Supporting Information

Exo/Endo Selectivity-control in Lewis-acid Catalyzed Tandem Heterocyclization/Formal [4+3] Cycloaddition: Synthesis of Polyheterocycles from 2-(1-Alkynyl)-2-alken-1-ones and 1, 3-Diphenylisobenzofuran.

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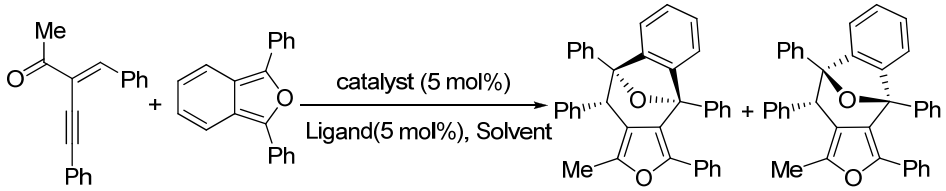
General Considerations: ^{1}H and ^{13}C spectra were generally recorded in a AV-300 Bruker using $CDCl_3$ as solvent at 300 or 75 MHz, respectively. Chemical shifts are reported in ppm relative to $CDCl_3$(δ 7.26 ppm) in indicated cases. Mass spectra (m/z) and HRMS were recorded under the conditions of electron impact (EI) and electrospray (ES). All reactions were monitored by thin-layer chromatography(TLC)

Optimization studies

Table 1. Optimization of the reaction conditions for the [4+3] tandem cycloaddition between **1a** and **2**.

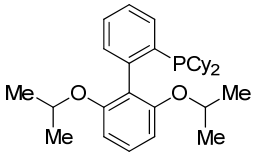


1a **2** **3a** **4a**

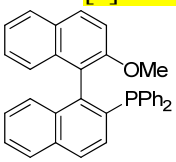
				exo	*endo*
Entry	Catalyst	Solvent	Conditions	Yield [%][a]	*exo*/*endo*[b]
1	$Yb(OTf)_3$	DCE	25 °C, 5 h	N.R.	-
2	$Y(OTf)_3$	DCE	25 °C, 5 h	N.R.	-
3	$In(OTf)_3$	DCE	25 °C, 5 h	N.R.	-
4	$Sc(OTf)_3$	DCE	25 °C, 5 h	N.R.	-
5	$AuCl_3$	DCE	25 °C, 12 h	trace	-
6	AuCl	DCE	25 °C, 12 h	trace	-
7	CuI	DCE	25 °C, 5 h	N.R.	-
8	$PtCl_2$	DCE	25 °C, 5 h	N.R.	-
9	AgOTf	DCE	25 °C, 12 h	trace	-
10	AgOTf	DCE	60 °C, 10 h	63	80:20
11	$Sn(OTf)_2$	DCE	25 °C, 5 h	80(16)[c]	50:50
12	$Cu(OTf)_2$	DCE	25 °C, 20 min	92	41:59
13	$AgSbF_6$	DCE	25 °C, 12 h	9(69)[c]	60:40
14	$Ph_3PAuCl/AgOTf$	DCE	25 °C, 10 min	95	63:37
15	IPrAuCl/AgOTf	DCE	25 °C, 24 h	70	49 : 51
16	L_1AuCl /AgOTf	DCE	25 °C, 10 min	95	89:11
17	$L_1AuCl/AgSbF_6$	DCE	25 °C, 15 min	127[d]	82 : 18
18	L_1AuCl/AgOMs	DCE	25 °C, 2 h	83 [d]	21 : 79
19	$L_1AuCl/C_3H_7CO_2Ag$	DCE	25 °C, 2 h	Complicated[e]	-
20	$L_1AuCl/AgBF_4$	DCE	25 °C, 15 min	131 [d]	82 : 18
21	$L_1AuCl/AgPF_6$	DCE	25 °C, 15 min	128 [d]	81 : 19
22	L_1AuCl/CF_3CO_2Ag	DCE	25 °C, 5 h	Complicated[e]	-
23	L_1AuCl /AgOTf	THF	25°C, 15 min	21	61 : 39
24	L_1AuCl /AgOTf	toluene	25°C, 30 min	53	80 : 20
25	L_1AuCl /AgOTf	CH_2Cl_2	25°C, 10 min	91	83 :17
26	L_2AuCl/AgOTf	DCE	18°C, 20 min	89	10:90
27	L_3AuCl/AgOTf	DCE	25°C, 6 h	92	34:66
28	L_4AuCl/AgOTf	DCE	25°C, 30 min	86	53:47
29	L_5AuCl/AgOTf	DCE	25°C, 15 min	95	74 : 26

30	L_6AuCl/AgOTf	DCE	25°C, 1 h	91	58 : 42
31	L_7AuCl/AgOTf	DCE	25°C, 15 min	95	86 : 14
32	L_8AuCl/AgOTf	DCE	25°C, 15 min	96	38 : 62
33	L_9AuCl/AgOTf	DCE	25°C, 10 min	86	29 : 71
34	L_{10}AuCl/AgOTf	DCE	25°C, 36 h	87(10)[c]	51 : 49
35	L_{11}AuCl/AgOTf	DCE	25°C, 10 min	79	44 : 56
36	L_1/AgOTf	DCE	30 °C, 72 h	trace	-
37	L_1/AgOTf	DCE	60 °C, 27 h	54(29)[c]	80:20
38	L_2/AgOTf	DCE	30 °C 48 h	89	6:94
39	L_9/AgOTf	DCE	60 °C, 3 h	67	79:21
40	L_{12}/AgOTf	DCE	30°C, 47 h	81(9) [c]	7: 93
41	L_{13}/AgOTf	DCE	30°C, 47 h	63(18) [c]	6 : 94
42	L_{14}/AgOTf	DCE	30°C, 34 h	trace	-
43	L_{15}/AgOTf	DCE	30°C, 46 h	70(21) [c]	51 : 49

[a] Yield of the isolated product. [b] Determined by ^{1}H NMR analysis of the crude product. [c] Recovery of the substrate **1a** in the parentheses. [d] NMR yield with CH_2Br_2 as internal standard. [e] A complicated mixture of products was obtained.



L_1



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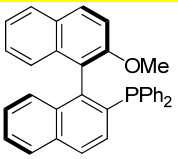
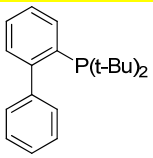


(*R*)-MOP



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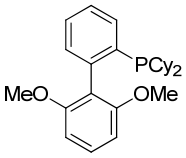

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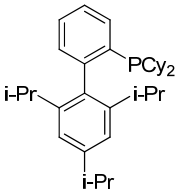

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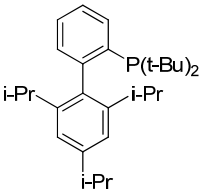

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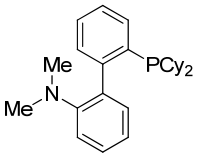

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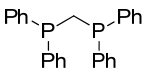

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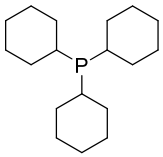

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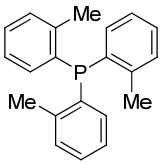
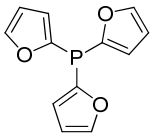
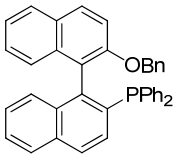


L_{10}



L_{11}



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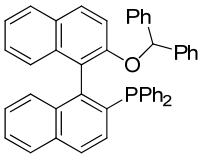
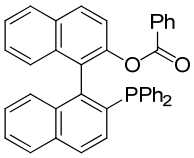


L_{13}



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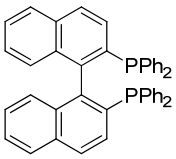


L_{15}

Experimental procedures:

General procedure of the gold(I) –catalyzed tandem heterobicyclization.

Typical procedure for the synthesis of the fused polycyclic compound 3a and 4a .

To a solution of $\mathbf{L_1}$AuCl (10.5 mg, 0.015 mmol) in DCE(1,2-dichlorethane, 1 mL) was added AgOTf (3.8 mg, 0.015 mmol) under an Ar atmosphere, and the mixture was stirred for 10 mins at room temperature. Then the solution of ketone **1a** (73.8 mg, 0.3 mmol) and diene **2** (89.1 mg, 0.33mmol) in DCE (2 mL) was added to this mixture. After being stirred for 15 min at room temperature, **1a** was consumed completely, which was determined by TLC analysis. The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the pure products **3a** (130.3 mg) and **4a** (16.6 mg) with the combined 95% total yield in a ratio of 89:11 as white solids.

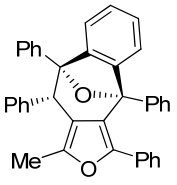
General procedure of the silver(I) –catalyzed tandem heterobicyclization.

Typical procedure for the synthesis of the fused polycyclic compound 3a and 4a .

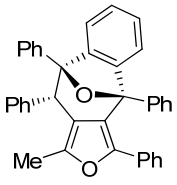
The mixture of $\mathbf{L_2}$ (7.0 mg, 0.015 mmol), AgOTf (3.8 mg, 0.015 mmol) in DCE(1,2-Dichlorethane, 1 mL) was stirred for 20 min at room temperature under an Ar atmosphere. Then the solution of ketone **1a** (73.8 mg, 0.3 mmol) and diene **2** (105.3 mg, 0.39mmol) in DCE (2 mL) was added to this mixture. After being stirred for 48h under Ar at 30^{o}C, **1a** was consumed completely, which was determined by TLC analysis. The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the pure products **3a** (7.8 mg) and **4a** (129.9 mg) with the combined 89% total yield in a ratio of 6:94 as white solids.

Data of the products:

1. **Fused polycyclic compound 3a and 4a .**



3a

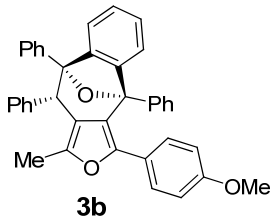


4a

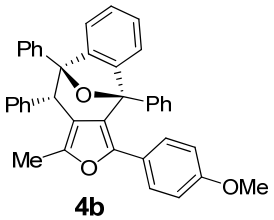
3a: white solid, m.p. 221-223 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 6.6 Hz, 2 H), 7.58 (d, *J* = 7.5 Hz, 3 H), 7.51-7.40 (m, 3 H), 7.39-6.99 (m, 16 H), 4.50 (s, 1 H), 1.95 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.3, 147.4, 146.9, 142.8, 141.8, 141.3, 136.4, 130.9, 129.9, 129.1, 128.9, 128.3, 127.63 (2 C), 127.60, 127.5 (2 C), 126.7, 126.51, 126.48, 126.0, 125.7, 122.7, 121.9, 120.8, 120.2, 88.2, 87.4, 47.3, 12.0 ppm; MS (EI) *m*/*z* (%): 516 [*M*+] (0.8), 57 (100); HRMS calcd for $C_{38}H_{28}O_2$: 516.2089, found: 516.2089.

4a : white solid, m.p. 237-238 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.2 Hz, 2 H), 7.59 (d, *J* = 7.5 Hz, 1 H), 7.55-7.48 (m, 2 H), 7.37 (t, *J* = 7.2 Hz, 1 H), 7.30-7.12 (m, 11 H), 7.10-6.95 (m, 5 H), 6.77 (d, *J* = 7.5 Hz, 1 H), 6.29 (d, *J* = 7.2 Hz, 1 H), 4.87 (s, 1 H), 1.62 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.2, 147.8, 142.9, 141.3, 141.1, 138.5, 136.2, 131.9, 130.9, 130.1, 129.1, 128.7, 128.2, 127.9, 127.8, 127.6, 127.5, 127.0, 126.92, 126.85, 126.7, 126.5, 126.1, 122.0, 121.1, 120.5, 88.3, 86.7, 49.6, 12.6 ppm; MS (EI) *m*/*z* (%): 516 [*M*+] (4.07), 411 (100); HRMS calcd for $C_{38}H_{28}O_2$: 516.2089, found: 516.2089.

2. Fused polycyclic compound 3b and 4b .



3b



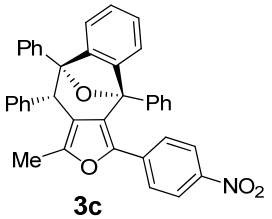
4b

The reaction of **1b** (83.8 mg, 0.3 mmol), **2** (89.1 mg, 0.33 mmol) afforded **3b** (77.5 mg) and **4b** (75.2 mg) with the combined 93% total yield in a ratio of 51:49 under the catalysis of $\mathbf{L_1}$AuOTf. **3b**: light yellow solid, m.p. 254-255 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.8 Hz, 2 H), 7.55-7.45 (m, 3 H), 7.44-7.32 (m, 3 H), 7.31-7.20 (m, 5 H), 7.19-7.09 (m, 4 H), 7.07-6.90 (m, 4 H), 6.61 (d, *J* = 8.7 Hz, 2 H), 4.41 (s, 1 H), 3.67 (s, 3 H), 1.86 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 158.2, 147.54, 147.53, 146.9, 142.7, 141.9, 141.4, 136.4, 129.8, 129.2, 128.9, 128.4, 128.1, 127.60 (2C), 127.56, 127.4, 126.5, 125.9, 125.7, 123.9, 122.6, 120.6, 120.4, 119.9, 113.0, 88.2, 87.4, 55.1, 47.3, 11.9 ppm; MS (EI) *m*/*z* (%): 546 [*M*+] (2.46), 441 (100); HRMS calcd for $C_{39}H_{30}O_3$: 546.2195, found: 546.2195.

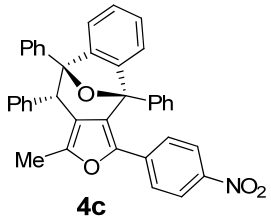
4b : light yellow solid, m.p. 195-197 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 6.9 Hz, 2 H), 7.58-7.49 (m, 3 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 7.30-6.90 (m, 13 H),

6.77 (d, J = 7.5 Hz, 1 H), 6.62 (d, J = 8.7 Hz, 2 H), 6.30 (d, J = 6.9 Hz, 1 H), 4.85 (s, 1 H), 3.70 (s, 3 H), 1.60 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 158.3, 148.4, 147.1, 142.9, 141.4, 141.2, 138.6, 136.2, 131.9, 130.1, 129.1, 128.7, 128.2, 128.1, 127.9, 127.1, 127.5, 127.0, 126.9, 126.8, 126.0, 123.9, 121.0, 120.6, 120.3, 113.0, 88.3, 86.7, 55.1, 49.8, 12.5 ppm; MS (EI) m/z (%): 546 [M+] (1.83), 441 (100); HRMS calcd for $C_{39}H_{30}O_3$: 546.2195, found: 546.2196.

3. Fused polycyclic compound 3c and 4c.



3c

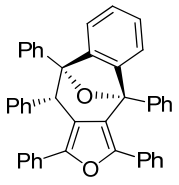


4c

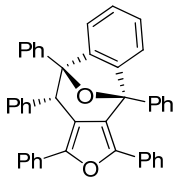
The reaction of **1c** (88.4 mg, 0.3 mmol), **2** (90.6 mg, 0.33 mmol) afforded **3c** (123.4 mg) and **4c** (32.3 mg) with the combined 93% total yield in a ratio of 77:23 under the catalysis of $\mathbf{L_1}$AuOTf. **3c**: yellow solid, m.p. 241-243 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.4 Hz, 2 H), 7.82 (d, J = 7.2 Hz, 2 H), 7.50 (d, J = 7.8 Hz, 3 H), 7.45-7.27 (m, 6 H), 7.26-7.20 (m, 4 H), 7.19-6.92 (m, 6 H), 4.42 (s, 1 H), 1.90 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 150.8, 146.7, 146.6, 145.3, 141.2, 140.8, 140.5, 136.6, 136.2, 129.8, 129.5, 128.9, 128.8, 127.9, 127.8, 127.7 (2C), 126.7, 126.5, 126.2 (2C), 125.6, 123.0, 122.9, 121.4, 120.5, 88.2, 87.1, 47.1, 12.1 ppm; MS (EI) m/z (%): 561 [M+] (4.00), 456 (100); HRMS calcd for $C_{38}H_{27}NO_4$: 561.1940, found: 561.1939.

4c: yellow solid, m.p. 235-237 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.4 Hz, 2 H), 7.69 (d, J = 7.5 Hz, 2 H), 7.60-7.45 (m, 3 H), 7.40 (t, J = 7.5 Hz, 1 H), 7.36-7.15 (m, 11 H), 7.12-6.95 (m, 2 H), 6.80 (d, J = 7.8 Hz, 1 H), 6.23 (d, J = 7.2 Hz, 1 H), 4.87 (s, 1 H), 1.65 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 150.3, 147.4, 145.4, 141.3, 140.7, 137.9, 136.6, 136.2, 132.0, 129.8, 129.3, 128.73, 128.70, 128.2, 127.9, 127.8 127.6, 127.2, 127.1, 126.88, 126.85, 126.6, 126.2, 123.0, 121.8, 120.8, 88.4, 86.5, 49.5, 12.7 ppm; MS (EI) m/z (%): 561 [M+] (3.97), 456 (100); HRMS calcd for $C_{38}H_{27}NO_4$: 561.1940, found: 561.1940.

4. Fused polycyclic compound 3d and 4d.



3d

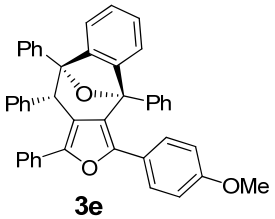


4d

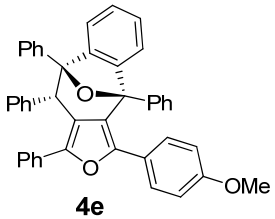
The reaction of **1d** (93.1 mg, 0.3 mmol), **2** (90.0 mg, 0.33 mmol) afforded **3d** (142.7 mg) and **4d** (23.7 mg) with the combined 96% total yield in a ratio of 87:13 under the catalysis of $\mathbf{L_1}$AuOTf. **3d**: white solid, m.p. 181-182 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90-7.80 (m, 2 H), 7.60-7.46 (m, 6 H), 7.41-7.22 (m, 7 H), 7.21-7.02 (m, 11 H), 6.98 (t, *J* = 7.5 Hz, 2 H), 6.92-6.85 (m, 1 H), 4.78 (s, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.11, 148.07, 145.9, 143.8, 141.2, 140.9, 136.2, 130.7, 130.6, 130.5, 129.1, 129.0, 128.5, 128.1, 127.8, 127.63, 127.56 (2C), 127.2 (3C), 127.0, 126.6, 126.1, 125.3 (2C), 123.6, 123.1, 121.6, 120.5, 88.0, 87.3, 48.6 ppm; MS (EI) *m*/*z* (%): 578 [*M*+] (2.93), 473 (100); HRMS calcd for $C_{43}H_{30}O_2$: 578.2246, found: 578.2244.

4d: white solid, m.p. 242-244 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82-7.55 (m, 5 H), 7.50-7.26 (m, 8 H), 7.25-6.85 (m, 13 H), 6.80-6.60 (m, 1 H), 6.53 (d, *J* = 7.5 Hz, 1 H), 6.12-5.92 (m, 1 H), 5.35 (s, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.2, 147.9, 144.3, 141.0, 140.7, 137.2, 136.0, 131.8, 130.6, 130.2, 129.6, 129.0, 128.8, 128.2, 128.01, 127.95, 127.6 (2C), 127.54 (2C), 127.48, 127.3, 127.1, 127.0, 126.7, 125.9, 125.8, 123.9, 121.8, 121.1, 88.9, 86.5, 50.4 ppm; MS (EI) *m*/*z* (%): 578 [*M*+] (2.90), 473 (100); HRMS calcd for $C_{43}H_{30}O_2$: 578.2246, found: 578.2247.

5. Fused polycyclic compound 3e and 4e.



3e



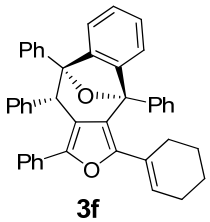
4e

The reaction of **1e** (101.9 mg, 0.3 mmol), **2** (90.9 mg, 0.33 mmol) afforded **3e** (70.8 mg) and **4e** (104.9 mg) with the combined 94% total yield in a ratio of 39:61 under the catalysis of $\mathbf{L_1}$AuOTf. **3e**: light yellow solid, m.p. 145-147 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 9.0 Hz, 2 H), 7.60-7.43 (m, 6 H), 7.42-7.30 (m, 5 H), 7.29-7.12 (m, 8 H), 7.11-7.01 (m, 2 H), 7.00-6.93 (m, 2 H), 6.90-6.83 (m, 1 H), 6.66 (d, *J* = 8.7 Hz, 2 H), 4.77 (s, 1 H), 3.69 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ

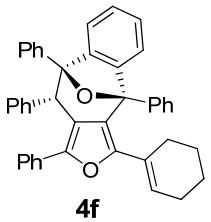
= 158.6, 148.2, 147.5, 145.9, 143.8, 141.2, 140.9, 136.3, 130.7, 130.6, 129.2, 129.0, 128.5 (2C), 128.1, 127.7, 127.6, 127.5, 127.1, 126.8, 126.6, 126.0, 125.3, 125.2, 123.5, 123.0, 122.2, 121.6, 120.3, 113.1, 88.0, 87.3, 55.1, 48.7 ppm; MS (EI) *m*/*z* (%): 608 [*M*+] (2.64), 503 (100); HRMS calcd for $C_{44}H_{32}O_3$: 608.2351, found: 608.2350.

4e: light yellow solid, m.p. 128-130 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73-7.67 (m, 4 H), 7.62 (d, *J* = 7.5 Hz, 1 H), 7.40-7.16 (m, 11 H), 7.10-6.90 (m, 7 H), 6.78-6.60 (m, 3 H), 6.52 (d, *J* = 7.8 Hz, 1 H), 6.04 (d, *J* = 6.9 Hz, 1 H), 5.34 (s, 1 H), 3.72 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 158.6, 148.1, 147.6, 144.3, 141.0, 140.8, 137.3, 136.0, 131.7, 130.3, 129.6, 129.1, 128.8, 128.5, 128.2, 128.0, 127.9, 127.5 (2C), 127.3, 127.1, 126.7, 126.5, 125.9, 125.7, 123.5, 122.4, 121.7, 121.0, 113.1, 88.9, 86.5, 55.2, 50.4 ppm; MS (EI) *m*/*z* (%): 608 [*M*+] (2.41), 503 (100); HRMS calcd for $C_{44}H_{32}O_3$: 608.2351, found: 608.2352.

6. Fused polycyclic compound 3f and 4f.



3f



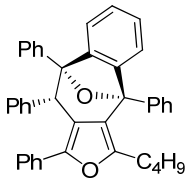
4f

The reaction of **1f** (94.7 mg, 0.3 mmol), **2** (90.6 mg, 0.33 mmol) afforded **3f** (92.7 mg) and **4f** (60.8 mg) with the combined 88% total yield in a ratio of 61:39 under the catalysis of $\mathbf{L_1}$AuOTf. **3f**: white solid, m.p. 94-96 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92-7.85 (m, 2 H), 7.60-7.40 (m, 8 H), 7.35 (d, *J* = 7.5 Hz, 3 H), 7.30-7.12 (m, 6 H), 7.11-7.00 (m, 2 H), 6.99-6.91 (m, 2 H), 6.89-6.81 (m, 1 H), 5.60 (s, 1 H), 4.73 (s, 1 H), 2.45-2.32 (m, 1 H), 2.21-2.03 (m, 1 H), 2.20-1.90 (m, 1 H), 1.70-1.43 (m, 4 H), 1.42-1.28 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.2, 146.6, 146.5, 146.1, 141.4, 141.0, 136.4, 130.8, 130.7, 130.5, 129.0, 128.9, 128.2, 128.0, 127.9, 127.6, 127.5, 127.3, 127.0, 126.6, 126.5, 125.9, 125.4, 125.1, 122.9, 122.0, 120.9, 120.7, 88.0, 87.1, 48.6, 26.9, 25.5, 22.4, 21.7 ppm; MS (EI) *m*/*z* (%): 582 [*M*+] (2.38), 477 (100); HRMS calcd for $C_{43}H_{34}O_2$: 582.2559, found: 582.2559.

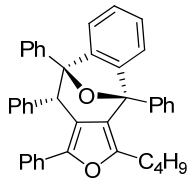
4f: light yellow solid, m.p. 105-107 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81-7.63 (m, 4 H), 7.49 (d, *J* = 7.5 Hz, 1 H), 7.44-7.28 (m, 7 H), 7.23 (d, *J* = 8.7 Hz, 2 H), 7.12-6.85 (m, 7 H), 6.78-6.60 (m, 1 H), 6.46 (d, *J* = 7.5 Hz, 1 H), 6.00 (d, *J* = 6.3 Hz, 1 H), 5.65 (s, 1 H), 5.30 (s, 1 H), 2.45-2.32 (m, 1 H), 2.15-1.90 (m, 2 H),

1.70-1.40 (m, 4 H), 1.35-1.15 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.0, 147.1, 146.7, 141.1, 140.8, 137.5, 136.4, 131.6, 130.51, 130.47, 128.8, 128.7, 128.1, 128.0, 127.92, 127.85, 127.7, 127.6, 127.5, 127.3, 127.2, 126.6, 126.3, 125.7, 125.5, 122.5, 121.4, 121.0, 88.9, 86.5, 50.3, 26.9, 25.5, 22.4, 21.7 ppm; MS (EI) *m*/*z* (%): 582 [*M*+] (1.95), 477 (100); HRMS calcd for $C_{43}H_{34}O_2$: 582.2559, found: 582.2559.

7. Fused polycyclic compound 3g and 4g.



3g

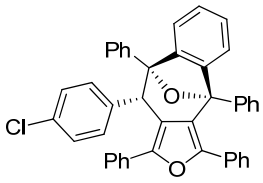


4g

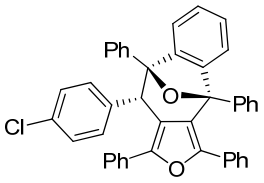
The reaction of **1g** (88.2 mg, 0.31 mmol), **2** (89.6 mg, 0.33 mmol) afforded **3g** (79.2 mg) and **4g** (80.2 mg) with the combined 93% total yield in a ratio of 50:50 under the catalysis of $\mathbf{L_1}$AuOTf. **3g**: light yellow solid, m.p. 98-99 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 6.3 Hz, 2 H), 7.62-7.45 (m, 6 H), 7.44-7.32 (m, 4 H), 7.31-7.12 (m, 7 H), 7.10-6.94 (m, 4 H), 6.93-6.84 (m, 1 H), 4.65 (s, 1 H), 2.45-2.20 (m, 2 H), 1.62-1.46 (m, 2 H), 1.32-1.14 (m, 2 H), 0.80 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.5, 146.6, 146.4, 145.5, 141.3, 141.0, 136.9, 130.9, 130.6, 129.3, 129.2, 128.6, 128.1, 127.6, 127.1 (3C), 126.5, 126.4, 126.0, 125.3, 124.6, 122.8, 122.3, 120.5, 119.8, 88.2, 86.6, 48.8, 30.0, 27.2, 22.5, 13.8 ppm; MS (EI) *m*/*z* (%): 558 [*M*+] (2.72), 453 (100); HRMS calcd for $C_{41}H_{34}O_2$: 558.2559, found: 558.2561.

4g: light yellow solid, m.p. 97-98 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.8 Hz, 2 H), 7.69 (d, *J* = 7.8 Hz, 2 H), 7.51-7.39 (m, 4 H), 7.38-7.25 (m, 4 H), 7.14 (d, *J* = 7.5 Hz, 2 H), 7.08-6.82 (m, 7 H), 6.75-6.60 (m, 1 H), 6.50 (d, *J* = 7.5 Hz, 1 H), 5.95 (d, *J* = 6.0 Hz, 1 H), 5.23 (s, 1 H), 2.39-2.14 (m, 2 H), 1.67-1.40 (m, 2 H), 1.35-1.15 (m, 2 H), 0.81 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.5, 146.9, 146.3, 140.7, 140.4, 137.1, 137.0, 131.9, 130.6, 129.6, 129.04, 128.98, 128.4, 128.0, 127.9, 127.8, 127.5, 127.4, 127.2, 126.6, 126.1, 125.5, 125.4, 122.8, 121.1, 119.7, 89.2, 85.8, 50.8, 30.1, 27.2, 22.5, 13.8 ppm; MS (EI) *m*/*z* (%): 558 [*M*+] (2.96), 453 (100); HRMS calcd for $C_{41}H_{34}O_2$: 558.2559, found: 558.2562.

8. Fused polycyclic compound 3h and 4h.



3h

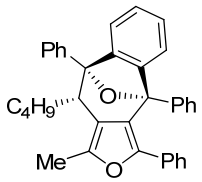


4h

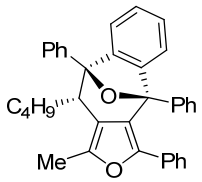
The reaction of **1h** (102.9 mg, 0.3 mmol), **2** (90.2 mg, 0.33 mmol) afforded **3h** (119.8 mg) and **4h** (56.5 mg) with the combined 96% total yield in a ratio of 68:32 under the catalysis of $\mathbf{L_1}$AuOTf. **3h**: white solid, m.p. 188-190 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80-7.65 (m, 2 H), 7.55-7.35 (m, 6 H), 7.32-6.92 (m, 18 H), 6.86 (d, *J* = 7.2 Hz, 2 H), 4.69 (s, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.2, 148.0, 145.6, 144.0, 140.9, 139.5, 136.1, 131.9, 131.8, 130.5, 130.3, 129.1 (2C), 128.5, 128.2 (2C), 127.9, 127.8, 127.63, 127.59, 127.3, 127.2, 127.1, 126.9, 125.3, 125.2, 123.3, 123.1, 121.2, 120.5, 87.9, 87.3, 48.0 ppm; MS (EI) *m*/*z* (%): 612 [*M*+] (2.63), 507 (100); HRMS calcd for $C_{43}H_{29}O_2Cl$: 612.1856, found: 612.1857.

