Electronic Supplementary Information

for

Catalytic vs. Uncatalyzed [2+2] Photocycloadditions of Quinones with Alkynes

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Contents

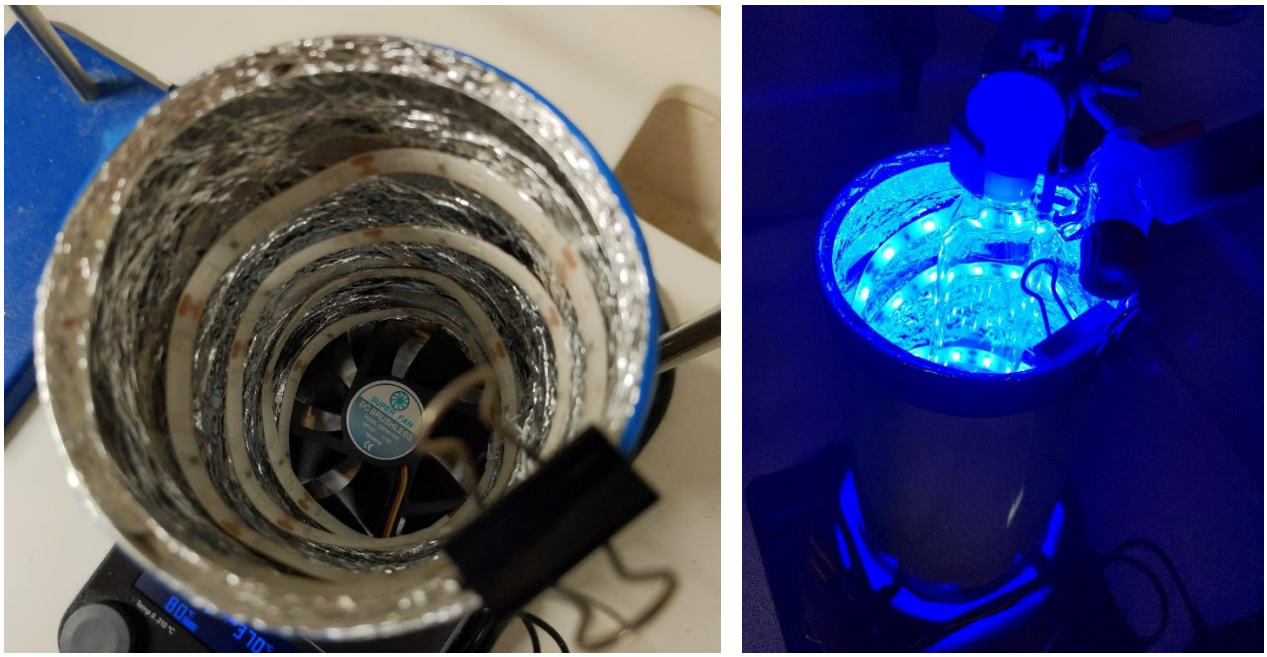
1 General

All reagents were purchased form commercial sources (Sigma-Aldrich, Acros Organics, Fluorochem and TCI Chemicals). Solvents were purified and dried by distillation. Other solvents and all reagents were used without further purification unless otherwise noted. During our initial studies, we did not observe any difference in the reaction outcome when special precautions (argon atmosphere, degassed solvents) were used for preparation of compounds **1**-**5**. Therefore, all the reactions were carried out under air atmosphere. Control experiments for the catalyst-free reactions were performed without stirring in a previously unused glassware to avoid false positive results. Column chromatography was performed on Merck Silica gel 60 from Sigma-Aldrich. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 coated aluminum sheets (254 nm UV light and neutral aqueous $KMnO_4$ were used for visualization). The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III HD Spectrometer (^{1}H at 400 MHz and ^{13}C at 101 MHz) as solutions in $CDCl_3$, CD_3OD and CD_3CN. Chemical shifts are given in parts per million (ppm) and referenced to the residual solvent peaks: $CDCl_3$ (^{1}H, $\delta = 7.26$; ^{13}C, $\delta = 77.2$), CD_3OD (^{1}H, $\delta = 3.31$; ^{13}C, $\delta = 49.0$) and CD_3CN (^{1}H, $\delta = 1.94$; ^{13}C, $\delta = 1.3$), coupling constants *J* are given in Hz (Hertz). The IR spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer in KBr powder and are reported in wave numbers (cm^{-1}). The MS spectra were recorded on LTQ Orbitrap XL (Thermo Scientific™). Crystallographic data were collected on Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube at 150 K. All melting points were determined on a meting point apparatus KB T3000.

Table S1. Nominal technical specifications of the diodes used for photoreactions

Color	Blue (monochrome)
Manufacturer	Epistar
Diode	SMD5050
LEDs per meter	60
Strip length	1 m
Wavelength maxima[1]	470 nm
Luminous flux	250 lm
Voltage	12 V DC
Power consumption	14,4 W/m
Protection	IP65

Picture S1. Experimental setup used for photochemical syntheses.

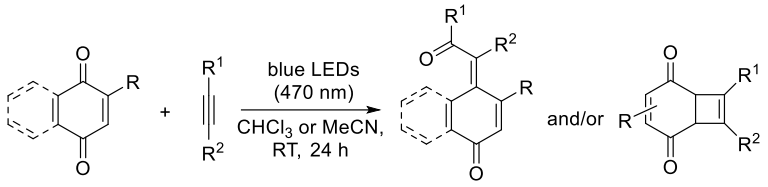


[1] The emission spectra of the SMD5050 LEDs can be found in the corresponding data sheet: https://www.iled.com/class/INNOVAEditor/assets/gallery2/5100-5105.pdf

2 Synthetic procedures

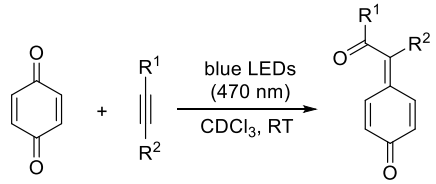
2.1 General procedures and other preparations

General procedure A: synthesis of photoproducts 1a–1f and 2a–2n



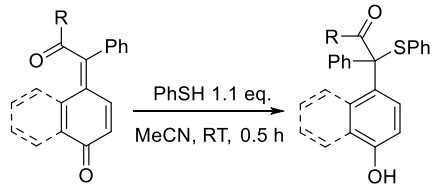
A solution of a quinone (1 mmol) and an alkyne (1.2 mmol) in MeCN or $CHCl_3$ (5 mL) in a 10 mL vial was irradiated with blue LEDs for 24 h at room temperature. The solvent was evaporated and the residue was purified by column chromatography on silica gel to give compounds **1** and/or **2**.

General procedure B: synthesis of *p*-QMs 1g–1j



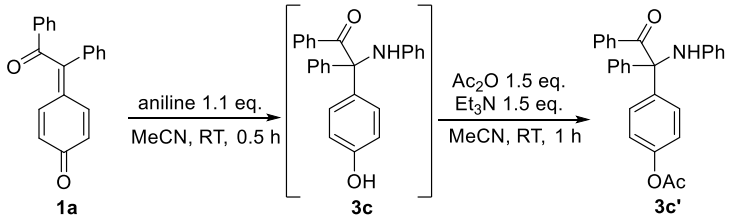
A solution of *p*-benzoquinone (0.10 mmol, 10.8 mg) and alkyne (0.10 mmol) in $CDCl_3$ (0.6 mL) was irradiated in an NMR tube with blue LEDs at room temperature. The reactions were monitored by NMR and product characterization was performed at the time of the highest *p*-QM signal intensity. The yields were measured in a separate set of experiments by adding internal standard (CH_2Br_2) after the same reaction time. When *p*-benzoquinone was used in excess (0.2 mmol, 21.6 mg), the yields were only slightly improved (<5%).

Synthesis of 3a and 3b



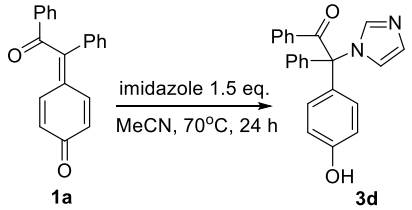
To a solution of **1a** (0.2 mmol, 57.2 mg) in MeCN (1 mL) was added thiophenol (0.22 mmol, 24 μl) and the reaction mixture was stirred for 0.5 h at room temperature, after which the bright yellow color faded and TLC showed full conversion of **1a**. The solvent was evaporated and the residue was purified by column chromatography on silica gel (**3a** was eluted with 12/1 hexanes/EtOAc) to give the product as a yellow oil (66.8 mg, 84% yield). Similarly, starting from *Z*-**1c** (0.2 mmol, 52.0 mg), **3b** was obtained as a pale yellow solid (71.8 mg, 97% yield).

Synthesis of 3c'



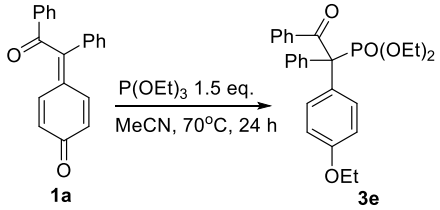
To a solution of **1a** (0.4 mmol, 114.4 mg) in MeCN (2 mL) was added freshly distilled aniline (0.44 mmol, 40 µl) and the reaction mixture was stirred for 3 h at room temperature, after which the bright yellow color faded and TLC showed nearly full conversion of **1a**. Next, Ac_2O (0.6 mmol, 57 µl) and Et_3N (0.6 mmol, 84 µl) were added to the reaction mixture and the stirring was continued for 1 h. After that, the volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (**3c'** was eluted with 25/1 hexanes/EtOAc) to give the product as a pale yellow powder (152.0 mg, 90% yield).

Synthesis of 3d



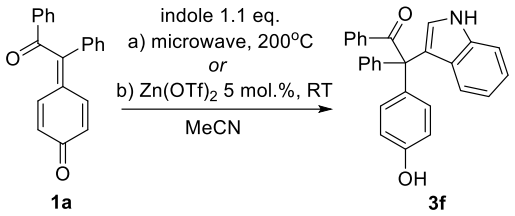
To a solution of **1a** (0.2 mmol, 57.2 mg) in MeCN (1 mL) was added imidazole (0.3 mmol, 20.4 mg) and the reaction mixture was stirred for 24 h at 70 °C, after which the bright yellow color faded and TLC showed full conversion of **1a**. The solvent was evaporated and the residue was dissolved in EtOAc (10 mL), washed with water (3×50 mL), and the organic layer was dried with Na_2SO_4. Evaporation of the solvent gave an oil, which was dissolved in MeOH (1 mL), water (5 mL) was added and thus formed solid was filtered, washed with water and dried *in vacuo* to give **3d** as a white powder (67.3 mg, 95% yield).

Synthesis of 3e



To a solution of **1a** (0.2 mmol, 57.2 mg) in MeCN (1 mL) was added triethyl phosphite (0.3 mmol, 51 µl) and the reaction mixture was stirred for 24 h at 70 °C, after which the bright yellow color faded and TLC showed full conversion of **1a**. The solvent was evaporated and the residue was purified by column chromatography on silica gel (**3e** was eluted with 20/1 DCM/Et_2O) to give the product as a pale yellow oil (59.7 mg, 66% yield).

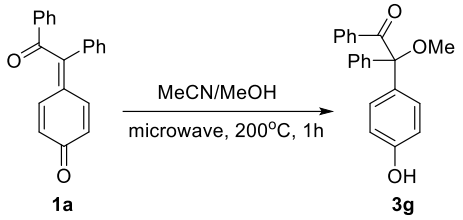
Synthesis of 3f



Microwave reaction: A solution of **1a** (0.2 mmol, 57.2 mg) and indole (0.22 mmol, 26 mg) in MeCN (1 mL) was stirred at 200 °C in a microwave reactor (Anton Paar Monowave 400) for 0.5 h after which the bright yellow color faded (monitored with an inside camera) and TLC showed full conversion of **1a**. The solvent was evaporated and the residue was purified by column chromatography on silica gel (**3f** was eluted with 4/1 hexanes/EtOAc) to give the product as a pink foam (66.7 mg, 83% yield).

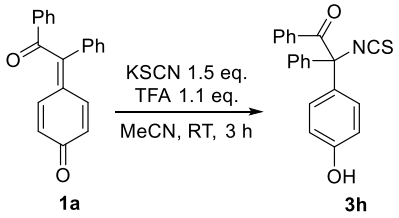
Catalytic reaction: To a solution of **1a** (0.2 mmol, 57.2 mg) and indole (0.22 mmol, 26 mg) in MeCN (1 mL) was added $Zn(OTf)_2$ (0.01 mmol, 3.6 mg) and the reaction mixture was stirred for 0.5 h at room temperature, after which the bright yellow color faded and TLC showed full conversion of **1a**. The solvent was evaporated and the residue was purified by column chromatography on silica gel (**3f** was eluted with 4/1 hexanes/EtOAc) to give the product as a pink foam (70.0 mg, 87% yield).

Synthesis of 3g



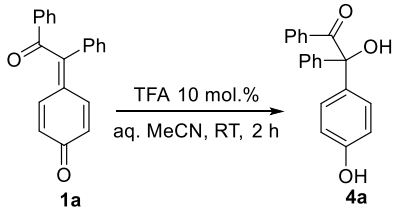
A solution of **1a** (0.2 mmol, 57.2 mg) in MeCN (1 mL), containing MeOH (0.1 mL) was stirred at 200 °C in a microwave reactor (Anton Paar Monowave 400) for 1 h (according to previous experiments, conversion of **1a** did not increase after this time). The solvent was evaporated and the residue was purified by column chromatography on silica gel (**3g** was eluted with 15/1 hexanes/EtOAc) to give the product as a pale yellow oil (29.8 mg, 47% isolated yield, 98% yield based on recovered **1a**).

Synthesis of 3h



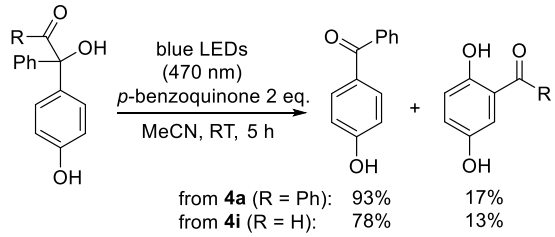
To a solution of **1a** (0.2 mmol, 57.2 mg) in MeCN (1 mL) was added potassium thiocyanate (0.3 mmol, 29.1 mg) followed by trifluoroacetic acid (0.22 mmol, 17 µl) and the reaction mixture was stirred for 3 h at room temperature, after which the bright yellow color faded and TLC showed full conversion of **1a**. The solvent was evaporated and the residue was purified by column chromatography on silica gel (**3h** was eluted with 15/1 hexanes/EtOAc) to give the product as a pale yellow oil (64.2 mg, 93% yield).

Synthesis of 4a from 1a



To a solution of **1a** (0.2 mmol, 57.2 mg) in MeCN (1 mL) was added aqueous trifluoroacetic acid (0.2 M, 0.1 mL) and the reaction mixture was stirred for 2 h at room temperature, after which the bright yellow color faded, and TLC showed full conversion of **1a**. The solvent was evaporated and the residue was purified by column chromatography on silica gel (**4a** was eluted with 13/1 hexanes/EtOAc) to give the product as a yellow oil (59.6 mg, 98% yield). When the reaction was performed in the absence of trifluoroacetic acid, only 40% of **1a** was converted into **4a** after 24 h at 70 °C.

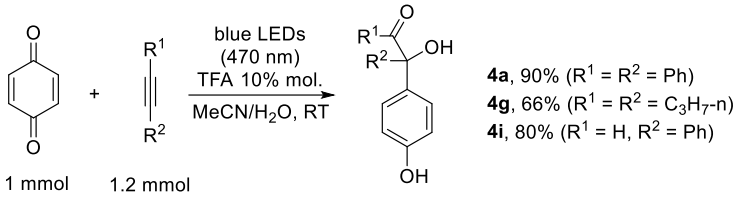
Synthesis of 4-hydroxybenzophenone from 4a or 4i



A solution of **4a** or **4i** (0.5 mmol) and *p*-benzoquinone (1 mmol, 108 mg) in MeCN (2.5 mL) in a 10 mL vial was irradiated with blue LEDs for 5 h at room temperature. The solvent was evaporated and the residue was purified by column chromatography on silica gel (4-hydroxybenzophenone was eluted with 10/1 hexanes/EtOAc) to give the product as a greenish yellow solid (92 mg, 93% yield from **4a** and 77 mg, 78% yield from **4i**). Small amounts of acylated hydroquinones were detected in the reaction mixtures and isolated. Thus, 2,5-

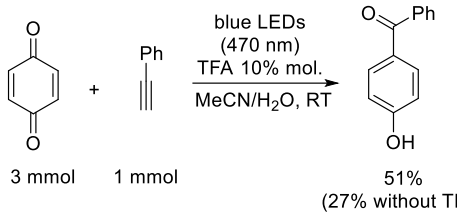
dihydroxybenzophenone (yellow solid, 18.0 mg, 17% yield, eluted with 20/1 hexanes/EtOAc) was obtained from **4a** and 2,5-dihydroxybenzaldehyde (yellow solid, 9.1 mg, 13% yield, eluted with 10/1 hexanes/EtOAc) was obtained from **4i**.

General procedure C: one-pot synthesis of 4a, 4g, 4i



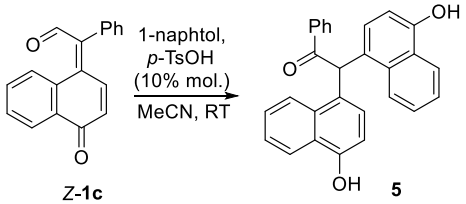
To a solution of a *p*-benzoquinone (1 mmol, 108 mg) and the corresponding alkyne (1.2 mmol) in MeCN (5 mL) in a 10 mL vial was added aqueous trifluoroacetic acid (0.2 M, 0.5 mL) and the reaction was irradiated with blue LEDs for 5 h at room temperature. The solvent was evaporated and the residue was purified by column chromatography on silica gel to give the corresponding product.

One-pot synthesis of 4-hydroxybenzophenone



To a solution of *p*-benzoquinone (3 mmol, 324 mg) and phenylacetylene (1 mmol, 110 µl) in MeCN (5 mL) was added aqueous trifluoroacetic acid (0.2 M, 0.5 mL) and the reaction was irradiated with blue LEDs for 24 h at room temperature. The solvent was evaporated and the residue was purified by column chromatography (4-hydroxybenzophenone was eluted with 10/1 hexanes/EtOAc) to give the product as a greenish yellow solid (101 mg, 51% yield). When the reaction was carried out with pure deionized water instead of trifluoroacetic acid solution, the product was obtained in 27% yield.

Synthesis of 5

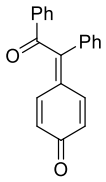


To a solution *Z*-**1c** (0.2 mmol, 52.0 mg) and 1-naphthol (0.4 mmol, 57.7 mg) in MeCN (1 mL) was added *p*-TsOH·H_2O (0.02 mmol, 3.8 mg) and the reaction mixture was stirred for 48 h at room temperature. The solvent was evaporated, and the residue was purified by column chromatography (4/1 hexanes/EtOAc) to give the crude product. It was then dissolved in DCM (3

mL) and hexane was added dropwise to the solution, causing impurities to precipitate as a dark oil. The solution was decanted and evaporated to give **5** as a pale brown solid (21.8 mg, 27% yield).

2.2 Compound characterization

4-(2-Oxo-1,2-diphenylethylidene)cyclohexa-2,5-dien-1-one (1a)



The title compound was prepared from *p*-benzoquinone (1 mmol, 108 mg) and diphenylacetylene (1.2 mmol, 214 mg) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (10/1 hexanes/EtOAc) yielded 249 mg (87%) of the title compound as a bright yellow solid. When the reaction was carried out in MeCN, the product was obtained in 82% isolated yield.

TLC R_f = 0.31 (2/1 hexanes/EtOAc);

M. p. 100 °C (lit. 105–106 °C[2]);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 – 7.88 (m, 2H), 7.63 – 7.57 (m, 1H), 7.52 (dd, *J* = 10.0, 2.5 Hz, 1H), 7.54 – 7.43 (m, 7H), 7.15 (dd, *J* = 10.0, 2.5 Hz, 1H), 6.51 (dd, *J* = 10.0, 2.0 Hz, 1H), 6.38 (dd, *J* = 10.0, 2.0 Hz, 1H);

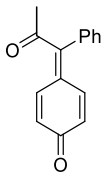
^{1}H NMR (400 MHz, CD_3CN): δ = 7.97 – 7.92 (m, 2H), 7.67 – 7.62 (m, 1H), 7.55 – 7.47 (m, 8H), 7.18 (dd, *J* = 10.0, 2.7 Hz, 1H), 6.44 (dd, *J* = 10.0, 2.1 Hz, 1H), 6.30 (dd, *J* = 10.0, 2.1 Hz, 1H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 195.9, 186.7, 154.5, 137.1, 136.9, 135.8, 134.7, 133.7, 130.9, 130.4, 130.1 (2C), 130.0 (2C), 129.9, 129.7, 129.3 (2C), 129.2 (2C);

IR (KBr): $\tilde{\nu}$ = 1655, 1633, 1593, 1531, 1444, 1385, 1336, 1309, 1248, 1217, 1171, 1076, 1030, 904, 862, 752, 712 cm^{-1};

HRMS (APCI): m/z calcd for $C_{20}H_{15}O_2^+$: 287.1067 $[M+H]^+$; found: 287.1060.

4-(2-Oxo-1-phenylpropylidene)cyclohexa-2,5-dien-1-one (1b)



The title compound was prepared from *p*-benzoquinone (1 mmol, 108 mg) and 1-phenyl-1-propyne (1.2 mmol, 139 mg, 150 µl) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (10/1 hexanes/EtOAc) yielded 190 mg (85%) of the title compound as a yellow oil.

TLC R_f = 0.38 (2/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 – 7.48 (m, 3H), 7.43 (dd, *J* = 10.0, 2.7 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.21 (dd, *J* = 10.0, 2.7 Hz, 1H), 6.47 (dd, *J* = 10.0, 2.0 Hz, 1H), 6.43 (dd, *J* = 10.0, 2.0 Hz, 1H), 2.29 (s, 3H);

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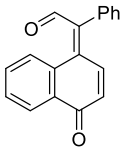
[2] H. E. Zimmerman, L. Craft, *Tetrahedron Lett*. **1964**, *5*, 2131−2136.

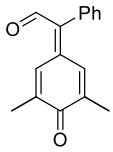
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 202.8, 186.9, 154.9, 137.4, 136.7, 133.7, 131.1, 130.4, 130.3, 129.9 (2C), 129.4, 129.3 (2C), 31.0;
IR (KBr): ṽ = 1712, 1631, 1604, 1502, 1446, 1352, 1230, 1163, 1032, 864, 829, 754, 698 cm^{-1};
HRMS (ESI): m/z calcd for $C_{15}H_{13}O_2^+$: 225.0910 $[M+H]^+$; found: 225.0910.

(*Z*)-2-(4-Oxonaphthalen-1(4H)-ylidene)-2-phenylacetaldehyde (1c)



The title compound was prepared according to the general procedure A using 3 mmol of 1,4-naphthoquinone (474 mg) and 3.6 mmol of phenylacetylene (0.4 mL) and MeCN as solvent (15 mL). Column chromatography (gradient elution with hexanes/EtOAc) yielded **2c** (96 mg, 12% yield) as a yellow solid together with **1c** (247 mg, 32% yield, 6/1 *Z*/*E*) as an orange oil. Crystallization of the latter from DCM/hexanes gave pure *Z*-**1c** as orange prisms (118 mg, >20/1 *Z*/*E*).
TLC R_f = 0.30 (2/1 hexanes/EtOAc);
M. p. 139 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.29 (s, 1H), 8.34 – 8.27 (m, 1H), 7.74 – 7.67 (m, 2H), 7.61 – 7.55 (m, 2H), 7.51 – 7.46 (m, 3H), 7.32 – 7.27 (m, 2H), 6.50 (d, *J* = 10.3 Hz, 1H);
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 192.6, 184.3, 145.6, 143.0, 142.7, 134.8, 133.0, 132.1, 131.9, 131.5 (2C), 131.3, 131.1, 130.2, 129.7, 128.8 (2C), 128.0;
IR (KBr): ṽ = 1666, 1628, 1587, 1441, 1398, 1331, 1298, 1255, 1167, 1124, 1076, 1053, 1022, 839, 768, 714 cm^{-1};
HRMS (APCI): m/z calcd for $C_{18}H_{13}O_2^+$: 261.0910 $[M+H]^+$; found: 261.0914.

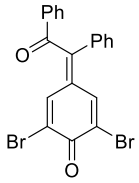
2-(3,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-2-phenylacetaldehyde (1d)



The title compound was prepared from 2,6-dimethylbenzoquinone (1 mmol, 136 mg) and phenylacetylene (1.2 mmol, 122 mg, 135 µl) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (gradient elution with hexanes/EtOAc) yielded **2d** (69 mg, 29% yield) as a yellow oil together with **1d** (96 mg, 40% yield) as an orange solid.
TLC R_f = 0.55 (3/1 hexanes/EtOAc);
M. p. 148 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.58 (s, 1H), 8.06 (dd, *J* = 2.6, 1.4 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.24 – 7.17 (m, 2H), 6.99 (dd, *J* = 2.6, 1.4 Hz, 1H), 2.14 (d, *J* = 1.4, 3H), 1.97 (d, *J* = 1.4, 3H);

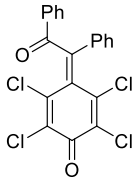
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 190.9, 186.8, 143.2, 140.4, 139.6, 138.9, 134.8, 133.7, 131.0 (2C), 129.9, 129.3, 128.5 (2C), 17.1, 16.9;
IR (KBr): ṽ = 1660, 1608, 1531, 1489, 1429, 1358, 1250, 1192, 1070, 1034, 916, 785, 771, 708 cm^{-1};
HRMS (ESI): m/z calcd for $C_{16}H_{15}O_2^+$: 239.1067 $[M+H]^+$; found: 239.1070.

2,6-Dibromo-4-(2-oxo-1,2-diphenylethylidene)cyclohexa-2,5-dien-1-one (1e)



The title compound was prepared from 2,6-dibromo-1,4-benzoquinone (0.5 mmol, 133 mg) and diphenylacetylene (0.6 mmol, 107 mg) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (15/1 hexanes/EtOAc) afforded the product as a 3:1 mixture of regioisomers (157 mg, 71% yield), from which the pure major isomer **1e** was isolated by crystallization from EtOAc (bright yellow microcrystals, 102 mg, 46% yield).
TLC R_f = 0.41 (3/1 hexanes/EtOAc);
M. p. 205 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 2.4 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.65 – 7.60 (m, 1H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.52 – 7.45 (m, 7H);
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 194.8, 172.9, 156.8, 138.41, 138.37, 135.3, 135.2, 133.3, 131.2, 130.3 (2C), 130.1 (2C), 129.7, 129.6 (2C), 129.4 (2C), 126.6, 125.5;
IR (KBr): ṽ = 1643, 1593, 1587, 1545, 1442, 1321, 1263, 1213, 1176, 1159, 1059, 1022, 908, 866, 764, 708 cm^{-1};
HRMS (ESI): m/z calcd for $C_{20}H_{13}Br_2O_2^+$: 444.9256 $[M+H]^+$; found: 444.9264.

2,3,5,6-Tetrachloro-4-(2-oxo-1,2-diphenylethylidene)cyclohexa-2,5-dien-1-one (1f)

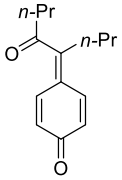


The title compound was prepared from chloranil (1 mmol, 246 mg) and diphenylacetylene (1.2 mmol, 214 mg) according to the general procedure A using $CHCl_3$ as solvent (reaction time 48 h). Column chromatography (60/1 hexanes/EtOAc) yielded 224 mg of **1f** as a bright yellow solid (53% isolated yield, 96% yield based on recovered diphenylacetylene).
TLC R_f = 0.47 (3/1 hexanes/EtOAc);
M. p. 176 °C (lit. 185–187 °C[3]);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 – 7.81 (m, 2H), 7.57 – 7.52 (m, 1H), 7.47 – 7.28 (m, 7H);

[3] J. A. Barltrop, B. Hesp, *J. Chem. Soc. C*, **1967**, 1625−1635.

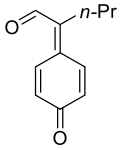
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 193.0, 170.7, 160.6, 141.6, 141.0, 136.1, 135.6, 135.1, 134.3, 132.8, 131.2, 130.8, 129.7 (2C), 129.4 (2C), 129.3, 129.2 (2C), 127.0;
IR (KBr): $\tilde{\nu}$ = 1655, 1564, 1516, 1450, 1315, 1259, 1132, 1109, 1055, 874, 731, 712, 694 cm^{-1};
HRMS (ESI): m/z calcd for $C_{20}H_{11}Cl_4O_2^+$: 424.9478 $[M+H]^+$; found: 424.9478.

4-(5-Oxooctan-4-ylidene)cyclohexa-2,5-dien-1-one (1g)



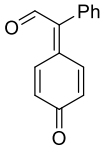
The title compound was prepared from *p*-benzoquinone (0.1 mmol, 10.8 mg) and 4-octyne (0.1 mmol, 11.0 mg) as a solution in $CDCl_3$ according to the general procedure B (reaction time 1 h).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (dd, *J* = 10.1, 2.7 Hz, 1H), 7.10 (dd, *J* = 10.1, 2.7 Hz, 1H), 6.48 (dd, *J* = 10.1, 1.8 Hz, 1H), 6.36 (dd, *J* = 10.1, 1.8 Hz, 1H), 2.70 – 2.58 (m, 4H), 1.76 – 1.66 (m, 2H), 1.62 – 1.52 (m, 2H), 1.02 – 0.95 (m, 6H);
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 207.6, 187.1, 159.7, 136.8, 134.8, 130.6, 129.1, 127.8, 44.9, 32.4, 22.9, 17.0, 14.2, 13.8;
HRMS (APCI): m/z calcd for $C_{14}H_{19}O_2^+$: 219.1380 $[M+H]^+$; found: 219.1371.

2-(4-Oxocyclohexa-2,5-dien-1-ylidene)pentanal (1h)



The title compound was prepared from *p*-benzoquinone (0.1 mmol, 10.8 mg) and 1-pentyne (0.1 mmol, 6.8 mg) as a solution in $CDCl_3$ according to the general procedure B (reaction time 1 h).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.58 (s, 1H), 8.13 (dd, *J* = 10.0, 2.4 Hz, 1H), 7.66 (dd, *J* = 10.0, 2.4 Hz, 1H), 6.60 – 6.52 (m, 2H), 2.72 – 2.61 (m, 2H), 1.60 – 1.43 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H);
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 190.2, 186.4, 148.9, 138.2, 136.4, 132.9, 132.2, 130.4, 28.7, 24.4, 14.4;
HRMS (APCI): m/z calcd for $C_{11}H_{13}O_2^+$: 177.0910 $[M+H]^+$; found: 177.0907.

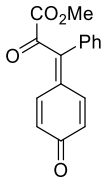
2-(4-Oxocyclohexa-2,5-dien-1-ylidene)-2-phenylacetaldehyde (1i)



The title compound was prepared from *p*-benzoquinone (0.1 mmol, 10.8 mg) and phenylacetylene (0.1 mmol, 10.2 mg) as a solution in $CDCl_3$ according to the general procedure B (reaction time 4 h).

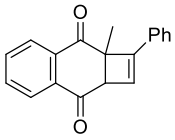
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.56 (s, 1H), 8.28 (dd, *J* = 10.2, 2.5 Hz, 1H), 7.58 – 7.45 (m, 3H), 7.40 – 7.21 (m, 3H), 6.64 (dd, *J* = 10.2, 1.8 Hz, 1H), 6.48 (dd, *J* = 10.2, 1.8 Hz, 1H);
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 190.9, 186.4, 146.1, 138.7, 137.4, 134.0, 133.2, 132.0, 131.5, 130.9 (2C), 130.0, 128.8 (2C);
HRMS (APCI): m/z calcd for $C_{14}H_{11}O_2^+$: 211.0754 $[M+H]^+$; found: 211.0756.

Methyl 2-oxo-3-(4-oxocyclohexa-2,5-dien-1-ylidene)-3-phenylpropanoate (1j)



The title compound was prepared from *p*-benzoquinone (0.1 mmol, 10.8 mg) and methyl phenylpropiolate (0.1 mmol, 16.0 mg) as a solution in $CDCl_3$ according to the general procedure B (reaction time 48 h).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 – 7.45 (m, 4H), 7.33 – 7.27 (m, 3H), 6.51 (dd, *J* = 10.1, 1.9 Hz, 1H), 6.47 (dd, *J* = 10.1, 1.9 Hz, 1H), 3.71 (s, 3H);
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 187.2, 186.8, 161.5, 148.7, 136.8, 135.9, 134.0, 132.2, 131.6, 131.0, 130.6, 130.4 (2C), 129.3 (2C), 53.4;
HRMS (ESI): m/z calcd for $C_{16}H_{12}NaO_4^+$: 291.0628 $[M+Na]^+$; found: 291.0625.

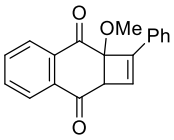
8a-Methyl-1-phenyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (2a)



The title compound was prepared from menadione (1 mmol, 172 mg) and phenylacetylene (1.2 mmol, 122 mg, 135 µl) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (40/1 hexanes/EtOAc) yielded 186 mg (68%) of a yellow oil, consisting of **2a** and its regioisomer (2a-methyl-1-phenyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione) in 5/1 ratio. Successive chromatographic separation afforded almost pure regioisomer **2a** (*rr* 25/1).
TLC R_f = 0.52 (2/1 hexanes/EtOAc);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 – 8.03 (m, 2H), 7.76 – 7.69 (m, 2H), 7.52 – 7.48 (m, 2H), 7.36 – 7.28 (m, 3H), 6.56 (d, *J* = 1.7 Hz, 1H), 3.79 (d, *J* = 1.7 Hz, 1H), 1.84 (s, 3H);
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 198.6, 196.9, 153.6, 134.6, 134.5, 133.9, 133.8, 131.7, 129.2, 128.8 (2C), 128.2, 127.7, 127.2, 125.7 (2C), 57.6, 57.3, 20.0;
HRMS (ESI): m/z calcd for $C_{19}H_{15}O_2^+$: 275.1067 $[M+H]^+$; found: 275.1066.
The recorded spectroscopic values agree with the previously reported data.[4]

[4] S.Farid, W.Kothe, G. Pfundt, *Tetrahedron Lett.* **1968**, *9*, 4151−4154.

8a-Methoxy-1-phenyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (2b)



The title compound was prepared from 2-methoxy-1,4-naphthoquinone (1 mmol, 188 mg) and phenylacetylene (1.2 mmol, 122 mg, 135 µl) according to the general procedure A using MeCN as solvent. Column chromatography (15/1 hexanes/EtOAc) yielded **2b** (200 mg, 69% yield) as a pale yellow oil.

TLC R_f = 0.41 (2/1 hexanes/EtOAc);

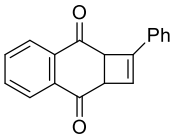
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 – 8.05 (m, 1H), 8.03 – 7.98 (m, 1H), 7.79 – 7.68 (m, 2H), 7.61 – 7.56 (m, 2H), 7.37 – 7.28 (m, 3H), 6.75 (d, *J* = 1.7 Hz, 1H), 4.15 (d, *J* = 1.7 Hz, 1H), 3.49 (s, 3H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 195.8, 194.8, 150.5, 134.9, 134.6, 133.5, 133.4, 131.6, 130.6, 129.7, 128.8 (2C), 128.5, 127.2, 126.2 (2C), 86.0, 55.5, 53.5;

HRMS (ESI): m/z calcd for $C_{19}H_{14}NaO_3^+$: 313.0835 [M+Na]$^+$; found: 313.0836.

The recorded spectroscopic values agree with the previously reported data.[5]

1-Phenyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (2c)



The title compound was prepared according to the general procedure A using 3 mmol of 1,4-naphthoquinone (474 mg) and 3.6 mmol of phenylacetylene (0.4 mL) and MeCN as solvent (15 mL). Column chromatography (gradient elution with hexanes/EtOAc) yielded **2c** (96 mg, 12% yield) as a yellow solid together with **1c** (247 mg, 32% yield, 6/1 *Z*/*E*) as an orange oil. Crystallization of the latter from DCM/hexanes gave pure *Z*-**1c** as orange prisms (118 mg, 48%).

TLC R_f = 0.37 (2/1 hexanes/EtOAc);

M. p. 125 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 – 8.07 (m, 1H), 8.05 – 8.00 (m, 1H), 7.77 – 7.69 (m, 2H), 7.58 – 7.53 (m, 2H), 7.37 – 7.27 (m, 3H), 6.60 – 6.53 (m, 1H), 4.53 (d, *J* = 3.7 Hz, 1H), 4.14 (dd, *J* = 3.7, 1.5 Hz, 1H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 195.8, 195.7, 149.3, 134.7, 134.6, 134.1, 133.8, 132.1, 129.3, 128.7, 128.6 (2C), 127.9, 127.7, 125.6 (2C), 52.3, 49.2;

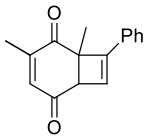
IR (KBr): $\tilde{\nu}$ = 1670, 1591, 1489, 1448, 1290, 1273, 1236, 1198, 1155, 1124, 933, 845, 758, 715 cm^{-1};

HRMS (APCI): m/z calcd for $C_{18}H_{13}O_2^+$: 261.0910 [M+H]$^+$; found: 261.0914.

The recorded spectroscopic values agree with the previously reported data.[4]

[5] S. Sultan, M. Bhat, M. A. Rizvi, B. A. Shah, *J. Org. Chem.* **2019**, *84*, 8948−8958.

1,3-Dimethyl-8-phenylbicyclo[4.2.0]octa-3,7-diene-2,5-dione (2d)



The title compound was prepared from 2,6-dimethylbenzoquinone (1 mmol, 136 mg) and phenylacetylene (1.2 mmol, 122 mg, 135 µl) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (gradient elution with hexanes/EtOAc) yielded **2d** (69 mg, 29% yield) as a yellow oil together with **1d** (96 mg, 40% yield) as an orange solid.

TLC R_f = 0.59 (3/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 – 7.47 (m, 2H), 7.37 – 7.29 (m, 3H), 6.53 (d, *J* = 1.8 Hz, 1H), 6.50 (dq, *J* = 2.4, 1.5 Hz, 1H), 3.52 (br. s, 1H), 2.00 (d, *J* = 1.5 Hz, 3H), 1.72 (s, 3H);

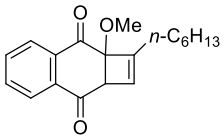
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 200.4, 198.1, 153.2, 148.7, 136.1, 131.7, 129.2, 128.8 (2C), 127.5, 125.7 (2C), 57.2, 56.0, 20.3, 17.1;

IR (KBr): $\tilde{\nu}$ = 1662, 1624, 1493, 1446, 1375, 1267, 1180, 1074, 1032, 972, 837, 758, 696 cm^{-1};

HRMS (ESI): m/z calcd for $C_{16}H_{15}O_2^+$: 239.1067 $[M+H]^+$; found: 239.1066.

The structure of this product was incorrectly assigned as 4-benzoyl-2,6-dimethylcyclohexa-2,5-dien-1-one.[6]

1-Hexyl-8a-methoxy-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (2e)



The title compound was prepared from 2-methoxy-1,4-naphthoquinone (1 mmol, 188 mg) and 1-octyne (1.2 mmol, 132 mg, 180 µl) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (25/1 hexanes/EtOAc) yielded **2e** (176 mg, 59% yield) as a colorless oil. When the reaction was carried out in MeCN, the product was obtained in 35% isolated yield, and a noticeable precipitate was formed during the reaction (42 mg, 22% yield after filtration and washing with EtOAc), which was not soluble in common organic solvents. Analytical data for this substance (M.p. > 200 °C; HRMS (APCI): m/z calcd for $C_{22}H_{17}O_6^+$: 377.1020 $[M+H]^+$; found: 377.1075) suggests a structure of the quinone dimer.[7]

TLC R_f = 0.60 (2/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 – 8.11 (m, 1H), 8.03 – 7.96 (m, 1H), 7.80 – 7.73 (m, 2H), 6.28 (td, *J* = 1.7, 1.4 Hz, 1H), 3.91 (td, *J* = 2.7, 1.4 Hz, 1H), 3.40 (s, 3H), 2.17 – 2.07 (m, 1H), 2.04 – 1.94 (m, 1H), 1.46 – 1.33 (m, 2H), 1.25 – 1.16 (m, 6H), 0.82 (t, *J* = 6.8 Hz, 3H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 196.6, 195.4, 155.9, 134.9, 134.5, 134.3, 133.5, 133.3, 127.9, 127.4, 86.0, 55.4, 53.9, 31.5, 29.0, 27.2, 25.5, 22.6, 14.1;

HRMS (ESI): m/z calcd for $C_{19}H_{22}NaO_3^+$: 321.1461 $[M+Na]^+$; found: 321.1461.

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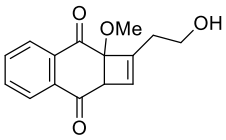
[6] A. Sagadevan, V. P. Charpe, A. Ragupathi, K. C. Hwang, *J. Am. Chem. Soc.* **2017**, *139*, 2896−2899.

[7] J. V. Ellis, J. E. Jones, *J. Org. Chem.* **1975**, *40*, 485–488.

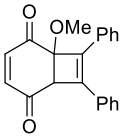
The recorded spectroscopic values agree with the previously reported data.[5]

1-(2-Hydroxyethyl)-8a-methoxy-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (2f)



The title compound was prepared from 2-methoxy-1,4-naphthoquinone (1 mmol, 188 mg) and but-3-yn-1-ol (1.2 mmol, 84 mg, 90 µl) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (3/1 DCM/EtOAc) yielded **2f** (120 mg, 69% yield) as a red oil.
TLC R_f = 0.16 (3/1 DCM/EtOAc);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 – 8.12 (m, 1H), 8.04 – 7.99 (m, 1H), 7.82 – 7.75 (m, 2H), 6.45 – 6.38 (m, 1H), 3.92 (td, *J* = 2.8, 1.5 Hz, 1H), 3.83 – 3.75 (m, 1H), 3.71 – 3.65 (m, 1H), 3.40 (s, 3H), 2.79 – 1.90 (m, 3H);
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 195.9, 195.1, 152.8, 137.0, 135.2, 134.7, 133.5, 133.3, 128.0, 127.5, 85.8, 59.9, 55.7, 54.6, 31.8;
IR (KBr): ṽ = 3431, 2935, 2831, 1682, 1593, 1462, 1286, 1252, 1119, 1043, 985, 897, 837, 789, 727 cm^{-1};
HRMS (ESI): m/z calcd for $C_{15}H_{14}NaO_4^+$: 281.0784 $[M+Na]^+$; found: 281.0787.

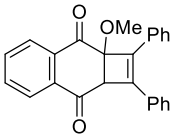
1-Methoxy-7,8-diphenylbicyclo[4.2.0]octa-3,7-diene-2,5-dione (2g)



The title compound was prepared from 2-methoxy-1,4-benzoquinone (1 mmol, 138 mg) and diphenylacetylene (1.2 mmol, 214 mg) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography provided **2g** (40 mg, 13% yield, eluted with 30/1 hexanes/EtOAc) as a yellow solid and unreacted diphenylacetylene (120 mg, 56% recovery, eluted with 50/1 hexanes/EtOAc). When the reaction was carried out in MeCN, **2g** was obtained in 15% isolated yield.
TLC R_f = 0.55 (2/1 hexanes/EtOAc);
M. p. 123 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 – 7.65 (m, 2H), 7.62 – 7.57 (m, 2H), 7.39 – 7.31 (m, 6H), 6.75 (d, *J* = 10.5 Hz, 1H), 6.52 (dd, *J* = 10.5, 1.2 Hz, 1H), 4.29 (d, *J* = 1.2 Hz, 1H), 3.41 (s, 3H);
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 197.2, 196.2, 143.8, 140.6, 139.0, 137.9, 132.2, 131.5, 130.0, 129.5, 128.9 (2C), 128.8 (2C), 127.7 (2C), 127.2 (2C), 82.8, 56.3, 53.3;
HRMS (APCI): m/z calcd for $C_{21}H_{17}O_3^+$: 317.1172 $[M+H]^+$; found: 317.1176.
The recorded spectroscopic values agree with the previously reported data.[8]

[8] (a) S. P. Pappas, B. C. Pappas, N. A. Portnoy, *J. Org. Chem.* **1969**, *34*, 520–525; (b) S. P. Pappas, B. C. Pappas, *Tetrahedron Lett.* **1967**, *8*, 1597−1600.

2a-Methoxy-1,2-diphenyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (2h)



The title compound was prepared from 2-methoxy-1,4-naphthoquinone (1 mmol, 188 mg) and diphenylacetylene (1.2 mmol, 214 mg) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (15/1 hexanes/EtOAc) yielded **2h** (201 mg, 55% yield) as a yellow powder.

TLC R_f = 0.50 (2/1 hexanes/EtOAc);

M. p. 128 °C;

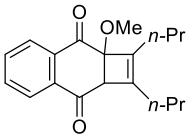
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 – 8.08 (m, 1H), 7.88 – 7.81 (m, 1H), 7.74 – 7.65 (m, 4H), 7.57 – 7.51 (m, 2H), 7.36 – 7.27 (m, 6H), 4.48 (s, 1H), 3.50 (s, 3H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 196.1, 195.2, 144.0, 141.3, 134.8, 134.5, 133.9, 133.7, 132.3, 131.7, 129.8, 129.3, 128.8 (2C), 128.7 (2C), 128.3, 127.5 (2C), 127.2 (2C), 127.1, 84.2, 57.0, 53.5;

HRMS (APCI): m/z calcd for $C_{25}H_{19}O_3^+$: 367.1329 $[M+H]^+$; found: 367.1320.

The recorded spectroscopic values agree with the previously reported data.[9]

2a-Methoxy-1,2-dipropyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (2i)



The title compound was prepared from 2-methoxy-1,4-naphthoquinone (1 mmol, 188 mg) and 4-octyne (1.2 mmol, 132 mg, 175 µl) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (20/1 hexanes/EtOAc) yielded **2i** (113 mg, 38% yield) as a pale yellow oil.

TLC R_f = 0.56 (2/1 hexanes/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 – 8.10 (m, 1H), 8.00 – 7.95 (m, 1H), 7.78 – 7.71 (m, 2H), 3.86 – 3.82 (m, 1H), 3.37 (s, 3H), 2.17 – 1.90 (m, 4H), 1.48 – 1.38 (m, 4H), 0.85 – 0.77 (m, 6H);

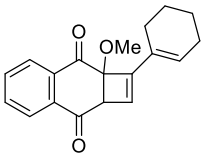
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 197.0, 196.1, 150.0, 146.2, 134.7, 134.4, 133.9, 133.5, 127.9, 127.1, 84.3, 57.4, 53.8, 30.2, 28.0, 20.5, 19.9, 14.3, 14.0;

IR (KBr): $\tilde{\nu}$ = 2958, 2871, 2829, 1682, 1593, 1456, 1379, 1284, 1250, 1151, 1095, 916, 795, 760, 714 cm^{-1};

HRMS (APCI): m/z calcd for $C_{19}H_{23}O_3^+$: 299.1642 $[M+H]^+$; found: 299.1642.

[9] (a) S. P. Pappas, N. A. Portnoy, *J. Org. Chem*. **1968**, *33*, 2200−2203; (b) S-B. Tan, C. Huang, X. Chen, Y. Wu, M. Zhou, C. Zhang, Y. Zhang, *Bioorg. Med. Chem.* **2013**, *21*, 6124–6131.

