$CuBr_2$-Catalyzed Enantioselective Routes to Highly Functionalized and Naturally Occurring Allenes

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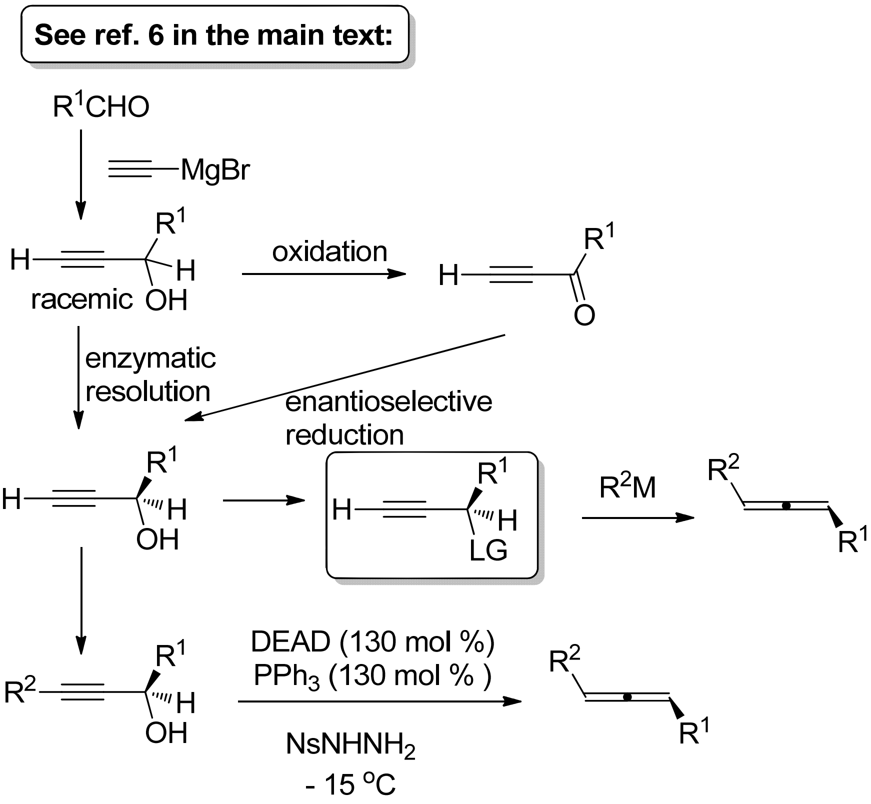
Supporting Information



See ref. 6 in the main text:

Problems:

(1) expensive nature of the terminal propargylic alcohols

(2) efficiency of chirality transfer

(3) R^1, R^2: simple alkyl or aryl

(4) Low synthetical efficiency with 4 or 5 steps

Figure S1. Enantioselective synthesis of simple 1,3-allenes via chirality transfer strategy.

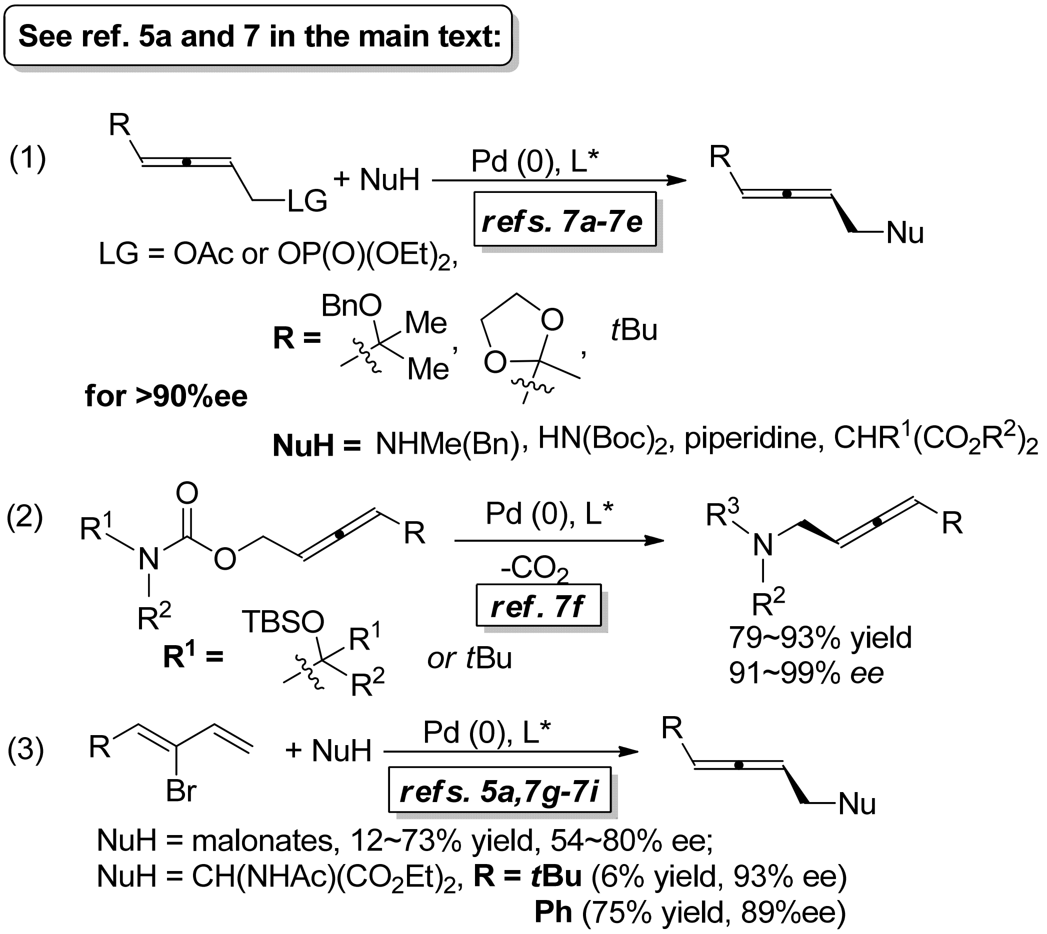


Figure S2. Pd-catalyzed enantioselective syntheses of amines and malonates with 1,3-disubstituted allene unit.

Figure S3. The photo of the apparatus for Typical Procedure I (130 ^{o}C).

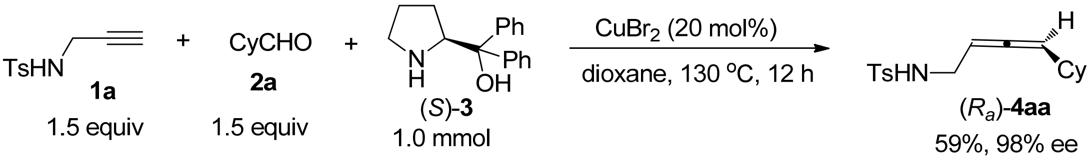
Figure S4. The photo of the apparatus for Typical Procedure II (70 ^{o}C).

General Experimental Methods

^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on an instrument operated at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR spectra. Infrared spectra were recorded from the films of pure samples on sodium chloride plates for liquid or in the form of KBr discs for the solid samples. Mass and HRMS spectra were carried out in EI or ESI mode. Thin layer chromatography was performed on pre-coated glass-back plates and visualized with UV light at 254 nm. Flash column chromatography was performed on silica gel. Copper(II) bromide was purchased from J&K. (*S*)-α,α-Diphenylprolinol and (*R*)-α,α-diphenylprolinol were purchased from Shanghai Darui Fine Chemicals. Aldehydes were distilled right before use. Dioxane were dried over sodium wire with benzophenone as the indicator and distilled freshly before use. All the temperatures are referred to the oil baths used.

Synthesis of functionalized axially chiral allenes (*R_a*)-4aa~(*R_a*)-4fa.

1. Preparation of (*R_a*)-*N*-(4-cyclohexylbuta-2,3-dienyl)-4-methylbenzenesulfonamide (*R_a*)-4aa. (hx-11-3)



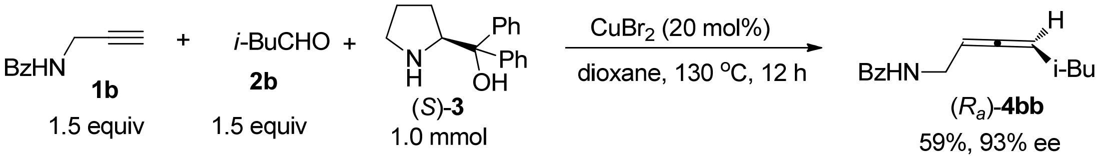
Typical Procedure I: To a flame-dried Schlenk tube with a polytetrafluoroethylene plug were added $CuBr_2$ (45.0 mg, 0.2 mmol), (*S*)-**3** (253.9 mg, 1.0 mmol), **1a** (313.4 mg, 1.5 mmol)/dioxane (1.5 mL), and **2a** (167.8 mg, 1.5 mmol)/dioxane (1.5 mL) sequentially under nitrogen atmosphere. The Schlenk tube was then sealed by screwing a polytetrafluoroethylene plug tightly with the outlet connected to the vacuum line and the nitrogen flow being closed (For an apparatus, see Fig. S3). The reaction was complete after being stirred in an oil bath preheated at 130 ^{o}C for 12 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 5/1). Then the resulting mixture was diluted with ether (30 mL) and washed with an aqueous solution of hydrochloric acid (3 M, 20 mL). The organic layer was separated, and the aqueous layer was extracted with ether (20 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography (eluent: petroleum ether/ethyl acetate = 5/1) on silica gel to afford (*R_a*)-**4aa** (180.0 mg, 59%) as a liquid:[1] 98% ee (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 95/5, 0.5 mL/min, $\lambda = 214$ nm, t_R(major) = 34.1 min, t_R(minor) = 35.6 min); $[\alpha]_D^{20} = -102.0$ (*c* = 1.05, $CHCl_3$) (reported value: 99% ee; $[\alpha]_D^{20} = -105.5$ (c = 1.07, $CHCl_3$)); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.72

(m, 2 H, ArH), 7.30 (d, *J* = 7.8 Hz, 2 H, ArH), 5.21-5.12 (m, 1 H, one proton of CH=C=CH), 5.11-5.01 (m, 1 H, one proton of CH=C=CH), 4.85 (t, *J* = 5.9 Hz, 1 H, NH), 3.60-3.50 (m, 2 H, NCH_2), 2.42 (s, 3 H, CH_3), 1.98-1.82 (m, 1 H, CH from Cy), 1.73-1.53 (m, 5 H, five protons from Cy), 1.32-0.89 (m, 5 H, five protons from Cy); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.3, 143.3, 137.0, 129.6, 127.0, 100.4, 88.4, 42.0, 36.7, 32.8, 32.7, 25.9, 25.8, 21.4; IR (neat) ν (cm^{-1}) 3284, 2924, 2850, 1962, 1598, 1495, 1418, 1329, 1161, 1094; MS (EI) m/z (%): 305 (M^+, 1.14), 91 (100).

The following compounds (R_a)-**4bb**~(R_a)-**4fa** were prepared at 130 °C according to the **Typical Procedure I** or at 70 °C according to the **Typical Procedure II** (see page S11) and their corresponding racemic enantiomers were prepared by following the same procedure using racemic diphenylprolinol ***rac*-3.**

2. Preparation of (R_a)-*N*-(6-methylhepta-2,3-dienyl)benzamide (R_a)-4bb.

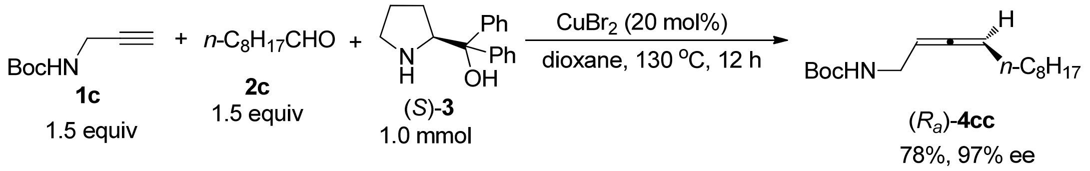
(hx-11-51)



The reaction of $CuBr_2$ (44.9 mg, 0.2 mmol), **1b** (238.4 mg, 1.5 mmol), (*S*)-**3** (254.3 mg, 1.0 mmol), and **2b** (129.9 mg, 1.5 mmol) in dioxane (3.0 mL) afforded (R_a)-**4bb** (136.8 mg, 59%) (eluent: petroleum ether/ethyl acetate = 5/1) as a liquid: 93% ee (HPLC conditions: Chiralcel AY-H column, hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 214 nm, t_R(major) = 9.8 min, t_R(minor) = 11.2 min); $[\alpha]_D^{20}$ = -92.5 (*c* = 0.78, $CHCl_3$);

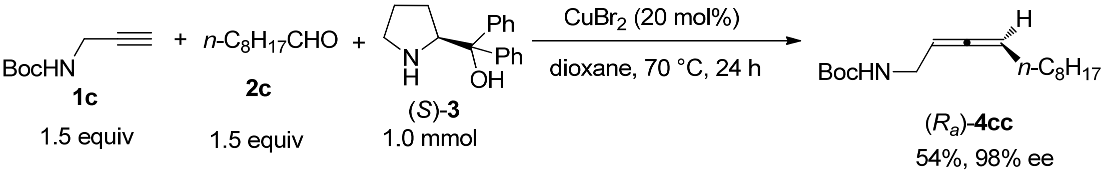
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.82-7.73 (m, 2 H, ArH), 7.51-7.35 (m, 3 H, ArH), 6.52 (bs, 1 H, NH), 5.30-5.19 (m, 2 H, CH=C=CH), 4.05-3.95 (m, 2 H, NCH$_2$), 1.96-1.86 (m, 2 H, CH$_2$), 1.73-1.55 (m, 1 H, CH), 0.894 (d, J = 6.6 Hz, 3 H, Me), 0.891 (d, J = 6.6 Hz, 3 H, Me); ^{13}C NMR (75 MHz, CDCl$_3$) δ 203.8, 167.3, 134.5, 131.3, 128.4, 126.8, 92.9, 87.8, 38.5, 38.0, 28.3, 22.1, 22.0; IR (neat) ν (cm^{-1}) 3320, 3064, 2955, 2927, 2869, 1964, 1727, 1644, 1603, 1578, 1538, 1489, 1465, 1308, 1076; MS (EI) m/z (%): 229 (M$^+$, 7.05), 105 (100); HRMS calcd for $C_{15}H_{19}NO$ [M$^+$]: 229.1467, found: 229.1469.

3. Preparation of (*R$_a$*)-*tert*-butyl (dodeca-2,3-dienyl)carbamate (*R$_a$*)-4cc. (zjs-3-097)



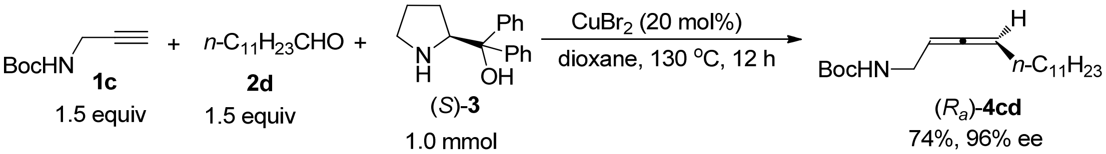
The reaction of CuBr$_2$ (45.4 mg, 0.2 mmol), **1c** (231.9 mg, 1.5 mmol), (*S*)-**3** (254.1 mg, 1.0 mmol), and **2c** (214.5 mg, 1.5 mmol) in dioxane (3.0 mL) afforded (*R$_a$*)-**4cc** (220.9 mg, 78%) (eluent: petroleum ether/ethyl acetate = 100/1) as a liquid: 97% ee (HPLC conditions: Chiralcel AD-R column, MeOH/H$_2$O = 85/15, 1.0 mL/min, λ = 214 nm, t_R(major) = 12.2 min, t_R(minor) = 16.2 min); $[\alpha]_D^{20}$ = -60.4 (c = 1.02, CHCl$_3$)); ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.28-5.22 (m, 1 H, one proton of CH=C=CH), 5.18-5.12 (m, 1 H, one proton of CH=C=CH), 4.72 (bs, 1 H, NH), 3.78-3.60 (m, 2 H, NCH$_2$), 2.00 (qd, J_1 = 6.8 Hz, J_2 = 2.8 Hz, 2 H, CH$_2$), 1.45 (s, 9 H, t-Bu), 1.43-1.27 (m, 12 H, (CH$_2$)$_6$), 0.88 (t, J = 6.8 Hz, 3 H, Me); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.1, 155.6, 93.9, 89.0, 79.1, 39.3, 31.8, 29.3, 29.2, 29.0, 28.6, 28.3, 22.6, 14.0; IR (neat) ν (cm^{-1}) 3354, 2925, 2854, 1965, 1696, 1503, 1458, 1389, 1366, 1247, 1167; MS (EI) m/z (%): 225 ((M-^{t}Bu+H)$^+$, 34.93), 57 (100); HRMS calcd for $C_{13}H_{23}NO_2$ [(M-^{t}Bu+H)$^+$]: 225.1729, found: 225.1732.

4. Preparation of (*R*$_a$)-*tert*-butyl (dodeca-2,3-dienyl)carbamate (*R*$_a$)-4cc at 70 °C. (tangy-1-113)



Typical Procedure II: To a flame-dried Schlenk tube with a rubber plug were added $CuBr_2$ (45.2 mg, 0.2 mmol), (*S*)-**3** (254.1 mg, 1.0 mmol), **1c** (231.9 mg, 1.5 mmol)/dioxane (1.5 mL), and **2c** (214.1 mg, 1.5 mmol)/dioxane (1.5 mL) sequentially under nitrogen atmosphere (For an apparatus, see Fig. S4). The reaction mixture was then stirred in an oil bath preheated at 70 °C for 24 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 10/1). The resulting mixture was diluted with ether (30 mL) and washed with an aqueous solution of hydrochloric acid (3 M, 20 mL). The organic layer was separated and the aqueous layer was extracted with ether (20 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography (eluent: petroleum ether/ethyl acetate = 100/1) on silica gel to afford (*R*$_a$)-**4cc** (153.6 mg, 54%) as a liquid: 98% ee (HPLC conditions: Chiralcel AD-R column, MeOH/H_2O = 85/15, 1.0 mL/min, λ = 214 nm, t_R(major) = 12.4 min, t_R(minor) = 16.1 min); $[\alpha]_D^{20}$ = -55.2 (*c* = 0.91, $CHCl_3$)); ^1H NMR (400 MHz, $CDCl_3$) δ 5.29-5.22 (m, 1 H, one proton of CH=C=CH), 5.17-5.15 (m, 1 H, one proton of CH=C=CH), 4.63 (bs, 1 H, NH), 3.75-3.65 (m, 2 H, NCH_2), 2.00 (qd, J_1 = 6.8 Hz, J_2 = 2.8 Hz, 2 H, CH_2), 1.45 (s, 9 H, t-Bu), 1.43-1.25 (m, 12 H, $(CH_2)_6$), 0.88 (t, J = 6.8 Hz, 3 H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 155.7, 94.0, 89.0, 79.2, 39.3, 31.8, 29.4, 29.2, 29.0, 28.7, 28.3, 22.6, 14.1.

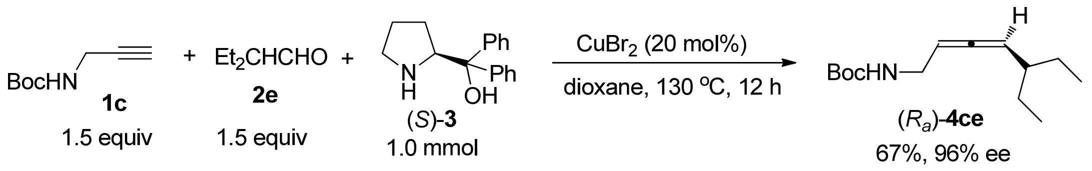
5. Preparation of (*R_a*)-*tert*-butyl (pentadeca-2,3-dienyl)carbamate (*R_a*)-4cd. (zjs-3-101)



The reaction of $CuBr_2$ (45.2 mg, 0.2 mmol), **1c** (233.5 mg, 1.5 mmol), (*S*)-**3** (253.3 mg, 1.0 mmol), and **2d** (275.9 mg, 1.5 mmol) in dioxane (3.0 mL) afforded (R_a)-**4cd** (239.2 mg, 74%) (eluent: petroleum ether/ethyl acetate = 100/1) as a liquid: 96% ee (HPLC conditions: Chiralcel AD-R column, MeOH/H_2O = 90/10, 0.5 mL/min, λ = 214 nm, t_R(major) = 27.8 min, t_R(minor) = 38.0 min); $[\alpha]_D^{20}$ = -50.4 (*c* = 1.00, $CHCl_3$)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28-5.21 (m, 1 H, one proton of CH=C=CH), 5.17-5.14 (m, 1 H, one proton of CH=C=CH), 4.75 (bs, 1 H, NH), 3.75-3.60 (m, 2 H, NCH_2), 2.00 (qd, J_1 = 6.8 Hz, J_2 = 2.8 Hz, 2 H, CH_2), 1.45 (s, 9 H, t-Bu), 1.43-1.26 (m, 18 H, $(CH_2)_9$), 0.88 (t, J = 6.8 Hz, 3 H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 155.6, 93.9, 89.0, 79.0, 39.2, 31.8, 29.6, 29.5, 29.4, 29.2, 29.0, 28.6, 28.3, 22.6, 14.0; IR (neat) ν (cm^{-1}) 3352, 2924, 2854, 1965, 1699, 1503, 1460, 1389, 1366, 1247, 1168, 1053; MS (EI) m/z (%): 267 ($(M-{}^tBu+H)^+$, 72.62), 57 (100); HRMS calcd for $C_{16}H_{29}NO_2$ [$(M-{}^tBu+H)^+$]: 267.2198, found: 267.2203.

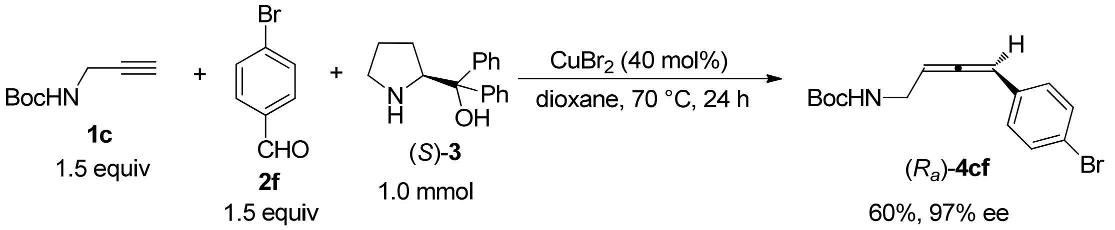
6. Preparation of (*R_a*)-*tert*-butyl (5-ethylhepta-2,3-dienyl)carbamate (*R_a*)-4ce.

(hx-11-52)



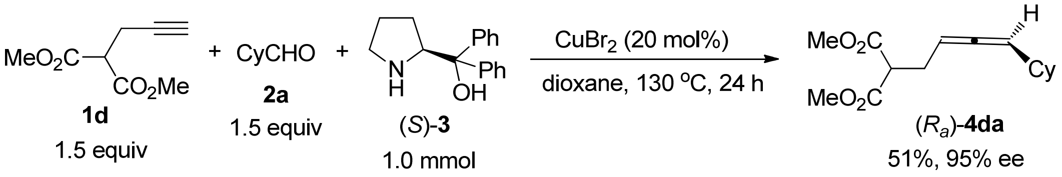
The reaction of $CuBr_2$ (44.9 mg, 0.2 mmol), **1c** (232.8 mg, 1.5 mmol), (*S*)-**3** (253.2 mg, 1.0 mmol), and **2e** (150.6 mg, 1.5 mmol) in dioxane (3.0 mL) afforded (*R$_a$*)-**4ce** (160.3 mg, 67%) (eluent: petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate = 20/1) as a liquid: 96% ee (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 100/0, 1.0 mL/min, λ = 214 nm, t_R(minor) = 19.7 min, t_R(major) = 20.4 min); $[\alpha]_D^{20}$ = -63.5 (*c* = 1.055, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 5.22-5.12 (m, 1 H, one proton of CH=C=CH), 5.11-5.03 (m, 1 H, one proton of CH=C=CH), 4.71 (bs, 1 H, NH), 3.77-3.63 (m, 2 H, NCH_2), 1.93-1.78 (m, 1 H, CH), 1.53-1.21 (m, 13 H, Me × 3 and CH_2 × 2), 0.90 (t, *J* = 7.4 Hz, 3 H, Me), 0.89 (t, *J* = 7.4 Hz, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.0, 155.6, 97.7, 89.0, 79.1, 42.7, 39.3, 28.3, 27.5, 27.2, 11.6, 11.4; IR (neat) ν (cm^{-1}) 3351, 2965, 2931, 2875, 1963, 1698, 1505, 1456, 1392, 1366, 1250, 1172, 1053; MS (EI) m/z (%): 239 (M^+, 0.01), 183 ($(M-{}^tBu+H)^+$, 45.91), 57 (100); HRMS calcd for $C_{14}H_{25}NO_2$ [M^+]: 239.1885, found: 239.1878.

7. Preparation of (*R$_a$*)-*tert*-butyl (4-bromophenyl-2,3-dienyl)carbamate (*R$_a$*)-4cf. (zjs-3-105)



The reaction of $CuBr_2$ (90.0 mg, 0.4 mmol), **1c** (233.1 mg, 1.5 mmol), (*S*)-**3** (254.0 mg, 1.0 mmol), and **2f** (278.2 mg, 1.5 mmol) in dioxane (3.0 mL) afforded (*R*$_a$)-**4cf** (195.0 mg, 60%) (eluent: petroleum ether/ethyl acetate = 25/1) as a oil: 97% ee (HPLC conditions: Chiralcel IB column, hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R(minor) = 7.5 min, t_R(major) = 8.1 min); $[\alpha]_D^{20}$ = -207.4 (*c* = 1.02, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.37 (m, 2 H, ArH), 7.13 (d, *J* = 8.4 Hz, 2 H, ArH), 6.23-6.17 (m, 1 H, one proton of CH=C=CH), 5.62 (q, *J* = 5.6 Hz, 1 H, one proton of CH=C=CH), 4.93 (bs, 1 H, NH), 3.93-3.70 (m, 2 H, NCH_2), 1.39 (s, 9 H, t-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 155.5, 132.8, 131.5, 128.3, 120.6, 96.3, 93.9, 79.3, 38.8, 28.2; IR (neat) ν (cm^{-1}) 3366, 2976, 2928, 1951, 1687, 1515, 1366, 1248, 1165, 1062, 1008; MS (EI) m/z (%): 269 ($(M(^{81}Br)\text{-}^tBu+H)^+$, 68.6), 267 ($(M(^{79}Br)\text{-}^tBu+H)^+$, 70.66), 57 (100); HRMS calcd for $C_{11}H_{10}NO_2{}^{79}Br$ [$(M(^{79}Br)\text{-}^tBu+H)^+$]: 266.9895, found: 266.9891.

8. Preparation of (*R*$_a$)-dimethyl 2-(4-cyclohexylbuta-2,3-dienyl)malonate (*R*$_a$)-4da. (hx-11-5)

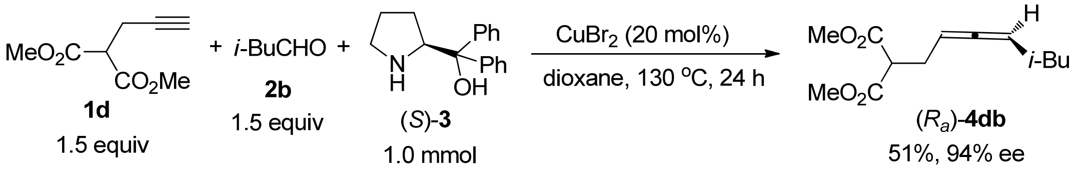


The reaction of $CuBr_2$ (44.8 mg, 0.2 mmol), **1d** (255.7 mg, 1.5 mmol), (*S*)-**3** (252.8 mg, 1.0 mmol), and **2a** (168.2 mg, 1.5 mmol) in dioxane (3.0 mL) afforded

(R_a)-**4da** (135.7 mg, 51%) (eluent: petroleum ether/ethyl acetate = 15/1) as a liquid:[1] 95% ee (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 100/1, 1.0 mL/min, λ = 214 nm, t_R(minor) = 9.0 min, t_R(major) = 9.6 min); $[\alpha]_D^{20}$ = -84.0 (*c* = 1.045, $CHCl_3$) (reported value: 99% ee; $[\alpha]_D^{20}$ = -85.4 (c = 1.05, $CHCl_3$)); ^1H NMR (300 MHz, $CDCl_3$) δ 5.20-5.08 (m, 2 H, CH=C=CH), 3.740 (s, 3 H, Me), 3.737 (s, 3 H, Me), 3.51 (t, *J* = 7.5 Hz, 1 H, CH), 2.63-2.54 (m, 2 H, CH_2), 2.00-1.85 (m, 1 H, CH from Cy), 1.78-1.57 (m, 5 H, five protons from Cy), 1.35-0.95 (m, 5 H, five protons from Cy); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.7, 169.33, 169.29, 98.9, 88.2, 52.4, 51.2, 37.1, 32.82, 32.78, 28.0, 26.0, 25.9; IR (neat) ν (cm^{-1}) 2926, 2851, 1959, 1757, 1738, 1617, 1436, 1343, 1233, 1155, 1035; MS (EI) m/z (%): 266 (M^+, 6.72), 91 (100).

9. Preparation of (*R*$_a$)-dimethyl 2-(6-methylhepta-2,3-dienyl)malonate (R_a)-4db.

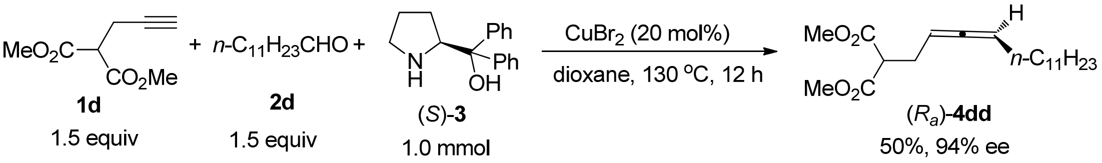
(hx-11-25)



The reaction of $CuBr_2$ (45.0 mg, 0.2 mmol), **1d** (255.7 mg, 1.5 mmol), (*S*)-**3** (252.5 mg, 1.0 mmol), and **2b** (129.6 mg, 1.5 mmol) in dioxane (3.0 mL) afforded (R_a)-**4db** (121.9 mg, 51%) (eluent: petroleum ether/ethyl acetate = 20/1) as a liquid: 94% ee (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 100/1, 0.7 mL/min, λ = 214 nm, t_R(minor) = 10.9 min, t_R(major) = 11.7 min); $[\alpha]_D^{20}$ = -64.4 (*c* = 0.87, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 5.15-5.04 (m, 2 H, CH=C=CH), 3.74 (s, 6 H, Me × 2), 3.51 (t, *J* = 7.5 Hz, 1 H, CH), 2.62-2.54 (m, 2 H, CH_2), 1.90-1.82 (m, 2 H, CH_2), 1.72-1.56 (m, 1 H, CH), 0.910 (d, *J* = 6.6 Hz, 3 H, Me), 0.906 (d, *J* = 6.6 Hz, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.6, 169.3, 169.2, 91.3, 86.6, 52.4, 51.3, 38.2, 28.3, 28.0, 22.09, 22.06; IR (neat) ν (cm^{-1}) 2956, 2927, 2869, 1964, 1754, 1739, 1436, 1342, 1271, 1232, 1154, 1044; MS (EI) m/z (%): 240 (M^+, 27.06), 97 (100); HRMS calcd for $C_{13}H_{20}O_4$ [M^+]: 240.1362, found: 240.1362.

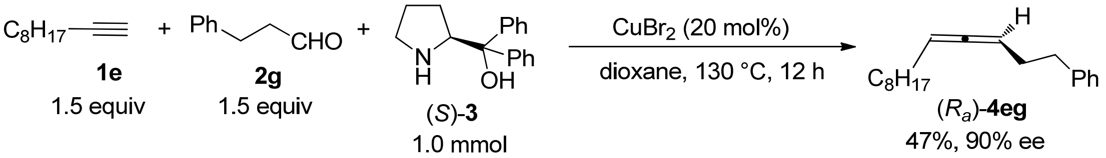
10. Preparation of (*R_a*)-dimethyl 2-(pentadeca-2,3-dienyl)malonate (*R_a*)-4dd.

(ty-1-68)



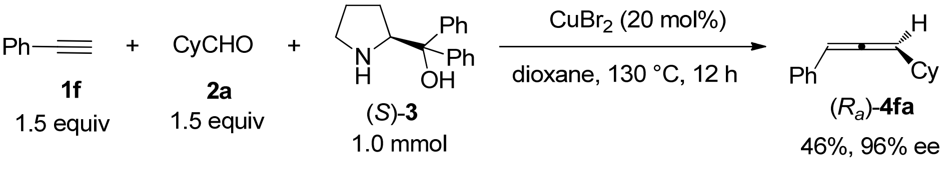
The reaction of $CuBr_2$ (45.1 mg, 0.2 mmol), **1d** (255.8 mg, 1.5 mmol), (*S*)-**3** (253.8 mg, 1.0 mmol), and **2d** (277.1 mg, 1.5 mmol) in dioxane (3.0 mL) afforded (R_a)-**4dd** (170.4 mg, 50%) (eluent: petroleum ether/ethyl acetate = 100/1) as a liquid: 94% ee (HPLC conditions: Chiralcel PC-4 column, MeOH/H_2O = 82/18, 0.7 mL/min, λ = 214 nm, t_R(minor) = 37.5 min, t_R(major) = 39.7 min); $[\alpha]_D^{26}$ = -49.9 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19-5.06 (m, 2 H, CH=C=CH), 3.74 (s, 6 H, Me × 2), 3.51 (t, *J* = 7.4 Hz, 1 H, CH), 2.63-2.53 (m, 2 H, CH_2), 1.98-1.90 (m, 2 H, CH_2), 1.42-1.24 (m, 18 H, $(CH_2)_9$), 0.88 (t, *J* = 6.6 Hz, 3 H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 169.4, 169.3, 93.0, 87.3, 52.5, 51.2, 31.9, 29.6, 29.5, 29.3, 29.15, 29.07, 28.8, 28.0, 22.7, 14.1; IR (neat) ν (cm^{-1}) 2923, 2853, 1964, 1755, 1738, 1436, 1340, 1262, 1230, 1151, 1080, 1041; MS (EI) m/z (%): 338 (M^+, 5.34), 138 (100); HRMS calcd for $C_{20}H_{34}O_4$ [M^+]: 338.2457, found: 338.2458.

11. Preparation of (*R_a*)-phenyltrideca-3,4-diene (*R_a*)-4eg. (hx-11-74)



The reaction of $CuBr_2$ (44.9 mg, 0.2 mmol), **1e** (207.8 mg, 1.5 mmol), (*S*)-**3** (253.4 mg, 1.0 mmol), and **2g** (201.5 mg, 1.5 mmol) in dioxane (3.0 mL) afforded (*R_a*)-**4eg** (119.3 mg, 47%) (eluent: petroleum ether) as a liquid: 90% ee (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 100/0, 0.3 mL/min, λ = 214 nm, t_R(minor) = 17.9 min, t_R(major) = 19.7 min); $[\alpha]_D^{20}$ = -50.0 (*c* = 0.84, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.30-7.21 (m, 2 H, ArH), 7.21-7.12 (m, 3 H, ArH), 5.16-5.02 (m, 2 H, CH=C=CH), 2.72 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.35-2.20 (m, 2 H, CH_2), 1.99-1.87 (m, 2 H, CH_2), 1.42-1.18 (m, 12 H, $CH_2 \times 6$), 0.88 (t, *J* = 6.8 Hz, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.0, 141.9, 128.5, 128.2, 125.8, 91.5, 90.2, 35.5, 31.9, 30.7, 29.4, 29.3, 29.2, 29.1, 28.9, 22.7, 14.1; IR (neat) ν (cm^{-1}) 3086, 3063, 3027, 2924, 2854, 1962, 1721, 1604, 1496, 1455, 1373, 1331, 1284, 1075, 1028; MS (EI) m/z (%): 256 (M^+, 12.85), 91 (100); HRMS calcd for $C_{19}H_{28}$ [M^+]: 256.2191, found: 256.2194.

12. Preparation of (*R_a*)-3-cyclohexyl-1-phenylpropa-1,2-diene (*R_a*)-4fa. (hx-11-18)



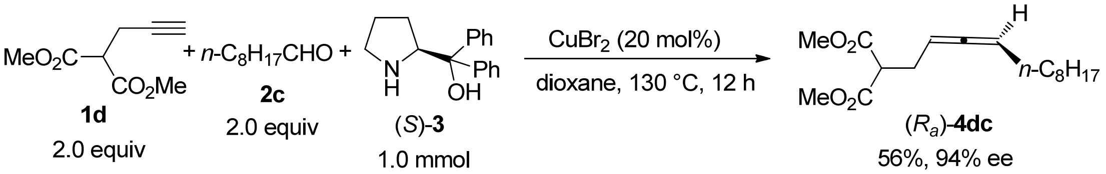
The reaction of $CuBr_2$ (44.8 mg, 0.2 mmol), **1f** (153.2 mg, 1.5 mmol), (*S*)-**3** (253.1 mg, 1.0 mmol), and **2a** (168.4 mg, 1.5 mmol) in dioxane (3.0 mL) afforded (*R_a*)-**4fa** (90.1 mg, 46%) (eluent: petroleum ether) as a liquid:[3] 96% ee (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 100/0, 0.3 mL/min, λ = 214 nm,

t_R(major) = 20.1 min, t_R(minor) = 22.1 min); $[\alpha]_D^{20}$ = -355.3 (*c* = 1.01, $CHCl_3$) (reported value: 99% ee; $[\alpha]_D^{19}$ = -330.3 (c = 0.94, $CHCl_3$)) (We repeated the reaction reported in ref. 3 and measured the ee and the specific optical rotation of this compound again: 99% ee; $[\alpha]_D^{20}$ = -379.0 (c = 1.125, $CHCl_3$), thus, the data in ref. 3 for this specific compound should be corrected); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.23 (m, 4 H, ArH), 7.21-7.11 (m, 1 H, ArH), 6.15 (dd, J_1 = 6.6 Hz, J_2 = 3.0 Hz, 1 H, one proton from CH=C=CH), 5.56 (t, *J* = 6.3 Hz, 1 H, one proton from CH=C=CH), 2.20-2.04 (m, 1 H, CH), 1.90-1.57 (m, 5 H, five protons from Cy), 1.38-1.09 (m, 5 H, five protons from Cy); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.1, 135.2, 128.5, 126.6, 126.4, 101.0, 95.4, 37.6, 33.2, 33.1, 26.1, 26.0; IR (neat) ν (cm^{-1}) 3082, 3062, 3030, 2924, 2851, 1946, 1597, 1496, 1458, 1257, 1071, 1028; MS (EI) m/z (%): 198 (M^+, 30.22), 130 (100).

Synthesis of naturally occurring allenes

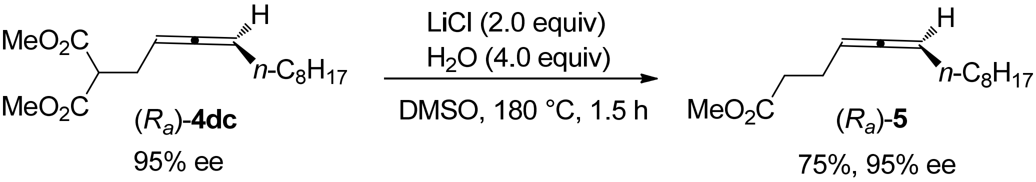
1. Synthesis of naturally occurring insect pheromone (*R_a*)-6

(1) Preparation of (*R*)-dimethyl 2-(dodeca-2,3-dienyl)malonate (*R_a*)-4rk on 4.0 mmol scale. (tangxj-8-154)



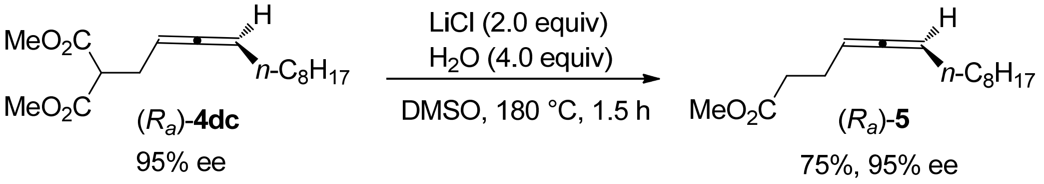
Following **Typical Procedure I**, the reaction of $CuBr_2$ (44.5 mg, 0.2 mmol), **1d** (340.2 mg, 2.0 mmol), (*S*)-**3** (254.1 mg, 1.0 mmol), and **2c** (285.1 mg, 2.0 mmol) in dioxane (3.0 mL) afforded (*R_a*)-**4dc** (166.3 mg, 56%) (eluent: petroleum ether/ethyl acetate = 50/1) as a liquid: 94% ee (HPLC conditions: Chiralcel PC-4 column, MeOH/H_2O = 82/18, 0.7 mL/min, λ = 214 nm, t_R(minor) = 19.9 min, t_R(major) = 21.0 min); $[\alpha]_D^{29.5}$ = -61.8 (c = 1.02, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.24-5.04 (m, 2 H, CH=C=CH), 3.74 (s, 6 H, 2 × CH_3), 3.51 (t, J = 7.6 Hz, 1 H, CH), 2.64-2.51 (m, 2 H, CH_2), 2.00-1.86 (m, 2 H, CH_2), 1.41-1.19 (m, 12 H, 6 × CH_2), 0.88 (t, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 169.34, 169.28, 93.0, 87.3, 52.4, 51.2, 31.8, 29.4, 29.2, 29.1, 29.0, 28.7, 28.0, 22.6, 14.0; IR (neat) ν (cm^{-1}) 2954, 2925, 2854, 1965, 1738, 1436, 1340, 1261, 1230, 1152, 1081, 1040; MS (EI) m/z (%): 296 (M^+, 4.51), 138 (100); HRMS calcd. for $C_{17}H_{28}O_4$ (M^+): 296.1988; Found: 296.1992.

