Supporting Information

Highly Endo and Enantioselective 1,3-Dipolar Cycloaddition of Azomethine Ylide with α-Enones Catalyzed by a Silver(I)/ThioClickFerrophos Complex

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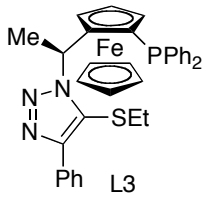
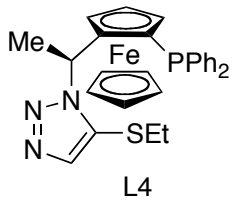
Experimental Procedure



L3

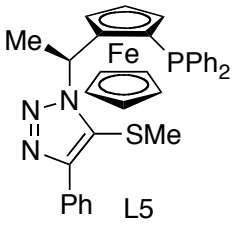
Preparation of ThioClickFerrophos. The following provides a typical experimental procedure for the preparation of ThioClickFerrophos. In a 20 mL Schlenk tube containing a magnetic stirring bar were charged (*Rp*)-1-(diphenylphosphino)-2-[(*S*)-1-[4-phenyl-1*H*-1,2,3-triazol-1-yl]ethyl]-ferrocene (0.15 g, 0.28 mmol) and dry THF (3.0 mL) under a slight pressure of nitrogen. The flask was cooled at –78°C and a hexane solution of *n*-BuLi (0.25 mL, 0.38 mmol, 1.5 M) was then added using a syringe through the septum with magnetic stirring. After 10 min, EtSSEt (42 μL, 0.34 mmol) was injected into the mixture at –78°C and stirred for 10 min. The mixture was allowed to warm to room temp. and then stirred for an additional 12 h. The reaction was quenched with saturated NH_4Cl, and the solution was then extracted with ethyl acetate (10 mL × 3). The combined extracts were washed (brine), dried ($MgSO_4$), filtered, and the solvent was removed on a rotary evaporator to leave a yellow residue. The crude product was purified by flash column chromatography (hexane/ethyl acetate = 4/1) to give pure ThioClickFerrophos **L-3** (R = Et). Yield, 150 mg, 0.25 mmol, 90%. Yellow solid, mp = 161-162°C. $[\alpha]_D^{25}$ = –232 (*c* =0.15, $CDCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, 3H, *J* = 7.3 Hz), 2.04 (d, 3H, *J* = 6.8 Hz), 2.41-2.59 (m, 2H), 3.70 (s, 1H), 4.15 (s, 5H), 4.41 (s, 1H), 4.93 (s, 1H), 6.2-6.3 (m, 1H), 6.7-6.9 (m, 5H), 7.2-7.5 (m, 8H), 7.75 (d, 2H, *J* = 7.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 21.9, 30.0, 52.47 (d, *J* = 8.9 Hz), 69.8, 69.9, 70.9 (d, *J* = 3.6 Hz), 71.6 (d, *J* = 4.3 Hz), 75.5 (d, *J* = 7.7 Hz), 92.1 (d, *J* = 24.4 Hz), 124.1, 126.9, 127.5, 127.6, 127.7, 127.8, 128.0 (d, *J* = 7.9 Hz), 129.1, 130.8, 131.3 (d, *J* = 18.2 Hz), 135.0 (d, *J* = 20.7 Hz), 136.4 (d, *J* = 8.2 Hz), 137.7 (d, *J* = 7.8 Hz), 147.4. ^{31}P NMR ($CDCl_3$) δ –25.0 (s). HRMS: cacld for $C_{34}H_{32}FeN_3PS$ ($M+Na^+$): 624.1302; found: 624.1309.



L4

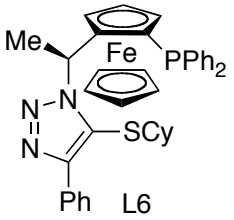
L4: The compound was prepared by using the 4-phenyl free triazole ferrocenyl phosphine as a precursor. Yield 68%, yellow solid, mp = 151-152°C. $[\alpha]_D^{25}$ = –254 (c = 0.15, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (t, 3H, *J* = 7.3 Hz), 1.95 (d, 3H, *J* = 6.8 Hz), 2.54 (dq, 1H, *J* = 7.2 Hz, 12.6 Hz), 2.66 (dq, 1H, *J* = 7.2 Hz, 12.6 Hz), 3.74 (s, 1H), 4.13 (s, 5H), 4.44 (s, 1H), 4.90 (s, 1H), 6.16 (ddd, 1H, *J* = 3.3, 6.8, 13.6 Hz), 6.67 (t, 2H, *J* = 7.6 Hz), 6.9-7.1 (m, 4H), 7.3-7.5 (m, 5H including TzH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 21.7, 30.0, 52.60 (d, *J* = 9.5 Hz), 69.9, 70.0, 70.8 (d, J = 3.6 Hz), 71.9 (d, J = 4.3 Hz), 75.8 (d, *J* = 8.2 Hz), 127.5, 127.8 (d, *J* = 6.2 Hz), 128.1 (d, *J* = 7.9 Hz), 128.4, 129.2, 131.5 (d, *J* = 18.1 Hz), 135.1 (d, *J* = 20.8 Hz),

136.3, 136.5 (d, J = 8.1 Hz), 137.9 (d, J = 7.9 Hz). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -25.3 (s). HRMS: cacld for $C_{28}H_{28}FeN_3PS$ ($M+Na^+$): 678.1771; found: 678.1773.



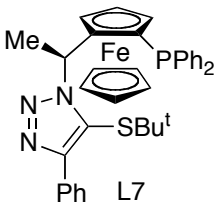
L5

L5: R = Me: Yield 72%, yellow solid, mp = 209-210°C. $[\alpha]_D^{25}$ = – 214 (*c* =0.11, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (d, 3H, J = 6.8 Hz), 2.04 (s, 3H), 3.72 (s, 1H), 4.17 (s, 5H), 4.44 (m, 1H), 4.95 (s, 1H), 6.33 (ddd, 1H, J = 3.3, 6.8, 10.3 Hz), 6.7-6.9 (m, 5H), 7.2 -7.8 (m, 8H), 7.76 (d, 2H, J = 8.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.7, 22.1, 52.7 (d, J = 9.3 Hz), 69.9, 69.9, 71.1 (d, J = 3.5 Hz), 71.8 (d, J = 4.6 Hz), 75.7 (d, J = 7.7 Hz), 91.91 (d, J = 24.8 Hz), 125.4, 126.8, 127.7, 127.8, 127.8 (d, J = 4.4 Hz), 128.1, 128.2, 129.2, 130.8, 131.5 (d, J = 18.2 Hz), 135.1 (d, J = 20.8 Hz), 136.5 (d, J = 8.0 Hz), 137.8 (d, J = 7.5 Hz), 147.1. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ –24.8 (s). HRMS: cacld for $C_{33}H_{30}FeN_3PS$ ($M+Na^+$): 672.1302; found: 672.1303.



L6

L6: R = Cy: Yield 89%, yellow solid, mp = 214-215°C. $[\alpha]_D^{25}$ = –223 (*c* =0.14, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.0-1.7 (m, 11H), 2.05 (d, 3H, J = 7.0 Hz), 2.71 (m, 1H), 3.69 (s, 1H), 4.13 (s, 5H), 4.39 (s, 1H), 4.90 (s, 1H), 6.2-6.3 (m, 1H), 6.6-6.9 (m, 5H), 7.2-7.5 (m, 8H), 7.75 (d, 2H, J = 6.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 25.2, 25.5, 25.6, 32.6, 33.6, 48.3 (d, J = 2.4 Hz), 52.3 (d, J = 9.8 Hz), 69.8, 70.9 (d, J = 3.5 Hz), 71.7 (d, J = 4.3 Hz), 75.6 (d, J = 8.5 Hz), 92.5 (d, J = 24.6 Hz), 123.8, 127.0, 127.5, 127.6, 127.7, 127.7, 127.9 (d, J = 7.8 Hz), 129.0, 130.9, 131.3 (d, J = 18.1 Hz), 135.0 (d, J = 20.9 Hz), 136.6 (d, 8.8 Hz), 137.8 (d, J = 8.2 Hz), 147.6. ^{31}P-NMR (121.5 MHz, $CDCl_3$) δ –25.3 (s). HRMS: cacld for $C_{38}H_{38}FeN_3PS$: ($M+Na^+$) 686.1458; found: 686.1428.

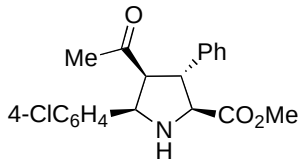


L7

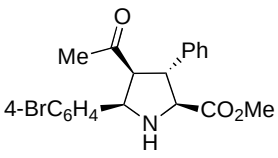
L7: R = *tert*-Bu: Yield 83%, yellow solid, mp = 189-190 °C. $[\alpha]_D^{25}$ = –236 (c = 0.15, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (s, 9H), 2.17 (d, J = 7.0 Hz, 3H), 3,63 (s, 1H), 4.12 (s, 5H), 4.34 (s, 1H), 4.80 (s, 1H,), 6.2-6.3 (m, 1H), 6.5-6.9 (m, 5H), 7.2-7.7 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.9, 31.2, 50.9, 51.7 (d, J = 7.1 Hz), 69.7, 69.8, 70.7 (d, J = 3.7 Hz), 71.4 (d, J = 4.2 Hz), 75.1 (d, J = 10.0 Hz), 123.8, 127.5, 127.6, 127.7, 127.8, 127.8, 127.8 (d, J = 7.8 Hz), 129.0, 131.1 (d, J = 17.5 Hz), 131.2, 135.0 (d, J = 21. 0 Hz), 137.0 (d, 9.5 Hz), 138.4 (d, J = 8.8 Hz). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ = –33.6 (s). HRMS: cacld for $C_{36}H_{36}FeN_3PS$ ($M+Na^+$)

706.0912; found: 706.0953. Crystals suitable for X-ray analysis was obtained by recrystalization from $CHCl_3$/hexane: CCDC 764088.

The reaction of azomethine ylide with α-enones. The following provide a typical experimental procedure of asymmetric 1,3-dipolar cycloaddition of azomethine ylide with α-enones. In a 20-mL Schlenk tube containing a stirring bar, AgOAc (1.30 mg, 0.01 mmol) and ThioClickFerrophos **L7** (6.80 mg, 0.011 mmol) were dissolved in CH_2Cl_2 (1.0 mL) and stirred at room temperature for 30 min under nitrogen. The mixture was cooled to 0 °C, and then a CH_2Cl_2 (1.0 mL) solution of methyl *N*-(*p*-chlorobenzylidene)glycinate (36 mg, 0.20 mmol), benzalacetone (44 mg, 0.30 mmol), and Et_3N (5.0 μL, 0.036 mmol) was added. The resulting solution was stirred at the same temperature for 5 h and then filtered through Celite and concentrated. The ^{1}H NMR measurement of the crude product showed the presence of a diastereomeric mixture of adducts (*endo*/*exo* = 85/15). The residue was purified by preparative TLC (*n*-hexane/EtOAc = 2:1) to afford (2*S*,3*R*,4*S*,5*R*)-methyl 4-acetyl-5-(4-chlorophenyl)-3-phenylpyrrolidine-2-carboxylate (*endo*) **3a** as a white solid, yield 65.0 mg (85%); mp 125-126°C.

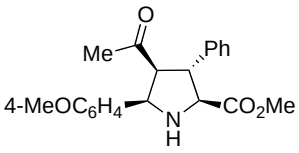


^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59 (s, 3H), 2.83 (br s, 1H), 3.62 (dd, 1H, *J* = 7.4, 8.4 Hz), 3.73 (s, 3H), 3.92 (dd, 1H, *J* = 7.4, 8.5 Hz), 4.04 (d, 1H, *J* = 8.4 Hz), 4.84 (d, 1H, *J* = 8.5 Hz), 7.2-7.4 (m, 9H). ^{13}C NMR ($CDCl_3$) δ 31.5, 51.7, 52.3, 64.8, 65.6, 67.6, 127.2, 127.6, 128.7, 128.82, 128.84, 133.8, 137.7, 140.7, 173.0, 207.2. HRMS: calcd for $C_{20}H_{20}ClNO_3$ ($M+H^+$): 358.1201; found: 358.1228. The enantiomeric excess (92% ee) was determined by HPLC (Daicel Chiralpak AS-H, *i*-PrOH/hexane 50:50, flow rate 0.7 mL/min, 210 nm): *t*R = 8.4 min (2*S*,3*R*,4*S*,5*R*)-isomer, 12.0 min (2*R*,3*S*,4*R*,5*S*)-isomer. CCDC 764086.

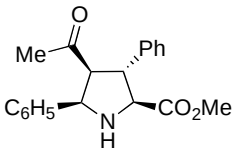


3b. White solid; mp 153-154 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59 (s, 3H), 2.63 (br s, 1H), 3.62 (dd, 1H, *J* = 7.4, 8.3 Hz), 3.72 (s, 3H), 3.92 (dd, 1H, *J* = 7.4, 8.5 Hz), 4.03 (d, 1H, *J* = 8.3 Hz), 4.84 (d, 1H, *J* = 8.5 Hz), 7.2-7.5 (m, 9H). ^{13}C NMR ($CDCl_3$) δ 31.4, 51.6, 52.2, 64.8, 65.5, 67.5, 121.9, 127.2, 127.5, 128.8, 129.0, 131.7, 138.2, 140.6, 172.9, 207.1. HRMS: calcd for $C_{20}H_{20}BrNO_3$ ($M+H^+$): 401.0627; found: 401.0642. HPLC: Daicel Chiralpak AS-H, *i*-PrOH/hexane 50:50, flow rate 0.7 mL/min, 210 nm): *t*R = 8.9 min (2*S*,3*R*,4*S*,5*R*)-isomer, 14.3 min

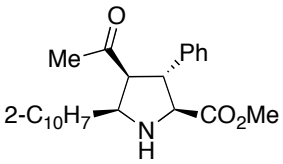
(2*R*,3*S*,4*R*,5*S*)-isomer.



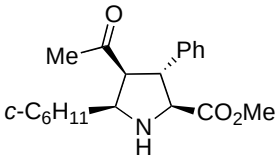
3c. White solid; mp 89-90°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56 (s, 3H), 2.84 (br s, 1H), 3.59 (dd, 1H, *J* = 7.0, 8.4 Hz), 3.72 (s, 3H), 3.79, (s, 3H), 3.93 (dd, 1H, *J* = 7.0, 8.6 Hz), 4.01 (d, 1H, *J* = 8.4 Hz), 4.84 (d, 1H, *J* = 8.6 Hz), 6.87 (d, 2H, *J* = 8.6 Hz), 7.2-7.4 (m, 7H). ^{13}C NMR ($CDCl_3$) δ 31.4, 51.9, 52.2, 55.2, 65.2, 65.9, 67.7, 114.0, 127.1, 127.6, 128.4, 128.8, 130.9, 141.0, 159.2, 173.1, 207.7. HRMS: calcd for $C_{21}H_{23}NO_4$ ($M+H^+$): 354.1705; found: 354.1703. HPLC: Daicel Chiralpak AS-H, *i*-PrOH/hexane 50:50, flow rate 0.7 mL/min, 210 nm): *t*R = 9.4 min (2*S*,3*R*,4*S*,5*R*)-isomer, 15.8 min (2*R*,3*S*,4*R*,5*S*)-isomer.



3d. Colerless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (s, 3H), 2.59 (br s, 1H), 3.62 (dd, 1H, *J* = 7.0, 8.3 Hz), 3.73 (s, 3H), 3.94 (dd, 1H, *J* = 7.0, 8.4 Hz), 4.03 (d, 1H, *J* = 8.3 Hz), 4.84 (d, 1H, *J* = 8.4 Hz), 7.2-7.4 (m, 9H). ^{13}C NMR ($CDCl_3$) δ 31.3, 52.0, 52.2, 65.8, 65.9, 67.8, 127.1, 127.2, 127.6, 128.0, 128.7, 128.8, 138.8, 141.0, 173.1, 207.6. HRMS: calcd for $C_{20}H_{21}NO_3$ ($M+H^+$): 324.1599; found: 324.1591. HPLC: Daicel Chiralpak AS-H, *i*-PrOH/hexane 50:50, flow rate 0.7 mL/min, 210 nm): *t*R = 7.5 min (2*S*,3*R*,4*S*,5*R*)-isomer, 11.1 min (2*R*,3*S*,4*R*,5*S*)-isomer.

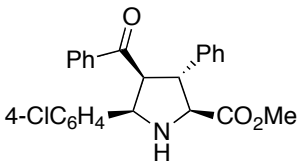


3e. Yellow solid; mp 105-106 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (s, 3H), 2.59 (br s, 1H), 3.62 (dd, 1H, *J* = 6.8, 8.3 Hz), 3.73 (s, 3H), 3.94 (dd, 1H, *J* = 6.8, 8.5 Hz), 4.03 (d, 1H, *J* = 8.3 Hz), 4.84 (d, 1H, *J* = 8.5 Hz), 7.2-7.4 (m, 9H). ^{13}C NMR ($CDCl_3$) δ 31.3, 52.0, 52.2, 65.8, 65.9, 67.8, 127.1, 127.2, 127.6, 128.0, 128.7, 128.8, 138.8, 141.0, 173.1, 207.6. HRMS: calcd for $C_{24}H_{23}NO_3$ ($M+H^+$): 374.1756; found: 374.1751. HPLC: Daicel Chiralpak AS-H, *i*-PrOH/hexane 50:50, flow rate 0.7 mL/min, 210 nm): *t*R = 9.2 min (2*S*,3*R*,4*S*,5*R*)-isomer, 16.2 min (2*R*,3*S*,4*R*,5*S*)-isomer.

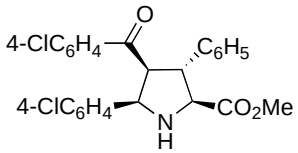


3f. Colerless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.0-1.7 (m, 11H), 1.96-2.02 (m, 1H), 2.12 (s, 3H), 2.53 (br s, 1H), 3.11-3.18 (m, 1H), 3.21 (dd, 1H, *J* = 3.5, 5.9 Hz), 3.35 (dd, 1H, *J* = 3.5, 7.0 Hz), 3.63 (s, 3H), 3.77 (d, 1H, *J* = 7.0 Hz), 7.1-7.3 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 25.6, 25.7, 31.4, 31.8, 32.5, 38.5, 52.0, 54.9, 61.8, 68.8, 70.4, 127.0, 127.2, 128.8, 142.7,

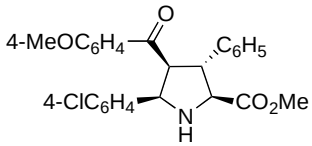
172.6, 210.7. HRMS: calcd for $C_{20}H_{27}NO_3$ ($M+H^+$): 330.2069; found: 330.2018. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 20:80, flow rate 0.8 mL/min, 210 nm): *t*R = 8.4 min (2*S*,3*R*,4*S*,5*R*)-isomer, 10.8 min (2*R*,3*S*,4*R*,5*S*)-isomer.



5. White solid, mp 151-152 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.0 (br s, 1H), 3.73 (s, 3H), 4.11 (dd, 1H, *J* = 8.1, 9.0 Hz), 4.18 (d, 1H, *J* = 9.0 Hz), 4.51 (dd, 1H, *J* = 8.1, 8.6 Hz), 4.97 (d, 1H, *J* = 8.6 Hz), 7.06 (s, 4H), 7.2-7.6 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 52.2, 52.3, 60.3, 65.7, 67.4, 127.2, 127.7, 128.0, 128.2, 128.4, 128.7, 128.8, 133.0, 133.3, 137.2, 137.9, 140.3, 173.3, 198.3. HRMS: calcd for $C_{25}H_{22}ClNO_3$ (M): 419.1288; found: 419.1285. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 10:90, flow rate 0.7 mL/min, 210 nm): *t*R = 33.2 min (2*R*,3*S*,4*R*,5*S*)-isomer, 42.7 min (2*S*,3*R*,4*S*,5*R*)-isomer.

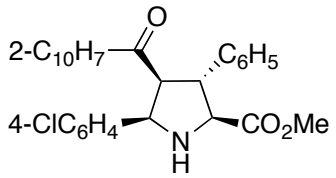


6. White solid, 140-142°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.0 (br s, 1H), 3.74 (s, 3H), 4.11 (dd, 1H, *J* = 8.1, 9.0 Hz), 4.17 (d, 1H, *J* = 9.0 Hz), 4.45 (dd, 1H, *J* = 8.1, 8.6 Hz), 4.96 (d, 1H, *J* = 8.6 Hz), 7.08 (s, 4H), 7.2-7.5 (m, 9H). ^{13}C NMR ($CDCl_3$) δ 52.2, 52.3, 60.3, 65.7, 67.4, 127.3, 127.7, 128.3, 128.6, 128.7, 128.8, 129.3, 133.5, 135.5, 137.7, 139.5, 140.2, 173.2, 197.2. HRMS: calcd for $C_{25}H_{22}Cl_2NO_3$(M): 453.0898; found: 453.0910. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 10:90, flow rate 0.7 mL/min, 210 nm): *t*R = 26.3 min (2*R*,3*S*,4*R*,5*S*)-isomer, 33.2 min (2*S*,3*R*,4*S*,5*R*)-isomer.