1-(Cyclohex-1-en-1-yl)-8a-methoxy-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (2j)



The title compound was prepared from 2-methoxy-1,4-naphthoquinone (1 mmol, 188 mg) and 1-ethynylcyclohexene (1.2 mmol, 127 mg, 140 µl) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (25/1 hexanes/EtOAc) yielded **2j** (176 mg, 60% yield) as a pale yellow oil.

TLC R_f = 0.50 (2/1 hexanes/EtOAc);

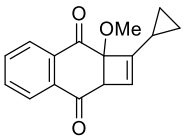
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 – 8.09 (m, 1H), 8.00 – 7.95 (m, 1H), 7.78 – 7.71 (m, 2H), 6.36 – 6.31 (m, 1H), 6.21 – 6.17 (m, 1H), 3.98 (br. s, 1H), 3.42 (s, 3H), 2.21 – 2.10 (m, 2H), 2.08 – 1.99 (m, 1H), 1.95 – 1.85 (m, 1H), 1.61 – 1.52 (m, 4H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 196.3, 195.1, 152.0, 134.7, 134.4, 133.6, 133.4, 132.4, 129.6, 128.8, 128.3, 127.2, 86.1, 55.3, 53.5, 25.6, 23.8, 21.9 (2C);

HRMS (ESI): m/z calcd for $C_{19}H_{19}O_3^+$: 295.1329 $[M+H]^+$; found: 295.1328.

The recorded spectroscopic values agree with the previously reported data.[5]

1-Cyclopropyl-8a-methoxy-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (2k)



The title compound was prepared from 2-methoxy-1,4-naphthoquinone (1 mmol, 188 mg) and cyclopropylacetylene (1.2 mmol, 79 mg, 105 µl) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (15/1 hexanes/EtOAc) yielded **2k** (150 mg, 59% yield) as pale yellow cubic crystals. When the reaction was carried out in MeCN, **2k** was obtained in 42% isolated yield.

TLC R_f = 0.40 (2/1 hexanes/EtOAc);

M. p. 115 °C;

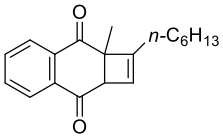
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 – 8.11 (m, 1H), 8.00 – 7.94 (m, 1H), 7.79 – 7.73 (m, 2H), 6.13 – 6.09 (m, 1H), 3.89 – 3.85 (m, 1H), 3.43 (s, 3H), 1.44 – 1.35 (m, 1H), 0.79 – 0.71 (m, 2H), 0.66 – 0.57 (m, 2H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 196.5, 195.4, 156.9, 134.8, 134.5, 133.6, 133.3, 131.1, 128.0, 127.3, 86.1, 54.8, 53.8, 9.2, 7.1, 6.9;

HRMS (ESI): m/z calcd for $C_{16}H_{14}NaO_3^+$: 277.0835 $[M+Na]^+$; found: 277.0838.

The recorded spectroscopic values agree with the previously reported data.[5]

1-Hexyl-8a-methyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (2l)



The title compound was prepared from menadione (1 mmol, 172 mg) and 1-octyne (1.2 mmol, 132 mg, 180 µl) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (25/1 hexanes/EtOAc) yielded **2l** (176 mg, 59% yield) as a colorless oil. When the reaction was carried out in MeCN, **2l** was obtained in 35% isolated yield.

TLC R_f = 0.65 (2/1 hexanes/EtOAc);

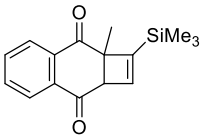
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 – 8.08 (m, 1H), 8.07 – 8.03 (m, 1H), 7.78 – 7.74 (m, 2H), 6.03 (td, *J* = 1.7, 1.4 Hz, 1H), 3.63 (td, *J* = 2.6, 1.4 Hz, 1H), 2.11 – 2.01 (m, 1H), 2.00 – 1.90 (m, 1H), 1.60 (s, 3H), 1.43 – 1.35 (m, 2H), 1.26 – 1.19 (m, 6H), 0.84 (t, *J* = 6.8 Hz, 3H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 198.2, 197.7, 159.3, 134.5, 134.4, 133.9, 133.6, 128.9, 127.8, 127.2, 58.1, 57.2, 31.6, 29.0, 27.5, 25.5, 22.6, 19.0, 14.1;

HRMS (APCI): m/z calcd for $C_{19}H_{23}O_2^+$: 283.1693 $[M+H]^+$; found: 283.1686.

The recorded spectroscopic values agree with the previously reported data.[5]

8a-Methyl-1-(trimethylsilyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (2m)



The title compound was prepared from menadione (1 mmol, 172 mg) and trimethylsilylacetylene (1.2 mmol, 118 mg, 165 µl) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (60/1 hexanes/EtOAc) yielded **2m** (108 mg, 40% yield) as a pale yellow oil.

TLC R_f = 0.69 (2/1 hexanes/EtOAc);

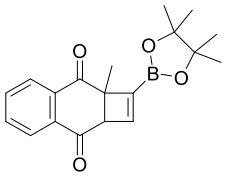
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 – 8.07 (m, 1H), 8.05 – 8.00 (m, 1H), 7.77 – 7.71 (m, 2H), 6.75 (d, *J* = 1.4 Hz, 1H), 3.83 (d, *J* = 1.4 Hz, 1H), 1.63 (s, 3H), 0.04 (s, 9H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 198.9, 196.9, 165.9, 148.2, 134.6, 134.3, 133.9, 133.8, 127.8, 127.2, 61.4, 58.9, 20.9, 2.0 (3C);

IR (KBr): $\tilde{\nu}$ = 2956, 1678, 1593, 1558, 1446, 1284, 1248, 1203, 982, 835, 756, 725 cm^{-1};

HRMS (APCI): m/z calcd for $C_{16}H_{19}O_2Si^+$: 271.1149 $[M+H]^+$; found: 271.1138.

8a-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (2n)



The title compound was prepared from menadione (1 mmol, 172 mg) and ethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.2 mmol, 182 mg) according to the general procedure A using $CHCl_3$ as solvent. Column chromatography (10/1 hexanes/EtOAc) yielded **2n** (74 mg, 23% yield, >20/1 regioisomeric ratio) as a pale orange solid. NMR analysis of the reaction mixture after 8 h indicated 32% product yield and 10/1 *rr*.

TLC R_f = 0.33 (2/1 hexanes/EtOAc);

M. p. 165 °C;

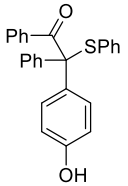
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 – 8.09 (m, 1H), 8.03 – 7.99 (m, 1H), 7.75 – 7.71 (m, 2H), 7.00 (d, *J* = 1.5 Hz, 1H), 3.82 (d, *J* = 1.5 Hz, 1H), 1.66 (s, 3H), 1.23 (s, 12H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 197.9, 196.4, 151.6, 134.7, 134.2 (2C), 134.0, 128.1, 127.1, 84.0 (2C), 61.4, 57.7, 24.9 (2C), 24.7 (2C), 20.3 (C-B carbon signal was not observed due to quadrupolar relaxation);

IR (KBr): ṽ = 2978, 2929, 1674, 1593, 1450, 1325, 1294, 1250, 1138, 1080, 1020, 852, 791, 742, 715 cm^{-1};

HRMS (APCI): m/z calcd for $C_{19}H_{22}BO_4^+$: 325.1606 $[M+H]^+$; found: 325.1606.

2-(4-Hydroxyphenyl)-1,2-diphenyl-2-(phenylthio)ethan-1-one (3a)



TLC R_f = 0.38 (2/1 hexanes/EtOAc);

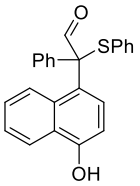
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 – 7.69 (m, 2H), 7.45 – 7.38 (m, 2H), 7.38 – 7.33 (m, 1H), 7.32 – 7.28 (m, 2H), 7.26 – 7.19 (m, 5H), 7.17 – 7.11 (m, 1H), 7.05 – 6.95 (m, 4H), 6.74 – 6.61 (m, 2H), 4.47 (br. s, 1H);

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 196.4, 154.9, 140.1, 136.4, 135.9 (2C), 132.4, 132.1, 131.8, 131.4 (2C), 130.7 (2C), 129.8 (2C), 128.6, 128.3 (2C), 128.1 (2C), 127.8 (2C), 127.5, 115.1 (2C), 74.7;

IR (KBr): ṽ = 3382, 3057, 1666, 1610, 1577, 1508, 1439, 1223, 1178, 1014, 908, 773, 731, 690 cm^{-1};

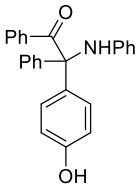
HRMS (ESI): m/z calcd for $C_{26}H_{20}NaO_2S^+$: 419.1076 $[M+Na]^+$; found: 419.1075.

2-(4-Hydroxynaphthalen-1-yl)-2-phenyl-2-(phenylthio)acetaldehyde (3b)



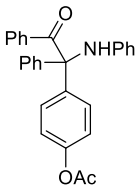
TLC R_f = 0.37 (2/1 hexanes/EtOAc);
M. p. 130 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.47 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.33 – 7.26 (m, 4H), 7.19 – 7.08 (m, 5H), 6.99 – 6.91 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H);
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 188.8, 152.7, 138.6, 137.9 (2C), 132.6, 129.9, 129.4 (2C), 129.2, 128.7 (2C), 128.1, 128.0 (2C), 127.6, 126.9, 126.0, 125.7, 125.3, 124.6, 122.6, 107.4, 70.0;
IR (KBr): $\tilde{\nu}$ = 3616, 3427, 3157, 1674, 1624, 1583, 1446, 1369, 1348, 1281, 1225, 1047, 1018, 922, 822, 752, 692 cm^{-1};
HRMS (APCI): m/z calcd for $C_{24}H_{17}O_2S^-$: 369.0955 $[M-H]^-$; found: 369.0952.

2-(4-Hydroxyphenyl)-1,2-diphenyl-2-(phenylamino)ethan-1-one (3c)



^{1}H NMR (400 MHz, CD_3CN): δ = 7.66 – 7.59 (m, 2H), 7.56 – 7.50 (m, 2H), 7.41 – 7.35 (m, 3H), 7.33 – 7.27 (m, 2H), 7.26 – 7.21 (m, 2H), 7.11 – 7.05 (m, 1H), 7.01 (br. s, 1H), 6.92 – 6.85 (m, 2H), 6.79 – 6.71 (m, 2H), 6.55 – 6.47 (m, 1H), 6.46 – 6.39 (m, 2H), 5.94 (br. s, 1H);
^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ = 200.0, 157.0, 146.5, 142.9, 137.4, 133.8, 133.0, 130.8, 130.2, 129.3, 129.1, 128.9, 128.8, 128.1, 118.5, 116.0, 115.9, 74.9.
HRMS (ESI): m/z calcd for $C_{26}H_{21}NNaO_2^+$: 402.1464 $[M+Na]^+$; found: 402.1464.

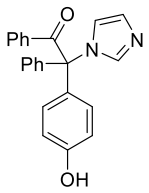
4-(2-Oxo-1,2-diphenyl-1-(phenylamino)ethyl)phenyl acetate (3c')



TLC R_f = 0.40 (2/1 hexanes/EtOAc);
M. p. 104 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 – 7.52 (m, 4H), 7.37 – 7.26 (m, 6H), 7.19 – 7.13 (m, 2H), 7.08 – 7.00 (m, 2H), 6.96 – 6.87 (m, 2H), 6.57 (t, *J* = 7.3 Hz, 1H), 6.38 – 6.32 (m, 2H), 5.55 (br. s, 1H), 2.27 (s, 3H);

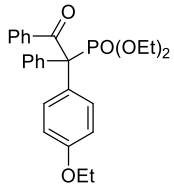
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 199.5, 169.3, 149.9, 144.7, 140.5, 137.2, 137.0, 131.9, 130.0 (2C), 129.7 (2C), 128.8 (2C), 128.7 (2C), 128.2 (2C), 128.0 (2C), 127.9, 121.3 (2C), 118.2, 115.7 (2C), 74.9, 21.3;
HRMS (ESI): m/z calcd for $C_{28}H_{23}NNaO_3^+$: 444.1570 $[M+Na]^+$; found: 444.1571.
The recorded spectroscopic values agree with the previously reported data.[10]

2-(4-Hydroxyphenyl)-2-(1*H*-imidazol-1-yl)-1,2-diphenylethan-1-one (3d)



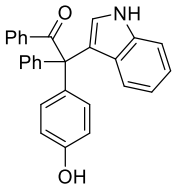
M. p. 110 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 – 7.59 (m, 2H), 7.42 – 7.37 (m, 1H), 7.37 – 7.29 (m, 4H), 7.25 – 7.19 (m, 4H), 7.09 – 7.03 (m, 2H), 7.01 (br. s, 1H), 6.87 – 6.81 (m, 2H), 6.80 (br. s, 1H);
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 195.1, 159.1, 138.7, 138.2, 136.1, 133.0, 131.2 (2C), 131.0 (2C), 129.7 (2C), 129.1, 128.8 (2C), 128.3 (2C), 127.3, 126.5, 122.4, 116.6 (2C), 78.6;
IR (KBr): $\tilde{\nu}$ = 3060, 3001, 2879, 2802, 2675, 2590, 1687, 1610, 1593, 1512, 1446, 1286, 1211, 1178, 1080, 920, 806, 748 cm^{-1};
HRMS (ESI): m/z calcd for $C_{23}H_{19}N_2O_2^+$: 355.1441 $[M+H]^+$; found: 355.1437.

Diethyl (1-(4-ethoxyphenyl)-2-oxo-1,2-diphenylethyl)phosphonate (3e)



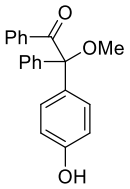
TLC R_f = 0.41 (3/1 DCM/Et_2O);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 – 7.56 (m, 2H), 7.53 – 7.47 (m, 4H), 7.34 – 7.25 (m, 4H), 7.16 – 7.09 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.05 – 3.94 (m, 4H), 3.88 – 3.77 (m, 2H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 6H);
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 198.8 (d, *J* = 4.3 Hz), 158.4, 137.4 (d, *J* = 4.3 Hz), 136.5 (d, *J* = 7.0 Hz), 131.8 (2C), 131.7, 130.6 (2C), 130.5 (2C), 128.3 (2C), 127.73 (d, *J* = 7.1 Hz), 127.67, 127.6 (2C), 114.2 (2C), 70.4 (d, *J* = 135.8 Hz), 63.5, 63.4 (2C), 16.3 (2C), 14.9;
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = 21.4;
IR (KBr): $\tilde{\nu}$ = 3057, 2979, 2929, 2906, 1674, 1608, 1508, 1446, 1244, 1186, 1016, 962, 804, 775, 741, 700 cm^{-1};
HRMS (ESI): m/z calcd for $C_{26}H_{29}NaO_5P^+$: 475.1645 $[M+Na]^+$; found: 475.1646.

2-(4-Hydroxyphenyl)-2-(1*H*-indol-3-yl)-1,2-diphenylethan-1-one (3f)



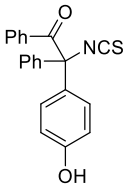
TLC R_f = 0.17 (2/1 hexanes/EtOAc);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 1.8 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.31 – 7.26 (m, 3H), 7.25 – 7.17 (m, 4H), 7.15 – 7.03 (m, 5H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.85 – 6.79 (m, 2H), 6.62 – 6.57 (m, 2H), 5.35 (br. s, 1H);
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 199.9, 154.3, 143.1, 137.8, 136.4, 134.8, 132.0, 131.7 (2C), 131.2 (2C), 130.4 (2C), 127.9 (2C), 127.7 (2C), 127.4, 126.7, 125.0, 122.2, 122.1, 119.7, 118.9, 114.8 (2C), 111.2, 65.7;
HRMS (APCI): m/z calcd for $C_{28}H_{20}NO_2^-$: 402.1500 $[M-H]^-$; found: 402.1486.
The recorded spectroscopic values agree with the previously reported data.[10]

2-(4-Hydroxyphenyl)-2-methoxy-1,2-diphenylethan-1-one (3g)



TLC R_f = 0.31 (3/1 hexanes/EtOAc);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 – 8.01 (m, 2H), 7.53 – 7.49 (m, 2H), 7.47 – 7.42 (m, 1H), 7.36 – 7.30 (m, 6H), 7.29 – 7.24 (m, 1H), 6.81 – 6.74 (m, 2H), 5.46 (br. s, 1H), 5.46 (s, 3H);
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 201.1, 155.3, 140.8, 136.8, 132.7, 132.5, 130.1 (4C), 128.3 (2C), 128.2 (2C), 128.1 (2C), 127.8, 115.1 (2C), 91.3, 53.5;
IR (KBr): ṽ = 3371, 3060, 3026, 2943, 1668, 1612, 1595, 1510, 1446, 1348, 1230, 1174, 1074, 982, 908, 822, 729, 698 cm^{-1};
HRMS (ESI): m/z calcd for $C_{21}H_{18}NaO_3^+$: 341.1148 $[M+Na]^+$; found: 341.1145.

2-(4-Hydroxyphenyl)-2-isothiocyanato-1,2-diphenylethan-1-one (3h)

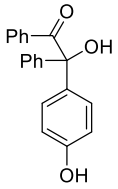


TLC R_f = 0.57 (2/1 hexanes/EtOAc);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 – 7.76 (m, 2H), 7.55 – 7.49 (m, 1H), 7.45 – 7.36 (m, 5H), 7.33 – 7.28 (m, 2H), 7.18 – 7.12 (m, 2H), 6.88 – 6.80 (m, 2H);

[10] A. Sharma, V. Dixit, S. Kumar, N. Jain, *Org. Lett.* **2021**, *23*, 3409−3414.

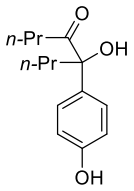
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 194.7, 156.0, 139.3, 138.2, 134.4, 133.4, 131.6, 130.5 (2C), 129.1 (2C), 128.92 (2C), 128.90, 128.6 (2C), 127.4 (2C), 115.7 (2C), 78.8;
IR (KBr): ṽ = 3408, 3060, 2954, 2025, 1693, 1612, 1597, 1512, 1446, 1230, 1176, 1014, 849, 820, 746 cm^{-1};
HRMS (ESI): m/z calcd for $C_{21}H_{14}NO_2S^-$: 344.0751 $[M-H]^-$; found: 344.0745.

2-Hydroxy-2-(4-hydroxyphenyl)-1,2-diphenylethan-1-one (4a)



The title compound was prepared from *p*-benzoquinone (1 mmol, 108 mg) and diphenylacetylene (1.2 mmol, 214 mg) according to the general procedure C. Column chromatography (13/1 hexanes/EtOAc) yielded 274 mg (90%) of the title compound as a yellow oil. Alternatively, **4a** was prepared from **1a** in 98% yield as described above.
TLC R_f = 0.31 (2/1 hexanes/EtOAc);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 – 7.67 (m, 2H), 7.47 – 7.40 (m, 3H), 7.37 – 7.26 (m, 5H), 7.25 – 7.20 (m, 2H), 6.76 – 6.67 (m, 2H), 5.56 (br. s, 1H), 5.10 (s, 1H);
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 201.1, 155.7, 141.9, 135.1, 133.9, 133.1, 131.0 (2C), 130.0 (2C), 128.5 (2C), 128.4 (2C), 128.3, 128.2 (2C), 115.4 (2C), 84.9;
IR (KBr): ṽ = 3359, 3059, 1666, 1595, 1510, 1444, 1348, 1227, 1174, 1049, 982, 822, 752, 698 cm^{-1};
HRMS (APCI): m/z calcd for $C_{20}H_{15}O_3^-$: 303.1027 $[M-H]^-$; found: 303.1034.

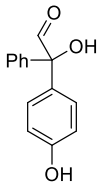
5-Hydroxy-5-(4-hydroxyphenyl)octan-4-one (4g)



The title compound was prepared from *p*-benzoquinone (1 mmol, 108 mg) and 4-octyne (1.2 mmol, 132 mg, 175 µl) according to the general procedure C. Column chromatography (50/1 DCM/Et_2O) yielded 156 mg (66%) of the title compound as a colorless oil.
TLC R_f = 0.15 (9/1 DCM/Et_2O);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 – 7.24 (m, 2H), 6.79 – 6.74 (m, 2H), 5.65 (br. s, 1H), 4.72 (s, 1H), 2.38 – 2.26 (m, 2H), 2.18 – 2.04 (m, 2H), 1.56 – 1.39 (m, 2H), 1.17 – 1.07 (m, 1H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.92 – 0.81 (m, 1H), 0.74 (t, *J* = 7.4 Hz, 3H);
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 212.2, 155.6, 133.0, 127.8 (2C), 115.6 (2C), 82.2, 38.6, 37.5, 17.4, 16.7, 14.5, 13.6;

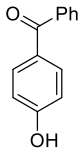
IR (KBr): $\tilde{\nu}$ = 3367, 2962, 2933, 2873, 1699, 1612, 1512, 1456, 1352, 1221, 1174, 1128, 1030, 976, 833, 746 cm^{-1};
HRMS (APCI): m/z calcd for $C_{14}H_{19}O_3^-$: 235.1340 $[M-H]^-$; found: 235.1338.

2-Hydroxy-2-(4-hydroxyphenyl)-2-phenylacetaldehyde (4i)



The title compound was prepared from *p*-benzoquinone (1 mmol, 108 mg) and phenylacetylene (1.2 mmol, 122 mg, 135 µl) according to the general procedure C. Column chromatography (10/1 hexanes/EtOAc) yielded 183 mg (80%) of the title compound as a white solid.
TLC R_f = 0.37 (2/1 hexanes/EtOAc);
M. p. 108 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.92 (s, 1H), 7.43 – 7.33 (m, 5H), 7.23 – 7.17 (m, 2H), 6.86 – 6.80 (m, 2H), 5.15 (br. s, 1H), 4.37 (s, 1H);
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 198.1, 155.9, 139.3, 131.6, 129.2 (2C), 129.0 (2C), 128.6, 127.5 (2C), 115.9 (2C), 83.3;
IR (KBr): $\tilde{\nu}$ = 3348, 2860, 1716, 1612, 1593, 1510, 1446, 1342, 1257, 1201, 1178, 1068, 974, 835, 779, 748, 698 cm^{-1};
HRMS (ESI): m/z calcd for $C_{14}H_{12}NaO_3^+$: 251.0679 $[M+Na]^+$; found: 251.0680.

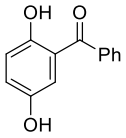
4-Hydroxybenzophenone



TLC R_f = 0.40 (2/1 hexanes/EtOAc);
M. p. 132 °C (lit. 133–135 °C[11]);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 – 7.73 (m, 4H), 7.62 – 7.53 (m, 1H), 7.52 – 7.44 (m, 2H), 6.97 – 6.89 (m, 2H), 6.67 (br. s, 1H);
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 196.6, 160.5, 138.2, 133.2 (2C), 132.3, 130.0 (2C), 129.9, 128.4 (2C), 115.4 (2C);
HRMS (ESI): m/z calcd for $C_{13}H_{11}O_2^+$: 199.0754 $[M+H]^+$; found: 199.0754.
The recorded spectroscopic values agree with the previously reported data.[11]

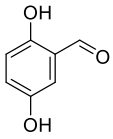
[11] H. Wu, A. Sumita, Y. Otani, T. Ohwada, *J. Org. Chem.* **2022**, *87*, 15224–15249.

2,5-Dihydroxybenzophenone



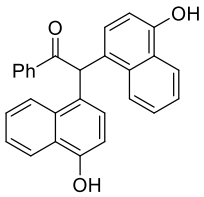
TLC R_f = 0.31 (2/1 hexanes/EtOAc);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.58 (s, 1H), 7.69 – 7.63 (m, 2H), 7.61 – 7.54 (m, 1H), 7.52 – 7.45 (m, 2H), 7.08 – 7.01 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 1H), 4.90 (br. s, 1H);
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 201.3, 157.4, 147.3, 137.8, 132.1, 129.2 (2C), 128.5 (2C), 125.0, 119.4, 119.0, 118.4;
The recorded spectroscopic values agree with the previously reported data.[12]

2,5-Dihydroxybenzaldehyde



TLC R_f = 0.28 (2/1 hexanes/EtOAc);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.60 (s, 1H), 9.82 (s, 1H), 7.08 (dd, *J* = 8.9, 3.0 Hz, 1H), 7.01 (d, *J* = 3.0 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 1H), 4.86 (br. s, 1H);
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 196.2, 156.0, 148.5, 125.7, 120.4, 118.9, 118.2;
The recorded spectroscopic values agree with the previously reported data.[13]

2,2-Bis(4-hydroxynaphthalen-1-yl)-1-phenylethan-1-one (5)

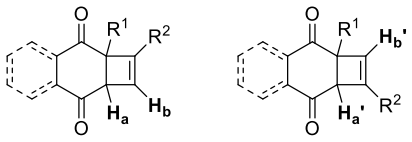


TLC R_f = 0.35 (1/1 hexanes/EtOAc);
^{1}H NMR (400 MHz, CD_3OD): δ = 8.34 – 8.27 (m, 2H), 8.04 – 7.97 (m, 2H), 7.88 – 7.80 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.46 – 7.37 (m, 6H), 7.33 (s, 1H), 6.83 (d, *J* = 7.9 Hz, 2H), 6.67 (d, *J* = 7.9 Hz, 2H);
^{13}C{^{1}H} NMR (101 MHz, CD_3OD): δ = 202.1, 154.4 (2C), 138.1, 134.4 (2C), 134.0 (2C), 129.9 (2C), 129.8 (2C), 129.1 (2C), 127.8 (2C), 127.2, 126.7 (2C), 125.5 (2C), 124.2 (2C), 124.0 (2C), 108.2 (2C), 52.6;
HRMS (APCI): m/z calcd for $C_{28}H_{19}O_3^-$: 403.1340 $[M-H]^-$; found: 403.1334.
The recorded spectroscopic values agree with the previously reported data.[14]

[12] P. H. Tran, H. Q. Phung, M. N. Duong, N.-N. Pham-Tran, *Tetrahedron Lett.* **2017**, *58*, 1558−1563.
[13] H. Naeimi, E. Zakerzadeh, *New J. Chem*., **2018**, *42*, 4590−4595.
[14] N. Chalotra, I. H. Shah, S. Raheem, M. A. Rizvi, B. A. Shah, *J. Org. Chem.* **2021**, *86*, 16770−16784.

2.3 Additional tables and charts

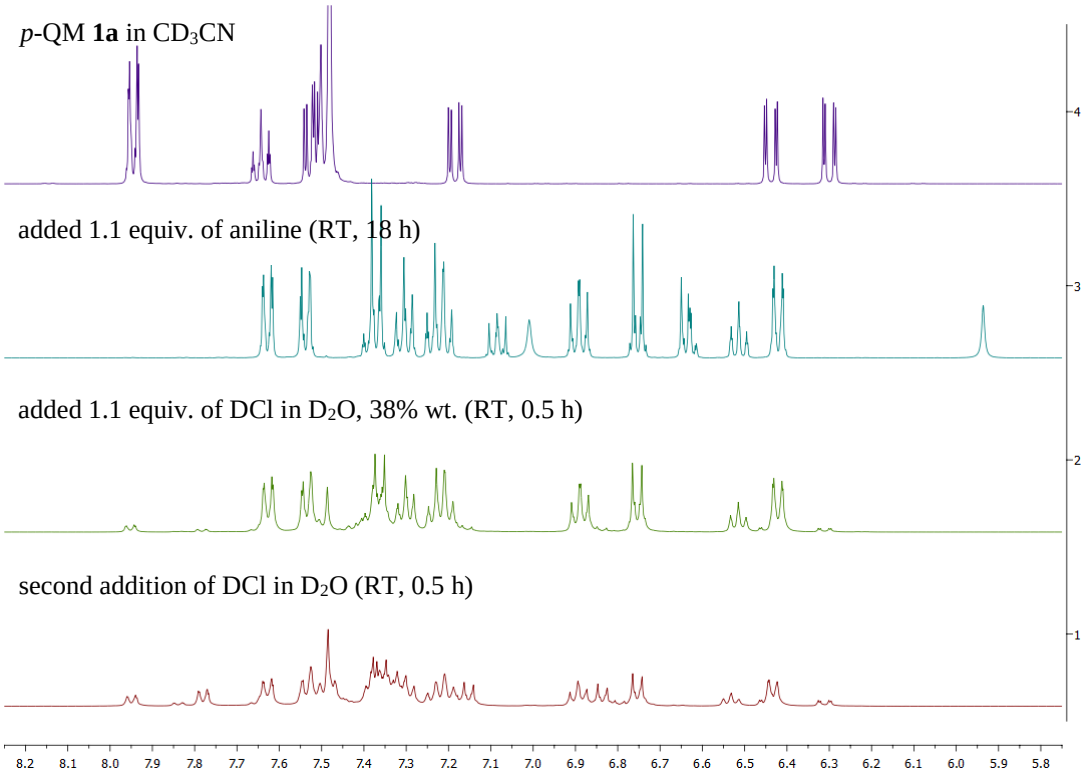
Table S2. Comparison of the NMR data for compounds **2**



Entry	Isomeric pair	Chemical shifts in $CDCl_3$ (ppm)			
		H_a	H_b	H_a'	H_b'
1	**2a** and **2a'** (R^1 = Me , R^2 = Ph)	3.79	6.56	4.16	6.57
2	**2b** and **2b'** (R^1 = OMe , R^2 = Ph)	4.15	6.75	-	-
3	**2d** and **2d'** (R^1 = Me , R^2 = Ph)	3.52	6.53	-	-
4	**2e** and **2e'** (R^1 = OMe , R^2 = *n*-C_6H_{13})	3.91	6.28	-	-
5	**2f** and **2f'** (R^1 = OMe , R^2 = CH_2CH_2OH)	3.92	6.42	-	-
6	**2j** and **2j**' (R^1 = OMe , R^2 = 1-cyclohexenyl)	3.98	6.19	-	-
7	**2k** and **2k**' (R^1 = OMe , R^2 = cyclopropyl)	3.87	6.11	-	-
8	**2l** and **2l'** (R^1 = Me , R^2 = *n*-C_6H_{13})	3.61	6.01	3.62	6.04
9	**2m** and **2m'** (R^1 = Me , R^2 = $SiMe_3$)	3.83	6.75	3.75	6.77
10	**2n** and **2n'** (R^1 = Me , R^2 = Bpin)	3.82	7.00	3.83*	7.04

* overlapped signal

Figure S1. NMR monitoring of the reaction between **1a** and aniline



3 Crystallographic data

The diffraction experiment for crystal structures determination was performed on Bruker D8 VENTURE Kappa Duo with PHOTONIII detector by IμS micro-focus sealed tube with MoKα (0.71073) radiation at a temperature 120(2) K. The structure was solved by intrinsic methods (XT)[15] and refined by full matrix least squares based on F^2 (SHELXL2018).[16] The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors either $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or $H_{iso}(H) = 1.5\ U_{eq}$ (pivot atom) for methyl moiety.

The compound *Z*-**1c** crystallizes in non-centrosymmetric space group but the absolute structure could not be determined reliably due to low anomalous dispersion of light atoms. Absolute structure parameter: 0.24(12).[17]

X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and can be obtained free of charge from the Centre via its website (www.ccdc.cam.ac.uk/getstructures).

[15] SHELXT: Sheldrick, G.M. (2015). *Acta Cryst*. **A71**, 3-8.
[16] SHELXL: Sheldrick, G.M. (2015). *Acta Cryst.* **C71**, 3-8.
[17] Parsons,S., Flack, H.D. and Wagner, T. (2013) *Acta Cryst*. **B69**, 249-259.

Table S3. Crystal data, data collection, and refinement parameters for ***Z*-1c** and **2k**.

Compound	***Z*-1c** (fa0516_3)	**2k** (fa0529)
CCDC	2240461	2240462
Formula	$C_{18}H_{12}O_2$	$C_{16}H_{14}O_3$
M.w.	260.28	254.27
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a [Å]	7.3664 (3)	12.4042 (4)
b [Å]	8.4028 (3)	8.1827 (2)
c [Å]	20.5541 (10)	12.1889 (4)
α [°]		
β [°]		99.910 (1)°
γ [°]		
Z	4	4
V[Å^3]	1272.27 (9)	1218.71 (6)
Temperature [K]	120	120
Wavelength [Å^3]	0.71073	0.71073
D_x [g cm^{-3}]	1.359	1.386
Crystal size [mm]	0.26 × 0.25 × 0.14	0.22 × 0.21 × 0.18
Crystal color, shape	Prism, yellow	Prism, colourless
μ [mm^{-1}]	0.09	0.10
T_{min},T_{max}	0.95, 0.99	0.96, 0.98
Measured reflections	64599	76544
Independent diffractions (R_{int}[a])	3710, (0.024)	2792, (0.020)
Observed diffract. [I>2σ(I)]	3670	2723
No. of parameters	181	176
R[b]	0.031	0.035
wR(F^2) for all data	0.089	0.089
GOF[c]	1.08	1.03
Residual electron density [e/Å^3]	0.31, −0.17	0.37, −0.18
Absolute structure parameter	0.24 (12)	

[a] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$; [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$;

[c] $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$

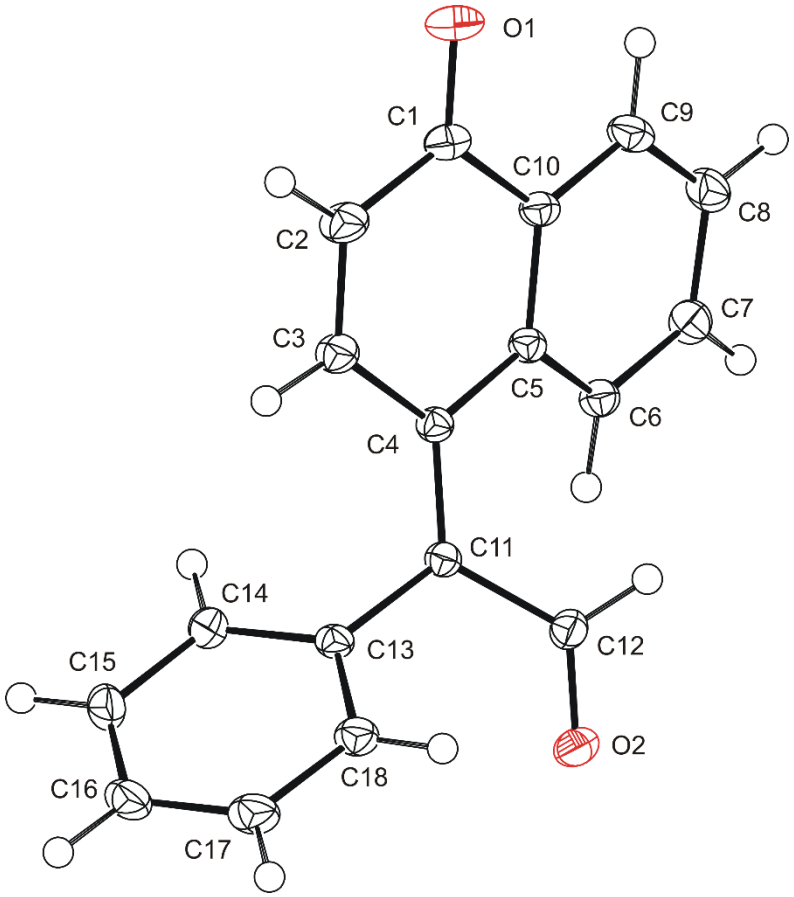


Figure S2. View on the ***Z*-1c** molecule. Displacement ellipsoid are drawn on 50% probability level.

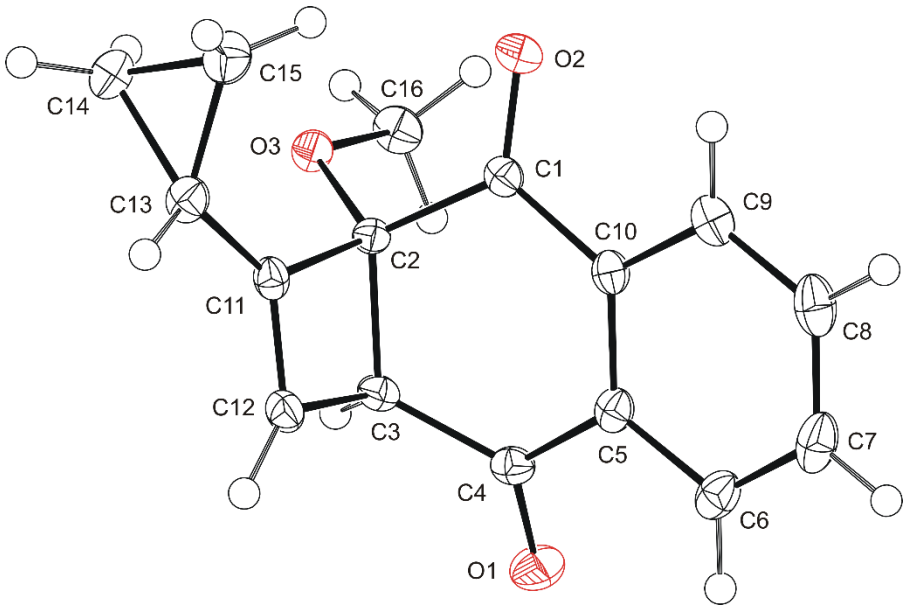
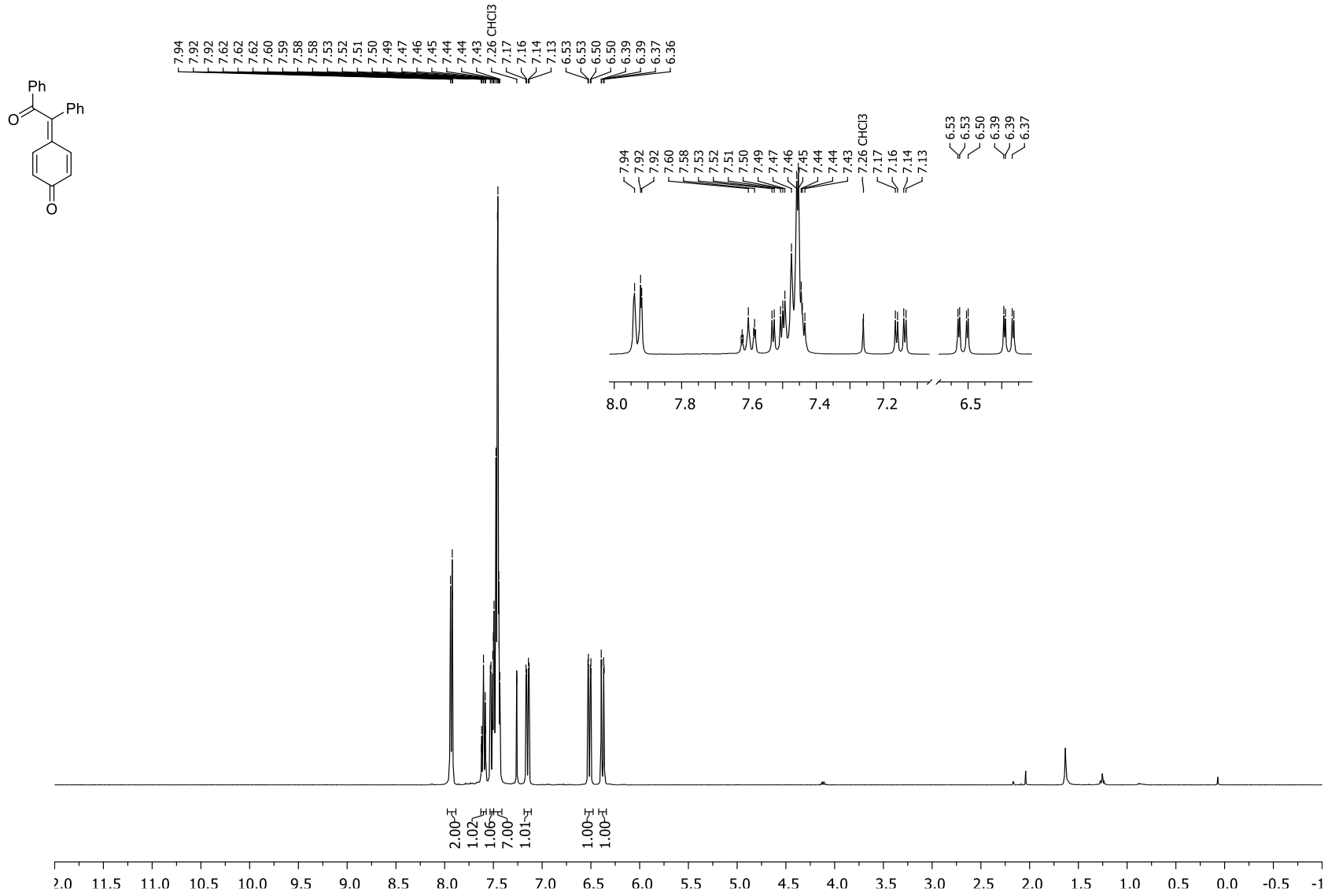


Figure S3. View on the **2k** molecule. Displacement ellipsoid are drawn on 50% probability level.