(2) Preparation of (*R*)-methyl tetradeca-4,5-dienoate (*R_a*)-5.[4] (hanyl-3-81)



To a Schlenk tube were added LiCl (145.0 mg, purity = 98%, 3.36 mmol), (R_a)-**4dc** (499.6 mg, 1.68 mmol), DMSO (9.0 mL), and H_2O (119.5 mg, 6.72 mmol) sequentially. The Schlenk tube was then equipped with a condenser and heasated with stirring with a preheated 180 °C oil bath. The reaction was complete after being stirred for 1.5 h as monitored by TLC. Then the resulting mixture was diluted with ethyl acetate (20 mL) and quenched with H_2O (7.0 mL). The organic layer was separated, washed with H_2O (3 × 10 mL) and brine (3 × 10 mL), and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford (R_a)-**5** (301.0 mg, 75%) as a liquid: 95% ee (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 100/0, 0.8 mL/min, λ = 214 nm, t_R(minor) = 12.7 min, t_R(major) = 13.4 min); $[\alpha]_D^{26.0}$ = -52.4 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400M Hz, $CDCl_3$) δ 5.21-5.09 (m, 2 H, C=CH), 3.72-3.65 (s, 3 H, CO_2CH_3), 2.43 (t, *J* = 7.4 Hz, 2 H, $COCH_2$), 2.35-2.26 (m, 2 H, $C=CCH_2$), 2.03-2.19 (m, 2 H, $C=CCH_2$), 1.42-1.21 (m, 12 H, 6×CH_2), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (100M Hz, $CDCl_3$) δ 203.6, 173.6, 92.6, 89.4, 51.5, 33.2, 31.8, 29.4, 29.3, 29.1, 28.8, 23.8, 22.6, 14.1; IR (neat) ν (cm^{-1}) 2954, 2924, 2854, 1963, 1699, 1458, 1436, 1362, 1298, 1254, 1224, 1197, 1159, 1058, 1017; MS (EI) m/z (%): 238 (M^+, 8.93), 80 (100); HRMS calcd. for $C_{15}H_{26}O_2$ (M^+): 238.1933; Found: 238.1930.

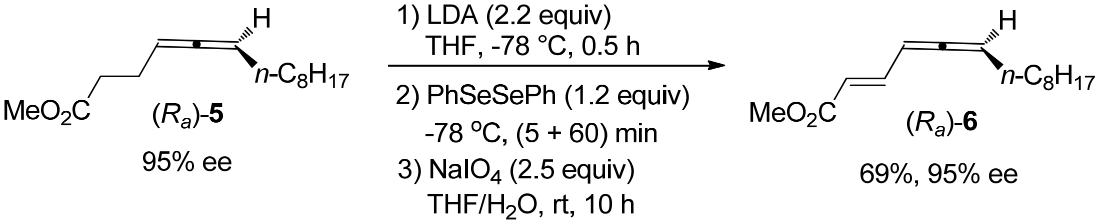
(3) Preparation of (*R*)-methyl tetradeca-4,5-dienoate (*R*$_a$)-5.[4] (hanyl-3-81)



To a Schlenk tube were added LiCl (145.0 mg, purity = 98%, 3.36 mmol), (*R*$_a$)-**4dc** (499.6 mg, 1.68 mmol), DMSO (9.0 mL), and H_2O (119.5 mg, 6.72 mmol) sequentially. The Schlenk tube was then equipped with a condenser and heated in an oil bath preheated at 180 °C. The reaction was complete after being stirred for 1.5 h as monitored by TLC. Then the resulting mixture was diluted with ethyl acetate (20 mL) and quenched with H_2O (7.0 mL). The organic layer was separated, washed with H_2O (3 × 10 mL) and brine (3 × 10 mL), and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford (*R*$_a$)-**5** (301.0 mg, 75%) as a liquid: 95% ee (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 100/0, 0.8

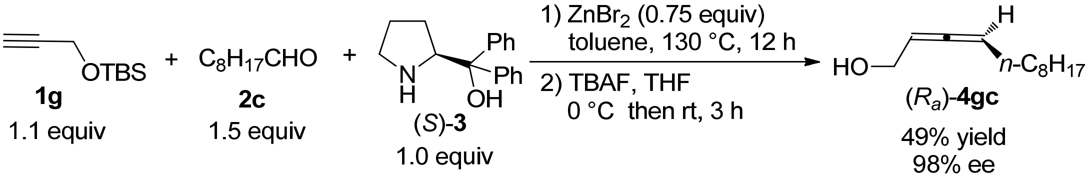
mL/min, λ = 214 nm, t_R(minor) = 12.7 min, t_R(major) = 13.4 min); $[\alpha]_D^{26.0}$ = -52.4 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21-5.09 (m, 2 H, CH=C=CH), 3.68 (s, 3 H, OCH_3), 2.43 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.35-2.25 (m, 2 H, CH_2), 2.03-1.90 (m, 2 H, CH_2), 1.42-1.20 (m, 12 H, 6 × CH_2), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 173.6, 92.6, 89.4, 51.5, 33.2, 31.8, 29.4, 29.3, 29.1, 28.9, 23.8, 22.6, 14.1; IR (neat) ν (cm^{-1}) 2954, 2924, 2854, 1963, 1741, 1458, 1436, 1362, 1298, 1254, 1224, 1197, 1159, 1058, 1017; MS (EI) m/z (%): 238 (M^+, 8.93), 80 (100); HRMS calcd. for $C_{15}H_{26}O_2$ (M^+): 238.1933; Found: 238.1930.

(4) Preparation of (*R*,*E*)-methyl tetradeca-2,4,5-trienoate (*R*$_a$)-6.[4] (zjs-3-109)



To a flame-dried Schlenk tube was added LDA (0.55 mL, 2 M in THF, 1.1 mmol) under nitrogen atmosphere. Then a solution of (*R*$_a$)-**5** (120.6 mg, 0.5 mmol) in THF (2.0 mL) was added dropwise in 5 minutes at -78 °C. After the reaction mixture was stirred for 0.5 h, a solution of PhSeSePh (191.1 mg, purity = 98%, 0.6 mmol) in THF (2.0 mL) was added dropwise in 5 minutes at -78 °C. After being stirred for another 1.0 h at -78 °C, the reaction was quenched with a saturated aq. solution of NH_4Cl (1.0 mL). The resulting mixture was extracted with ether (10 mL) and the organic layer was separated, which was washed with brine (3 × 3 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography (eluent: petroleum ether/ethyl acetate = 50/1) on silica gel to afford a yellow oil, which was transferred to another Schlenk tube with THF (2.0 mL). Then a solution of $NaIO_4$ (268.7 mg, 1.25 mmol) in water (1.0 mL) was added. After being stirred for 10 h at room temperature, the resulting mixture was diluted with ether (15.0 mL) and washed with brine (3 × 3 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography (eluent: petroleum ether/ethyl acetate = 500/1) on silica gel to afford (R_a)-**6** (82.6 mg, 69%) as a liquid: 95% ee (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 95/5, 0.5 mL/min, λ = 214 nm, t_R(minor) = 9.0 min, t_R(major) = 10.3 min); $[\alpha]_D^{26.0}$ = -130.9 (*c* = 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J_1 = 15.4 Hz, J_2 = 11.0 Hz, 1 H, =CH), 5.96-5.80 (m, 2 H, one proton of CH=C=CH and =CH), 5.44 (q, *J* = 6.4 Hz, 1 H, one proton of CH=C=CH), 3.73 (s, 3 H, Me), 2.12-2.00 (m, 2 H, CH_2), 1.49-1.19 (m, 12 H, CH_2 × 6), 0.88 (t, *J* = 6.6 Hz, 3 H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.5, 167.1, 142.9, 118.8, 92.9, 92.8, 51.4, 31.8, 29.3, 29.2, 29.0, 28.8, 28.0, 22.6, 14.0; IR (neat) ν (cm^{-1}) 2924, 2854, 1942, 1719, 1628, 1460, 1436, 1304, 1263, 1240, 1175, 1137, 1094, 1039, 1016; MS (EI) m/z (%): 236 (M^+, 4.79), 79 (100); HRMS calcd. for $C_{15}H_{24}O_2$ (M^+): 236.1776; Found: 236.1773.

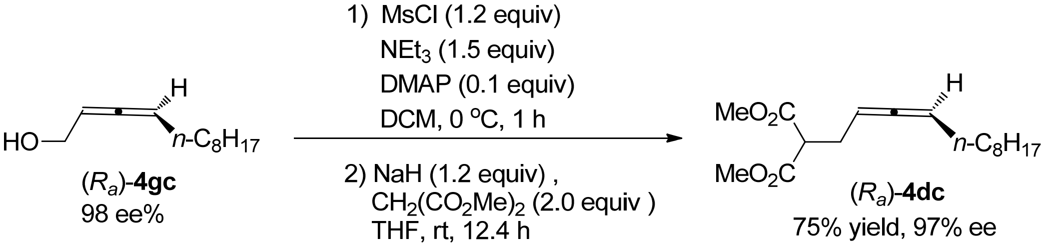
(5) Preparation of (*R*)-2,3-dodecadien-1-ol (*Ra*)-4gc**[1] (yq-11-63, yq-11-71)



To a flame-dried three-necked 250-mL round-bottom flask was added $ZnBr_2$ powder (3.3341 g, 15 mmol) under an argon atmosphere. Then the flask was dried under vacuum with a heating gun for about 1 minute. After cooling to room temperature, (*S*)-**3** (5.0631 g, 20 mmol) and **1g** (3.7430 g, 22 mmol) were added sequentially with stirring under argon atmosphere at room temperature. The suspension was allowed to stir for 5 minutes at room temperature before 60 mL of freshly distilled toluene were added. Then freshly distilled aldehyde **2c** (5.1 mL, d = 0.83 g/mL, 4.23 g, 30 mmol) was added. The resulting mixture was stirred for 3 minutes at room temperature. The flask was then heated in a pre-heated oil bath of 130 °C for 12 h with stirring. After cooling to room temperature, the crude reaction mixture was concentrated by rotary evaporation, flash chromatography on silica gel (eluent: petroleum ether/ethyl ether = 40/1) afforded an orange-red liquid.

To a 250-mL flask cooled with an ice-water bath were added the crude product prepared above, 60 mL of THF, and TBAF (5.2203 g, 20 mmol) sequentially. Then the ice-water bath was removed and the resulting mixture was allowed to stir at room temperature. After 3 h, the reaction was complete as monitored by TLC, and the resulting mixture was poured into 30 mL of water and extracted with ethyl ether (100 mL). The organic layer was separated, washed sequentially with water (3 × 20 mL) and brine (3 × 20 mL), and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford (R_a)-**4gc** (1.7847 g, 49% yields over the two steps) as an oil:[5] 98% ee (HPLC conditions: Chiralcel AS-H column, hexane/i-PrOH = 200/1, 1.0 mL/min, λ = 214 nm, t_R(major) = 10.3 min, t_R(minor) = 11.0 min); $[\alpha]_D^{22}$ = - 69.1 (c = 1.02, hexane) (reported value: 95% ee; $[\alpha]_D^{26.1}$ = -61.7 (*c* = 0.98, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 5.36-5.24 (m, 2 H, CH=C=CH), 4.15-4.07 (m, 2 H, OCH_2), 2.08-1.94 (m, 2 H, CH_2), 1.53-1.15 (m, 13 H, OH and 6 × CH_2), 0.88 (t, $J = 6.8$ Hz, 3 H, CH_3).

(6) Synthesis of (*R*)-dimethyl 2-(2,3-dodecadienyl)maloate (*R*)

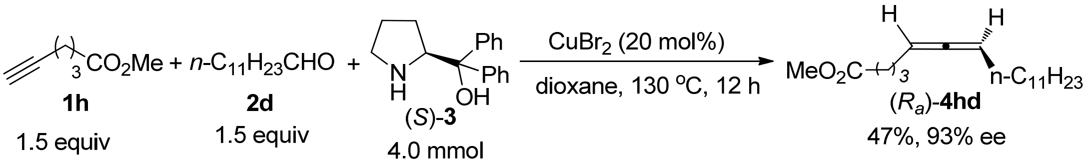


To a flame-dried 100 mL Schlenk bottle were added DMAP (122.4 mg, 1 mmol), anhydrous NEt_3 (2.1 mL, d = 0.726 g/mL, 1.515 g, 12 mmol), (R_a)-**4gc** (1.8209 mg, 10 mmol, 98% ee), and dry DCM (30 mL) sequentially under Ar atmosphere at room temperature. MsCl (0.9 mL, d =1.475, 1.33 g, 0.6 mmol) was added dropwise within 10 min via a syringe at 0 °C. The resulting mixture was stirred at 0 °C for 1 h and quenched with sat. $NaHCO_3$ (aq., 5 mL). DCM (50 mL) was added and the organic layer was washed sequentially with water (3 × 10 mL) and brine (3 × 10 mL), and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was used in the next step without further purification.

To another flame-dried Schlenk bottle were added NaH (480.7 mg, 12 mmol, 60% in mineral oil) and dry THF (30 mL). Dimethyl malonate (2.3 mL, d = 1.151 g/mL, 2.64 g, 12 mmol) were then added dropwise within 5 min via a syringe at Ar atmosphere at room temperature. The resulting mixture was allowed to stir for 30 min at rt. The crude mesylate prepared above was then dissolved in 10 mL of dry THF and added dropwise within 5 h via a syringe pump (2 mL/hour) at rt. After 12.4 h, the reaction was complete as monitored by TLC, quenched with H_2O (5 mL), and extracted with Et_2O (50 mL). The organic layer was separated, washed with H_2O (3 × 10 mL) and brine (3 × 10 mL), and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on silica gel to afford (R_a)-**4dc** (2.2201 g, 75% over the two steps) (eluent: petroleum ether/ethyl ether = 30/1) as a liquid: 97% ee (HPLC conditions: Chiralcel OD-H column, hexane/i-PrOH = 100/1, 1 mL/min, λ = 214 nm, t_R(minor) = 8.3 min, t_R(major) = 9.0 min); $[\alpha]_D^{22}$ = - 58.2 (c = 1.01, hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 5.19-5.05 (m, 2 H, CH=C=CH), 3.74 (s, 6 H, 2 × OCH_3), 3.50 (t, J = 7.7 Hz, 1 H, CH), 2.61-2.53 (m, 2 H, CH_2), 1.99-1.87 (m, 2 H, CH_2), 1.43-1.18 (m, 12 H, 6 × CH_2), 0.87 (t, J = 6.8 Hz, 3 H, CH_3).

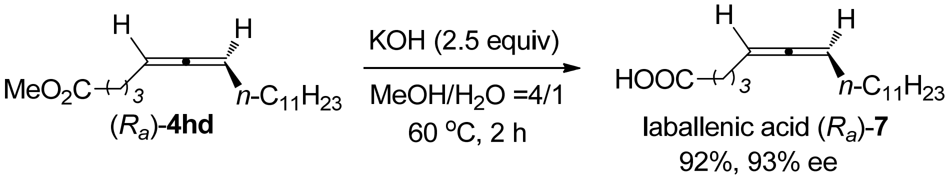
2. Preparation of (*R*)-octadeca-5,6-dienoic acid (laballenic acid)

(1) Preparation of (*R*)-methyl octadeca-5,6-dienoate (R_a)-4hd. (jxg-1-55)



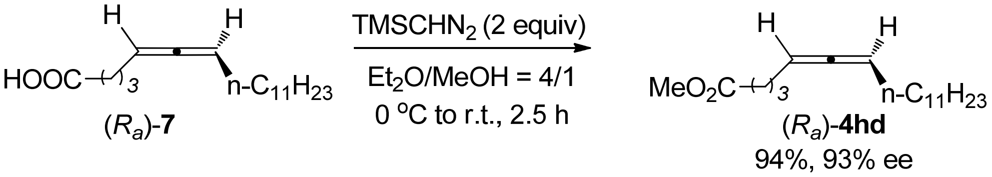
Following **Typical Procedure I**, the reaction of $CuBr_2$ (178.4 mg, 0.8 mmol), **1h** (781.0 mg, 6.0 mmol), (*S*)-**3** (1.0181 g, 4.0 mmol), and **2d** (1106.2 mg, 6.0 mmol) in dioxane (12 mL) afforded (R_a)-**4hd** (560.6 mg, 47%) (eluent: petroleum ether/ethyl ether = 200/1) as a liquid:[6] 93% ee (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 100/0, 0.5 mL/min, λ = 214 nm, t_R(major) = 21.0 min, t_R(minor) = 20.0 min); $[\alpha]_D^{27.1}$ = -41.0 (*c* = 1.03, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.13-5.00 (m, 2 H, CH=C=CH), 3.67 (s, 3 H, CH_3), 2.36 (t, J = 7.4 Hz, 2 H, CH_2), 2.06-1.94 (m, 4 H, 2 × CH_2), 1.74 (quint, J = 7.4 Hz, 2 H, CH_2), 1.43-1.20 (m, 18 H, 9 × CH_2), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 174.0, 91.4, 89.7, 51.4, 33.3, 31.9, 29.65, 29.61, 29.5, 29.3, 29.2, 29.1, 28.9, 28.3, 24.2, 22.7, 14.1; IR (neat, cm^{-1}): 2923, 2853, 1962, 1741, 1458, 1437, 1364, 1242, 1199, 1154, 1061, 1018; MS (EI) m/z (%): 294 (M$^+$, 2.11), 80 (100).

(2) Preparation of (*R*)-octadeca-5,6-dienoic acid (laballenic acid) (*R*$_a$)-**7.** (jxg-1-66)



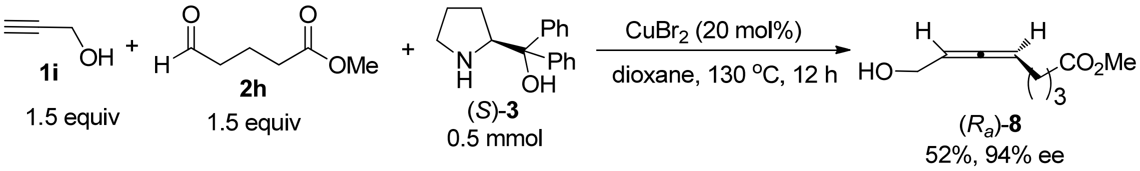
To a round bottom flask, KOH (140.8 mg, 2.5 mmol), mixed solvent (5 mL, MeOH/H_2O = 4/1 by volume), and (*R*$_a$)-**4hd** (294.7 mg, 1 mmol)/mixed solvent (5 mL, MeOH/H_2O = 4/1 by volume) were added sequentially. The resulting mixture was then stirred at 60 ^{o}C. After 2 h as monitored by TLC, the reaction was complete. HCl (3 M, 1 mL) was added dropwise after the mixture was cooled with an ice bath. MeOH was removed by rotary evaporation. 30 mL of CH_2Cl_2 and water were added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (15 mL × 3). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on silica gel to afford (*R*$_a$)-**7** (257.6 mg, 92%) (eluent: petroleum ether/ethyl acetate = 10/1 to 2/1) as a liquid:[6] 93% ee (determined after esterification; HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 100/0, 0.5 mL/min, λ = 214 nm, t_R(major) = 21.7 min, t_R(minor) = 21.0 min); $[\alpha]_D^{27.0}$ = -50.6 (*c* = 1.025, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.99 (br s, 1 H, COOH) 5.15-5.01 (m, 2 H, CH=C=CH), 2.40 (t, *J* = 7.6 Hz, 2 H, CH_2), 2.08-1.94 (m, 4 H, 2 × CH_2), 1.75 (quint, *J* = 7.4 Hz, 2 H, CH_2), 1.45-1.22 (m, 18 H, 9 × CH_2), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 180.3, 91.6, 89.6, 33.3, 31.9, 29.67, 29.65, 29.5, 29.4, 29.2, 29.1, 28.9, 28.2, 23.9, 22.7, 14.1; IR (neat, cm^{-1}): 2922, 2853, 1962, 1708, 1457, 1439, 1413, 1378, 1287, 1240, 1204, 1157, 1061, 1056; MS (EI) m/z (%): 280 (M^+, 1.65), 140 (100).

(3) Determination of ee for (*R*)-octadeca-5,6-dienoic acid. (jxg-1-69)



To a round bottom flask, (*R*$_a$)-**7** (55.9 mg, 0.2 mmol) and mixed solvent (5 mL, Et_2O/MeOH = 4/1 by volume) were added. $TMSCHN_2$ (2 M in hexane, 0.2 mL, 0.4 mmol) was added dropwise after the mixture was cooled to 0 °C. The reaction mixture was then warmed up to room temperature naturally. When the reaction was complete as monitored by TLC after 2.5 h, the solvent was evaporated under vacuum, and the residue was purified by chromatography on silica gel on silica gel to afford (*R$_a$*)-**4hd** (55.0 mg, 94%) (eluent: petroleum ether then petroleum ether /ethyl acetate = 50/1) as a liquid:[6] 93% ee (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 100/0, 0.5 mL/min, λ = 214 nm, t_R(major) = 21.7 min, t_R(minor) = 21.0 min); $[\alpha]_D^{27.2}$ = -44.4 (*c* = 0.970, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15-4.99 (m, 2 H, CH=C=CH), 3.67 (s, 3 H, CH_3), 2.36 (t, *J* = 7.6 Hz, 2 H, CH_2), 2.09-1.91 (m, 4 H, 2 × CH_2), 1.74 (quint, *J* = 7.4 Hz, 2 H, CH_2), 1.45-1.19 (m, 18 H, 9 × CH_2), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 174.0, 91.5, 89.7, 51.4, 33.3, 31.9, 29.65, 29.62, 29.5, 29.3, 29.2, 29.1, 28.9, 28.3, 24.3, 22.7, 14.1

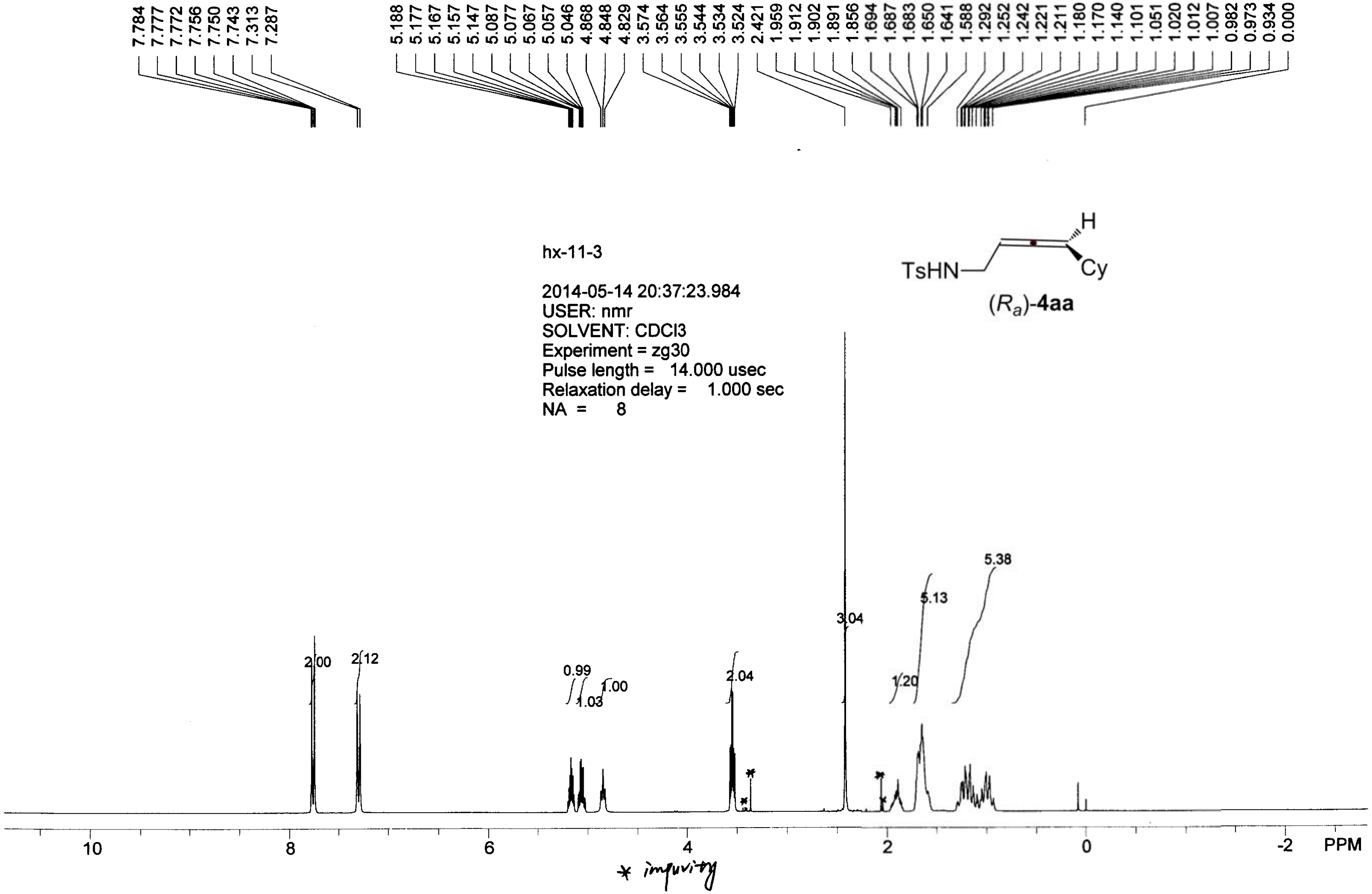
3. Preparation of (*R*)-methyl 8-hydroxyocta-5,6-dienoate (*R*$_a$)-8. (jxg-1-74)



Following **Typical Procedure I**, the reaction of $CuBr_2$ (22.5 mg, 0.1 mmol), **1i** (42.5 mg, 0.75 mmol), (*S*)-**3** (126.9 mg, 0.5 mmol), and **2h** (97.9 mg, 0.75 mmol) in dioxane (1.5 mL) afforded (*R*$_a$)-**8** (44.6 mg, 52%) (eluent: petroleum ether/ethyl acetate = 10/1 to 8/1 to 6/1) as a liquid:[7,8] 94% ee (HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 95/5, 0.6 mL/min, λ = 214 nm, t_R(major) = 25.7 min, t_R(minor) = 27.3 min); $[\alpha]_D^{27.0}$ = -48.9 (*c* = 0.99, $CHCl_3$) (reported value: 90% ee; $[\alpha]_D^{22}$ = -42.0 (c = 0.3, $CHCl_3$); from nature: $[\alpha]_D^{12}$ = -51.3 (c = 0.94, $CHCl_3$)); ^1H NMR (400 MHz, $CDCl_3$) δ 5.39-5.32 (m, 1 H, CH), 5.30-5.22 (m, 1 H, CH), 4.12 (dd, J_1 = 6.0 Hz, J_2 = 2.8 Hz, 2 H, OCH_2), 3.68 (s, 3 H, OCH_3), 2.41-2.35 (m, 2 H, CH_2), 2.16-2.03 (m, 3 H, CH_2 and OH), 1.84-1.72 (m, 2 H, CH_2) ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 174.2, 92.32, 92.29, 60.6, 51.6, 33.1, 27.7, 24.0; IR (neat) ν (cm^{-1}) 3404, 2951, 2869, 1963, 1732, 1438, 1365, 1317, 1244, 1201, 1154, 1056, 1009; MS (EI) m/z (%): 170 (M^+, 1.64), 110 (100).

References

1. J. Ye, W. Fan, S. Ma, *Chem. Eur. J.*, 2013, **19**, 716.
2. J. Ye, S. Li, B. Chen, W. Fan, J. Kuang, J. Liu, Y. Liu, B. Miao, B. Wan, Y. Wang, X. Xie, Q. Yu, W. Yuan, S. Ma, *Org. Lett.*, 2012, **14**, 1346.
3. R. Lü, J. Ye, T. Cao, B. Chen, W. Fan, W. Lin, J. Liu, H. Luo, B. Miao, S. Ni, X. Tang, N. Wang, Y. Wang, X. Xie, Q. Yu, W. Yuan, W. Zhang, C. Zhu, S. Ma, *Org. Lett.*, 2013, **15**, 2254.
4. M. Ogasawara, T. Nagano, T. Hayashi, *J. Org. Chem.*, 2005, **70**, 5764.
5. X. Huang, T. Cao, Y. Han, X. Jiang, W. Lin, J. Zhang, S. Ma, *Chem. Commun.*, 2015, **51**, 6956.
6. S. R. Landor, B. J. Miller, A. R. Tatchell, *J. Chem. Soc. C*, 1966, 1822.
7. O. W. Gooding, C. C. Beard, D. Y. Jackson, D. L. Wren, G. F. Cooper, *J. Org. Chem.*, 1991, **56**, 1083.
8. Y. Zhang, H. Hao, Y. Wu, *Synlett*, 2010, 905.



(R_a)-**4aa**

hx-11-3

2014-05-14 20:37:23.984
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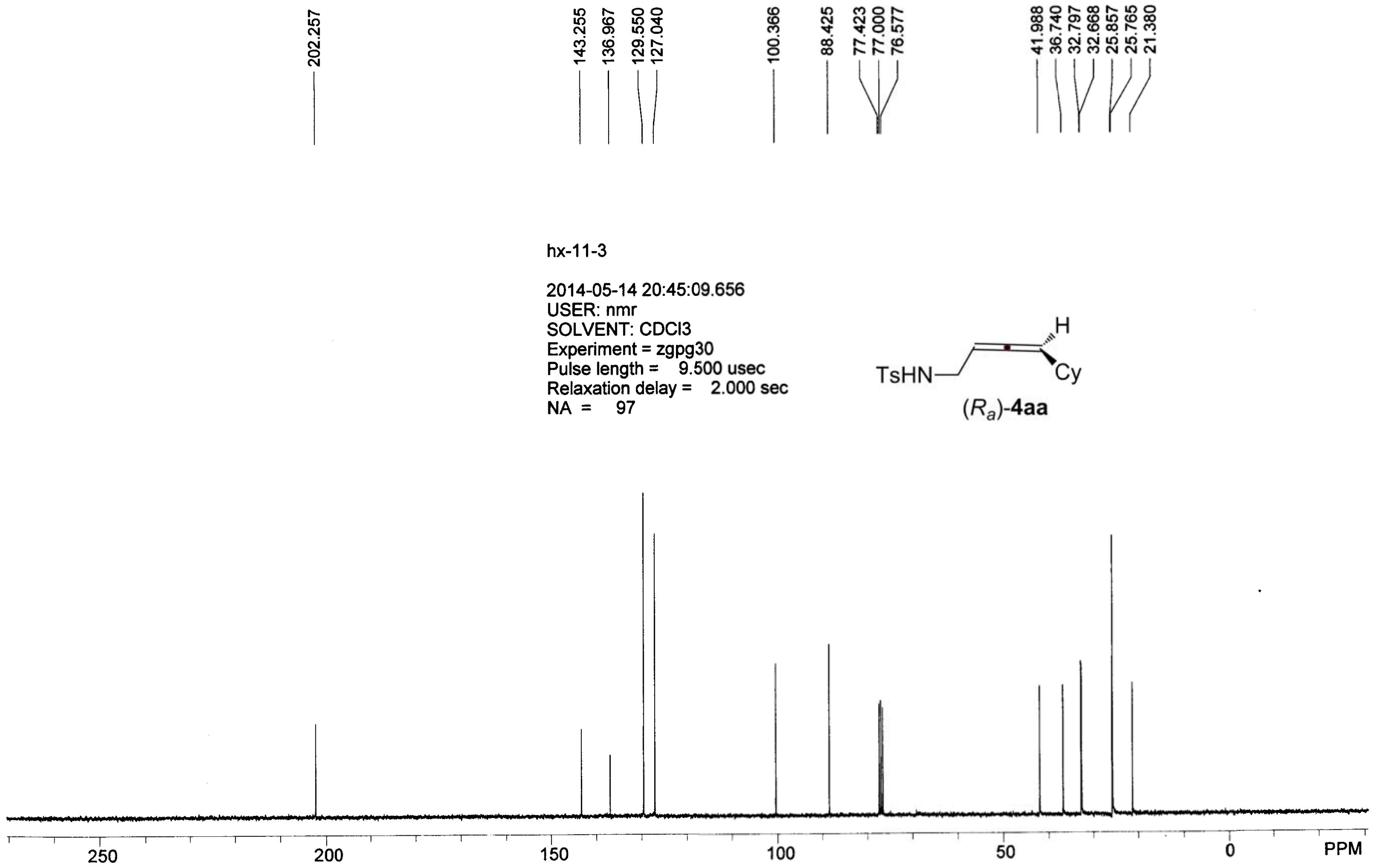
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8

* impurity



hx-11-3

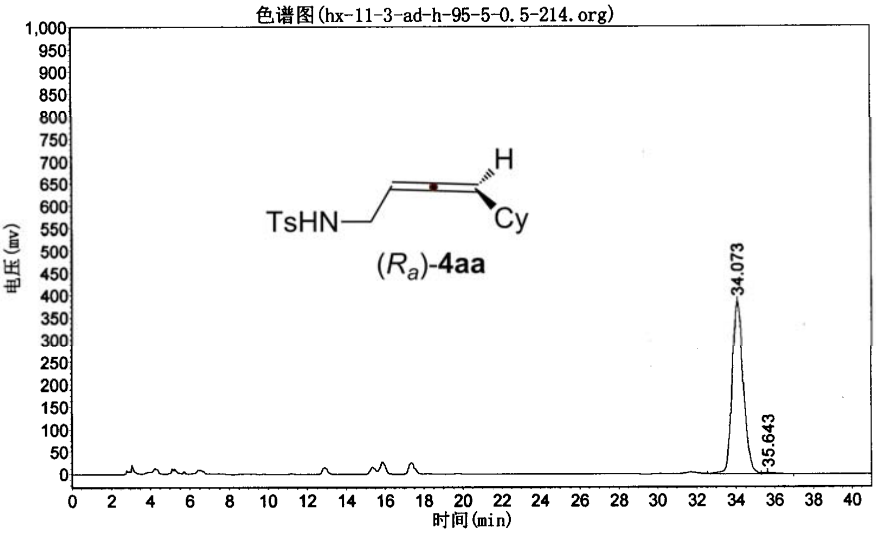
2014-05-14 20:45:09.656
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 97

(R_a)-**4aa**

hx-11-3-ad-h-95-5-0.5-214

实验时间：2014-05-20,17:43:15　　报告时间：2014-05-20,19:28:39
谱图文件:D:\zhuguangjiong\hx\20140515\hx-11-3-ad-h-95-5-0.5-214.org

实验内容简介:
ad-h 95/5
0.5ml/min 214nm



分析结果表

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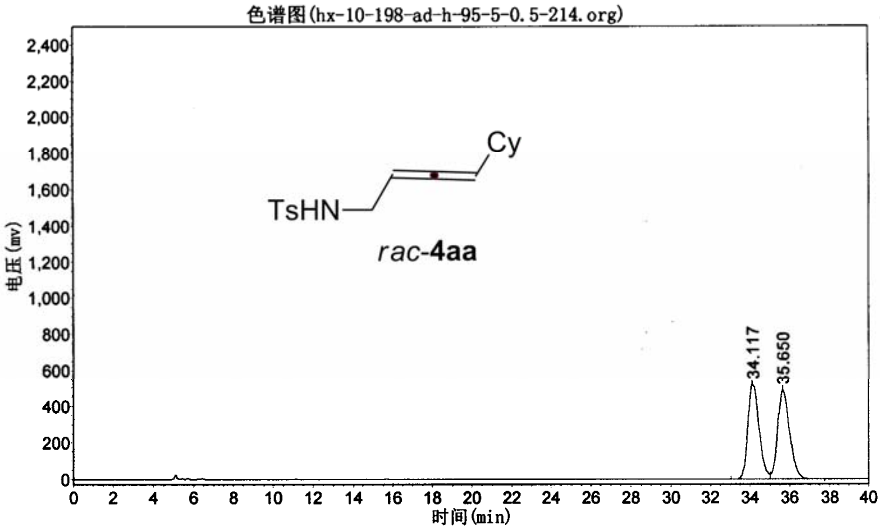
2		35.643	3234.943	131301.094	0.8400
总计			389117.286	15630891.094	100.0000

hx-10-198-ad-h-95-5-0.5-214

实验时间：2014-05-20,17:00:14　　　　　　　　　　报告时间：2014-05-20,19:23:40
谱图文件:D:\zhuguangjiong\hx\20140515\hx-10-198-ad-h-95-5-0.5-214.org

实验内容简介：

色谱图(hx-10-198-ad-h-95-5-0.5-214.org)



分析结果表

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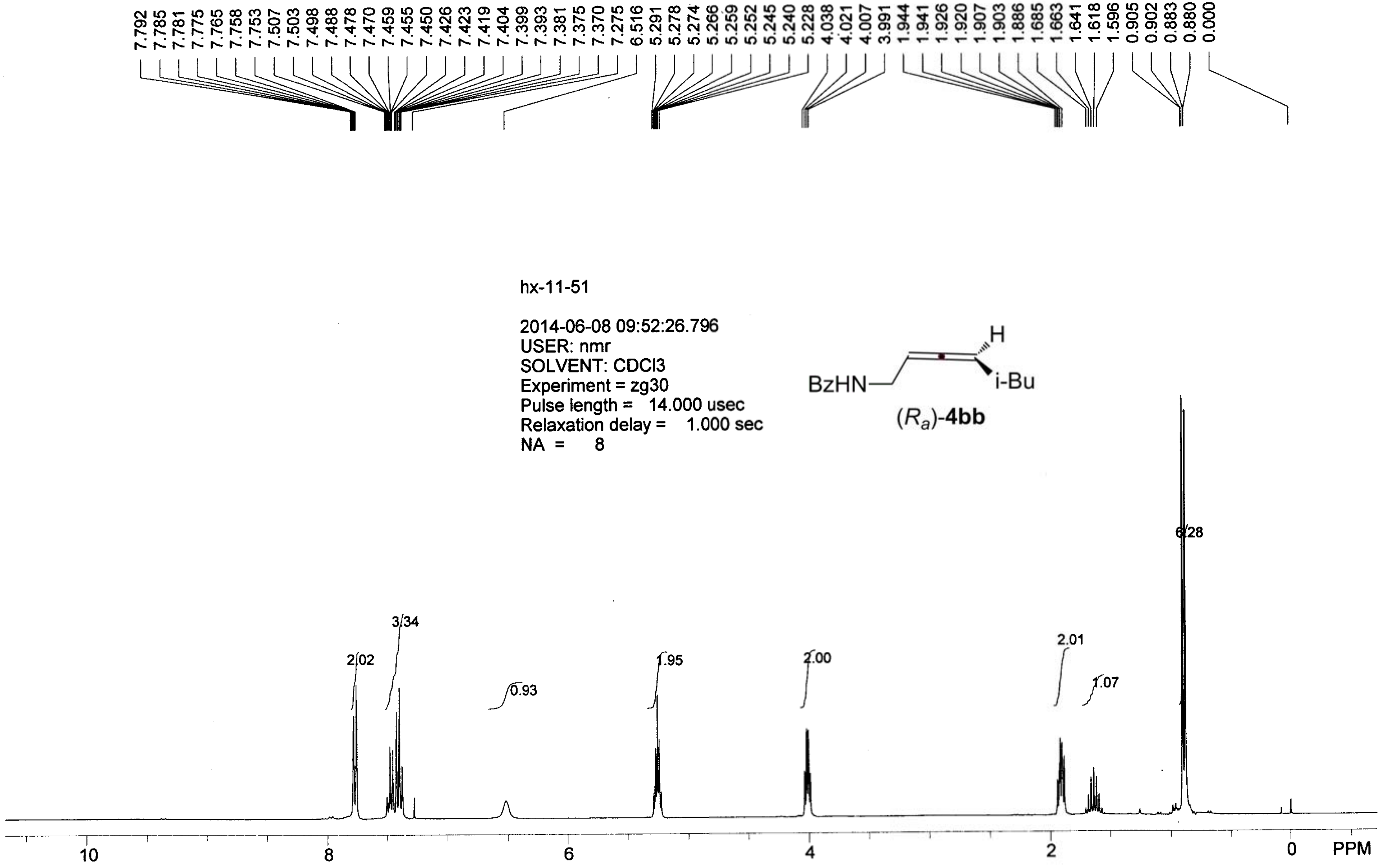

