Supplementary Information

Nickel-Catalyzed [2+2+2] Cycloaddition of Aryne and Unactivated Alkene: Synthesis of 9,10-Dihydrophenanthrene Derivatives

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General Procedure for Ni-catalyzed [2+2+2] Cycloaddition of Aryne and Alkene.

A suspension of $Ni(cod)_2$ (10 mol% to a diene), 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro imidazolium tetrafluoroborate (SIMes·HBF_4, 10 mol% to the diene) and CsF (6.0 equiv to the diene) in CH_3CN (1.0 mL) was stirred at room temperature for 10 min. To the mixture were successively added a solution of alkene **1** and aryne **4** (3.0 equiv to the diene) in THF (4.0 mL) at 0°C, and the mixture was stirred at 50°C. To the mixture was flitted with Celite®, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **5** and **6**.

Dimethyl 2-allyl-2-[(9,10-dihydrophenanthren-10-yl)methyl]malonate (5aa) and Dimethyl 2-allyl-2-[3-(biphenyl-2-yl)prop-2-en-1-yl]malonate (*E*- and *Z*-6aa) (Table 1, run 5). According to the General Procedure, a crude product, which was obtained from **1a** (106.5 mg, 0.50 mmol), **4a** (0.38 mL, 1.5 mmol), $Ni(cod)_2$ (14.2 mg, 0.052 mmol), SIMes·HBF_4 (19.4 mg, 0.049 mmol) and CsF (455.1 mg, 3.0 mmol) in CH_3CN (5.0 mL), was roughly purified by flash column chromatography on silica gel (hexane/AcOEt = 100/1~10/1) to give an inseparable mixture of **5aa** and **6aa**. Further purification was performed by recycling preparative gel permeation chromatography [column: JAIGEL-1H-A, JAIGEL-2H-A, eluent: $CHCl_3$, flow rate: 3.7 mL/min, detector: UV (254 nm)] to give **5aa** (130.6 mg, 71%) as a colorless solid and a mixture of *E*- and *Z*-**6aa** (23.5 mg, 13%, *E*/*Z* = 2.3/1) as a colorless oil, respectively. Analytically pure samples of *E*-**6aa** and *Z*-**6aa** were obtained through further purification by recycling gel permeation chromatography (same conditions as above). For **5aa**: mp. 99~100 °C; Anal. Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 76.08; H, 6.69; IR (film, CH_2Cl_2) 1733, 1211, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.69 (m, 2H), 7.34-7.14 (m, 6H), 5.59 (ddt, *J* = 7.3, 11.1, 15.9 Hz, 1H), 5.07 (d, *J* = 11.1 Hz, 1H), 5.06 (d, *J* = 15.9 Hz, 1H), 3.65 (s, 3H), 3,49 (s, 3H), 3.10-3.00 (m, 2H), 2.76 (dt, *J* = 1.4, 7.3 Hz, 2H), 2.68 (d, *J* = 12.7 Hz, 1H), 2.08 (dd, *J* = 6.1, 14.8 Hz, 1H), 2.01 (dd, *J* = 7.2, 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 171.3, 140.2, 134.7, 134.0, 133.6, 132.3, 129.1, 128.2, 127.5, 127.4, 127.3, 127.1, 124.1, 123.3, 119.1, 56.9, 52.3, 52.1, 37.4, 35.0, 34.6, 34.2; EI-LRMS *m*/*z* 364 (M^+), 333, 301, 273, 192, 178; EI-HRMS calcd for $C_{23}H_{24}O_4$ 364.1675, found 364.1657. For (*E*)-**6aa**: IR (film, CH_2Cl_2) 1733, 1265, 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55-7.50 (m, 1H), 7.43-7.24 (m, 8H), 6.44 (d, *J* = 15.4 Hz, 1H), 5.93 (dt, *J* = 7.7, 15.4 Hz, 1H), 5.63 (ddt, *J* = 7.4, 10.5, 16.4 Hz, 1H), 5.09-4.98 (m, 2H), 3.68 (s, 6H), 2.71 (d, *J* = 7.4 Hz, 2H), 2.66 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.6, 140.9, 140.5, 135.2, 133.2, 132.2, 130.1, 129.7, 129.4, 129.3, 128.1, 127.6, 127.4, 127.0, 126.2, 124.7, 119.3, 57.9, 52.4 (2C),

37.1, 36.3; EI-LRMS *m/z* 364 (M^+), 333, 301, 273, 245, 192, 178; EI-HRMR calcd for $C_{23}H_{24}O_4$ 364.1675, found 364.1661. For (*Z*)-**6aa**: IR (film, CH_2Cl_2) 1735, 1214, 742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.28 (m, 9H), 6.41 (d, *J* = 11.7 Hz, 1H), 5.52 (ddt, *J* = 7.4, 10.0, 16.9 Hz, 1H), 5,44 (dt, *J* = 7.3, 11.7 Hz, 1H), 5.01 (*J* = 16.9 Hz, 1H), 5.00 (d, *J* = 10.0 Hz, 1H), 3.68 (s, 6H), 2.89 (dd, *J* = 1.7, 7.3 Hz, 2H), 2.65 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3 (2C), 141.2, 141.0, 134.5, 132.4, 132.1, 129.9, 129.7, 129.6, 129.6, 128.0, 127.9, 127.9, 127.4, 127.0, 125.0, 119.2, 57.7, 52.4, 37.2, 31.1, 29.7; EI-LRMS *m/z* 364 (M^+), 332, 300, 273, 245, 192, 178; EI-HRMS calcd for $C_{23}H_{24}O_4$ 364.1675, found 364.1665.

5-Allyl-5-[(9,10-dihydrophenanthren-10-yl)methyl]-2,2-dimethyl-1,3-dioxane (5ba) and (*Z*)-5-Allyl-5-[3-(biphenyl-2-yl)prop-2-en-1-yl]-2,2-dimethyl-1,3-dioxane (*Z*-6ba). According to the General Procedure, a crude product, which was obtained from **1b** (97.5 mg, 0.47 mmol), **4a** (0.37 mL, 1.5 mmol), $Ni(cod)_2$ (14.0 mg, 0.051 mmol), SIMes·HBF_4 (20.1 mg, 0.051 mmol) and CsF (454.6 mg, 3.0 mmol) in CH_3CN (5.0 mL), was purified by flash column chromatography on silica gel (hexane/AcOEt = 100/1~10/1) to give a mixture of **5ba** and **6ba**. Further purification was performed by recycling preparative gel permeation chromatography [column: JAIGEL-1H-A, JAIGEL-2H-A, eluent: $CHCl_3$, flow rate: 3.7 mL/min, detector: UV (254 nm).] to give **5ba** (58.4 mg, 36%) as a colorless solid and (*Z*)-**6ba** (19.4 mg, 12%) as a colorless amorphous solid, respectively. For **5ba**: mp. 51~52 °C; IR (film, CH_2Cl_2) 1198, 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77-7.71 (m, 2H), 7.35-7.19 (m, 6H), 5.70 (ddt, *J* = 7.4, 10.3, 16.5 Hz, 1H), 5.09 (d, *J* = 16.5 Hz, 1H), 5.08 (d, *J* = 10.3 Hz, 1H), 3.64 (d, *J* = 11.5 Hz, 1H), 3.57 (d, *J* = 11.5 Hz, 1H), 3.49 (d, *J* = 12.0 Hz, 1H), 3.32 (d, *J* = 12.0, 1H), 3.15-3.09 (m, 2H), 2.79 (dd, *J* = 4.6, 16.6 Hz, 1H), 2.38 (dd, *J* = 7.4, 13.6 Hz, 1H), 2.34 (dd, *J* = 7.4, 13.6 Hz, 1H), 1.50 (dd, *J* = 6.9, 14.9 Hz, 1H), 1.38 (s, 3H), 1.31 (s, 3H), 1.28 (dd, *J* = 5.2, 14.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 135.1, 134.2, 133.5, 133.4, 129.2, 127.8, 127.6, 127.6, 127.1, 127.0, 124.2, 123.3, 118.5, 97.8, 67.8, 67.6, 36.3, 36.1, 35.6, 35.3, 33.9, 25.1, 22.6; EI-LRMS *m/z* 348 (M^+), 306, 290, 247, 192, 179; EI-HRMS calcd for $C_{24}H_{28}O_2$ 348.2090, Found 348.2078. For (*Z*)-**6ba**: IR (film, CH_2Cl_2) 1198, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43-7.30 (m, 9H), 6.41 (d, *J* = 11.7 Hz, 1H), 5.65 (ddt, *J* = 7.4, 10.8, 16.0 Hz, 1H), 5.62 (dt, *J* = 7.3, 11.7 Hz, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 5.04 (d, *J* = 10.8 Hz, 1H), 3.59 (d, *J* = 11.5 Hz, 2H), 3.55 (d, *J* = 11.5 Hz, 2H), 2.36 (dd, *J* = 2.0, 7.4 Hz, 2H), 2.15 (d, *J* = 7.3 Hz, 2H), 1.41 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 135.1, 133.0, 131.6, 129.8, 129.8, 129.6 (2C), 127.9 (2C), 127.1, 126.9, 126.8, 126.1, 118.4, 98.0, 67.3 (2C), 36.7, 36.0 (2C), 30.6, 24.0, 23.6; EI-LRMS *m/z* 348 (M^+), 290, 249, 191, 178; EI-HRMS calcd for $C_{24}H_{28}O_2$

348.2090, found 348.2086.

***N*-Allyl-*N*-[(9,10-dihydrophenanthren-9-yl)methyl]-*p*-toluenesulfonamide (5ca) and *N*-Allyl-*N*-[3-(biphenyl-2-yl)prop-2-en-1-yl]-*p*-toluenesulfonamide (*E*- and *Z*-6ca).** According to the General Procedure, a crude product, which was obtained from **1c** (125.7 mg, 0.50 mmol), **4a** (0.38 mL, 1.5 mmol), $Ni(cod)_2$ (13.7 mg, 0.051 mmol), SIMes·HBF_4 (20.2 mg, 0.051 mmol) and CsF (456.7 mg, 3.0 mmol) in CH_3CN (5.0 mL), was purified by flash column chromatography on silica gel (hexane/AcOEt = 100/1~10/1) to give a mixture of **5ca** and **6ca**. Further purification was performed by recycling preparative Gel Permeation Chromatography [column: JAIGEL-1H-A, JAIGEL-2H-A, eluent: $CHCl_3$, flow rate: 3.7 mL/min, detector: UV (254 nm).] to give **5ca** (50.4 mg, 25%) as a colorless amorphous solid and an inseparable mixture of *E*- and *Z*-**6ca** (24.1 mg, 12%, *E*/*Z* = 1.5/1) as a colorless oil, respectively. For **5ca**: IR (film, CH_2Cl_2) 1344, 1161, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.61 (dt, *J* = 1.7, 6.3 Hz, 2H), 7.36-7.21 (m, 8H), 5.20 (ddt, *J* = 6.7, 10.2, 17.1 Hz, 1H), 4.83 (dd, *J* = 1.1, 10.2 Hz, 1H), 4.74 (*J* = 1.1, 17.1 Hz, 1H), 3.62 (dd, *J* = 6.7, 15.2 Hz, 1H), 3.58 (dd, *J* = 6.7, 15.2 Hz, 1H), 3.38 (dddd, *J* = 2.3, 6.1, 6.1, 8.8 Hz, 1H), 3.11 (dd, *J* = 6.1, 15.9 Hz, 1H), 3.03 (dd, *J* = 8.8, 14.3 Hz, 1H), 2.97 (dd, *J* = 2.3, 15.9 Hz, 1H), 2.86 (dd, *J* = 6.1, 14.3 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.4, 136.5, 134.2, 133.8, 133.5, 132.3, 129.6, 129.6 (2C), 129.1, 127.7, 127.7, 127.7, 127.2 (2C), 127.1, 123.8, 123.3, 119.5, 52.2, 49.4, 38.2, 30.8, 21.5; EI-LRMS *m*/*z* 403 (M^+), 363, 248, 224, 192, 178; EI-HRMS calcd for $C_{25}H_{25}NO_2S$ 403.1606, found 403.1599. For *E*- and *Z*-**6ca**: IR (film, CH_2Cl_2) 1343, 1160, 738 cm^{-1}; EI-LRMS *m*/*z* 403 (M^+), 363, 248, 224, 191, 178; EI-HRMS calcd for $C_{25}H_{25}NO_2S$ 403.1606, found 403.1610; ^1H NMR (500 MHz, $CDCl_3$) for *E*-**6ca**: δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.44-7.24 (m, 13H), 6.40 (d, *J* = 15.5 Hz, 1H), 5.90 (dt, *J* = 6.9, 15.5 Hz, 1H), 5.58 (ddt, *J* = 6.4, 10.5, 17.0 Hz, 1H), 5.08 (d, *J* = 10.5 Hz, 1H), 5.05 (d, *J* = 17.0 Hz, 1H), 3.85 (d, *J* = 6.9 Hz, 1H), 3.78 (d, *J* = 6.4 Hz, 1H), 2.42 (s, 3H); ^1H NMR (500 MHz, $CDCl_3$) for *Z*-**6ca**: δ 7.65 (dt, *J* = 2.0, 8.4 Hz, 2H), 7.44-7.24 (m, 13H), 7.16 (d, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 11.5 Hz, 1H), 5.58 (ddt, *J* = 6.4, 10.5, 17.0 Hz, 1H), 5.46 (dt, *J* = 6.3, 11.5 Hz, 1H), 5.05 (d, *J* = 10.3 Hz, 1H), 5.05 (d, *J* = 17.0 Hz, 1H), 3.94 (d, *J* = 6.7 Hz, 1H), 3.70 (d, *J* = 6.4 Hz, 1H), 2.42 (s, 3H).

Allyl (9,10-dihydrophenanthren-10-yl)methyl ether (5da) and Allyl 3-(biphenyl-2-yl)prop-2-en-1-yl ether (*E*- and *Z*-6da). According to the General Procedure, a crude product, which was obtained from **1d** (185 μL, 1.5 mmol), **4a** (1.15 mL, 4.6 mmol), $Ni(cod)_2$ (41.3 mg, 0.15 mmol),

SIMes·HBF_4 (58.4 mg, 0.15 mmol) and CsF (1.3725 g, 9.1 mmol) in CH_3CN (15.0 mL), was purified by flash column chromatography on silica gel (hexane/AcOEt = 100/1~20/1) to give a mixture of **5da** and **6da**. Further purification was performed by recycling preparative gel permeation chromatography [column: JAIGEL-1H-A, JAIGEL-2H-A, eluent: $CHCl_3$, flow rate: 3.7 mL/min, detector: UV (254 nm).] to give **5da** (94.4 mg, 25%) as a colorless oil and an inseparable mixture of *E*- and *Z*-**6da** (35.3 mg, 9%, *E*/*Z* = 1.3/1) as a colorless oil, respectively. For **5da**: IR (film, CH_2Cl_2) 1091, 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.4 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.36-7.21 (m, 6H), 5.85 (ddt, *J* = 5.3, 10.6, 17.7 Hz, 1H), 5.20 (d, *J* = 17.7 Hz, 1H), 5.12 (d, *J* = 10.6 Hz, 1H), 3.91 (dd, *J* = 5.0, 12.9 Hz, 1H), 3.88 (dd, *J* = 5.0, 12.9 Hz, 1H), 3.42 (dd, *J* = 5.0, 9.4 Hz, 1H), 3.30 (dd, *J* = 9.4, 9,4 Hz, 1H), 3.20 (dddd, *J* = 5.0, 5.0, 5.0, 9.4 Hz, 1H), 3.06 (d, *J* = 5.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.3, 134.9, 134.8, 134.1, 133.7, 129.2, 128.7, 127.6, 127.5, 127.5, 126.9, 123.8, 123.4, 116.7, 71.8, 71.4, 38.9, 30.7; EI-LRMS *m*/*z* 250 (M^+), 192, 178, 165; EI-HRMS Calcd for $C_{18}H_{18}O$ 250.1358, found 250.1368. For *E*- and *Z*-**6da**: IR (film, CH_2Cl_2) 1094, 746 cm^{-1}; EI-LRMS *m*/*z* 250 (M^+), 209, 192, 178, 165; EI-HRMS calcd for $C_{18}H_{18}O$ 250.1358, found 250.1362; ^1H NMR (400 MHz, $CDCl_3$) for *E*-**6da**: δ 7.44-7.22 (m, 9H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 6.1, 15.9 Hz, 1H), 5.90 (ddt, *J* = 5.4, 10.8, 16.9 Hz, 1H), 5.25 (d, *J* = 16.9 Hz, 1H), 5.17 (d, *J* = 10.8 Hz, 1H), 4.07 (dd, *J* = 1.4, 6.1 Hz, 2H), 3.97 (dd, *J* = 1.4, 5.4 Hz, 2H); ^1H NMR (400 MHz, $CDCl_3$) for *Z*-**6ca**: δ 7.44-7.22 (m, 9H), 6.46 (d, *J* = 11.8 Hz, 1H), 5.94 (ddt, *J* = 6.0, 10.6, 17.0 Hz, 1H), 5.80 (dt, *J* = 6.6, 11.8 Hz, 1H), 5.27 (d, *J* = 17.0 Hz, 1H), 5.18 (d, *J* = 10.6 Hz, 1H), 4.21 (dd, *J* = 1.6, 6.6 Hz, 2H), 3.99 (dd, *J* = 1.4, 6.0 Hz, 2H).

