

Chiral Phosphoric Acid Catalyzed Asymmetric Oxidative Dearomatization of Naphthols with Quinones

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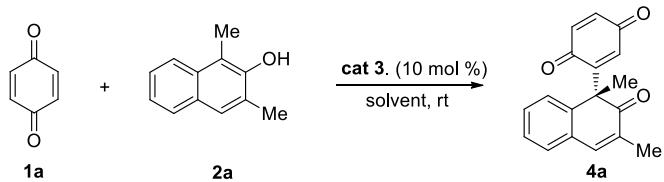
1. General information

Unless stated otherwise, all reactions were carried out in flame dried glassware. All solvents were purified and dried according to standard methods prior to use. 2-naphthols¹ and Cat. 3² were prepared according to literature, quinones were purchased from commercial suppliers. ¹H and ¹³C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ¹H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet or unresolved, coupling constant(s) in Hz, integration). Data for ¹³C NMR are reported in terms of chemical shift (δ , ppm). IR spectra were recorded on a FT-IR spectrometer and only major peaks were reported in cm^{-1} . Optical rotations were reported as follows: $[\alpha]_D^{rt}$ (c: g/100 mL, in solvent). High resolution mass spectra (HRMS) were obtained by the ESI ionization sources. The ee value determination was carried out using chiral HPLC with Daicel Chiracel column on Waters with a 996 UV-detector.

[1] (a) A. Rudolph, P. H. Bos, A. Meetsma, A. J. Minnaard, B. L. Feringa, *Angew. Chem. Int. Ed.* 2011, **50**, 5834–5838. (b) T. Oguma, T. Katsuki, *J. Am. Chem. Soc.*, 2012, **134**, 20017–20020. (c) J. Zheng, S.-B. Wang, C. Zheng, S.-L. You, *J. Am. Chem. Soc.*, 2015, **137**, 4880–4883.

[2] (a) S. Müller, M. J. Webber, B. List, *J. Am. Chem. Soc.*, 2011, **133**, 18534–18537. (b) I. Čorić, S. Müller, B. List, *J. Am. Chem. Soc.*, 2010, **132**, 17370–17373. (c) I. T. Crouch, R. K. Neff, D. E. Frantz, *J. Am. Chem. Soc.*, 2013, **135**, 4970–4973. (d) F. R-Michailidis, L. Guenée, A. Alexakis, *Angew. Chem. Int. Ed.* **2013**, **52**, 9266–9270. (e) M. Yamanaka, J. Itoh, K. Fuchibe, T. Akiyama, *J. Am. Chem. Soc.* **2007**, **129**, 6756–6764.

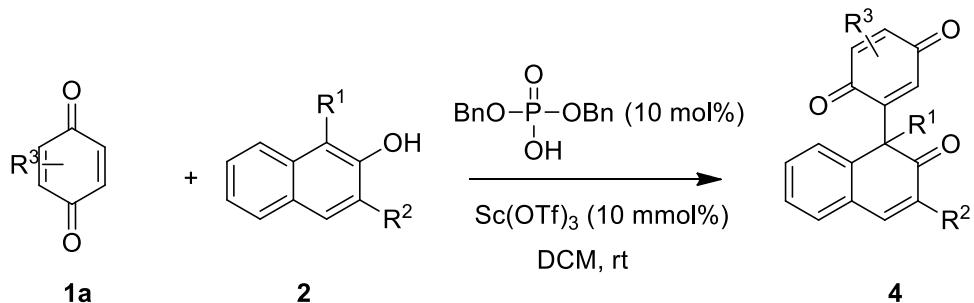
2. Optimization of the reaction condition



entry	cat.	solvent	2a:1a	time (h)	conv. (%)	ee (%)
1	3a	toluene	1:3	air 48	45	69
2	3b	toluene	1:3	air 48	>95	42
3	3c	toluene	1:3	air 48	>95	35
4	3d	toluene	1:3	air 48	>95 (77)	75
5	3e	toluene	1:3	air 48	>95	23
6	3f	toluene	1:3	air 48	30	24
7	3g	toluene	1:3	air 48	89	91
8	3g	DCM	1:3	air 36	>95(78)	98
9	3g	DCE	1:3	air 36	>95	97
10	3g	xylene	1:3	air 48	>95	89
11	3g	mesitylene	1:3	air 48	>95	86
12	3g	PhF	1:3	air 48	>95	93
13	3g	THF	1:3	air 48	<5	--
14	3g	Et ₂ O	1:3	air 48	<5	--
15	3g	DCM	1:4	air 36	>95(76)	97
16	3g	DCM	1:6	air 36	>95(68)	97
17	3g	DCM	1:2	air 36	76 (53)	98
18	3g	DCM	1:1	air 36	45 (28)	98
19	3g	DCM	1:3	A _r 36	>95(77)	98
20	3g	DCM	1:3	O ₂ 36	>95(75)	98
21	3g	DCM	1:3	DDQ 48	>95	Complex mixtures
22	3g	DCM	1:3	PhI(OAc) ₂ 48	<5	-
23	3g	DCM	1:3	IBX 48	<5	-
24	3g	DCM	1:3	Dess-Martin 48	<5	-
25	3g	DCM	1:3	'BuOOH 48	<5	-

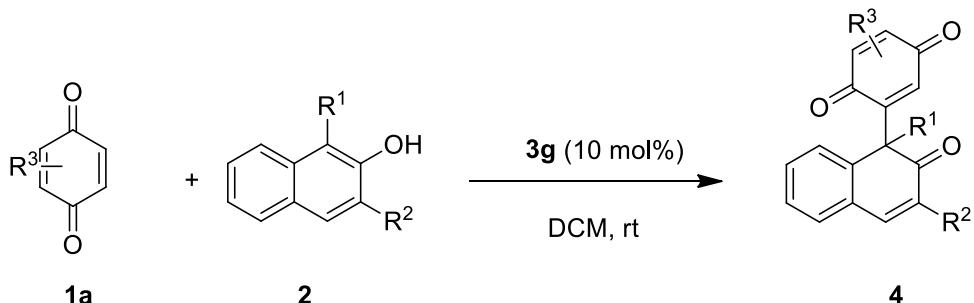
Isolated yield was given in the parentheses.

3. General procedure for preparation of racemic samples



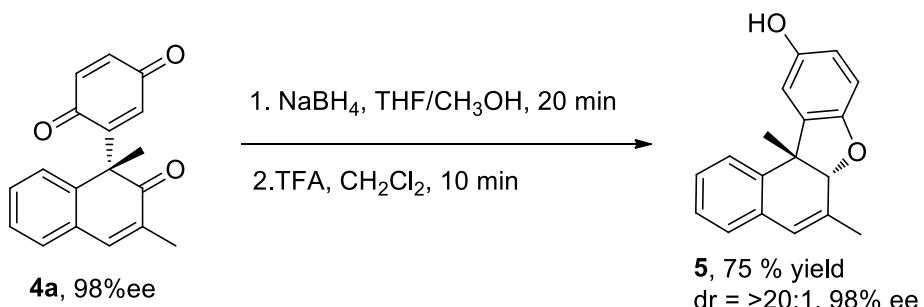
In an ordinary vial, quinone **1a** (0.30 mmol) was added to a stirred mixture of dibenzyl phosphate (10 mol%), $\text{Sc}(\text{OTf})_3$ (10 mol%) and substituted 2-naphthol **2** (0.10 mmol) in CH_2Cl_2 (1.0 mL) at room temperature. The mixture was stirred at this temperature for the requisite amount of time as monitored by TLC. The solvent was removed under vacuum and residue was chromatographed on silica gel and fractions were collected and concentrated in vacuo to provide the pure desired products.

4. General experimental procedure for dearomatization of 2-naphthols with quinone



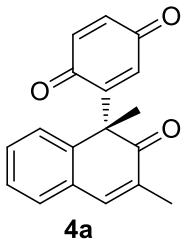
In an ordinary vial, quinone **1a** (0.60 mmol) was added to a stirred mixture of 2-naphthols **2** (0.20 mmol) and catalyst **3g** (0.02 mmol) in CH_2Cl_2 (2.0 mL) at room temperature. The mixture was stirred at this temperature for the requisite amount of time as monitored by TLC. The solvent was removed under vacuum and residue was chromatographed on silica gel (petroleum ether/AcOEt 20:1 - 6:1) and fractions were collected and concentrated in vacuo to provide the pure desired products **4**.

5. Further Transformations of the Products



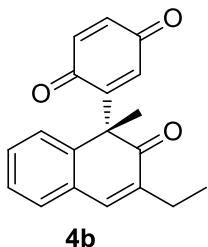
In an ordinary vial, NaBH_4 (0.90 mmol, 4.5eq) was added to a stirred mixture of (*R*)-2-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione **4a** (0.20 mmol) in THF (0.5 mL) at 0°C, followed by the dropwise addition of 0.5 mL of MeOH. The mixture was stirred at this temperature for 20 min. The solvent was removed under vacuum and the residue was added TFA (trifluoroacetic acid, 0.2 mL) at 0°C. The mixture was stirred at this temperature for 10 min. The solvent was removed under vacuum and residue was chromatographed on silica gel (petroleum ether/AcOEt 15:1) and fractions were collected and concentrated in vacuo to provide the pure desired products.

6. Characterization of 4 and 5



(R)-2-(1,3-dimethyl-2-oxo-1,2-dihydroronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4a

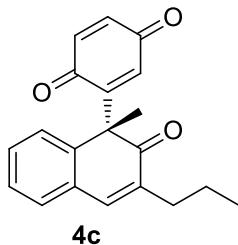
Using 10 mol % cat. 3g at rt with 36 h, 43.9 mg (78 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 10:1) as a yellow solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.41 (s, 1H), 7.38 – 7.32 (m, 1H), 7.31 – 7.18 (m, 2H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.96 – 6.87 (m, 1H), 6.77 (dd, *J* = 10.1, 2.4 Hz, 1H), 6.61 (d, *J* = 10.1 Hz, 1H), 2.06 (d, *J* = 0.9 Hz, 3H), 1.50 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 200.7, 187.5, 185.7, 151.8, 143.6, 141.3, 136.7, 136.1, 133.8, 131.4, 129.3, 129.1, 129.0, 127.3, 125.2, 53.1, 26.5, 16.0; **IR:** 3314, 2924, 1663, 1555, 1373, 1286, 1097, 1034, 995, 919, 738 cm⁻¹; [α]_D^{rt} = -40 °c = 1.00, CHCl₃); HRMS (ESI): C₁₈H₁₄O₃+H, Calc: 279.1016, Found: 279.1017; HPLC: DAICEL CHIRALCEL IC, Hexane/EtOH = 1/1, flow rate = 1.0 ml/min, retention time: t_{major} = 7.3, t_{minor} = 6.2, 98% ee.



(R)-2-(3-ethyl-1-methyl-2-oxo-1,2-dihydroronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4b

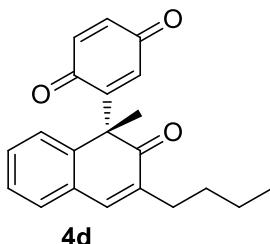
Using 10 mol % cat. 3g at rt with 10 h, 46 mg (79 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.43 – 7.30 (m, 2H), 7.30 – 7.16 (m, 2H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.98 – 6.84 (m, 1H), 6.76 (dd, *J* = 10.1, 2.4 Hz, 1H), 6.61 (d, *J* = 10.1 Hz, 1H), 2.47 (q, *J* = 7.5 Hz, 2H), 1.49 (s, 3H), 1.18 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 200.2, 187.5, 185.6, 151.9, 143.4, 139.5, 136.9, 136.7, 136.1, 133.8, 129.5, 129.1, 129.0, 127.3, 125.1, 53.2, 26.4, 22.3, 12.4; **IR:** 3312, 2927, 1657, 1457, 1385, 1337, 1286, 1096, 992, 917, 760 cm⁻¹; [α]_D^{rt} = -42 °c =

1.00, CHCl₃); C₁₉H₁₆O₃+H, Calc: 293.1172, Found: 293.1172; HPLC: DAICEL CHIRALCEL IC, Hexane/EtOH = 8/2, flow rate = 1.0 ml/min, retention time: t_{major} = 11.0, t_{minor} = 8.2, 98% ee.



(R)-2-(1-methyl-2-oxo-3-propyl-1,2-dihydroronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4c

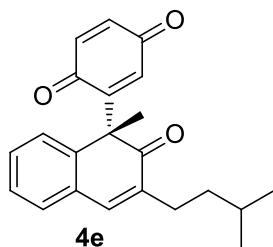
Using 10 mol % cat. 3g at rt with 22 h, 43 mg (71 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; ¹H NMR (300 MHz, CDCl₃) δ 7.42 – 7.32 (m, 2H), 7.30 – 7.16 (m, 2H), 7.03 (d, J = 2.4 Hz, 1H), 6.97 – 6.85 (m, 1H), 6.77 (dd, J = 10.1, 2.4 Hz, 1H), 6.61 (d, J = 10.1 Hz, 1H), 2.58 – 2.27 (m, 2H), 1.69 – 1.52 (m, 2H), 1.49 (s, 3H), 0.98 (t, J = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 200.3, 187.5, 185.6, 151.9, 143.5, 140.6, 136.7, 136.1, 135.4, 133.8, 129.5, 129.0, 129.0, 127.3, 125.1, 53.3, 31.4, 26.4, 21.6, 13.8; IR: 3313, 2926, 1659, 1456, 1382, 1286, 1096, 997, 919, 758 cm⁻¹; [α]_D^{rt} = -39 (c = 1.00, CHCl₃); C₂₀H₁₉O₃+H, Calc: 307.1329, Found: 307.1331; HPLC: DAICEL CHIRALCEL IC, Hexane/EtOH = 8/2, flow rate = 1.0 ml/min, retention time: t_{major} = 9.4, t_{minor} = 7.4, 98% ee.



(R)-2-(3-butyl-1-methyl-2-oxo-1,2-dihydroronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4d

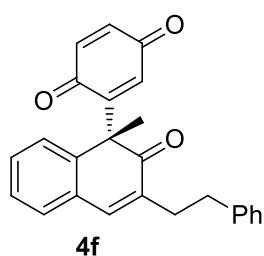
Using 10 mol % cat. 3g at rt with 48 h, 44 mg (69 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; ¹H NMR (300 MHz, CDCl₃) δ 7.41 – 7.30 (m, 2H), 7.30 – 7.15 (m, 2H), 7.03 (d, J = 2.4 Hz, 1H),

6.96 – 6.85 (m, 1H), 6.76 (dd, J = 10.1, 2.4 Hz, 1H), 6.61 (d, J = 10.1 Hz, 1H), 2.58 – 2.32 (m, 2H), 1.62 – 1.46 (m, 5H), 1.45 – 1.37 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, CDCl_3) δ 200.3, 187.5, 185.6, 151.9, 143.5, 140.4, 136.7, 136.0, 135.7, 133.8, 129.4, 129.1, 129.0, 127.3, 125.1, 53.3, 30.5, 29.0, 26.4, 22.4, 13.9; **IR**: 3312, 2928, 1659, 1456, 1382, 1285, 1202, 1097, 995, 919, 759 cm^{-1} ; $[\alpha]_D^{rt} = +35$ (c = 1.00, CHCl_3); $\text{C}_{21}\text{H}_{20}\text{O}_3+\text{H}$, Calc: 321.1485, Found: 321.1486; HPLC: DAICEL CHIRALCEL IC, Hexane/EtOH = 6/4, flow rate = 1.0 ml/min, retention time: $t_{\text{major}} = 6.3$, $t_{\text{minor}} = 5.2$, 96% ee.



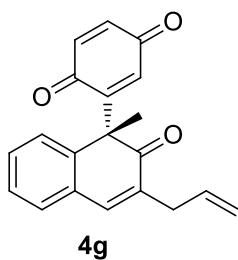
(R)-2-(3-isopentyl-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4e

Using 10 mol % cat. 3g at rt with 37 h, 45 mg (68 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; **^1H NMR** (300 MHz, CDCl_3) δ 7.45 – 7.31 (m, 2H), 7.31 – 7.14 (m, 2H), 7.03 (d, J = 2.4 Hz, 1H), 6.97 – 6.85 (m, 1H), 6.76 (dd, J = 10.1, 2.4 Hz, 1H), 6.61 (d, J = 10.1 Hz, 1H), 2.64 – 2.25 (m, 2H), 1.76 – 1.54 (m, 1H), 1.54 – 1.34 (m, 5H), 0.95 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (75 MHz, CDCl_3) δ 200.3, 187.5, 185.6, 151.9, 143.5, 140.3, 136.7, 136.1, 136.0, 133.8, 129.4, 129.1, 129.0, 127.3, 125.1, 53.3, 37.4, 27.9, 27.3, 26.4, 22.5, 22.5; **IR**: 3314, 2925, 1659, 1457, 1383, 1285, 1097, 997, 918, 758 cm^{-1} ; $[\alpha]_D^{rt} = -35$ (c = 1.00, CHCl_3); $\text{C}_{22}\text{H}_{22}\text{O}_3+\text{H}$, Calc: 335.1642, Found: 335.1644; HPLC: DAICEL CHIRALCEL IC, Hexane/iPrOH = 8/2, flow rate = 1.0 ml/min, retention time: $t_{\text{major}} = 7.8$, $t_{\text{minor}} = 6.0$, 96% ee.



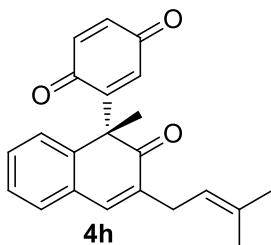
(R)-2-(1-methyl-2-oxo-3-phenethyl-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione e, 4f

Using 10 mol % cat. 3g at rt with 21 h, 52 mg (70 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.35 – 7.09 (m, 9H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.96 – 6.85 (m, 1H), 6.76 (dd, *J* = 10.0, 2.4 Hz, 1H), 6.62 (d, *J* = 10.1 Hz, 1H), 2.96 – 2.80 (m, 2H), 2.80 – 2.65 (m, 2H), 1.46 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 200.2, 187.4, 185.6, 151.8, 143.6, 141.4, 141.3, 136.7, 136.1, 134.3, 133.8, 129.5, 129.2, 128.8, 128.6, 128.3, 127.3, 125.9, 125.1, 53.3, 34.6, 31.6, 26.4; **IR**: 3312, 2925, 1661, 1454, 1383, 1286, 1202, 1096, 995, 919, 757 cm⁻¹; **[α]_D^{rt}** = -39 (c = 1.00, CHCl₃); C₂₅H₂₀O₃+H, Calc: 369.1485, Found: 369.1491; HPLC: DAICEL CHIRALCEL IA, Hexane/iPrOH = 8/2, flow rate = 1.0 ml/min, retention time: t_{major} = 18.3, t_{minor} = 8.7, 99% ee.



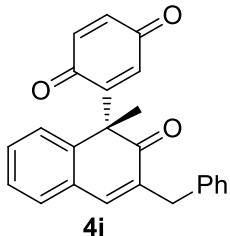
(R)-2-(3-allyl-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4g

Using 10 mol % cat. 3g at rt with 24 h, 38 mg (63 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.45 – 7.33 (m, 2H), 7.33 – 7.18 (m, 2H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.96 – 6.86 (m, 1H), 6.77 (dd, *J* = 10.1, 2.4 Hz, 1H), 6.62 (d, *J* = 10.1 Hz, 1H), 6.04 – 5.86 (m, 1H), 5.54 – 4.68 (m, 2H), 3.55 – 2.77 (m, 2H), 1.50 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 199.8, 187.5, 185.6, 151.8, 143.6, 141.2, 136.7, 136.1, 134.9, 133.8, 133.5, 129.7, 129.3, 128.9, 127.4, 125.2, 117.2, 53.3, 33.2, 26.5; **IR**: 3383, 2924, 1744, 1657, 1460, 1380, 1264, 1097, 918, 742 cm⁻¹; **[α]_D^{rt}** = -39 (c = 1.00, CHCl₃); HRMS (ESI): C₂₀H₁₆O₃+H, Calc: 305.1172, Found: 305.1169; HPLC: DAICEL CHIRALCEL IC, Hexane/iPrOH = 9/1, flow rate = 1.0 ml/min, retention time: t_{major} = 16.5, t_{minor} = 14.7, 93% ee.



(R)-2-(1-methyl-3-(3-methylbut-2-en-1-yl)-2-oxo-1,2-dihydronephthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4h

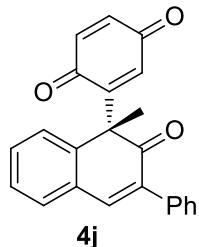
Using 10 mol % cat. 3g at rt with 37 h, 41 mg (61 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 30:1 - 20:1) as a yellow solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.43 – 7.34 (m, 1H), 7.31 (s, 1H), 7.29 – 7.16 (m, 2H), 7.03 (d, J = 2.4 Hz, 1H), 6.98 – 6.87 (m, 1H), 6.77 (dd, J = 10.1, 2.4 Hz, 1H), 6.61 (d, J = 10.1 Hz, 1H), 5.36 – 5.21 (m, 1H), 3.47 – 2.77 (m, 2H), 1.80 (s, 3H), 1.70 (s, 3H), 1.50 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 200.3, 187.5, 185.6, 151.9, 143.5, 140.3, 136.7, 136.1, 134.6, 134.5, 133.8, 129.6, 129.1, 129.1, 127.3, 125.1, 120.1, 53.4, 27.5, 26.4, 25.8, 17.8; **IR:** 3405, 2924, 1657, 1448, 1382, 1286, 1097, 998, 919, 759 cm⁻¹; [α]_D^{rt} = +25 (c = 1.00, CHCl₃); C₂₂H₂₀O₃+H, Calc: 333.1485, Found: 333.1484; HPLC: DAICEL CHIRALCEL AD, Hexane/EtOH = 7/3, flow rate = 1.0 ml/min, retention time: t_{major} = 8.3, t_{minor} = 6.8, 96% ee.



(R)-2-(3-benzyl-1-methyl-2-oxo-1,2-dihydronephthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4i

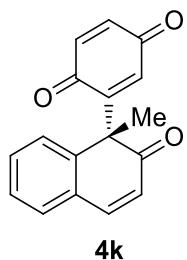
Using 10 mol % cat. 3g at rt with 24 h, 51 mg (72 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 10:1) as a yellow solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.37 – 7.15 (m, 9H), 7.02 (d, J = 2.4 Hz, 1H), 6.97 – 6.88 (m, 1H), 6.75 (dd, J = 10.1, 2.4 Hz, 1H), 6.61 (d, J = 10.1 Hz, 1H), 3.77 (dd, J = 37.9, 15.8 Hz, 2H), 1.46 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 199.9, 187.4, 185.6, 151.7, 143.6, 141.7, 138.9, 136.7, 136.1, 134.8, 133.8, 129.8, 129.3, 129.1, 128.8, 128.5, 127.3, 126.3, 125.1, 53.4, 35.2, 26.3; **IR:** 3314, 2926, 1663, 1454, 1382, 1286, 1096, 998, 919, 739 cm⁻¹; [α]_D^{rt} = -10 (c = 1.00, CHCl₃); HRMS

(ESI): C₂₄H₁₈O₃+H, Calc: 355.1329, Found: 355.1331; HPLC: DAICEL CHIRALCEL IC, Hexane/EtOH = 1/1, flow rate = 1.0 ml/min, retention time: t_{major} = 6.4, t_{minor} = 8.5, 95% ee.



(R)-2-(1-methyl-2-oxo-3-phenyl-1,2-dihydroronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4j

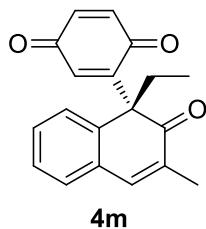
Using 10 mol % cat. 3g at rt with 48 h, 15 mg (22 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; ¹H NMR (300 MHz, CDCl₃) δ 7.68 (s, 1H), 7.55 (dd, J = 8.0, 1.5 Hz, 2H), 7.52 – 7.45 (m, 1H), 7.45 – 7.34 (m, 3H), 7.34 – 7.28 (m, 2H), 7.07 (d, J = 2.4 Hz, 1H), 6.99 – 6.91 (m, 1H), 6.79 (dd, J = 10.1, 2.4 Hz, 1H), 6.64 (d, J = 10.1 Hz, 1H), 1.62 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 199.0, 187.5, 185.7, 151.9, 143.9, 142.3, 136.7, 136.2, 135.4, 134.3, 133.8, 130.5, 129.9, 129.0, 128.8, 128.2, 128.2, 127.6, 125.3, 54.1, 26.5; IR: 3398, 2924, 1658, 1456, 1375, 1285, 1096, 1028, 919, 740 cm⁻¹; [α]_D^{rt} = -24 (c = 1.00, CHCl₃); C₂₃H₁₆O₃+H, Calc: 341.1172, Found: 341.1174; HPLC: DAICEL CHIRALCEL IC, Hexane/EtOH = 9/1, flow rate = 1.0 ml/min, retention time: t_{major} = 20.3, t_{minor} = 18.1, 91% ee.



(R)-2-(1-methyl-2-oxo-1,2-dihydroronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4k

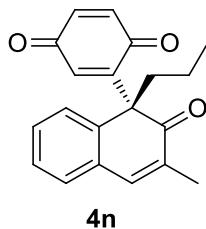
Using 10 mol % cat. 3g at rt with 60 h, 15 mg (28 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, J = 9.9 Hz, 1H), 7.51 – 7.40 (m, , 1H), 7.35 – 7.28 (m, 2H),

7.05 (d, $J = 2.4$ Hz, 1H), 6.99 – 6.90 (m, 1H), 6.78 (dd, $J = 10.1, 2.4$ Hz, 1H), 6.63 (d, $J = 10.1$ Hz, 1H), 6.29 (d, $J = 9.9$ Hz, 1H), 1.53 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 200.5, 187.4., 185.6, 151.5, 145.0, 144.2, 136.7, 136.2, 134.0, 130.3, 130.3, 128.4, 127.5, 125.5, 124.0, 53.4, 26.4. IR: 3313, 2926, 1656, 1598, 1452, 1398, 1338, 1287, 1097, 919, 830, 761, 607 cm^{-1} ; $[\alpha]_D^{rt} = -2$ $\text{c} = 1.00$, CHCl_3); HRMS (ESI): $\text{C}_{17}\text{H}_{12}\text{O}_3 + \text{H}$, Calc: 265.0859, Found: 265.0857; HPLC: DAICEL CHIRALCEL IA, Hexane/iPrOH = 8/2, flow rate = 1.0 ml/min, retention time: $t_{\text{major}} = 14.9$, $t_{\text{minor}} = 13.3$, 58% ee.



