Supporting Information for

General Palladium-Catalyzed Cross Coupling of Cyclopropenyl Esters

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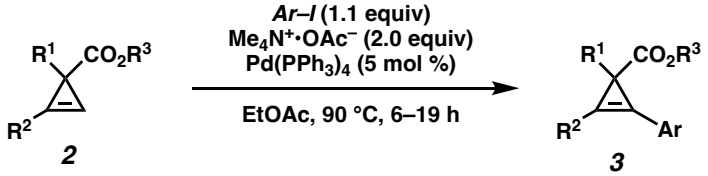
Materials and Methods

EtOAc and CH_2Cl_2 (AR grade) were purchased from Bio-Lab Ltd. and used as received. THF and Et_2O were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC), which was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV (254 nm) fluorescence quenching or by staining with $KMnO_4$ or anisaldehyde. Silica gel flash chromatography was performed using Zeochem ZEOprep 60 silica gel (40–63 μm). Automated flash chromatography was performed using a Teledyne ISCO CombiFlash Rf+ system with RediSep Rf cartridges (silica gel). NMR spectra were recorded on Bruker Avance III 400 MHz and Bruker Avance NEO 500 MHz spectrometers. Shifts are reported relative to residual $CHCl_3$ (^{1}H NMR: δ 7.26 ppm; ^{13}C NMR: δ 77.16 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). Some reported spectra include minor solvent impurities of water (δ 1.56 ppm), ethyl acetate (δ 4.12, 2.05, 1.26 ppm), methylene chloride (δ 5.30 ppm), acetone (δ 2.17 ppm), grease (δ 1.26, 0.86 ppm), and/or silicon grease (δ 0.07 ppm), which do not impact product assignments. The optical rotation of compound **3i** was measured with a UniPol L1000 polarimeter operating on the sodium D-line (589 nm), using a 50 mm path-length cell. High resolution mass spectra (HRMS) were obtained in the Technion Mass Spectrometry Lab using a Bruker maXis Impact QTof instrument in atmospheric pressure chemical ionization (APCI+) mode. Chiral HPLC was performed using an Agilent 1260 Infinity analytical HPLC system equipped with a Daicel Chiralpak AD-H column (4.6 mm x 250 mm).

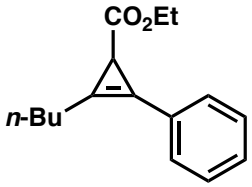
Cross-Coupling Reactions



General Procedure for Cross-Coupling

To a 4 mL glass vial equipped with a PTFE-coated magnetic stir bar were added $Pd(PPh_3)_4$ (29 mg, 0.025 mmol, 5 mol %) and Me_4NOAc (133 mg, 1.00 mmol, 2.0 equiv). The ammonium salt was weighed out and transferred rapidly due to its hygroscopic nature. In cases where the aryl iodide and/or the cyclopropene were solids at ambient temperature, the solid reagents were also

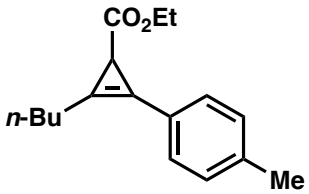
added at this stage (1.1 and 1.0 equiv, respectively). The vial was sealed with a rubber septum, evacuated, and backfilled with argon (3x). EtOAc (2 mL, sparged for 15 min with argon prior to use) was injected, followed by the appropriate aryl iodide (1.1 equiv) and cyclopropene starting material (1.0 equiv) (when the latter reagents were liquid). The rubber septum was replaced with a PTFE/silicone septum cap under a stream of argon, and the vial was heated with stirring in a 90 °C metal heating block. After the indicated time, the reaction mixture was allowed to cool to room temperature. The vial was then opened to air, and water (1.5 mL) and saturated aq. $NaHCO_3$ (0.5 mL) were added. The phases were separated, and the aqueous phase was extracted with EtOAc (3 x 1 mL). The combined organic phases were dried over Na_2SO_4, concentrated under reduced pressure, and purified as indicated.



Ethyl 2-butyl-3-phenylcycloprop-2-ene-1-carboxylate (3a)

Prepared according to the general procedure using cyclopropene **2a** and iodobenzene with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→3→18% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (102 mg, 0.417 mmol, 84% yield). All characterization data matched those reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.44 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.28 (m, 1H), 4.23 – 4.05 (m, 2H), 2.68 (td, *J* = 7.3, 1.6 Hz, 2H), 2.43 (s, 1H), 1.73 (p, *J* = 7.4 Hz, 2H), 1.51 – 1.39 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H).



Ethyl 2-butyl-3-(p-tolyl)cycloprop-2-ene-1-carboxylate (3b)

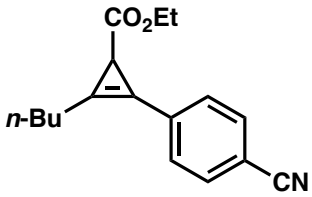
Prepared according to the general procedure using cyclopropene **2a** and 4-iodotoluene with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→3→25% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (98.2 mg, 0.380 mmol, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.33 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 4.21 – 4.07 (m,

2H), 2.66 (td, *J* = 7.2, 1.5 Hz, 2H), 2.41 (s, 1H), 2.36 (s, 3H), 1.77 – 1.66 (m, 2H), 1.51 – 1.40 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.2, 138.7, 129.5, 129.3, 124.4, 109.2, 104.6, 60.1, 29.6, 25.2, 22.5, 22.2, 21.5, 14.5, 13.9.

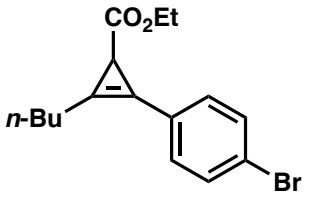
HRMS (APCI+): *m/z* calculated for $C_{17}H_{23}O_2$ $[M+H]^+$: 259.1693, found 259.1706.



Ethyl 2-butyl-3-(4-cyanophenyl)cycloprop-2-ene-1-carboxylate (3c)

Prepared according to the general procedure using cyclopropene **2a** and 4-cyano-1-iodobenzene with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→5→40% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (91.4 mg, 0.339 mmol, 68% yield). All characterization data matched those reported in the literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 – 7.64 (m, 2H), 7.56 – 7.50 (m, 2H), 4.15 (qd, *J* = 7.2, 4.3 Hz, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.48 (s, 1H), 1.77 – 1.68 (m, 2H), 1.49 – 1.40 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H).



Ethyl 2-(4-bromophenyl)-3-butylcycloprop-2-ene-1-carboxylate (3d)

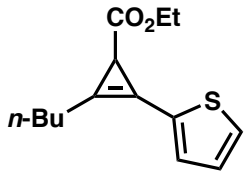
Prepared according to the general procedure using cyclopropene **2a** and 1-bromo-4-iodobenzene with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→2→25% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (121 mg, 0.374 mmol, 75% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 – 7.49 (m, 2H), 7.34 – 7.29 (m, 2H), 4.20 – 4.08 (m, 2H), 2.66 (td, *J* = 7.2, 1.3 Hz, 2H), 2.42 (s, 1H), 1.75 – 1.66 (m, 2H), 1.49 – 1.38 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 175.6, 132.0, 130.8, 126.3, 122.8, 111.8, 104.0, 60.3, 29.5, 25.3,

22.6, 22.3, 14.5, 13.9.

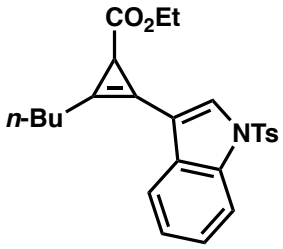
HRMS (APCI+): *m/z* calculated for $C_{16}H_{20}BrO_2$ $[M+H]^+$: 323.0641, found 323.0651.



Ethyl 2-butyl-3-(thiophen-2-yl)cycloprop-2-ene-1-carboxylate (3e)

Prepared according to the general procedure using cyclopropene **2a** and 2-iodothiophene with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→3→25% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (81.5 mg, 0.326 mmol, 65% yield). All characterization data matched those reported in the literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.10 (dd, *J* = 3.7, 1.4 Hz, 1H), 7.05 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.22 – 4.07 (m, 2H), 2.68 – 2.56 (m, 2H), 2.48 (s, 1H), 1.76 – 1.65 (m, 2H), 1.50 – 1.41 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H).



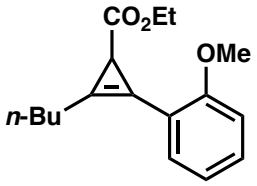
Ethyl 2-butyl-3-(1-tosyl-1*H*-indol-3-yl)cycloprop-2-ene-1-carboxylate (3f)

Prepared according to the general procedure using cyclopropene **2a** and *N*-tosyl-3-iodoindole[4] with a 17 h reaction time. Purification by automated silica gel flash chromatography (0→5→20% EtOAc/petroleum ether, 12 g "gold" column) afforded the product (130 mg, 0.297 mmol, 59% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.67 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.65 (s, 1H), 7.36 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.30 (td, *J* = 7.4, 1.1 Hz, 1H), 7.25 – 7.21 (m, 2H), 4.22 – 4.11 (m, 2H), 2.81 – 2.69 (m, 2H), 2.46 (s, 1H), 2.34 (s, 3H), 1.73 – 1.65 (m, 2H), 1.49 – 1.39 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 175.8, 145.4, 135.3, 135.0, 130.1, 129.4, 127.1, 126.4, 125.5, 123.9, 120.5, 113.8, 110.9, 108.9, 96.2, 60.4, 29.2, 25.6, 22.6, 21.7, 21.7, 14.5, 13.9.

HRMS (APCI+): *m/z* calculated for $C_{25}H_{28}NO_4S$ $[M+H]^+$: 438.1734, found 438.1739.



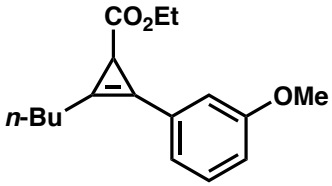
Ethyl 2-butyl-3-(2-methoxyphenyl)cycloprop-2-ene-1-carboxylate (3g)

Prepared according to the general procedure using cyclopropene **2a** and 2-iodoanisole with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→35% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (117 mg, 0.426 mmol, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.21 (m, 2H), 6.96 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 4.22 – 4.06 (m, 2H), 3.90 (s, 3H), 2.72 (td, *J* = 7.4, 2.6 Hz, 2H), 2.37 (s, 1H), 1.69 – 1.58 (m, 2H), 1.47 – 1.36 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.4, 158.2, 130.7, 130.2, 120.6, 116.6, 111.3, 110.3, 100.8, 60.1, 55.5, 29.0, 25.3, 22.5, 21.2, 14.6, 13.9.

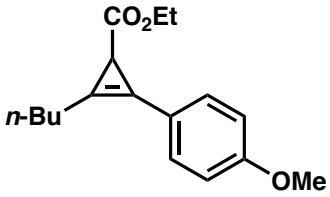
HRMS (APCI+): *m/z* calculated for $C_{17}H_{23}O_3$ $[M+H]^+$: 275.1642, found 275.1634.



Ethyl 2-butyl-3-(3-methoxyphenyl)cycloprop-2-ene-1-carboxylate (3h)

Prepared according to the general procedure using cyclopropene **2a** and 3-iodoanisole with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→3→35% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (118 mg, 0.430 mmol, 86% yield). All characterization data matched those reported in the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 2.1 Hz, 1H), 6.87 (dd, *J* = 8.3, 2.8 Hz, 1H), 4.20 – 4.07 (m, 2H), 3.83 (s, 3H), 2.71 – 2.62 (m, 2H), 2.43 (s, 1H), 1.72 (p, *J* = 7.3 Hz, 2H), 1.51 – 1.39 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H).



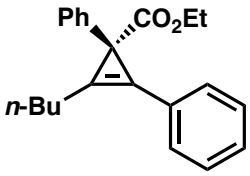
Ethyl 2-butyl-3-(4-methoxyphenyl)cycloprop-2-ene-1-carboxylate (3i)

Prepared according to the general procedure using cyclopropene **2a** and 4-iodoanisole with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→3→35% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (124 mg, 0.452 mmol, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.36 (m, 2H), 6.94 – 6.89 (m, 2H), 4.19 – 4.07 (m, 2H), 3.82 (s, 3H), 2.64 (td, *J* = 7.3, 1.4 Hz, 2H), 2.39 (s, 1H), 1.75 – 1.64 (m, 2H), 1.51 – 1.37 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.3, 160.0, 130.8, 119.9, 114.3, 107.7, 104.1, 60.1, 55.4, 29.7, 25.2, 22.6, 22.3, 14.5, 13.9.

HRMS (APCI+): *m/z* calculated for $C_{17}H_{23}O_3$ $[M+H]^+$: 275.1642, found 275.1667.



Ethyl (*S*)-2-butyl-1,3-diphenylcycloprop-2-ene-1-carboxylate (3j)

Prepared according to the general procedure using enantioenriched cyclopropene **2b** (81% ee) and iodobenzene with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→2→20% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (122 mg, 0.381 mmol, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.48 (m, 2H), 7.43 – 7.28 (m, 5H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.12 (m, 1H), 4.24 – 4.09 (m, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 1.73 (p, *J* = 7.4 Hz, 2H), 1.48 – 1.36 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H).

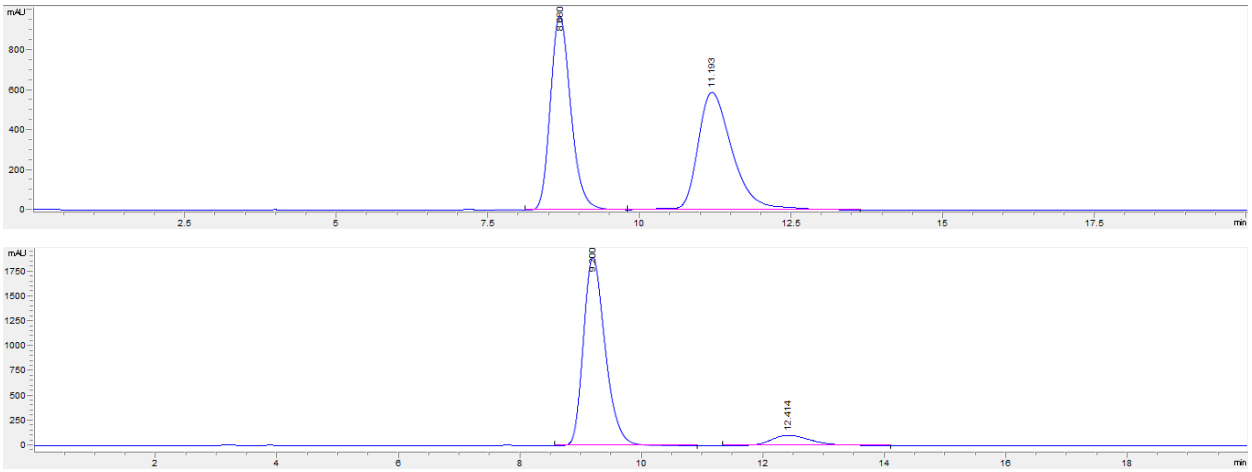
^{13}C NMR (101 MHz, $CDCl_3$): δ 174.9, 141.5, 129.4, 128.9, 128.8, 128.3, 128.1, 126.9, 126.2, 115.7, 107.8, 60.6, 35.6, 29.8, 24.7, 22.6, 14.5, 13.9.

HRMS (APCI+): *m/z* calculated for $C_{22}H_{25}O_2$ $[M+H]^+$: 321.1849, found 321.1881.

$[\alpha]_D^{20.0}$ –81.62 (*c* 1.0, $CHCl_3$).

HPLC: AD-H, *i*-PrOH/*n*-hexane = 0.6/99.4, flow rate = 1.0 mL/min, 40 °C column temperature,

λ = 245 nm. t_R: 9.2 min (major), 12.4 min (minor). 82% ee.



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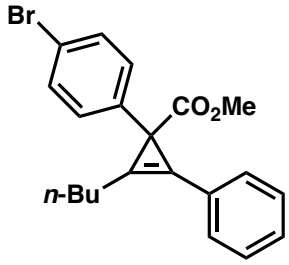
2	12.414	BB	0.6907	4583.31885	102.50298	8.8969
Totals :				5.15157e4	1991.16387	



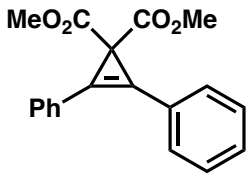
Methyl 1-(4-bromophenyl)-2-butyl-3-phenylcycloprop-2-ene-1-carboxylate (3k)

Prepared according to the general procedure using cyclopropene **2c** and iodobenzene with a 17 h reaction time. Purification by automated silica gel flash chromatography (0→2→20% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (177 mg, 0.459 mmol, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.48 (m, 2H), 7.45 – 7.39 (m, 2H), 7.39 – 7.33 (m, 3H), 7.27 – 7.21 (m, 2H), 3.69 (s, 3H), 2.72 (td, *J* = 7.3, 1.3 Hz, 2H), 1.72 (p, *J* = 7.4 Hz, 2H), 1.48 – 1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.0, 140.4, 131.2, 130.0, 129.4, 129.07, 129.09, 126.3, 120.1, 115.3, 107.3, 52.1, 34.9, 29.7, 24.6, 22.6, 13.9.

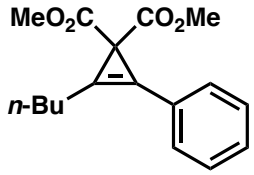
HRMS (APCI+): *m/z* calculated for $C_{21}H_{22}BrO_2$ $[M+H]^+$: 385.0798, found 385.0790.



Dimethyl 2,3-diphenylcycloprop-2-ene-1,1-dicarboxylate (3l)

Prepared according to the general procedure using cyclopropene **2d** and iodobenzene with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→70% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (112 mg, 0.363 mmol, 73% yield). All characterization data matched those reported in the literature.[6]

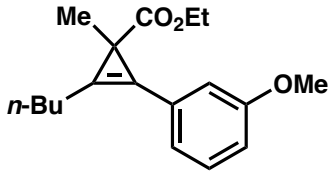
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.69 (m, 4H), 7.54 – 7.39 (m, 6H), 3.73 (s, 6H).



Dimethyl 2-butyl-3-phenylcycloprop-2-ene-1,1-dicarboxylate (3m)

Prepared according to the general procedure using cyclopropene **2e** and iodobenzene with a 6 h reaction time. Purification by automated silica gel flash chromatography (0→55% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (91.4 mg, 0.317 mmol, 63% yield). All characterization data matched those reported in the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.49 (m, 2H), 7.44 – 7.33 (m, 3H), 3.71 (s, 6H), 2.71 (t, *J* = 7.4 Hz, 2H), 1.75 (p, *J* = 7.5 Hz, 2H), 1.51 – 1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).



Ethyl 2-butyl-3-(3-methoxyphenyl)-1-methylcycloprop-2-ene-1-carboxylate (3n)

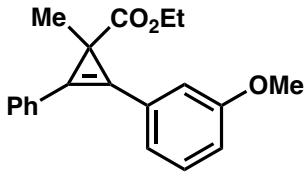
Prepared according to the general procedure using cyclopropene **2f** and 3-iodoanisole with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→3→25% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (106 mg, 0.368 mmol, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, *J* = 7.9 Hz, 1H), 7.02 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.93 (dd, *J* = 2.6, 1.5 Hz, 1H), 6.86 (ddd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 4.18 – 3.99 (m, 2H), 3.82 (s, 3H), 2.63

(t, J = 7.3 Hz, 2H), 1.74 – 1.62 (m, 2H), 1.51 – 1.39 (m, 5H), 1.17 (t, J = 7.1 Hz, 3H), 0.96 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 177.2, 159.8, 129.8, 128.7, 121.7, 116.3, 114.3, 114.2, 110.2, 60.3, 55.4, 29.8, 26.8, 24.6, 22.6, 18.7, 14.5, 13.9.

HRMS (APCI+): *m/z* calculated for $C_{18}H_{25}O_3$ $[M+H]^+$: 289.1798, found 289.1824.



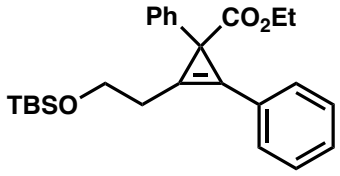
Ethyl 2-(3-methoxyphenyl)-1-methyl-3-phenylcycloprop-2-ene-1-carboxylate (3o)

Prepared according to the general procedure using cyclopropene **2g** and 3-iodoanisole with a 19 h reaction time. Purification by automated silica gel flash chromatography (0→5→35% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (117 mg, 0.379 mmol, 76% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 – 7.60 (m, 2H), 7.49 – 7.44 (m, 2H), 7.41 – 7.35 (m, 2H), 7.25 (dt, J = 7.0, 1.3 Hz, 1H), 7.14 (dd, J = 2.7, 1.6 Hz, 1H), 6.94 (ddd, J = 8.2, 2.7, 0.9 Hz, 1H), 4.12 (q, J = 7.0 Hz, 2H), 3.87 (s, 3H), 1.67 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 176.2, 160.0, 130.1, 129.8, 129.2, 129.0, 128.6, 127.3, 122.4, 114.92, 114.87, 113.4, 113.0, 60.6, 55.5, 26.8, 18.1, 14.5.

HRMS (APCI+): *m/z* calculated for $C_{20}H_{21}O_3$ $[M+H]^+$: 309.1485, found 309.1501.



Ethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-1,3-diphenylcycloprop-2-ene-1-carboxylate (3p)

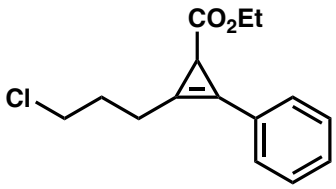
Prepared according to the general procedure using cyclopropene **2h** and iodobenzene with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→2.5→12% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (128 mg, 0.303 mmol, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.55 (m, 2H), 7.43 – 7.30 (m, 5H), 7.26 – 7.22 (m, 2H), 7.20 – 7.14 (m, 1H), 4.24 – 4.10 (m, 2H), 4.02 – 3.90 (m, 2H), 2.95 (t, J = 6.9 Hz, 2H), 1.20 (t, J

= 7.1 Hz, 3H), 0.88 (s, 9H), 0.06 (d, *J* = 5.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.7, 141.3, 129.6, 129.0, 128.8, 128.2, 128.1, 126.7, 126.2, 112.4, 108.9, 60.9, 60.7, 35.3, 29.0, 26.0, 18.4, 14.5, –5.2.

HRMS (APCI+): *m/z* calculated for $C_{26}H_{35}O_3Si$ $[M+H]^+$: 423.2350, found 423.2349.



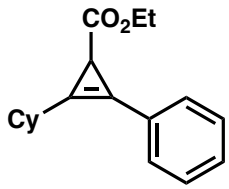
Ethyl 2-(3-chloropropyl)-3-phenylcycloprop-2-ene-1-carboxylate (3q)

Prepared according to the general procedure using cyclopropene **2i** and iodobenzene with a 19 h reaction time. Purification by automated silica gel flash chromatography (0→50% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (51.3 mg, 0.194 mmol, 39% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 – 7.44 (m, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.32 (m, 1H), 4.21 – 4.08 (m, 2H), 3.72 – 3.60 (m, 2H), 2.98 – 2.79 (m, 2H), 2.46 (s, 1H), 2.20 (p, *J* = 6.7 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 175.7, 129.5, 129.1, 128.9, 126.8, 108.6, 106.4, 60.4, 44.2, 30.3, 22.9, 22.3, 14.5.

HRMS (APCI+): *m/z* calculated for $C_{15}H_{18}ClO_2$ $[M+H]^+$: 265.0990, found 265.0999.



Ethyl 2-cyclohexyl-3-phenylcycloprop-2-ene-1-carboxylate (3r)

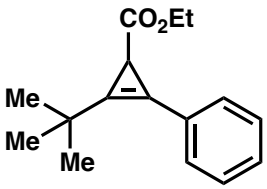
Prepared according to the general procedure using cyclopropene **2j** and iodobenzene with a 15 h reaction time. Purification by automated silica gel flash chromatography (0→2.5→11% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (92.2 mg, 0.341 mmol, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.0 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.34 – 7.27 (m, 1H), 4.22 – 4.07 (m, 2H), 2.74 (td, *J* = 9.8, 5.2 Hz, 1H), 2.44 (s, 1H), 2.11 – 1.97 (m, 2H), 1.81 – 1.70 (m, 2H), 1.69 – 1.62 (m, 1H), 1.61 – 1.49 (m, 2H), 1.46 – 1.37 (m, 2H), 1.36 – 1.28 (m, 1H),

1.24 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 176.2, 129.6, 128.74, 128.65, 127.3, 114.2, 103.9, 60.2, 35.0, 31.0, 30.9, 26.1, 25.55, 25.49, 21.7, 14.5.

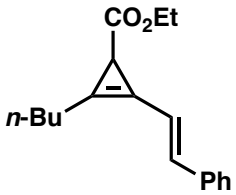
HRMS (APCI+): *m/z* calculated for $C_{18}H_{23}O_2$ $[M+H]^+$: 271.1693, found 271.1695.



Ethyl 2-(*tert*-butyl)-3-phenylcycloprop-2-ene-1-carboxylate (3s)

Prepared according to the general procedure using cyclopropene **2k** and iodobenzene with a 15 h reaction time. Purification twice by automated silica gel flash chromatography (0→2.5→11% Et_2O/petroleum ether, then 0→100% polar component/petroleum ether where the polar component is 2% EtOAc/CH_2Cl_2, 12 g "gold" column) afforded the product (98.2 mg, 0.402 mmol, 80% yield). All characterization data matched those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.46 (m, 2H), 7.42 – 7.35 (m, 2H), 7.35 – 7.29 (m, 1H), 4.24 – 4.05 (m, 2H), 2.45 (s, 1H), 1.32 (s, 9H), 1.23 (t, J = 7.1 Hz, 3H).

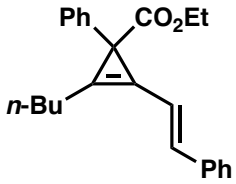


Ethyl (*E*)-2-butyl-3-styrylcycloprop-2-ene-1-carboxylate (3t)

To a 7 mL flame-dried reaction tube with a PTFE needle-valve stopcock and containing a PTFE magnetic stir bar were added Ag_2O (116 mg, 0.500 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (29 mg, 0.025 mmol, 5 mol %). The tube was evacuated and backfilled with argon (3x). THF (5.0 mL, 0.1 M) was added, followed immediately by (*E*)-β-iodostyrene[9,10] (0.10 mL, 0.75 mmol, 1.5 equiv) and cyclopropene **2a** (88 wt%, 95.6 mg, 0.500 mmol, 1.0 equiv). The reaction tube was sealed and heated with stirring in a 50 °C metal vial block for 20 h. Then, the reaction mixture was allowed to cool to ambient temperature and filtered through a PTFE syringe filter, which was subsequently rinsed with Et_2O. The filtrate was concentrated under reduced pressure and purified by automated silica gel flash chromatography (0→12% Et_2O/petroleum ether, 12 g "gold" column) to afford the

product (104 mg, 0.385 mmol, 77% yield). All characterization data matched those reported in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.41 (m, 2H), 7.37 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 6.90 (d, *J* = 15.6 Hz, 1H), 6.71 (d, *J* = 15.6 Hz, 1H), 4.21 – 4.06 (m, 2H), 2.59 (t, *J* = 7.3 Hz, 2H), 2.32 (s, 1H), 1.68 – 1.59 (m, 2H), 1.47 – 1.37 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H).



