The Versatile Roles of Ammonium Salt Catalysts in Enantioselective Reduction and Alkylation of α,β-Unsaturated Aldehydes: Iminium Catalysis, Enamine Catalysis, and Acid Catalysis

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Supporting Information

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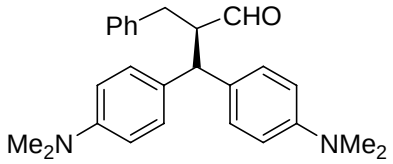
General Remarks

General: All manipulations were conducted with Schlenk tube. ^{1}H-NMR spectra were recorded on Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. 13C-NMR spectra were obtained by the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). Mass spectra were obtained using electron impact ionization (EI) mass spectrometer or electrospray ionization (ESI) mass spectrometer. Optical rotations were measured as follows: $[\alpha]_D^{rt}$ (c in g per 100 mL of solvent). HPLC analysis was performed on Agilent 1200 using AD-H or OD-H columns. Unless otherwise noted, materials and solvents obtained from commercial suppliers were used without further purification. **1f-1h** were prepared according to literature methods.[1]

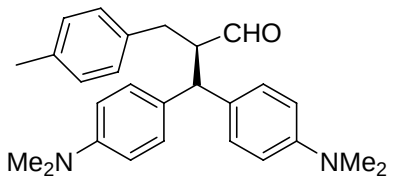
Experimental Section

(*R*)-2-Benzyl-3,3-bis(4-(dimethylamino)phenyl)propanal **(4aa)**



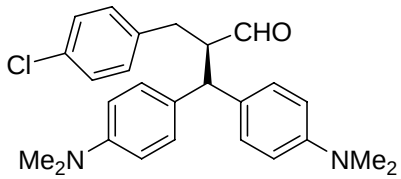
Typical Procedure (1): Catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch esters **2** (60.7 mg, 0.24 mmol) were mixtured in 2.0 mL toluene. The *trans*-Cinnamaldehyde **1a** (39.6 mg, 0.3 mmol) was added after the reaction mixture was cooled to -5 ℃. The reaction was stirred for one day at -5 ℃, then bis(4-dimethylamino-phenyl)methanol **3a** (54.0 mg, 0.2mmol) was added and the reaction continues for another four days. The crude reaction mixture was directly purified by flash chromatography column using hexane/Et_2O = 5/1 as the eluent to afford 73.4 mg (95 % yield, 87% ee) of **4aa**. HPLC analysis on a AD-H column at 0℃: hexane/*i*-PrOH = 90/10, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 28.1 min., $^{\tau}$minor = 31.2 min.; $[\alpha]_D^{rt}$ = -10.5 (*c* = 1.14, $CHCl_3$, 87% ee); IR:(KBr) ν_{max} 2921, 2856, 2799, 1720, 1612, 1520, 1350, 816 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.53 (d, *J* = 3.6 Hz, 1H), 7.25-7.04 (m, 9H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 4.02 (d, *J* = 10.8 Hz, 1H), 3.52-3.44 (m, 1H), 2.92-2.76 (m, 2H), 2.90 (s, 6H), 2.85 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 204.8, 149.3, 149.2, 139.1, 130.7, 130.1, 129.0, 128.58, 128.55, 128.3, 126.2, 113.0, 112.9, 57.8, 50.7, 40.6, 40.5, 34.8; MS (70 eV): m/z (%): 253.2 (100), 386.3 (10) $[M]^+$. HRMS m/z (ESI): Calcd. for $C_{26}H_{31}N_2O$ $[M+H]^+$ 387.24309, Found: 387.24292.

(*R*)-3,3-Bis(4-(dimethylamino)phenyl)-2-(4-methylbenzyl)propanal **(4ba)**



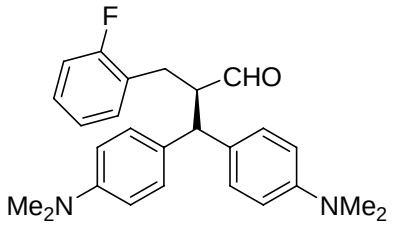
The reaction was carried out following the typical procedure (1) at the appointed temperature. The reaction of catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch esters **2** (60.7 mg, 0.24 mmol), 4-methyl-Cinnamaldehyde **1b** (43.8 mg, 0.3 mmol), bis(4-dimethylamino-phenyl)methanol **3a** (54.0 mg, 0.2mmol) in toluene (2.0 mL) afford 74.0 mg (93 % yield, 81% ee) of **4ba**. HPLC analysis on a AD-H column at 0℃: hexane/*i*-PrOH = 90/10, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 30.5 min., $^{\tau}$minor = 28.6 min.; $[\alpha]_D^{rt}$ = +5.0 (*c* = 2.39, $CHCl_3$, 81% ee); IR:(KBr) ν_{max} 2916, 2883, 2854, 2798, 1716, 1613, 1519, 1348, 804 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.51 (d, *J* = 3.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 7.2 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 4.01 (d, *J* = 10.8 Hz, 1H),3.48-3.42 (m, 1H), 2.89-2.73 (m, 2H), 2.88 (s, 6H), 2.84 (s, 6H), 2.27 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 204.9, 149.2, 149.15, 135.8, 135.6, 130.8, 130.2, 129.0, 128.8, 128.5, 112.9, 112.8, 57.8, 50.6, 40.6, 40.5, 34.4, 20.9; MS (70 eV): m/z (%): 253.2 (100), 400.4 (10) $[M]^+$. HRMS m/z (ESI): Calcd. for $C_{27}H_{33}N_2O$ $[M+H]^+$ 401.25874, Found: 401.25878

(*R*)-2-(4-Chlorobenzyl)-3,3-bis(4-(dimethylamino)phenyl)propanal **(4ca)**



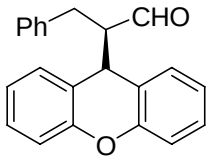
The reaction was carried out following the typical procedure (1) at the appointed temperature. The reaction of catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch esters **2** (60.7 mg, 0.24 mmol), 4-chloro-Cinnamaldehyde **1c** (50.0 mg, 0.3 mmol), bis(4-dimethylamino-phenyl)methanol **3a** (54.0 mg, 0.2mmol) in toluene (2.0 mL) afford 73.3 mg (87 % yield, 80% ee) of **4ca**. HPLC analysis on a AD-H column at 0℃: hexane/*i*-PrOH = 90/10, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 49.8 min., $^{\tau}$minor = 30.3 min.; $[\alpha]_D^{rt}$ = -19.8 (*c* = 2.63, $CHCl_3$, 80% ee); IR:(KBr) ν_{max} 2931, 2886, 2859, 2803, 1714, 1612, 1520, 1350, 807 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.51 (s, 1H), 7.17-7.09 (m, 6H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.68 (d, *J* = 7.6 Hz, 2H), 6.61 (d, *J* = 7.2 Hz, 2H), 3.98 (d, *J* = 10.4 Hz, 1H), 3.44-3.41 (m, 1H), 3.04-2.68 (m, 2H), 2.89 (s, 6H), 2.85 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 204.5, 149.3, 149.2, 137.6, 131.9, 130.4, 130.3, 129.8, 128.5,128.47, 128.4, 112.9, 112.8, 57.7, 50.7, 40.55, 40.48, 34.0; MS (70 eV): m/z (%): 253.2 (100), 420.3 (10) $[M]^+$. HRMS m/z (ESI): Calcd. for $C_{26}H_{30}ClN_2O$ $[M+H]^+$ 421.20412, Found: 421.20390.

(*R*)-3,3-Bis(4-(dimethylamino)phenyl)-2-(2-fluorobenzyl)propanal **(4da)**



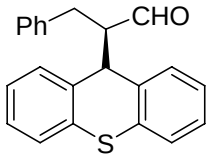
The reaction was carried out following the typical procedure (1) at the appointed temperature. The reaction of catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch esters **2** (60.7 mg, 0.24 mmol), 2-fluoro-Cinnamaldehyde **1d** (45.0 mg, 0.3 mmol), bis(4-dimethylamino-phenyl)methanol **3a** (54.0 mg, 0.2mmol) in toluene (2.0 mL) afford 76.7 mg (95 % yield, 90% ee) of **4da**. HPLC analysis on a AD-H column at 0℃: hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 35.5 min., $^{\tau}$minor = 47.5 min.; $[\alpha]_D^{rt}$ = -11.5 (*c* = 1.75, CHCl3, 90% ee); IR:(KBr) ν_{max} 2920, 2884, 2795, 1723, 1614, 1520, 1348, 1227, 803, 758 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.51 (d, *J* = 3.2 Hz, 1H), 7.23-6.92 (m, 8H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 4.02 (d, *J* = 10.8 Hz, 1H), 3.55-3.49 (m, 1H), 2.90-2.78 (m, 2H), 2.89 (s, 6H), 2.85 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 204.0, 161.0 (d, *J* = 243Hz), 149.3, 149.27, 131.44, 131.39, 130.5, 130.1, 128.56, 128.54, 128.09, 128.01, 126.1, 125.9, 123.93, 123.90, 115.3, 115.1, 112.95, 112.86, 56.6, 51.1, 40.6, 40.5, 28.6; HRMS m/z (ESI): Calcd. for $C_{26}H_{30}FN_2O$ $[M+H]^+$ 405.23367, Found: 405.23324.

(*R*)-3-Phenyl-2-(9H-xanthen-9-yl)propanal **(4ab)**



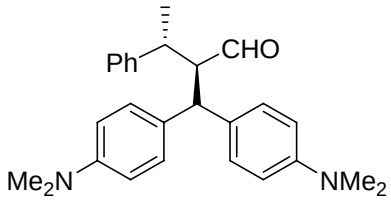
The reaction was carried out following the typical procedure (1) at the appointed temperature. The reaction of catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch esters **2** (60.7 mg, 0.24 mmol), *trans*-Cinnamaldehyde **1a** (39.6 mg, 0.3 mmol), 9H-xanthen-9-ol **3b** (39.6 mg, 0.2mmol) in $MeNO_2$ (2.0 mL) afford 60.3 mg (96 % yield, 70% ee) of **4ba**. HPLC analysis on a AD-H column at 0℃: hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 16.4 min., $^{\tau}$ minor = 19.2 min.; $[\alpha]_D^{rt}$ = -23.9 (*c* = 2.51, $CHCl_3$, 70% ee); IR:(KBr) ν_{max} 2925, 1722, 1477, 1457, 1247, 754 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.64 (d, *J* = 1.2 Hz, 1H), 7.29-7.06 (m, 11H), 6.96 (d, *J* = 7.2 Hz, 2H), 4.59 (d, *J* = 4.0 Hz, 1H), 3.01-2.96 (m, 1H), 2.83-2.76 (m, 1H), 2.72-2.66 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 203.5, 152.9, 152.86, 138.8, 129.0, 128.8, 128.6, 128.5, 128.4, 126.3, 123.7, 123.5, 122.6, 121.7, 116.8, 117.77, 62.4, 39.5, 31.2; MS (70 eV): m/z (%): 181.0 (100); HRMS m/z (ESI): Calcd. for $C_{22}H_{18}NaO_2$ $[M+Na]^+$ 337.11990, Found: 337.12018.

(*R*)-3-Phenyl-2-(9H-thioxanthen-9-yl)propanal **(4ac)**



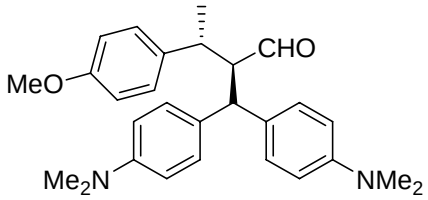
The reaction was carried out following the typical procedure (1) at the appointed temperature. The reaction of catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch esters **2** (60.7 mg, 0.24 mmol), *trans*-Cinnamaldehyde **1a** (39.6 mg, 0.3 mmol), 9H-thioxanthen-9-ol **3c** (42.8 mg, 0.2mmol) in $MeNO_2$ (2.0 mL) afford 56.8 mg (86 % yield, 67% ee) of **4ca**. HPLC analysis on a AD-H column at 0℃: hexane/i-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 25.2 min., $^{\tau}$ minor = 19.5 min.; $[\alpha]_D^{rt}$ = +25.0 (*c* = 1.20, $CHCl_3$, 67% ee); IR:(KBr) ν_{max} 2932, 1715, 1462, 1442, 762, 750, 694 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.43 (d, *J* = 2.8 Hz, 1H), 7.48-7.42 (m, 2H), 7.32-7.10 (m, 9H), 6.96 (d, *J* = 7.2 Hz, 2H), 4.38 (d, *J* = 9.6 Hz, 1H), 3.56-3.53 (m, 1H), 2.86 (dd, J_1 = 14.0 Hz, J_2 = 10.4 Hz, 1H), 2.52 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 203.9, 138.5, 135.3, 135.2, 133.2, 133.1, 130.1, 129.6, 128.7, 128.4, 127.5, 127.45, 127.2, 127.1, 126.7, 126.5, 126.3, 52.6, 50.0, 34.7; HRMS m/z (ESI): Calcd. for $C_{22}H_{18}NaOS$ $[M+Na]^+$ 353.09706, Found: 353.09736.

(*2R,3R*)-2-(Bis(4-(dimethylamino)phenyl)methyl-3-phenylbutanal **(4ea)**



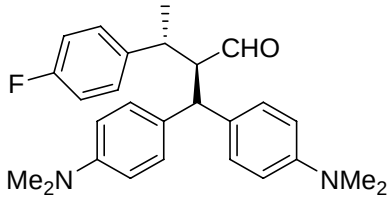
Typical Procedure (2): Catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch Esters **2** (60.7 mg, 0.24 mmol) were mixtured in 2.0 mL toluene. The 3-phenylbut-2-enal **1e** (43.8 mg, 0.3 mmol, *E/Z* = 3/1) was added after the reaction mixture was cooled to -5 ℃. The reaction was stirred for 1.5 day at -5 ℃, then bis(4-dimethylamino-phenyl)methanol **3a** (54.0 mg, 0.2mmol) was added and the temperature was rised to +20℃ to react for another four days. The crude reaction mixture was directly purified by flash chromatography column using hexane/Et_2O = 5/1 as the eluent to afford 65.6 mg (82 % yield, 93% ee, 7:1 dr) of **4ea**. HPLC analysis on a AD-H column at 0℃: hexane/i-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 27.1 min., $^{\tau}$minor = 38.3 min., $^{\tau'}$ major = 20.1 min., $^{\tau'}$ minor = 45.4 min.; $[\alpha]_D^{rt}$ = -9.6 (*c* = 2.09, $CHCl_3$, 93% ee, 7:1 dr); IR:(KBr) ν_{max} 2971, 2931, 2879, 2796, 1696, 1608, 1517, 1343, 803, 697 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.60 (d, *J* = 3.2 Hz, 1H), 7.31-7.04 (m, 9H), 6.72-6.67 (m, 2H), 6.59-6.57 (m, 2H), 4.19 (d, *J* = 10.0 Hz, 1H), 3.52-3.48 (m, 1H), 3.10-3.06 (m, 1H), 2.91 (s, 6H), 2.90 (s, 6H), 1.35-1.28 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 205.5, 149.2, 149.1, 144.7, 131.2, 130.4, 128.8, 128.5, 128.4, 127.5, 126.4, 113.0, 112.8, 61.0, 48.6, 40.64, 40.56, 39.0, 15.5; MS (70 eV): m/z (%): 253.3 (100), 400.6 (2) $[M]^+$. HRMS m/z (ESI): Calcd. for $C_{27}H_{33}N_2O$ $[M+H]^+$ 401.25874, Found: 401.25850.

(*2R,3R*)-2-(Bis(4-(dimethylamino)phenyl)methyl)-3-(4-methoxyphenyl)butanal **(4fa)**



The reaction was carried out following the typical procedure (2) at the appointed temperature. The reaction of catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch esters **2** (60.7 mg, 0.24 mmol), (*E*)-3-(4-methoxyphenyl)but-2-enal **1f** (52.8 mg, 0.3 mmol), bis(4-dimethylamino-phenyl)methanol **3a** (54.0 mg, 0.2mmol) in toluene (2.0 mL) afford 63.4 mg (74 % yield, 94% ee, 6:1 dr) of **4fa**. HPLC analysis on a AD-H column at 0℃: hexane/i-PrOH = 90/10, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 24.9 min., $^{\tau}$minor = 30.6 min., $^{\tau'}$major = 20.6 min., $^{\tau'}$minor = 39.7 min.; $[\alpha]_D^{rt}$ = -17.6 (*c* = 2.27, $CHCl_3$, 94% ee, 6:1 dr); IR:(KBr) ν_{max} 2927, 2831, 2802, 1719, 1611, 1514, 1348, 1247, 1027, 829, 810 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.59 (d, *J* = 4.0 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 6.8 Hz, 4H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.17 (d, *J* = 10.0 Hz, 1H), 3.77 (s, 3H), 3.47-3.45 (m, 1H), 3.04-2.97 (m, 1H), 2.89 (s, 6H), 2.84 (s, 6H), 1.28 (d, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 205.7, 158.0, 149.11, 149.06, 136.8, 131.2, 130.4, 128.8, 128.4, 128.3, 113.8, 113.5, 113.1, 113.0, 112.8, 61.2, 55.1, 48.5, 40.6, 40.5, 38.2, 15.7; MS (70 eV): m/z (%): 253.1 (100), 430.6 (3) $[M]^+$; HRMS m/z (ESI): Calcd. for $C_{28}H_{35}N_2O_2$ $[M+H]^+$ 431.26930, Found: 431.26886.

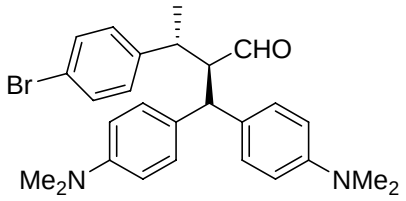
(*2R,3R*)-2-(Bis(4-(dimethylamino)phenyl)methyl)-3-(4-fluorophenyl)butanal **(4ga)**



The reaction was carried out following the typical procedure (2) at the appointed temperature. The reaction of catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch esters **2** (60.7 mg, 0.24 mmol), (E)-3-(4-fluorophenyl)but-2-enal **1g** (49.2 mg, 0.3 mmol), bis(4-dimethylamino-phenyl)methanol **3a** (54.0 mg, 0.2mmol) in toluene (2.0 mL) afford 50.8 mg (61 % yield, 99% ee, 7:1 dr) of **4ga**. HPLC analysis on a AD-H column at 0℃: hexane/i-PrOH = 90/10, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 18.6 min., $^{\tau}$minor = 23.0 min., $^{\tau'}$major = 14.3 min., $^{\tau'}$minor = 29.3 min.; $[\alpha]_D^{rt}$ = +12.6 (*c* = 1.90, $CHCl_3$, 96% ee, 7:1 dr); IR:(KBr) ν_{max} 2970, 2925, 2853, 2799, 1696, 1610, 1513, 1345, 1220, 800 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.59 (d, *J* = 4.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.08-6.93 (m, 6H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.16 (d, *J* = 10.0 Hz, 1H), 3.44-3.38 (m, 1H), 3.07-3.03 (m, 1H), 2.89 (s, 6H), 2.85 (s, 6H), 1.29 (d, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$,

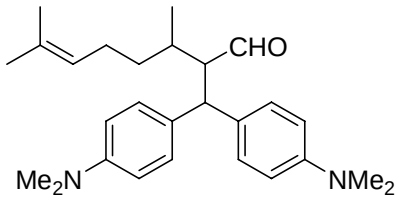
ppm) δ 205.4, 149.20, 149.15, 140.4, 131.0, 130.1, 128.9, 128.8, 128.78, 128.3, 115.3, 115.0, 113.0, 112.8, 61.2, 48.7, 40.6, 40.5, 38.4, 15.6; MS (70 eV): m/z (%): 253.2 (100), 418.4 (7) $[M]^+$; HRMS m/z (ESI): Calcd. for $C_{27}H_{32}FN_2O$ $[M+H]^+$ 419.24932, Found: 419.24921.

(*2R,3R*)-2-(Bis(4-(dimethylamino)phenyl)methyl-3-(4-bromophenyl)butanal **(4ha)**



The reaction was carried out following the typical procedure (2) at the appointed temperature. The reaction of catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch esters **2** (60.7 mg, 0.24 mmol), (E)-3-(4-bromophenyl)but-2-enal **1h** (67.5 mg, 0.3 mmol), bis(4-dimethylamino-phenyl)methanol **3a** (54.0 mg, 0.2mmol) in toluene (2.0 mL) afford 57.2 mg (60% yield, >99% ee, 6:1 dr) of **4ha**. HPLC analysis on a AD-H column at 0℃: hexane/i-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 31.3 min., $^{\tau'}$ major = 19.0 min., $^{\tau'}$ minor = 50.5 min.; $[\alpha]_D^{rt}$ = -15.8 (*c* = 1.77, $CHCl_3$, >99% ee, 6:1 dr); IR:(KBr) ν_{max} 2966, 2916, 2883, 2854, 2793, 1718, 1613, 1521, 1349, 806 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.58 (s, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.23-6.90 (m, 6H), 6.66 (d, *J* = 7.2 Hz, 2H), 6.58 (d, *J* = 7.2 Hz, 2H), 4.15 (d, *J* = 10.0 Hz, 1H), 3.42-3.40 (m, 1H), 3.02-3.00 (m, 1H), 2.89 (s, 6H), 2.84 (s, 6H), 1.30-1.25 (m, 3H); MS (70 eV): m/z (%): 253.2 (100); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 205.1, 149.2, 149.1, 143.8, 131.4, 130.8, 130.0, 129.2, 128.8, 128.3, 120.1, 113.0, 112.7, 60.9, 48.8, 40.6, 40.5, 38.6, 15.5; HRMS m/z (ESI): Calcd. for $C_{27}H_{32}BrN_2O$ $[M+H]^+$ 479.16925, Found: 479.16884.

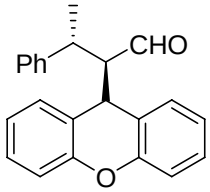
2-(Bis(4-(dimethylamino)phenyl)methyl)-3,7-dimethyloct-6-enal **(4ia)**



The reaction was carried out following the typical procedure (2) at the appointed temperature. The reaction of catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch esters **2** (60.7 mg, 0.24 mmol), citral (*E* + *Z*) **1i** (45.6 mg, 0.3 mmol), bis(4-dimethylamino-phenyl)methanol **3a** (54.0 mg, 0.2mmol) in toluene (2.0 mL) afford 48.1 mg (59 % yield, 85% ee, 2:1 dr) of **4ia**. HPLC analysis on a AD-H column at 0℃: hexane/i-PrOH = 99/1, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$ major = 34.3 min., $^{\tau}$ minor = 25.4 min., $^{\tau'}$ major = 31.7 min., $^{\tau'}$ minor = 26.7 min.; $[\alpha]_D^{rt}$ = +173.6 (*c* = 1.82, $CHCl_3$, 85% ee, 2:1 dr); IR:(KBr) ν_{max} 2922, 2854, 2803, 1718, 1613, 1520, 1349, 808 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.61 (d, *J* = 4.8 Hz, 1H), 7.13-7.09 (m, 4H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 2H),

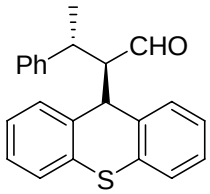
5.01-4.97 (m, 1H), 4.29-4.23 (m, 1H), 3.17-3.11 (m, 1H), 2.87 (s, 6H), 2.84 (s, 6H), 2.01-1.97 (m, 2H), 1.64 (s, 3H), 1.58 (s, 3H), 1.47-1.41 (m, 1H), 1.32-1.21 (m, 2H), 1.01-0.97 (m, 3H); MS (70 eV): m/z (%): 253.3 (100), 406.7 (6) $[M]^+$; HRMS m/z (ESI): Calcd. for $C_{27}H_{39}N_2O$ $[M+H]^+$ 407.30569, Found: 407.30563.

