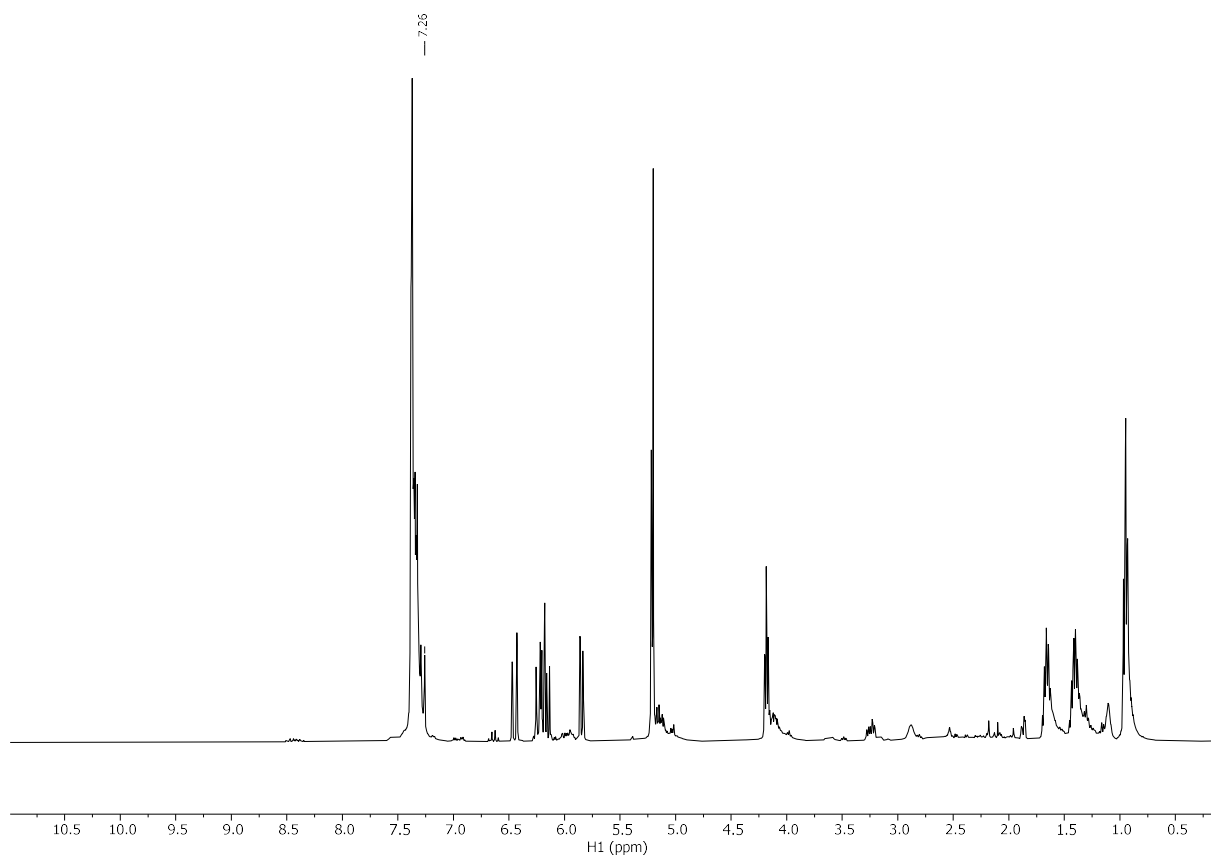
^bIsolated yield after purification by column chromatography, ratio of *E,E*:*Z,E* isomers displayed in brackets.

n.d. = not determined.

Reluctant substrates:

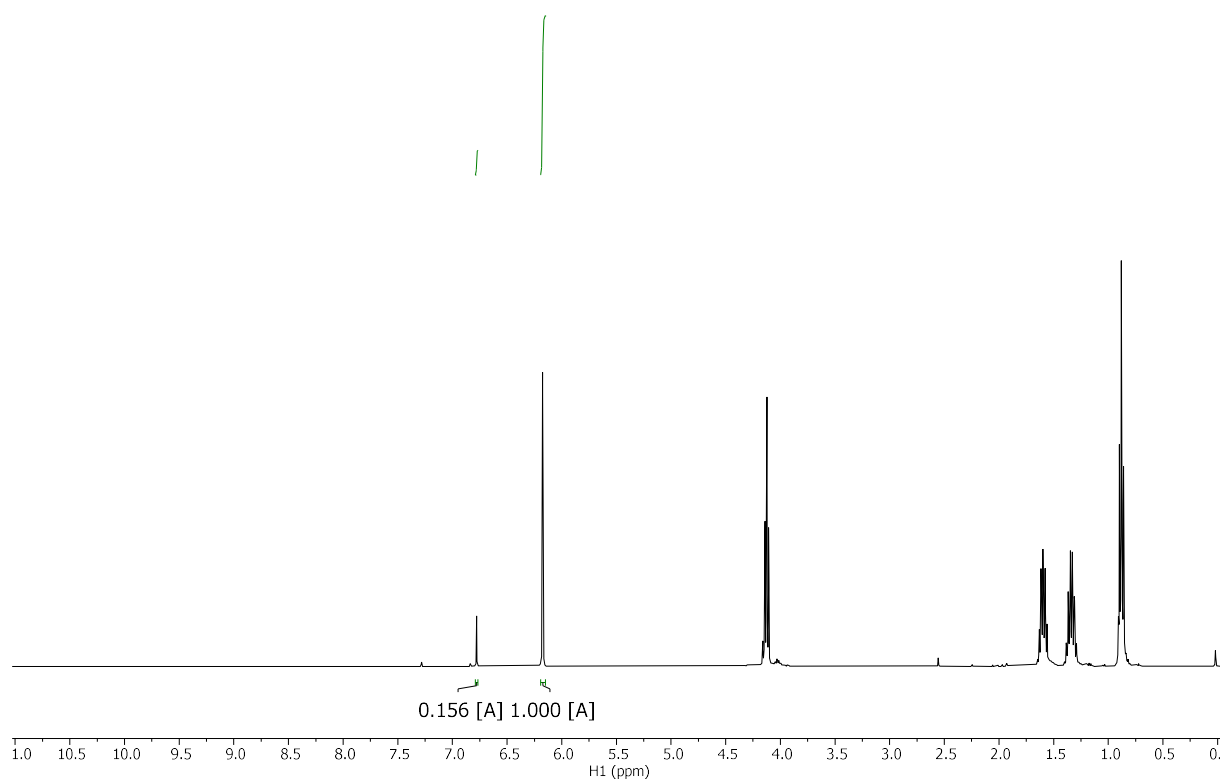


Cross-coupling studies between butyl acrylate and benzyl acrylate: In a dry Schlenk tube under argon atmosphere, butyl acrylate (71 μ L, 64 mg, 0.5 mmol), benzyl acrylate (73 μ L, 81 mg, 0.5 mmol), [RuCl₂(*p*-cymene)]₂ (0.05 mmol, 31 mg), AgSbF₆ (0.2 mmol, 69 mg), Cu(OAc)₂·H₂O (1 mmol, 200 mg) and dry 1,2-dichloroethane (3 mL) were added and the reaction mixture was placed in a preheated oil bath at 140 °C and stirred for 24 h. Then, the reaction mixture was cooled down to room temperature and further diluted with ethyl acetate 10 mL prior filtration over a pad of celite. NEt₃ (5 mL) were added to the solution and then evaporated to dryness. The crude residue was purified by column chromatography with a mixture of heptane and ethyl acetate as the eluent affording a mixture of products **2** in a combined 68% yield with a ratio of **2c** : **2k** : cross-coupled product of 8 : 31 : 29 (see also **Scheme 3B** in the main text). We were unable to isolate pure samples of each product due to the similar polarity (see NMR below):



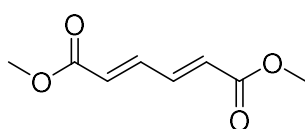
Cross-coupling studies between butyl acrylate and styrene: In a dry Schlenk tube under argon atmosphere, butyl acrylate (71 μ L, 64 mg, 0.5 mmol), styrene (57 μ L, 52 mg, 0.5 mmol), [RuCl₂(*p*-cymene)]₂ (0.05 mmol, 31 mg), AgSbF₆ (0.2 mmol, 69 mg), Cu(OAc)₂·H₂O (1 mmol, 200 mg) and dry 1,2-dichloroethane (3 mL) were added and the reaction mixture was placed in a preheated oil bath at 140 °C and stirred for 24 h. Then, the reaction mixture was cooled down to room temperature and further diluted with ethyl acetate 10 mL prior filtration over a pad of celite. NEt₃ (5 mL) were added to the solution and then evaporated to dryness. The crude residue was purified by column chromatography with a mixture of heptane and ethyl acetate as the eluent affording exclusively the product derived from homo-coupling of butyl acrylate (**2c**).

Mechanistic investigations: In a dry Schlenk tube under argon atmosphere, dibutyl maleate (228 mg, 1 mmol), [RuCl₂(*p*-cymene)]₂ (0.05 mmol, 31 mg), AgSbF₆ (0.2 mmol, 69 mg), Cu(OAc)₂·H₂O (1 mmol, 200 mg) and dry 1,2-dichloroethane (3 mL) were added and the reaction mixture was placed in a preheated oil bath at 140 °C and stirred for 24 h. Then, the reaction mixture was cooled down to room temperature and further diluted with ethyl acetate 10 mL prior filtration over a pad of celite. NEt₃ (5 mL) were added to the solution and then evaporated to dryness. The crude residue was analysed by ¹H NMR spectroscopy showing a 87:13 ratio of dibutyl maleate : fumarate species (see below). Note: the reaction performed in the absence of [RuCl₂(*p*-cymene)]₂ led to no isomerization.

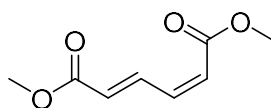


General procedure for the tandem ruthenium-catalyzed oxidative coupling/hydrogenation: In a dry Schlenk tube under argon atmosphere, the vinyl derivative **2** (1 mmol), [RuCl₂(*p*-cymene)]₂ (0.05 mmol, 31 mg), AgSbF₆ (0.2 mmol, 69 mg), Cu(OAc)₂·H₂O (1 mmol, 200 mg) and dry 1,2-dichloroethane (3 mL) were added and the reaction mixture was placed in a preheated oil bath at 140 °C and stirred for 24 h. Then, the reaction mixture was cooled down to room temperature and further diluted with ethyl acetate 10 mL prior filtration over a pad of celite. The remaining solution was placed in a dry Schlenk tube capped with a balloon filled with H₂ (1 bar) and the reaction mixture was stirred at 75 °C for 18 h. Back at to room temperature, the pressure was slowly released and the solvents were evaporated under vacuum. The crude reaction mixture was purified by column chromatography with a mixture of heptane and ethyl acetate (90:10) to afford the corresponding product **3**.

3. Characterization of products.



dimethyl (2*E*,4*E*)-hexa-2,4-dienedioate (**2a**)

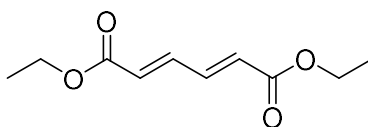


dimethyl (2*Z*,4*E*)-hexa-2,4-dienedioate (**2a**)

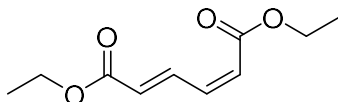
2a (163 mg, 0.96 mmol, 96% yield) was obtained as an inseparable mixture of *E,E* and *Z,E* isomers in a 90:10 ratio according to ¹H NMR spectroscopy. The analytical data is in agreement with previous reports.^[2]

¹H NMR (400 MHz, CDCl₃): δ = 8.46 (1H, dd, *J* = 15.0, 10.0, *Z,E*, minor), 7.35-7.27 (2H, m, *E,E*, major), 6.70 (1H, dd, *J* = 10.0, 10.0, *Z,E*, minor), 6.23-6.18 (2H, m, *E,E*, major), 6.17 (1H, d, *J* = 15.0, *Z,E*, minor), 6.01 (1H, d, *J* = 10.0, *Z,E*, minor), 3.82 (6H, s, *Z,E*, minor), 3.78 (6H, s, *E,E*, major) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 166.4 (*Z,E*, minor), 166.2 (*E,E*, major), 165.6 (*Z,E*, minor), 140.9 (*E,E*, major), 140.6 (*Z,E*, minor), 138.6 (*Z,E*, minor), 128.6 (*Z,E*, minor), 128.0 (*E,E*, major), 124.2 (*Z,E*, minor), 51.9 (*E,E*, major), 51.8 (*Z,E*, minor), 51.6 (*Z,E*, minor) ppm.



diethyl (2*E*,4*E*)-hexa-2,4-dienedioate (**2b**)

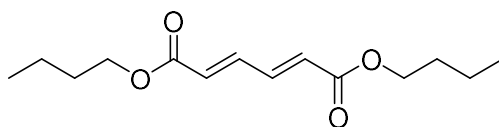


diethyl (2*Z*,4*E*)-hexa-2,4-dienedioate (**2b**)

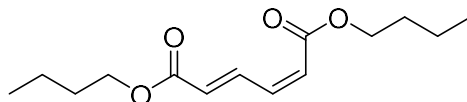
2b (143 mg, 0.72 mmol, 72% yield) was obtained as an inseparable mixture of *E,E* and *Z,E* isomers in a 85:15 ratio according to ^1H NMR spectroscopy. The analytical data is in agreement with previous reports.^[3]

^1H NMR (400 MHz, CDCl_3): δ = 8.40 (1H, dd, J = 15.6, 10.5, *Z,E*, minor), 7.32 (2H, dd, J = 11.5, 3.2, *E,E*, major), 6.64 (1H, t, J = 11.5, *Z,E*, minor), 6.20 (2H, dd, J = 11.5, 3.2, *E,E*, major), 6.10 (2H, dd, J = 11.5, 3.2, *E,E*, major), 5.95 (1H, d, J = 11.5, *Z,E*, minor), 4.27-4.22 (4H, q, J = 7.1, *E,E*, major + *Z,E*, minor), 1.33 (6H, t, J = 7.1, *E,E*, major + *Z,E*, minor) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 166.0 (*Z,E*, minor), 165.9 (*E,E*, major), 165.2 (*Z,E*, minor), 140.8 (*E,E*, major), 140.4 (*Z,E*, minor), 138.4 (*Z,E*, minor), 128.9 (*Z,E*, minor), 128.4 (*E,E*, major), 124.6 (*Z,E*, minor), 60.8 (*E,E*, major), 60.7 (*Z,E*, minor), 60.5 (*Z,E*, minor), 14.2 (*E,E*, major + *Z,E*, minor) ppm.



dibutyl (2*E*,4*E*)-hexa-2,4-dienedioate (**2c**)

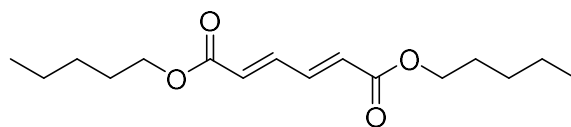


dibutyl (2*Z*,4*E*)-hexa-2,4-dienedioate (**2c**)

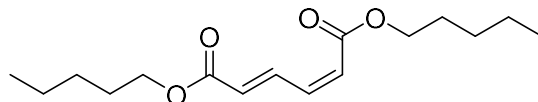
2c (188 mg, 0.74 mmol, 74% yield) was obtained as an inseparable mixture of *E,E* and *Z,E* isomers in a 87:11 ratio according to ^1H NMR spectroscopy. The analytical data is in agreement with previous reports.^[3]