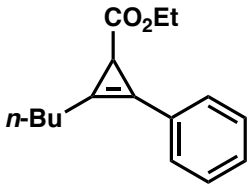
Ethyl (*E*)-2-butyl-1-phenyl-3-styrylcycloprop-2-ene-1-carboxylate (3u)

To a 7 mL flame-dried reaction tube with a PTFE needle-valve stopcock and containing a PTFE magnetic stir bar were added Ag_2O (116 mg, 0.500 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (29 mg, 0.025 mmol, 5 mol %). The tube was evacuated and backfilled with argon (3x). THF (5.0 mL, 0.1 M) was added, followed immediately by (*E*)-β-iodostyrene[9,10] (0.10 mL, 0.75 mmol, 1.5 equiv) and cyclopropene **rac-2b** (122 mg, 0.500 mmol, 1.0 equiv). The reaction tube was sealed and heated with stirring in a 50 °C metal vial block for 24 h. Then, the reaction mixture was allowed to cool to ambient temperature and filtered through a PTFE syringe filter, which was subsequently rinsed with Et_2O. The filtrate was concentrated under reduced pressure and purified by automated silica gel flash chromatography (0→20% Et_2O/petroleum ether, 12 g "gold" column) to afford the product (123 mg, 0.355 mmol, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.30 (m, 4H), 7.29 – 7.23 (m, 3H), 7.20 – 7.14 (m, 1H), 6.94 (d, *J* = 15.8 Hz, 1H), 6.85 (d, *J* = 15.8 Hz, 1H), 4.26 – 4.10 (m, 2H), 2.64 (t, *J* = 7.4 Hz, 2H), 1.63 (p, *J* = 7.3 Hz, 2H), 1.46 – 1.33 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.93 – 0.87 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.7, 141.4, 137.6, 136.3, 128.8, 128.7, 128.4, 128.1, 127.1, 126.1, 117.4, 112.3, 106.4, 60.6, 35.3, 29.4, 24.8, 22.5, 14.5, 13.9.

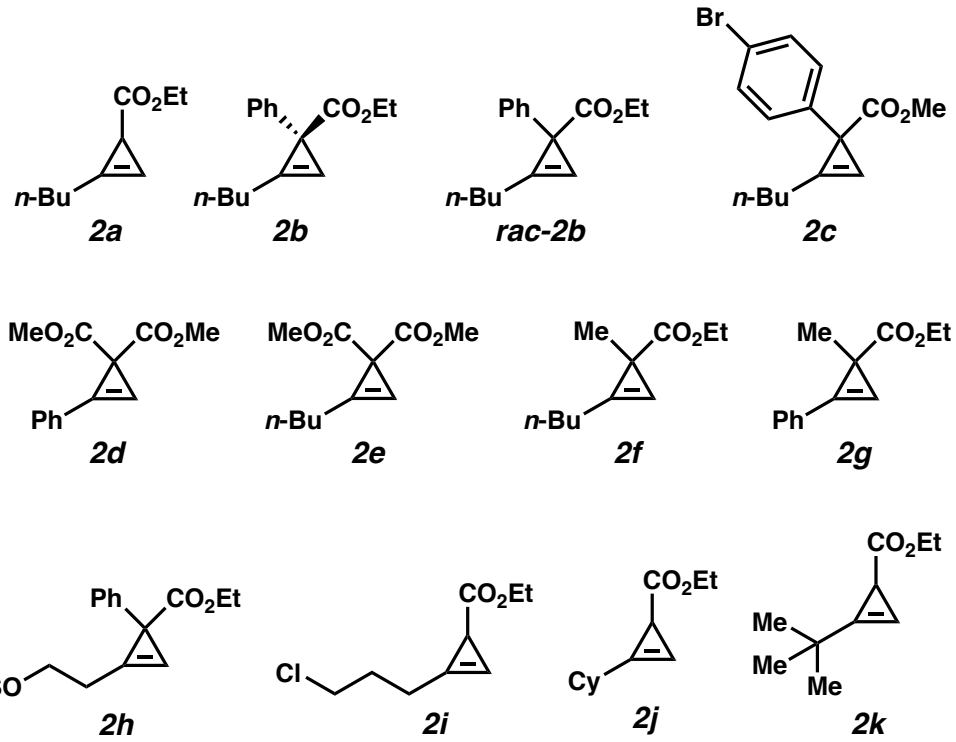
HRMS (APCI+): *m/z* calculated for $C_{24}H_{27}O_2$ $[M+H]^+$: 347.2006, found 347.1997.



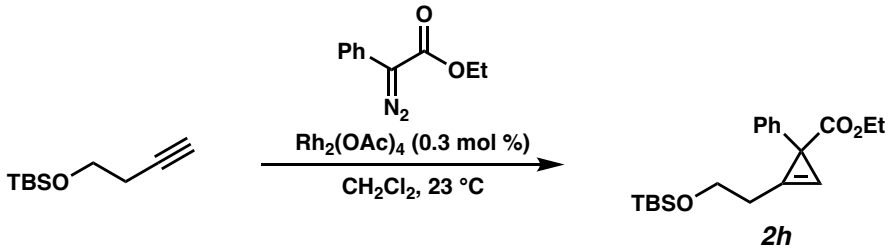
Large-Scale Preparation of Cyclopropene 3a

A 250 mL Schlenk vessel with a PTFE needle-valve stopcock and containing a PTFE magnetic stir bar was charged with $Pd(PPh_3)_4$ (580 mg, 0.500 mmol, 5 mol %) and Me_4NOAc (2.66 g, 20.0 mmol, 2.0 equiv). The vessel was evacuated and purged with argon (3x). EtOAc (40 mL, sparged for 15 min with argon prior to use) was added, followed by iodobenzene (1.2 mL, 11.0 mmol, 1.1 equiv) and cyclopropene **2a** (88 wt%, 1.91 g, 10.0 mmol, 1.0 equiv). The vessel was sealed and stirred at 90 °C in an oil bath for 18 h. The reaction mixture was then allowed to cool to ambient temperature and washed with a mixture of saturated aqueous $NaHCO_3$ (40 mL) and water (20 mL). The aqueous phase was extracted with EtOAc (3 x 15 mL), and the combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by automated silica gel flash chromatography (0→3→25% Et_2O/petroleum ether, 80 g column) afforded the product (1.98 g, 8.10 mmol, 81% yield) as a colorless oil. All characterization data matched those reported above for **3a** and in the literature.[2]

Preparation of Starting Materials



Cyclopropenes **2a**,[11] **2b**,[12] **2c**,[13] **2d**,[14] **2e**,[14] **2f**,[2] **2g**,[15] **2i**,[16] **2j**,[16] and **2k**[17] were prepared by literature procedures.



Ethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-1-phenylcycloprop-2-ene-1-carboxylate (2h)

To a 25 mL round-bottom flask containing a PTFE-coated magnetic stir bar was added $Rh_2(OAc)_4$ (6.6 mg, 0.015 mmol, 0.3 mol %). The flask was purged with argon, and CH_2Cl_2 (4 mL) and (but-3-yn-1-yloxy)(*tert*-butyl)dimethylsilane[18] (1.84 g, 10.0 mmol, 2.0 equiv) were added. Then, a solution of ethyl diazo(phenyl)acetate[19] (951 mg, 5.00 mmol, 1.0 equiv) in CH_2Cl_2 (3.5 mL) was added dropwise with stirring over 15 h via syringe pump. The reaction mixture was then concentrated under reduced pressure and purified twice by automated silica gel flash chromatography (0→20% Et_2O/petroleum ether, 24 g column) to afford the product (458 mg, 1.32 mmol, 26% yield) as a thick, colorless oil.

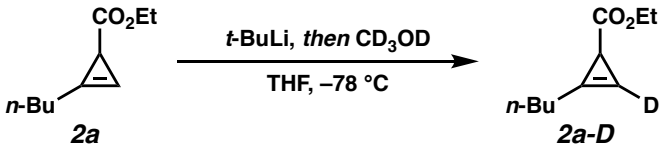
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.27 (m, 4H), 7.22 – 7.16 (m, 1H), 6.73 (t, J = 1.5 Hz, 1H),

4.15 (qd, *J* = 7.1, 1.5 Hz, 2H), 3.83 (t, *J* = 6.9 Hz, 2H), 2.79 (td, *J* = 7.0, 1.6 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.04 (d, *J* = 4.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 175.4, 141.8, 128.3, 128.1, 126.3, 118.1, 98.4, 60.8, 60.5, 32.8, 28.6, 26.0, 18.4, 14.5, –5.3.

HRMS (APCI+): *m/z* calculated for $C_{20}H_{31}O_3Si$ $[M+H]^+$: 347.2037, found 347.2057.

Kinetic Isotope Effect Determination



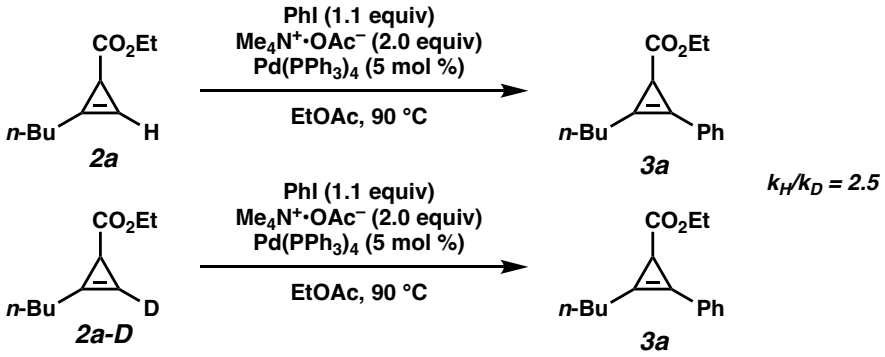
Ethyl 2-butylcycloprop-2-ene-1-carboxylate-3-d (2a-D)

To a flame-dried 50 mL round-bottom flask containing a PTFE-coated magnetic stir bar was added cyclopropene **2a** (88 wt%, 956 mg, 5.00 mmol, 1.0 equiv). The flask was sealed with a rubber septum and evacuated and backfilled with argon (3x). THF (17 mL) was added, and the resulting solution was cooled to –78 °C in a dry ice/acetone bath. *t*-BuLi (3.7 mL, 1.47 M in pentane, 5.5 mmol, 1.1 equiv) was then added dropwise over 8 min. After stirring for an additional 3 min, CD_3OD (0.41 mL, 10 mmol, 2.0 equiv) was rapidly added, followed by saturated aq. $NaHCO_3$ (10 mL). The resulting mixture was diluted with water and extracted with Et_2O (3 x 15 mL). The combined organic extracts were dried over Na_2SO_4, concentrated under reduced pressure, and purified by automated silica gel flash chromatography (0→25% Et_2O/petroleum ether, 80 g column) to afford the product (299 mg, 1.77 mmol, 35% yield, 97% D by ^{1}H NMR).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.19 – 4.05 (m, 2H), 2.50 (t, *J* = 7.3 Hz, 2H), 2.12 (s, 1H), 1.59 – 1.55 (m, 2H), 1.44 – 1.34 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 176.8, 115.5, 94.0, 93.8, 93.5, 60.3, 28.9, 24.8, 22.3, 19.7, 14.5, 13.9.

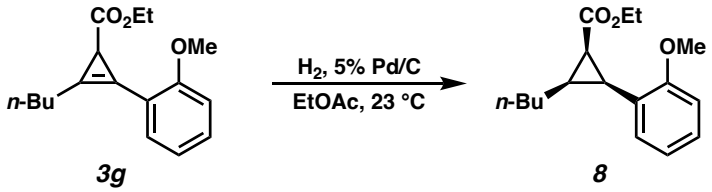
HRMS (APCI+): *m/z* calculated for $C_{10}H_{16}DO_2$ $[M+H]^+$: 170.1286, found 170.1289.



Procedure for KIE Determination

To two parallel 7 mL flame-dried reaction tubes with PTFE needle-valve stopcocks and containing PTFE magnetic stir bars were added $Pd(PPh_3)_4$ (29 mg, 0.025 mmol, 5 mol %), Me_4NOAc (133 mg, 1.00 mmol, 2.0 equiv), and 1,3,5-trimethoxybenzene (28.0 mg, 0.167 mmol, 0.33 equiv). The tubes were evacuated and backfilled with argon (3x). EtOAc (2 mL, sparged for 15 min with argon prior to use) was injected, followed by iodobenzene (62 µL, 0.55 mmol, 1.1 equiv) and either **2a** or **2a-D** (0.500 mmol, 1.0 equiv). The tubes were sealed and heated with stirring in a 90 °C metal heating block. ~50 µL aliquots were taken at reaction times of 20 min, 49 min, 81 min, and 112 min. The time during which the reaction mixtures were cooled to ambient temperature to enable aliquoting was not counted in the overall reaction time. Each reaction aliquot was concentrated under reduced pressure, taken up in $CDCl_3$, and passed through a PTFE syringe filter, then subjected to ^1H NMR analysis. The product yield and amount of unreacted starting material were determined relative to the 1,3,5-trimethoxybenzene internal standard. The natural log of the fraction of unreacted starting material was plotted against the reaction time for both reactions, revealing a linear relationship, and taking the ratio of the slopes of the resulting lines gave $k_H/k_D = 2.5$.

Derivatization of Cross-Coupling Products



Ethyl 2-butyl-3-(2-methoxyphenyl)cyclopropane-1-carboxylate (8)

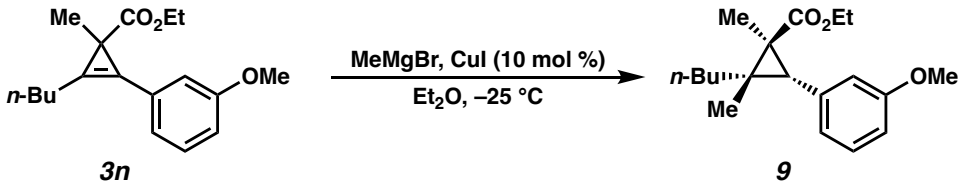
A 30 mL glass vial containing cyclopropene **3g** (117 mg, 0.426 mmol, 1.0 equiv) was charged with a PTFE-coated magnetic stir bar and EtOAc (4.3 mL), covered with a rubber septum, and

purged with argon. 5% Pd/C (117 mg, 5 wt% Pd) was added under a flow of argon, whereafter the vial was purged with H_2 from a balloon and stirred under an H_2 atmosphere. After 28 min, the reaction mixture was filtered through a PTFE syringe filter, which was subsequently rinsed with EtOAc. The filtrate was concentrated under reduced pressure. A crude ^{1}H NMR spectrum was measured, indicating product formation in >20:1 dr. Purification by automated silica gel flash chromatography (0→40% Et_2O/petroleum ether, 12 g "gold" column) afforded the product (80.4 mg, 0.291 mmol, 68% yield, >20:1 dr) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.16 (m, 2H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 4.00 (qd, *J* = 7.1, 1.3 Hz, 2H), 3.76 (s, 3H), 2.40 (t, *J* = 8.6 Hz, 1H), 2.13 – 2.04 (m, 1H), 1.84 – 1.75 (m, 1H), 1.72 – 1.58 (m, 2H), 1.38 – 1.25 (m, 4H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.4, 159.0, 131.3, 127.9, 124.1, 120.0, 109.9, 59.6, 55.1, 32.3, 26.0, 24.5, 23.9, 22.7, 22.4, 14.4, 14.3.

HRMS (APCI+): *m/z* calculated for $C_{17}H_{25}O_3$ $[M+H]^+$: 277.1798, found 277.1790.



3n ***9***

Ethyl 2-butyl-3-(3-methoxyphenyl)-1,2-dimethylcyclopropane-1-carboxylate (9)

A Schlenk tube was charged with cyclopropene **3n** (106 mg, 0.368 mmol, 1.0 equiv). Toluene (~1 mL) was added and removed under reduced pressure in order to azeotropically remove traces of water. CuI (7.0 mg, 0.037 mmol, 0.1 equiv) and a PTFE-coated magnetic stir bar were then added to the tube, which was subsequently sealed with a rubber septum and evacuated and backfilled with argon (3x). Et_2O (3.7 mL) was added, and the reaction mixture was cooled in a –25 °C acetone bath. MeMgBr in Et_2O (0.25 mL, 3.0 M, 0.74 mmol, 2.0 equiv) was added dropwise over 7 min with stirring, and the reaction mixture was stirred for an additional 2 hours at –25 °C. Then, saturated aq. NH_4Cl (4 mL) and 28% aq. NH_4OH were added, and the mixture was extracted with Et_2O (3x5 mL). The combined organic phases were dried over Na_2SO_4, concentrated under reduced pressure, and purified by automated silica gel flash chromatography (0→25% Et_2O/petroleum ether, 12 g "gold" column) to afford the product (73.1 mg, 0.240 mmol, 65% yield,

>20:1 dr) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.9 Hz, 1H), 6.79 – 6.71 (m, 2H), 6.71 – 6.67 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.77 (s, 1H), 1.53 (ddd, *J* = 14.5, 9.8, 4.7 Hz, 2H), 1.32 – 1.23 (m, 9H), 1.22 (s, 3H), 1.14 (td, *J* = 14.3, 4.8 Hz, 1H), 0.87 (t, *J* = 7.1 Hz, 3H).

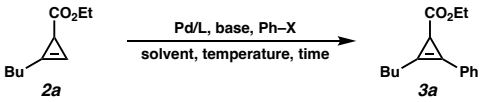
^{13}C NMR (101 MHz, $CDCl_3$): δ 174.7, 159.5, 138.1, 129.2, 123.2, 116.5, 111.7, 60.7, 55.3, 37.6, 33.2, 32.6, 31.4, 28.8, 23.4, 20.3, 14.6, 14.3, 13.4.

HRMS (APCI+): *m/z* calculated for $C_{19}H_{29}O_3$ $[M+H]^+$: 305.2111, found 305.2122.

Additional Optimization Details

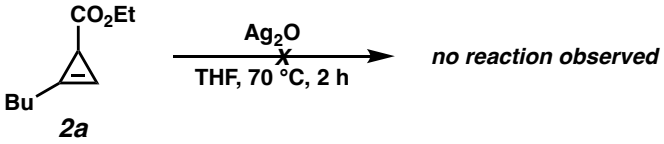
General Procedure for Reaction Optimization

To either a 7 mL flame-dried reaction tube with a PTFE needle-valve stopcock or a 4 mL glass vial, containing a PTFE magnetic stir bar, were added the appropriate palladium source and other appropriate solid reagents. The reaction vessel was evacuated and backfilled with argon (3x). The solvent, phenyl halide or triflate, and then cyclopropene **2a** (0.2–0.3 mmol) were added, and the reaction vessel was sealed and stirred at the indicated temperature for the indicated reaction time. Ag_2O/Cu_2O-mediated reactions were filtered through a PTFE syringe filter and concentrated under reduced pressure, while other reactions were subjected to an extractive workup, dried over magnesium sulfate, and concentrated under reduced pressure. Conversion and yield were determined relative to a 1,3,5-trimethoxybenzene internal standard.



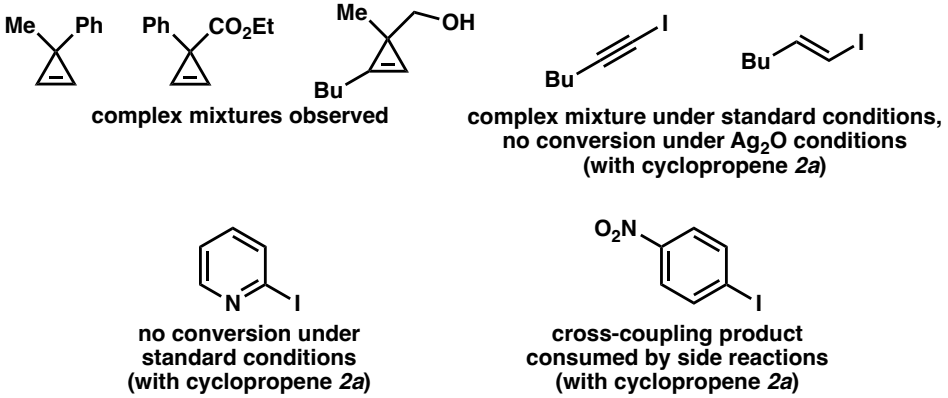
entry	Pd/L	base	additive	Ph–X	solvent	temperature	time	% RSM	% yield
1	$Pd(OAc)_2$ (14.5 mol %)	K_2CO_3	--	PhI	DMF	30 °C	3 d	1%	1%
2	$Pd(PPh_3)_4$ (14.5 mol %)	DIPEA	AgI (29 mol %)	PhI	DMF	23 °C	17 h	n.d.	--
3	$Pd(PPh_3)_4$ (14.5 mol %)	DIPEA	AgI (29 mol %)	PhI	THF	70 °C	17 h	n.d.	--
4	$Pd(PPh_3)_4$ (14.5 mol %)	Cs_2CO_3	AgI (29 mol %)	PhI	THF	70 °C	23 h	n.d.	--
5	$Pd(PPh_3)_4$ (7.2 mol %)	AgOAc	--	PhI	THF	70 °C	18 h	--	39%
6	$Pd(PPh_3)_4$ (7.2 mol %)	Ag_2O	--	PhI	THF	70 °C	2 h	--	84%
7	$Pd(PPh_3)_4$ (7.2 mol %)	Ag_2O	--	PhI	THF	23 °C	18 h	51%	28%
8	$Pd(PPh_3)_4$ (7.2 mol %)	Cu_2O	--	PhI	THF	70 °C	23 h	n.d.	--
9	$Pd(PPh_3)_4$ (7.2 mol %)	Ag_2O	--	PhBr	THF	70 °C	4 h	--	--
10	Pd_2dba_3 (3.6 mol %), JohnPhos (14.5 mol %)	Ag_2O	--	PhI	THF	70 °C	17 h	--	4%
11	$Pd(PPh_3)_4$ (7.2 mol %)	TBAF	--	PhI	THF	70 °C	21 h	42%	22%
12	$Pd(PPh_3)_4$ (7.2 mol %)	KOPh	--	PhI	THF	70 °C	16 h	20%	33%
13	$Pd(PPh_3)_4$ (7.2 mol %)	CsOAc	--	PhI	THF	70 °C	17 h	23%	20%
14	$Pd(PPh_3)_4$ (7.2 mol %)	Me_4NOAc	AgI (29 mol %)	PhI	THF	70 °C	16 h	19%	68%
15	$Pd(PPh_3)_4$ (7.2 mol %)	Me_4NOAc	AgI (29 mol %)	PhI	THF	70 °C	3 d	--	84%
16	$Pd(PPh_3)_4$ (5.7 mol %)	Me_4NOAc	AgI (23 mol %)	PhI	THF	90 °C	17 h	--	84%
17	$Pd(PPh_3)_4$ (5.7 mol %)	Me_4NOAc	AgI (23 mol %)	PhI	EtOAc	90 °C	17 h	--	85%
18	$Pd(PPh_3)_4$ (5.7 mol %)	TBAOAc	AgI (23 mol %)	PhI	EtOAc	90 °C	17 h	--	51%
19	$Pd(PPh_3)_4$ (5.7 mol %)	Me_4NOAc	--	PhI	EtOAc	90 °C	19 h	--	86%
20	$Pd(PPh_3)_4$ (7.2 mol %)	Me_4NOAc + KOPh	--	PhI	EtOAc	70 °C	15 h	35%	41%
21	$Pd(PPh_3)_4$ (2.8 mol %)	Me_4NOAc	--	PhI	EtOAc	90 °C	19 h	--	86%
22	$Pd(PPh_3)_4$ (1.1 mol %)	Me_4NOAc	--	PhI	EtOAc	90 °C	15 h	--	77%
23	$Pd(OAc)_2$ (1.1 mol %), PPh_3 (4.5 mol%)	Me_4NOAc	--	PhI	EtOAc	90 °C	15 h	--	60%
24	$Pd(OAc)_2$ (1.1 mol %), $P(2\text{-furyl})_3$ (4.5 mol%)	Me_4NOAc	--	PhI	EtOAc	90 °C	15 h	--	57%
25	$Pd(OAc)_2$ (1.1 mol %)	Me_4NOAc	--	PhI	EtOAc	90 °C	15 h	--	--
26	PEPPSI-IPr (1.1 mol %)	Me_4NOAc	--	PhI	EtOAc	90 °C	15 h	9%	5%
27	$Pd(dppf)Cl_2$ (1.1 mol %)	Me_4NOAc	--	PhI	EtOAc	90 °C	15 h	--	35%
28	$Pd(PPh_3)_4$ (5.7 mol %)	Me_4NOAc	AgI (23 mol %)	PhBr	EtOAc	90 °C	5 h	--	6%
29	Pd_2dba_3 (2.8 mol %), $P(t\text{-Bu})_3{\cdot}HBF_4$ (11.4 mol %)	Me_4NOAc	--	PhI	THF	70 °C	25 h	--	20%
30	$Pd(PPh_3)_4$ (5 mol %)	Me_4NOAc	--	PhBr	EtOAc	90 °C	19 h	--	--
31	$Pd(PPh_3)_4$ (5 mol %)	Me_4NOAc	--	PhOTf	EtOAc	90 °C	19 h	--	--

Control Experiment Demonstrating that Ag-Mediated C–H Activation is Inoperative



To a 7 mL flame-dried reaction tube with a PTFE needle-valve stopcock and containing a PTFE magnetic stir bar was added Ag_2O (69.5 mg, 0.300 mmol, 1.0 equiv). The vessel was evacuated and backfilled with argon (3x). Then, THF (3.0 mL) and cyclopropene **2a** (88 wt%, 57.4 mg, 0.300 mmol, 1.0 equiv) were added, and the vessel was sealed and heated with stirring in a 70 °C metal vial block for 2 hours. The reaction mixture was then allowed to cool to ambient temperature. CD_3OD (0.5 mL) was added, and the mixture was passed through a PTFE syringe filter and concentrated under reduced pressure. 1,3,5-trimethoxybenzene (16.8 mg, 0.100 mmol, 0.33 equiv) and $CDCl_3$ were then added, and the ^1H NMR spectrum of the resulting mixture was measured. No consumption or deuteration of cyclopropene **2a** was observed.