(*2R,3R*)-3-Phenyl-2-(9H-xanthen-9-yl)butanal **(4eb)**



The reaction was carried out following the typical procedure (2) at the appointed temperature. The reaction of catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch esters **2** (60.7 mg, 0.24 mmol), The 3-phenylbut-2-enal **1e** (43.8 mg, 0.3 mmol, *E/Z* = 3/1), 9H-xanthen-9-ol **3b** (39.6 mg, 0.2mmol) in $MeNO_2$ (2.0 mL) afford 37.9 mg (58% yield, 99% ee, >25:1 dr) of **4eb**. HPLC analysis on a OD-H column at 0℃: hexane/i-PrOH = 99/1, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 21.5 min., $^{\tau}$minor = 26.0 min.; $[\alpha]_D^{rt}$ = -44.4 (*c* = 2.07, $CHCl_3$, 90% ee, >25:1 dr); IR:(KBr) ν_{max} 2961, 2926, 2849, 1708, 1478, 1455, 1252, 753, 702 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.39 (d, *J* = 4.0 Hz, 1H), 7.46-7.41 (m, 2H), 7.33-7.20 (m, 6H), 7.12-7.05 (m, 5H), 4.18 (d, *J* = 3.2 Hz, 1H), 3.25-3.19 (m, 1H), 2.94-2.89 (m, 1H), 1.12 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 203.4, 153.1, 152.6, 144.4, 129.2, 129.0, 128.5, 128.3, 128.1, 127.7, 126.9, 124.4, 123.8, 123.3, 121.5, 116.8, 116.6, 66.3, 38.5, 37.4, 21.4; MS (70 eV): m/z (%): 181.0 (100); HRMS m/z (ESI): Calcd. for $C_{23}H_{20}NaO_2$ $[M+Na]^+$ 351.13555, Found: 351.13559.

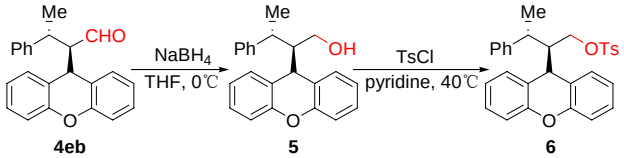
(*2R,3R*)-3-Phenyl-2-(9H-thioxanthen-9-yl)butanal **(4ec)**



The reaction was carried out following the typical procedure (2) at the appointed temperature. The reaction of catalyst **D** (4.1 mg, 0.015 mmol), catalyst **B** (19.9 mg, 0.06 mmol), ethyl Hantzsch esters **2** (60.7 mg, 0.24 mmol), The 3-phenylbut-2-enal **1e** (43.8 mg, 0.3 mmol, *E/Z* = 3/1), 9H-thioxanthen-9-ol **3c** (42.8 mg, 0.2mmol) in $MeNO_2$ (2.0 mL) afford 26.6 mg (39 % yield, 86% ee, >25:1 dr) of **4ec**. HPLC analysis on a AD-H column at 0℃: hexane/i-PrOH = 99/1, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 22.5 min., $^{\tau}$minor = 27.8 min.; $[\alpha]_D^{rt}$ = +18.2 (*c* = 1.32, $CHCl_3$, 86% ee, >25:1 dr); IR:(KBr) ν_{max} 2961, 2927, 1721, 1460, 1443, 757, 701 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 9.44 (d, 1H, *J* = 3.2 Hz), 7.47-7.43 (m, 1H), 7.40-7.37 (m, 1H), 7.35-7.29 (m, 3H), 7.26-7.14 (m, 8H), 4.55 (d, 1H, *J* = 8.0 Hz), 3.48-3.44 (m, 1H), 2.79-2.75 (m, 1H), 1.24 (d, 1H, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz,

$CDCl_3$, ppm) δ 203.0, 114.1, 136.0, 135.5, 133.4, 133.3, 130.3, 129.3, 128.7, 127.4, 127.3, 127.0, 126.9, 126.7, 126.6, 126.4, 58.9, 47.1, 38.3, 16.5; MS (70 eV): m/z (%): 197.1 (100); HRMS m/z (ESI): Calcd. for $C_{23}H_{20}NaOS$ $[M+Na]^+$ 367.11271, Found: 367.11295.

The synthesis of the compound **6**



The compound **6** were prepared according to literature methods.[2] Compound **4eb** (131.7 mg, 0.4 mmol, 90% ee, >25:1 dr) was dissolved in dry THF (5 mL) and the mixture was cooled to 0 °C. Then solid $NaBH_4$ (4 mmol, 10 equiv) was added in one portion. Frothing occurs but is readily controllable through magnetic stirring of the solution. After 30 minutes the mixture was quenched with few drops of water. Brine (10 mL) was added and the resulting mixture extracted with AcOEt (3 × 10 mL). The combined organics were washed with brine (5 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. The crude residue was dissolved in 7 mL of dry pyridine and tosyl chloride (1.2 mmol, 10 equiv) was added in one portion. The reaction was stirred 2 day at 40℃. Water (20 mL) and diethyl ether were added. After separation of the two phases, the aqueous phase was further extracted with diethyl ether (2x20 mL). The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The product was purified by flash chromatography on silica gel to afford 156.8 mg (81 % yield, 88% ee, >25:1 dr) of **6**. HPLC analysis on a AD-H column which was cooled to 0℃: hexane/i-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm: $^{\tau}$major = 22.4 min., $^{\tau}$minor = 23.6 min.; $[\alpha]_D^{rt}$ = -35.3 (*c* = 1.02, $CHCl_3$, 88% ee, >25:1 dr); IR:(KBr) ν_{max} 2925, 1477, 1357, 1255, 1173, 937, 757, 552 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.71-7.13 (m, 8H), 7.06-6.94 (m, 7H), 4.11-4.04 (m, 2H), 3.90-3.85 (m, 1H), 3.00-2.92 (m, 1H), 2.47 (s, 3H), 2.19-2.13 (m, 1H), 1.01 (d, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 153.0, 152.9, 145.8, 144.6, 132.7, 129.7, 128.9, 128.72, 128.7, 127.97, 127.92, 127.2, 126.3, 124.0, 123.3, 123.2, 123.0, 116.6, 116.55, 68.2, 53.2, 38.5, 38.4, 21.6, 17.6; HRMS m/z (ESI): Calcd. for $C_{30}H_{28}NaO_4S$ $[M+Na]^+$ 507.16005, Found: 507.15948.

Single crystals of compund **6** suitable for X-ray crystallographic analysis were obtained by means of slow crystallization from a mixture of Hexane-Et_2O.

Reference:

(1) M. Stadler, B. List, *synlett* 2008, 597.
(2) R. R. Shaikh, A. Mazzanti, M. Petrini, G. Bartoli, P. Melchiorre, *Angew. Chem. Int. Ed.* 2008, **47**, 8707.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

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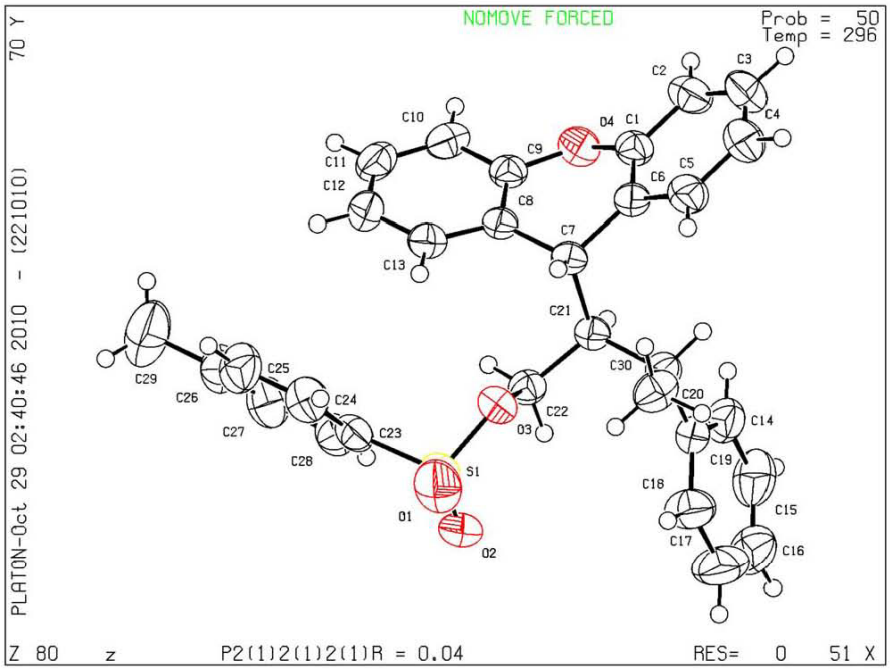
PLATON version of 22/10/2010; check.def file version of 11/10/2010

