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Supporting Information

Studies on Thermal Reactivity of β-(1,2-Allenyl)butenolides and 2-Allyl-3-allenylcyclohex-2-enones

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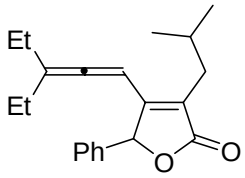
Synthesis of the starting materials β-allenylfuran-2(5*H*)-ones 1c-t

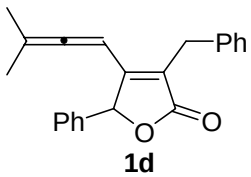
(1) Synthesis of 3-Isobutyl-4-(3'-ethylpenta-1',2'-dienyl)-5-phenylfuran-2(5*H*)-one (1c)



1c

A mixture of 2-isobutyl-4-phenylbuta-2,3-dienoic acid (108 mg, 0.50 mmol), methyl 3-ethylpent-1-yn-3-yl carbonate (170 mg, 1.00 mmol), $Pd(OAc)_2$ (5 mg, 0.025 mmol), TFP (11 mg, 0.050 mmol), and K_2CO_3 (69 mg, 0.50 mmol) in 2 mL of DMSO was stirred at 35 ^oC for 14 h to afford **1c** (76 mg, 49%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.39-7.30 (m, 3 H), 7.21-7.12 (m, 2 H), 6.15 (pentet, *J* = 3.0 Hz, 1 H), 5.70 (s, 1 H), 2.39-2.23 (m, 2 H), 2.12-1.82 (m, 3 H), 1.62-1.45 (m, 1 H), 1.45-1.30 (m, 1 H), 1.06-0.93 (m, 9 H), 0.28 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.7, 12.1, 22.4, 22.5, 24.9, 25.2, 27.9, 32.5, 83.0, 87.7, 112.1, 125.4, 127.6, 128.5, 129.0, 136.1, 156.1, 174.1, 206.7; MS(EI): *m/z* (%) 310 (M^+, 31.06), 281 (100); IR (neat): 1942, 1753, 1642, 1456, 1083, 1005 cm^{-1}; HRMS: calcd. for $C_{21}H_{26}O_2$ [M^+]: 310.1933; Found: 310.1934.

(2) Synthesis of 3-Benzyl-4-(3'-methylbuta-1',2'-dienyl)-5-phenylfuran-2(5*H*)-one (1d)

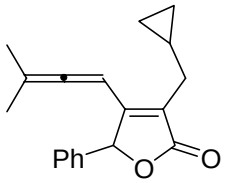


1d

A mixture of 2-benzyl-4-phenylbuta-2,3-dienoic acid (62 mg, 0.25 mmol), methyl

2-methylbut-3-yn-2-yl carbonate (71 mg, 0.50 mmol), $Pd(OAc)_2$ (3 mg, 0.0125 mmol), TFP (6 mg, 0.025 mmol), and K_2CO_3 (34 mg, 0.25 mmol) in 1 mL of DMSO was stirred at 35 ^oC for 5 h to afford **1d** (31 mg, 39%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.41-7.30 (m, 6 H), 7.30-7.20 (m, 2 H), 7.20-7.12 (m, 2 H), 5.96 (heptet, *J* = 3.0 Hz, 1 H), 5.73 (s, 1 H), 3.77 (s, 2 H), 1.64 (d, *J* = 3.0 Hz, 3 H), 1.03 (d, *J* = 3.0 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 18.8, 19.4, 29.6, 83.2, 83.8, 100.0, 125.3, 126.5, 127.6, 128.4, 128.6, 129.0, 135.9, 138.1, 156.1, 173.8, 208.5; MS(EI): *m/z* (%) 316 (M^+, 31.86), 301 (M^+-CH_3, 63.30), 105 (100); IR (neat): 1949, 1751, 1643, 1602, 1495, 1455, 1302, 1083, 1002 cm^{-1}; HRMS: calcd. for $C_{22}H_{20}O_2$ [M^+]: 316.1463; Found: 316.1461.

(3) Synthesis of 3-(Cyclopropylmethenyl)-4-(3'-methylbuta-1',2'-dienyl)-5-phenylfuran-2(5*H*)-one (1e)

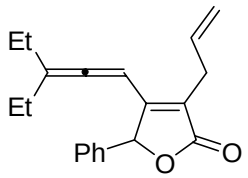


1e

A mixture of 2-cyclopropylmethenyl-4-phenylbuta-2,3-dienoic acid (107 mg, 0.50 mmol), methyl 2-methylbut-3-yn-2-yl carbonate (142 mg, 1.00 mmol), $Pd(OAc)_2$ (5 mg, 0.025 mmol), TFP (11 mg, 0.050 mmol), and K_2CO_3 (69 mg, 0.50 mmol) in 2 mL of DMSO was stirred at 30 ^oC for 9 h to afford **1e** (63 mg, 45%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.40-7.27 (m, 3 H), 7.25-7.15 (m, 2 H), 5.96 (heptet, *J* = 3.0 Hz, 1 H), 5.71 (s, 1 H), 2.35 (d, *J* = 6.3 Hz, 2 H), 1.66 (d, *J* = 3.0 Hz, 3 H), 1.11-0.98 (m, 1 H), 1.04 (d, *J* = 3.0 Hz, 3 H), 0.55-0.45 (m, 2 H), 0.28-0.21 (m, 2 H); ^{13}C NMR (75.4

MHz, $CDCl_3$): δ 4.5, 4.6, 10.1, 18.9, 19.4, 28.0, 83.1, 83.8, 99.8, 126.3, 127.6, 128.6, 128.9, 136.1, 155.2, 174.2, 208.1; MS(EI): *m/z* (%) 280 (M^+, 5.50), 77 (100); IR (neat): 1950, 1751, 1644, 1456, 1301, 1082, 1002 cm^{-1}; HRMS: calcd. for $C_{19}H_{20}O_2$ [M^+]: 280.1463; Found: 280.1469.

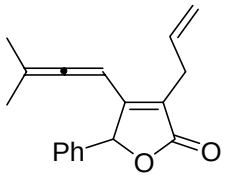
(4) Synthesis of 3-Allyl-4-(3'-ethylpenta-1',2'-dienyl)-5-phenylfuran-2(5*H*)-one (1f)



1f

A mixture of 2-allyl-4-phenylbuta-2,3-dienoic acid (50 mg, 0.25 mmol), methyl 3-ethylpent-1-yn-3-yl carbonate (85 mg, 0.50 mmol), $Pd(OAc)_2$ (3 mg, 0.0125 mmol), TFP (6 mg, 0.025 mmol), and K_2CO_3 (34 mg, 0.25 mmol) in 1 mL of DMSO was stirred at 35 ^oC for 10 h to afford **1f** (53 mg, 72%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.40-7.28 (m, 3 H), 7.21-7.12 (m, 2 H), 6.17 (pentet, *J* = 2.7 Hz, 1 H), 6.01-5.85 (m, 1 H), 5.71 (s, 1 H), 5.22-5.09 (m, 2 H), 3.21 (d, *J* = 6.3 Hz, 2 H), 2.06-1.82 (m, 2 H), 1.60-1.46 (m, 1 H), 1.46-1.30 (m, 1 H), 1.02 (t, *J* = 7.5 Hz, 3 H), 0.30 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.8, 12.2, 25.0, 25.3, 27.7, 83.2, 87.5, 112.2, 116.5, 123.6, 127.7, 128.6, 129.1, 133.5, 135.9, 156.4, 173.7, 207.0; MS(EI): *m/z* (%) 294 (M^+, 10.52), 265 (M^+-C_2H_5, 75.55), 105 (100); IR (neat): 1941, 1753, 1643, 1455, 1300, 1080, 1002 cm^{-1}; HRMS: cacld. for $C_{20}H_{22}O_2$ [M^+] 294.1620; Found, 294.1633.

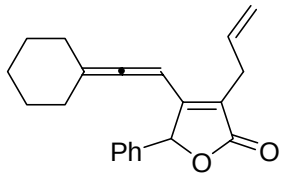
(5) Synthesis of 3-Allyl-4-(3'-methylbuta-1',2'-dienyl)-5-phenylfuran-2(5*H*)-one (1g)



1g

A mixture of 2-allyl-4-phenylbuta-2,3-dienoic acid (50 mg, 0.25 mmol), methyl 2-methylbut-3-yn-2-yl carbonate (72 mg, 0.51 mmol), $Pd(OAc)_2$ (3 mg, 0.0125 mmol), TFP (6 mg, 0.025 mmol), and K_2CO_3 (34 mg, 0.25 mmol) in 3 mL of DMSO was stirred at 30 ^oC for 21 h to afford **1g** (40 mg, 60%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.40-7.27 (m, 3 H), 7.22-7.13 (m, 2 H), 6.00-5.85 (m, 2 H), 5.72 (s, 1 H), 5.22-5.08 (m, 2 H), 3.19 (d, *J* = 6.3 Hz, 2 H), 1.66 (d, *J* = 3.0 Hz, 3 H), 1.05 (d, *J* = 3.0 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 18.9, 19.4, 27.8, 83.2, 83.7, 99.9, 116.6, 124.0, 127.7, 128.6, 129.0, 133.5, 135.9, 156.3, 173.7, 208.4; MS(EI): *m/z* (%) 266 (M^+, 29.73), 77 (100); IR (neat): 1951, 1752, 1645, 1300, 1083, 1002 cm^{-1}; HRMS: cacld. for $C_{18}H_{18}O_2$ [M^+] 266.1307; Found, 266.1292.

(6) Synthesis of 3-Allyl-4-(3',3'-pentamethylenepropa-1',2'-dienyl)-5-phenylfuran-2(5*H*)-one (1h)

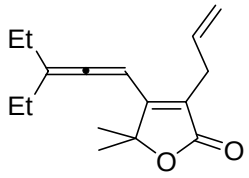


1h

A mixture of 2-allyl-4-phenylbuta-2,3-dienoic acid (50 mg, 0.25 mmol), methyl 1,1-pentamethyleneprop-2-ynyl carbonate (91 mg, 0.50 mmol), $Pd(OAc)_2$ (3 mg, 0.0125 mmol), TFP (6 mg, 0.025 mmol), and K_2CO_3 (33 mg, 0.24 mmol) in 1 mL of DMSO was stirred at 35 ^oC for 10 h to afford **1h** (48 mg, 63%). ^1H NMR (300 MHz,

$CDCl_3$): δ 7.34-7.20 (m, 3 H), 7.18-7.08 (m, 2 H), 5.95-5.90 (m, 1 H), 5.90-5.78 (m, 1 H), 5.68 (s, 1 H), 5.18-5.00 (m, 2 H), 3.13 (d, *J* = 6.3 Hz, 2 H), 2.10-1.92 (m, 2 H), 1.58-1.40 (m, 3 H), 1.40-1.24 (m, 3 H), 1.24-1.17 (m, 1 H), 1.18-1.03 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 25.4, 25.8, 26.5, 27.8, 29.6, 30.2, 83.1, 83.6, 105.9, 116.5, 123.8, 127.8, 128.6, 129.1, 133.5, 136.0, 156.2, 173.6, 205.0; MS(EI): *m/z* (%) 306 (M^+, 30.77), 105 (100); IR (neat): 1945, 1753, 1643, 1450, 1300, 1081, 1006 cm^{-1}; HRMS: cacld. for $C_{21}H_{23}O_2$ [M^++1] 307.1693; Found, 307.1695.

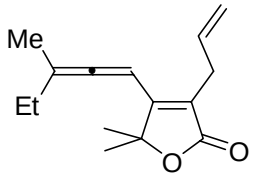
(7) Synthesis of 3-Allyl-4-(3'-ethylpenta-1',2'-dienyl)-5,5-dimethylfuran-2(5*H*)-one (1i)



1i

A mixture of 2-allyl-4-methylpenta-2,3-dienoic acid (77 mg, 0.51 mmol), methyl 3-ethylpent-1-yn-3-yl carbonate (170 mg, 1.00 mmol), $Pd(OAc)_2$ (6 mg, 0.025 mmol), TFP (12 mg, 0.050 mmol), and K_2CO_3 (69 mg, 0.50 mmol) in 2 mL of DMSO was stirred at 35 ^{o}C for 10 h to afford **1i** (103 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.13 (pentet, *J* = 3.3 Hz, 1 H), 5.89-5.72 (m, 1 H), 5.07-4.96 (m, 2 H), 3.03 (d, *J* = 6.0 Hz, 2 H), 2.20-1.95 (m, 4 H), 1.43 (s, 6 H), 1.00 (t, *J* = 7.5 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 11.7, 25.1, 25.9, 27.3, 84.9, 86.3, 110.8, 115.9, 122.4, 133.5, 160.9, 172.4, 206.4; MS(EI): *m/z* (%) 247 (M^++1, 56.34), 246 (M^+, 12.25), 43 (100); IR (neat): 1939, 1751, 1640, 1458, 1293, 1196, 1067 cm^{-1}; HRMS: cacld. for $C_{16}H_{22}O_2$ [M^+] 246.1620; Found, 246.1612.

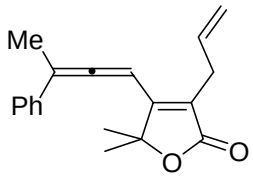
(8) Synthesis of 3-Allyl-4-(3'-methylpenta-1',2'-dienyl)-5,5-dimethylfuran-2(5*H*)-one (1j)



1j

A mixture of 2-allyl-4-methylpenta-2,3-dienoic acid (76 mg, 0.50 mmol), methyl 3-methylpent-1-yn-3-yl carbonate (156 mg, 1.00 mmol), $Pd(OAc)_2$ (5 mg, 0.022 mmol), TFP (12 mg, 0.050 mmol), and K_2CO_3 (69 mg, 0.50 mmol) in 2 mL of DMSO was stirred at 25 ^oC for 10 h to afford **1j** (77 mg, 66%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.10-6.03 (m, 1 H), 5.90-5.75 (m, 1 H), 5.10-4.98 (m, 2 H), 3.05 (d, *J* = 6.3 Hz, 2 H), 2.17-1.96 (m, 2 H), 1.79 (d, *J* = 3.0 Hz, 3 H), 1.46 (s, 3 H), 1.44 (s, 3 H), 1.03 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 11.7, 18.2, 25.7, 25.8, 26.6, 27.3, 84.5, 84.9, 104.5, 116.0, 122.6, 133.6, 160.9, 172.4, 207.1; MS(EI): *m/z* (%) 232 (M^+, 1.94), 217 (M^+-CH_3, 22.21), 43 (100); IR (neat): 1943, 1752, 1640, 1459, 1292, 1196, 1067 cm^{-1}; HRMS: cacld. for $C_{15}H_{20}O_2$ [M^+] 232.1463; Found, 232.1461.

(9) Synthesis of 3-Allyl-4-(3'-phenylbuta-1',2'-dienyl)-5,5-dimethylfuran-2(5*H*)-one (1k)

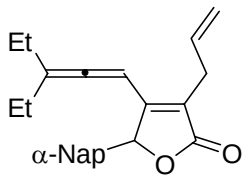


1k

A mixture of 2-allyl-4-methylpenta-2,3-dienoic acid (76 mg, 0.50 mmol), methyl 3-phenylbuta-1-yn-3-yl carbonate (153 mg, 0.75 mmol), $Pd(OAc)_2$ (5 mg, 0.022

mmol), TFP (12 mg, 0.052 mmol), and K_2CO_3 (69 mg, 0.50 mmol) in 2 mL of DMSO was stirred at 25 ^oC for 11 h to afford **1j** (111 mg, 79%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.42-7.20 (m, 5 H), 6.49 (q, *J* = 3.0 Hz, 1 H), 5.98-5.80 (m, 1 H), 5.18-5.02 (m, 2 H), 3.13 (d, *J* = 6.0 Hz, 2 H), 2.22 (d, *J* = 3.0 Hz, 3 H), 1.49 (s, 3 H), 1.37 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 16.5, 25.7, 27.6, 85.0, 86.8, 104.1, 116.3, 124.0, 125.9, 127.8, 128.7, 133.5, 134.0, 159.8, 172.2, 211.0; MS(EI): *m/z* (%) 280 (M^+, 15.45), 265 (M^+-CH_3, 51.25), 43 (100); IR (neat): 1929, 1748, 1642, 1597, 1494, 1288, 1195, 1067 cm^{-1}; HRMS: cacld. for $C_{19}H_{20}O_2$ [M^+] 280.1463; Found, 280.1465.

(10) Synthesis of 3-Allyl-4-(3'-ethylpenta-1',2'-dienyl)-5-(naphth-1'-yl)furan-2(5*H*)-one (1l)

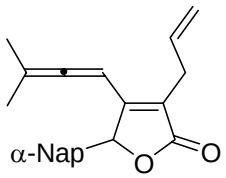


1l

A mixture of 2-allyl-4-(naphth-1'-yl)buta-2,3-dienoic acid (125 mg, 0.50 mmol), methyl 3-ethylpent-1-yn-3-yl carbonate (170 mg, 1.00 mmol), $Pd(OAc)_2$ (5 mg, 0.022 mmol), TFP (12 mg, 0.052 mmol), and K_2CO_3 (69 mg, 0.50 mmol) in 2 mL of DMSO was stirred at 25 ^oC for 12 h to afford **1l** (137 mg, 80%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.1 Hz, 1 H), 7.85 (t, *J* = 9.0 Hz, 2 H), 7.58-7.45 (m, 2 H), 7.42 (t, *J* = 7.5 Hz, 1 H), 7.27 (d, *J* = 7.2 Hz, 1 H), 6.61 (s, 1 H), 6.23 (pentet, *J* = 3.0 Hz, 1 H), 6.07-5.92 (m, 1 H), 5.28-5.12 (m, 2 H), 3.28 (d, *J* = 6.3 Hz, 2 H), 1.85-1.60 (m, 2 H), 1.15-0.98 (m, 1 H), 0.90 (t, *J* = 7.5 Hz, 3 H), 0.73-0.56 (m, 1 H), 0.02 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.7, 12.0, 24.3, 24.9, 27.9, 78.3, 87.6, 112.4,

116.6, 122.3, 124.0, 125.2, 125.5, 125.7, 126.5, 128.8, 129.7, 131.7, 131.8, 133.5, 133.8, 157.3, 173.8, 206.9; MS(EI): *m/z* (%) 344 (M^+, 70.30), 315 (M^+-C_2H_5, 97.71), 127 (100); IR (neat): 1939, 1754, 1644, 1298, 1075, 1035, 990, 779 cm^{-1}; HRMS: cacld. for $C_{24}H_{24}O_2$ [M^+] 344.1776; Found, 344.1773.

(11) Synthesis of 3-Allyl-4-(3'-methylbuta-1',2'-dienyl)-5-(naphth-1'-yl)-furan-2(5*H*)-one (1m)

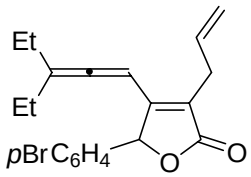


1m

A mixture of 2-allyl-4-(naphth-1'-yl)buta-2,3-dienoic acid (125 mg, 0.50 mmol), methyl 3-methylbuta-1-yn-3-yl carbonate (142 mg, 1.00 mmol), $Pd(OAc)_2$ (5 mg, 0.022 mmol), TFP (11 mg, 0.050 mmol), and K_2CO_3 (69 mg, 0.50 mmol) in 2 mL of DMSO was stirred at 25 ^oC for 10 h to afford **1m** (100 mg, 63%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 1 H), 7.78 (d, *J* = 8.1 Hz, 1 H), 7.73 (d, *J* = 8.4 Hz, 1 H), 7.50-7.39 (m, 2 H), 7.35 (t, *J* = 7.8 Hz, 1 H), 7.16 (d, *J* = 7.2 Hz, 1 H), 6.53 (s, 1 H), 5.98-5.80 (m, 2 H), 5.20-5.01 (m, 2 H), 3.17 (d, *J* = 6.6 Hz, 2 H), 1.34 (d, *J* = 2.7 Hz, 3 H), 0.38 (d, *J* = 2.7 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 18.0, 19.2, 27.9, 78.3, 83.8, 100.1, 116.6, 122.4, 124.3, 125.2, 125.7, 126.6, 128.8, 129.5, 131.8, 133.5, 133.8, 157.1, 173.8, 208.3; MS(EI): *m/z* (%) 316 (M^+, 65.71), 301 (M^+-CH_3, 33.62), 127 (100); IR (neat): 1949, 1753, 1644, 1512, 1297, 1036, 989, 778 cm^{-1}; HRMS: cacld. for $C_{22}H_{20}O_2$ [M^+] 316.1463; Found, 316.1459.

(12) Synthesis of 3-Allyl-4-(3'-ethylpenta-1',2'-dienyl)-5-(4'-bromophenyl)furan-

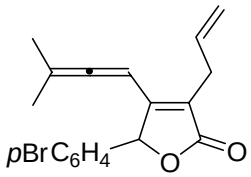
2(5*H*)-one (1n)



1n

A mixture of 2-allyl-4-(4'-bromophenyl)buta-2,3-dienoic acid (209 mg, 0.75 mmol), methyl 3-ethylpent-1-yn-3-yl carbonate (193 mg, 1.13 mmol), $Pd(OAc)_2$ (8 mg, 0.038 mmol), TFP (18 mg, 0.078 mmol), and K_2CO_3 (103 mg, 0.75 mmol) in 3 mL of DMSO was stirred at 25 ^oC for 12 h to afford **1n** (164 mg, 59%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.4 Hz, 2 H), 6.98 (d, *J* = 8.4 Hz, 2 H), 6.11 (pentet, *J* = 3.0 Hz, 1 H), 5.93-5.88 (m, 1 H), 5.61 (s, 1 H), 5.17-5.01 (m, 2 H), 3.13 (d, *J* = 6.6 Hz, 2 H), 2.02-1.78 (m, 2 H), 1.62-1.30 (m, 2 H), 0.94 (t, *J* = 7.5 Hz, 3 H), 0.30 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.8, 12.2, 25.1, 25.2, 27.7, 82.2, 87.4, 112.4, 116.6, 123.1, 123.8, 129.4, 131.7, 133.3, 135.1, 156.0, 173.4, 207.0; MS(EI): *m/z* (%) 373 [(^{81}Br)M^+-1, 6.14], 371 [(^{79}Br)M^+-1, 6.08], 91 (100); IR (neat): 1940, 1757, 1643, 1488, 1407, 1299, 1070, 1004 cm^{-1}; HRMS: cacld. for $C_{20}H_{21}O_2Br$ [(^{79}Br)M^+] 372.0725; Found, 372.0740.

(13) Synthesis of 3-Allyl-4-(3'-methylbuta-1',2'-dienyl)-5-(4'-bromophenyl)-furan-2(5*H*)-one (1o)

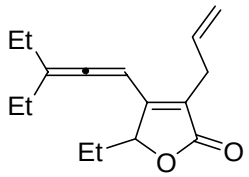


1o

A mixture of 2-allyl-4-(4'-bromophenyl)buta-2,3-dienoic acid (279 mg, 1.00

mmol), methyl 3-methylbuta-1-yn-3-yl carbonate (213 mg, 1.50 mmol), $Pd(OAc)_2$ (11 mg, 0.050 mmol), TFP (23 mg, 0.10 mmol), and K_2CO_3 (138 mg, 1.00 mmol) in 4 mL of DMSO was stirred at 25 ^oC for 14 h to afford **1o** (157 mg, 46%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 9.0 Hz, 2 H), 7.05 (d, *J* = 9.0 Hz, 2 H), 6.00-5.82 (m, 2 H), 5.68 (s, 1 H), 5.21-5.08 (m, 2 H), 3.18 (d, *J* = 6.0 Hz, 2 H), 1.66 (d, *J* = 3.0 Hz, 3 H), 1.12 (d, *J* = 3.0 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 19.0, 19.4, 27.8, 82.2, 83.6, 99.9, 116.7, 123.0, 124.2, 129.3, 131.8, 133.3, 135.1, 155.9, 173.4, 208.3; MS(EI): *m/z* (%) 346 [(^{81}Br)M^+, 1.32], 344 [(^{79}Br)M^+, 1.52], 345 [(^{81}Br)M^+-1, 3.84], 343 [(^{79}Br)M^+-1, 4.00], 84 (100); IR (neat): 1949, 1754, 1643, 1488, 1299, 1071, 1004 cm^{-1}; HRMS: cacld. for $C_{18}H_{17}O_2Br$ [(^{79}Br)M^+] 344.0412; Found, 344.0400.

(14) Synthesis of 3-Allyl-4-(3'-ethylpenta-1',2'-dienyl)-5-ethylfuran-2(5*H*)-one (1p)

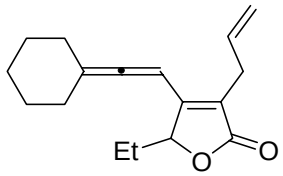


1p

A mixture of 2-allylhexa-2,3-dienoic acid (76 mg, 0.50 mmol), methyl 3-ethylpent-1-yn-3-yl carbonate (170 mg, 1.00 mmol), $Pd(OAc)_2$ (5 mg, 0.022 mmol), TFP (11 mg, 0.047 mmol), and K_2CO_3 (69 mg, 0.50 mmol) in 2 mL of DMSO was stirred at 35 ^oC for 10 h to afford **1p** (88 mg, 72%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.16 (pentet, *J* = 3.0 Hz, 1 H), 5.88-5.71 (m, 1 H), 5.08-4.96 (m, 2 H), 4.87-4.80 (m, 1 H), 3.04 (d, *J* = 6.0 Hz, 2 H), 2.18-1.90 (m, 5 H), 1.68-1.50 (m, 1 H), 1.00 (t, *J* = 7.5 Hz, 3 H), 0.96 (t, *J* = 7.8 Hz, 3 H), 0.82 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75.4 MHz,

$CDCl_3$): δ 7.6, 11.7, 12.1, 25.0, 25.3, 25.9, 27.5, 81.7, 87.2, 111.8, 116.0, 123.7, 133.5, 156.3, 173.7, 205.7; MS(ESI): *m/z* 247 (M^++1); IR (neat): 1940, 1751, 1643, 1458, 1328, 1048 cm^{-1}; HRMS: cacld. for $C_{16}H_{23}O_2$ [M^++1] 247.1693; Found, 247.1695.

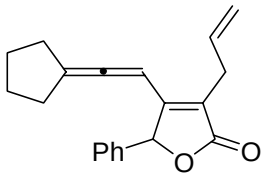
(15) Synthesis of 3-Allyl-4-(3',3'-pentamethylenepropa-1',2'-dienyl)-5-ethylfuran-2(5*H*)-one (1q)



1q

A mixture of 2-allylhexa-2,3-dienoic acid (76 mg, 0.50 mmol), methyl 1,1-pentamethyleneprop-2-ynyl carbonate (196 mg, 1.00 mmol), $Pd(OAc)_2$ (6 mg, 0.027 mmol), TFP (12 mg, 0.052 mmol), and K_2CO_3 (69 mg, 0.50 mmol) in 2 mL of DMSO was stirred at 35 ^oC for 12 h to afford **1q** (79 mg, 58%). ^1H NMR (300 MHz, $CDCl_3$): δ 5.98 (s, 1 H), 5.88-5.70 (m, 1 H), 5.12-4.94 (m, 2 H), 4.88-4.78 (m, 1 H), 3.04 (d, *J* = 6.3 Hz, 2 H), 2.23-2.07 (m, 4 H), 2.07-1.85 (m, 1 H), 1.77-1.40 (m, 7 H), 0.85 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 8.0, 25.5, 26.3, 26.4, 26.9, 27.5, 30.43, 30.45, 81.8, 83.5, 105.6, 116.0, 123.5, 133.5, 156.6, 173.7, 203.6; MS(EI): *m/z* (%) 259 [(M^++1), 15.57], 258 (M^+, 7.46), 91 (100); IR (neat): 1945, 1751, 1643 1446, 1330, 1047 cm^{-1}; HRMS: cacld. for $C_{17}H_{22}O_2$ [M^+] 258.1620; Found, 258.1629.

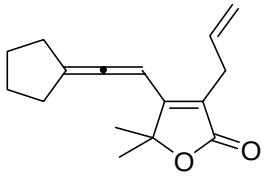
(16) Synthesis of 3-Allyl-4-(3',3'-tetramethylenepropa-1',2'-dienyl)-5-phenyl-furan-2(5*H*)-one (1r)



1r

A mixture of 2-allyl-4-phenylbuta-2,3-dienoic acid (100 mg, 0.50 mmol), methyl 1,1-tetramethyleneprop-2-ynyl carbonate (168 mg, 1.00 mmol), $Pd(OAc)_2$ (5 mg, 0.022 mmol), TFP (11 mg, 0.047 mmol), and K_2CO_3 (70 mg, 0.51 mmol) in 2 mL of DMSO was stirred at 35 ^oC for 8 h to afford **1r** (62 mg, 43%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.32-7.18 (m, 3 H), 7.15-7.02 (m, 2 H), 6.02-5.93 (m, 1 H), 5.93-5.78 (m, 1 H), 5.64 (s, 1 H), 5.17-4.98 (m, 2 H), 3.12 (d, *J* = 6.3 Hz, 2 H), 2.40-2.18 (m, 2 H), 1.96-1.80 (m, 1 H), 1.60-1.22 (m, 4 H), 1.22-1.07 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 26.8, 27.0, 27.7, 30.7, 31.2, 83.1, 85.8, 107.8, 116.4, 123.6, 127.7, 128.6, 129.0, 133.5, 136.0, 156.4, 173.6, 203.7; MS(EI): *m/z* (%) 292 (M^+, 13.25), 77 (100); IR (neat): 1945, 1754, 1643, 1497, 1456, 1300, 1082, 1004 cm^{-1}; HRMS: cacld. for $C_{20}H_{20}O_2$ [M^+] 292.1463; Found, 292.1459.

(17) Synthesis of 3-Allyl-4-(3',3'-tetramethylenepropa-1',2'-dienyl)-5,5-dimethylfuran-2(5*H*)-one (1s)

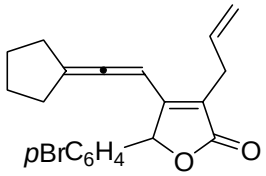


1s

A mixture of 2-allyl-4-methylpenta-2,3-dienoic acid (116 mg, 0.75 mmol), methyl 1,1-tetramethyleneprop-2-ynyl carbonate (253 mg, 1.50 mmol), $Pd(OAc)_2$ (5 mg, 0.022 mmol), TFP (10 mg, 0.043 mmol), and K_2CO_3 (104 mg, 0.75 mmol) in 3 mL of

DMSO was stirred at 30 ^{o}C for 11 h to afford **1s** (135 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.00 (pentet, *J* = 4.2 Hz, 1 H), 5.83-5.68 (m, 1 H), 5.03-4.90 (m, 2 H), 2.97 (d, *J* = 6.3 Hz, 2 H), 2.55-2.28 (m, 4 H), 1.78-1.60 (m, 4 H), 1.38 (s, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 25.6, 27.0, 27.2, 31.4, 84.7, 84.9, 106.6, 115.8, 122.2, 133.4, 161.2, 172.2, 203.1; MS(EI): *m/z* (%) 244 (M^+, 3.21), 229 (M^+-CH_3, 40.69), 43 (100); IR (neat): 1944, 1751, 1640, 1433, 1362, 1291, 1196, 1067 cm^{-1}; HRMS: cacld. for $C_{16}H_{20}O_2$ [M^+] 244.1463; Found, 244.1461.

(18) Synthesis of 3-Allyl-4-(3',3'-tetramethylenepropa-1',2'-dienyl)-5-(4'-bromophenyl)furan-2(5*H*)-one (1t)



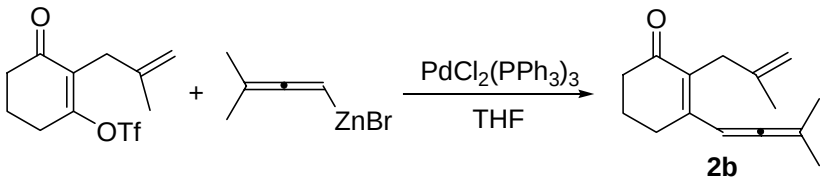
1t

A mixture of 2-allyl-4-(4'-bromophenyl)buta-2,3-dienoic acid (70 mg, 0.25 mmol), methyl 1,1-tetramethyleneprop-2-ynyl carbonate (84 mg, 0.50 mmol), $Pd(OAc)_2$ (2 mg, 0.009 mmol), TFP (6 mg, 0.026 mmol), and K_2CO_3 (35 mg, 0.25 mmol) in 1 mL of DMSO was stirred at 35 ^{o}C for 9 h to afford **1t** (41 mg, 44%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.7 Hz, 2 H), 7.05 (d, *J* = 8.7 Hz, 2 H), 6.03 (pentet, *J* = 3.9 Hz, 1 H), 5.98-5.80 (m, 1 H), 5.67 (s, 1 H), 5.20-5.05 (m, 2 H), 3.17 (d, *J* = 6.6 Hz, 2 H), 2.50-2.22 (m, 2 H), 2.10-1.93 (m, 1 H), 1.68-1.50 (m, 3 H), 1.50-1.28 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 26.8, 27.1, 27.7, 30.9, 31.3, 82.2, 85.7, 107.9, 116.6, 123.0, 123.9, 129.4, 131.7, 133.3, 135.2, 156.1, 173.3, 203.7; MS(EI): *m/z* (%) 372 [(^{81}Br)M^+, 4.88], 370 [(^{79}Br)M^+, 6.54], 371 [(^{81}Br)M^+-1, 19.55], 369 [(^{79}Br)M^+-1,

18.37], 91 (100); IR (neat): 1943, 1754, 1643, 1448, 1299, 1070, 1007 cm^{-1}; HRMS: cacld. for $C_{20}H_{20}O_2Br$ [(^{79}Br)M^++1] 371.0641; Found, 371.0649.

2. The synthesis of 2-allylic 3-allenylic cyclohex-2-enone derivatives 2b-d

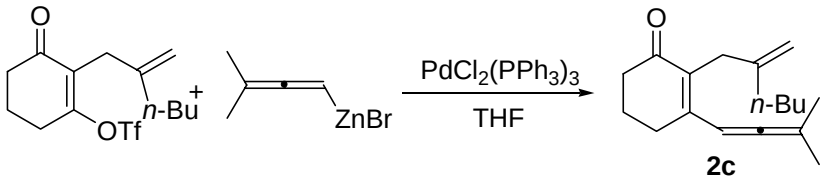
(1) Synthesis of 2-(2'-methylallyl)-3-(3'-methylbuta-1',2'-dienyl)cyclohex-2-enone (2b)



2b

In a flame dried Schlenk tube, a mixture of $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), 2-(2'-methylallyl)-3-(trifluoromethanesulfonyloxy)cyclohex-2-enone[1] (149 mg, 0.50 mmol), the allenyl zinc reagent (0.625 mol/L in THF) (1.2 mL, 0.75 mmol), and 3 mL of THF was stirred at rt for 2.5 h. After complete consumption of the starting material as monitored by TLC, THF was removed by evaporation and the residue was purified via flash chromatography on silica gel to afford 87 mg (81%) of **2b**. ^1H NMR (300 MHz, $CDCl_3$): δ 6.08 (heptet, *J* = 2.7 Hz, 1 H), 4.70 (s, 1 H), 4.51 (s, 1 H), 3.10 (s, 2 H), 2.48-2.37 (m, 4 H), 2.02-1.88 (m, 2 H), 1.78 (d, *J* = 2.7 Hz, 6 H), 1.72 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 19.9, 22.2, 22.9, 27.6, 32.0, 38.0, 92.3, 98.7, 109.9, 132.1, 143.8, 152.4, 198.5, 207.4; MS(EI): *m/z* (%) 216 (M^+, 24.56), 145 (100); IR (neat): 1944, 1661, 1592, 1430, 1365, 1217, 1182, 1136, 1039 cm^{-1}; HRMS: cacld. for $C_{15}H_{20}O$ [M^+] 216.1514; Found, 216.1511.

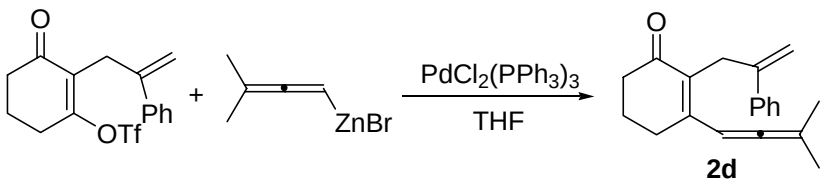
(2) Synthesis of 2-(2'-butylallyl)-3-(3'-methylbuta-1',2'-dienyl)cyclohex-2-enone (2c)



2c

In a flame dried Schlenk tube, a mixture of $Pd(PPh_3)_2Cl_2$ (4 mg, 0.005 mmol), 2-(2'-butylallyl)-3-(trifluoromethanesulfonyloxy)cyclohex-2-enone[1] (84 mg, 0.25 mmol), the allenyl zinc reagent (0.625 mol/L in THF) (2.4 mL, 1.50 mmol), and 1.5 mL of THF was stirred at rt for 1.5 h. After complete consumption of the starting material as monitored by TLC, THF was removed by evaporation and the residue was purified via flash chromatography on silica gel to afford 52 mg (81%) of **2c** together with another unidentified byproduct. **2c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.03 (heptet, *J* = 2.7 Hz, 1 H), 4.67 (s, 1 H), 4.47 (s, 1 H), 3.07 (s, 2 H), 2.45-2.35 (m, 4 H), 2.05-1.88 (m, 4 H), 1.75 (d, *J* = 2.7 Hz, 6 H), 1.52-1.38 (m, 2 H), 1.38-1.20 (m, 2 H), 0.88 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 13.9, 19.8, 22.1, 22.4, 27.5, 29.9, 30.5, 36.4, 38.0, 92.3, 98.6, 108.6, 132.2, 147.7, 152.2, 198.4, 207.3; MS(ESI): *m/z* 259 (M^++1); IR (neat): 1946, 1662, 1594, 1363, 1182 cm^{-1}; HRMS: calcd. for $C_{18}H_{27}O$ [M^++1]: 259.2056; Found: 259.2058.

(3) Synthesis of 2-(2'-phenylallyl)-3-(3'-methylbuta-1',2'-dienyl)cyclohex-2-enone (2c)



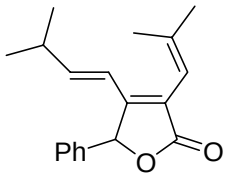
2d

In a flame dried Schlenk tube, a mixture of $Pd(PPh_3)_2Cl_2$ (28 mg, 0.040 mmol), 2-(2'-phenylallyl)-3-(trifluoromethanesulfonyloxy)cyclohex-2-enone[1] (431 mg, 1.20

mmol), the allenyl zinc reagent (0.625 mol/L in THF) (4.8 mL, 3.00 mmol), and 5.0 mL of THF was stirred at rt for 2.5 h. After complete consumption of the starting material as monitored by TLC, THF was removed by evaporation and the residue was purified via preparative TLC to afford 186 mg (56%) of **2d**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52-7.45 (m, 2 H), 7.38-7.20 (m, 3 H), 6.07 (heptet, *J* = 3.0 Hz, 1 H), 5.27 (s, 1 H), 4.79 (s, 1 H), 3.57 (s, 2 H), 2.52-2.40 (m, 4 H), 2.02-1.90 (m, 2 H), 1.77 (d, *J* = 2.7 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 19.9, 22.2, 27.7, 29.6, 38.0, 92.4, 98.7, 111.9, 126.1, 127.3, 128.1, 132.0, 141.8, 146.0, 152.9, 198.4, 207.5; MS(ESI): *m/z* 279 (M^++1); IR (neat): 1946, 1660, 1594, 1363, 1183 cm^{-1}; HRMS: calcd. for $C_{20}H_{23}O$ [M^++1]: 279.1743; Found: 279.1746.

3. Sequential 1,5-H Shift and 1,7-H Shift Reactions of 3-Alkyl-4-allenylfuran-2(5*H*)-ones.

(1) Synthesis of 3-(2'-methylprop-1'-enyl)-4-(3'-methylbut-1'(*E*)-enyl)-5-phenylfuran-2(5*H*)-one (*E*-3b)

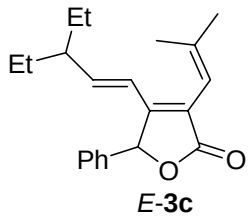


E-**3b**

Under an argon atmosphere, a mixture of **1b** (50 mg, 0.18 mmol) in 4 mL of xylene was stirred under reflux for 3.5 h. After complete consumption of the starting material as monitored by TLC, the mixture was directly purified via flash chromatography on silica gel to afford *E*-**3b** (36 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.31 (m, 3 H), 7.30-7.20 (m, 2 H), 6.09 (d, *J* = 16.5 Hz, 1 H), 5.92 (s, 1 H), 5.85 (s, 1 H), 5.78

(dd, *J* = 6.6, 16.5 Hz, 1 H), 2.37-2.20 (m, 1 H), 1.94 (s, 3 H), 1.71 (s, 3 H), 0.89 (d, *J* = 6.6 Hz, 3 H), 0.84 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 20.8, 21.39, 21.45, 26.2, 31.8, 82.6, 113.2, 118.5, 124.3, 127.7, 128.8, 129.2, 136.2, 142.6, 148.8, 155.1, 173.2; MS(EI): *m/z* (%) 282 (M^+, 43.25), 239 (M^+-C_3H_7, 93.22), 91 (100); IR (neat): 1753, 1642, 1456, 1301, 1101, 1008 cm^{-1}; HRMS: calcd. for $C_{19}H_{22}O_2$ [M^+]: 282.1620; Found: 282.1608.

(2) Synthesis of 3-(2'-methylprop-1'-enyl)-4-(3'-ethylpent-1'(*E*)-enyl)-5-phenylfuran-2(5*H*)-one (*E*-3c)

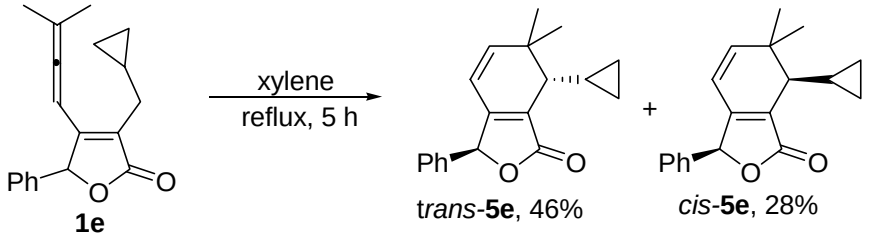


E-**3c**

Under an argon atmosphere, a mixture of **1c** (61 mg, 0.20 mmol) in 4 mL of xylene was stirred under reflux for 6 h. The mixture was directly purified via flash chromatography on silica gel to afford *E*-**3c** (40 mg, 66%) as well as **1c** (6 mg, 10%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.32 (m, 3 H), 7.32-7.22 (m, 2 H), 6.11 (d, *J* = 16.2 Hz, 1 H), 5.96 (s, 1 H), 5.87 (s, 1 H), 5.53 (dd, *J* = 9.0, 16.2 Hz, 1 H), 1.96 (s, 3 H), 1.88-1.70 (m, 1 H), 1.74 (s, 3 H), 1.43-1.10 (m, 3 H), 1.07-0.82 (m, 1 H), 0.76 (t, *J* = 7.5 Hz, 3 H), 0.46 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 11.2, 11.7, 20.8, 26.2, 27.1, 27.3, 47.5, 82.6, 113.3, 121.4, 124.1, 127.7, 128.8, 129.2, 136.4, 142.6, 146.9, 155.1, 173.2; MS(EI): *m/z* (%) 310 (M^+, 25.40), 91 (100); IR (neat): 1755, 1642, 1456, 1101, 1008 cm^{-1}; HRMS: calcd. for $C_{21}H_{26}O_2$ [M^+]: 310.1933; Found: 310.1931.

4. Sequential 1,5-H Shift and 6π-Electrocyclization Reaction of 3-Benzyl (or Cyclopropylmethylene)-4-allenylfuran-2(5*H*)-ones.