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SOLVENT: CDCl3
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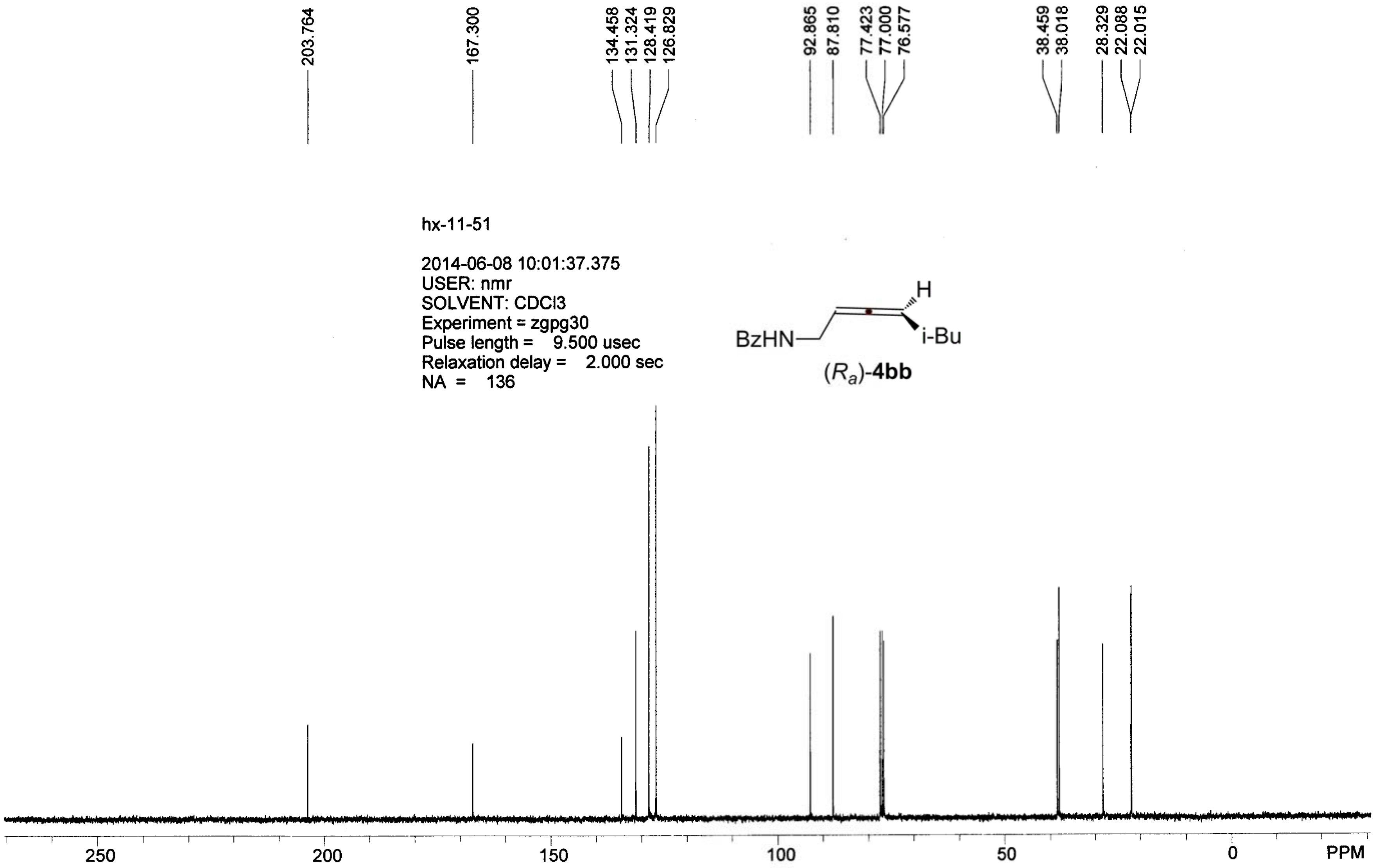
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8

(R_a)-**4bb**



hx-11-51

2014-06-08 10:01:37.375
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 136

(*R*$_a$)-**4bb**

hx-11-51-ay-h-90-10-1-214

实验时间：2014-06-10,14:53:46 报告时间：2014-06-12,16:56:01
谱图文件:D:\zhuguangjiong\hx\20140610\hx-11-51-ay-h-90-10-1-214..org

实验内容简介：

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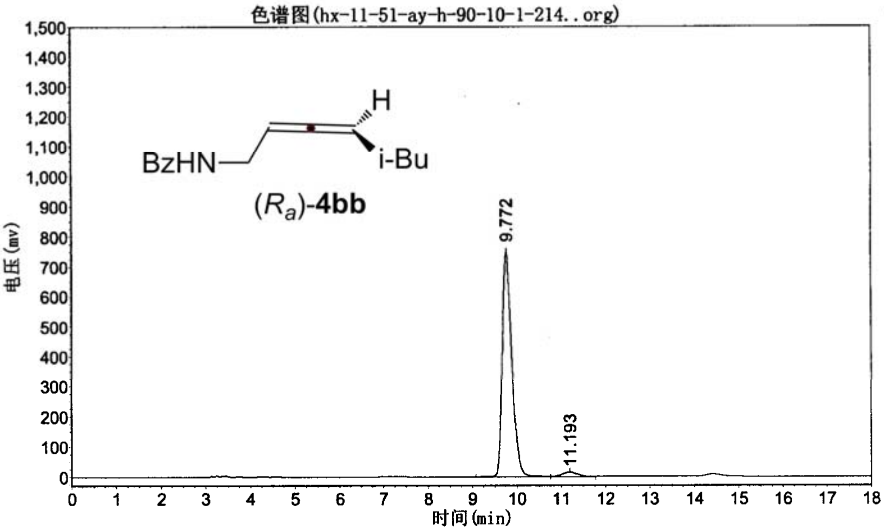

分析结果表

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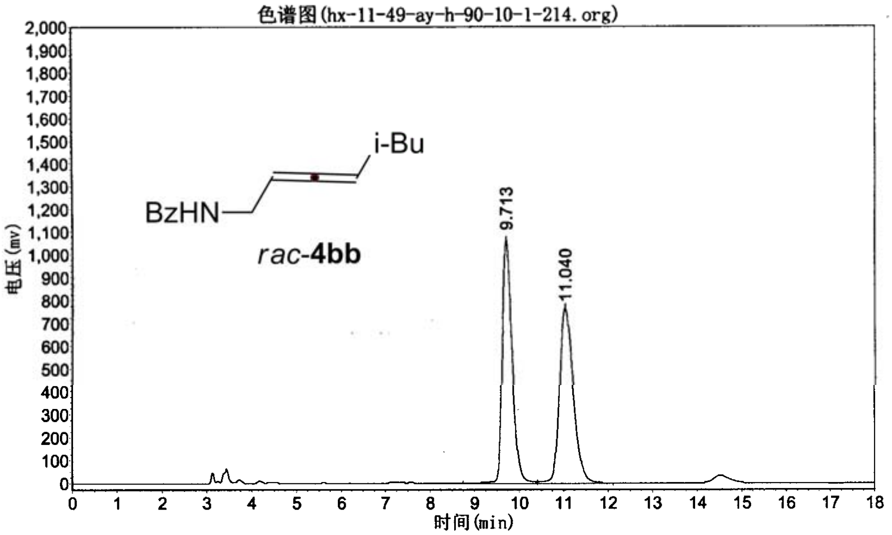
2		11.193	16124.151	397754.438	3.4096
总计			764788.589	11665790.438	100.0000

hx-11-49-ay-h-90-10-1-214

实验时间：2014-06-10,14:03:24 报告时间：2014-06-12,16:54:25
谱图文件:D:\zhuguangjiong\hx\20140610\hx-11-49-ay-h-90-10-1-214.org

实验内容简介：



分析结果表

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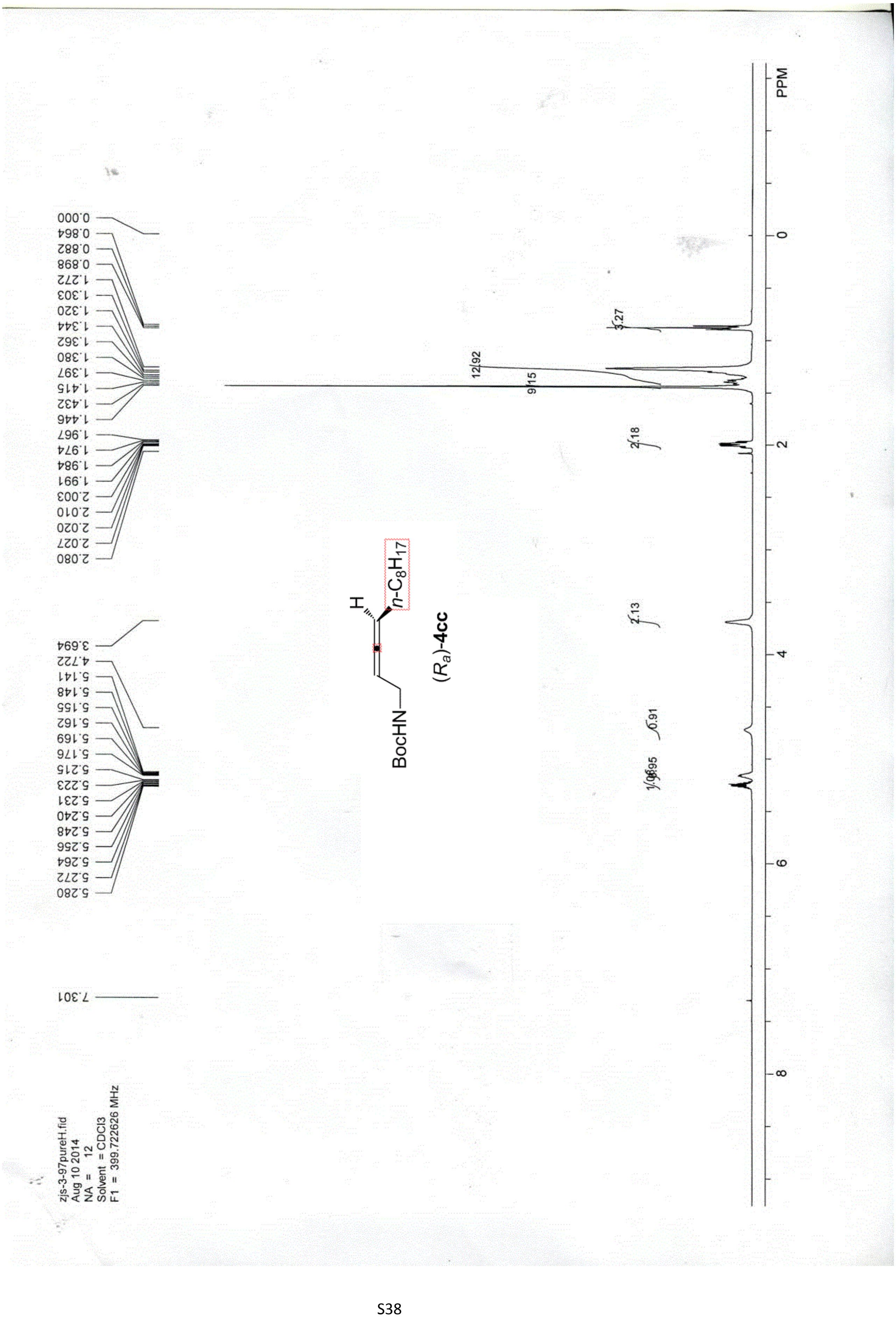
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Aug 10 2014
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Solvent = CDCl3
F1 = 399.722626 MHz
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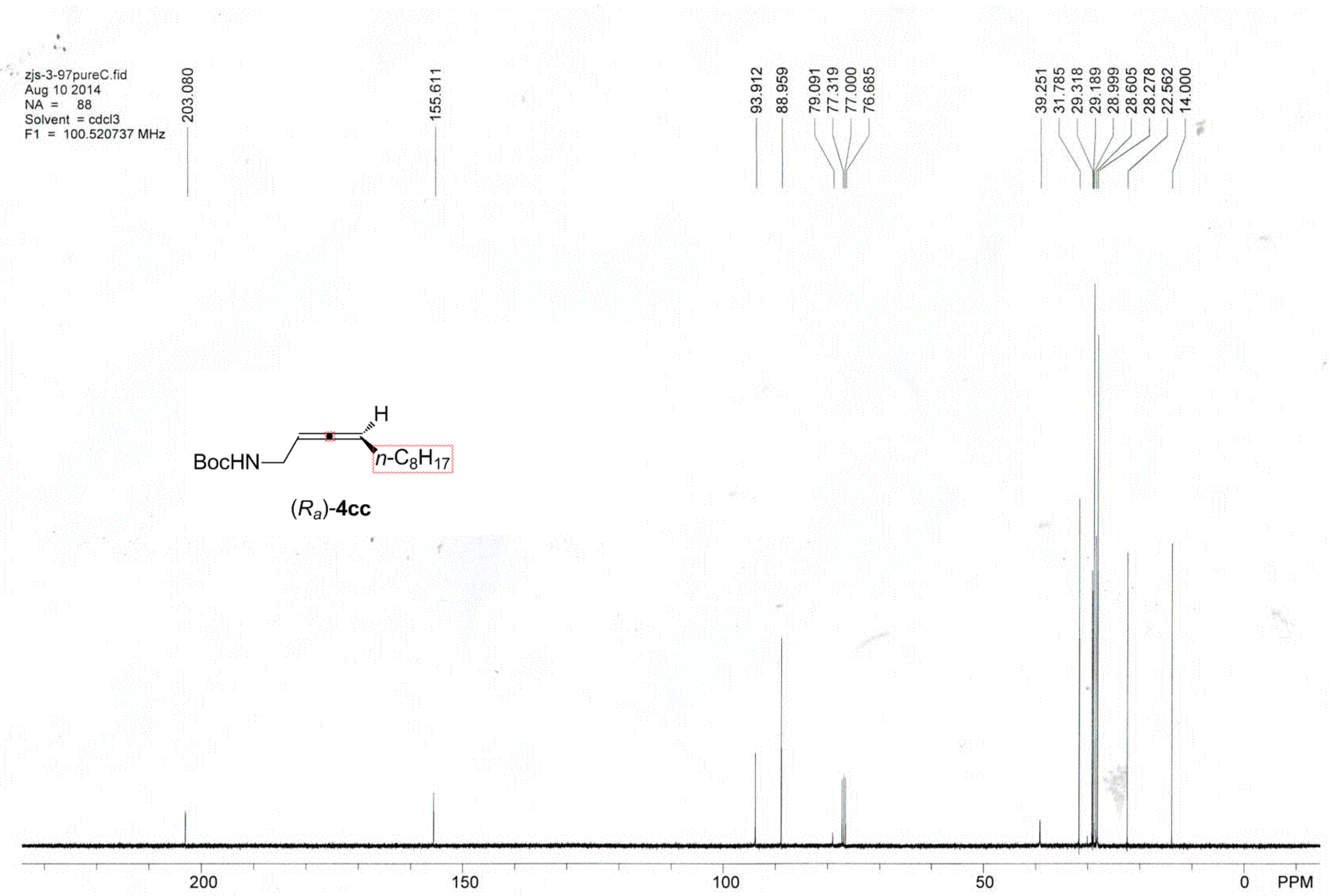
5.280
5.272
5.264
5.256
5.248
5.240
5.231
5.223
5.215
5.176
5.169
5.162
5.155
5.148
5.141
4.722
3.694
2.080
2.027
2.020
2.010
2.003
1.991
1.984
1.974
1.967
1.446
1.432
1.415
1.397
1.380
1.362
1.344
1.320
1.303
1.272
0.898
0.882
0.864
0.000
BocHN
H
n-C8H17
1.06
0.95
0.91
2.13
2.18
9.15
12.92
3.27
8
6
4
2
0
PPM

(*R*a)-**4cc**


zjs-3-97pureC.fid
Aug 10 2014
NA = 88
Solvent = cdcl3
F1 = 100.520737 MHz
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88.959
79.091
77.319
77.000
76.685
39.251
31.785
29.318
29.189
28.999
28.605
28.278
22.562
14.000
H
BocHN
n-C8H17
(Ra)-4cc
200
150
100
50
0
PPM

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Sample Name: ZJS-97 AD-R M85W15 214 1 20

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      Acq. Instrument : instr1                          Location : Vial 85
      Injection Date  : 18/08/2014 11:46:51
                                                      Inj Volume : 5.000 µl
      Acq. Method     : D:\CHEM32\1\DATA\WXL\WXL.M
      Last changed    : 18/08/2014 11:42:46 by WXL
                        (modified after loading)
      Analysis Method : D:\CHEM32\1\DATA\WXL\WXL.M
      Last changed    : 20/08/2014 09:34:23 by LXG
                        (modified after loading)
      Additional Info : Peak(s) manually integrated
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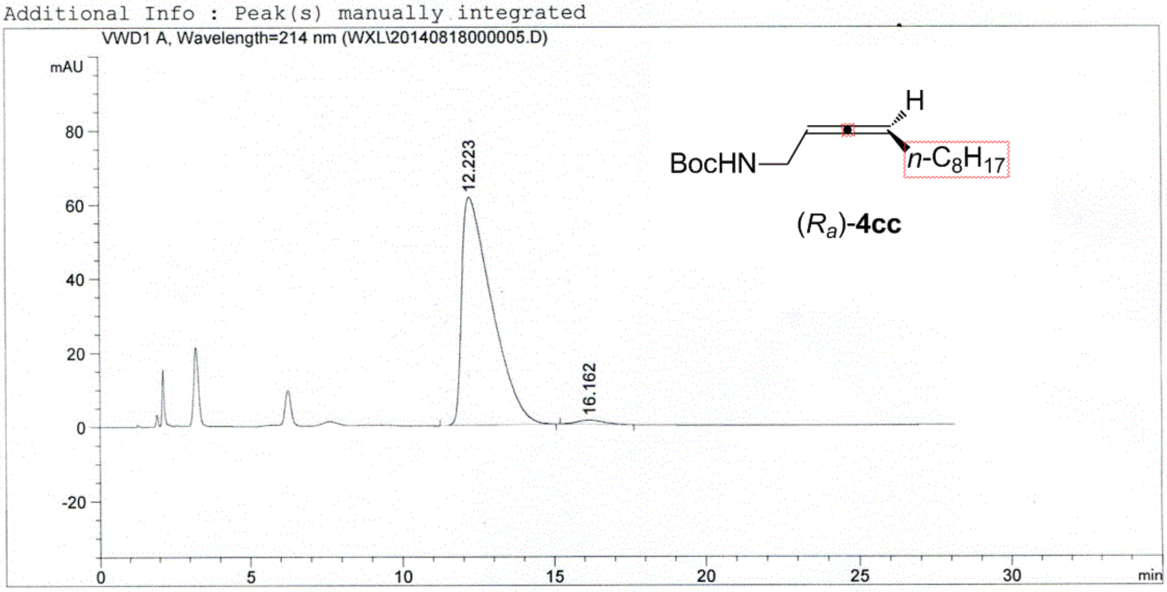

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      =====================================================================
                              Area Percent Report
      =====================================================================

      Sorted By             :      Signal
      Multiplier:                  :       1.0000
      Dilution:                    :       1.0000
      Use Multiplier & Dilution Factor with ISTDs


      Signal 1: VWD1 A, Wavelength=214 nm

      Peak RetTime Type  Width     Area      Height     Area
        #   [min]        [min]   [mAU*s]     [mAU]       %
      ----|-------|----|-------|----------|----------|--------|
         1  12.223 BB    0.9529 4230.80811   61.66743  98.3233
         2  16.162 VB    0.7410   72.14684    1.14052   1.6767

      Totals :                  4302.95495   62.80795

      =====================================================================
                               *** End of Report ***



instr1 20/08/2014 09:35:11 LXG                                  Page    1 of 1
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    =====================================================================
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    Acq. Instrument : instr1                        Location : Vial 81
    Injection Date  : 18/08/2014 11:13:03
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\CHEM32\1\DATA\WXL\WXL.M
    Last changed    : 18/08/2014 11:09:10 by WXL
                      (modified after loading)
    Analysis Method : D:\CHEM32\1\DATA\WXL\WXL.M
    Last changed    : 20/08/2014 09:34:23 by LXG
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
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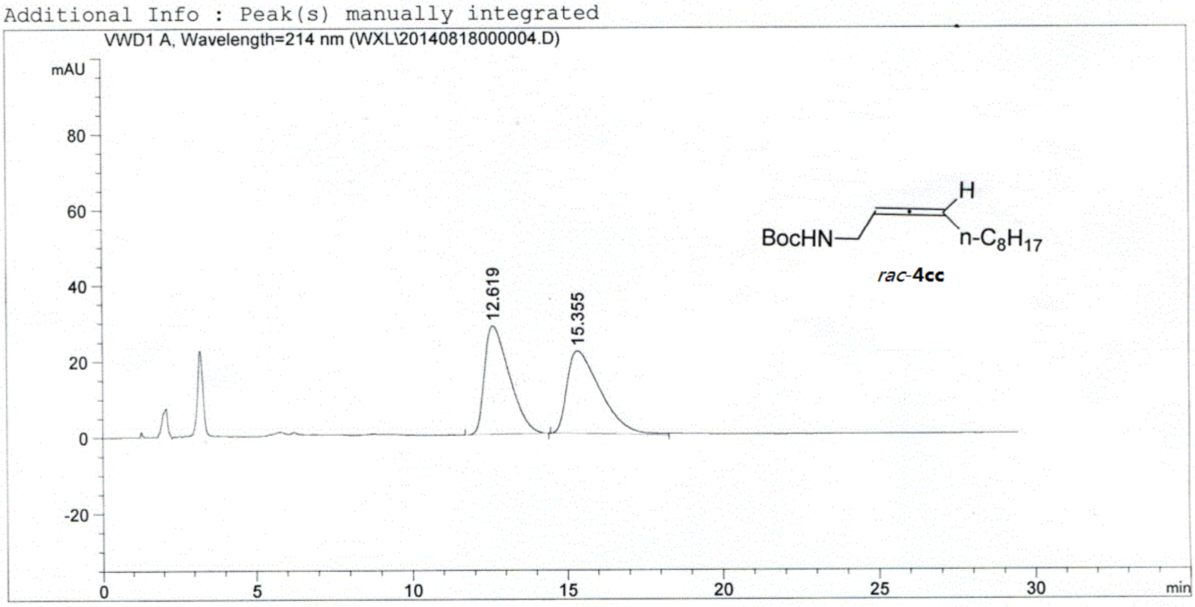

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                             Area Percent Report
    =====================================================================

    Sorted By                 :      Signal
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    Dilution:                         :       1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=214 nm

    Peak RetTime Type  Width      Area       Height      Area
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    ----|-------|----|-------|----------|----------|--------|
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       2  15.355 MM    1.2415 1613.19897   21.65615  50.3236

    Totals :                  3205.64905   50.23858


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                             *** End of Report ***



instr1 20/08/2014 09:34:31 LXG                                  Page    1 of 1
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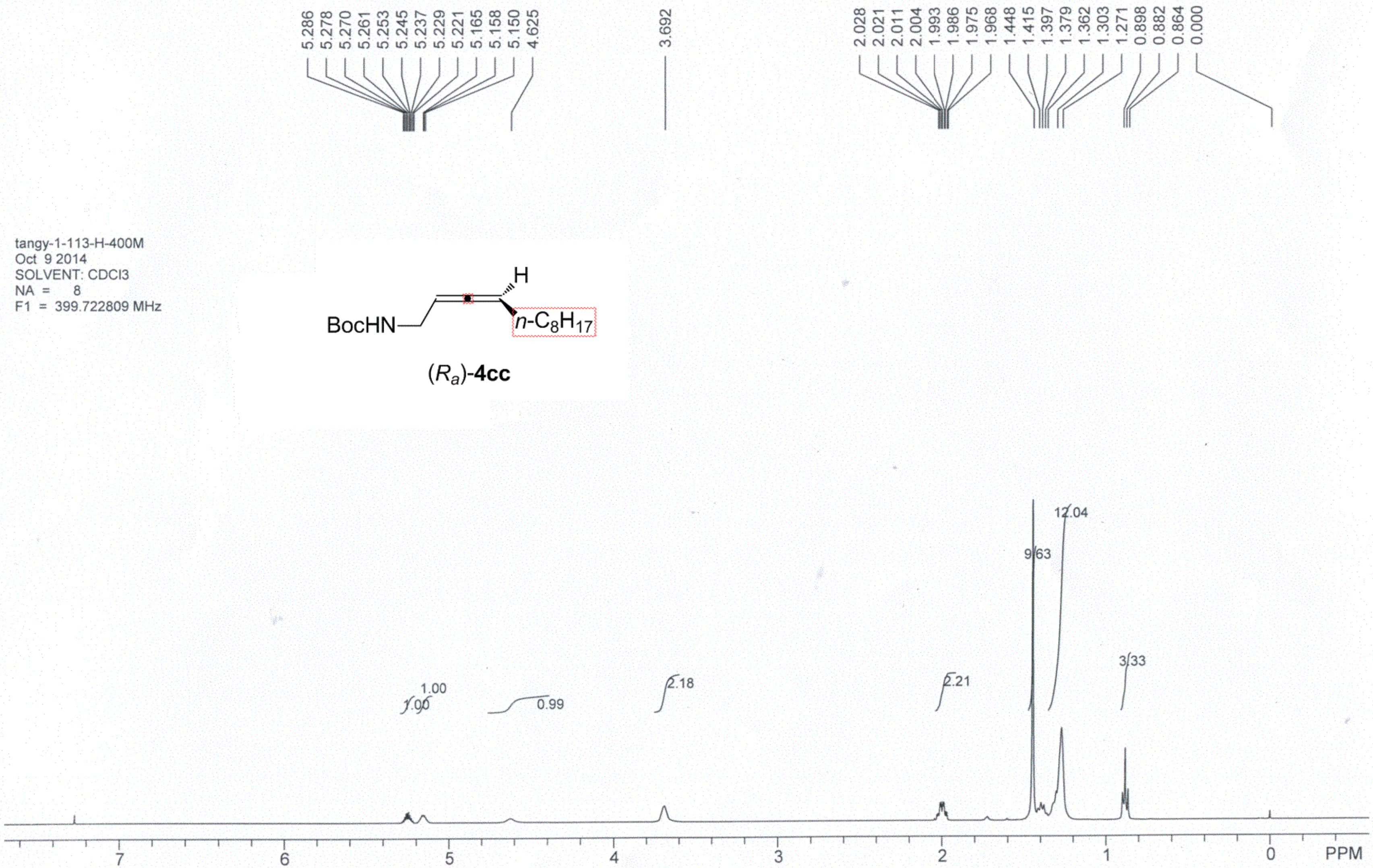
tangy-1-113-H-400M
Oct 9 2014
SOLVENT: CDCl3
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F1 = 399.722809 MHz
BocHN
H
n-C_8H_{17}
5.286
5.278
5.270
5.261
5.253
5.245
5.237
5.229
5.221
5.165
5.158
5.150
4.625
3.692
2.028
2.021
2.011
2.004
1.993
1.986
1.975
1.968
1.448
1.415
1.397
1.379
1.362
1.303
1.271
0.898
0.882
0.864
0.000
1.00
1.00
0.99
2.18
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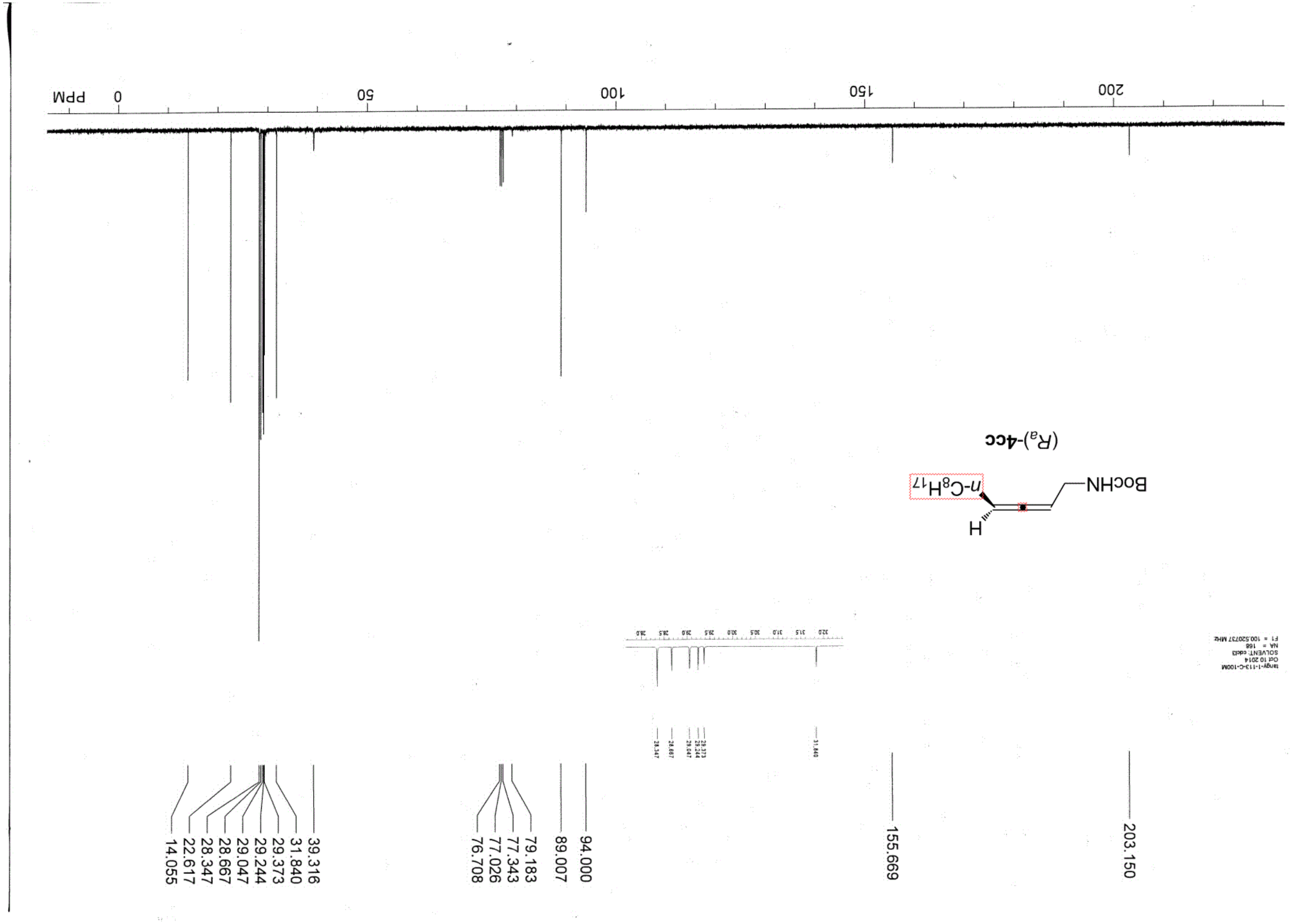
9.63
12.04
3.33
7
6
5
4
3
2
1
0
PPM

(R_a)-**4cc**


PPM
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100
150
200
14.055
22.617
28.347
28.667
29.047
29.244
29.373
31.840
39.316
76.708
77.026
77.343
79.183
89.007
94.000
155.669
203.150
28.347
28.667
29.047
29.244
29.373
31.840
28.0
28.5
29.0
29.5
30.0
30.5
31.0
31.5
32.0
BocHN
H
n-C8H17
tangy-1-113-C-100M
Oct 10 2014
SOLVENT: cdcl3
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F1 = 100.520737 MHz

(R_a)-**4cc**

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                                                   Inj Volume : 3.000 µl
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     Last changed    : 10/10/2014 17:29:42 by WXL
                       (modified after loading)
     Analysis Method : D:\CHEM32\1\DATA\WXL\WXL.M
     Last changed    : 08/10/2014 15:26:25 by WXL
                       (modified after loading)
     Additional Info : Peak(s) manually integrated
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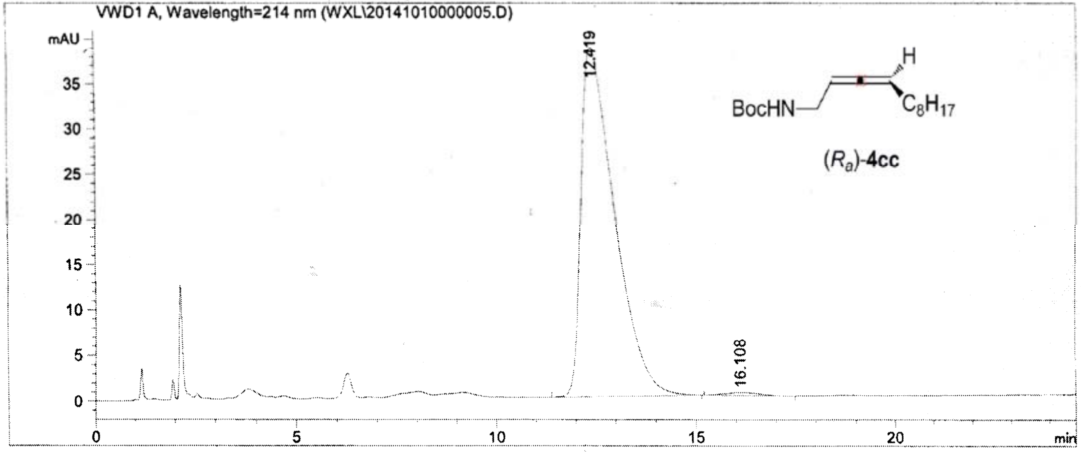
VWD1 A, Wavelength=214 nm (WXL\20141010000005.D)

(R_a)-**4cc**

```
     =====================================================================
                              Area Percent Report
     =====================================================================

     Sorted By             :      Signal
     Multiplier:                  :       1.0000
     Dilution:                    :       1.0000
     Use Multiplier & Dilution Factor with ISTDs


     Signal 1: VWD1 A, Wavelength=214 nm

     Peak RetTime Type  Width      Area       Height      Area
       #   [min]        [min]   [mAU*s]       [mAU]        %
     ----|-------|----|-------|----------|----------|--------|
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        2  16.108 BB    0.6670   17.88317 3.14224e-1   0.7921

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                              *** End of Report ***



 instr1 10/10/2014 17:56:50 WXL                                    Page    1 of 1
```

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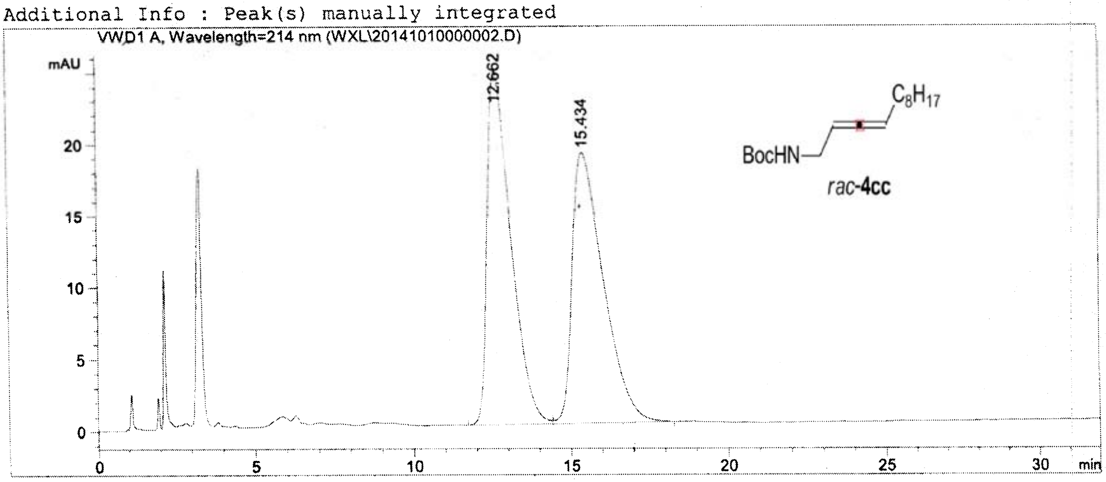
    =====================================================================
    Acq. Operator   : WXL
    Acq. Instrument : instrl                        Location : Vial 41
    Injection Date  : 10/10/2014 12:01:44
                                                  Inj Volume : 3.000 µl
    Acq. Method     : D:\CHEM32\1\DATA\WXL\WXL.M
    Last changed    : 10/10/2014 11:37:24 by WXL
                      (modified after loading)
    Analysis Method : D:\CHEM32\1\DATA\WXL\WXL.M
    Last changed    : 08/10/2014 15:26:25 by WXL
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



```
    =====================================================================
                             Area Percent Report
    =====================================================================

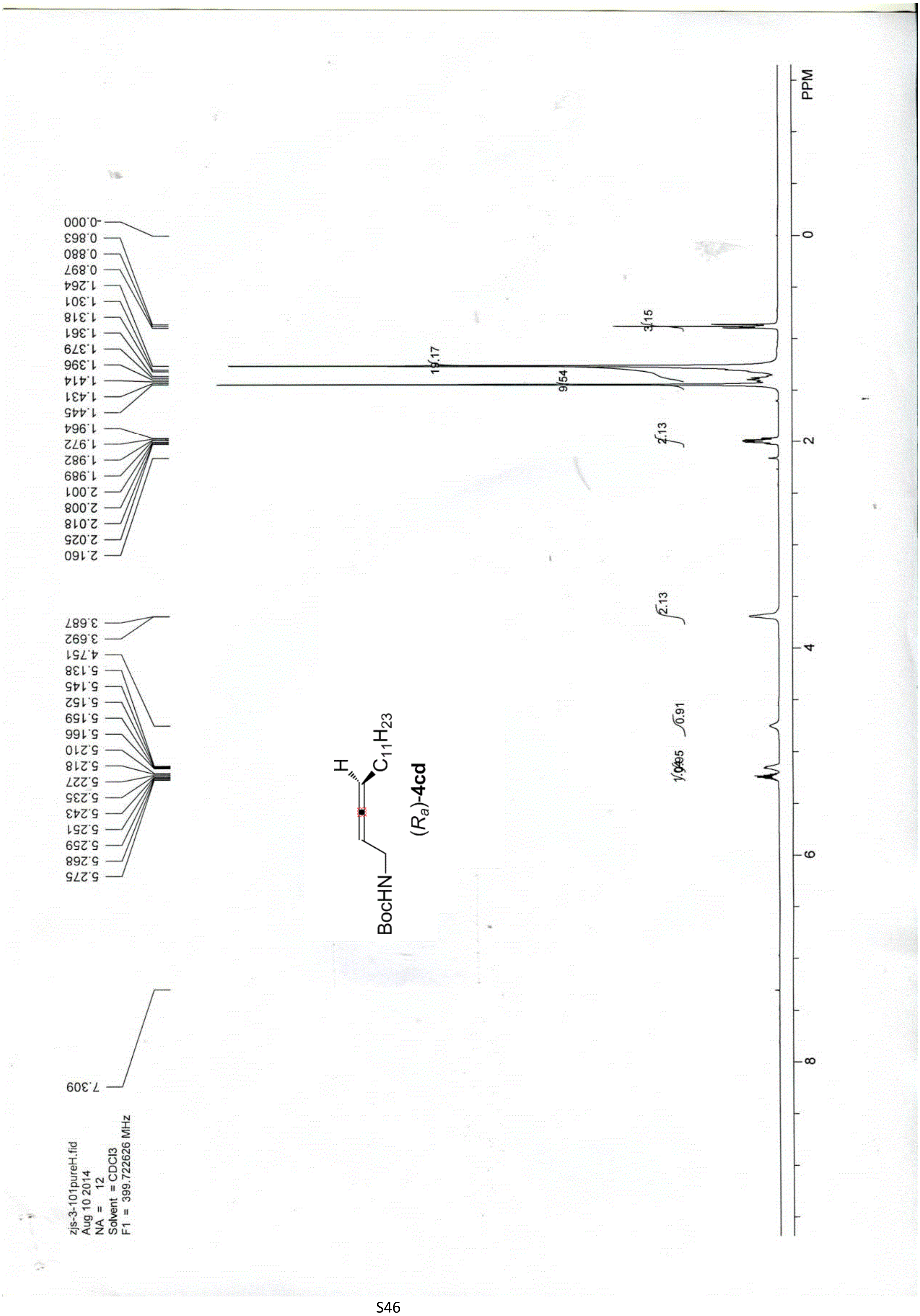
    Sorted By             :      Signal
    Multiplier:                  :      1.0000
    Dilution:                    :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=214 nm

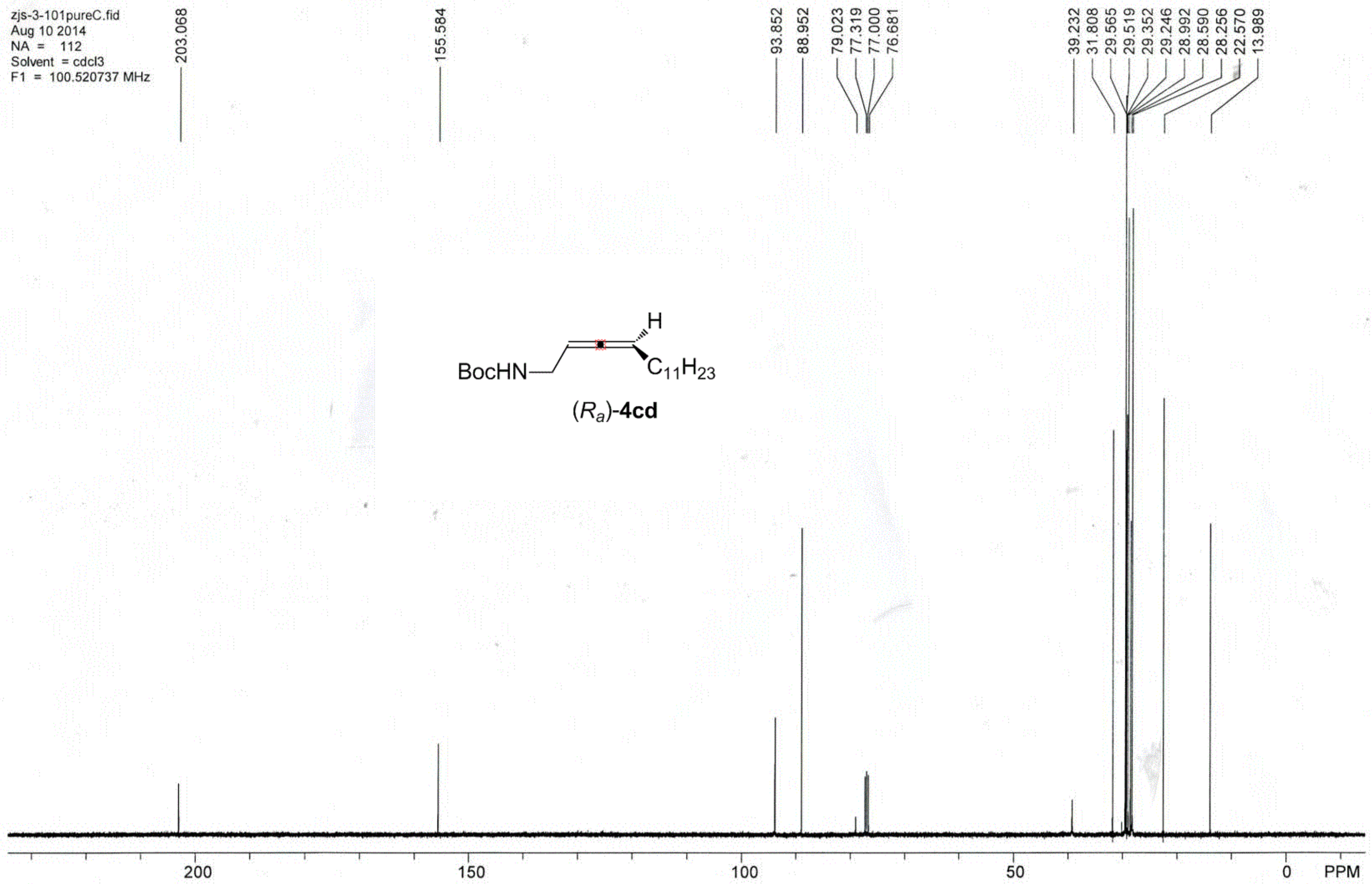
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  12.662 BV    0.7813 1289.85254   24.61849  49.8284
       2  15.434 VB    1.0115 1298.73401   18.85631  50.1716

    Totals :                  2588.58655   43.47481

    =====================================================================
                             *** End of Report ***
```


zjs-3-101pureH.fid
Aug 10 2014
NA = 12
Solvent = CDCl3
F1 = 399.722626 MHz
7.309
5.275
5.268
5.259
5.251
5.243
5.235
5.227
5.218
5.210
5.166
5.159
5.152
5.145
5.138
4.751
3.692
3.687
2.160
2.025
2.018
2.008
2.001
1.989
1.982
1.972
1.964
1.445
1.431
1.414
1.396
1.379
1.361
1.318
1.301
1.264
0.897
0.880
0.863
-0.000
BocHN
H
C11H23
1.95
0.91
2.13
2.13
9.54
19.17
3.15
PPM
8
6
4
2
0