(R)-2-(1-ethyl-3-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4m

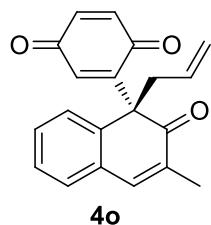
Using 10 mol % cat. 3g at rt with 24 h, 41 mg (71 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 7.38 (s, 1H), 7.36 – 7.31 (m, 1H), 7.30 – 7.17 (m, 2H), 7.04 (d, $J = 2.4$ Hz, 1H), 7.01 – 6.83 (m, 1H), 6.73 (dd, $J = 10.1, 2.4$ Hz, 1H), 6.57 (d, $J = 10.1$ Hz, 1H), 2.27 – 2.08 (m, 1H), 2.04 (d, $J = 1.1$ Hz, 3H), 2.00 – 1.83 (m, 1H), 0.59 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 200.9, 187.6, 185.7, 152.6, 141.8, 141.5, 136.7, 135.8, 133.7, 133.4, 131.1, 128.8, 128.8, 127.3, 125.6, 56.1, 34.7, 15.6, 7.3; IR: 3319, 2925, 1663, 1460, 1378, 1265, 1094, 909, 740 cm^{-1} ; $[\alpha]_D^{rt} = -73$ $\text{c} = 1.00$, CHCl_3); HRMS (ESI): $\text{C}_{19}\text{H}_{16}\text{O}_3 + \text{H}$, Calc: 293.1172, Found: 293.1171; HPLC: DAICEL CHIRALCEL IC, Hexane/EtOH = 9/1, flow rate = 1.0 ml/min, retention time: $t_{\text{major}} = 20.2$, $t_{\text{minor}} = 17.2$, 98% ee.



(R)-2-(3-methyl-2-oxo-1-propyl-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione,

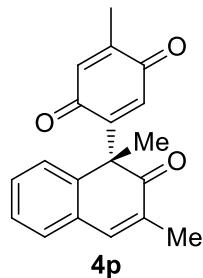
4n

Using 10 mol % cat. 3g at rt with 10 h, 41 mg (67 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.37 (s, 1H), 7.35 – 7.28 (m, 1H), 7.28 – 7.18 (m, 2H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.97 – 6.88 (m, 1H), 6.73 (dd, *J* = 10.1, 2.4 Hz, 1H), 6.57 (d, *J* = 10.1 Hz, 1H), 2.15 – 1.95 (m, 4H), 1.80 (td, *J* = 12.0, 3.2 Hz, 1H), 1.19 – 0.98 (m, 1H), 0.91 – 0.79 (m, 1H), 0.75 (t, *J* = 6.3 Hz, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 200.9, 187.7, 185.7, 152.6, 142.2, 141.4, 136.7, 135.8, 133.6, 133.4, 130.9, 128.9, 128.8, 127.3, 125.6, 55.9, 43.9, 15.9, 15.7, 14.3; **IR:** 3312, 2925, 1657, 1458, 1378, 1281, 1090, 902, 761 cm⁻¹; **[α]_D^{rt}** = -56 (c = 1.00, CHCl₃); C₂₀H₁₈O₃+H, Calc: 307.1329, Found: 307.1328; HPLC: DAICEL CHIRALCEL IC, Hexane/EtOH = 8/2, flow rate = 1.0 ml/min, retention time: t_{major} = 8.9, t_{minor} = 7.0, 99% ee.



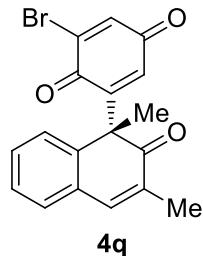
(R)-2-(1-allyl-3-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4o

Using 10 mol % cat. 3g at rt with 24 h, 38 mg (63 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.38 – 7.29 (m, 2H), 7.28 – 7.20 (m, 2H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.97 (dd, *J* = 6.1, 2.7 Hz, 1H), 6.75 (dd, *J* = 10.1, 2.4 Hz, 1H), 6.59 (d, *J* = 10.1 Hz, 1H), 5.38 – 5.18 (m, 1H), 4.94 – 4.75 (m, 2H), 2.71 (ddd, *J* = 18.9, 12.4, 7.3 Hz, 2H), 2.00 (d, *J* = 1.3 Hz, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 200.2, 187.5, 185.6, 151.9, 141.5, 141.4, 136.7, 135.9, 133.6, 130.7, 130.0, 128.9, 128.9, 127.5, 125.7, 119.3, 56.0, 45.5, 15.6; **IR:** 3317, 2924, 1660, 1460, 1379, 1265, 1092, 1017, 913, 741 cm⁻¹; **[α]_D^{rt}** = -75 (c = 1.00, CHCl₃); HRMS (ESI): C₂₀H₁₆O₃+H, Calc: 305.1172, Found: 305.1172; HPLC: DAICEL CHIRALCEL IC, Hexane/iPrOH = 9/1, flow rate = 1.0 ml/min, retention time: t_{major} = 16.8, t_{minor} = 14.2, 95% ee.



(R)-2-(1,3-dimethyl-2-oxo-1,2-dihydroronaphthalen-1-yl)-5-methylcyclohexa-2,5-diene-1,4-dione, 4p.

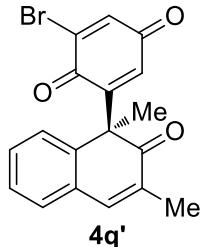
Using 10 mol % cat. 3g at rt with 48 h, 20 mg (35 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.38 (s, 1H), 7.36 – 7.30 (m, 1H), 7.29 – 7.15 (m, 2H), 7.01 (s, 1H), 6.95 – 6.88 (m, 1H), 6.44 (d, *J* = 1.6 Hz, 1H), 2.05 (t, *J* = 1.6 Hz, 6H), 1.48 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 200.7, 188.0, 185.9, 151.9, 145.6, 143.8, 141.2, 133.8, 133.5, 131.5, 129.3, 129.1, 129.0, 127.3, 125.3, 52.9, 26.6, 16.0, 15.4. **IR:** 3280, 2924, 1743, 1656, 1440, 1376, 1342, 1249, 1203, 1102, 1033, 918, 760, 737 cm⁻¹; [α]_D^{rt} = -4 (c = 1.00, CHCl₃); HRMS (ESI): C₁₉H₁₆O₃+H, Calc: 293.1172, Found: 293.1184; HPLC: DAICEL CHIRALCEL IC, Hexane/iPrOH = 8/2, flow rate = 1.0 ml/min, retention time: t_{major} = 11.3, t_{minor} = 8.7, 82% ee.



(R)-2-bromo-6-(1,3-dimethyl-2-oxo-1,2-dihydroronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione, 4q

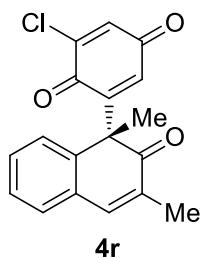
Using 10 mol % cat. 3g at rt with 36 h, 15 mg (21 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 15:1 - 10:1) as a yellow solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.40 (s, 1H), 7.36 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.21 (s, 1H), 7.12 (s, 1H), 6.93 – 6.85 (m, 1H), 2.05 (d, *J* = 1.3 Hz, 3H), 1.50 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 200.4, 183.1, 179.5, 152.4, 143.3, 141.5, 138.1, 137.3, 133.2, 131.4, 129.4, 129.1, 129.0, 127.5, 125.2, 53.2, 26.6, 15.9. **IR:** 3313, 2925, 1656, 1745, 1665, 1655, 1594, 1459, 1377,

1197, 1035, 1001, 912, 759, 737 cm^{-1} ; $[\alpha]_D^{rt} = -15$ ($c = 1.00, \text{CHCl}_3$); HRMS (ESI): $C_{18}\text{H}_{13}\text{BrO}_3\text{Na}$, Calc: 378.9940, Found: 378.9951; HPLC: DAICEL CHIRALCEL IA, Hexane/iPrOH = 8/2, flow rate = 1.0 ml/min, retention time: $t_{\text{major}} = 12.5$, $t_{\text{minor}} = 10.5$, 74% ee.



(S)-2-bromo-6-(1,3-dimethyl-2-oxo-1,2-dihydroronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione e, 4q'.

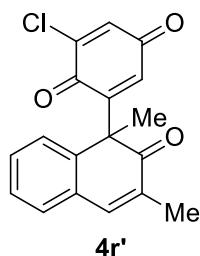
Using 10 mol % cat. 3g at rt with 22 h, 39 mg (55 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; **$^1\text{H NMR}$** (300 MHz, CDCl_3) δ 7.40 (s, 1H), 7.35 (dd, $J = 7.2, 1.7$ Hz, 1H), 7.31 – 7.22 (m, 2H), 7.21 (s, 1H), 7.12 (s, 1H), 6.94 – 6.82 (m, 1H), 2.05 (d, $J = 1.2$ Hz, 3H), 1.50 (s, 3H). **$^{13}\text{C NMR}$** (75 MHz, CDCl_3) δ 200.4, 183.1, 179.5, 152.4, 143.3, 141.5, 138.1, 137.3, 133.2, 131.4, 129.4, 129.1, 129.0, 127.5, 125.2, 53.2, 26.6, 15.9. **IR:** 3301, 2925, 1743, 1666, 1595, 1458, 1375, 1259, 1197, 1001, 912, 738 cm^{-1} ; $[\alpha]_D^{rt} = 24$ ($c = 1.00, \text{CHCl}_3$); HRMS (ESI): $C_{18}\text{H}_{13}\text{ClO}_3\text{Na}$, Calc: 378.9940, Found: 378.9956; HPLC: DAICEL CHIRALCEL IA, Hexane/iPrOH = 8/2, flow rate = 1.0 ml/min, retention time: $t_{\text{major}} = 11.0$, $t_{\text{minor}} = 13.0$, 45% ee.



(R)-2-chloro-6-(1,3-dimethyl-2-oxo-1,2-dihydroronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione e, 4r

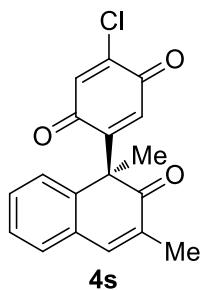
Using 10 mol % cat. 3g at rt with 40 h, 32 mg (51 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; **$^1\text{H NMR}$**

NMR (300 MHz, CDCl₃) δ 7.40 (s, 1H), 7.39 – 7.32 (m, 1H), 7.31 – 7.18 (m, 2H), 7.17 (s, 1H), 6.96 – 6.86 (m, 1H), 6.84 (s, 1H), 2.05 (d, *J* = 1.1 Hz, 3H), 1.51 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 200.4, 183.5, 179.6, 152.5, 143.9, 143.3, 141.5, 133.8, 133.5, 131.4, 129.5, 129.2, 129.0, 127.5, 125.2, 53.2, 26.6, 16.0. **IR:** 3394, 2924, 1656, 1593, 1457, 1379, 1261, 1027, 808, 607 cm⁻¹; [α]_D^{rt} = -33 (c = 1.00, CHCl₃); HRMS (ESI): C₁₈H₁₃ClO₃+H, Calc: 313.0626, Found: 313.0624; HPLC: DAICEL CHIRALCEL IC, Hexane/iPrOH = 9/1, flow rate = 1.0 ml/min, retention time: t_{major} = 12.5, t_{minor} = 13.4, 89% ee.



**2-chloro-6-(1,3-dimethyl-2-oxo-1,2-dihydronephthalen-1-yl)cyclohexa-2,5-diene-1,4-dione,
4r'**

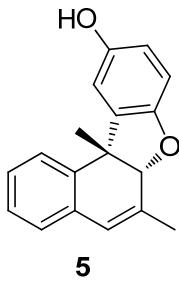
Using 10 mol % cat. 3g at rt with 22 h, 40 mg (64 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 10:1) as a yellow solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.40 (s, 1H), 7.39 – 7.32 (m, 1H), 7.31 – 7.18 (m, 2H), 7.17 (s, 1H), 6.96 – 6.86 (m, 1H), 6.84 (s, 1H), 2.05 (d, *J* = 1.1 Hz, 3H), 1.51 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 200.4, 183.5, 179.6, 152.5, 143.9, 143.3, 141.5, 133.8, 133.5, 131.4, 129.5, 129.2, 129.0, 127.5, 125.2, 53.2, 26.6, 16.0. **IR:** 3394, 2924, 1656, 1593, 1457, 1379, 1261, 1027, 808, 607 cm⁻¹; HRMS (ESI): C₁₈H₁₃ClO₃+H, Calc: 313.0626, Found: 313.0624.



(S)-2-chloro-5-(1,3-dimethyl-2-oxo-1,2-dihydronephthalen-1-yl)cyclohexa-2,5-diene-1,4-dion

e, 4s.

Using 10 mol % cat. 3g at rt with 30 h, 26 mg (41 % yield) of the pure product was obtained by silica gel column chromatography (petroleum/ethyl acetate = 20:1 - 15:1) as a yellow solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.41 (s, 1H), 7.36 (dd, J = 7.3, 1.6 Hz, 1H), 7.31 – 7.18 (m, 2H), 7.05 (d, J = 2.4 Hz, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.94 – 6.86 (m, 1H), 2.06 (d, J = 1.2 Hz, 3H), 1.51 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 200.3, 184.9, 178.3, 151.8, 144.2, 143.1, 141.6, 134.2, 133.4, 131.5, 129.5, 129.2, 129.1, 127.6, 125.1, 53.6, 26.9, 15.9. **IR:** 3304, 3054, 2926, 1662, 1594, 1458, 1422, 1265, 1014, 896, 739 cm⁻¹; [α]_D^{rt} = 7°(c = 1.00, CHCl₃); HRMS (ESI): C₁₈H₁₃ClO₃+H, Calc: 313.0626, Found: 313.0640; HPLC: DAICEL CHIRALCEL IA, Hexane/iPrOH = 8/2, flow rate = 1.0 ml/min, retention time: t_{major} = 7.6, t_{minor} = 9.3, 18% ee.



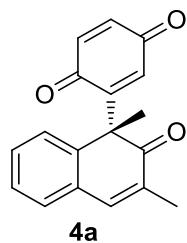
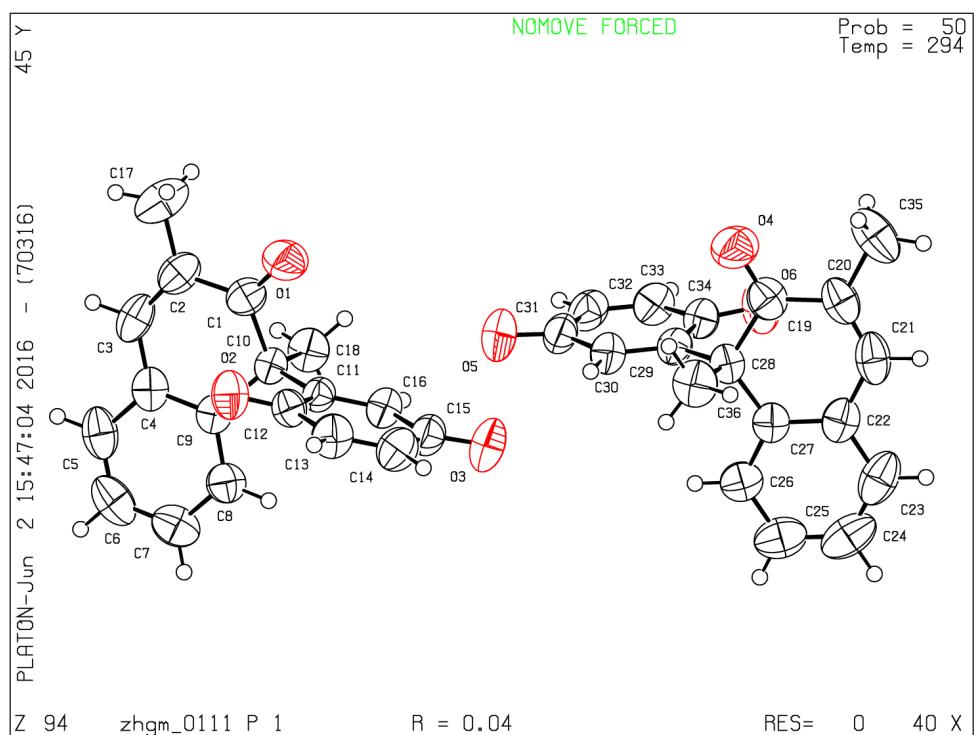
5

(6aR,11bR)-6,11b-dimethyl-6a,11b-dihydronaphtho[2,1-b]benzofuran-10-ol, 5

The solvent was removed under vacuum and residue was chromatographed on silica gel (petroleum ether/AcOEt 15:1) to provide the pure desired products 40 mg (75 % yield) as a white solid; **¹H NMR** (300 MHz, CDCl₃) δ 7.49 – 7.38 (m, 1H), 7.23 – 7.08 (m, 2H), 7.04 (dd, J = 7.2, 1.6 Hz, 1H), 6.86 (d, J = 2.6 Hz, 1H), 6.66 (d, J = 8.4 Hz, 1H), 6.56 (dd, J = 8.5, 2.6 Hz, 1H), 6.42 (s, 1H), 4.82 (s, 1H), 4.58 (s, 1H), 2.09 (d, J = 0.8 Hz, 3H), 1.58 (s, 3H), **¹³C NMR** (75 MHz, CDCl₃) δ 152.3, 149.8, 137.2, 136.3, 131.0, 130.7, 127.6, 127.1, 126.9, 126.9, 126.1, 114.3, 111.6, 109.7, 90.8, 47.5, 27.9, 21.1; **IR:** 3395, 2923, 1656, 1602, 1489, 1376, 1268, 1192, 1068, 947, 812, 753 cm⁻¹; [α]_D^{rt} = 117 °(c = 1.00, CHCl₃); HRMS (ESI): C₁₈H₁₆O₂+H, Calc: 265.1223, Found: 265.1225; HPLC: DAICEL CHIRALCEL IA, Hexane/EtOH = 95/5, flow rate = 1.0 ml/min, retention time: t_{major} = 9.7, t_{minor} = 13.7, 98% ee.

7. Determination of the absolute configuration 4.

X-ray Structure of 4a:



Bond precision:

C-C = 0.0069 Å

Wavelength=1.54184

Cell:

a=7.6607(7)

b=9.2315(7)

c=11.1270(8)

alpha=72.019(7)

beta=79.887(7)

gamma=74.428(7)

Temperature: 294 K

	Calculated	Reported
Volume	717.29(11)	717.29(11)
Space group	P 1	P 1
Hall group	P 1	P 1

Moiety formula	C18 H14 O3	C18 H14 O3
Sum formula	C18 H14 O3	C18 H14 O3
Mr	278.29	278.29
Dx,g cm ⁻³	1.288	1.289
Z	2	2
Mu (mm ⁻¹)	0.708	0.708
F000	292.0	292.0
F000'	292.91	
h,k,lmax	9,11,13	9,11,13
Nref	5446[2723]	4653
Tmin,Tmax	0.887,0.906	0.869,1.000
Tmin'	0.887	

Correction method= # Reported T Limits: Tmin=0.869 Tmax=1.000 AbsCorr =

MULTI-SCAN

Data completeness= 1.71/0.85 Theta(max)= 69.915

R(reflections)= 0.0429(3320) wR2(reflections)= 0.1185(4653)

S = 1.056 Npar= 383

8. HPLC Analytic Conditions of 4 and 5:

All products are separated by using DAICEL CHIRALCEL column.

entry	product	Chiralcel column	Mobile phase	flow rate ml/min	Retention Time (min)	ee (%)
1		IC	H/E = 1/1	1.0	$t_{\text{major}} = 7.3, t_{\text{minor}} = 6.2$	98
2		IC	H/E = 8/2	1.0	$t_{\text{major}} = 11.0, t_{\text{minor}} = 8.2$	98
3		IC	H/E = 8/2	1.0	$t_{\text{major}} = 9.4, t_{\text{minor}} = 7.4$	98
4		IC	H/E = 6/4	1.0	$t_{\text{major}} = 6.3, t_{\text{minor}} = 5.2$	96
5		IC	H/E = 8/2	1.0	$t_{\text{major}} = 7.8, t_{\text{minor}} = 6.0$	96

6		IA	H/E = 8/2	1.0	$t_{\text{major}} = 18.3, t_{\text{minor}} = 8.7$	99
7		IC	H/E = 9/1	1.0	$t_{\text{major}} = 16.5, t_{\text{minor}} = 14.7$	93
8		AD	H/E = 7/3	1.0	$t_{\text{major}} = 8.3, t_{\text{minor}} = 6.8$	96
9		IC	H/E = 1/1	1.0	$t_{\text{major}} = 8.5, t_{\text{minor}} = 6.4$	95
10		IC	H/E = 9/1	1.0	$t_{\text{major}} = 20.4, t_{\text{minor}} = 18.1$	91
11		IA	H/I=8/2	1.0	$t_{\text{major}} = 14.9, t_{\text{minor}} = 13.3$	58

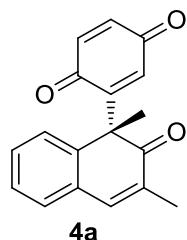
12		IC	H/I = 9/1	1.0	$t_{\text{major}} = 20.2, t_{\text{minor}} = 17.2$	98
13		IC	H/I = 8/2	1.0	$t_{\text{major}} = 8.9, t_{\text{minor}} = 7.0$	99
14		IC	H/E = 9/1	1.0	$t_{\text{major}} = 16.8, t_{\text{minor}} = 14.2$	95
15		IC	H/E = 8/2	1.0	$t_{\text{major}} = 11.3, t_{\text{minor}} = 8.7$	82
16		IA	H/E = 8/2	1.0	$t_{\text{major}} = 12.5, t_{\text{minor}} = 10.5$	74
17		IA	H/E = 8/2	1.0	$t_{\text{major}} = 11.0, t_{\text{minor}} = 13.0$	45

18		IC	H/E = 9/1	1.0	$t_{\text{major}} = 12.5, t_{\text{minor}} = 13.4$	89
19		IA	H/E=8/2	1.0	$t_{\text{major}} = 7.6, t_{\text{minor}} = 9.3$	18
20		IA	H/I = 95/5	1.0	$t_{\text{major}} = 13.7, t_{\text{minor}} = 9.7$	98

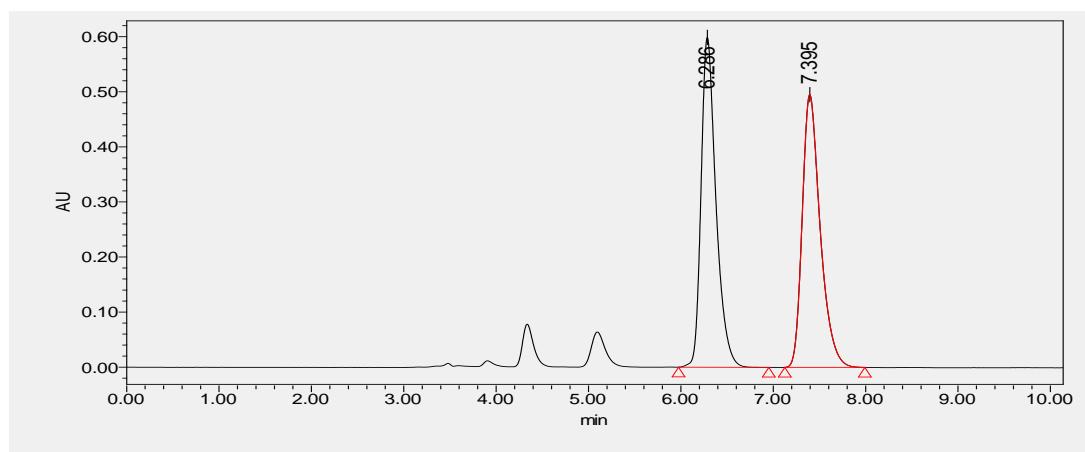
9. Copies of HPLC spectra for 4 and 5.