Synthesis of 7-cyclopropyl-6,6-dimethyl-3-phenyl-6,7-dihydro-isobenzofuran-1(3*H*)-one (5e):



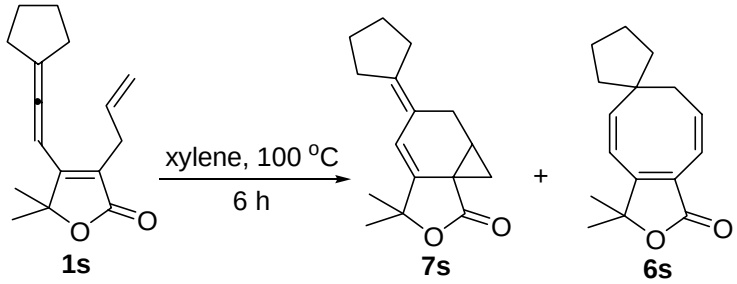
1e *trans*-**5e**, 46% *cis*-**5e**, 28%

Under an argon atmosphere, a mixture of **1e** (50 mg, 0.18 mmol) in 4 mL of xylene in a Schlenk tube with a screw cap was stirred at 160 ^{o}C for 6 h. The mixture was directly purified via flash chromatography on silica gel to afford *trans*-**5e** (less polar, 23 mg, 46%) and *cis*-**5e** (more polar, 14 mg, 28%). *trans*-**5e**: Solid, m.p. 132-133 ^{o}C (ethyl acetate/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.32 (m, 3 H), 7.25-7.17 (m, 2 H), 5.96 (d, *J* = 9.6 Hz, 1 H), 5.91 (s, 1 H), 5.89 (d, *J* = 9.6 Hz, 1 H), 1.68 (d, *J* = 9.6 Hz, 1 H), 1.32 (s, 3 H), 0.98 (s, 3 H), 0.84-0.70 (m, 1 H), 0.70-0.51 (m, 2 H), 0.41-0.30 (m, 1 H), 0.26-0.15 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 1.9, 6.6, 10.8, 25.1, 27.1, 38.1, 45.7, 82.2, 116.2, 126.0, 126.9, 128.9, 129.2, 134.7, 148.9, 155.6, 173.5; MS(EI): *m/z* (%) 280 (M^+, 23.52), 105 (100); IR (KBr): 1745, 1654, 1574, 1303, 1234, 1023 cm^{-1}; Anal. calcd. for $C_{19}H_{20}O_2$: (%) C 81.40, H 7.19; Found, C 81.05, H 7.43. *cis*-**5e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.32 (m, 3 H), 7.30-7.20 (m, 2 H), 5.97 (d, *J* = 9.6 Hz, 1 H), 5.82 (d, *J* = 9.6 Hz, 1 H), 5.80 (s, 1 H), 1.70 (d, *J* = 9.6 Hz, 1 H), 1.32 (s, 3 H), 1.04 (s, 3 H), 0.84-0.70 (m, 1 H), 0.70-0.52 (m, 2 H), 0.46-0.37 (m, 1 H), 0.30-0.19 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 1.6, 6.5, 10.9,

25.1, 27.2, 38.1, 45.1, 82.0, 116.0, 125.9, 127.0, 129.0, 129.3, 134.8, 148.8, 155.4, 173.6; MS(EI): *m/z* (%) 280 (M^+, 10.76), 84 (100); IR (neat): 1752, 1655, 1579, 1300, 1234, 1024, 1001 cm^{-1}; HRMS: calcd. for $C_{19}H_{20}O_2$ [M^+]: 280.1463; Found: 280.1467.

5. Cycloisomeriztion of 3-Allyl-4-allenylfuran-2(5*H*)-ones

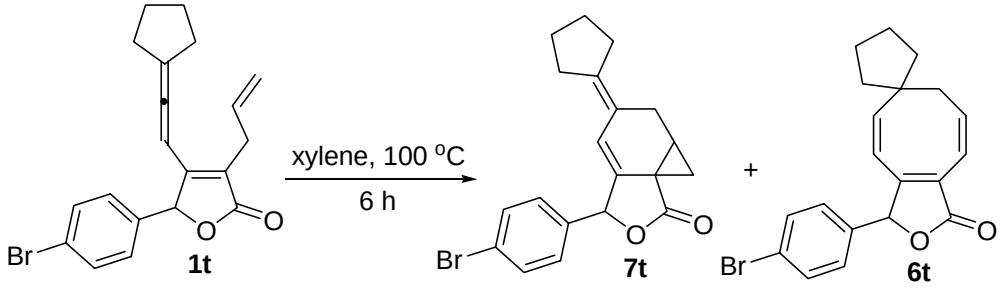
(1) Synthesis of (3a*Z*,4*Z*,8*Z*)-6,6-tetramethylene-3,3-dimethyl-6,7-dihydrocycloocta[*c*]furan-1(3*H*)-one (6s) and 7s:



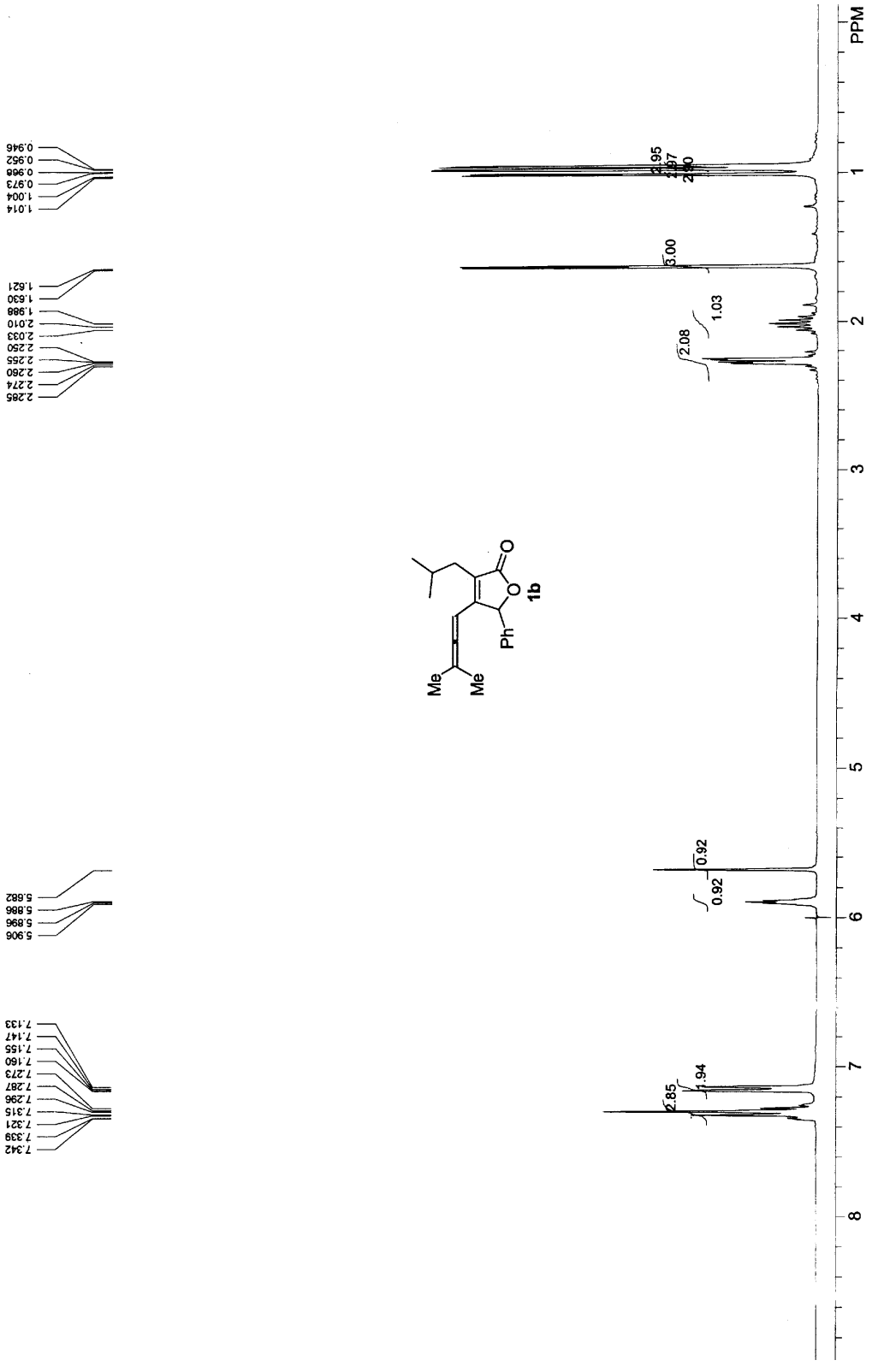
A solution of **1s** (124 mg, 0.51 mmol) in 5 mL of xylene was stirred at 100 °C for 6 h. After complete consumption of the starting material as monitored by TLC, the mixture was directly purified via flash chromatography on silica gel to afford **7s** (17 mg, 14%) and **6s** (92 mg, 74%). **7s**: Solid, 119-121 °C (ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.77 (s, 1 H), 2.62 (d, *J* = 15.3 Hz, 1 H), 2.32-2.02 (m, 6 H), 1.68-1.50 (m, 5 H), 1.50 (s, 3 H), 1.48 (s, 3 H), 0.99 (dd, *J* = 3.6, 6.9 Hz, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 24.1, 24.5, 25.0, 26.2, 26.3, 26.4, 27.1, 29.0, 30.7, 30.9, 86.0, 112.8, 119.5, 142.4, 143.8, 177.3; MS(EI): *m/z* (%) 244 (M^+, 21.67), 229 (M^+-CH_3, 81.83), 43 (100); IR (neat): 1771, 1281, 1121, 1046 cm^{-1}; HRMS: calcd. for $C_{16}H_{20}O_2$ [M^+]: 244.1463; Found: 244.1467. **6s**: Solid, m.p. 72-74 °C (ethyl ether/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.32-6.20 (m, 2 H), 6.08 (d, *J* = 13.2 Hz, 1 H), 5.71 (d, *J* = 13.2 Hz, 1 H), 2.20-2.08 (m, 2 H), 1.80-1.62 (m, 4 H),

1.60-1.45 (m, 4 H), 1.46 (s, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 24.1, 25.6, 34.5, 42.6, 51.3, 85.8, 114.0, 121.3, 122.3, 137.6, 152.8, 161.0, 171.6; MS(EI): *m/z* (%) 244 (M^+, 12.24), 229 (M^+-CH_3, 31.20), 43 (100); IR (neat): 1747, 1619, 1453, 1366, 1282, 1197, 1083, 1053 cm^{-1}; Anal. calcd. for $C_{16}H_{20}O_2$: (%) C 78.65, H 8.25; Found, C 78.47, H 8.27.

(2) Synthesis of (3a*Z*,4*Z*,8*Z*)-6,6-tetramethylene-3-(4'-bromophenyl)-6,7-dihydrocycloocta[*c*]furan-1(3*H*)-one (6t) and 7t