Datablock z - ellipsoid plot



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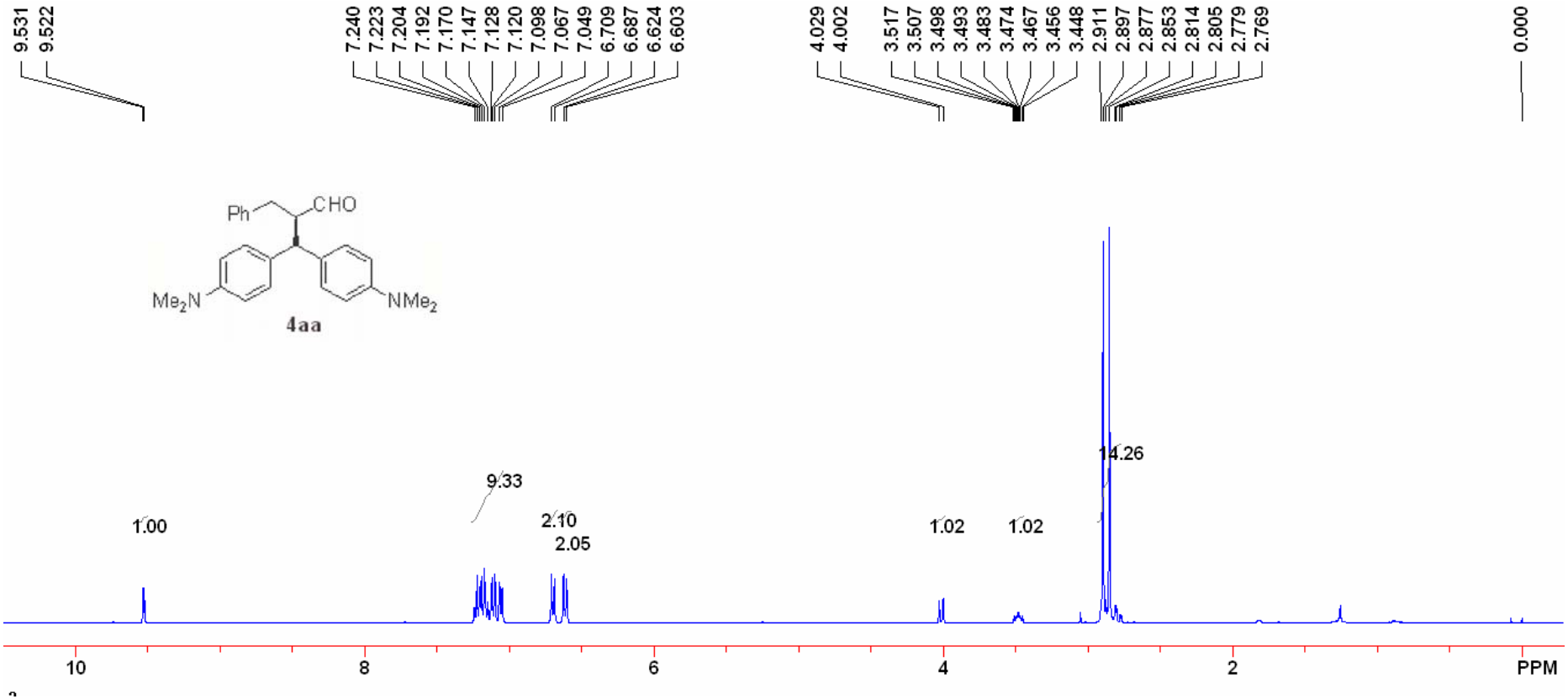
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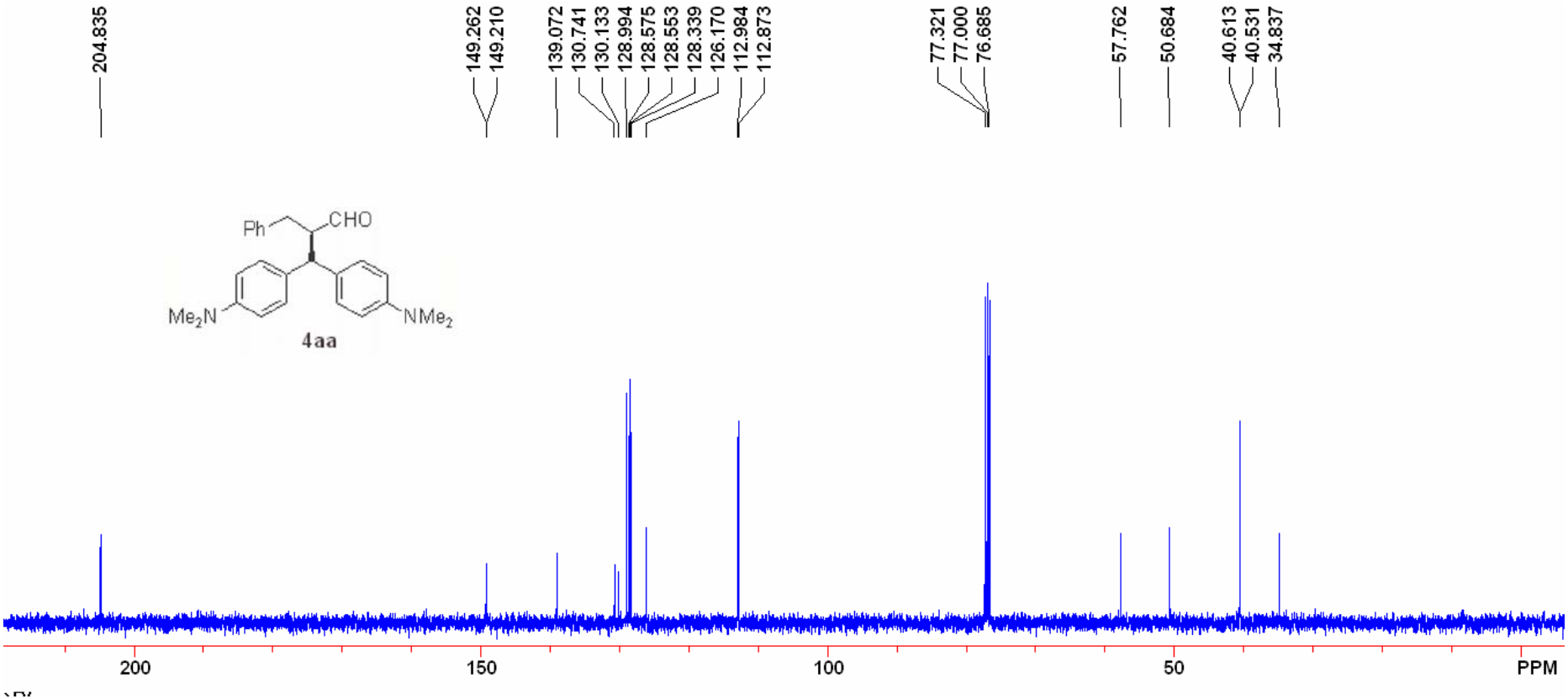
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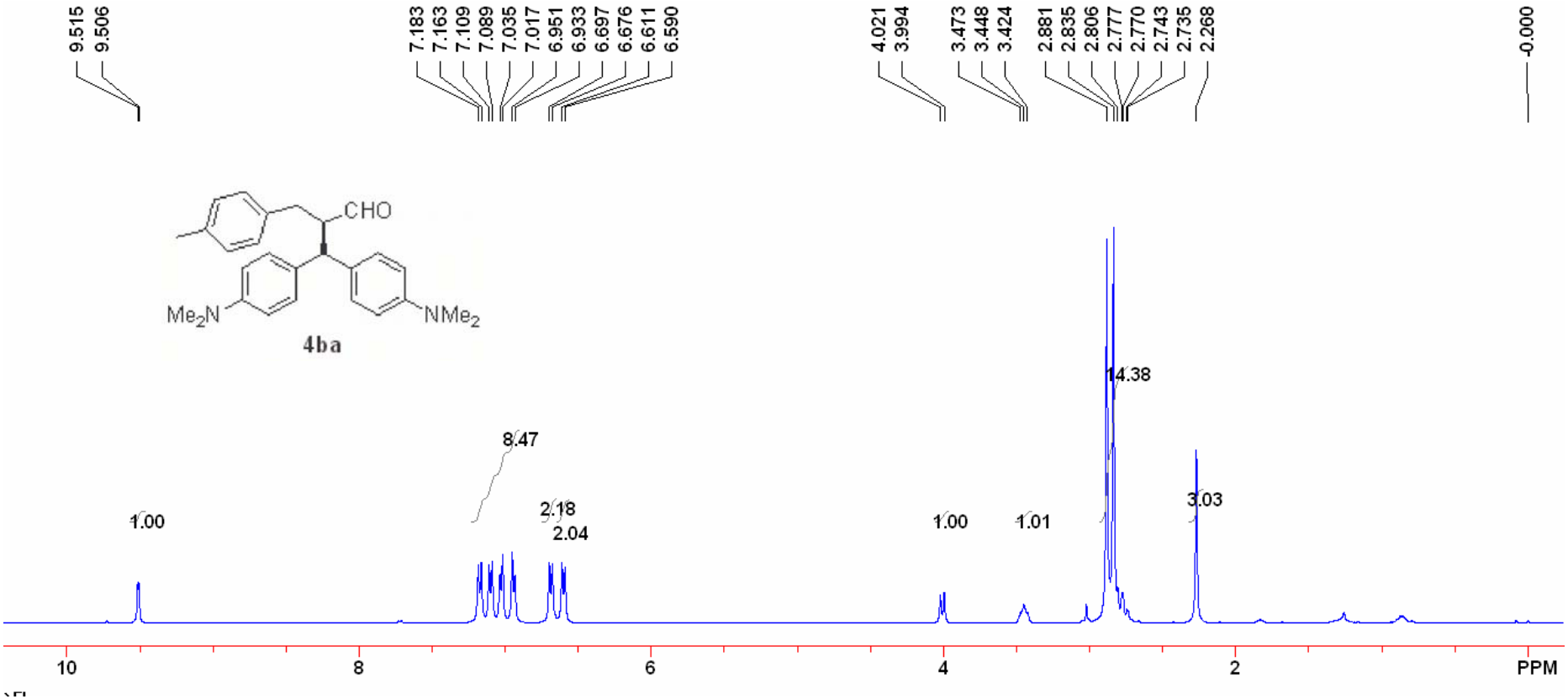
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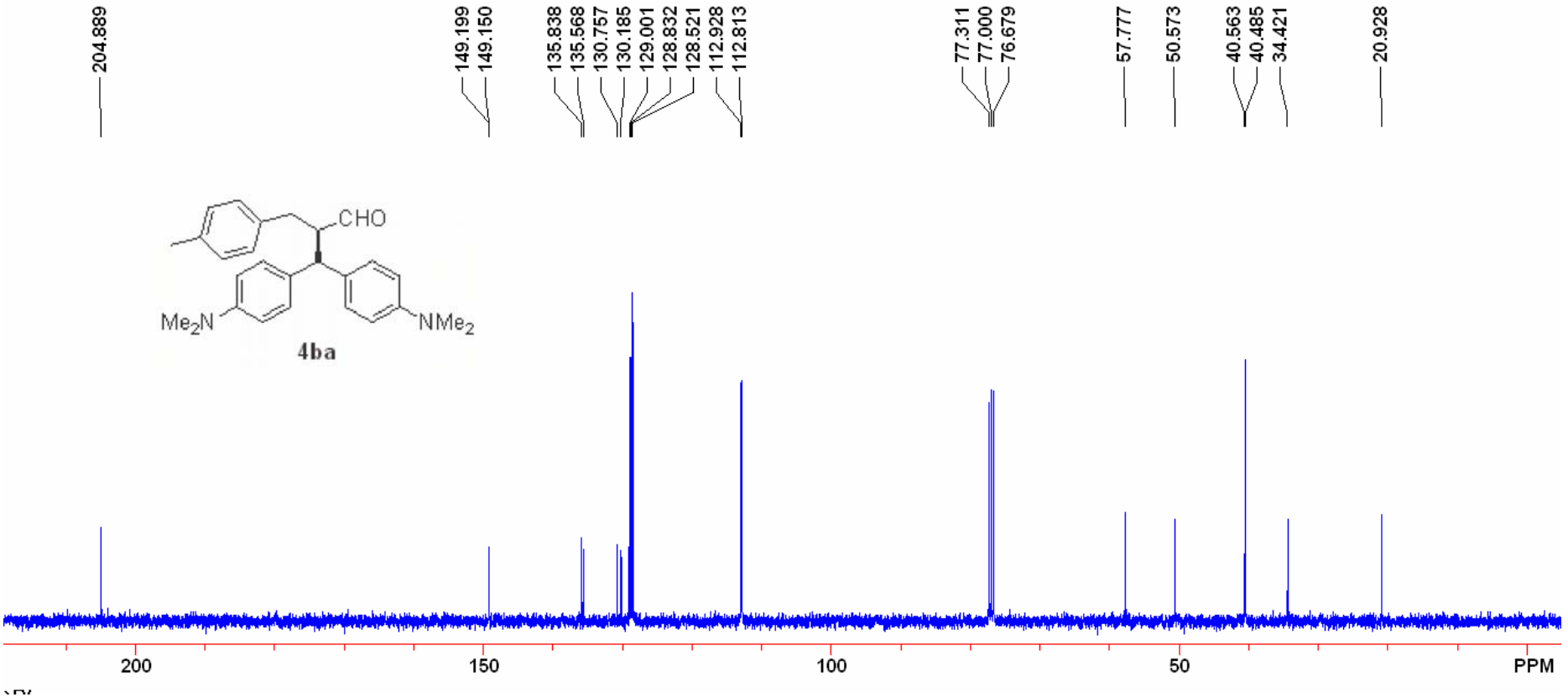
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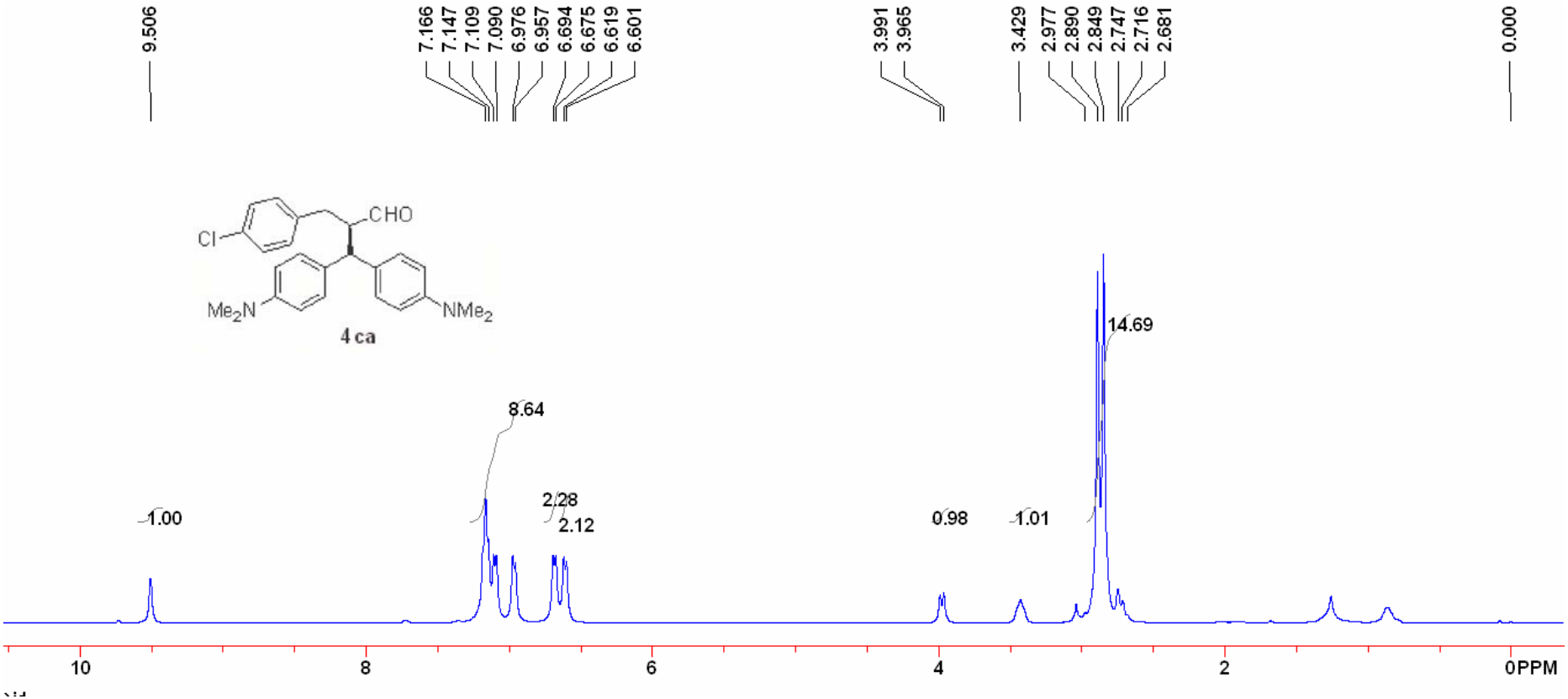
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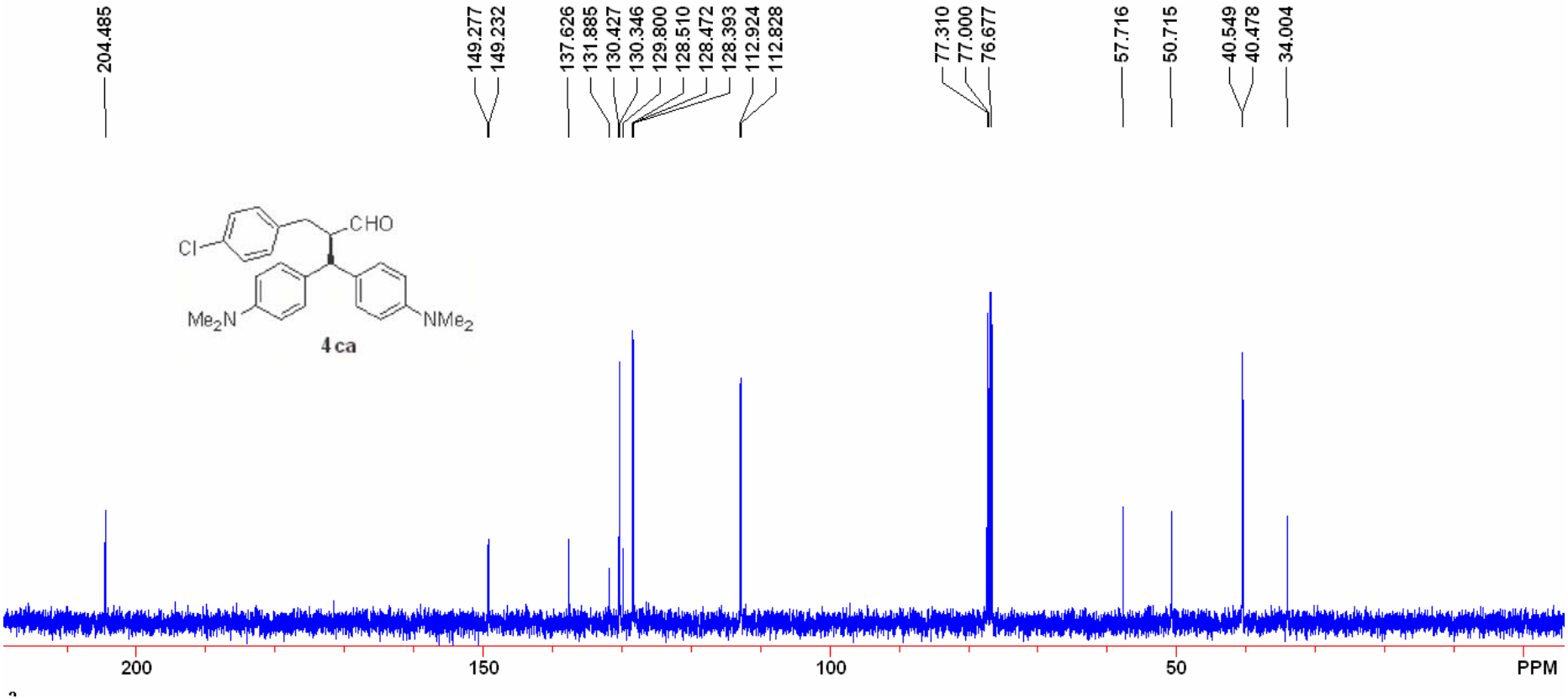
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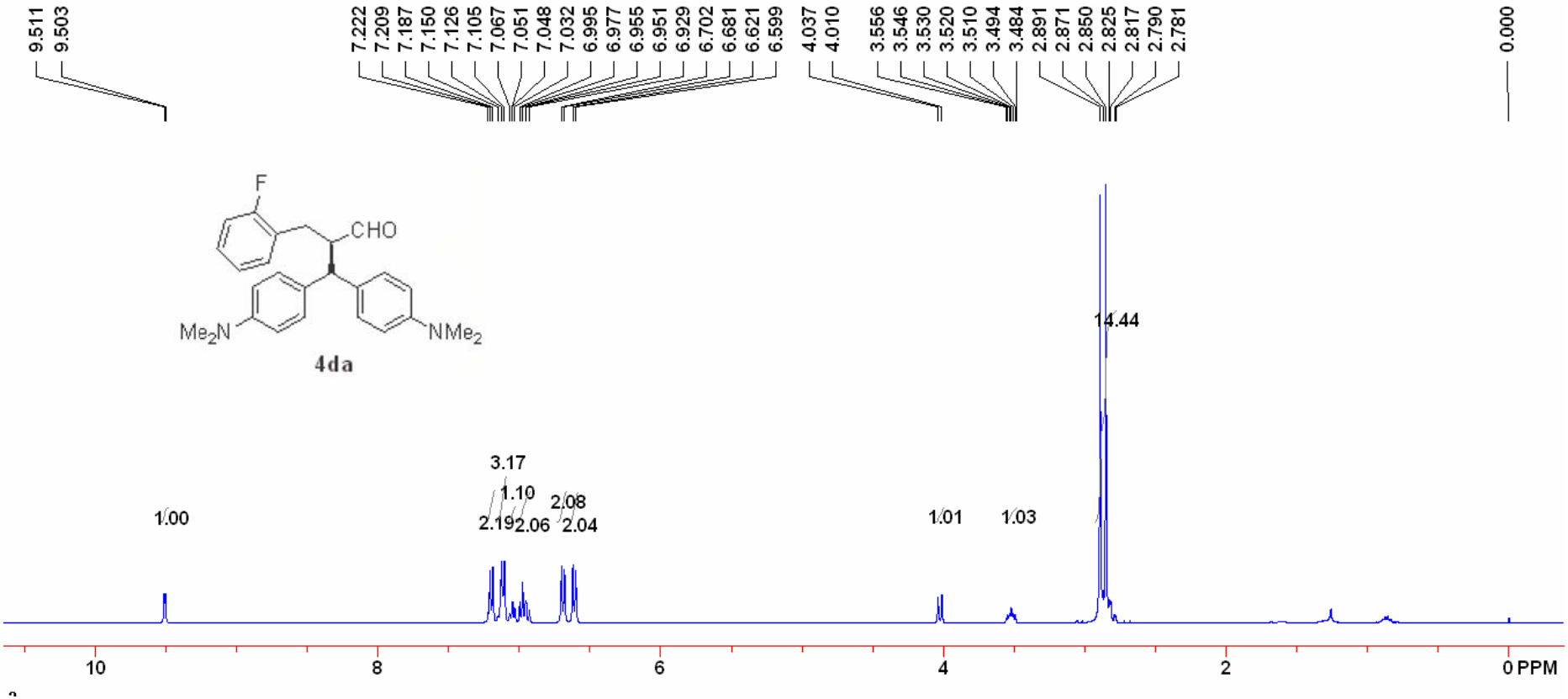
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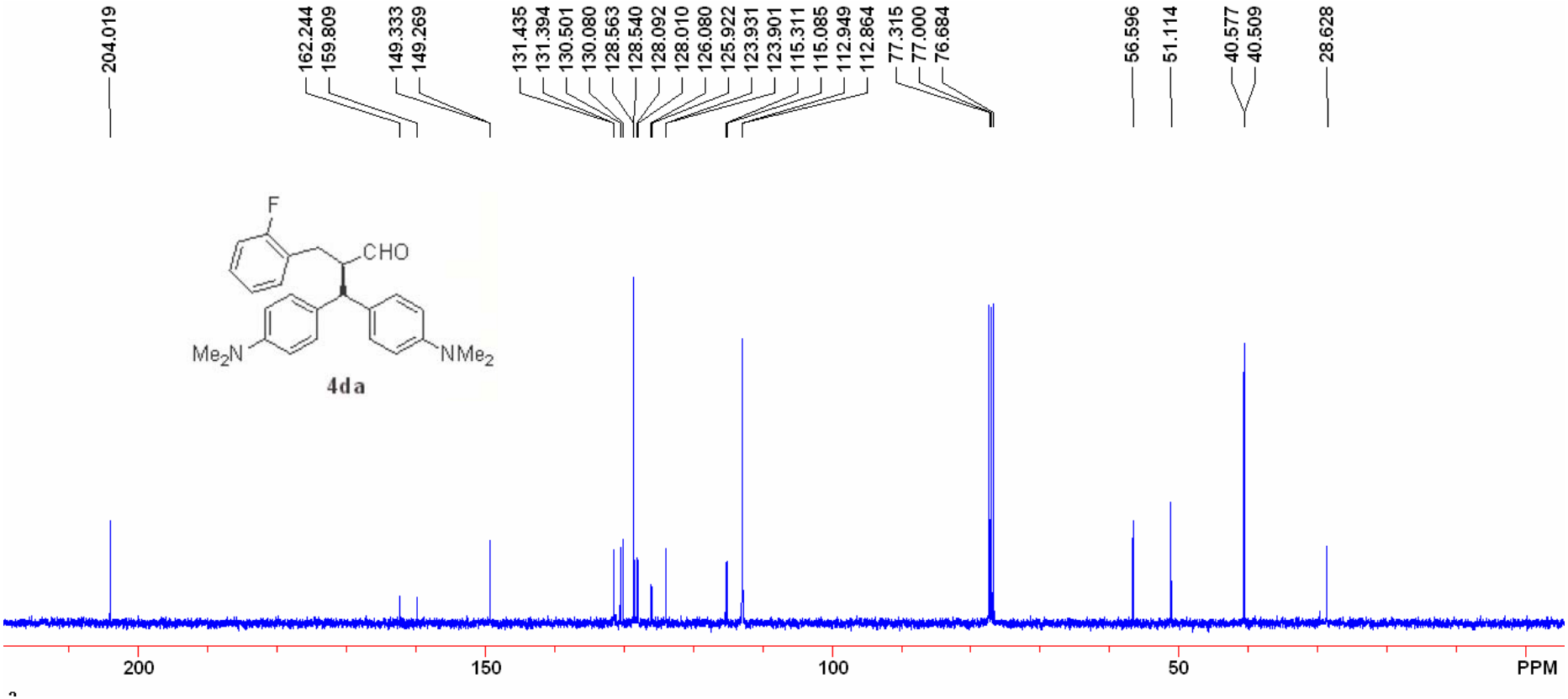
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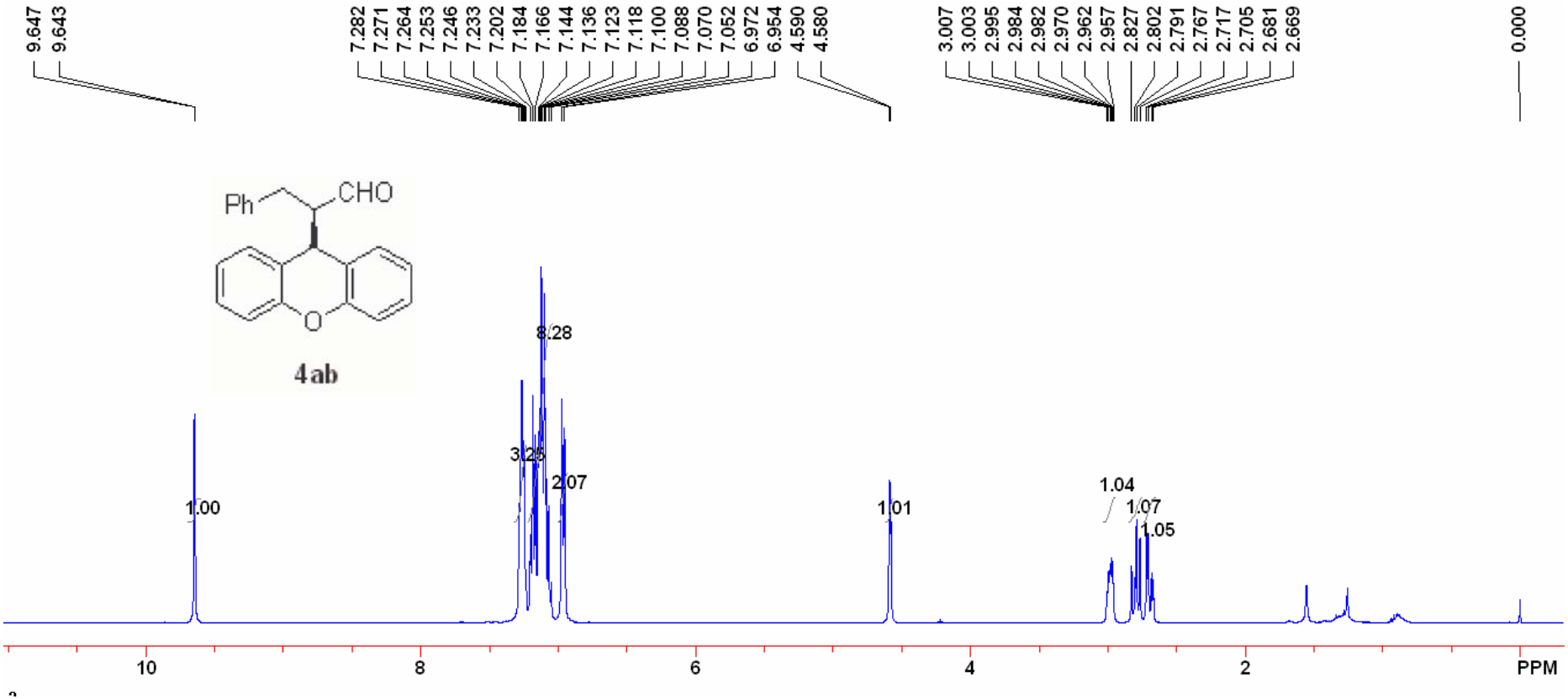
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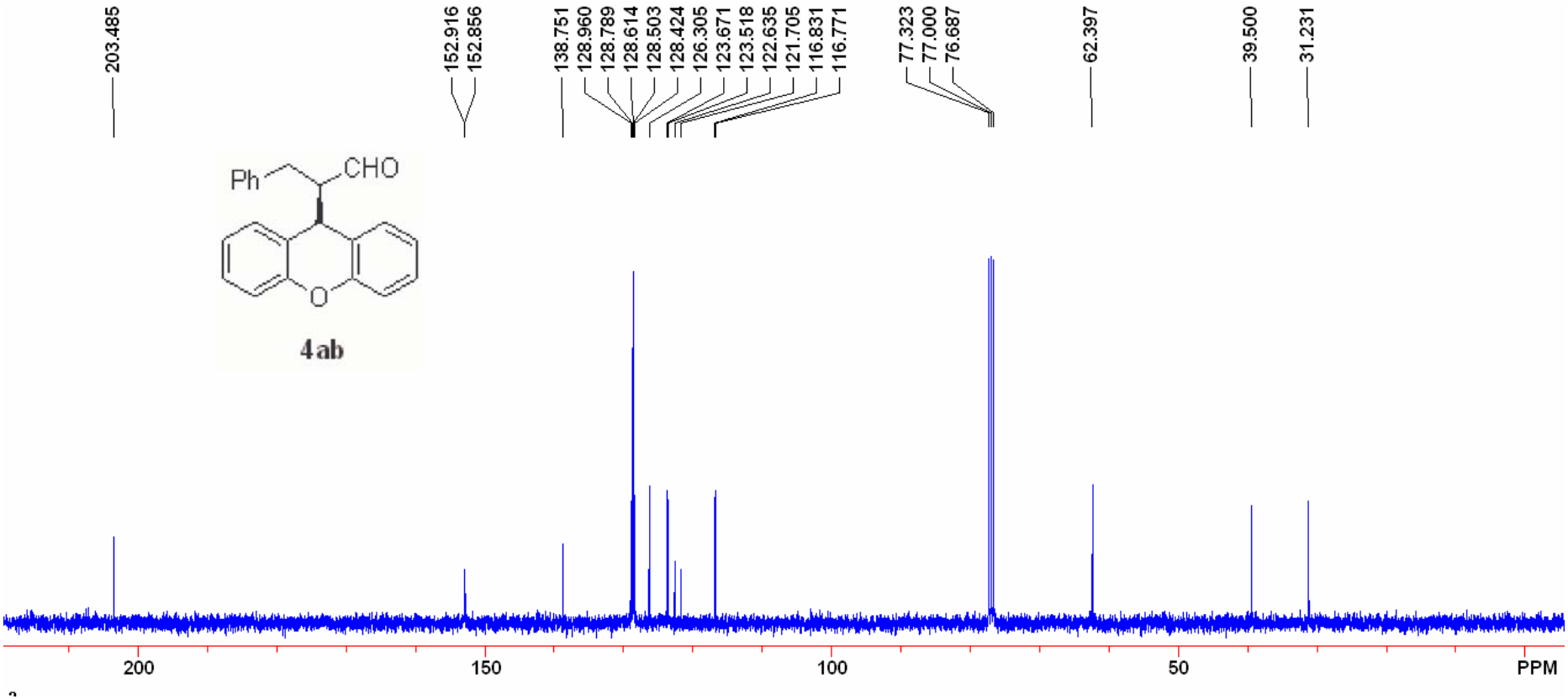
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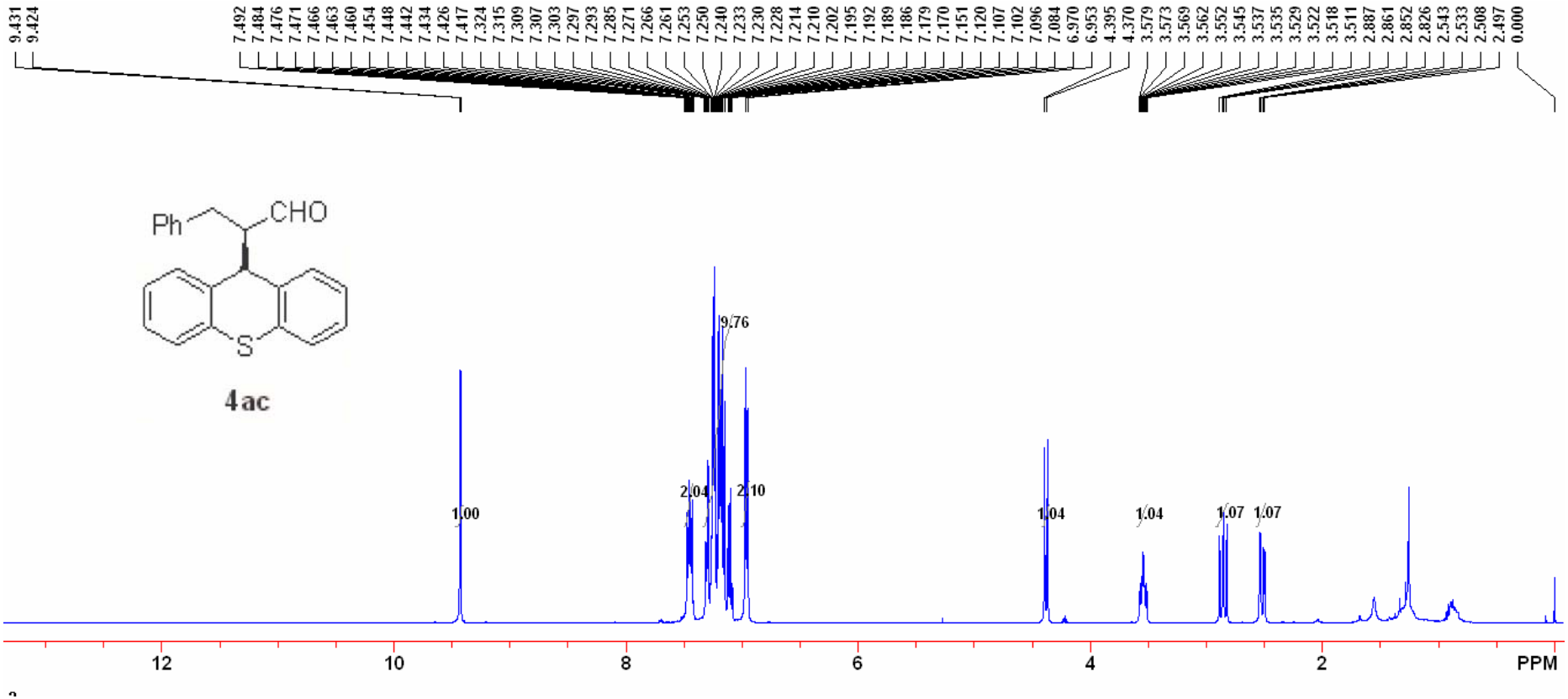
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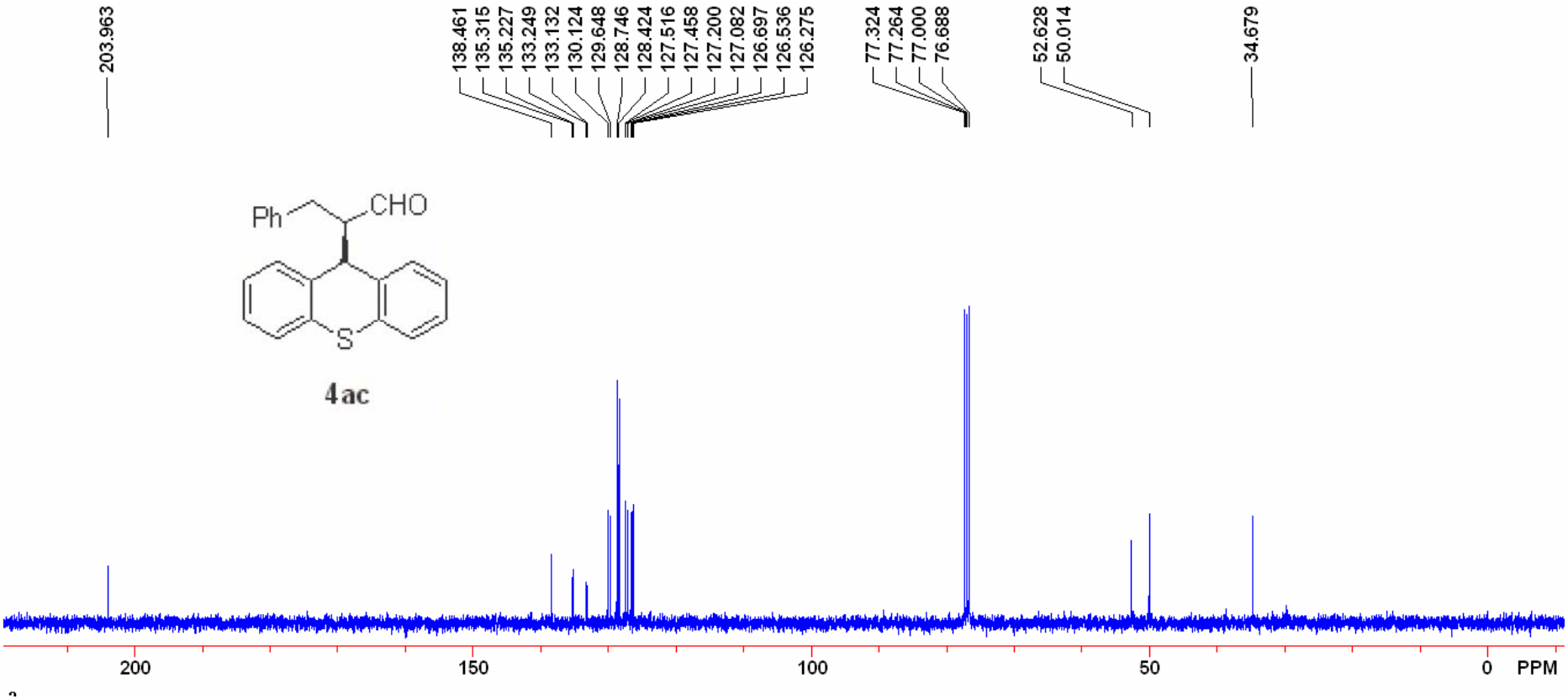
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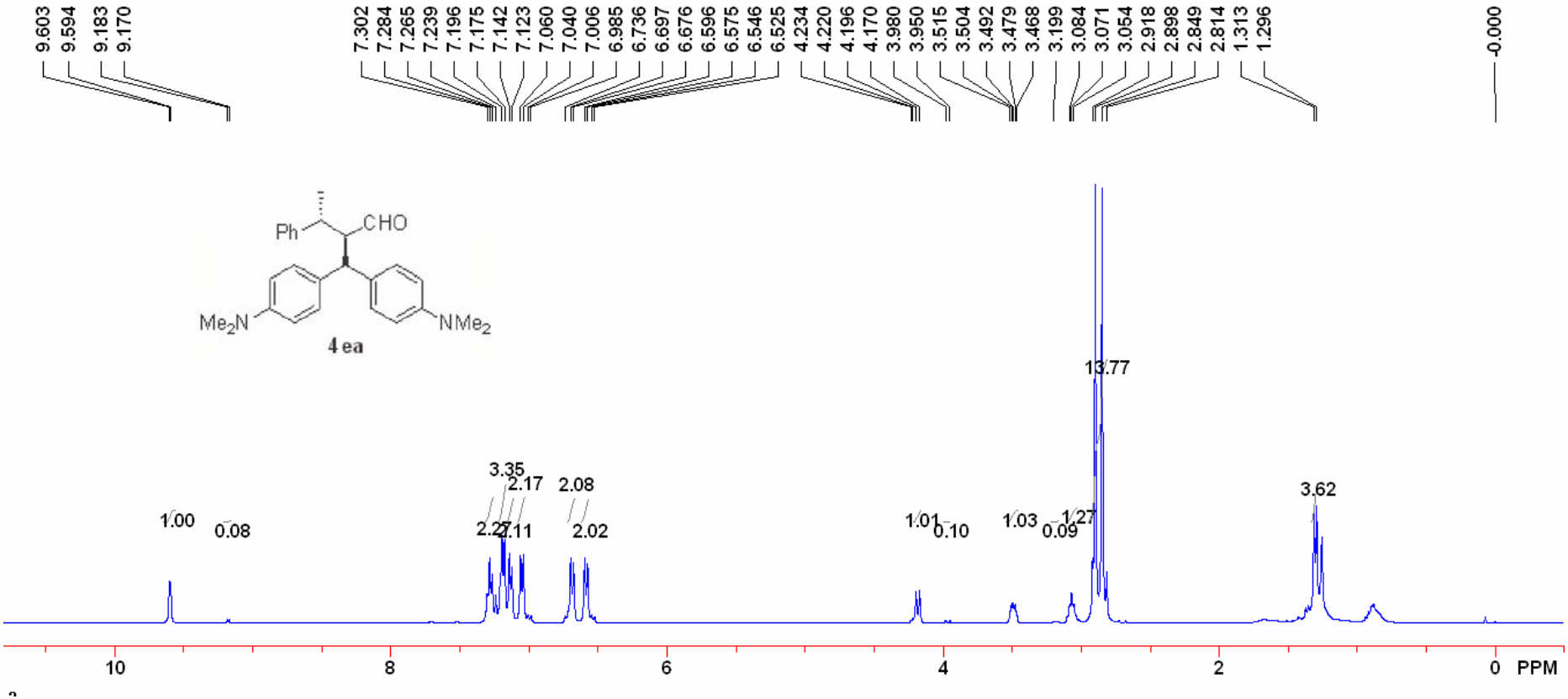
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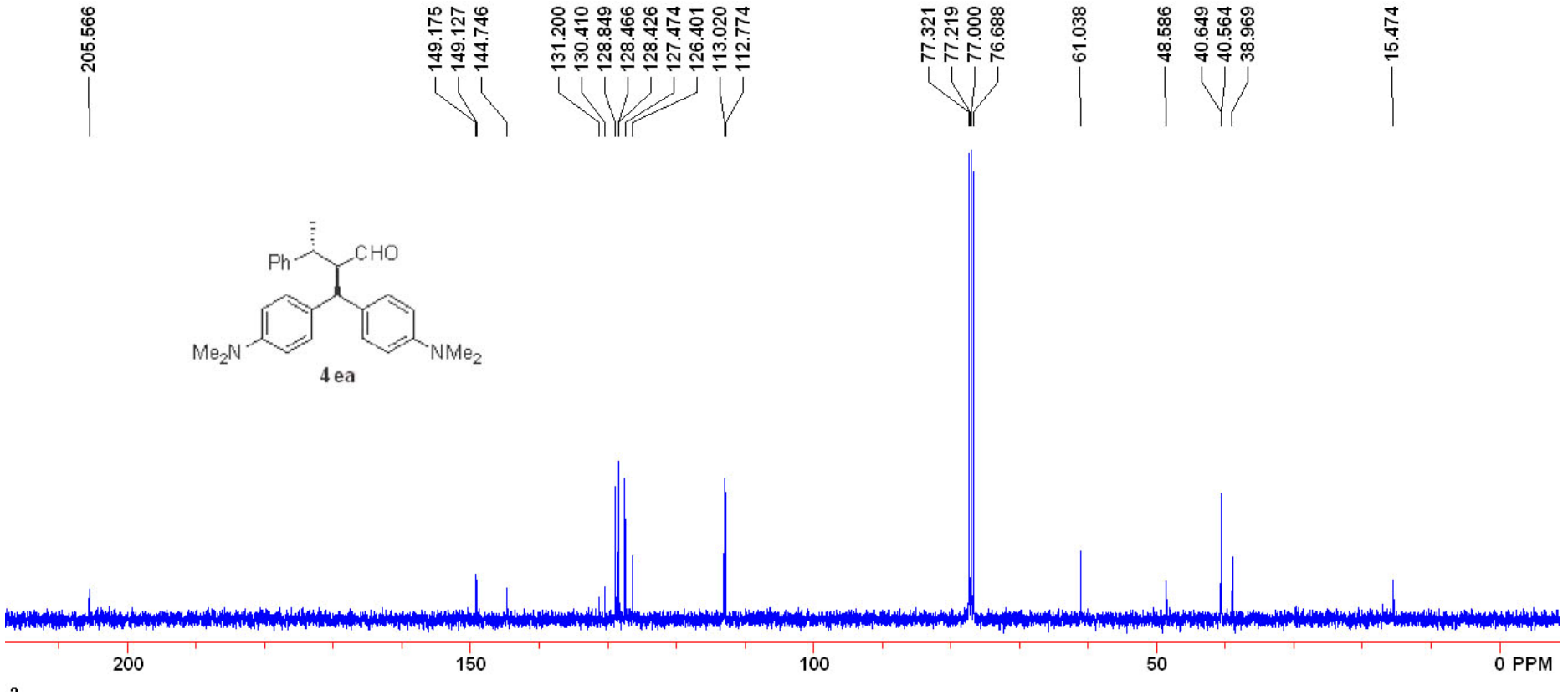