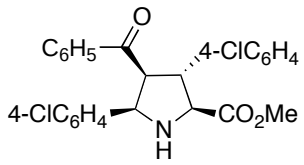


7. White solid, 132-133°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.0 (br s, 1H), 3.73 (s, 3H), 3.80 (s, 3H), 4.07 (dd, 1H, *J* = 8.1, 9.0 Hz), 4.18 (d, 1H, *J* = 9.0 Hz), 4.45 (dd, 1H, *J* = 8.1, 8.6 Hz), 4.95 (d, 1H, *J* = 8.6 Hz), 6.74 (d, 2H, *J* = 8.0 Hz), 7.06 (s, 4H), 7.2-7.3 (m, 6H), 7.56 (d, 2H, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$) δ 52.2, 52.3, 55.4, 59.8, 65.8, 67.4, 113.5, 127.0, 127.7, 128.1, 128.6, 128.7, 130.3, 133.1, 133.7, 138.1, 140.5, 163.4, 173.3, 196.5. HRMS: calcd for $C_{26}H_{24}ClNO_4$ (M): 449.1394; found: 449.1360. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 10:90, flow rate 0.7 mL/min, 210 nm): *t*R = 23.2 min (2*S*,3*R*,4*S*,5*R*)-isomer, 32.0 min (2*R*,3*S*,4*R*,5*S*)-isomer.

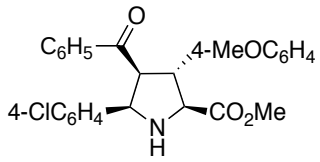
8. White solid, 159-160°C.^{1}H NMR (300 MHz, $CDCl_3$) δ 3.0 (br s, 1H), 3.74 (s, 3H), 4.16 (dd,



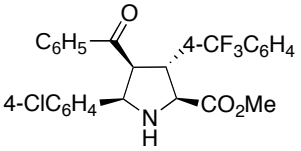
1H, *J* = 8.1, 9.0 Hz), 4.24 (d, 1H, *J* = 9.0 Hz), 4.70 (dd, 1H, *J* = 8.1, 8.6 Hz), 5.05 (d, 1H, *J* = 8.6 Hz), 7.0-7.8 (m, 15H), 8.11 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 52.2, 52.3, 60.3, 65.7, 67.4, 123.6, 127.2, 127.7, 128.2, 128.3, 128.5, 128.7, 128.8, 129.4, 129.7, 132.1, 133.2, 134.6, 135.3, 138.1, 140.2, 173.4, 198.0. HRMS: calcd for $C_{29}H_{24}ClNO_3$ ($M+H^+$): 469.1445; found: 469.1432. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 10:90, flow rate 0.7 mL/min, 210 nm): *t*R = 25.0 min (2*S*,3*R*,4*S*,5*R*)-isomer, 27.5 min (2*R*,3*S*,4*R*,5*S*)-isomer.



9. White solid, 162-163°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.9 (br s, 1H), 3.74 (s, 3H), 4.11 (dd, 1H, *J* = 8.0, 9.3 Hz), 4.17 (d, 1H, *J* = 9.3 Hz), 4.47 (dd, 1H, *J* = 8.0, 8.9 Hz), 4.96 (d, 1H, *J* = 8.9 Hz), 7.08 (s, 4H), 7.2-7.5 (m, 9H). ^{13}C NMR ($CDCl_3$) δ 51.2, 52.3, 60.4, 65.4, 67.1, 128.0, 128.2, 128.4, 128.7, 128.9, 129.1, 133.0, 133.2, 133.4, 137.1, 137.9, 138.5, 173.1, 197.6. HRMS: calcd for $C_{25}H_{22}Cl_2NO_3$ ($M+H^+$): 453.0898; found: 453.0903. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 50:50, flow rate 0.7 mL/min, 210 nm): *t*R = 11.3 min (2*R*,3*S*,4*R*,5*S*)-isomer, 16.7 min (2*S*,3*R*,4*S*,5*R*)-isomer.

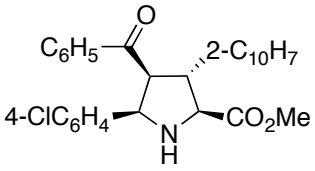


10. Yellow solid, 168-169°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.9 (br s, 1H), 3.74 (s, 3H), 3.78 (s, 3H), 4.06 (dd, 1H, *J* = 8.4, 9.2 Hz), 4.14 (d, 1H, *J* = 9.2 Hz), 4.47 (dd, 1H, *J* = 8.2, 8.7 Hz), 4.95 (d, 1H, *J* = 8.7 Hz), 6.86 (d, 2H, J = 8.0 Hz), 7.06 (s, 4H), 7.2-7.5 (m, 6H), 7.56 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$) δ 51.5, 52.3, 55.2, 60.3, 65.5, 67.4, 114.1, 128.0, 128.2, 128.4, 128.6, 128.7, 132.1, 133.0, 133.2, 137.2, 138.1, 158.6, 173.3, 198.2. HRMS: calcd for $C_{26}H_{24}ClNO_4$ ($M+H^+$): 449.1394; found: 449.1390. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 50:50, flow rate 0.7 mL/min, 210 nm): *t*R = 10.7 min (2*R*,3*S*,4*R*,5*S*)-isomer, 14.1 min (2*S*,3*R*,4*S*,5*R*)-isomer.

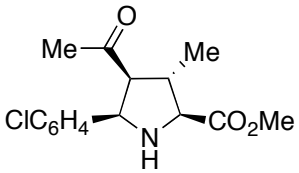


11. White solid, 153-154°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.0 (br s, 1H), 3.74 (s, 3H), 4.2 (m, 2H), 4.17 (d, 1H, *J* = 9.3 Hz), 4.5-4.6 (m, 1H), 5.00 (d, 1H, *J* = 8.9 Hz), 7.05 (s, 4H), 7.2-7.6 (m, 9H). ^{13}C NMR ($CDCl_3$) δ 51.2, 52.4, 60.4, 65.4, 67.0, 125.7 (q, *J*= 3.8 Hz), 127.0 (q, *J* = 260 Hz), 128.0, 128.2, 128.3, 128.4, 128.8, 133.8 (d, *J* = 6.7 Hz), 133.2, 133.4,

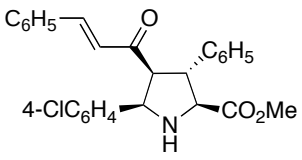
137.0, 137.9, 144.1, 173.0, 197.4. HRMS: calcd for $C_{26}H_{21}ClF_3NO_3$ (M): 487.1162; found: 487.116x1. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 50:50, flow rate 0.7 mL/min, 210 nm): *t*R = 10.9 (2*S*,3*R*,4*S*,5*R*)-isomer, 15.4 min min (2*R*,3*S*,4*R*,5*S*)-isomer.



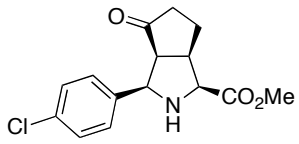
12. White solid, 174-175°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.1 (br s, 1H), 3.72 (s, 3H), 4.28 (dd, 1H, *J* = 7,7, 9.0 Hz), 4.32 (d, 1H, *J* = 9.0 Hz), 4.62 (dd, 1H, *J* = 7.8, 8.6 Hz), 5.04 (d, 1H, *J* = 8.6 Hz), 7.08 (s, 4H), 7.2-7.6 (m, 8H), 7.8-7.9 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 52.3, 52.4, 60.4, 65.7, 67.3, 125.5, 125.8, 126.2, 126.8, 127.6, 127.8, 128.0, 128.2, 128.4, 128.6, 128.7, 132.6, 133.0, 133.3, 137.2, 137.6, 137.9, 173.3, 198.2. HRMS: calcd for $C_{29}H_{24}ClNO_3$ ($M+H^+$): 469.1445; found: 469.1453. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 50:50, flow rate 0.7 mL/min, 210 nm): *t*R = 9.1 min (2*R*,3*S*,4*R*,5*S*)-isomer, 15.8 min(2*S*,3*R*,4*S*,5*R*)-isomer.



13. White solid, 85-86°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (d, 3H, J = 6.7 Hz), 1.69 (s, 3H), 2.5 (br s, 1H), 2.72 (sext, 1H, *J* = 7.1 Hz), 3.12 (dd, 1H, *J* = 7.9, 8.6 Hz), 3.41 (d, 1H, *J* = 8.4 Hz), 3.82 (s, 3H), 4.64 (d, 1H, *J* = 8.6 Hz), 7.2-7.3 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 18.1, 31.1, 40.8, 52.3, 63.7, 65.3, 67.9, 128.5, 128.7, 133.6, 138.3, 173.5, 207.5. HRMS: calcd for $C_{15}H_{18}ClNO_3$ ($M+H^+$): 296.1053; found: 296.1057. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 50:50, flow rate 0.7 mL/min, 210 nm): *t*R = 6.1 min (2*S*,3*R*,4*S*,5*R*)-isomer, 7.8 min, (2*R*,3*S*,4*R*,5*S*)-isomer.



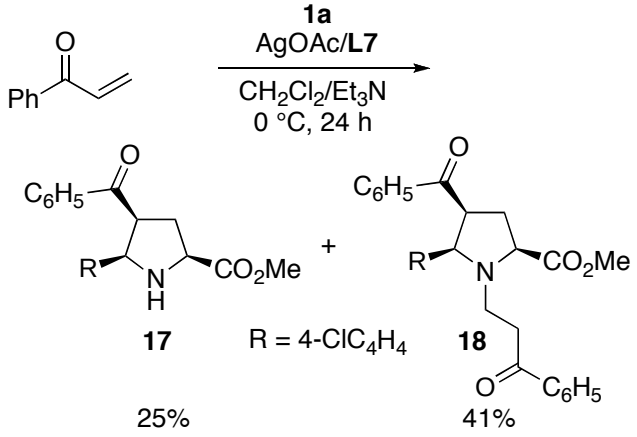
14. Yellow solid, 62-63°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.8 (br s, 1H), 3.76 (s, 3H), 3.93 (dd, 1H, *J* = 7.0, 8.2 Hz), 4.04 (dd, 1H, *J* = 7.0, 8.2 Hz), 4.13 (d, 1H, *J* = 8.2 Hz), 4.94 (d, 1H, *J* = 8.2 Hz), 6.29 (d, 1H, 16.0 Hz), 7.16-7.36 (m, 15H). ^{13}C NMR ($CDCl_3$) δ 51.9, 52.3, 63.2, 65.5, 67.5, 126.2, 127.1, 127.6, 128.2, 128.5, 128.6, 128.8, 130.5, 133.5, 134.1, 137.6, 140.9, 142.7, 173.2, 198.0. HRMS: calcd for $C_{27}H_{24}ClNO_3$ ($M+H^+$): 455.1445; found: 455.1450. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 50:50, flow rate 0.7 mL/min, 210 nm): *t*R = 10.7 (2*S*,3*R*,4*S*,5*R*)-isomer, 16.5 min min (2*R*,3*S*,4*R*,5*S*)-isomer.



16. Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.8-2.2 (m, 4H), 2.3 (br s, 1H), 2.89 (dd, 1H, *J* = 8.8, 9.1 Hz), 3.17-3.27 (m, 1H), 3.82 (s, 3H), 4.11 (d, 1H, *J* = 6.8 Hz), 4.45 (d, 1H, *J* = 9.4 Hz), 7.30 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 23.8, 39.7, 42.2, 52.0, 55.3, 64.0, 64.1, 128.4, 130.9, 133.3, 137.0, 171.9, 217.0. HRMS: calcd for $C_{15}H_{16}ClNO_3$ ($M+H^+$): 294.0897; found: 294.0886. HPLC: Daicel Chiralpak IB, *i*-PrOH-hexane 90/10, flow rate 0.7 mL/min, 210 nm), *t*R: 31.9 min for (1*S*,3*R*,3a*S*,6a*R*)-isomer and 39.6 min for (1*R*,3*S*,3a*R*,6a*S*)-isomer.

The reaction with 1-phenyl-2-propen-1-one

The reaction with 1-phenyl-2-propen-1-one produced a mixture of **17** and **18** in 25% and 41% yields, respectively (below Scheme). Compound **18** probably resulted from the Michael addition of the pyrrolidine group to 1-phenyl-2-propen-1-one. In each product the *endo*-selectivity and ee% were high (98% ee). When the reaction was carried out using more than twice the amount of 1-phenyl-2-propen-1-one, **18** was the major product.



17. White solid, mp 84-85°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (dt, 1H, *J* = 7.4, 13.2 Hz), 2.60 (dt, 1H, *J* = 7.1, 13.2 Hz), 2.80 (br s, 1H), 3.86 (s, 3H), 4.03 (dd, *J* = 8.2, 8.2 Hz), 4.35 (dt, *J* = 7.4, 8.0 Hz), 4.70 (d, 1H, *J* = 8.0 Hz), 7.0 (s, 4H), 7.2-7.6 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 33.3, 51.0, 52.4, 59.8, 66.0, 128.0, 128.1, 128.3, 128.5, 132.9, 133.0, 133.1, 137.2, 137.7, 174.0, 199.0. HRMS: calcd for $C_{28}H_{27}ClNO_4$ ($M+H^+$): 343.0975; found: 343.0982. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 10:90, flow rate 1.0 mL/min, 210 nm): *t*R = 24.1 min (2*S*,3*R*,4*S*,5*R*)-isomer, 28.6 min (2*R*,3*S*,4*R*,5*S*)-isomer.

18. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60 (br s, 1H), 2.25 (dt, 1H, *J* = 6.4, 12.7 Hz), 2.28 (dt, 1H, *J* = 10.0, 12.7 Hz), 2.89 (dt, 1H, *J* = 7.4, 17.0 Hz), 2.99 (dt, 1H, *J* = 7.4, 17.0 Hz), 3.18 (t, 1H, *J* = 7.4 Hz), 3.19 (t, 1H, *J* = 7.4 Hz), 3.77 (dd, *J* = 6.4, 10.0 Hz), 3.81 (s, 3H), 4.33 (dt, *J* = 6.4, 10.0 Hz), 4.37 (d, *J* = 10.0 Hz), 6.90 (d, 2H, *J* = 8.4 Hz), 6.98 (d, 2H, *J* = 8.4 Hz), 7.36 (m, 4H), 7.50 (m, 2H), 7.64 (d, 2H, *J* = 7.8 Hz), 7.69 (d, 2H, *J* = 7.8 Hz). ^{13}C NMR ($CDCl_3$) δ 31.2, 37.5, 58.9, 50.3, 52.1, 65.6, 70.2, 127.7, 127.8, 128.1, 128.4, 129.6, 132.9, 133.0, 133.1, 136.5, 137.2, 139.3, 174.0, 197.4, 199.0. HRMS: calcd for $C_{28}H_{26}ClNO_4$ ($M+H^+$): 476.1628; found: 476.1624. HPLC: Daicel Chiralpak IA, *i*-PrOH/hexane 90:10, flow rate 0.7 mL/min, 210 nm): *t*R = 10.7 min (2*S*,3*R*,4*S*,5*R*)-isomer, 16.5 min (2*R*,3*S*,4*R*,5*S*)-isomer.

Discussion on the mechanism of the reaction

As illustrated in Figure 1, the high stereoselectivity of the reaction may be explained based on Carretero's Cu/Fesulphos-azomethine complex intermediate although the central metal is silver not copper.[2] The O and N atoms of the azomethine ylide should coordinate to the silver atom of the Ag/ThioClickFerrophos complex to form a tetrahedral structure where the azomethine species adopts a stable geometry. X-ray crystallographic structure of AgOAc/**L5** complex (Figure 2), where acetoxy and triazole group coordinate in addition to phosphorus and sulfur, may support the tetrahedral structure. The α-enone approaches from the less hindered site (*Re* face of C=N bond) avoiding the bulky *tert*-Bu group. At this point, the carbonyl group may coordinate to the silver atom, such that it is arranged *endo* to the azomethine species. The stereocenters of C-2 and C-5 would be *S* and *R*, respectively.

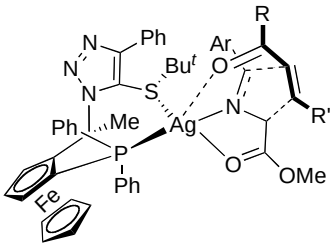


Figure 1.

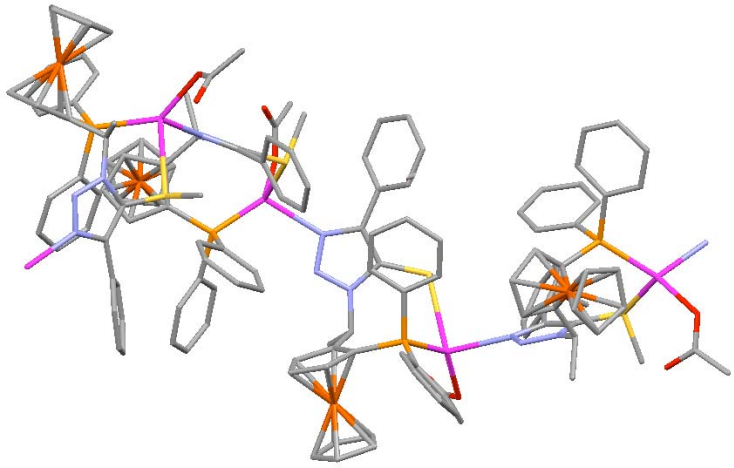
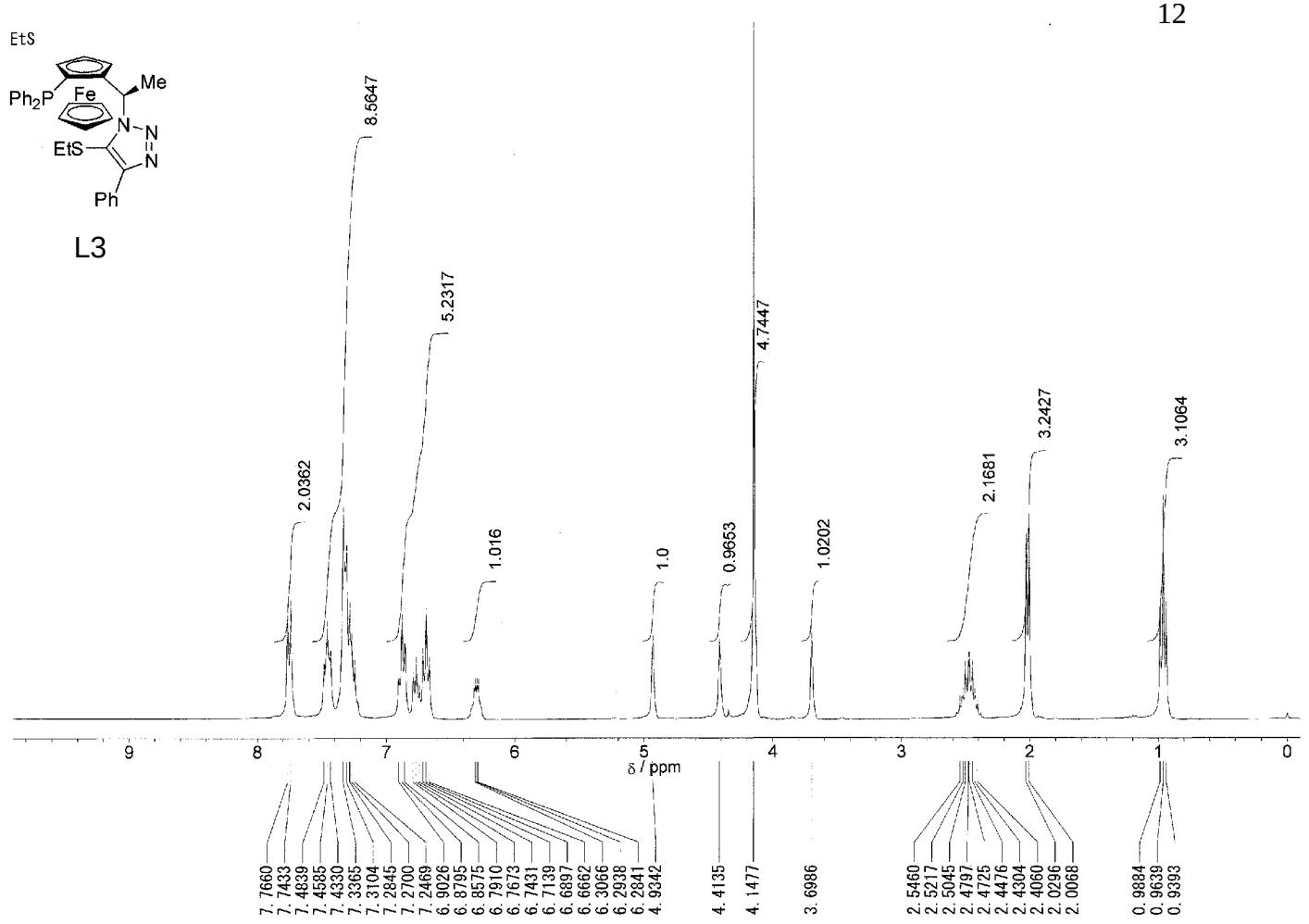


Figure 2.

References

1. Ligands **L1**, **L2, and L8** have been reported: (a) Fukuzawa, S.-i.; Oki, H.; Hosaka, M.; Sugasawa, J.; Kikuchi, S. *Org. Lett.* **2007**, *9*, 5557-5560. (b) Kato, M.; Nakamura T.; Ogata, K.; Fukuzawa S-i. *Eur. J. Org. Chem.* **2009**, 5232-5238.