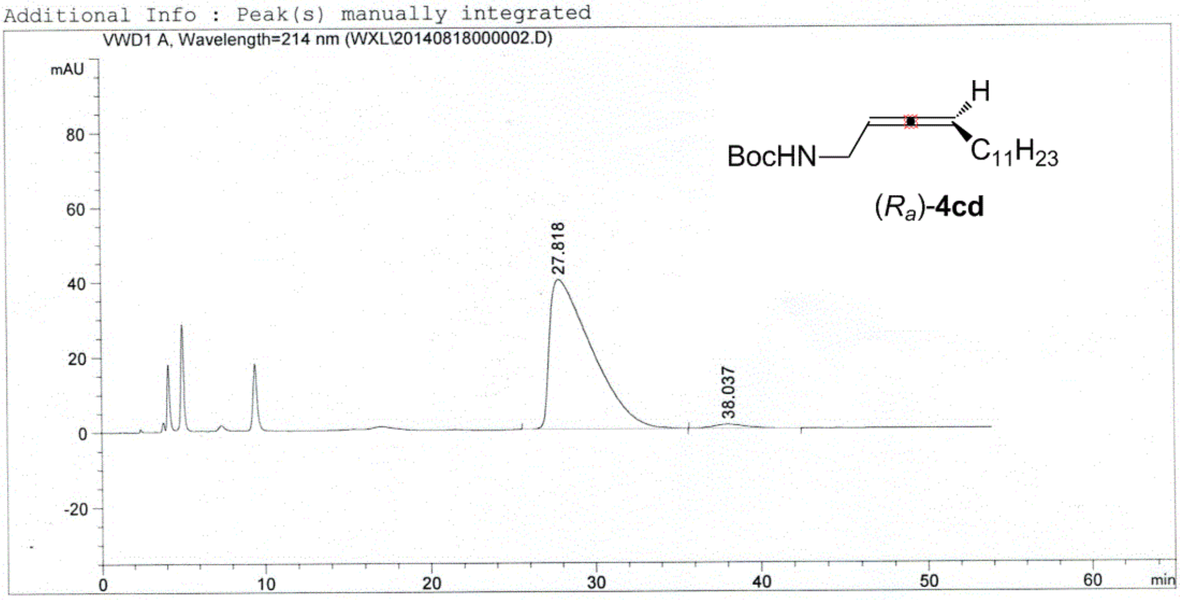
(*R*$_a$)-**4cd**


zjs-3-101pureC.fid
Aug 10 2014
NA = 112
Solvent = cdcl3
F1 = 100.520737 MHz
203.068
155.584
93.852
88.952
79.023
77.319
77.000
76.681
39.232
31.808
29.565
29.519
29.352
29.246
28.992
28.590
28.256
22.570
13.989
BocHN
H
$C_{11}H_{23}$
200
150
100
50
0
PPM

(R_a)-**4cd**

```
Data File D:\CHEM32\1\DATA\WXL\20140818000002.D
Sample Name: ZJS-101 AD-R M9W1 214 0.5 20

    =====================================================================
    Acq. Operator   : WXL
    Acq. Instrument : instr1                          Location : Vial 84
    Injection Date  : 18/08/2014 09:41:20
                                                    Inj Volume : 5.000 µl
    Acq. Method     : D:\CHEM32\1\DATA\WXL\WXL.M
    Last changed    : 18/08/2014 09:40:37 by WXL
                      (modified after loading)
    Analysis Method : D:\CHEM32\1\DATA\WXL\WXL.M
    Last changed    : 20/08/2014 09:32:49 by LXG
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



(R_a)-**4cd**

```
    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier:                  :       1.0000
    Dilution:                    :       1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=214 nm

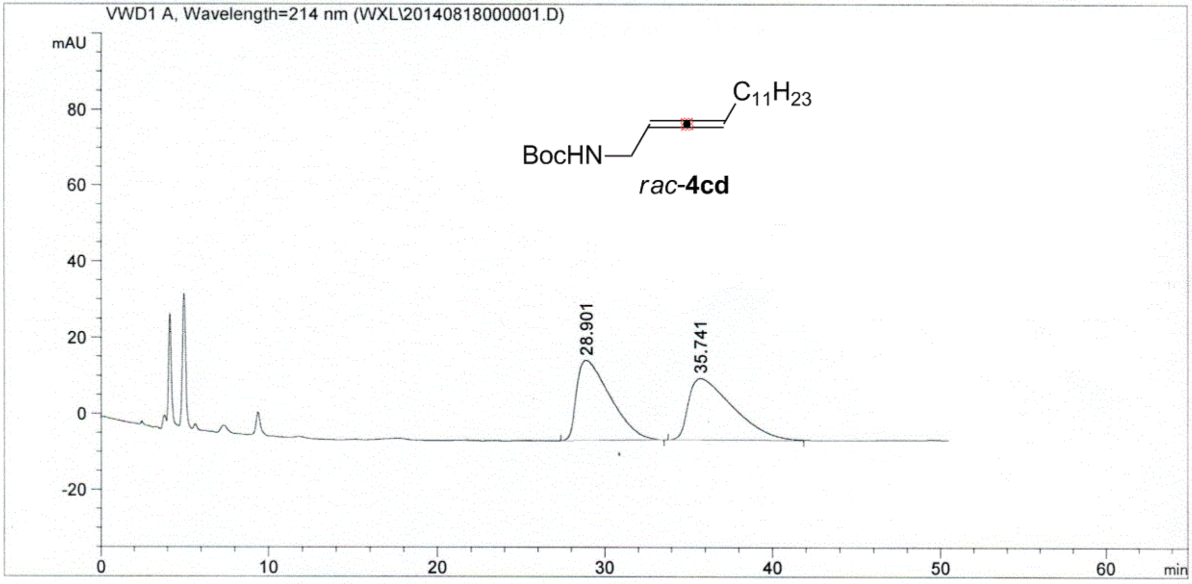
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1  27.818 MM    2.9673 7086.52100   39.80346  97.9571
       2  38.037 MM    2.2627  147.78818    1.08858   2.0429

    Totals :                   7234.30917   40.89205


    =====================================================================
                             *** End of Report ***
```

```
Data File D:\CHEM32\1\DATA\WXL\20140818000001.D
Sample Name: ZJS-102+- AD-R M9W1 214 0.5 20

    =====================================================================
    Acq. Operator   : WXL
    Acq. Instrument : instr1                          Location : Vial 83
    Injection Date  : 18/08/2014 08:49:35
                                                    Inj Volume : 10.000 µl
    Acq. Method     : D:\CHEM32\1\DATA\WXL\WXL.M
    Last changed    : 18/08/2014 08:37:35 by WXL
                      (modified after loading)
    Analysis Method : D:\CHEM32\1\DATA\WXL\WXL.M
    Last changed    : 20/08/2014 09:23:13 by LXG
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



```
    =====================================================================
                             Area Percent Report
    =====================================================================

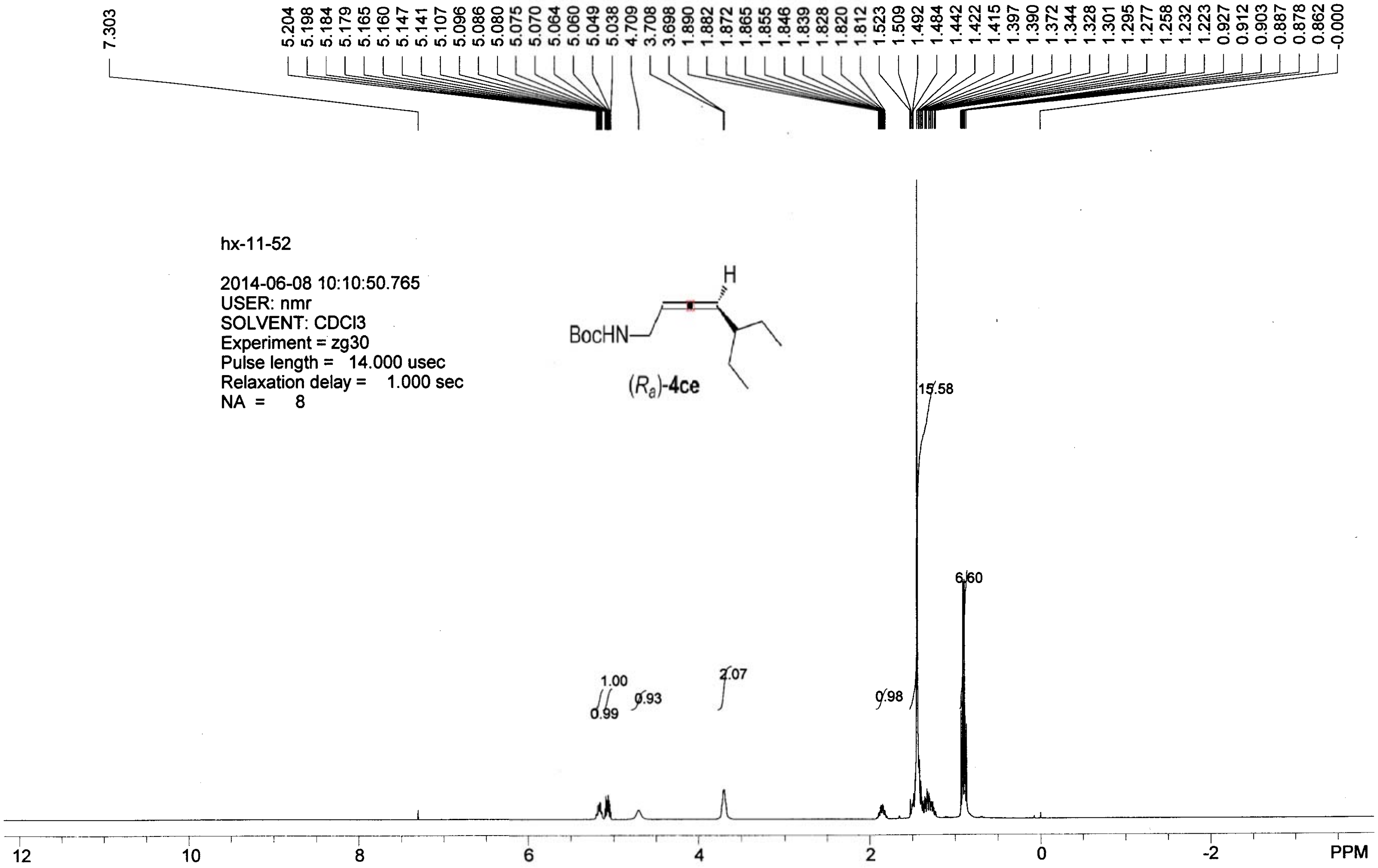
    Sorted By             :      Signal
    Multiplier:                   :       1.0000
    Dilution:                     :       1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=214 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  28.901 BB     1.6369 2946.37671   21.05761 49.7033
       2  35.741 BV     2.1551 2981.55591   16.15548 50.2967

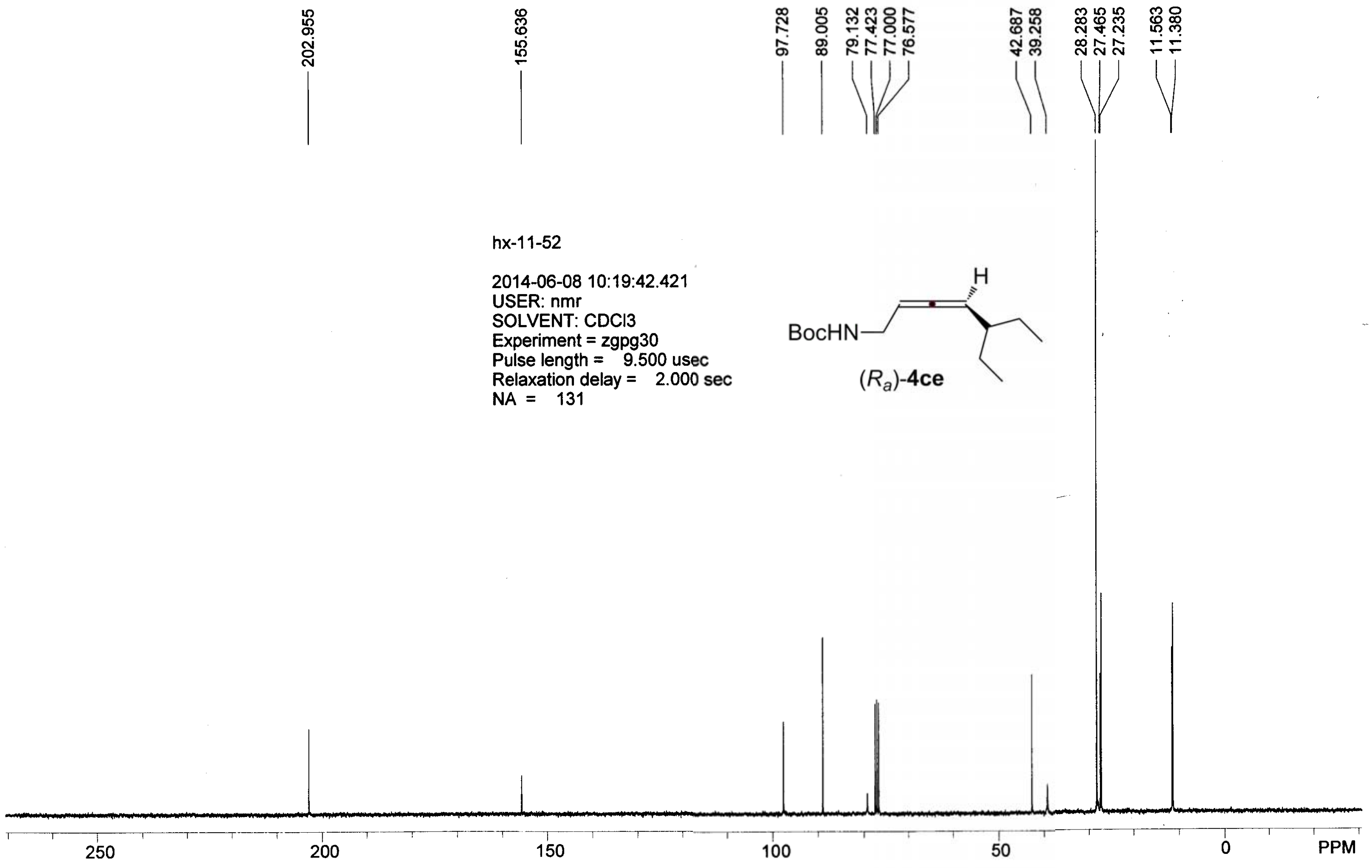
    Totals :                   5927.93262   37.21308


    =====================================================================
                             *** End of Report ***
```


hx-11-52

2014-06-08 10:10:50.765
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8

(R_a)-**4ce**


202.955
155.636
97.728
89.005
79.132
77.423
77.000
76.577
42.687
39.258
28.283
27.465
27.235
11.563
11.380
hx-11-52
2014-06-08 10:19:42.421
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 131
BocHN
H
(R_a)-**4ce**
250
200
150
100
50
0
PPM

中国科学院上海有机化学研究所

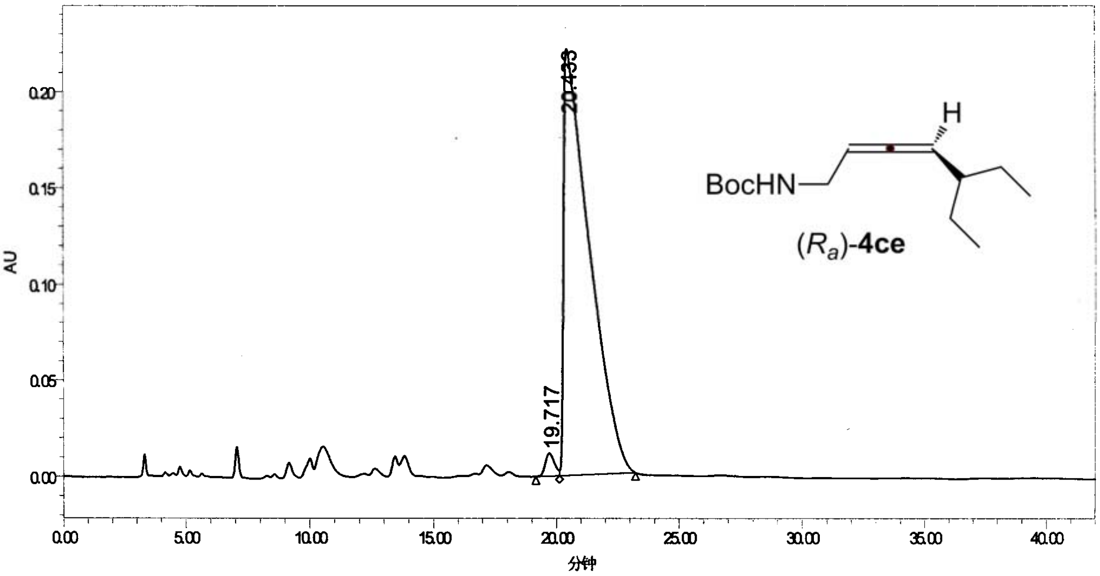
Project Name: defaults for copy

Reported by User: Breeze user (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	hx-11-52-od-100-0-1-214	Acquired By:	Breeze
Sample Type:	未知	Date Acquired:	2014/6/11 11:18:59 CST
Vial:	1	Acq. Method:	zgj100
Injection #:	10	Date Processed:	2014/6/11 13:20:51 CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.00 Minutes	Channel Desc.:	W2489 ChA 214nm
Column Type:		Sample Set Name:	



	RT (min)	Area (礦sec)	%Area	Height (礦)	% Height
1	19.717	308558	1.88	11803	5.06
2	20.433	16106249	98.12	221549	94.94

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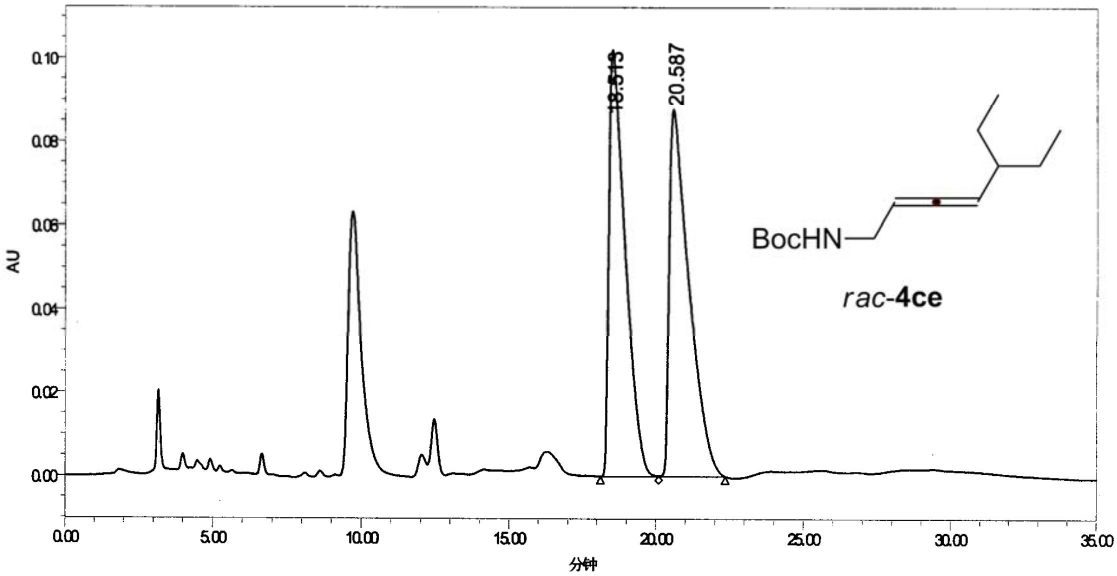
Project Name: defaults for copy

Reported by User: Breeze user (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	hx-11-50-1-od-100-0-1-214	Acquired By:	Breeze
Sample Type:	未知	Date Acquired:	2014/6/11 14:20:22 CST
Vial:	1	Acq. Method:	zgj100
Injection #:	15	Date Processed:	2014/6/11 14:57:10 CST
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	35.00 Minutes	Channel Desc.:	W2489 ChA 214nm
Column Type:		Sample Set Name:	



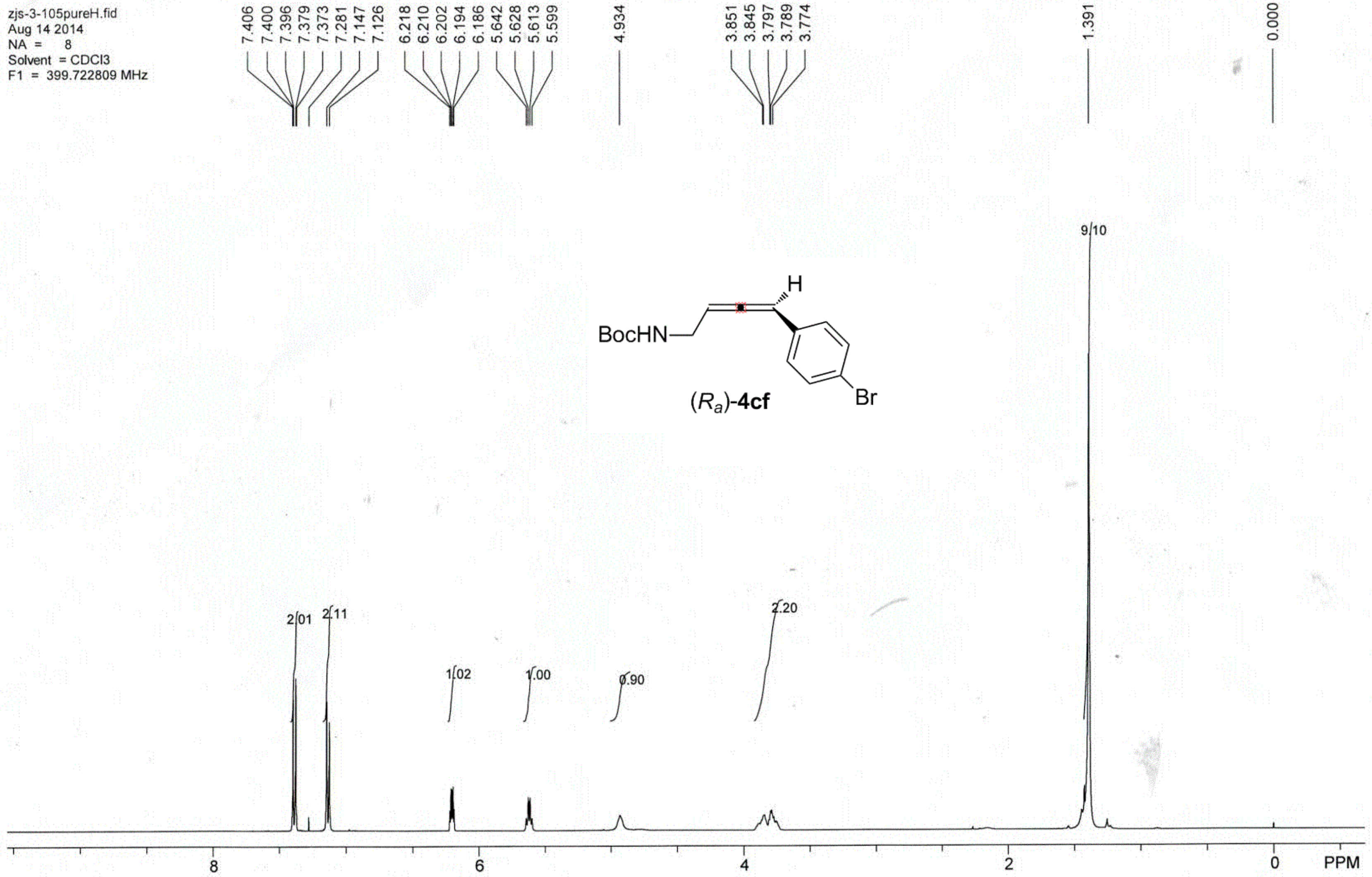
rac-**4ce**

	RT (min)	Area (磺sec)	%Area	Height (磺)	% Height
1	18.513	3931021	49.03	102129	53.77
2	20.587	4086407	50.97	87806	46.23

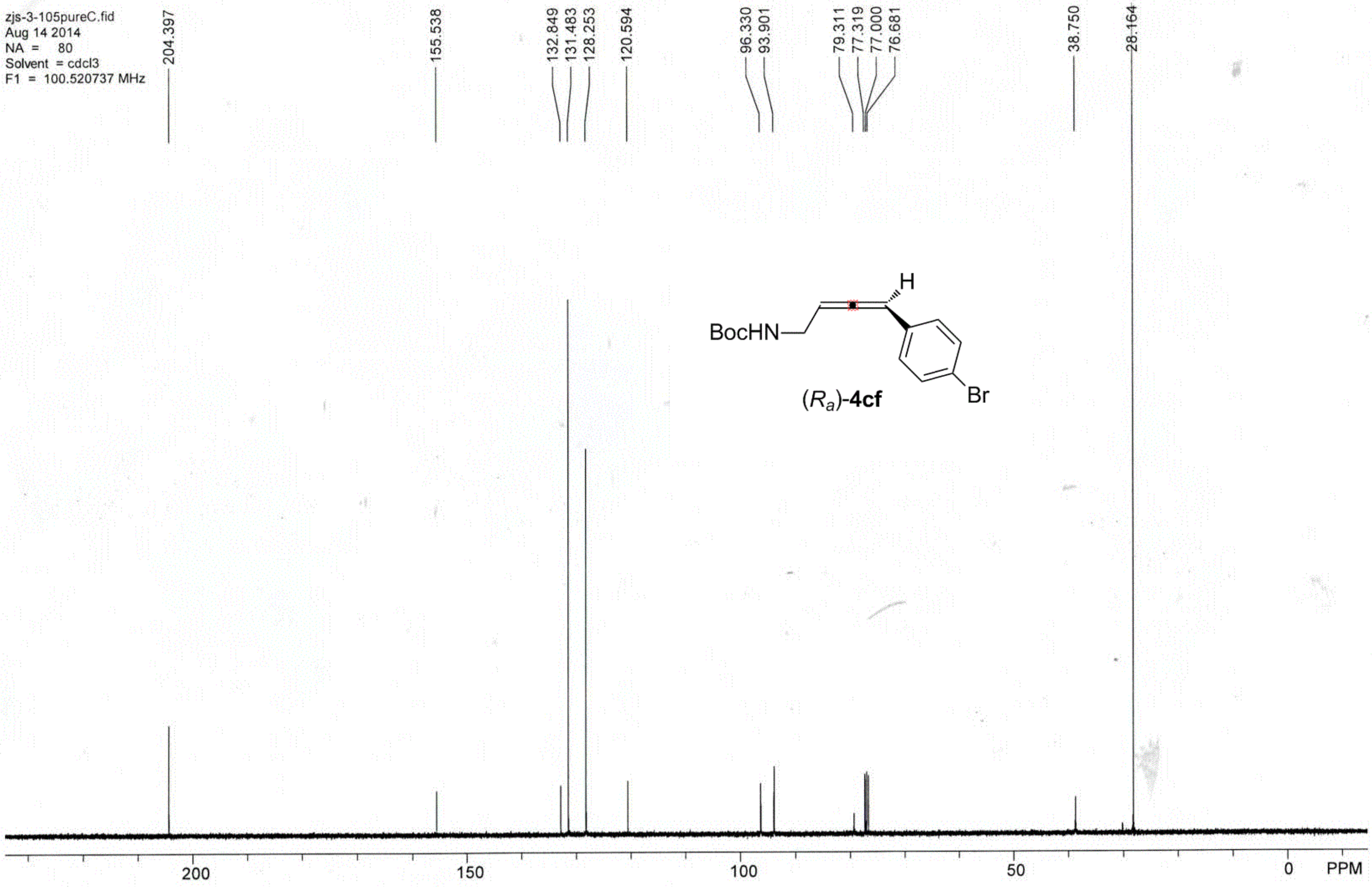
Report Method: Individual Report HP

Page: 1 (共计 1)

Printed: 2014/6/12 16:19:36 PRC


zjs-3-105pureH.fid
Aug 14 2014
NA = 8
Solvent = CDCl3
F1 = 399.722809 MHz
7.406
7.400
7.396
7.379
7.373
7.281
7.147
7.126
6.218
6.210
6.202
6.194
6.186
5.642
5.628
5.613
5.599
4.934
3.851
3.845
3.797
3.789
3.774
1.391
0.000
BocHN
H
Br
2.01
2.11
1.02
1.00
0.90
2.20
9.10
8
6
4
2
0
PPM

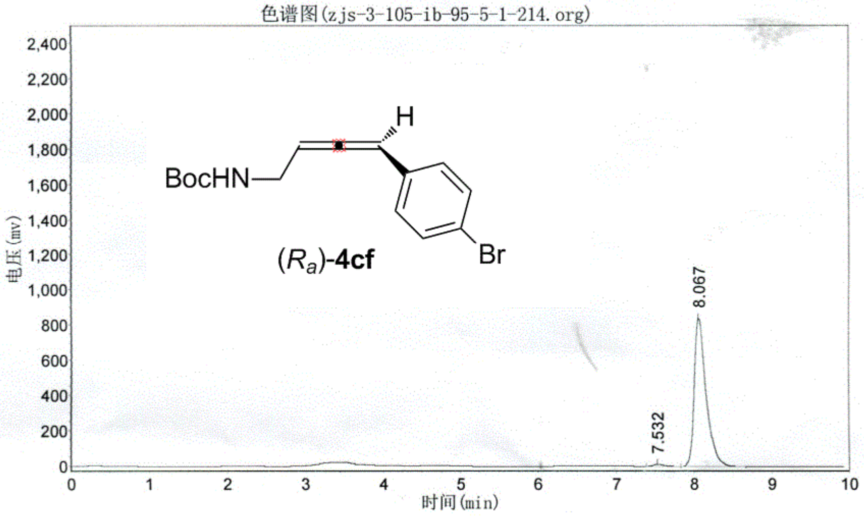
(*R*$_a$)-**4cf**


zjs-3-105pureC.fid
Aug 14 2014
NA = 80
Solvent = cdcl3
F1 = 100.520737 MHz
204.397
155.538
132.849
131.483
128.253
120.594
96.330
93.901
79.311
77.319
77.000
76.681
38.750
28.164
BocHN
H
Br
(*R*a)-**4cf**
200
150
100
50
0
PPM

zjs-3-105-ib-95-5-1-214

实验时间：2014-08-14,16:10:31　　报告时间：2014-08-14,16:30:08
谱图文件:D:\zhuguangjiong\zjs\20140814\zjs-3-105-ib-95-5-1-214.org

实验内容简介：



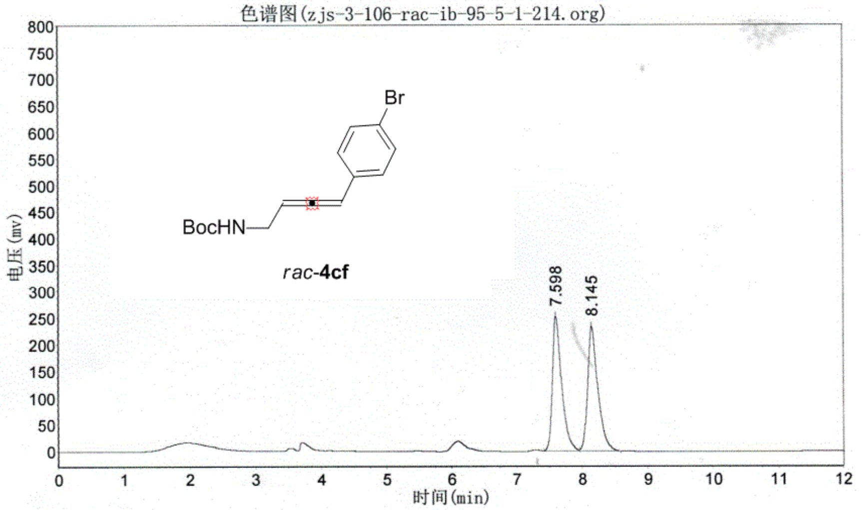
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		7.532	12360.554	111866.688	1.2539
2		8.067	839946.438	8809319.000	98.7461
总计			852306.991	8921185.688	100.0000

zjs-3-106-rac-ib-95-5-1-214

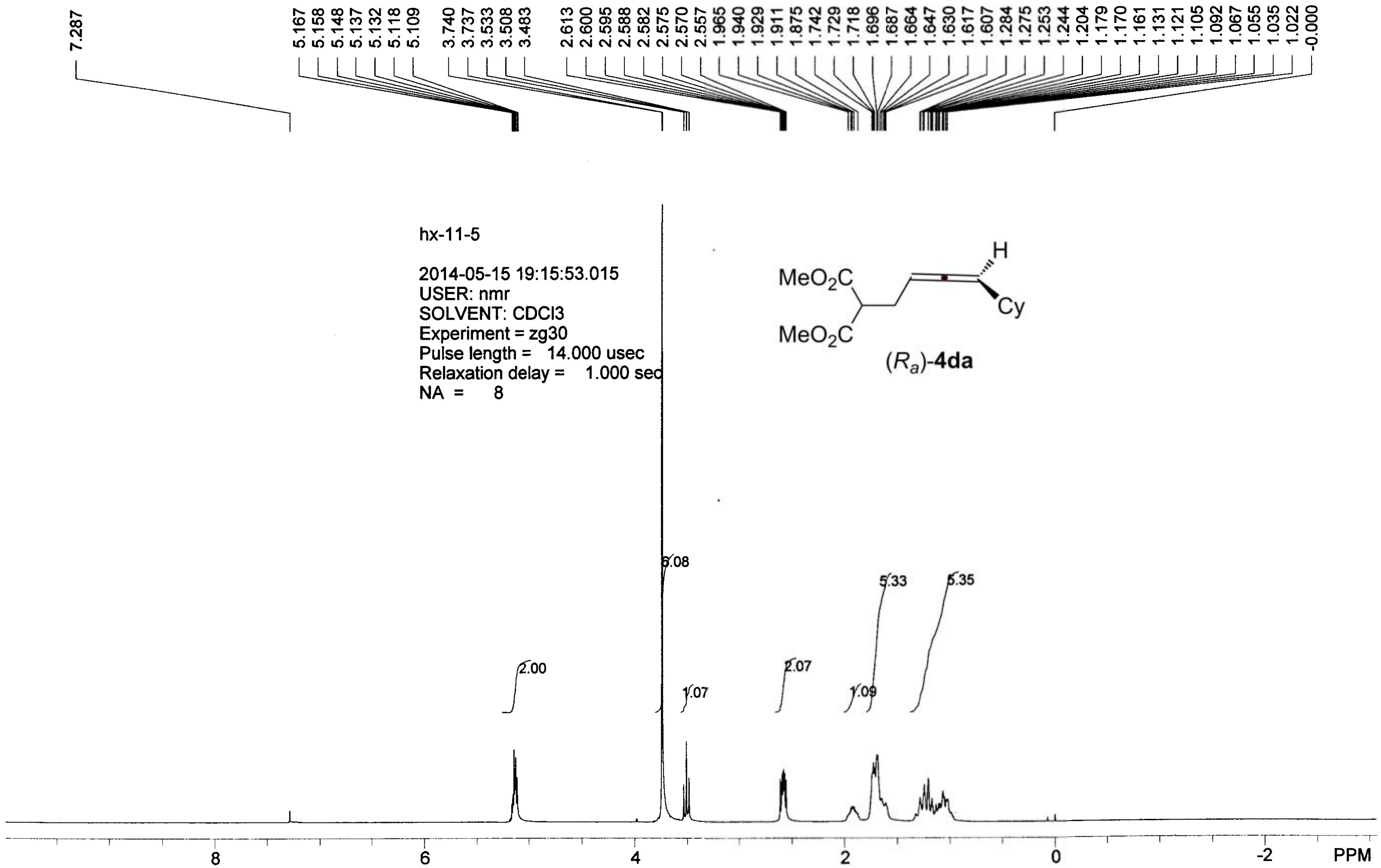
实验时间：2014-08-14, 15:43:54　　　　　　　　　　报告时间：2014-08-14, 16:28:29
谱图文件:D:\zhuguangjiong\zjs\20140814\zjs-3-106-rac-ib-95-5-1-214.org