Limitations



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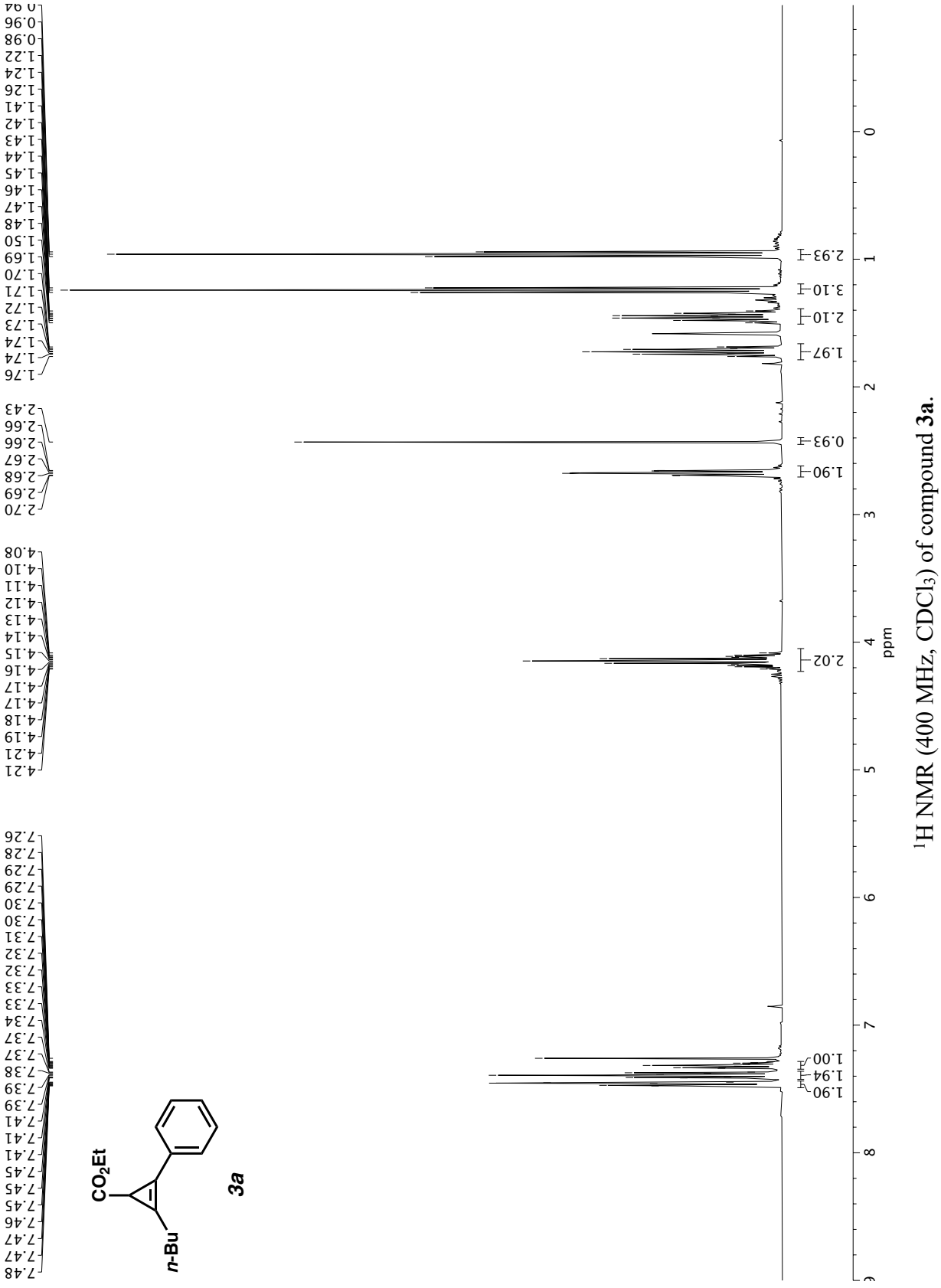
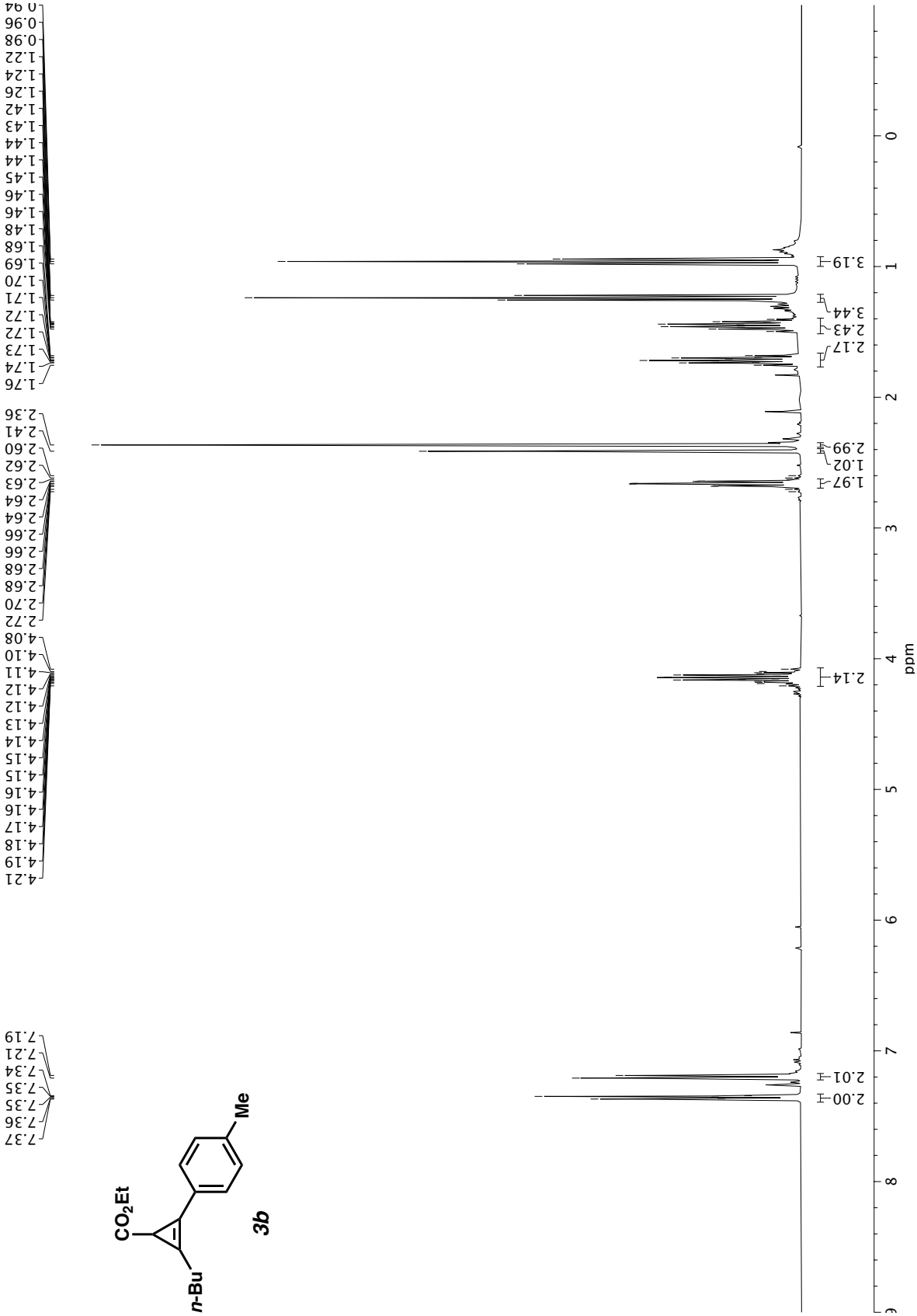
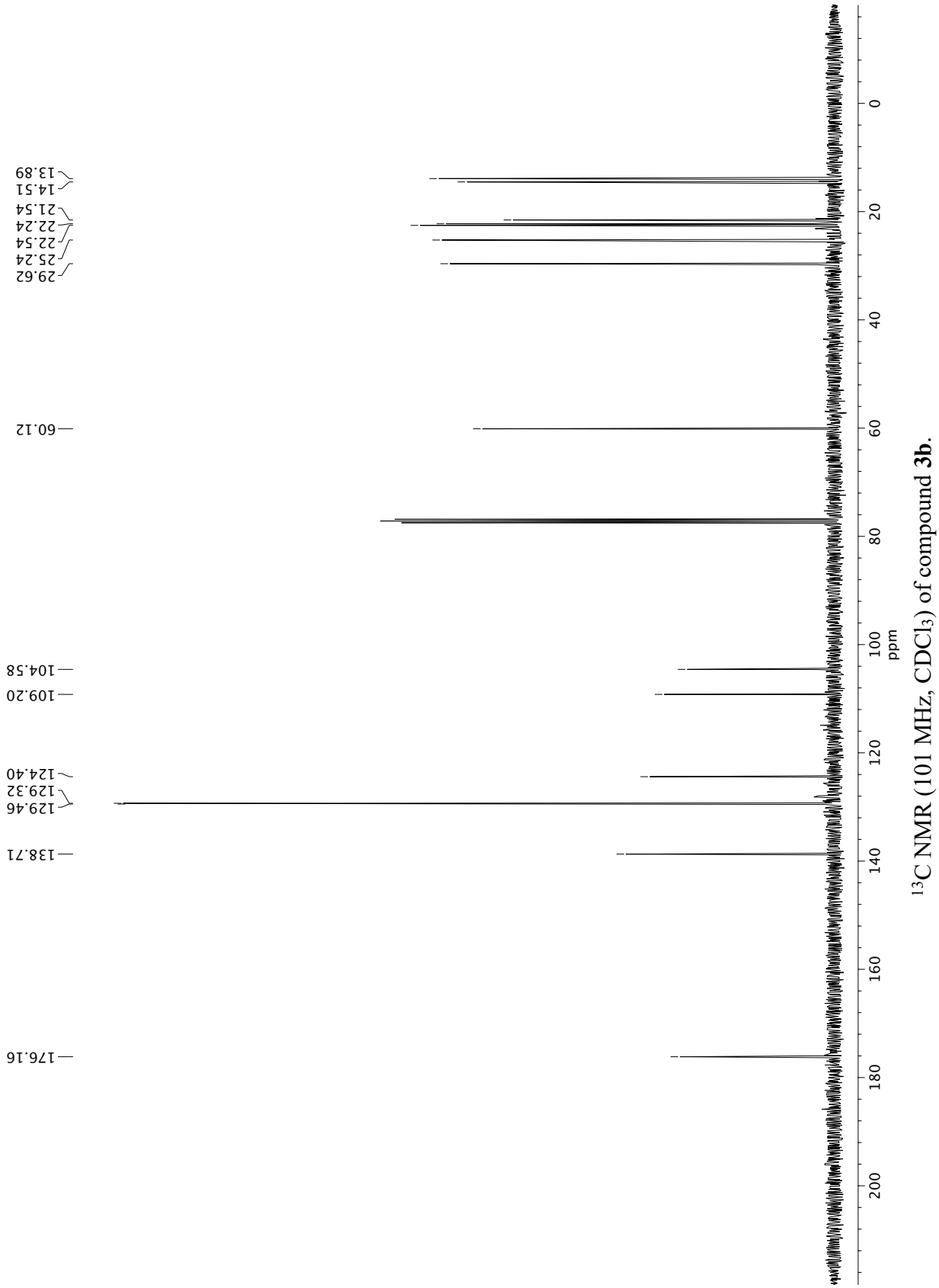
NMR Spectra of New Compounds



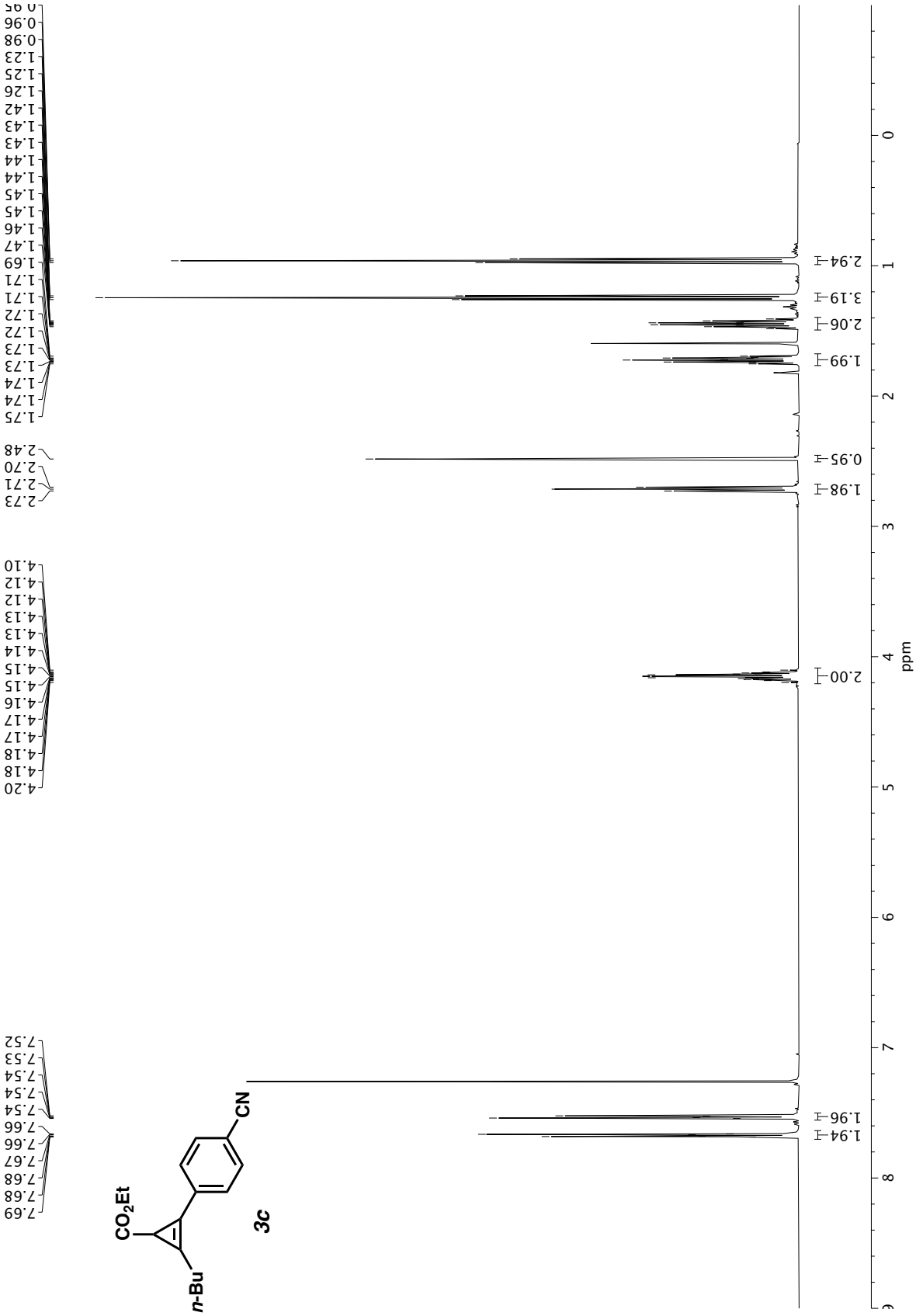
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**.



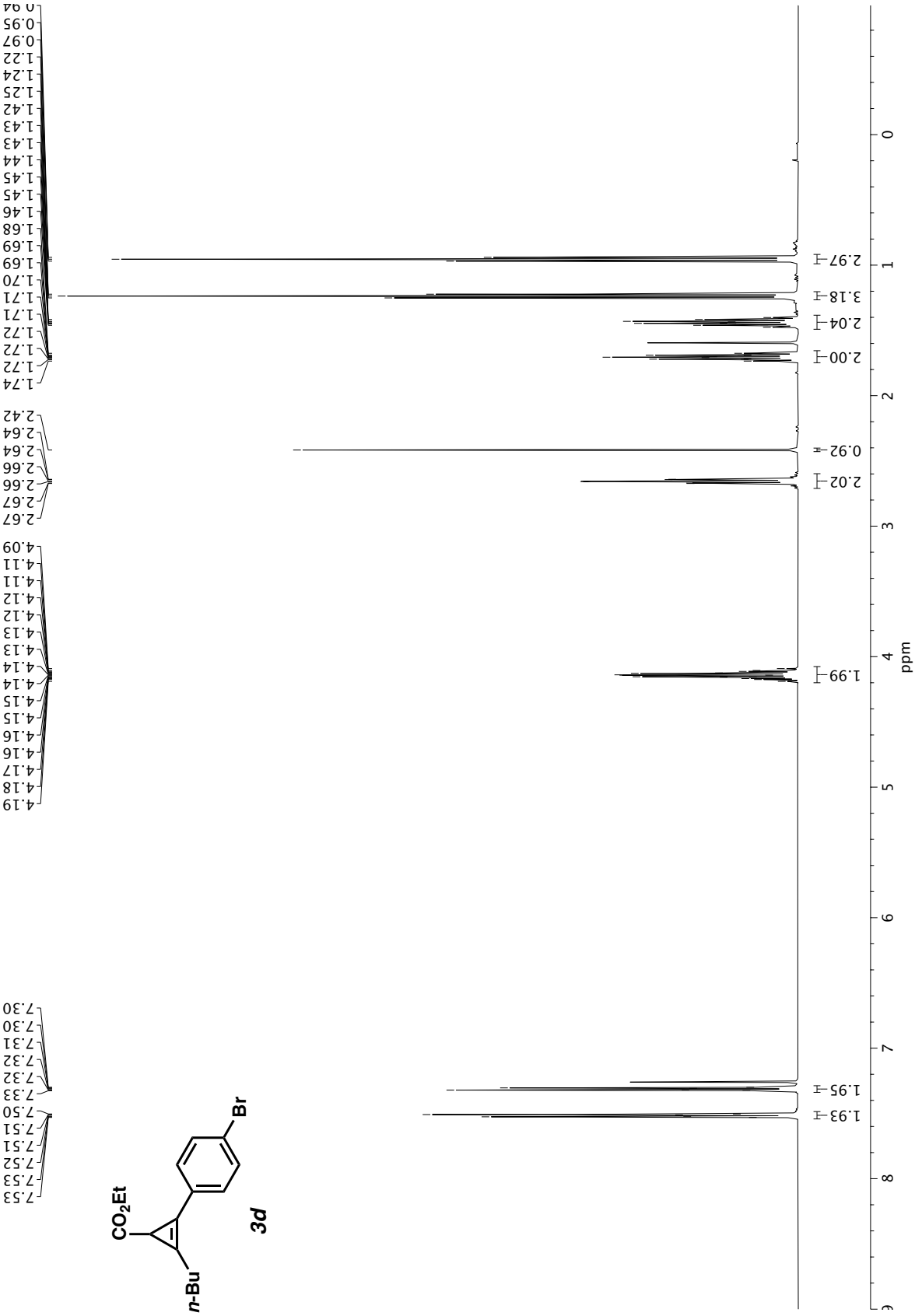
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**.



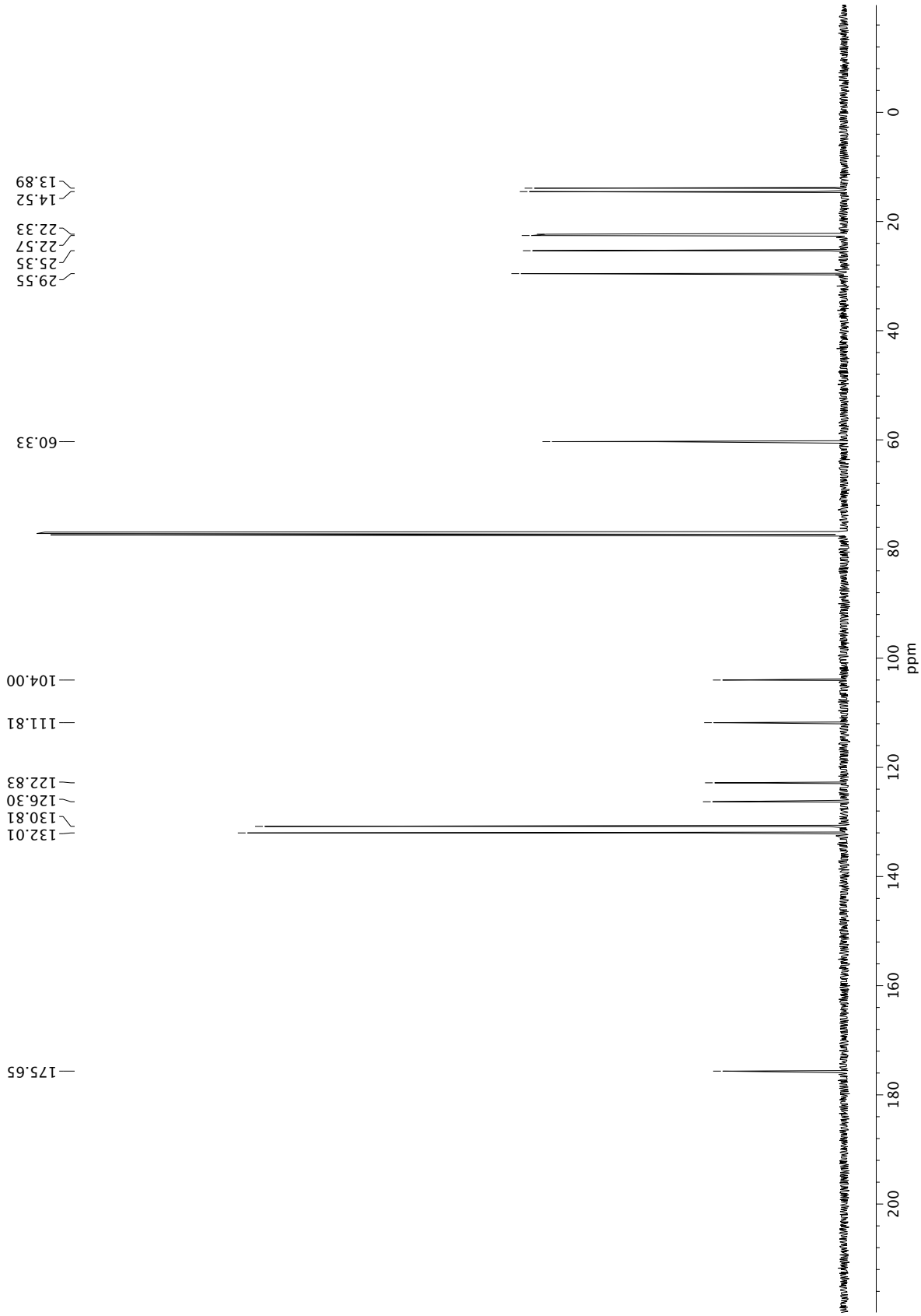
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3b**.



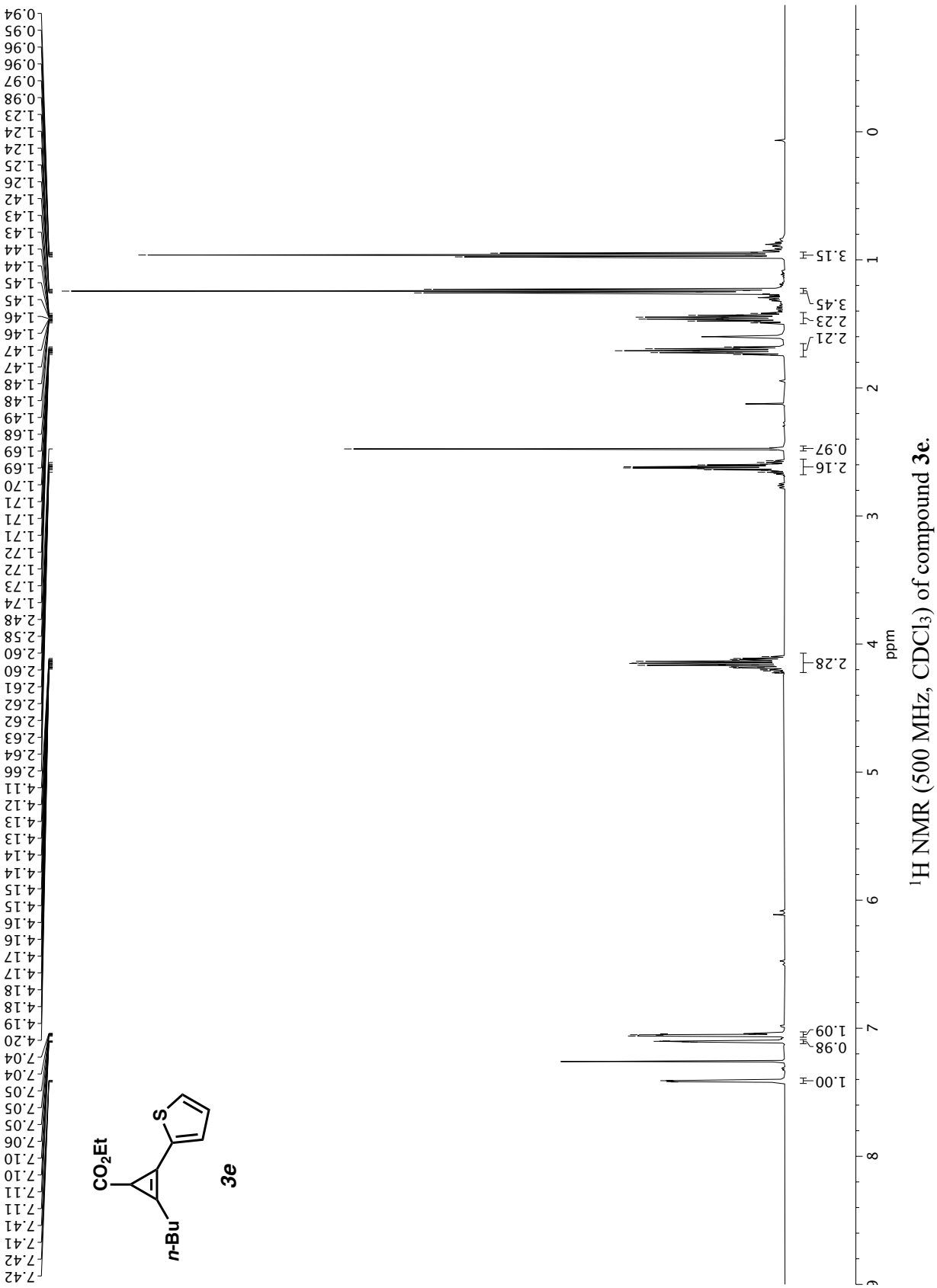
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3c**.