^1H NMR (400 MHz, CDCl_3): δ = 8.39 (1H, dd, J = 15.6, 11.5, *Z,E*, minor), 7.31 (2H, dd, J = 11.5, 3.2, *E,E*, major), 6.64 (1H, t, J = 11.5, *Z,E*, minor), 6.21 (2H, dd, J = 11.5, 3.2, *E,E*, major), 6.11 (1H, d, J = 15.6, *Z,E*, minor), 5.96 (1H, d, J = 11.5, *Z,E*, minor), 4.17 (4H, t, J = 6.7, *E,E*, major + *Z,E*, minor), 1.65 (4H, m, *E,E*, major + *Z,E*, minor), 1.39 (4H, m, *E,E*, major + *Z,E*, minor), 0.93 (6H, t, J = 7.3, *E,E*, major + *Z,E*, minor) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 170.4 (*Z,E*, minor), 167.5 (*Z,E*, minor), 165.9 (*E,E*, major), 140.7 (*E,E*, major), 140.3 (*Z,E*, minor), 138.4 (*Z,E*, minor), 130.7 (*Z,E*, minor), 128.9 (*Z,E*, minor), 128.4 (*E,E*, major), 60.9 (*Z,E*, minor), 64.7 (*E,E*, major), 60.6 (*Z,E*, minor), 30.7 (*Z,E*, minor), 30.6 (*E,E*, major), 30.5 (*Z,E*, minor), 19.2 (*Z,E*, minor), 19.0 (*E,E*, major), 18.9 (*Z,E*, minor), 13.7 (*Z,E*, minor), 13.6 (*E,E*, major), 12.7 (*Z,E*, minor) ppm.



dipentyl (2*E*,4*E*)-hexa-2,4-dienedioate (**2d**)

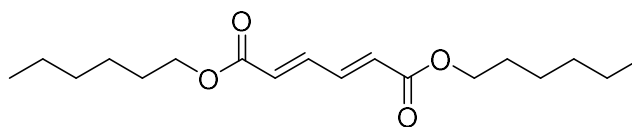


dipentyl (2*Z*,4*E*)-hexa-2,4-dienedioate (**2d**)

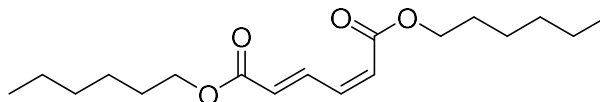
2d (229 mg, 0.81 mmol, 81% yield) was obtained as an inseparable mixture of *E,E* and *Z,E* isomers in a 93:7 ratio according to ¹H NMR spectroscopy. The analytical data is in agreement with previous reports.^[4]

¹H NMR (400 MHz, CDCl₃): δ = 8.38 (1H, dd, *J* = 15.6, 11.6, *Z,E*, minor), 7.31 (2H, dd, *J* = 11.5, 3.0, *E,E*, major), 6.63 (1H, t, *J* = 11.5, *Z,E*, minor), 6.19 (2H, dd, *J* = 11.5, 3.1, *E,E*, major), 6.10 (1H, d, *J* = 15.6, *Z,E*, minor), 5.96 (1H, d, *J* = 11.4, *Z,E*, minor), 4.17 (4H, t, *J* = 6.8, *E,E*, major), 4.38-4.08 (4H, m, *Z,E*, minor), 1.70-1.56 (4H, m, *E,E*, major + *Z,E*, minor), 1.37-1.23 (8H, m, *E,E*, major + *Z,E*, minor), 0.92 (6H, m, *E,E*, major + *Z,E*, minor) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 166.0 (*E,E*, major), 140.8 (*E,E*, major), 128.4 (*E,E*, major), 65.1 (*E,E*, major), 29.7 (*E,E*, major), 28.3 (*E,E*, major), 28.0 (*Z,E*, minor), 22.3 (*E,E*, major), 13.9 (*E,E*, major) ppm.



dihexyl (2*E*,4*E*)-hexa-2,4-dienedioate (**2e**)

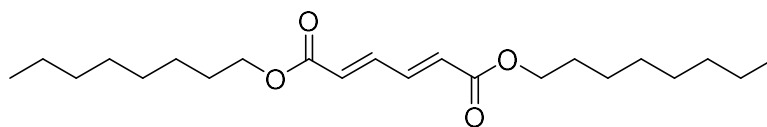


dihexyl (2*Z*,4*E*)-hexa-2,4-dienedioate (**2e**)

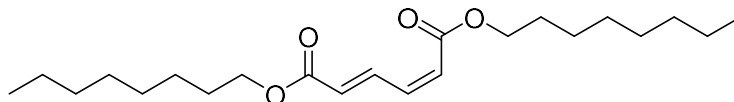
2e (233 mg, 0.75 mmol, 75% yield) was obtained as an inseparable mixture of *E,E* and *Z,E* isomers in a 96:4 ratio according to ^1H NMR spectroscopy. The analytical data is in agreement with previous reports.^[4]

^1H NMR (400 MHz, CDCl_3): δ = 8.37 (1H, dd, J = 15.6, 11.6, *Z,E*, minor), 7.29 (2H, dd, J = 11.5, 3.0, *E,E*, major), 6.61 (1H, t, J = 11.5, *Z,E*, minor), 6.18 (2H, dd, J = 11.5, 3.1, *E,E*, major), 6.08 (1H, d, J = 15.6, *Z,E*, minor), 5.94 (1H, d, J = 11.4, *Z,E*, minor), 4.16 (4H, t, J = 6.8, *E,E*, major), 4.37-4.06 (4H, m, *Z,E*, minor), 1.66 (4H, p, J = 6.8, *E,E*, major + *Z,E*, minor), 1.40-1.24 (12H, m, *E,E*, major + *Z,E*, minor), 0.86 (6H, t, J = 7.4, *E,E*, major + *Z,E*, minor) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 166.1 (*Z,E*, minor), 166.0 (*E,E*, major), 165.4 (*Z,E*, minor), 140.7 (*E,E*, major), 140.4 (*Z,E*, minor), 138.5 (*Z,E*, minor), 129.0 (*Z,E*, minor), 128.4 (*E,E*, major), 124.7 (*Z,E*, minor), 65.1 (*E,E*, major), 64.9 (*Z,E*, minor), 64.8 (*Z,E*, minor), 31.9 (*Z,E*, minor), 31.4 (*E,E*, major), 30.9 (*Z,E*, minor), 29.7 (*Z,E*, minor), 29.3 (*Z,E*, minor), 28.5 (*E,E*, major), 25.6 (*E,E*, major), 22.7 (*Z,E*, minor), 22.5 (*E,E*, major), 14.1 (*Z,E*, minor), 14.0 (*E,E*, major) ppm.



dioctyl (2*E*,4*E*)-hexa-2,4-dienedioate (**2f**)

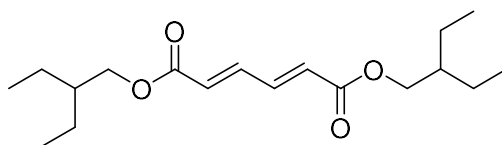


dioctyl (2*Z*,4*E*)-hexa-2,4-dienedioate (**2f**)

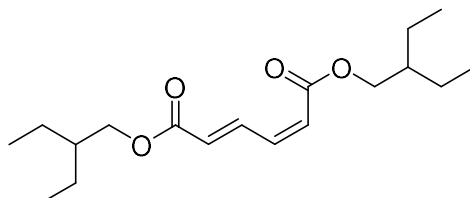
2f (330 mg, 0.90 mmol, 90% yield) was obtained as an inseparable mixture of *E,E* and *Z,E* isomers in a 95:5 ratio according to ^1H NMR spectroscopy. The analytical data is in agreement with previous reports.^[4]

^1H NMR (400 MHz, CDCl_3): δ = 8.38 (1H, dd, J = 15.6, 11.6, *Z,E*, minor), 7.30 (2H, dd, J = 11.5, 3.0, *E,E*, major), 6.63 (1H, t, J = 11.5, *Z,E*, minor), 6.20 (2H, dd, J = 11.5, 3.1, *E,E*, major), 6.10 (1H, d, J = 15.6, *Z,E*, minor), 5.95 (1H, d, J = 11.4, *Z,E*, minor), 4.17 (4H, t, J = 6.8, *E,E*, major), 4.18-4.03 (4H, m, *Z,E*, minor), 1.67 (4H, m, *E,E*, major + *Z,E*, minor), 1.40-1.25 (20H, m, *E,E*, major + *Z,E*, minor), 0.87 (6H, t, J = 7.3, *E,E*, major + *Z,E*, minor) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 166.0 (*E,E*, major), 140.8 (*E,E*, major), 128.4 (*E,E*, major), 65.1 (*E,E*, major), 31.8 (*E,E*, major), 29.2 (*E,E*, major), 29.1 (*E,E*, major), 28.6 (*E,E*, major), 25.9 (*E,E*, major), 22.6 (*E,E*, major), 14.1 (*E,E*, major) ppm.



bis(2-ethylbutyl) (2*E*,4*E*)-hexa-2,4-dienedioate (**2g**)

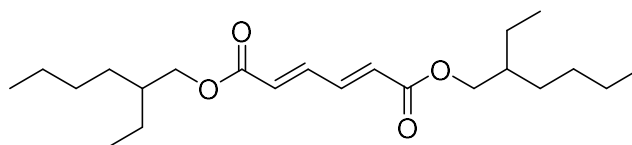


bis(2-ethylbutyl) (2*Z*,4*E*)-hexa-2,4-dienedioate (**2g**)

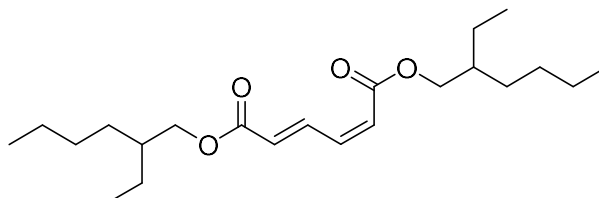
2g (227 mg, 0.73 mmol, 73% yield) was obtained as an inseparable mixture of *E,E* and *Z,E* isomers in a 94:6 ratio according to ^1H NMR spectroscopy. The analytical data is in agreement with previous reports.^[5]

^1H NMR (400 MHz, CDCl_3): δ = 8.37 (1H, dd, J = 15.6, 11.6, *Z,E*, minor), 7.30 (2H, dd, J = 11.5, 3.0, *E,E*, major), 6.63 (1H, t, J = 11.5, *Z,E*, minor), 6.21 (2H, dd, J = 11.5, 3.1, *E,E*, major), 6.11 (1H, d, J = 15.6, *Z,E*, minor), 5.96 (1H, d, J = 11.4, *Z,E*, minor), 4.11 (4H, d, J = 5.9, *E,E*, major + *Z,E*, minor), 1.57 (2H, hept, J = 6.2, *E,E*, major + *Z,E*, minor), 1.39 (4H, p, J = 7.2, *E,E*, major + *Z,E*, minor), 1.29-1.26 (4H, m, *E,E*, major + *Z,E*, minor), 0.91 (6H, t, J = 7.5, *E,E*, major), 0.88-0.86 (6H, *Z,E*, minor) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 166.1 (*E,E*, major), 140.7 (*E,E*, major), 128.4 (*E,E*, major), 67.0 (*E,E*, major), 53.4 (*E,E*, major), 40.3 (*E,E*, major), 40.2 (*Z,E*, minor), 31.9 (*Z,E*, minor), 29.5 (*Z,E*, minor), 29.4 (*Z,E*, minor), 29.7 (*E,E*, major), 23.3 (*E,E*, major), 22.7 (*Z,E*, minor), 14.1 (*Z,E*, minor), 11.0 (*E,E*, major) ppm.



bis(2-ethylhexyl) (2*E*,4*E*)-hexa-2,4-dienedioate (**2h**)

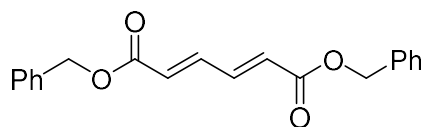


bis(2-ethylhexyl) (2*Z*,4*E*)-hexa-2,4-dienedioate (**2h**)

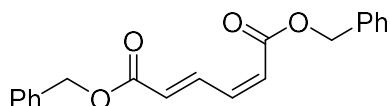
2h (268 mg, 0.73 mmol, 73% yield) was obtained as an inseparable mixture of *E,E* and *Z,E* isomers in a 93:7 ratio according to ^1H NMR spectroscopy. The analytical data is in agreement with previous reports.^[5]

^1H NMR (400 MHz, CDCl_3): δ = 8.38 (1H, dd, J = 15.6, 11.6, *Z,E*, minor), 7.30 (2H, dd, J = 11.5, 3.0, *E,E*, major), 6.63 (1H, t, J = 11.5, *Z,E*, minor), 6.21 (2H, dd, J = 11.5, 3.1, *E,E*, major), 6.11 (1H, d, J = 15.6, *Z,E*, minor), 5.96 (1H, d, J = 11.4, *Z,E*, minor), 4.10 (4H, m, *E,E*, major + *Z,E*, minor), 1.62 (2H, hept, J = 6.0, *E,E*, major + *Z,E*, minor), 1.38 (4H, p, J = 7.2, *E,E*, major + *Z,E*, minor), 1.35-1.26 (12H, m, *E,E*, major + *Z,E*, minor), 0.91 (6H, t, J = 7.5, *E,E*, major + *Z,E*, minor), 0.90 (6H, t, J = 7.5, *Z,E*, minor) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 166.1 (*E,E*, major), 140.7 (*E,E*, major), 128.4 (*E,E*, major), 67.3 (*E,E*, major), 53.4 (*E,E*, major), 38.8 (*E,E*, major), 30.4 (*E,E*, major), 29.7 (*Z,E*, minor), 28.9 (*E,E*, major), 23.8 (*Z,E*, minor), 23.0 (*E,E*, major), 14.0 (*E,E*, major), 11.0 (*E,E*, major) ppm.



dibenzyl (2*E*,4*E*)-hexa-2,4-dienedioate (**2j**)

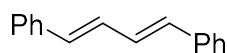


dibenzyl (2*Z*,4*E*)-hexa-2,4-dienedioate (**2j**)

2j (213 mg, 0.66 mmol, 66% yield) was obtained as an inseparable mixture of *E,E* and *Z,E* isomers in a 87:13 ratio according to ¹H NMR spectroscopy. The analytical data is in agreement with previous reports.^[6]

¹H NMR (400 MHz, CDCl₃): δ = 8.47 (1H, ddd, *J* = 15.3, 11.6, 1.1, *Z,E*, minor), 7.39 (12H, m, *E,E*, major + *Z,E*, minor), 6.66 (1H, t, *J* = 11.7, *Z,E*, minor), 6.25 (2H, dd, *J* = 11.5, 3.1, *E,E*, major), 6.15 (1H, d, *J* = 15.7, *Z,E*, minor), 6.01 (1H, d, *J* = 11.5, *Z,E*, minor), 5.24 (4H, m, *Z,E*, minor), 5.23 (4H, s, *E,E*, major) ppm.

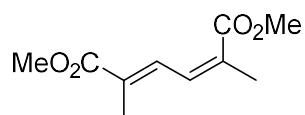
¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 165.7 (*E,E*, major), 141.2 (*E,E*, major), 135.7 (*E,E*, major), 128.8 (*E,E*, major), 128.4 (*E,E*, major), 128.3 (*E,E*, major), 128.2 (*E,E*, major), 66.7 (*E,E*, major) ppm.



