

**Asymmetric construction of pyrido[1,2-*a*]-1*H*-indole derivatives via a
gold-catalyzed cycloisomerization**

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Supporting Information

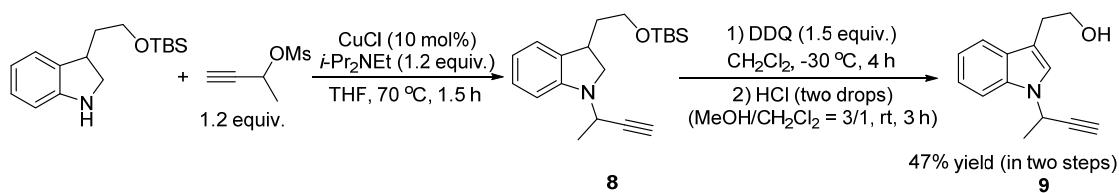
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1. General Information

¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra were recorded in CDCl₃ using a Bruker AM 300 MHz NMR spectrometer (¹H at 300 MHz, ¹³C at 75 MHz, ¹⁹F at 282 MHz) or a Bruker AM 400 MHz NMR spectrometer (¹H at 400 MHz, ¹³C at 100 MHz, ¹⁹F at 376 MHz) or a Bruker AM 500 MHz NMR spectrometer (¹H at 500 MHz, ¹³C at 125 MHz) using TMS (¹H, δ = 0), residual CHCl₃ (7.26 ppm) in CDCl₃, CDCl₃ (¹³C CDCl₃, 77.0 ppm), and CFCl₃ (¹⁹F CFCl₃, δ = 0) as the internal standards, respectively. IR spectra were recorded with a Perkin–Elmer 983G instrument. Elemental analyses were measured with a Carlo-Erba EA1110 elementary analysis instrument. Mass spectrometry was performed with an HP 5989A system. High-resolution mass spectrometry was determined with a Finnigan MAT 8430 or Bruker APEXIII instrument. IPrAuCl, and AgPF₆ were purchased from *Strem*. AgSbF₆ was purchased from *Strem and Aladdin*. CHCl₃ was stirred with CaH₂ and distilled right before use. Petroleum ether (60-90 °C) was used for chromatography on silica gel unless noted otherwise. Other commercially available chemicals including indoles were purchased and used without additional purification unless noted otherwise. Disubstituted indoles¹⁻² and 3-ethylindole³ were prepared according to the literature procedures. *N*-propargylindoles⁴ was prepared according to the literature procedures.

2. Synthesis of 2-((but-3-yn-2-yl)-1*H*-indol-3-yl)ethanol **9** (jf-5-088, jf-5-089)



To an oven-dried Schlenk tube were added CuCl (0.0700 g, 0.7 mmol), 3-((*tert*-butyldimethylsilyl)oxy)ethylindoline (1.9200 g, 7 mmol), and THF (25 mL) under nitrogen atmosphere sequentially. The suspension was stirred for 5 min at room temperature, after which *i*-Pr₂NEt (1.42 mL, d = 0.782 g/mL, 1.1074 g, 8.4 mmol) was added dropwise in 4 min. The resulting suspension was allowed to stir for 10 min, and a solution of but-3-yn-2-yl methanesulfonate (1.2445 g, 8.4 mmol) in THF (10 mL) was added over the period of 10 min. The reaction was complete after being stirred at 70 °C for 1.5 h as monitored by TLC. After filtration through a short column of celite (3 cm × 2 cm) [eluent: ethyl acetate (10 mL × 4)] and evaporation, the crude product was purified by column chromatography on silica gel to afford **8** (2.0438 g) [eluent: petroleum ether/ethyl acetate = 50/1] as a liquid which was used in the next step without further purification.

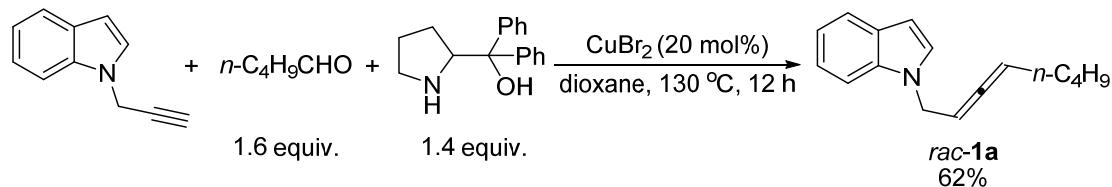
To an oven-dried Schlenk tube were added **8** (2.0438 g) and DCM (60 mL) under nitrogen atmosphere sequentially. Then the solution was cooled to -30 °C, and DDQ (2.0415 g, 9 mmol) was added. The reaction was complete after being stirred at -30 °C for 4 h as monitored by TLC. The resulting mixture was filtrated through a pad of celite (3 cm × 2 cm) [eluent: ethyl acetate (20 mL × 3)] and washed sequentially with saturated NaHCO₃ (20 mL × 3), water (20 mL), brine, and dried over anhydrous Na₂SO₄. After filtration and evaporation, the residue was purified by column chromatography on silica gel to afford 1-(but-3-yn-2-yl)-3-((*tert*-butyldimethylsilyl)oxy)ethyl-1*H*-indole (1.0526 g) [eluent: petroleum ether/ethyl acetate = 50/1] as a liquid, which was used in the next step without further purification.

To a round-bottomed flask were added the crude product and 9 mL of mixed solvent (V_{MeOH}/V_{DCM} = 3/1), and HCl (2 drops) sequentially. The reaction was

complete after being stirred at room temperature for 3 h as monitored by TLC. The resulting mixture was quenched with H₂O (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 2). The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. After filtration and evaporation, the crude product was purified by column chromatography on silica gel to afford **9** (0.6890 g, 47%) [eluent: petroleum ether/ethyl acetate = 3/1] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.61 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.41 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.28-7.20 (m, 2H, Ar-H), 7.13 (t, *J* = 7.4 Hz, 1H, Ar-H), 5.35-5.20 (m, 1H, CH), 3.90 (t, *J* = 6.5 Hz, 2H, OCH₂), 3.03 (t, *J* = 6.3 Hz, 2H, CH₂), 2.47 (d, *J* = 1.8 Hz, 1H, ≡CH), 1.74 (d, *J* = 6.9 Hz, 3H, CH₃), 1.55 (s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 135.2, 128.4, 123.2, 121.6, 119.2, 119.1, 111.7, 109.4, 82.2, 72.7, 62.3, 43.0, 28.5, 22.2; IR (neat) ν (cm⁻¹) 3394, 3288, 3051, 2985, 2935, 2116, 1612, 1553, 1462, 1398, 1360, 1297, 1227, 1195, 1157, 1091, 1075, 1045, 1012; MS (70 ev, EI) *m/z* (%) 214 (M⁺ + 1, 5.26), 213 (M⁺, 36.41), 182 (100); HRMS calcd for C₁₄H₁₆NO⁺[M⁺ + H]: 214.1226, Found: 214.1225.

3. Synthesis of racemic *N*-allenyl indoles ⁵⁻⁶

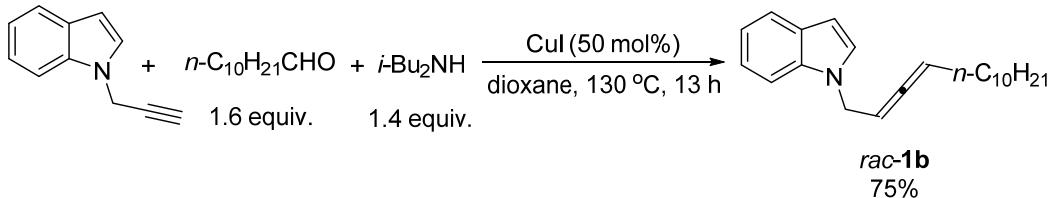
3.1 Synthesis of 1-(octa-2,3-dienyl)-1*H*-indole *rac*-**1a** (jf-1-117)



Typical Procedure I: To a flame-dried Schlenk tube with a polytetrafluoroethylene plug were added CuBr₂ (0.3606 g, 1.6 mmol, 99%), α,α-diphenylprolinol (2.8918 g, 11.2 mmol, 98%), 1-(prop-2-ynyl)-1*H*-indole (1.2404 g, 8 mmol), pentanal (1.4 mL, d = 0.81 g/mL, 1.134 g, 12.8 mmol, 98%), and dioxane (24 mL) sequentially. The Schlenk tube was then sealed by screwing the polytetrafluoroethylene plug tightly with the outlet connected to the vacuum line. The reaction was complete after being stirred in an oil bath preheated at 130 °C for 12 h as monitored by TLC. The resulting mixture was cooled to room temperature, diluted with diethyl ether and washed with an aqueous solution of hydrochloric acid (1.2 M). The organic layer was separated

and the aqueous layer was extracted with diethyl ether. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 . After filtration and evaporation, the residue was purified by column chromatography on silica gel to afford *rac*-**1a** (1.1087 g, 62%) [eluent: petroleum ether] as a liquid: ^1H NMR (300 MHz, CDCl_3) δ 7.62 (d, $J = 8.1$ Hz, 1H, Ar-H), 7.36 (dd, $J_1 = 8.1$ Hz, $J_2 = 0.9$ Hz, 1H, Ar-H), 7.22-7.13 (m, 1H, Ar-H), 7.13-7.06 (m, 2H, Ar-H), 6.48 (dd, $J_1 = 3.2$ Hz, $J_2 = 0.8$ Hz, 1H, Ar-H), 5.31-5.15 (m, 2H, $\text{CH}=\text{C}=\text{CH}$), 4.68 (dd, $J_1 = 6.5$ Hz, $J_2 = 2.9$ Hz, 2H, NCH_2), 2.02-1.88 (m, 2H, CH_2), 1.36-1.22 (m, 4H, $\text{CH}_2 \times 2$), 0.87 (t, $J = 7.1$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 204.4, 135.9, 128.7, 127.5, 121.3, 120.9, 119.3, 109.7, 101.2, 93.5, 87.9, 46.0, 31.1, 28.2, 22.1, 13.8; IR (neat) ν (cm^{-1}) 3056, 2957, 2929, 2858, 1964, 1511, 1484, 1464, 1396, 1378, 1334, 1313, 1253, 1180, 1051, 1012; MS (70 ev, EI) m/z (%) 226 (M^++1 , 4.34), 225 (M^+ , 30.42), 182 (100); HRMS calcd for $\text{C}_{16}\text{H}_{19}\text{N} [\text{M}^+]$: 225.1517, Found: 225.1517.

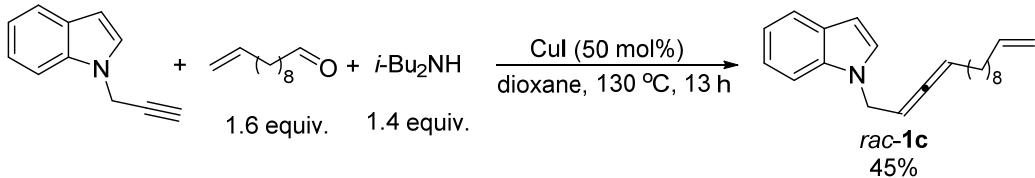
3.2 Synthesis of 1-(tetradeca-2,3-dienyl)-1*H*-indole *rac*-**1b** (jf-2-009)



Following **Typical Procedure I**, the reaction of CuI (0.3842 g, 2 mmol, 99%), diisobutylamine (0.98 mL, d = 0.74 g/mL, 0.7237 g, 5.6 mmol), 1-(prop-2-ynyl)-1*H*-indole (0.6204 g, 4 mmol), undecanal (1.0910 g, 6.4 mmol), and dioxane (8 mL) for 13 h at 130 °C afforded *rac*-**1b** (0.9233 g, 75%) [eluent: petroleum ether/diethyl ether = 200/1] as a liquid: ^1H NMR (300 MHz, CDCl_3) δ 7.61 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.35 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.22-7.13 (m, 1H, Ar-H), 7.13-7.04 (m, 2H, Ar-H), 6.47 (dd, $J_1 = 3.2$ Hz, $J_2 = 0.8$ Hz, 1H, Ar-H), 5.29-5.14 (m, 2H, $\text{CH}=\text{C}=\text{CH}$), 4.66 (dd, $J_1 = 6.3$ Hz, $J_2 = 2.7$ Hz, 2H, NCH_2), 2.00-1.87 (m, 2H, CH_2), 1.40-1.14 (m, 16H, $\text{CH}_2 \times 8$), 0.88 (t, $J = 6.8$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 204.5, 136.0, 128.8, 127.5, 121.4, 120.9, 119.3, 109.7, 101.3, 93.5, 87.9, 46.0, 31.9, 29.6, 29.4, 29.3, 29.1, 29.0, 28.6, 22.7, 14.1; IR (neat) ν (cm^{-1}) 3056, 2925, 2853, 1964, 1613, 1512, 1484, 1464, 1395, 1378, 1335, 1313, 1250, 1180, 1123, 1087,

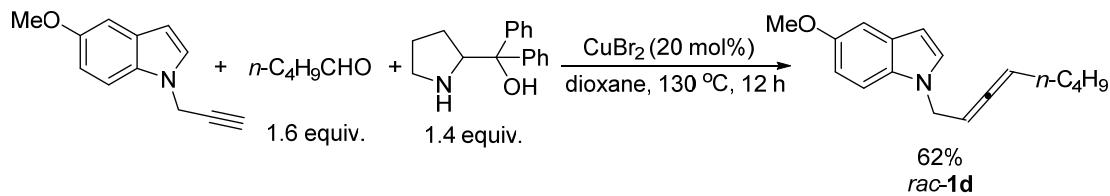
1055, 1012; MS (70 ev, EI) m/z (%) 310 (M^++1 , 8.13), 309 (M^+ , 30.46), 130 (100); HRMS calcd for $C_{22}H_{31}N$ [M^+]: 309.2457, Found: 309.2458.

3.3 Synthesis of 1-(tetradeca-2,3,13-trienyl)-1*H*-indole *rac*-**1c** (jf-2-029)



Following **Typical Procedure I**, the reaction of CuI (0.3840 g, 2 mmol, 99%), diisobutylamine (0.98 mL, $d = 0.74$ g/mL, 0.7237 g, 5.6 mmol), 1-(prop-2-ynyl)-1*H*-indole (0.6210 g, 4 mmol), undecenal (1.1020 g, 6.4 mmol, 97%), and dioxane (8 mL) for 13 h at 130 °C afforded *rac*-**1c** (0.5547 g, 45%) [eluent: petroleum ether] as a liquid: 1H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, $J = 8.1$ Hz, 1H, Ar-H), 7.34 (d, $J = 8.1$ Hz, 1H, Ar-H), 7.19 (t, $J = 7.7$ Hz, 1H, Ar-H), 7.13-7.05 (m, 2H, Ar-H), 6.48 (dd, $J_1 = 3.2$ Hz, $J_2 = 0.8$ Hz, 1H, Ar-H), 5.88-5.73 (m, 1H, CH=), 5.30-5.15 (m, 2H, CH=C=CH), 5.05-4.89 (m, 2H, =CH₂), 4.67 (dd, $J_1 = 6.0$ Hz, $J_2 = 2.7$ Hz, 2H, NCH₂), 2.09-1.97 (m, 2H, CH₂), 1.99-1.88 (m, 2H, CH₂), 1.47-1.19 (m, 12H, $CH_2 \times 6$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.4, 139.1, 135.9, 128.7, 127.5, 121.3, 120.8, 119.3, 114.1, 109.6, 101.2, 93.5, 87.9, 45.9, 33.8, 29.4, 29.3, 29.1, 29.0, 28.93, 28.86, 28.5; IR (neat) ν (cm⁻¹) 3057, 2977, 2925, 2852, 1964, 1640, 1613, 1512, 1484, 1464, 1396, 1334, 1313, 1254, 1180, 1012; MS (70 ev, EI) m/z (%) 308 (M^++1 , 5.38), 307 (M^+ , 20.24), 130 (100); HRMS calcd for $C_{22}H_{29}N$ [M^+]: 307.2300, Found: 307.2302.

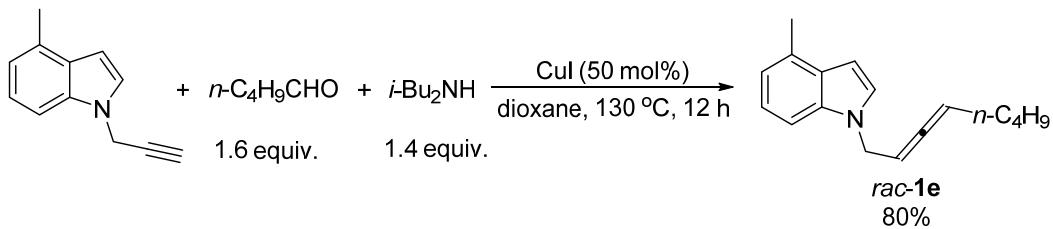
3.4 Synthesis of 5-methoxy-1-(octa-2,3-dienyl)-1*H*-indole *rac*-**1d** (jf-1-196)



Following **Typical Procedure I**, the reaction of CuBr₂ (0.1338 g, 0.6 mmol, 99%), α,α -diphenylprolinol (1.0845 g, 4.2 mmol, 98%), 5-methoxy-1-(prop-2-ynyl)-1*H*-indole (0.5552 g, 3 mmol), pentanal (0.52 mL, $d =$

0.81 g/mL, 0.4212 g, 4.8 mmol, 98%), and dioxane (9.0 mL) for 12 h at 130 °C afforded *rac*-**1d** (0.4760 g, 62%) [eluent: petroleum ether/diethyl ether = 200/1] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.25 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.09 (d, *J* = 3.0 Hz, 2H, Ar-H), 6.86 (dd, *J*₁ = 8.7 Hz, *J*₂ = 2.4 Hz, 1H, Ar-H), 6.41 (d, *J* = 3.0 Hz, 1H, Ar-H), 5.32-5.13 (m, 2H, CH=C=CH), 4.66 (dd, *J*₁ = 6.3 Hz, *J*₂ = 2.7 Hz, 2H, NCH₂), 3.85 (s, 3H, OCH₃), 2.07-1.86 (m, 2H, CH₂), 1.37-1.22 (m, 4H, CH₂ × 2), 0.88 (t, *J* = 5.9 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.4, 154.0, 131.4, 129.1, 128.1, 111.7, 110.4, 102.6, 100.8, 93.5, 88.0, 55.9, 46.2, 31.1, 28.2, 22.1, 13.8; IR (neat) ν (cm⁻¹) 3101, 2991, 2958, 2929, 2868, 2855, 2829, 1964, 1622, 1575, 1486, 1447, 1394, 1378, 1336, 1295, 1237, 1183, 1151, 1131, 1089, 1033; MS (70 ev, EI) *m/z* (%) 256 (M⁺+1, 11.16), 225 (M⁺, 53.83), 212 (100); HRMS calcd for C₁₇H₂₁NO [M⁺]: 255.1623, Found: 255.1622.

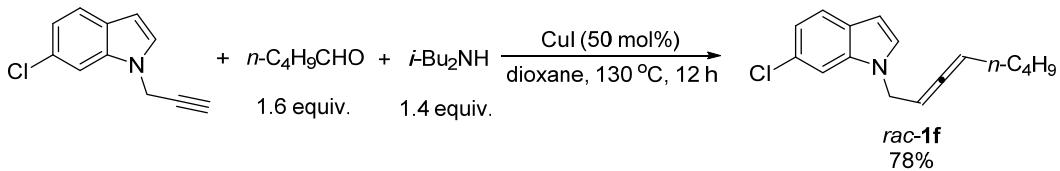
3.5 Synthesis of 4-methyl-1-(octa-2,3-dienyl)-1*H*-indole *rac*-**1e** (jf-2-034)



Typical Procedure II: To a flame-dried Schlenk tube with a polytetrafluoroethylene plug were added CuI (0.3849 g, 2 mmol, 99%), diisobutylamine (0.98 mL, d = 0.74 g/mL, 0.7237 g, 5.6 mmol), 4-methyl-1-(prop-2-ynyl)-1*H*-indole (0.6739 g, 4 mmol)/dioxane (2 mL), pentanal (0.68 mL, d = 0.81 g/mL, 0.5504 g, 6.4 mmol, 98%), and dioxane (6 mL) sequentially. The Schlenk tube was then sealed by screwing the polytetrafluoroethylene plug tightly with the outlet connected to the vacuum line. The reaction was complete after being stirred in an oil bath preheated at 130 °C for 12 h as monitored by TLC. The resulting mixture was cooled to room temperature and diluted with diethyl ether and washed with an aqueous solution of hydrochloric acid (1.2 M). The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. After

filtration and evaporation, the residue was purified by column chromatography on silica gel to afford *rac*-**1e** (0.7584 g, 80%) [eluent: petroleum ether/diethyl ether = 200/1] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.18 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.11 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.07 (d, *J* = 3.0 Hz, 1H, Ar-H), 6.89 (d, *J* = 6.6 Hz, 1H, Ar-H), 6.49 (dd, *J*₁ = 3.2 Hz, *J*₂ = 0.8 Hz, 1H, Ar-H), 5.33-5.12 (m, 2H, CH=C=CH), 4.64 (dd, *J*₁ = 6.0 Hz, *J*₂ = 2.7 Hz, 2H, NCH₂), 2.54 (s, 3H, CH₃), 2.05-1.90 (m, 2H, CH₂), 1.37-1.17 (m, 4H, CH₂ × 2), 0.87 (t, *J* = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.4, 135.7, 130.3, 128.6, 126.8, 121.5, 119.5, 107.3, 99.7, 93.4, 88.0, 46.1, 31.1, 28.2, 22.1, 18.7, 13.8; IR (neat) ν (cm⁻¹) 3050, 2957, 2927, 2858, 1964, 1605, 1585, 1514, 1493, 1456, 1423, 1398, 1378, 1338, 1297, 1246, 1200, 1158, 1136, 1069, 1051; MS (70 ev, EI) *m/z* (%) 240 (M⁺+1, 7.89), 239 (M⁺, 37.75), 196 (100); HRMS calcd for C₁₇H₂₁N [M⁺]: 239.1674, Found: 239.1676.

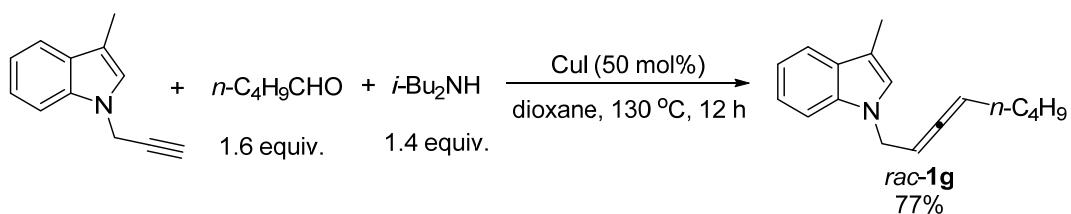
3.6 Synthesis of 6-chloro-1-(octa-2,3-dienyl)-1*H*-indole *rac*-**1f** (jf-2-060)



Following **Typical Procedure I**, the reaction of CuI (0.3830 g, 2 mmol, 99%), diisobutylamine (0.98 mL, d = 0.74 g/mL, 0.7237 g, 5.6 mmol), 6-chloro-1-(prop-2-ynyl)-1*H*-indole (0.7582 g, 4 mmol), pentanal (0.68 mL, d = 0.81 g/mL, 0.5504 g, 6.4 mmol, 98%), and dioxane (8 mL) for 12 h at 130 °C afforded *rac*-**1f** (0.8068 g, 78%) [eluent: petroleum ether] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.49 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.34 (s, 1H, Ar-H), 7.13-6.99 (m, 2H, Ar-H), 6.44 (d, *J* = 3.0 Hz, 1H, Ar-H), 5.28-5.13 (m, 2H, CH=C=CH), 4.66-4.53 (m, 2H, NCH₂), 2.03-1.85 (m, 2H, CH₂), 1.37-1.16 (m, 4H, CH₂ × 2), 0.86 (t, *J* = 6.9 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.4, 136.4, 128.4, 127.4, 127.3, 121.6, 120.0, 109.9, 101.4, 93.9, 87.6, 46.1, 31.1, 28.2, 22.1, 13.8; IR (neat) ν (cm⁻¹) 2957, 2928, 2858, 1964, 1689, 1611, 1564, 1508, 1465, 1392, 1338, 1313, 1269, 1240, 1204, 1182, 1126, 1101, 1063, 1053; MS (70 ev, EI) *m/z* (%) 262 (M⁺(³⁷Cl) + 1, 1.69), 261 (M⁺(³⁷Cl), 9.78), 260 (M⁺(³⁵Cl) + 1, 5.93), 259 (M⁺(³⁵Cl), 25.88), 216 (100); HRMS

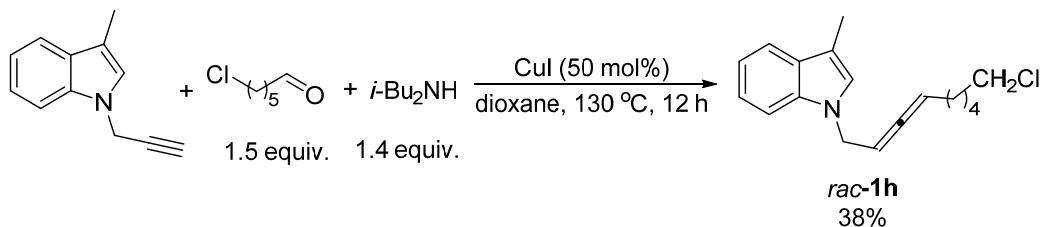
calcd for C₁₆H₁₈N³⁵Cl [M⁺]: 259.1128, Found: 259.1128.

3.7 Synthesis of 3-methyl-1-(octa-2,3-dienyl)-1*H*-indole *rac*-1g (jf-2-080)



Following **Typical Procedure II**, the reaction of CuI (0.3850 g, 2 mmol, 99%), diisobutylamine (0.98 mL, d = 0.74 g/mL, 0.7237 g, 5.6 mmol), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (0.6758 g, 4 mmol)/dioxane (2 mL), pentanal (0.68 mL, d = 0.81 g/mL, 0.5504 g, 6.4 mmol, 98%), and dioxane (6 mL) for 12 h at 130 °C afforded *rac*-1g (0.7384 g, 77%) [eluent: petroleum ether] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.55 (dd, *J*₁ = 7.8 Hz, *J*₂ = 0.6 Hz, 1H, Ar-H), 7.31 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.19 (td, *J*₁ = 7.4 Hz, *J*₂ = 1.4 Hz, 1H, Ar-H), 7.09 (td, *J*₁ = 7.4 Hz, *J*₂ = 0.9 Hz, 1H, Ar-H), 6.87 (s, 1H, Ar-H), 5.30-5.15 (m, 2H, CH=C=CH), 4.62 (dd, *J*₁ = 5.9 Hz, *J*₂ = 3.2 Hz, 2H, NCH₂), 2.32 (d, *J* = 0.9 Hz, 3H, CH₃), 2.06-1.90 (m, 2H, CH₂), 1.38-1.23 (m, 4H, CH₂ × 2), 0.88 (t, *J* = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.4, 136.3, 129.0, 125.2, 121.3, 119.0, 118.6, 110.4, 109.5, 93.3, 88.1, 45.7, 31.2, 28.3, 22.1, 13.9, 9.6; IR (neat) ν (cm⁻¹) 3055, 2956, 2928, 2859, 1964, 1614, 1560, 1482, 1466, 1386, 1329, 1252, 1179, 1126, 1104, 1013; MS (70 ev, EI) *m/z* (%) 240 (M⁺+1, 7.35), 239 (M⁺, 40.31), 144 (100); HRMS calcd for C₁₇H₂₁N [M⁺]: 239.1674, Found: 239.1676.

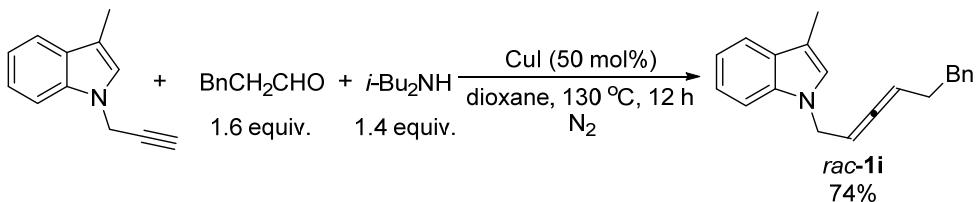
3.8 Synthesis of 1-(9-chloronona-2,3-dienyl)-3-methyl-1*H*-indole *rac*-1h (jf-2-149)



Following **Typical Procedure II**, the reaction of CuI (0.3837 g, 2 mmol, 99%), diisobutylamine (0.98 mL, d = 0.74 g/mL, 0.7237 g, 5.6 mmol), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (0.6751 g, 4 mmol)/dioxane (2 mL),

6-chlorohexanal (0.8025 g, 6.4 mmol), and dioxane (6 mL) for 12 h at 130 °C afforded *rac*-**1h** (0.4410 g, 38%, 98% purity) [eluent: petroleum ether/diethyl ether = 200/1] as a liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.30 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.19 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.09 (t, *J* = 7.2 Hz, 1H, Ar-H), 6.87 (s, 1H, Ar-H), 5.32-5.14 (m, 2H, CH=C=CH), 4.63 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2.8 Hz, 2H, NCH₂), 3.49 (t, *J* = 6.8 Hz, 2H, CH₂Cl), 2.32 (s, 3H, CH₃), 2.00-1.92 (m, 2H, CH₂), 1.76-1.68 (m, 2H, CH₂), 1.44-1.27 (m, 4H, CH₂ × 2); ¹³C NMR (100 MHz, CDCl₃) δ 204.4, 136.3, 129.0, 125.2, 121.3, 119.0, 118.6, 110.4, 109.4, 93.0, 88.4, 45.6, 45.0, 32.4, 28.3, 28.1, 26.2, 9.6; IR (neat) ν (cm⁻¹) 3054, 2933, 2859, 1963, 1614, 1558, 1481, 1466, 1386, 1363, 1329, 1257, 1179, 1126, 1102, 1038, 1013; MS (70 ev, EI) *m/z* (%) 289 (M⁺(³⁷Cl), 5.57), 287 (M⁺(³⁵Cl), 14.93), 144 (100); HRMS calcd for C₁₈H₂₂N³⁵Cl [M⁺]: 287.1441, Found: 287.1438.

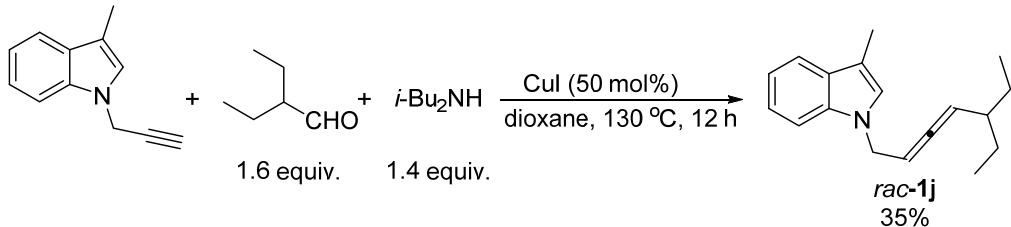
3.9 Synthesis of 3-methyl-1-(6-phenylhexa-2,3-dienyl)-1*H*-indole *rac*-**1i** (jf-3-019)



Following **Typical Procedure II**, the reaction of CuI (0.3845 g, 2 mmol, 99%), diisobutylamine (0.98 mL, d = 0.74 g/mL, 0.7237 g, 5.6 mmol), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (0.6762 g, 4 mmol)/dioxane (2 mL), 3-phenylpropanal (0.8591 g, 6.4 mmol), and dioxane (6 mL) for 12 h at 130 °C afforded *rac*-**1i** (0.8396 g, 74%) [eluent: petroleum ether/diethyl ether = 200/1] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.30-7.22 (m, 3H, Ar-H), 7.22-7.05 (m, 5H, Ar-H), 6.81 (d, *J* = 0.9 Hz, 1H, Ar-H), 5.26-5.17 (m, 2H, CH=C=CH), 4.57-4.50 (m, 2H, NCH₂), 2.59 (t, *J* = 7.7 Hz, 2H, CH₂Ph), 2.35-2.19 (m, 5H, CH₃ + CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 204.5, 141.5, 136.2, 128.9, 128.5, 128.3, 125.9, 125.2, 121.3, 119.0, 118.6, 110.4, 109.4, 92.5, 88.6, 45.4, 35.2, 30.3, 9.6; IR (neat) ν (cm⁻¹) 3084, 3057, 3026, 2916, 2858, 1965, 1614, 1603, 1583, 1559, 1496, 1481, 1465, 1454, 1386, 1329, 1257, 1209, 1180, 1126, 1105, 1078, 1030, 1013; MS (70 ev, EI) *m/z* (%) 288 (M⁺+1, 1.3), 287 (M⁺, 6.0), 196 (100); HRMS calcd for

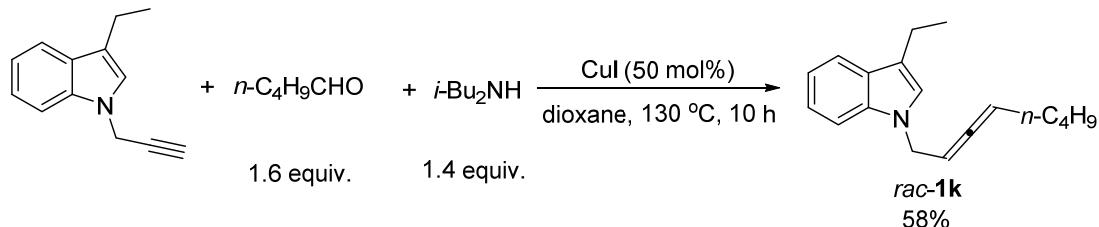
$C_{21}H_{21}N$ [M $^+$]: 287.1674, Found: 287.1674.