2. Compound **18** has been reported: Hernández-Torbio, J.; Arrayás, R. G.; Martín-Mature, B.; Carretero, J. C. *Org. Lett.* **2009**, *11*, 393-396.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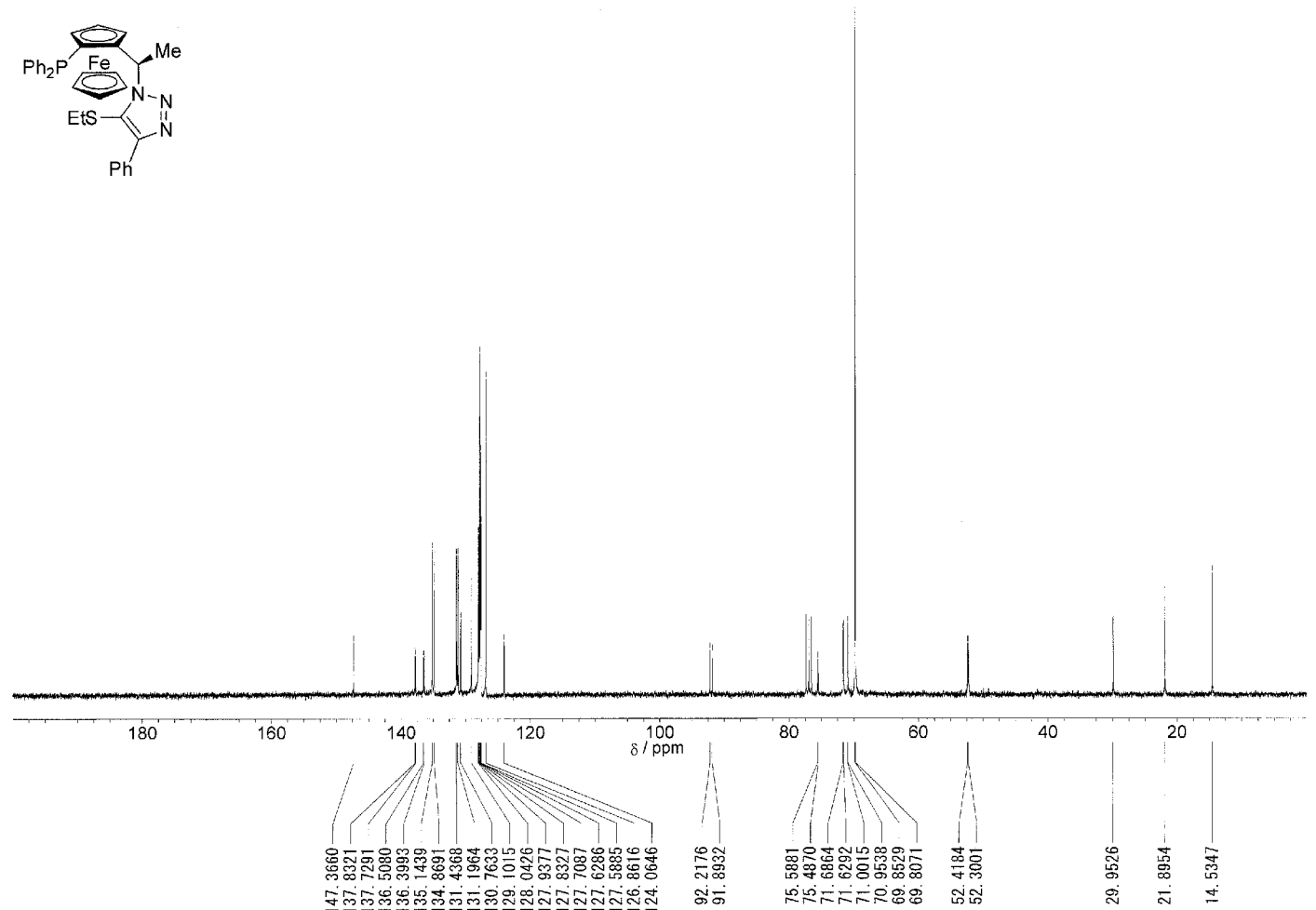
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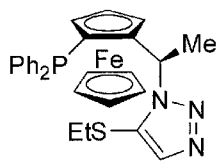
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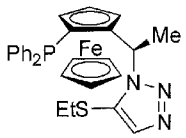
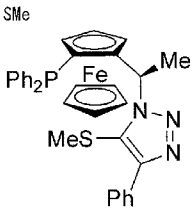
1.0864
0.8609

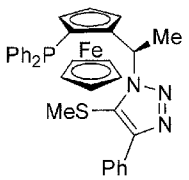

Ph2P
Fe
Me
N
N
N
EtS

180
160
140
120
100
80
60
40
20
δ / ppm
137.9504
137.8455
136.5939
136.4871
136.2734
135.2679
134.9913
131.6066
131.3662
129.2160
128.3803
128.1380
128.0331
127.8556
127.7736
127.5179
91.9715
91.6414
75.8324
75.7236
71.9402
71.8830
70.8928
70.8451
69.9846
69.9064
52.6530
52.5271
30.0480
30.0117
21.6817
14.6224

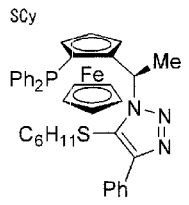

SMe
Ph2P
Fe
Me
N
N
N
MeS
Ph

L5

9.4032
4.7462
4.6741
6.0284
1.7899
0.9481
1.0
0.8634
0.9275
δ / ppm
7.7813
7.7760
7.7536
7.7491
7.5022
7.4958
7.4700
7.4595
7.4540
7.4437
7.3631
7.3430
7.3180
7.3090
7.3036
7.2983
7.2896
7.2806
7.2611
6.9137
6.9087
6.8908
6.8859
6.8657
6.8160
6.7917
6.7677
6.7124
6.7075
6.6830
6.6601
6.3663
6.3541
6.3427
6.3318
6.3196
6.3092
6.2969
6.2872
4.9518
4.4481
4.4398
4.4312
4.1661
3.7282
3.7242
3.7204
2.0360
2.0268
2.0037

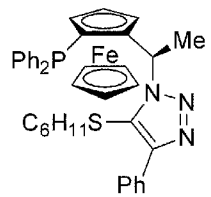

Ph2P
Fe
Me
N
N
N
MeS
Ph

δ / ppm
147.0760
137.8684
137.7654
136.5348
136.4279
135.2813
135.0046
131.6276
131.3872
130.7576
129.2427
128.1857
128.0750
127.8366
127.8003
127.7774
127.7545
126.8444
125.4230
92.0630
91.7406
77.1984
75.7579
75.6568
71.8582
71.8009
71.1732
71.1274
69.9407
52.7503
52.6282
22.1377
18.7245
18.6844


SCy
Ph2P
Fe
Me
N
N
N
C6H11S
Ph

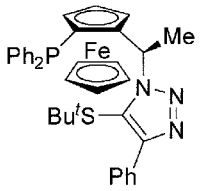
L6

2.0674
8.6409
5.3738
1.0361
1.0
1.0823
4.8767
0.9916
1.0316
3.0915
10.5831
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.7663
7.7439
7.4795
7.4540
7.4283
7.3270
7.2939
7.2688
7.2565
7.2336
6.9014
6.8781
6.8565
6.7772
6.7532
6.7230
6.6986
6.6751
6.2714
6.2579
6.2487
4.8899
4.3905
4.1372
3.6893
2.7171
2.0529
2.0301
1.5945
1.5598
1.4404
1.1945
1.1679
1.1202
1.0856
1.0554


Ph2P
Fe
Me
N
N
N
C6H11S
Ph

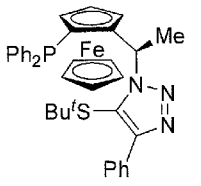
180
160
140
120
100
80
60
40
20
δ / ppm
147.5854
137.8875
137.7787
136.7160
136.5996
135.1019
134.8253
131.4005
131.1601
130.9178
129.0118
127.9758
127.8728
127.6782
127.5847
127.4645
126.9761
123.7822
92.6144
92.2882
75.6397
75.5271
71.6635
71.6063
70.8889
70.8431
69.7594
52.2753
52.1589
48.3392
48.3068
33.5586
32.6256
25.6388
25.5358
25.1828
21.7275

tBuS

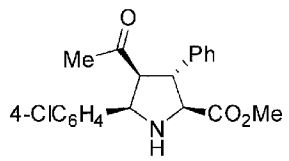

Ph2P
Fe
Me
N
N
N
But S
Ph

L7

10.8891
5.3432
1.0167
1.0
0.9334
4.9786
1.0093
3.0732
9.5999
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.6574
7.6357
7.4395
7.3221
7.2534
7.2315
6.9111
6.8879
6.8399
6.8178
6.7019
6.6786
6.6561
6.2362
6.2154
4.8027
4.3467
4.1262
3.6370
2.1847
2.1630
1.0406

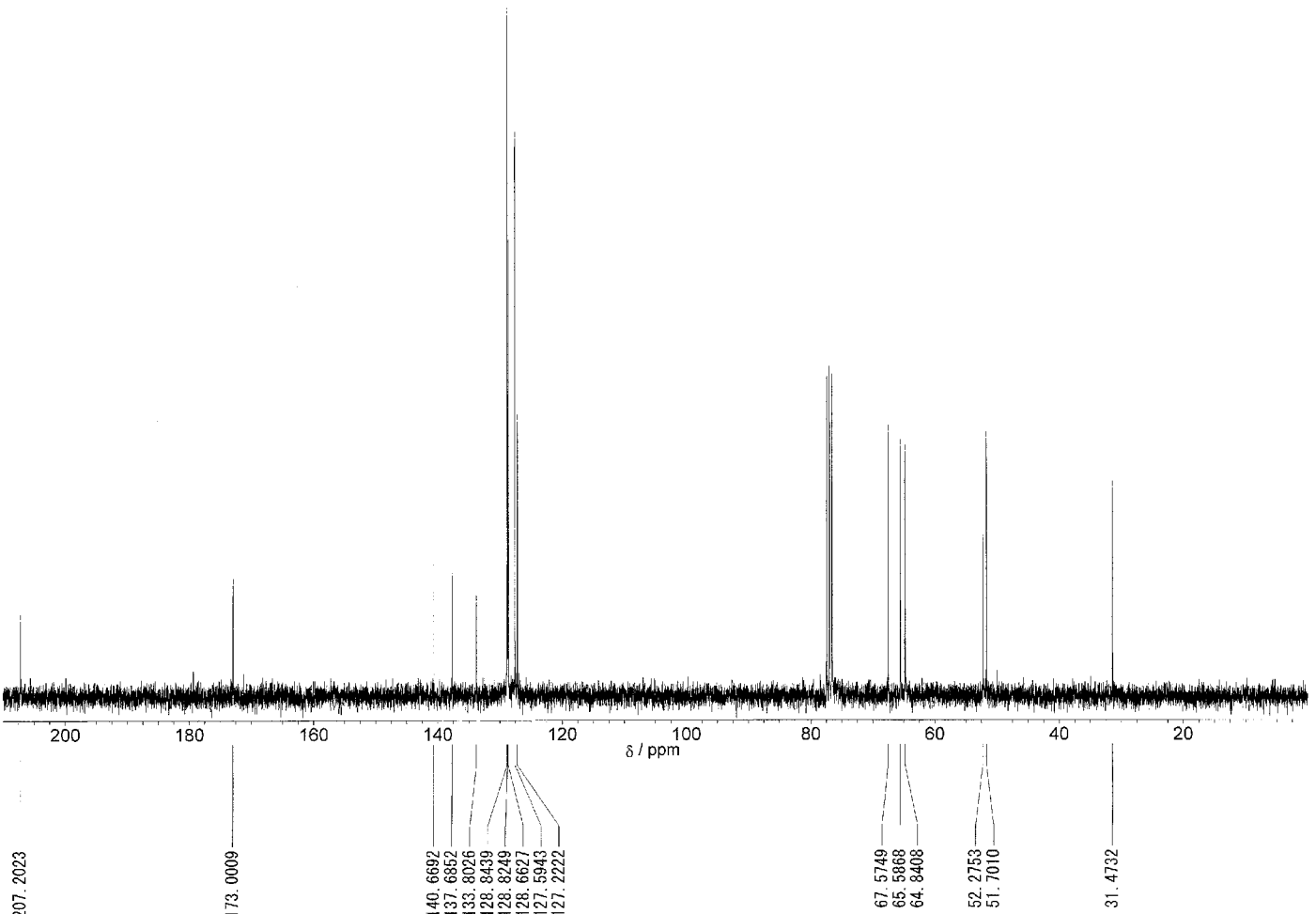

Ph2P
Fe
Me
N
N
N
But S
Ph

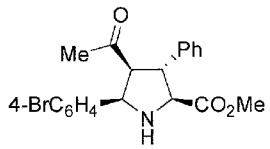
180
160
140
120
100
80
60
40
20
δ / ppm
149.2129
138.4923
138.3759
137.1186
136.9927
135.1763
134.8978
131.3166
131.2307
131.0838
128.9794
127.9167
127.8137
127.7602
127.6648
127.5542
127.4702
123.8223
93.9366
93.6065
75.1150
74.9833
71.4861
71.4308
70.7592
70.7096
69.7709
69.7194
51.7315
51.6380
50.9225
31.2443
21.9336


O
Me
Ph
4-ClC6H4
N
H
CO2Me

3a

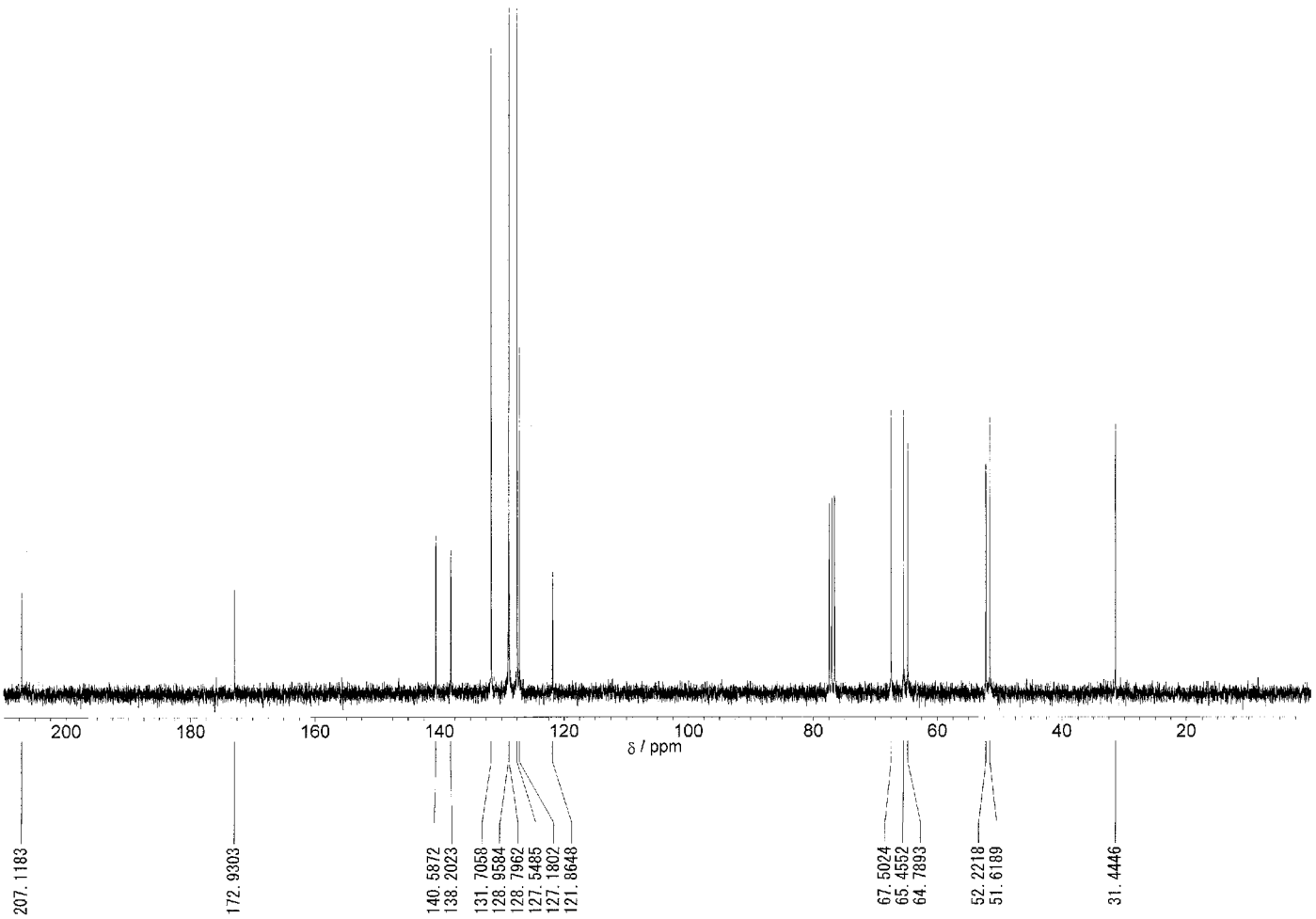
9.1096
1.0
1.935
2.8426
0.9401
0.6607
2.9466
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.3709
7.3468
7.3426
7.3165
7.3044
7.2825
7.2612
7.2384
4.8629
4.8342
4.0442
4.0163
3.9434
3.9189
3.8920
3.7258
3.6435
3.6152
3.5913
1.5873

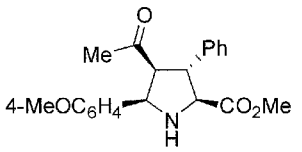

200
180
160
140
120
100
80
60
40
20
δ / ppm
207.2023
173.0009
140.6692
137.6852
133.8026
128.8439
128.8249
128.6627
127.5943
127.2222
67.5749
65.5868
64.8408
52.2753
51.7010
31.4732


O
Me
Ph
4-BrC6H4
N
H
CO2Me

3b

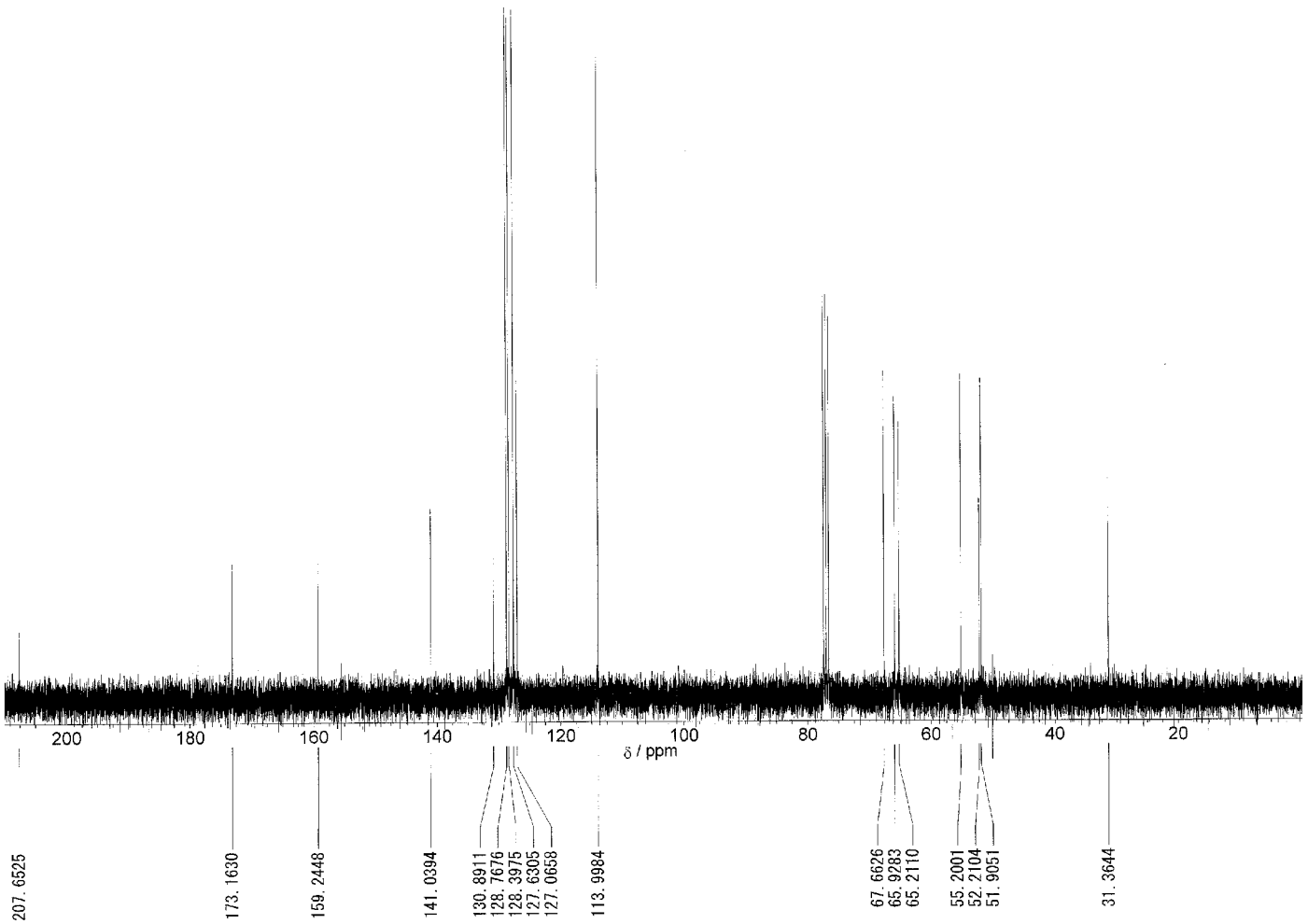
9.6059
1.0
1.8087
2.522
0.7188
0.7236
2.9786
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.4877
7.4606
7.3688
7.3449
7.3211
7.3036
7.2812
7.2643
7.2377
4.8465
4.8181
4.0435
4.0158
3.9400
3.9153
3.8890
3.7225
3.6459
3.6189
3.5932
2.6340
1.5915