实验内容简介：

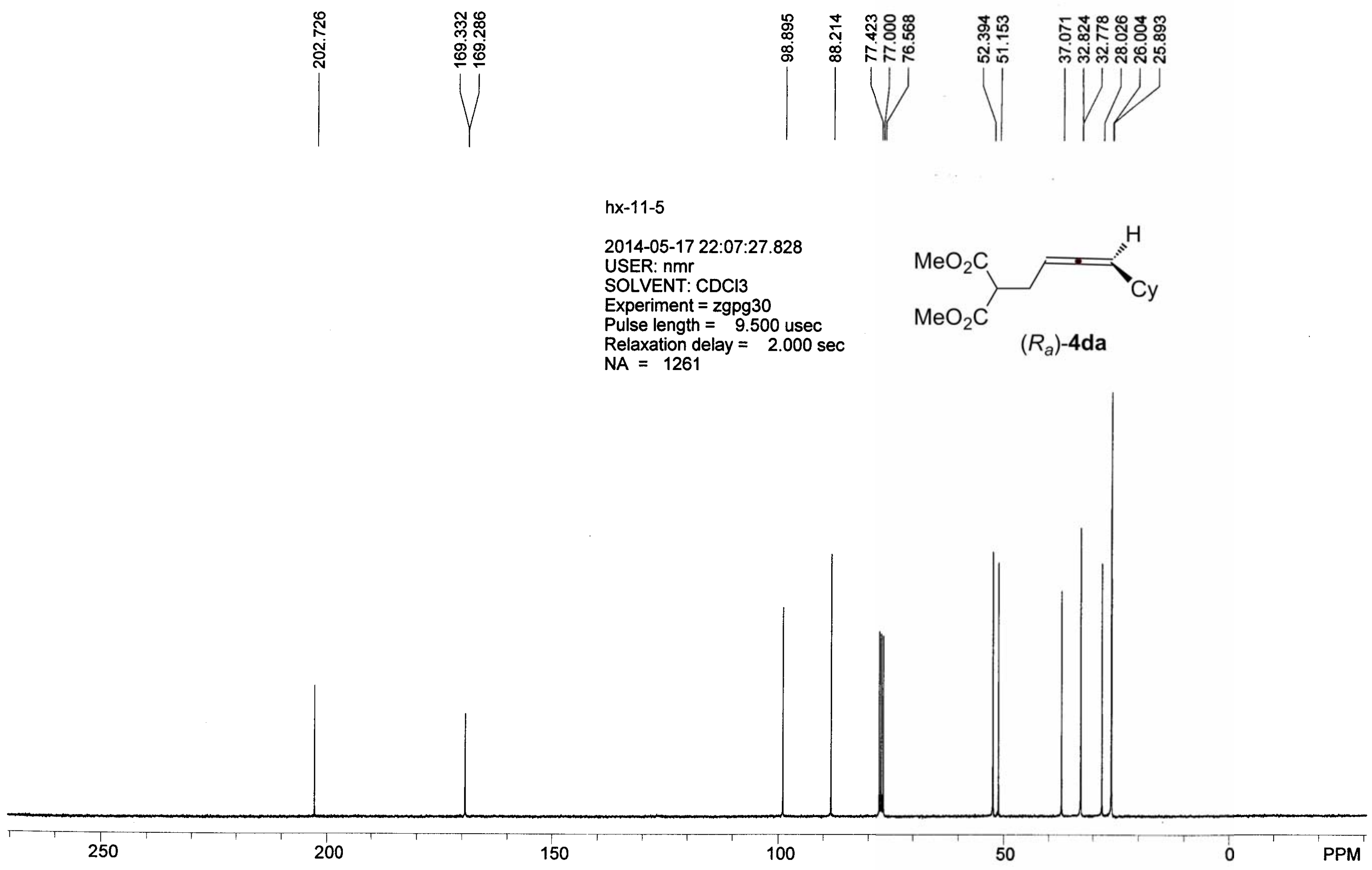


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		7.598	251911.641	2491649.500	49.5503
2		8.145	233443.719	2536876.000	50.4497
总计			485355.359	5028525.500	100.0000


7.287
5.167
5.158
5.148
5.137
5.132
5.118
5.109
3.740
3.737
3.533
3.508
3.483
2.613
2.600
2.595
2.588
2.582
2.575
2.570
2.557
1.965
1.940
1.929
1.911
1.875
1.742
1.729
1.718
1.696
1.687
1.664
1.647
1.630
1.617
1.607
1.284
1.275
1.253
1.244
1.204
1.179
1.170
1.161
1.131
1.121
1.105
1.092
1.067
1.055
1.035
1.022
-0.000
hx-11-5
2014-05-15 19:15:53.015
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
MeO2C
MeO2C
H
Cy
6.08
5.33
5.35
2.00
2.07
1.07
1.09
8
6
4
2
0
-2
PPM

(R_a)-**4da**



hx-11-5

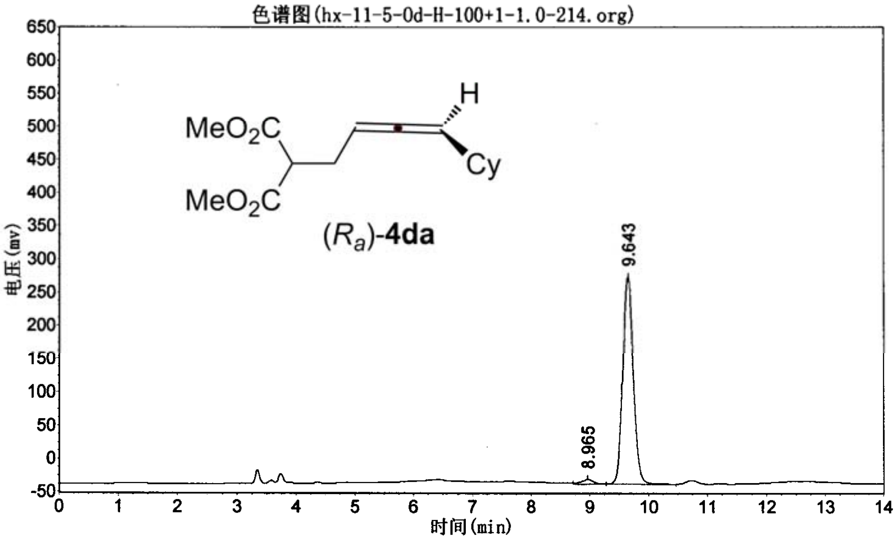
2014-05-17 22:07:27.828
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 1261

(*R*$_a$)-**4da**

hx-11-5

实验时间：2014-05-20,18:29:25　　报告时间：2014-05-20,18:33:05
谱图文件:F:\slf\huangxin\hx-11-5\新建文件夹 (3)\hx-11-5-0d-H-100+1-1.0-214.org

实验内容简介：
OD-H　100+1
214nm　1.0ml/min



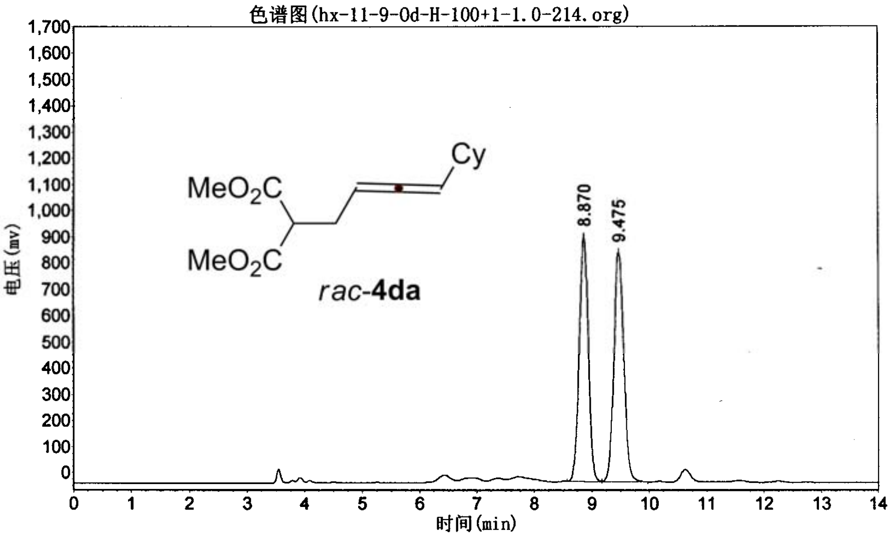
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.965	6980.922	92922.148	2.3503
2		9.643	311130.375	3860662.250	97.6497
总计			318111.297	3953584.398	100.0000

hx-11-9

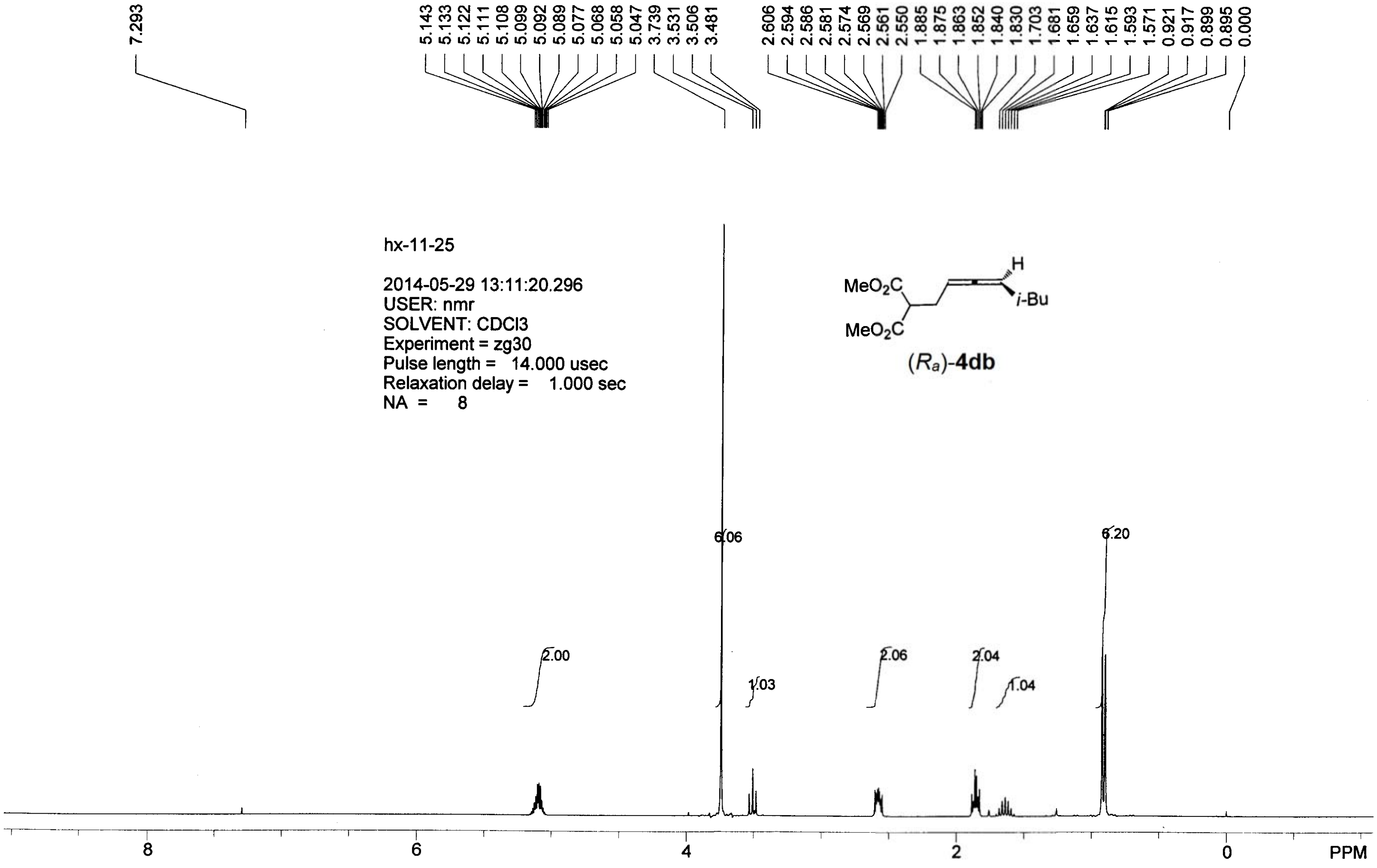
实验时间：2014-05-20,17:31:11　　　　　　　　　报告时间：2014-05-20,17:35:07
谱图文件:F:\slf\huangxin\hx-11-9\新建文件夹\hx-11-9-0d-H-100+1-1.0-214.org

实验内容简介：
OD-H　100+1
214nm　1.0ml/min

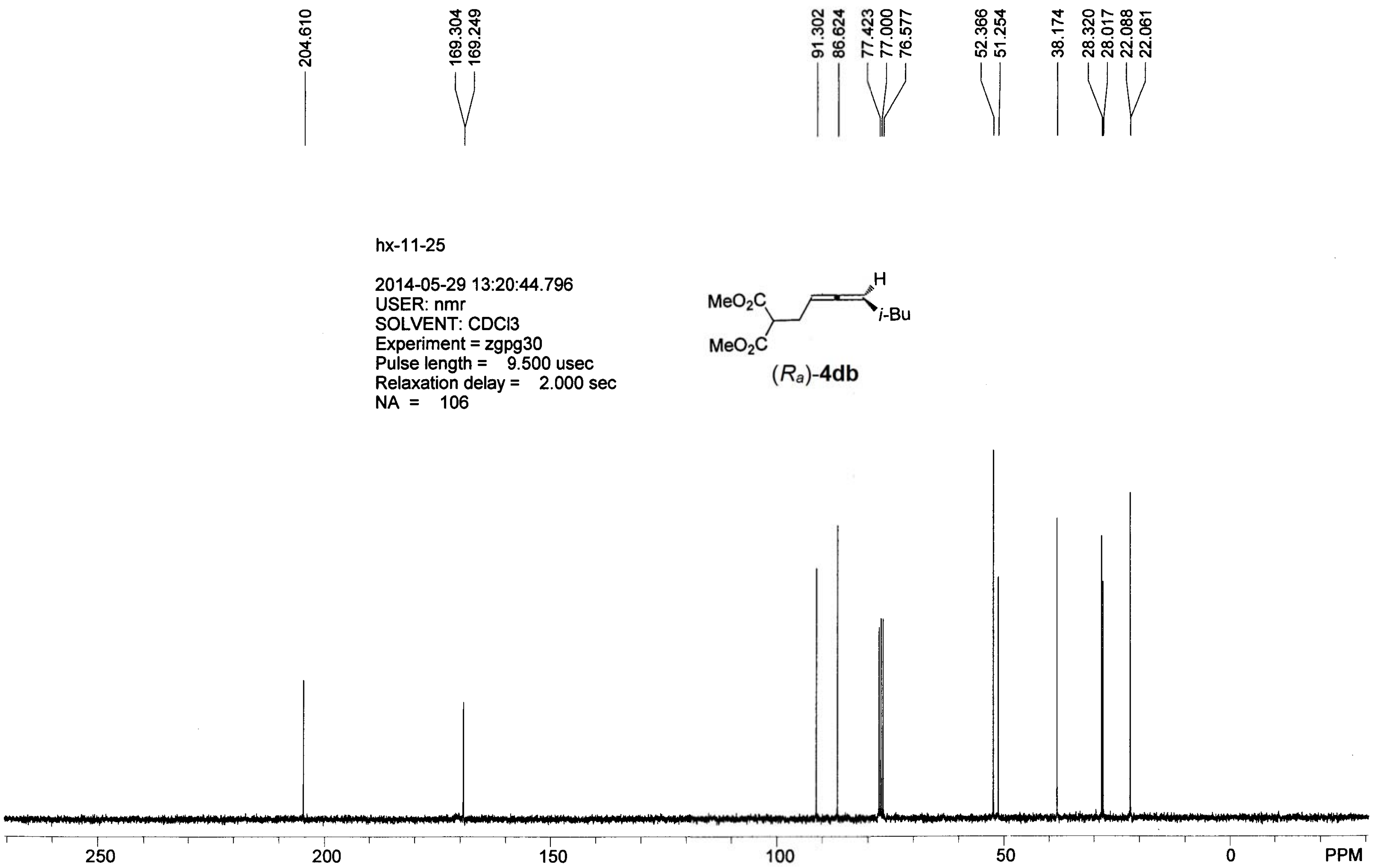


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.870	931001.375	10305495.000	49.6255
2		9.475	872660.125	10461015.000	50.3745
总计			1803661.500	20766510.000	100.0000


7.293
5.143
5.133
5.122
5.111
5.108
5.099
5.092
5.089
5.077
5.068
5.058
5.047
3.739
3.531
3.506
3.481
2.606
2.594
2.586
2.581
2.574
2.569
2.561
2.550
1.885
1.875
1.863
1.852
1.840
1.830
1.703
1.681
1.659
1.637
1.615
1.593
1.571
0.921
0.917
0.899
0.895
0.000
hx-11-25
2014-05-29 13:11:20.296
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
MeO2C
MeO2C
H
i-Bu
6.06
6.20
2.00
1.03
2.06
2.04
1.04
8
6
4
2
0
PPM

(R_a)-**4db**



(R_a)-**4db**

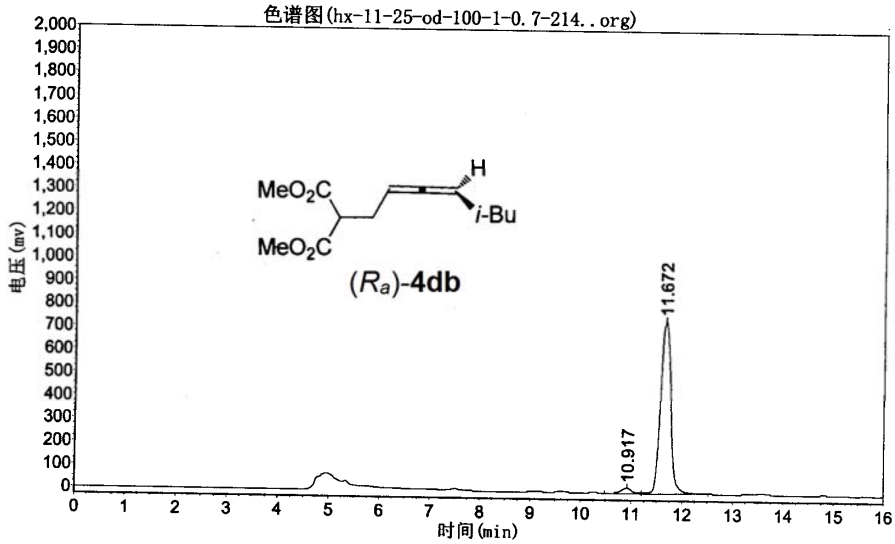
hx-11-25

2014-05-29 13:20:44.796
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 106

hx-11-25-od-h-100-1-0.7-214

实验时间：2014/5/27,15:54:23　　　　报告时间：2014/5/27,16:27:20
谱图文件:D:\zhuguangjiong\hx\20140527\hx-11-25-od-100-1-0.7-214..org

实验内容简介：



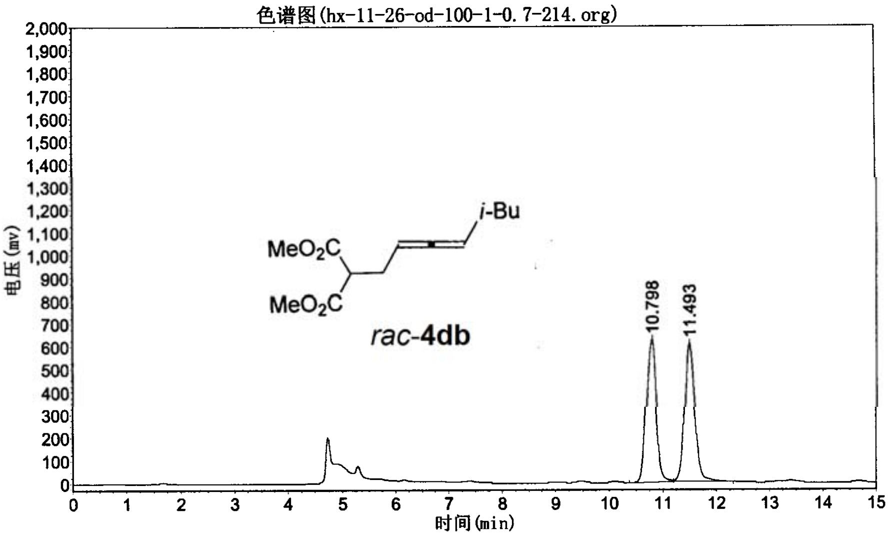
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		10.917	23981.508	314672.219	2.9362
2		11.672	745760.313	10402385.000	97.0638
总计			769741.820	10717057.219	100.0000

hx-11-26-od-h-100-1-0.7-214

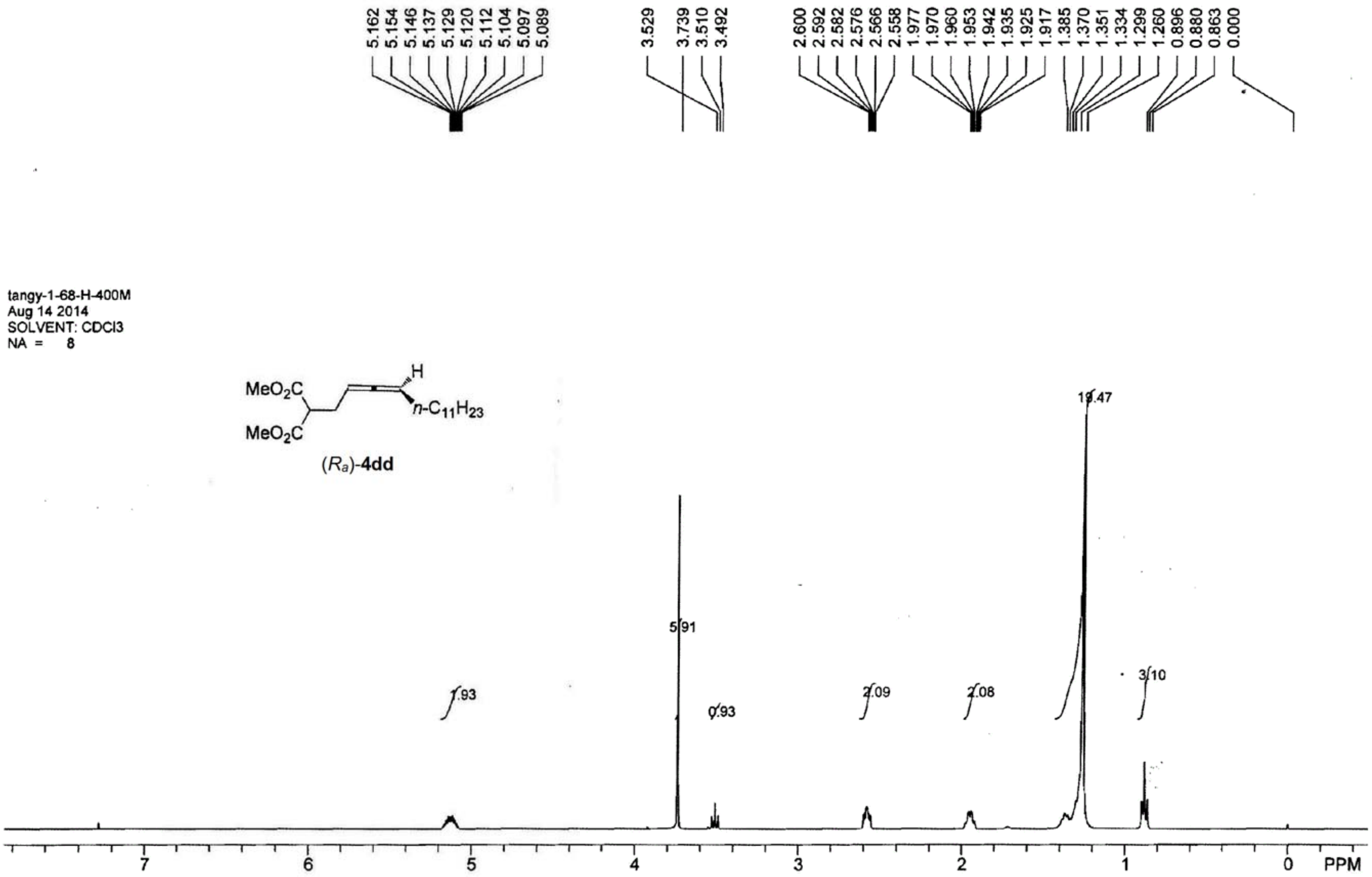
实验时间：2014/5/27,15:17:20　　　　　　　　　　报告时间：2014/5/27,16:24:54
谱图文件:D:\zhuguangjiong\hx\20140527\hx-11-26-od-100-1-0.7-214.org

实验内容简介：

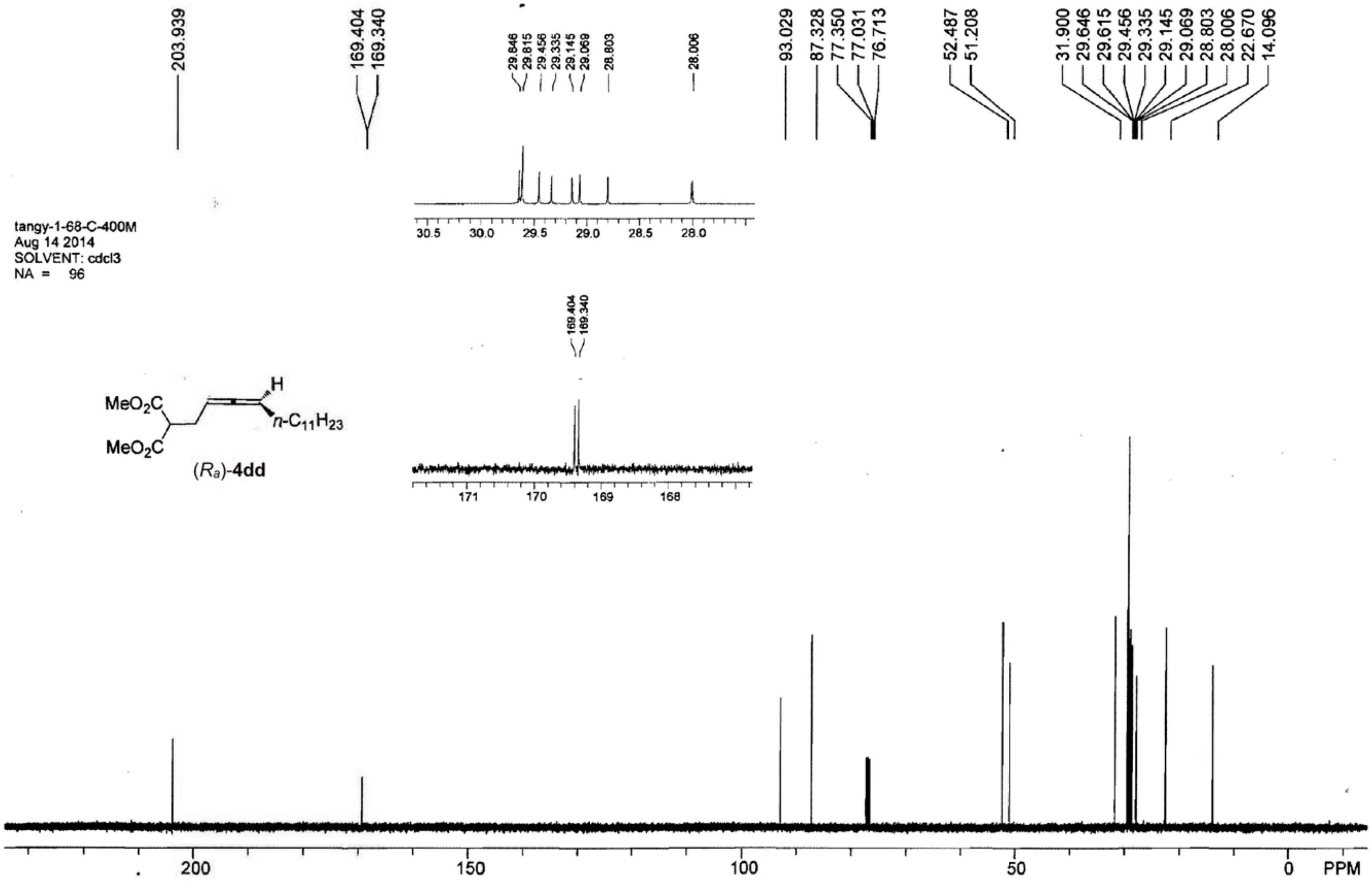


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		10.798	623178.313	8022705.500	49.8512
2		11.493	605930.188	8070587.000	50.1488
总计			1229108.500	16093292.500	100.0000


5.162
5.154
5.146
5.137
5.129
5.120
5.112
5.104
5.097
5.089
3.529
3.739
3.510
3.492
2.600
2.592
2.582
2.576
2.566
2.558
1.977
1.970
1.960
1.953
1.942
1.935
1.925
1.917
1.385
1.370
1.351
1.334
1.299
1.260
0.896
0.880
0.863
0.000
tangy-1-68-H-400M
Aug 14 2014
SOLVENT: CDCl3
NA = 8
MeO2C
MeO2C
H
n-C11H23
1.93
5.91
0.93
2.09
2.08
19.47
3.10
7
6
5
4
3
2
1
0
PPM

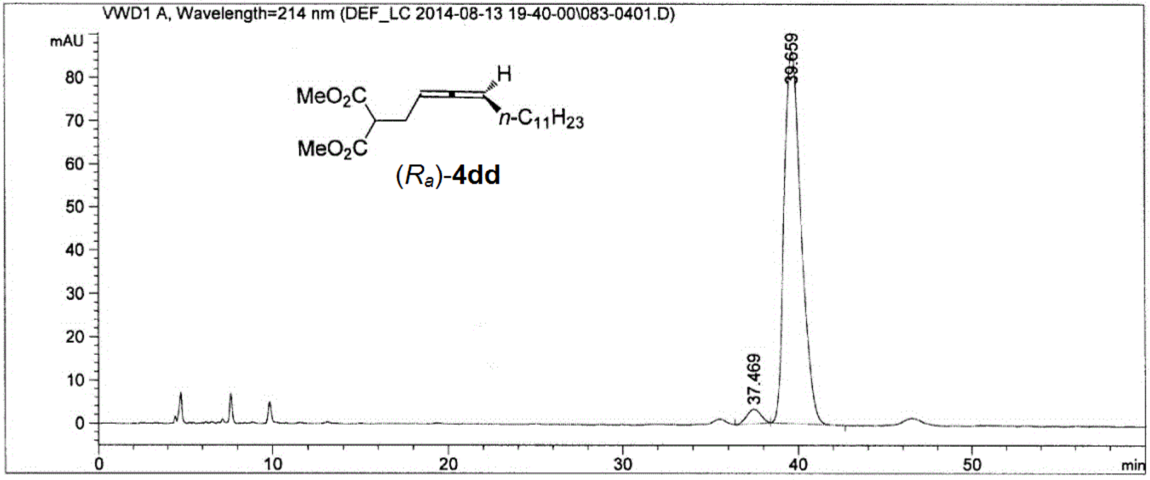
(R_a)-**4dd**


203.939
169.404
169.340
29.846
29.815
29.456
29.335
29.145
29.069
28.803
28.006
93.029
87.328
77.350
77.031
76.713
52.487
51.208
31.900
29.646
29.615
29.456
29.335
29.145
29.069
28.803
28.006
22.670
14.096
30.5
30.0
29.5
29.0
28.5
28.0
169.404
169.340
171
170
169
168
tangy-1-68-C-400M
Aug 14 2014
SOLVENT: cdcl3
NA = 96
MeO2C
MeO2C
H
n-C11H23
200
150
100
50
0
PPM

(R_a)-**4dd**

```
Data File D:\CHEM32\1\DATA\DEF_LC 2014-08-13 19-40-00\083-0401.D
Sample Name: SLF-1-68 PC-4 M82W18 214 0.7 20

    =====================================================================
    Acq. Operator   : WXL                              Seq. Line :    4
    Acq. Instrument : instr1                            Location : Vial 83
    Injection Date  : 13/08/2014 22:42:54                    Inj :    1
                                                      Inj Volume : 3.000 µl
    Acq. Method     : D:\CHEM32\1\DATA\DEF_LC 2014-08-13 19-40-00\WXL.M
    Last changed    : 13/08/2014 19:40:00 by WXL
    Analysis Method : D:\CHEM32\1\DATA\WXL\WXL.M
    Last changed    : 14/08/2014 08:24:50 by LXG
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



```
    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :       Signal
    Multiplier:                   :       1.0000
    Dilution:                     :       1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=214 nm

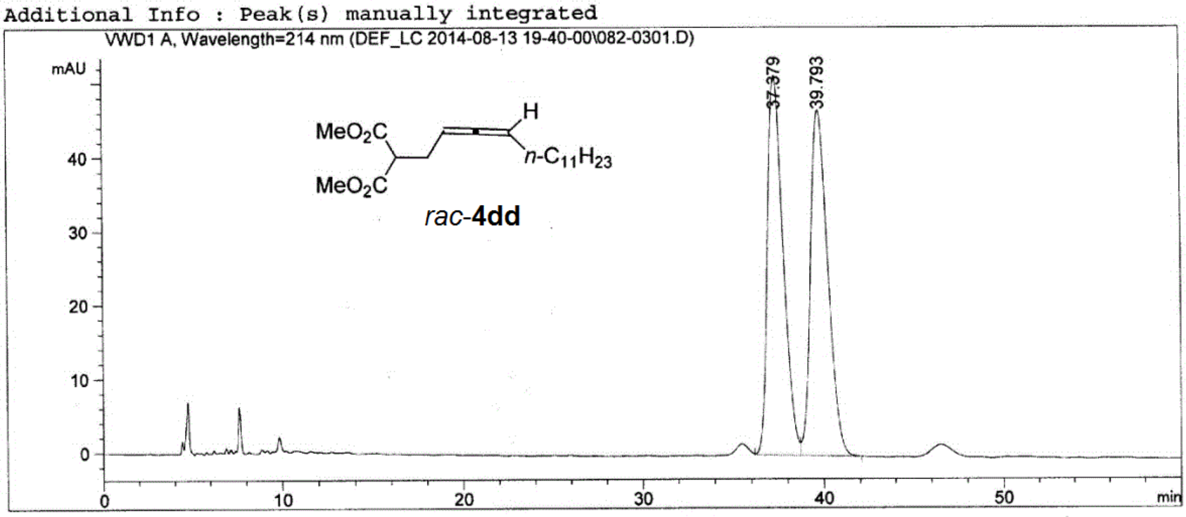
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1  37.469 MM    0.9260  183.95093    3.31099   3.1003
       2  39.659 MM    1.1114 5749.43115   86.21941  96.8997

    Totals :                  5933.38208   89.53040

    =====================================================================
                            *** End of Report ***
```

```
Data File D:\CHEM32\1\DATA\DEF_LC 2014-08-13 19-40-00\082-0301.D
Sample Name: SLF-1-68+- PC-4 M82W18 214 0.7 20