4h: white solid, m.p. 225-227 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95-7.65 (m, 5 H), 7.55-7.34 (m, 8 H), 7.33-7.05 (m, 11 H), 7.04-6.90 (m, 1 H), 6.76 (d, *J* = 6.9 Hz, 1 H), 6.70-6.60 (m, 1 H), 6.20-5.95 (m, 1 H), 5.42 (d, *J* = 1.8 Hz, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.2, 147.9, 144.4, 140.5, 140.3, 135.9, 135.8, 132.8, 132.5, 130.9, 130.4, 130.0, 129.0, 128.9, 128.3, 128.2 (2C), 127.7, 127.6, 127.4 (2C), 127.2, 127.1 (2C), 127.0, 126.9, 126.1, 125.8, 123.6, 121.3, 88.8, 86.6, 49.9 ppm; MS (EI) *m*/*z* (%): 612 [*M*+] (2.42), 507 (100); HRMS calcd for $C_{43}H_{29}O_2Cl$: 612.1856, found: 612.1859.

9. Fused polycyclic compound 3i and 4i.



3i



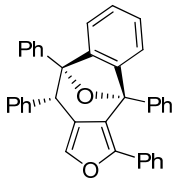
4i

The reaction of **1i** (69.6 mg, 0.31 mmol), **2** (90.4 mg, 0.33 mmol) afforded **3i** (82.2 mg) and **4i** (60.7 mg) with the combined 94% total yield in a ratio of 58:42 under the catalysis of $\mathbf{L_1}$AuOTf. **3i**: white solid, m.p. 83-85 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.5 Hz, 2 H), 7.63 (d, *J* = 7.5 Hz, 2 H), 7.45-7.31 (m, 3 H), 7.30-7.10 (m, 9 H), 7.09-7.00 (m, 3 H), 3.42-3.30 (m, 1 H), 2.23 (s, 3 H), 1.82-1.58

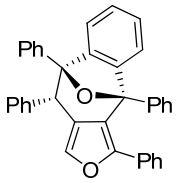
(m, 2 H), 1.48-1.15 (m, 2 H), 1.14-0.95 (m, 2 H), 0.70 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 147.7, 147.0, 146.8, 142.6, 141.8, 136.6, 131.1, 129.1, 128.8, 128.3, 128.1, 127.4, 127.24, 127.15, 126.8, 126.6, 126.3, 125.3, 122.8, 122.7, 120.1, 119.5, 88.1, 87.3, 39.6, 32.8, 28.3, 23.2, 13.8, 13.1 ppm; MS (EI) *m*/*z* (%): 496 [*M*+] (14.64), 105 (100); HRMS calcd for $C_{36}H_{32}O_2$: 496.2402, found: 496.2405.

4i: white solid, m.p. 183-185 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.5 Hz, 2 H), 7.63-7.50 (m, 3 H), 7.45-7.23 (m, 6 H), 7.22-7.00 (m, 8 H), 4.10-4.00 (m, 1 H), 2.33 (s, 3 H), 1.85-1.55 (m, 2 H), 1.30-1.08 (m, 3 H), 1.05-0.85 (m, 1 H), 0.76 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 147.8, 146.5, 143.3, 143.0, 141.1, 136.2, 130.9, 128.9, 128.7, 128.2, 128.1 (3C), 127.8, 127.4, 126.8, 126.7, 126.5, 125.6, 122.1, 121.7, 120.8, 88.6, 86.6, 38.0, 30.8, 30.2, 23.2, 13.8, 13.7 ppm; MS (EI) *m*/*z* (%): 496 [*M*+] (10.82), 105 (100); HRMS calcd for $C_{36}H_{32}O_2$: 496.2402, found: 496.2403.

10. Fused polycyclic compound 3j and 4j.



3j



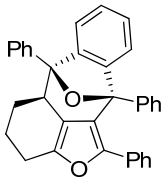
4j

The reaction of **1j** (70.2 mg, 0.3 mmol), **2** (105.6 mg, 0.39 mmol) afforded **3j** (45.9 mg) and **4j** (59.3 mg) with the combined 70% total yield in a ratio of 42:58 under the catalysis of $\mathbf{L_2}$AgOTf. **3j**: yellow solid, m.p. 90-91 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.5 Hz, 2 H), 7.62-7.41 (m, 7 H), 7.38-7.21 (m, 6 H), 7.20-7.10 (m, 5 H), 7.09-7.01 (m, 1 H), 6.76 (d, *J* = 7.5 Hz, 1 H), 6.62 (d, *J* = 7.5 Hz, 2 H), 6.14 (s, 1 H), 4.92 (s, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 153.2, 152.6, 151.3, 141.2, 139.6, 137.6, 136.2, 131.0, 130.9, 128.7, 128.6, 128.5, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.2, 126.6, 126.4, 126.1, 123.4, 121.8, 119.3, 106.5, 90.0, 85.1, 52.5 ppm; MS (EI) *m*/*z* (%): 502 [*M*+] (26.73), 105 (100); HRMS calcd for $C_{37}H_{26}O_2$: 502.1933, found: 502.1931.

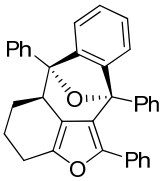
4j: light yellow solid, m.p. 113-115 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.5 Hz, 2 H), 7.58 (d, *J* = 7.5 Hz, 1 H), 7.46 (d, *J* = 4.8 Hz, 2 H), 7.36 (d, *J* = 7.5 Hz, 1 H), 7.26-7.05 (m, 15 H), 6.90-6.82 (m, 2 H), 6.76 (d, *J* = 7.5 Hz, 2 H), 4.91 (s, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.5, 145.0, 141.3, 141.0, 139.5, 136.1, 131.0,

130.8, 129.1, 128.9, 128.3, 128.0, 127.8, 127.7, 127.6 (2C), 127.4, 127.3, 127.0 (2C), 126.8 (2C), 126.7, 126.3, 121.6, 121.0, 88.3, 86.8, 49.8 ppm; MS (EI) *m*/*z* (%): 502 [*M*+] (4.06), 397 (100); HRMS calcd for $C_{37}H_{26}O_2$: 502.1933, found: 502.1934.

11. Fused polycyclic compound 3k and 4k .



3k

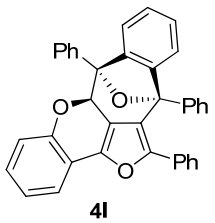


4k

The reaction of **1k** (59.2 mg, 0.3 mmol), **2** (91.0 mg, 0.34 mmol) afforded **3k** (21.3 mg) and **4k** (105.5 mg) with the combined 91% total yield in a ratio of 17:83 under the catalysis of $\mathbf{L_1}$AuOTf. **3k**: white solid, m.p. 229-231 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70-7.50 (m, 5 H), 7.45-7.30 (m, 4 H), 7.29-7.20 (m, 2 H), 7.19-7.10 (m, 5 H), 7.09-7.00 (m, 3 H), 3.10 (d, *J* = 11.4 Hz, 1 H), 2.81-2.53 (m, 2 H), 2.20-2.04 (m, 1 H), 1.90-1.70 (m, 2 H), 1.15-0.95 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 149.2, 148.7, 145.7, 144.1, 140.0, 136.1, 130.9, 128.9, 128.5, 128.1, 127.9 (2C), 127.6, 127.5, 127.1, 127.0, 126.7, 125.5, 122.5, 122.4, 121.7, 121.6, 87.7, 85.7, 42.6, 26.1, 23.1, 22.9 ppm; MS (EI) *m*/*z* (%): 446 [*M*+] (13.55), 361 (100); HRMS calcd for $C_{34}H_{26}O_2$: 466.1933, found: 466.1933.

4k: white solid, m.p. 235-236 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80-7.70 (m, 2 H), 7.62 (d, *J* = 7.5 Hz, 2 H), 7.42-7.27 (m, 7 H), 7.26-7.15 (m, 4 H), 7.13-7.02 (m, 4 H), 3.81 (d, *J* = 10.2 Hz, 1 H), 2.80-2.65 (m, 1 H), 2.55-2.40 (m, 1 H), 2.39-2.25 (m, 1 H), 2.24-2.10 (m, 1 H), 2.09-1.90 (m, 1 H), 1.20-1.00 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 149.9, 149.7, 143.8, 143.0, 141.3, 136.6, 131.1, 129.3, 129.1, 128.7, 128.1, 128.0, 127.8, 127.69, 127.66, 127.0, 126.2, 125.8, 124.5, 121.5, 121.4, 119.9, 88.7, 88.5, 40.8, 25.2, 22.8 (2C) ppm; MS (EI) *m*/*z* (%): 446 [*M*+] (19.59), 361 (100); HRMS calcd for $C_{34}H_{26}O_2$: 466.1933, found: 466.1932.

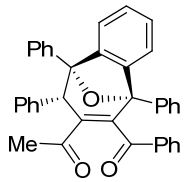
12. Fused polycyclic compound 4l.



4l

The reaction of **1l** (74.4 mg, 0.3 mmol), **2** (91.1 mg, 0.33 mmol) afforded **4l** (139.1mg) in 90% yield under the catalysis of $\mathbf{L_1}$AuOTf. **4l**: light yellow solid, m.p. 146-148 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.5 Hz, 2 H), 7.82-7.75 (m, 2 H), 7.50-7.25 (m, 10 H), 7.23-6.96 (m, 8 H), 6.95-6.80 (m, 1 H), 6.07 (s, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 154.2, 147.5, 146.6, 145.3, 142.4, 141.2, 135.7, 130.3, 129.5, 129.4, 128.9, 128.8, 128.3, 128.24, 128.20, 128.0, 127.8, 127.1, 126.7, 125.8, 125.7, 122.3, 122.2, 120.4, 119.8, 118.5, 117.8, 117.5, 89.6, 87.5, 74.5 ppm; MS (EI) *m*/*z* (%): 516 [*M*+] (30.89), 105 (100); HRMS calcd for $C_{37}H_{24}O_3$: 516.1725, found: 516.1727.

13. Oxabicyclic alkene 5.

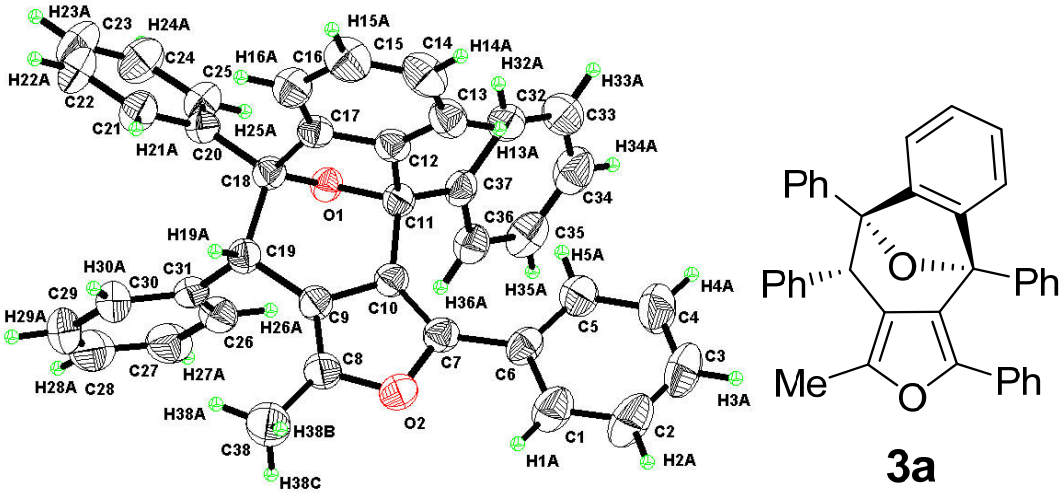


5

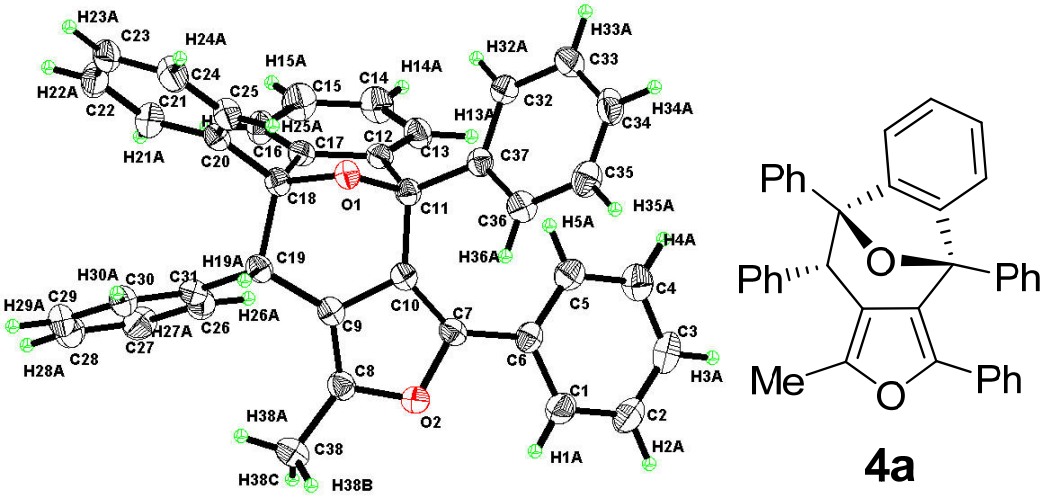
Fused polycyclic compound **3a** (155.3 mg, 0.3 mmol) was added to the suspension of 3-chlorobenzoperoxoic acid (*m*-CPBA, 85%) (93.5 mg, 0.45 mmol) in CH_2Cl_2 (3 mL) at 0 ^{o}C under Ar atmosphere. The mixture was stirred for 3 h, which was determined by TLC analysis. The mixture was neutralized by saturated solution of $NaHCO_3$ at room tempreture. The extracts with CH_2Cl_2 were dried over anhydrous $MgSO_4$ and passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the pure product **5** (145.6 mg) in 91% yield as white solid.

5: white solid, m.p. 215-217 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.5 Hz, 2 H), 7.65-7.50 (m, 7 H), 7.49-7.40 (m, 1 H), 7.39-7.30 (m, 1 H), 7.29-6.95 (m, 13 H), 4.27 (s, 1 H), 1.72 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 199.2, 197.2, 151.4, 148.6, 144.1, 140.1, 137.6, 137.0, 136.5, 136.3, 132.8, 130.7, 128.6, 128.17, 128.15, 128.1 (2C), 128.0, 127.8, 127.4, 127.0 (2C), 126.9, 125.1, 122.3, 121.2, 87.7, 86.4, 49.0, 29.0 ppm; MS (EI) *m*/*z* (%): 532 [*M*+] (5.56), 105 (100); HRMS calcd for $C_{38}H_{28}O_3$: 532.2038, found: 532.2037.

X-Ray Structures

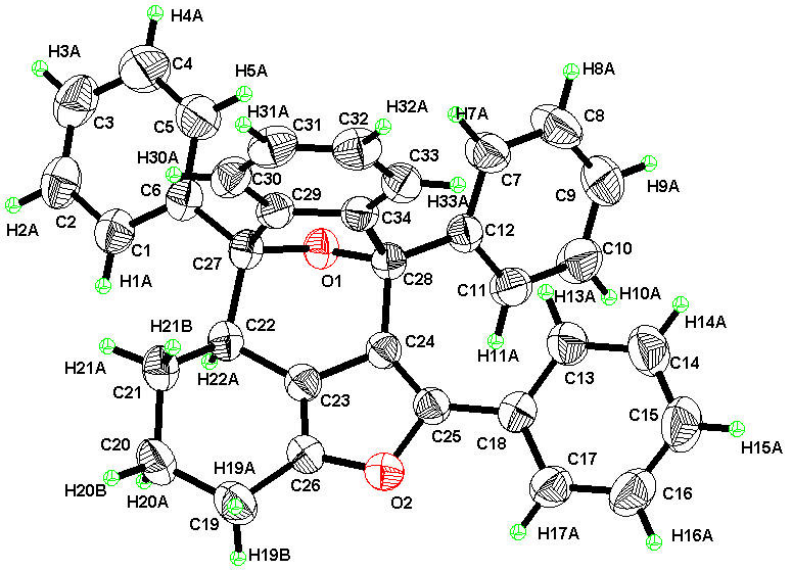


3a (*exo*)

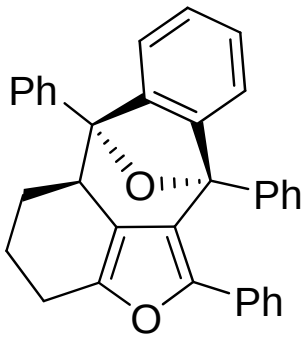


4a (*endo*)

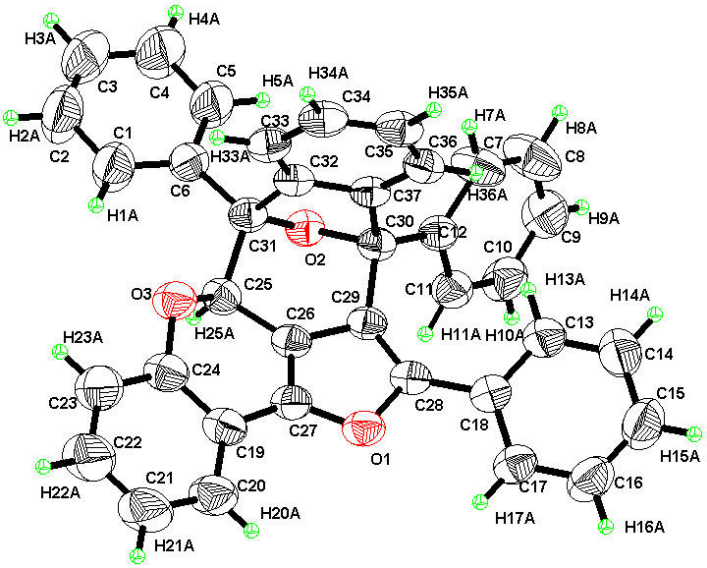
Figure 1. X-ray structure of **3a** and **4a**.



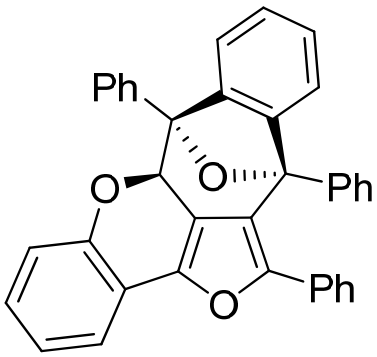
4k (*endo*)



4k



4l (*endo*)



4l

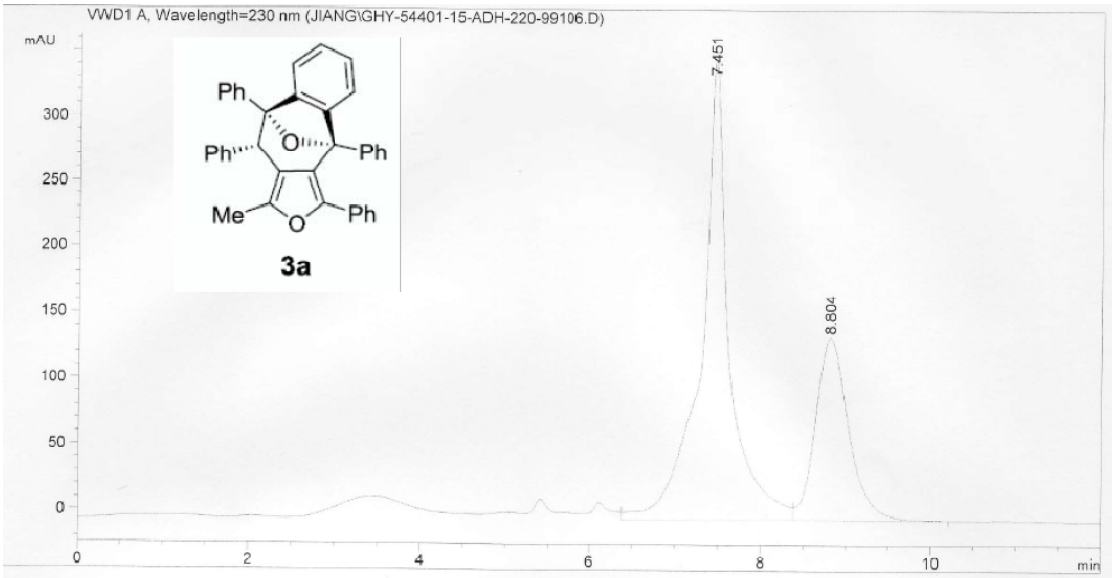
Figure 2. X-ray structure of **4k** and **4l**.

Typical procedure for asymmetric gold-catalyzed cycloaddition.

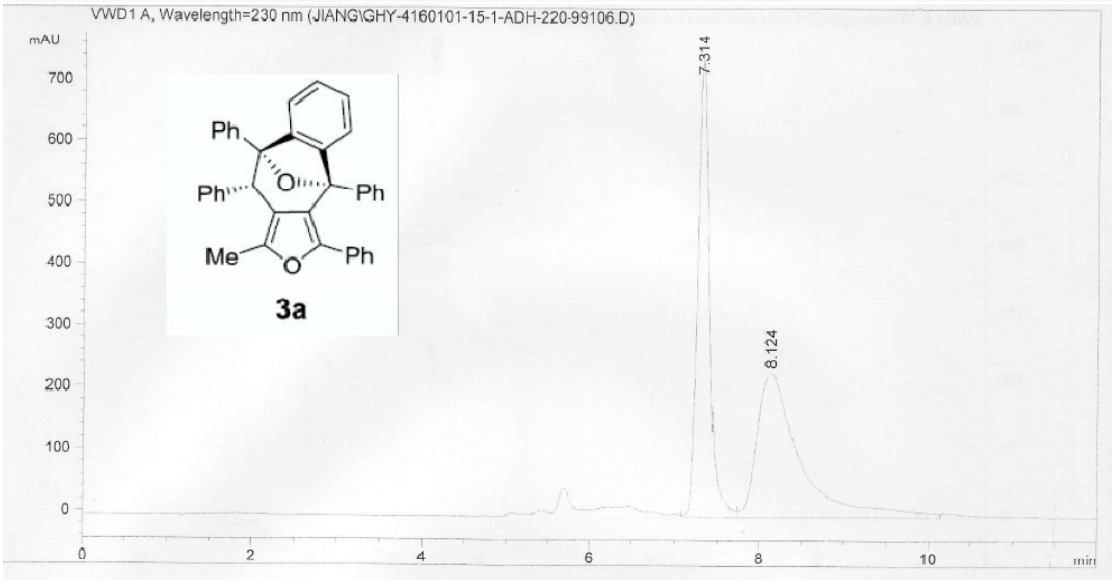
After the solution of ligand ((*R*)-MOP) (7.1 mg, 0.015 mmol) and Me_2SAuCl(4.4 mg, 0.015mmol) in CH_2Cl_2(2 mL) was stirred at rt for 2 h, the solvent was removed in vacuum. Then a solution of AgOTf (3.8 mg, 0.015mmol) in DCE (1 mL) was added to the residue and the mixture was stirred at 20^{o}C for 15 mins. A solution of **1a** (73.8 mg, 0.3 mmol) and **2** (89.1 mg, 0.33 mmol) in DCE (2 mL) at 20^{o}C was transferred into the above catalyst solution. The reaction was determined by TLC, after the less component was consumed, the solution was removed under reduced pressure. The diastereomeric ratio was determined by crude ^{1}H NMR, the resulting crude mixture was passed through a short silica gel column to afford the pure products **3a** (16.5 mg) and **4a** (132.0 mg) with the combined 96% total yield in a ratio of 10:90 as white solids.

The enantionmeric excesses of the products were determined by chiral stationary phase HPLC using a Chiralcel OD-H and Chiralpak AD-H.

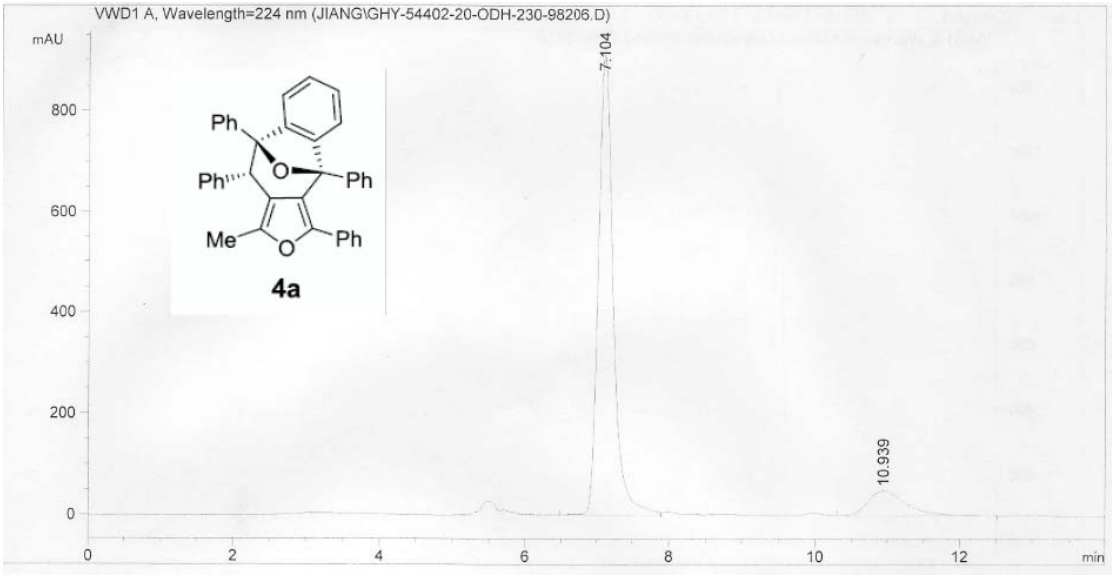
Ee% of **3a**: 36%, determined by Chiralpak AD-H *i*-PrOH/hexane = 1/99, flow rate 0.6 mL/min, t = 8.8 (minor), t = 7.5 (major), etection at 230 nm, sample **3a;** ee% of **4a**: 75%, determined by Chiralcel OD-H *i*-PrOH/hexane = 2/98, flow rate 0.6 mL/min, t = 10.9 (minor), t = 7.1(major), etection at 224 nm, sample **4a.**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.451	VV	0.3078	8048.36914	351.57571	67.8133
2	8.804	VB	0.4180	3820.06152	138.43840	32.1867
Totals :				1.18684e4	490.01411	



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.314	VV	0.1507	7382.92285	744.24615	46.9326
2	8.124	VV	0.5117	8347.97461	234.31458	53.0674
Totals :				1.57309e4	978.56073	



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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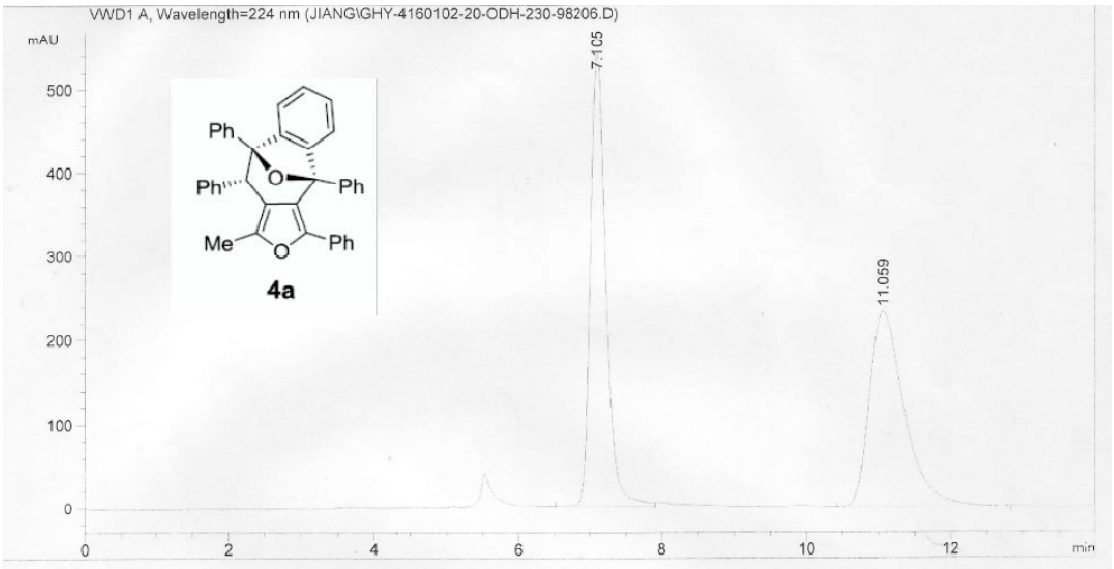
2	10.939	VB	0.5608	1858.73206	49.95578	12.3674
Totals :				1.50292e4	959.99368	