Dimethyl 2-crotyl-2-[3-(biphenyl-2-yl)prop-2-en-1-yl]malonate (5ea) and Dimethyl 2-crotyl-2-[3-(biphenyl-2-yl)prop-2-en-1-yl]malonate (*E*- and *Z*-6ea). According to the General Procedure, a crude product, which was obtained from **1e** (112.9 mg, 0.50 mmol), **4a** (0.37 mL, 1.5 mmol), $Ni(cod)_2$ (13.7 mg, 0.050 mmol), SIMes·HBF_4 (19.4 mg, 0.049 mmol) and CsF (456.6 mg, 3.0 mmol) in CH_3CN (5.0 mL), was purified by flash column chromatography on silica gel (hexane/AcOEt = 100/1~10/1) to give **5ea** (86.0 mg, 46%) as a colorless oil and an inseparable mixture of *E*- and *Z*-**6ea** (12.4 mg, 7%, *E*/*Z* = 3.0/1) as a colorless oil. For **5ea**: IR (film, CH_2Cl_2) 1732, 1266, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.34-7.14 (m, 6H), 5.45 (dq, *J* = 6.3, 15.0 Hz, 1H), 5.17 (dtq, *J* = 1.4, 7.5, 15.0 Hz, 1H), 3.65 (s, 3H), 3,49 (s, 3H), 3.10-2.98 (m, 2H), 2.71-2.64 (m, 3H), 2.06 (dd, *J* = 6.7, 15.0 Hz, 1H), 1.99 (dd, *J* = 6.7, 15.0 Hz, 1H), 1.62 (dd, *J* = 1.4, 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 171.3, 140.3, 134.8, 134.1, 133.7, 129.8, 129.2, 128.2, 127.5, 127.4, 127.3, 127.1, 124.5, 124.0,

123.3, 57.1, 52.2, 52.1, 36.2, 34.8, 34.6, 34.2, 12.3; EI-LRMS *m/z* 378 (M^+), 347, 315, 287, 192, 178; EI-HRMS Calcd for $C_{24}H_{26}O_4$ 378.1831, found 378.1839. For *E*- and *Z*-**6ea**: IR (film, CH_2Cl_2) 1734, 1206, 739 cm^{-1}; EI-LRMS *m/z* 378 (M^+), 347, 313, 193, 178; EI-HRMS calcd for $C_{24}H_{26}O_4$ 378.1831, found 378.1820; ^1H NMR (500 MHz, $CDCl_3$) for *E*-**6ea**: δ 7.42-7.23 (m, 9H), 6.42 (d, *J* = 15.3 Hz, 1H), 5.93 (dt, *J* = 7.6, 15.3 Hz, 1H), 5.50-5.34 (m, 1H), 5.22 (dtq, *J* = 1.6, 7.4, 14.9 Hz, 1H), 3.68 (s, 6H), 2.69 (dd, *J* = 1.1, 7.6 Hz, 2H), 2.59 (d, *J* = 7.4 Hz, 2H), 1.61 (dd, *J* = 1.6, 6.3 Hz, 3H); ^1H NMR (500 MHz, $CDCl_3$) for *E*-**6ea**: δ 7.42-7.23 (m, 9H), 6.39 (d, *J* = 9.7 Hz, 1H), 5.50-5.34 (m, 2H), 5.10 (dtq, *J* = 1.4, 7.4, 15.2 Hz, 1H), 3.67 (s, 6H), 2.87 (dd, *J* = 2.0, 7.4 Hz, 2H), 2.60-2.55 (m, 2H), 1.51 (dd, *J* = 1.4, 6.3 Hz, 3H).

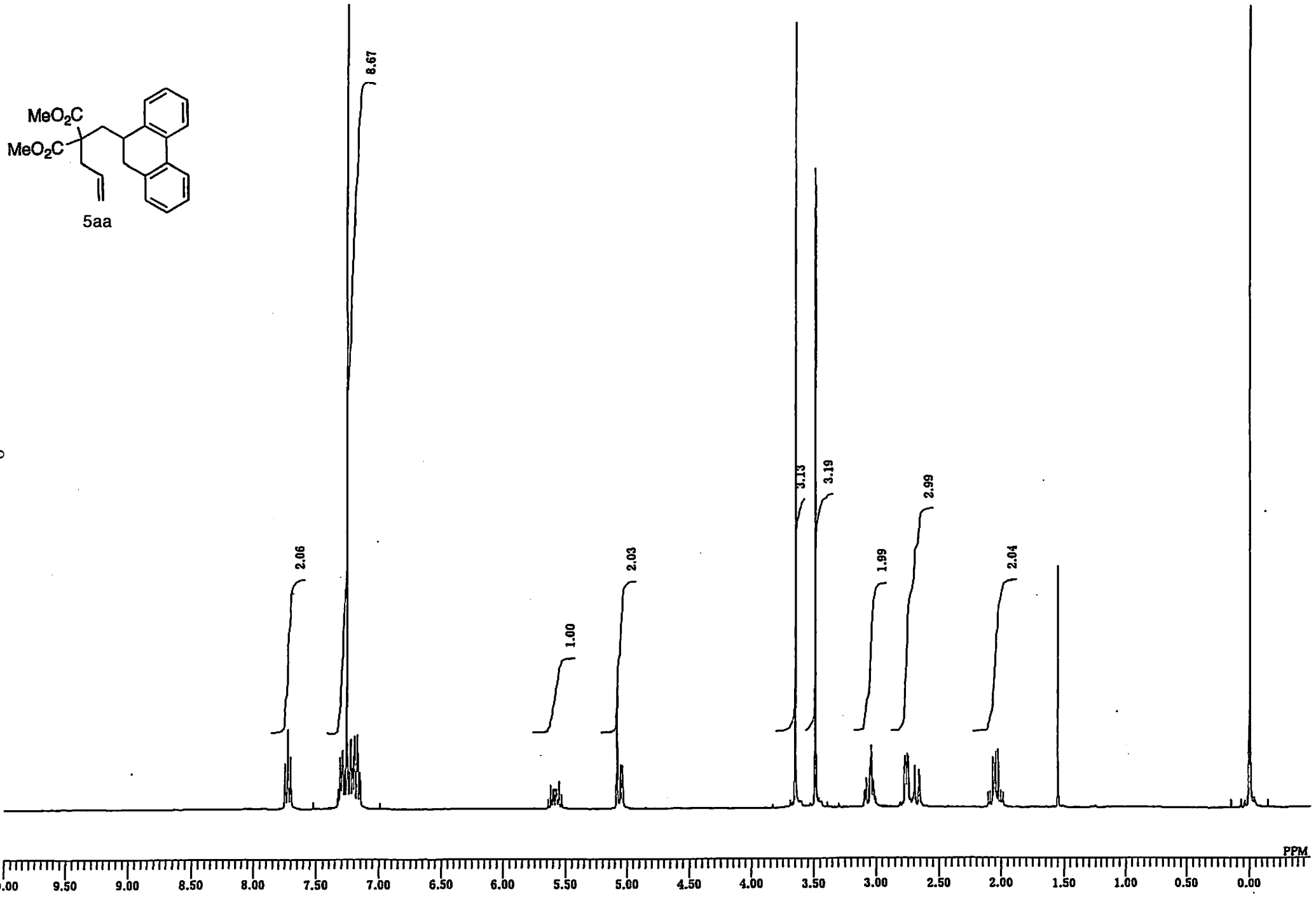
Dimethyl 2-allyl-2-(2,3,6,7-tetramethoxy-9,10-dihydrophenanthren-9-yl)methylmalonate (5ab) and Dimethyl 2-allyl-2-[3-(3',4,4',5-tetramethoxybiphenyl-2-yl)prop-2-en-1yl]malonate (*E*- and *Z*-6ab). According to the General Procedure, a crude product, which was obtained from **1a** (106.3 mg, 0.50 mmol), **4b** (543.0 mg, 1.5 mmol), $Ni(cod)_2$ (13.8 mg, 0.050 mmol), SIMes·HBF_4 (19.6 mg, 0.050 mmol) and CsF (456.9 mg, 3.0 mmol) in CH_3CN (5.0 mL), was purified by flash column chromatography on silica gel (hexane/AcOEt = 20/1~10/1~3/1) to give a mixture of **5ab** and **6ab**. Further purification was performed by recycling preparative gel permeation chromatography [column: JAIGEL-1H-A, JAIGEL-2H-A, eluent: $CHCl_3$, flow rate: 3.7 mL/min, detector: UV (254 nm).] to give **5ab** (164.4 mg, 68%) as a colorless solid and an inseparable mixture of *E*- and *Z*-**6ab** (34.6 mg, 14%, *E*/*Z* = 2.5/1) as a colorless oil, respectively. For **5ab**: mp. 95~97 °C; IR (film, CH_2Cl_2) 1731, 1248, 1210, 733 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.14 (s, 1H), 7.10 (s, 1H), 6.72 (s, 1H), 6.69 (s, 1H), 5.57 (ddt, *J* = 7.1, 11.2, 16.2 Hz, 1H), 5.07 (d, *J* = 11.2 Hz, 1H), 5.06 (d, *J* = 16.2 Hz, 1H), 3.98 (s, 3H), 3,96 (s, 3H), 3.94 (s, 3H), 3.92 (s, 3H), 3.66 (s, 3H), 3.53 (s, 3H), 3.01 (dd, *J* = 6.2, 15.0 Hz, 1H), 2.90 (dddd, *J* = 2.1, 6.2, 6.2, 6.2 Hz, 1H), 2.74 (d, *J* = 7.1 Hz, 2H), 2.56 (dd, *J* = 2.0, 15.0 Hz, 1H), 2.07 (dd, *J* = 6.2, 14.7 Hz, 1H), 2.00 (dd, *J* = 6.2, 14.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 171.4, 148.1, 148.0, 147.9, 147.6, 132.4, 132.1, 126.7, 126.5, 126.2, 119.0, 112.4, 111.8, 107.1, 106.7, 56.9, 56.2, 56.2, 55.9, 55.8, 52.2, 52.2, 37.5, 35.3, 34.7, 34.1; EI-LRMS *m/z* 484 (M^+), 312, 299, 268; EI-HRMS calcd for $C_{27}H_{32}O_8$ 484.2097, found 484.2096. For *E*- and *Z*-**6ab**: IR (film, CH_2Cl_2) 1733, 1251, 1211, 737 cm^{-1}; EI-LRMS *m/z* 484 (M^+), 312, 299, 269; EI-HRMS calcd for $C_{27}H_{32}O_8$ 484.2097, found 484.2097; ^1H NMR (400 MHz, $CDCl_3$) for *E*-**6ab**: δ 6.99 (s, 1H), 6.92-6.88 (s, 1H), 6.84-6.80 (m, 2H), 6.77-6.73 (m, 1H), 6.37 (d, *J* = 15.5 Hz, 1H), 5.79 (dt, *J* = 7.6, 15.5 Hz, 1H), 5.63 (ddt, *J* = 7.4, 10.4, 16.7 Hz, 1H), 5.06 (d, *J* = 10.4 Hz, 1H), 5.04 (d, *J* = 16.7 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.89 (s, 3H), 3.88 (s,

3H), 3.68 (s, 6H), 2.69 (dd, *J* = 1.1, 7.4 Hz, 2H), 2.64 (d, *J* = 7.6 Hz, 2H); ^{1}H NMR (400 MHz, $CDCl_3$) for *Z*-**6ab**: δ 7.00-6.71 (m, 5H), 6.38 (d, *J* = 11.8 Hz, 1H), 5.63 (ddt, *J* = 7.5, 10.7, 15.3 Hz, 1H), 5.39 (dt, *J* = 7.3, 11.8 Hz, 1H), 5.03 (d, *J* = 15.3 Hz, 1H), 5.02 (d, *J* = 10.7 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.92 (s, 3H), 3.89 (s, 3H), 3.67 (s, 6H), 2.93 (dd, *J* = 1.6, 7.5 Hz, 2H), 2.64 (d, *J* = 7.3 Hz, 2H).

Dimethyl 2-allyl-2-{(5,6-dihydro[1,3]dioxolo[4',5':6,7]phenanthro[2,3-*d*][1,3]dioxol-5-yl) methyl}malonate (5ac) and Dimethyl 2-allyl-2-{3-(5,5'-bibenzo[*d*][1,3]dioxol-6-yl)prop-2-en-1-yl}malonate (*E*- and *Z*-6ac). According to the General Procedure, a crude product, which was obtained from **1a** (106.5 mg, 0.50 mmol), **4c** (0.38 mL, 1.5 mmol), $Ni(cod)_2$ (14.2 mg, 0.052 mmol), SIMes·HBF_4 (19.4 mg, 0.049 mmol) and CsF (455.1 mg, 3.0 mmol) in CH_3CN (5.0 mL), was purified by flash column chromatography on silica gel (hexane/AcOEt = 20/1~5/1) to give a mixture of **5ac** and **6ac**. Further purification was performed by recycling preparative gel permeation chromatography [column: JAIGEL-1H-A, JAIGEL-2H-A, eluent: $CHCl_3$, flow rate: 3.7 mL/min, detector: UV (254 nm).] to give **5ac** (130.6 mg, 71%) as a white solid and an inseparable mixture of *E*- and *Z*-**6ac** (7.0 mg, 4%, *E*/*Z* = 2.6/1) as a colorless oil, respectively. For **5ac**: mp. 131~132 °C; IR (film, CH_2Cl_2) 1730, 1265, 1235, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (s, 1H), 7.04 (s, 1H), 6.67 (s, 1H), 6.63 (s, 1H), 5.98-5.93 (m, 4H), 5.57 (ddt, *J* = 7.3, 10.7, 16.3 Hz, 1H), 5.08 (d, *J* = 10.7 Hz, 1H), 5.07 (d, *J* = 16.3 Hz, 1H), 3.68 (s, 3H), 3.59 (s, 3H), 2.92 (dd, *J* = 6.4, 15.0 Hz, 1H), 2.86 (dddd, *J* = 2.0, 6.4, 6.4, 6.4 Hz, 1H), 2.56 (dd, *J* = 6.4, 14.3 Hz, 1H), 2.71 (dd, *J* = 6.4, 14.3 Hz, 1H), 2.52 (dd, *J* = 2.0, 15.0 Hz, 1H), 1.99 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 171.3, 147.0, 146.9, 146.3, 146.1, 133.7, 132.3, 128.0, 127.7 (2C), 119.1, 109.4, 108.4, 104.1, 103.7, 100.9, 100.8, 56.8, 52.3, 52.2, 37.5, 34.7, 34.5 (2C); EI-LRMS *m*/*z* 452 (M^+), 280, 267, 237, EI-HRMS Calcd for $C_{25}H_{24}O_8$ 452.1471, Found 452.1474. For *E*- and *Z*-**6ac**: IR (film, CH_2Cl_2) 1732, 1266, 1227, 738 cm^{-1}; EI-LRMS *m*/*z* 452 (M^+), 280, 267, 251, 237; EI-HRMS Calcd for $C_{25}H_{24}O_8$ 452.1471, Found 452.1465; ^{1}H NMR (500 MHz, $CDCl_3$) for *E*-**6ac**: δ 6.98(s, 1H), 6.83-6.56 (m, 4H), 6.33 (d, *J* = 15.3 Hz, 1H), 6.00-5.90 (m, 4H), 5.79 (dt, *J* = 7.6, 15.3 Hz, 1H), 5.69-5.50 (m, 1H), 5.07 (d, *J* = 16.6 Hz, 1H), 5.05 (d, *J* = 9.2 Hz, 1H), 3.70 (s, 6H), 2.69 (d, *J* = 7.6 Hz, 2H), 2.66 (d, *J* = 6.9 Hz, 2H); ^{1}H NMR (500 MHz, $CDCl_3$) for *Z*-**6ac**: δ 6.83-6.56 (m, 5H), 6.27 (d, *J* = 11.5 Hz, 1H), 6.00-5.90 (m, 4H), 5.69-5.50 (m, 1H), 5.38 (dt, *J* = 7.6, 11.5 Hz, 1H), 5.07 (d, *J* = 16.6 Hz, 1H), 5.05 (d, *J* = 9.2 Hz, 1H), 3.70 (s, 6H), 2.77 (d, *J* = 7.6 Hz, 2H), 2.70-2.63 (m, 2H).