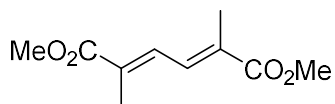
(1*E*,3*E*)-1,4-diphenylbuta-1,3-diene (**2m**)

2l (41 mg, 0.20 mmol, 20% yield) was obtained as light-sensitive material prone to decompose, as such only ¹H NMR spectroscopy is provided. The analytical data is in agreement with previous reports.^[7]

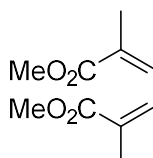
¹H NMR (400 MHz, CDCl₃): δ = 7.45 (4H, d, *J* = 7.6), 7.34 (4H, t, *J* = 7.6), 7.23 (2H, d, *J* = 8.9), 6.97 (2H, dd, *J* = 14.7, 8.9), 6.68 (2H, dd, *J* = 14.8, 9.0) ppm.



dimethyl (2*Z*,4*E*)-2,5-dimethylhexa-2,4-dienedioate (**2m**)



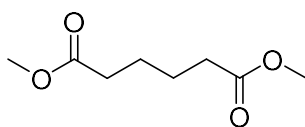
dimethyl (2*E*,4*E*)-2,5-dimethylhexa-2,4-dienedioate (**2m**)



dimethyl (2*Z*,4*Z*)-2,5-dimethylhexa-2,4-dienedioate (**2m**)

2m (42 mg, 0.21 mmol, 21% yield) was obtained as an inseparable mixture of *Z,E* and *E,E* and *Z,Z* isomers in a 80:14:6 ratio according to ^1H NMR spectroscopy. The analytical data is in agreement with previous reports.^[8]

^1H NMR (400 MHz, CDCl_3): δ = 7.99 (1H, ddd, J = 11.9, 1.6, 0.7, *Z,E*, major), 7.44 (2H, s, *Z,Z*, minor), 6.69 (1H, dq, J = 11.8, 1.6, *Z,E*, major), 6.15 (1H, d, J = 1.3, *E,E*, minor), 5.50 (1H, s, *E,E*, minor), 3.79 (3H, s, *Z,E*, major), 3.78 (3H, s, *E,E*, minor), 3.76 (3H, s, *Z,E*, major), 3.74 (3H, s, *E,E*, minor), 2.48 (2H, s, *E,E*, minor), 2.06 (3H, dd, J = 1.5, 0.8, *Z,E*, major), 2.04 (6H, s, *Z,Z*, minor) 1.98 (3H, dd, J = 1.6, 0.8, *Z,E*, major) ppm.

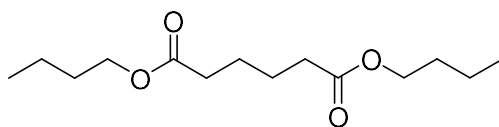


dimethyl adipate (**3a**)

3a (132 mg, 0.76 mmol, 76% yield) was obtained after purification by column chromatography and the analytical data is in agreement with previous reports.^[9]

^1H NMR (400 MHz, CDCl_3): δ = 3.66 (6H, s), 2.32 (4H, m), 1.65 (4H, m) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 173.7, 51.5, 33.6, 24.3 ppm.



dibutyl adipate (**3c**)

3c (212 mg, 0.82 mmol, 82% yield) was obtained after purification by column chromatography and the analytical data is in agreement with previous reports.^[10]

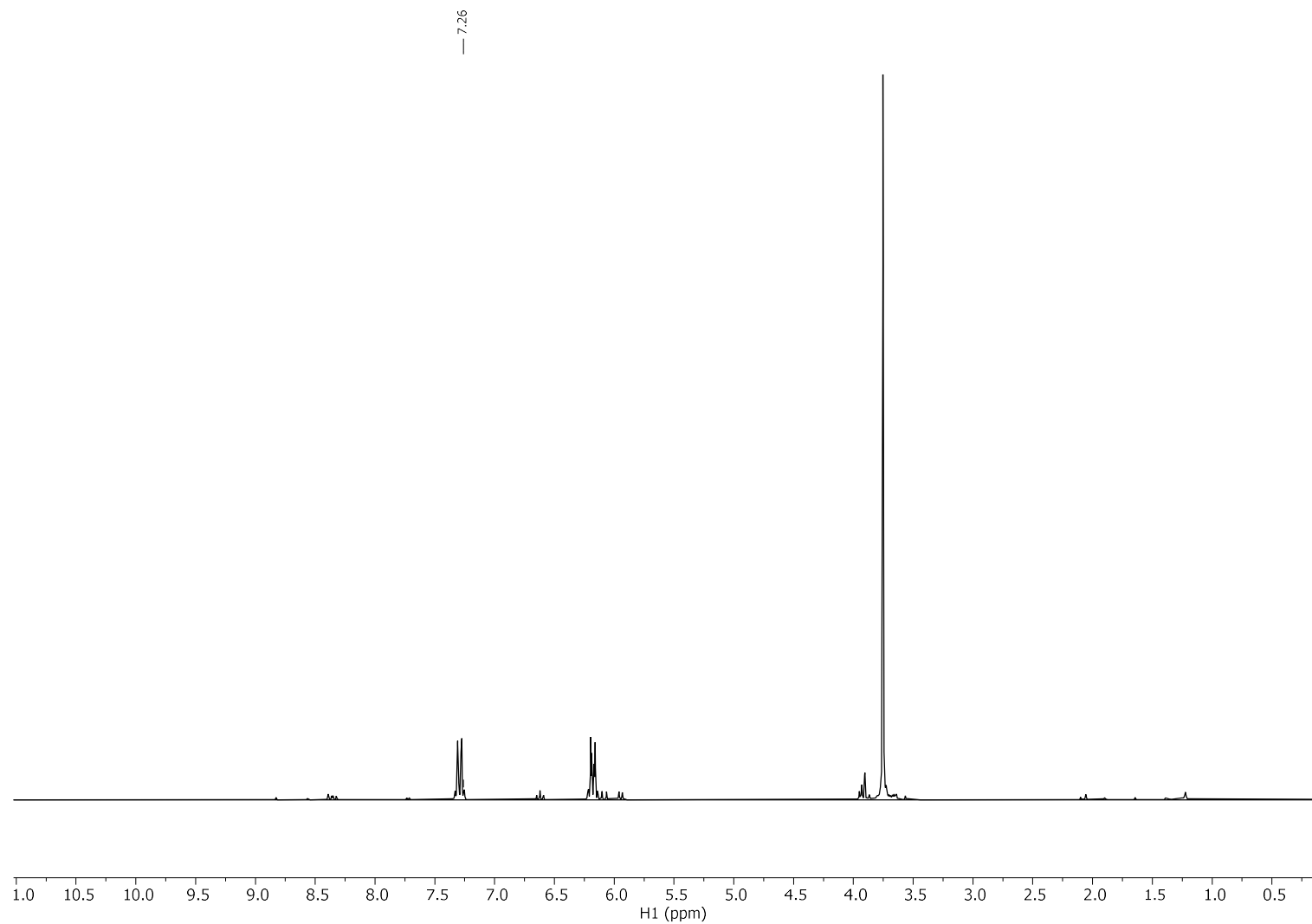
¹H NMR (400 MHz, CDCl₃): δ = 4.06 (4H, t, J = 6.7), 2.31 (4H, m), 1.65 (4H, m), 1.59 (4H, m), 1.36 (4H, m), 0.92 (6H, t, J = 7.4) ppm.

¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 173.4, 64.2, 33.9, 30.6, 24.4, 19.1, 13.7 ppm.

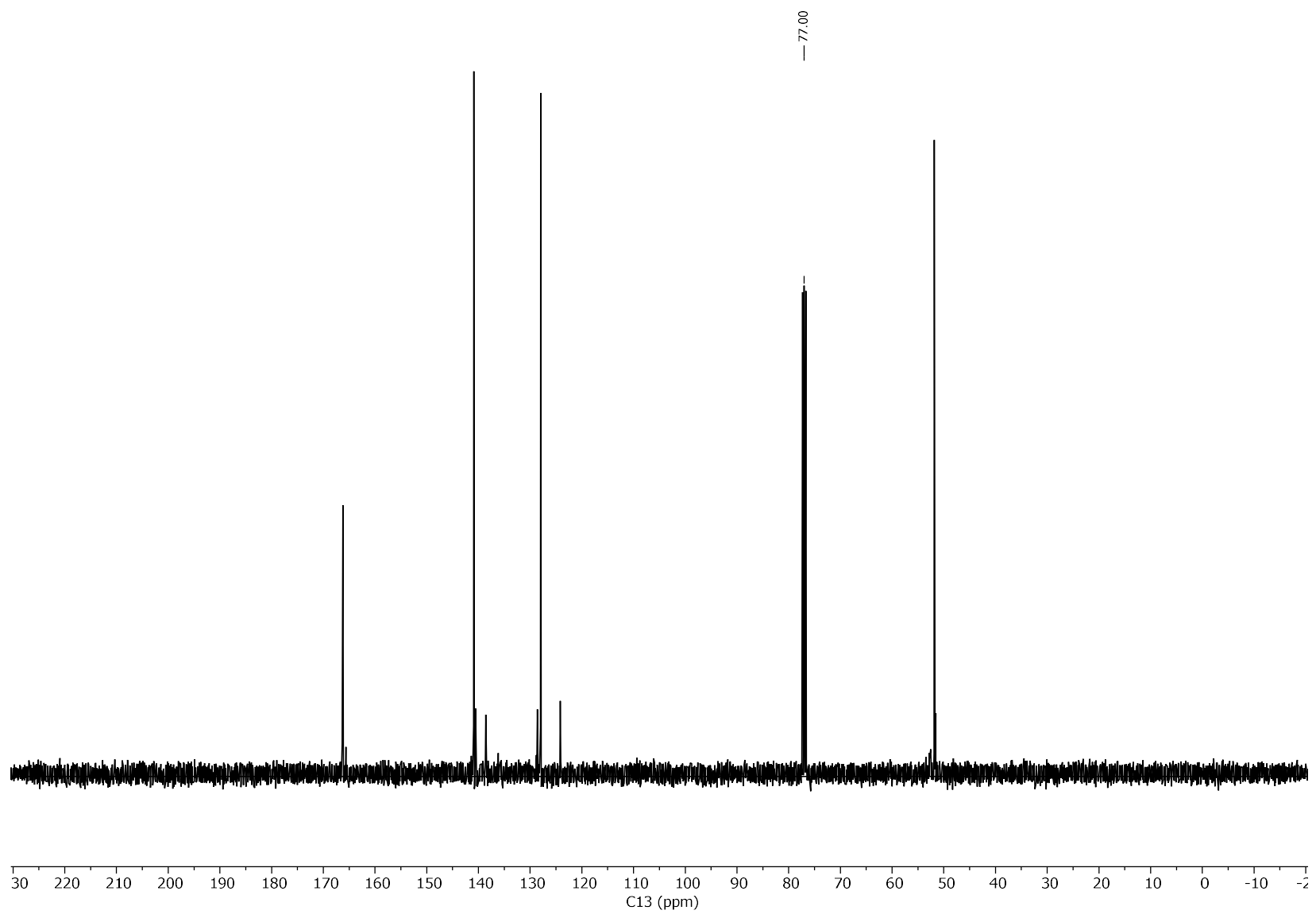
4. References.

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- [2] (a) For NMR data from *E,E* isomer of **2a**, see: L. Boisvert, F. Beaumier and C. Spino, *Org. Lett.*, 2007, **9**, 5361–5363; (b) For NMR data from *Z,E* isomer of **2a**, see: M.-E. Martin, D. Planchenault and F. Huet, *Tetrahedron*, 1995, **51**, 4985–4990.
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- [8] (a) For NMR data from *Z,E* and *E,E* isomer of **2n**, see: H. A. Dieck and R. F. Heck, *J. Org. Chem.*, 1975, **40**, 1083–1090; (b) For NMR data from *Z,Z* isomer of **2n**, see: M. Wiessler, *Tetrahedron Lett.*, 1977, **3**, 233–234.
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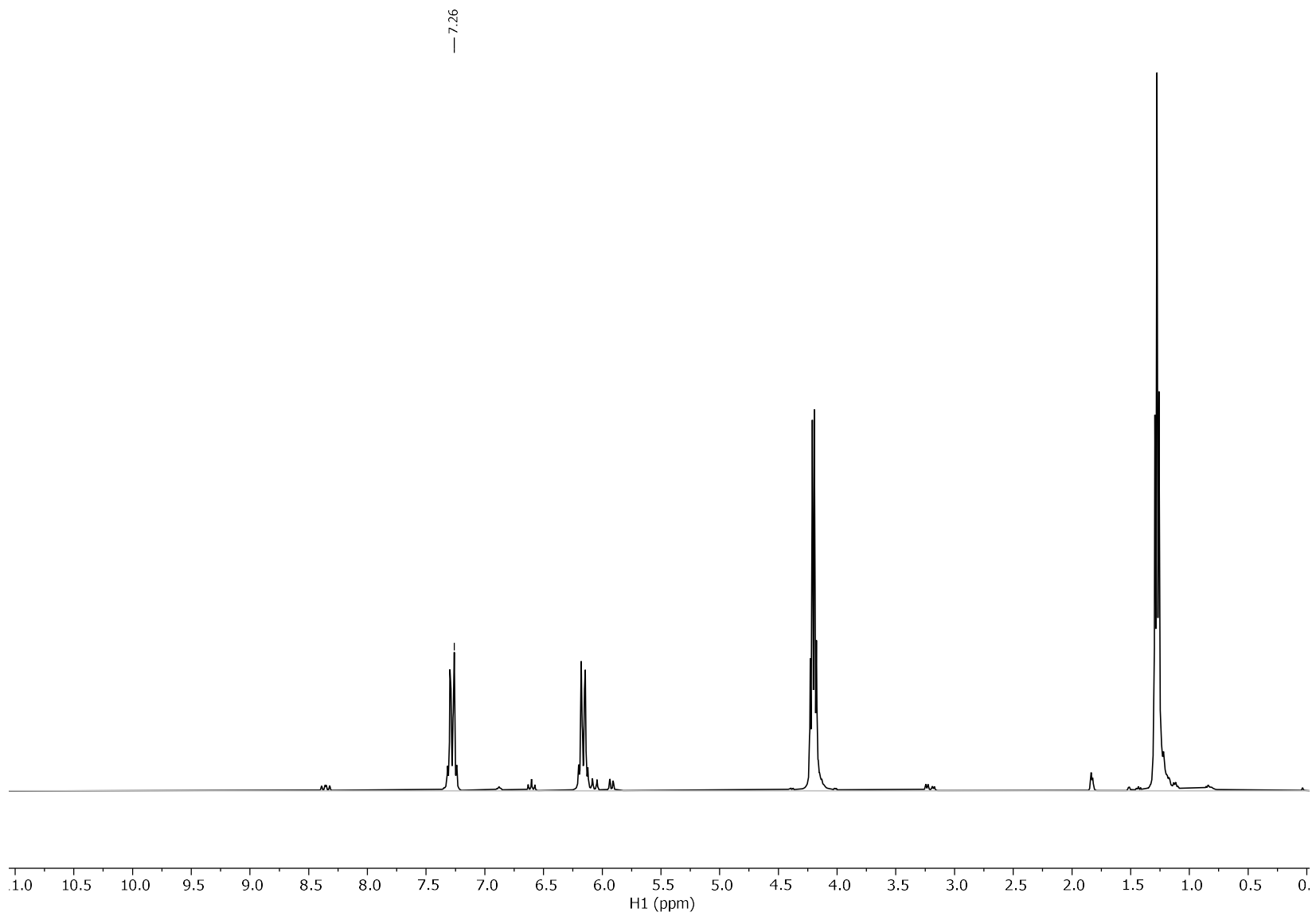
5. NMR spectra.