(R)-2-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

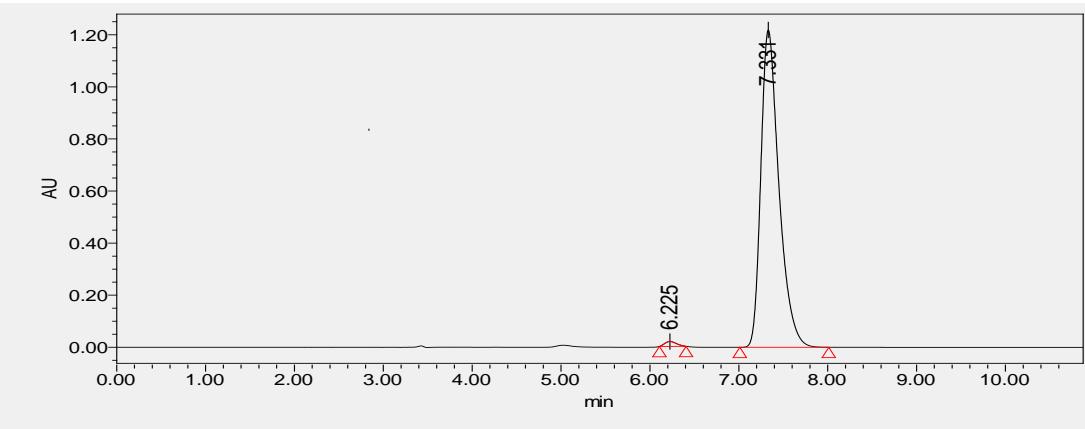
4a (Table 2)



Chiralpak IC column, hexane/EtOH (1:1), flow rate 1.0 mL/min



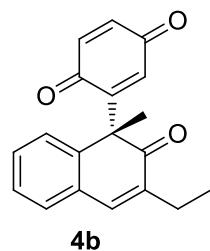
	Retention time	Area	% Area	Height	Integral type
1	6.286	6703713	50.03	598924	bb
2	7.395	6695800	49.97	495218	bb



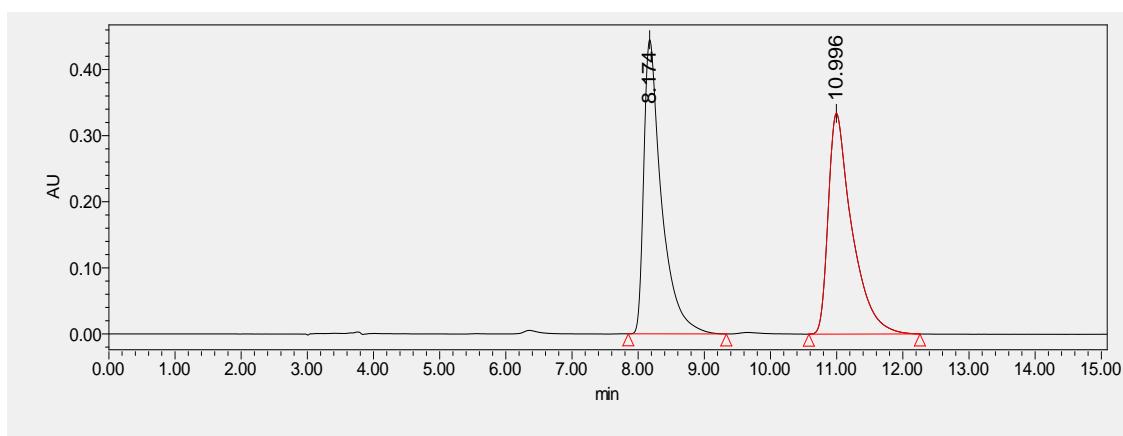
	Retention time	Area	% Area	Height	Integral type
1	6.225	172225	0.99	18739	bb
2	7.331	17223772	99.01	1218144	bb

(R)-2-(3-ethyl-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

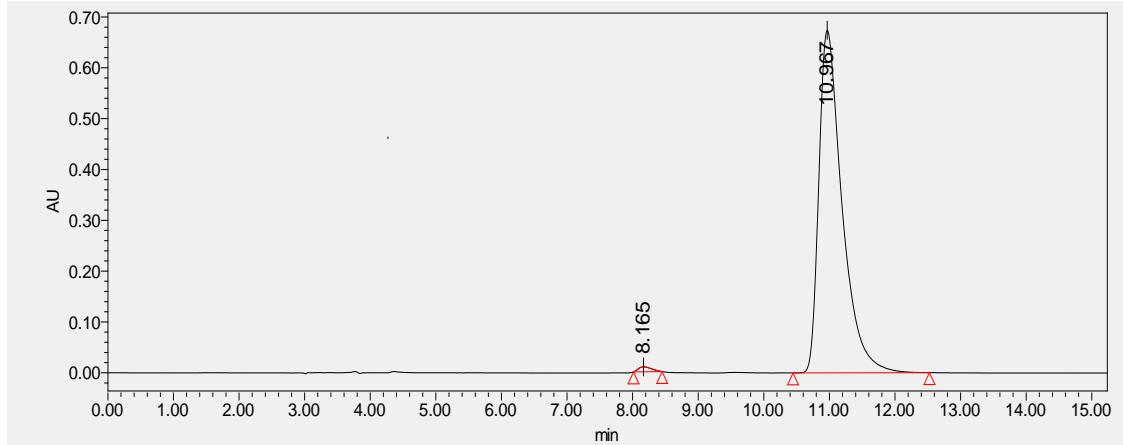
4b (Table 2)



Chiralpak IC column, hexane/EtOH (8:2), flow rate 1.0 mL/min



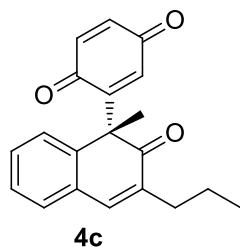
	Retention time	Area	% Area	Height	Integral type
1	8.174	8266822	49.88	444993	bb
2	10.996	8307541	50.12	333850	bb



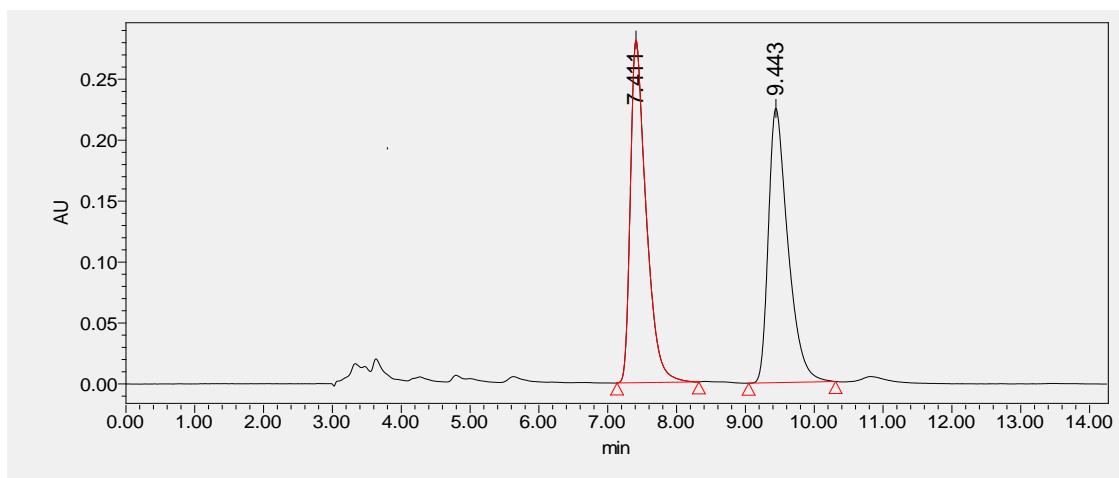
	Retention time	Area	% Area	Height	Integral type
1	8.165	139575	0.84	9976	bb
2	10.967	16557871	99.16	673993	bb

(R)-2-(1-methyl-2-oxo-3-propyl-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

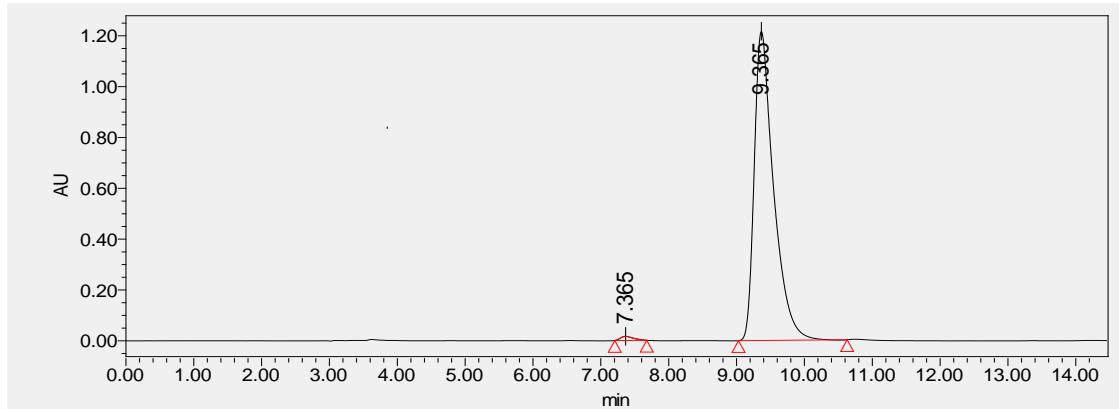
4c (Table 2)



Chiralpak IC column, hexane/EtOH (8:2), flow rate 1.0 mL/min



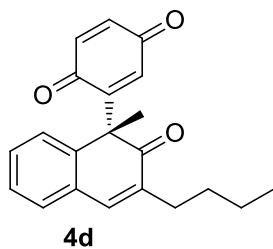
	Retention time	Area	% Area	Height	Integral type
1	7.411	4458380	50.14	281075	bb
2	9.443	4433817	49.86	225089	bb



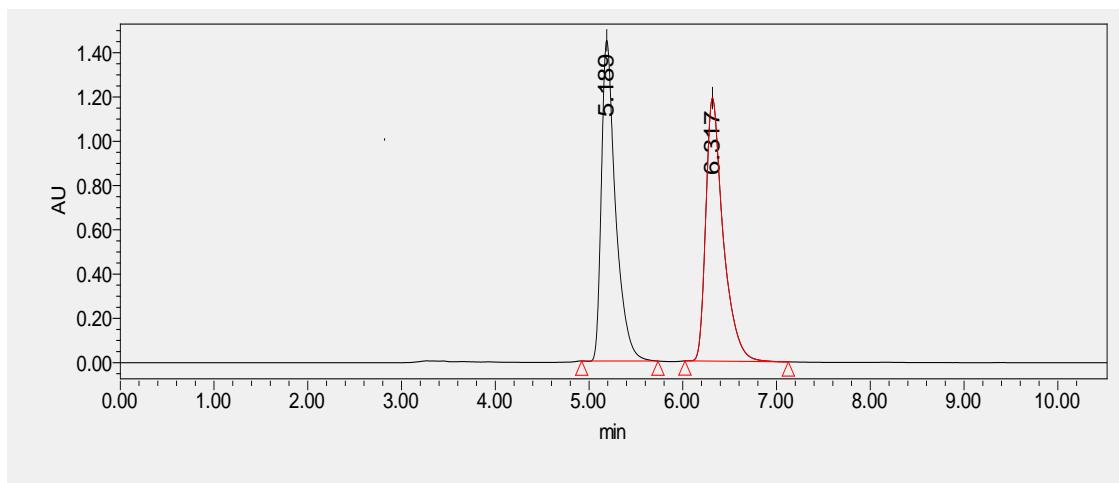
	Retention time	Area	% Area	Height	Integral type
1	7.365	212672	0.88	16211	bb
2	9.365	24087752	99.12	1216435	bb

(R)-2-(3-butyl-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

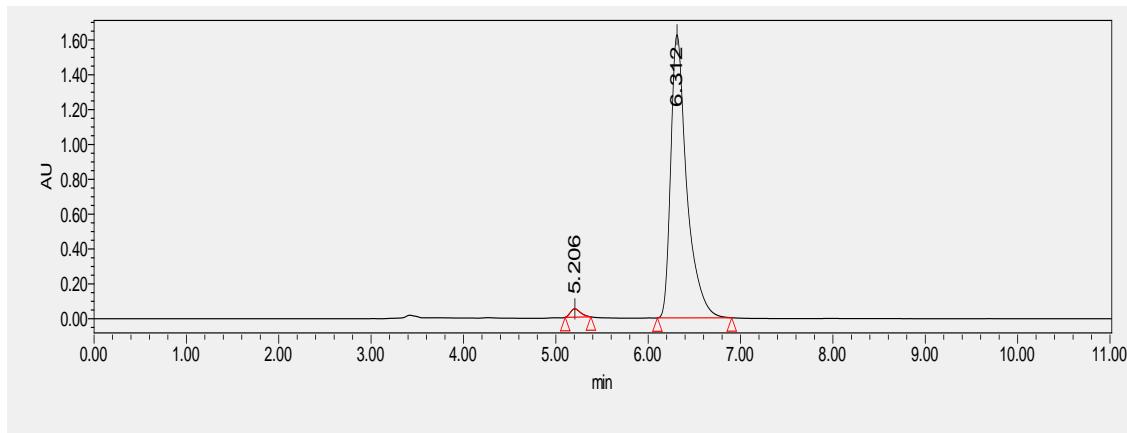
4d (Table 2)



Chiralpak IC column, hexane/EtOH (6:4), flow rate 1.0 mL/min



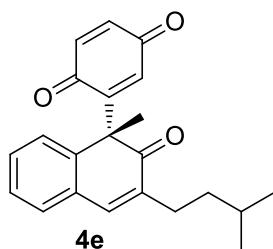
	Retention time	Area	% Area	Height	Integral type
1	5.189	15165442	49.81	1448855	bb
2	6.317	15283257	50.19	1188509	bb



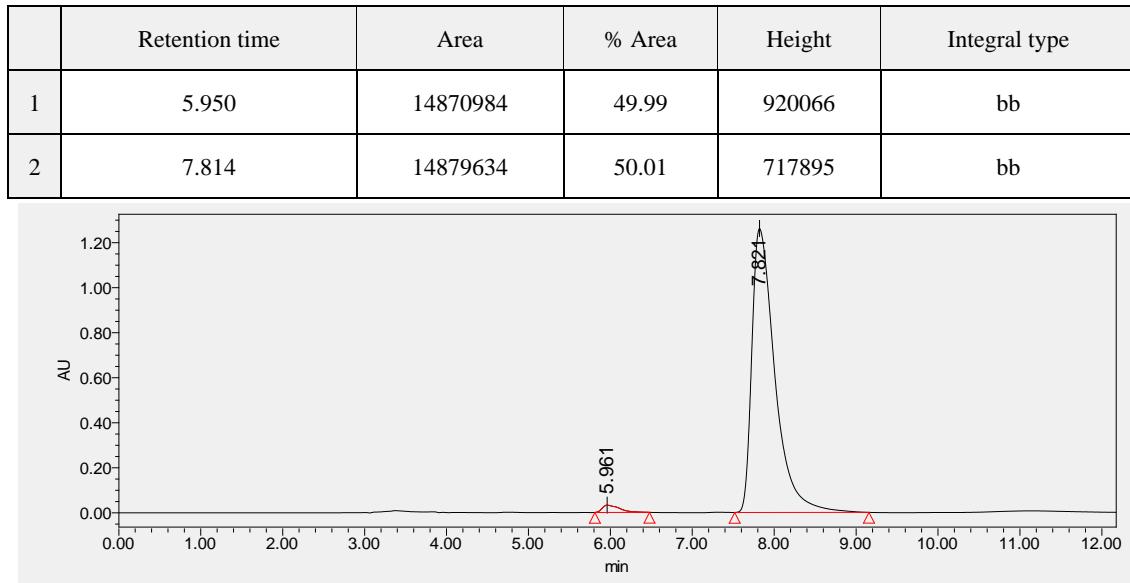
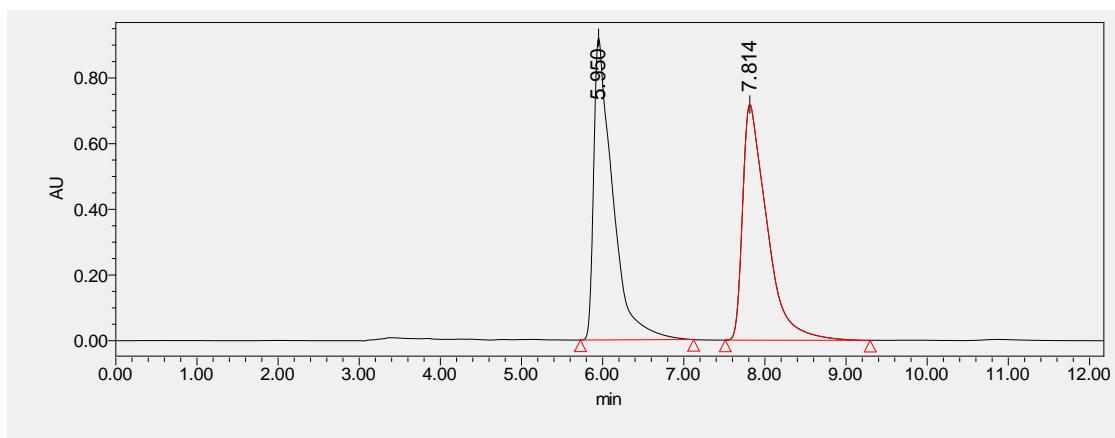
	Retention time	Area	% Area	Height	Integral type
1	5.206	364486	1.83	47728	bb
2	6.312	19567242	98.17	1625305	bb

(R)-2-(3-isopentyl-1-methyl-2-oxo-1,2-dihydroronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

4e (Table 2)

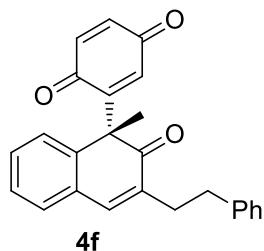


Chiralpak IC column, hexane/EtOH (8:2), flow rate 1.0 mL/min

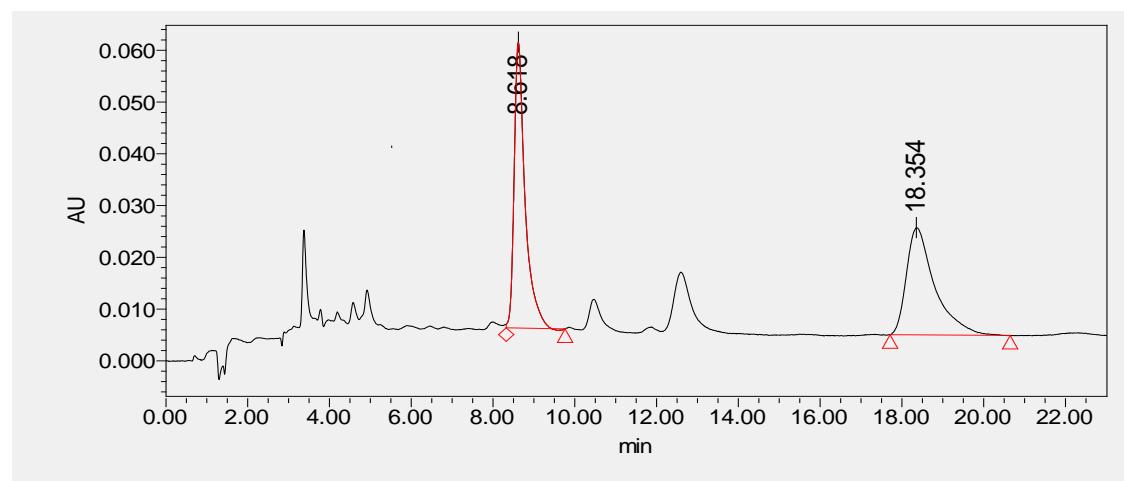


(R)-2-(1-methyl-2-oxo-3-phenethyl-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

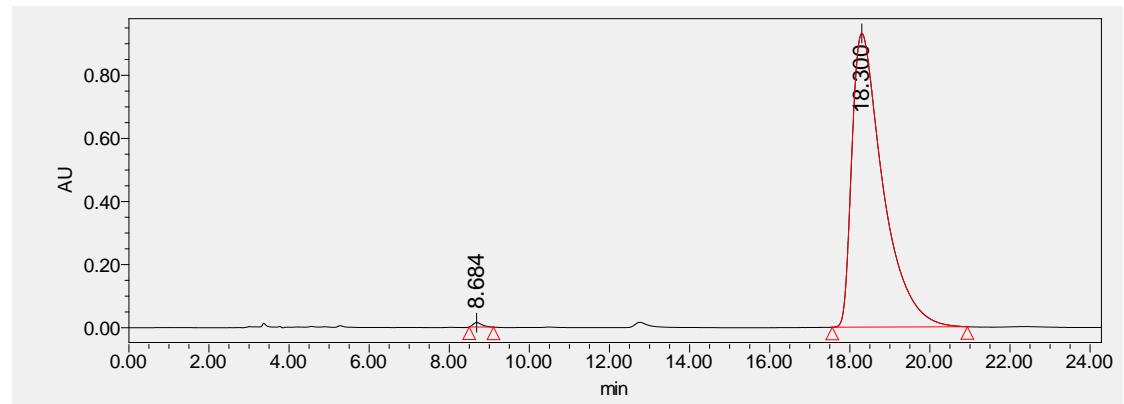
4f (Table 2)



Chiralpak IA column, hexane/EtOH (8:2), flow rate 1.0 mL/min



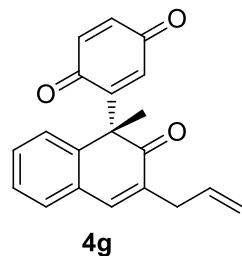
	Retention time	Area	% Area	Height	Integral type
1	8.618	1024247	50.73	55193	vb
2	18.354	994605	49.27	20725	bb



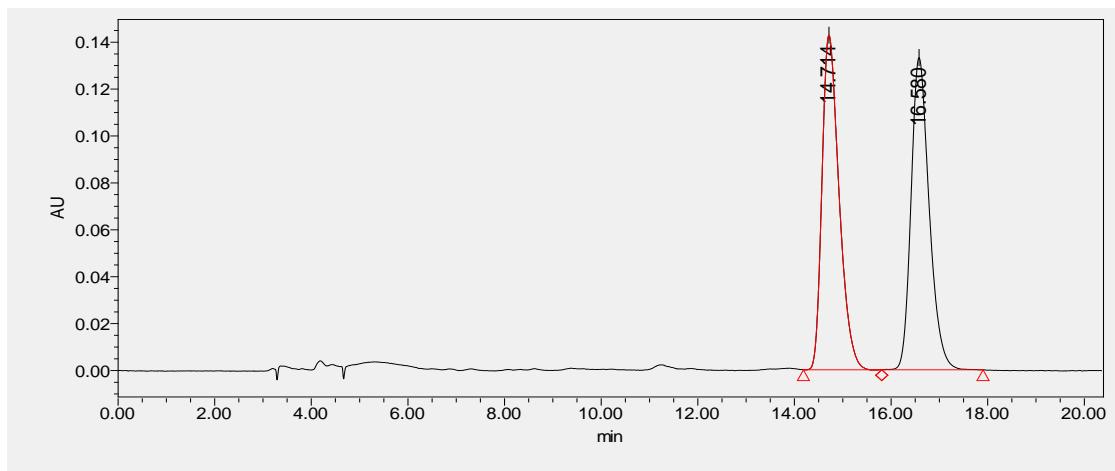
	Retention time	Area	% Area	Height	Integral type
1	8.684	219647	0.44	14178	bb
2	18.300	49967050	99.56	930727	bb

(R)-2-(3-allyl-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

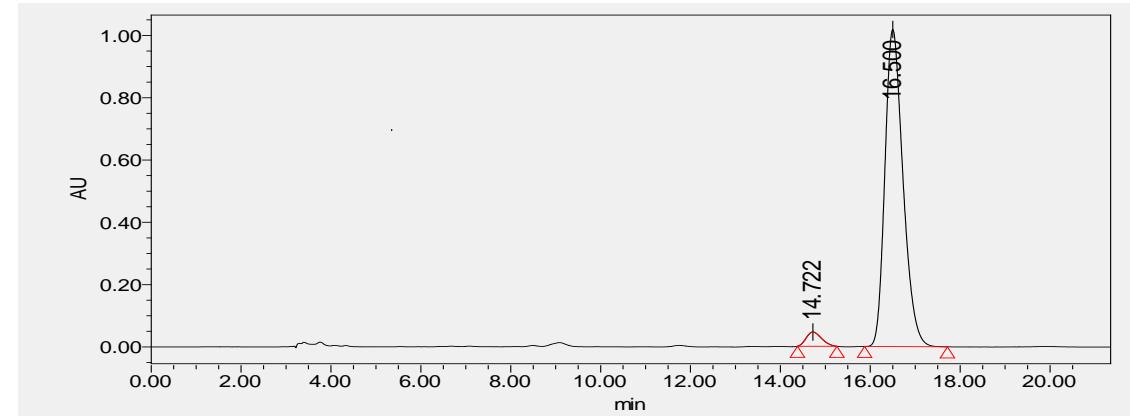
4g (Table 2)



Chiralpak IC column, hexane/EtOH (9:1), flow rate 1.0 mL/min



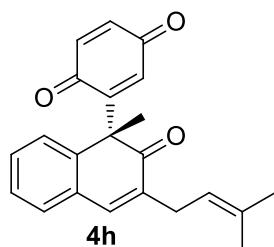
	Retention time	Area	% Area	Height	Integral type
1	14.714	3500299	50.23	142646	bv
2	16.580	3467893	49.77	133081	vb



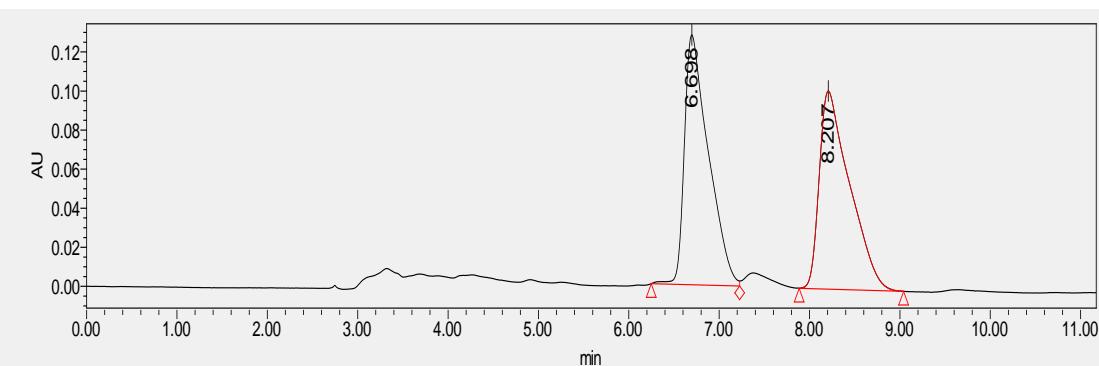
	Retention time	Area	% Area	Height	Integral type
1	14.722	1084102	3.67	45952	bb
2	16.500	28469181	96.33	1018032	bb

(R)-2-(1-methyl-3-(3-methylbut-2-en-1-yl)-2-oxo-1,2-dihydroronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

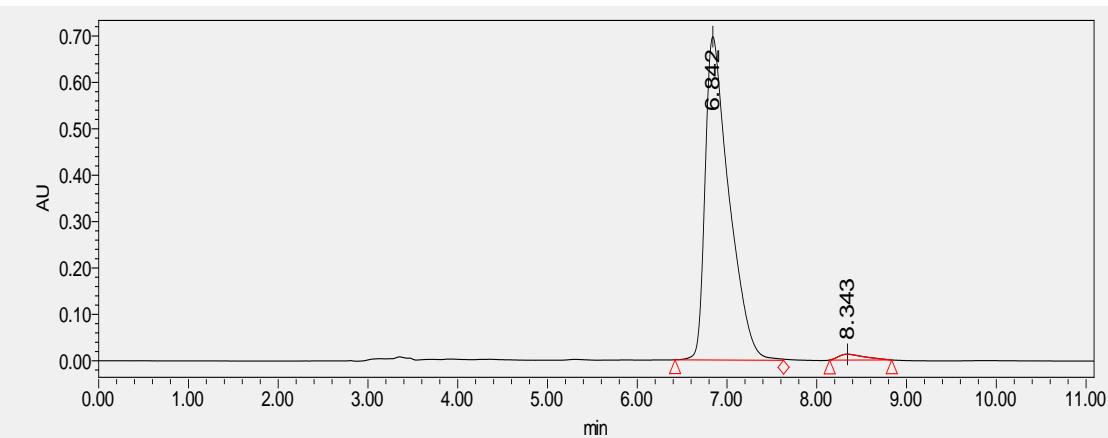
4h (Table 2)



Chiralpak AD column hexane/EtOH (7:3), flow rate 1.0 mL/min



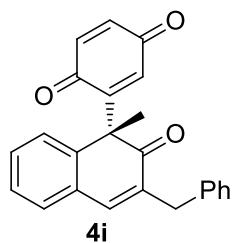
	Retention time	Area	% Area	Height	Integral type
1	6.698	2365282	49.99	127851	bv
2	8.207	2366468	50.01	101432	bb



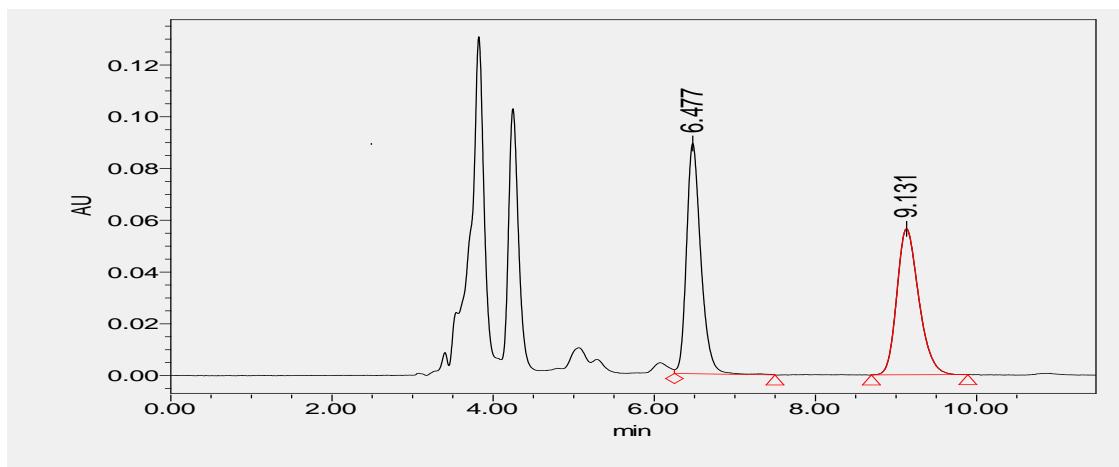
	Retention time	Area	% Area	Height	Integral type
1	6.842	12854338	98.08	696610	bv
2	8.343	251814	1.92	12468	bb