Dimethyl 2-cinnamyl-2-propylmalonate (9). According to the General Procedure, a crude product, which was obtained from **8** (107.4 mg, 0.50 mmol), **4a** (0.38 mL, 1.5 mmol), $Ni(cod)_2$ (13.6 mg, 0.049 mmol), SIMes·HBF_4 (19.7 mg, 0.050 mmol) and CsF (455.4 mg, 3.0 mmol) in CH_3CN (5.0 mL), was purified by flash column chromatography on silica gel (hexane/AcOEt = 100/1~10/1) to give **9** (16.0 mg, 11%) as a colorless oil. For **9**: IR(neat) 1735, 1234, 744 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.12 (m, 5H), 6.05 (d, *J* = 15.9 Hz, 1H), 5.69 (dt, *J* = 6.9, 15.9 Hz, 1H), 3.72 (s, 6H), 3.42 (d, *J* = 6.9 Hz, 2H), 2.03-1.98 (m, 2H), 1.27-1.18 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3 (2C), 139.7, 131.0, 128.4 (2C), 128.4 (2C), 128.2, 126.2, 59.4, 52.6 (2C), 39.0, 37.6, 17.7, 14.3; EI-LRMS *m/z* 290 (M^+), 247, 231, 199, 171; EI-HRMS Calcd for $C_{17}H_{22}O_4$ 290.1518, Found 290.1502.

9-(Pent-4-enyl)-9,10-dihydrophenanthrene (5fa) and 2-(Hepta-1,6-dienyl)biphenyl (*E*- and *Z*-6fa). According to the General Procedure, a crude product, which was obtained from **1f** (67.5 μL, 0.50 mmol), **4a** (0.38 mL, 1.5 mmol), $Ni(cod)_2$ (13.4 mg, 0.049 mmol), SIMes·HBF_4 (19.9 mg, 0.051 mmol) and CsF (456.5 mg, 3.0 mmol) in CH_3CN (5.0 mL), was purified by flash column chromatography on silica gel (hexane only ~ hexane/AcOEt = 50/1) to give a mixture of **5f** and **6f**. Further purification was performed by recycling preparative Gel Permeation Chromatography [column: JAIGEL-1H-A, JAIGEL-2H-A, eluent: $CHCl_3$, flow rate: 3.7 mL/min, detector: UV (254 nm).] to give **5f** (38.3 mg, 31%) as a colorless oil and an inseparable mixture of *E*- and *Z*-**6f** (4.1 mg, 3%, *E*/*Z* = 1/1) as a colorless oil. For **5f**: IR (neat) 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.78-7.72 (m, 2H), 7.36-7.17 (m, 6H), 5.74 (ddt, *J* = 6.7, 10.3, 17.0 Hz, 1H), 4.94 (d, *J* = 17.0 Hz, 1H), 4.89 (d, *J* = 10.3 Hz, 1H), 3.10 (dd, *J* = 5.2, 14.9 Hz, 1H), 2.87-2.81 (m, 1H), 2.78 (dd, *J* = 3.4, 14.9 Hz, 1H), 1.97 (dt, *J* = 6.8, 6.8 Hz, 2H), 1.62-1.24 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 138.8, 135.4, 134.0, 133.4, 128.9, 128.1, 127.4, 127.3, 126.9, 126.8, 124.0, 123.4, 114.4, 38.4, 33.9, 33.7, 32.8, 26.9; EI-LRMS m/z 248 (M^+), 191, 179; EI-HRMS Calcd for $C_{19}H_{20}$ 248.1571, found 248.1572. For *E*- and *Z*-**6f**: IR (film, CH_2Cl_2) 740 cm^{-1}; EI-LRMS *m/z* 248 (M^+), 205, 191, 179, 165; EI-HRMS Calcd for $C_{19}H_{20}$ 248.1571, Found 248.1565; ^1H NMR (500 MHz, $CDCl_3$) for *E*-**6f**: δ 7.43-7.25 (m, 9H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 7.2, 15.8 Hz, 1H), 5.80 (ddt, *J* = 6.7, 10.3, 17.0 Hz, 1H), 4.99 (d, *J* = 17.0 Hz, 1H), 4.93 (d, *J* = 10.3 Hz, 1H), 2.14 (dt, *J* = 7.2, 7.4 Hz, 2H), 2.06 (dt, *J* = 6.7, 7.3 Hz, 2H), 1.50 (tt, *J* = 7.3, 7.4 Hz, 2H); ^1H NMR (500 MHz, $CDCl_3$) for *Z*-**6f**: δ 7.43-7.25 (m, 9H), 6.27 (d, *J* = 11.5 Hz, 1H), 5.80 (ddt, *J* = 6.7, 10.3, 17.0 Hz, 1H), 5.58 (dt, *J* = 7.4, 11.5 Hz, 1H), 4.99 (d, *J* = 17.0 Hz, 1H), 4.93 (d, *J* = 10.3 Hz, 1H), 2.27 (dt, *J* = 7.4, 7.5 Hz, 2H), 2.06 (dt, *J* = 6.7, 7.3 Hz, 2H), 1.50 (tt, *J* = 7.3, 7.5 Hz, 2H).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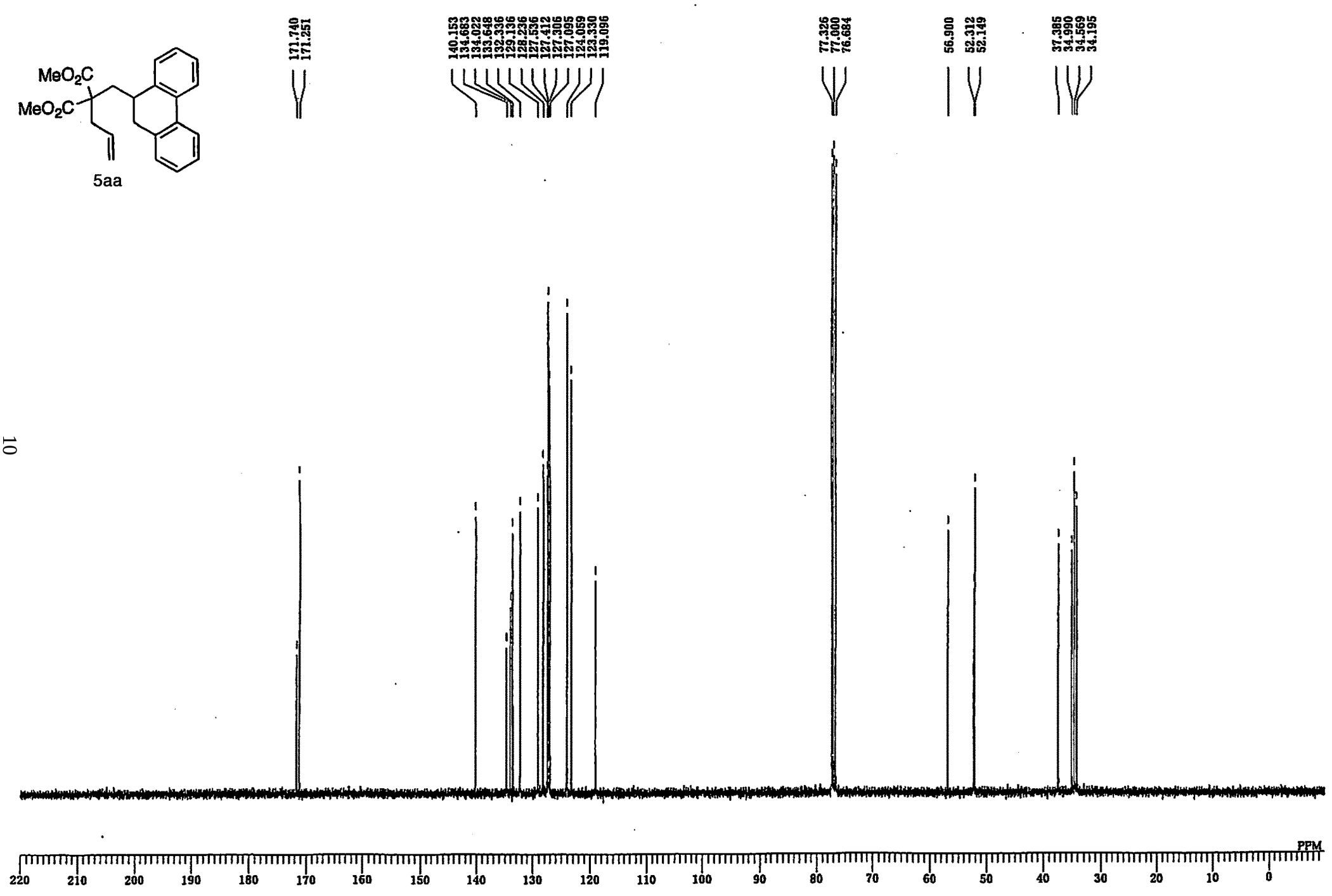
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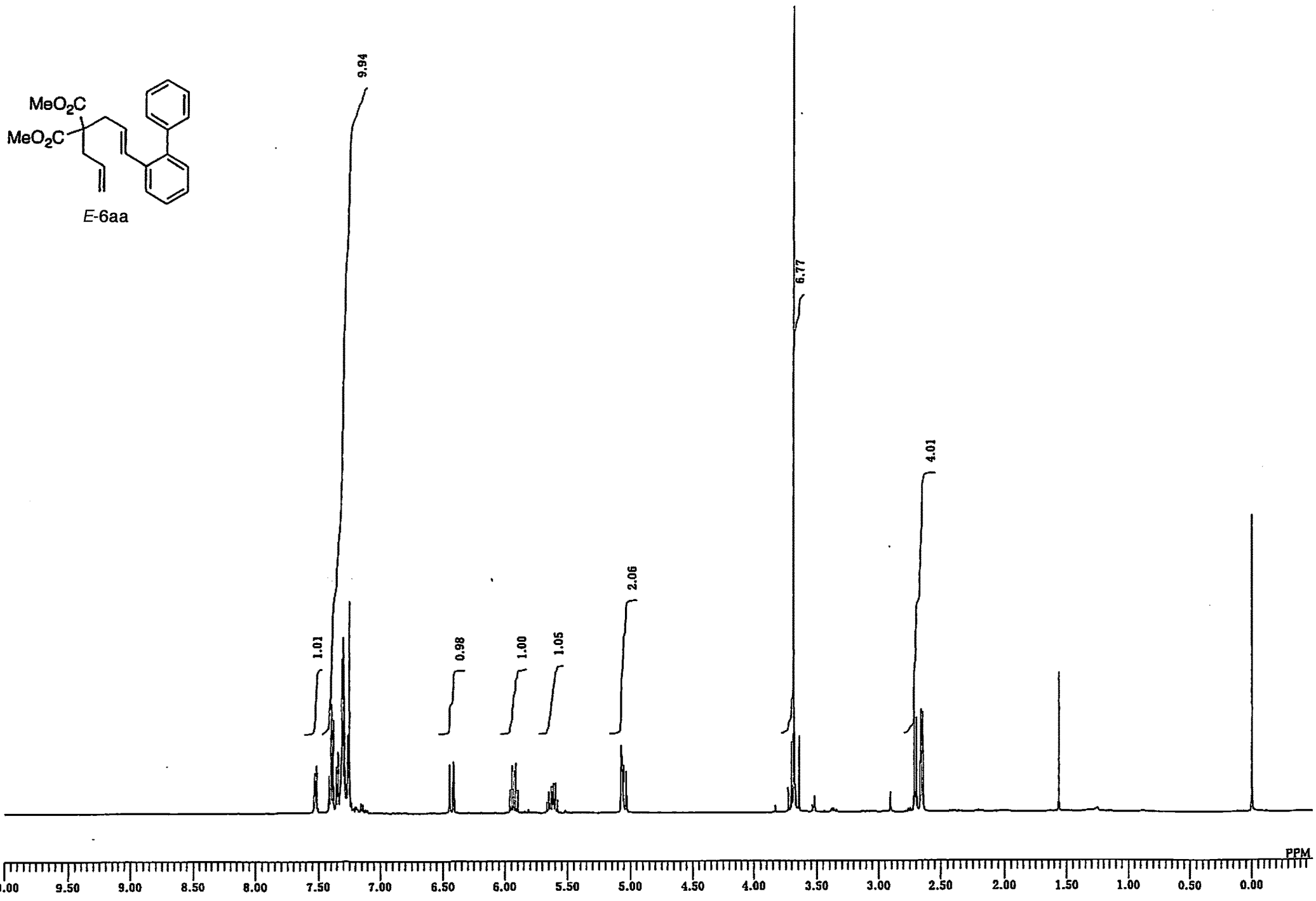
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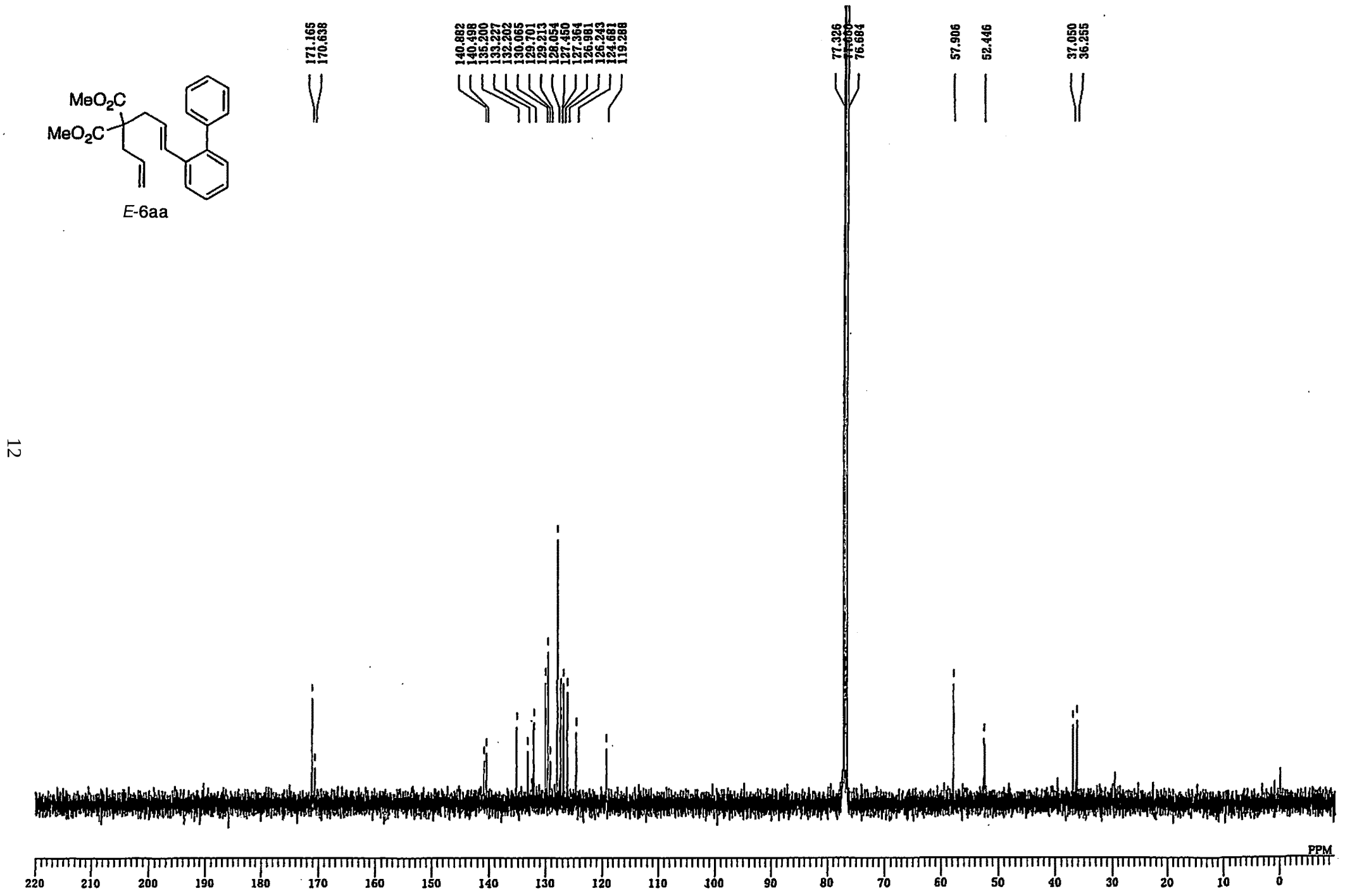
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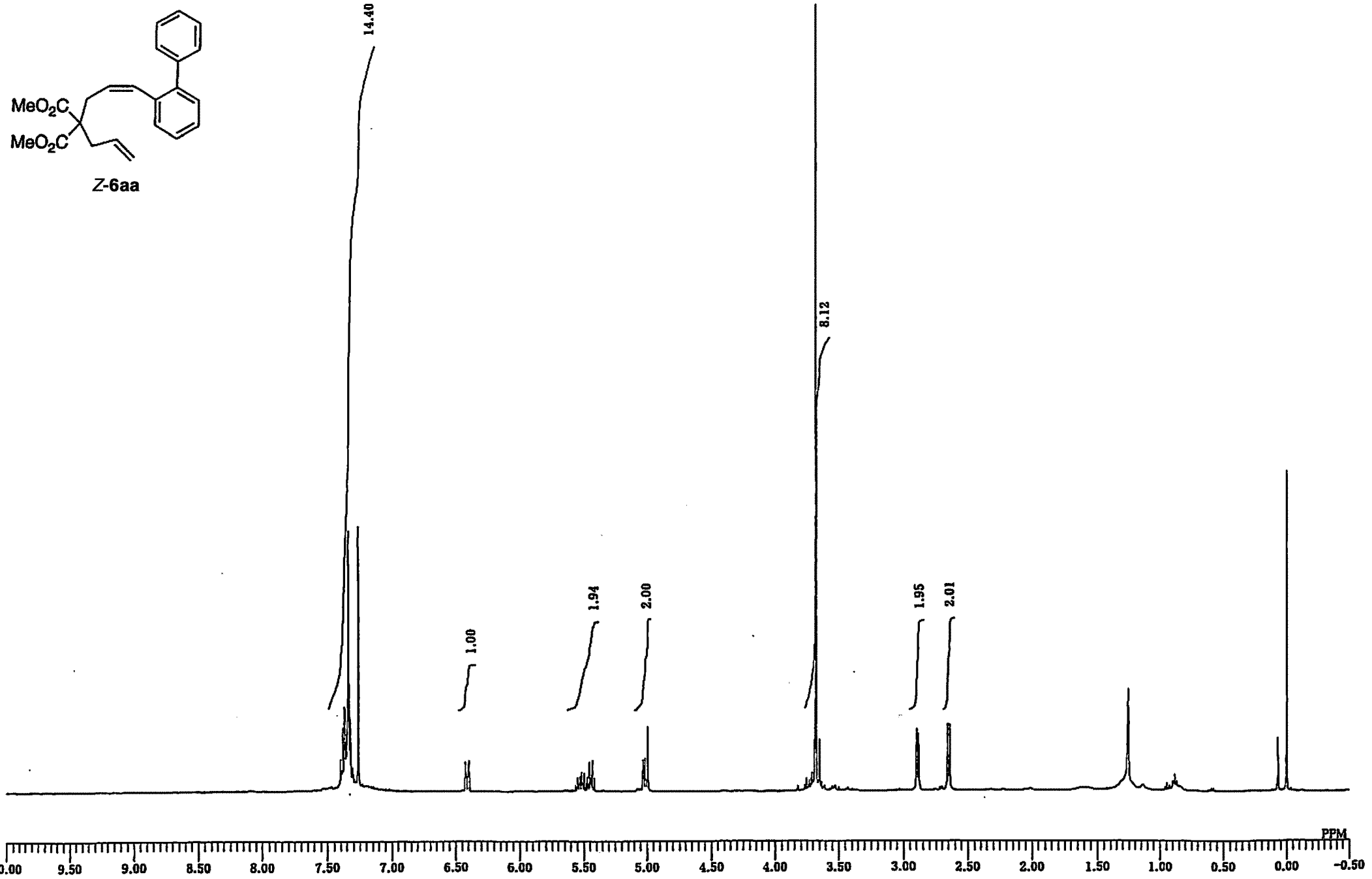
MeO2C