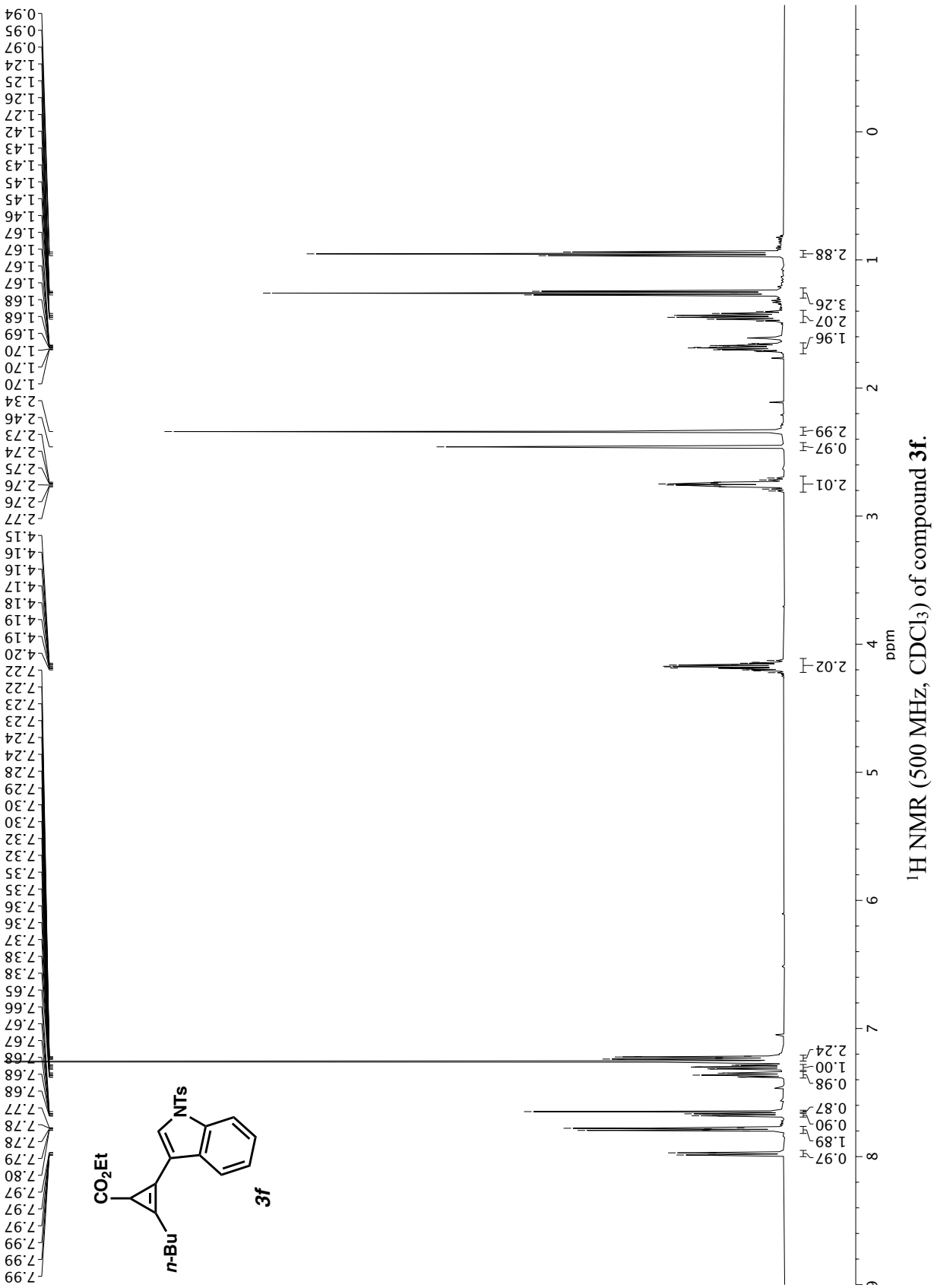
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3d**.



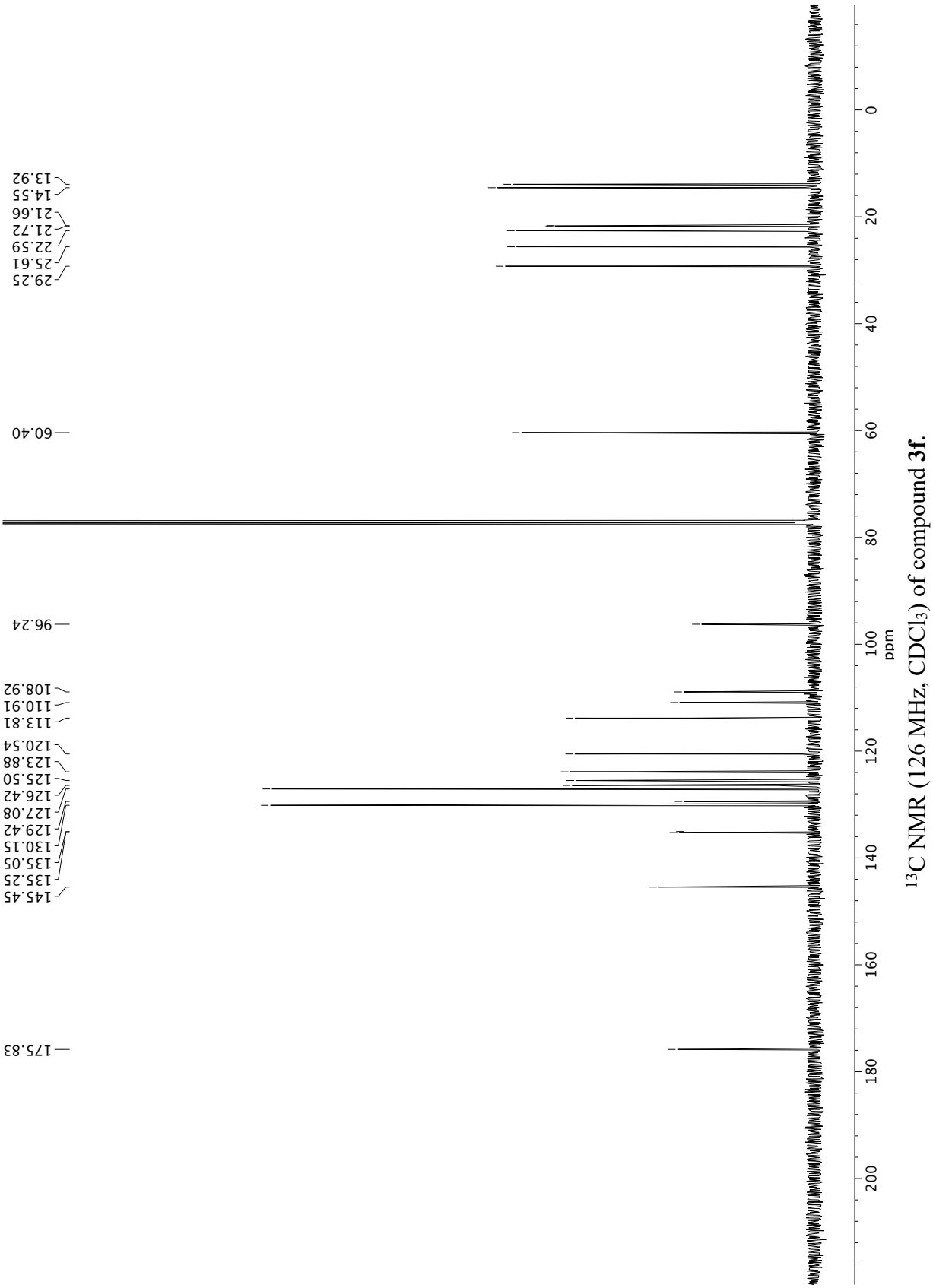
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3d**.



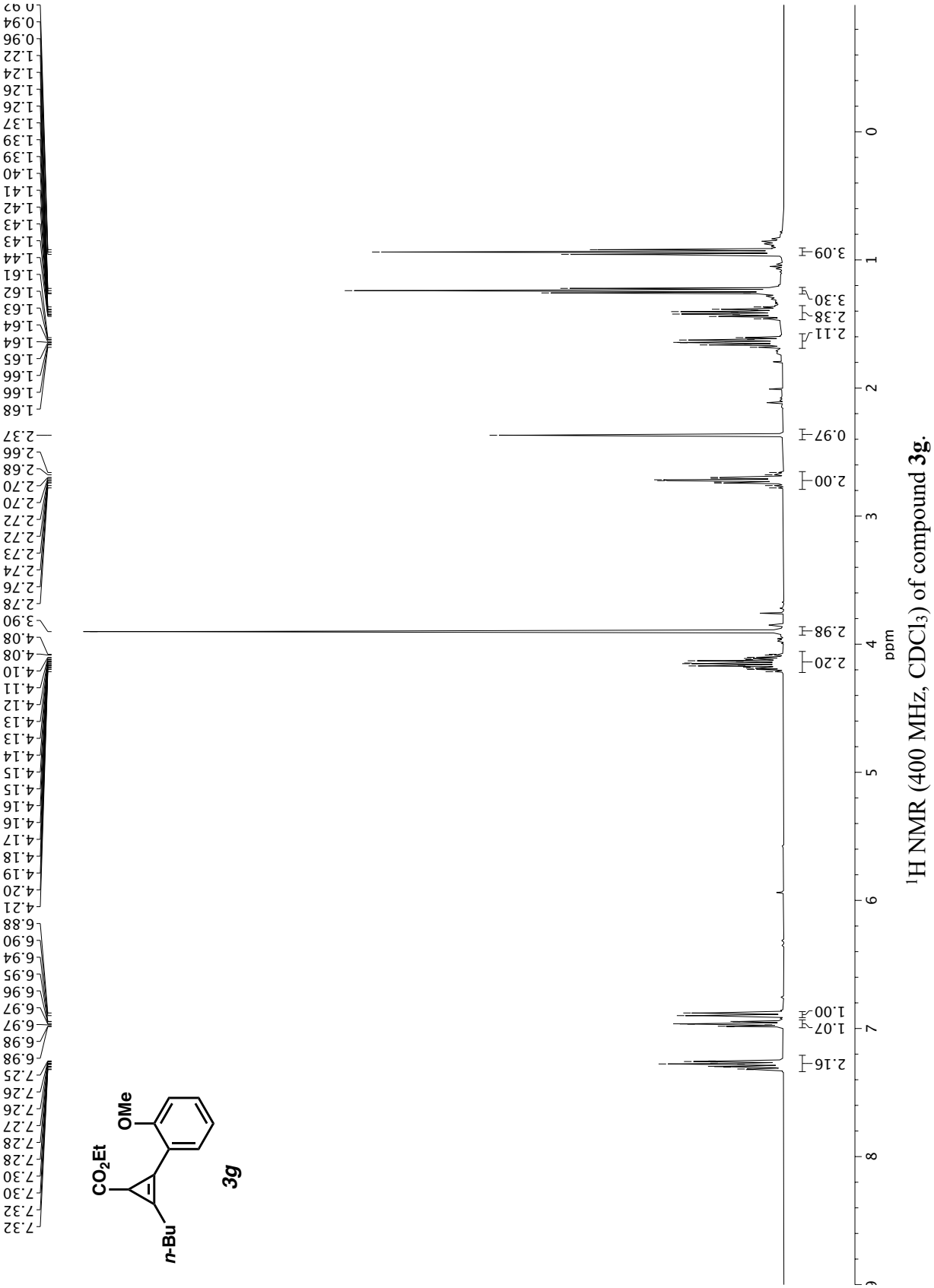
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3e**.



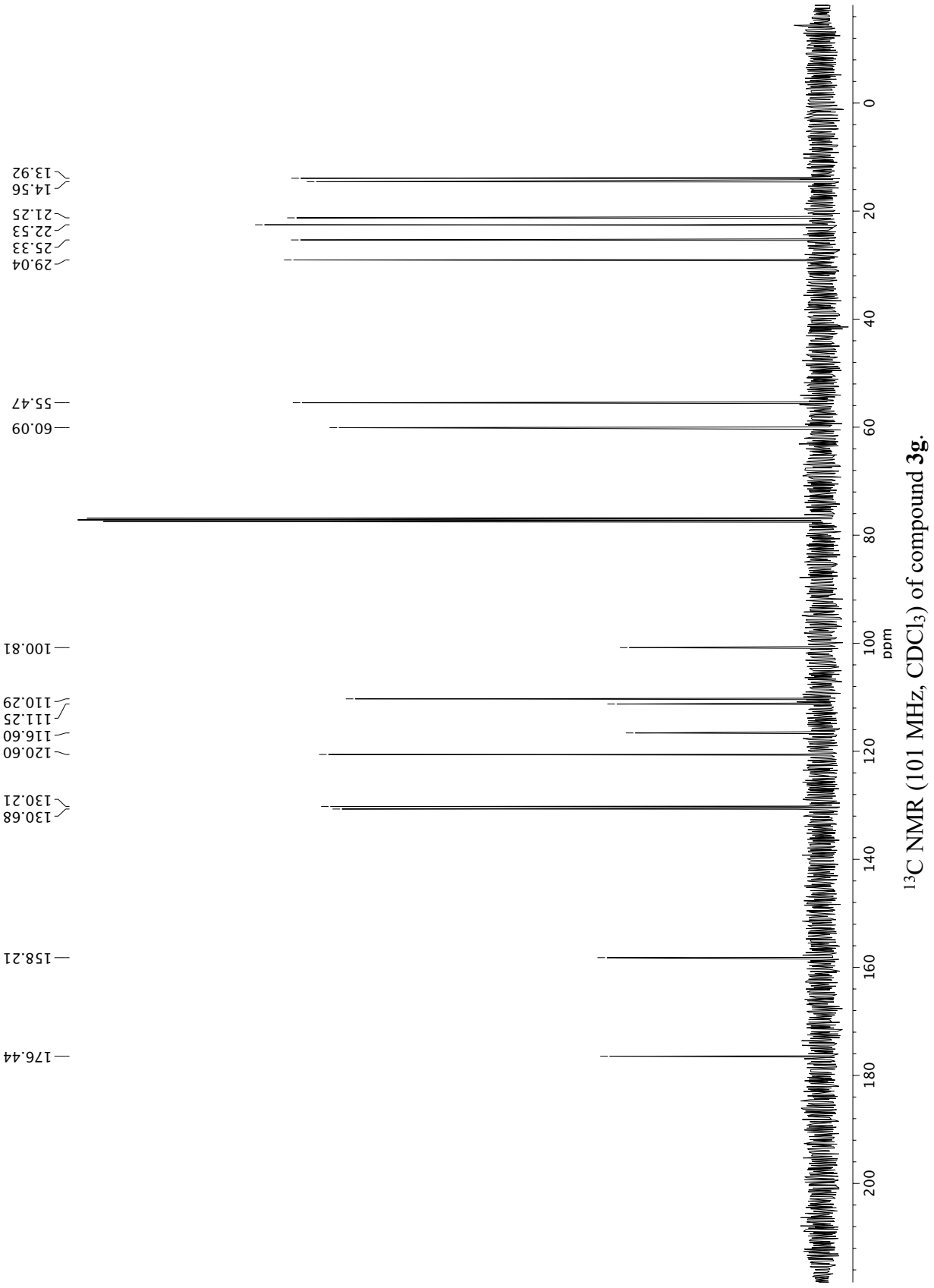
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3f**.



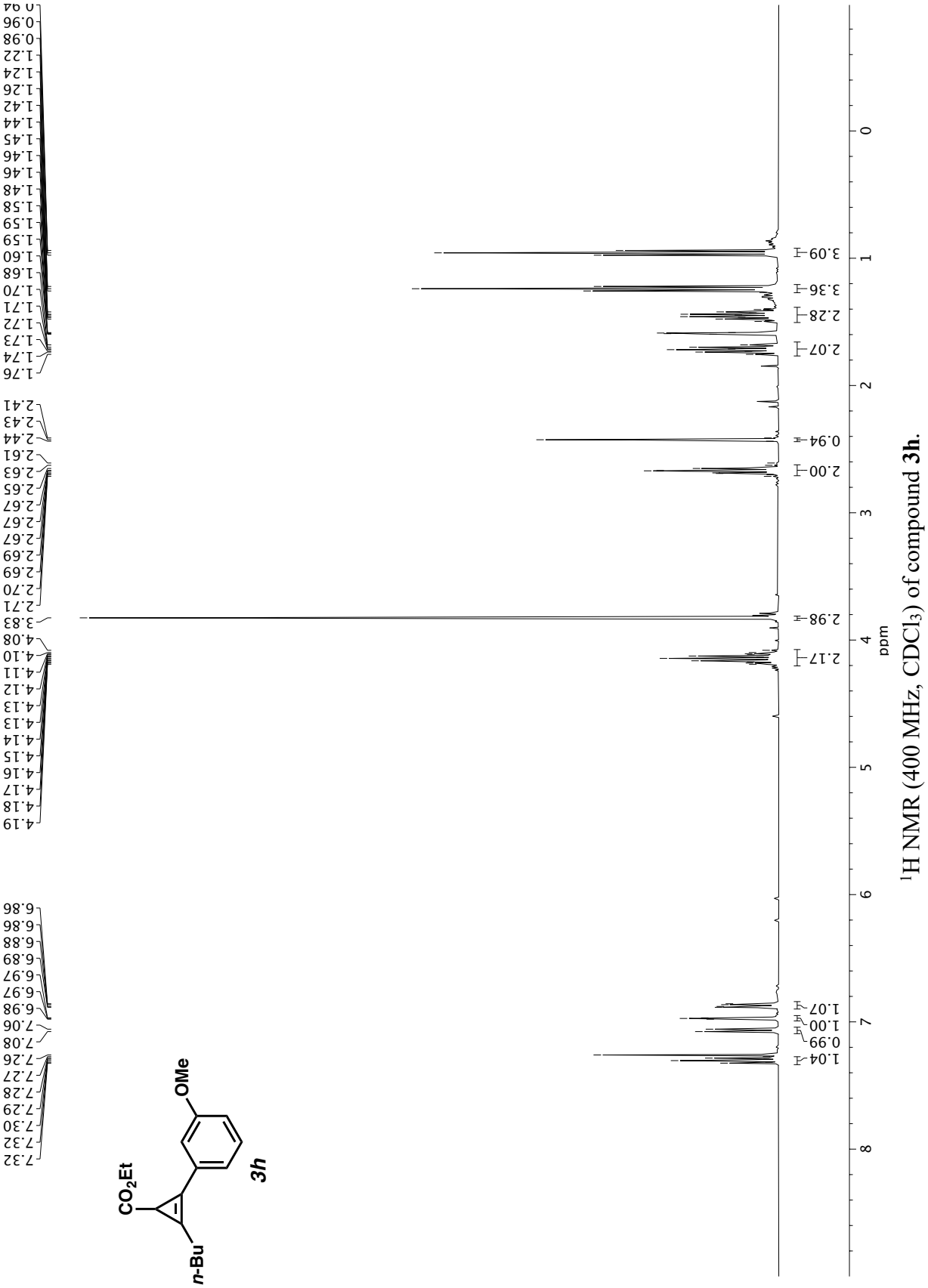
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3f**.



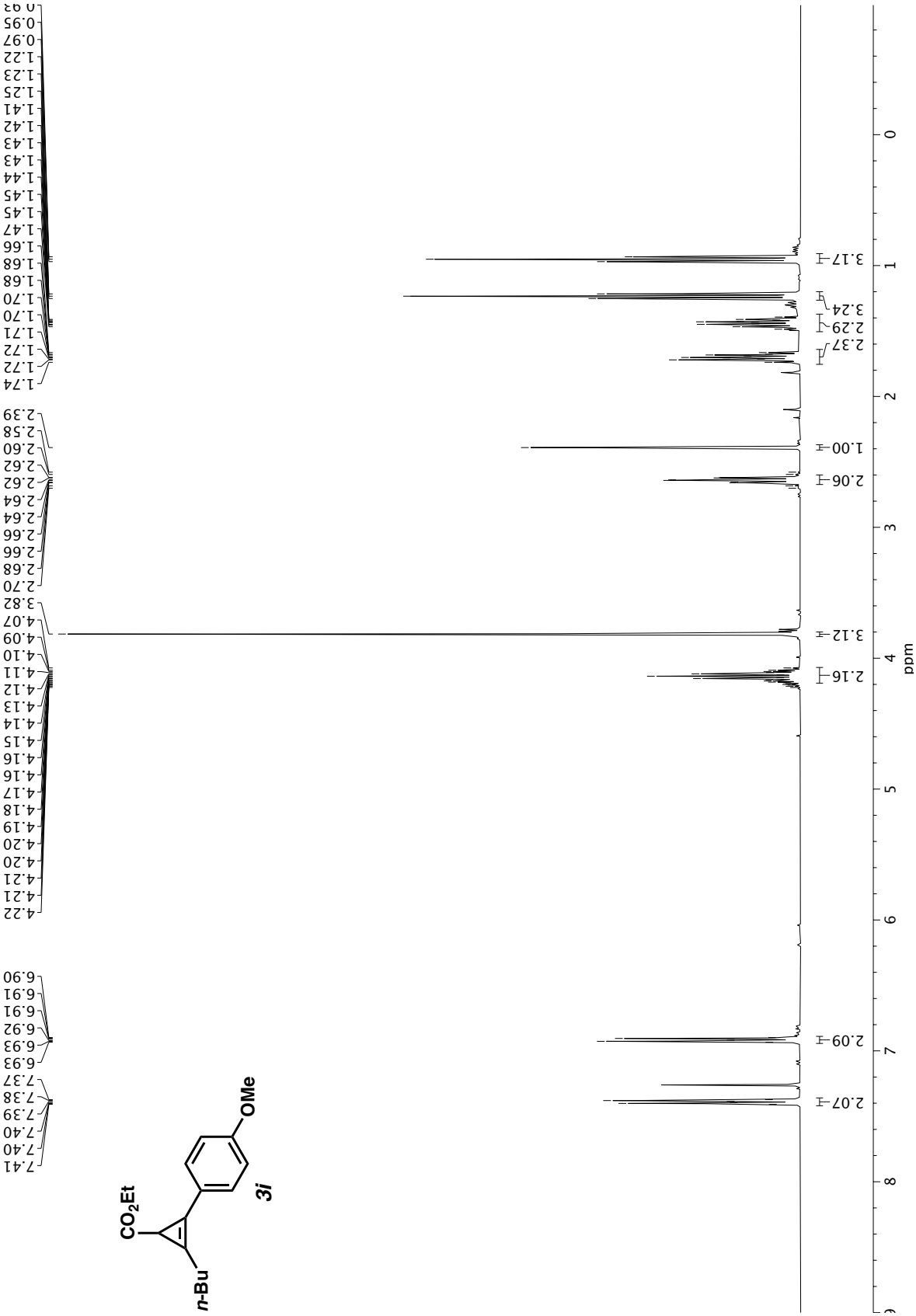
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**.



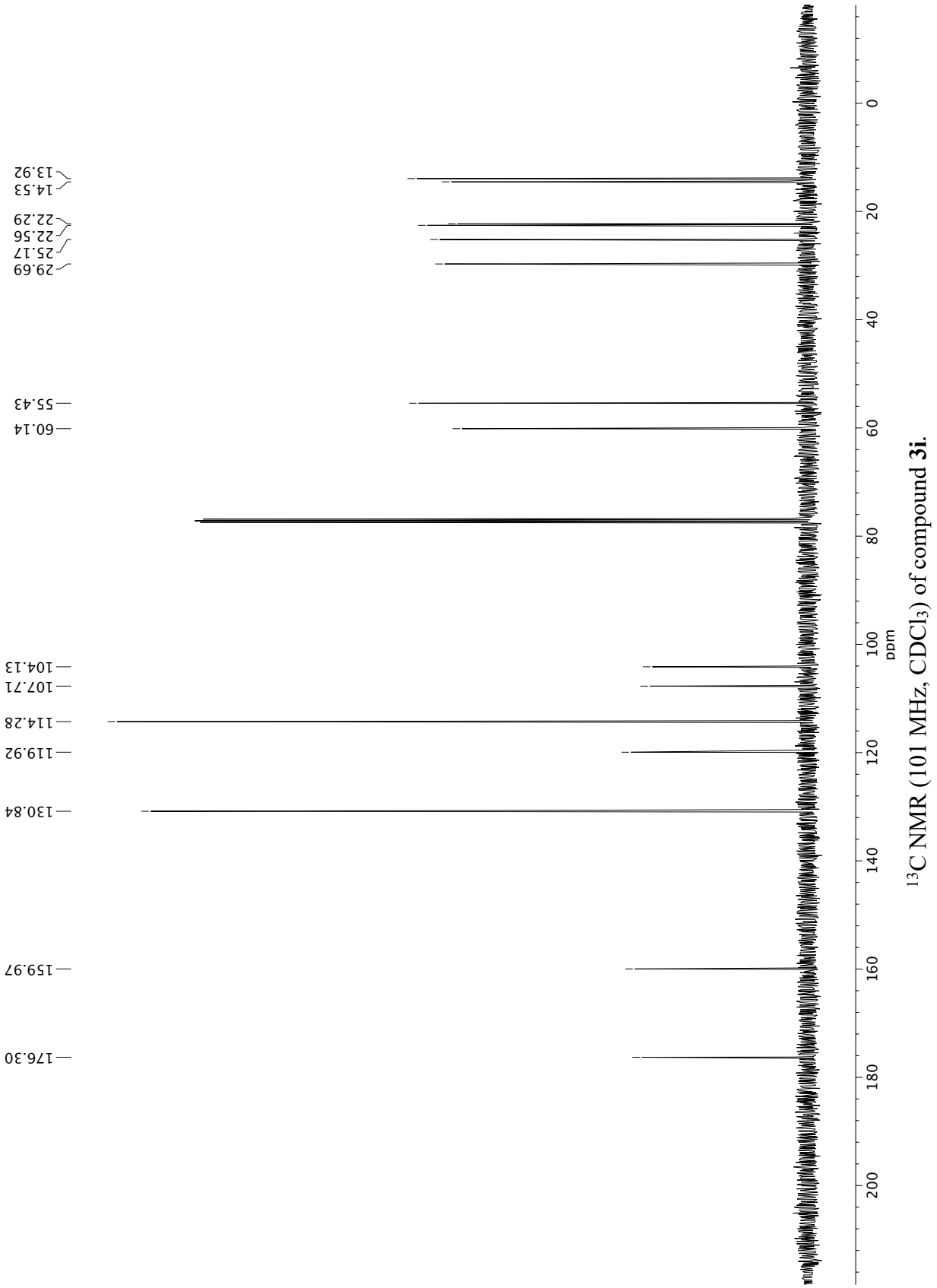
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3g**.



