Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Regioselective and Stereoselective Cyclizations of Cyclohexadienones Tethered to Active Methylene Groups.

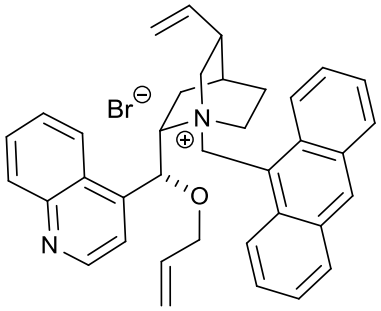
Rodolfo Tello-Aburto, Kyle A. Kalstabakken, Kelly A. Volp, and Andrew M. Harned*

University of Minnesota, Department of Chemistry, 207 Pleasant Street SE, Minneapolis, MN, USA 55455

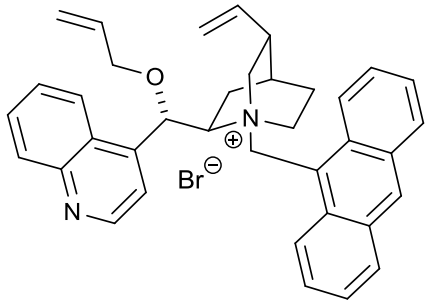
SUPPORTING INFORMATION

Table of Contents

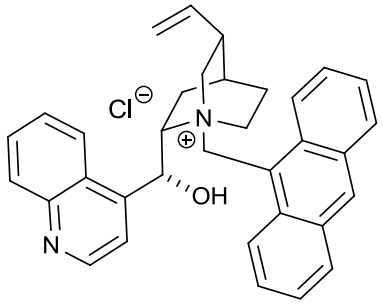
Structures of Catalysts



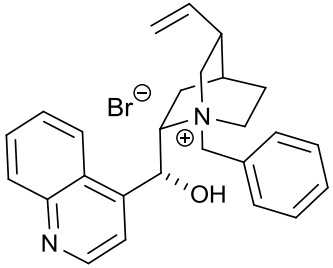
Catalyst **A**



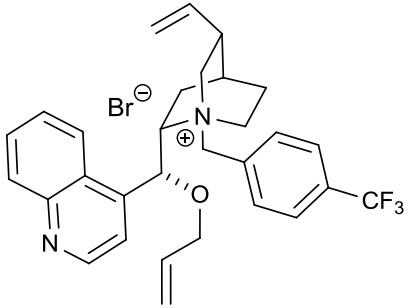
Catalyst **B**



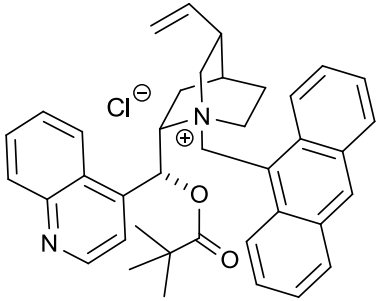
Catalyst **C**



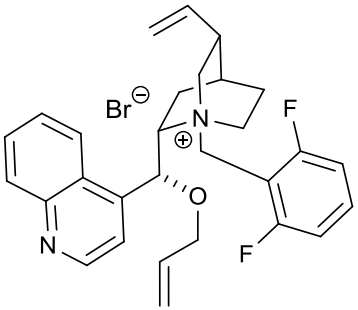
Catalyst **D**



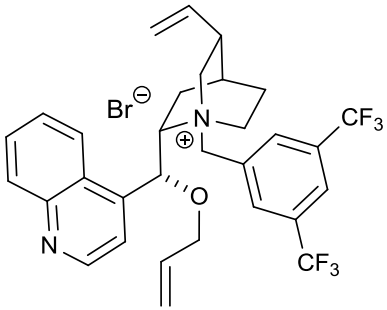
Catalyst **E**



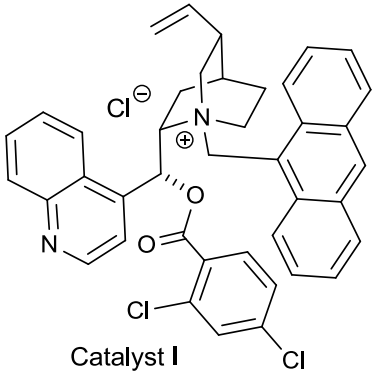
Catalyst **F**



Catalyst **G**



Catalyst **H**



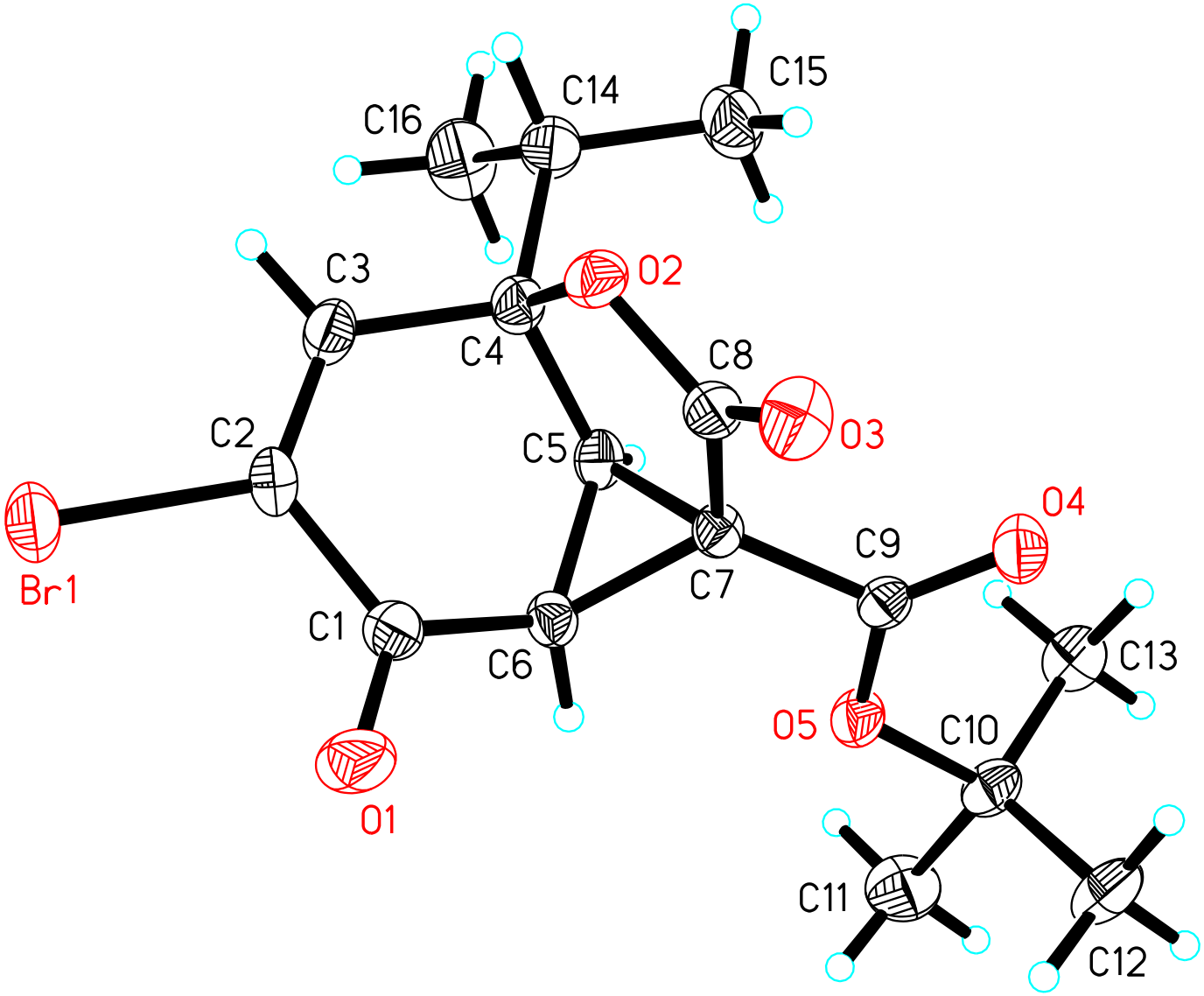
Catalyst **I**

Optimization of Desymmetrization Reaction [a]

Entry	Substrate	Catalyst	Base[b]	Solvent	Additive	Time (h)	Yield (%)	er[c]
1[d]	**2**	**A**	Cs_2CO_3	CH_2Cl_2	–	24	75	64 : 36
2	**2**	**A**	$CsOH•H_2O$[e]	CH_2Cl_2	–	9	75	65 : 35
3	**2**	**C**	Cs_2CO_3	CH_2Cl_2	–	2	ND	58 : 42
4[d]	**2**	**D**	Cs_2CO_3	CH_2Cl_2	–	7.5	>99	48 : 52
5[d]	**3**	**A**	Cs_2CO_3	CH_2Cl_2	–	6.5	99	59 : 41
6	**4a**	**A**	Cs_2CO_3	CH_2Cl_2	–	1	79	71 : 29
7	**4a**	**B**	Cs_2CO_3	CH_2Cl_2	–	2	97	29 : 71
8	**4a**	**A**	K_2CO_3	CH_2Cl_2	–	4.5	77	71 : 29
9	**4a**	**A**	Cs_2CO_3[f]	CH_2Cl_2	–	0.33	63	71 : 29
10	**4a**	**A**	$KF•2H_2O$[g]	CH_2Cl_2	–	96	ND	68 : 32
11	**4a**	**A**	$KF•2H_2O$[h]	CH_2Cl_2	–	24	ND	67 : 33
12[d]	**4a**	**A**	Cs_2CO_3	toluene	–	19	92	63 : 37
13	**4a**	**A**	Cs_2CO_3	THF	–	3.5	82	67 : 33
14	**4a**	**E**	Cs_2CO_3	CH_2Cl_2	–	2	85	59 : 41
15	**4a**	**F**	Cs_2CO_3	CH_2Cl_2	–	1	83	70 : 30
16	**4a**	**F**	Cs_2CO_3[i]	CH_2Cl_2	–	1	90	41 : 59
17[d]	**4a**	**A**	Cs_2CO_3	"wet" CH_2Cl_2[j]	–	5	85	73 : 27
18[d]	**4a**	**A**	Cs_2CO_3	CH_2Cl_2	4Å mol. sieves	18	88	74 : 26
19	**4a**	**A**	Cs_2CO_3	$CF_3C_6H_5$	4Å mol. sieves	2	79	75 : 25
20	**4a**	**G**	Cs_2CO_3	$CF_3C_6H_5$	4Å mol. sieves	2.5	96	69 : 31
21	**4a**	**H**	Cs_2CO_3	$CF_3C_6H_5$	4Å mol. sieves	7	81	59 : 41
22	**4a**	**I**	Cs_2CO_3	$CF_3C_6H_5$	4Å mol. sieves	7	99	74 : 26

[a] All reactions run at 0 ºC unless otherwise noted. ND: Not determined. [b] 1 equiv used, unless otherwise noted. [c] Determined by chiral HPLC analysis with monitoring at 225 nm. [d] Performed at −78 ºC → r.t. [e] Performed at −78 ºC. [f] Aq. saturated solution. [g] Performed at 0 °C → r.t. [h] 10 equiv base. [i] 0.1 equiv base. [j] CH_2Cl_2 was shaken with H_2O and separated before use.

X-ray Structure of 12r[1]



[1] See CIF file for more information.

Materials and Methods

Unless otherwise stated, reactions were performed in flame- or oven-dried glassware under an argon or nitrogen atmosphere using anhydrous solvents. Acetonitrile, CH_2Cl_2 and DME were dried by passage through an activated alumina column under argon. THF was distilled from sodium/benzophenone ketyl. Powdered 4Å molecular sieves were activated by heating under vacuum and kept at 90 ºC until use. Microwave reactions were prepared in sealed reaction tubes and conducted in a Biotage Initiator 8 microwave reactor equipped with an IR sensor to monitor reaction temperature. Thin-layer chromatography (TLC) was performed using plates precoated with silica gel XHL w/ UV254 (250 μm) or alumina W/ UV and visualized by UV light or $KMnO_4$, phosphomolybdic acid, or anisaldehyde stains, followed by heating. Silica gel (particle size 32-63 μm) was used for flash chromatography. ^1H and ^{13}C NMR spectra are reported relative to the residual solvent peak (δ 7.26 and δ 77.2 for ^1H and ^{13}C in $CDCl_3$, δ 7.16 and δ 128.0 for ^1H and ^{13}C in C_6D_6, respectively). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Spectra are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, bs = broad singlet. IR samples were prepared on NaCl plates either neat or by evaporation from $CHCl_3$ or CH_2Cl_2.

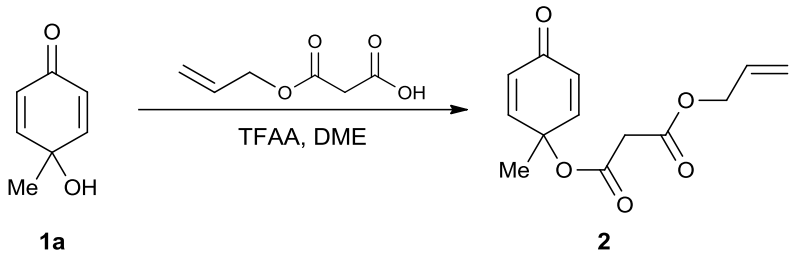
Experimental Details and Characterization Data

General method A: Dearomatization of phenols using $PhI(OAc)_2$. A solution of the corresponding phenol (1 equiv) in 3:1 MeCN–H_2O (0.1 M in substrate) was cooled to 0 ºC and treated with $PhI(OAc)_2$ (1.1 equiv). The reaction mixture was stirred until consumption of the starting material (usually within 1 h), then diluted with CH_2Cl_2, washed with saturated aq. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated.

General method B: Coupling of phenols using trifluoroacetic anhydride. A procedure by Stork[2] was adapted. Trifluoroacetic anhydride (2 mL per mmol of substrate) was added to a flask containing the mono-alkyl malonate (2.5 equiv). The mixture was stirred for 30 min before it was placed it under high vacuum to remove formed TFA and excess trifluoroacetic anhydride. The flask was back-filled with nitrogen and a solution of the appropriate quinol (1 equiv) in DME (0.05 M in substrate) was added. The solution was stirred until consumption of the starting material (usually between 1 and 3 h), at which point it was quenched by addition of saturated aq. $NaHCO_3$. The mixture was extracted with CH_2Cl_2 and the organic layer dried over Na_2SO_4, filtered, and concentrated.

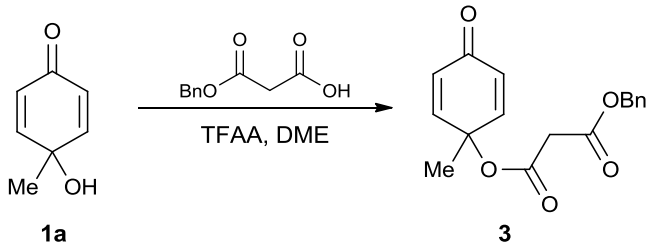
General method C: Coupling of phenols using DCC. DCC (3 equiv) was added to a solution of the appropriate quinol (1 equiv), the corresponding acid (3 equiv), and DMAP (10 mol%) in CH_2Cl_2 (0.4 M in substrate). The mixture was stirred until consumption of the starting material (usually between 1 and 3 h), then diluted with Et_2O, filtered, and concentrated.

[2] G. Stork, J. J. La Clair, P. Spargo, R. P. Nargund, and N. Totah, *J. Am. Chem. Soc.* 1996, **118**, 5304.



1a **2**

Allyl-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl) malonate (2). Using general method B, mono-allyl malonate[3] was coupled to quinol **1a**[4] to give **2** in 66% yield after flash-column chromatography (3:1 hexanes–EtOAc). **IR** (thin film) 2983, 2941, 1736, 1668, 1631, 1329, 1270, 1150, 1053, 992, 858 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.90 (d, *J* = 10.2 Hz, 2 H), 6.25 (d, *J* = 10.2 Hz, 2 H), 6.00–5.81 (m, 1 H), 5.35 (ddd, *J* = 17.2, 2.6, 1.2 Hz, 1 H), 5.28 (ddd, *J* = 10.4, 2.3, 1.2 Hz, 1 H), 4.65 (d, *J* = 5.8 Hz, 2 H), 3.40 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 185.0 (C), 166.0 (C), 165.0 (C), 148.4 (CH × 2), 131.4 (CH), 128.6 (CH × 2), 119.3 (CH_2), 75.5 (C), 66.4 (CH_2), 41.8 (CH_2); 26.3 (CH_3); **HRMS** (ESI+) 273.0733 calcd for $C_{13}H_{14}O_5Na$, found 273.0742.



1a **3**

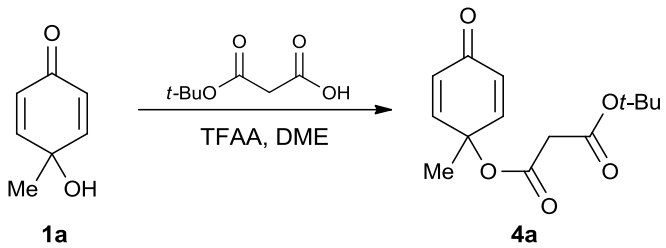
Benzyl (1-methyl-4-oxocyclohexa-2,5-dien-1-yl) malonate (3). Using general method B, mono-benzyl malonate[5] was coupled to quinol **1a** to give **3** in 63% yield after flash-column chromatography (3:1 hexanes–EtOAc). **IR** (thin film) 3036, 2983, 2937, 1734, 1666, 1630, 1328, 1266, 1149, 1152, 858 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 (s, 5 H), 6.78 (d, *J* = 10.2 Hz, 2 H), 6.20 (d, *J* = 10.2 Hz, 2 H), 5.18 (s, 2 H), 3.41 (s,

[3] Prepared according to: I. Navarro, J.-F. Basset, S. Hebbe, S. M. Major, T. Werner, C. Howsham, J. Bräckow, and A. G. M. Barret, *J. Am. Chem. Soc.* 2008, **130**, 10293.

[4] M. C. Carreño, M. González-López, and A. Urbano, *Angew. Chem. Int. Ed.* 2006, **45**, 2737.

[5] S. A.-L. Thetiot-Laurent, B. Nadal, and T. Le Gall, *Synthesis* 2010, 1697.

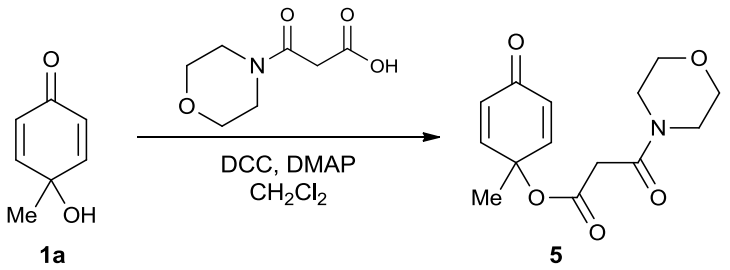
2 H), 1.49 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 184.9(C), 166.1(C), 164.9(C), 148.4 (CH × 2), 135.1(C), 128.8 (CH × 4), 128.7 (CH), 128.5 (CH × 2), 75.4(C), 67.5 (CH_2), 41.9 (CH_2), 26.2 (CH_3); **HRMS** (ESI+) 323.0890 calcd for $C_{17}H_{16}O_5Na$, found 323.0898.



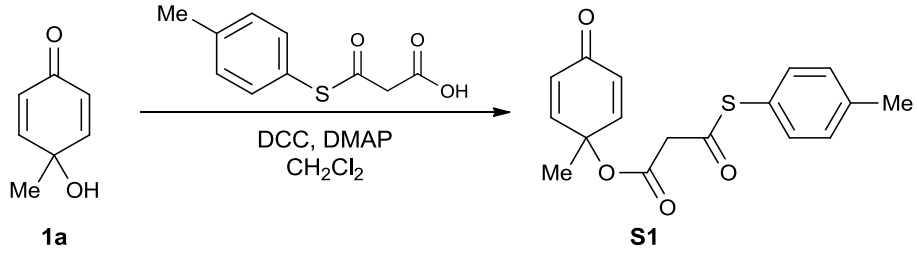
1a **4a**

***tert*-Butyl (1-methyl-4-oxocyclohexa-2,5-dien-1-yl) malonate (4a).** Using general method B, mono-*tert*-butyl malonate[6] was coupled to quinol **1a** to give **4a** in 43% yield after flash-column chromatography (3:1 hexanes–EtOAc). **IR** (thin film) 2983, 2937, 1755, 1728, 1671, 1629, 1144, 1055, 854 cm^{-1}; **^{1}H NMR** (300 MHz, C_6D_6) δ 6.35 (d, *J* = 10.2 Hz, 2 H), 6.07 (d, *J* = 10.2 Hz, 2 H), 2.97 (s, 2 H), 1.30 (s, 9 H), 1.04 (s, 3 H); **^{13}C NMR** (75 MHz, C_6D_6, DEPT) δ 189.6 (C), 165.4 (C), 165.1 (C), 147.8 (CH × 2), 128.6 (CH × 2), 81.7 (C), 75.0 (C), 43.0 (CH_2), 27.9 (CH_3 × 3), 25.9 (CH_3); **HRMS** (ESI+) 289.1046 calcd for $C_{14}H_{18}O_5Na$, found 289.1059.

[6] Although this substrate is commercially available, it is also easily obtained by DCC coupling of malonic acid with 1 equiv of *t*-BuOH; see: R. Shelkov, M. Nahmany, and A. Melman, *J. Org. Chem.* **2002**, *67*, 8975.



1-Methyl-4-oxocyclohexa-2,5-dien-1-yl 3-morpholino-3-oxopropanoate (5). Using general method C, mono-morpholine malonic acid[7] was coupled to quinol **1a** to give **5** in 96% yield after flash-column chromatography (2:1 hexanes–acetone). **IR** (thin film) 3497, 3288, 2925, 2856, 1744, 1657, 1444, 1313, 1230, 1052, 857 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.89 (d, *J* = 10.2 Hz, 2 H), 6.20 (d, *J* = 10.2 Hz, 2 H), 3.69–3.55 (m, 6 H), 3.40 (s, 2 H), 3.43–3.34 (m, 2 H) 1.54 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 184.9 (C), 166.0 (C), 164.3 (C), 148.6 (CH × 2), 128.4 (CH × 2), 75.3 (C), 66.6 (CH_2), 66.4 (CH_2), 46.6 (CH_2), 42.2 (CH_2), 41.1 (CH_2), 26.3 (CH_3); **HRMS** (ESI+) 302.0999 calcd for $C_{14}H_{17}NO_5Na$, found 302.0990.

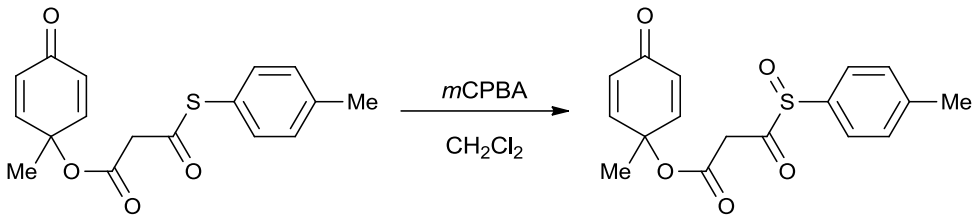


1-Methyl-4-oxocyclohexa-2,5-dien-1-yl 2-(*p*-tolylthio)acetate (S1). Using general method C, 2-(*p*-tolylthio)acetic acid[8] was coupled to **1a** to give sulfide **S1** in 65% yield after flash-column chromatography (3:1 hexanes–EtOAc). **IR** (thin film) 3022, 2779, 2924, 1739, 1668, 1631, 1269, 1134, 1052, 857 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 6.72 (d, *J* = 10.2 Hz, 2 H), 6.17 (d, *J* =

[7] (a) M. R. Angelastro, L. E. Baugh, P. Bey, J. P. Burkhart, T.-M. Chen, S. L. Durham, C. M. Hare, E. W. Huber, M. J. Janusz, J. R. Koehl, A. L. Marquart, S. Mehdi, and N. P. Peet, *J. Med. Chem.* 1994, **37**, 4538. (b) B. Rigo, D. Fasseur, P. Cauliez, and D. Couturier, *Tetrahedron Lett.* 1989, **30**, 3073.

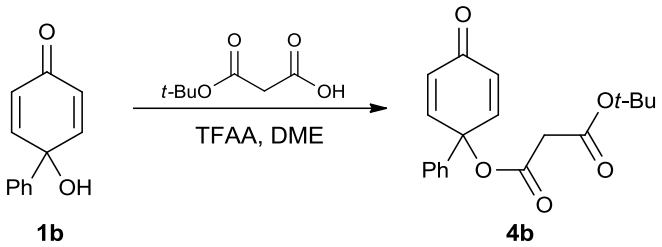
[8] (a) Prepared according to W. J. Kenney, J. A. Walsh, and D. A. Davenport, *J. Am. Chem. Soc.* 1961, **83**, 4019. (b) Y. Nagao, S. Miyamoto, M. Miyamoto, H. Takeshige, K. Hayashi, S. Sano, M. Shiro, K. Yamaguchi, and Y. Sei, *J. Am. Chem. Soc.* 2006, **128**, 9722.

10.2 Hz, 2 H), 3.52 (s, 2 H), 2.31 (s, 3 H), 1.45 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 184.9 (C), 168.3 (C), 148.5 (CH × 2), 137.8 (C), 131.4 (CH × 2), 130.6 (C), 129.9 (CH × 2), 128.3 (CH × 2), 75.0 (C), 37.5 (CH_2), 26.0 (CH_3), 21.1 (CH_3); **HRMS** (ESI+) 311.0712 calcd for $C_{16}H_{16}O_3SNa$, found 311.0708.



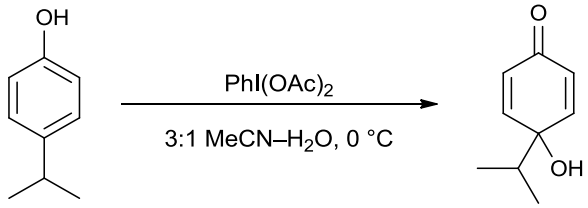
S1 **6**

1-Methyl-4-oxocyclohexa-2,5-dien-1-yl 2-tosylacetate (6). Sulfide **S1** (89 mg, 0.30 mmol) was dissolved in CH_2Cl_2 (5 mL) and treated with 77% *m*-chloroperbenzoic acid (207 mg, 0.9 mmol). The mixture was stirred for 2 h before being quenched with saturated aq. $NaHCO_3$ (10 mL). The phases were separated and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to give **6** (87.3 mg, 88% yield) after flash-column chromatography (2:1→1:1 hexanes–EtOAc). **IR** (thin film) 3051, 2992, 2937, 1746, 1669, 1632, 1391, 1320, 1280, 1152, 1050, 859 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 6.78 (d, *J* = 10.2 Hz, 2 H), 6.18 (d, *J* = 10.2 Hz, 2 H), 4.07 (s, 2 H), 2.43 (s, 3 H), 1.50 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 184.7 (C), 160.9 (C), 147.5 (CH × 2), 145.8 (C), 135.7 (C), 130.0 (CH × 2), 128.7 (CH × 2), 128.5 (CH × 2), 76.3 (C), 61.4 (CH_2), 25.9 (CH_3), 21.8 (CH_3); **HRMS** (ESI+) 343.0611 calcd for $C_{16}H_{16}O_5SNa$, found 343.0616.



1b **4b**

***tert*-Butyl (4-oxo-1,4-dihydro-[1,1'-biphenyl]-1-yl) malonate (4b).** Using general method B, mono-*tert*-butyl malonate was coupled to quinol **1b**[9] to give **4b** in 36% yield after flash-column chromatography (4:1 hexanes–EtOAc). **IR** (thin film) 1729, 1670, 1625, 1325, 1135, 994, 842 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47–7.30 (m, 5 H), 6.97 (d, *J* = 10.1 Hz, 2 H), 6.34 (d, *J* = 10.1 Hz, 2 H), 3.40 (s, 2 H), 1.48 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 185.5 (C), 165.3 (C), 165.0 (C), 147.1 (CH × 2), 136.1 (C), 129.2 (CH × 2), 129.0 (CH), 128.4 (CH × 2), 125.4 (CH × 2), 82.7 (C), 78.2 (C), 43.4 (CH_2), 28.1 (CH_3 × 3); **HRMS** (ESI+) 351.1203 calcd for $C_{19}H_{20}O_5Na$, found 351.1199.



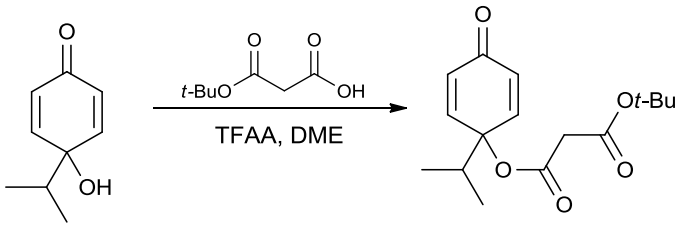
1c

4-Hydroxy-4-isopropylcyclohexa-2,5-dienone (1c). Using general method A, 4-isopropyl phenol was converted into quinol **1c** in 73% yield after flash-column chromatography (3:1 hexanes–EtOAc). This compound has been prepared and characterized before;[10] however, our ^{1}H NMR spectrum differs from the literature data. **IR** (thin film) 3343, 2960, 1648, 1641, 1496, 1454, 1367, 1311, 1186, 1028, 968, 865, 774 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.80 (d, *J* = 10.2 Hz, 2 H), 6.14 (d, *J* = 10.2 Hz, 2 H), 3.14 (bs, 1 H), 1.96 (hept, *J* = 6.9 Hz, 1 H), 0.91 (d, *J* = 6.9 Hz, 6 H). **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 186.3 (C), 151.1 (CH × 2),

[9] Prepared according to: F.-X. Felpin, *Tetrahedron Lett*. 2007, **48**, 409.

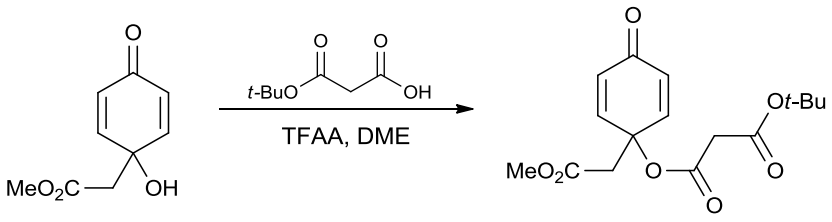
[10] J. McKinley, A. Aponick, J. C. Raber, C. Fritz, D. Montgomery, and C. T. Wigal, *J. Org. Chem.* 1997, **62**, 4874.

128.8 (CH × 2), 72.3 (C), 36.7 (CH), 17.0 (CH_3 × 2); **HRMS** (ESI+) 175.0740 calcd for $C_9H_{12}O_2Na$, found 175.0741.



1c **4c**

***tert*-butyl (1-isopropyl-4-oxocyclohexa-2,5-dien-1-yl) malonate (4c).** Using general method B, mono-*tert*-butyl malonate was coupled to **1c** to give **4c** in 56% yield after flash-column chromatography (5:1 hexanes–EtOAc). **IR** (thin film) 2976, 2937, 2880, 1751, 1730, 1670, 1629, 1461, 1333, 1272, 1146, 1005 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.77 (d, *J* = 10.3 Hz, 2 H), 6.31 (d, *J* = 10.3 Hz, 2 H), 3.27 (s, 2 H), 2.11 (hept, *J* = 6.9 Hz, 1 H), 1.45 (s, 9 H), 0.93 (d, *J* = 6.9 Hz, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 185.3 (C), 165.5 (C), 165.3 (C), 146.8 (CH × 2), 130.1 (CH × 2), 82.5 (C), 80.4 (C), 43.2 (CH_2), 36.5 (CH), 28.0 (CH_3 × 3), 16.9 (CH_3); **HRMS** (ESI+) 317.1359 calcd for $C_{16}H_{22}O_5Na$, found 317.1417.

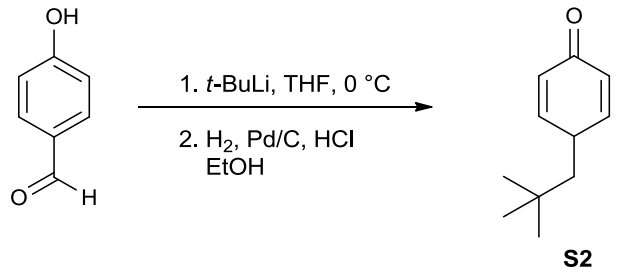


1d **4d**

***tert*-Butyl (1-(2-methoxy-2-oxoethyl)-4-oxocyclohexa-2,5-dien-1-yl) malonate (4d).** Using general method B, mono-*tert*-butyl malonate was coupled to jacaranone[11] (**1d)** to give **4d** in 38% yield after flash-column chromatography (3:1 hexanes–EtOAc). **IR** (thin film) 2980, 1734, 1672, 1633, 1333, 1249, 1154, 1032, 855 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 10.2 Hz, 2 H), 6.29 (d, *J* = 10.2 Hz, 2 H), 3.67 (s, 3 H), 3.26 (s,

[11] K. A. Parker and J. R. Andrade, *J. Org. Chem.* 1979, **44**, 3964.

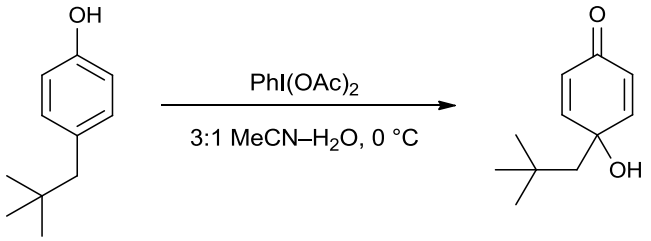
2 H), 2.82 (s, 2 H), 1.44 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 184.7 (C), 168.0 (C), 165.1 (C), 146.2 (CH × 2), 129.4 (CH), 82.7 (C), 74.5 (C), 52.3 (CH_3), 43.8 (CH_2), 43.0 (CH_2), 28.0 (CH_3 × 3); **HRMS** (ESI+) 347.1101 calcd for $C_{16}H_{20}O_7Na$, found 347.1126.



S2

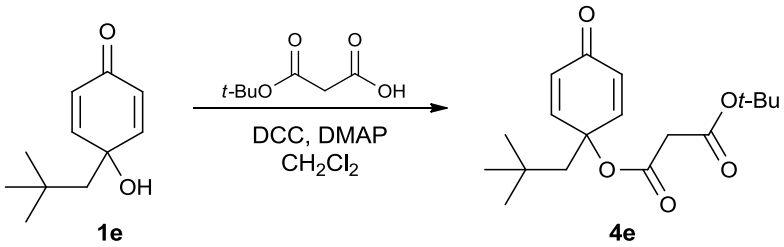
4-neopentylphenol (S2). A solution of 4-hydroxybenzaldehyde (1.0 g, 8.2 mmol) in THF (40 mL) was cooled to 0 ºC and treated with *t*-BuLi (1.28 M in pentane, 14.0 mL, 18.0 mmol). The mixture was stirred for 1 h before being quenched with 10% aq. HCl (1 mL). The mixture was diluted with brine and acidified with 10% aq. HCl until a clear solution was obtained. Extraction with Et_2O followed by drying over $MgSO_4$ and concentration gave a residue that was purified by flash-column chromatography (3:1 hexanes–EtOAc). Further purification was achieved by suspending the obtained solid in chloroform, followed by filtration to give 471 mg of the intermediate benzylic alchohol. This material was dissolved in EtOH (35 mL), treated with 100 mg Pd/C (10% w/w) and 1 drop of conc. HCl. The mixture was stirred under an atmosphere of H_2 (ballon) for 14 h, then filtered through a short plug of Celite. Solvent was removed in vacuo and the residue purified by flash-column chromatography (19:1 hexanes–EtOAc) to give **S2** (387 mg, 24% yield over 2 steps). Identity was verified by comparison of ^{1}H NMR spectrum with literature data.[12]

[12] R. B. Bates and T. J. Siahaan, *J. Org. Chem.* 1986, **51**, 1432.



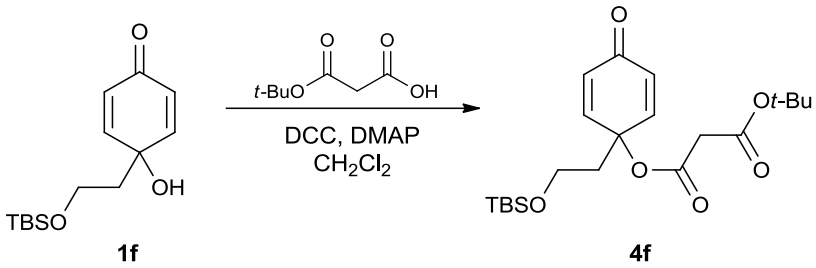
S2 **1e**

4-Hydroxy-4-neopentylcyclohexa-2,5-dienone (1e). Using general method A, phenol **S2** was converted into **1e** in 31% yield after flash-column chromatography (3:1 hexanes–EtOAc). **IR** (thin film) 3429, 2960, 2873, 1661, 1621, 1470, 1397, 1279, 1074 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.91 (d, *J* = 10.1 Hz, 2 H), 6.12 (d, *J* = 10.1 Hz, 2 H), 2.42 (bs, 1 H), 1.85 (s, 2 H), 0.93 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 186.1 (C), 152.7 (CH × 2), 127.2 (CH × 2), 69.6 (C), 53.8 (CH_2), 31.3 (CH_3 × 3), 30.9 (C); **HRMS** (ESI+) 203.1043 calcd for $C_{11}H_{16}O_2Na$, found 203.1059.



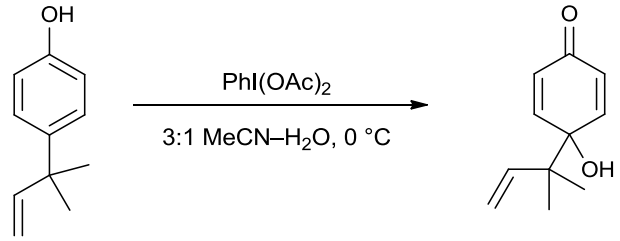
1e **4e**

***tert*-Butyl (1-neopentyl-4-oxocyclohexa-2,5-dien-1-yl) malonate (4e).** Using general method C, mono-*tert*-butyl malonate was coupled to quinol **1e** to give **4e** in quantitative yield after flash-column chromatography (5:1 hexanes–EtOAc). **IR** (thin film) 2976, 2935, 2870, 1732, 1671, 1630, 1368, 1331, 1143, 1046, 853 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.99 (d, *J* = 10.2 Hz, 2 H), 6.22 (d, *J* = 10.2 Hz, 2 H), 3.24 (s, 2 H), 1.81 (s, 2 H), 1.44 (s, 9 H), 0.99 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 185.4 (C), 165.4 (C), 165.2 (C), 149.0 (CH × 2), 128.0 (CH × 2), 82.6 (C), 78.5 (C), 53.1 (CH_2), 43.3 (CH_2), 31.8 (C), 31.5 (CH_3 × 3), 28.0 (CH_3 × 3); **HRMS** (ESI+) 345.1672 calcd for $C_{18}H_{26}O_5Na$, found 345.1679.



1f **4f**

***tert*-Butyl (1-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-4-oxocylcohexa-2,5-dien-1-yl) malonate (4f).** Using general method C, mono-*tert*-butyl malonate was coupled to quinol **1f**[13] to give **4f** as a white solid in 74% yield after flash-column chromatography (10:1 hexanes/EtOAc). **IR** (thin film) 2955, 2929, 2857, 1757, 1730, 1674, 1632, 1258, 1148, 1100, 839, 778 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.93 (d, *J* = 10.2 Hz, 2 H), 6.24 (d, *J* = 10.2 Hz, 2 H), 3.72 (t, *J* = 6.1 Hz, 2 H), 3.27 (s, 2 H), 2.03 (t, *J* = 6.1 Hz, 2 H), 1.46 (s, 9 H), 0.85 (s, 9 H), 0.00 (s, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 185.3 (C), 165.4 (C), 165.3 (C), 148.1 (CH × 2), 128.6 (CH × 2), 82.6 (C), 76.8 (C), 57.8 (CH_2), 43.2 (CH_2), 42.9 (CH_2), 28.1 (CH_3 × 3), 25.9 (CH_3 × 3), 18.2 (C), −5.4 (CH_3 × 2); **HRMS** (ESI+) 433.2017 calcd for $C_{21}H_{34}O_6SiNa$, found 433.2028.



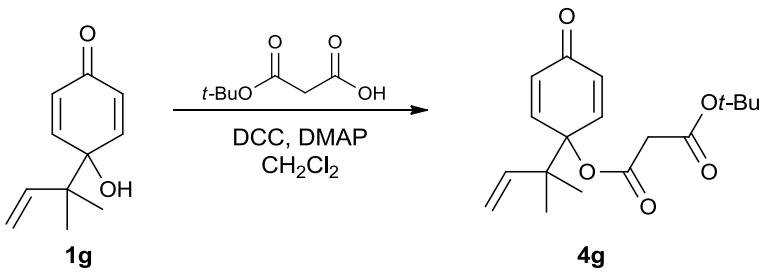
1g

4-Hydroxy-4-(2-methylpent-4-en-2-yl)cyclohexa-2,5-dienone (1g). Using general procedure A, 4-(2-methylpent-4-en-2-yl)phenol[14] was converted into quinol **1g** in 37% yield after flash-column chromatography (3:1 hexanes–EtOAc). **IR** (thin film) 3398, 2970, 1667, 1620, 1385, 1463, 1173, 1063, 955, 916, 859 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.99 (d, *J* = 10.4 Hz, 2 H), 6.18 (d, *J* = 10.4 Hz, 2 H), 5.80 (ddt, *J* = 17.7, 10.3, 7.4 Hz, 1 H), 5.10–4.97 (m, 2 H), 2.66 (s, 1 H), 2.14 (d, *J* = 7.4 Hz, 1 H), 0.98 (s, 6 H); **^{13}C NMR** (75 MHz,

[13] Prepared according to: Z. You, A. H. Hoveyda, and M. L. Snapper, *Ang. Chem. Int. Ed.* 2009, **48**, 547.

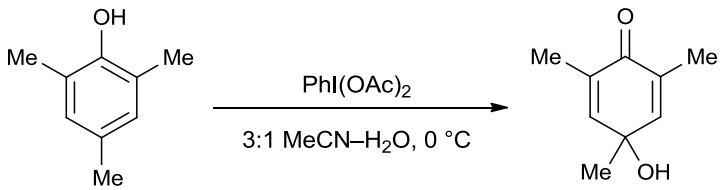
[14] J. A. Cella, *J. Org. Chem.* 1982, **47**, 2125.

$CDCl_3$, DEPT) δ 185.7 (C), 150.5 (CH × 2), 134.8 (CH), 129.0 (CH × 2), 118.2 (CH_2), 74.1 (C), 41.8 (C, overlapped), 41.8 (CH_2), 21.9 (CH_3 × 2); **HRMS** (ESI+) 215.1043 calcd for $C_{12}H_{16}O_2Na$, found 215.1059.



1g **4g**

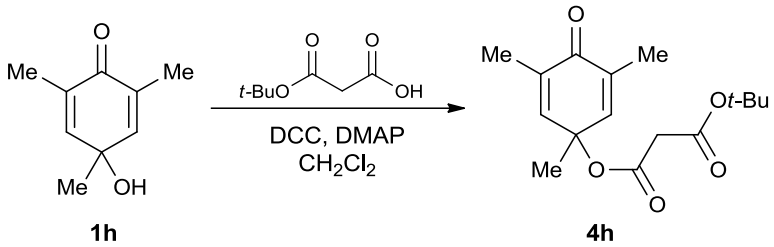
***tert*-Butyl (1-(2-methylpent-4-en-2-yl)-4-oxocyclohexa-2,5-dien-1-yl) malonate (4g).** Using general method C, mono-*tert*-butyl malonate was coupled to quinol **1g** to give **4g** in 50% yield after flash-column chromatography (3:1 hexanes–Et_2O). **IR** (thin film) 2977, 2941, 1759, 1731, 1671, 1629, 1332, 1257, 1143, 1000, 914, cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.88 (d, *J* = 10.3 Hz, 2 H), 6.35 (d, *J* = 10.3 Hz, 2 H), 5.75 (ddt, *J* = 17.3, 10.0, 7.4 Hz, 1 H), 5.07 (d, *J* = 10.3 Hz, 1 H), 5.02 (d, *J* = 17.2 Hz, 1 H) 3.31 (s, 2 H), 2.15 (d, *J* = 7.4 Hz, 2 H), 1.47 (s, 9 H), 0.98 (s, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 185.0 (C), 165.5 (C), 165.2 (C), 146.9 (CH × 2), 134.0 (CH), 130.4 (CH × 2); 118.6 (CH_2), 82.7 (C), 82.0 (C), 43.3 (C), 43.2 (CH_2), 41.5 (CH_2), 28.1 (CH_3 × 3), 21.9 (CH_3 × 2); **HRMS** (ESI+) 357.1672 calcd for $C_{19}H_{26}O_5Na$, found 357.1690.



1h

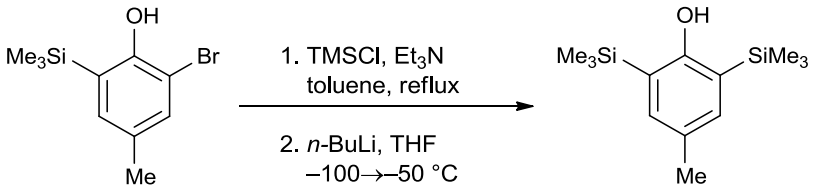
4-Hydroxy-2,4,6-trimethylcyclohexa-2,5-dienone (1h). Using general method A, 2,4,6-trimethylphenol was converted into **1h** in 78% yield after flash-column chromatography (4:1→3:1 hexanes–EtOAc). Identity was verified by comparison of ^{1}H NMR spectrum with literature data.[4,15]

[15] M. Ochiai, K. Miyamoto, M. Shiro, T. Ozawa, and K. Yamaguchi, *J. Am. Chem. Soc.* 2003, **125**, 13006.



1h **4h**

***tert*-Butyl (1,3,5-trimethyl-4-oxocyclohexa-2,5-dien-1-yl) malonate (4h).** Using general method C, mono-*tert*-butyl malonate was coupled to quinol **1h** to give **4h** in quantitative yield after flash-column chromatography (9:1 hexanes–EtOAc). **IR** (thin film) 2979, 2930, 1731, 1679, 1644, 1370, 1333, 1144, 1048, 971, 847 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.65 (s, 2 H), 3.22 (s, 2 H), 1.87 (s, 6 H), 1.52 (s, 3 H), 1.45 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 186.4 (C), 165.7 (C), 165.5 (C), 143.4 (CH × 2), 134.9 (C × 2), 82.3 (C), 75.9 (C), 43.5 (CH_2), 28.1 (CH_3 × 3), 26.4 (CH_3), 16.0 (CH_3 × 2); **HRMS** (ESI+) 317.1359 calcd for $C_{16}H_{22}O_5Na$, found 317.1373.

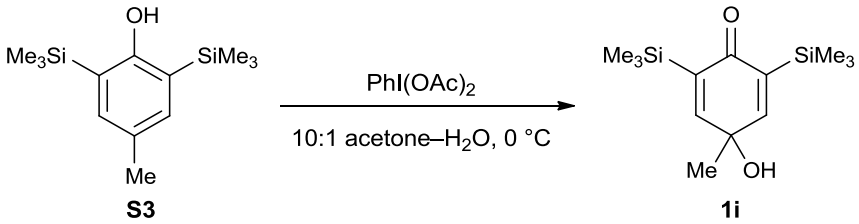


S3

4-Methyl-2,6-bis(trimethylsilyl)phenol (S3). A mixture of 2-bromo-4-methyl-6-(trimethylsilyl)phenol[16] (660 mg, 2.54 mmol), TMSCl (0.64 mL, 5.1 mmol) and Et_3N (0.71 mL, 5.1 mmol) was dissolved in toluene (20 mL) and refluxed for 12 h. The mixture was then allowed to cool to r.t. and concentrated. Full conversion of the phenol to the TMS ether was confirmed by ^{1}H NMR analysis. The residue was then dissolved in 20 mL THF and cooled to −100 ºC. *n*-BuLi (2.5 M in hexanes, 1.01 mL, 2.54 mmol) was added and the mixture was allowed to gradually warm to −50 ºC, at which point it was quenched with saturated aq. NH_4Cl (1 mL). The cooling bath was removed and the mixture was diluted with Et_2O, washed with brine, dried over $MgSO_4$,

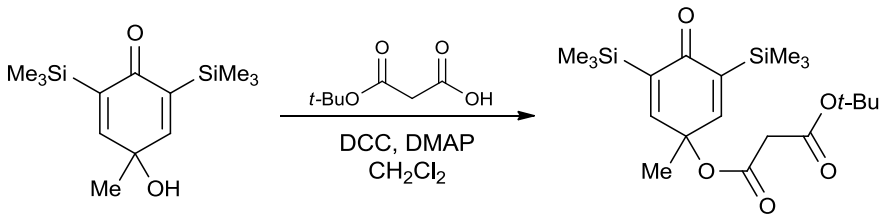
[16] S. Akai, T. Ikawa, S.-i. Takayanagi, Y. Morikawa, S. Mohri, M. Tsubakiyama, M. Egi, Y. Wada, and Y. Kita, *Angew. Chem. Int. Ed.* 2008, **47**, 7673.

filtered, and concentrated. Flash-column chromatography (100% petroleum ether) afforded phenol **S3** (564.2 mg, 87% yield over 2 steps). **IR** (thin film) 3599, 2951, 1572, 1403, 1241, 1169, 832 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.17 (s, 2 H), 4.85 (s, 1 H), 2.29 (s, 3 H), 0.34 (s, 18 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 163.4 (C), 137.3 (CH × 2), 129.2 (C), 124.1 (C × 2), 20.8 (CH_3), −0.3 (CH_3 × 6); **HRMS** (ESI–) 251.1282 calcd for $C_{13}H_{23}OSi_2$, found 251.0992.



S3 **1i**

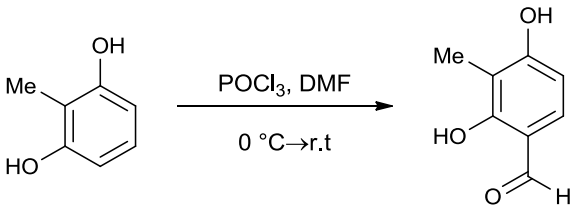
4-Hydroxy-4-methyl-2,6-bis(trimethylsilyl)cyclohexa-2,5-dienone (1i). Using a modification of general method A in which 10:1 acetone–H_2O was used as solvent, **S3** was converted into **1i** in 67% yield after flash-column chromatography (19:1 hexanes–EtOAc). **IR** (thin film) 3464, 1619, 1351, 1246, 1032, 841, 740 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.97 (s, 2 H), 1.84 (bs, 1 H), 1.42 (s, 3 H), 0.17 (s, 18 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 190.9 (C), 158.7 (CH × 2), 140.2 (C × 2), 66.6 (C), 27.3 (CH_3), −1.3 (CH_3 × 6); **HRMS** (ESI+) 291.1207 calcd for $C_{13}H_{24}O_2Si_2Na$, found 291.1209.



1i **4i**

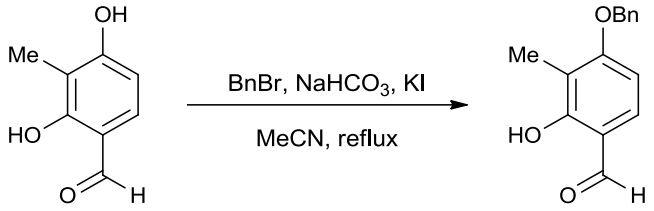
***tert*-Butyl (1-methyl-4-oxo-3,5-bis(trimethylsilyl)cyclohexa-2,5-dien-1-yl) malonate (4i)** Using general method C, mono-*tert*-butyl malonate was coupled to quinol **1i** to give **4i** in 86% yield after flash-column chromatography (19:1 hexanes–EtOAc). **IR** (thin film) 2953, 1725, 1630, 1313, 1244, 1157, 1047, 843 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.99 (s, 2 H), 3.26 (s, 2 H), 1.50 (s, 3 H), 1.47 (s, 9 H), 0.16 (s, 18 H); **^{13}C NMR**

(75 MHz, $CDCl_3$, DEPT) δ 190.7 (C), 165.5(C), 165.3(C), 155.1 (CH × 2), 140.9 (C × 2), 82.2 (C), 75.3 (C), 43.5 (CH_2), 28.1 (CH_3 ×3), 26.6 (CH_3), −1.3 (CH_3 ×6); **HRMS** (ESI+) 433.1837 calcd for $C_{20}H_{34}O_5Si_2Na$, found 433.1853.



S4

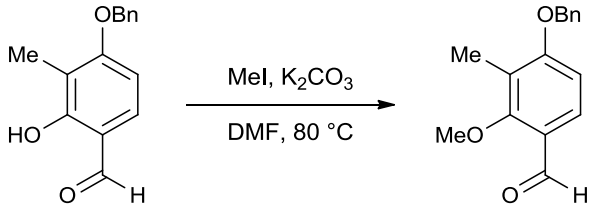
2,4-Dihydroxy-3-methylbenzaldehyde (S4). Phosphorous oxychloride (83 mL, 0.89 mol) was added dropwise to DMF (250 mL) at 0 °C. This was transferred via cannula to a solution of 2-methylresorcinol (50.0 g, 0.40 mol) in DMF (250 mL) at 0 °C. The reaction was stirred for 1.5 h, gradually warming to r.t. The mixture was then cooled to 0 °C and quenched with 2 M NaOH until pH 6. The product was extracted with EtOAc and concentrated. The resulting residue was recrystallized from hot 10% IPA–H_2O to give **S4** (30.30 g) as beige crystalline needles. A second crop of crystals yielded an additional 6.99 g for a total of 37.29 g (61% yield). **mp** 153.0–154.4 °C (uncorrected); **IR** (neat)**:** 3276, 2780, 1622,1596, 1493, 1435, 1306, 1251, 1217, 1095 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 11.67 (s, 1 H), 9.69 (s, 1 H), 7.29 (d, *J* = 8.5 Hz, 1 H), 6.47 (d, *J* = 8.5 Hz, 1 H), 5.62 (s, 1 H), 2.14 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 194.8, 162.4, 161.2, 133.1, 115.3, 111.2, 108.2, 7.2; **HRMS** (ESI+) 151.0390 calcd for $C_8H_7O_3$, found 151.0399.



S4 **S5**

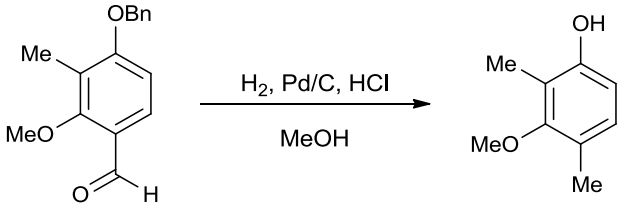
4-(Benzyloxy)-2-hydroxy-3-methylbenzaldehyde (S5). A literature procedure was adapted.[17] 2,4-Dihydroxy-3-methylbenzaldehyde (**S4**) (30.0 g, 0.197 mol), sodium bicarbonate (18.88 g, 0.23 mol), and KI (6.54 g, 0.039 mol) were dissolved in MeCN (500 mL). The flask was fitted with a reflux condenser and slowly warmed to 60 °C. At this time, the benzyl bromide (28.3 mL, 0.236 mol) was added and the mixture was warmed to 80 °C. After refluxing overnight, $KHCO_3$ (9.86 g, 0.099 mol) was added and the mixture was stirred for an additional 5 h, then cooled to r.t. and concentrated. The residue was quenched with 10% aq. HCl (100 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated. The resulting oil was purified by flash-column chromatography using 100% hexanes until removal of benzyl bromide, then 6:1 hexanes–EtOAc to afford a **S5** as a yellow solid (46.89 g, 98% yield). **IR** (thin film, NaCl) 3030, 2923, 2839, 1641, 1626, 1498, 1289, 1250, 1111 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 11.47 (s, 1 H), 9.71 (s, 1 H), 7.42–7.34 (m, 6 H), 6.61 (d, J = 8.7, 1H), 5.19 (s, 2 H), 2.17 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 194.9, 163.5, 161.3, 136.4, 133.3, 128.8, 128.3, 127.2, 115.6, 104.4, 104.2, 70.4, 7.7; **MS** (CI, CH_4) 243.1016 calcd for $C_{15}H_{15}O_3$, found 243.1031.

[17] W. L. Mendelson, M. Holmes, and J. Dougherty, *Synth. Commun.* 1996, **26**, 593.



S5 **S6**

4-(Benzyloxy)-2-methoxy-3-methylbenzaldehyde (S6). To a solution of benzaldehyde **S5** (18.5 g, 0.076 mol) in DMF (300 mL) was added K_2CO_3 (31.7 g, 0.229 mol) and MeI (5.14 mL, 0.826 mol). The flask was fitted with a reflux condenser and the solution was heated to 80 °C for 3 hours. The reaction was then cooled to r.t., poured onto H_2O and extracted with Et_2O. The combined organic layers were washed with H_2O, 10% aq. NaOH and brine; dried over $MgSO_4$; filtered; and concentrated to obtain **S6** as a yellow solid (19.1 g, 97% yield). **IR** (neat) 2934, 2861, 1678, 1591, 1277, 1256, 1100 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.24 (s, 1 H), 7.73 (d, *J* = 8.7 Hz, 1 H), 7.46–7.32 (m, 5 H), 6.81 (d, *J* = 8.7 Hz, 1 H), 5.16 (s, 2 H), 3.87 (s, 3 H), 2.23 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 189.3, 163.2, 162.8, 136.4, 128.8, 128.3, 128.0, 127.3, 123.1, 120.7, 107.9, 70.4, 63.4, 8.9; **HRMS** (ESI+) 279.0992 calcd for $C_{16}H_{16}NaO_3$, found 279.0986.

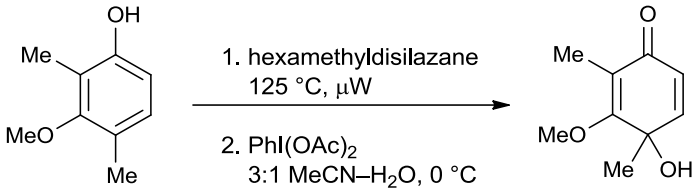


S6 **S7**

3-Methoxy-2,4-dimethylphenol (S7). Benzaldehyde **S6** (15.0 g, 58.5 mmol) 10% Pd/C[18] (3 mol %, 3.2 g) were suspended in MeOH (250 mL) and placed under a H_2 atmosphere (balloon). The mixture was stirred for 3 h. After such time, 1 drop of conc. HCl was added and the reaction was stirred overnight. The mixture was then filtered through a pad of Celite and concentrated. The crude residue was purified by flash-column chromatography (3:1 hexanes–EtOAc) to give **S7** as a pale yellow crystalline solid (8.6 g, 96% yield). **IR** (neat)

[18] Pd/C catalyst obtained from Johnson Matthey (56% H_2O, Type 10R39).

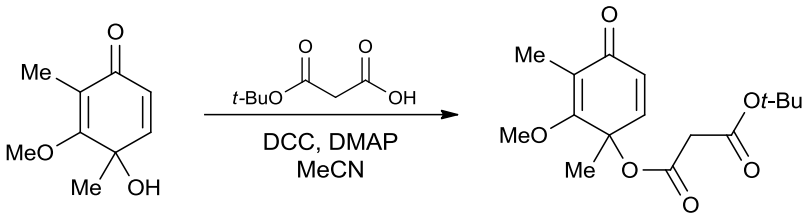
3388, 2940, 2861, 1603, 1496, 1469, 1411, 1285, 1079, 999 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.87 (d, *J* = 8.1 Hz, 1 H), 6.50 (d, *J* = 8.2, 1 H), 4.58 (s, H), 3.71 (s, 3 H), 2.21 (s, 3 H), 2.18 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.5, 153.0, 128.2, 122.9, 117.4, 110.8, 60.1, 15.8, 9.0; **HRMS** (CI, CH_4) 153.0910 calcd for $C_9H_{13}O_2$, found 153.0930.



S7 **1j**

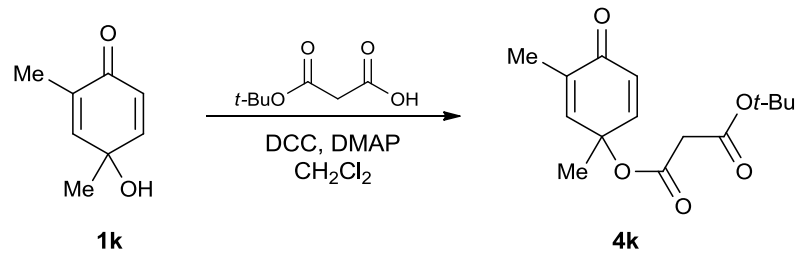
4-Hydroxy-3-methoxy-2,4-dimethylcyclohexa-2,5-dienone (1j). A mixture of phenol **S7** (53 mmol, 8.0 g) and hexamethyldisilazane (17 mL) was heated at 125 °C for 10 minutes in a microwave reactor.[19] General method A was then used to convert the resulting TMS phenol to quinol **1j** in 80% yield after flash-column chromatography (1:0→1:1 hexanes–EtOAc). **IR** (neat) 3391, 2981, 2932, 2851, 1662, 1608, 1456, 1214, 1094 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.66 (d, *J* = 9.9 Hz, 1 H), 6.09 (d, *J* = 9.9 Hz, 1 H), 4.02 (s, 3 H), 2.61 (s, 1 H), 1.87 (s, 3 H), 1.51 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 188.5 (C), 171.5 (C), 147.8 (CH), 126.5 (CH), 117.5 (C), 69.8 (C), 61.7 (CH_3), 26.5 (CH_3), 9.2 (CH_3); **HRMS** (ESI+) 191.0679 calcd for $C_9H_{12}NaO_3$, found 191.0674.

[19] M. M. Mojtahedi, M. R. Saidi, M. Bolourtchian, and M. M. Heravi, *Phosphorus, Sulfur Silicon Relat. Elem.* 2002, **177**, 289.



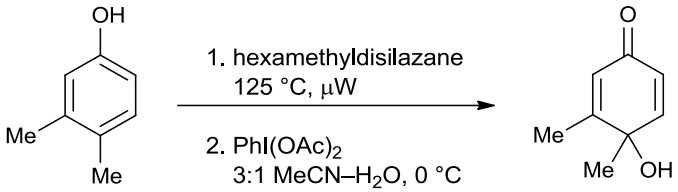
1j **4j**

***tert*-Butyl (2-methoxy-1,3-dimethyl-4-oxocyclohexa-2,5-dien-1-yl) malonate (4j).** Using a modification of general method C, in which MeCN was used as solvent, mono-*tert*-butyl malonate was coupled to quinol **1j** to give **4j** in 98% yield (3:1 hexanes–EtOAc). **IR** (neat) 2987, 2922, 1753, 1730, 1665, 1614, 1321, 1143, 1056 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.61 (d, *J* = 10.0 Hz, 1H), 6.22 (d, *J* = 10.0 Hz, 1 H), 3.91 (s, 3 H), 3.29 (s, 2 H), 1.92 (s, 3 H), 1.56 (s, 3 H), 1.48 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.7, 170.1, 165.40, 165.35, 144.4, 128.0, 118.2, 82.4, 76.6, 61.5, 43.1, 28.1, 25.4, 9.7; **HRMS** (ESI+) 333.1309 calcd for $C_{16}H_{22}NaO_6$, found 333.1307.



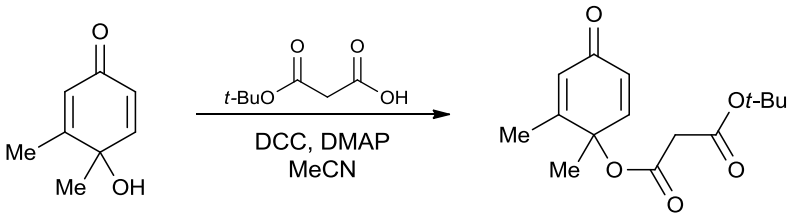
1k **4k**

***tert*-Butyl (1,3-dimethyl-4-oxocyclohexa-2,5-dien-1-yl) malonate (4k).** Using general method C, mono-*tert*-butyl malonate was coupled to quinol **1k**[4] to give **4k**, in 95% yield (9:1 hexanes–EtOAc). **IR** (thin film) 2980, 1753, 1730, 1673, 1645, 1369, 1333, 1144, 1051, 969 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.82 (dd, *J* = 10.1, 3.2 Hz, 1 H), 6.61 (dq, *J* = 3.2, 1.4 Hz, 1 H), 6.15 (d, *J* = 10.1 Hz, 1 H) 3.19 (s, 3 H), 1.82 (d, *J* = 1.4 Hz, 3 H), 1.48 (s, 3 H), 1.40 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 185.5 (C), 165.4 (C), 165.3 (C), 148.3 (CH), 143.6 (CH), 135.1 (C), 128.1 (CH), 82.2 (C), 75.6 (C), 43.1 (CH_2), 27.9 (CH_3 × 3), 26.2 (CH_3), 15.6 (CH_3); **HRMS** (ESI+) 303.1203 calcd for $C_{15}H_{20}O_5Na$, found 303.1196.



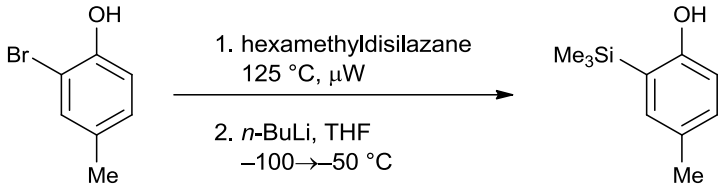
1l

4-Hydroxy-3,4-dimethylcyclohexa-2,5-dienone (1l). A mixture of 3,4-dimethylphenol (8.84 mmol, 1.08 g) and hexamethyldisilazane (2 mL) was heated at 125 °C for 10 min in a microwave reactor.[19] General method A was then used to convert the resulting TMS phenol to quinol **1l** in 48% yield (two steps) after flash-column chromatography (1:0→1:1 hexanes–EtOAc). Identity was verified by comparison of ^{1}H NMR spectrum with literature data.[4]



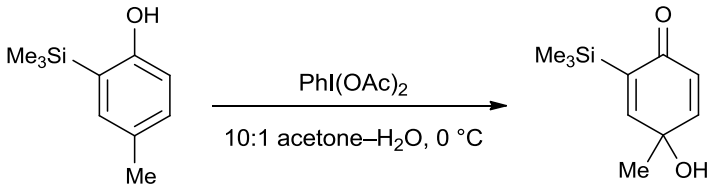
1l **4l**

***tert*-Butyl (1,2-dimethyl-4-oxocyclohexa-2,5-dien-1-yl) malonate (4l).** Using a modification of general method C, in which MeCN was used as solvent, mono-*tert*-butyl malonate was coupled to quinol **1l** to give **4l**, in 73% yield (9:1 hexanes–EtOAc). **IR** (neat) 2979, 2932, 1753, 1729, 1670, 1635, 1142, 1958 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.83 (d, J = 10.1, 1 H), 6.21 (dd, J =1.9, 10.0, 1 H), 6.10–6.08 (m, 1 H), 3.29 (s, 2 H), 1.97 (d, J = 1.4 Hz, 3 H), 1.51 (s, 3 H), 1.47 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 185.4 (C), 165.4 (C), 165.1 (C), 158.7 (C), 149.2 (CH), 128.2 (CH), 127.0 (CH), 82.6 (C), 77.3 (C), 43.0 (CH_2), 28.1 (CH_3 × 3), 26.3 (CH_3), 17.9 (CH_3); **HRMS** (ESI+) 303.1203 calcd for $C_{15}H_{20}O_5Na$, found 303.1206.



S8

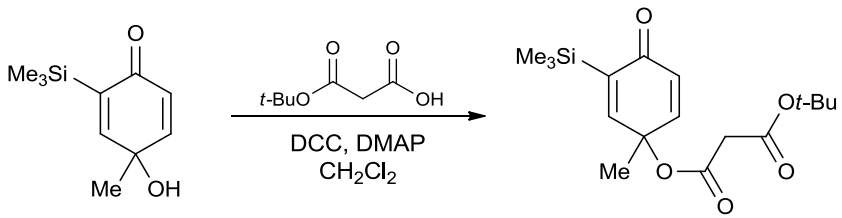
4-Methyl-2-(trimethylsilyl)phenol (S8). A solution of 2-bromo-4-methyl phenol (500 mg, 2.67 mmol) in 1 mL of hexamethyldisilazane was heated at 125 ºC for 20 min in a microwave reactor.[19] After excess hexamethyldisilazane was removed in vacuo, the resulting TMS ether was dissolved in 15 mL of dry THF and cooled to −100 ºC. *n*-BuLi (2.5 M in hexanes, 1.06 mL, 2.65 mmol) was added slowly, then the mixture was allowed to warm to −50 ºC. The reaction was then quenched with saturated aq. NH_4Cl (10 mL). The cooling bath was removed and the mixture was diluted with Et_2O, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash-column chromatography (95:5 hexanes–EtOAc) afforded phenol **S8** (343.1 mg, 62% yield over 2 steps). **IR** (thin film) 3533, 2953, 1599, 1490, 1389, 1244, 1181, 1073, 890, 839 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.16 (d, *J* = 1.7 Hz, 1 H), 7.04 (dd, *J* = 8.1, 2.3 Hz, 1 H), 6.59 (d, *J* = 8.1, 1 H), 4.62 (s, 1 H), 2.29 (s, 3 H), 0.31 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 158.3 (C), 135.8 (CH), 131.2 (CH), 129.5 (C), 125.2 (C), 114.5 (CH), 20.7 (CH_3), −0.8 (CH_3 × 3); **HRMS** (ESI–) 179.0887 calcd for $C_{10}H_{15}OSi$, found 179.1305.



S8 **1m**

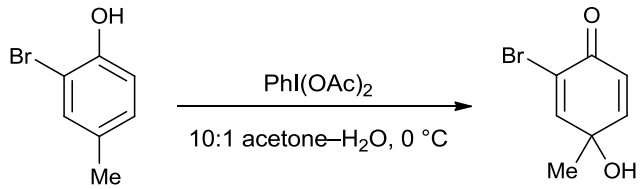
4-Hydroxy-4-methyl-2-(trimethylsilyl)cyclohexa-2,5-dienone (1m). Using a modification of general method A in which 10:1 acetone–H_2O was used as solvent, phenol **S8** was converted into quinol **1m** in 51% yield after flash-column chromatography (5:1 hexanes–EtOAc). **IR** (thin film) 3381, 2958, 1649, 1611, 1361, 1242, 1138, 1050, 841 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.99 (d, *J* = 3.1 Hz, 1 H), 6.83 (dd, *J* = 10.0, 3.1 Hz,

1 H), 2.12 (bs, 1 H), 1.44 (s, 3 H), 0.17 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 188.5 (C), 160.0 (CH), 151.7 (CH), 139.0 (C), 127.8 (CH), 66.8 (C), 27.0 (CH_3), −1.4 (CH_3 × 3); **HRMS** (ESI+) 219.0812 calcd for $C_{10}H_{16}O_2SiNa$, found 219.0825.



1m **4m**

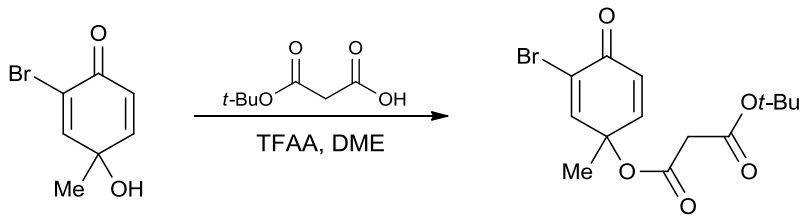
***tert*-Butyl (1-methyl-4-oxo-3-(trimethylsilyl)cyclohexa-2,5-dien-1-yl) malonate (4m).** Using general method C, mono-*tert*-butyl malonate was coupled to quinol **1m** to give **4m** in 82% yield after flash-column chromatography (9:1 hexanes–EtOAc). **IR** (thin film) 2978, 1754, 1732, 1657, 1628, 1369, 1333, 1248, 1140, 1055, 845 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.94 (d, J = 3.1 Hz, 1 H), 6.85 (dd, J = 10.0, 3.1 Hz, 1 H), 6.15 (d, J = 10.0 Hz, 1 H), 3.23 (s, 2 H), 1.50 (s, 3 H), 1.43 (s, 9 H), 0.14 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 187.8 (C), 165.4 (C), 165.3 (C), 155.6 (CH), 147.6 (CH), 140.4 (C), 129.0 (CH), 82.3 (C), 75.2 (C), 43.3 (CH_2), 28.0 (CH_3 × 3), 26.4 (CH_3), −1.5 (CH_3 × 3); **HRMS** (ESI+) 361.1442 calcd for $C_{17}H_{26}O_5SiNa$, found 361.1443.



1n

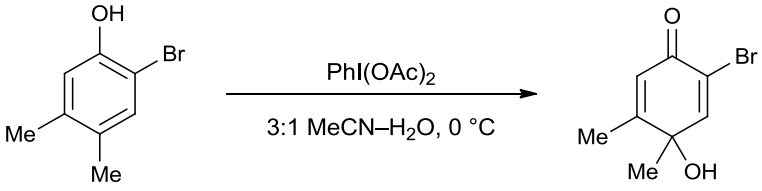
2-Bromo-4-hydroxy-4-methylcyclohexa-2,5-dienone (1n). Using a modification of general method A, in which 10:1 acetone–H_2O was used as solvent, 2-bromo-4-methylphenol gave **1n** as a yellow/orange solid in 76% yield after flash-column chromatography (3:1 hexanes–EtOAc). **IR** (thin film) 3474, 3045, 2980, 2937, 1660, 1594, 1052 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 (d, J = 2.8 Hz, 1 H), 6.92 (dd, J = 10.0, 2.8 Hz,

1 H), 6.27 (d, 10.0 Hz, 1 H), 2.04 (bs, 1 H), 1.53 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 178.6 (C), 152.9 (CH), 152.7 (CH), 125.6 (CH), 123.4 (C), 70.1 (C), 26.5 (CH_3); **HRMS** (ESI+) 224.9522 calcd for $C_7H_7BrO_2Na$, found 224.9531.



1n **4n**

3-Bromo-1-methyl-4-oxocyclohexa-2,5-dien-1-yl *tert*-butyl malonate (4n). Using a modification of general method B, in which the concentration was 0.2 M in quinol, **1n** gave **4n** as a yellow oil in 69% yield after flash-column chromatography (3:1 hexanes–EtOAc). **IR** (neat) 3050, 2981, 2934, 1759, 1728, 1672, 1640, 1606, 1334, 1146, 1056, 965, 824 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 2.9 Hz, 1 H), 6.94 (dd, *J* = 10.0, 2.9 Hz, 1 H), 6.37 (d, *J* = 10.0 Hz, 1 H), 3.30 (s, 2 H), 1.62 (s, 3 H), 1.49 (s, 9 H); **^{13}C NMR** (MHz, $CDCl_3$, DEPT) δ 177.9 (C), 165.3 (C), 165.2 (C), 148.79 (CH), 148.72 (CH), 126.7 (CH), 124.6 (C), 82.7 (C), 76.7 (C), 43.0 (CH_2), 28.0 (CH_3 × 3), 25.9 (CH_3); **HRMS** (ESI+) 367.0152 calcd for $C_{14}H_{17}BrO_5Na$, found 367.0143.

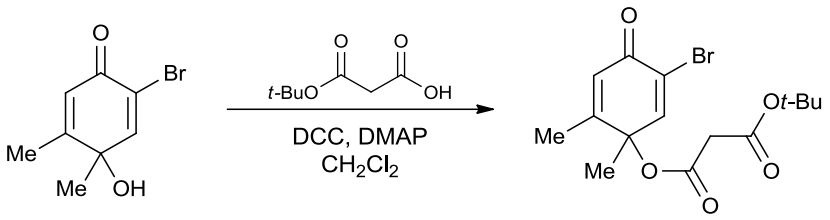


1o

2-Bromo-4-hydroxy-4,5-dimethylcyclohexa-2,5-dienone (1o). Using general method A, 2-bromo-4,5-dimethylphenol[20] was converted into quinol **1o** in 74% yield after flash-column chromatography (3:1 hexanes–EtOAc). **IR** (thin film) 3457, 3038, 2986, 2934, 1648, 1626, 1596, 1363, 1231, 1132, 1041, cm^{-1}; **^{1}H NMR**

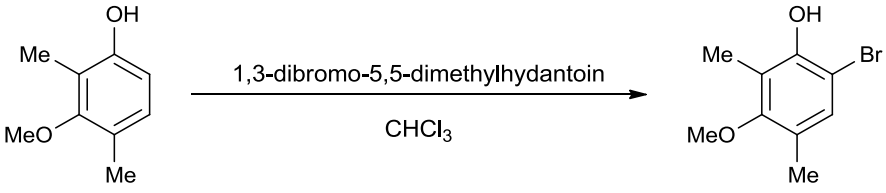
[20] S. Kajigaeshi, T. Kakinami, T. Okamoto, H. Nakamura, M. Fujikawa, and T. Ube, *Bull Chem. Soc. Jpn.* 1987, **60**, 4187.

(300 MHz, $CDCl_3$) δ 7.29 (s, 1 H), 5.95 (q, *J* = 1.4 Hz, 1 H), 3.64 (s, 1 H), 2.05 (d, *J* = 1.4 Hz, 3 H), 1.41 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 179.3 (C), 164.1 (C), 154.1 (CH), 123.8 (CH), 122.6 (C), 71.7 (C), 25.9 (CH_3), 18.2 (CH_3); **HRMS** (ESI+) 238.9678 calcd for $C_8H_9OBr_2Na$, found 238.9736.



1o **4o**

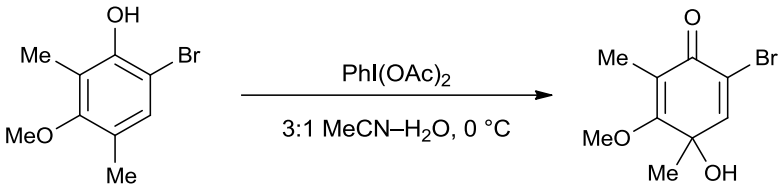
5-Bromo-1,2-dimethyl-4-oxocyclohexa-2,5-dien-1-yl tert-butyl malonate (4o). Using general method C, mono-*tert*-butyl malonate was coupled to quinol **1o** to give **4o** in 96% yield after flash-column chromatography (5:1 hexanes–EtOAc). **IR** (thin film) 2979, 2933, 2859, 1729, 1666, 1332, 1222, 1145 1030 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.27 (s, 1 H), 6.20 (q, *J* = 1.3 Hz, 1 H), 3.30 (s, 2 H), 1.99 (d, *J* = 1.3 Hz, 3 H), 1.55 (s, 3 H) 1.47 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 177.9 (C), 165.0 (C), 164.8 (C), 159.3 (C), 149.2 (CH), 124.8 (CH), 124.0 (C), 82.4 (C), 78.4 (C), 42.6 (CH_2), 27.8 (CH_3 × 3), 25.7 (CH_3), 17.5 (CH_3); **HRMS** (ESI+) 381.0308 calcd for $C_{15}H_{19}O_5BrNa$, found 381.0337.



S7 **S9**

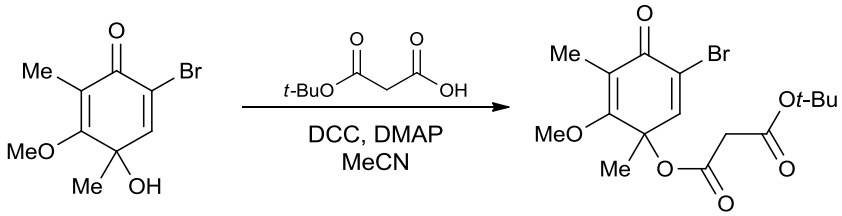
6-Bromo-3-methoxy-2,4-dimethylphenol (S9). Phenol **S7** (500 mg, 3.29 mmol) was dissolved in chloroform (30 mL). To this, 1,3-dibromo-5,5-dimethylhydantoin (70 mg, 2.5 mmol) was added portion-wise. The reaction mixture was protected from light and stirred overnight before being quenched with 10% aq. $Na_2S_2O_3$ and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The resulting brown solid was purified by flash-column chromatography (9:1 hexanes–EtOAc) to

afford **S9** as a yellow solid (39 mg, 51% yield), which quickly turned brown upon standing (product is suspected to be light sensitive).; **IR** (neat) 3511, 2939, 1596, 1470, 1405, 1308, 1235, 1209, 1085, 1003, 778 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.12 (s, 1 H), 5.42 (s, 1 H), 3.69 (s, 3 H), 2.23 (s, 3 H), 2.20 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 157.3 (C), 149.3 (C), 129.8 (CH), 124.3 (C), 119.2 (C), 104.7 (C), 60.1 (CH_3), 15.6 (CH_3), 10.1 (CH_3); **HRMS** (ESI+) 229.9937 calcd for $C_9H_{11}BrO_2$, found 229.0151.



S9 **1p**

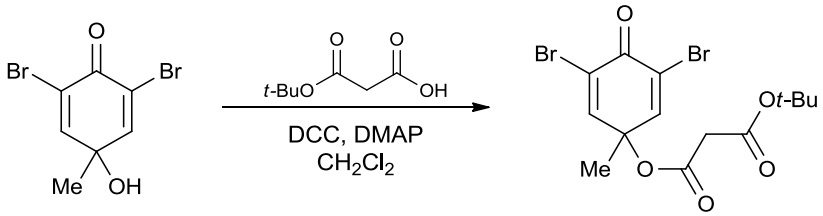
6-Bromo-4-hydroxy-3-methoxy-2,4-dimethylcyclohexa-2,5-dienone (1p). Using general method A, phenol **S9** was converted into quinol **1p** in 51% after flash-column chromatography (1:0→1:1 hexanes–EtOAc). **IR** (neat) 3397, 2928, 2853, 1640, 1601, 1370, 1299, 1208, 1150, 1062, 868, 762 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.08 (s, 1 H), 4.05 (s, 3 H), 1.85 (s, 3 H), 1.51 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 181.6 (C), 171.7 (C), 148.7 (CH), 122.7 (C), 116.8 (C), 71.6 (C), 61.6 (CH_3), 25.8 (CH_3 × 3), 9.9 (CH_3); **HRMS** (ESI+) 268.9784 calcd for $C_9H_{11}BrO_3Na$, found 268.9781.



1p **4p**

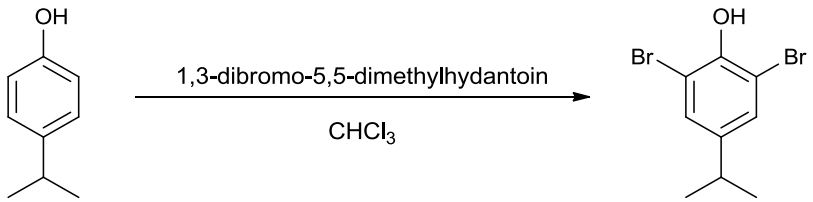
5-Bromo-2-methoxy-1,3-dimethyl-4-oxocyclohexa-2,5-dien-1-yl-*tert*-butyl malonate (4p). Using a modification of general method C, in which MeCN was used as solvent, mono-*tert*-butyl malonate was coupled to quinol **1p** to give **4p** in 55% yield and 19% of recovered **1p** after flash-column chromatography (9:1

hexanes–EtOAc). **IR** (neat) 2979, 2933, 2853, 1754, 1730, 1657, 1651, 1613, 1309, 1214, 1143, 1054 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.04 (s, 1 H), 3.90 (s, 3 H), 3.28 (s, 2 H), 1.95 (s, 3 H), 1.56 (s, 3 H), 1.46 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 180.5 (C), 170.2 (C), 165.3 (C), 165.1 (C), 144.1 (CH), 124.7 (C), 117.0 (C), 82.5 (C), 77.6 (C), 61.7 (CH_3), 42.9 (CH_2), 28.0 (CH_3 × 3), 25.1 (CH_3), 10.6 (CH_3); **HRMS** (ESI+) 441.0414 calcd for $C_{16}H_{21}BrO_6Na$, found 411.0432.



1q **4q**

***tert*-Butyl (3,5-dibromo-1-methyl-4-oxocyclohexa-2,5-dien-1-yl) malonate (4q).** Using general method C, mono-*tert*-butyl malonate was coupled to quinol **1q**[21]Error! Bookmark not defined. to give **4q** in quantitative yield after flash-column chromatography (5:1 hexanes–EtOAc). **IR** (thin film) 3051, 2977, 2927, 1729, 1681, 1600, 1310, 1142, 1052, 698 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 (s, 2 H), 3.30 (s, 2 H), 1.63 (s, 3 H), 1.48 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 165.3 (C × 2), 165.1 (C), 148.9 (CH × 2), 82.9 (C), 77.7(C), 42.9 (CH_2), 28.1 (CH_3 × 3), 25.7 (CH_3); **HRMS** (ESI+) 444.9257 calcd for $C_{14}H_{16}Br_2O_5Na$, found 444.9250.

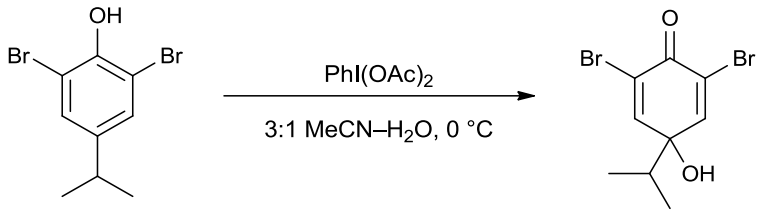


S10

2,6-dibromo-4-isopropyl phenol (S10). A solution of 4-isopropyl phenol (266 mg, 1.95 mmol) in 15 mL of dry CH_2Cl_2 was treated with 1,3-dibromo-5,5-dimethylhydantoin (614.3 mg, 2.14 mmol) in small portions. The

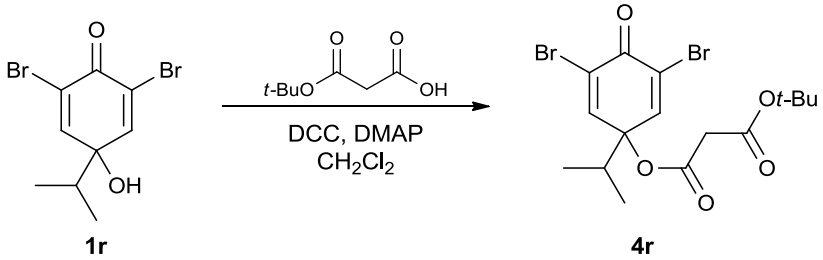
[21] Prepared according to: A. McKillop, L. McLaren, and R. J. K. Taylor, *J. Chem. Soc., Perkin Trans. 1* 1994, 2047.

mixture was then protected from light and stirred. After 16 h, the mixture was diluted with CH_2Cl_2 and washed with 10% HCl solution, dried over Na_2SO_4, filtered and concentrated. Crude product was purified by flash-column chromatography (39:1 hexanes-EtOAc) to give 285.8 mg of **S10** in 49% yield. Identity was verified by comparison of ^{1}H NMR spectrum with literature data.[22]



S10 **1r**

2,6-Dibromo-4-hydroxy-4-isopropylcyclohexa-2,5-dienone (1r). Using general method A, **S10** was converted into quinol **1r** in 78% yield after flash-column chromatography (5:1 hexanes–EtOAc). **IR** (thin film) 3434, 1671, 1596, 1461, 1358, 997, 692 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 (s, 2 H), 2.29 (bs, 1 H), 2.06 (hept, J = 6.9 Hz, 1 H), 1.01 (d, J = 6.9 Hz, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 172.5 (C), 151.0 (CH × 2), 122.2 (C × 2), 77.3 (C), 37.3 (CH), 17.1 (CH_3 × 2); **HRMS** (ESI+) 330.8940 calcd for $C_9H_{10}Br_2O_2Na$, found 330.8940.

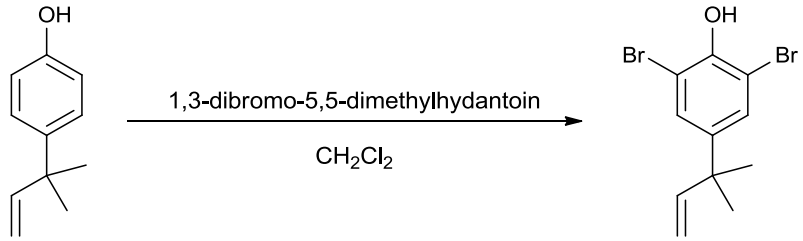


1r **4r**

***tert*-Butyl (3,5-dibromo-1-isopropyl-4-oxocyclohexa-2,5-dien-1-yl) malonate (4r).** Using general method C, mono-*tert*-butyl malonate was coupled to quinol **1r** to give **4r** in 95% yield after flash-column

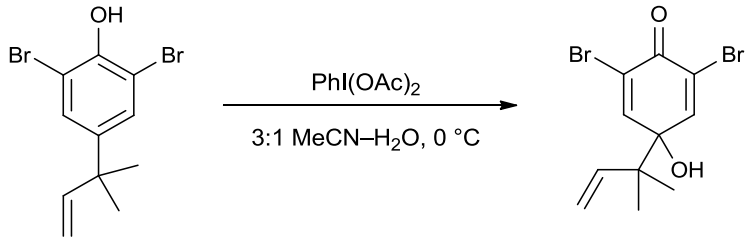
[22] (a) A. O. Fitton, A. Rigby, and R. J. Hurlock, *J. Chem. Soc. C* 1968, 1000. (b) J. Eriksson, S. Rahm, N. Green, Å. Bergman, E. Jakobsson, *Chemosphere* 2004, **54**, 117.

chromatography (9:1 hexanes–EtOAc). **IR** (thin film) 2976, 2934, 1730, 1682, 1599, 1463, 1329, 1255, 1147, 1002, 842 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 (s, 2 H), 3.35 (s, 2 H), 2.22 (hept, *J* = 6.9 Hz 1 H), 1.49 (s, 9 H), 1.01 (d, *J* = 6.9 Hz, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 172.2 (C), 165.1 (C), 165.0 (C), 147.6 (CH × 2), 122.6 (C), 82.8 (C), 82.6 (C), 42.8 (CH_2), 36.9 (CH), 27.9 (CH_3 × 3), 16.9 (CH_3 × 2); **HRMS** (ESI+) 474.9550 calcd for $C_{16}H_{20}{}^{81}Br_2O_5$, found 474.9569.