Z-6aa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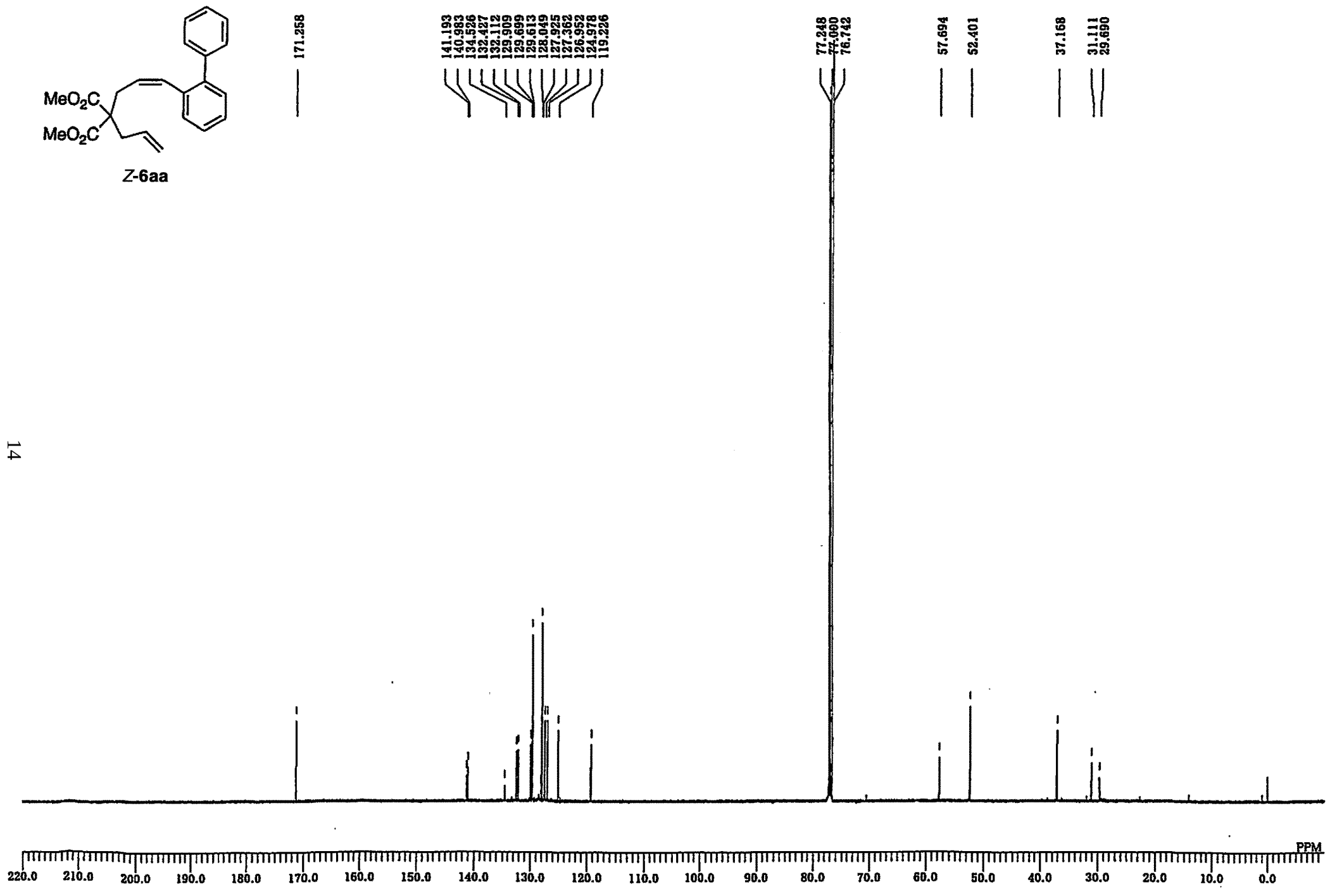
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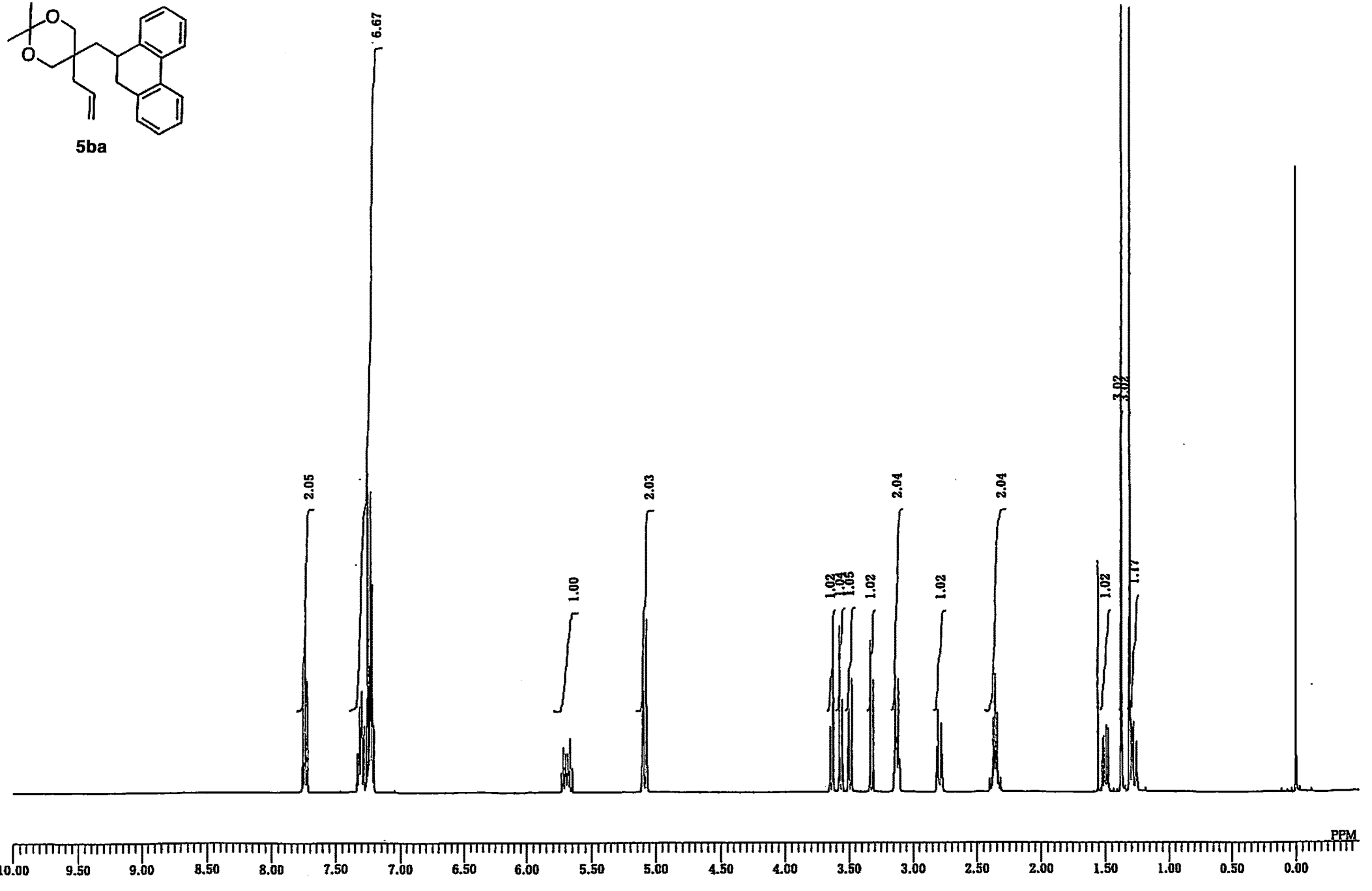
5ba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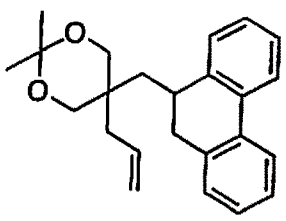

5ba

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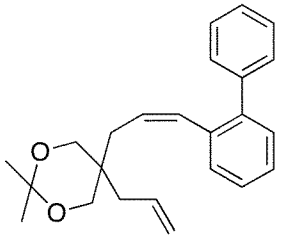
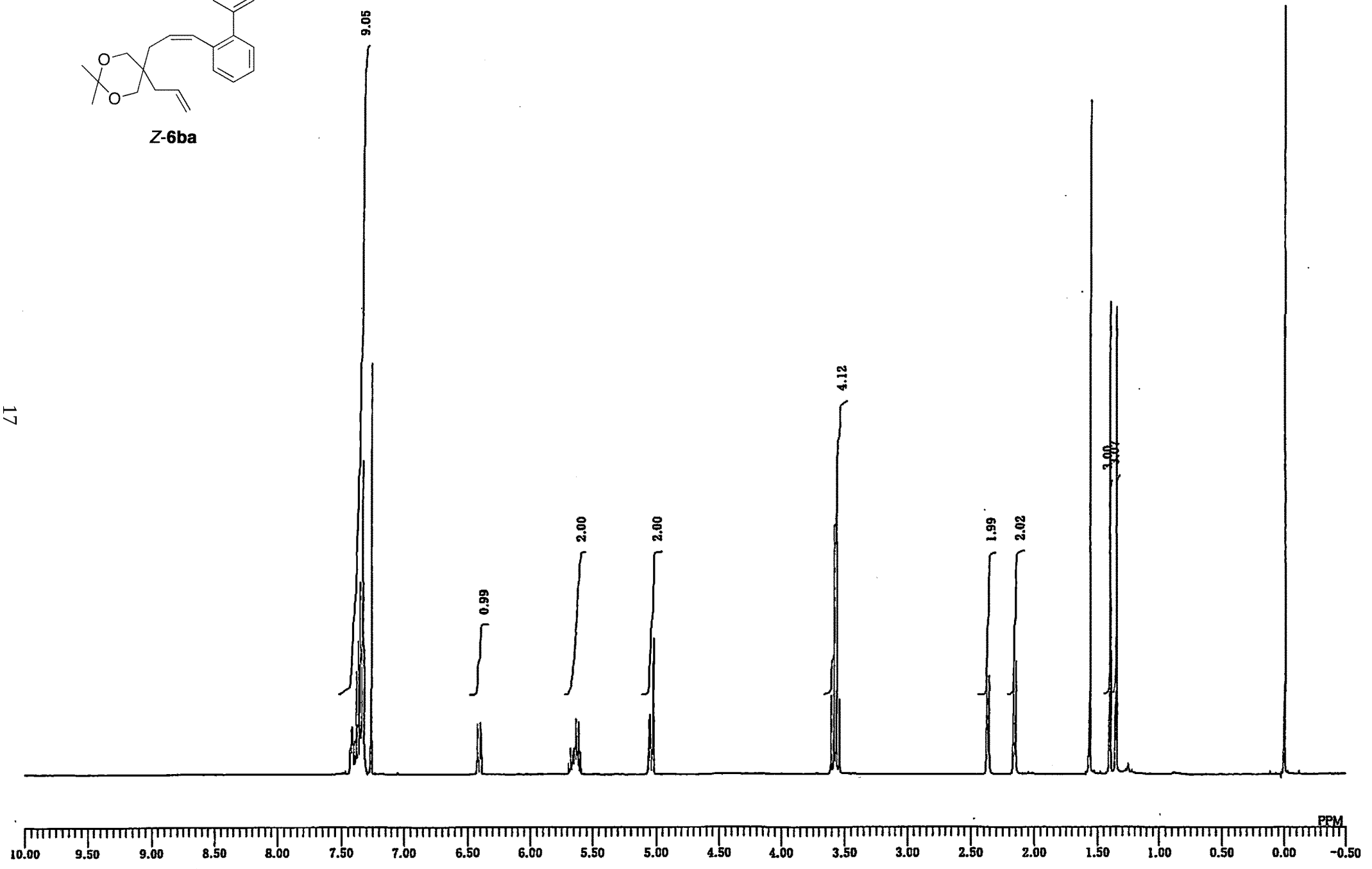


Z-6ba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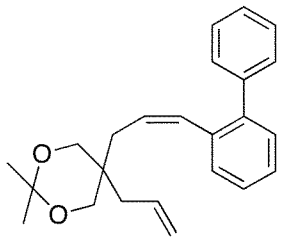