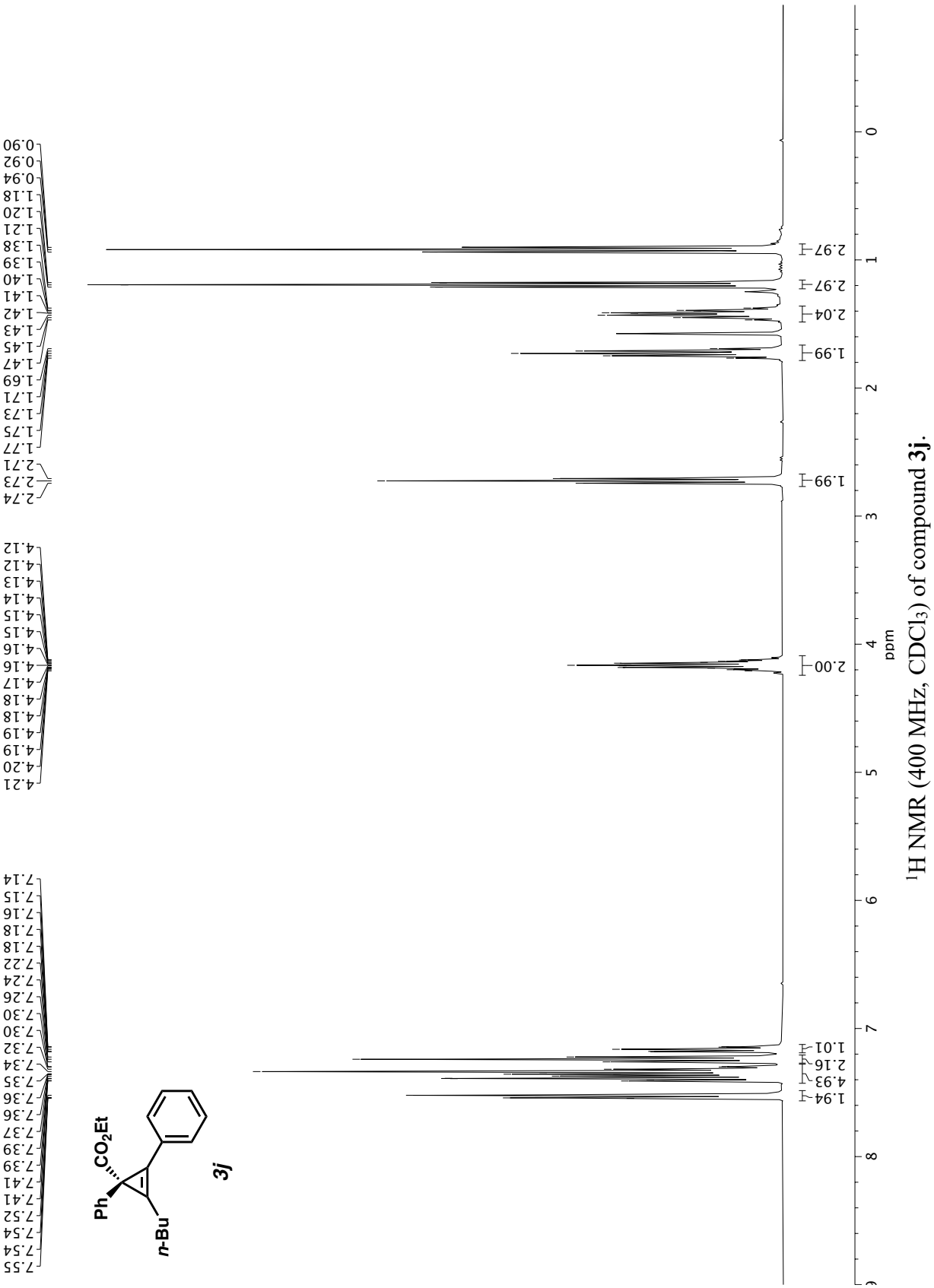
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**.



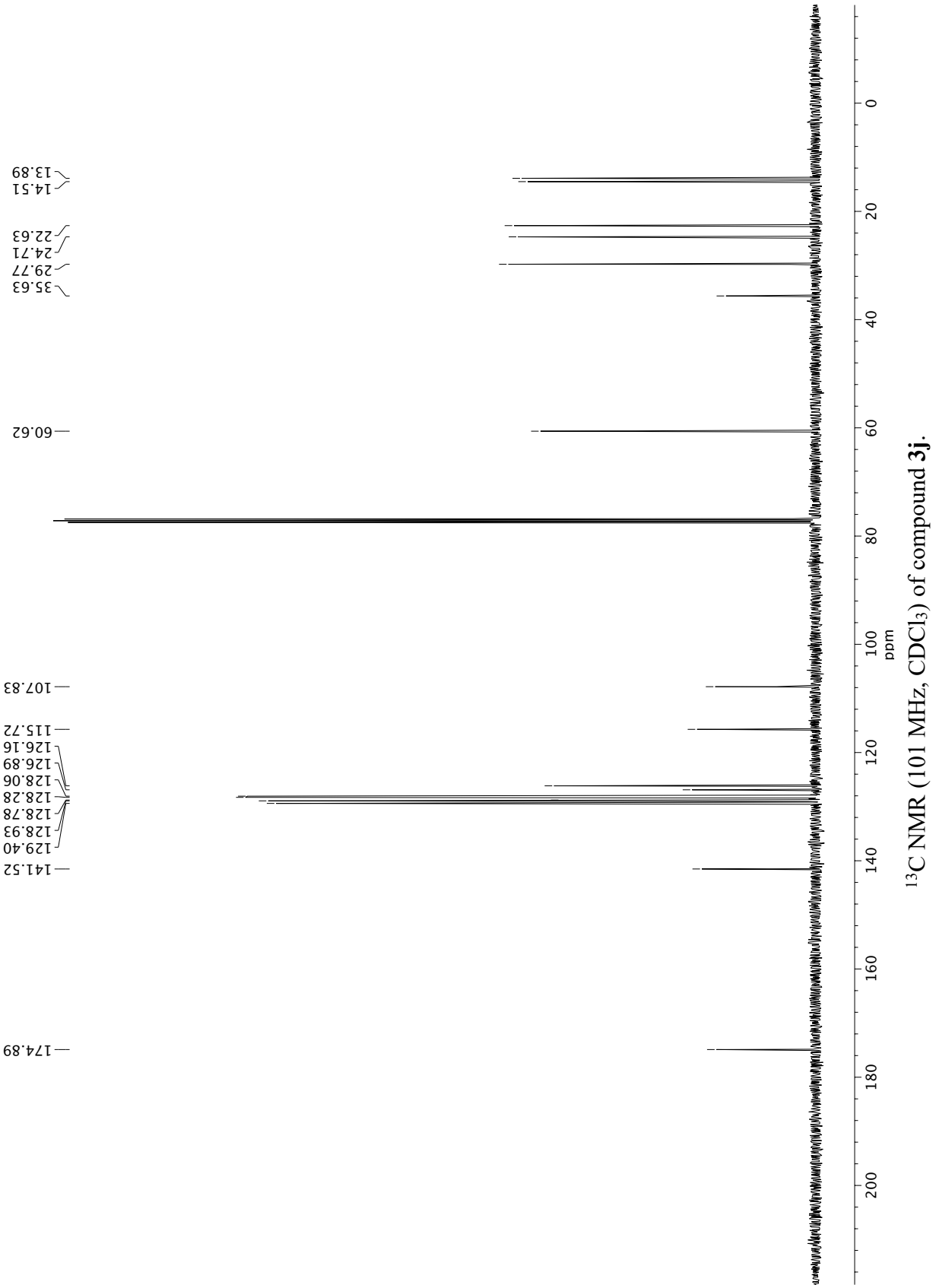
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**.



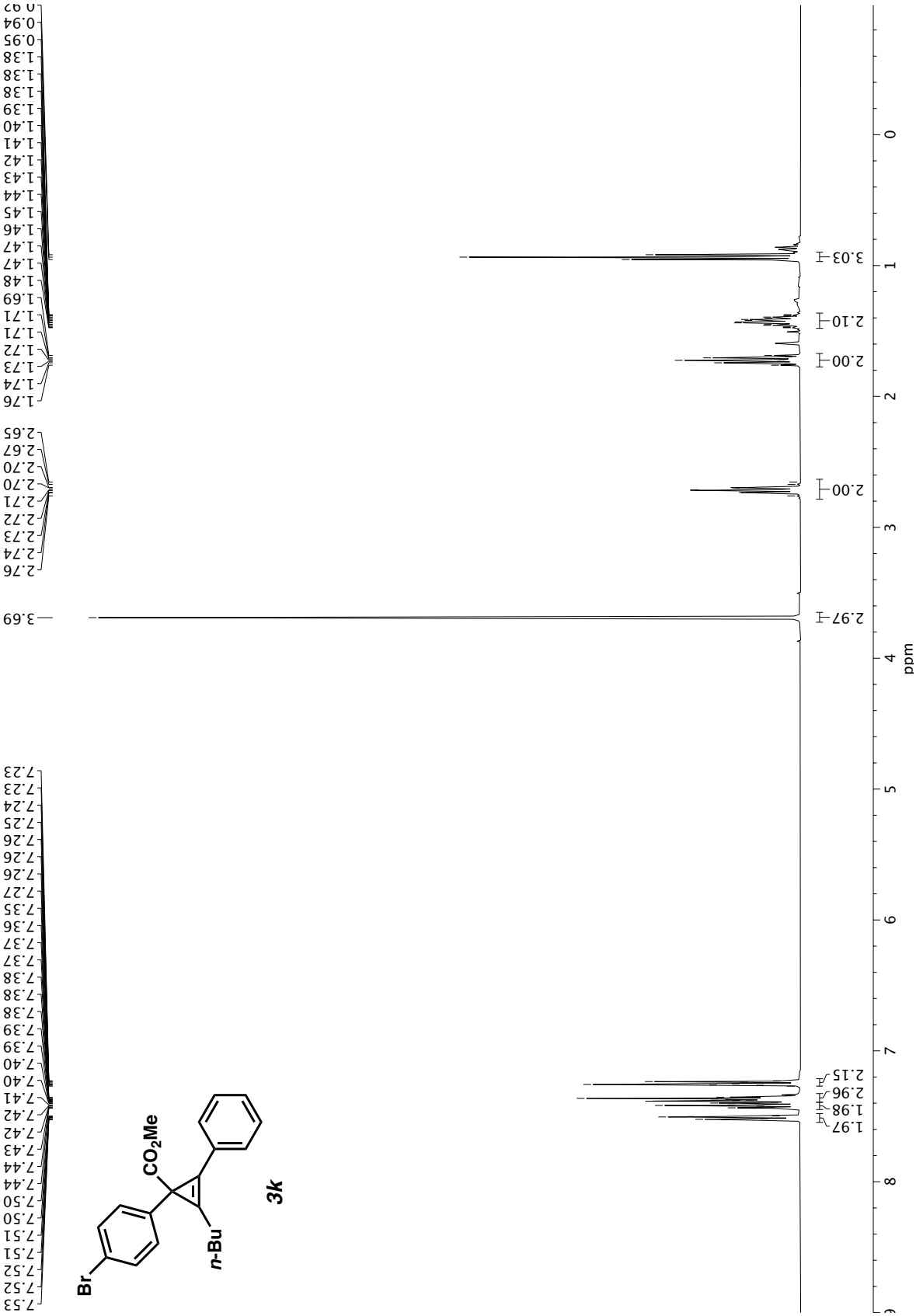
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3i**.



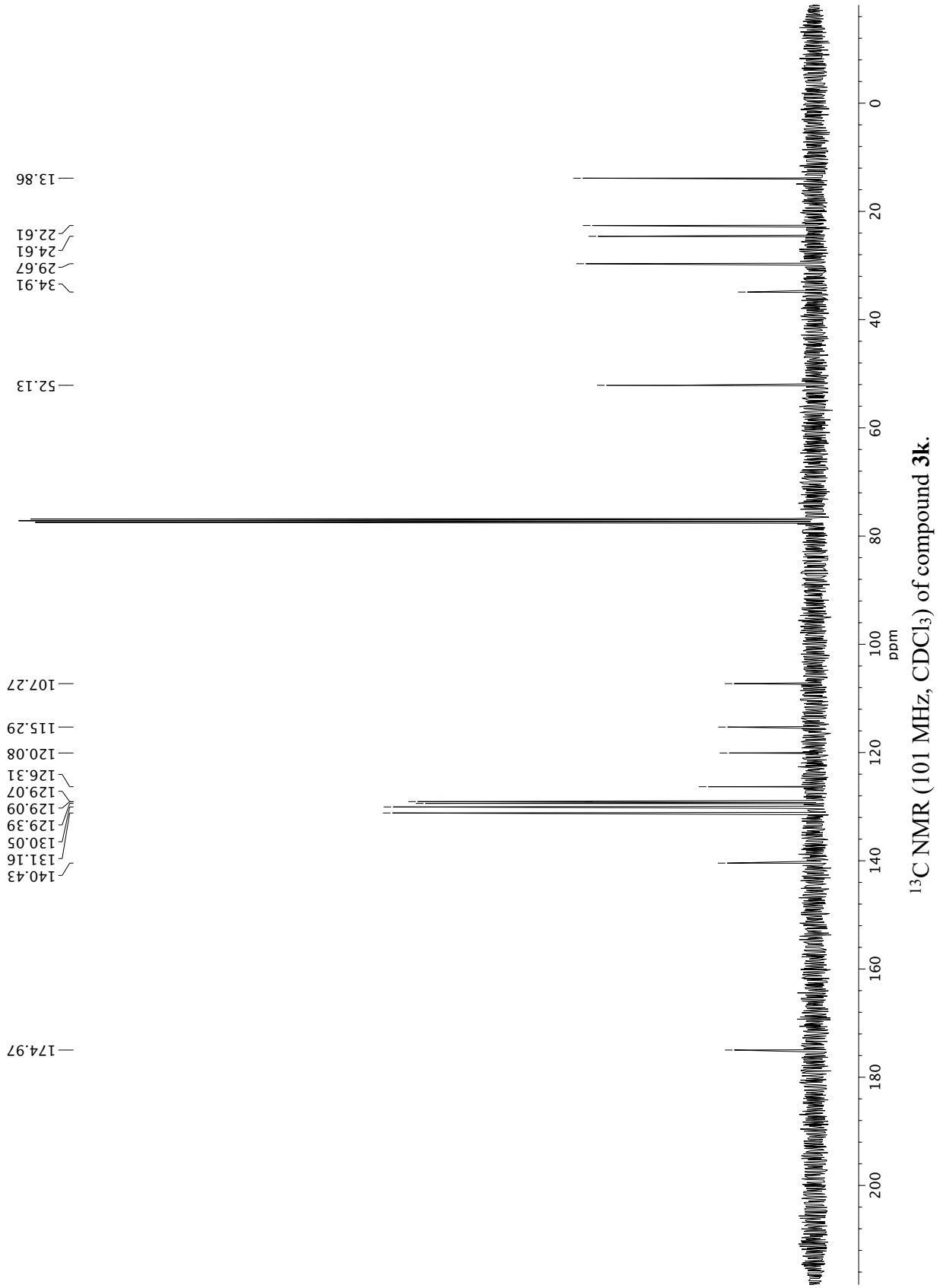
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**.



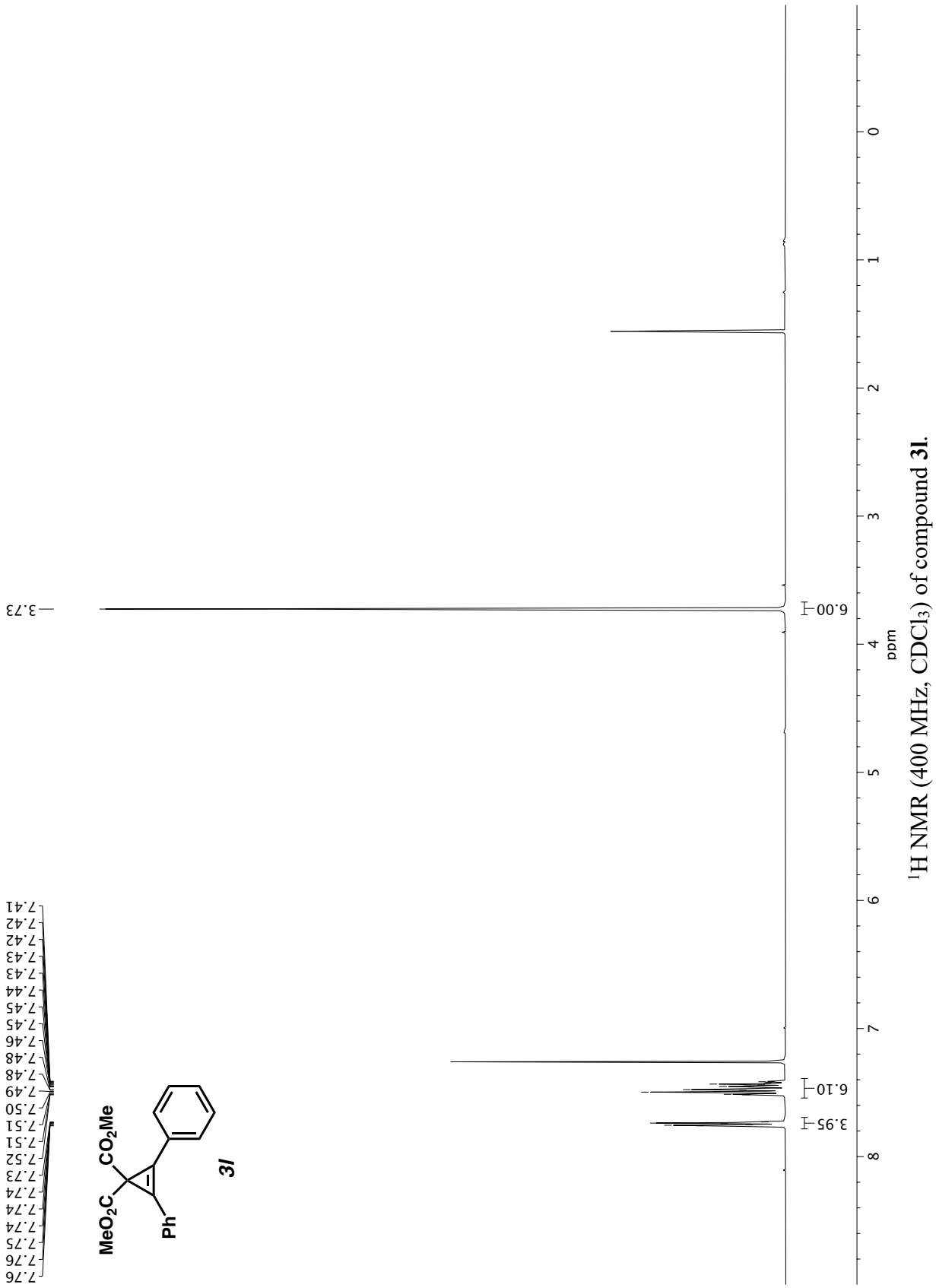
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3j**.



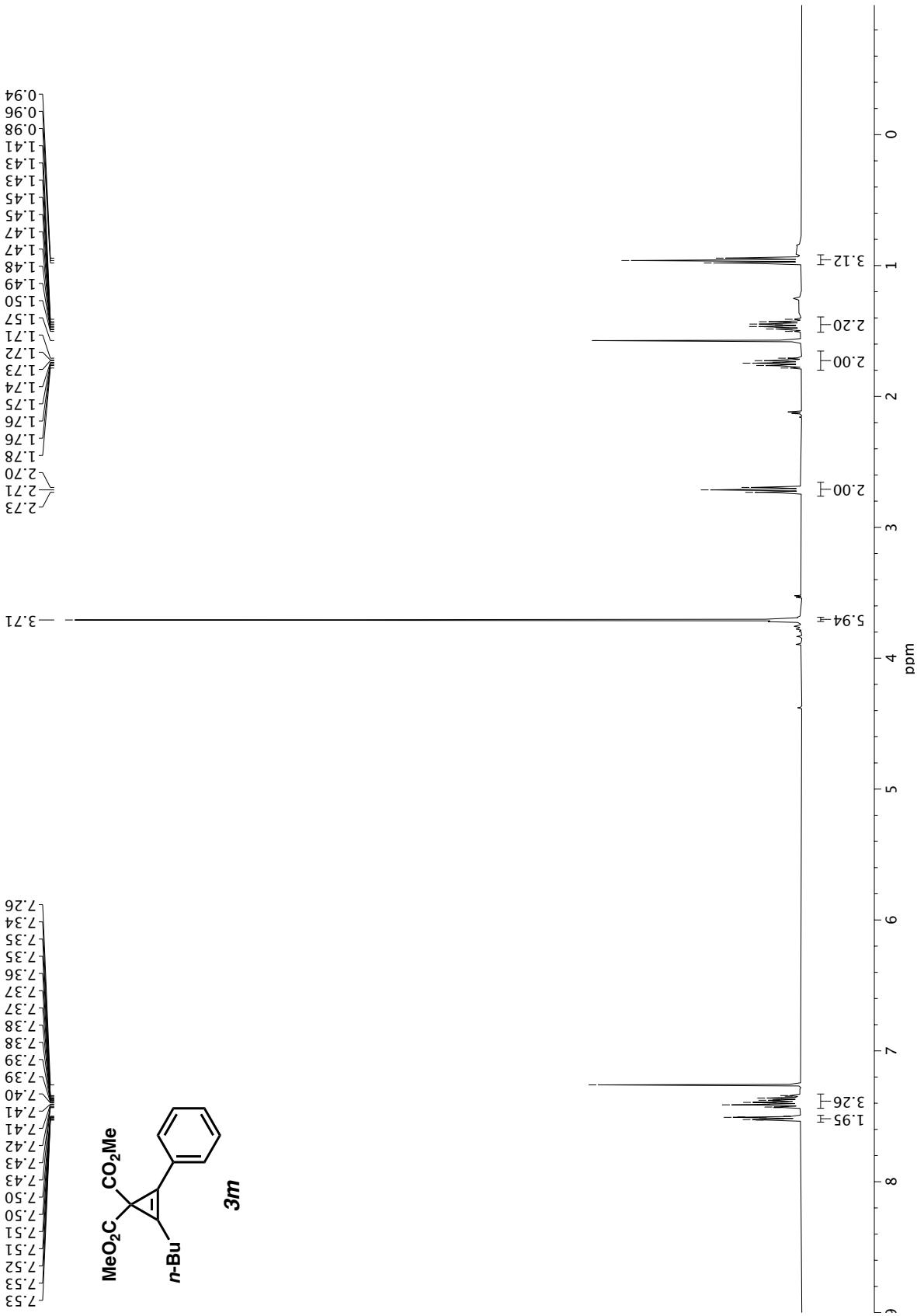
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k**.



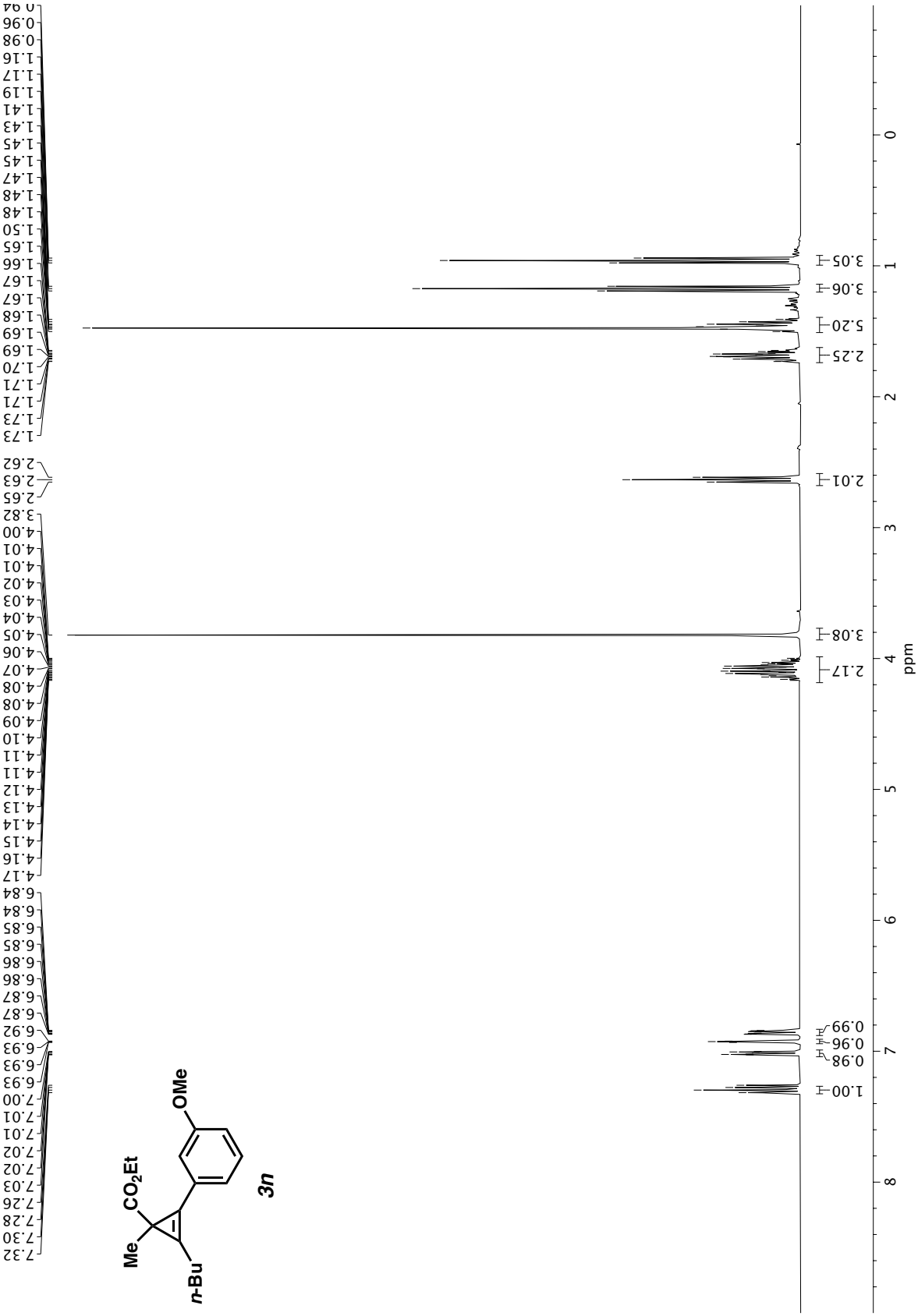
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3k**.