    =====================================================================
    Acq. Operator   : WXL                              Seq. Line :    3
    Acq. Instrument : instr1                            Location : Vial 82
    Injection Date  : 13/08/2014 21:42:11                    Inj :    1
                                                     Inj Volume : 3.000 µl
    Acq. Method     : D:\CHEM32\1\DATA\DEF_LC 2014-08-13 19-40-00\WXL.M
    Last changed    : 13/08/2014 19:40:00 by WXL
    Analysis Method : D:\CHEM32\1\DATA\WXL\WXL.M
    Last changed    : 14/08/2014 08:24:50 by LXG
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



```
    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier:                  :      1.0000
    Dilution:                    :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=214 nm

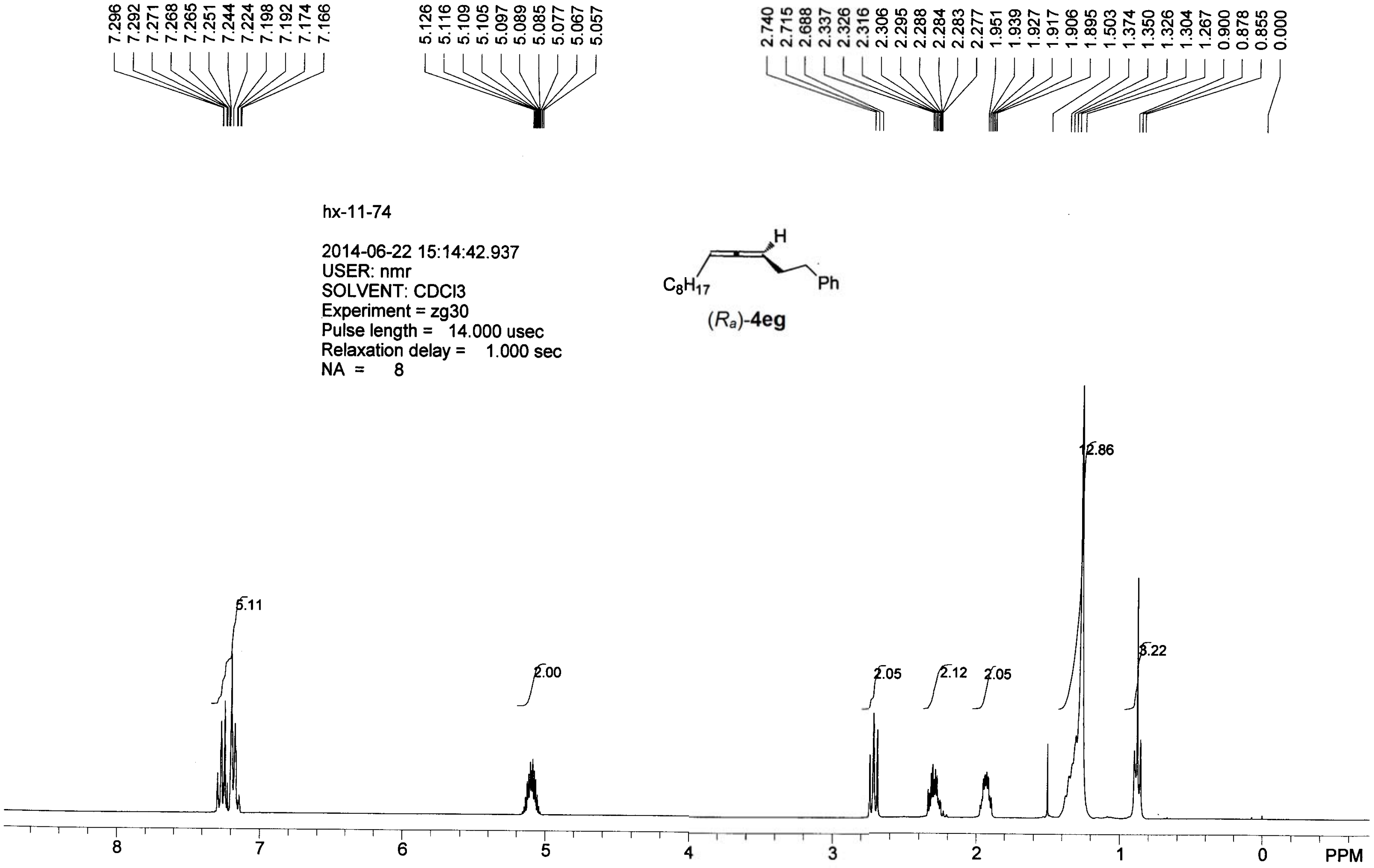
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1  37.379 MF    1.0040 3099.37500   51.45283  50.0926
       2  39.793 FM    1.0977 3087.91040   46.88557  49.9074

    Totals :                  6187.28540   98.33840

    =====================================================================
                             *** End of Report ***



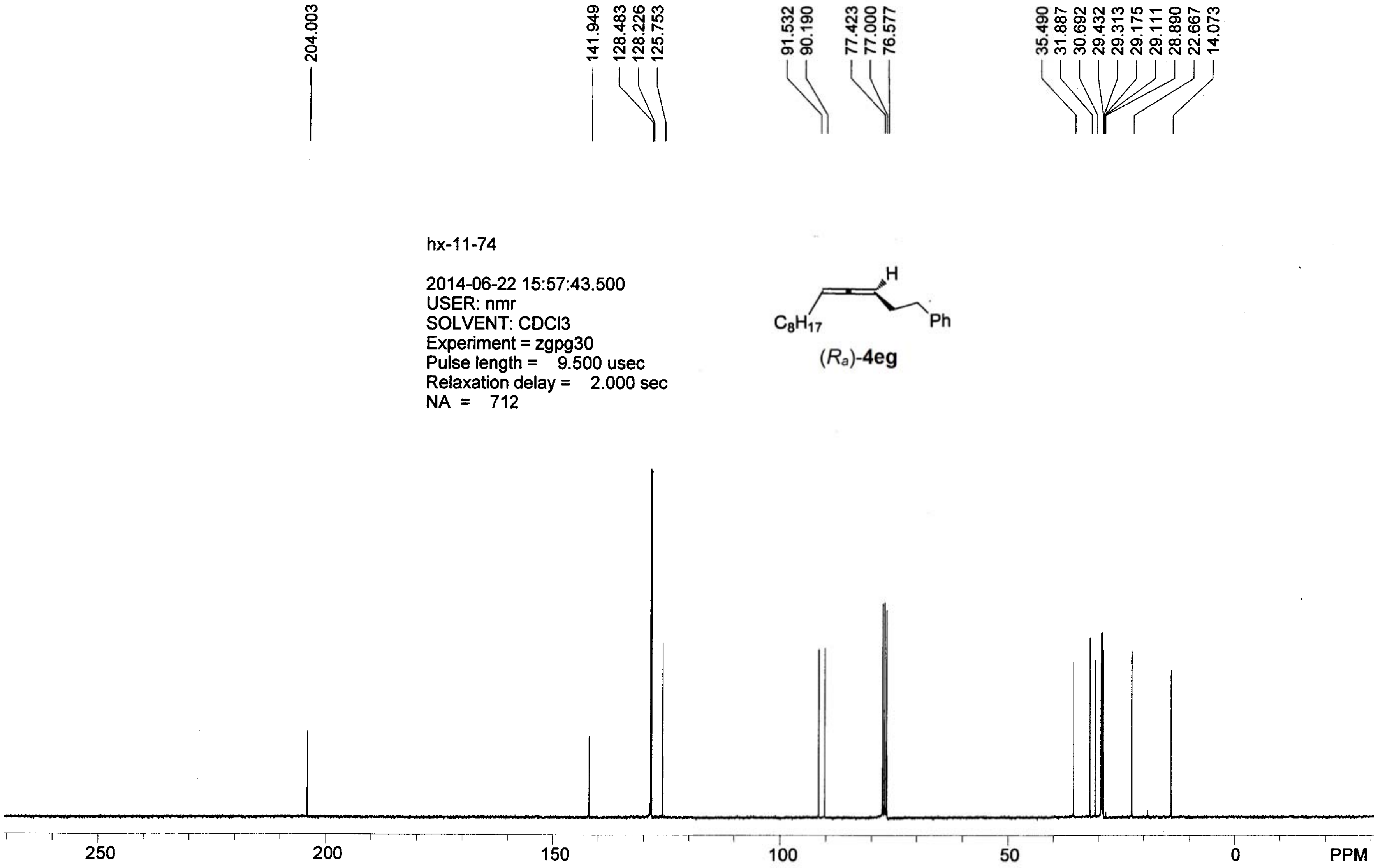
 instr1 14/08/2014 08:38:22 LXG                                Page    1 of 1
```



hx-11-74

2014-06-22 15:14:42.937
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8

(R_a)-**4eg**



(*R*$_a$)-**4eg**

hx-11-74

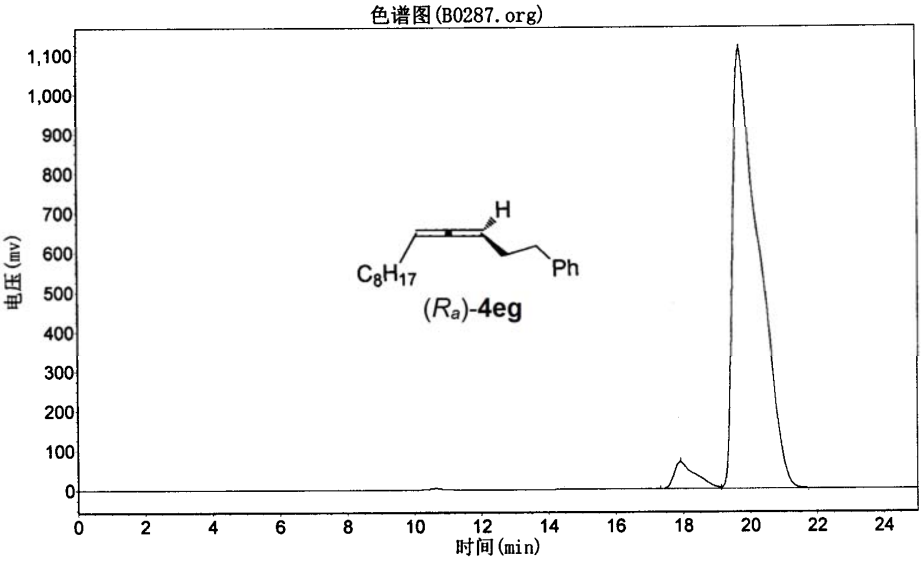
2014-06-22 15:57:43.500
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 712

hx-11-74

实验单位：zju
实验时间：2014-06-27, 18:20:05
谱图文件:D:\浙大智达\N2000\样品\B0287.org

实验者：hx
报告时间：2014-06-27, 18:46:31
积分方法:面积归一法

实验内容简介：
OD-H column, n-hexane/iPrOH = 100/0, 214 nm, 0.3 ml/min



分析结果表

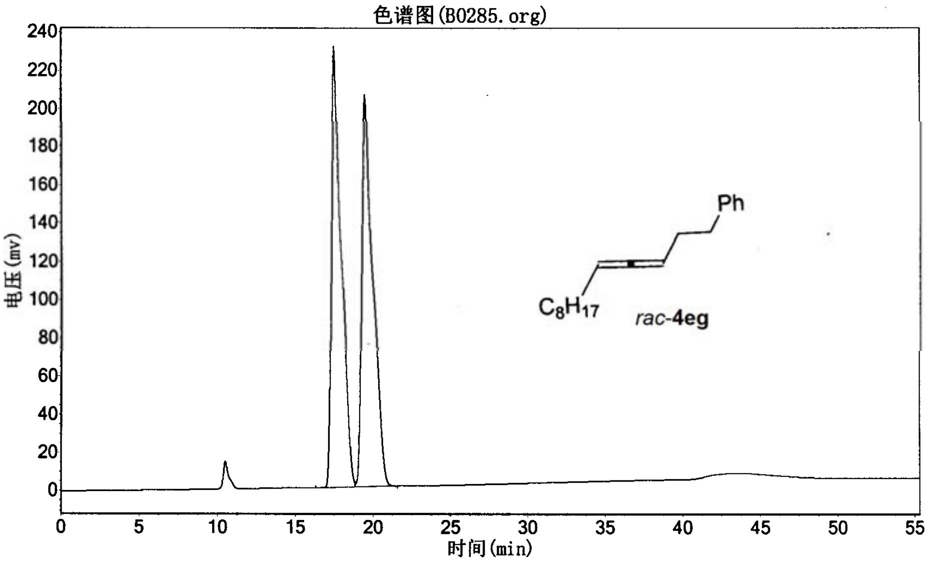
峰号	峰名	保留时间	峰高	峰面积	含量
1		17.917	67656.680	3023257.000	4.8138
2		19.735	1109539.625	59780280.000	95.1862
总计			1177196.305	62803537.000	100.0000

hx-11-60

实验单位：zju
实验时间：2014-06-27,16:38:14
谱图文件:D:\浙大智达\N2000\样品\B0285.org

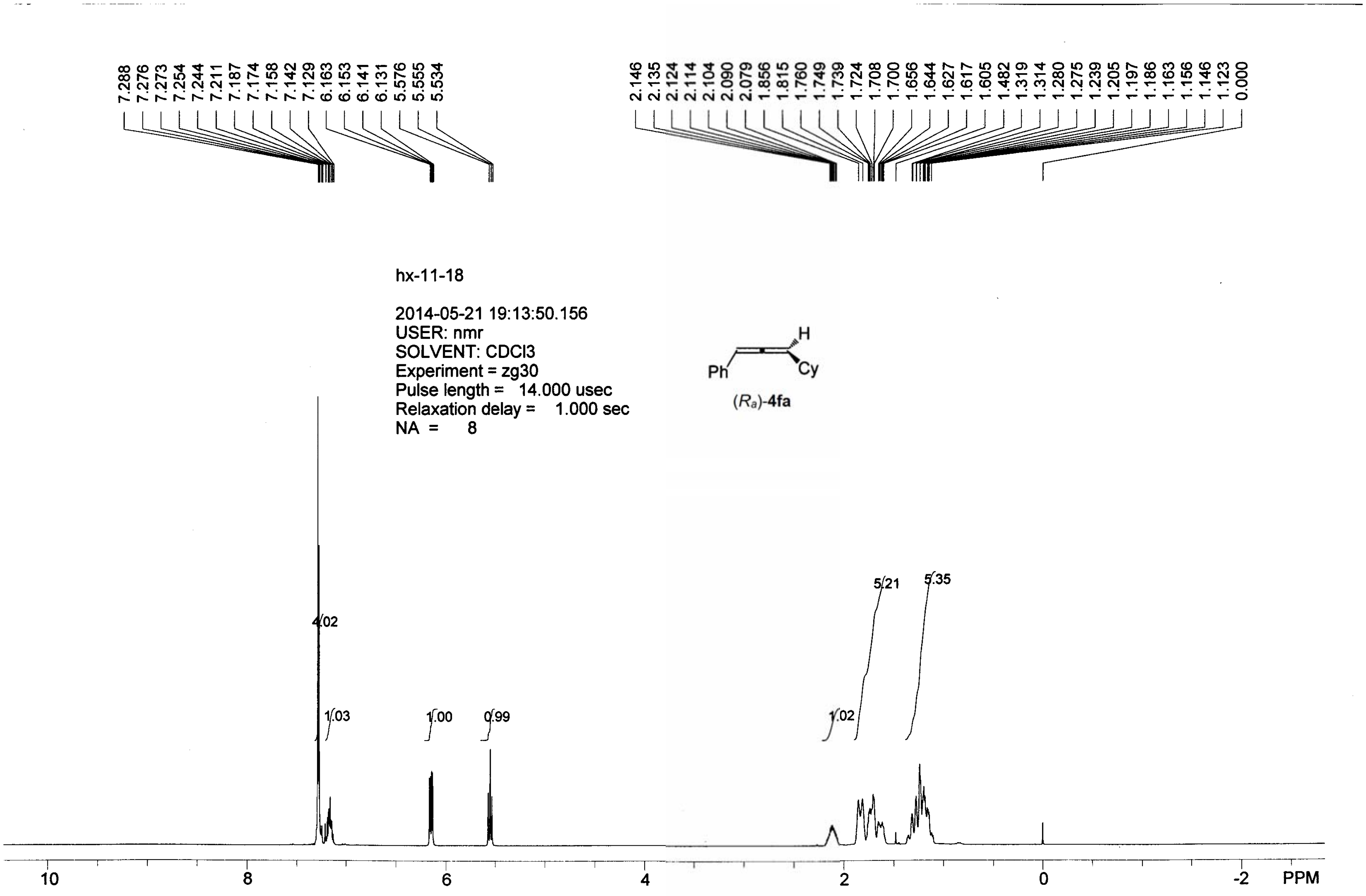
实验者：hx
报告时间：2014-06-27,17:48:18
积分方法:面积归一法

实验内容简介：
OD-H column, n-hexane/iPrOH = 100/0, 214 nm, 0.3 ml/min



分析结果表

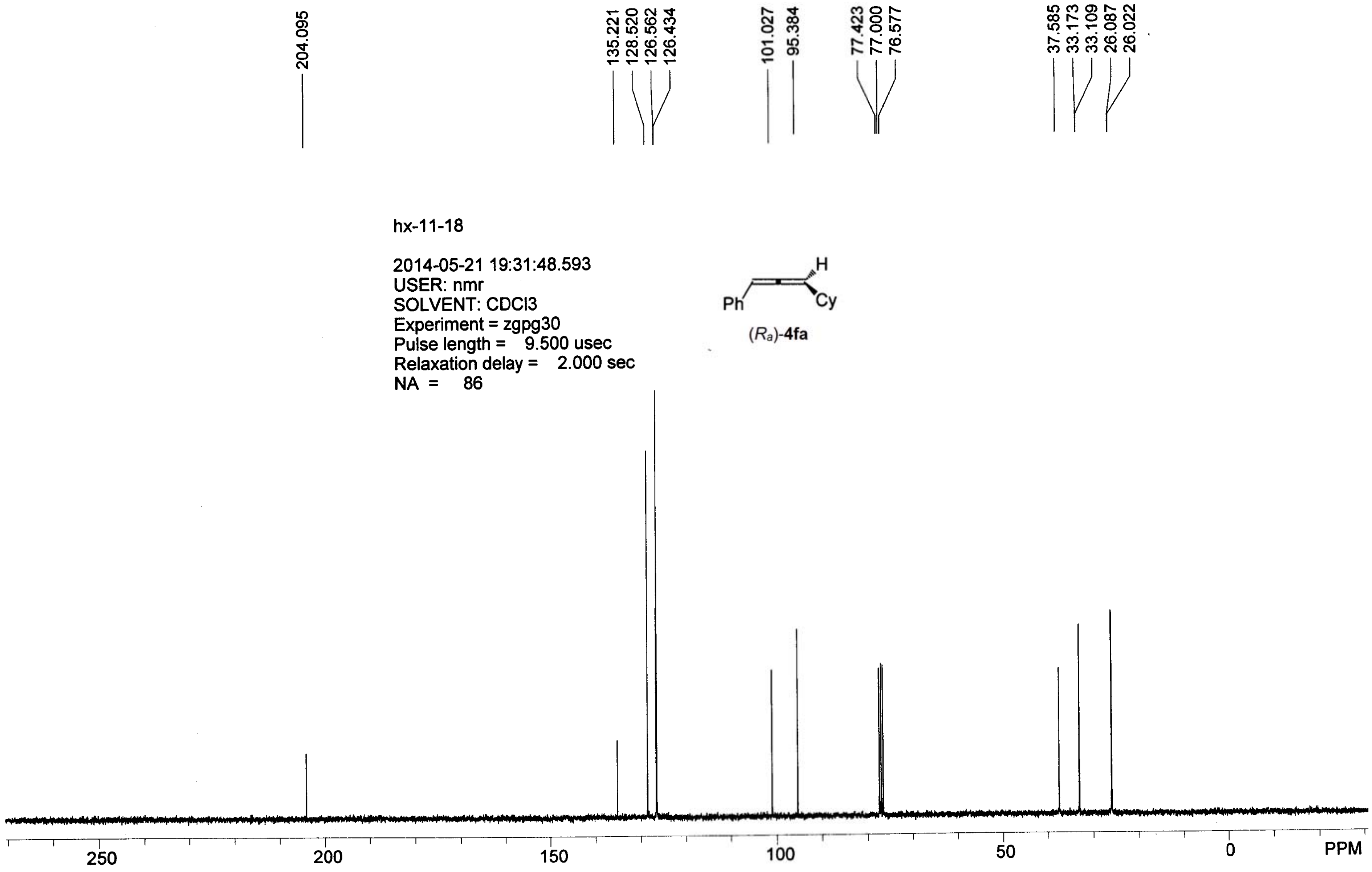
峰号	峰名	保留时间	峰高	峰面积	含量
1		17.490	228847.828	10030968.000	49.8641
2		19.465	203229.078	10085638.000	50.1359
总计			432076.906	20116606.000	100.0000



hx-11-18

2014-05-21 19:13:50.156
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8

(R_a)-**4fa**



(*R*$_a$)-**4fa**

hx-11-18

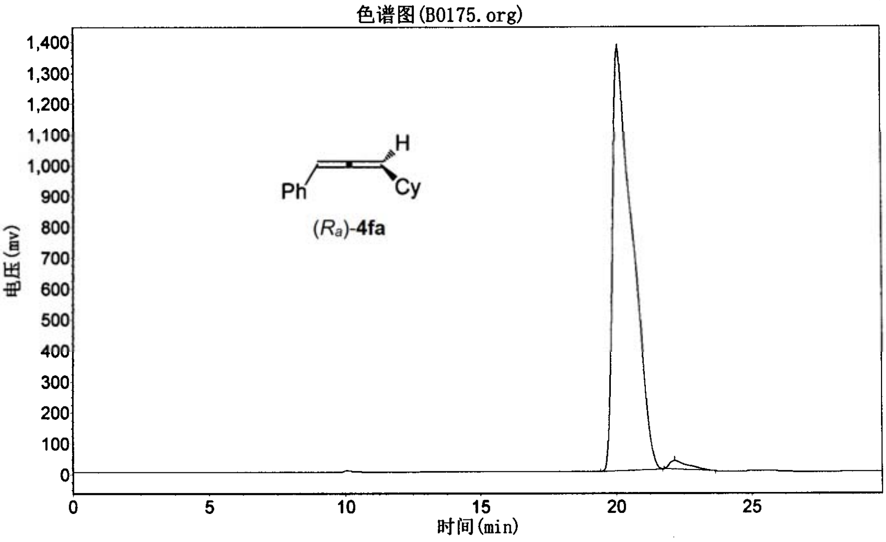
2014-05-21 19:31:48.593
USER: nmr
SOLVENT: CDCl3
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 86

hx-11-18

实验单位：zju
实验时间：2014-05-21,19:31:00
谱图文件:D:\浙大智达\N2000\样品\B0175.org

实验者：hx
报告时间：2014-05-21,20:03:25
积分方法:面积归一法

实验内容简介：
OD-H column, n-hexane/iPrOH = 100/0, 214 nm, 0.3 ml/min



分析结果表

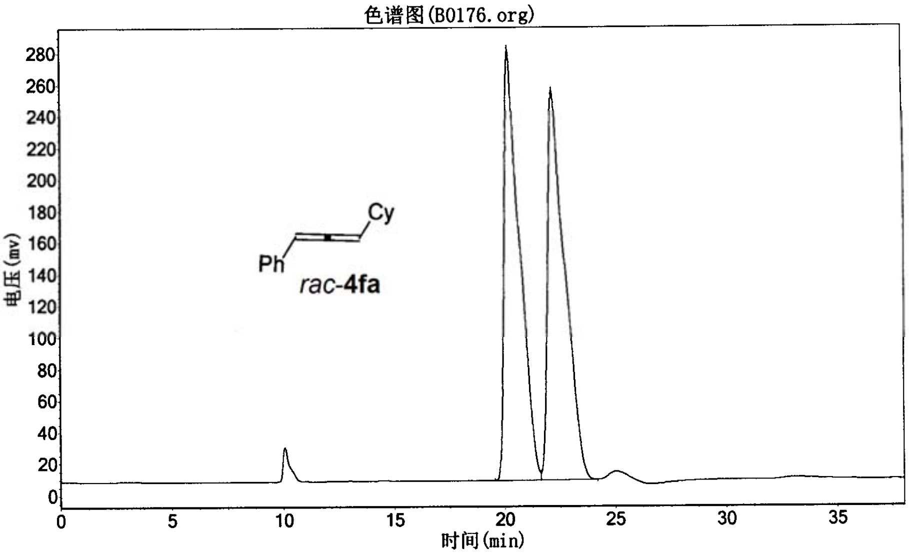
峰号	峰名	保留时间	峰高	峰面积	含量
1		20.102	1365809.875	69352888.000	98.1229
2		22.147	27621.168	1326733.250	1.8771
总计			1393431.043	70679621.250	100.0000

hx-11-19

实验单位：zju
实验时间：2014-05-21,20:05:59
谱图文件:D:\浙大智达\N2000\样品\B0176.org

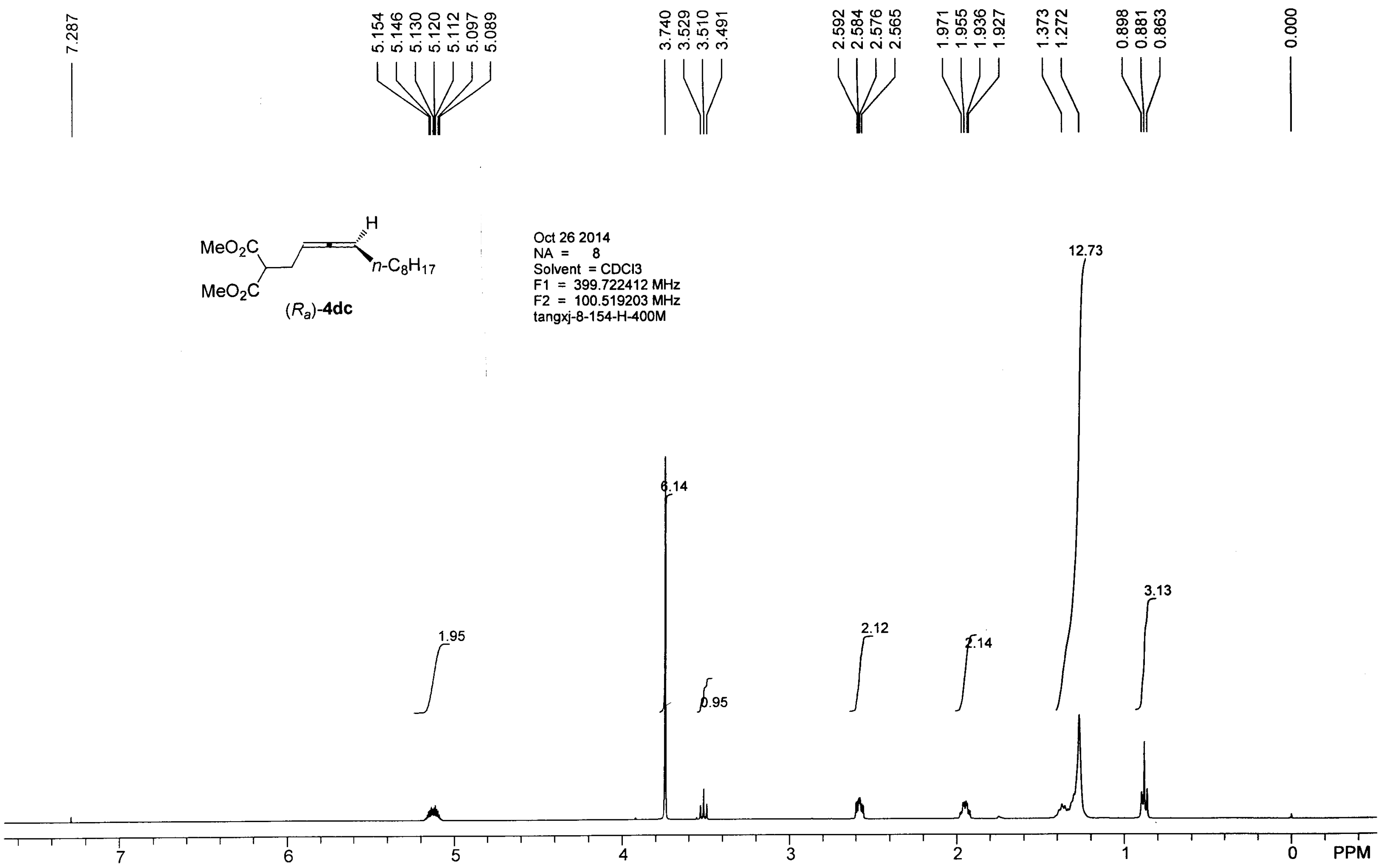
实验者：hx
报告时间：2014-05-21,20:45:28
积分方法:面积归一法

实验内容简介：
OD-H column, n-hexane/iPrOH = 100/0, 214 nm, 0.3 ml/min

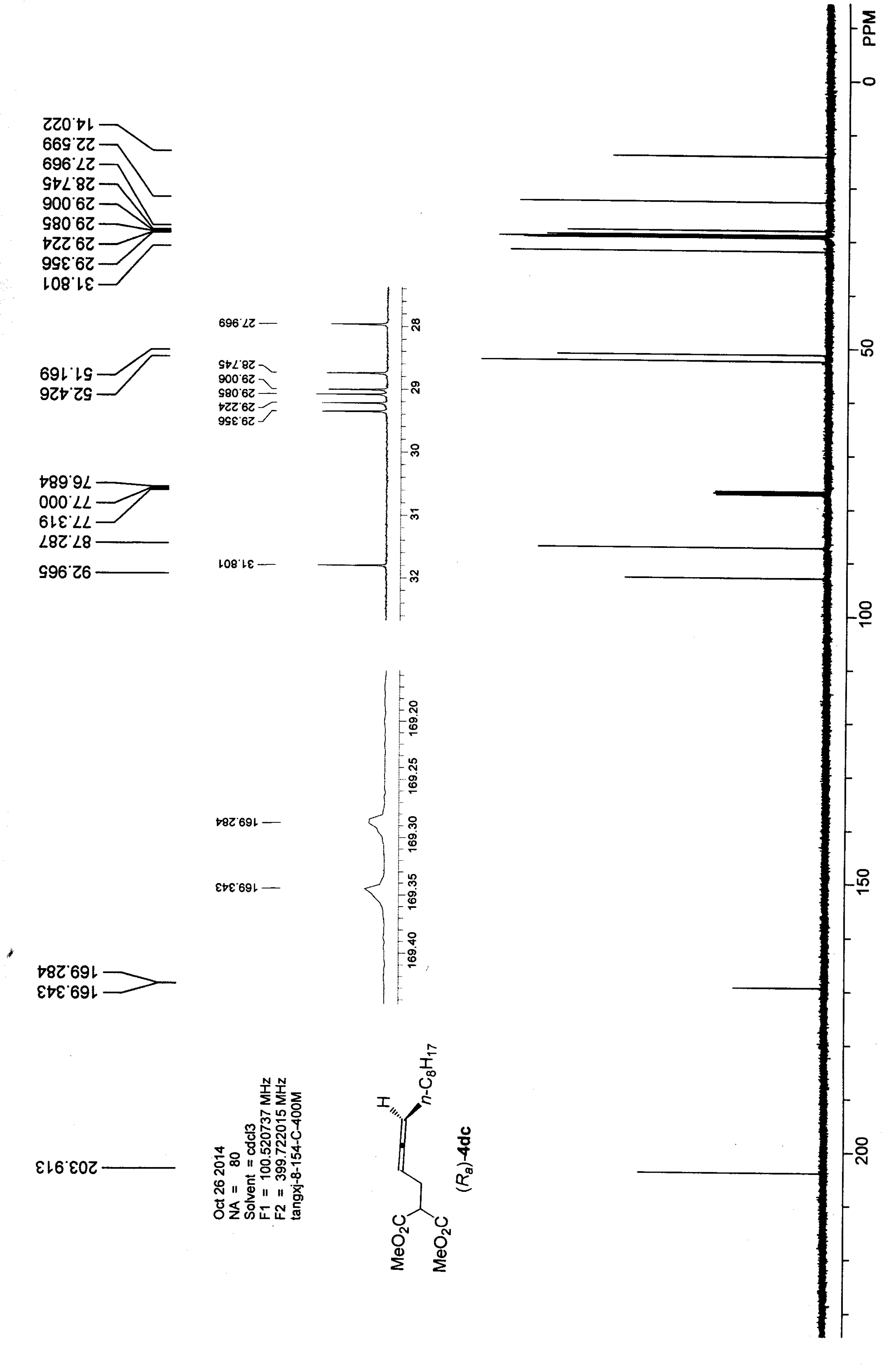


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		20.228	272890.219	13287882.000	49.9622
2		22.210	246186.547	13307984.000	50.0378
总计			519076.766	26595866.000	100.0000

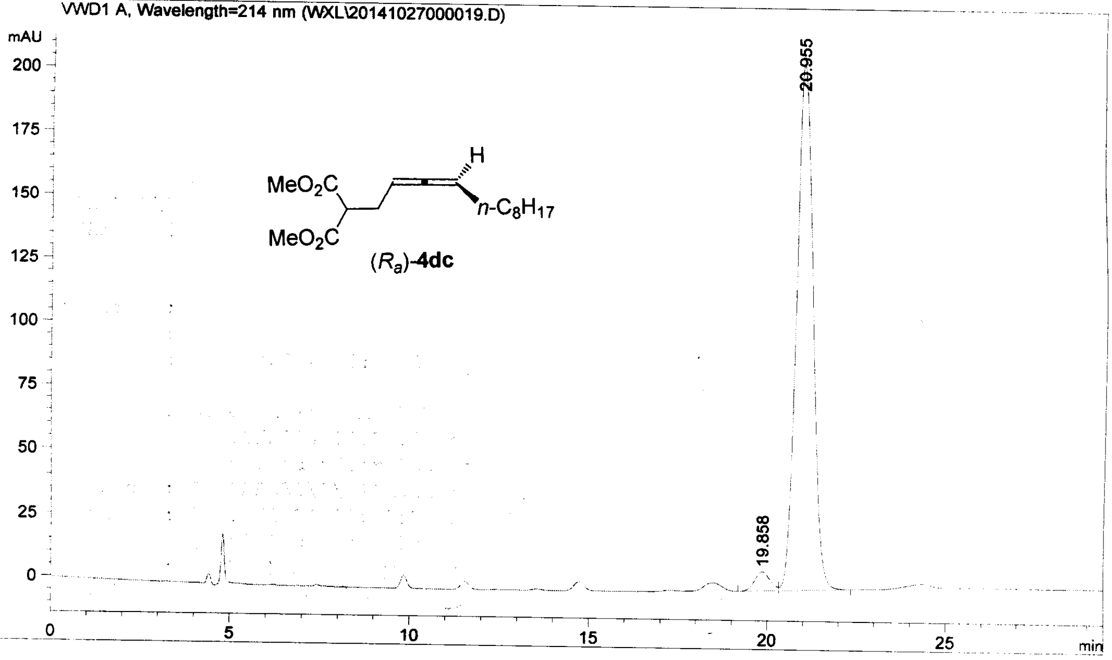

(*R*$_a$)-**4dc**

Oct 26 2014
NA = 8
Solvent = CDCl3
F1 = 399.722412 MHz
F2 = 100.519203 MHz
tangxj-8-154-H-400M


14.022
22.599
27.969
28.745
29.006
29.085
29.224
29.356
31.801
51.169
52.426
76.684
77.000
77.319
87.287
92.965
169.284
169.343
203.913
27.969
28.745
29.006
29.085
29.224
29.356
31.801
28
29
30
31
32
169.284
169.343
169.20
169.25
169.30
169.35
169.40
Oct 26 2014
NA = 80
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
tangxj-8-154-C-400M
MeO$_2$C
MeO$_2$C
H
n-C$_8$H$_{17}$
(R_a)-4dc
PPM
0
50
100
150
200

```
Data File D:\CHEM32\1\DATA\WXL\20141027000019.D
Sample Name: TANGXJ-8-154 M82W18 214 0.7 20

    =====================================================================
    Acq. Operator   : WXL
    Acq. Instrument : instr1                    Location : Vial 81
    Injection Date  : 27/10/2014 10:16:51
                                              Inj Volume : 5.000 µl
    Acq. Method     : D:\CHEM32\1\DATA\WXL\WXL.M
    Last changed    : 27/10/2014 10:16:05 by WXL
                      (modified after loading)
    Analysis Method : D:\CHEM32\1\DATA\WXL\WXL.M
    Last changed    : 27/10/2014 09:50:37 by WXL
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



```
    =====================================================================
                         Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier:                  :       1.0000
    Dilution:                    :       1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=214 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1  19.858 BV    0.4573  218.14836    7.34882   3.1946
       2  20.955 VB    0.5020 6610.51025  206.18468  96.8054

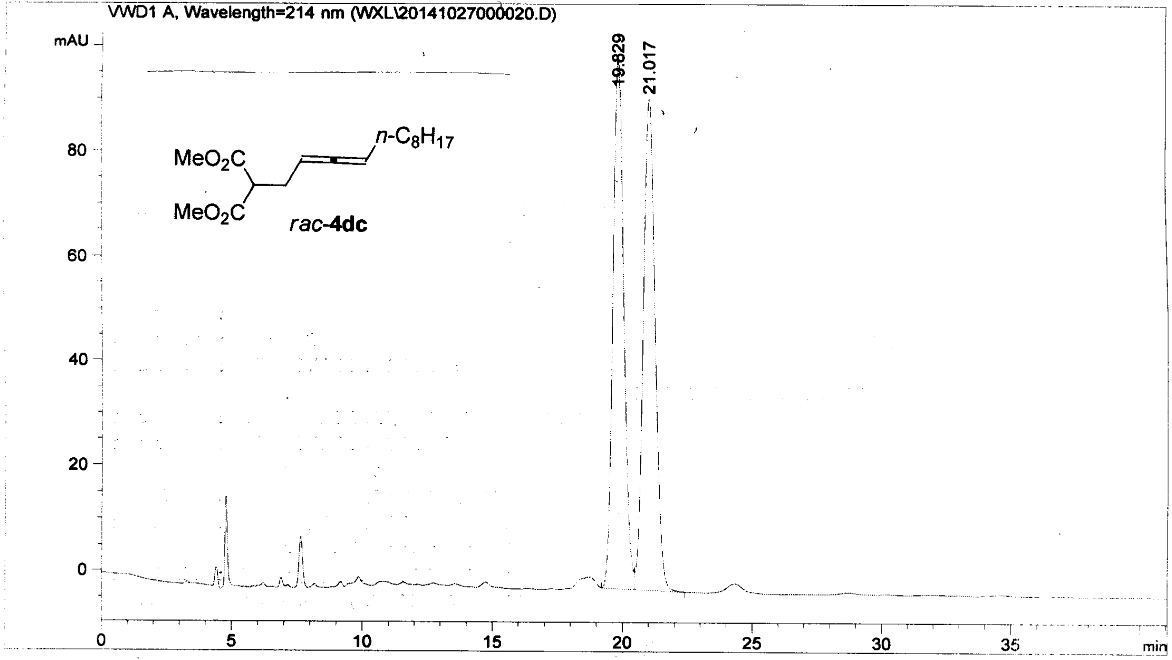
    Totals :                  6828.65862  213.53350

    =====================================================================
                          *** End of Report ***

instr1 27/10/2014 16:03:28 WXL                                Page    1 of 1
```

```
Data File D:\CHEM32\1\DATA\WXL\20141027000020.D
Sample Name: TANGY-1-66+- M82W18 214 0.7 20

=====================================================================
Acq. Operator   : WXL
Acq. Instrument : instr1                     Location : Vial 82
Injection Date  : 27/10/2014 10:47:48
                                           Inj Volume : 5.000 µl
Acq. Method     : D:\CHEM32\1\DATA\WXL\WXL.M
Last changed    : 27/10/2014 10:46:37 by WXL
                  (modified after loading)
Analysis Method : D:\CHEM32\1\DATA\WXL\WXL.M
Last changed    : 27/10/2014 09:50:37 by WXL
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



```
=====================================================================
                         Area Percent Report
=====================================================================

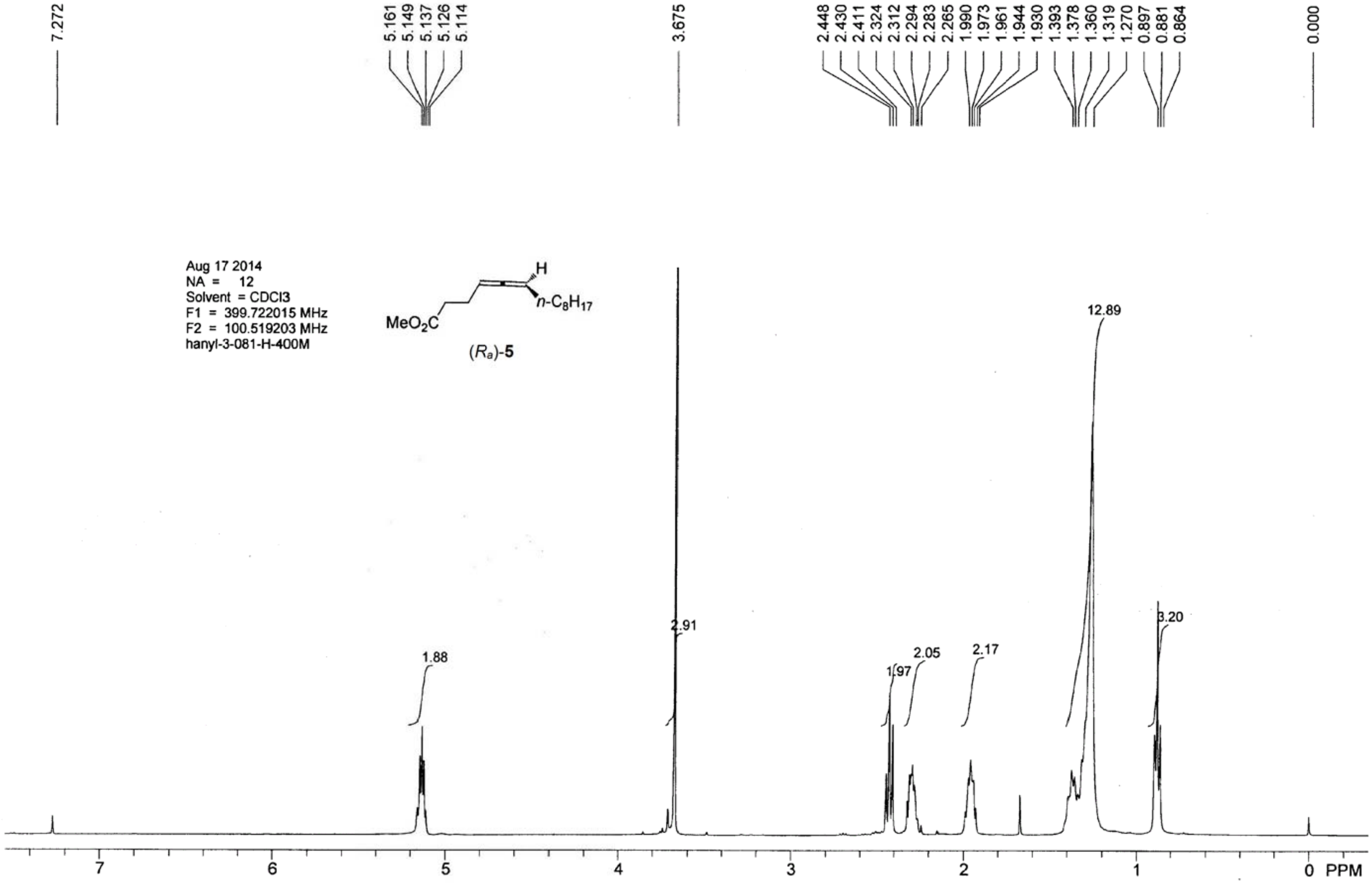
Sorted By             :      Signal
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=214 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.829 BV    0.4537 2932.67017  100.72310  49.8216
   2  21.017 VB    0.4921 2953.67358   93.62585  50.1784

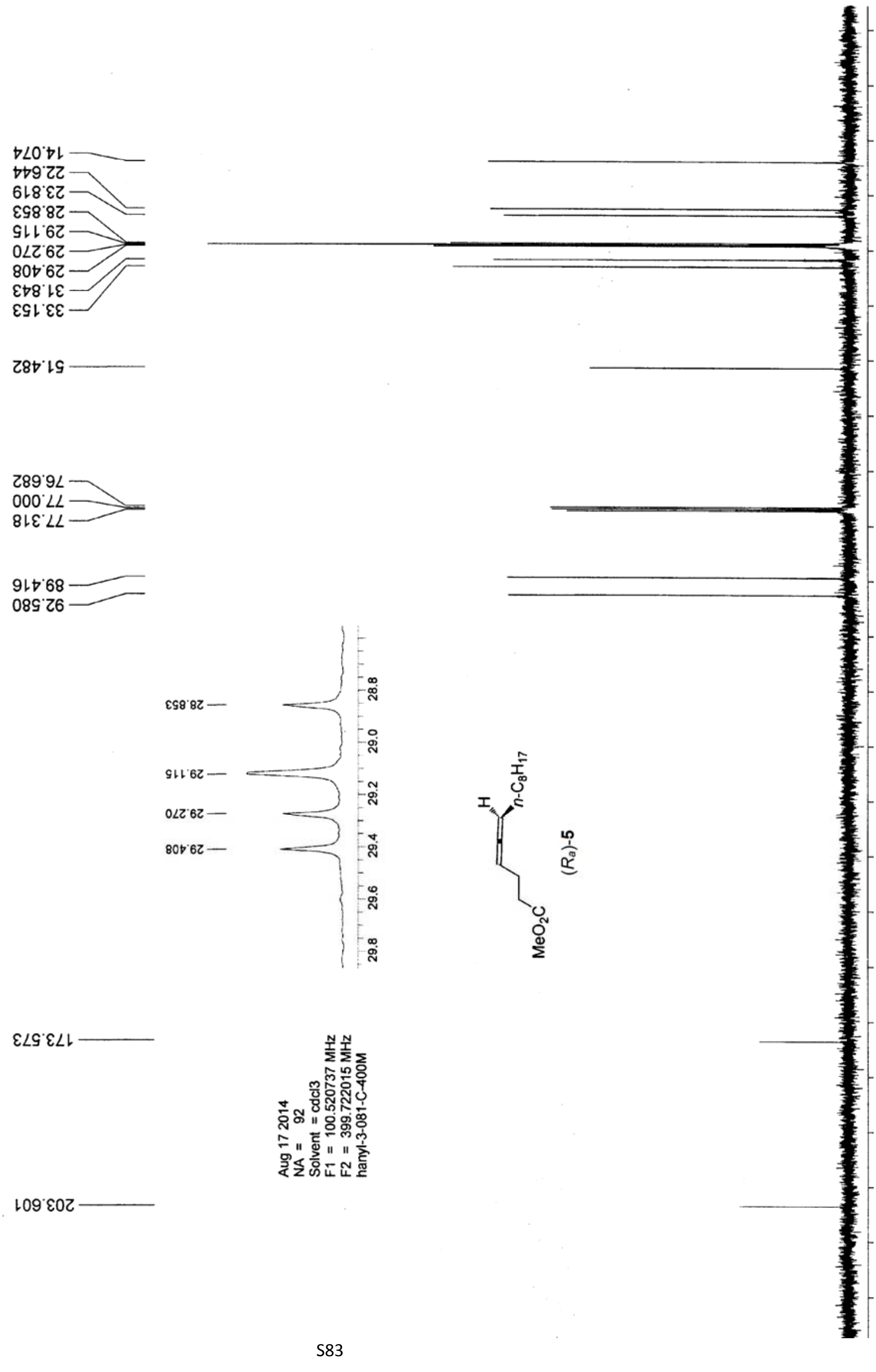
Totals :                  5886.34375  194.34895

=====================================================================
                         *** End of Report ***
```