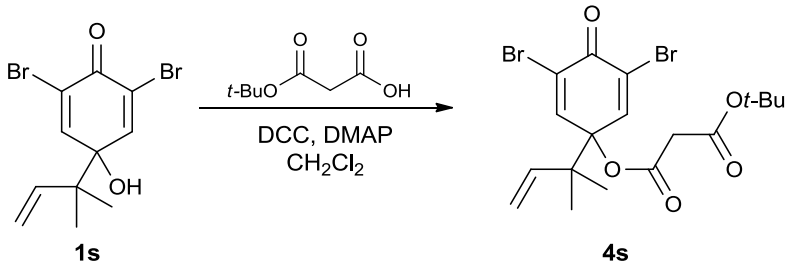
S11

2,6-Dibromo-4-(2-methylpent-4-en-2-yl)phenol (S11). A solution of 4-(2-methylpent-4-en-2-yl)phenol[14] (159.9 mg, 0.90 mmol) in 12 mL of CH_2Cl_2 was treated with 1,3-dibromo-5,5-dimethylhydantoin (259.3 mg, 0.9 mmol). The reaction flask was protected from light and stirred for 16 h. The mixture was then diluted with CH_2Cl_2, washed with 10% aq. HCl and brine, dried over Na_2SO_4, filtered, and concentrated. Flash-column chromatography (20:1 hexanes–Et_2O) provided **S11** (243 mg, 80% yield). **IR** (thin film) 3498, 2964, 1555, 1475, 1393, 1285, 1163, 998, 917, 733 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38 (s, 2 H), 5.74 (s, 1 H), 5.61–5.42 (m, 1 H), 4.99 (s, 1 H), 4.97–4.90 (m, 1 H), 2.28 (d, *J* = 7.3 Hz, 2 H), 1.24 (s, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 147.2 (C), 144.2 (C), 134.6 (CH), 129.8 (CH × 2), 117.8 (CH_2), 48.7 (CH_2), 37.4 (C), 28.5 (CH_3 × 2); **HRMS** (ESI–) 333.9386 calcd for $C_{12}H_{14}Br_2O$, found 333.1305.



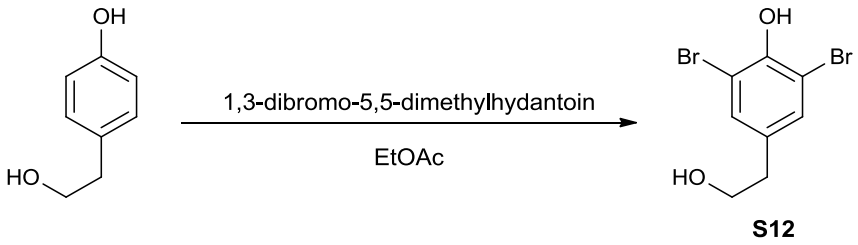
S11 **1s**

2,6-Dibromo-4-hydroxy-4-(2-methylpent-4-en-2-yl)cyclohexa-2,5-dienone (1s). Using general method A, phenol **S11** was converted into quinol **1s** in 74% yield after flash-column chromatography (5:1 hexanes–EtOAc). **IR** (thin film) 3470, 2970, 1677, 1592, 1467, 1312, 988, 918 cm^{-1} ; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.48 (s, 2 H), 5.79 (ddt, *J* = 17.5, 10.1, 7.4 Hz, 1 H), 5.11 (d, *J* = 10.1 Hz, 1 H), 5.07 (d, *J* = 17.5 Hz, 1 H), 3.08 (s, 2 H) 2.17 (d, *J* = 7.4 Hz, 2 H), 1.04 (s, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 172.5 (C), 151.5 (CH × 2), 134.0 (CH), 121.8 (C × 2), 118.7 (CH_2), 79.0 (C), 43.0 (C), 42.0 (CH_2), 22.2 (CH_3 × 2); **HRMS** (ESI+) 370.9253 calcd for $C_{12}H_{14}Br_2O_2Na$, found 370.9264.



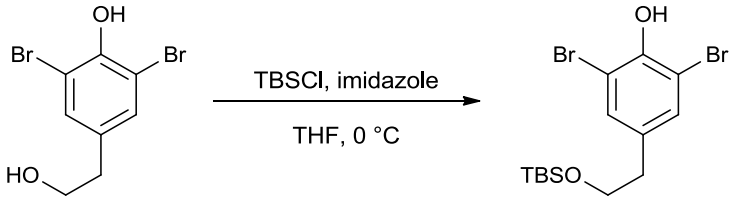
1s **4s**

***tert*-Butyl (3,5-dibromo-1-(2-methylpent-4-en-2-yl)-4-oxocyclohexa-2,5-dien-1-yl) malonate (4s).** Using general method C, mono-*tert*-butyl malonate was coupled to quinol **1s** to give **4s** in 81% yield after flash-column chromatography (19:1 hexanes–EtOAc). **IR** (thin film) 2974, 1730, 1682, 1595, 1466, 1313, 1254, 1145, 991, 697 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 (s, 2 H), 5.75 (ddt, *J* = 17.3, 10.1, 7.4 Hz, 1 H), 5.12 (d, *J* = 10.1 Hz, 1 H), 5.06 (d, *J* = 17.3 Hz, 1 H), 3.35 (s, 2 H) 2.17 (d, *J* = 7.4 Hz, 2 H), 1.50 (s, 9 H), 1.03 (s, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 172.1 (C), 165.1 (C), 165.0 (C), 147.8 (CH × 2), 133.2 (CH), 122.7 (C), 119.2 (CH_2), 84.7 (C), 82.9 (C), 44.3 (C), 42.9 (CH_2), 41.8 (CH_2), 28.1 (CH_3 × 3), 22.3 (CH_3 × 2); **HRMS** (ESI+) 514.9864 calcd for $C_{19}H_{24}Br_2O_5Na$, found 514.9882.



S12

2,6-Dibromo-4-(2-hydroxyethyl)phenol (S12). To a solution of 2-(4-hydroxyphenyl)ethanol[23] (150 mg, 1.09 mmol) in EtOAc (11 mL) was added 1,3-dibromo-5,5-dimethylhydantoin (312 mg, 1.09 mmol). The solution was protected from light and stirred for 15 h. The reaction was then diluted with EtOAc and quenched with 10% aq. HCl. The organic layer was washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated. The crude material was purified by flash-column chromatography (2:1 hexanes/EtOAc) to give **S12** as a yellow solid (190 mg, 59% yield). **IR** (thin film) 3389, 2975, 2952, 2891, 1557, 1475, 1408, 1238, 1012, 997, 736 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 (s, 2 H), 5.80 (bs, 1 H), 3.83 (t, *J* = 6.4 Hz, 2 H), 2.76 (t, *J* = 6.4 Hz, 2 H), 1.47 (s, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 148.1 (C), 133.5 (C), 132.6 (CH × 2), 109.9 (C × 2), 63.4 (CH_2), 37.7 (CH_2); **HRMS** (ESI–) 292.8818 calcd for $C_8H_7Br_2O_2$, found 292.8810.

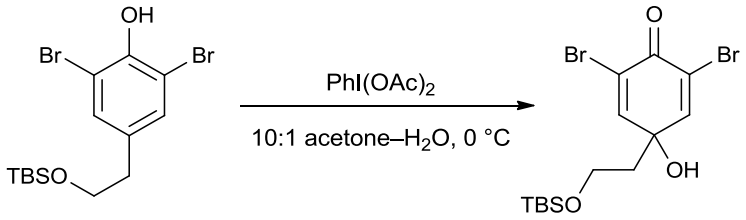


S12 **S13**

2,6-Dibromo-4-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)phenol (S13). Imidazole (48 mg, 0.71 mmol) was added to a solution of alcohol **S12** (175 mg, 0.591 mmol) in THF (6 mL). The solution was cooled to 0 °C and TBSCl (107 mg, 0.710 mmol) was added. The mixture was stirred for 7 h, then quenched with saturated aq. $NaHCO_3$ (10 mL). The mixture was diluted with Et_2O and the organic layer was washed with H_2O and brine, dried over $MgSO_4$, and concentrated. The crude material, a mixture of alkyl and aryl silyl ethers, was purified

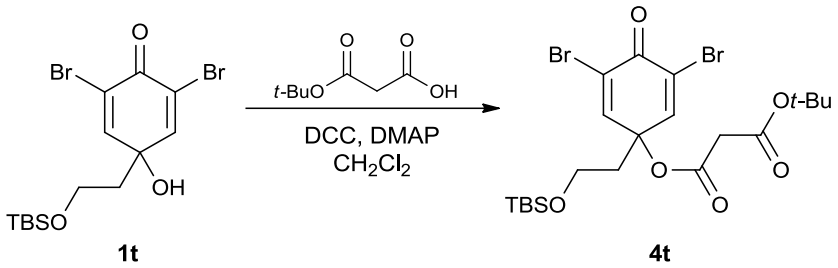
[23] Although this substrate is commercially available, we chose to prepare it by LAH reduction of the less expensive methyl 4-hydroxyphenylacetate.

by flash-column chromatography (5:1 toluene–petroleum ether) to give **S13** as a yellow oil (65 mg, 27% yield). **IR** (thin film) 3512, 2955, 2928, 2858, 1563, 1472, 1256, 1163, 1100, 836, 778, 738 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 (s, 2 H), 5.77 (s, 1 H), 3.74 (t, *J* = 6.4 Hz, 2 H), 2.69 (t, *J* = 6.4 Hz, 2 H), 0.87 (s, 9 H), –0.03 (s, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 147.7 (C), 134.4 (C), 132.8 (CH × 2), 109.5 (C × 2), 63.9 (CH_2), 38.0 (CH_2), 26.0 (CH_3 × 3), 18.4 (C), −5.3 (CH_3 × 2); **HRMS** (ESI–) 406.9683 calcd for $C_{14}H_{21}Br_2O_2Si$, found 406.9683.



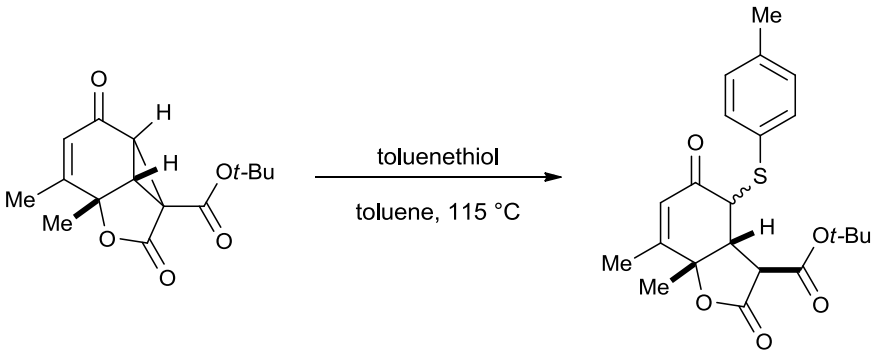
S13 **1t**

2,6-Dibromo-4-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-4-hydroxycyclohexa-2,5-dienone (1t). Using a modification of general method A, in which 10:1 acetone–H_2O was used as solvent, **S13** gave **1t** as a yellow solid in 42% yield after flash-column chromatography (5:1 hexanes/EtOAc). **IR** (thin film) 3466, 3036, 2926, 2856, 1668, 1592, 1471, 1349, 1093, 992, 840, 770, 701 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42 (s, 2 H), 4.51 (s, 1 H), 3.96 (t, *J* = 5.4 Hz, 2 H), 1.99 (t, *J* = 5.4 Hz, 2 H), 0.91 (s, 9 H), 0.11 (s, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.4 (C), 151.7 (CH × 2), 121.0 (C × 2), 74.3 (C), 60.4 (CH_2), 41.0 (CH_2), 25.9 (CH_3 × 3), 18.1 (C), 5.5 (CH_3 × 2); **HRMS** (ESI+) 446.9608 calcd for $C_{17}H_{22}Br_2O_3SiNa$, found 446.9600.



1t **4t**

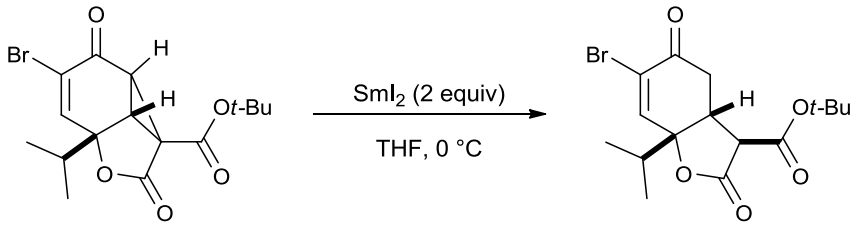
***tert*-Butyl (3,5-dibromo-1-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-4-oxocylcohexa-2,5-dien-1-yl) malonate (4t).** Using general method C, mono-*tert*-butyl malonate was coupled to quinol **1t** to give **4t** as a colorless oil in 96% yield after flash-column chromatography (10:1 hexanes/EtOAc). **IR** (thin film) 2953, 2929, 2856, 1757, 1732, 1682, 1599, 1369, 1257, 1142, 1099, 838, 779 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (s, 2 H), 3.79 (t, 5.5 Hz, 2 H), 3.30 (s, 2 H), 2.08 (t, 5.5 Hz, 2 H), 1.48 (s, 9 H), 0.88 (s, 9 H), 0.05 (s, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 172.5 (C), 165.0 (C × 2, overlapped), 148.7 (CH × 2), 121.9 (C × 2), 82.9 (C), 79.5 (C), 57.5 (CH_2), 43.0 (CH_2), 42.7 (CH_2), 28.1 (CH_3 × 3), 26.0 (CH_3 × 3), −5.3 (CH_3 × 2); **HRMS** (ESI+) 589.0227 calcd for $C_{21}H_{32}Br_2O_6SiNa$, found 589.0229.



12o **13**

(3S,3a*R*,7a*S*)-*tert*-Butyl 7,7a-dimethyl-2,5-dioxo-4-(*p*-tolylthio)-2,3,3a,4,5,7a-hexahydrobenzofuran-3-carboxylate (13). A mixture of crude cyclopropane **12o** (68 mg, 0.24 mmol) and *p*-toluenethiol (30.3 mg, 0.24 mmol) was dissolved in 5 mL toluene. A condenser was attached to the flask and the reaction was heated to 115 ºC for 1 h. The mixture was allowed to cool to r.t. The solvent was removed in vacuo and the residue purified by flash-column chromatography to give **13** (36.7 mg, 37.2% yield from **4o**), as a 2:1 inseparable

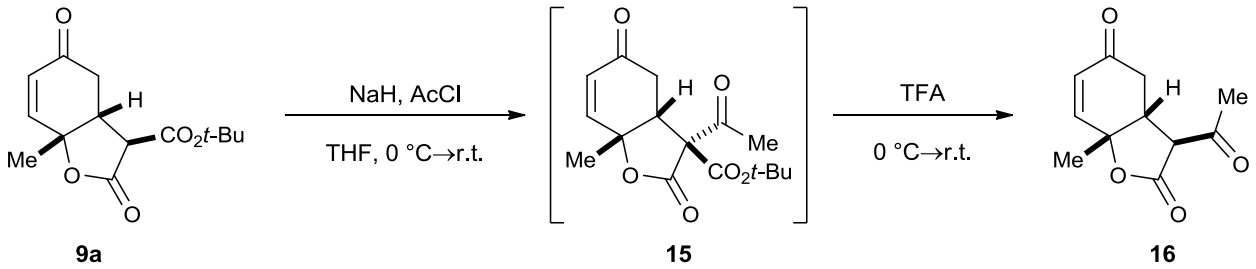
mixture of diastereomers. **IR** (thin film) 2979, 2928, 1787, 1731, 1675, 1370, 1293, 1257, 1153, 1090, 952 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$, *denotes minor diastereomer) δ *7.39 (d, *J* = 8.2 Hz), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.16 (d, *J* = 7.9 Hz, 2 H), *7.15 (d, *J* = 8.4 Hz), *6.02 (q, *J* = 1.4 Hz), 5.94 (dq, *J* = 1.3, 1.3 Hz, 1 H), *4.16 (d, *J* = 5.0 Hz), 3.74 (dd, *J* = 1.9, 1.2 Hz, 1 H), *3.66 (dd, *J* = 11.9, 5.0 Hz), 3.48 (dd, *J* = 12.5, 2.0 Hz, 1 H), *3.37 (d, *J* = 11.9 Hz), 3.32 (d, *J* = 12.5, Hz, 1 H), 2.34 (s, 3 H) *2.34 (s), 2.06 (d, *J* = 1.4 Hz, 3 H), *2.01 (d, *J* = 1.3 Hz), 1.90 (s, 3 H), *1.66 (s), *1.53 (s), 1.46 (s, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$, mixture of diastereomers) δ 191.2 (C), 190.5 (C), 169.7 (C), 168.5 (C), 166.3 (C), 164.9 (C), 157.1 (C), 156.0 (C), 139.5 (C), 138.5 (C), 133.9 (CH), 132.8 (CH), 130.3 (CH), 130.2 (CH), 129.6 (C), 128.6 (C), 127.0 (CH), 126.0 (CH), 84.0 (C), 83.4 (C), 83.3 (C), 81.9 (C), 56.3 (CH), 52.7 (CH), 51.9 (CH), 51.7 (CH), 51.3 (CH), 50.0 (CH), 28.04 (CH_3), 28.02 (CH_3), 25.5 (CH_3), 22.5 (CH_3), 21.4 (CH_3), 21.3 (CH_3), 18.6 (CH_3), 18.3 (CH_3); **HRMS** (ESI+) 425.1393 calcd for $C_{22}H_{26}O_5SNa$, found 425.1403.



12r **14**

(3S,3aR,7aS)-*tert*-Butyl 6-bromo- 7a-isopropyl- 2,5-dioxo- 2,3,3a,4,5,7a-hexahydrobenzofuran-3-carboxylate (14). A solution of SmI_2 in THF (4.5 mL, ~0.16 mmol) was added slowly to cyclopropane **12r** (22 mg, 0.059 mmol) at 0 °C. The reaction mixture was stirred for ~5 min before quenching with 0.5 mL of 10% aq. HCl. The cooling bath was removed and the mixture was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude material was purified by flash-column chromatography (5:1 hexanes–EtOAc) to give **14** (8.7 mg, 39% yield). **IR** (thin film) 2978, 2927, 1785, 1716, 1699, 1371, 1152, 994, 948 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 1.7 Hz, 1 H), 3.47 (dtd, *J* = 11.9, 3.8, 1.7 Hz, 1 H), 3.35 (d, *J* = 12.0 Hz, 1 H), 2.84 (d, *J* = 3.8 Hz, 2 H), 2.27 (hept, *J* = 6.9 Hz, 1 H), 1.50 (s, 9 H), 1.14 (d, *J* =

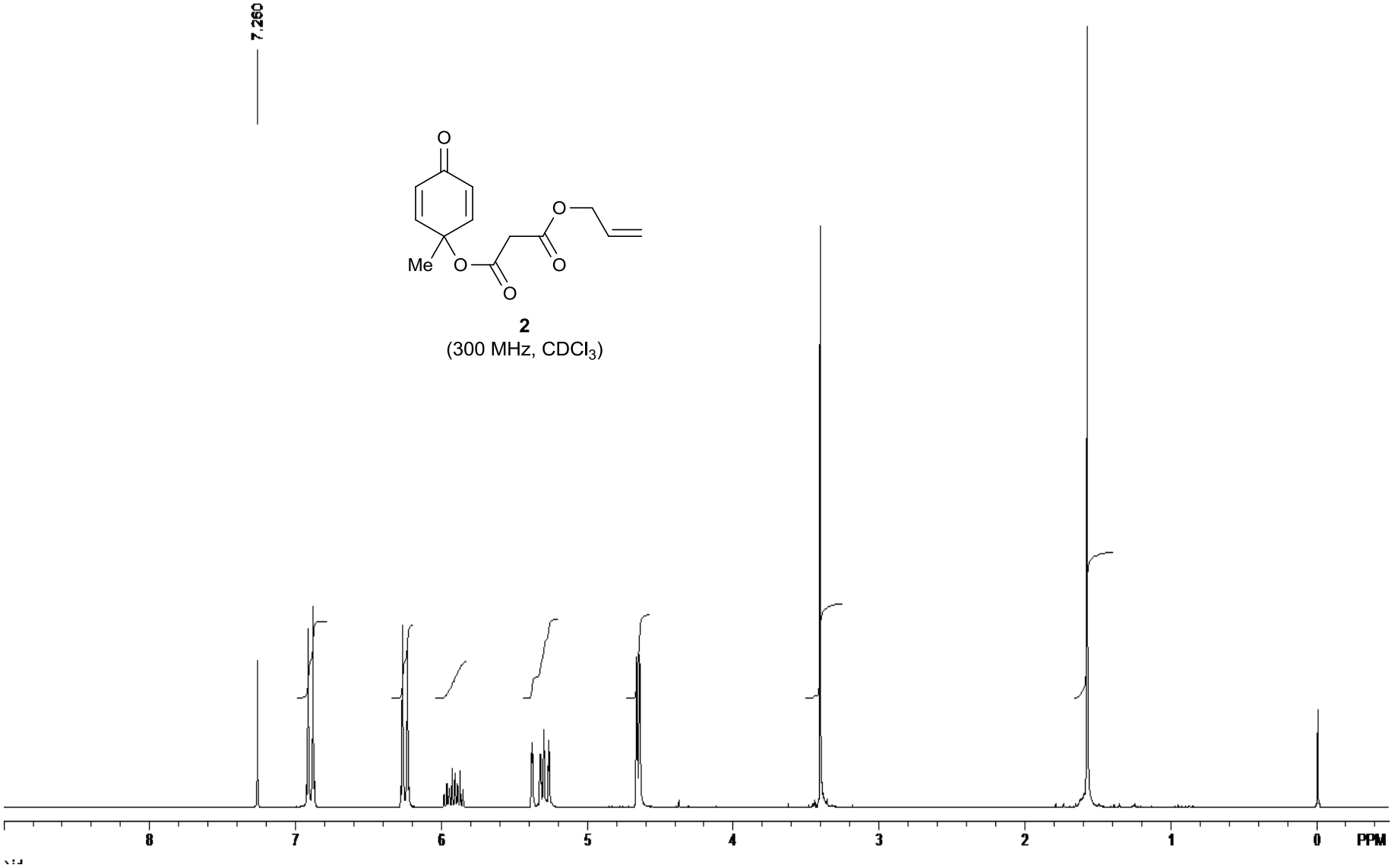
6.9 Hz, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 187.3 (C), 168.8 (C), 165.2 (C), 146.4 (CH), 126.5 (C), 86.5 (C), 84.2 (C), 53.3 (CH), 40.0 (CH), 37.4 (CH_2), 36.1 (CH), 28.1 (CH_3 × 3), 17.7 (CH_3), 16.9 (CH_3); **HRMS** (ESI+) 395.0465 calcd for $C_{16}H_{21}BrO_5Na$, found 395.0445.



3-Acetyl-7a-methyl-3a,4-dihydrobenzofuran-2,5(3*H*,7a*H*)-dione (16). Compound **9a** (20 mg, 0.075 mmol) was added to a suspension of NaH (60% in mineral oil, 7.2 mg, 1.8 mmol) in THF (0.75 mL) at 0 °C. After 15 min, acetyl chloride (11 µL, 0.15 mmol) was added. The mixture was allowed to warm to r.t. and stirred for 16 h, at which point the THF was removed under reduced pressure. The remaining residue[24] was cooled to 0 °C and TFA (2 mL) was added. The solution was allowed to warm to r.t. and stirred for 4 h. It was then quenched with saturated aq. $NaHCO_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. The crude material was purified by flash-column chromatography (3:1 hexanes/EtOAc) to give **16** (7.3 mg, 46% yield). **IR** (thin film) 2980, 2925, 1769, 1715, 1685, 1372, 1237, 1095, 957 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.68 (dd, *J* = 10.4, 2.1 Hz, 1 H), 6.08 (d, 10.4 Hz, 1 H), 3.52 (d, 12.0 Hz, 1 H), 3.38 (dddd, *J* = 12.0, 5.5, 2.1, 2.1 Hz, 1 H), 2.73 (dd, *J* = 17.7, 5.5 Hz, 1 H), 2.55 (d, *J* = 17.7 Hz, 1 H), 2.46 (s, 3 H), 1.71 (s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$, DEPT) δ 199.3 (C), 195.0 (C), 169.5 (C), 147.0 (CH), 129.7 (CH), 80.4 (C), 57.8 (CH), 41.9 (CH), 36.3 (CH_2), 30.3 (CH_3), 24.0 (CH_3); **HRMS** (ESI–) 207.0663 calcd for $C_{11}H_{11}O_4$, found 207.0684.

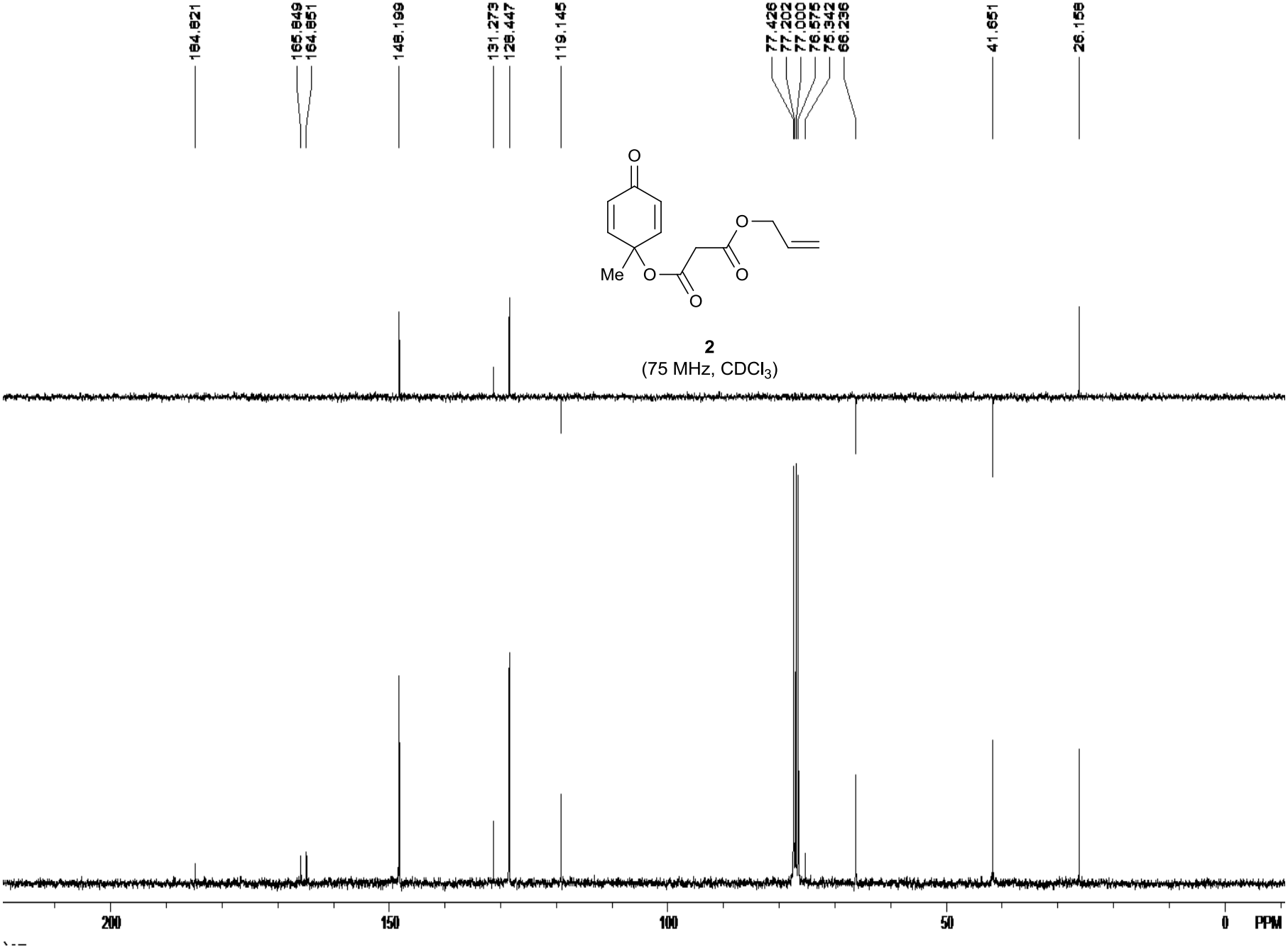
[24] The crude residue was identified as intermediate **15** by ^{1}H NMR.

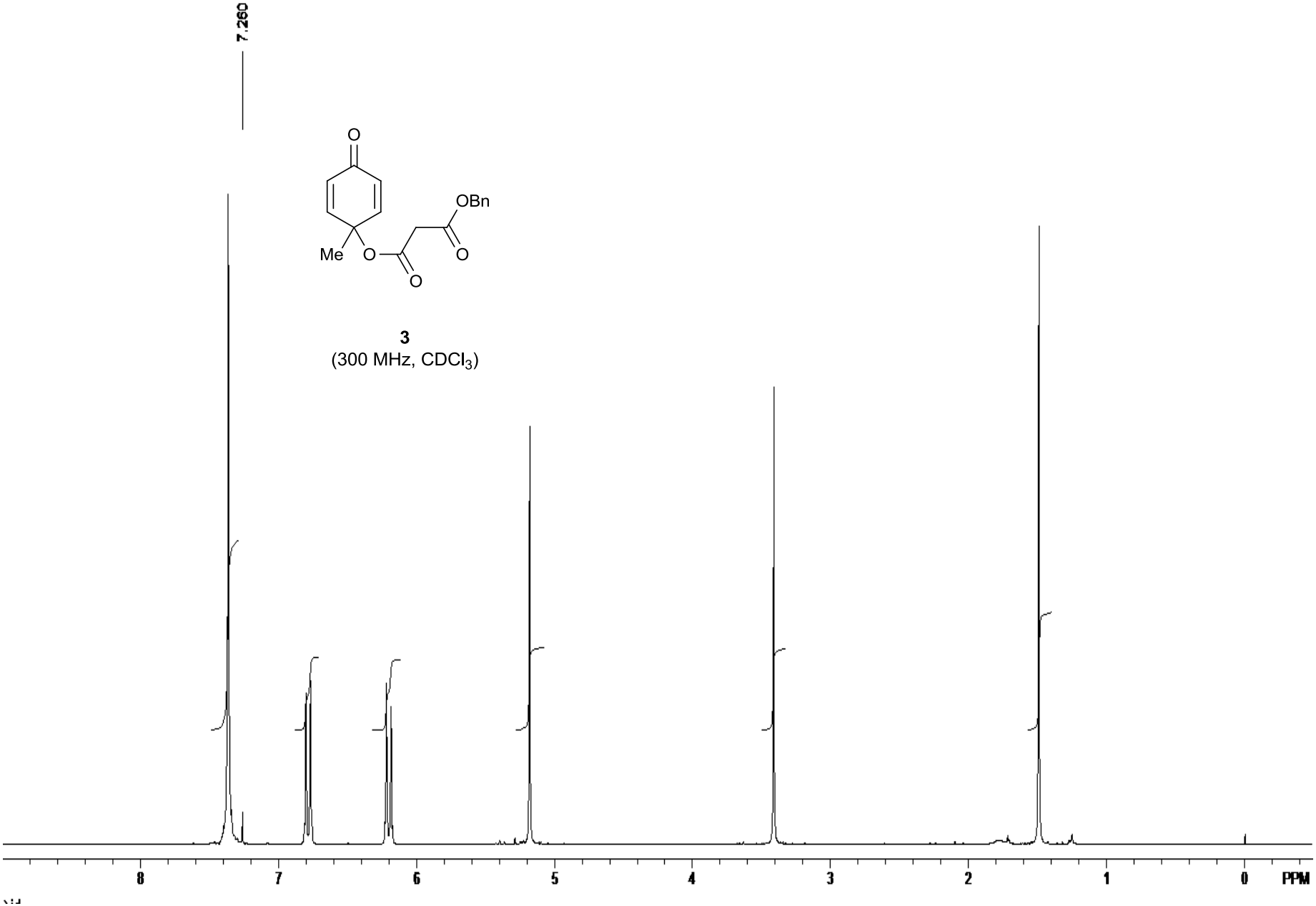
Copies of ^{1}H and ^{13}C NMR spectra



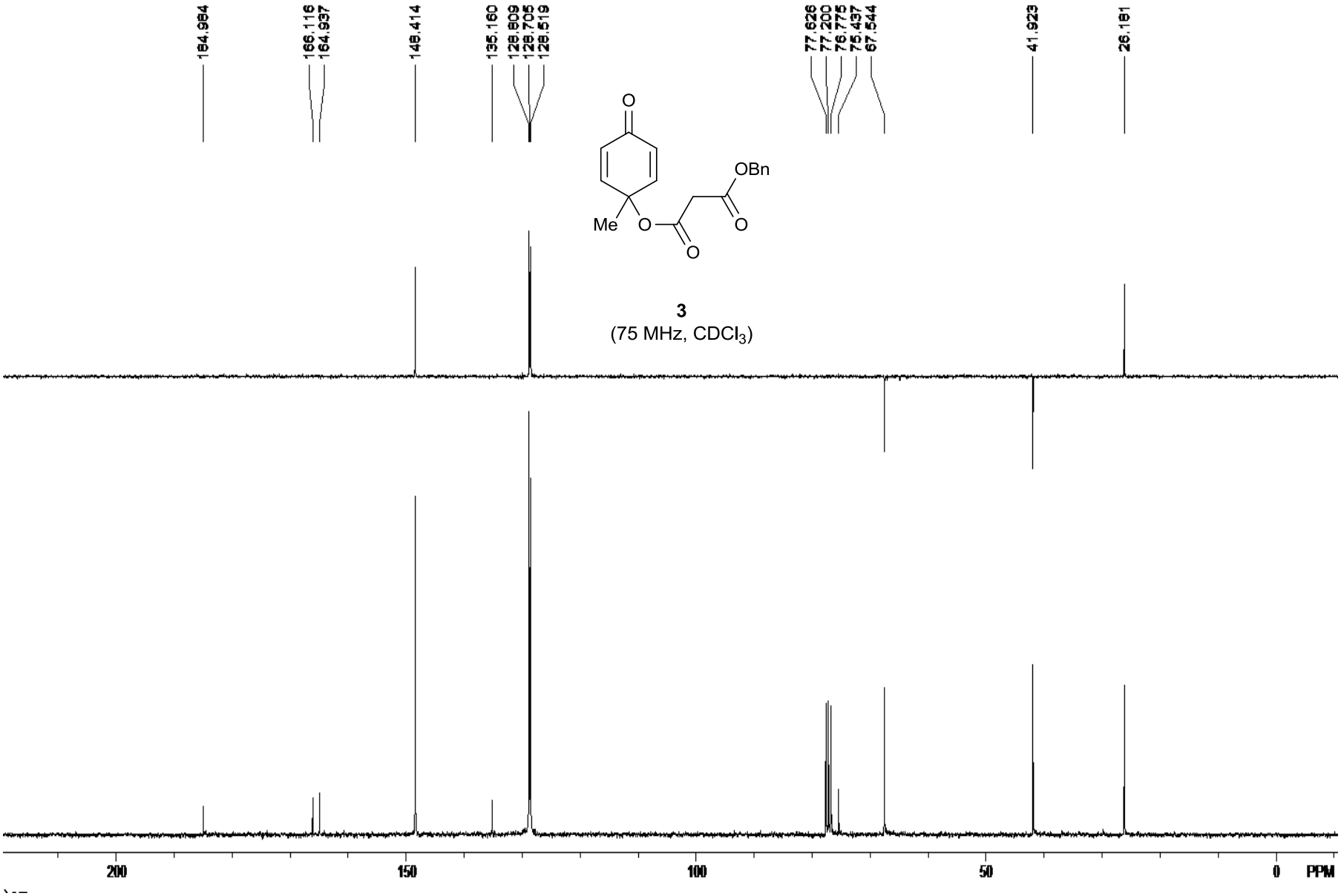
2

(300 MHz, $CDCl_3$)

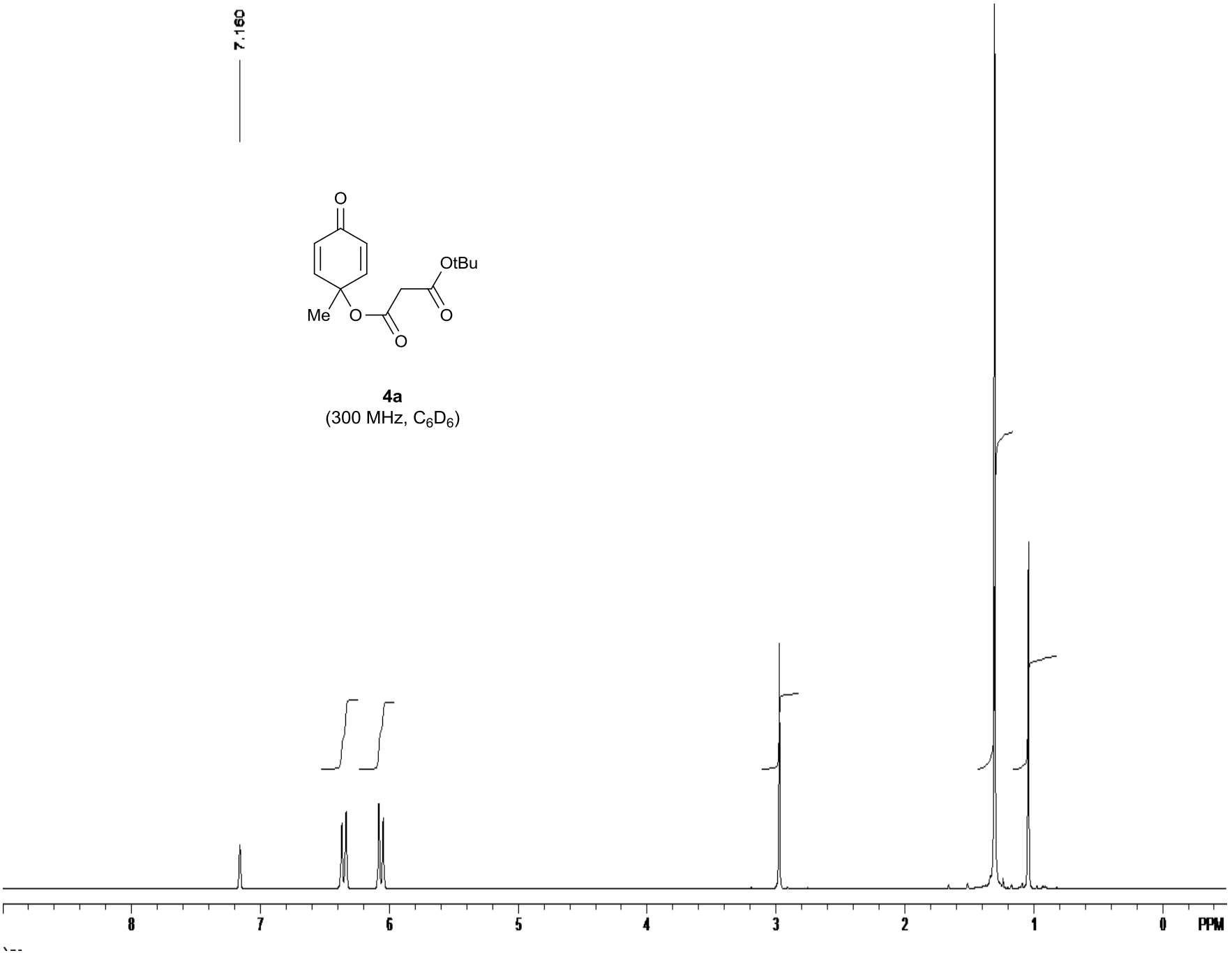




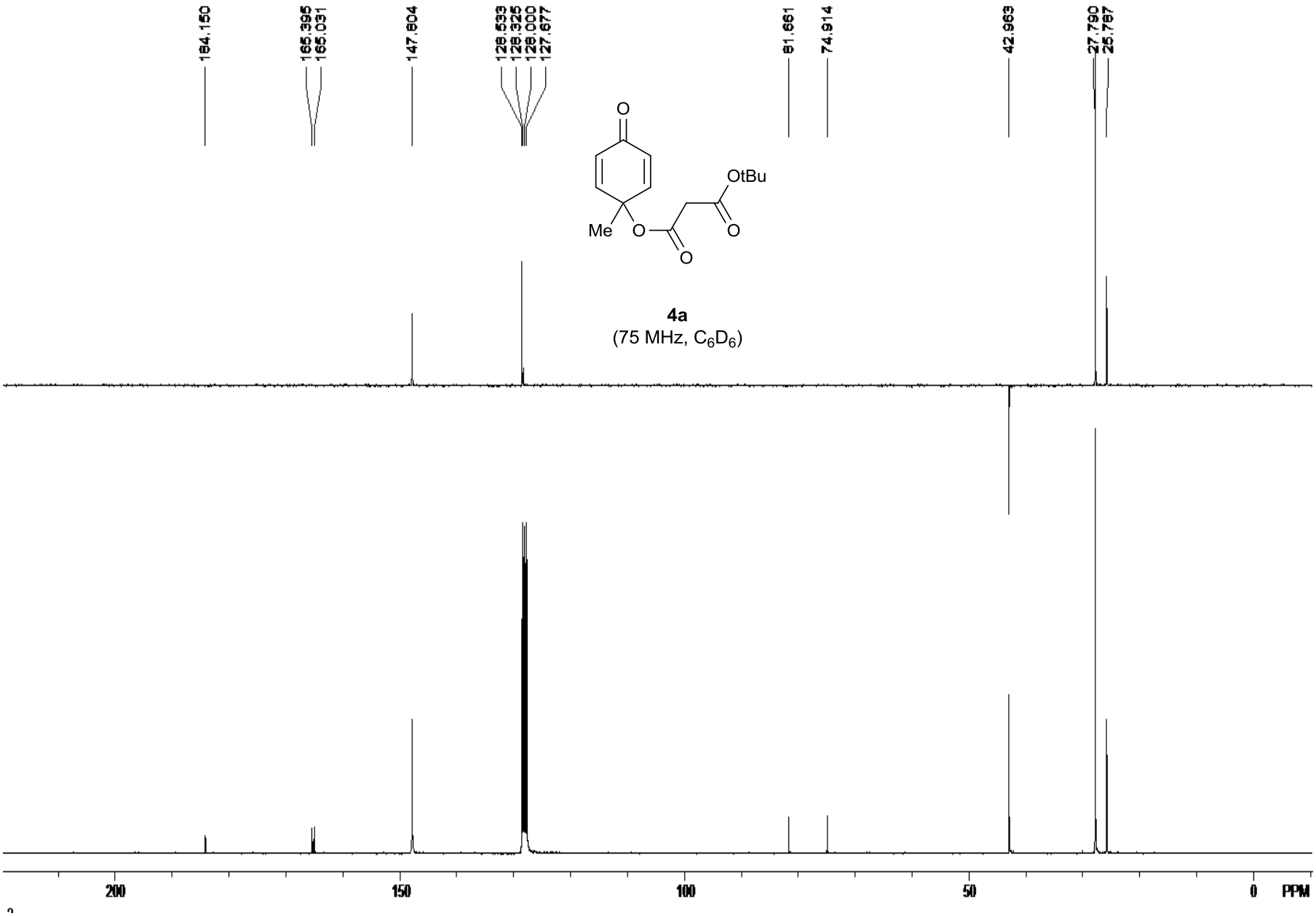
3
(300 MHz, $CDCl_3$)



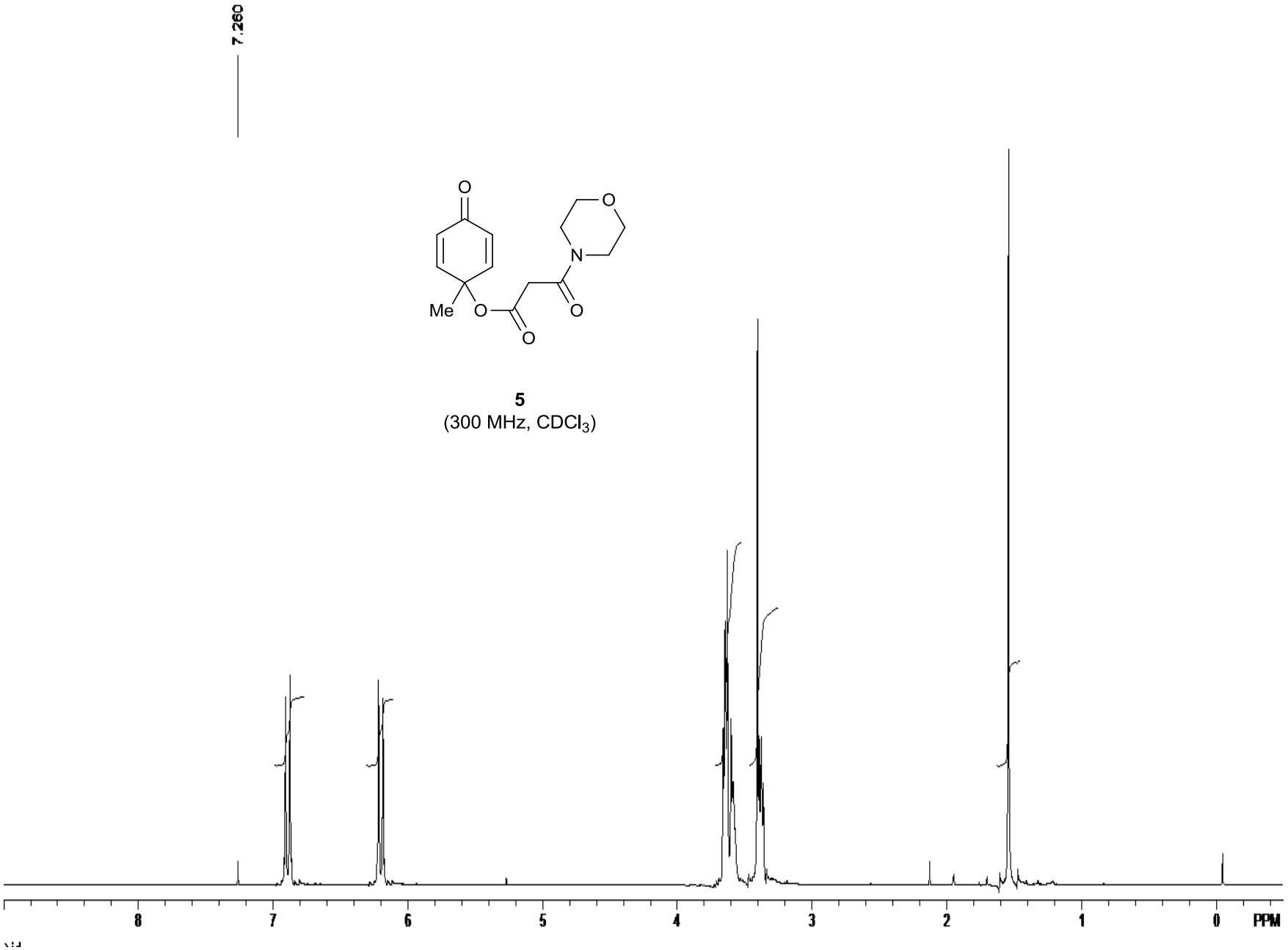
3
(75 MHz, $CDCl_3$)



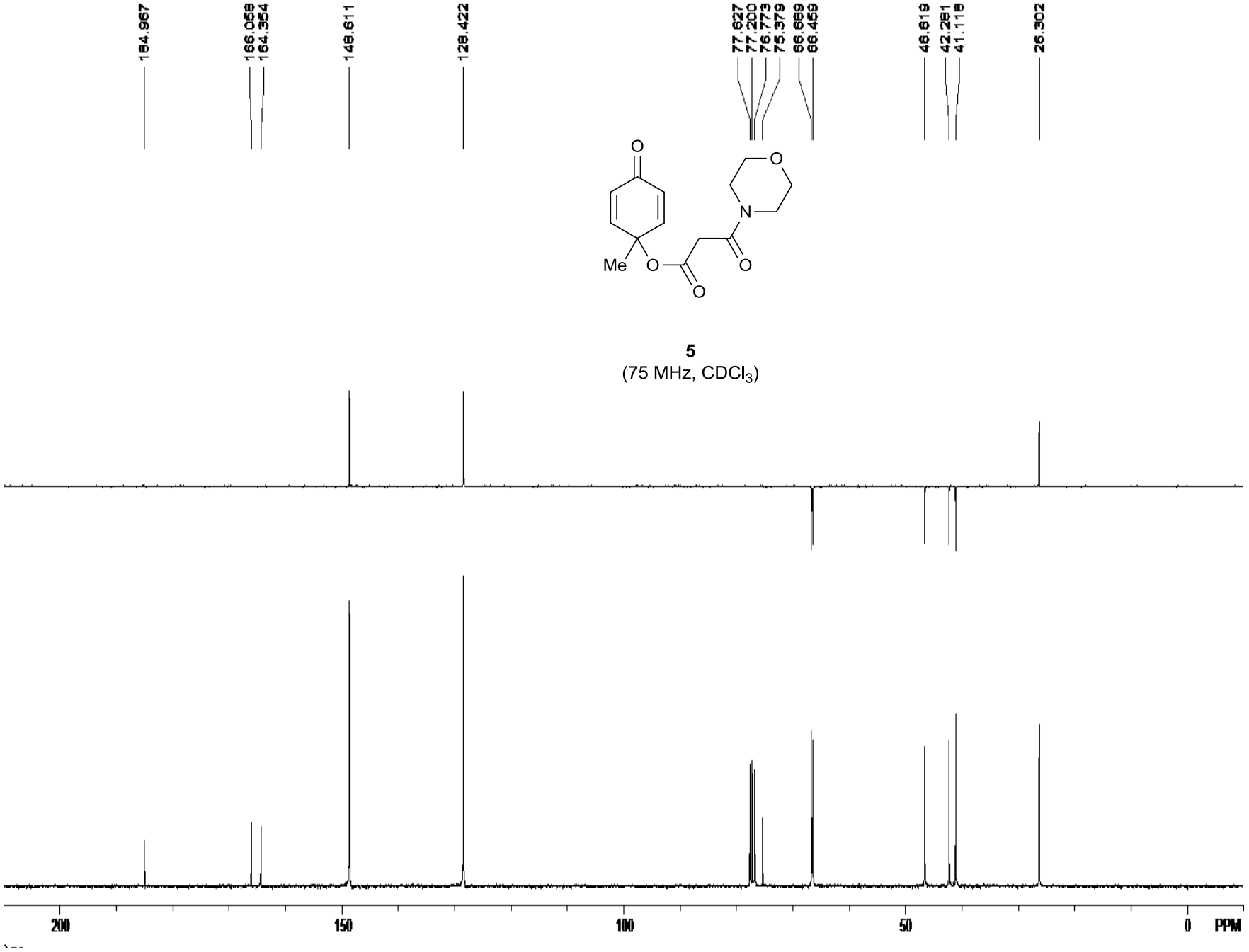
4a
(300 MHz, C_6D_6)



4a
(75 MHz, C_6D_6)

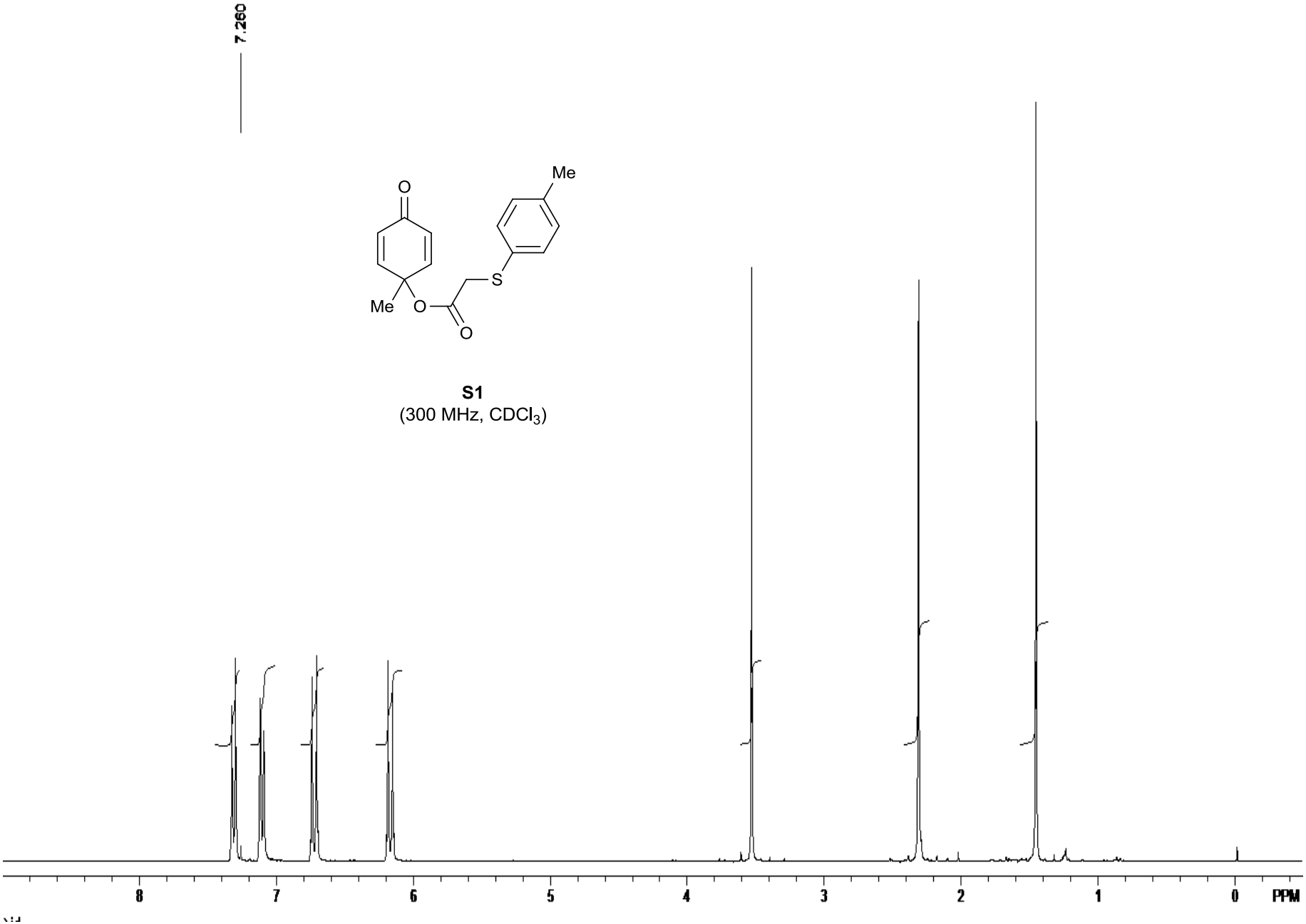


5
(300 MHz, $CDCl_3$)

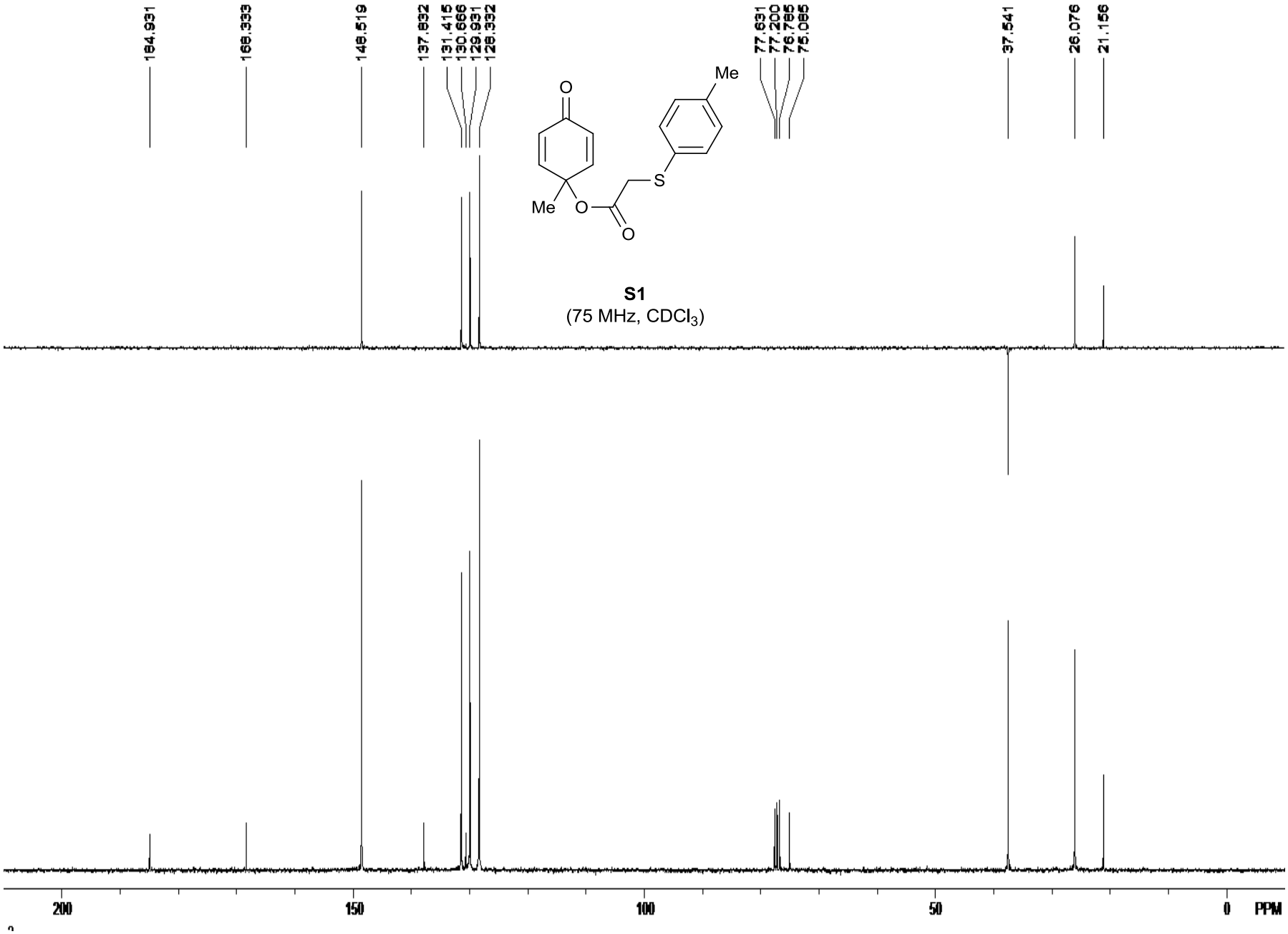


5

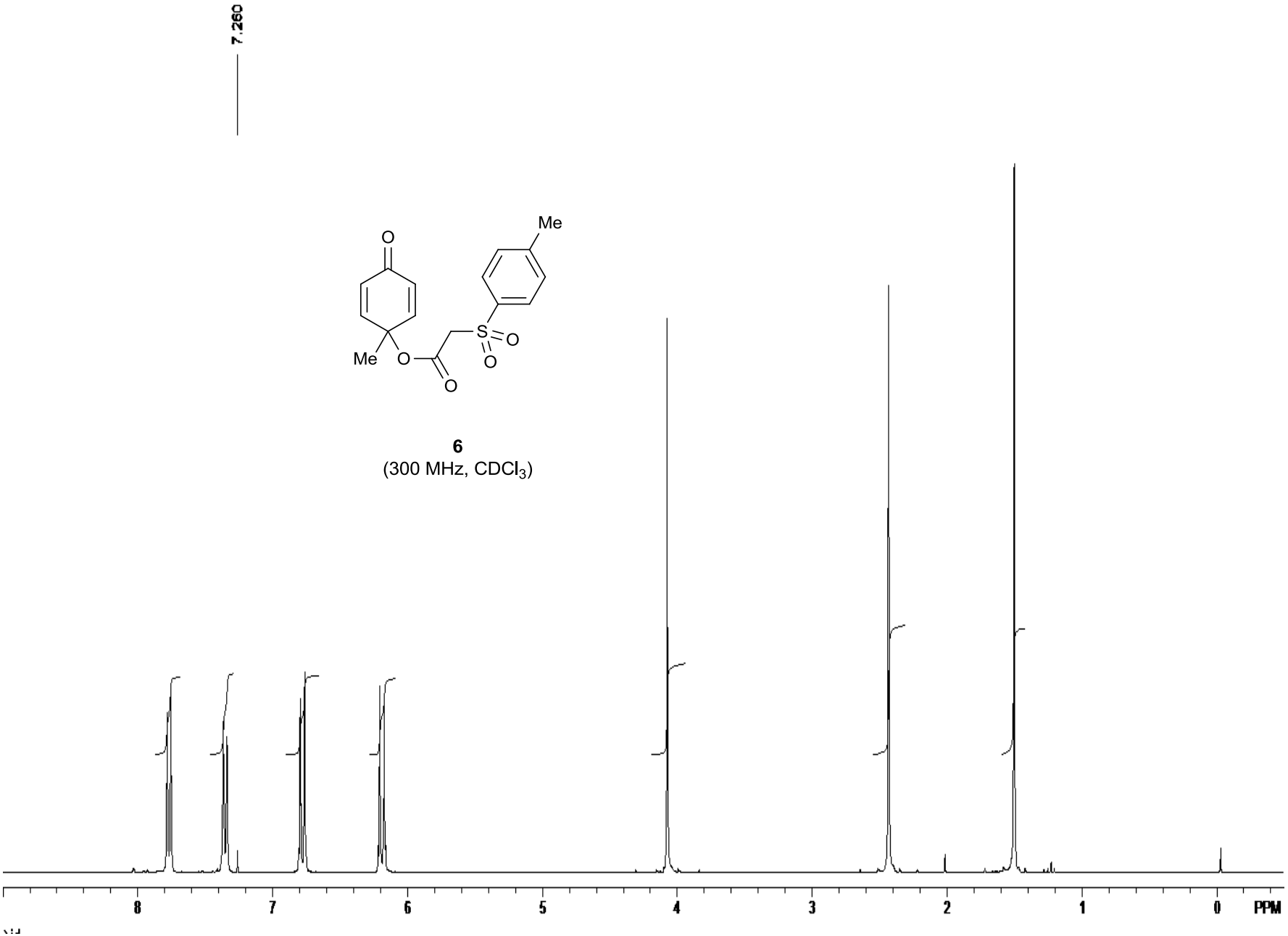
(75 MHz, $CDCl_3$)



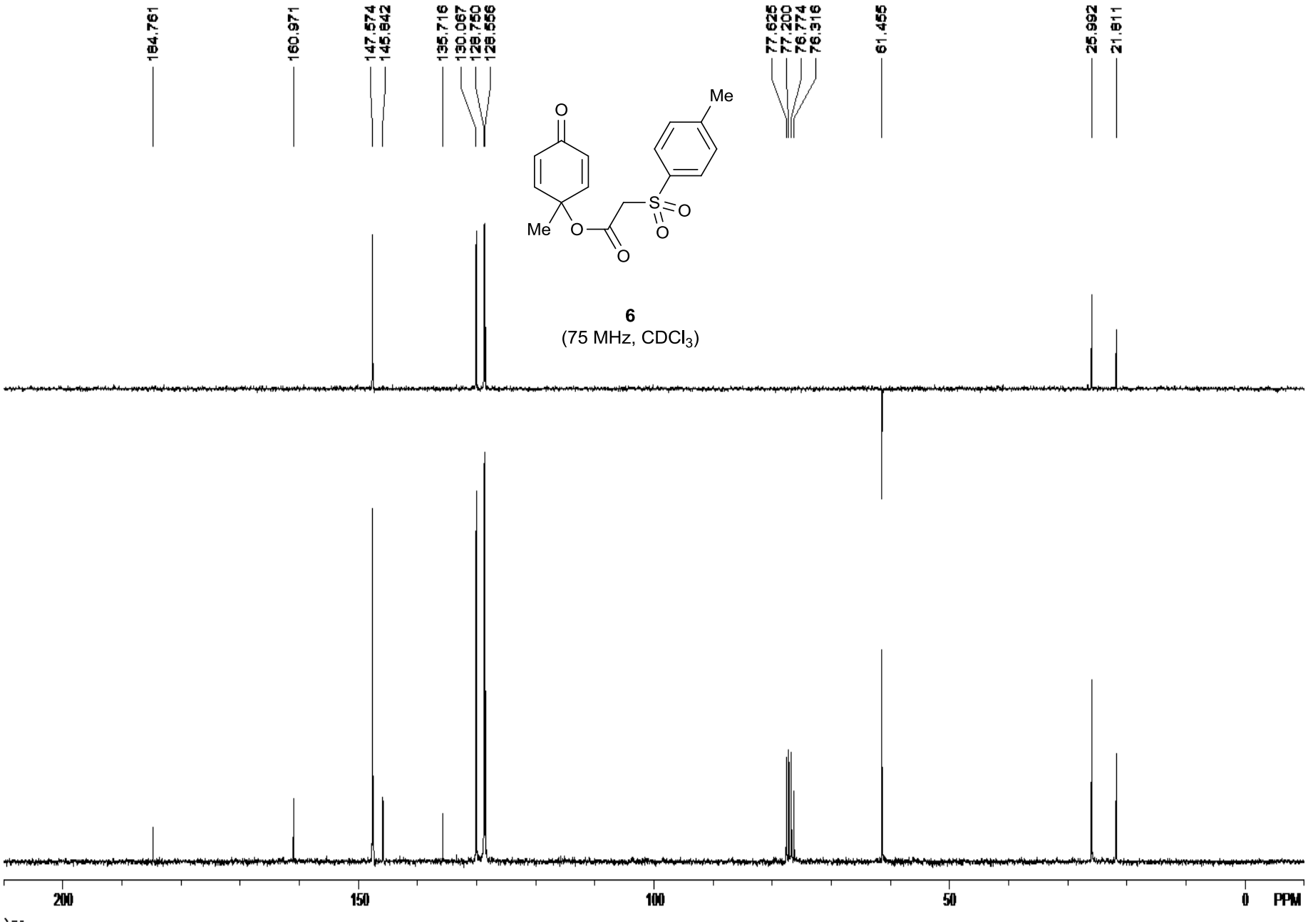
S1
(300 MHz, $CDCl_3$)



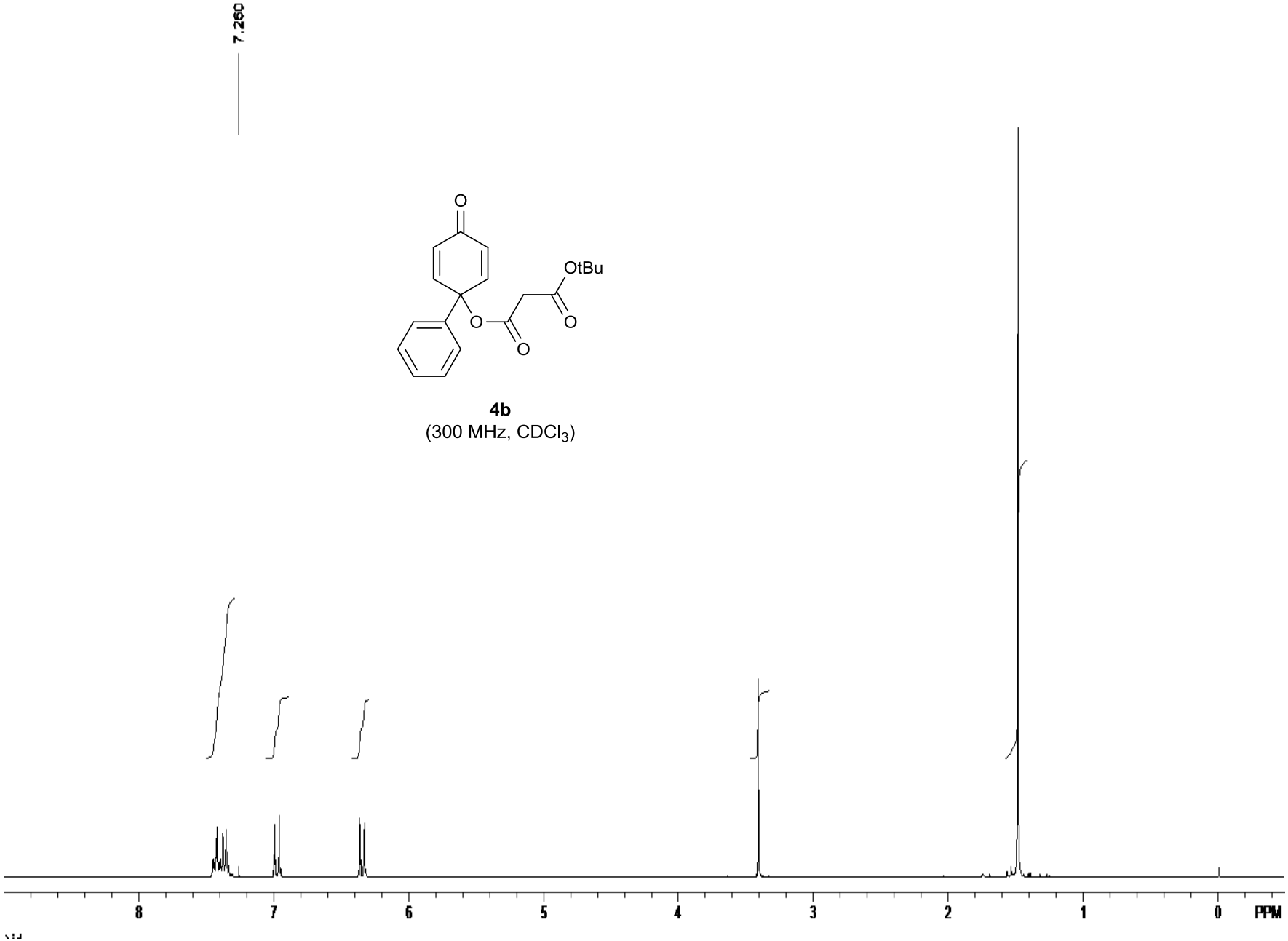
S1
(75 MHz, $CDCl_3$)



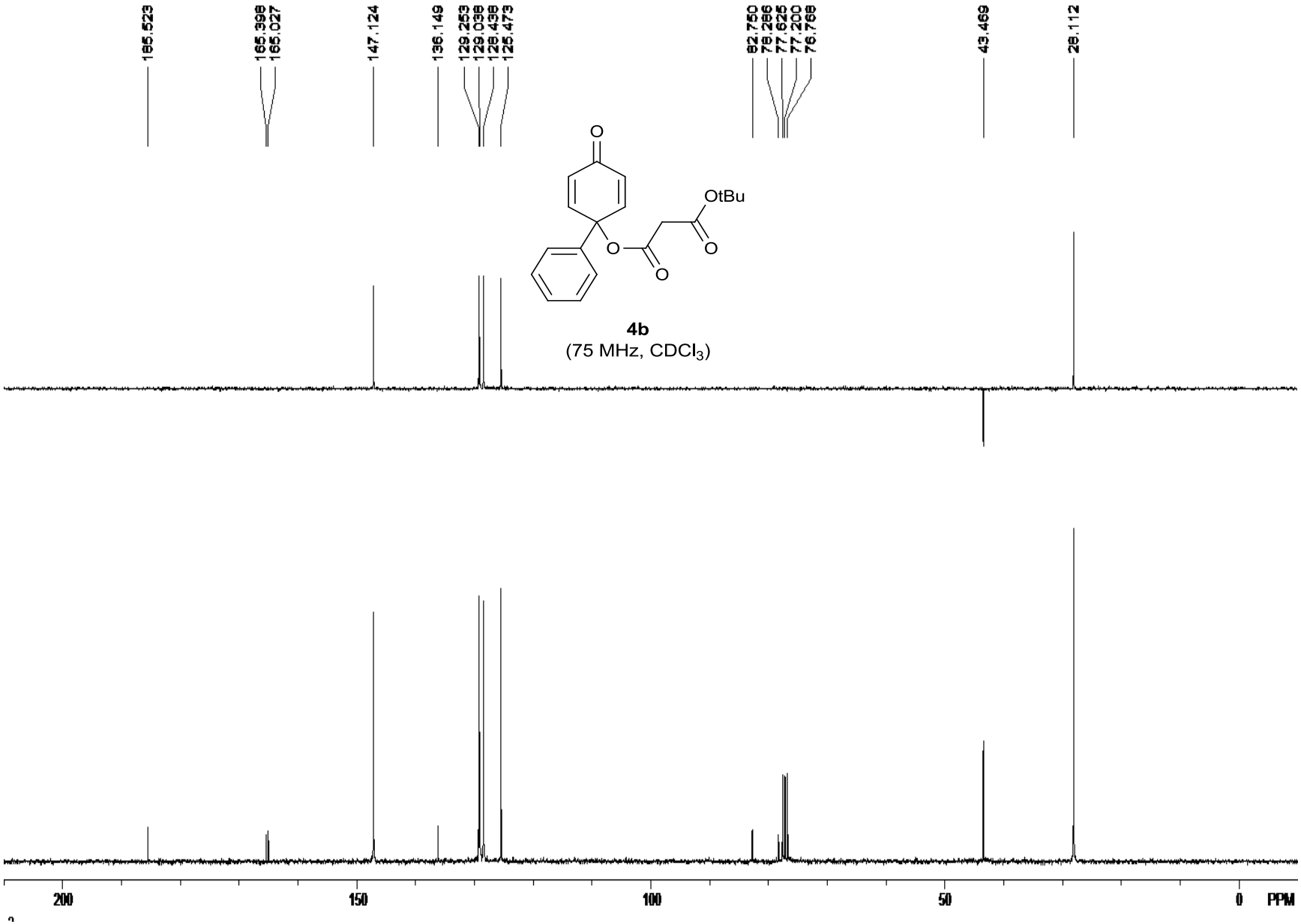
6
(300 MHz, $CDCl_3$)



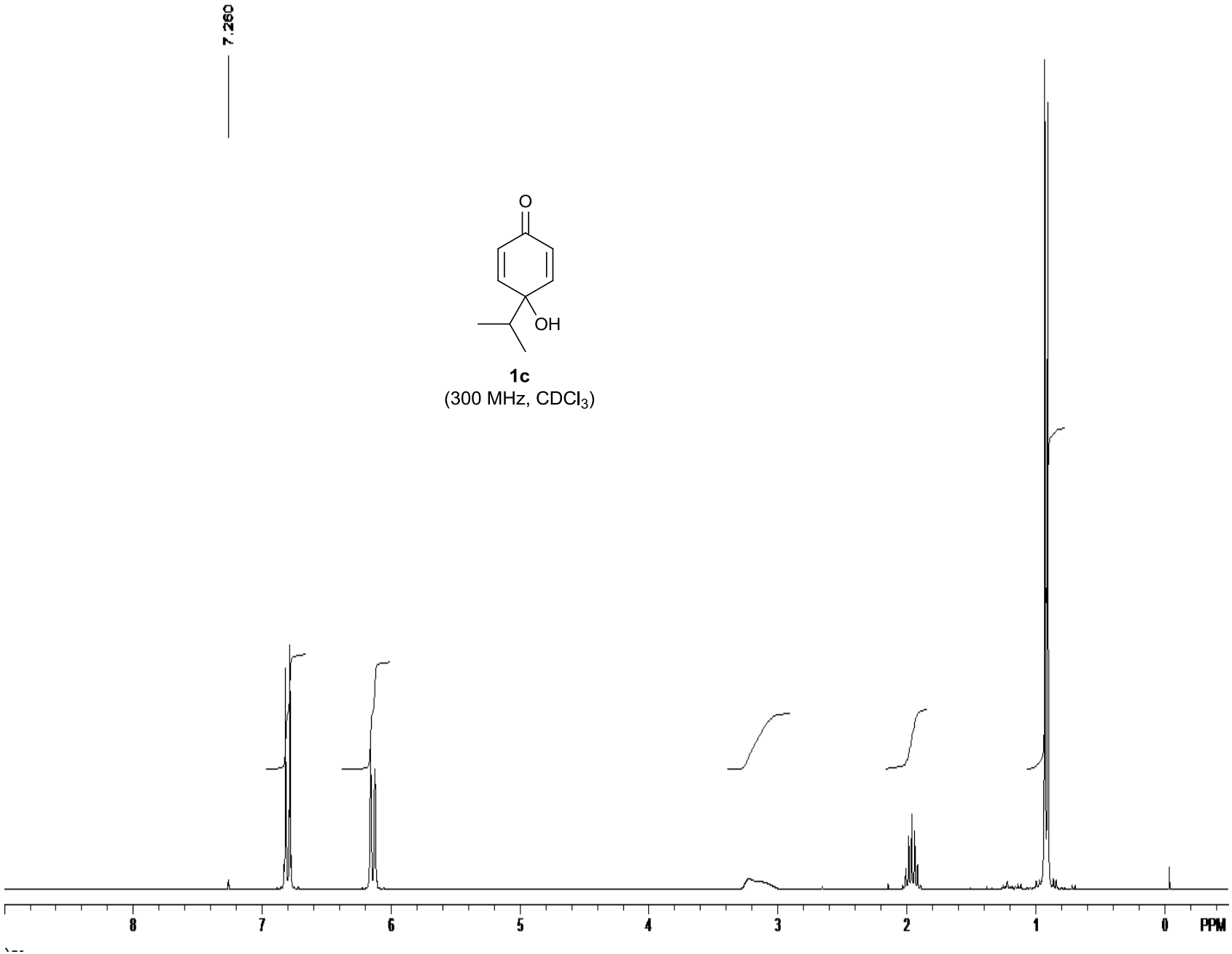
6
(75 MHz, $CDCl_3$)



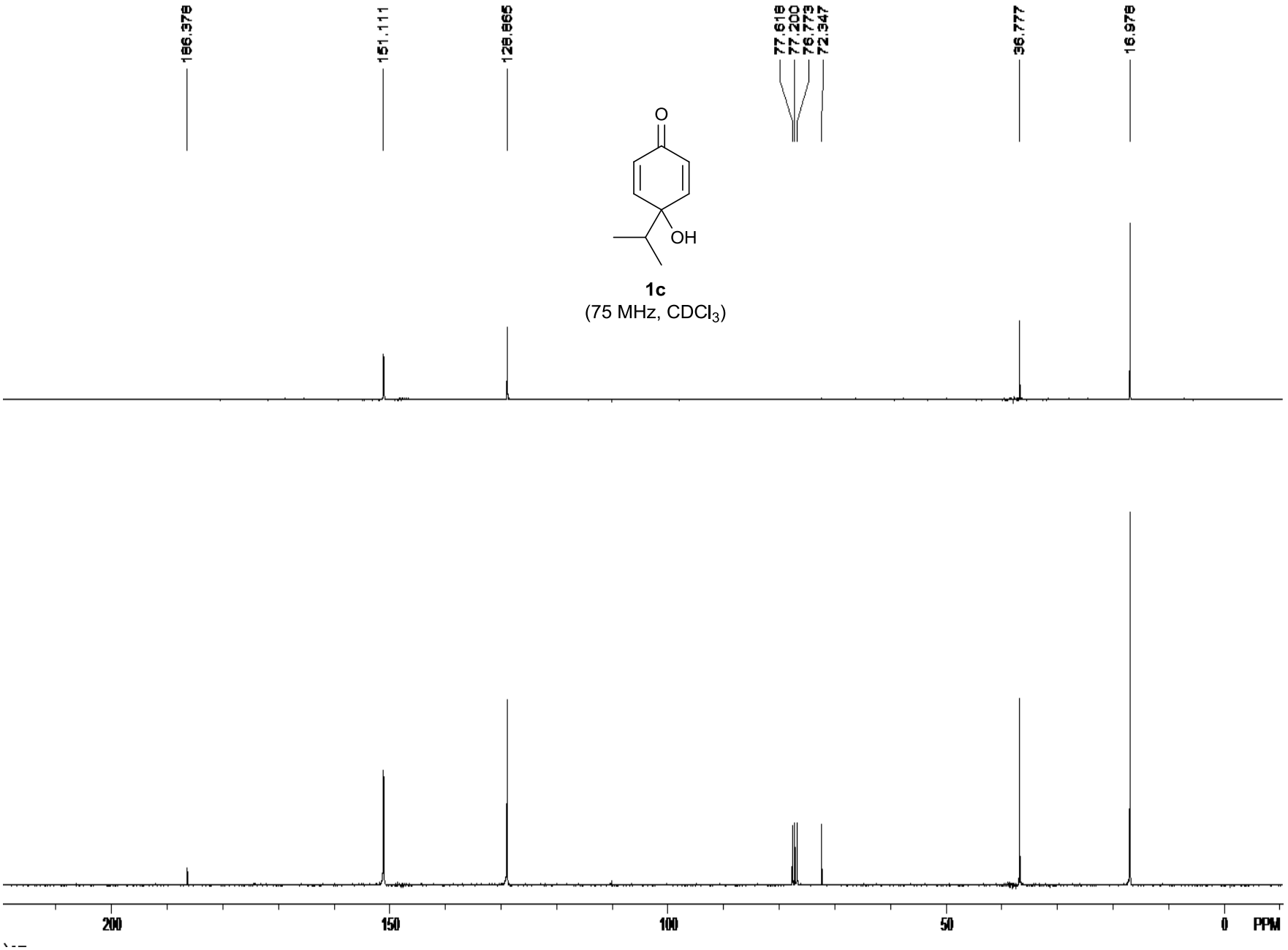
4b
(300 MHz, $CDCl_3$)



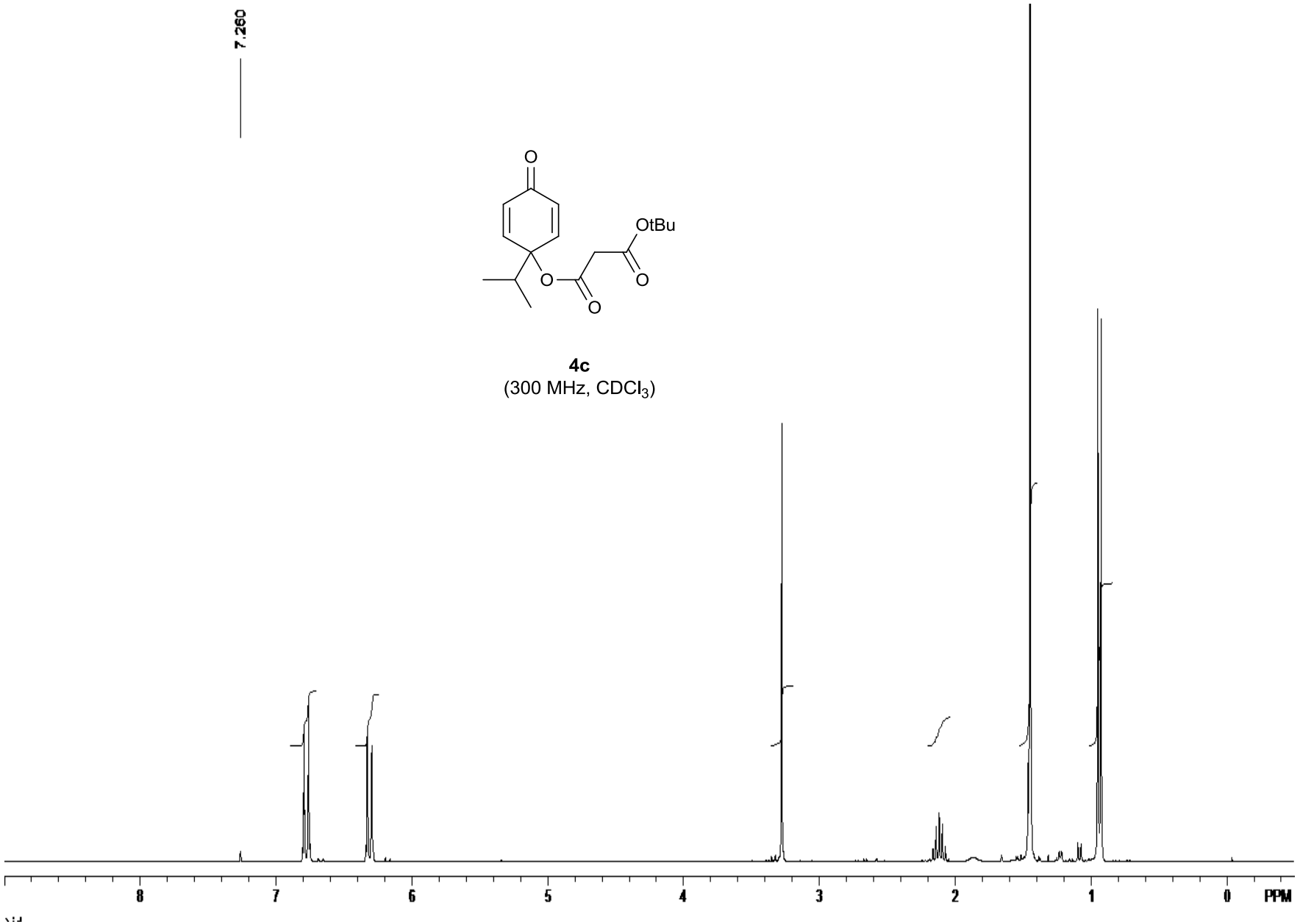
4b
(75 MHz, $CDCl_3$)



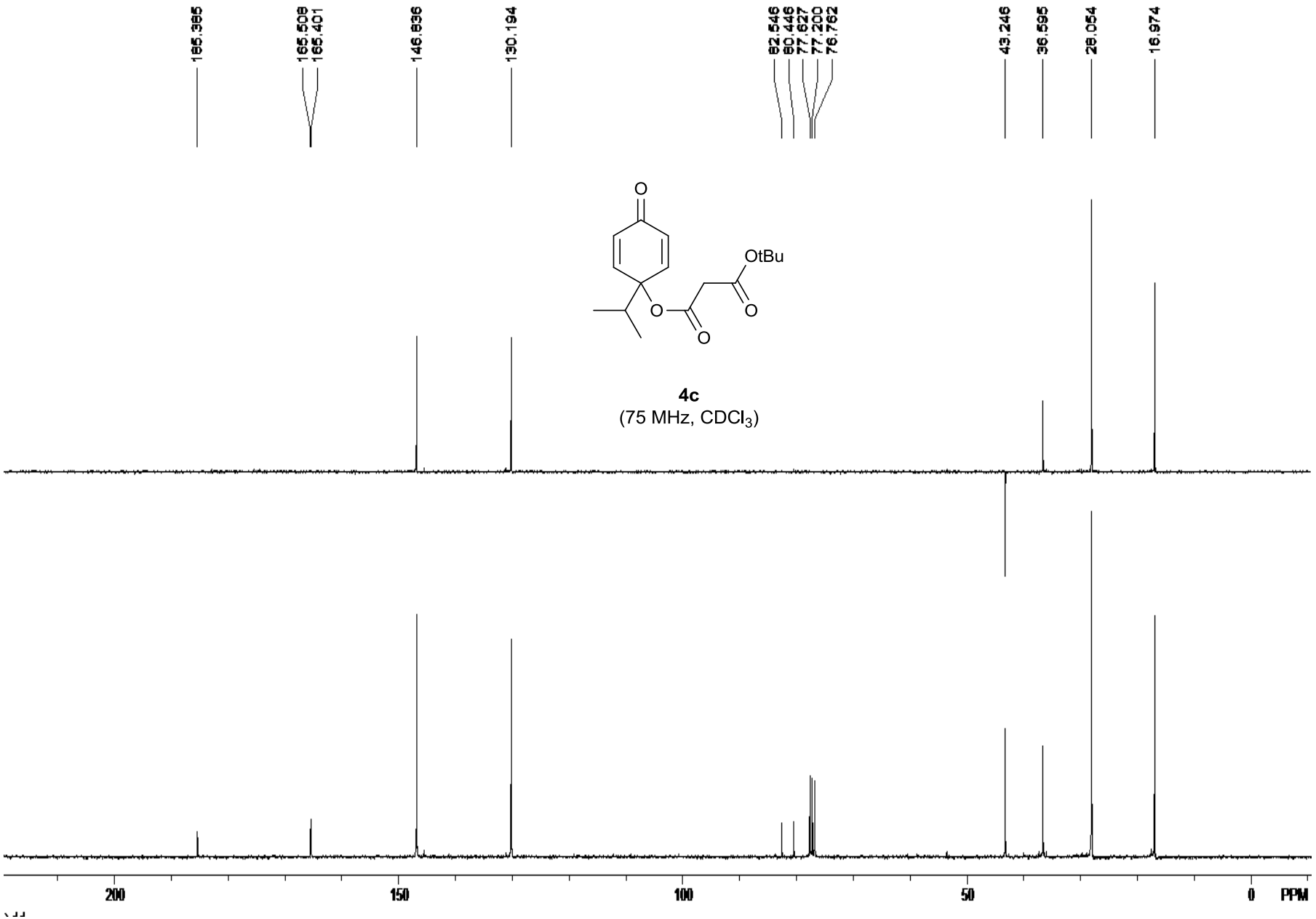
1c
(300 MHz, $CDCl_3$)



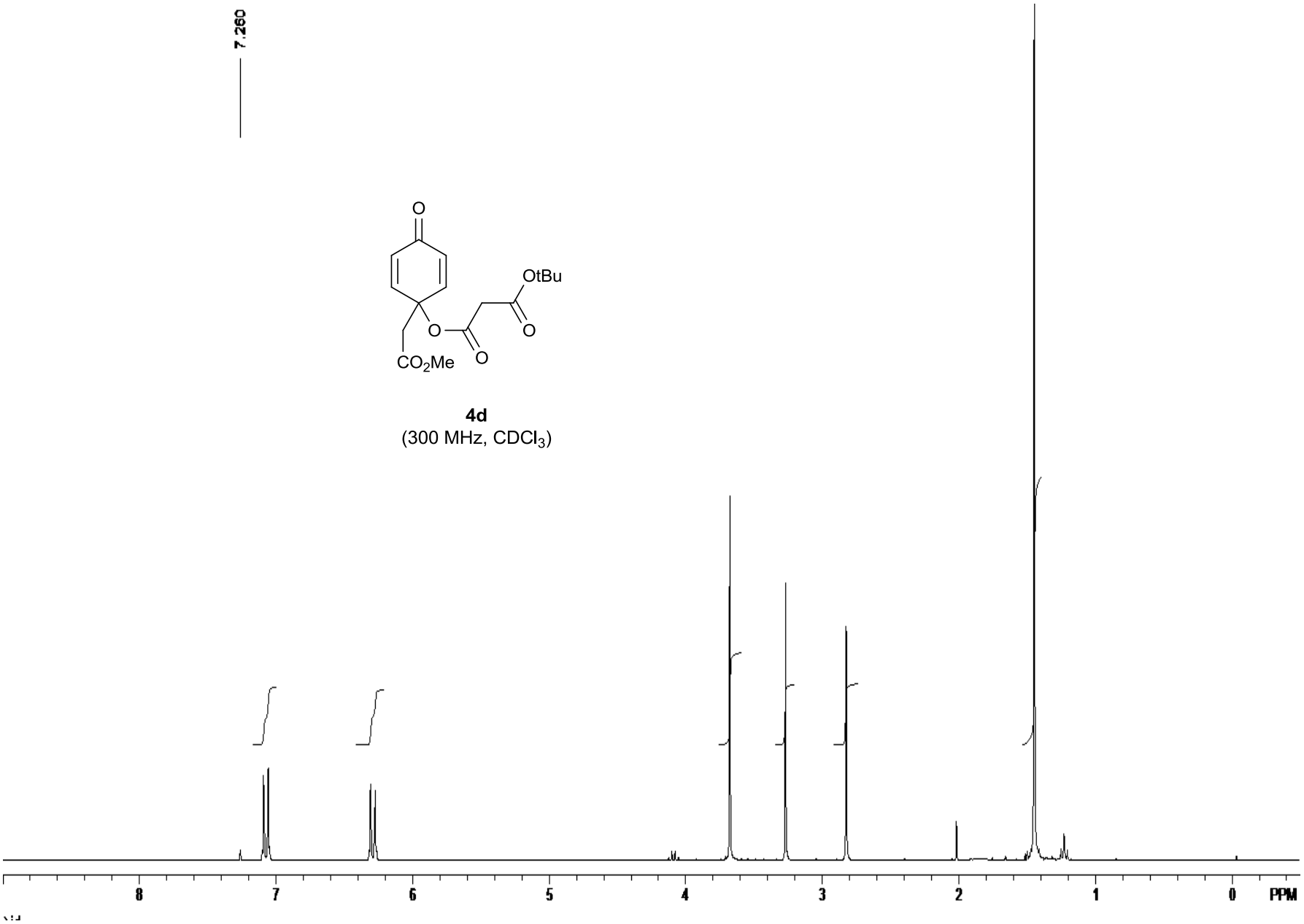
1c
(75 MHz, $CDCl_3$)