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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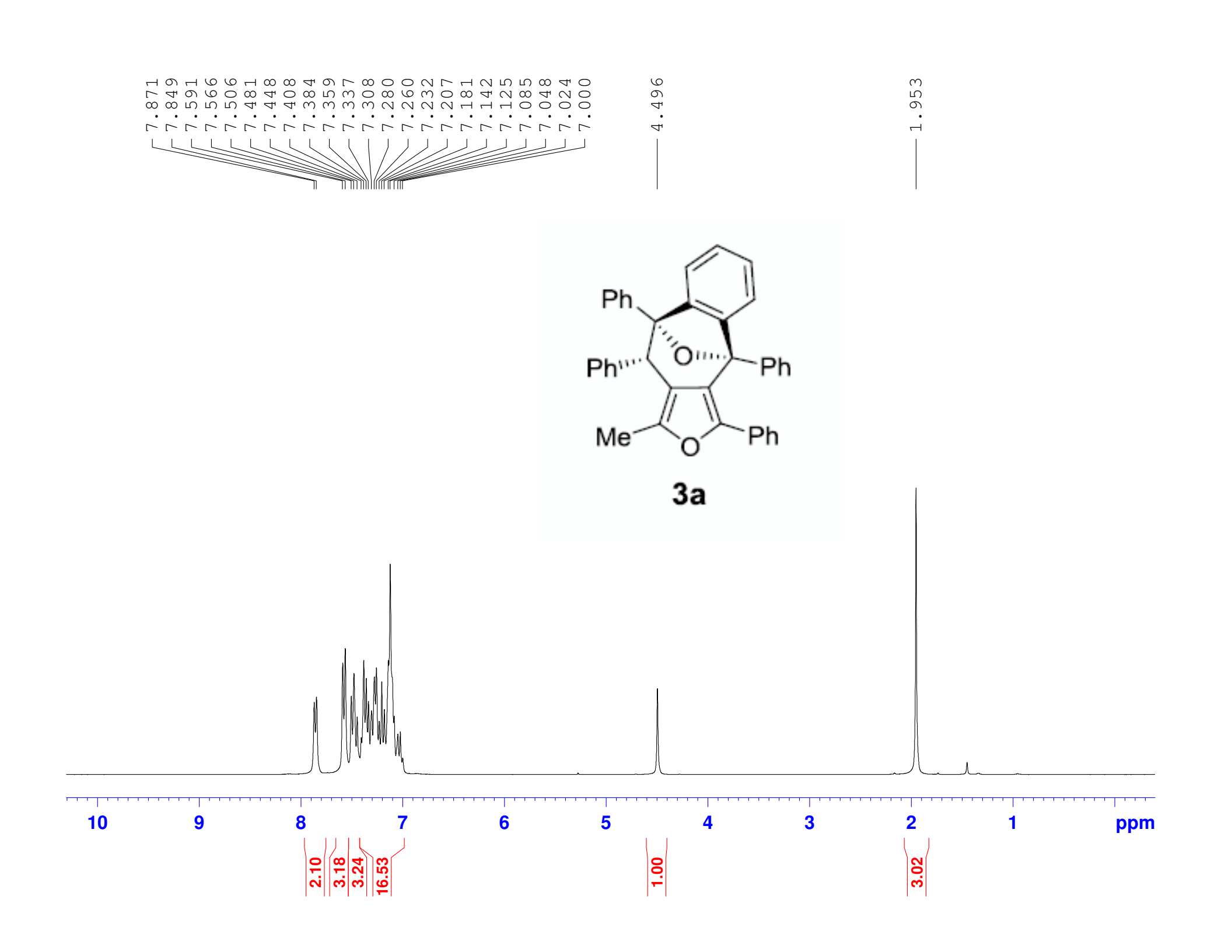
Totals :				1.61316e4	774.77327	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7.207
7.181
7.142
7.125
7.085
7.048
7.024
7.000
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1.953
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Ph
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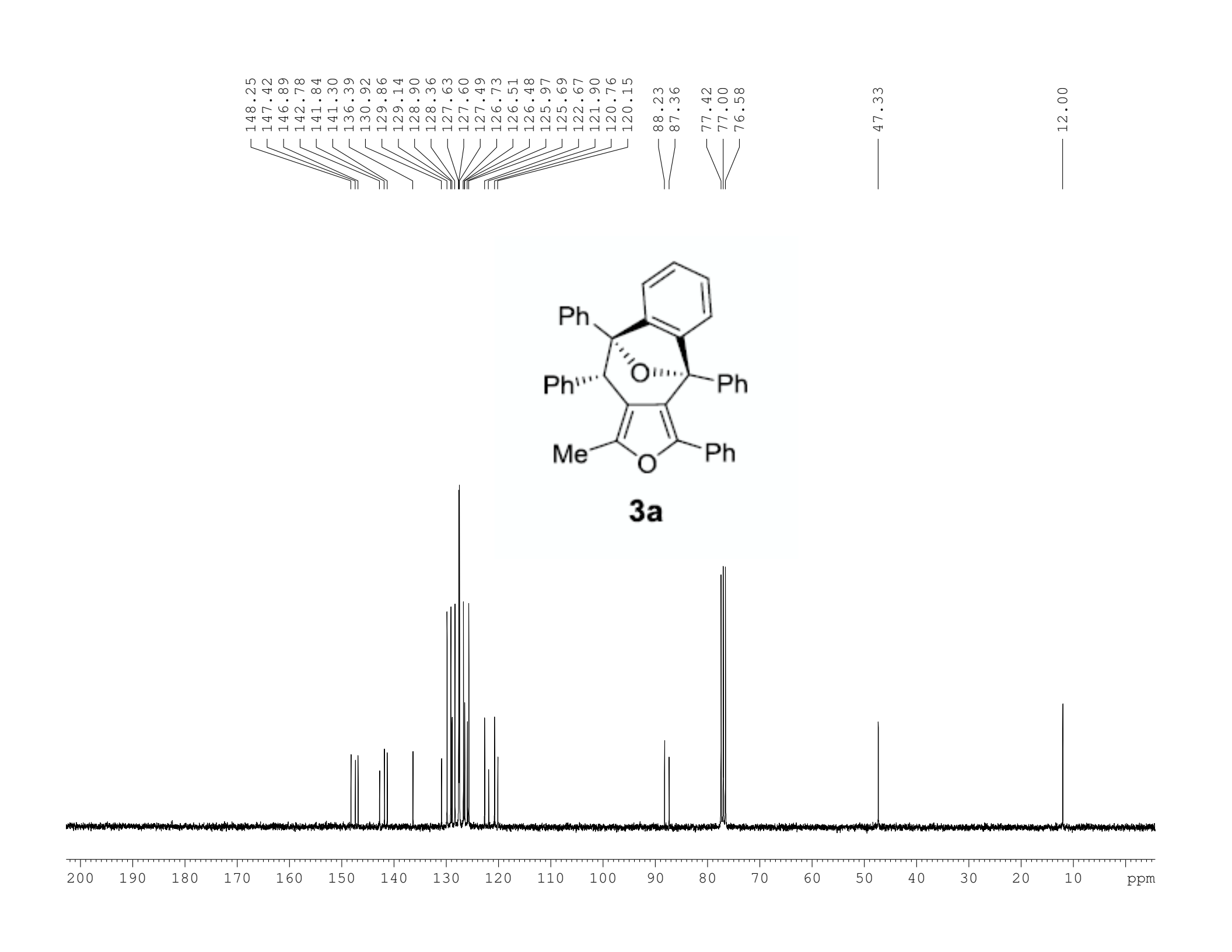
3.02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77.00
76.58
47.33
12.00
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Ph
Me
O
Ph
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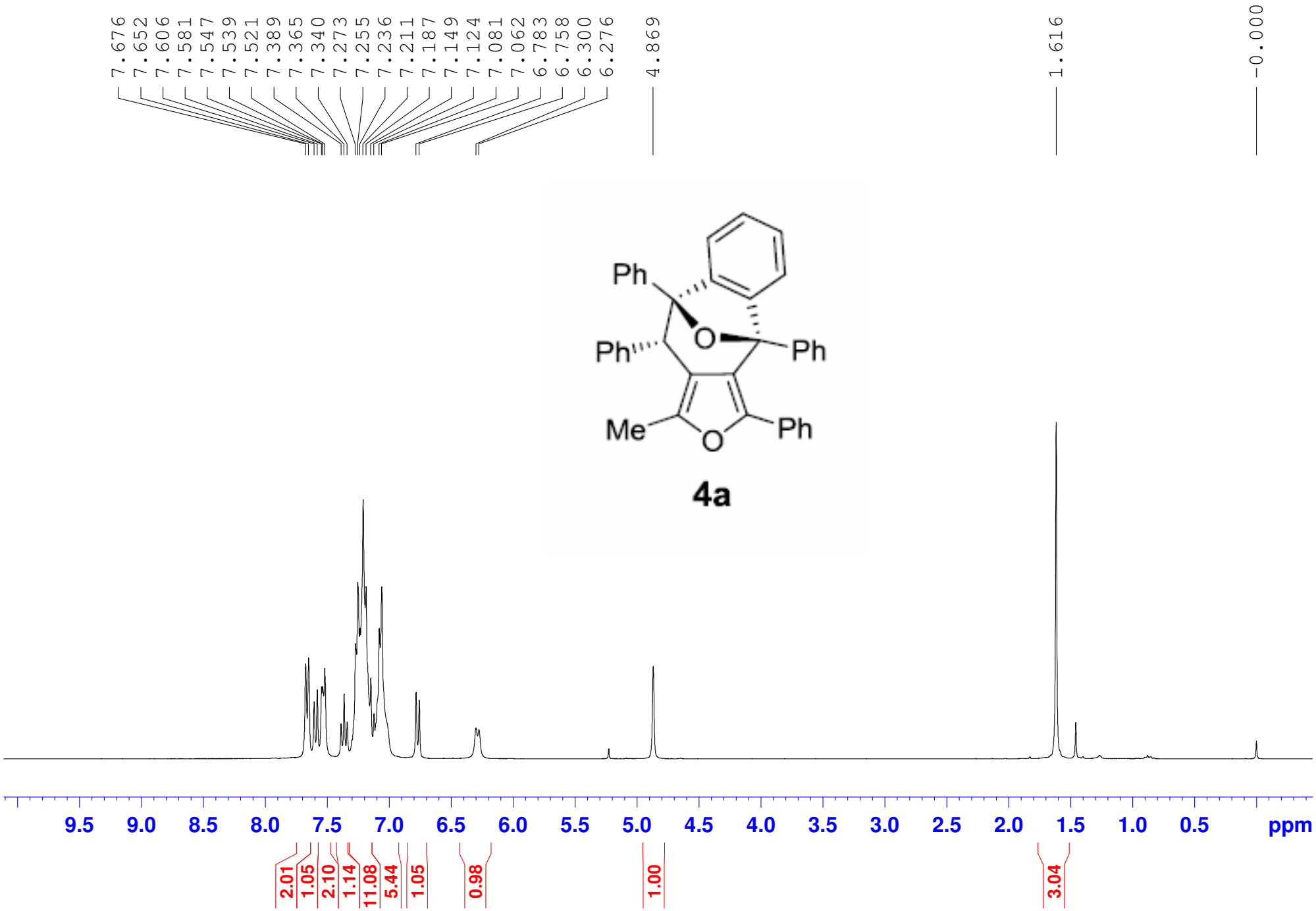
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7.124
7.081
7.062
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6.758
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6.276
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1.616
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Ph
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O
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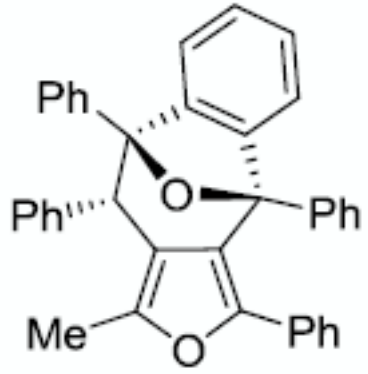
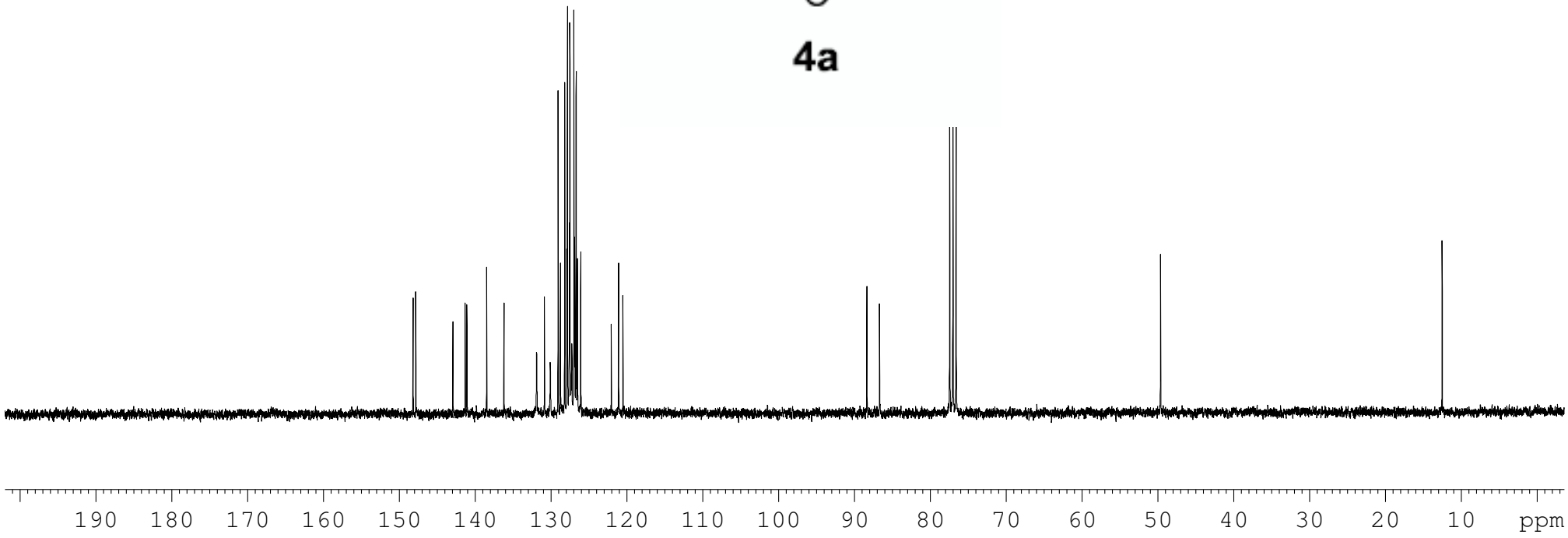
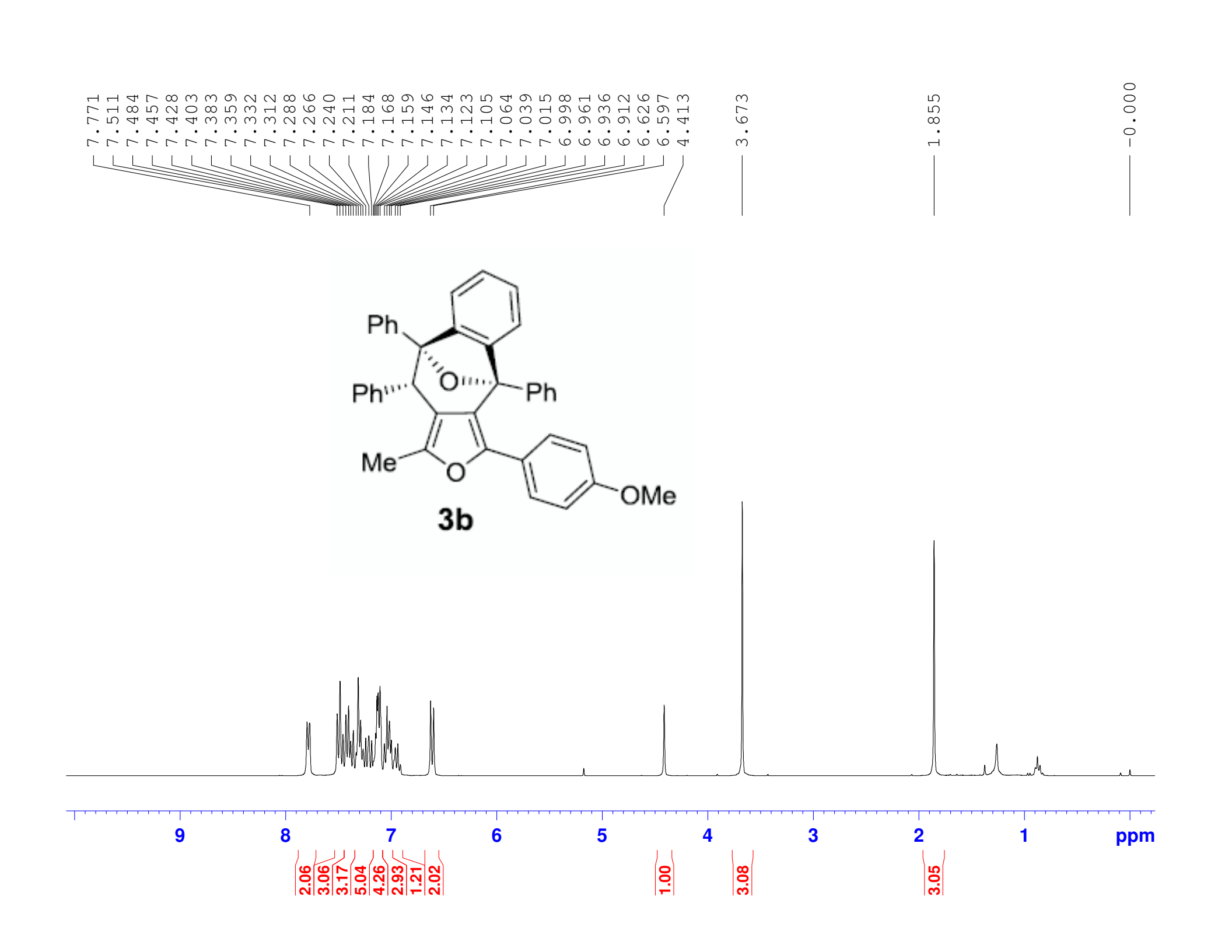


4a

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Ph
Me
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OMe
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2.02
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3.05

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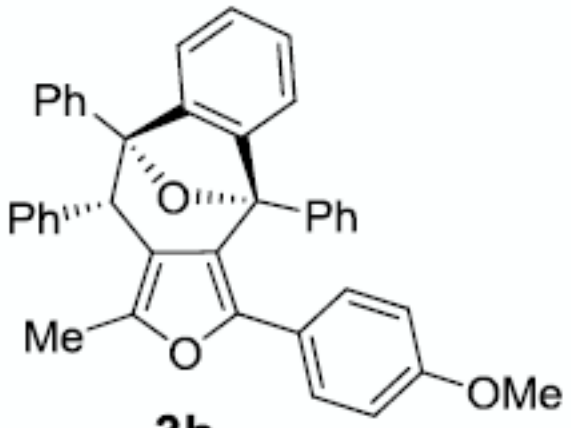
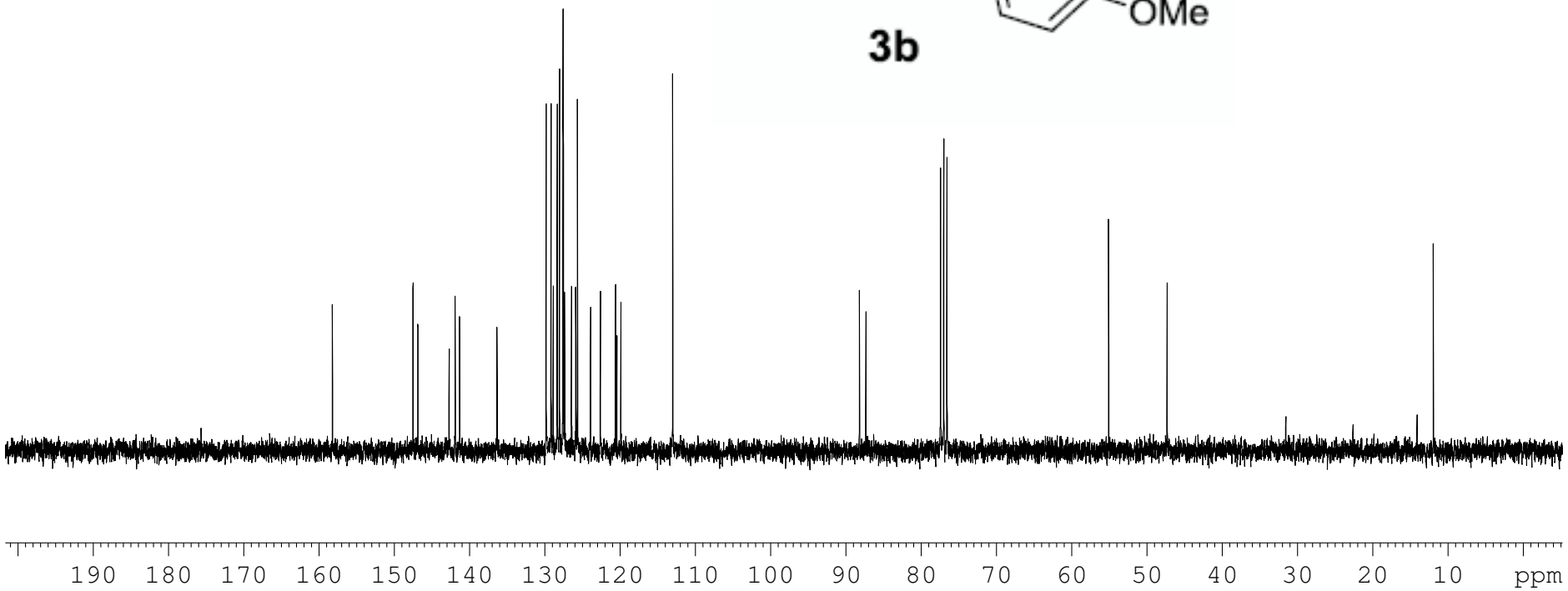
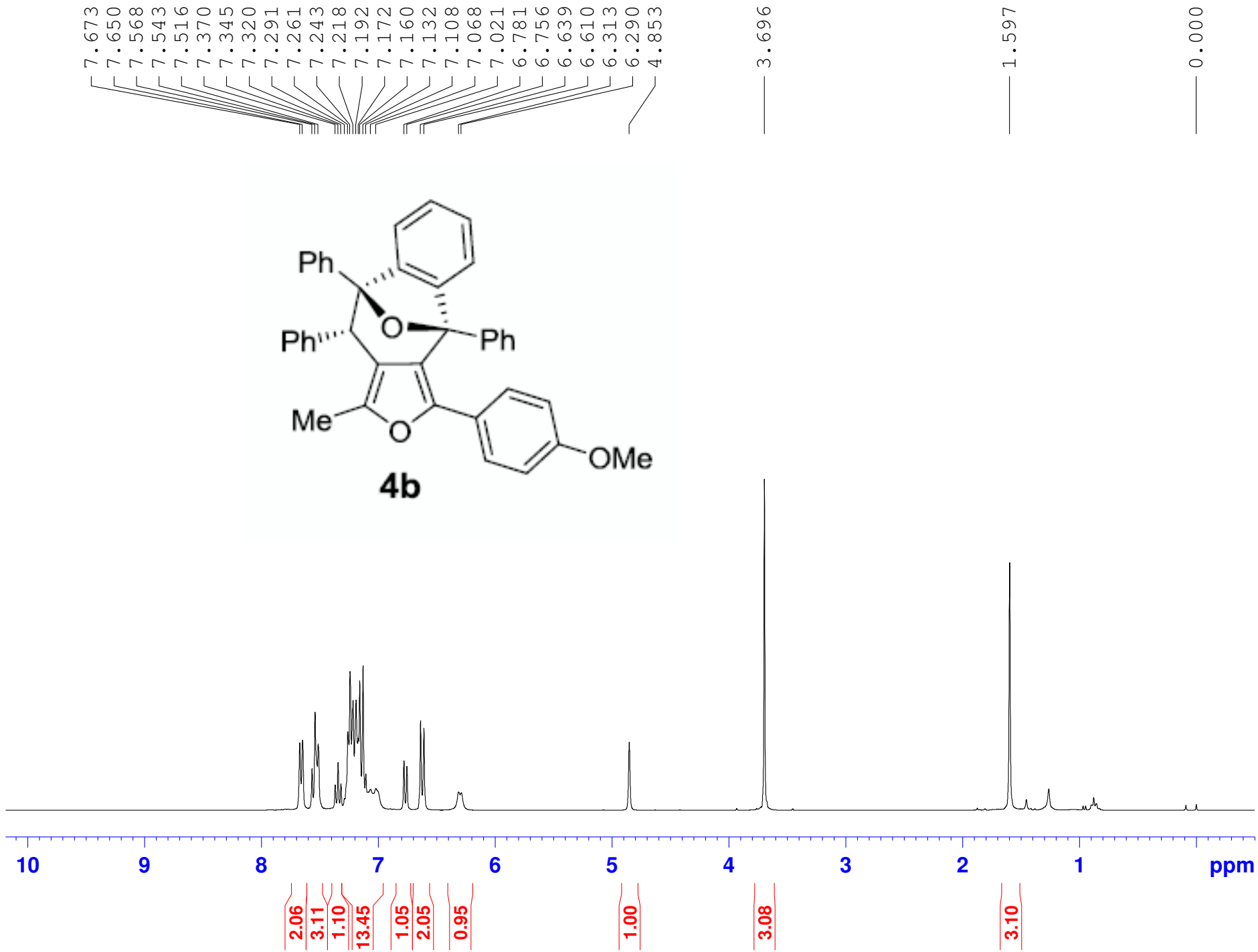