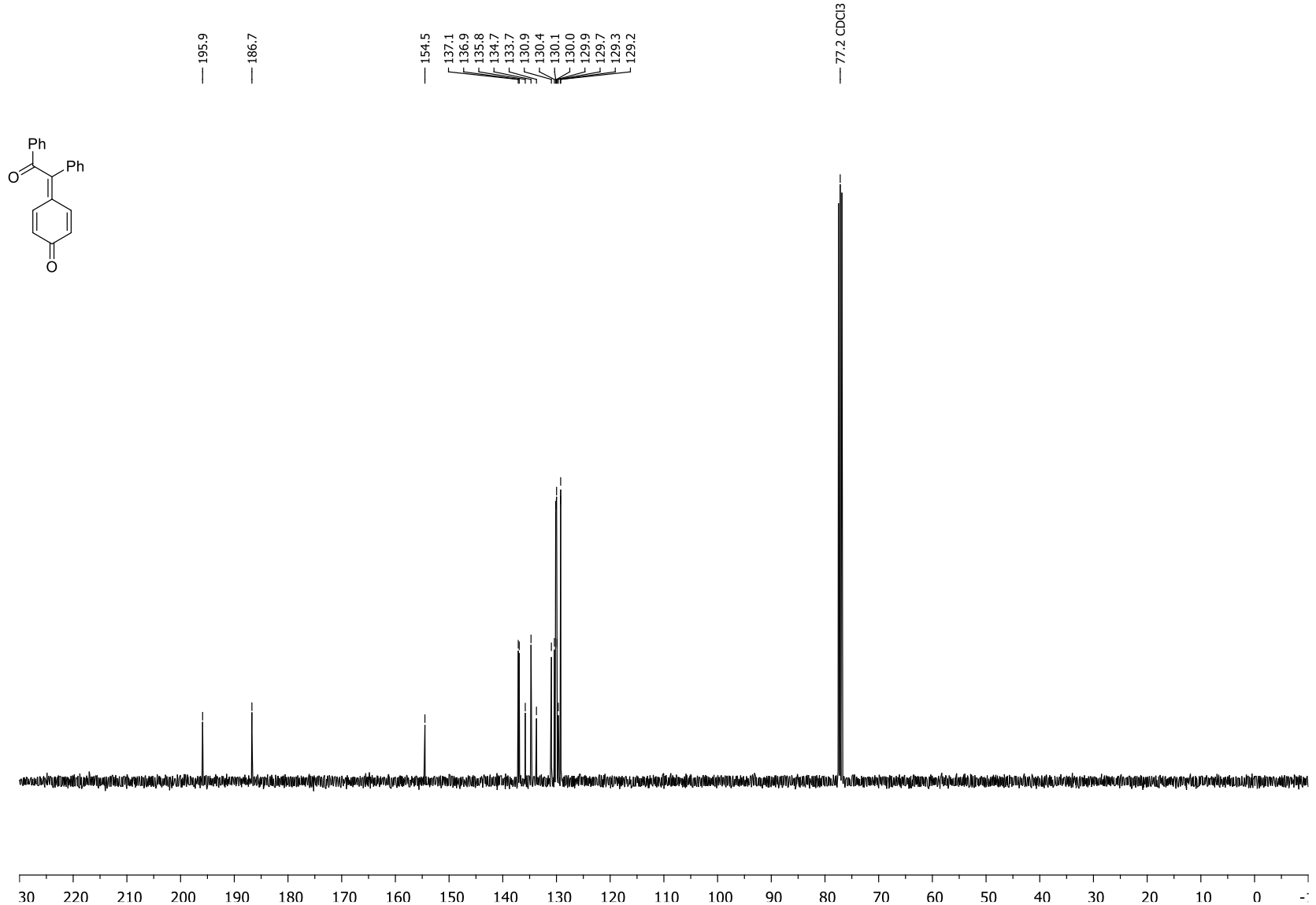
4 Copies of ^{1}H and ^{13}C spectra

4-(2-Oxo-1,2-diphenylethylidene)cyclohexa-2,5-dien-1-one (1a)

^{1}H NMR (400 MHz, $CDCl_3$)

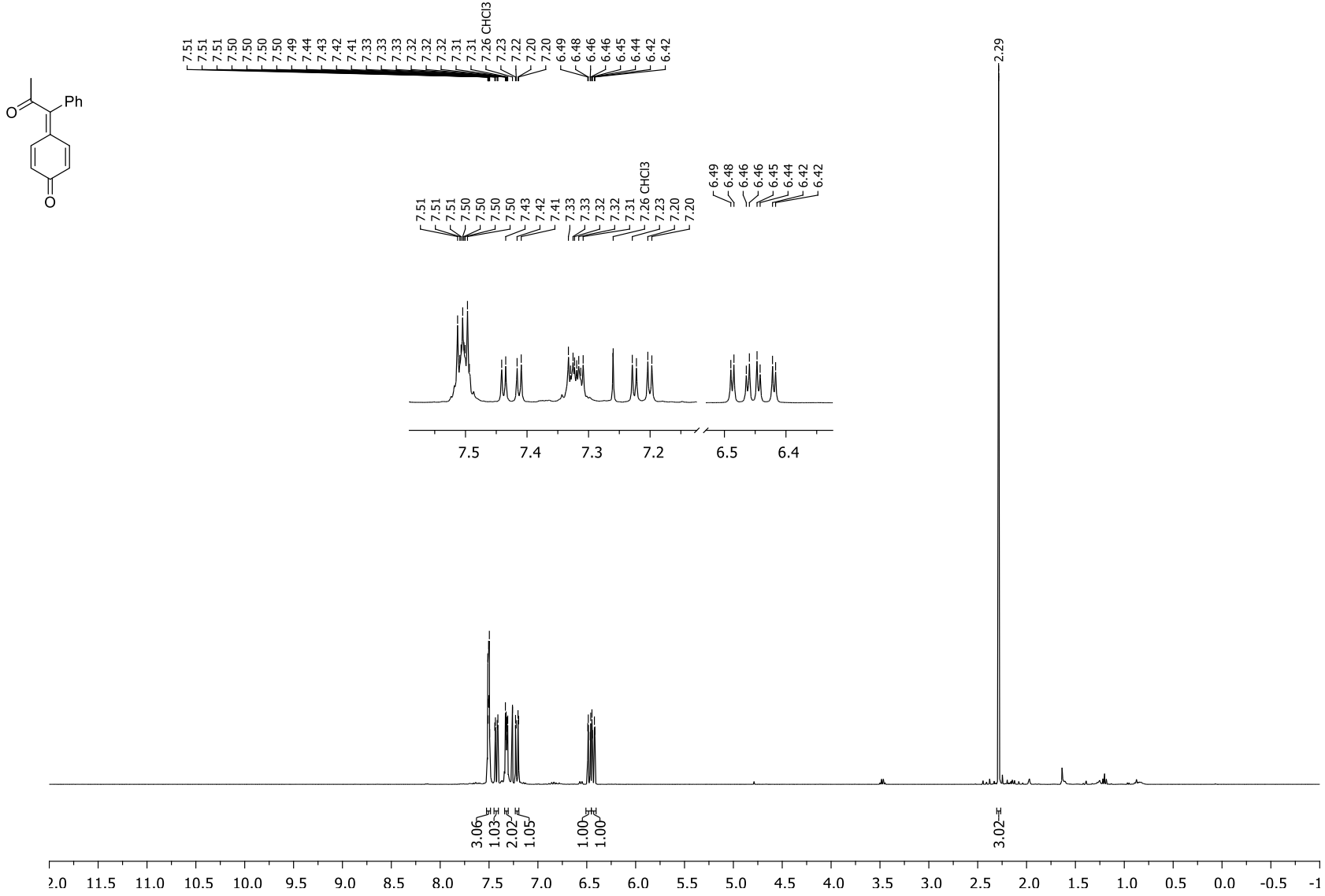


^{13}C NMR (101 MHz, $CDCl_3$)

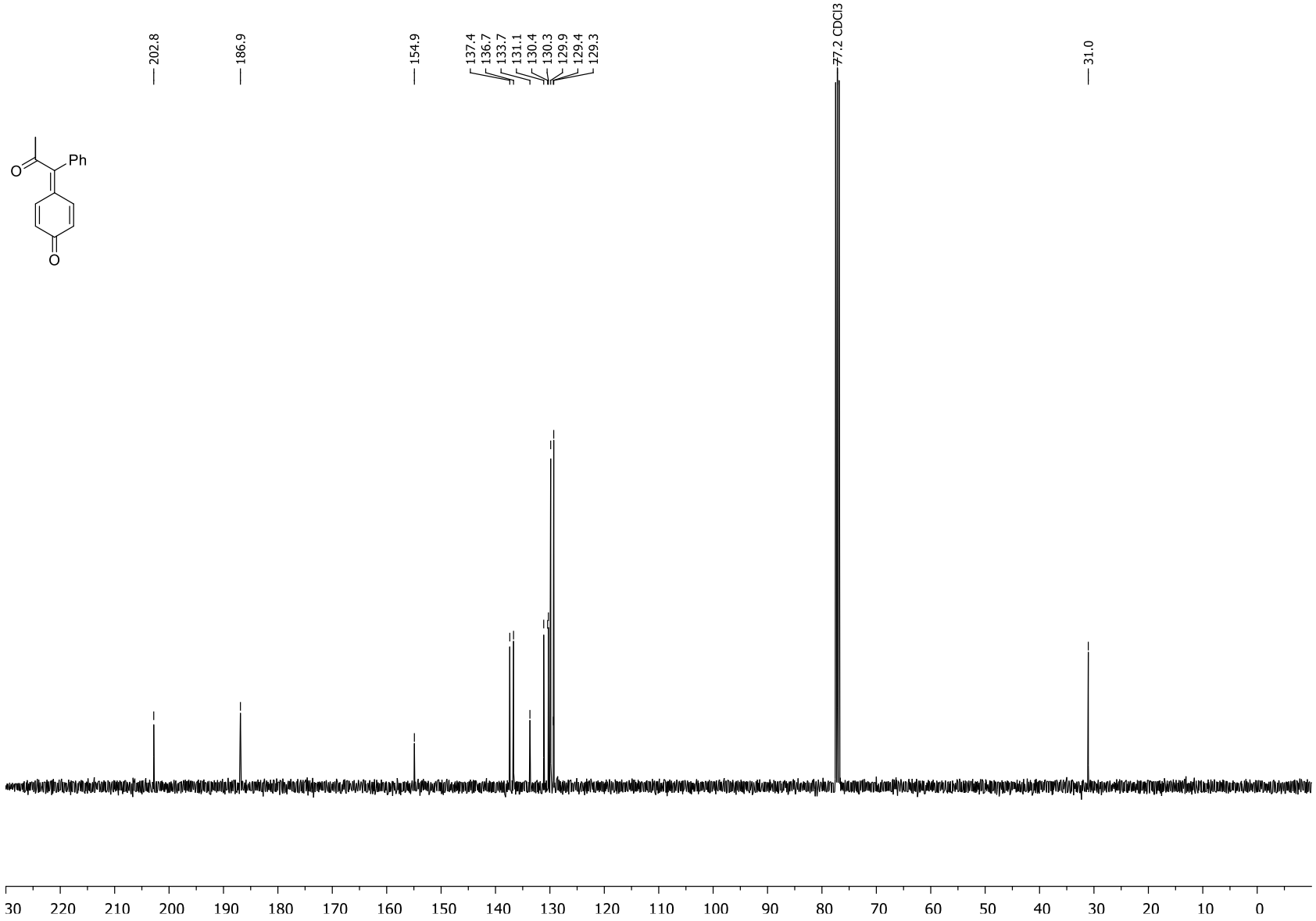


4-(2-Oxo-1-phenylpropylidene)cyclohexa-2,5-dien-1-one (1b)

^{1}H NMR (400 MHz, $CDCl_3$)

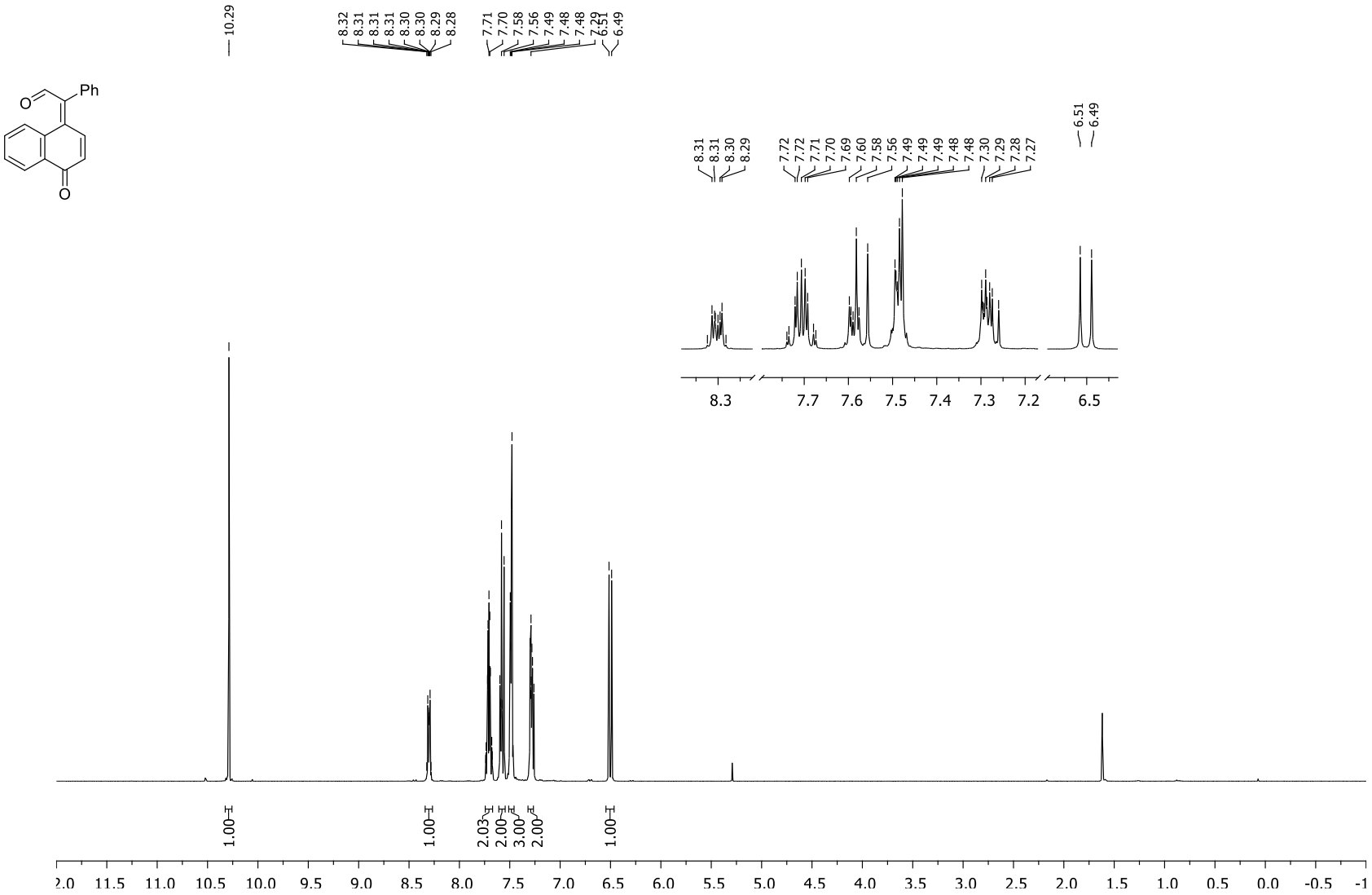


^{13}C NMR (101 MHz, $CDCl_3$)

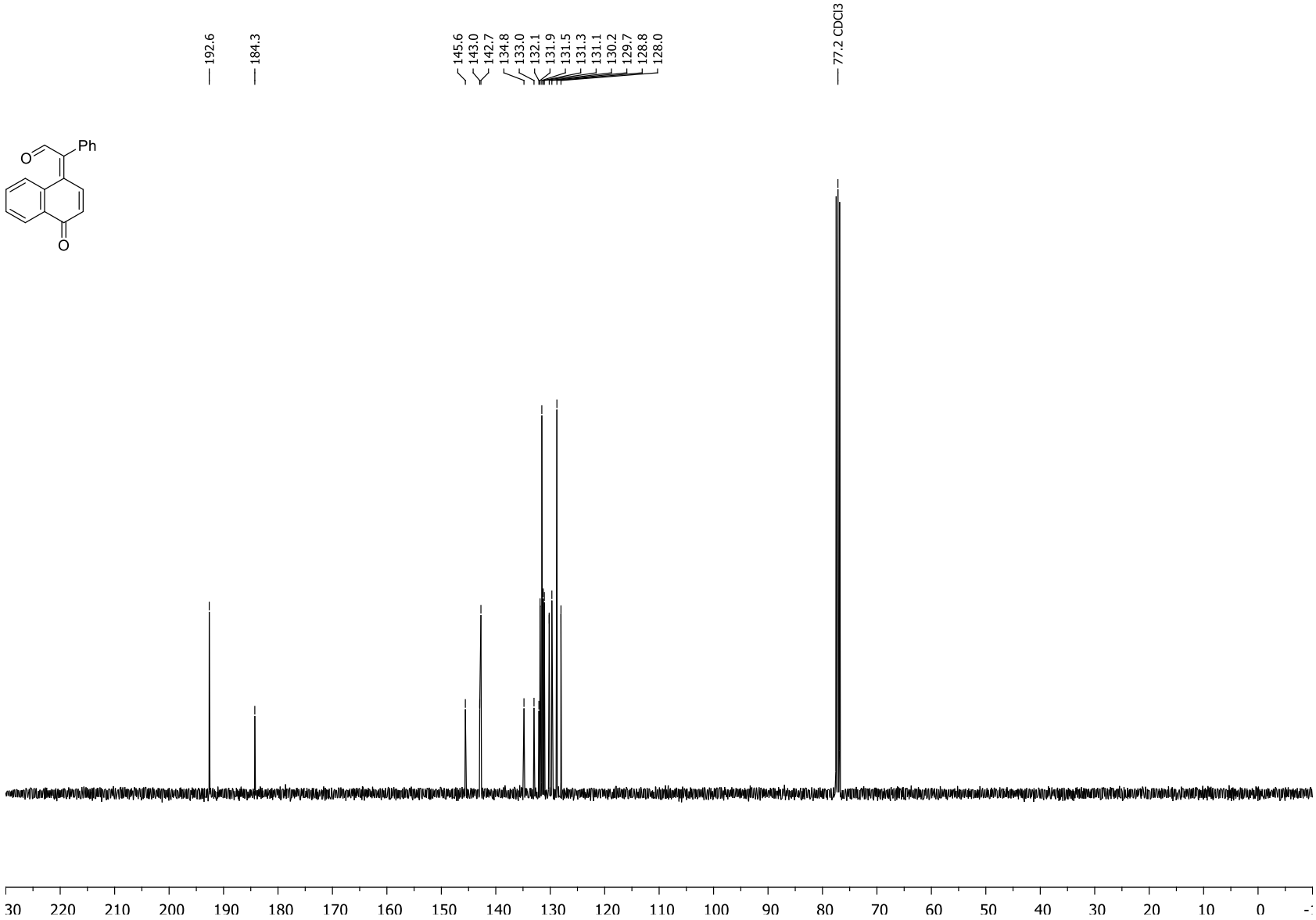


(*Z*)-2-(4-Oxonaphthalen-1(4*H*)-ylidene)-2-phenylacetaldehyde (1c)

^{1}H NMR (400 MHz, $CDCl_3$)

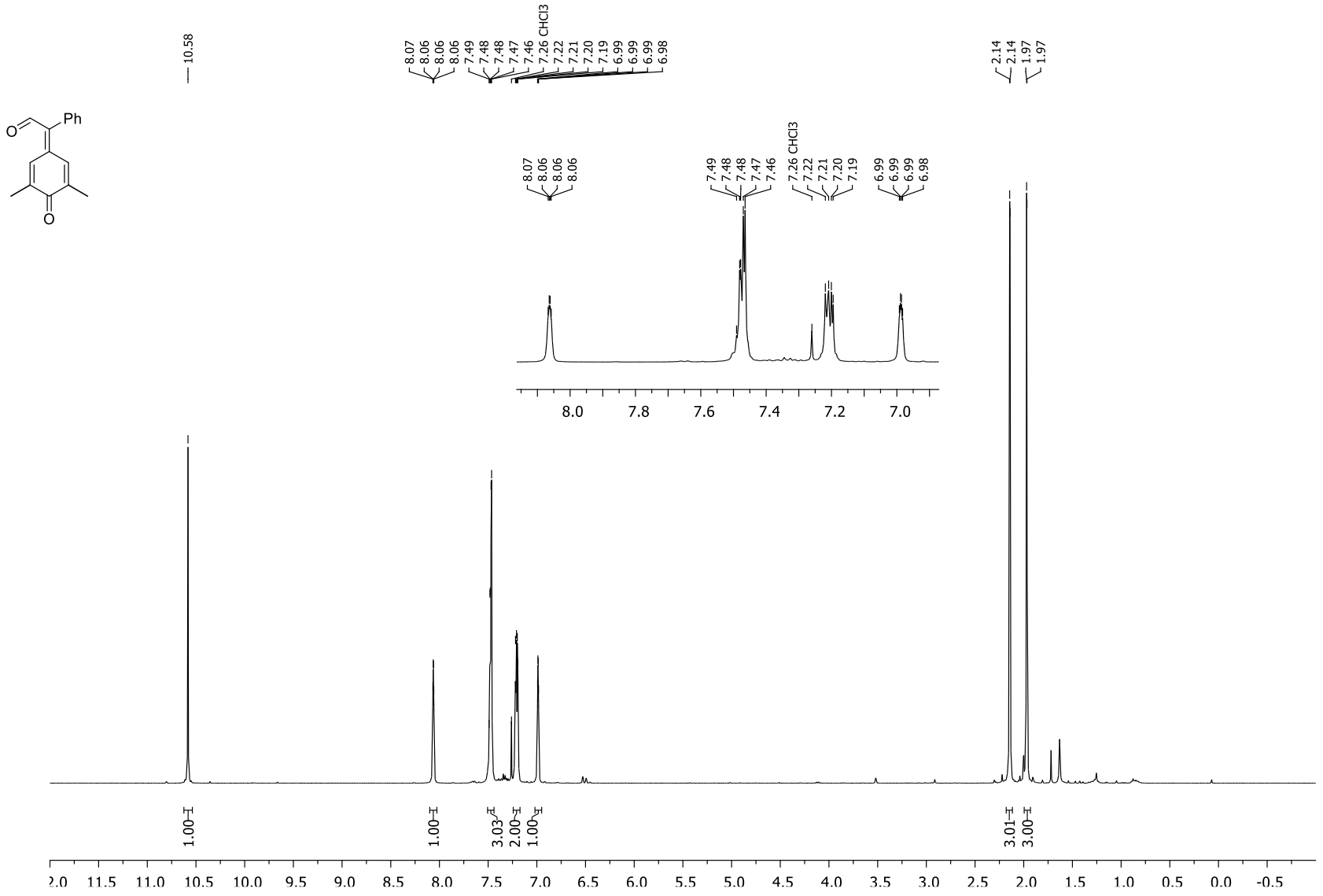


^{13}C NMR (101 MHz, $CDCl_3$)

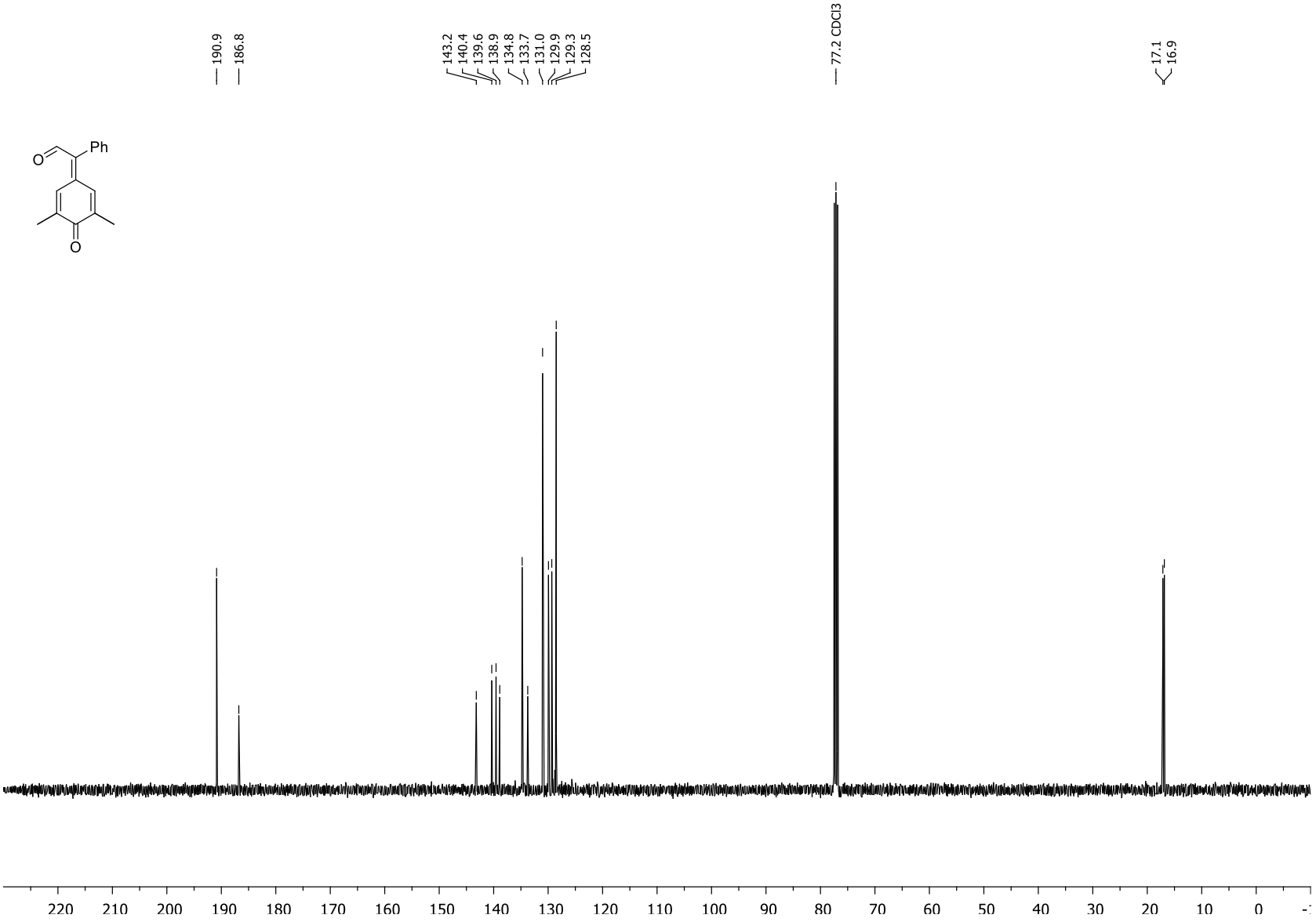


2-(3,5-Dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-2-phenylacetaldehyde (1d)

^{1}H NMR (400 MHz, $CDCl_3$)

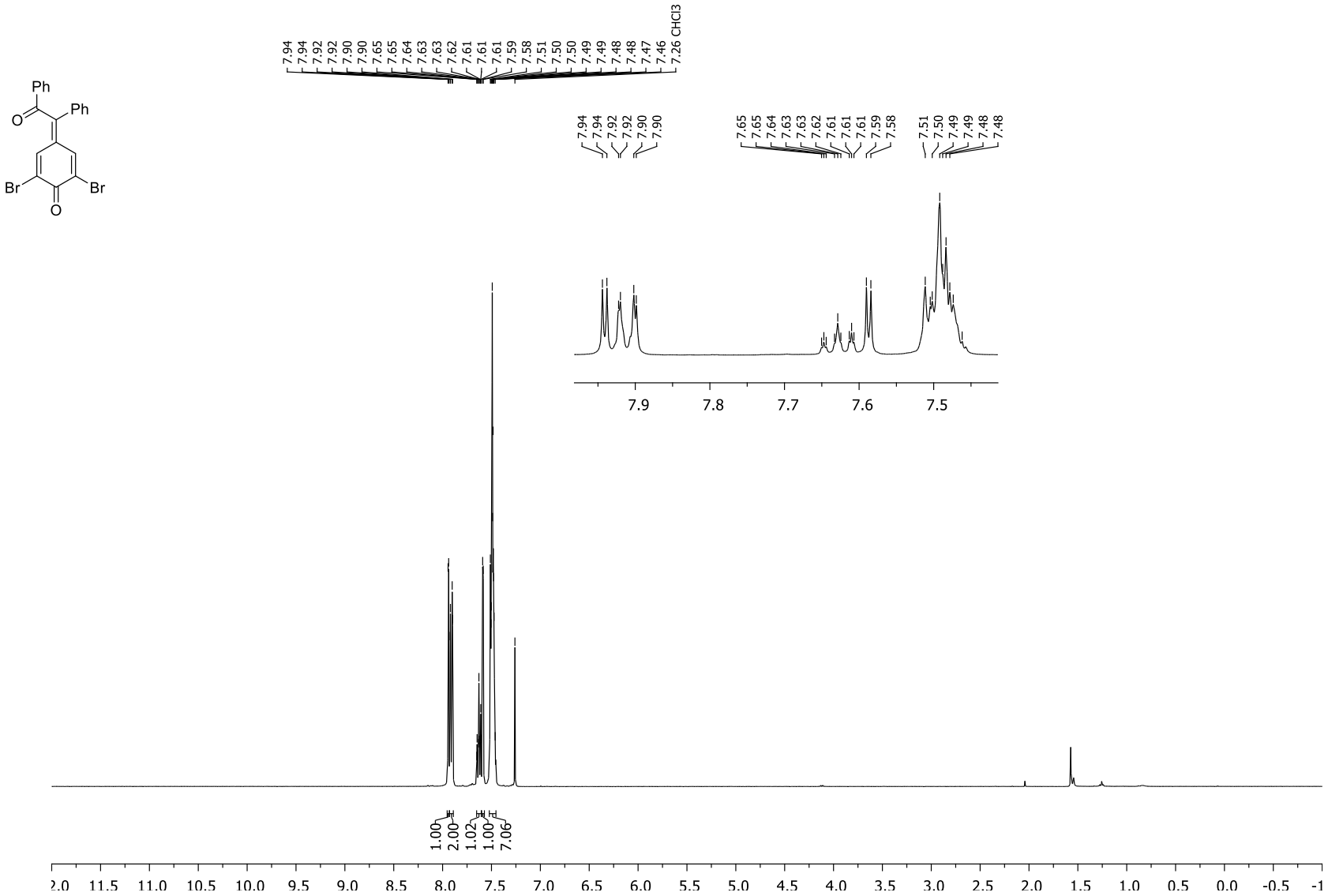


^{13}C NMR (101 MHz, $CDCl_3$)

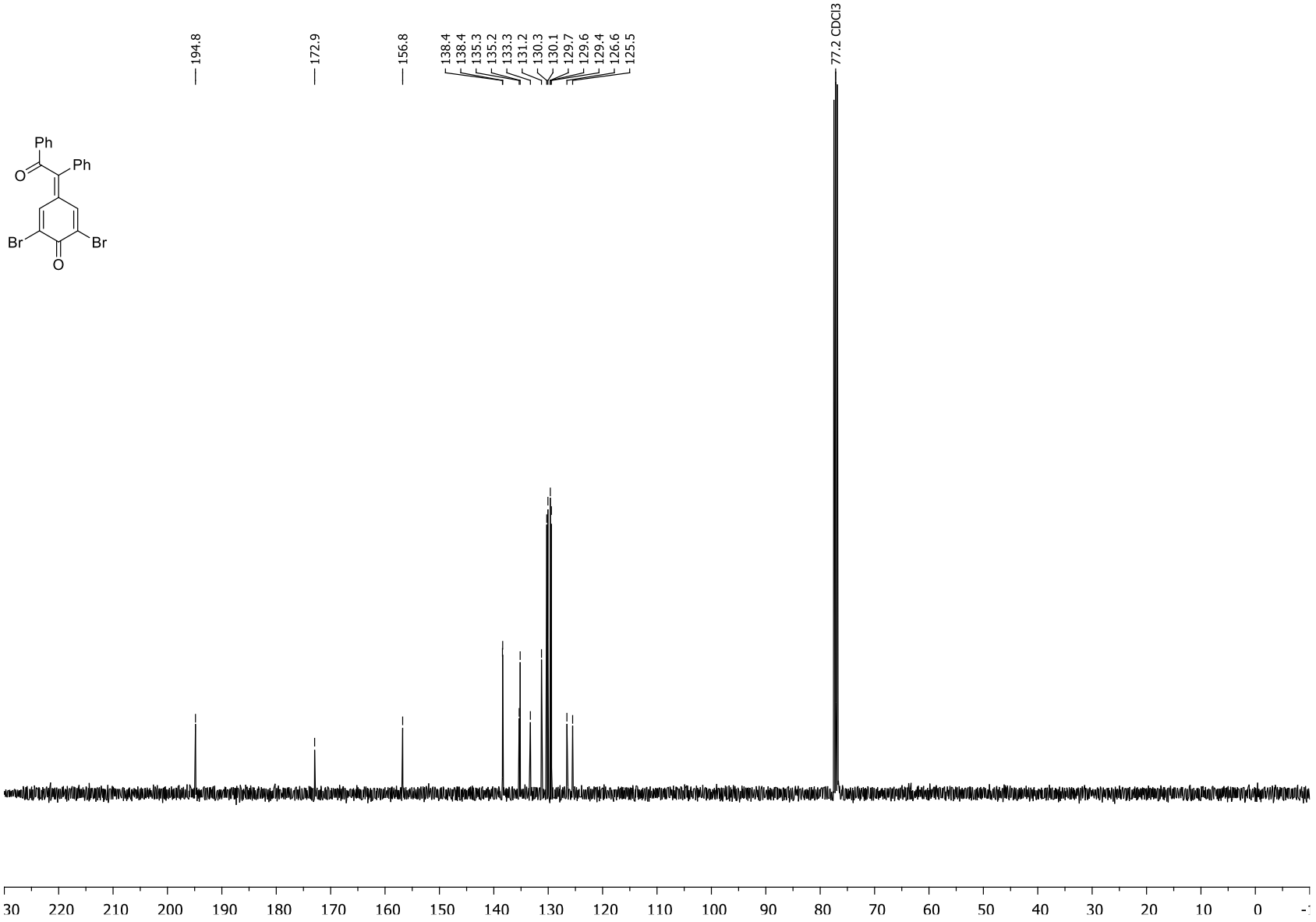


2,6-Dibromo-4-(2-oxo-1,2-diphenylethylidene)cyclohexa-2,5-dien-1-one (1e)

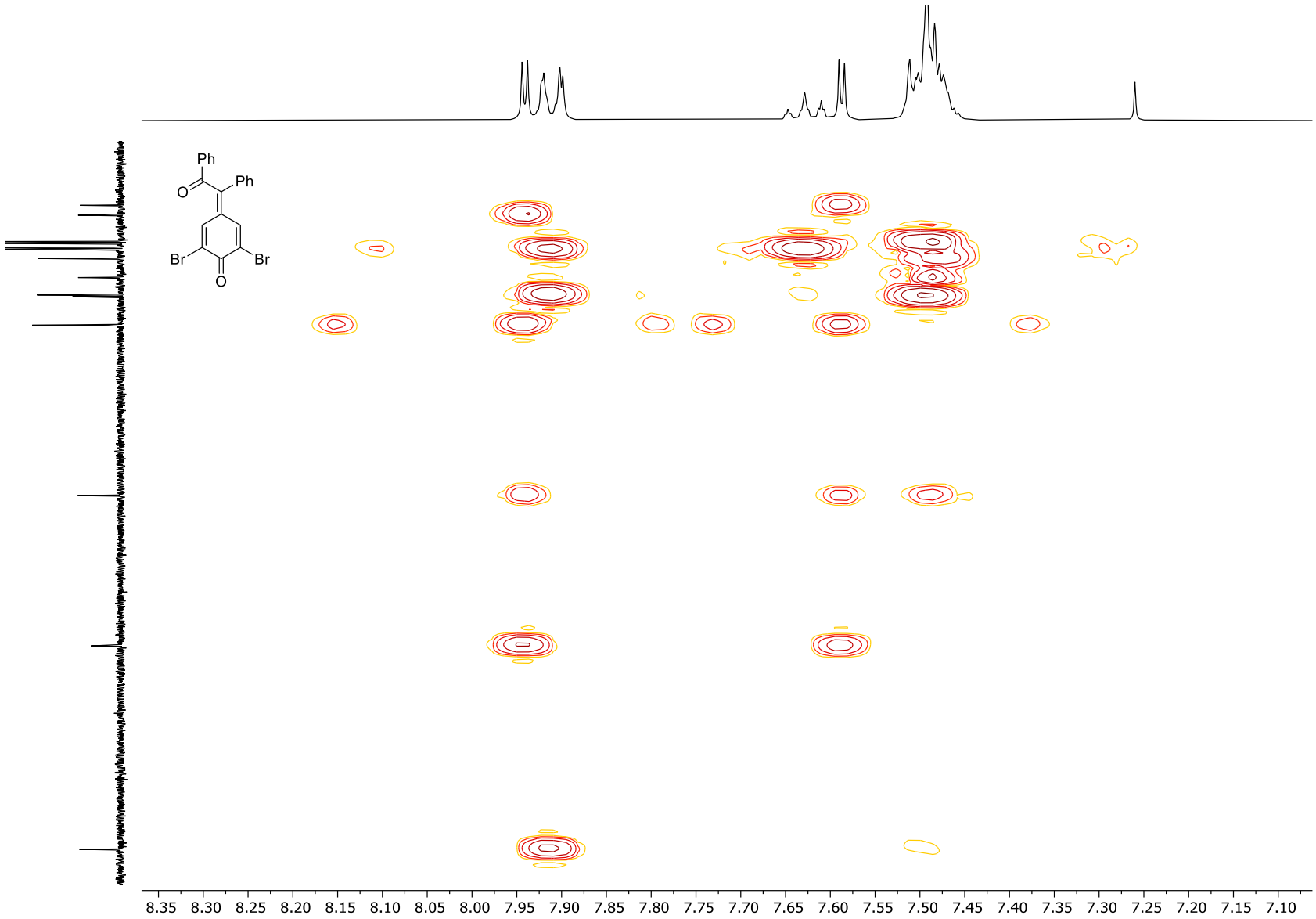
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

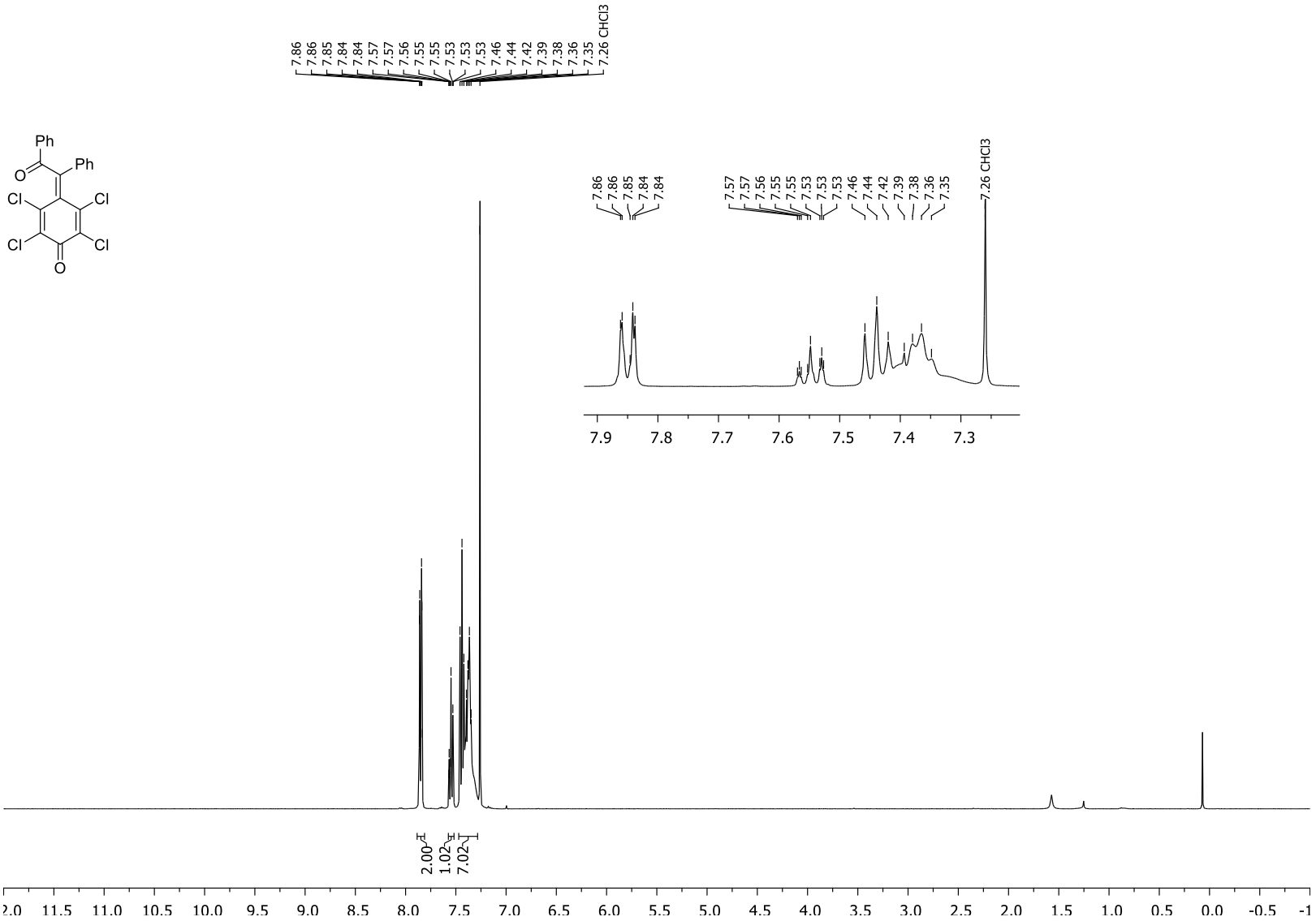


HMBC (400 MHz, $CDCl_3$)

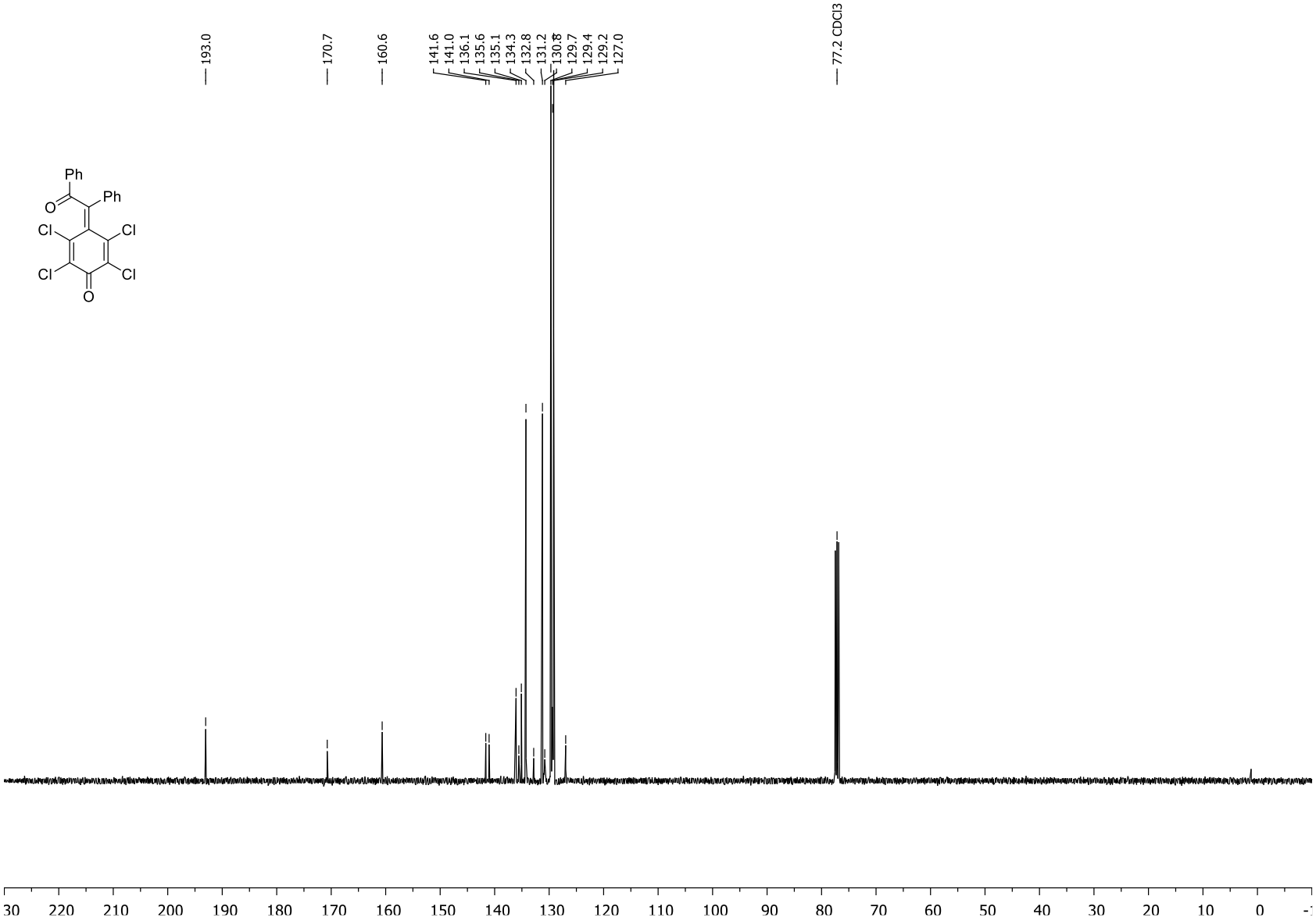


2,3,5,6-Tetrachloro-4-(2-oxo-1,2-diphenylethylidene)cyclohexa-2,5-dien-1-one (1f)

^{1}H NMR (400 MHz, $CDCl_3$)

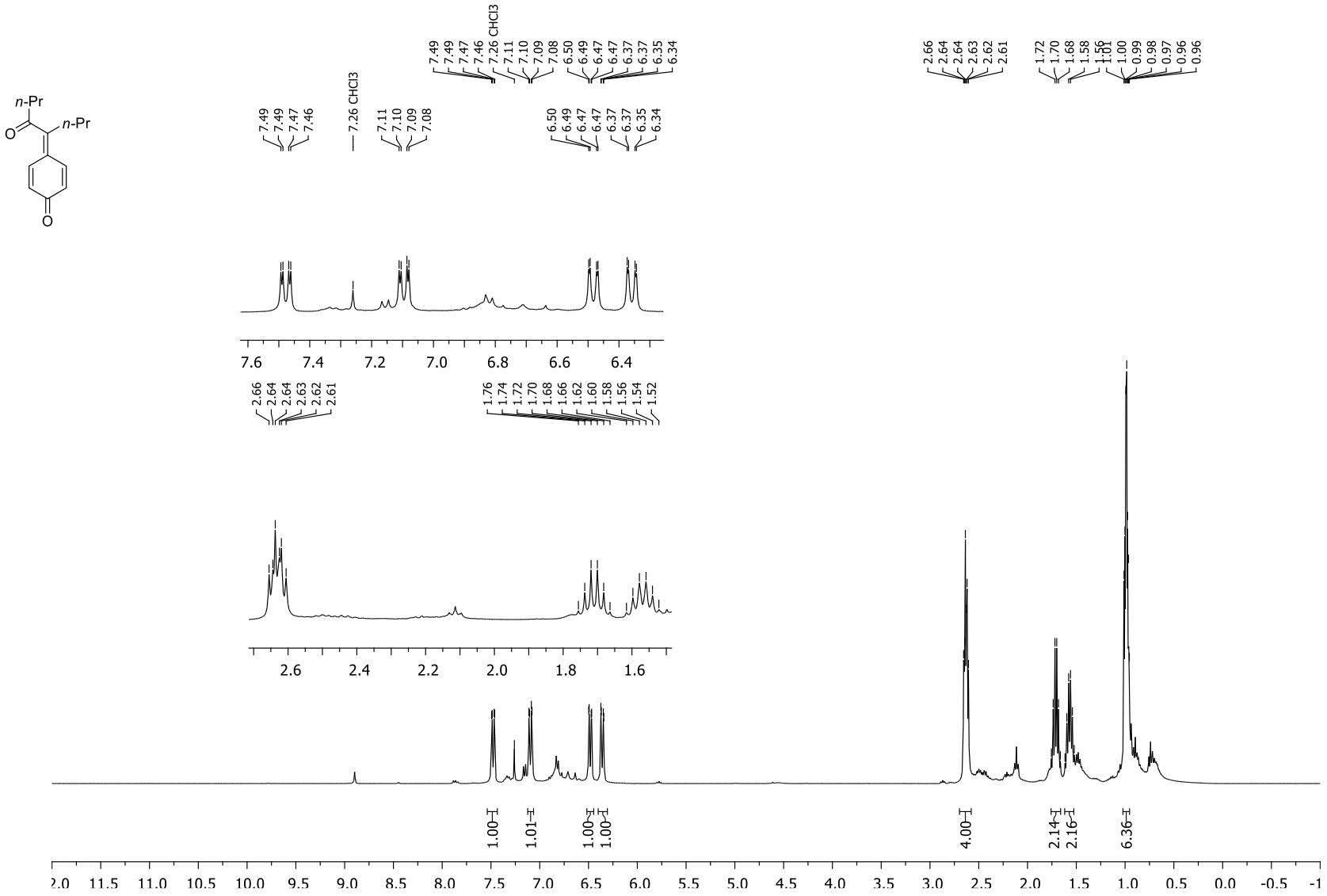


^{13}C NMR (101 MHz, $CDCl_3$)

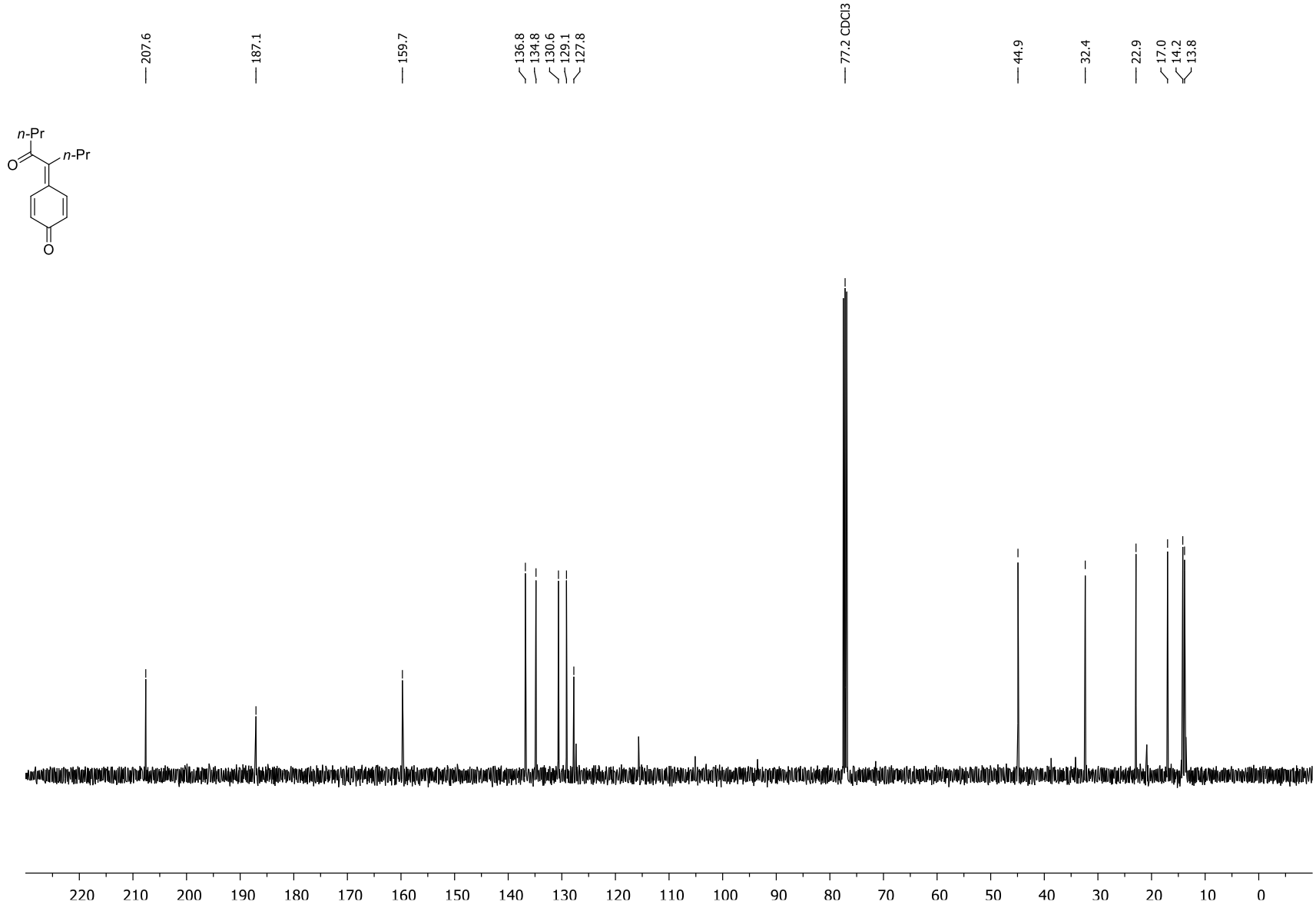


4-(5-Oxooctan-4-ylidene)cyclohexa-2,5-dien-1-one (1g)

^{1}H NMR (400 MHz, $CDCl_3$)