3.10 Synthesis of 1-(5-ethylhepta-2,3-dienyl)-3-methyl-1*H*-indole *rac*-1j (jf-3-092)



Following **Typical Procedure II**, the reaction of CuI (0.3850 g, 2 mmol, 99%), diisobutylamine (0.98 mL, $d = 0.74$ g/mL, 0.7237 g, 5.6 mmol), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (0.6779 g, 4 mmol)/dioxane (2 mL), 2-ethylbutanal (0.82 mL, $d = 0.814$ g/mL, 0.6675 g, 6.4 mmol, 97%), and dioxane (6 mL) for 12 h at 130 °C afforded *rac*-1j (0.3548 g, 35%) [eluent: petroleum ether] as a liquid: 1H NMR (300 MHz, CDCl₃) δ 7.55 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.32 (d, $J = 8.1$ Hz, 1H, Ar-H), 7.19 (t, $J = 7.4$ Hz, 1H, Ar-H), 7.09 (t, $J = 7.4$ Hz, 1H, Ar-H), 6.89 (s, 1H, Ar-H), 5.31-5.20 (m, 1H, one proton of CH=C=CH), 5.10-4.97 (m, 1H, one proton of CH=C=CH), 4.70-4.59 (m, 2H, NCH₂), 2.32 (s, 3H, Ar-CH₃), 1.93-1.75 (m, 1H, CH), 1.50-1.16 (m, 4H, CH₂ \times 2), 0.85 (t, $J = 7.1$ Hz, 6H, CH₃ \times 2); ^{13}C NMR (75 MHz, CDCl₃) δ 204.2, 136.3, 129.0, 125.2, 121.3, 118.9, 118.6, 110.4, 109.4, 97.0, 88.1, 45.8, 42.8, 27.6, 27.3, 11.6, 11.5, 9.6; IR (neat) ν (cm $^{-1}$) 3056, 2961, 2921, 2873, 1963, 1615, 1558, 1482, 1466, 1386, 1329, 1256, 1179, 1126, 1013; MS (70 ev, EI) m/z (%) 254 (M $^+$ +1, 4.81), 253 (M $^+$, 24.75), 224 (100); HRMS calcd for C₁₈H₂₃N [M $^+$]: 253.1830, Found: 253.1832.

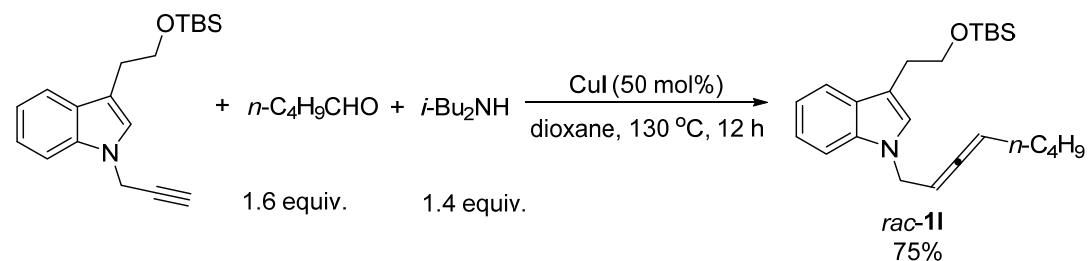
3.11 Synthesis of 3-ethyl-1-(octa-2,3-dienyl)-1*H*-indole *rac*-1k (jf-3-074)



Following **Typical Procedure II**, the reaction of CuI (0.3758 g, 2 mmol, 99%), diisobutylamine (0.98 mL, $d = 0.74$ g/mL, 0.7235 g, 5.6 mmol), 3-ethyl-1-(prop-2-ynyl)-1*H*-indole (0.7222 g, 4 mmol)/dioxane (2 mL), pentanal (0.69

mL, d = 0.81 g/mL, 0.5616 g, 6.4 mmol, 98%), and dioxane (6 mL) for 10 h at 130 °C afforded *rac*-**1k** (0.5763 g, 58%) [eluent: petroleum ether/ethyl acetate = 100/1] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.31 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.19 (t, *J* = 6.9 Hz, 1H, Ar-H), 7.08 (t, *J* = 7.1 Hz, 1H, Ar-H), 6.88 (s, 1H, Ar-H), 5.31-5.16 (m, 2H, CH=C=CH), 4.63 (dd, *J*₁ = 6.0 Hz, *J*₂ = 2.7 Hz, 2H, NCH₂), 2.77 (q, *J* = 7.5 Hz, 2H, Ar-CH₂), 2.03-1.91 (m, 2H, CH₂), 1.40-1.22 (m, 7H, CH₂ × 2 + CH₃), 0.88 (t, *J* = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.4, 136.4, 128.1, 124.0, 121.3, 119.0, 118.5, 117.6, 109.5, 93.3, 88.1, 45.8, 31.1, 28.3, 22.1, 18.3, 14.5, 13.9; IR (neat) ν (cm⁻¹) 3055, 2960, 2929, 2871, 2856, 1964, 1614, 1556, 1467, 1417, 1392, 1371, 1333, 1314, 1270, 1177, 1126, 1105, 1064, 1013; MS (70 ev, EI) *m/z* (%) 254 (M⁺+1, 9.84), 253 (M⁺, 50.58), 210 (100); HRMS calcd for C₁₈H₂₃N [M⁺]: 253.1830, Found: 253.1832.

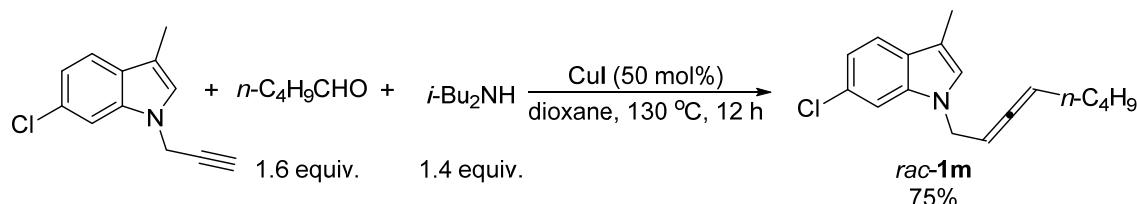
3.12 Synthesis of 3-((*tert*-butyldimethylsilyl)oxy)ethyl)-1-(octa-2,3-dienyl)-1*H*-indole *rac*-**1l** (jf-3-058)



Following **Typical Procedure II**, the reaction of CuI (0.5712 g, 3 mmol, 99%), diisobutylamine (1.46 mL, d = 0.74 g/mL, 1.0853 g, 8.4 mmol), 3-((*tert*-butyldimethylsilyl)oxy)ethyl)-1-(prop-2-ynyl)-1*H*-indole (1.8820 g, 6 mmol)/dioxane (2 mL), pentanal (1.02 mL, d = 0.81 g/mL, 0.8262 g, 9.6 mmol, 98%), and dioxane (10 mL) for 12 h at 130 °C afforded *rac*-**1l** (1.7205 g, 75%) [eluent: petroleum ether/ethyl acetate = 100/1] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.62 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.36 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.23 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.13 (t, *J* = 7.1 Hz, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 5.34-5.16 (m, 2H, CH=C=CH), 4.68 (dd, *J*₁ = 5.7 Hz, *J*₂ = 3.3 Hz, 2H, NCH₂), 3.90 (t, *J* = 7.5 Hz, 2H, CH₂), 3.02 (t, *J* = 7.5 Hz, 2H, CH₂), 2.09-1.93 (m, 2H, CH₂), 1.43-1.27 (m, 4H, CH₂ × 2 + CH₃).

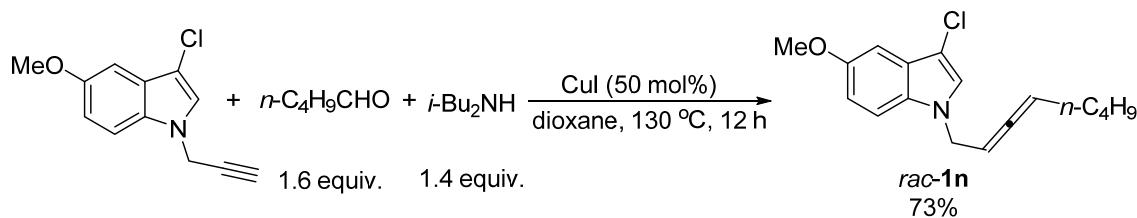
2), 1.00-0.86 (m, 12H, $\text{CH}_3 + \text{CH}_3 \times 3$), 0.075 (s, 6H, $\text{CH}_3 \times 2$); ^{13}C NMR (75 MHz, CDCl_3) δ 204.4, 136.1, 128.4, 125.6, 121.3, 119.0, 118.7, 111.8, 109.6, 93.3, 88.0, 64.0, 45.8, 31.2, 29.0, 28.3, 26.0, 22.1, 18.4, 13.9, -5.29; IR (neat) ν (cm^{-1}) 3056, 2956, 2928, 2857, 1964, 1614, 1553, 1470, 1386, 1360, 1332, 1255, 1215, 1174, 1093, 1053, 1013; MS (70 ev, EI) m/z (%) 384 ($\text{M}^+ + 1$, 9.69), 383 (M^+ , 31.68), 208 (100); HRMS calcd for $\text{C}_{24}\text{H}_{37}\text{NOSi} [\text{M}^+]$: 383.2644, Found: 383.2646.

3.13 Synthesis of 6-chloro-3-methyl-1-(octa-2,3-dienyl)-1*H*-indole *rac*-**1m** (jf-2-191)



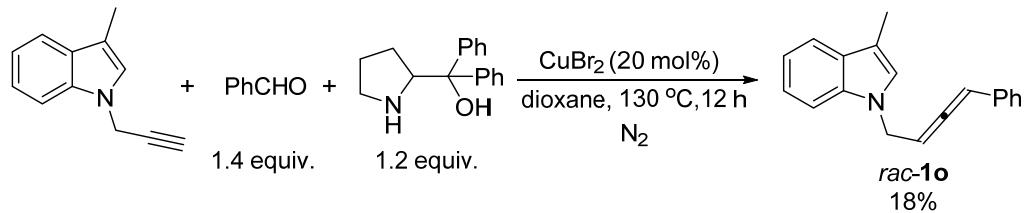
Following **Typical Procedure II**, the reaction of CuI (0.3850 g, 2 mmol, 99%), diisobutylamine (0.98 mL, d = 0.74 g/mL, 0.7237 g, 5.6 mmol), 6-chloro-3-methyl-1-(prop-2-ynyl)-1*H*-indole (0.8148 g, 4 mmol)/dioxane (2 mL), pentanal (0.70 mL, d = 0.81 g/mL, 0.5670 g, 6.4 mmol, 98%), and dioxane (6 mL) for 12 h at 130 °C afforded **rac-1m** (0.8200 g, 75%) [eluent: petroleum ether] as a liquid: ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, J = 8.4 Hz, 1H, Ar-H), 7.30 (d, J = 1.6 Hz, 1H, Ar-H), 7.05 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H, Ar-H), 6.86 (s, 1H, Ar-H), 5.26-5.15 (m, 2H, $\text{CH}=\text{C}=\text{CH}$), 4.60-4.55 (m, 2H, NCH_2), 2.28 (s, 3H, CH_3), 2.02-1.91 (m, 2H, CH_2), 1.34-1.22 (m, 4H, $\text{CH}_2 \times 2$), 0.87 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 204.5, 136.7, 127.6, 127.4, 126.0, 119.8, 119.3, 110.7, 109.6, 93.7, 87.7, 45.8, 31.2, 28.2, 22.1, 13.8, 9.5; IR (neat) ν (cm^{-1}) 2957, 2928, 2860, 1965, 1612, 1552, 1468, 1386, 1362, 1326, 1243, 1177, 1135, 1067; MS (70 ev, EI) m/z (%) 275 ($\text{M}^+(\text{Cl})$, 27.33), 273 ($\text{M}^+(\text{Cl})$, 83.53), 230 (100); HRMS calcd for $\text{C}_{17}\text{H}_{20}\text{N}^{35}\text{Cl} [\text{M}^+]$: 273.1284, Found: 273.1284.

3.14 Synthesis of 3-chloro-5-methoxy-1-(octa-2,3-dienyl)-1*H*-indole *rac*-**1n** (jf-3-082)



Following **Typical Procedure II**, the reaction of CuI (0.2891 g, 1.5 mmol, 99%), diisobutylamine (0.73 mL, $d = 0.74$ g/mL, 0.5426 g, 4.2 mmol), 3-chloro-5-methoxy-1-(prop-2-ynyl)-1*H*-indole (0.6598 g, 3 mmol)/dioxane (2 mL), pentanal (0.52 mL, $d = 0.81$ g/mL, 0.4212 g, 4.8 mmol, 98%), and dioxane (4 mL) for 12 h at 130 °C afforded *rac*-1n (0.6375 g, 73%) [eluent: petroleum ether/ethyl acetate = 100/1] as a liquid: ^1H NMR (300 MHz, CDCl_3) δ 7.22 (d, $J = 8.7$ Hz, 1H, Ar-H), 7.06 (s, 1H, Ar-H), 7.02 (d, $J = 2.7$ Hz, 1H, Ar-H), 6.89 (dd, $J_1 = 8.9$ Hz, $J_2 = 2.6$ Hz, 1H, Ar-H), 5.27-5.15 (m, 2H, $\text{CH}=\text{C}=\text{CH}$), 4.65-4.55 (m, 2H, NCH_2), 3.87 (s, 3H, OCH_3), 2.01-1.86 (m, 2H, CH_2), 1.34-1.17 (m, 4H, $\text{CH}_2 \times 2$), 0.87 (t, $J = 7.1$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 204.5, 154.5, 130.3, 126.2, 124.5, 113.3, 111.0, 104.1, 99.3, 93.8, 87.6, 85.7, 46.2, 31.1, 28.2, 22.1, 13.8; IR (neat) ν (cm^{-1}) 3123, 2956, 2929, 2856, 1964, 1624, 1576, 1489, 1451, 1388, 1334, 1292, 1252, 1220, 1177, 1126, 1089, 1035; MS (70 ev, EI) m/z (%) 292 ($\text{M}^{+}(^{37}\text{Cl}) + 1$, 1.17), 291 ($\text{M}^{+}(^{37}\text{Cl})$, 5.79), 290 ($\text{M}^{+}(^{35}\text{Cl}) + 1$, 5.79), 289 ($\text{M}^{+}(^{35}\text{Cl})$, 16.88), 254 (100); HRMS calcd for $\text{C}_{17}\text{H}_{20}\text{NO}^{35}\text{Cl} [\text{M}^+]$: 289.1233, Found: 289.1235.

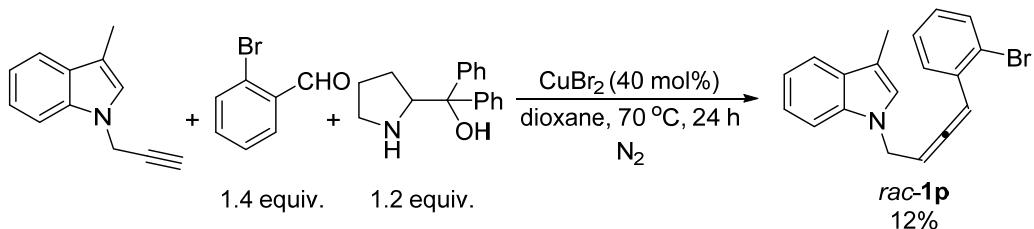
3.15 Synthesis of 3-methyl-1-(4-phenylbuta-2,3-dienyl)-1*H*-indole *rac*-1o (jf-2-157)



Following **Typical Procedure II**, the reaction of CuBr₂ (0.1818 g, 0.8 mmol, 99%), α,α -diphenylprolinol (1.2142 g, 4.8 mmol, 98%), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (0.6764 g, 4 mmol)/dioxane (2 mL), benzaldehyde (0.5997 g, 5.6 mmol), and dioxane (4 mL) for 12 h at 130 °C afforded *rac*-1o (0.1868 g, 18%)

[eluent: petroleum ether] as a liquid: ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.33-7.16 (m, 7H, Ar-H), 7.11 (t, $J = 7.2$ Hz, 1H, Ar-H), 6.90 (s, 1H, Ar-H), 6.27 (dt, $J_1 = 6.4$ Hz, $J_2 = 2.3$ Hz, 1H, CH=), 5.68 (q, $J = 6.7$ Hz, 1H, CH=), 4.75 (dd, $J_1 = 6.8$ Hz, $J_2 = 2.4$ Hz, 2H, NCH₂), 2.32 (s, 3H, CH₃); ^{13}C NMR (100 MHz, CDCl_3) δ 205.7, 136.2, 133.5, 129.1, 128.6, 127.3, 127.0, 125.1, 121.5, 119.1, 118.8, 110.9, 109.5, 96.4, 92.1, 45.3, 9.6; IR (neat) ν (cm⁻¹) 3050, 3030, 2916, 2856, 1950, 1614, 1597, 1495, 1481, 1465, 1386, 1364, 1328, 1265, 1178, 1126, 1101, 1072, 1041, 1013; MS (70 ev, EI) m/z (%) 260 (M^++1 , 14.68), 259 (M^+ , 76.85), 258 (100); HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{N} [M^+]$: 259.1361, Found: 259.1361.

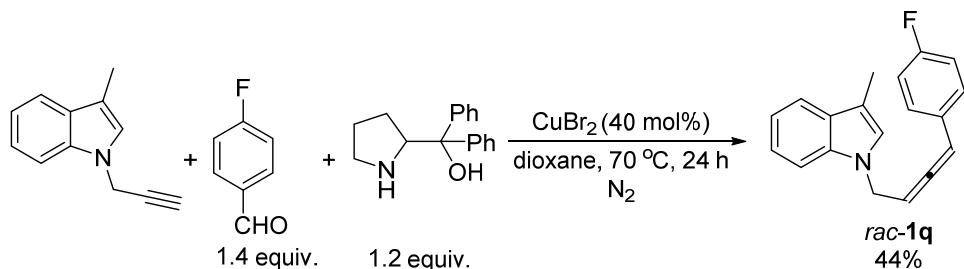
3.16 Synthesis of 1-(4-(2-bromophenyl)buta-2,3-dienyl)-3-methyl-1*H*-indole *rac*-1p (jf-2-172)



Typical Procedure III: To a flame-dried Schlenk tube with a rubber plug were added CuBr_2 (0.5458 g, 2.4 mmol, 99%), α,α -diphenylprolinol (1.8600 g, 7.2 mmol, 98%), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (1.0143 g, 6 mmol)/dioxane (2 mL), 2-bromobenzaldehyde (1.6380 g, 8.4 mmol, 95%), and dioxane (7 mL) sequentially under nitrogen atmosphere. The reaction was complete after being stirred in an oil bath preheated at 70 °C for 24 h as monitored by TLC. The resulting mixture was diluted with ether, and washed with an aqueous solution of hydrochloric acid (1.2 M). The organic layer was separated, and the aqueous layer was extracted with ether. 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 on silica gel to afford *rac*-1p (0.2463 g, 12%) [eluent: petroleum ether] as a liquid: ^1H NMR (300 MHz, CDCl_3) δ 7.57 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.51 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.34-7.25 (m, 2H, Ar-H), 7.23-6.98 (m, 4H, Ar-H), 6.89 (s, 1H, Ar-H), 6.74 (dt, $J_1 = 6.2$ Hz, $J_2 = 2.4$ Hz, 1H, CH=), 5.72 (q, $J = 6.6$ Hz, 1H, CH=), 4.76 (dd, $J_1 = 6.8$ Hz,

$J_2 = 2.3$ Hz, 2H, NCH₂), 2.32 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 206.5, 136.2, 132.99, 132.95, 129.1, 128.65, 128.56, 127.4, 125.1, 122.6, 121.6, 119.1, 118.9, 111.1, 109.4, 95.5, 92.4, 45.1, 9.6; IR (neat) ν (cm⁻¹) 3054, 2916, 2883, 2859, 1951, 1614, 1588, 1561, 1465, 1439, 1403 1385, 1364, 1328, 1287, 1260, 1178, 1126, 1022; MS (70 ev, EI) *m/z* (%) 339 (M⁺(⁸¹Br), 28.38), 337 (M⁺(⁷⁹Br), 30.63), 168 (100); HRMS calcd for C₁₉H₁₆N⁷⁹Br [M⁺]: 337.0466, Found: 337.0464.

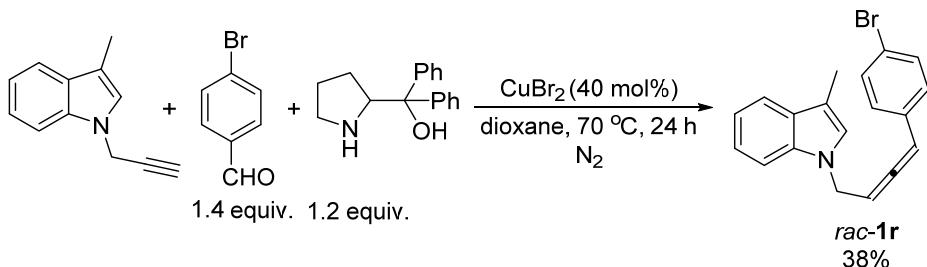
3.17 Synthesis of 1-(4-(4-fluorophenyl)buta-2,3-dienyl)-3-methyl-1*H*-indole *rac*-1q (jf-3-033)



Following **Typical Procedure III**, the reaction of CuBr₂ (0.5461 g, 2.4 mmol, 99%), α,α-diphenylprolinol (1.8580 g, 7.2 mmol, 98%), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (1.0110 g, 6 mmol)/dioxane (2 mL), 4-fluorobenzaldehyde (1.0394 g, 8.4 mmol, 99%), and dioxane (7 mL) for 24 h at 70 °C afforded *rac*-1q (0.7268 g, 44%) [eluent: petroleum ether/ethyl acetate = 200/1] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.56 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.26 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.21-7.06 (m, 4H, Ar-H), 6.93 (t, *J* = 8.7 Hz, 2H, Ar-H), 6.84 (s, 1H, Ar-H), 6.19 (dt, *J*₁ = 5.9 Hz, *J*₂ = 2.5 Hz, 1H, CH=), 5.64 (q, *J* = 6.5 Hz, 1H, CH=), 4.68 (dd, *J*₁ = 6.8 Hz, *J*₂ = 2.6 Hz, 2H, NCH₂), 2.30 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 205.3 (d, *J* = 2.0 Hz), 162.0 (d, *J* = 245.4 Hz), 136.1, 129.4 (d, *J* = 3.5 Hz), 129.1, 128.4 (d, *J* = 8.3 Hz), 125.1, 121.5, 119.1, 118.8, 115.5 (d, *J* = 22.1 Hz), 110.9, 109.4, 95.5, 92.4, 45.2, 9.5; ¹⁹F NMR (282 MHz, CDCl₃) δ -115.2; IR (neat) ν (cm⁻¹) 3048, 2917, 2887, 2861, 1950, 1889, 1603, 1506, 1481, 1464, 1386, 1328, 1299, 1264, 1226, 1178, 1156, 1126, 1092, 1041, 1013; MS (70 ev, EI) *m/z* (%) 278 (M⁺+1, 11.19), 277 (M⁺, 59.28), 167 (100); HRMS calcd for C₁₉H₁₆NF [M⁺]: 277.1267, Found: 277.1266.

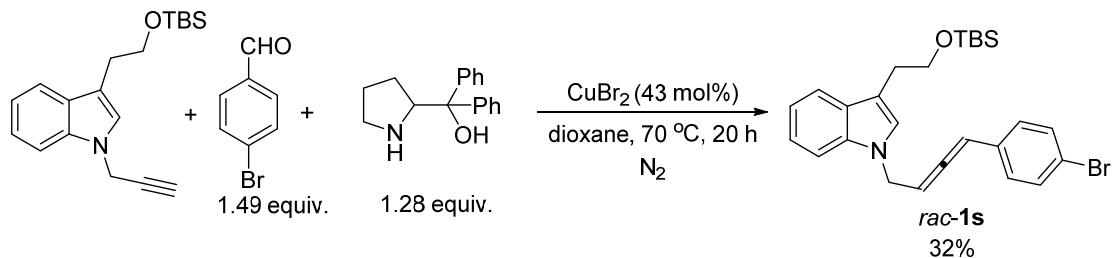
3.18 Synthesis of 1-(4-(4-bromophenyl)buta-2,3-dienyl)-3-methyl-1*H*-indole

***rac*-1r (jf-3-017)**



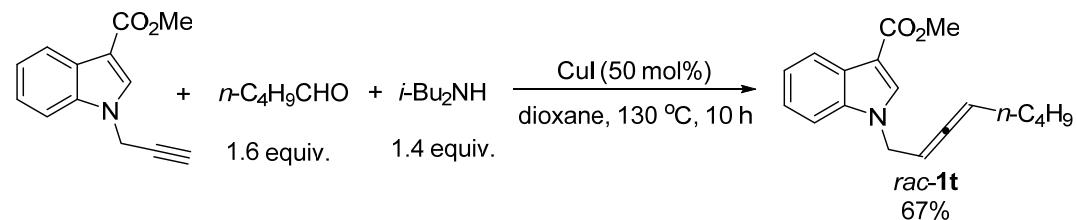
Following **Typical Procedure III**, the reaction of CuBr₂ (0.5466 g, 2.4 mmol, 99%), α,α -diphenylprolinol (1.8580 g, 7.2 mmol, 98%), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (1.0133 g, 6 mmol)/dioxane (2 mL), 4-bromobenzaldehyde (1.5548 g, 8.4 mmol, 99%), and dioxane (7 mL) for 24 h at 70 °C afforded *rac*-1r (0.7616 g, 38%) [eluent: petroleum ether (800 mL) to petroleum ether/diethyl ether = 200/1 (800 mL)] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.35 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.25 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.17 (td, *J*₁ = 7.4 Hz, *J*₂ = 1.0 Hz, 1H, Ar-H), 7.11 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.02 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.84 (s, 1H, Ar-H), 6.15 (dt, *J*₁ = 6.3 Hz, *J*₂ = 2.4 Hz, 1H, ArCH=), 5.64 (q, *J* = 6.5 Hz, 1H, CH=), 4.69 (dd, *J*₁ = 6.8 Hz, *J*₂ = 2.3 Hz, 2H, NCH₂), 2.30 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 205.6, 136.1, 132.4, 131.6, 129.1, 128.4, 125.0, 121.6, 120.9, 119.1, 118.9, 111.0, 109.4, 95.7, 92.6, 45.0, 9.6; IR (neat) ν (cm⁻¹) 3046, 2916, 2883, 2859, 1951, 1614, 1586, 1487, 1464, 1386, 1363, 1328, 1262, 1177, 1126, 1095, 1069, 1042, 1010; MS (70 ev, EI) *m/z* (%) 339 (M⁺(⁸¹Br), 18.41), 337 (M⁺(⁷⁹Br), 17.35), 168 (100); HRMS calcd for C₁₉H₁₆N⁷⁹Br [M⁺]: 337.0466, Found: 337.0463.

3.19 Synthesis of 1-(4-(4-bromophenyl)buta-2,3-dienyl)-3-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-1*H*-indole *rac*-1s (jf-3-085)



Following **Typical Procedure III**, the reaction of CuBr₂ (0.9005 g, 4 mmol, 99%), α,α -diphenylprolinol (3.0970 g, 12 mmol, 98%), 3-((tert-butyldimethylsilyl)oxy)-ethyl)-1-(prop-2-ynyl)-1*H*-indole (2.9504 g, 9.4 mmol)/dioxane (2 mL), 4-bromobenzaldehyde (2.6154 g, 14 mmol, 99%), and dioxane (13 mL) for 20 h at 70 °C afforded *rac*-**1s** (1.4622 g, 32%) [eluent: petroleum ether/diethyl ether = 50/1] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.61 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.41 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.31 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.21 (td, *J*₁ = 7.4 Hz, *J*₂ = 1.0 Hz, 1H, Ar-H), 7.14 (dd, *J*₁ = 7.7 Hz, *J*₂ = 1.1 Hz, 1H, Ar-H), 7.09 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.98 (s, 1H, Ar-H), 6.22 (td, *J*₁ = 6.0 Hz, *J*₂ = 2.5 Hz, 1H, =CH), 5.72 (q, *J* = 6.6 Hz, 2H, CH=), 4.79 (dd, *J*₁ = 6.6 Hz, *J*₂ = 2.7 Hz, 2H, NCH₂), 3.85 (t, *J* = 7.4 Hz, 2H, CH₂), 2.99 (t, *J* = 7.5 Hz, 2H, CH₂), 0.92 (m, 9H, CH₃ × 3), 0.05 (s, 6H, CH₃ × 2); ¹³C NMR (75 MHz, CDCl₃) δ 205.7, 136.1, 132.5, 131.7, 128.6, 128.5, 125.5, 121.6, 121.0, 119.2, 119.0, 112.5, 109.5, 95.8, 92.6, 63.9, 45.2, 28.9, 26.0, 18.4, -5.28; IR (neat) ν (cm⁻¹) 3045, 2953, 2927, 2856, 1952, 1614, 1588, 1488, 1465, 1387, 1356, 1332, 1254, 1174, 1094, 1010; MS (70 ev, EI) *m/z* (%) 484 (M⁺(⁸¹Br) + 1, 4.70), 483 (M⁺(⁸¹Br), 13.28), 482 (M⁺(⁷⁹Br) + 1, 5.57), 481 (M⁺(⁷⁹Br), 13.49), 167 (100); HRMS calcd for C₂₆H₃₂⁷⁹BrNOSi [M⁺]: 481.1437, Found: 481.1434.

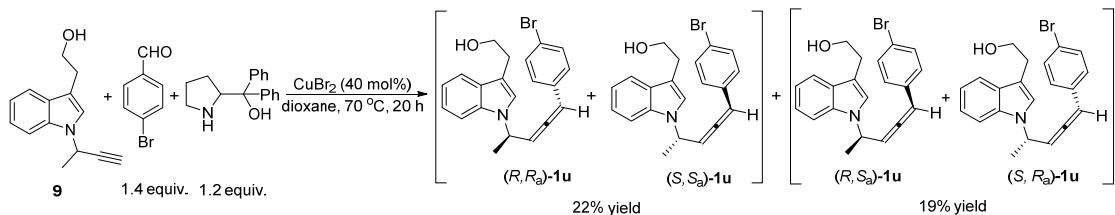
3.20 Synthesis of methyl 1-(octa-2,3-dienyl)-1*H*-indole-3-carboxylate *rac*-**1t** (jf-3-112)



Following **Typical Procedure II**, the reaction of CuI (0.5720 g, 3 mmol, 99%), diisobutylamine (1.47 mL, d = 0.74 g/mL, 0.7237 g, 8.4 mmol), methyl 1-(prop-2-ynyl)-1*H*-indole-3-carboxylate (1.2780 g, 6 mmol)/dioxane (2 mL), pentanal (1.04 mL, d = 0.81 g/mL, 0.8424 g, 9.6 mmol, 98%), and dioxane (10 mL) for 10 h at 130 °C afforded *rac*-**1t** (1.1348 g, 67%) [eluent: petroleum ether/ ethyl

acetate = 15/1] as a liquid: ^1H NMR (300 MHz, CDCl_3) δ 8.24-8.07 (m, 1H, Ar-H), 7.83 (s, 1H, Ar-H), 7.41-7.31 (m, 1H, Ar-H), 7.31-7.18 (m, 2H, Ar-H), 5.35-5.12 (m, 2H, $\text{CH}=\text{C}=\text{CH}$), 4.68 (dd, $J_1 = 5.9$ Hz, $J_2 = 2.9$ Hz, 2H, NCH_2), 3.90 (s, 3H, OCH_3), 2.01-1.81 (m, 2H, CH_2), 1.36-1.13 (m, 4H, $\text{CH}_2 \times 2$), 0.85 (t, $J = 6.3$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 204.6, 165.4, 136.4, 134.1, 126.8, 122.6, 121.8, 121.6, 110.2, 107.0, 94.2, 87.0, 50.8, 46.3, 31.0, 28.0, 22.0, 13.7; IR (neat) ν (cm^{-1}) 3120, 3054, 2955, 2925, 2872, 1965, 1705, 1615, 1537, 1486, 1466, 1381, 1340, 1267, 1239, 1179, 1121, 1091, 1029, 1014; MS (70 ev, EI) m/z (%) 284 ($\text{M}^+ + 1$, 9.91), 283 (M^+ , 48.42), 180 (100); HRMS calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2$ [M^+]: 283.1572, Found: 283.1570.