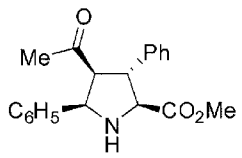

200
180
160
140
120
100
80
60
40
20
δ / ppm
207.1183
172.9303
140.5872
138.2023
131.7058
128.9584
128.7962
127.5485
127.1802
121.8648
67.5024
65.4552
64.7893
52.2218
51.6189
31.4446


O
Me
Ph
4-MeOC6H4
CO2Me
N
H

3c

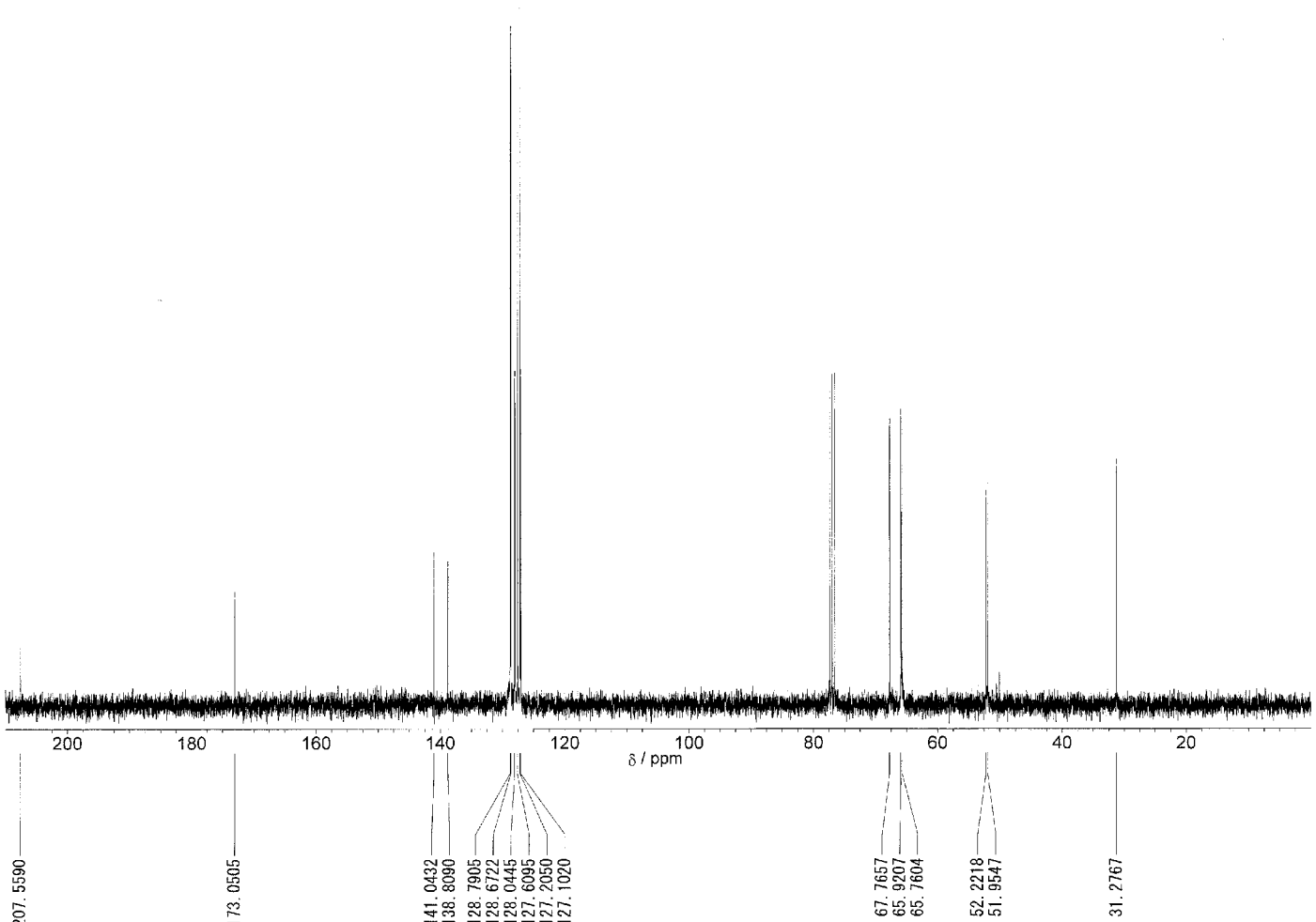
7.2934
2.0005
1.0
1.8134
5.7746
0.875
0.8103
2.8716
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.3670
7.3393
7.3183
7.3114
7.2843
7.2554
6.8882
6.8821
6.8594
4.8500
4.8213
4.0216
3.9935
3.9547
3.9314
3.9035
3.7941
3.7214
3.6148
3.5861
3.5629
2.8484
1.5559

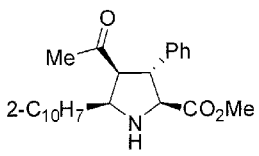

200
180
160
140
120
100
80
60
40
20
δ / ppm
207.6525
173.1630
159.2448
141.0394
130.8911
128.7676
128.3975
127.6305
127.0658
113.9984
67.6626
65.9283
65.2110
55.2001
52.2104
51.9051
31.3644


O
Me
Ph
C6H5
N
H
CO2Me

3d

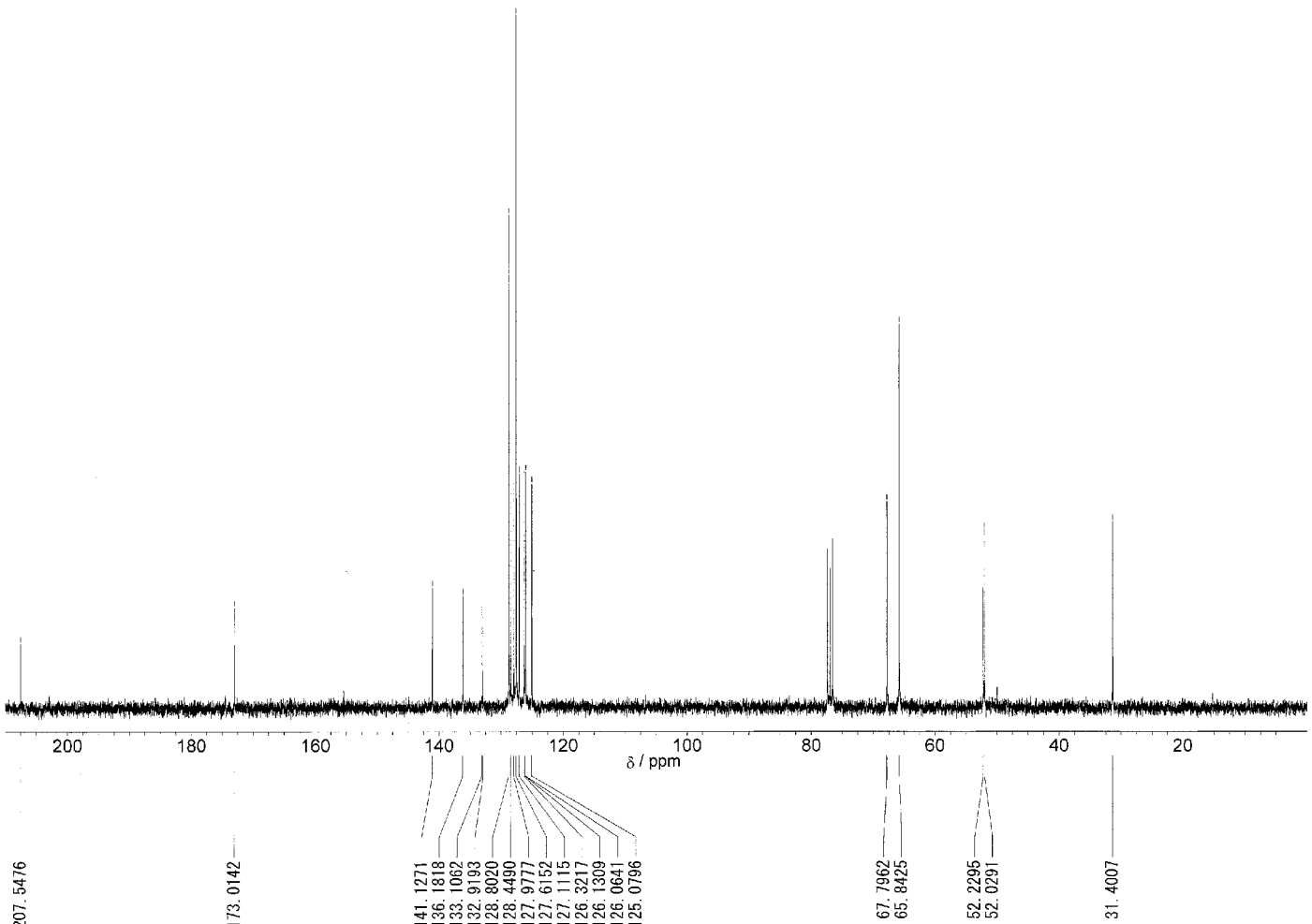
10.494
1.0
2.0906
2.7105
0.8527
0.7629
2.974
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.3579
7.3444
7.3263
7.3204
7.2973
7.2820
7.2601
4.8893
4.8608
4.0490
4.0214
3.9625
3.9397
3.9129
3.7326
3.6442
3.6162
3.5932
1.5269

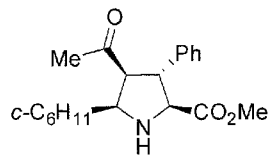

200
180
160
140
120
100
80
60
40
20
δ / ppm
207.5590
173.0505
141.0432
138.8090
128.7905
128.6722
128.0445
127.6095
127.2050
127.1020
67.7657
65.9207
65.7604
52.2218
51.9547
31.2767


Me
O
Ph
2-C10H7
N
H
CO2Me

3e

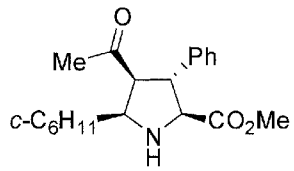
9.2831
4.308
4.074
1.9543
3.339
1.0
0.7133
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.8598
7.8461
7.8303
7.8186
7.8054
7.4984
7.4843
7.4705
7.4674
7.4523
7.4424
7.4373
7.3660
7.3585
7.3485
7.3023
7.2945
7.2737
7.2563
5.0547
5.0261
4.1080
4.0807
4.0320
4.0103
3.9829
3.7621
3.7255
3.6983
3.6758
3.0556
1.5101


200
180
160
140
120
100
80
60
40
20
δ / ppm
207.5476
173.0142
141.1271
136.1818
133.1062
132.9193
128.8020
128.4490
127.9777
127.6152
127.1115
126.3217
126.1309
126.0641
125.0796
67.7962
65.8425
52.2295
52.0291
31.4007

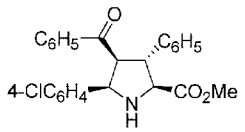

O
Me
Ph
c-C6H11
N
H
CO2Me

3f

5.7731
1.0
2.9603
1.0861
2.1946
0.9551
3.0291
1.0561
12.6162
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2876
7.2648
7.2402
7.2040
7.1676
7.1448
3.7946
3.7710
3.6284
3.3660
3.3543
3.3433
3.3311
3.2366
3.2166
3.2048
3.1650
3.1338
3.1138
2.5361
2.1203
2.0231
1.9823
1.9628
1.6568
1.6011
1.4908
1.4575
1.1324
1.1144
1.0732
1.0348
0.9984

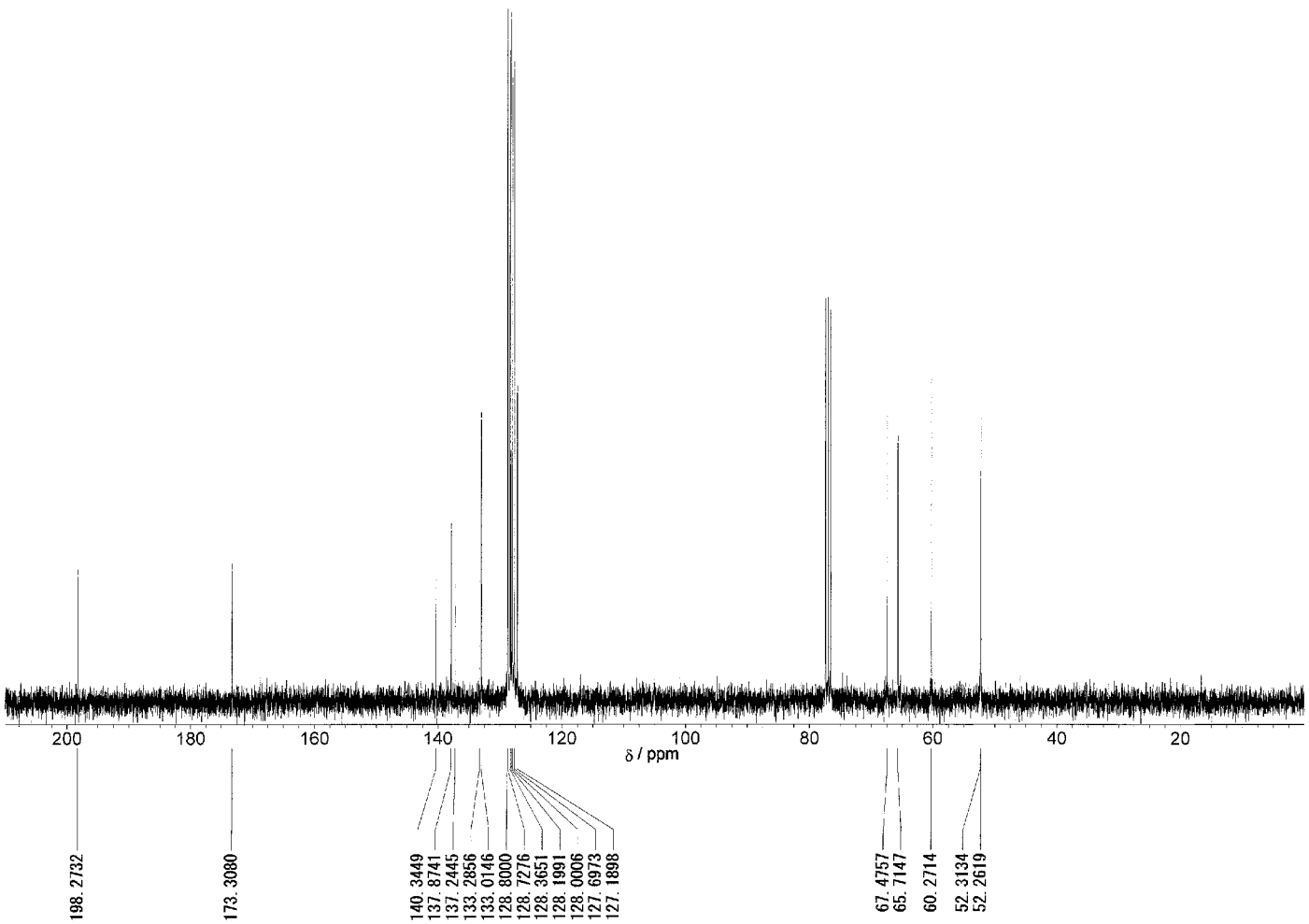

O
Me
Ph
c-C6H11
N
H
CO2Me

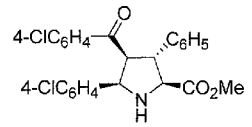
200
180
160
140
120
100
80
60
40
20
δ / ppm
210.6899
172.5754
142.6535
128.8210
127.2069
127.0295
77.4274
77.0019
76.5784
70.3643
68.7673
61.8206
54.9215
52.0806
38.5134
32.4672
31.8300
31.3912
26.1806
25.7342
25.6674


C6H5
C6H5
4-ClC6H4
CO2Me
N
H
O

5

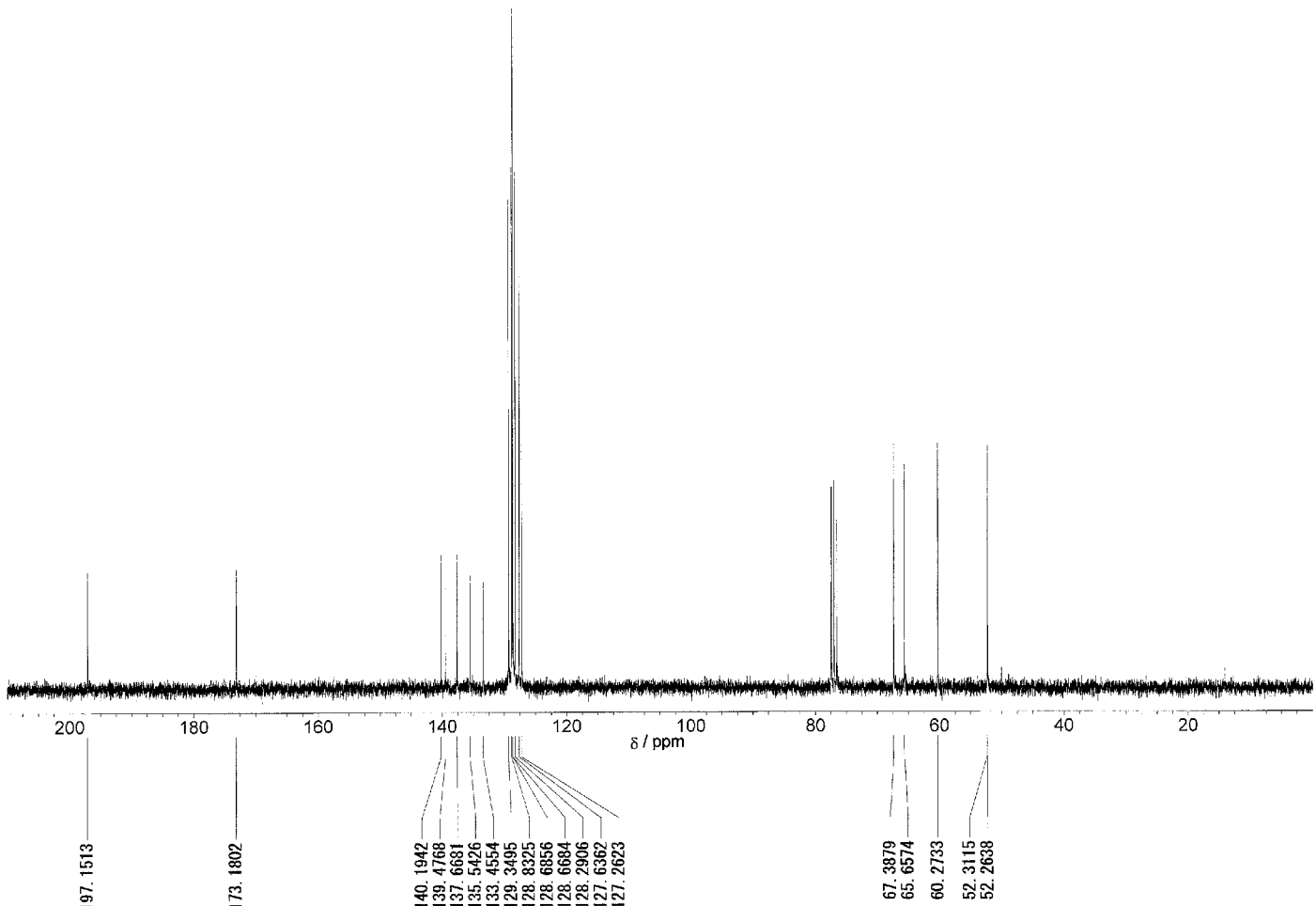
10.5097
4.0704
1.0
1.0297
2.0467
3.0758
0.5088
δ / ppm
7.5653
7.5382
7.4557
7.4314
7.4067
7.3840
7.3563
7.3316
7.3055
7.2793
7.2557
7.0595
4.9845
4.9557
4.5419
4.5143
4.4875
4.1981
4.1681
4.1316
4.1049
4.0761
3.7365

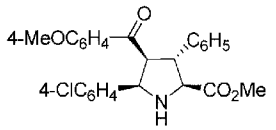

δ / ppm
198.2732
173.3080
140.3449
137.8741
137.2445
133.2856
133.0146
128.8000
128.7276
128.3651
128.1991
128.0006
127.6973
127.1898
67.4757
65.7147
60.2714
52.3134
52.2619