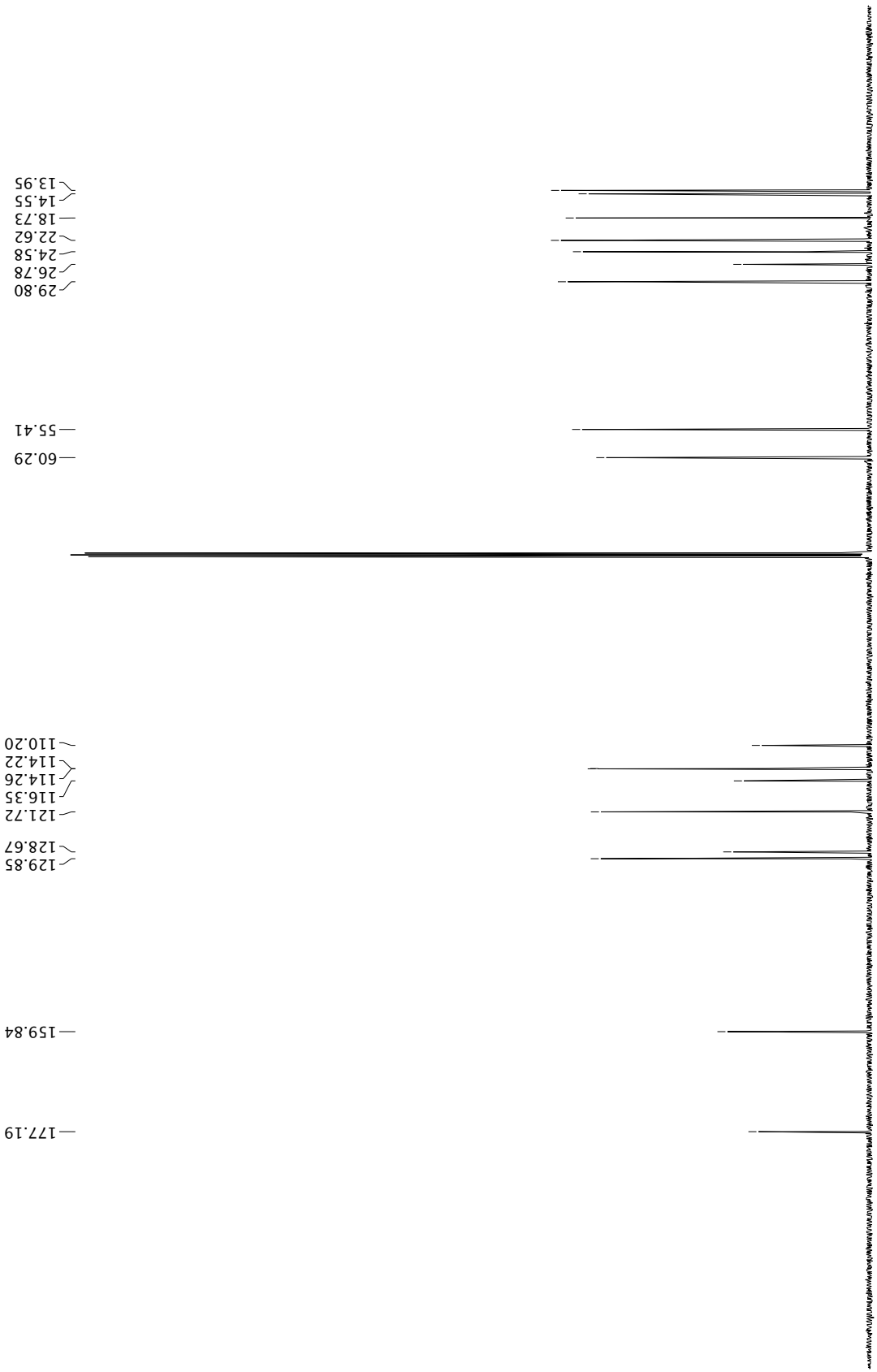
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l**.



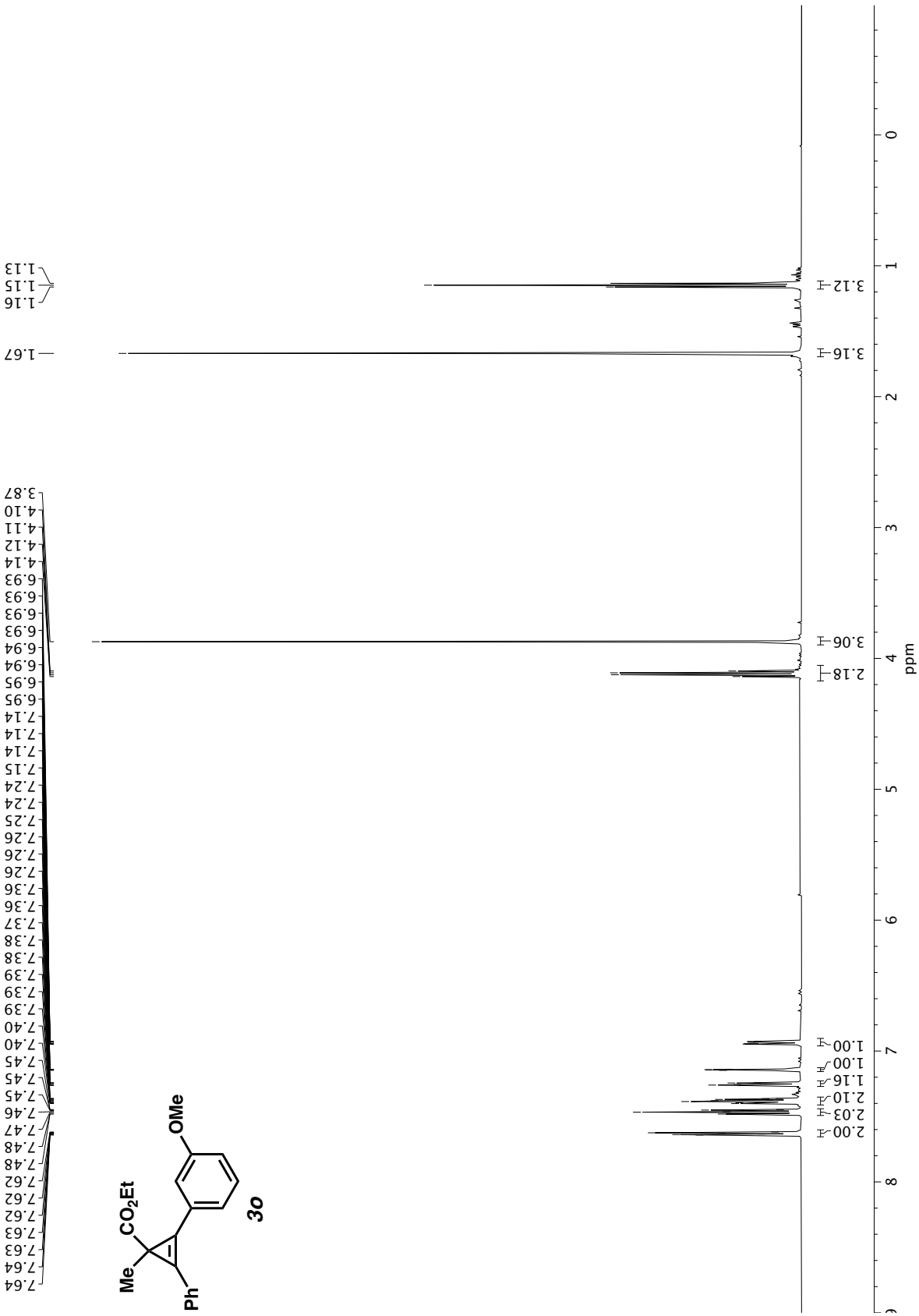
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m**.



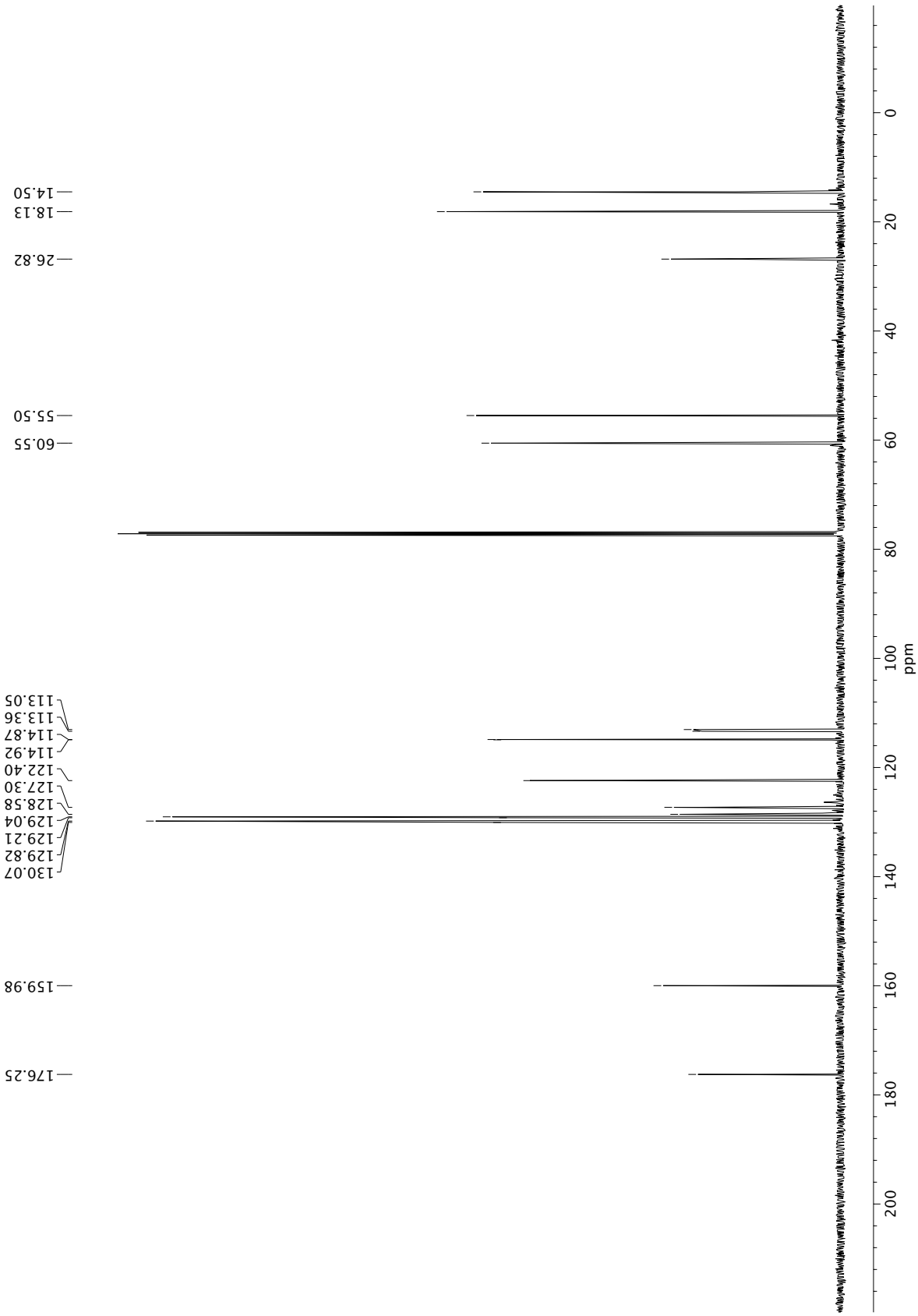
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3n**.



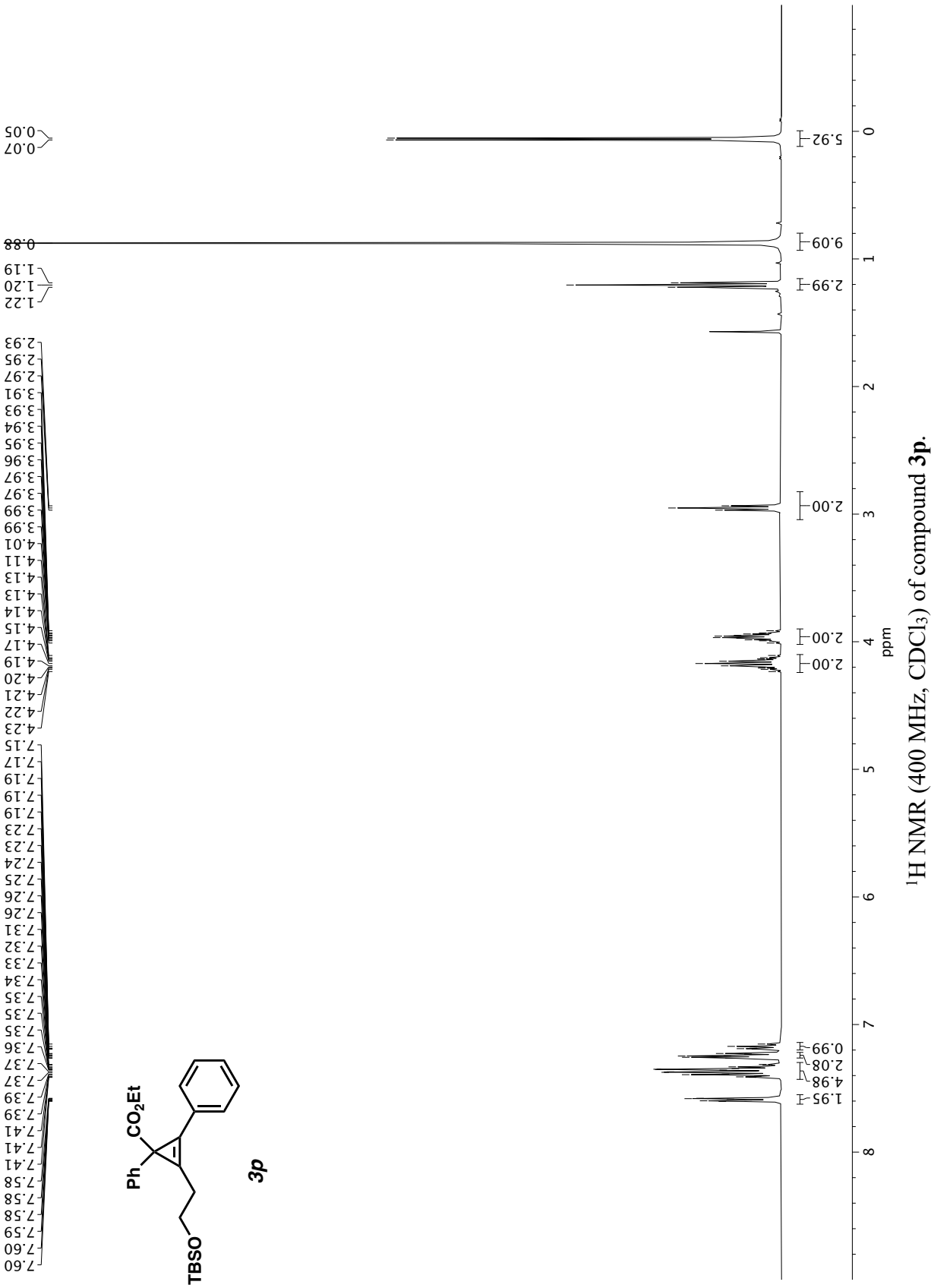
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3n**.



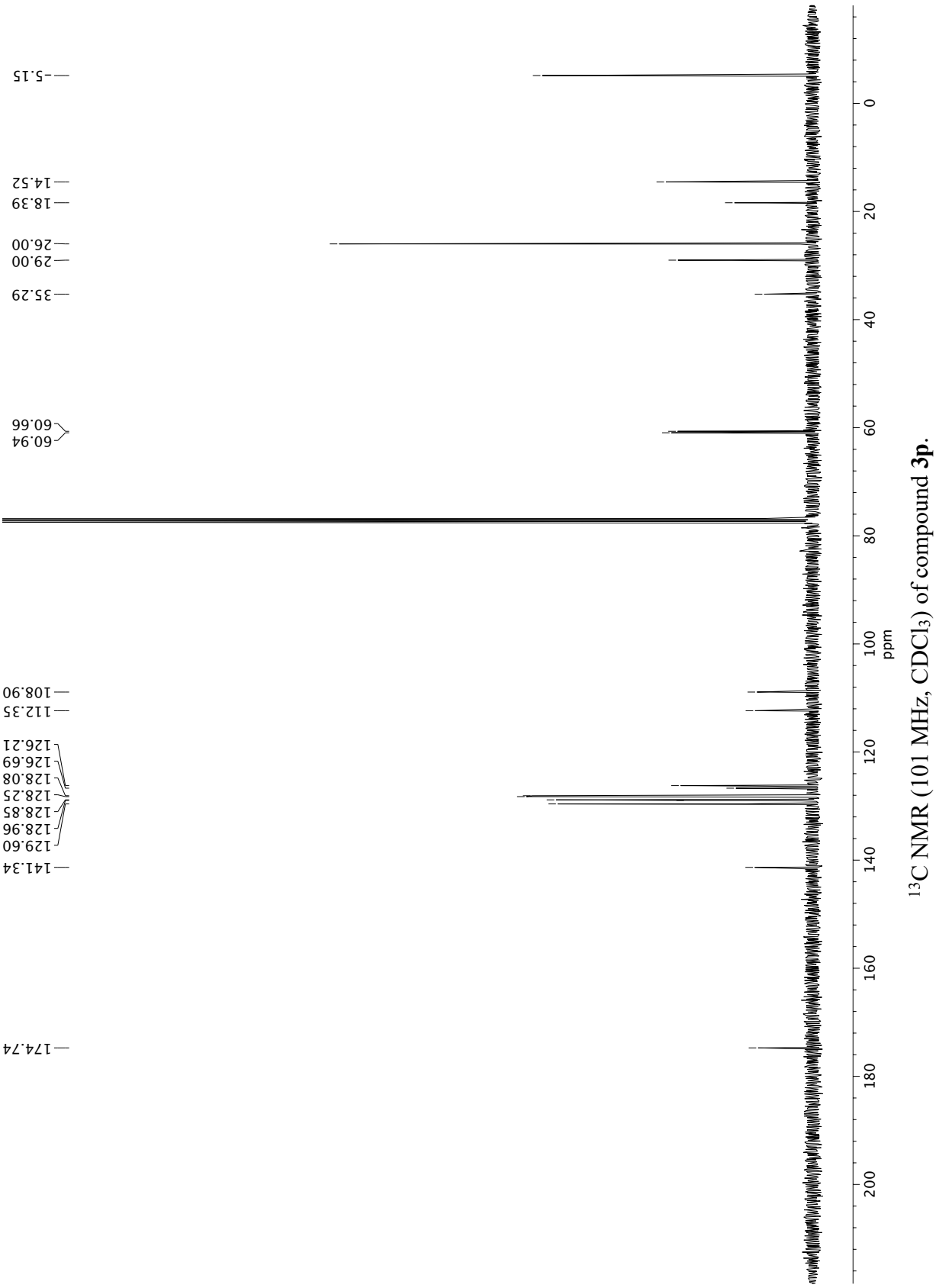
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3o**.



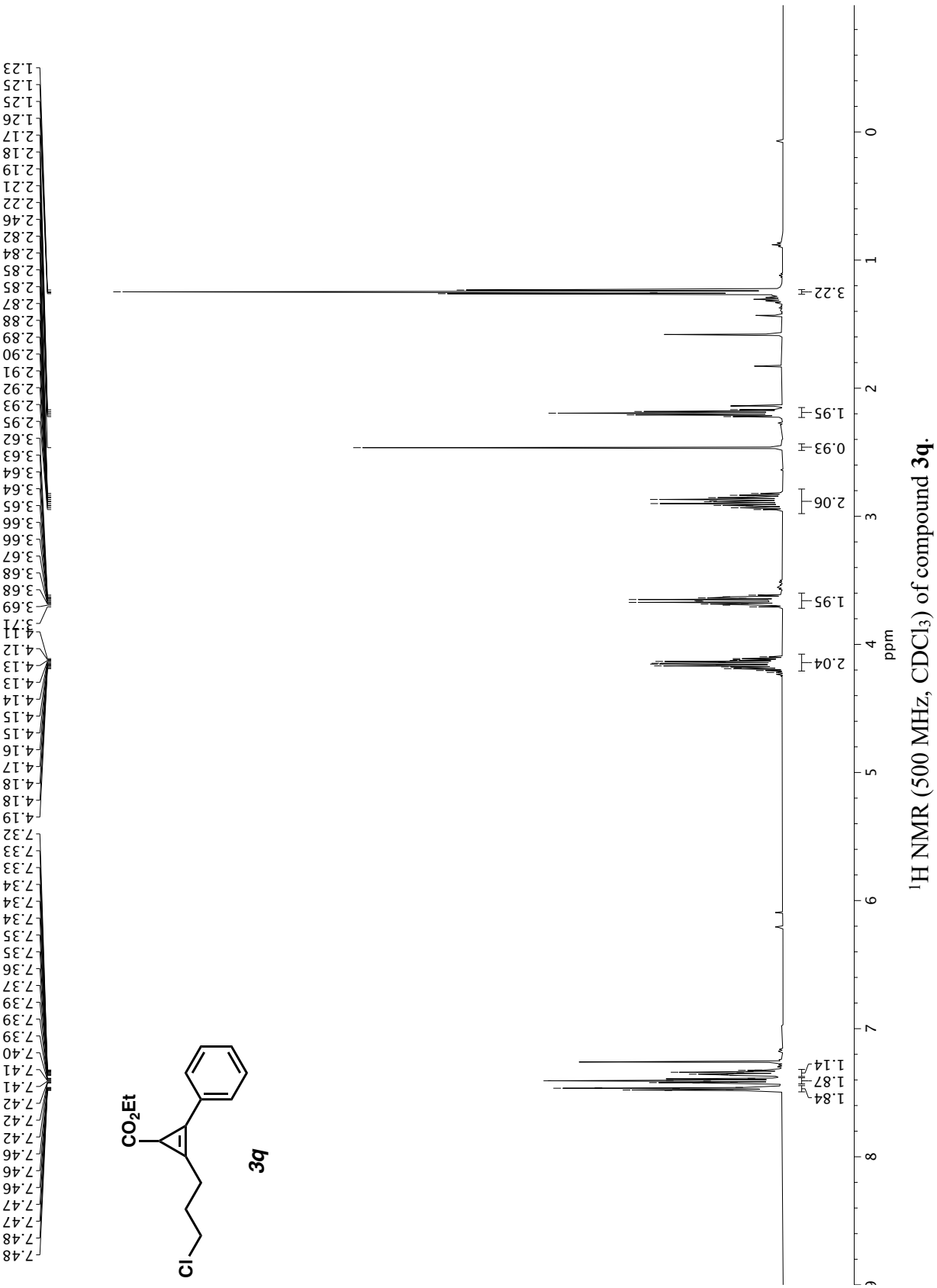
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3o**.



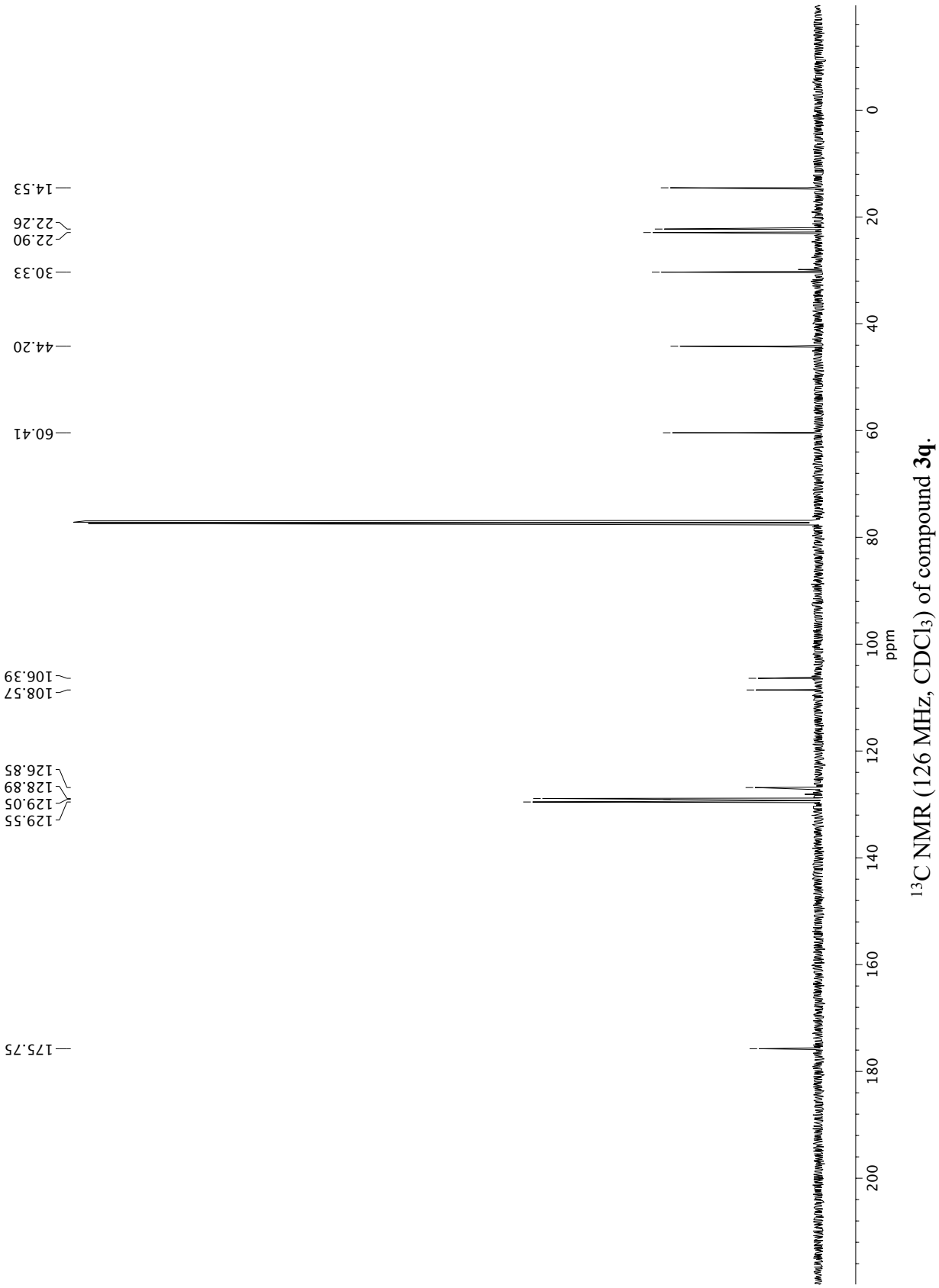
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3p**.