Z-**6ba**

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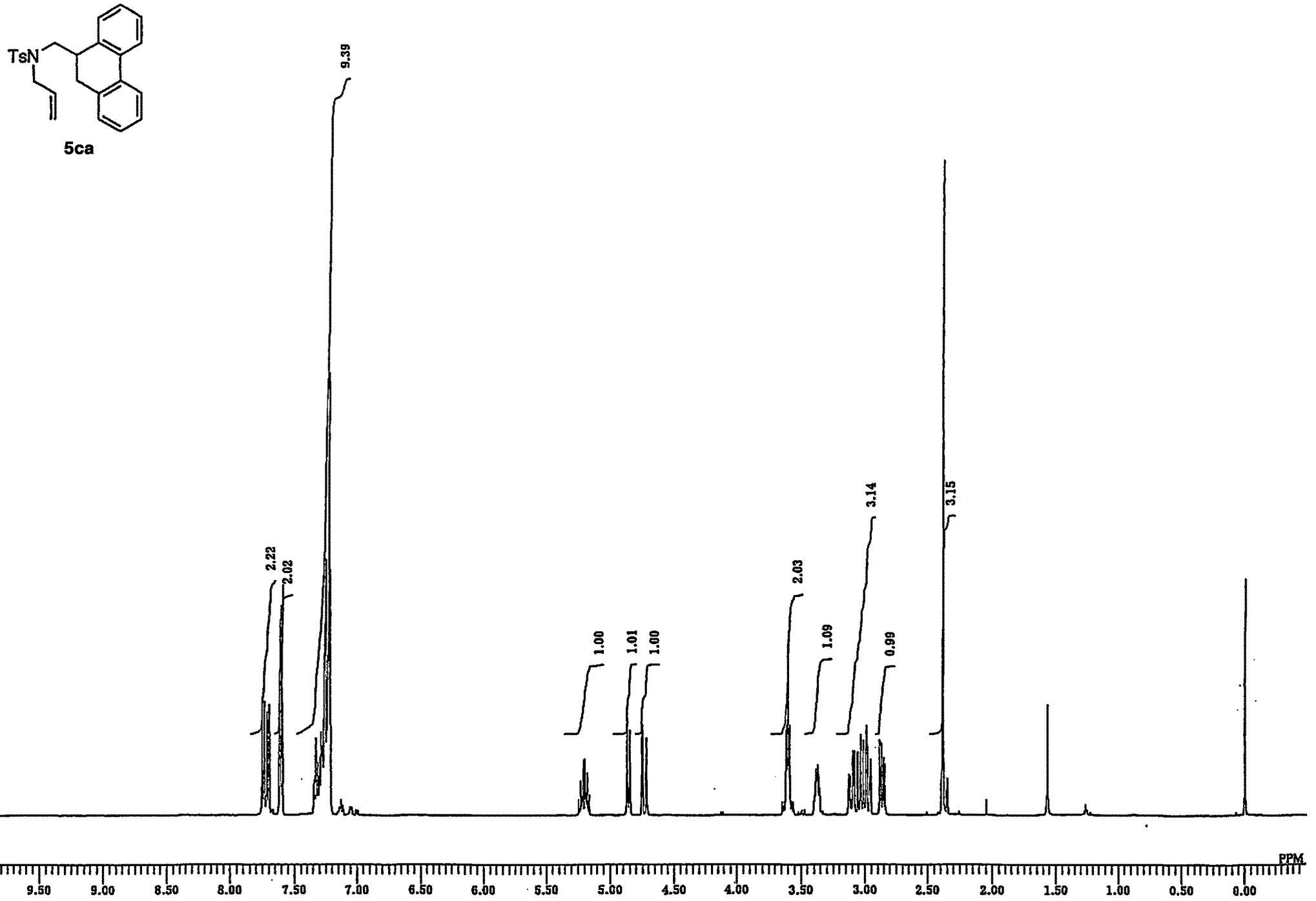
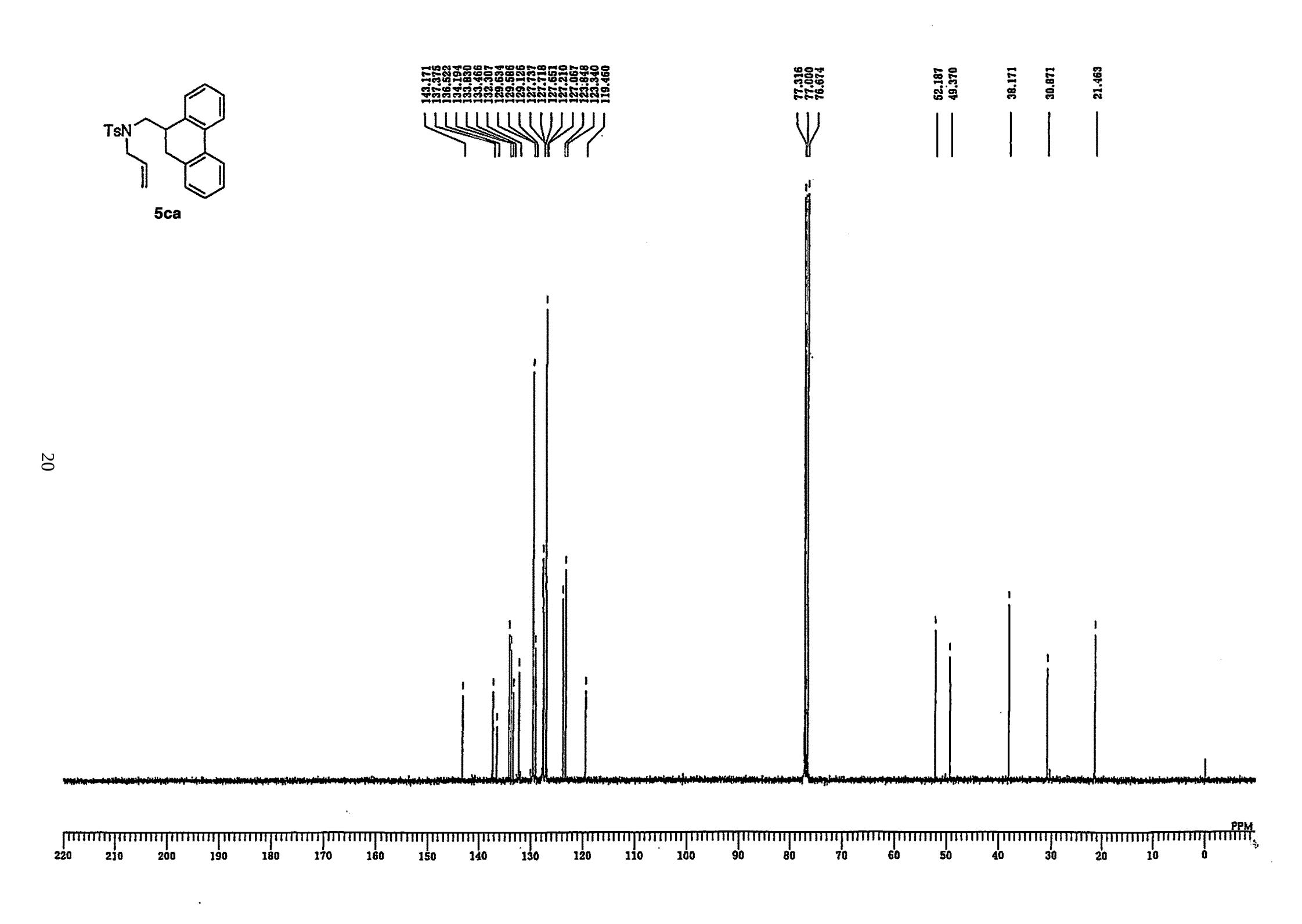
126.875
126.808
126.109
118.406
97.962
77.316
77.000
76.674
67.257
36.744
35.977
30.583
24.030
23.551

PPM

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


TsN
5ca
9.39
2.22
2.02
1.00
1.01
1.00
2.03
1.09
3.14
0.99
3.15
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00


TsN
5ca
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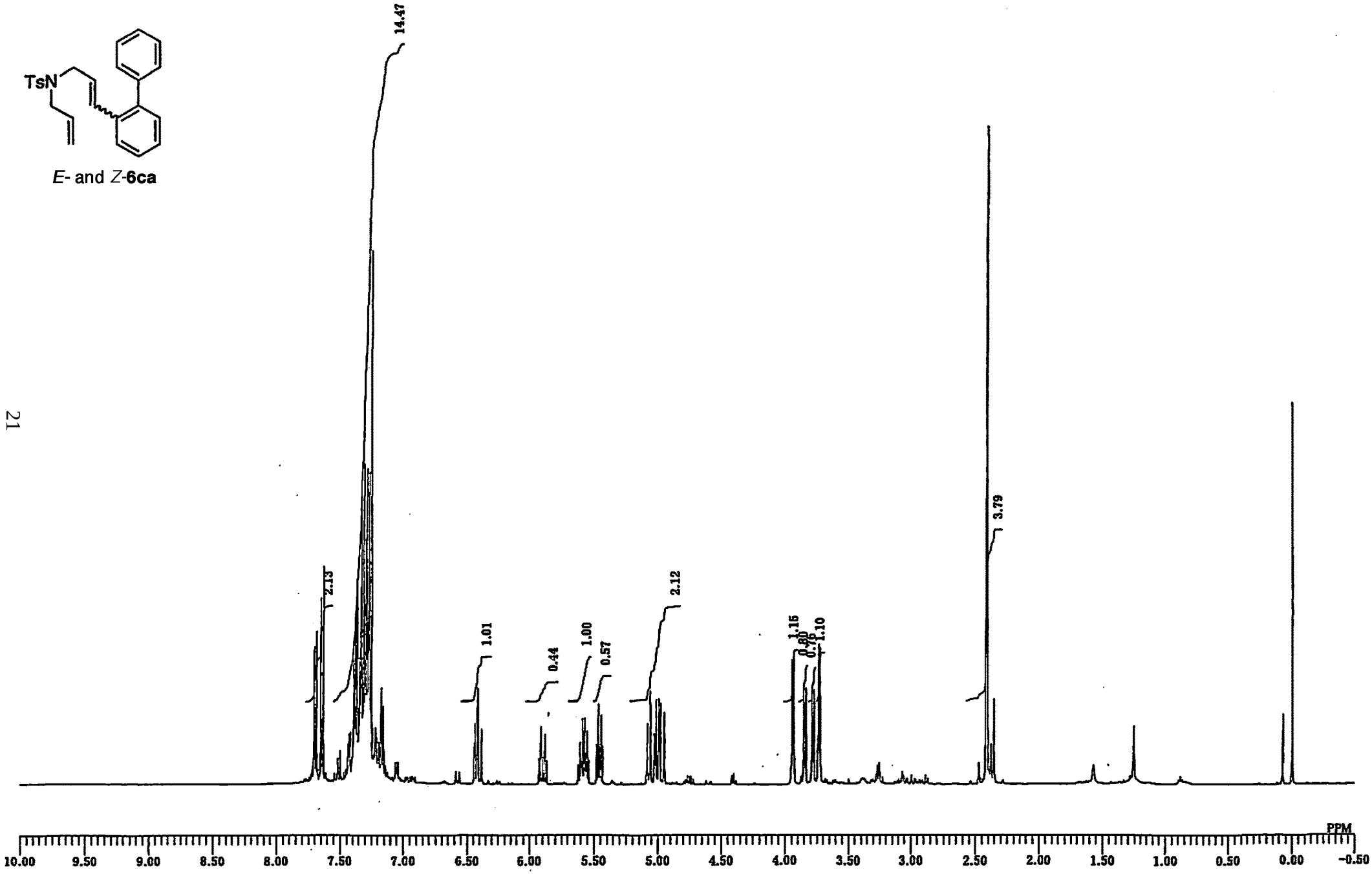
136.522
134.194
133.830
133.466
132.307
129.634
129.586
129.126
127.737
127.718
127.651
127.210
127.067
123.848
123.340
119.460
77.316
77.000
76.674
52.187
49.370
38.171
30.871
21.463
PPM
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

TsN

E- and *Z*-**6ca**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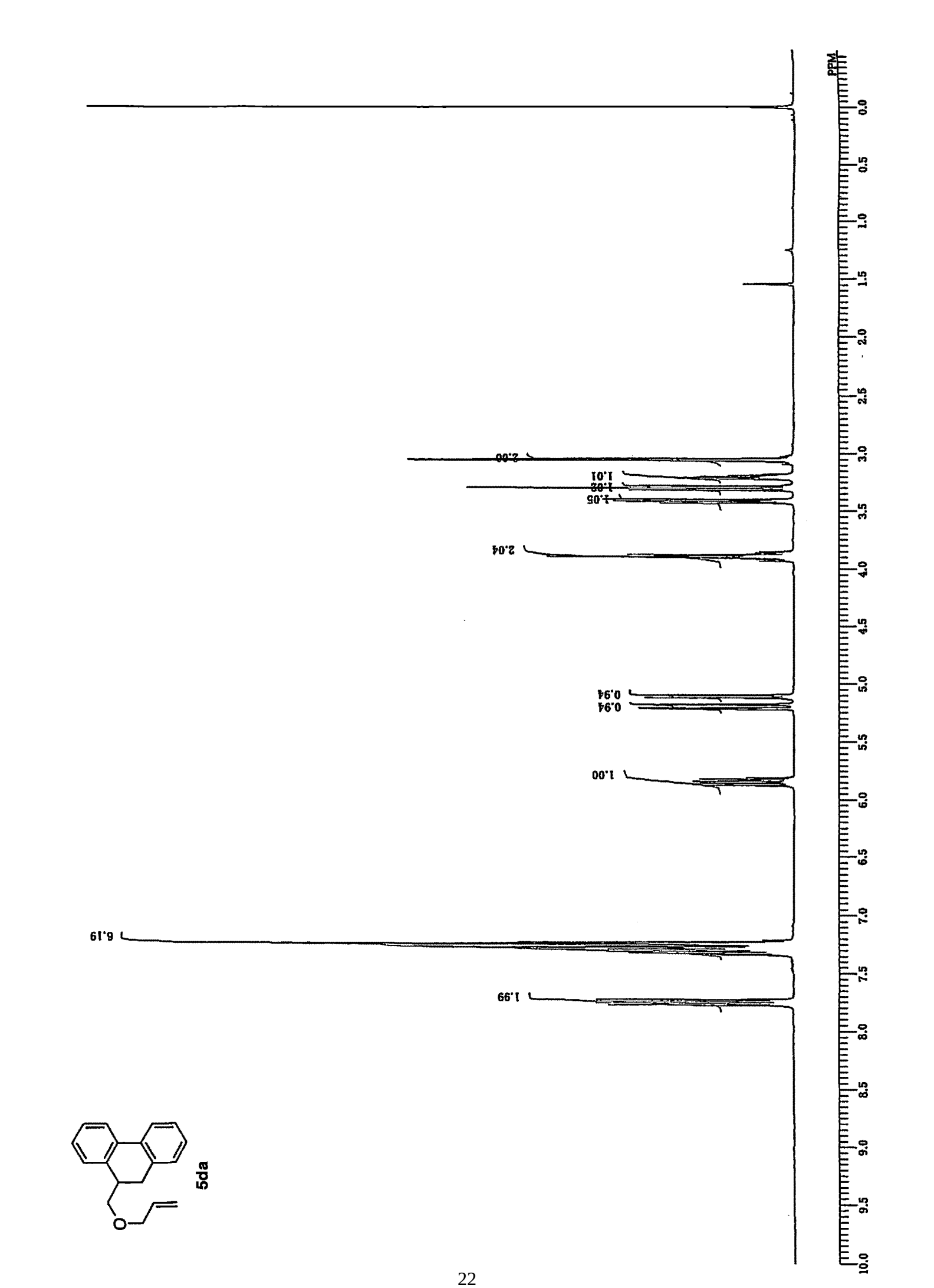
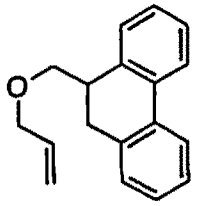
2.13
1.01
0.44
1.00
0.57
2.12
1.15
0.80
0.78
1.10
3.79
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50


6.19
1.99
2.04
0.94
0.94
1.00
2.00
1.01
1.05
PPM
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
O
5da



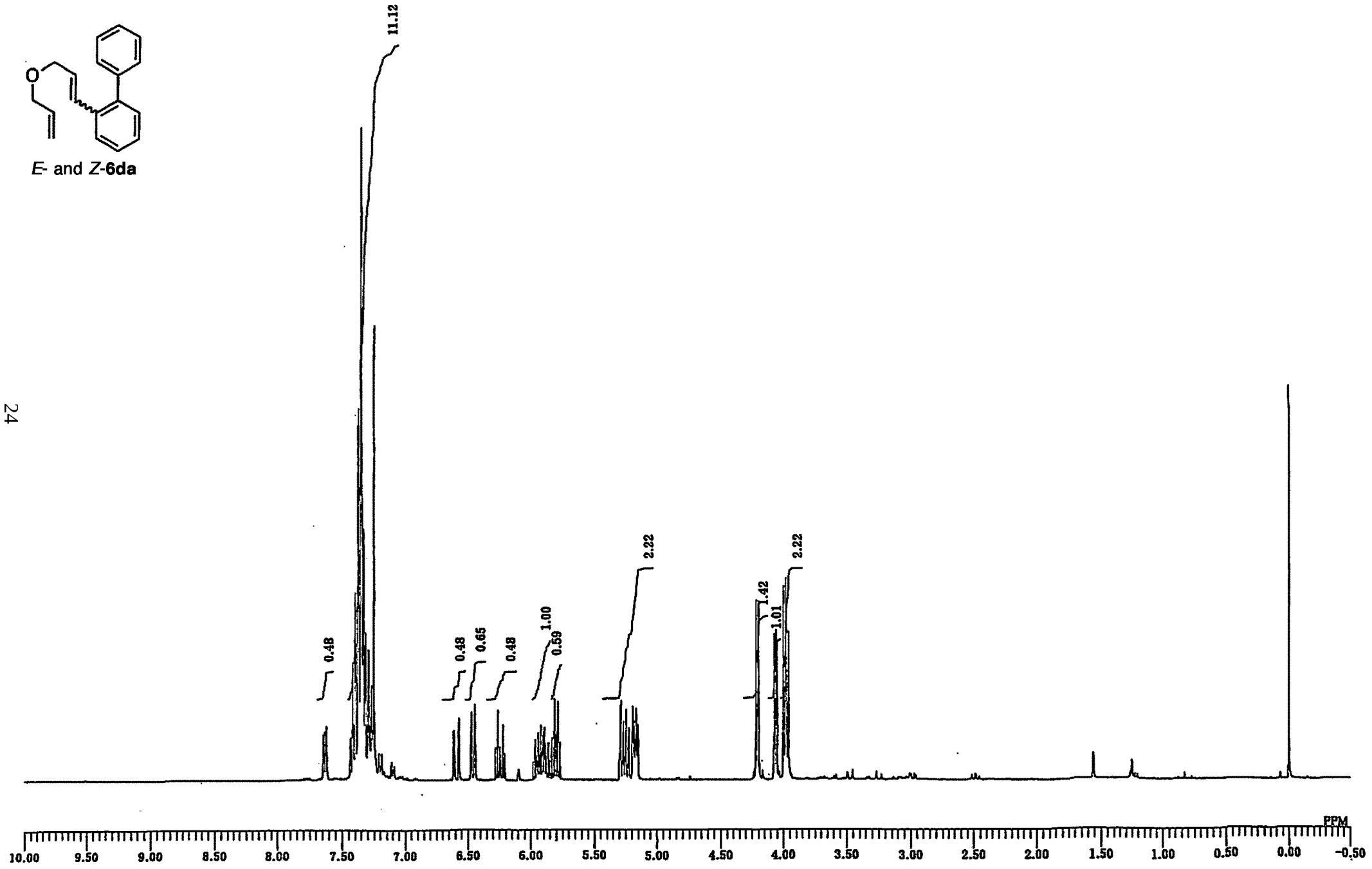
5da

137.330
134.859
134.764
134.087
133.734
129.175
128.660
127.620
127.534
127.458
126.905
123.805
123.366
116.651
77.258
77.060
76.742
71.849
71.411
38.875
30.672