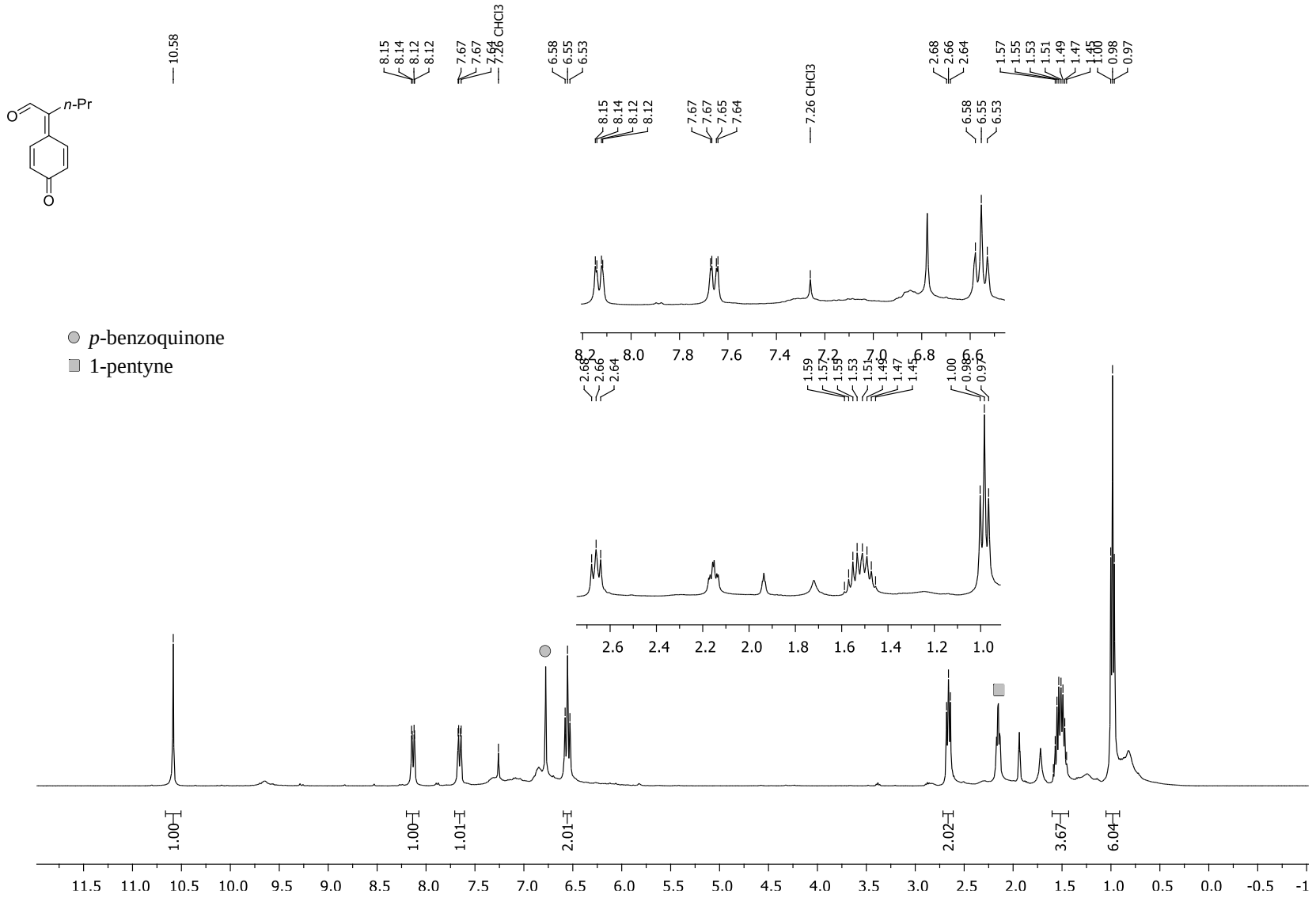


^{13}C NMR (101 MHz, $CDCl_3$)

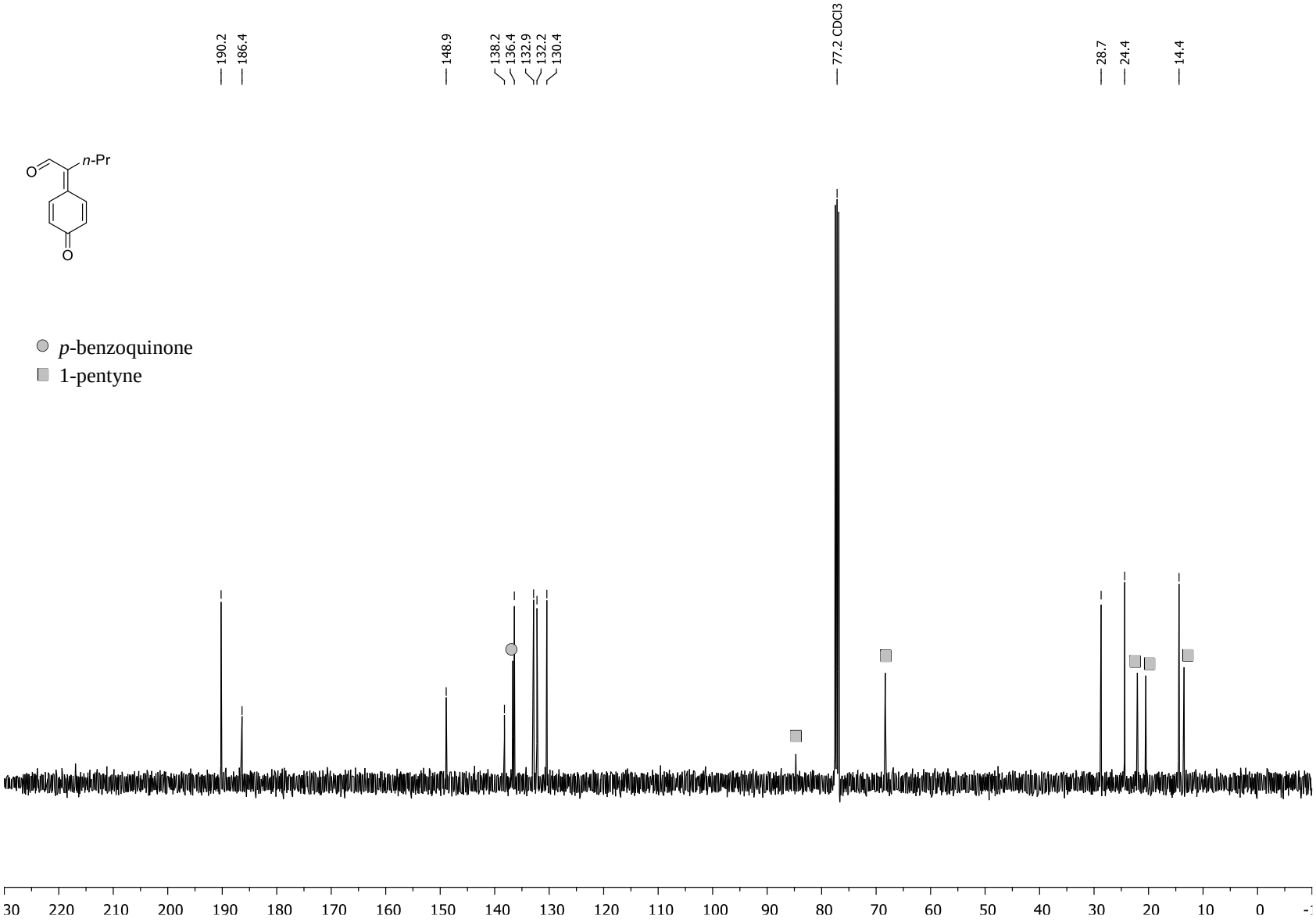


2-(4-Oxocyclohexa-2,5-dien-1-ylidene)pentanal (1h)

^{1}H NMR (400 MHz, $CDCl_3$)

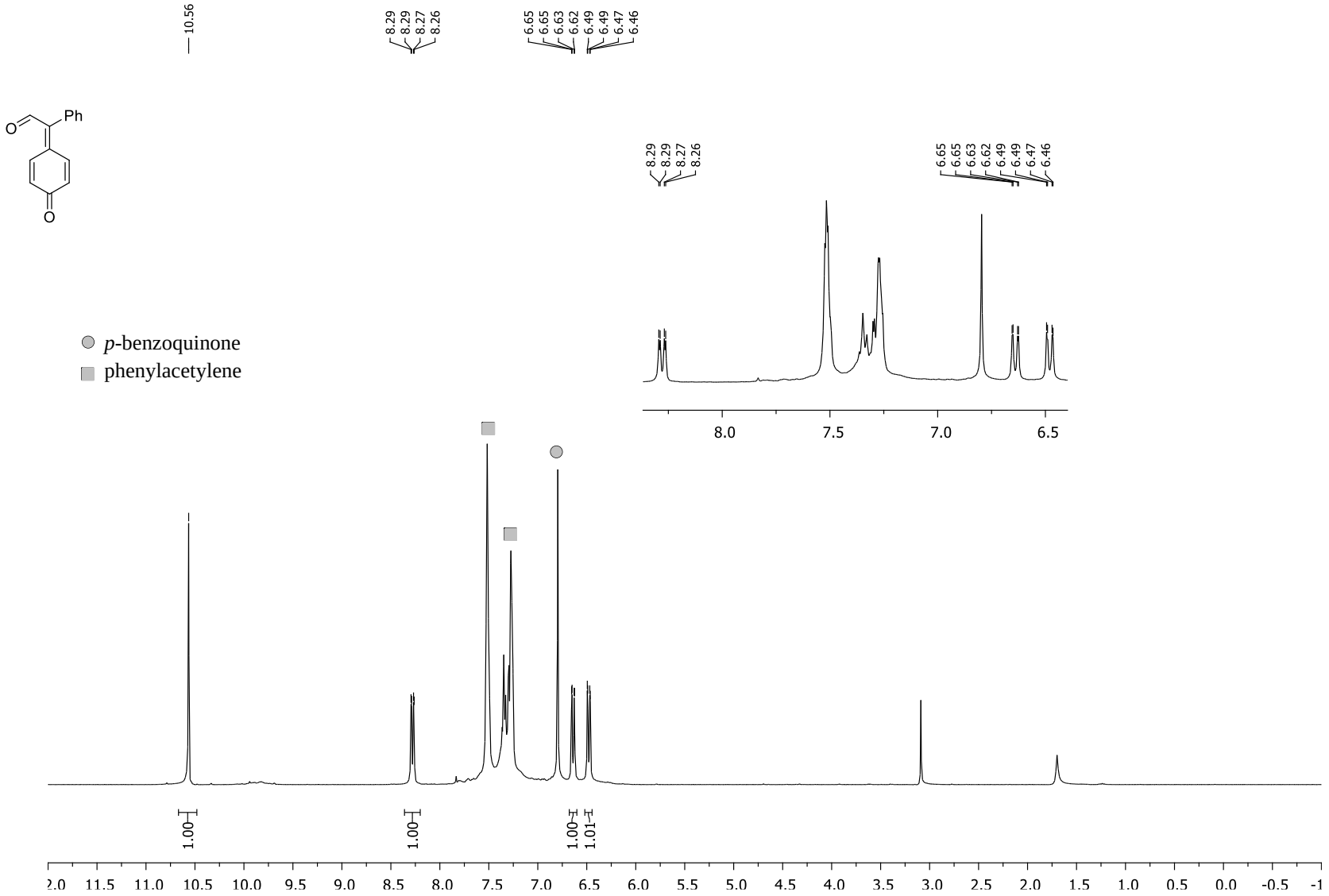


^{13}C NMR (101 MHz, $CDCl_3$)

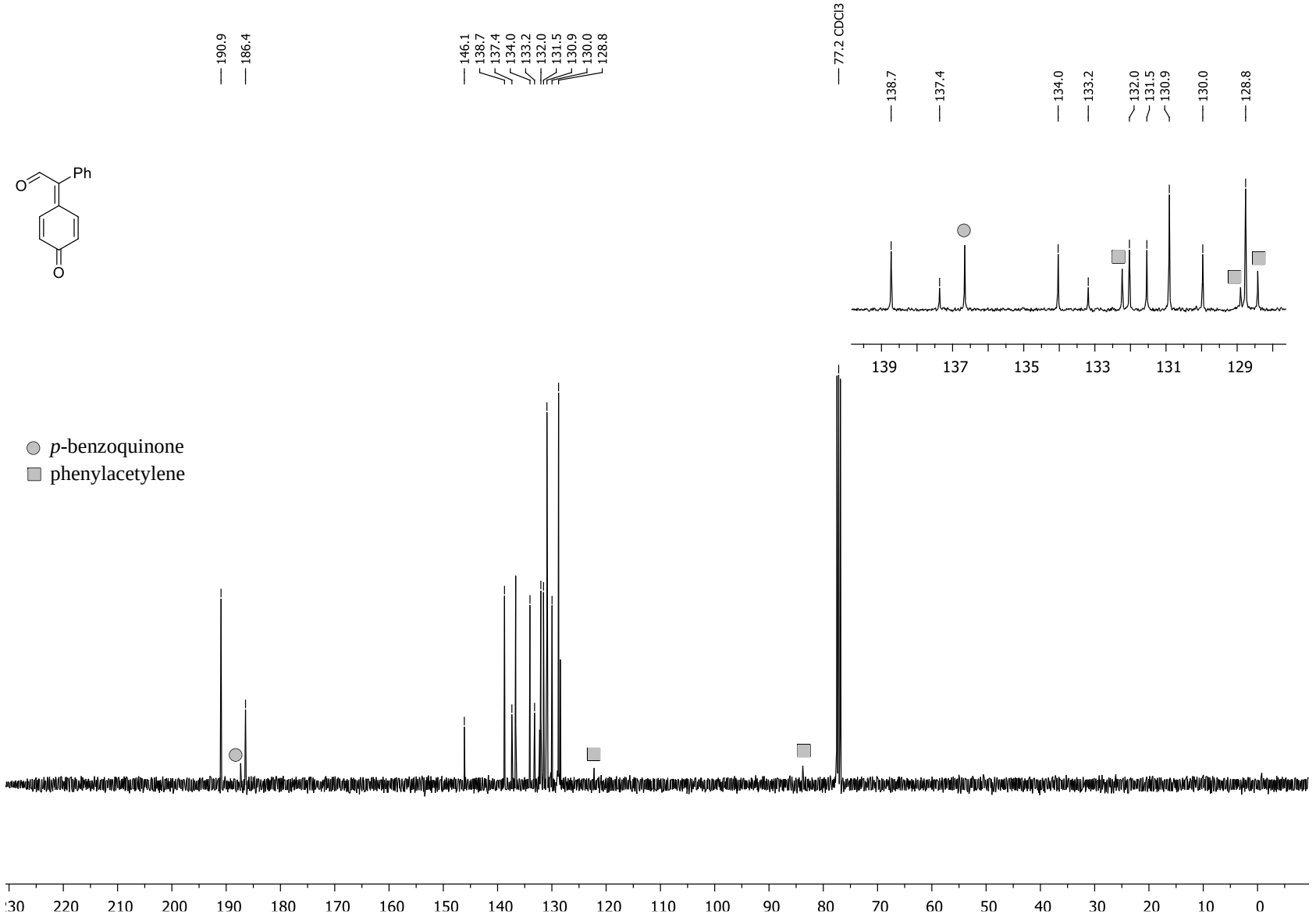


2-(4-Oxocyclohexa-2,5-dien-1-ylidene)-2-phenylacetaldehyde (1i)

^{1}H NMR (400 MHz, $CDCl_3$)

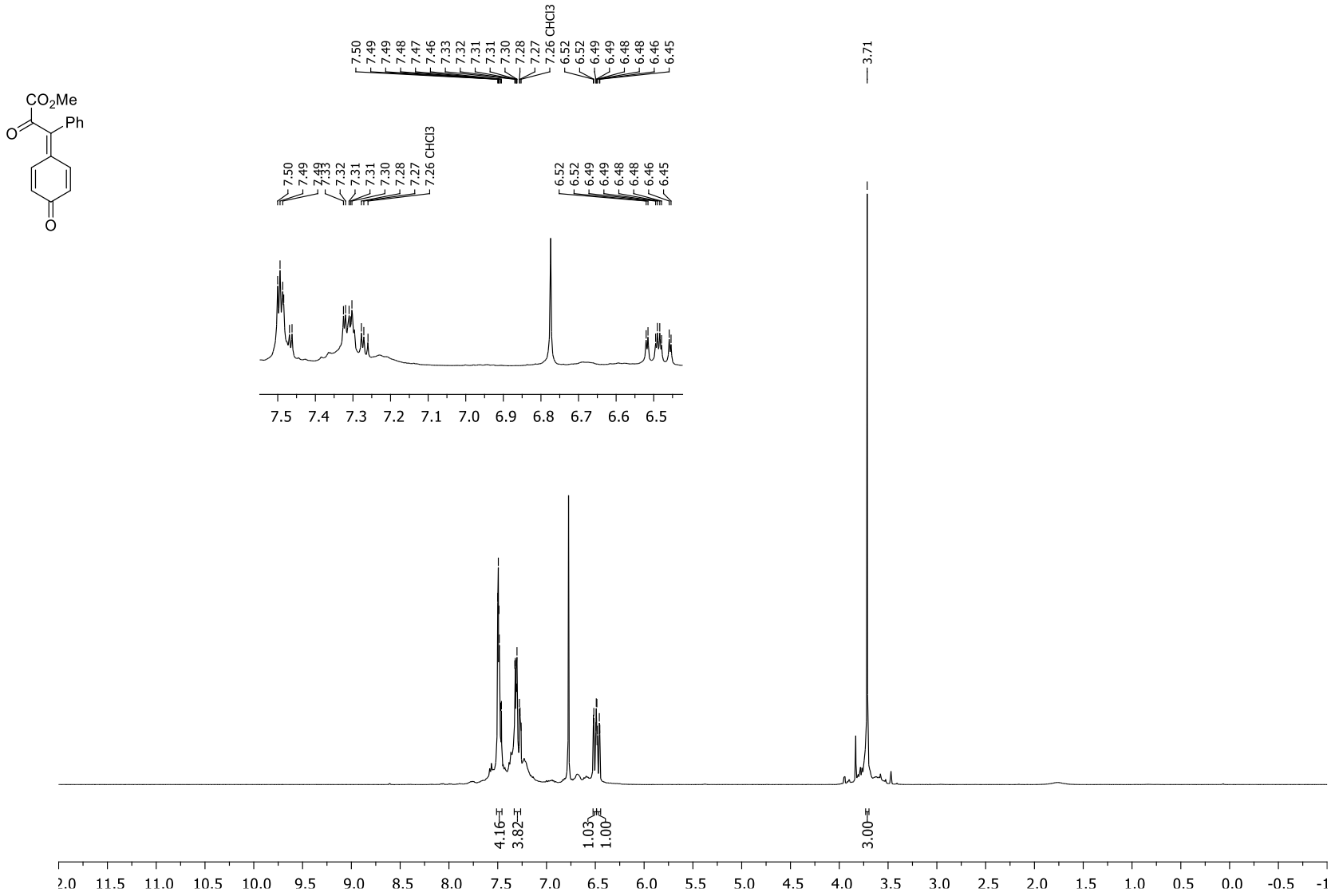


^{13}C NMR (101 MHz, $CDCl_3$)

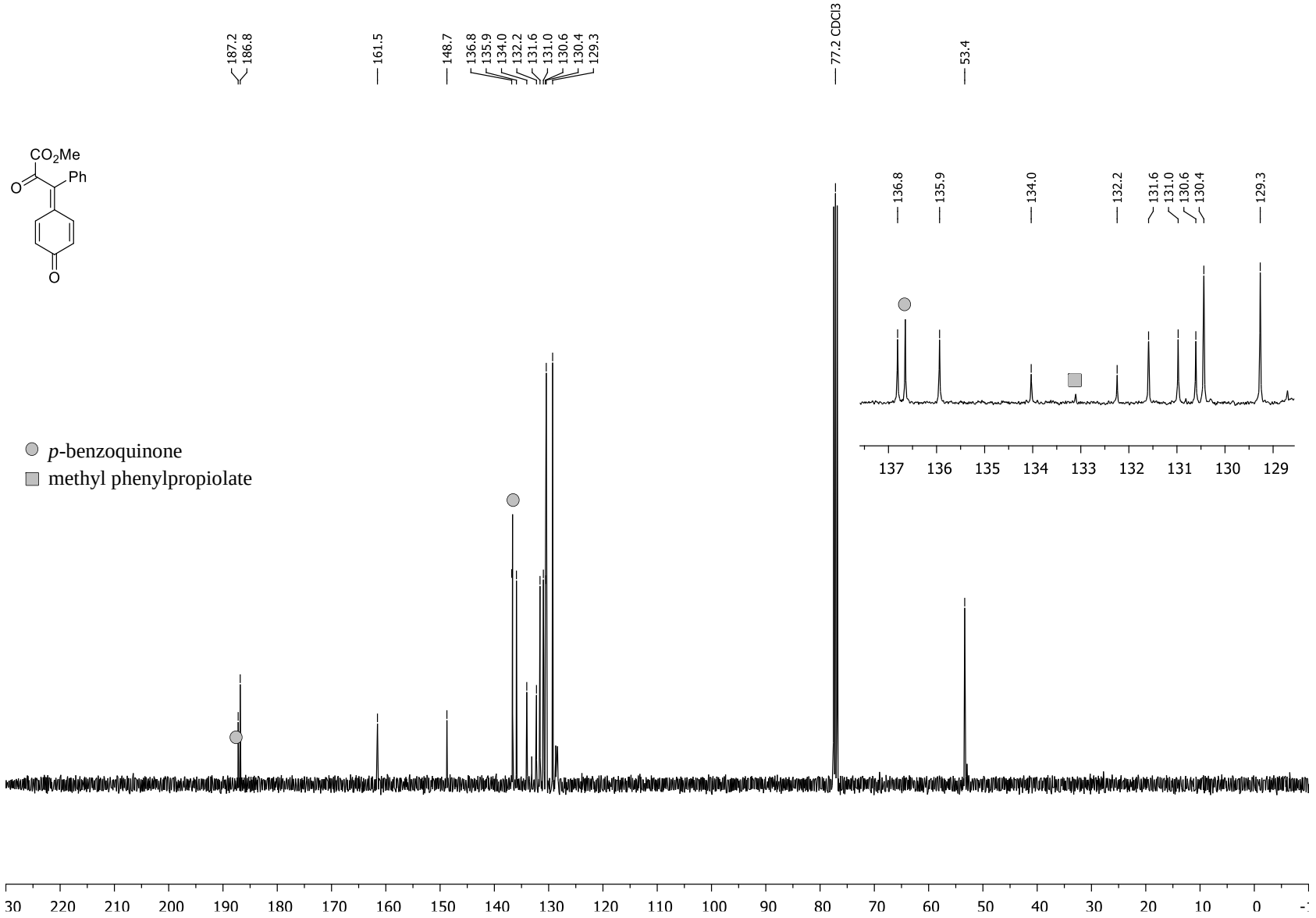


Methyl 2-oxo-3-(4-oxocyclohexa-2,5-dien-1-ylidene)-3-phenylpropanoate (1j)

^{1}H NMR (400 MHz, $CDCl_3$)

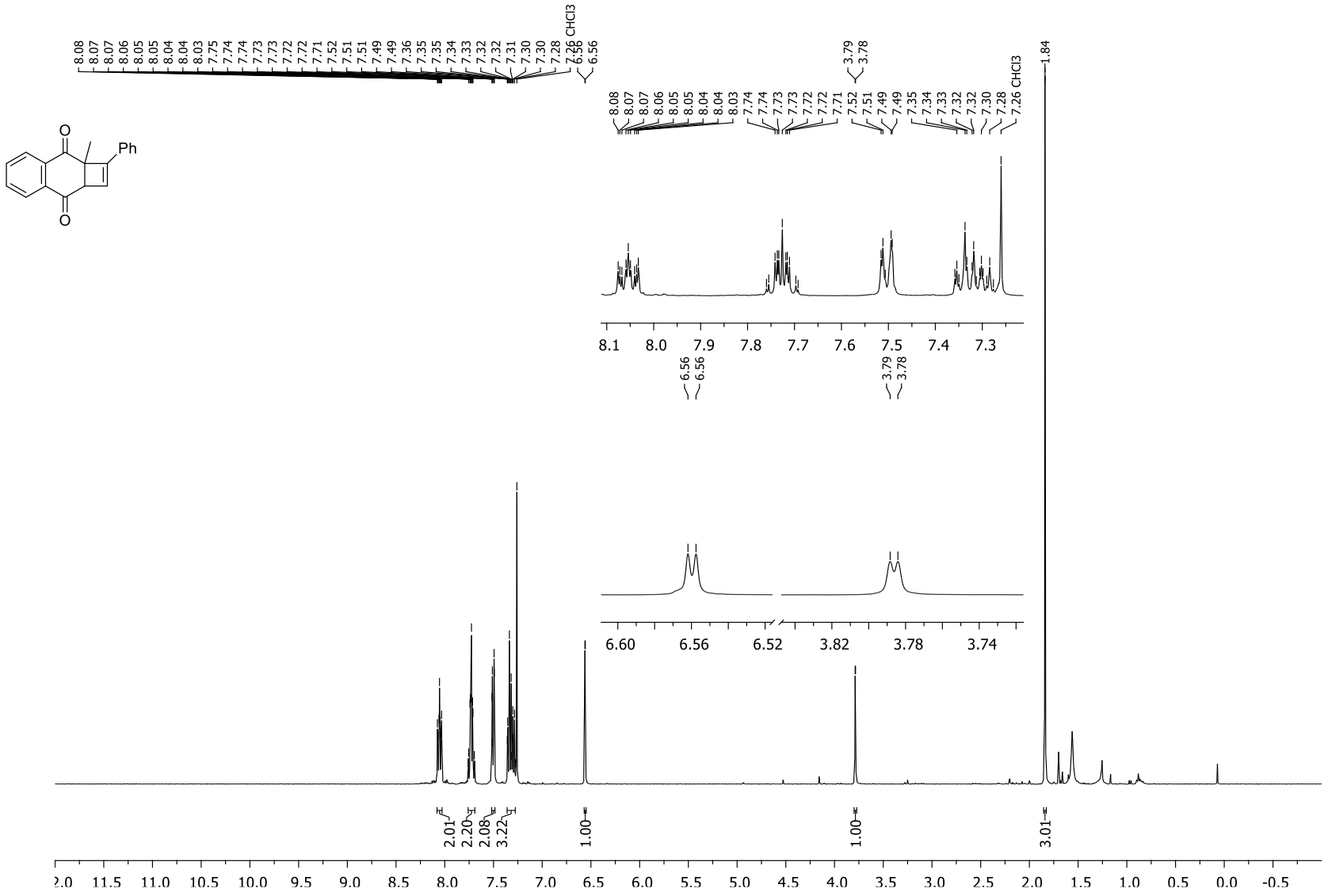


^{13}C NMR (101 MHz, $CDCl_3$)

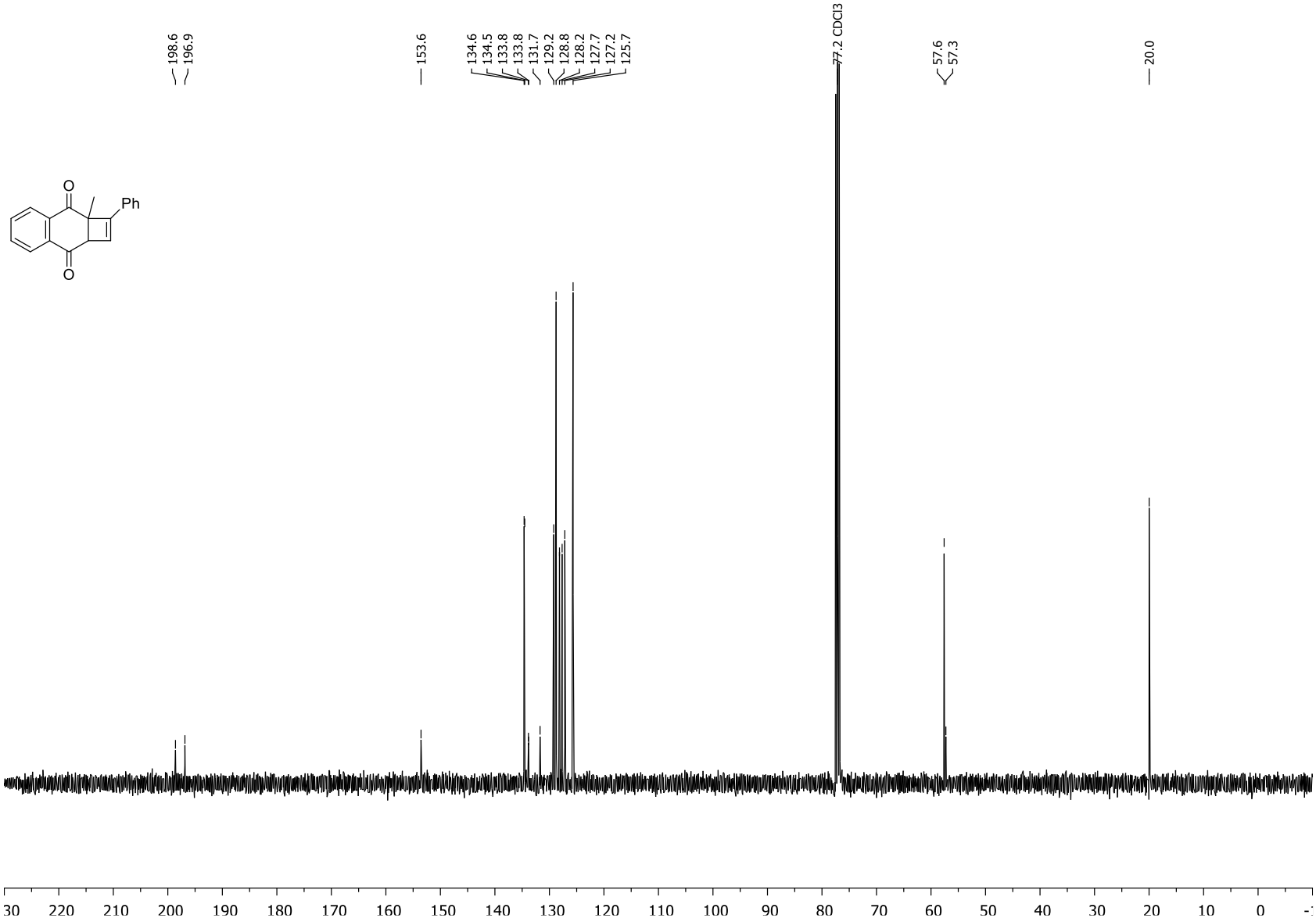


8a-Methyl-1-phenyl-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione (2a)

^{1}H NMR (400 MHz, $CDCl_3$)

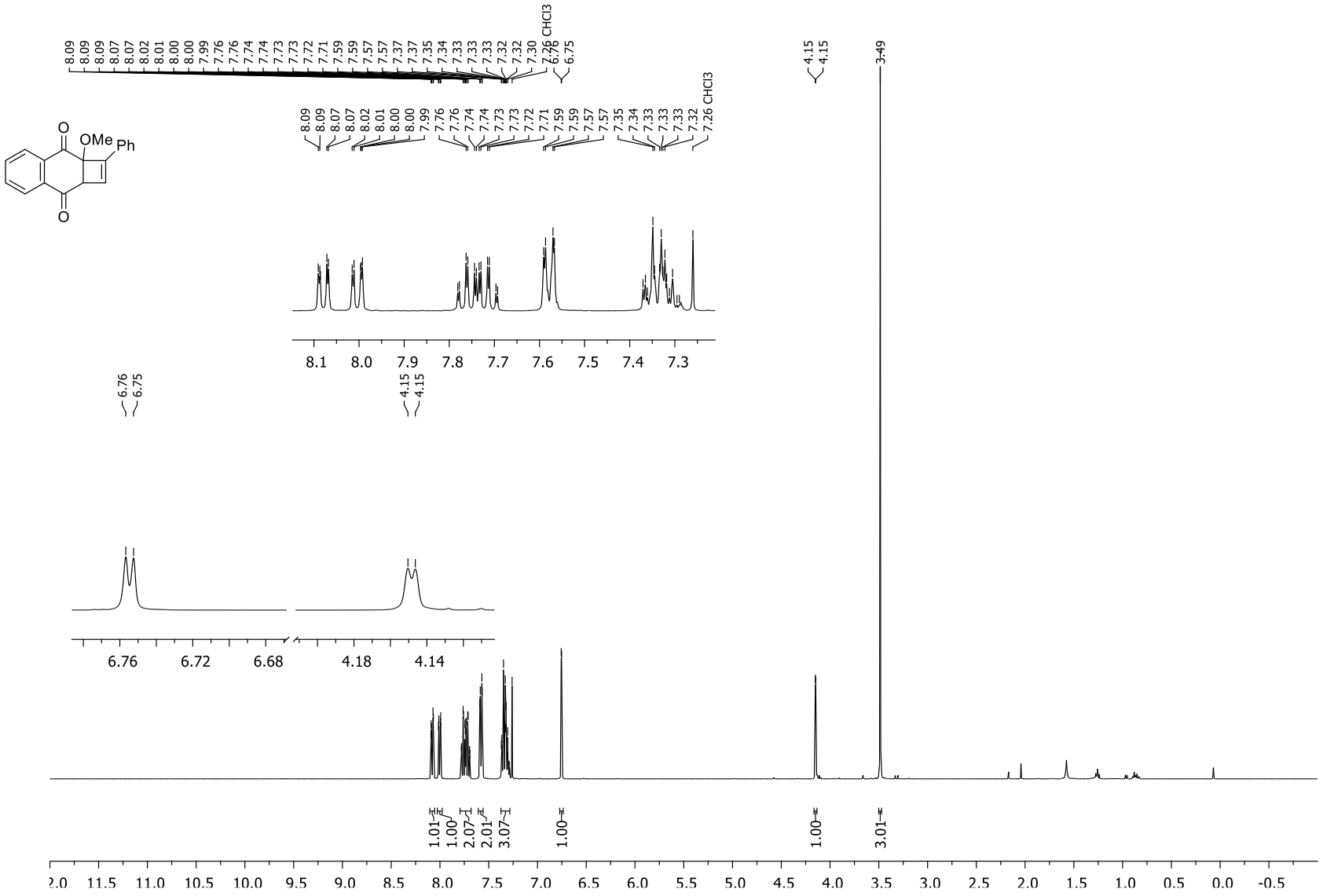


^{13}C NMR (101 MHz, $CDCl_3$)

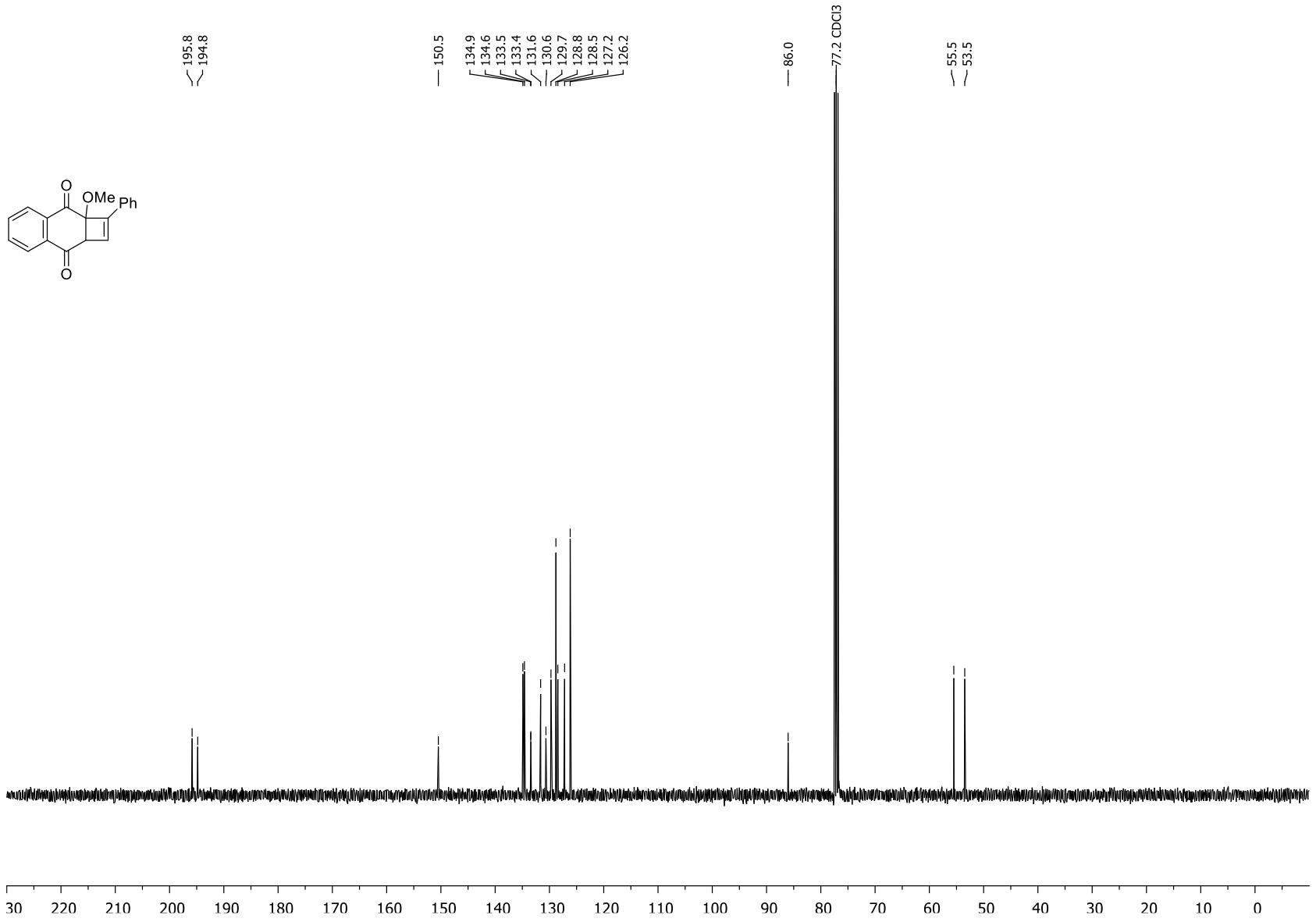


8a-Methoxy-1-phenyl-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione (2b)

^{1}H NMR (400 MHz, $CDCl_3$)

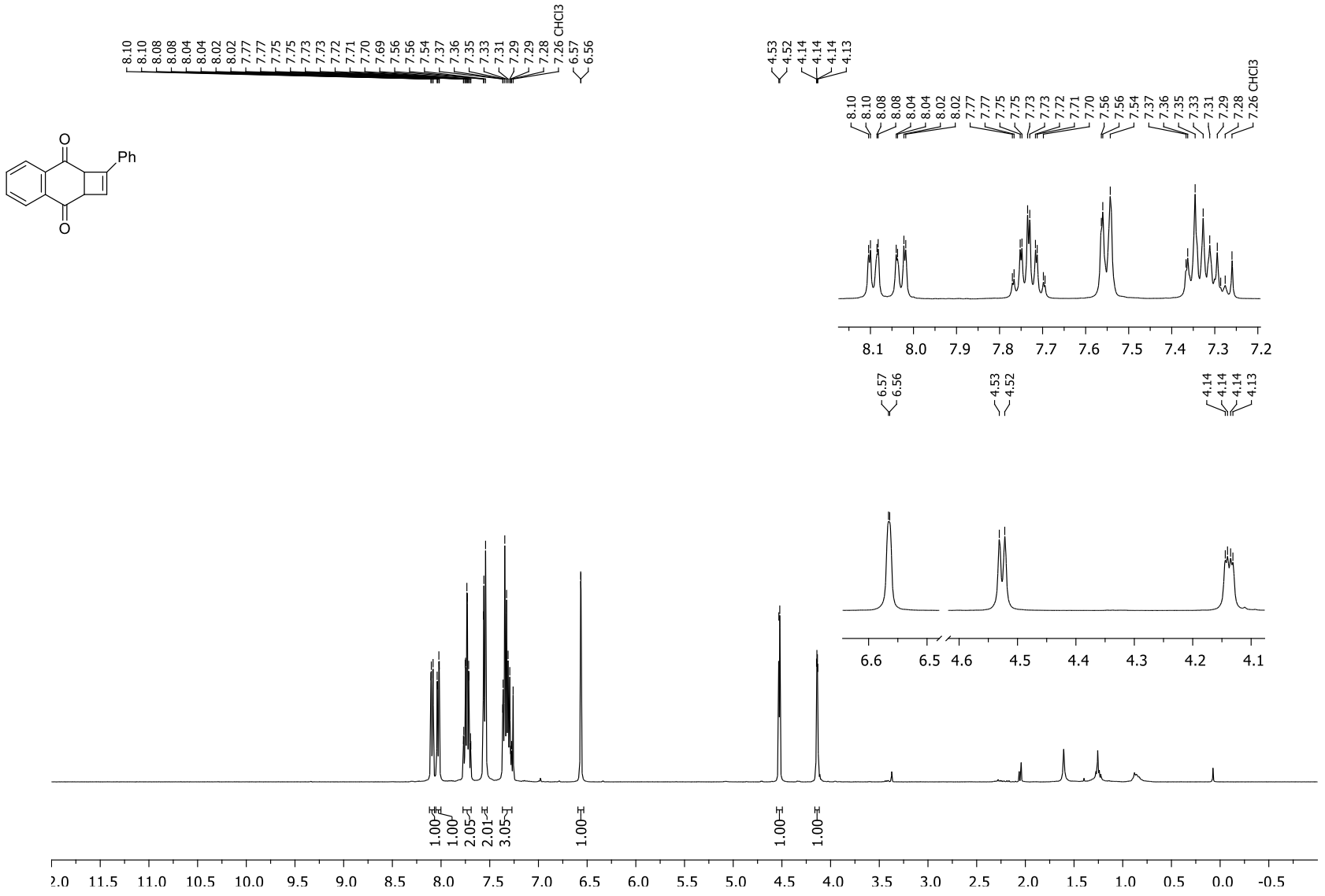


^{13}C NMR (101 MHz, $CDCl_3$)

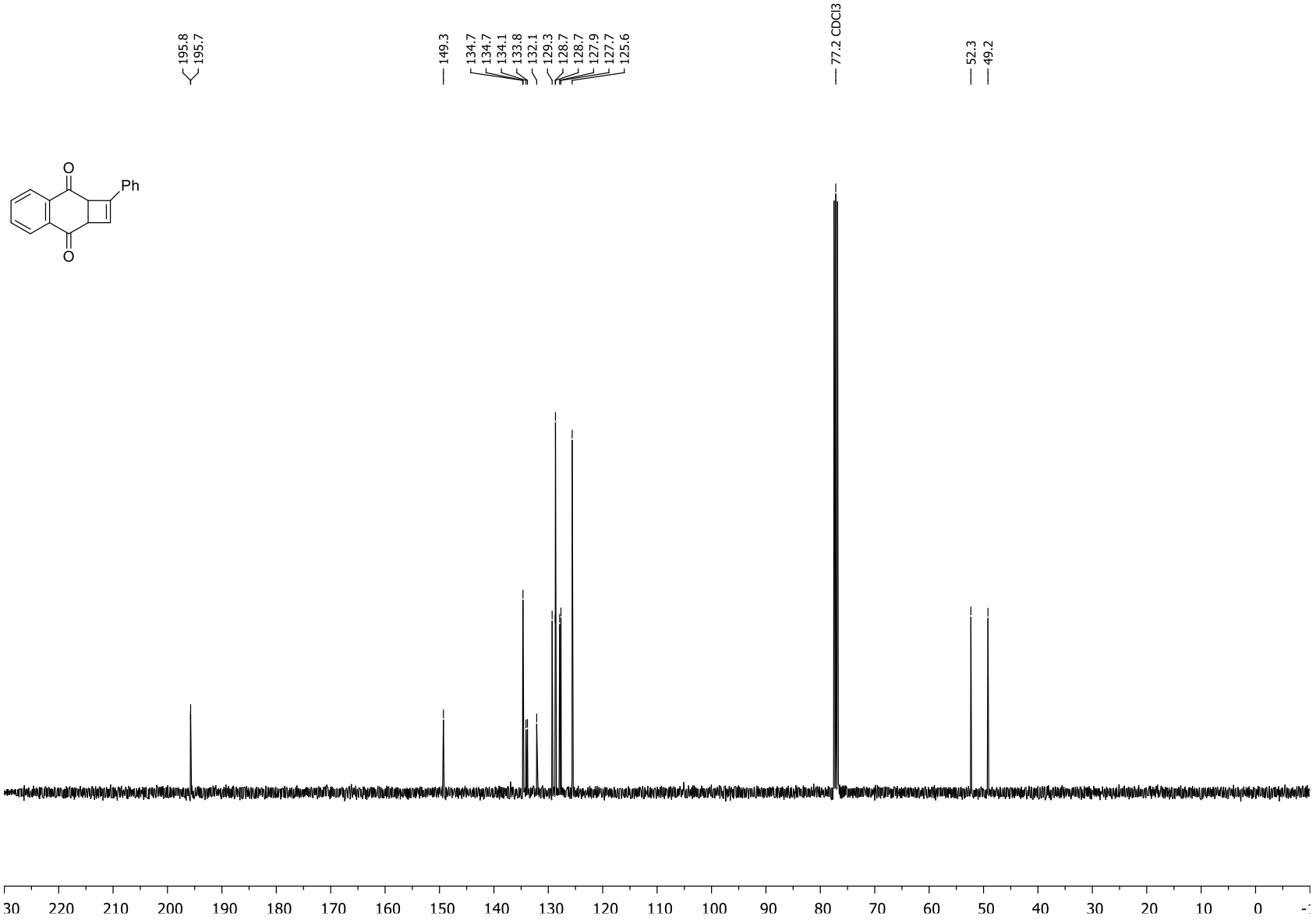


1-Phenyl-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione (2c)

^{1}H NMR (400 MHz, $CDCl_3$)