A solution of **1t** (79 mg, 0.213 mmol) in 4 mL of xylene was stirred at 100 °C for 6 h. After complete consumption of the starting material as monitored by TLC, the mixture was directly purified via flash chromatography on silica gel to afford **7t** (9 mg, 11%) and **6t**[2] (52 mg, 66%). **7t**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60-7.45 (m, 2 H), 7.30-7.20 (m, 2 H), [6.10 (s), 5.57 (s), 6.06 (s), 5.97 (s), 2 H], 2.80-2.65 (m, 1 H), 2.50-2.37 (m, 1 H), 2.35-2.05 (m, 5 H), 1.79-1.70 (m, 1 H), 1.70-1.45 (m, 4 H), 1.23-1.07 (m, 1 H); MS(EI): *m/z* (%) 372 [(^{81}Br)M^+, 7.29], 370 [(^{79}Br)M^+, 7.02], 91 (100); IR (neat): 1776, 1488, 1290, 1099, 1011 cm^{-1}; HRMS: calcd. for $C_{20}H_{19}O_2Br$ [(^{79}Br)M^+]: 370.0568; Found: 370.0552.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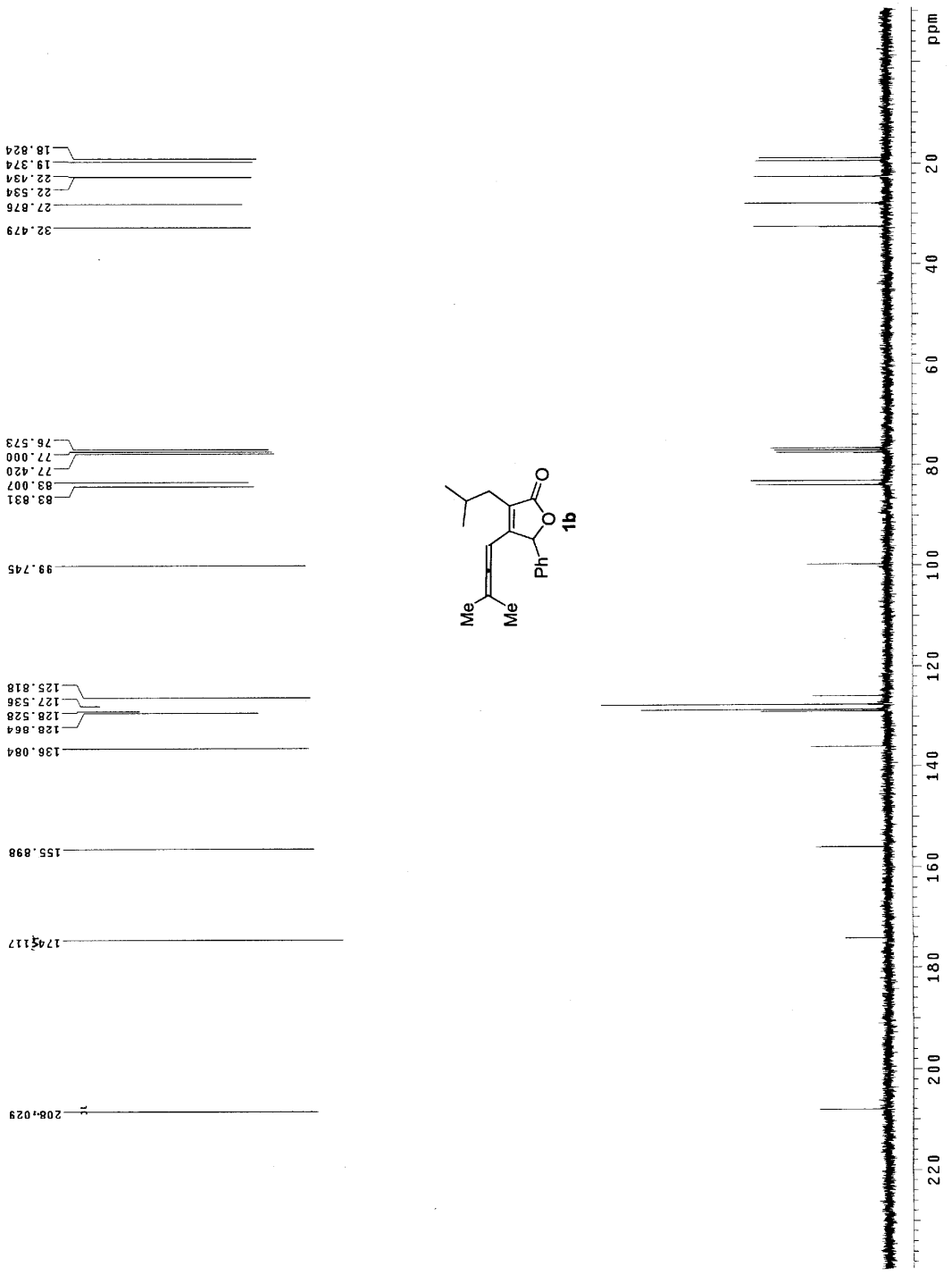
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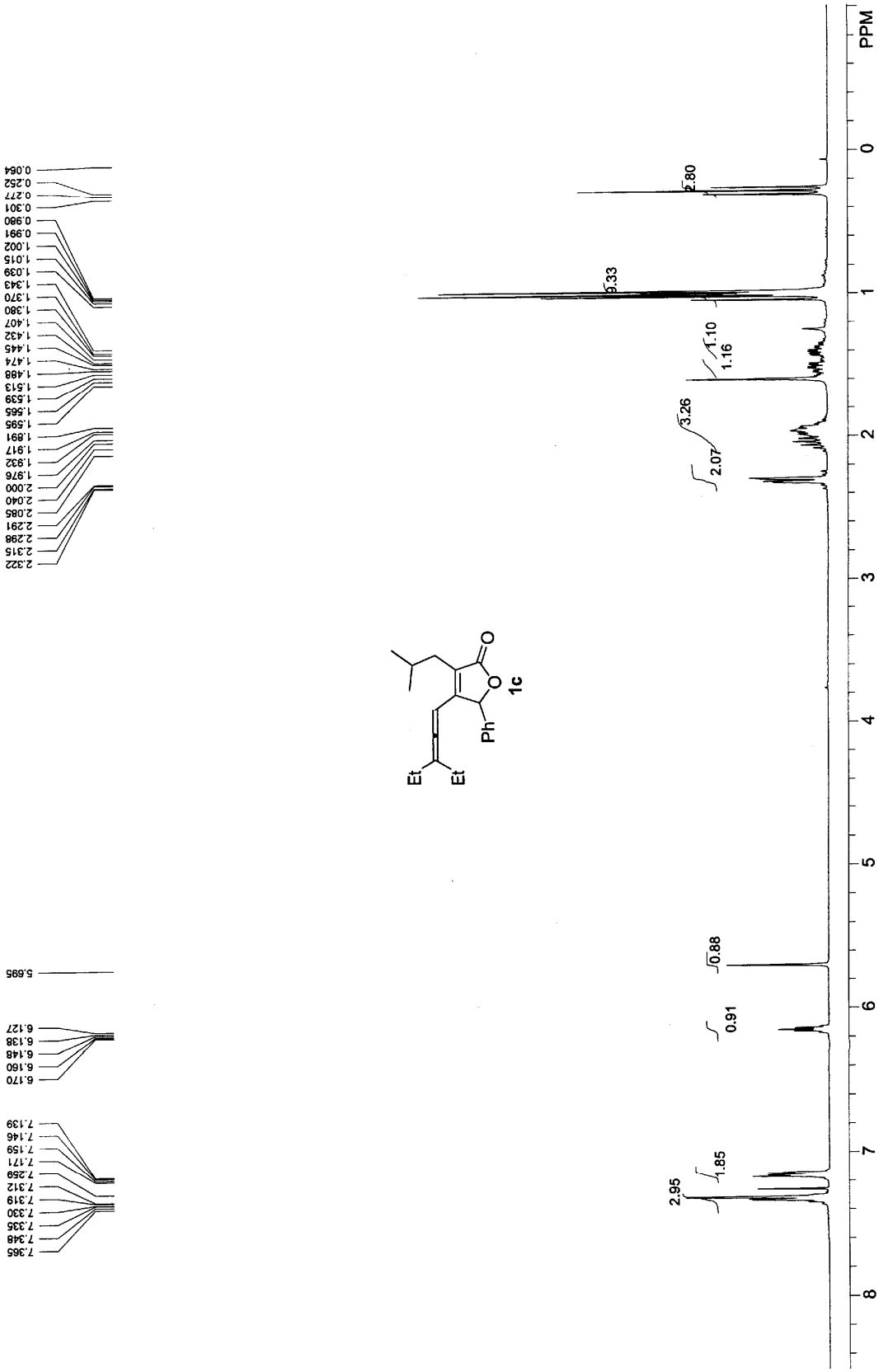
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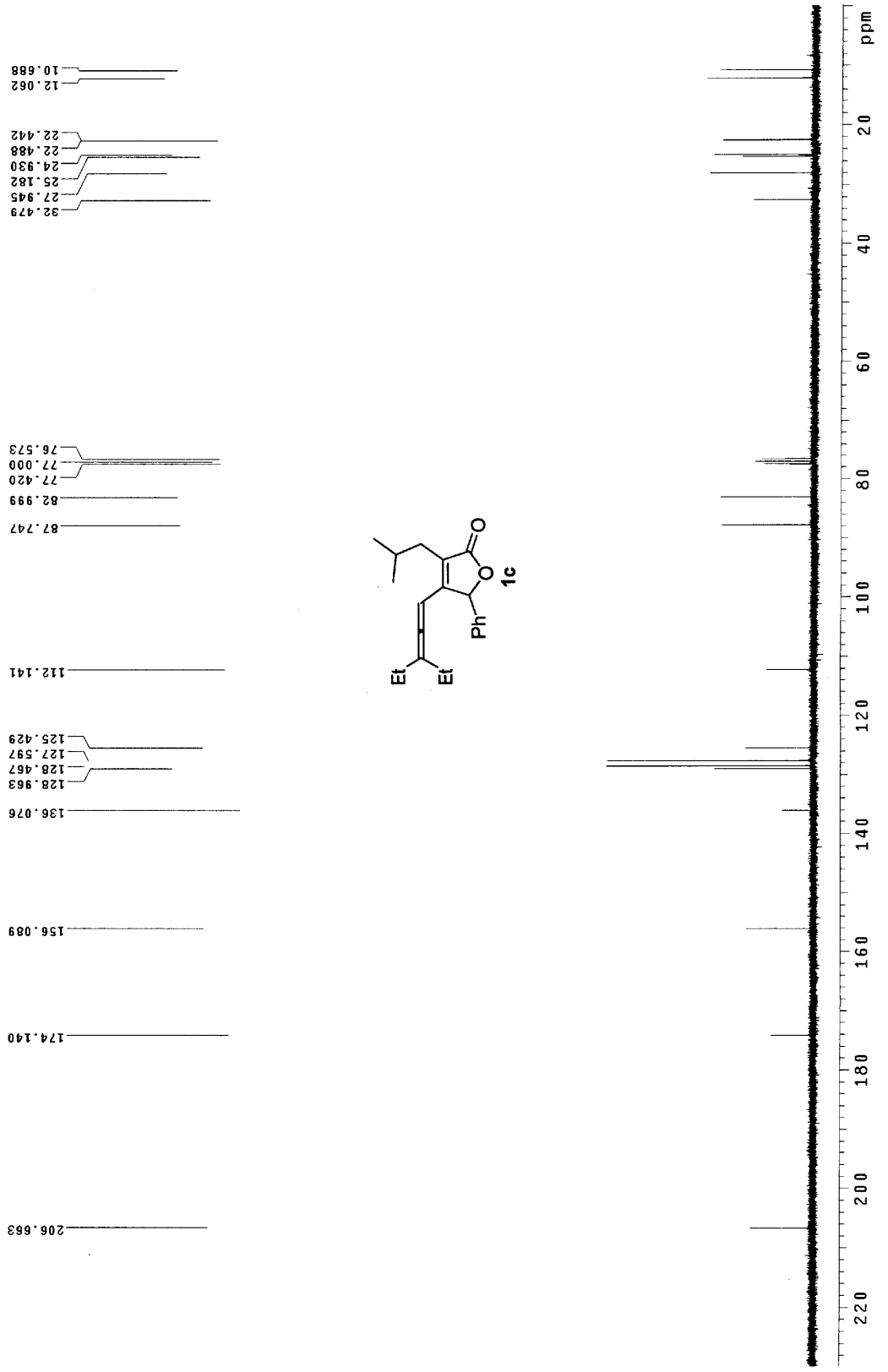
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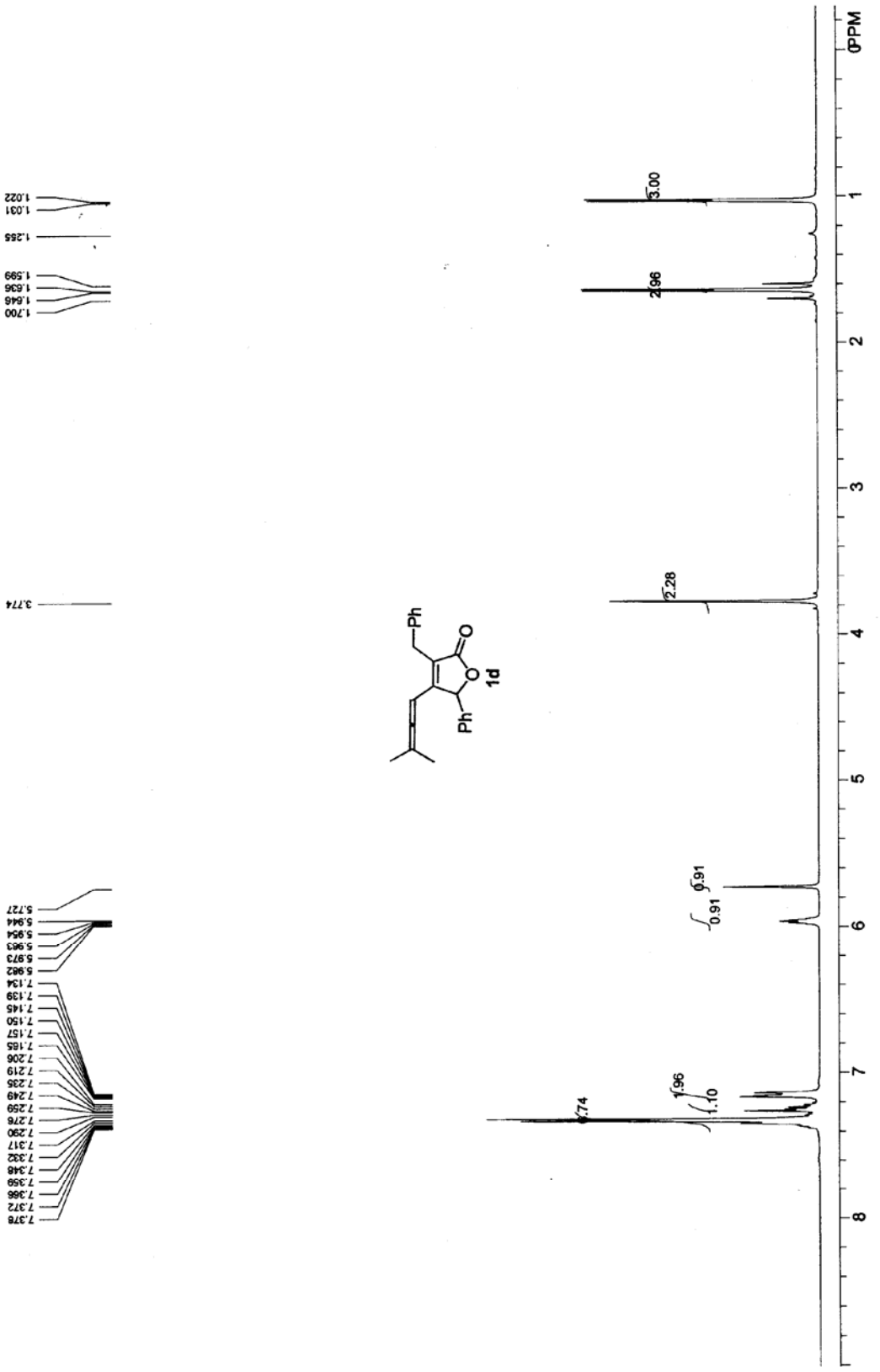
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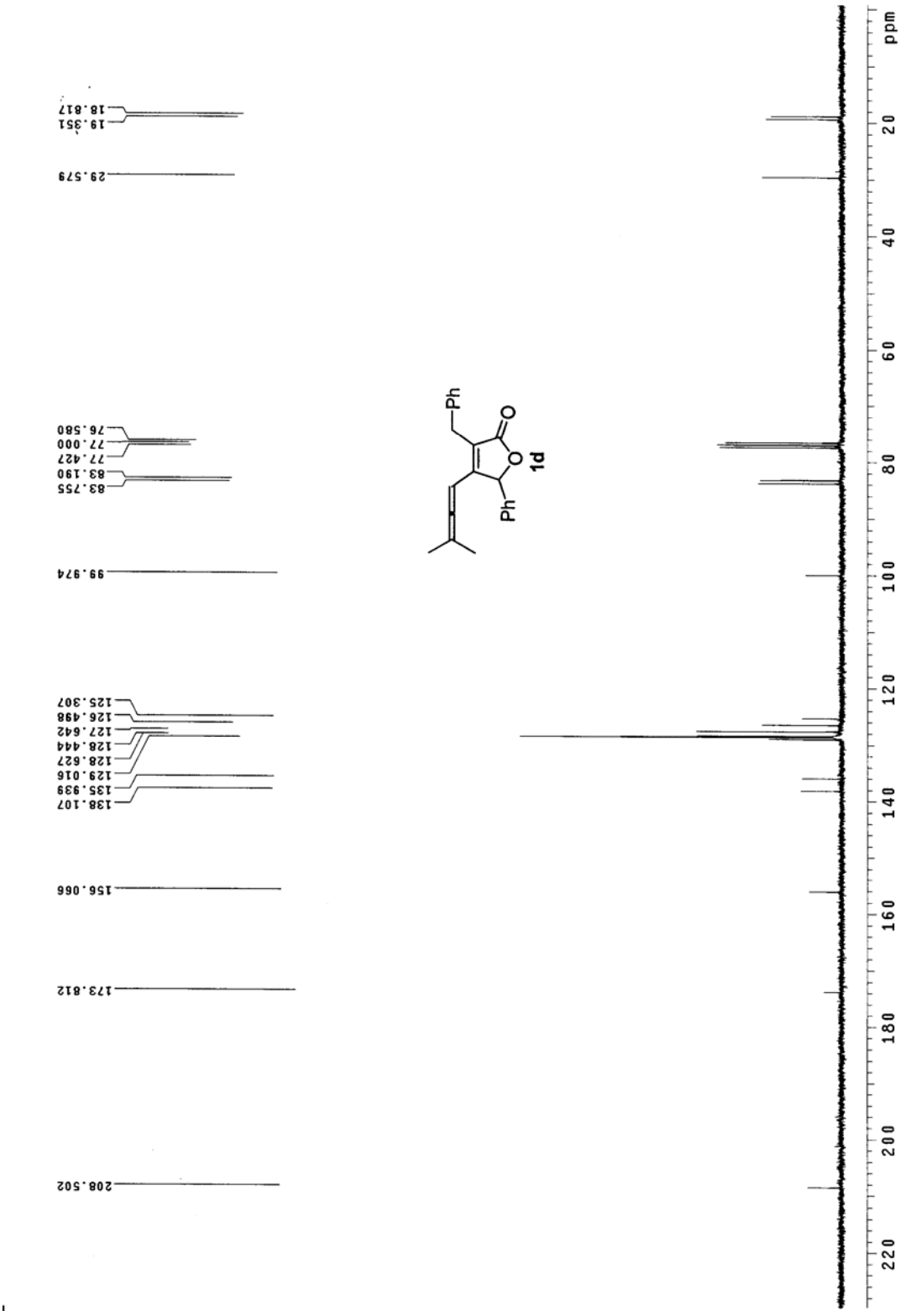
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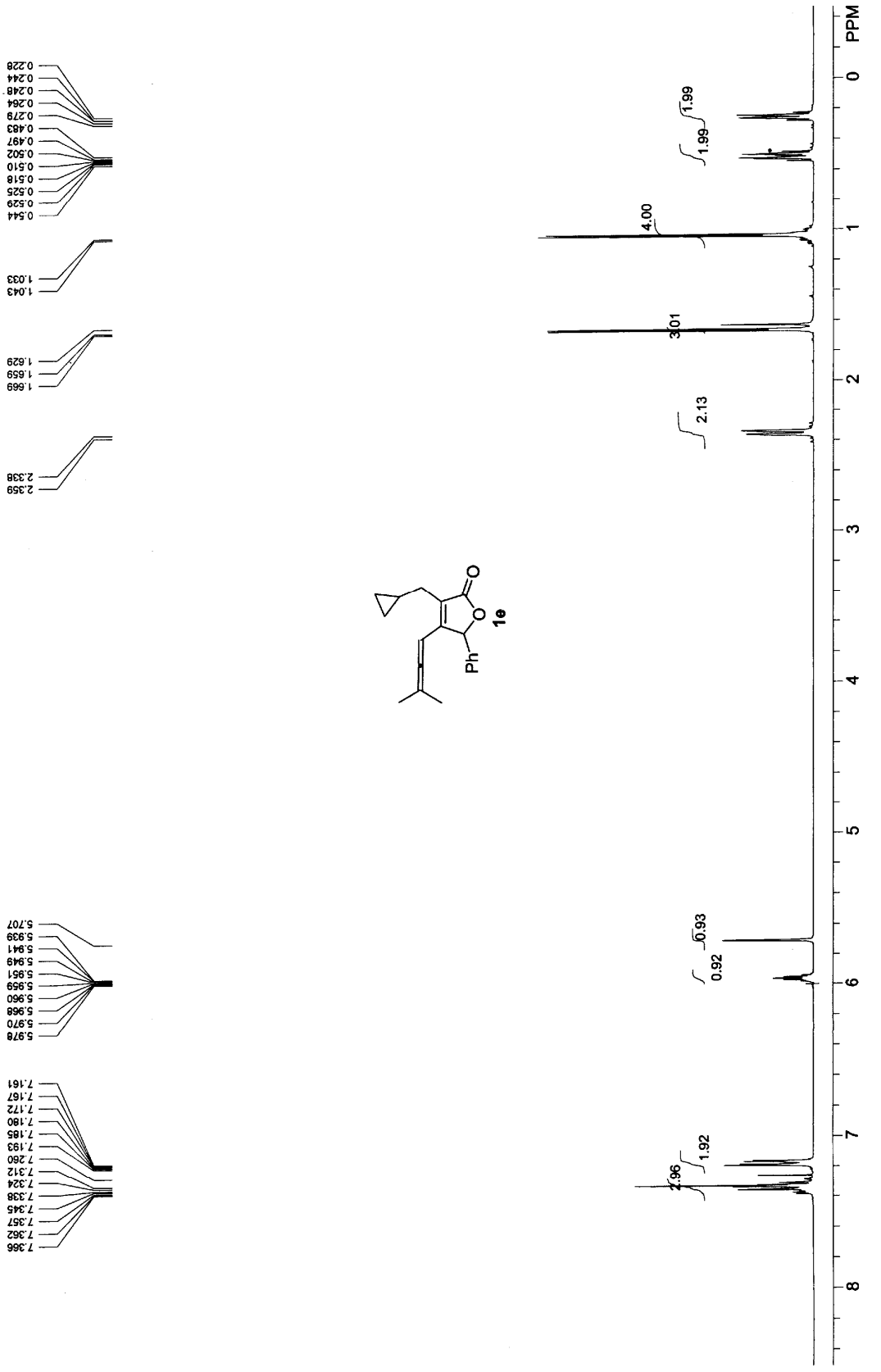
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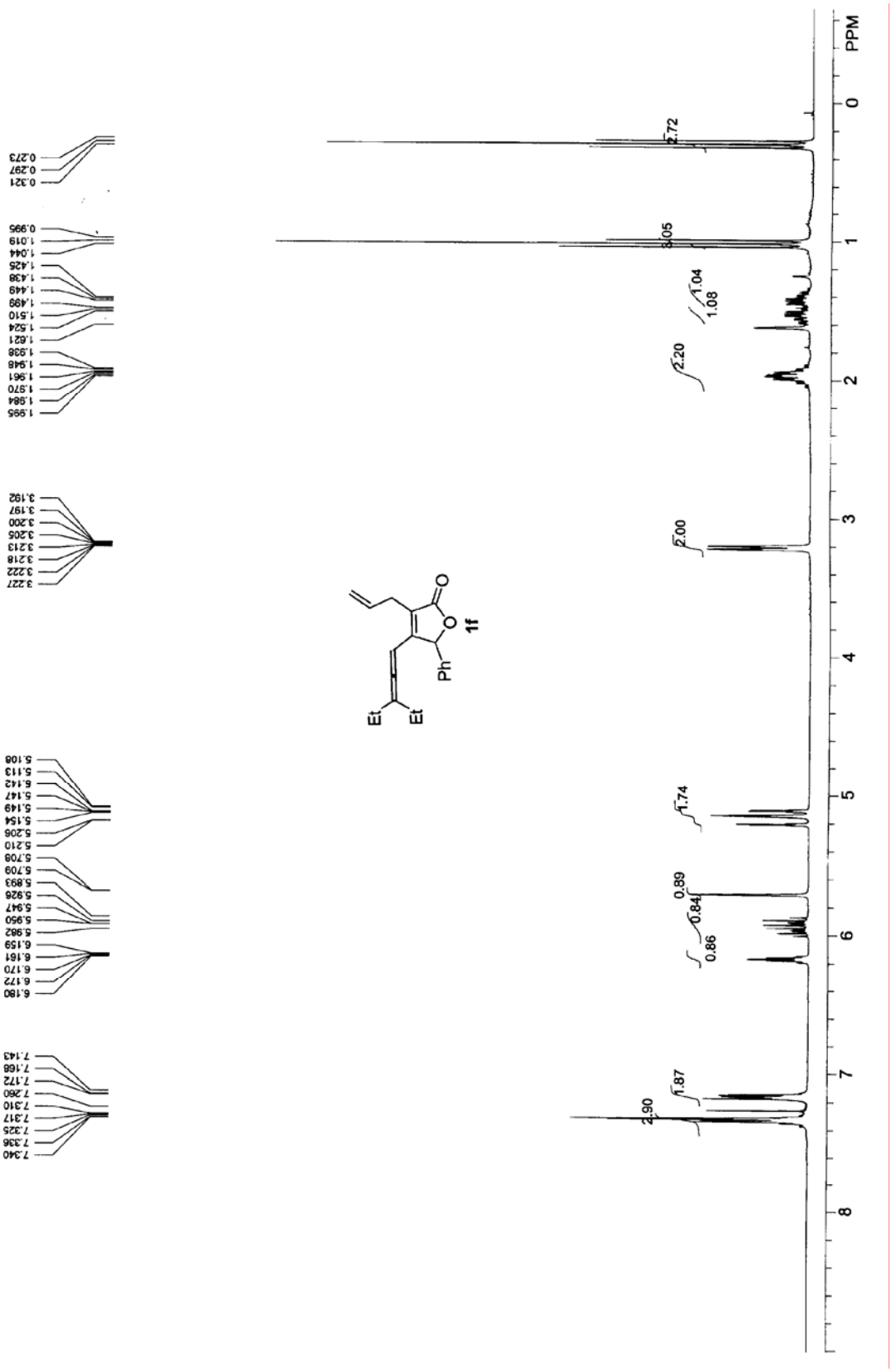
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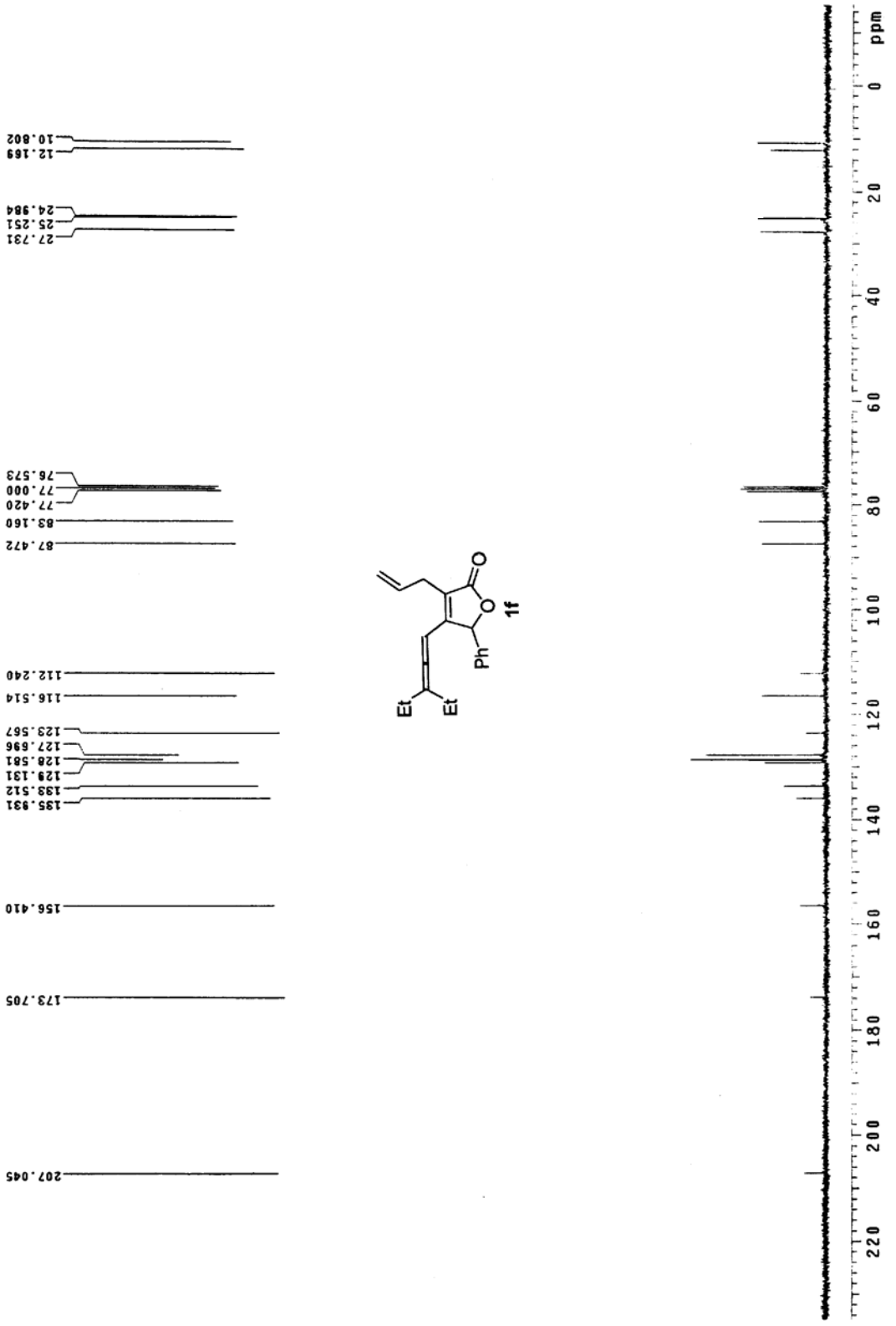
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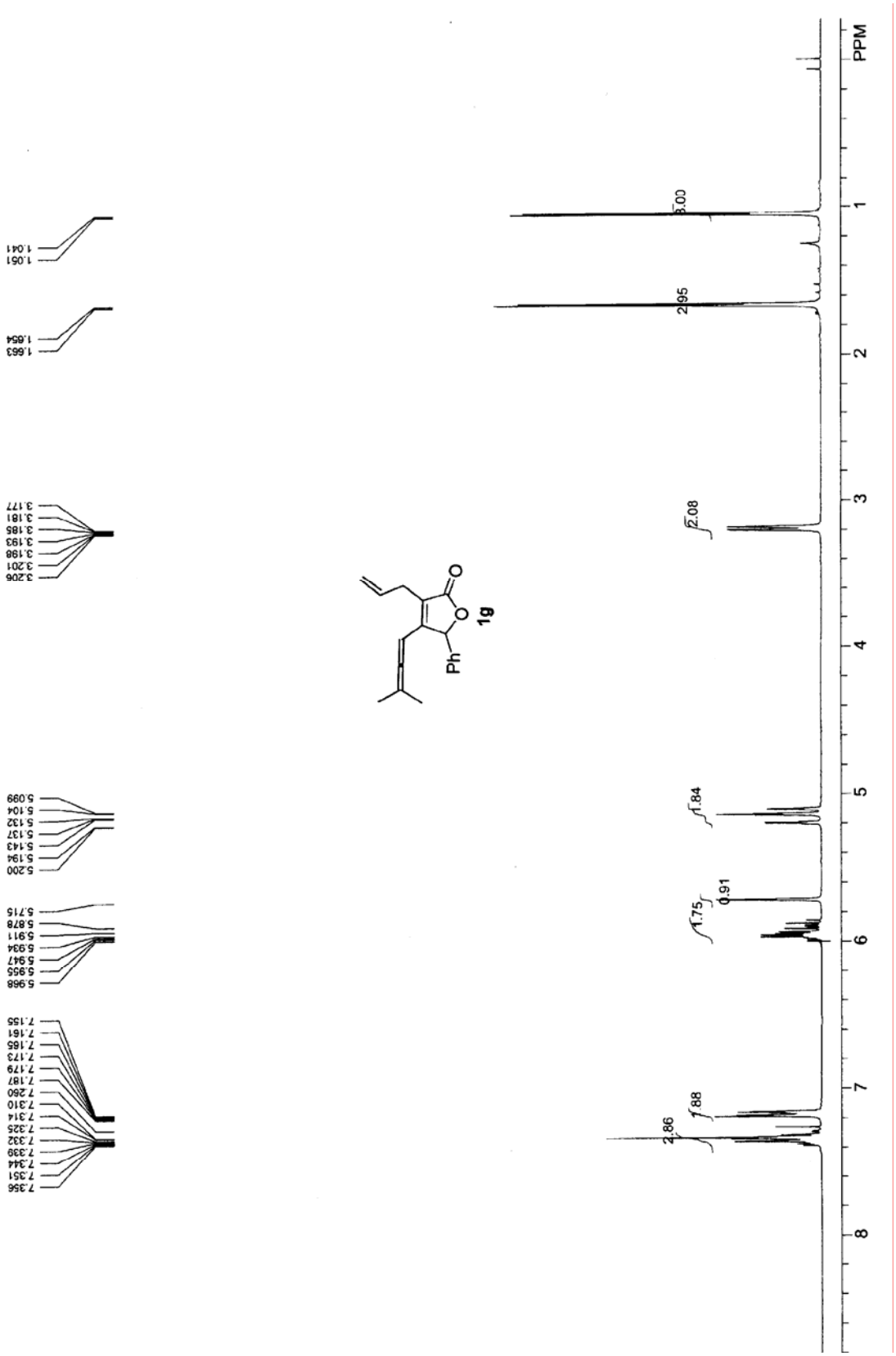
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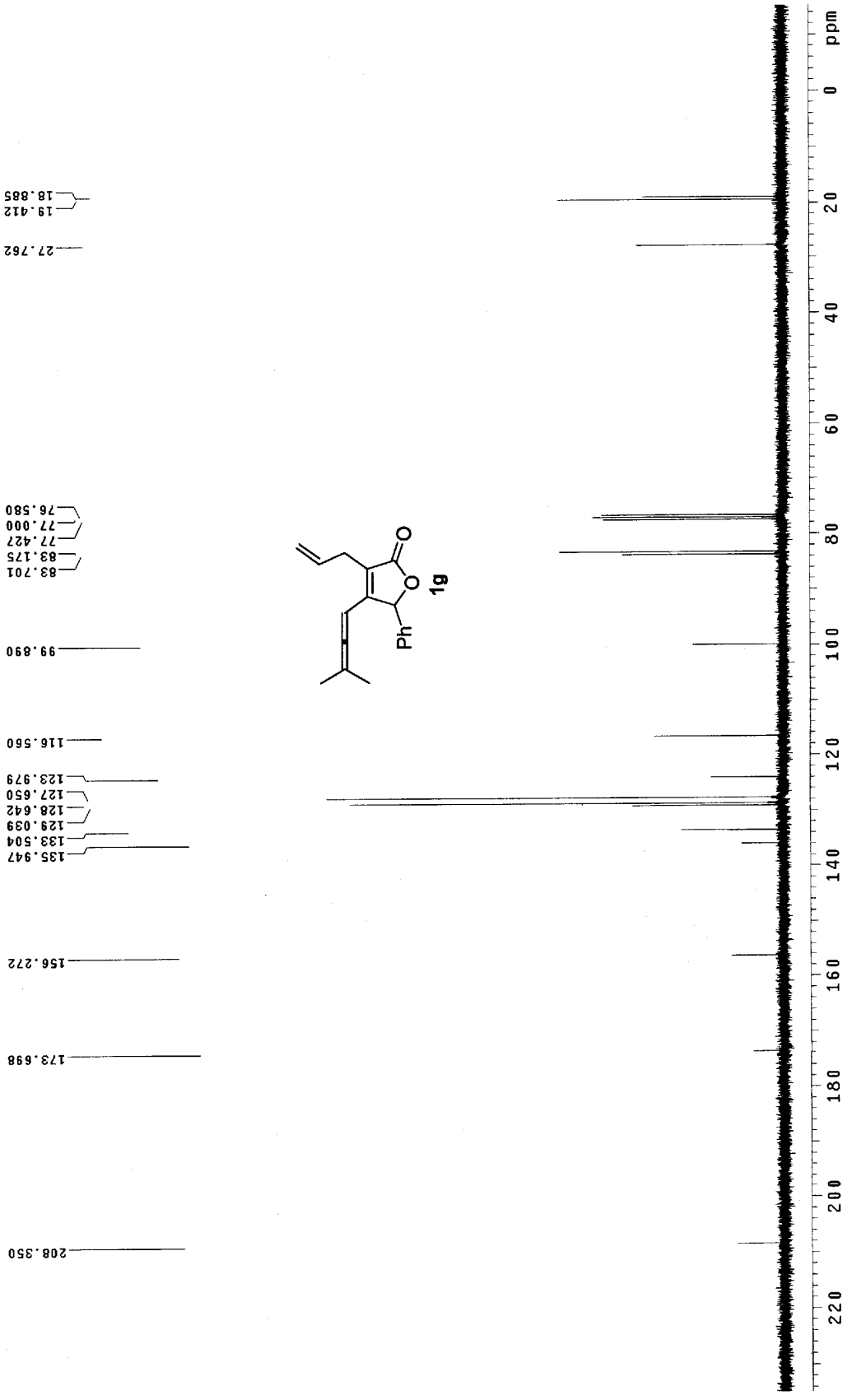
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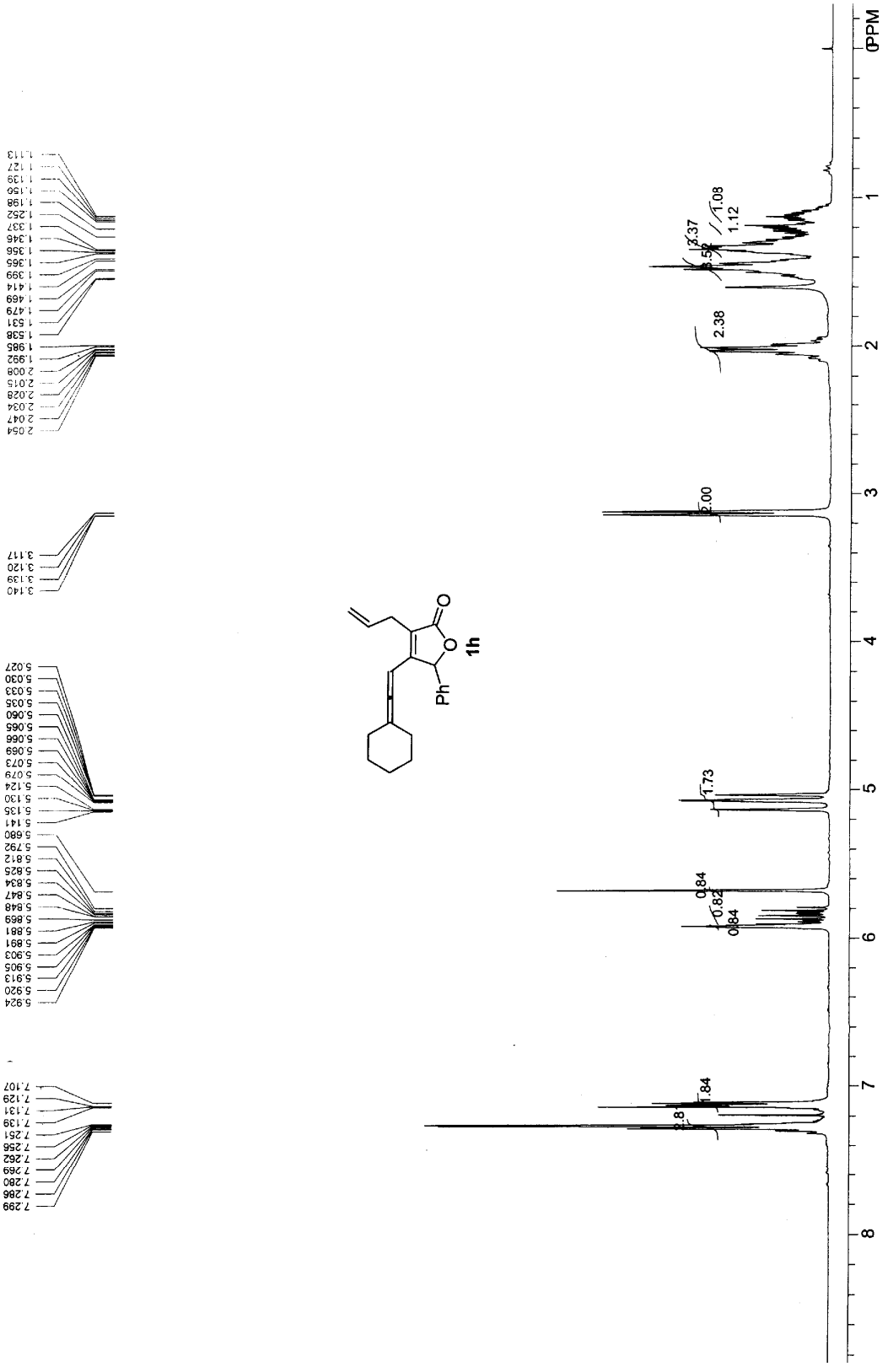
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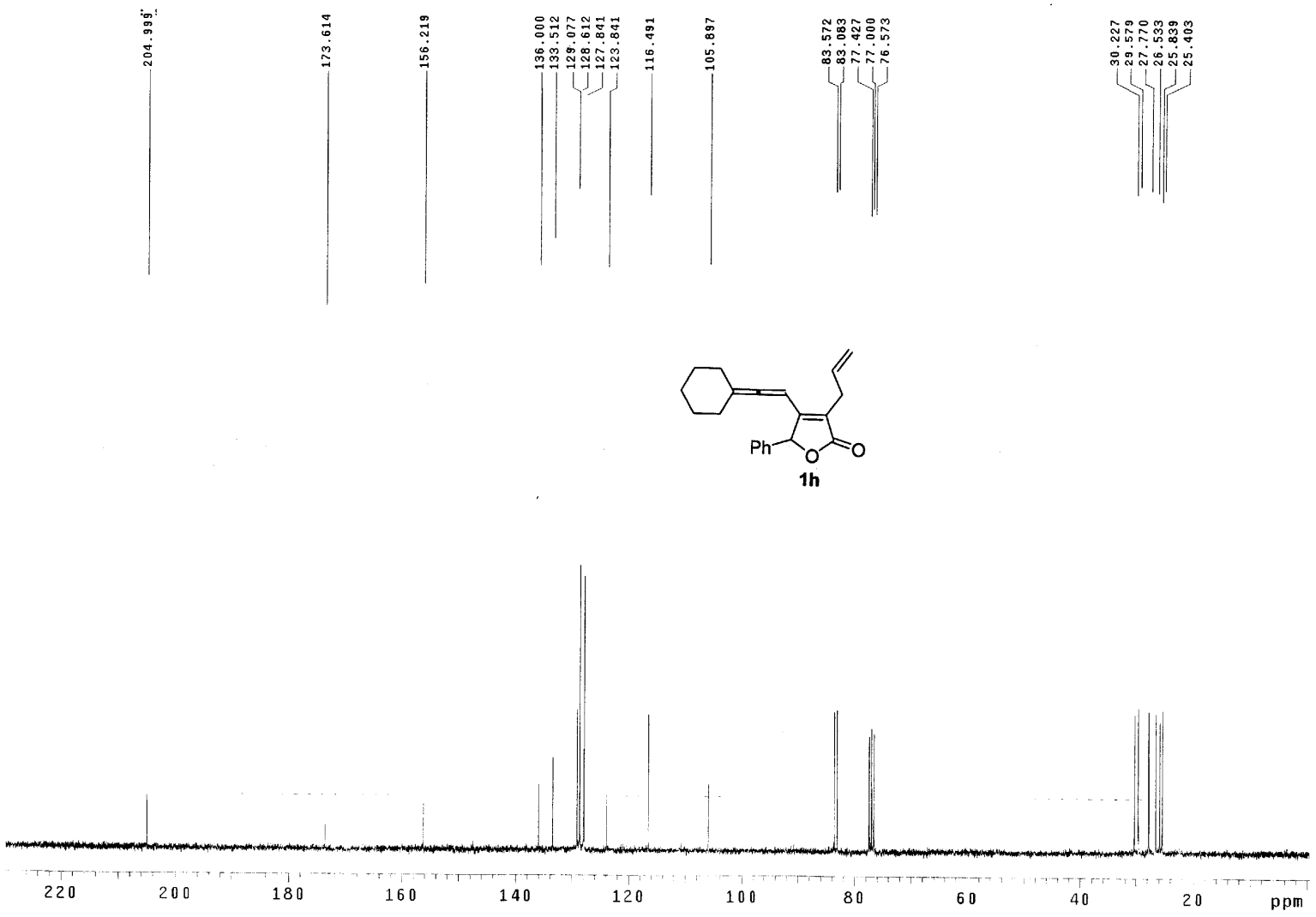
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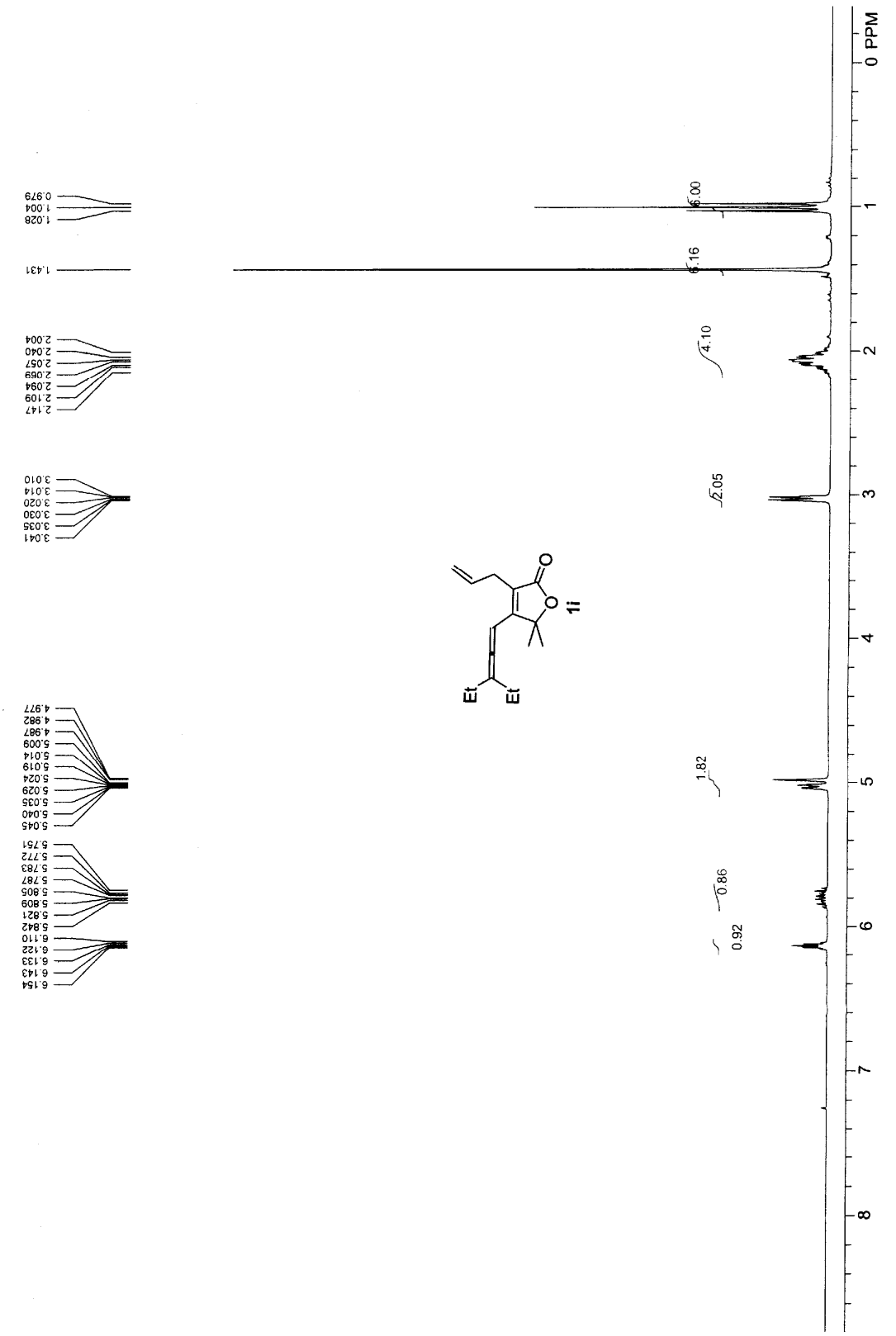
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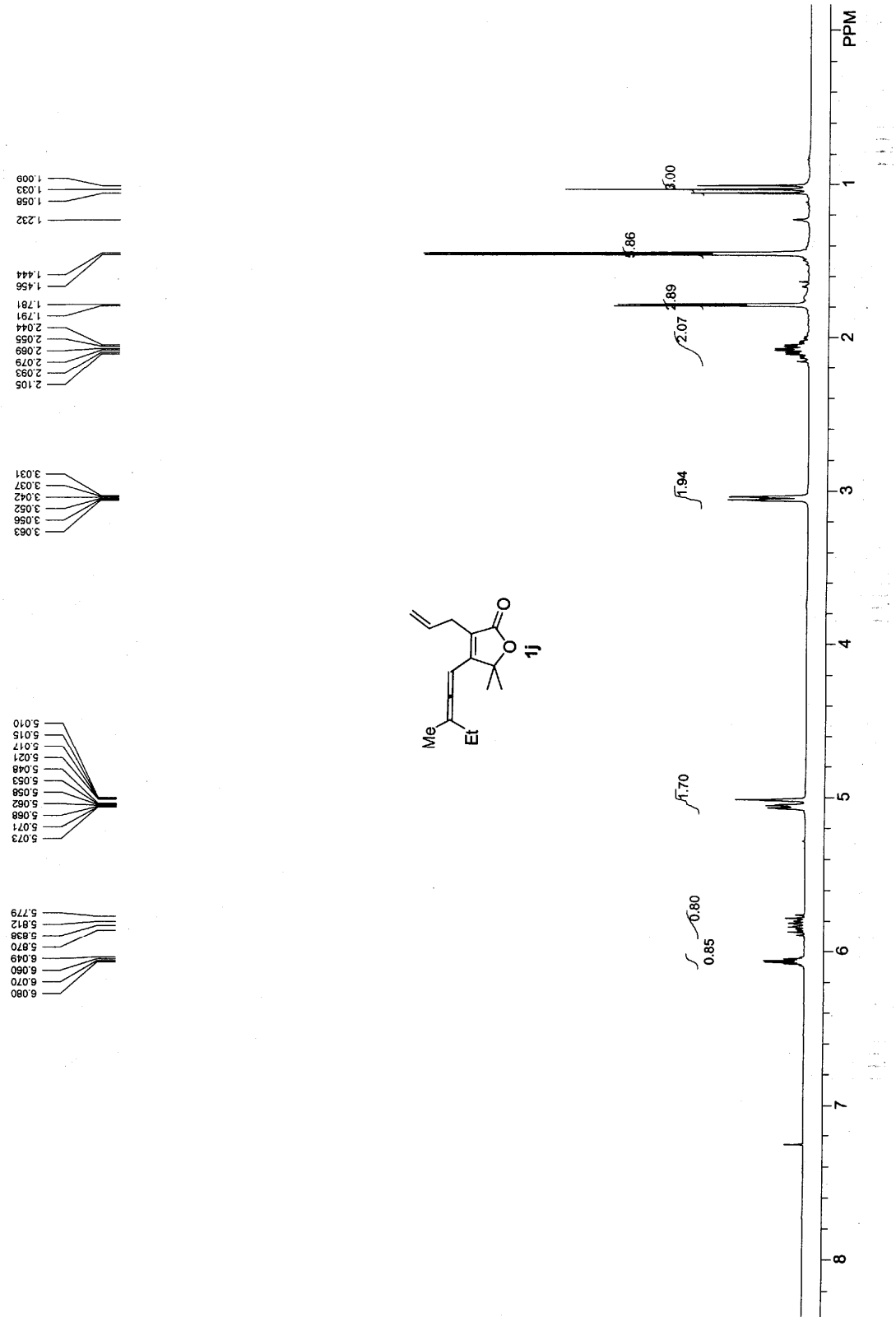
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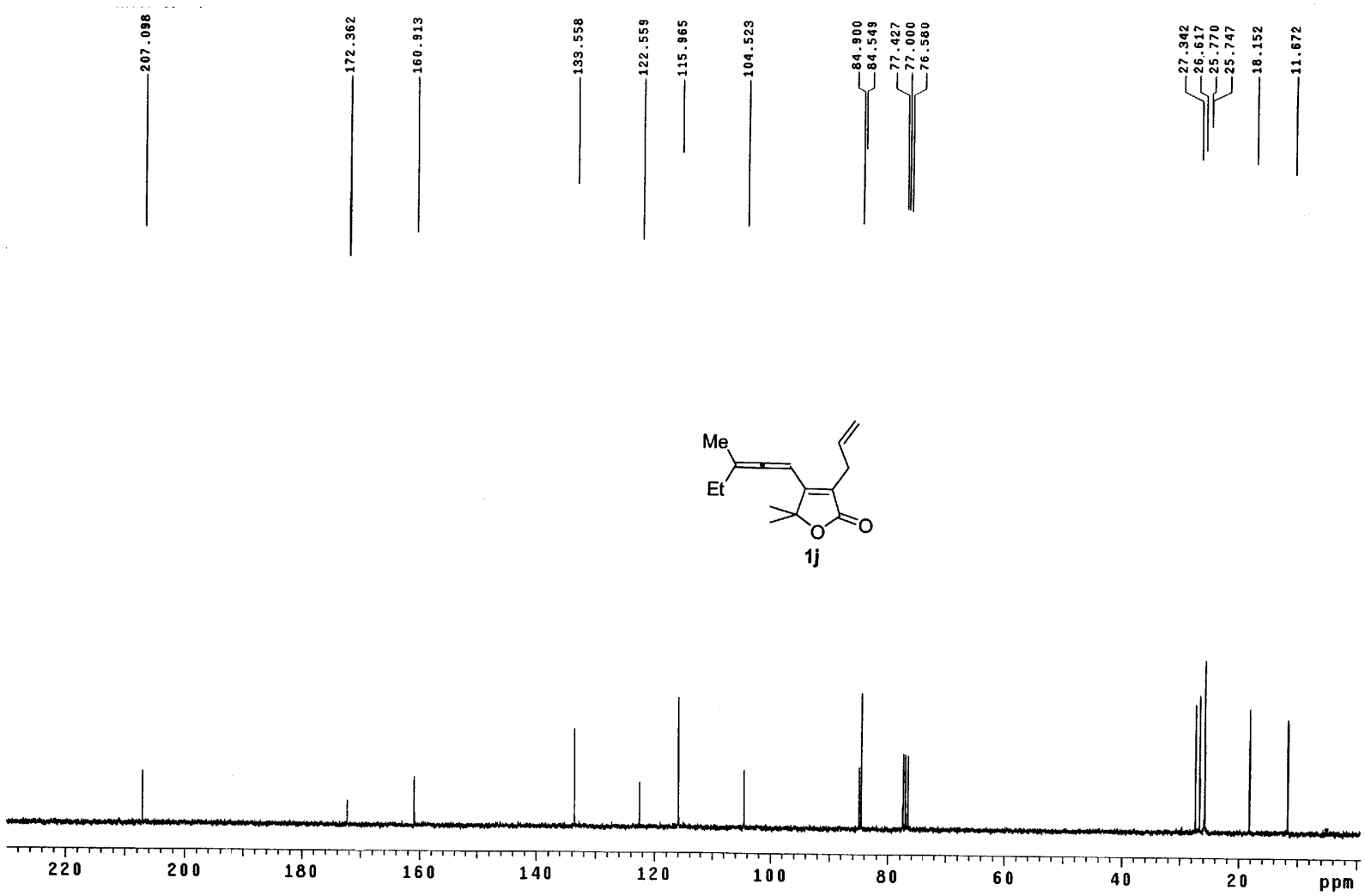
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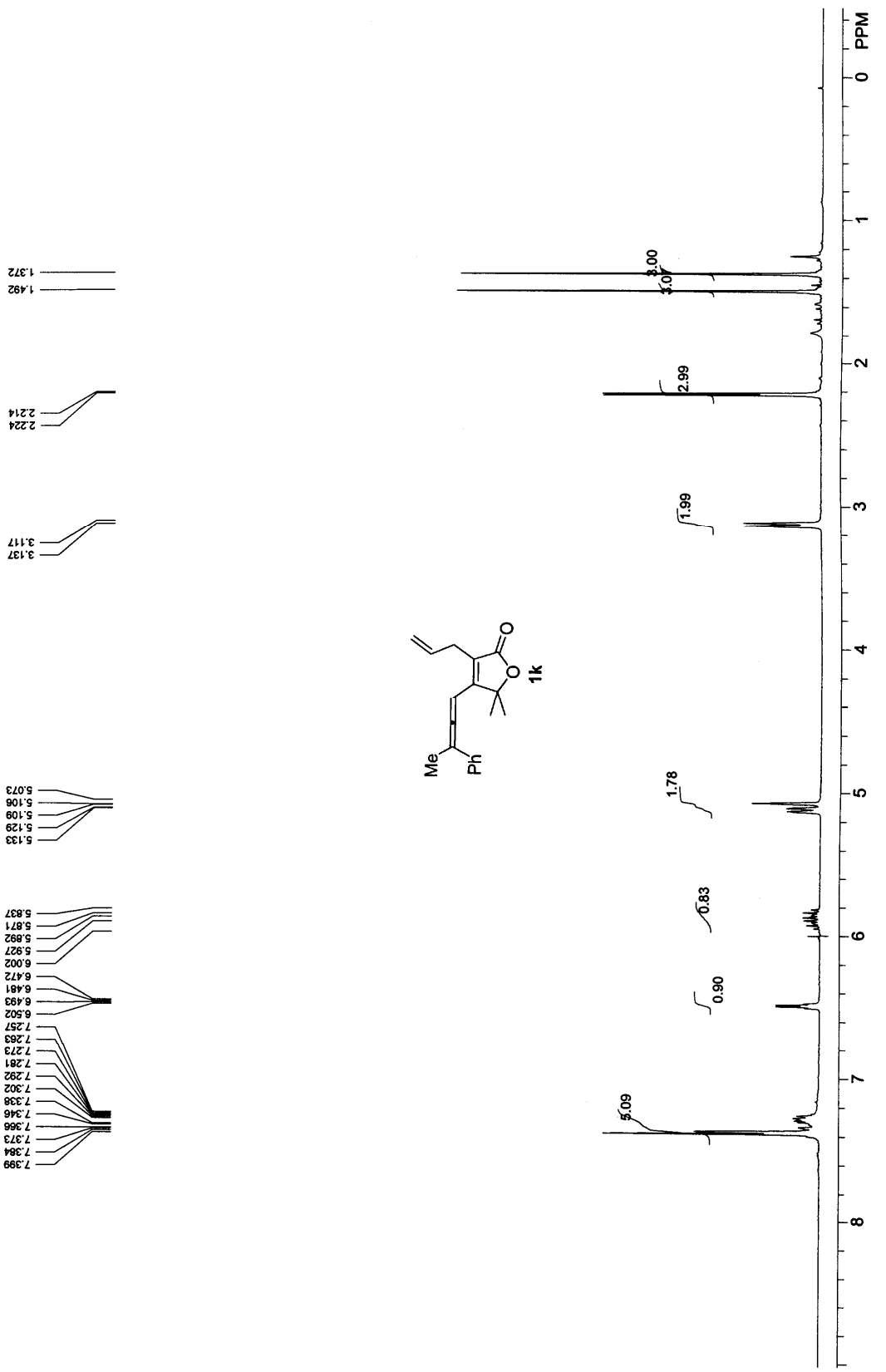
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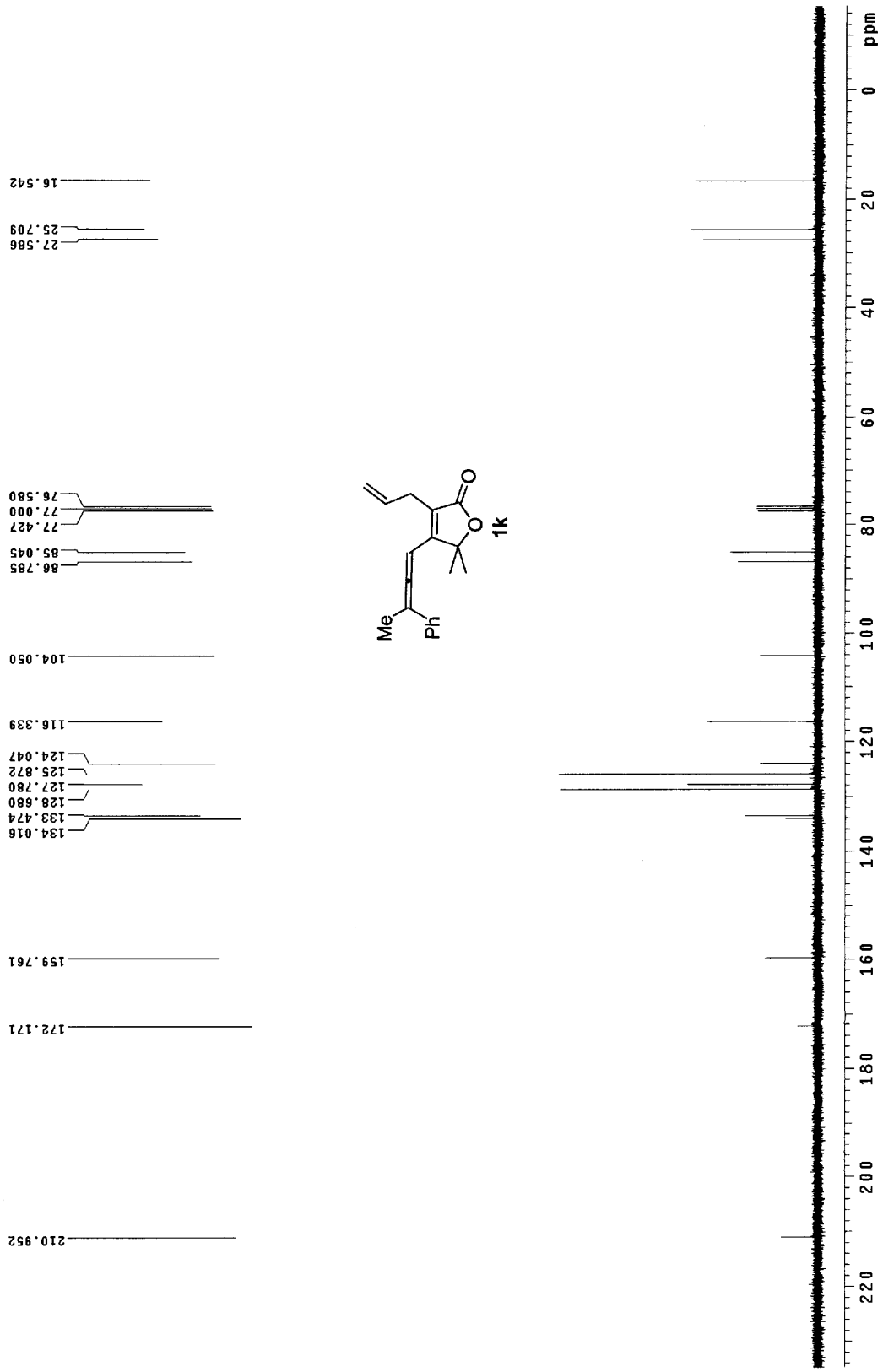
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77.000
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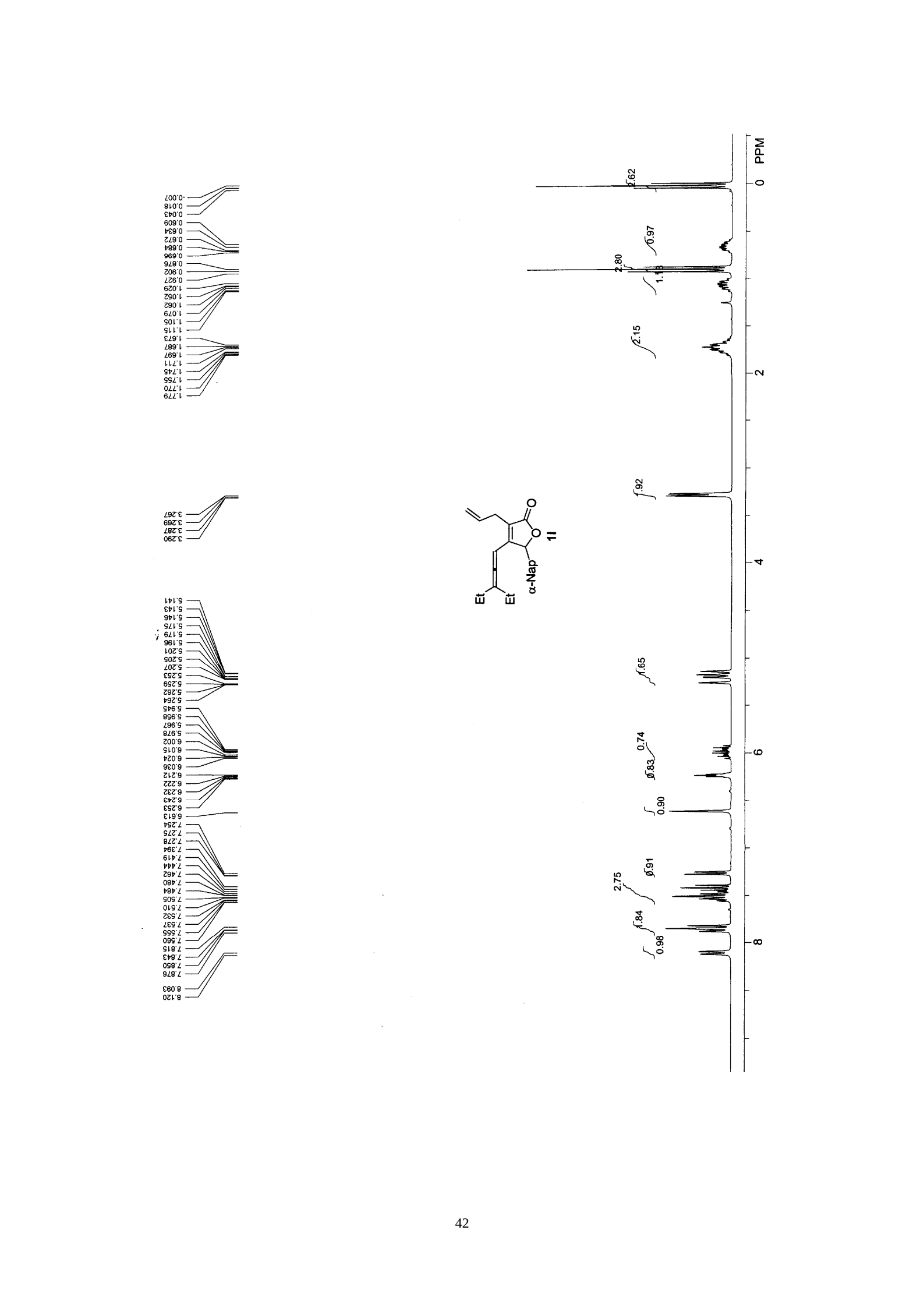
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1.115
1.673
1.687
1.697
1.711
1.745
1.755
1.770
1.779
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3.269
3.287
3.290
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5.196
5.201
5.205
5.207
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7.444
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7.510
7.532
7.537
7.555
7.560
7.815
7.843
7.850
7.876
8.093
8.120
Et
Et
α-Nap
11
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1.84
2.75
0.91
0.90
0.83
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1.92
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2.62
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4
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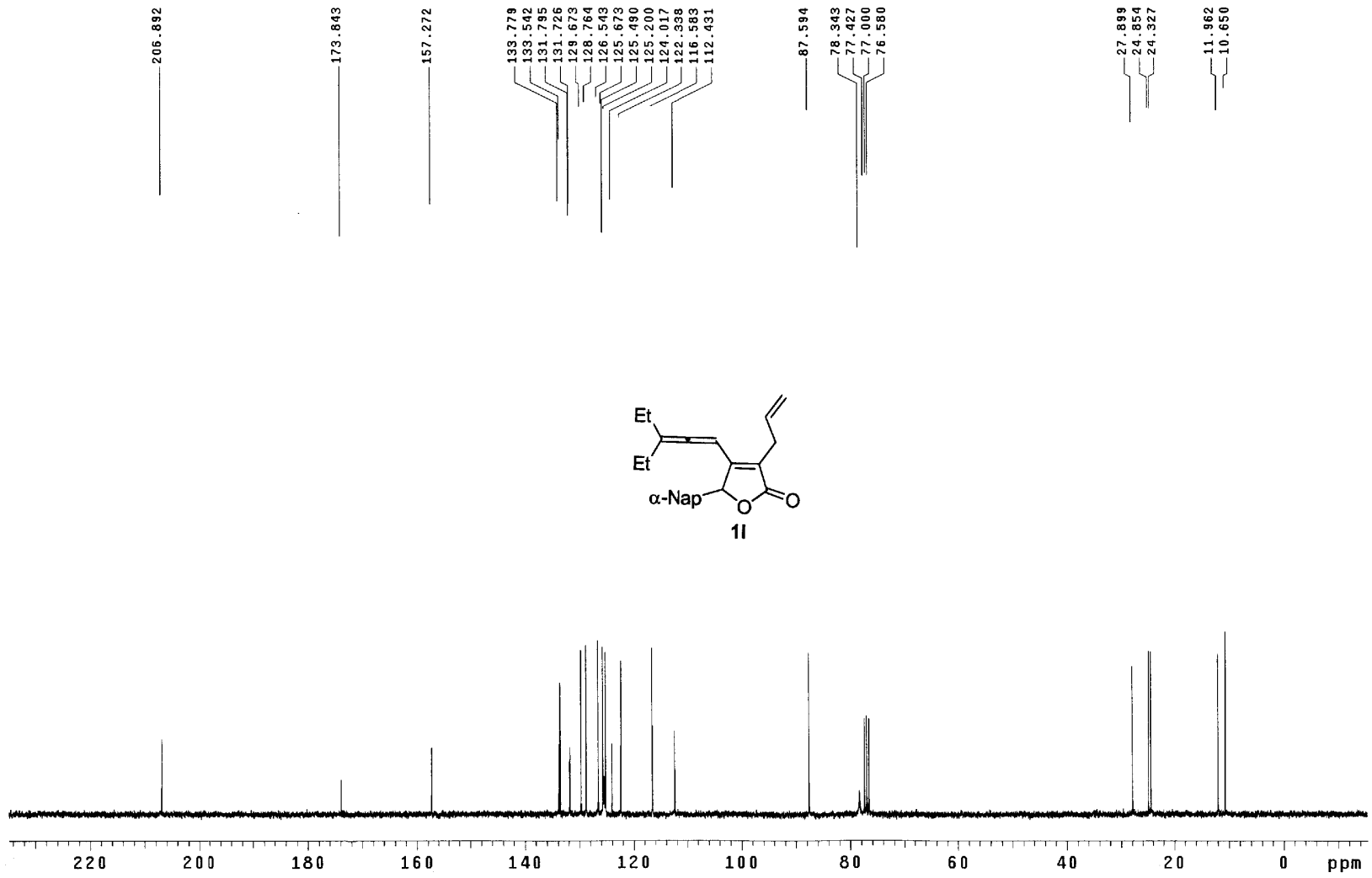
PPM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24.327
11.962
10.650
Et
Et
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O
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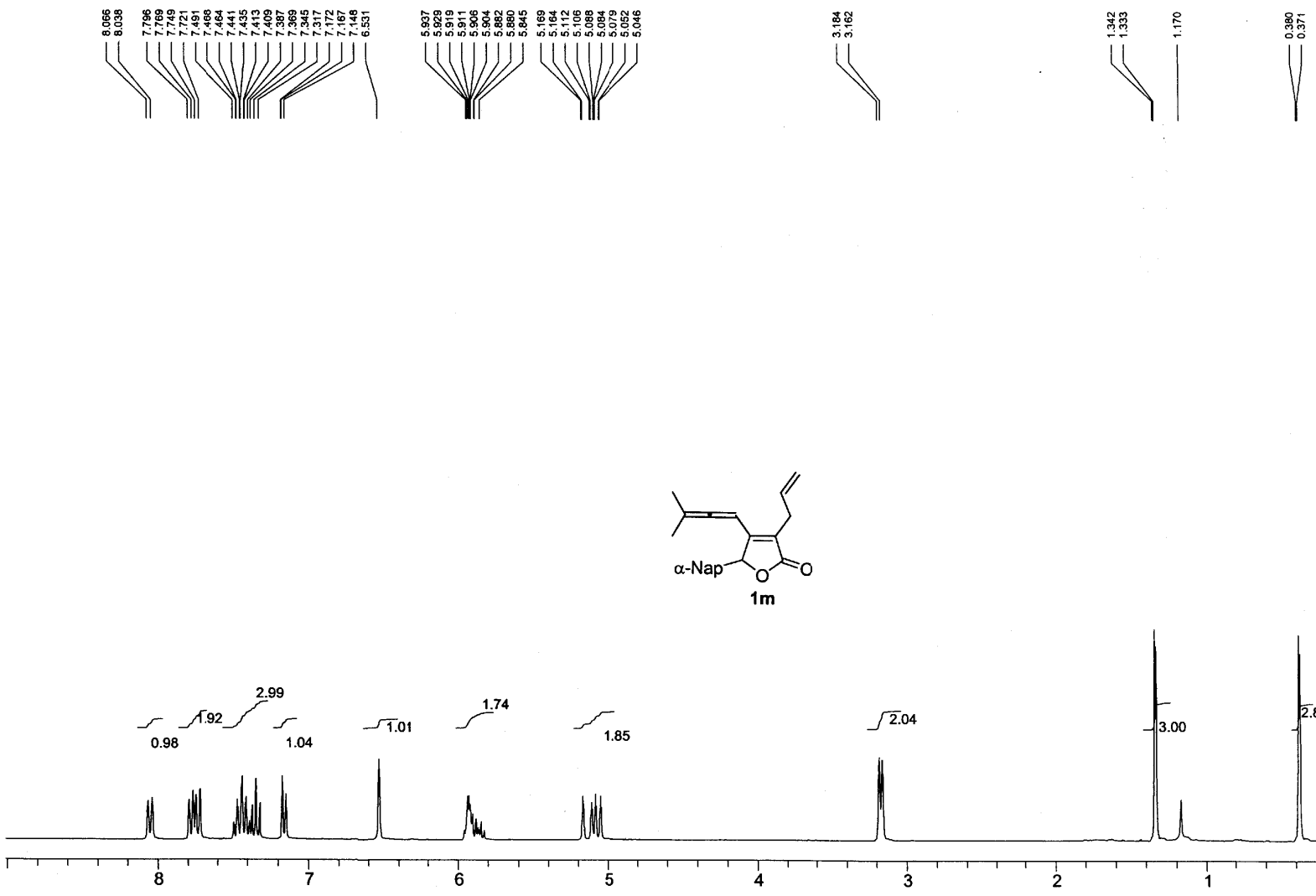
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5.929
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5.164
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5.106
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5.046
3.184
3.162
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0.371
α-Nap
O
O
1m
0.98
1.92
2.99
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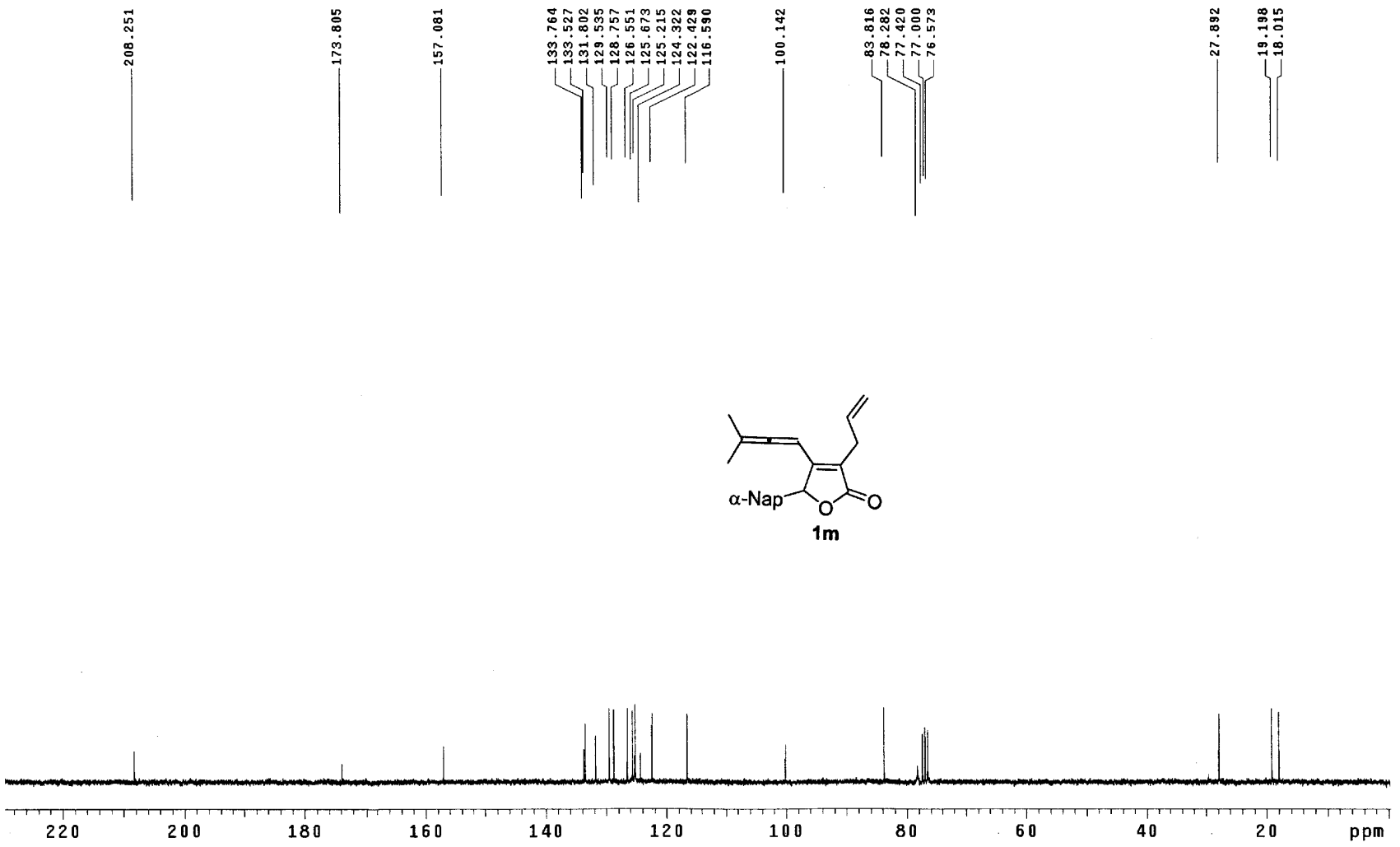
6
5
4
3
2
1
PPM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O
O
1m
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140
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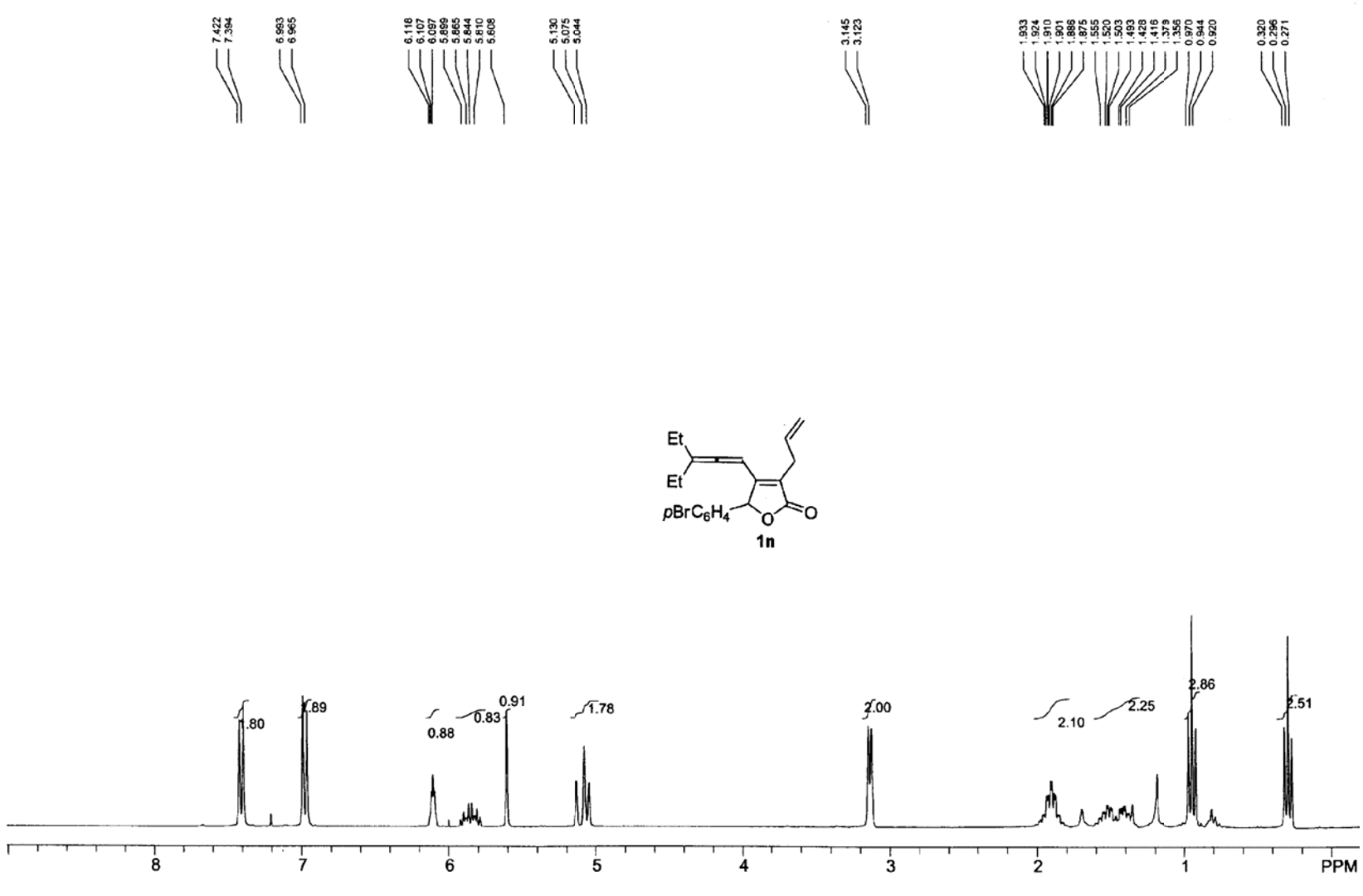
20
ppm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5.844
5.810
5.608
5.130
5.075
5.044
3.145
3.123
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1.910
1.901
1.886
1.875
1.555
1.520
1.503
1.493
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1.416
1.373
1.356
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0.920
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0.271
Et
Et
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O
O
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2
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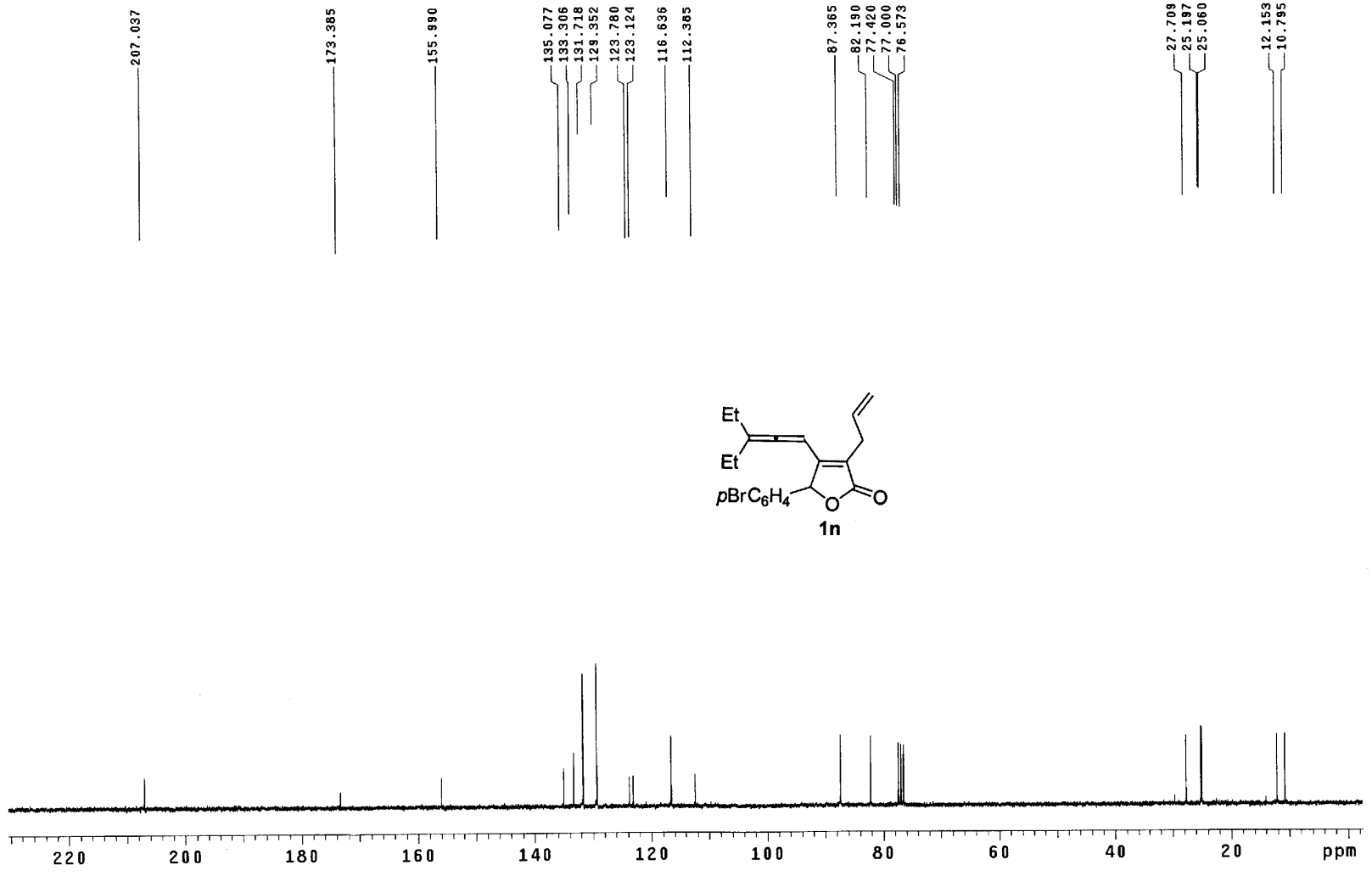
PPM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82.190
77.420
77.000
76.573
27.709
25.197
25.060
12.153
10.795
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Et
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O
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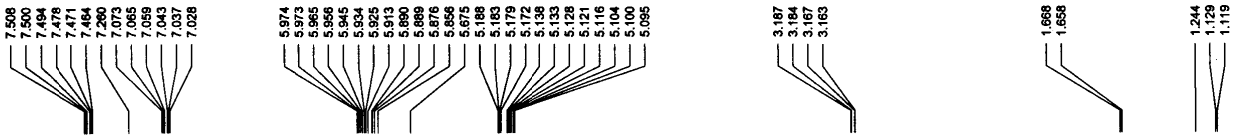
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7.464
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7.073
7.065
7.059
7.043
7.037
7.028
5.974
5.973
5.965
5.956
5.945
5.934
5.925
5.913
5.890
5.889
5.876
5.856
5.675
5.188
5.183
5.179
5.172
5.138
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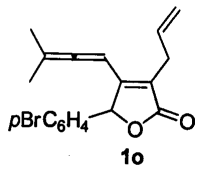
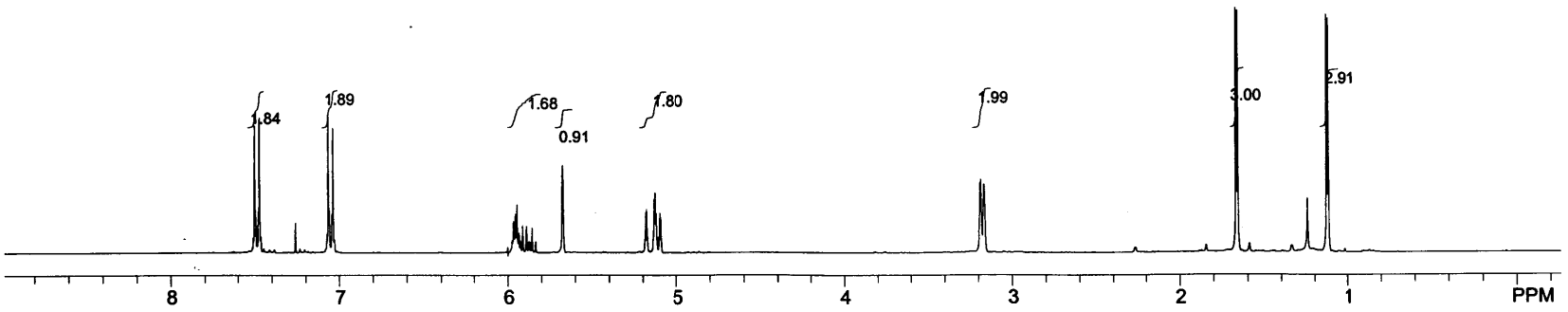
1.119