PPM

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

E- and *Z*-**6da**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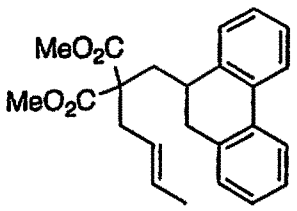
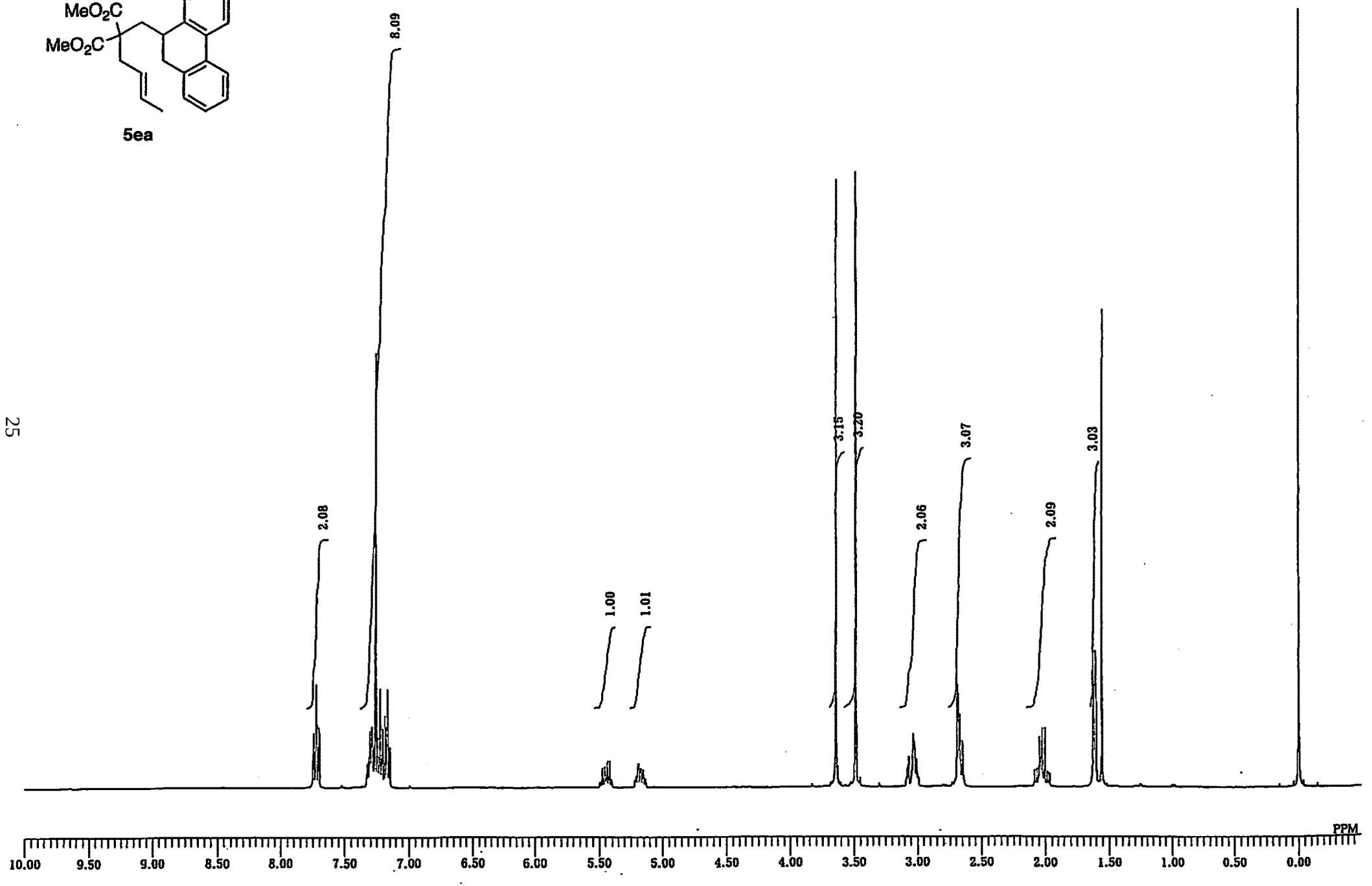
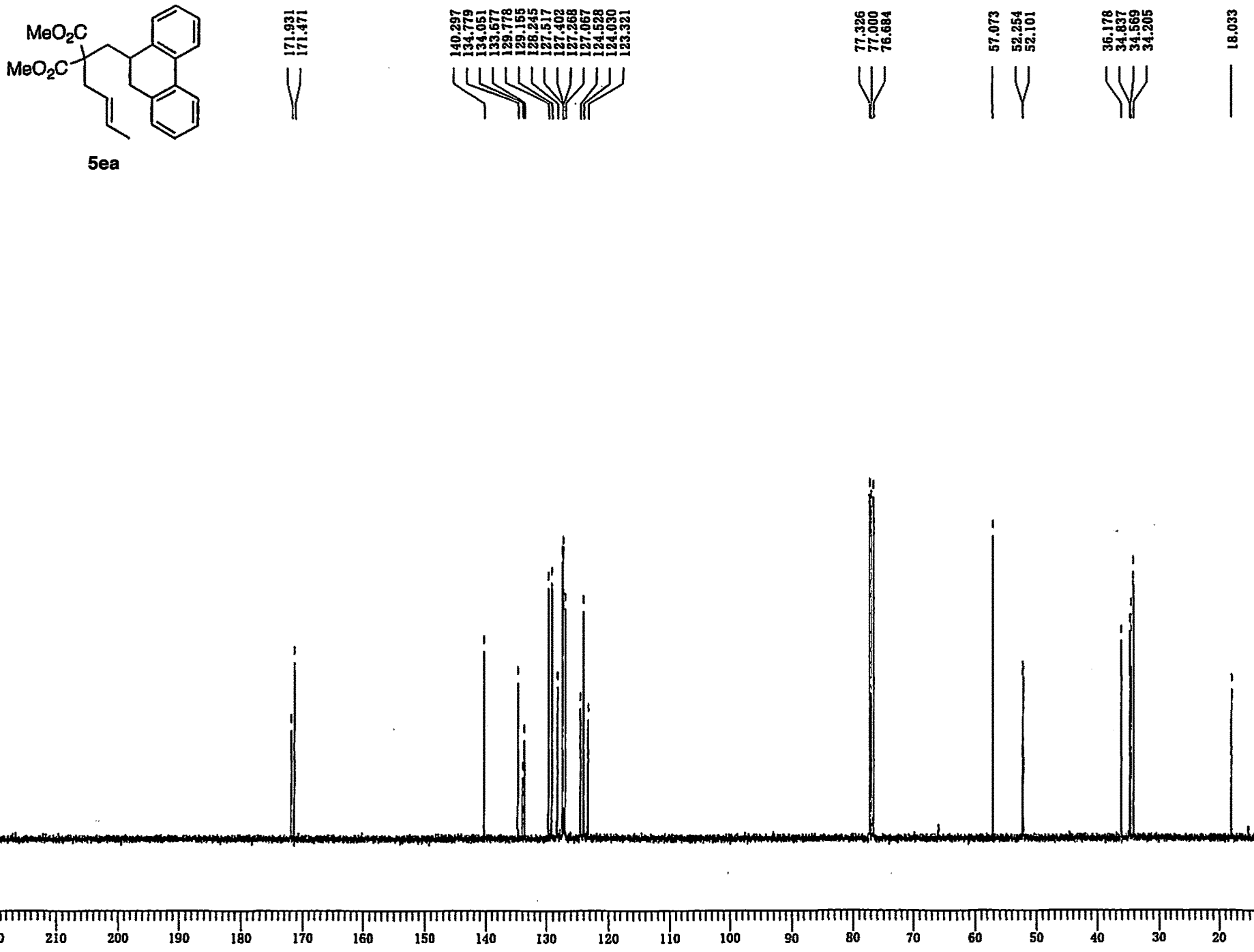
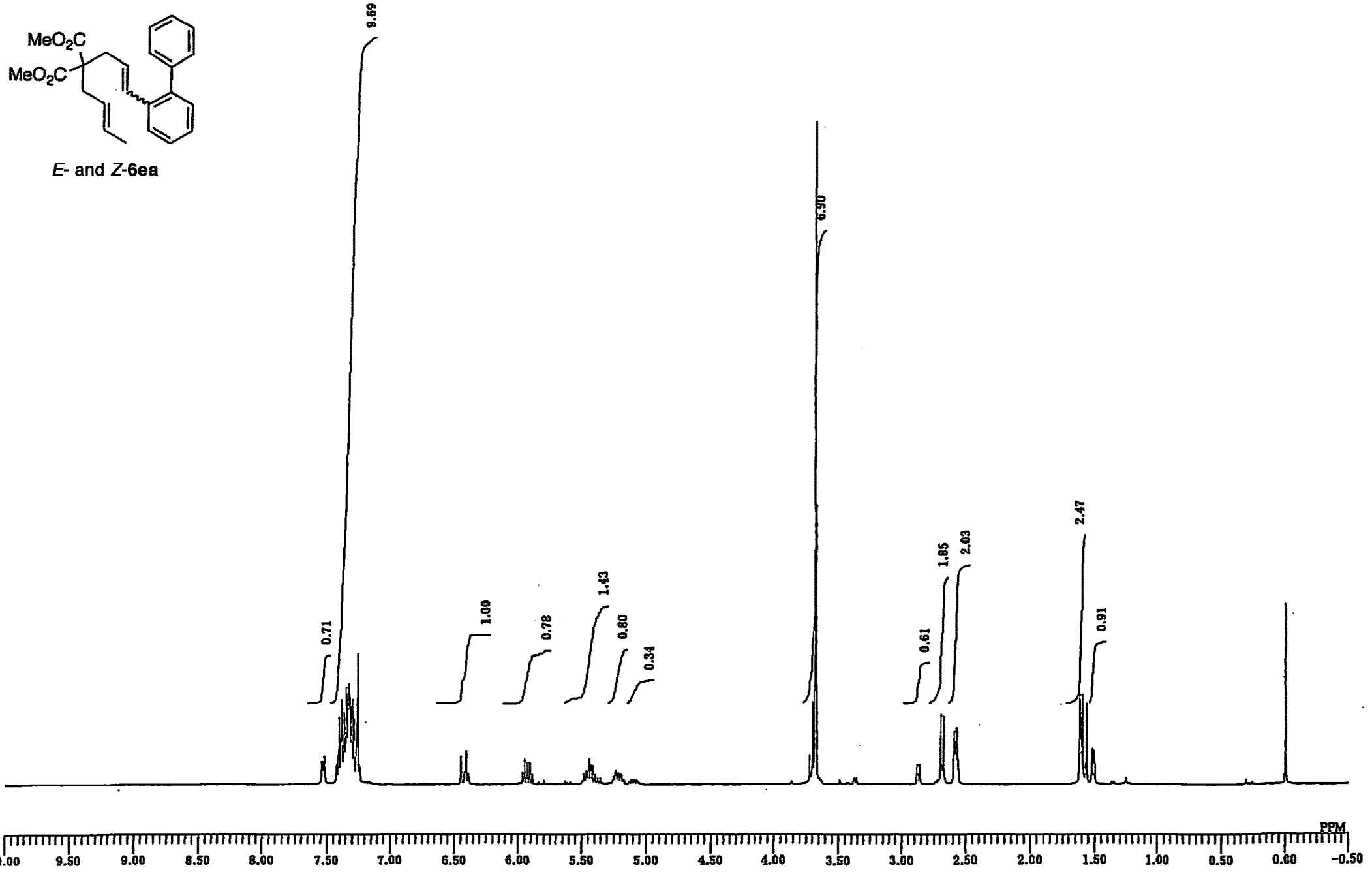
0.48
0.48
0.65
0.48
1.00
0.59
2.22
1.42
1.01
2.22
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50

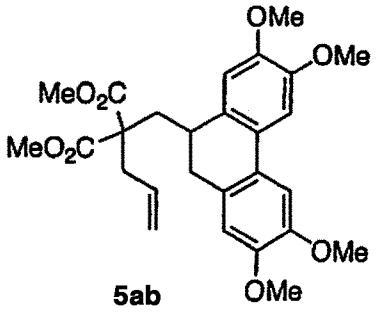

MeO2C
MeO2C

5ea

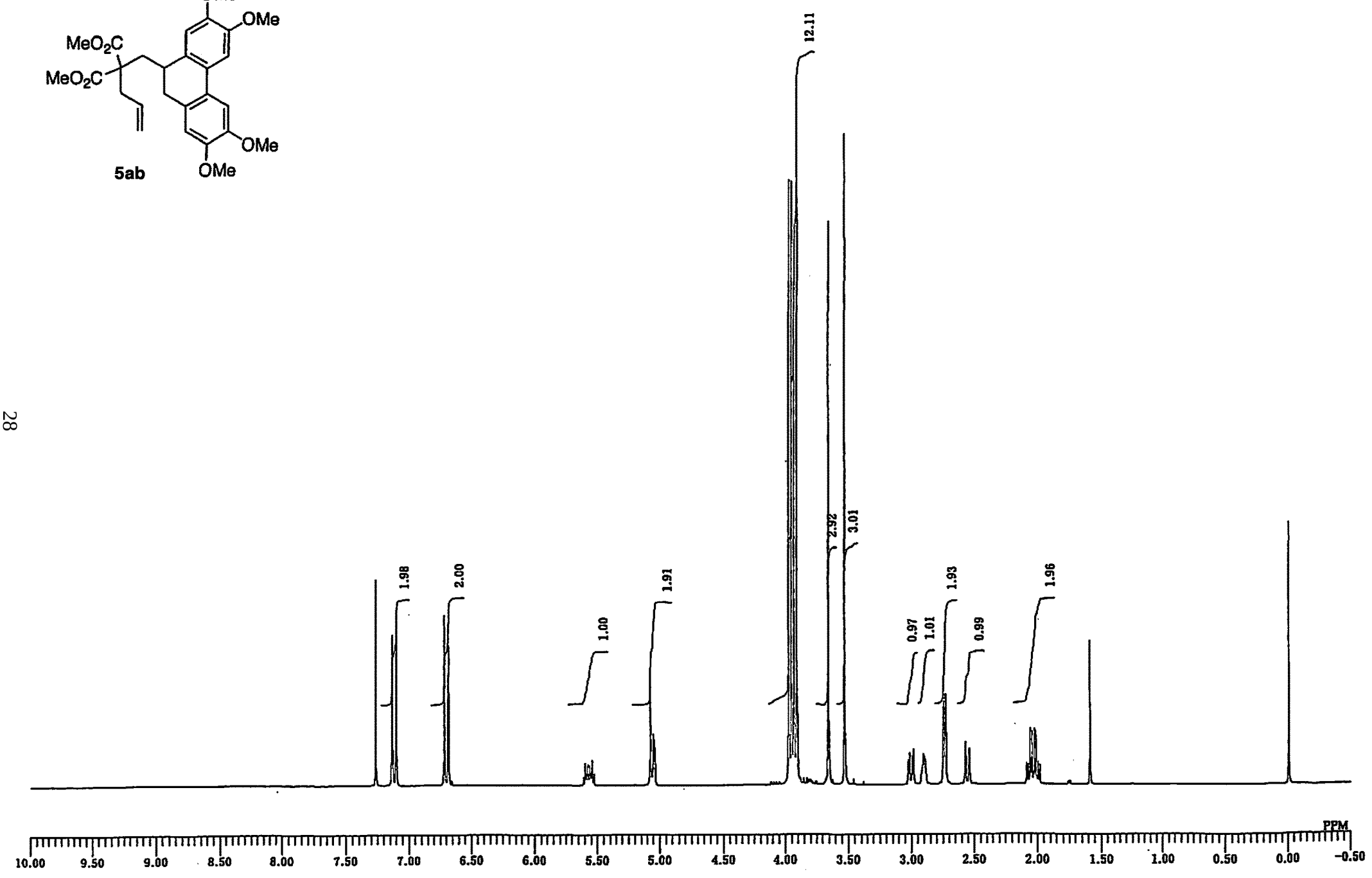

8.09
2.08
1.00
1.01
3.15
3.20
2.06
3.07
2.09
3.03
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00