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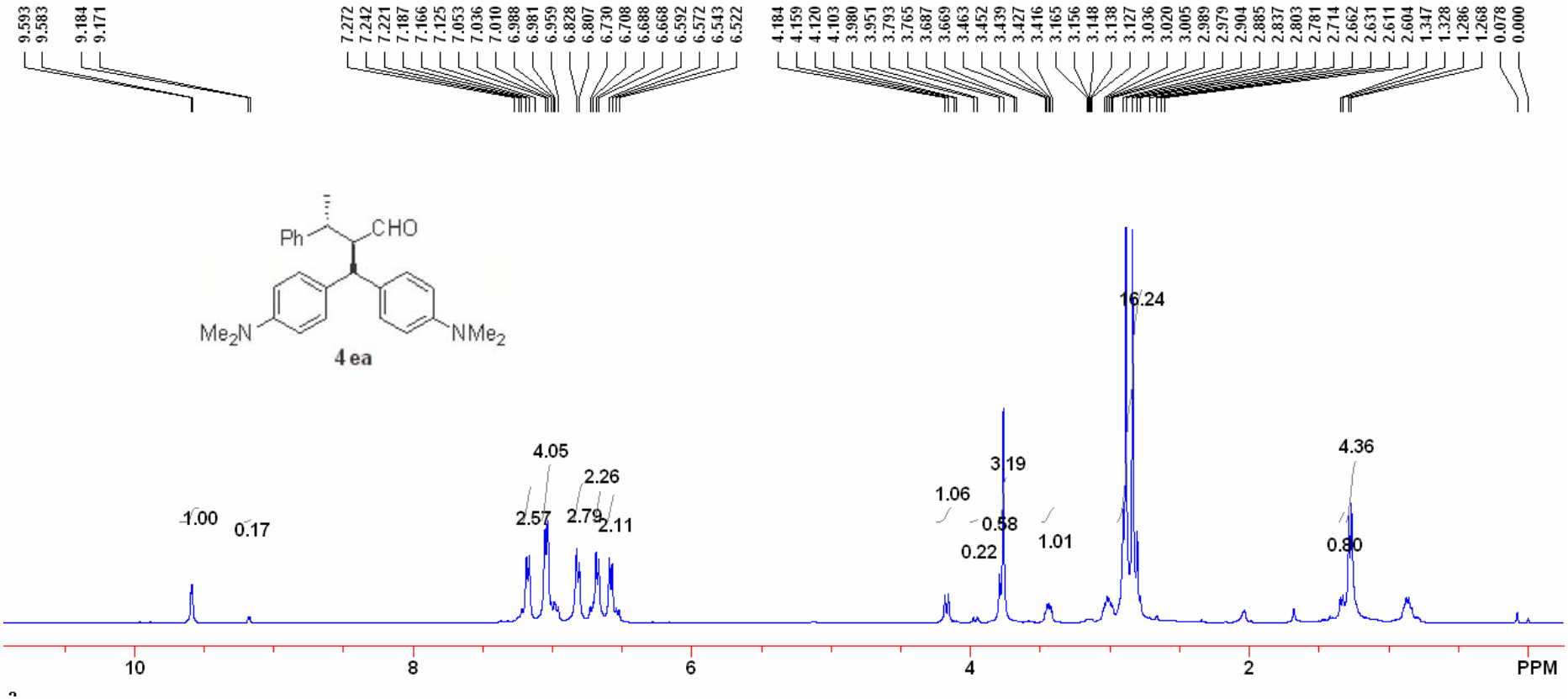
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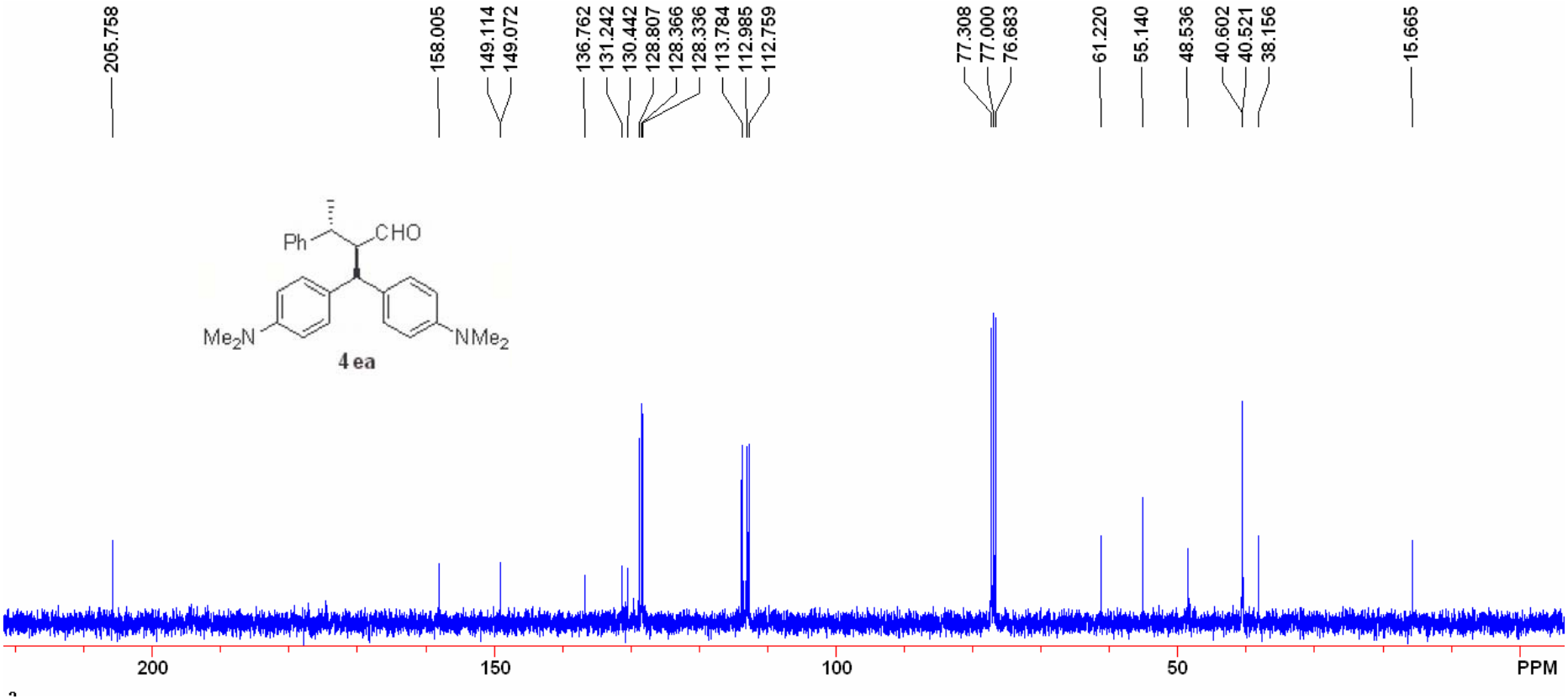
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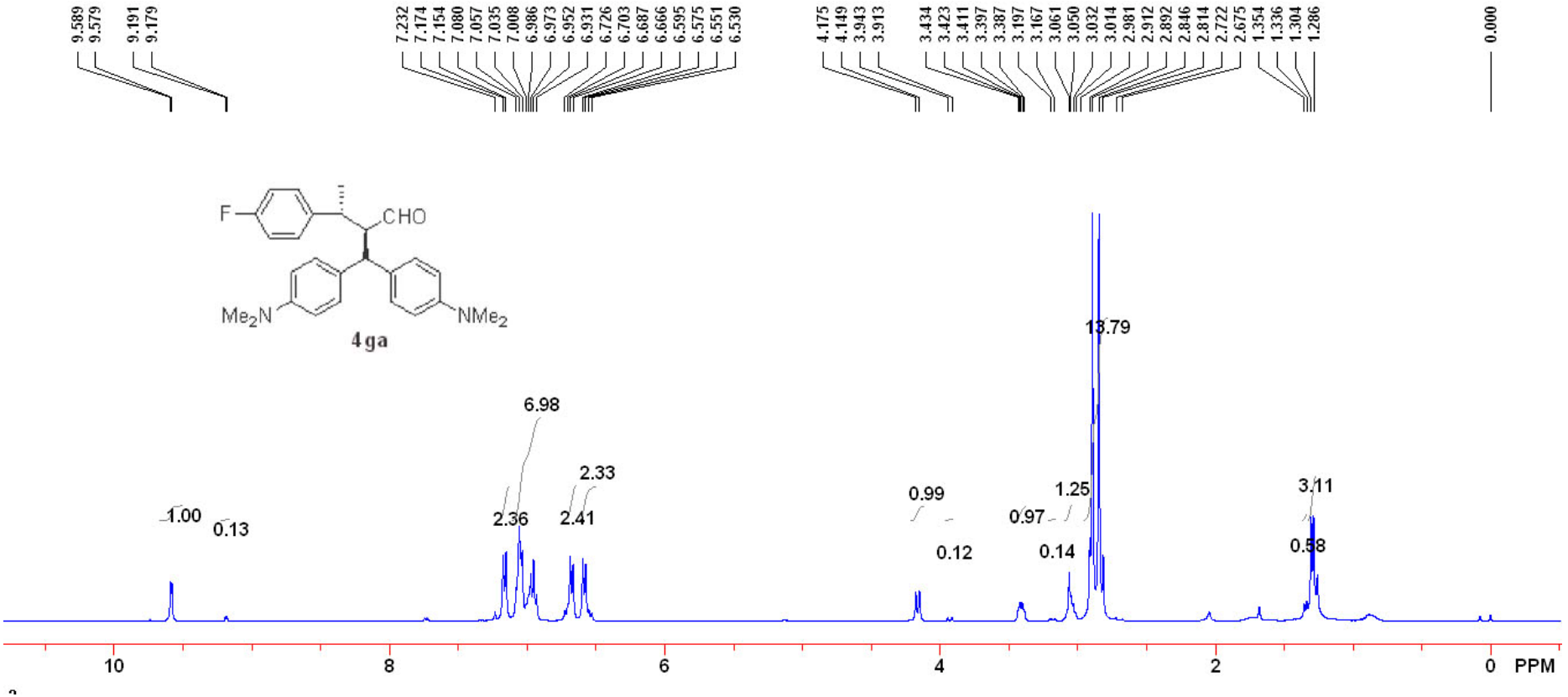
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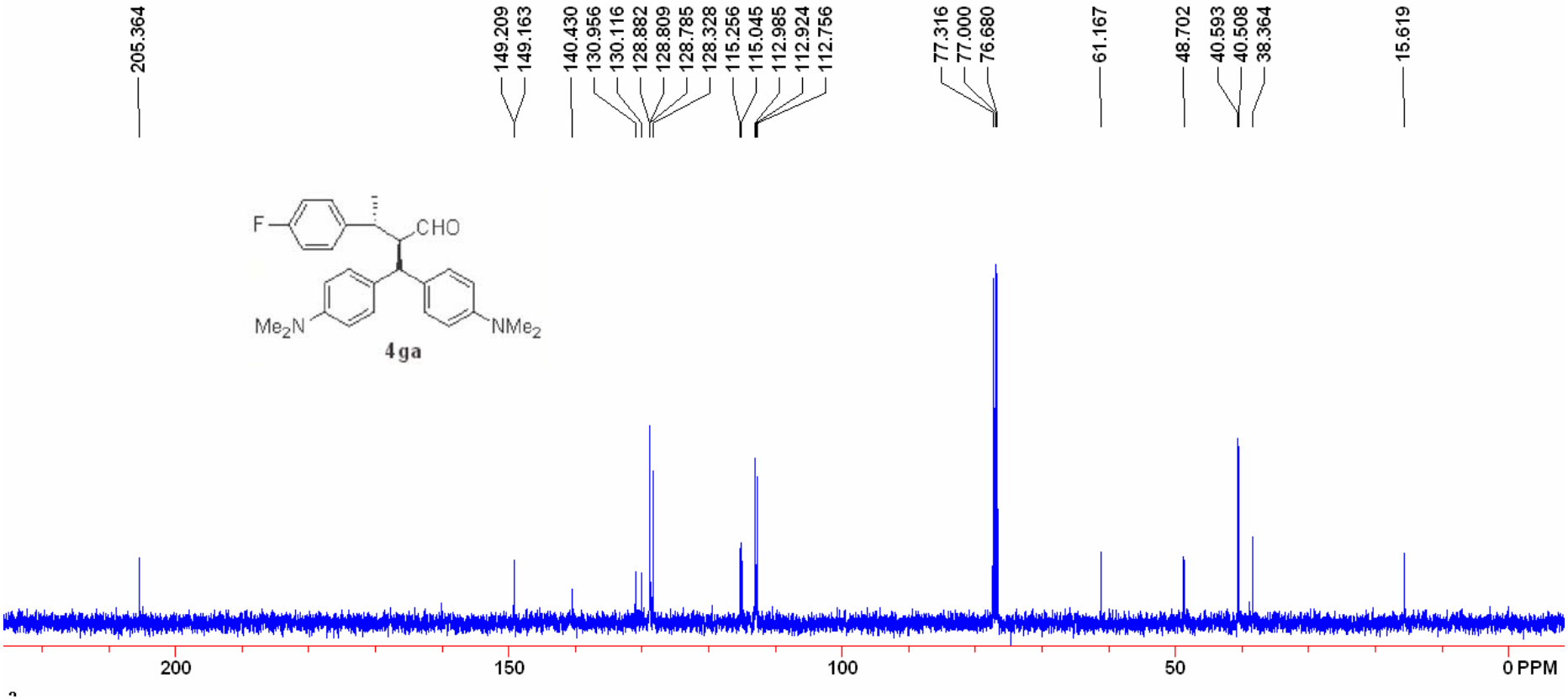
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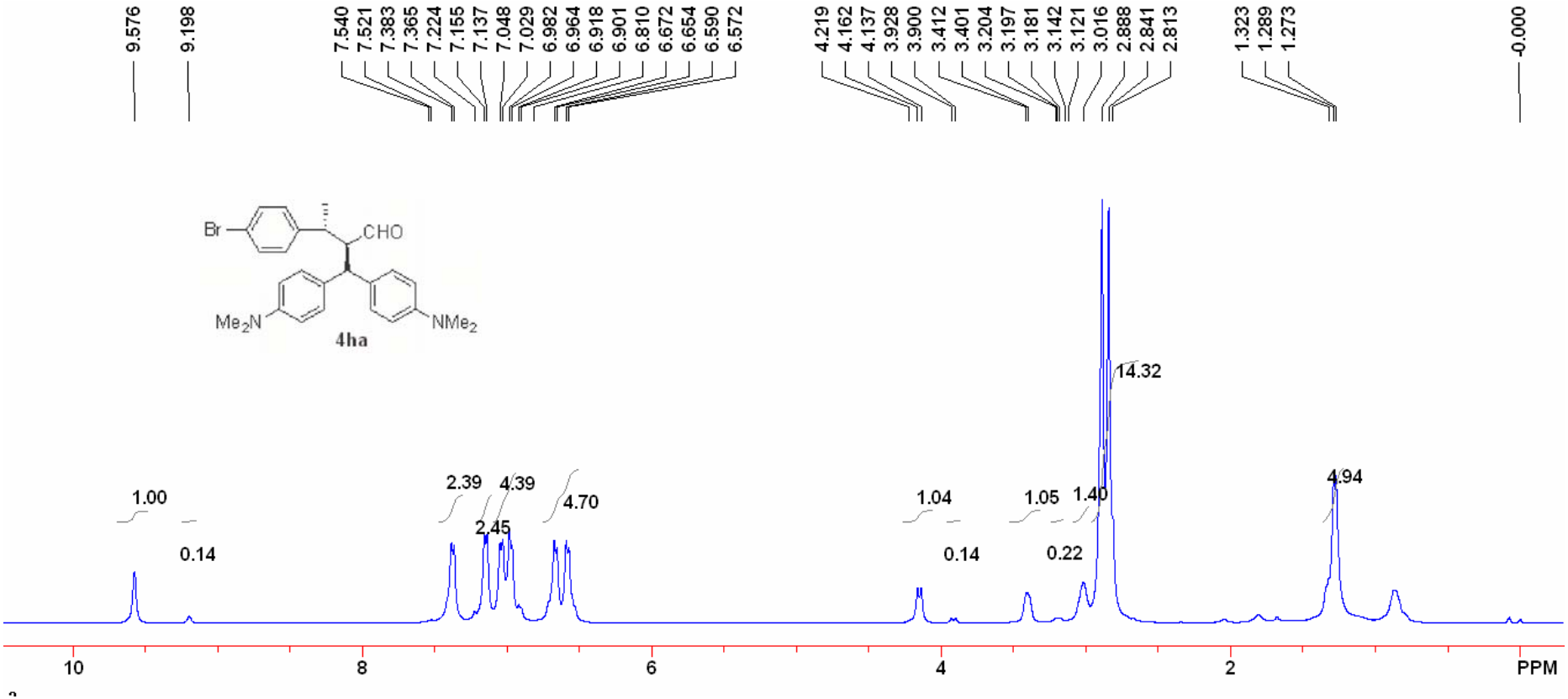
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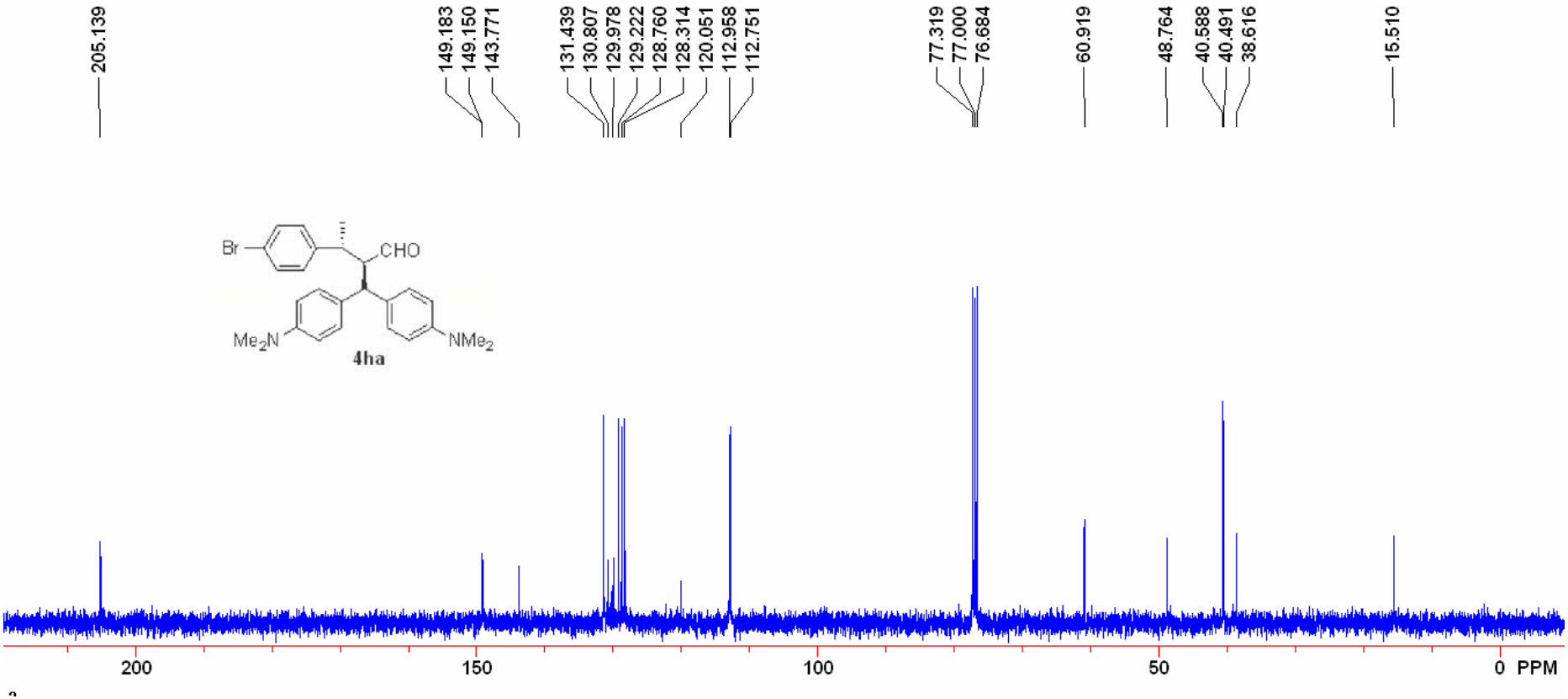
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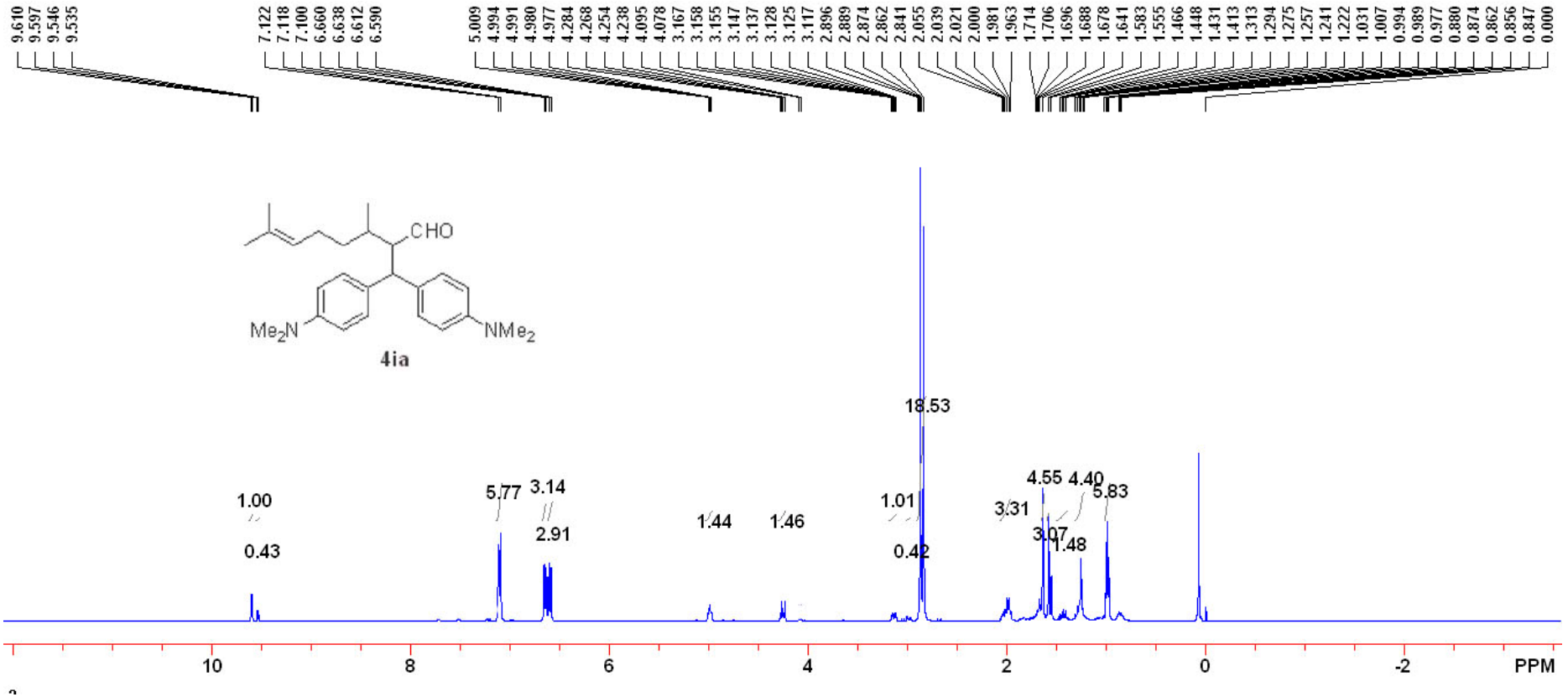
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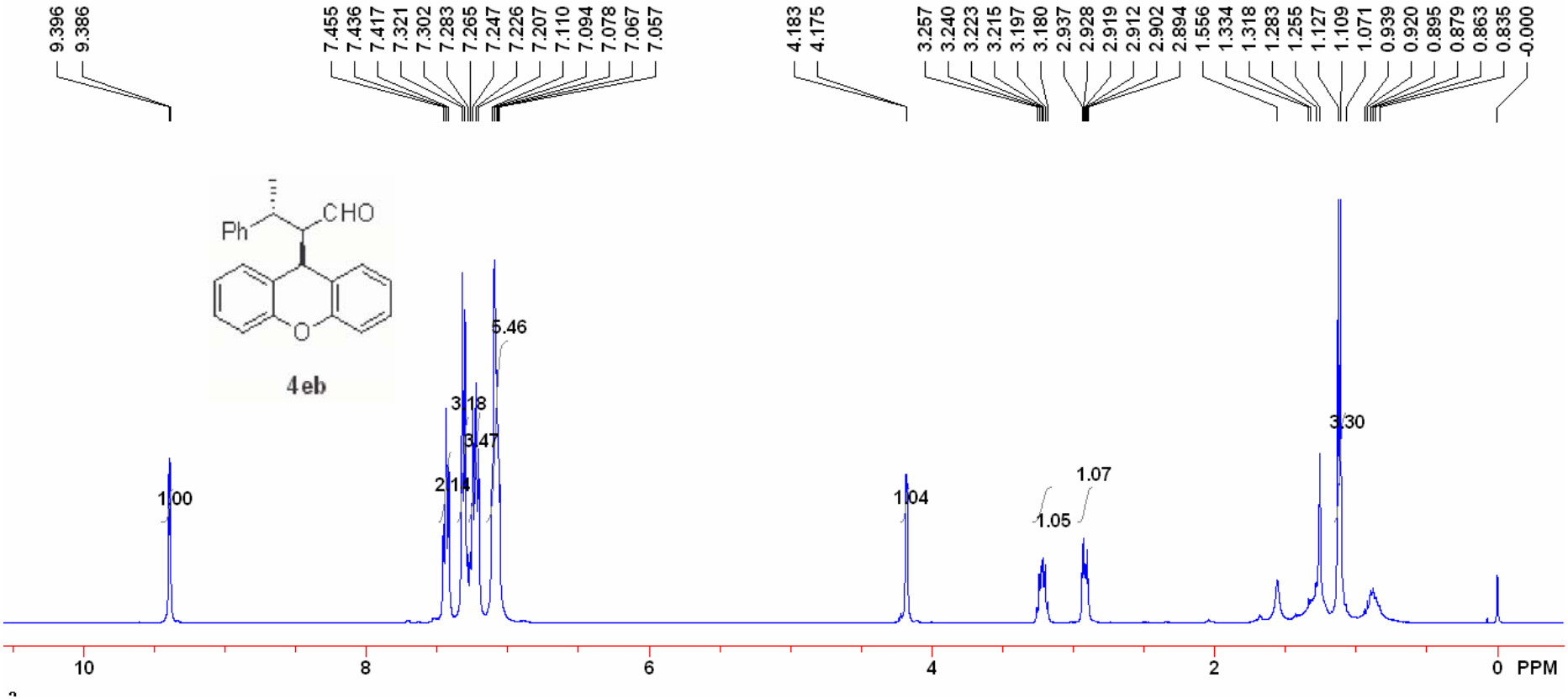
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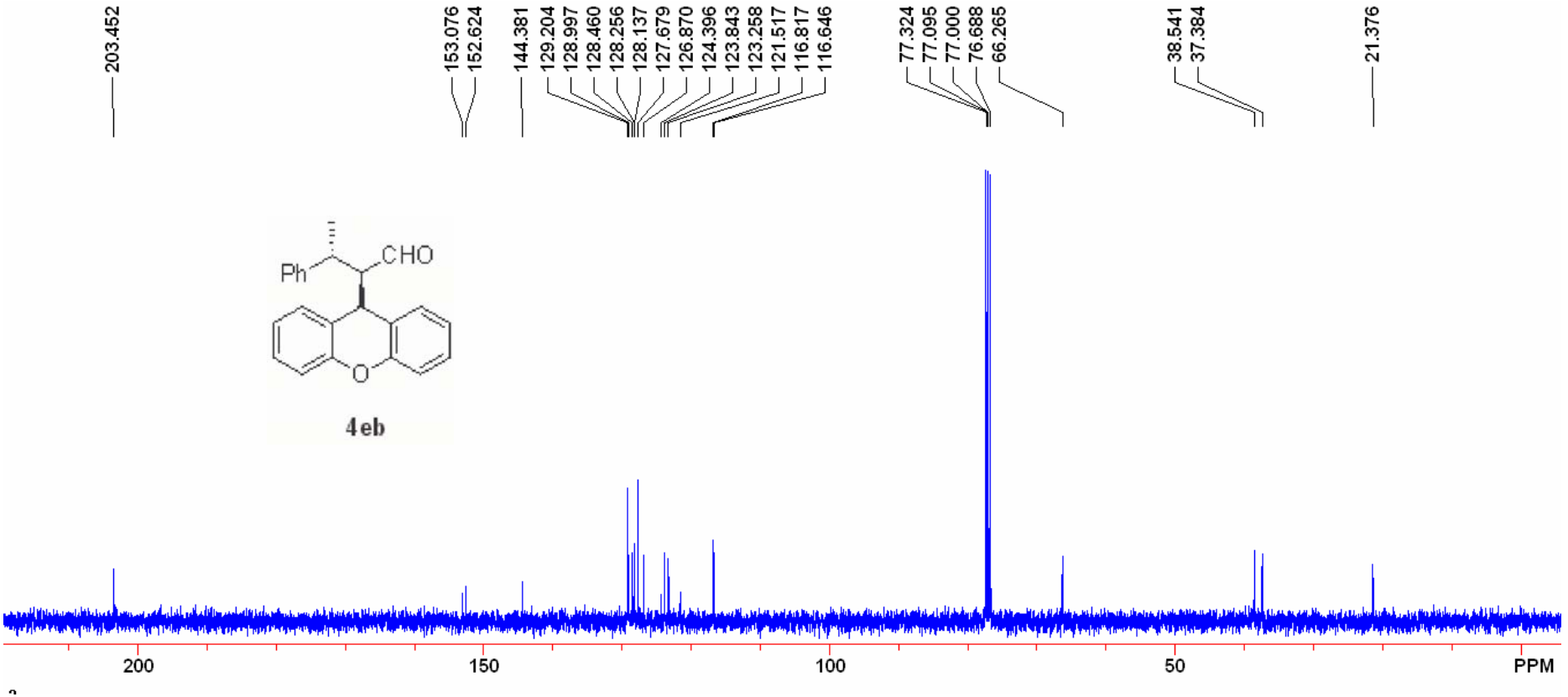
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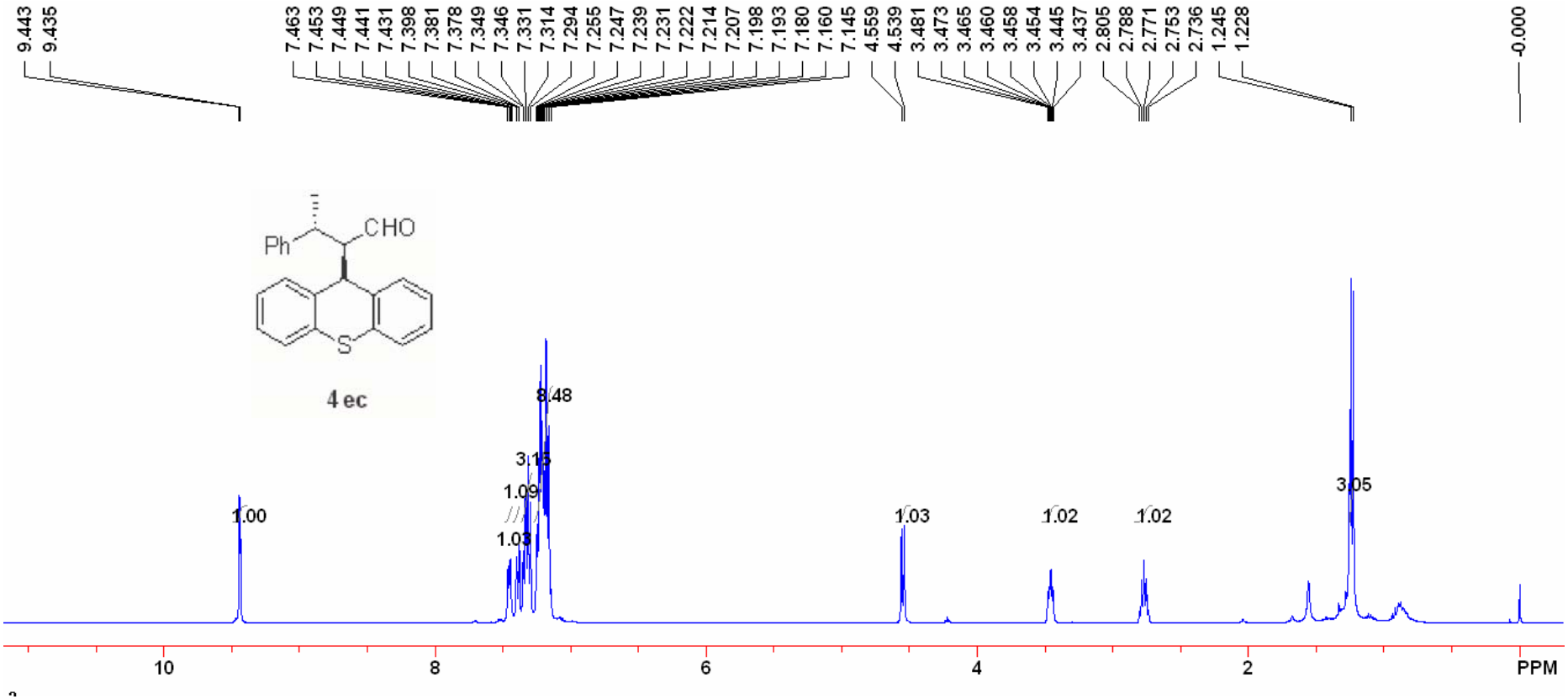
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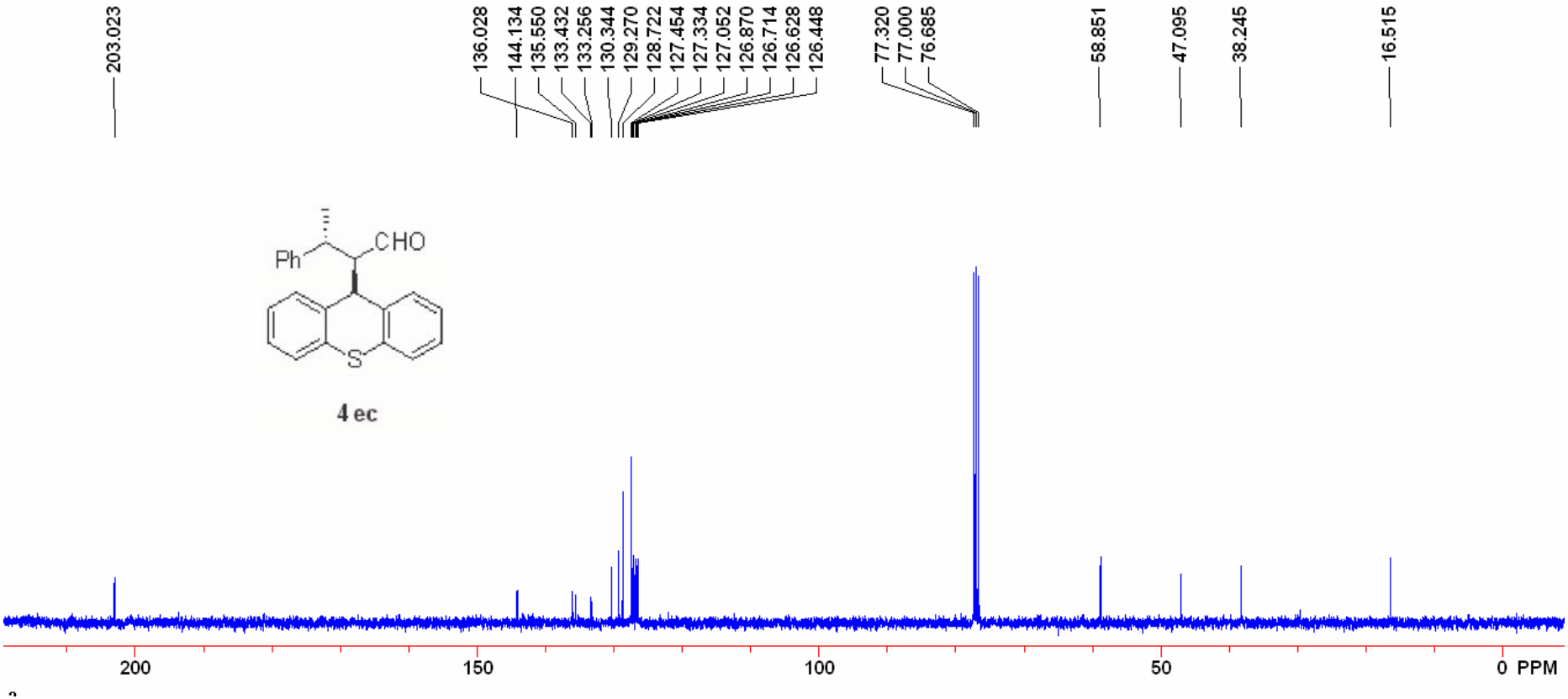
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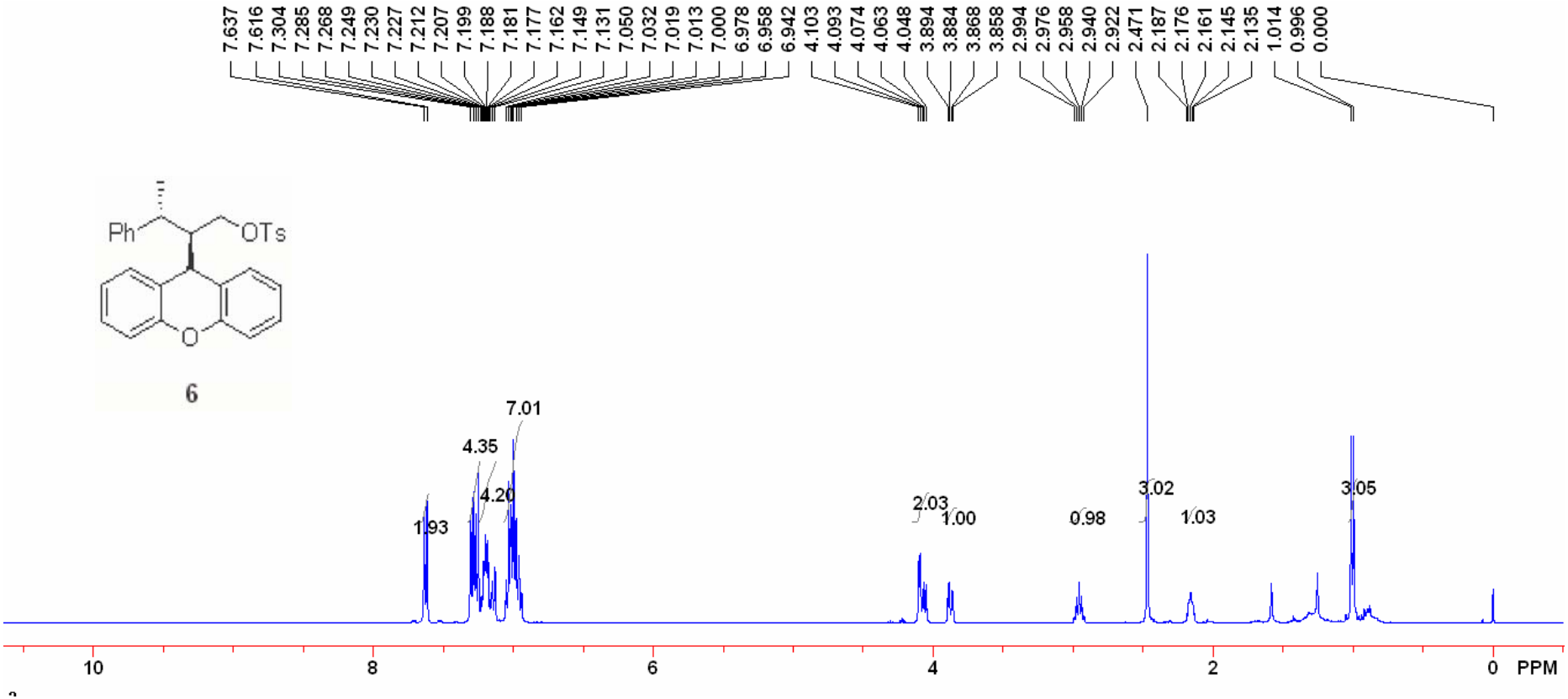
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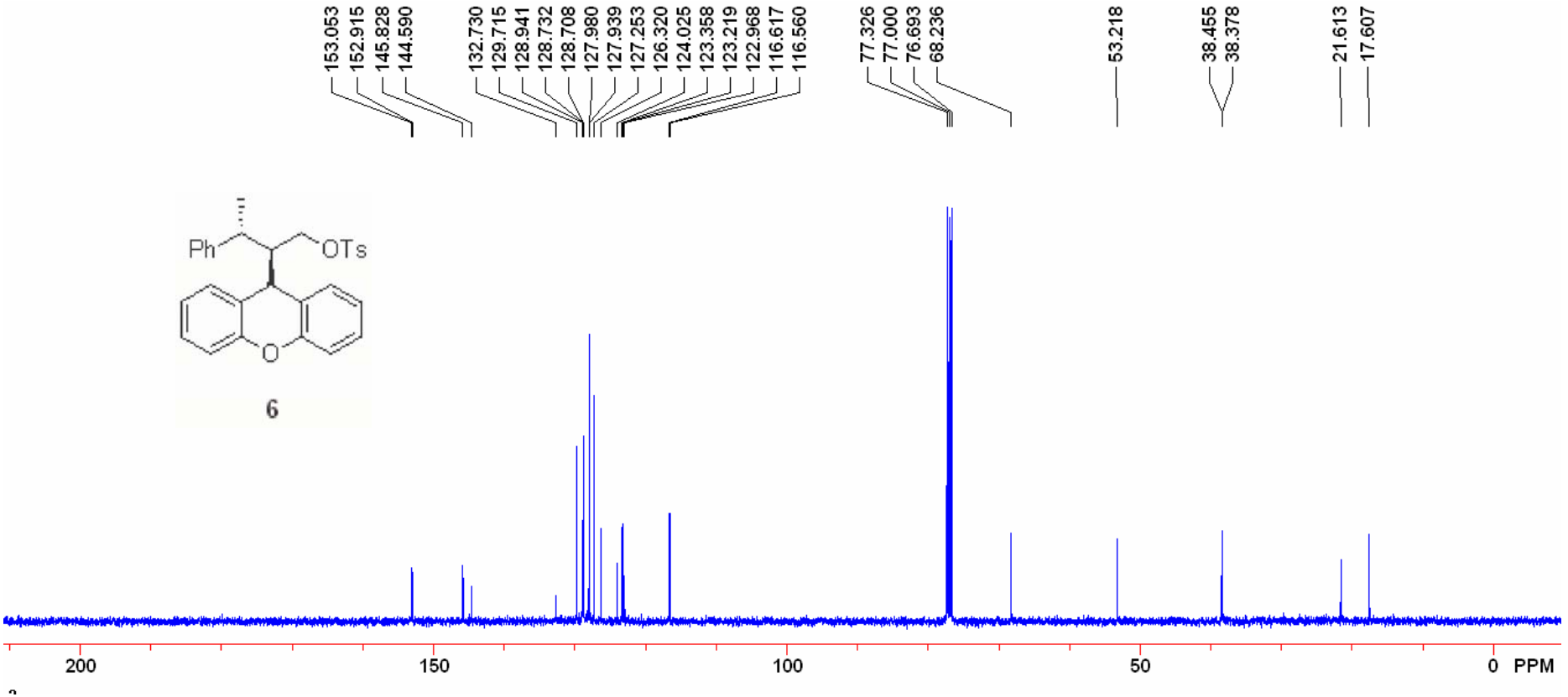
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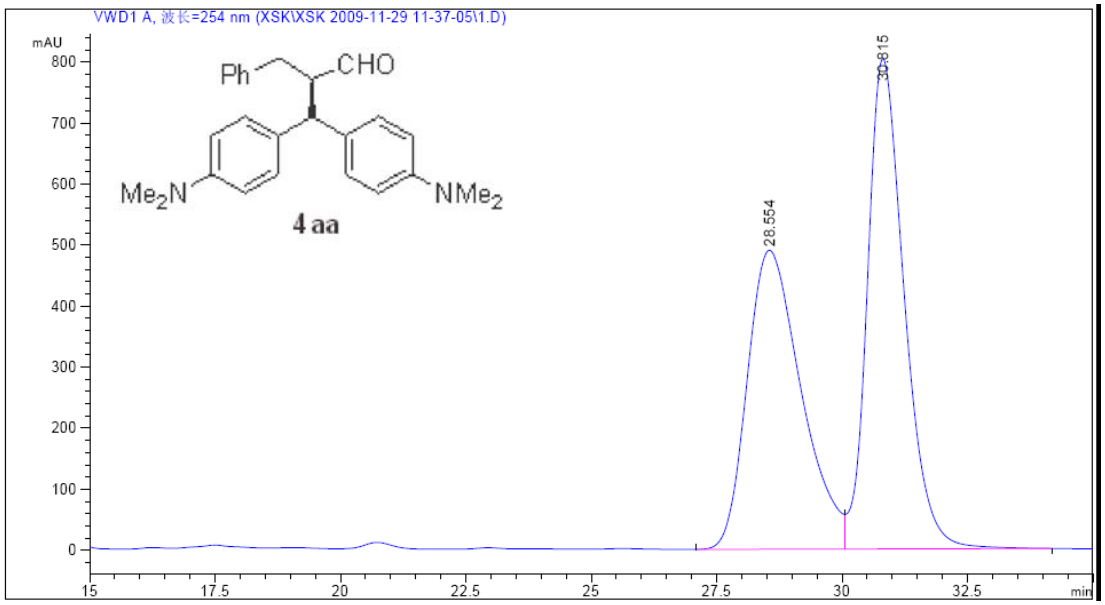
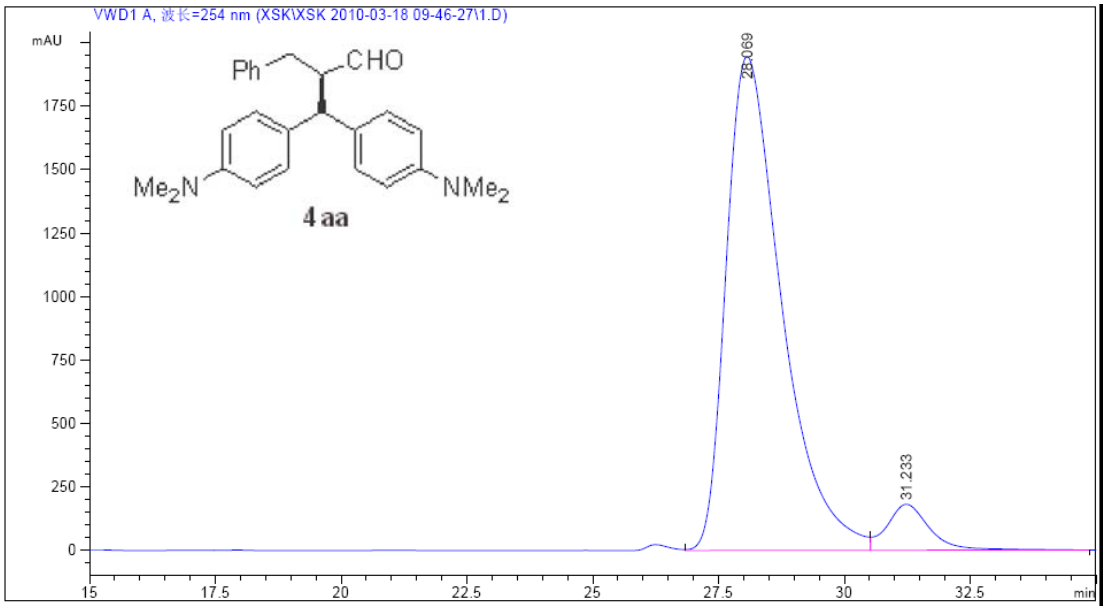
Racemic