3.21 Synthesis of (*R,R_a*)-2-((5-(4-bromophenyl)penta-3,4-dien-2-yl)-1*H*-indol-3-yl)ethanol (*R,R_a*)-1u**, (*S,S_a*)-2-((5-(4-bromophenyl)penta-3,4-dien-2-yl)-1*H*-indol-3-yl)ethanol (*S,S_a*)-**1u**, (*R,S_a*)-2-((5-(4-bromophenyl)penta-3,4-dien-2-yl)-1*H*-indol-3-yl)-ethanol (*R,S_a*)-**1u**, and (*S,R_a*)-2-((5-(4-bromophenyl)penta-3,4-dien-2-yl)-1*H*-indol-3-yl)-ethanol (*S,R_a*)-**1u** (jf-5-116)**



Following **Typical Procedure III**, the reaction of CuBr_2 (0.4500 g, 2.0 mmol, 99%), α,α -diphenylprolinol (1.5482 g, 6 mmol, 98%), **9** (1.0625 g, 5 mmol)/dioxane (2 mL), 4-bromobenzaldehyde (1.2974 g, 7 mmol, 99%), and dioxane (5.5 mL) for 20 h at 70 $^\circ\text{C}$ afforded ((*R,R_a*)-**1u** + (*S,S_a*)-**1u**) (0.4172 g, 22%) (0.2329 g) and ((*R,S_a*)-**1u** + (*S,R_a*)-**1u**) (0.3735 g, 19%) [first round eluent: petroleum ether/ ethyl acetate = 8/1 (450 mL) to 6/1 (500 mL) to 5/1 (500 mL); second round eluent: petroleum ether/ ethyl acetate = 8/1 (500 mL) to 5/1 (500 mL)].

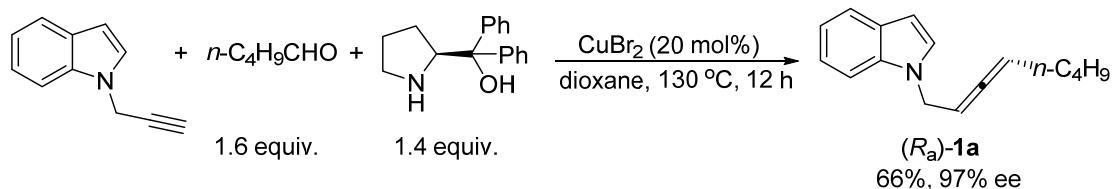
((*R,R_a*)-**1u** + (*S,S_a*)-**1u**): liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.59 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.45-7.31 (m, 3H, Ar-H), 7.28-7.17 (m, 1H, Ar-H), 7.17-6.96 (m, 4H, Ar-H), 6.25 (dd, $J_1 = 6.2$ Hz, $J_2 = 2.9$ Hz, 1H, =CH), 5.80 (t, $J = 5.9$ Hz, 1H, CH=), 5.23-5.07

(m, 1H, NCH), 3.85 (t, J = 6.5 Hz, 2H, OCH₂), 3.00 (t, J = 6.3 Hz, 2H, CH₂), 1.80-1.58 (m, 4H, CH₃ + OH); ¹³C NMR (75 MHz, CDCl₃) δ 204.6, 136.1, 132.6, 131.7, 128.2, 122.7, 121.7, 121.0, 119.2, 119.1, 111.6, 109.7, 98.3, 96.9, 62.6, 50.1, 28.7, 20.2; IR (neat) ν (cm⁻¹) 3396, 3048, 2972, 2926, 2852, 1950, 1611, 1488, 1460, 1427, 1361, 1312, 1224, 1193, 1069, 1045, 1010; MS (70 ev, EI) *m/z* (%) 383 (M⁺(⁸¹Br), 8.15), 381 (M⁺(⁷⁹Br), 7.37), 363 (100); HRMS calcd for C₂₁H₂₀NO⁷⁹Br [M⁺]: 381.0728, Found: 381.0725.

((R,S_a)-**1u** + (S,R_a)-**1u**): liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, J = 7.5 Hz, 1H, Ar-H), 7.47-7.27 (m, 3H, Ar-H), 7.27-6.98 (m, 5H, Ar-H), 6.25 (dd, J ₁ = 6.6 Hz, J ₂ = 2.1 Hz, 1H, =CH), 5.77 (t, J = 6.0 Hz, 1H, CH=), 5.28-5.08 (m, 1H, NCH), 3.84 (t, J = 6.3 Hz, 2H, OCH₂), 2.99 (t, J = 6.3 Hz, 2H, CH₂), 1.78-1.53 (m, 4H, CH₃ + OH); ¹³C NMR (75 MHz, CDCl₃) δ 204.7, 136.0, 132.4, 131.7, 128.3, 128.2, 122.7, 121.7, 121.0, 119.2, 119.1, 111.5, 109.8, 98.2, 96.8, 62.6, 50.0, 28.7, 20.1; IR (neat) ν (cm⁻¹) 3391, 3048, 2976, 2929, 1950, 1611, 1488, 1460, 1427, 1361, 1224, 1193, 1068, 1045, 1010; MS (70 ev, EI) *m/z* (%) 383 (M⁺(⁸¹Br), 14.64), 381 (M⁺(⁷⁹Br), 14.61), 212 (100); HRMS calcd for C₂₁H₂₀NO⁷⁹Br [M⁺]: 381.0728, Found: 381.0726.

4. Synthesis of optically active *N*-allenylindoles⁵

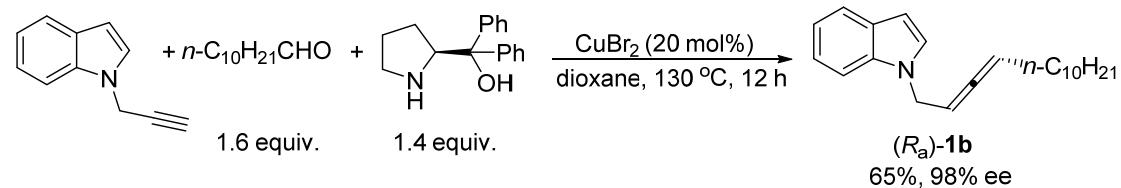
4.1 Synthesis of (R_a)-1-(octa-2,3-dienyl)-1*H*-indole (R_a)-**1a**. (jf-1-155)



Following **Typical Procedure I**, the reaction of CuBr₂ (0.6823 g, 3 mmol, 99%), (S)-α,α-diphenylprolinol (5.4215 g, 21 mmol, 98%), 1-(prop-2-ynyl)-1*H*-indole (2.3249 g, 15 mmol), pentanal (2.6 mL, d = 0.81 g/mL, 2.1060 g, 24 mmol, 98%), and dioxane (45 mL) for 12 h at 130 °C afforded (R_a)-**1a** (2.2244 g, 66%) [eluent: petroleum ether] as a liquid: 97% ee (HPLC conditions: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 200/1, 0.7 mL/min, λ = 214 nm, *t*_R (major) = 6.9 min, *t*_R (minor) = 6.5 min); [α]_D²⁰ = -38.2 (*c* = 0.945, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.62 (d, J

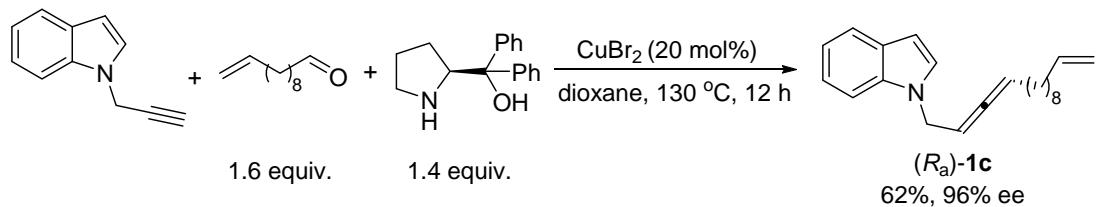
$= 7.8$ Hz, 1H, Ar-H), 7.37 (dd, $J_1 = 8.1$ Hz, $J_2 = 0.9$ Hz, 1H, Ar-H), 7.20 (td, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz, 1H, Ar-H), 7.16-7.05 (m, 2H, Ar-H), 6.49 (dd, $J_1 = 3.0$ Hz, $J_2 = 0.9$ Hz, 1H, Ar-H), 5.32-5.13 (m, 2H, CH=C=CH), 4.70 (dd, $J_1 = 6.2$ Hz, $J_2 = 2.9$ Hz, 2H, NCH₂), 2.03-1.86 (m, 2H, CH₂), 1.38-1.20 (m, 4H, CH₂ × 2), 0.87 (t, $J = 7.1$ Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.5, 136.0, 128.8, 127.5, 121.3, 120.9, 119.3, 109.7, 101.3, 93.5, 87.9, 45.9, 31.1, 28.2, 22.1, 13.8; IR (neat) ν (cm⁻¹) 3056, 2951, 2928, 2858, 1963, 1613, 1511, 1484, 1464, 1420, 1396, 1378, 1334, 1313, 1253, 1180, 1123, 1088, 1054, 1012; MS (70 ev, EI) *m/z* (%) 226 (M⁺+1, 3.48), 225 (M⁺, 20.97), 130 (100); HRMS calcd for C₁₆H₁₉N [M⁺]: 225.1517, Found: 225.1517.

4.2 Synthesis of (*R*_a)-1-(tetradeca-2,3-dienyl)-1*H*-indole (*R*_a)-1b. (jf-2-008)



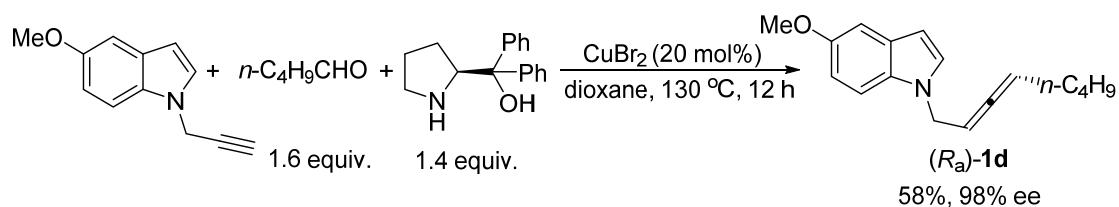
Following **Typical Procedure I**, the reaction of CuBr₂ (0.3629 g, 1.6 mmol, 99%), (S)- α,α -diphenylprolinol (2.8914 g, 11.2 mmol, 98%), 1-(prop-2-ynyl)-1*H*-indole (1.2405 g, 8 mmol), undecanal (2.1831 g, 12.8 mmol), and dioxane (24 mL) for 12 h at 130 °C afforded (*R*_a)-1b (1.6153 g, 65%) [eluent: petroleum ether /diethyl ether = 200/1] as a liquid: 98% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/i-PrOH = 200/1, 0.7 mL/min, $\lambda = 214$ nm, t_R (major) = 15.4 min, t_R (minor) = 14.8 min); $[\alpha]_D^{20} = -30.4$ (*c* = 1.355, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.61 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.34 (d, $J = 8.1$ Hz, 1H, Ar-H), 7.19 (td, $J_1 = 7.6$ Hz, $J_2 = 1.3$ Hz, 1H, Ar-H), 7.13-7.03 (m, 2H, Ar-H), 6.47 (dd, $J_1 = 3.3$ Hz, $J_2 = 0.6$ Hz, 1H, Ar-H), 5.29-5.15 (m, 2H, CH=C=CH), 4.66 (dd, $J_1 = 6.2$ Hz, $J_2 = 2.9$ Hz, 2H, NCH₂), 2.02-1.86 (m, 2H, CH₂), 1.37-1.17 (m, 16H, CH₂ × 8), 0.88 (t, $J = 6.6$ Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.4, 135.9, 128.7, 127.5, 121.3, 120.9, 119.3, 109.7, 101.2, 93.5, 87.9, 46.0, 31.9, 29.6, 29.4, 29.3, 29.1, 29.0, 28.6, 22.7, 14.1; IR (neat) ν (cm⁻¹) 3056, 2925, 2853, 1964, 1613, 1575, 1512, 1485, 1464, 1396, 1335, 1313, 1254, 1180, 1123, 1080, 1055, 1012; MS (70 ev, EI) *m/z* (%) 310 (M⁺+1, 3.52), 309 (M⁺, 14.88), 130 (100); HRMS calcd for C₂₂H₃₁N [M⁺]: 309.2457, Found: 309.2457.

4.3 Synthesis of (*R*_a)-1-(tetradeca-2,3,13-trienyl)-1*H*-indole (*R*_a)-1c. (jf-2-065)



Following **Typical Procedure I**, the reaction of CuBr₂ (0.3621 g, 1.6 mmol, 99%), (S)- α,α -diphenylprolinol (2.8918 g, 11.2 mmol, 98%), 1-(prop-2-ynyl)-1*H*-indole (1.2391 g, 8 mmol), undecenal (2.1914 g, 12.8 mmol, 98%), and dioxane (24 mL) for 12 h at 130 °C afforded (*R*_a)-1c (1.5325 g, 62%) [eluent: petroleum ether] as a liquid: 96% ee (HPLC conditions: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/1, 1.0 mL/min, λ = 214 nm, t_R (major) = 13.2 min, t_R (minor) = 13.9 min); $[\alpha]_D^{20} = -30.7$ (c = 1.75, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.62 (d, J = 7.8 Hz, 1H, Ar-H), 7.35 (d, J = 8.1 Hz, 1H, Ar-H), 7.19 (td, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H, Ar-H), 7.14-7.03 (m, 2H, Ar-H), 6.48 (d, J = 3.0 Hz, 1H, Ar-H), 5.90-5.72 (m, 1H, CH=), 5.30-5.14 (m, 2H, CH=C=CH), 5.05-4.88 (m, 2H, =CH₂), 4.68 (dd, J_1 = 6.3 Hz, J_2 = 2.7 Hz, 2H, NCH₂), 2.08-1.99 (m, 2H, CH₂), 1.99-1.87 (m, 2H, CH₂), 1.43-1.15 (m, 12H, CH₂ × 6); ¹³C NMR (75 MHz, CDCl₃) δ 204.4, 139.2, 136.0, 128.7, 127.5, 121.3, 120.9, 119.3, 114.1, 109.7, 101.2, 93.5, 87.9, 46.0, 33.8, 29.4, 29.3, 29.1, 29.01, 28.96, 28.9, 28.5; IR (neat) ν (cm⁻¹) 3058, 2975, 2925, 2853, 1965, 1640, 1613, 1512, 1485, 1464, 1396, 1335, 1313, 1253, 1180, 1012; MS (70 ev, EI) *m/z* (%) 308 (M⁺+1, 6.80), 307 (M⁺, 29.80), 130 (100); HRMS calcd for C₂₂H₂₉N [M⁺]: 307.2300, Found: 307.2301.

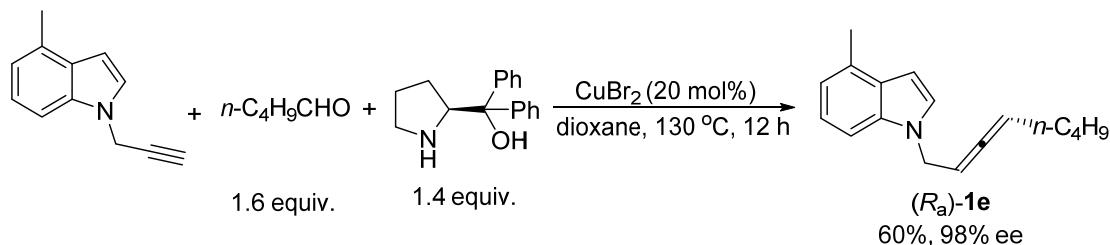
4.4 Synthesis of (*R*_a)-5-methoxy-1-(octa-2,3-dienyl)-1*H*-indole (*R*_a)-1d (jf-1-192)



Following **Typical Procedure I**, the reaction of CuBr₂ (0.2736 g, 1.2 mmol, 99%), (S)- α,α -diphenylprolinol (2.1681 g, 8.4 mmol, 98%), 5-methoxy-1-(prop-2-ynyl)-1*H*-indole (1.1107 g, 6 mmol), pentanal (1.04 mL, d = 0.81 g/mL, 0.8424 g, 9.6 mmol, 98%), and dioxane (18 mL) for 12 h at 130 °C

afforded (*R*_a)-**1d** (0.8924 g, 58%) [eluent: petroleum ether/diethyl ether = 200/1] as a liquid: 98% ee (HPLC conditions: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (major) = 23.9 min, t_R (minor) = 21.2 min); $[\alpha]_D^{20}$ = -32.4 (c = 0.995, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.24 (d, J = 8.7 Hz, 1H, Ar-H), 7.10-7.05 (m, 2H, Ar-H), 6.86 (dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz, 1H, Ar-H), 6.40 (dd, J_1 = 3.2 Hz, J_2 = 0.8 Hz, 1H, Ar-H), 5.31-5.13 (m, 2H, CH=C=CH), 4.64 (dd, J_1 = 6.2 Hz, J_2 = 2.9 Hz, 2H, NCH₂), 3.84 (s, 3H, OCH₃), 2.02-1.88 (m, 2H, CH₂), 1.36-1.22 (m, 4H, CH₂ × 2), 0.87 (t, J = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.4, 154.0, 131.3, 129.1, 128.1, 111.7, 110.4, 102.5, 100.7, 93.4, 88.0, 55.8, 46.2, 31.1, 28.2, 22.1, 13.8; IR (neat) ν (cm⁻¹) 2956, 2924, 2873, 2858, 2829, 1964, 1622, 1575, 1509, 1489, 1464, 1447, 1436, 1394, 1376, 1333, 1295, 1235, 1183, 1151, 1130, 1089, 1033; MS (70 ev, EI) m/z (%) 256 (M⁺+1, 8.24), 225 (M⁺, 47.36), 212 (100); HRMS calcd for C₁₇H₂₁NO [M⁺]: 255.1623, Found: 255.1626.

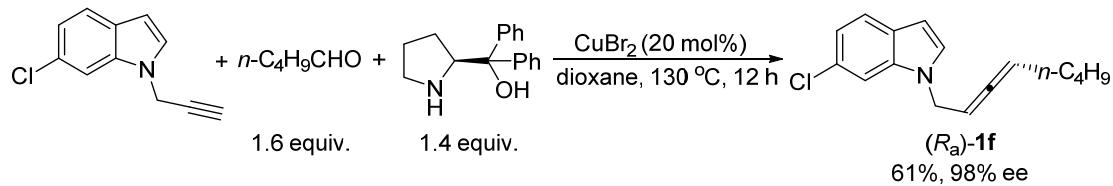
4.5 Synthesis of (*R*_a)-4-methyl-1-(octa-2,3-dienyl)-1*H*-indole (*R*_a)-**1e** (jf-2-030)



Following **Typical Procedure II**, the reaction of CuBr₂ (0.3648 g, 1.6 mmol, 99%), (S)- α,α -diphenylprolinol (2.8950 g, 11.2 mmol, 98%), 4-methyl-1-(prop-2-ynyl)-1*H*-indole (1.3546 g, 8 mmol)/dioxane (2 mL), pentanal (1.40 mL, d = 0.81 g/mL, 1.1340 g, 12.8 mmol, 98%), and dioxane (22 mL) for 12 h at 130 °C afforded (*R*_a)-**1e** (1.1896 g, 60%, 97% purity) [eluent: petroleum ether /diethyl ether = 200/1] as a liquid: 98% ee (HPLC conditions: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, 1.0 mL/min, λ = 214 nm, t_R (major) = 26.8 min, t_R (minor) = 31.9 min); $[\alpha]_D^{20}$ = -34.9 (c = 1.56, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.18 (d, J = 8.4 Hz, 1H, Ar-H), 7.11 (d, J = 6.9 Hz, 1H, Ar-H), 7.06 (d, J = 3.3 Hz, 1H, Ar-H), 6.89 (d, J = 6.9 Hz, 1H, Ar-H), 6.48 (dd, J_1 = 3.2 Hz, J_2 = 0.8 Hz, 1H, Ar-H),

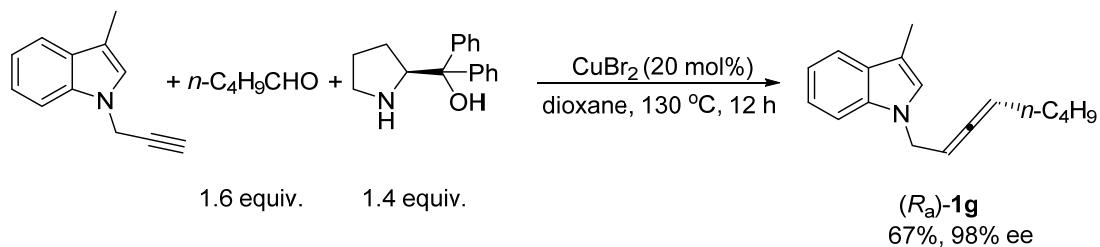
5.27-5.13 (m, 2H, CH=C=CH), 4.62 (dd, $J_1 = 6.2$ Hz, $J_2 = 2.9$ Hz, 2H, NCH₂), 2.54 (s, 3H, CH₃), 2.04-1.87 (m, 2H, CH₂), 1.37-1.20 (m, 4H, CH₂ × 2), 0.86 (t, $J = 7.1$ Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.5, 135.7, 130.3, 128.7, 126.9, 121.6, 119.6, 107.3, 99.8, 93.4, 88.0, 46.1, 31.2, 28.3, 22.1, 18.7, 13.9; IR (neat) ν (cm⁻¹) 3050, 2957, 2927, 2858, 1963, 1604, 1585, 1513, 1492, 1456, 1423, 1396, 1378, 1338, 1297, 1246, 1201, 1158, 1138, 1067, 1053; MS (70 ev, EI) *m/z* (%) 240 (M⁺+1, 10.43), 239 (M⁺, 47.67), 196 (100); HRMS calcd for C₁₇H₂₁N [M⁺]: 239.1674, Found: 239.1676.

4.6 Synthesis of (*R*_a)-6-chloro-1-(octa-2,3-dienyl)-1*H*-indole (*R*_a)-1f (jf-2-061)



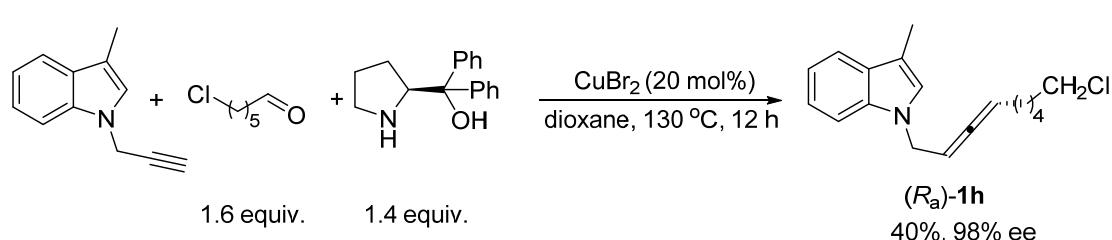
Following **Typical Procedure I**, the reaction of CuBr₂ (0.2733 g, 1.2 mmol, 99%), (S)- α,α -diphenylprolinol (2.1665 g, 8.4 mmol, 98%), 6-chloro-1-(prop-2-ynyl)-1*H*-indole (1.1355 g, 6 mmol), pentanal (1.02 mL, d = 0.81 g/mL, 0.8424 g, 9.6 mmol, 98%), and dioxane (18 mL) for 12 h at 130 °C afforded (R_a)-1f (0.9430 g, 61%) [eluent: petroleum ether] as a liquid: 98% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 20/1, 0.6 mL/min, $\lambda = 254$ nm, t_R (major) = 8.5 min, t_R (minor) = 8.1 min); $[\alpha]_D^{20} = -10.2$ (*c* = 1.065, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.50 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.40-7.31 (m, 1H, Ar-H), 7.12-7.00 (m, 2H, Ar-H), 6.44 (dd, $J_1 = 3.3$ Hz, $J_2 = 0.6$ Hz, 1H, Ar-H), 5.28-5.14 (m, 2H, CH=C=CH), 4.62 (dd, $J_1 = 5.3$ Hz, $J_2 = 3.5$ Hz, 2H, NCH₂), 2.02-1.86 (m, 2H, CH₂), 1.35-1.17 (m, 4H, CH₂ × 2), 0.86 (t, $J = 7.1$ Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.4, 136.4, 128.4, 127.4, 127.3, 121.7, 120.0, 109.9, 101.4, 93.9, 87.6, 46.0, 31.1, 28.2, 22.1, 13.8; IR (neat) ν (cm⁻¹) 2957, 2928, 2872, 2858, 1965, 1612, 1564, 1509, 1465, 1392, 1338, 1313, 1240, 1183, 1125, 1101, 1063, 1051; MS (70 ev, EI) *m/z* (%) 262 (M⁺(³⁷Cl) + 1, 1.48), 261 (M⁺(³⁷Cl), 9.06), 260 (M⁺(³⁵Cl) + 1, 6.15), 259 (M⁺(³⁵Cl), 27.19), 216 (100); HRMS calcd for C₁₆H₁₈N³⁵Cl [M⁺]: 259.1128, Found: 259.1126.

4.7 Synthesis of (*R*_a)-3-methyl-1-(octa-2,3-dienyl)-1*H*-indole (*R*_a)-1g (jf-2-081)



Following **Typical Procedure II**, the reaction of CuBr₂ (0.3646 g, 1.6 mmol, 99%), (S)- α,α -diphenylprolinol (2.8903 g, 11.2 mmol, 98%), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (1.3565 g, 8 mmol)/dioxane (2 mL), pentanal (1.39 mL, d = 0.81 g/mL, 1.1259 g, 12.8 mmol, 98%), and dioxane (22 mL) for 12 h at 130 °C afforded (*R*_a)-1g (1.2777 g, 67%) [eluent: petroleum ether] as a liquid: 98% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 100/1, 0.5 mL/min, λ = 214 nm, t_R (major) = 18.8 min, t_R (minor) = 17.5 min); $[\alpha]_D^{20} = -37.9$ (c = 1.23, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, J = 5.7 Hz, 1H, Ar-H), 7.31 (d, J = 6.0 Hz, 1H, Ar-H), 7.19 (t, J = 5.4 Hz, 1H, Ar-H), 7.09 (t, J = 5.6 Hz, 1H, Ar-H), 6.88 (s, 1H, Ar-H), 5.28-5.16 (m, 2H, CH=C=CH), 4.63 (dd, J_1 = 4.7 Hz, J_2 = 2.3 Hz, 2H, NCH₂), 2.32 (s, 3H, CH₃), 2.06-1.92 (m, 2H, CH₂), 1.36-1.22 (m, 4H, CH₂ × 2), 0.88 (t, J = 5.3 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.4, 136.3, 129.0, 125.2, 121.3, 118.9, 118.6, 110.4, 109.5, 93.3, 88.1, 45.7, 31.2, 28.3, 22.1, 13.9, 9.6; IR (neat) ν (cm⁻¹) 3055, 2956, 2928, 2859, 1964, 1614, 1558, 1482, 1466, 1386, 1363, 1329, 1255, 1179, 1126, 1104, 1041, 1013; MS (70 ev, EI) m/z (%) 240 (M⁺+1, 9.23), 239 (M⁺, 45.55), 196 (100); HRMS calcd for C₁₇H₂₁N [M⁺]: 239.1674, Found: 239.1674.

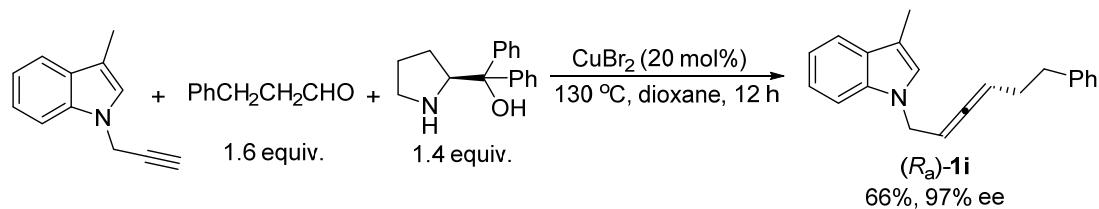
4.8 Synthesis of (*R*_a)-1-(9-chloronona-2,3-dienyl)-3-methyl-1*H*-indole (*R*_a)-1h (jf-2-140)



Following **Typical Procedure II**, the reaction of CuBr₂ (0.2728 g, 1.2 mmol, 99%), (S)- α,α -diphenylprolinol (2.1683 g, 8.4 mmol, 98%),

3-methyl-1-(prop-2-ynyl)-1*H*-indole (1.0034 g, 6 mmol)/dioxane (2 mL), 6-chlorohexanal (1.2916 g, 9.6 mmol), and dioxane (16 mL) for 12 h at 130 °C afforded (*R*_a)-**1h** (0.7006 g, 40%, 97% purity) [eluent: petroleum ether/diethyl ether = 200/1] as a liquid: 98% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 100/1, 1.0 mL/min, λ = 254 nm, t_R (major) = 14.9 min, t_R (minor) = 15.6 min); $[\alpha]_D^{20}$ = -30.3 (c = 0.92, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 7.6 Hz, 1H, Ar-H), 7.30 (d, J = 8.4 Hz, 1H, Ar-H), 7.19 (t, J = 7.6 Hz, 1H, Ar-H), 7.09 (t, J = 7.2 Hz, 1H, Ar-H), 6.87 (s, 1H, Ar-H), 5.32-5.12 (m, 2H, CH=C=CH), 4.63 (dd, J_1 = 6.4 Hz, J_2 = 2.8 Hz, 2H, NCH₂), 3.49 (t, J = 6.8 Hz, 2H, CH₂Cl), 2.32 (s, 3H, CH₃), 2.00-1.91 (m, 2H, CH₂), 1.76-1.67 (m, 2H, CH₂), 1.44-1.27 (m, 4H, CH₂ × 2); ¹³C NMR (100 MHz, CDCl₃) δ 204.4, 136.3, 128.9, 125.2, 121.3, 119.0, 118.6, 110.4, 109.4, 93.0, 88.4, 45.6, 45.0, 32.4, 28.3, 28.1, 26.2, 9.6; IR (neat) ν (cm⁻¹) 3054, 2932, 2860, 1964, 1614, 1559, 1481, 1465, 1386, 1329, 1257, 1209, 1180, 1126, 1104, 1040, 1013; MS (70 ev, EI) m/z (%) 289 (M⁺(³⁷Cl), 9.90), 287 (M⁺(³⁵Cl), 28.45), 144 (100); HRMS calcd for C₁₈H₂₂N³⁵Cl [M⁺]: 287.1441, Found: 287.1440.

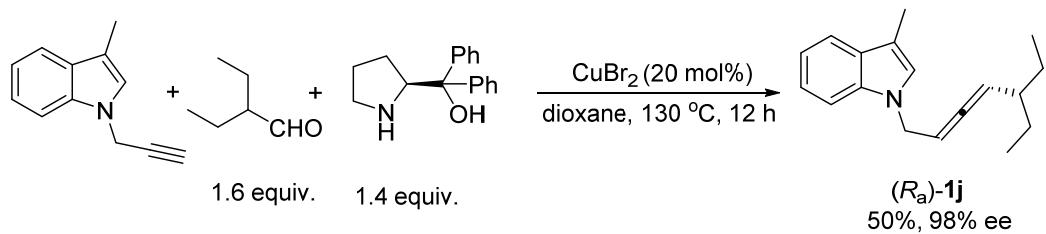
4.9 Synthesis of (*R*_a)-3-methyl-1-(6-phenylhexa-2,3-dienyl)-1*H*-indole (*R*_a)-**1i** (jf-3-018)



Following **Typical Procedure II**, the reaction of CuBr₂ (0.2727 g, 1.2 mmol, 99%), (S)- α,α -diphenylprolinol (2.1687 g, 8.4 mmol, 98%), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (1.0173 g, 6 mmol)/dioxane (2 mL), 3-phenylpropanal (1.3154 g, 9.6 mmol), and dioxane (16 mL) for 12 h at 130 °C afforded (*R*_a)-**1i** (1.1060 g, 66%) [eluent: petroleum ether/diethyl ether = 200/1] as a liquid: 97% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, λ = 254 nm, t_R (major) = 15.1 min, t_R (minor) = 13.2 min); $[\alpha]_D^{20}$ = -21.0 (c = 1.17, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, J = 7.5 Hz, 1H, Ar-H),

7.30-7.23 (m, 3H, Ar-H), 7.22-7.05 (m, 5H, Ar-H), 6.81 (s, 1H, Ar-H), 5.28-5.13 (m, 2H, CH=C=CH), 4.58-4.47 (m, 2H, NCH₂), 2.59 (t, *J* = 7.7 Hz, 2H, CH₂Ph), 2.37-2.17 (m, 5H, CH₂ + CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.4, 141.4, 136.2, 128.9, 128.5, 128.3, 125.9, 125.2, 121.3, 119.0, 118.6, 110.4, 109.4, 92.5, 88.6, 45.4, 35.2, 30.3, 9.6; IR (neat) ν (cm⁻¹) 3084, 3057, 3026, 2916, 2858, 1965, 1614, 1603, 1579, 1555, 1496, 1481, 1466, 1454, 1386, 1329, 1257, 1209, 1180, 1126, 1104, 1077, 1031, 1013; MS (70 ev, EI) *m/z* (%) 288 (M⁺+1, 2.3), 287 (M⁺, 7.3), 196 (100); HRMS calcd for C₂₁H₂₁N [M⁺]: 287.1674, Found: 287.1672.