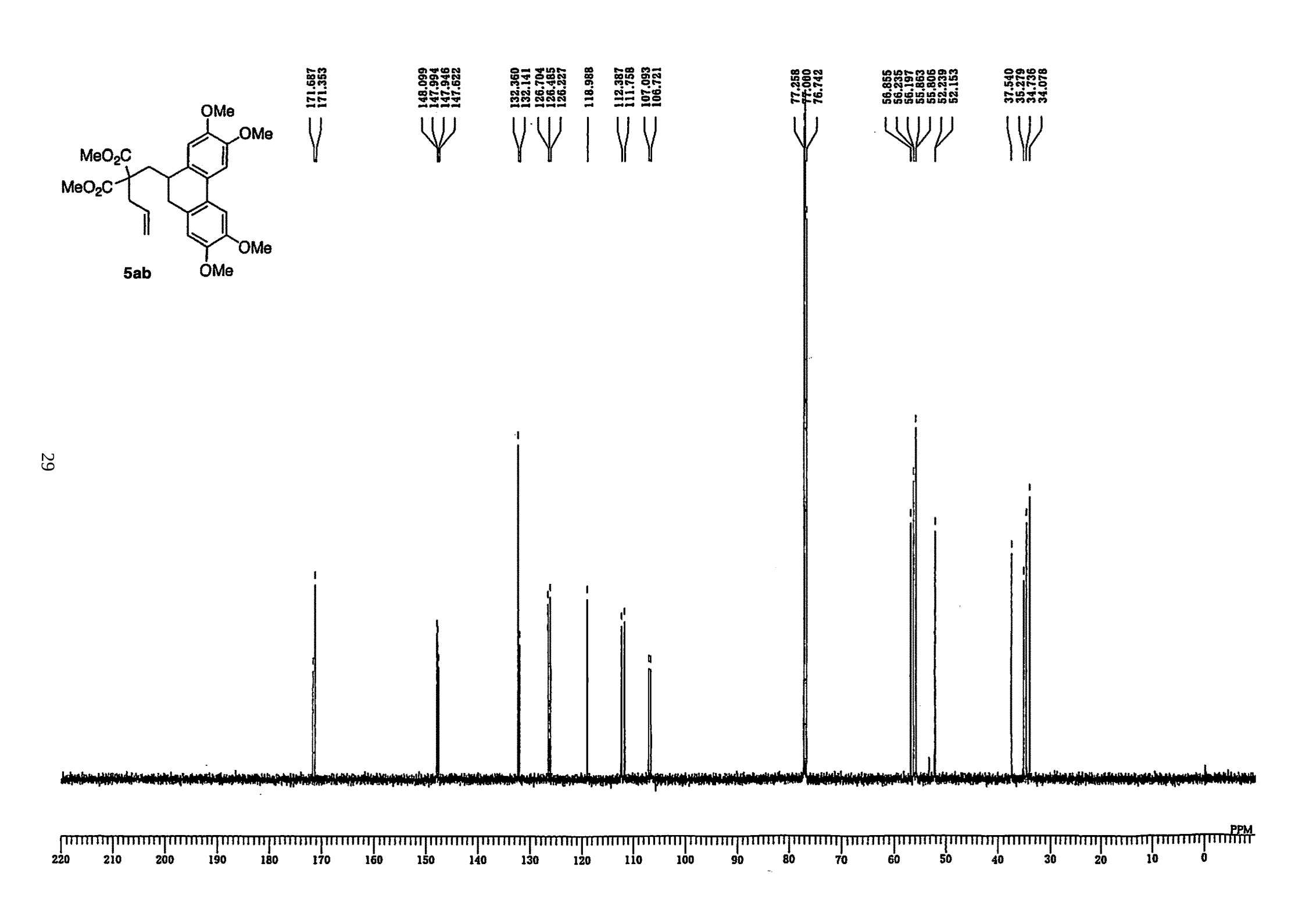

MeO2C
MeO2C
5ea
171.931
171.471
140.297
134.779
134.051
133.677
129.778
129.155
128.245
127.517
127.402
127.268
127.067
124.528
124.030
123.321
77.326
77.000
76.684
57.073
52.254
52.101
36.178
34.837
34.569
34.205
18.033
PPM
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

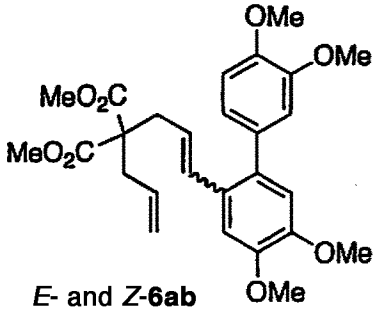

MeO2C
MeO2C
E- and Z-6ea
9.69
6.90
0.71
1.00
0.78
1.43
0.80
0.34
0.61
1.85
2.03
2.47
0.91
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50


OMe
OMe
MeO2C
MeO2C
OMe
OMe

5ab

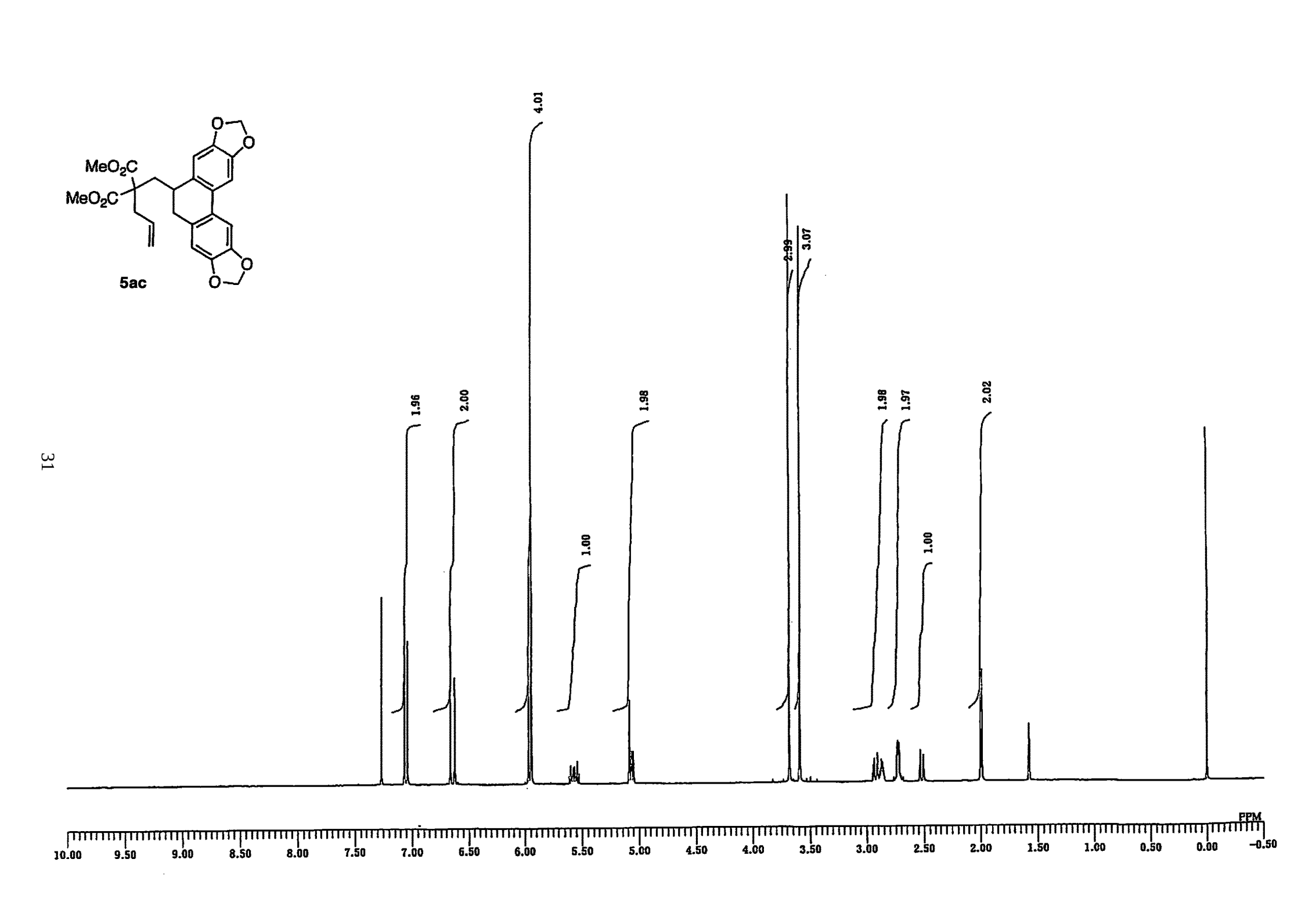

12.11
2.92
3.01
1.98
2.00
1.00
1.91
0.97
1.01
1.93
0.99
1.96
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50

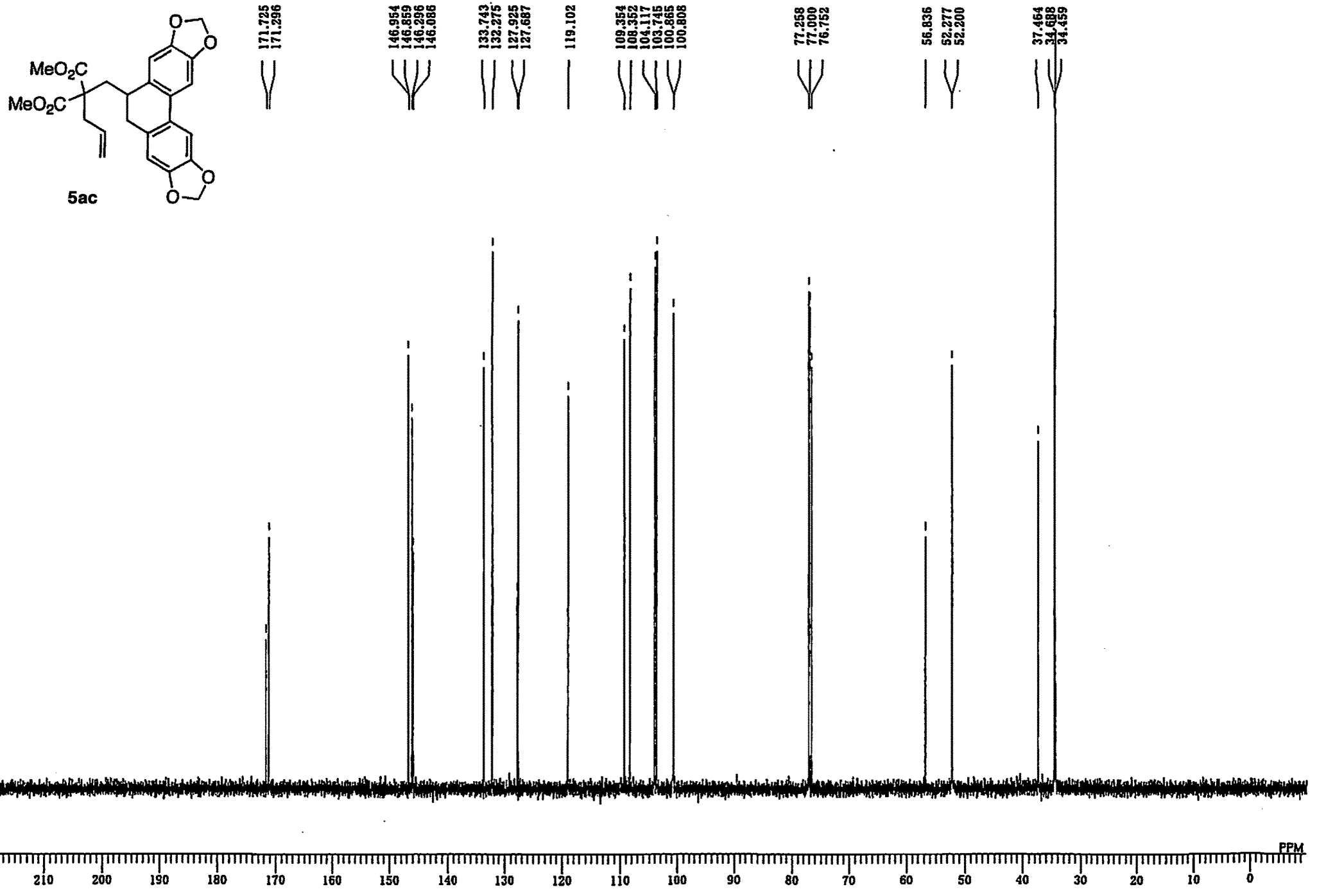

171.687
171.353
148.099
147.994
147.946
147.622
132.360
132.141
126.704
126.485
126.227
118.988
112.387
111.758
107.093
106.721
77.258
77.060
76.742
56.855
56.235
56.197
55.863
55.806
52.239
52.153
37.540
35.279
34.736
34.078
OMe
OMe
MeO2C
MeO2C
OMe
OMe
5ab
PPM
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OMe
OMe
MeO2C
MeO2C
OMe
OMe

E- and *Z*-**6ab**

15.33
7.30
6.61
2.38
1.98
1.36
1.14
1.00
0.82
0.52
0.29
0.28
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50


MeO2C
MeO2C
5ac
4.01
1.96
2.00
1.00
1.98
2.99
3.07
1.98
1.97
1.00
2.02
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50


MeO2C
MeO2C
5ac
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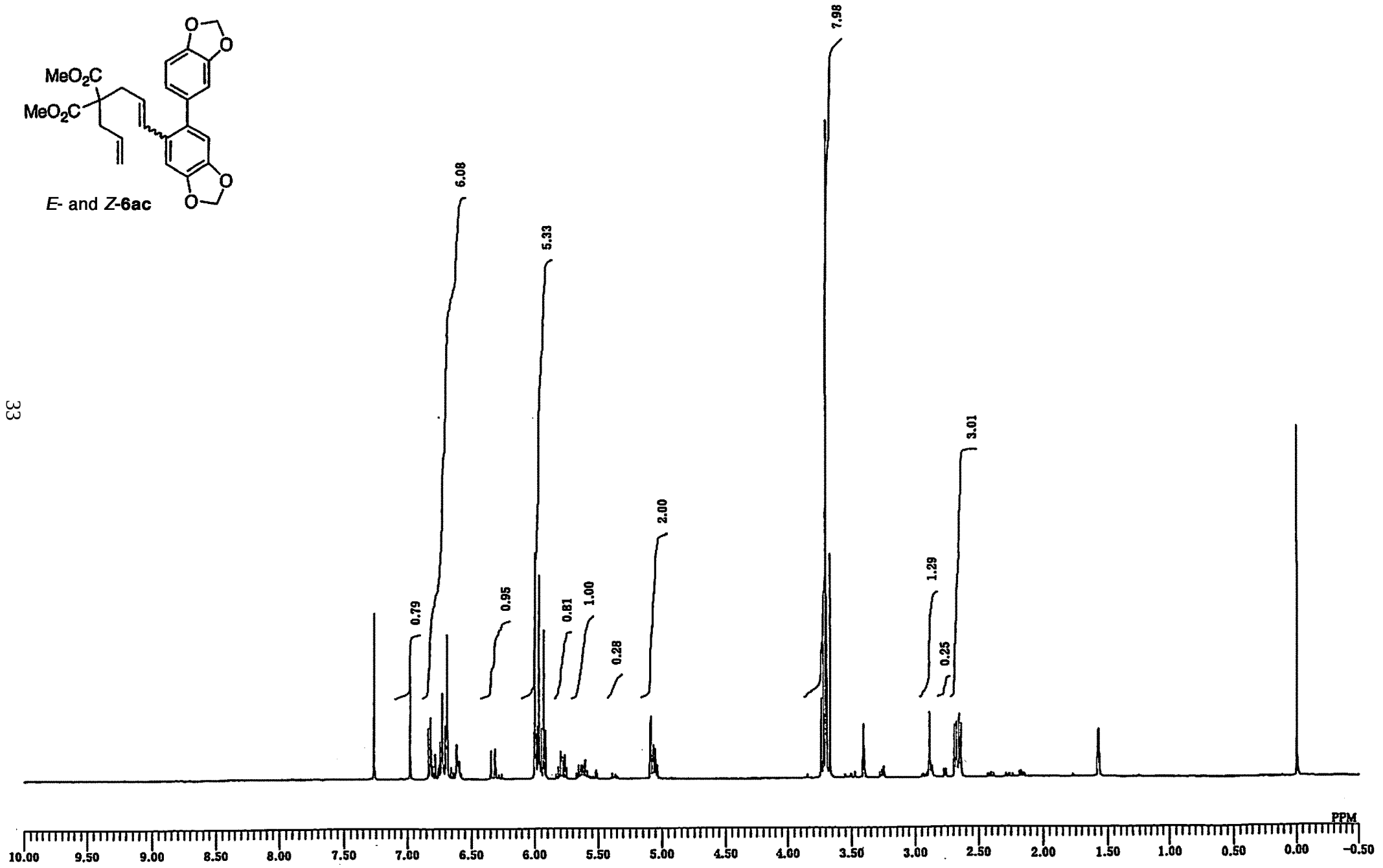
146.859
146.296
146.086
133.743
132.275
127.925
127.687
119.102
109.354
108.352
104.117
103.745
100.865
100.808
77.258
77.000
76.752
56.836
52.277
52.200
37.464
34.688
34.459
PPM
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