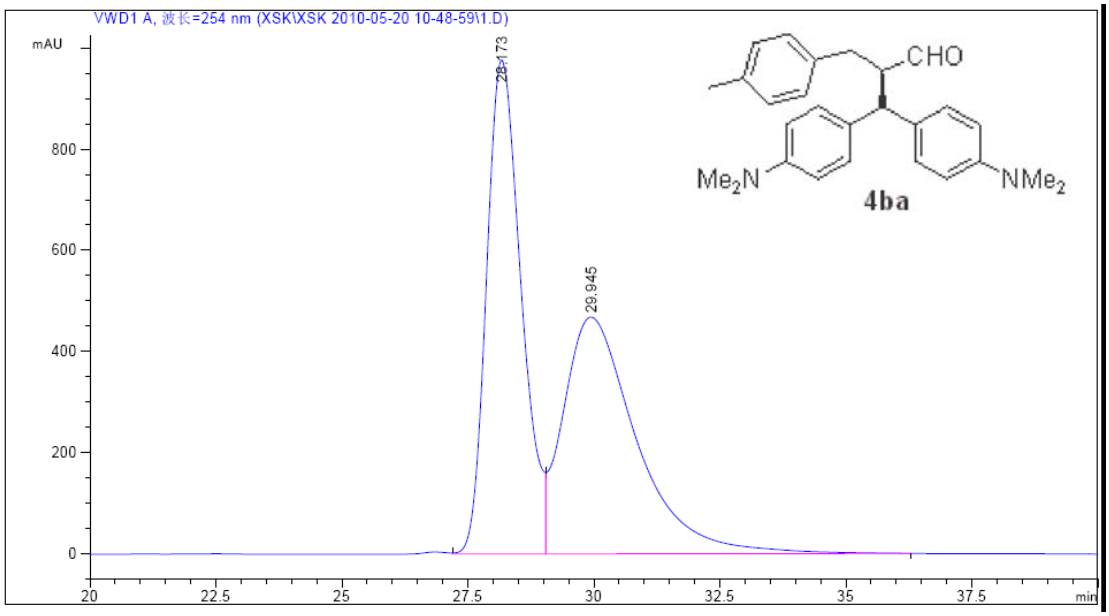
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	28.554	BV	1.1421	3.65918e4	489.94943	47.1403
2	30.815	VB	0.7776	4.10314e4	803.72809	52.8597