3b

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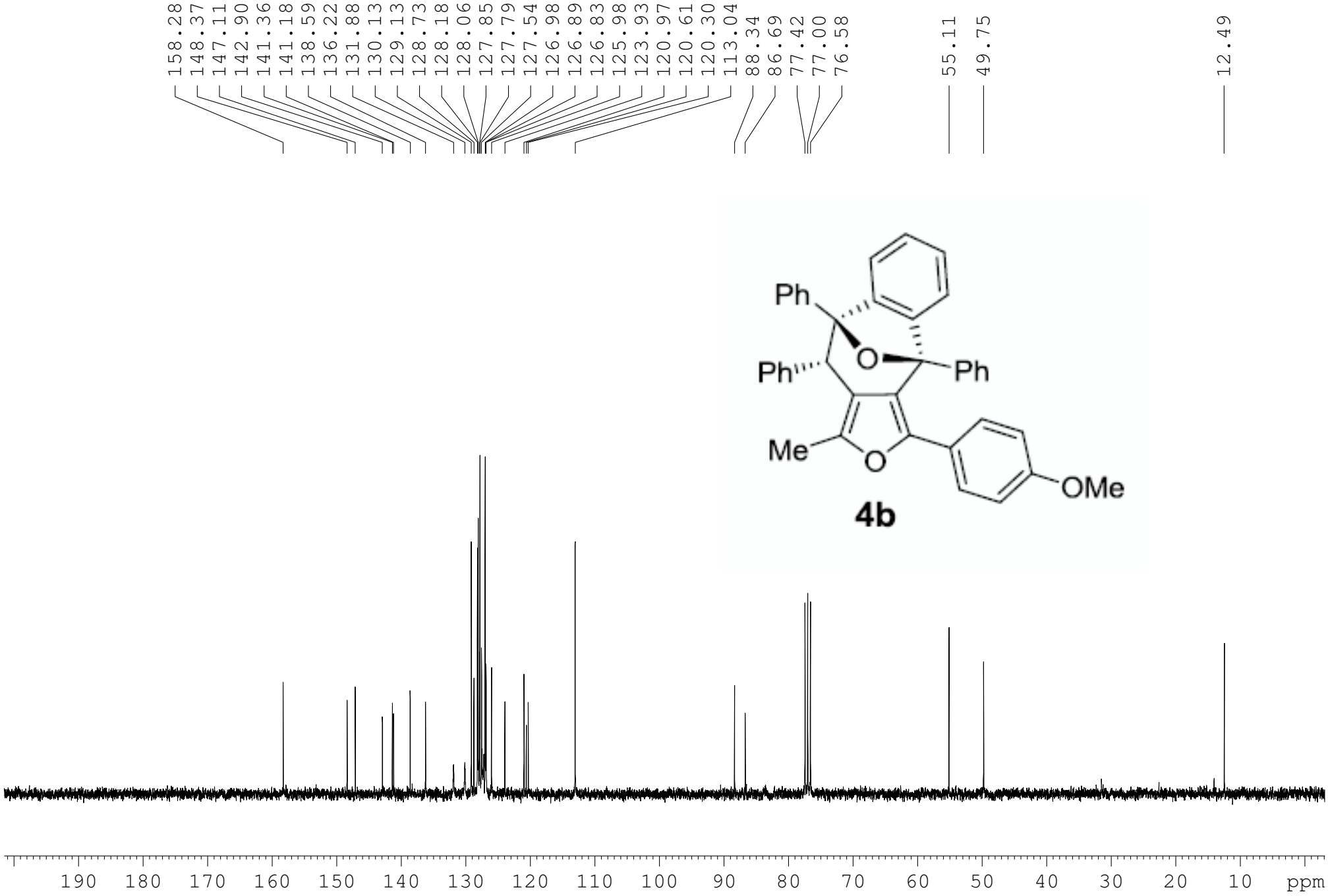
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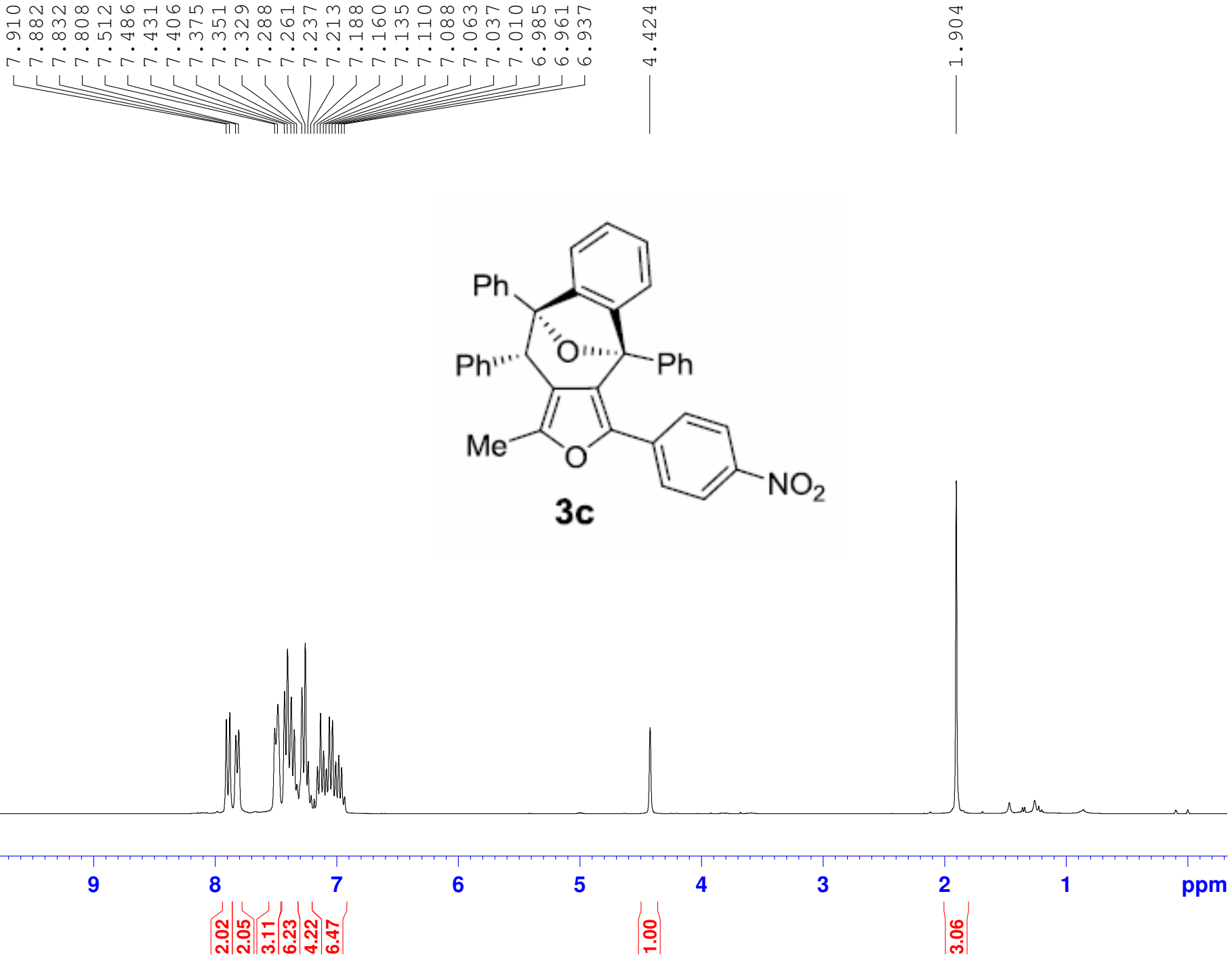
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6.961
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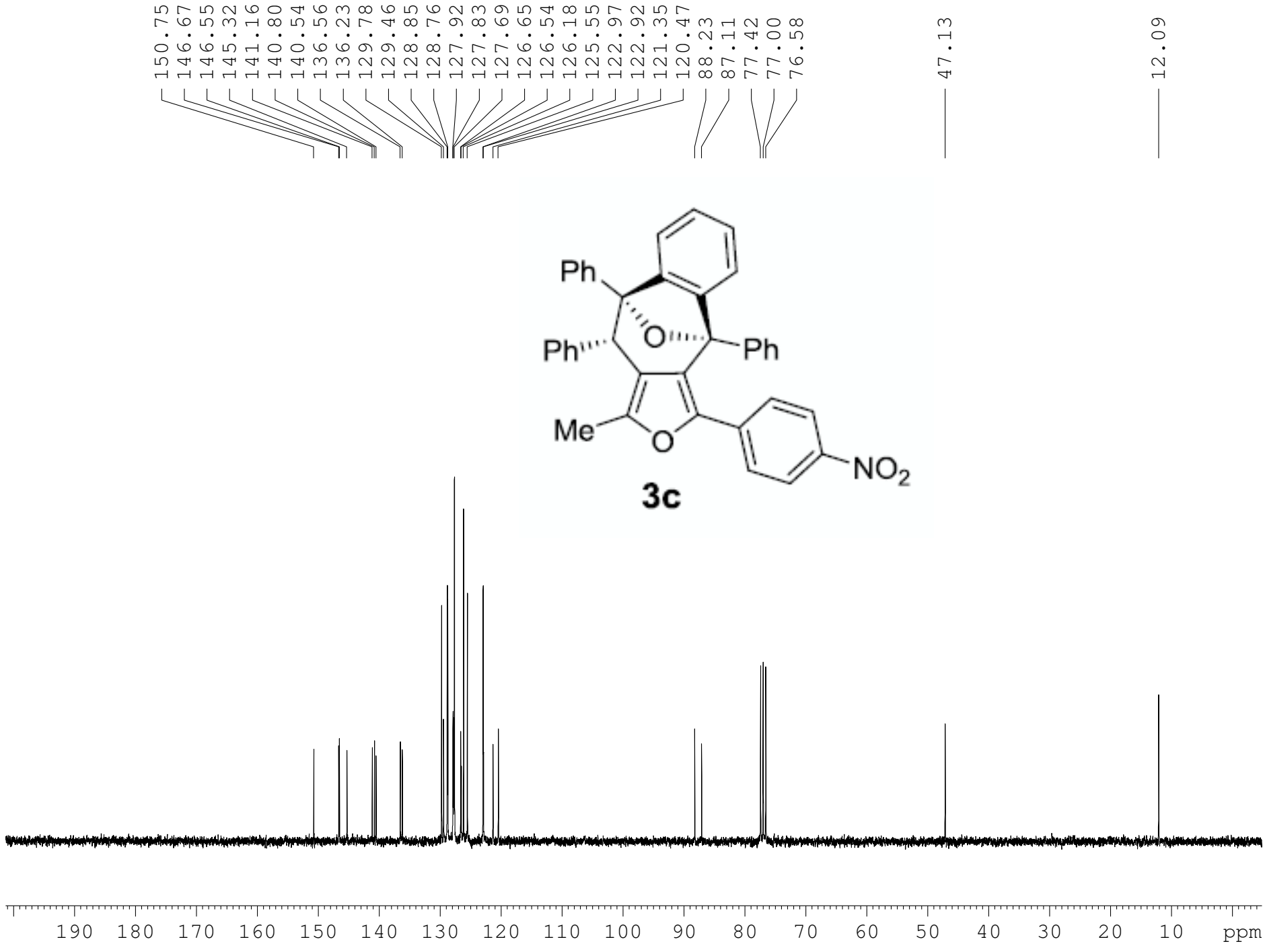
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122.97
122.92
121.35
120.47
88.23
87.11
77.42
77.00
76.58
47.13
12.09
Ph
Ph
O
Ph
Me
O
NO2
3c
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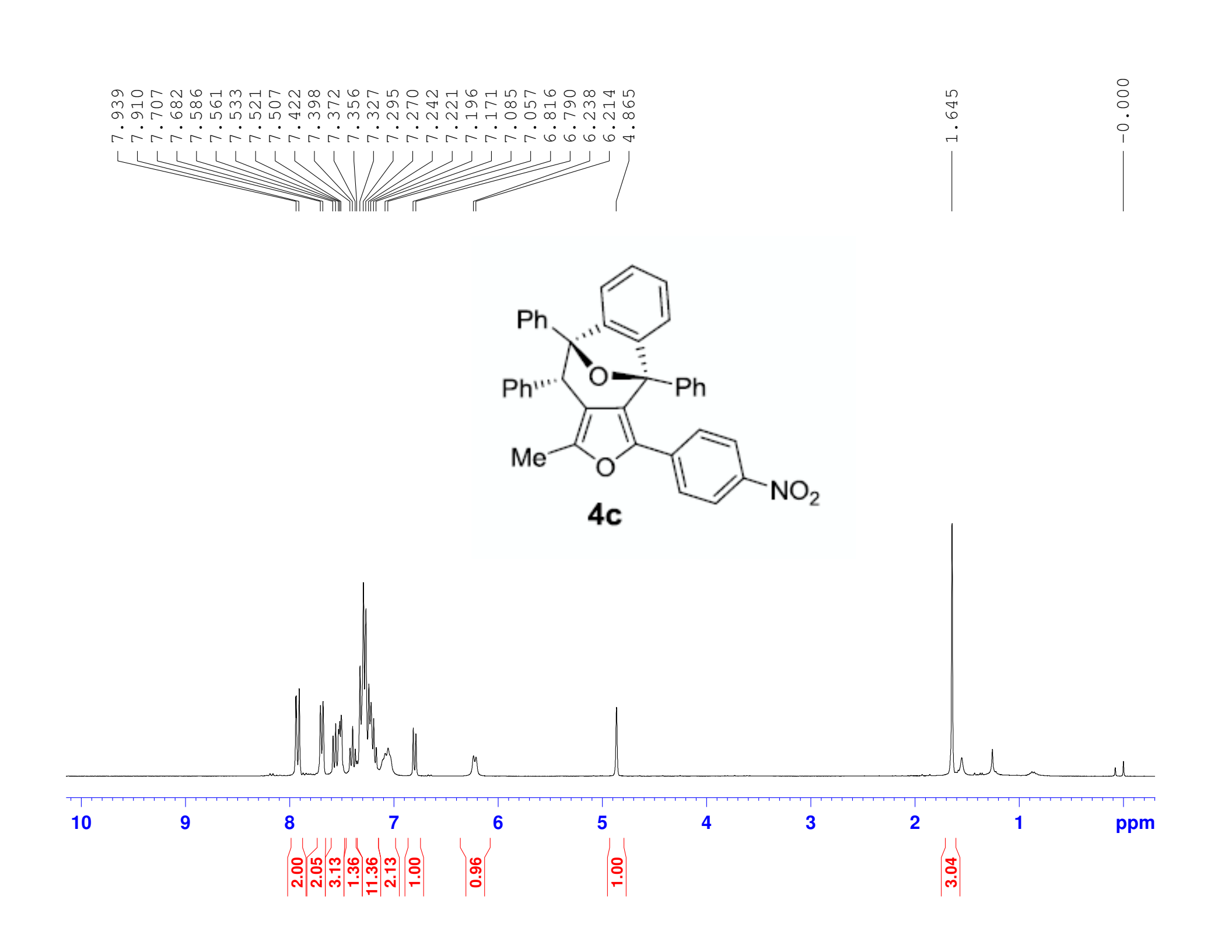
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7.356
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7.242
7.221
7.196
7.171
7.085
7.057
6.816
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6.238
6.214
4.865
1.645
0.000
Ph
Ph
O
Ph
Me
O
NO2
4c
10
9
8
7
6
5
4
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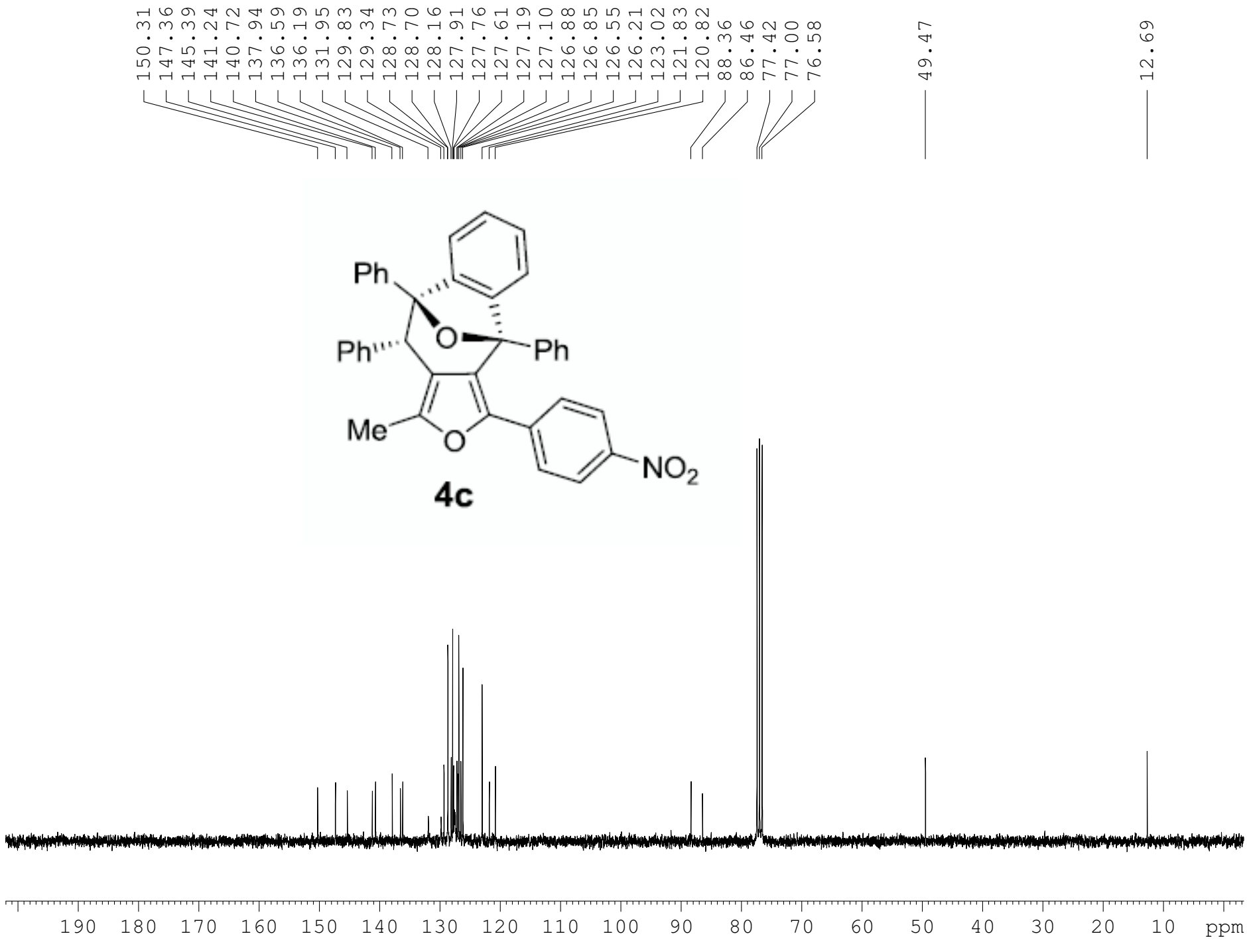
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129.34
128.73
128.70
128.16
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127.76
127.61
127.19
127.10
126.88
126.85
126.55
126.21
123.02
121.83
120.82
88.36
86.46
77.42
77.00
76.58
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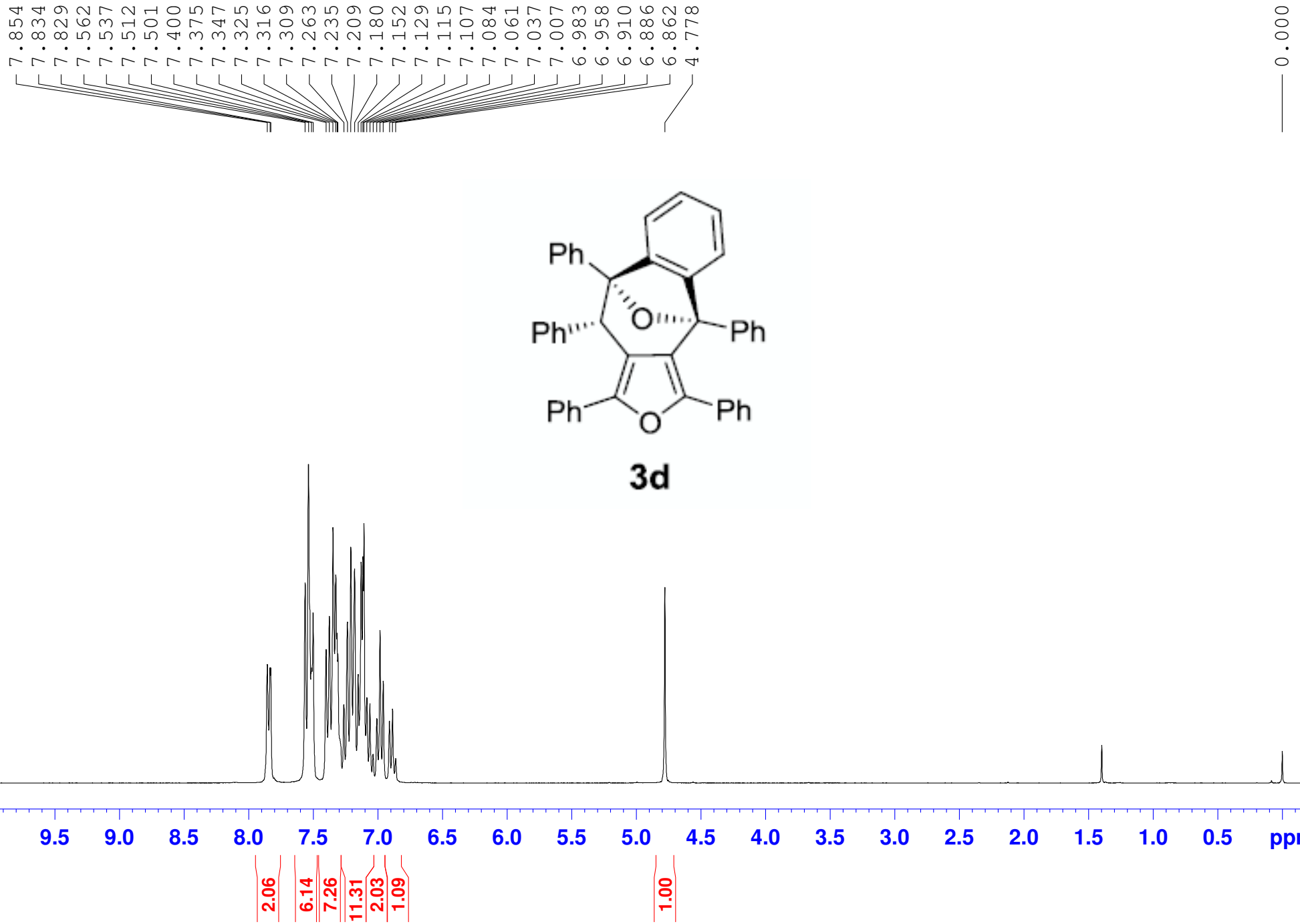
Ph
Ph
O
Ph
Me
O
NO2
4c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.309
7.263
7.235
7.209
7.180
7.152
7.129
7.115
7.107
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7.061
7.037
7.007
6.983
6.958
6.910
6.886
6.862
4.778
0.000
Ph
Ph
O
Ph
Ph
O
Ph
3d
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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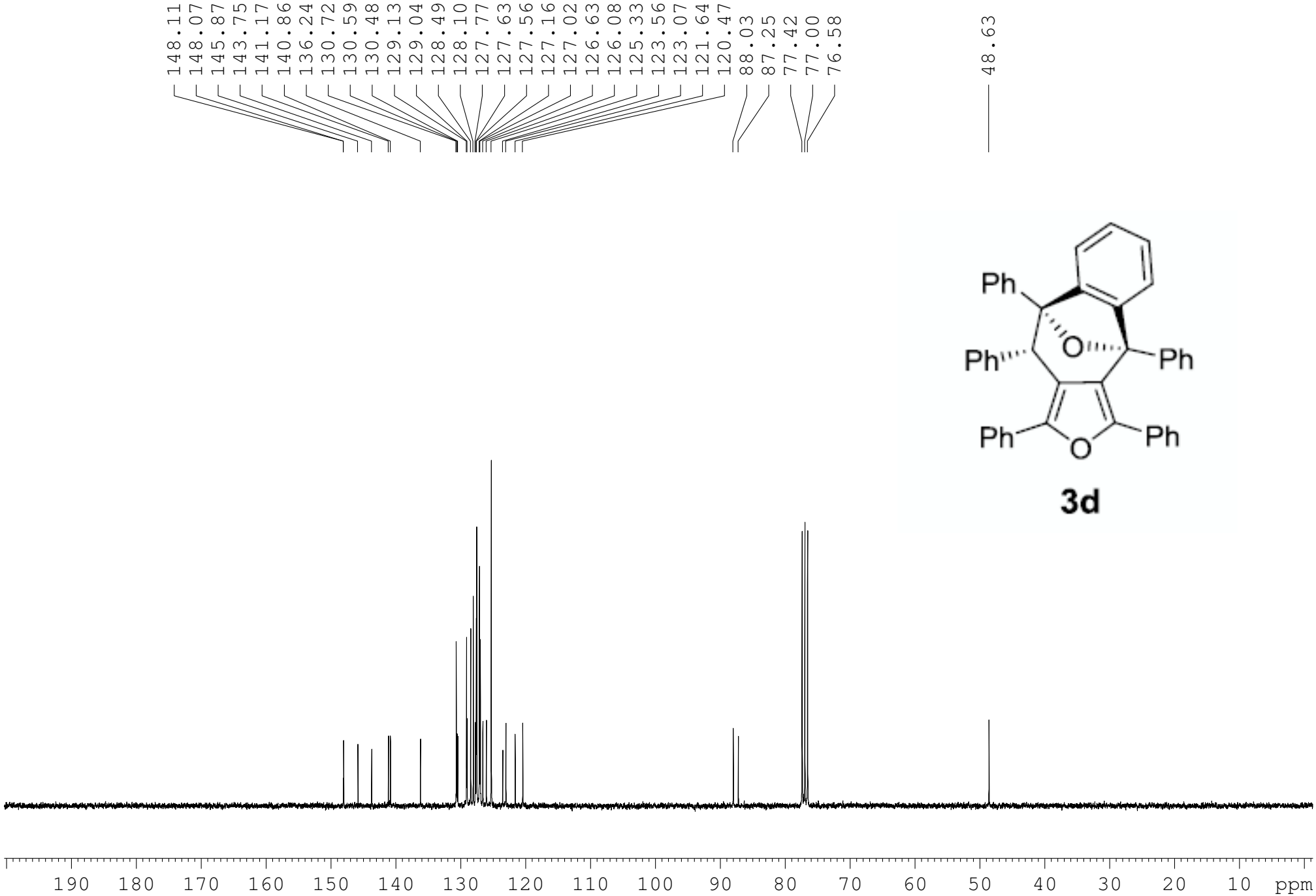
1.09
1.00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136.24
130.72
130.59
130.48
129.13
129.04
128.49
128.10
127.77
127.63
127.56
127.16
127.02
126.63
126.08
125.33
123.56
123.07
121.64
120.47
88.03
87.25
77.42
77.00
76.58
48.63
Ph
Ph
O
Ph
Ph
O
Ph
3d
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180
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140
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120
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100
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80
70
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30
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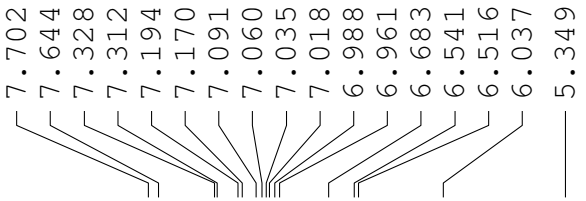
10
ppm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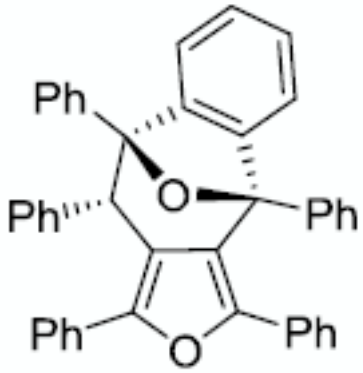
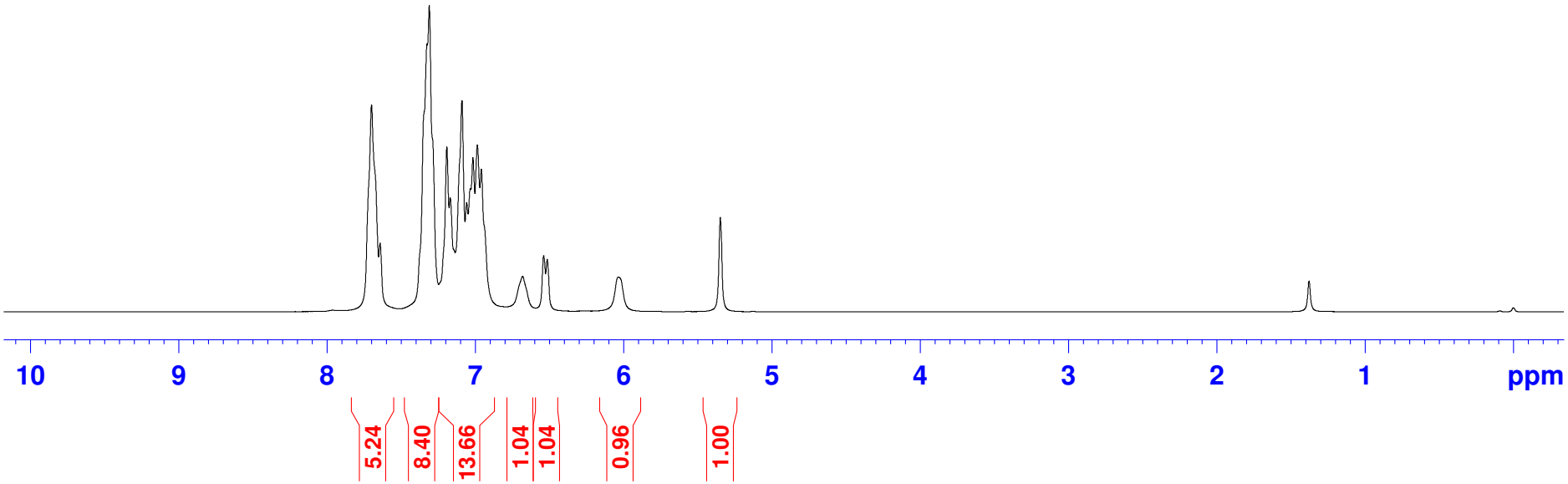

Ph
Ph
O
Ph
Ph
O
Ph

4d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8
7
6
5
4
3
2
1
ppm
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1.04
1.04
0.96
1.00

148.20
147.88
144.26
140.99
140.71
137.19
136.04
131.75
130.56
130.22
129.57
129.03
128.79
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128.01
127.95
127.57
127.54
127.48
127.31
127.11
127.01
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123.86
121.82
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86.54
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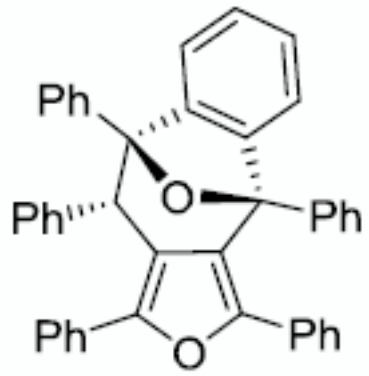
77.00
76.57
50.39



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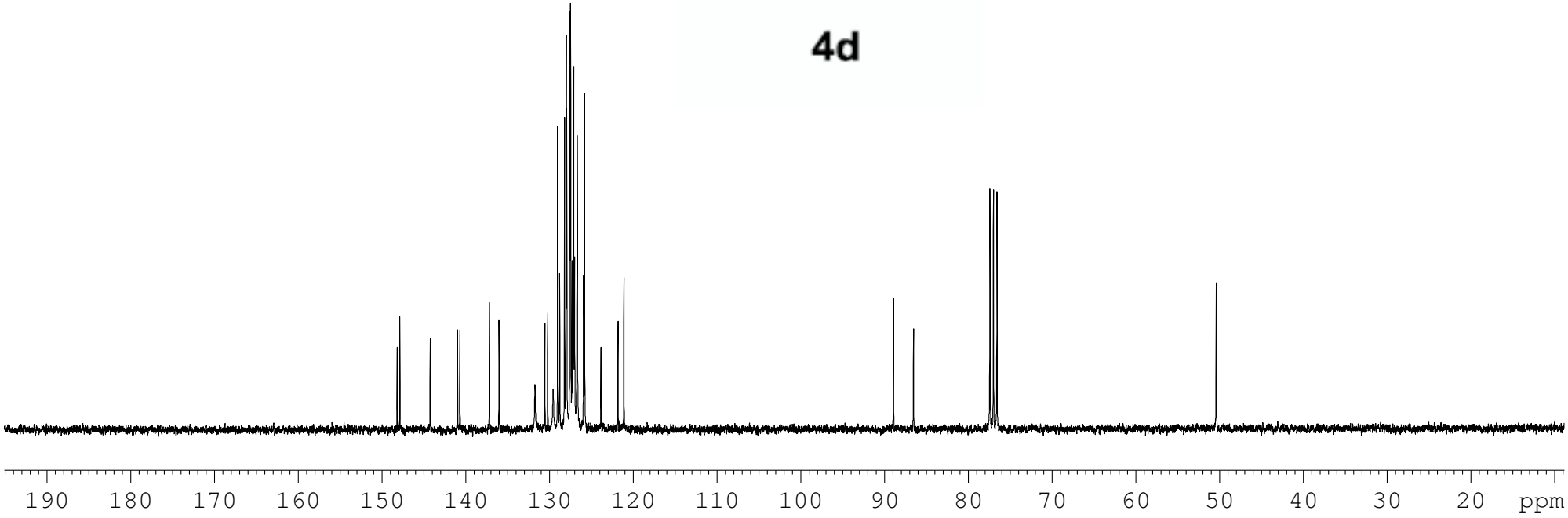