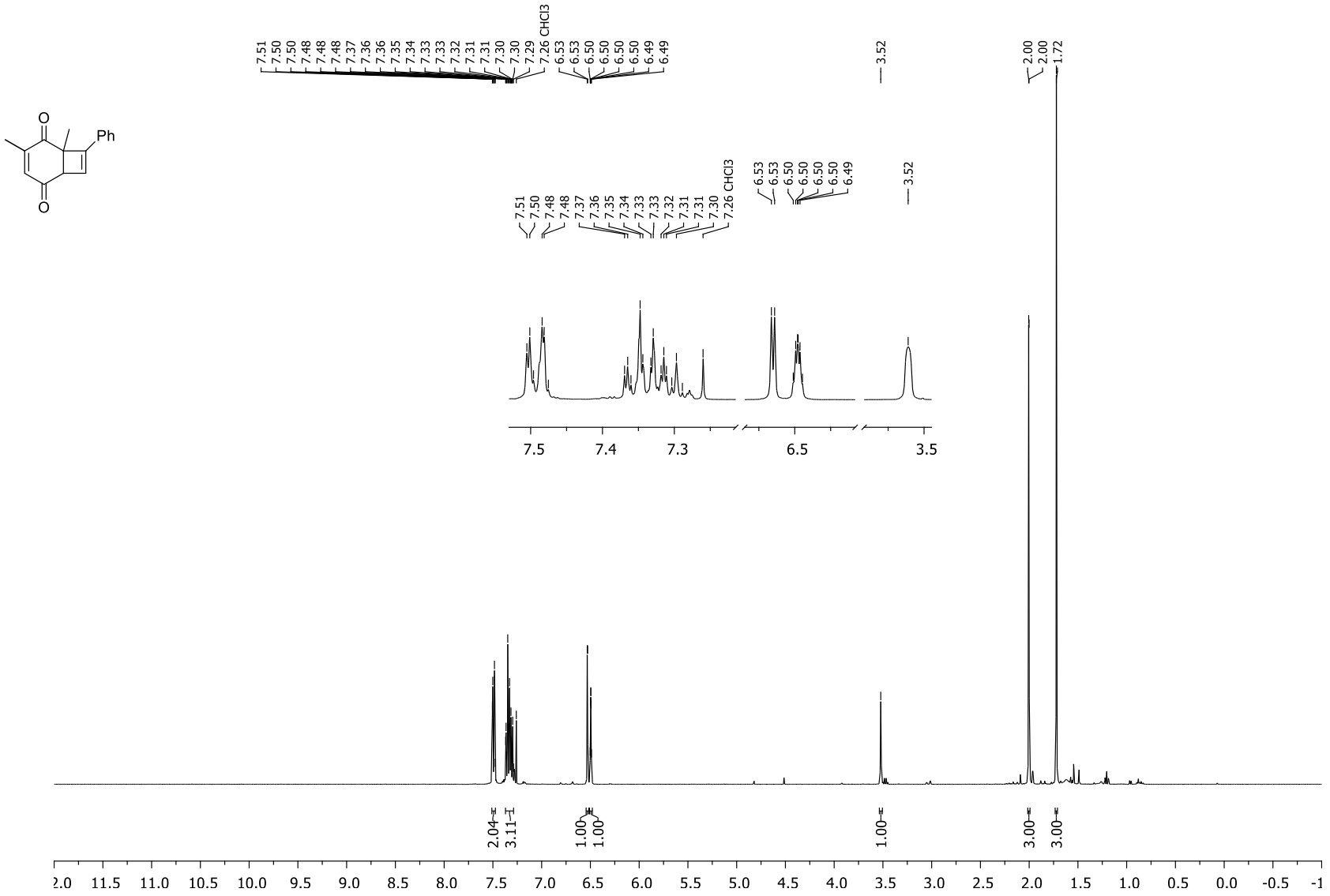


^{13}C NMR (101 MHz, $CDCl_3$)

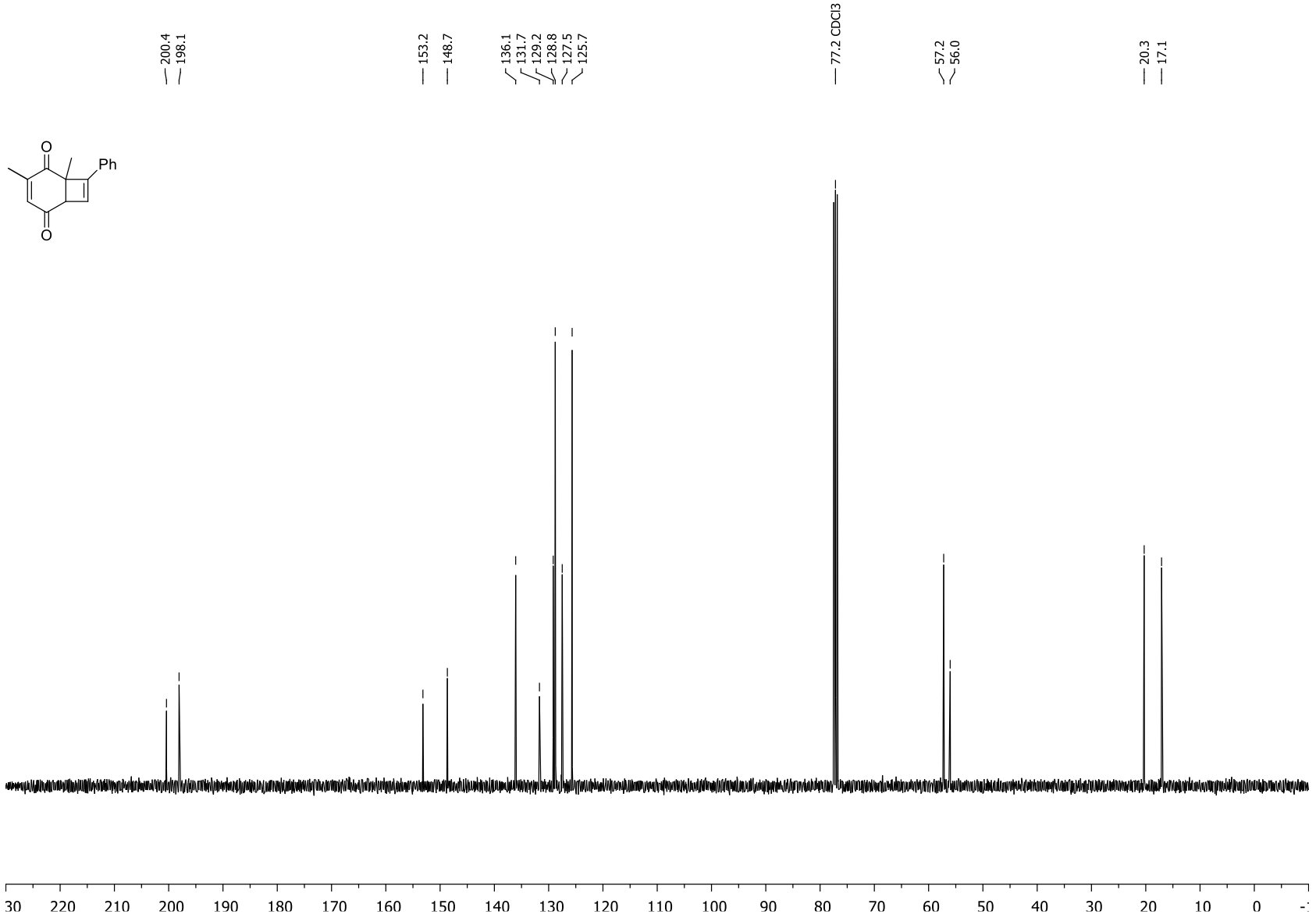


1,3-Dimethyl-8-phenylbicyclo[4.2.0]octa-3,7-diene-2,5-dione (2d)

^{1}H NMR (400 MHz, $CDCl_3$)

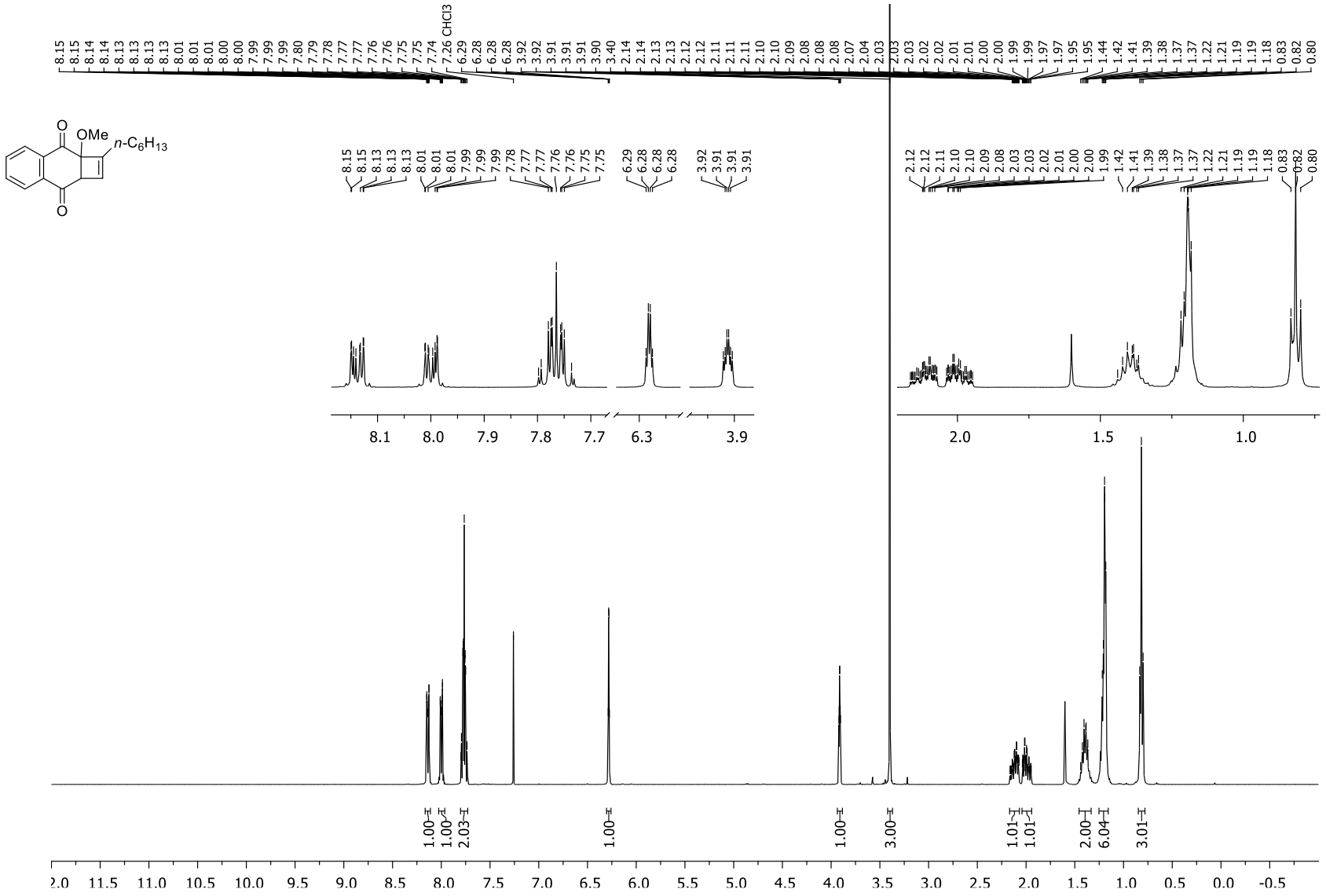


^{13}C NMR (101 MHz, $CDCl_3$)

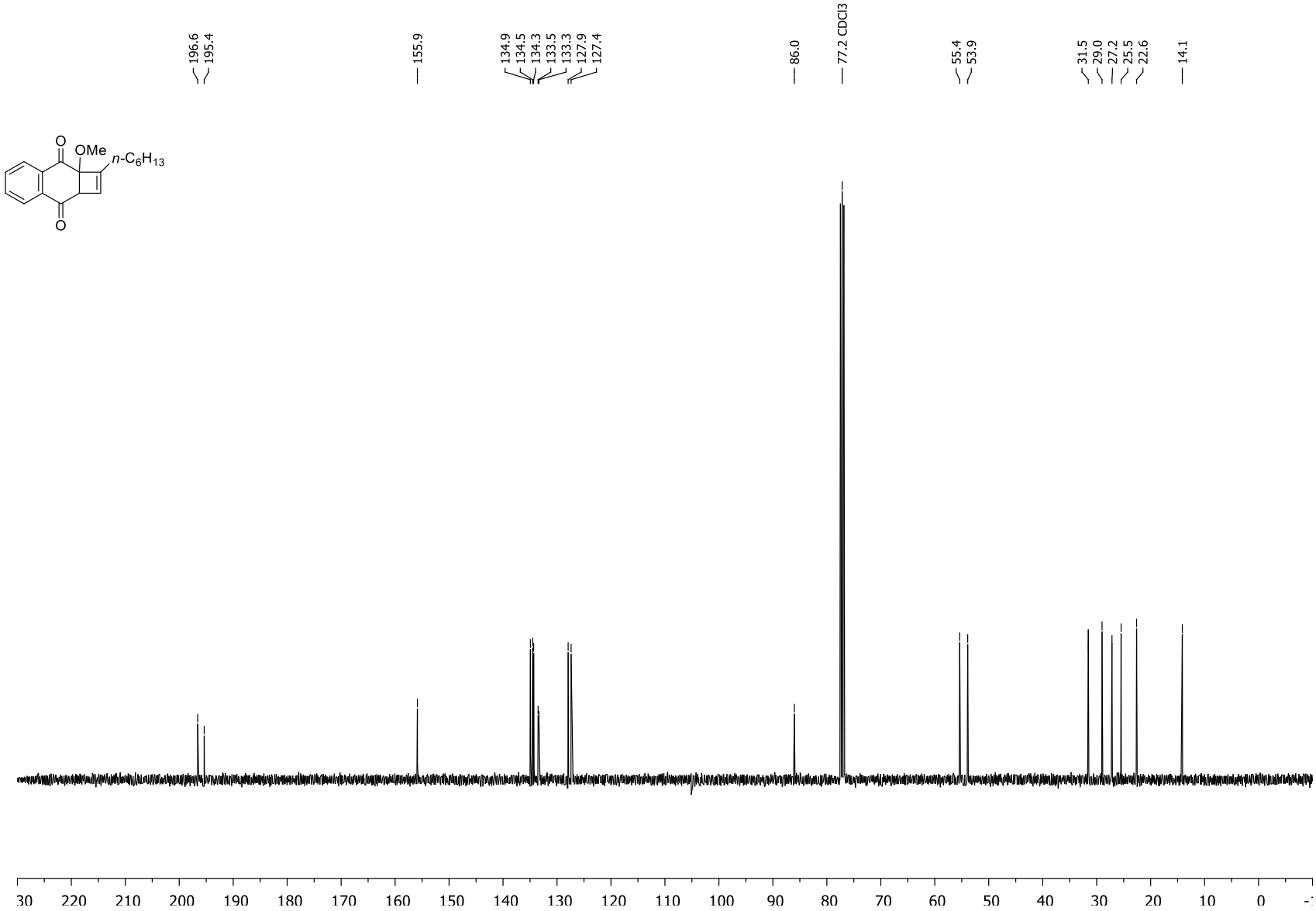


1-Hexyl-8a-methoxy-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione (2e)

^{1}H NMR (400 MHz, $CDCl_3$)

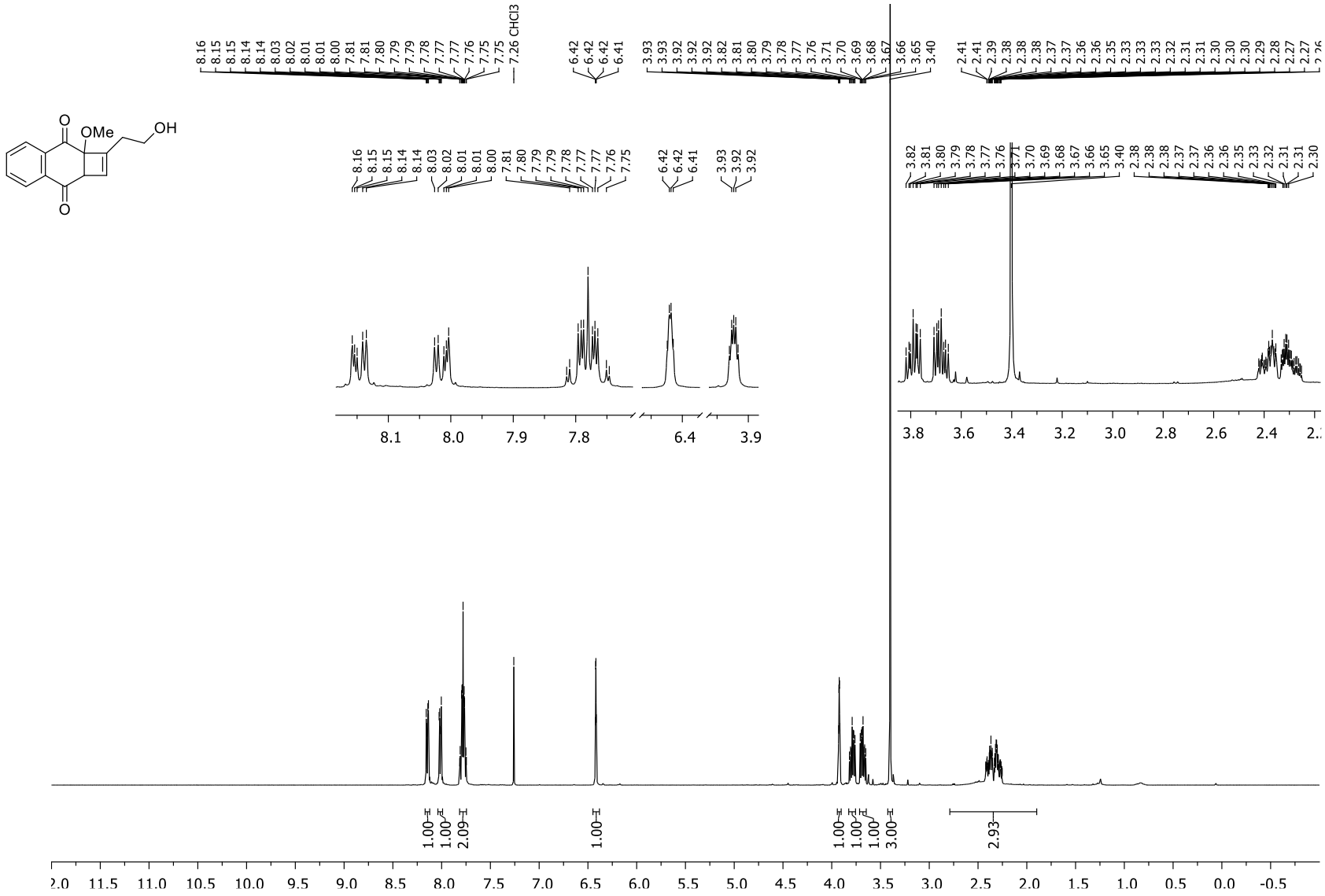


^{13}C NMR (101 MHz, $CDCl_3$)

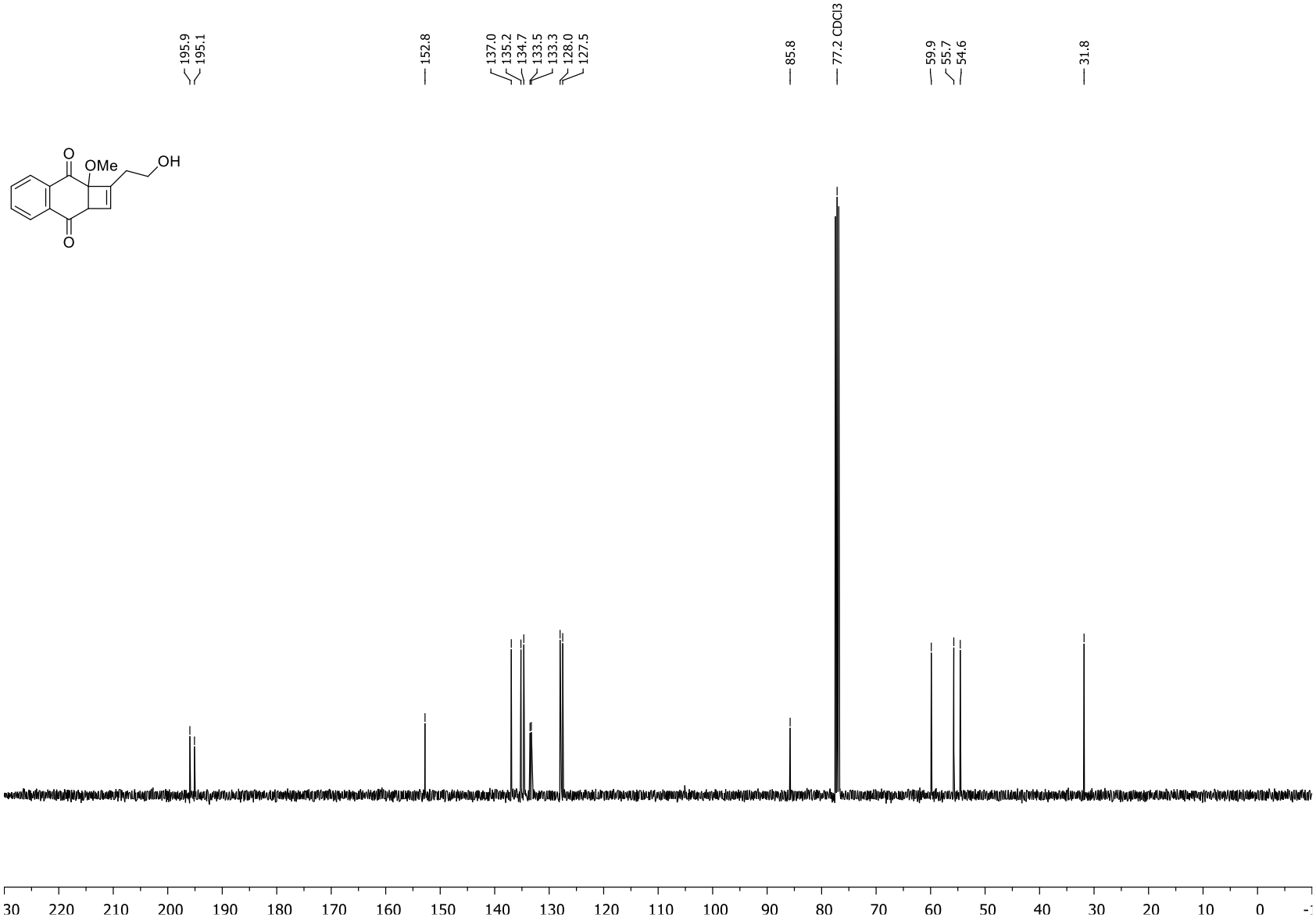


1-(2-Hydroxyethyl)-8a-methoxy-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione (2f)

^{1}H NMR (400 MHz, $CDCl_3$)

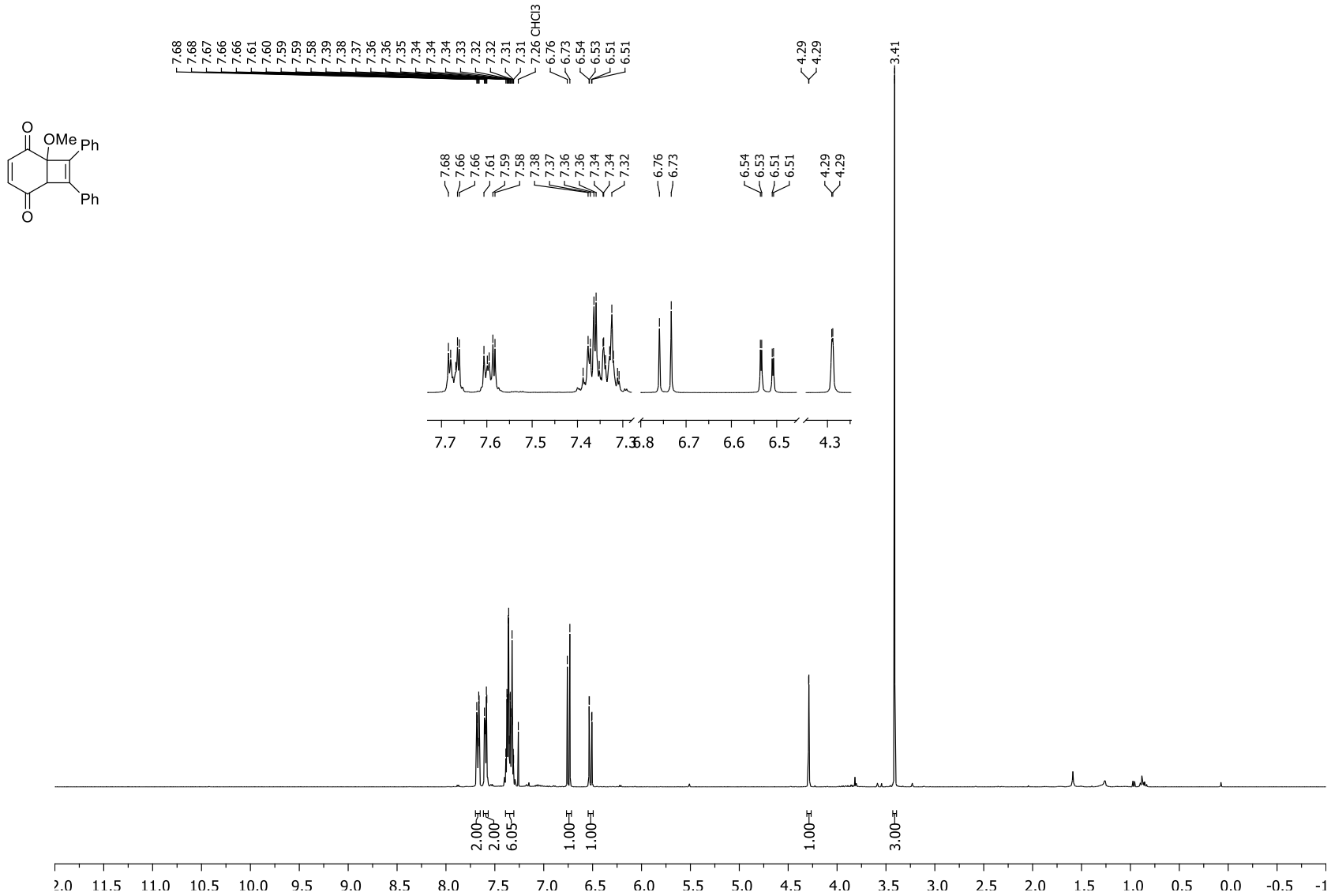


^{13}C NMR (101 MHz, $CDCl_3$)

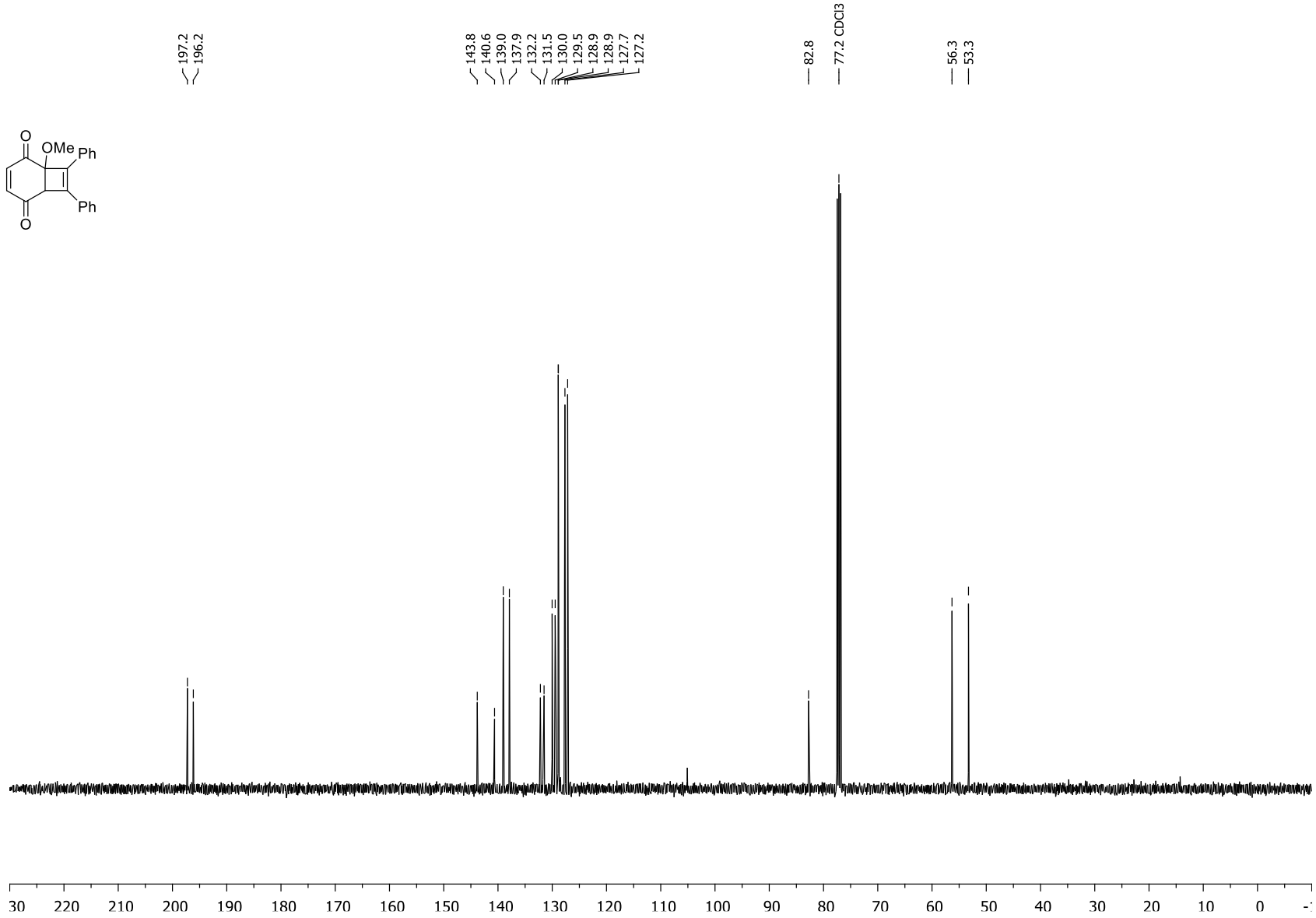


1-Methoxy-7,8-diphenylbicyclo[4.2.0]octa-3,7-diene-2,5-dione (2g)

^{1}H NMR (400 MHz, $CDCl_3$)

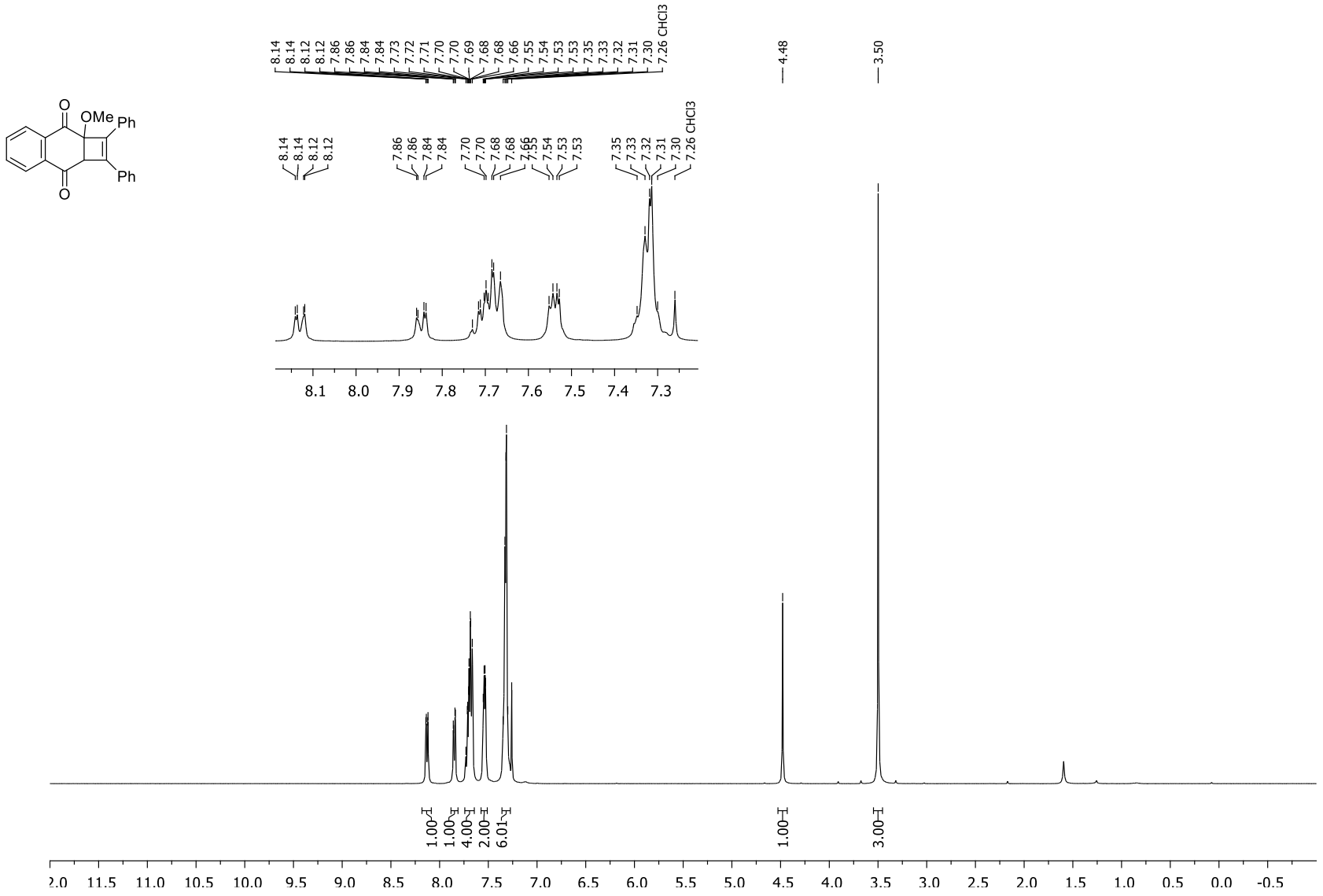


^{13}C NMR (101 MHz, $CDCl_3$)

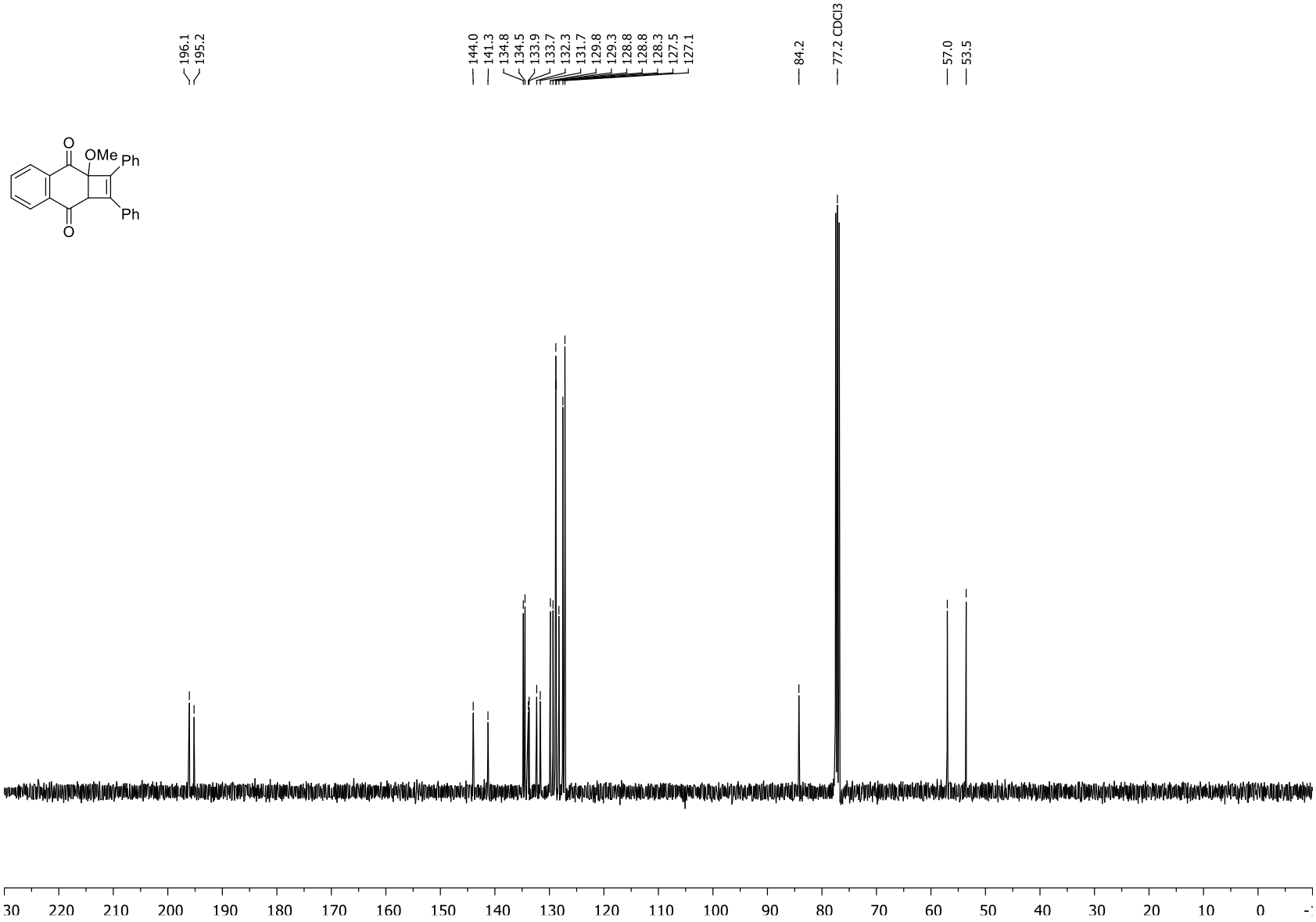


2a-Methoxy-1,2-diphenyl-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione (2h)

^{1}H NMR (400 MHz, $CDCl_3$)

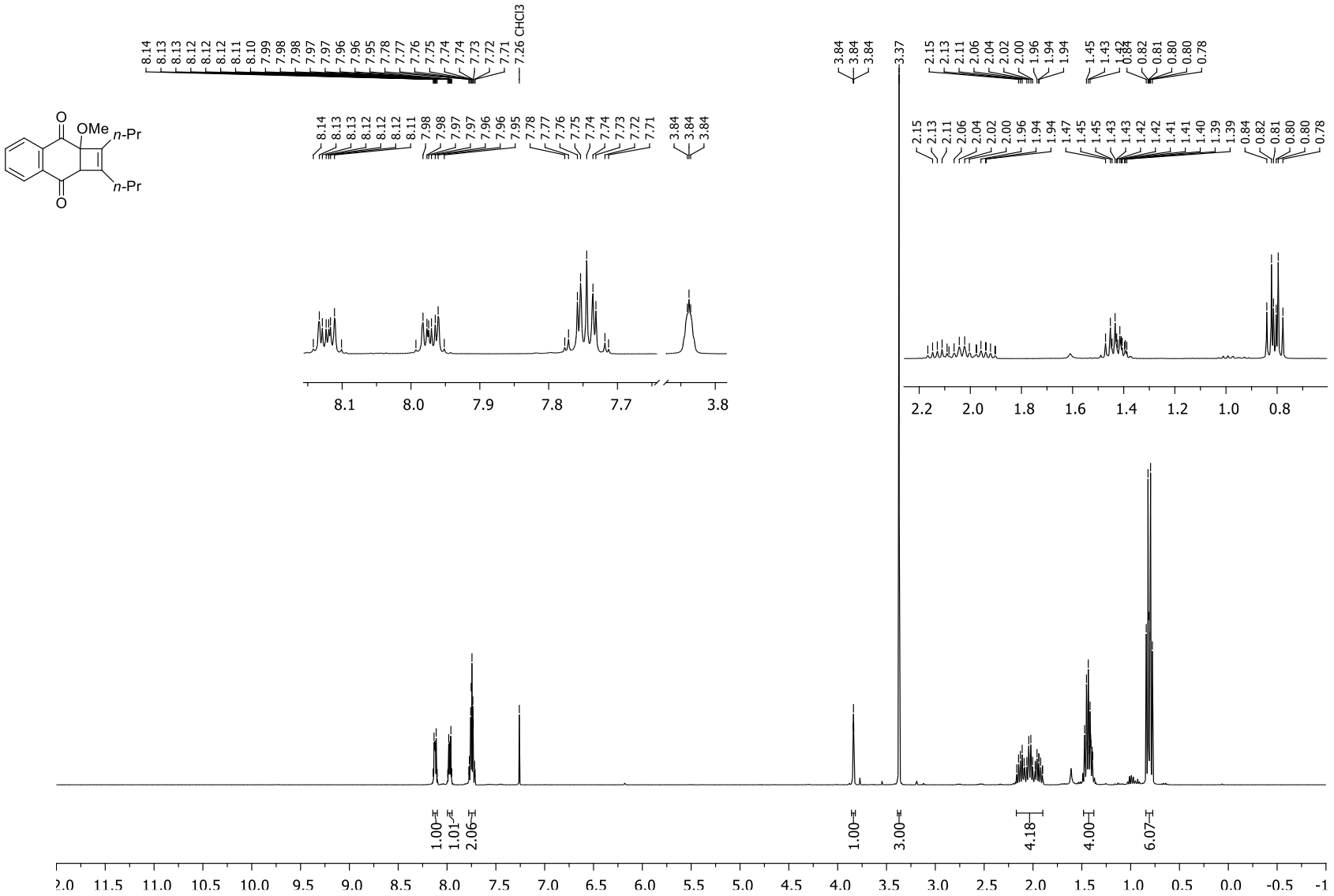


^{13}C NMR (101 MHz, $CDCl_3$)

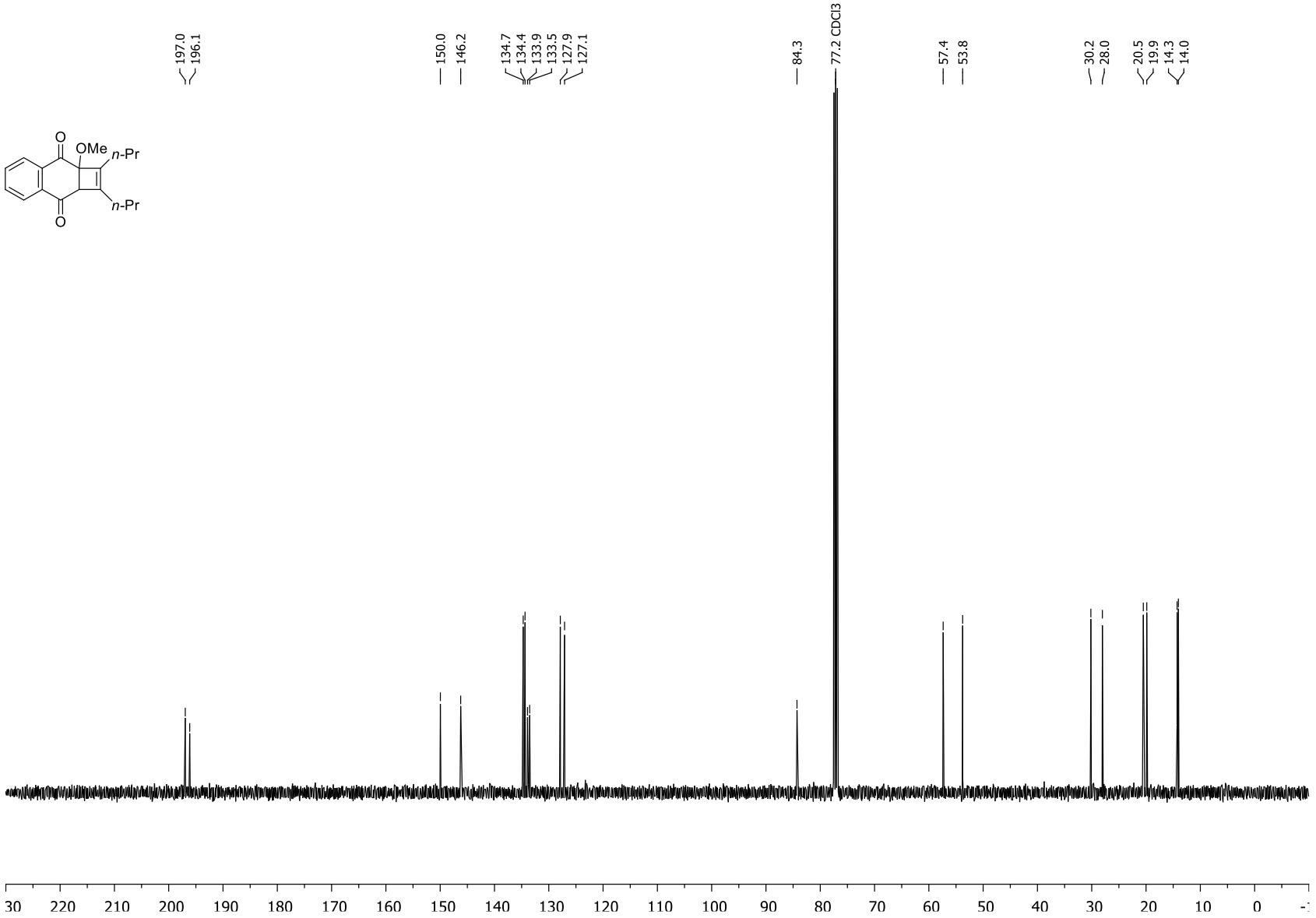


2a-Methoxy-1,2-dipropyl-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione (2i)

^{1}H NMR (400 MHz, $CDCl_3$)

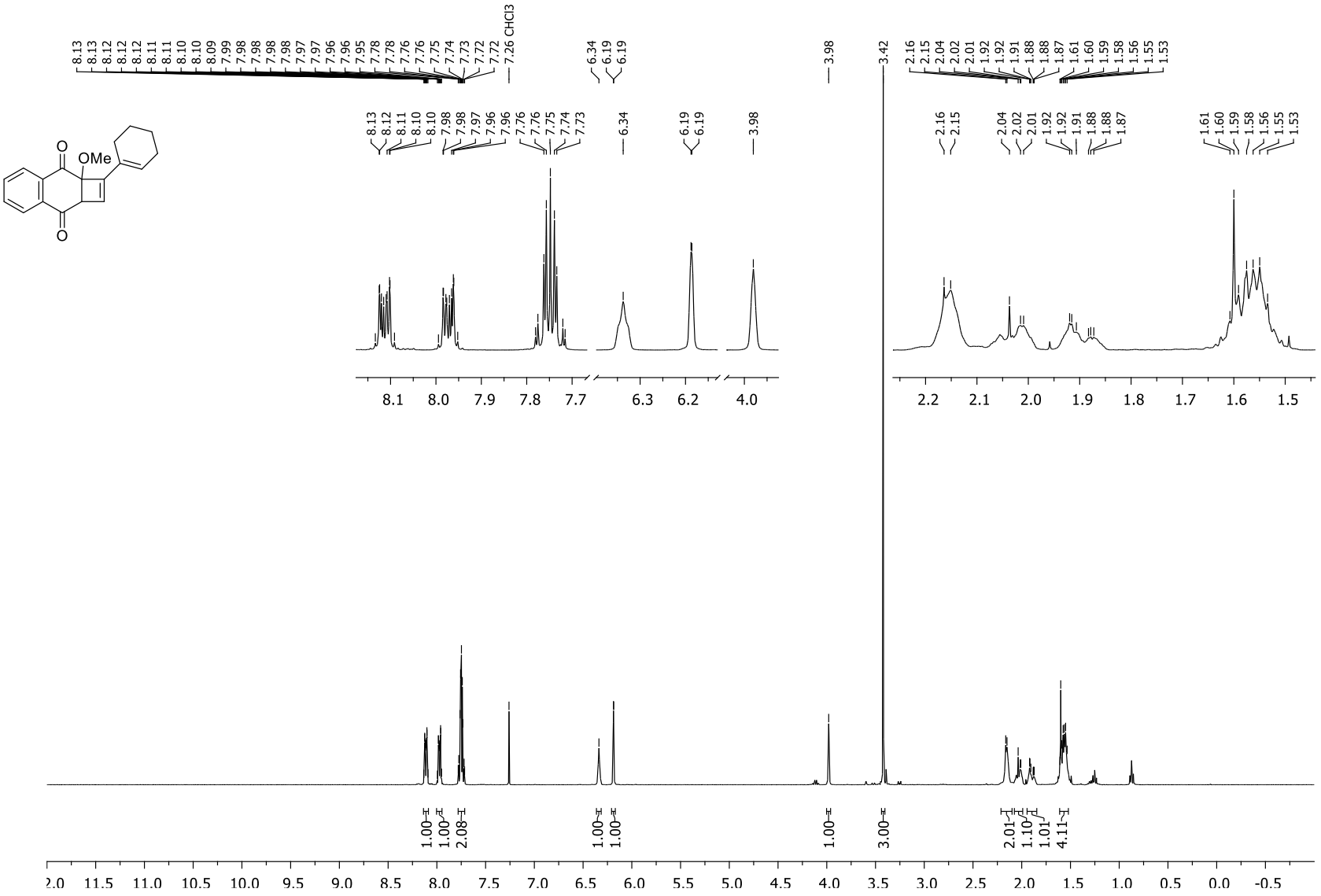


^{13}C NMR (101 MHz, $CDCl_3$)