pBrC6H4
O
O

1o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7
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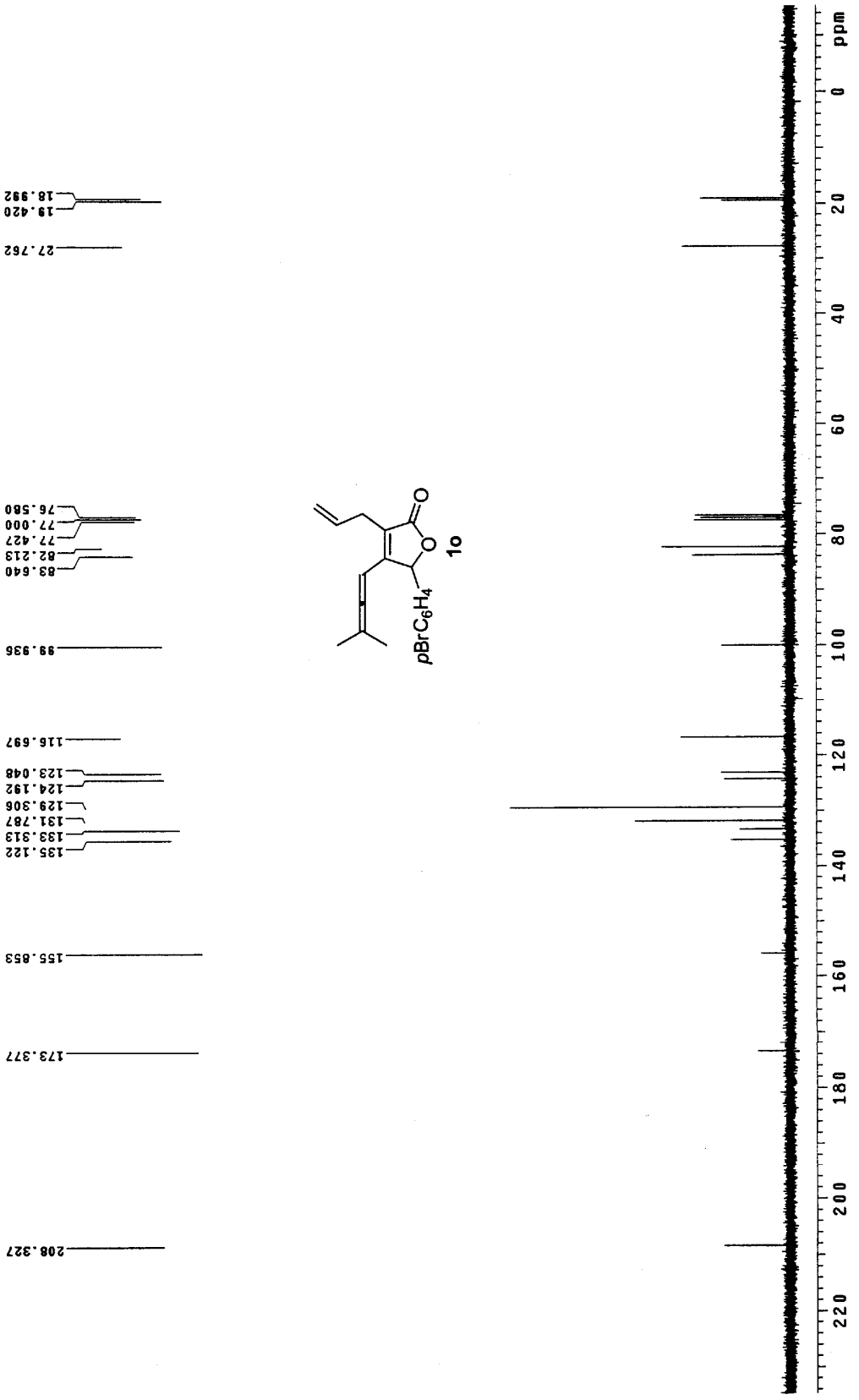
5
4
3
2
1
PPM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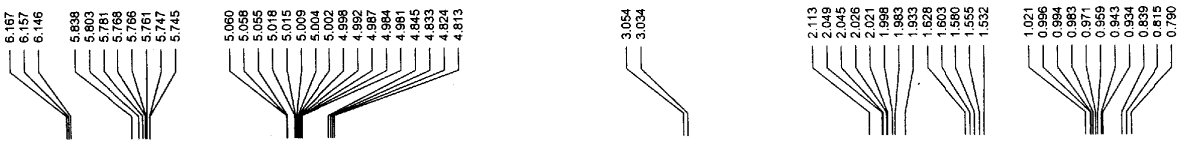
pBrC6H4
ppm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5.055
5.018
5.015
5.009
5.004
5.002
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4.987
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4.824
4.813
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2.049
2.045
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2.021
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1.532
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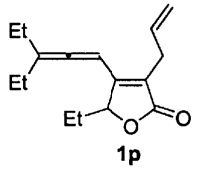
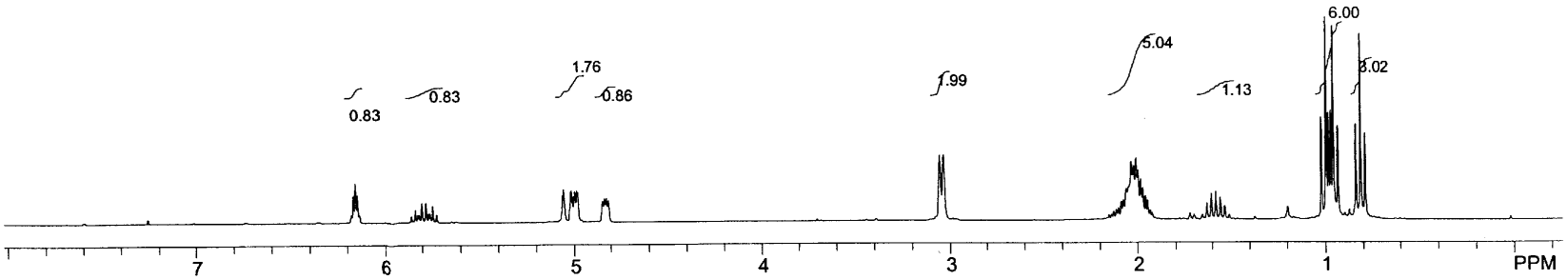
0.790


Et
Et
Et
O
O

1p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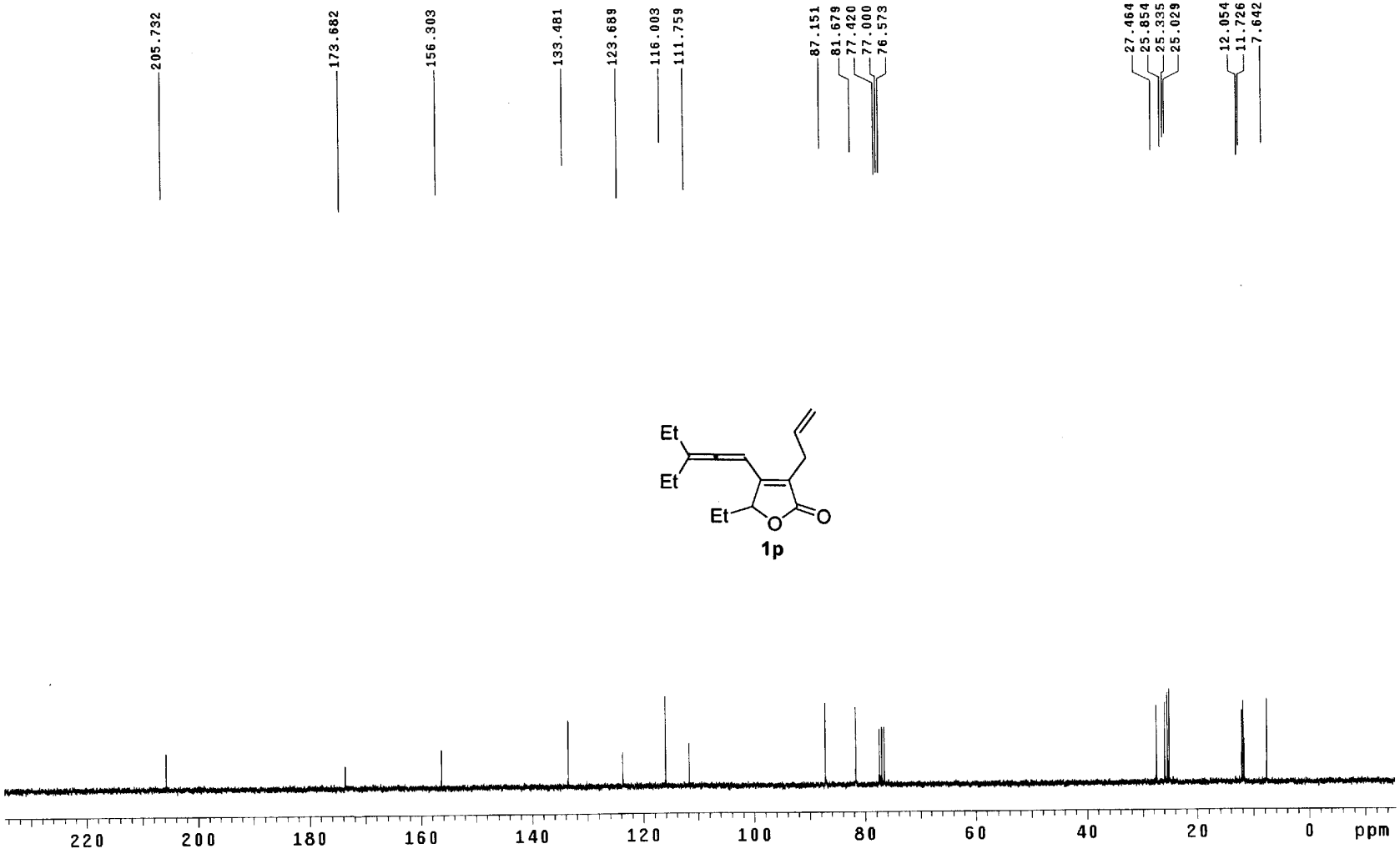
6.00
3.02
7
6
5
4
3
2
1
PPM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27.464
25.854
25.335
25.029
12.054
11.726
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Et
Et
Et
O
O
1p
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200
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120
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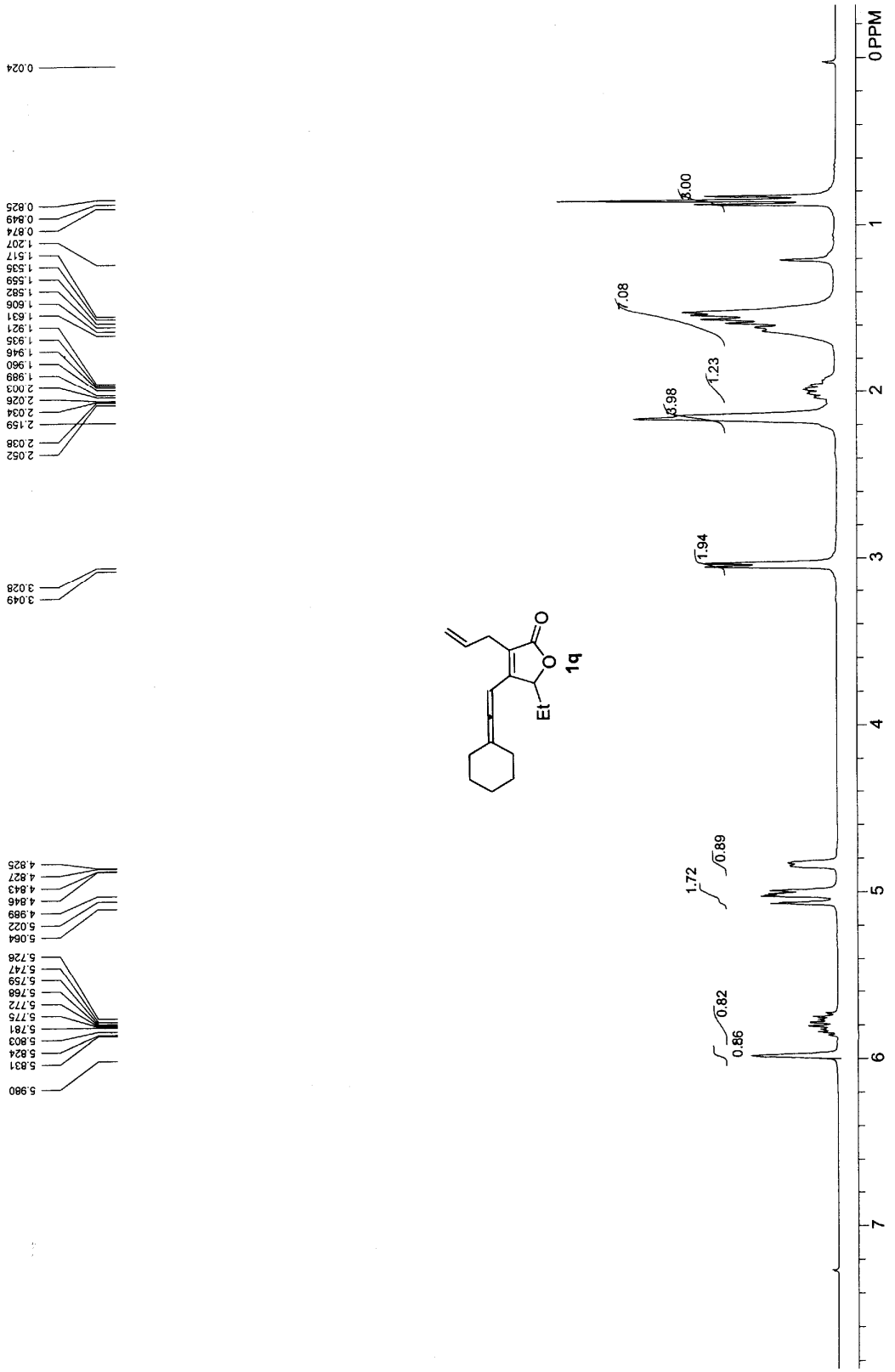
0
ppm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1.935
1.946
1.960
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2.038
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3.028
3.049
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4.827
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0.86
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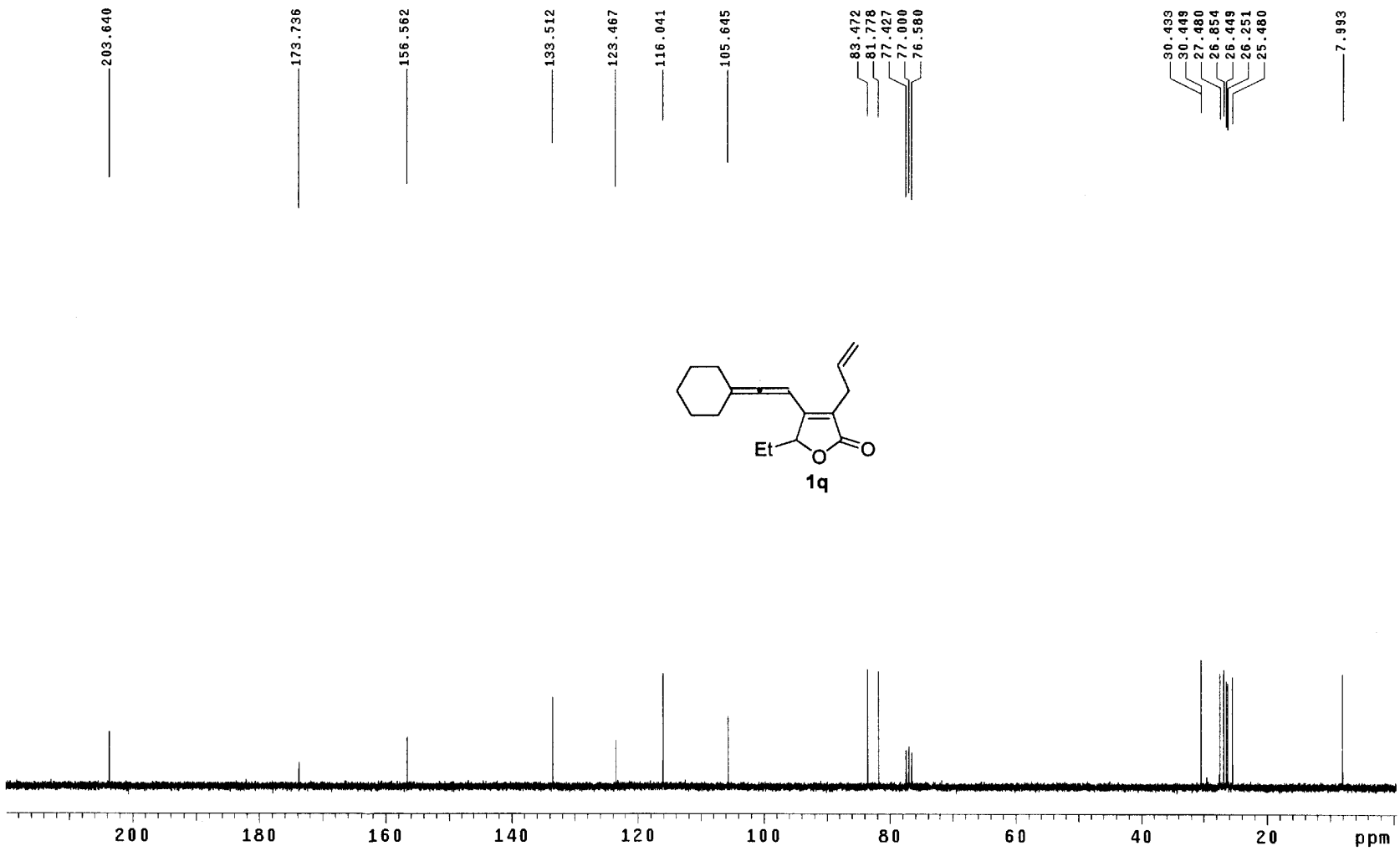
7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27.480
26.854
26.449
26.251
25.480
7.993
Et
O
O
1q
200
180
160
140
120
100
80
60
40
20
ppm


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7.258
7.256
7.242
7.121
7.113
7.095
7.089
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5.973
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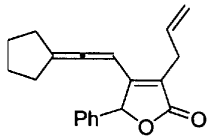
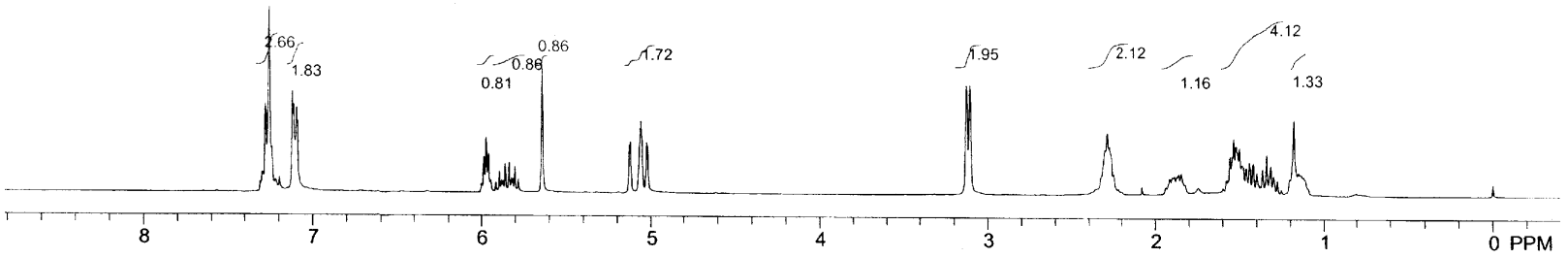
1.142


Ph
O
O

1r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1.33
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7
6
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4
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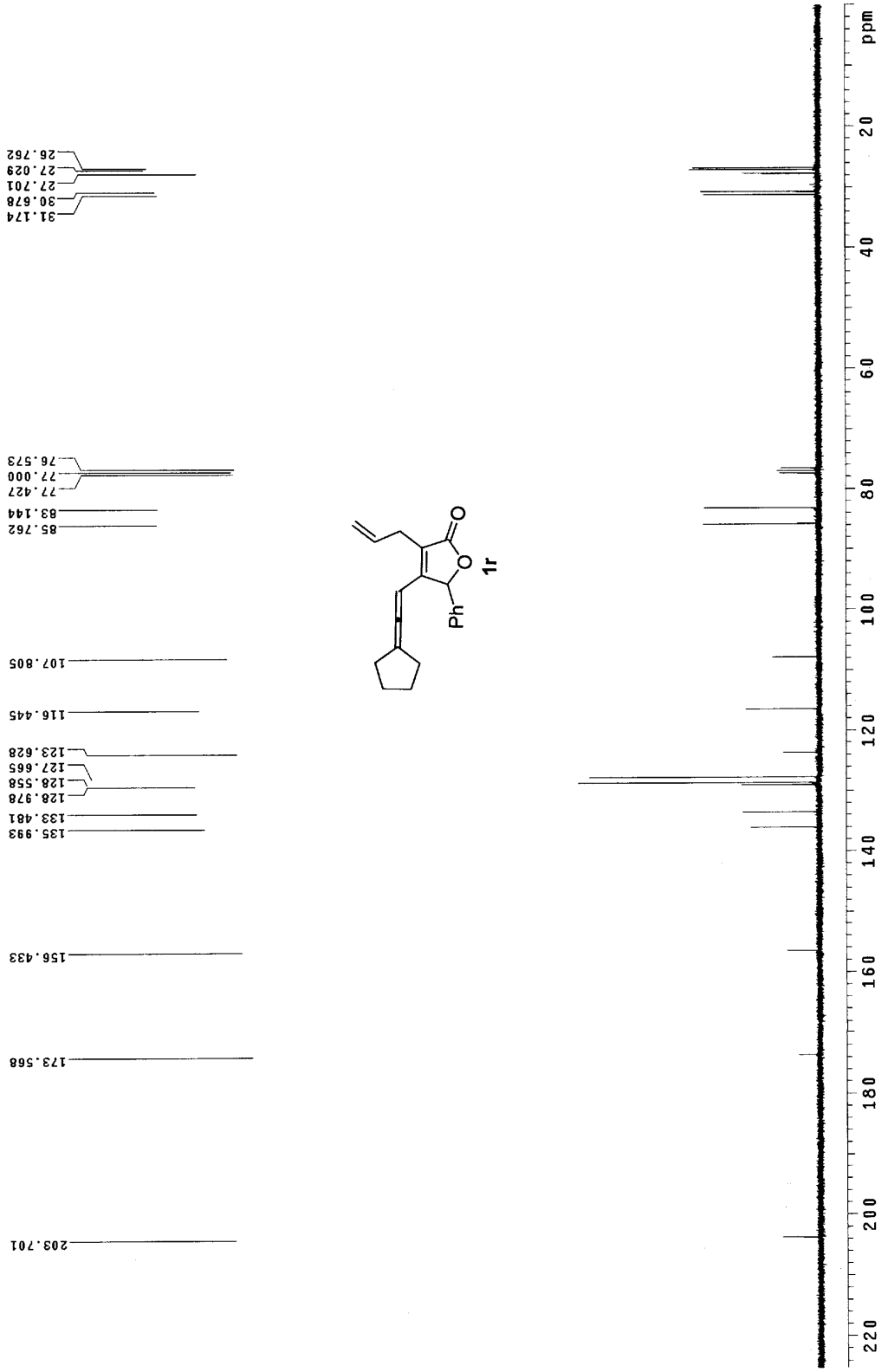
2
1
0 PPM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123.628
127.665
128.558
128.978
133.481
135.993
156.433
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1r
Ph
O
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160
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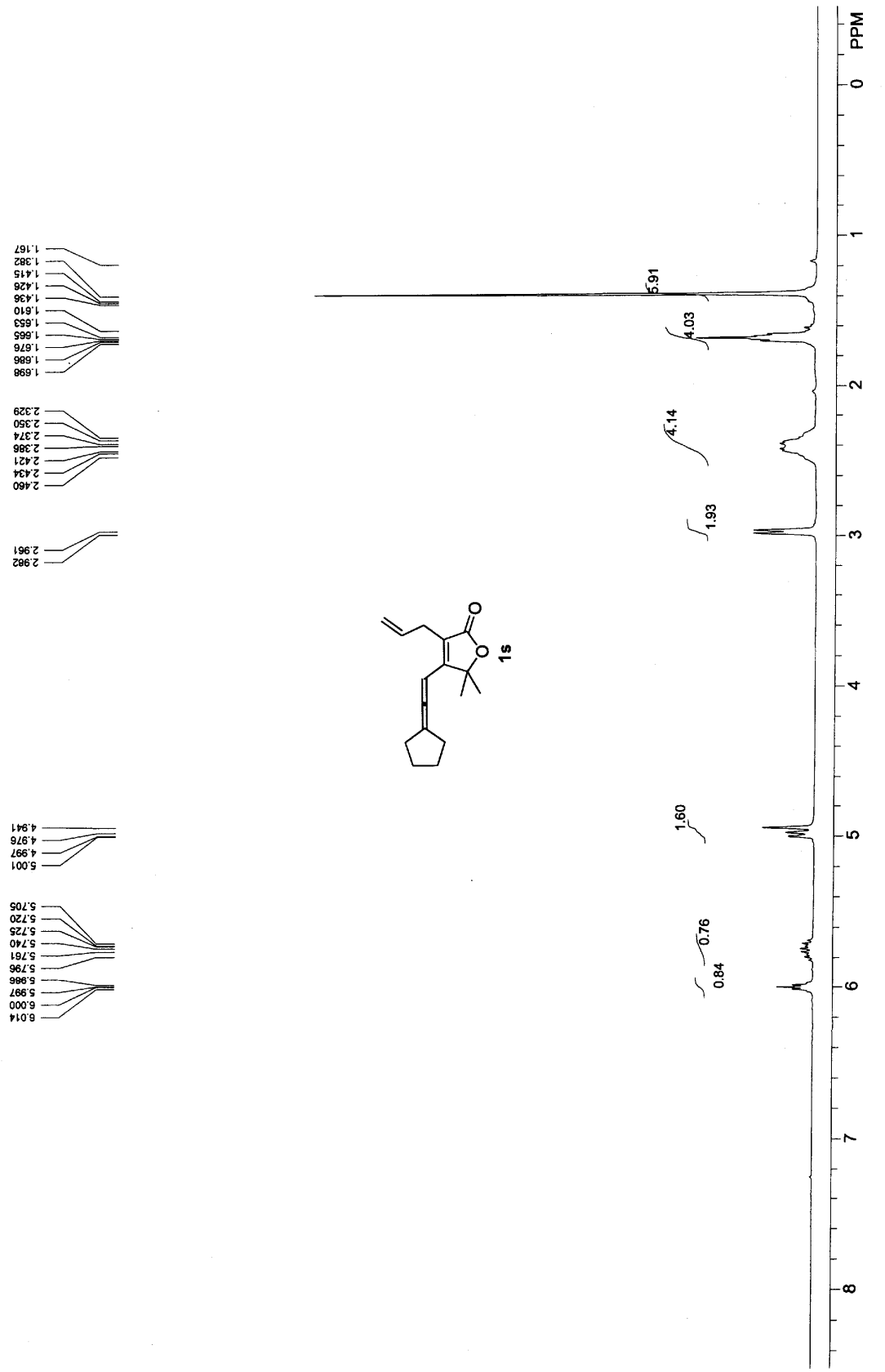
200
220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PPM
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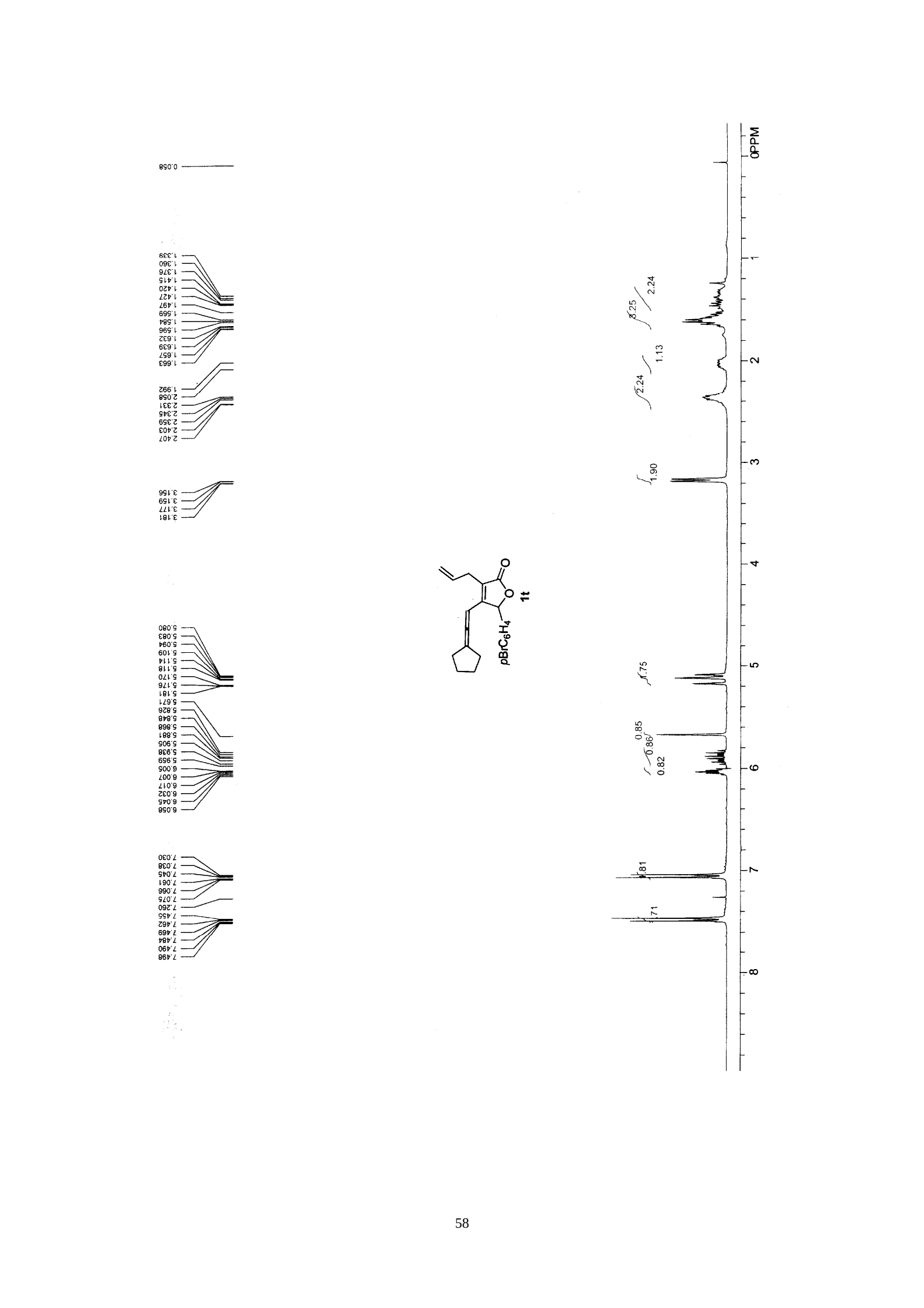
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pBrC6H4
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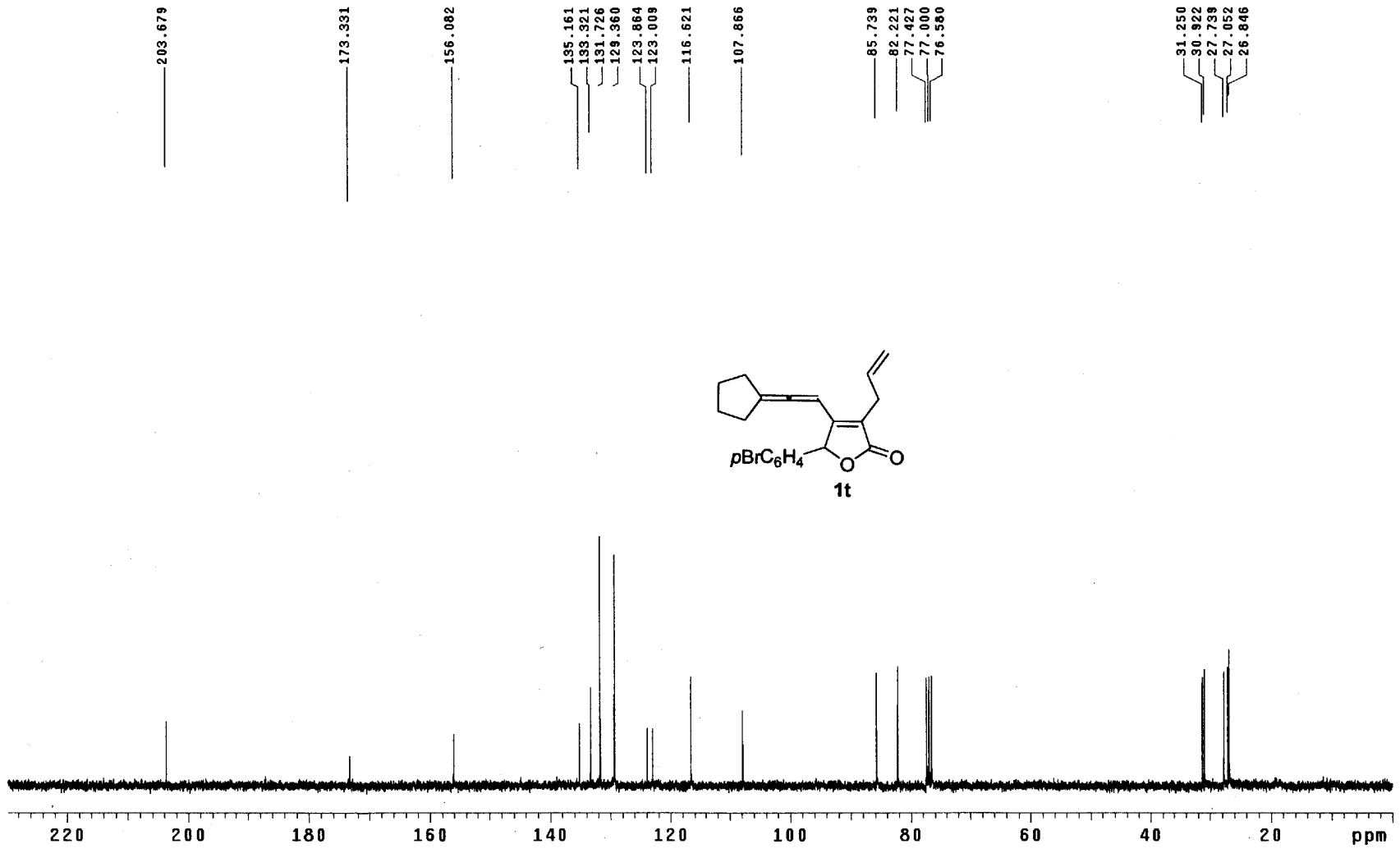
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77.427
77.000
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31.250
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O
1t
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200
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140
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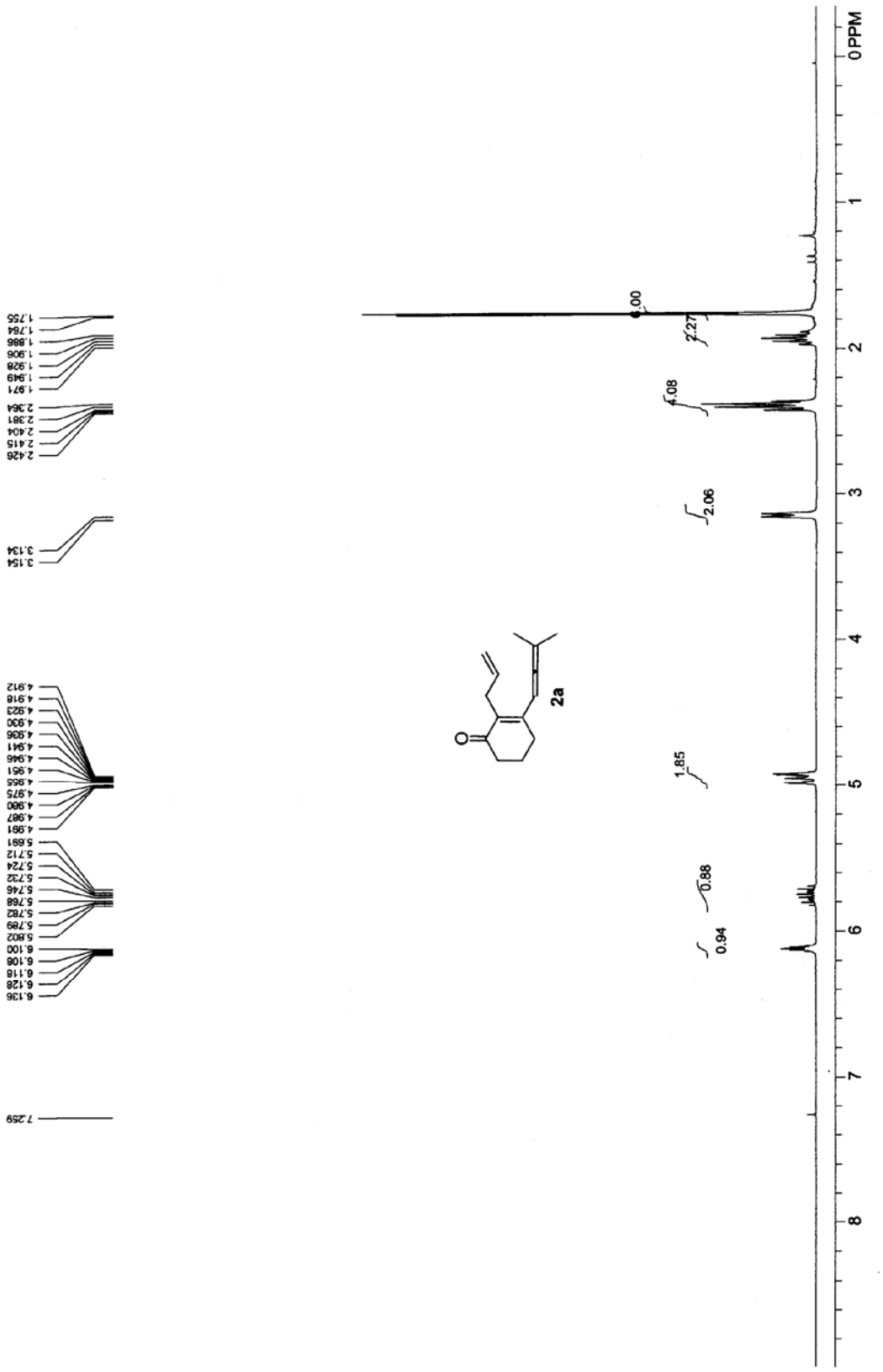
20
ppm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1.755
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0.94
0 PPM