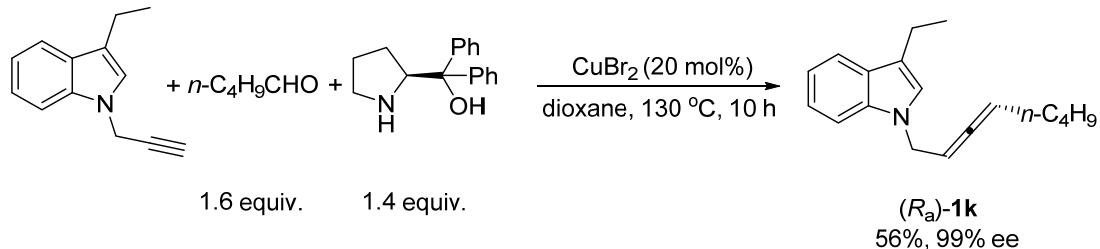
4.10 Synthesis of (*R*_a)-1-(5-ethylhepta-2,3-dienyl)-3-methyl-1*H*-indole (*R*_a)-1j (jf-3-093)



Following **Typical Procedure II**, the reaction of CuBr₂ (0.2735 g, 1.2 mmol, 99%), (S)- α,α -diphenylprolinol (2.1690 g, 8.4 mmol, 98%), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (1.0122 g, 6 mmol)/dioxane (2 mL), 2-ethylbutanal (1.2 mL, d = 0.814 g/mL, 0.9917 g, 9.6 mmol, 97%), and dioxane (16 mL) for 12 h at 130 °C afforded (*R*_a)-1j (0.7625 g, 50%) [eluent: petroleum ether] as a liquid: 98% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 200/1, 0.5 mL/min, λ = 214 nm, *t*_R (major) = 26.2 min, *t*_R (minor) = 25.1 min); [α]_D²⁰ = -40.5 (c = 1.38, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.31 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.25-7.15 (m, 1H, Ar-H), 7.12-7.05 (m, 1H, Ar-H), 6.87 (s, 1H, Ar-H), 5.28-5.20 (m, 1H, one proton of CH=C=CH), 5.08-4.97 (m, 1H, one proton of CH=C=CH), 4.63 (dd, *J*₁ = 6.5 Hz, *J*₂ = 2.6 Hz, 2H, NCH₂), 2.31 (s, 3H, Ar-CH₃), 1.91-1.76 (m, 1H, CH), 1.51-1.15 (m, 4H, CH₂ × 2), 0.84 (t, *J* = 7.4 Hz, 6H, CH₃ × 2); ¹³C NMR (75 MHz, CDCl₃) δ 204.2, 136.3, 129.0, 125.2, 121.3, 118.9, 118.6, 110.4, 109.4, 97.0, 88.1, 45.8, 42.8, 27.6, 27.3, 11.6, 11.5, 9.6; IR (neat) ν (cm⁻¹) 3055, 2961, 2920, 2873, 1963, 1614, 1561, 1482, 1466, 1385, 1329, 1256, 1208, 1179,

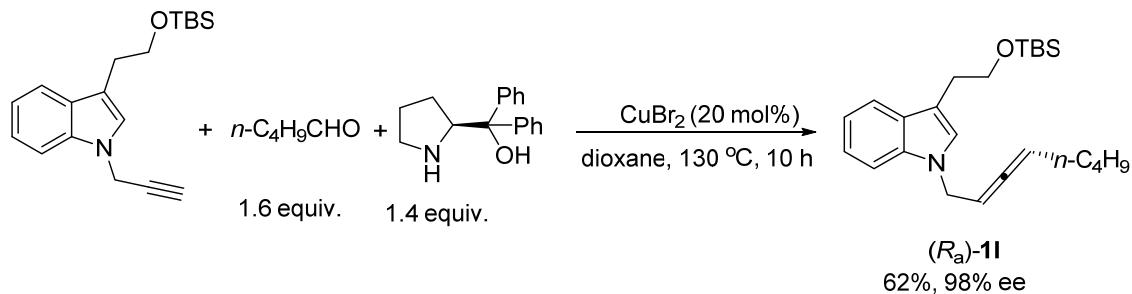
1126, 1104, 1013, 1013; MS (70 ev, EI) m/z (%) 254 (M^++1 , 3.57), 253 (M^+ , 22.43), 224 (100); HRMS calcd for $C_{18}H_{23}N$ [M^+]: 253.1830, Found: 253.1829.

4.11 Synthesis of (R_a)-3-ethyl-1-(octa-2,3-dienyl)-1*H*-indole (R_a)-**1k** (jf-3-073)



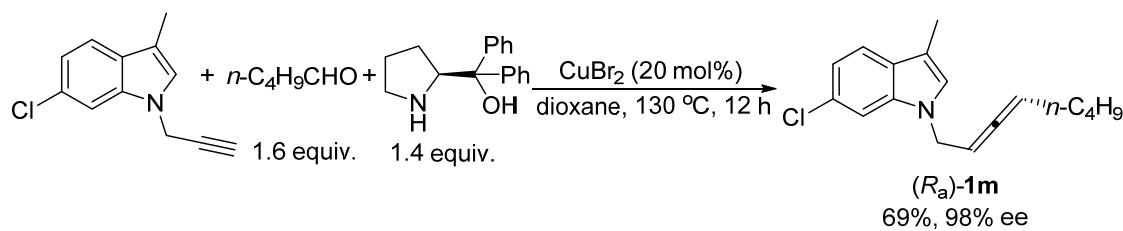
Following **Typical Procedure II**, the reaction of CuBr_2 (0.2745 g, 1.2 mmol, 99%), (*S*)- α,α -diphenylprolinol (2.1682 g, 8.4 mmol, 98%), 3-ethyl-1-(prop-2-ynyl)-1*H*-indole (1.0992 g, 6 mmol)/dioxane (2 mL), pentanal (1.04 mL, d = 0.81 g/mL, 0.8424 g, 9.6 mmol, 98%), and dioxane (16 mL) for 10 h at 130 °C afforded (R_a)-**1k** (0.8537 g, 56%) [eluent: petroleum ether/ethyl acetate = 100/1] as a liquid: 99% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 200/1, 1.0 mL/min, λ = 214 nm, t_R (major) = 12.7 min, t_R (minor) = 12.1 min); $[\alpha]_D^{20}$ = -33.5 (c = 1.26, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.59 (d, J = 7.8 Hz, 1H, Ar-H), 7.31 (d, J = 8.1 Hz, 1H, Ar-H), 7.19 (t, J = 7.7 Hz, 1H, Ar-H), 7.08 (t, J = 7.5 Hz, 1H, Ar-H), 6.88 (s, 1H, Ar-H), 5.30-5.15 (m, 2H, $\text{CH}=\text{C}=\text{CH}$), 4.63 (dd, J_1 = 6.2 Hz, J_2 = 2.9 Hz, 2H, NCH_2), 2.77 (q, J = 7.5 Hz, 2H, Ar- CH_2), 2.05-1.88 (m, 2H, CH_2), 1.39-1.21 (m, 7H, $\text{CH}_2 \times 2 + \text{CH}_3$), 0.88 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 204.4, 136.4, 128.1, 124.1, 121.3, 119.0, 118.5, 117.6, 109.6, 93.3, 88.1, 45.8, 31.2, 28.3, 22.1, 18.3, 14.6, 13.9; IR (neat) ν (cm^{-1}) 3055, 2960, 2929, 2871, 2856, 1964, 1614, 1557, 1481, 1467, 1418, 1392, 1371, 1333, 1314, 1270, 1207, 1177, 1128, 1105, 1063, 1013; MS (70 ev, EI) m/z (%) 254 (M^++1 , 10.50), 253 (M^+ , 61.79), 158 (100); HRMS calcd for $C_{18}H_{23}N$ [M^+]: 253.1830, Found: 253.1831.

4.12 Synthesis of (R_a)-3-((*tert*-butyldimethylsilyl)oxy)ethyl-1-(octa-2,3-dienyl)-1*H*-indole (R_a)-**1l** (jf-3-056)



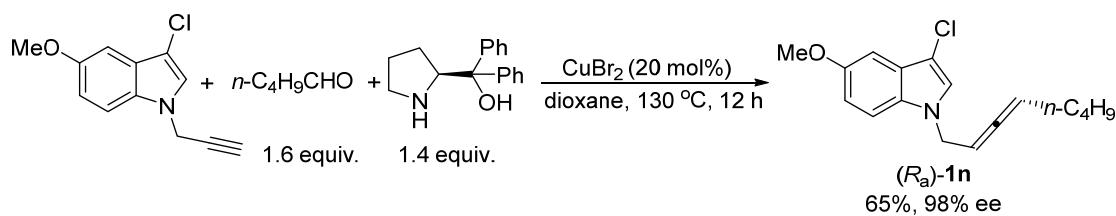
Following **Typical Procedure II**, the reaction of CuBr_2 (0.3592 g, 1.6 mmol, 99%), (*S*)- α,α -diphenylprolinol (2.8918 g, 11.2 mmol, 98%), 3-((*tert*-butyldimethylsilyl)oxy)ethyl-1-(prop-2-ynyl)-1*H*-indole (2.5108 g, 8 mmol) (2 mL), pentanal (1.4 mL, d = 0.81 g/mL, 1.1232 g, 12.8 mmol, 98%), and dioxane (22 mL) for 10 h at 130 °C afforded (*R*_a)-**1l** (1.8994 g, 62%) [eluent: petroleum ether/ethyl acetate = 100/1] as a liquid: 98% ee (HPLC conditions: Chiralcel IB-H column, *n*-hexane/*i*-PrOH = 100/0, 1.0 mL/min, λ = 214 nm, t_R (major) = 36.2 min, t_R (minor) = 32.0 min); $[\alpha]_D^{20} = -24.1$ (c = 1.09, CHCl_3); ¹H NMR (300 MHz, CDCl_3) δ 7.63 (d, J = 7.8 Hz, 1H, Ar-H), 7.36 (d, J = 8.1 Hz, 1H, Ar-H), 7.23 (td, J_1 = 7.5 Hz, J_2 = 0.6 Hz, 1H, Ar-H), 7.13 (t, J = 7.4 Hz, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 5.34-5.20 (m, 2H, $\text{CH}=\text{C}=\text{CH}$), 4.68 (dd, J_1 = 5.9 Hz, J_2 = 3.2 Hz, 2H, NCH₂), 3.90 (t, J = 7.5 Hz, 2H, CH₂), 3.02 (t, J = 7.5 Hz, 2H, CH₂), 2.10-1.91 (m, 2H, CH₂), 1.44-1.25 (m, 4H, $\text{CH}_2 \times 2$), 1.02-0.86 (m, 12H, $\text{CH}_3 + \text{CH}_3 \times 3$), 0.08 (s, 6H, $\text{CH}_3 \times 2$); ¹³C NMR (75 MHz, CDCl_3) δ 204.4, 136.2, 128.4, 125.6, 121.3, 119.0, 118.7, 111.8, 109.6, 93.3, 88.0, 64.0, 45.8, 31.2, 29.0, 28.3, 26.0, 22.1, 18.4, 13.9, -5.3; IR (neat) ν (cm⁻¹) 3056, 2928, 2856, 1965, 1615, 1555, 1469, 1386, 1360, 1332, 1255, 1215, 1174, 1093, 1053, 1013; MS (70 ev, EI) m/z (%) 384 ($\text{M}^+ + 1$, 15.85), 383 (M^+ , 51.96), 208 (100); HRMS calcd for $\text{C}_{24}\text{H}_{37}\text{NOSi} [\text{M}^+]$: 383.2644, Found: 383.2643.

4.13 Synthesis of (*R*_a)-6-chloro-3-methyl-1-(octa-2,3-dienyl)-1*H*-indole (*R*_a)-**1m** (jf-2-190)



Following **Typical Procedure II**, the reaction of CuBr_2 (0.3645 g, 1.6 mmol, 99%), (*S*)- α,α -diphenylprolinol (2.8910 g, 11.2 mmol, 98%), 6-chloro-3-methyl-1-(prop-2-ynyl)-1*H*-indole (1.6302 g, 8 mmol)/dioxane (2 mL), pentanal (1.4 mL, $d = 0.81$ g/mL, 1.134 g, 12.8 mmol, 98%), and dioxane (22 mL) for 12 h at 130 °C afforded (*R*_a)-**1m** (1.5115 g, 69%) [eluent: petroleum ether] as a liquid: 98% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 100/1, 0.5 mL/min, $\lambda = 254$ nm, t_R (major) = 13.6 min, t_R (minor) = 13.0 min); $[\alpha]_D^{20} = -15.9$ ($c = 1.27$, CHCl_3); ¹H NMR (300 MHz, CDCl_3) δ 7.43 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.29 (s, 1H, Ar-H), 7.04 (d, $J = 8.4$ Hz, 1H, Ar-H), 6.83 (s, 1H, Ar-H), 5.29-5.06 (m, 2H, $\text{CH}=\text{C}=\text{CH}$), 4.62-4.47 (m, 2H, NCH_2), 2.27 (s, 3H, CH_3), 2.04-1.86 (m, 2H, CH_2), 1.36-1.20 (m, 4H, $\text{CH}_2 \times 2$), 0.93-0.81 (m, 3H, CH_3); ¹³C NMR (75 MHz, CDCl_3) δ 204.4, 136.6, 127.6, 127.4, 126.0, 119.8, 119.2, 110.6, 109.6, 93.7, 87.7, 45.8, 31.2, 28.2, 22.1 13.9, 9.5; IR (neat) ν (cm⁻¹) 2956, 2928, 2859, 1965, 1612, 1552, 1468, 1386, 1362, 1326, 1243, 1177, 1135, 1067; MS (70 ev, EI) m/z (%) 275 ($\text{M}^+(\text{Cl})$, 24.87), 273 ($\text{M}^+(\text{Cl})$, 77.10), 272 (100); HRMS calcd for $\text{C}_{17}\text{H}_{20}\text{ClN}$ [M^+]: 273.1284, Found: 273.1283.

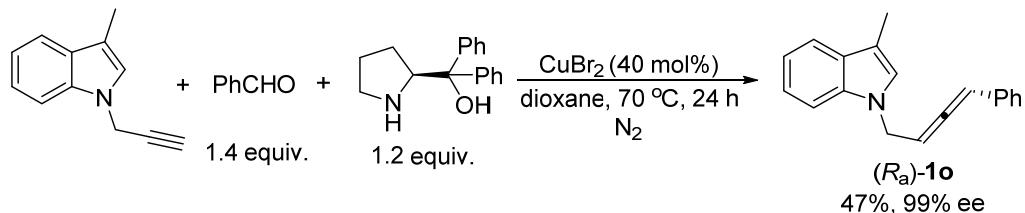
4.14 Synthesis of (*R*_a)-3-chloro-5-methoxy-1-(octa-2,3-dienyl)-1*H*-indole (*R*_a)-**1n** (jf-3-083)



Following **Typical Procedure II**, the reaction of CuBr_2 (0.2234 g, 1 mmol, 99%), (*S*)- α,α -diphenylprolinol (1.8078 g, 7 mmol, 98%), 3-chloro-5-methoxy-1-(prop-2-ynyl)-1*H*-indole (1.0985 g, 5 mmol)/dioxane (2 mL),

pentanal (0.87 mL, d = 0.81 g/mL, 0.7047 g, 8 mmol, 98%), and dioxane (13 mL) for 12 h at 130 °C afforded (*R*_a)-**1n** (0.9410 g, 65%) [eluent: petroleum ether/ethyl acetate = 100/1] as a liquid: 98% ee (HPLC conditions: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 98/2, 3.0 mL/min, λ = 214 nm, t_R (major) = 9.0 min, t_R (minor) = 8.6 min); $[\alpha]_D^{20} = -34.3$ (c = 1.165, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.22 (d, J = 9.0 Hz, 1H, Ar-H), 7.05 (s, 1H, Ar-H), 7.02 (d, J = 2.7 Hz, 1H, Ar-H), 6.89 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H, Ar-H), 5.27-5.14 (m, 2H, CH=C=CH), 4.64-4.56 (m, 2H, NCH₂), 3.87 (s, 3H, OCH₃), 2.02-1.85 (m, 2H, CH₂), 1.35-1.20 (m, 4H, CH₂ × 2), 0.87 (t, J = 6.6 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.5, 154.5, 130.3, 126.3, 124.5, 113.3, 111.0, 104.1, 99.4, 93.8, 87.6, 55.8, 46.2, 31.1, 28.2, 22.1, 13.8; IR (neat) ν (cm⁻¹) 3123, 2956, 2929, 2858, 1964, 1624, 1575, 1488, 1451, 1388, 1334, 1292, 1252, 1220, 1177, 1126, 1089, 1035; MS (70 ev, EI) m/z (%) 292 (M⁺(³⁷Cl)) + 1, 1.35), 291 (M⁺(³⁷Cl)), 6.66), 290 (M⁺(³⁵Cl)) + 1, 4.55), 289 (M⁺(³⁵Cl)), 20.64), 254 (100); HRMS calcd for C₁₇H₂₀NO³⁵Cl [M⁺]: 289.1233, Found: 289.1235.

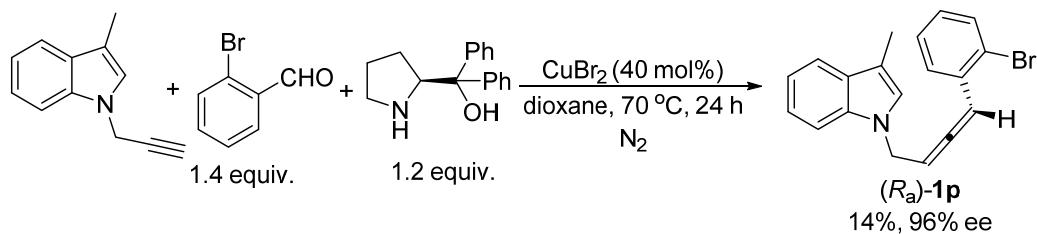
4.15 Synthesis of (*R*_a)-3-methyl-1-(4-phenylbuta-2,3-dienyl)-1*H*-indole (*R*_a)-**1o** (jf-2-153)



Following **Typical Procedure III**, the reaction of CuBr₂ (0.7280 g, 3.2 mmol, 99%), (S)- α,α -diphenylprolinol (2.4288 g, 9.6 mmol, 98%), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (1.3524 g, 8 mmol)/dioxane (2 mL), benzaldehyde (1.1872 g, 11.2 mmol), and dioxane (10 mL) for 24 h at 70 °C afforded (*R*_a)-**1o** (0.9693 g, 47%) [eluent: petroleum ether] as a liquid: 99% ee (HPLC conditions: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 99/1, 0.7 mL/min, λ = 214 nm, t_R (major) = 8.4 min, t_R (minor) = 7.7 min); $[\alpha]_D^{20} = -192.0$ (c = 0.835, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 8.0 Hz, 1H, Ar-H), 7.35-7.17 (m, 7H, Ar-H), 7.12 (t, J = 7.4 Hz, 1H, Ar-H), 6.92 (s, 1H, Ar-H), 6.28 (dt, J_1 = 6.1 Hz, J_2 =

2.6 Hz, 1H, CH=), 5.70 (q, J = 6.7 Hz, 1H, CH=), 4.77 (dd, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 2H, NCH₂), 2.32 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 205.7, 136.2, 133.5, 129.1, 128.6, 127.3, 127.0, 125.1, 121.6, 119.1, 118.8, 110.9, 109.5, 96.4, 92.2, 45.3, 9.6; IR (neat) ν (cm⁻¹) 3054, 3030, 2916, 2860, 1950, 1614, 1595, 1557, 1495, 1481, 1464, 1386, 1328, 1265, 1178, 1126, 1102, 1071, 1040, 1012; MS (70 ev, EI) *m/z* (%) 260 (M⁺+1, 10.67), 259 (M⁺, 54.40), 144 (100); HRMS calcd for C₁₉H₁₇N [M⁺]: 259.1361, Found: 259.1359.

4.16 Synthesis of (*R*_a)-1-(4-(2-bromophenyl)buta-2,3-dienyl)-3-methyl-1*H*-indole (*R*_a)-1p (jf-2-169)

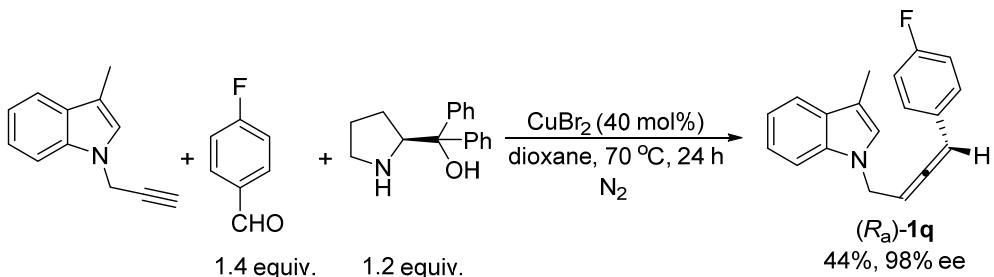


Following **Typical Procedure III**, the reaction of CuBr₂ (0.7280 g, 3.2 mmol, 99%), (S)- α,α -diphenylprolinol (2.4290 g, 9.6 mmol, 98%), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (1.3523 g, 8 mmol)/dioxane (2 mL), 2-bromobenzaldehyde (2.1842 g, 11.2 mmol, 95%), and dioxane (10 mL) for 24 h at 70 °C afforded (*R*_a)-1p (0.3916 g, 14%) [eluent: petroleum ether] as a liquid: 96% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, λ = 254 nm, t_R (major) = 21.0 min, t_R (minor) = 20.0 min); $[\alpha]_D^{20}$ = -101.4 (c = 0.93, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.57 (d, J = 7.8 Hz, 1H, Ar-H), 7.51 (d, J = 8.1 Hz, 1H, Ar-H), 7.34-7.25 (m, 2H, Ar-H), 7.22-7.08 (m, 3H, Ar-H), 7.07-6.98 (m, 1H, Ar-H), 6.89 (s, 1H, Ar-H), 6.74 (dt, J_1 = 6.6 Hz, J_2 = 2.4 Hz, 1H, ArCH=), 5.71 (q, J = 6.7 Hz, 1H, CH=), 4.76 (dd, J_1 = 6.9 Hz, J_2 = 2.4 Hz, 2H, NCH₂), 2.32 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 206.5, 136.2, 133.0, 132.9, 129.1, 128.65, 128.56, 127.4, 125.1, 122.6, 121.6, 119.1, 118.9, 111.1, 109.4, 95.5, 92.4, 45.1, 9.6; IR (neat) ν (cm⁻¹) 3054, 2915, 2884, 2859, 1951, 1614, 1587, 1561, 1465, 1439, 1401 1385, 1363, 1328, 1287, 1260, 1178, 1123, 1022; MS (70 ev, EI) *m/z* (%) 339 (M⁺(⁸¹Br)), 28.78), 337 (M⁺(⁷⁹Br), 29.02), 168 (100); HRMS calcd for C₁₉H₁₆N⁷⁹Br [M⁺]:

337.0466, Found: 337.0466.

4.17 Synthesis of (*R*_a)-1-(4-(4-fluorophenyl)buta-2,3-dienyl)-3-methyl-1*H*-indole

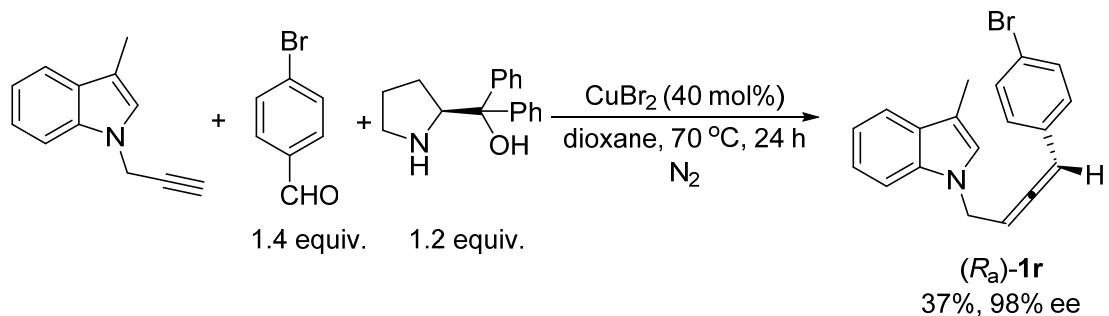
(*R*_a)-1q (jf-3-031)



Following **Typical Procedure III**, the reaction of CuBr₂ (0.5436 g, 2.4 mmol, 99%), (*S*)- α,α -diphenylprolinol (1.8543 g, 7.2 mmol, 98%), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (1.0105 g, 6 mmol)/dioxane (2 mL), 4-fluorobenzaldehyde (1.0429 g, 8.4 mmol, 99%), and dioxane (7 mL) for 24 h at 70 °C afforded (*R*_a)-1q (0.7275 g, 44%) [eluent: petroleum ether/ethyl acetate = 200/1] as a liquid: 98% ee (HPLC conditions: Chiralcel IA-H column, *n*-hexane/*i*-PrOH = 100/1, 0.5 mL/min, λ = 254 nm, t_R (major) = 11.4 min, t_R (minor) = 11.0 min); $[\alpha]_D^{20}$ = -174.4 (*c* = 1.3, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.57 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.30 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.24-7.08 (m, 4H, Ar-H), 6.97 (t, *J* = 8.7 Hz, 2H, Ar-H), 6.90 (s, 1H, Ar-H), 6.24 (dt, *J*₁ = 6.3 Hz, *J*₂ = 2.6 Hz, 1H, CH=), 5.69 (q, *J* = 6.6 Hz, 1H, CH=), 4.76 (dd, *J*₁ = 6.6 Hz, *J*₂ = 2.4 Hz, 2H, NCH₂), 2.32 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 205.4 (d, *J* = 2.0 Hz), 162.0 (d, *J* = 244.7 Hz), 136.2, 129.4 (d, *J* = 3.5 Hz), 129.1, 128.4 (d, *J* = 8.3 Hz), 125.1, 121.6, 119.1, 118.8, 115.5 (d, *J* = 21.4 Hz), 111.0, 109.4, 95.5, 92.4, 45.3, 9.6; ¹⁹F NMR (282 MHz, CDCl₃) δ -115.2; IR (neat) ν (cm⁻¹) 3048, 2917, 2887, 2861, 1950, 1886, 1680, 1604, 1505, 1481, 1464, 1386, 1328, 1299, 1264, 1226, 1178, 1156, 1126, 1092, 1041, 1013; MS (70 ev, EI) *m/z* (%) 278 (M⁺+1, 17.45), 277 (M⁺, 91.01), 144 (100); HRMS calcd for C₁₉H₁₆NF [M⁺]: 277.1267, Found: 277.1267.

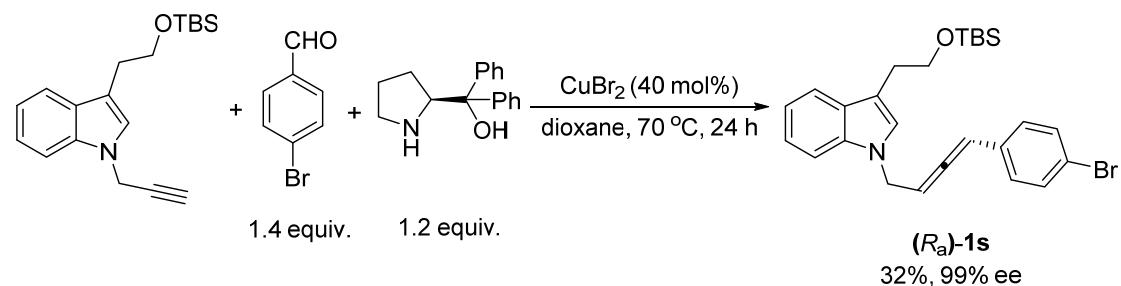
4.18 Synthesis of (*R*_a)-1-(4-(4-bromophenyl)buta-2,3-dienyl)-3-methyl-1*H*-indole

(*R*_a)-1r (jf-3-016)



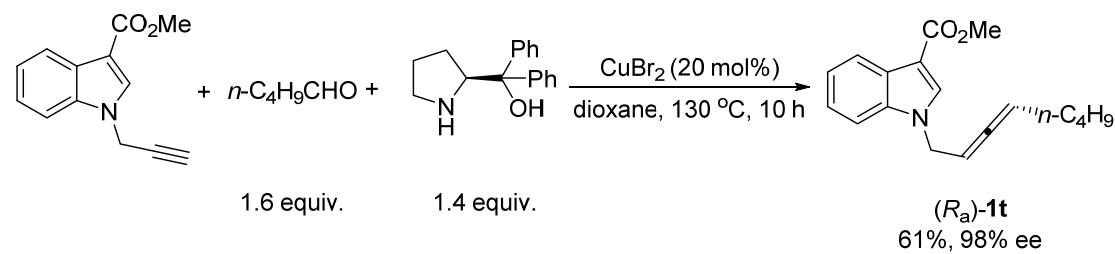
Following **Typical Procedure III**, the reaction of CuBr₂ (0.5472 g, 2.4 mmol, 99%), (S)-*α,α*-diphenylprolinol (1.8591 g, 7.2 mmol, 98%), 3-methyl-1-(prop-2-ynyl)-1*H*-indole (1.0145 g, 6 mmol)/dioxane (2 mL), 4-bromobenzaldehyde (1.5543 g, 8.4 mmol, 99%), and dioxane (7 mL) for 24 h at 70 °C afforded (R_a)-1r (0.7435 g, 37%) [eluent: petroleum ether (800 mL) to petroleum ether/diethyl ether = 200/1 (800 mL)] as a liquid: 98% ee (HPLC conditions: Chiralcel IA-H column, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 214 nm, t_R (major) = 6.9 min, t_R (minor) = 6.6 min); $[\alpha]_D^{20}$ = -153.7 (*c* = 1.065, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.53 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.31 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.25-7.05 (m, 3H, Ar-H), 6.96 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.77 (s, 1H, Ar-H), 6.13-6.04 (m, 1H, CH=), 5.58 (q, *J* = 6.5 Hz, 1H, CH=), 4.61 (dd, *J*₁ = 6.9 Hz, *J*₂ = 2.4 Hz, 2H, NCH₂), 2.28 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 205.5, 136.1, 132.4, 131.6, 129.0, 128.4, 125.0, 121.5, 120.8, 119.0, 118.8, 110.9, 109.3, 95.6, 92.5, 44.9, 9.5; IR (neat) ν (cm⁻¹) 3046, 2915, 2885, 2859, 1951, 1614, 1586, 1559, 1487, 1464, 1386, 1363, 1328, 1262, 1177, 1126, 1095, 1069, 1042, 1010; MS (70 ev, EI) *m/z* (%) 339 (M⁺(⁸¹Br), 21.61), 337 (M⁺(⁷⁹Br), 20.59), 168 (100); HRMS calcd for C₁₉H₁₆N⁷⁹Br [M⁺]: 337.0466, Found: 337.0468.

4.19 Synthesis of (R_a)-1-(4-(4-bromophenyl)buta-2,3-dienyl)-3-(2-((tert-butyldimethylsilyl)oxy)ethyl)-1*H*-indole (R_a)-1s (jf-3-086)



Following **Typical Procedure III**, the reaction of CuBr₂ (1.0820 g, 4.8 mmol, 99%), (S)- α,α -diphenylprolinol (3.7166 g, 14.4 mmol, 98%), 3-((tert-butyldimethylsilyl)oxy)ethyl-1-(prop-2-ynyl)-1*H*-indole (3.7652 g, 12 mmol)/dioxane (2 mL), 4-bromobenzaldehyde (3.1388 g, 16.8 mmol, 99%), and dioxane (16 mL) for 24 h at 70 °C afforded (*R*_a)-**1s** (1.8278 g, 32%) [eluent: petroleum ether/diethyl ether = 50/1] as a liquid: 99% ee (HPLC conditions: Chiralcel IA-H column, *n*-hexane/*i*-PrOH = 200/1, 0.7 mL/min, λ = 254 nm, t_R (major) = 9.5 min, t_R (minor) = 9.0 min); $[\alpha]_D^{20}$ = -111.3 (*c* = 0.87, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.62 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.42 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.32 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.22 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.18-7.05 (m, 3H, Ar-H), 6.99 (s, 1H, Ar-H), 6.29-6.16 (m, 1H, =CH), 5.73 (q, *J* = 6.6 Hz, 1H, CH=), 4.80 (dd, *J*₁ = 6.8 Hz, *J*₂ = 2.6 Hz, 2H, NCH₂), 3.86 (t, *J* = 7.4 Hz, 2H, CH₂), 3.00 (t, *J* = 7.4 Hz, 2H, CH₂), 0.93 (m, 9H, CH₃ × 3), 0.06 (s, 6H, CH₃ × 2); ¹³C NMR (75 MHz, CDCl₃) δ 205.7, 136.0, 132.4, 131.7, 128.52, 128.46, 125.5, 121.6, 121.0, 119.2, 119.0, 112.4, 109.5, 95.8, 92.6, 63.9, 45.1, 28.9, 26.0, 18.4, -5.3; IR (neat) ν (cm⁻¹) 3055, 2953, 2927, 2856, 1952, 1613, 1583, 1488, 1465, 1387, 1360, 1332, 1254, 1174, 1094, 1010; MS (70 ev, EI) *m/z* (%) 484 (M⁺(⁸¹Br) + 1, 5.26), 483 (M⁺(⁸¹Br), 10.68), 482 (M⁺(⁷⁹Br) + 1, 3.84), 481 (M⁺(⁷⁹Br), 16.21), 167 (100); HRMS calcd for C₂₆H₃₂⁷⁹BrNOSi [M⁺]: 481.1437, Found: 481.1435.