4-ClC6H4
C6H5
4-ClC6H4
CO2Me
N
H
O

6

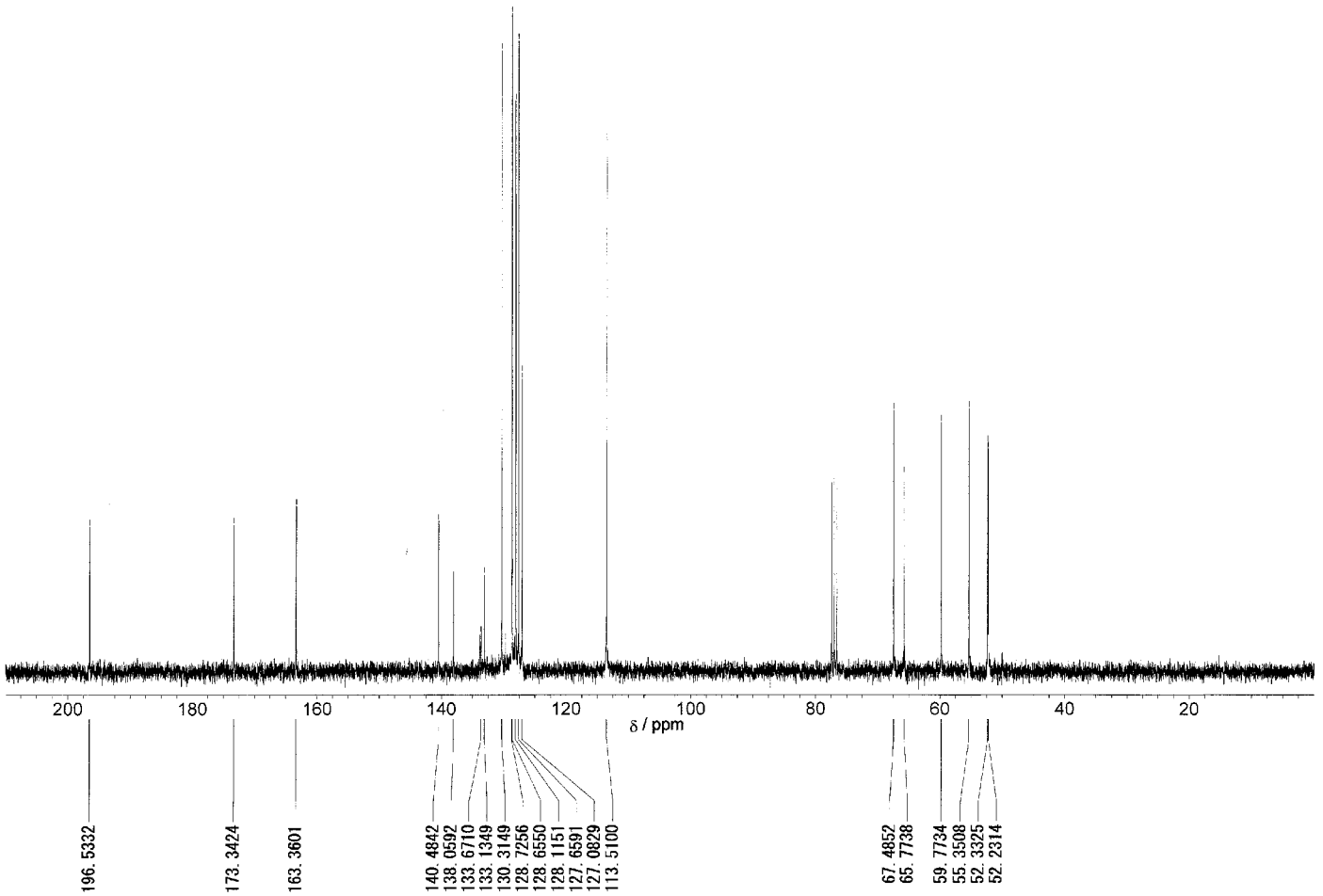
9.1422
3.8491
1.0
0.997
2.1519
2.949
0.6525
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.5024
7.4741
7.3547
7.3349
7.3097
7.2663
7.2383
7.0758
4.9704
4.9416
4.4656
4.4383
4.4113
4.1911
4.1613
4.1213
4.0949
4.0663
3.7358
2.9723

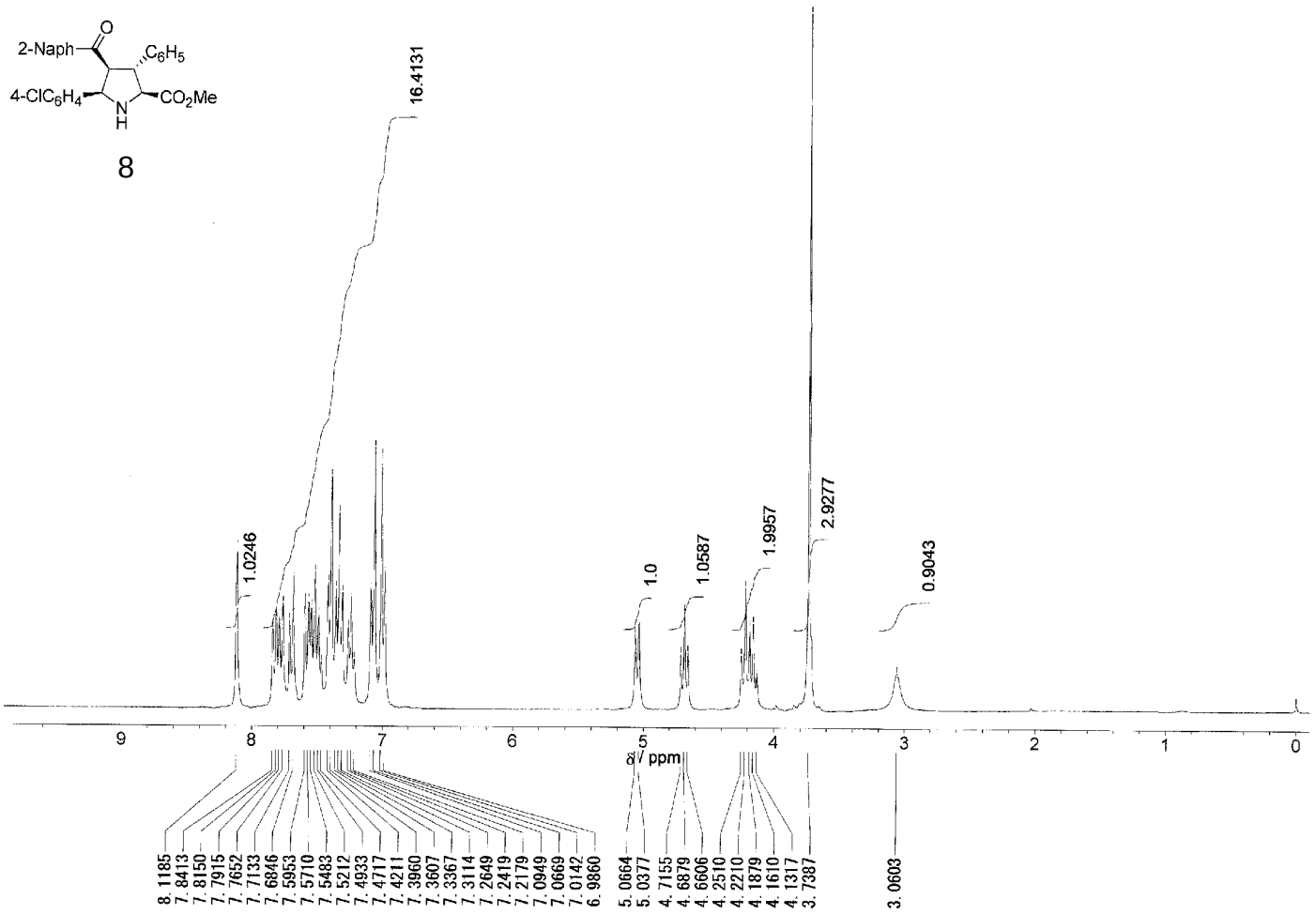

200
180
160
140
120
100
80
60
40
20
δ / ppm
197.1513
173.1802
140.1942
139.4768
137.6681
135.5426
133.4554
129.3495
128.8325
128.6856
128.6684
128.2906
127.6362
127.2623
67.3879
65.6574
60.2733
52.3115
52.2638

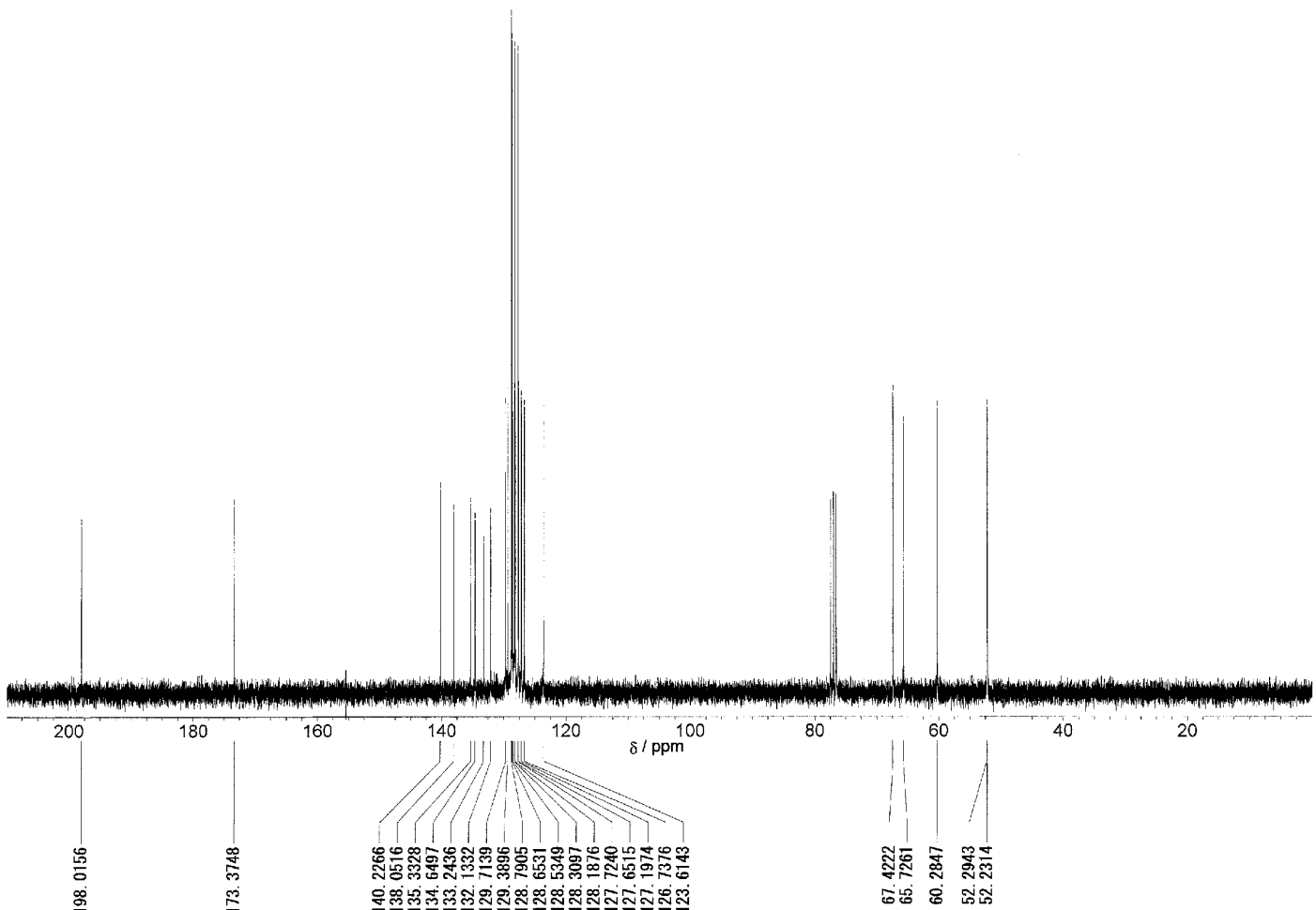

4-MeOC6H4
C6H5
4-ClC6H4
CO2Me
H
N
O

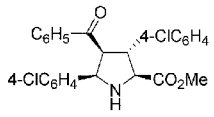
7

6.1847
6.6325
4.0479
1.8727
1.914
2.0705
1.0659
1.0
0.9715
δ / ppm
7.5841
7.5545
7.3721
7.3458
7.3230
7.2970
7.2580
7.2346
7.0798
6.7747
6.7451
4.9582
4.9299
4.4822
4.4548
4.4279
4.1867
4.1570
4.1032
4.0757
4.0478
3.7985
3.7321
3.0317


δ / ppm
196.5332
173.3424
163.3601
140.4842
138.0592
133.6710
133.1349
130.3149
128.7256
128.6550
128.1151
127.6591
127.0829
113.5100
67.4852
65.7738
59.7734
55.3508
52.3325
52.2314


2-Naph
C6H5
4-ClC6H4
CO2Me
N
H
8
16.4131
1.0246
1.0
1.0587
1.9957
2.9277
0.9043
δ / ppm
8.1185
7.8413
7.8150
7.7915
7.7652
7.7133
7.6846
7.5953
7.5710
7.5483
7.5212
7.4933
7.4717
7.4211
7.3960
7.3607
7.3367
7.3114
7.2649
7.2419
7.2179
7.0949
7.0669
7.0142
6.9860
5.0664
5.0377
4.7155
4.6879
4.6606
4.2510
4.2210
4.1879
4.1610
4.1317
3.7387
3.0603


δ / ppm
198.0156
173.3748
140.2266
138.0516
135.3328
134.6497
133.2436
132.1332
129.7139
129.3896
128.7905
128.6531
128.5349
128.3097
128.1876
127.7240
127.6515
127.1974
126.7376
123.6143
67.4222
65.7261
60.2847
52.2943
52.2314


C6H5
4-ClC6H4
4-ClC6H4
CO2Me
N
H

9

9.9484
4.1799
1.0
0.9982
1.9333
3.2092
0.5132
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.5754
7.5514
7.5475
7.4844
7.4591
7.4351
7.3327
7.3056
7.2826
7.2640
7.2178
7.0799
7.0473
4.9843
4.9548
4.4977
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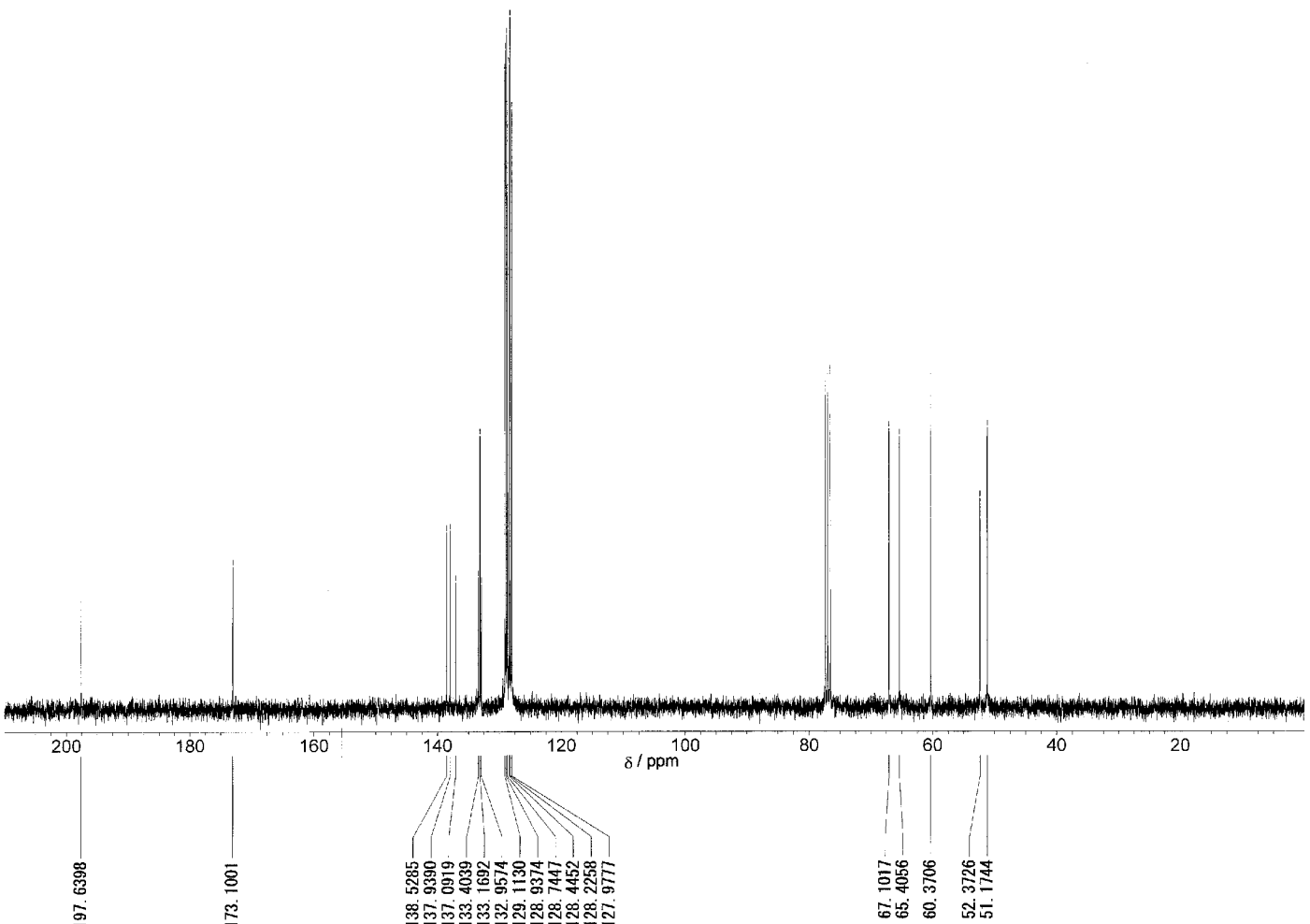
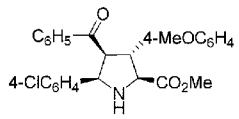
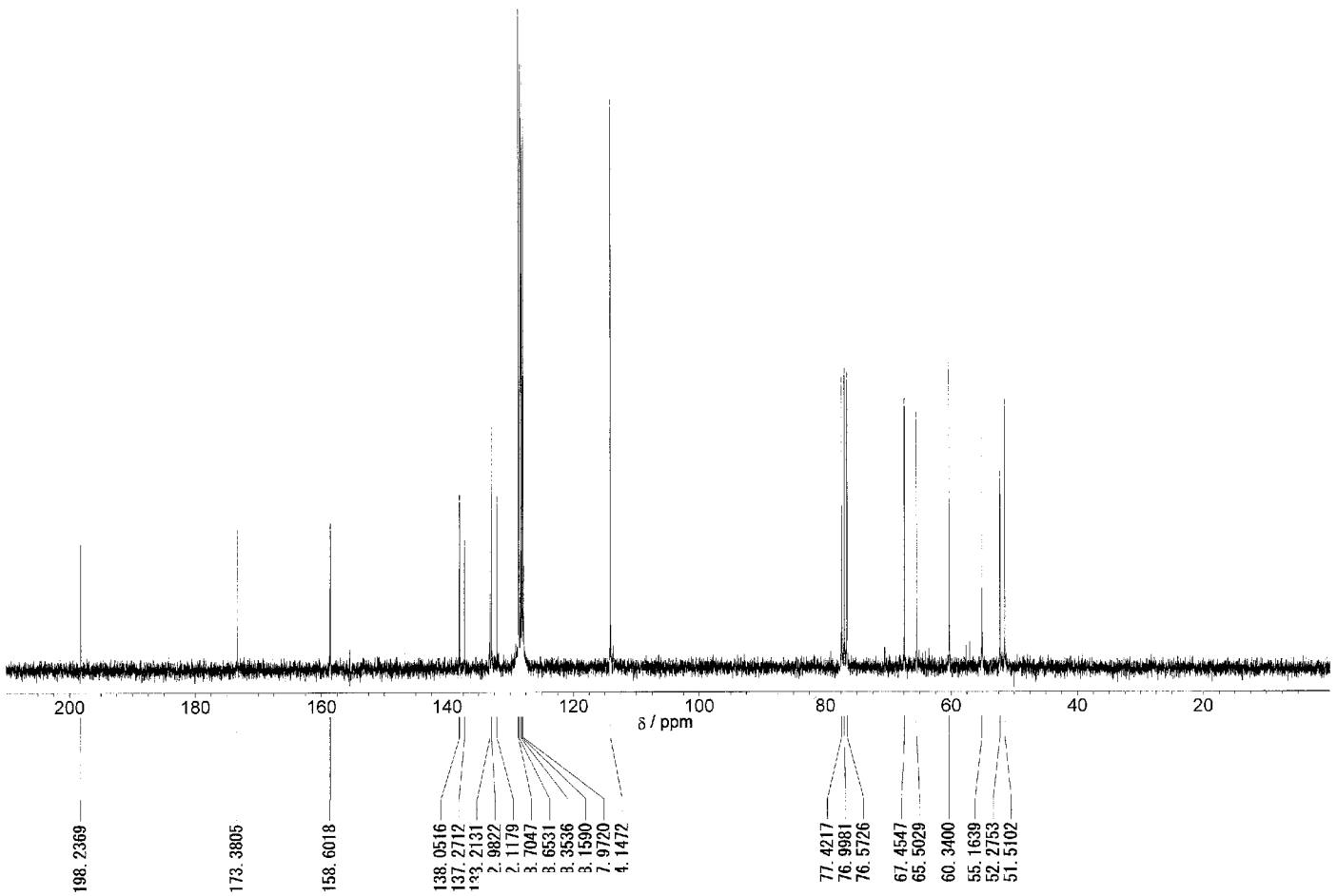
4.4421
4.1615
4.1307
4.1205
4.0940
4.0628
3.7412
2.9166