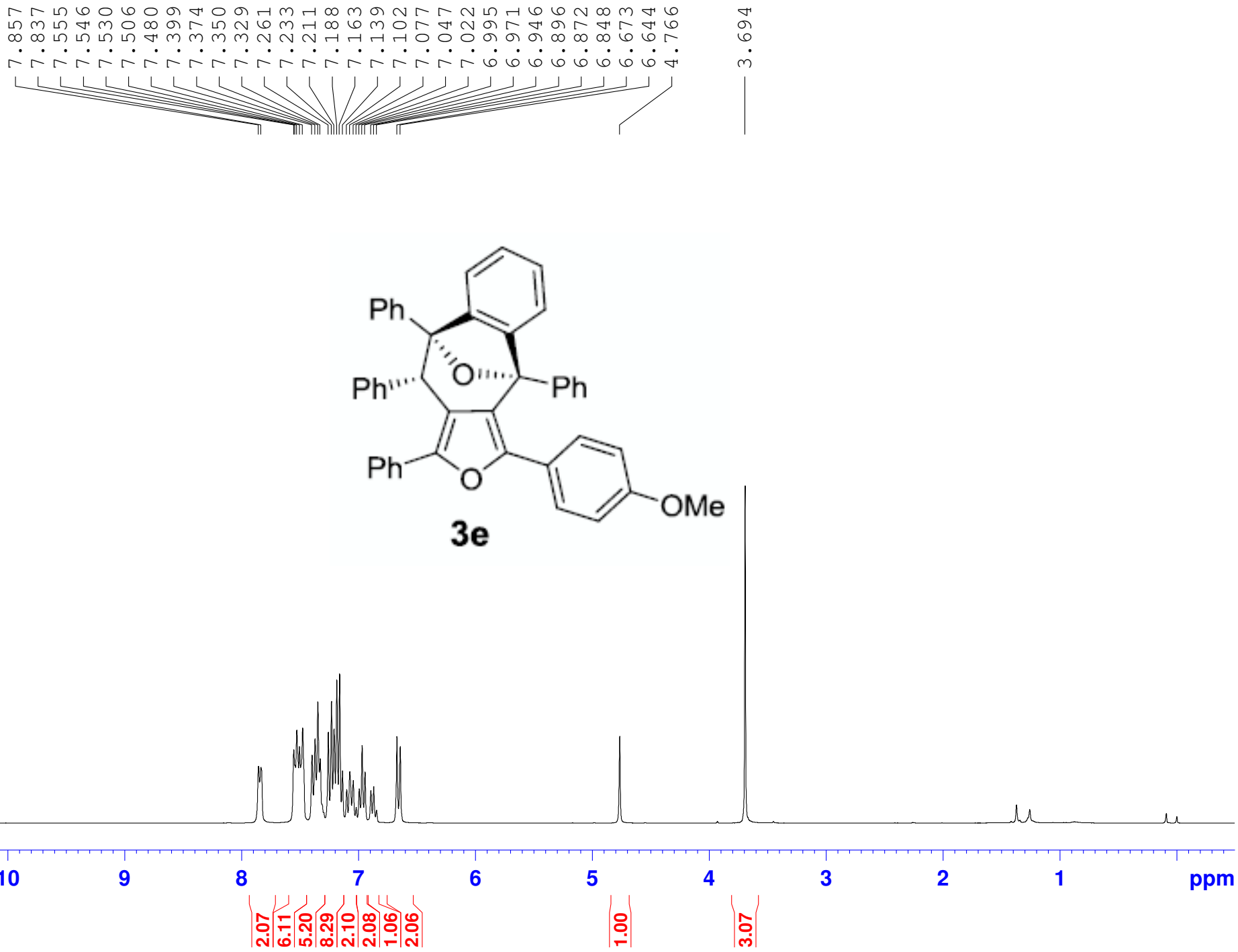
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7.261
7.233
7.211
7.188
7.163
7.139
7.102
7.077
7.047
7.022
6.995
6.971
6.946
6.896
6.872
6.848
6.673
6.644
4.766
3.694
Ph
Ph
O
Ph
Ph
O
OMe
3e
10
9
8
7
6
5
4
3
2
1
ppm
2.07
6.11
5.20
8.29
2.10
2.08
1.06
2.06
1.00
3.07

158.63
148.20
147.50
145.86
143.82
141.23
140.93
136.27
130.73
130.59
129.18
129.04
128.52
128.07
127.72
127.61
127.47
127.11
126.81
126.60
126.03
125.33
125.19
123.51
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121.56
120.31
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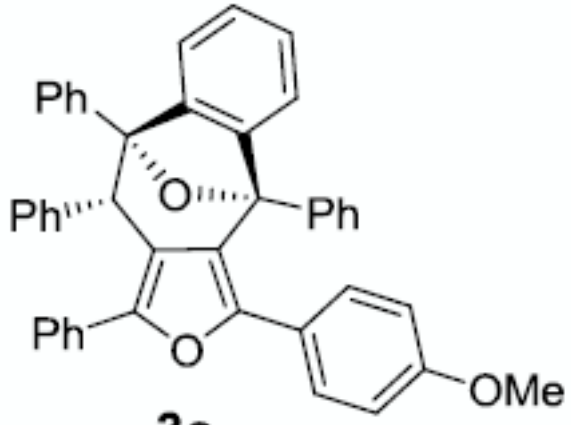
77.00
76.58
55.13
48.66



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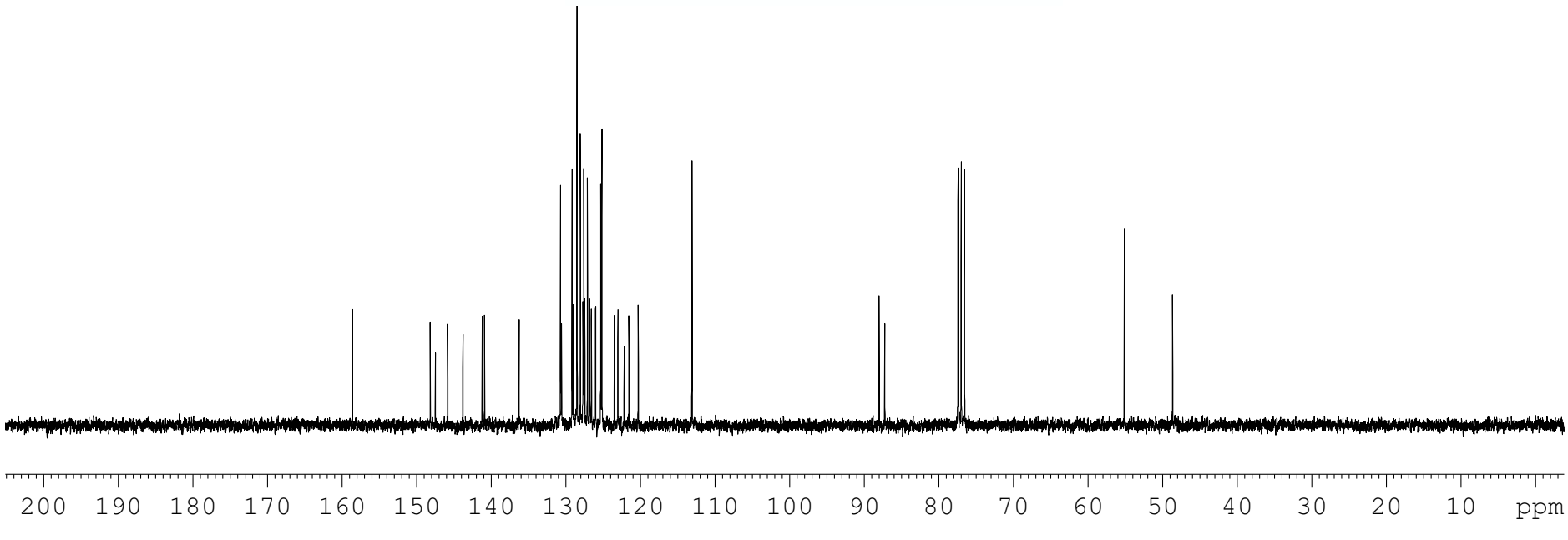

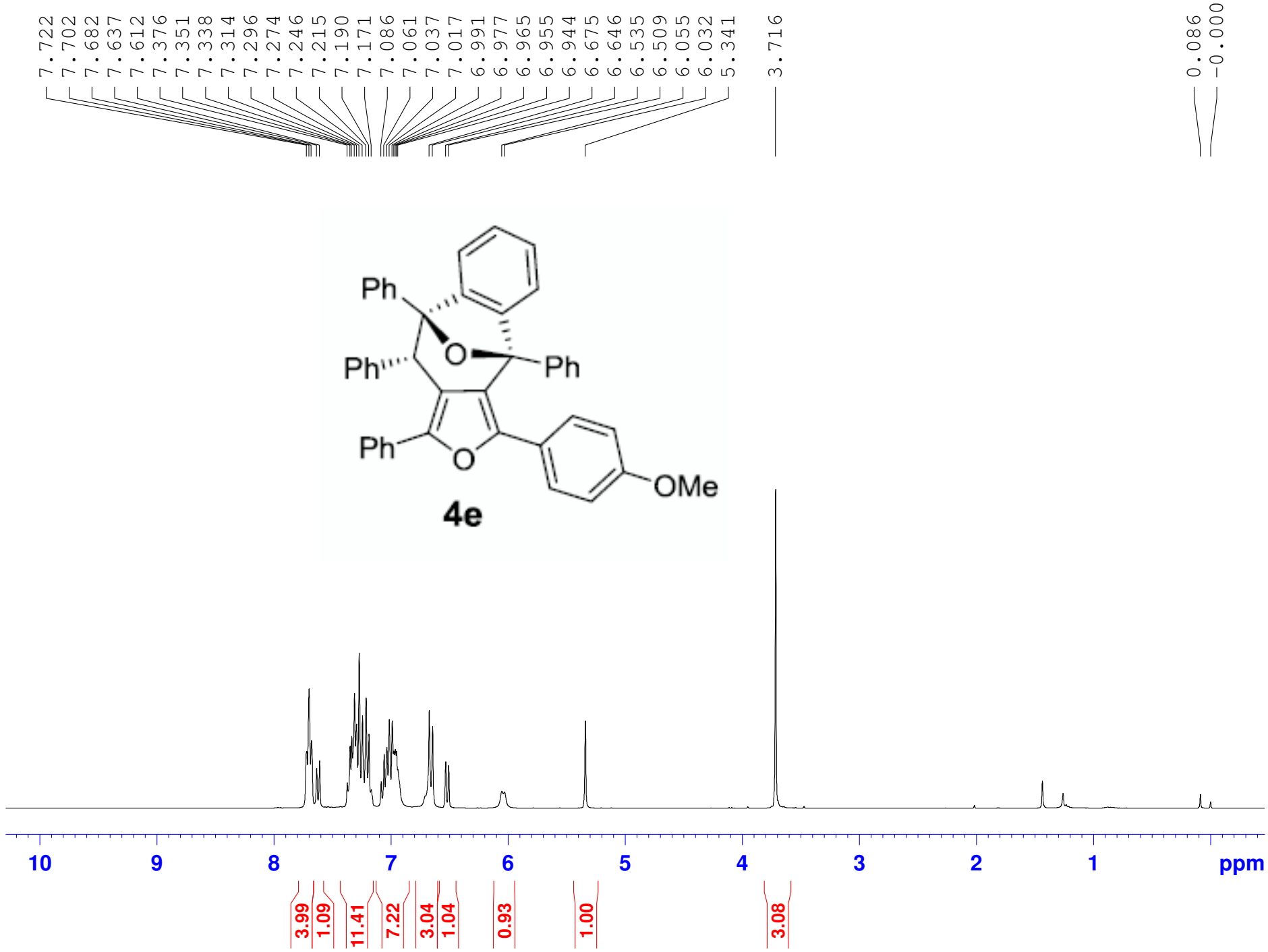
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7.314
7.296
7.274
7.246
7.215
7.190
7.171
7.086
7.061
7.037
7.017
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6.977
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6.955
6.944
6.675
6.646
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6.509
6.055
6.032
5.341
3.716
0.086
-0.000
Ph
Ph
O
Ph
Ph
O
OMe
4e
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9
8
7
6
5
4
3
2
1
ppm
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1.09
11.41
7.22
3.04
1.04
0.93
1.00
3.08

158.64
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144.28
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140.75
137.26
136.00
131.74
130.31
129.60
129.09
128.81
128.47
128.23
128.00
127.90
127.50
127.31
127.13
126.68
126.51
125.86
125.71
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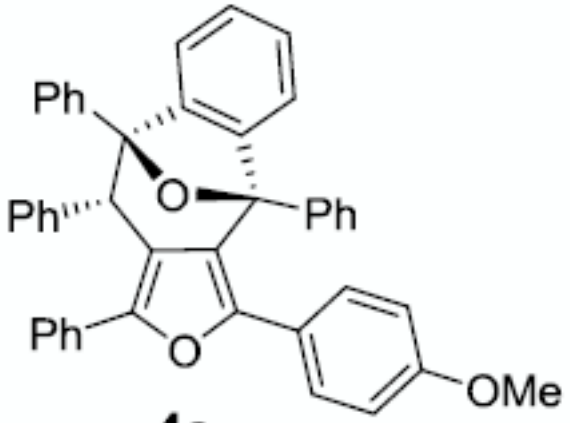
50.42



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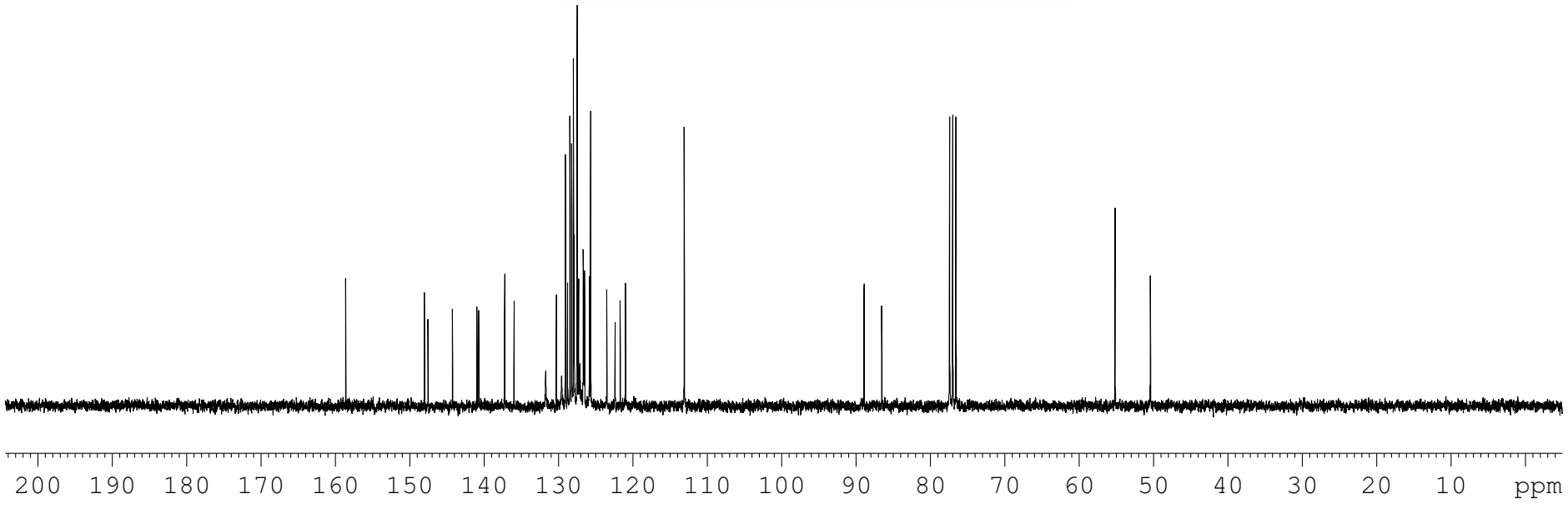

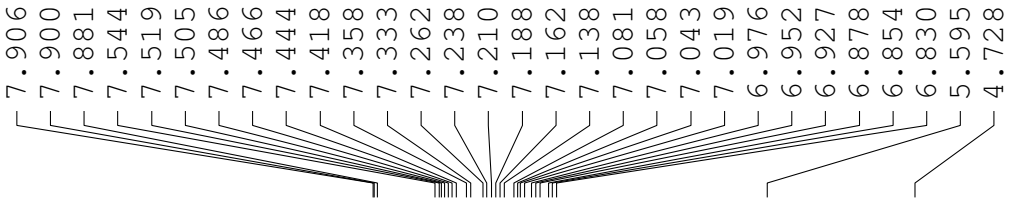
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7.444
7.418
7.358
7.333
7.262
7.238
7.210
7.188
7.162
7.138
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7.019
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6.927
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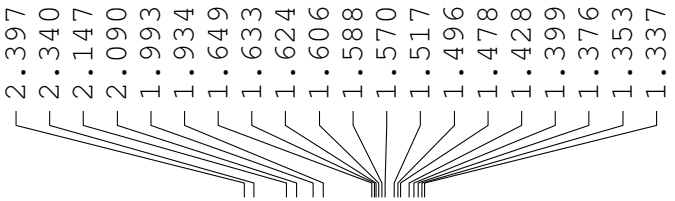
5.595
4.728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1.517
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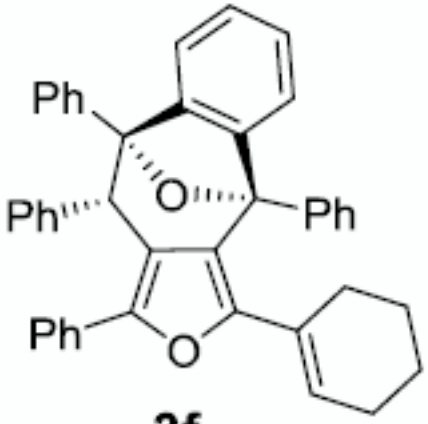
1.376
1.353
1.337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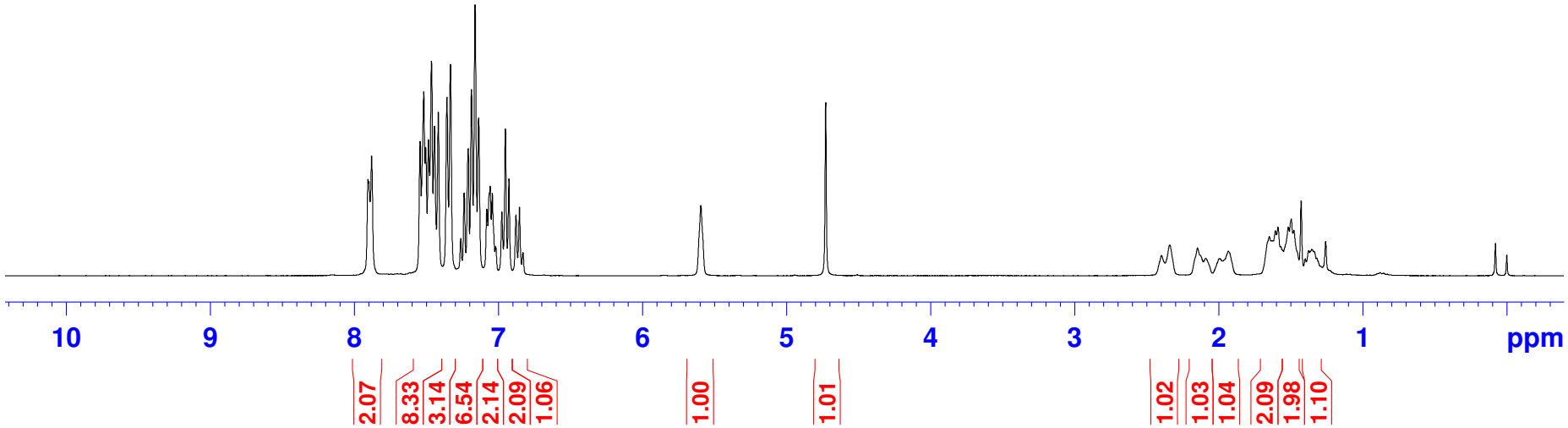
Ph
O
Ph
Ph
O

3f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3
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ppm
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3.14
6.54
2.14
2.09
1.06
1.00
1.01
1.02
1.03
1.04
2.09
1.98
1.10

148.22
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146.48
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141.36
140.96
136.44
130.77
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130.54
129.02
128.86
128.24
127.96
127.92
127.57
127.53
127.27
127.03
126.58
126.53
125.93
125.38
125.05
122.93
122.01
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77.00
76.58

48.64

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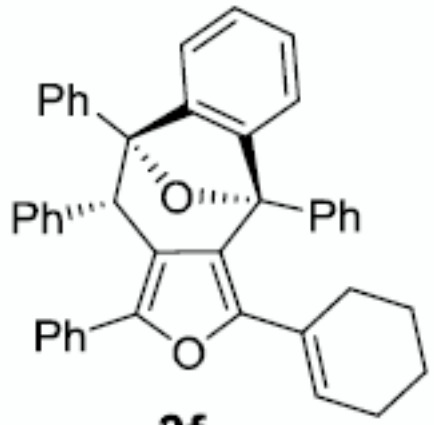
21.71



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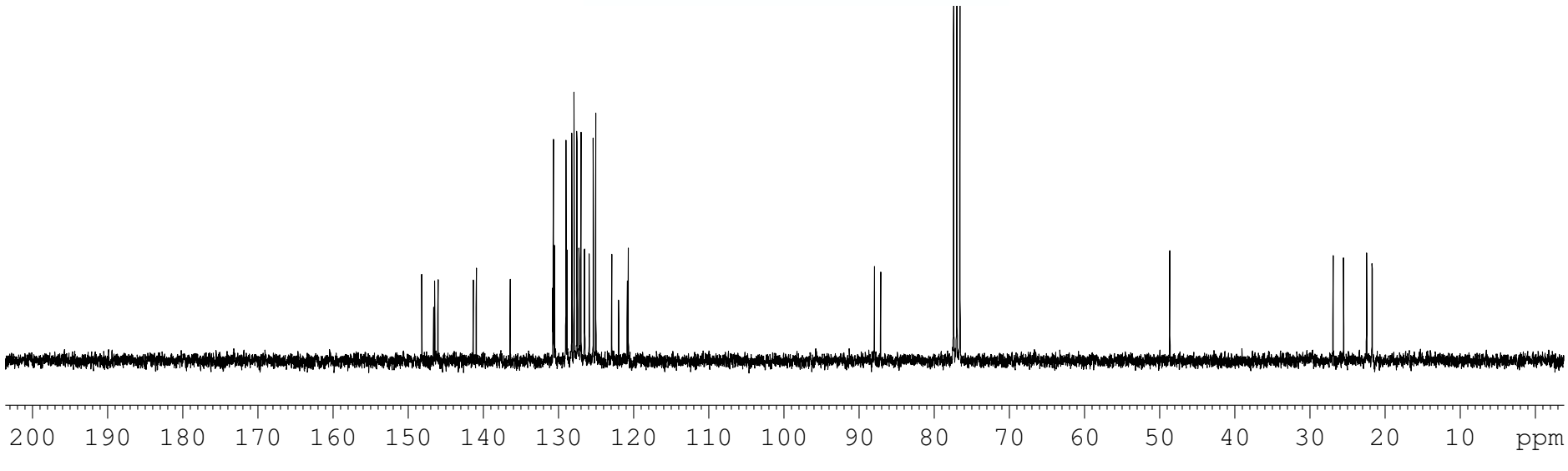

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7.064
7.039
7.009
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6.950
6.926
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6.013
5.992
5.646
5.300

2.414
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2.115
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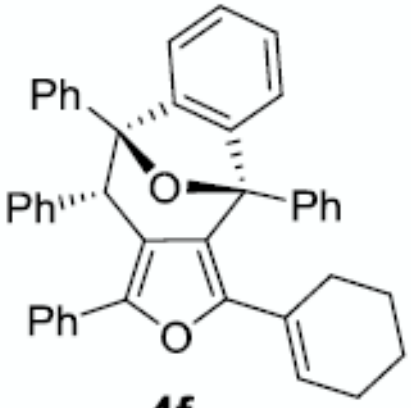
1.257



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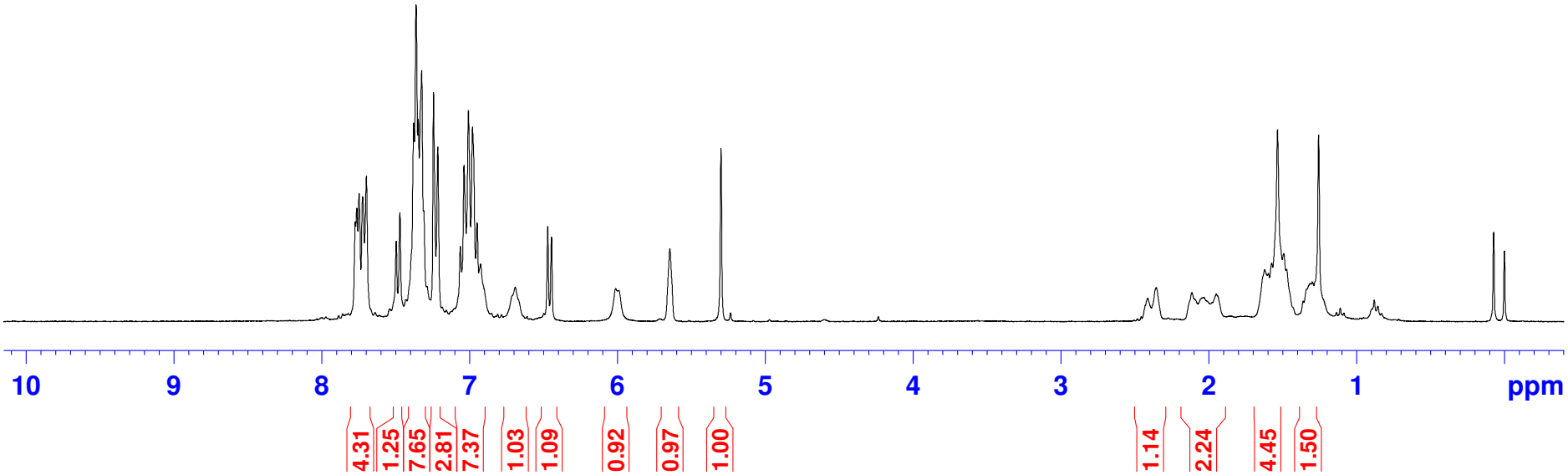

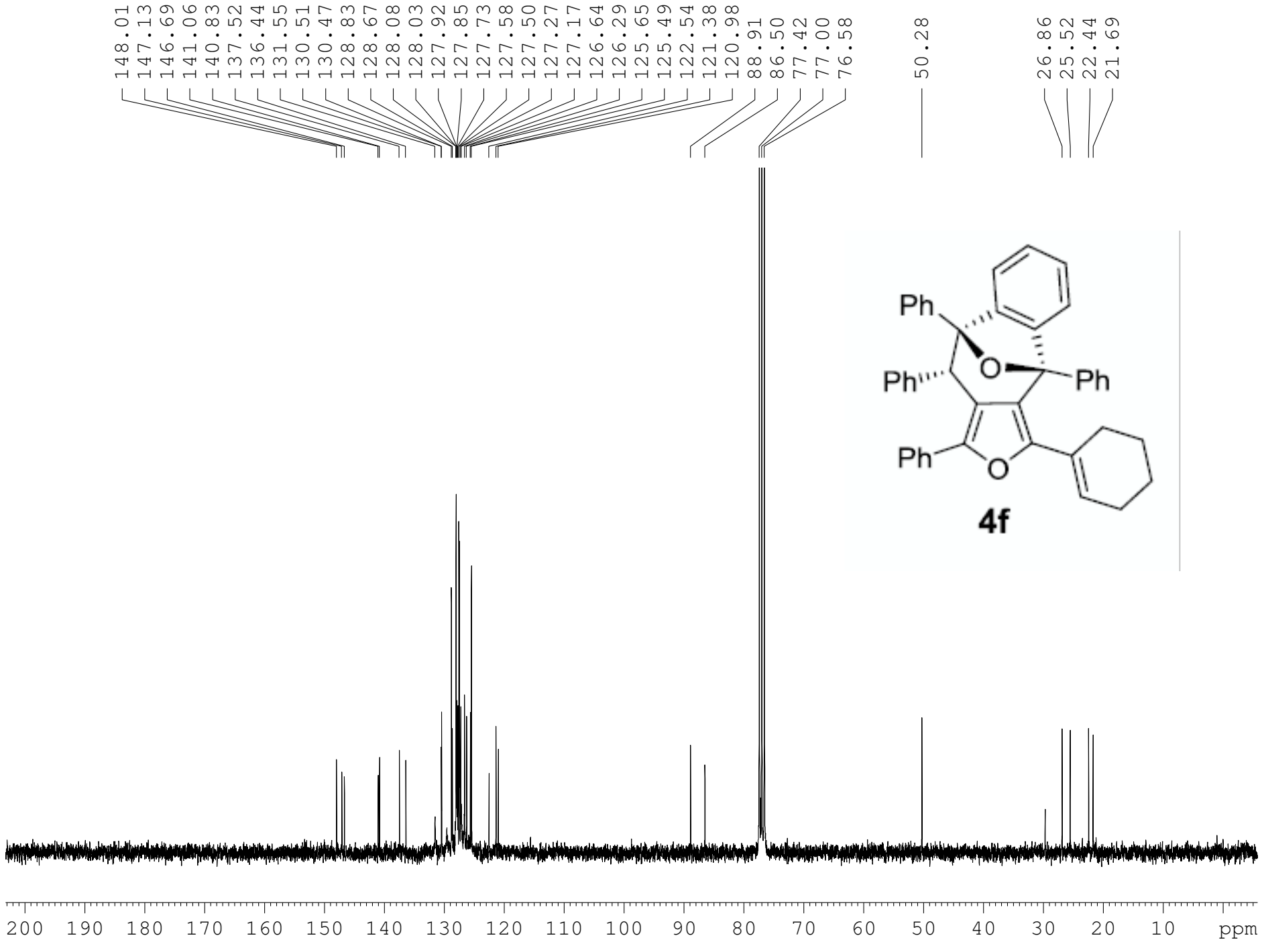
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126.29
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125.49
122.54
121.38
120.98
88.91
86.50
77.42
77.00
76.58
50.28
26.86
25.52
22.44
21.69
Ph
Ph
O
Ph
Ph
O
4f
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140
130
120
110
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30
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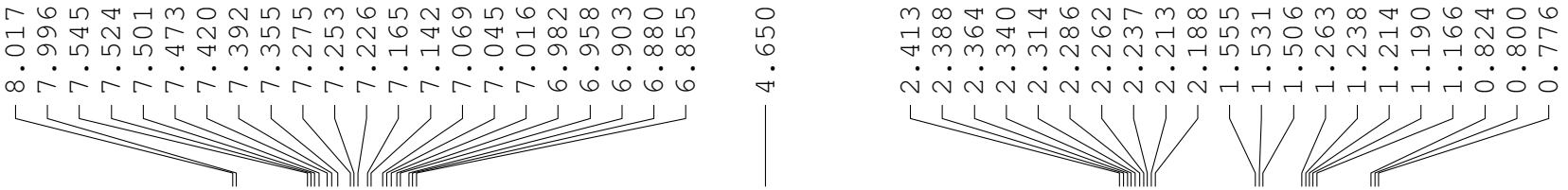
10
ppm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7.226
7.165
7.142
7.069
7.045
7.016
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6.958
6.903
6.880
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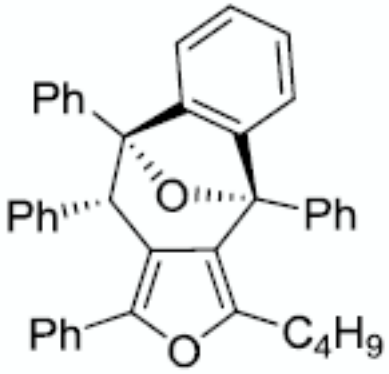
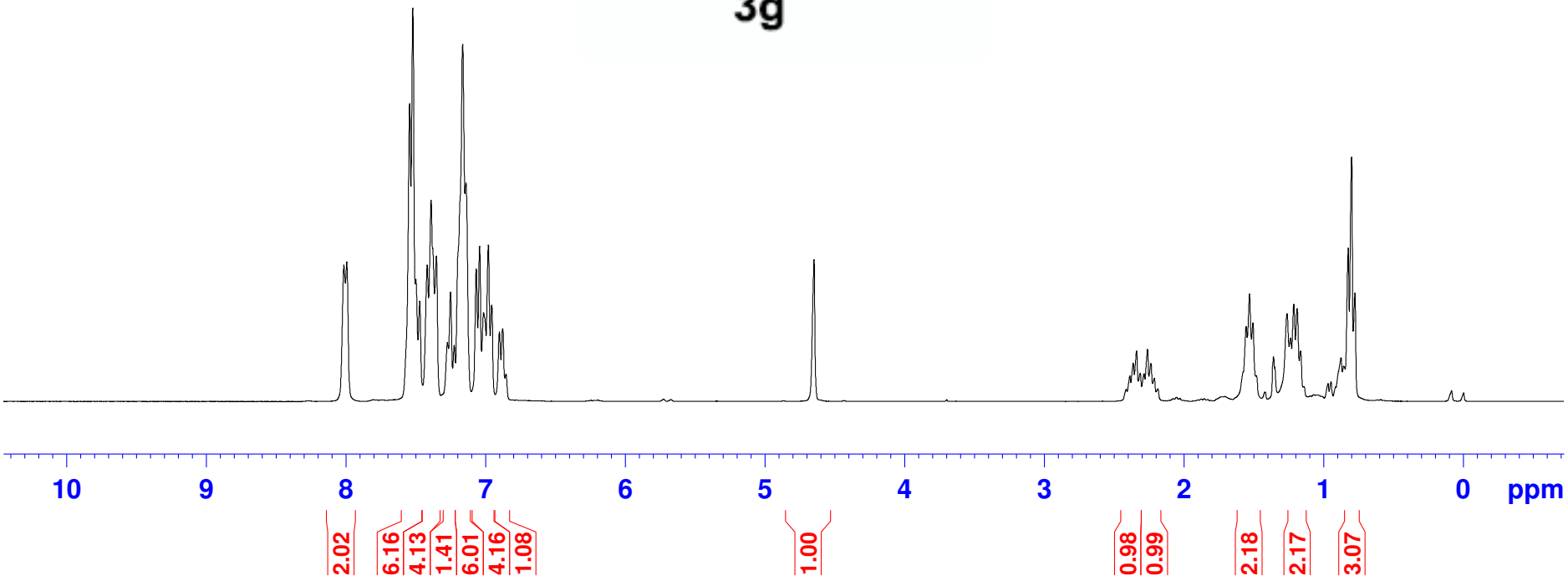