(R)-2-(3-benzyl-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

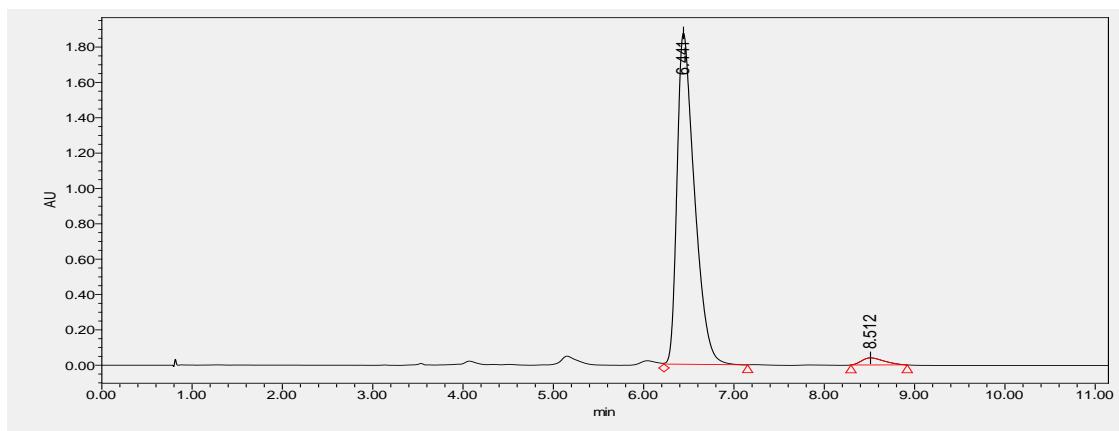
4i (Table 2)



Chiralpak IC column, hexane/EtOH (1:1), flow rate 1.0 mL/min



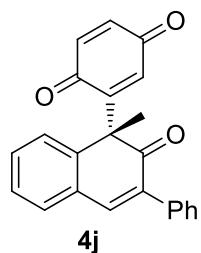
	Retention time	Area	% Area	Height	Integral type
1	6.477	1101256	50.82	88996	vb
2	9.131	1065755	49.18	56405	bb



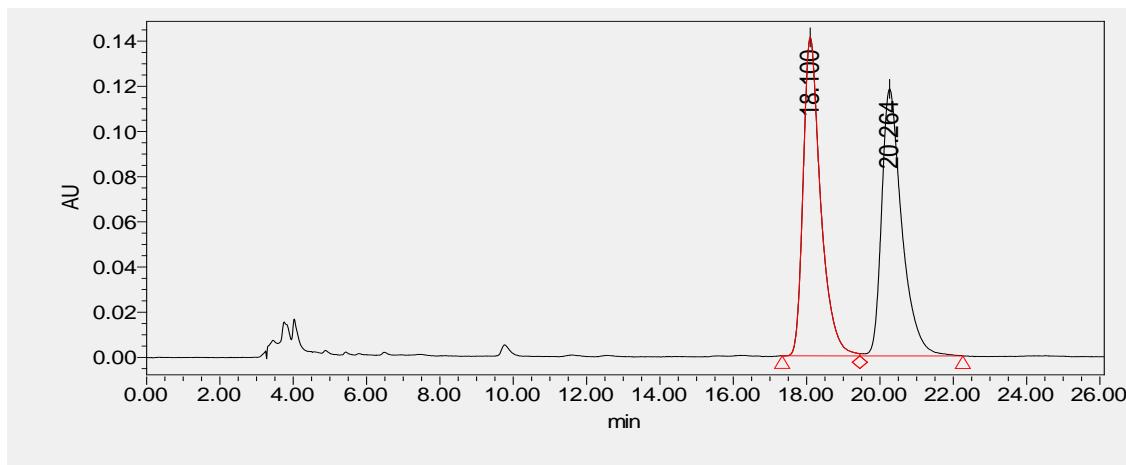
	Retention time	Area	% Area	Height	Integral type
1	6.441	25072607	97.30	1874404	vb
2	8.512	695034	2.70	40307	bb

(R)-2-(1-methyl-2-oxo-3-phenyl-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

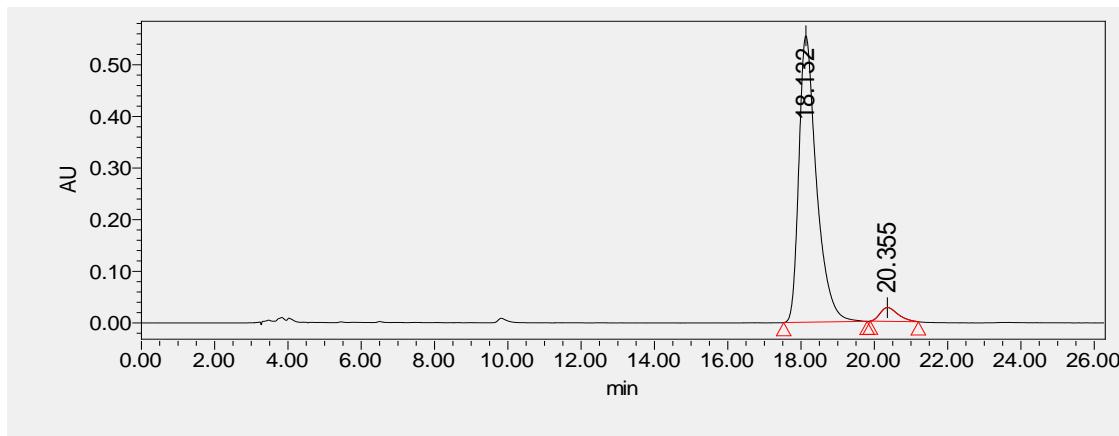
4j (Table 2)



Chiralpak IC column, hexane/EtOH (9:1), flow rate 1.0 mL/min



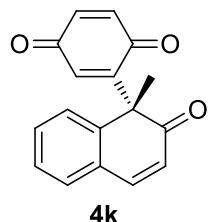
	Retention time	Area	% Area	Height	Integral type
1	18.100	4665316	50.74	140942	bv
2	20.264	4528427	49.26	118177	vb



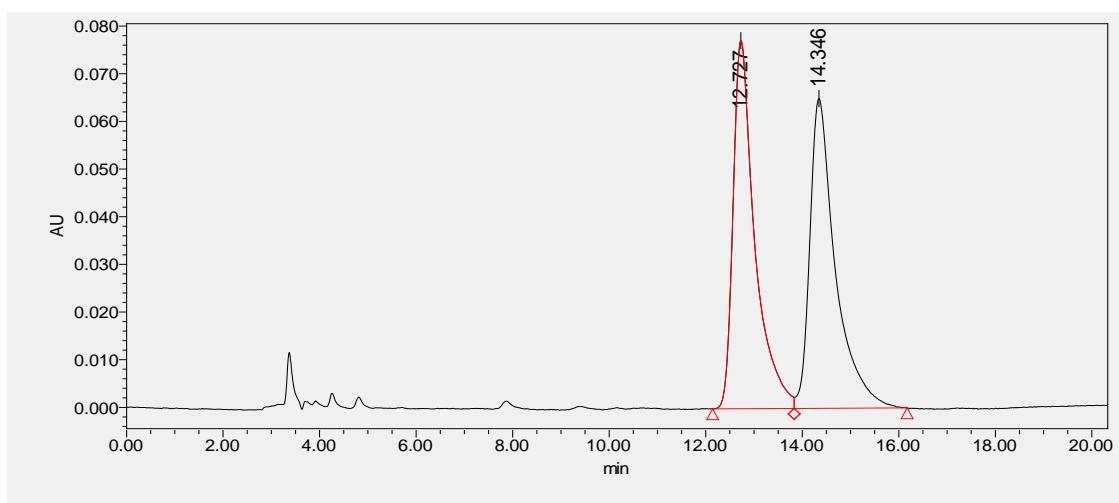
	Retention time	Area	% Area	Height	Integral type
1	18.132	18511410	95.35	554939	bb
2	20.355	902732	4.65	26745	bb

(R)-2-(1-methyl-2-oxo-1,2-dihydroronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

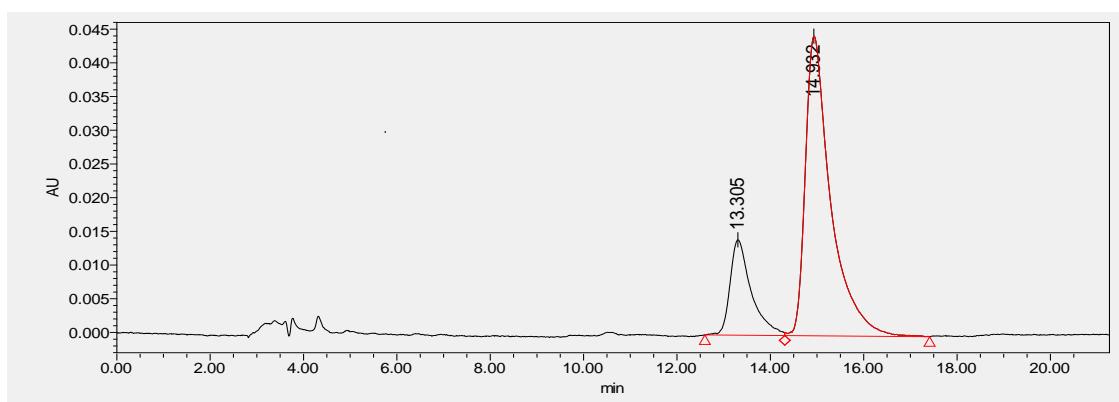
4k (Table 2)



Chiralpak IA column, hexane/iPrOH (8:2), flow rate 1.0 mL/min



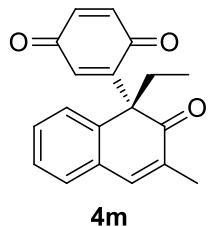
	Retention time	Area	% Area	Height	Integral type
1	12.727	2415085	50.26	77207	bv
2	14.346	2390033	49.74	65006	vb



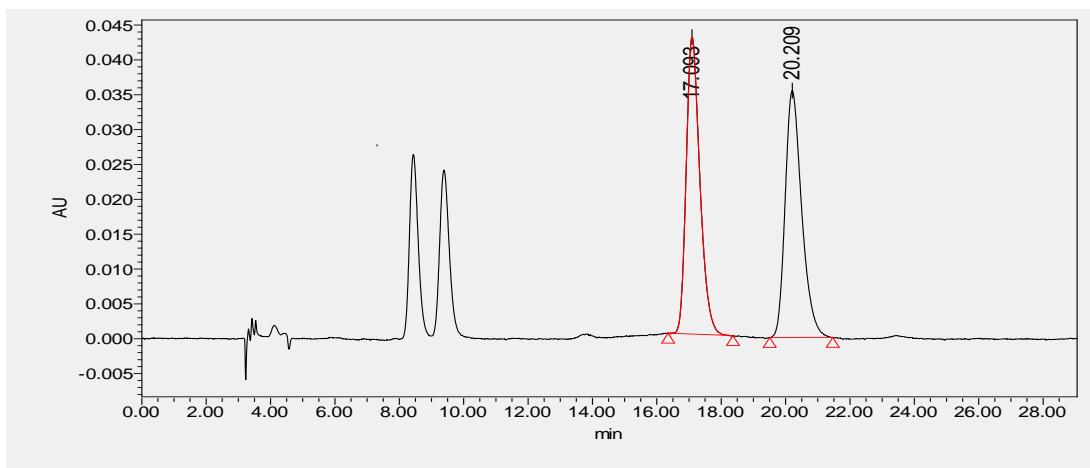
	Retention time	Area	% Area	Height	Integral type
1	13.305	445649	20.94	14156	bv
2	14.932	1682452	79.06	44441	vb

(R)-2-(1-ethyl-3-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

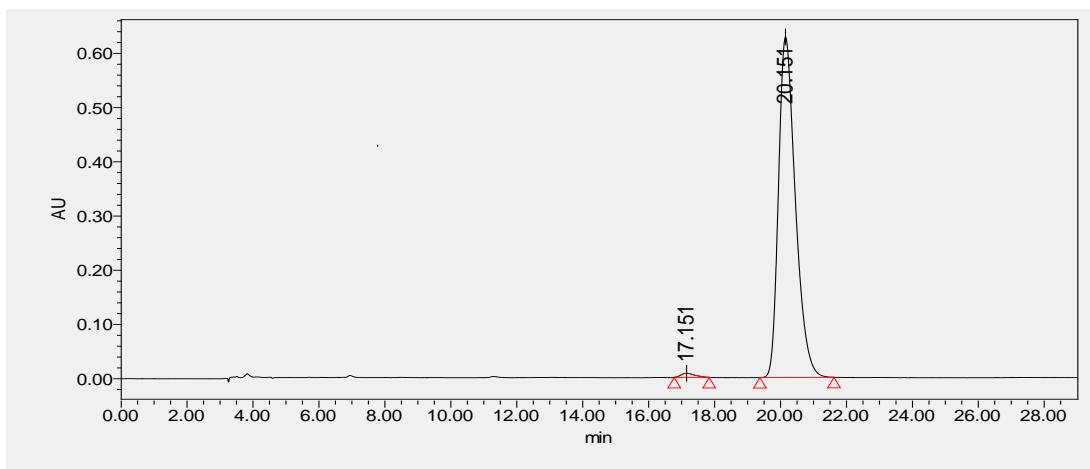
4m (Table 2)



Chiralpak IC column, hexane/EtOH (9:1), flow rate 1.0 mL/min



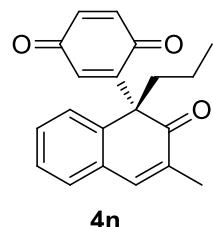
	Retention time	Area	% Area	Height	Integral type
1	17.093	1258384	49.89	42592	bb
2	20.209	1263874	50.11	35417	bb



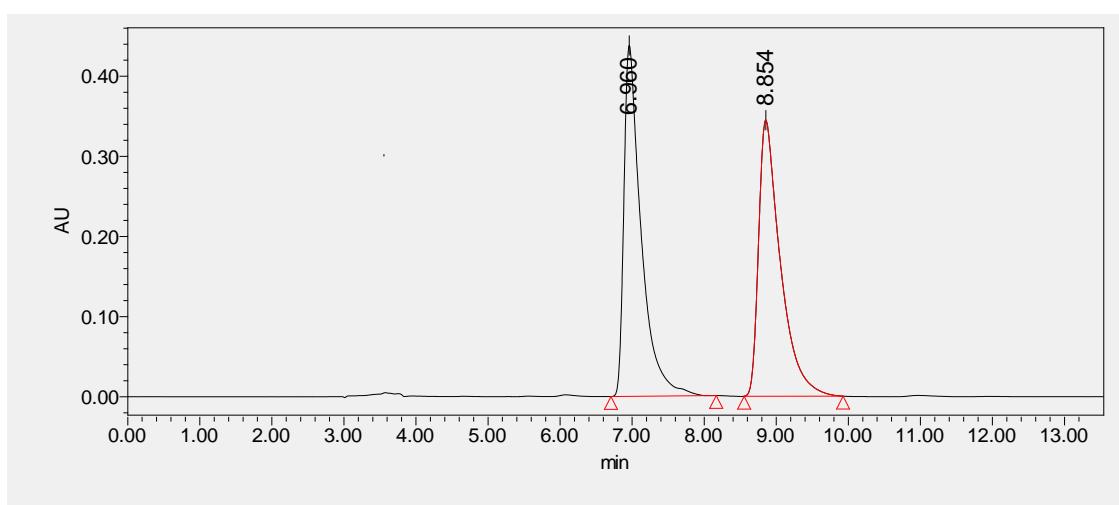
	Retention time	Area	% Area	Height	Integral type
1	17.151	221407	0.98	7715	bb
2	20.151	22316737	99.02	627929	bb

(R)-2-(3-methyl-2-oxo-1-propyl-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

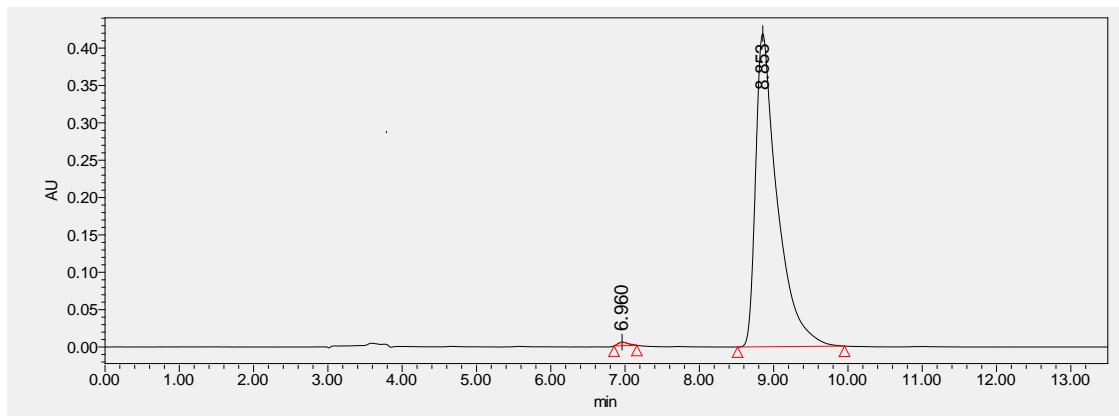
4n (Table 2)



Chiralpak IC column, hexane/EtOH (8:2), flow rate 1.0 mL/min



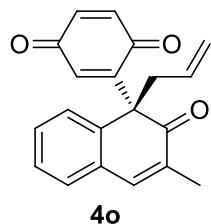
	Retention time	Area	% Area	Height	Integral type
1	6.960	7280866	50.18	437792	bb
2	8.854	7228408	49.82	344624	bb



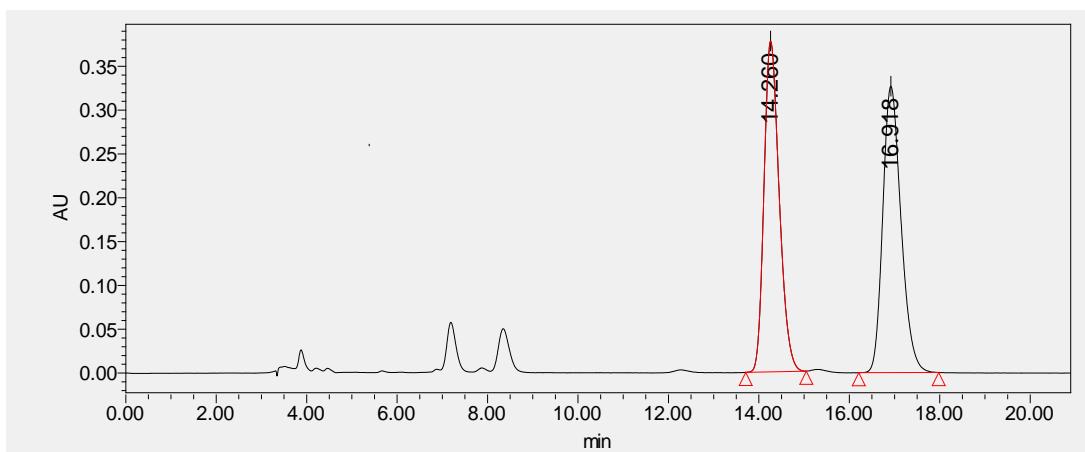
	Retention time	Area	% Area	Height	Integral type
1	6.960	45632	0.54	4782	bb
2	8.853	8471271	99.46	419168	bb

(R)-2-(1-allyl-3-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

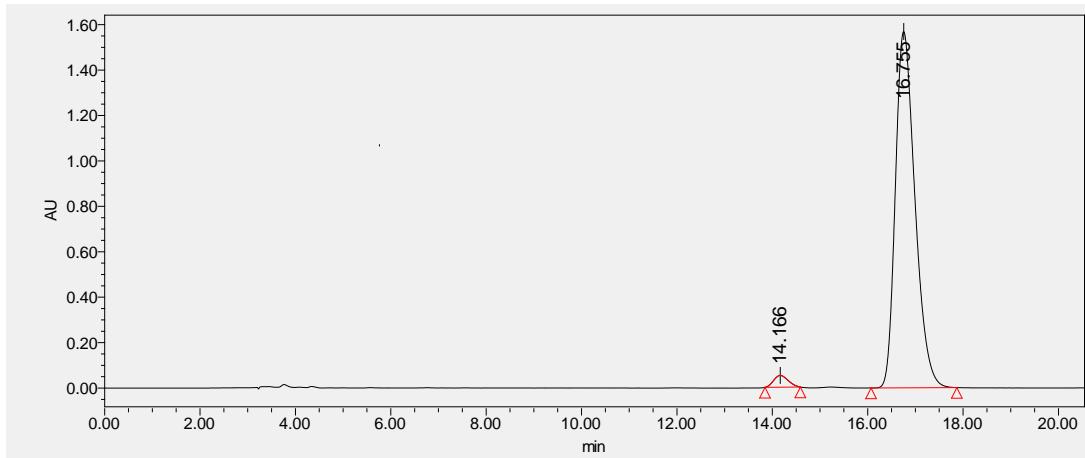
4o (Table 2)



Chiraldak IC column, hexane/EtOH (9:1), flow rate 1.0 mL/min



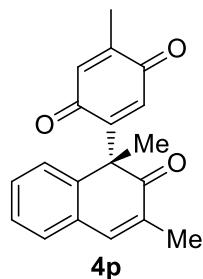
	Retention time	Area	% Area	Height	Integral type
1	14.260	8819131	49.06	377465	bb
2	16.918	9158585	50.94	326711	bb



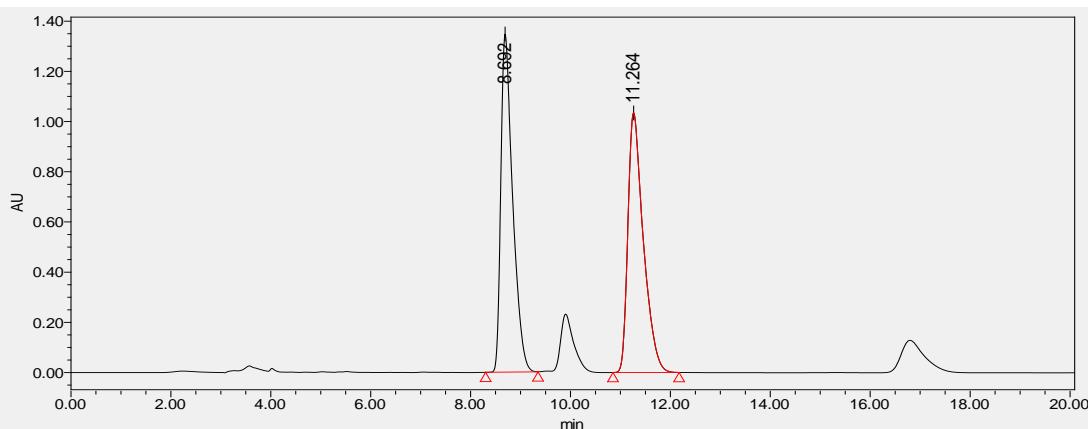
	Retention time	Area	% Area	Height	Integral type
1	14.166	1098694	2.40	52052	bb
2	16.755	44730385	97.60	1568599	bb

(R)-2-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-5-methylcyclohexa-2,5-diene-1,4-dione

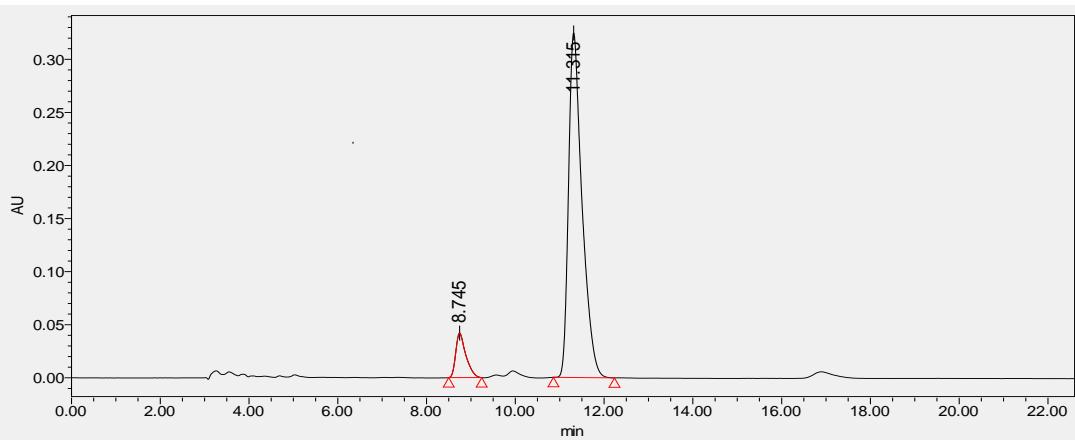
4p (Scheme 3)



Chiralpak IC column, hexane/EtOH (8:2), flow rate 1.0 mL/min



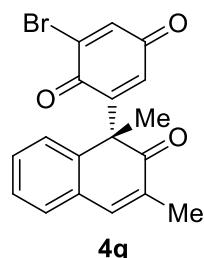
	Retention time	Area	% Area	Height	Integral type
1	8.692	22133515	49.95	1346651	bb
2	11.264	22177012	50.05	1034359	bb



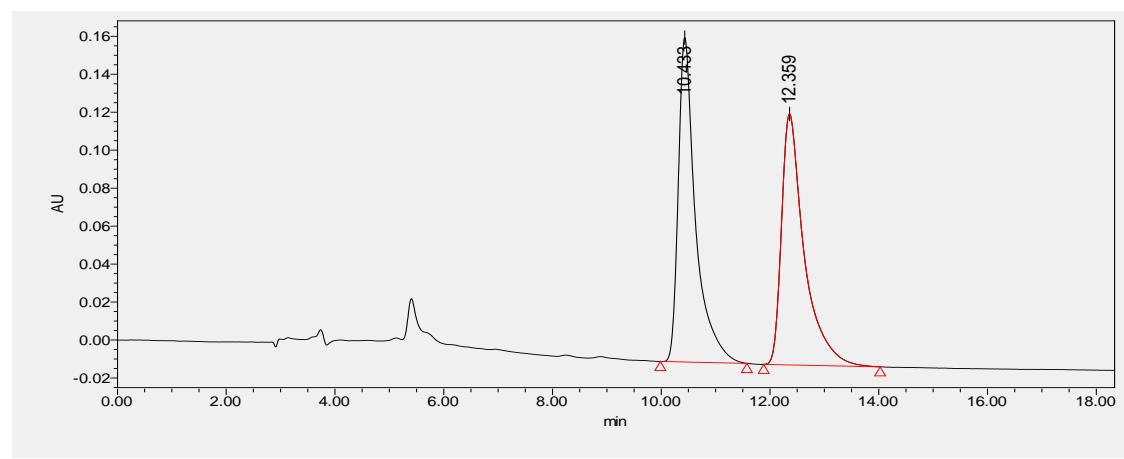
	Retention time	Area	% Area	Height	Integral type
1	8.745	663970	8.82	42031	bb
2	11.315	6864662	91.18	324603	bb