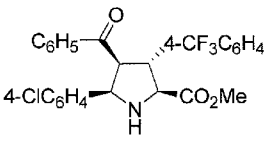

200
180
160
140
120
100
80
60
40
20
δ / ppm
197.6398
173.1001
138.5285
137.9390
137.0919
133.4039
133.1692
132.9574
129.1130
128.9374
128.7447
128.4452
128.2258
127.9777
67.1017
65.4056
60.3706
52.3726
51.1744


C6H5
4-MeOC6H4
4-ClC6H4
CO2Me
N
H
O

10

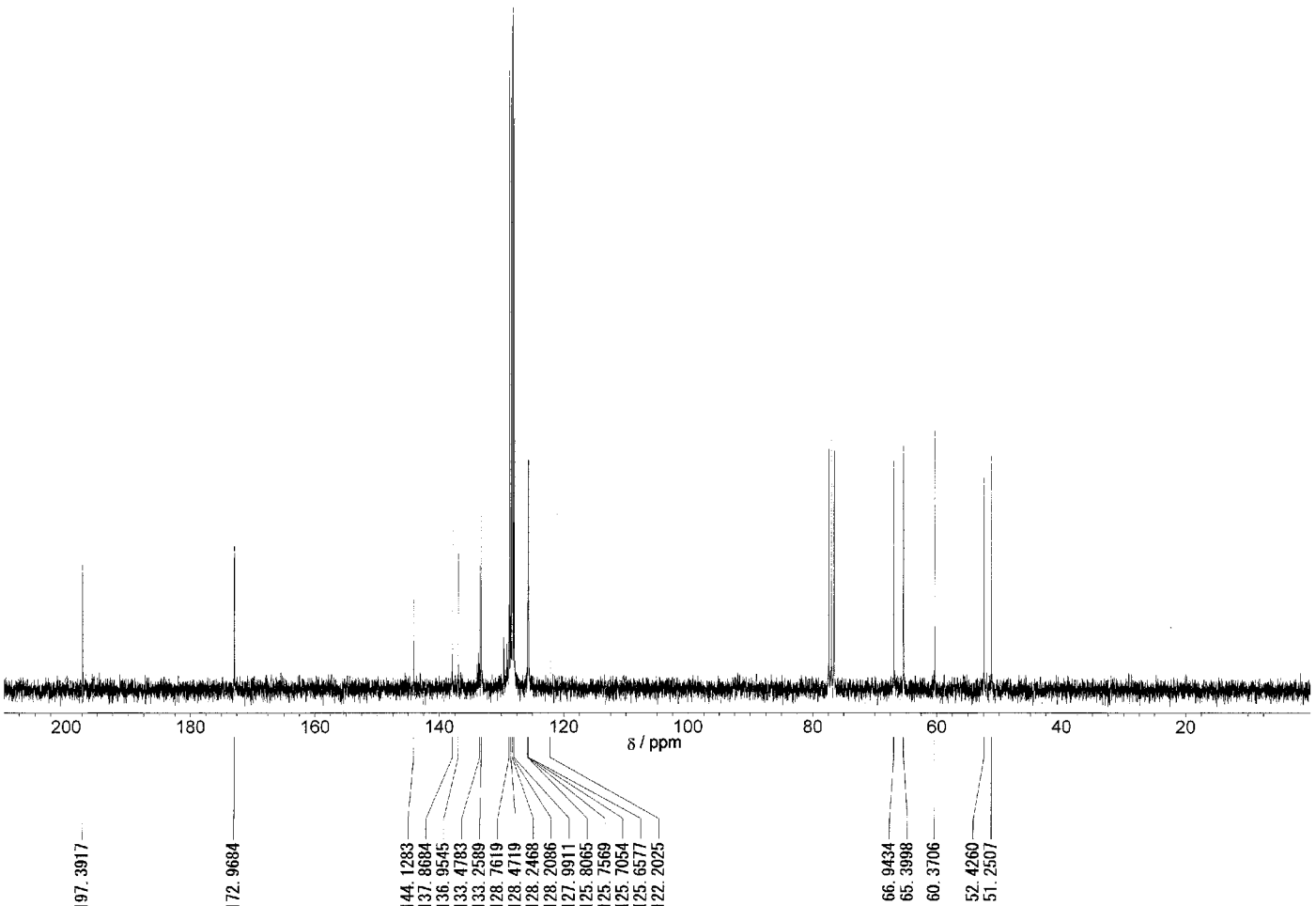
8.1355
4.0474
1.8973
1.0
1.0361
1.9386
6.526
0.4665
δ / ppm
7.5752
7.5515
7.5471
7.4666
7.4418
7.4173
7.3176
7.2922
7.2699
7.2626
7.0605
6.8806
6.8516
4.9693
4.9403
4.5039
4.4759
4.4484
4.1532
4.1227
4.0822
4.0541
4.0253
3.7812
3.7543
3.7425
2.9305

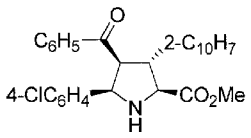

δ / ppm
198.2369
173.3805
158.6018
138.0516
137.2712
133.2131
2.9822
2.1179
3.7047
3.6531
3.3536
3.1590
7.9720
4.1472
77.4217
76.9981
76.5726
67.4547
65.5029
60.3400
55.1639
52.2753
51.5102


C6H5
4-CF3C6H4
4-ClC6H4
CO2Me
N
H

11

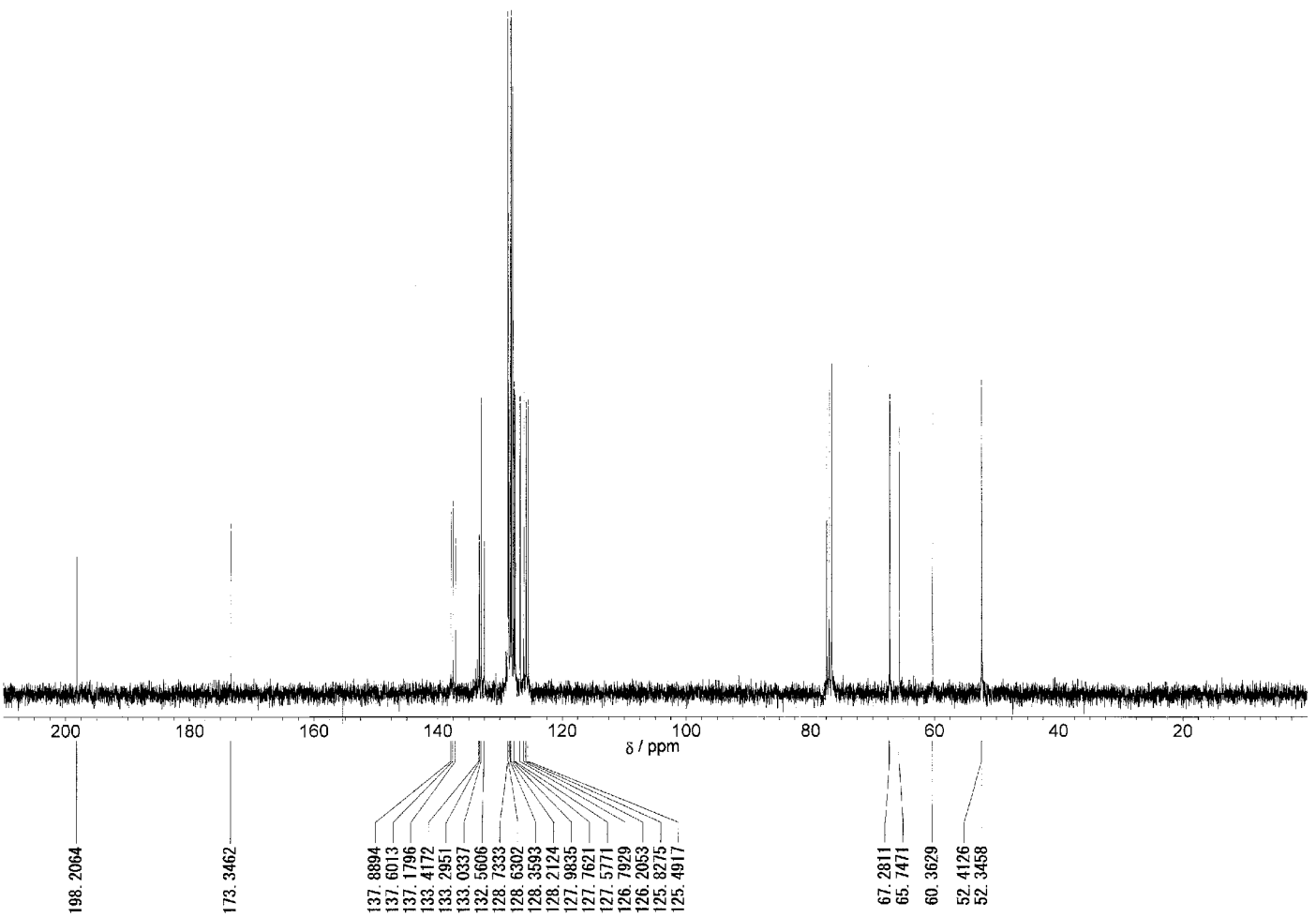
11.1903
4.1035
1.0
1.038
2.0303
3.0588
0.9685
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.6100
7.5836
7.5631
7.5587
7.5194
7.4928
7.4699
7.4453
7.4070
7.3832
7.3421
7.3156
7.2915
7.2690
7.2368
7.2097
7.0882
7.0603
7.0531
7.0233
5.0236
4.9939
4.5357
4.5212
4.5057
4.4920
4.2117
4.1956
3.7480
2.9660

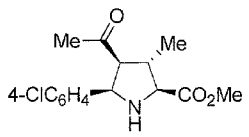

200
180
160
140
120
100
80
60
40
20
δ / ppm
197.3917
172.9684
144.1283
137.8684
136.9545
133.4783
133.2589
128.7619
128.4719
128.2468
128.2086
127.9911
125.8065
125.7569
125.7054
125.6577
122.2025
66.9434
65.3998
60.3706
52.4260
51.2507


C6H5
2-C10H7
4-ClC6H4
CO2Me
N
H
O

12

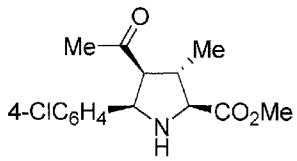
9.121
4.0707
3.8311
2.9788
2.0373
1.014
1.0
0.8203
δ / ppm
7.8599
7.8306
7.8034
7.5728
7.5490
7.5448
7.5242
7.4960
7.4879
7.4802
7.4679
7.4552
7.4496
7.4300
7.4054
7.3025
7.2764
7.2648
7.2589
7.2518
7.0897
5.0601
5.0313
4.6429
4.6158
4.5898
4.3485
4.3185
4.3109
4.2853
4.2554
3.7241
3.0702


δ / ppm
198.2064
173.3462
137.8894
137.6013
137.1796
133.4172
133.2951
133.0337
132.5606
128.7333
128.6302
128.3593
128.2124
127.9835
127.7621
127.5771
126.7929
126.2053
125.8275
125.4917
67.2811
65.7471
60.3629
52.4126
52.3458

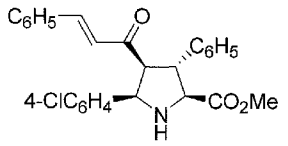

Me
Me
4-ClC6H4
CO2Me
N
H

13

4.3106
3.2275
3.1156
3.3952
1.0
0.9462
1.0425
0.8328
0.3429
δ / ppm
7.3032
7.2742
7.2468
7.2185
4.6422
4.6136
3.8235
3.5274
3.4992
3.1477
3.1204
3.0941
2.7961
2.7722
2.7484
2.7241
2.7001
2.6775
2.5164
1.6912
1.2150
1.1928

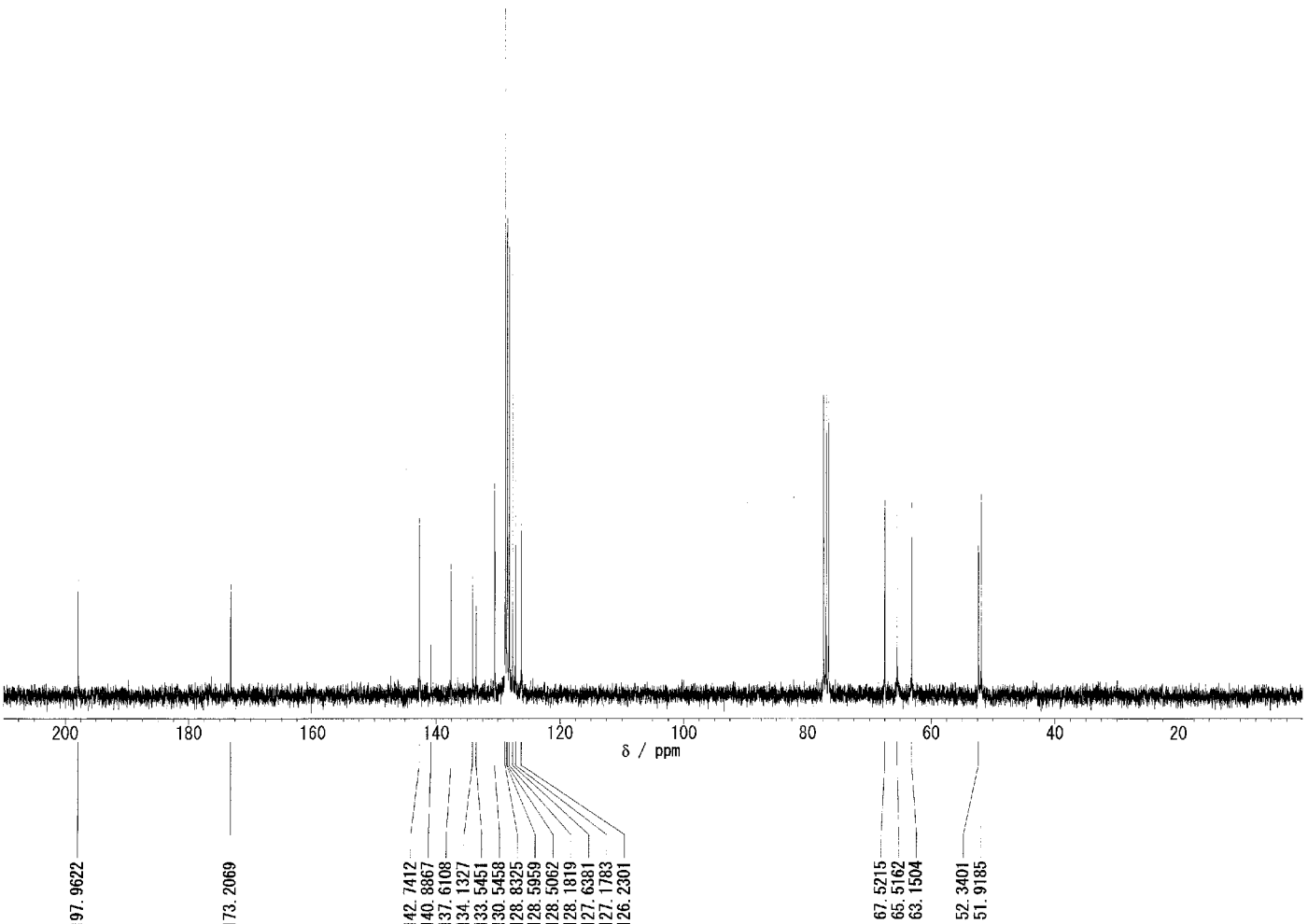

Me
Me
4-ClC6H4
CO2Me
N
H

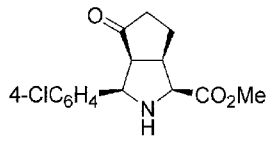
δ / ppm
207.4942
173.5313
138.3282
133.5909
128.7237
128.5329
67.0063
65.3025
63.7266
52.2867
40.8029
31.1374
18.0796


C6H5
O
C6H5
4-ClC6H4
N
H
CO2Me

14

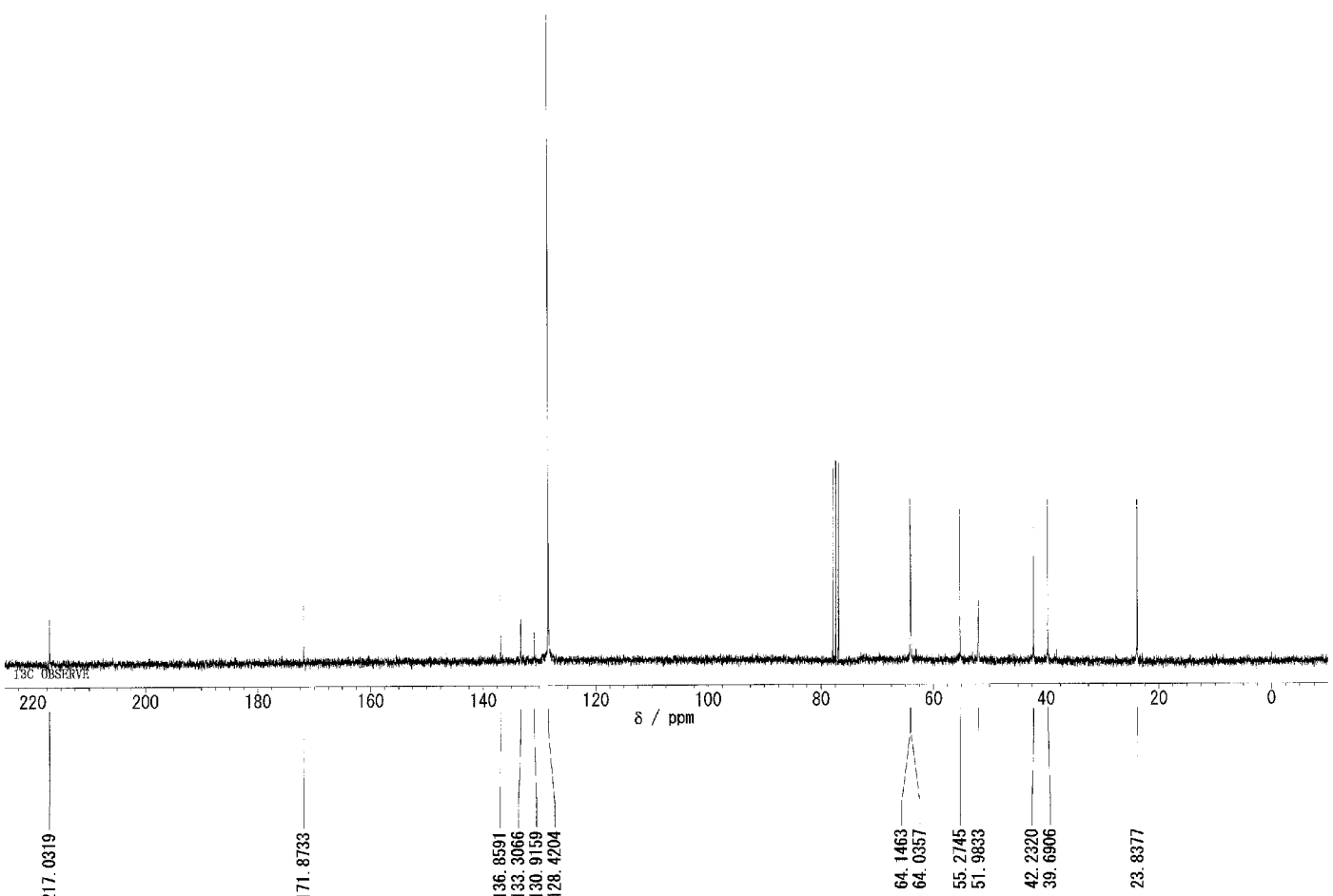
16.7562
1.036
1.0
2.9017
2.9595
0.7148
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.3622
7.3489
7.3283
7.3070
7.2778
7.2300
7.2028
7.1685
6.3193
6.2659
4.9618
4.9346
4.1563
4.1290
4.0665
4.0437
4.0171
3.9575
3.9316
3.9082
3.7621
2.8134