Aug 17 2014
NA = 12
Solvent = CDCl3
F1 = 399.722015 MHz
F2 = 100.519203 MHz
hanyl-3-081-H-400M

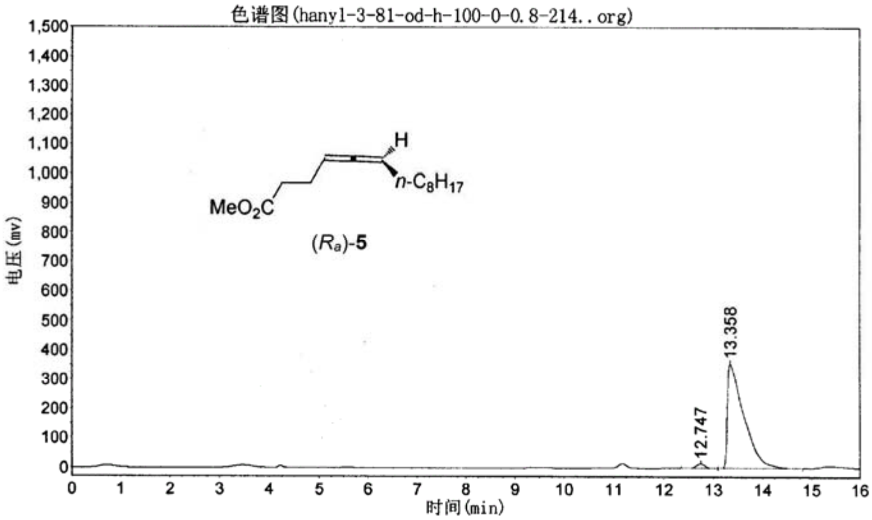
(R_a)-**5**


14.074
22.644
23.819
28.853
29.115
29.270
29.408
31.843
33.153
51.482
76.682
77.000
77.318
89.416
92.580
173.573
203.601
28.853
29.115
29.270
29.408
28.8
29.0
29.2
29.4
29.6
29.8
H
n-C_8H_{17}
MeO_2C
(R_a)-**5**
Aug 17 2014
NA = 92
Solvent = cdcl3
F1 = 100.520737 MHz
F2 = 399.722015 MHz
hanyl-3-081-C-400M

hanyl-3-81-od-h-100-0-1-214

实验时间：2014-08-17, 16:49:22　　　　报告时间：2014-08-17, 18:03:28
谱图文件:D:\zhuguangjiong\20140817\hanyl-3-81-od-h-100-0-0.8-214..org

实验内容简介：



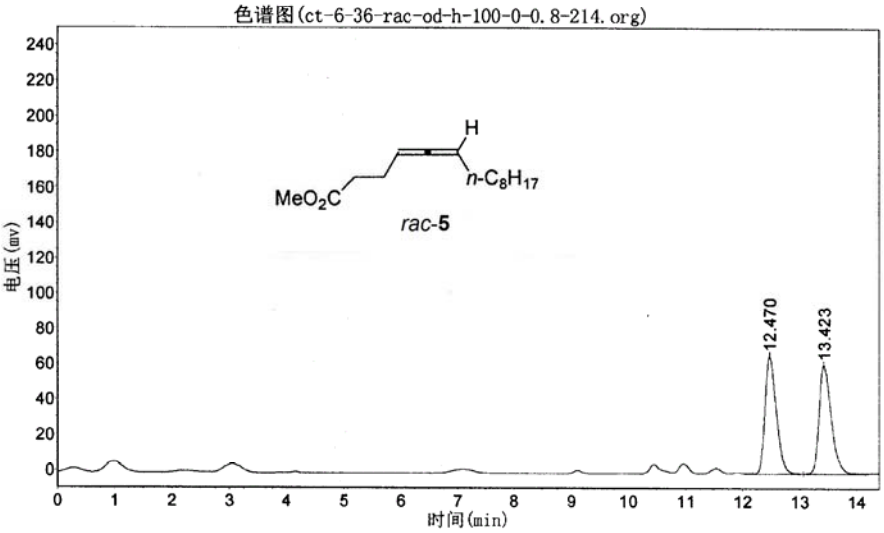
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		12.747	15958.741	204877.016	2.4229
2		13.358	357070.156	8251119.500	97.5771
总计			373028.897	8455996.516	100.0000

ct-6-36-rac-od-h-100-0-0.8-214

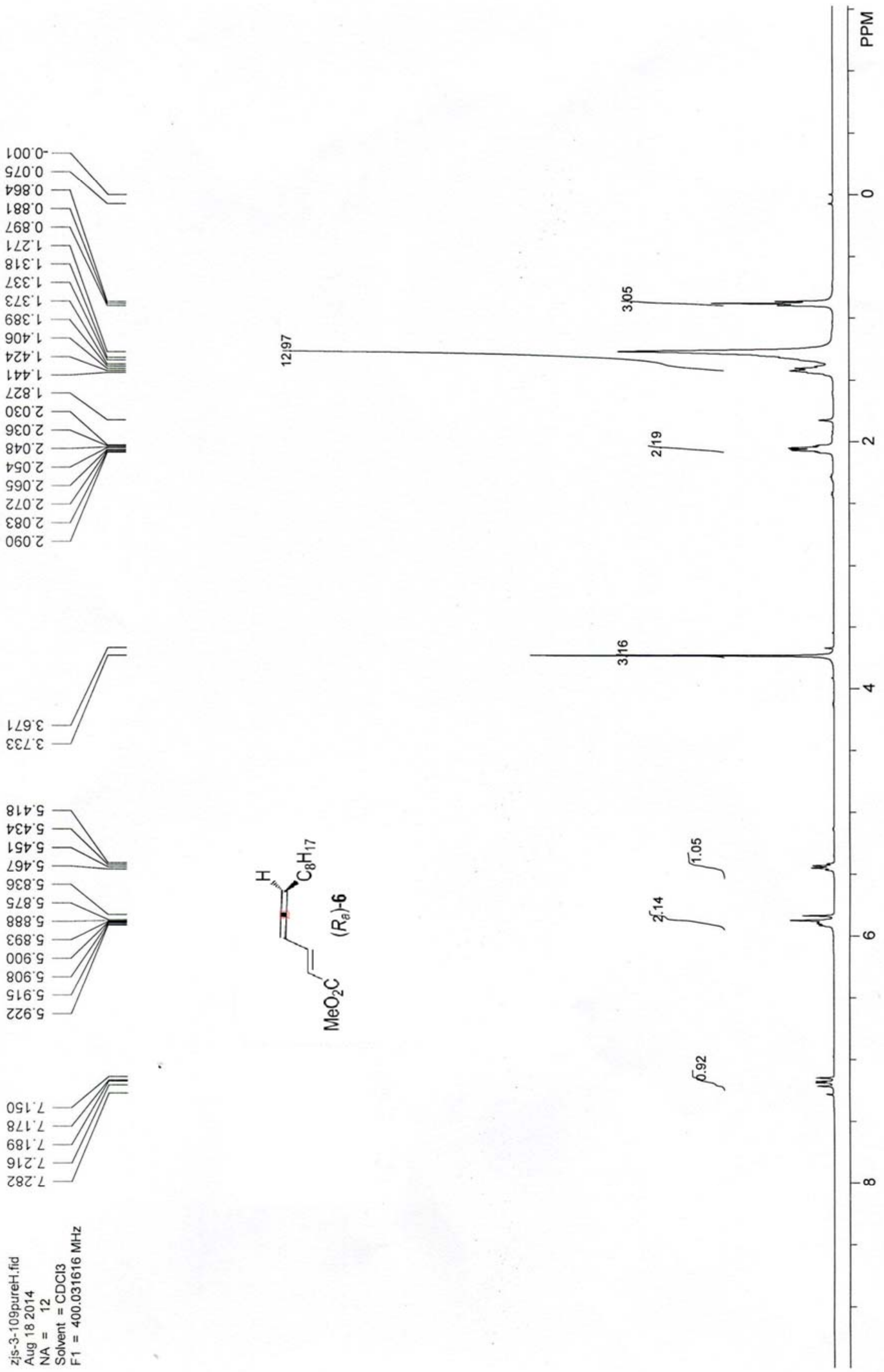
实验时间：2014-08-17,17:41:24　　报告时间：2014-08-17,17:59:38
谱图文件:D:\zhuguangjiong\20140817\ct-6-36-rac-od-h-100-0-0.8-214.org

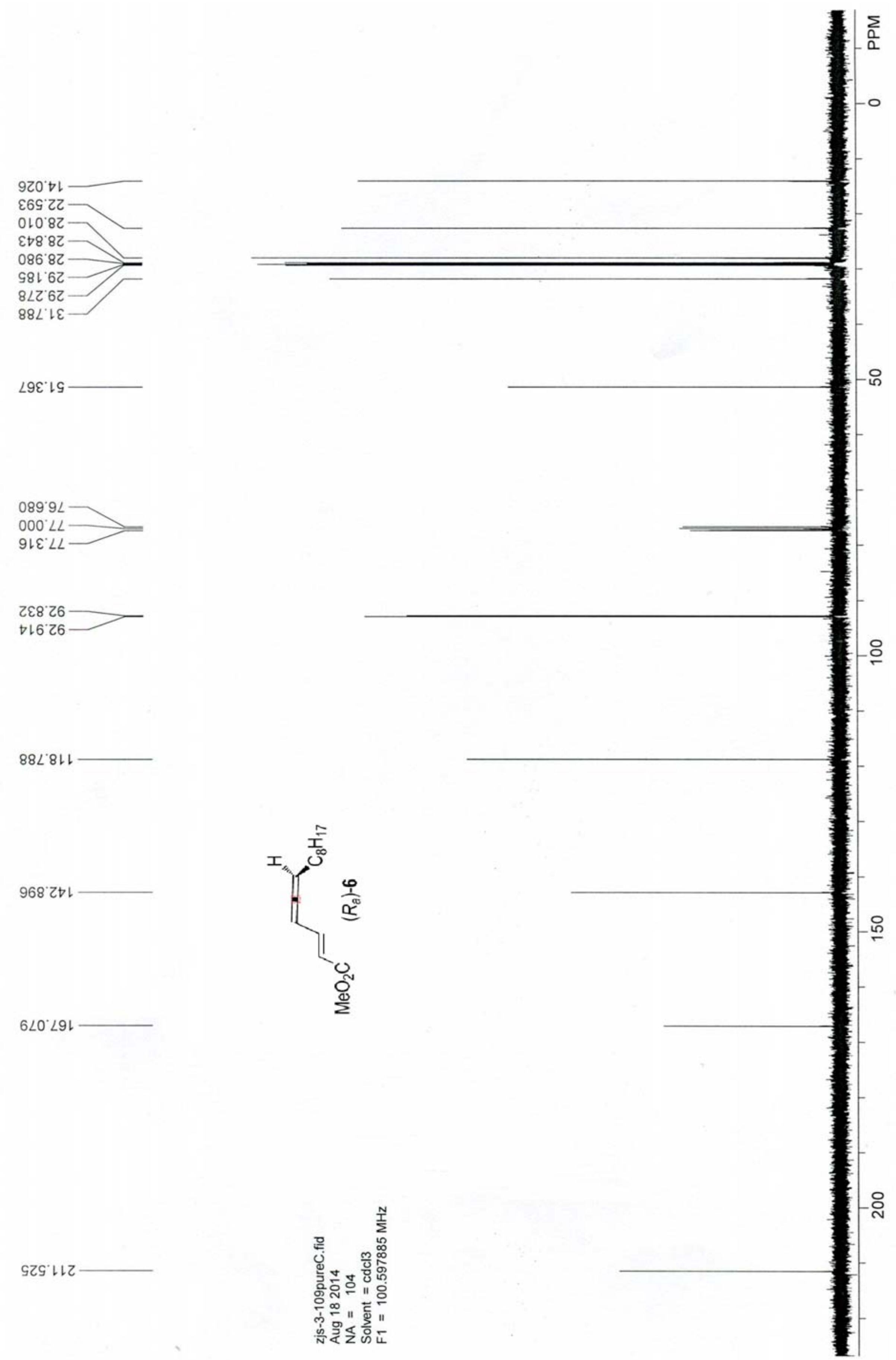
实验内容简介：



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		12.470	66481.930	920333.750	49.5642
2		13.423	61443.684	936517.688	50.4358
总计			127925.613	1856851.438	100.0000


zjs-3-109pureH.fid
Aug 18 2014
NA = 12
Solvent = CDCl3
F1 = 400.031616 MHz
7.282
7.216
7.189
7.178
7.150
5.922
5.915
5.908
5.900
5.893
5.888
5.875
5.836
5.467
5.451
5.434
5.418
3.733
3.671
2.090
2.083
2.072
2.065
2.054
2.048
2.036
2.030
1.827
1.441
1.424
1.406
1.389
1.373
1.337
1.318
1.271
0.897
0.881
0.864
0.075
-0.001
MeO$_2$C
H
C$_8$H$_{17}$
(R_a)-6
0.92
2.14
1.05
3.16
2.19
12.97
3.05
8
6
4
2
0
PPM

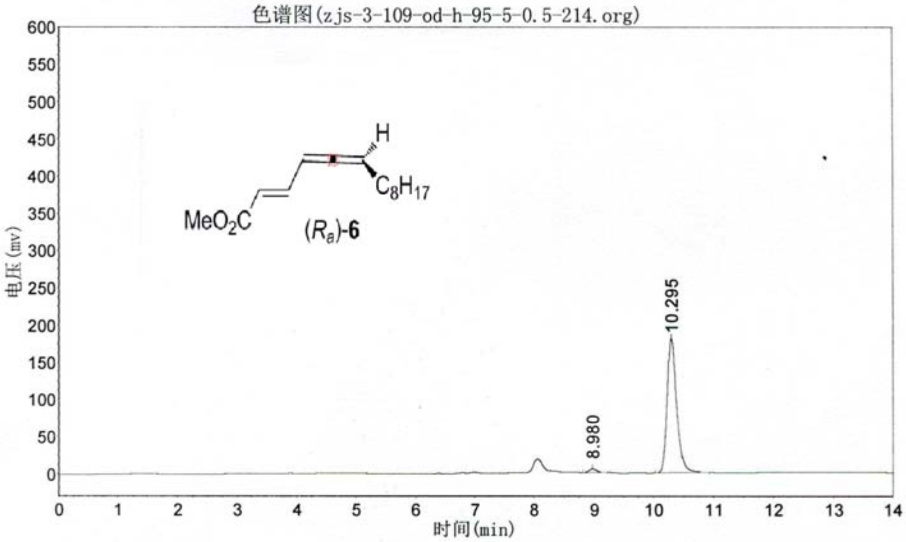

14.026
22.593
28.010
28.843
28.980
29.185
29.278
31.788
51.367
76.680
77.000
77.316
92.832
92.914
118.788
142.896
167.079
211.525
MeO2C
H
C8H17
zjs-3-109pureC.fid
Aug 18 2014
NA = 104
Solvent = cdcl3
F1 = 100.597885 MHz
PPM
0
50
100
150
200

(R_a)-**6**

zjs-3-109-od-h-95-5-0.5-214

实验时间：2014-08-18, 16:44:35　　　　报告时间：2014-08-18, 17:03:04
谱图文件:D:\zhuguangjiong\20140818\zjs-3-109-od-h-95-5-0.5-214.org

实验内容简介：



分析结果表

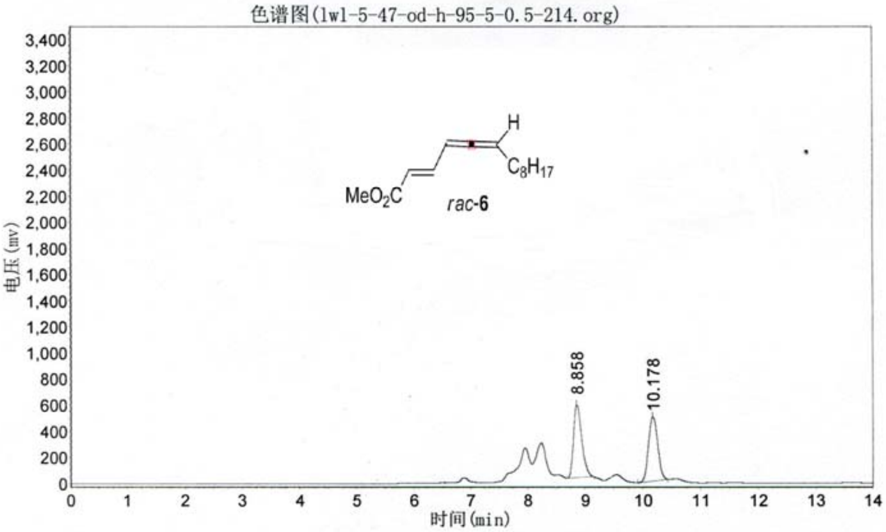
峰号	峰名	保留时间	峰高	峰面积	含量
1		8.980	5142.119	45658.051	2.2475
2		10.295	181023.938	1985832.375	97.7525
总计			186166.057	2031490.426	100.0000

lwl-5-47-rac-od--95-5-0.5-214

实验时间：2014-08-18, 15:49:19　　　　报告时间：2014-08-18, 16:55:00
谱图文件:D:\zhuguangjiong\20140818\lwl-5-47-od-h-95-5-0.5-214.org

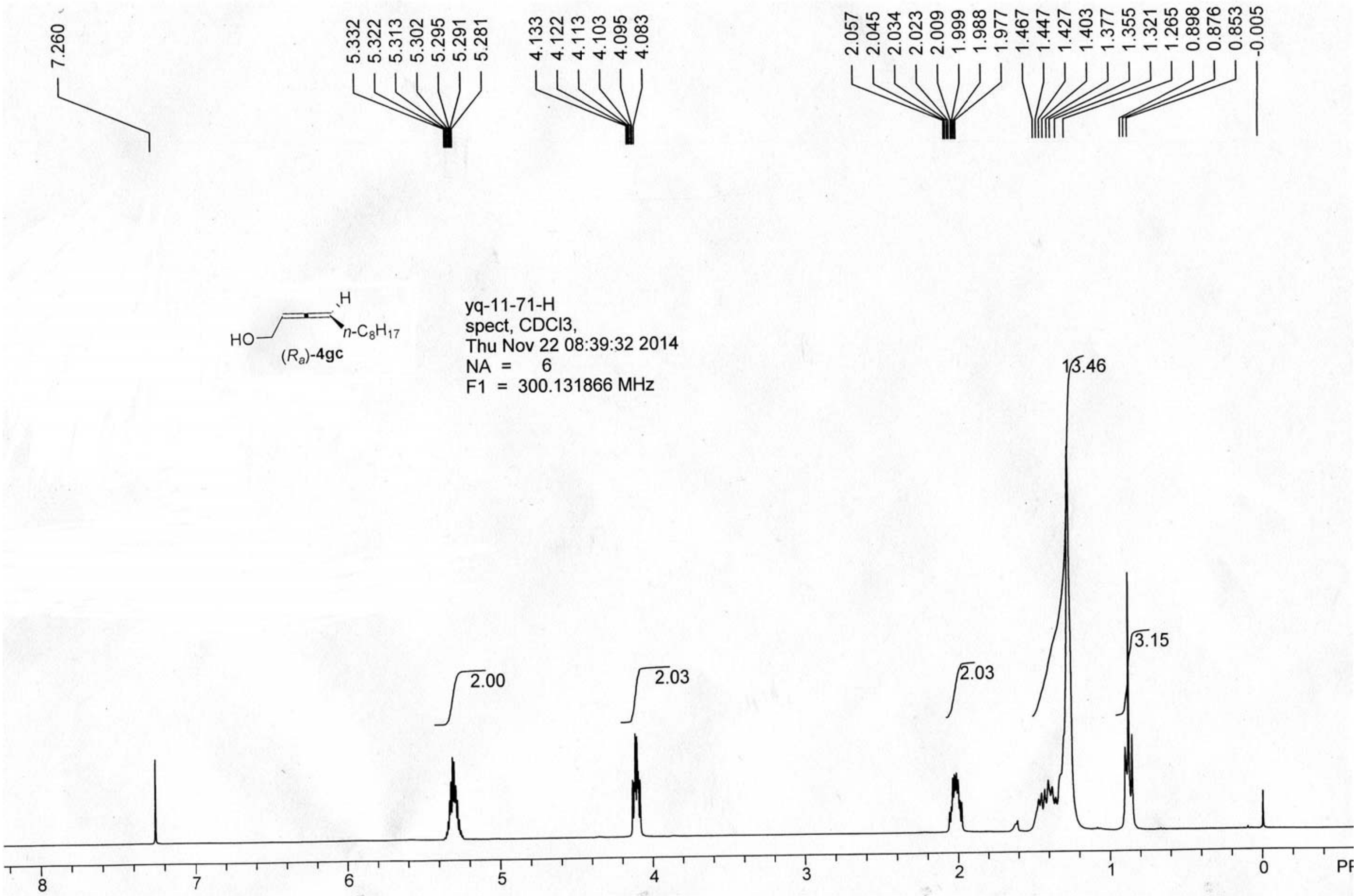
实验内容简介：

色谱图(lwl-5-47-od-h-95-5-0.5-214.org)



分析结果表

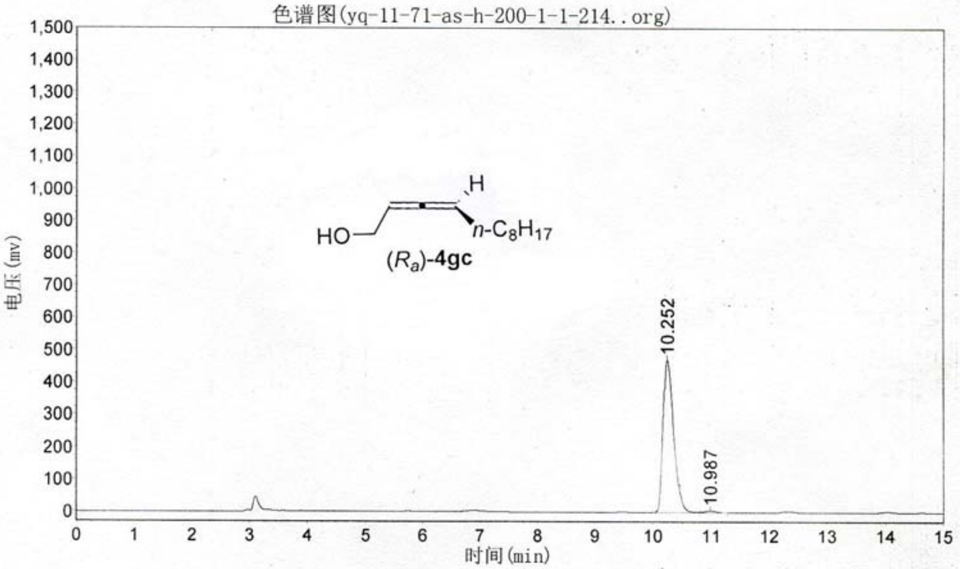
峰号	峰名	保留时间	峰高	峰面积	含量
1		8.858	561110.500	5481465.500	49.9752
2		10.178	494296.656	5486912.500	50.0248
总计			1055407.156	10968378.000	100.0000


7.260
5.332
5.322
5.313
5.302
5.295
5.291
5.281
4.133
4.122
4.113
4.103
4.095
4.083
2.057
2.045
2.034
2.023
2.009
1.999
1.988
1.977
1.467
1.447
1.427
1.403
1.377
1.355
1.321
1.265
0.898
0.876
0.853
-0.005
HO
H
n-C_8H_{17}
(R_a)-**4gc**
yq-11-71-H
spect, CDCl3,
Thu Nov 22 08:39:32 2014
NA = 6
F1 = 300.131866 MHz
2.00
2.03
2.03
13.46
3.15
8
7
6
5
4
3
2
1
0
PF

yq-11-71-as-h-200-1-1-214

实验时间：2014-01-06, 12:09:04 报告时间：2014-01-06, 15:52:00
谱图文件:D:\zhuguangjiong\yq\20140106\yq-11-71-as-h-200-1-1-214..org

实验内容简介：



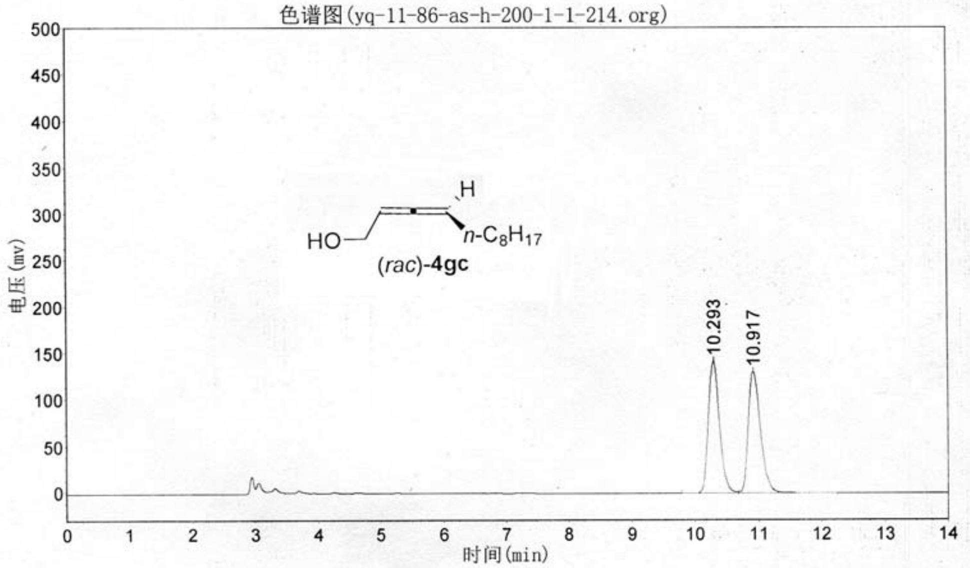
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		10.252	470790.906	6028986.000	98.8182
2		10.987	5669.209	72105.344	1.1818
总计			476460.115	6101091.344	100.0000

yq-11-86-as-h-200-1-1-214

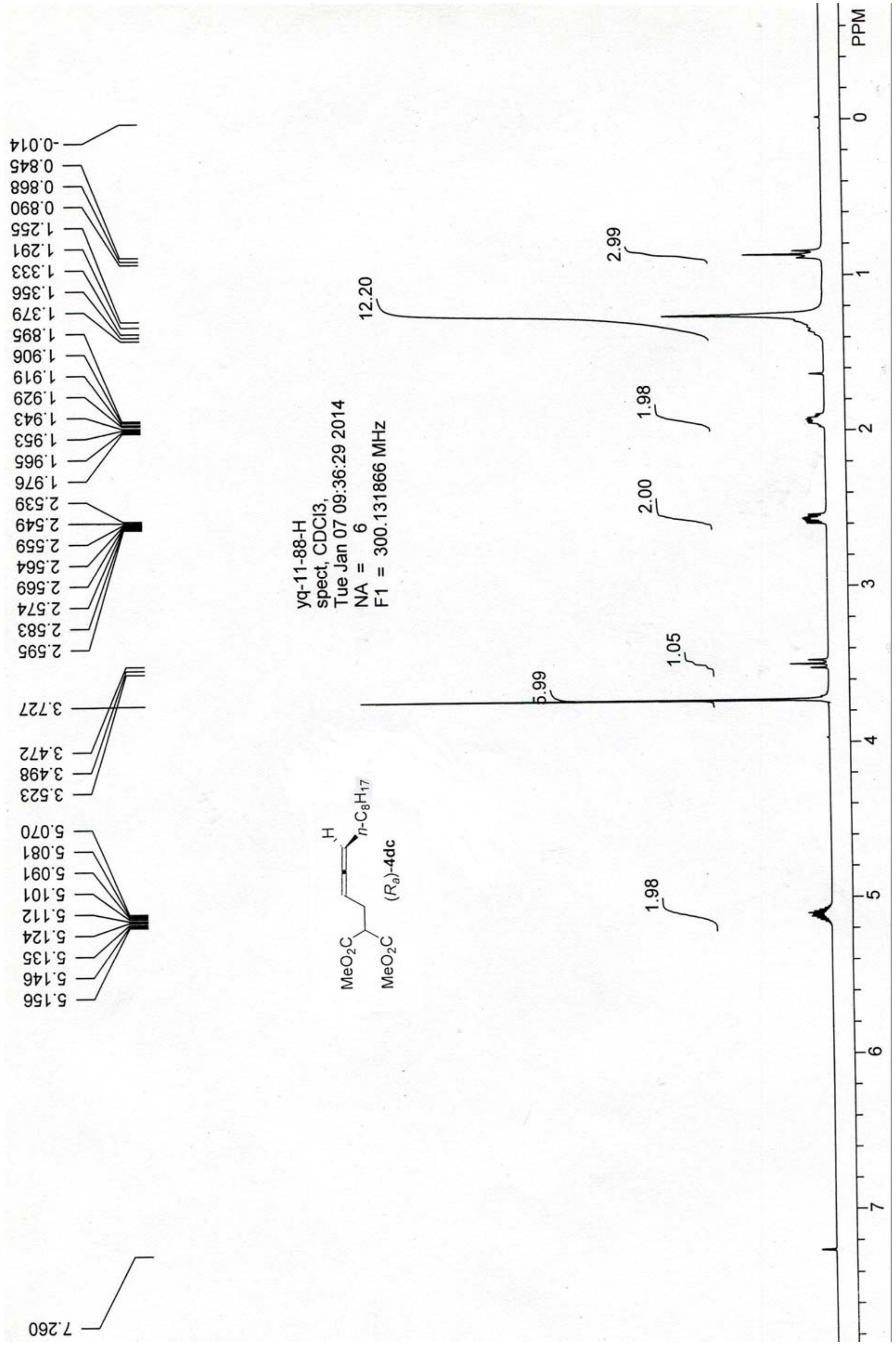
验时间：2014-01-06,11:28:09　　　　　　　　报告时间：2014-01-06,15:50:12
图文件:D:\zhuguangjiong\yq\20140106\yq-11-86-as-h-200-1-1-
4.org

验内容简介：



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		10.293	141502.078	1704717.500	49.6836
2		10.917	129714.195	1726429.500	50.3164
总计			271216.273	3431147.000	100.0000



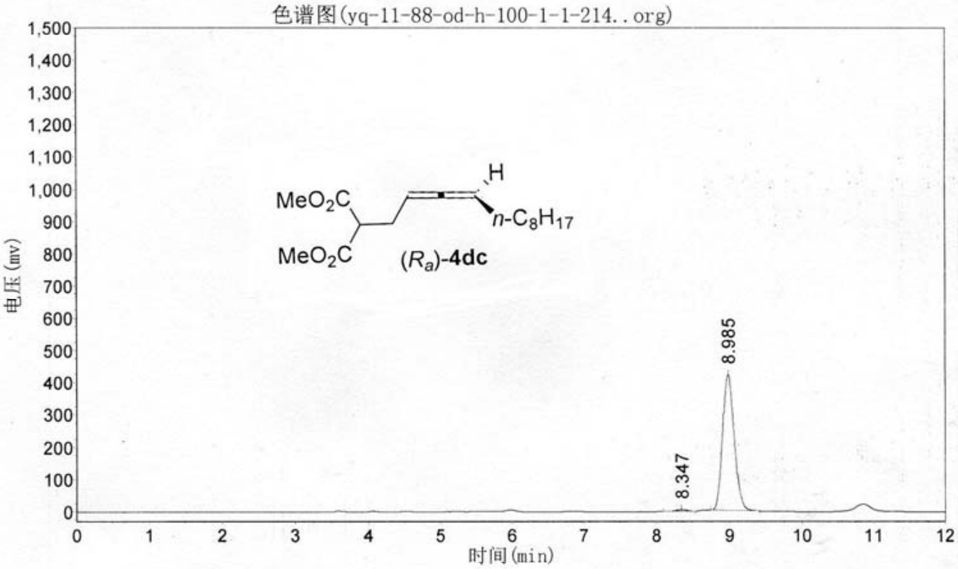
yq-11-88-H
spect, CDCl3,
Tue Jan 07 09:36:29 2014
NA = 6
F1 = 300.131866 MHz

(R_a)-**4dc**

yq-11-88-od-h-100-1-1-214

实验时间：2014-01-06,15:17:43　　　　　　　　　　报告时间：2014-01-06,15:54:18
谱图文件:D:\zhuguangjiong\yq\20140106\yq-11-88-od-h-100-1-1-214..org

实验内容简介：



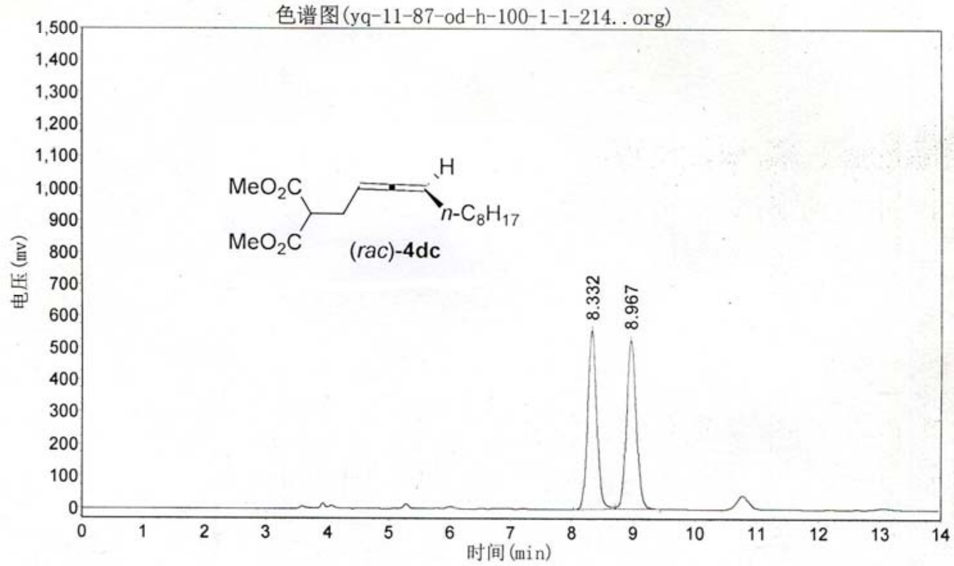
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.347	6206.786	61485.645	1.2879
2		8.985	420678.813	4712760.000	98.7121
总计			426885.599	4774245.645	100.0000

yq-11-87-od-h-100-1-1-214

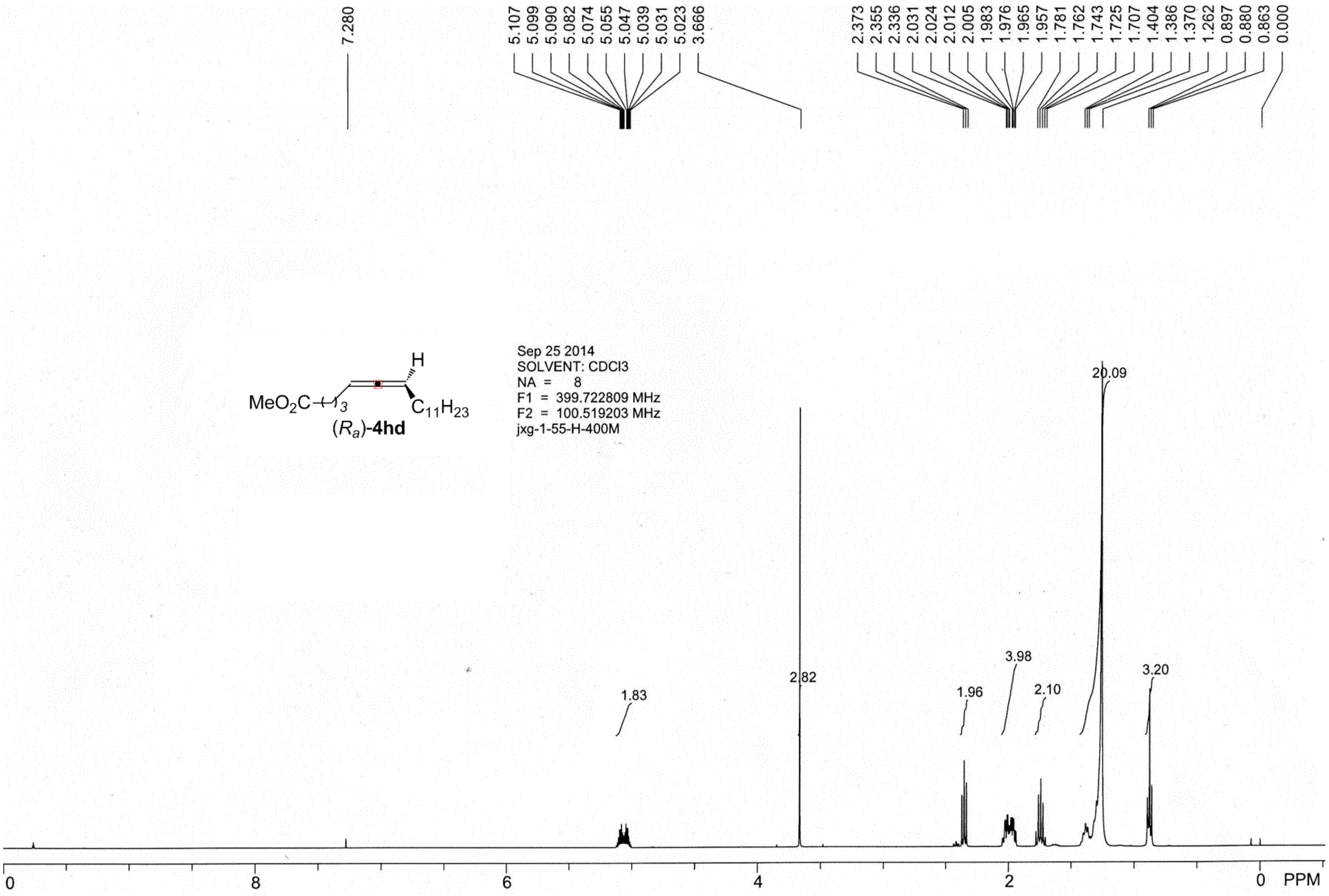
验时间：2014-01-06,14:54:37　　　　　　　　　　报告时间：2014-01-06,15:52:57
图文件:D:\zhuguangjiong\yq\20140106\yq-11-87-od-h-100-1-1-4..org