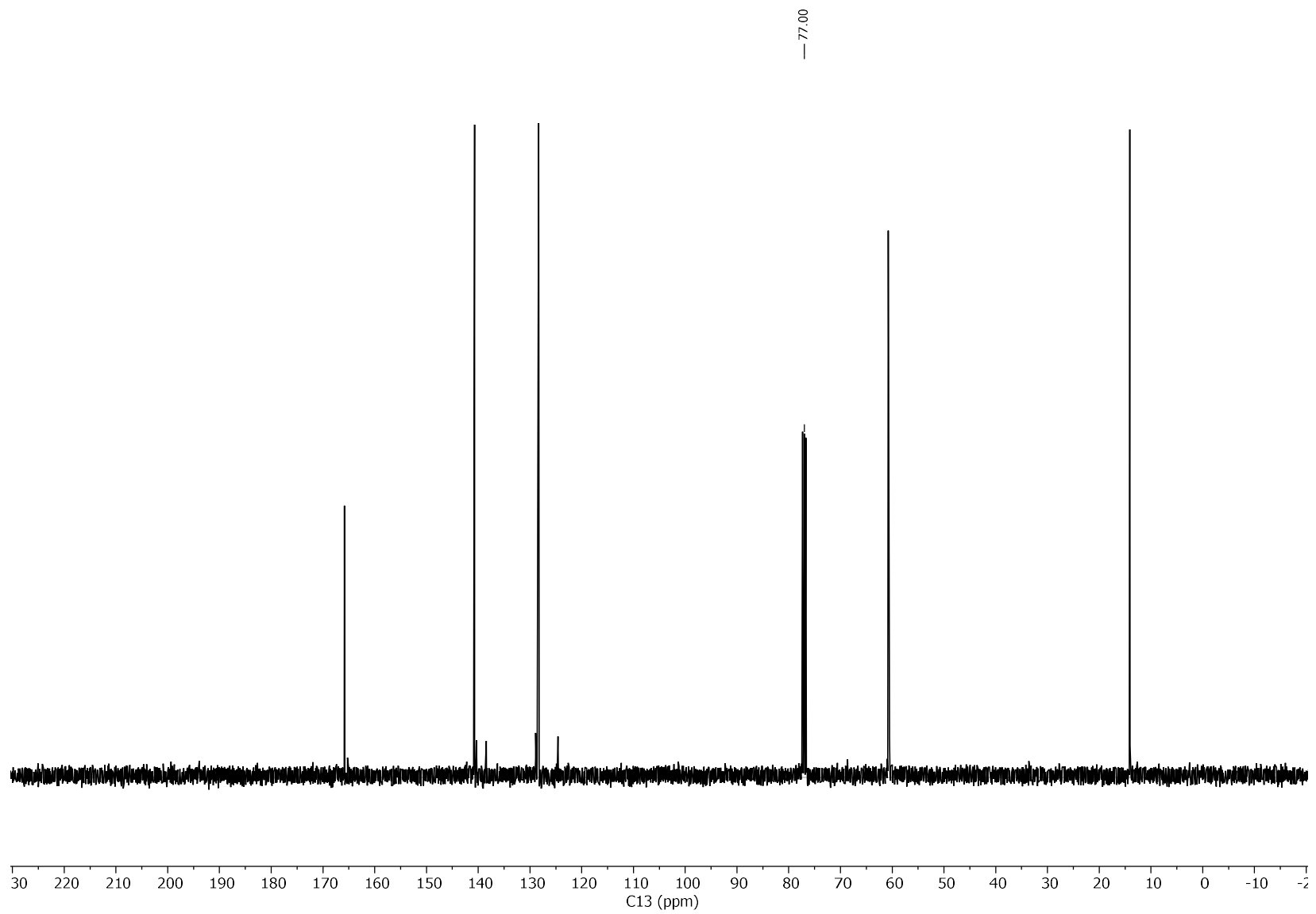
^1H NMR (CDCl_3 , 400 MHz) spectrum of **2a**.



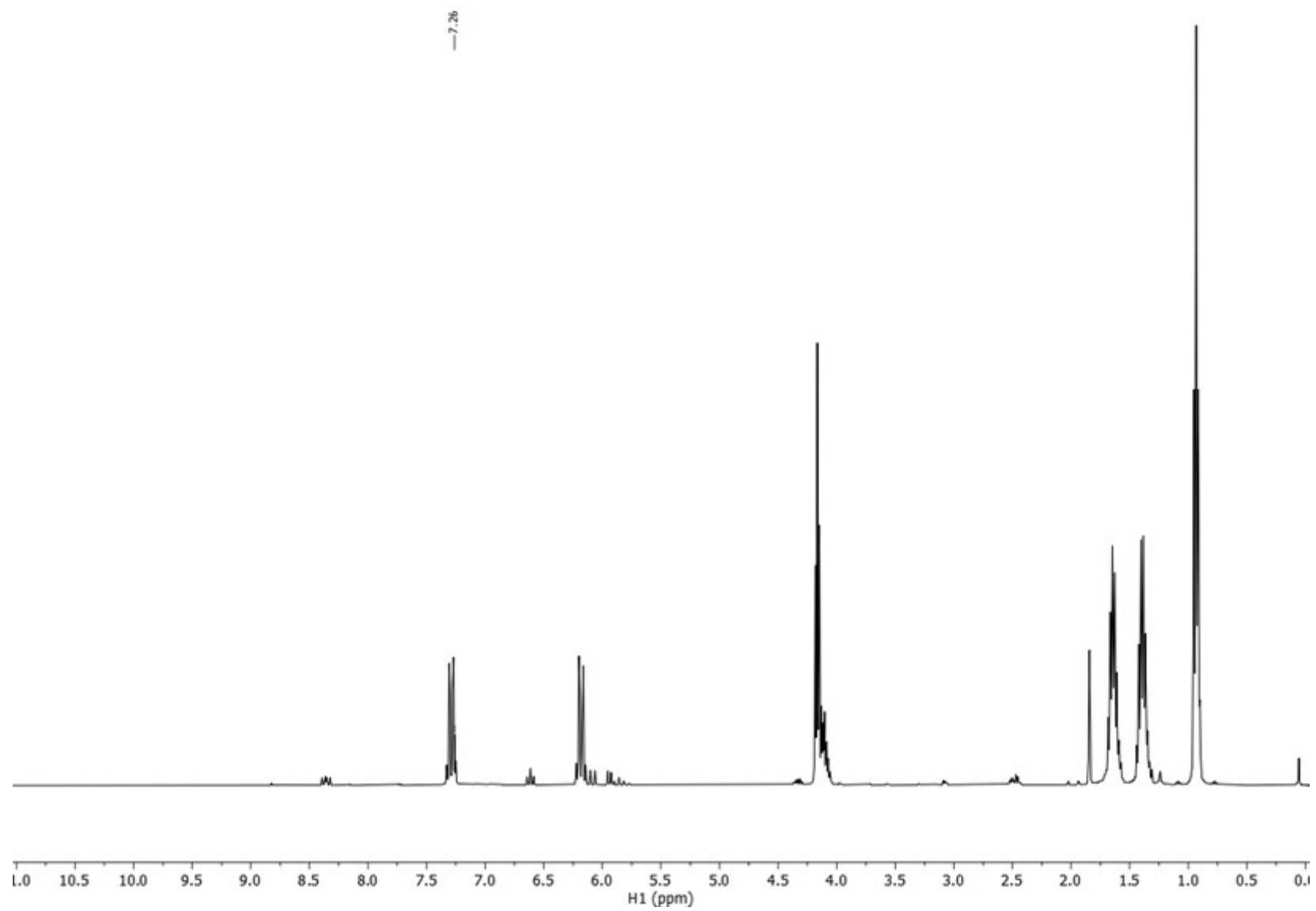
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **2a**.



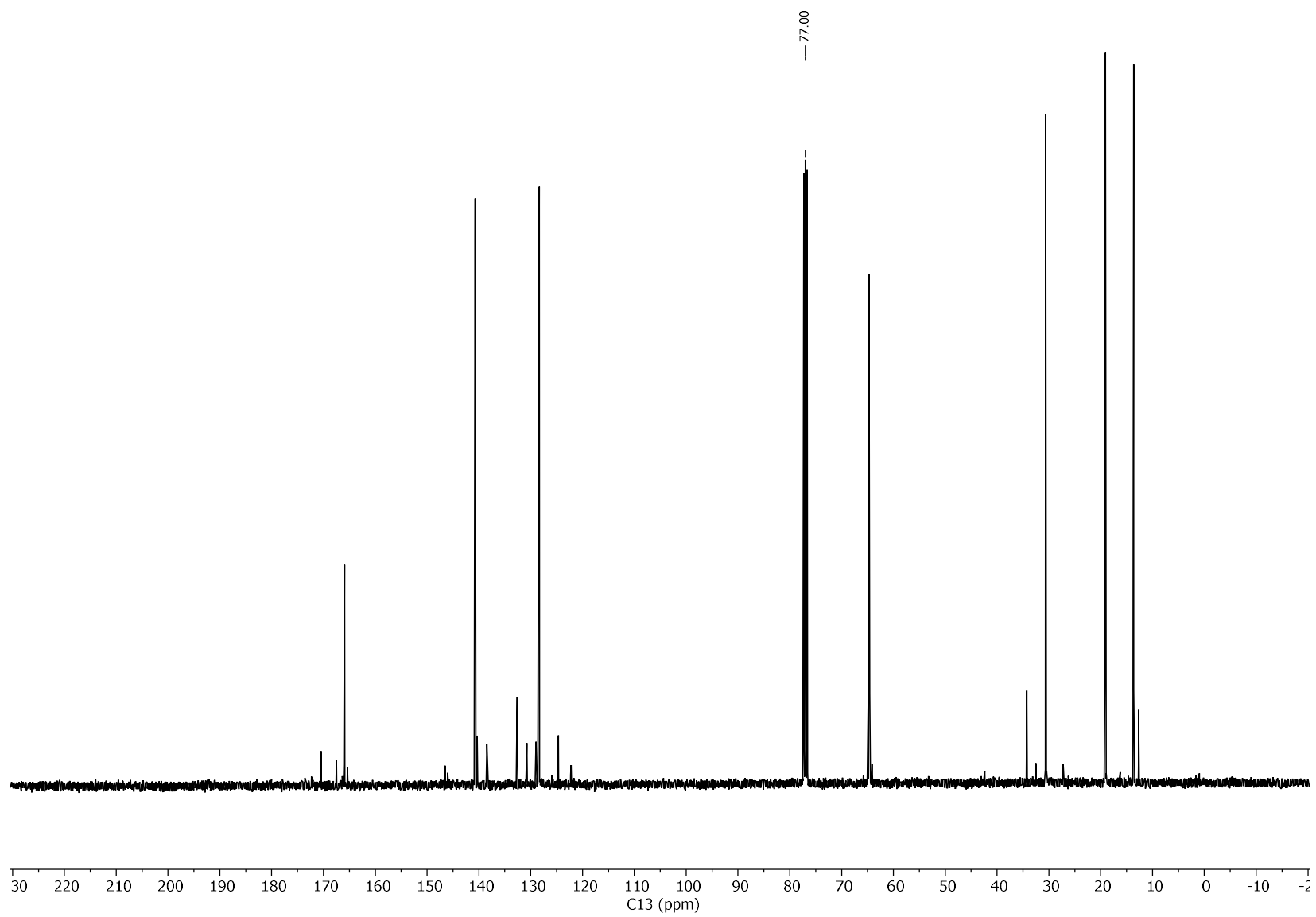
^1H NMR (CDCl_3 , 400 MHz) spectrum of **2b**.



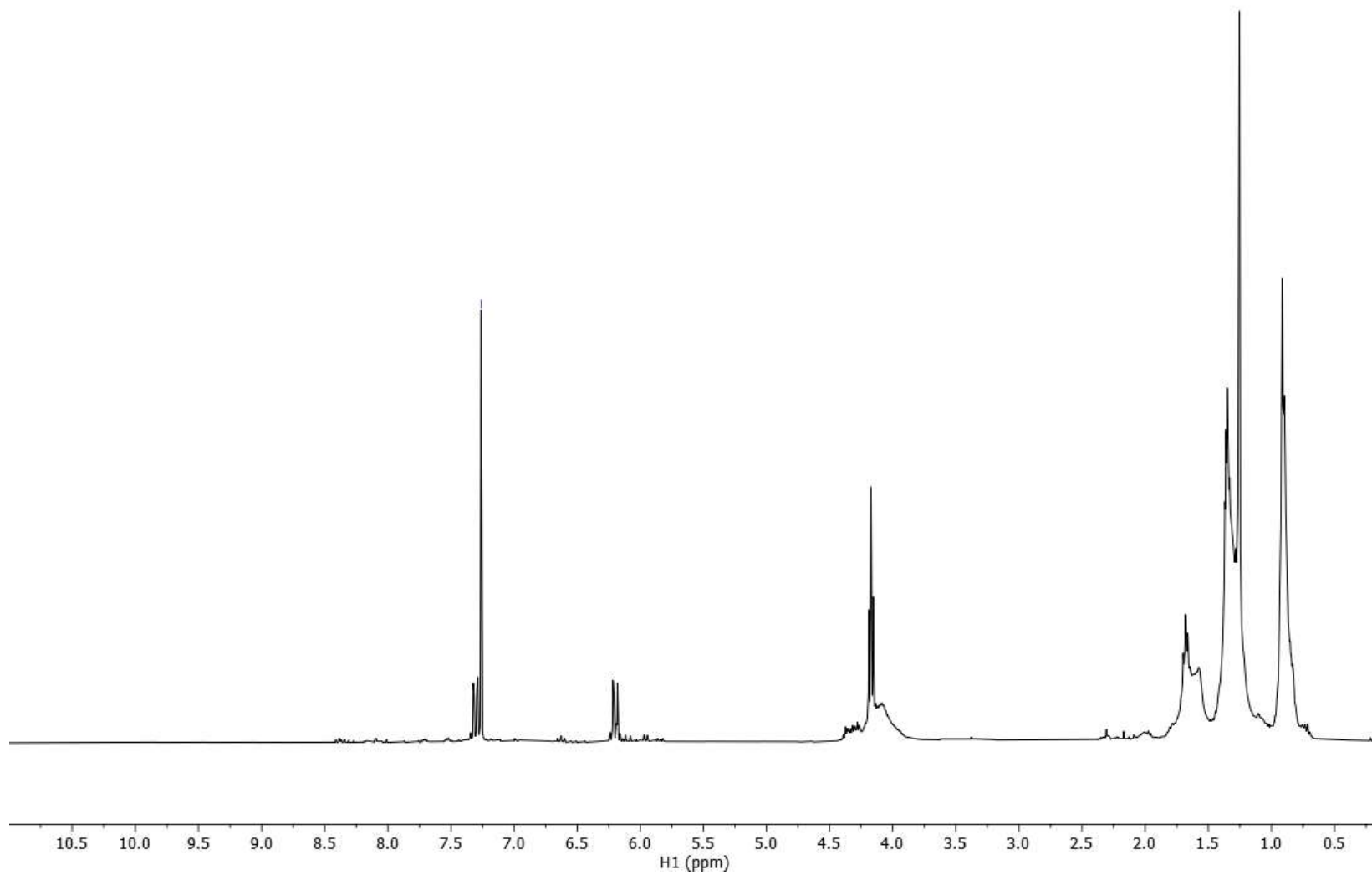
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **2b**.