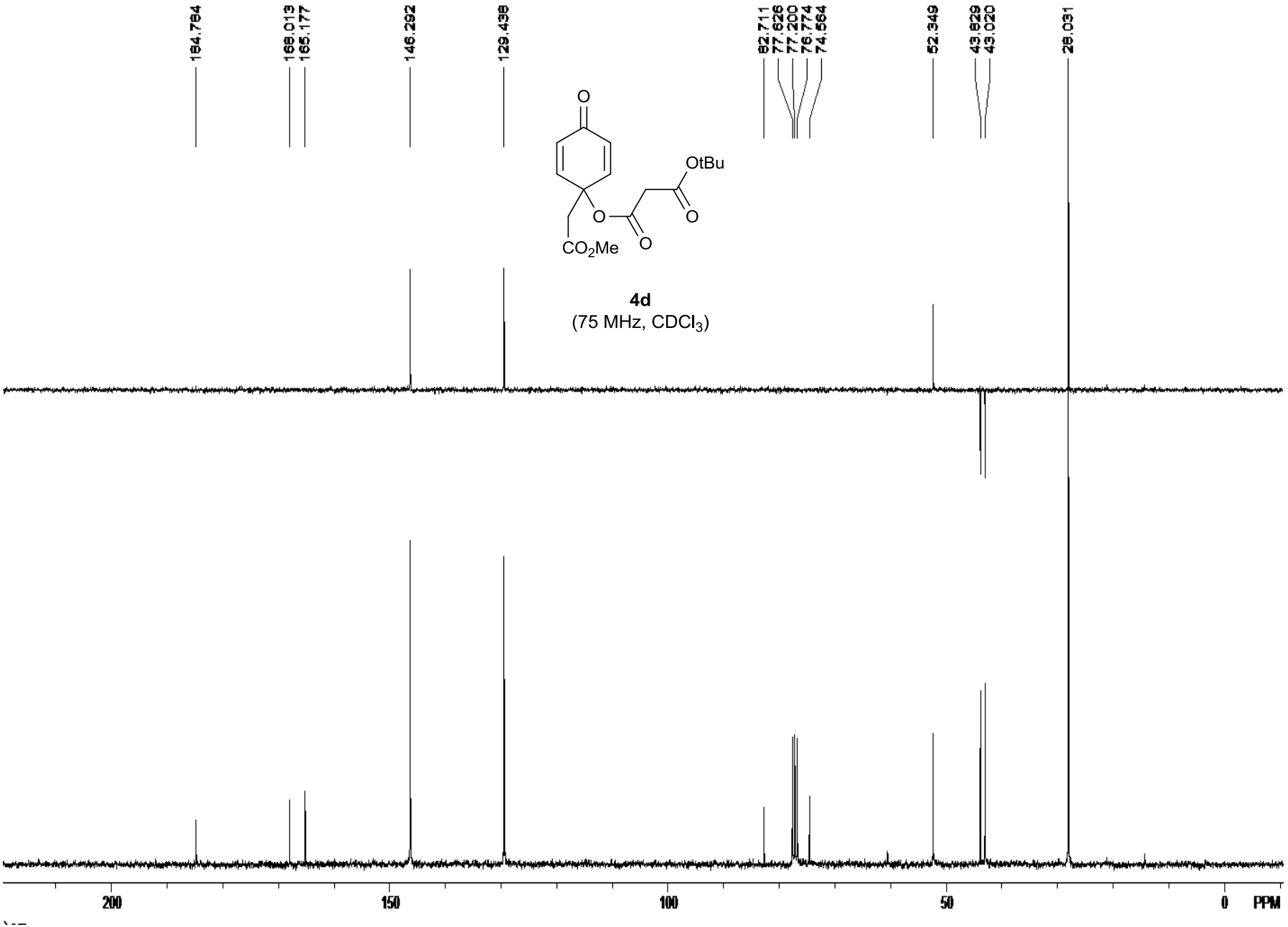
4c
(300 MHz, $CDCl_3$)

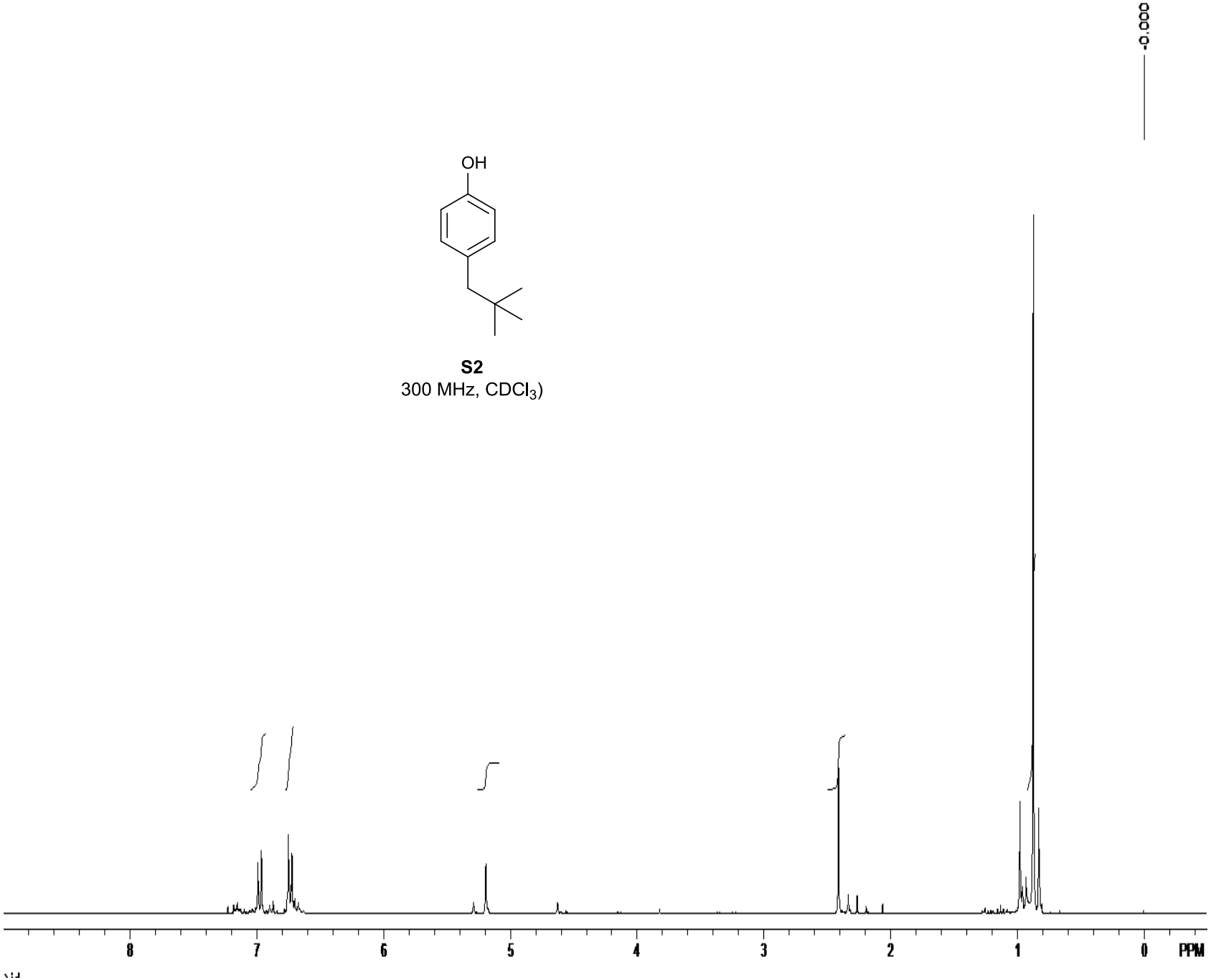


4c
(75 MHz, $CDCl_3$)

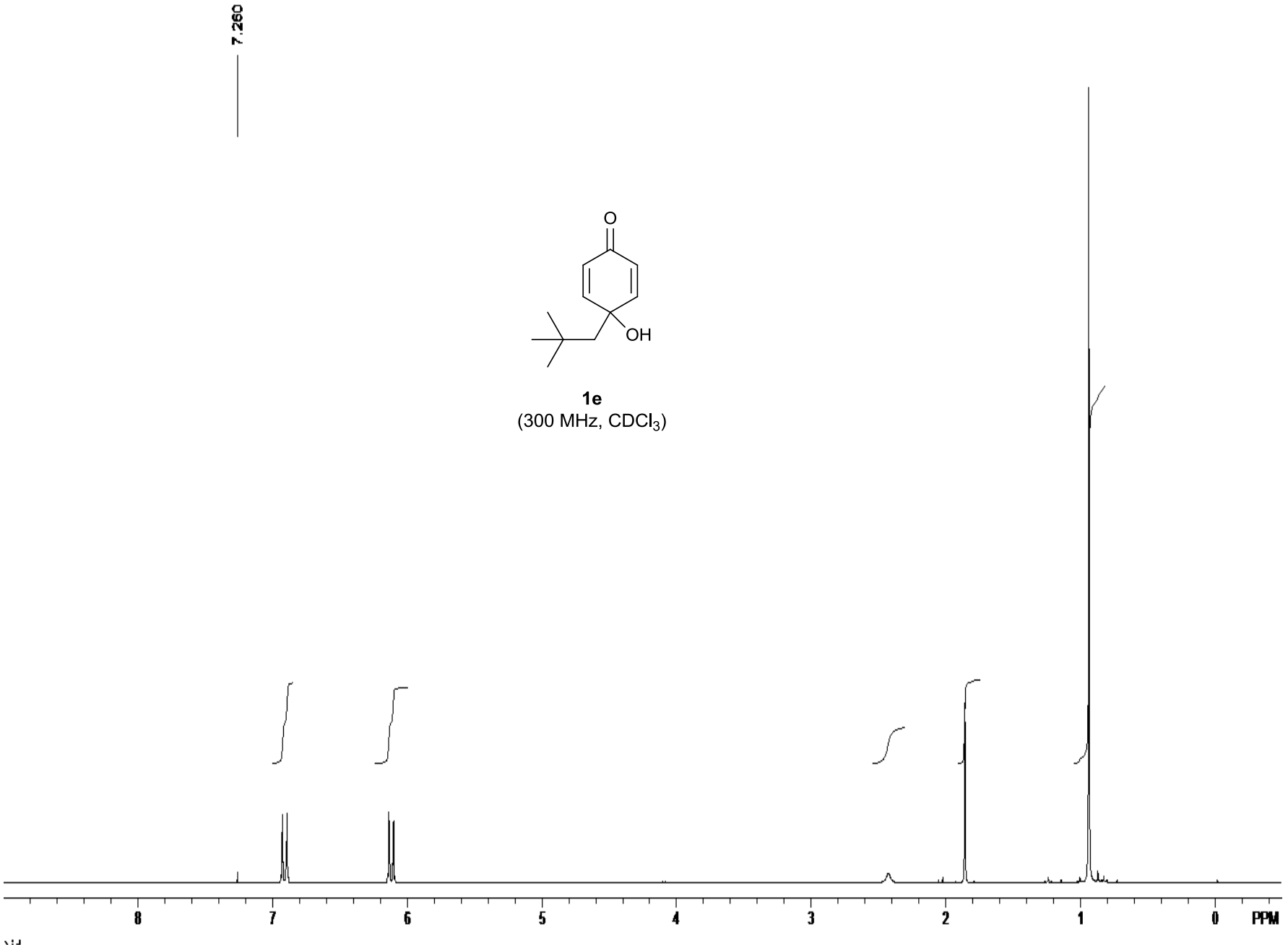


4d
(300 MHz, $CDCl_3$)

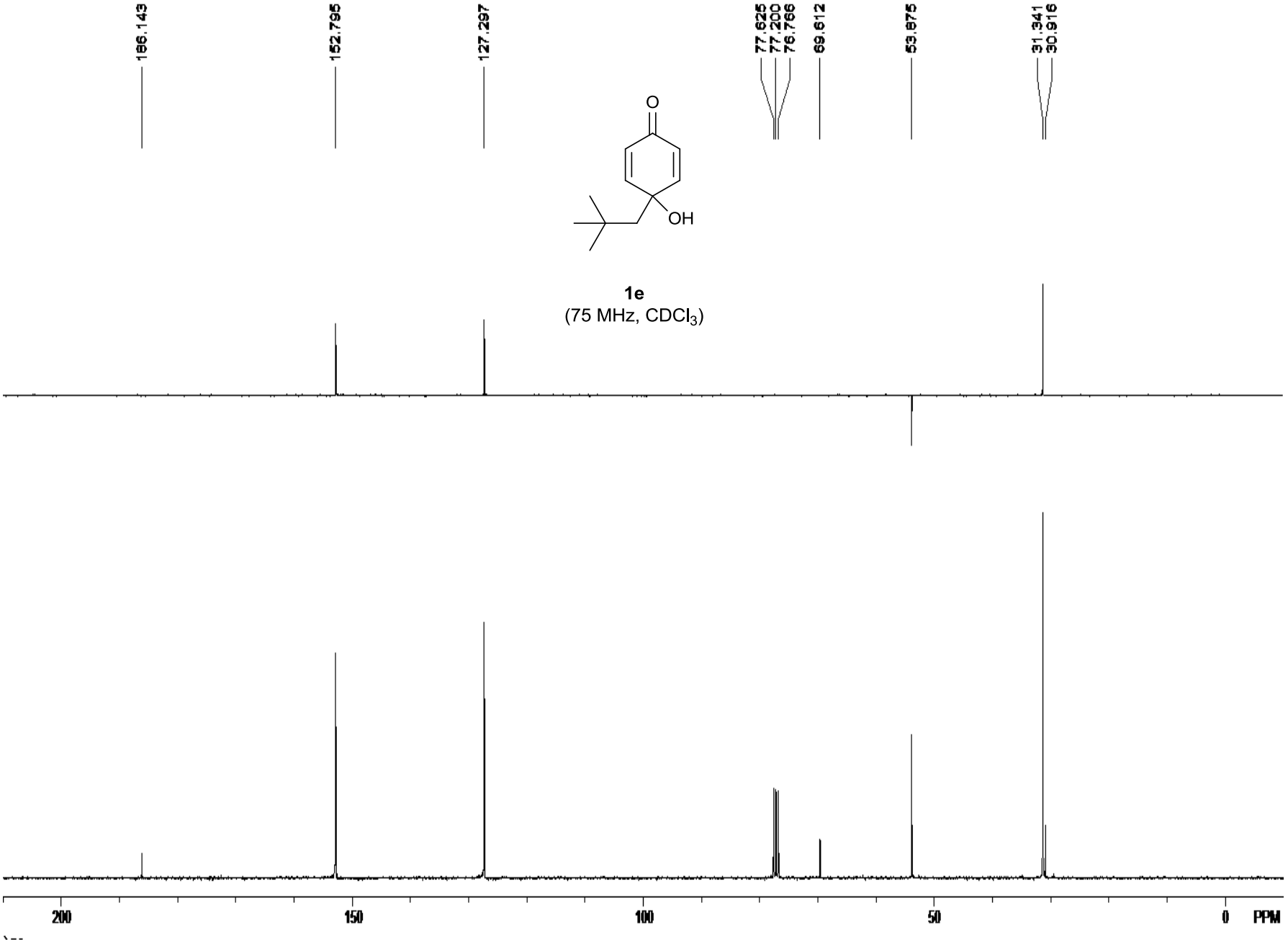




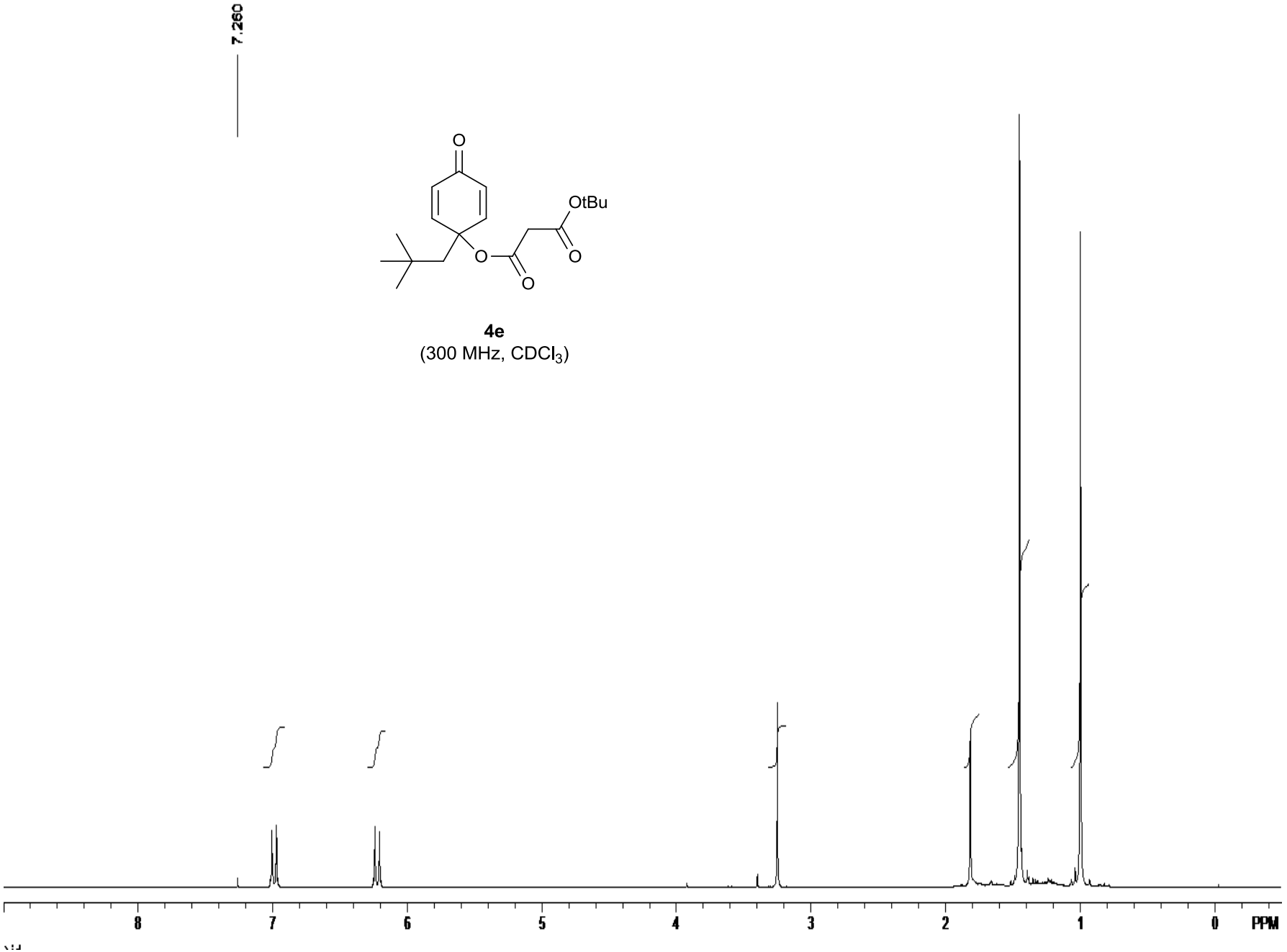
S2
300 MHz, $CDCl_3$)



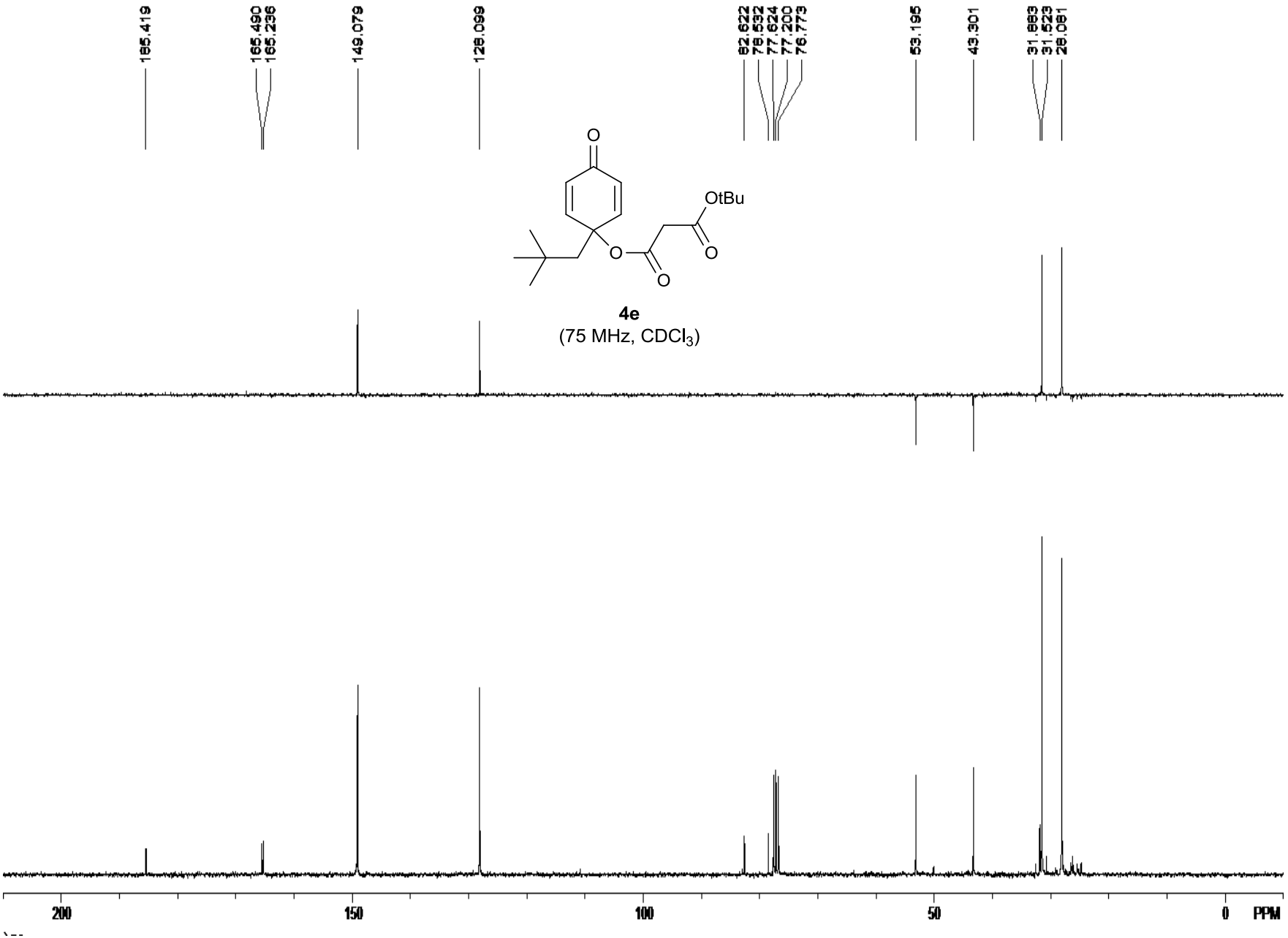
1e
(300 MHz, $CDCl_3$)



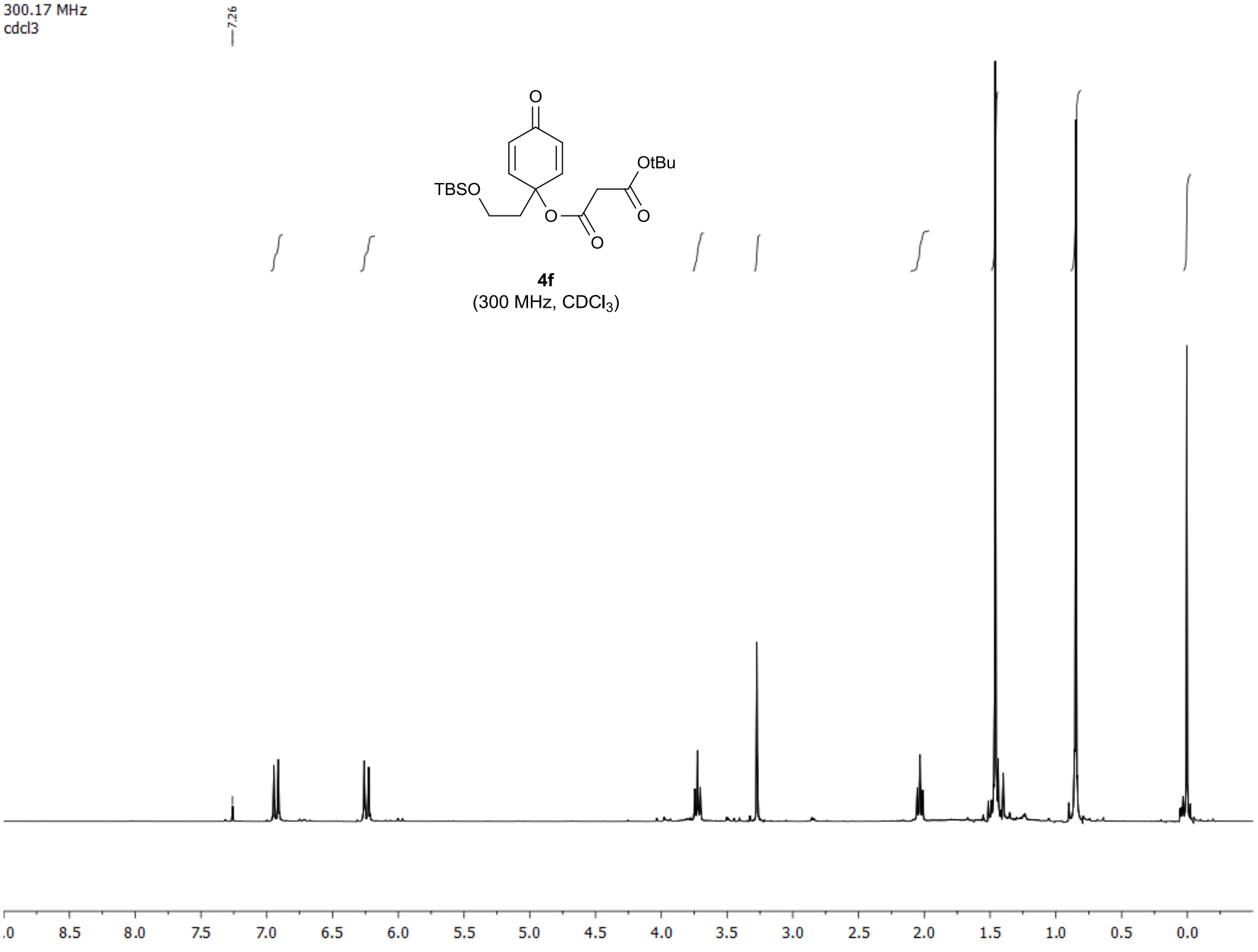
1e
(75 MHz, $CDCl_3$)

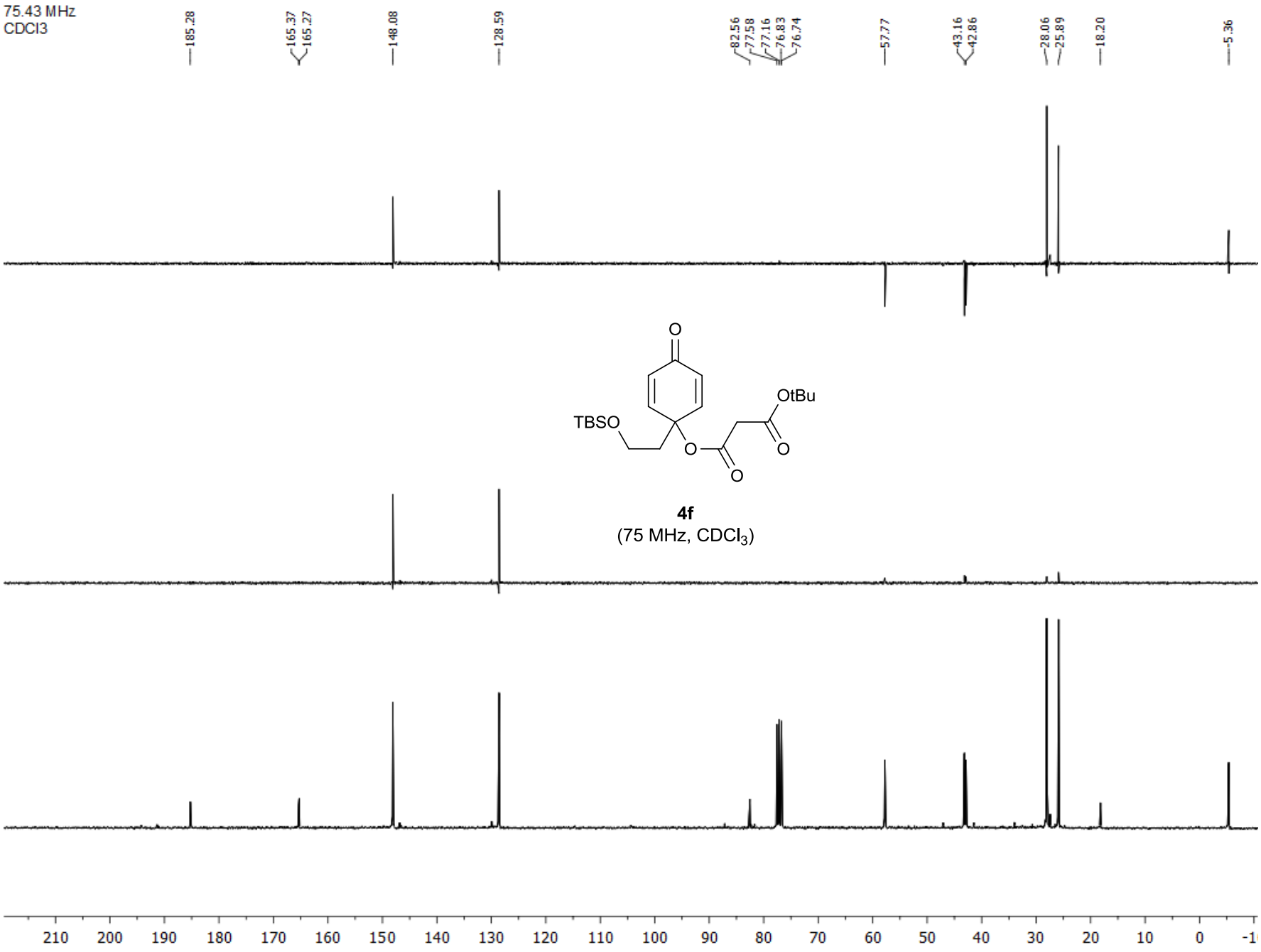


4e
(300 MHz, $CDCl_3$)

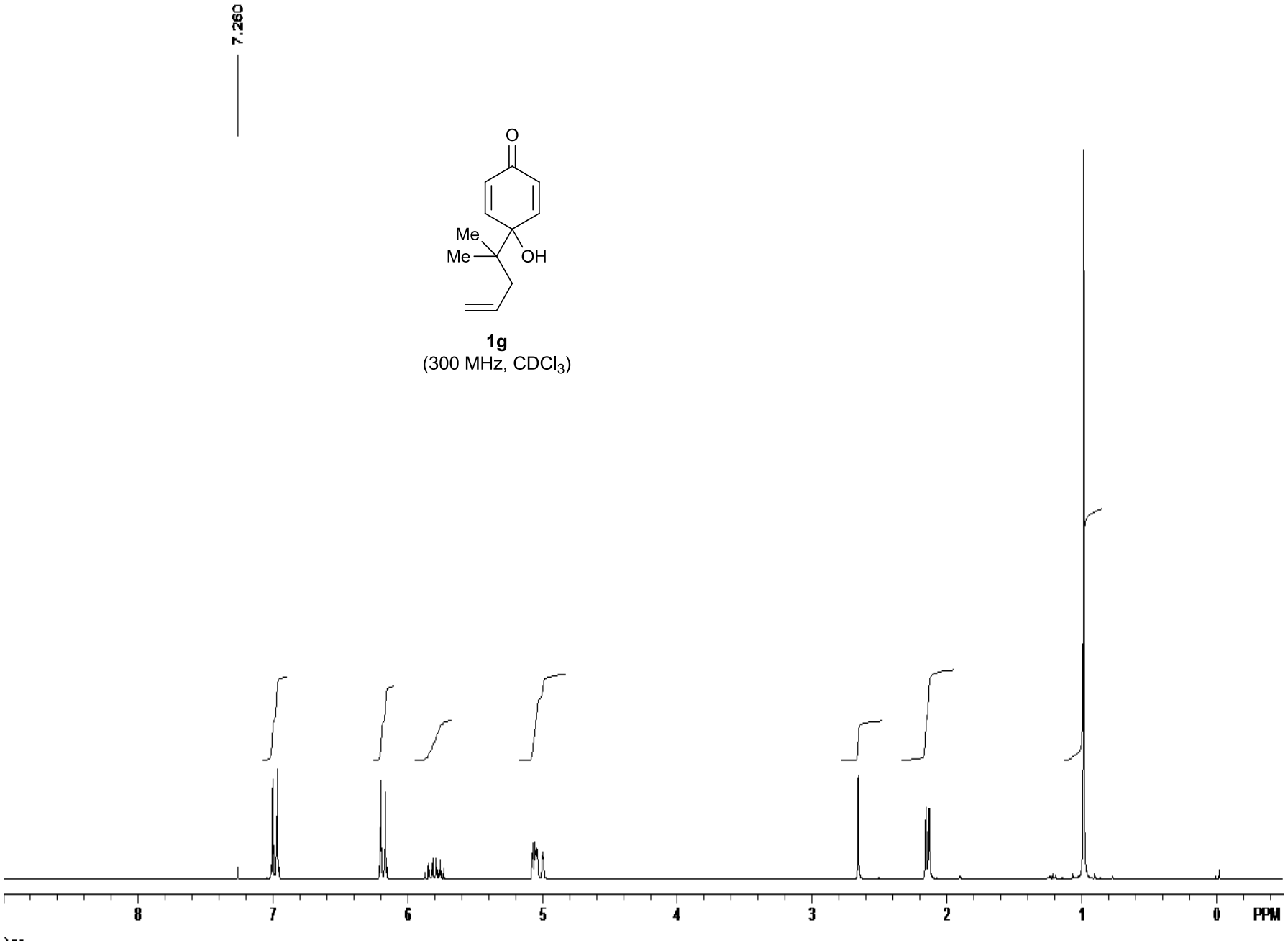


4e
(75 MHz, $CDCl_3$)

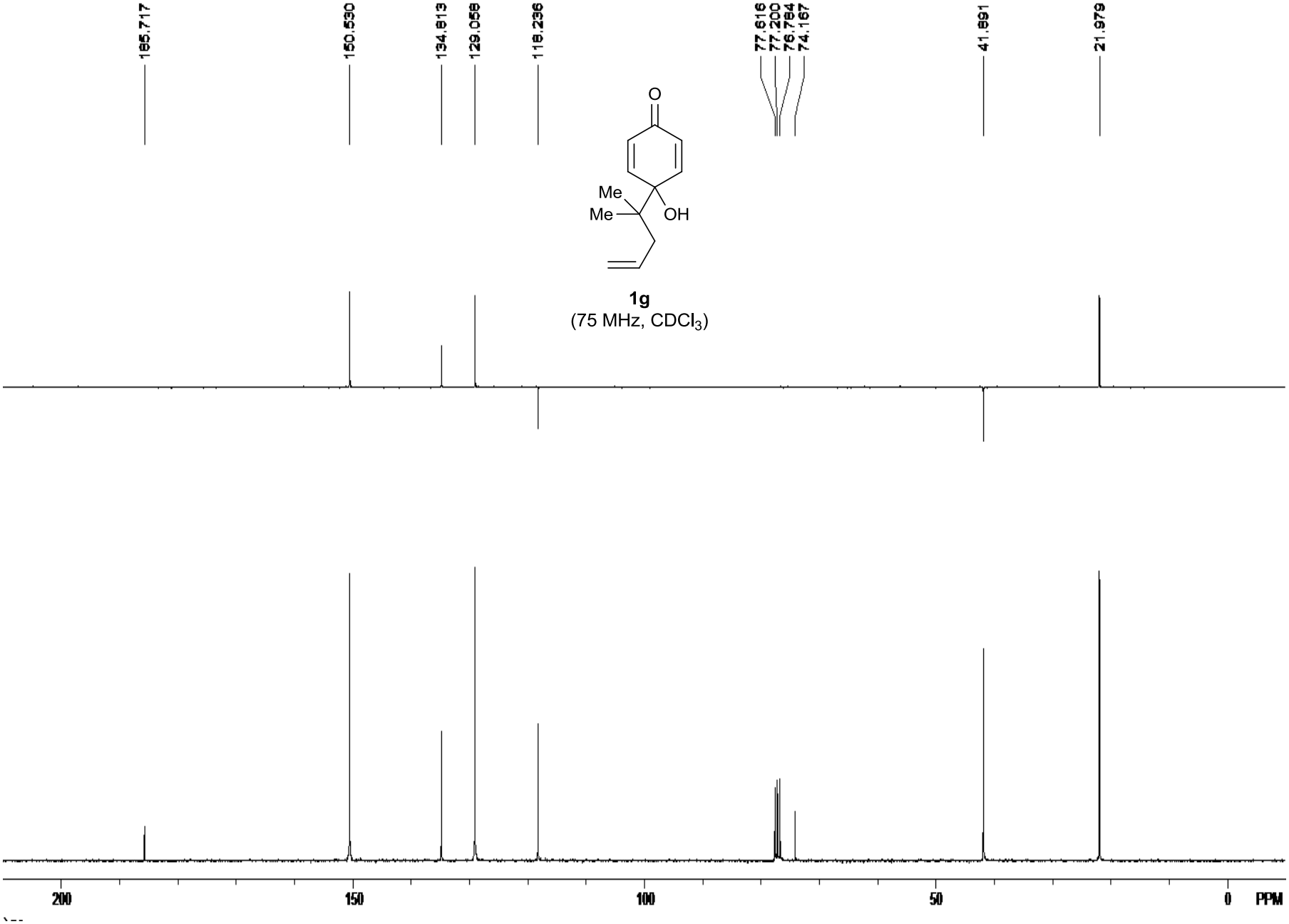




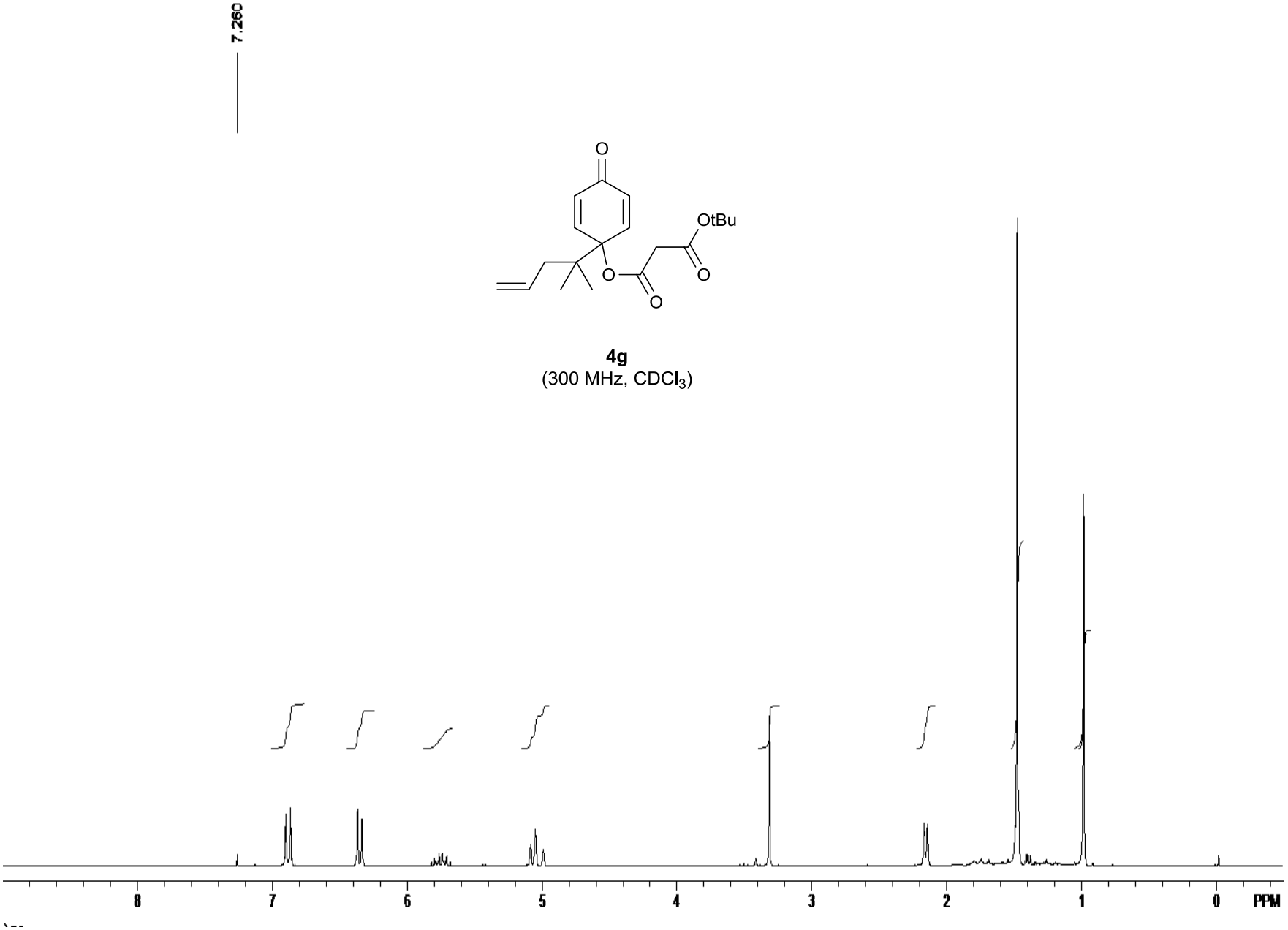
4f
(75 MHz, $CDCl_3$)



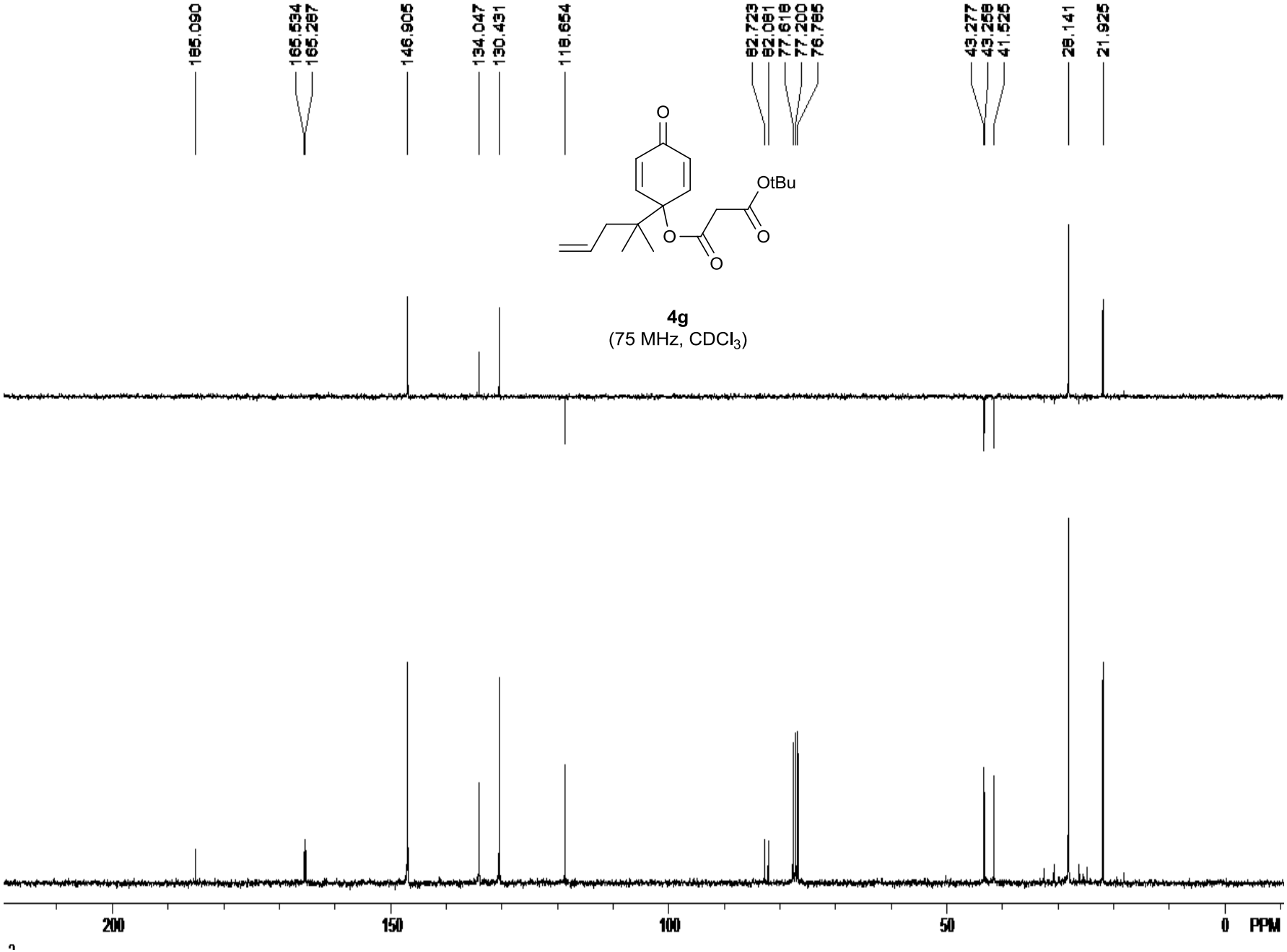
1g
(300 MHz, $CDCl_3$)



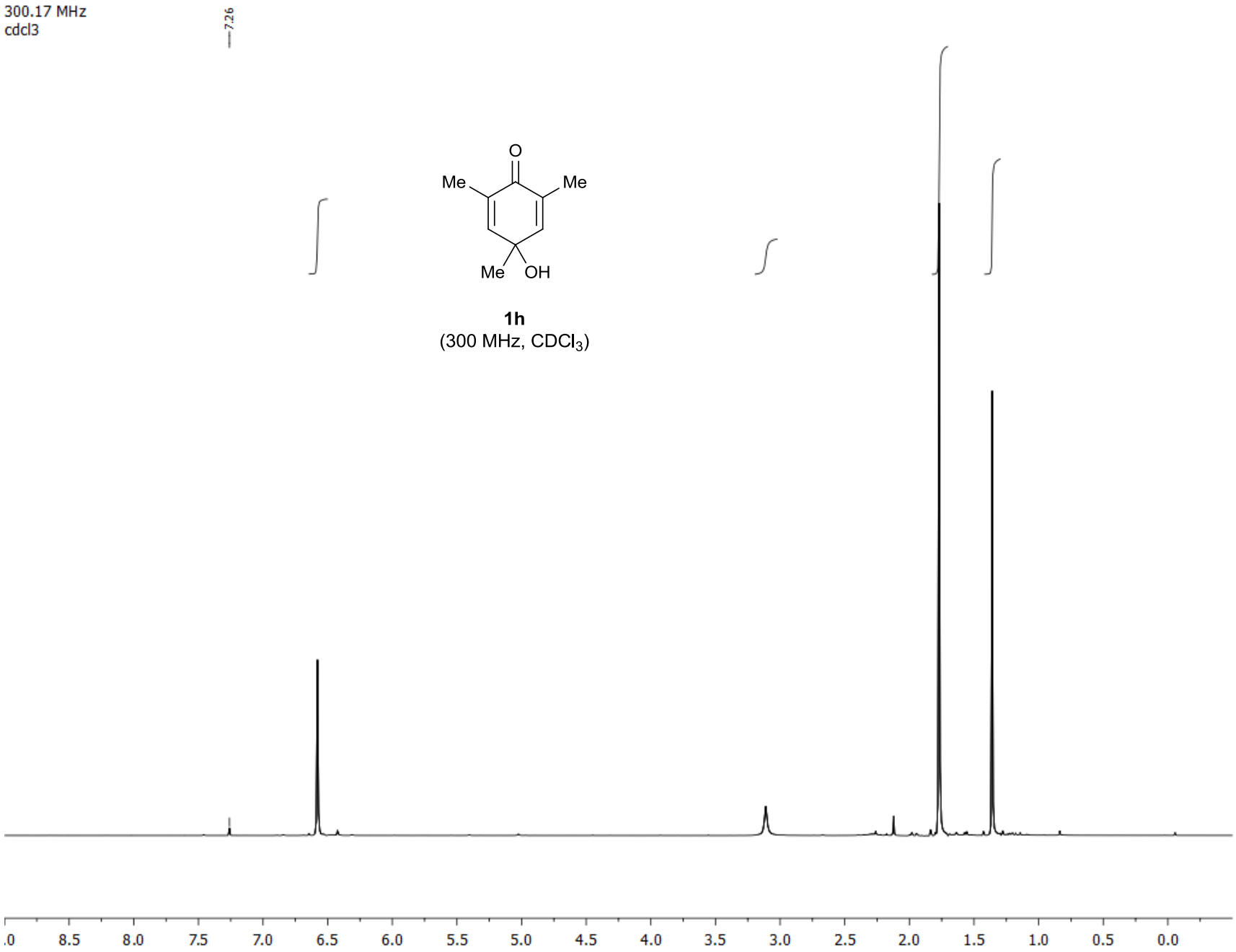
1g
(75 MHz, $CDCl_3$)



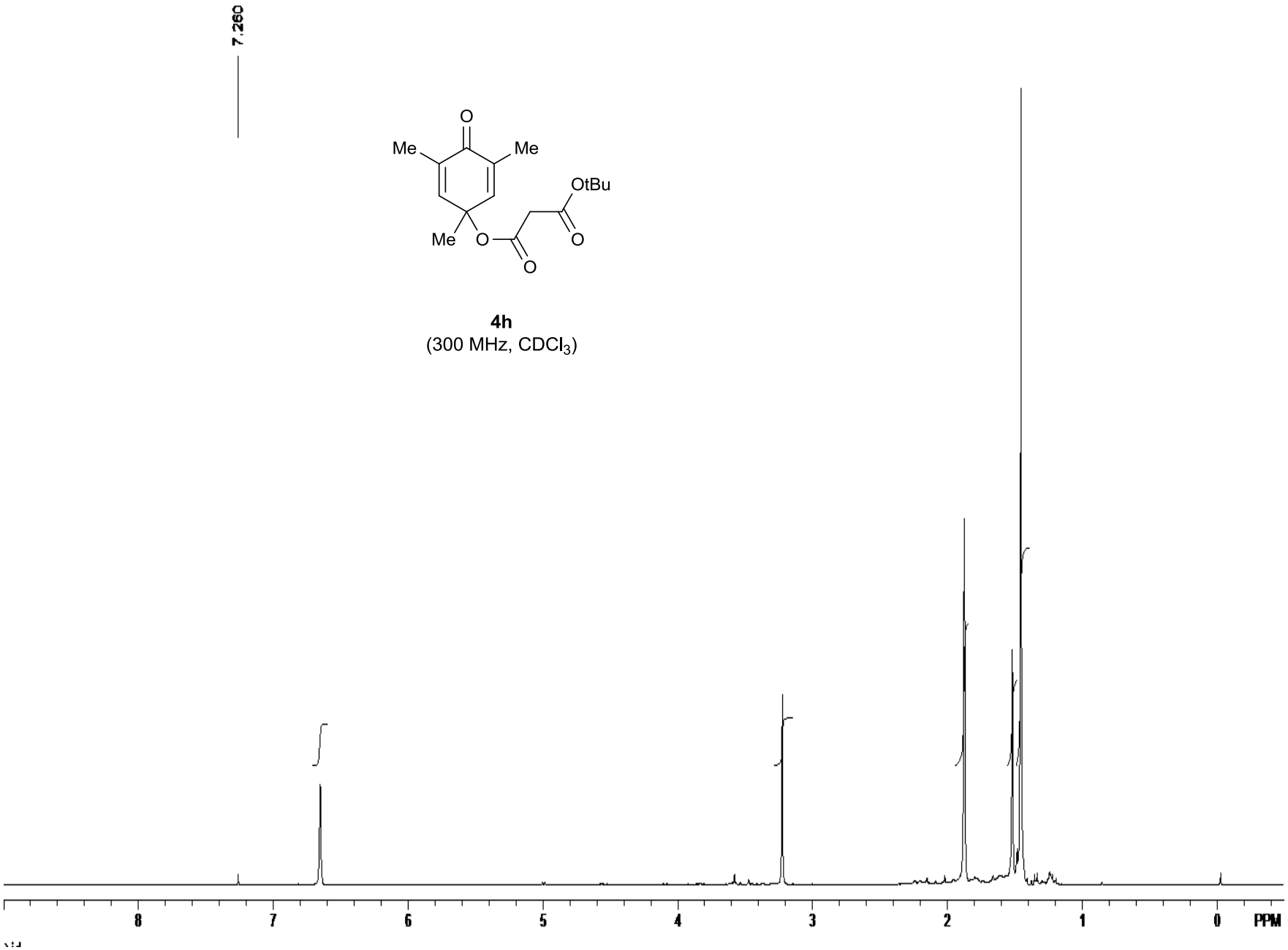
4g
(300 MHz, $CDCl_3$)



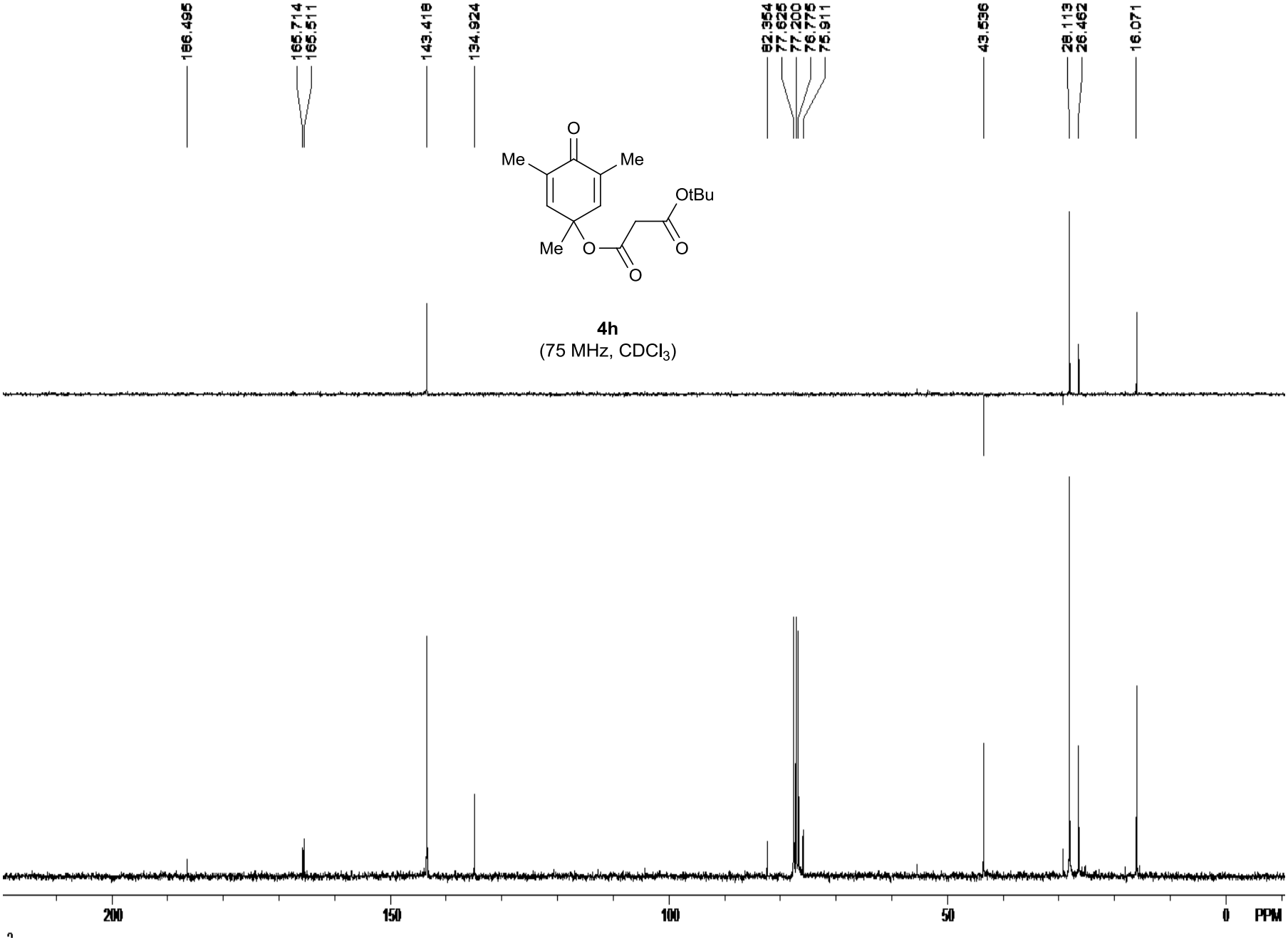
4g
(75 MHz, $CDCl_3$)



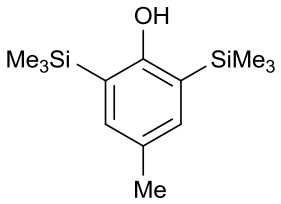
1h
(300 MHz, $CDCl_3$)



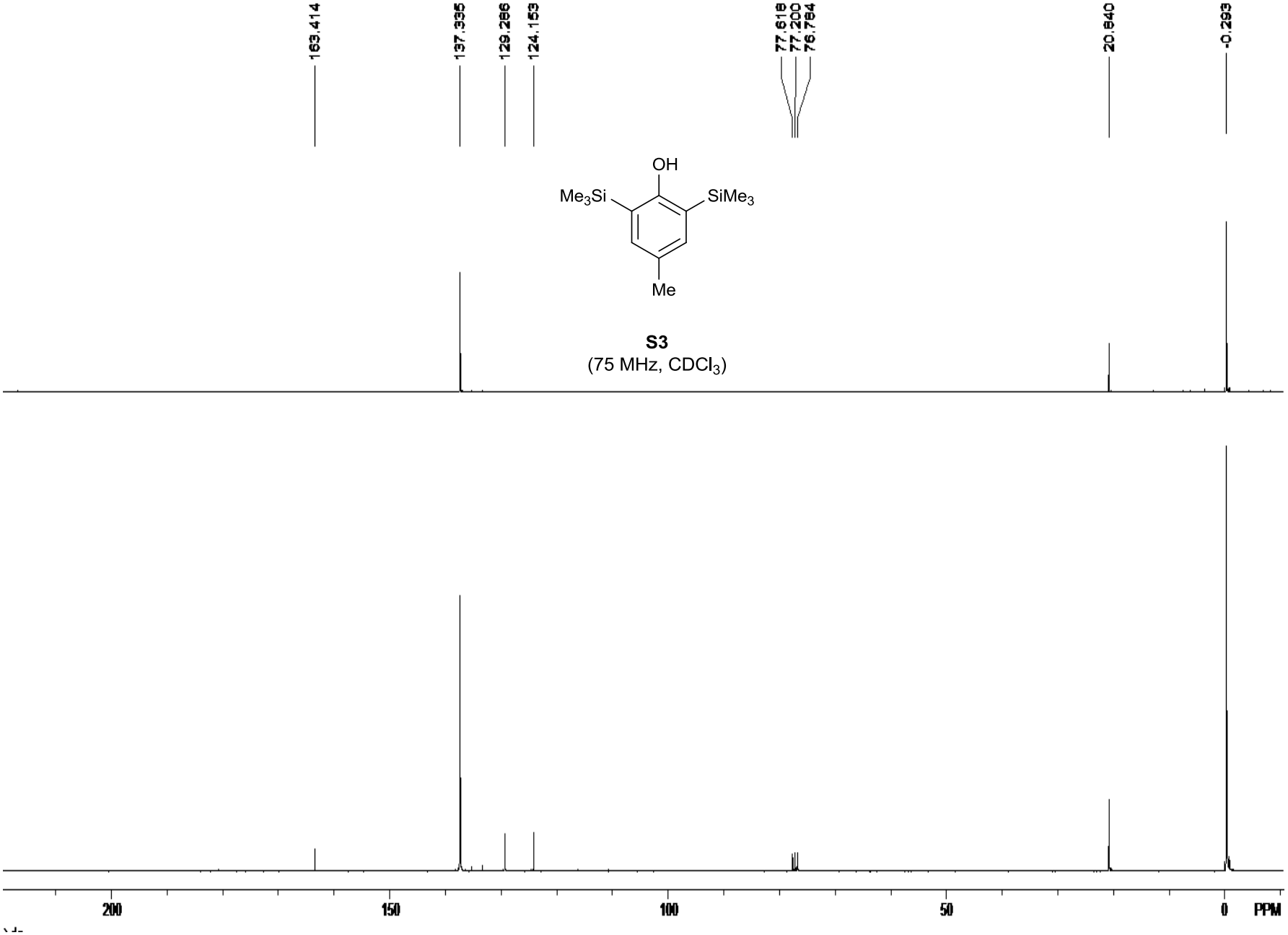
4h
(300 MHz, $CDCl_3$)



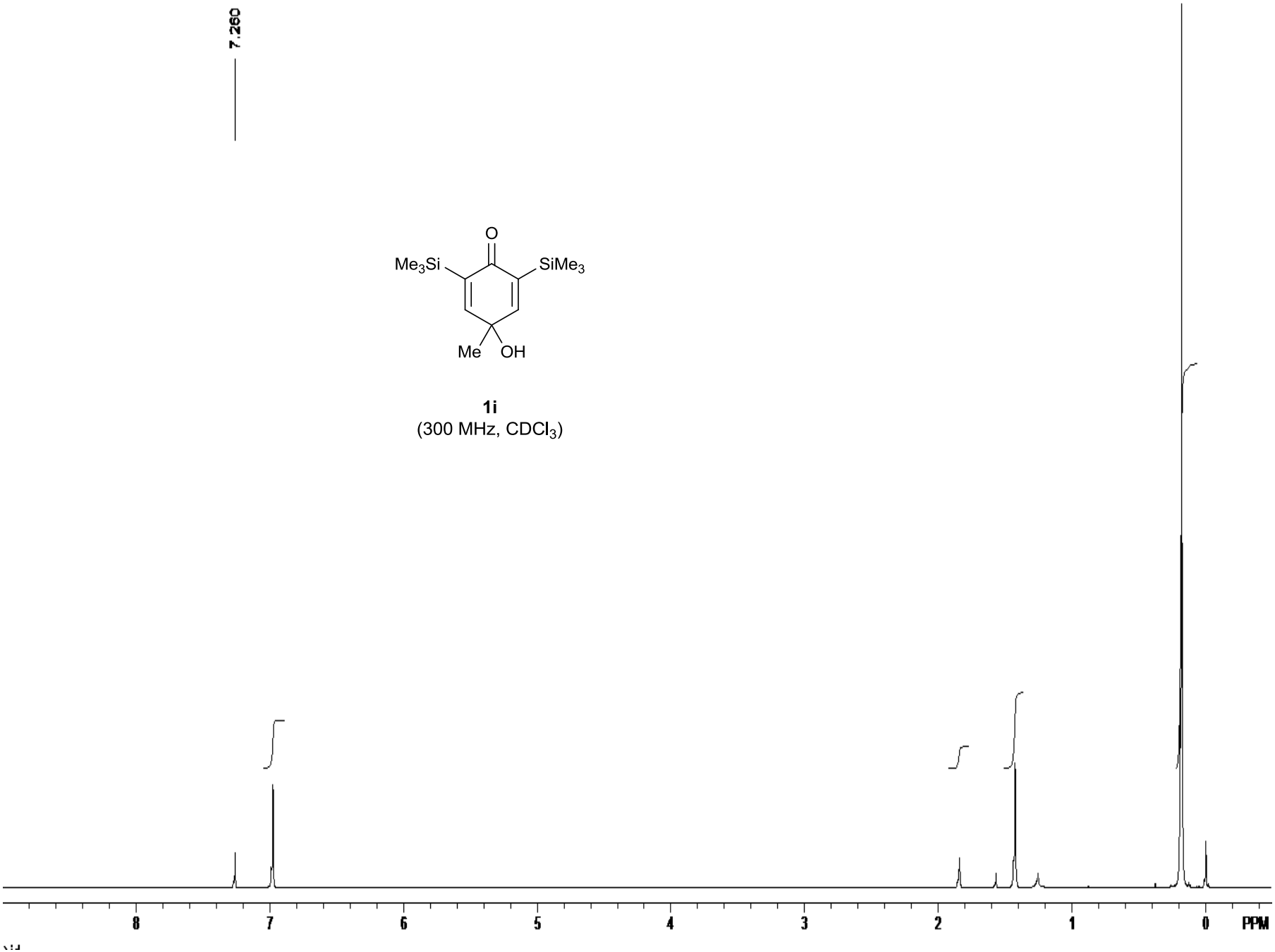
4h
(75 MHz, $CDCl_3$)



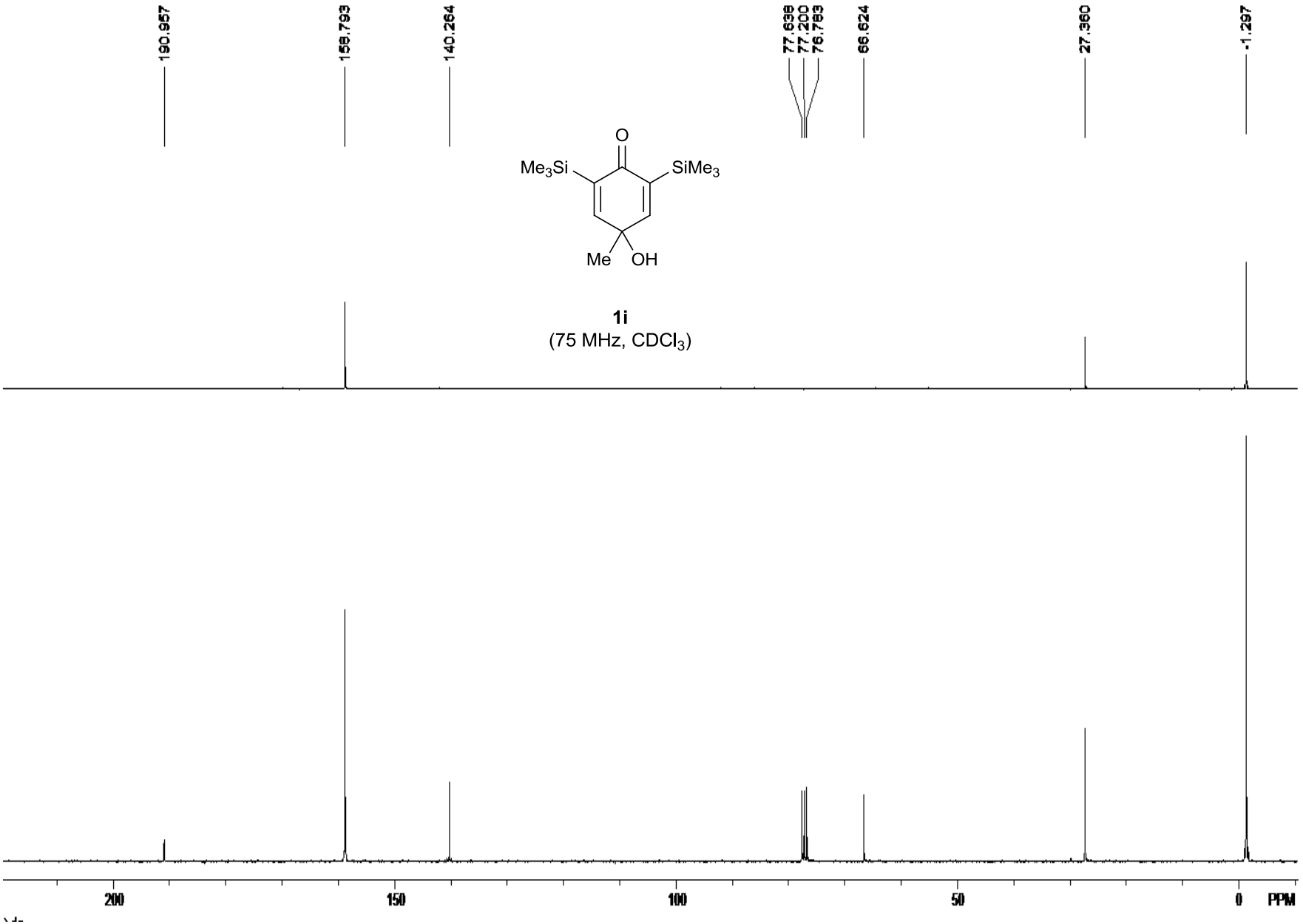
S3
(300 MHz, $CDCl_3$)



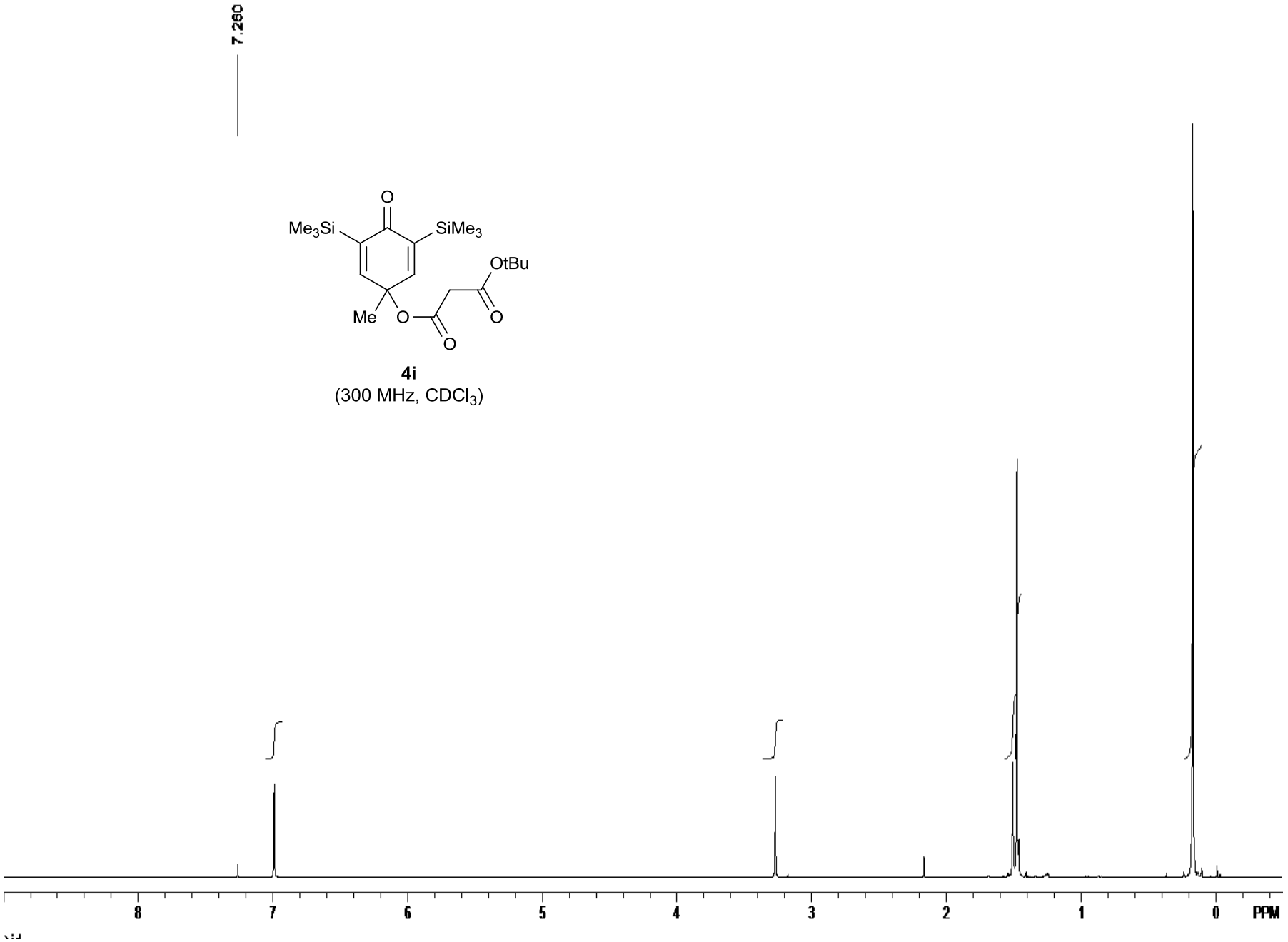
S3
(75 MHz, $CDCl_3$)



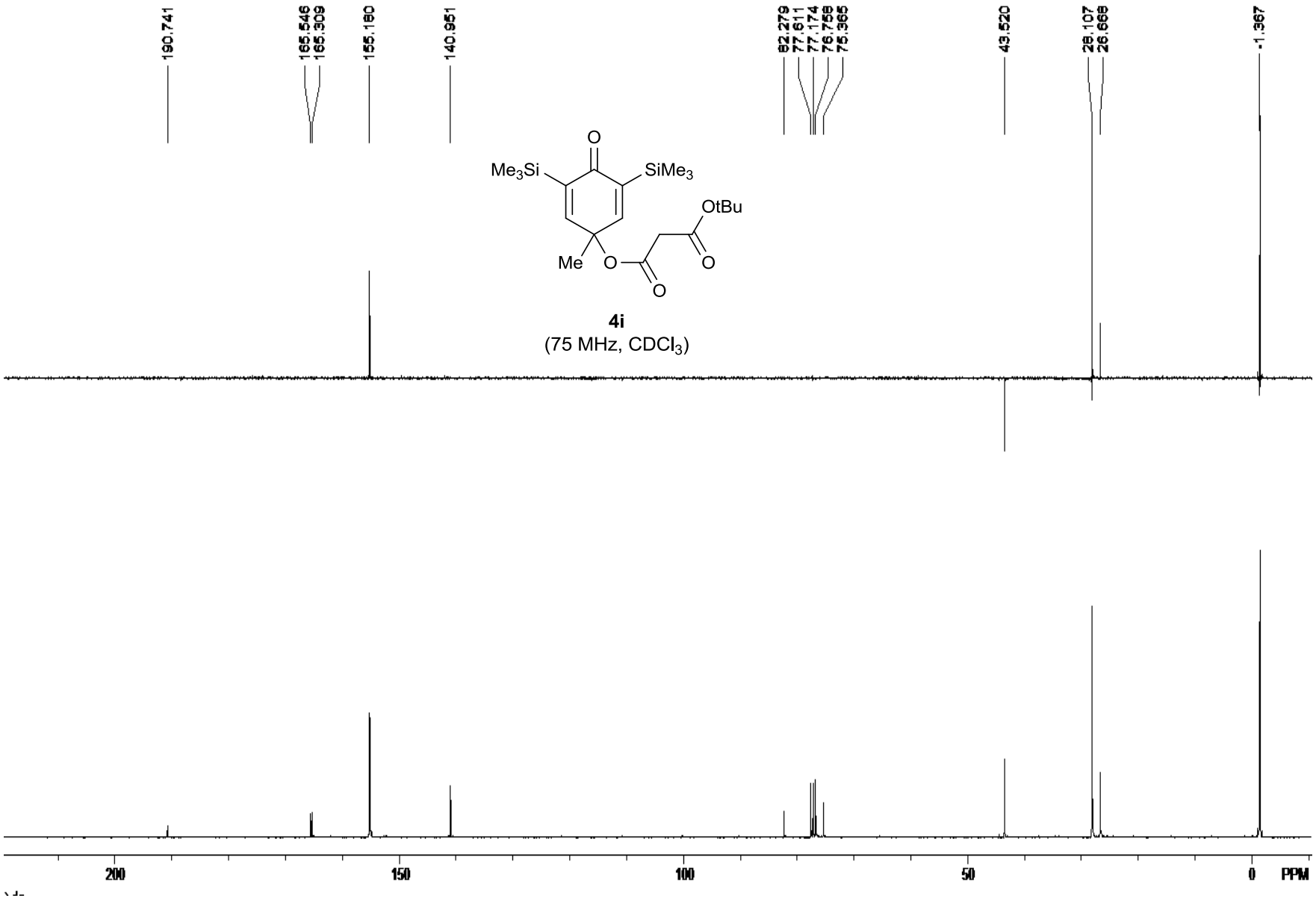
1i
(300 MHz, $CDCl_3$)



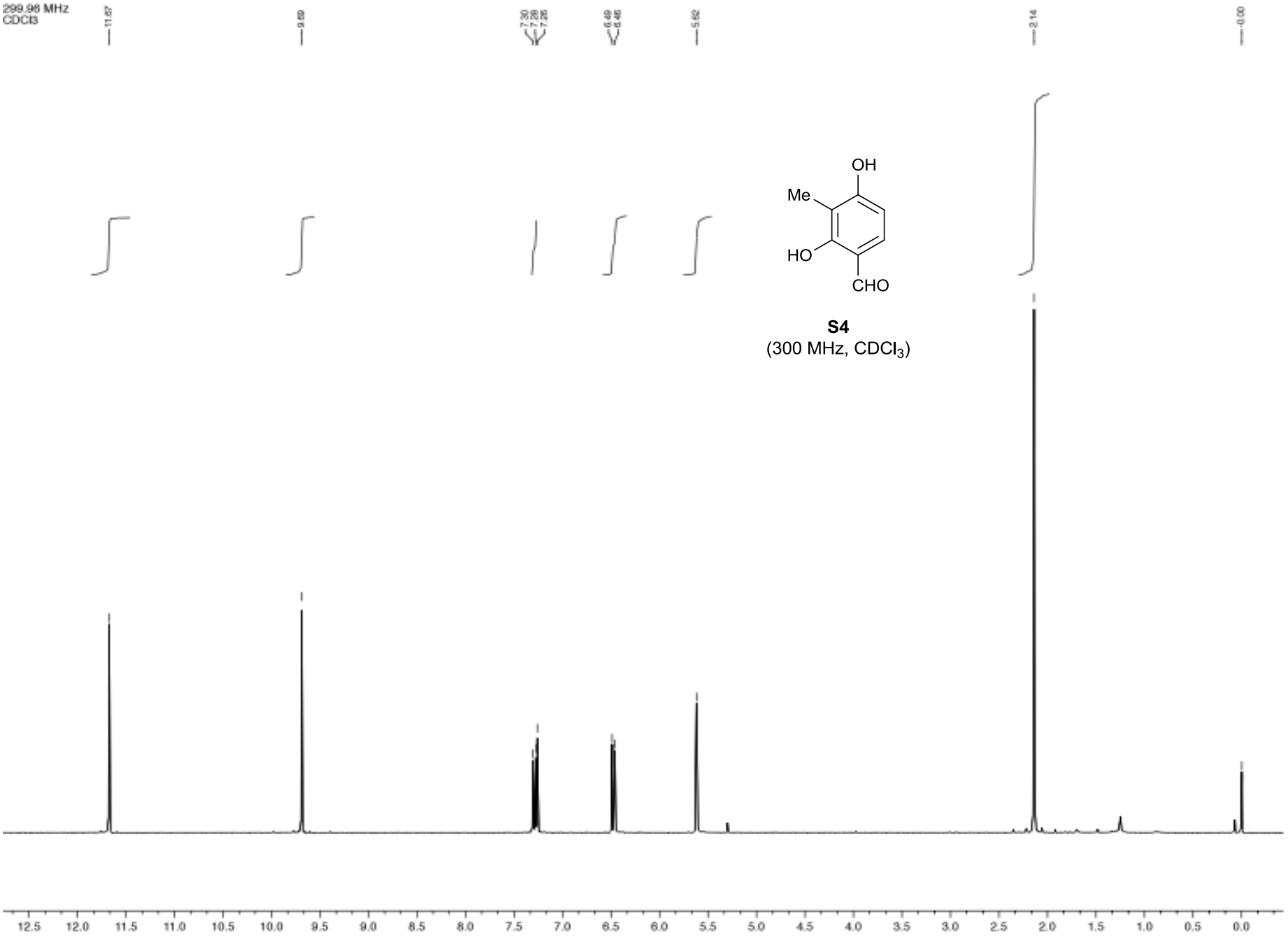
1i
(75 MHz, $CDCl_3$)



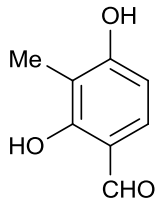
4i
(300 MHz, $CDCl_3$)



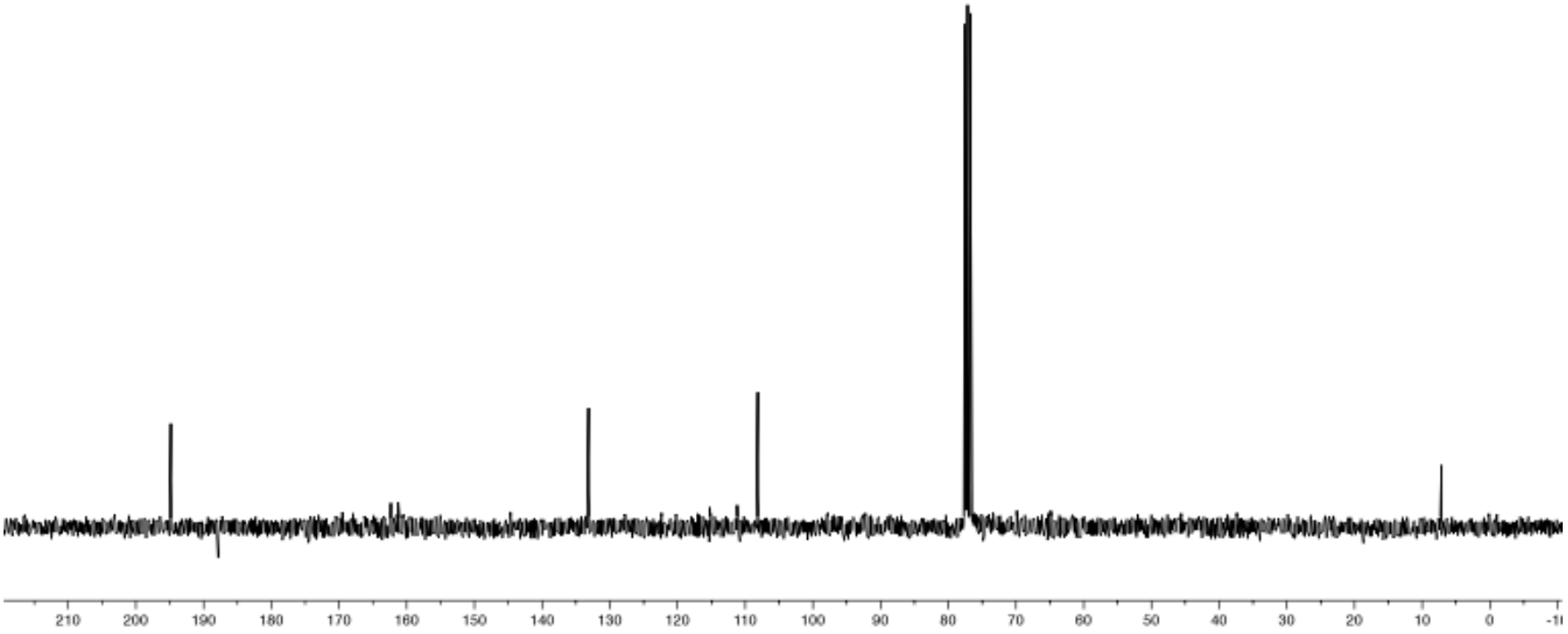
4i
(75 MHz, $CDCl_3$)

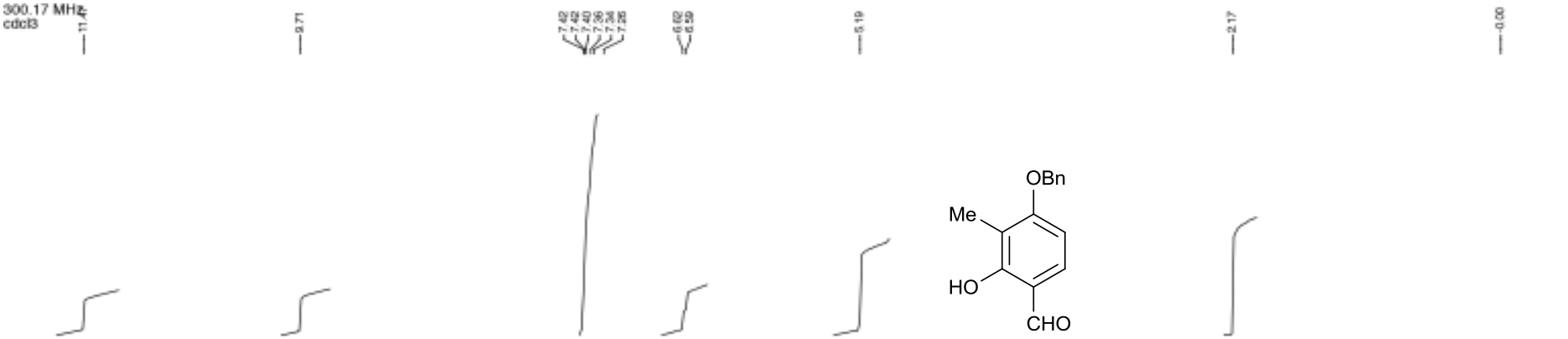


S4
(300 MHz, $CDCl_3$)

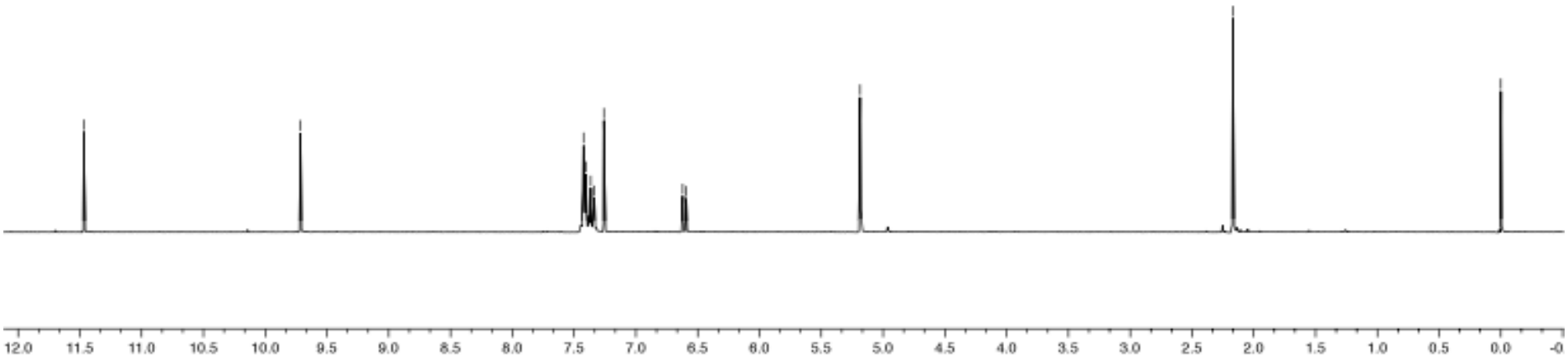


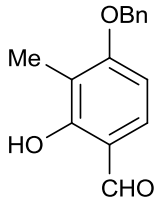
S4
(75 MHz, $CDCl_3$)



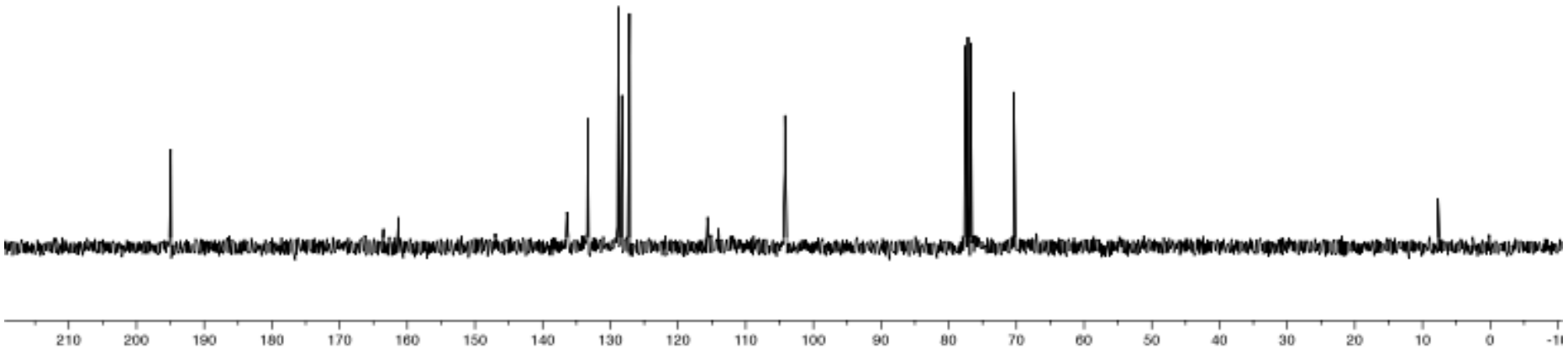


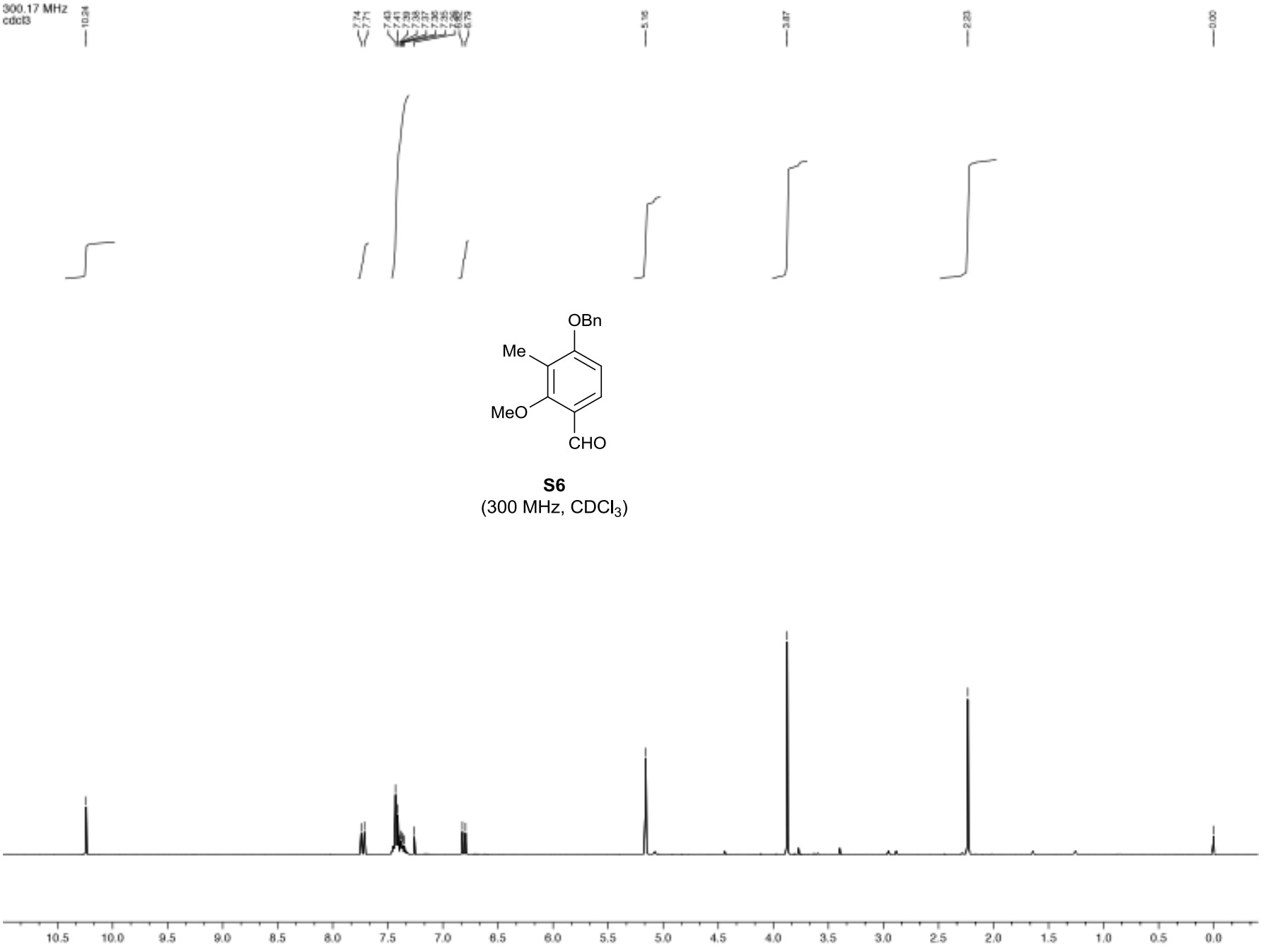
S5
(300 MHz, $CDCl_3$)