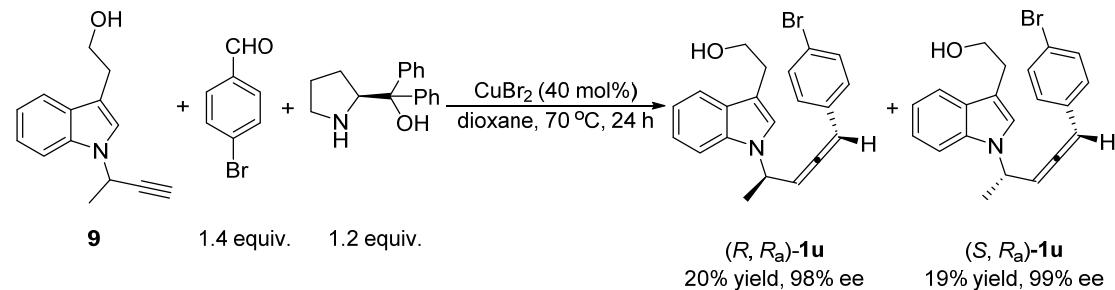
4.20 Synthesis of methyl (*R*_a)-1-(octa-2,3-dienyl)-1*H*-indole-3-carboxylate (*R*_a)-**1t** (jf-3-111)



Following **Typical Procedure II**, the reaction of CuBr₂ (0.2725 g, 1.2 mmol, 99%), (S)- α,α -diphenylprolinol (2.1681 g, 8.4 mmol, 98%), methyl

1-(prop-2-ynyl)-1*H*-indole-3-carboxylate (1.2782 g, 6 mmol)/dioxane (2 mL), pentanal (1.04 mL, d = 0.81 g/mL, 0.8424 g, 9.6 mmol, 98%), and dioxane (16 mL) for 10 h at 130 °C afforded (*R_a*)-**1t** (1.0435 g, 61%) [eluent: petroleum ether/ ethyl acetate = 15/1] as a liquid: 98% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, λ = 214 nm, t_R (major) = 25.6 min, t_R (minor) = 26.7 min); $[\alpha]_D^{20} = -45.3$ (c = 1.19, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 8.22-8.13 (m, 1H, Ar-H), 7.84 (s, 1H, Ar-H), 7.41-7.31 (m, 1H, Ar-H), 7.31-7.22 (m, 2H, Ar-H), 5.32-5.17 (m, 2H, CH=C=CH), 4.69 (dd, J_1 = 6.2 Hz, J_2 = 2.9 Hz, 2H, NCH₂), 3.90 (s, 3H, OCH₃), 2.00-1.82 (m, 2H, CH₂), 1.34-1.13 (m, 4H, CH₂ × 2), 0.85 (t, J = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 204.7, 165.4, 136.5, 134.1, 126.8, 122.6, 121.8, 121.7, 110.2, 107.1, 94.2, 87.0, 50.9, 46.4, 31.0, 28.1, 22.0, 13.8; IR (neat) ν (cm⁻¹) 3120, 3054, 2951, 2928, 2856, 1965, 1698, 1615, 1533, 1487, 1465, 1380, 1339, 1266, 1237, 1177, 1121, 1090, 1031; MS (70 ev, EI) *m/z* (%) 284 (M⁺+1, 10.12), 283 (M⁺, 49.94), 224 (100); HRMS calcd for C₁₈H₂₁NO₂ [M⁺]: 283.1572, Found: 283.1573.

4.21 Synthesis of (*R, R_a*)-2-((5-(4-bromophenyl)penta-3,4-dien-2-yl)-1*H*-indol-3-yl)ethanol (*R, R_a*)-**1u** and (*S, R_a*)-2-((5-(4-bromophenyl)penta-3,4-dien-2-yl)-1*H*-indol-3-yl)ethanol (*S, R_a*)-**1u** (jf-5-117)



Following **Typical Procedure III**, the reaction of CuBr₂ (0.6300 g, 2.8 mmol, 99%), (*S*)- α,α -diphenylprolinol (2.1657 g, 8.4 mmol, 98%), **9** (1.4754 g, 7 mmol)/dioxane (2 mL), 4-bromobenzaldehyde (1.8330 g, 9.8 mmol, 99%), and dioxane (8.5 mL) for 24 h at 70 °C afforded (*R, R_a*)-**1u** (0.5117 g), (*S, R_a*)-**1u** (0.2574 g), mixture of [(*R, R_a*)-**1u** and (*S, R_a*)-**1u**] (0.2675 g) [eluent: petroleum ether/ ethyl acetate = 8/1 (450 mL) to 6/1 (500 mL) to 5/1 (500 mL)], then the mixture was purified by column

chromatography on silica gel again to afford (*R, R_a*)-**1u** (0.0210 g) and (*S, R_a*)-**1u** (0.2408 g) [eluent: petroleum ether/ ethyl acetate = 8/1 (500 mL) to 5/1 (500 mL)]

(*R, R_a*)-**1u** (0.5327 g, 20%) as a liquid: 98% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t_R (major) = 17.6 min, t_R (minor) = 21.1 min); $[\alpha]_D^{20} = -32.4$ (c = 0.875, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, J = 7.8 Hz, 1H, Ar-H), 7.46-7.35 (m, 3H, Ar-H), 7.27-7.18 (m, 1H, Ar-H), 7.16-7.03 (m, 4H, Ar-H), 6.27 (dd, J_1 = 6.5 Hz, J_2 = 2.9 Hz, 1H, =CH), 5.81 (t, J = 6.2 Hz, 1H, CH=), 5.27-5.10 (m, 1H, NCH), 3.87 (t, J = 6.3 Hz, 2H, OCH₂), 3.02 (t, J = 6.5 Hz, 2H, CH₂), 1.68 (d, J = 6.9 Hz, 3H, CH₃), 1.57 (s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 204.6, 136.2, 132.6, 131.8, 128.3, 122.7, 121.8, 121.0, 119.3, 119.1, 111.6, 109.8, 98.4, 97.0, 62.6, 50.1, 28.8, 20.3; IR (neat) ν (cm⁻¹) 3391, 3048, 2976, 2930, 1950, 1611, 1488, 1461, 1427, 1360, 1312, 1224, 1194, 1069, 1045, 1010; MS (70 ev, EI) *m/z* (%) 383 (M⁺(⁸¹Br), 7.30), 381 (M⁺(⁷⁹Br), 5.85), 363 (100); HRMS calcd for C₂₁H₂₀NO⁷⁹Br [M⁺]: 381.0728, Found: 381.0728.

(*S, R_a*)-**1u** (0.4982 g, 19%) as a liquid: 99% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t_R (major) = 35.9 min, t_R (minor) = 18.2 min); $[\alpha]_D^{20} = -275.8$ (c = 1.030, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.61 (d, J = 7.8 Hz, 1H, Ar-H), 7.46-7.29 (m, 3H, Ar-H), 7.26-7.00 (m, 5H, Ar-H), 6.27 (dd, J_1 = 6.5 Hz, J_2 = 2.6 Hz, 1H, =CH), 5.79 (t, J = 6.0 Hz, 1H, CH=), 5.30-5.10 (m, 1H, NCH), 3.96-3.77 (m, 2H, OCH₂), 3.01 (t, J = 6.5 Hz, 2H, CH₂), 1.67 (d, J = 6.6 Hz, 3H, CH₃), 1.51 (s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 204.8, 136.1, 132.4, 131.8, 128.4, 128.3, 122.8, 121.8, 121.0, 119.3, 119.1, 111.6, 109.8, 98.2, 96.8, 62.6, 50.1, 28.8, 20.1; IR (neat) ν (cm⁻¹) 3391, 3048, 2976, 2929, 1950, 1611, 1488, 1460, 1427, 1361, 1224, 1193, 1068, 1045, 1010; MS (70 ev, EI) *m/z* (%) 383 (M⁺(⁸¹Br), 13.20), 381 (M⁺(⁷⁹Br), 13.20), 212 (100); HRMS calcd for C₂₁H₂₀NO⁷⁹Br [M⁺]: 381.0728, Found: 381.0729.

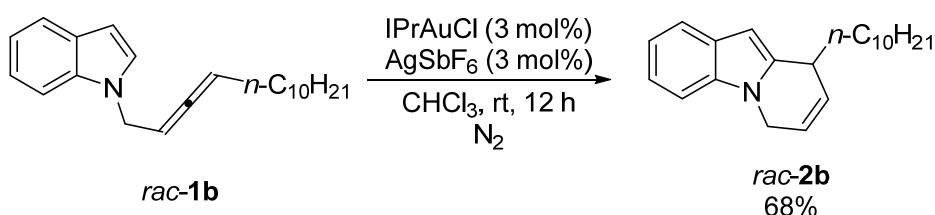
5. Gold(I) catalyzed cyclization of racemic *N*-allenylindoles

5.1 Synthesis of 9-butyl-6,9-dihdropyrido[1,2-*a*]indole *rac*-**2a** (jf-2-026)



Typical Procedure IV: To an oven-dried Schlenk tube were added IPrAuCl (0.0197 g, weighed in a glove box, 0.03 mmol, 95%), AgSbF₆ (0.0105 g, weighed in a glove box, 0.03 mmol, 98%), *rac*-**1a** (0.2554 g, 1 mmol), and CHCl₃ (5 mL) under nitrogen atmosphere sequentially. The reaction was complete after being stirred at room temperature for 12 h as monitored by TLC. After filtration through a short column of silica gel (3 cm × 2 cm) [eluent: DCM (8 mL × 4)] and evaporation, the crude product was purified by column chromatography on silica gel to afford *rac*-**2a** (0.1600 g, 71%) [eluent: petroleum ether] as a powder solid: m.p. 39.2-42.9 °C (without recrystallization); ¹H NMR (300 MHz, CDCl₃) δ 7.62-7.55 (m, 1H, Ar-H), 7.30 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.22-7.08 (m, 2H, Ar-H), 6.35-6.25 (m, 1H, Ar-H), 6.09-5.94 (m, 2H, =CH × 2), 4.63-4.52 (m, 2H, NCH₂), 3.79-3.66 (m, 1H, CH), 1.87-1.70 (m, 2H, CH₂), 1.43-1.17 (m, 4H, CH₂ × 2), 0.94-0.79 (m, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 138.5, 135.5, 128.3, 127.6, 120.2, 120.1, 119.8, 108.8, 96.8, 41.8, 36.4, 34.2, 28.0, 22.8, 14.0; IR (KBr) ν (cm⁻¹) 3043, 2956, 2929, 2858, 1667, 1541, 1472, 1456, 1420, 1362, 1329, 1315, 1225, 1184, 1169, 1014; MS (70 ev, EI) *m/z* (%) 226 (M⁺+1, 9.74), 225 (M⁺, 46.55), 168 (100); HRMS calcd for C₁₆H₁₉N [M⁺]: 225.1517, Found: 225.1519.

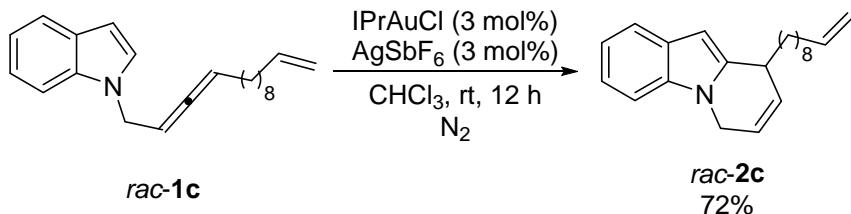
5.2 Synthesis of 9-decyl-6,9-dihydropyrido[1,2-*a*]indole *rac*-**2b** (jf-2-012)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0195 g, 0.03 mmol, 95%), AgSbF₆ (0.0106 g, 0.03 mmol, 98%), *rac*-**1b** (0.3099 g, 1 mmol), and CHCl₃ (5 mL) for 12 h at room temperature afforded *rac*-**2b** (0.2116 g, 68%) [eluent: petroleum

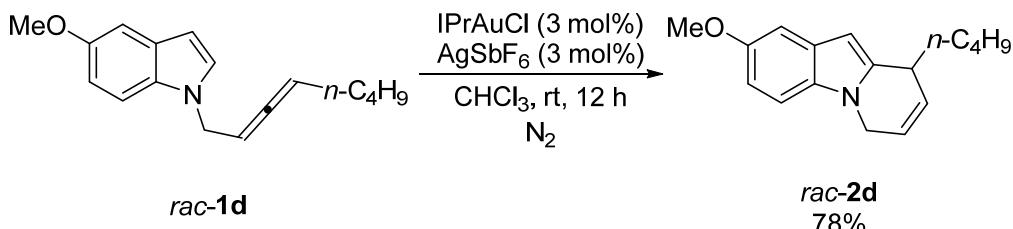
ether/diethyl ether = 100/1] as a liquid: ^1H NMR (300 MHz, CDCl_3) δ 7.59 (d, J = 7.2 Hz, 1H, Ar-H), 7.29 (d, J = 7.8 Hz, 1H, Ar-H), 7.21-7.07 (m, 2H, Ar-H), 6.32 (s, 1H, Ar-H), 6.10-5.92 (m, 2H, =CH \times 2), 4.67-4.52 (m, 2H, NCH_2), 3.78-3.65 (m, 1H, CH), 1.88-1.70 (m, 2H, CH_2), 1.44-1.15 (m, 16H, $\text{CH}_2 \times 8$), 0.88 (t, J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 138.5, 135.5, 128.3, 127.6, 120.2, 120.1, 119.8, 108.8, 96.8, 41.8, 36.7, 34.3, 31.9, 29.8, 29.6, 29.58, 29.53, 29.3, 25.8, 22.7, 14.1; IR (neat) ν (cm^{-1}) 3042, 2924, 2854, 1667, 1541, 1471, 1456, 1421, 1362, 1315, 1227, 1185, 1170, 1012; MS (70 ev, EI) m/z (%) 310 (M^+ +1, 8.77), 309 (M^+ , 38.48), 168 (100); HRMS calcd for $\text{C}_{22}\text{H}_{31}\text{N}$ [M^+]: 309.2457, Found: 309.2458.

5.3 Synthesis of 9-(dec-9-enyl)-6,9-dihydropyrido[1,2-*a*]indole *rac*-2c (jf-2-037)



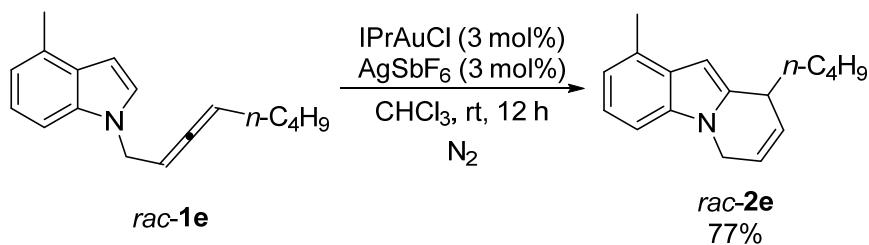
Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0195 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), *rac*-1c (0.3101 g, 1 mmol), and CHCl₃ (5 mL) for 12 h at room temperature afforded *rac*-2c (0.2385 g, 72%, 93% purity) [eluent: petroleum ether] as a liquid: ^1H NMR (300 MHz, CDCl_3) δ 7.57 (d, J = 6.6 Hz, 1H, Ar-H), 7.24 (d, J = 7.8 Hz, 1H, Ar-H), 7.18-7.05 (m, 2H, Ar-H), 6.29 (s, 1H, ArH), 6.02-5.88 (m, 2H, =CH \times 2), 5.86-5.70 (m, 1H, CH=), 5.03-4.87 (m, 2H, =CH₂), 4.56-4.46 (m, 2H, NCH_2), 3.74-3.58 (m, 1H, CH), 2.07-1.95 (m, 2H, CH_2), 1.81-1.69 (m, 2H, CH_2), 1.40-1.19 (m, 12H, $\text{CH}_2 \times 6$); ^{13}C NMR (75 MHz, CDCl_3) δ 139.1, 138.3, 135.4, 128.3, 127.5, 120.2, 120.1, 119.7, 114.1, 108.7, 96.8, 41.7, 36.6, 34.2, 33.7, 29.7, 29.43, 29.41, 29.0, 28.8, 25.8; IR (neat) ν (cm^{-1}) 3044, 2926, 2854, 1668, 1640, 1612, 1539, 1471, 1456, 1418, 1362, 1316, 1227, 1185, 1170, 1151; MS (70 ev, EI) m/z (%) 308 (M^+ +1, 7.47), 307 (M^+ , 32.57), 168 (100); HRMS calcd for $\text{C}_{22}\text{H}_{29}\text{N}$ [M^+]: 307.2300, Found: 307.2398.

5.4 Synthesis of 9-butyl-2-methoxy-6,9-dihydropyrido[1,2-*a*]indole *rac*-2d (jf-2-004)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0105 g, 0.03 mmol, 98%), *rac*-**1d** (0.2526 g, 1 mmol), and CHCl₃ (5 mL) for 12 h at room temperature afforded *rac*-**2d** (0.1971 g, 78%) [eluent: petroleum ether/diethyl ether = 100/1 to 50/1] as a powder solid: m.p. 82.1-84.5 °C (without recrystallization); ¹H NMR (300 MHz, CDCl₃) δ 7.16 (d, *J* = 9.0 Hz, 1H, Ar-H), 7.06 (d, *J* = 2.1 Hz, 1H, Ar-H), 6.82 (dd, *J*₁ = 8.7 Hz, *J*₂ = 2.4 Hz, 1H, Ar-H), 6.24 (s, 1H, Ar-H), 6.06-5.91 (m, 2H, =CH × 2), 4.59-4.46 (m, 2H, NCH₂), 3.85 (s, 3H, OCH₃), 3.74-3.62 (m, 1H, CH), 1.85-1.70 (m, 2H, CH₂), 1.40-1.16 (m, 4H, CH₂ × 2), 0.86 (t, *J* = 6.9 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 154.3, 139.1, 130.8, 128.6, 127.4, 120.1, 110.1, 109.4, 101.9, 96.4, 55.9, 41.8, 36.3, 34.3, 27.9, 22.8, 14.0; IR (KBr) ν (cm⁻¹) 2957, 2925, 2857, 1617, 1483, 1450, 1425, 1367, 1349, 1333, 1320, 1280, 1237, 1210, 1185, 1166, 1138, 1122, 1032; MS (70 ev, EI) *m/z* (%) 256 (M⁺+1, 5.20), 255 (M⁺, 30.22), 198 (100); HRMS calcd for C₁₇H₂₁NO [M⁺]: 255.1623, Found: 255.1621.

5.5 Synthesis of 9-butyl-1-methyl-6,9-dihydropyrido[1,2-*a*]indole *rac*-**2e** (**jf-2-045**)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0194 g, 0.03 mmol, 95%), AgSbF₆ (0.0106 g, 0.03 mmol, 98%), *rac*-**1e** (0.2368 g, 1 mmol), and CHCl₃ (5 mL) for 12 h at room temperature afforded *rac*-**2e** (0.1900 g, 77%, 96% purity) [eluent: petroleum ether] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.18-7.03 (m, 2H, Ar-H), 6.92 (d, *J* = 6.9 Hz, 1H, Ar-H), 6.32 (s, 1H, Ar-H), 6.12-5.92 (m, 2H, =CH × 2), 4.66-4.52 (m, 2H, NCH₂), 3.80-3.64 (m, 1H, CH), 2.55 (s, 3H, CH₃), 1.88-1.72

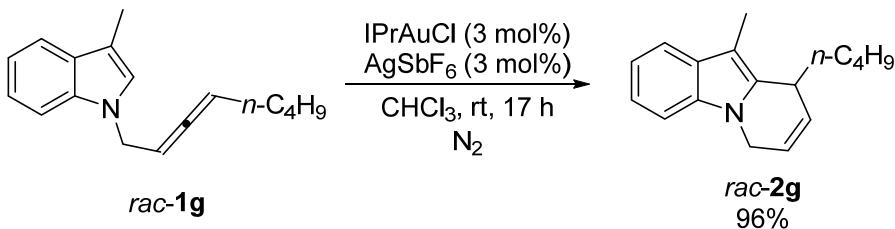
(m, 2H, CH₂), 1.42-1.18 (m, 4H, CH₂ × 2), 0.87 (t, *J* = 6.9 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 137.9, 135.1, 129.2, 128.1, 127.6, 120.4, 120.2, 120.0, 106.4, 95.3, 41.9, 36.5, 34.3, 28.0, 22.8, 18.7, 14.0; IR (neat) ν (cm⁻¹) 3044, 2956, 2929, 2858, 1668, 1585, 1538, 1495, 1456, 1429, 1362, 1319, 1240, 1174, 1155, 1101, 1079, 1032; MS (70 ev, EI) *m/z* (%) 240 (M⁺+1, 6.58), 239 (M⁺, 30.01), 182 (100); HRMS calcd for C₁₇H₂₁N [M⁺]: 239.1674, Found: 239.1673.

5.6 Synthesis of 9-butyl-3-chloro-6,9-dihydropyrido[1,2-*a*]indole *rac*-2f (jf-2-107)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), *rac*-1f (0.2604 g, 1 mmol), and CHCl₃ (5 mL) for 12 h at room temperature afforded *rac*-2f (0.2252 g, 84%, 98% purity) [eluent: petroleum ether] as a powder solid: m.p. 53.4-55.4 °C (without recrystallization); ¹H NMR (300 MHz, CDCl₃) δ 7.45 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.24 (s, 1H, Ar-H), 7.06 (dd, *J*₁ = 8.3 Hz, *J*₂ = 2.0 Hz, 1H, Ar-H), 6.26 (s, 1H, Ar-H), 6.03-5.87 (m, 2H, =CH × 2), 4.55-4.40 (m, 2H, NCH₂), 3.75-3.57 (m, 1H, CH), 1.76 (q, *J* = 7.0 Hz, 2H, CH₂), 1.40-1.12 (m, 4H, CH₂ × 2), 0.85 (t, *J* = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 139.2, 135.8, 127.4, 126.7, 126.1, 120.5, 120.2, 119.8, 108.8, 96.9, 41.8, 36.2, 34.1, 27.9, 22.8, 14.0; IR (KBr) ν (cm⁻¹) 3041, 2956, 2931, 2858, 1667, 1607, 1569, 1540, 1475, 1456, 1417, 1352, 1319, 1276, 1223, 1169, 1121, 1101, 1063; MS (70 ev, EI) *m/z* (%) 261 (M⁺(³⁷Cl), 13.36), 259 (M⁺(³⁵Cl), 41.40), 202 (100); HRMS calcd for C₁₆H₁₈³⁵ClN [M⁺]: 259.1128, Found: 259.1128.

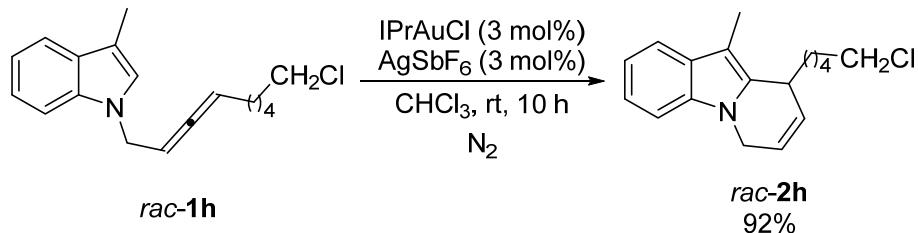
5.7 Synthesis of 9-butyl-10-methyl-6,9-dihydropyrido[1,2-*a*]indole *rac*-2g (jf-2-097)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), ***rac-1g*** (0.2389 g, 1 mmol), and CHCl₃ (5 mL) for 17 h at room temperature afforded ***rac-2g*** (0.2292 g, 96%) [eluent: petroleum ether] as a powder solid: m.p. 40.1-41.1 °C (without recrystallization); ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.26 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.22-7.07 (m, 2H, Ar-H), 6.14-5.97 (m, 2H, =CH × 2), 4.64-4.50 (m, 2H, NCH₂), 3.82-3.68 (m, 1H, CH), 2.30 (s, 3H, CH₃), 1.85-1.67 (m, 2H, CH₂), 1.36-1.18 (m, 3H, CH₂ + one proton of CH₂), 1.16-1.02 (m, 1H, one proton of CH₂), 0.83 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 135.2, 134.0, 128.8, 127.8, 120.7, 120.2, 119.0, 117.8, 108.5, 104.1, 42.0, 35.6, 33.2, 27.6, 22.8, 14.0, 8.9; IR (neat) ν (cm⁻¹) 3042, 2951, 2929, 2858, 1662, 1615, 1568, 1462, 1426, 1384, 1369, 1329, 1313, 1241, 1196, 1169, 1011; MS (70 ev, EI) *m/z* (%) 240 (M⁺+1, 6.68), 239 (M⁺, 33.76), 182 (100); HRMS calcd for C₁₇H₂₁N [M⁺]: 239.1674, Found: 239.1673.

5.8 Synthesis of 9-(5-chloropentyl)-10-methyl-6,9-dihydropyrido[1,2-*a*]indole

rac-2h (jf-2-152)

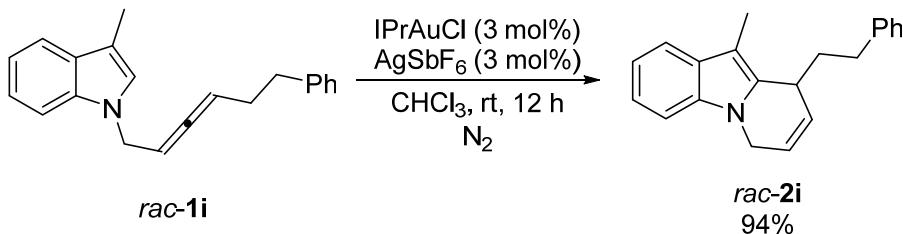


Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0194 g, 0.03 mmol, 95%), AgSbF₆ (0.0105 g, 0.03 mmol, 98%), ***rac-1h*** (0.2886 g, 1 mmol), and CHCl₃ (5 mL) afforded ***rac-2h*** (0.2654 g, 92%) [eluent: petroleum ether] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.56-7.50 (m, 1H, Ar-H), 7.26-7.21 (m, 1H, Ar-H), 7.19-7.08 (m, 2H, Ar-H), 6.09-5.93 (m, 2H, =CH × 2), 4.66-4.40 (m, 2H, NCH₂), 3.81-3.70 (m, 1H, CH), 3.44 (t, *J* = 6.6 Hz, 2H, CH₂Cl), 2.29 (s, 3H, CH₃), 1.84-1.61 (m, 4H, CH₂ × 2),

1.44-1.23 (m, 3H, CH₂ + one proton of CH₂), 1.15-1.00 (m, 1H, one proton of CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 135.2, 133.5, 128.7, 127.5, 120.9, 120.3, 119.0, 117.8, 108.5, 104.1, 45.0, 42.0, 35.5, 33.1, 32.4, 26.9, 24.6, 8.9; IR (neat) ν (cm⁻¹) 3042, 2934, 2858, 1665, 1615, 1568, 1471, 1461, 1385, 1368, 1328, 1312, 1240, 1197, 1169, 1054, 1011; MS (70 ev, EI) *m/z* (%) 290 (M^{+(³⁷Cl)} + 1, 1.26), 289 (M^{+(³⁷Cl)}), 6.87), 288 (M^{+(³⁵Cl)} + 1, 4.36), 287 (M^{+(³⁵Cl)}), 20.42), 182 (100); HRMS calcd for C₁₈H₂₂N³⁵Cl [M⁺]: 287.1441, Found: 287.1440.}}}}

5.9 Synthesis of 10-methyl-9-phenethyl-6,9-dihydropyrido[1,2-*a*]indole *rac*-2*i*

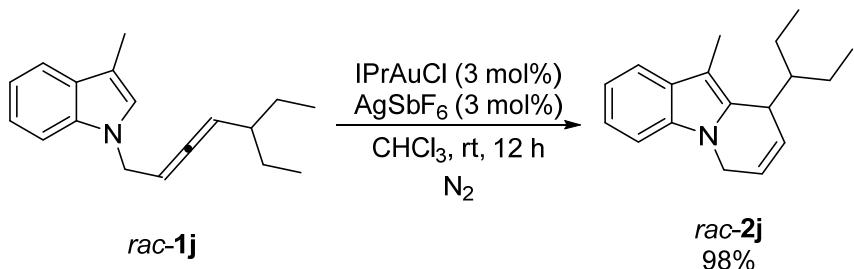
(jf-3-030)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0194 g, 0.03 mmol, 95%), AgSbF₆ (0.0105 g, 0.03 mmol, 98%), *rac*-1*i* (0.2881 g, 1 mmol), and CHCl₃ (5 mL) for 12 h at room temperature afforded *rac*-2*i* (0.2706 g, 94%) [eluent: petroleum ether/diethyl ether = 50/1] as a needle solid: m.p. 91.5-92.2 °C (DCM/hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.56 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.30-7.04 (m, 8H, Ar-H), 6.16-6.01 (m, 2H, =CH × 2), 4.66-4.51 (m, 2H, NCH₂), 3.89-3.72 (m, 1H, CH), 2.65-2.51 (m, 1H, one proton of PhCH₂), 2.45-2.33 (m, 1H, one proton of PhCH₂), 2.30 (s, 3H, CH₃), 2.20-1.93 (m, 2H, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 142.0, 135.2, 133.1, 128.7, 128.2, 127.0, 125.7, 121.2, 120.3, 119.0, 117.8, 108.5, 104.2, 41.8, 37.3, 32.9, 31.5, 8.9; IR (KBr) ν (cm⁻¹) 3030, 2947, 2917, 2859, 1667, 1601, 1579, 1500, 1471, 1462, 1369, 1313, 1238, 1197, 1167, 1119, 1083; MS (70 ev, EI) *m/z* (%) 288 (M⁺¹, 4.84), 287 (M⁺, 21.40), 182 (100); Anal. Calcd. for C₂₁H₂₁N (%): C 87.76, H 7.37, N 4.87, Found: C 87.65, H 7.35, N 4.66.

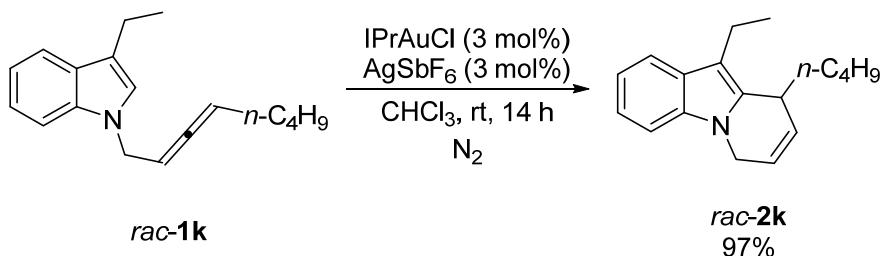
5.10 Synthesis of 10-methyl-9-(pentan-3-yl)-6,9-dihydropyrido[1,2-*a*]indole *rac*-2*j*

(jf-3-094)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), *rac*-**1j** (0.2530 g, 1 mmol), and CHCl₃ (5 mL) for 12 h at room temperature afforded *rac*-**2j** (0.2481 g, 98%) [eluent: petroleum ether] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, *J* = 6.9 Hz, 1H, Ar-H), 7.24 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.20-7.08 (m, 2H, Ar-H), 6.13-5.95 (m, 2H, =CH × 2), 4.59-4.50 (m, 2H, NCH₂), 4.00-3.82 (m, 1H, CH), 2.30 (s, 3H, Ar-CH₃), 1.86-1.69 (m, 1H, CH), 1.67-1.51 (m, 1H, one proton of CH₂), 1.43-1.25 (m, 1H, one proton of CH₂), 1.12 (t, *J* = 7.4 Hz, 3H, CH₃), 1.02 (quint, *J* = 7.2 Hz, 2H, CH₂), 0.65 (t, *J* = 7.5 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 135.2, 134.1, 128.9, 124.2, 122.0, 120.1, 118.9, 117.7, 108.4, 103.8, 47.5, 42.2, 35.1, 23.7, 23.0, 12.5, 12.2, 9.0; IR (neat) ν (cm⁻¹) 3042, 2959, 2928, 2873, 1665, 1613, 1567, 1462, 1425, 1385, 1368, 1312, 1241, 1198, 1173, 1058, 1012; MS (70 ev, EI) *m/z* (%) 254 (M⁺+1, 3.21), 253 (M⁺, 15.57), 182 (100); HRMS calcd for C₁₈H₂₃N [M⁺]: 253.1830, Found: 253.1830.