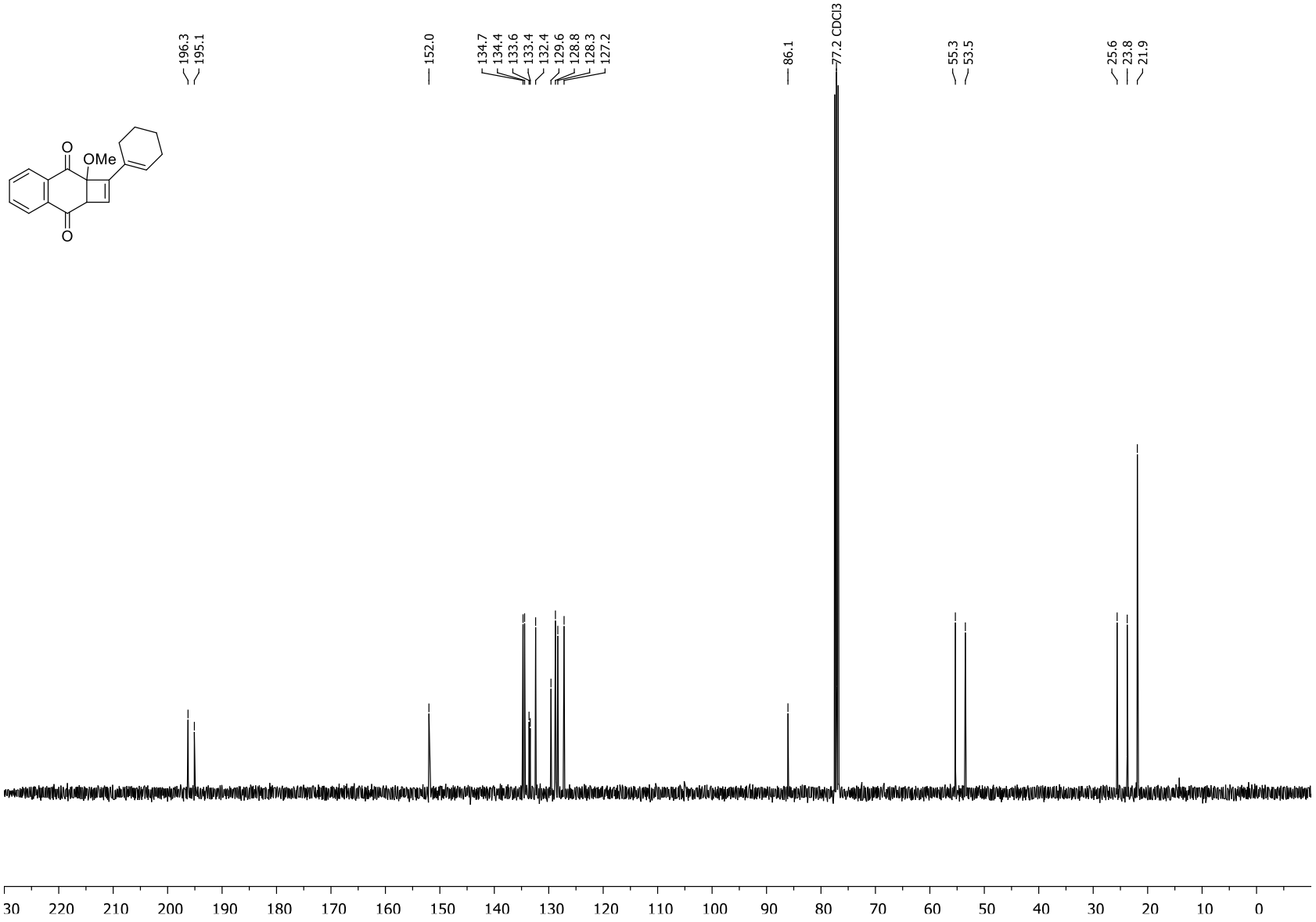


1-(Cyclohex-1-en-1-yl)-8a-methoxy-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione (2j)

^{1}H NMR (400 MHz, $CDCl_3$)

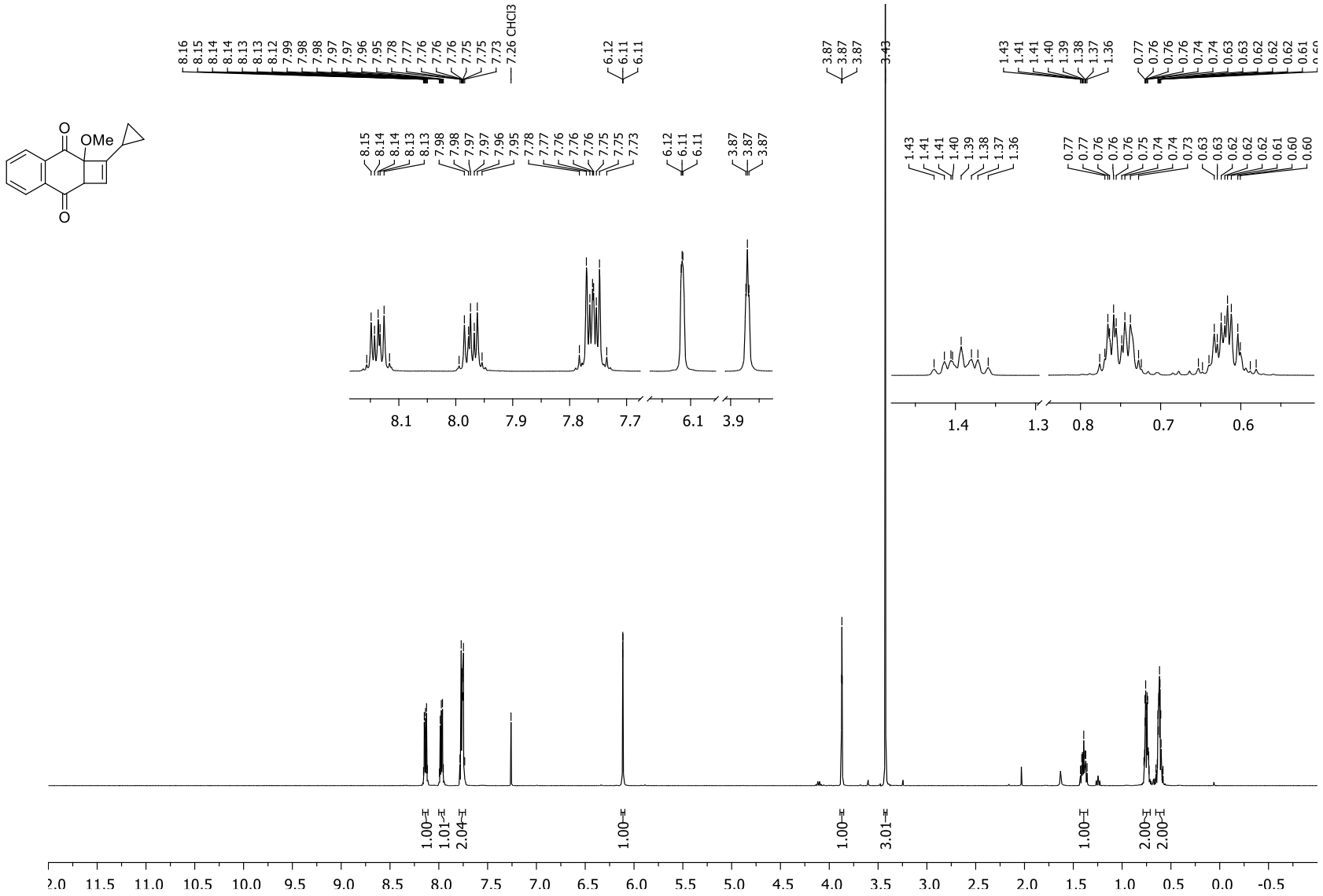


^{13}C NMR (101 MHz, $CDCl_3$)

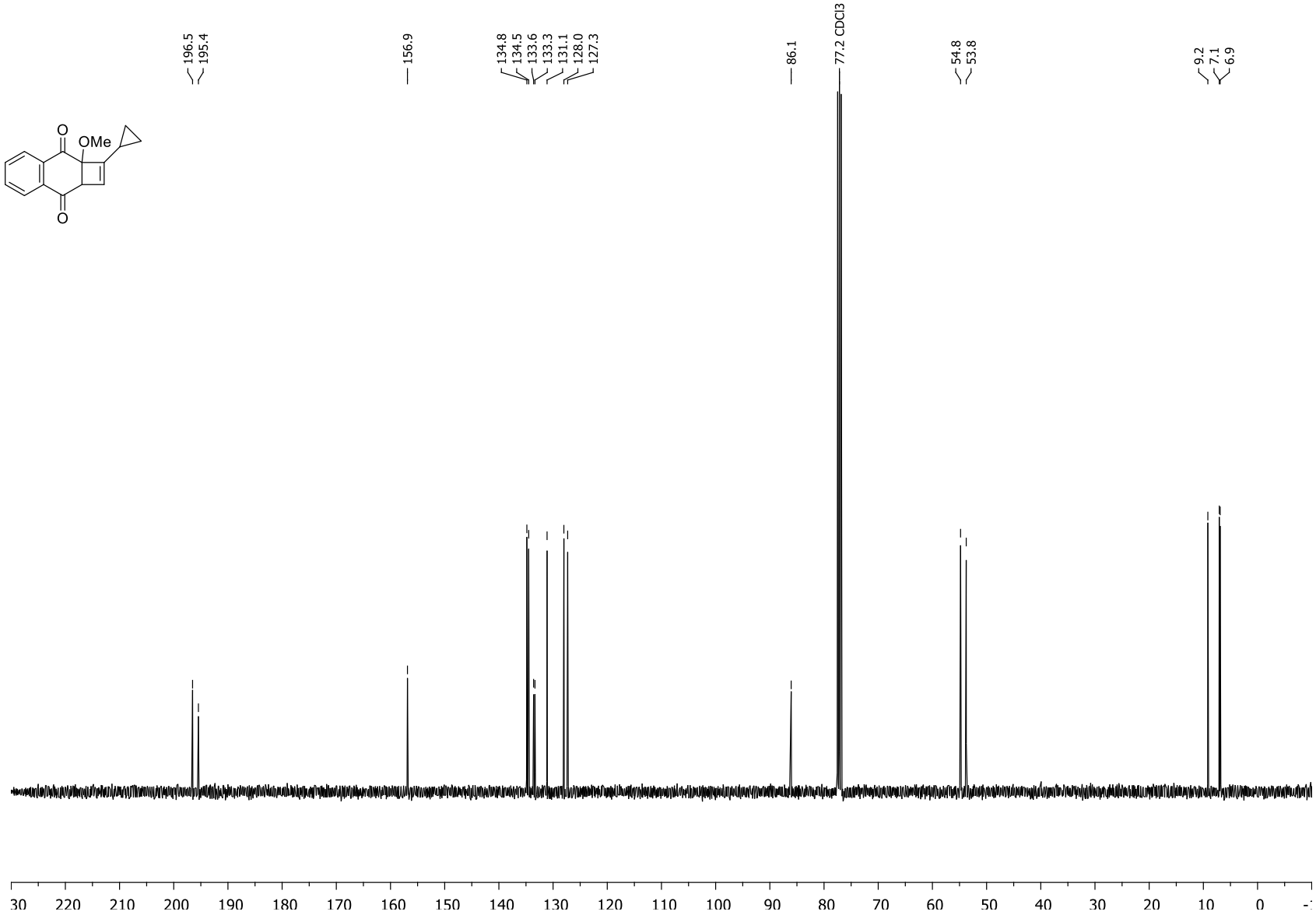


1-Cyclopropyl-8a-methoxy-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione (2k)

^{1}H NMR (400 MHz, $CDCl_3$)

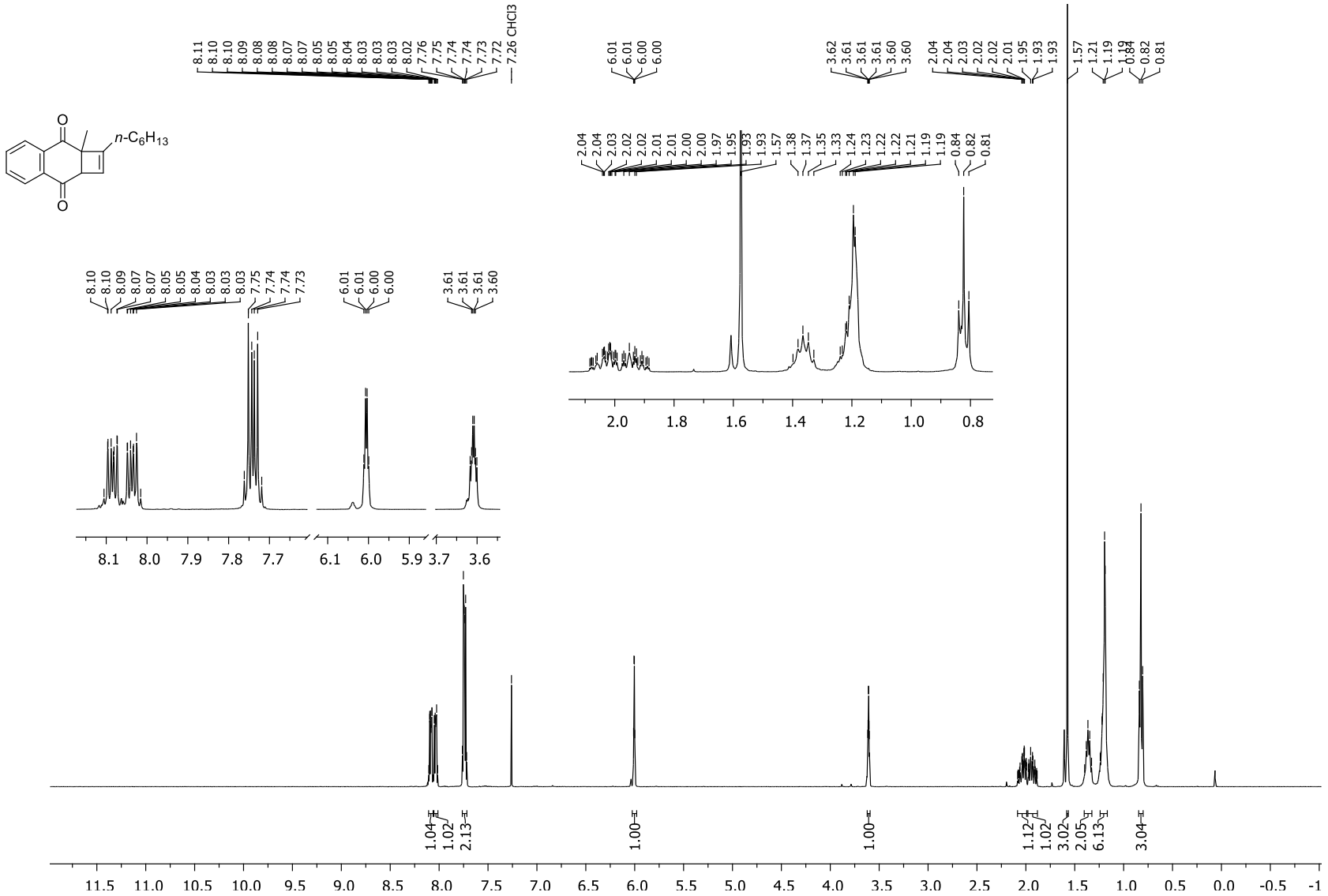


^{13}C NMR (101 MHz, $CDCl_3$)

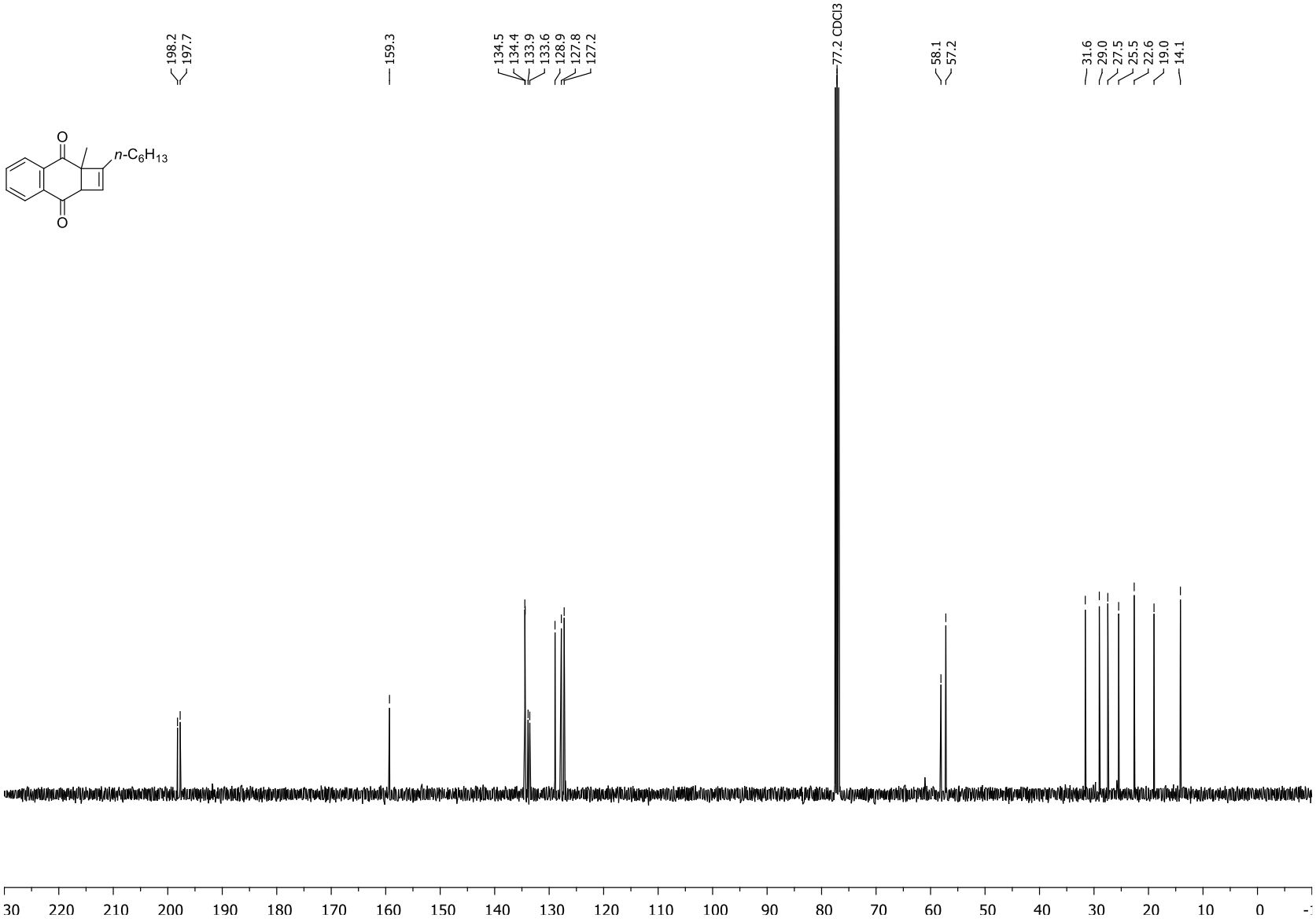


1-Hexyl-8a-methyl-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione (2l)

^{1}H NMR (400 MHz, $CDCl_3$)

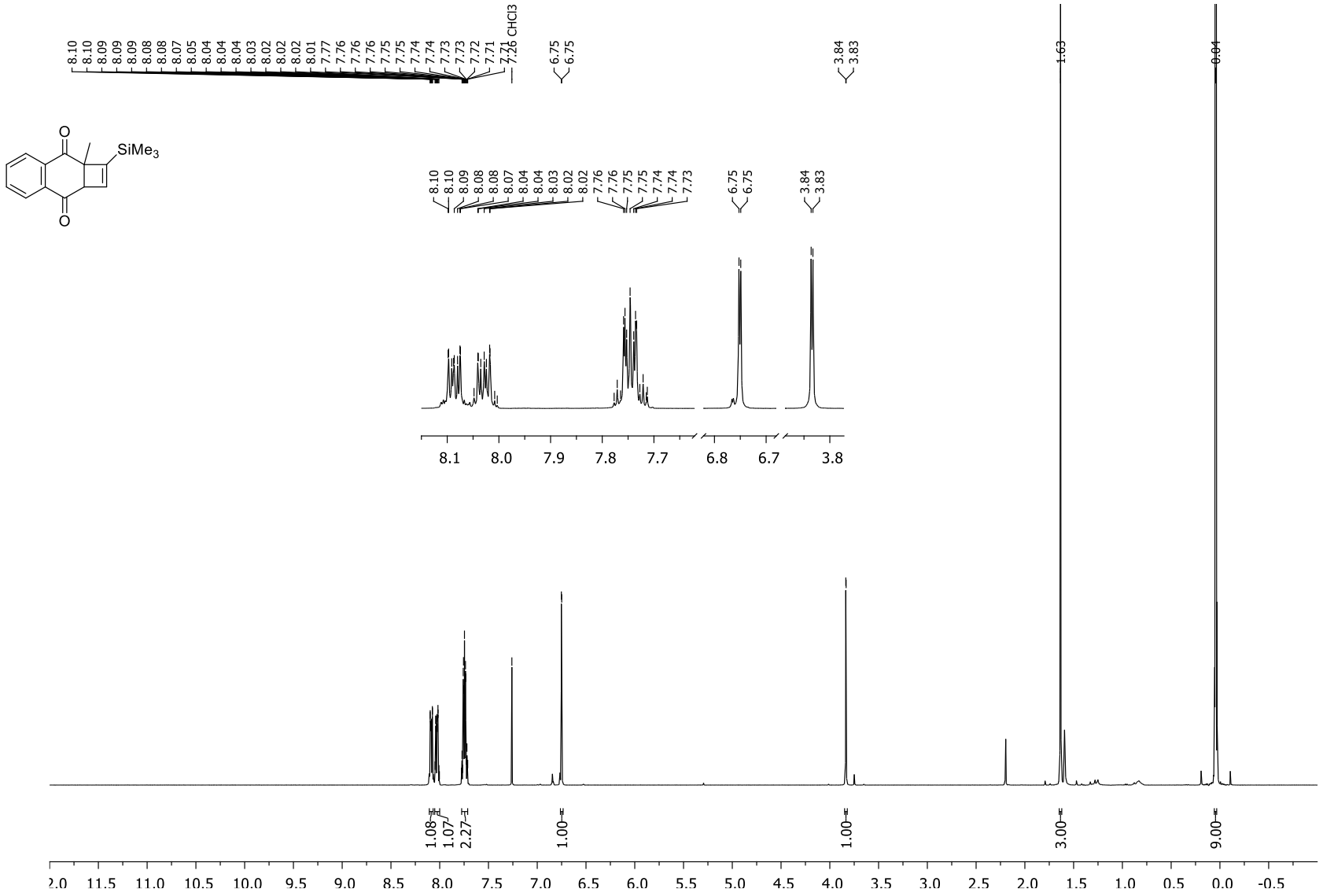


^{13}C NMR (101 MHz, $CDCl_3$)

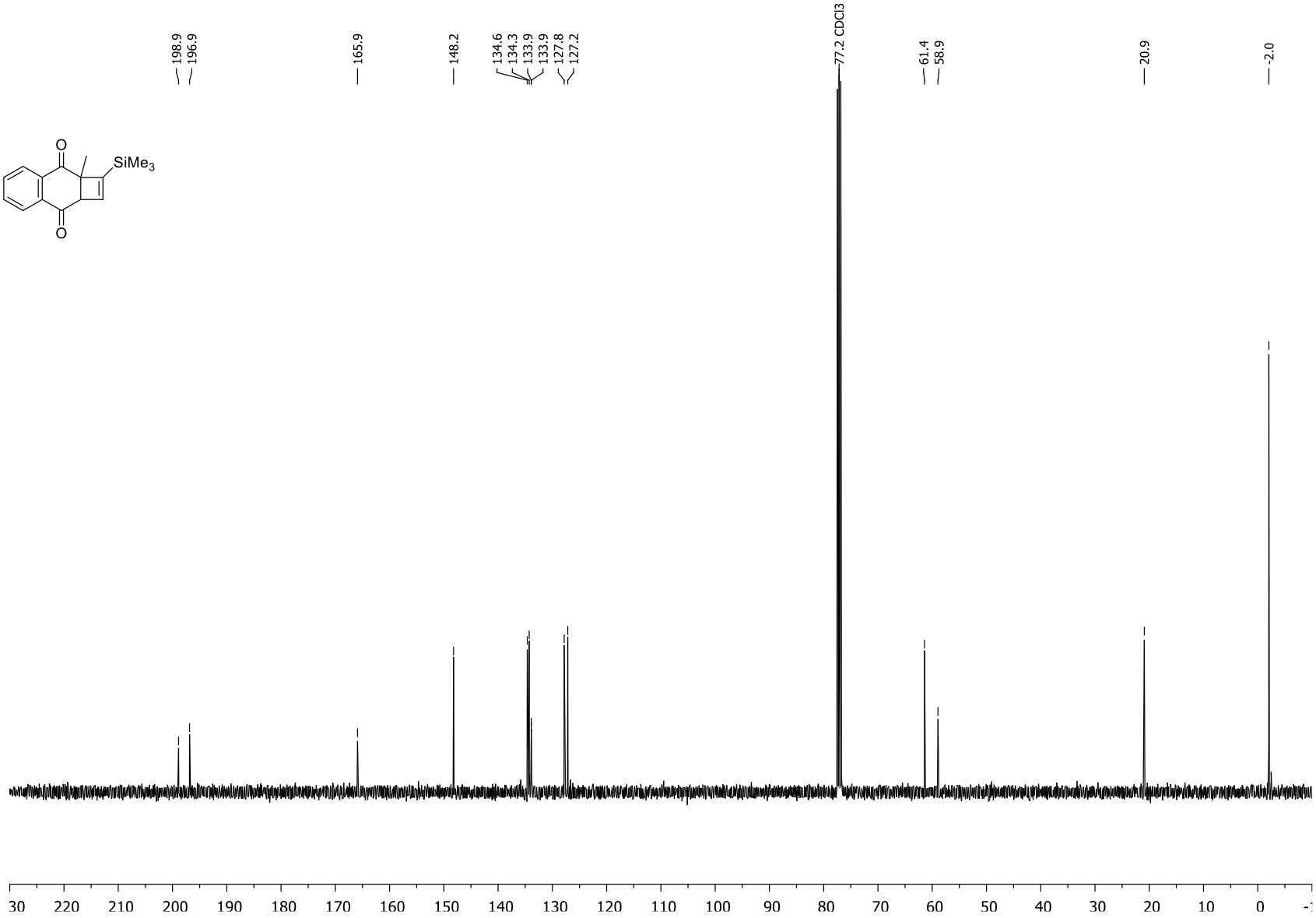


8a-Methyl-1-(trimethylsilyl)-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione (2m)

^{1}H NMR (400 MHz, $CDCl_3$)

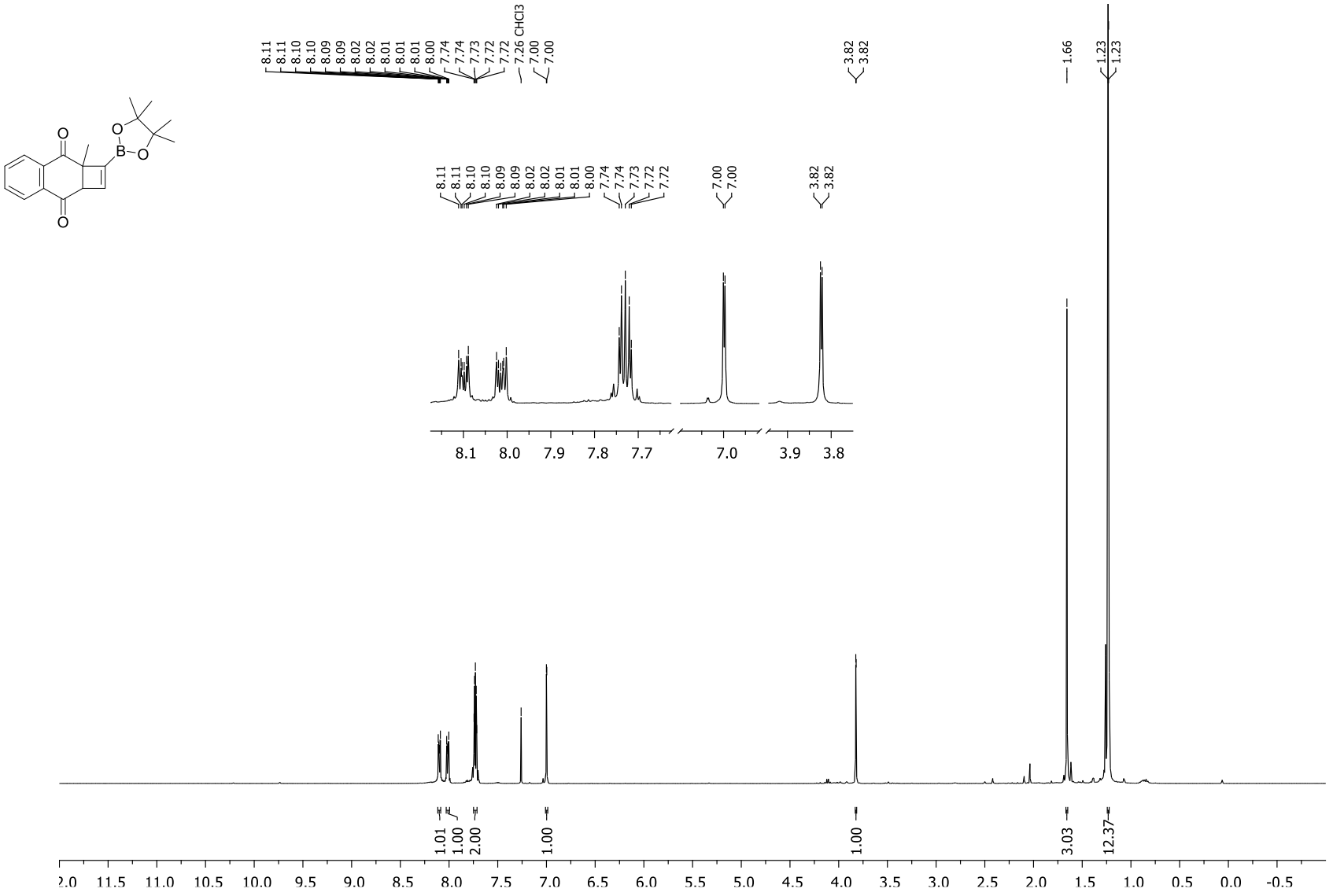


^{13}C NMR (101 MHz, $CDCl_3$)

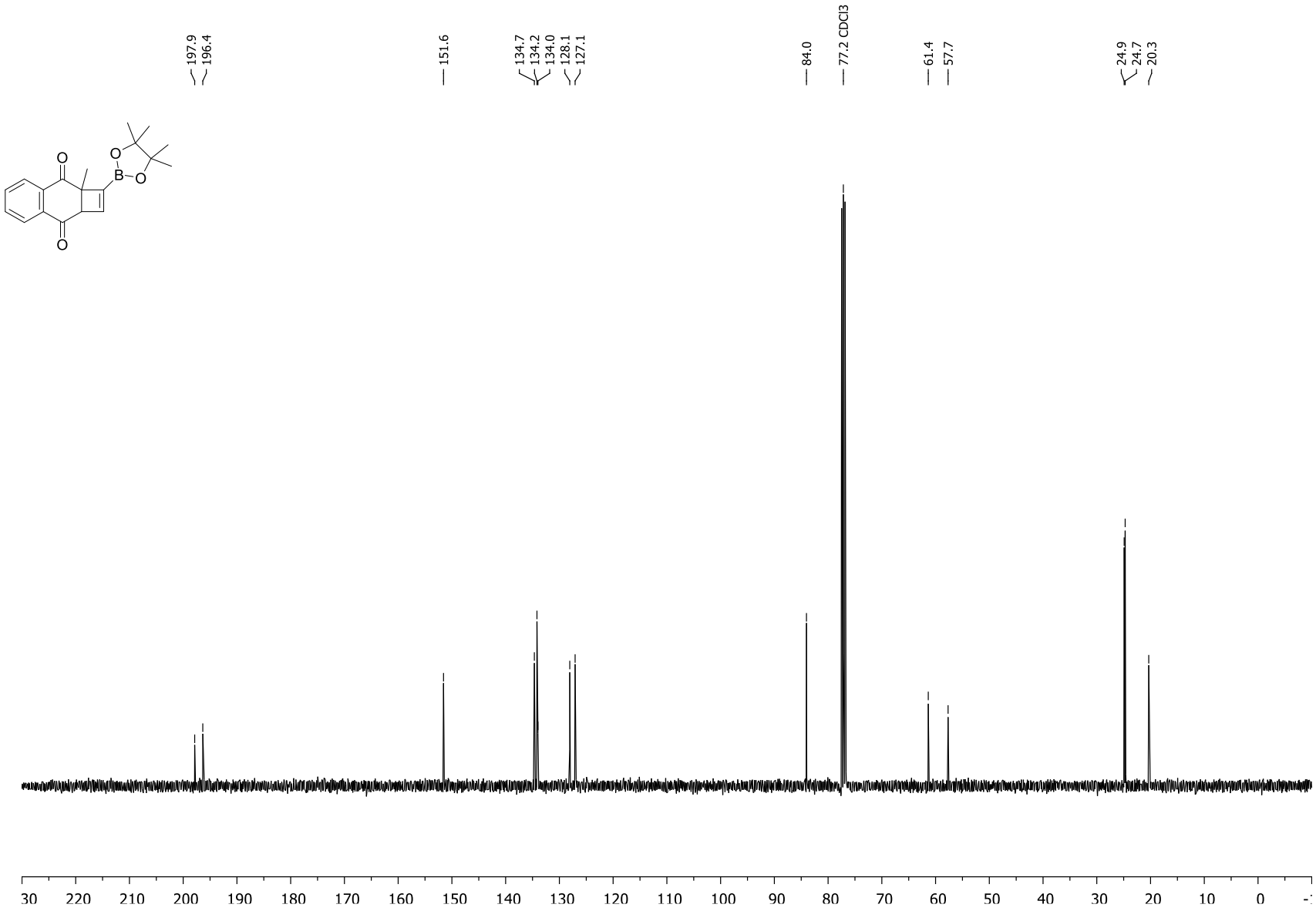


8a-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2a,8a-dihydrocyclobuta[*b*]naphthalene-3,8-dione (2n)

^{1}H NMR (400 MHz, $CDCl_3$)

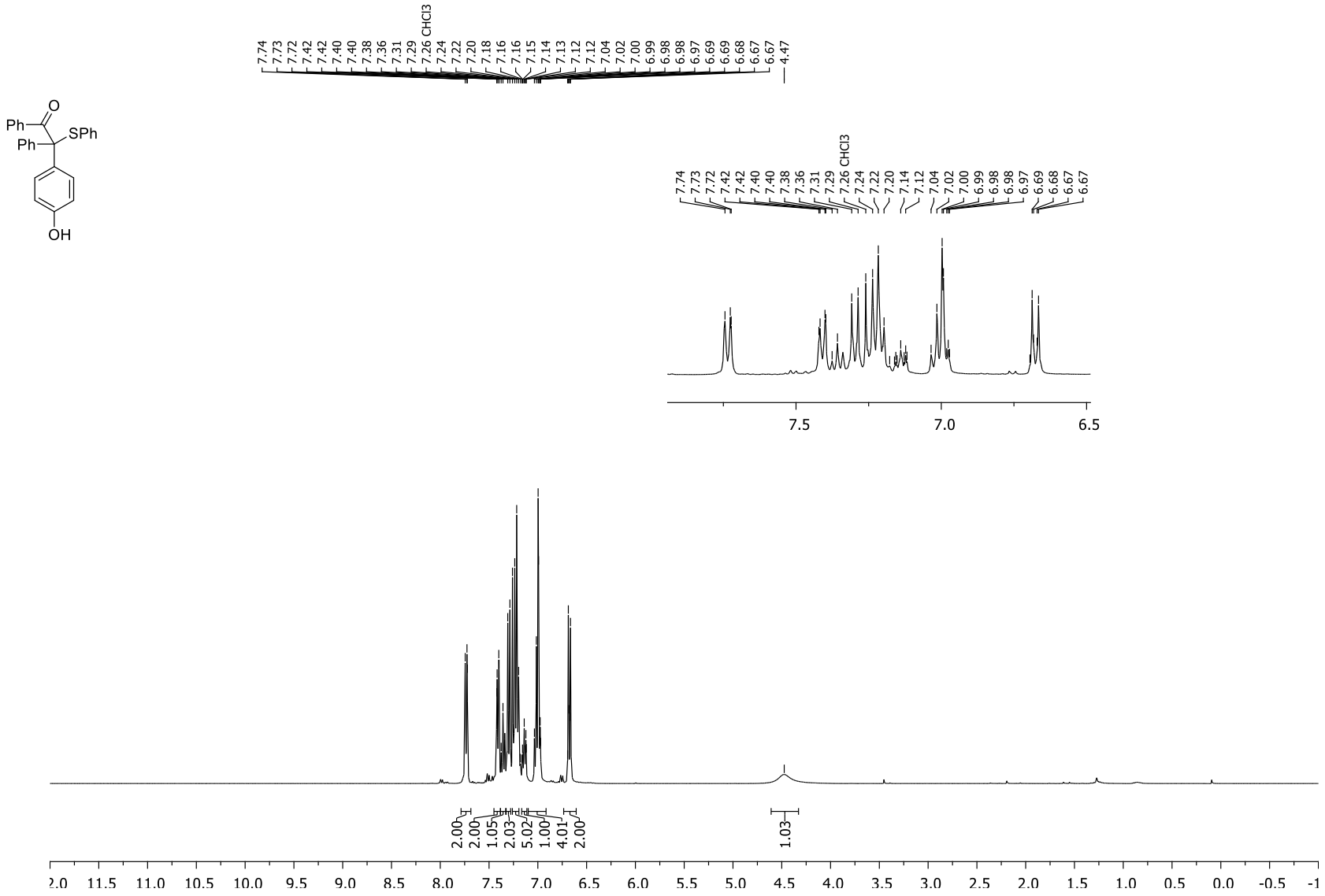


^{13}C NMR (101 MHz, $CDCl_3$)

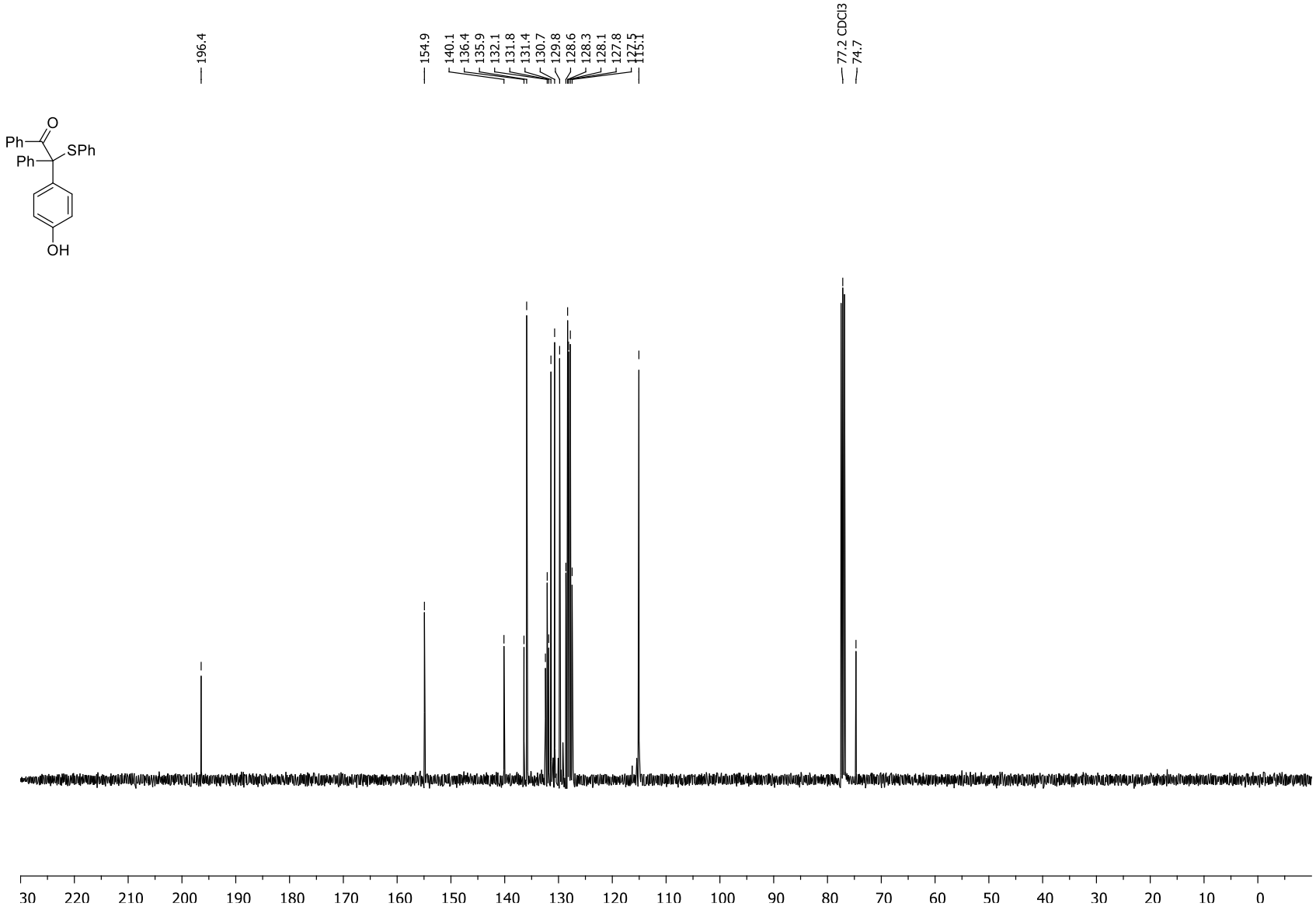


2-(4-Hydroxyphenyl)-1,2-diphenyl-2-(phenylthio)ethan-1-one (3a)

^{1}H NMR (400 MHz, $CDCl_3$)

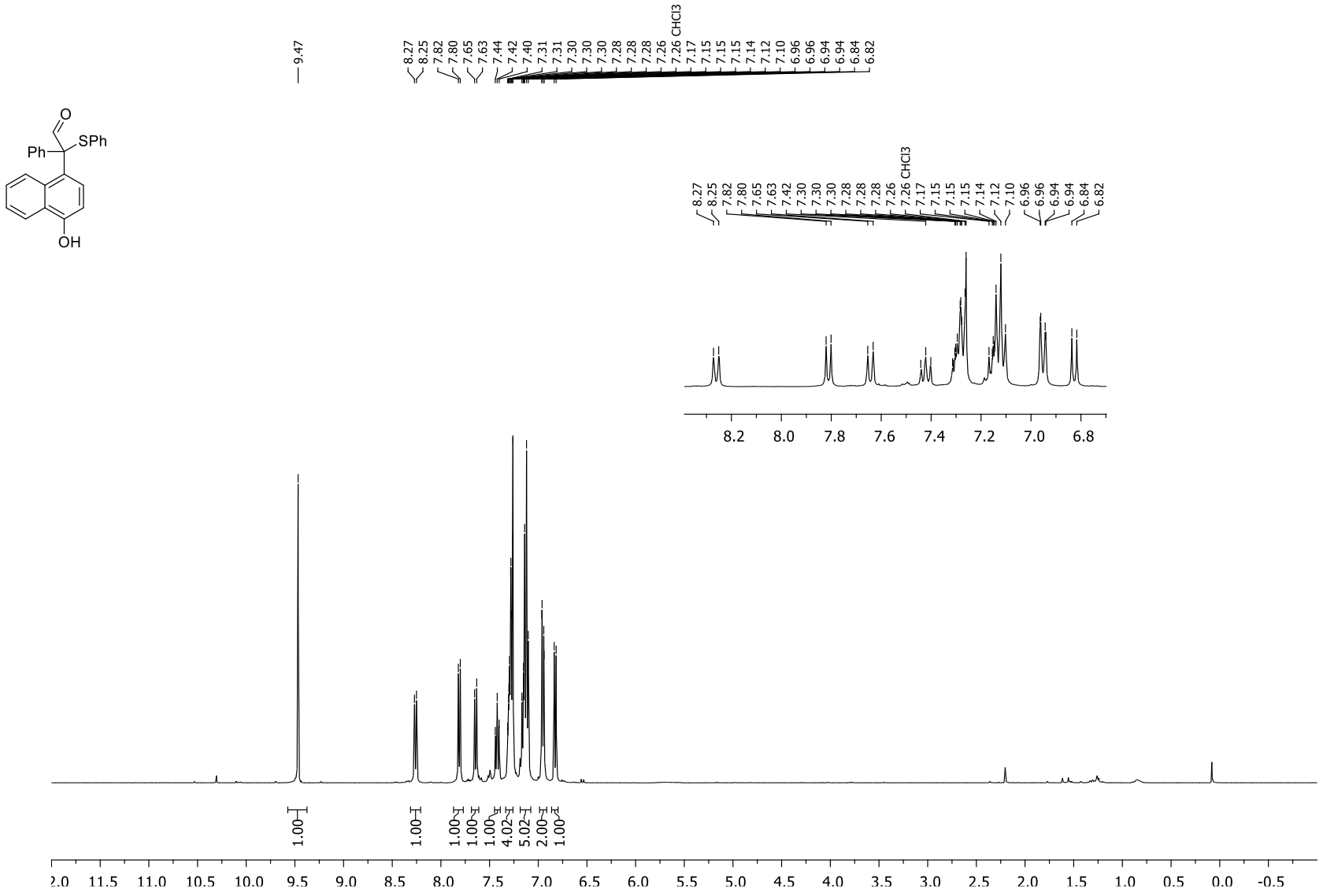


^{13}C NMR (101 MHz, $CDCl_3$)