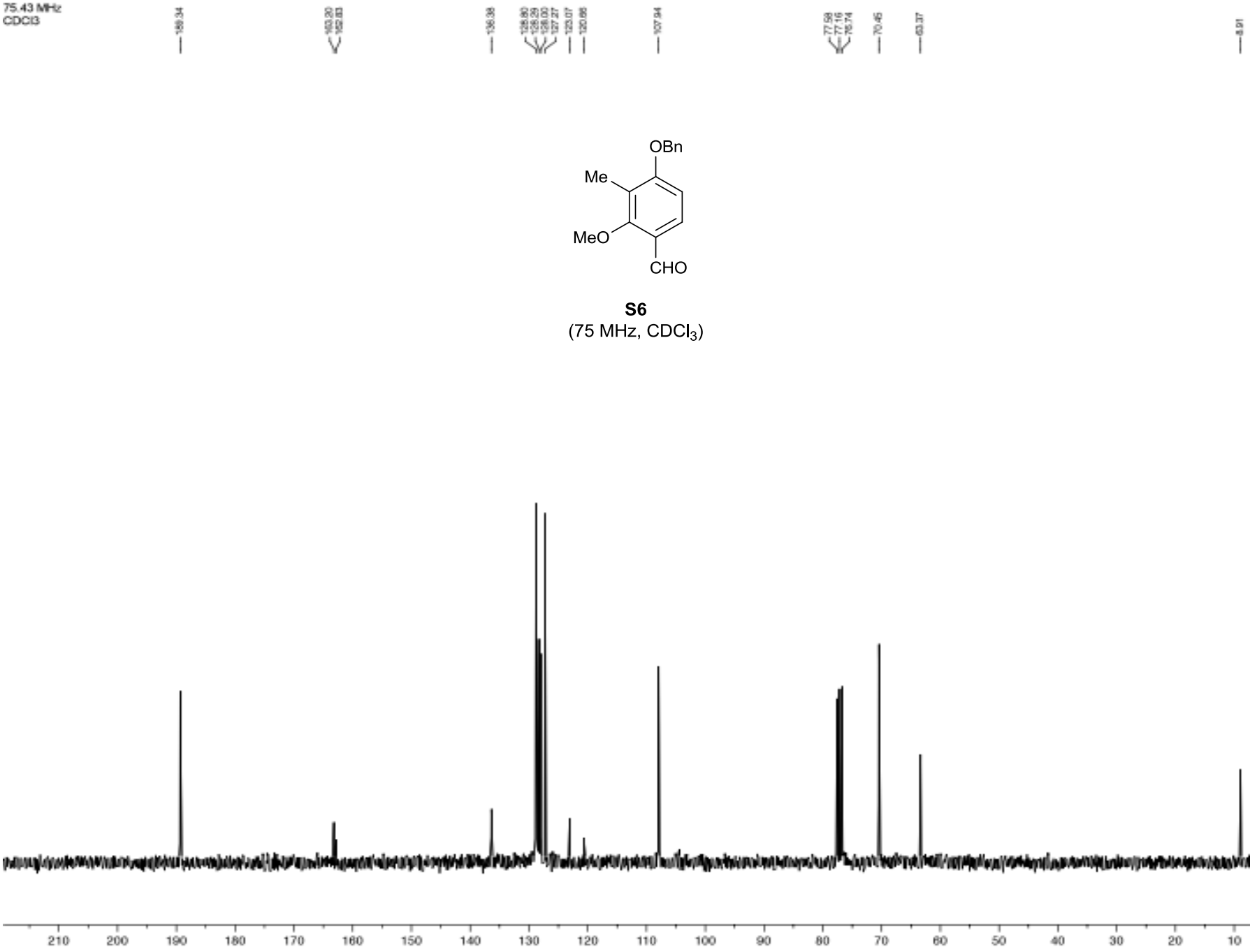


S5
(75 MHz, $CDCl_3$)

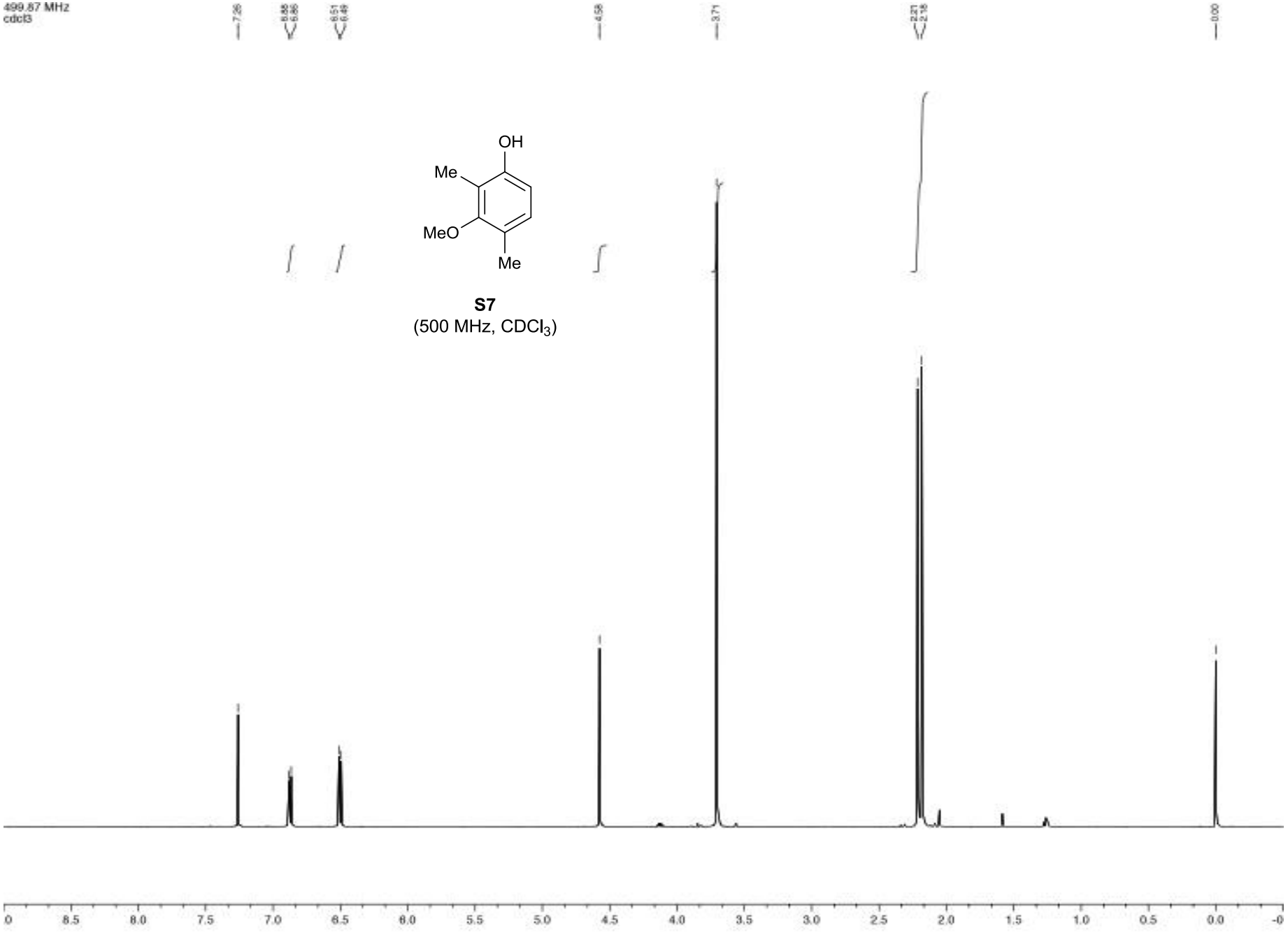




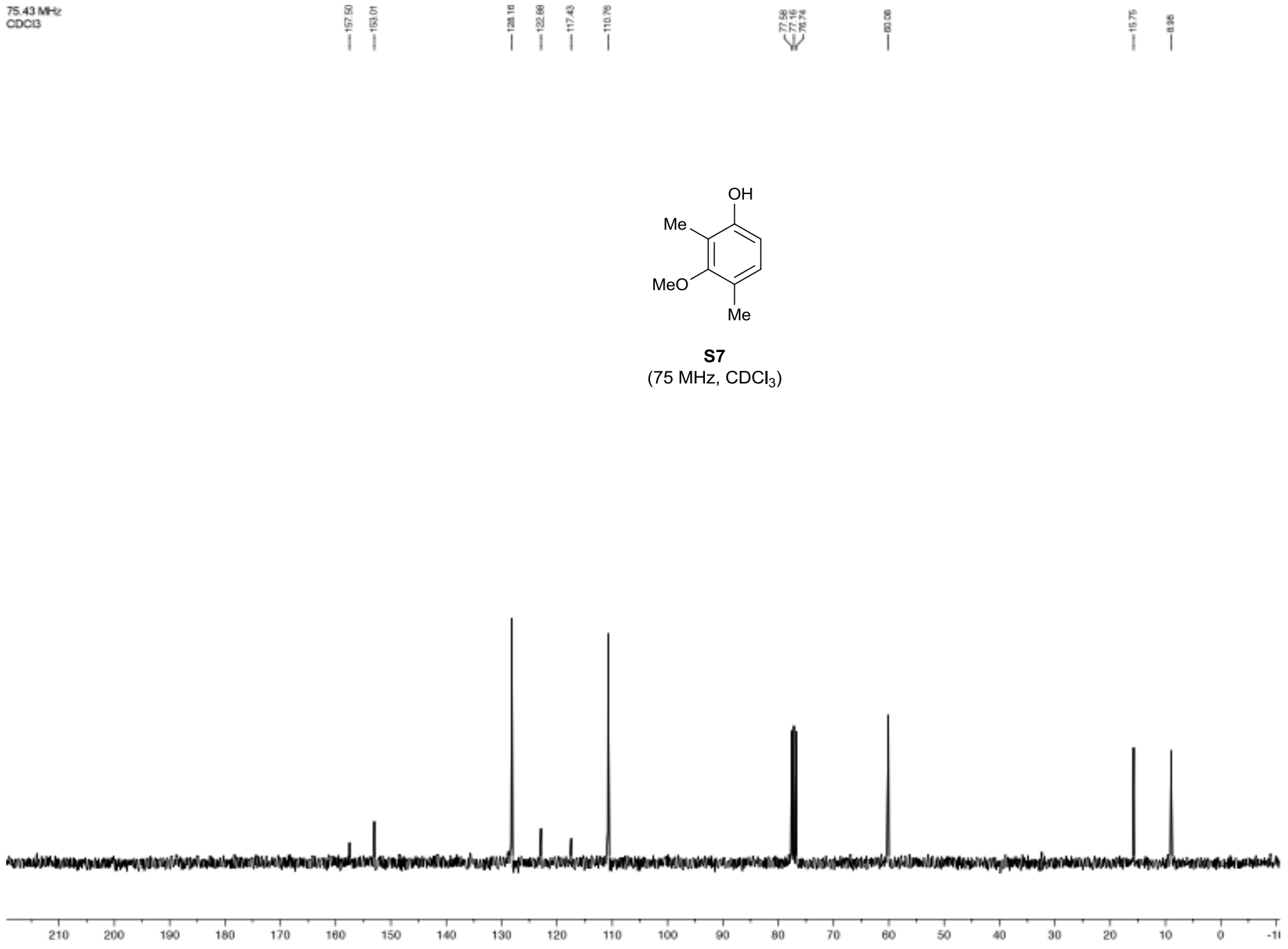
S6
(300 MHz, $CDCl_3$)



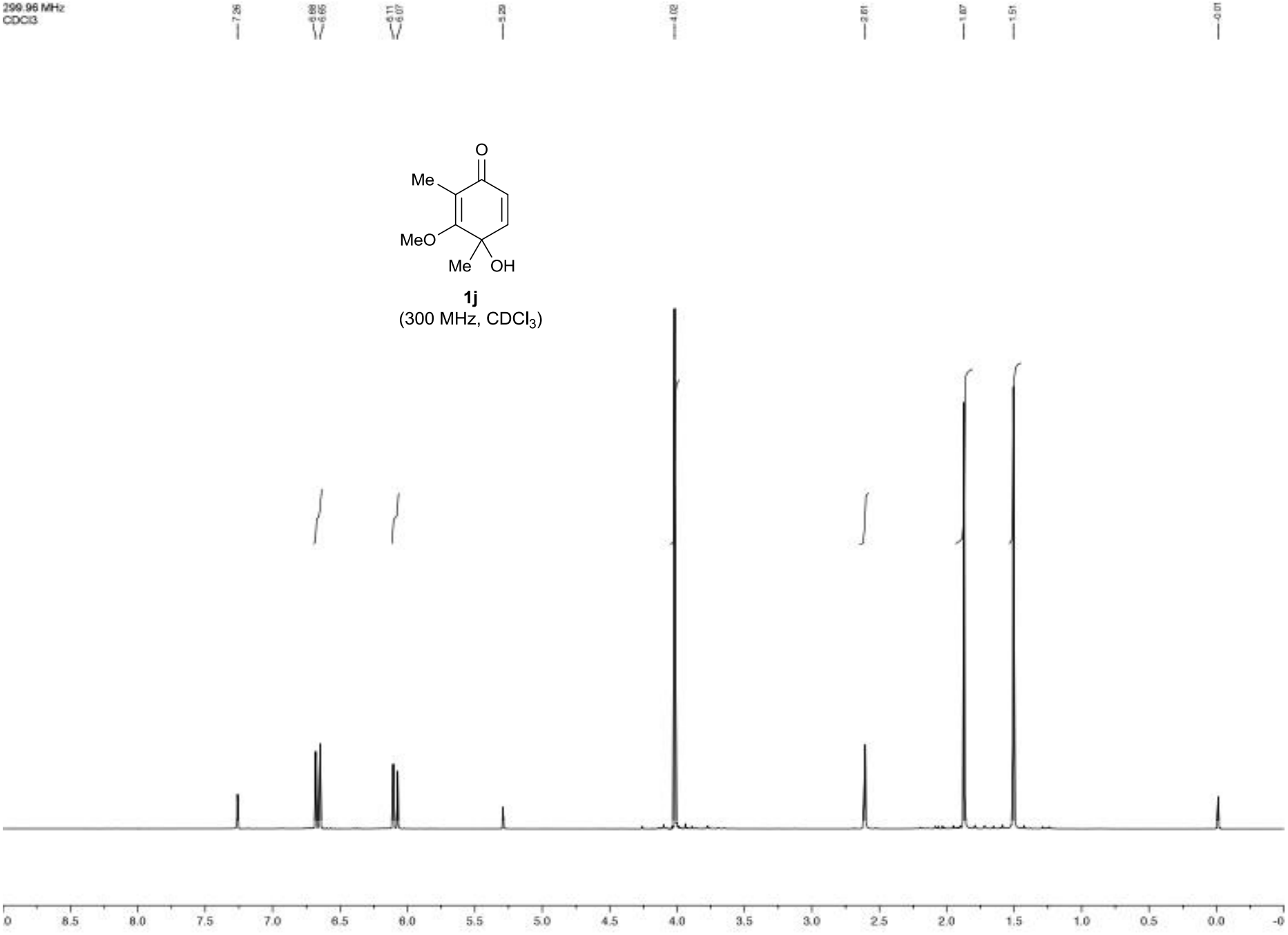
S6
(75 MHz, $CDCl_3$)



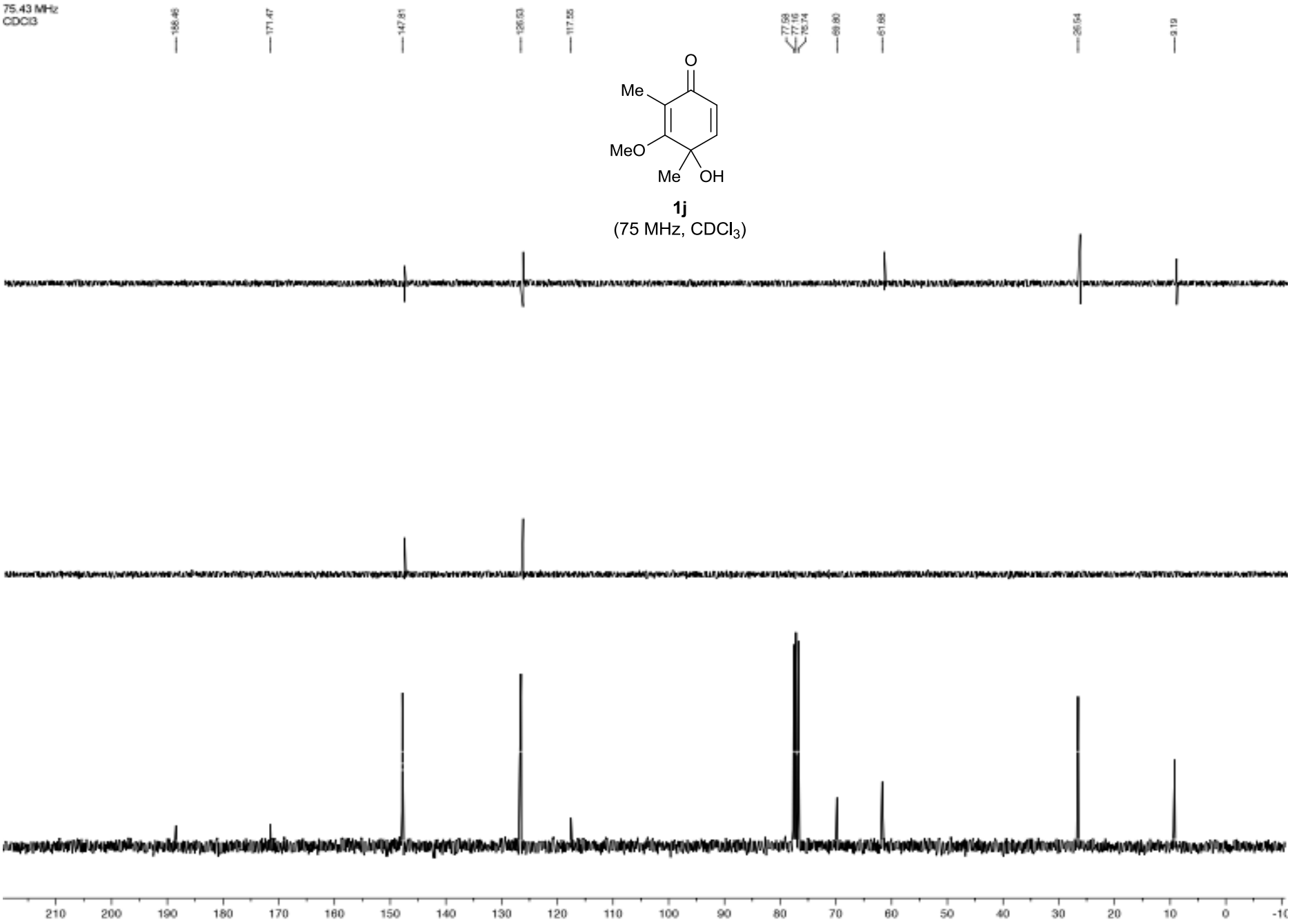
S7
(500 MHz, $CDCl_3$)



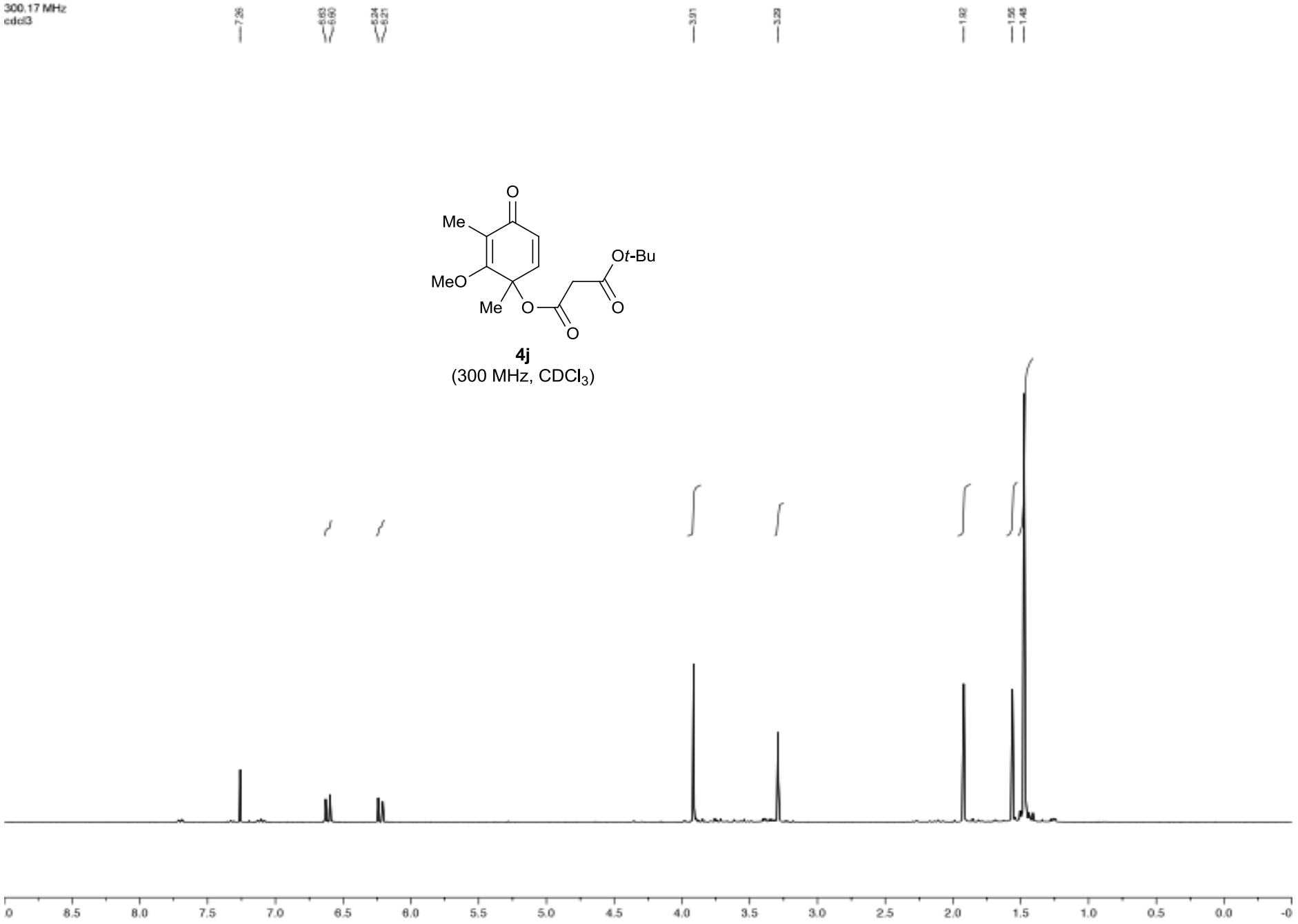
S7
(75 MHz, $CDCl_3$)

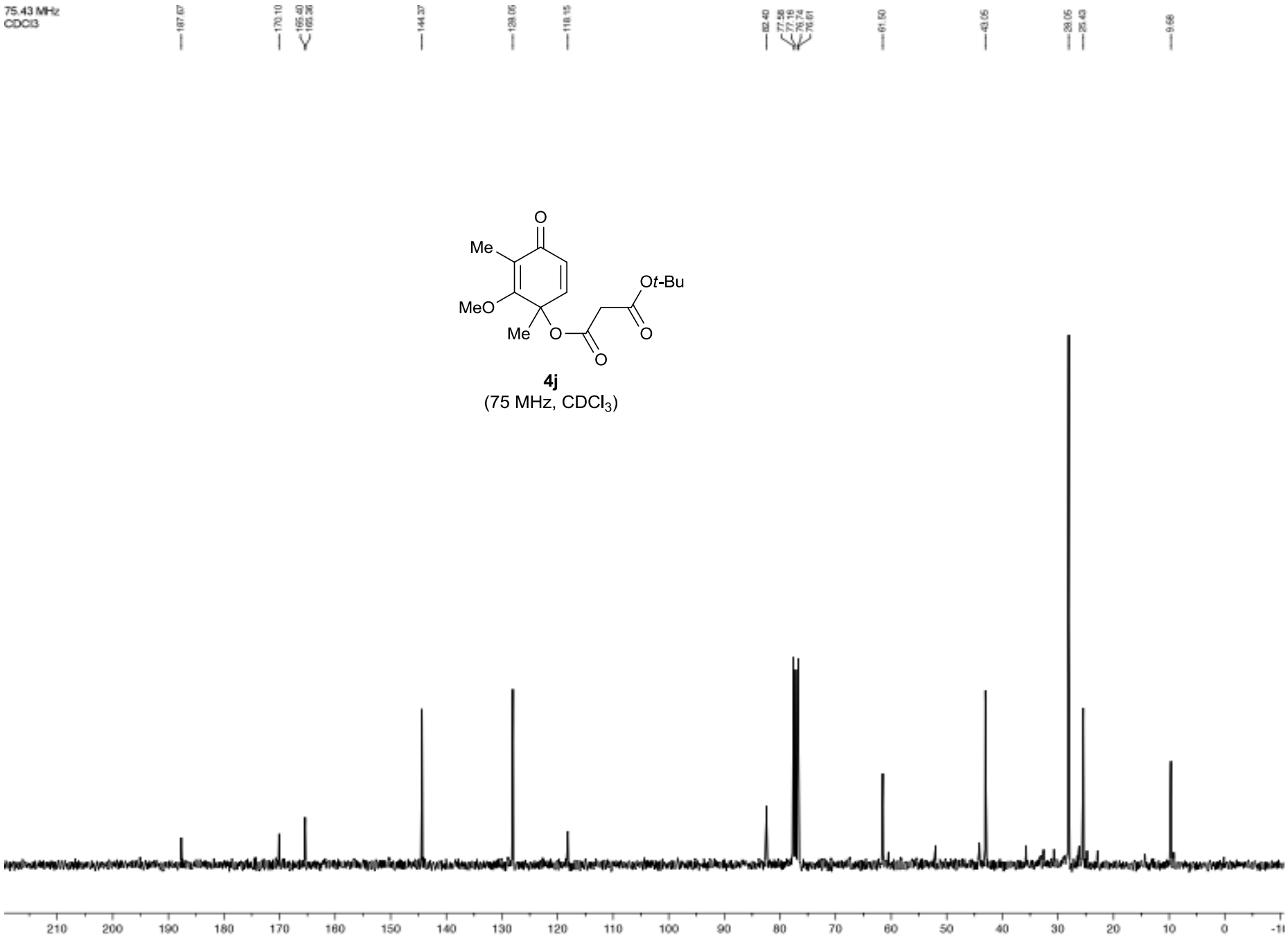


1j
(300 MHz, $CDCl_3$)

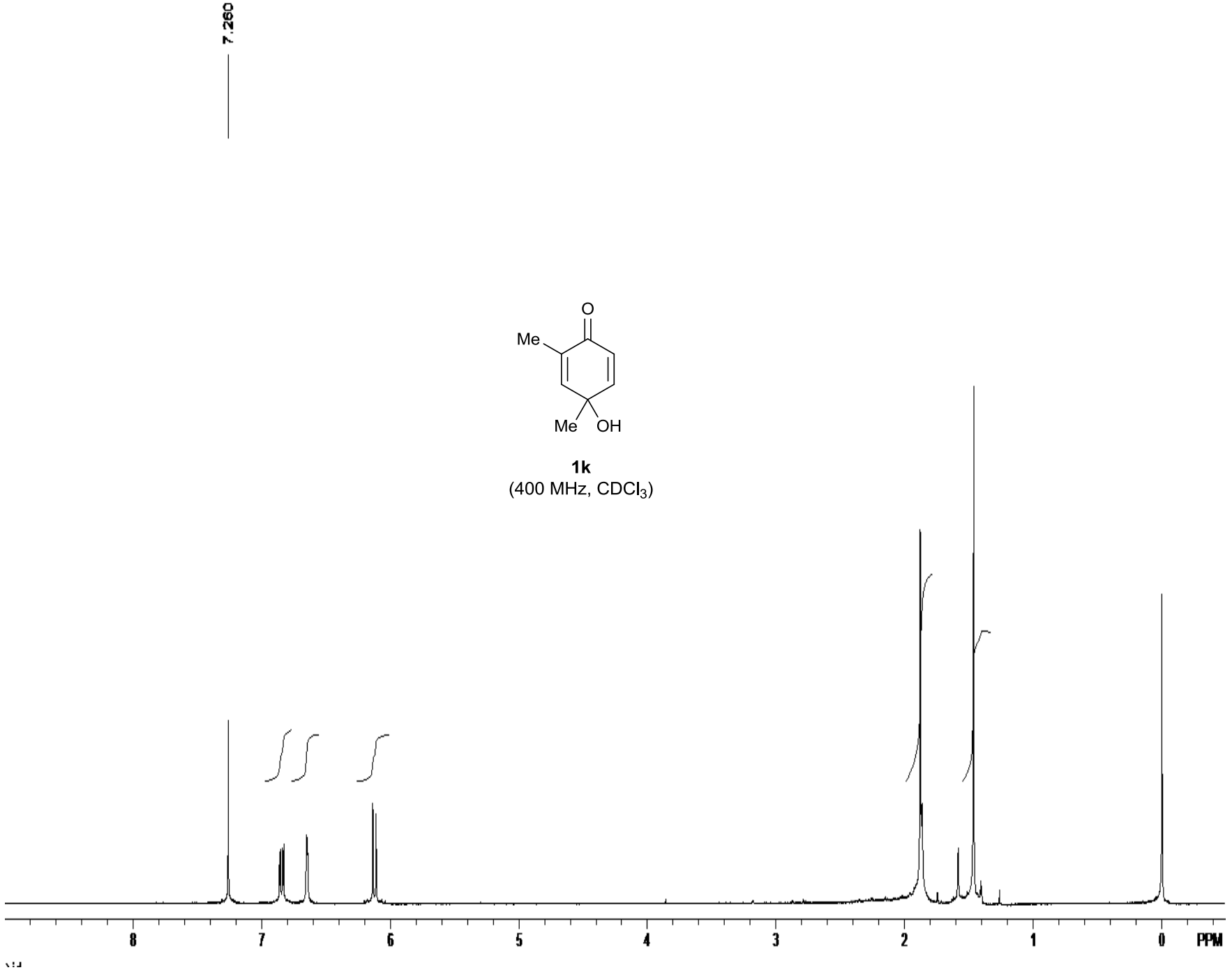


1j
(75 MHz, $CDCl_3$)

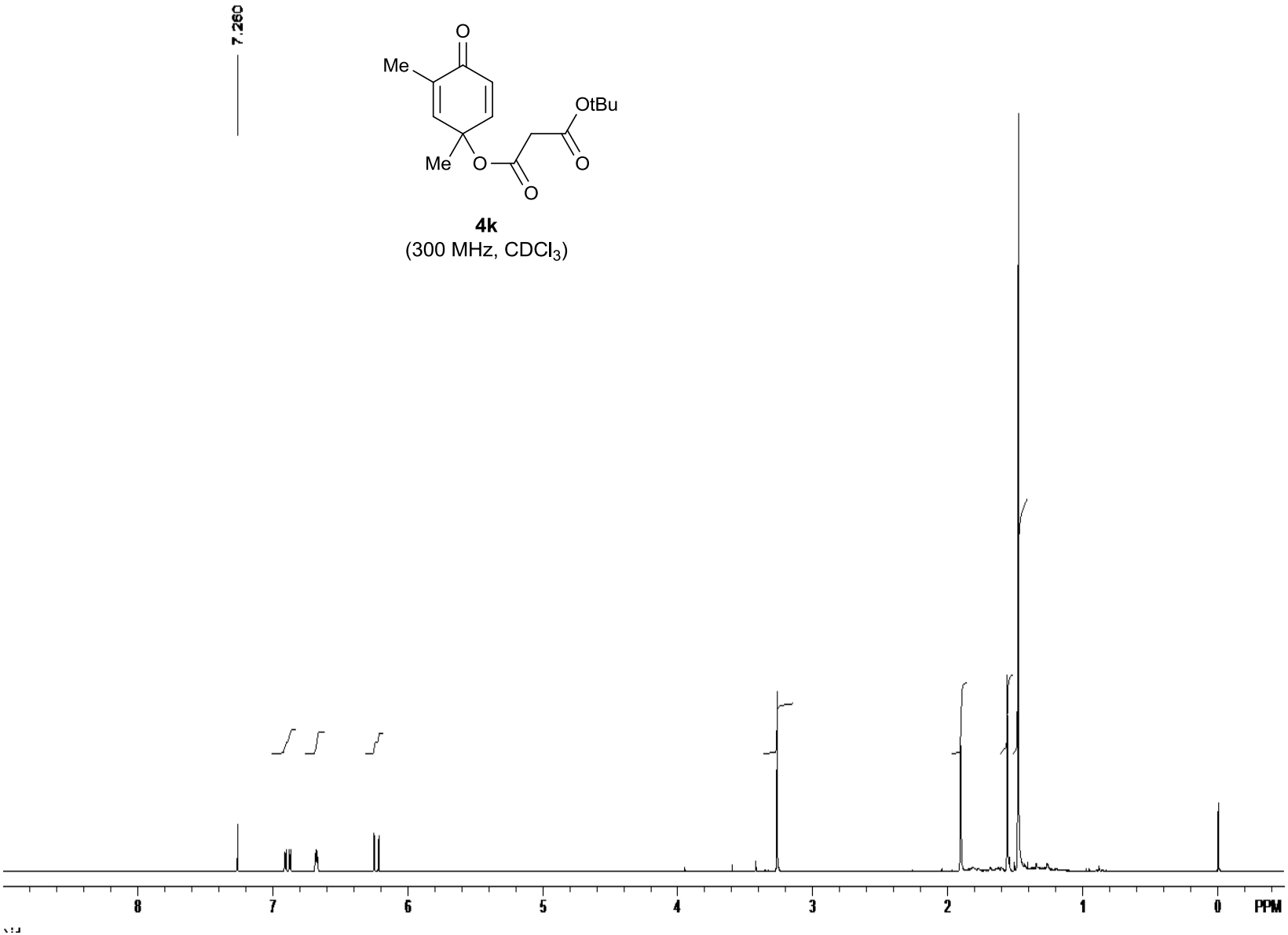




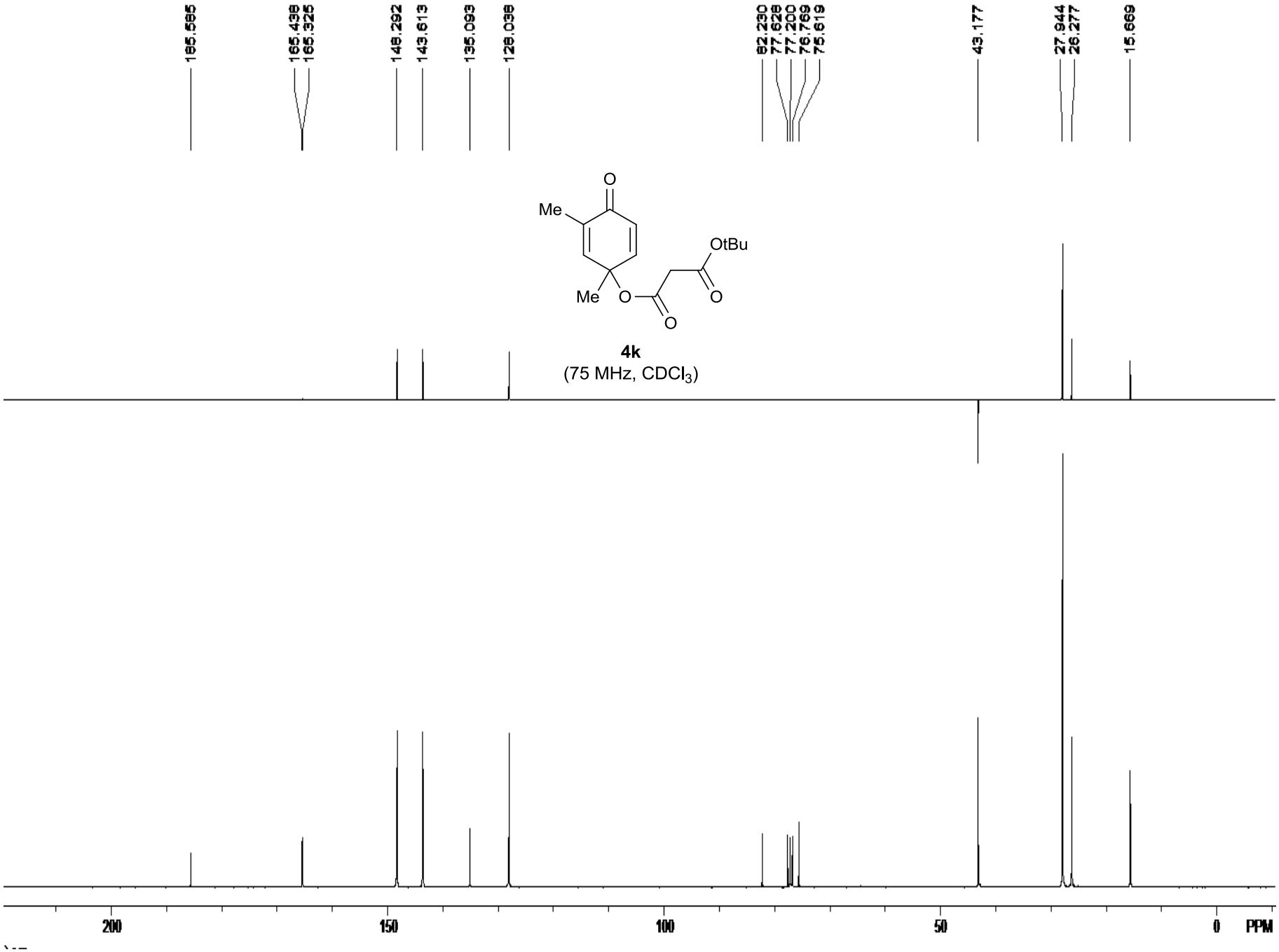
4j
(75 MHz, $CDCl_3$)



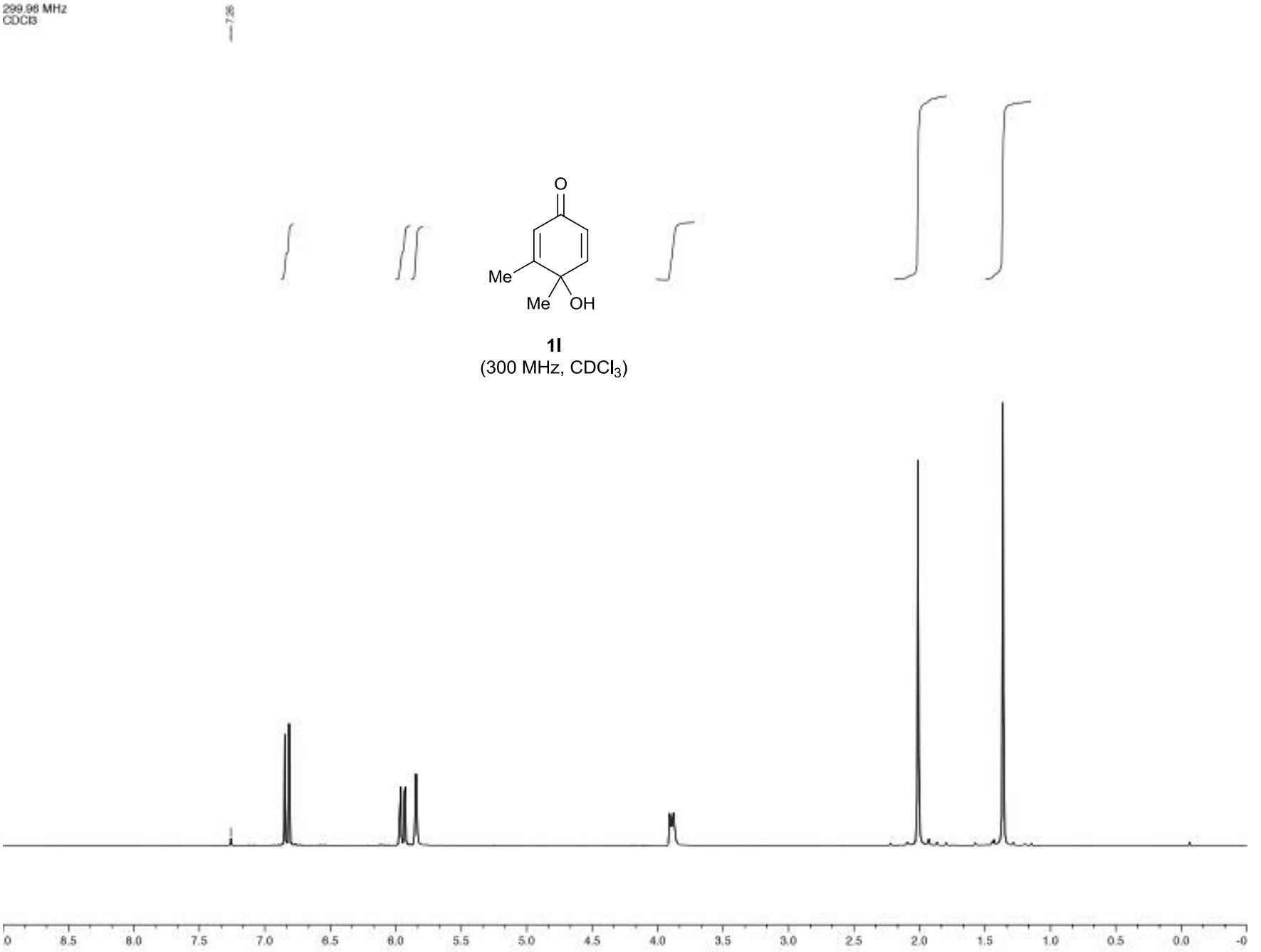
1k
(400 MHz, $CDCl_3$)



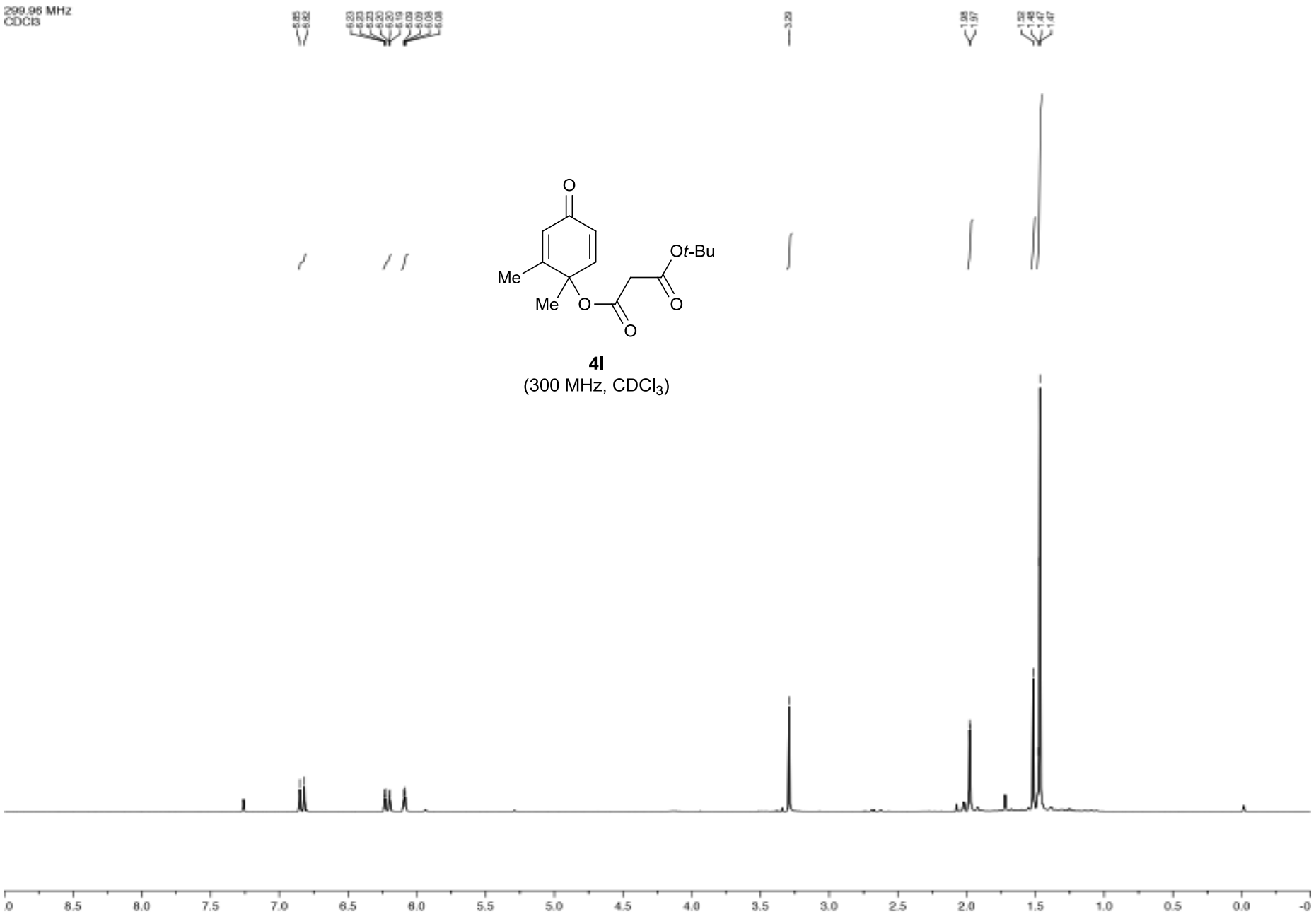
4k
(300 MHz, $CDCl_3$)



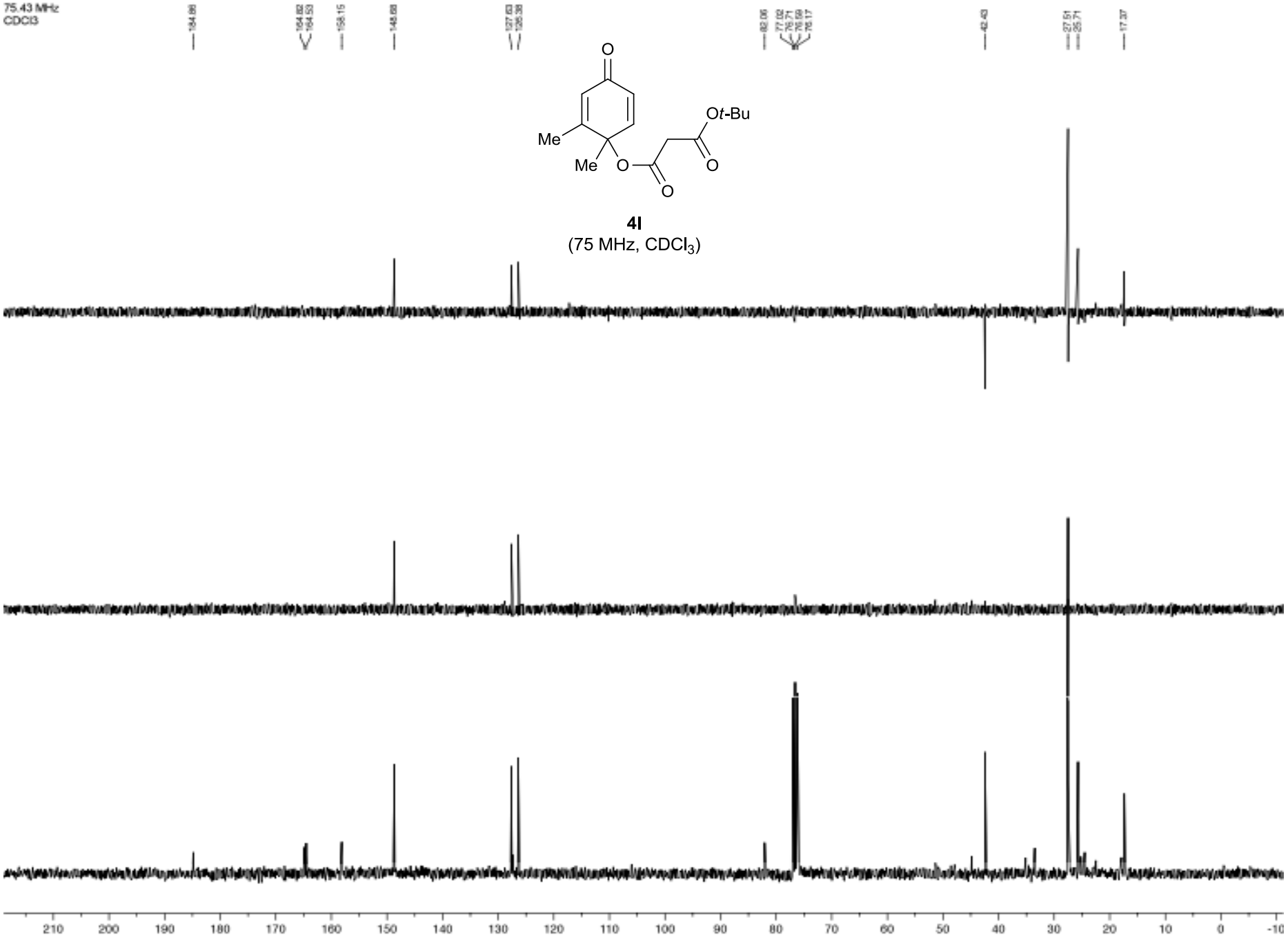
4k
(75 MHz, $CDCl_3$)



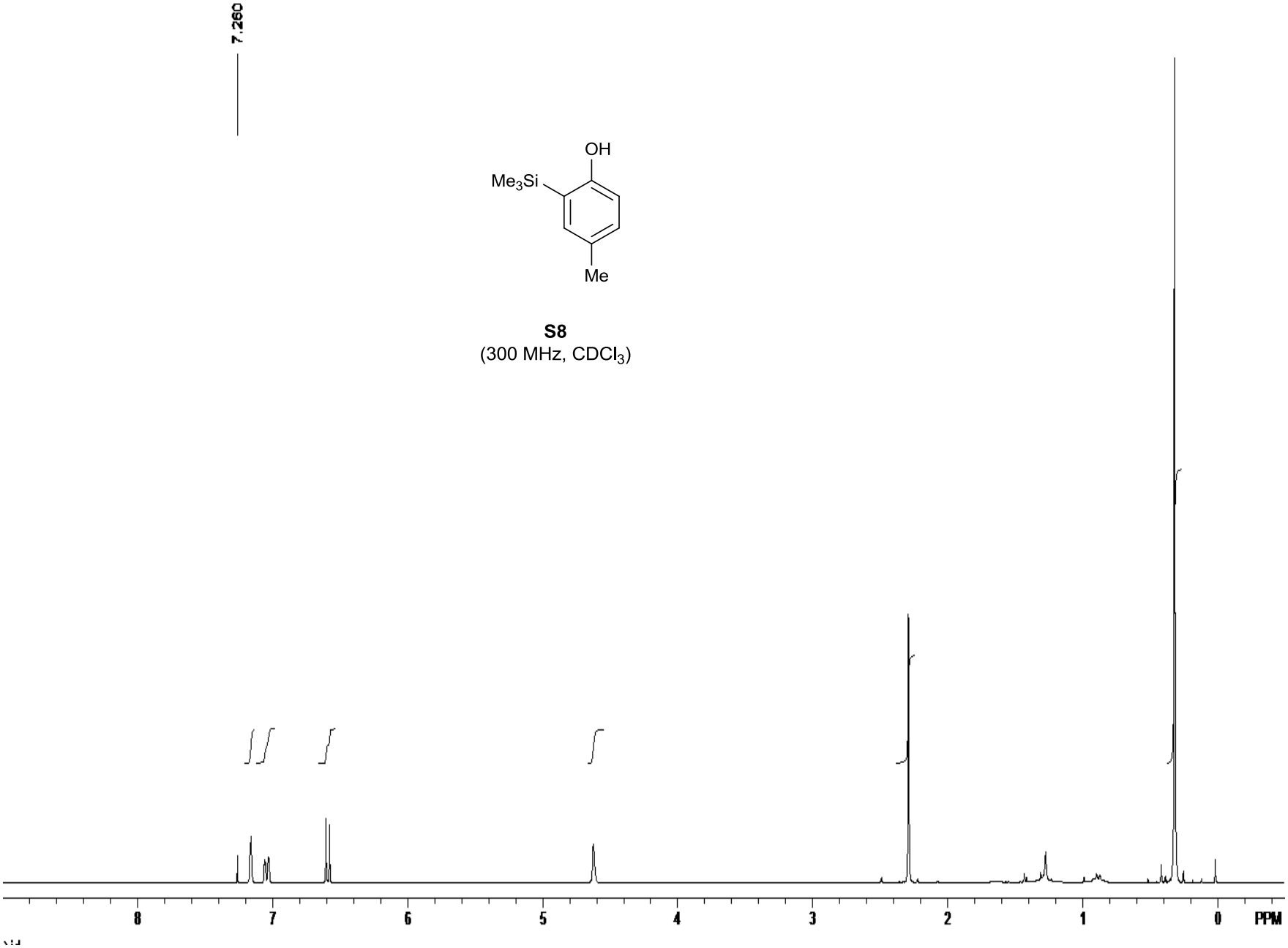
1l
(300 MHz, $CDCl_3$)



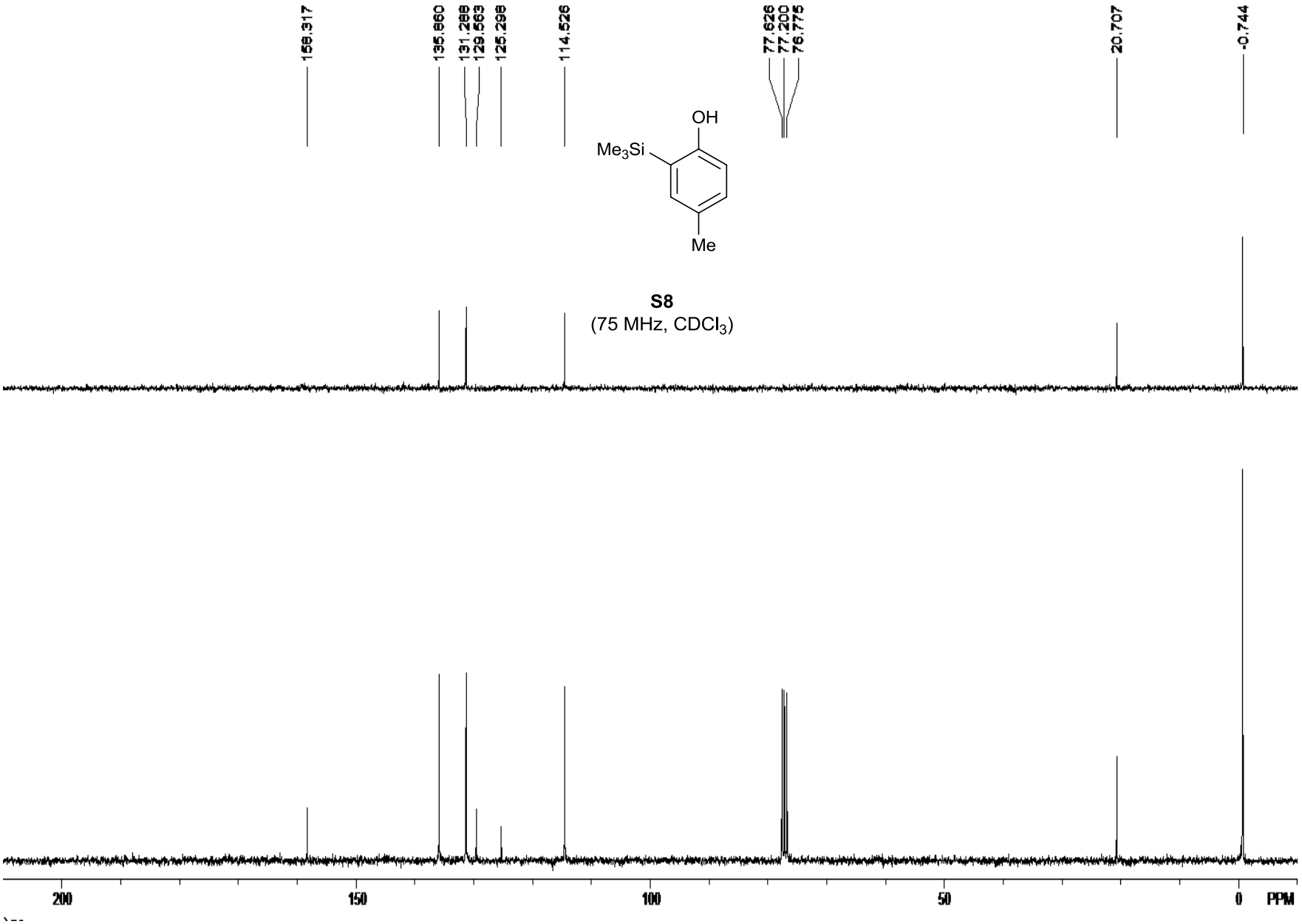
4l
(300 MHz, $CDCl_3$)



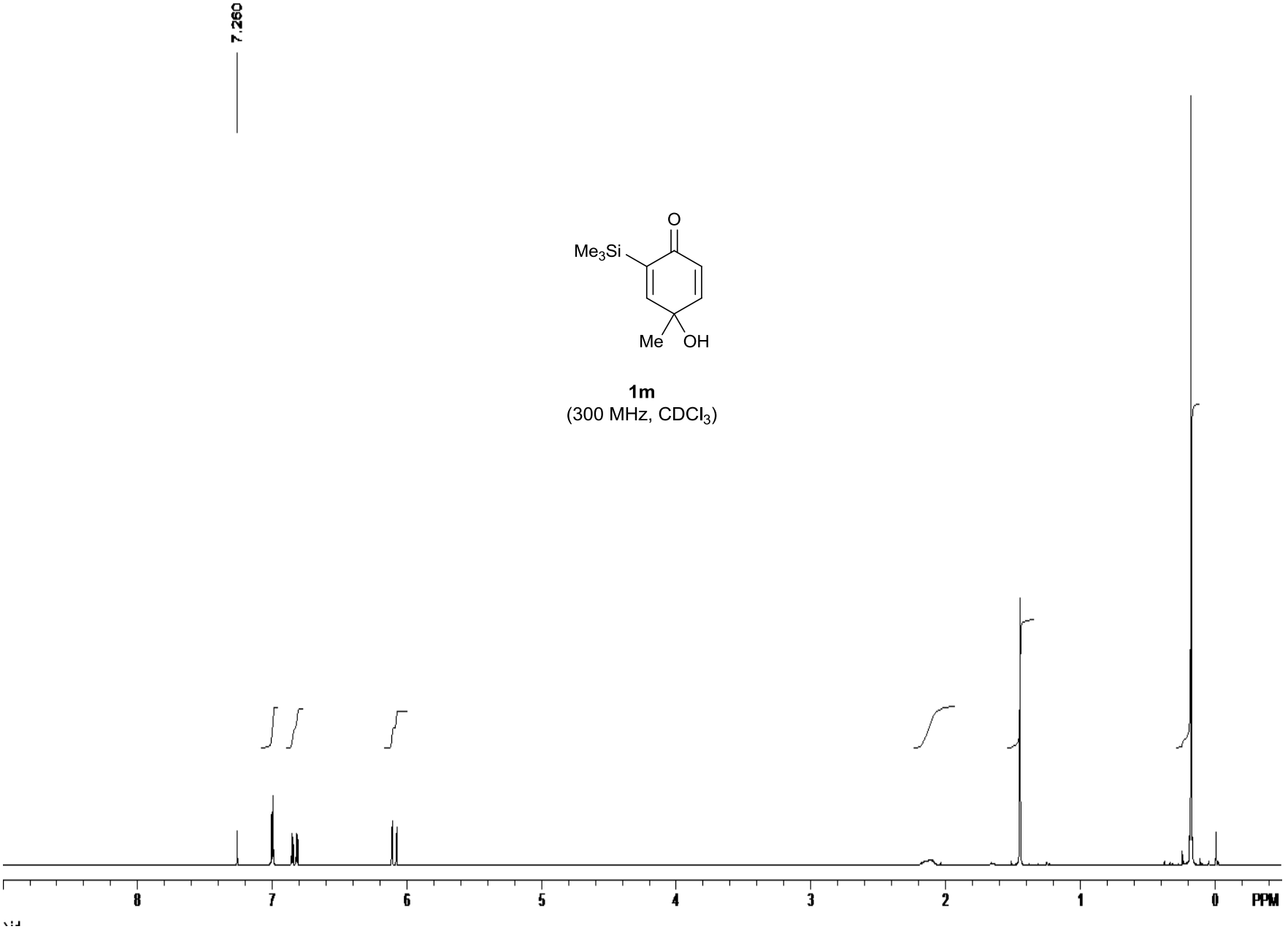
4l
(75 MHz, $CDCl_3$)

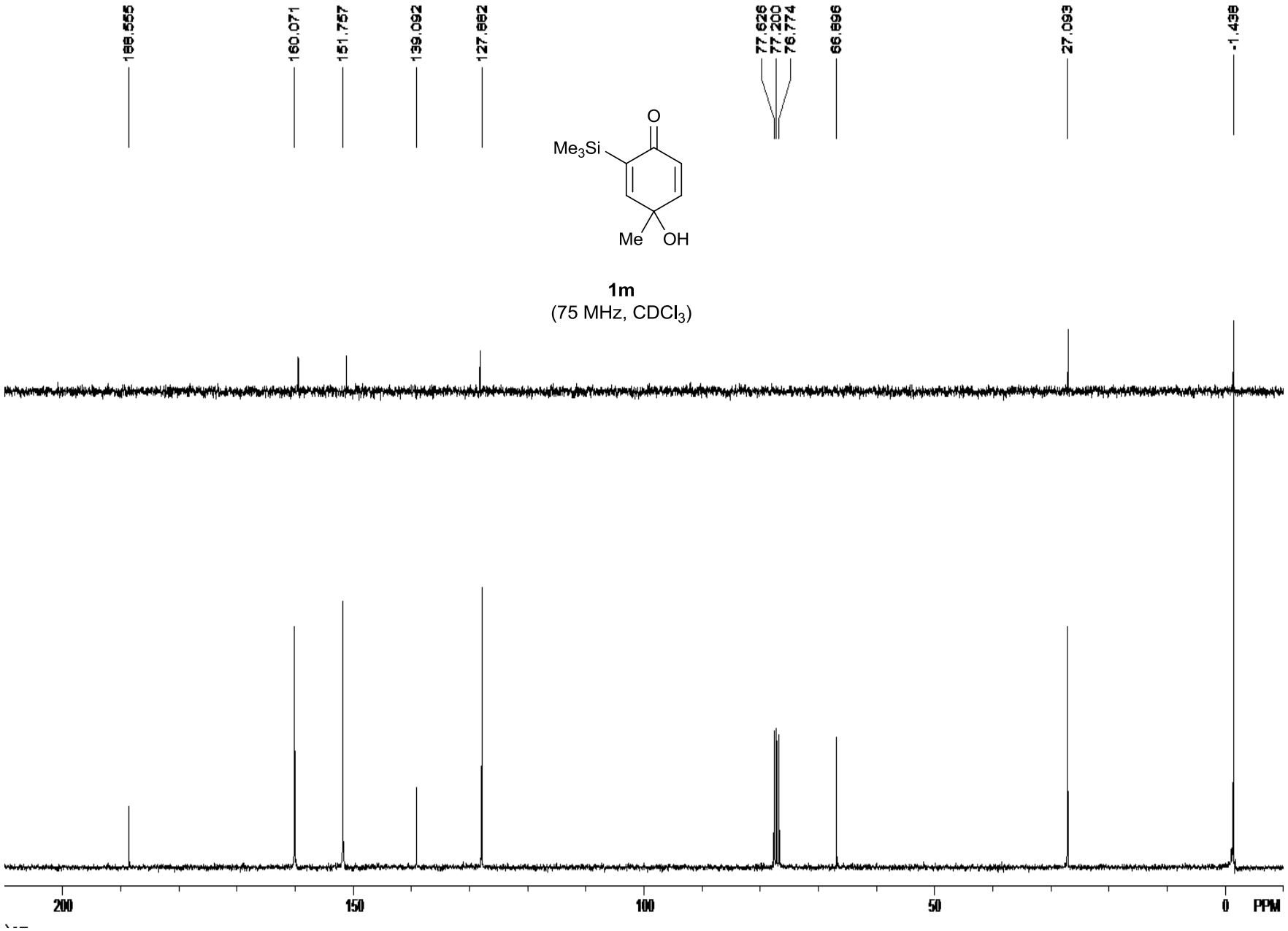


S8
(300 MHz, $CDCl_3$)

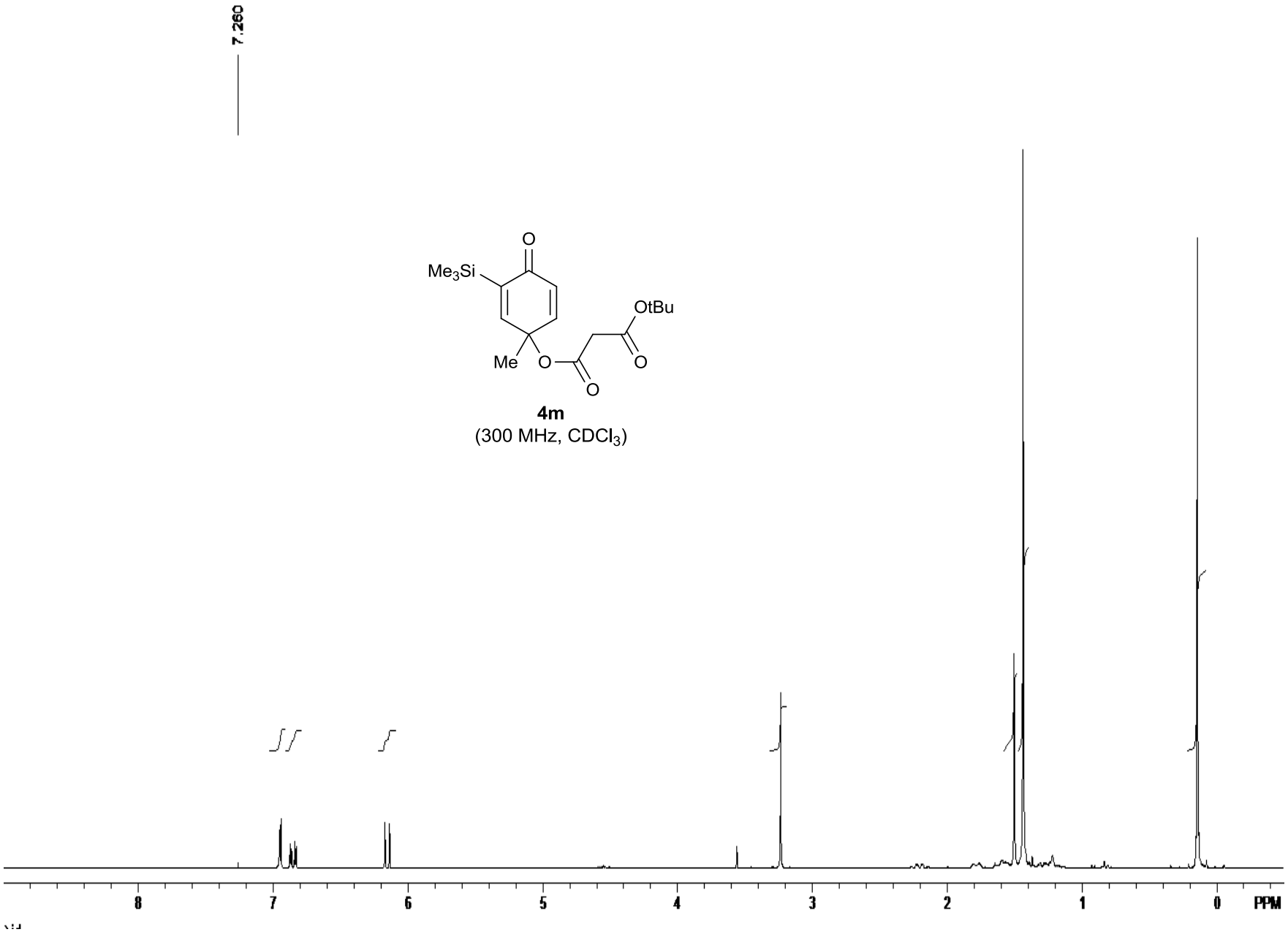


S8
(75 MHz, $CDCl_3$)

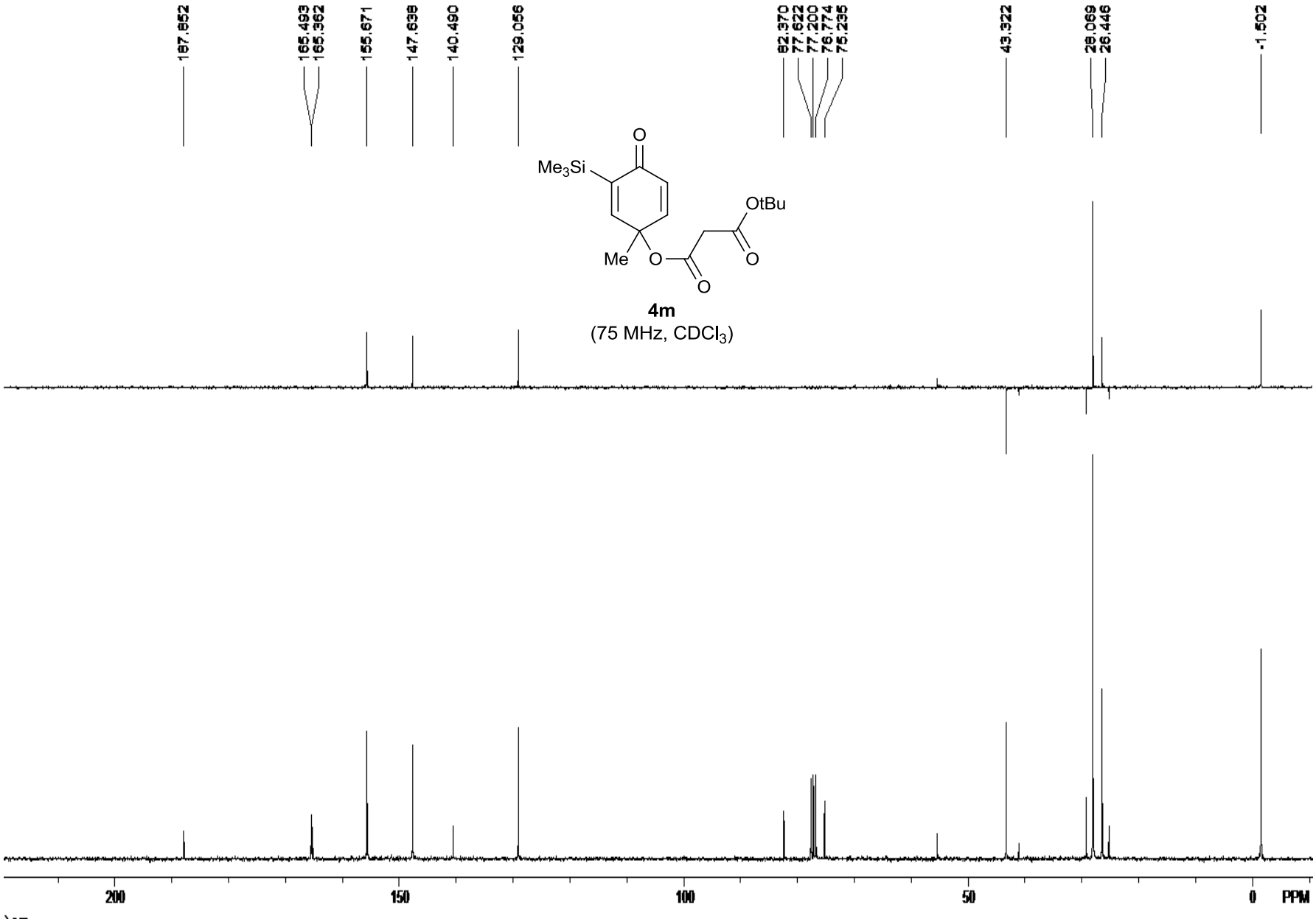


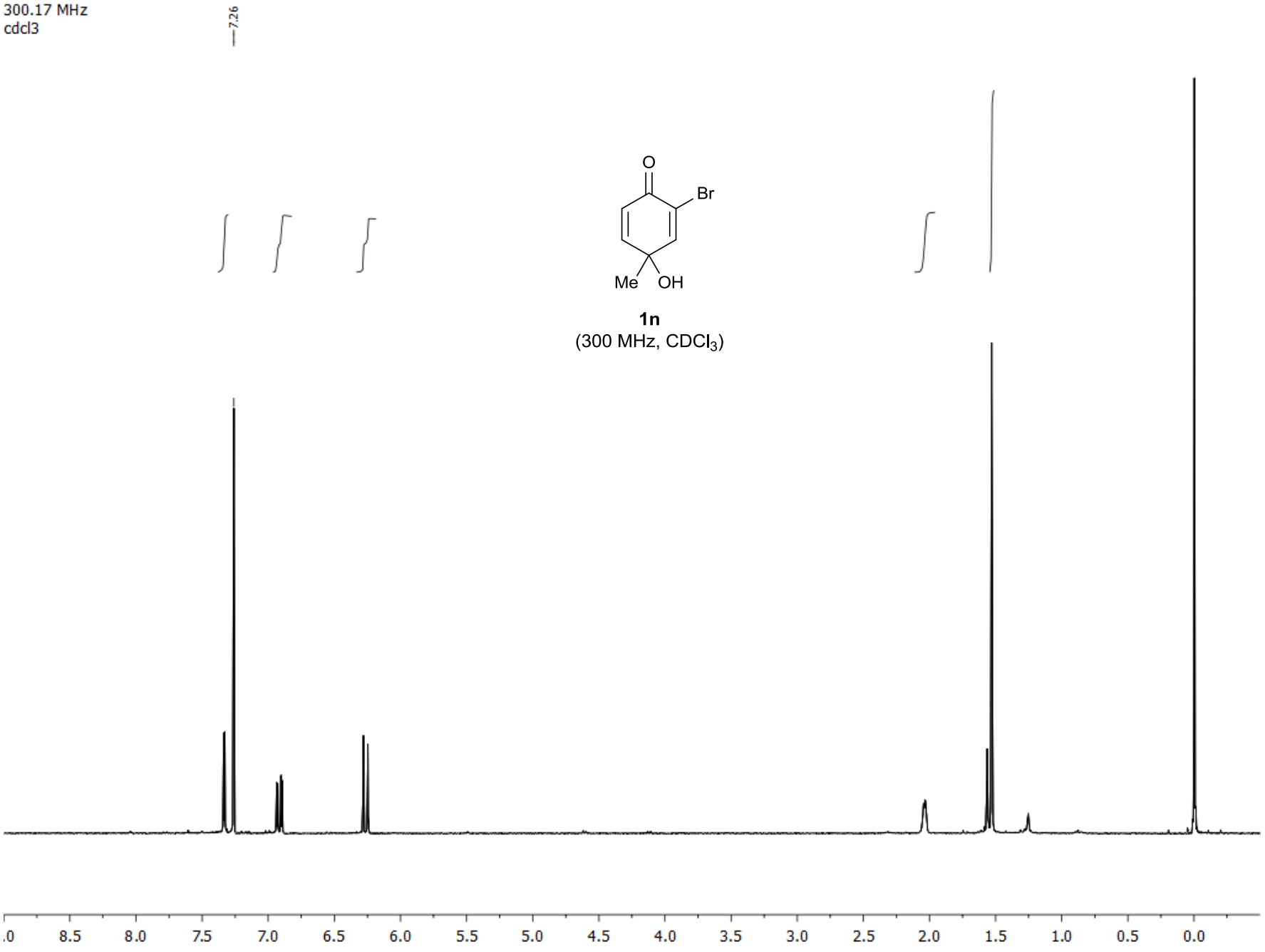


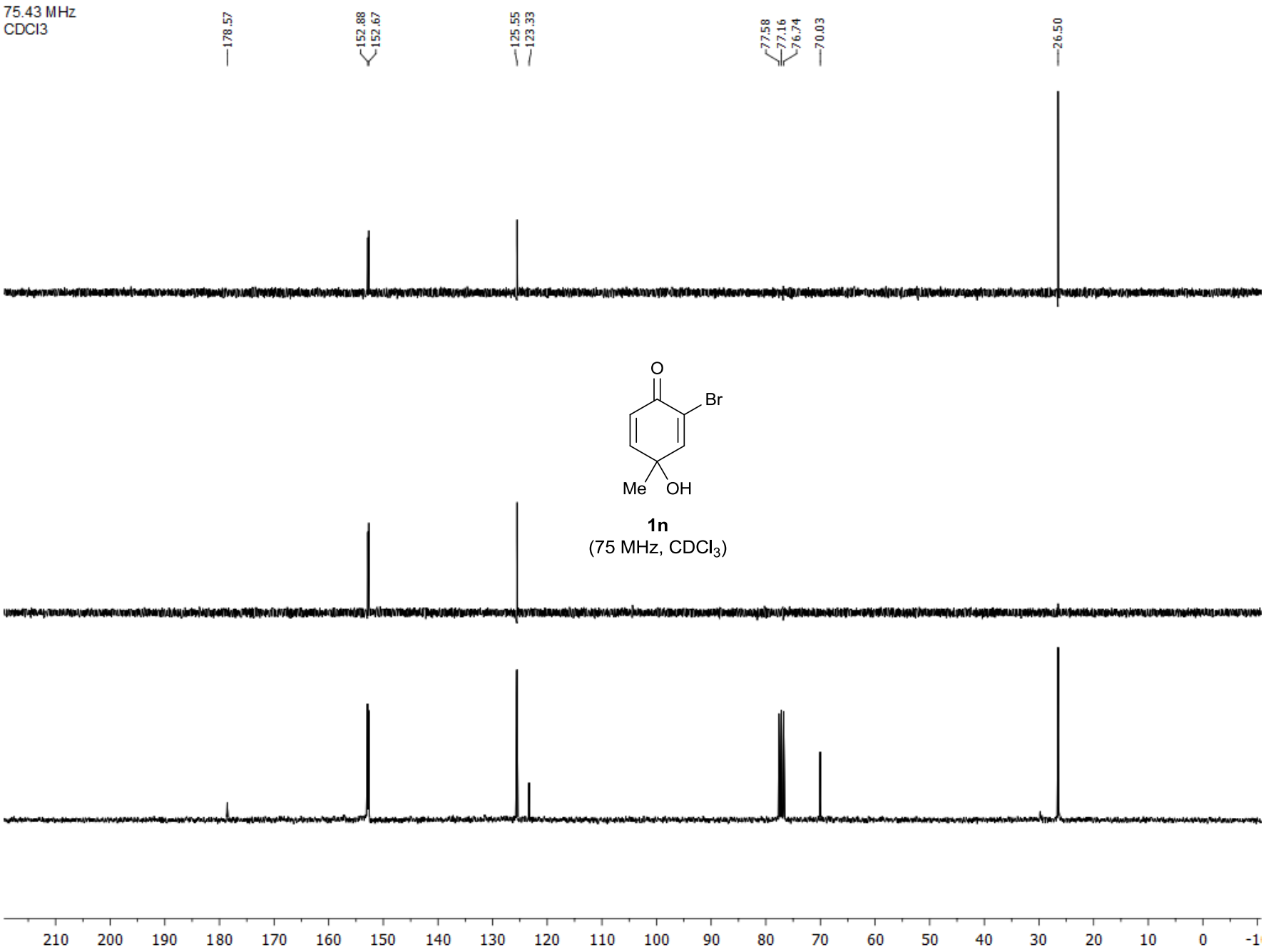
1m
(75 MHz, $CDCl_3$)



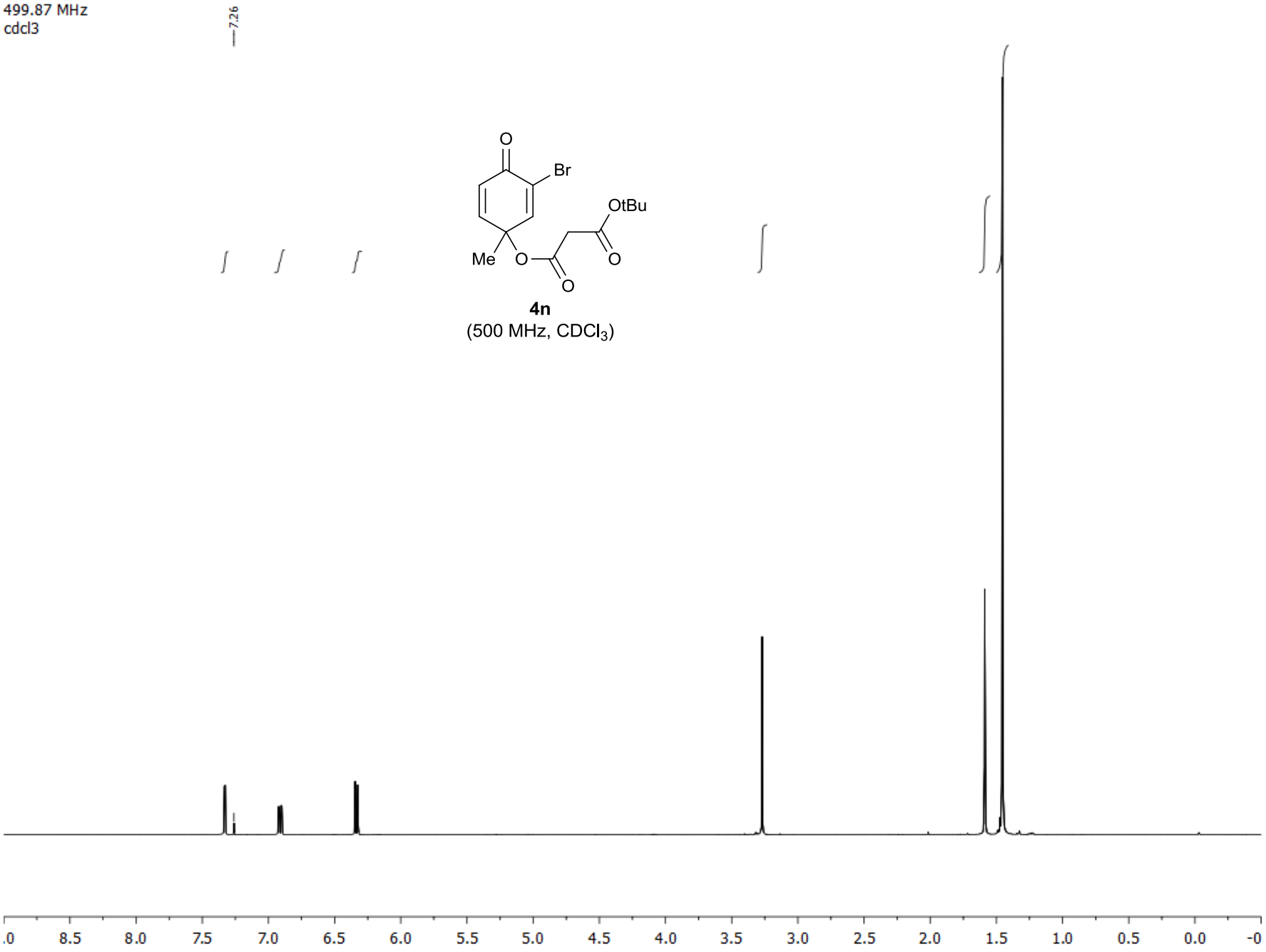
4m
(300 MHz, $CDCl_3$)

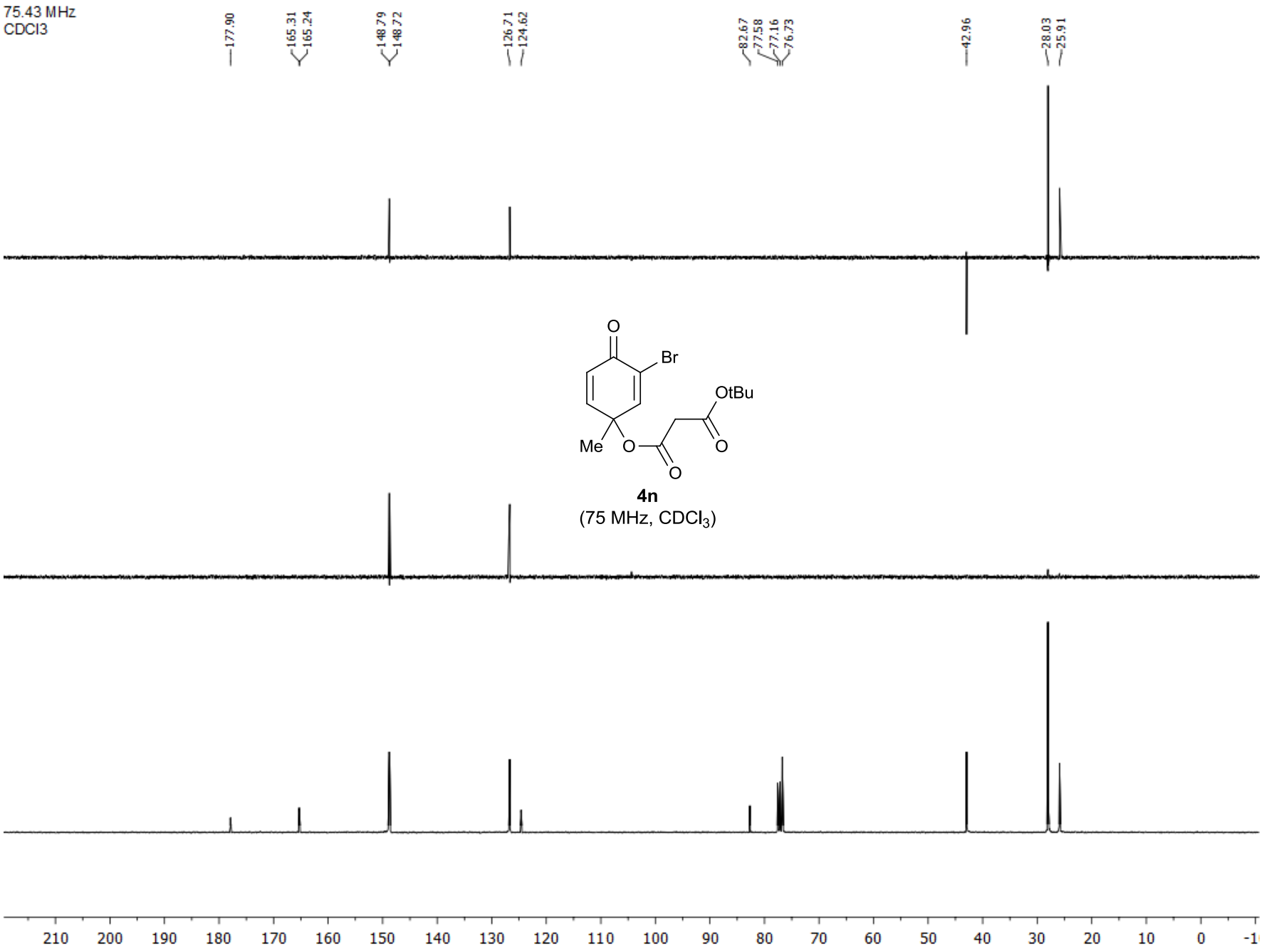




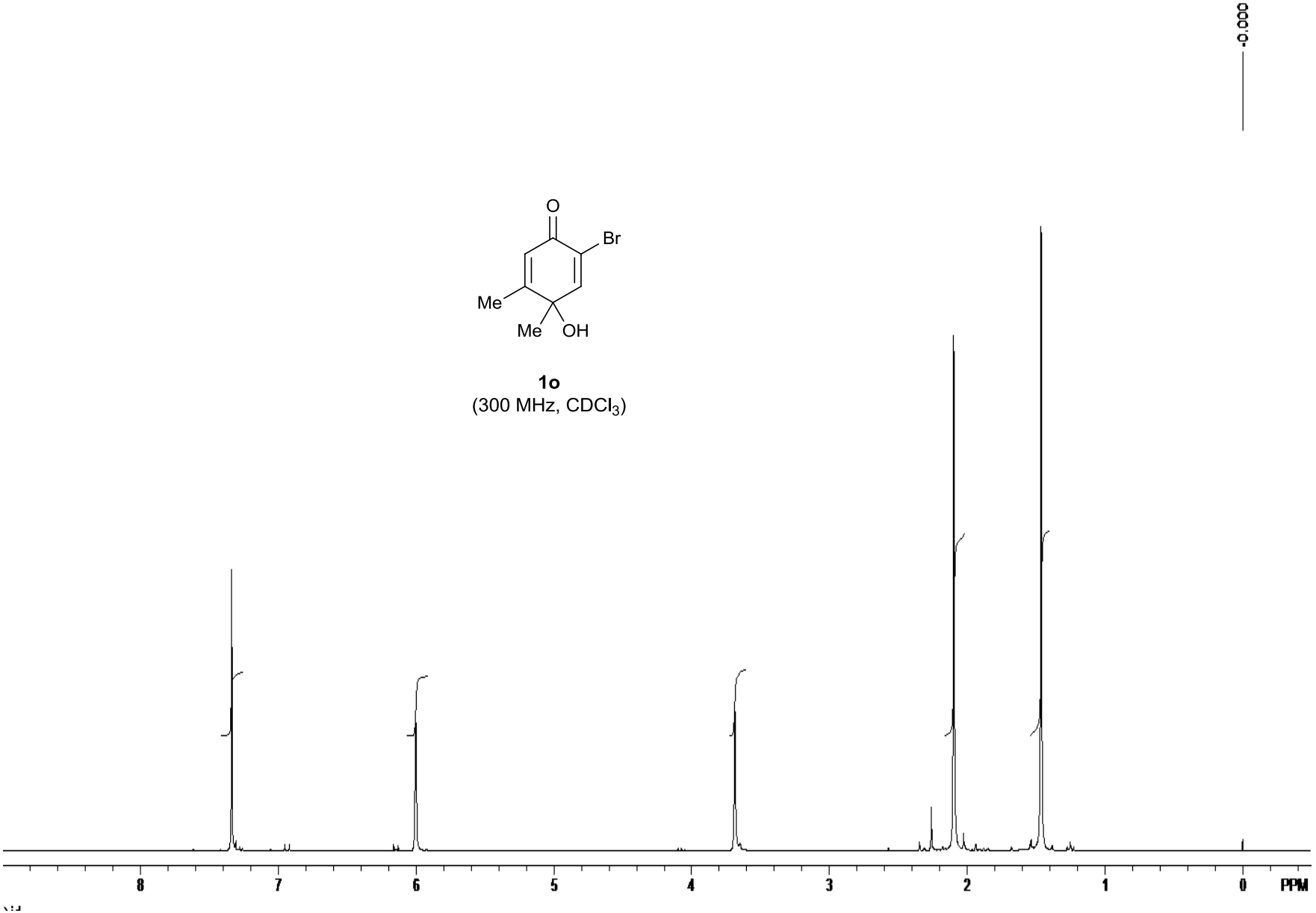


1n
(75 MHz, $CDCl_3$)