(R)-2-bromo-6-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

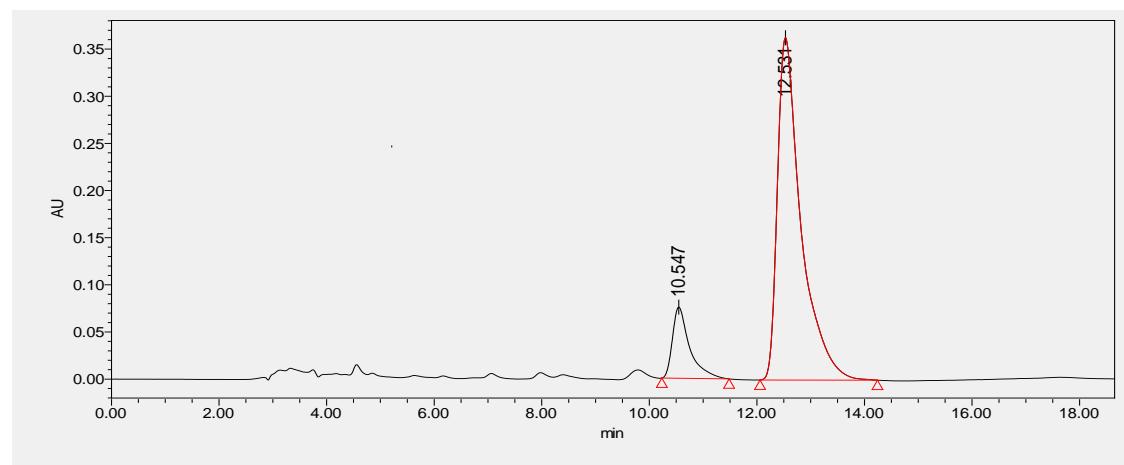
4q (Scheme 3)



Chiralpak IA column, hexane/EtOH (8:2), flow rate 1.0 mL/min



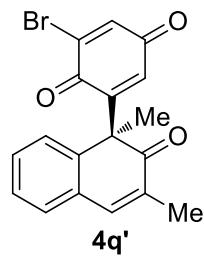
	Retention time	Area	% Area	Height	Integral type
1	10.433	3768801	49.70	170907	bb
2	12.359	3814506	50.30	132234	bb



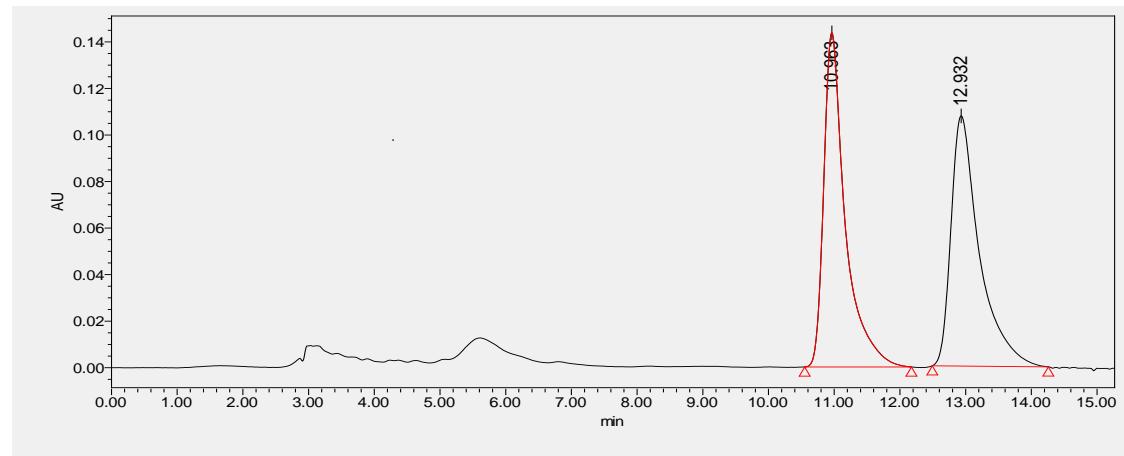
	Retention time	Area	% Area	Height	Integral type
1	10.547	1670398	13.11	75528	bb
2	12.531	11068416	86.89	363065	bb

(S)-2-bromo-6-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

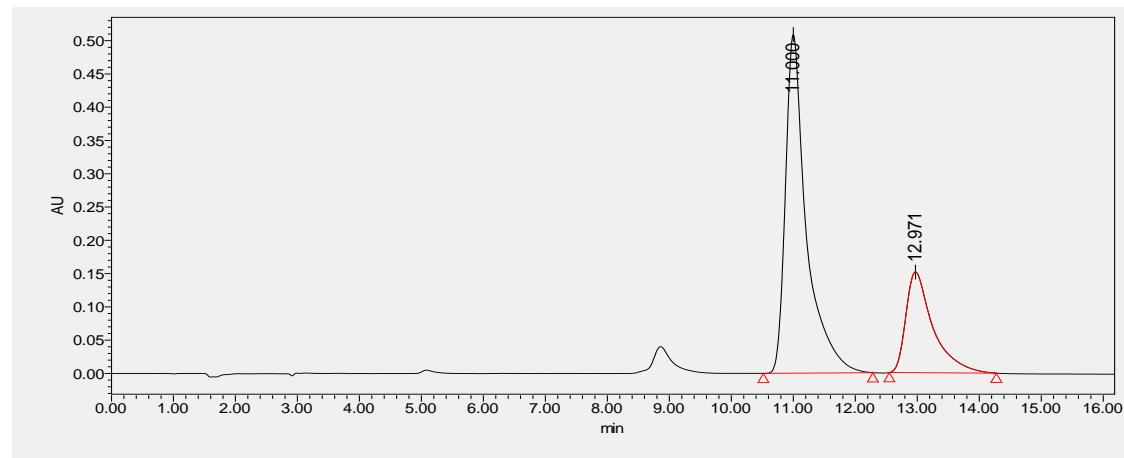
4q' (Scheme 3)



Chiralpak IA column, hexane/EtOH (8:2), flow rate 1.0 mL/min



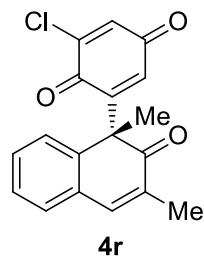
	Retention time	Area	% Area	Height	Integral type
1	10.963	3257438	50.31	143605	bb
2	12.932	3216723	49.69	107532	bb



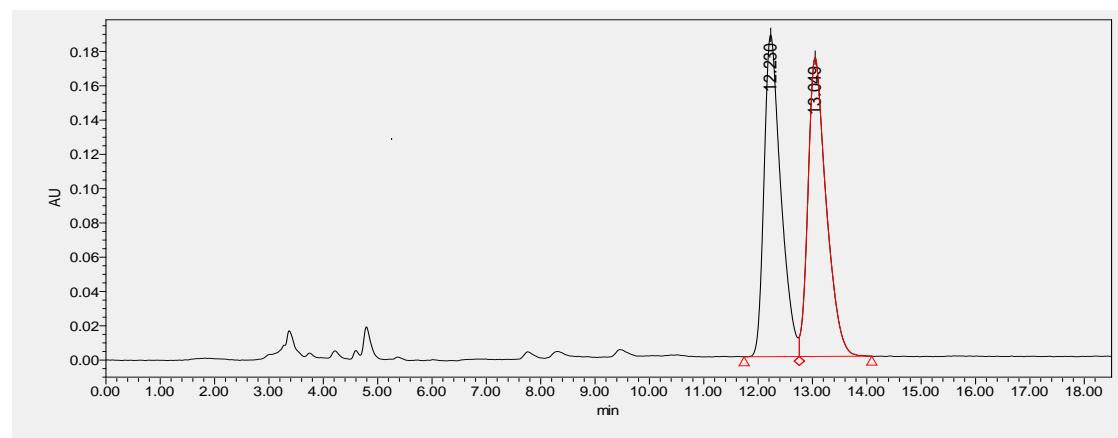
	Retention time	Area	% Area	Height	Integral type
1	11.000	11921945	72.26	508799	bb
2	12.971	4576798	27.74	151276	bb

(R)-2-chloro-6-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

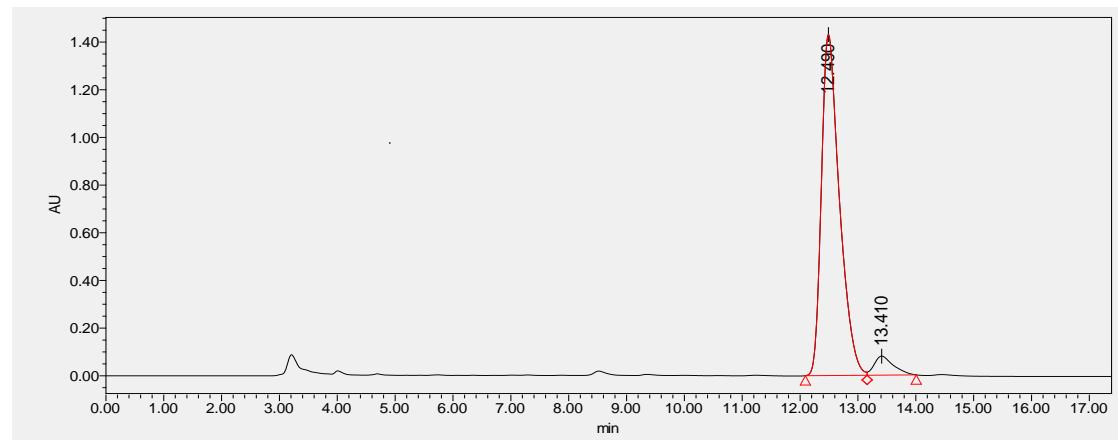
4r (Scheme 3)



Chiralpak IC column, hexane/EtOH (9:1), flow rate 1.0 mL/min



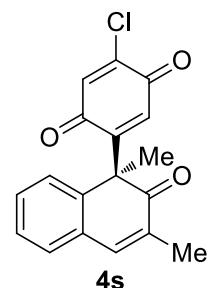
	Retention time	Area	% Area	Height	Integral type
1	12.230	4018701	49.83	187742	bv
2	13.049	4046684	50.17	174244	vb



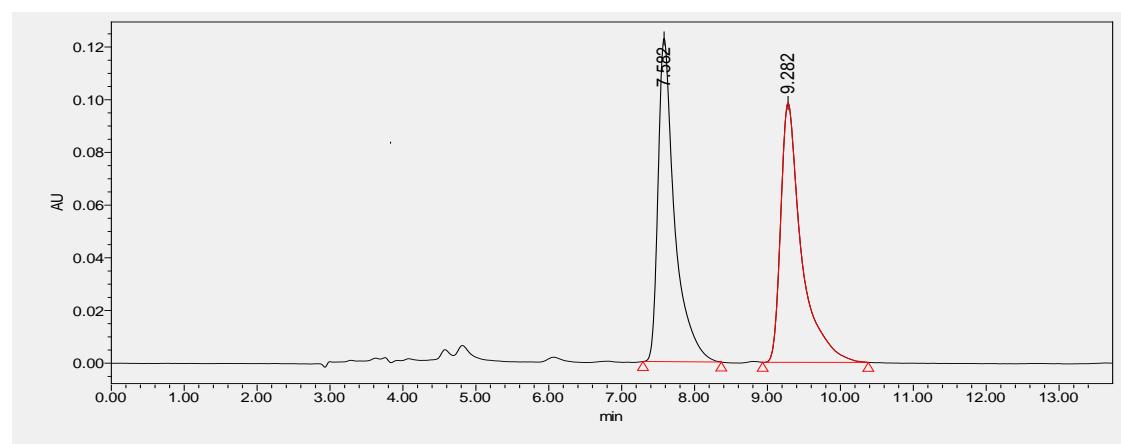
	Retention time	Area	% Area	Height	Integral type
1	12.490	30983103	94.39	1430641	bv
2	13.410	1842602	5.61	80003	vb

(S)-2-chloro-5-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)cyclohexa-2,5-diene-1,4-dione

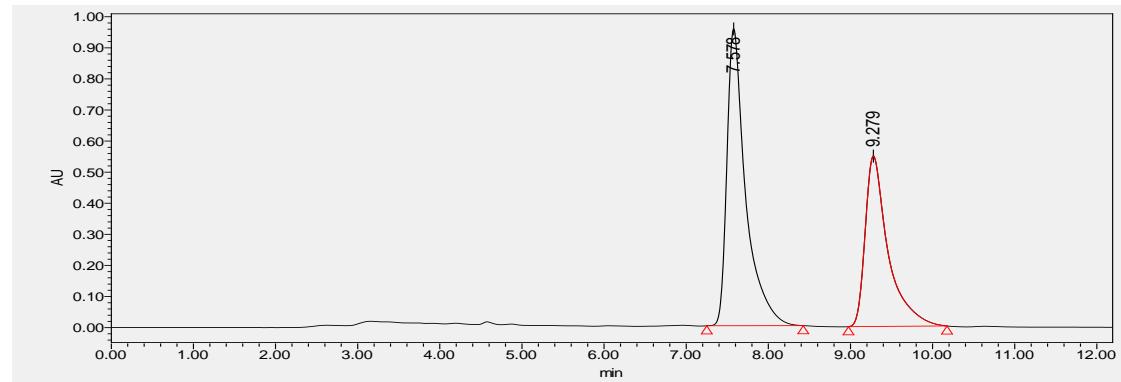
4S (Scheme 3)



Chiralpak IA column, hexane/EtOH (8:2), flow rate 1.0 mL/min



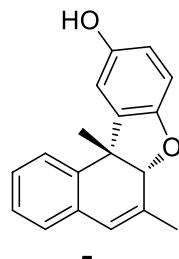
	Retention time	Area	% Area	Height	Integral type
1	7.582	1927828	49.83	122659	bb
2	9.282	1941197	50.17	98423	bb



	Retention time	Area	% Area	Height	Integral type
1	7.578	15126910	58.81	955940	bb
2	9.279	10593369	41.19	548548	bb

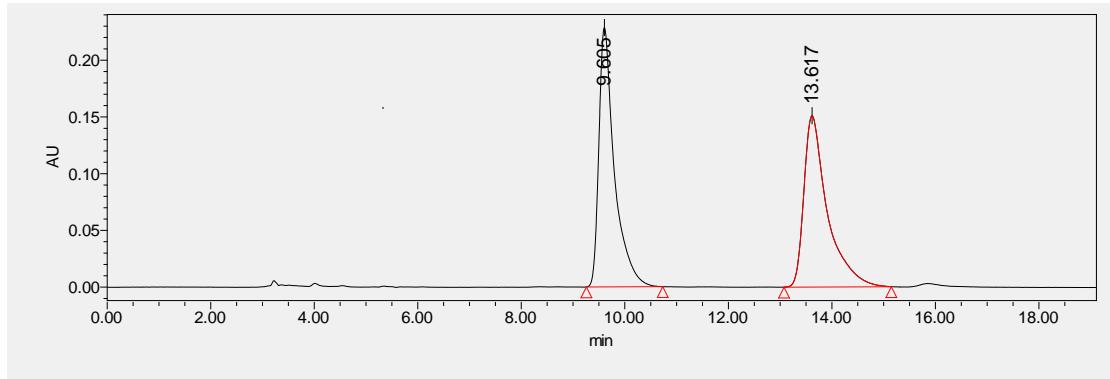
(6aR,11bR)-6,11b-dimethyl-6a,11b-dihydronaphtho[2,1-b]benzofuran-10-ol

5 (Scheme 3)

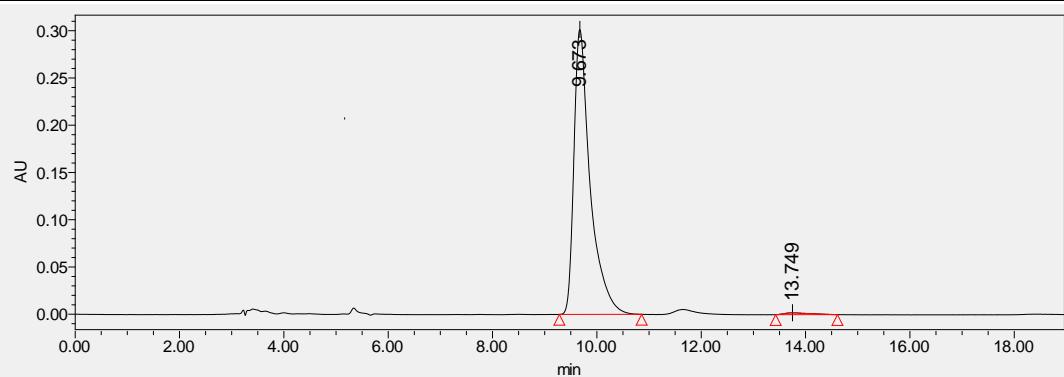


5

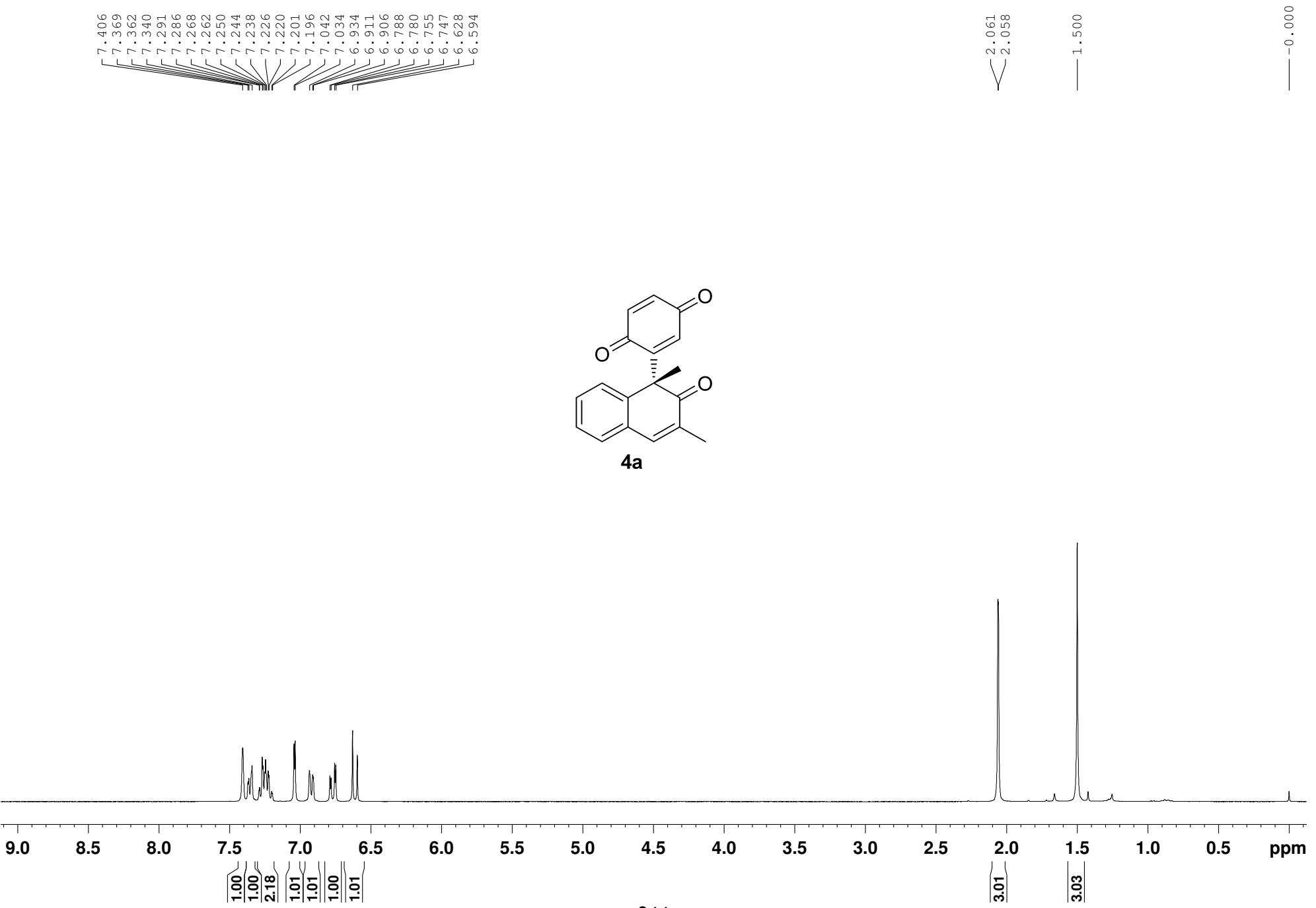
Chiralpak IA column, hexane/EtOH (95:5), flow rate 1.0 mL/min

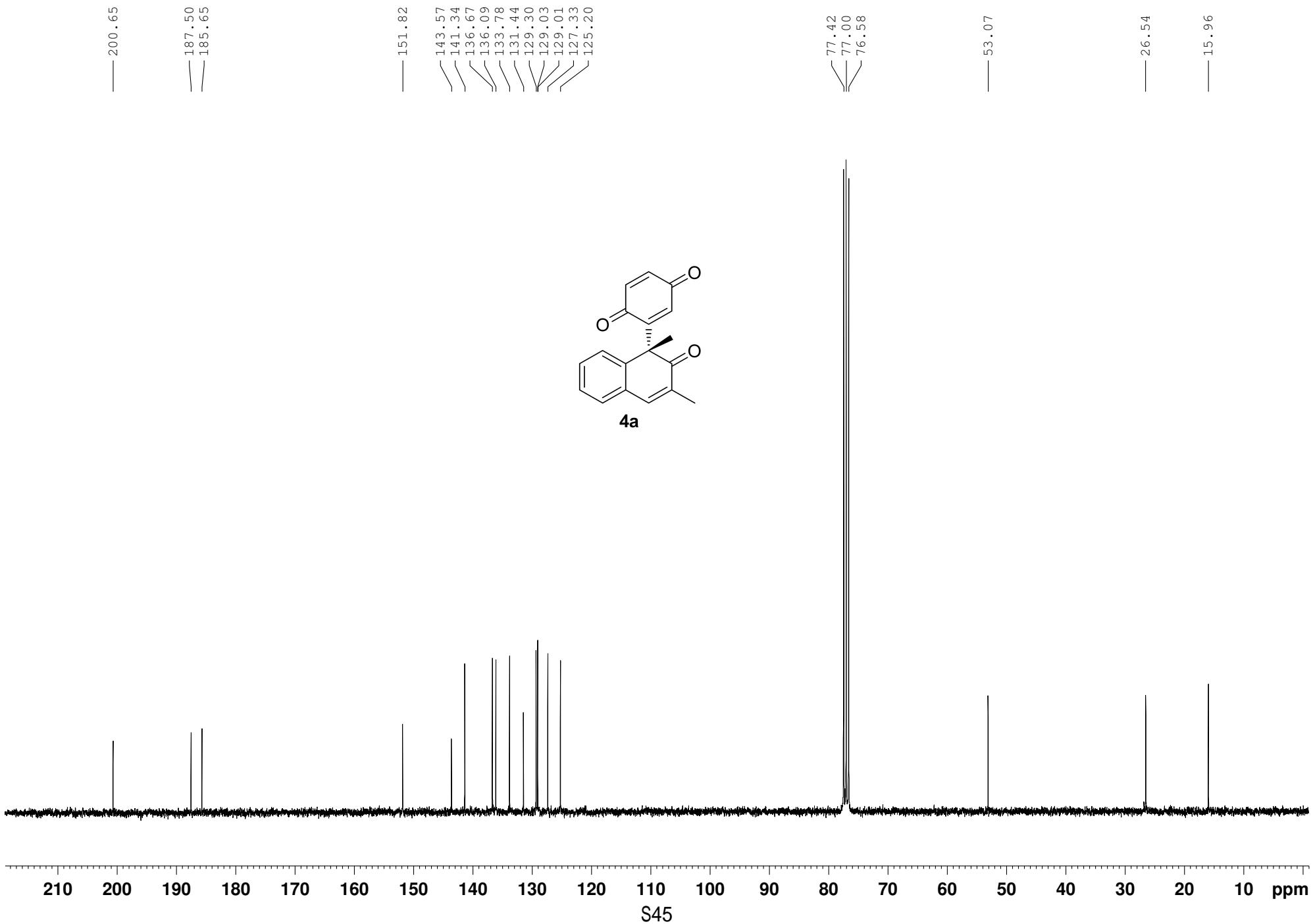


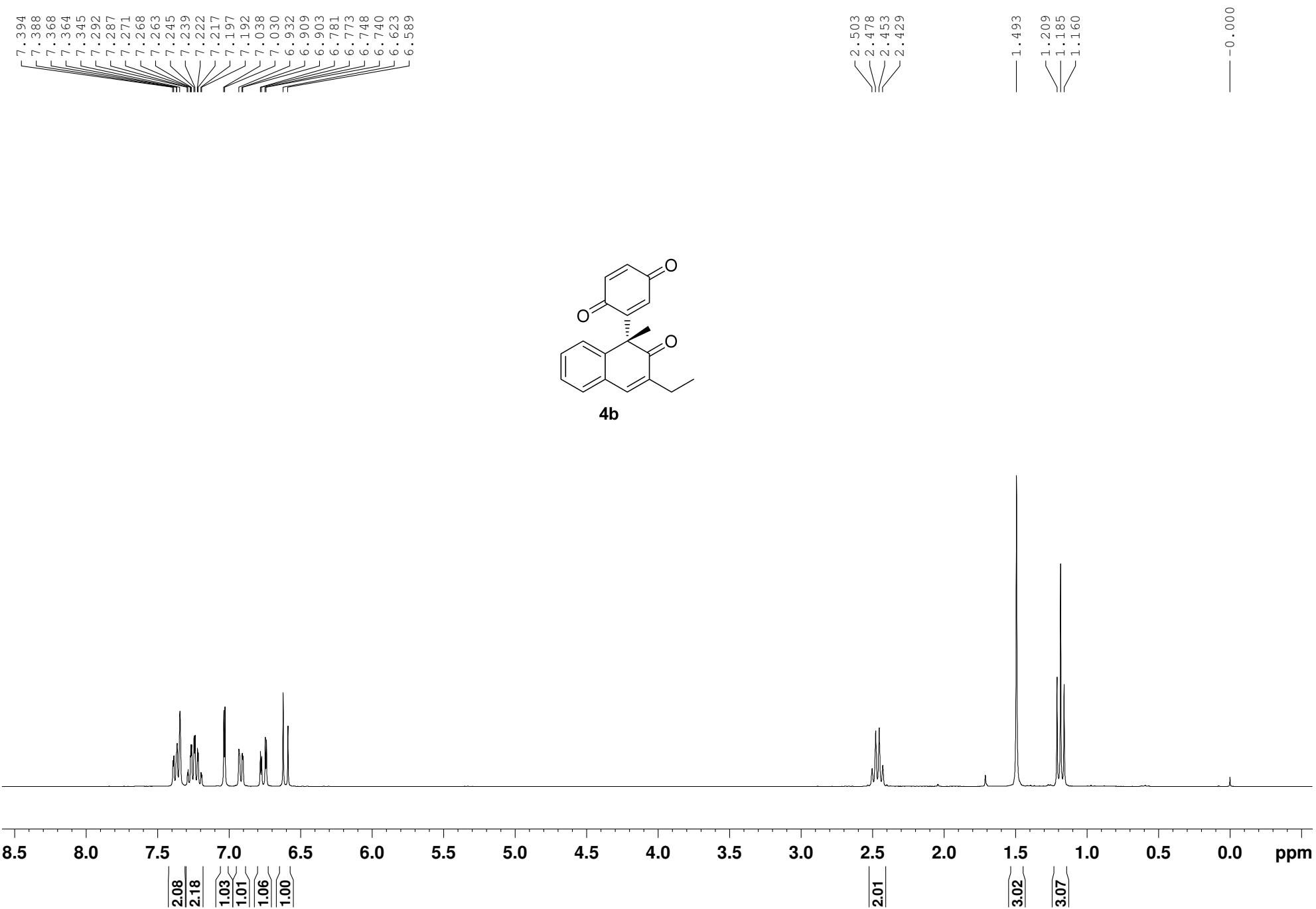
	Retention time	Area	% Area	Height	Integral type
1	9.605	4755993	50.06	228538	bb
2	13.617	4745510	49.94	150987	bb