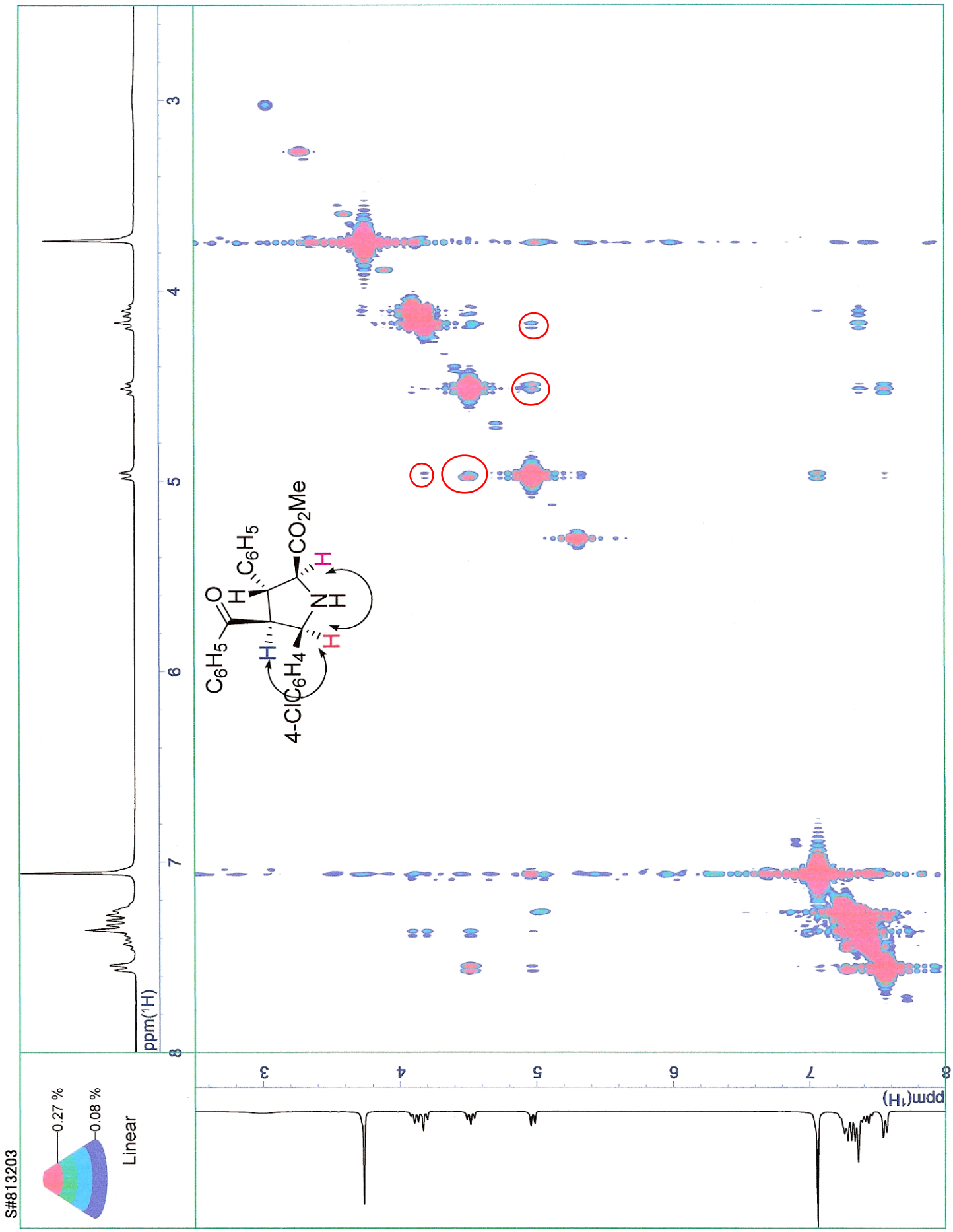

200
180
160
140
120
100
80
60
40
20
δ / ppm
197.9622
173.2069
142.7412
140.8867
137.6108
134.1327
133.5451
130.5458
128.8325
128.5959
128.5062
128.1819
127.6381
127.1783
126.2301
67.5215
65.5162
63.1504
52.3401
51.9185


O
4-ClC6H4
N
H
CO2Me

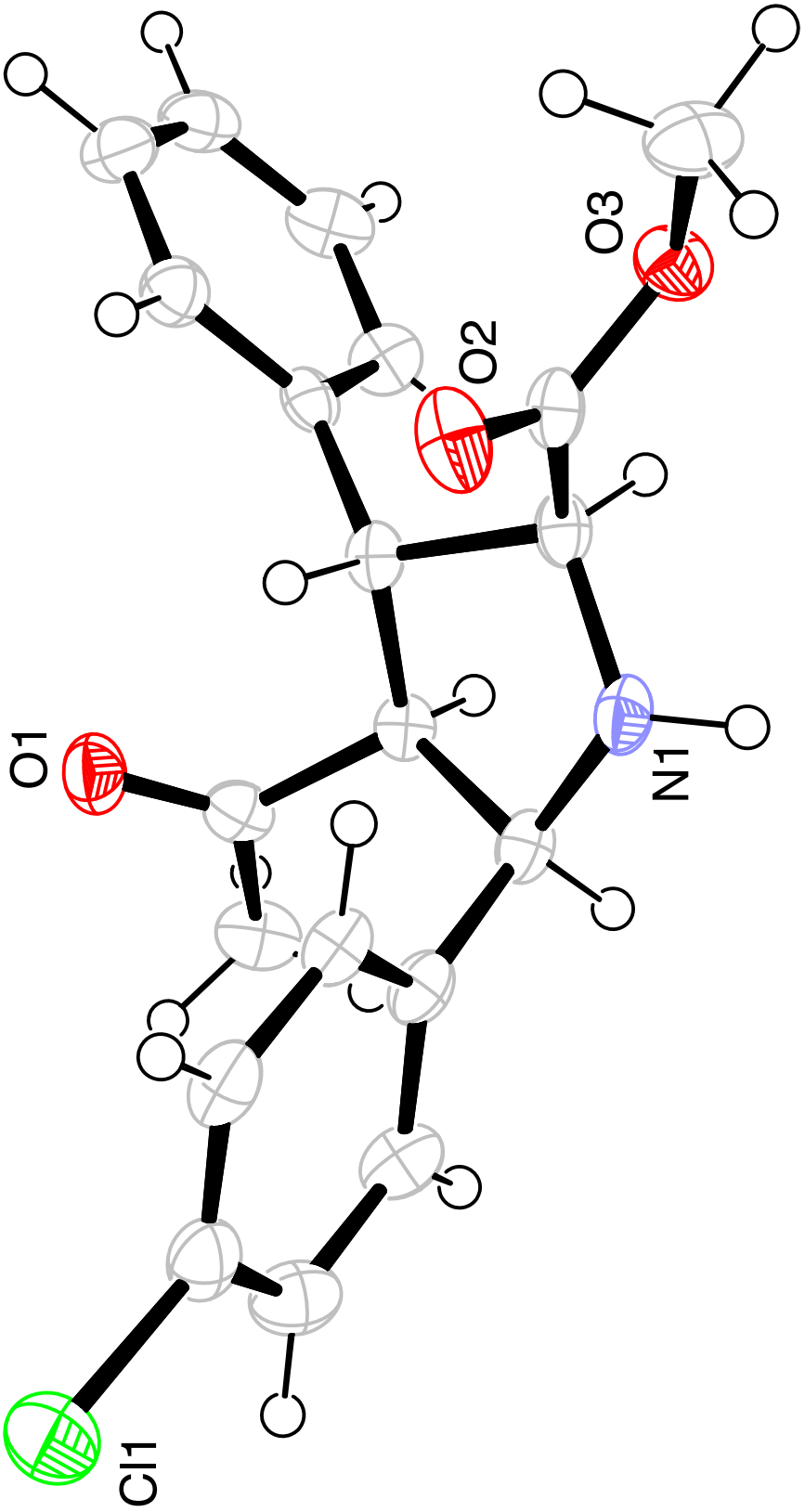
16

5.2896
4.0772
3.0541
1.0
1.036
0.9482
1.0933
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.3183
7.2887
7.2624
4.4748
4.4436
4.1297
4.1073
3.8267
3.2720
3.2430
3.2215
3.2021
3.1755
2.9210
2.8906
2.8631
2.4065
2.3185
2.2289
2.1957
2.1668
2.1520
2.1271
2.1012
2.0622
2.0455
2.0180
1.9903
1.8631
1.8440
1.8251
1.8143
1.7915
1.5760
-0.0004

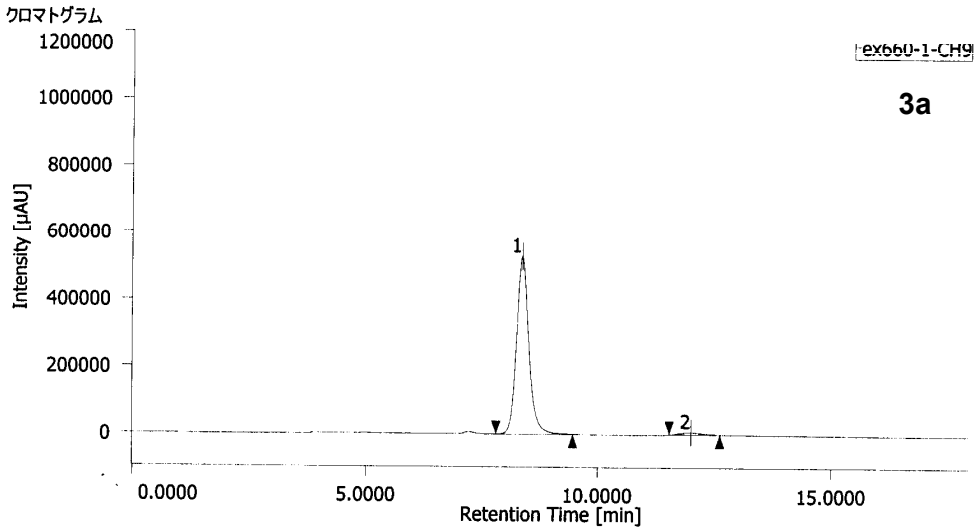

13C OBSERVE
220
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
217.0319
171.8733
136.8591
133.3066
130.9159
128.4204
64.1463
64.0357
55.2745
51.9833
42.2320
39.6906
23.8377


S#813203
0.27 %
0.08 %
Linear
ppm(¹H)
3
4
5
6
7
8
C6H5
O
H
C6H5
CO2Me
H
N
H
H
4-ClC6H4

X-ray structure of 3a



Jasco_HPLC analytical result

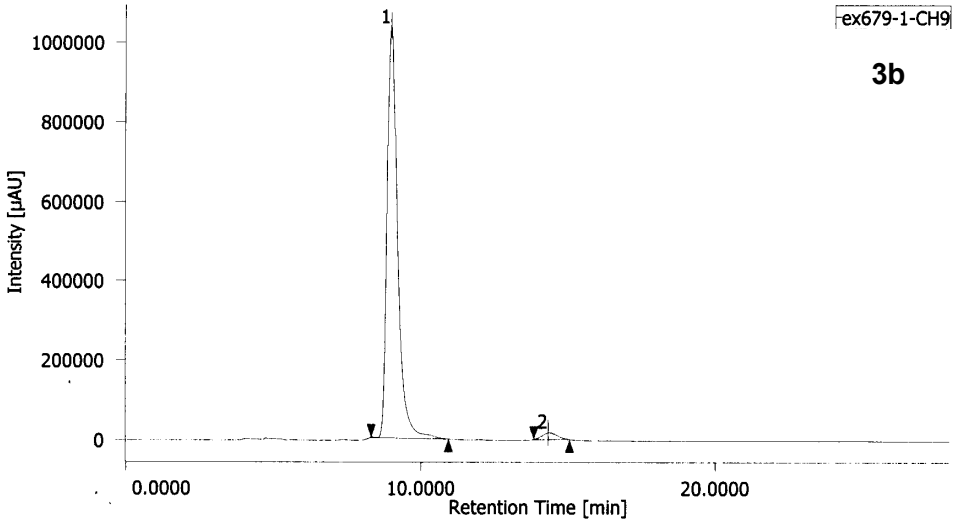


Table

	#name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1	Unknown	9	8.360	9788343	529633	97.835	98.712
2	Unknown	9	11.987	216590	6909	2.165	1.288

hex50 0.8mL 30min AS-H ex679-1 2010/01/14 18:57:15

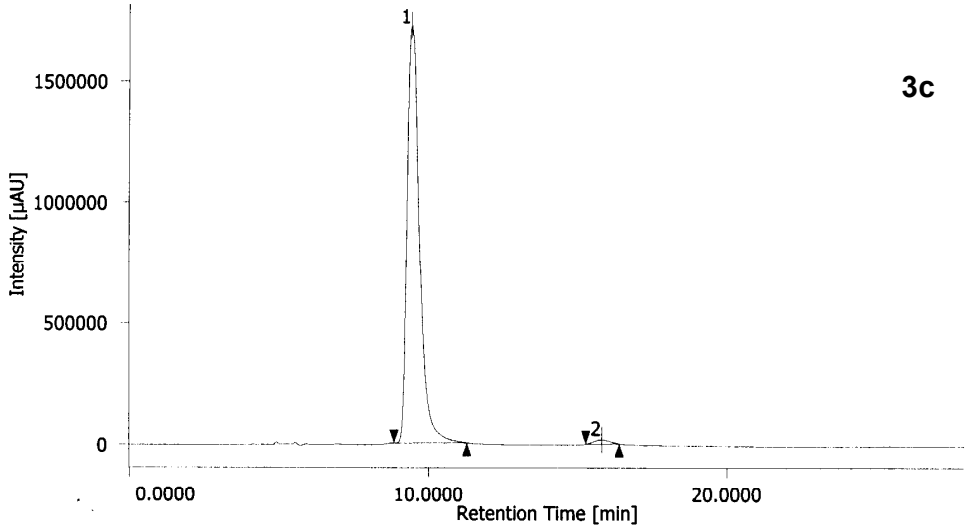
Jasco_HPLC analytical result



Table

	#name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1	Unknown	9	8.973	25911557	1038044	97.709	98.400
2	Unknown	9	14.347	607678	16877	2.291	1.600

Jasco_HPLC analytical result

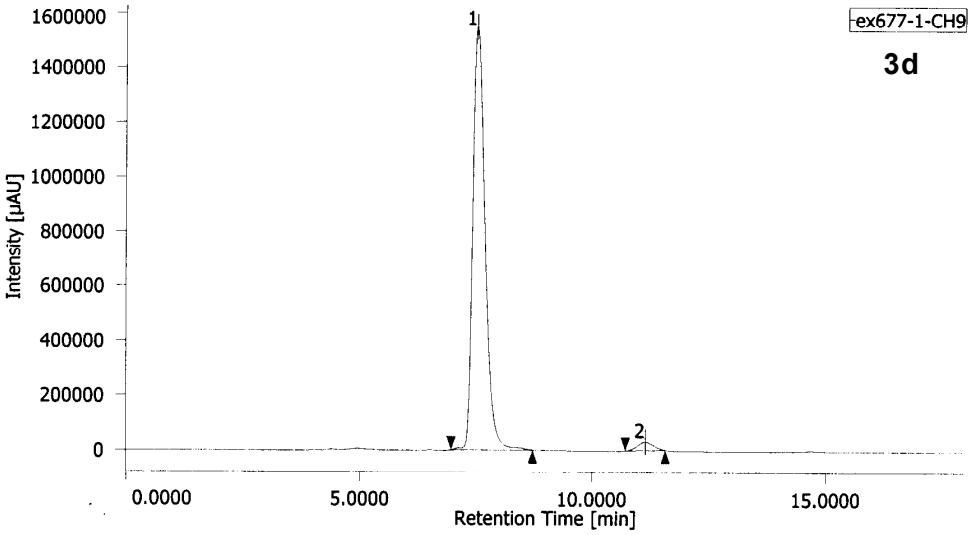


Table

	#name	CH	tR [min]	area [uV·sec]	hight [uV]	area%	hight%
1	Unknown	9	9.413	50111306	1725805	98.741	98.984
2	Unknown	9	15.813	638737	17713	1.259	1.016

hex50 0.8mL 20min AS-H ex677-1 2010/01/14 18:59:48

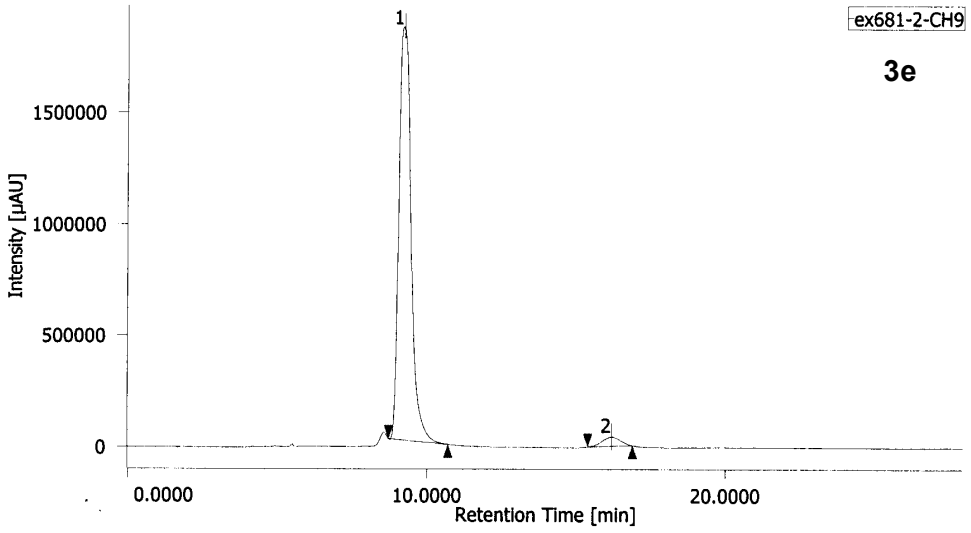
Jasco_HPLC analytical result



Table

	#name	CH	tR [min]	area [uV·sec]	hight [uV]	area%	hight%
1	Unknown	9	7.507	28533879	1546429	97.457	98.021
2	Unknown	9	11.133	744550	31229	2.543	1.979

Jasco_HPLC analytical result

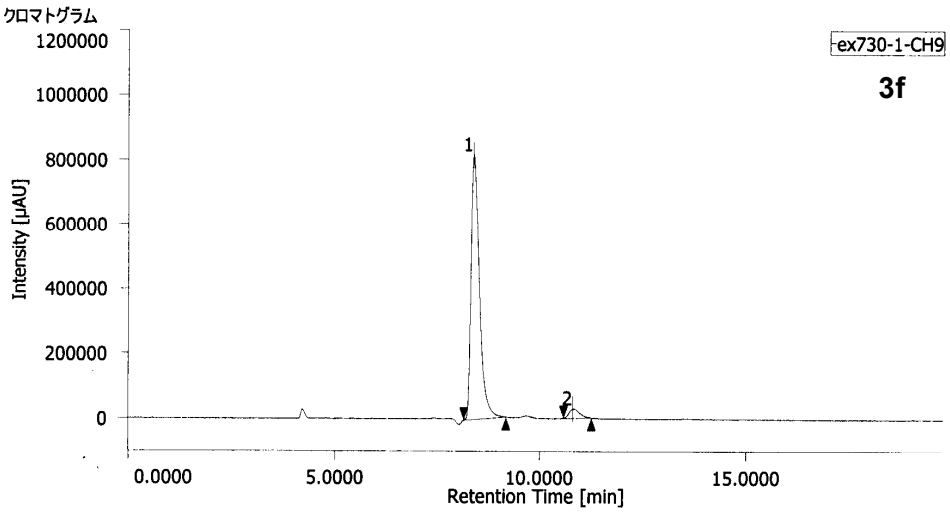


Table

#name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1 Unknown	9	9.227	52832363	1854506	96.740	97.806
2 Unknown	9	16.200	1780529	41595	3.260	2.194

hex80 0.7mL 30min AS-H ex730-1 2010/01/14 18:20:04

Jasco_HPLC analytical result

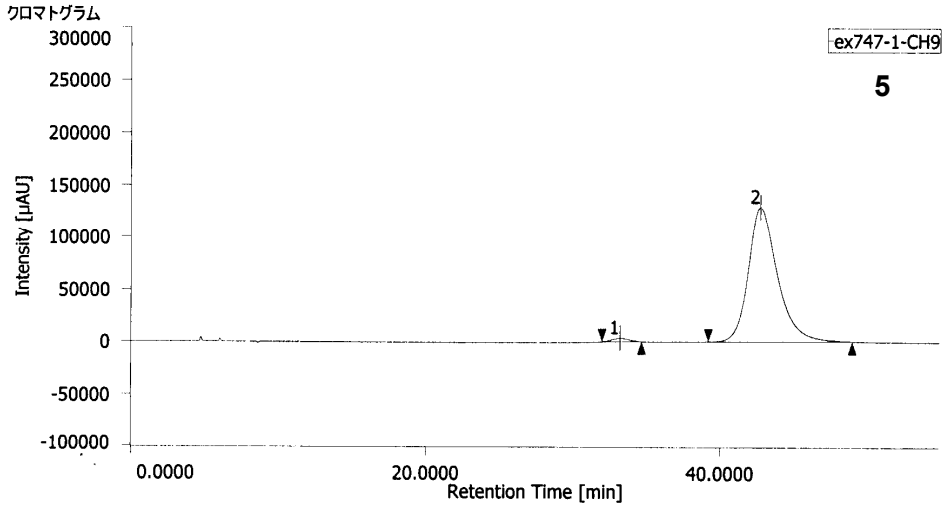


Table

#name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1 Unknown	9	8.373	11398193	818289	95.549	96.550
2 Unknown	9	10.800	531029	29237	4.451	3.450