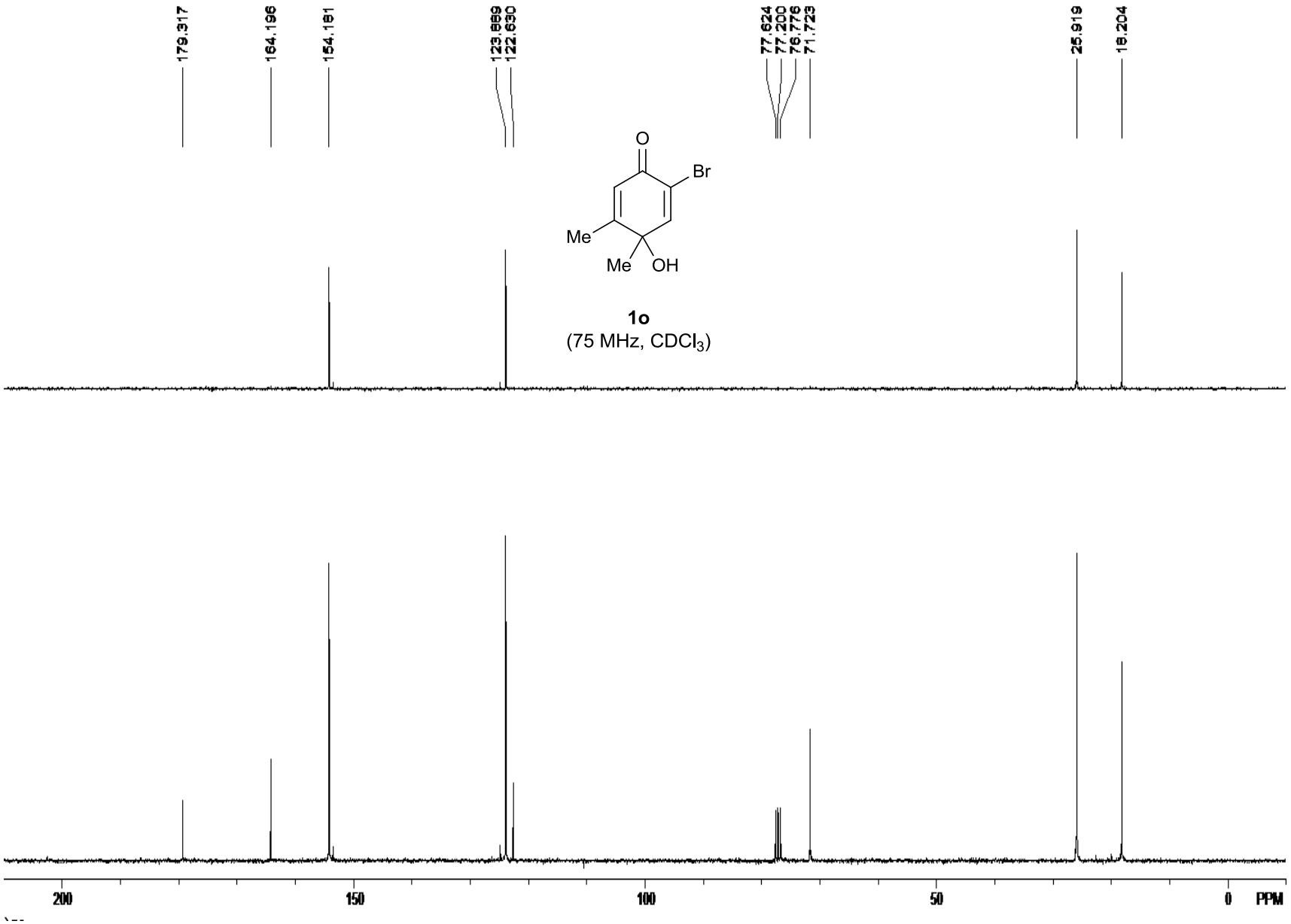

499.87 MHz
cdcl3
7.26
O
Br
OtBu
Me
O
O
O
4n
(500 MHz, CDCl3)
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

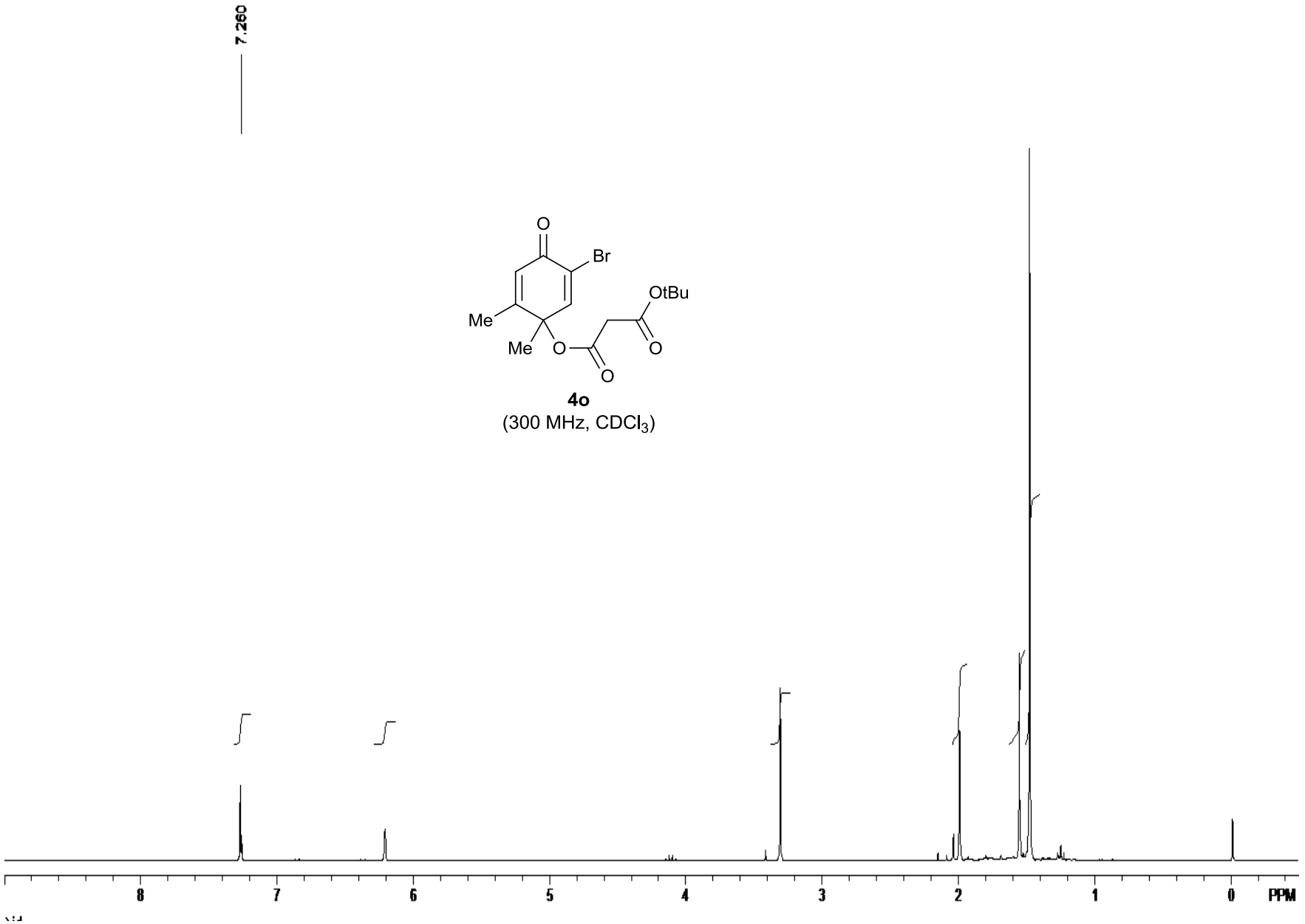


4n
(75 MHz, $CDCl_3$)



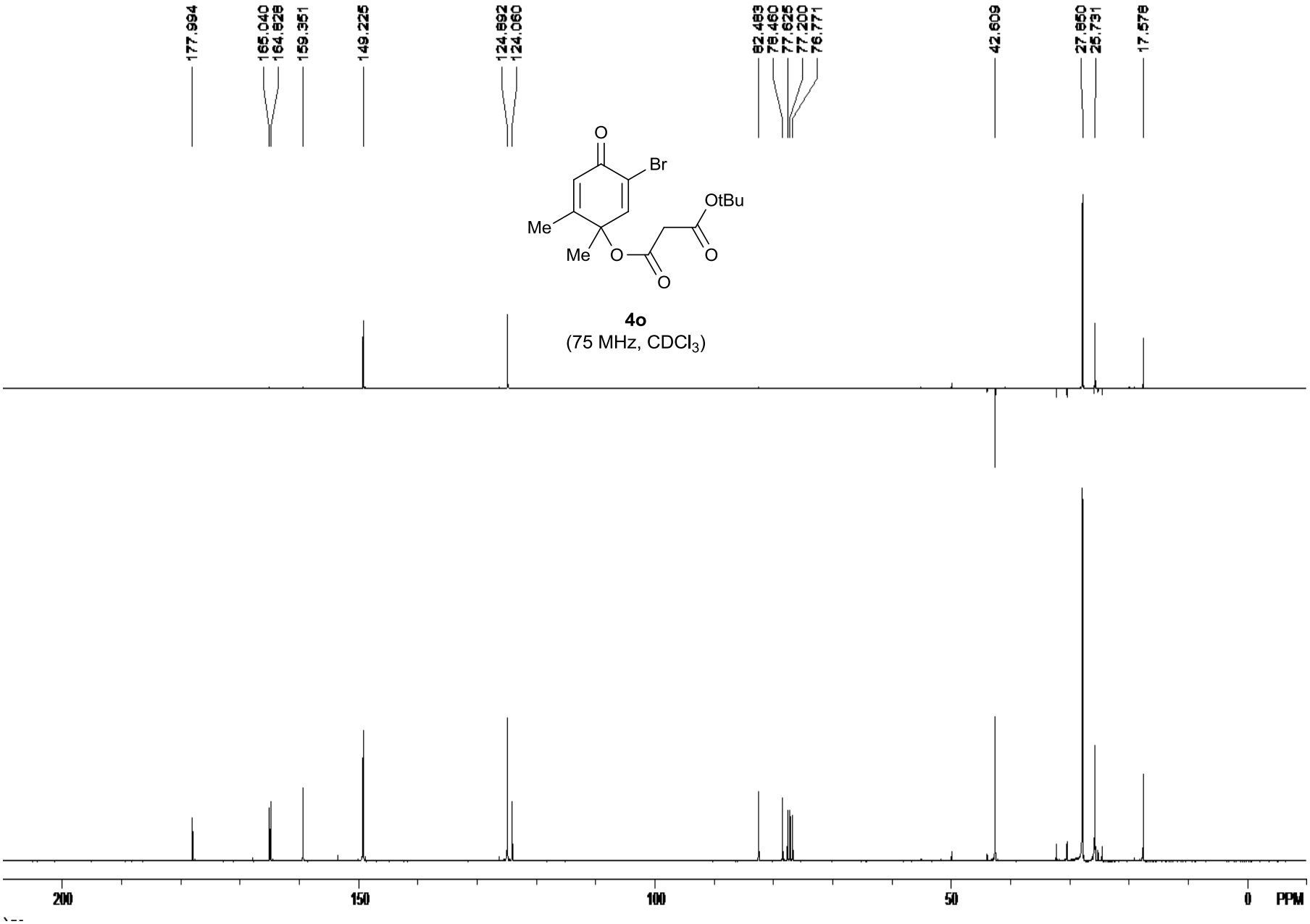
1o
(300 MHz, $CDCl_3$)



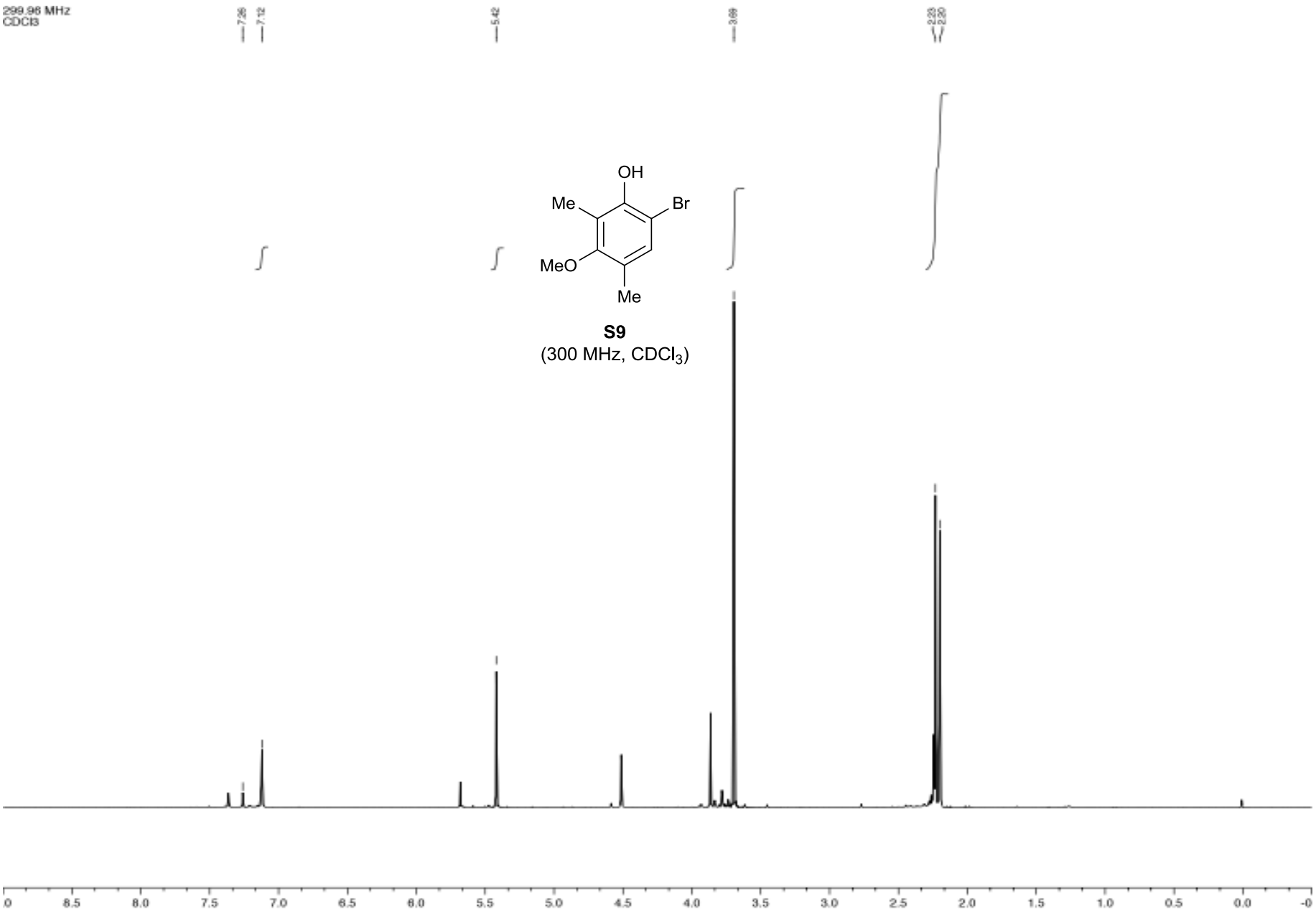


4o

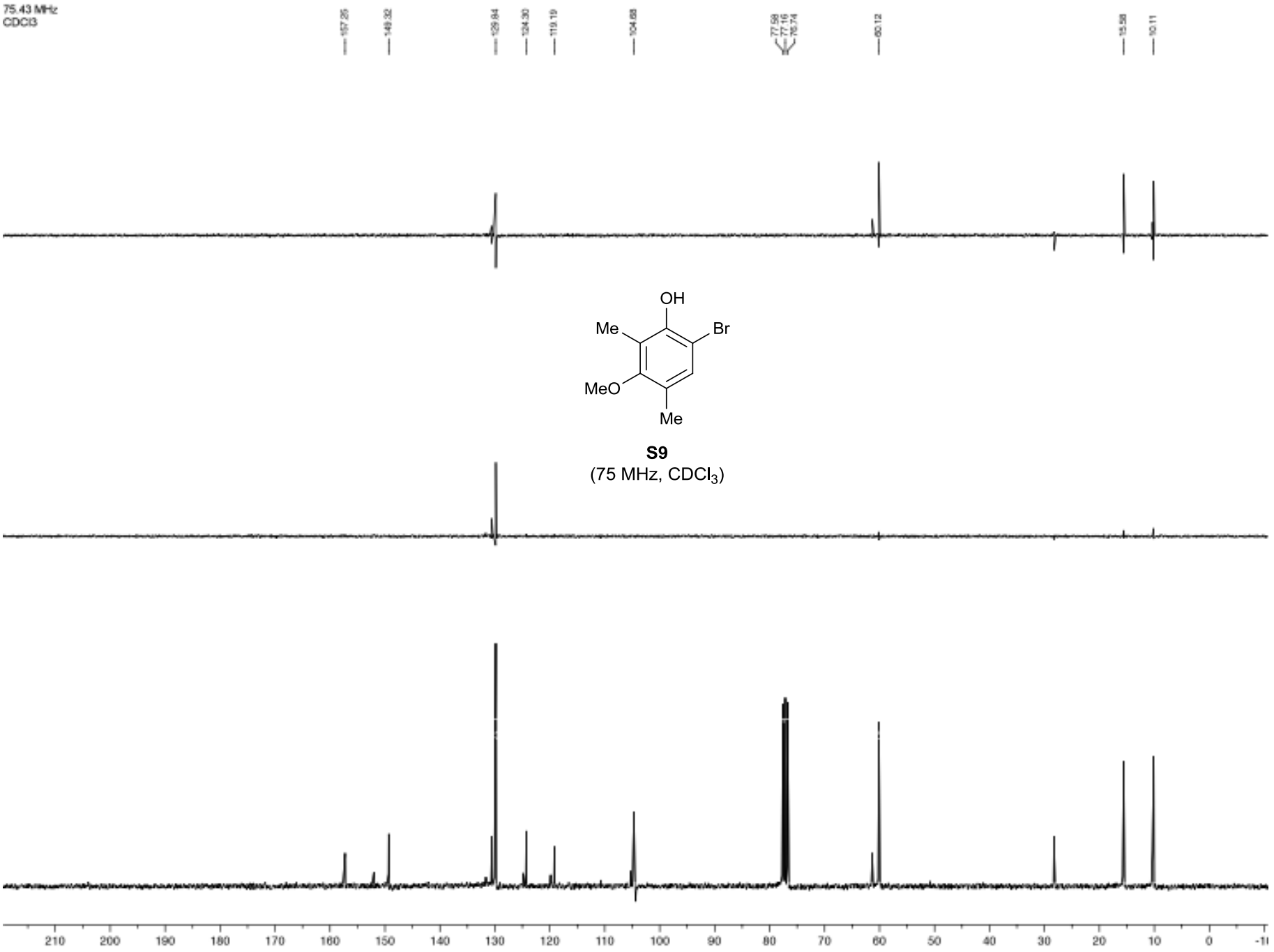
(300 MHz, $CDCl_3$)



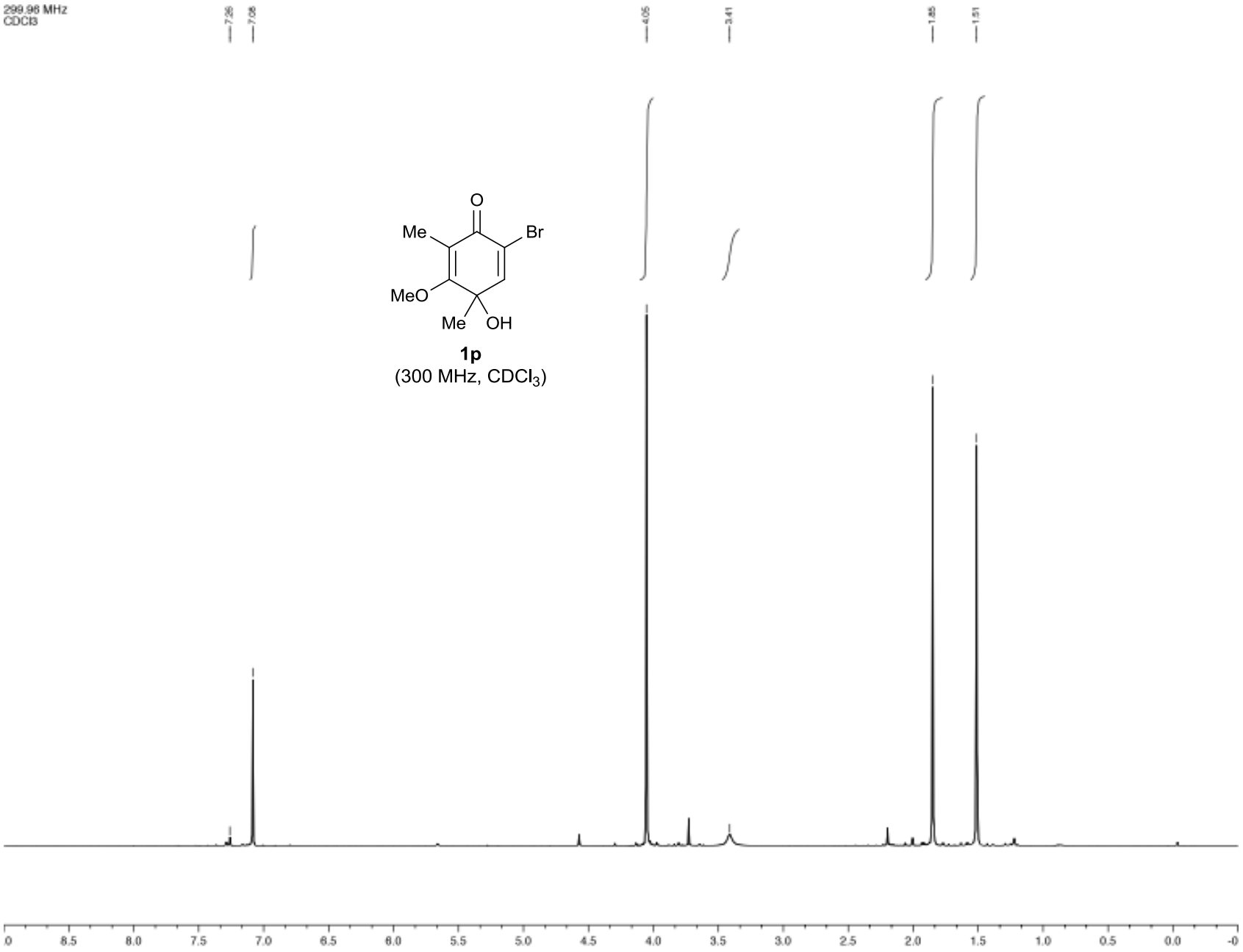
4o
(75 MHz, $CDCl_3$)

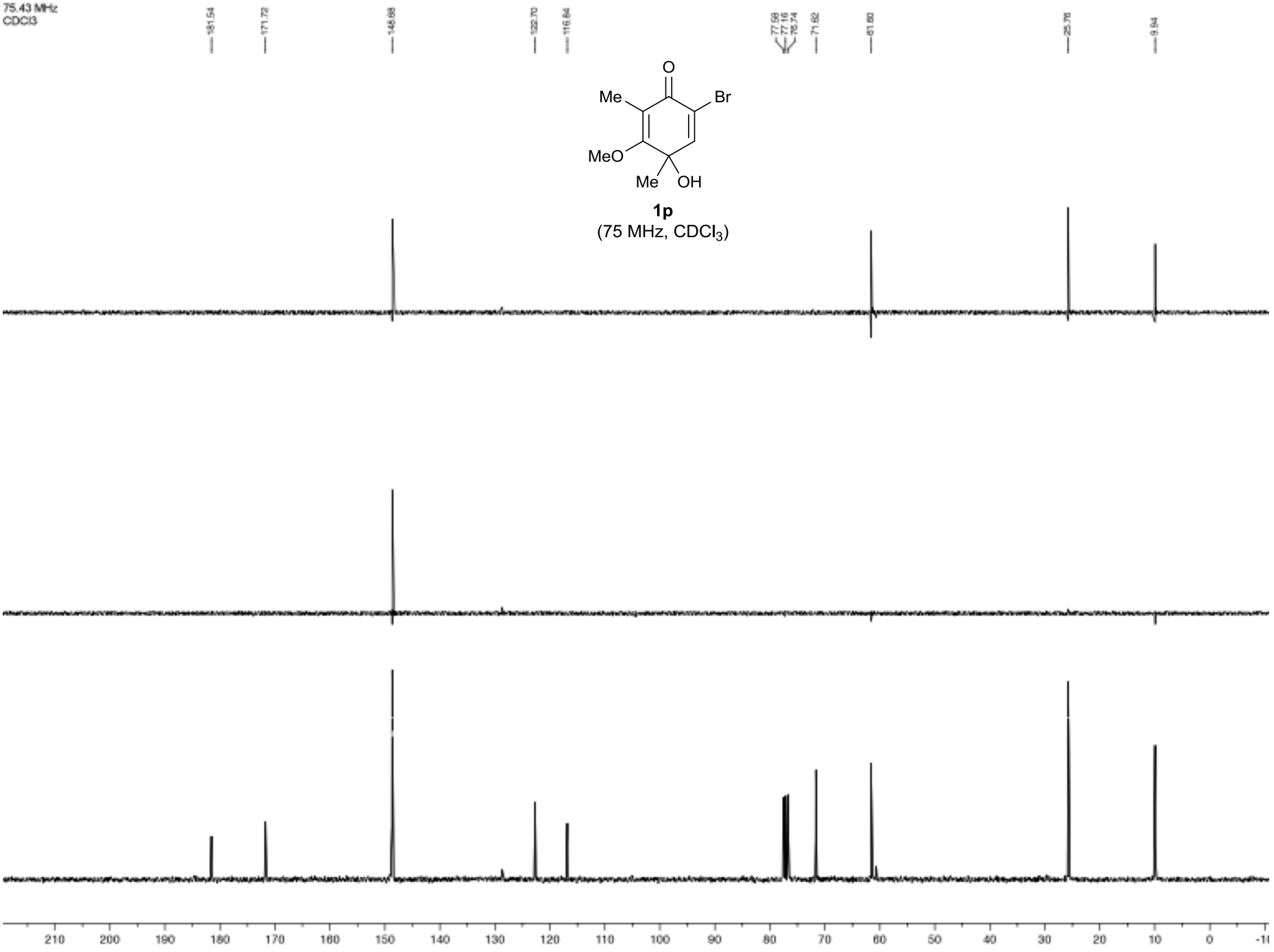


S9
(300 MHz, $CDCl_3$)

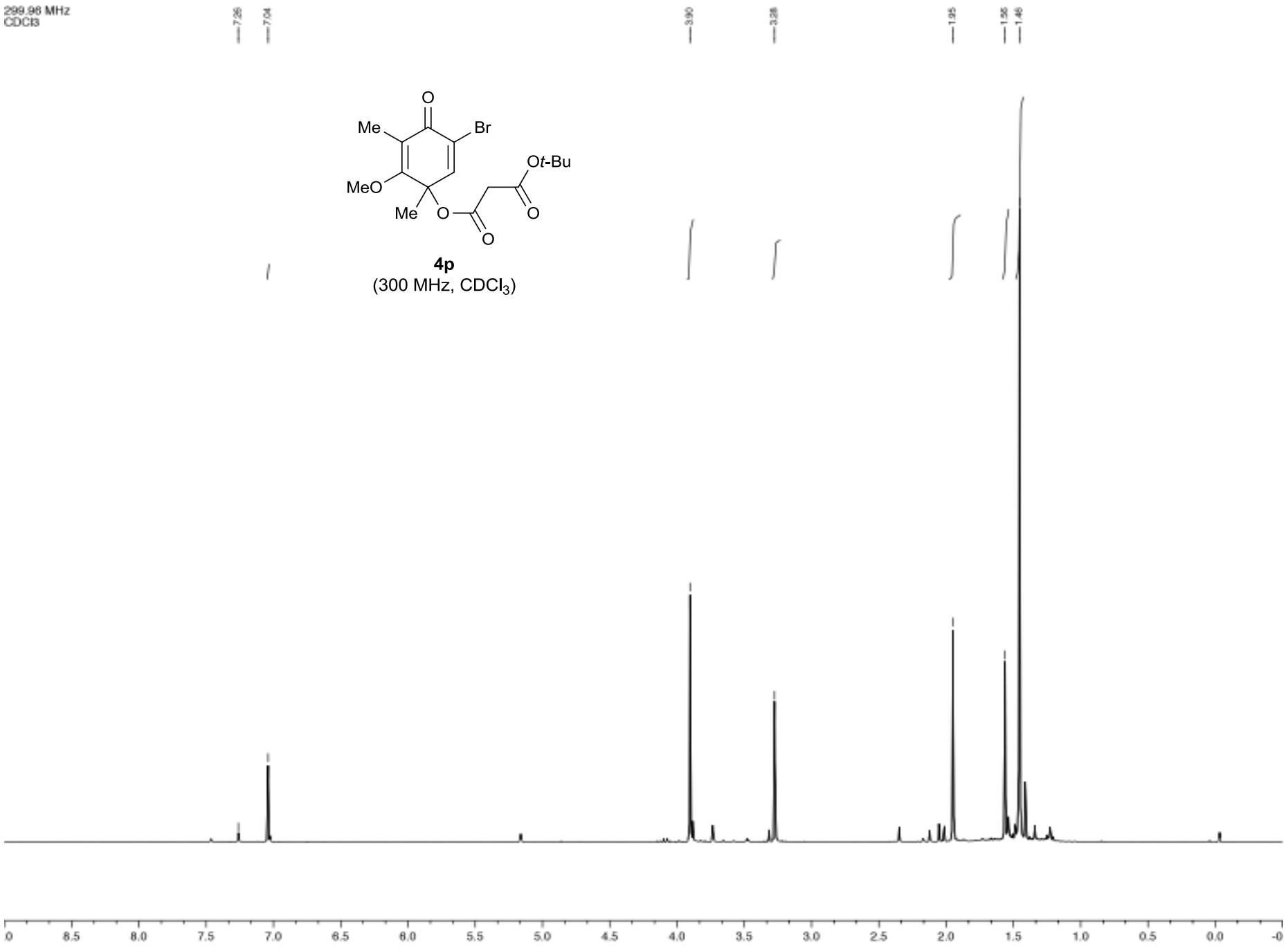


S9
(75 MHz, $CDCl_3$)

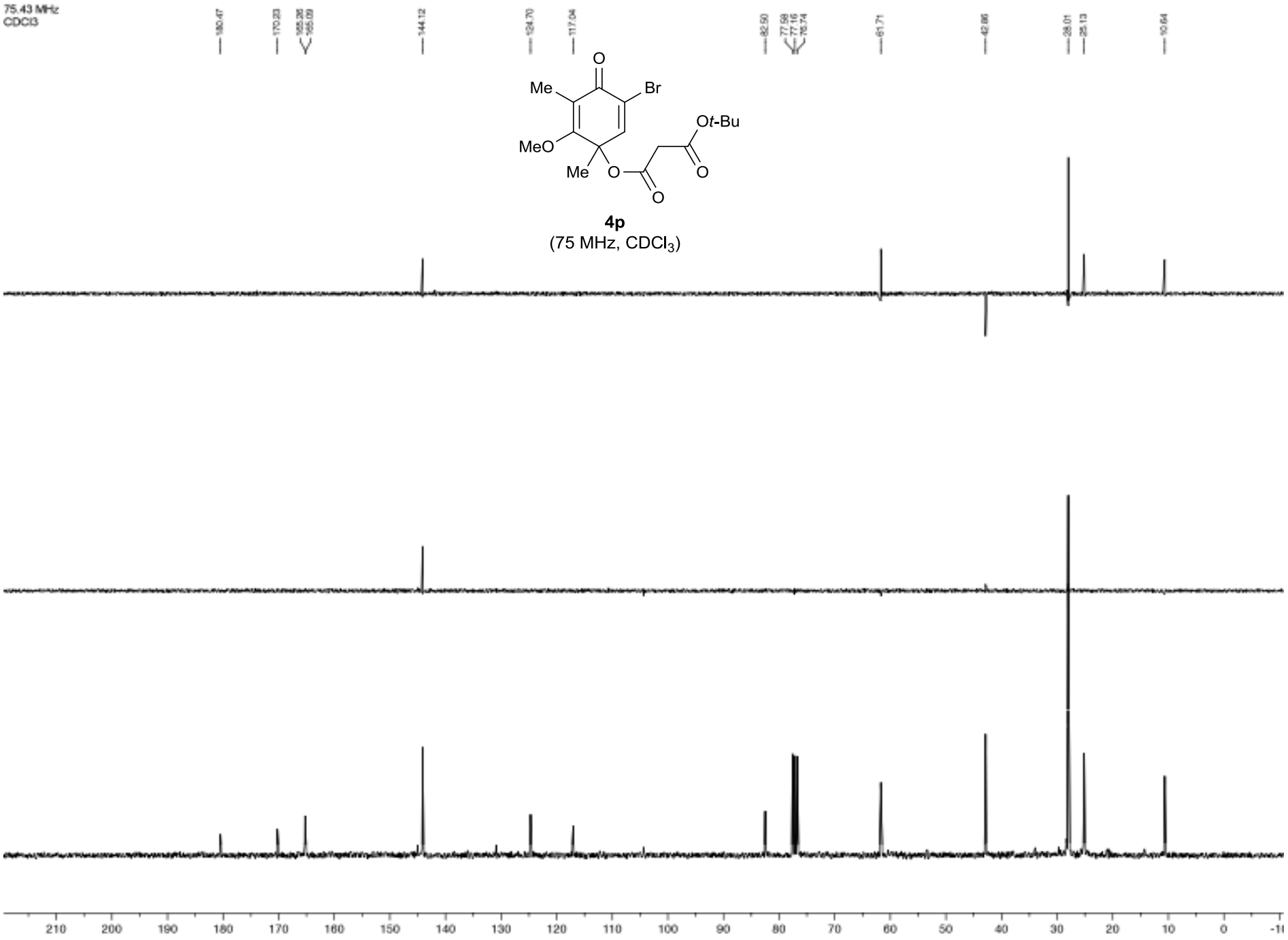




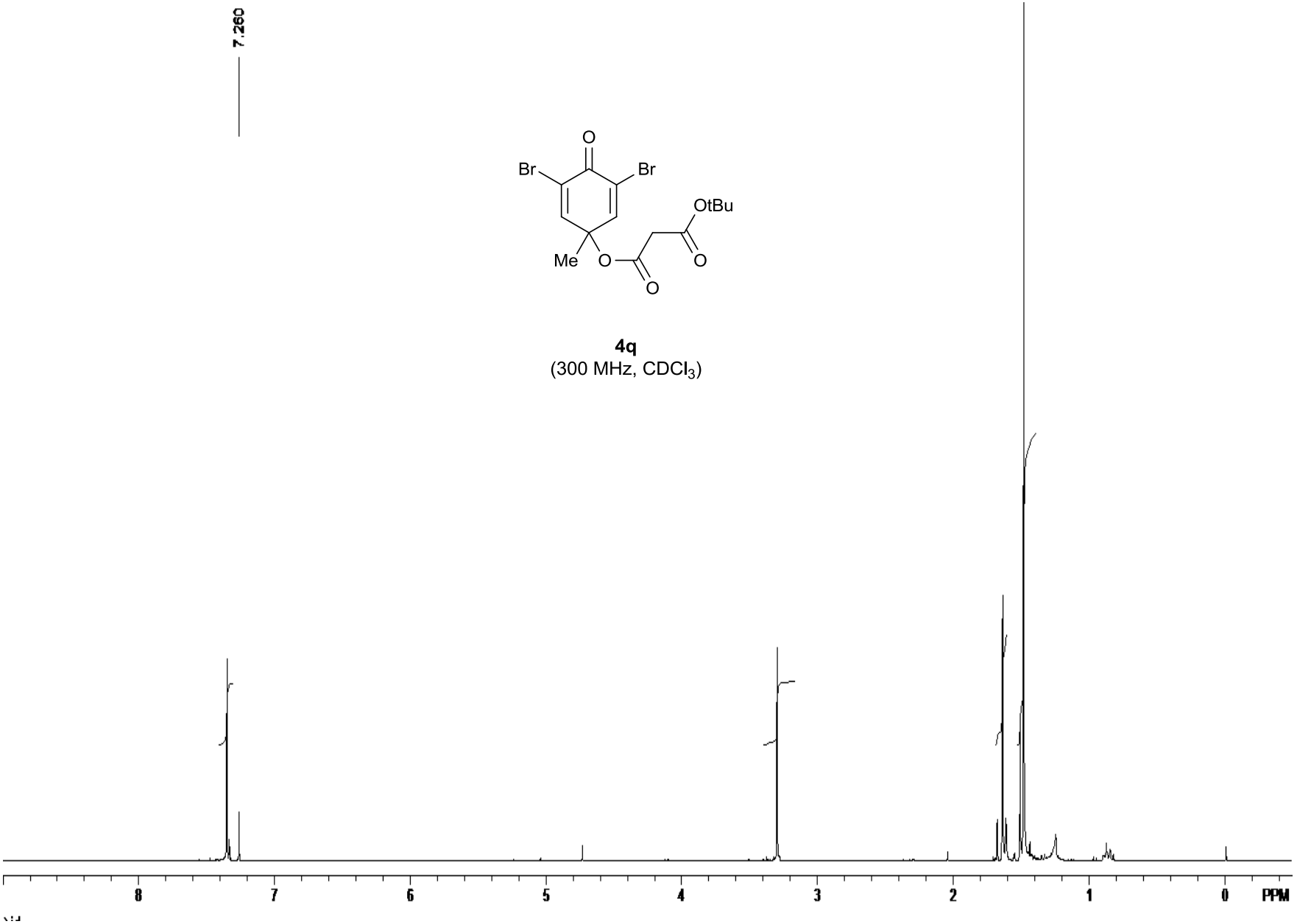
1p
(75 MHz, $CDCl_3$)



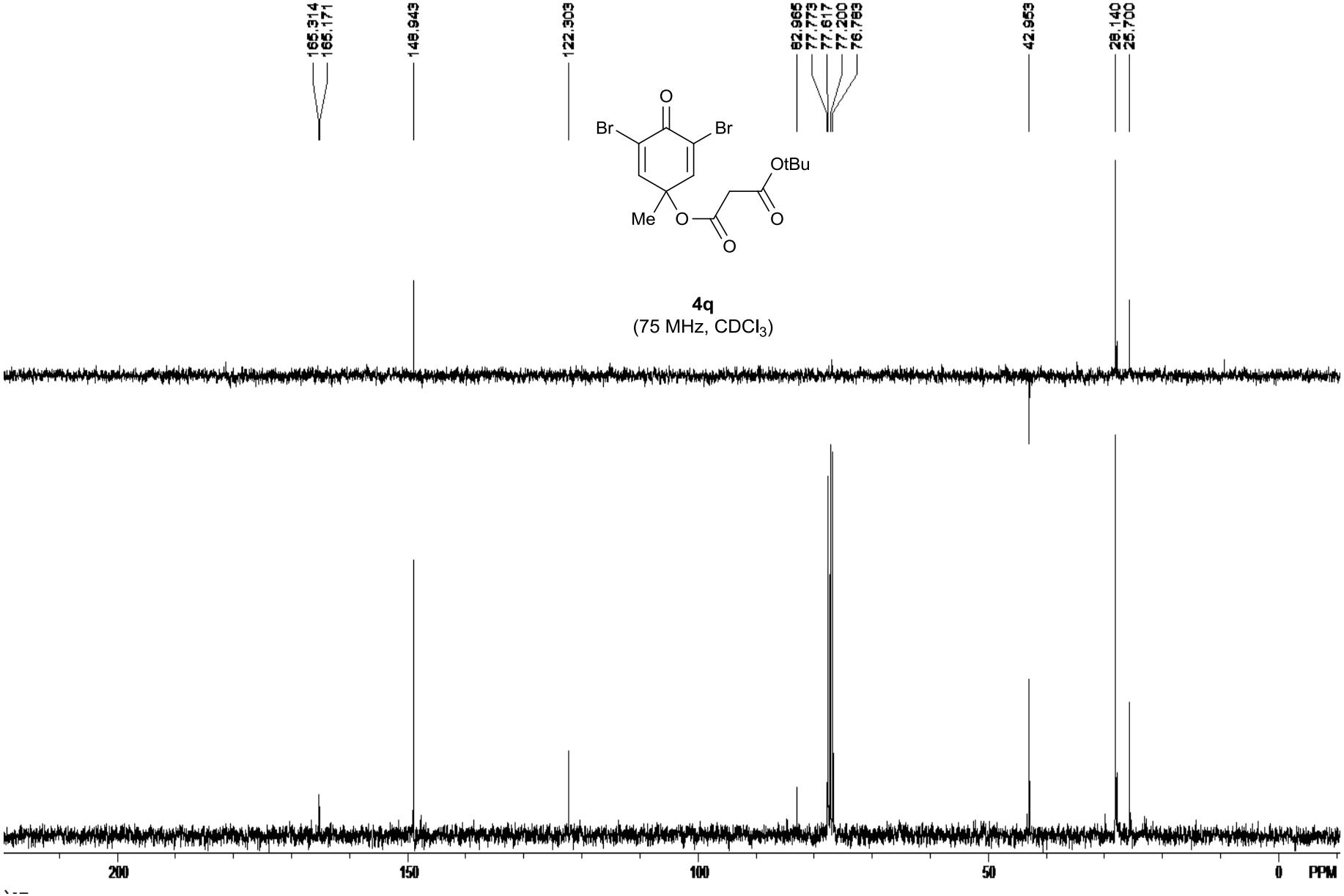
4p
(300 MHz, $CDCl_3$)



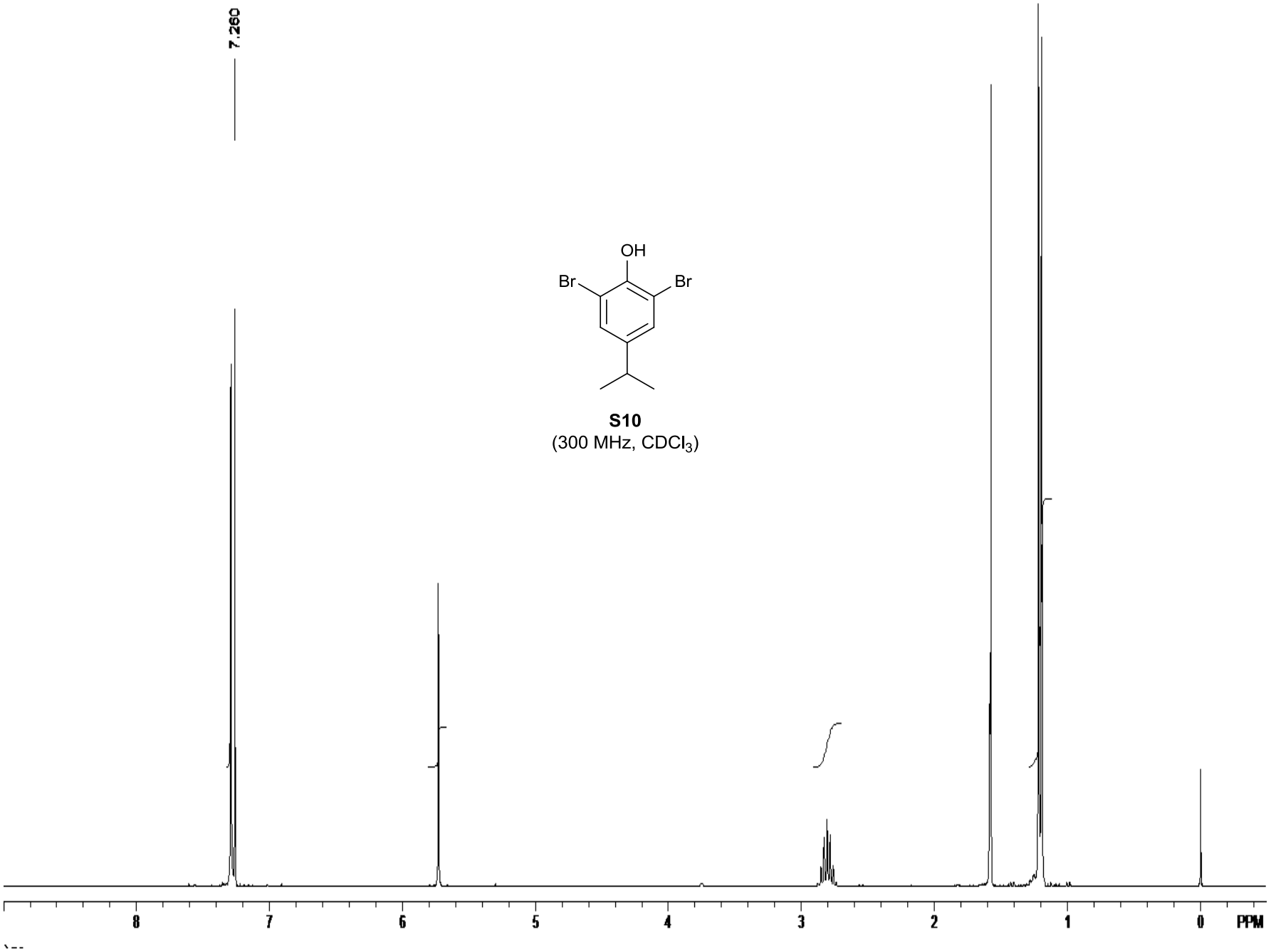
4p
(75 MHz, $CDCl_3$)



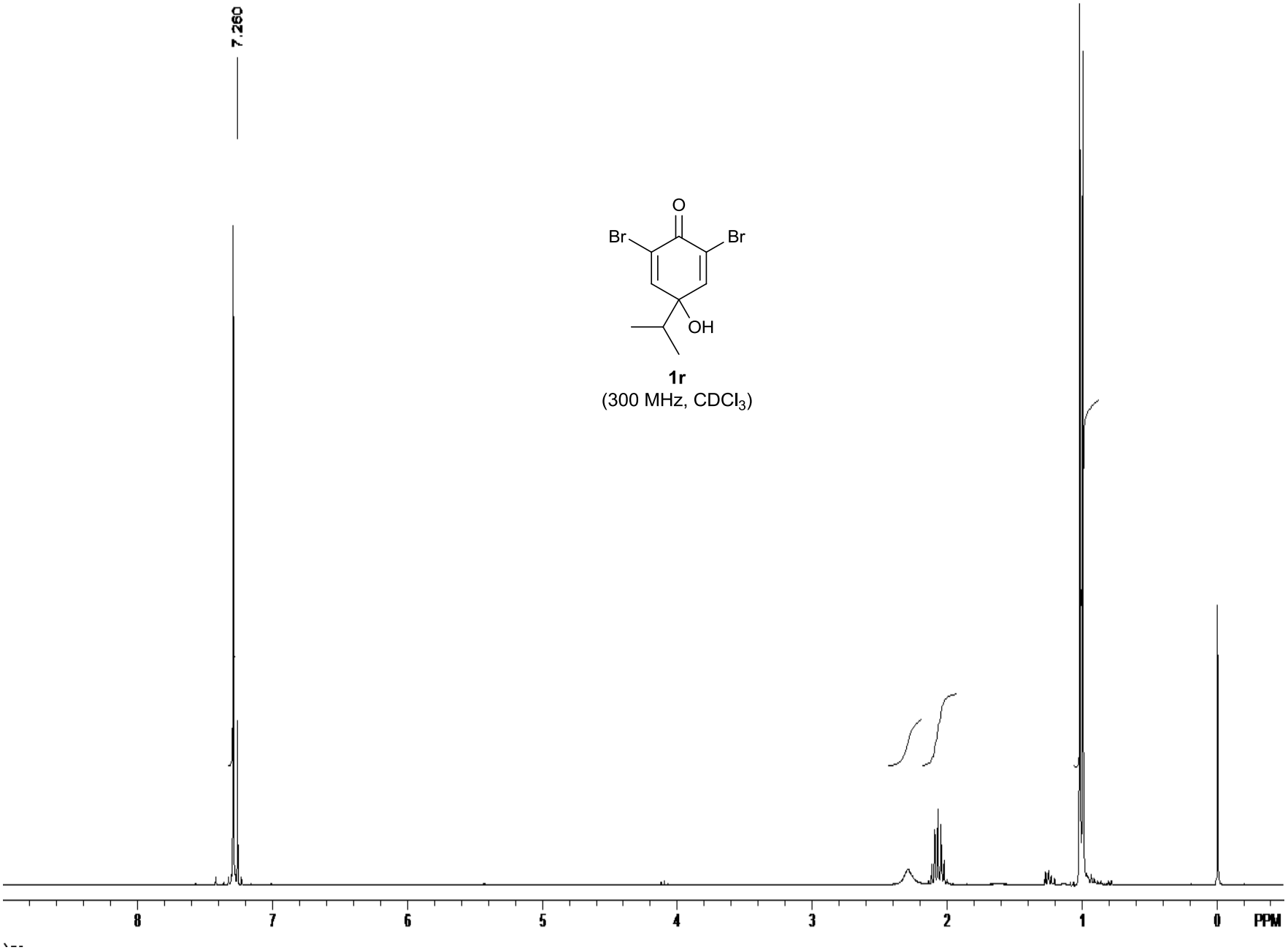
4q
(300 MHz, $CDCl_3$)



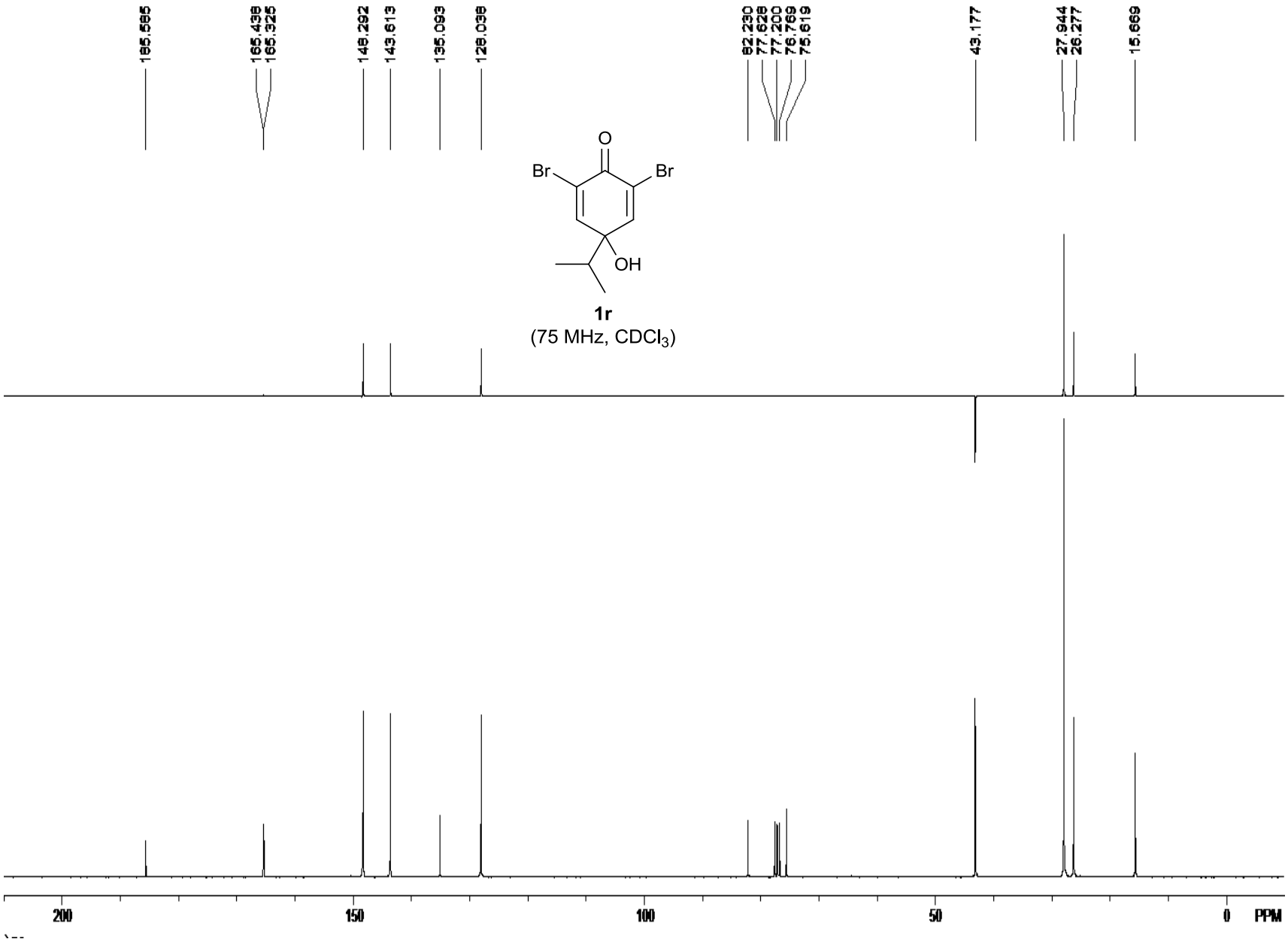
4q
(75 MHz, $CDCl_3$)



S10
(300 MHz, $CDCl_3$)

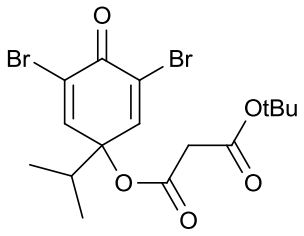


1r
(300 MHz, $CDCl_3$)

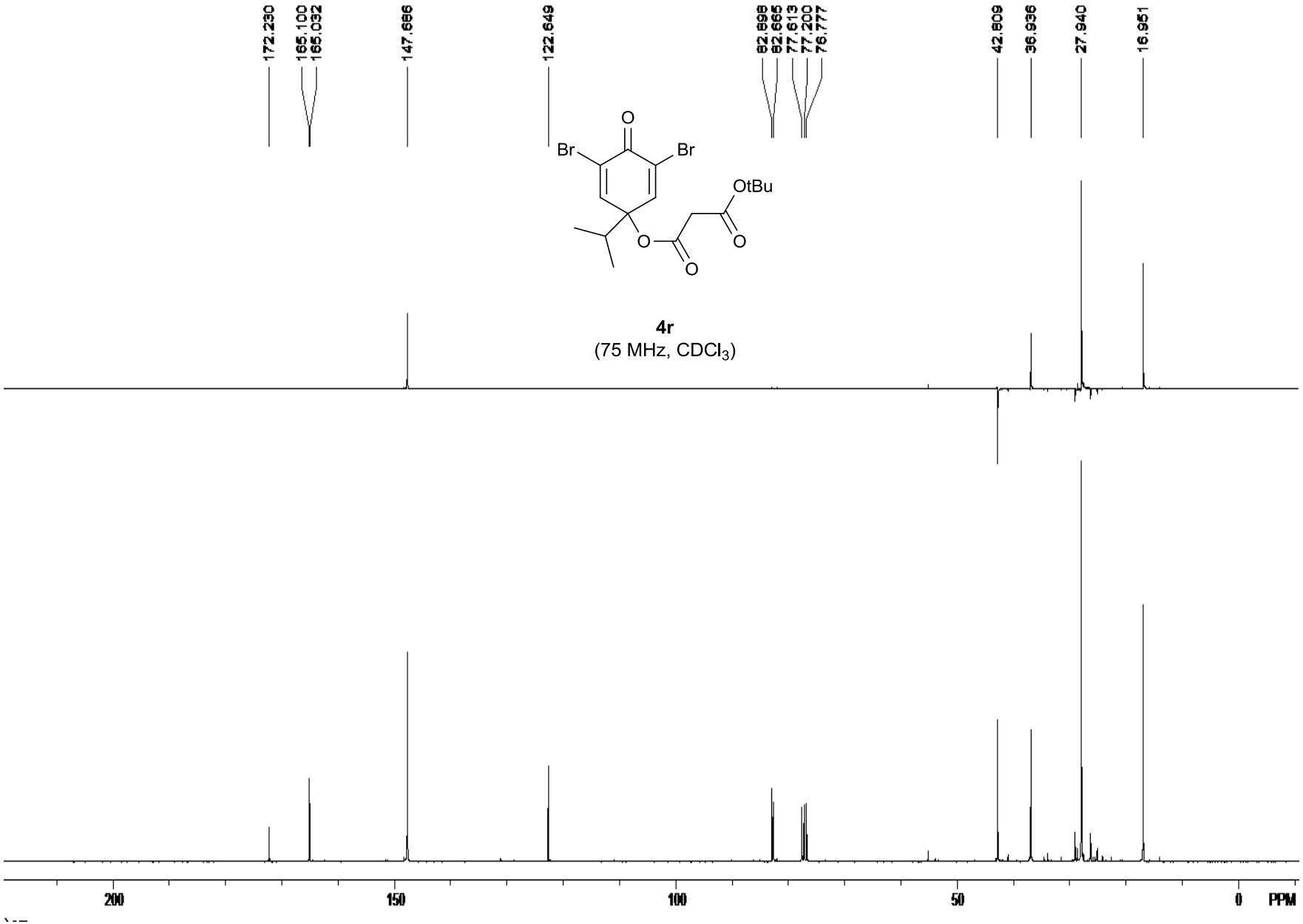


1r

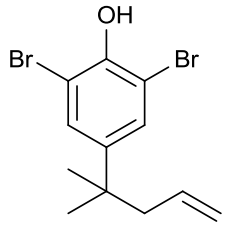
(75 MHz, $CDCl_3$)



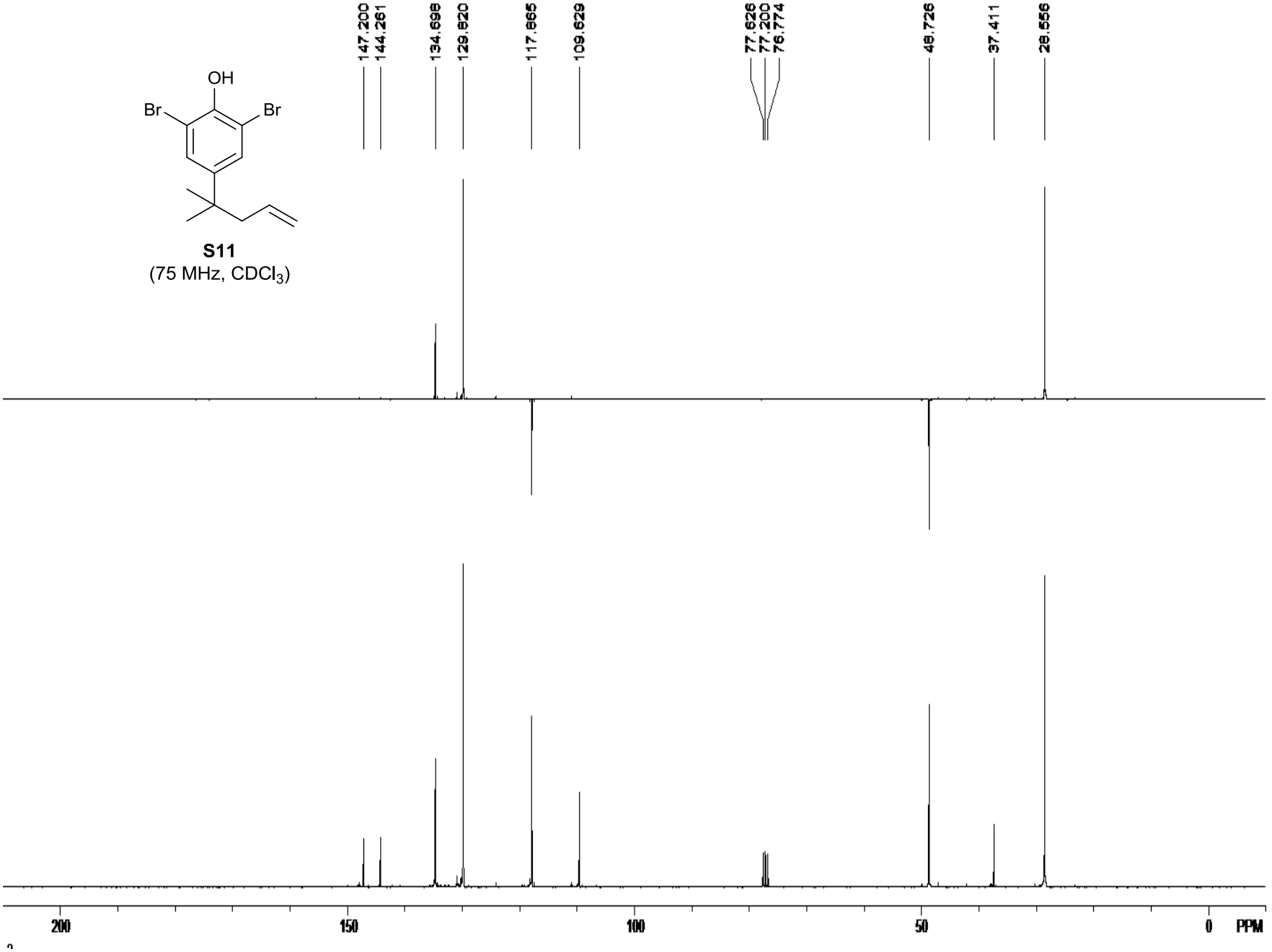
4r
(300 MHz, $CDCl_3$)



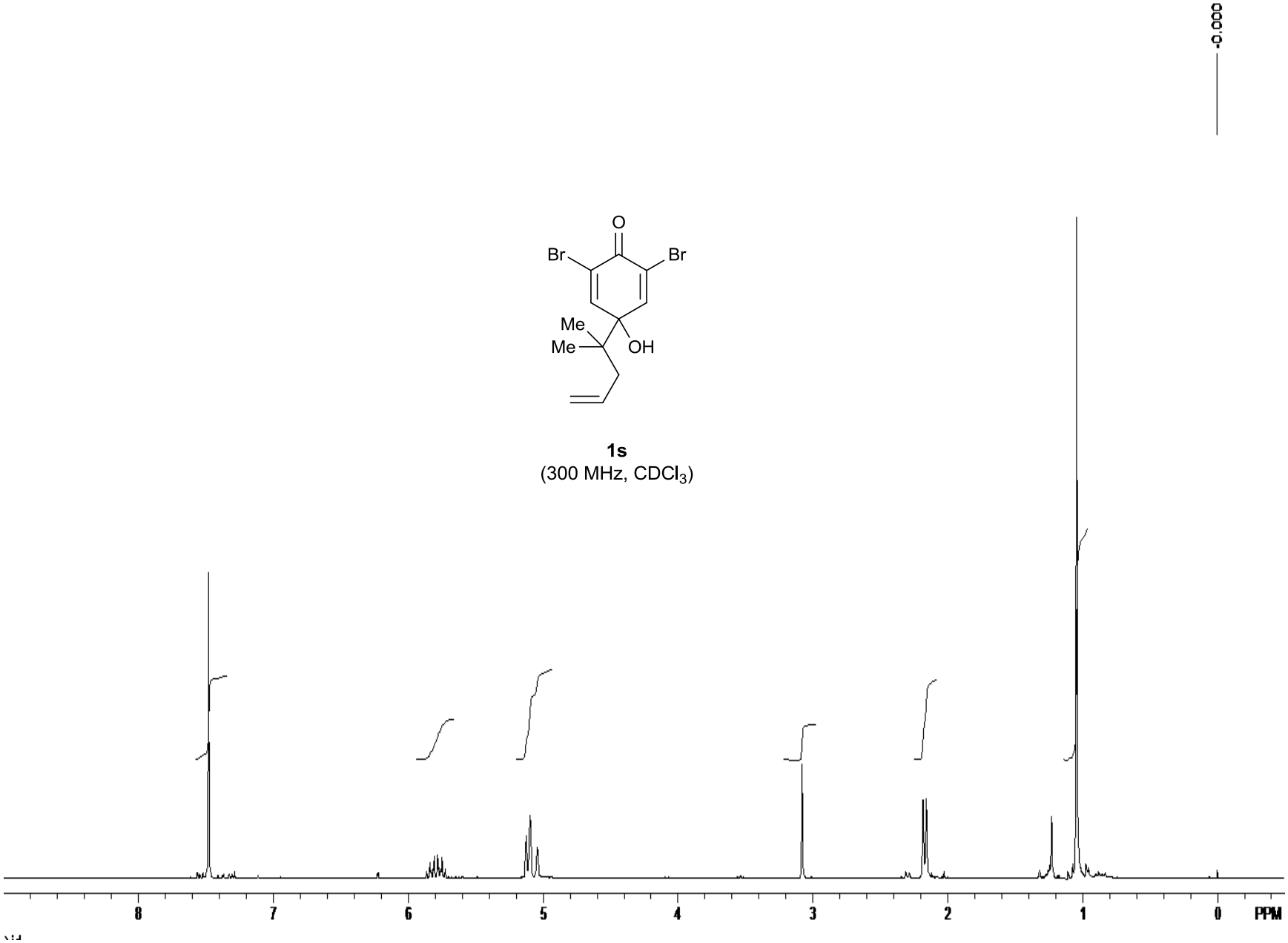
4r
(75 MHz, $CDCl_3$)



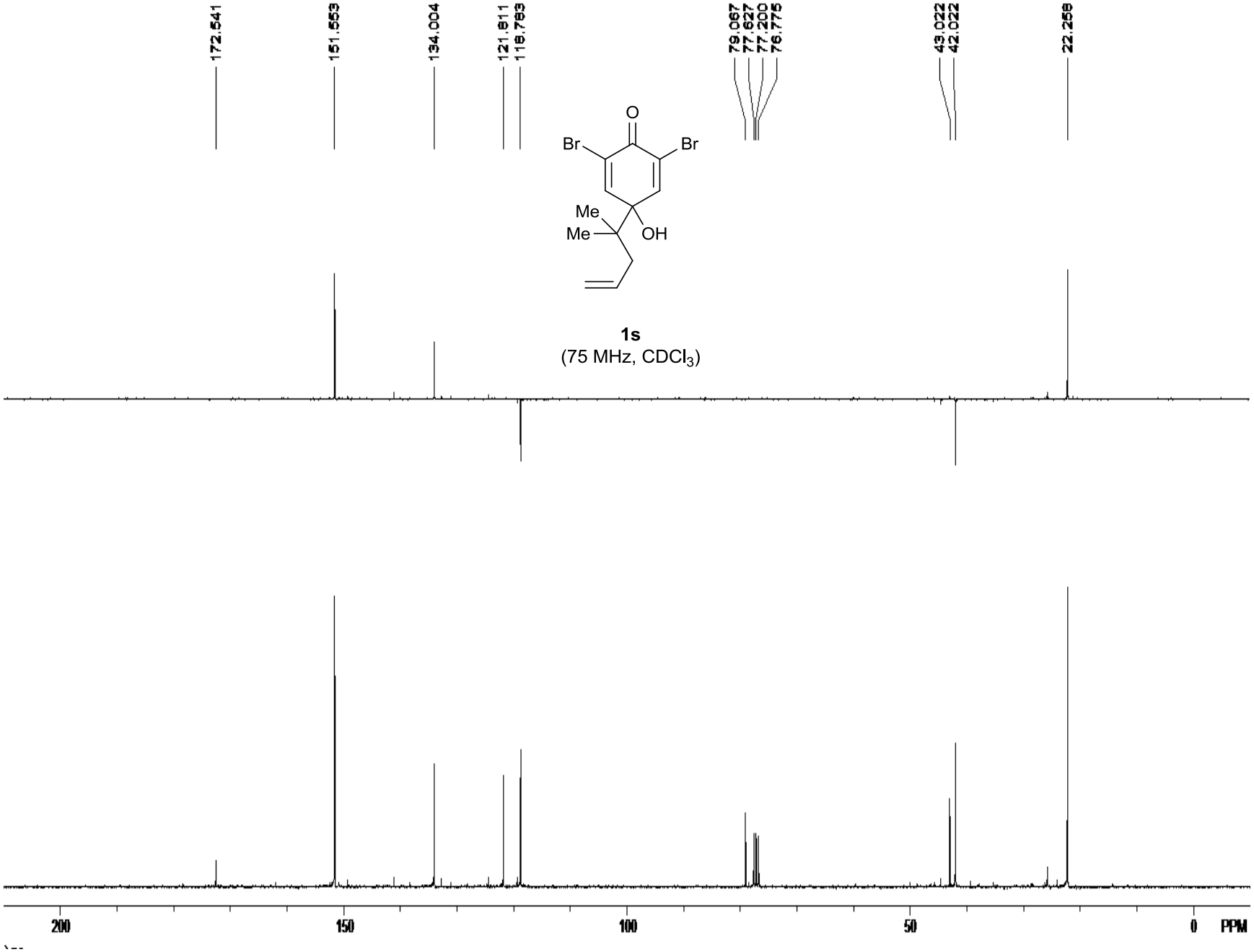
S11
(300 MHz, $CDCl_3$)



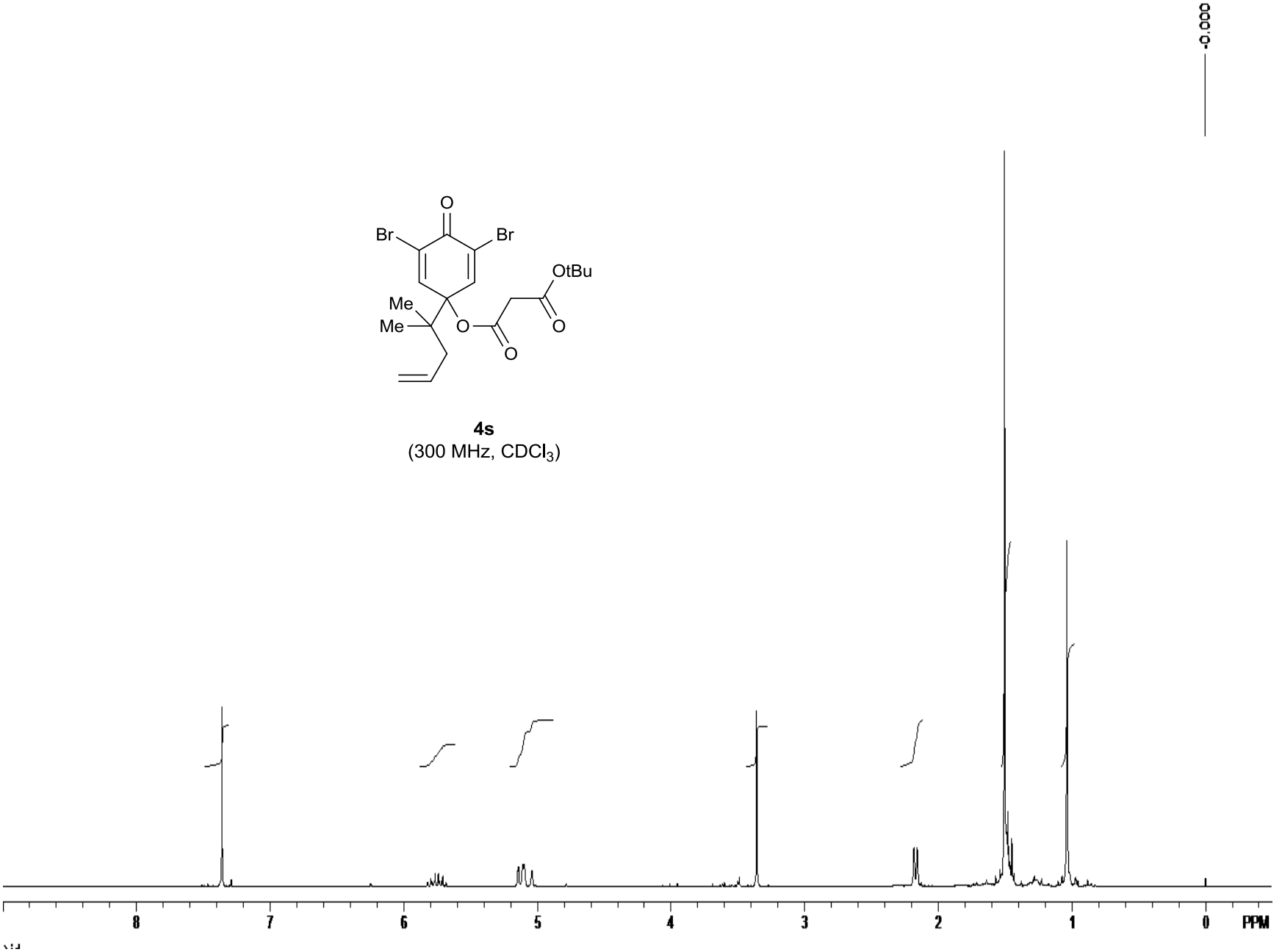
S11
(75 MHz, $CDCl_3$)



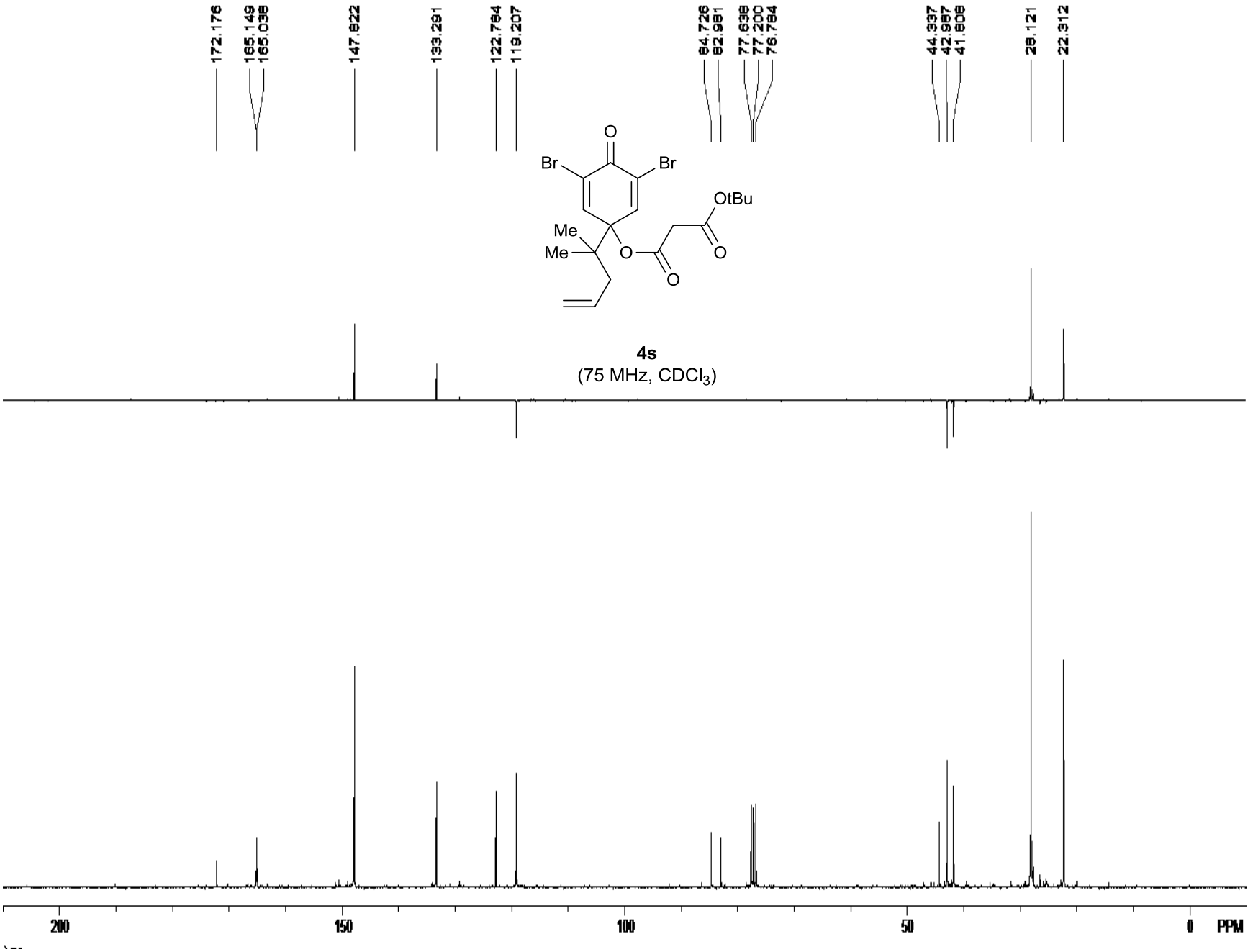
1s
(300 MHz, $CDCl_3$)

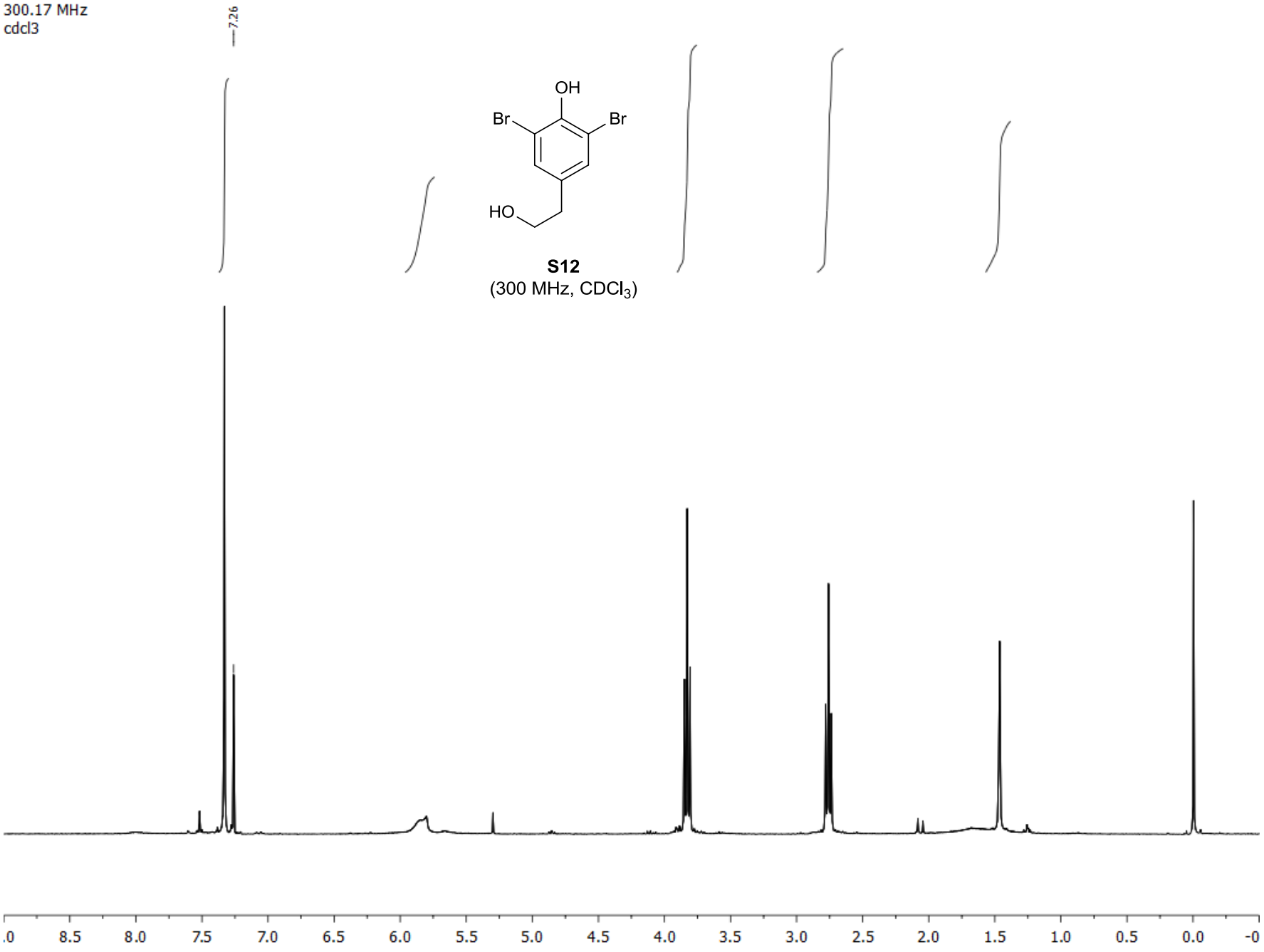


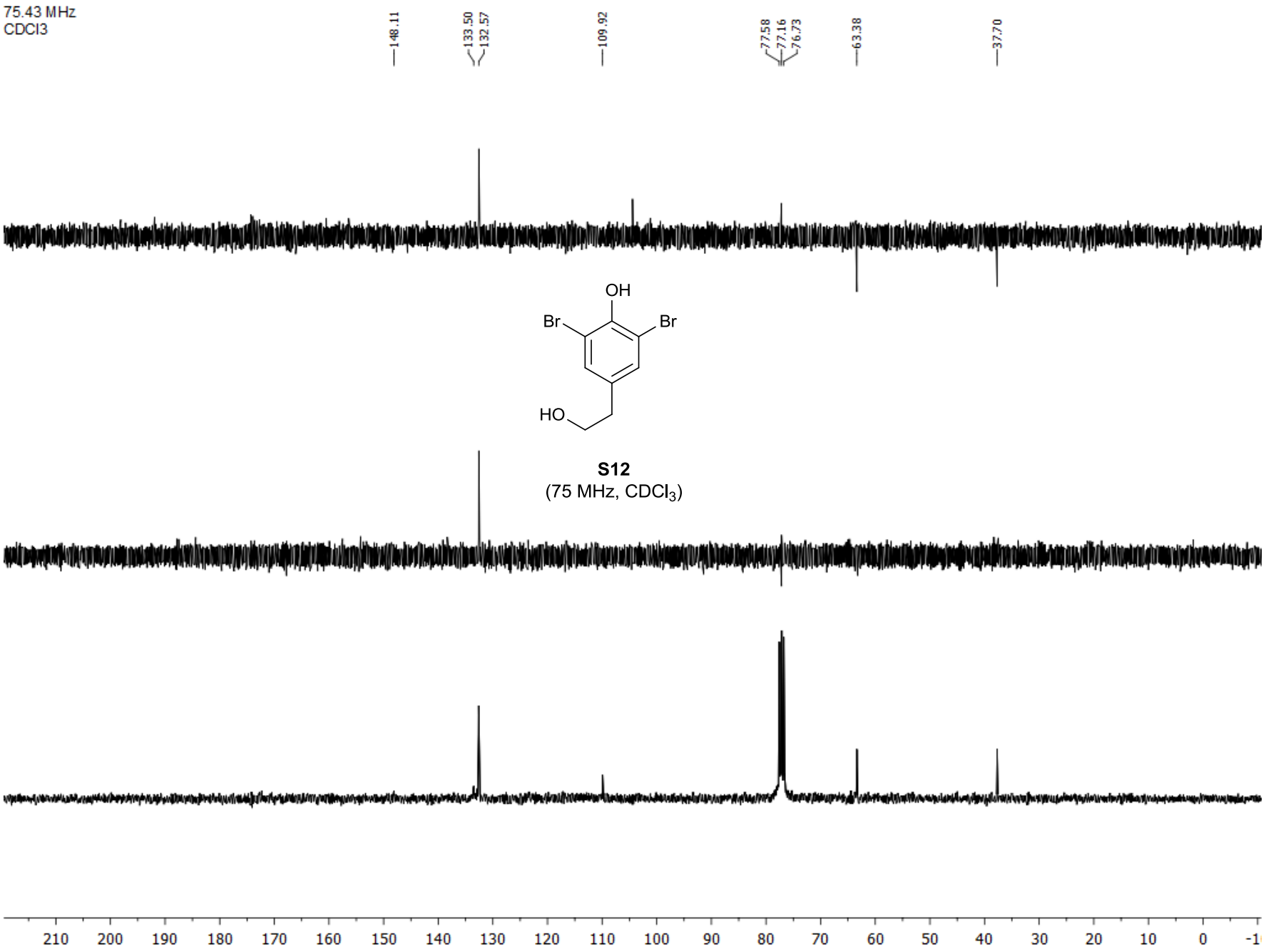
1s
(75 MHz, $CDCl_3$)



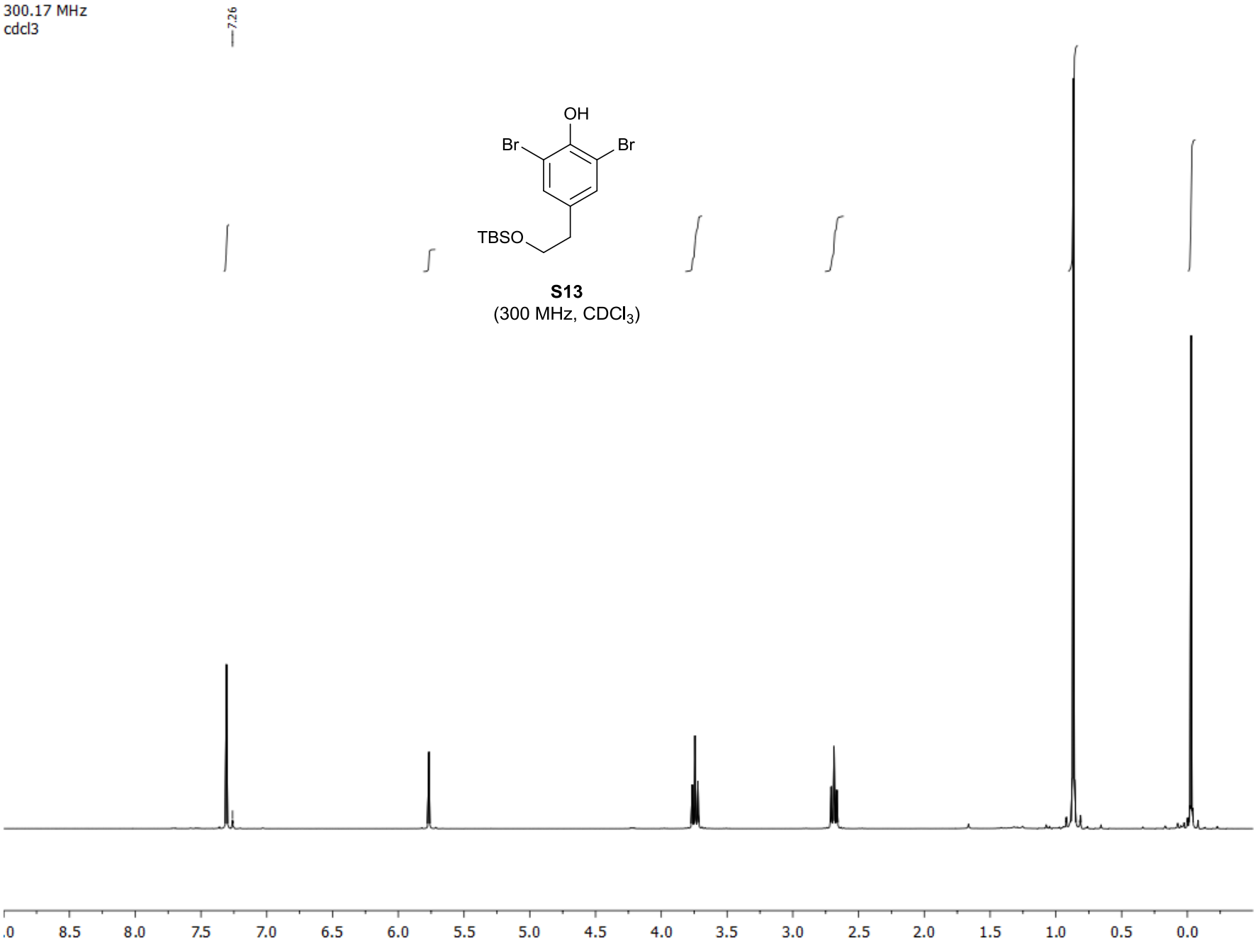
4s
(300 MHz, $CDCl_3$)