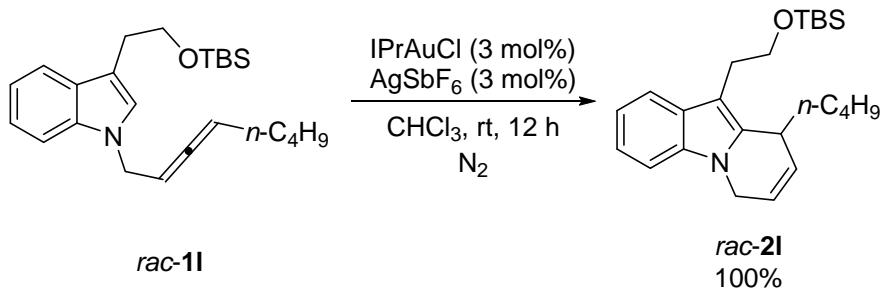
5.11 Synthesis of 9-butyl-10-ethyl-6,9-dihydropyrido[1,2-*a*]indole *rac*-**2k** (jf-3-077)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), *rac*-**1k** (0.2564 g, 1 mmol), and CHCl₃ (5 mL) for 14 h at room temperature afforded *rac*-**2k** (0.2485 g, 97%) [eluent: petroleum ether/diethyl ether = 50/1] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.25 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.20-7.07 (m, 2H, Ar-H), 6.09-5.95 (m,

2H, =CH × 2), 4.60-4.48 (m, 2H, NCH₂), 3.85-3.66 (m, 1H, CH), 2.78 (q, *J* = 7.5 Hz, 2H, Ar-CH₂), 1.84-1.61 (m, 2H, CH₂), 1.38-1.17 (m, 6H, CH₂ + one proton of CH₂ + CH₃), 1.15-0.97 (m, 1H, one proton of CH₂), 0.83 (t, *J* = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 135.5, 133.3, 127.9, 127.8, 120.7, 120.2, 119.0, 118.2, 111.0, 108.6, 42.0, 36.3, 33.3, 27.3, 22.8, 17.7, 15.4, 14.0; IR (neat) ν (cm⁻¹) 3042, 2959, 2929, 2857, 1666, 1612, 1566, 1471, 1456, 1423, 1372, 1331, 1314, 1235, 1193, 1169, 1126, 1069, 1015; MS (70 ev, EI) *m/z* (%) 254 (M⁺+1, 6.31), 253 (M⁺, 30.62), 196 (100); HRMS calcd for C₁₈H₂₃N [M⁺]: 253.1830, Found: 253.1829.

5.12 Synthesis of 9-butyl-10-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-6,9-dihydro-pyrido[1,2-*a*]indole *rac*-2l (jf-3-060)

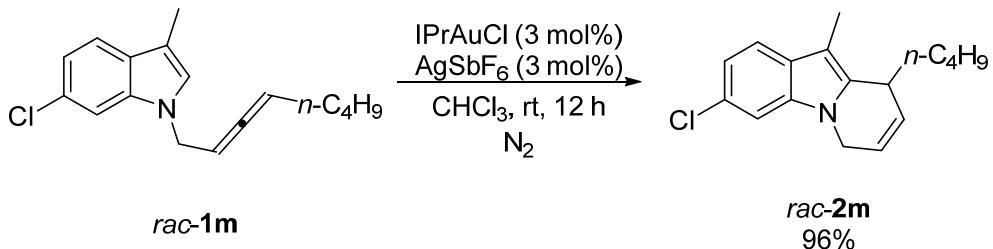


Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0193 g, 0.03 mmol, 95%), AgSbF₆ (0.0106 g, 0.03 mmol, 98%), *rac*-11 (0.3838 g, 1 mmol), and CHCl₃ (5 mL) for 12 h at room temperature afforded *rac*-2l (0.3836 g, 100%) [eluent: petroleum ether/diethyl ether = 100/1] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.27 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.22-7.09 (m, 2H, Ar-H), 6.14-6.00 (m, 2H, =CH × 2), 4.65-4.48 (m, 2H, NCH₂), 3.93-3.75 (m, 3H, OCH₂ + CH), 3.03 (t, *J* = 8.0 Hz, 2H, Ar-CH₂), 1.84-1.67 (m, 2H, CH₂), 1.37-1.19 (m, 3H, CH₂ + one proton of CH₂), 1.17-1.02 (m, 1H, one proton of CH₂), 0.92 (s, 9H, CH₃ × 3), 0.83 (t, *J* = 7.1 Hz, 3H, CH₃), 0.06 (s, 3H, CH₃), 0.05 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 135.4, 134.9, 128.3, 127.8, 120.7, 120.3, 119.2, 118.1, 108.7, 105.2, 63.8, 42.1, 36.4, 33.2, 28.6, 27.4, 26.0, 22.8, 18.4, 14.0, -5.24, -5.28; IR (KBr) ν (cm⁻¹) 3043, 2955, 2929, 2857, 1665, 1613, 1566, 1471, 1461, 1425, 1370, 1330, 1314, 1254, 1213, 1191, 1169, 1094, 1067, 1014; MS (70 ev, EI) *m/z* (%) 384 (M⁺+1, 16.36), 383 (M⁺, 54.53), 238 (100); HRMS calcd for C₂₄H₃₇NOSi [M⁺]: 383.2644, Found:

383.2642.

5.13 Synthesis of 9-butyl-3-chloro-10-methyl-6,9-dihydropyrido[1,2-*a*]indole

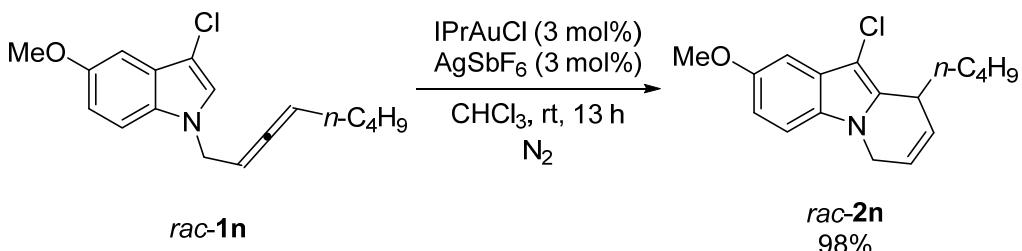
rac-1m (jf-3-003)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0197 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), *rac*-1m (0.2762 g, 1 mmol), and CHCl₃ (5 mL) for 12 h at room temperature afforded *rac*-2m (0.2647 g, 96%) [eluent: petroleum ether] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.43 (d, *J* = 6.3 Hz, 1H, Ar-H), 7.24 (d, *J* = 1.5 Hz, 1H, Ar-H), 7.07 (dd, *J*₁ = 6.3 Hz, *J*₂ = 1.8 Hz, 1H, Ar-H), 6.10-5.98 (m, 2H, =CH × 2), 4.58-4.46 (m, 2H, NCH₂), 3.78-3.66 (m, 1H, CH), 2.27 (s, 3H, CH₃), 1.81-1.69 (m, 2H, CH₂), 1.35-1.18 (m, 3H, CH₂ + one proton of CH₂), 1.14-1.01 (m, 1H, one proton of CH₂), 0.83 (t, *J* = 5.3 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 135.6, 134.7, 127.7, 127.4, 126.2, 120.4, 119.5, 118.6, 108.6, 104.4, 42.0, 35.4, 33.3, 27.5, 22.7, 14.0, 8.8; IR (neat) ν (cm⁻¹) 3039, 2953, 2924, 2858, 1839, 1665, 1608, 1584, 1556, 1474, 1463, 1417, 1385, 1364, 1342, 1319, 1281, 1233, 1198, 1169, 1101, 1066, 1050, 1001; MS (70 ev, EI) *m/z* (%) 276 (M⁺(³⁷Cl) + 1, 1.33), 275 (M⁺(³⁷Cl), 10.67), 274 (M⁺(³⁵Cl) + 1, 5.96), 273 (M⁺(³⁵Cl), 30.66), 216 (100); HRMS calcd for C₁₇H₂₀N³⁵Cl [M⁺]: 273.1284, Found: 273.1282.

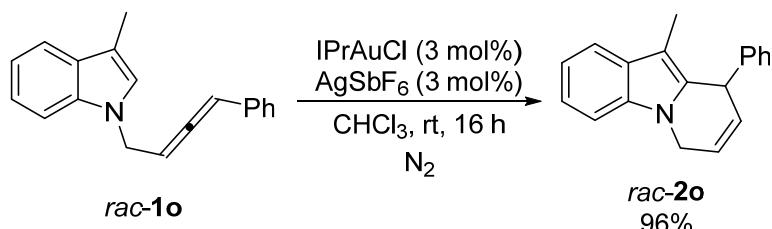
5.14 Synthesis of 9-butyl-10-chloro-2-methoxy-6,9-dihydropyrido[1,2-*a*]indole

rac-2n (jf-3-090)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0106 g, 0.03 mmol, 98%), *rac*-**1n** (0.2902 g, 1 mmol), and CHCl₃ (5 mL) for 13 h at room temperature afforded *rac*-**2n** (0.2839 g, 98%) [eluent: petroleum ether/diethyl ether = 20/1] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.16 (d, *J* = 9.0 Hz, 1H, Ar-H), 7.03 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.85 (dd, *J*₁ = 8.7 Hz, *J*₂ = 2.4 Hz, 1H, Ar-H), 6.06-5.96 (m, 2H, =CH × 2), 4.57-4.48 (m, 2H, NCH₂), 3.88 (s, 3H, OMe), 3.82-3.73 (m, 1H, CH), 2.03-1.76 (m, 2H, CH₂), 1.37-1.19 (m, 3H, CH₂ + one proton of CH₂), 1.15-0.98 (m, 1H, one proton of CH₂), 0.84 (t, *J* = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 154.8, 133.8, 129.3, 127.1, 126.0, 120.2, 111.8, 109.9, 99.5, 98.8, 55.8, 42.1, 33.9, 33.1, 27.4, 22.6, 14.0; IR (neat) ν (cm⁻¹) 3036, 3008, 2950, 2925, 2868, 1619, 1577, 1486, 1450, 1370, 1342, 1287, 1220, 1185, 1164, 1030; MS (70 ev, EI) *m/z* (%) 292 (M⁺(³⁷Cl) + 1, 1.97), 291 (M⁺(³⁷Cl), 10.79), 290 (M⁺(³⁵Cl) + 1, 5.54), 289 (M⁺(³⁵Cl), 35.41), 232 (100); HRMS calcd for C₁₇H₂₀NO³⁵Cl [M⁺]: 289.1233, Found: 289.1232.

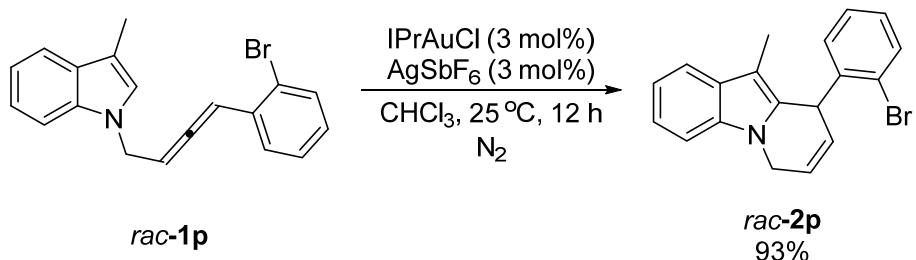
5.15 Synthesis of 10-methyl-9-phenyl-6,9-dihydropyrido[1,2-*a*]indole *rac*-**2o** (jf-2-162)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0039 g, 0.006 mmol, 95%), AgSbF₆ (0.0021 g, 0.006 mmol, 98%), *rac*-**1o** (0.0526 g, 0.2 mmol), and CHCl₃ (5 mL) for 16 h at room temperature afforded *rac*-**2o** (0.0504 g, 96%) [eluent: petroleum ether/ethyl acetate = 100/1] as a powder solid: m.p. 153.8-154.8 °C (without recrystallization); ¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.33 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.29-7.08 (m, 7H, Ar-H), 6.12-5.96 (m, 2H, =CH × 2), 4.86-4.60 (m, 3H, NCH₂ + CH), 1.97 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 143.3, 135.2, 132.2, 128.7, 128.6, 128.0, 127.8, 126.5, 120.6, 119.2, 119.0, 118.1, 108.7, 105.9, 41.9, 40.6, 8.6; IR (KBr) ν (cm⁻¹) 3041, 3022, 2912, 2854, 1654,

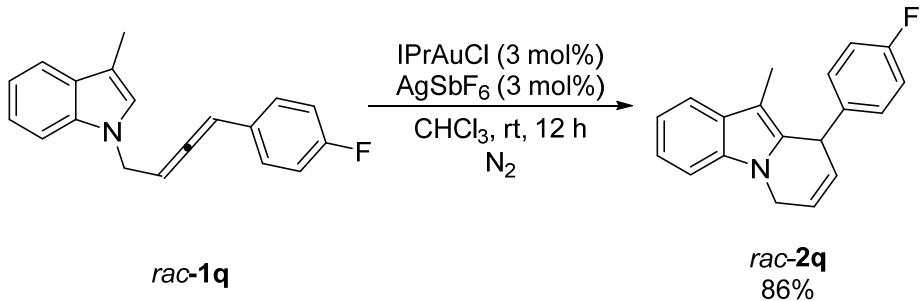
1618, 1600, 1577, 1561, 1489, 1471, 1463, 1453, 1426, 1390, 1369, 1314, 1240, 1199, 1183, 1166, 1074, 1027, 1009; MS (70 ev, EI) m/z (%) 260 ($M^+ + 1$, 19.71), 259 (100); HRMS calcd for $C_{19}H_{17}N$ [M^+]: 259.1361, Found: 259.1359.

5.16 Synthesis of 9-(2-bromophenyl)-10-methyl-6,9-dihydropyrido[1,2-*a*]indole *rac*-2p (jf-2-182)



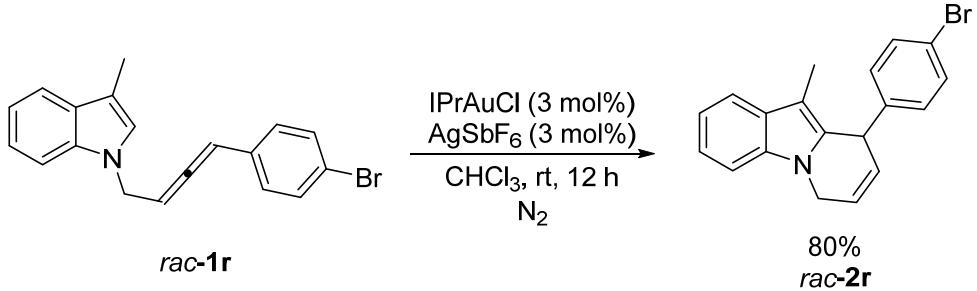
Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0038 g, 0.006 mmol, 95%), AgSbF₆ (0.0021 g, 0.006 mmol, 98%), *rac*-1p (0.0678 g, 0.2 mmol), and CHCl₃ (5 mL) for 12 h at 25 °C afforded *rac*-2p (0.0631 g, 93%) [eluent: petroleum ether] as a powder solid: m.p. 135.7-136.6 °C (without recrystallization); ¹H NMR (300 MHz, CDCl₃) δ 7.55 (t, $J = 8.3$ Hz, 2H, Ar-H), 7.36 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.27-6.98 (m, 4H, Ar-H), 6.78 (d, $J = 7.2$ Hz, 1H, Ar-H), 6.08 (q, $J = 10.5$ Hz, 2H, =CH × 2), 5.50-5.26 (m, 1H, CH), 4.78 (d, $J = 19.2$ Hz, 1H, one proton of NCH₂), 4.67 (d, $J = 19.2$ Hz, 1H, one proton of NCH₂), 1.93 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 142.4, 135.3, 132.6, 132.0, 130.1, 128.6, 128.1, 128.0, 125.9, 123.2, 120.8, 119.6, 119.4, 118.2, 108.8, 106.2, 41.9, 39.6, 8.4; IR (KBr) ν (cm⁻¹) 3045, 2913, 2885, 2853, 1611, 1585, 1559, 1460, 1432, 1386, 1366, 1315, 1307, 1262, 1242, 1200, 1173, 1044, 1023, 1010; MS (70 ev, EI) m/z (%) 339 ($M^+ + ^{81}Br$, 79.29), 337 ($M^+ + ^{79}Br$, 100); HRMS calcd for $C_{19}H_{16}N^{79}Br$ [M^+]: 337.0466, Found: 337.0466.

5.17 Synthesis of 9-(4-fluorophenyl)-10-methyl-6,9-dihydropyrido[1,2-*a*]indole *rac*-2q (jf-3-037)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0195 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), *rac*-**1q** (0.2816 g, 1 mmol), and CHCl₃ (5 mL) for 12 h at room temperature afforded *rac*-**2q** (0.2433 g, 86%) [eluent: petroleum ether/diethyl ether = 50/1] as a powder solid: m.p. 115.3-116.7 °C (without recrystallization); ¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.32 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.25-7.17 (m, 1H, Ar-H), 7.17-7.04 (m, 3H, Ar-H), 6.93 (t, *J* = 8.7 Hz, 2H, Ar-H), 6.07-5.95 (m, 2H, =CH × 2), 4.83-4.58 (m, 3H, NCH₂ + CH), 1.96 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 161.4 (d, *J* = 243.3 Hz), 139.0 (d, *J* = 2.8 Hz), 135.2, 131.9, 129.3 (d, *J* = 7.6 Hz), 128.6, 127.8, 120.8, 119.3, 119.2, 118.1, 115.4 (d, *J* = 21.4 Hz), 108.7, 105.9, 41.8, 39.7, 8.6; ¹⁹F NMR (282 MHz, CDCl₃) δ -108.7; IR (KBr) v (cm⁻¹) 3041, 2939, 2909, 2887, 2852, 2883, 1665, 1654, 1603, 1561, 1506, 1472, 1462, 1388, 1369, 1319, 1293, 1280, 1227, 1167, 1156, 1093, 1011; MS (70 ev, EI) *m/z* (%) 278 (M⁺+1, 19.43), 277 (100); Anal. Calcd. for C₁₉H₁₆FN (%): C 82.28, H 5.82, N 5.05, Found: C 82.25, H 5.87, N 4.96.

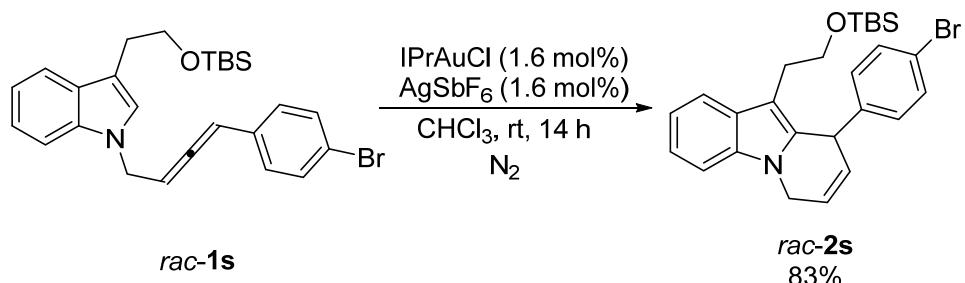
5.18 Synthesis of 9-(4-bromophenyl)-10-methyl-6,9-dihydropyrido[1,2-*a*]indole *rac*-**2r** (jf-3-021)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0194 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), *rac*-**1r** (0.3390 g, 1 mmol), and CHCl₃ (5

mL) for 12 h at room temperature afforded *rac*-**2r** (0.2712 g, 80%) [eluent: petroleum ether/diethyl ether = 50/1] as a needle solid: m.p. 152.0-154.3 °C (DCM/hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.51 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.38-7.25 (m, 3H, Ar-H), 7.24-7.08 (m, 2H, Ar-H), 6.95 (d, *J* = 8.1 Hz, 2H, Ar-H), 6.06-5.88 (m, 2H, =CH × 2), 4.79-4.50 (m, 3H, NCH₂ + CH), 1.94 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 142.3, 135.2, 131.7, 131.5, 129.5, 128.6, 127.3, 120.8, 120.2, 119.43, 119.36, 118.1, 108.7, 106.0, 41.8, 39.9, 8.6; IR (KBr) ν (cm⁻¹) 3044, 2963, 2916, 2861, 1561, 1485, 1461, 1426, 1402, 1385, 1367, 1313, 1263, 1241, 1200, 1180, 1166, 1067, 1008; MS (70 ev, EI) *m/z* (%) 340 (M^{+(⁸¹Br)} + 1, 20.90), 339 (M^{+(⁸¹Br)}, 91.05), 338 (M^{+(⁷⁹Br)} + 1, 100), 337 (M^{+(⁷⁹Br)}, 85.87); Anal. Calcd. for C₁₉H₁₆BrN (%): C 67.47, H 4.77, N 4.14, Found: C 67.20, H 4.77, N 4.00.

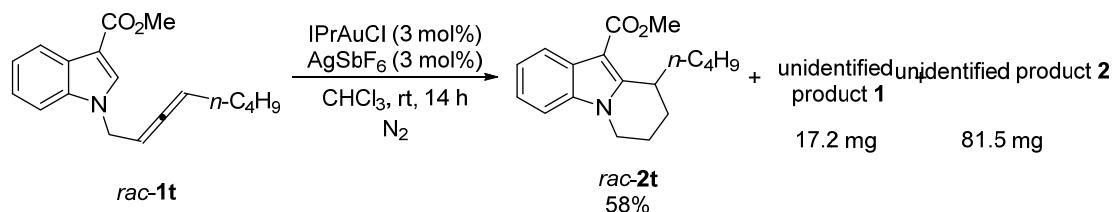
5.19 Synthesis of 9-(4-bromophenyl)-10-((tert-butyldimethylsilyl)oxy)ethyl)-6,9-dihydropyrido[1,2-*a*]indole *rac*-**2s** (jf-3-124)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0296 g, 0.045 mmol, 95%), AgSbF₆ (0.0158 g, 0.045 mmol, 98%), *rac*-**1s** (1.3720 g, 2.8 mmol), and CHCl₃ (15 mL) for 14 h at room temperature afforded *rac*-**2s** (1.1381 g, 83%) [eluent: petroleum ether/diethyl ether = 100/1] as a powder solid: m.p. 109.4-110.4 °C (without recrystallization); ¹H NMR (300 MHz, CDCl₃) δ 7.56 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.34 (t, *J* = 8.4 Hz, 3H, Ar-H), 7.21 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.13 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.00 (d, *J* = 8.1 Hz, 2H, Ar -H), 6.07-5.94 (m, 2H, =CH × 2), 4.95-4.83 (m, 1H, CH), 4.76 (d, *J* = 18.3 Hz, 1H, one proton of NCH₂), 4.65 (d, *J* = 17.7 Hz, 1H, one proton of NCH₂), 3.62-3.46 (m, 1H, one proton of OCH₂), 3.29 (td, *J*₁ = 9.3 Hz, *J*₂ = 5.4 Hz, 1H, one proton of OCH₂), 2.82-2.61 (m, 2H, Ar-CH₂), 0.83 (s, 9H, CH₃ × 3), -0.08 (s, 3H, CH₃), -0.10 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃)

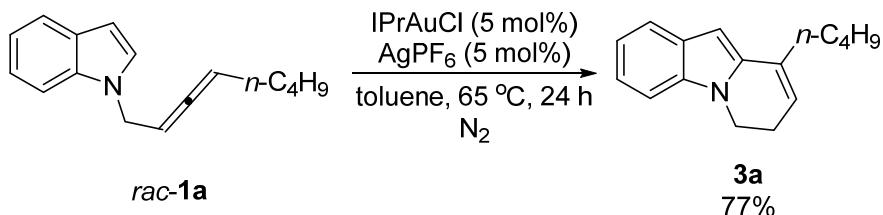
δ 143.0, 135.4, 132.6, 131.8, 129.5, 128.3, 127.5, 121.0, 120.5, 119.6, 119.3, 118.5, 108.9, 107.4, 63.0, 41.9, 39.9, 28.1, 26.0, 18.4, -5.38, -5.44; IR (KBr) ν (cm⁻¹) 3054, 2951, 2928, 2856, 1485, 1470, 1401, 1387, 1369, 1314, 1291, 1251, 1168, 1087, 1011; MS (70 ev, EI) m/z (%) 484 ($M^+({}^{81}\text{Br}) + 1$, 6.16), 483 ($M^+({}^{81}\text{Br})$, 18.98), 482 ($M^+({}^{79}\text{Br}) + 1$, 6.88), 481 ($M^+({}^{79}\text{Br})$, 18.33), 336 (100); Anal. Calcd. for C₂₆H₃₂BrNOSi (%): C 64.72, H 6.68, N 2.90, Found: C 64.70, H 6.68, N 2.66.

5.20. Synthesis of methyl 9-butyl-6,9-dihydropyrido[1,2-*a*]indole-10-carboxylate *rac*-2t (jf-4-174)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0198 g, 0.03 mmol, 95%), AgSbF₆ (0.0107 g, 0.03 mmol, 98%), *rac*-1t (0.2845 g, 1 mmol), and CHCl₃ (5 mL) for 14 h at room temperature afforded *rac*-2t (0.1648 g, 58%), unidentified product 1 (17.2 mg), and unidentified product 2 (81.5 mg) [eluent: petroleum ether/ethyl acetate = 15/1 (500 mL) to 7/1 (400 mL)] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 8.15 (d, J = 7.2 Hz, 1H, Ar-H), 7.34-7.08 (m, 3H, Ar-H), 6.13-5.85 (m, 2H, =CH × 2), 4.56-4.38 (m, 2H, NCH₂), 4.36-4.23 (m, 1H, CH), 3.91 (s, 3H, OCH₃), 1.95-1.71 (m, 2H, CH₂), 1.43-1.14 (m, 3H, CH₂ + one proton of CH₂), 1.11-0.91 (m, 1H, one proton of CH₂), 0.82 (t, J = 7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 165.7, 147.2, 135.3, 127.7, 126.7, 122.0, 121.7, 121.3, 119.4, 108.9, 101.3, 50.5, 42.1, 35.7, 34.5, 27.7, 22.5, 13.9; IR (neat) ν (cm⁻¹) 3050, 2951, 2924, 2860, 1692, 1531, 1455, 1435, 1379, 1356, 1314, 1257, 1209, 1158, 1116, 1040, 1017; MS (70 ev, EI) m/z (%) 284 ($M^+ + 1$, 13.54), 283 (M^+ , 59.70), 226 (100); HRMS calcd for C₁₈H₂₁NO₂ [M⁺]: 283.1572, Found: 283.1575.

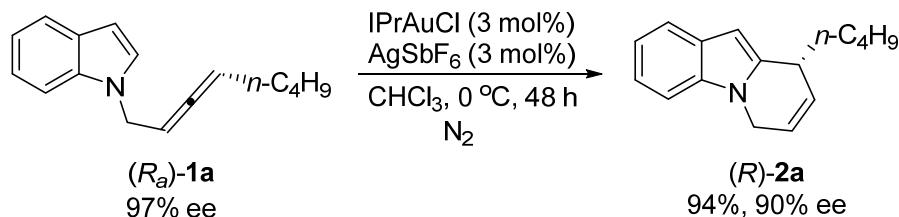
6. Synthesis of 9-butyl-6,7-dihydropyrido[1,2-*a*]indole 3a (jf-4-067)



To an oven-dried Schlenk tube were added IPrAuCl (0.0065 g, weighed in a glove box, 0.01 mmol, 95%), AgPF₆ (0.0026 g, weighed in a glove box, 0.01 mmol, 99%), *rac*-**1a** (0.0453 g, 0.2 mmol), and toluene (5 mL) at room temperature under nitrogen atmosphere sequentially. The reaction was complete after being stirred at 65 °C for 24 h as monitored by TLC. After filtration through a short column of silica gel (3 cm × 2 cm) [eluent: DCM (5 mL × 4)] and evaporation, the crude product was purified by column chromatography on silica gel to afford **3a** (0.0351 g, 77%) [eluent: petroleum ether] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.57 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.24 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.21-7.13 (m, 1H, Ar-H), 7.08-7.01 (m, 1H, Ar-H), 6.44 (s, 1H, Ar-H), 5.72 (t, *J* = 4.4 Hz, 1H, =CH), 4.03 (t, *J* = 7.2 Hz, 2H, NCH₂), 2.64-2.50 (m, 2H, CH₂), 2.43 (t, *J* = 7.7 Hz, 2H, CH₂), 1.66-1.53 (m, 2H, CH₂), 1.46-1.32 (m, 2H, CH₂), 0.94 (t, *J* = 7.4 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 136.8, 136.6, 132.1, 128.3, 121.6, 120.5, 119.43, 119.37, 108.6, 97.2, 39.5, 32.2, 31.0, 24.1, 22.5, 14.0; IR (KBr) ν (cm⁻¹) 3053, 2956, 2930, 2859, 1456, 1414, 1382, 1360, 1335, 1312, 1248, 1161, 1010; MS (70 ev, EI) *m/z* (%) 226 (M⁺+1, 11.14), 225 (M⁺, 63.85), 183 (100); HRMS calcd for C₁₆H₁₉N [M⁺]: 225.1517, Found: 225.1517.

7. Gold(I) catalyzed cyclization of axially chiral *N*-allenylindoles

7.1 Synthesis of (*R*)-9-butyl-6,9-dihydropyrido[1,2-*a*]indole (*R*)-**2a** (jf-2-023)



Typical Procedure V: To an oven-dried Schlenk tube were added IPrAuCl (0.0196 g, weighed in a glove box, 0.03 mmol, 95%), AgSbF₆ (0.0105 g, weighed in a glove

box, 0.03 mmol, 98%), (*R*_a)-**1a** (0.2228 g, 1 mmol), and CHCl₃ (25 mL) at room temperature under nitrogen atmosphere sequentially. The reaction was complete after being stirred at 0 °C for 48 h as monitored by TLC. Filtration through a short column of silica gel (3 cm × 2 cm) [eluent: petroleum ether (10 mL × 5)] and evaporation afforded (*R*)-**2a** (0.2092 g, 94%) as a powder solid: m.p. 61.8-63.3 °C (without recrystallization); 90% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 100/1, 1.0 mL/min, λ = 214 nm, t_R (major) = 8.3 min, t_R (minor) = 7.8 min); ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, J = 6.9 Hz, 1H, Ar-H), 7.29 (d, J = 8.4 Hz, 1H, Ar-H), 7.20-7.08 (m, 2H, Ar-H), 6.32 (s, 1H, Ar-H), 6.09-5.92 (m, 2H, =CH × 2), 4.66-4.50 (m, 2H, NCH₂), 3.81-3.61 (m, 1H, CH), 1.86-1.73 (m, 2H, CH₂), 1.41-1.18 (m, 4H, CH₂ × 2), 0.86 (t, J = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 138.4, 135.5, 128.3, 127.5, 120.2, 120.1, 119.7, 108.7, 96.8, 41.8, 36.4, 34.2, 27.9, 22.8, 14.0; IR (KBr) ν (cm⁻¹) 2959, 2949, 2924, 2859, 1535, 1467, 1459, 1419, 1362, 1313, 1227, 1183, 1169, 1154, 1010, 1000; MS (70 ev, EI) *m/z* (%) 226 (M⁺+1, 8.18), 225 (M⁺, 40.51), 168 (100); HRMS calcd for C₁₆H₁₉N [M⁺]: 225.1517, Found: 225.1517.

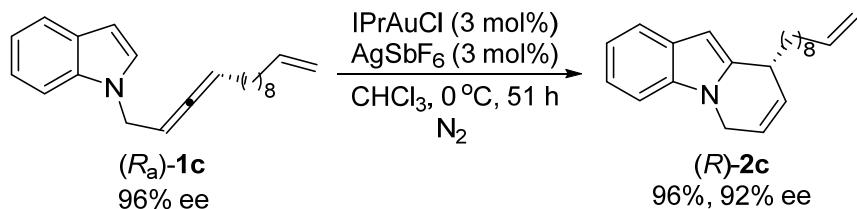
7.2 Synthesis of (*R*)-9-decyl-6,9-dihydropyrido[1,2-*a*]indole (*R*)-**2b** (jf-2-015)



To an oven-dried Schlenk tube were added IPrAuCl (0.0196 g, weighed in a glove box, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, weighed in a glove box, 0.03 mmol, 98%), (*R*_a)-**1b** (0.3078 g, 1 mmol), and CHCl₃ (25 mL) under nitrogen atmosphere sequentially. The reaction was complete after being stirred at 0 °C for 48 h as monitored by TLC. Filtration through a short column of neutral alumina (2 cm × 2 cm) [eluent: DCM (8 mL × 4)] and evaporation. The crude product was then purified by column chromatography on neutral alumina to afford (*R*)-**2b** (0.2936 g, 95%) [eluent: petroleum ether] as a liquid: 90% ee (HPLC conditions: Chiralcel OD-H

column, *n*-hexane/*i*-PrOH = 100/1, 1.0 mL/min, λ = 214 nm, t_R (major) = 7.5 min, t_R (minor) = 8.0 min; $[\alpha]_D^{20} = -86.0$ ($c = 0.86$, THF); ^1H NMR (300 MHz, CDCl_3) δ 7.58 (d, $J = 6.9$ Hz, 1H, Ar-H), 7.27 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.19-7.07 (m, 2H, Ar-H), 6.31 (s, 1H, Ar-H), 6.07-5.92 (m, 2H, =CH \times 2), 4.63-4.50 (m, 2H, NCH_2), 3.78-3.61 (m, 1H, CH), 1.85-1.70 (m, 2H, CH_2), 1.38-1.16 (m, 16H, $\text{CH}_2 \times 8$), 0.87 (t, $J = 6.6$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 138.4, 135.5, 128.3, 127.5, 120.2, 120.1, 119.7, 108.7, 96.8, 41.8, 36.7, 34.3, 31.9, 29.8, 29.63, 29.58, 29.53, 29.3, 25.8, 22.7, 14.1; IR (neat) ν (cm^{-1}) 3043, 2924, 2853, 1668, 1541, 1471, 1456, 1419, 1362, 1316, 1227, 1185, 1170, 1150, 1012; MS (70 ev, EI) m/z (%) 310 ($M^+ + 1$, 9.95), 309 (M^+ , 41.78), 168 (100); HRMS calcd for $\text{C}_{22}\text{H}_{31}\text{N}$ [M^+]: 309.2457, Found: 309.2458.