Sample



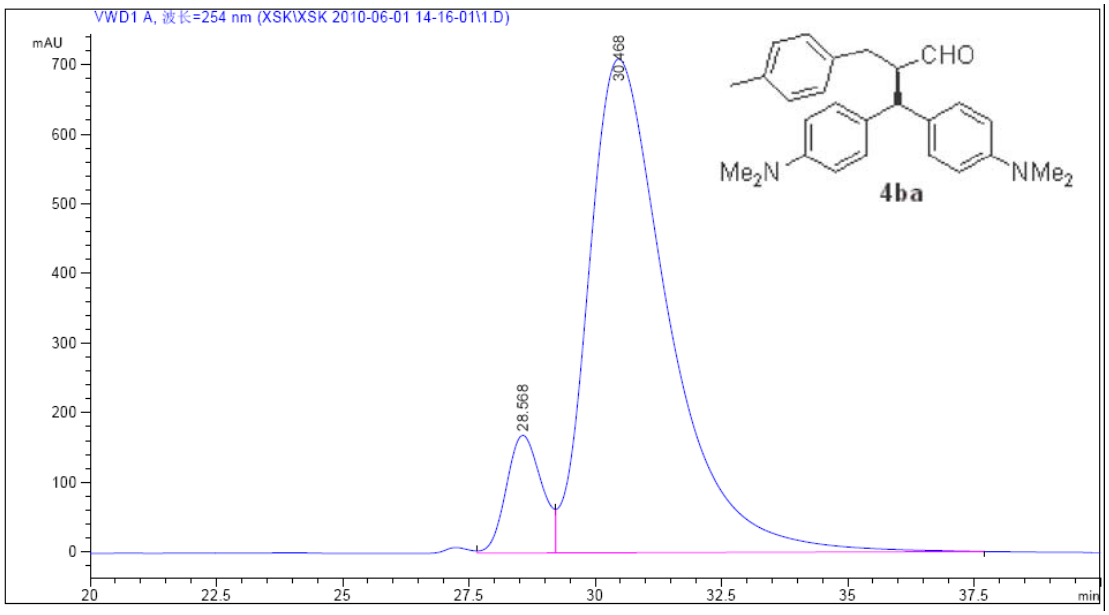
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	28.069	VV	1.1485	1.49112e5	1946.62720	93.3164
2	31.233	VB	0.8807	1.06799e4	180.97691	6.6836

Racemic



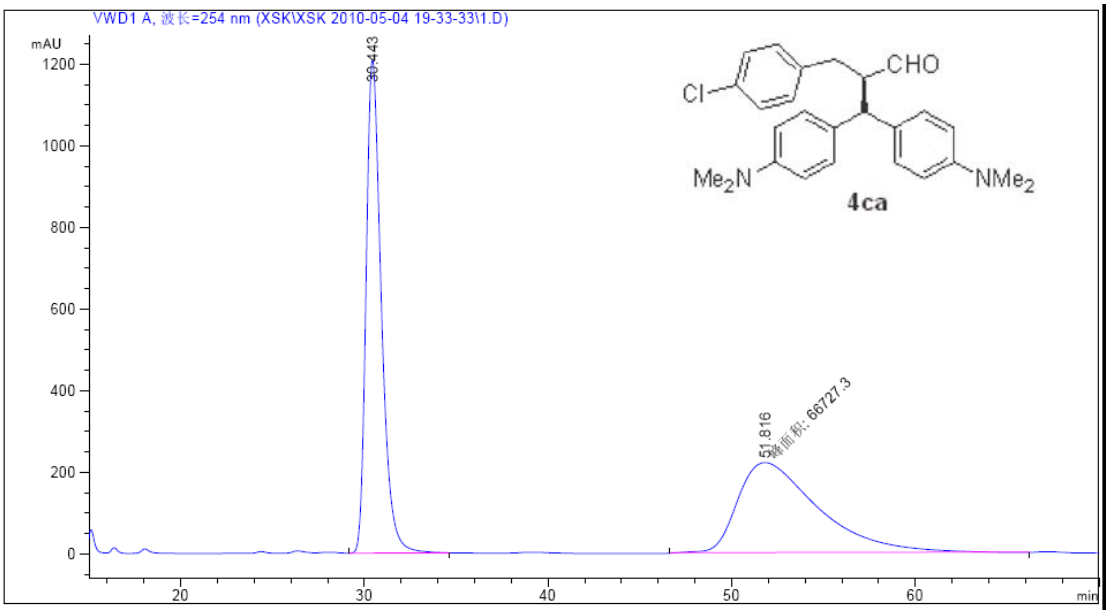
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	28.173	VV	0.7328	4.67656e4	977.63123	49.6040
2	29.945	VB	1.4797	4.75123e4	468.67648	50.3960

Sample



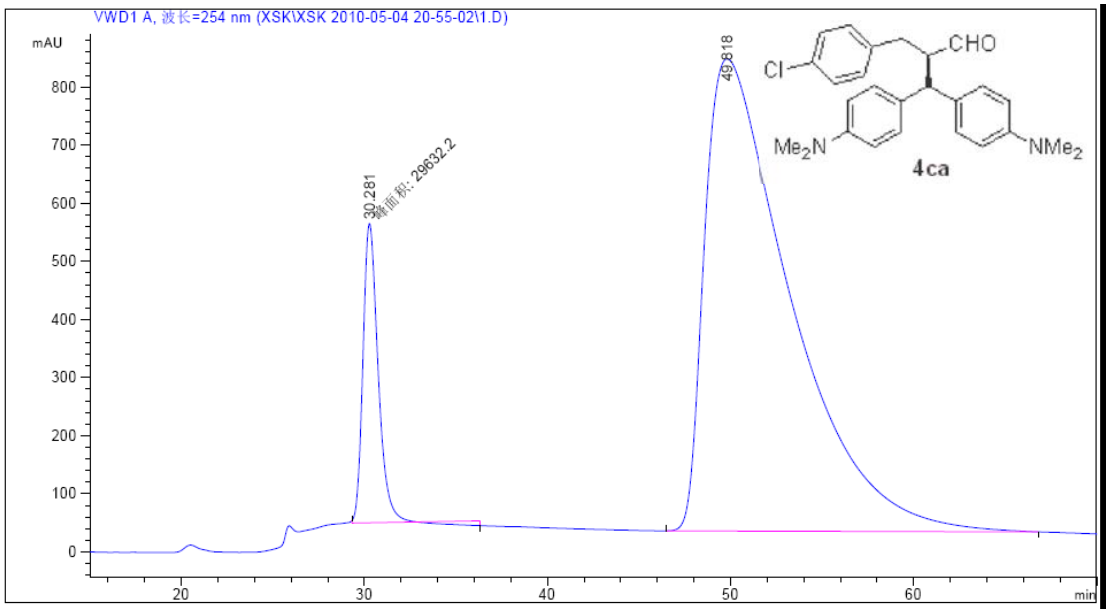
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	28.568	VV	0.7447	8222.42773	169.17261	9.5428
2	30.468	VB	1.6170	7.79415e4	709.23816	90.4572

Racemic



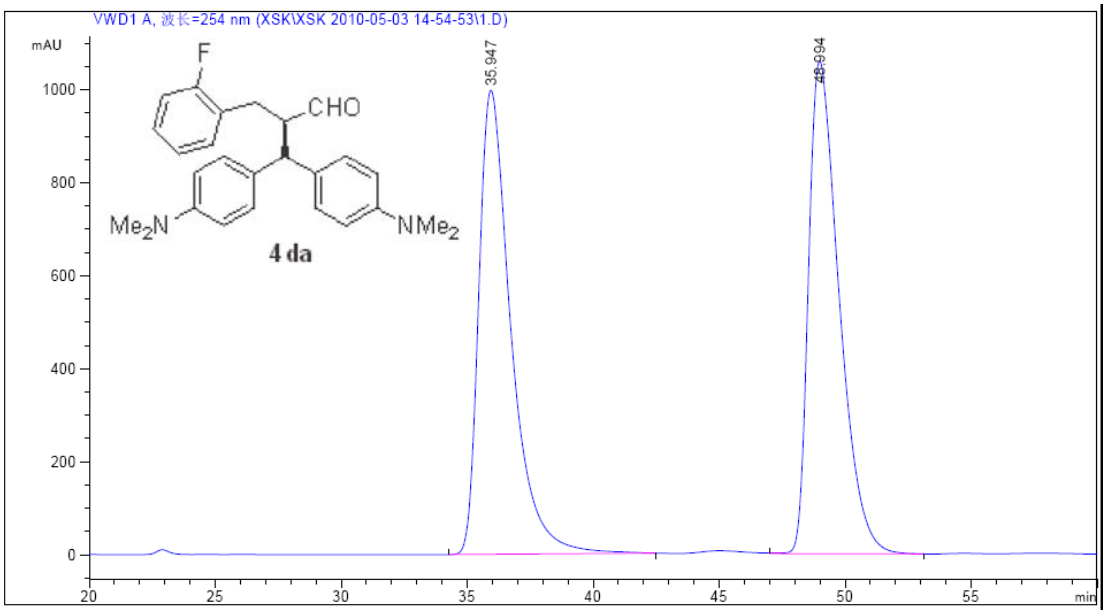
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	30.443	VB	0.8694	6.97009e4	1208.62671	51.0898
2	51.816	MM	5.0429	6.67273e4	220.53209	48.9102

Sample



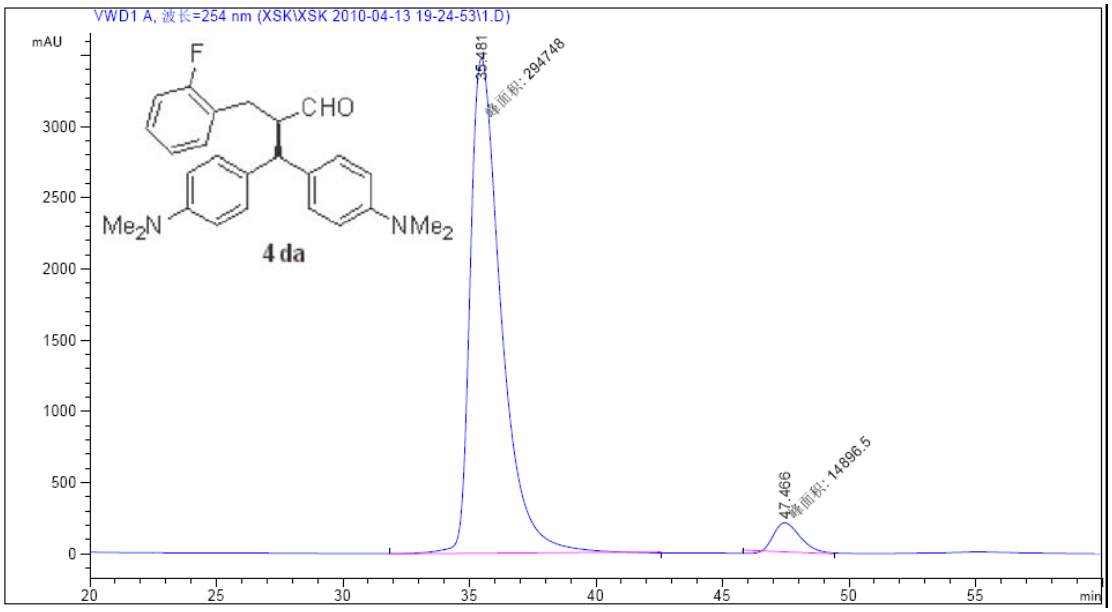
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	30.281	MM	0.9591	2.96322e4	514.92493	10.0746
2	49.818	BB	4.4837	2.64497e5	812.48944	89.9254

Racemic



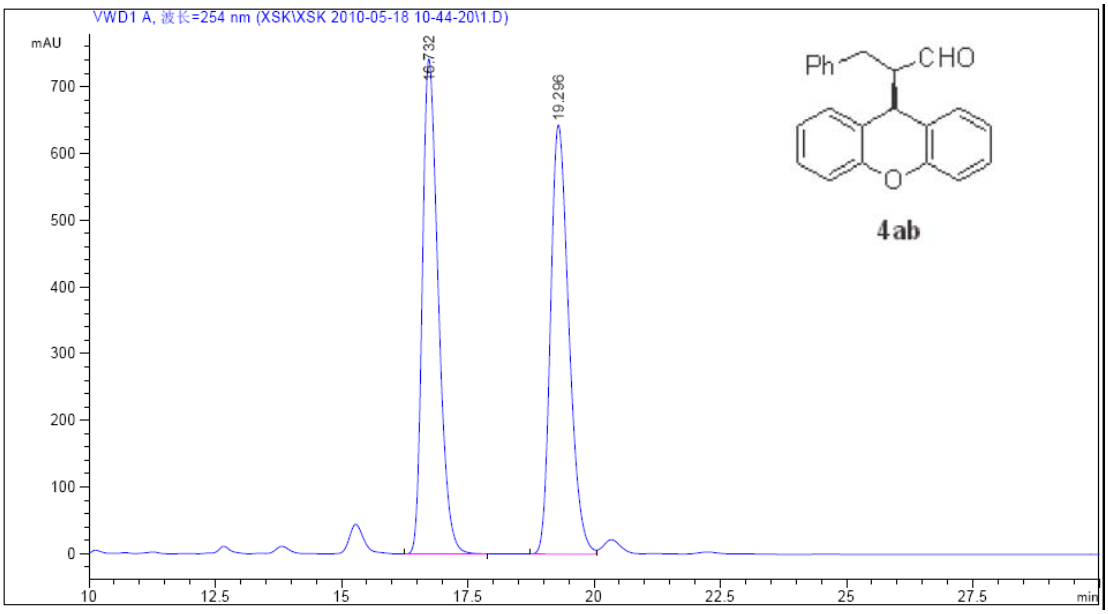
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	35.947	BB	1.3129	8.85349e4	998.20557	49.7911
2	48.994	VB	1.2610	8.92776e4	1059.64209	50.2089