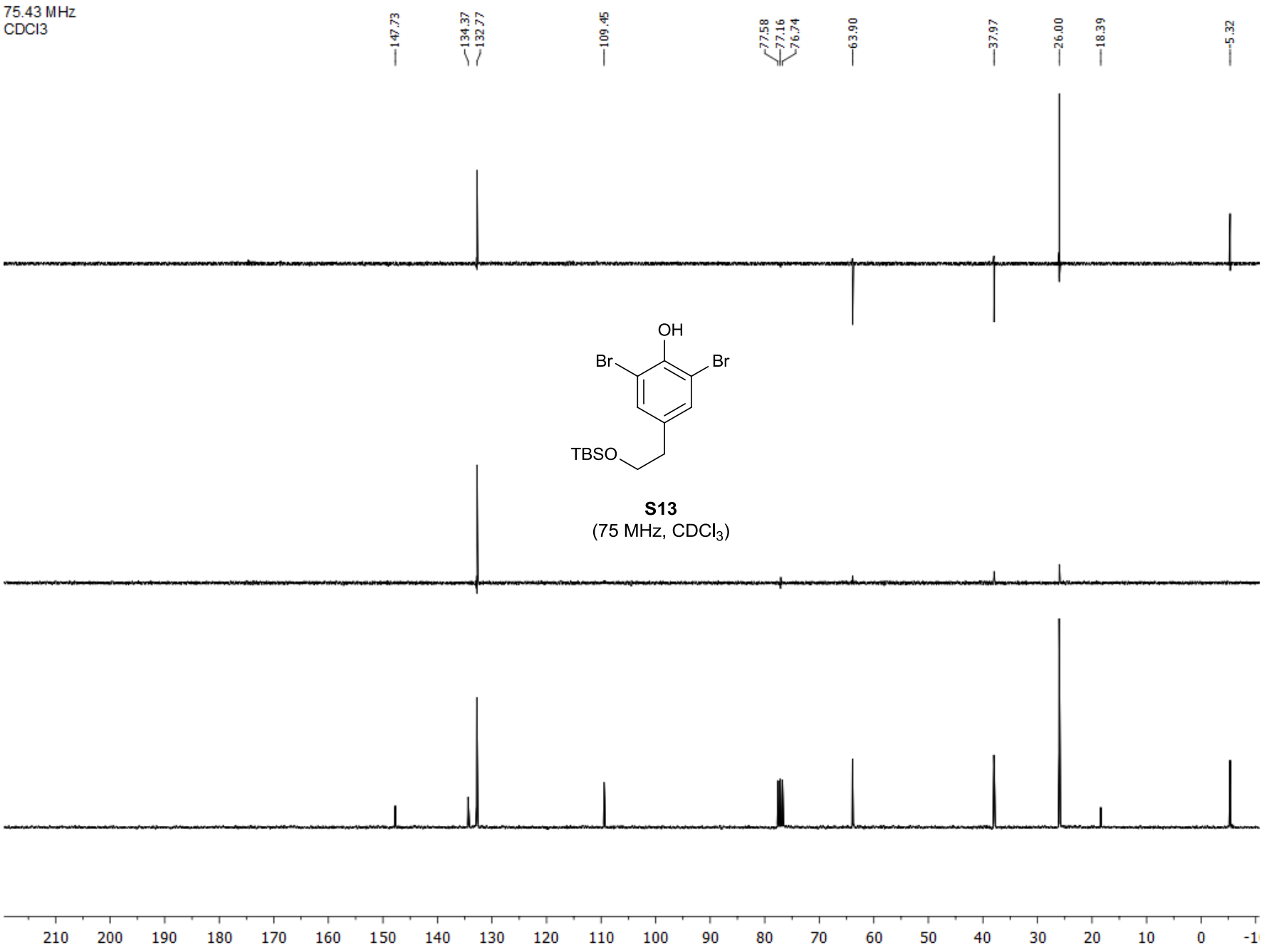




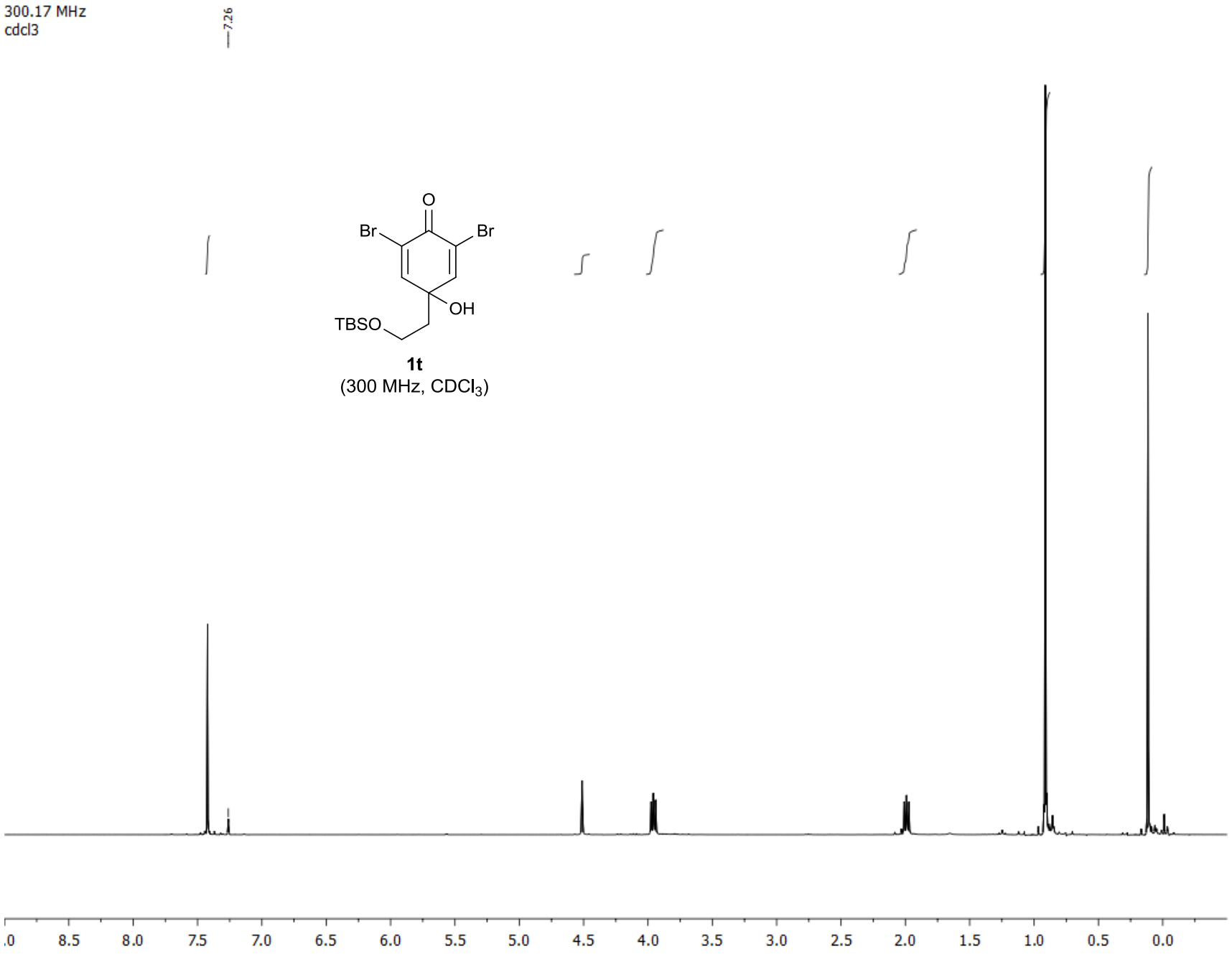
S12
(75 MHz, $CDCl_3$)

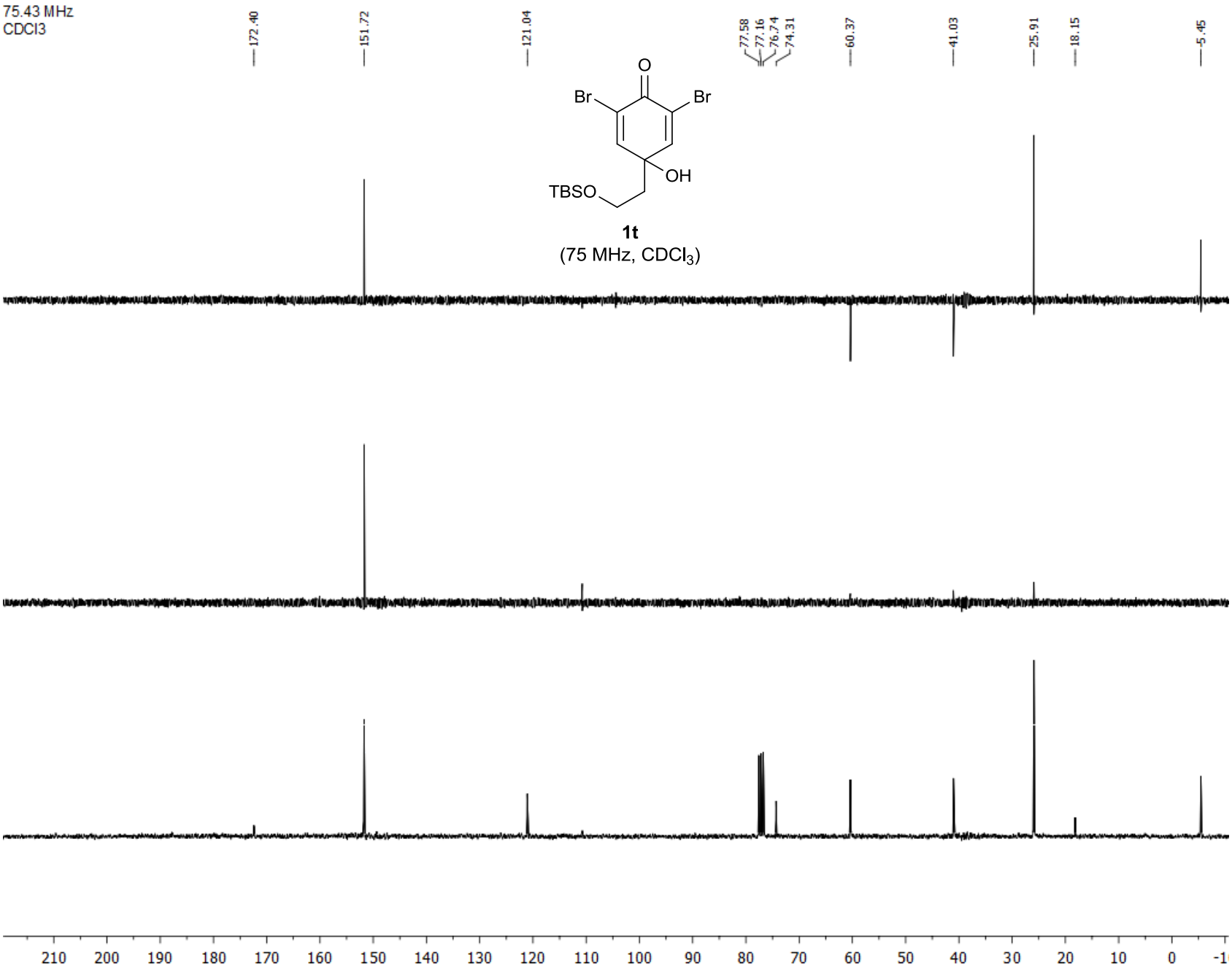


S13
(300 MHz, $CDCl_3$)

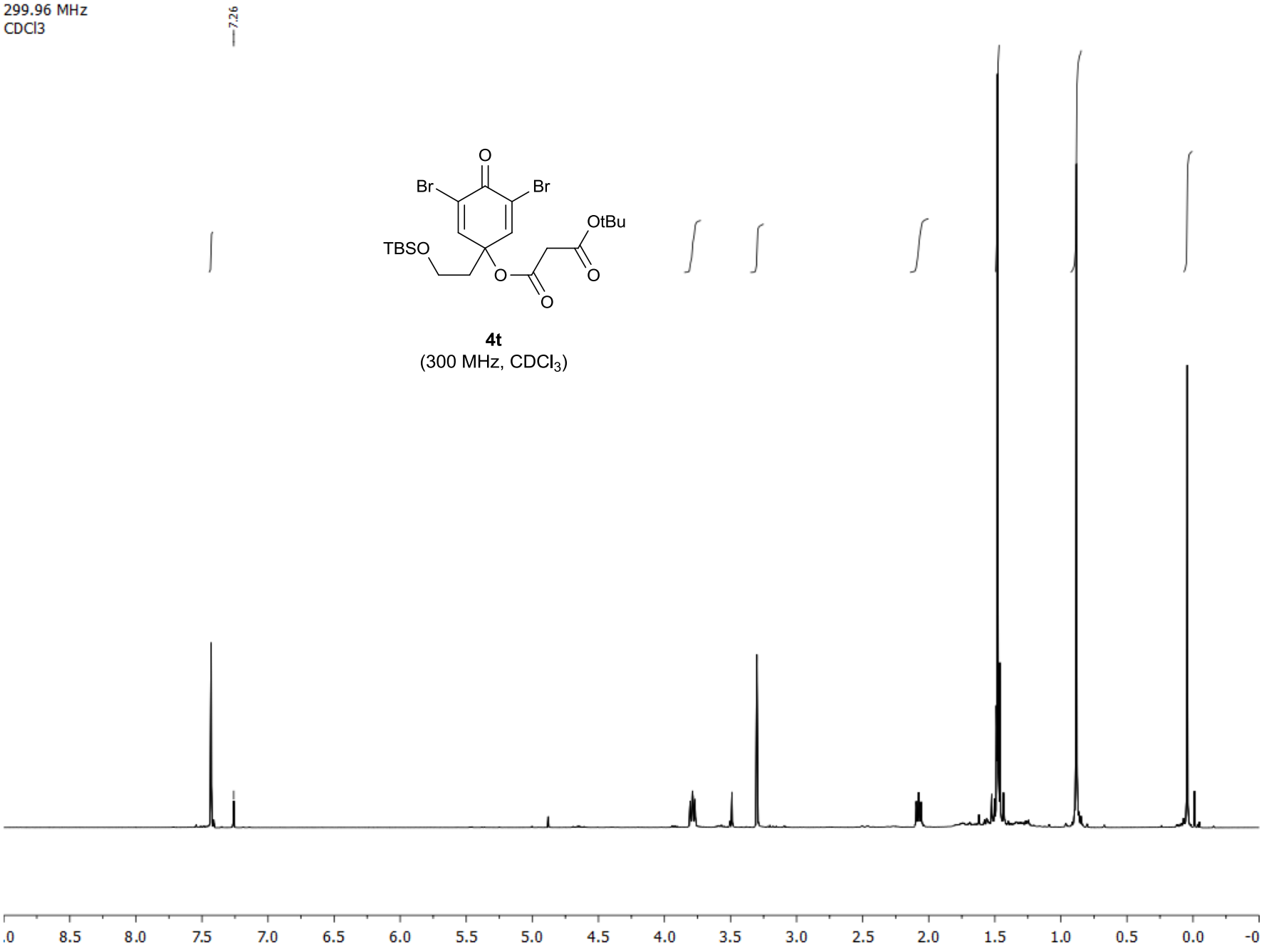


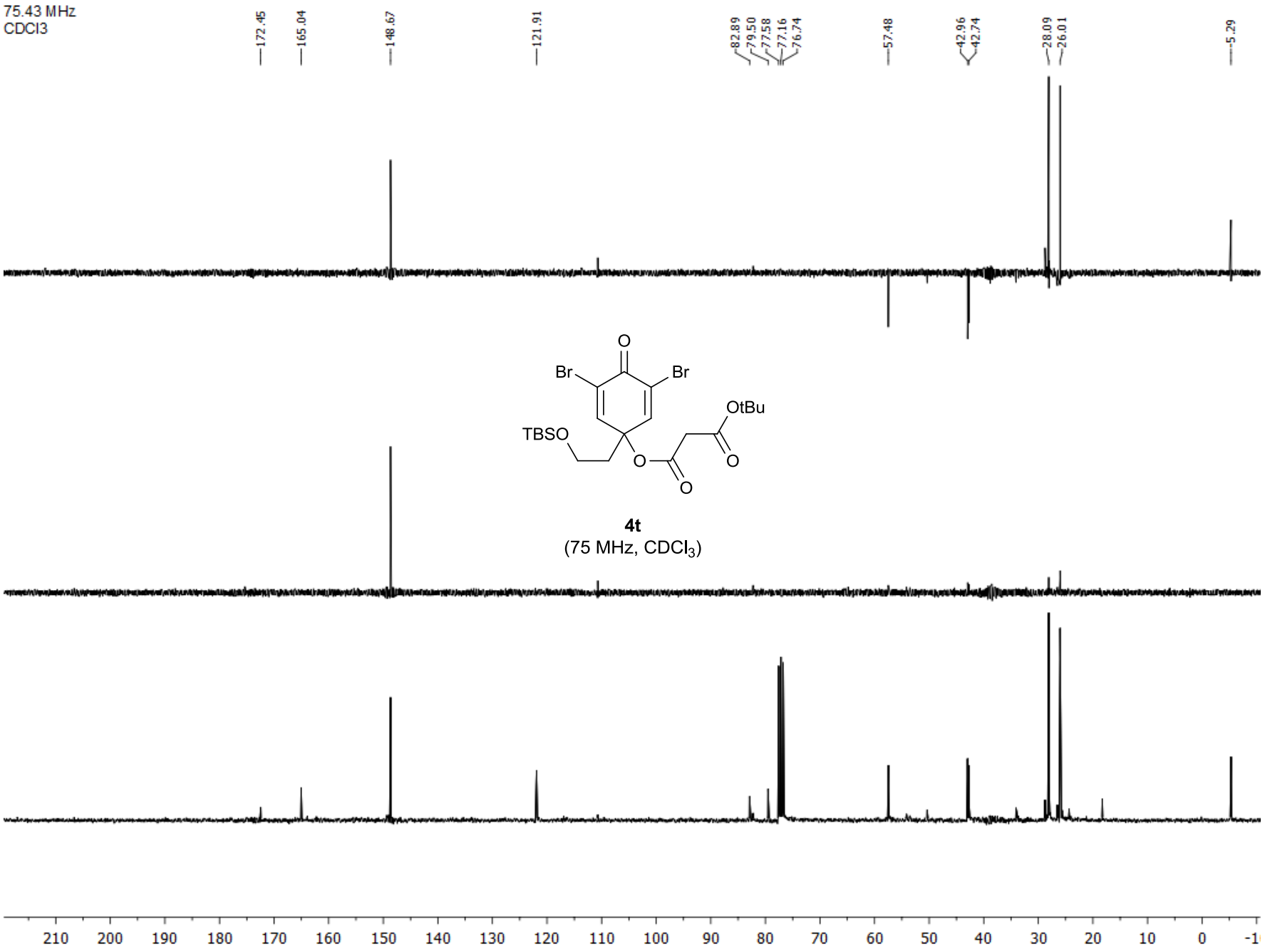
S13
(75 MHz, $CDCl_3$)



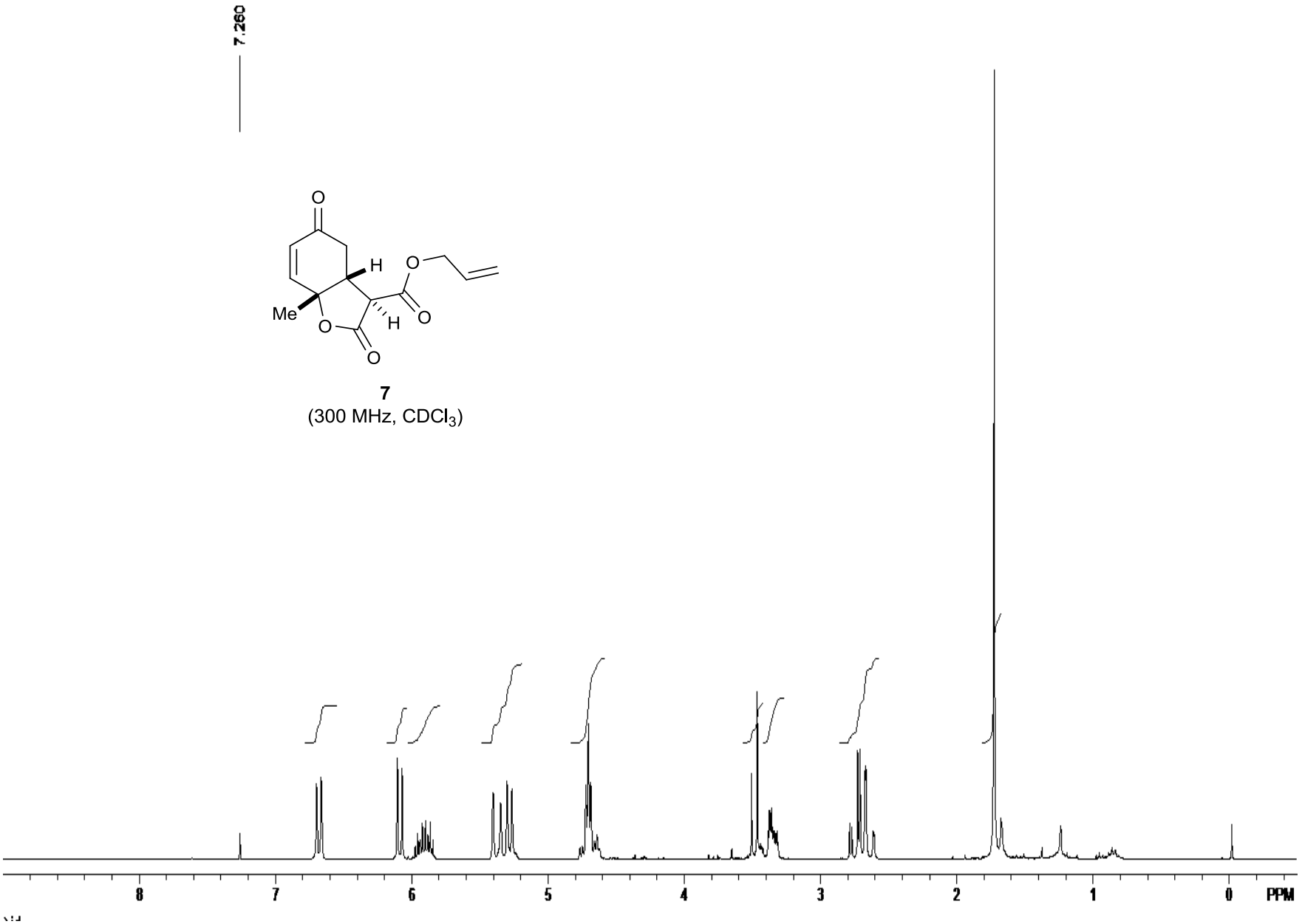


1t
(75 MHz, $CDCl_3$)

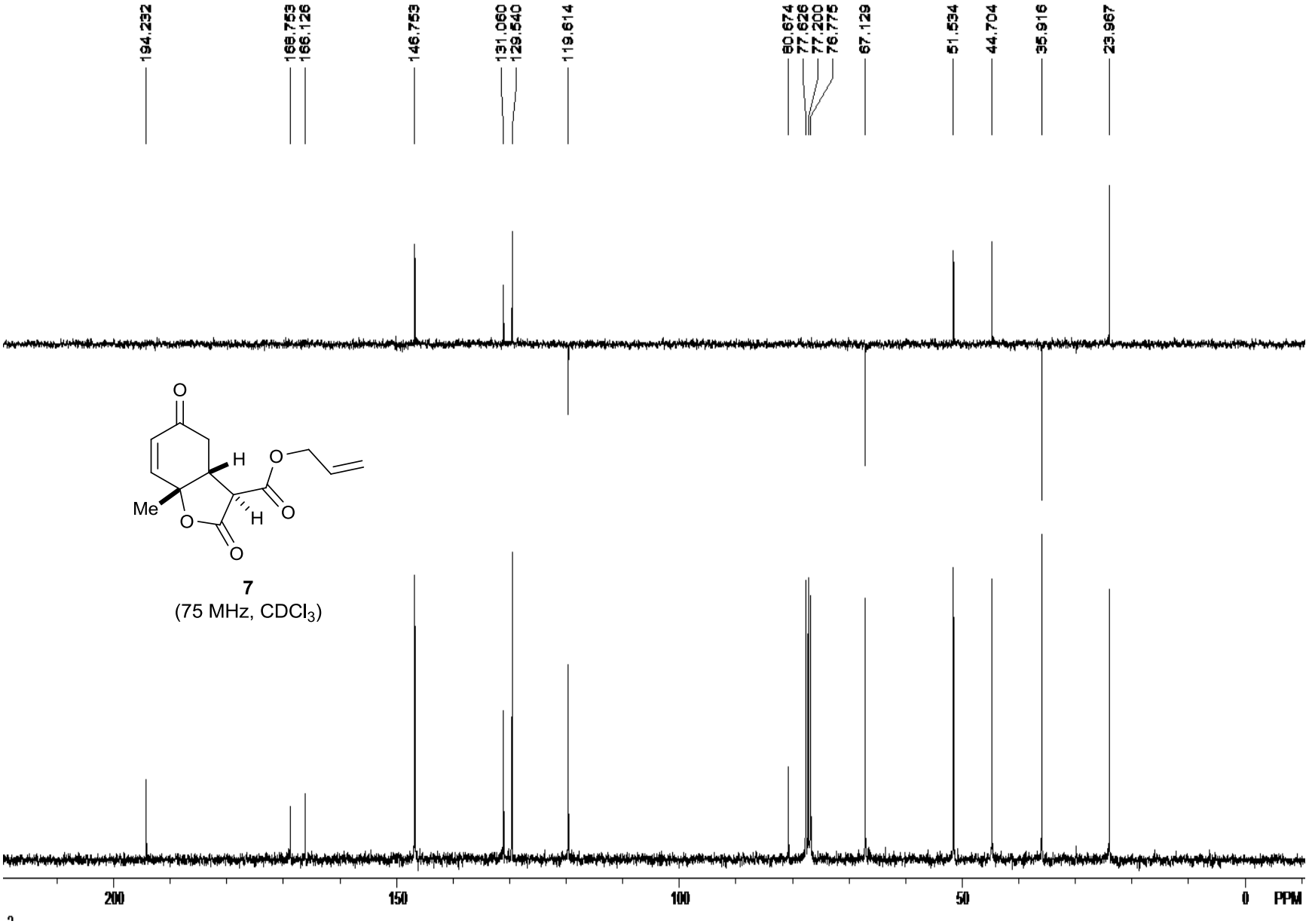




4t
(75 MHz, $CDCl_3$)

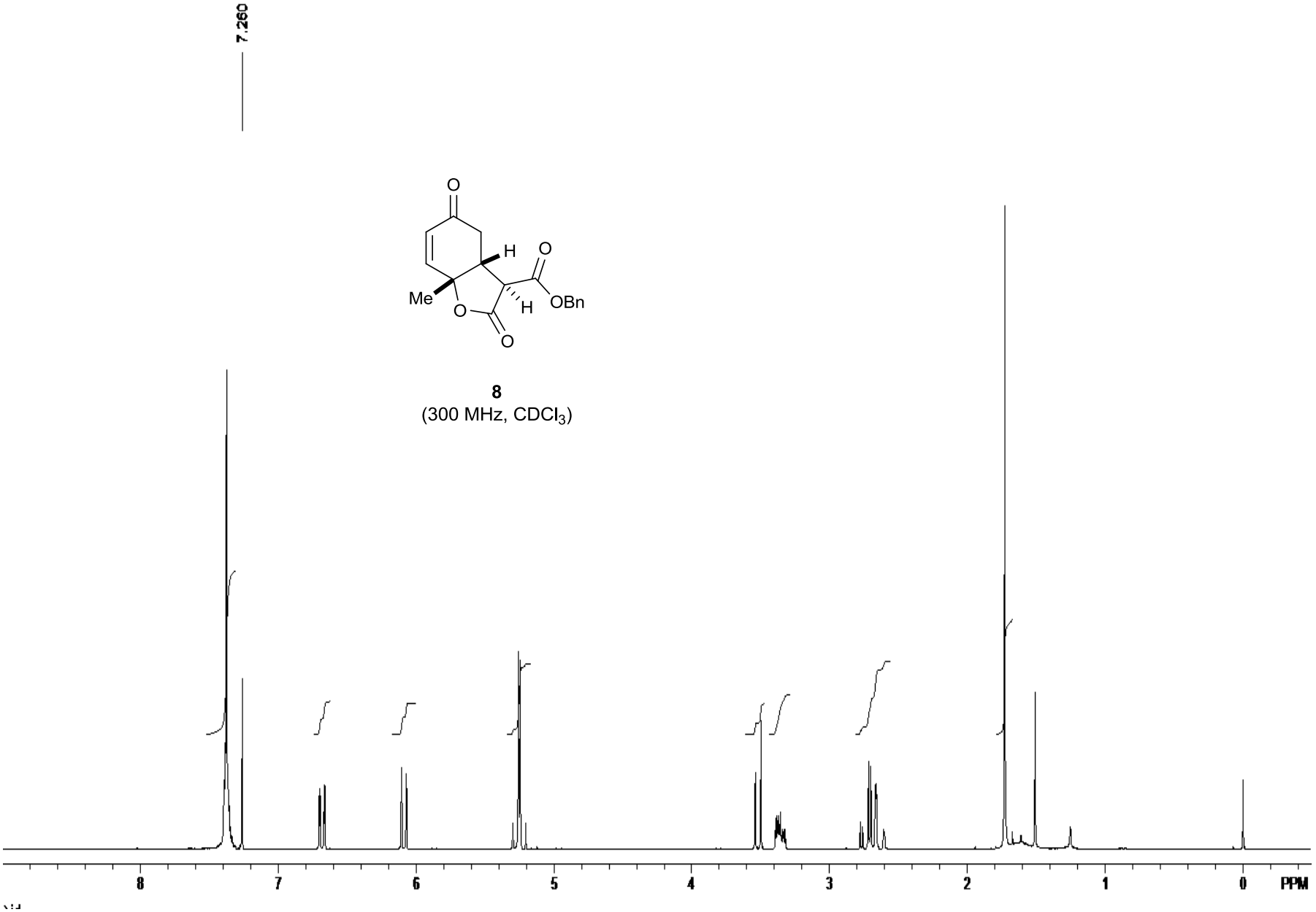


7
(300 MHz, $CDCl_3$)

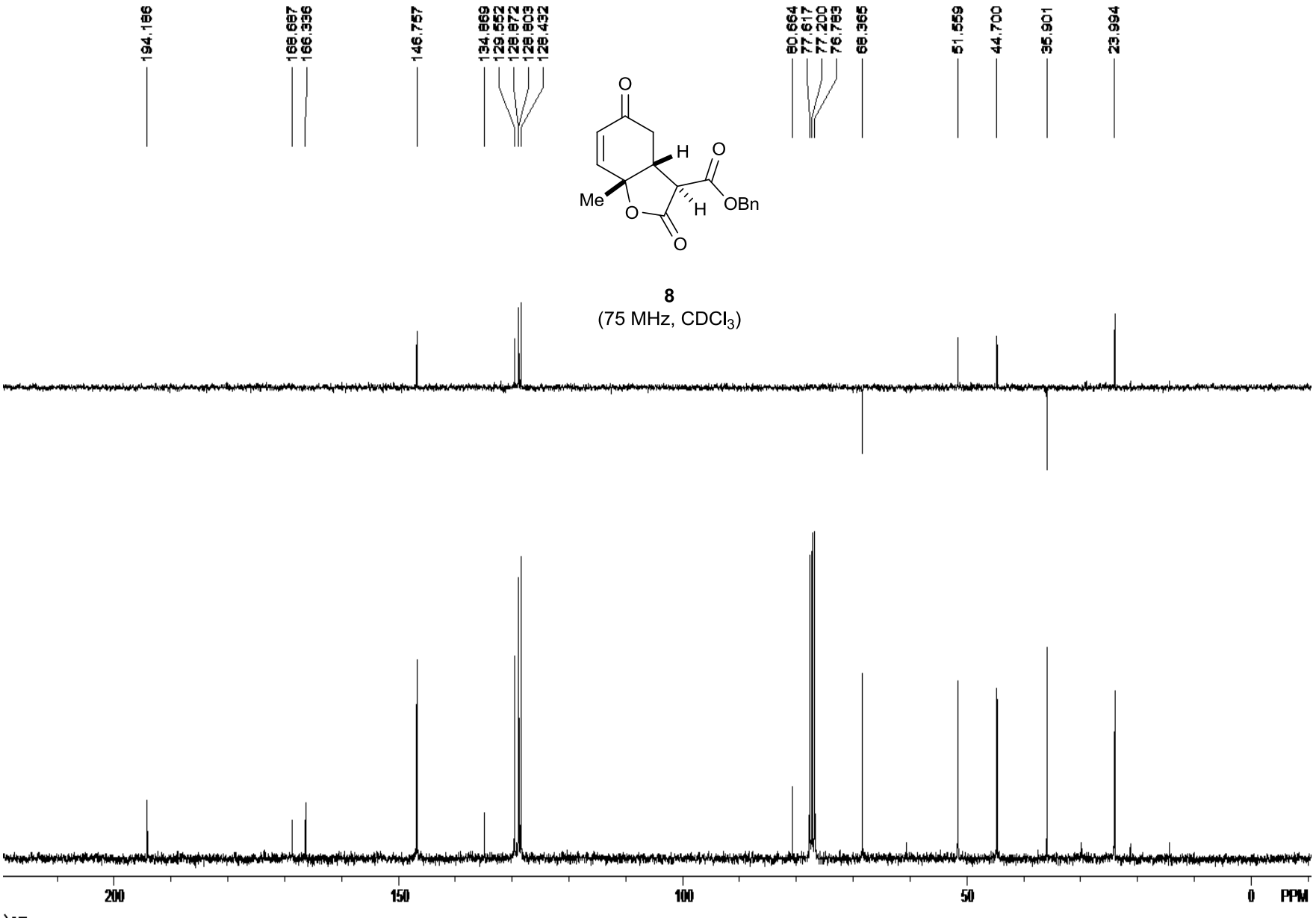


7

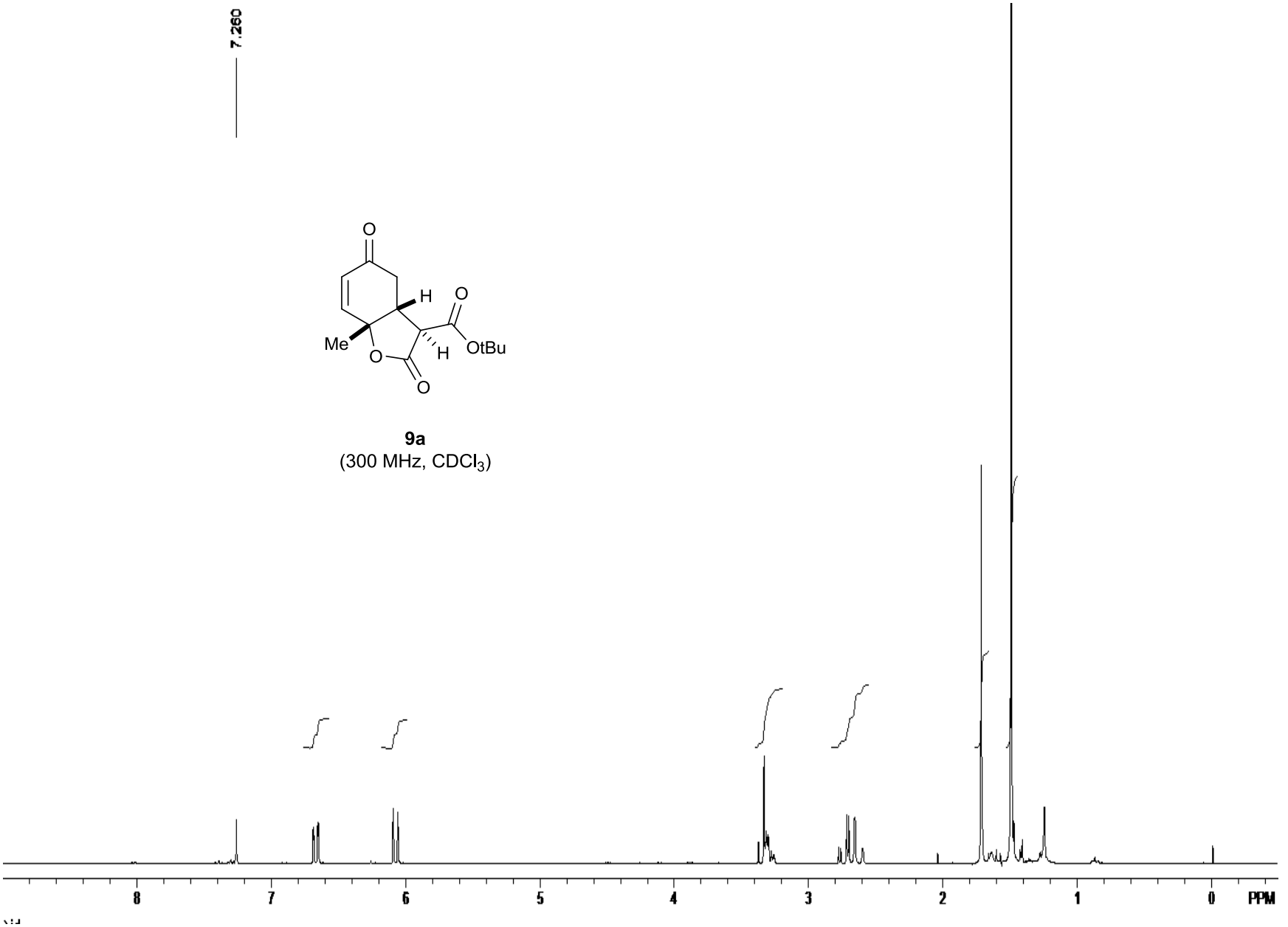
(75 MHz, $CDCl_3$)



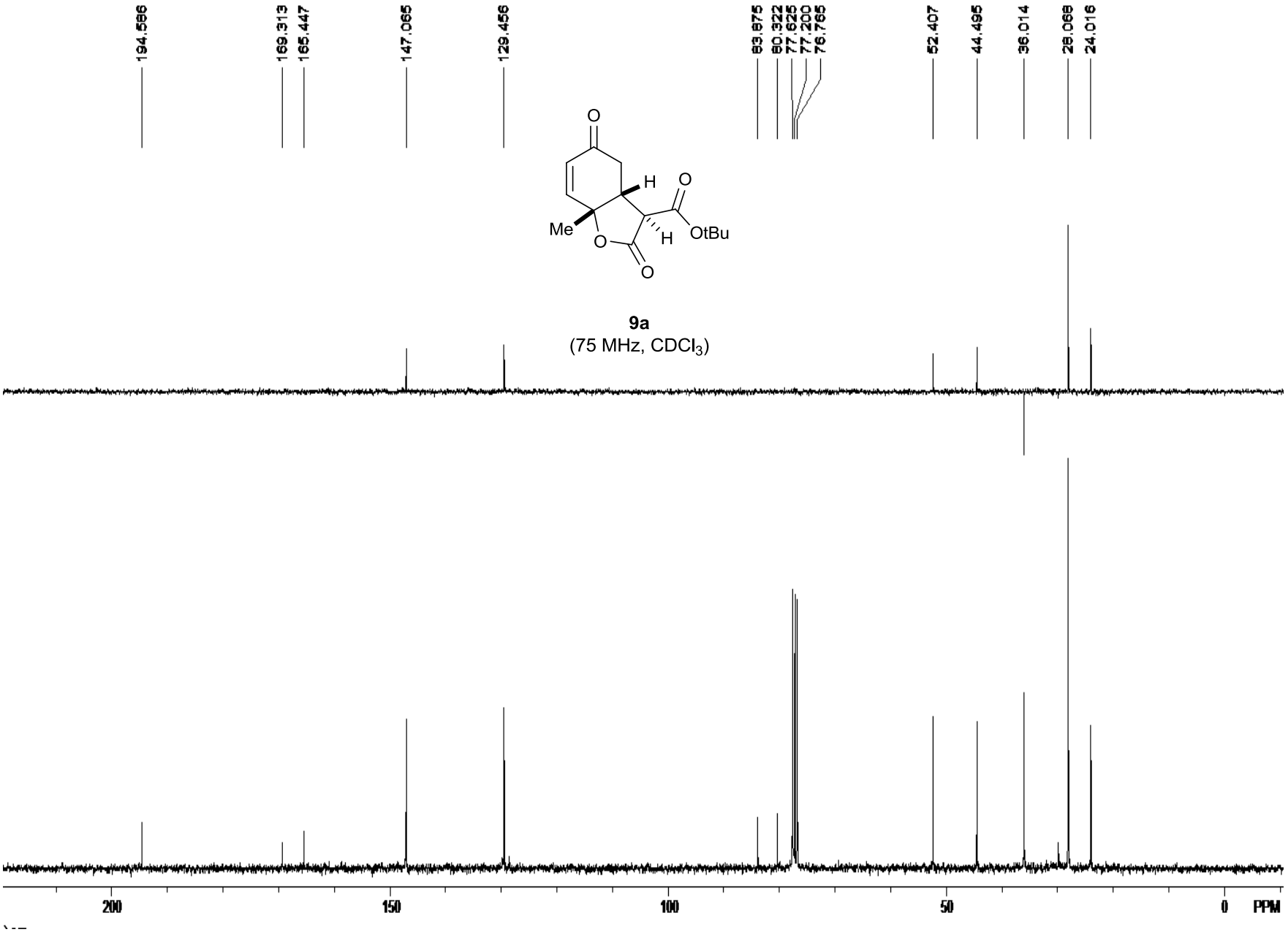
(300 MHz, $CDCl_3$)



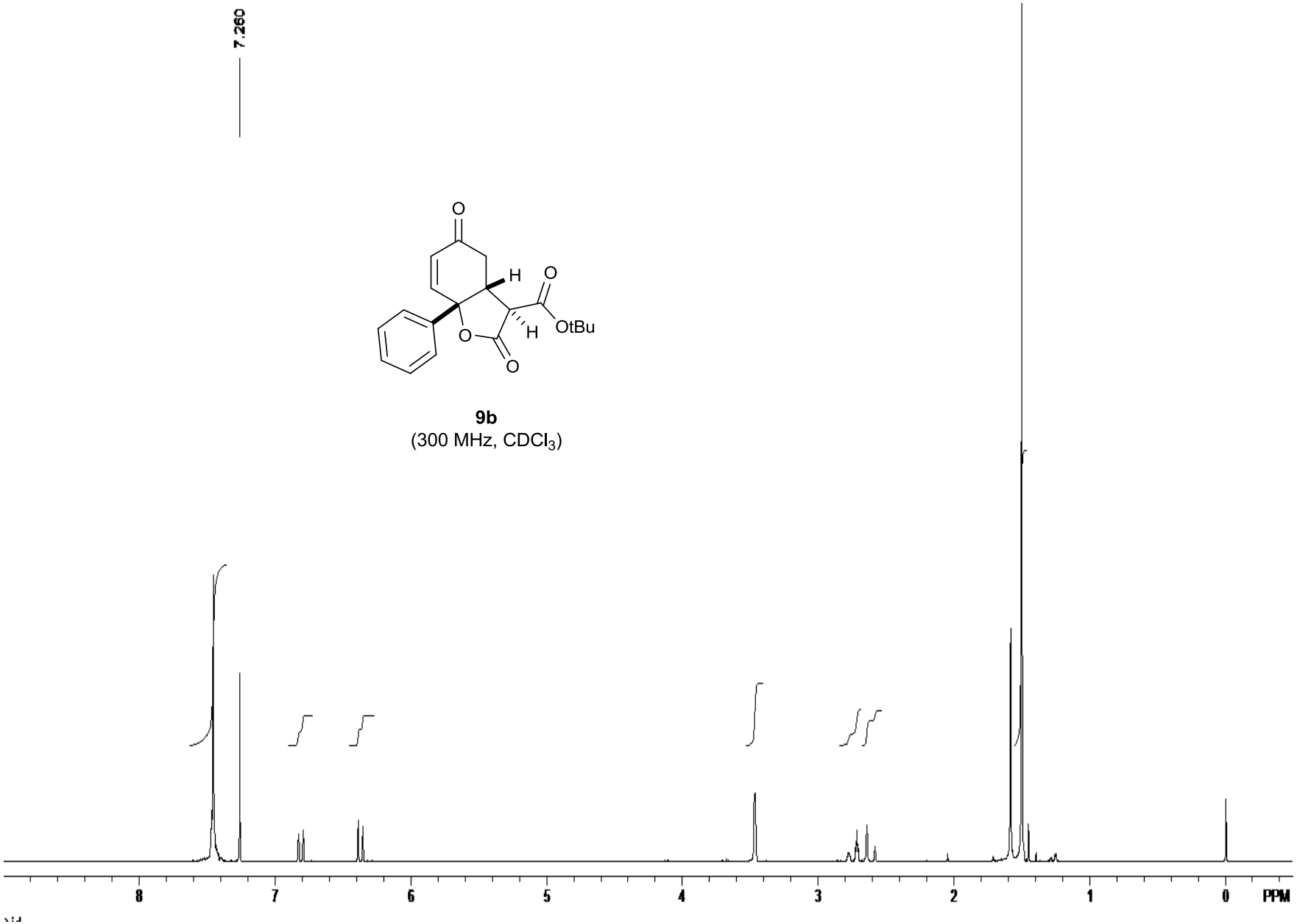
8
(75 MHz, $CDCl_3$)



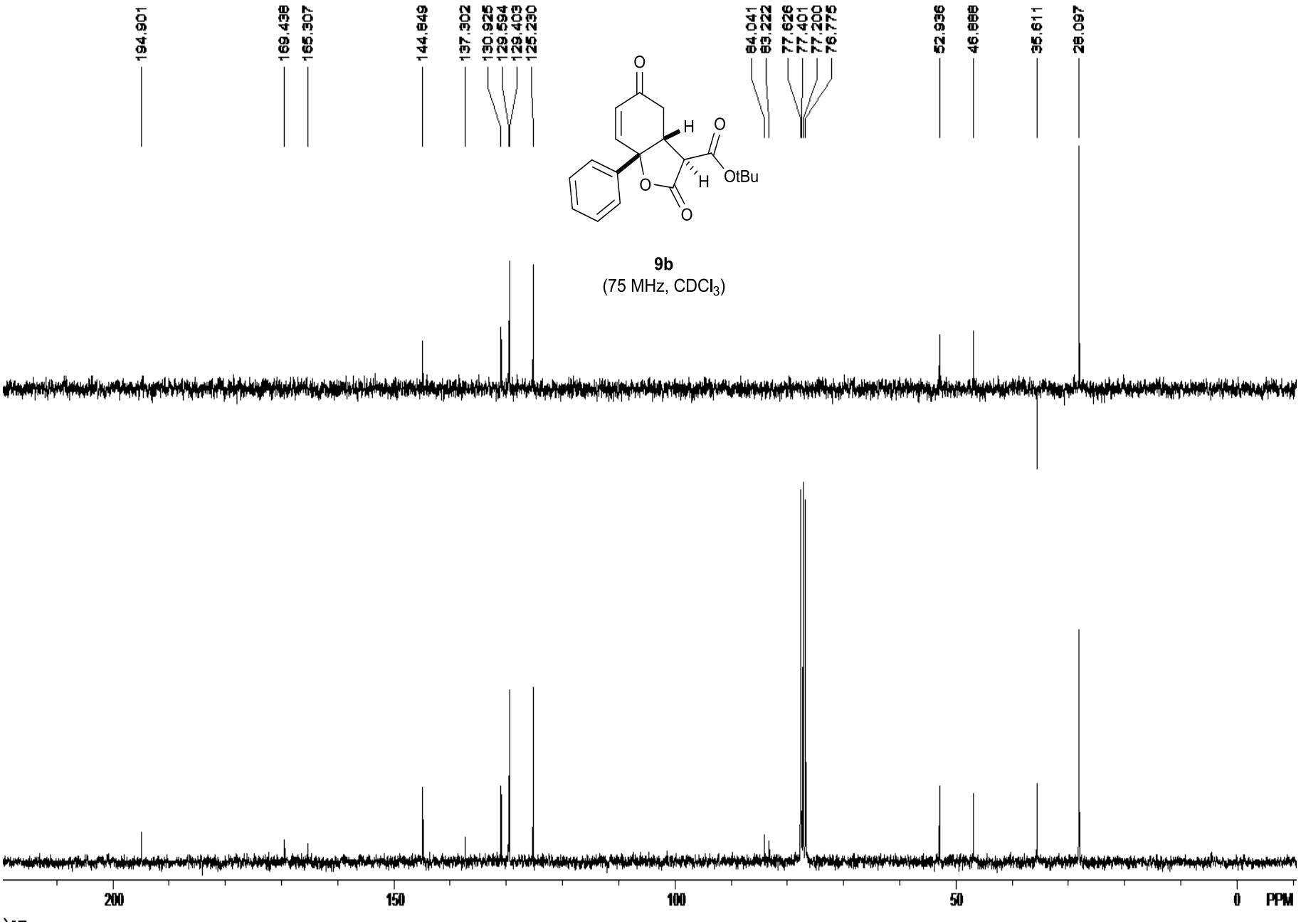
9a
(300 MHz, $CDCl_3$)

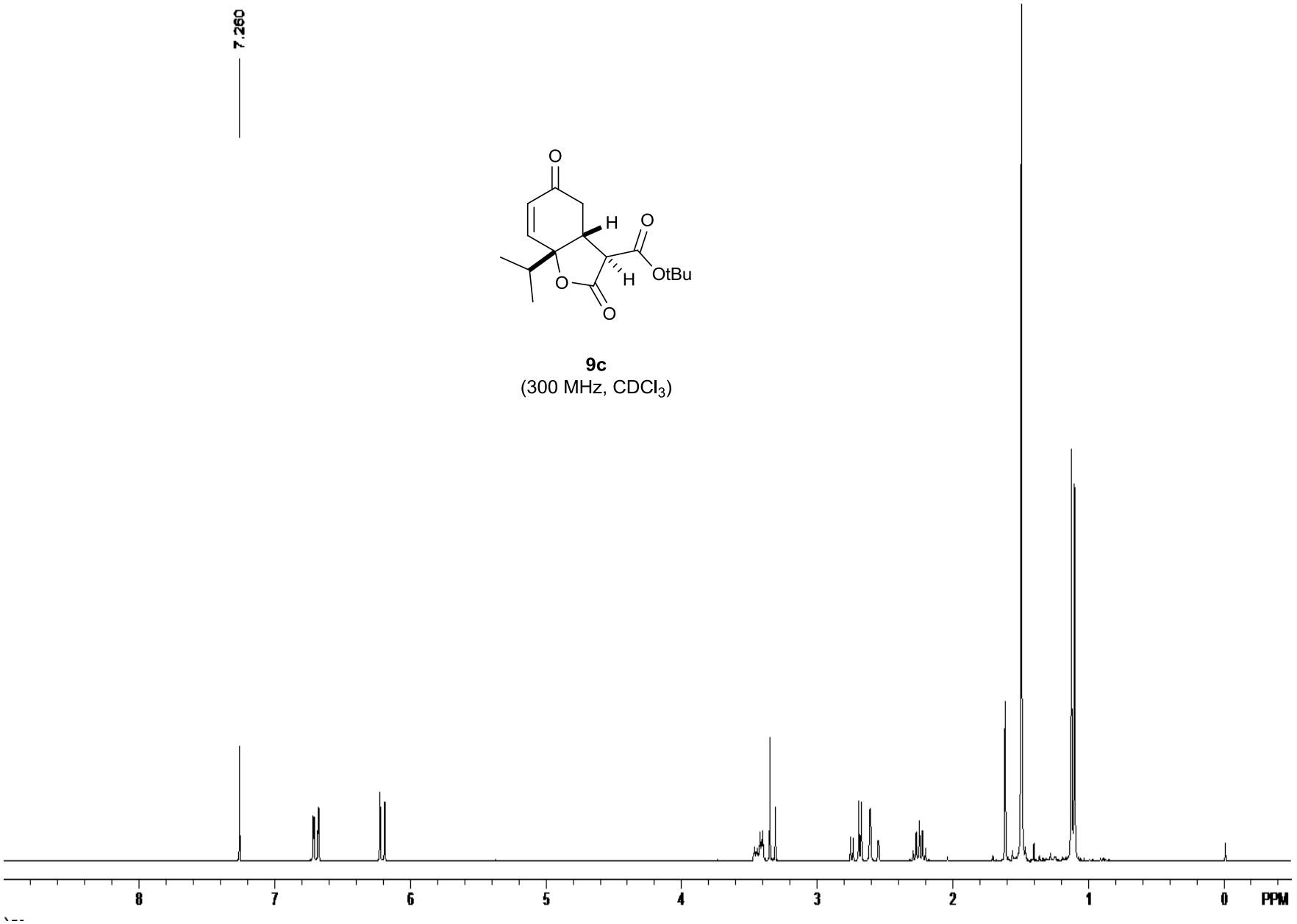


9a
(75 MHz, $CDCl_3$)

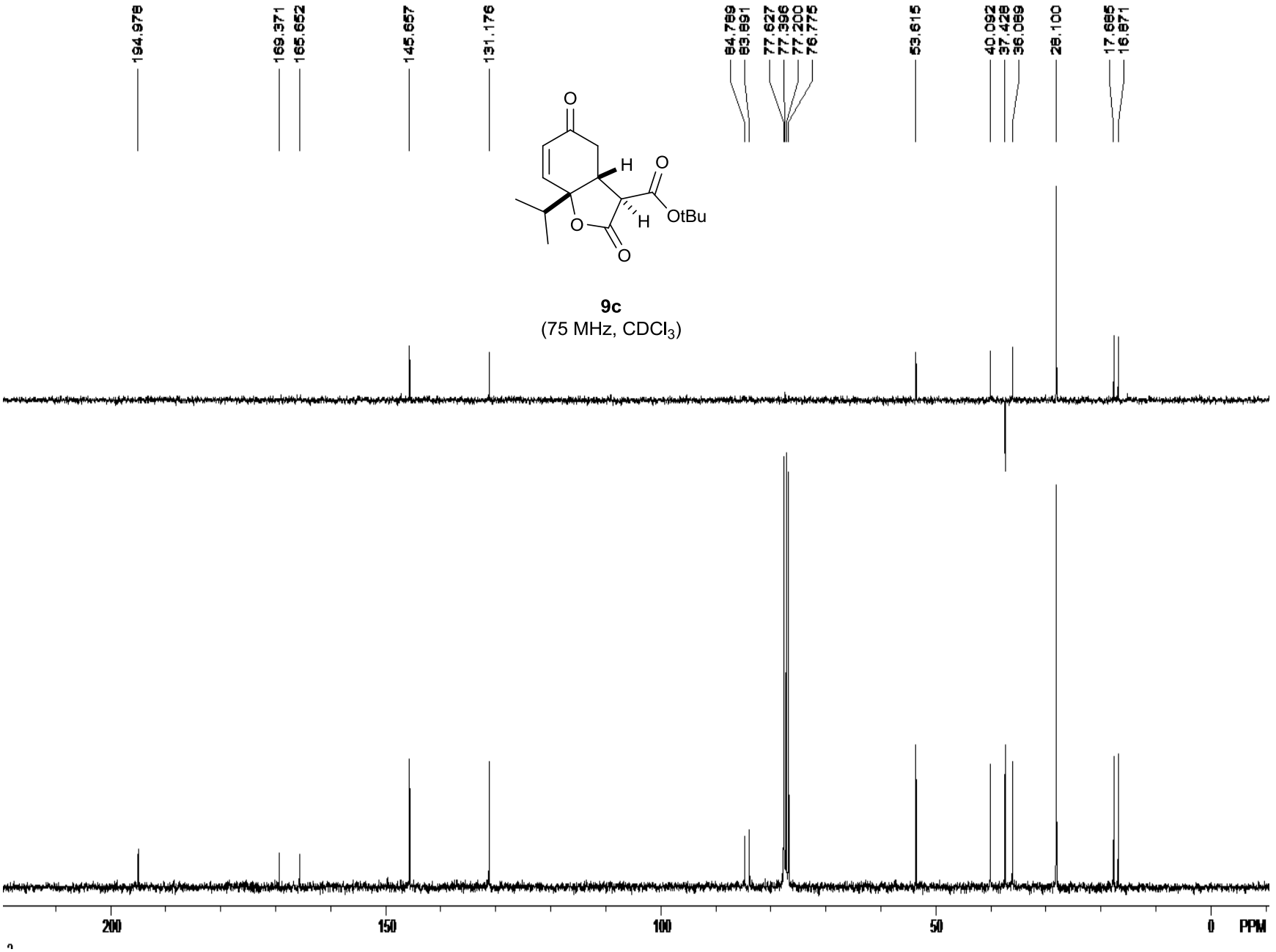


9b
(300 MHz, $CDCl_3$)

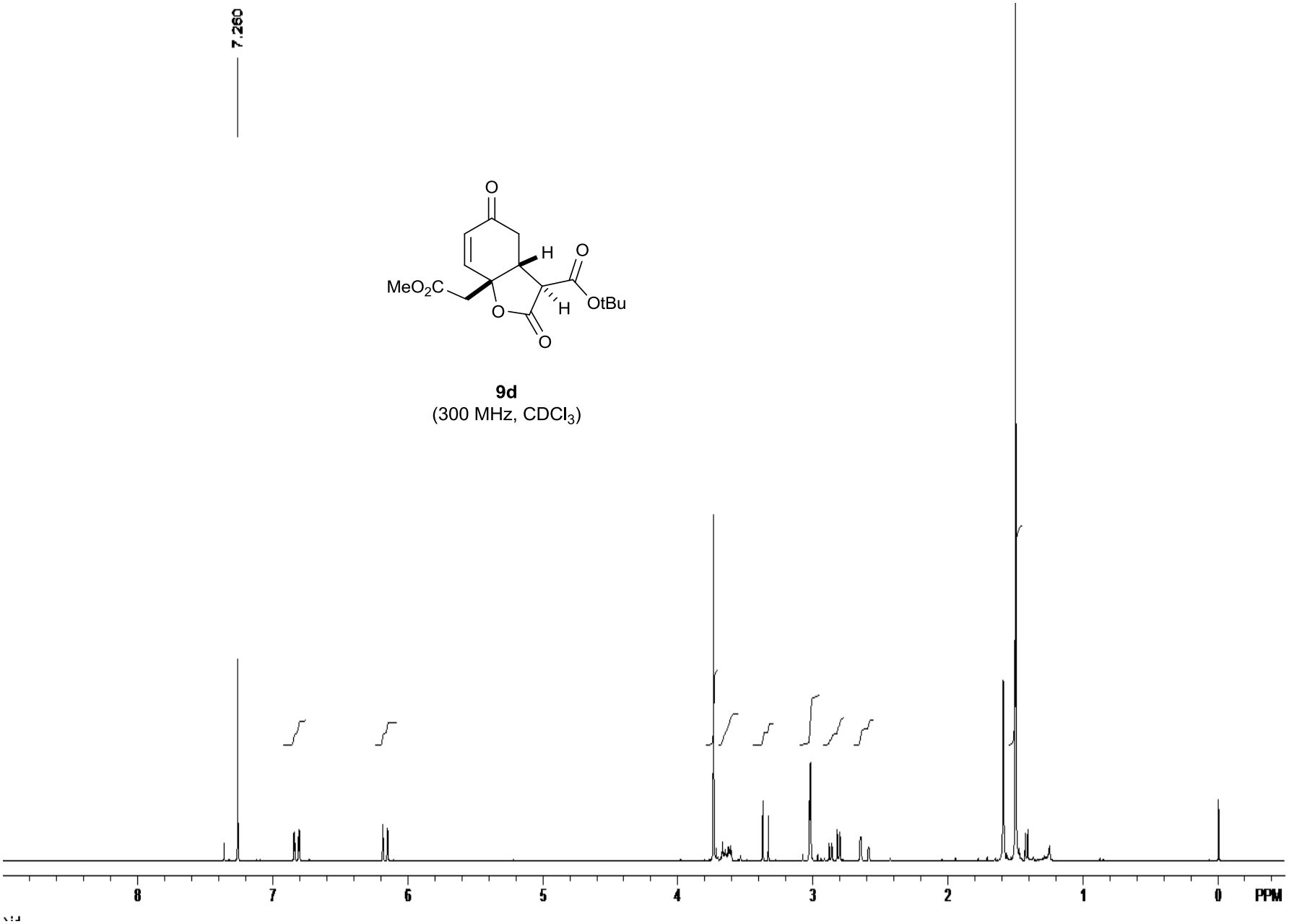




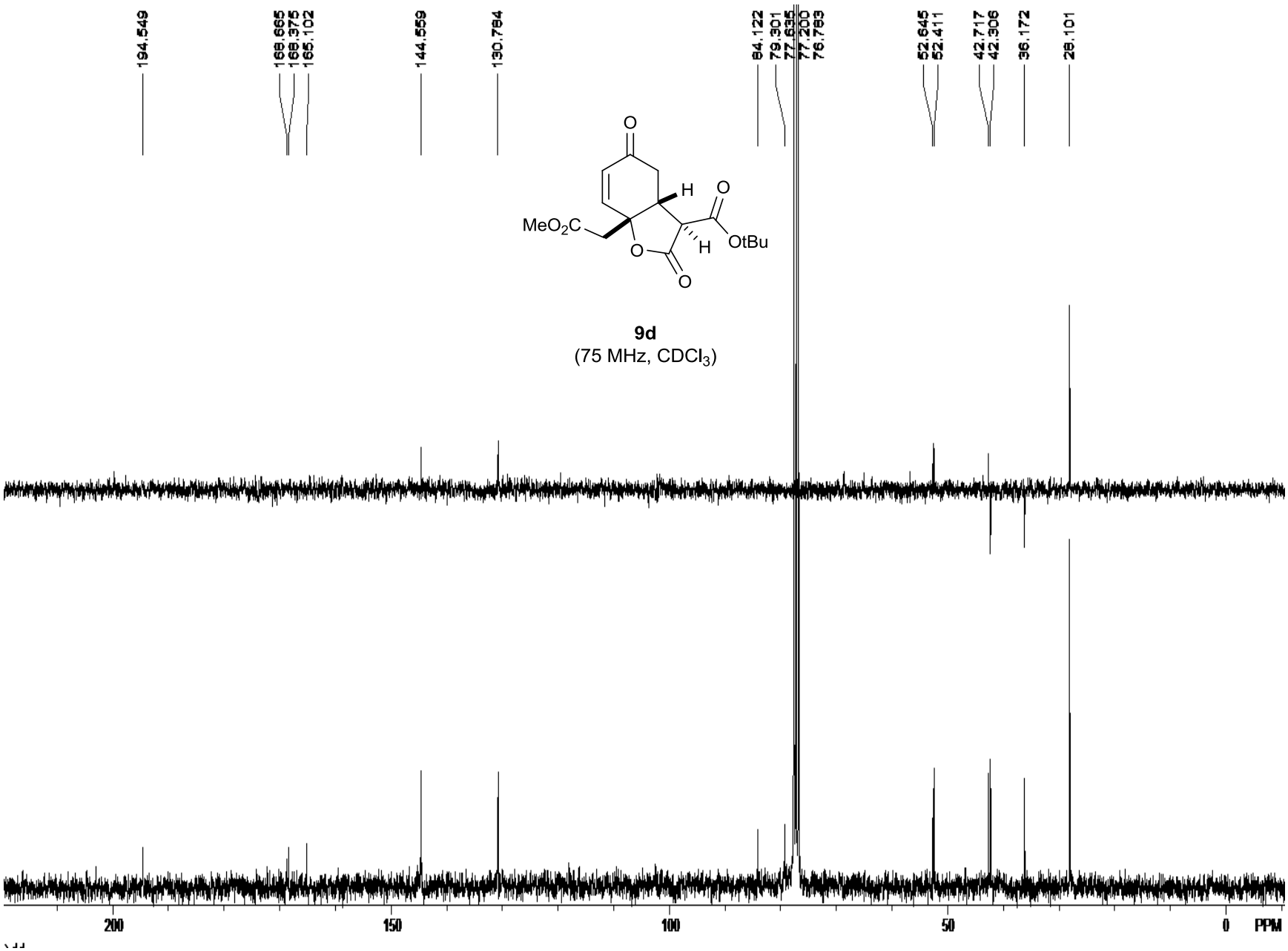
9c
(300 MHz, $CDCl_3$)



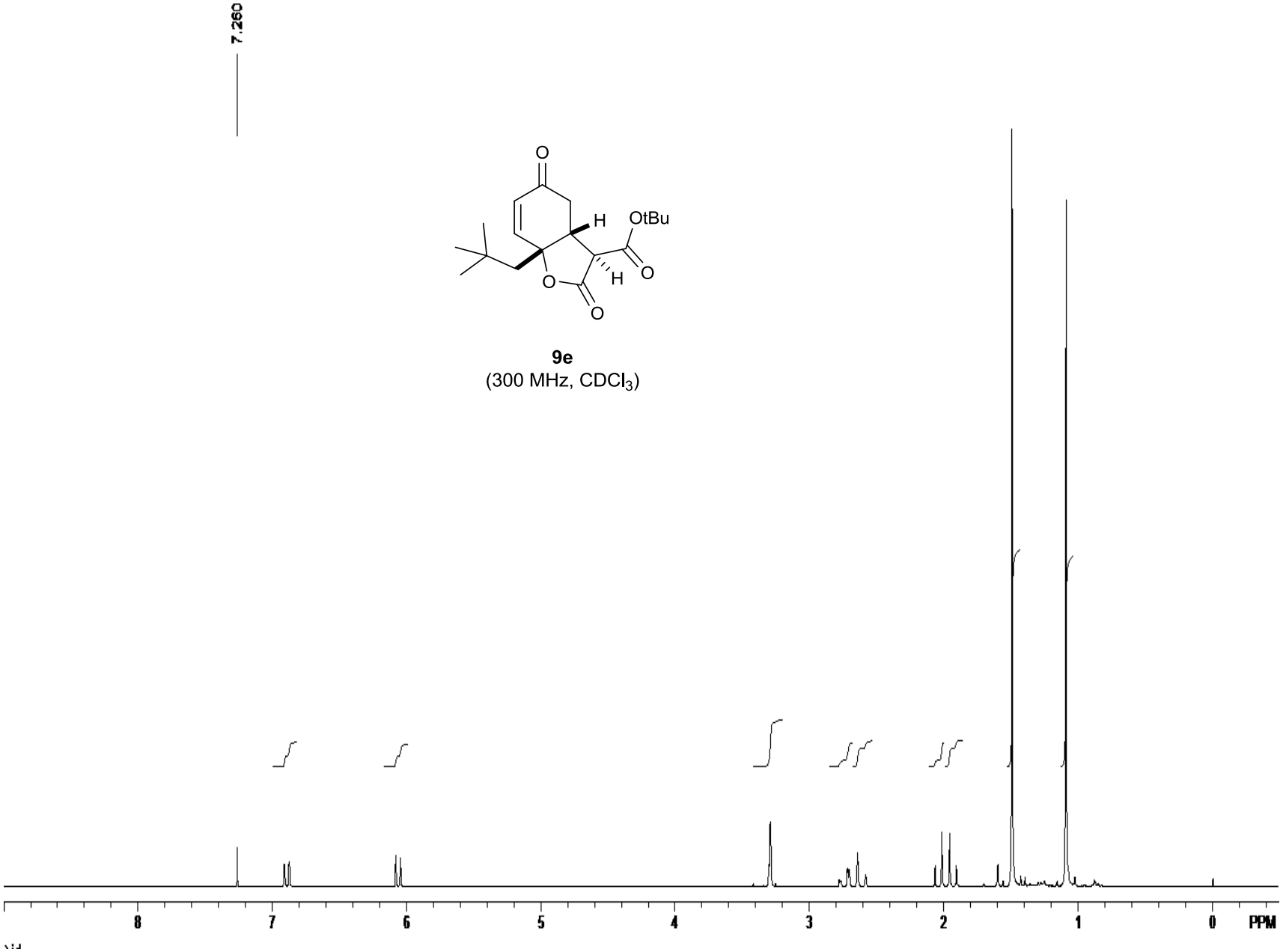
9c
(75 MHz, $CDCl_3$)



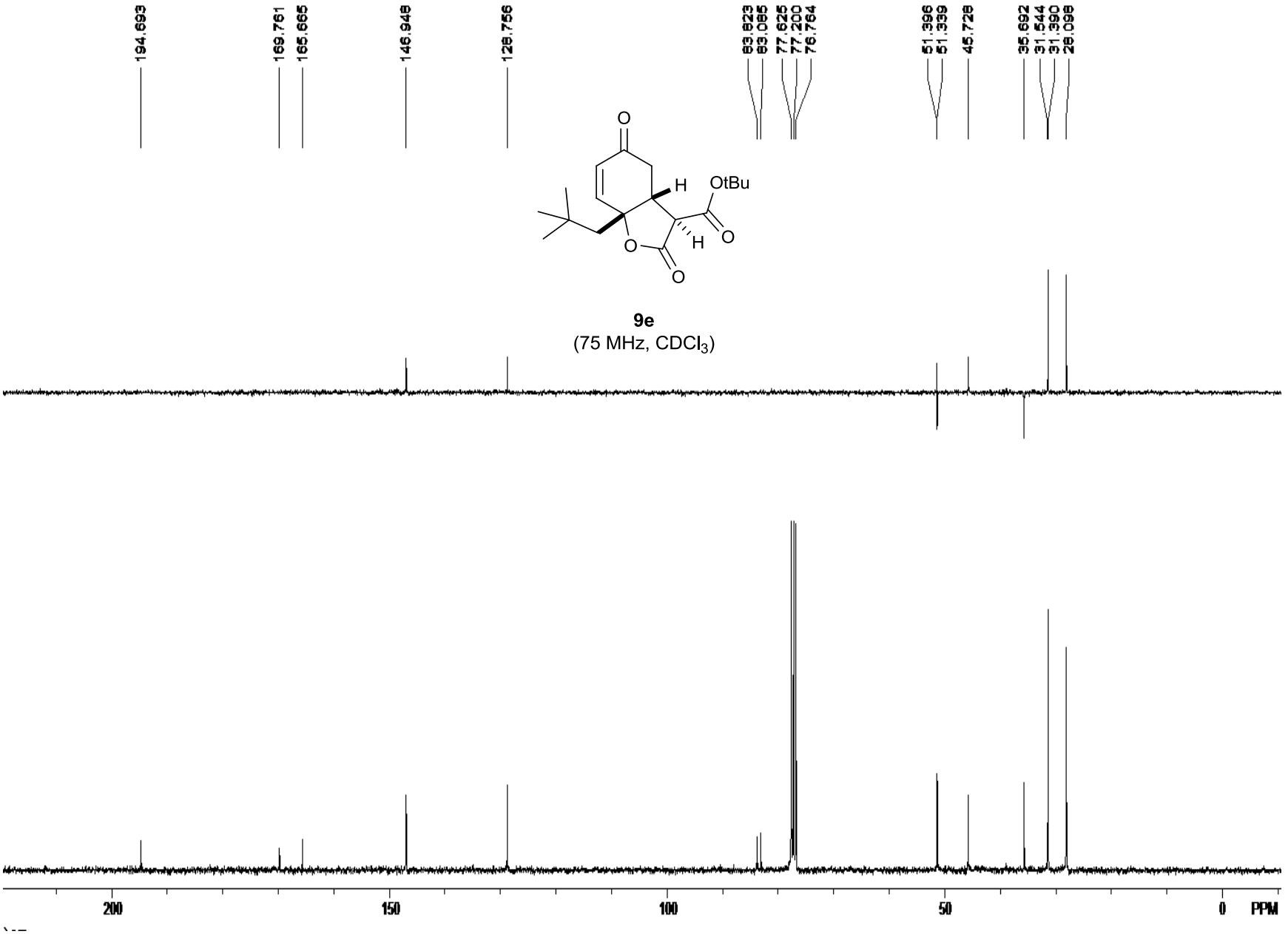
9d
(300 MHz, $CDCl_3$)



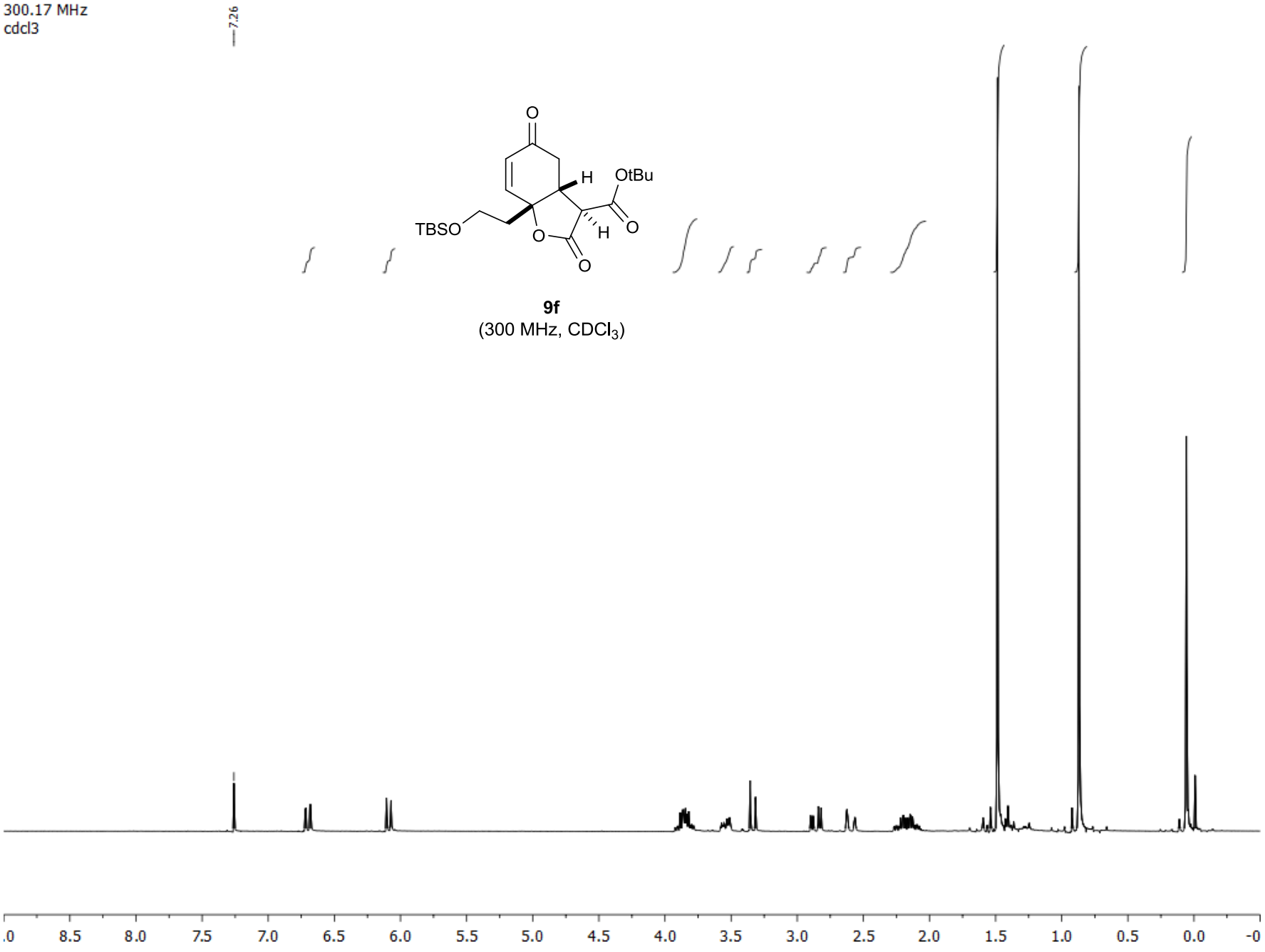
9d
(75 MHz, $CDCl_3$)



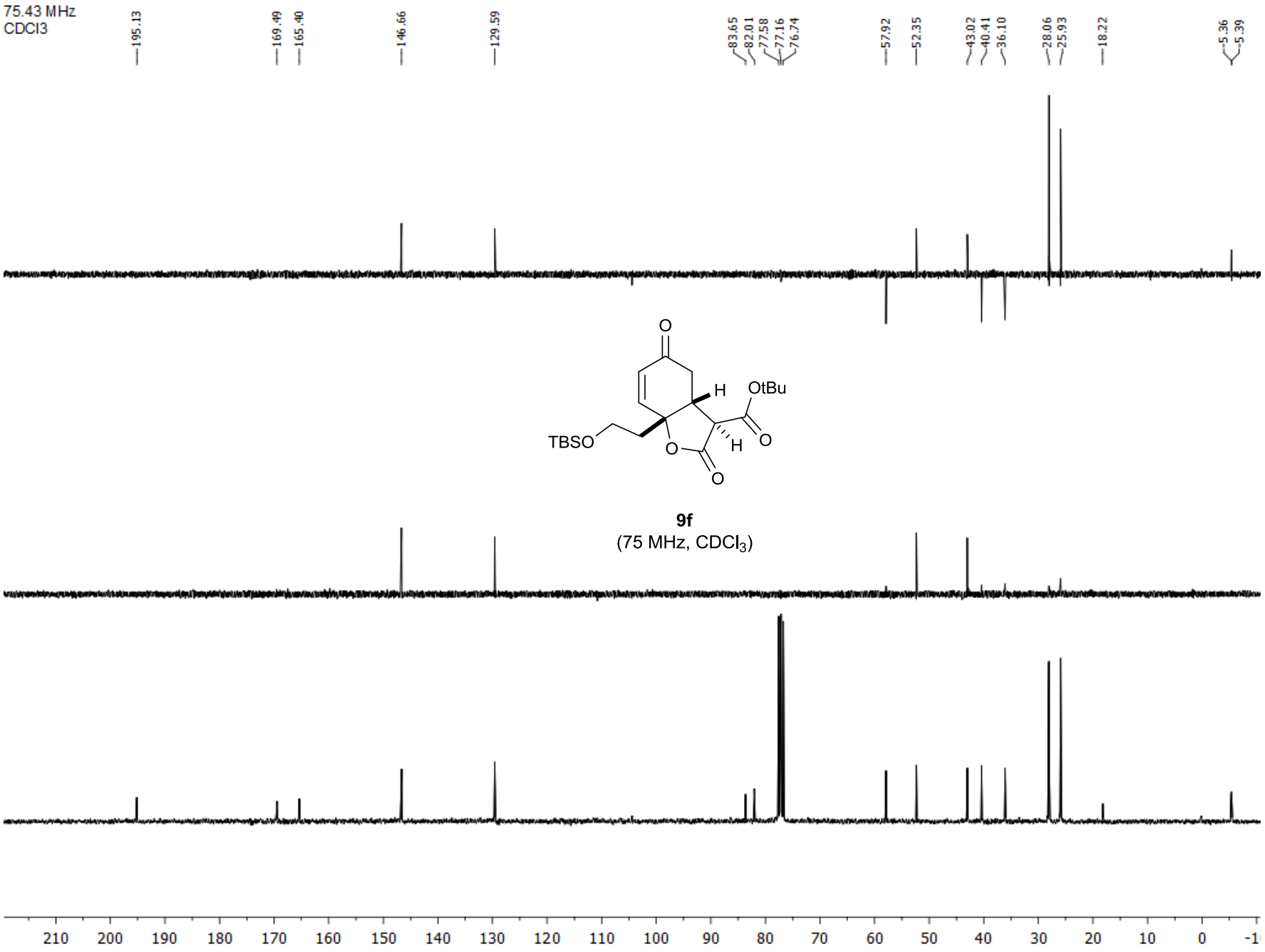
9e
(300 MHz, $CDCl_3$)



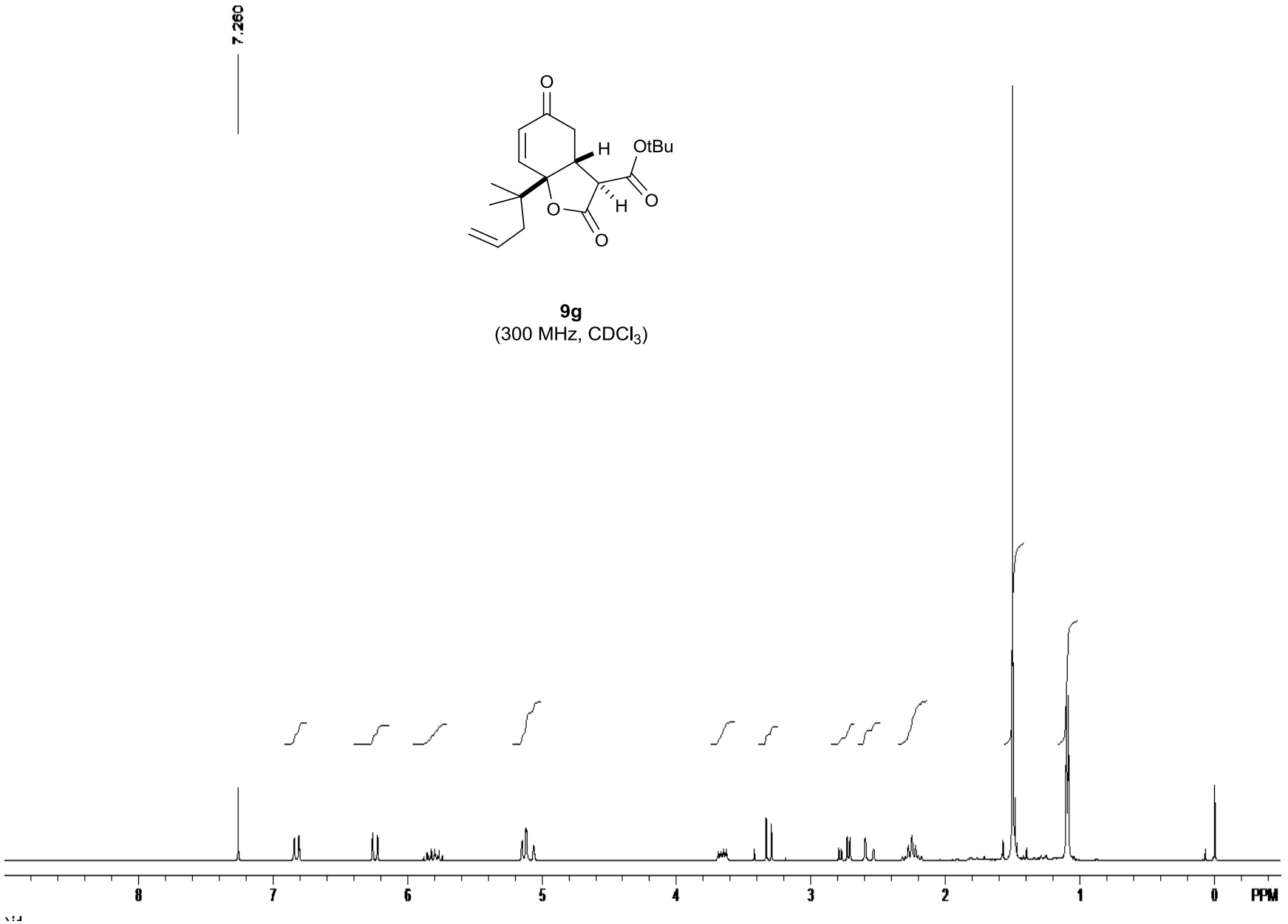
9e
(75 MHz, $CDCl_3$)



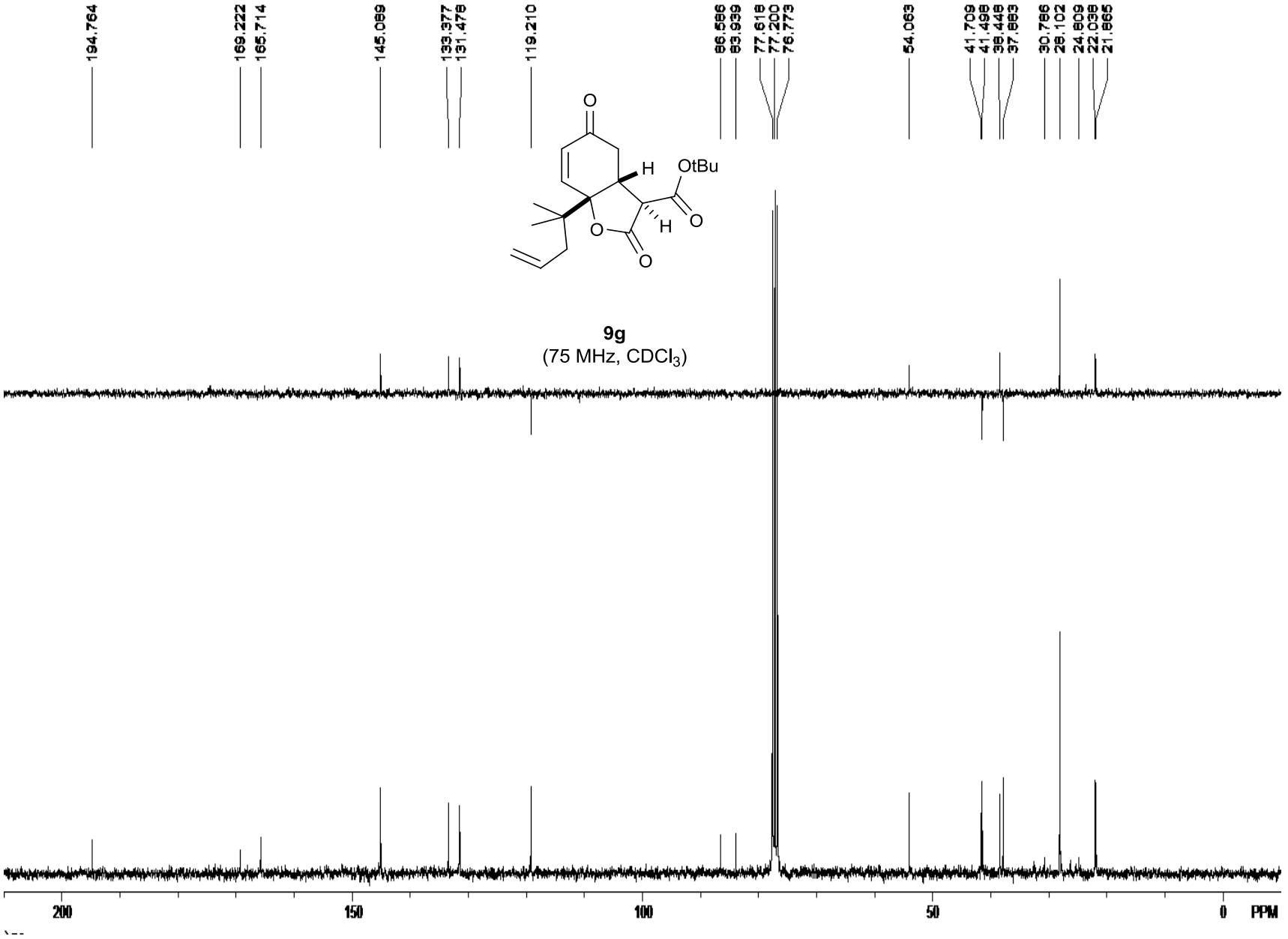
9f
(300 MHz, $CDCl_3$)

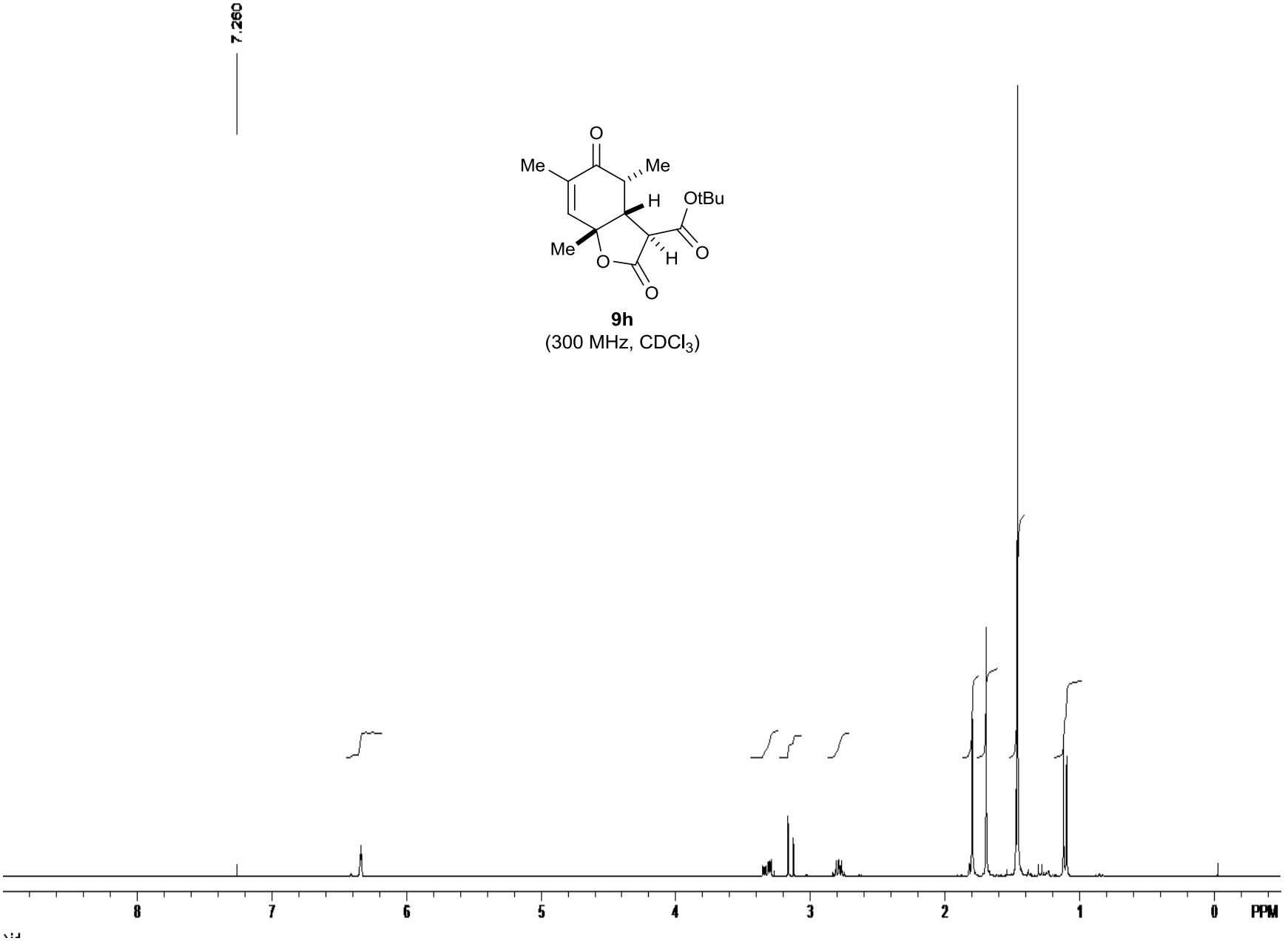


9f
(75 MHz, $CDCl_3$)