hex90 0.7mL 60min AS-H ex747-1 2010/01/14 18:25:15

Jasco_HPLC analytical result

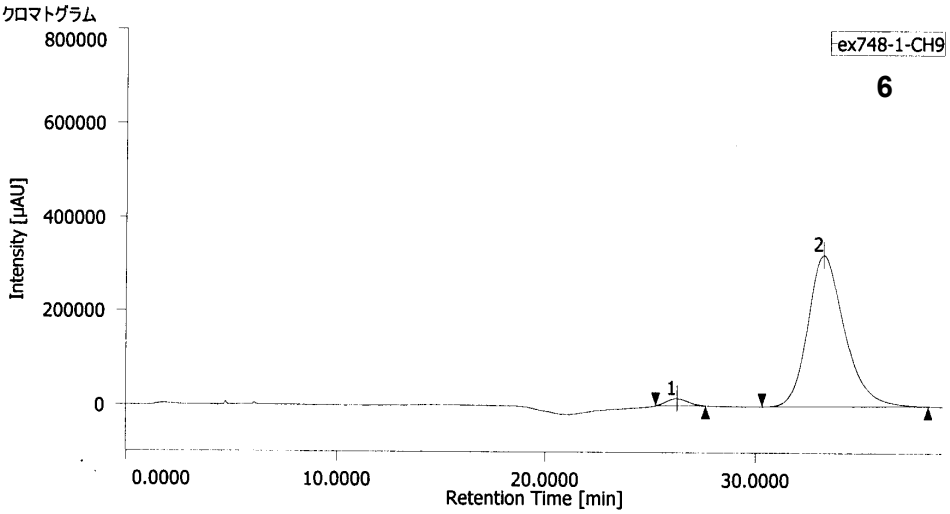


Table

	#name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1	Unknown	9	33.200	266507	3497	1.480	2.643
2	Unknown	9	42.667	17735925	128826	98.520	97.357

hex90 0.7mL 40min AS-H ex748-1 2010/01/14 18:27:38

Jasco_HPLC analytical result

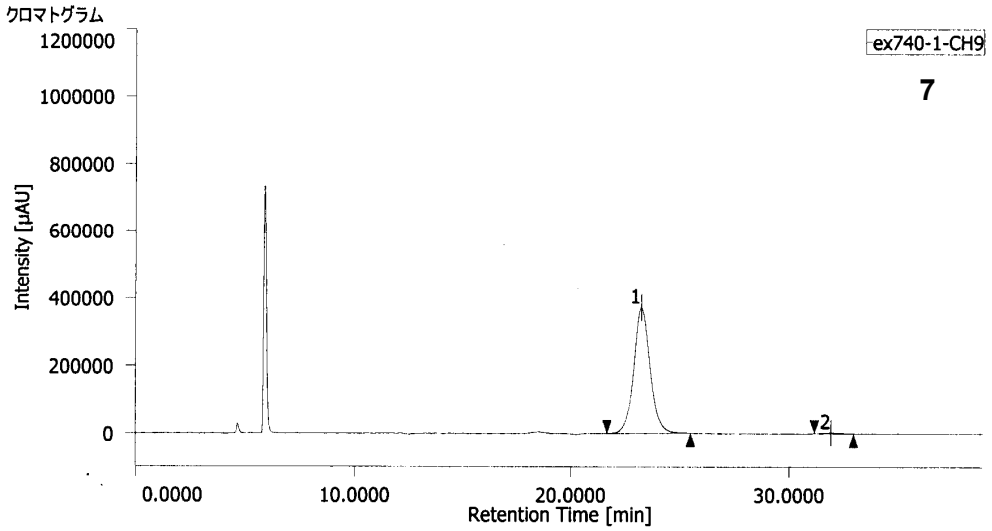


Table

	#name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1	Unknown	9	26.253	1071287	15201	2.636	4.520
2	Unknown	9	33.213	39566877	321114	97.364	95.480

hex90 0.7mL 40min AS-H ex740-1 2010/01/14 18:22:11

Jasco_HPLC analytical result

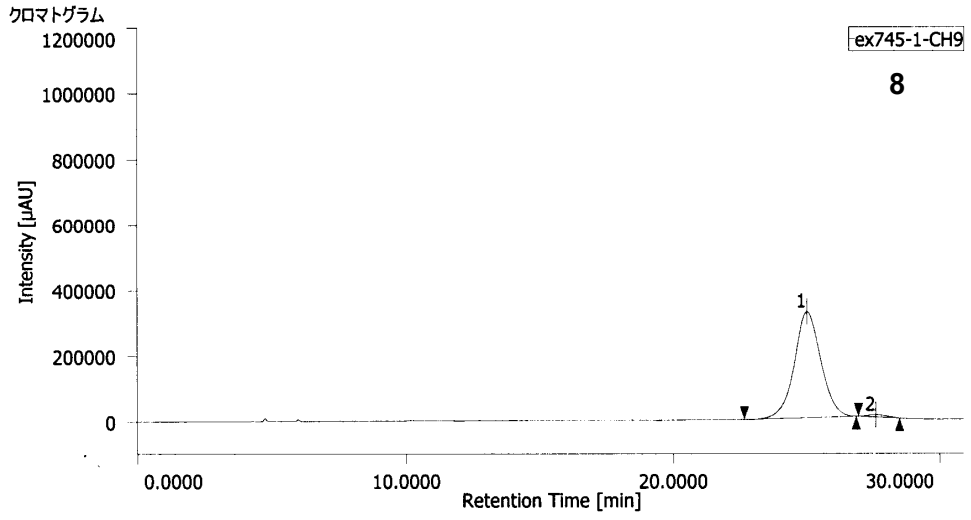


Table

#name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1 Unknown	9	23.227	19375346	371922	99.227	99.276
2 Unknown	9	31.907	150931	2712	0.773	0.724

hex90 0.7mL 40min AS-H ex745-1 2010/01/14 18:23:58

Jasco_HPLC analytical result

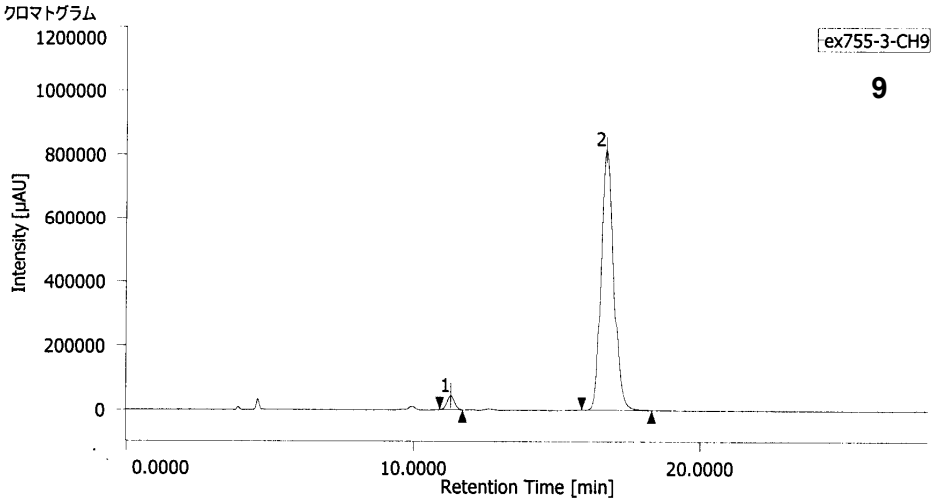


Table

#name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1 Unknown	9	24.960	22399645	323148	98.335	97.737
2 Unknown	9	27.547	379317	7483	1.665	2.263

hex50 0.8mL 30min AS-H ex755-3 2010/01/15 11:31:02

Jasco_HPLC analytical result

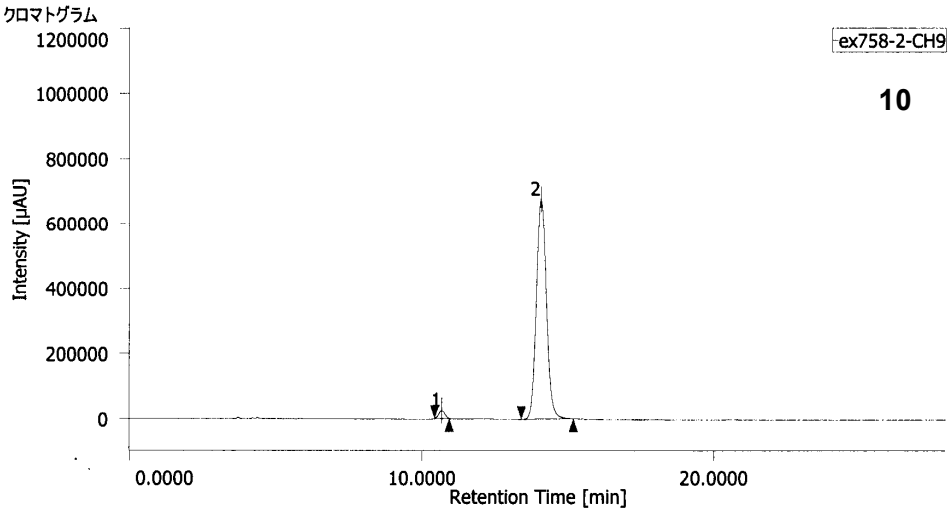


Table

#	name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1	Unknown	9	11.307	812138	44893	3.173	5.218
2	Unknown	9	16.707	24783517	815490	96.827	94.782

hex50 0.8mL 30min AS-H ex758-2 2010/01/13 17:45:29

Jasco_HPLC analytical result

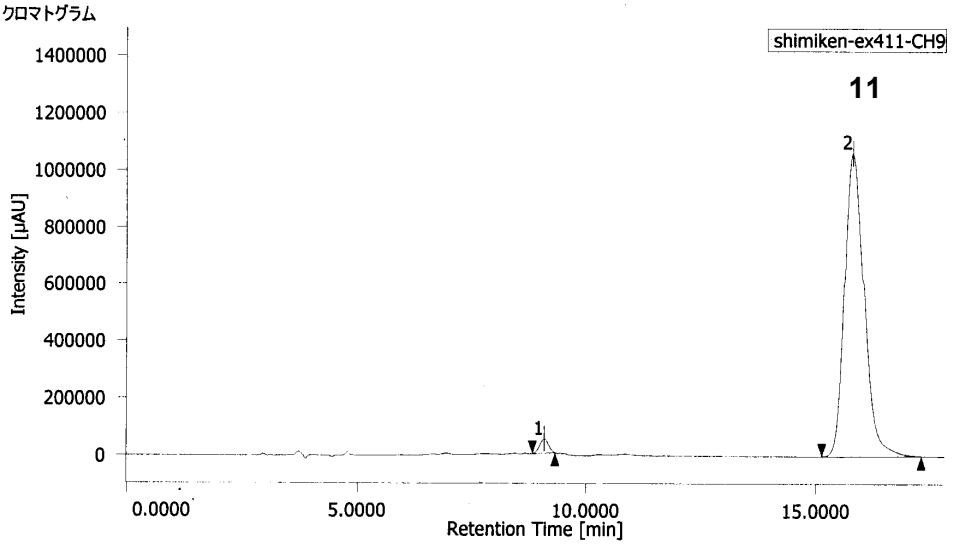


Table

#	name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1	Unknown	9	10.680	359905	24703	2.165	3.527
2	Unknown	9	14.080	16267250	675601	97.835	96.473

hex70 1.0ml 40min IA shimiken-ex411 2010/01/15 12:23:16

Jasco_HPLC analytical result

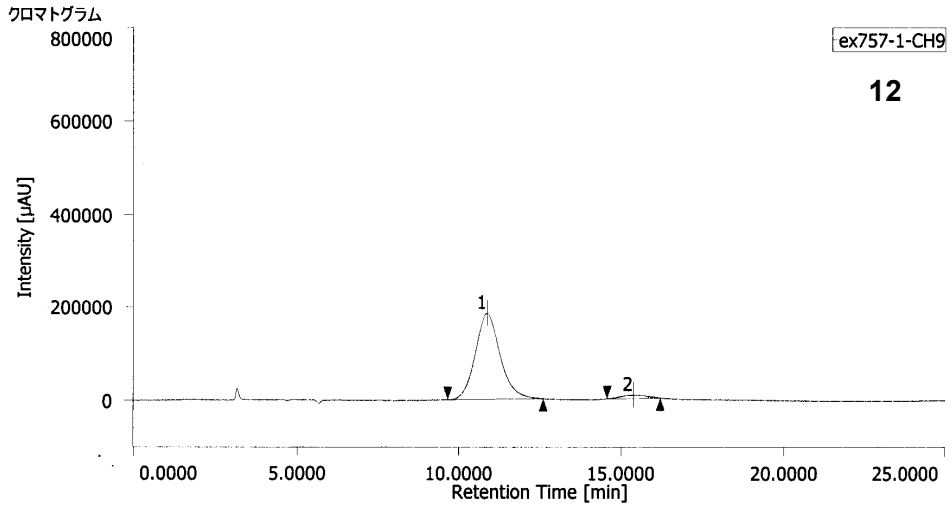


ピーク情報

#	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1	9	9.080	671118	50295	2.084	4.521
2	9	15.773	31525164	1062217	97.916	95.479

hex70 1.0mL 30min AS-H ex757-1 2010/01/15 11:30:23

Jasco_HPLC analytical result

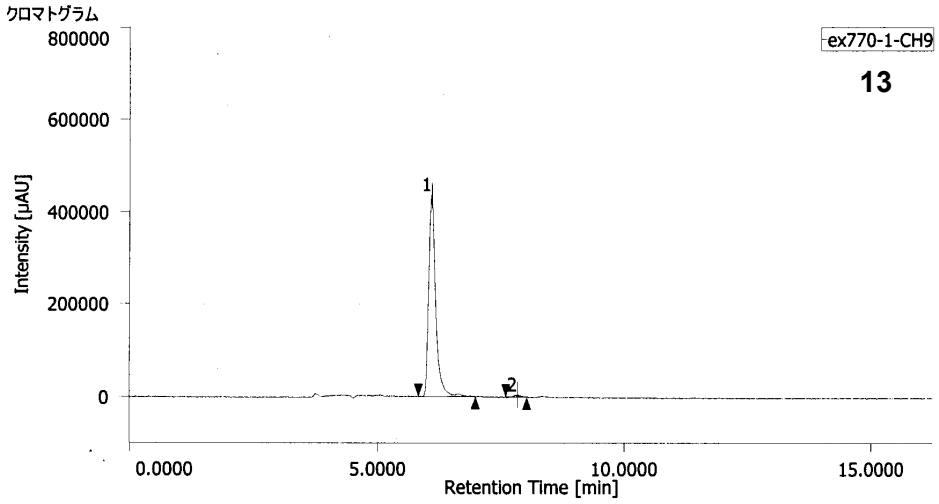


Table

#	name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1	Unknown	9	10.867	9718456	184855	95.944	95.903
2	Unknown	9	15.360	410858	7897	4.056	4.097

hex50 0.8mL 30min AS-H ex770-1 2010/01/26 20:42:51

Jasco_HPLC analytical result

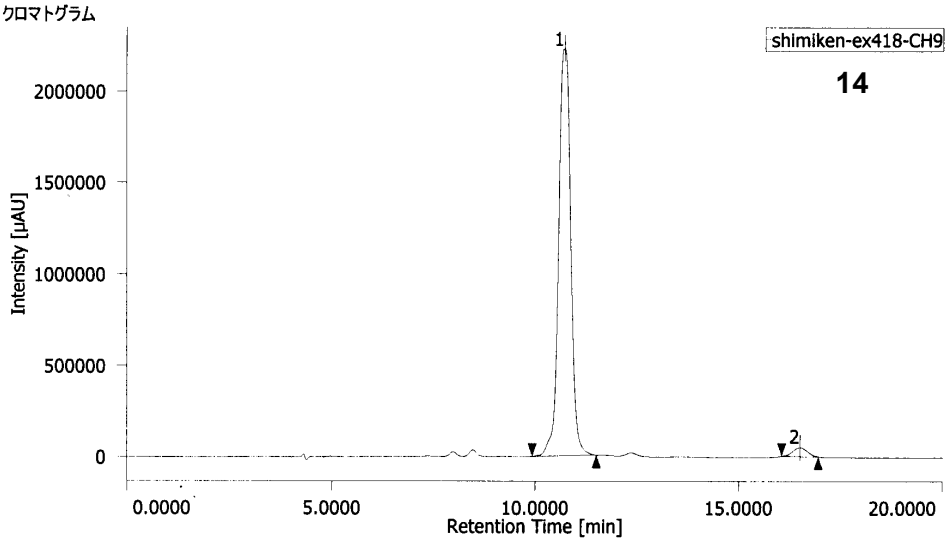


Table

#name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1 Unknown	9	6.093	4307576	436506	99.119	99.114
2 Unknown	9	7.840	38276	3903	0.881	0.886

hex50 0.8ml 20min IA shimiken-ex418 2010/01/19 15:41:17

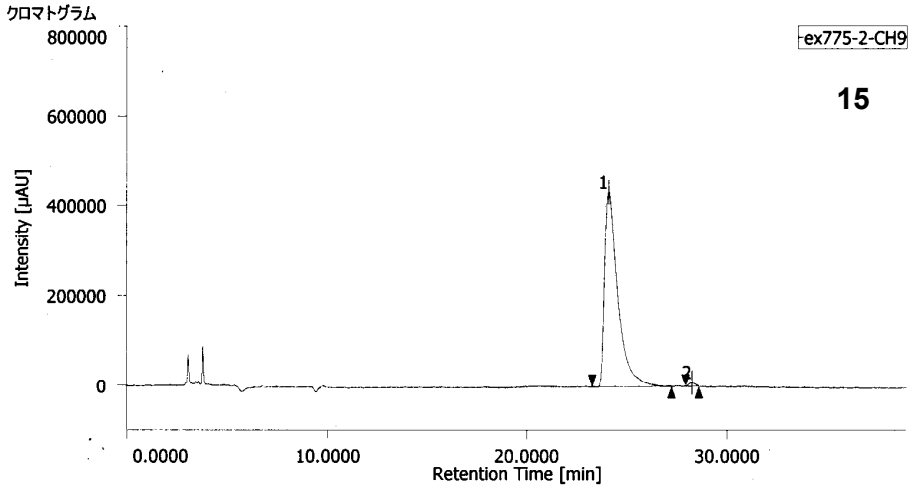
Jasco_HPLC analytical result



ピーク情報

#	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1	9	10.720	45969079	2226606	97.450	97.891
2	9	16.493	1202867	47977	2.550	2.109

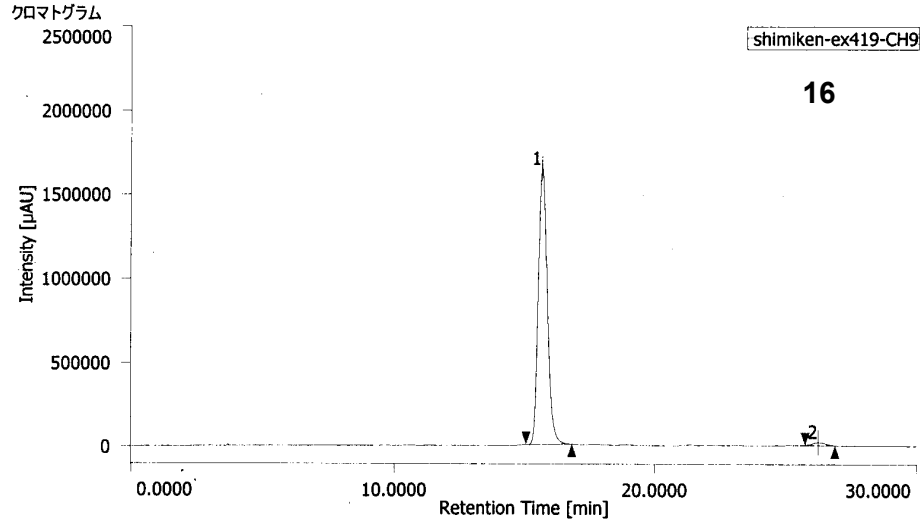
Jasco_HPLC analytical result



Table

#	name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1	Unknown	9	24.080	19848206	431124	99.050	98.110
2	Unknown	9	28.640	190361	8304	0.950	1.890

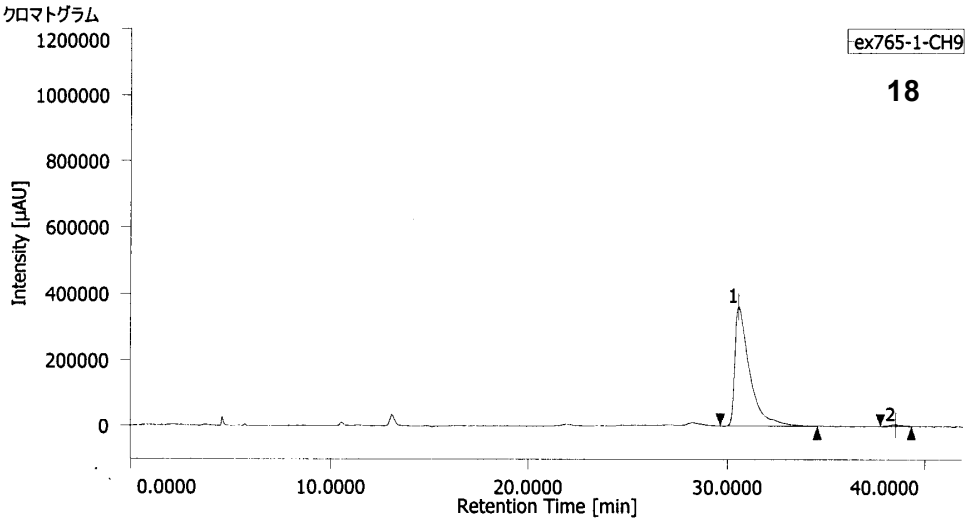
Jasco_HPLC analytical result



ピーク情報

#	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1	9	15.653	39852382	1645469	98.544	98.935
2	9	26.200	588829	17716	1.456	1.065

Jasco_HPLC analytical result



Table

	#name	CH	tR [min]	area [μV·sec]	hight [μV]	area%	hight%
1	Unknown	9	30.533	18906746	362479	98.690	98.579
2	Unknown	9	38.493	251044	5224	1.310	1.421