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ppm
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200
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140
120
100
80
60
40
20


7.258
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4.513
3.102
2.450
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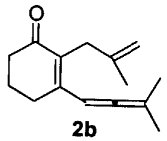
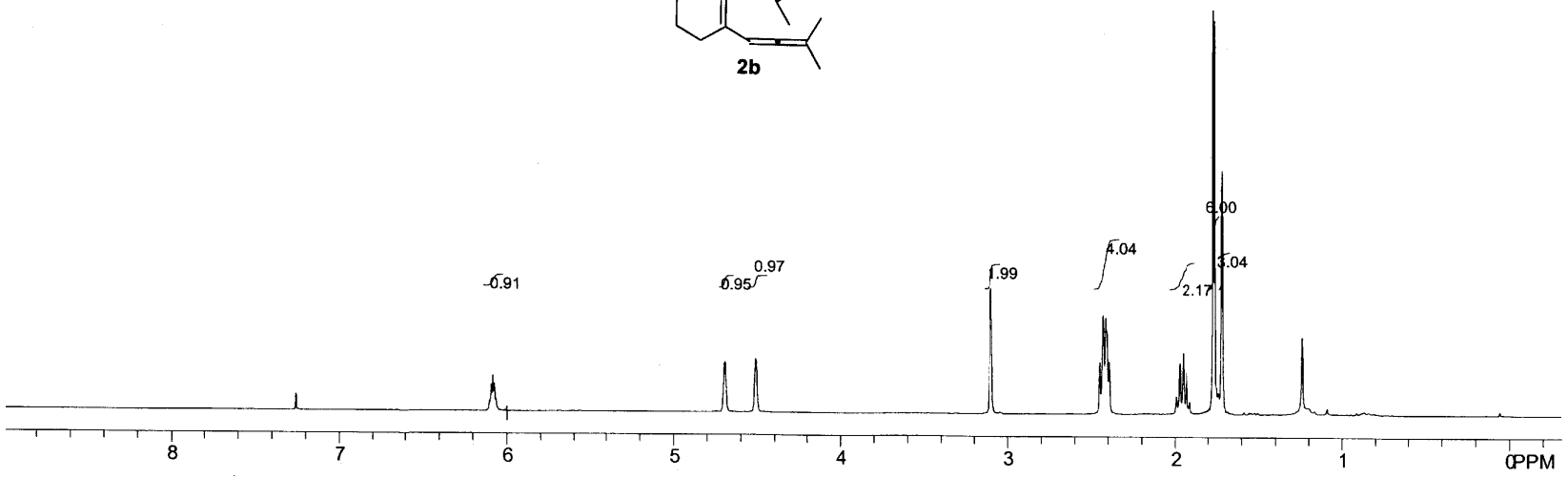


2b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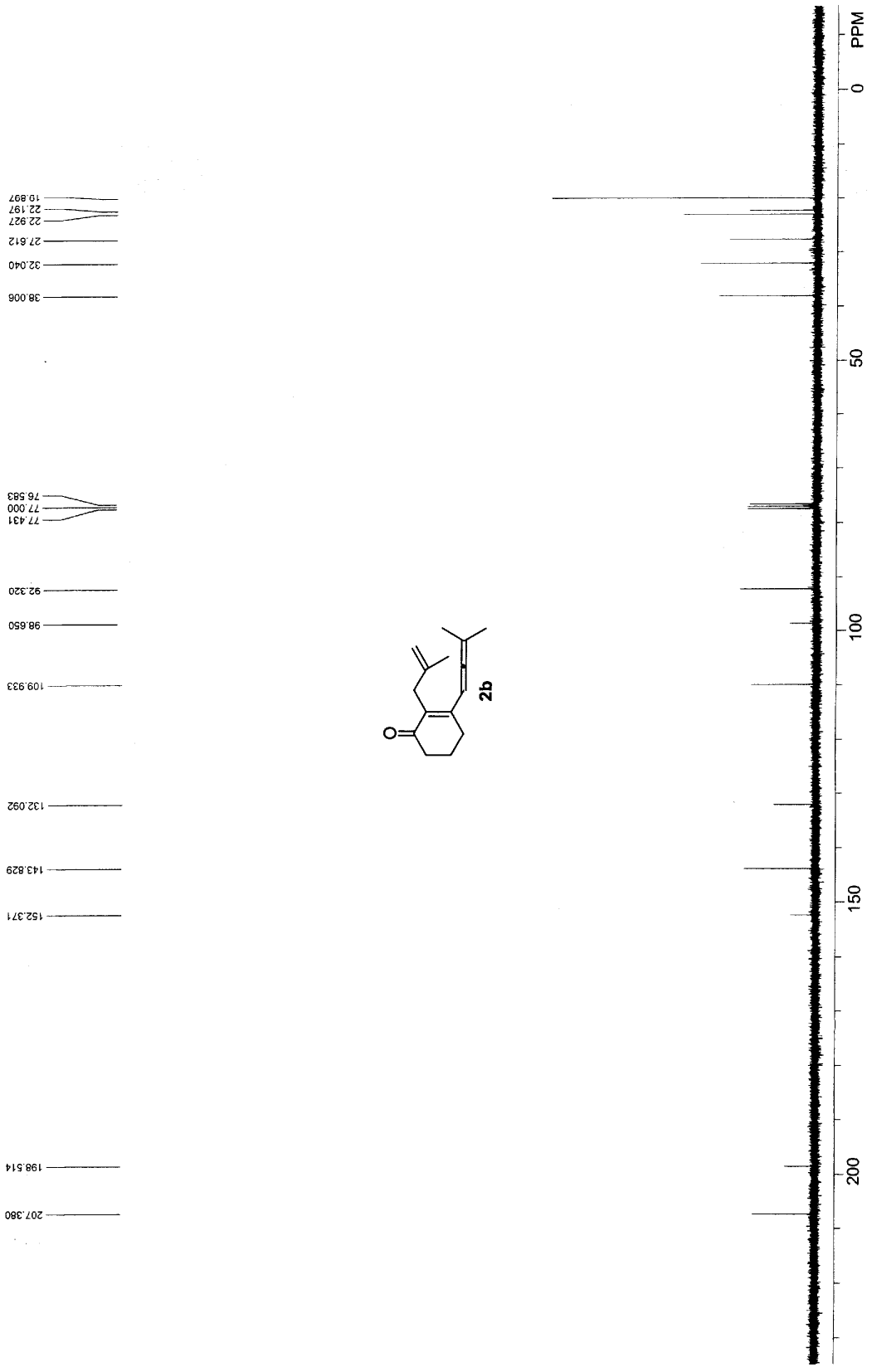
0.95
0.97
1.99
4.04
2.17
6.00
3.04
8
7
6
5
4
3
2
1
0PPM


PPM
0
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100
150
200
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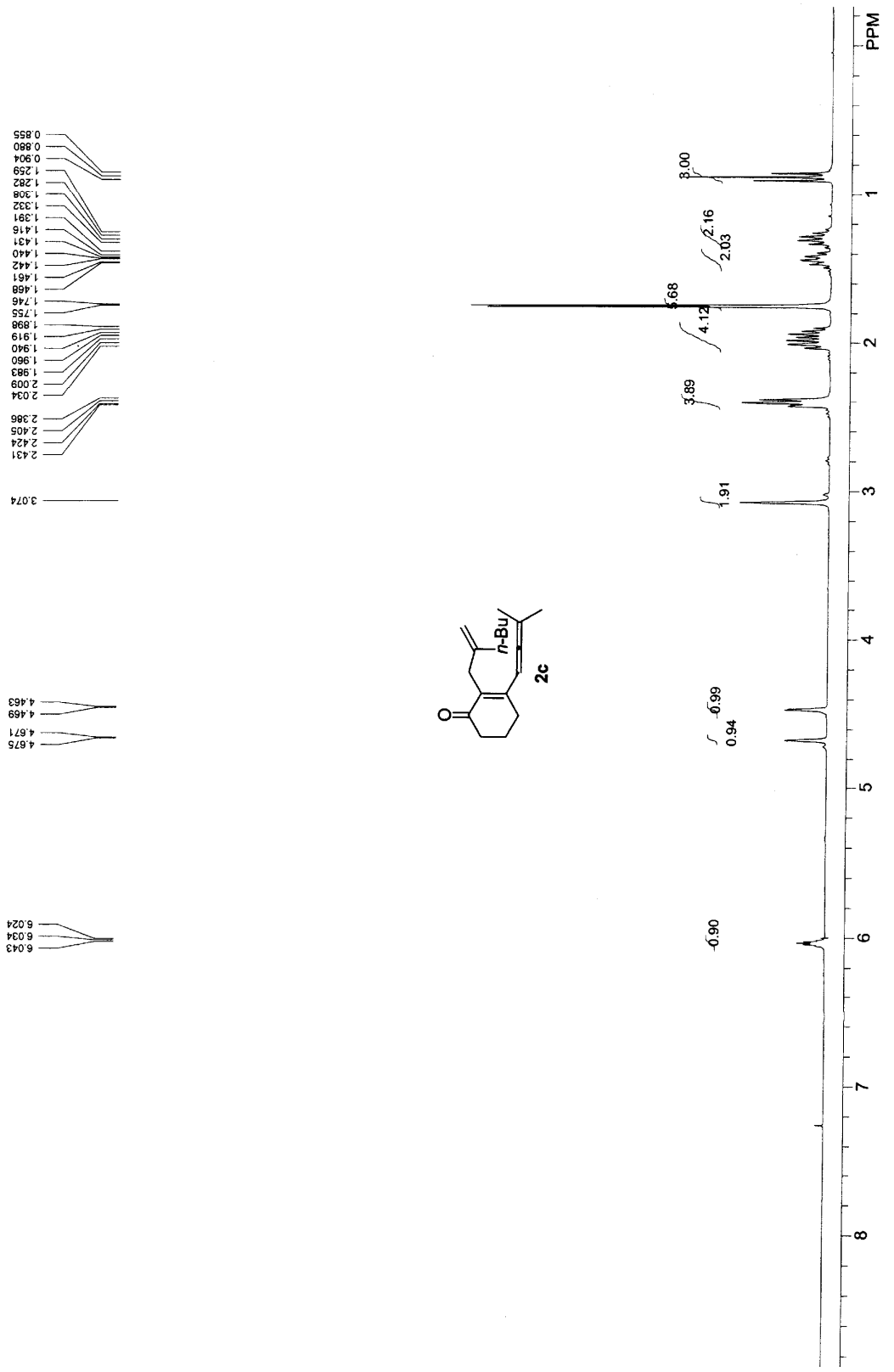
22.197
22.927
27.612
32.040
38.006
76.583
77.000
77.431
92.320
98.650
109.933
132.092
143.829
152.371
198.514
207.380
O
2b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1.391
1.416
1.431
1.440
1.442
1.461
1.468
1.746
1.755
1.898
1.919
1.940
1.960
1.983
2.009
2.034
2.386
2.405
2.424
2.431
3.074
4.463
4.469
4.671
4.675
6.024
6.034
6.043
n-Bu
2c
0.90
0.94
0.99
1.91
3.89
4.12
5.68
2.03
2.16
3.00
PPM

13.939
19.839
22.144
22.396
27.525
29.899
30.533
36.394
37.967
76.573
77.000
77.420
92.334
98.555
108.576
132.161
147.670
152.166
198.397
207.289
n-Bu
2c
O
ppm
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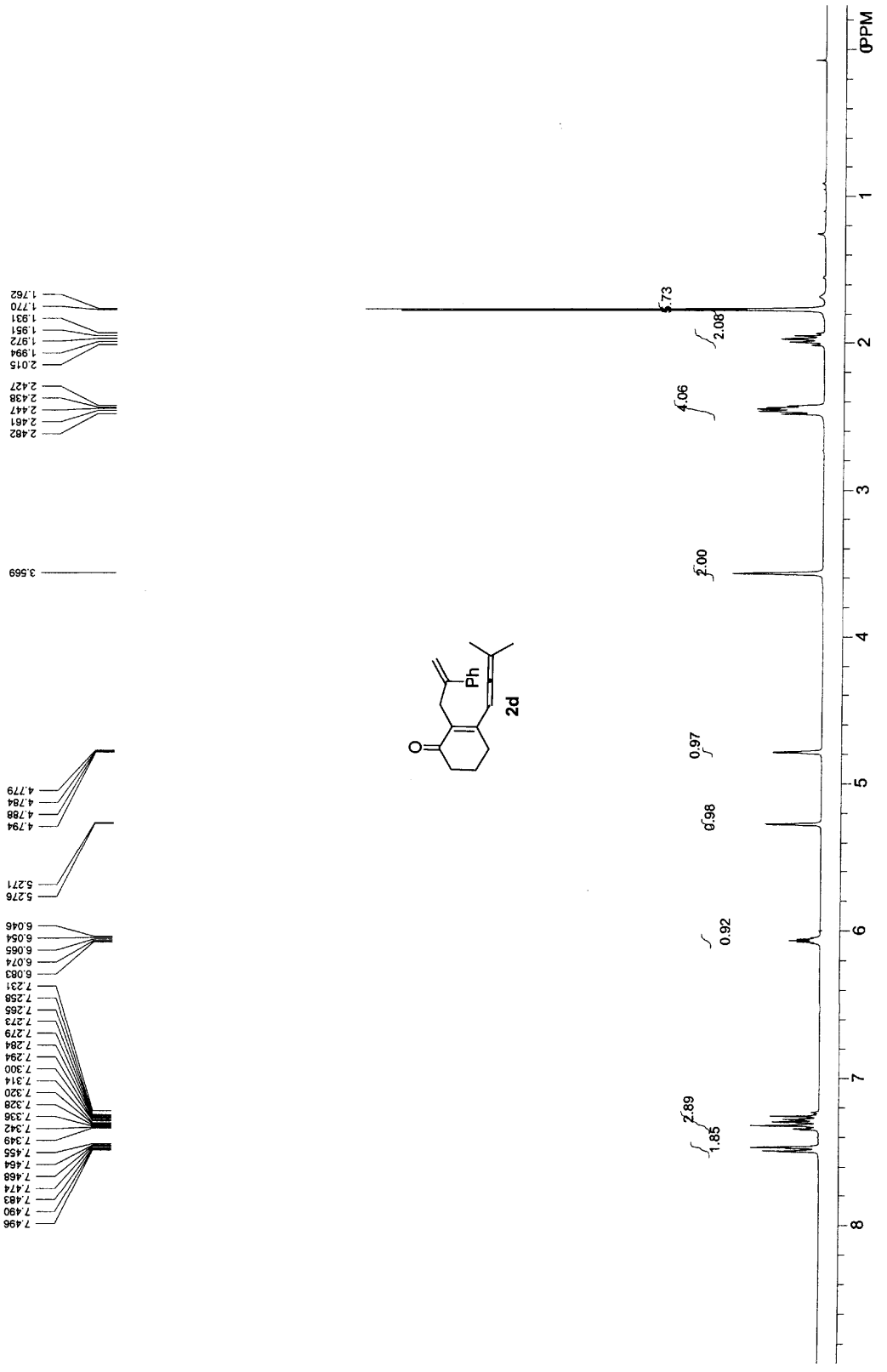
200
180
160
140
120
100
80
60
40
20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2.447
2.461
2.482
3.569
4.779
4.784
4.788
4.794
5.271
5.276
6.046
6.054
6.065
6.074
6.083
7.231
7.258
7.265
7.273
7.279
7.284
7.294
7.300
7.314
7.320
7.328
7.336
7.342
7.349
7.455
7.464
7.468
7.474
7.483
7.490
7.496
Ph
O
2d
5.73
2.08
4.06
2.00
0.97
0.98
0.92
2.89
1.85
PPM

198.351
207.533
141.778
145.968
152.922
131.985
128.077
127.322
126.093
111.935
98.715
92.441
77.427
77.000
76.580
37.990
29.601
27.670
22.183
19.870
Ph
O
2d
ppm
220
200
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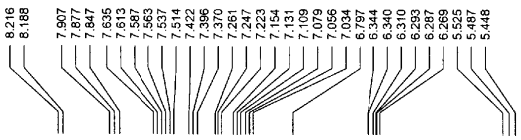
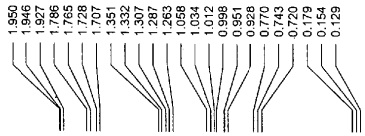
160
140
120
100
80
60
40
20


8.216
8.188
7.907
7.877
7.847
7.635
7.613
7.587
7.563
7.537
7.514
7.422
7.396
7.370
7.261
7.247
7.223
7.154
7.131
7.109
7.079
7.056
7.034
6.797
6.344
6.340
6.310
6.293
6.287
6.269
5.525
5.487
5.448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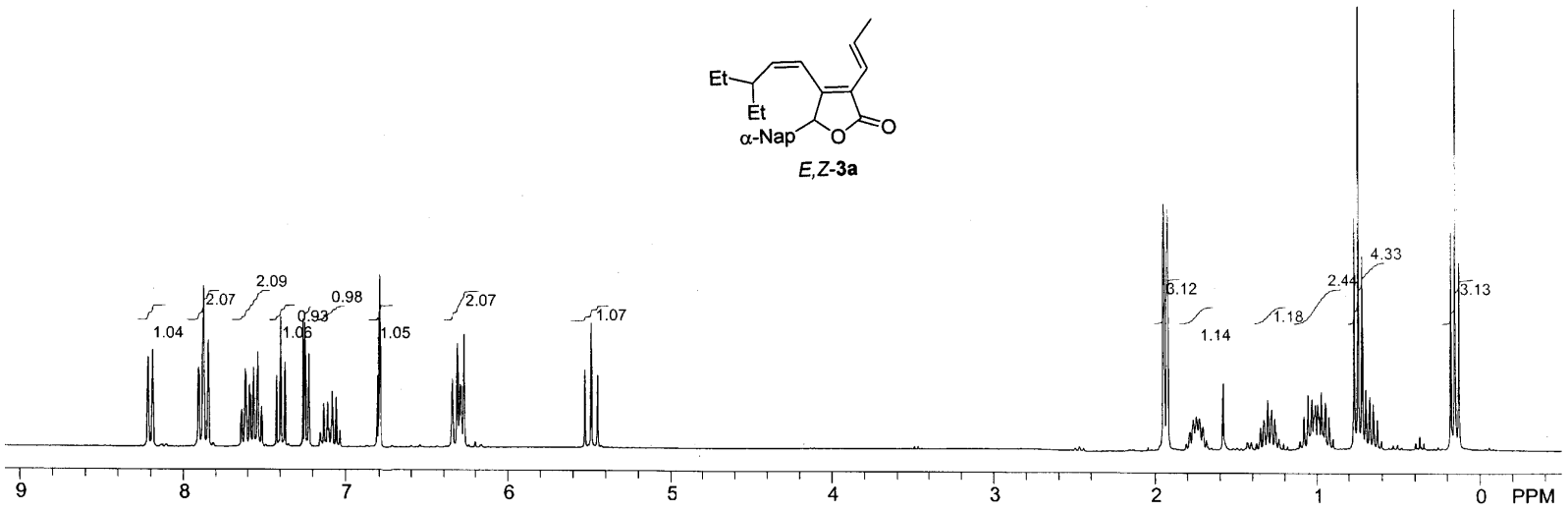
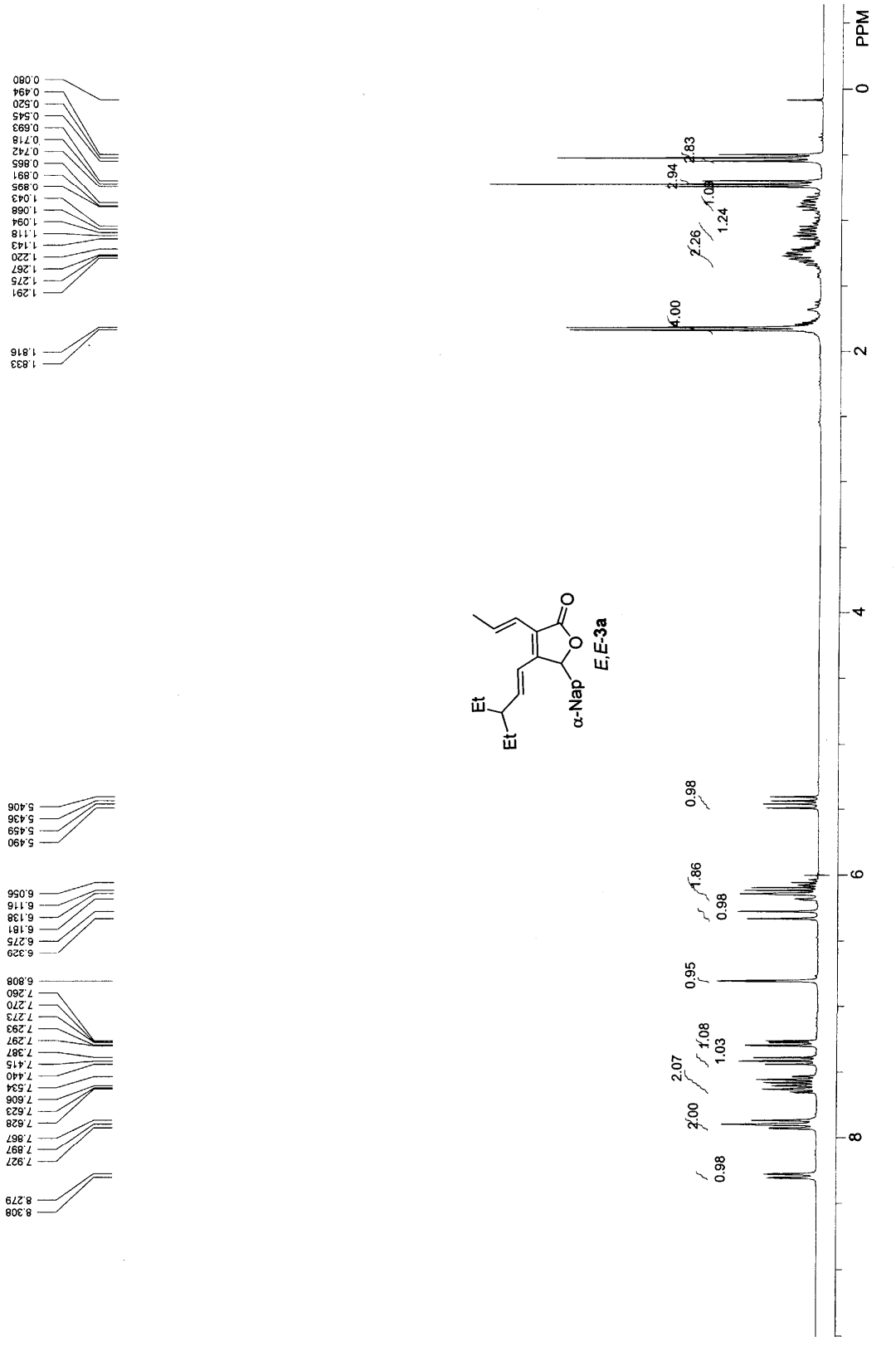
1.946
1.927
1.786
1.765
1.728
1.707
1.351
1.332
1.307
1.287
1.263
1.058
1.034
1.012
0.998
0.951
0.928
0.770
0.743
0.720
0.179
0.154
0.129


Et
Et
α-Nap
O
O
E,Z-3a
1.04
2.07
2.09
0.93
1.06
0.98
1.05
2.07
1.07
6.12
1.14
1.18
2.44
4.33
3.13
9
8
7
6
5
4
3
2
1
0
PPM

10.810
11.680
19.488
26.899
27.128
42.875
76.573
77.000
77.420
78.954
118.354
119.346
122.635
124.406
125.238
125.704
126.047
127.017
128.932
130.001
131.260
131.718
133.840
134.222
145.373
153.242
171.88
Et
Et
α-Nap
O
O
E,Z-3a
ppm
20
40
60
80
100
120
140
160
180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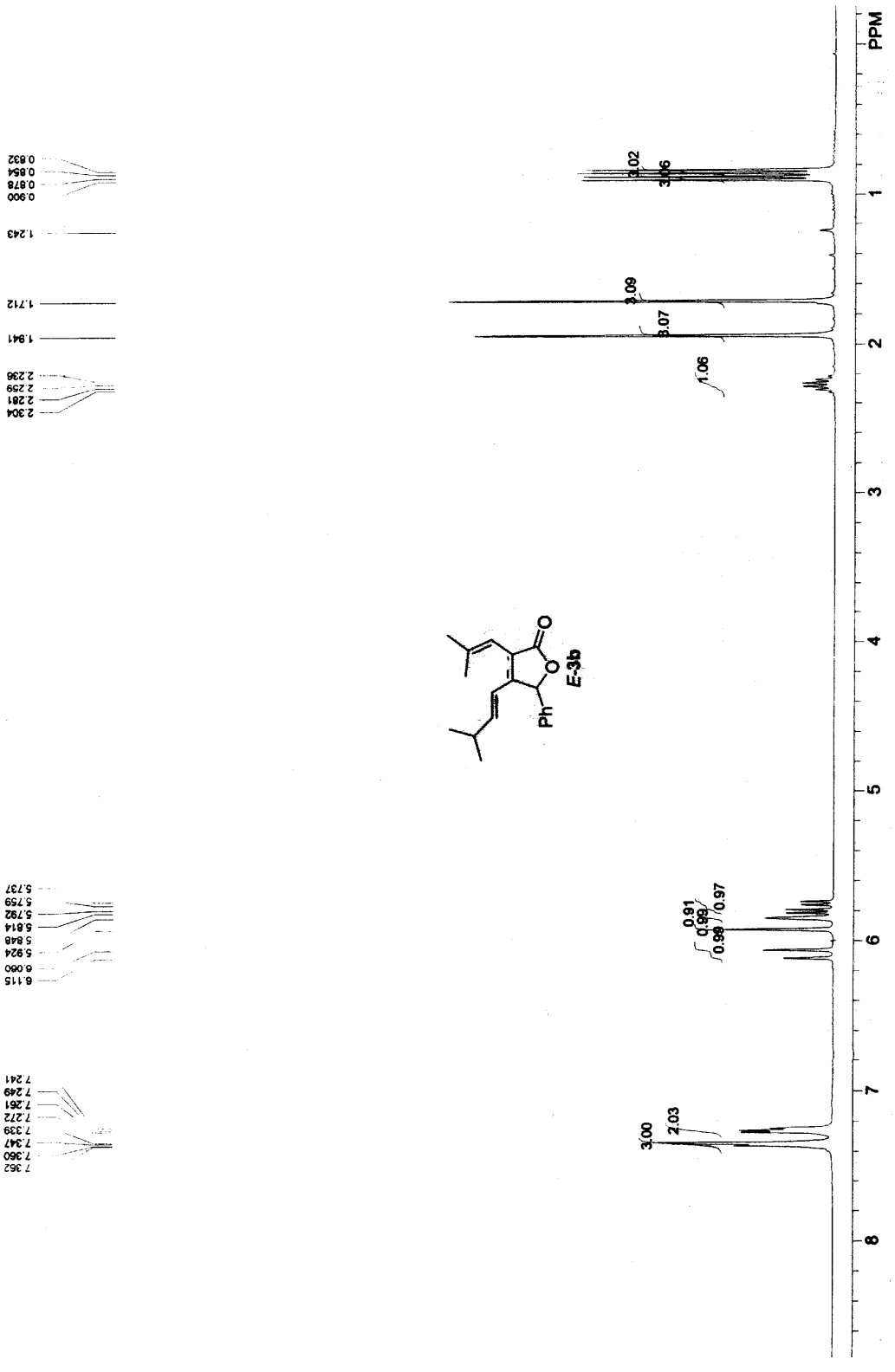
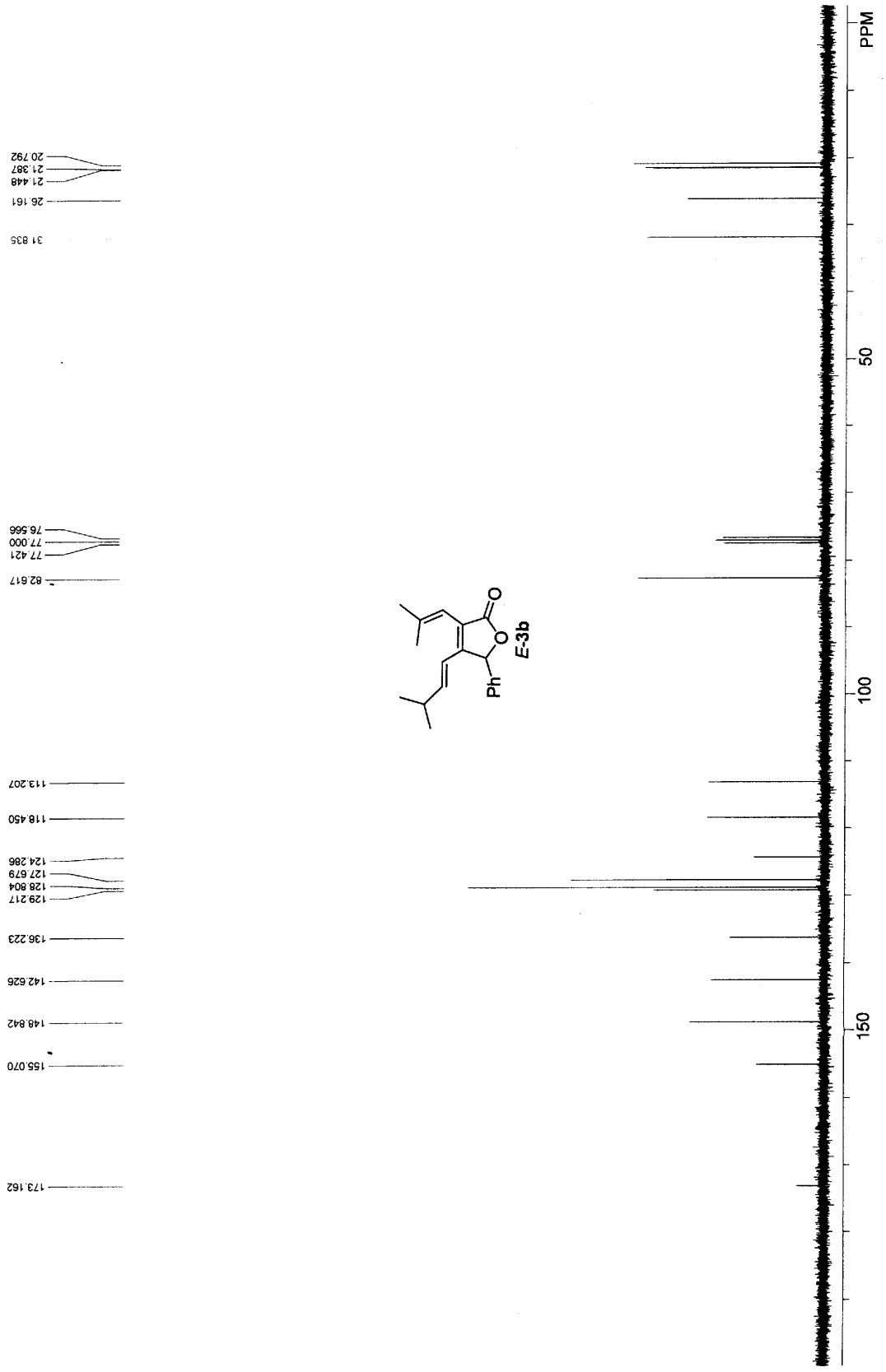
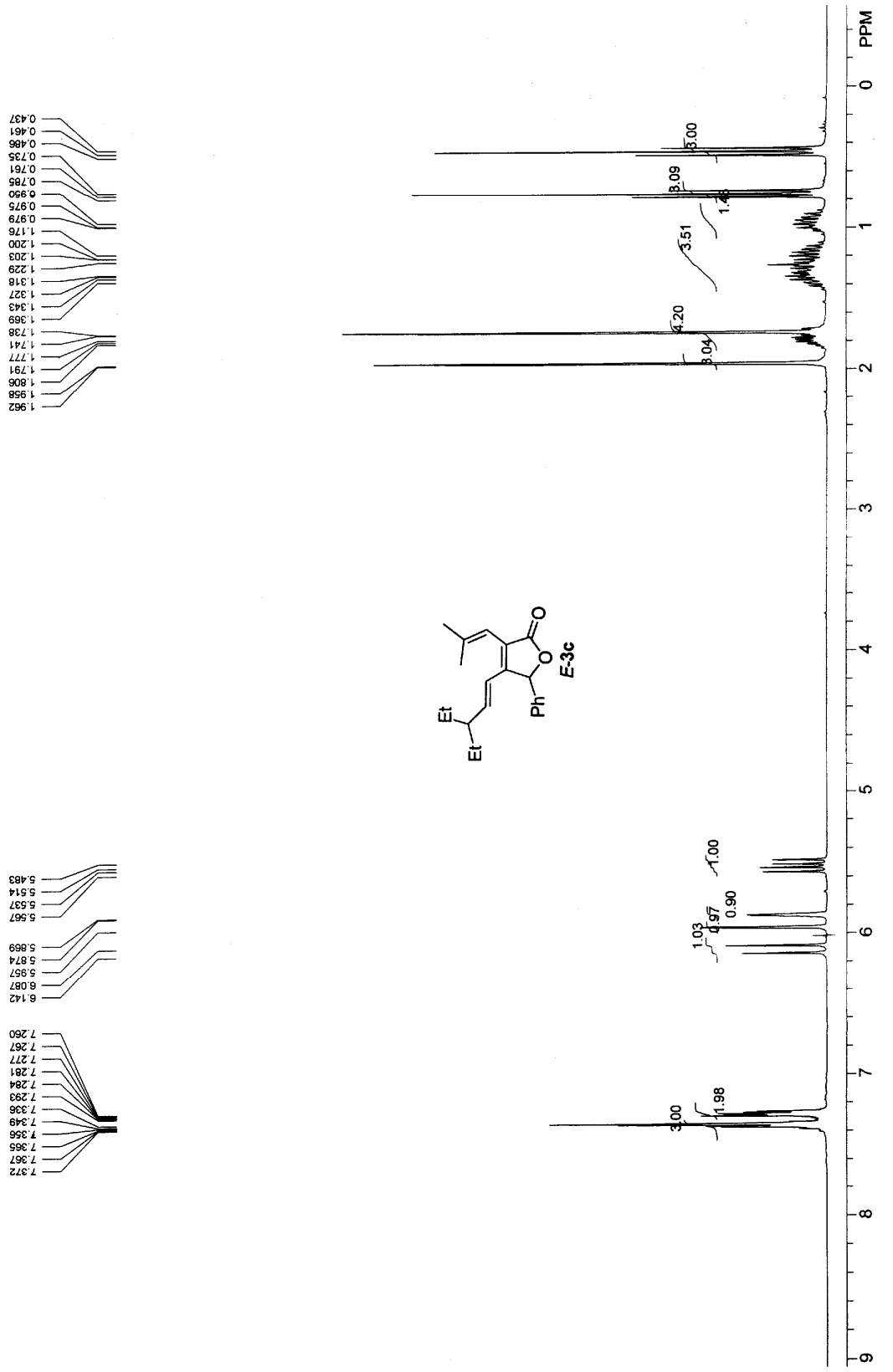
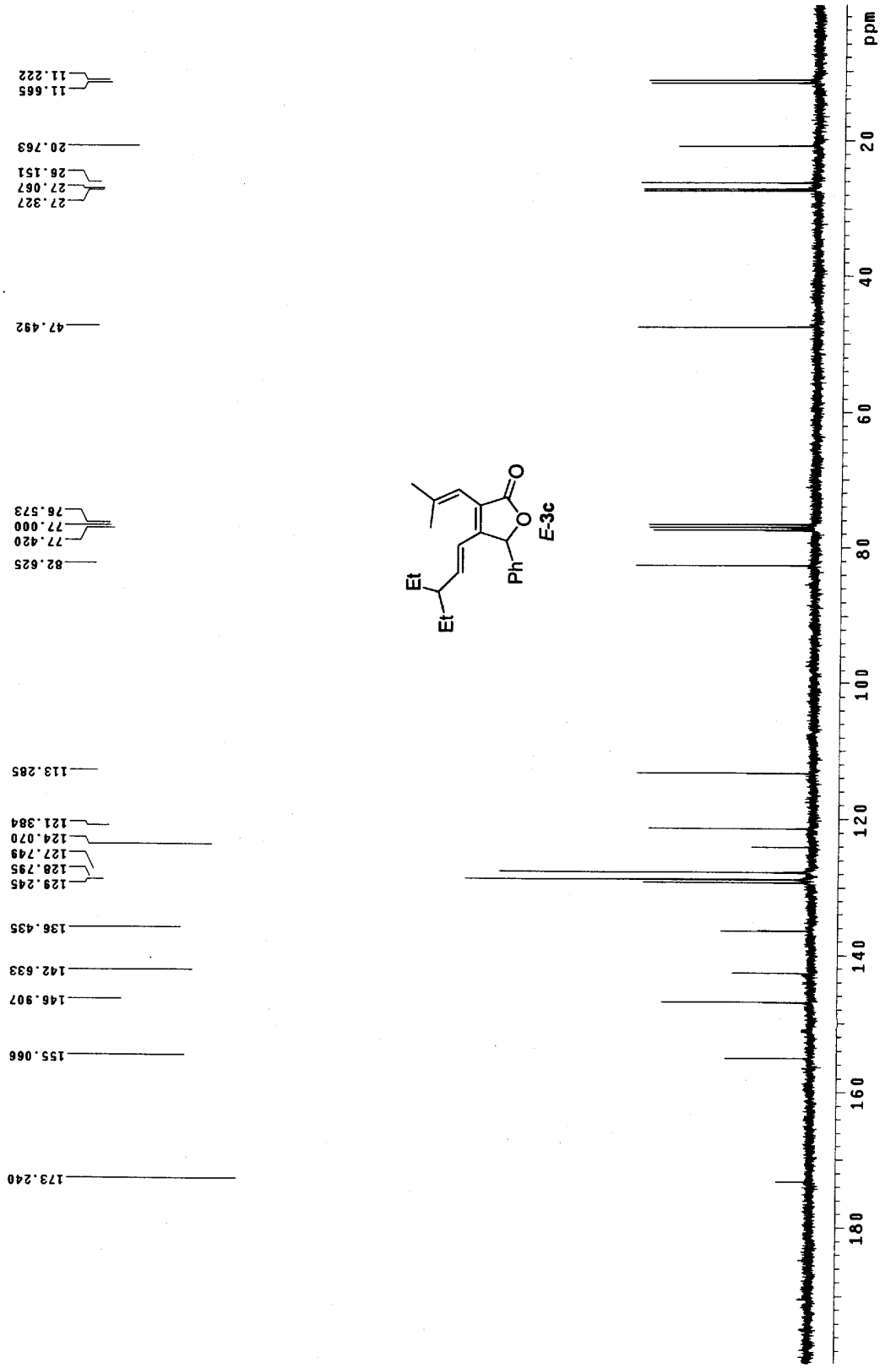
0.494
0.520
0.545
0.693
0.718
0.742
0.865
0.891
0.895
1.043
1.068
1.094
1.118
1.143
1.220
1.267
1.275
1.291
1.816
1.833
5.406
5.436
5.459
5.490
6.056
6.116
6.138
6.181
6.275
6.329
6.808
7.260
7.270
7.273
7.293
7.297
7.387
7.415
7.440
7.534
7.606
7.623
7.628
7.867
7.897
7.927
8.279
8.308
Et
Et
α-Nap
E,E-3a
0.98
1.86
0.98
0.95
2.07
1.08
1.03
2.00
0.98
4.00
2.26
1.24
1.08
2.94
2.83
PPM
0
2
4
6
8

11.474
11.695
16.122
26.930
27.212
47.630
76.573
77.000
77.420
78.786
118.285
121.735
123.017
124.170
125.032
126.062
126.345
126.948
128.887
130.108
131.833
131.917
133.573
133.825
147.915
155.769
172.637
Et
Et
α-Nap
E,E-3a
ppm
20
40
60
80
100
120
140
160
180
200


PPM
1
2
3
4
5
6
7
8
3.02
3.06
3.09
3.07
1.06
0.91
0.99
0.99
0.97
3.00
2.03
O
O
Ph
E-3b
0.900
0.878
0.854
0.832
1.243
1.712
1.841
2.236
2.259
2.281
2.304
5.737
5.759
5.792
5.814
5.848
5.924
6.060
6.115
7.241
7.249
7.261
7.272
7.339
7.347
7.360
7.362


20.792
21.387
21.448
26.161
31.835
76.566
77.000
77.421
82.617
113.207
118.450
124.286
127.679
128.804
129.217
136.223
142.626
148.842
155.070
173.162
O
O
Ph
E-3b
PPM
50
100
150