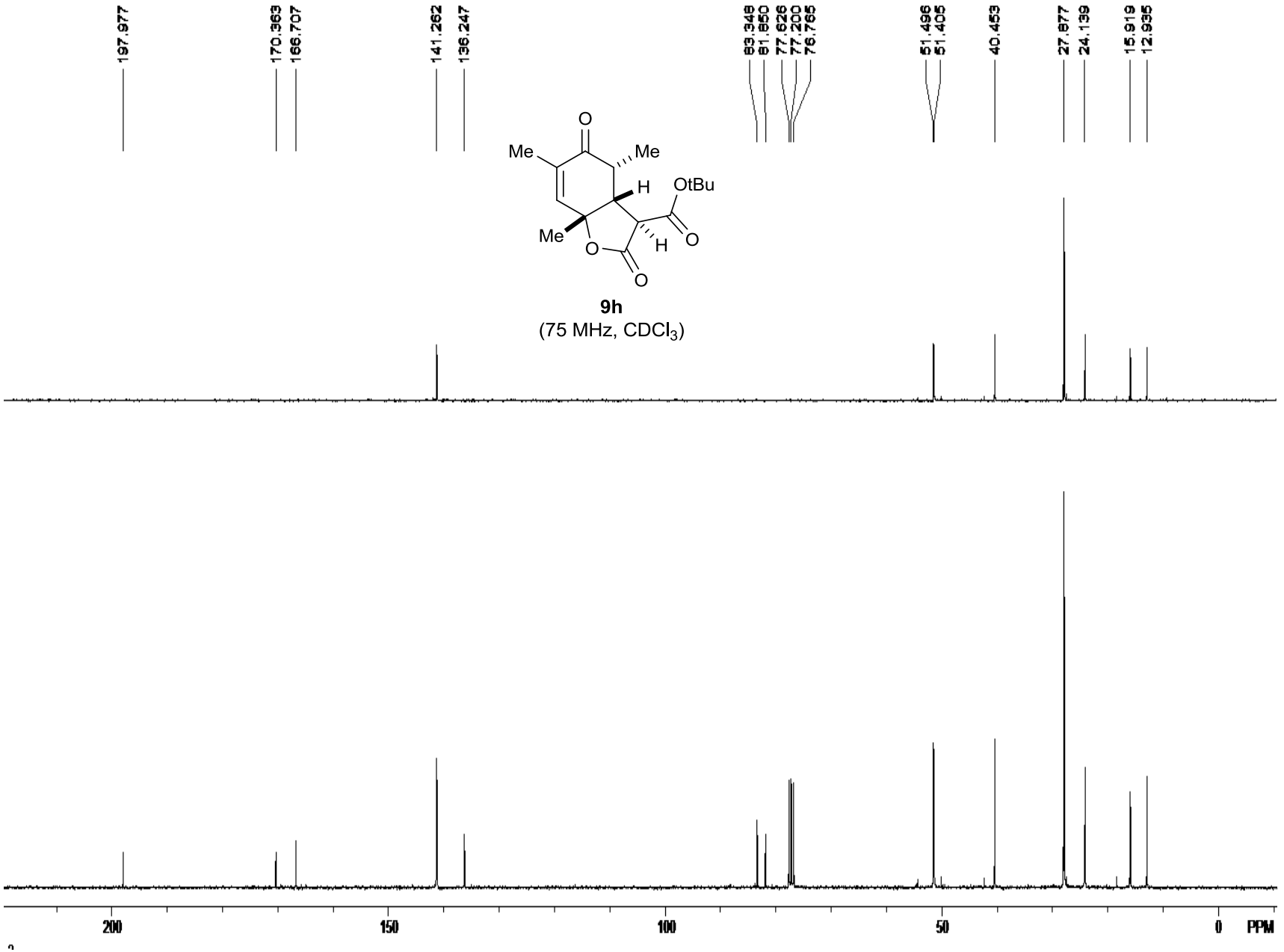


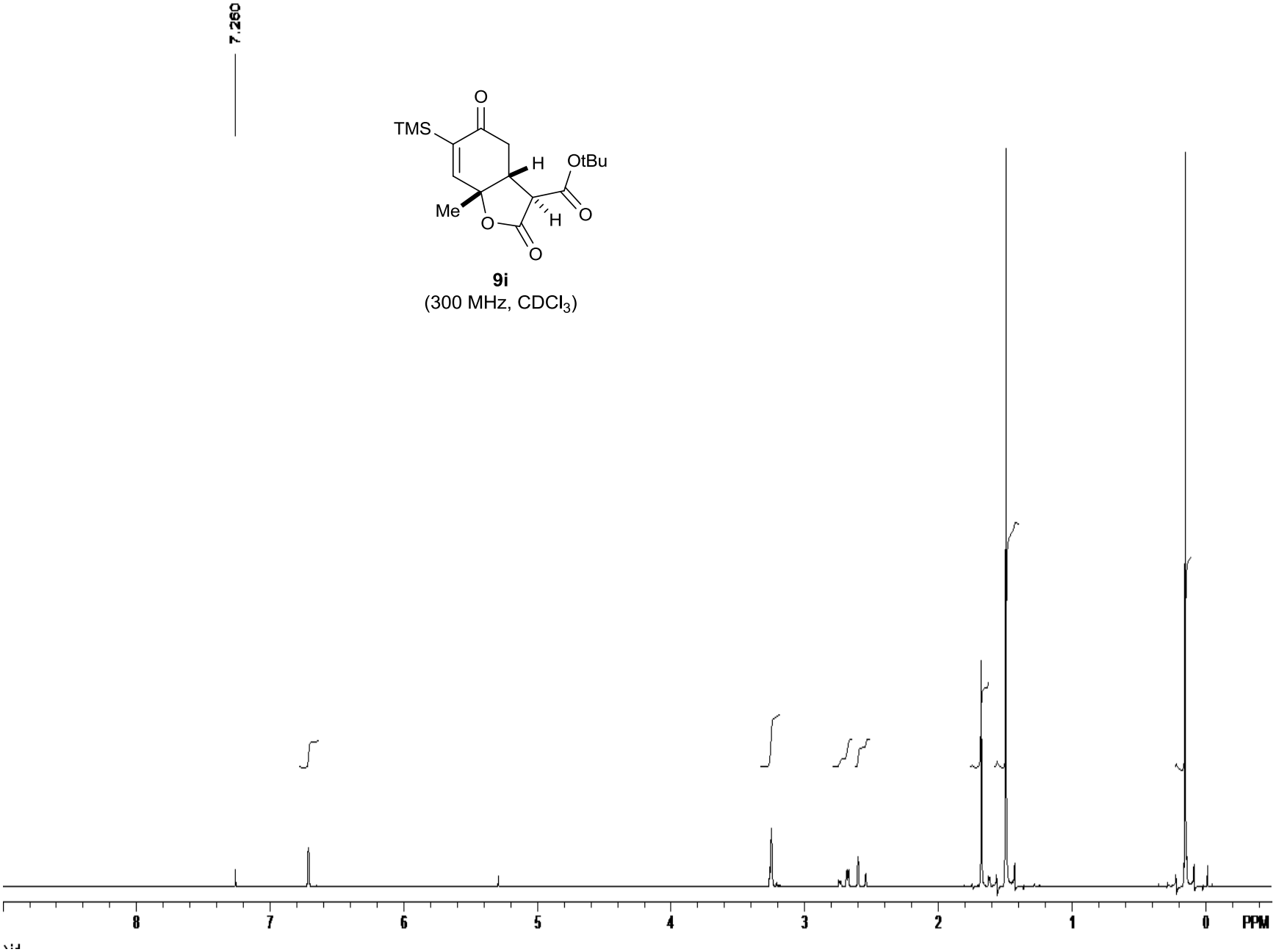
9g
(300 MHz, $CDCl_3$)



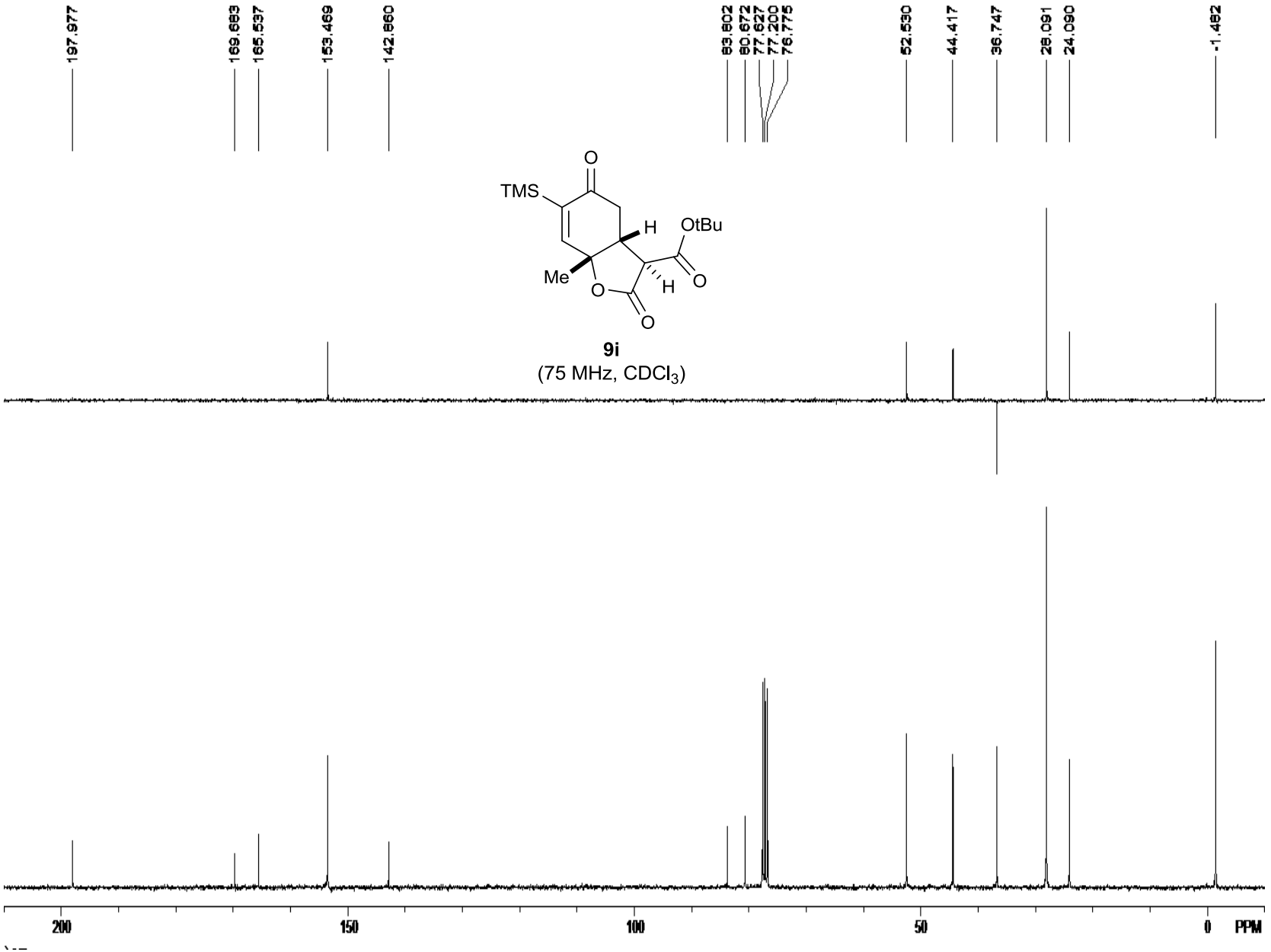


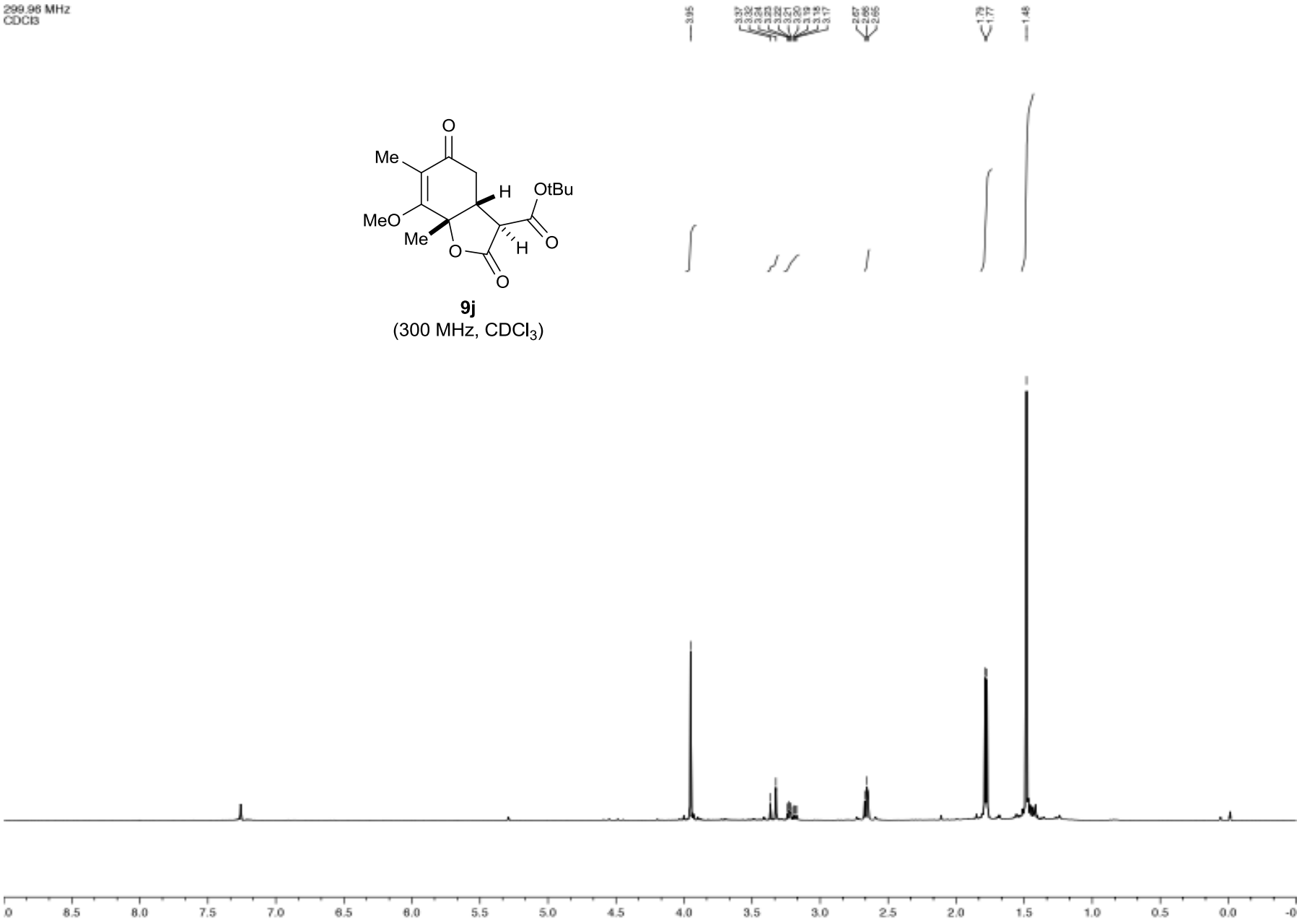
9h
(300 MHz, $CDCl_3$)



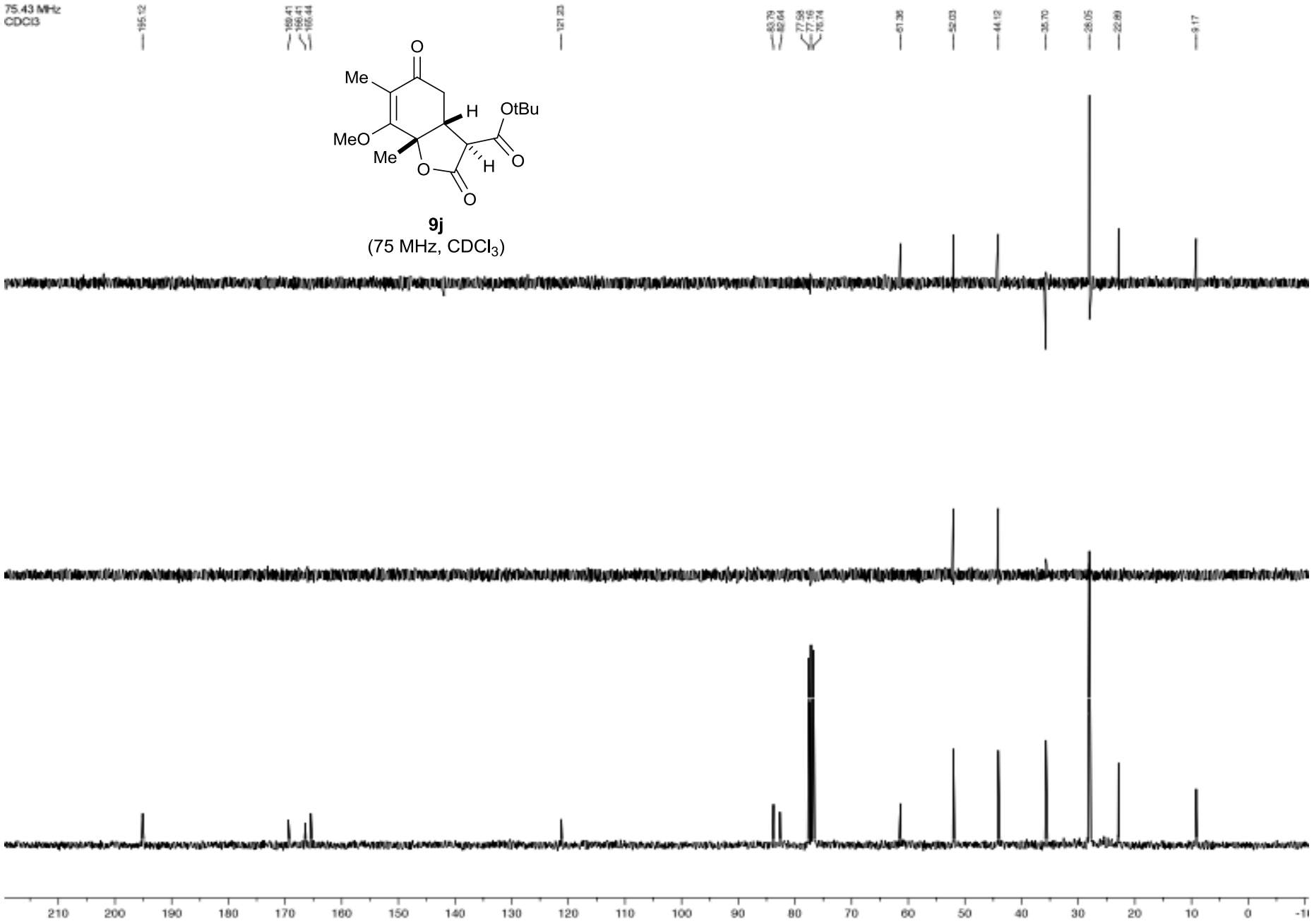


9i
(300 MHz, $CDCl_3$)

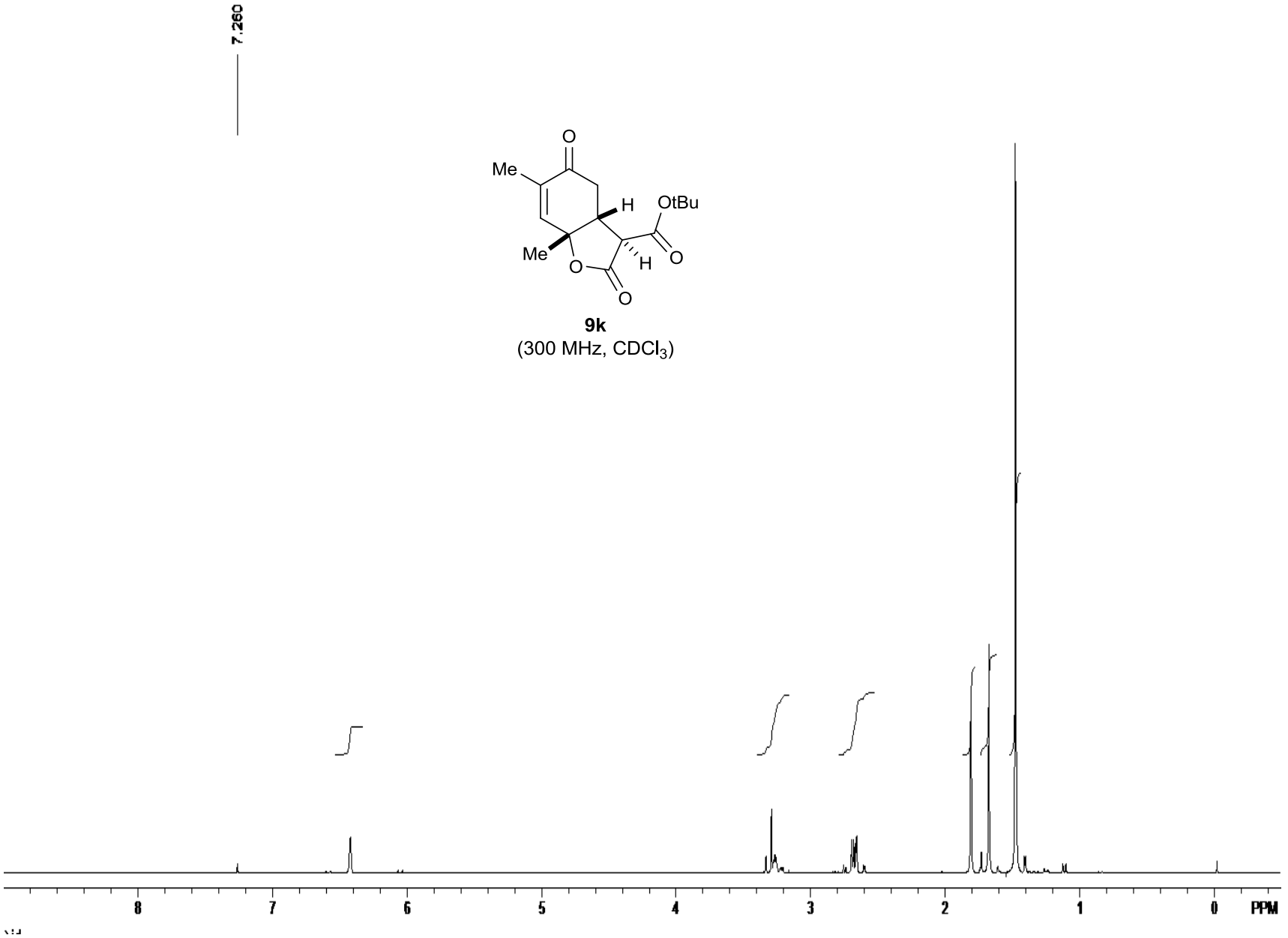




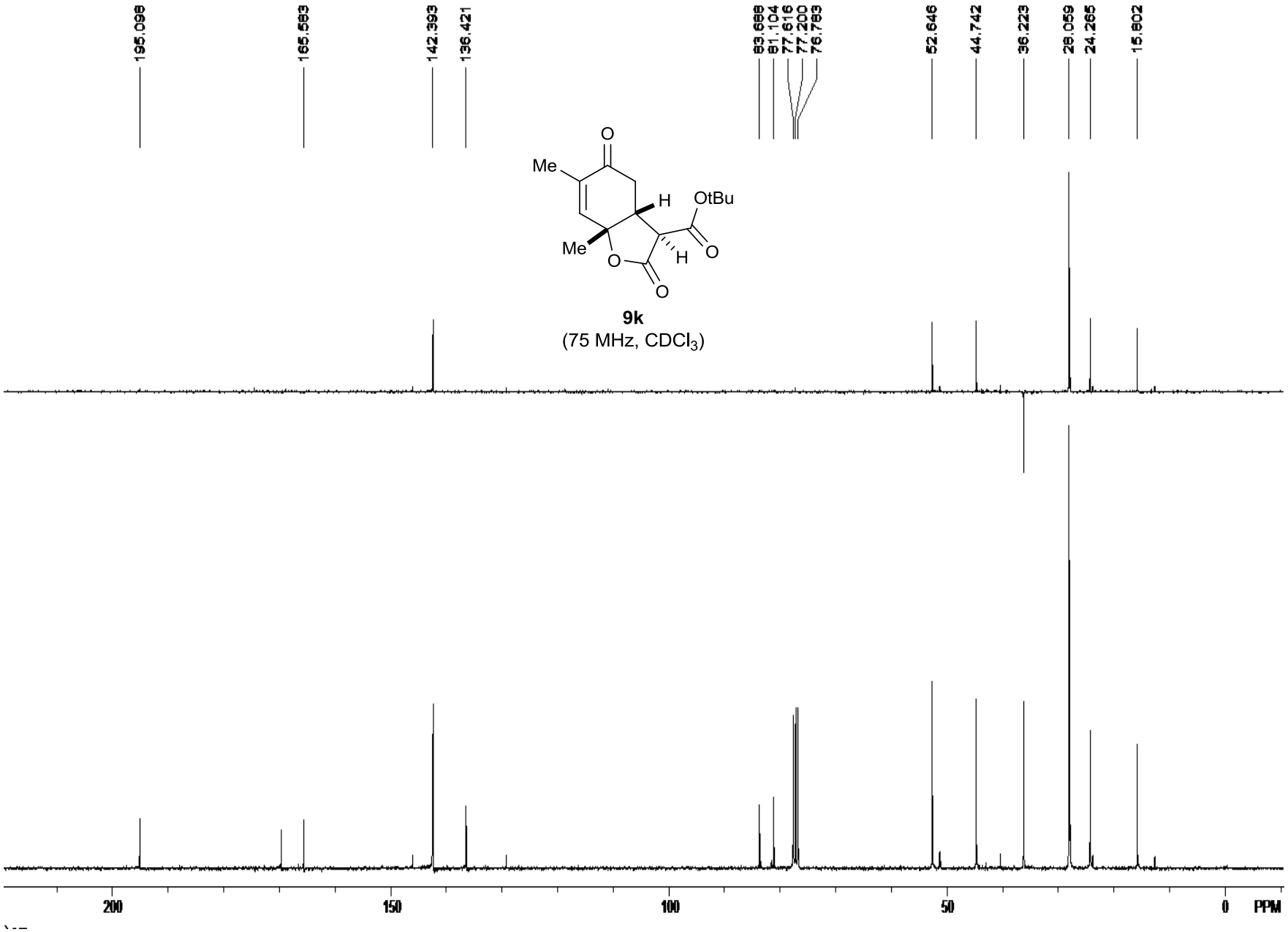
9j
(300 MHz, $CDCl_3$)



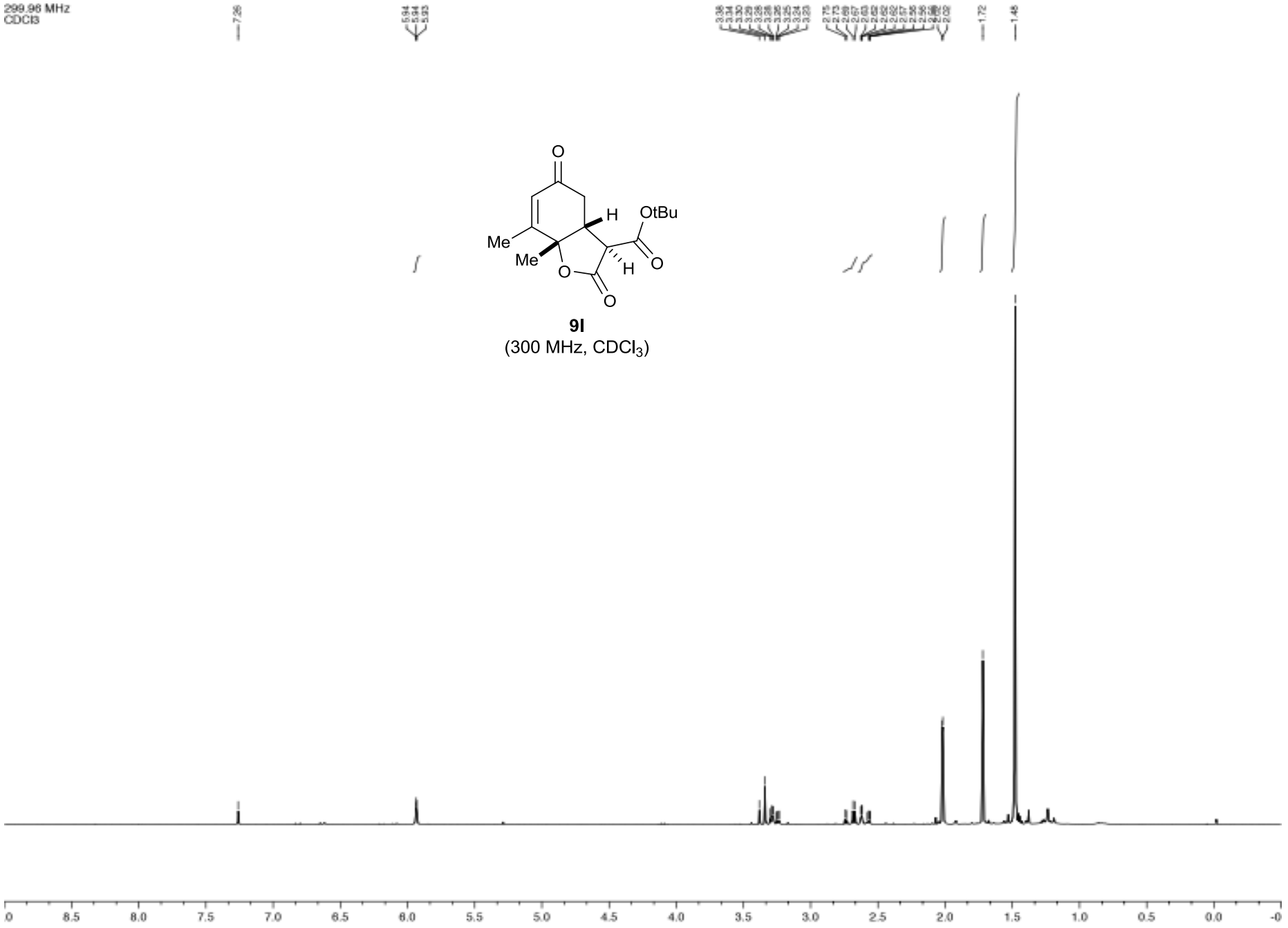
9j
(75 MHz, $CDCl_3$)



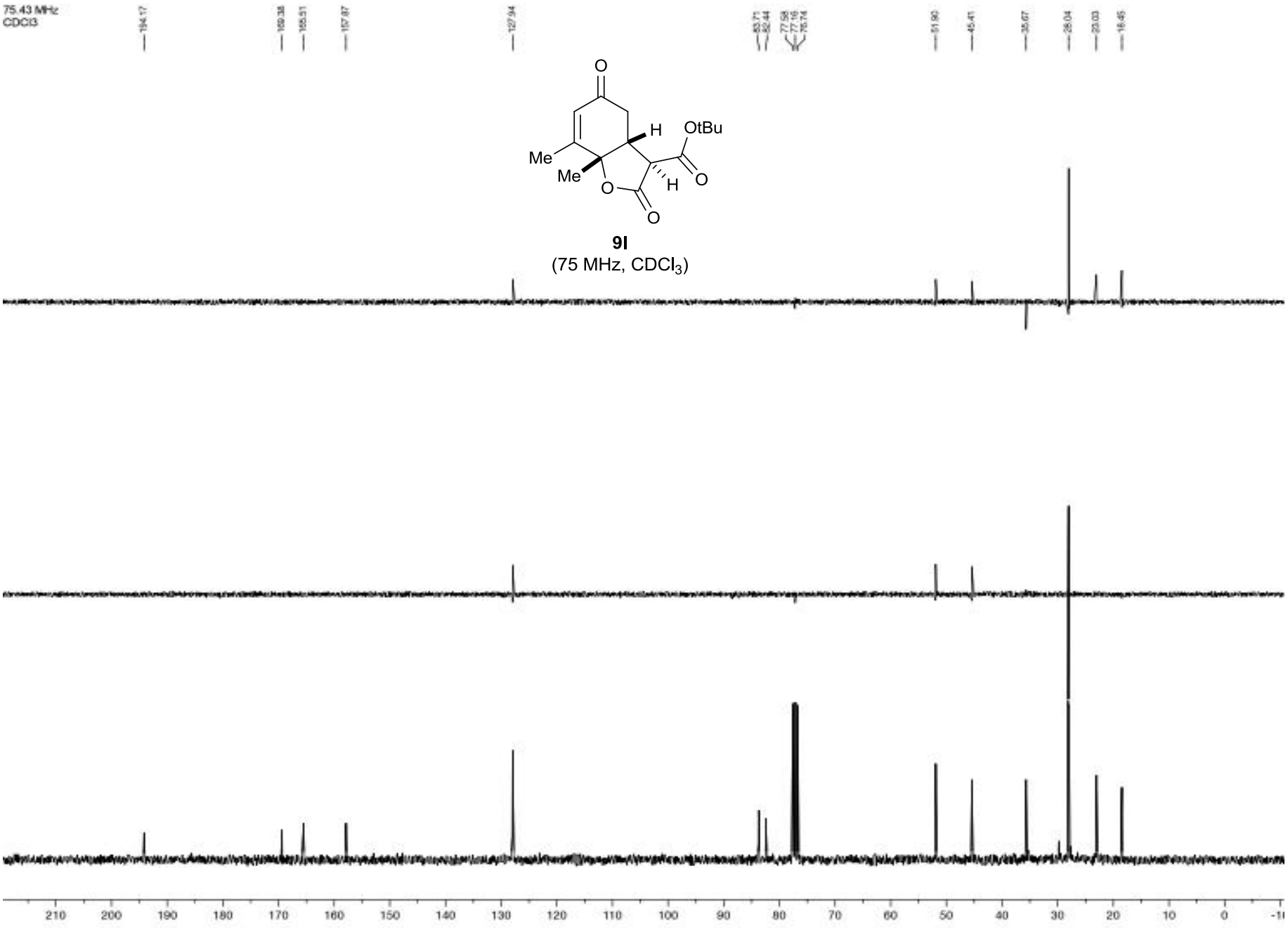
9k
(300 MHz, $CDCl_3$)



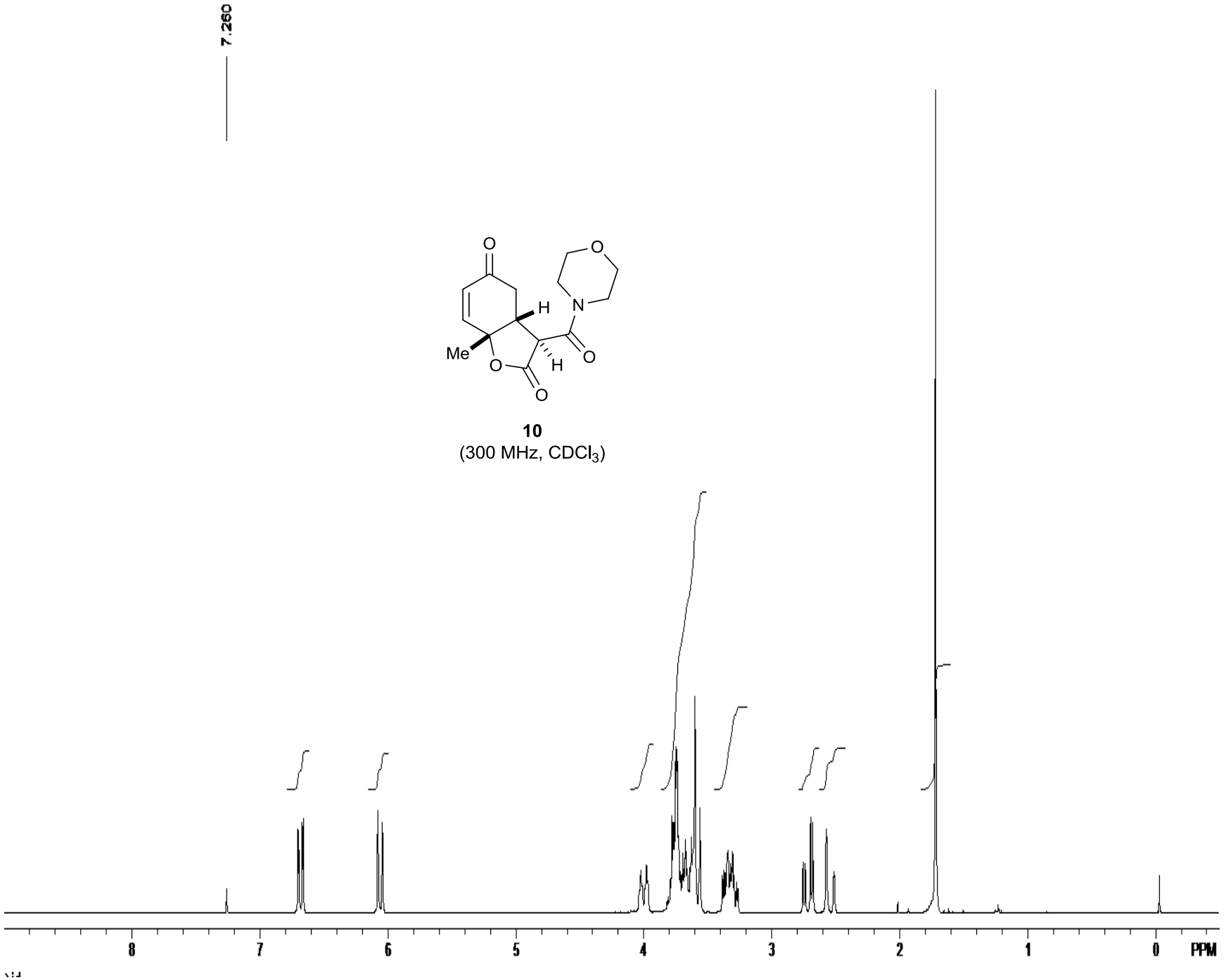
9k
(75 MHz, $CDCl_3$)



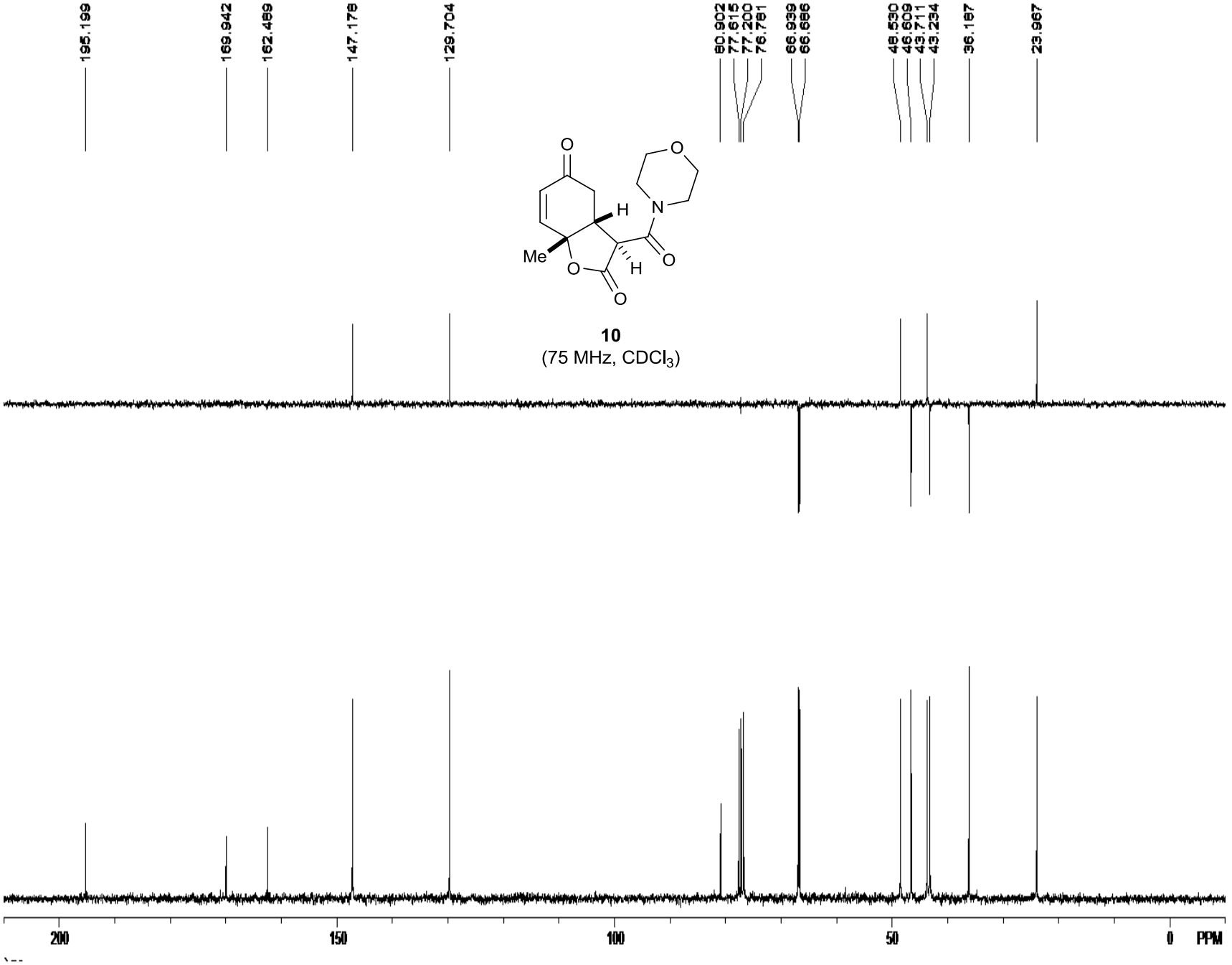
9l
(300 MHz, $CDCl_3$)



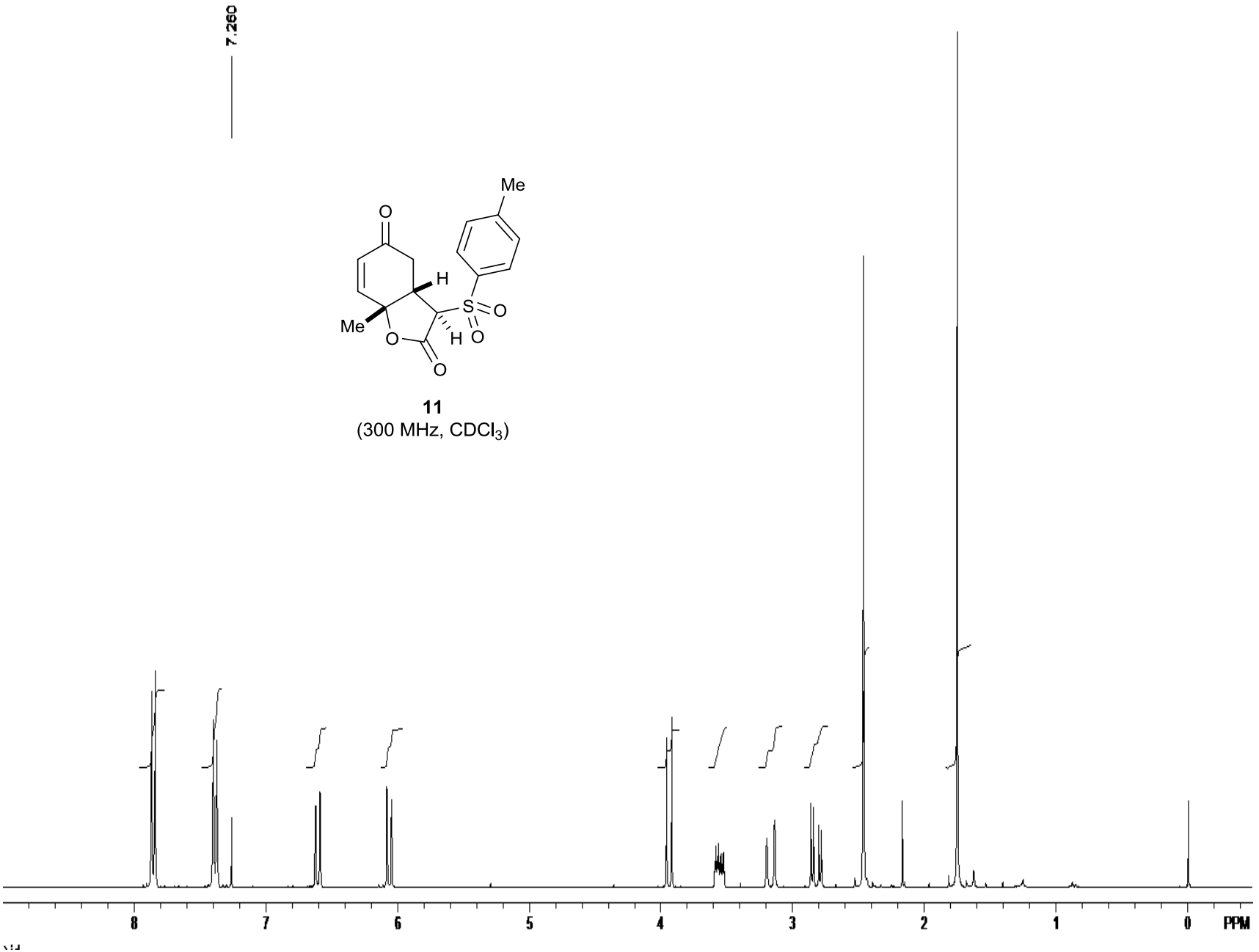
9l
(75 MHz, $CDCl_3$)



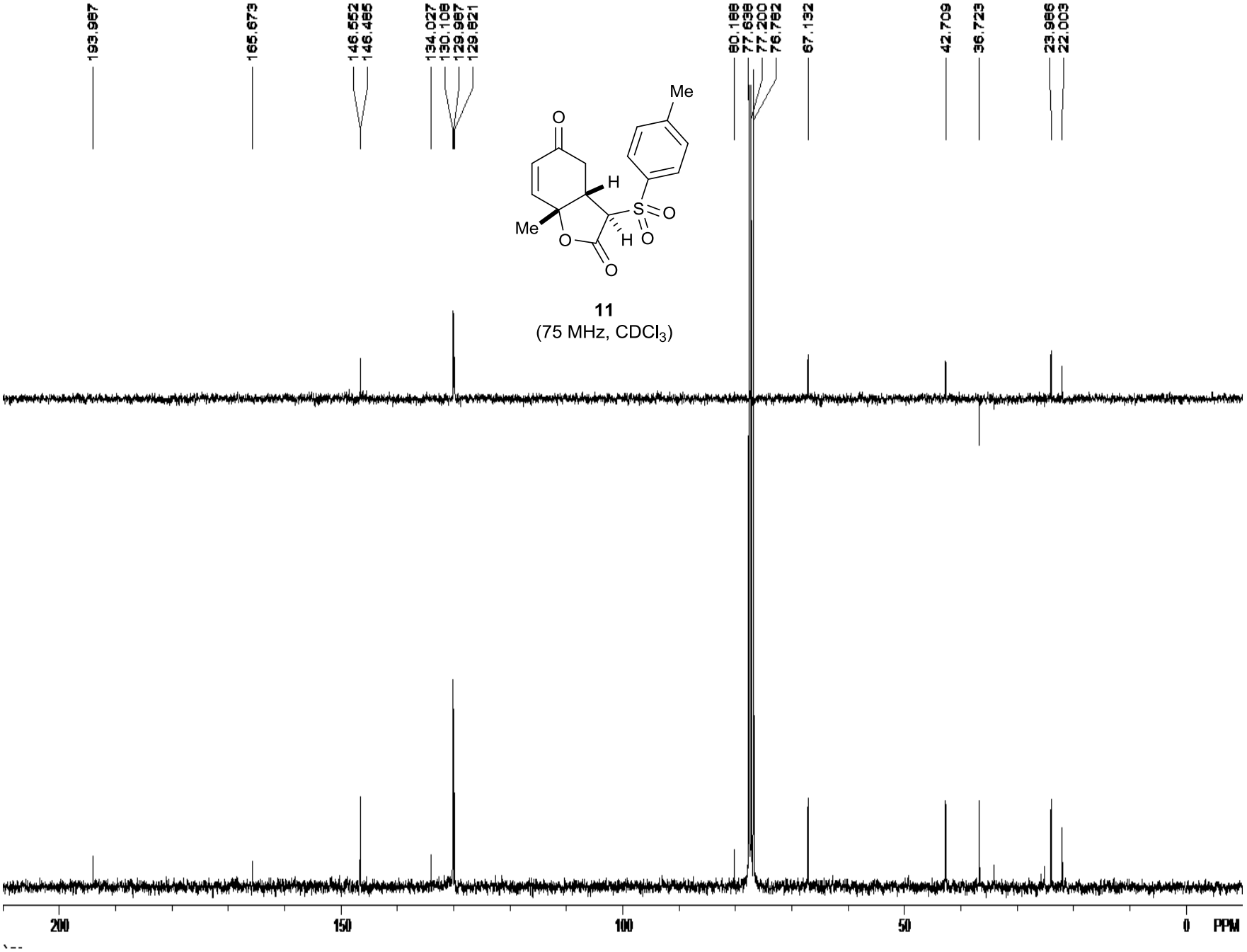
10
(300 MHz, $CDCl_3$)



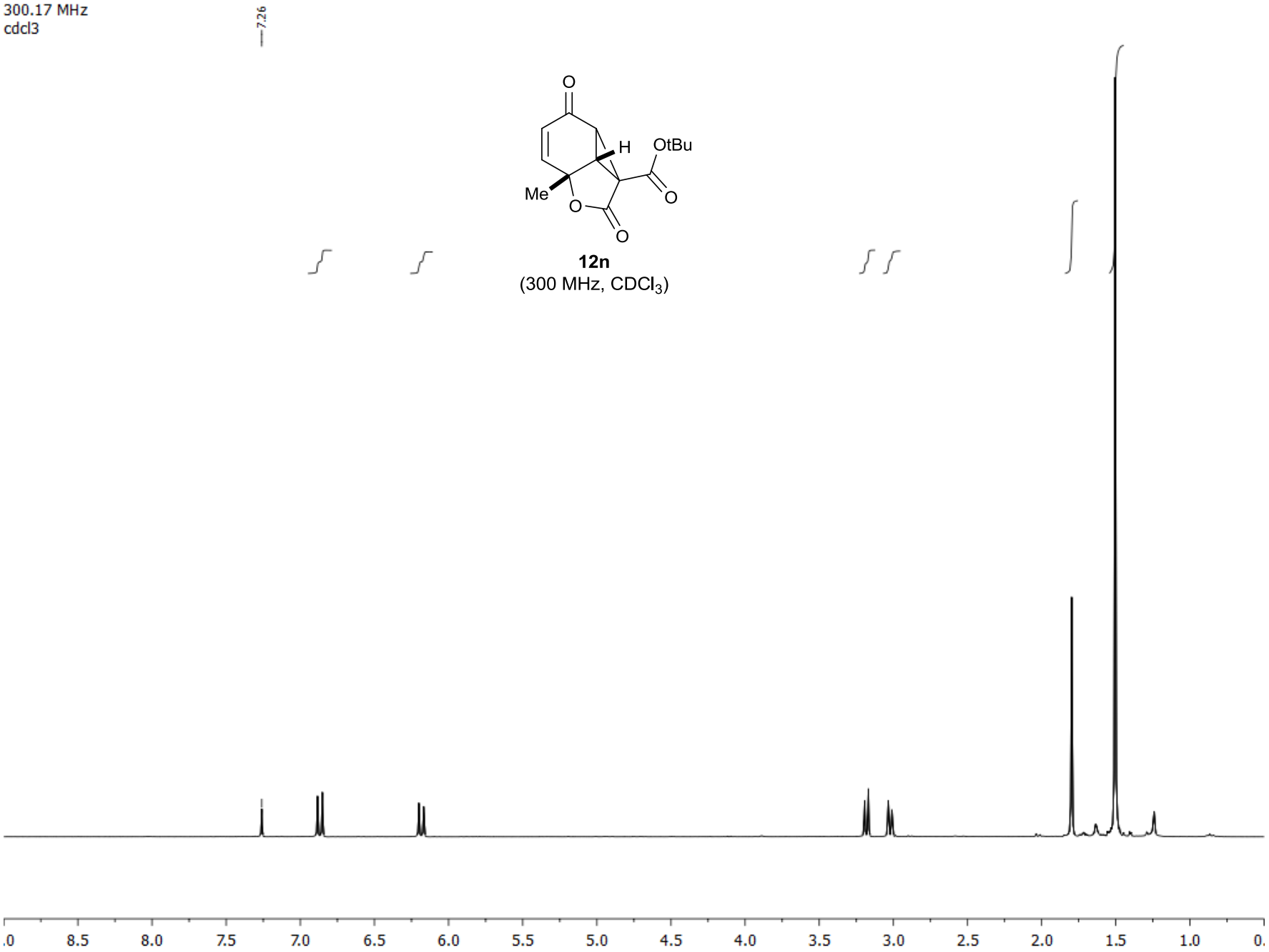
10
(75 MHz, $CDCl_3$)

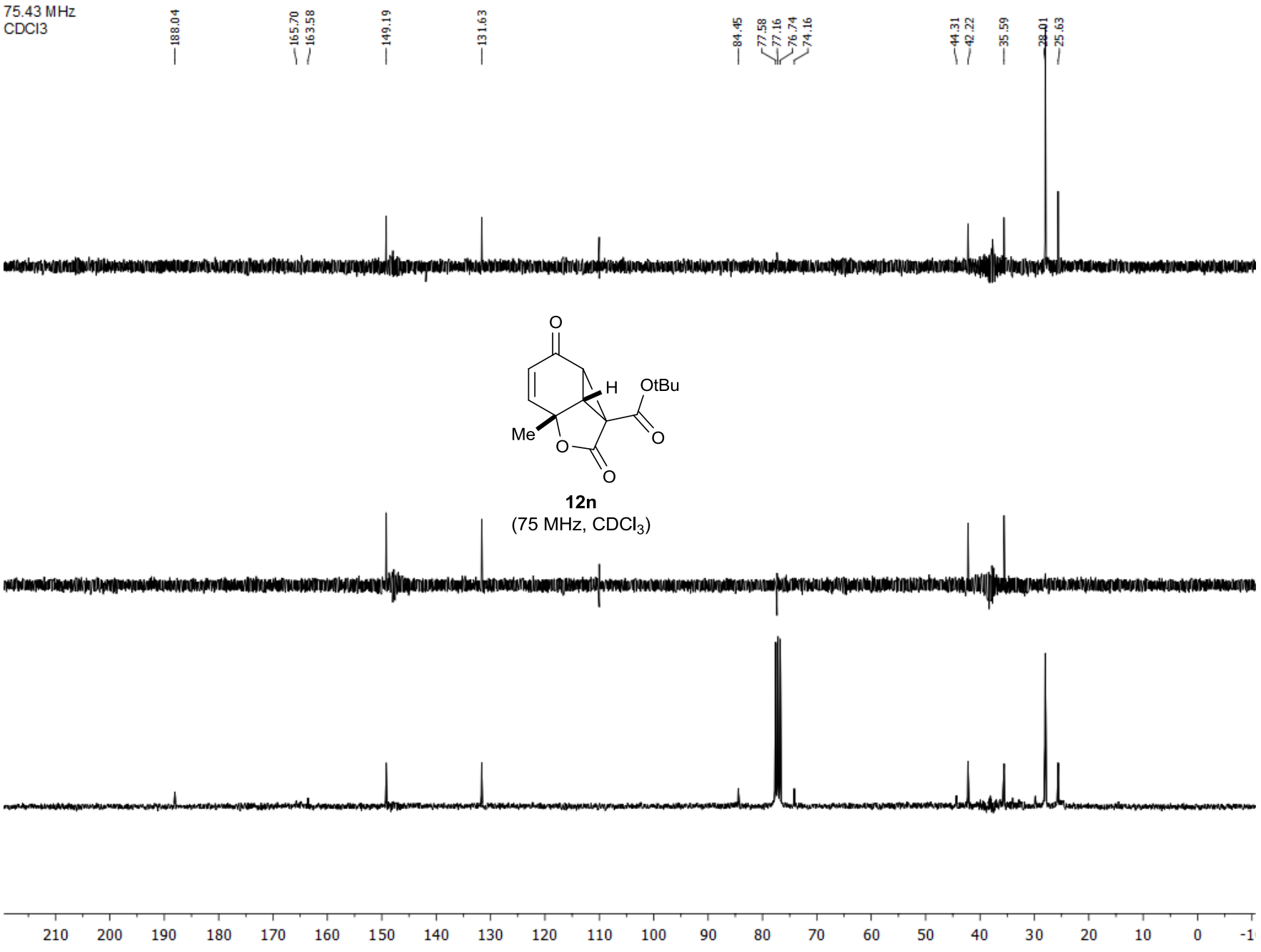


11
(300 MHz, $CDCl_3$)

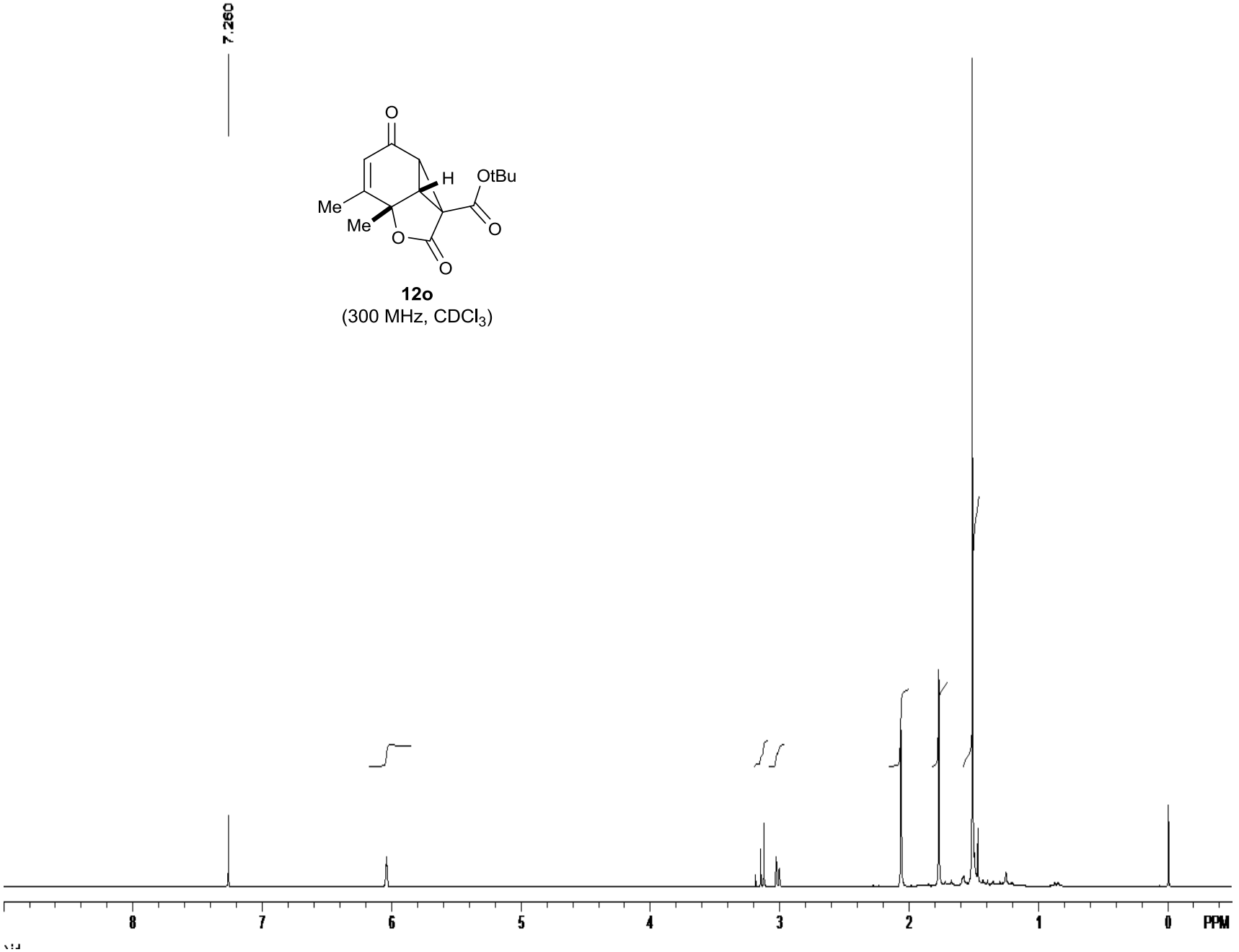


11
(75 MHz, $CDCl_3$)

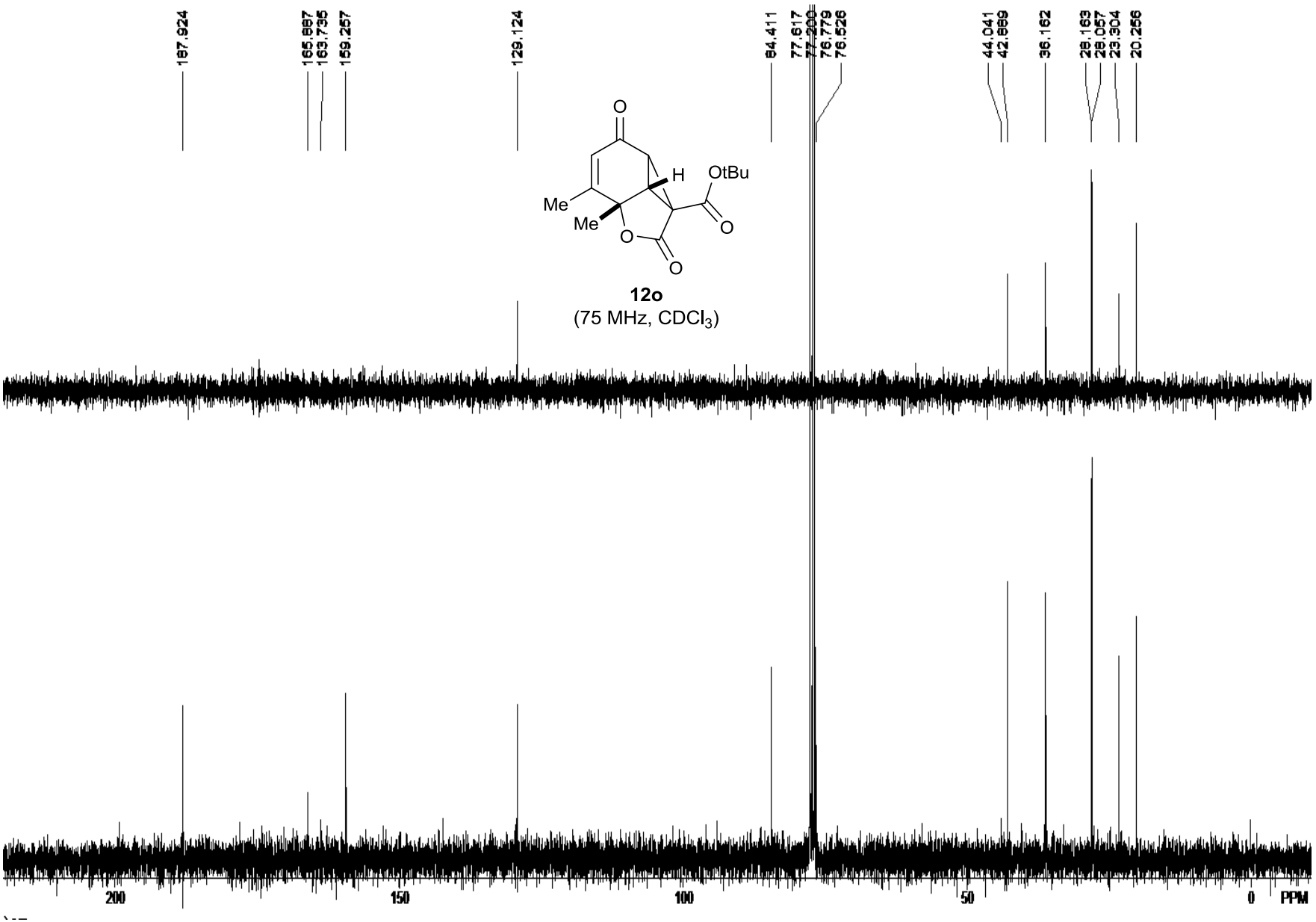

300.17 MHz
cdcl3
7.26
O
H
OtBu
Me
O
O
O
12n
(300 MHz, CDCl3)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0



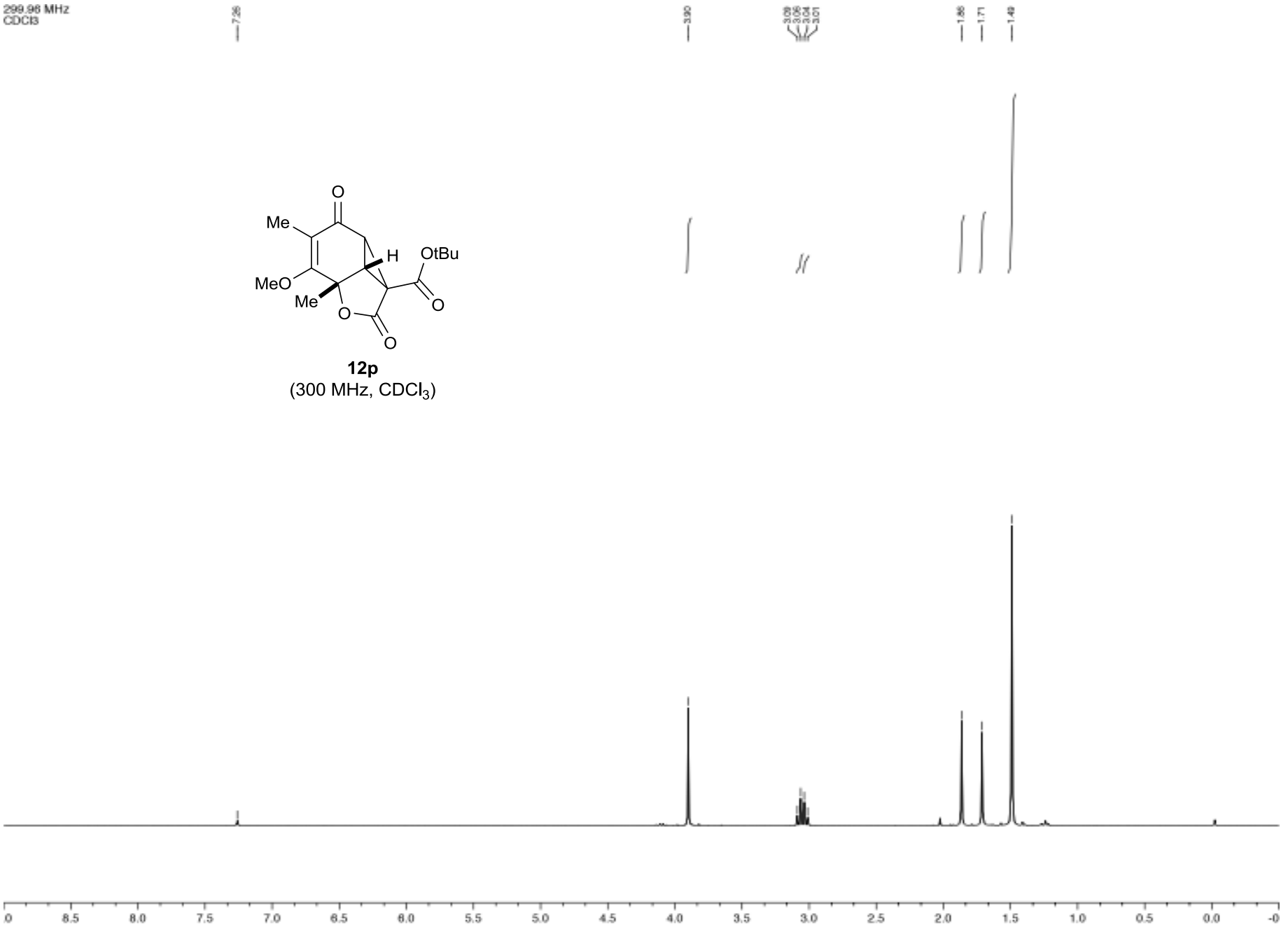
12n
(75 MHz, $CDCl_3$)

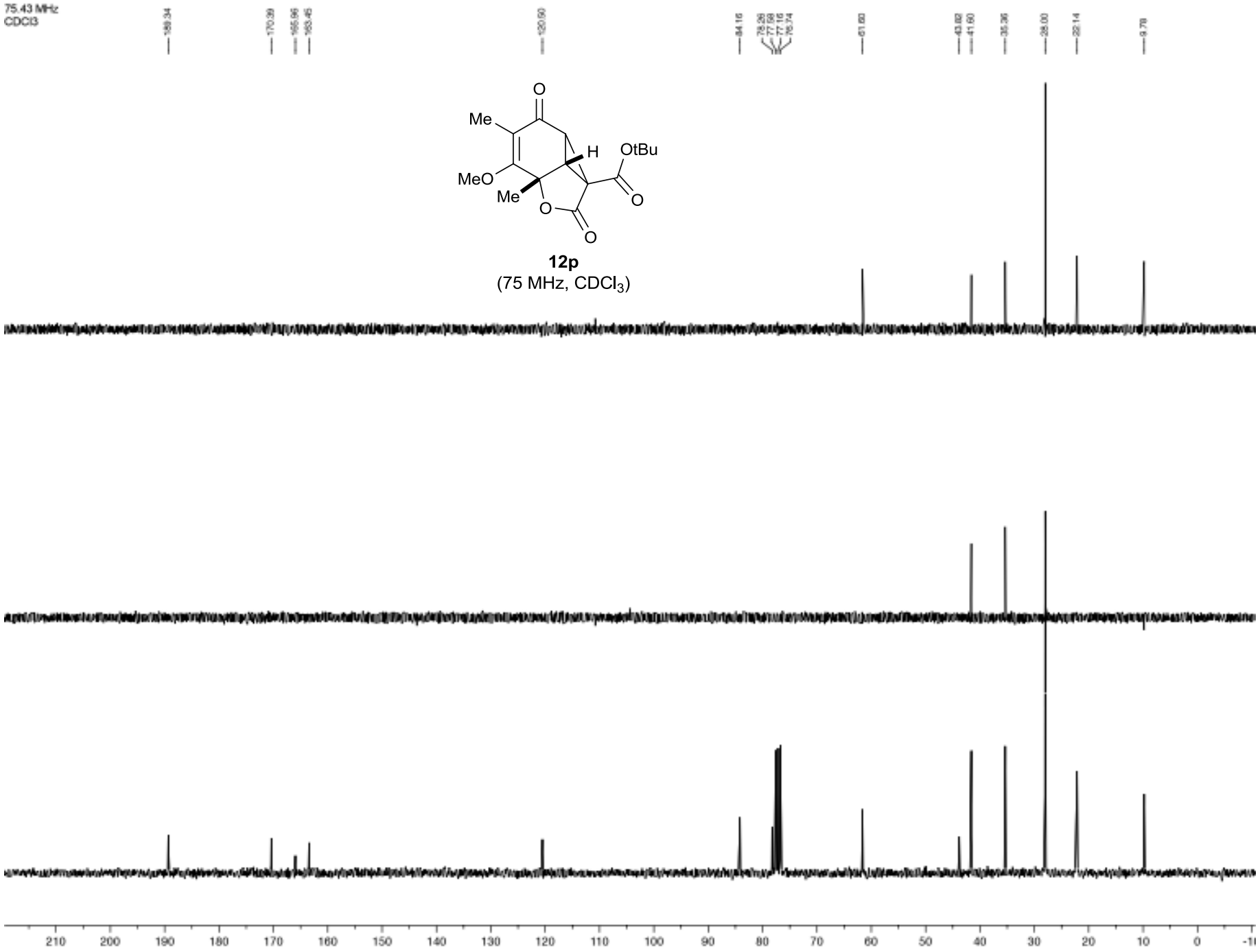


12o
(300 MHz, $CDCl_3$)

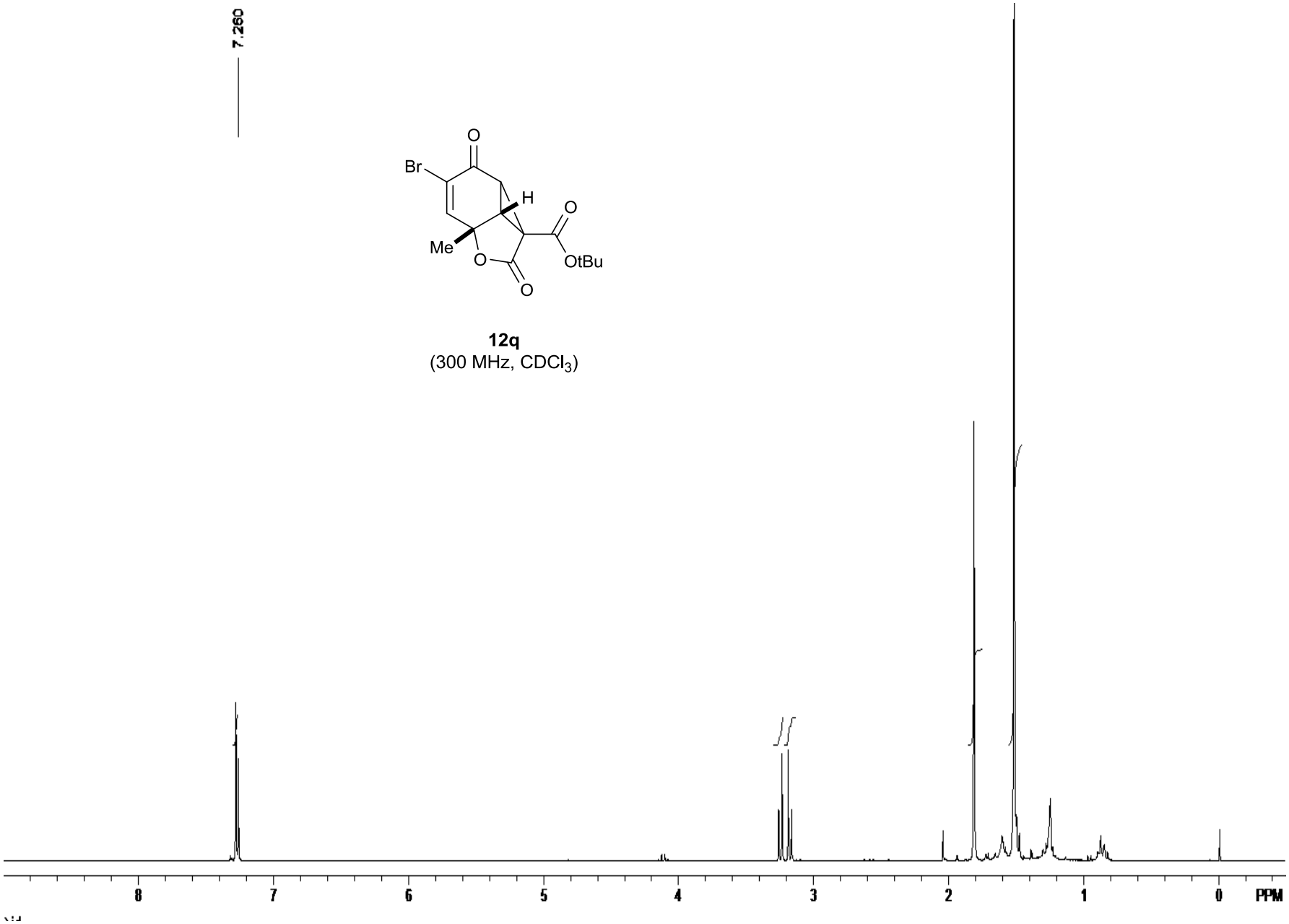


12o
(75 MHz, $CDCl_3$)

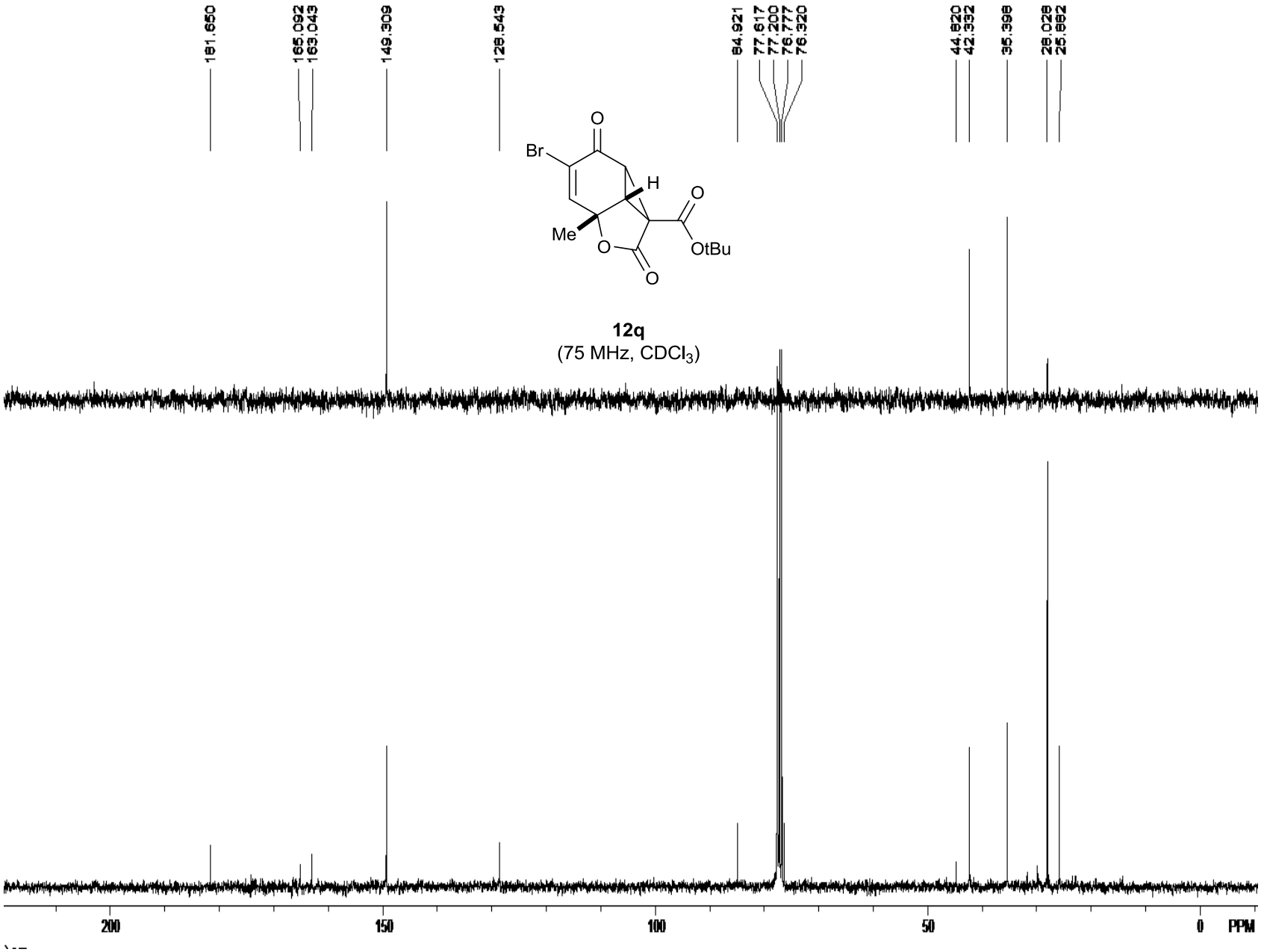


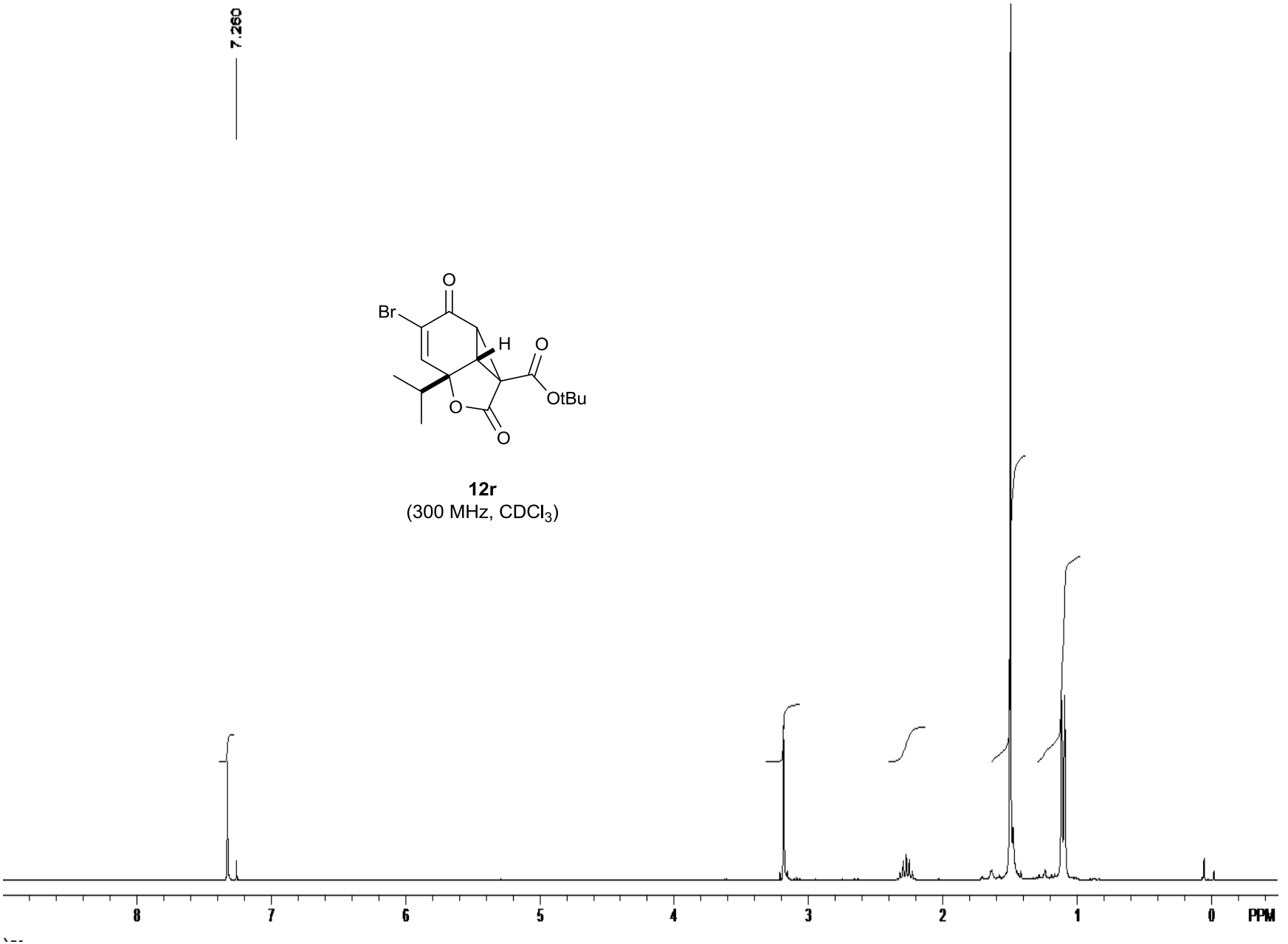


12p
(75 MHz, $CDCl_3$)

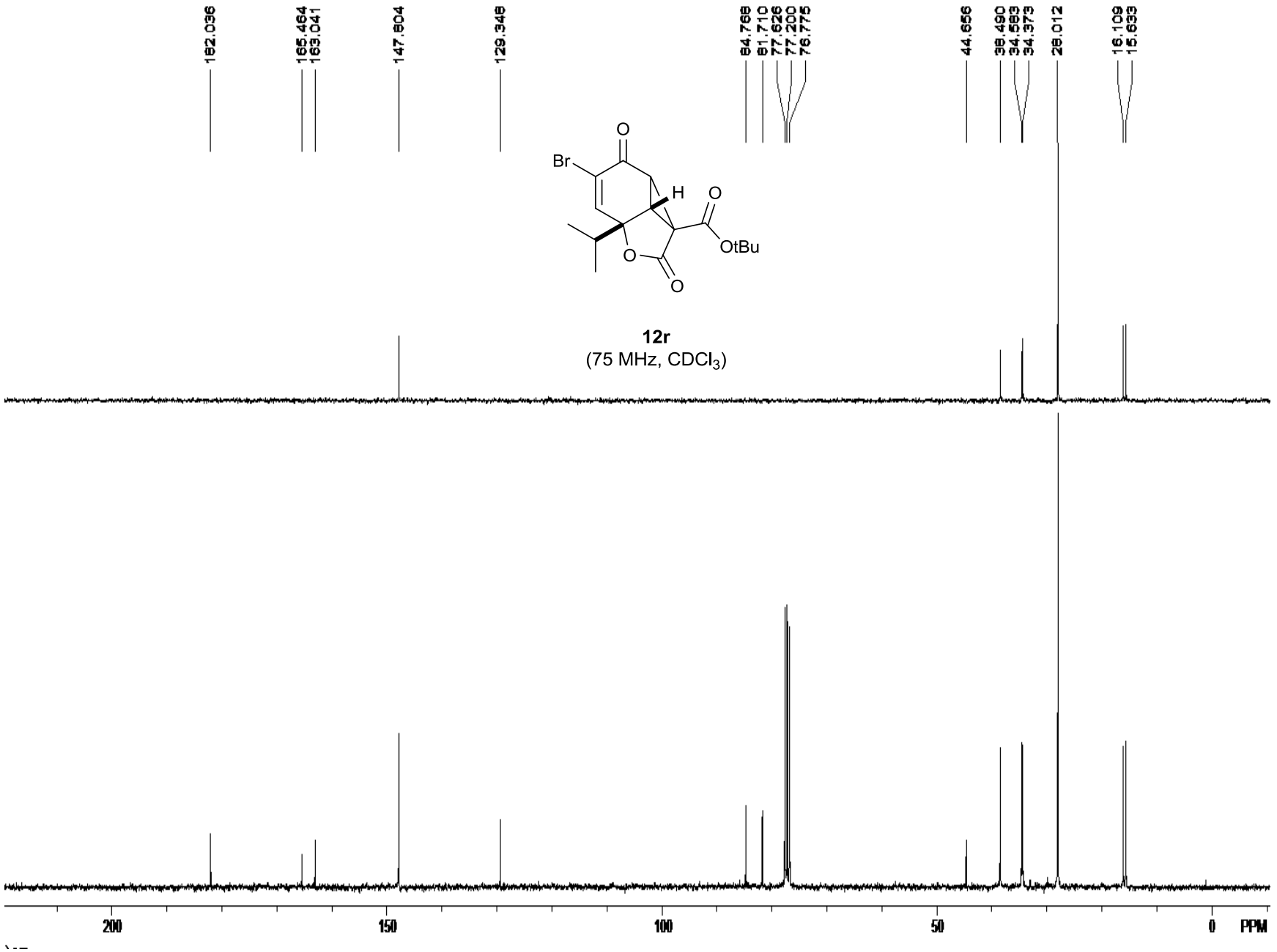


12q
(300 MHz, $CDCl_3$)

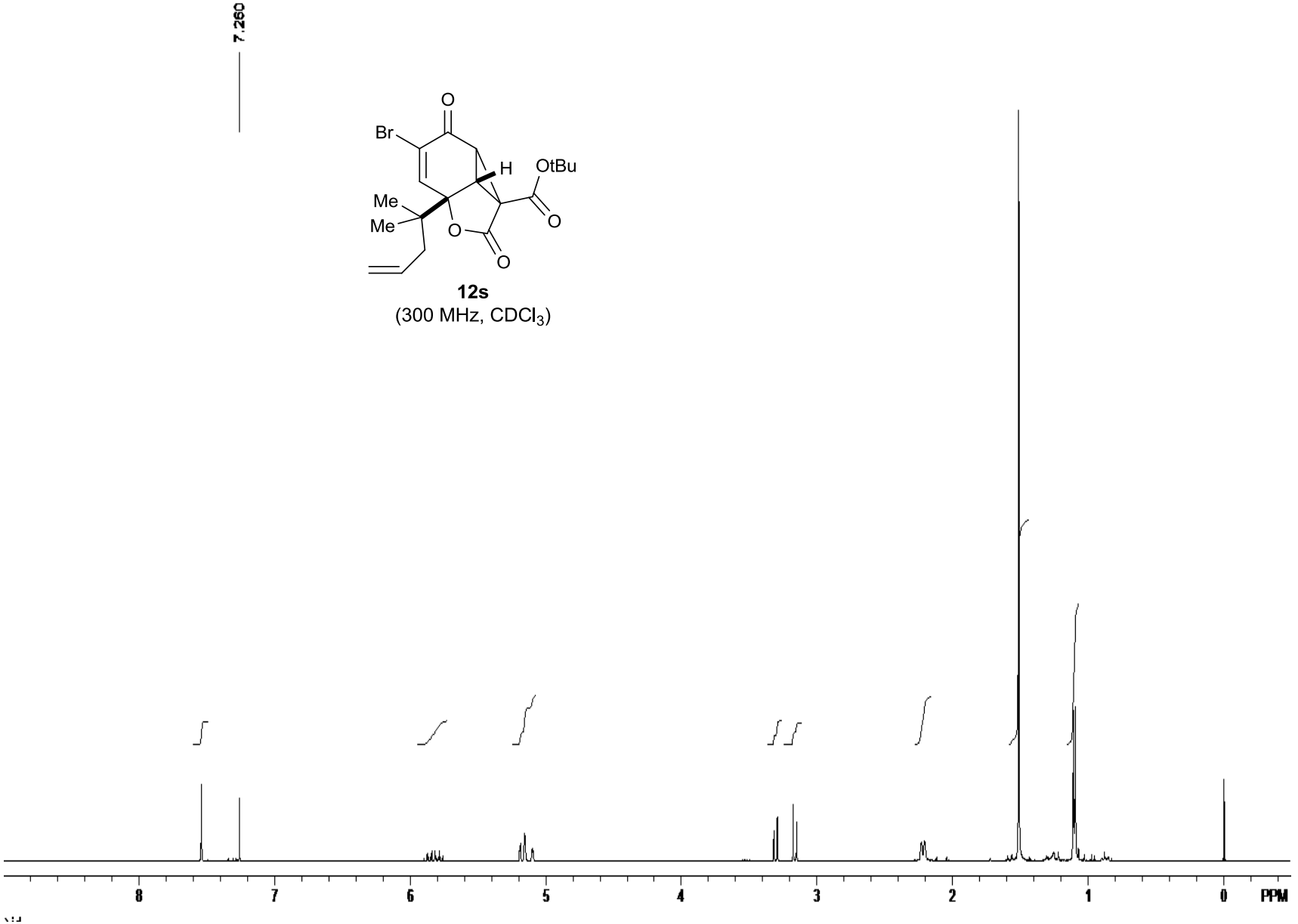




12r
(300 MHz, $CDCl_3$)

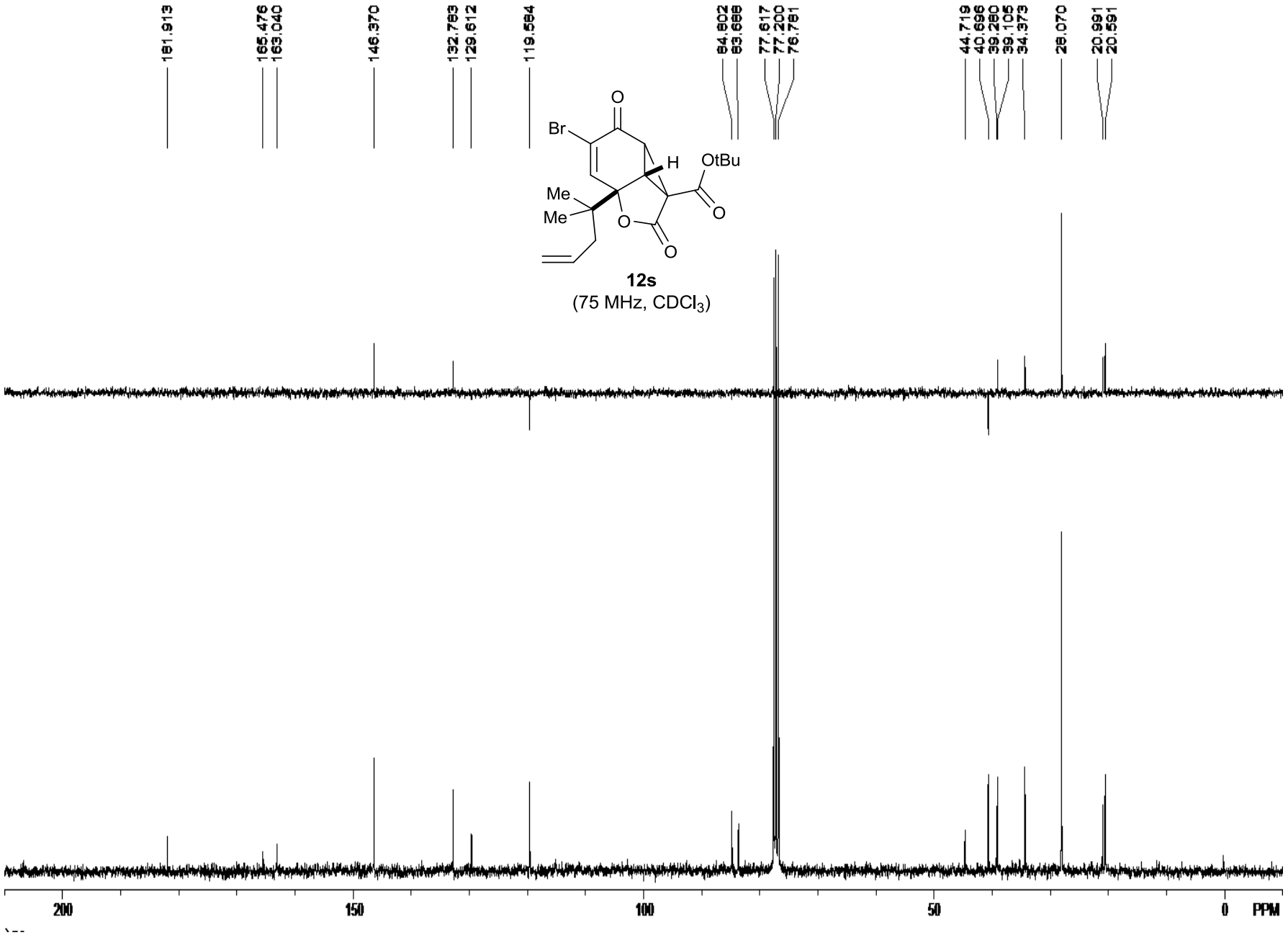


12r
(75 MHz, $CDCl_3$)