Ph
Ph
O
Ph
Ph
O
C_4H_9

3g


10
9
8
7
6
5
4
3
2
1
0
ppm
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4.16
1.08
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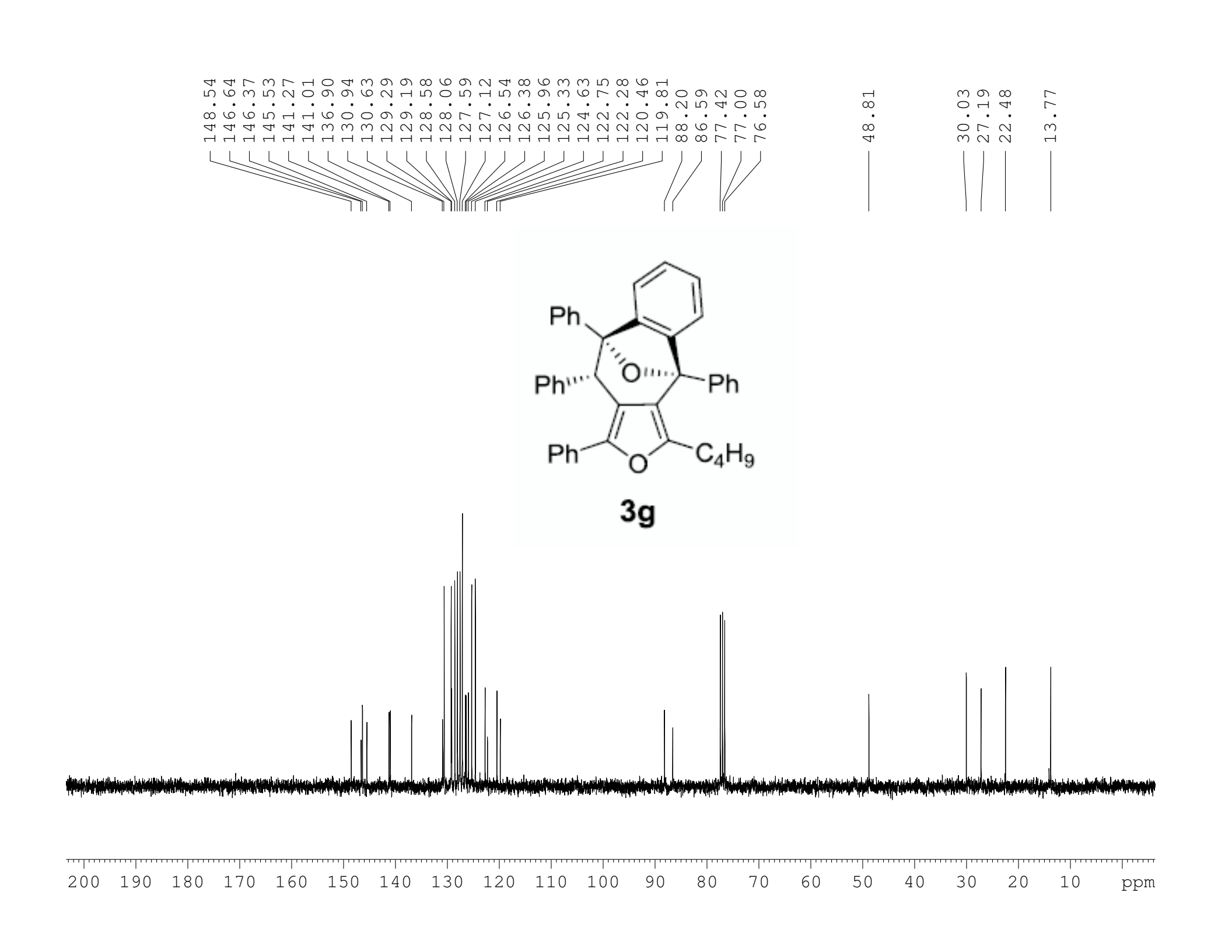
2.17
3.07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124.63
122.75
122.28
120.46
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88.20
86.59
77.42
77.00
76.58
48.81
30.03
27.19
22.48
13.77
Ph
Ph
O
Ph
Ph
O
C4H9
3g
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150
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110
100
90
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70
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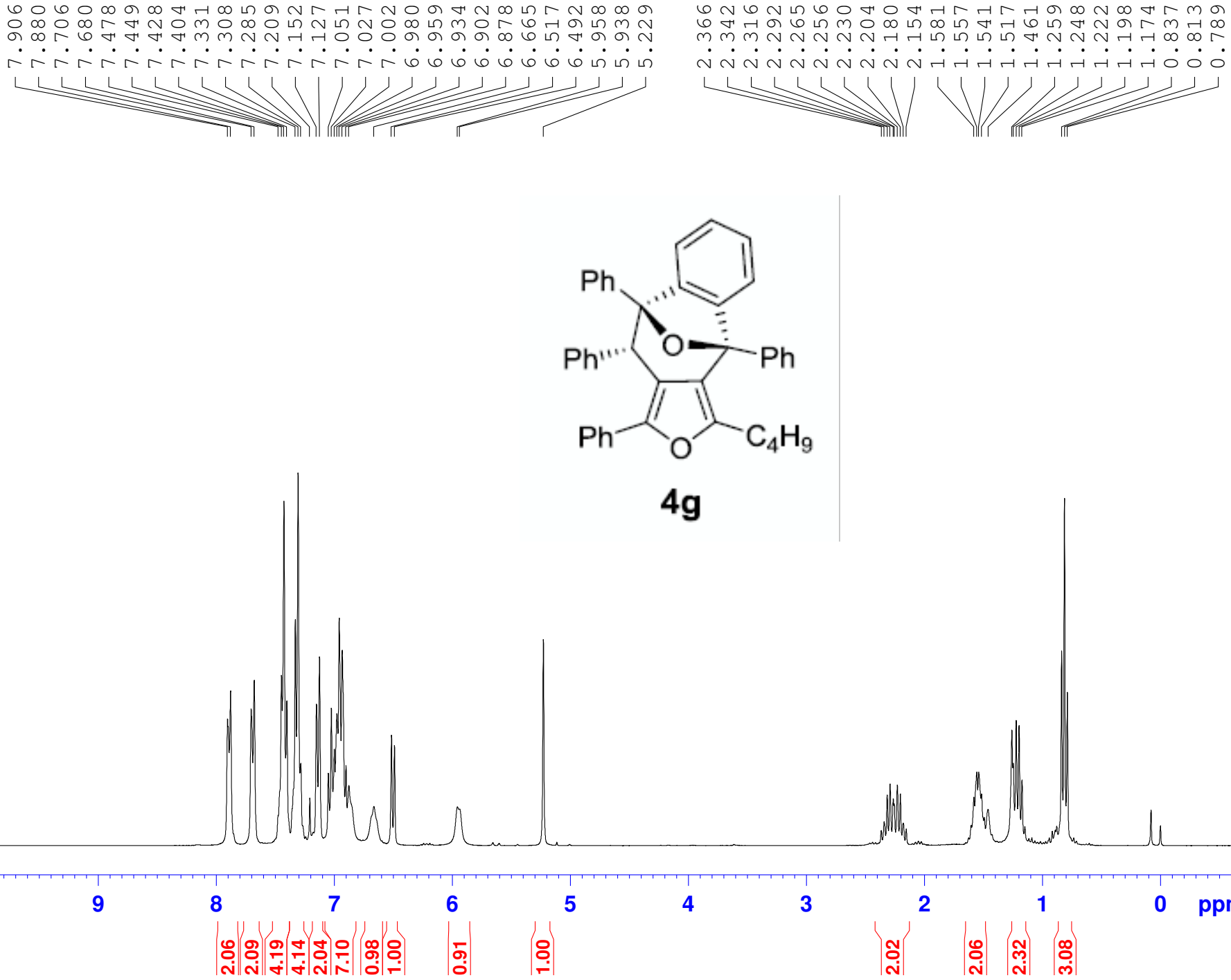
30
20
10
ppm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7.002
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6.492
5.958
5.938
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1.557
1.541
1.517
1.461
1.259
1.248
1.222
1.198
1.174
0.837
0.813
0.789
Ph
Ph
O
Ph
Ph
O
C4H9
4g
10
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8
7
6
5
4
3
2
1
0
ppm
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2.09
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0.91
1.00
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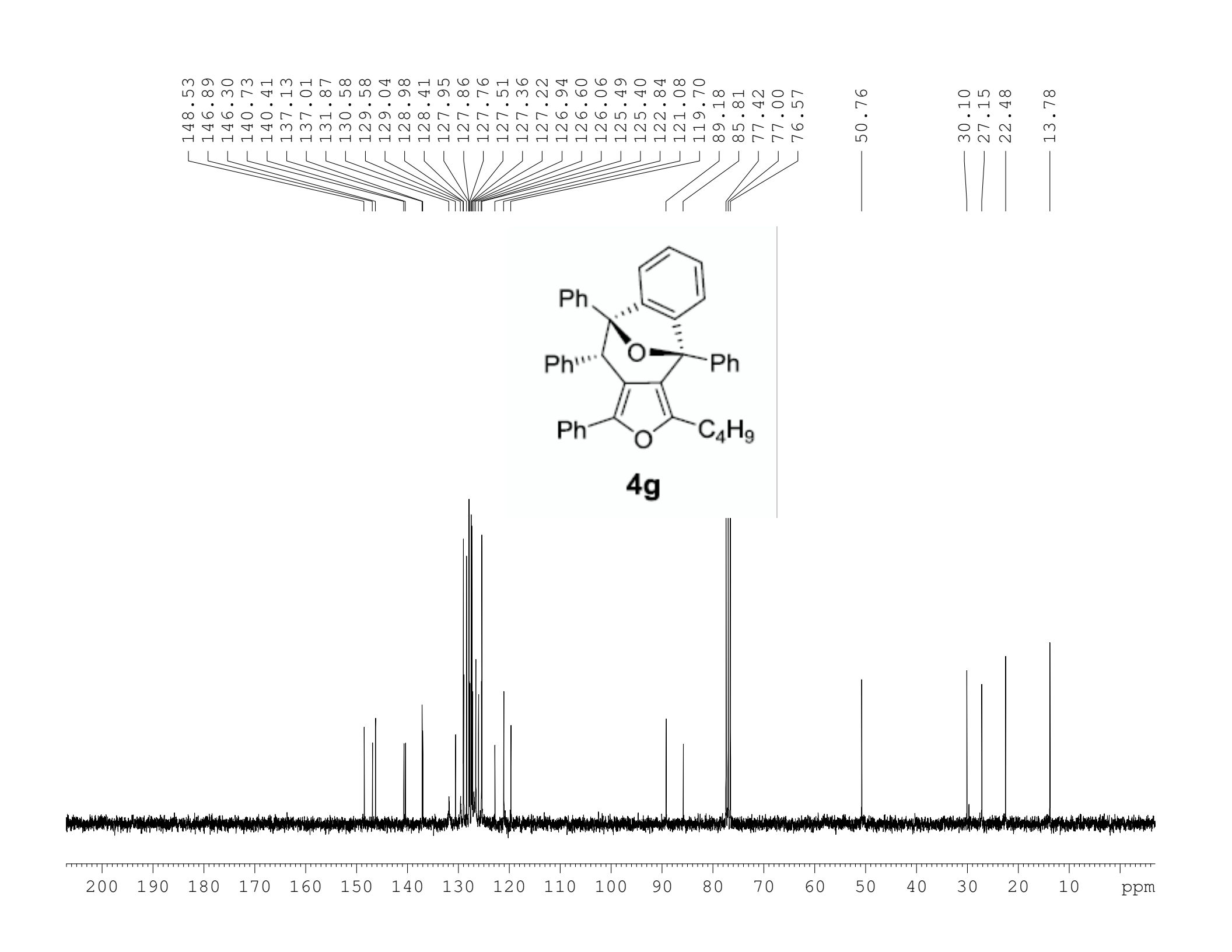
2.06
2.32
3.08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127.86
127.76
127.51
127.36
127.22
126.94
126.60
126.06
125.49
125.40
122.84
121.08
119.70
89.18
85.81
77.42
77.00
76.57
50.76
30.10
27.15
22.48
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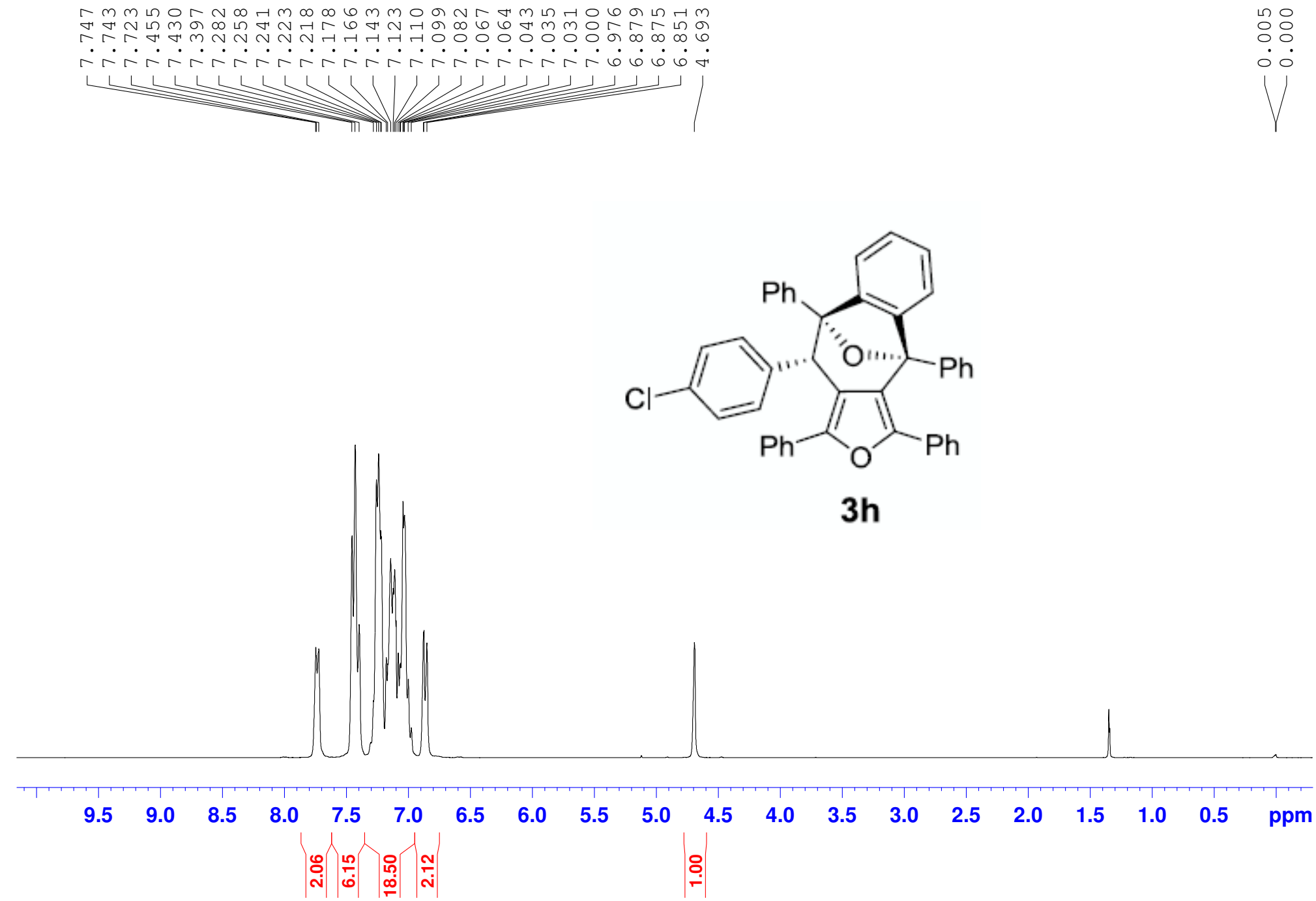
Ph
O
Ph
Ph
O
C4H9
4g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.241
7.223
7.218
7.178
7.166
7.143
7.123
7.110
7.099
7.082
7.067
7.064
7.043
7.035
7.031
7.000
6.976
6.879
6.875
6.851
4.693
0.005
0.000
Ph
O
Ph
Cl
Ph
O
Ph
3h
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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ppm
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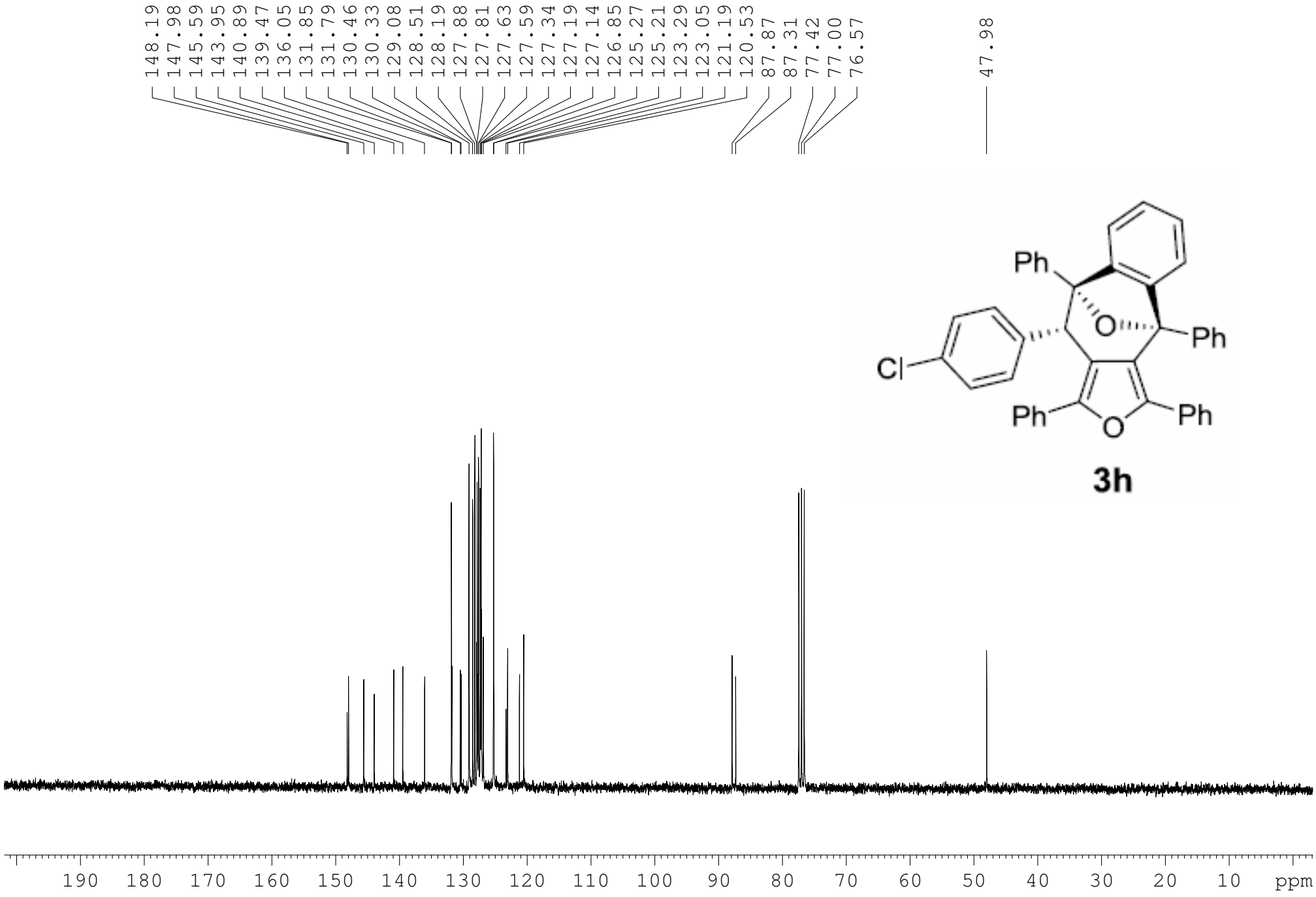
1.00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127.81
127.63
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127.34
127.19
127.14
126.85
125.27
125.21
123.29
123.05
121.19
120.53
87.87
87.31
77.42
77.00
76.57
47.98
Ph
O
Ph
Cl
Ph
O
Ph
3h
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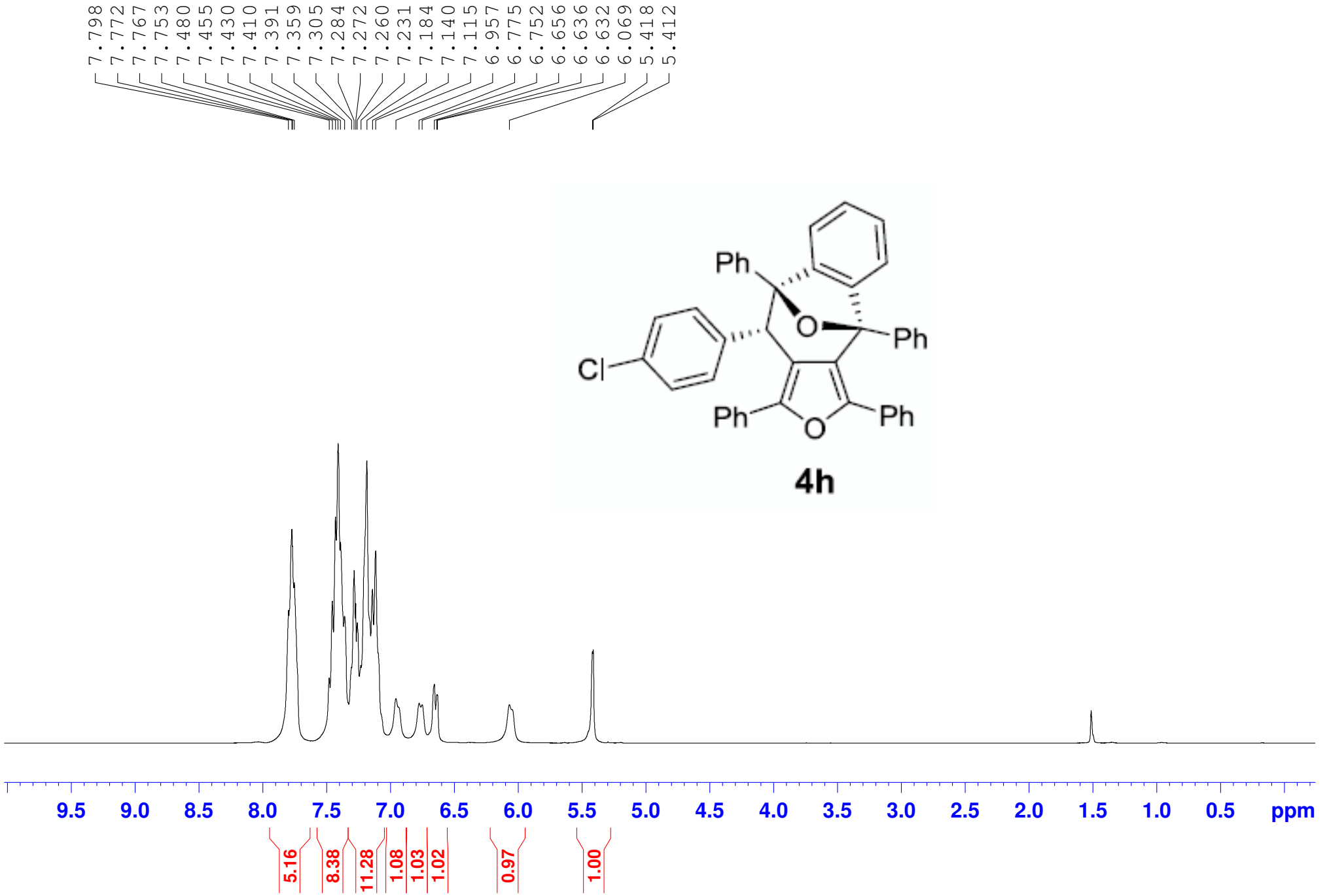
ppm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7.410
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7.305
7.284
7.272
7.260
7.231
7.184
7.140
7.115
6.957
6.775
6.752
6.656
6.636
6.632
6.069
5.418
5.412
Ph
O
Ph
Cl
Ph
O
Ph
4h
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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ppm
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1.08
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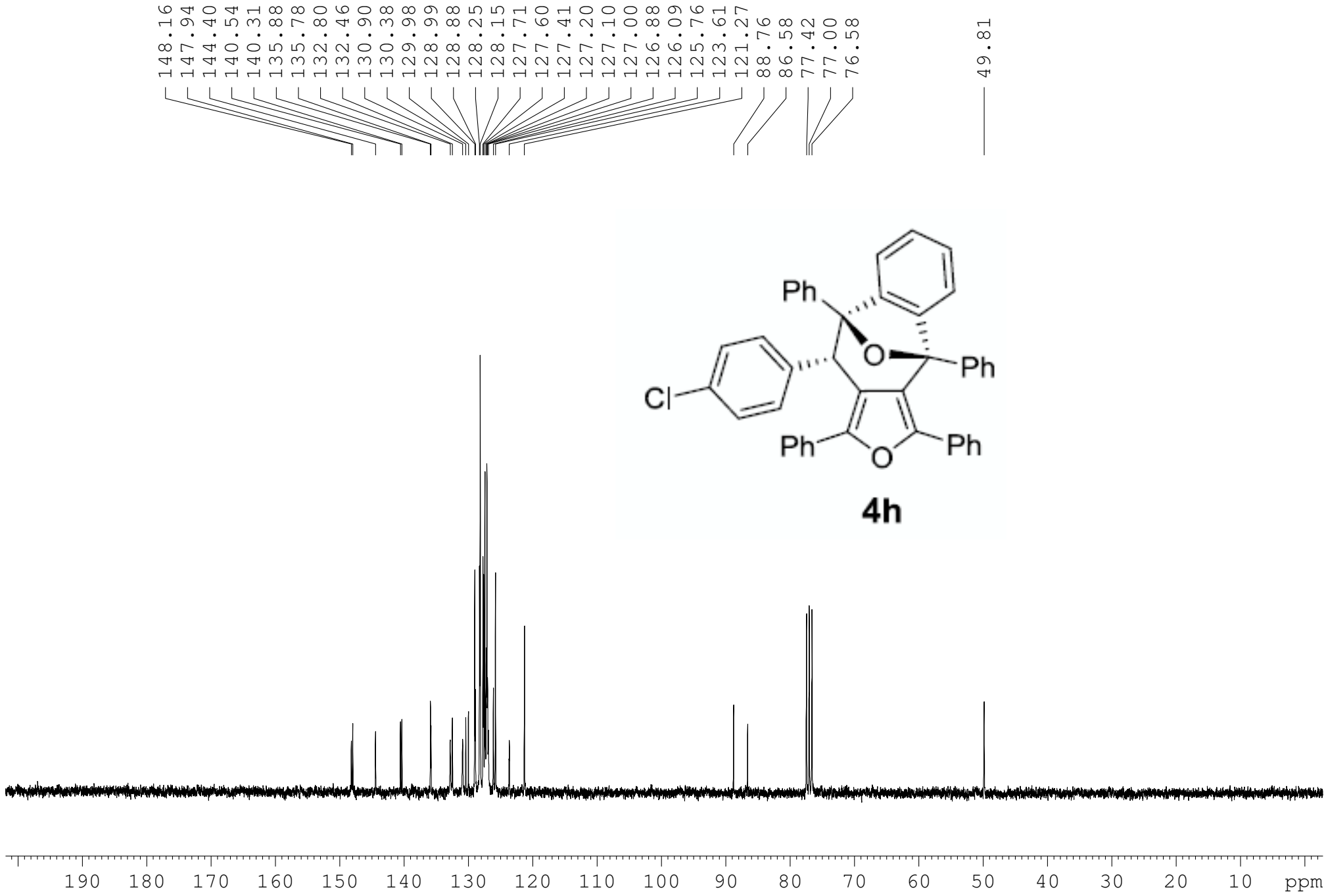
1.02
0.97
1.00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128.88
128.25
128.15
127.71
127.60
127.41
127.20
127.10
127.00
126.88
126.09
125.76
123.61
121.27
88.76
86.58
77.42
77.00
76.58
49.81
Ph
O
Ph
Cl
Ph
O
Ph
4h
190
180
170
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150
140
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100
90
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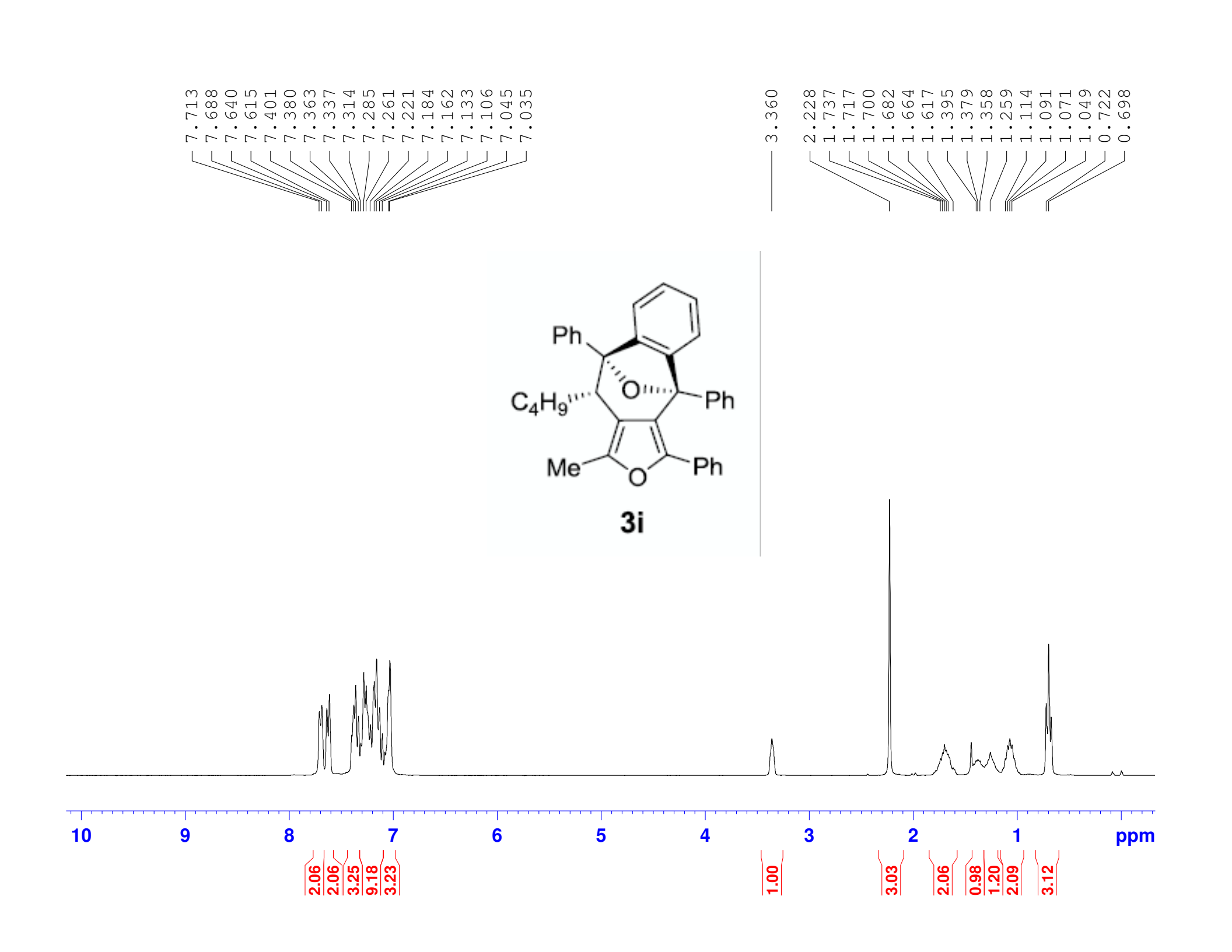
30
20
10
ppm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7.615
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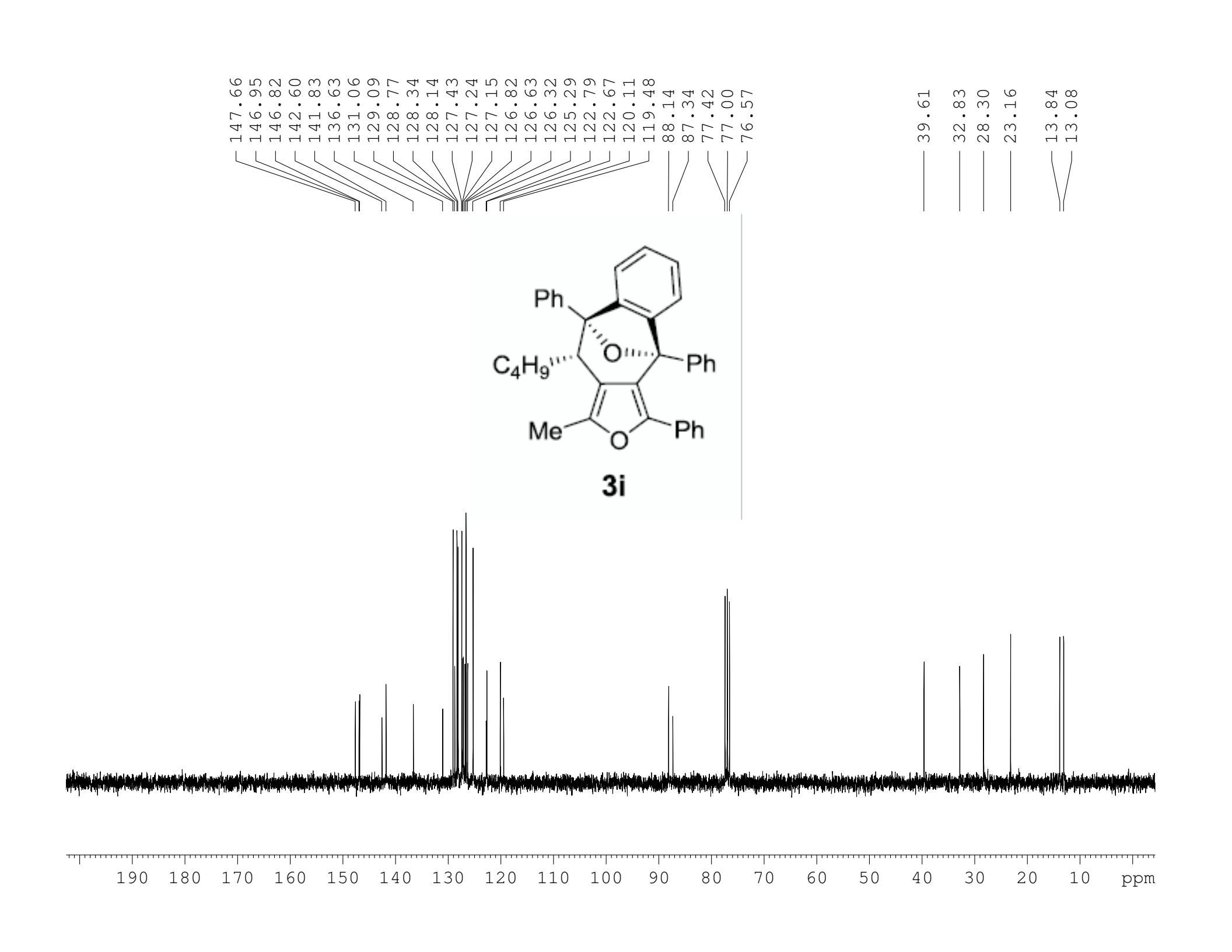
7.380
7.363
7.337
7.314
7.285
7.261
7.221
7.184
7.162
7.133
7.106
7.045
7.035
3.360
2.228
1.737
1.717
1.700
1.682
1.664
1.617
1.395
1.379
1.358
1.259
1.114
1.091
1.071
1.049
0.722
0.698
Ph
O
Ph
C4H9
Me
O
Ph
3i
10
9
8
7
6
5
4
3
2
1
ppm
2.06
2.06
3.25
9.18
3.23
1.00
3.03
2.06
0.98
1.20
2.09
3.12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136.63
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128.14
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127.24
127.15
126.82
126.63
126.32
125.29
122.79
122.67
120.11
119.48
88.14
87.34
77.42
77.00
76.57
39.61
32.83
28.30
23.16
13.84
13.08
Ph
O
Ph
C4H9
Me
O
Ph
3i
190
180
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150
140
130
120
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60
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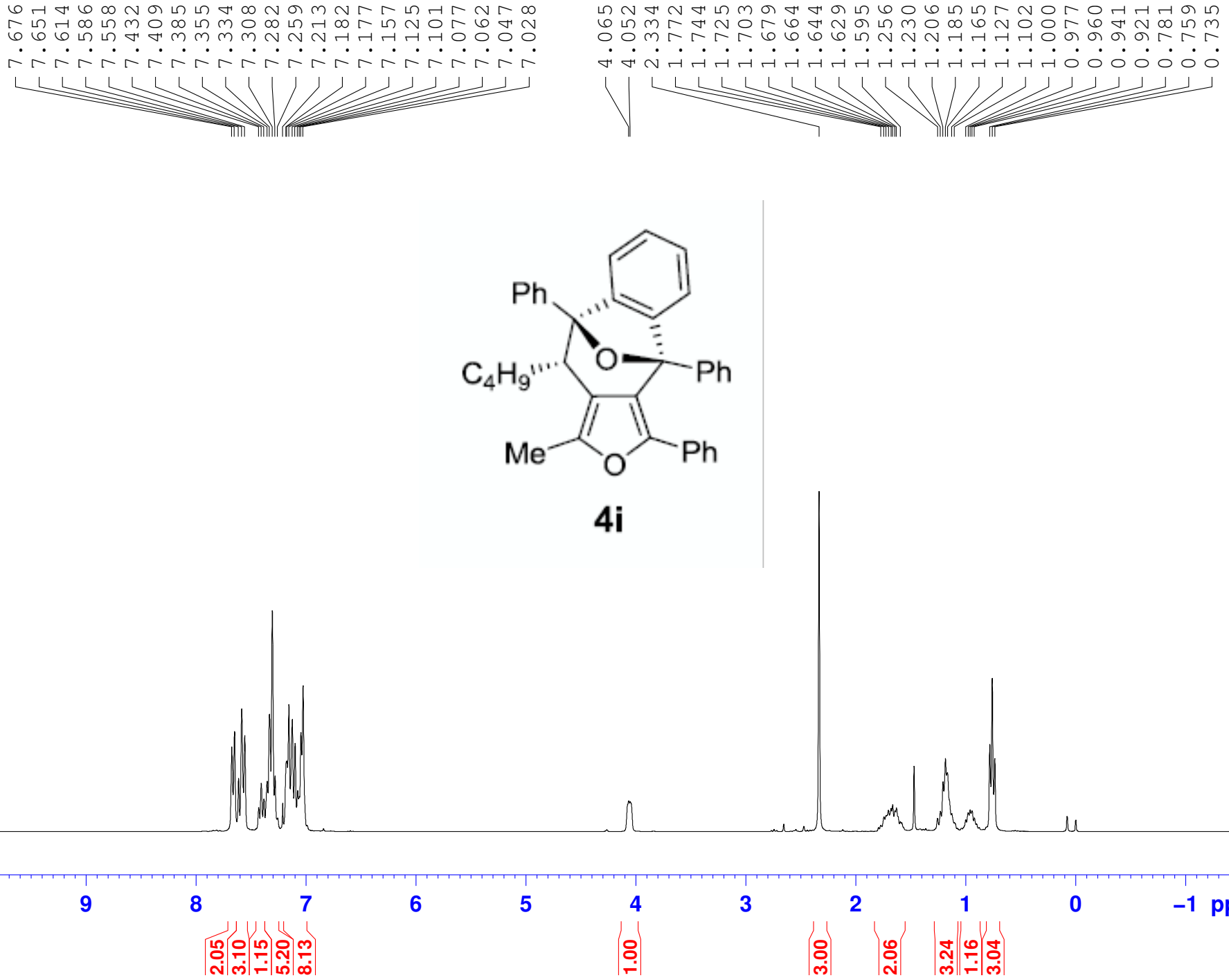
40
30
20
10
ppm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7.385
7.355
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7.282
7.259
7.213
7.182
7.177
7.157
7.125
7.101
7.077
7.062
7.047
7.028
4.065
4.052
2.334
1.772
1.744
1.725
1.703
1.679
1.664
1.644
1.629
1.595
1.256
1.230
1.206
1.185
1.165
1.127
1.102
1.000
0.977
0.960
0.941
0.921
0.781
0.759
0.735
Ph
O
Ph
C4H9
Me
O
Ph
4i
9
8
7
6
5
4
3
2
1
0
–1 ppm
2.05
3.10
1.15
5.20
8.13
1.00
3.00
2.06
3.24
1.16
3.04