E-3c
Et
Et
Ph
O
O
PPM
0
1
2
3
4
5
6
7
8
9
3.00
1.98
1.03
0.97
0.90
1.00
4.20
3.04
3.51
8.09
1.46
3.00
7.372
7.367
7.365
7.356
7.349
7.336
7.293
7.284
7.281
7.277
7.267
7.260
8.142
6.087
5.957
5.874
5.869
5.567
5.537
5.514
5.483
1.962
1.958
1.806
1.791
1.777
1.741
1.736
1.369
1.343
1.327
1.318
1.229
1.203
1.200
1.176
0.979
0.975
0.930
0.785
0.761
0.735
0.486
0.461
0.437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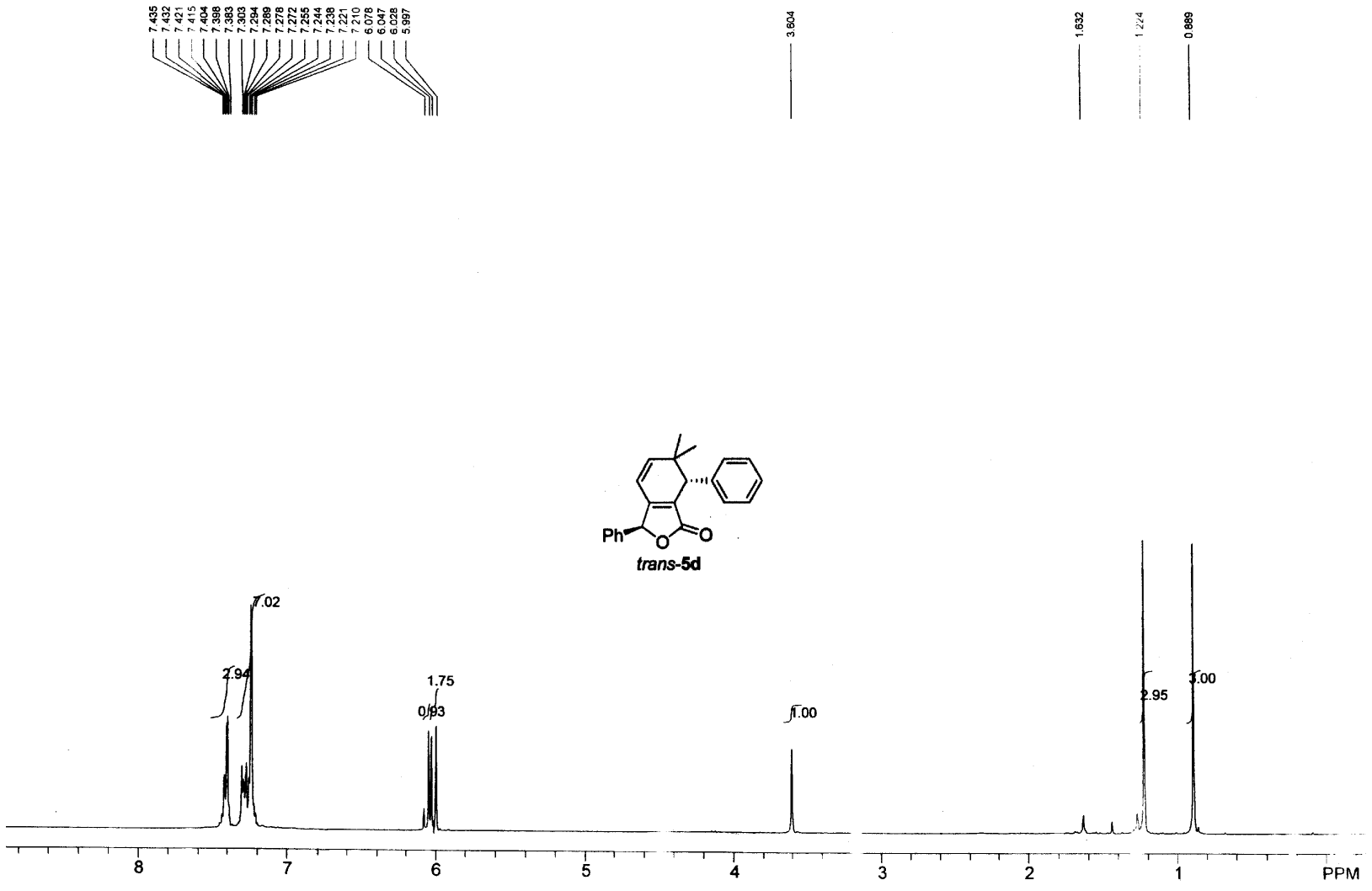
11.665
20.763
26.151
27.067
27.327
47.492
76.573
77.000
77.420
82.625
113.285
121.384
124.070
127.749
128.795
129.245
136.435
142.633
146.907
155.066
173.240
Et
Et
Ph
O
O
E-3c
ppm
20
40
60
80
100
120
140
160
180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7.432
7.421
7.415
7.404
7.398
7.383
7.303
7.294
7.289
7.278
7.272
7.255
7.244
7.238
7.221
7.210
6.078
6.047
6.028
5.997
3.804
1.632
1.224
0.889
Ph
O
O
trans-5d
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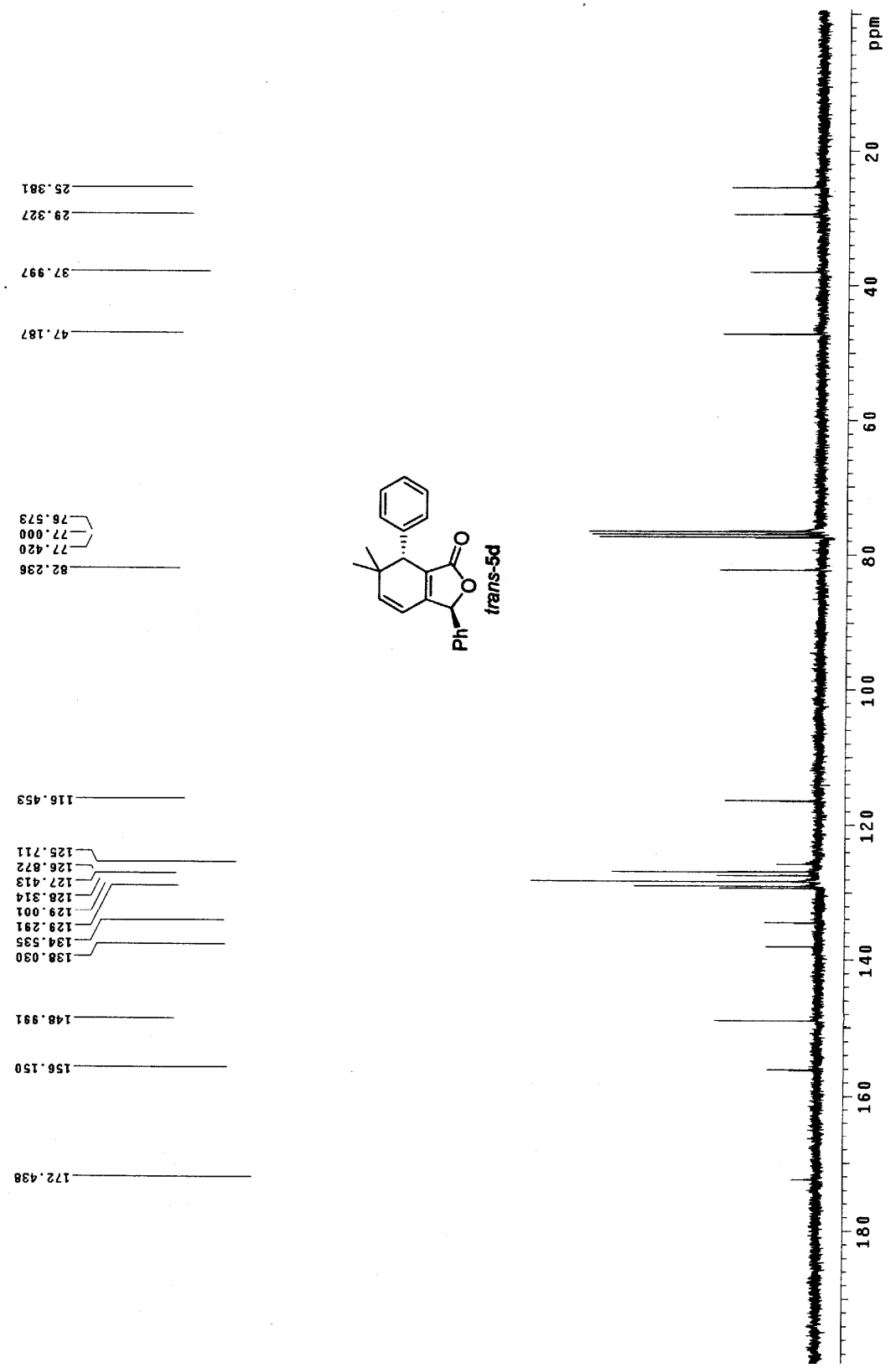
0.93
1.00
2.95
3.00
8
7
6
5
4
3
2
1
PPM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76.573
77.000
77.420
82.236
116.453
125.711
126.872
127.413
128.314
129.001
129.291
134.535
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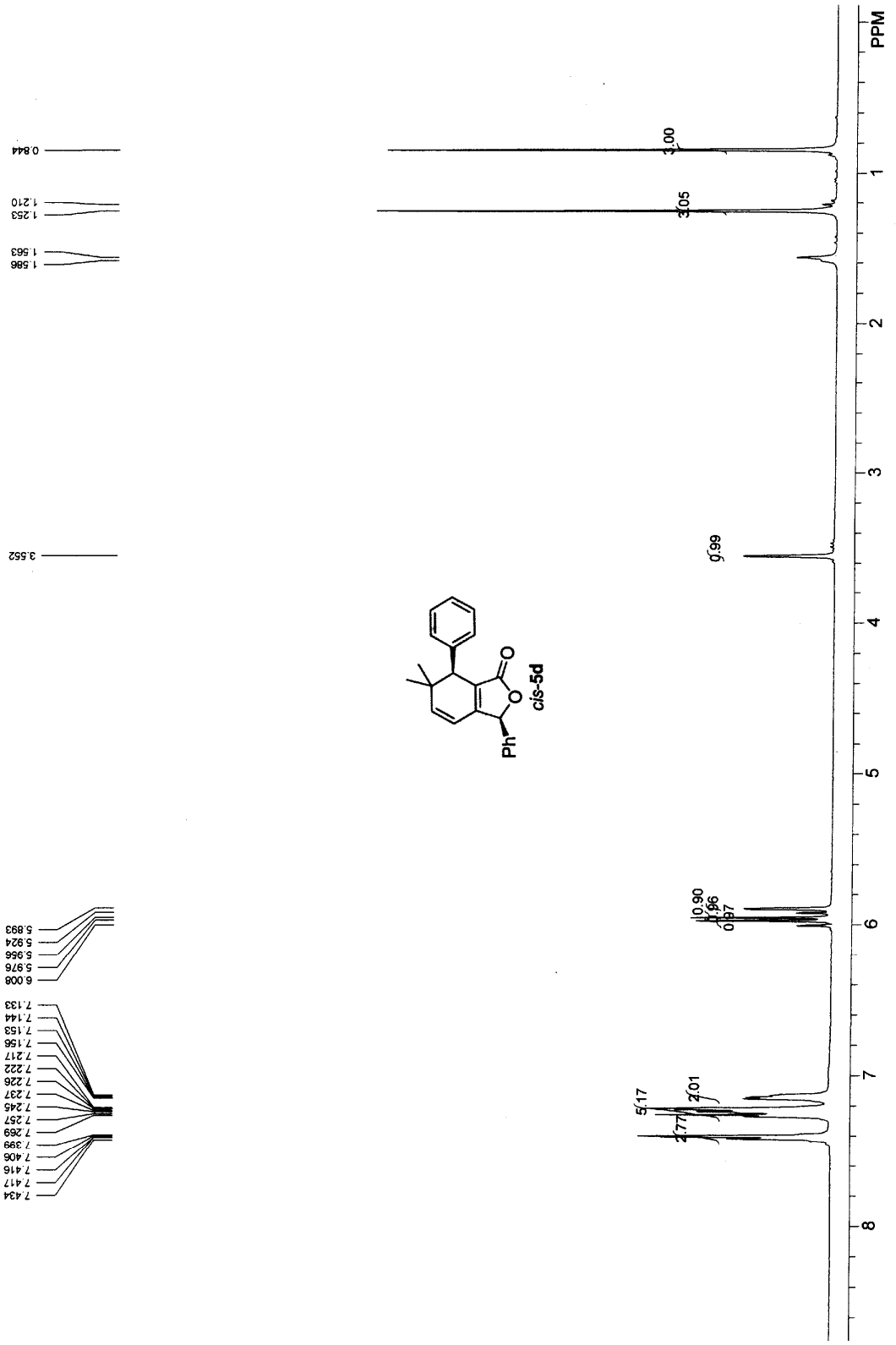
156.150
172.438
Ph
trans-5d
ppm
20
40
60
80
100
120
140
160
180


PPM
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2
3
4
5
6
7
8
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3.05
6.99
10.90
0.96
0.87
5.17
2.01
2.77
cis-5d
Ph
O
O
0.844
1.210
1.253
1.563
1.586
3.552
5.893
5.924
5.956
5.976
6.008
7.133
7.144
7.153
7.156
7.217
7.222
7.226
7.237
7.245
7.257
7.269
7.399
7.406
7.416
7.417
7.434

25.426
29.456
38.089
46.653
76.573
77.000
77.420
82.175
116.232
125.376
126.788
127.398
128.245
128.352
129.039
129.283
134.726
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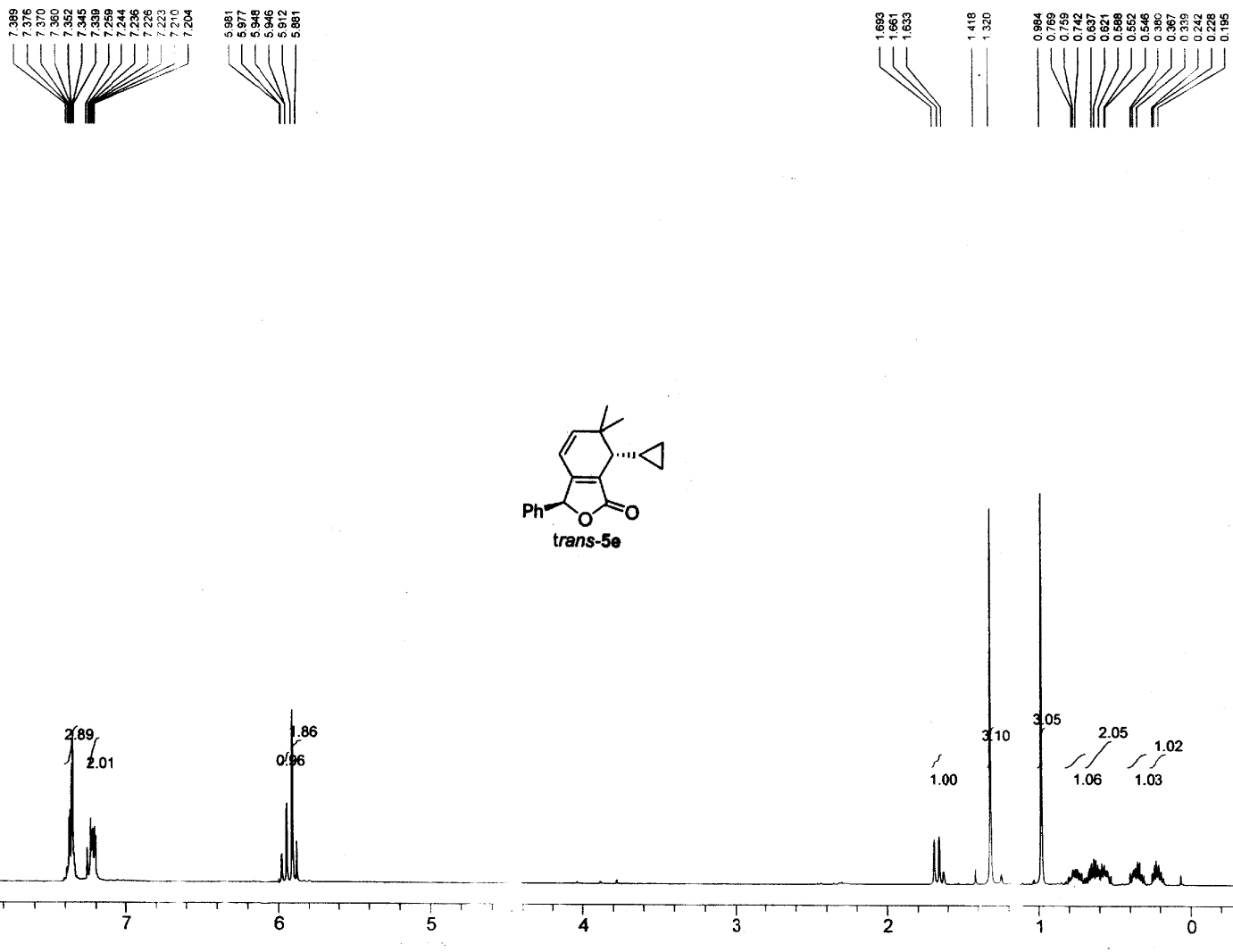
156.150
172.606
Ph
cis-5d
ppm
20
40
60
80
100
120
140
160
180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7.345
7.339
7.259
7.244
7.236
7.226
7.223
7.210
7.204
5.981
5.977
5.948
5.946
5.912
5.881
1.693
1.661
1.633
1.418
1.320
0.984
0.769
0.759
0.742
0.637
0.621
0.588
0.552
0.546
0.380
0.367
0.339
0.242
0.228
0.195
Ph
O
O
trans-5e
2.89
2.01
1.86
0.96
1.00
3.10
3.05
2.05
1.06
1.02
1.03
8
7
6
5
4
3
2
1
0
PPM

1.918
6.589
10.787
25.106
27.060
38.074
45.691
76.573
77.000
77.420
82.244
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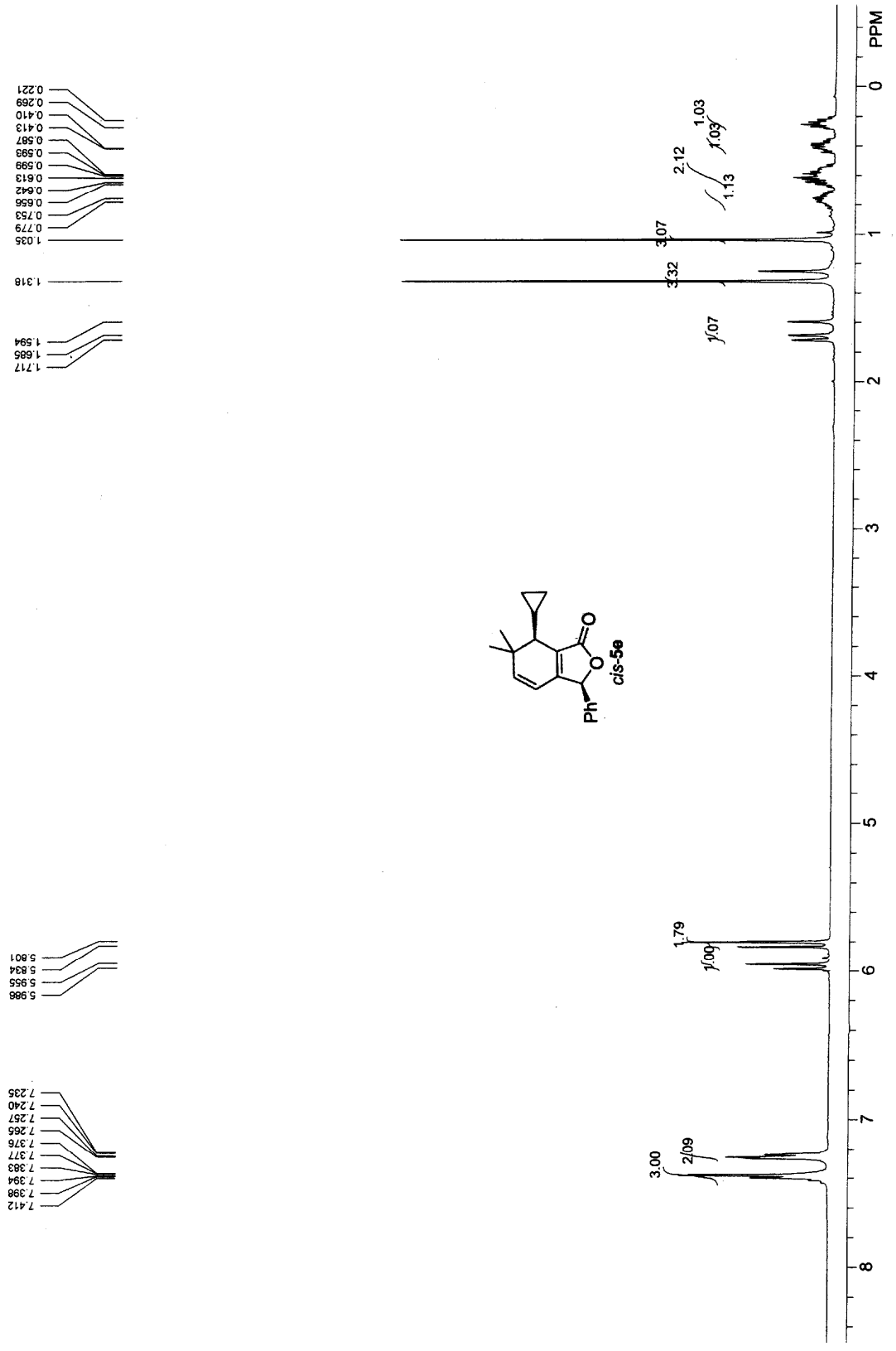
126.864
128.932
129.184
134.733
148.945
155.563
173.499
Ph
trans-5e
ppm


0.221
0.269
0.410
0.413
0.587
0.589
0.599
0.613
0.642
0.656
0.753
0.779
1.035
1.318
1.594
1.685
1.717
5.801
5.834
5.955
5.986
7.235
7.240
7.257
7.265
7.376
7.377
7.383
7.394
7.398
7.412
3.00
2.09
1.79
1.00
1.07
3.07
3.32
2.12
1.13
1.03
1.03
cis-5e
Ph
O
O
PPM
0
1
2
3
4
5
6
7
8

1.628
6.467
10.886
25.083
27.159
38.112
45.080
76.580
77.000
77.427
82.045
115.987
125.856
126.963
129.016
129.276
134.794
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155.395
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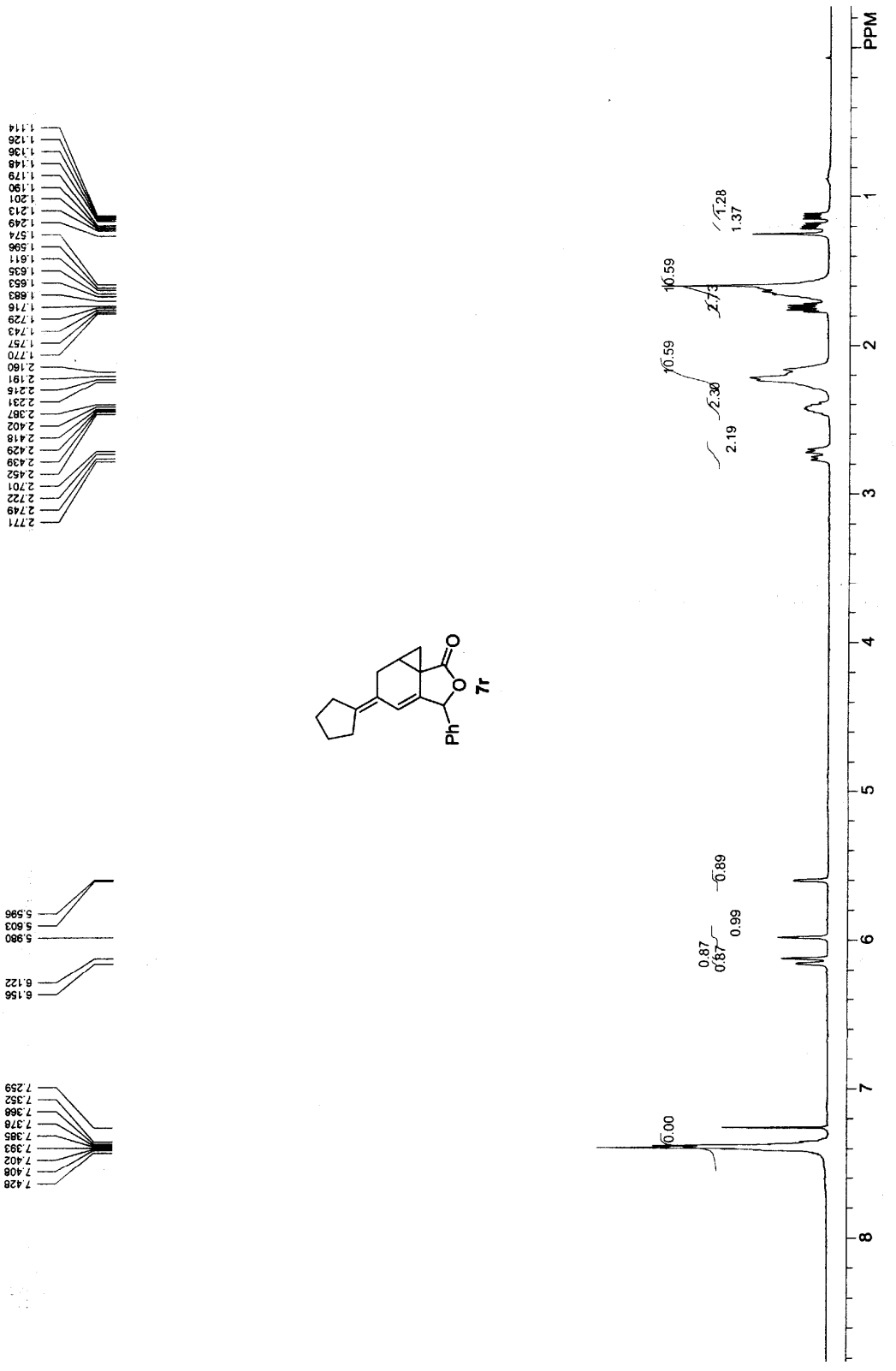
Ph
O
O
cis-5e
0
20
40
60
80
100
120
140
160
180
ppm


7r
Ph
O
O
PPM
1 2 3 4 5 6 7 8
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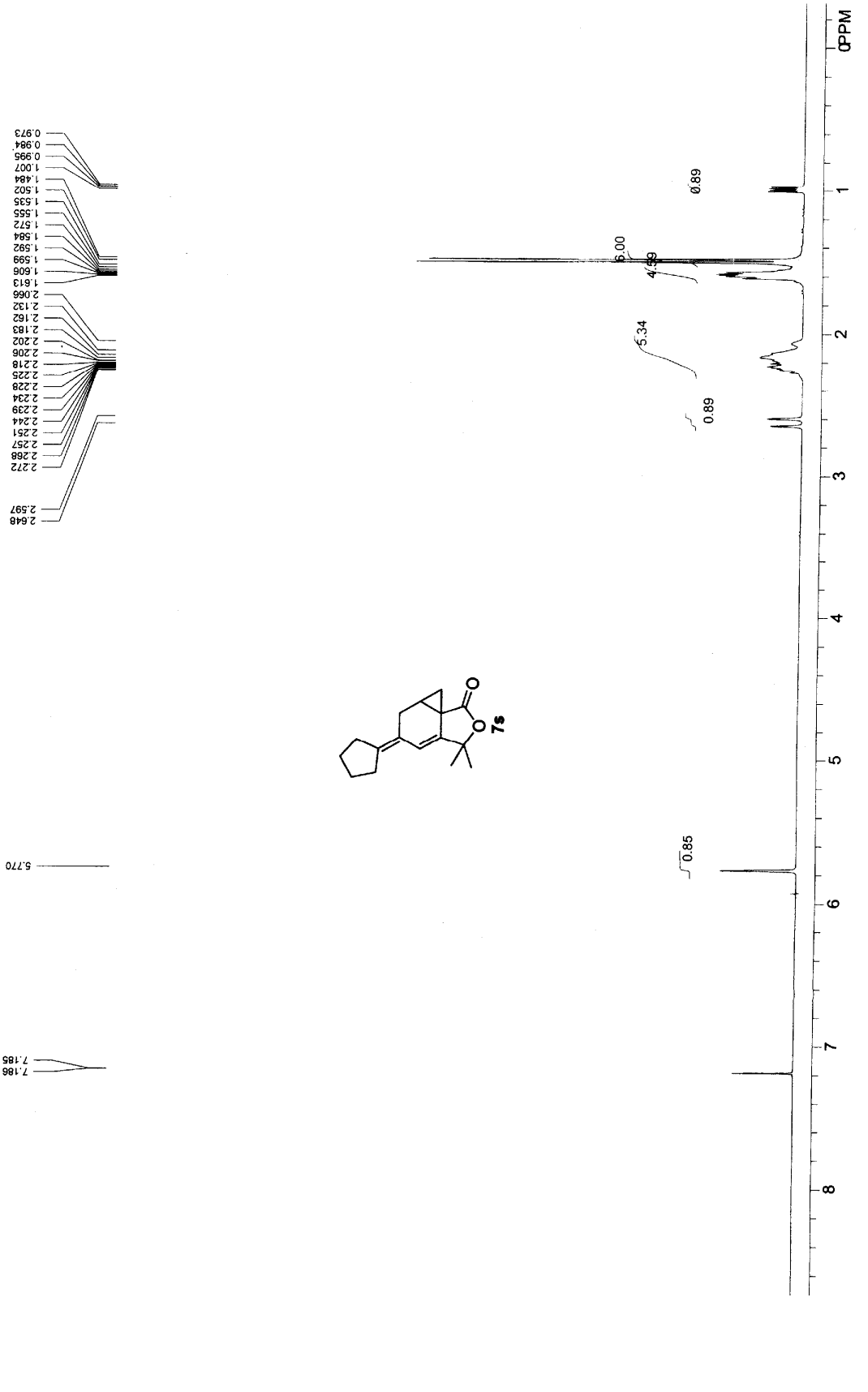
0.87
0.87
0.99
0.89
10.59
2.30
2.19
10.59
2.13
1.28
1.37
7.428 7.408 7.402 7.393 7.385 7.378 7.368 7.352 7.259
6.156 6.122
5.980 5.603 5.586
2.771 2.749 2.722 2.701 2.452 2.439 2.429 2.418 2.402 2.387 2.231 2.215 2.191 2.160 1.770 1.757 1.743 1.729 1.716 1.683 1.653 1.635 1.611 1.596 1.574 1.249 1.213 1.201 1.190 1.179 1.148 1.136 1.126 1.114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1.502
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1.555
1.572
1.584
1.592
1.599
1.606
1.613
2.066
2.132
2.162
2.183
2.202
2.206
2.218
2.225
2.228
2.234
2.239
2.244
2.251
2.257
2.268
2.272
2.597
2.648
5.770
7.185
7.186
7s
0.85
0.89
5.34
4.89
6.00
0.89
PPM

177.277
143.801
142.358
119.460
112.774
85.999
77.427
77.008
76.580
80.922
30.723
28.976
27.106
26.442
26.296
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25.014
24.541
24.083
7s
ppm
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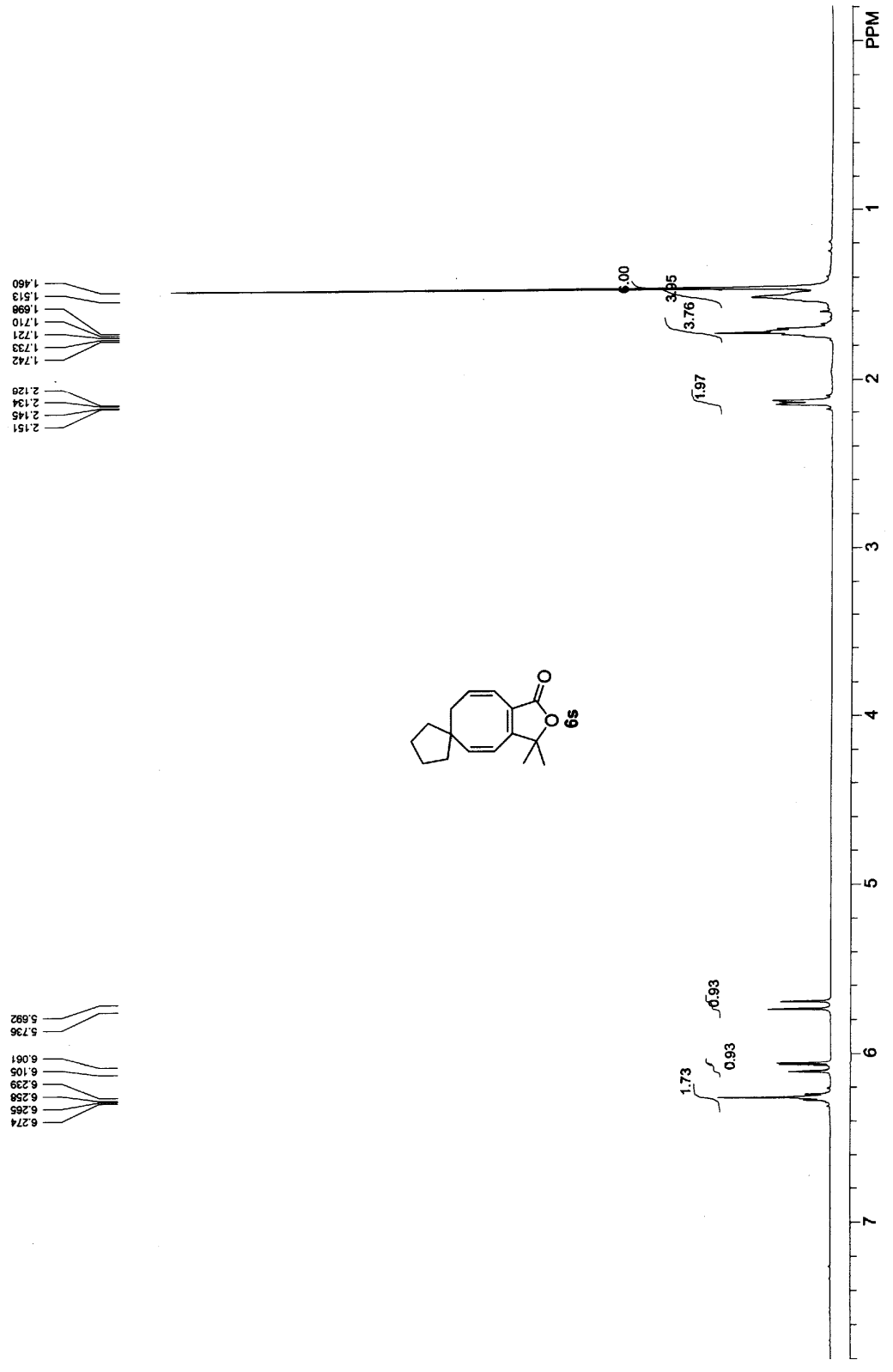
160
140
120
100
80
60
40
20


PPM
1
2
3
4
5
6
7
6.00
3.95
3.76
1.97
0.93
0.93
1.73
6s
1.460
1.513
1.698
1.710
1.721
1.733
1.742
2.126
2.134
2.145
2.151
5.692
5.736
6.061
6.105
6.239
6.258
6.265
6.274

24.136
25.602
34.517
42.615
51.301
76.573
77.000
77.420
85.793
114.018
121.277
122.269
137.572
152.830
160.982
171.599
6s
ppm
20
40
60
80
100
120
140
160
180


7.546
7.538
7.531
7.517
7.510
7.504
7.283
7.261
7.256
7.232
7.227
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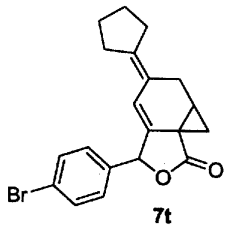
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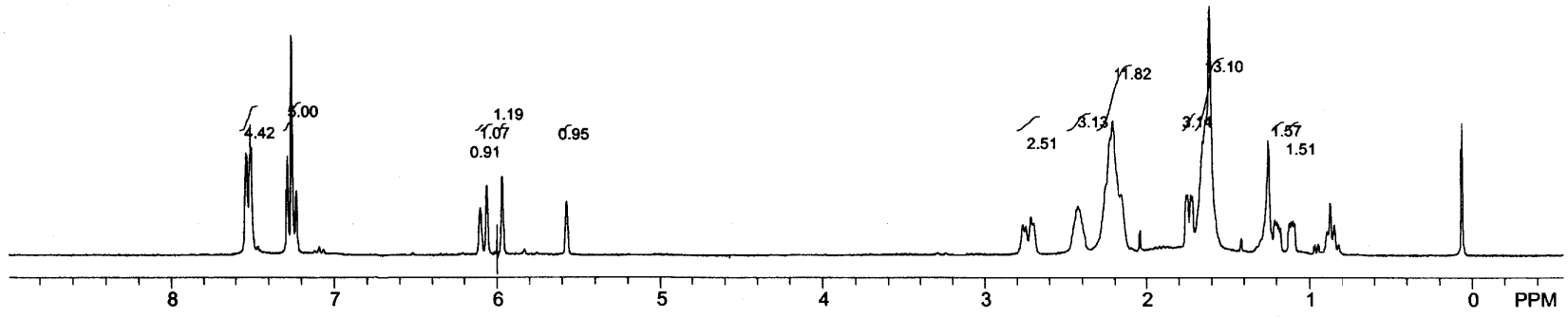
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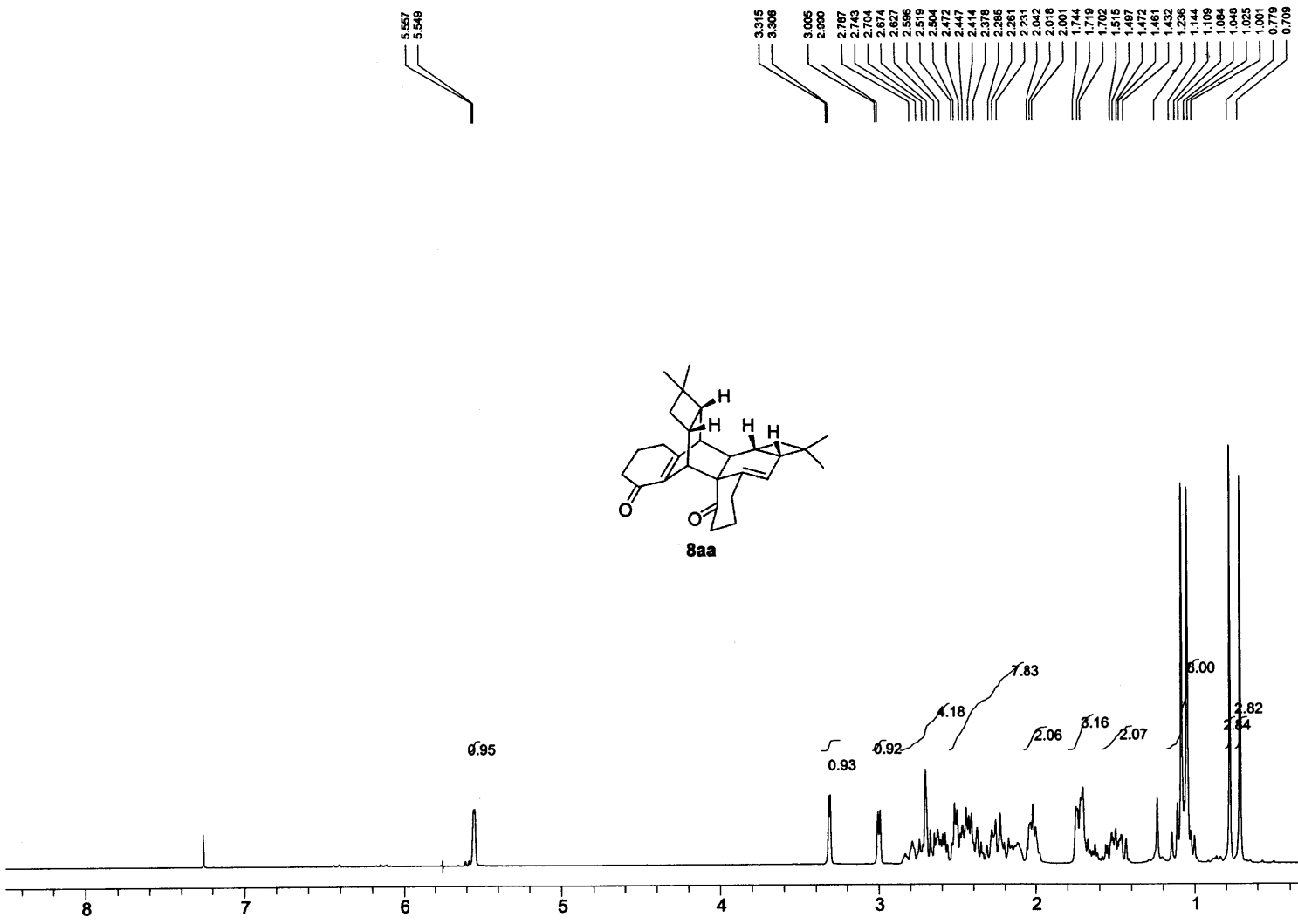
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1.025
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H
H
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O
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PPM

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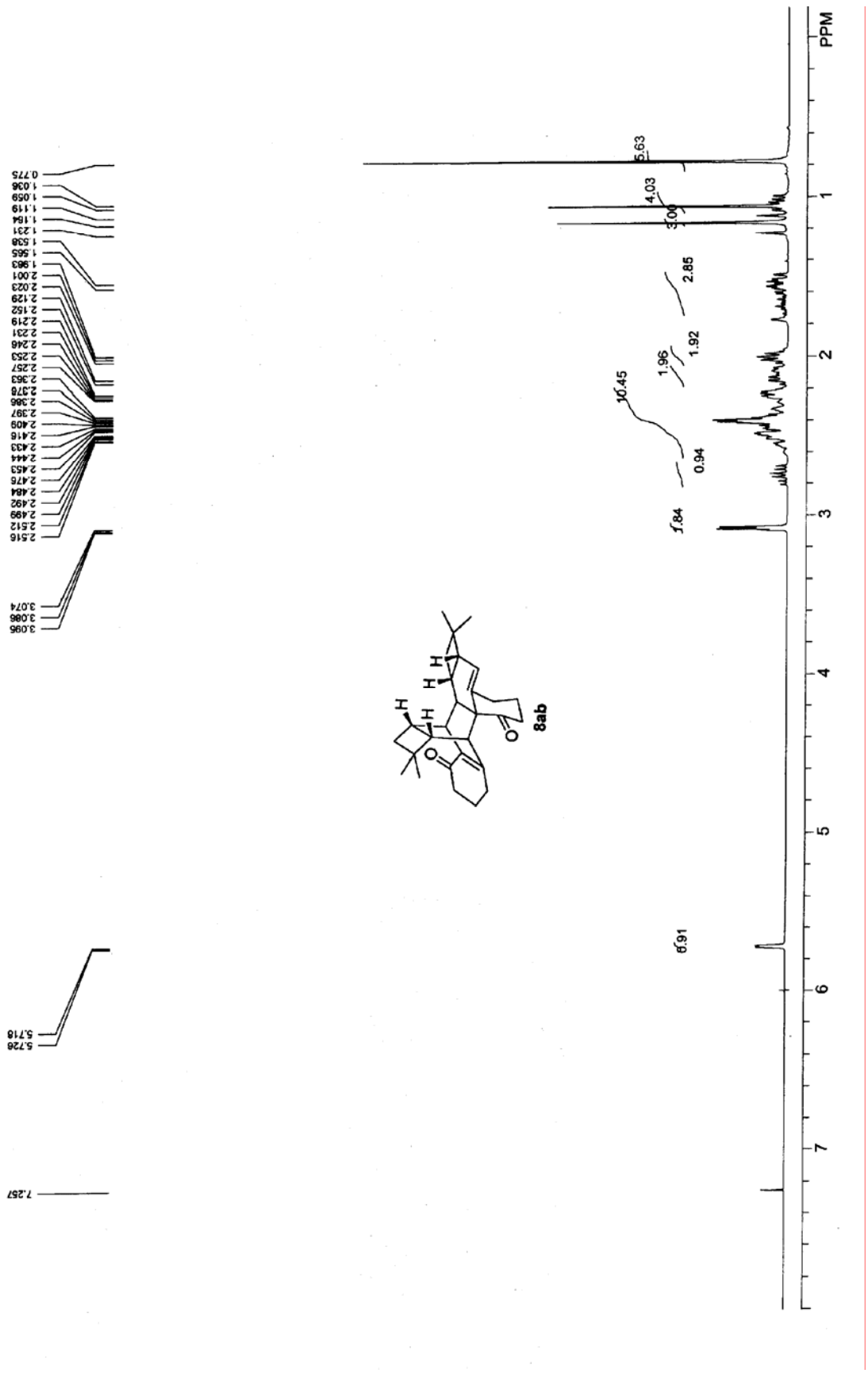
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8ab
PPM

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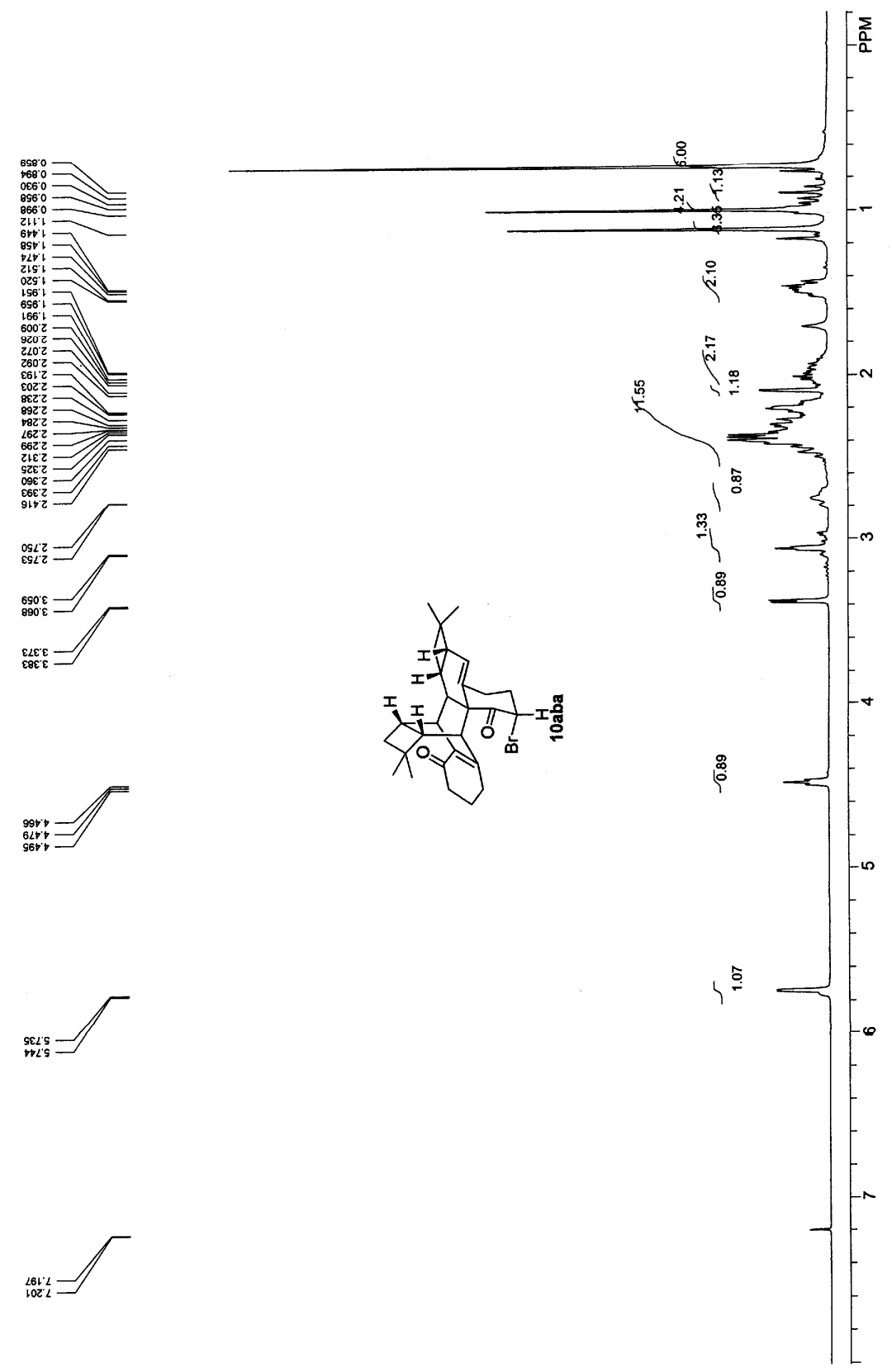
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0.894
0.930
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2.299
2.312
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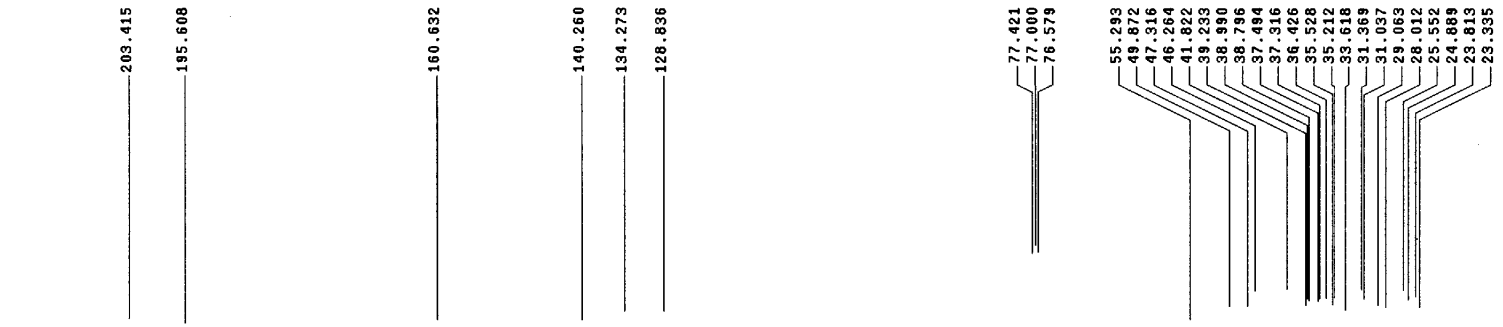
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46.264
41.822
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38.796
37.494
37.316
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35.212
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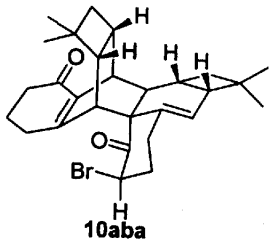
24.889
23.813
23.335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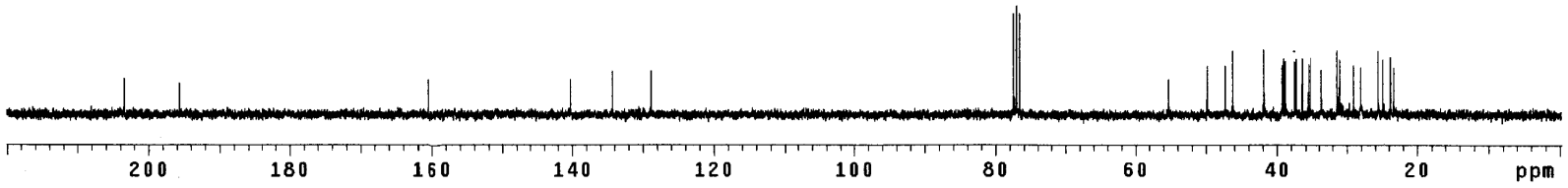
O
O
Br
H