MeO2C
MeO2C
O
O
O
O

E- and *Z*-**6ac**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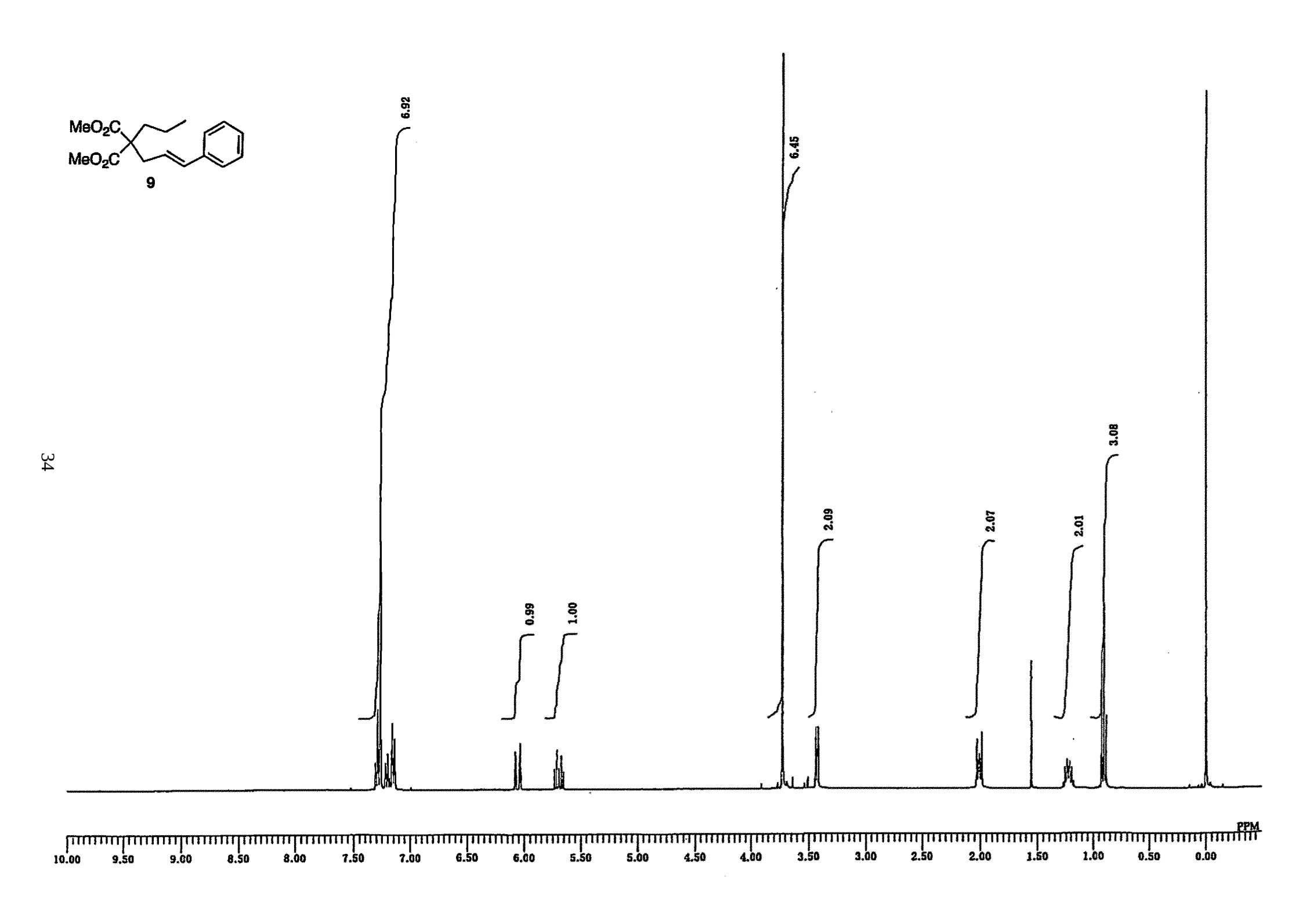
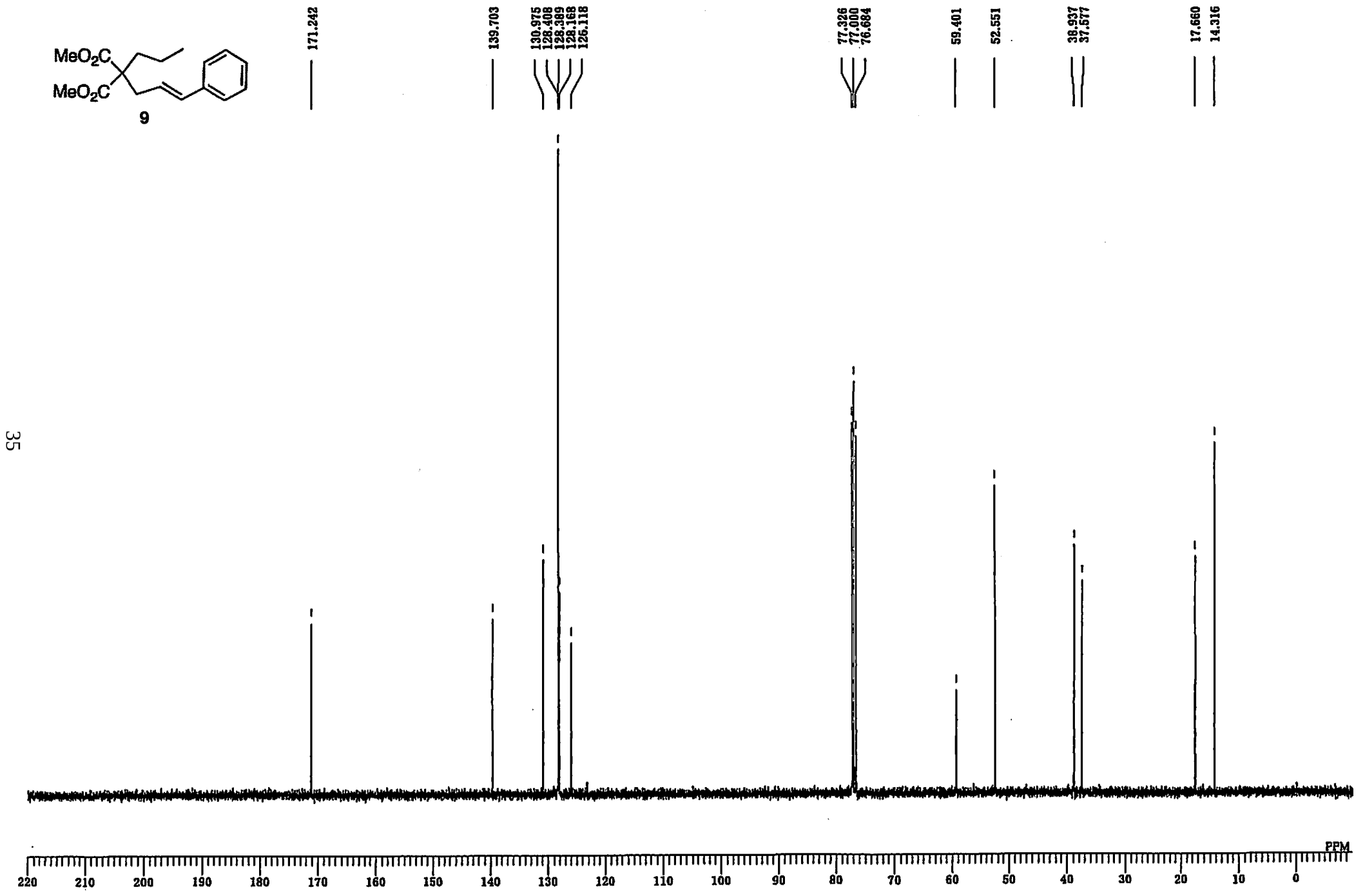
6.08
5.33
3.01
2.00
1.29
1.00
0.95
0.81
0.79
0.28
0.25
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50


MeO2C
MeO2C
9
6.92
6.45
0.99
1.00
2.09
2.07
2.01
3.08
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00


MeO2C
MeO2C
9
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128.389
128.168
126.118
77.326
77.000
76.684
59.401
52.551
38.937
37.677
17.660
14.316
PPM
220
210
200
190
180
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150
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120
110
100
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70
60
50
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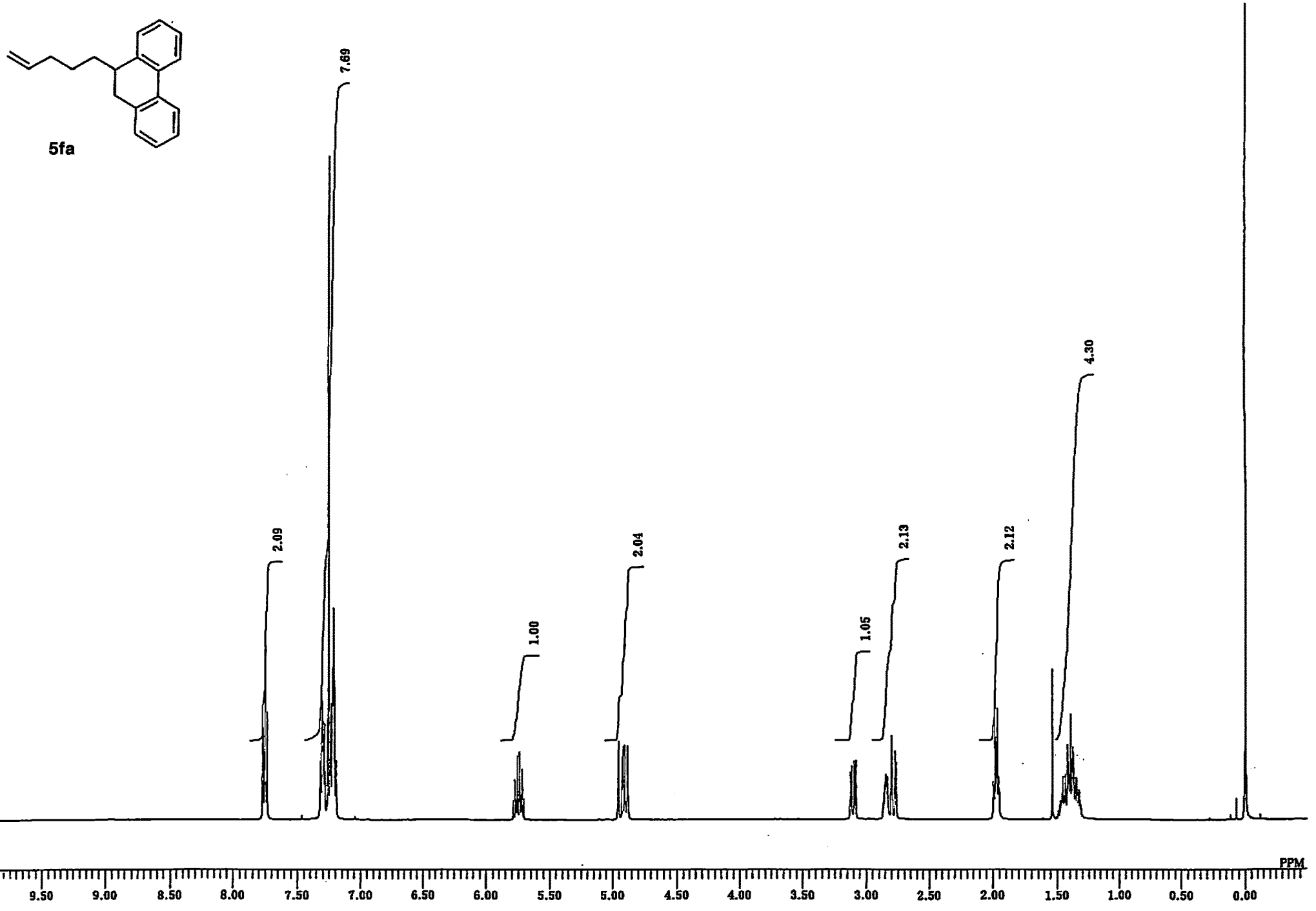
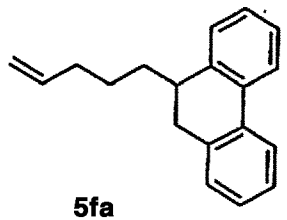
30
20
10
0


5fa
7.69
2.09
1.00
2.04
1.05
2.13
2.12
4.30
PPM
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00

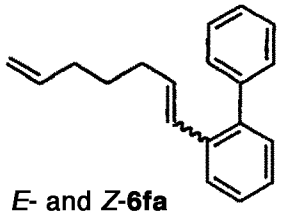


5fa

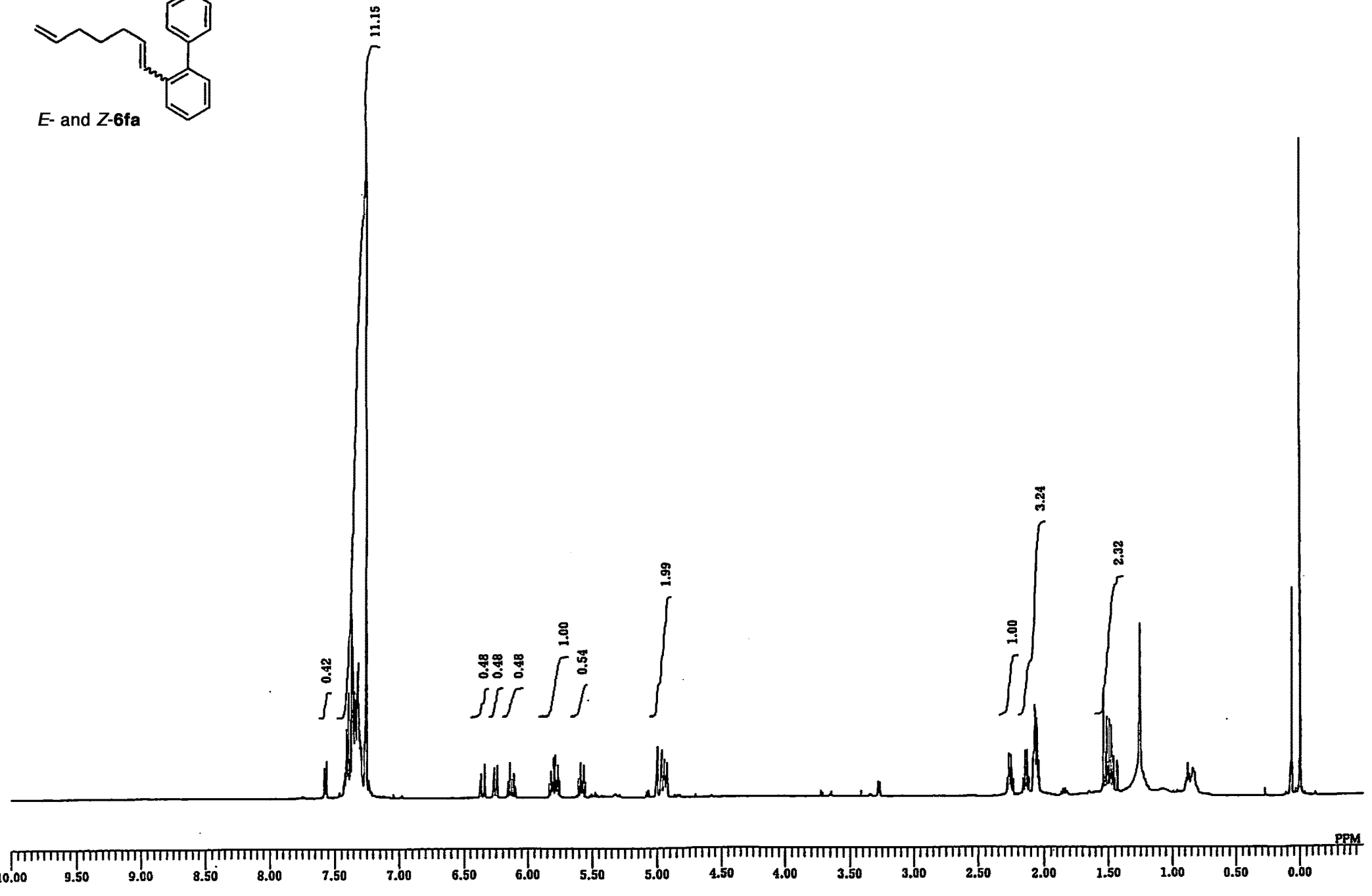
141.078
138.799
135.441
134.020
133.457
128.917
128.183
127.448
127.305
126.905
126.838
123.986
123.375
114.352
77.258
77.000
76.752
38.437
33.934
33.715
32.838
26.914

PPM

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



E- and *Z*-**6fa**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0.48
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1.00
0.54
1.99
1.00
3.24
2.32
PPM
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9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00