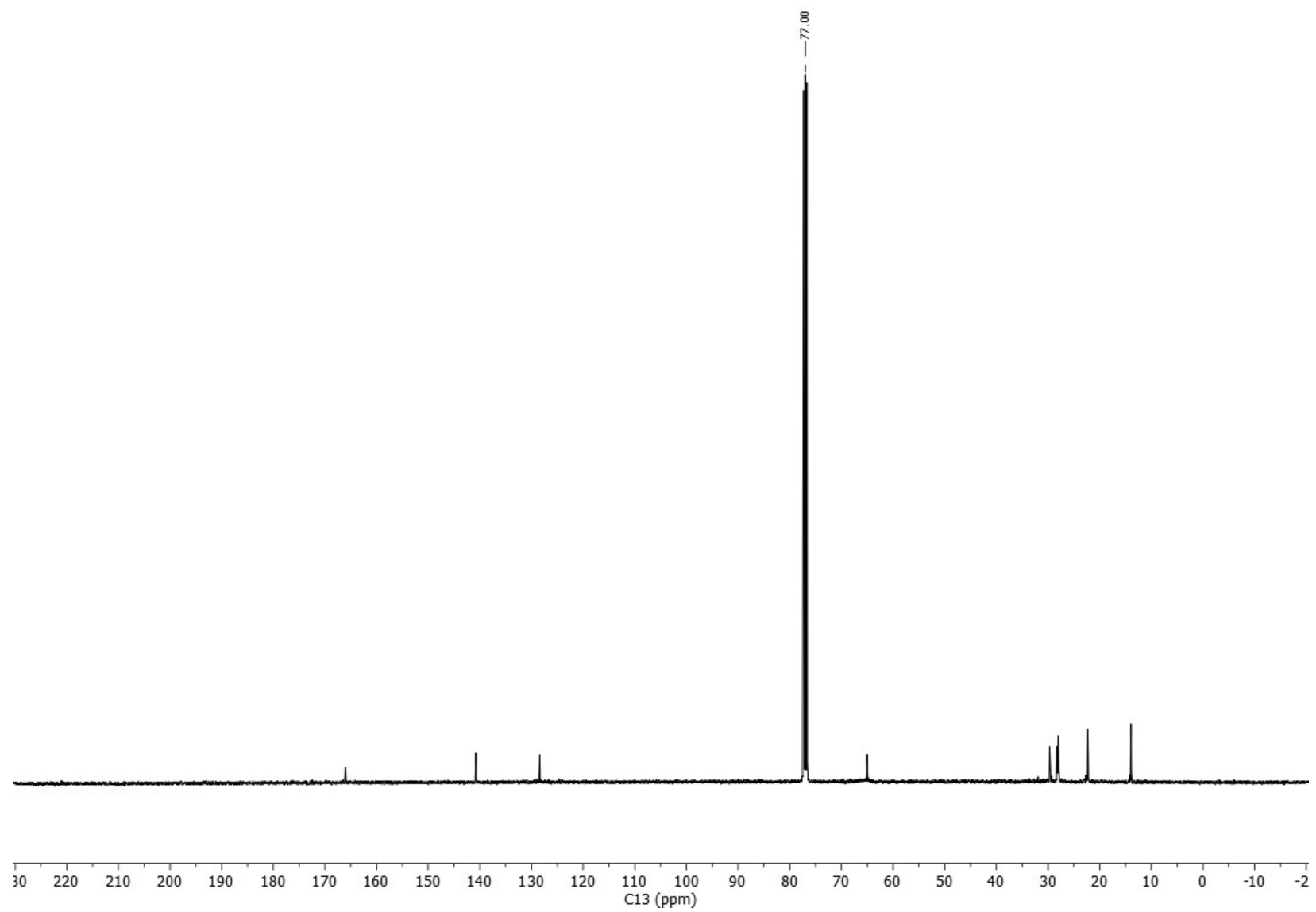
^1H NMR (CDCl_3 , 400 MHz) spectrum of **2c**.



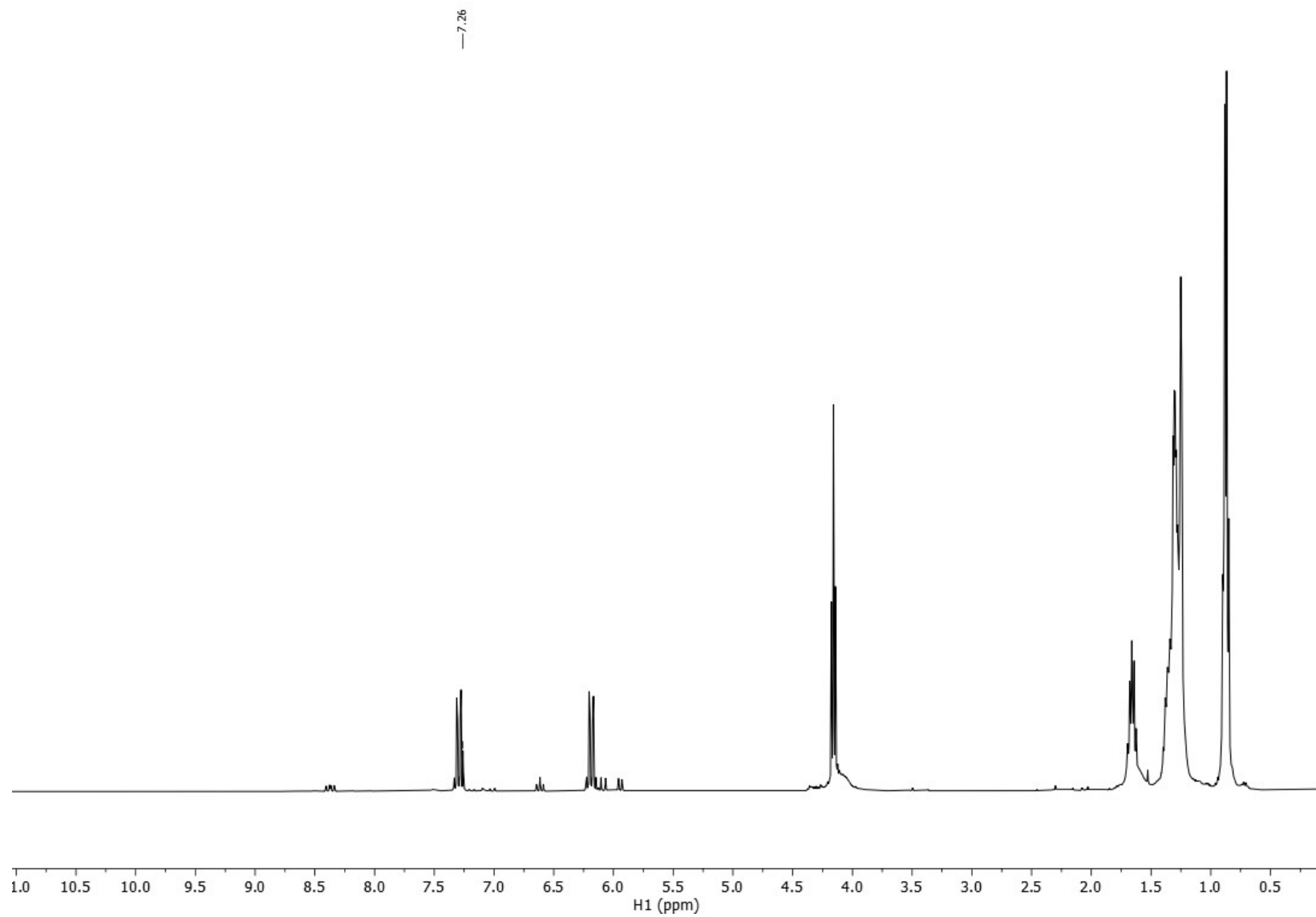
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **2c**.



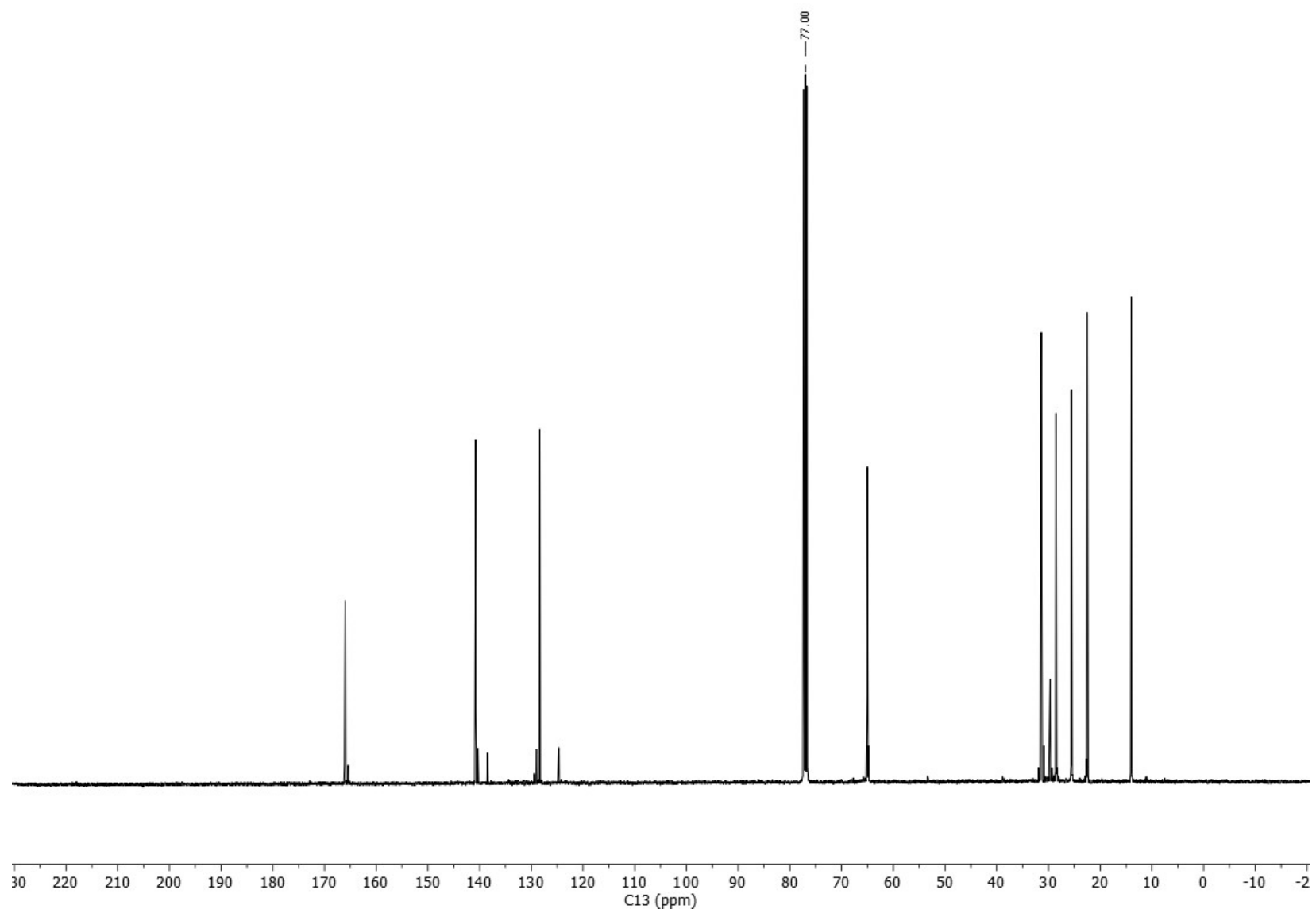
^1H NMR (CDCl_3 , 400 MHz) spectrum of **2d**.



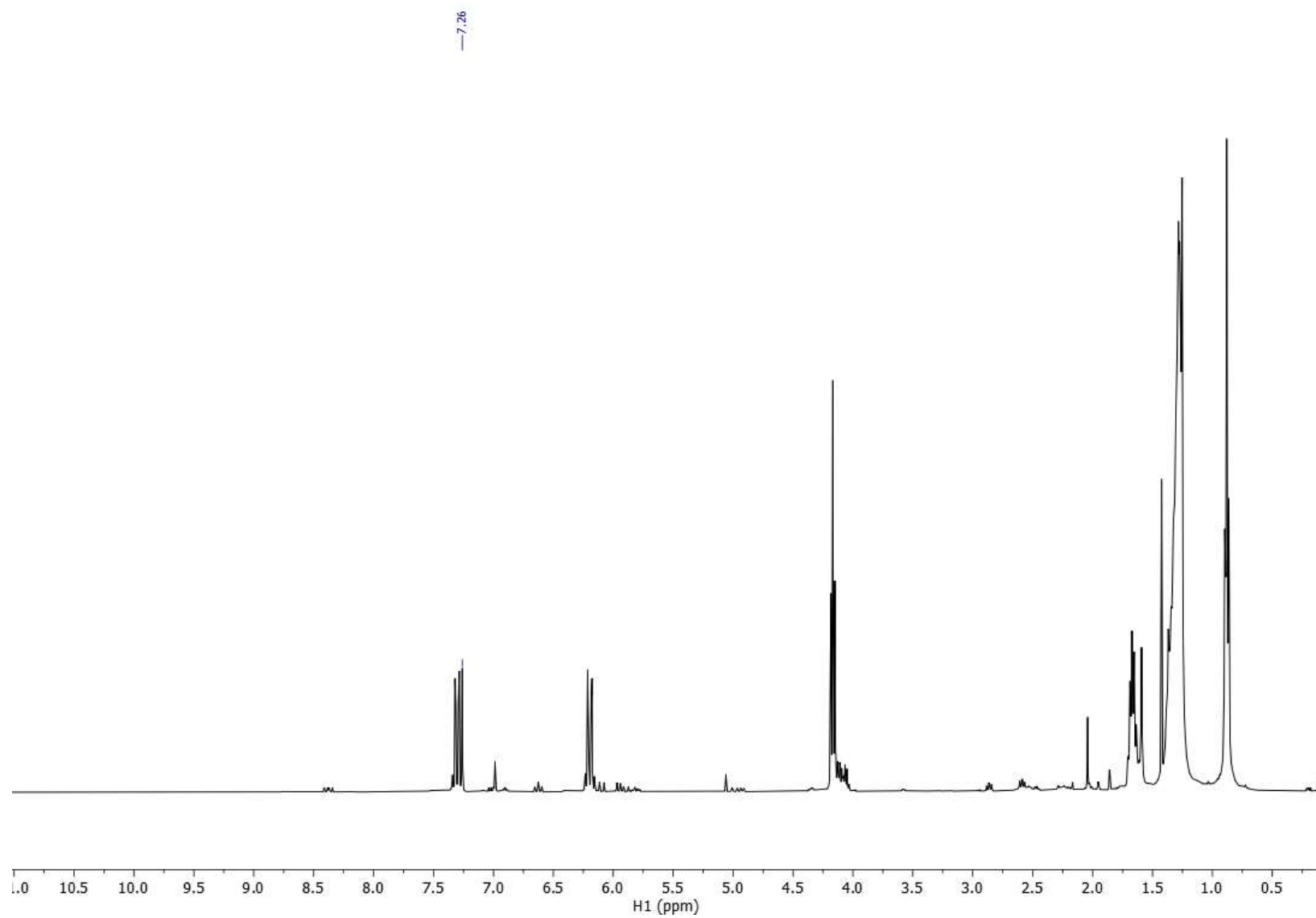
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **2d**.



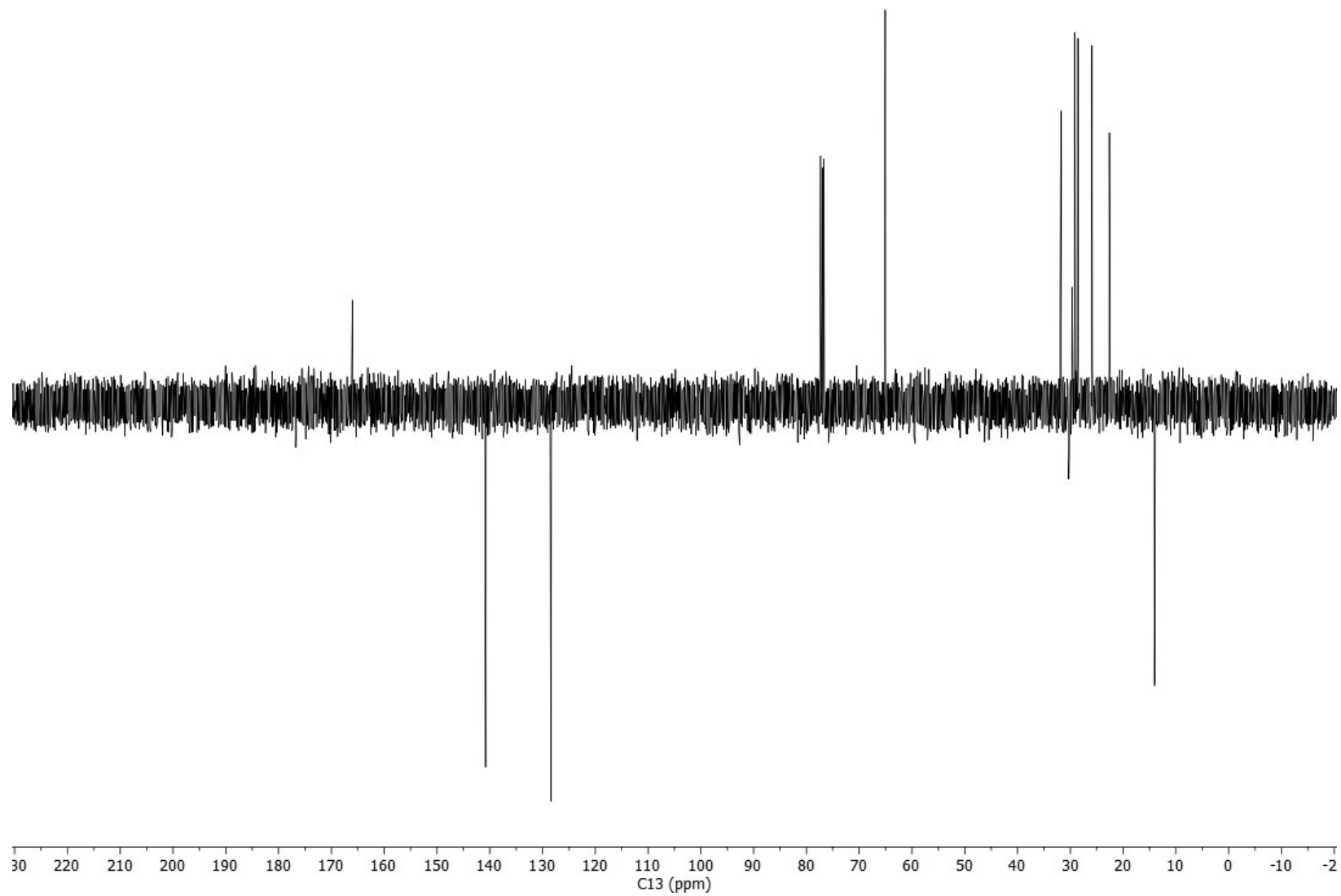
^1H NMR (CDCl_3 , 400 MHz) spectrum of **2e**.