10aba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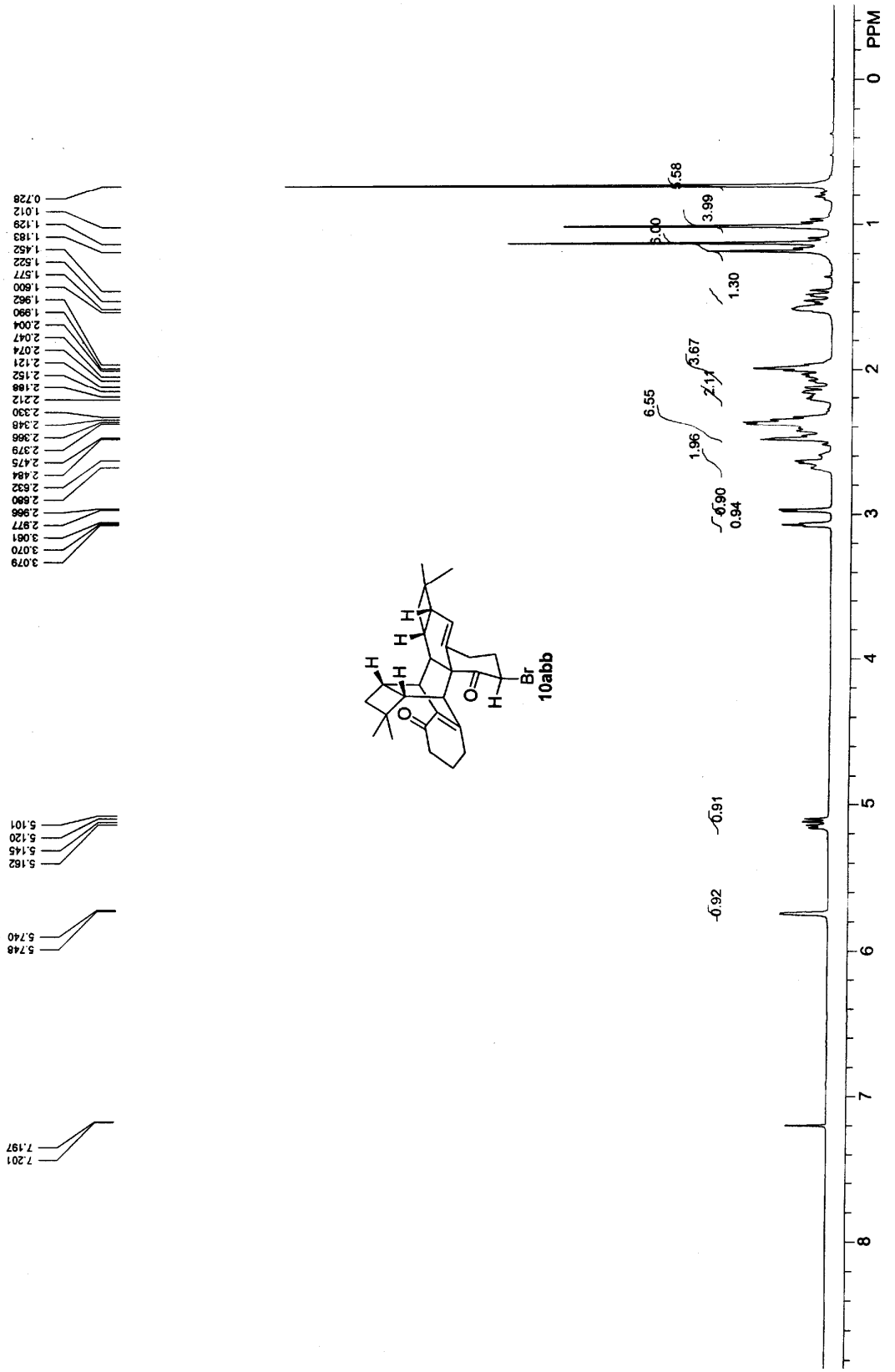
ppm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6.55
1.96
0.90
0.94
0.91
0.92
Br
10abb
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1.012
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1.577
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2.366
2.379
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2.632
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2.966
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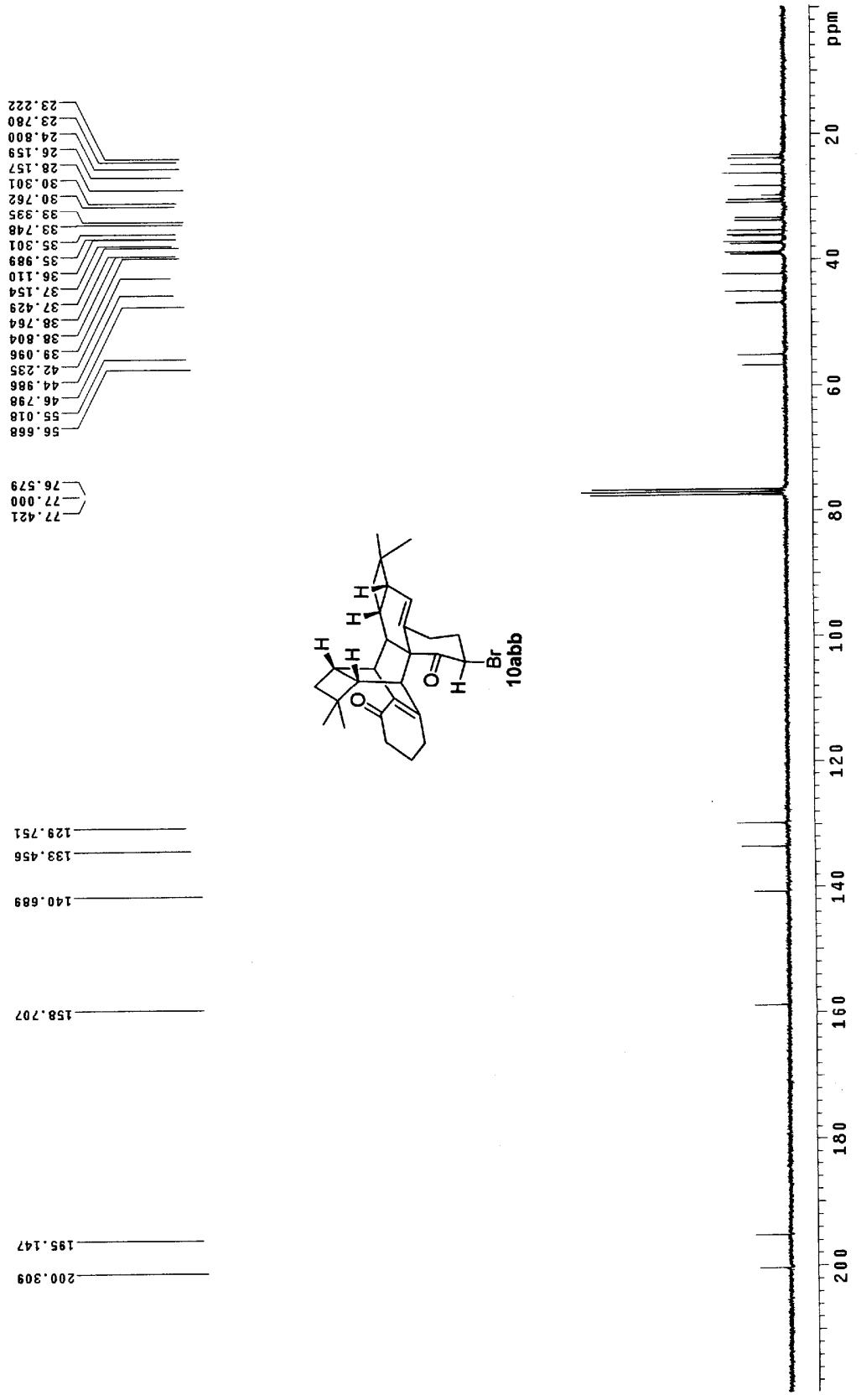
7.201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77.000
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180
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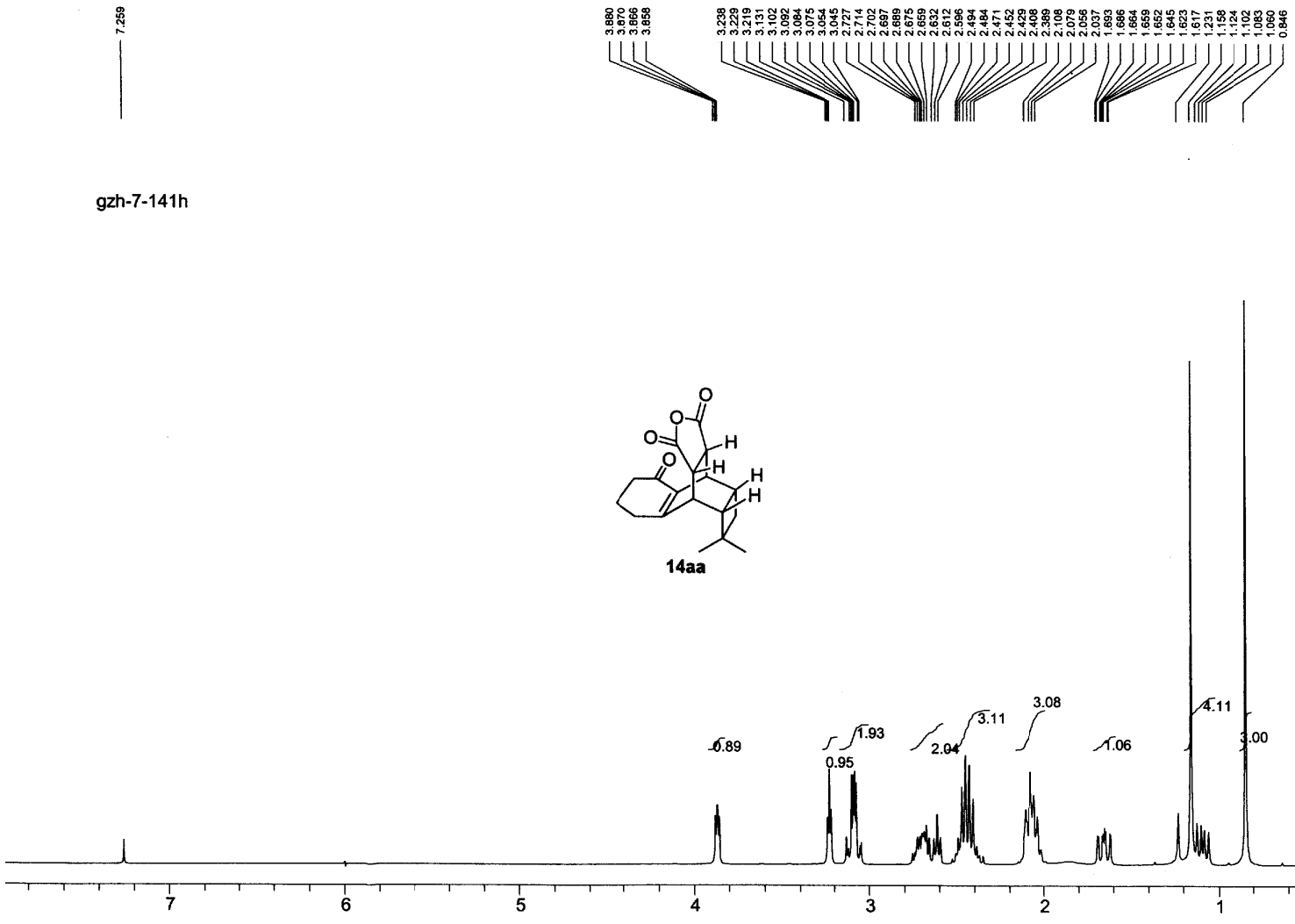
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2.596
2.494
2.484
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1.158
1.124
1.102
1.083
1.060
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O
O
O
H
H
H
H
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0.95
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3.08
1.06
4.11
3.00
7
6
5
4
3
2
1
PPM


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76.573
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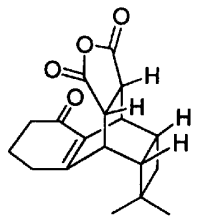
22.999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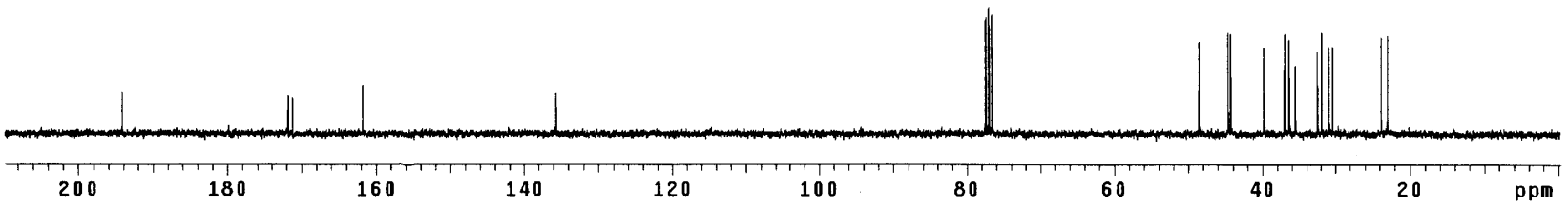
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140
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100
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40
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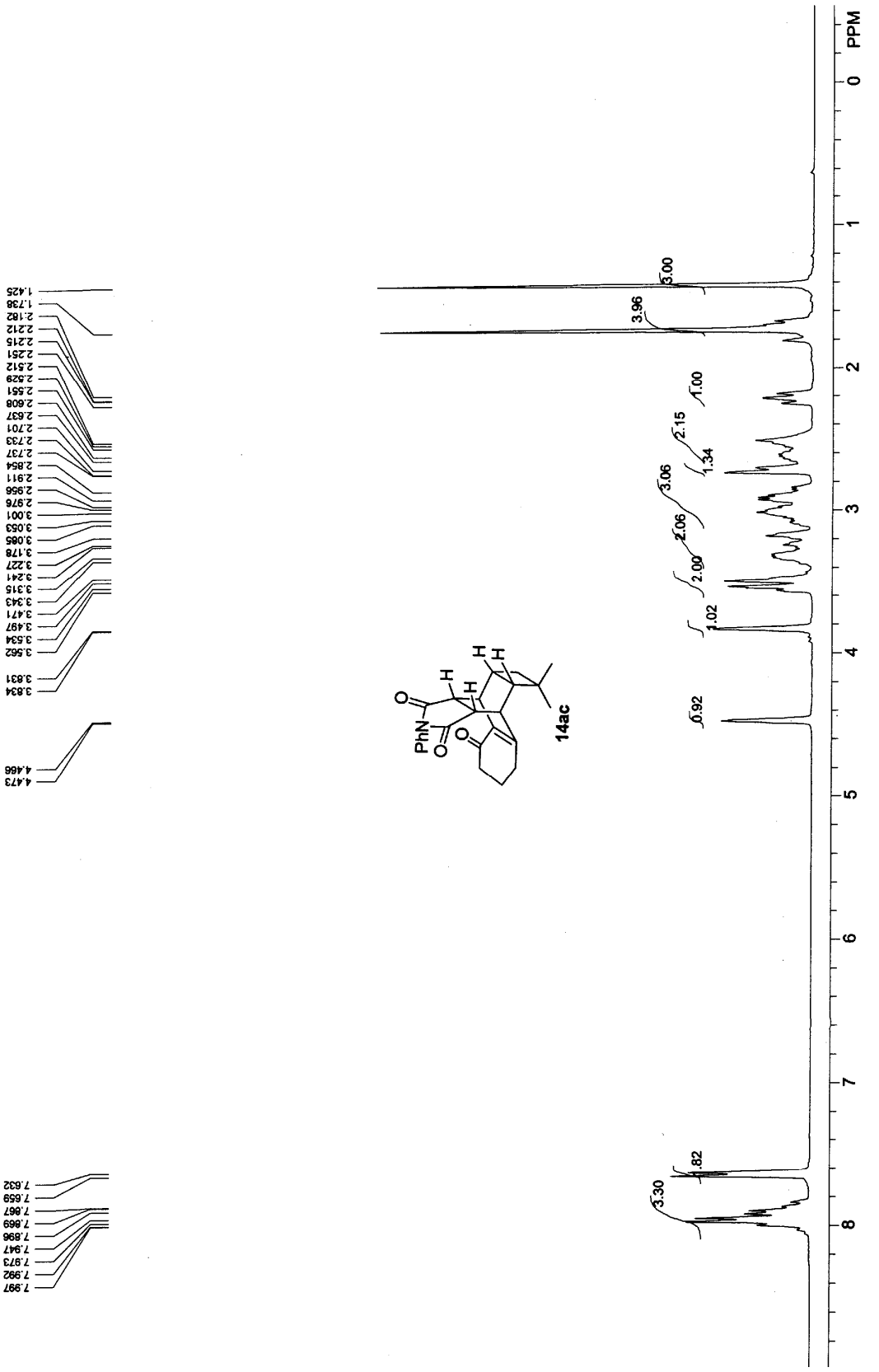
ppm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3.06
2.06
2.00
1.02
6.92
1.82
3.30
PhN
O
O
O
H
H
H
H
14ac
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1.738
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2.551
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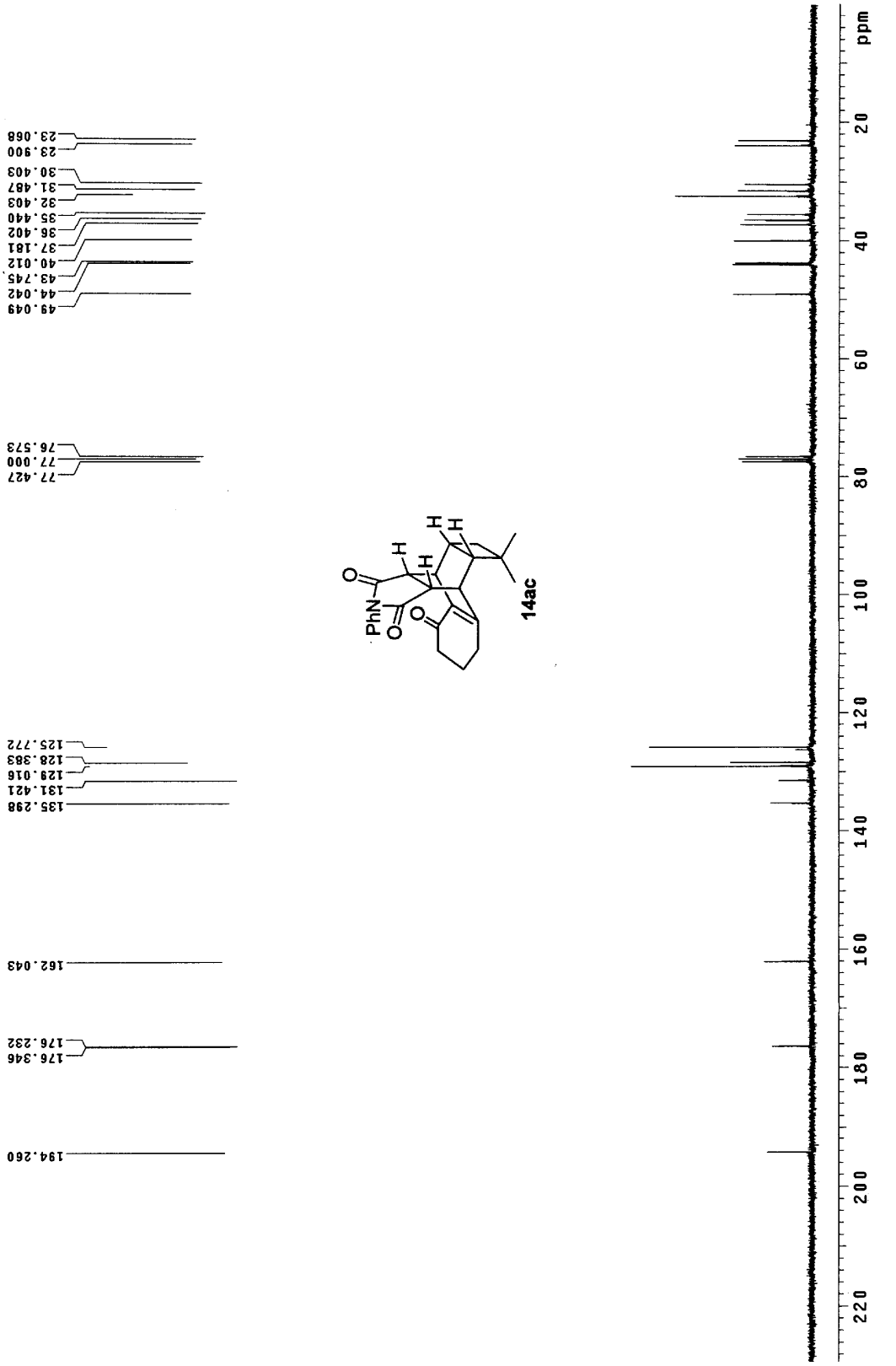
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77.427
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128.383
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131.421
135.298
162.043
176.232
176.346
194.260
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H
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ppm
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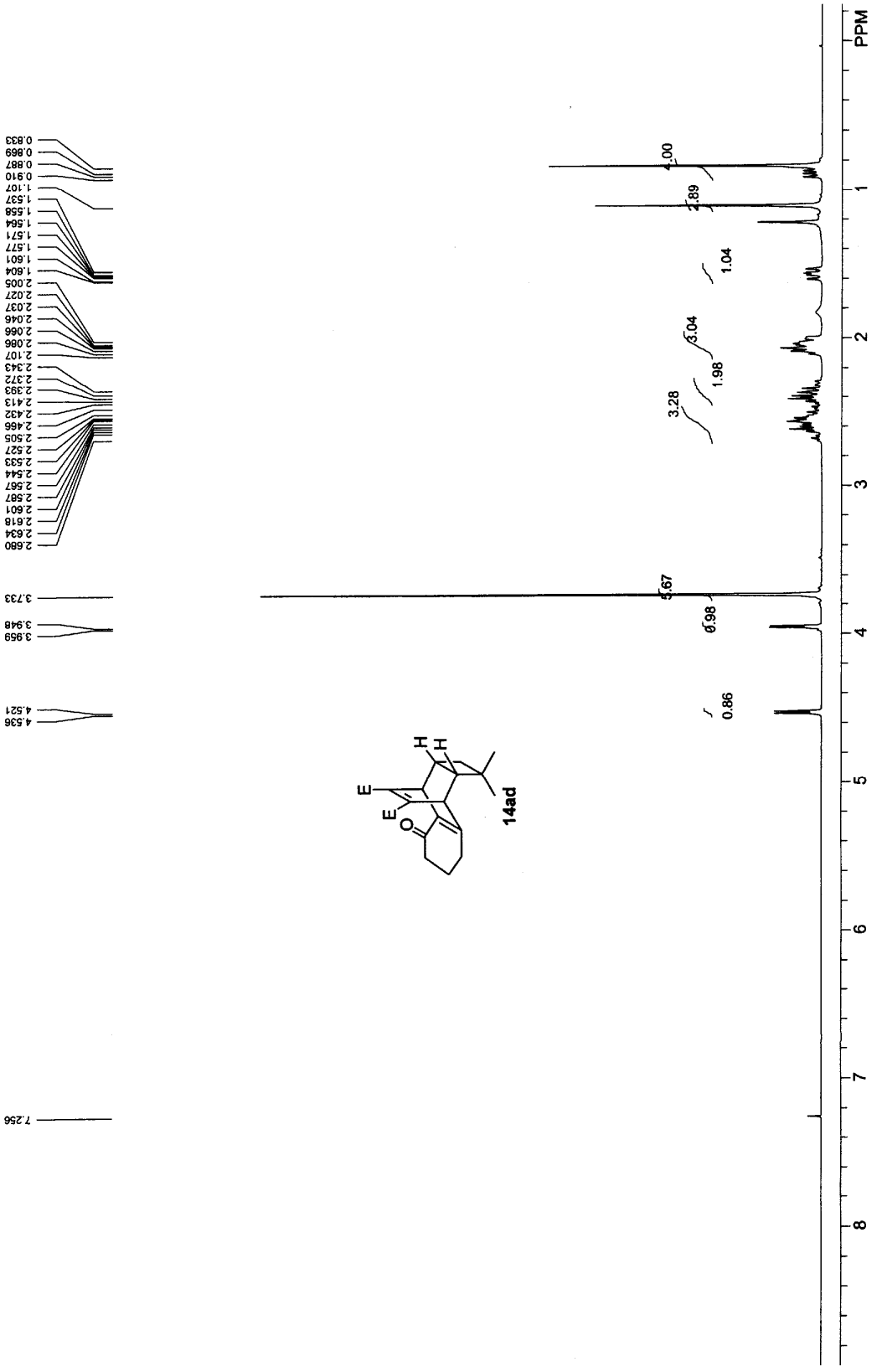
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1.601
1.604
2.005
2.027
2.037
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2.107
2.343
2.372
2.393
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2.432
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2.587
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3.959
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4.536
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2.89
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3.04
1.98
3.28
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E
E
O
H
H
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PPM
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6
7
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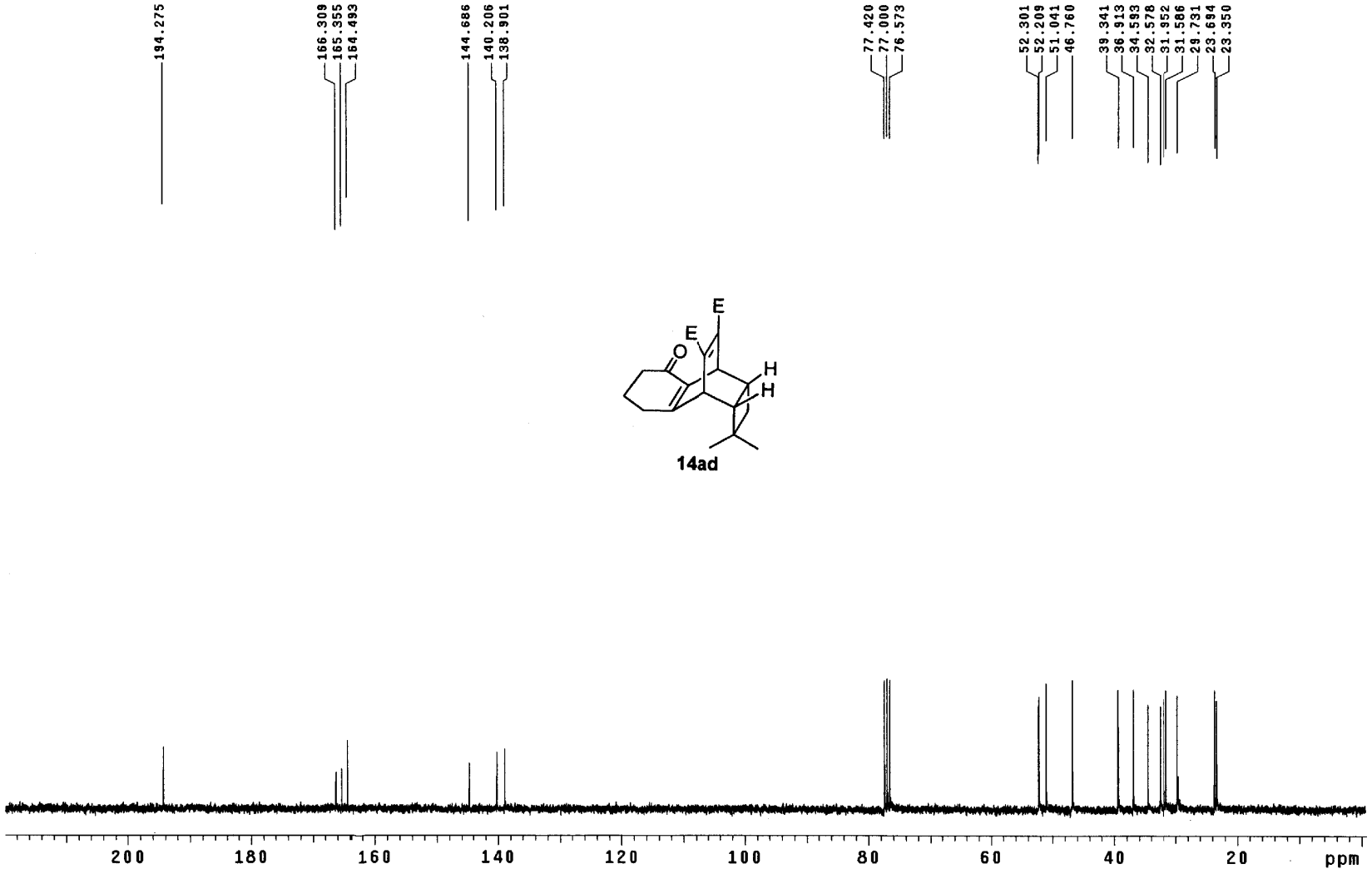
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34.593
32.578
31.952
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29.731
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E
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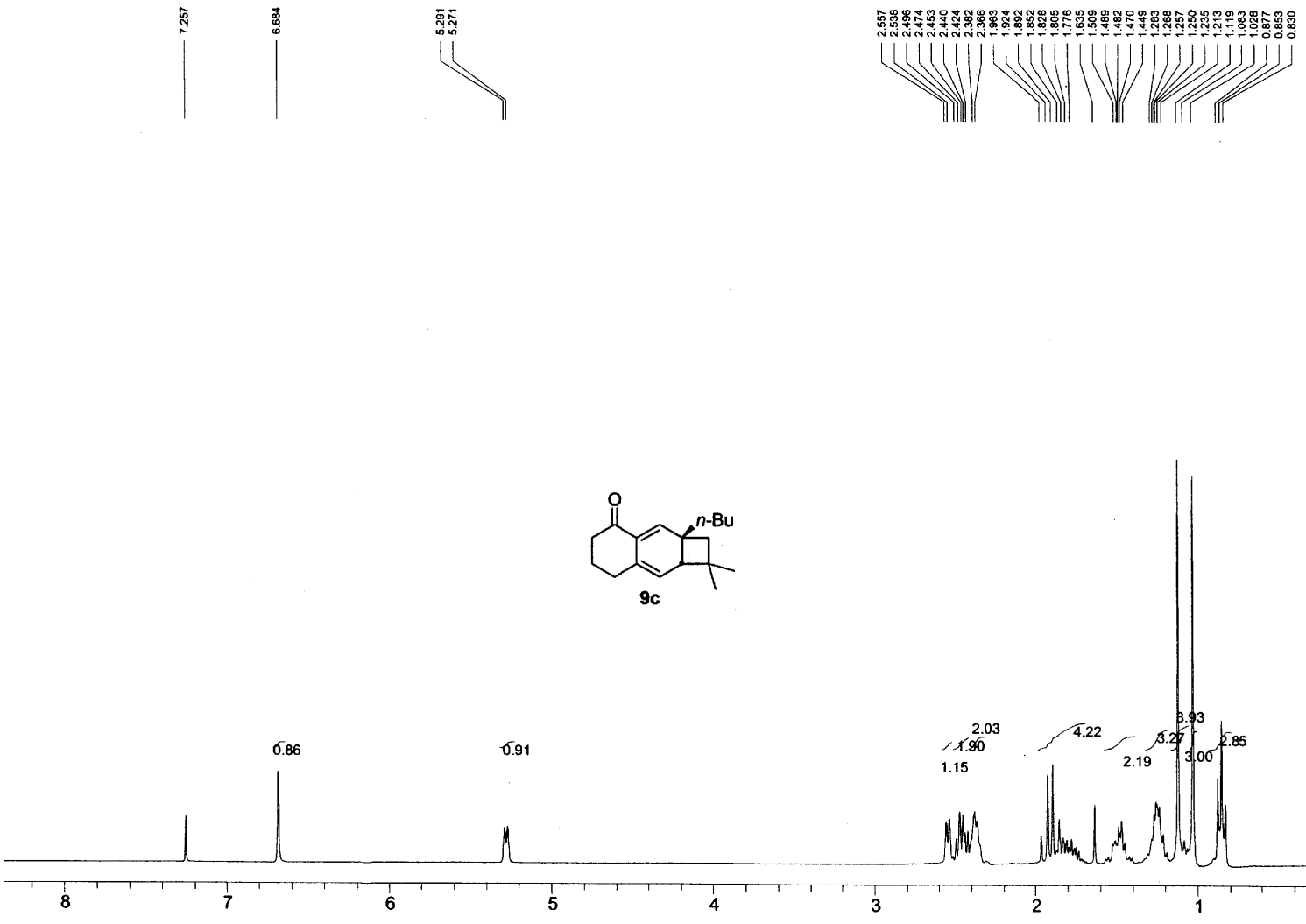
20
ppm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2.440
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2.366
1.963
1.924
1.892
1.852
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1.283
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1.083
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0.853
0.830
O
n-Bu
9c
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2
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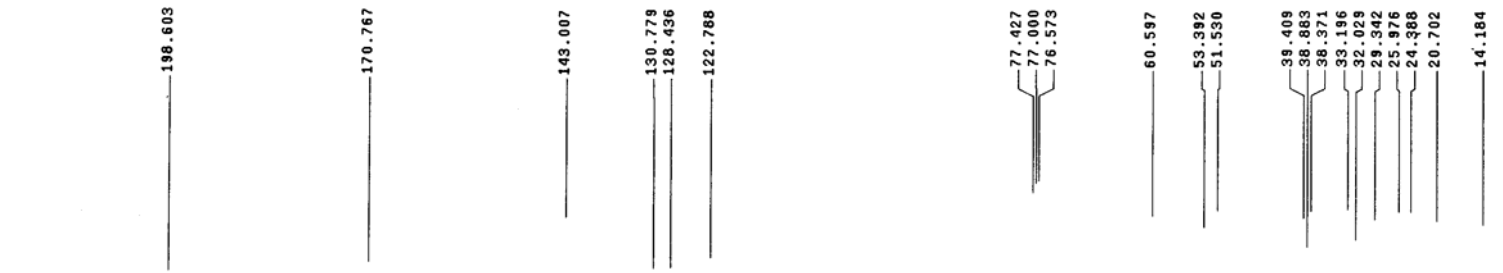
0 PPM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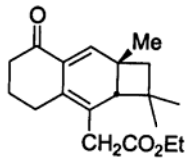
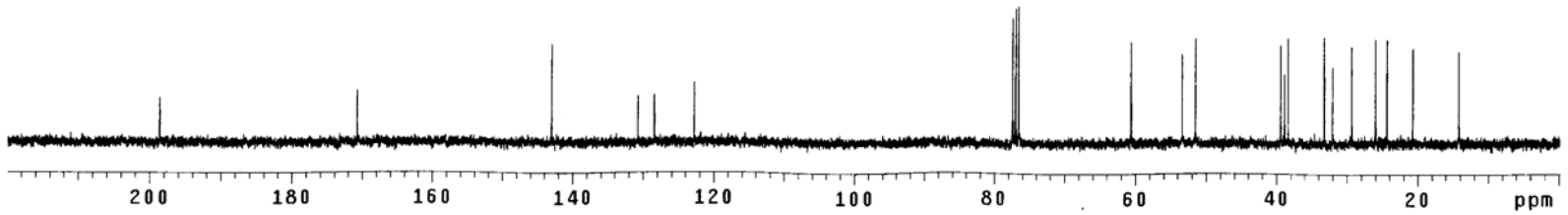

O
Me
CH2CO2Et

9e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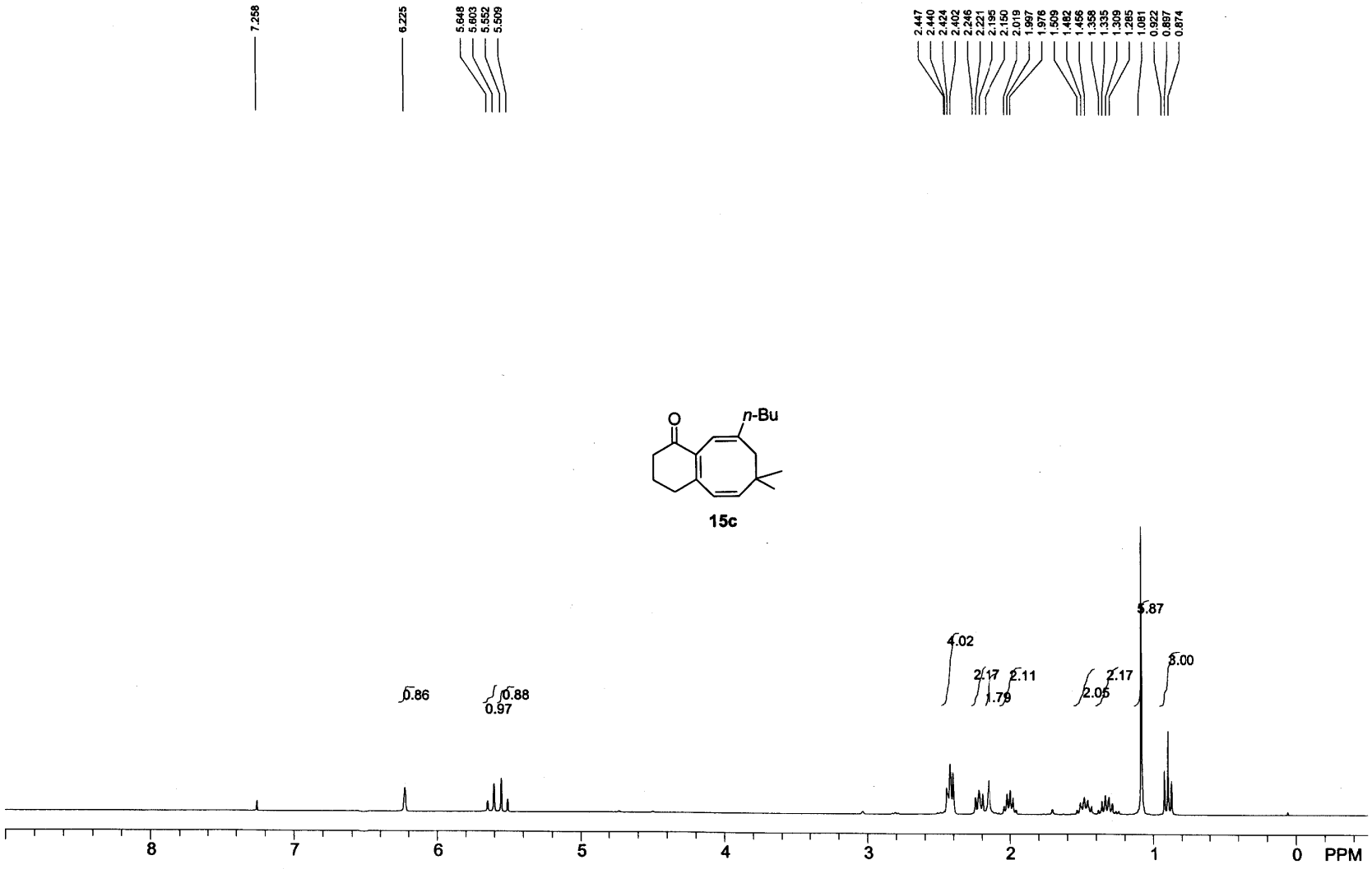
20
ppm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2.424
2.402
2.246
2.221
2.195
2.150
2.019
1.997
1.976
1.509
1.482
1.456
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1.335
1.309
1.285
1.081
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0.897
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O
n-Bu
15c
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0.97
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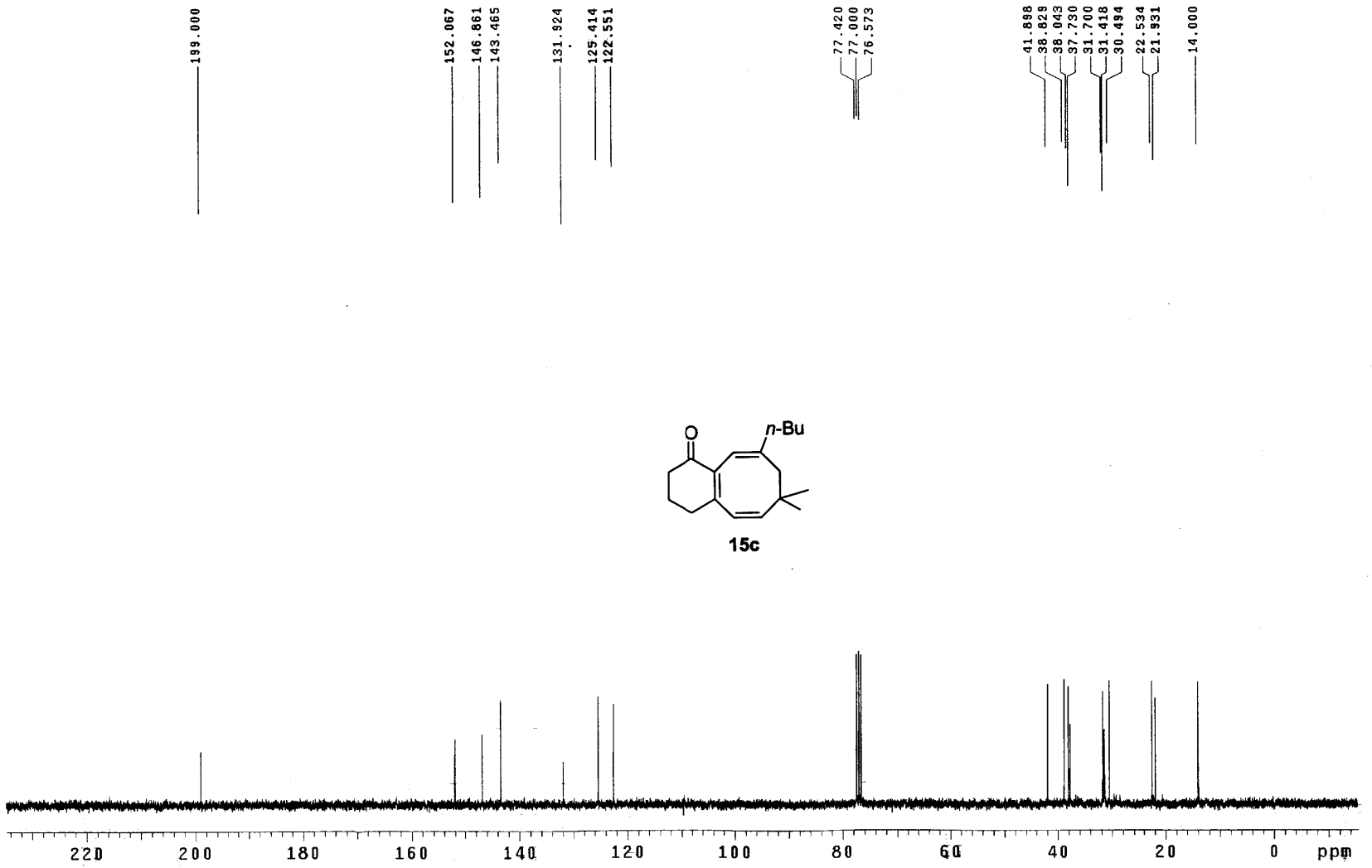
PPM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37.730
31.700
31.418
30.494
22.534
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n-Bu
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80
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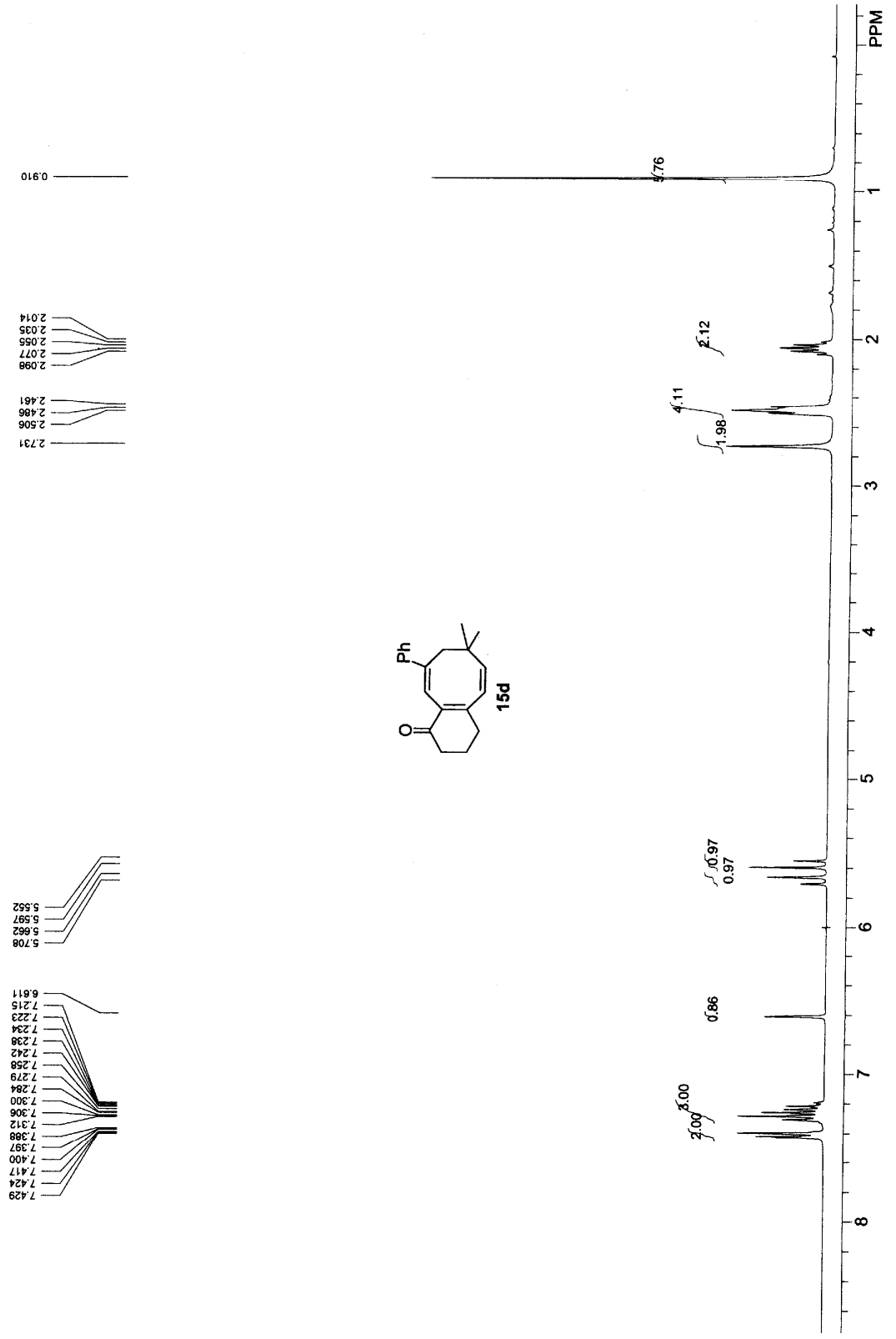
0
ppm