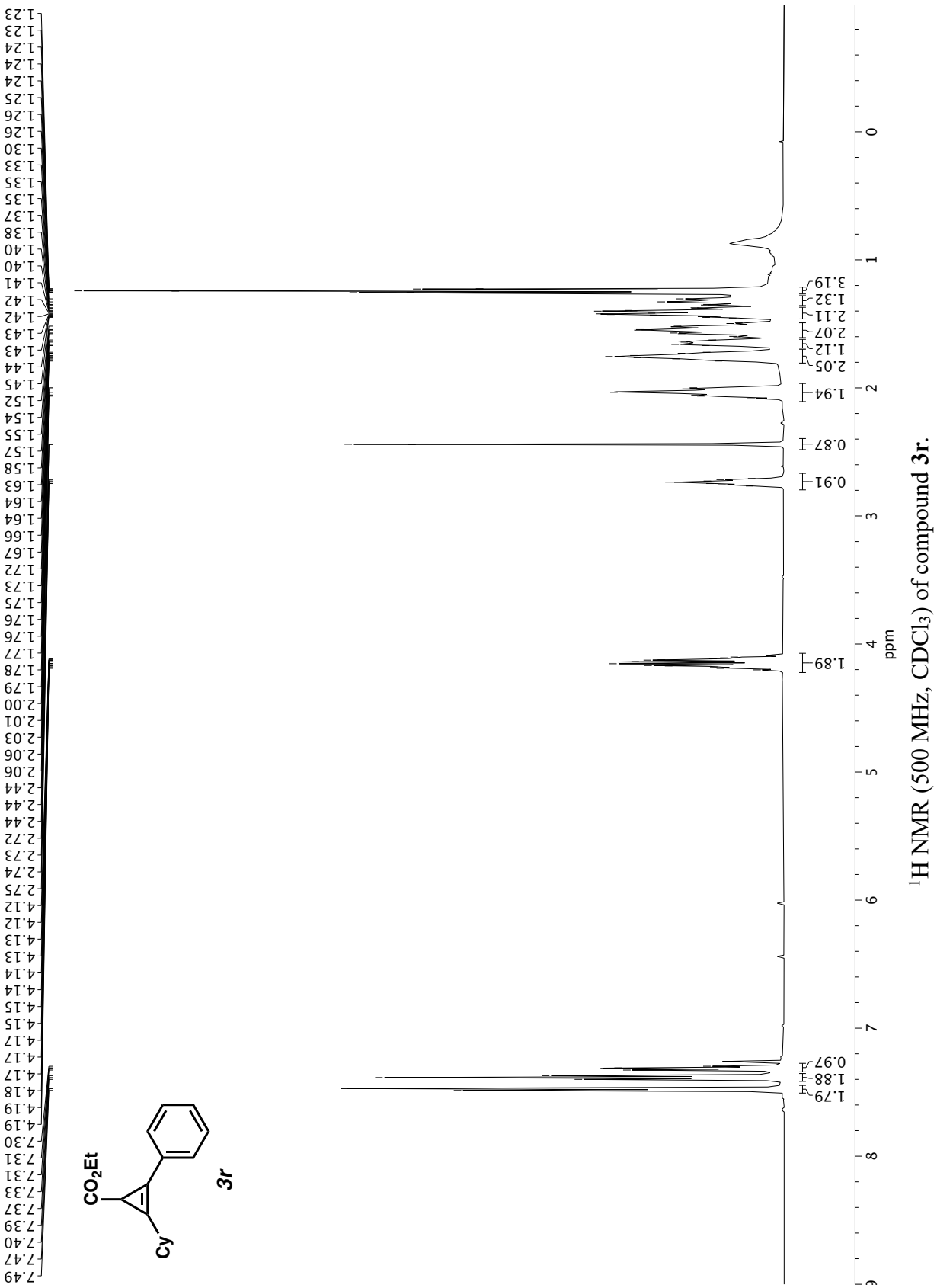
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3p**.



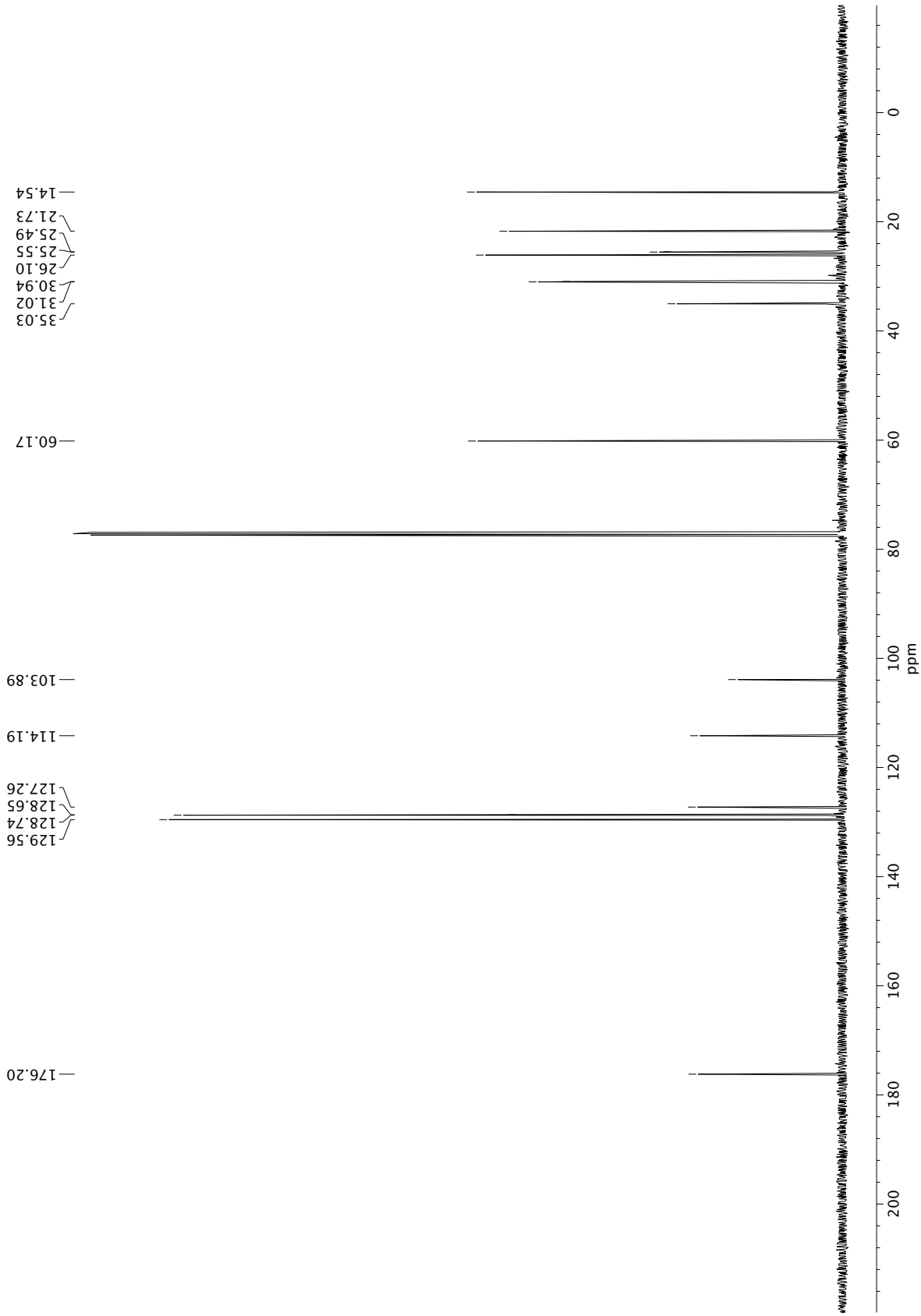
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3q**.



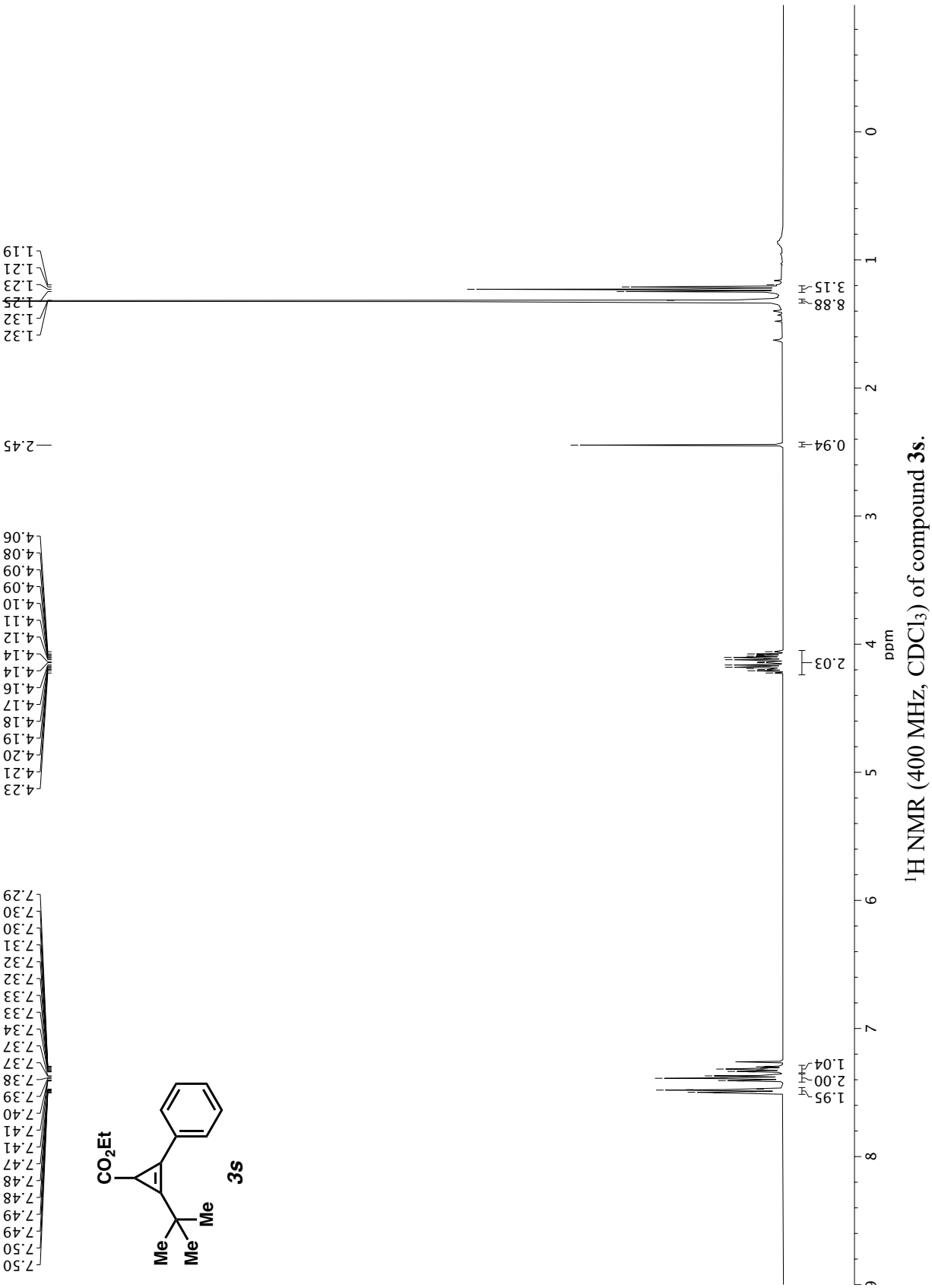
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3q**.



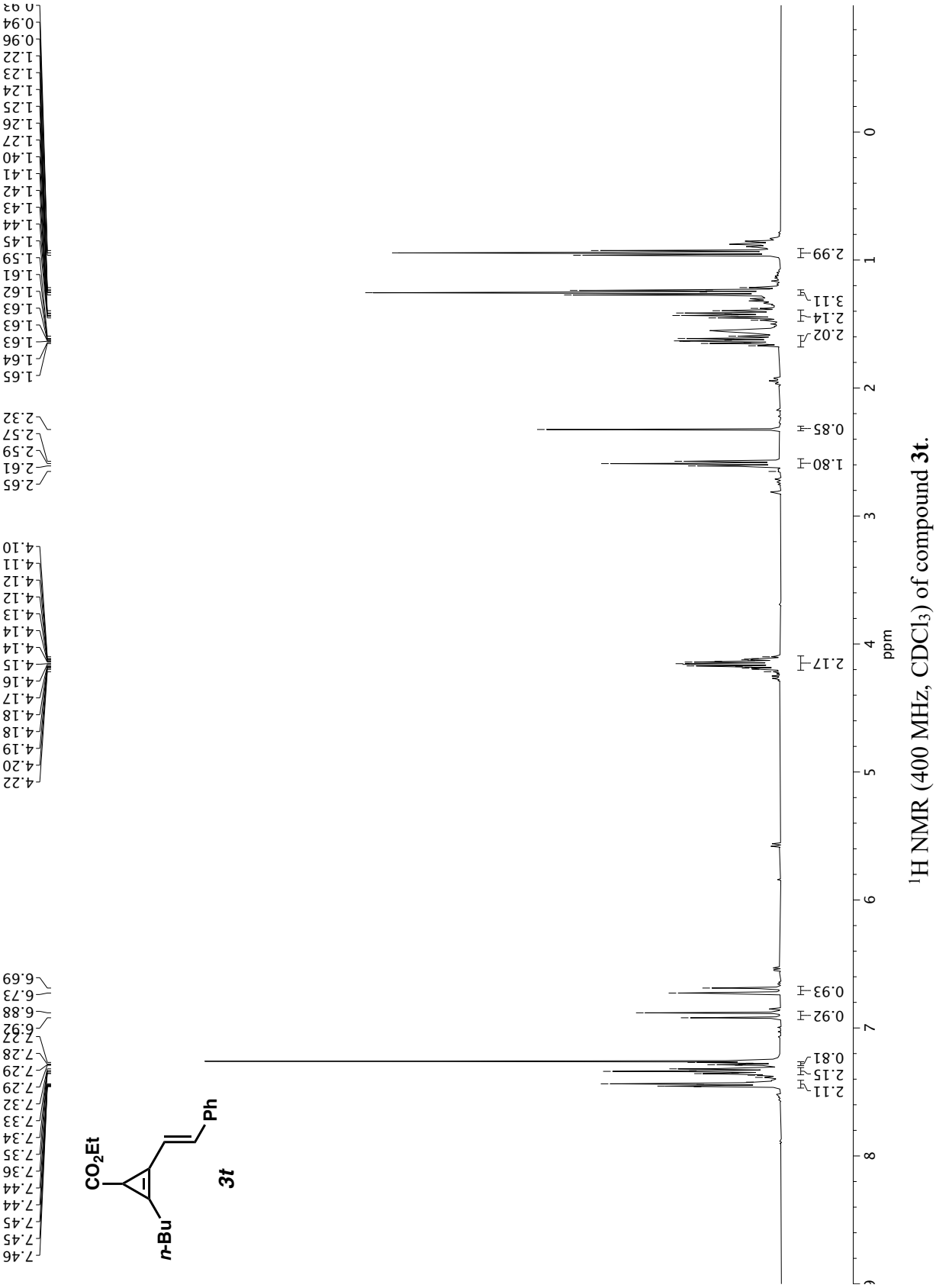
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3r**.



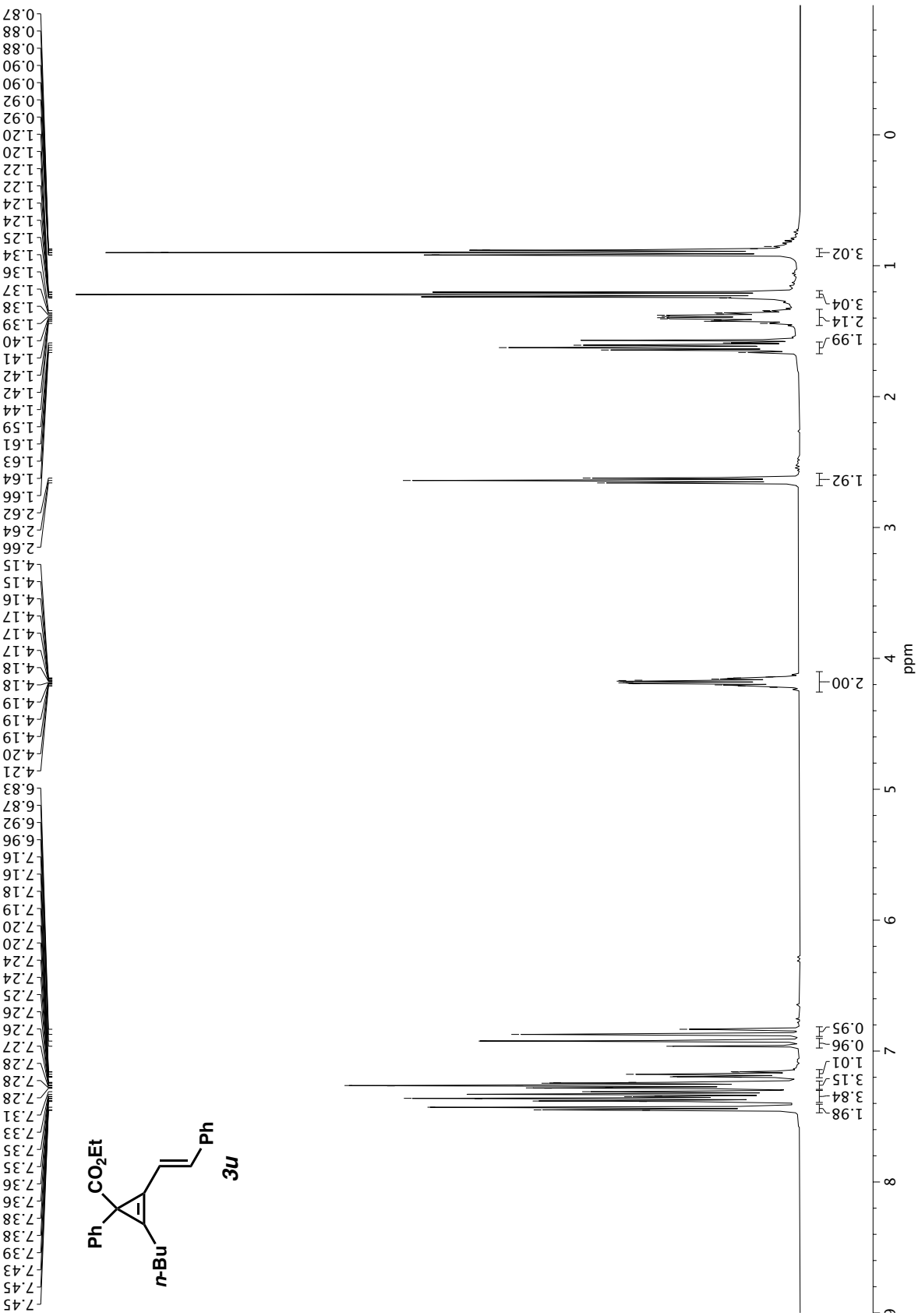
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3r**.



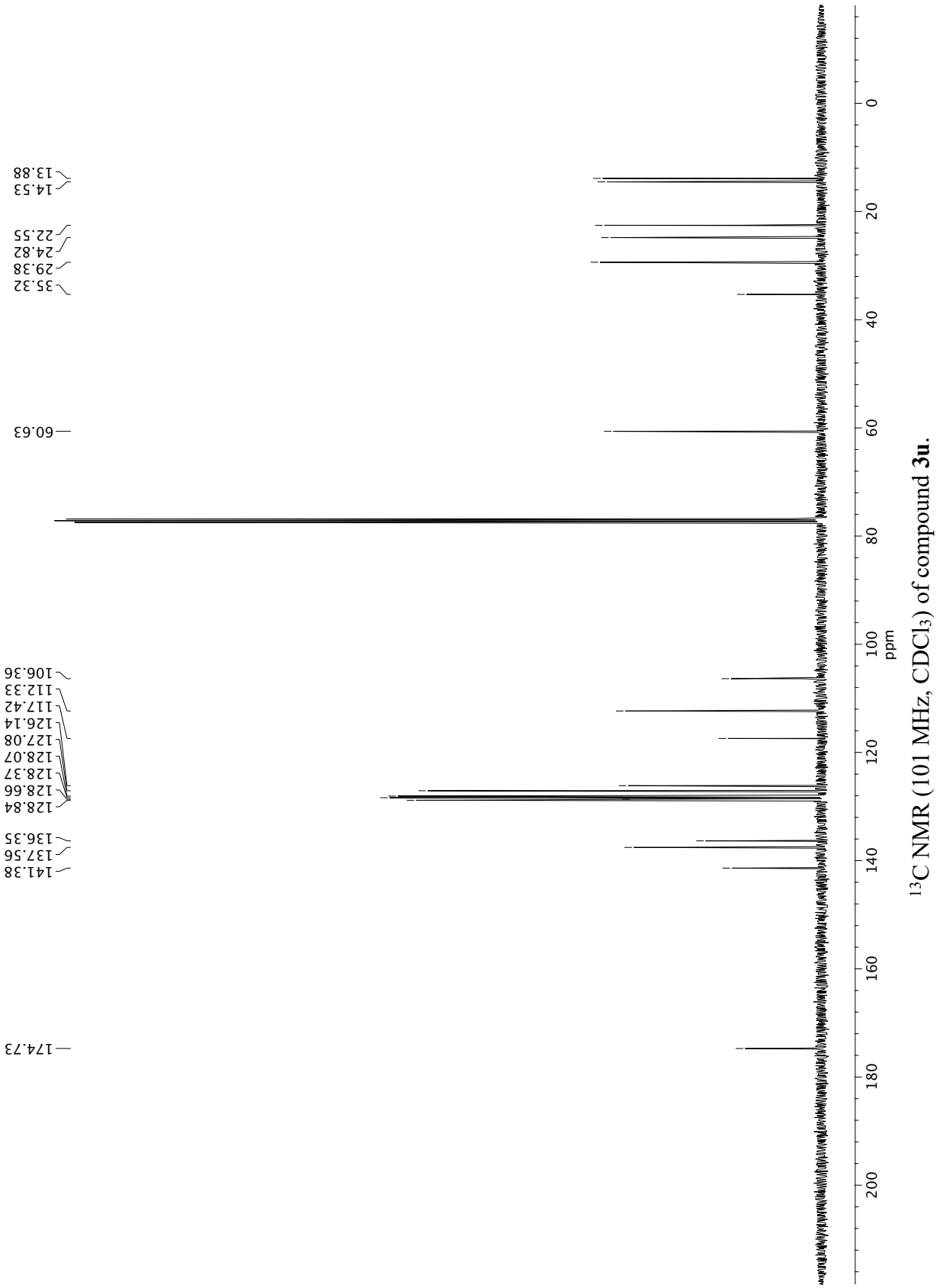
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3s**.



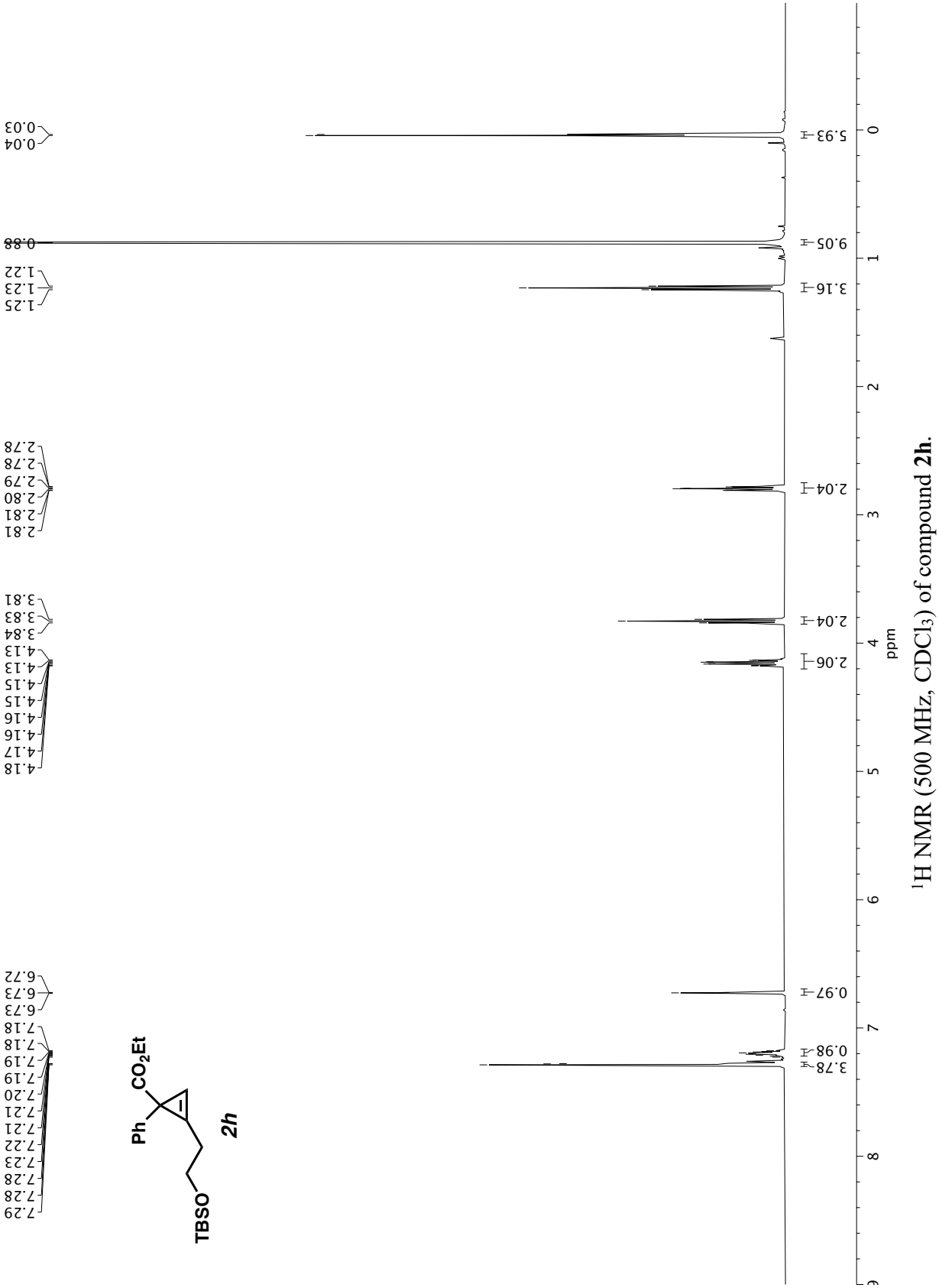
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3t**.