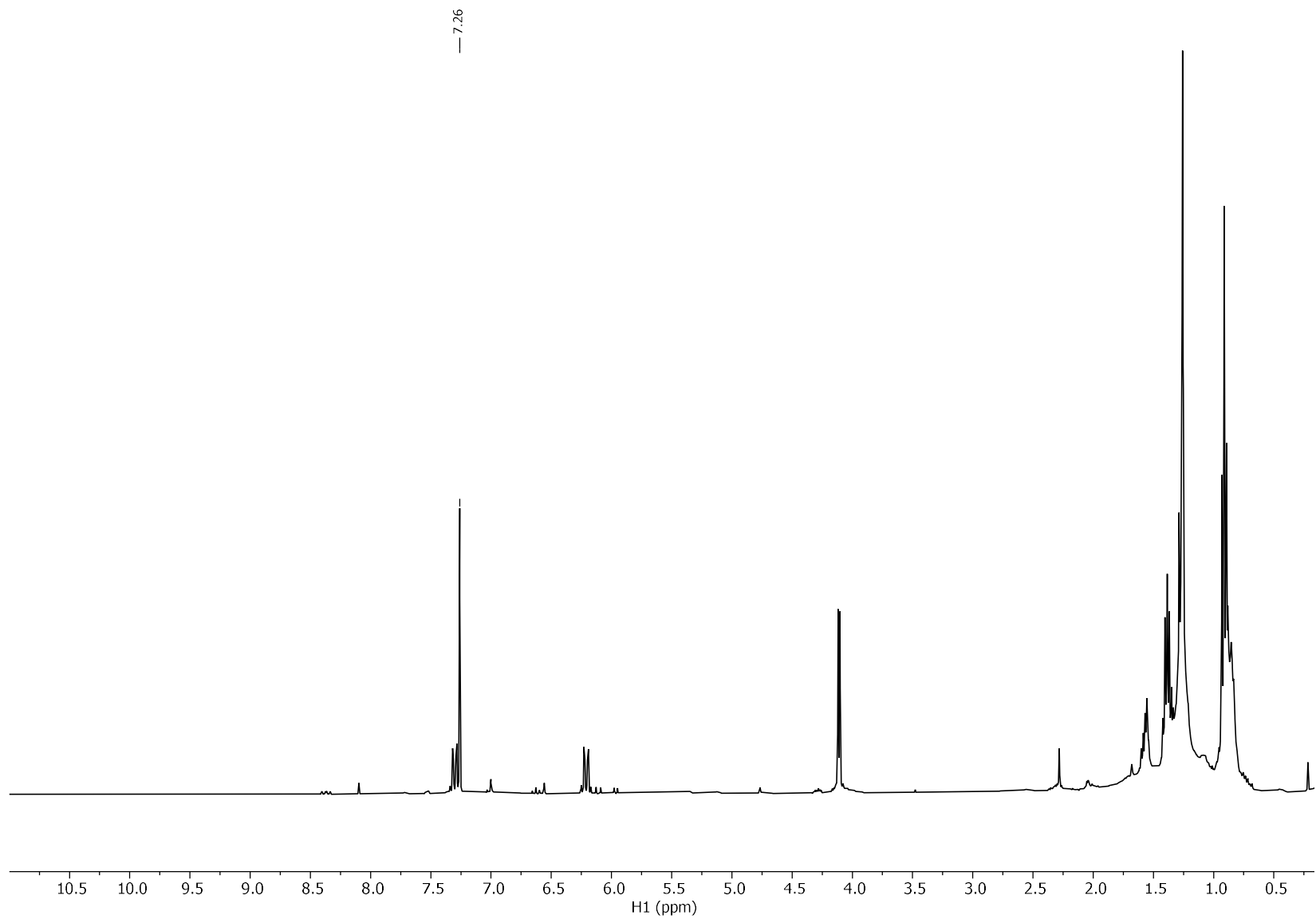
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **2e**.



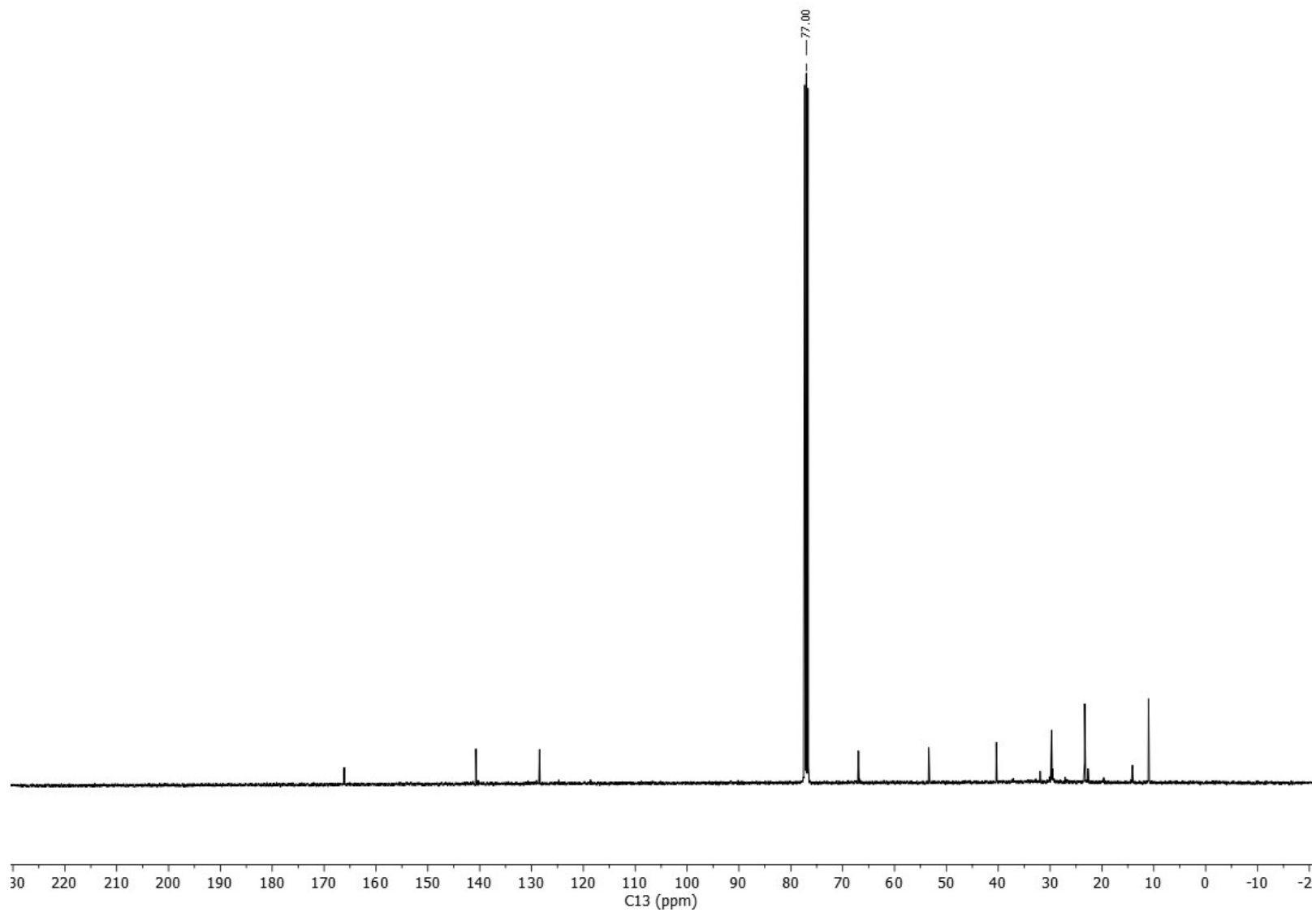
^1H NMR (CDCl_3 , 400 MHz) spectrum of **2f**.



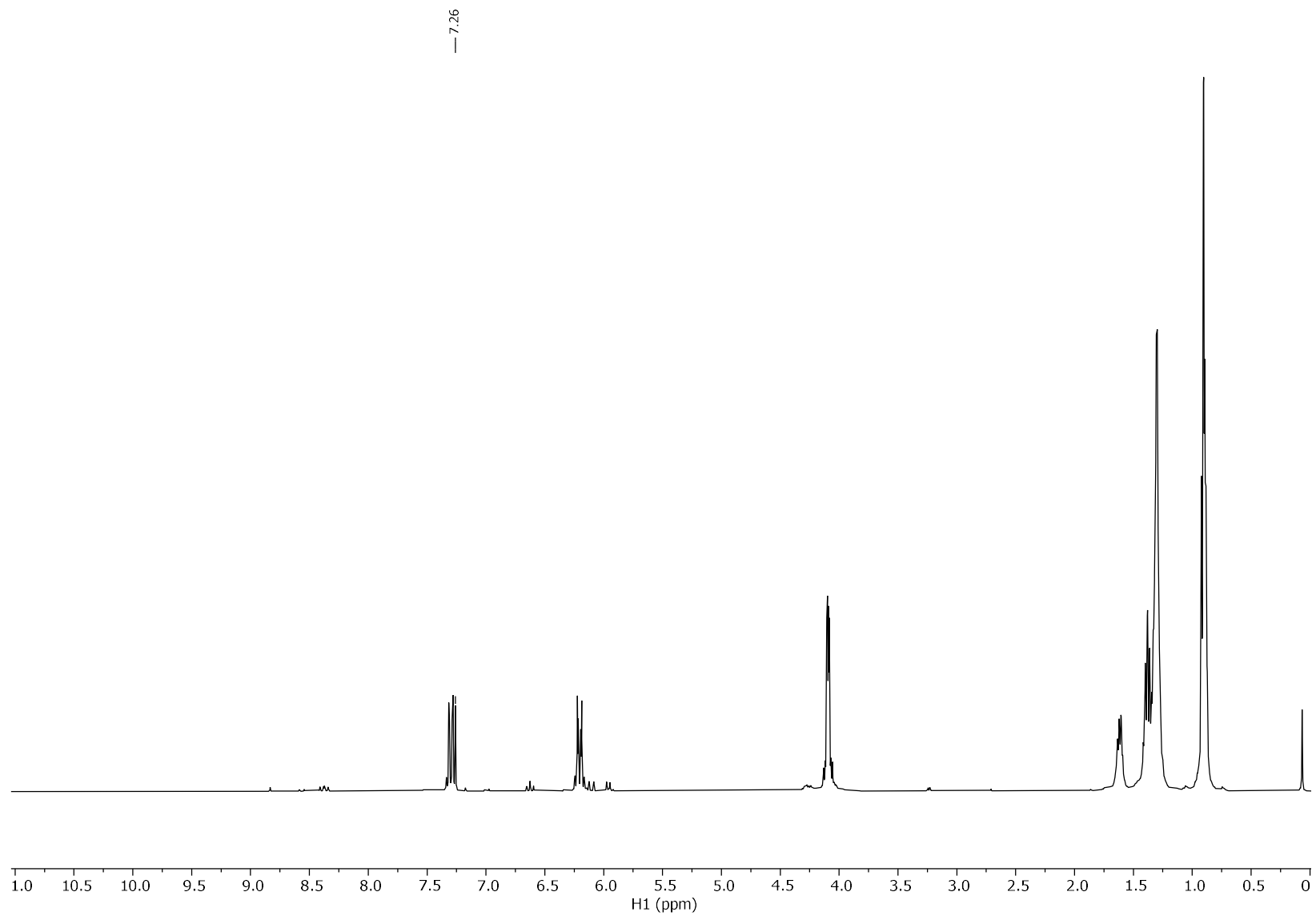
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) JMOD spectrum of **2f**.



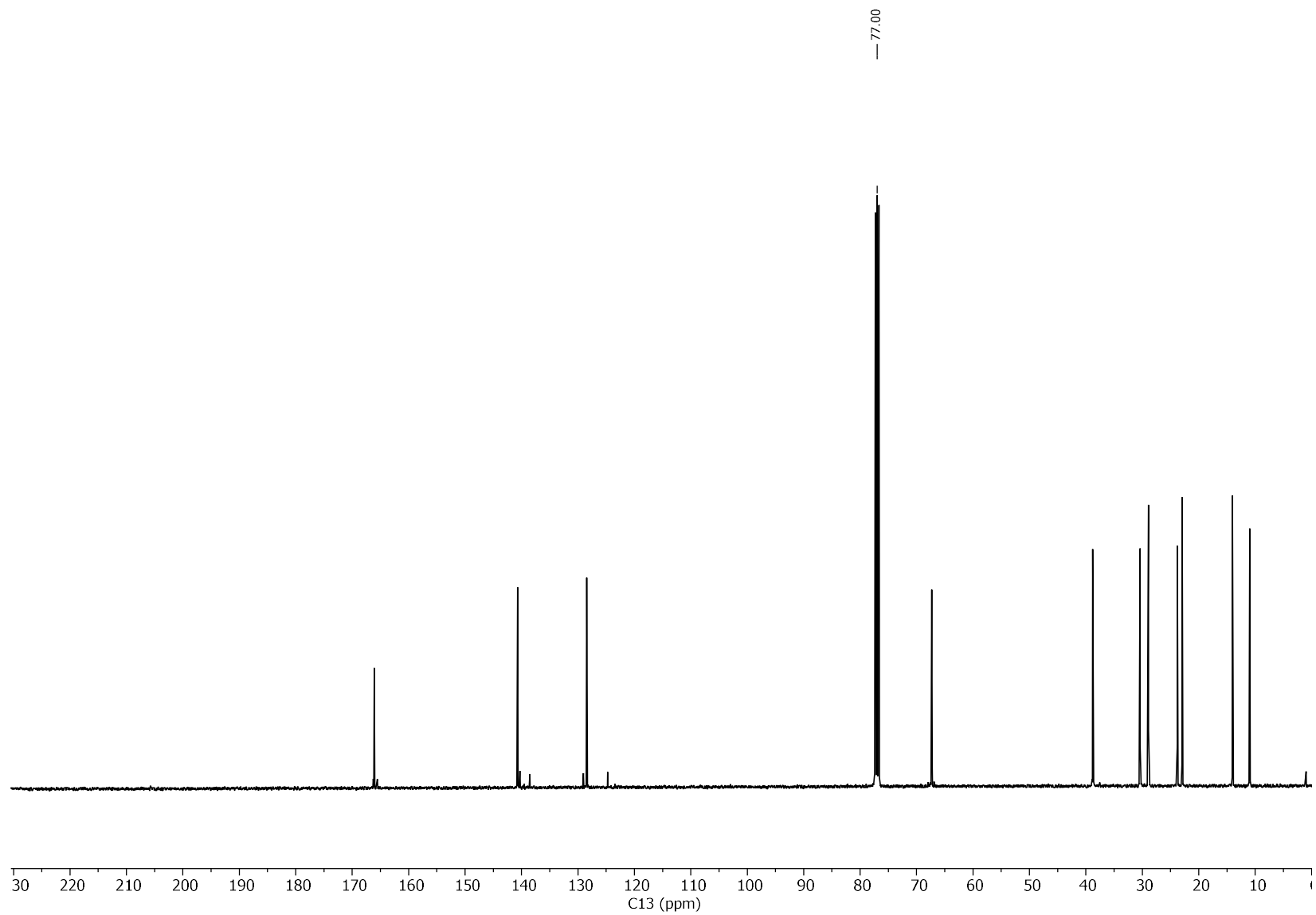
^1H NMR (CDCl_3 , 400 MHz) spectrum of **2g**.