15c


PPM
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0.97
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2.00
2.00
Ph
O
15d
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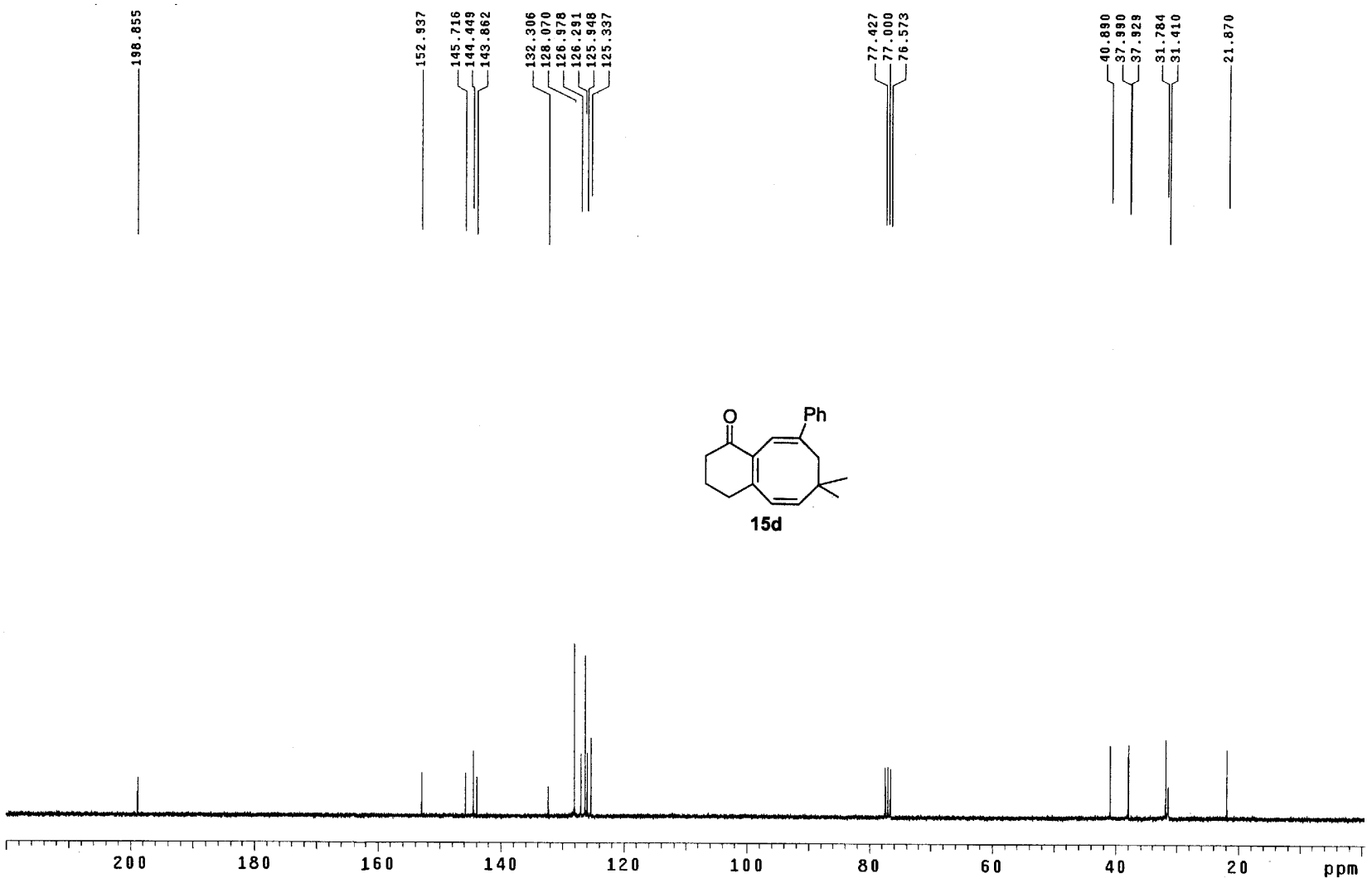
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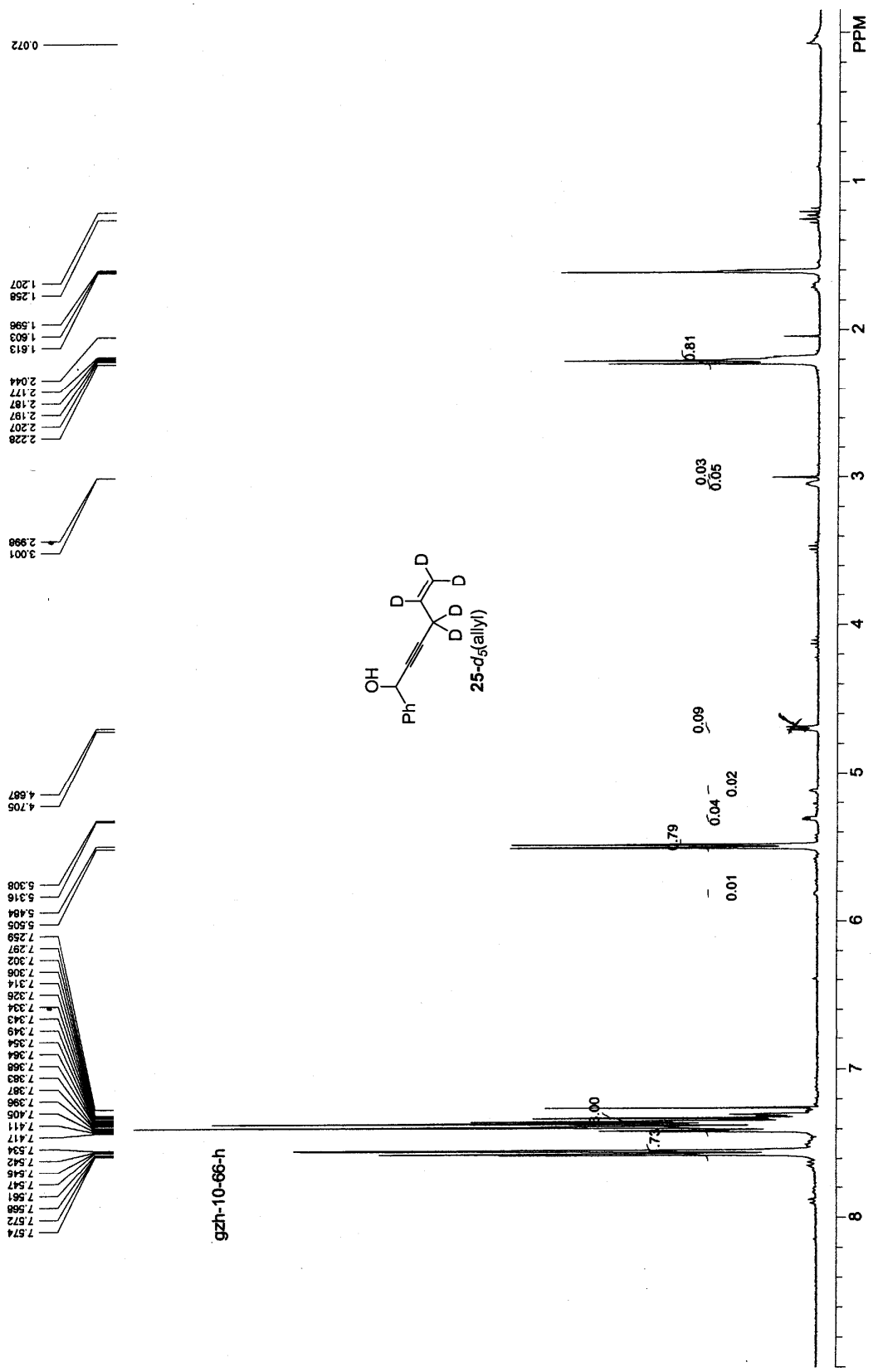
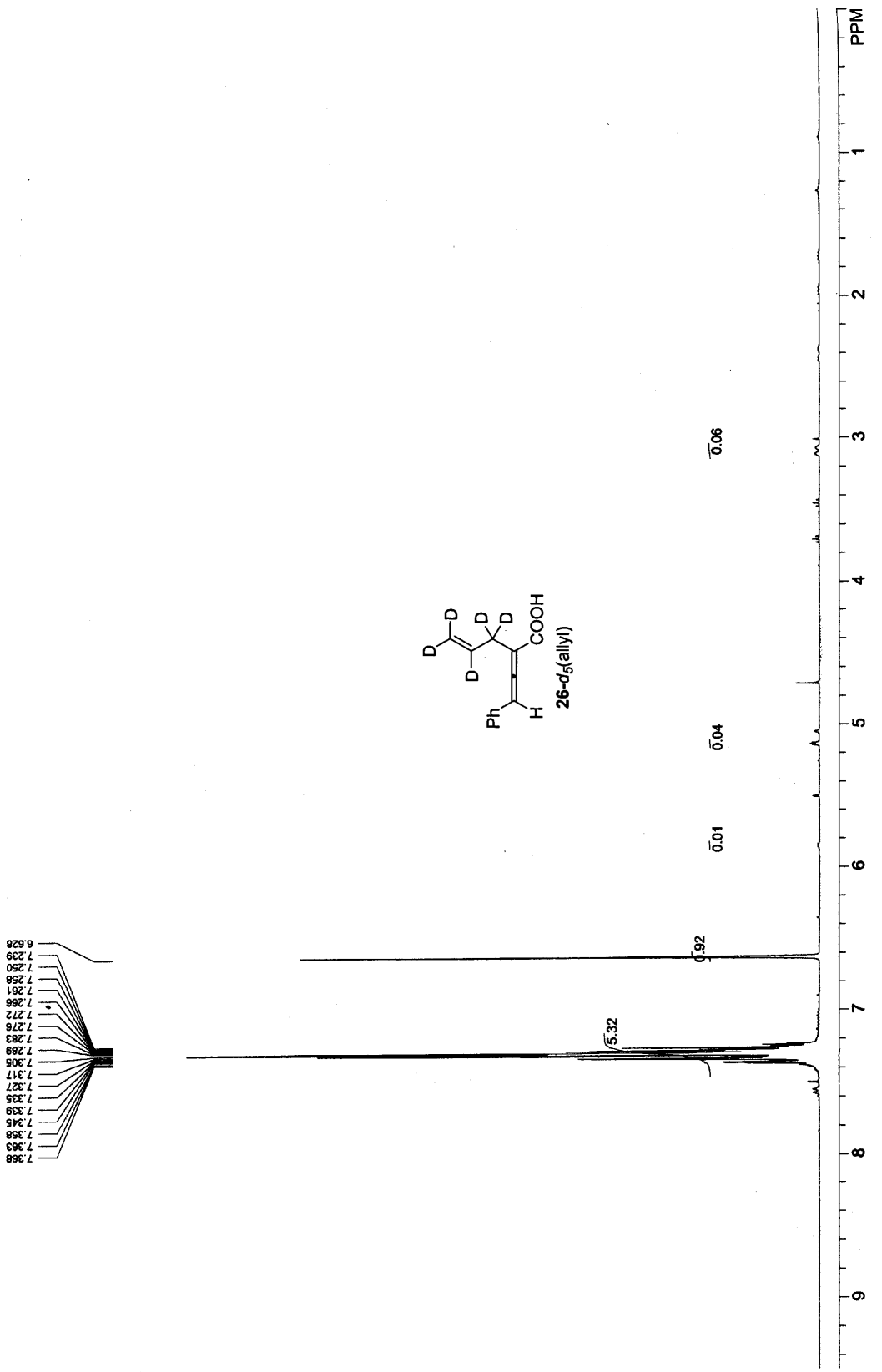
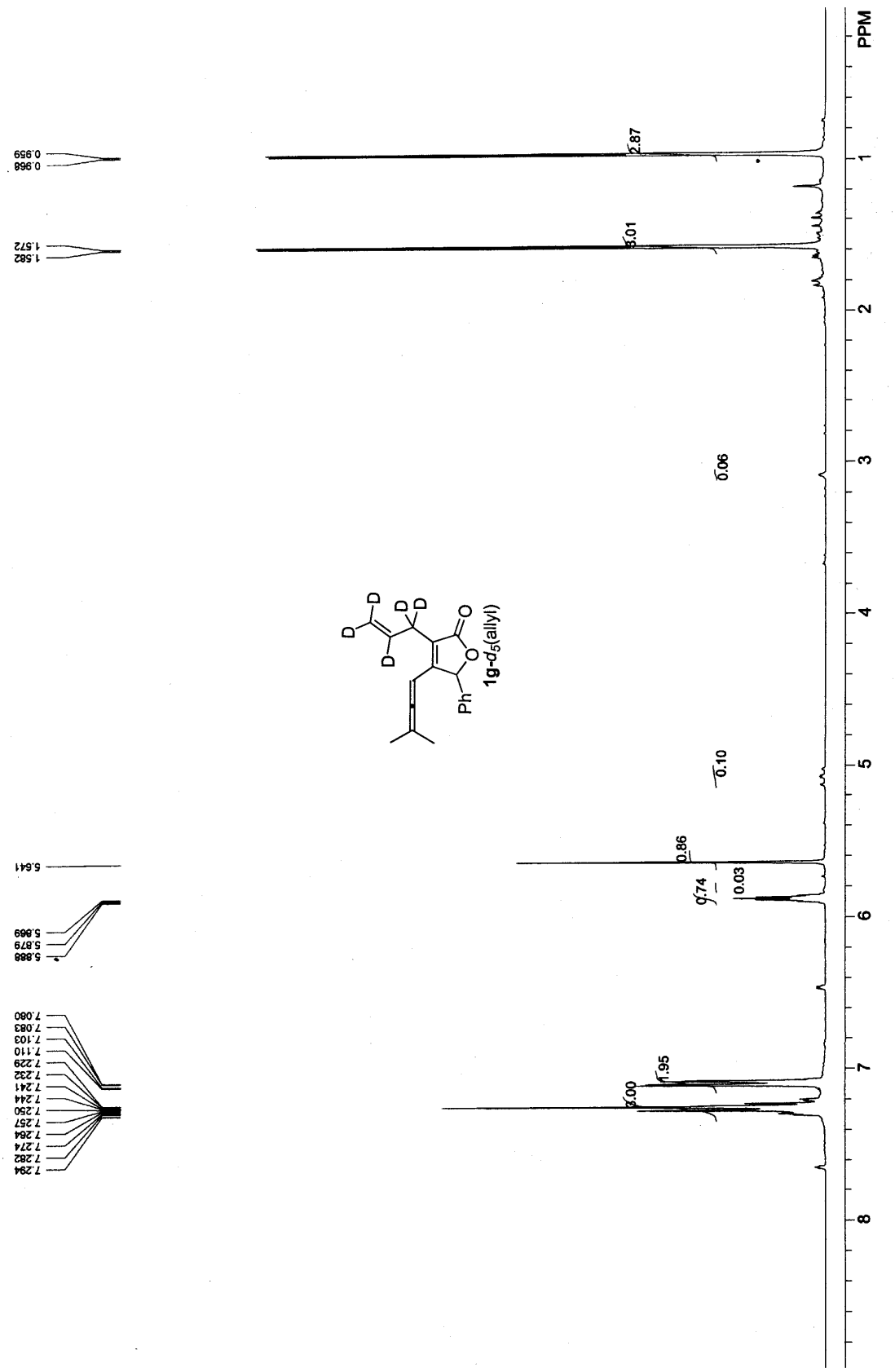
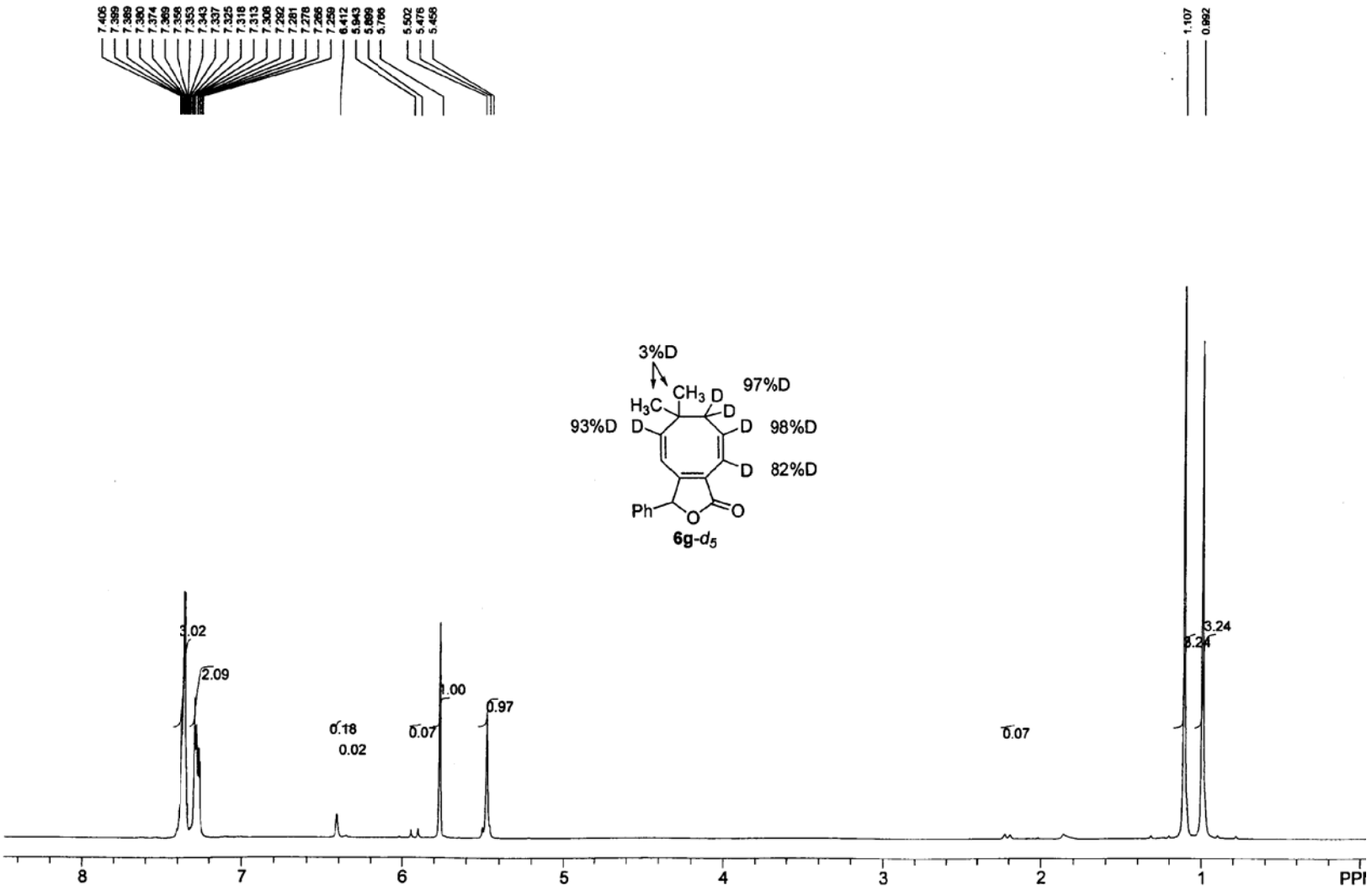
O
Ph
15d
200
180
160
140
120
100
80
60
40
20
ppm

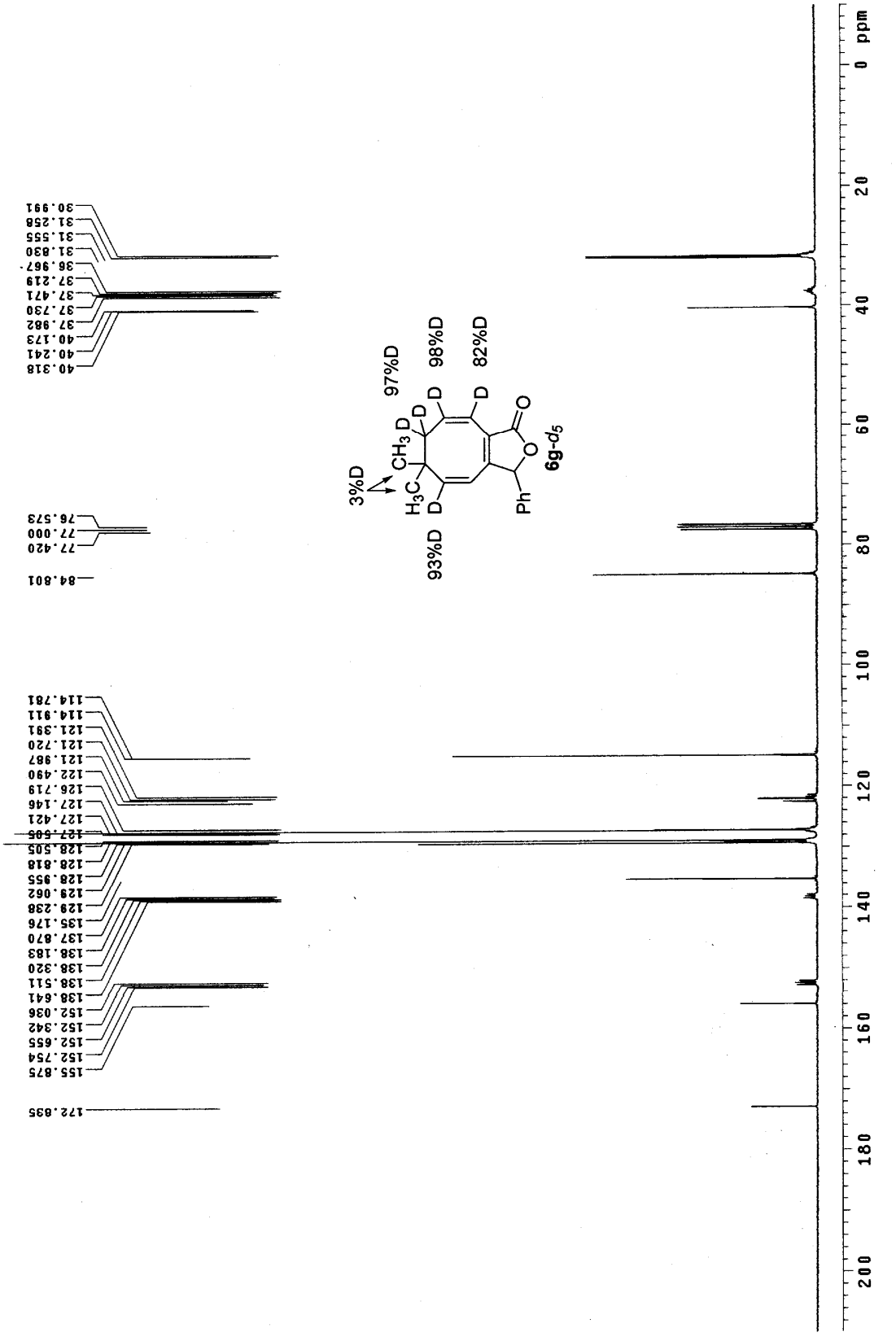

gzh-10-66-h
25-d_5(allyl)
OH
Ph
D
PPM
0.072
1.207
1.258
1.598
1.603
1.613
2.044
2.177
2.187
2.197
2.207
2.228
2.998
3.001
4.687
4.705
5.308
5.316
5.484
5.505
7.259
7.297
7.302
7.306
7.314
7.326
7.334
7.343
7.349
7.354
7.364
7.368
7.383
7.387
7.396
7.405
7.411
7.417
7.534
7.542
7.546
7.547
7.561
7.568
7.572
7.574
0.81
0.03
0.05
0.09
0.04
0.02
0.79
0.01
8.00
7.73

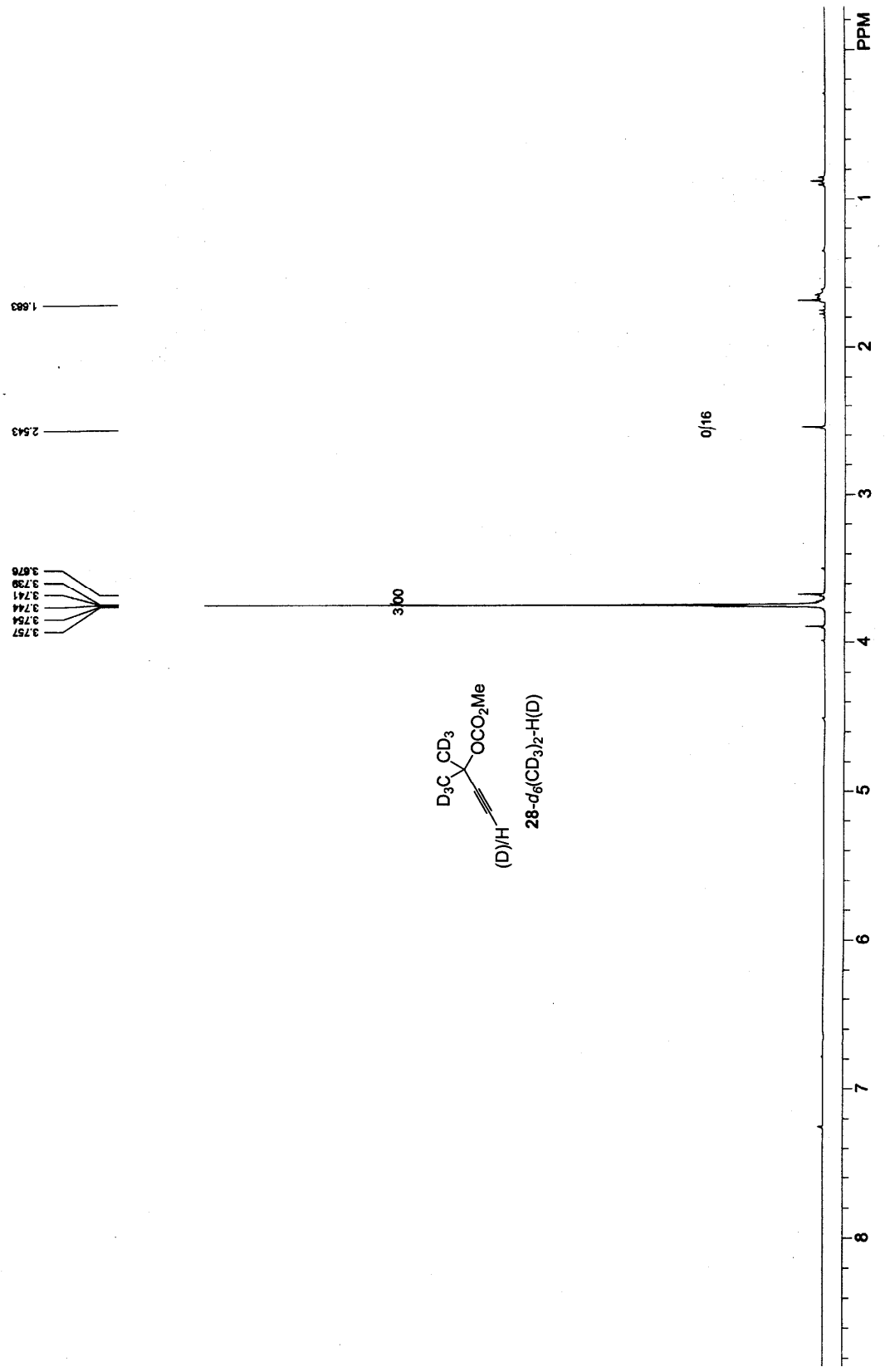

6.628
7.239
7.250
7.258
7.261
7.266
7.272
7.276
7.283
7.289
7.305
7.317
7.327
7.335
7.339
7.345
7.358
7.363
7.368
5.32
0.92
0.01
0.04
0.06
D
D
D
D
D
COOH
Ph
H
26-d5(allyl)
PPM
1
2
3
4
5
6
7
8
9


0.959
0.968
1.572
1.582
7.294
7.262
7.274
7.264
7.257
7.250
7.244
7.241
7.232
7.229
7.110
7.103
7.083
7.080
5.641
5.869
5.879
5.888
2.87
3.01
0.06
0.10
0.86
0.74
0.03
1.95
3.00
D
D
D
D
O
O
Ph
1g-d5(allyl)
PPM
1
2
3
4
5
6
7
8

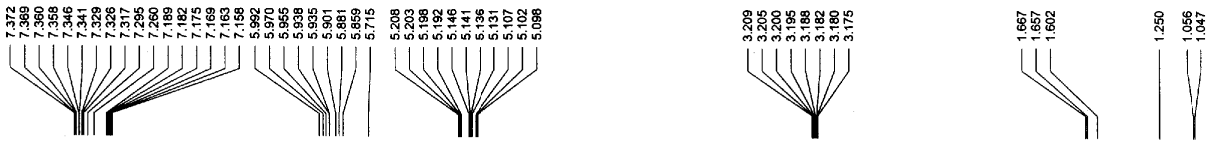
18.786
19.297
76.573
77.000
77.420
83.083
83.617
99.791
123.880
127.558
128.551
128.932
135.931
156.143
173.553
208.266
ppm
1g-d_5(allyl)

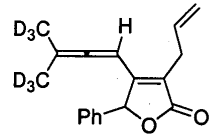

7.405
7.399
7.389
7.380
7.374
7.369
7.358
7.353
7.343
7.337
7.325
7.318
7.313
7.308
7.292
7.281
7.270
7.265
7.259
6.412
5.943
5.899
5.706
5.502
5.476
5.456
1.107
0.992
3%D
97%D
CH3 D
H3C
D
93%D D
D
98%D
D
82%D
Ph
O
O
6g-d5
3.02
2.09
0.18
0.02
0.07
1.00
0.97
0.07
3.24
3.24
8
7
6
5
4
3
2
1
PPI


3%D
97%D
98%D
82%D
93%D
6g-d5
Ph
O
CH3
H3C
D
0 ppm
20
40
60
80
100
120
140
160
180
200
30.991
31.258
31.555
31.830
36.967
37.219
37.471
37.730
37.982
40.173
40.241
40.318
76.573
77.000
77.420
84.801
114.781
114.911
121.391
121.720
121.987
122.490
126.719
127.146
127.421
127.505
128.505
128.818
128.955
129.062
129.238
135.176
137.870
138.183
138.320
138.511
138.641
152.036
152.342
152.655
152.754
155.875
172.835

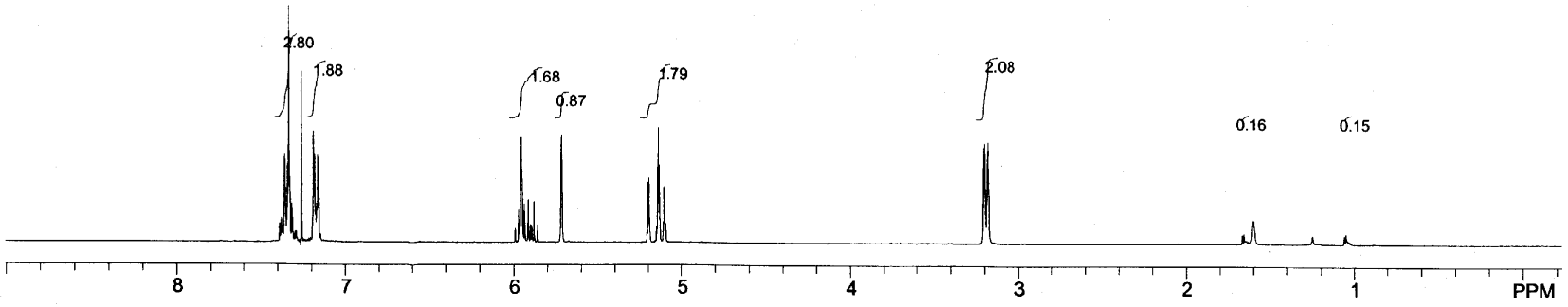

1.663
2.543
3.676
3.739
3.741
3.744
3.754
3.757
3.00
0.16
PPM
1
2
3
4
5
6
7
8
D3C
CD3
OCO2Me
(D)/H
28-d6(CD3)2-H(D)

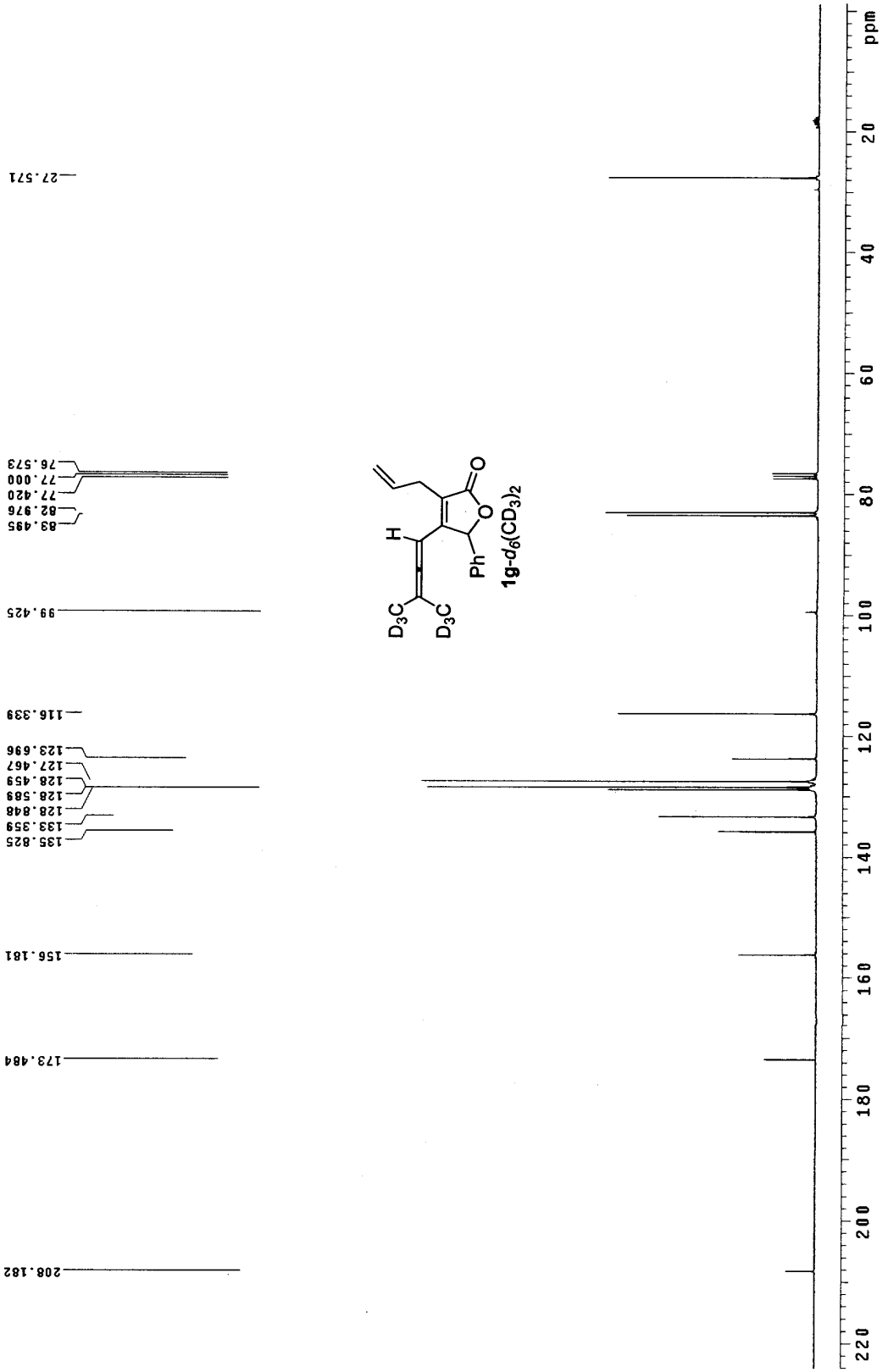
0.899
2.555
3.762
1.00
0.81
3.31
1.59
PPM
1
2
3
4
5
6
7
8
D3C
CD3
OCO2Me
H
28-d6(CD3)2


7.372
7.369
7.360
7.358
7.346
7.341
7.329
7.326
7.317
7.295
7.260
7.189
7.182
7.175
7.169
7.163
7.158
5.992
5.970
5.955
5.938
5.935
5.901
5.881
5.859
5.715
5.208
5.203
5.198
5.192
5.146
5.141
5.136
5.131
5.107
5.102
5.098
3.209
3.205
3.200
3.195
3.188
3.182
3.160
3.175
1.667
1.657
1.602
1.250
1.056
1.047

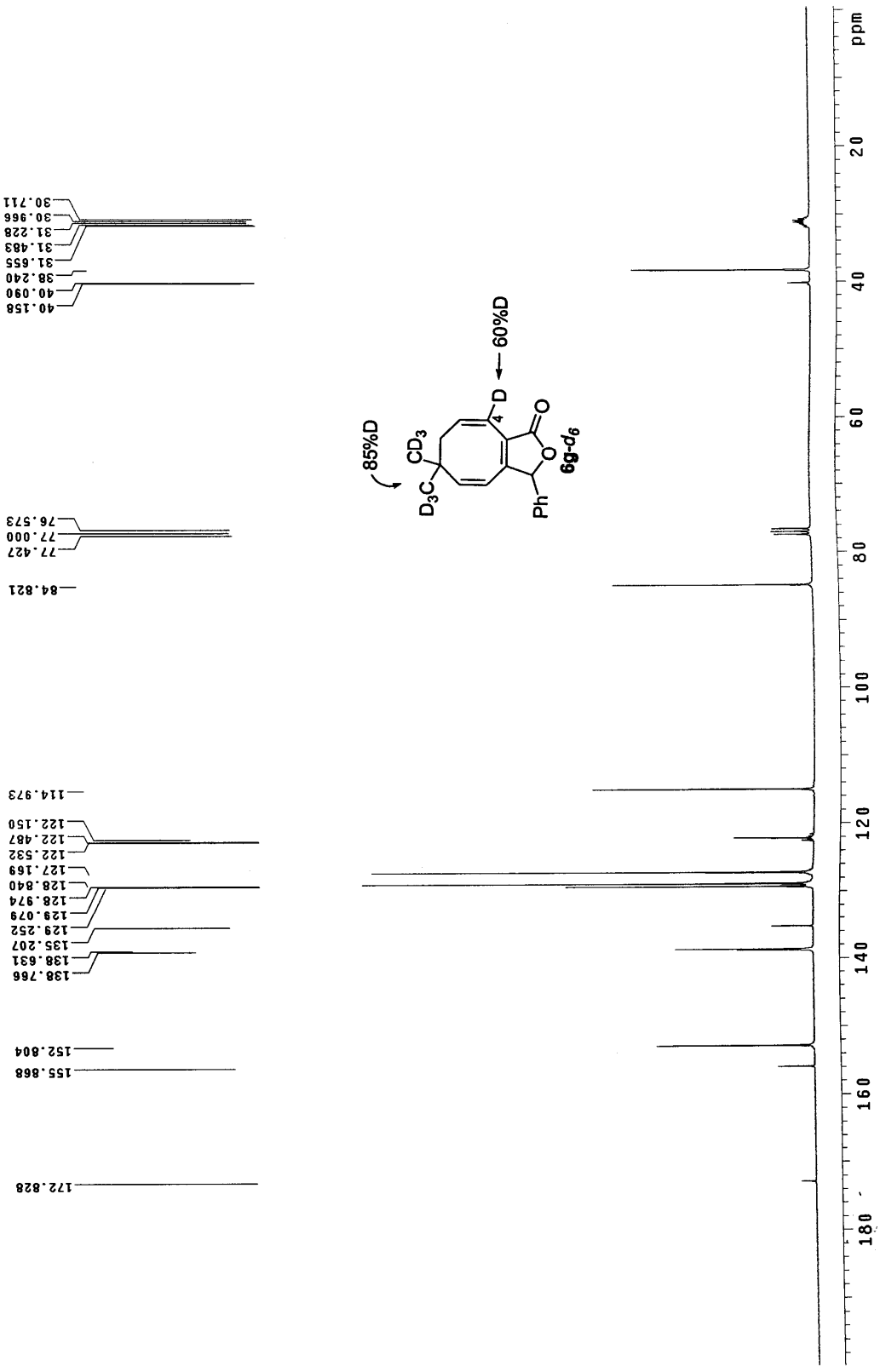

D3C
H
D3C
Ph
O
O

1g-d_6(CD_3)$_2$


2.80
1.88
1.68
0.87
1.79
2.08
0.16
0.15
8
7
6
5
4
3
2
1
PPM


27.571
76.573
77.000
77.420
82.976
89.495
99.425
116.339
123.696
127.467
128.459
128.589
128.848
133.359
135.825
156.181
173.484
208.182
ppm
20
40
60
80
100
120
140
160
180
200
220
O
O
H
Ph
D3C
D3C
1g-d6(CD3)2

PPM
0.45
0.45
2.04
0.94
0.88
0.94
1.22
7.14
2.04
85%D
CD3
D3C
4
D
60%D
O
O
Ph
6g-d6
7.403
7.389
7.384
7.373
7.366
7.359
7.352
7.314
7.299
7.286
7.274
7.266
7.250
6.447
6.408
6.399
6.383
6.371
6.358
6.348
6.343
5.951
5.907
5.766
5.501
5.457
1.816
2.302
2.274
2.256
2.249
2.231
2.220
2.207
1.118
1.081
1.009
0.971


30.711
30.966
31.228
31.483
31.655
38.240
40.090
40.158
76.573
77.000
77.427
84.821
114.973
122.150
122.487
122.532
127.169
128.840
128.974
129.079
129.252
135.207
138.631
138.766
152.804
155.868
172.828
85%D
CD3
D3C
4
D
60%D
O
O
Ph
6g-d6
ppm
20
40
60
80
100
120
140
160
180

References:

1. K. Shin, B. D. Gregory, *J. Am. Chem. Soc.* **2005**, *127*, 5028.

2. S. Ma, Z. Gu, *J. Am. Chem. Soc.* **2006**, *128*, 4942.