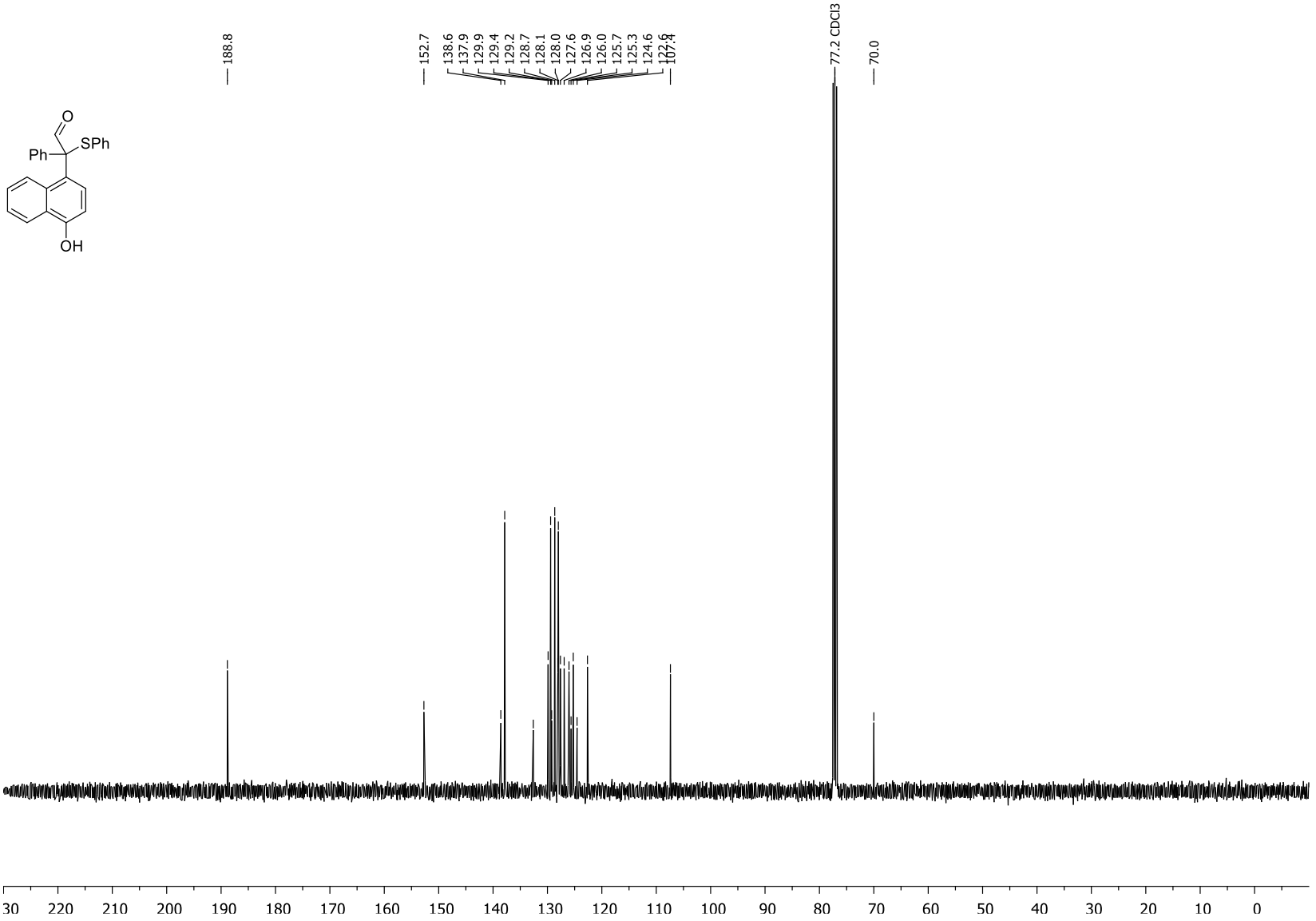


2-(4-Hydroxynaphthalen-1-yl)-2-phenyl-2-(phenylthio)acetaldehyde (3b)

^{1}H NMR (400 MHz, $CDCl_3$)

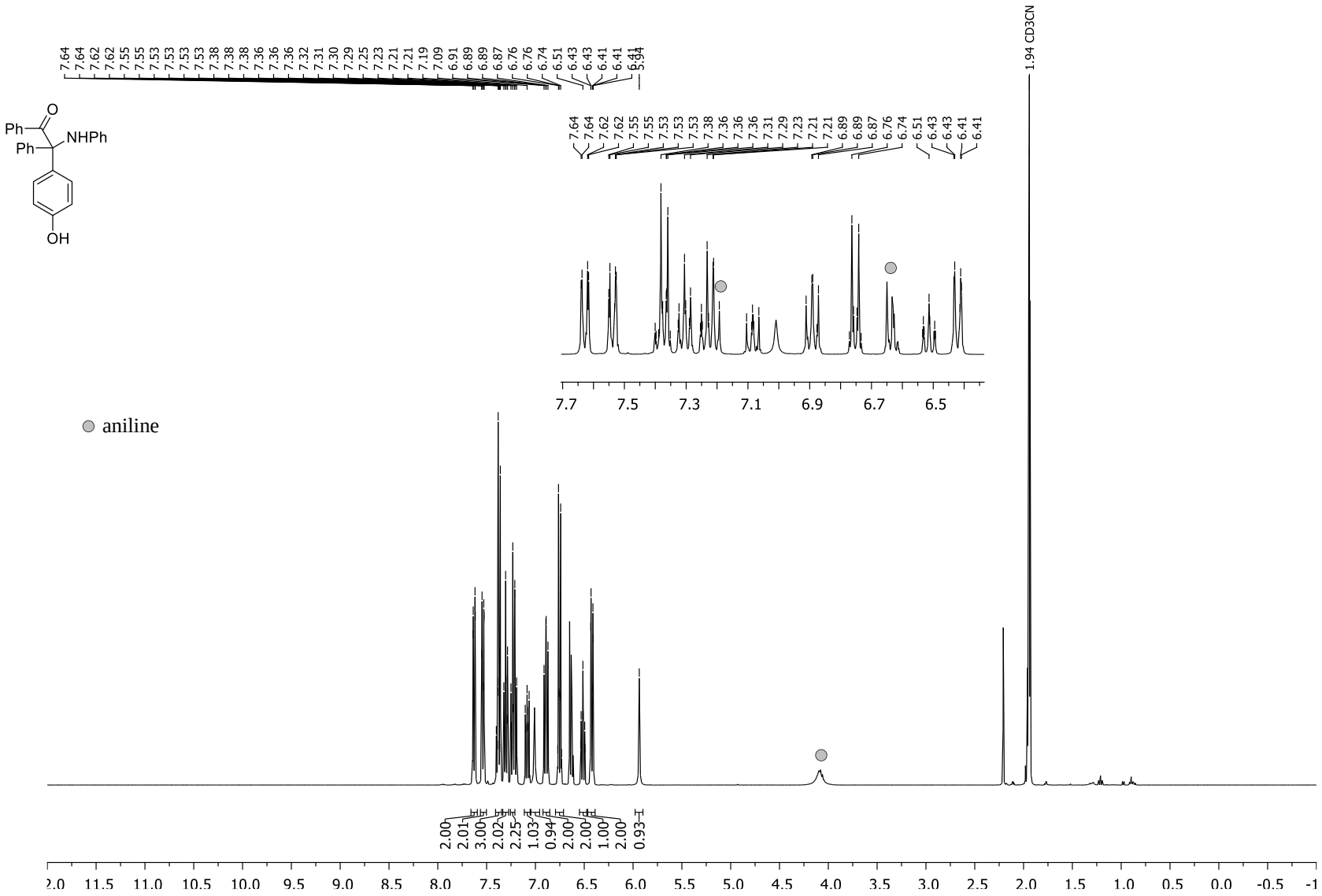


^{13}C NMR (101 MHz, $CDCl_3$)

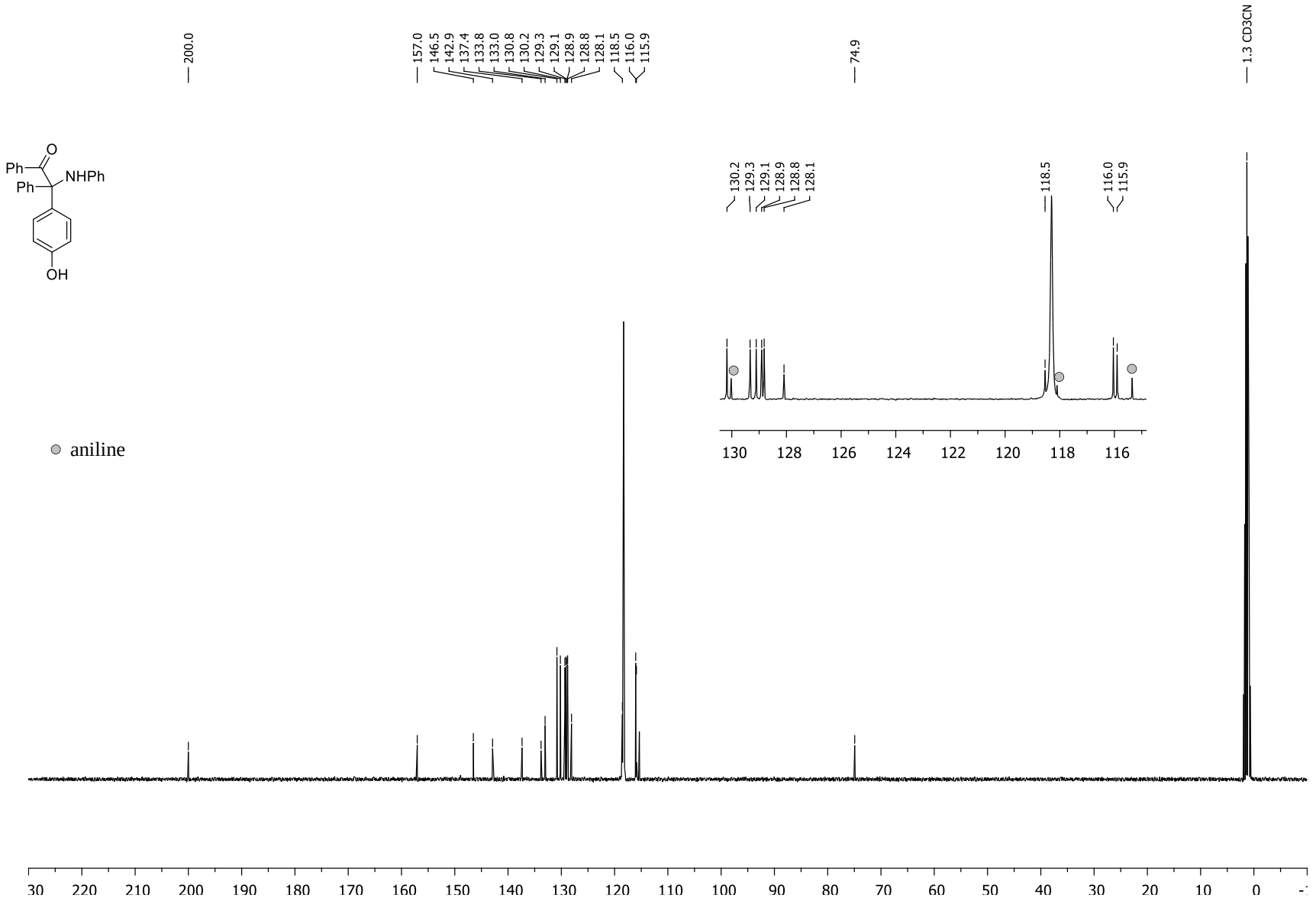


2-(4-Hydroxyphenyl)-1,2-diphenyl-2-(phenylamino)ethan-1-one (3c)

^{1}H NMR (400 MHz, CD_3CN)

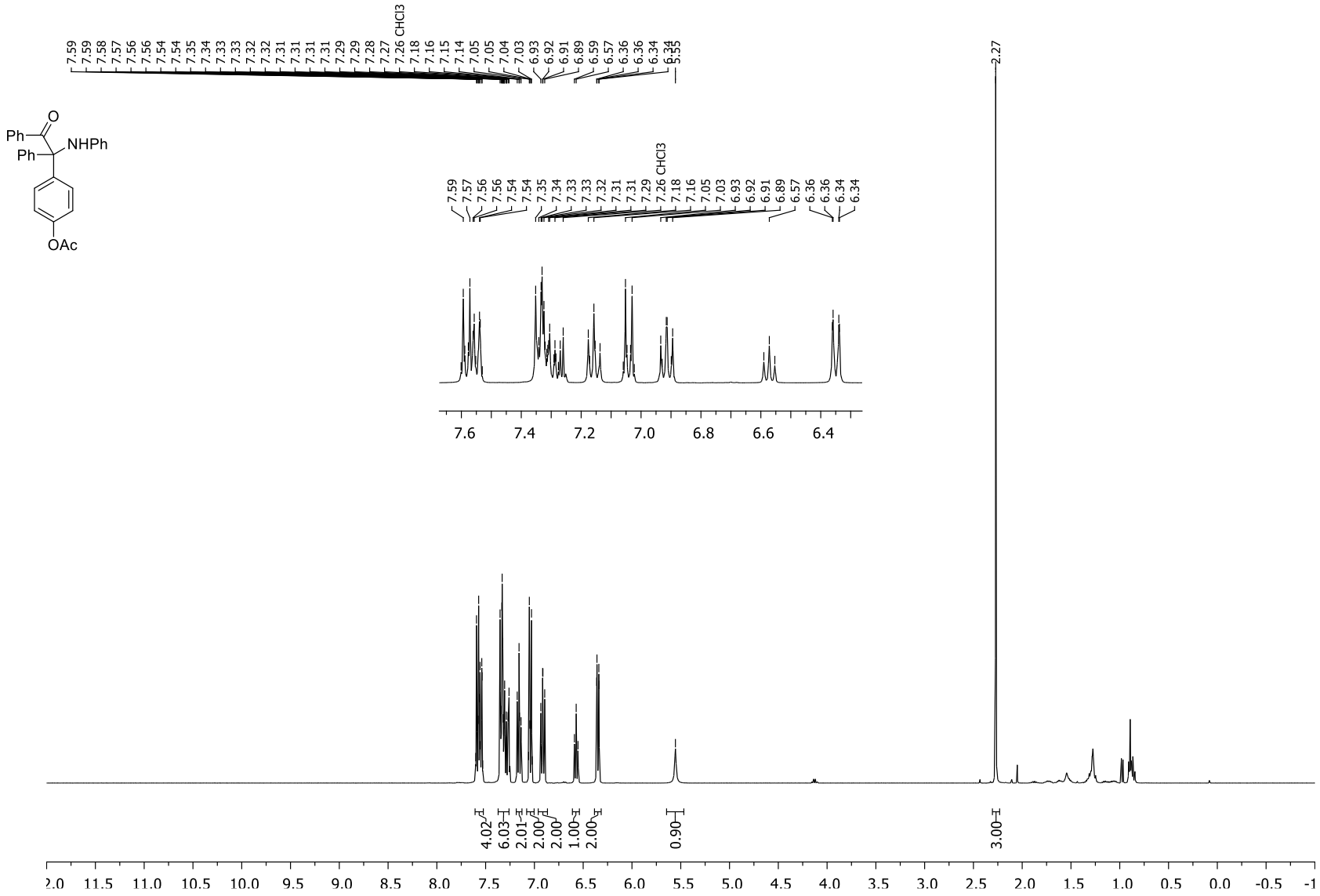


^{13}C NMR (101 MHz, CD_3CN)

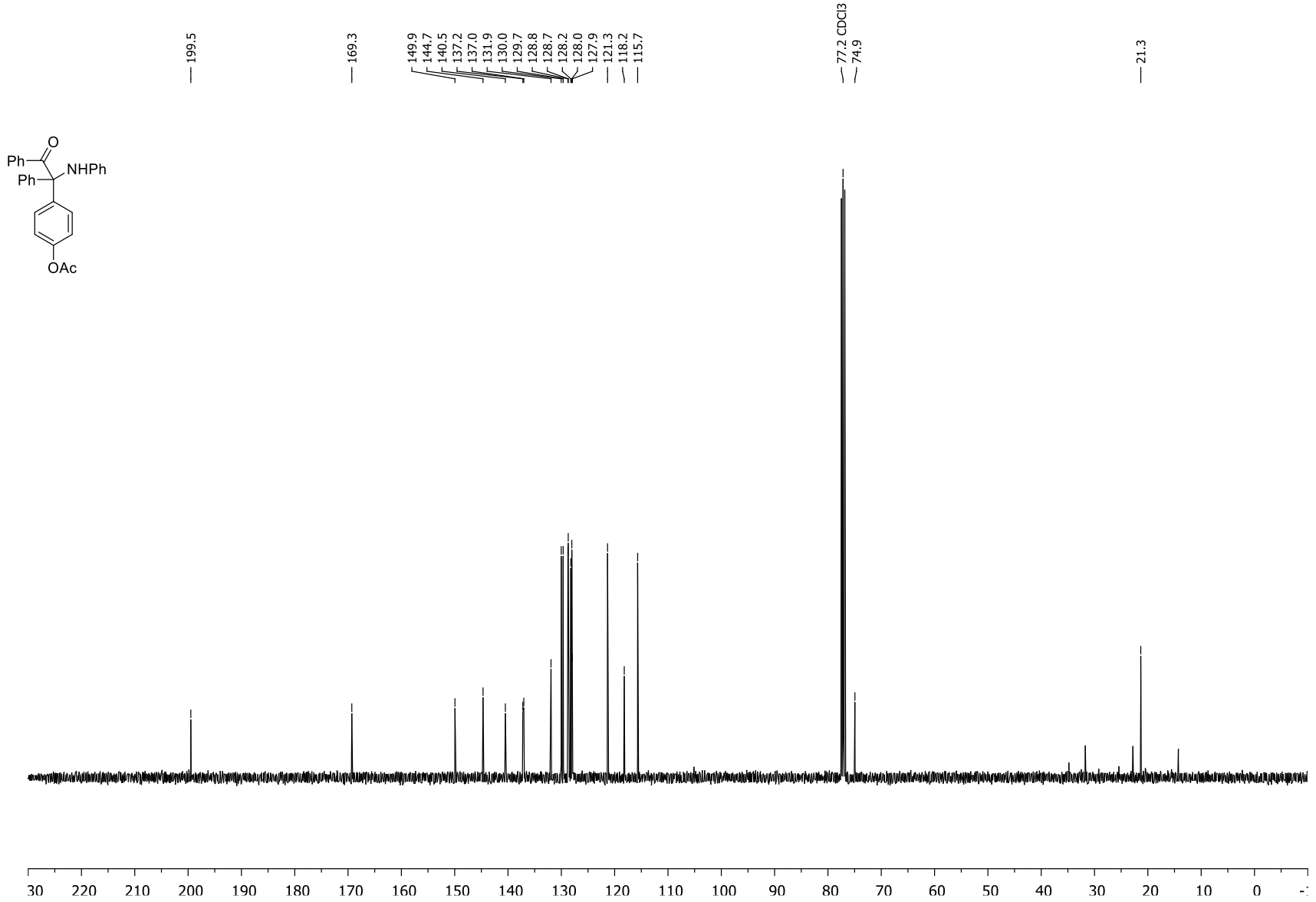


4-(2-Oxo-1,2-diphenyl-1-(phenylamino)ethyl)phenyl acetate (3c')

^{1}H NMR (400 MHz, $CDCl_3$)

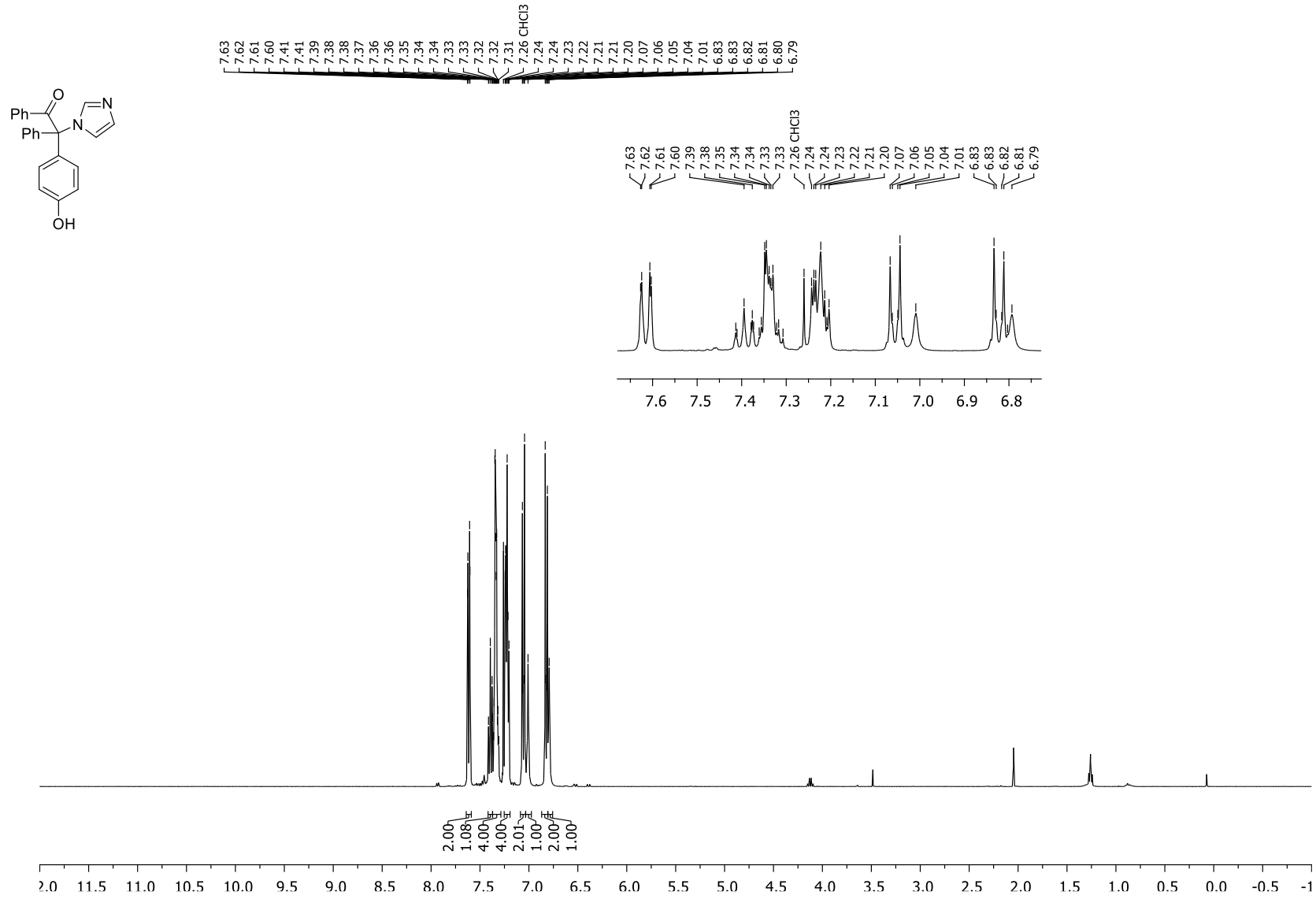


^{13}C NMR (101 MHz, $CDCl_3$)

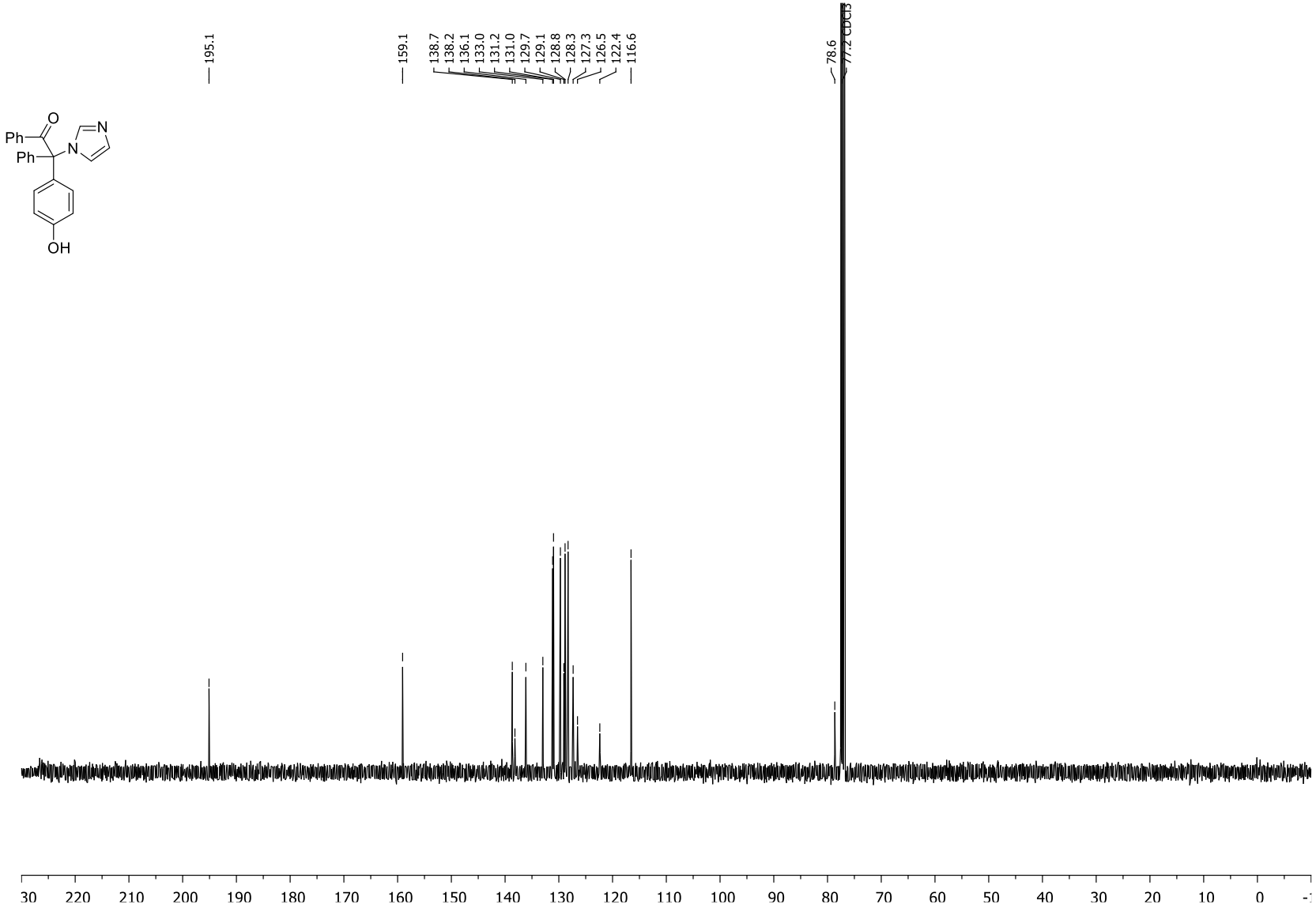


2-(4-Hydroxyphenyl)-2-(1*H*-imidazol-1-yl)-1,2-diphenylethan-1-one (3d)

^{1}H NMR (400 MHz, $CDCl_3$)

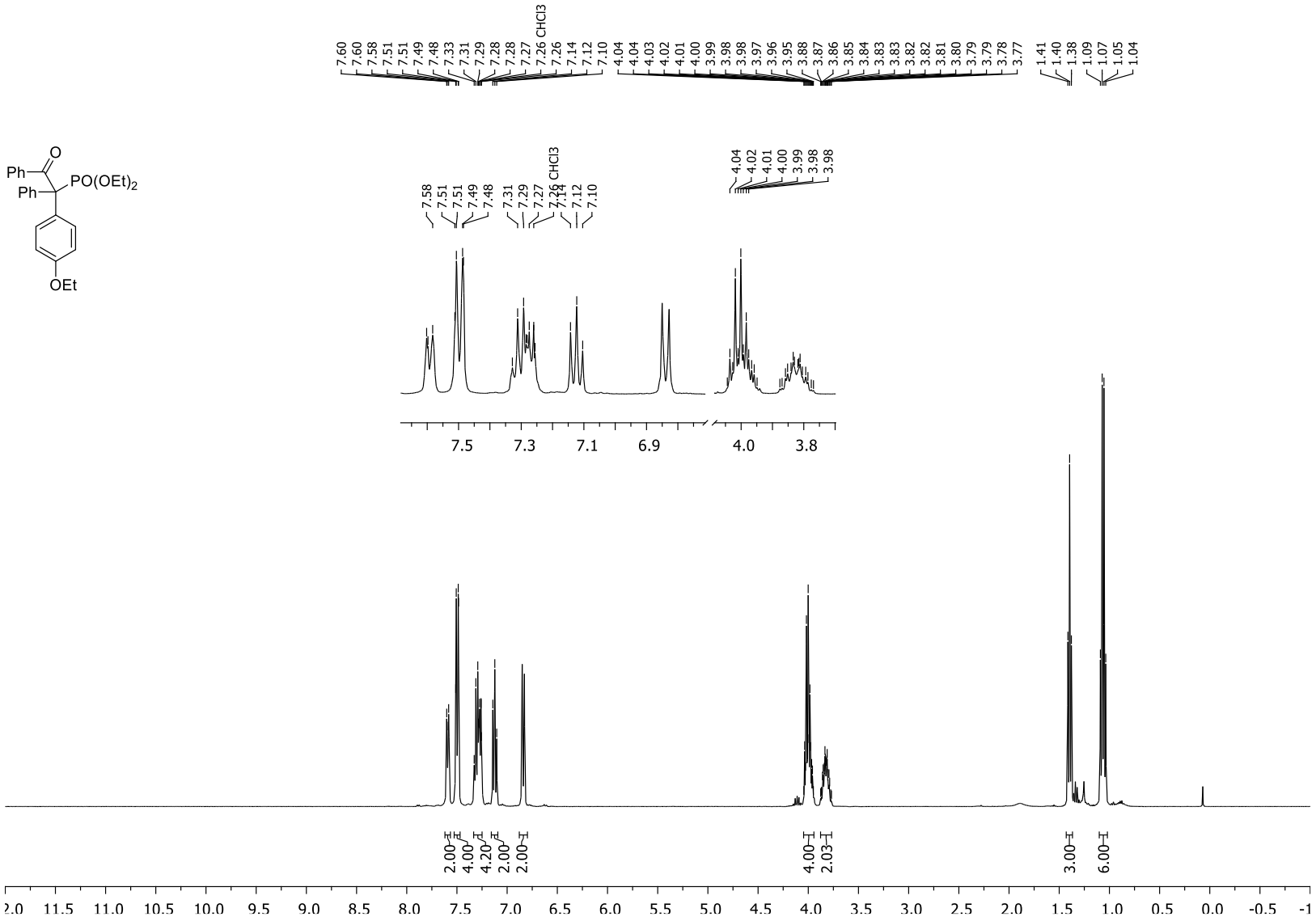


^{13}C NMR (101 MHz, $CDCl_3$)

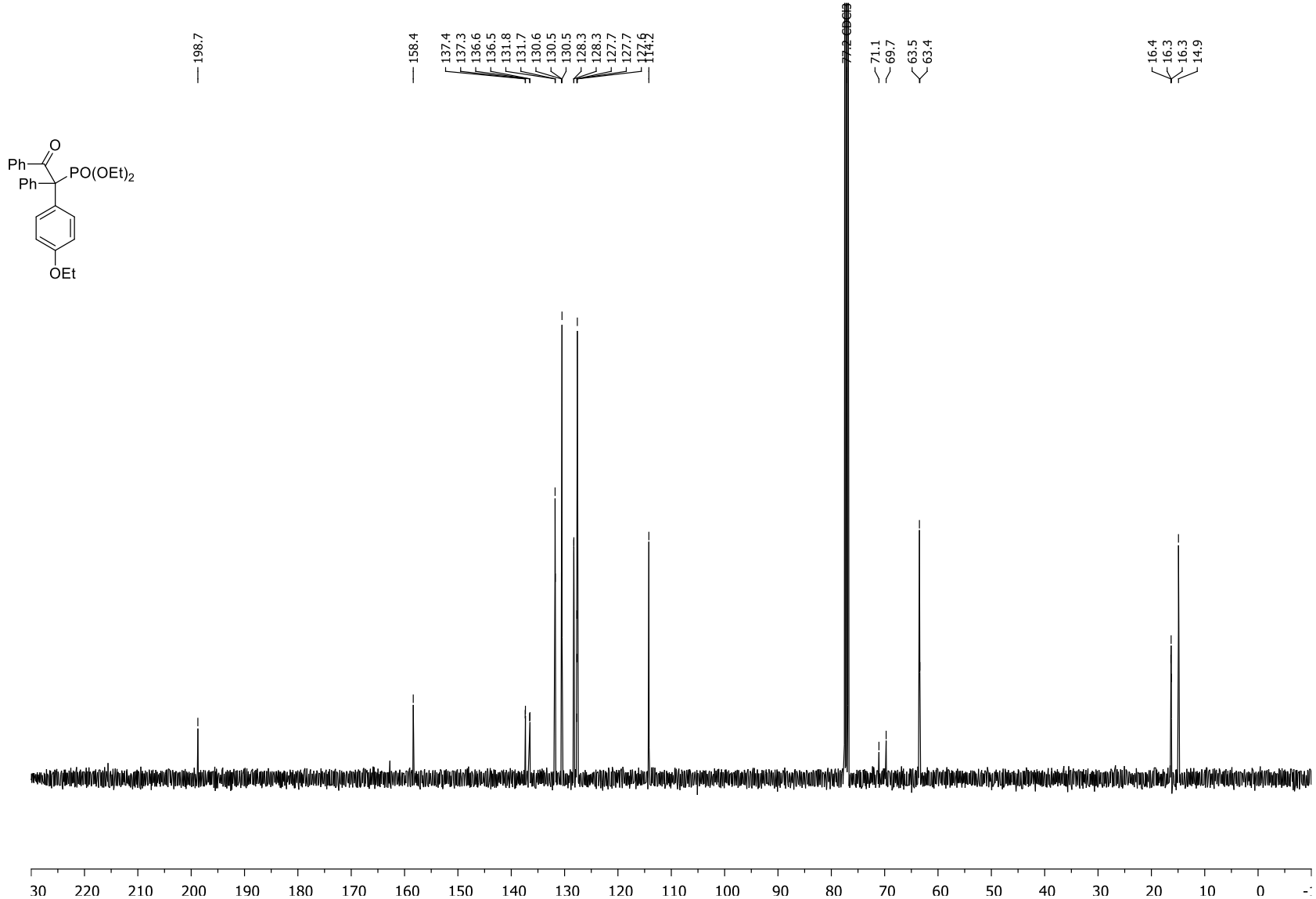


Diethyl (1-(4-ethoxyphenyl)-2-oxo-1,2-diphenylethyl)phosphonate (3e)

^{1}H NMR (400 MHz, $CDCl_3$)

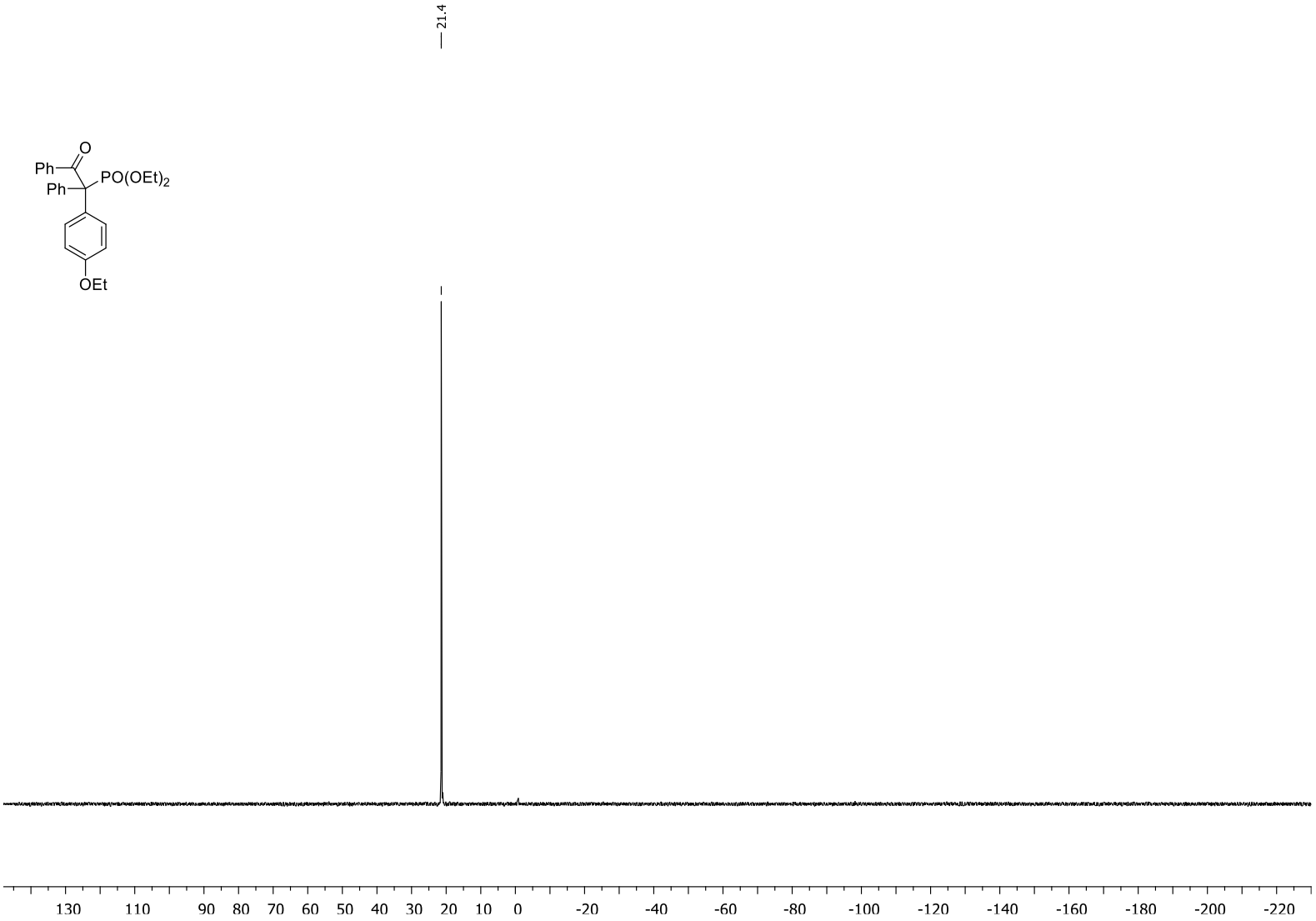


^{13}C NMR (101 MHz, $CDCl_3$)



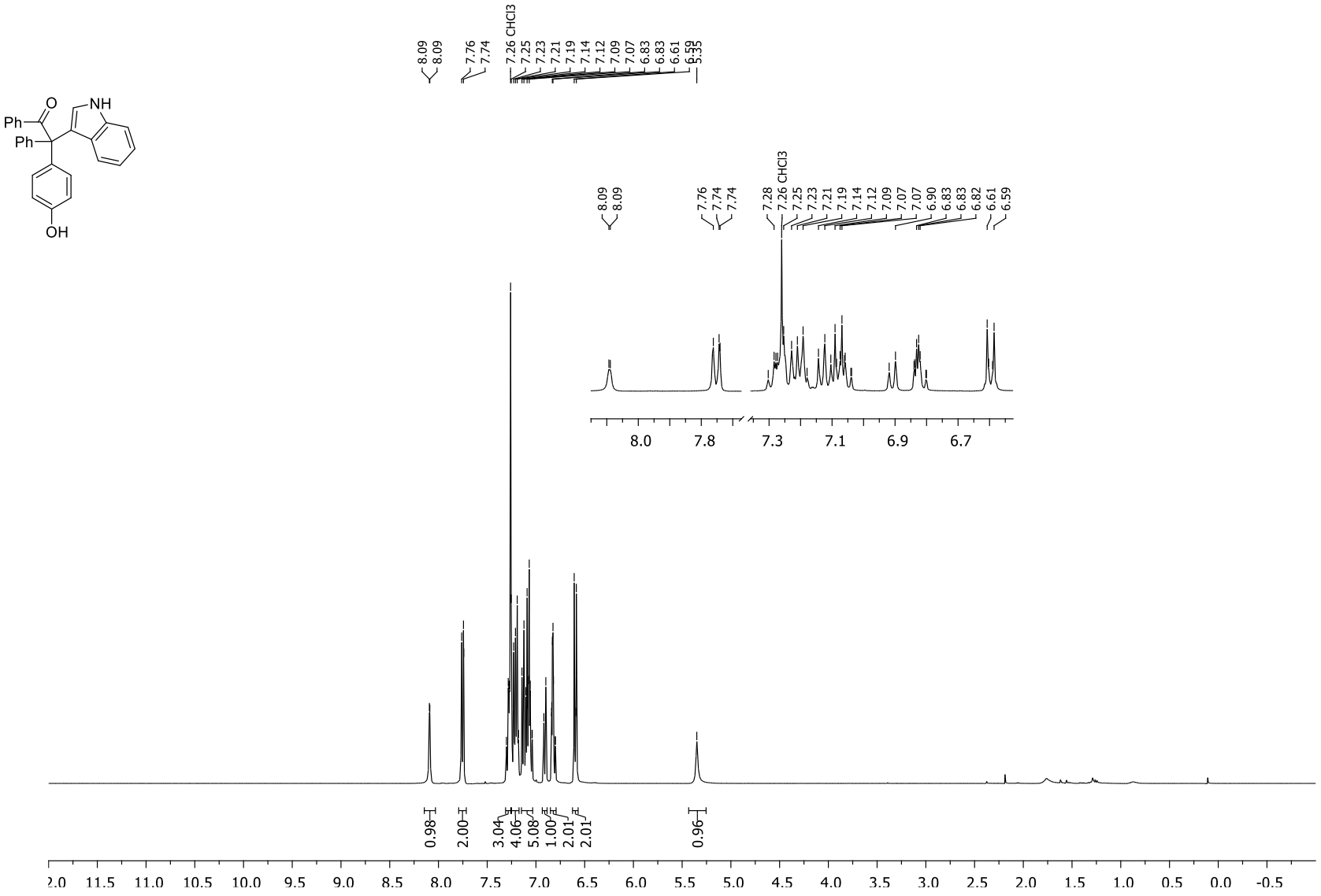
Diethyl (1-(4-ethoxyphenyl)-2-oxo-1,2-diphenylethyl)phosphonate (3e)

^{31}P NMR (162 MHz, $CDCl_3$)

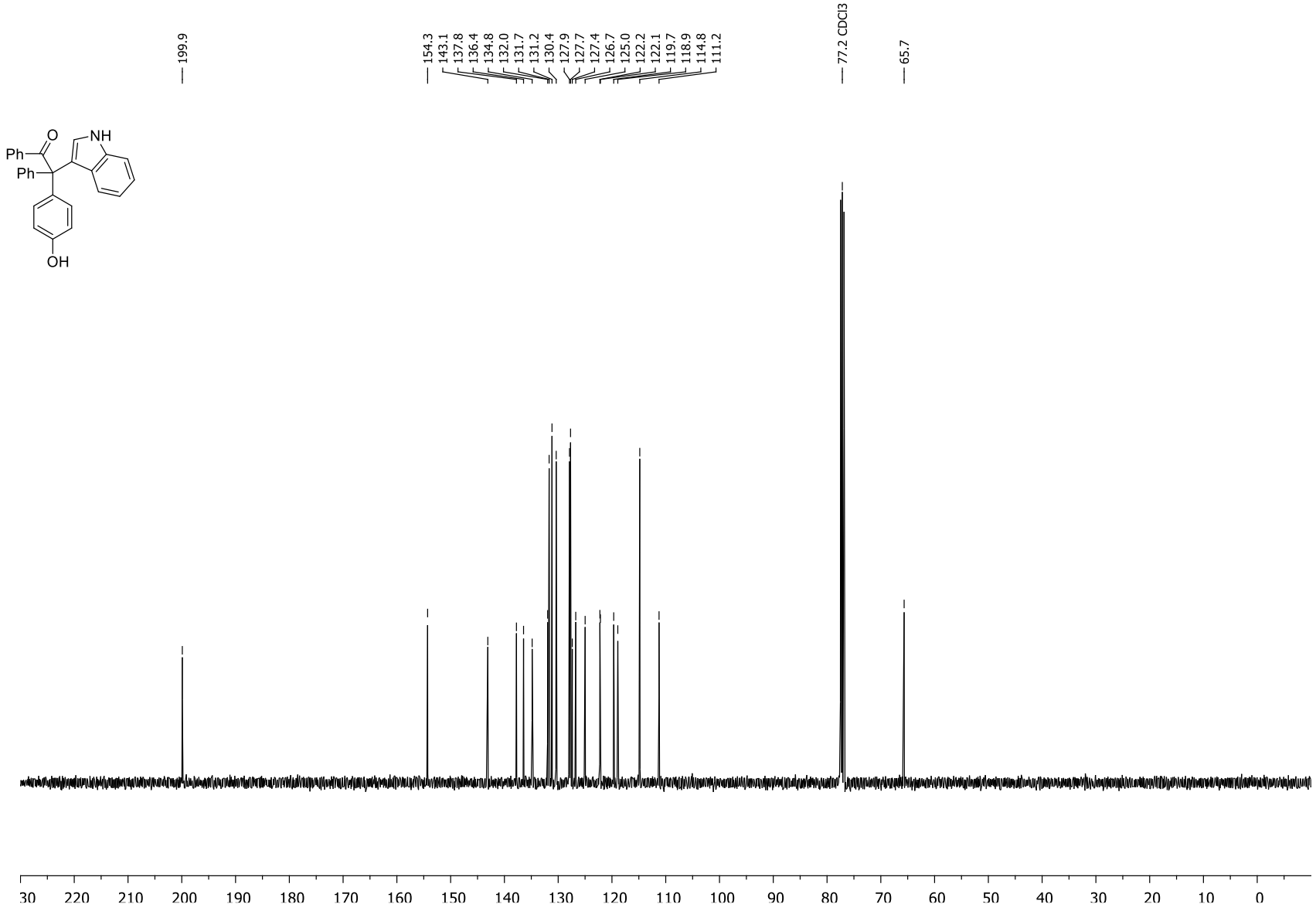


2-(4-Hydroxyphenyl)-2-(1*H*-indol-3-yl)-1,2-diphenylethan-1-one (3f)

^{1}H NMR (400 MHz, $CDCl_3$)

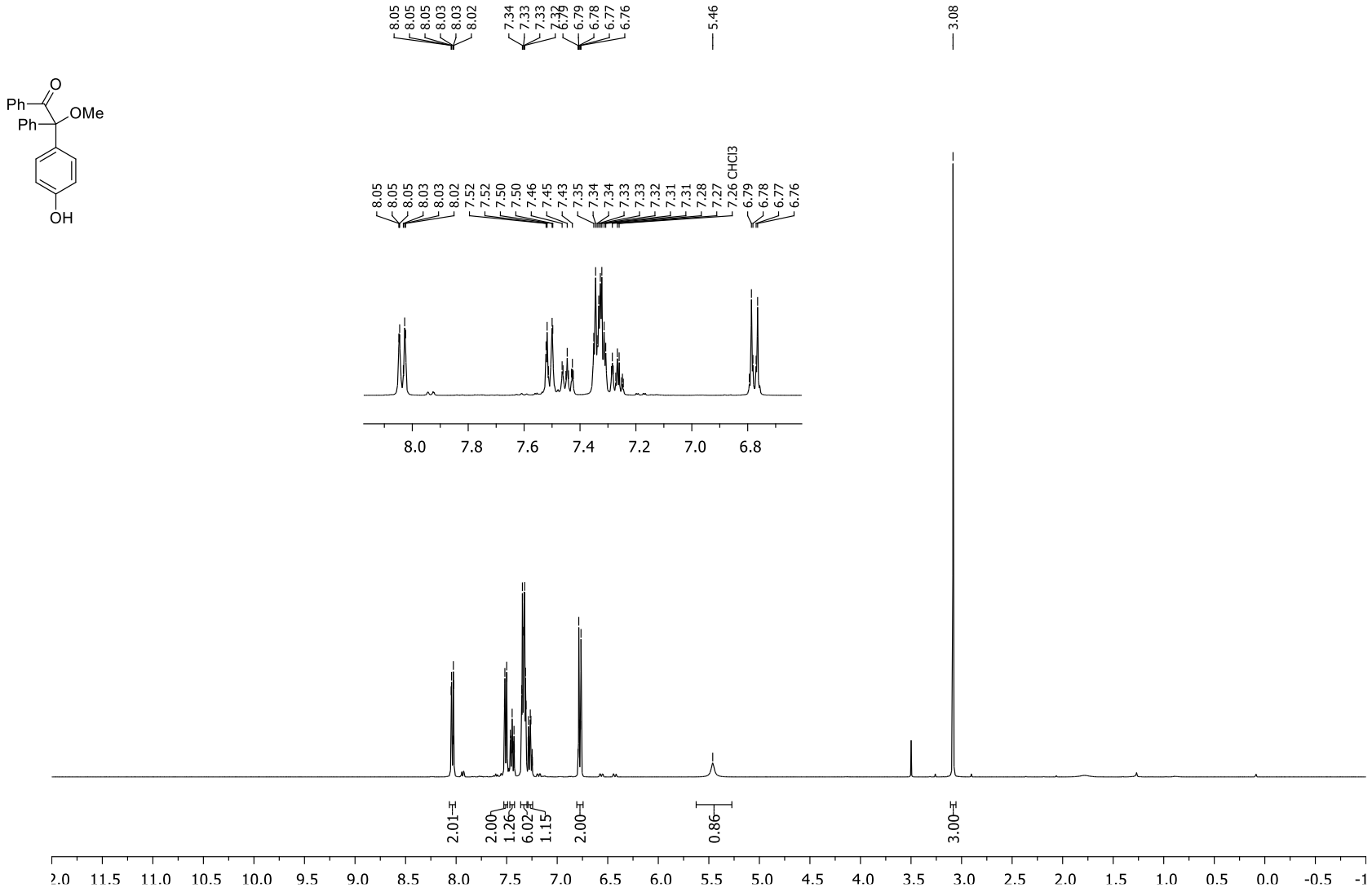


^{13}C NMR (101 MHz, $CDCl_3$)