147.84
146.49
143.31
143.02
141.06
136.17
130.93
128.86
128.56
128.17
128.05
127.82
127.41
126.81
126.71
126.45
125.63
122.05
121.65
120.76

88.59
86.59

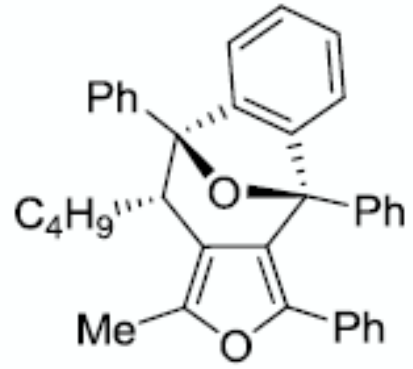
77.42
77.00
76.58

38.02

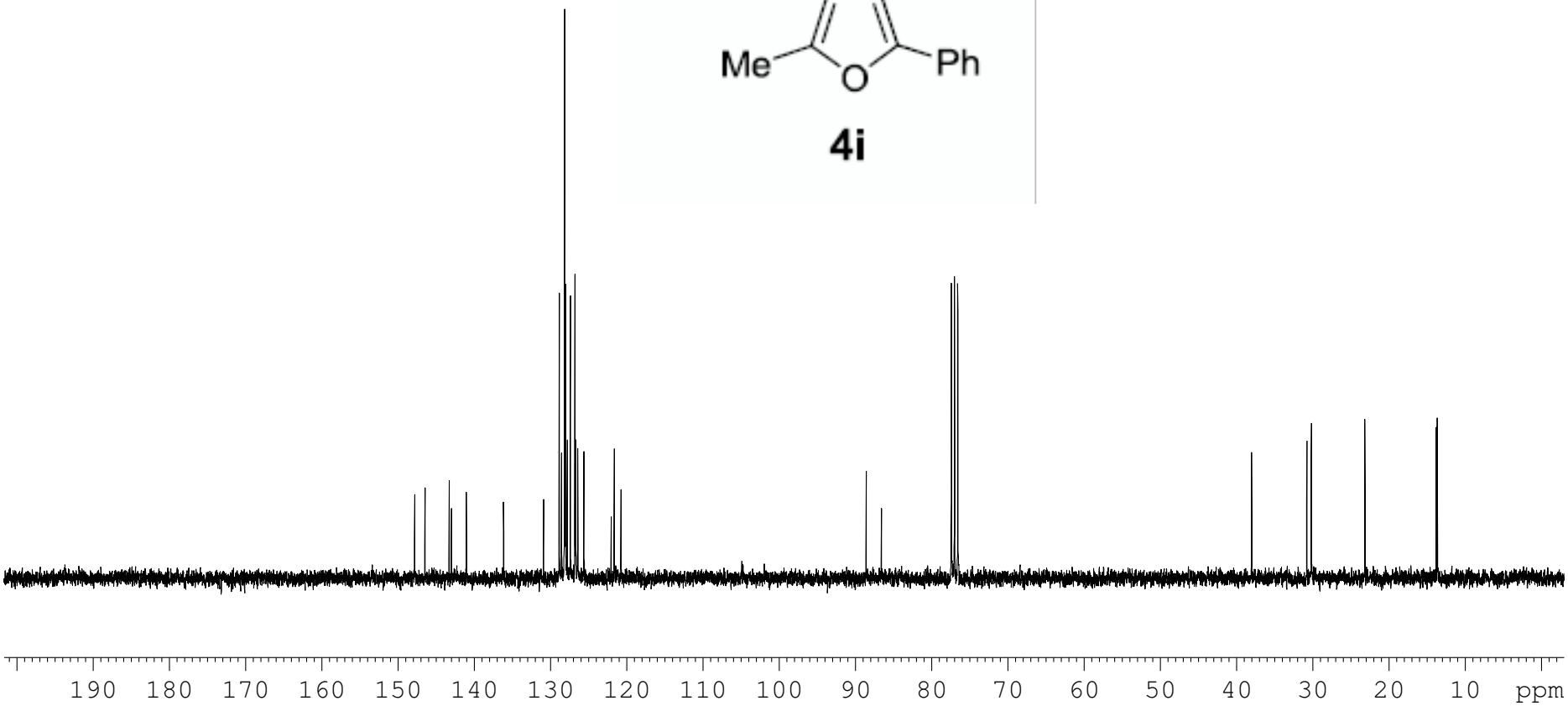
30.77
30.19

23.16

13.79
13.65



4i



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7.513
7.486
7.462
7.439
7.370
7.354
7.330
7.300
7.275
7.259
7.235
7.214
7.172
7.153
7.128
7.083
7.074
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7.040
7.030
6.772
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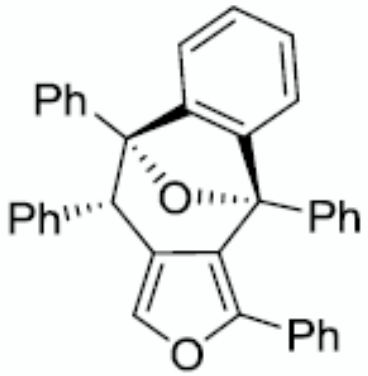
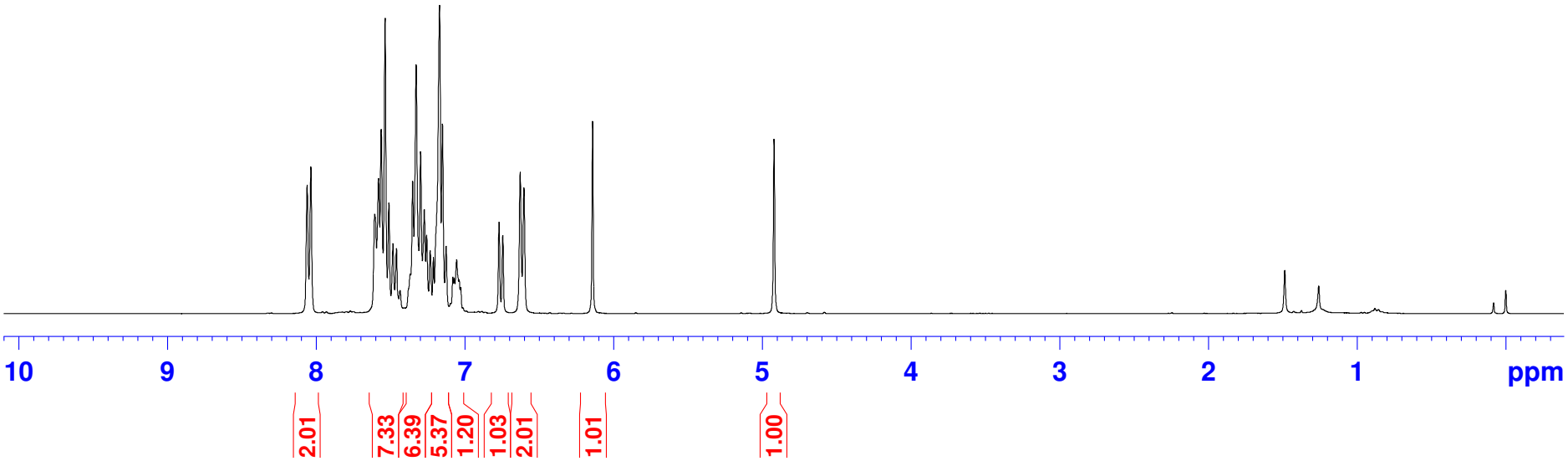
6.630
6.605
6.143
4.922

0.001



3j



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152.56
151.25
141.17
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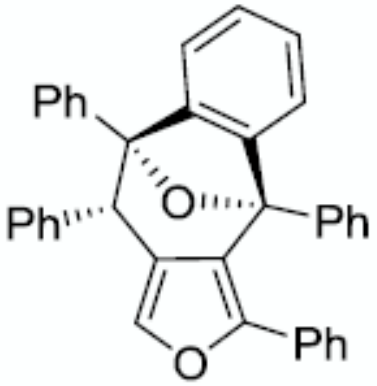
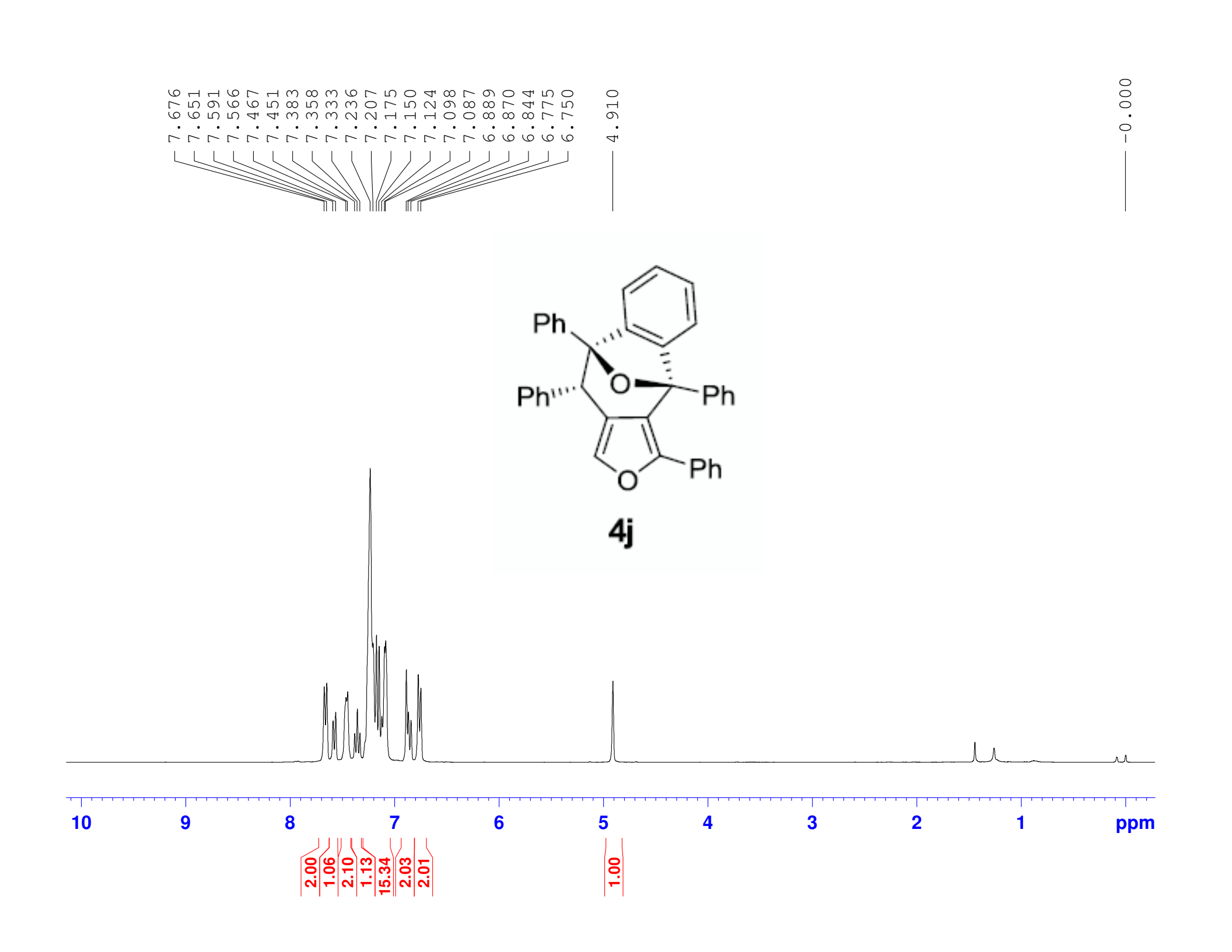
136.17
130.96
130.81
128.73
128.59
128.50
128.02
127.92
127.71
127.64
127.46
127.37
127.06
126.61
126.43
126.13
123.37
121.84
119.34
106.48
90.01
85.08
77.42
77.00
76.58