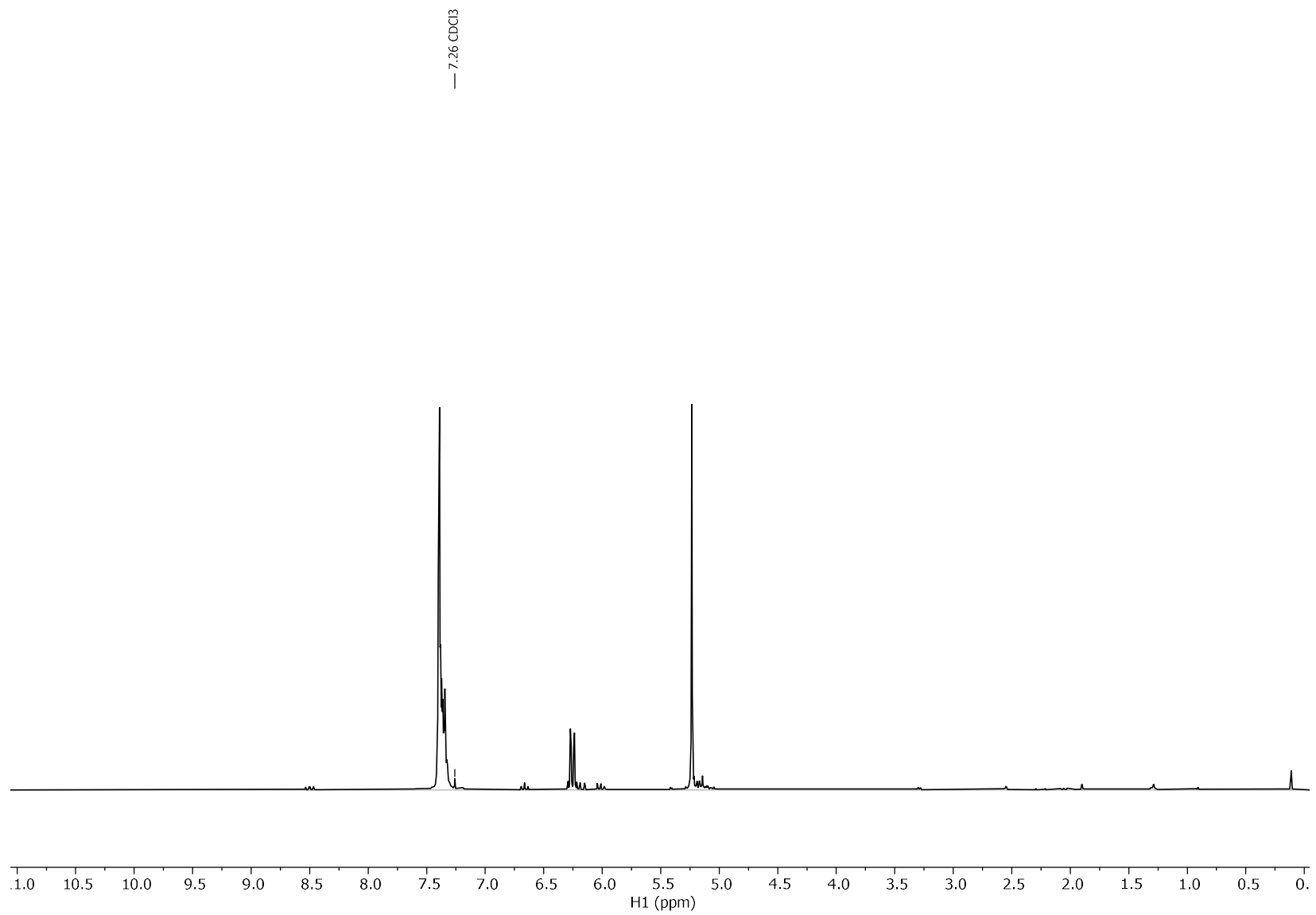
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **2g**.



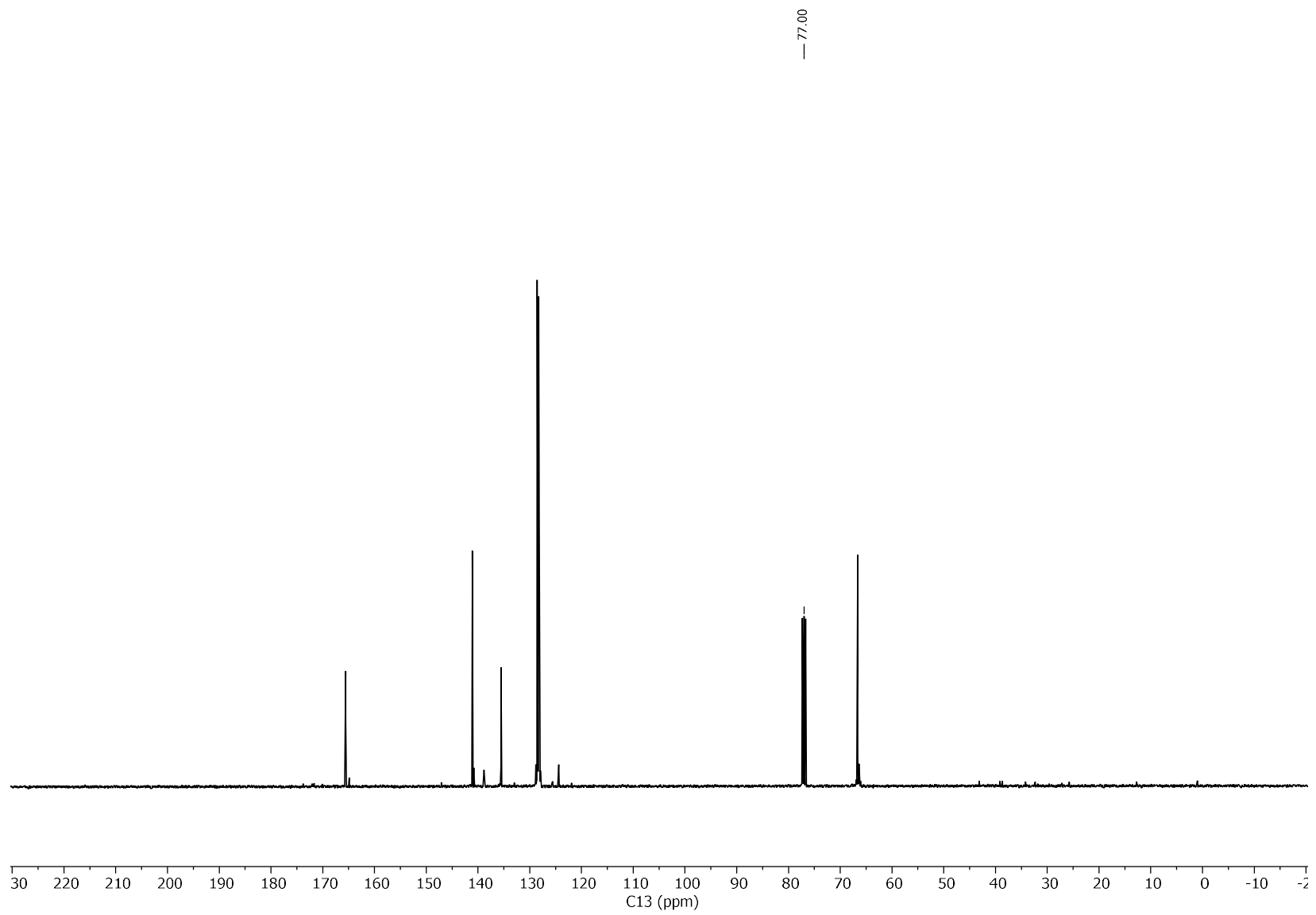
^1H NMR (CDCl_3 , 400 MHz) spectrum of **2h**.



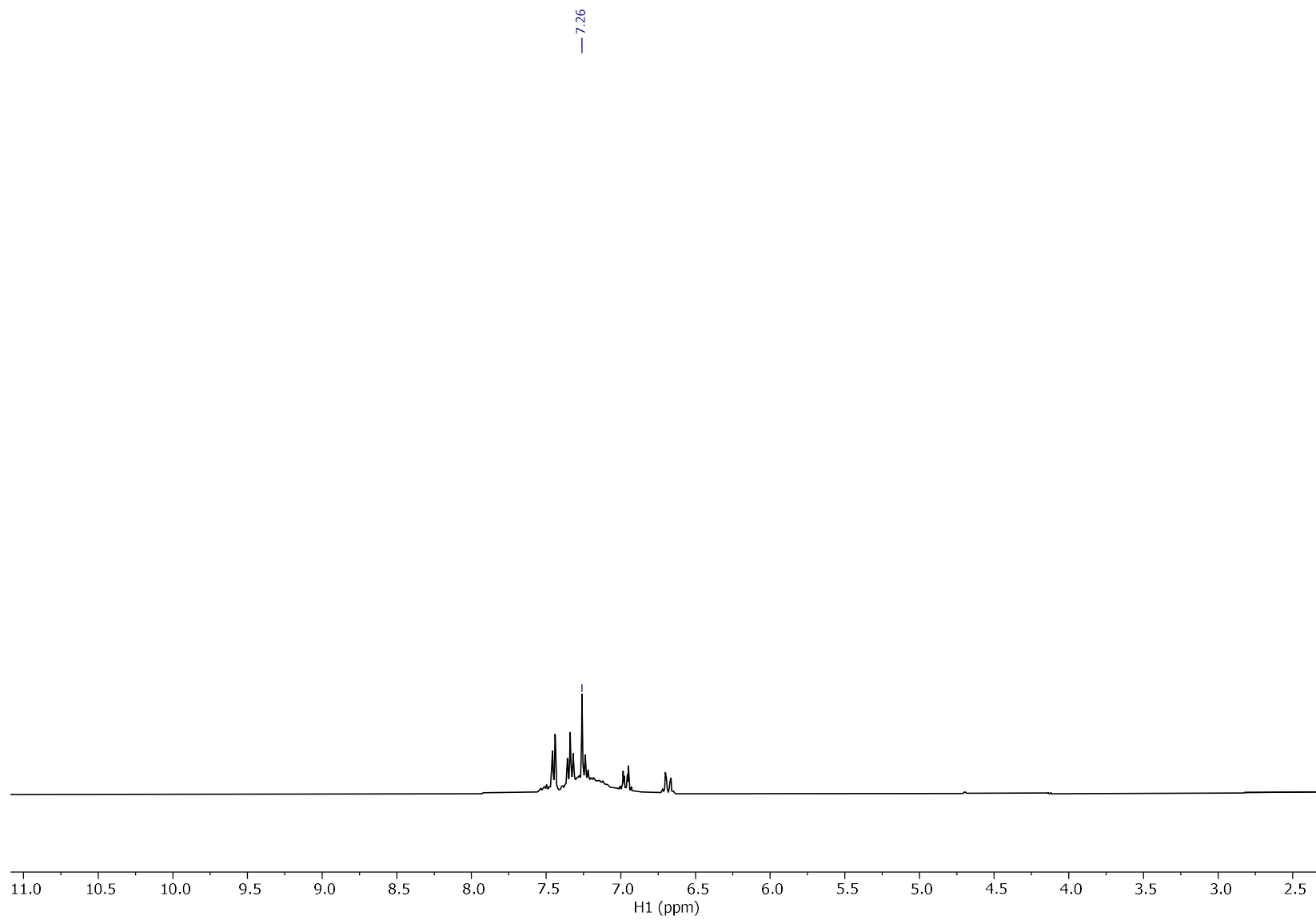
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **2h**.



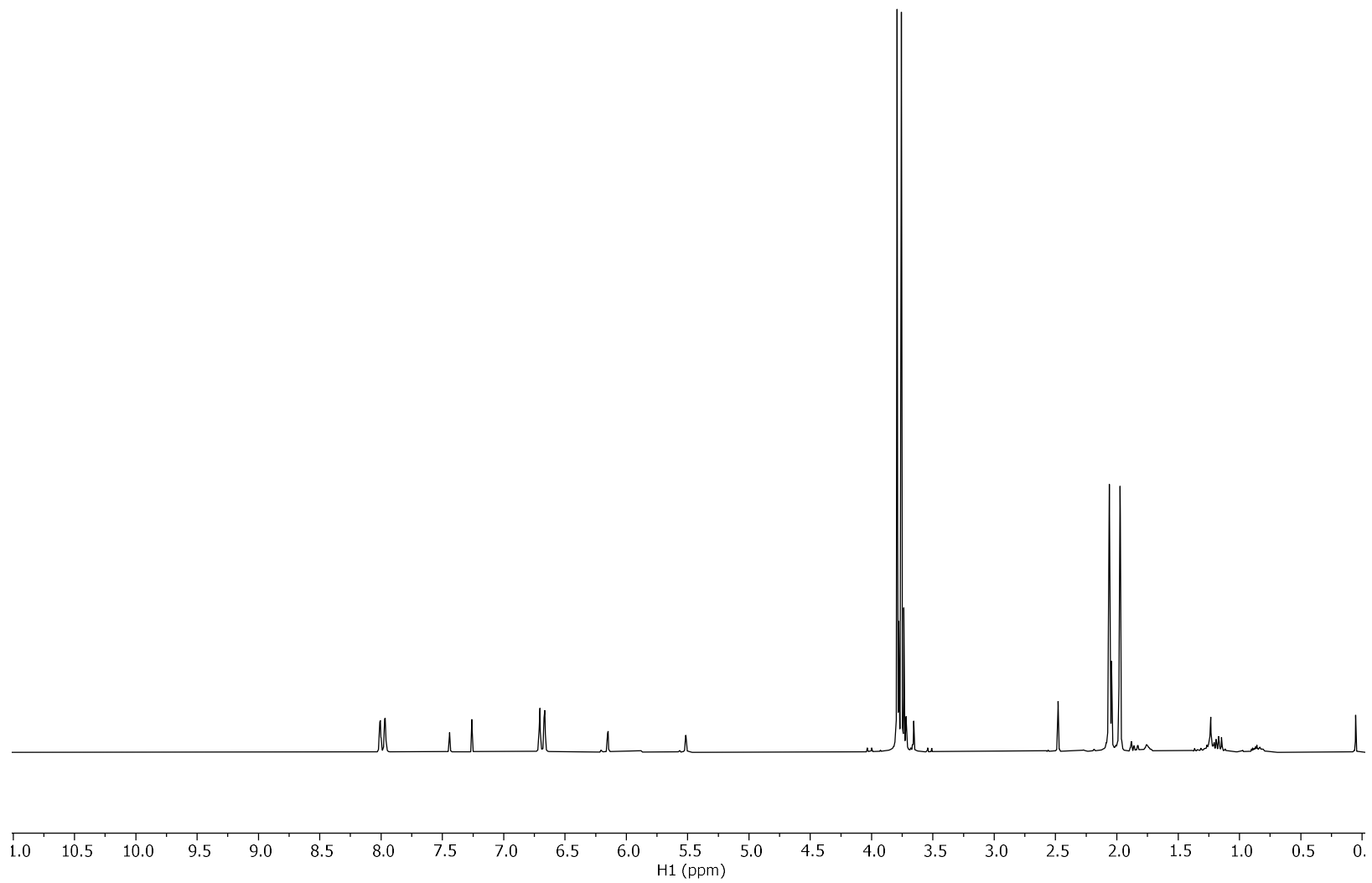
^1H NMR (CDCl_3 , 400 MHz) spectrum of **2j**.