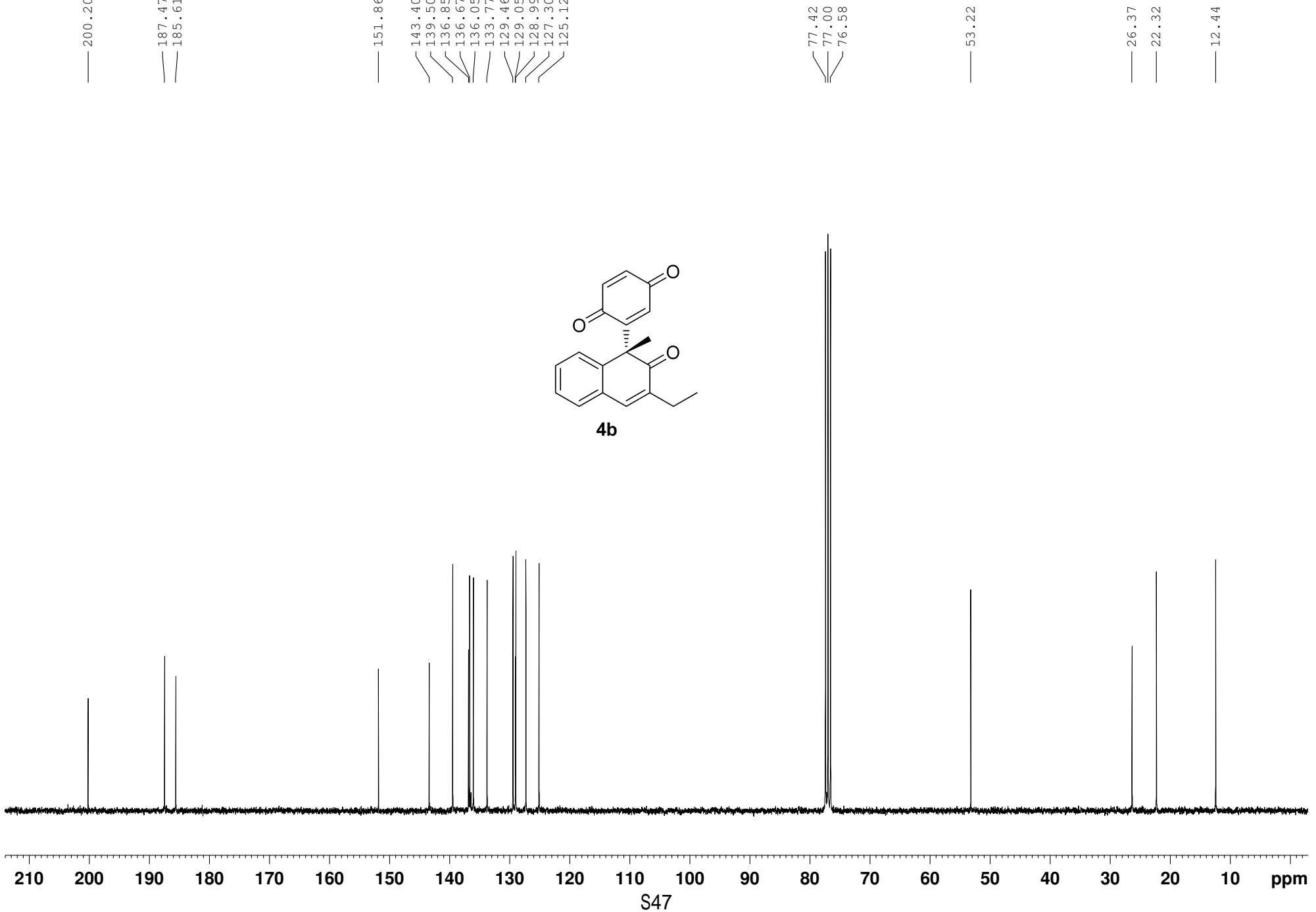


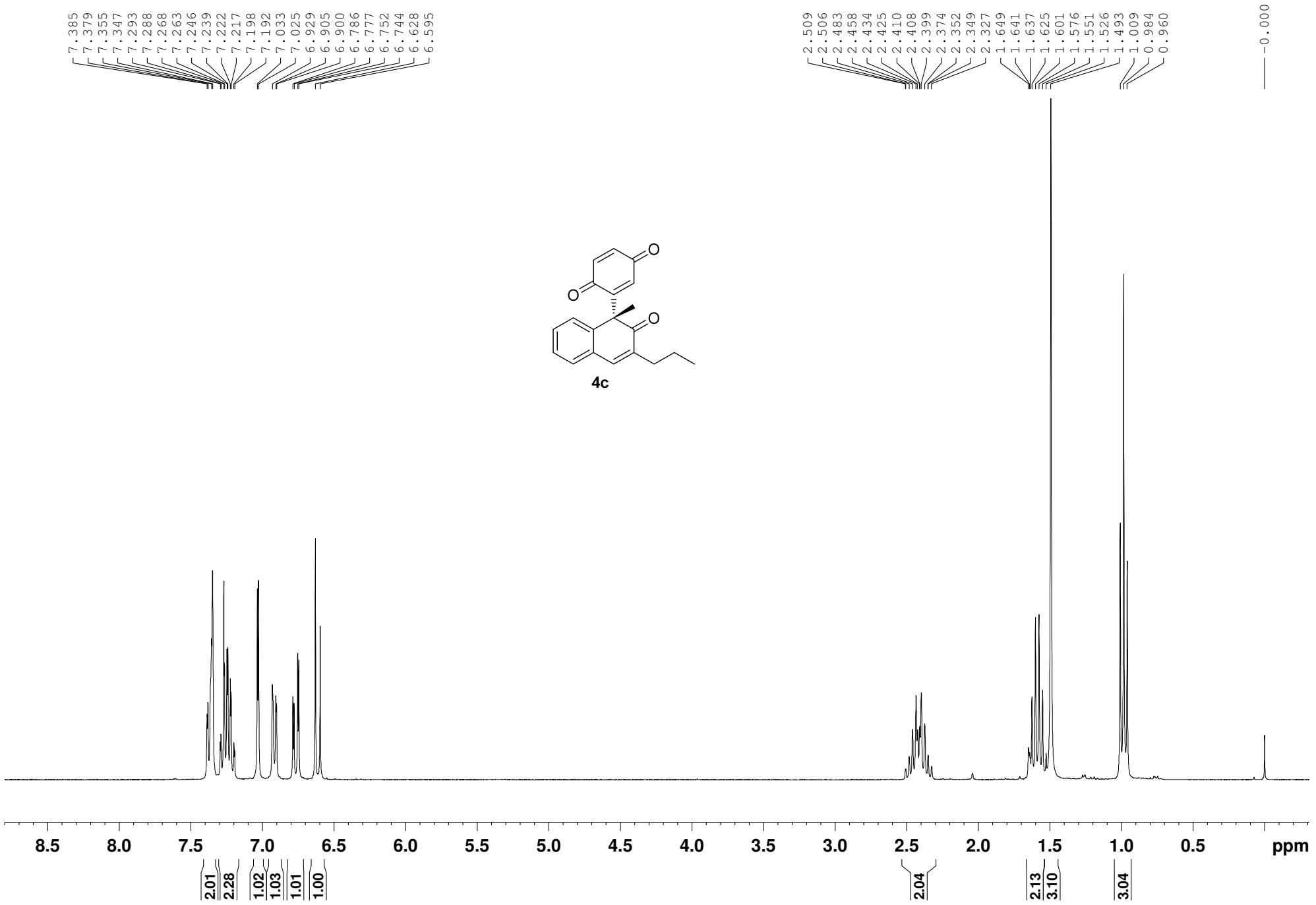
	Retention time	Area	% Area	Height	Integral type
1	9.673	6525752	99.00	301449	bb
2	13.749	65833	1.00	2018	bb

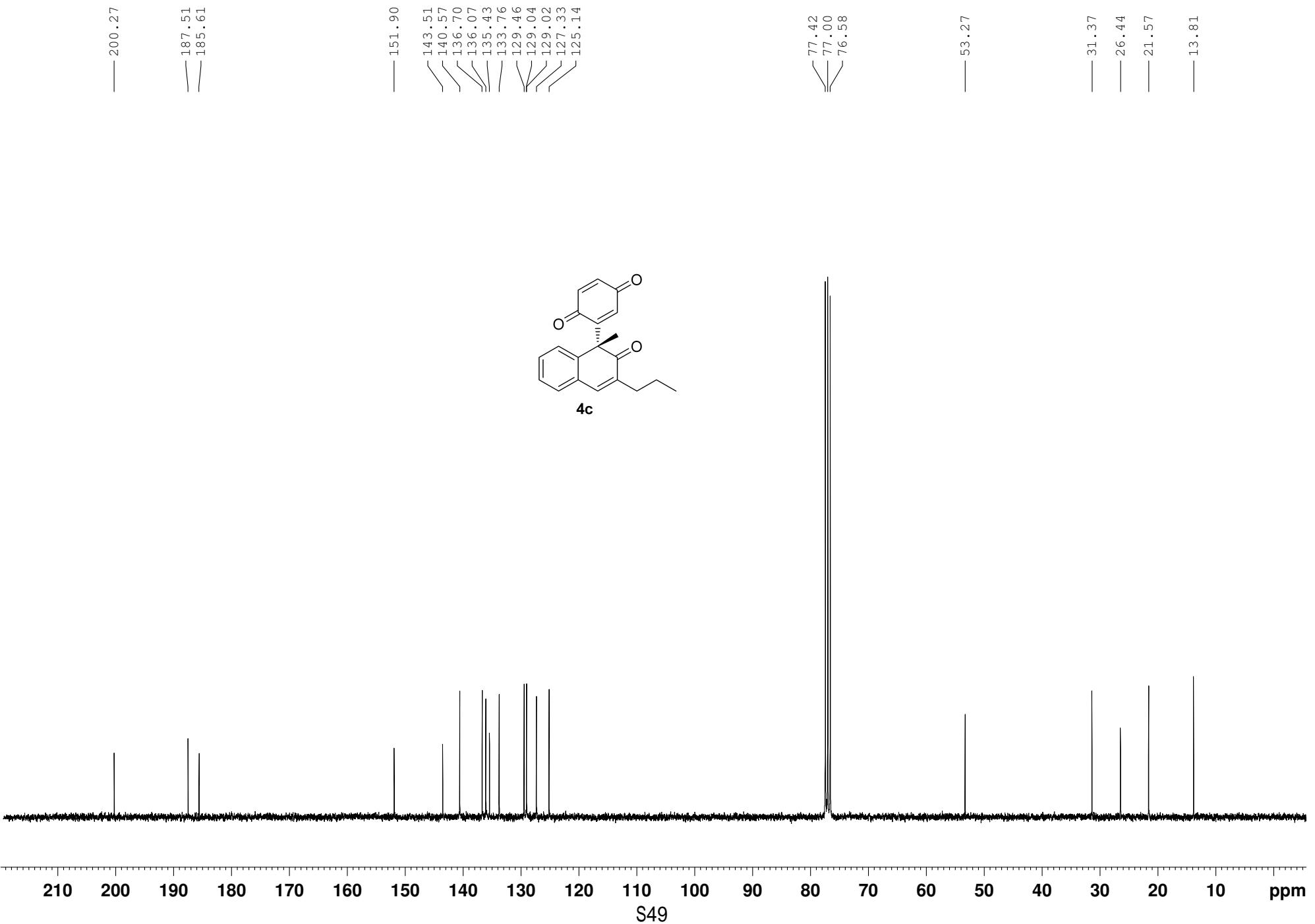


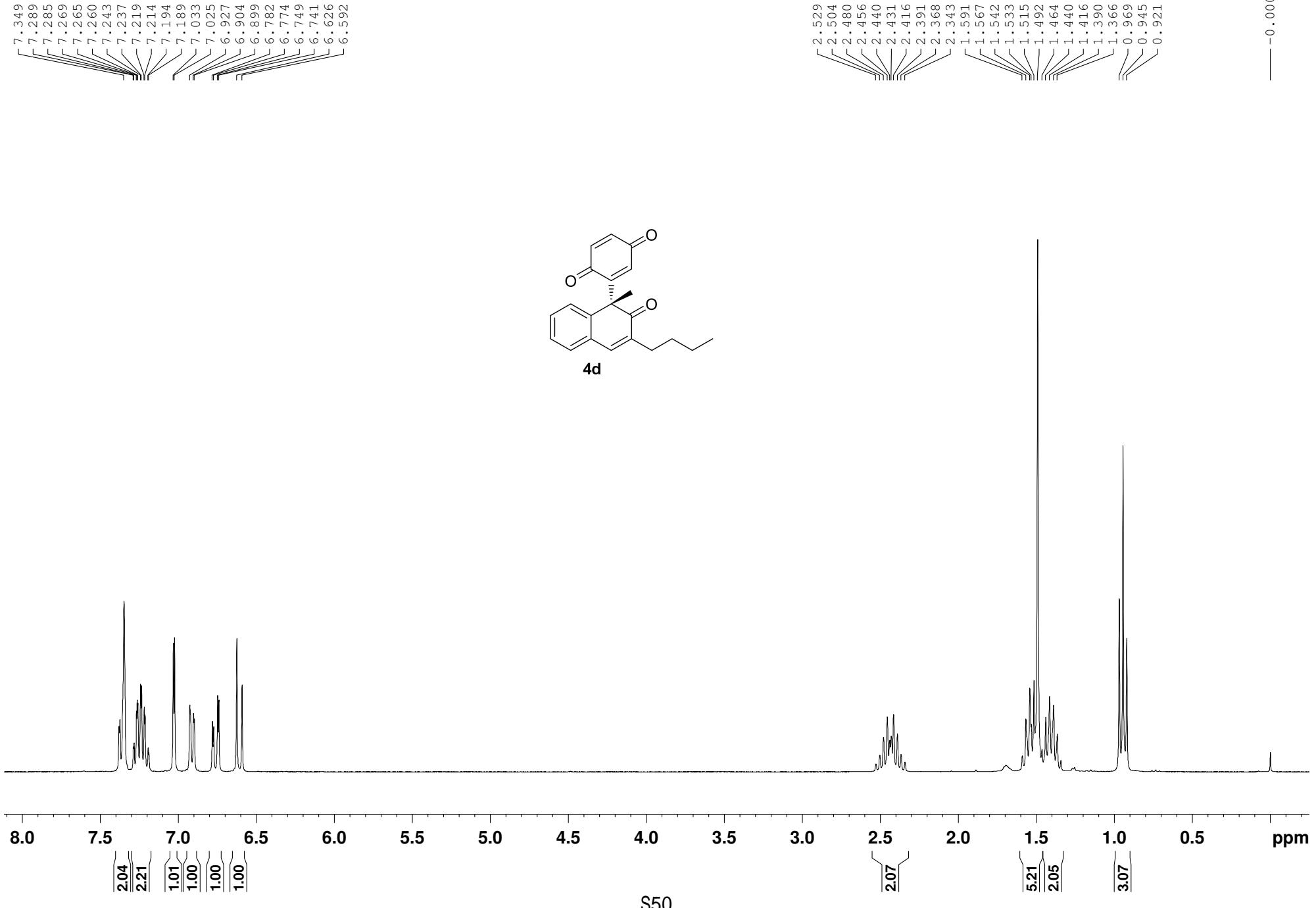


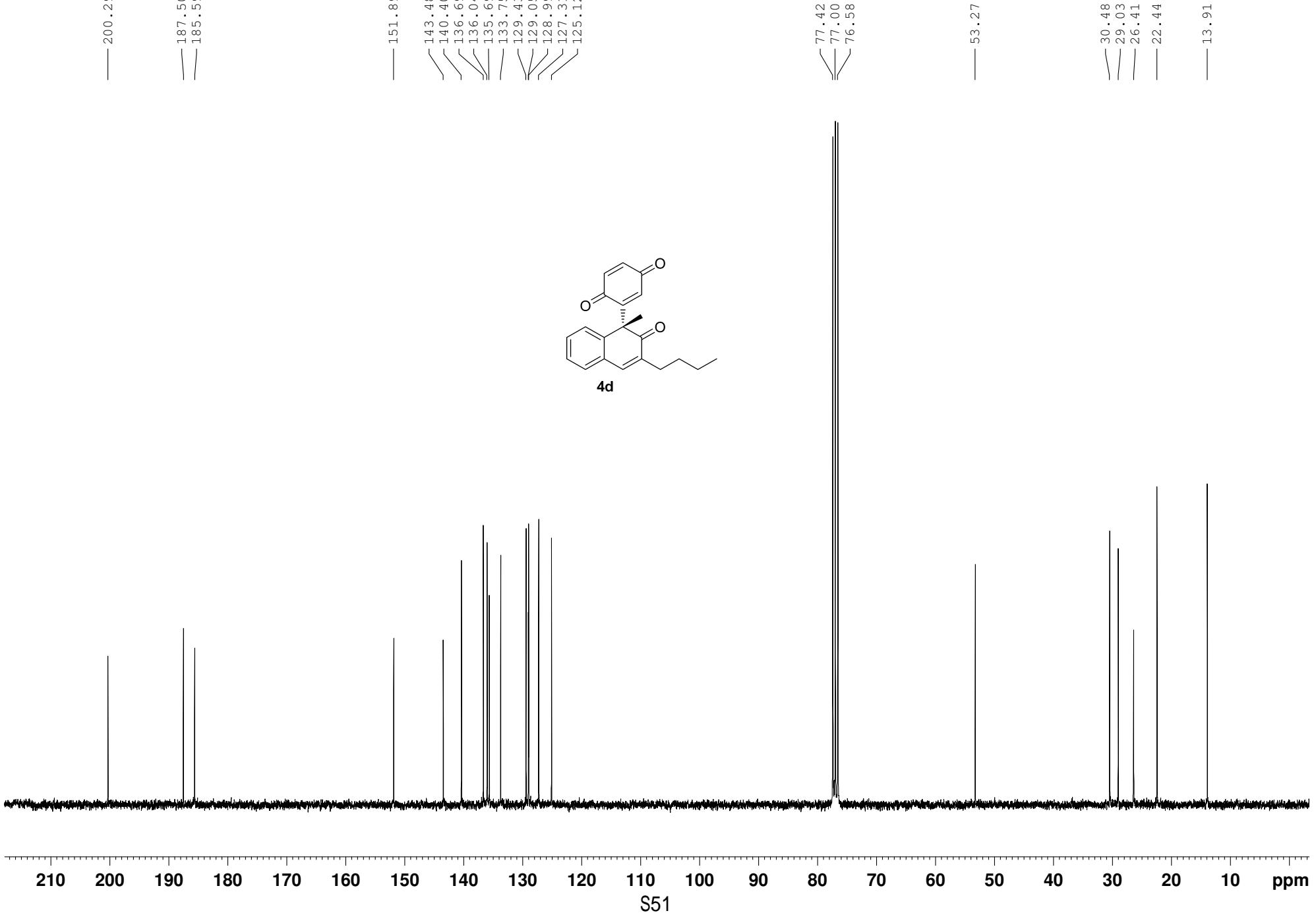


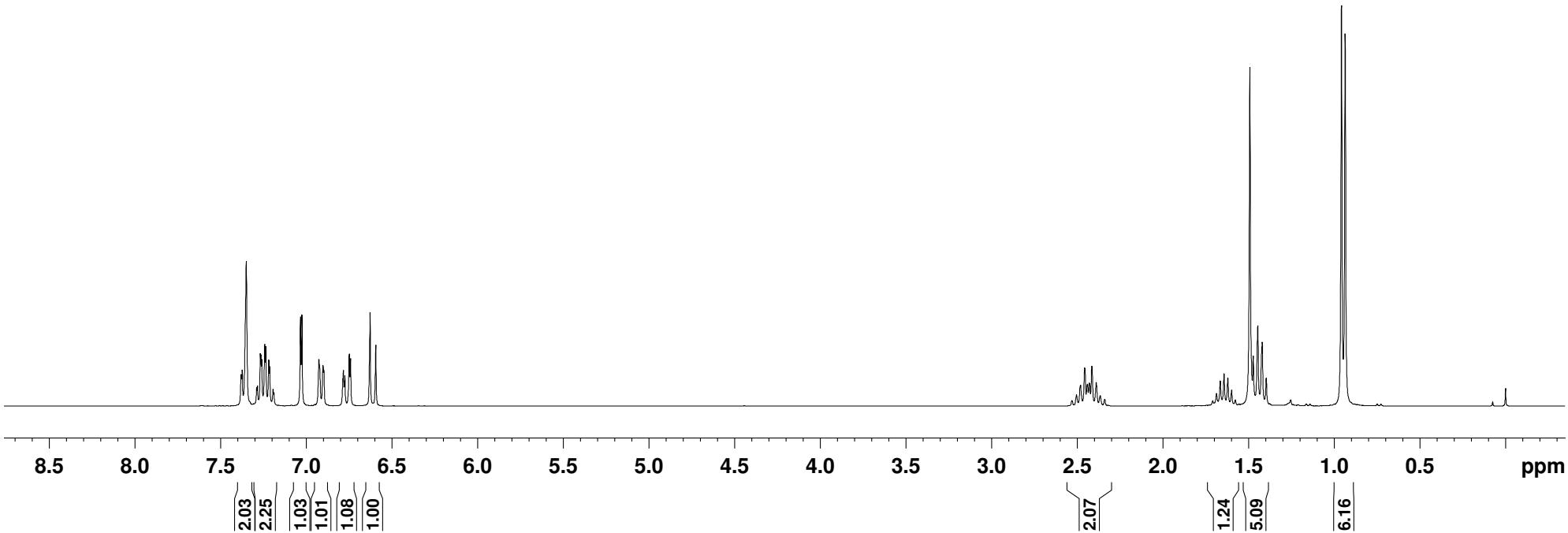
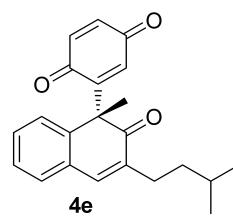
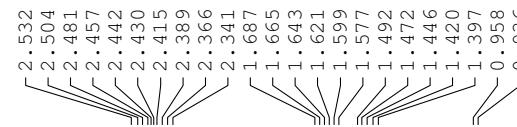
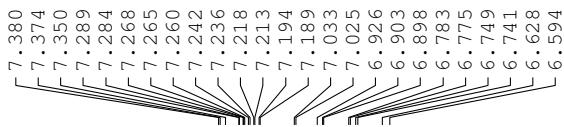