验内容简介：



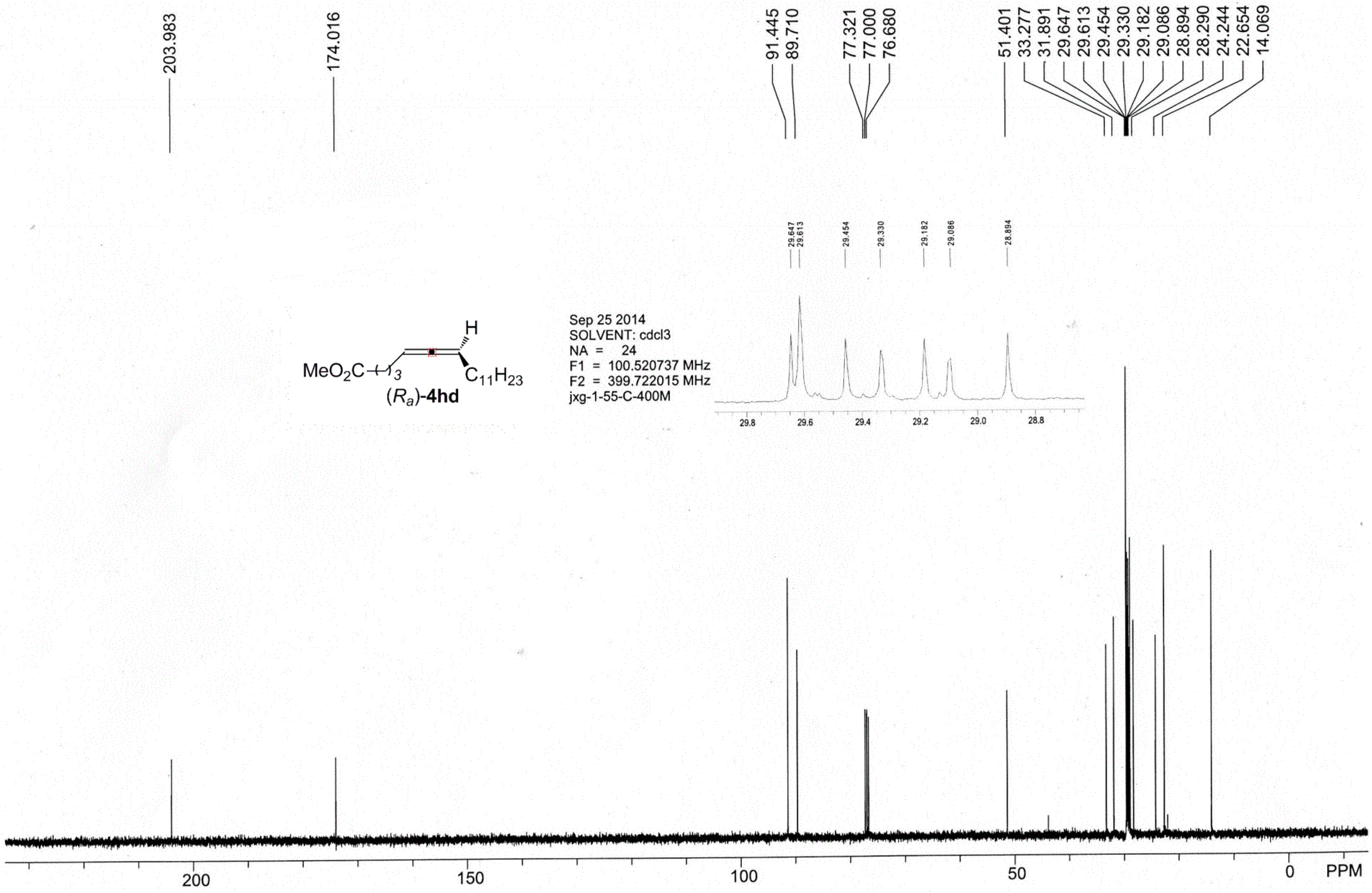
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.332	555762.063	5801182.000	49.7512
2		8.967	525134.188	5859211.500	50.2488
总计			1080896.250	11660393.500	100.0000



(*R*$_a$)-**4hd**

Sep 25 2014
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
F2 = 100.519203 MHz
jxg-1-55-H-400M



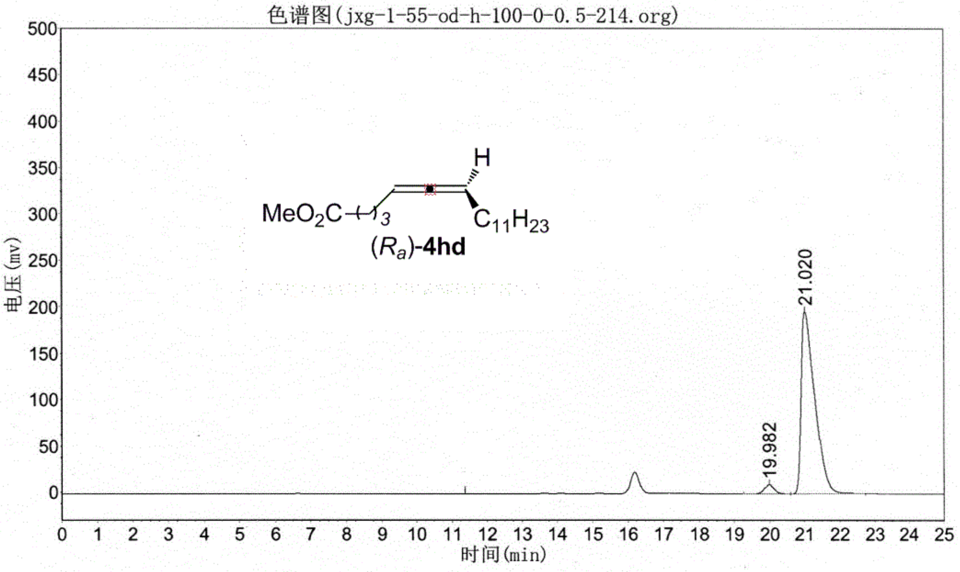
(R_a)-**4hd**

Sep 25 2014
SOLVENT: cdcl3
NA = 24
F1 = 100.520737 MHz
F2 = 399.722015 MHz
jxg-1-55-C-400M

jxg-1-55-od-h-100-0-0.5-214

验时间：2014-09-28,16:16:24　　　　　　　　　　报告时间：2014-09-28,17:15:03
图文件:D:\zhuguangjiong\jxg\20140928\jxg-1-55-od-h-100-0-5-214.org

验内容简介：



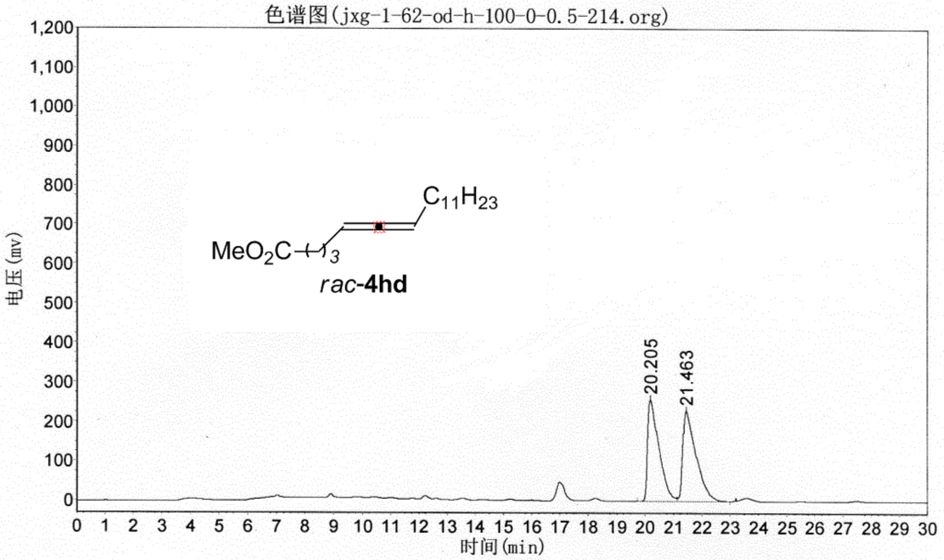
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		19.982	9589.253	187023.844	3.4458
2		21.020	196304.203	5240627.500	96.5542
总计			205893.456	5427651.344	100.0000

jxg-1-62-od-h-100-0-0.5-214

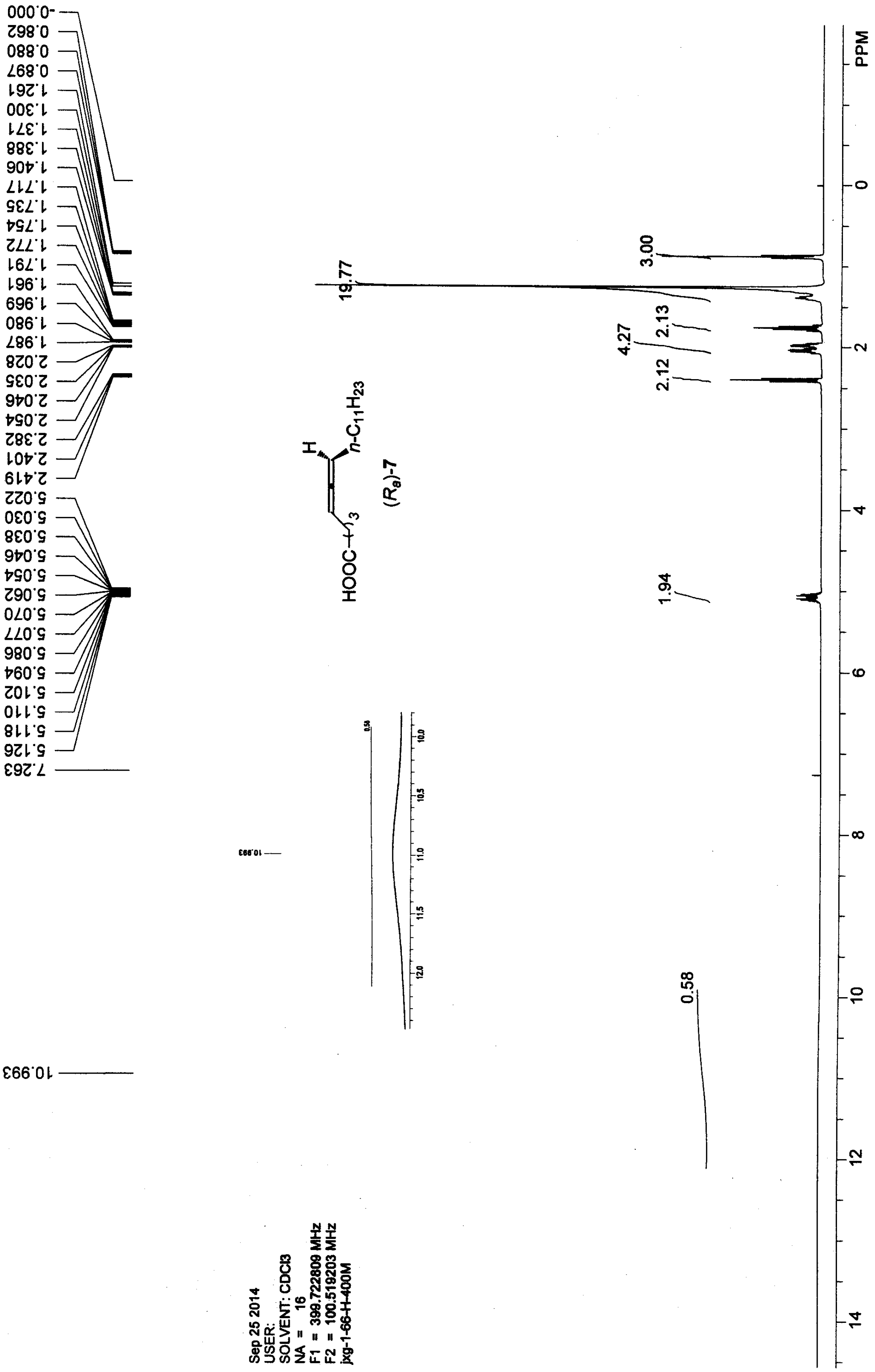
实验时间：2014-09-29,14:55:52　　　　报告时间：2014-09-29,16:56:18
谱图文件:D:\zhuguangjiong\jxg\20140929\jxg-1-62-od-h-100-0-0.5-214.org

实验内容简介：

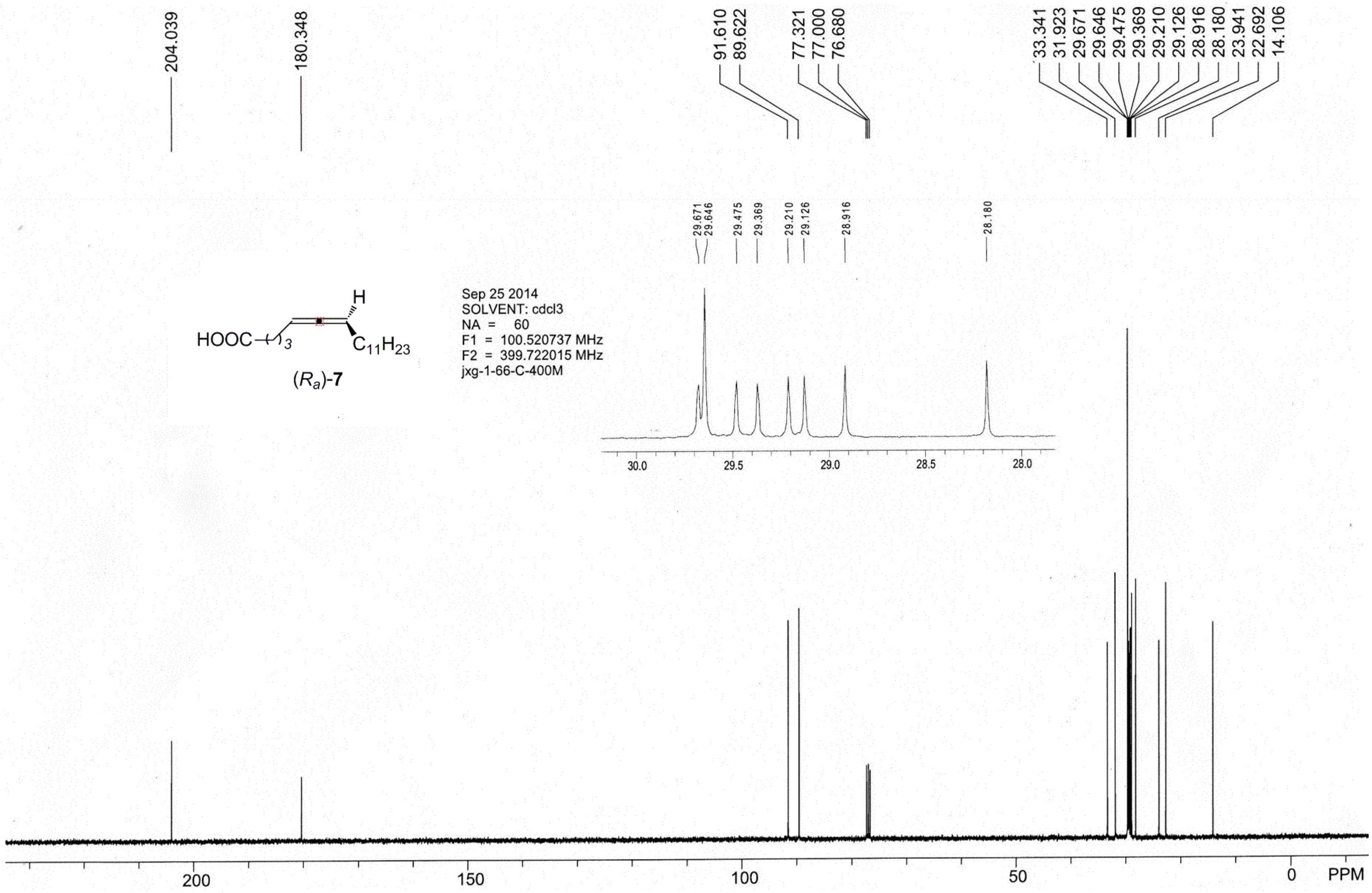


分析结果表

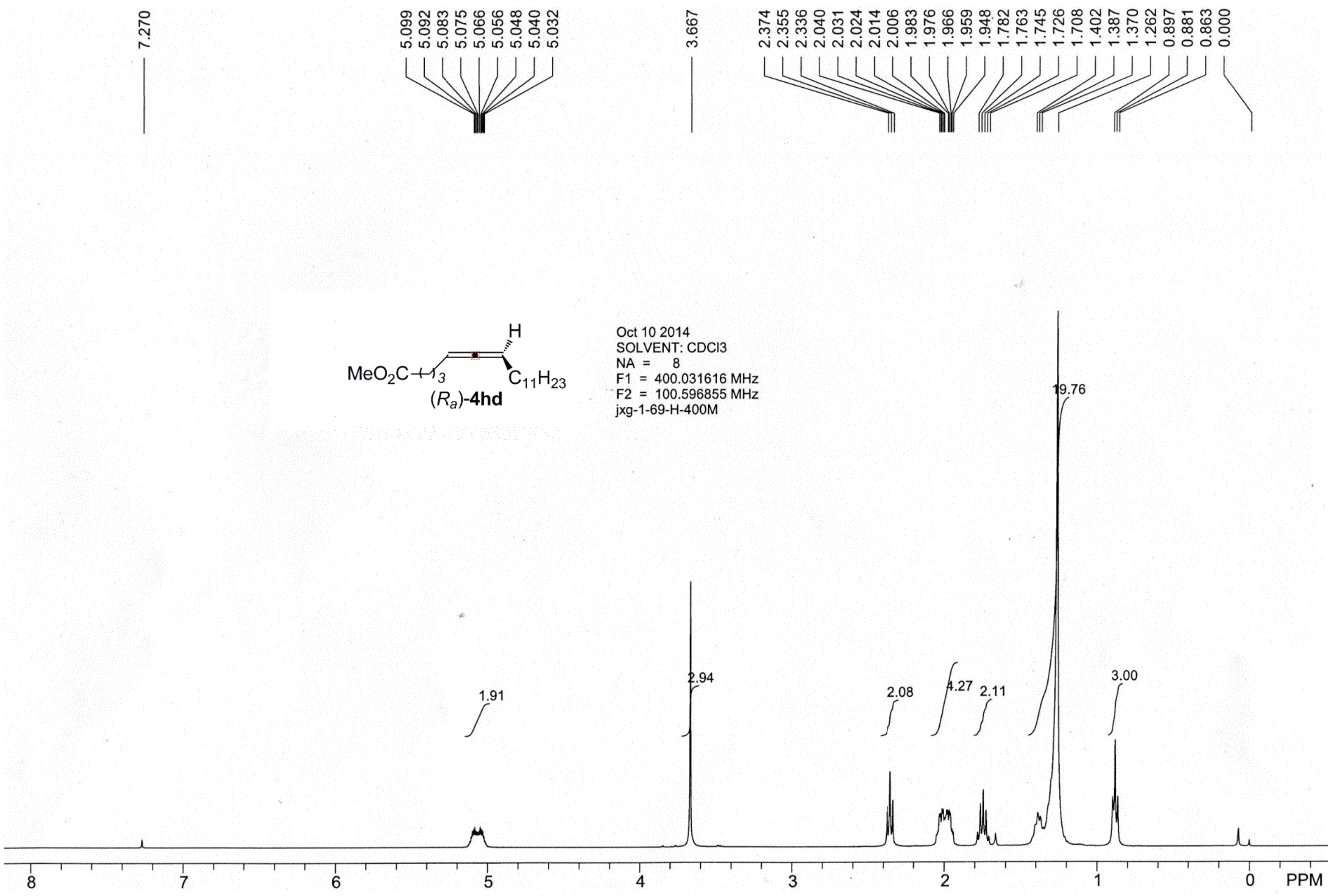
峰号	峰名	保留时间	峰高	峰面积	含量
1		20.205	257249.156	7231222.500	49.2490
2		21.463	227788.125	7451751.500	50.7510
总计			485037.281	14682974.000	100.0000



Sep 25 2014
USER:
SOLVENT: CDCl3
NA = 16
F1 = 399.722809 MHz
F2 = 100.519203 MHz
jxg-1-66-H-400M

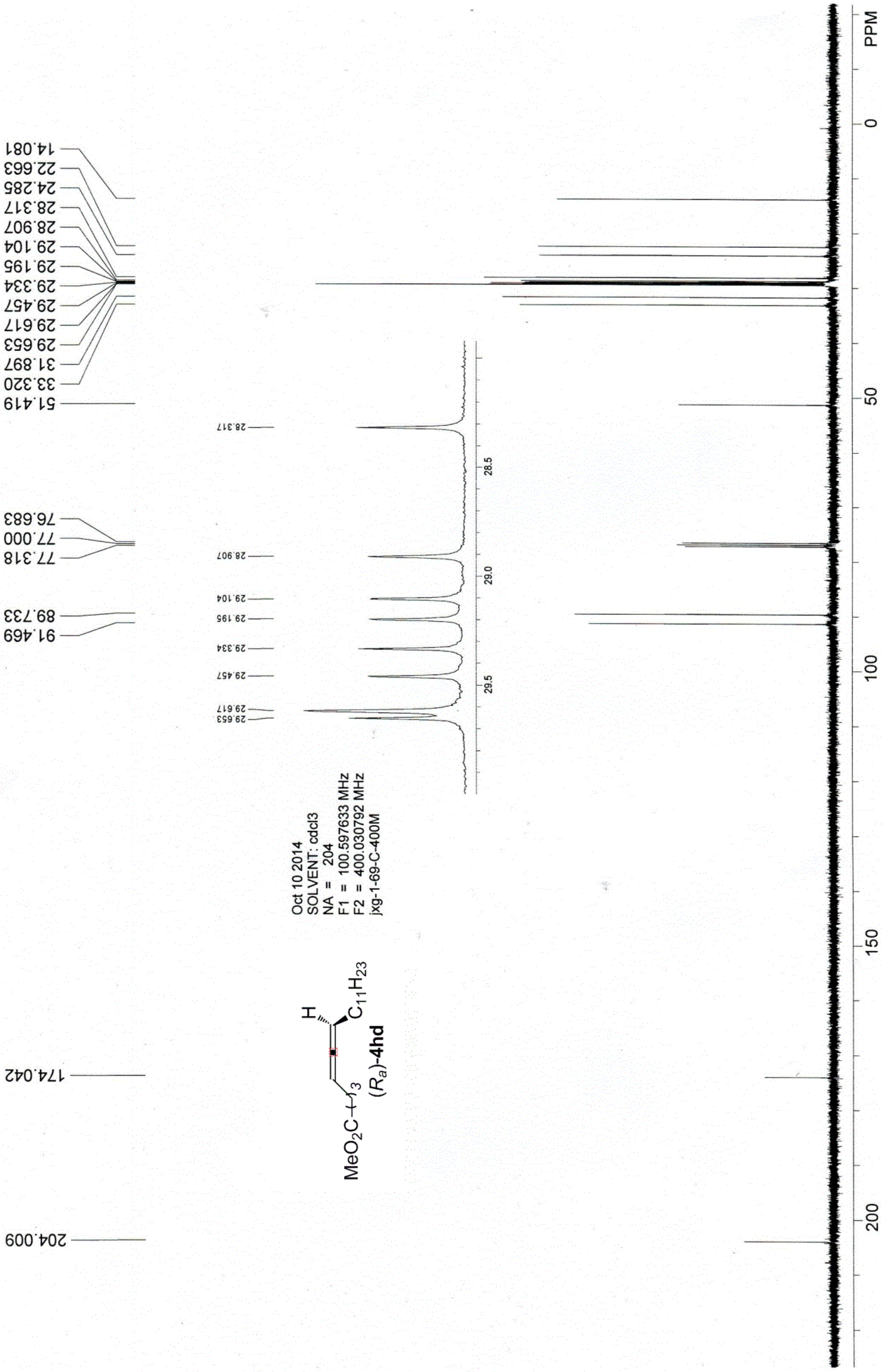

204.039
180.348
91.610
89.622
77.321
77.000
76.680
33.341
31.923
29.671
29.646
29.475
29.369
29.210
29.126
28.916
28.180
23.941
22.692
14.106
HOOC
3
H
C11H23
Sep 25 2014
SOLVENT: cdcl3
NA = 60
F1 = 100.520737 MHz
F2 = 399.722015 MHz
jxg-1-66-C-400M
29.671
29.646
29.475
29.369
29.210
29.126
28.916
28.180
30.0
29.5
29.0
28.5
28.0
200
150
100
50
0
PPM

(R_a)-**7**



(*R*$_a$)-**4hd**

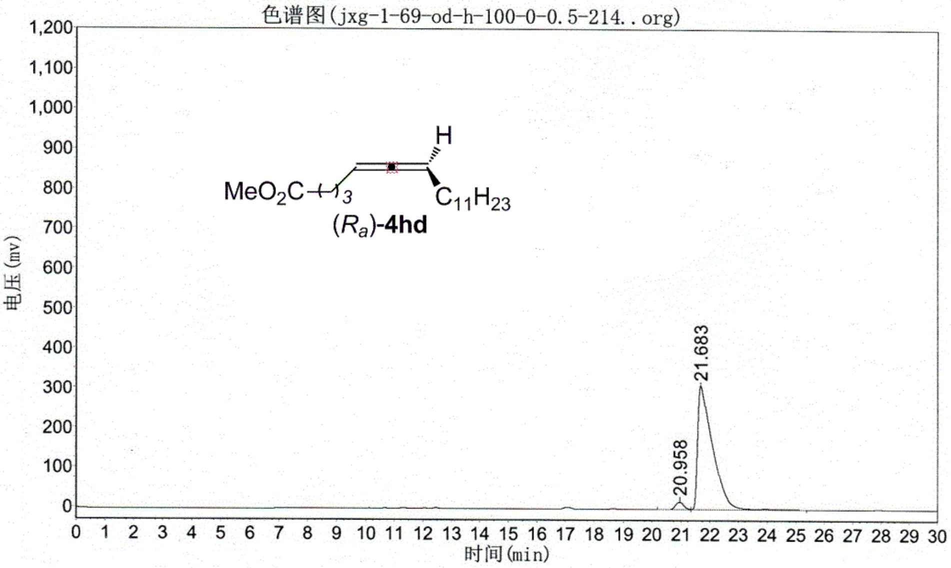
Oct 10 2014
SOLVENT: CDCl3
NA = 8
F1 = 400.031616 MHz
F2 = 100.596855 MHz
jxg-1-69-H-400M


14.081
22.663
24.285
28.317
28.907
29.104
29.195
29.334
29.457
29.617
29.653
31.897
33.320
51.419
76.683
77.000
77.318
89.733
91.469
174.042
204.009
28.317
28.907
29.104
29.195
29.334
29.457
29.617
29.653
28.5
29.0
29.5
Oct 10 2014
SOLVENT: cdcl3
NA = 204
F1 = 100.597633 MHz
F2 = 400.030792 MHz
jxg-1-69-C-400M
H
$C_{11}H_{23}$
MeO_2C
3
(R_a)-**4hd**
PPM
0
50
100
150
200

jxg-1-69-od-h-100-0-0.5-214

实验时间：2014-09-29,16:01:38　　　　报告时间：2014-09-29,16:57:45
谱图文件:D:\zhuguangjiong\jxg\20140929\jxg-1-69-od-h-100-0-0.5-214..org

实验内容简介：



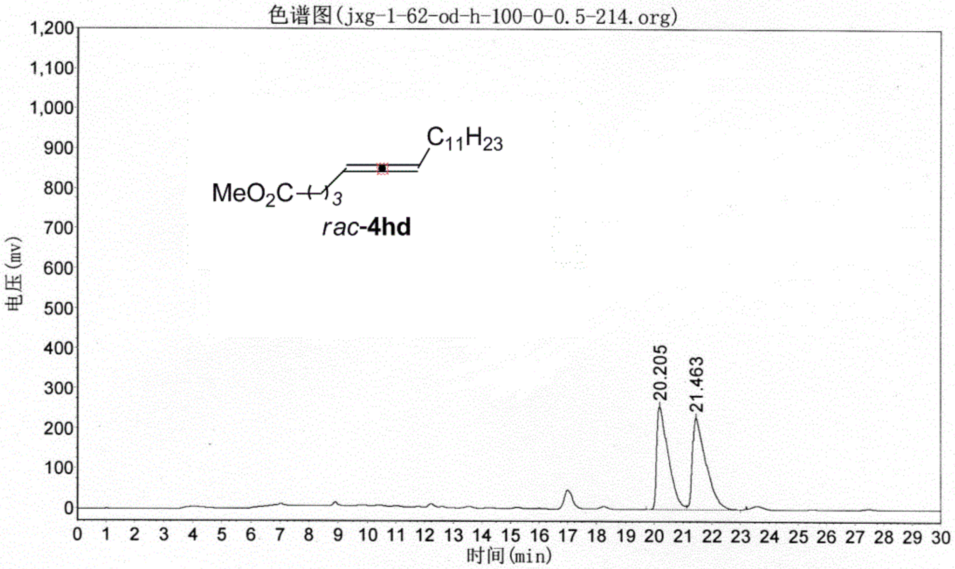
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		20.958	19871.551	402086.531	3.4339
2		21.683	310348.094	11307082.000	96.5661
总计			330219.645	11709168.531	100.000

jxg-1-62-od-h-100-0-0.5-214

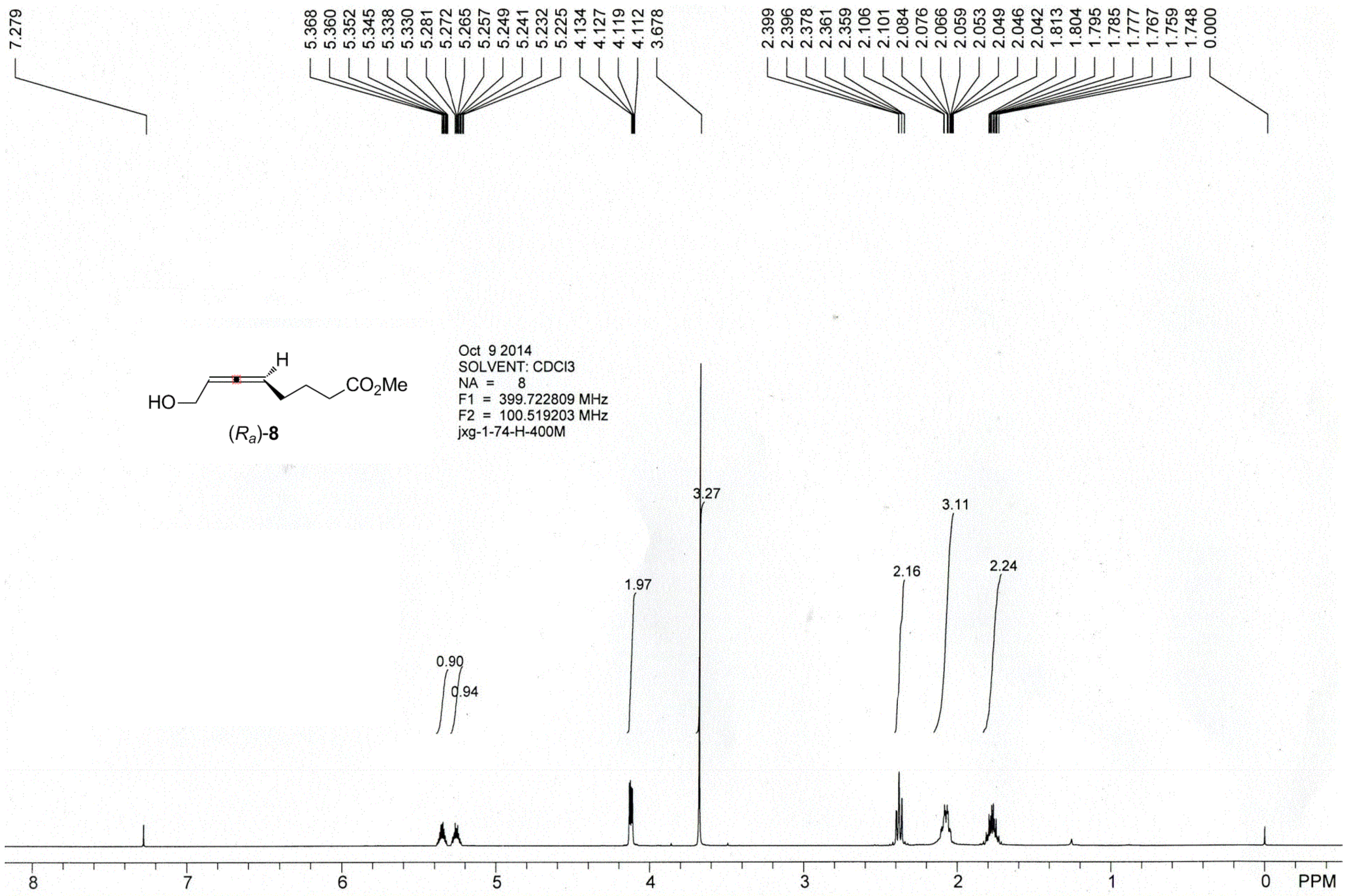
实验时间：2014-09-29,14:55:52　　报告时间：2014-09-29,16:56:18
谱图文件:D:\zhuguangjiong\jxg\20140929\jxg-1-62-od-h-100-0-0.5-214.org

实验内容简介：



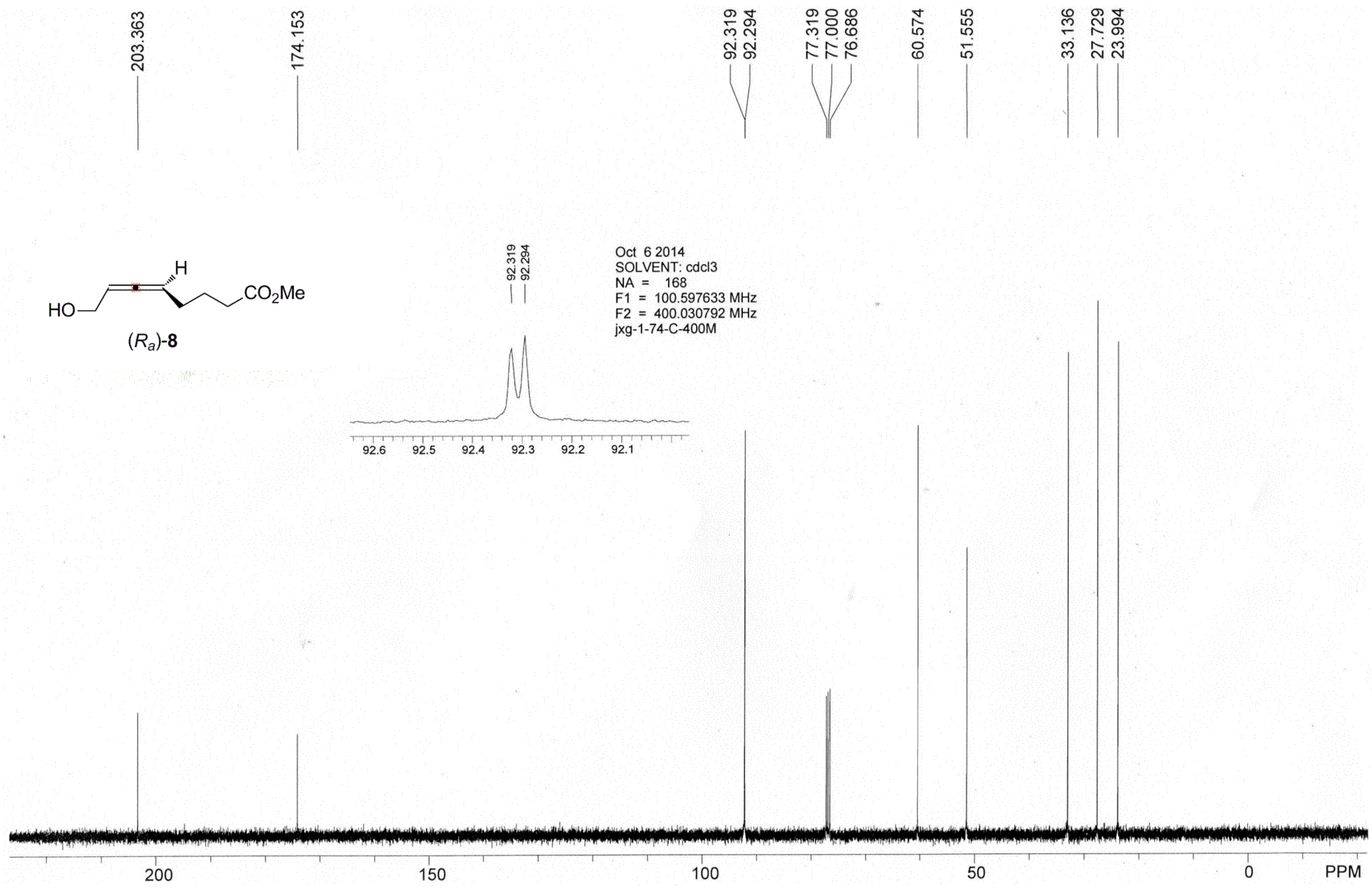
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		20.205	257249.156	7231222.500	49.2490
2		21.463	227788.125	7451751.500	50.7510
总计			485037.281	14682974.000	100.0000



(*R*$_a$)-**8**

Oct 9 2014
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
F2 = 100.519203 MHz
jxg-1-74-H-400M



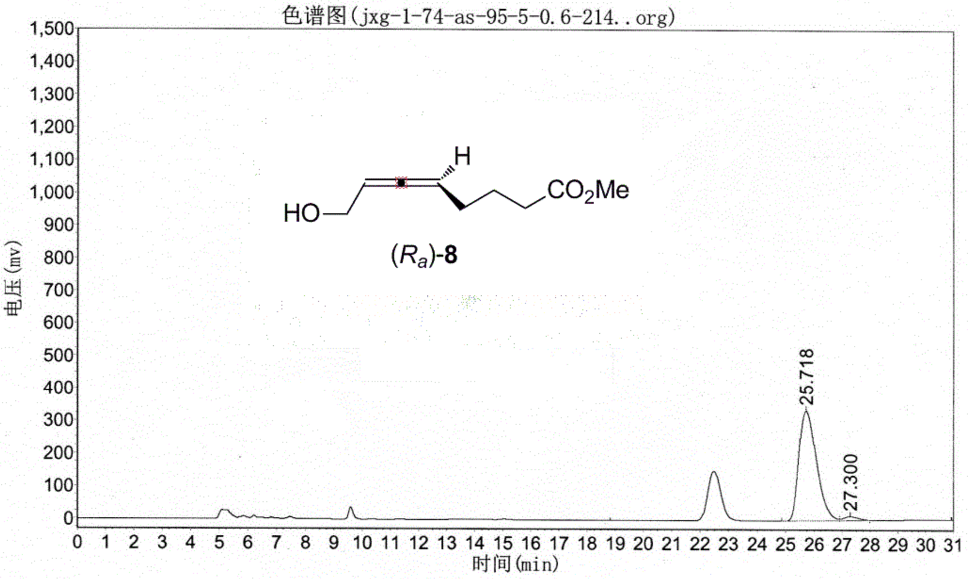
(R_a)-**8**

203.363
174.153
92.319
92.294
77.319
77.000
76.686
60.574
51.555
33.136
27.729
23.994
HO
H
CO2Me
Oct 6 2014
SOLVENT: cdcl3
NA = 168
F1 = 100.597633 MHz
F2 = 400.030792 MHz
jxg-1-74-C-400M
92.6
92.5
92.4
92.3
92.2
92.1
200
150
100
50
0
PPM

jxg-1-74-as-95-5-0.6-214

实验时间：2014-10-10,15:20:00　　　　　　报告时间：2014-10-10,16:16:58
谱图文件:D:\zhuguangjiong\jxg\20141009\jxg-1-74-as-95-5-0.6-214..org

实验内容简介：



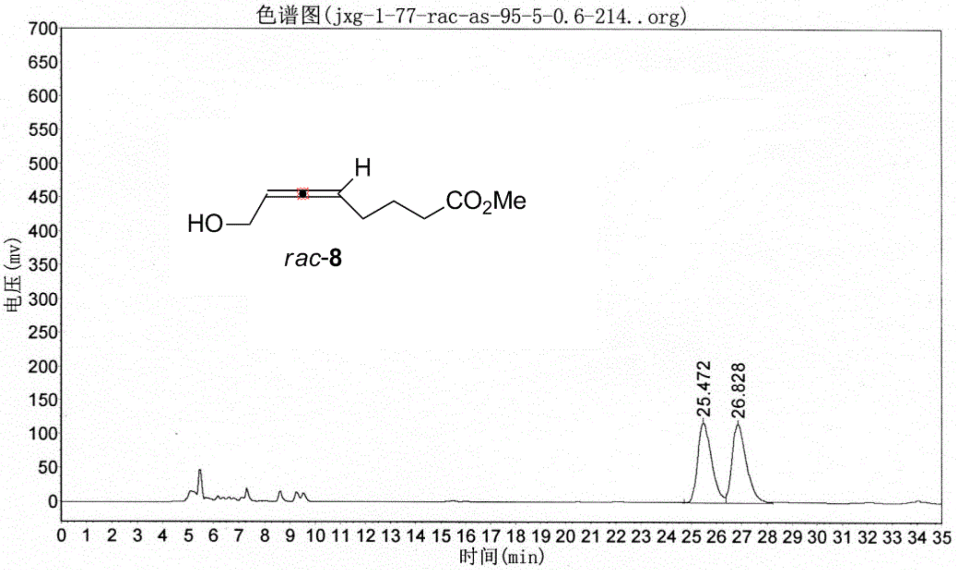
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		25.718	335966.844	14645433.000	97.2489
2		27.300	11620.171	414312.875	2.7511
总计			347587.015	15059745.875	100.0000

jxg-1-77-rac-as-95-5-0. 6-214

验时间：2014-10-10, 13:51:18　　　　　　　　报告时间：2014-10-10, 16:13:08
图文件:D:\zhuguangjiong\jxg\20141009\jxg-1-77-rac-as-95-5-
6-214..org

验内容简介：



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		25. 472	118111. 883	4550166. 000	49. 8643
2		26. 828	116403. 398	4574926. 000	50. 1357
总计			234515. 281	9125092. 000	100. 0000