7.3 Synthesis of (*R*)-9-(dec-9-enyl)-6,9-dihydropyrido[1,2-*a*]indole (*R*)-2c (jf-2-066)

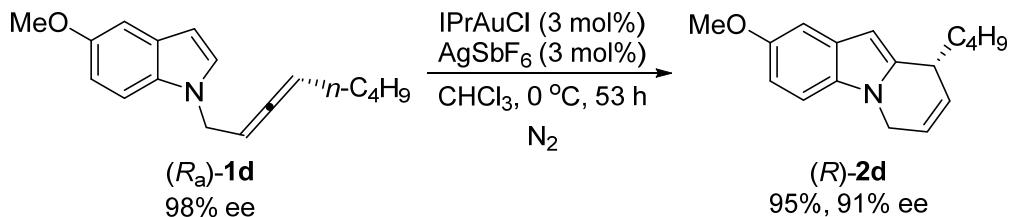


Following **Typical Procedure V**, the reaction of IPrAuCl (0.0195 g, 0.03 mmol, 95%), AgSbF₆ (0.0105 g, 0.03 mmol, 98%), (*R*_a)-1c (0.3075 g, 1 mmol), and CHCl₃ (25 mL) for 51 h at 0 °C afforded (*R*)-2c (0.2941 g, 96%) as a liquid: 92% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 100/1, 1.0 mL/min, λ = 214 nm, t_R (major) = 8.8 min, t_R (minor) = 9.3 min); $[\alpha]_D^{20} = -86.7$ ($c = 1.095$, CHCl₃); ^1H NMR (300 MHz, CDCl_3) δ 7.58 (dd, $J_1 = 6.9$ Hz, $J_2 = 1.2$ Hz, 1H, Ar-H), 7.28 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.19-7.07 (m, 2H, Ar-H), 6.31 (s, 1H, ArH), 6.08-5.92 (m, 2H, CH=CH), 5.88-5.71 (m, 1H, CH=), 5.05-4.86 (m, 2H, =CH₂), 4.63-4.51 (m, 2H, NCH_2), 3.78-3.64 (m, 1H, CH), 2.02 (q, $J = 7.0$ Hz, 2H, CH_2), 1.84-1.69 (m, 2H, CH_2), 1.41-1.15 (m, 12H, $\text{CH}_2 \times 6$); ^{13}C NMR (75 MHz, CDCl_3) δ 139.2, 138.4, 135.4, 128.2, 127.5, 120.2, 120.1, 119.7, 114.1, 108.8, 96.7, 41.8, 36.6, 34.2, 33.8, 29.7, 29.45, 29.42, 29.1, 28.9, 25.8; IR (neat) ν (cm^{-1}) 3044, 2926, 2854, 1668, 1640,

1542, 1471, 1456, 1419, 1362, 1316, 1227, 1185, 1170; MS (70 ev, EI) m/z (%) 308 ($M^+ + 1$, 9.70), 307 (M^+ , 35.39), 168 (100); HRMS calcd for $C_{22}H_{29}N$ [M^+]: 307.2300, Found: 307.2303.

7.4 Synthesis of (*R*)-9-butyl-2-methoxy-6,9-dihydropyrido[1,2-*a*]indole (*R*)-2d

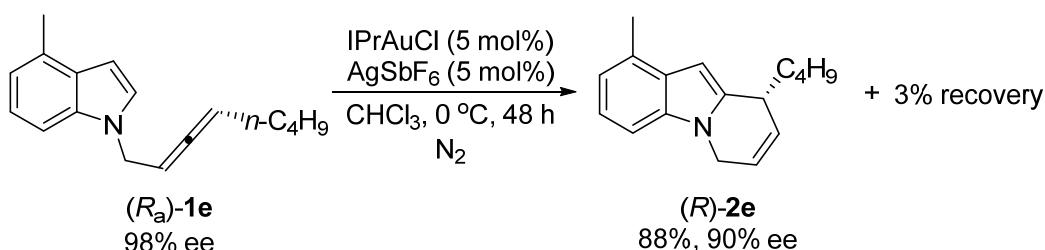
(jf-1-198)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), (R_a)-1d (0.2561 g, 1 mmol), and CHCl₃ (25 mL) for 53 h at 0 °C afforded (*R*)-2d (0.2424 g, 95%) [eluent: petroleum ether/ethyl acetate = 50/1] as a powder solid: m.p. 105.3-105.8 °C (without recrystallization); 91% ee (HPLC conditions: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (major) = 9.9 min, t_R (minor) = 8.6 min); ¹H NMR (300 MHz, CDCl₃) δ 7.16 (d, J = 9.0 Hz, 1H, Ar-H), 7.06 (d, J = 2.4 Hz, 1H, Ar-H), 6.82 (dd, J_1 = 8.7 Hz, J_2 = 2.7 Hz, 1H, Ar-H), 6.24 (s, 1H, Ar-H), 6.08-5.89 (m, 2H, =CH × 2), 4.60-4.49 (m, 2H, NCH₂), 3.85 (s, 3H, OCH₃), 3.75-3.60 (m, 1H, CH), 1.86-1.70 (m, 2H, CH₂), 1.40-1.15 (m, 4H, CH₂ × 2), 0.86 (t, J = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 154.4, 139.1, 130.9, 128.6, 127.4, 120.1, 110.2, 109.4, 101.9, 96.5, 55.9, 41.8, 36.3, 34.3, 27.9, 22.8, 14.0; IR (KBr) ν (cm⁻¹) 3045, 2961, 2940, 2923, 2856, 1616, 1483, 1448, 1367, 1278, 1238, 1210, 1167, 1137, 1118, 1034; MS (70 ev, EI) m/z (%) 255 (M^+ , 99.46), 213 (100); HRMS calcd for C₁₇H₂₁NO [M^+]: 255.1623, Found: 255.1622.

7.5 Synthesis of (*R*)-9-butyl-1-methyl-6,9-dihydropyrido[1,2-*a*]indole (*R*)-2e

(jf-2-039)



Following **Typical Procedure V**, the reaction of IPrAuCl (0.0326 g, 0.05 mmol, 95%), AgSbF₆ (0.0176 g, 0.05 mmol, 98%), (R_a)-1e (0.2389 g, 1 mmol), and CHCl₃ (25 mL) for 48 h at 0 °C afforded (R)-2e (0.2308 g, 88%, 91% purity) as a liquid: 90% ee (HPLC conditions: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 95/5, 0.6 mL/min, λ = 214 nm, t_R (major) = 9.8 min, t_R (minor) = 12.2 min); ¹H NMR (300 MHz, CDCl₃) δ 7.09-6.99 (m, 2H, Ar-H), 6.94-6.85 (m, 1H, Ar-H), 6.28 (s, 1H, Ar-H), 5.95-5.83 (m, 2H, =CH \times 2), 4.41 (d, J = 4.5 Hz, 2H, NCH₂), 3.74-3.56 (m, 1H, CH), 2.53 (s, 3H, CH₃), 1.75 (q, J = 7.1 Hz, 2H, CH₂), 1.38-1.13 (m, 4H, CH₂ \times 2), 0.85 (t, J = 6.9 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 137.7, 135.1, 129.0, 128.0, 127.3, 120.4, 120.1, 119.9, 106.4, 95.2, 41.8, 36.4, 34.2, 27.9, 22.8, 18.7, 14.0; IR (neat) ν (cm⁻¹) 3049, 2956, 2928, 2858, 1536, 1491, 1455, 1432, 1360, 1319, 1235, 1156; MS (70 ev, EI) *m/z* (%) 240 (M⁺+1, 22.62), 239 (M⁺, 52.14), 182 (100); HRMS calcd for C₁₇H₂₁N [M⁺]: 239.1674, Found: 239.1676.

7.6 Synthesis of (*R*)-9-butyl-3-chloro-6,9-dihydropyrido[1,2-*a*]indole (*R*)-2f (jf-2-062)

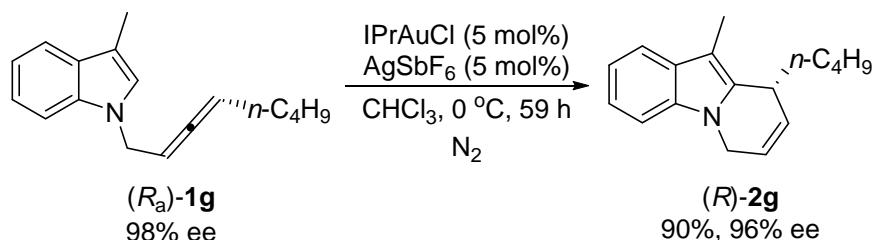


Following **Typical Procedure V**, the reaction of IPrAuCl (0.0195 g, 0.03 mmol, 95%), AgSbF₆ (0.0106 g, 0.03 mmol, 98%), (R_a)-1f (0.2594 g, 1 mmol), and CHCl₃ (25 mL) for 58 h at 0 °C afforded (R)-2f (0.2408 g, 93%) as a powder solid: m.p. 77.5-78.9 °C (without recrystallization); 78% ee (HPLC conditions: Chiralcel OZ-H column, *n*-hexane/*i*-PrOH = 100/0, 1 mL/min, λ = 214 nm, t_R (major) = 22.4

min, t_R (minor) = 16.8 min); $[\alpha]_D^{20} = -65.7$ ($c = 1.01$, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.46 (d, $J = 8.1$ Hz, 1H, Ar-H), 7.26 (s, 1H, Ar-H), 7.07 (dd, $J_1 = 8.3$ Hz, $J_2 = 2.0$ Hz, 1H, Ar-H), 6.28 (s, 1H, Ar-H), 6.07-5.92 (m, 2H, =CH \times 2), 4.59-4.46 (m, 2H, NCH_2), 3.76-3.60 (m, 1H, CH), 1.84-1.69 (m, 2H, CH_2), 1.41-1.13 (m, 4H, $\text{CH}_2 \times 2$), 0.86 (t, $J = 7.1$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 139.3, 135.9, 127.5, 126.8, 126.1, 120.5, 120.3, 119.8, 108.9, 96.9, 41.8, 36.3, 34.2, 27.9, 22.8, 14.0; IR (KBr) ν (cm^{-1}) 3041, 2956, 2922, 2858, 1664, 1605, 1561, 1536, 1467, 1458, 1414, 1392, 1351, 1318, 1275, 1222, 1183, 1169, 1145, 1104, 1059; MS (70 ev, EI) m/z (%) 261 ($\text{M}^{+}(^{37}\text{Cl})$, 14.04), 259 ($\text{M}^{+}(^{35}\text{Cl})$, 38.66), 202 (100); HRMS calcd for $\text{C}_{16}\text{H}_{18}^{35}\text{ClN}$ [M^+]: 259.1128, Found: 259.1129.

7.7 Synthesis of (*R*)-9-butyl-10-methyl-6,9-dihydropyrido[1,2-*a*]indole (*R*)-2g

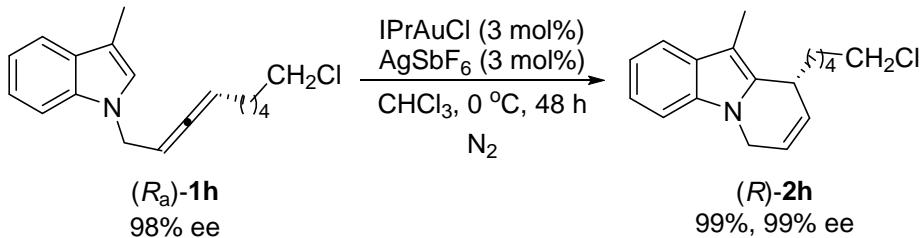
(jf-2-096)



Following **Typical Procedure V**, the reaction of IPrAuCl (0.0327 g, 0.05 mmol, 95%), AgSbF₆ (0.0175 g, 0.05 mmol, 98%), (*R*_a)-1g (0.2390 g, 1 mmol), and CHCl₃ (25 mL) for 59 h at 0 °C afforded (*R*)-2g (0.2149 g, 90%) as a powder solid: m.p. 64.5-65.5 °C (without recrystallization); 96% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 100/1, 0.4 mL/min, $\lambda = 254$ nm, t_R (major) = 17.1 min, t_R (minor) = 18.0 min); $[\alpha]_D^{20} = -149.7$ ($c = 0.93$, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.59-7.52 (m, 1H, Ar-H), 7.30-7.23 (m, 1H, Ar-H), 7.20-7.07 (m, 2H, Ar-H), 6.10-5.97 (m, 2H, =CH \times 2), 4.62-4.51 (m, 2H, NCH_2), 3.80-3.69 (m, 1H, CH), 2.30 (s, 3H, CH_3), 1.82-1.67 (m, 2H, CH_2), 1.35-1.17 (m, 3H, $\text{CH}_2 +$ one proton of CH_2), 1.17-1.01 (m, 1H, one proton of CH_2), 0.83 (t, $J = 7.1$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 135.2, 133.8, 128.8, 127.6, 120.7, 120.2, 119.0, 117.8, 108.4, 104.0, 41.9, 35.5, 33.2, 27.5, 22.7, 14.0, 8.8; IR (neat) ν (cm^{-1}) 3042, 2956, 2929, 2858, 1665, 1615, 1568, 1462, 1426, 1384, 1368, 1328, 1313, 1241, 1196, 1169, 1056, 1011; MS

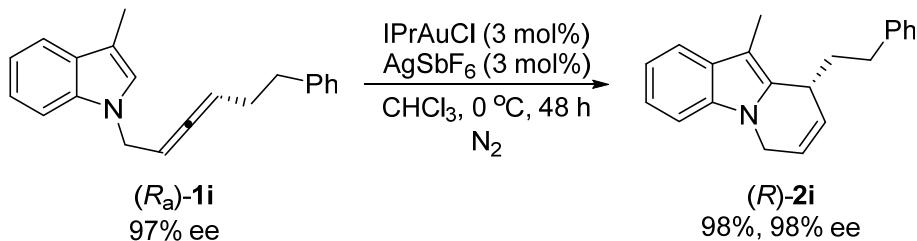
(70 ev, EI) m/z (%) 240 ($M^+ + 1$, 5.34), 239 (M^+ , 29.45), 182 (100); HRMS calcd for $C_{17}H_{21}N$ [M^+]: 239.1674, Found: 239.1672.

7.8 Synthesis of (*R*)-9-(5-chloropentyl)-10-methyl-6,9-dihydropyrido[1,2-*a*]indole (*R*)-2h (jf-2-144)



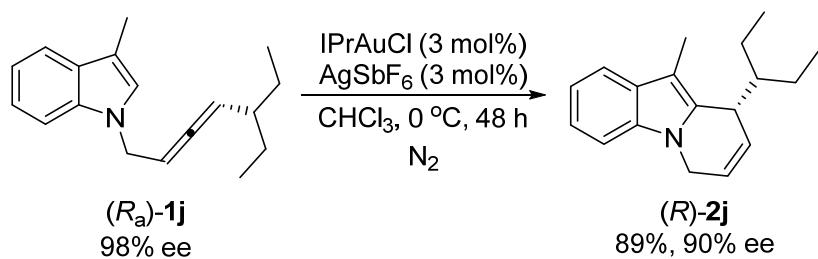
Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), (*R*_a)-1h (0.2862 g, 1 mmol, 97%), and CHCl₃ (25 mL) for 48 h at 0 °C afforded (*R*)-2h (0.2849 g, 99%, 96% purity) [eluent: petroleum ether] as a liquid: 99% ee (HPLC conditions: Chiralcel IA-H column, *n*-hexane/*i*-PrOH = 100/1, 0.7 mL/min, λ = 254 nm, t_R (major) = 7.2 min, t_R (minor) = 7.8 min); $[\alpha]_D^{20} = -136.7$ ($c = 1.41$, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.55-7.47 (m, 1H, Ar-H), 7.20-7.06 (m, 3H, Ar-H), 6.00-5.89 (m, 2H, =CH × 2), 4.51-4.38 (m, 2H, NCH₂), 3.72-3.63 (m, 1H, CH), 3.37 (t, $J = 6.6$ Hz, 2H, CH₂Cl), 2.26 (s, 3H, CH₃), 1.82-1.52 (m, 4H, CH₂ × 2), 1.39-1.15 (m, 3H, CH₂ + one proton of CH₂), 1.15-0.96 (m, 1H, one proton of CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 135.1, 133.4, 128.7, 127.3, 120.8, 120.2, 119.0, 117.7, 108.4, 104.0, 44.9, 41.8, 35.4, 33.0, 32.4, 26.8, 24.5, 8.8; IR (neat) ν (cm⁻¹) 3042, 2934, 2858, 1666, 1613, 1568, 1471, 1462, 1385, 1368, 1328, 1313, 1284, 1240, 1197, 1169, 1150, 1122, 1054, 1011; MS (70 ev, EI) m/z (%) 290 ($M^+(^{37}\text{Cl}) + 1$, 1.00), 289 ($M^+(^{37}\text{Cl})$, 5.11), 288 ($M^+(^{35}\text{Cl}) + 1$, 3.17), 287 ($M^+(^{35}\text{Cl})$, 16.00), 182 (100); HRMS calcd for $C_{18}H_{22}N^{35}\text{Cl}$ [M^+]: 287.1441, Found: 287.1438.

7.9 Synthesis of (*R*)-10-methyl-9-phenethyl-6,9-dihydropyrido[1,2-*a*]indole (*R*)-2i (jf-3-065)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0106 g, 0.03 mmol, 98%), (R_a)-1i (0.2856 g, 1 mmol), and CHCl₃ (25 mL) for 48 h at 0 °C afforded (R)-2i (0.2794 g, 98%) [eluent: petroleum ether/diethyl ether = 50/1] as a needle solid: m.p. 101.1-102.2 °C (DCM/hexane); 98% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 254 nm, t_R (major) = 11.9 min, t_R (minor) = 12.9 min); $[\alpha]_D^{20} = -141.7$ ($c = 0.78$, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.56 (d, J = 7.2 Hz, 1H, Ar-H), 7.30-7.07 (m, 8H, Ar-H), 6.17-6.00 (m, 2H, =CH × 2), 4.60 (d, J = 3.6 Hz, 2H, NCH₂), 3.89-3.77 (m, 1H, CH), 2.66-2.51 (m, 1H, one proton of PhCH₂), 2.46-2.33 (m, 1H, one proton of PhCH₂), 2.30 (s, 3H, CH₃), 2.20-1.98 (m, 2H, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 142.1, 135.3, 133.2, 128.9, 128.3, 127.2, 125.7, 121.3, 120.4, 119.1, 117.9, 108.5, 104.4, 42.0, 37.4, 33.0, 31.6, 8.9; IR (KBr) ν (cm⁻¹) 3026, 2947, 2921, 2858, 1601, 1577, 1560, 1494, 1471, 1463, 1425, 1386, 1369, 1328, 1312, 1240, 1197, 1167, 1122, 1080; MS (70 ev, EI) m/z (%) 288 (M⁺+1, 4.32), 287 (M⁺, 21.04), 182 (100); Anal. Calcd. for C₂₁H₂₁N (%): C 87.76, H 7.37, N 4.87, Found: C 87.76, H 7.29, N 4.67.

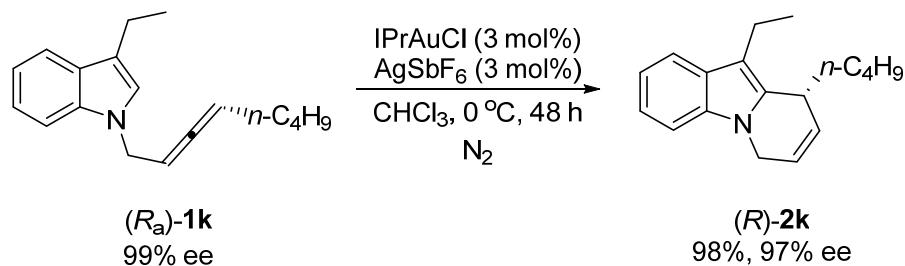
7.10 Synthesis of (R)-10-methyl-9-(pentan-3-yl)-6,9-dihydropyrido[1,2-*a*]indole (R)-2j (jf-3-095)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), (R_a)-1j (0.2520 g, 1 mmol), and CHCl₃ (25 mL) for 48 h at 0 °C afforded (R)-2j (0.2239 g, 89%) [eluent: petroleum ether] as

a liquid: 90% ee (HPLC conditions: Chiralcel OZ-H column, *n*-hexane/*i*-PrOH = 100/0, 1.0 mL/min, λ = 214 nm, t_R (major) = 11.4 min, t_R (minor) = 10.4 min); $[\alpha]_D^{20}$ = -145.8 (c = 0.89, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.54 (d, J = 7.5 Hz, 1H, Ar-H), 7.24 (d, J = 7.5 Hz, 1H, Ar-H), 7.21-7.07 (m, 2H, Ar-H), 6.14-5.94 (m, 2H, =CH × 2), 4.66-4.42 (m, 2H, NCH₂), 3.98-3.80 (m, 1H, CH), 2.30 (s, 3H, Ar-CH₃), 1.84-1.70 (m, 1H, CH), 1.65-1.52 (m, 1H, one proton of CH₂), 1.42-1.24 (m, 1H, one proton of CH₂), 1.12 (t, J = 7.4 Hz, 3H, CH₃), 1.02 (quint, J = 7.2 Hz, 2H, CH₂), 0.65 (t, J = 7.5 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 135.2, 134.1, 128.9, 124.2, 122.0, 120.1, 118.9, 117.8, 108.4, 103.8, 47.5, 42.3, 35.1, 23.7, 23.0, 12.5, 12.2, 9.0; IR (neat) ν (cm⁻¹) 3042, 2959, 2928, 2873, 1665, 1567, 1462, 1426, 1385, 1369, 1312, 1241, 1198, 1173, 1122, 1094, 1058, 1012; MS (70 ev, EI) *m/z* (%) 254 (M⁺+1, 3.24), 253 (M⁺, 15.66), 182 (100); HRMS calcd for C₁₈H₂₃N [M⁺]: 253.1830, Found: 253.1832.

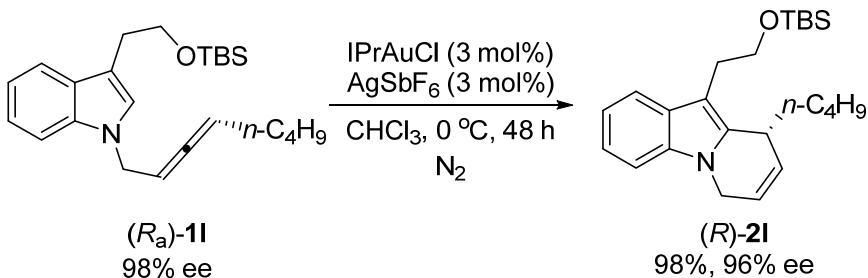
7.11 Synthesis of (*R*)-9-butyl-10-ethyl-6,9-dihydropyrido[1,2-*a*]indole (*R*)-2k (jf-3-075)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0197 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), (*R*_a)-1k (0.2541 g, 1 mmol), and CHCl₃ (25 mL) for 48 h at 0 °C afforded (*R*)-2k (0.2501 g, 98%) [eluent: petroleum ether/diethyl ether = 50/1] as a liquid: 97% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (major) = 4.4 min, t_R (minor) = 4.9 min); $[\alpha]_D^{20}$ = -185.9 (c = 1.05, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, J = 6.6 Hz, 1H, Ar-H), 7.25 (d, J = 7.5 Hz, 1H, Ar-H), 7.20-7.07 (m, 2H, Ar-H), 6.11-5.97 (m, 2H, =CH × 2), 4.61-4.49 (m, 2H, NCH₂), 3.83-3.70 (m, 1H, CH), 2.78 (q, J = 7.5 Hz, 2H, Ar-CH₂), 1.82-1.68 (m, 2H, CH₂), 1.35-1.18 (m, 6H, CH₂ +

one proton of $\text{CH}_2 + \text{CH}_3$), 1.15-1.00 (m, 1H, one proton of CH_2), 0.83 (t, $J = 7.1$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 135.5, 133.3, 127.9, 127.8, 120.7, 120.2, 119.0, 118.2, 111.0, 108.6, 42.0, 36.2, 33.2, 27.3, 22.8, 17.7, 15.4, 14.0; IR (neat) ν (cm^{-1}) 3042, 2959, 2929, 2857, 1665, 1612, 1565, 1471, 1456, 1423, 1372, 1331, 1315, 1235, 1193, 1169, 1126, 1069, 1015; MS (70 ev, EI) m/z (%) 254 ($\text{M}^+ + 1$, 7.59), 253 (M^+ , 33.67), 196 (100); HRMS calcd for $\text{C}_{18}\text{H}_{23}\text{N}$ [M^+]: 253.1830, Found: 253.1829.

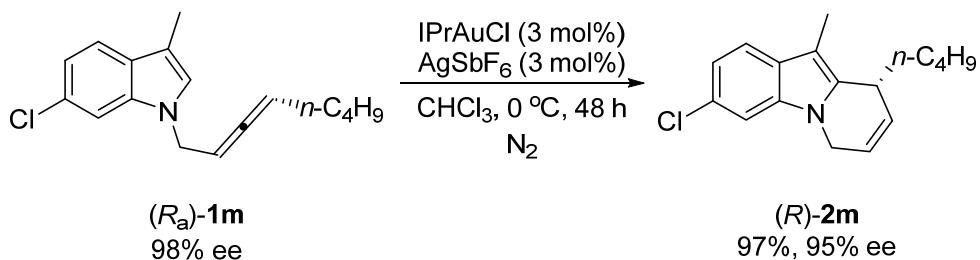
7.12 Synthesis of (*R*)-9-butyl-10-(2-((*tert*-butyldimethylsilyl)oxy)-ethyl)-6,9-dihydropyrido[1,2-*a*]indole (*R*)-2I (jf-3-057)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0195 g, 0.03 mmol, 95%), AgSbF₆ (0.0105 g, 0.03 mmol, 98%), (*R*_a)-1I (0.3796 g, 1 mmol), and CHCl₃ (25 mL) for 48 h at 0 °C afforded (*R*)-2I (0.3749 g, 98%) [eluent: petroleum ether/ethyl acetate = 100/1] as a liquid: 96% ee (HPLC conditions: Chiralcel IF-H column, *n*-hexane/*i*-PrOH = 100/0, 1.0 mL/min, $\lambda = 214$ nm, t_R (major) = 10.2 min, t_R (minor) = 10.9 min); $[\alpha]_D^{20} = -118.8$ ($c = 0.825$, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.60 (d, $J = 7.2$ Hz, 1H, Ar-H), 7.28 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.22-7.10 (m, 2H, Ar-H), 6.14-6.00 (m, 2H, =CH × 2), 4.64-4.48 (m, 2H, NCH₂), 3.94-3.72 (m, 3H, OCH₂ + CH), 3.04 (t, $J = 8.0$ Hz, 2H, CH₂), 1.79 (q, $J = 6.9$ Hz, 2H, CH₂), 1.39-1.19 (m, 3H, CH₂ + one proton of CH₂), 1.17-1.02 (m, 1H, one proton of CH₂), 0.93 (s, 9H, CH₃ × 3), 0.85 (t, $J = 6.9$ Hz, 3H, CH₃), 0.06 (s, 6H, CH₃ × 2); ^{13}C NMR (75 MHz, CDCl_3) δ 135.4, 134.9, 128.3, 127.7, 120.7, 120.3, 119.2, 118.1, 108.6, 105.2, 63.8, 42.1, 36.4, 33.2, 28.6, 27.4, 26.0, 22.8, 18.4, 14.0, -5.24, -5.29; IR (neat) ν (cm^{-1}) 3043, 2955, 2929, 2857, 1666, 1611, 1565, 1471, 1461, 1425, 1370, 1330, 1314, 1254,

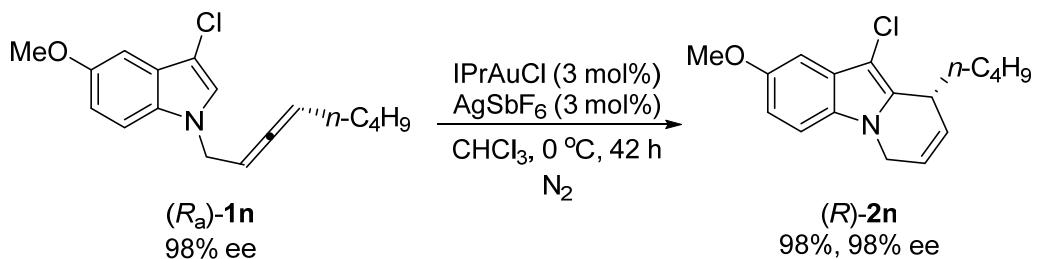
1213, 1191, 1169, 1093, 1067, 1014; MS (70 ev, EI) m/z (%) 384 ($M^+ + 1$, 18.59), 383 (M^+ , 56.82), 238 (100); HRMS calcd for $C_{24}H_{37}NOSi$ [M^+]: 383.2644, Found: 383.2644.

7.13 Synthesis of (*R*)-9-butyl-3-chloro-10-methyl-6,9-dihydropyrido[1,2-*a*]indole (*R*)-2m (jf-2-200)



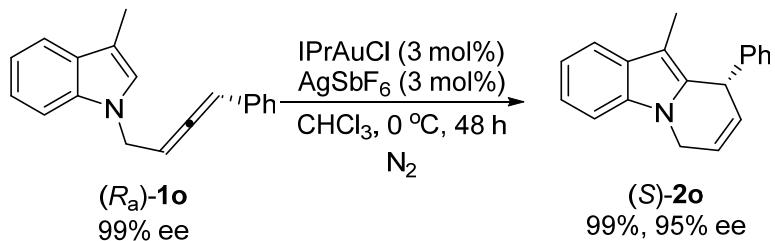
Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0194 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), (*R*_a)-1m (0.2736 g, 1 mmol), and CHCl₃ (25 mL) for 48 h at 0 °C afforded (*R*)-2m (0.2067 g, 97%) [eluent: petroleum ether] as a liquid: 95% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 100/1, 1.0 mL/min, λ = 254 nm, t_R (major) = 5.0 min, t_R (minor) = 6.2 min); $[\alpha]_D^{20}$ = -122.7 (c = 0.99, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.41 (d, J = 8.4 Hz, 1H, Ar-H), 7.22 (s, 1H, Ar-H), 7.06 (dd, J_1 = 8.4 Hz, J_2 = 1.5 Hz, 1H, Ar-H), 6.12-5.93 (m, 2H, =CH × 2), 4.58-4.37 (m, 2H, NCH₂), 3.75-3.64 (m, 1H, CH), 2.25 (s, 3H, CH₃), 1.79-1.63 (m, 2H, CH₂), 1.36-1.15 (m, 3H, CH₂ + one proton of CH₂), 1.15-0.98 (m, 1H, one proton of CH₂), 0.83 (t, J = 6.9 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 135.5, 134.7, 127.6, 127.3, 126.1, 120.4, 119.5, 118.6, 108.5, 104.3, 42.0, 35.4, 33.2, 27.5, 22.7, 14.0, 8.8; IR (neat) ν (cm⁻¹) 3040, 2956, 2929, 2858, 1854, 1667, 1611, 1560, 1475, 1462, 1422, 1385, 1365, 1322, 1281, 1236, 1198, 1169, 1068, 1003; MS (70 ev, EI) m/z (%) 275 ($M^+(^{37}\text{Cl})$, 11.56), 273 ($M^+(^{35}\text{Cl})$, 32.44), 216 (100); HRMS calcd for C₁₇H₂₀N³⁵Cl [M⁺]: 273.1284, Found: 273.1284.

7.14 Synthesis of (*R*)-9-butyl-10-chloro-2-methoxy-6,9-dihydropyrido[1,2-*a*]indole (*R*)-2n (jf-3-084)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), (R_a)-1n (0.2888 g, 1 mmol), and CHCl₃ (25 mL) for 42 h at 0 °C afforded (R)-2n (0.2818 g, 98%) [eluent: petroleum ether/diethyl ether = 20/1] as a prism solid: m.p. 98.7-99.3 °C (DCM/hexane): 98% ee (HPLC conditions: Chiralcel OD-H column, n-hexane/i-PrOH = 95/5, 0.5 mL/min, λ = 214 nm, t_R (major) = 10.0 min, t_R (minor) = 11.8 min); $[\alpha]_D^{20} = -181.4$ ($c = 0.87$, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.17 (d, J = 8.7 Hz, 1H, Ar-H), 7.03 (d, J = 2.4 Hz, 1H, Ar-H), 6.85 (dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz, 1H, Ar-H), 6.08-5.98 (m, 2H, =CH \times 2), 4.54 (d, J = 3.6 Hz, 2H, NCH₂), 3.88 (s, 3H, OMe), 3.83-3.74 (m, 1H, CH), 2.03-1.76 (m, 2H, CH₂), 1.37-1.18 (m, 3H, CH₂ + one proton of CH₂), 1.18-0.99 (m, 1H, one proton of CH₂), 0.84 (t, J = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 154.8, 133.8, 129.3, 127.1, 126.0, 120.2, 111.8, 109.9, 99.5, 98.8, 55.8, 42.2, 33.9, 33.1, 27.4, 22.6, 14.0; IR (KBr) ν (cm⁻¹) 3035, 3008, 2950, 2925, 2860, 1661, 1620, 1576, 1486, 1466, 1450, 1426, 1371, 1340, 1287, 1220, 1185, 1164, 1030; MS (70 ev, EI) m/z (%) 291 (M⁺(³⁷Cl), 12.33), 289 (M⁺(³⁵Cl), 34.06), 232 (100); Anal. Calcd. for C₁₇H₂₀ClN (%): C 70.46, H 6.96, N 4.83, Found: C 70.45, H 6.96, N 4.60.