52.45



3j

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.207
7.175
7.150
7.124
7.098
7.087
6.889
6.870
6.844
6.775
6.750
4.910
-0.000
Ph
Ph
O
Ph
Ph
O
4j
10
9
8
7
6
5
4
3
2
1
ppm
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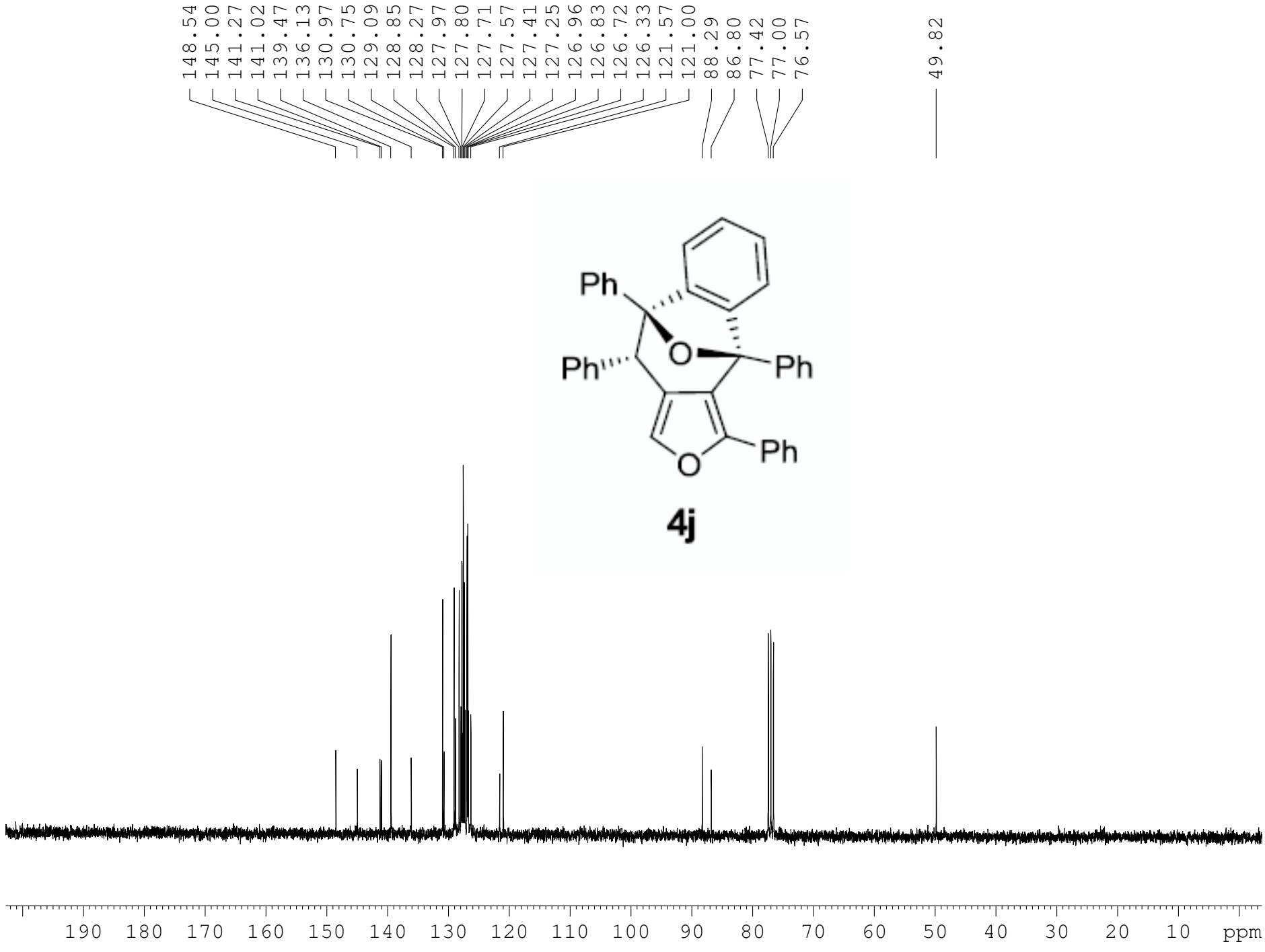
1.06
2.10
1.13
15.34
2.03
2.01
1.00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127.97
127.80
127.71
127.57
127.41
127.25
126.96
126.83
126.72
126.33
121.57
121.00
88.29
86.80
77.42
77.00
76.57
49.82
Ph
Ph
O
Ph
Ph
O
4j
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150
140
130
120
110
100
90
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70
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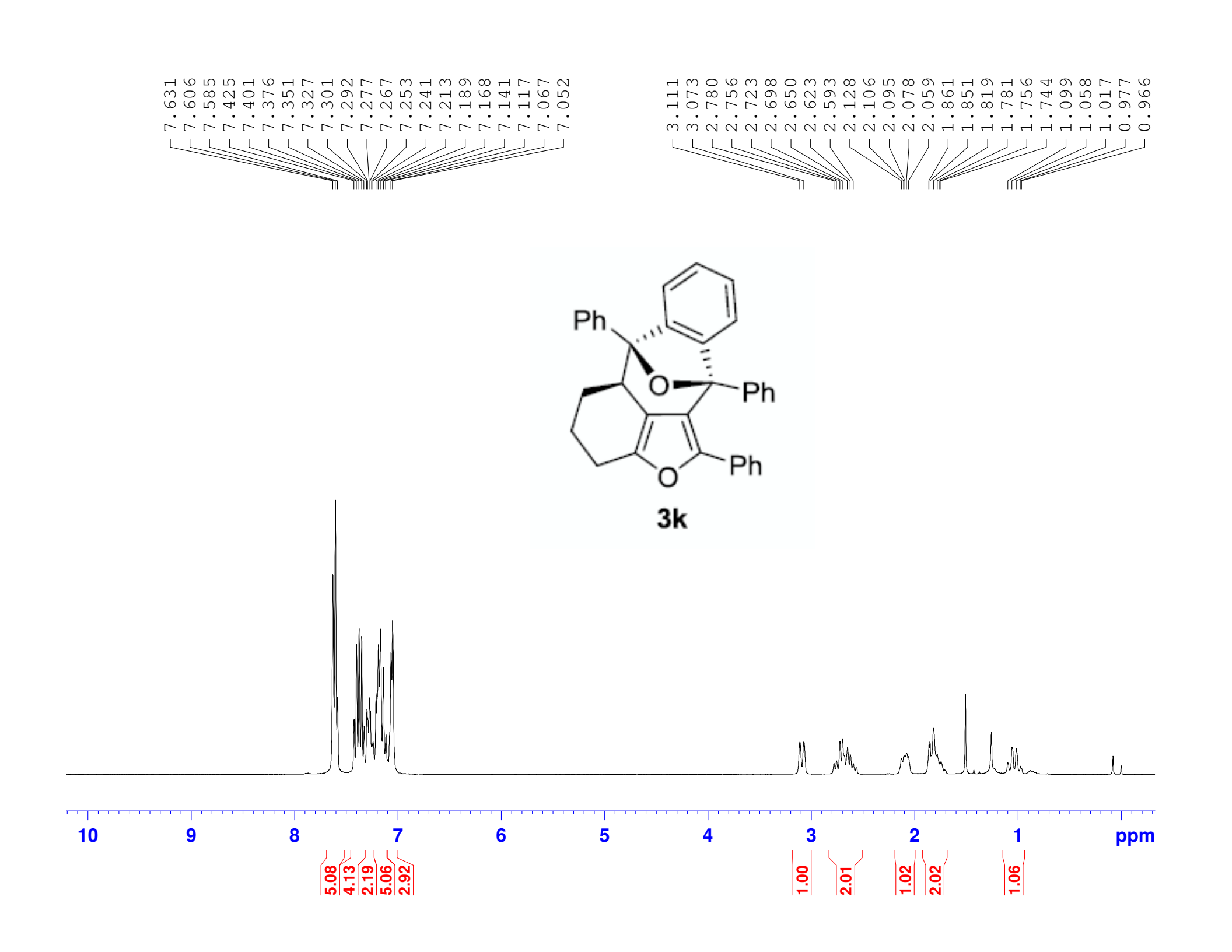
30
20
10
ppm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7.241
7.213
7.189
7.168
7.141
7.117
7.067
7.052
3.111
3.073
2.780
2.756
2.723
2.698
2.650
2.623
2.593
2.128
2.106
2.095
2.078
2.059
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1.851
1.819
1.781
1.756
1.744
1.099
1.058
1.017
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0.966
Ph
O
Ph
Ph
O
3k
10
9
8
7
6
5
4
3
2
1
ppm
5.08
4.13
2.19
5.06
2.92
1.00
2.01
1.02
2.02
1.06

149.16
148.73
145.69
144.14
140.00
136.07
130.88
128.86
128.48
128.08
127.85
127.56
127.47
127.05
126.97
126.70
125.53
122.51
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76.58
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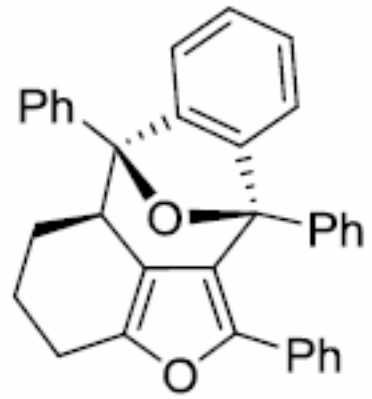
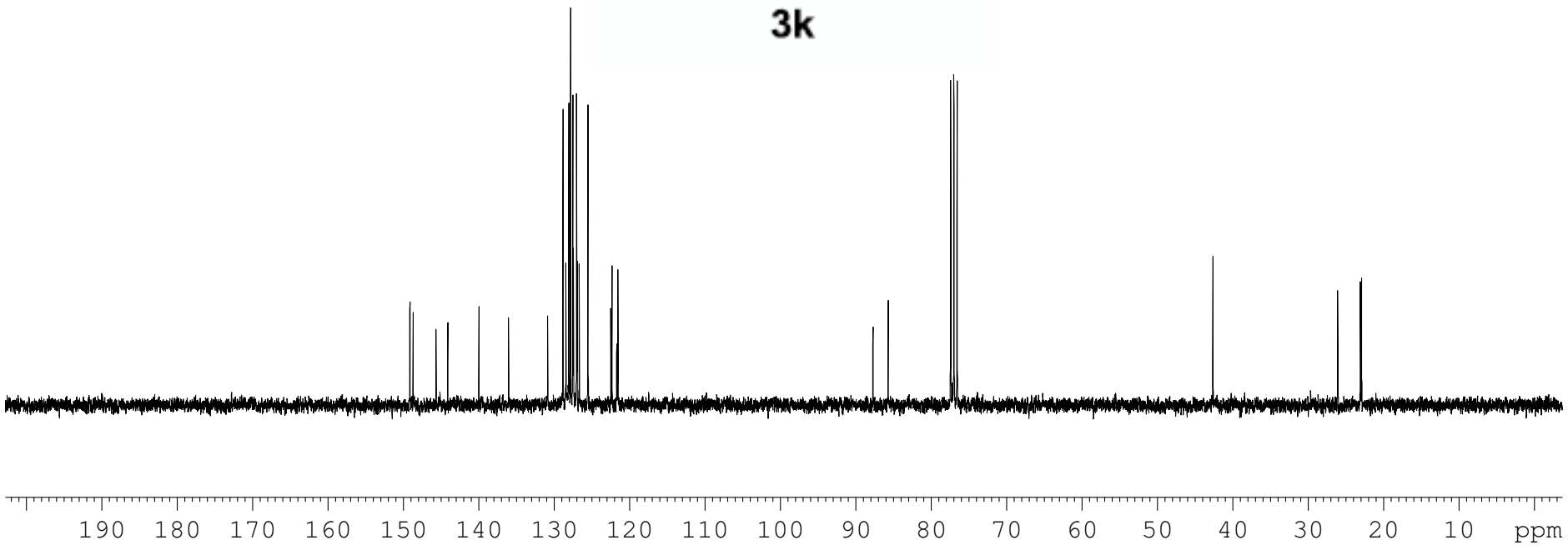
26.09
23.09
22.92



3k



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7.218
7.209
7.203
7.186
7.160
7.100
7.080
7.057
3.825
3.791
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2.700
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2.177
2.143
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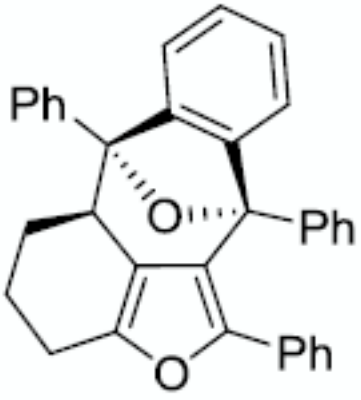
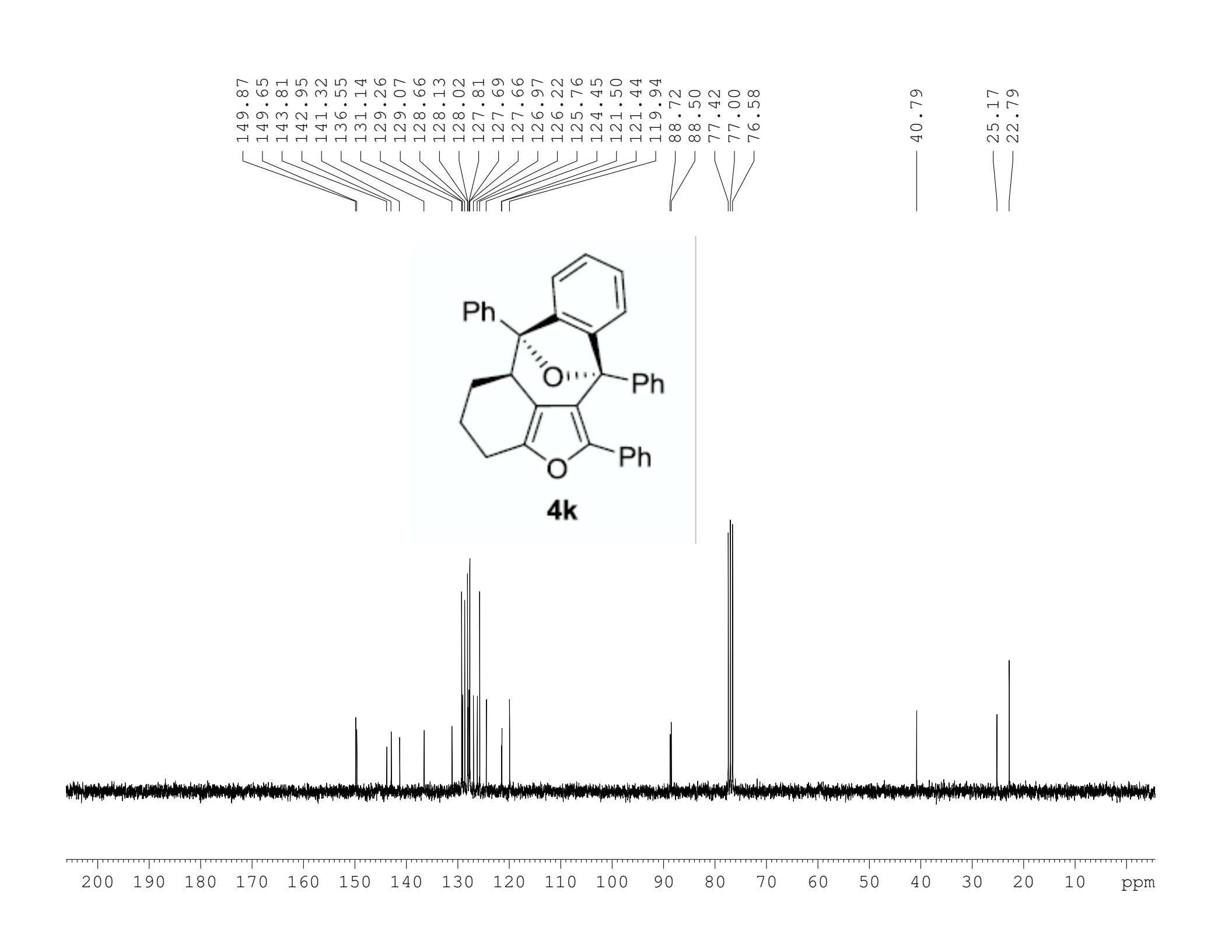
1.040



4k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128.13
128.02
127.81
127.69
127.66
126.97
126.22
125.76
124.45
121.50
121.44
119.94
88.72
88.50
77.42
77.00
76.58
40.79
25.17
22.79
Ph
O
Ph
Ph
O
4k
200
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170
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150
140
130
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70
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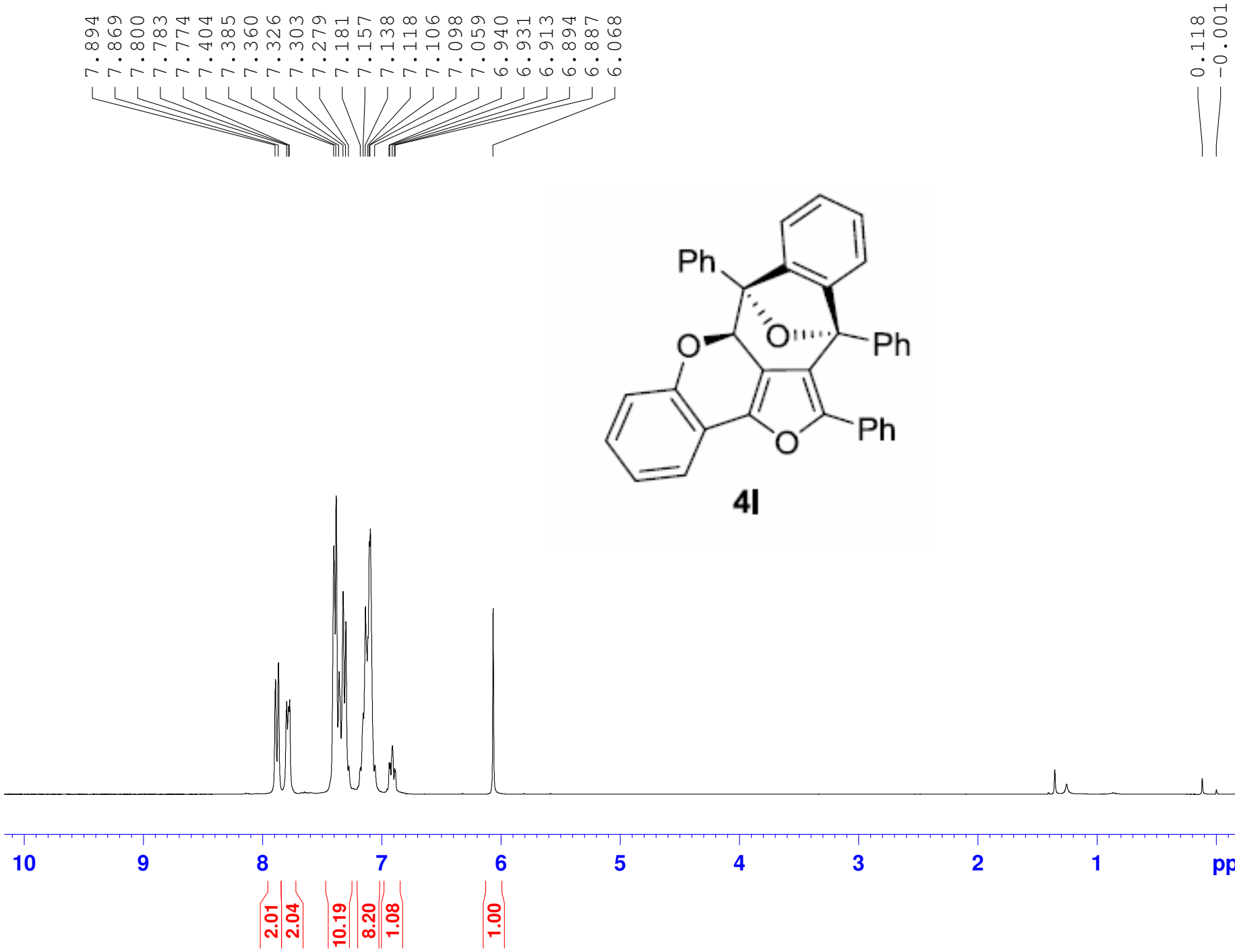
30
20
10
ppm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7.303
7.279
7.181
7.157
7.138
7.118
7.106
7.098
7.059
6.940
6.931
6.913
6.894
6.887
6.068
0.118
-0.001
Ph
O
O
Ph
O
Ph
4l
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5
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3
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2.04
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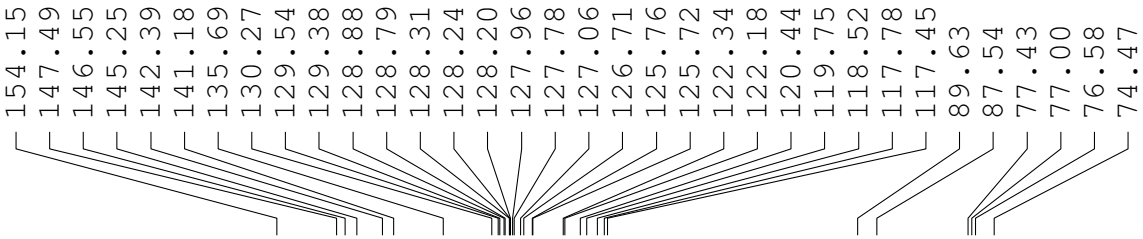
8.20
1.08
1.00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129.38
128.88
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128.31
128.24
128.20
127.96
127.78
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126.71
125.76
125.72
122.34
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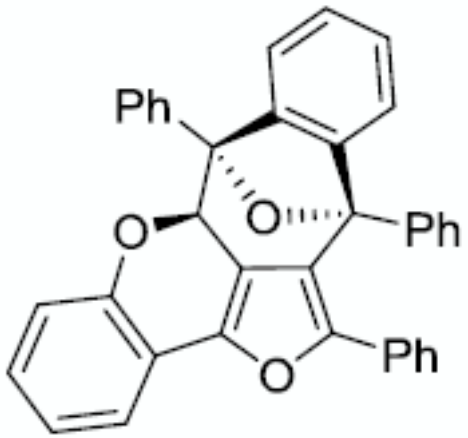
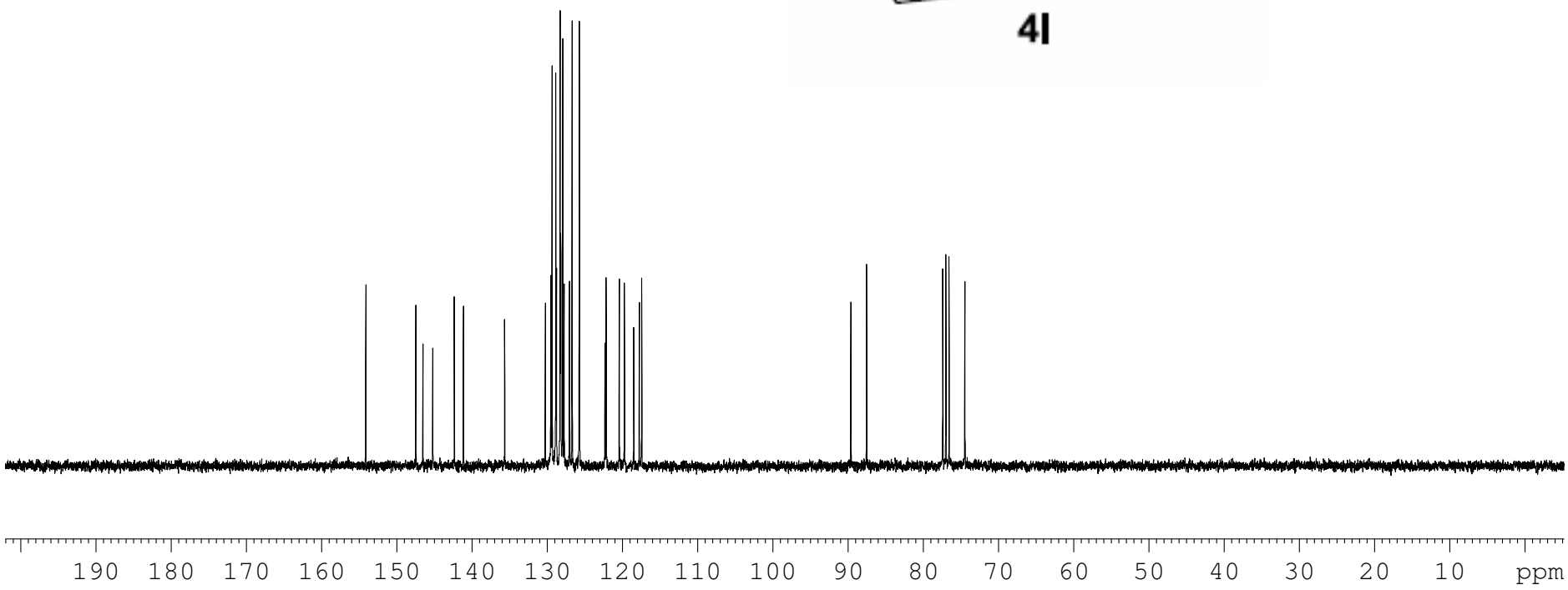
76.58
74.47


Ph
O
O
Ph
O
Ph

4l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150
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130
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110
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90
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70
60
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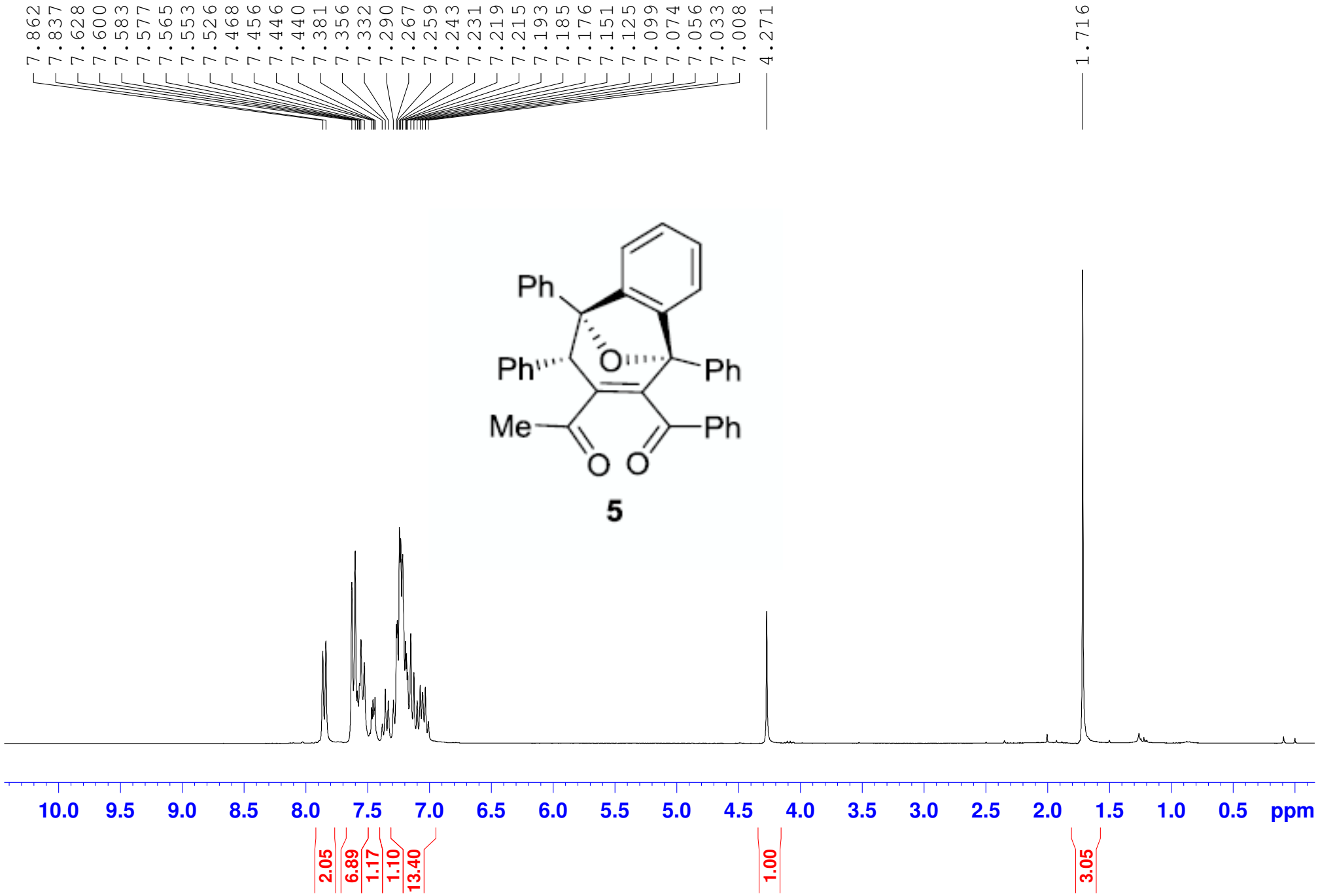
40
30
20
10
ppm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7.440
7.381
7.356
7.332
7.290
7.267
7.259
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7.231
7.219
7.215
7.193
7.185
7.176
7.151
7.125
7.099
7.074
7.056
7.033
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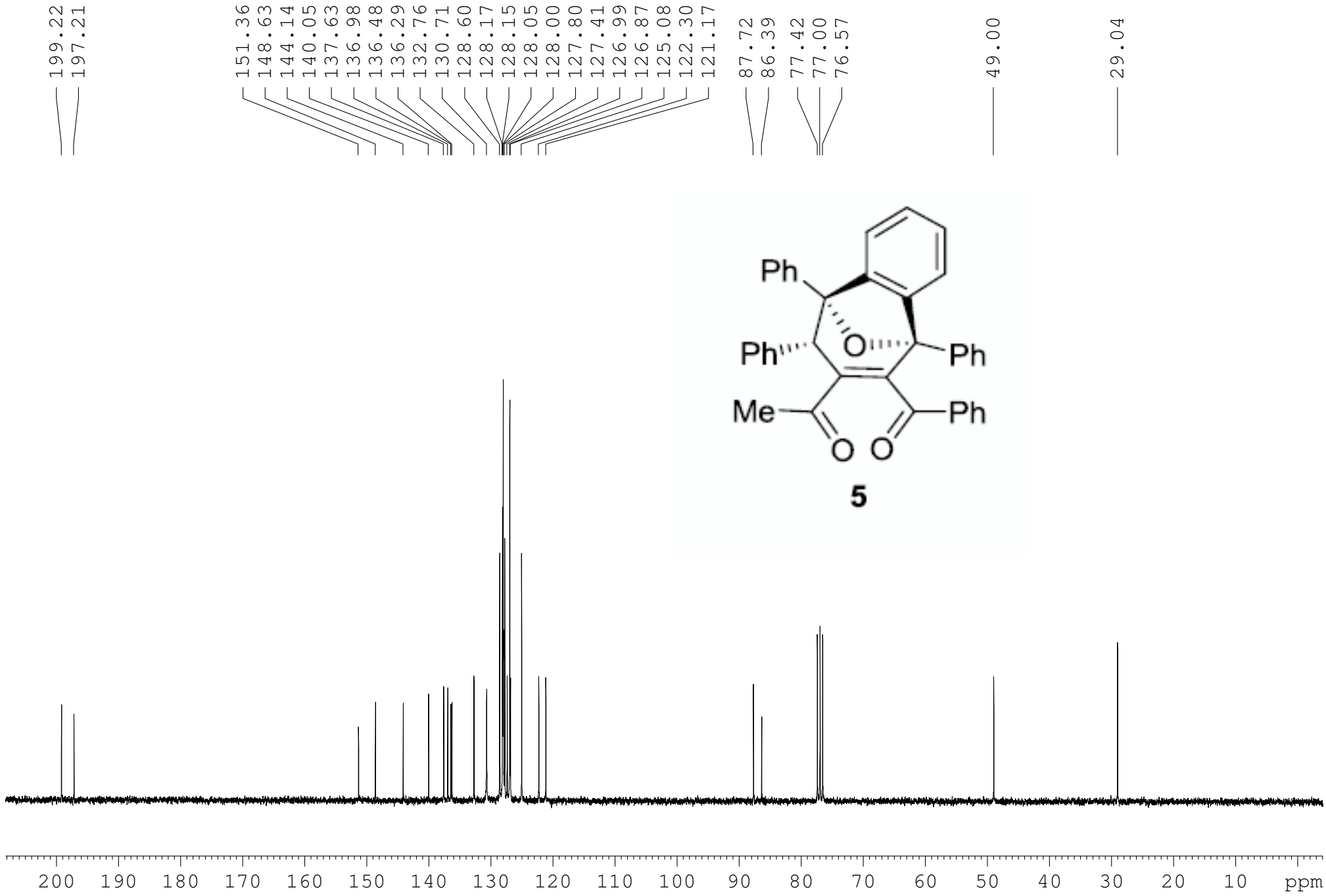
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