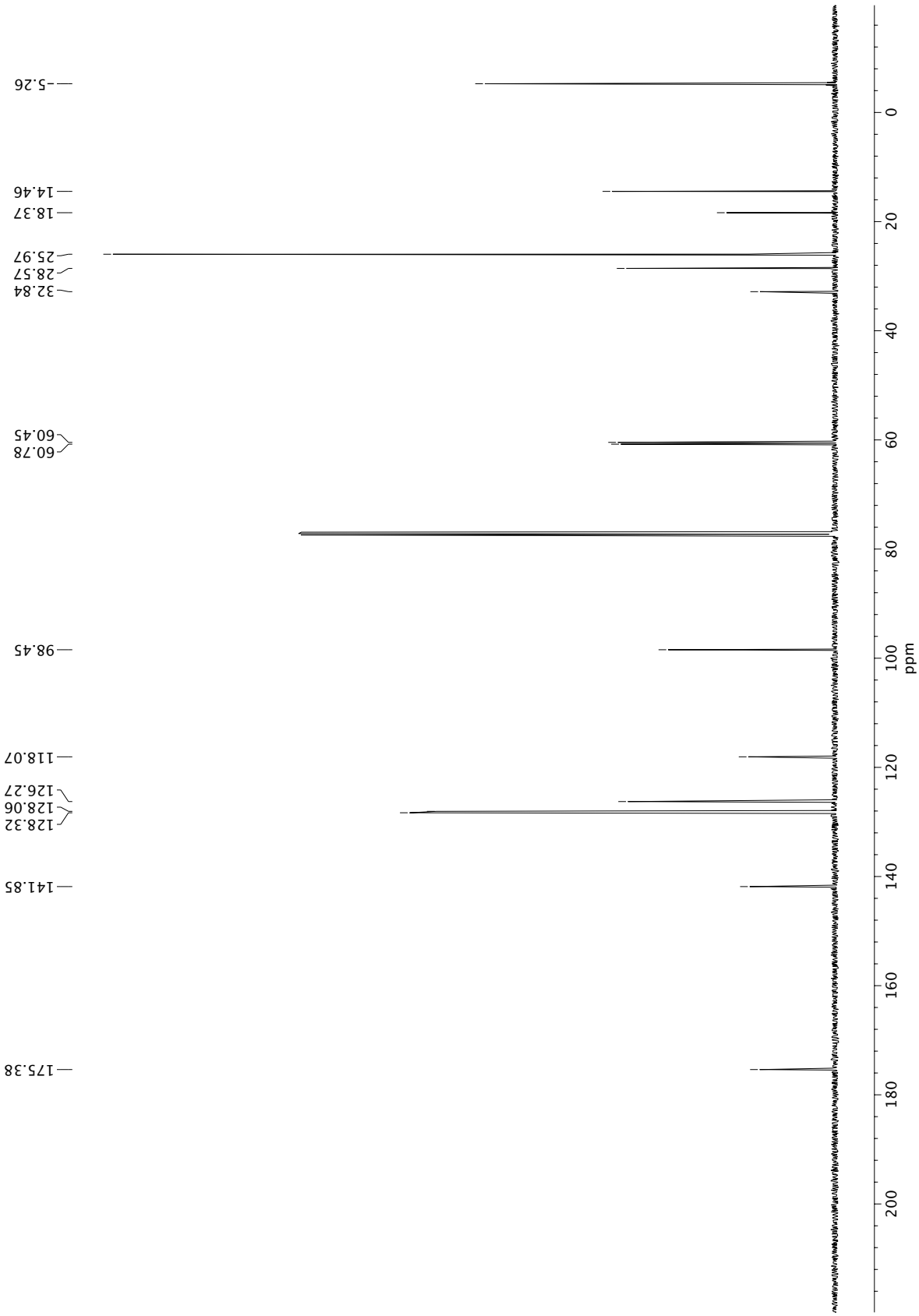
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3u**.



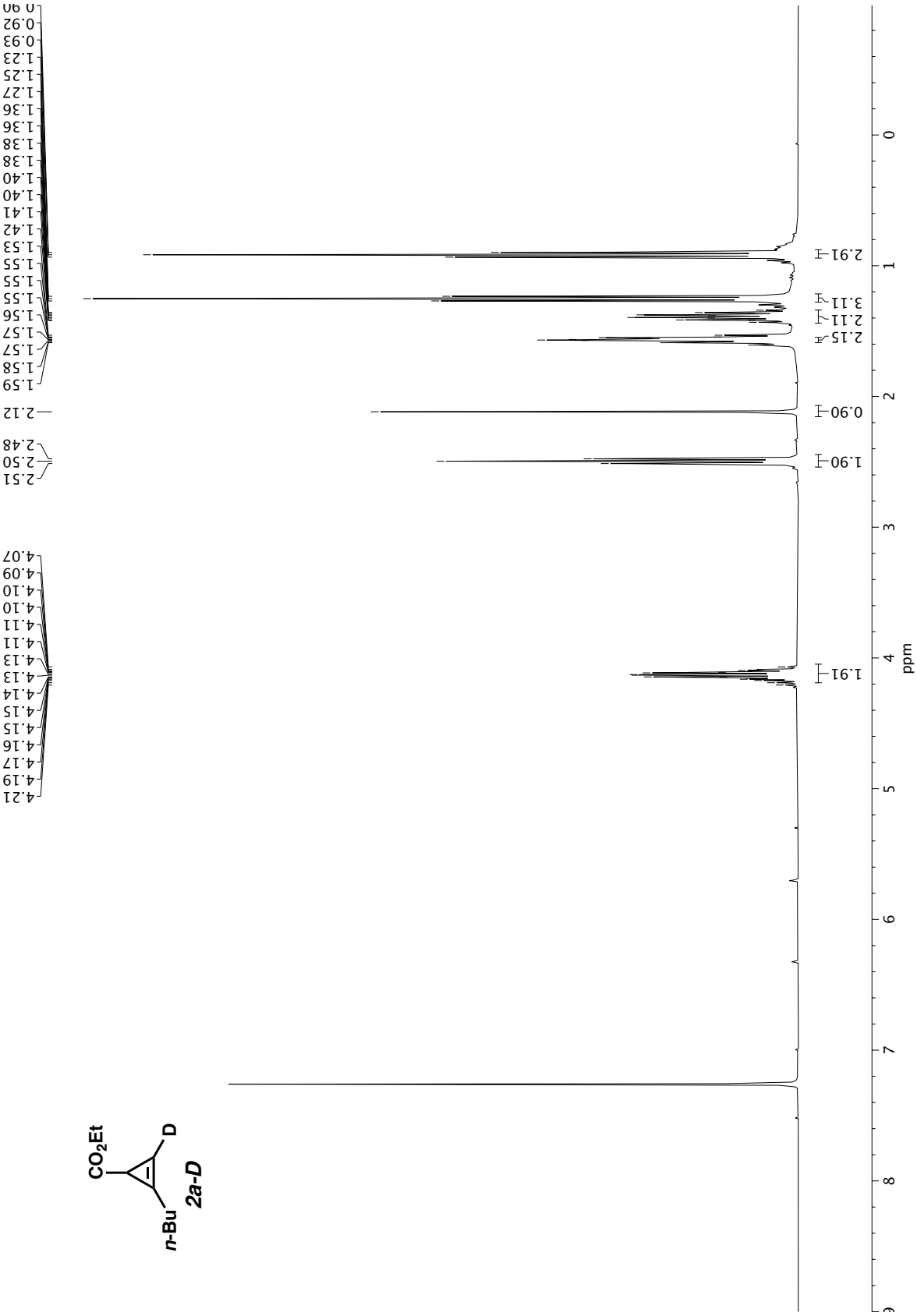
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3u**.



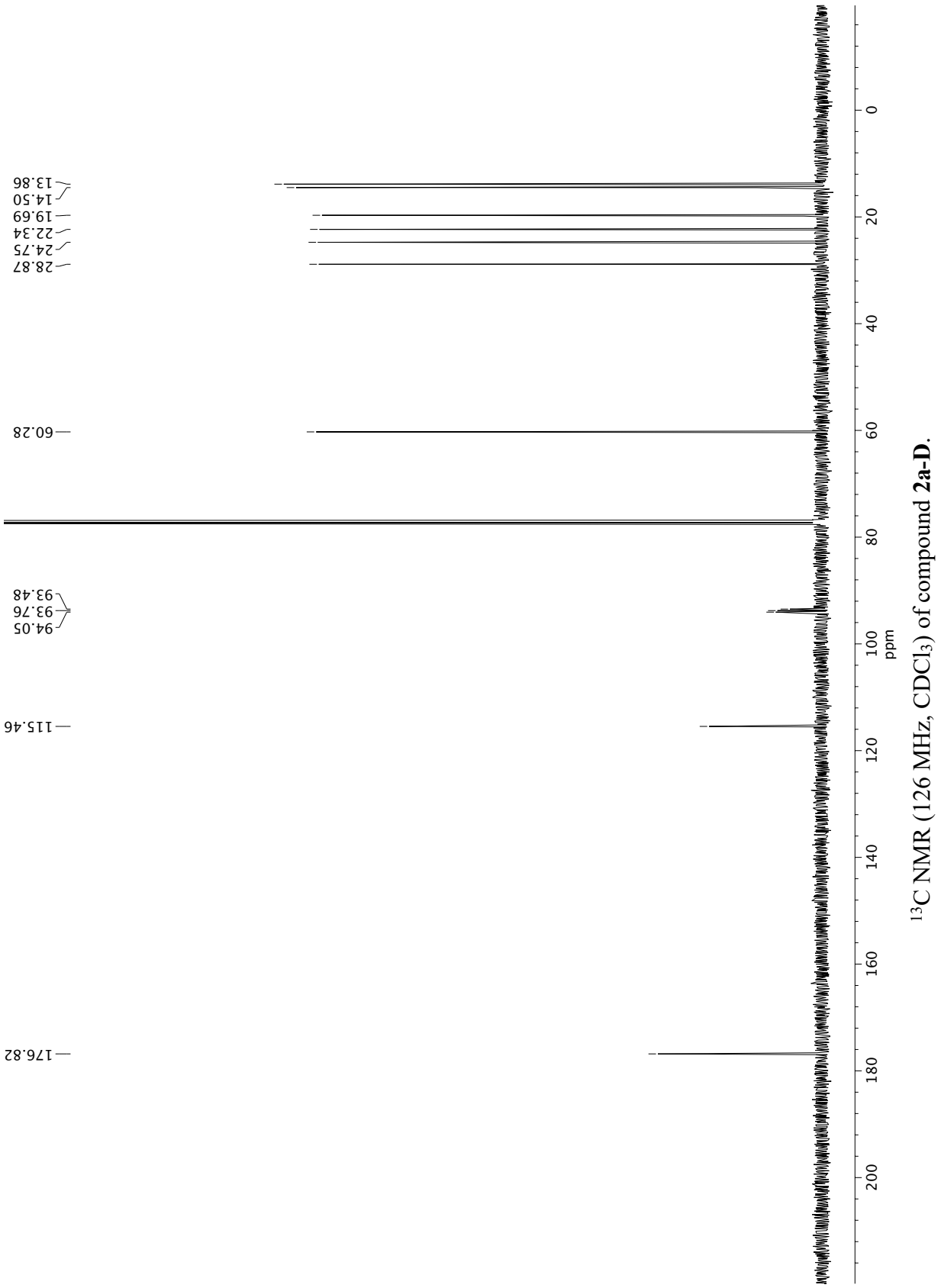
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2h**.



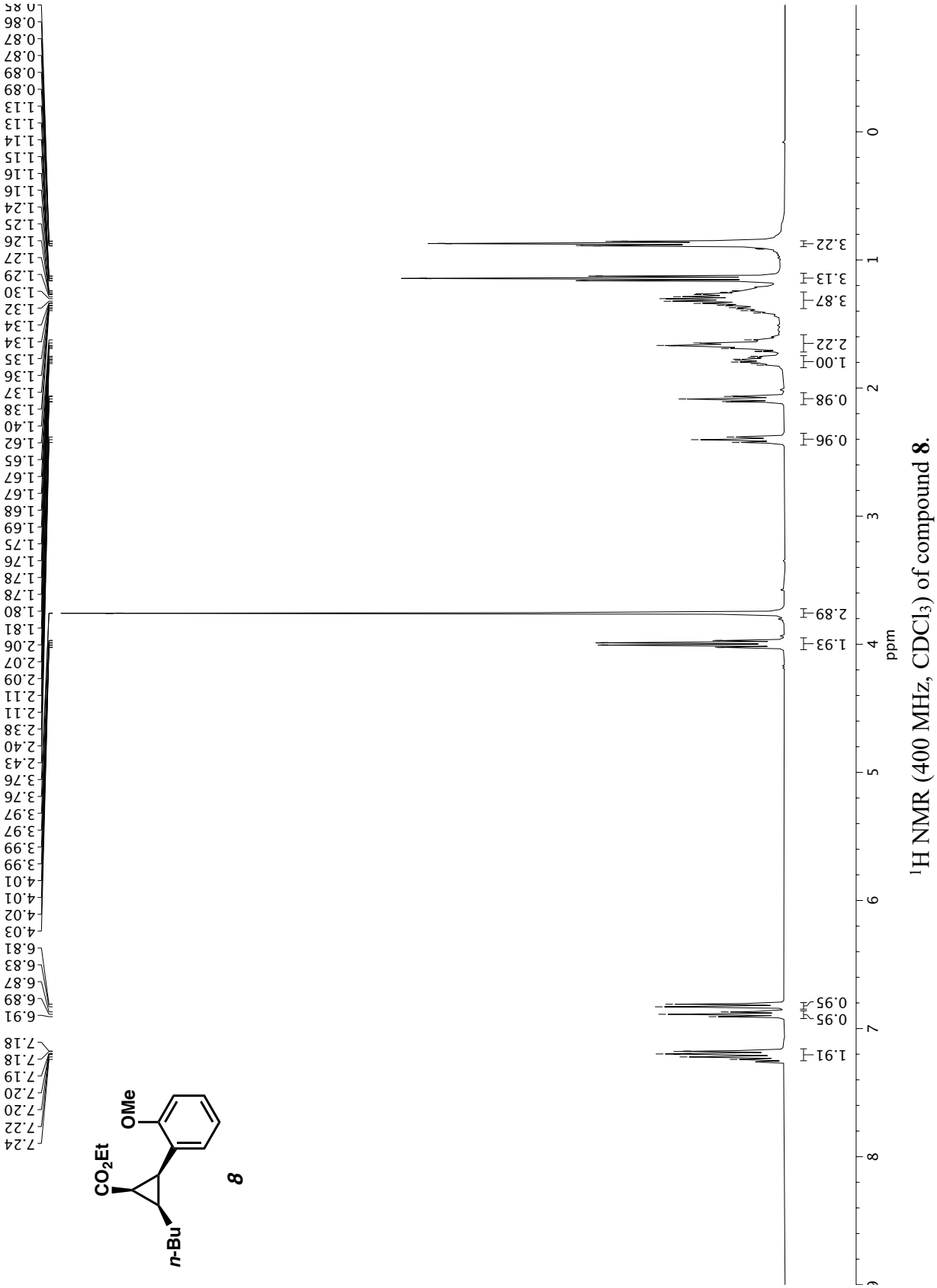
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2h**.



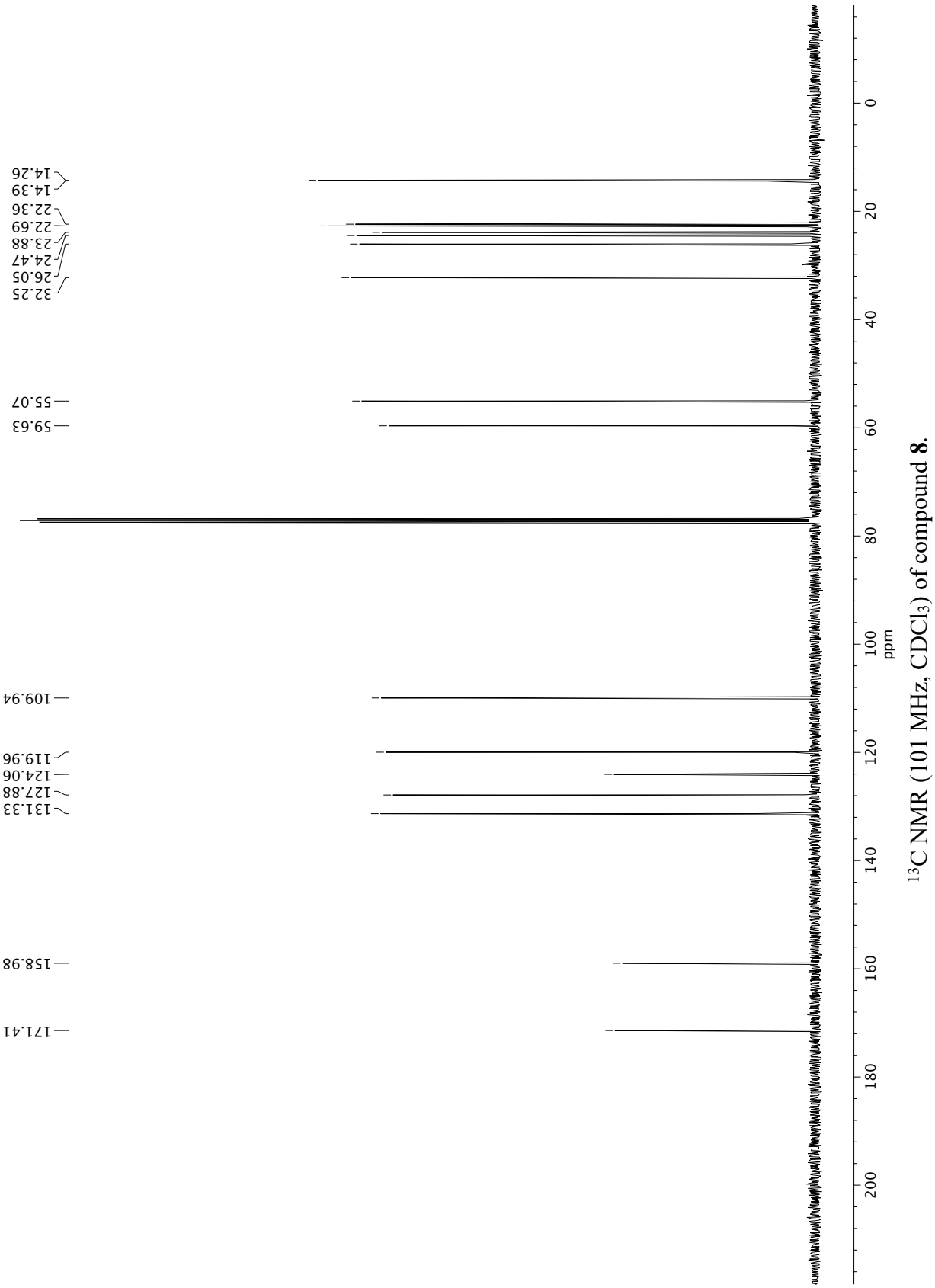
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a-D**.



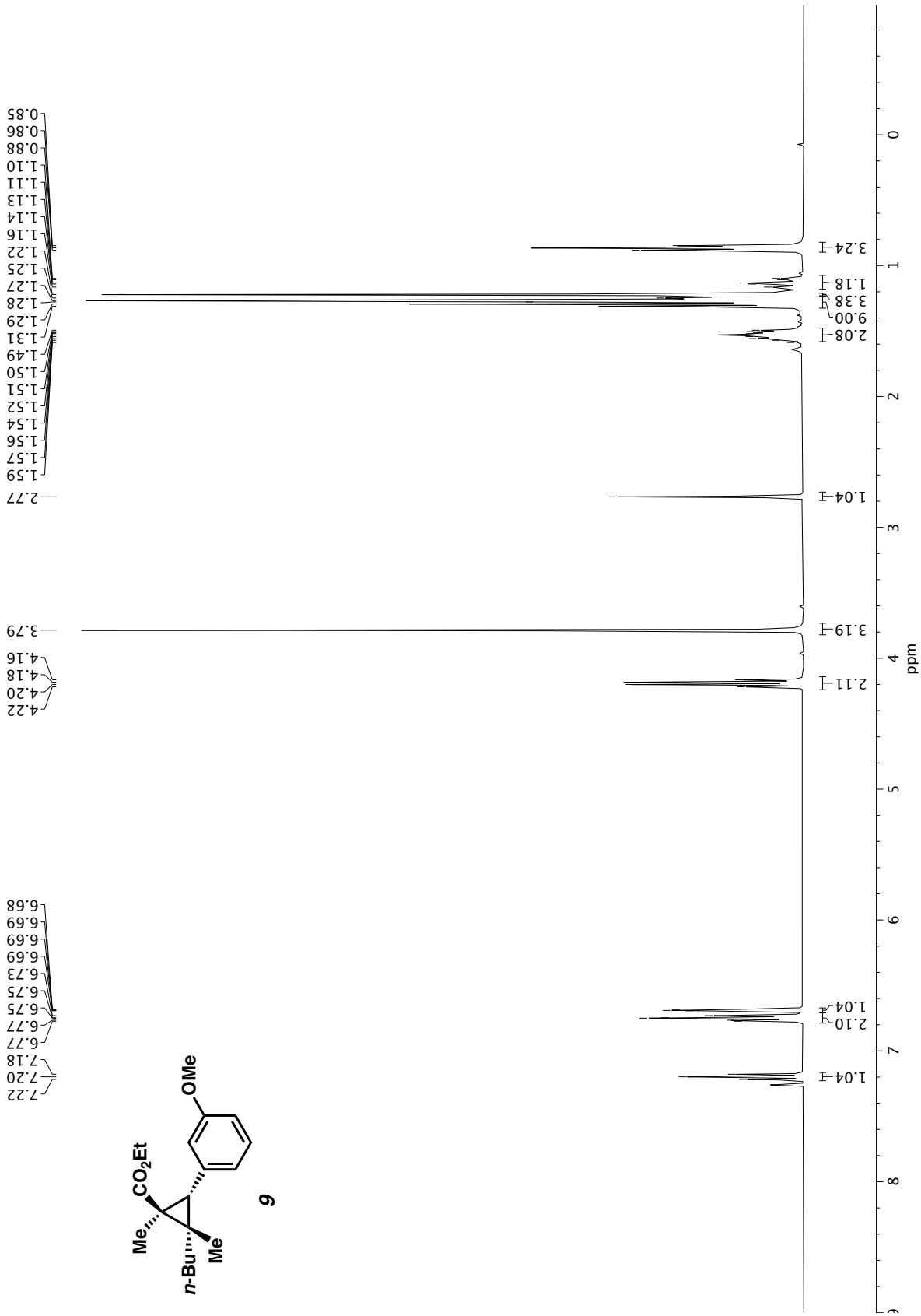
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2a-D**.



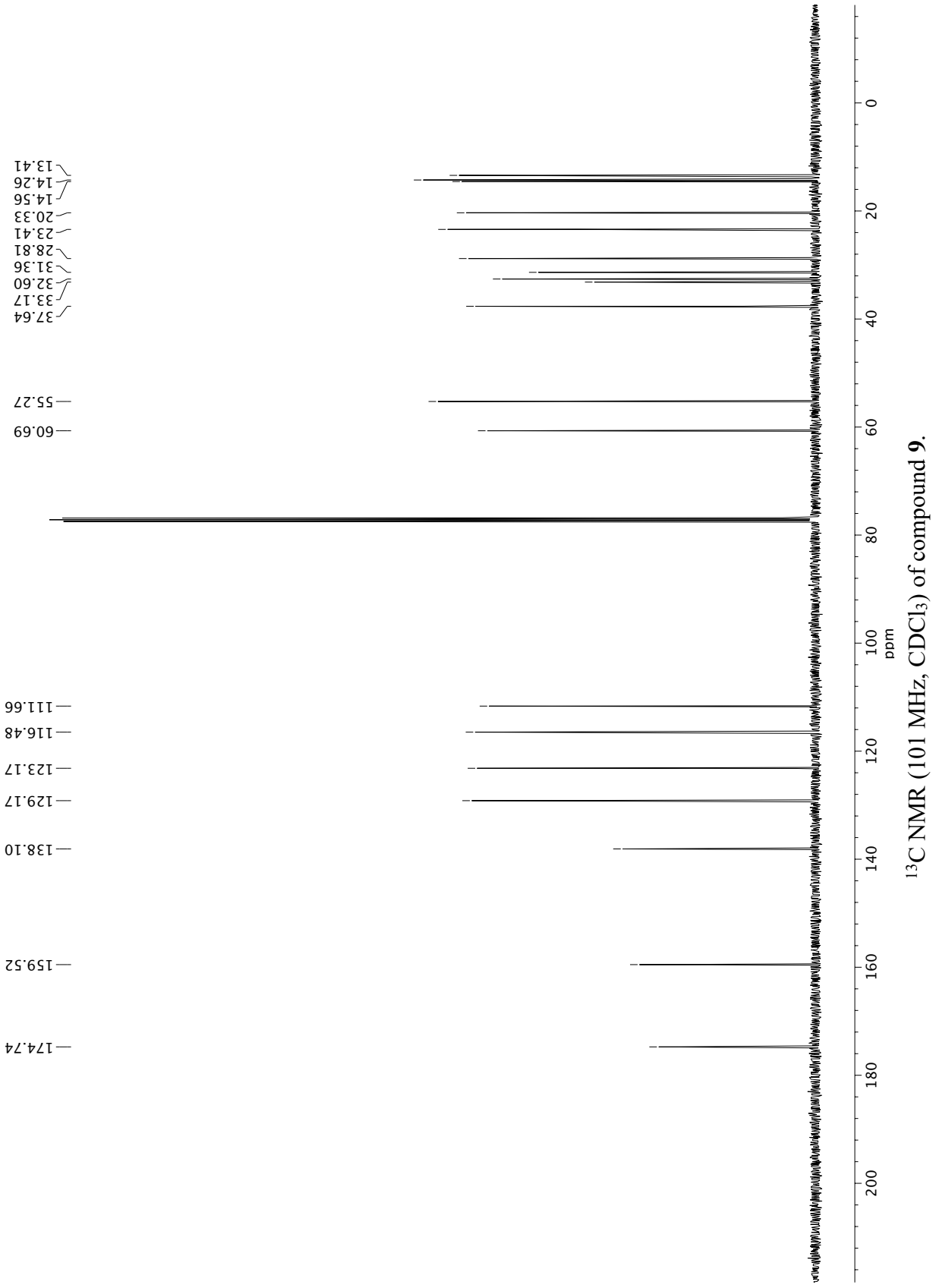
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8**.



^{13}C NMR (101 MHz, $CDCl_3$) of compound **8**.



^{1}H NMR (400 MHz, $CDCl_3$) of compound **9**.



^{13}C NMR (101 MHz, $CDCl_3$) of compound **9**.