Sample



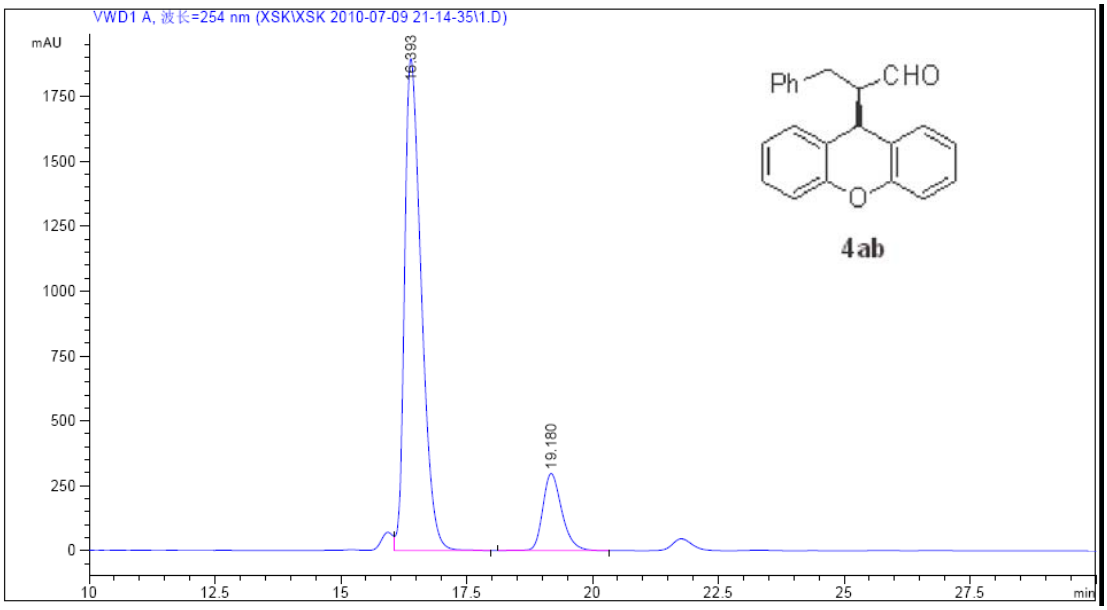
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	35.481	MM	1.4120	2.94748e5	3479.16309	95.1892
2	47.466	MM	1.2179	1.48965e4	203.85295	4.8108

Racemic



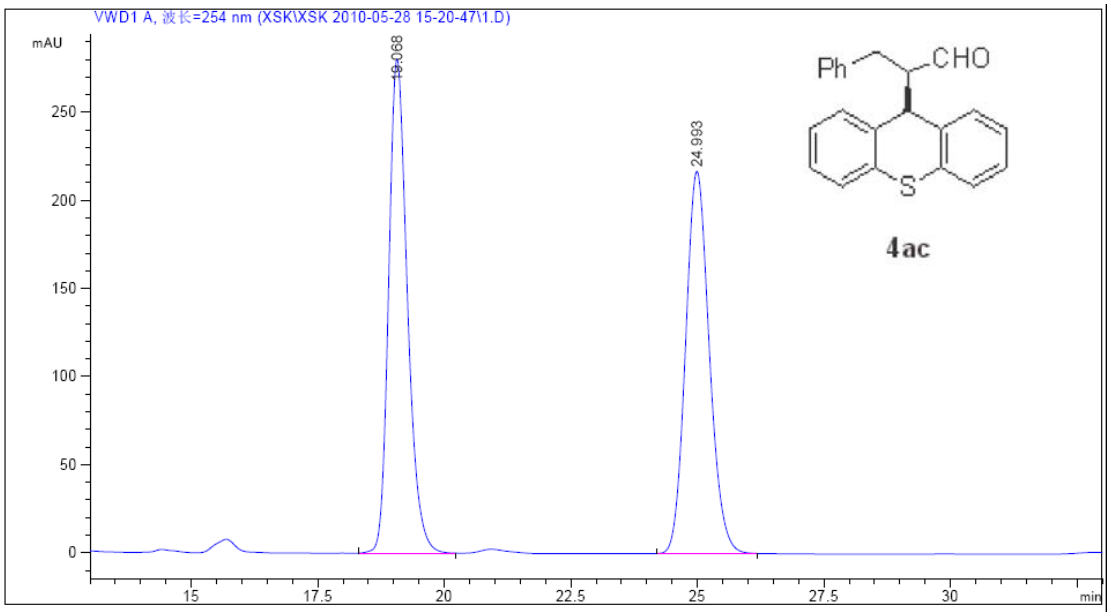
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	16.732	BB	0.3400	1.62495e4	741.85345	49.9817
2	19.296	BV	0.3926	1.62614e4	643.10303	50.0183

Sample



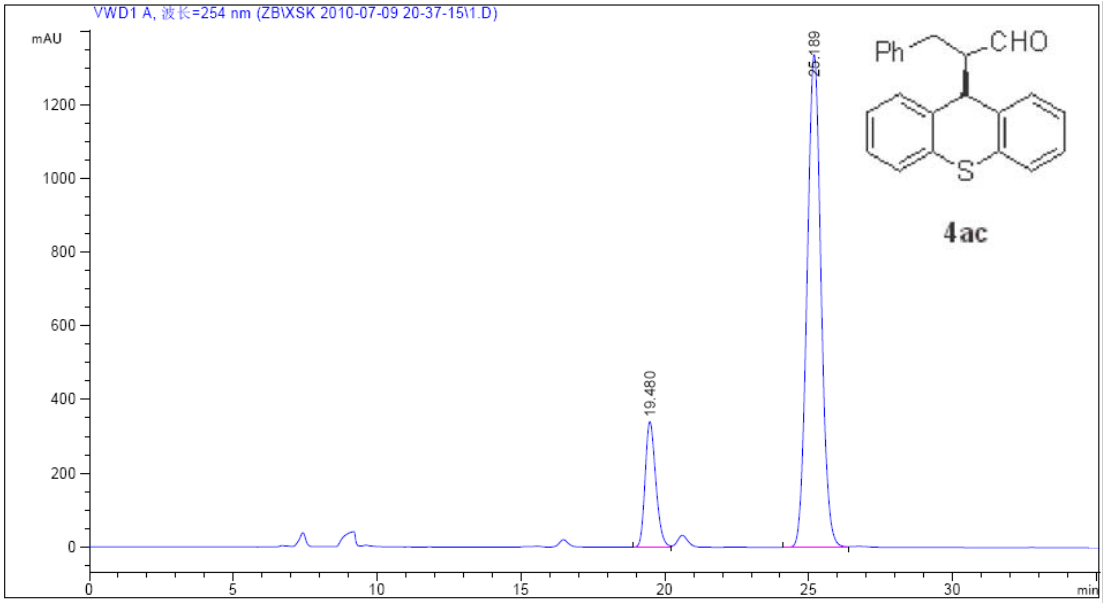
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	16.393	VB	0.3591	4.39057e4	1895.34058	84.8933
2	19.180	BB	0.4044	7812.96289	297.05502	15.1067

Racemic



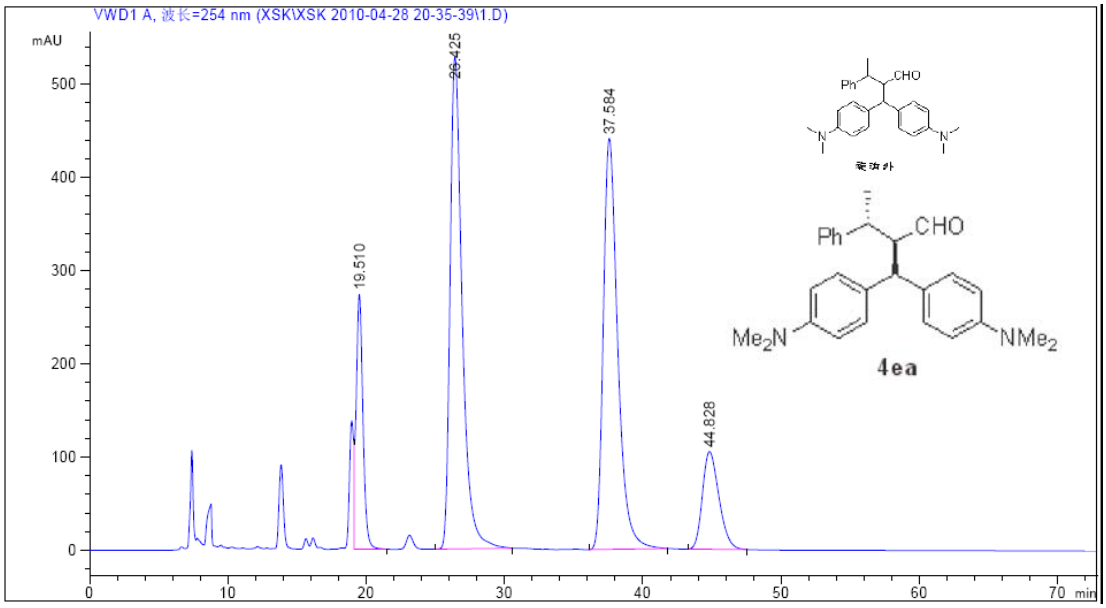
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	19.068	BB	0.3943	7204.54492	280.50629	50.4915
2	24.993	BB	0.4992	7064.27344	216.99493	49.5085

Sample



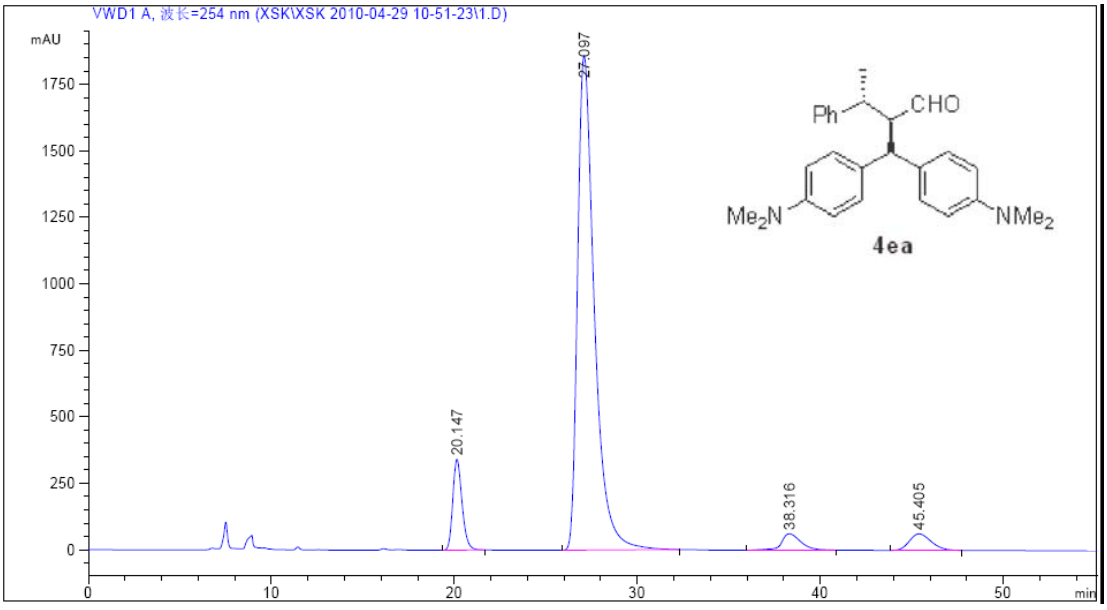
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	19.480	VV	0.3980	8783.63477	341.12457	16.3025
2	25.189	BB	0.5200	4.50955e4	1337.59424	83.6975

Racemic



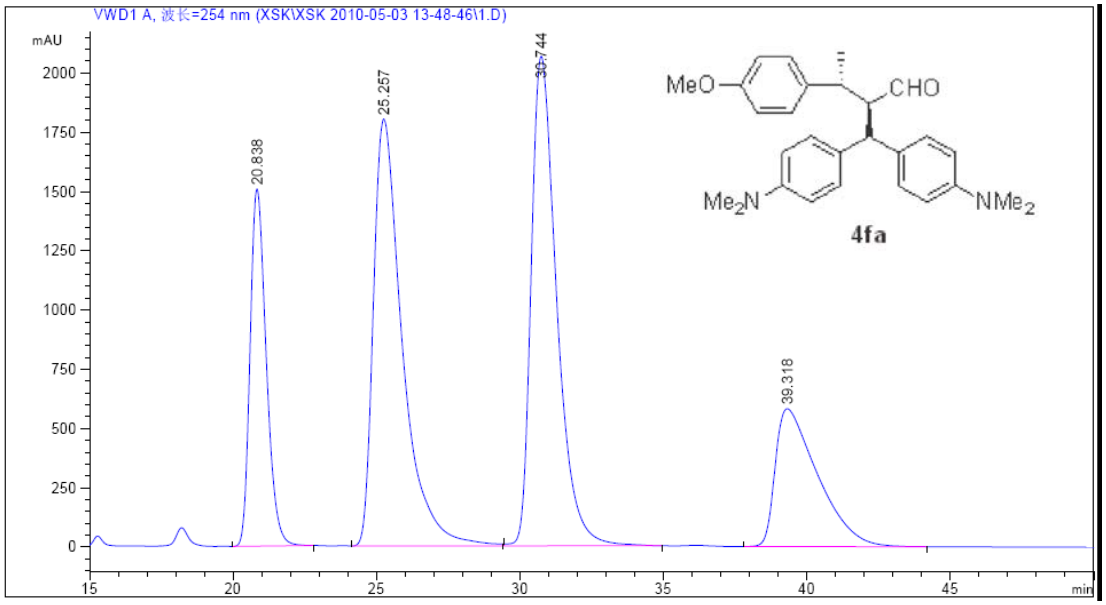
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	19.510	VB	0.5059	9295.18555	273.35315	11.3404
2	26.425	BB	0.9060	3.20400e4	528.00201	39.0898
3	37.584	BB	1.0822	3.19213e4	440.81558	38.9451
4	44.828	BB	1.2624	8708.49219	104.77153	10.6247

Sample



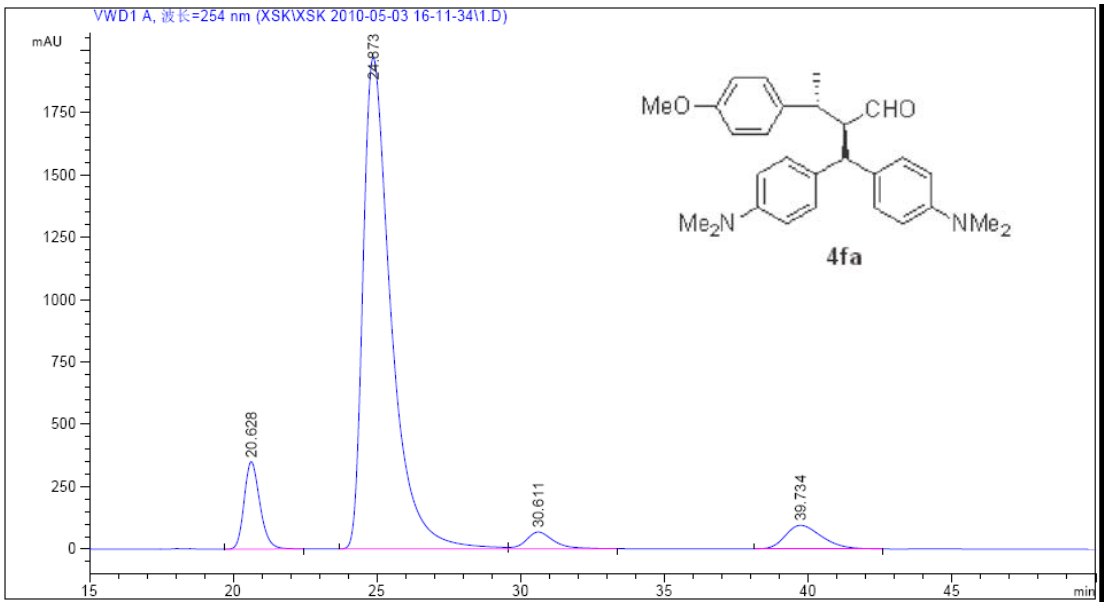
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	20.147	BB	0.5334	1.20378e4	341.58600	8.5614
2	27.097	BB	0.9454	1.18881e5	1859.24731	84.5494
3	38.316	BB	1.0910	4502.23096	61.42187	3.2020
4	45.405	BB	1.2451	5184.46533	62.45428	3.6872

Racemic



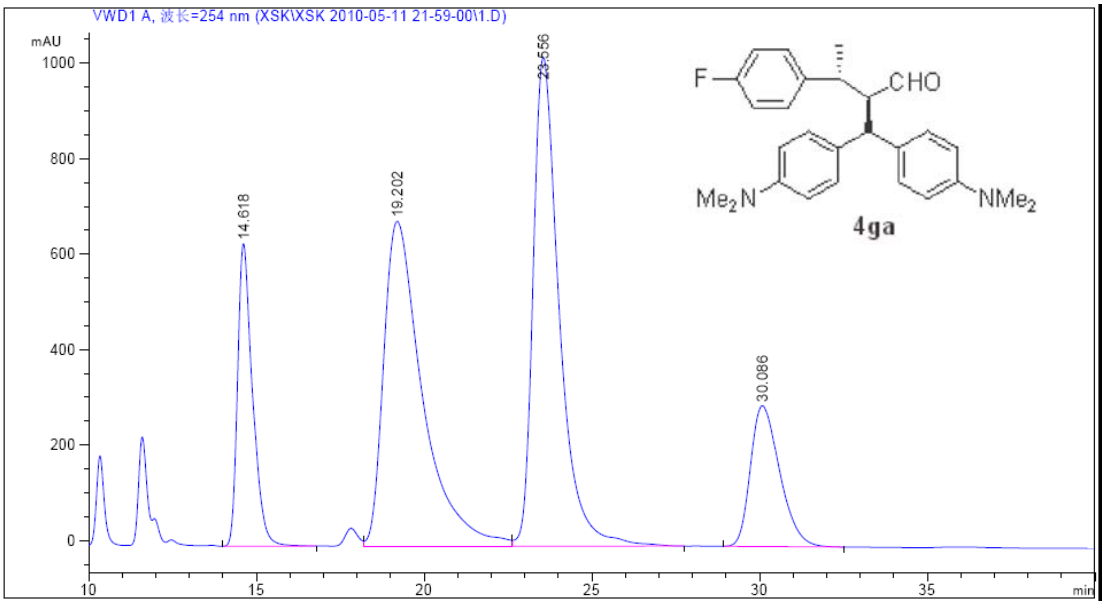
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	20.838	BB	0.5974	5.89230e4	1506.95850	15.8300
2	25.257	VB	1.0356	1.26145e5	1800.98804	33.8896
3	30.744	BB	0.9358	1.27514e5	2065.27881	34.2575
4	39.318	BB	1.4737	5.96411e4	581.28168	16.0229

Sample



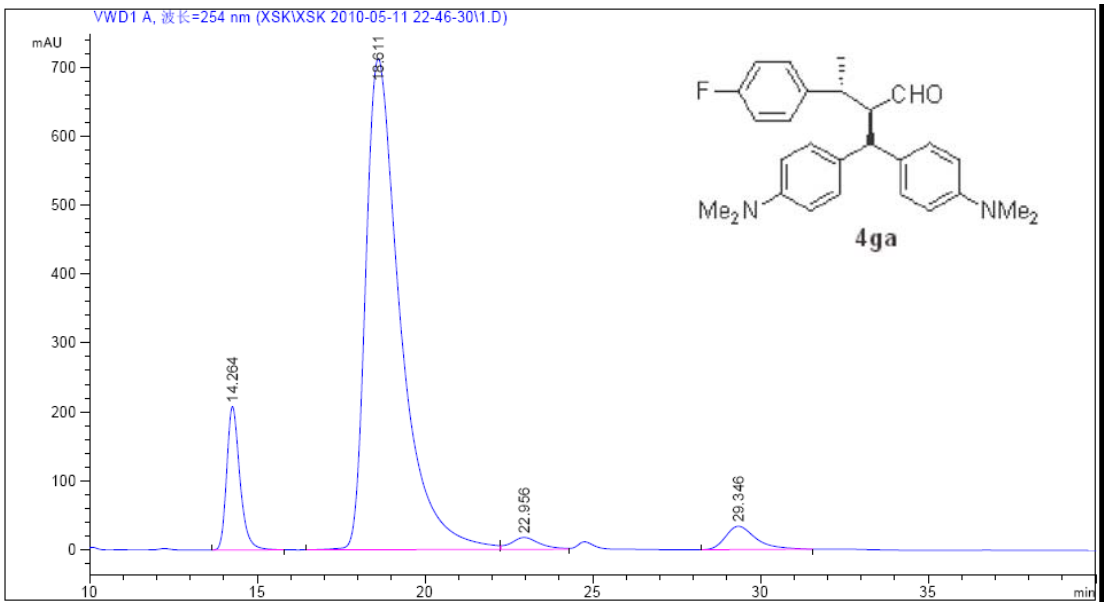
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	20.628	VB	0.5867	1.33257e4	350.11600	8.3637
2	24.873	BB	1.0065	1.33262e5	1969.20251	83.6401
3	30.611	BB	0.9882	4453.52832	67.11514	2.7952
4	39.734	BB	1.3181	8286.70996	94.55170	5.2010

Racemic



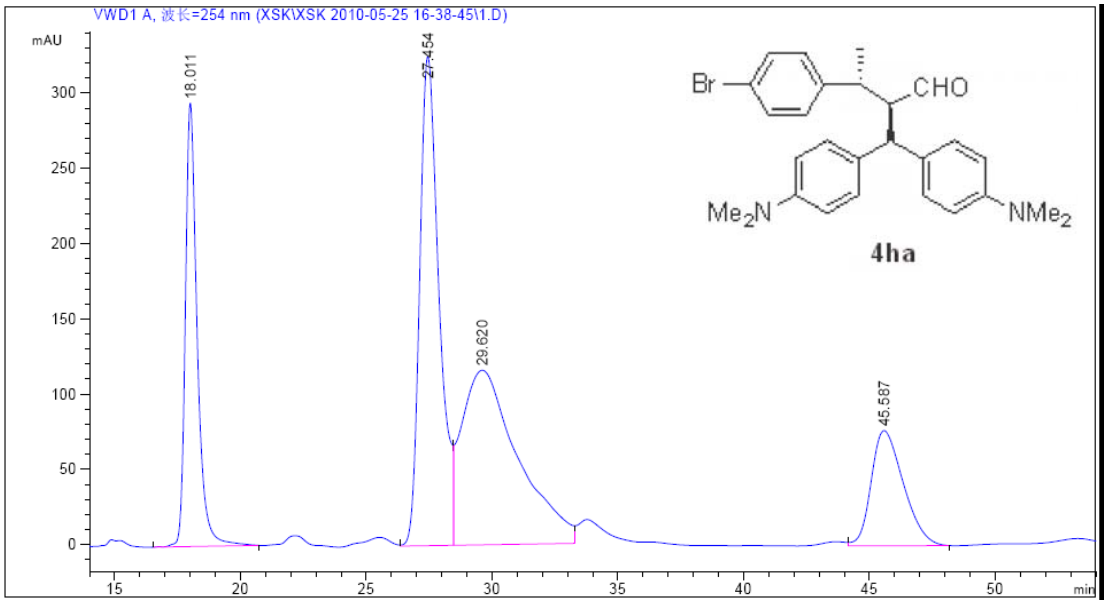
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	14.618	VB	0.4558	1.96283e4	634.03271	13.2683
2	19.202	VV	1.1909	5.47110e4	680.82300	36.9832
3	23.556	VB	0.8237	5.56895e4	1024.07239	37.6447
4	30.086	BB	0.9398	1.79057e4	294.92010	12.1038

Sample



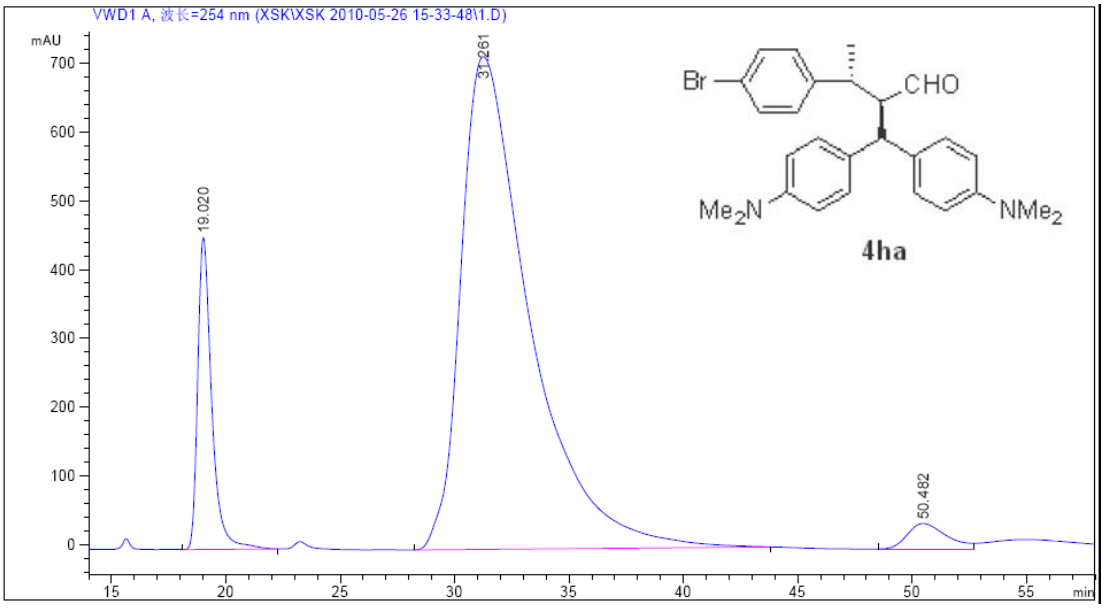
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	14.264	BB	0.4163	5696.16748	208.51686	9.4916
2	18.611	BB	1.0671	5.11478e4	714.16455	85.2282
3	22.956	BB	0.8531	1028.44629	17.35118	1.7137
4	29.346	BB	0.9475	2140.35254	33.91241	3.5665