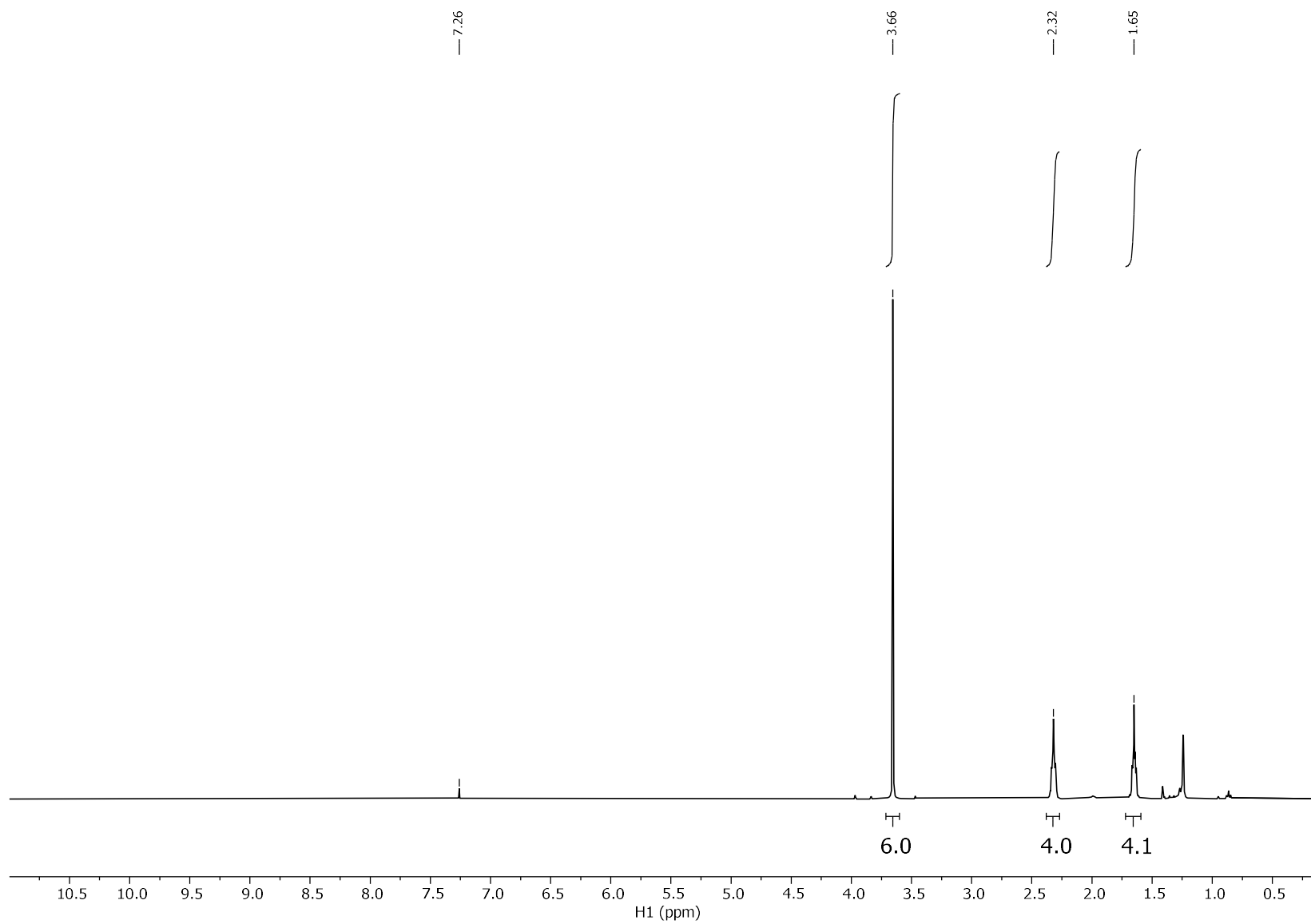
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **2j**.



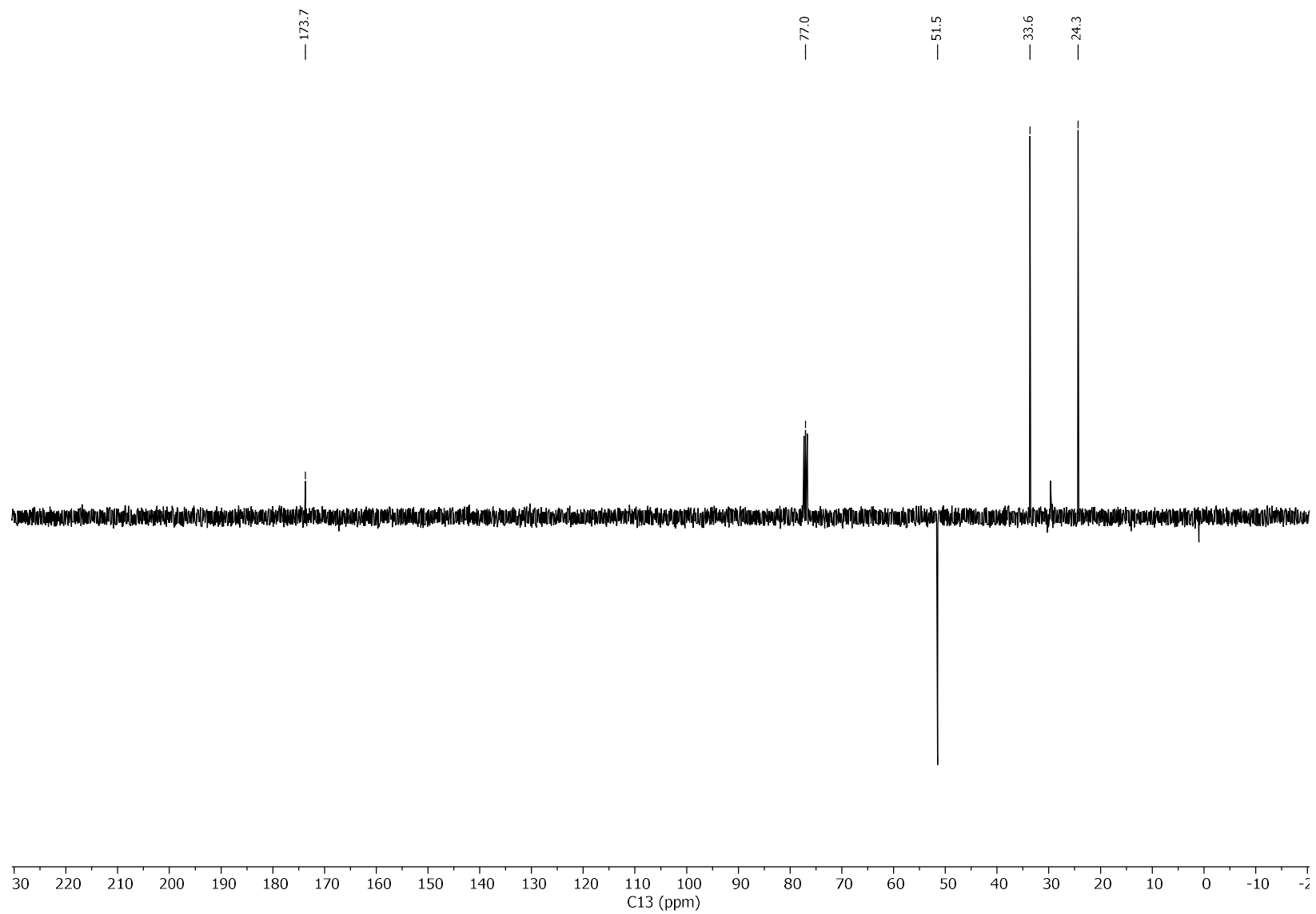
^1H NMR (CDCl_3 , 400 MHz) spectrum of **2l**.



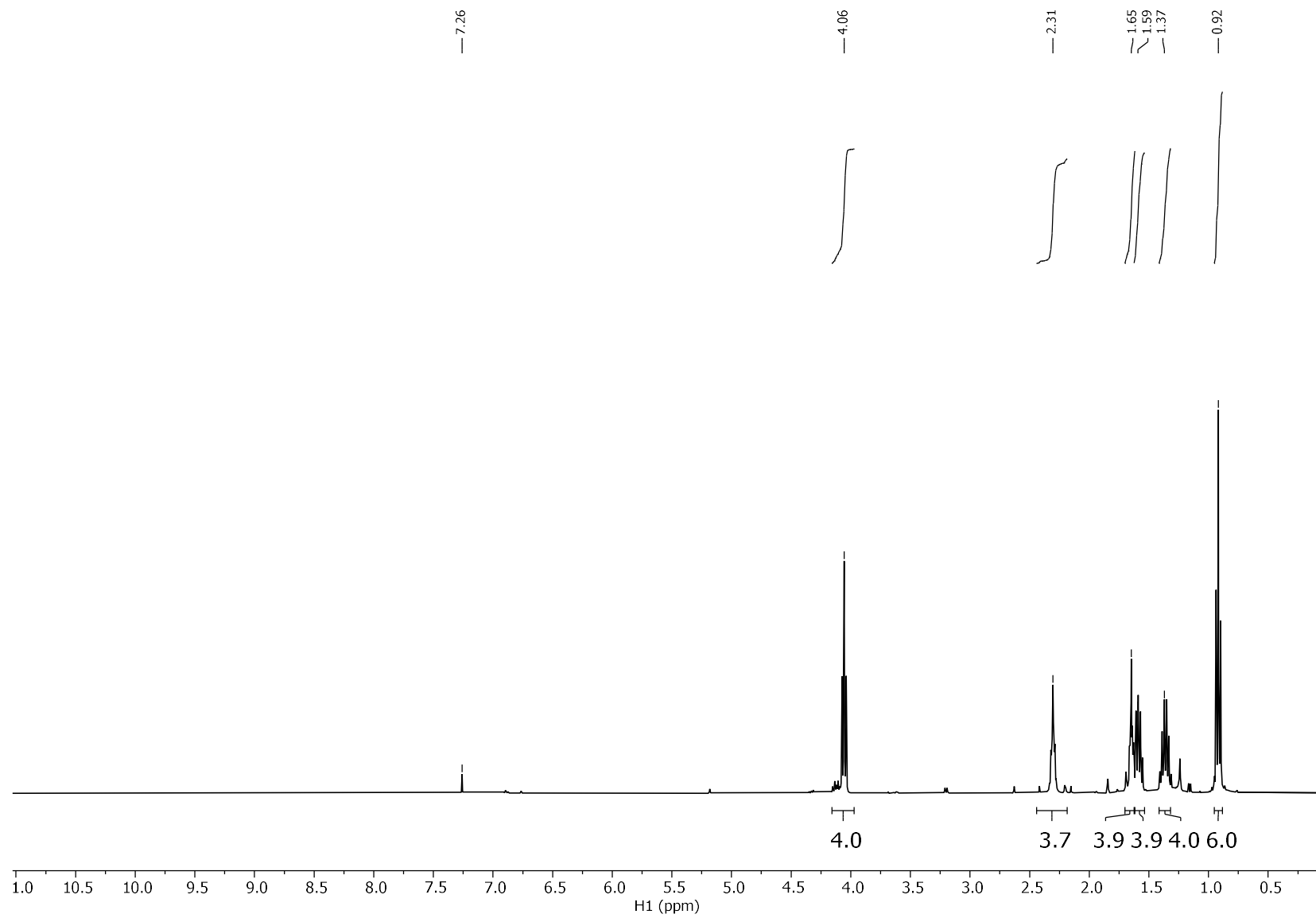
^1H NMR (CDCl_3 , 400 MHz) spectrum of **2m**.



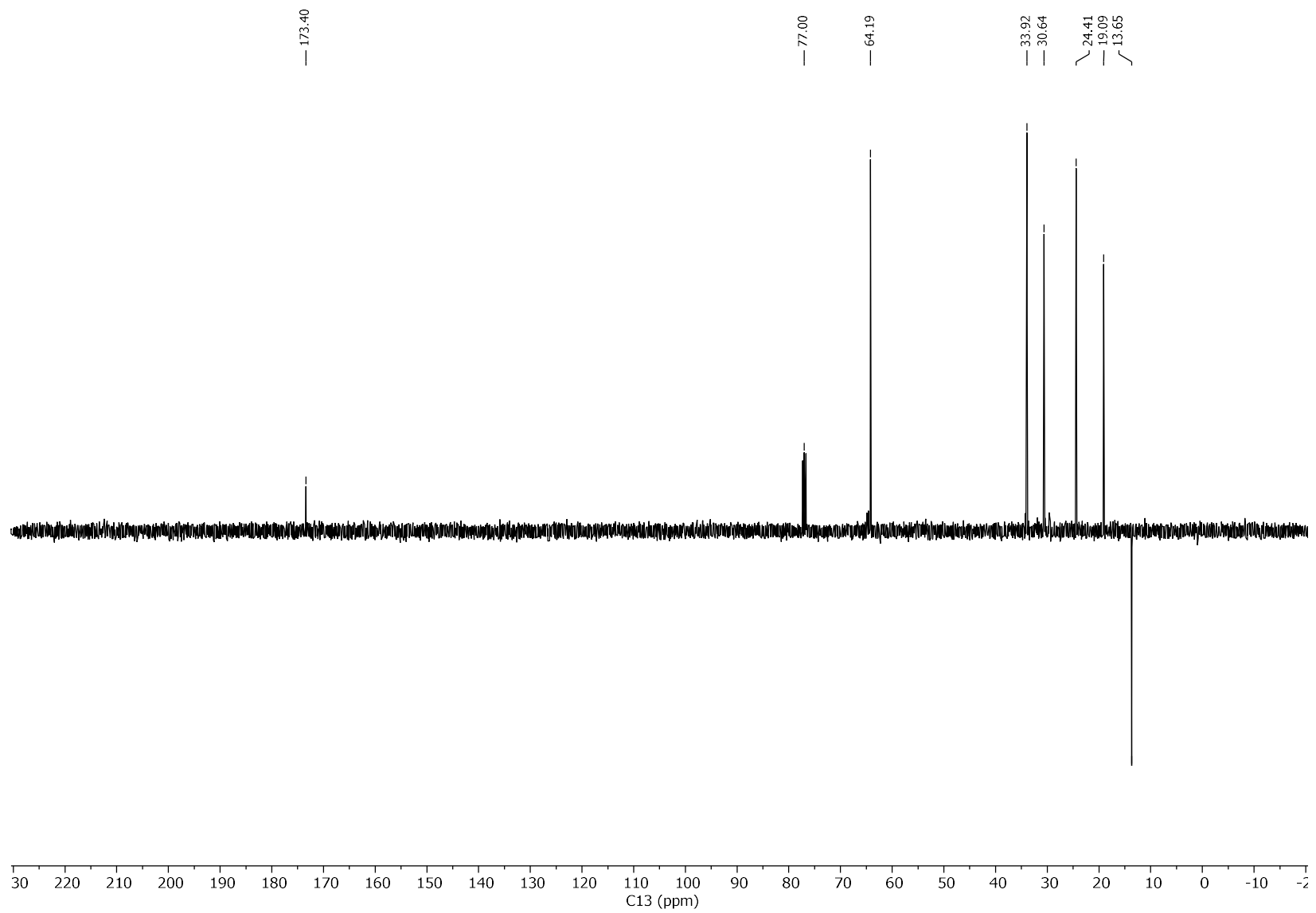
^1H NMR (CDCl_3 , 400 MHz) spectrum of **3a**.



$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) JMOD spectrum of **3a**.



^1H NMR (CDCl_3 , 400 MHz) spectrum of **3c**.



$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) JMOD spectrum of **3c**.