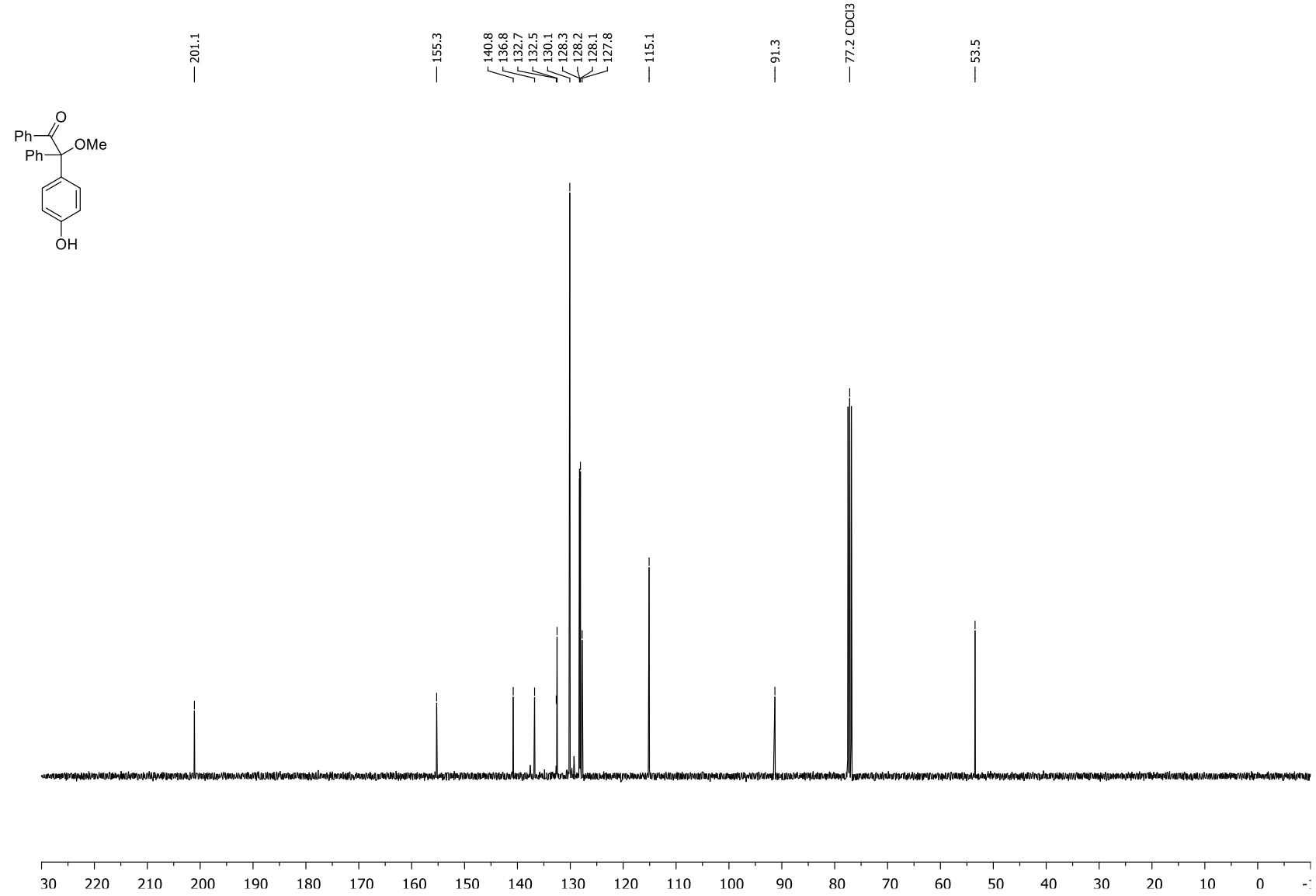


2-(4-Hydroxyphenyl)-2-methoxy-1,2-diphenylethan-1-one (3g)

^{1}H NMR (400 MHz, $CDCl_3$)

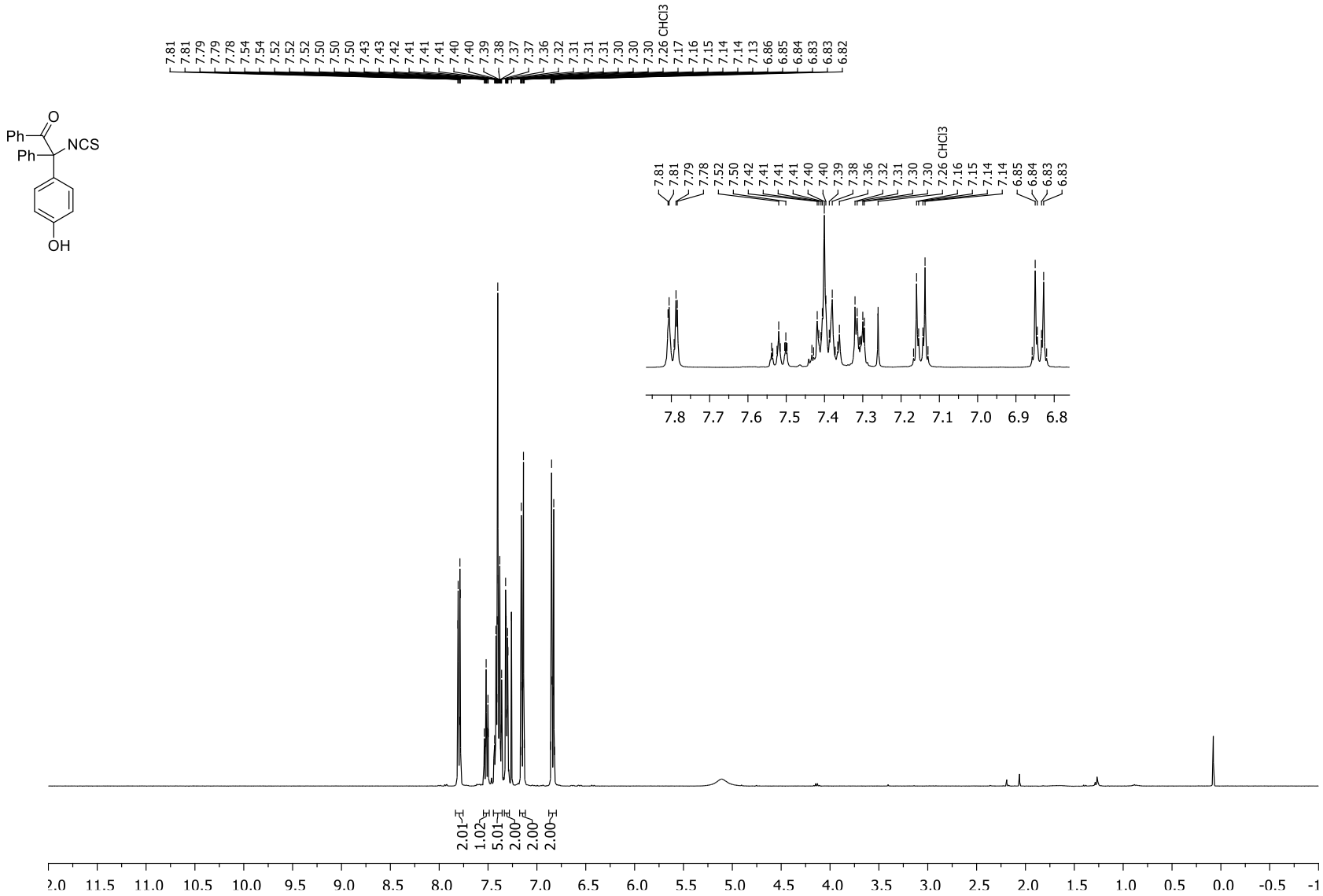


^{13}C NMR (101 MHz, $CDCl_3$)

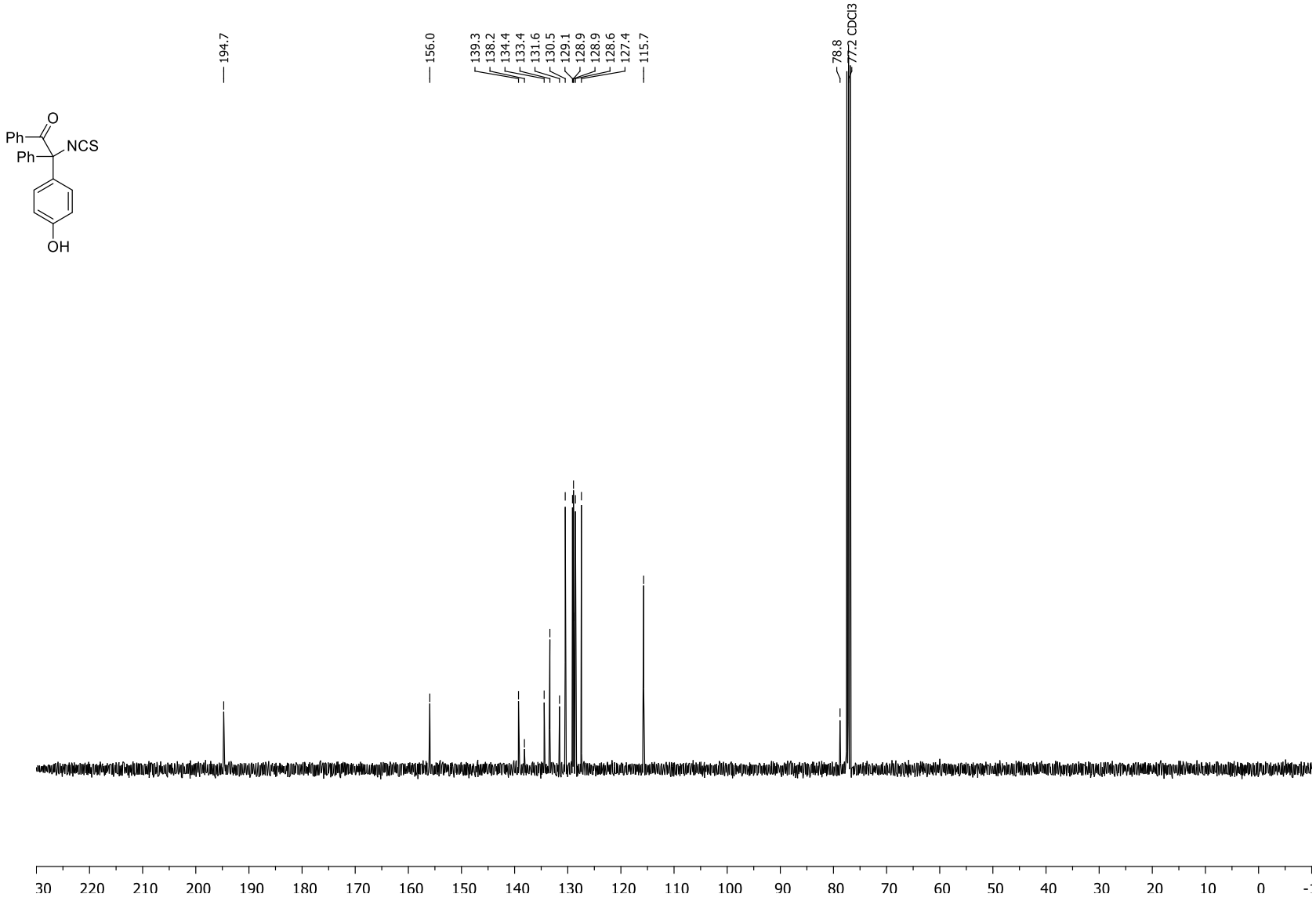


2-(4-Hydroxyphenyl)-2-isothiocyanato-1,2-diphenylethan-1-one (3h)

^{1}H NMR (400 MHz, $CDCl_3$)

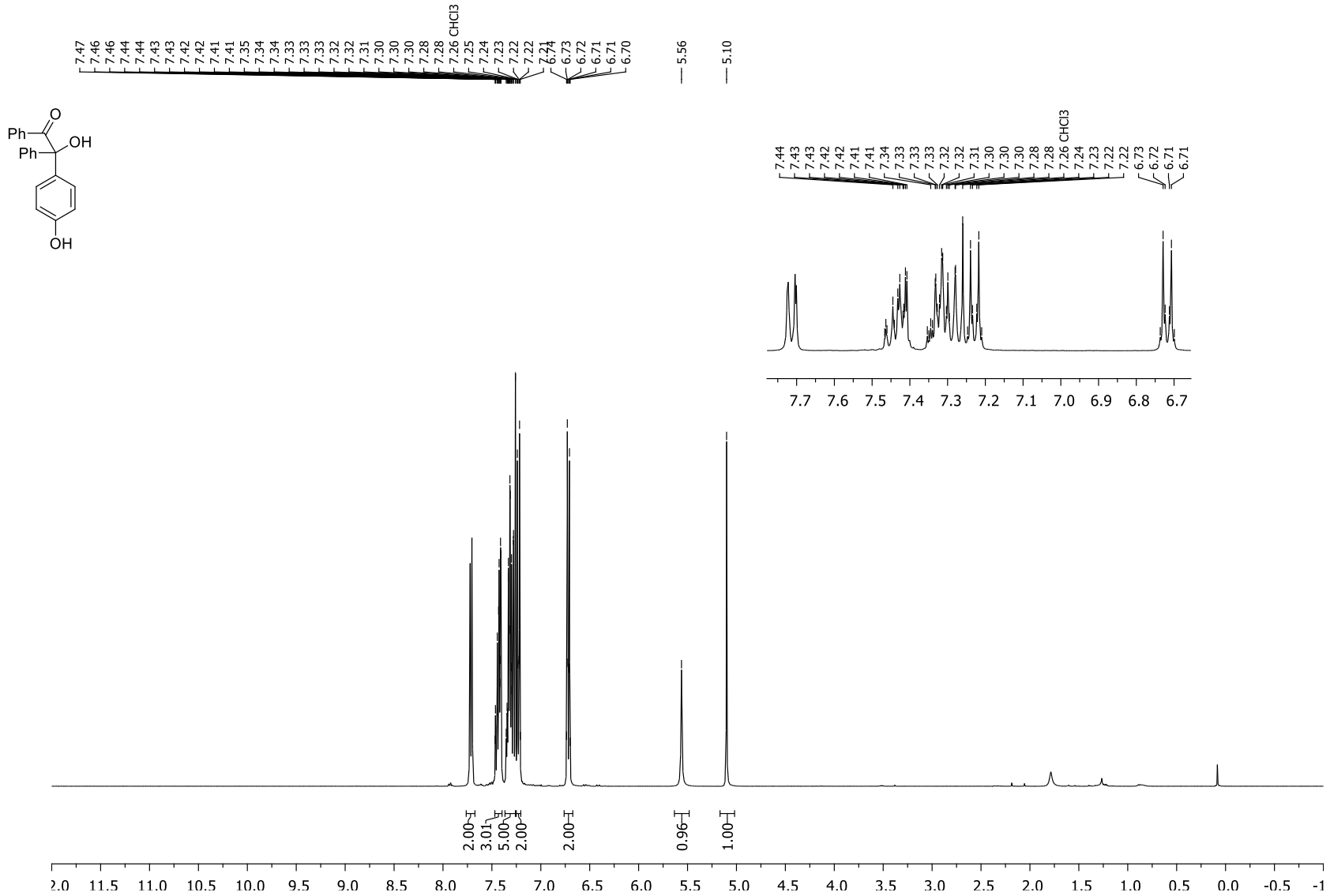


^{13}C NMR (101 MHz, $CDCl_3$)

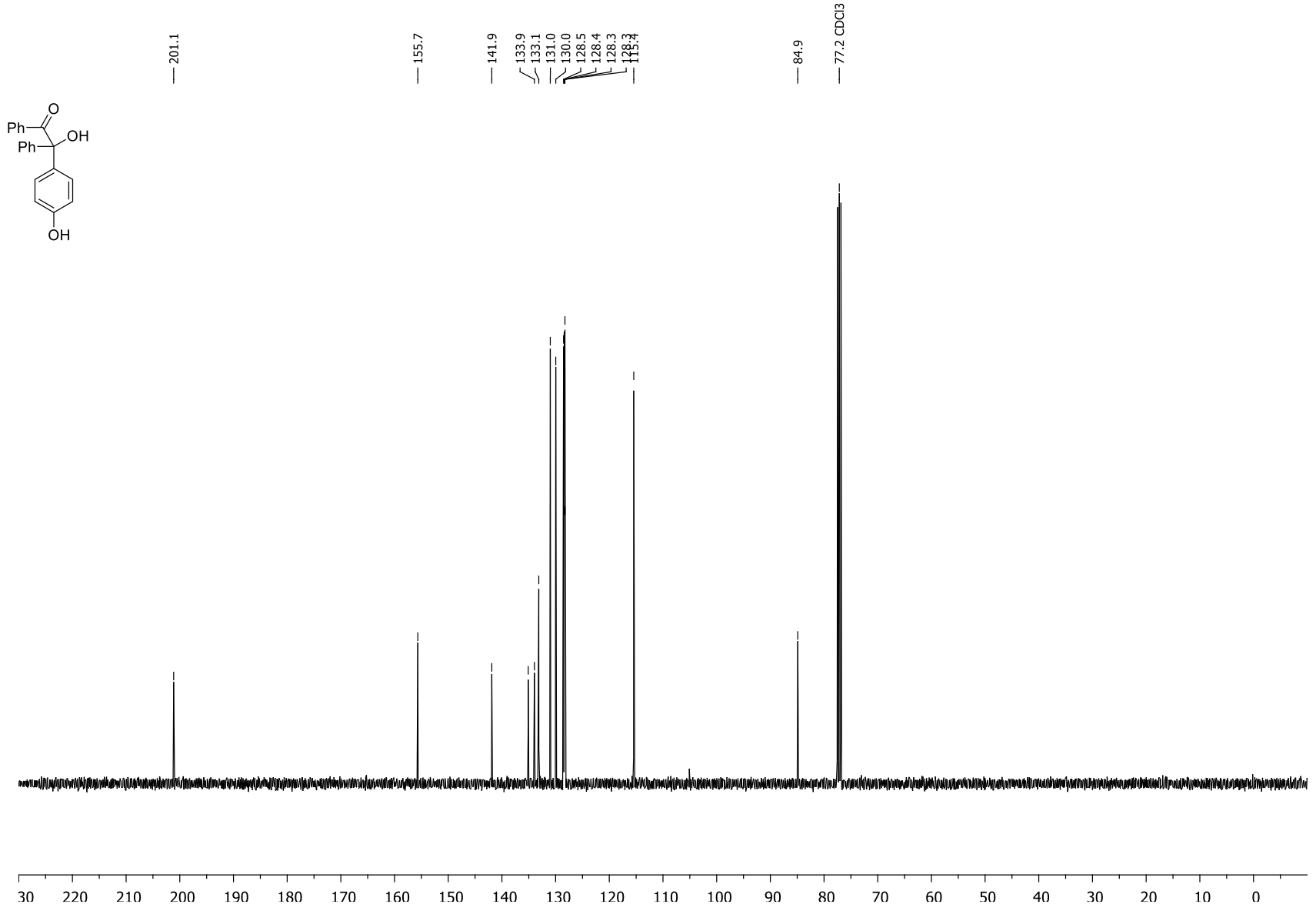


2-Hydroxy-2-(4-hydroxyphenyl)-1,2-diphenylethan-1-one (4a)

^{1}H NMR (400 MHz, $CDCl_3$)

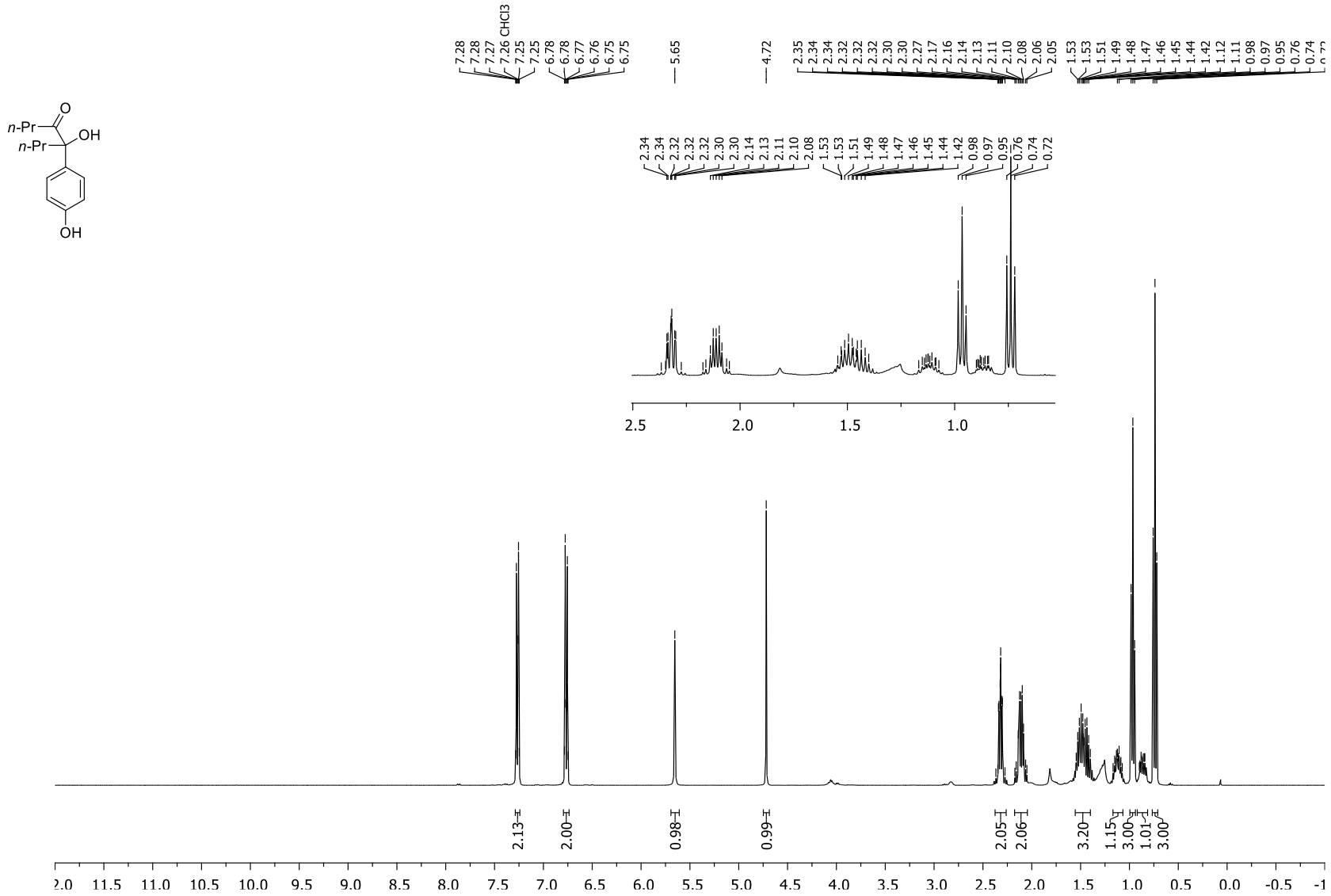


^{13}C NMR (101 MHz, $CDCl_3$)

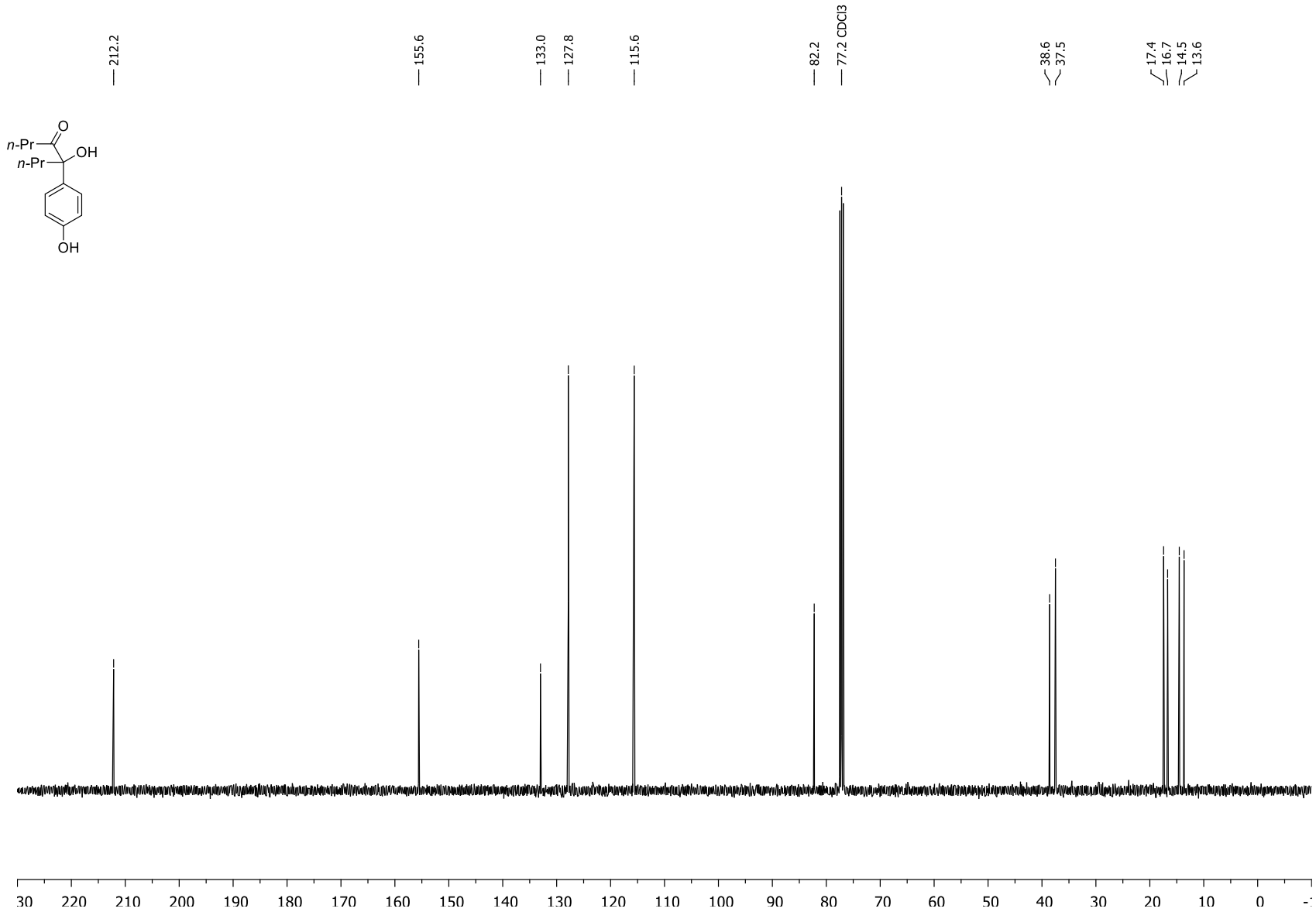


5-Hydroxy-5-(4-hydroxyphenyl)octan-4-one (4g)

^{1}H NMR (400 MHz, $CDCl_3$)

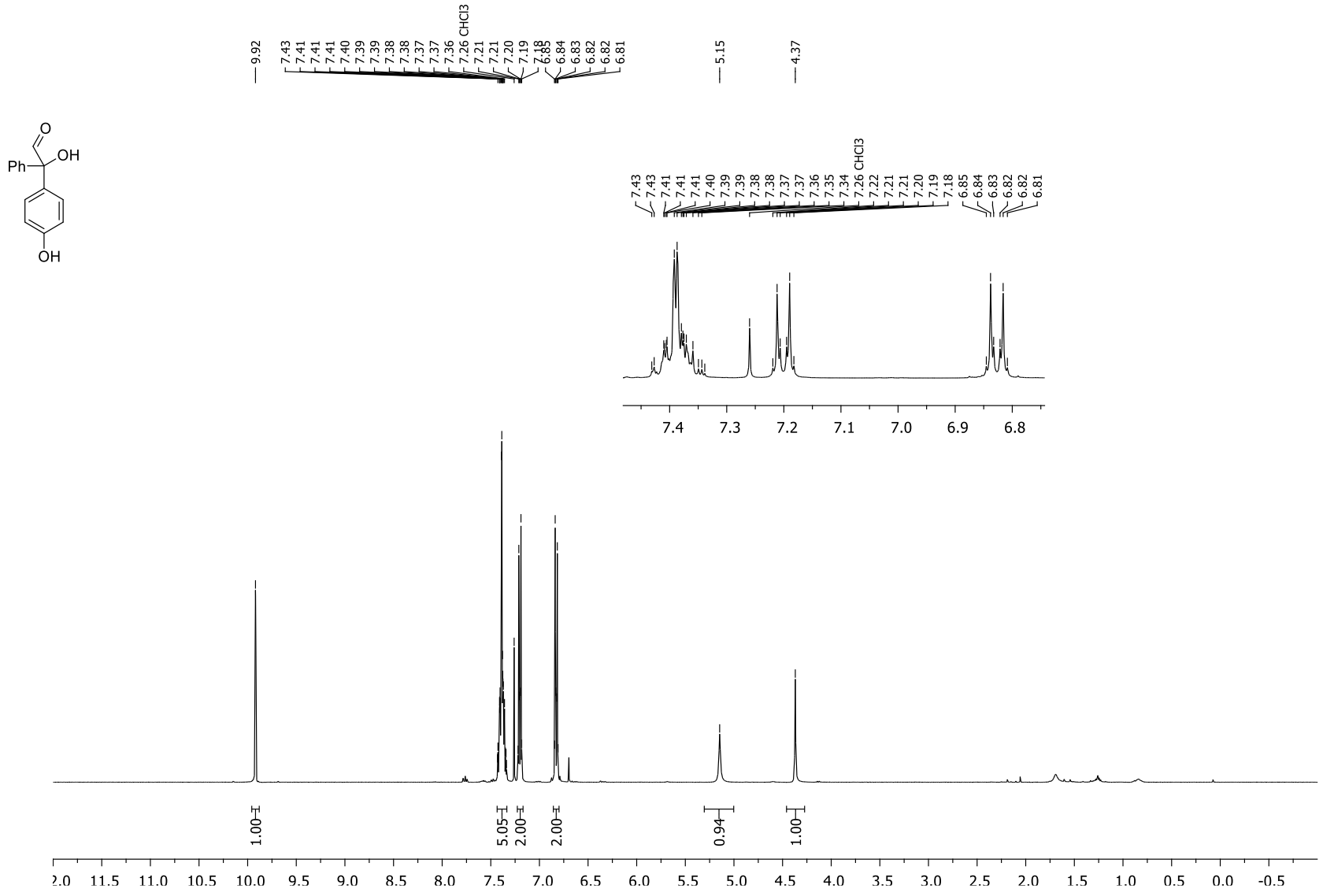


^{13}C NMR (101 MHz, $CDCl_3$)

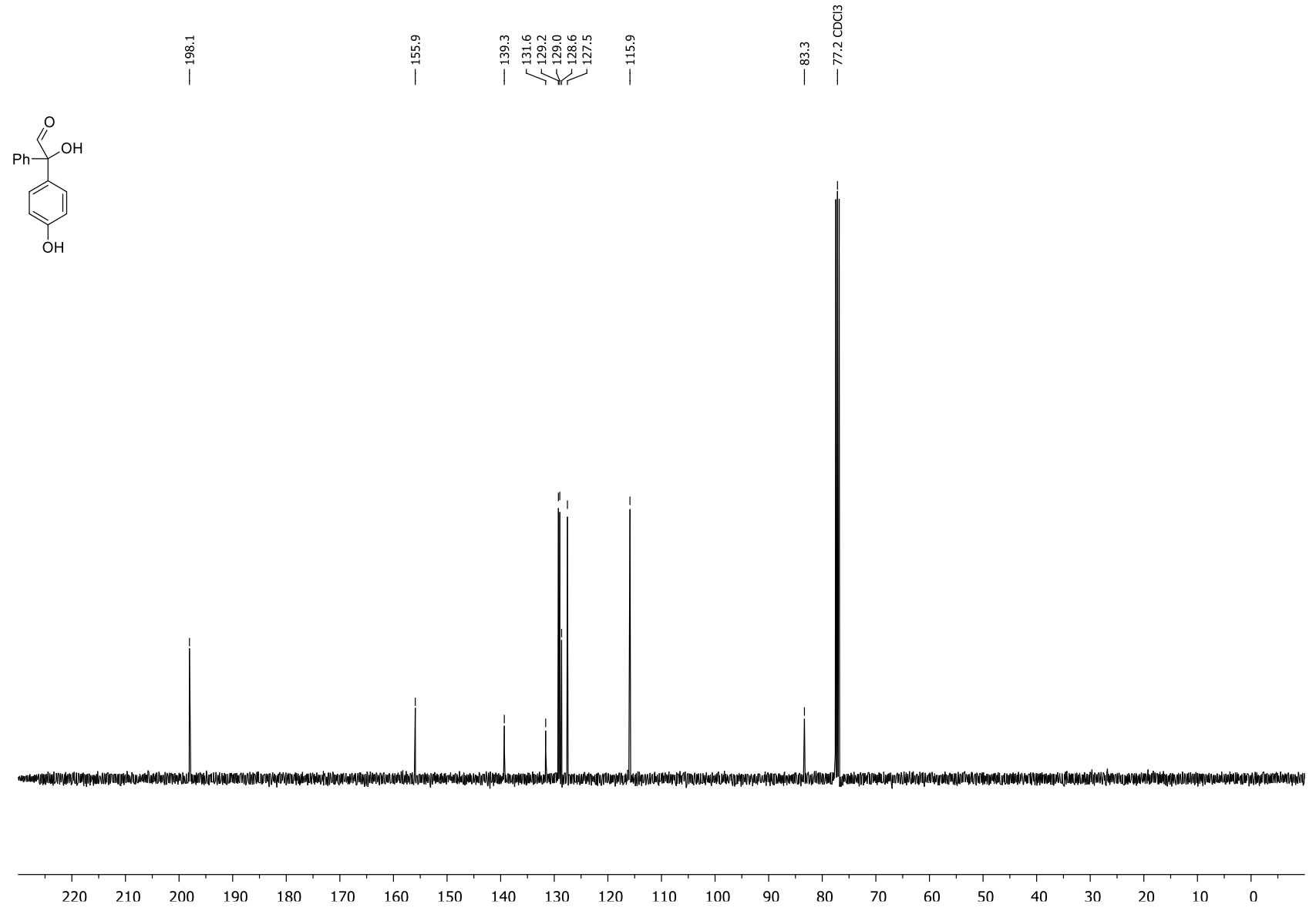


2-Hydroxy-2-(4-hydroxyphenyl)-2-phenylacetaldehyde (4i)

^{1}H NMR (400 MHz, $CDCl_3$)

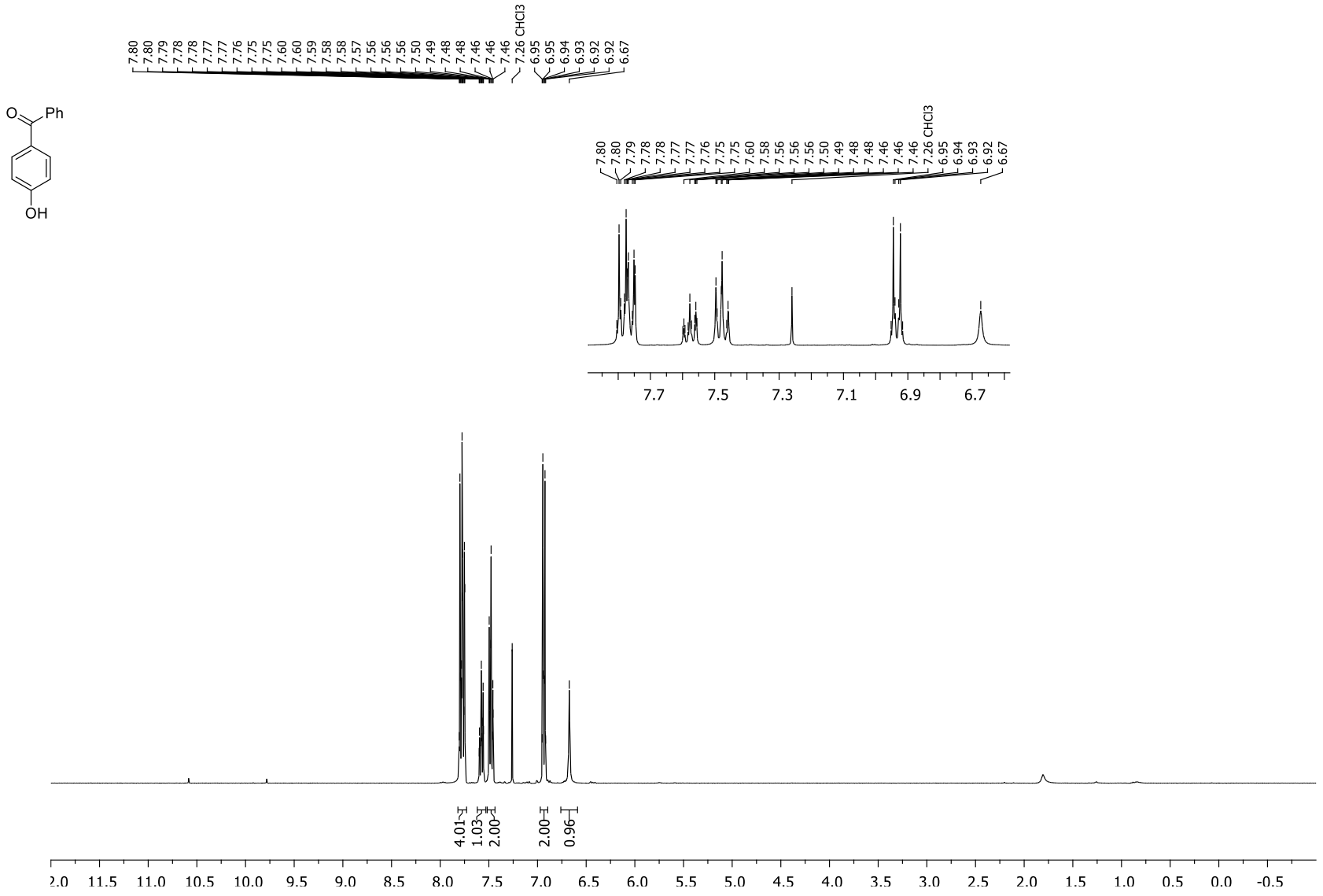


^{13}C NMR (101 MHz, $CDCl_3$)

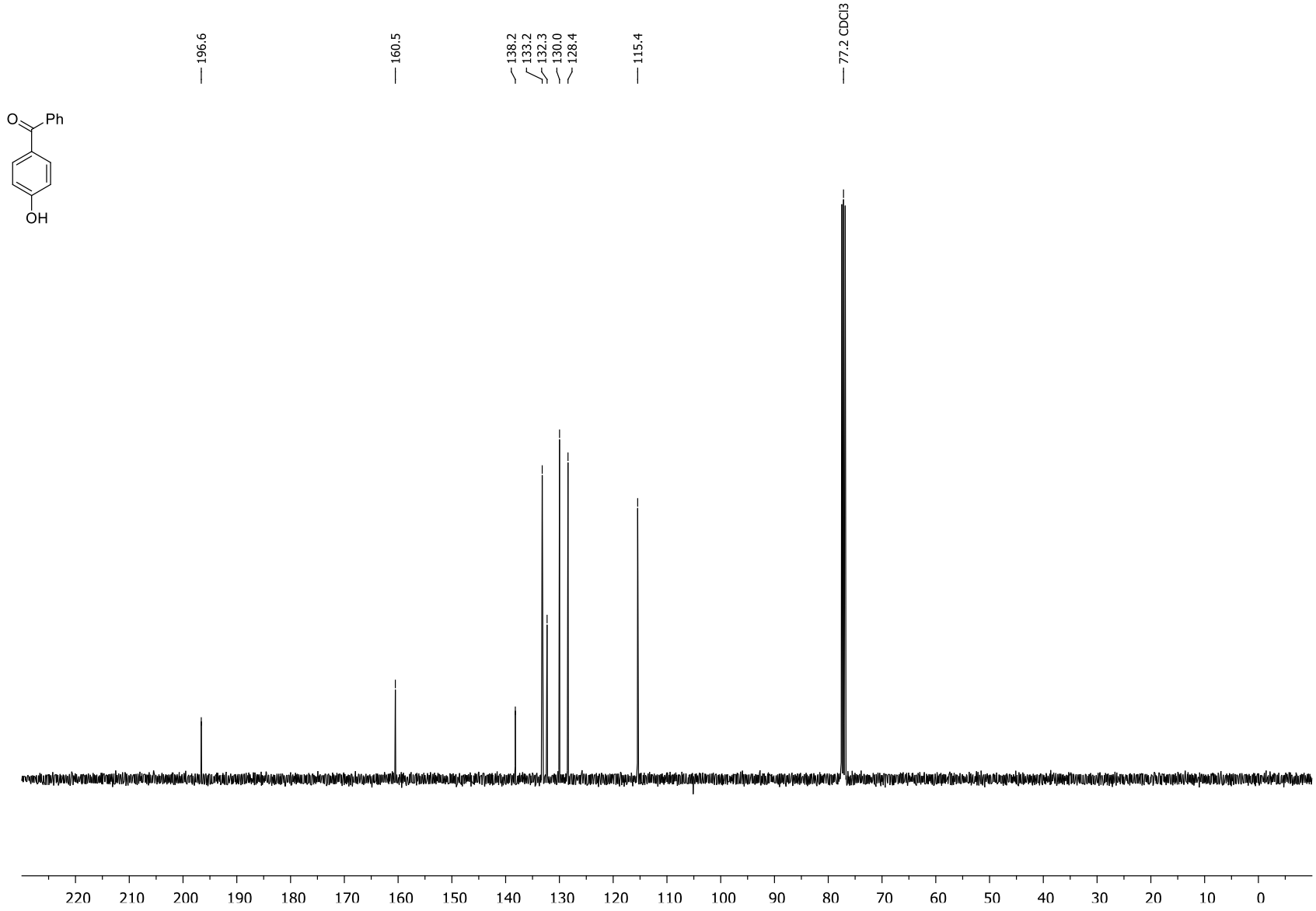


4-Hydroxybenzophenone

^{1}H NMR (400 MHz, $CDCl_3$)

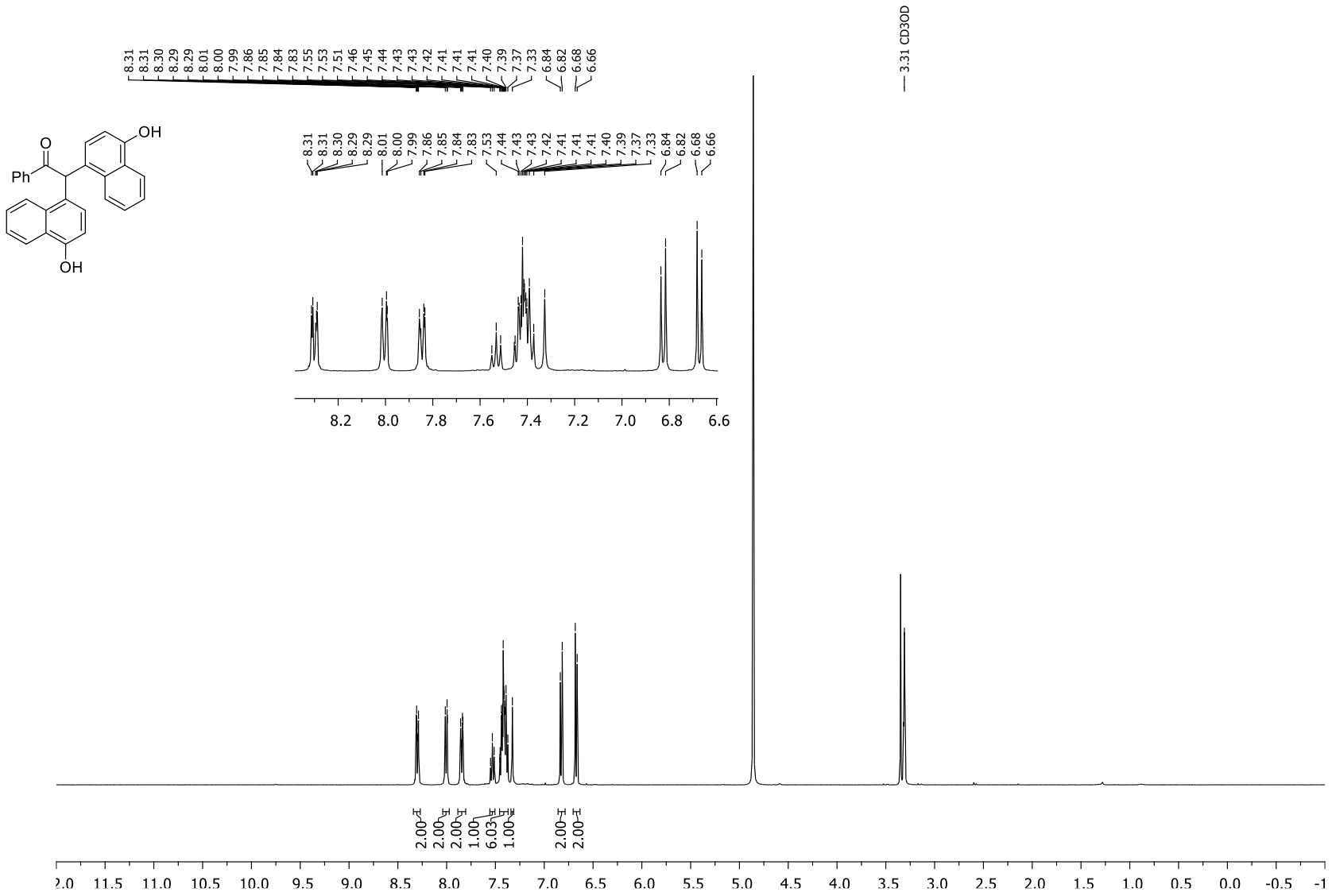


^{13}C NMR (101 MHz, $CDCl_3$)



2,2-Bis(4-hydroxynaphthalen-1-yl)-1-phenylethan-1-one (5)

^{1}H NMR (400 MHz, CD_3OD)



^{13}C NMR (101 MHz, CD_3OD)