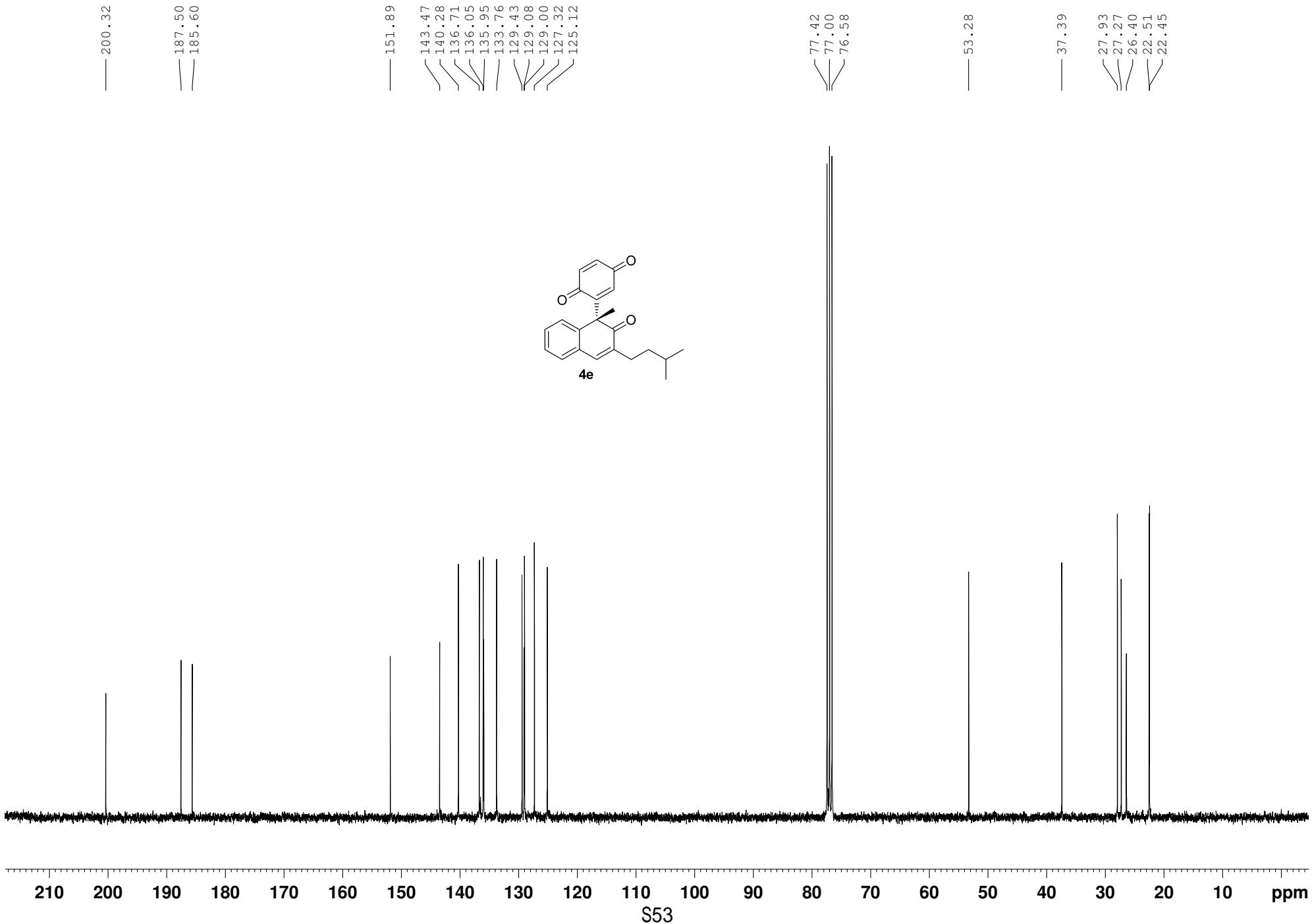


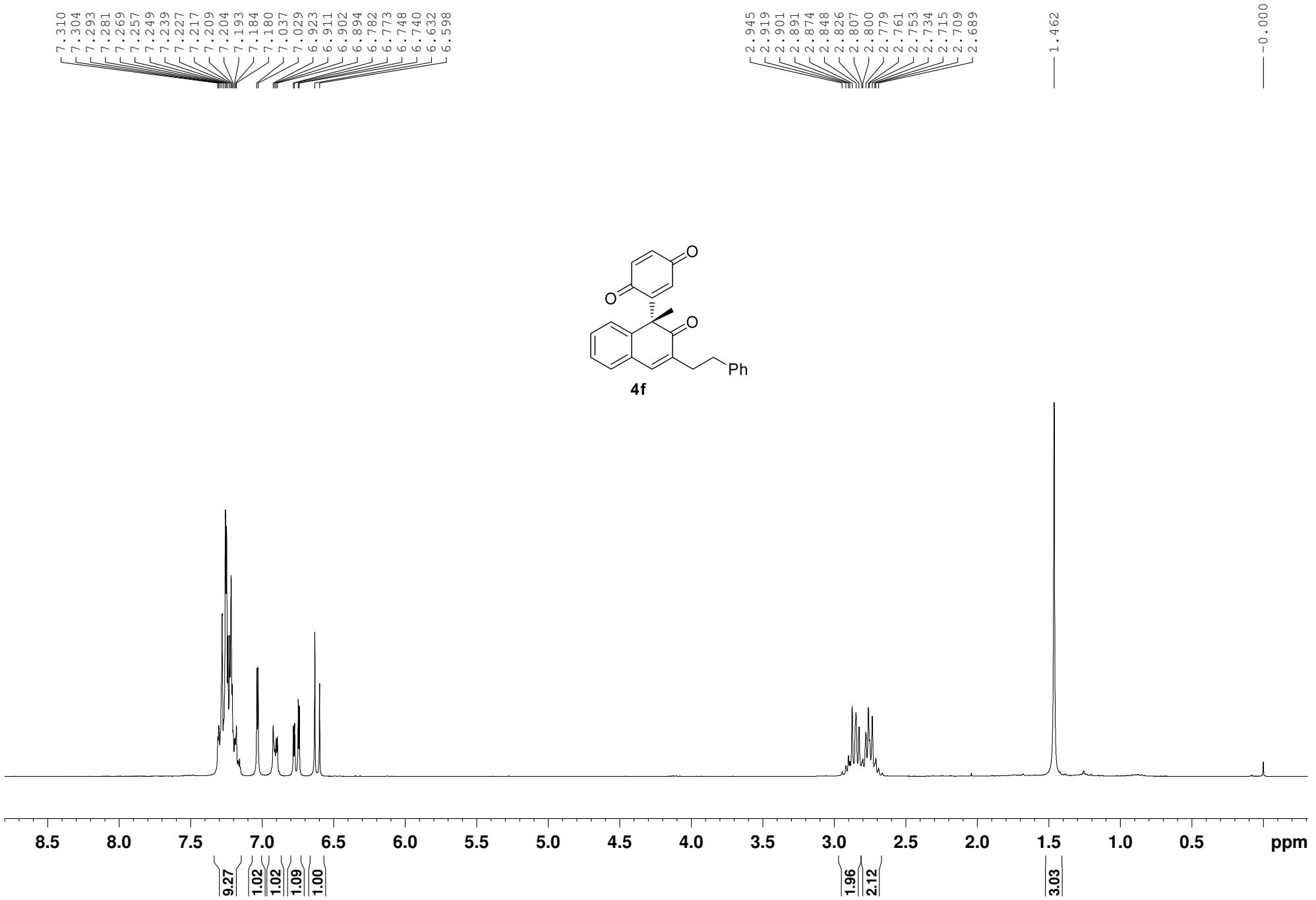


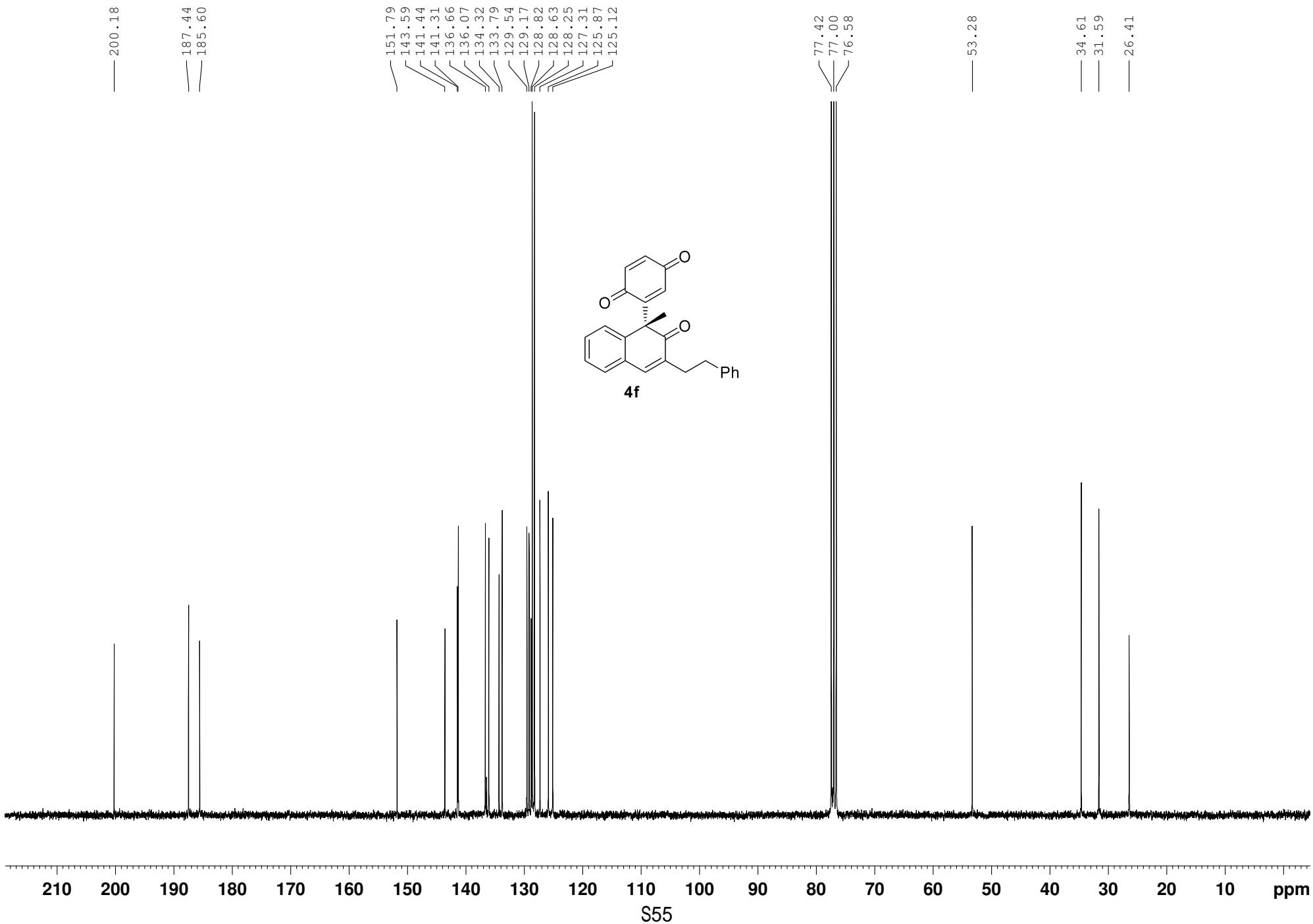


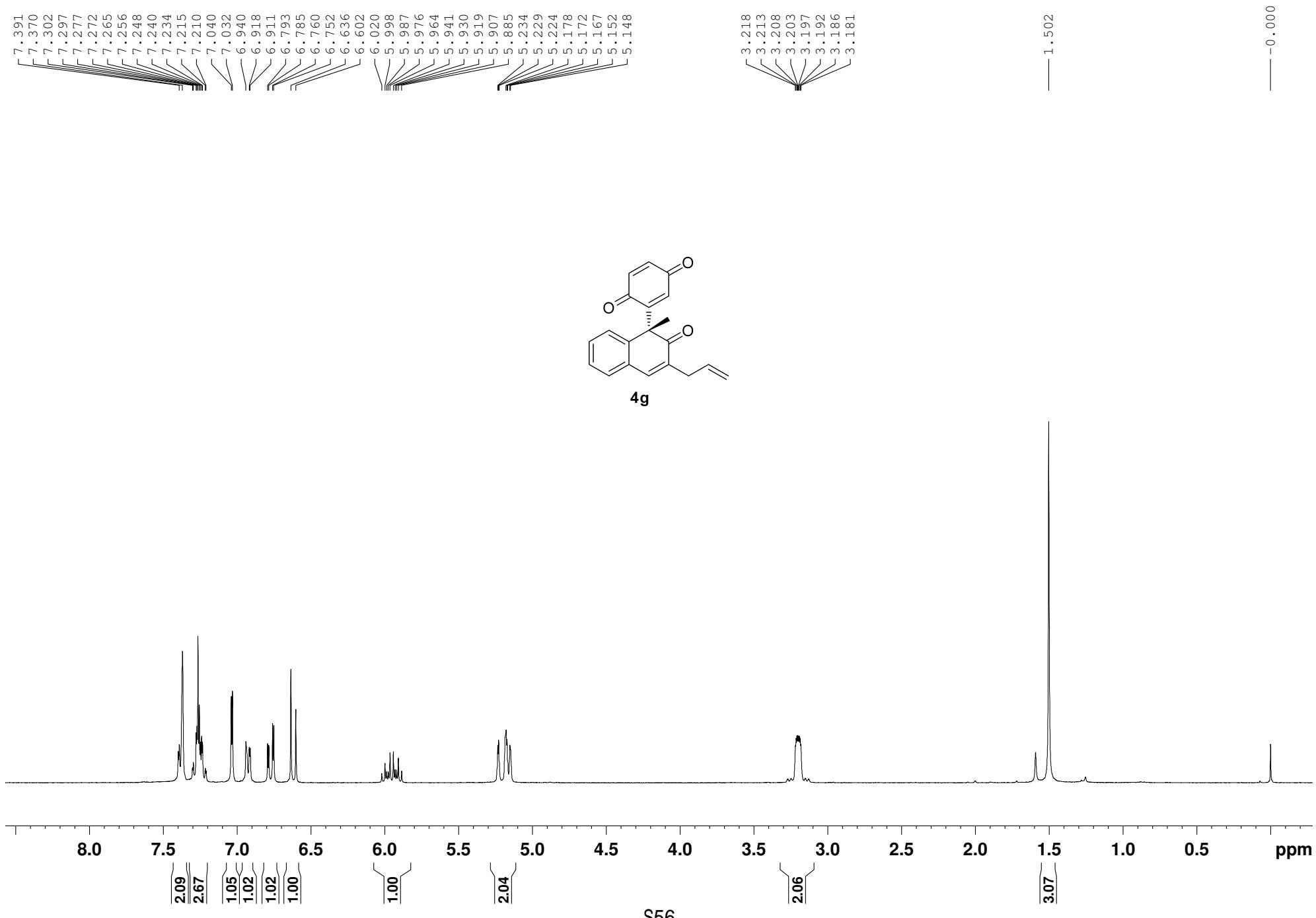


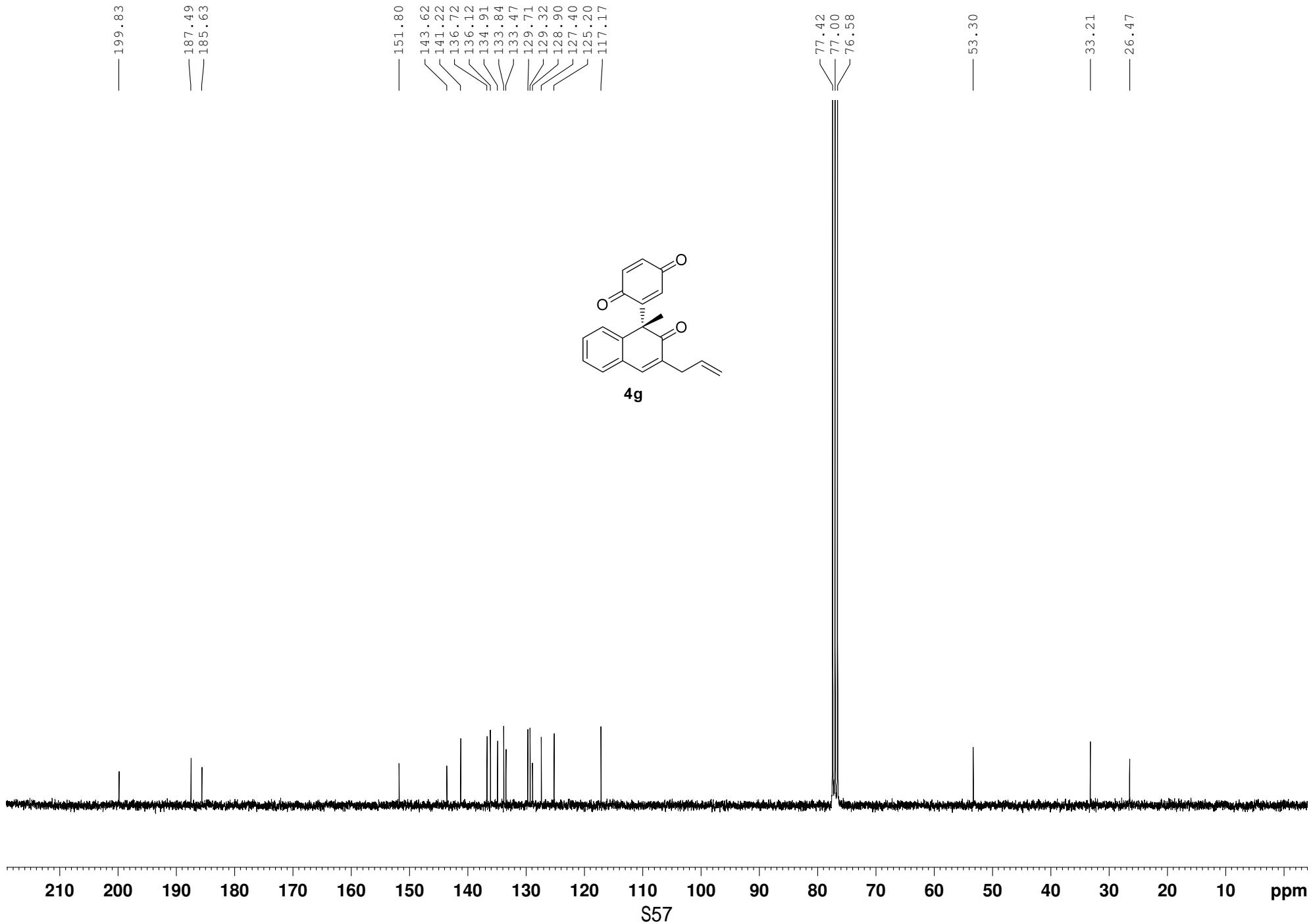


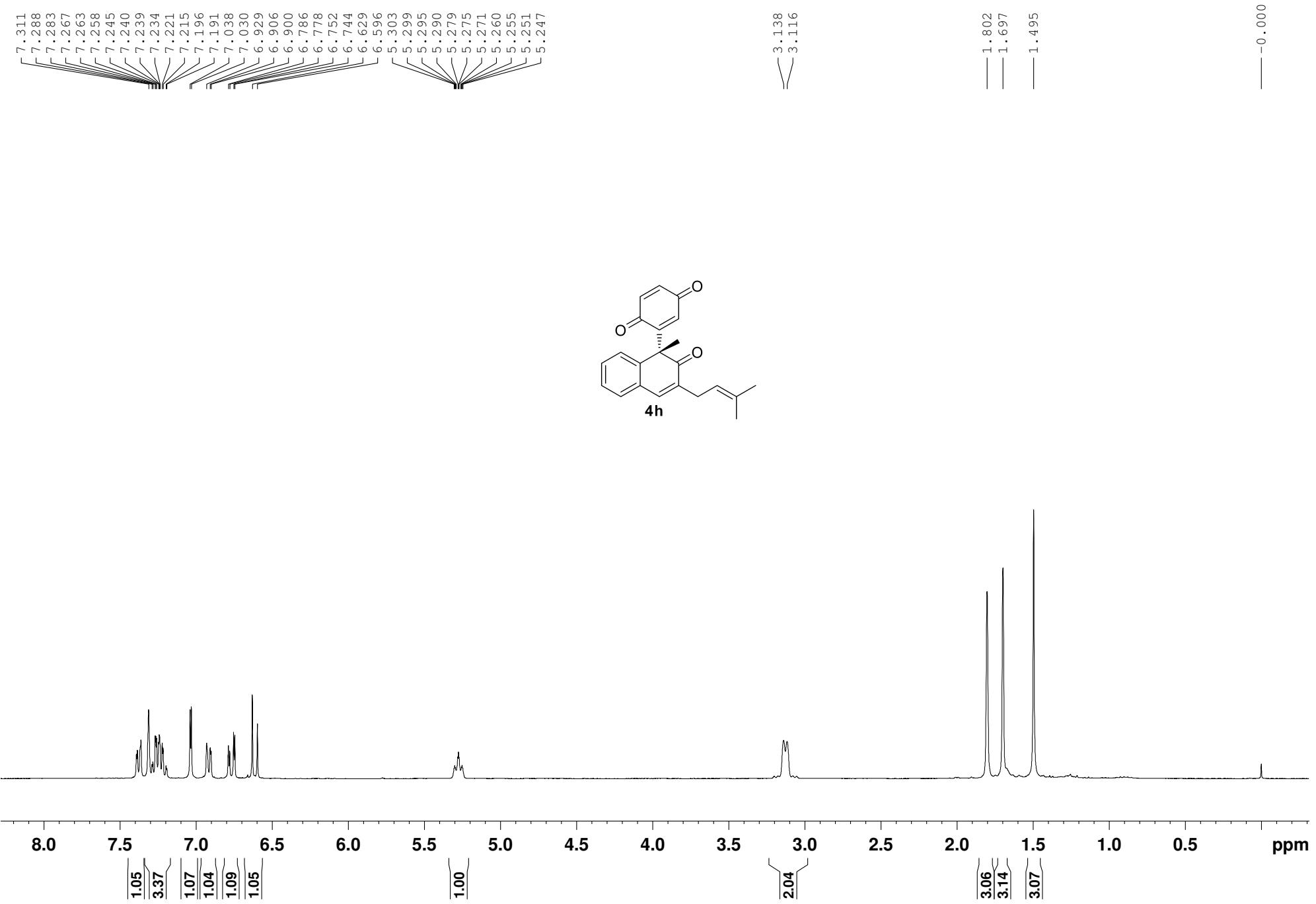


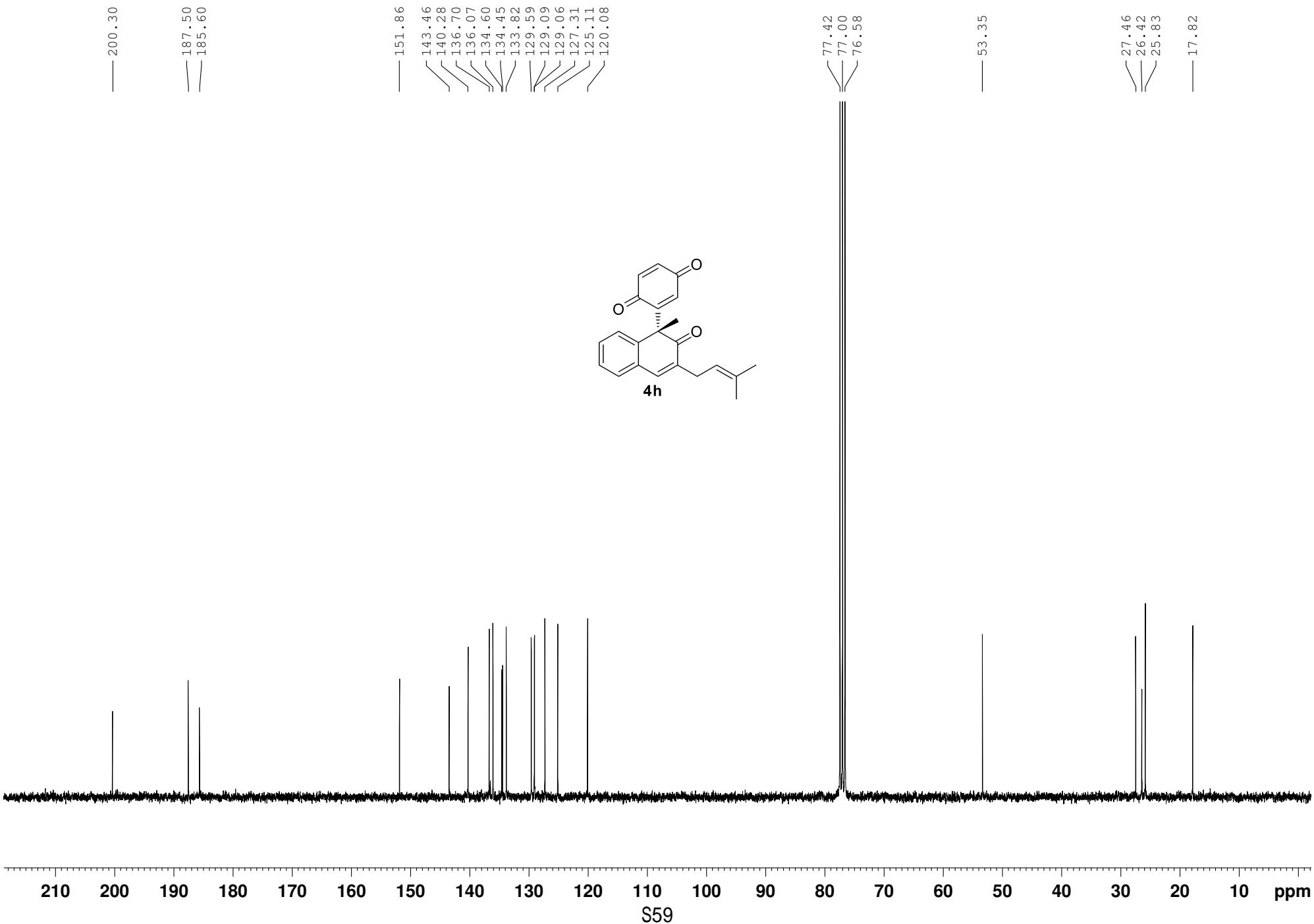


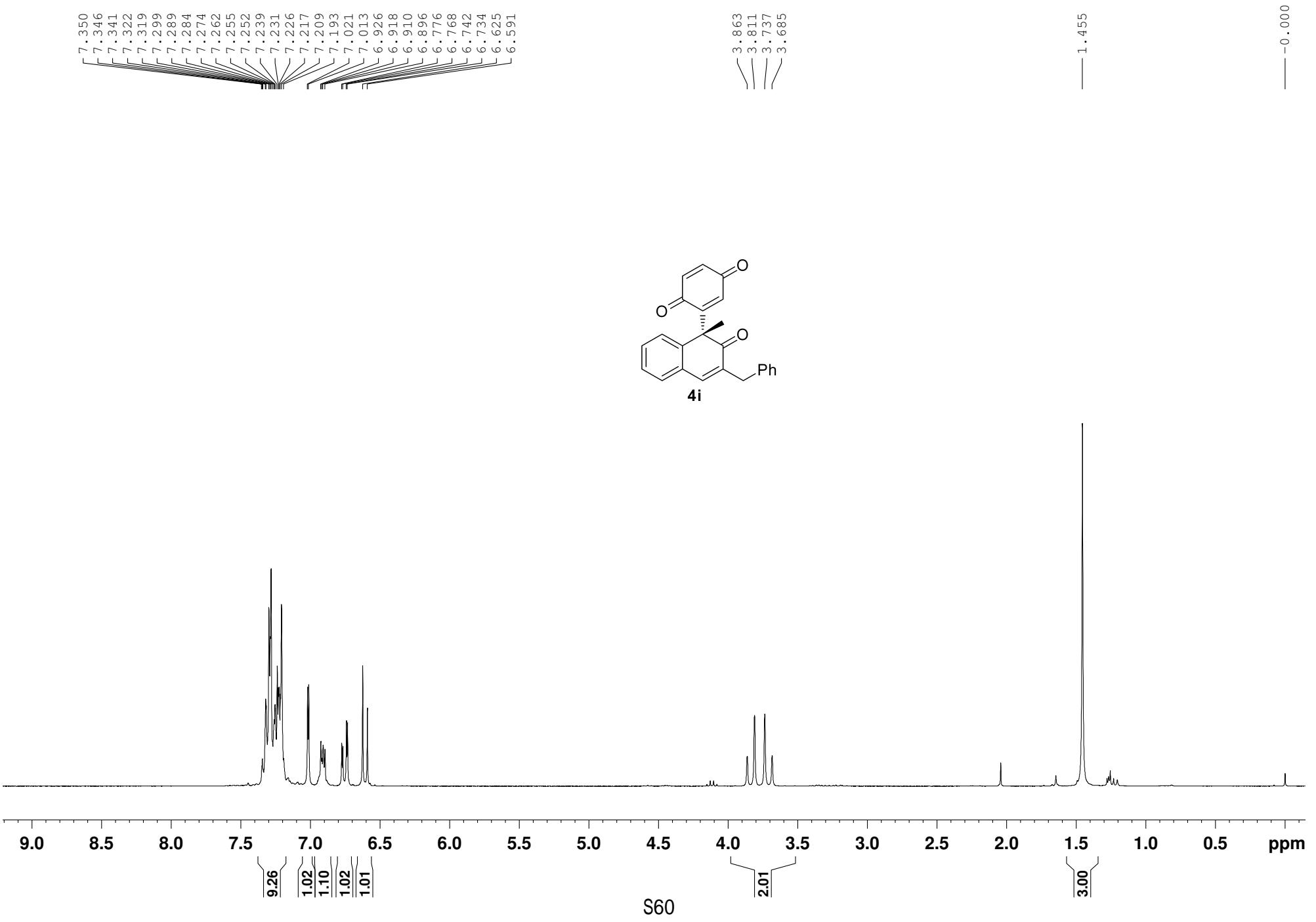


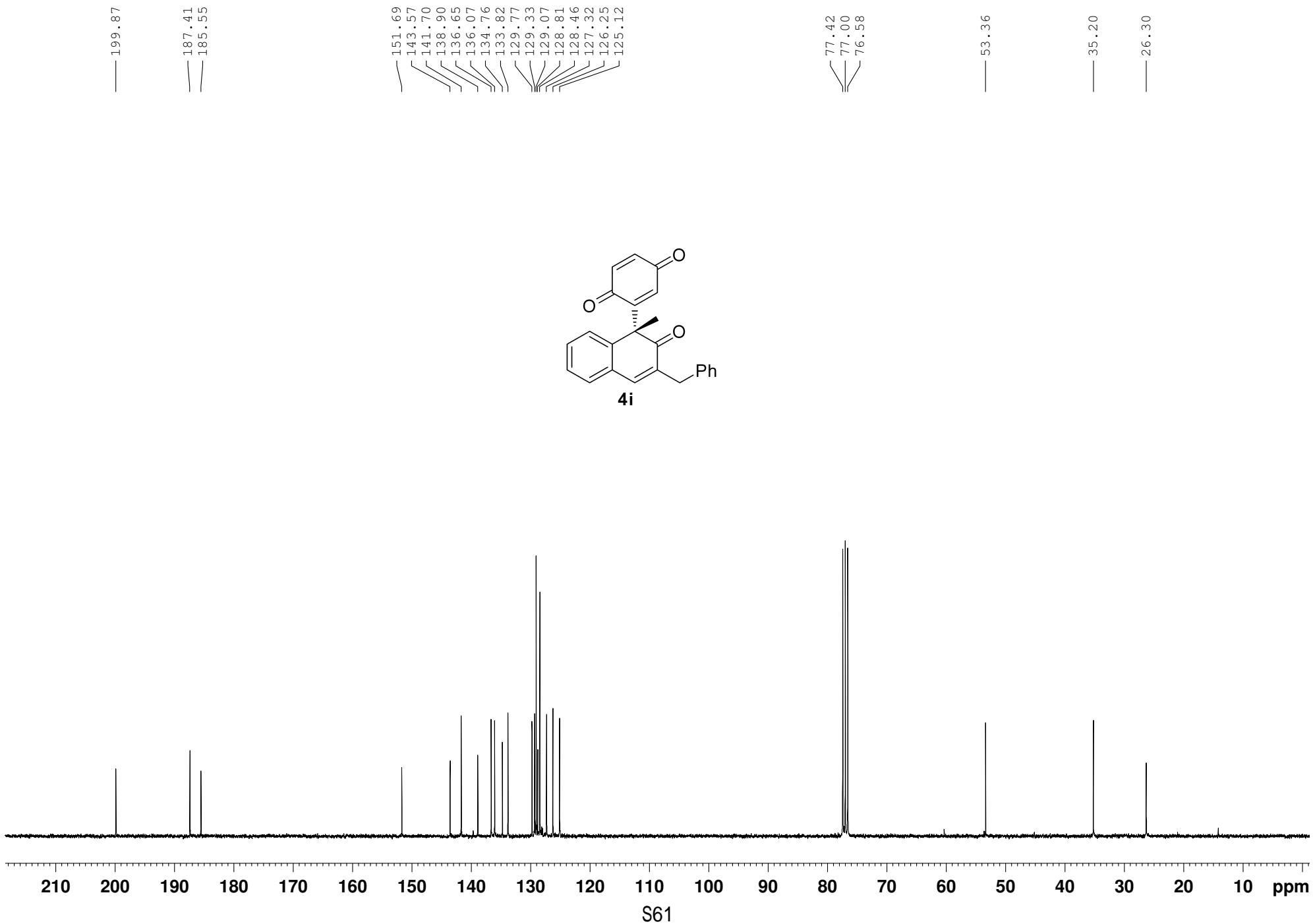