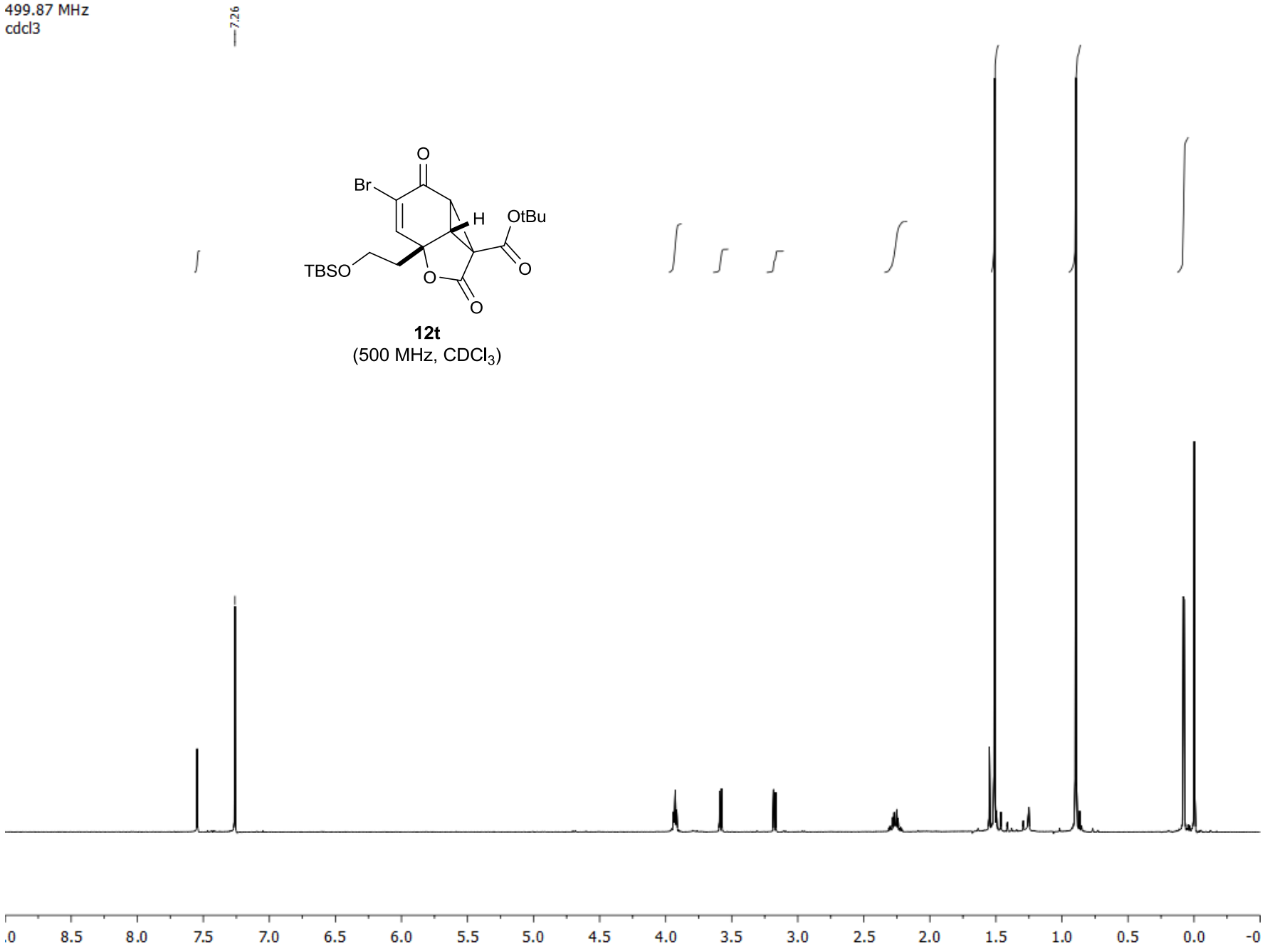


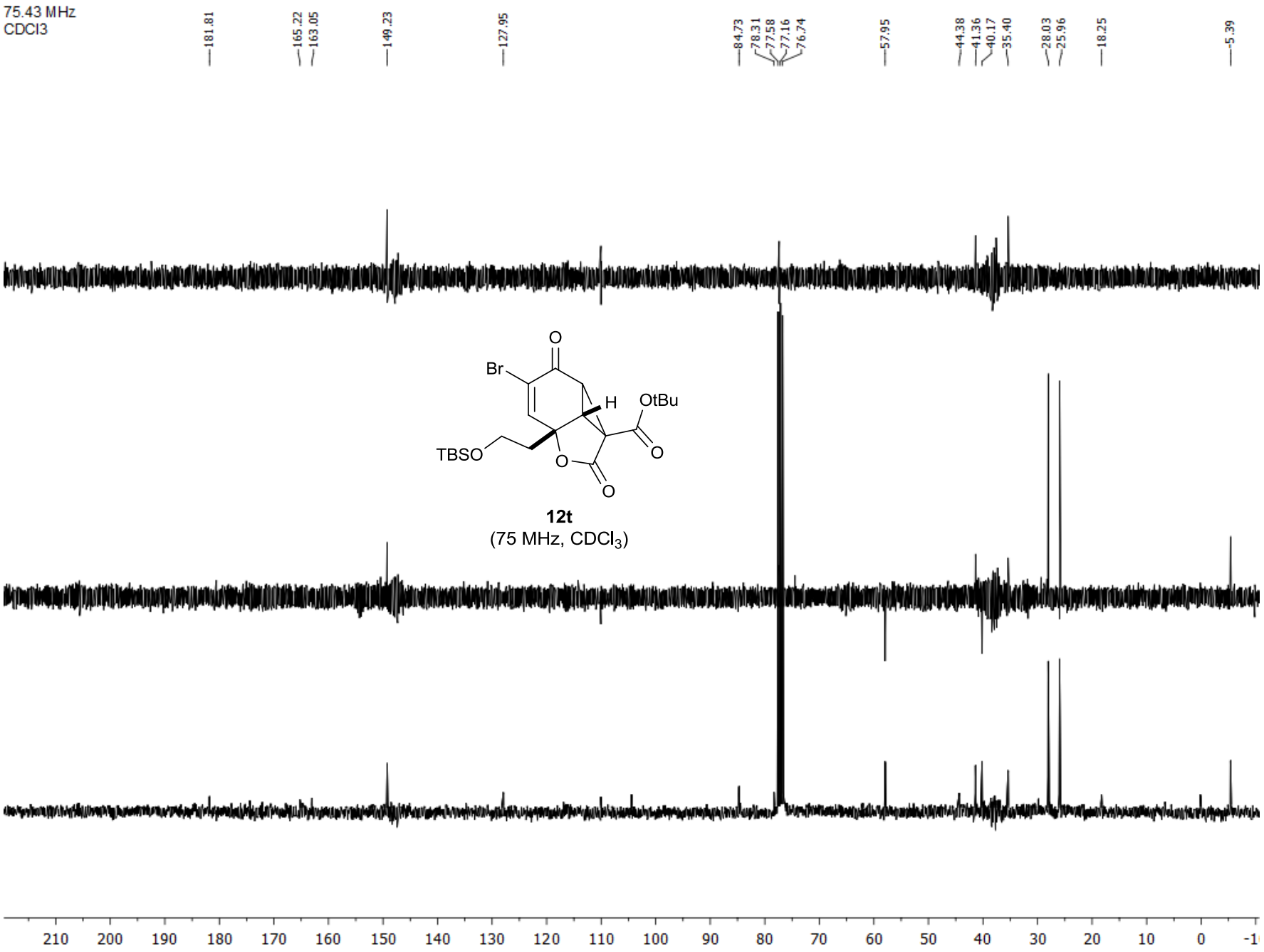
12s

(300 MHz, $CDCl_3$)

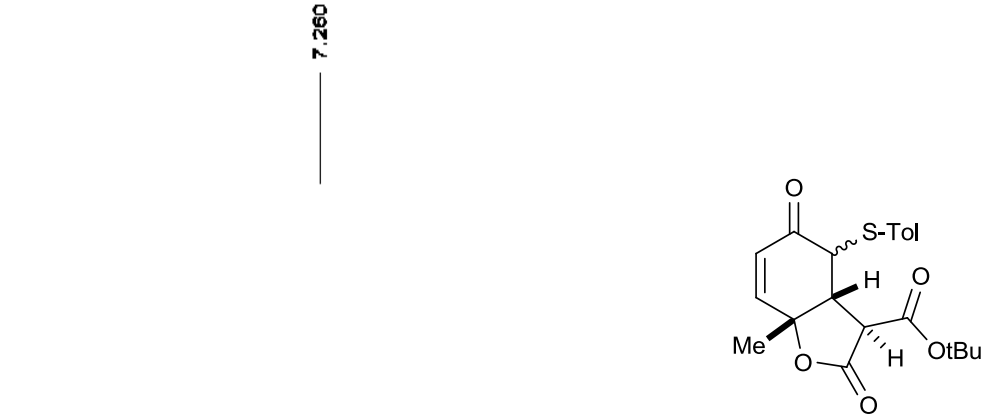


12s
(75 MHz, $CDCl_3$)

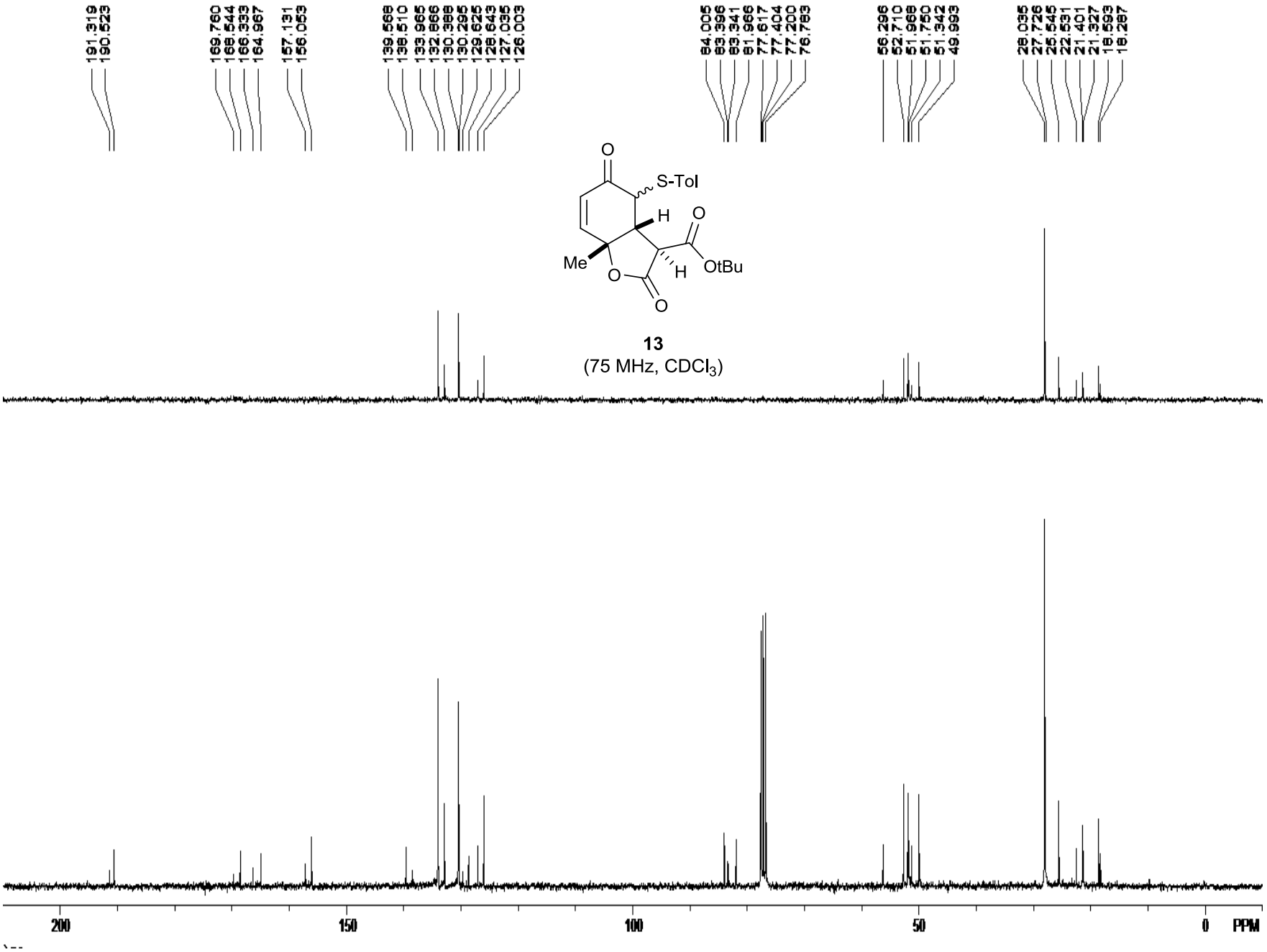




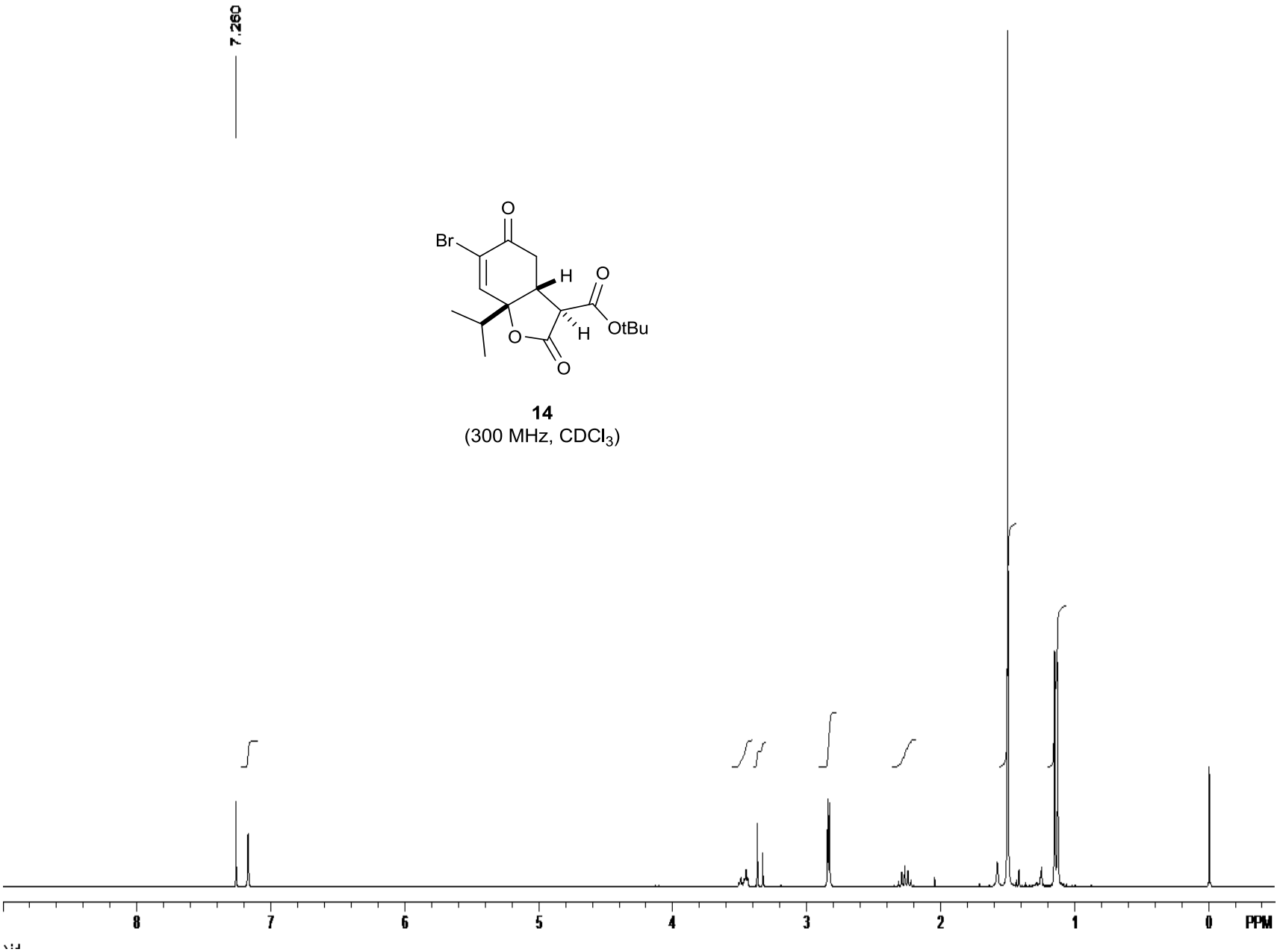
12t
(75 MHz, $CDCl_3$)



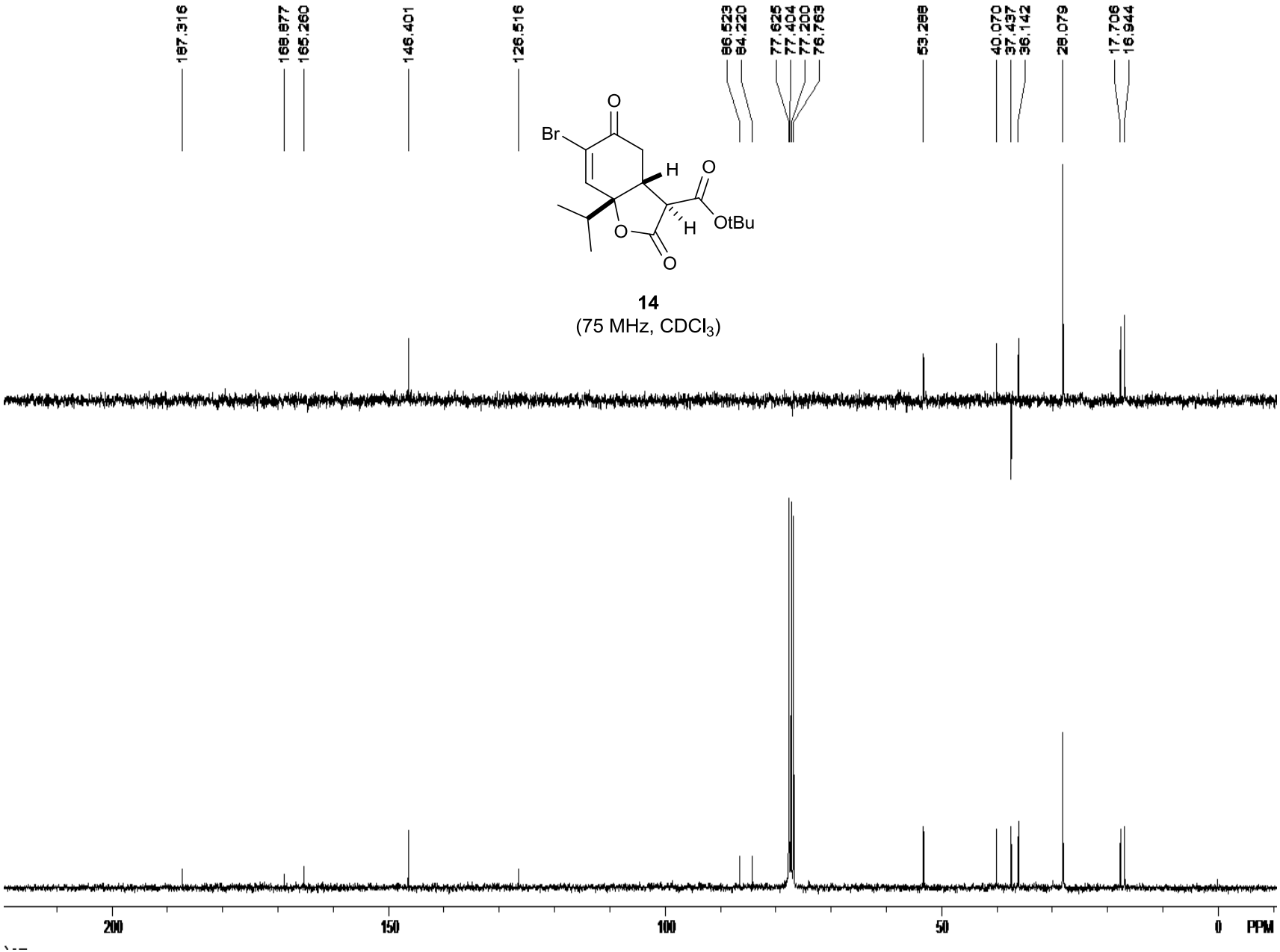
13
(300 MHz, $CDCl_3$)



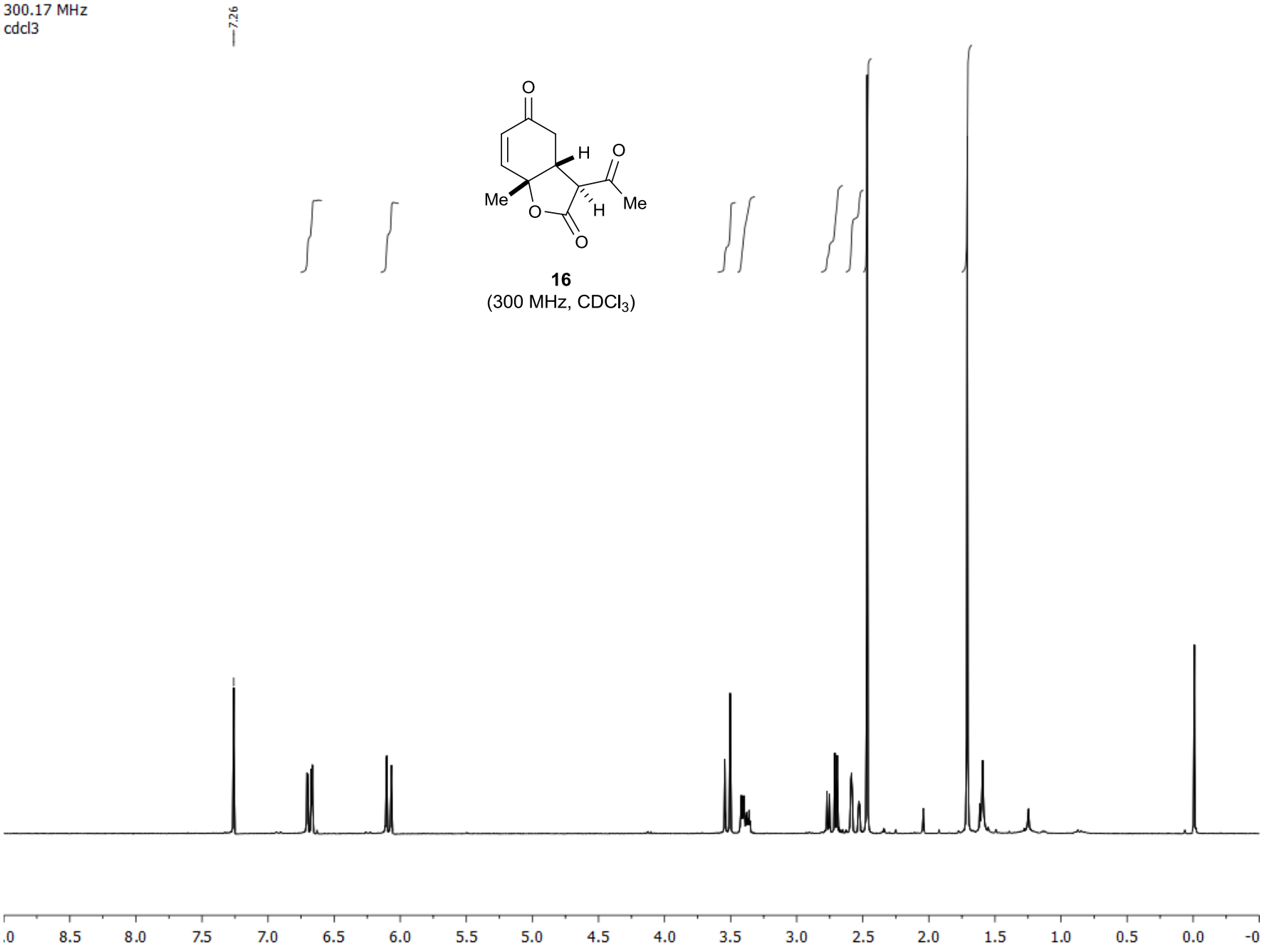
13
(75 MHz, $CDCl_3$)

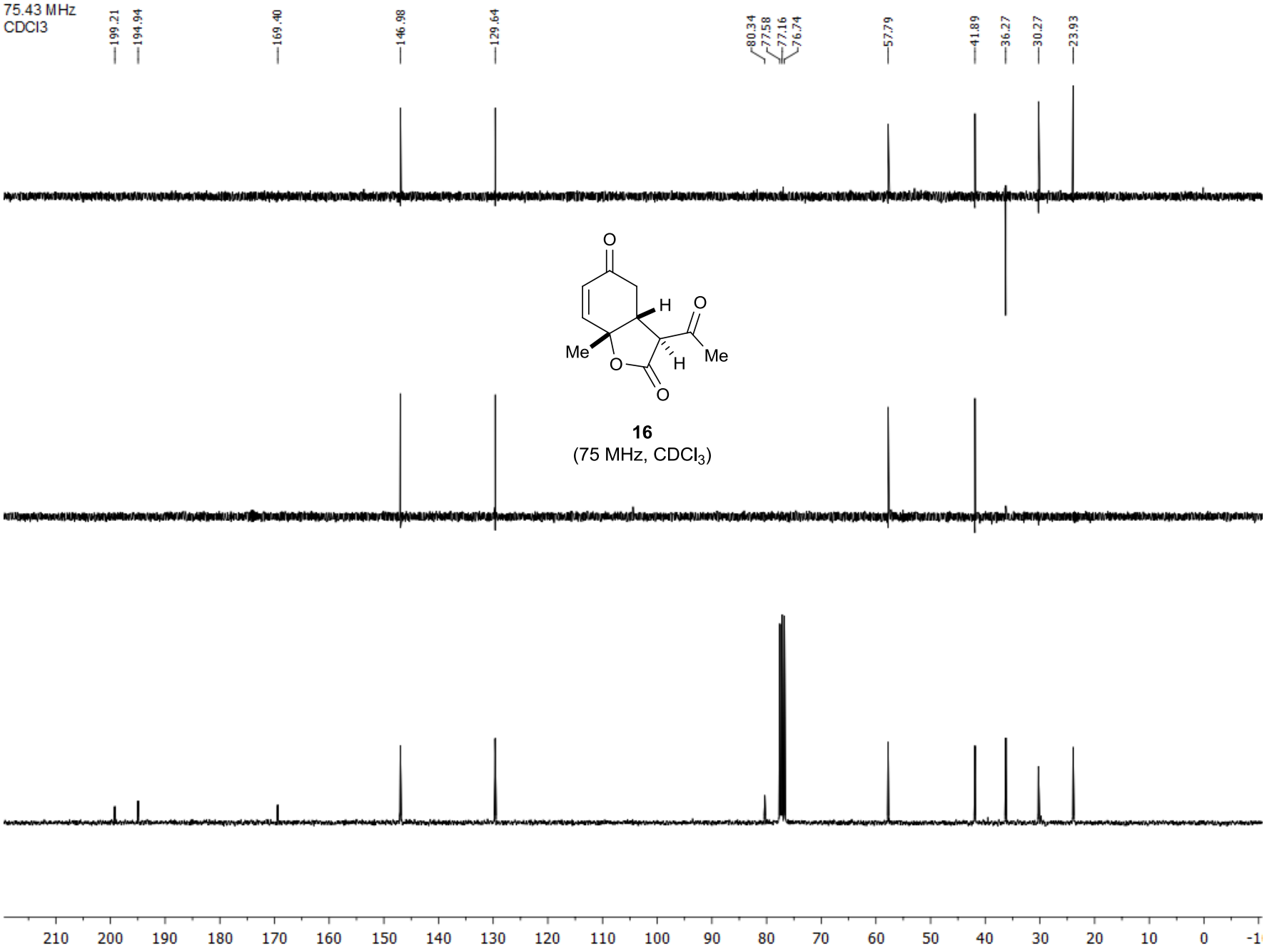


14
(300 MHz, $CDCl_3$)



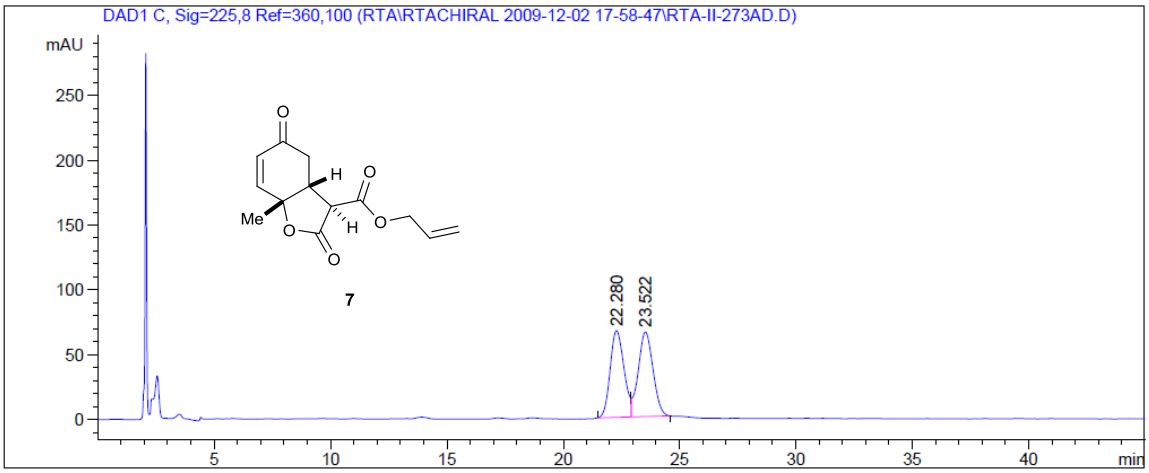
14
(75 MHz, $CDCl_3$)





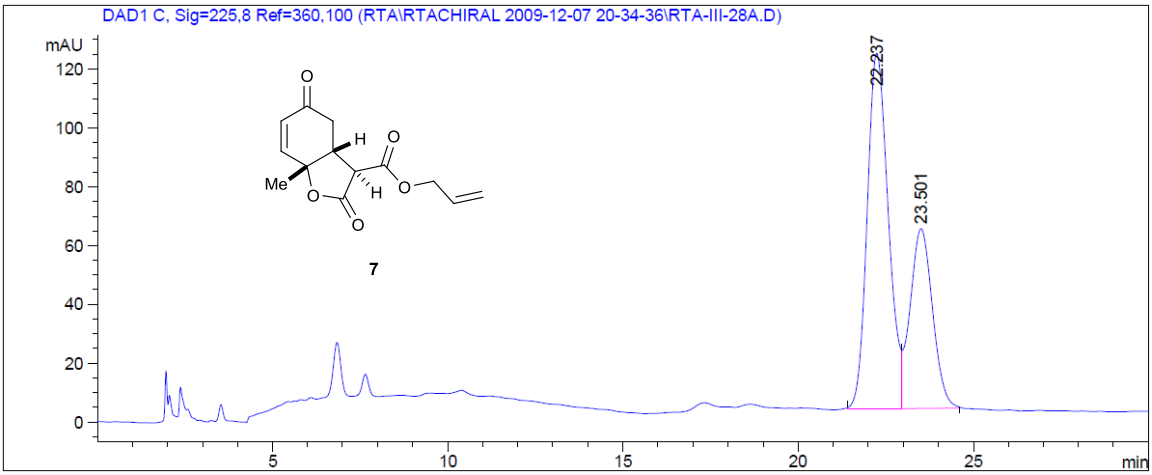
16
(75 MHz, $CDCl_3$)

HPLC Chromatograms



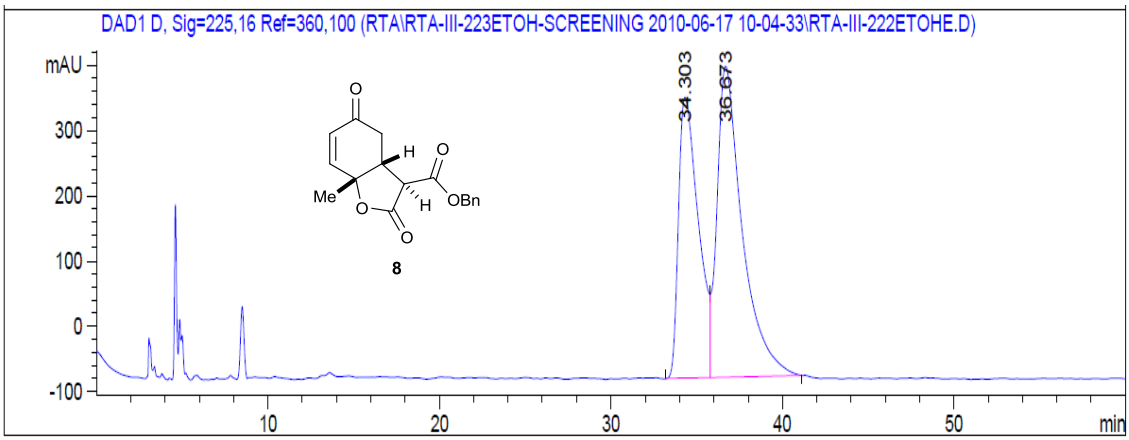
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.280	BV	0.6444	2795.66748	67.33952	49.0167
2	23.522	VB	0.6810	2907.83618	65.61931	50.9833
Totals :				5703.50366	132.95883	



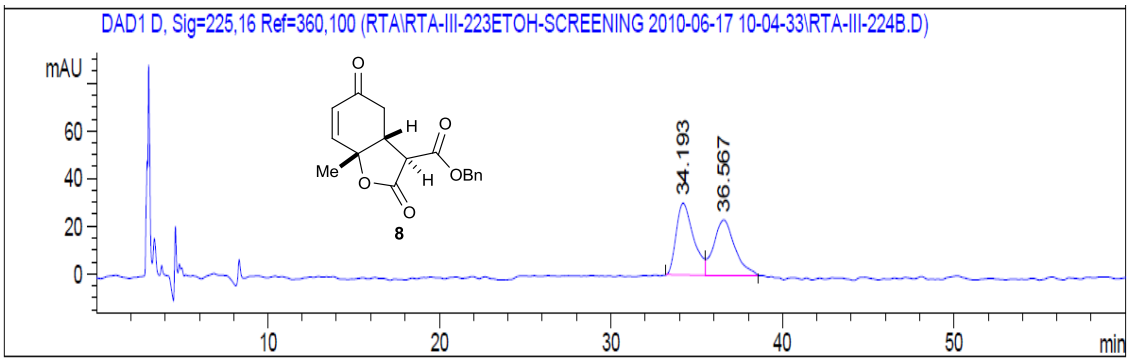
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.237	BV	0.6541	5080.52344	120.93938	65.0589
2	23.501	VB	0.6860	2728.58838	61.21568	34.9411
Totals :				7809.11182	182.15506	



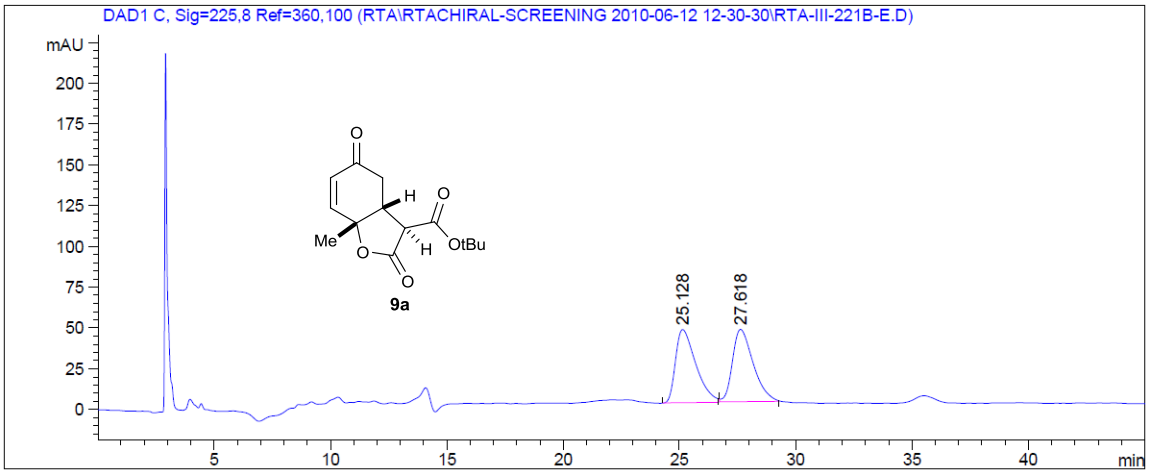
Signal 3: DAD1 D, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.303	BV	1.1955	3.44614e4	430.69736	41.3495
2	36.673	VB	1.5104	4.88805e4	476.65475	58.6505
Totals :				8.33419e4	907.35211	



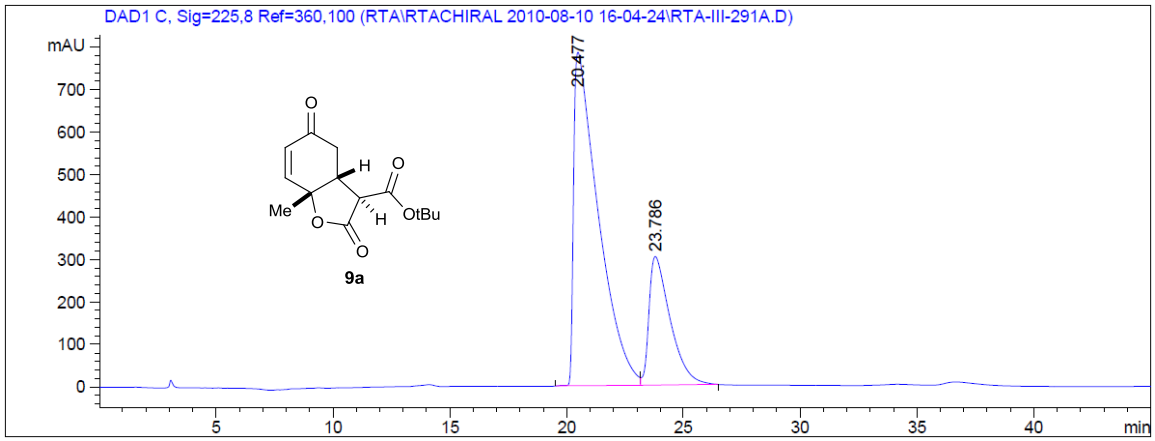
Signal 2: DAD1 D, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.193	BV	1.0614	2150.87451	30.25681	51.8370
2	36.567	VB	1.2581	1998.42957	23.31288	48.1630
Totals :				4149.30408	53.56969	



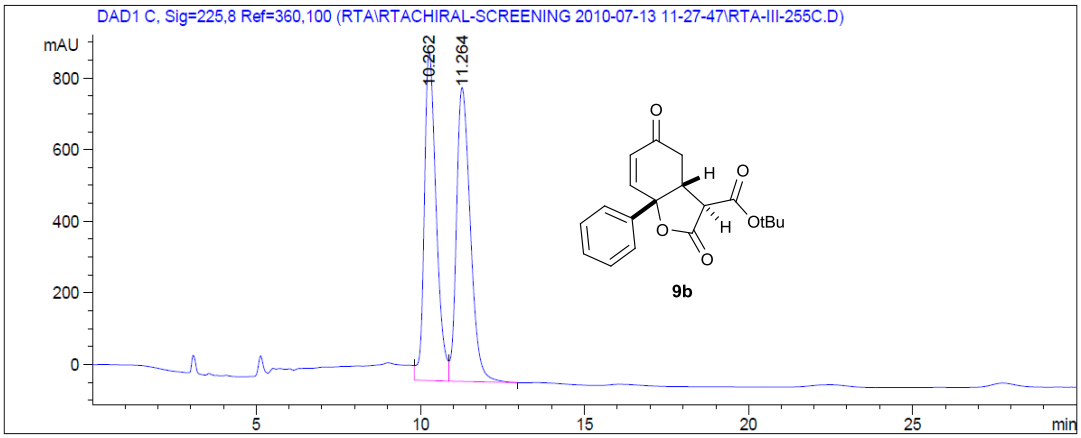
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.128	BB	0.9114	2732.88379	44.94476	49.5701
2	27.618	BB	0.9339	2780.28638	44.56203	50.4299
Totals :				5513.17017	89.50679	



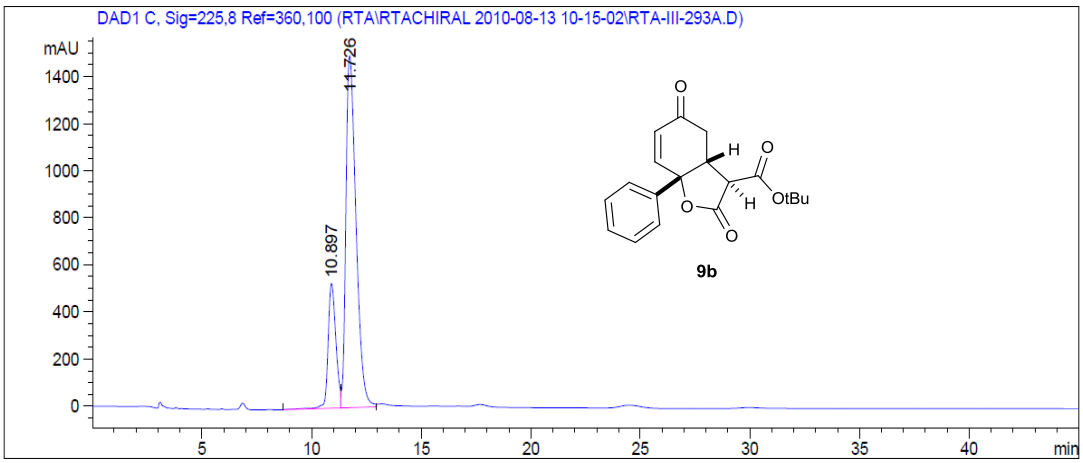
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.477	BV	1.0418	5.78117e4	786.26599	75.0149
2	23.786	VB	0.9444	1.92552e4	303.42371	24.9851
Totals :				7.70670e4	1089.68970	



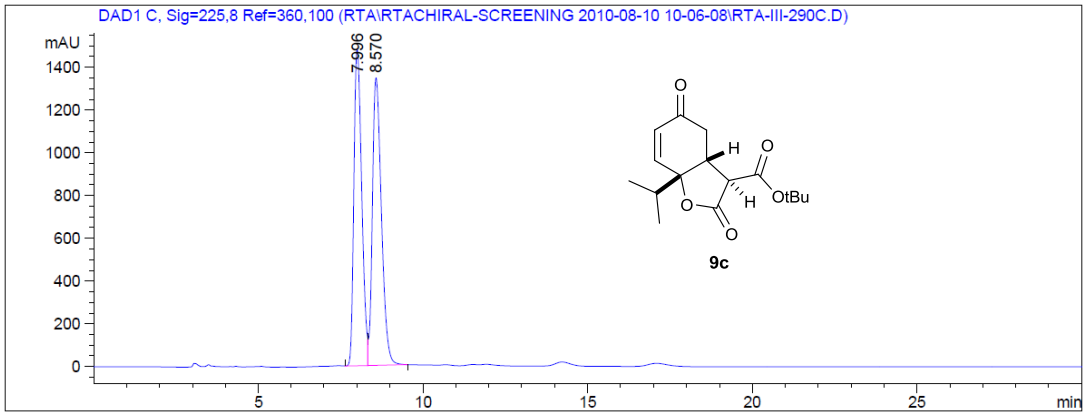
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.262	VV	0.3848	2.30434e4	918.14948	48.8320
2	11.264	VB	0.4591	2.41457e4	820.97662	51.1680
Totals :				4.71892e4	1739.12610	



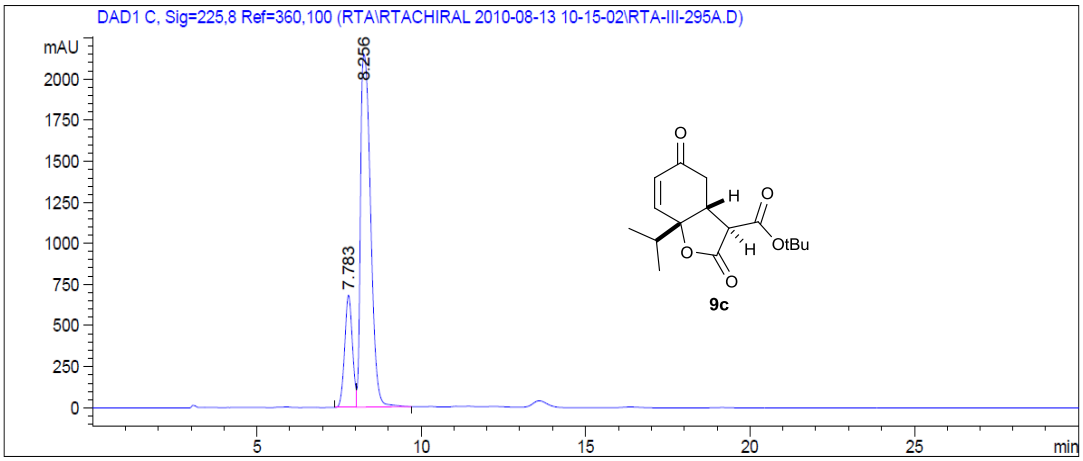
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.897	BV	0.3796	1.31531e4	529.92493	21.5763
2	11.726	VB	0.4950	4.78077e4	1495.37183	78.4237
Totals :				6.09608e4	2025.29675	



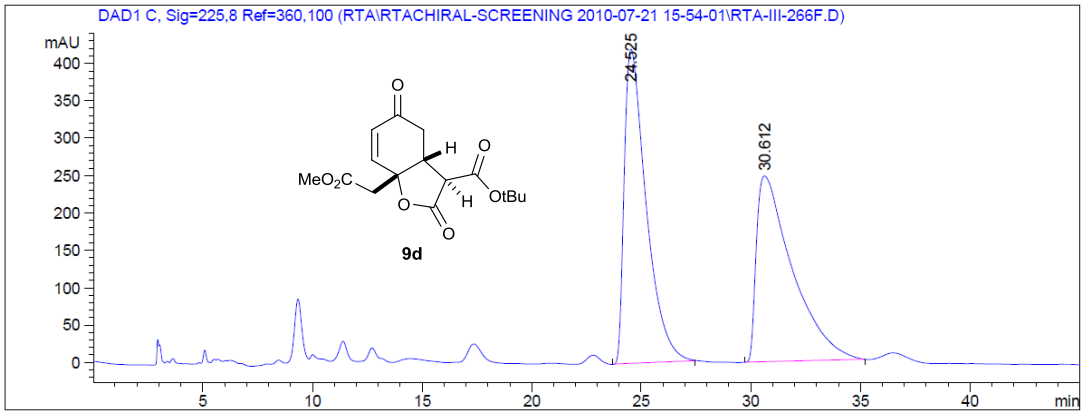
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.996	VV	0.2597	2.45907e4	1481.15747	49.0026
2	8.570	VB	0.2938	2.55918e4	1345.97168	50.9974
Totals :				5.01825e4	2827.12915	



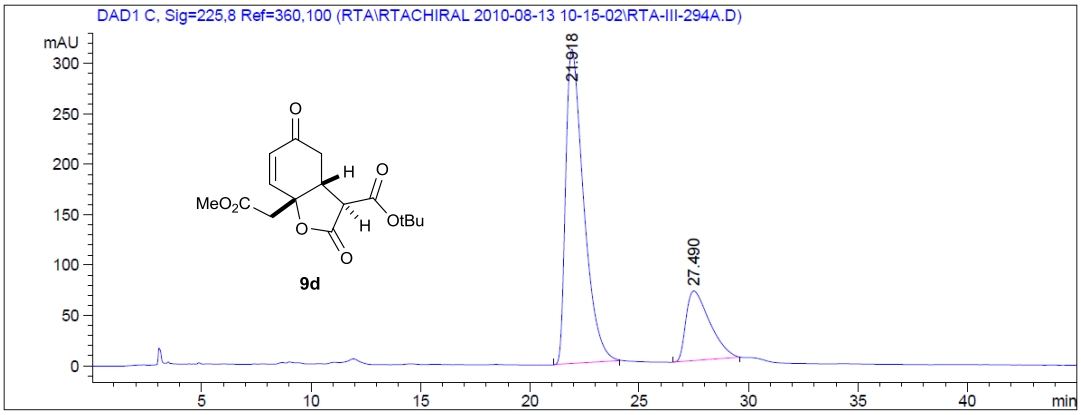
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.783	BV	0.2503	1.11395e4	683.06348	19.5405
2	8.256	VB	0.3392	4.58678e4	2147.51904	80.4595
Totals :				5.70074e4	2830.58252	



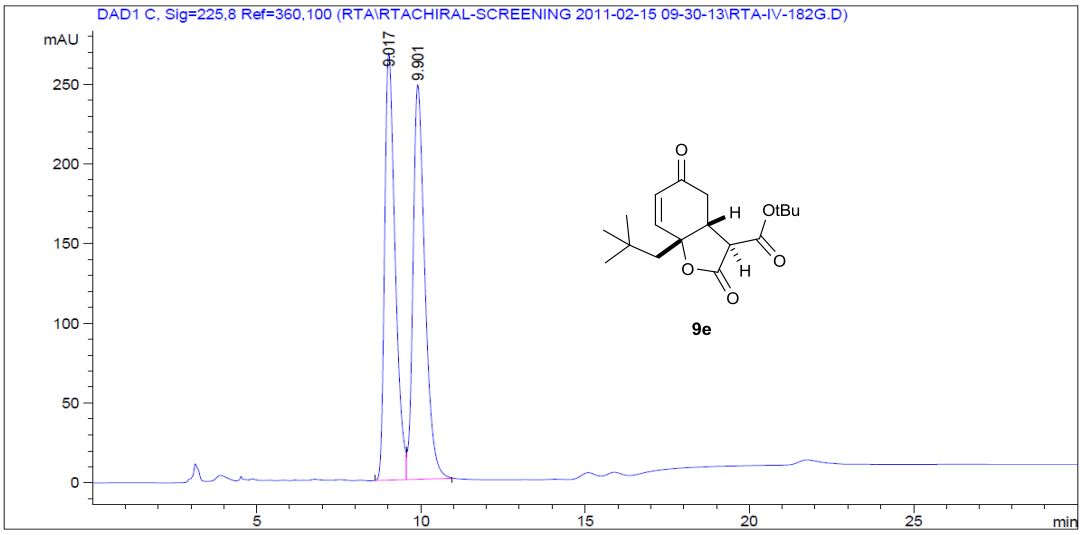
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.525	VB	1.0519	2.93265e4	420.38501	50.7998
2	30.612	BB	1.6125	2.84031e4	248.67615	49.2002
Totals :				5.77296e4	669.06116	



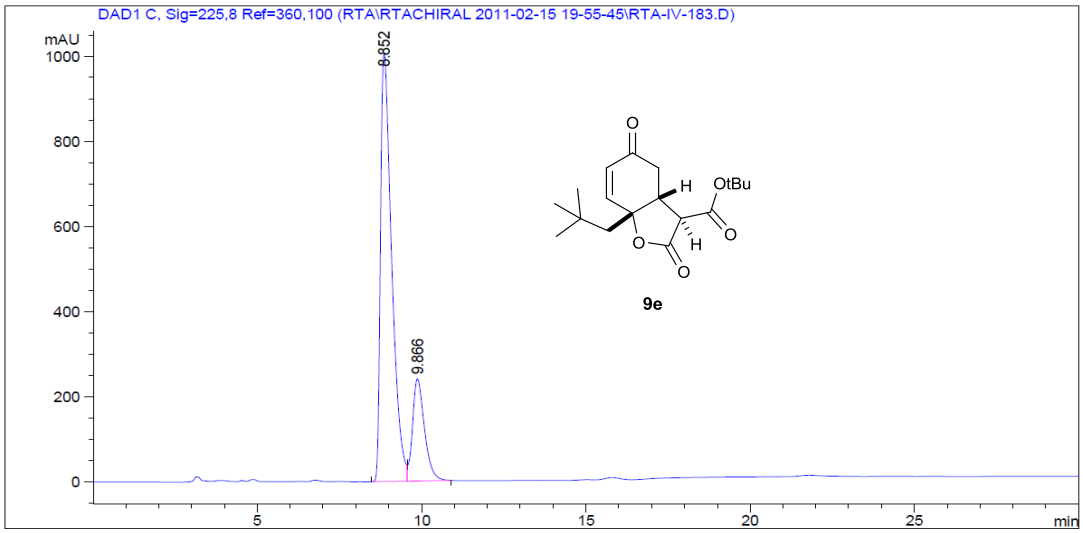
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.918	BB	0.8675	1.79123e4	312.11633	77.3304
2	27.490	BB	1.1444	5251.05518	69.26980	22.6696
Totals :				2.31634e4	381.38613	



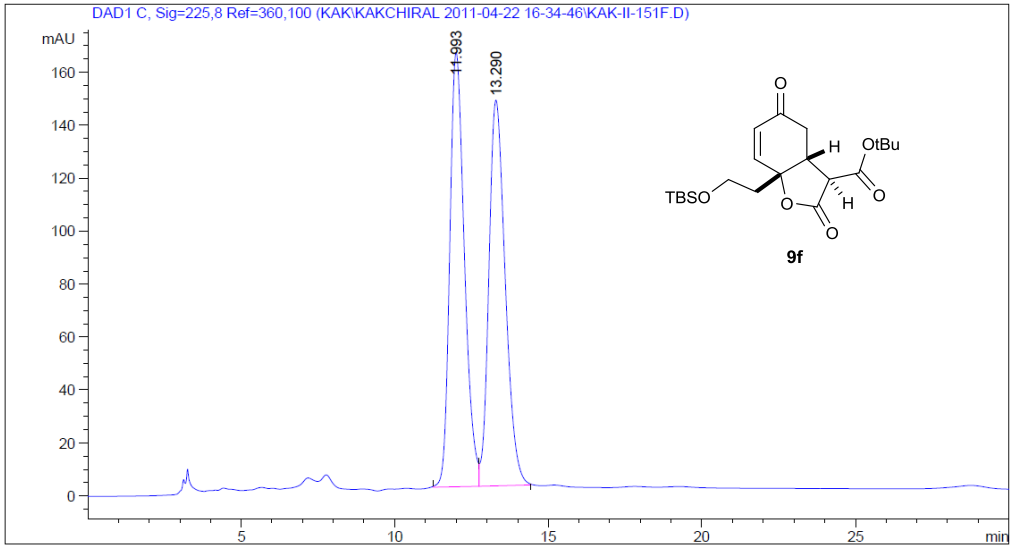
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.017	BV	0.3384	5987.78760	268.27936	49.0460
2	9.901	VB	0.3790	6220.72998	247.67616	50.9540
Totals :				1.22085e4	515.95552	



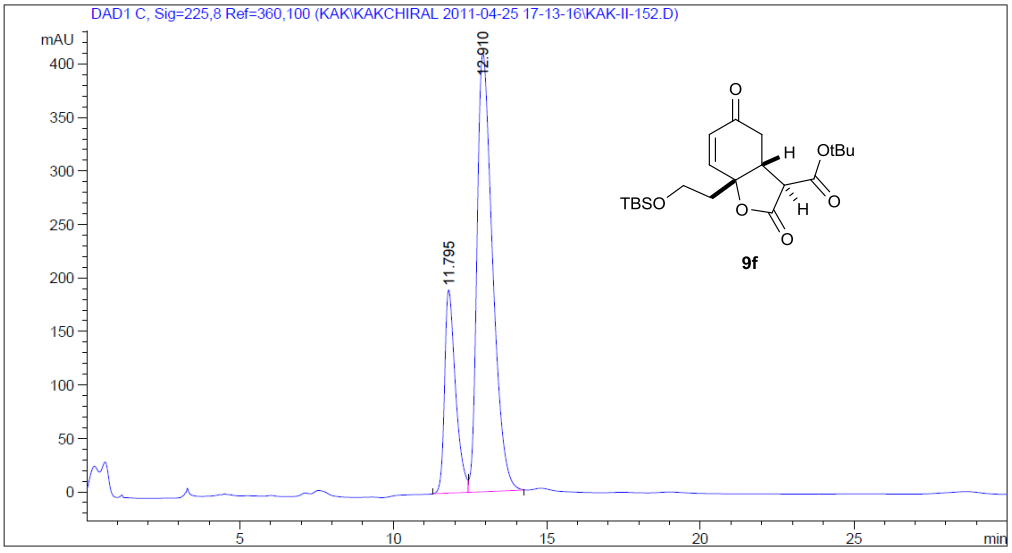
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.852	BV	0.3555	2.37998e4	1007.76569	79.5687
2	9.866	VB	0.3846	6111.21484	240.36726	20.4313
Totals :				2.99110e4	1248.13295	



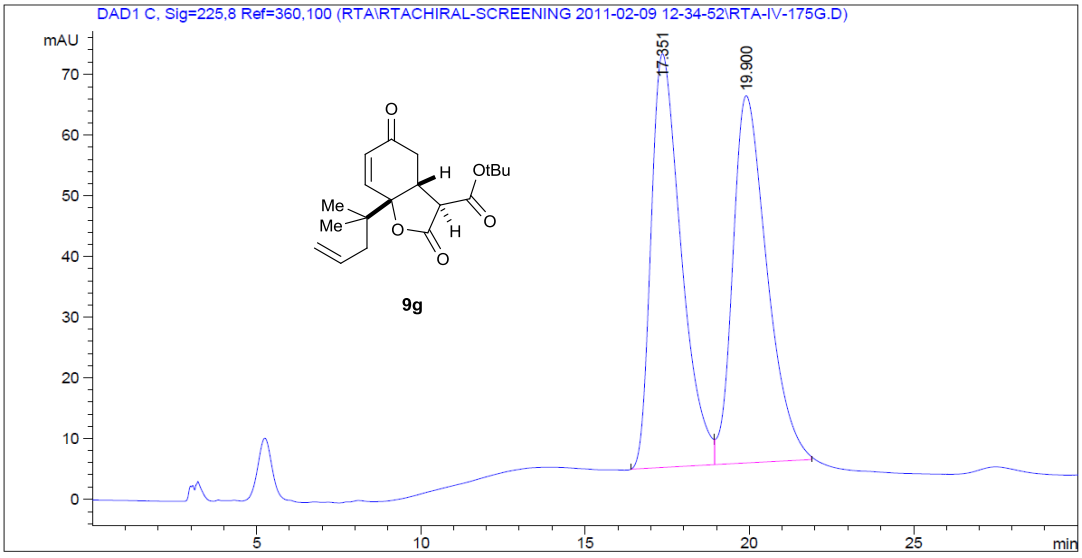
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.993	BV	0.5121	5460.72900	164.16624	50.3019
2	13.290	VB	0.5699	5395.17236	145.72881	49.6981
Totals :				1.08559e4	309.89505	



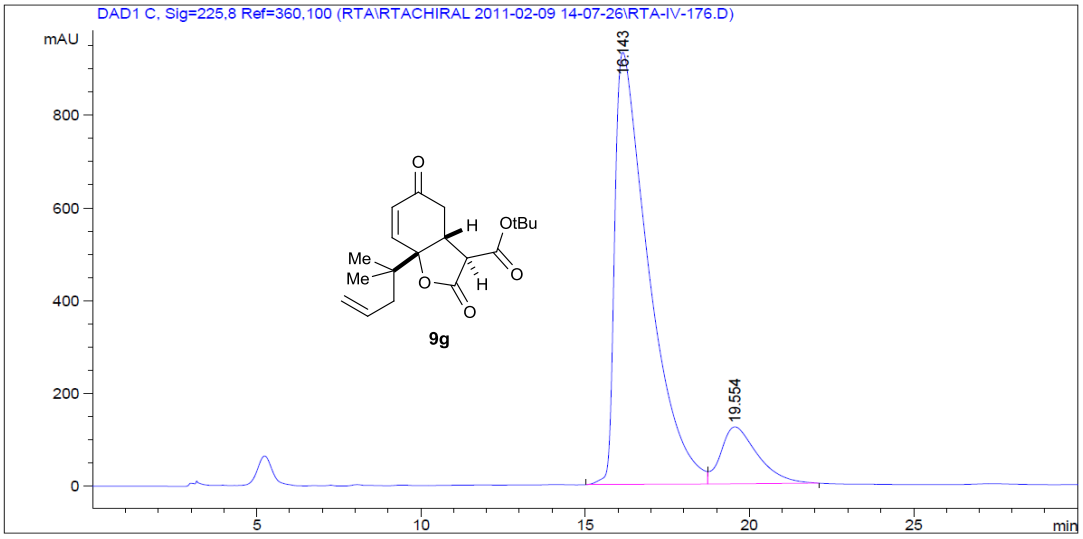
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.795	BV	0.3738	4756.44775	190.15103	24.6850
2	12.910	VB	0.5388	1.45121e4	410.17517	75.3150
Totals :				1.92686e4	600.32620	



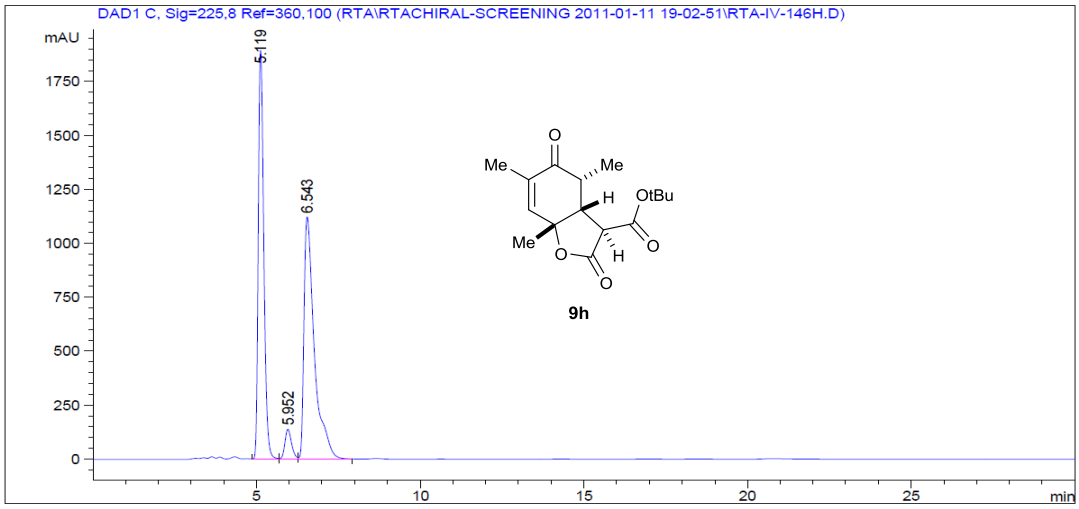
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.351	BV	0.9796	4358.75537	68.20110	49.8197
2	19.900	VB	1.0800	4390.29785	60.54633	50.1803
Totals :				8749.05322	128.74743	



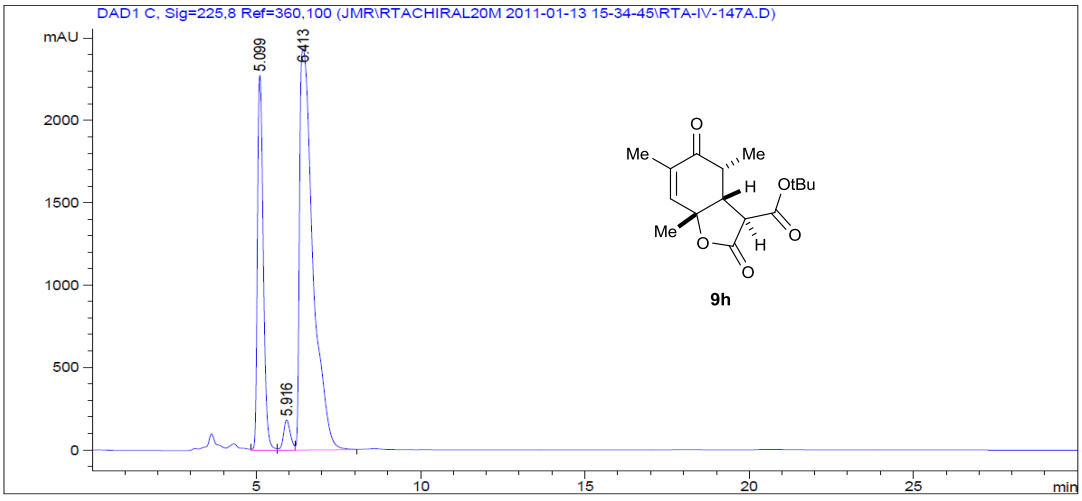
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.143	BV	1.0349	6.67601e4	932.88239	87.4301
2	19.554	VB	1.1545	9598.15430	122.99047	12.5699
Totals :				7.63582e4	1055.87286	



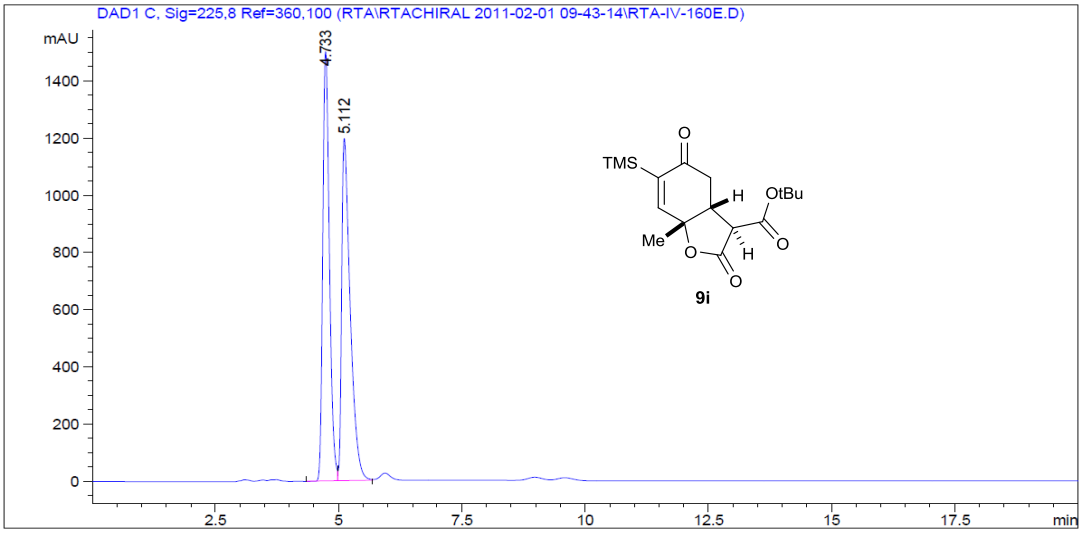
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.119	VV	0.1803	2.21447e4	1895.46582	45.3031
2	5.952	VV	0.2205	1975.79810	138.44162	4.0420
3	6.543	VB	0.3275	2.47607e4	1121.99731	50.6549
Totals :				4.88812e4	3155.90475	



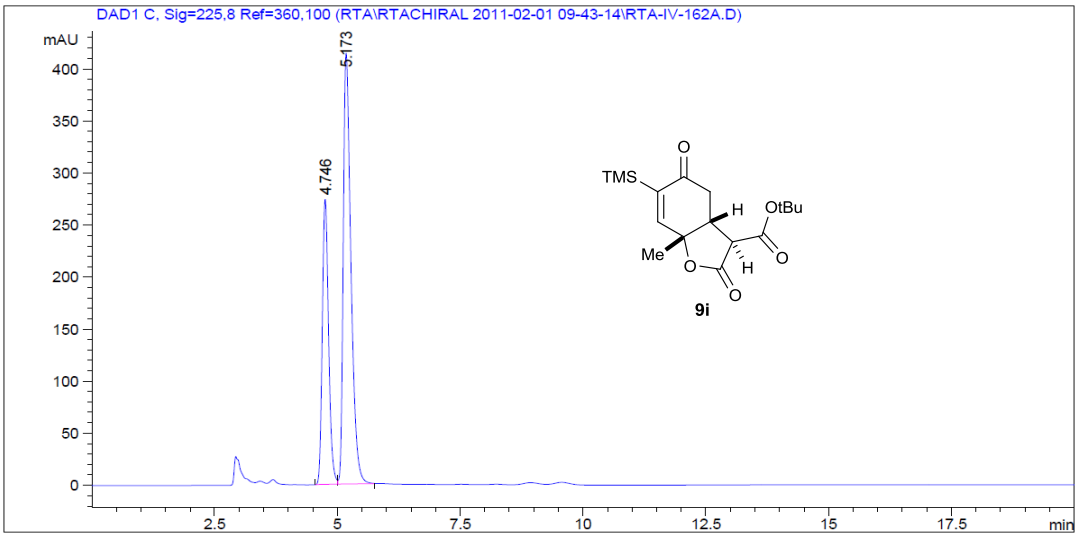
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.099	VV	0.1945	2.81788e4	2275.27051	28.2121
2	5.916	VV	0.2217	2670.45532	183.64128	2.6736
3	6.413	VB	0.4309	6.90325e4	2433.61670	69.1142
Totals :				9.98818e4	4892.52849	



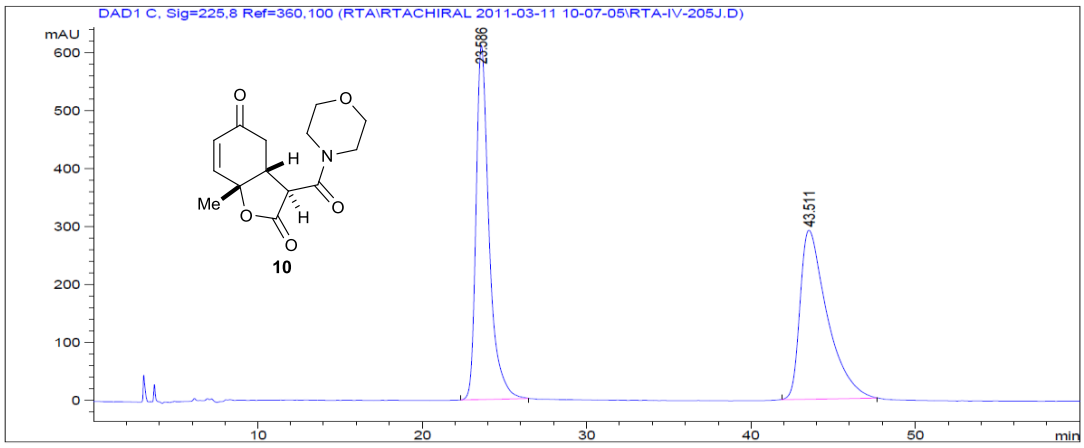
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.733	VV	0.1452	1.40737e4	1503.52515	49.2863
2	5.112	VV	0.1790	1.44813e4	1198.34216	50.7137
Totals :				2.85550e4	2701.86731	



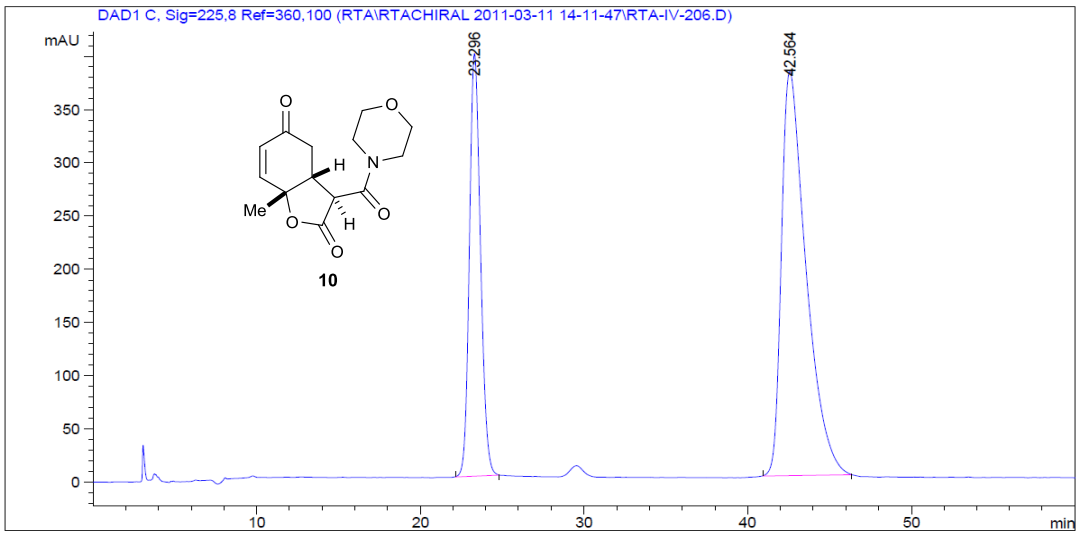
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.746	BV	0.1359	2441.79980	274.21561	35.2086
2	5.173	VB	0.1646	4493.44629	414.24277	64.7914
Totals :				6935.24609	688.45837	



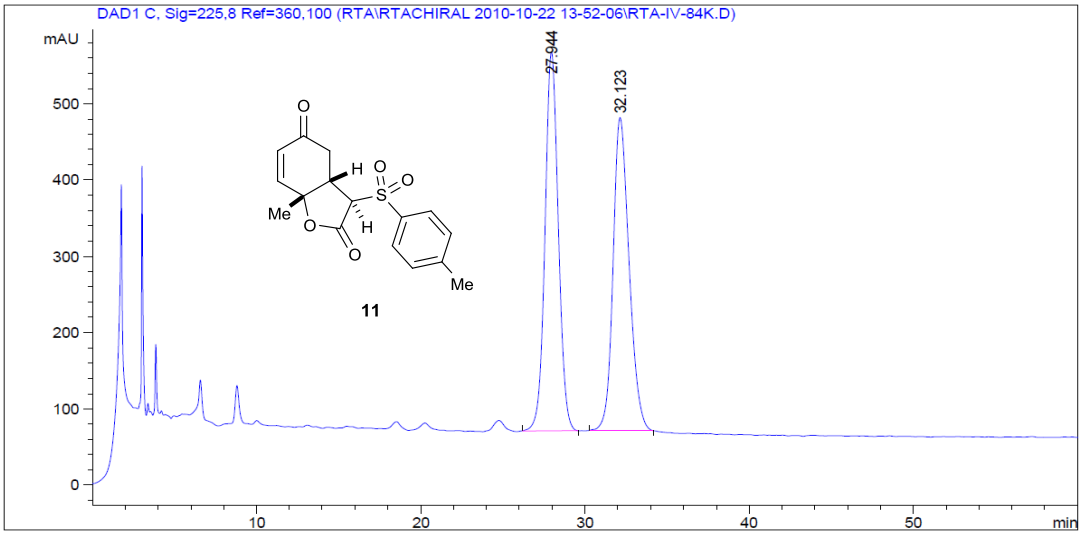
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.586	BB	0.8247	3.37105e4	611.93066	50.0626
2	43.511	BB	1.6687	3.36262e4	292.17975	49.9374
Totals :				6.73367e4	904.11041	



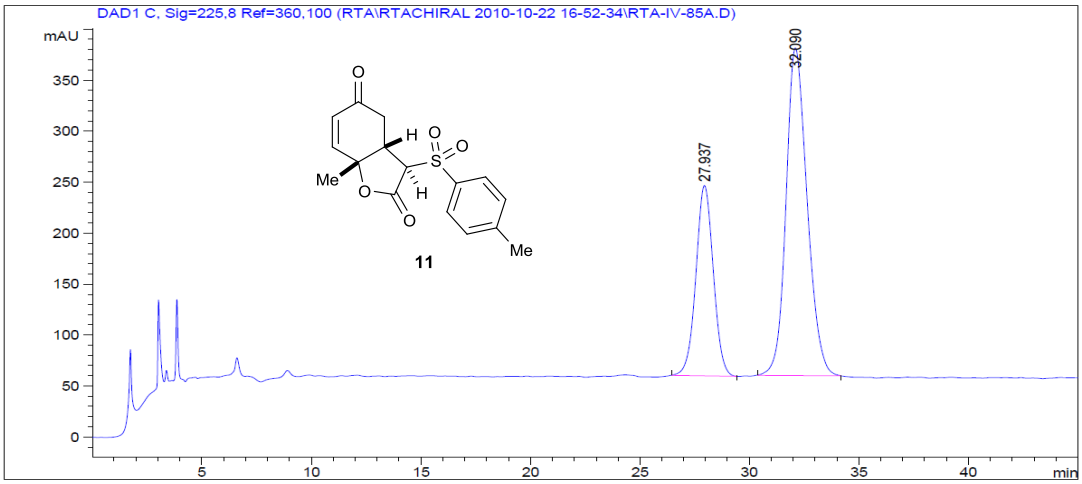
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.296	BB	0.7258	1.87056e4	396.94693	31.9701
2	42.564	BB	1.5509	3.98040e4	379.73398	68.0299
Totals :				5.85097e4	776.68091	



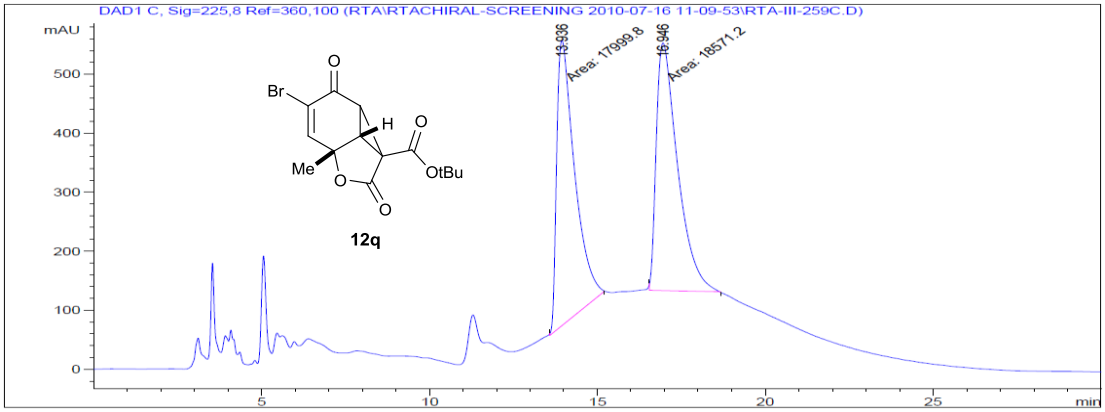
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.944	BB	0.8683	2.80527e4	497.19113	50.1618
2	32.123	BB	1.0442	2.78717e4	410.48291	49.8382
Totals :				5.59243e4	907.67404	



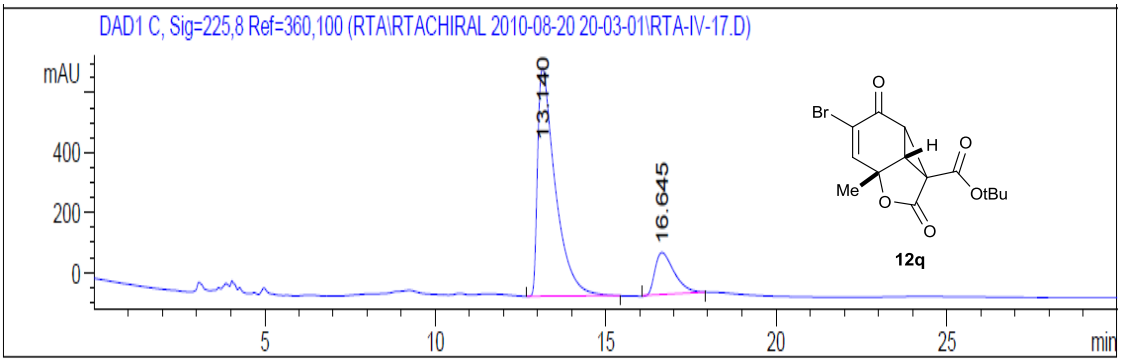
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.937	BB	0.8573	1.03660e4	186.84067	32.4235
2	32.090	BB	1.0356	2.16047e4	321.65137	67.5765
Totals :				3.19707e4	508.49203	



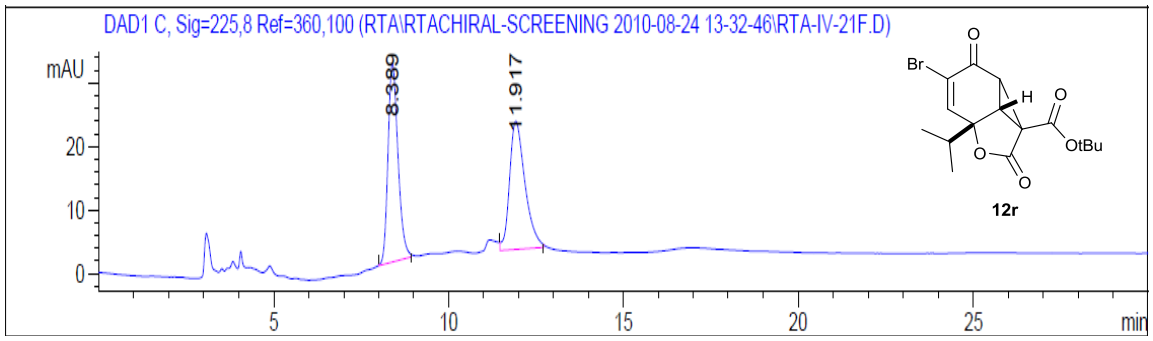
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.936	MM	0.6193	1.79998e4	484.44879	49.2189
2	16.946	MM	0.7369	1.85712e4	420.01151	50.7811
Totals :				3.65710e4	904.46030	



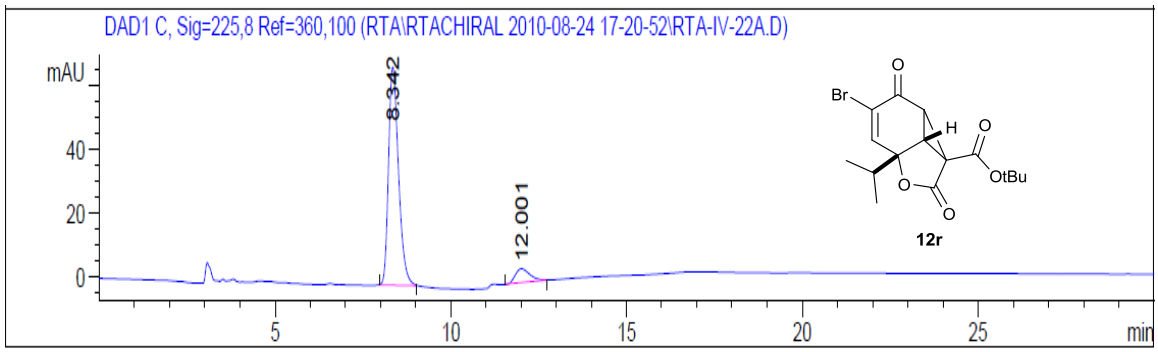
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.140	VB	0.5291	2.75291e4	762.63934	82.9901
2	16.645	BB	0.6034	5642.45020	142.04649	17.0099
Totals :				3.31715e4	904.68584	



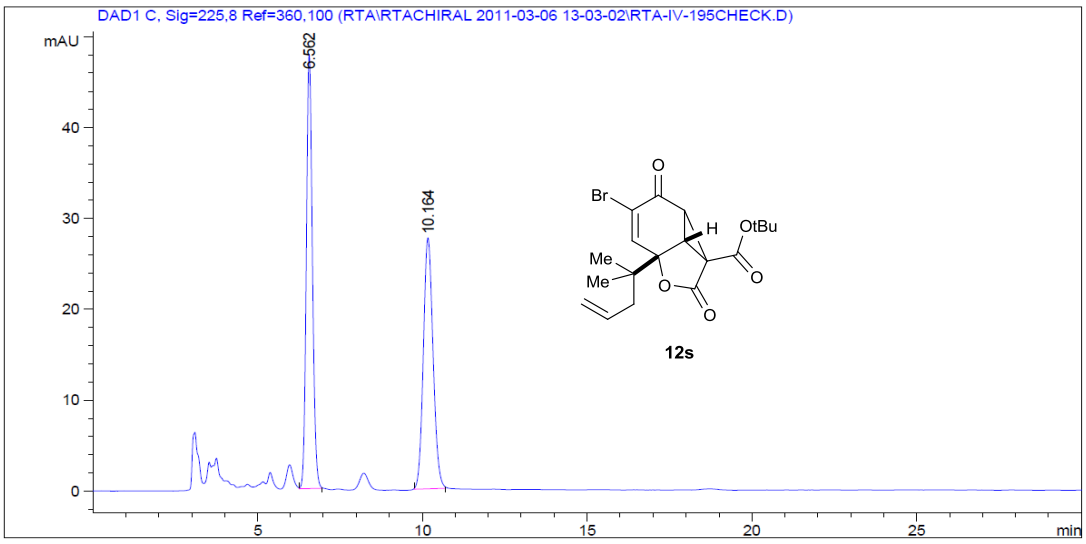
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.389	BB	0.3062	621.01746	31.20434	50.0388
2	11.917	BB	0.4643	620.05469	20.18884	49.9612
Totals :				1241.07214	51.39318	



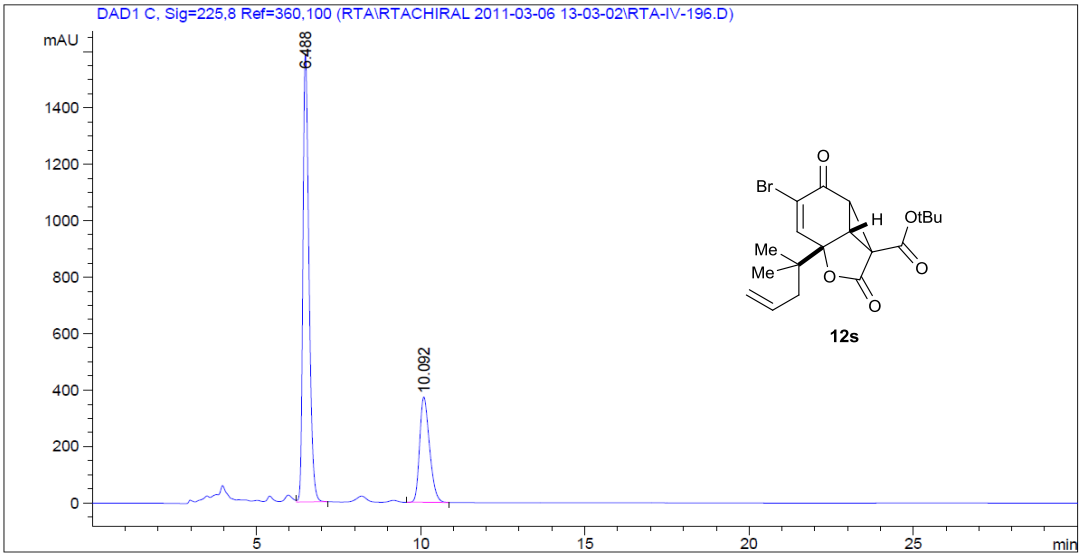
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.342	BB	0.3026	1357.14783	68.67429	91.0858
2	12.001	BB	0.4555	132.81891	4.48435	8.9142
Totals :				1489.96674	73.15865	



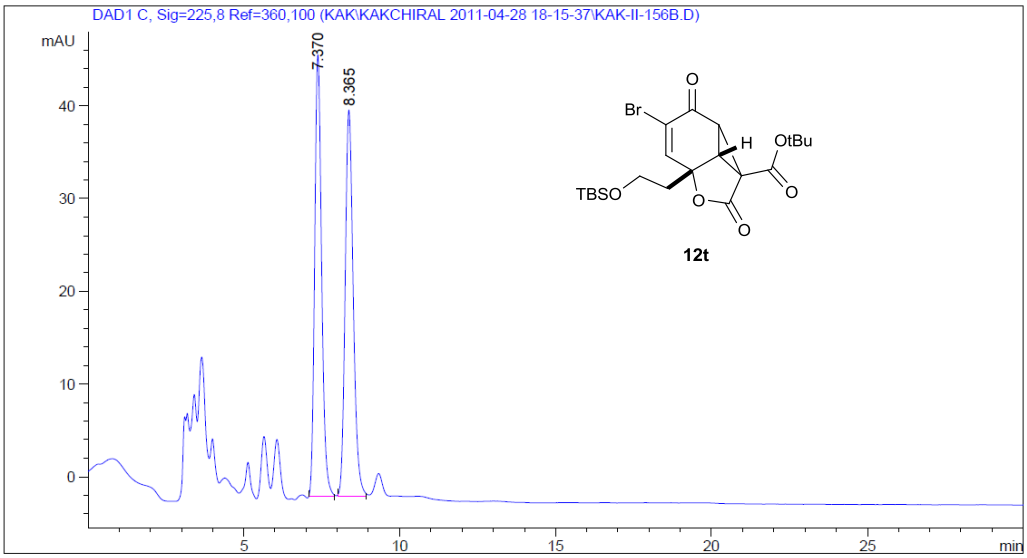
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.562	VB	0.1968	610.60992	47.86470	51.8827
2	10.164	BB	0.3169	566.29553	27.65885	48.1173
Totals :				1176.90546	75.52355	



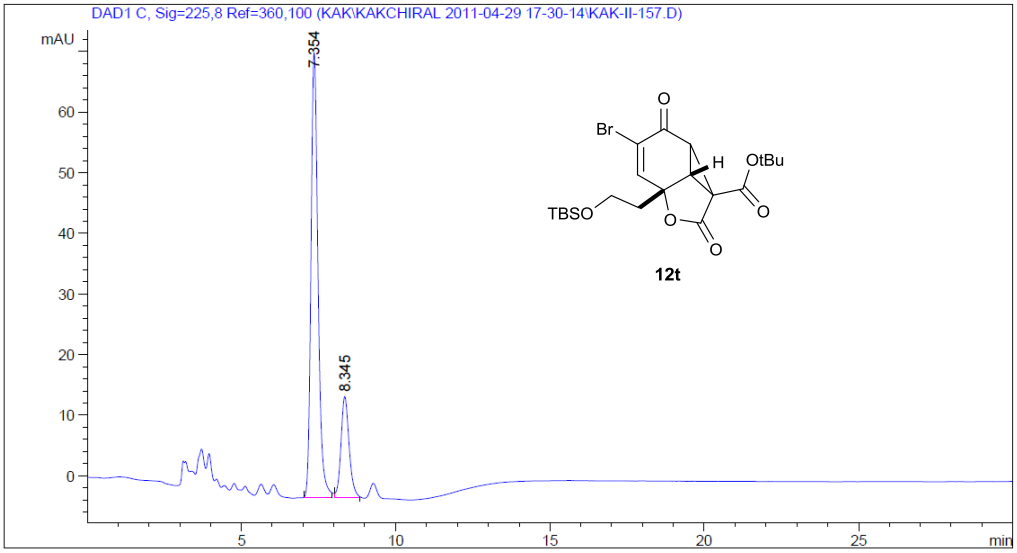
Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.488	VB	0.1953	2.03476e4	1589.64600	72.1979
2	10.092	VB	0.3225	7835.46924	373.82523	27.8021
Totals :				2.81830e4	1963.47122	



Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.370	BB	0.2386	737.87378	47.67091	49.4908
2	8.365	BB	0.2787	753.05872	41.68877	50.5092
Totals :				1490.93250	89.35967	



Signal 1: DAD1 C, Sig=225,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.354	BB	0.2405	1160.50854	73.36861	79.0275
2	8.345	BB	0.2811	307.97888	16.70793	20.9725
Totals :				1468.48743	90.07654	