Racemic



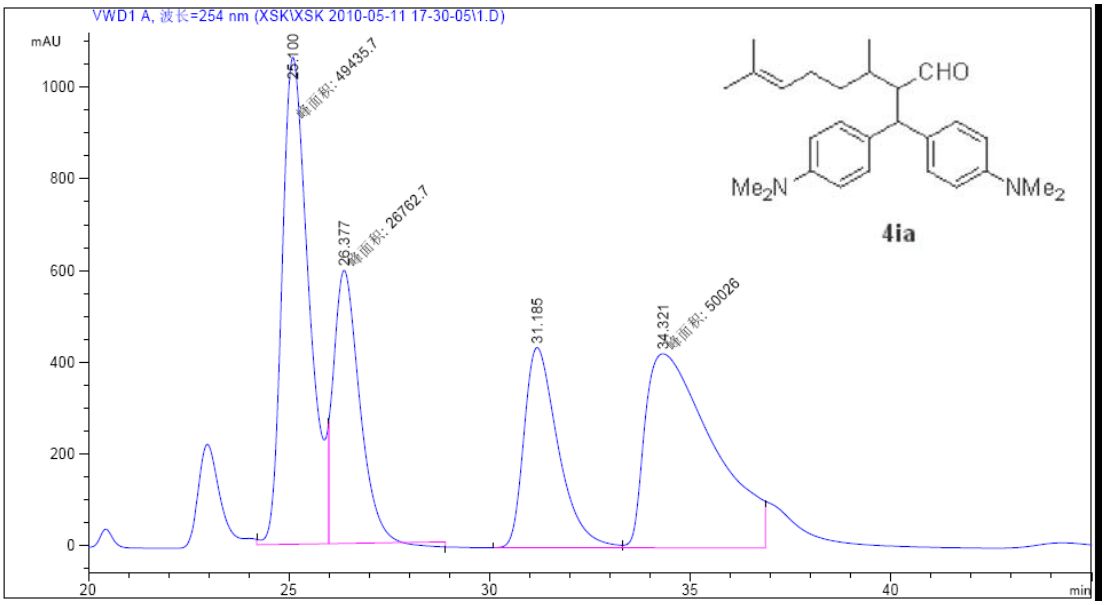
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	18.011	BB	0.4895	9603.44434	294.58002	18.5206
2	27.454	VV	0.8006	1.73556e4	325.04794	33.4709
3	29.620	VV	2.1967	1.80839e4	115.94669	34.8754
4	45.587	VB	1.3201	6809.89258	76.45879	13.1331

Sample



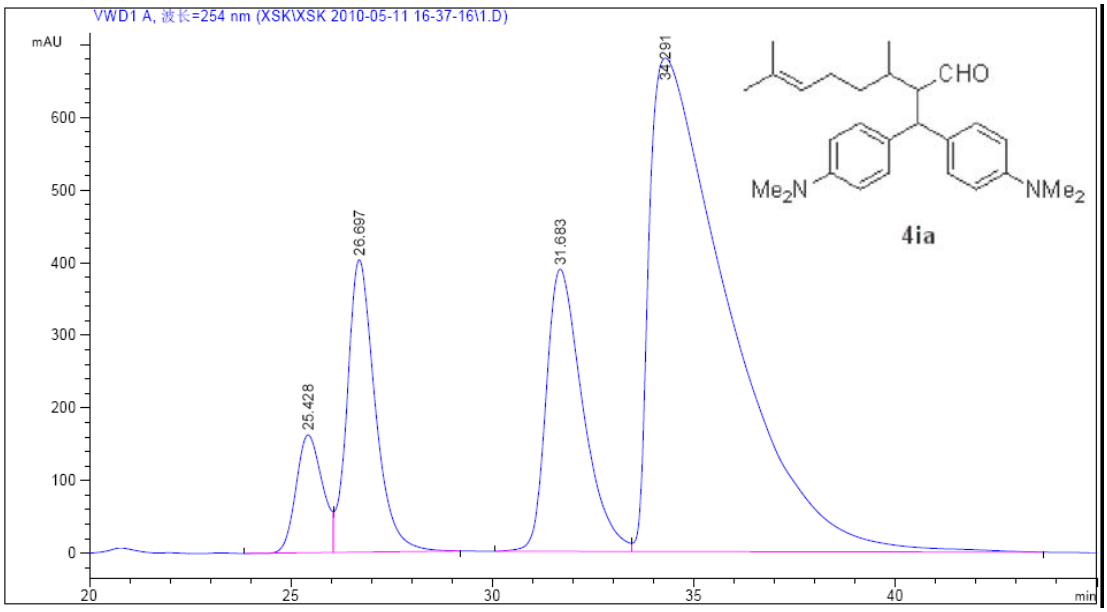
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	19.020	VB	0.6340	1.92757e4	453.67825	11.1085
2	31.261	BB	2.9458	1.49798e5	716.93311	86.3272
3	50.482	BV	1.7103	4449.68359	37.19183	2.5643

Racemic



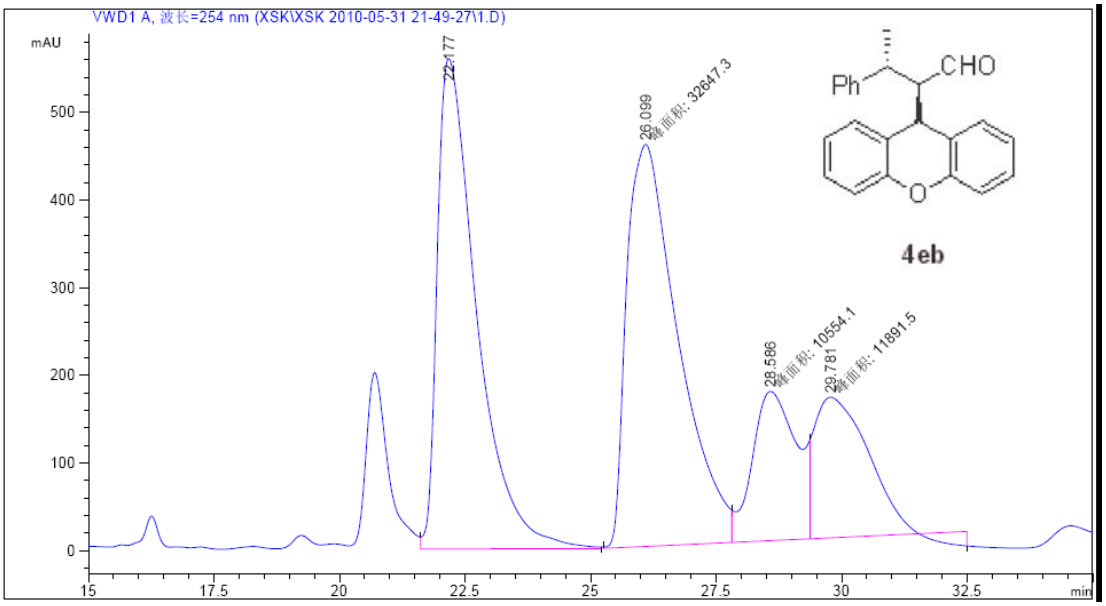
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	25.100	MF	0.7763	4.94357e4	1061.38159	32.5110
2	26.377	FM	0.7490	2.67627e4	595.53955	17.6003
3	31.185	BV	0.8986	2.58338e4	436.55292	16.9894
4	34.321	MF	1.9710	5.00260e4	423.02014	32.8992

Sample



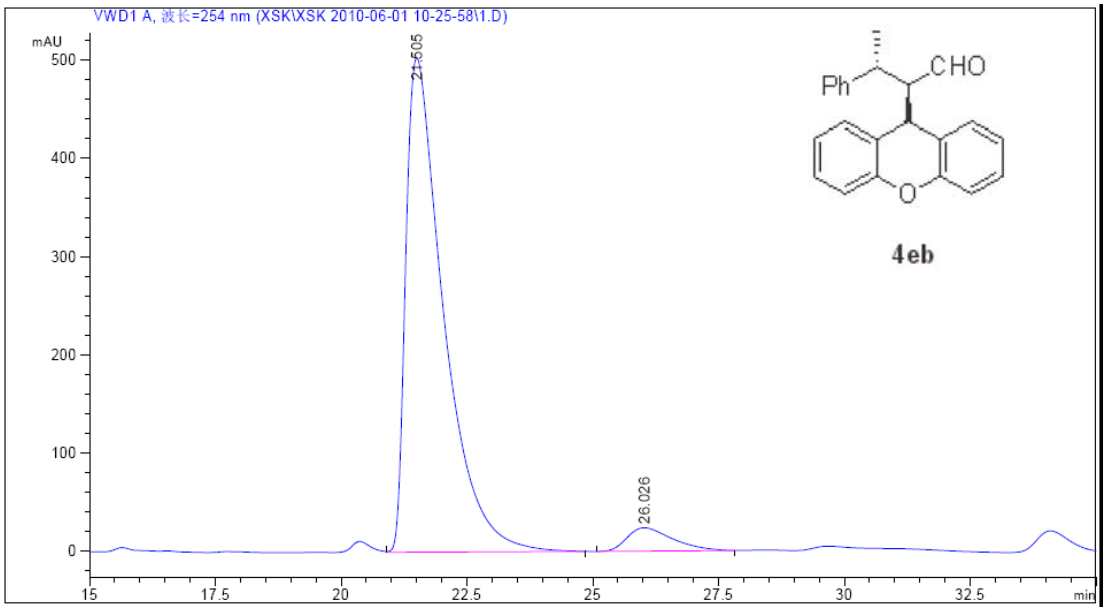
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	25.428	VV	0.7016	7367.71826	162.24649	5.0973
2	26.697	VB	0.7215	1.94249e4	402.65524	13.4390
3	31.683	BV	0.9528	2.45000e4	388.41849	16.9502
4	34.291	VB	1.9154	9.32483e4	679.54285	64.5135

Racemic



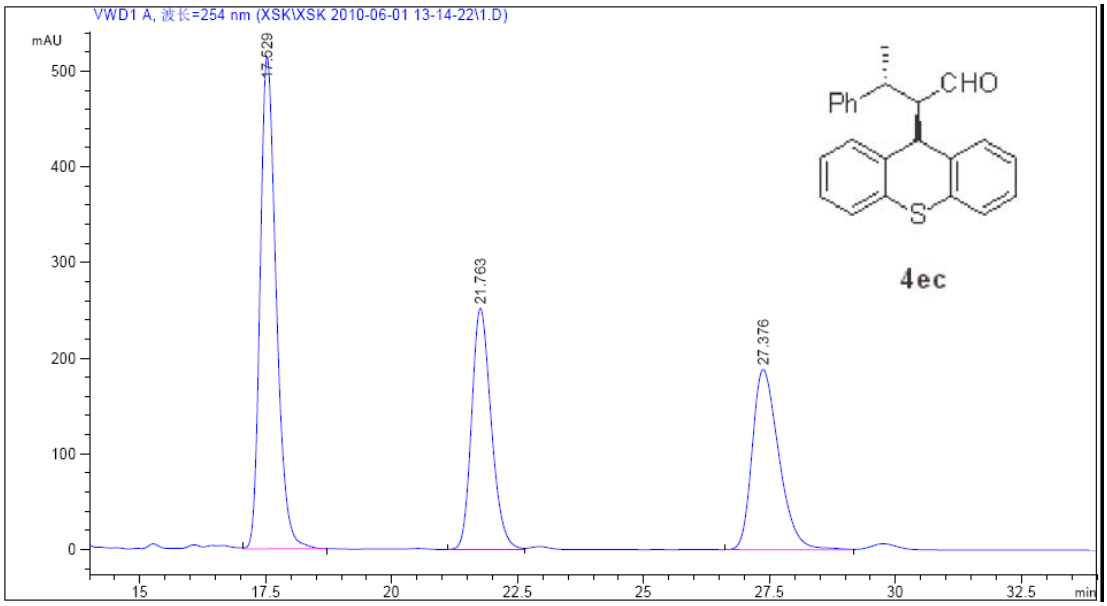
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	22.177	VB	0.8214	3.05131e4	559.28235	35.6436
2	26.099	MF	1.1866	3.26473e4	458.54257	38.1366
3	28.586	MF	1.0334	1.05541e4	170.22038	12.3287
4	29.781	FM	1.2363	1.18915e4	160.31342	13.8910

Sample



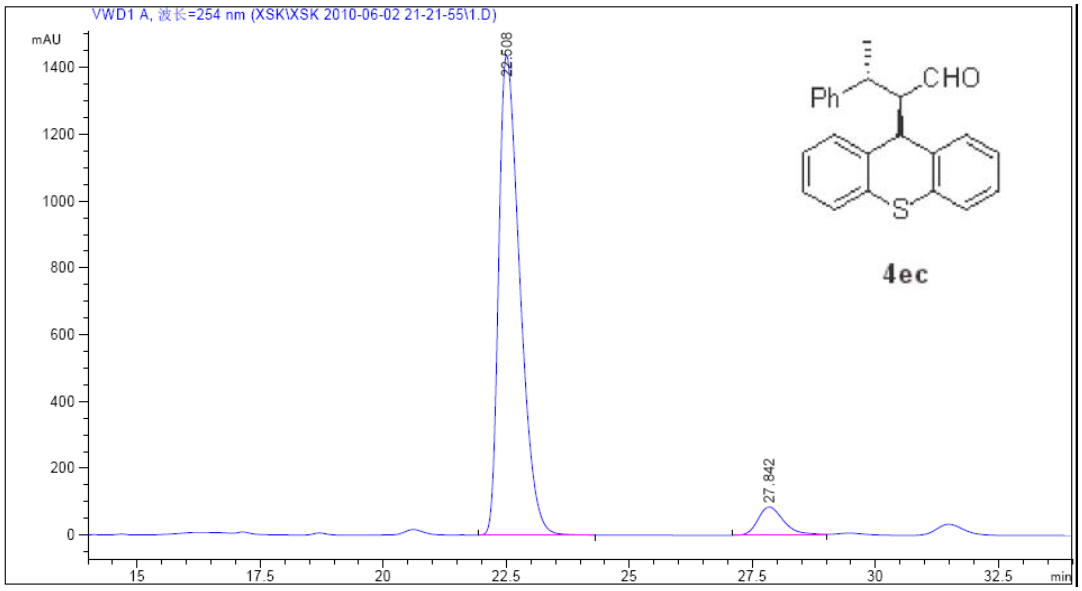
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	21.505	VB	0.7560	2.61968e4	503.12851	94.6075
2	26.026	BB	0.9309	1493.17358	23.76908	5.3925

Racemic



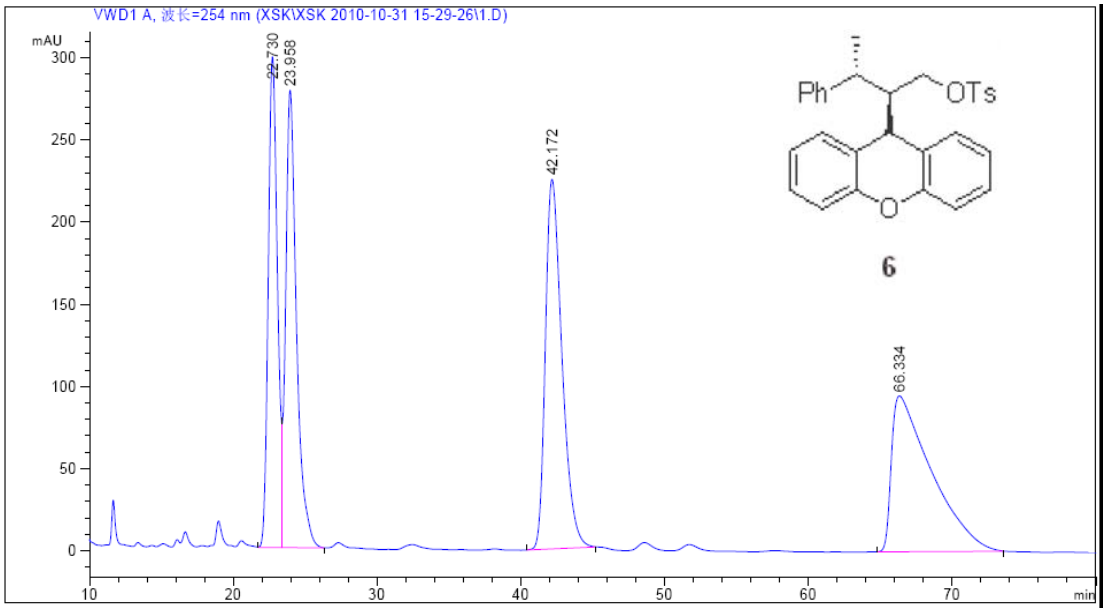
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	17.529	VB	0.3391	1.14229e4	514.56842	45.3462
2	21.763	BV	0.4161	6818.76807	252.05048	27.0690
3	27.376	BB	0.5670	6948.72266	188.45505	27.5848

Sample



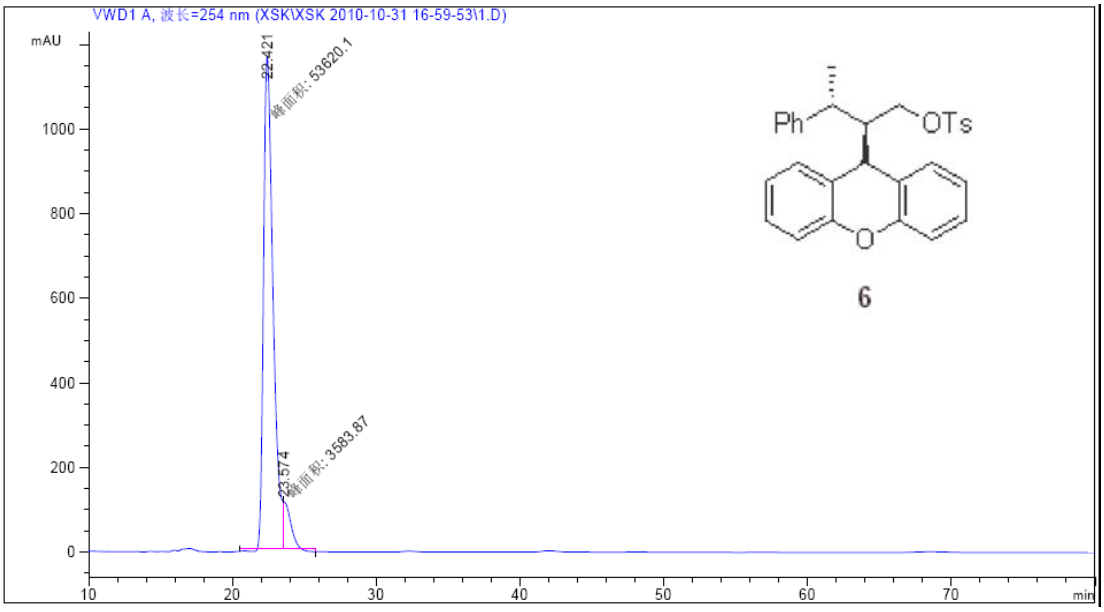
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	22.508	BB	0.4528	4.28645e4	1437.32715	93.1671
2	27.842	BV	0.5666	3143.68188	84.76650	6.8329

Racemic

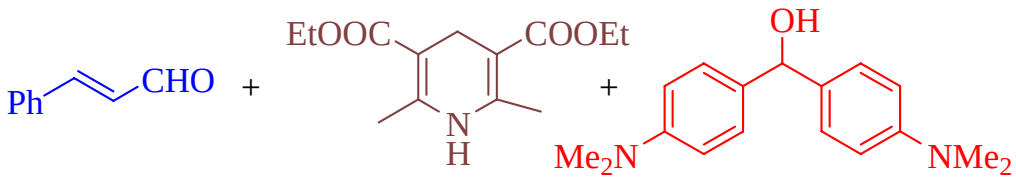


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	22.730	VV	0.6718	1.31770e4	298.77783	20.5754
2	23.958	VB	0.7689	1.45954e4	278.39587	22.7902
3	42.172	BB	1.1903	1.79864e4	225.00516	28.0851
4	66.334	BB	2.5272	1.82837e4	94.84215	28.5493

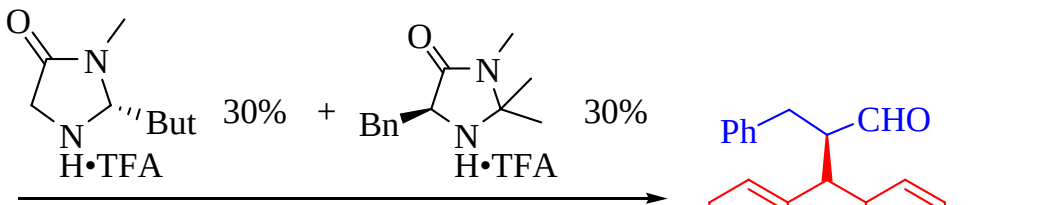
Sample



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	22.421	MF	0.7691	5.36201e4	1162.03333	93.7349
2	23.574	FM	0.5436	3583.87231	109.87580	6.2651

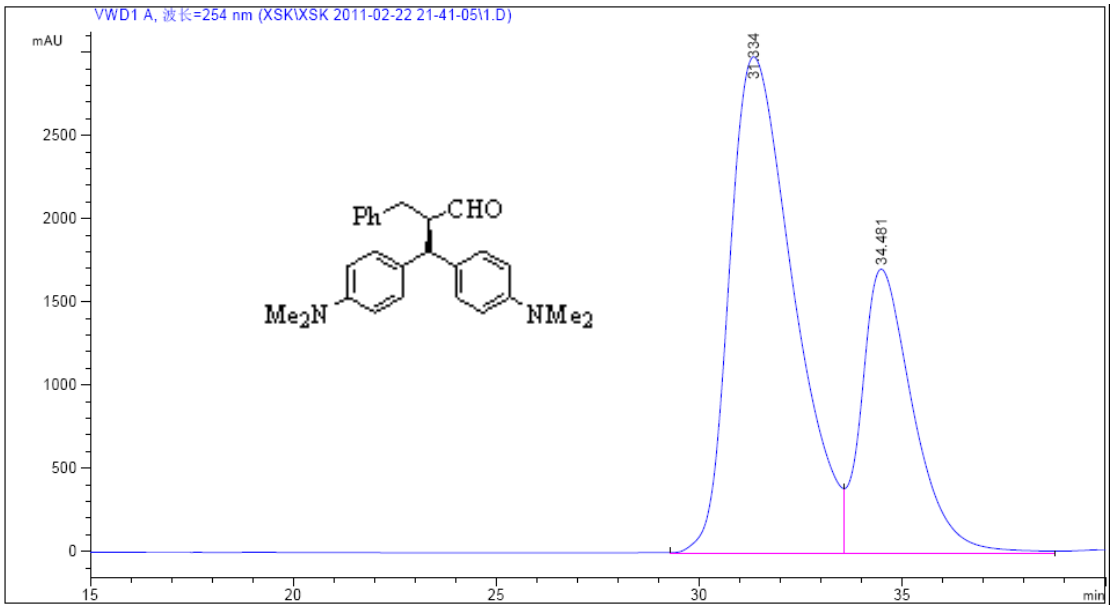


1a **2** **3a**



4aa

entry 12, Table 1; yield = 99%; ee = 37%



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	31.334	VV	1.5329	3.24670e5	2980.52734	68.3904
2	34.481	VB	1.2845	1.50060e5	1705.08545	31.6096