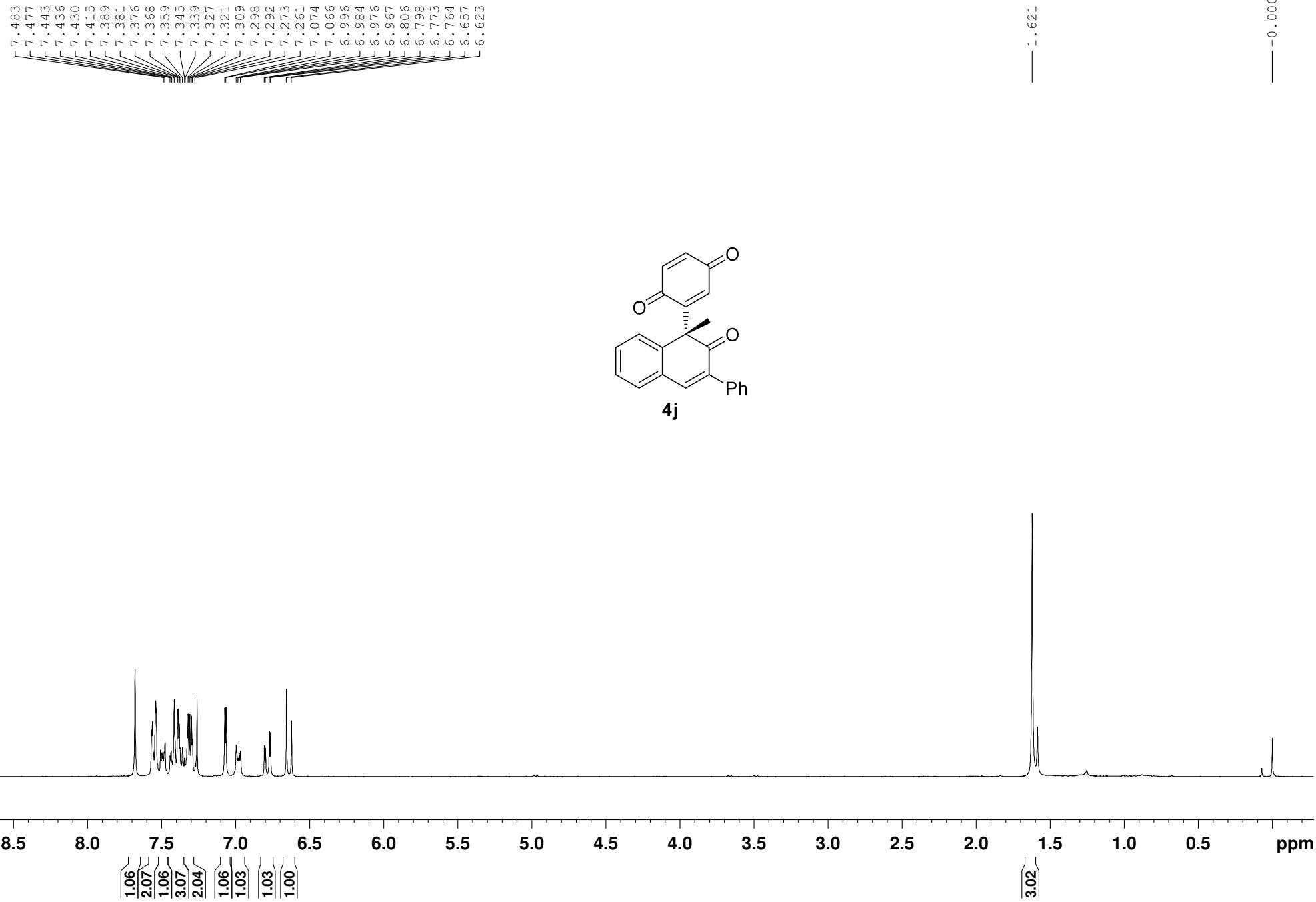


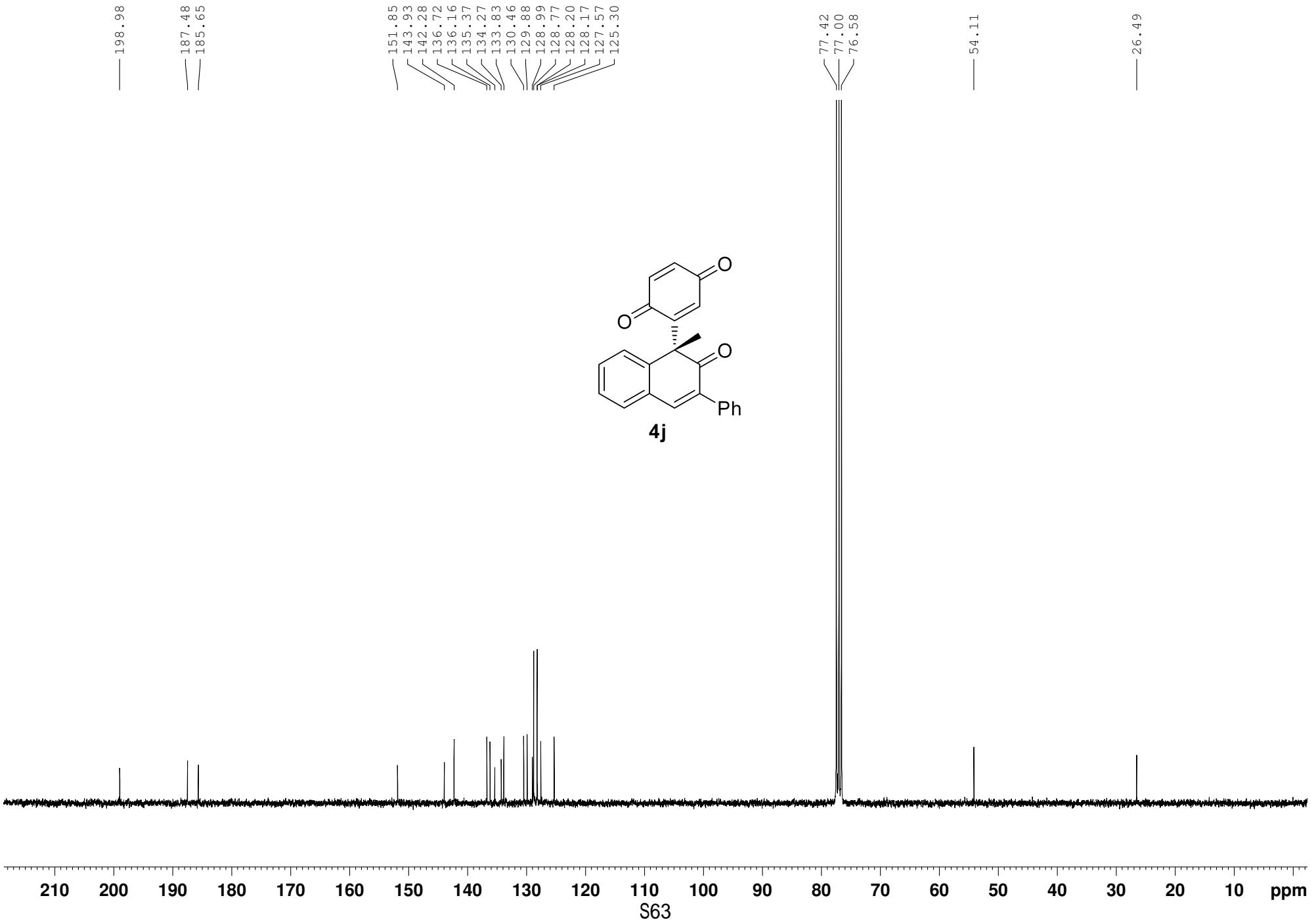


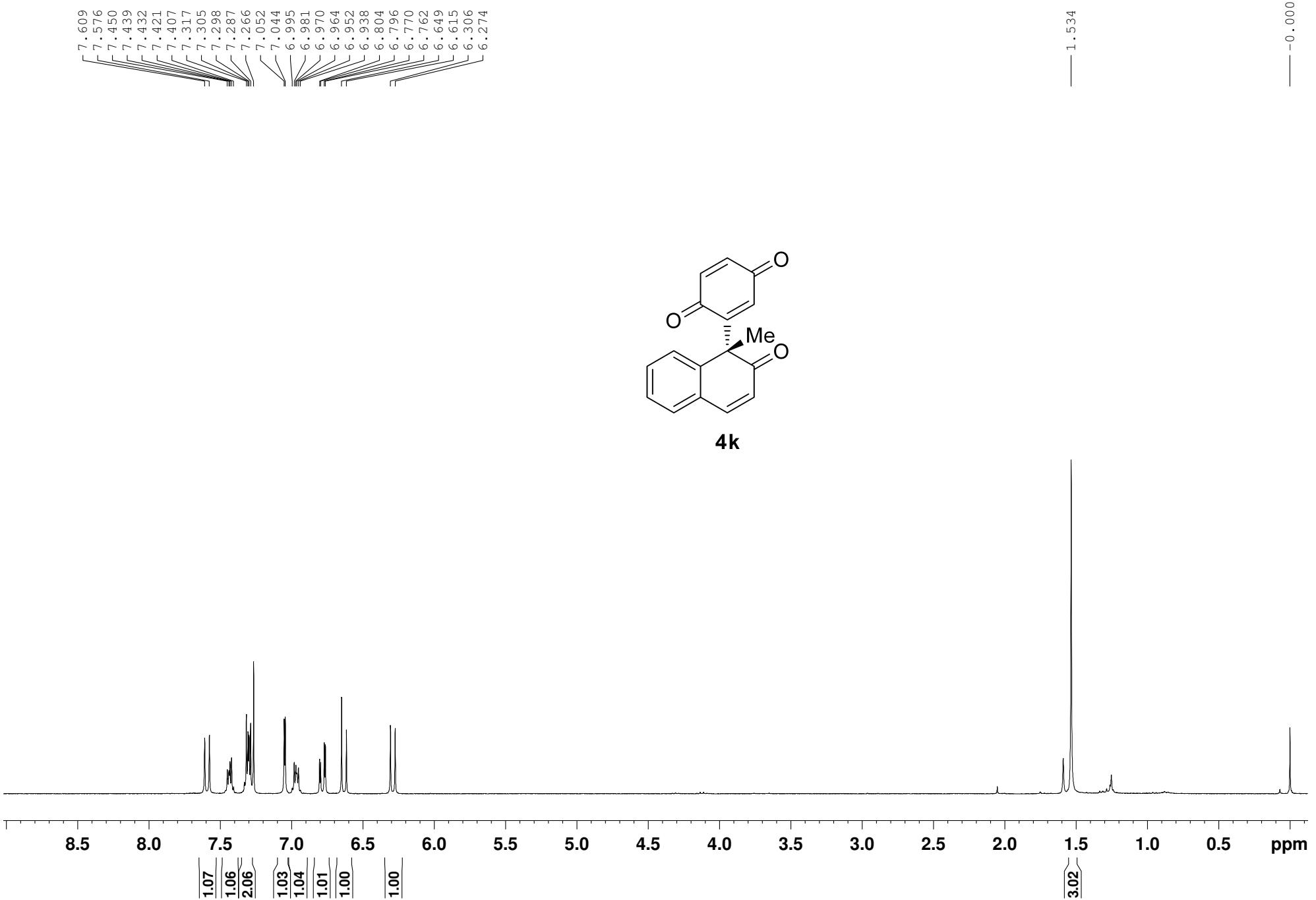


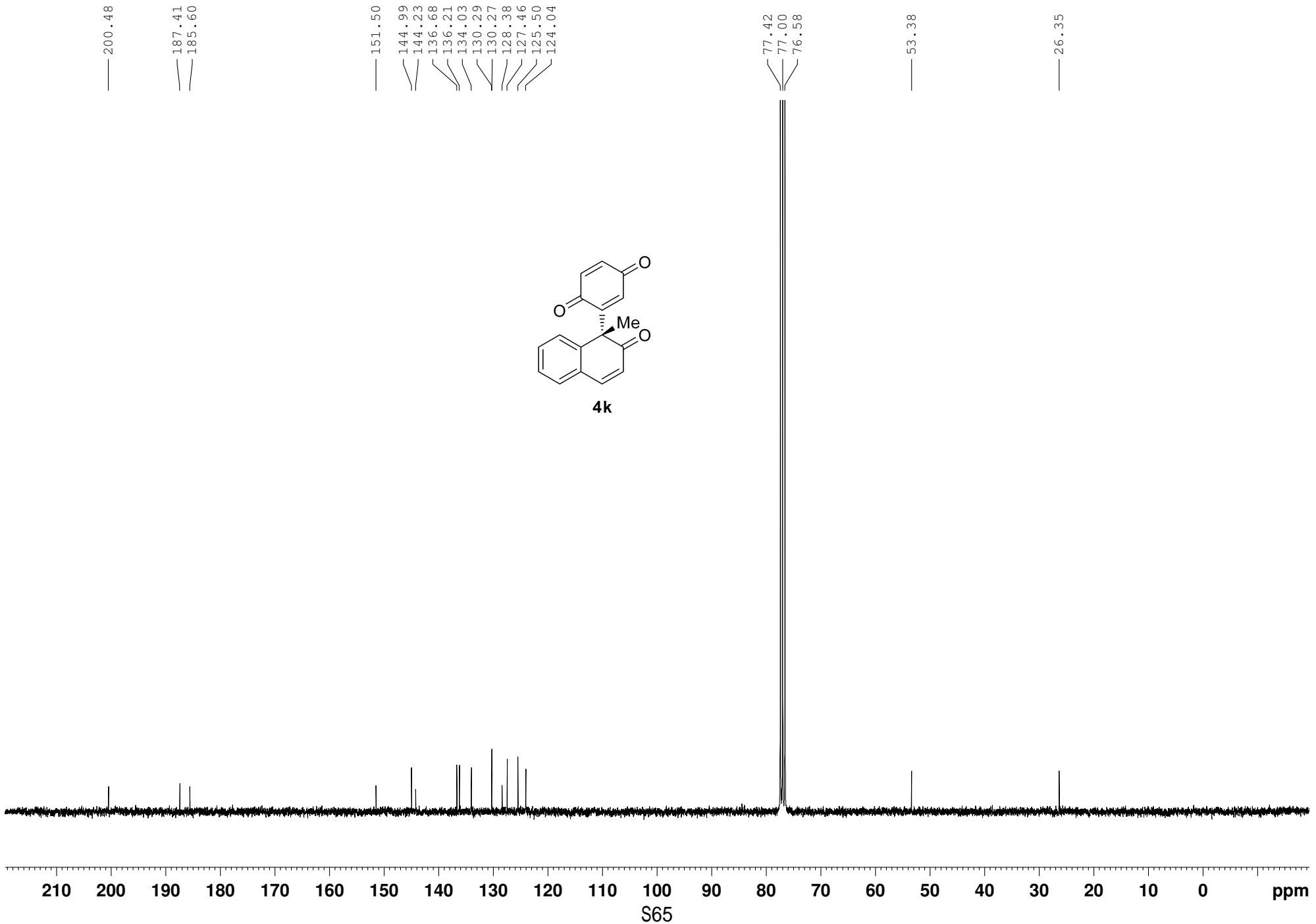


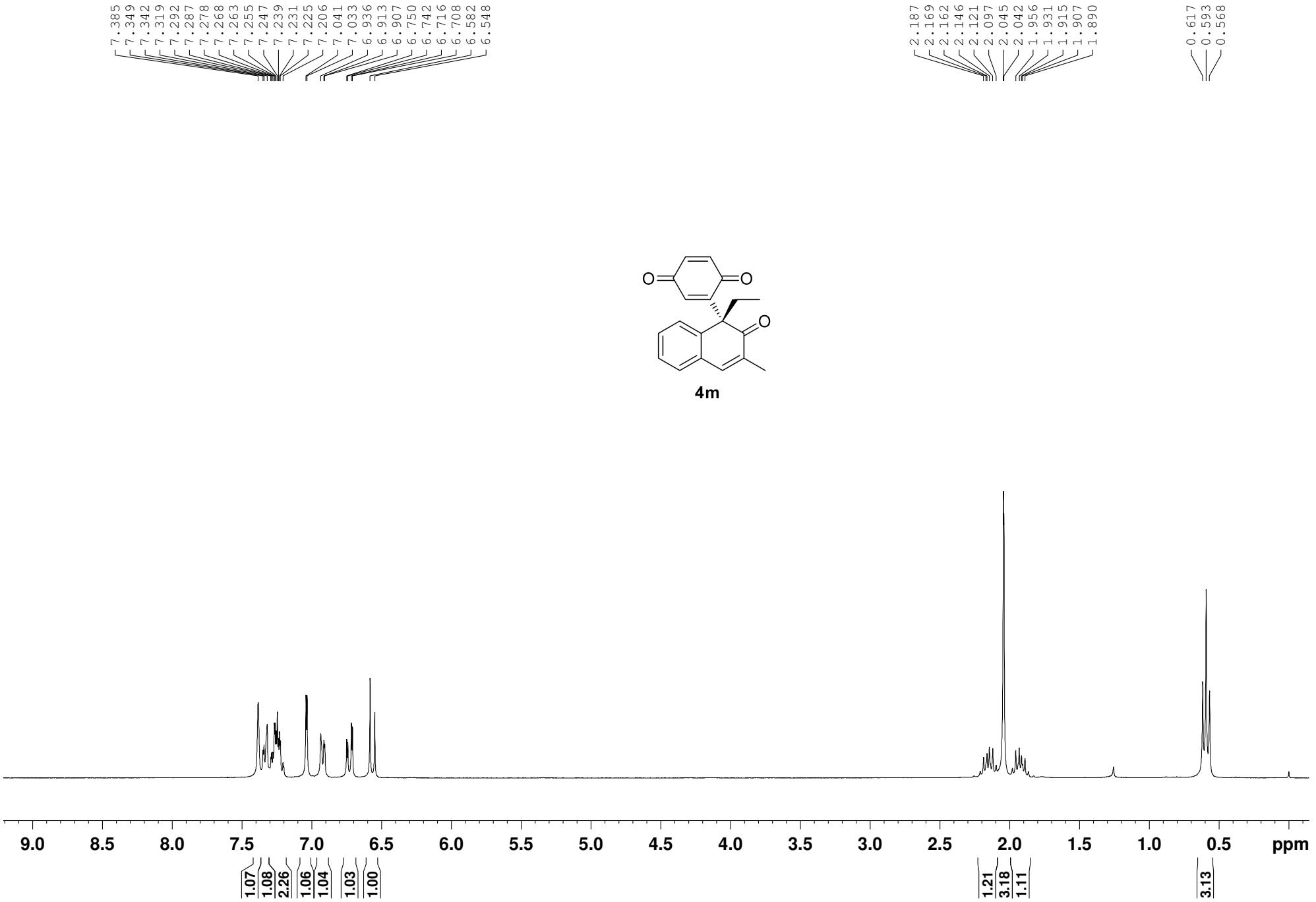


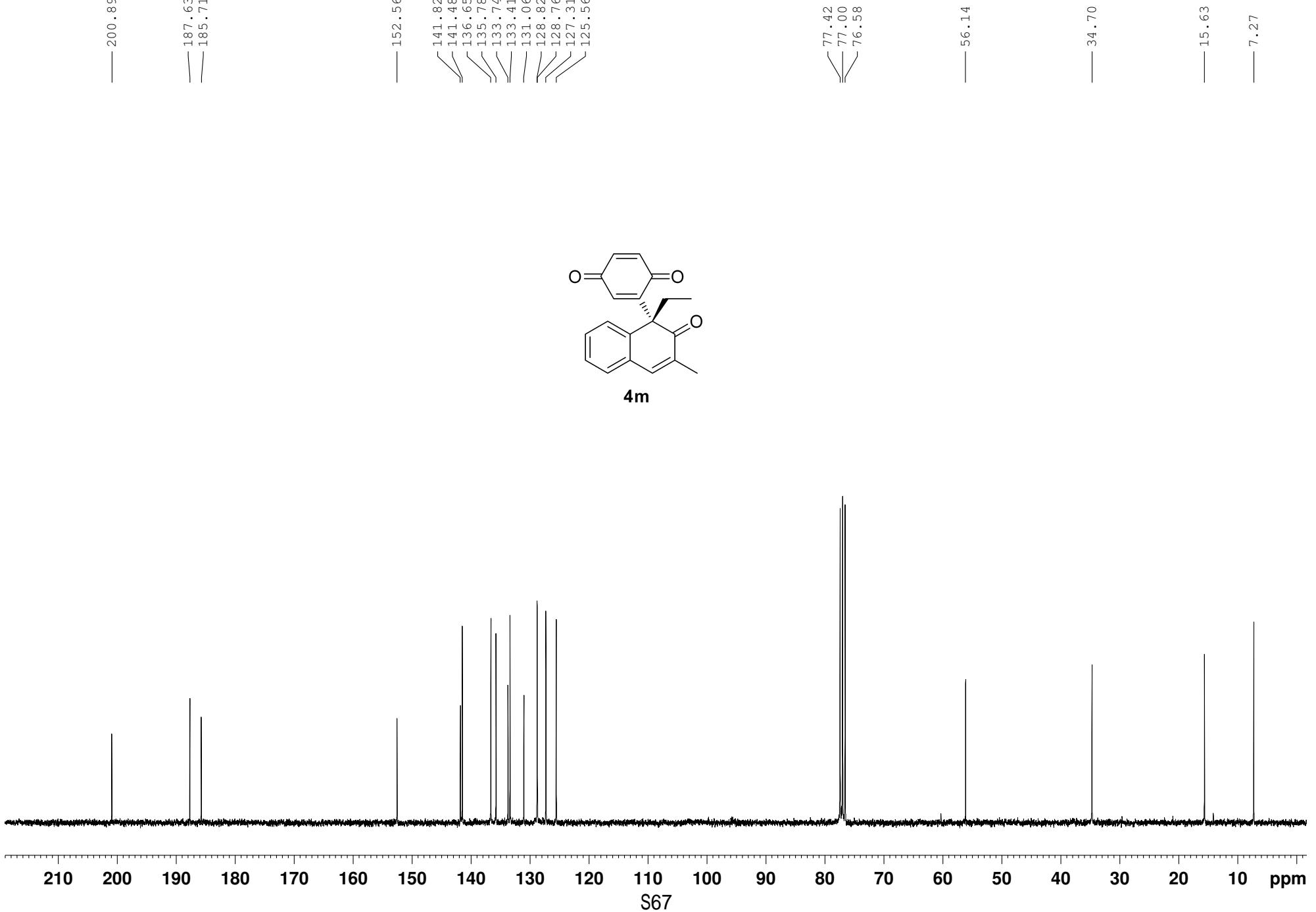


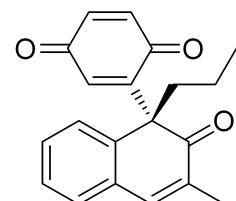












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