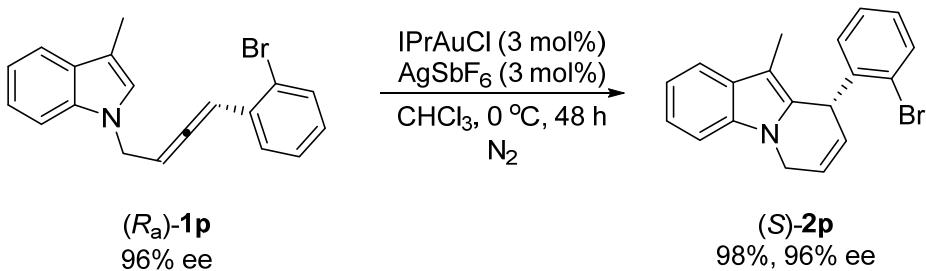
7.15 Synthesis of (S)-10-methyl-9-phenyl-6,9-dihydropyrido[1,2-a]indole (S)-2o (jf-2-158)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0195 g, 0.03 mmol, 95%), AgSbF₆ (0.0106 g, 0.03 mmol, 98%), (R_a)-1o (0.2591 g, 1 mmol), and CHCl₃

(25 mL) for 48 h at 0 °C afforded (*S*)-**2o** (0.2575 g, 99%) [eluent: petroleum ether] as a powder solid: m.p. 143.8–146.3 °C (without recrystallization); 95% ee (HPLC conditions: Chiralcel IA-H column, *n*-hexane/*i*-PrOH = 100/1, 0.7 mL/min, λ = 254 nm, t_R (major) = 9.9 min, t_R (minor) = 10.6 min); $[\alpha]_D^{20}$ = -207.1 (c = 1.03, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, J = 7.8 Hz, 1H, Ar-H), 7.32 (d, J = 8.1 Hz, 1H, Ar-H), 7.28–7.09 (m, 7H, Ar-H), 6.10–5.96 (m, 2H, =CH × 2), 4.86–4.58 (m, 3H, NCH₂ + CH), 1.97 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 143.3, 135.2, 132.2, 128.7, 128.6, 128.0, 127.8, 126.4, 120.6, 119.2, 119.0, 118.0, 108.7, 105.9, 41.9, 40.5, 8.6; IR (KBr) ν (cm⁻¹) 3050, 3024, 2912, 2857, 1488, 1470, 1459, 1452, 1418, 1388, 1367, 1315, 1242, 1197, 1167; MS (70 ev, EI) *m/z* (%) 260 (M⁺+1, 19.64), 259 (M⁺, 100); HRMS calcd for C₁₉H₁₇N [M⁺]: 259.1361, Found: 259.1361.

7.16 Synthesis of (*S*)-9-(2-bromophenyl)-10-methyl-6,9-dihydropyrido-[1,2-*a*]indole (*S*)-**2p** (jf-2-174)

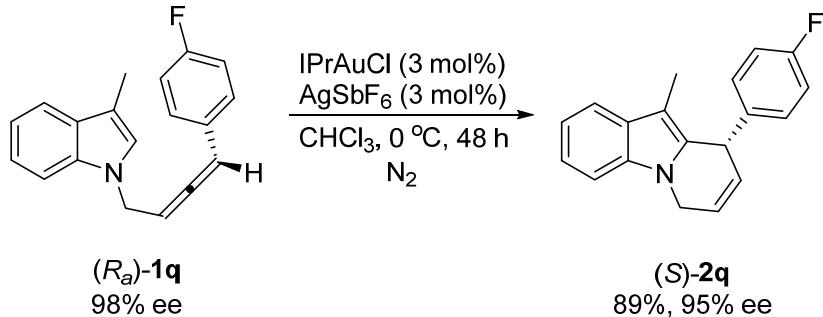


Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0194 g, 0.03 mmol, 95%), AgSbF₆ (0.0106 g, 0.03 mmol, 98%), (R_a)-**1p** (0.3287 g, 1 mmol), and CHCl₃ (25 mL) for 48 h at 0 °C afforded (*S*)-**2p** (0.3220 g, 98%) [eluent: petroleum ether] as a powder solid: m.p. 91.1–92.1 °C (without recrystallization); 96% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, λ = 254 nm, t_R (major) = 9.6 min, t_R (minor) = 12.7 min); $[\alpha]_D^{20}$ = -131.7 (c = 0.625, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.55 (t, J = 8.0 Hz, 2H, Ar-H), 7.35 (d, J = 8.1 Hz, 1H, Ar-H), 7.27–6.98 (m, 4H, Ar-H), 6.78 (d, J = 7.2 Hz, 1H, Ar-H), 6.08 (q, J = 10.7 Hz, 2H, =CH × 2), 5.49–5.30 (m, 1H, CH), 4.78 (d, J = 19.8 Hz, 1H, one proton of NCH₂), 4.66 (d, J = 19.5 Hz, 1H, one proton of NCH₂), 1.93 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 142.4, 135.3, 132.6, 131.9, 130.0, 128.6, 128.1, 128.0, 125.8, 123.1, 120.8,

119.5, 119.4, 118.2, 108.7, 106.1, 41.8, 39.5, 8.4; IR (KBr) ν (cm⁻¹) 3045, 2913, 1471, 1460, 1438, 1432, 1386, 1366, 1315, 1307, 1266, 1241, 1200, 1172, 1044, 1023, 1010; MS (70 ev, EI) m/z (%) 339 ($M^+{^{81}\text{Br}}$, 76.10), 337 ($M^+{^{79}\text{Br}}$, 100); HRMS calcd for C₁₉H₁₆N⁷⁹Br [M⁺]: 337.0466, Found: 337.0467.

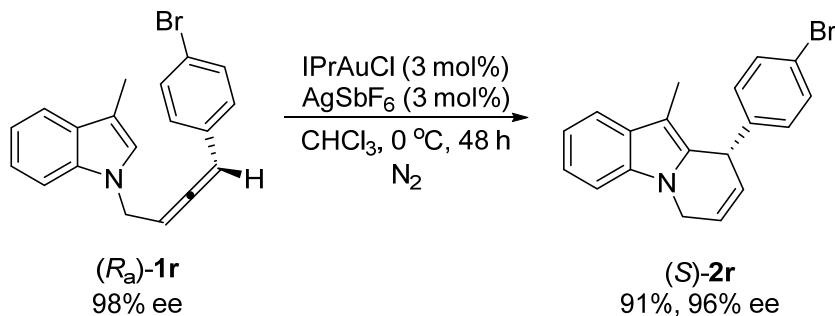
7.17 Synthesis of

(S)-9-(4-fluorophenyl)-10-methyl-6,9-dihydropyrido[1,2-*a*]indole (*S*)-2q (jf-3-034)



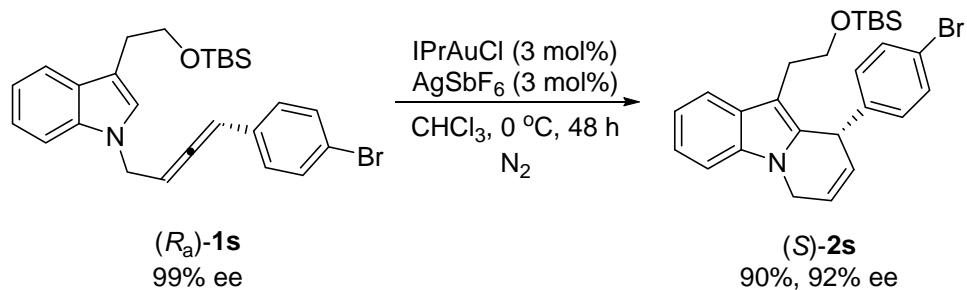
Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0194 g, 0.03 mmol, 95%), AgSbF₆ (0.0105 g, 0.03 mmol, 98%), (*R*_a)-**1q** (0.2800 g, 1 mmol), and CHCl₃ (25 mL) for 48 h at 0 °C afforded (*S*)-**2q** (0.2500 g, 89%) [eluent: petroleum ether/diethyl ether = 50/1] as a needle solid: m.p. 123.1-124.2 °C (DCM/hexane); 95% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (major) = 9.3 min, t_R (minor) = 7.8 min); $[\alpha]_D^{20} = -205.1$ (c = 1.20, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.51 (d, J = 7.8 Hz, 1H, Ar-H), 7.29 (d, J = 7.8 Hz, 1H, Ar-H), 7.23-7.16 (m, 1H, Ar-H), 7.16-7.09 (m, 1H, Ar-H), 7.09-7.01 (m, 2H, Ar-H), 6.90 (t, J = 8.6 Hz, 2H, Ar-H), 6.03-5.91 (m, 2H, =CH × 2), 4.82-4.51 (m, 3H, NCH₂ + CH), 1.95 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 161.4 (d, J = 243.4 Hz), 139.0 (d, J = 2.8 Hz), 135.2, 131.9, 129.2 (d, J = 7.6 Hz), 128.6, 127.7, 120.8, 119.3, 119.2, 118.1, 115.4 (d, J = 21.4 Hz), 108.7, 105.9, 41.8, 39.7, 8.6; ¹⁹F NMR (282 MHz, CDCl₃) δ -117.0; IR (KBr) ν (cm⁻¹) 1601, 1561, 1505, 1472, 1461, 1414, 1388, 1370, 1315, 1279, 1245, 1223, 1168, 1156, 1093, 1012; MS (70 ev, EI) m/z (%) 278 (M^++1 , 18.95), 277 (M^+ , 100); Anal. Calcd. for C₁₉H₁₆FN (%): C 82.28, H 5.82, N 5.05, Found: C 82.15, H 5.82, N 4.93.

7.18 Synthesis of (S)-9-(4-bromophenyl)-10-methyl-6,9-dihydropyrido-[1,2-*a*]indole (*S*)-2r (jf-3-020)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0195 g, 0.03 mmol, 95%), AgSbF₆ (0.0102 g, 0.03 mmol, 98%), (R_a)-1r (0.3390 g, 1 mmol), and CHCl₃ (25 mL) for 48 h at 0 °C afforded (S)-2r (0.3089 g, 91%) [eluent: petroleum ether/diethyl ether = 100/ 1] as a needle solid: m.p. 156.5-157.2 °C (DCM/hexane); 96% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, λ = 254 nm, t_R (major) = 11.7 min, t_R (minor) = 9.5 min); $[\alpha]_D^{20} = -227.2$ ($c = 1.02$, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.40-7.30 (m, 3H, Ar-H), 7.25-7.18 (m, 1H, Ar-H), 7.14 (t, $J = 7.1$ Hz, 1H, Ar-H), 7.01 (d, $J = 8.4$ Hz, 2H, Ar-H) 6.09-5.96 (m, 2H, =CH × 2), 4.84-4.59 (m, 3H, NCH₂ + CH), 1.96 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 142.4, 135.3, 131.7, 131.5, 129.5, 128.6, 127.4, 120.9, 120.3, 119.5, 119.4, 118.2, 108.7, 106.1, 41.9, 40.0, 8.6; IR (KBr) ν (cm⁻¹) 3038, 1485, 1473, 1462, 1427, 1402, 1388, 1370, 1319, 1245, 1201, 1180, 1165, 1149, 1101, 1069, 1008; MS (70 ev, EI) *m/z* (%) 339 (M⁺(⁸¹Br), 80.04), 337 (M⁺(⁷⁹Br), 100); Anal. Calcd. for C₁₉H₁₆BrN (%): C 67.47, H 4.77, N 4.14, Found: C 67.23, H 4.91, N 3.96.

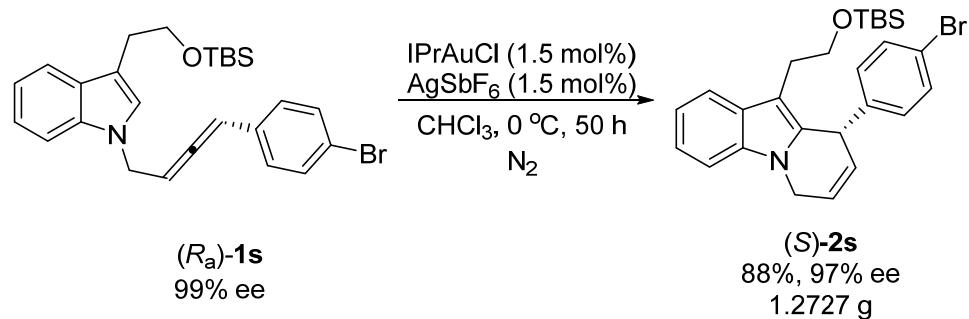
7.19 Synthesis of (S)-9-(4-bromophenyl)-10-((tert-butylidimethylsilyl)oxy)-ethyl)-6,9-dihydropyrido[1,2-*a*]indole (S)-2s (jf-3-096)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0195 g, 0.03 mmol,

95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), (*R*_a)-**1s** (0.4824 g, 1 mmol), and CHCl₃ (25 mL) for 48 h at 0 °C afforded (*S*)-**2s** (0.4328 g, 90%) [eluent: petroleum ether/ethyl acetate = 50/1] as a powder solid: m.p. 66.3-68.7 °C (without recrystallization); 92% ee (HPLC conditions: Chiralcel IF-H column, *n*-hexane/*i*-PrOH = 100/0, 1.0 mL/min, λ = 214 nm, t_R (major) = 22.3 min, t_R (minor) = 24.9 min); $[\alpha]_D^{20} = -184.9$ ($c = 0.73$, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, J = 7.8 Hz, 1H, Ar-H), 7.38 (t, J = 7.7 Hz, 3H, Ar-H), 7.25 (t, J = 7.5 Hz, 1H, Ar-H), 7.17 (t, J = 7.4 Hz, 1H, Ar-H), 7.04 (d, J = 8.4 Hz, 2H, Ar-H), 6.12-5.99 (m, 2H, =CH × 2), 4.96-4.87 (m, 1H, CH), 4.81 (d, J = 18.3 Hz, 1H, one proton of NCH₂), 4.69 (d, J = 18.9 Hz, 1H, one proton of NCH₂) 3.65-3.50 (m, 1H, one proton of OCH₂), 3.31 (td, J_1 = 9.5 Hz, J_2 = 5.7 Hz, 1H, one proton of OCH₂), 2.85-2.65 (m, 2H, Ar-CH₂), 0.86 (s, 9H, CH₃ × 3), -0.06 (s, 3H, CH₃), -0.07 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 143.0, 135.4, 132.6, 131.8, 129.5, 128.3, 127.5, 121.0, 120.5, 119.6, 119.3, 118.5, 108.9, 107.4, 63.0, 41.9, 39.9, 28.1, 26.0, 18.4, -5.38, -5.44; IR (KBr) ν (cm⁻¹) 3047, 2951, 2926, 2856, 1586, 1485, 1471, 1459, 1422, 1403, 1388, 1373, 1359, 1317, 1256, 1247, 1212, 1169, 1109, 1068, 1011; MS (70 ev, EI) m/z (%) 484 (M⁺(⁸¹Br) + 1, 6.86), 483 (M⁺(⁸¹Br), 20.43), 482 (M⁺(⁷⁹Br) + 1, 7.54), 481 (M⁺(⁷⁹Br), 19.74), 336 (100); Anal. Calcd. for C₂₆H₃₂BrNOSi (%): C 64.72, H 6.68, N 2.90, Found: C 64.74, H 6.69, N 2.69.

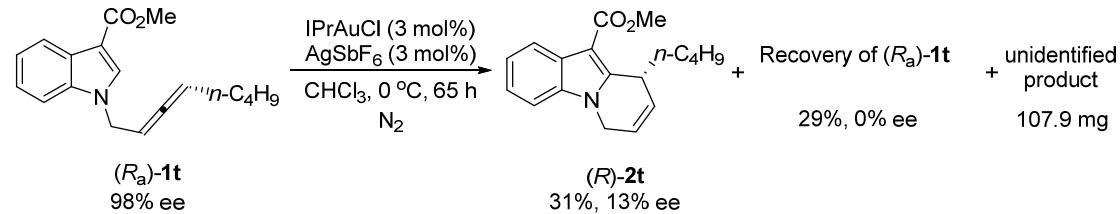
Gram-scale



To an oven-dried three-neck bottle were added IPrAuCl (0.0296 g, 0.045 mmol, 95%), AgSbF₆ (0.0158 g, 0.045 mmol, 98%), and CHCl₃ (40 mL) under nitrogen atmosphere sequentially. After stirring at room temperature for 15 min, the reaction was cooled down to 0 °C and then (*R*_a)-**1s** (1.4450 g, 0.5 mmol), and CHCl₃ (35 mL)

were added. The reaction was complete after being stirred at 0 °C for 50 h as monitored by TLC. After filtration through a short column of silica gel eluted with DCM (15 mL × 4) and evaporation, the crude product was then purified by column chromatography on silica gel to afford (*S*)-**2s** (1.2727 g, 88%) [eluent: petroleum ether/diethyl ether = 100/1] as a powder solid: 97% ee (HPLC conditions: Chiralcel IF-H column, *n*-hexane/*i*-PrOH = 100/0, 1.0 mL/min, λ = 214 nm, t_R (major) = 20.0 min, t_R (minor) = 22.7 min); $[\alpha]_D^{20} = -187.1$ ($c = 0.93$, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, J = 7.8 Hz, 1H, Ar-H), 7.38 (t, J = 7.5 Hz, 3H, Ar-H), 7.24 (t, J = 7.5 Hz, 1H, Ar-H), 7.16 (t, J = 7.4 Hz, 1H, Ar-H), 7.03 (d, J = 8.4 Hz, 2H, Ar-H), 6.12-5.99 (m, 2H, =CH × 2), 4.96-4.87 (m, 1H, CH), 4.80 (d, J = 18.6 Hz, 1H, one proton of NCH₂), 4.69 (d, J = 18.9 Hz, 1H, one proton of NCH₂), 3.63-3.50 (m, 1H, one proton of OCH₂), 3.31 (td, J_1 = 9.5 Hz, J_2 = 5.7 Hz, 1H, one proton of OCH₂), 2.85-2.65 (m, 2H, Ar-CH₂), 0.85 (s, 9H, CH₃ × 3), -0.066 (s, 3H, CH₃), -0.076 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 142.9, 135.4, 132.6, 131.8, 129.5, 128.3, 127.5, 121.0, 120.5, 119.6, 119.3, 118.5, 108.9, 107.4, 63.0, 41.9, 39.9, 28.1, 26.0, 18.4, -5.38, -5.44.

7.20 Synthesis of methyl (*R*)-9-butyl-6,9-dihydropyrido[1,2-*a*]indole-10-carboxylate (*R*)-**2t** (jf-4-173)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0104 g, 0.03 mmol, 98%), (R_a)-**1t** (0.2865 g, 1 mmol), and CHCl₃ (25 mL) for 65 h at 0 °C afforded (*R*)-**2t** (0.0911 g, 31%, 98% purity), recovery of (R_a)-**1t** (0.0814 g, 29%), and unidentified product (107.9 mg) [eluent: petroleum ether/ethyl acetate = 15/1 (500 mL) to 7/1 (400 mL)].

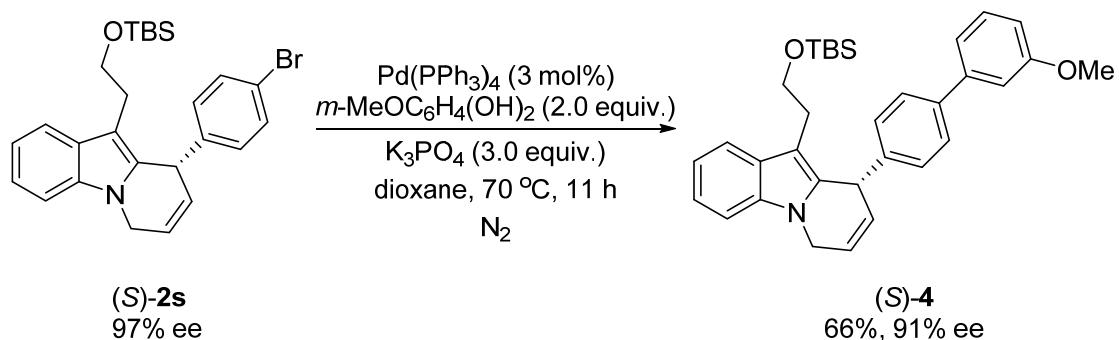
(*R*)-**2t** as a liquid: 13% ee (HPLC conditions: Chiralcel IA-H column, *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, λ = 214 nm, t_R (major) = 5.7 min, t_R (minor) =

6.7 min); $[\alpha]_D^{20} = -36.1$ ($c = 1.19$, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 8.16 (d, $J = 7.2$ Hz, 1H, Ar-H), 7.36-7.13 (m, 3H, Ar-H), 6.18-5.97 (m, 2H, =CH \times 2), 4.68-4.46 (m, 2H, NCH₂), 4.40-4.27 (m, 1H, CH), 3.93 (s, 3H, OCH₃), 1.99-1.77 (m, 2H, CH₂), 1.41-1.16 (m, 3H, CH₂ + one proton of CH₂), 1.13-0.97 (m, 1H, one proton of CH₂), 0.83 (t, $J = 7.1$ Hz, 3H, CH₃); ^{13}C NMR (75 MHz, CDCl_3) δ 165.9, 147.4, 135.4, 128.0, 126.8, 122.1, 121.8, 121.4, 119.5, 109.0, 101.4, 50.6, 42.3, 35.8, 34.6, 27.8, 22.6, 14.0; IR (neat) ν (cm⁻¹) 3045, 2956, 2925, 2858, 1694, 1532, 1457, 1435, 1378, 1356, 1315, 1259, 1209, 1159, 1114, 1040; MS (70 ev, EI) m/z (%) 284 ($M^+ + 1$, 13.70), 283 (M^+ , 62.11), 226 (100); HRMS calcd for $C_{18}\text{H}_{21}\text{NO}_2$ [M^+]: 283.1572, Found: 283.1573.

Recovery of (*R*_a)-**1t** as a liquid: 0% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, $\lambda = 214$ nm, t_R (major) = 25.0 min, t_R (minor) = 23.9 min); ^1H NMR (300 MHz, CDCl_3) δ 8.22-8.13 (m, 1H, Ar-H), 7.84 (s, 1H, Ar-H), 7.41-7.32 (m, 1H, Ar-H), 7.30-7.20 (m, 2H, Ar-H), 5.33-5.14 (m, 2H, CH=C=CH), 4.69 (dd, $J_1 = 6.0$ Hz, $J_2 = 2.7$ Hz, 2H, NCH₂), 3.90 (s, 3H, OCH₃), 2.00-1.82 (m, 2H, CH₂), 1.32-1.14 (m, 4H, CH₂ \times 2), 0.85 (t, $J = 7.1$ Hz, 3H, CH₃).

8. Syntheses of simplified analogues of (-)-Goniomitine.

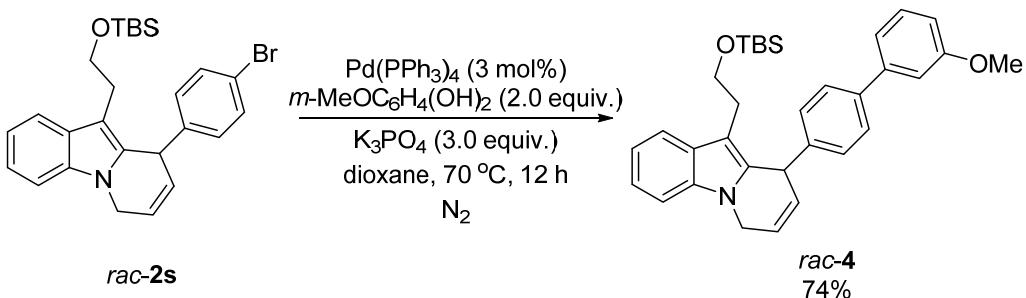
8.1 Synthesis of (*S*)-10-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-9-(3'-methoxy-[1,1'-biphenyl]-4-yl)-6,9-dihydropyrido[1,2-*a*]indole (*S*)-4⁷ (jf-3-140)



To an oven-dried Schlenk tube were added K_3PO_4 (127.4 mg, 0.4 mmol), $\text{Pd}(\text{PPh}_3)_4$ (7.2 mg, 0.006 mmol), (*S*)-**2s** (97.0 mg, 0.2 mmol), 3-methoxyphenylboronic acid

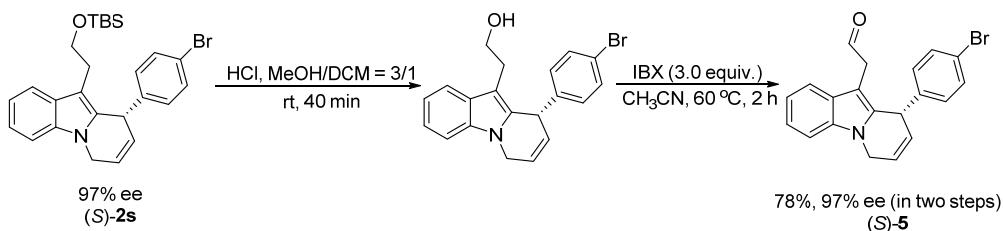
(62.6 mg, 0.4 mmol), and dioxane (2 mL) under nitrogen atmosphere sequentially. The reaction was complete after being stirred at 70 °C for 11 h as monitored by TLC. The resulting mixture was diluted with H₂O (5 mL) and DCM (5 mL). The organic layer was separated and the aqueous layer was extracted with DCM (5 mL × 2). The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. After filtration and evaporation, the residue was purified by column chromatography on silica gel to afford (*S*)-**4** (67.2 mg, 66%) [eluent: petroleum ether/ethyl acetate = 50/1] as a liquid: 91% ee (HPLC conditions: Chiralcel IA-H column, *n*-hexane/*i*-PrOH = 100/1, 0.5 mL/min, λ = 214 nm, t_R (major) = 15.8 min, t_R (minor) = 19.8 min); $[\alpha]_D^{20}$ = -207.5 (c = 1.14, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.58 (d, J = 7.5 Hz, 1H, Ar-H), 7.47 (d, J = 8.4 Hz, 2H, Ar-H), 7.35 (d, J = 7.7 Hz, 1H, Ar-H), 7.31 (d, J = 7.8 Hz, 1H, Ar-H), 7.26-7.09 (m, 5H, Ar-H), 7.09-7.04 (m, 1H, Ar-H), 6.87 (ddd, J_1 = 8.3 Hz, J_2 = 2.6 Hz, J_3 = 0.9 Hz, 1H, Ar-H), 6.17-5.99 (m, 2H, CH=CH), 5.02-4.91 (m, 1H, CH), 4.81 (d, J = 17.4 Hz, 1H, one proton of NCH₂), 4.69 (d, J = 17.4 Hz, 1H, one proton of NCH₂), 3.84 (s, 3H, OCH₃), 3.64-3.50 (m, 1H, one proton of OCH₂), 3.34 (td, J_1 = 9.3 Hz, J_2 = 5.6 Hz, 1H, one proton of OCH₂), 2.89-2.68 (m, 2H, Ar-CH₂), 0.80 (s, 9H, CH₃ × 3), -0.012 (s, 3H, CH₃), -0.013 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 159.9, 143.1, 142.3, 139.5, 135.4, 133.1, 129.7, 128.4, 128.1, 127.9, 127.5, 120.8, 119.6, 119.5, 119.0, 118.5, 112.7, 112.6, 108.8, 107.2, 63.0, 55.2, 42.0, 40.1, 28.2, 26.0, 18.3, -5.4; IR (neat) ν (cm⁻¹) 3044, 2951, 2928, 2855, 1600, 1566, 1471, 1460, 1403, 1370, 1317, 1295, 1254, 1213, 1169, 1093, 1032, 1015; MS (70 ev, EI) m/z (%) 510 (M⁺+1, 17.52), 509 (M⁺, 43.55), 364 (100); HRMS calcd for C₃₃H₃₉NO₂Si [M⁺]: 509.2750, Found: 509.2752.

8.2 Synthesis of 10-((*tert*-butyldimethylsilyl)oxy)ethyl)-9-(3'-methoxy-[1,1'-biphenyl]-4-yl)-6,9-dihydropyrido[1,2-*a*]indole *rac*-4**⁷ (jf-**3-158**).**



Following the preparation of (*S*)-4, the reaction of K_3PO_4 (128.0 mg, 0.6 mmol), $\text{Pd}(\text{PPh}_3)_3$ (7.3 mg, 0.006 mmol), *rac-2s* (96.6 mg, 0.2 mmol), 3-methoxyphenylboronic acid (63.0 mg, 0.4 mmol), and dioxane (2 mL) for 12 h at 70 $^\circ\text{C}$ afforded *rac-4* (75.2 mg, 74%) [eluent: petroleum ether/ethyl acetate = 50/1] as a powder solid: m.p. 97.3-98.7 $^\circ\text{C}$ (without recrystallization); ^1H NMR (300 MHz, CDCl_3) δ 7.58 (d, J = 7.8 Hz, 1H, Ar-H), 7.46 (d, J = 8.1 Hz, 2H, Ar-H), 7.37-7.27 (m, 2H, Ar-H), 7.25-7.08 (m, 5H, Ar-H), 7.08-7.04 (m, 1H, Ar-H), 6.85 (ddd, J_1 = 8.1 Hz, J_2 = 2.4 Hz, J_3 = 0.6 Hz, 1H, Ar-H), 6.12-5.96 (m, 2H, CH=CH), 5.00-4.89 (m, 1H, CH), 4.78 (d, J = 17.4 Hz, 1H, one proton of NCH_2), 4.65 (d, J = 17.4 Hz, 1H, one proton of NCH_2), 3.82 (s, 3H, OCH_3), 3.62-3.50 (m, 1H, one proton of OCH_2), 3.34 (td, J_1 = 9.5 Hz, J_2 = 5.7 Hz, 1H, one proton of OCH_2), 2.90-2.69 (m, 2H, Ar-CH₂), 0.81 (s, 9H, $\text{CH}_3 \times 3$), -0.012 (s, 3H, CH_3), -0.013 (s, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 159.9, 143.1, 142.3, 139.5, 135.4, 133.1, 129.7, 128.4, 128.1, 127.9, 127.5, 120.8, 119.54, 119.49, 119.0, 118.5, 112.7, 112.6, 108.8, 107.2, 63.0, 55.2, 42.0, 40.1, 28.2, 26.0, 18.3, -5.4; IR (neat) ν (cm^{-1}) 3052, 3028, 3002, 2925, 2854, 1608, 1584, 1566, 1471, 1459, 1437, 1402, 1369, 1315, 1297, 1256, 1210, 1169, 1087, 1055, 1030, 1014; MS (70 ev, EI) m/z (%) 510 ($\text{M}^+ + 1$, 13.58), 509 (M^+ , 33.87), 364 (100); HRMS calcd for $\text{C}_{33}\text{H}_{39}\text{NO}_2\text{Si} [\text{M}^+]$: 509.2750, Found: 509.2751.

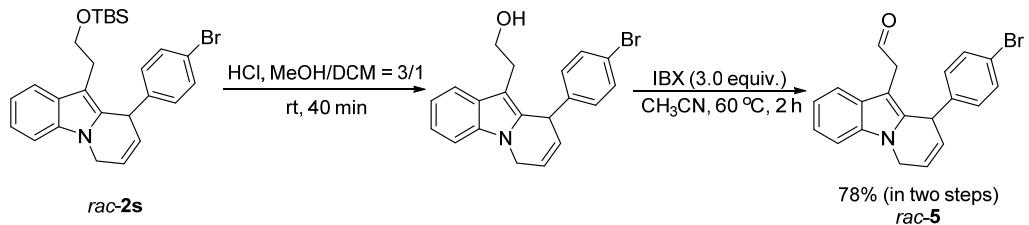
8.3 Synthesis of (*S*)-9-(4-bromophenyl)-6,9-dihydropyrido[1,2-*a*]indole-10-aldehyde (*S*)-5⁸⁻⁹ (jf-3-136, jf-3-137)



To a reaction tube were added (*S*)-**2s** (96.9 mg, 0.2 mmol), V_{MeOH}/V_{DCM} = 3/1 (4 mL), and HCl (30 µL) sequentially. The reaction was complete after being stirred at room temperature for 40 min as monitored by TLC. The resulting mixture was diluted with H₂O (10 mL) and ethyl acetate (10 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 2). The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. After filtration and evaporation, the crude product was submitted to the next step without further purification.

To a reaction tube were added the crude product prepared above, acetonitrile (4 mL), and IBX (0.1680 g, 0.6 mmol) sequentially. The reaction was complete after being stirred at 60 °C for 2 h as monitored by TLC. After filtration through a short column of celite, eluted with DCM (8 mL × 4), and evaporation, the crude product was then purified by column chromatography on silica gel to afford (*S*)-**5** (0.0573 g, 78%) [eluent: petroleum ether/ethyl acetate = 10/1] as an oil: 97% ee (HPLC conditions: Chiralcel OZ-H column, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (major) = 18.5 min, t_R (minor) = 28.4 min); $[\alpha]_D^{20} = -150.9$ ($c = 1.055$, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 9.26 (dd, J_1 = 3.0 Hz, J_2 = 1.8 Hz, 1H, CHO), 7.47 (d, J = 7.8 Hz, 1H, Ar-H), 7.38 (d, J = 8.4 Hz, 3H, Ar-H), 7.26 (td, J_1 = 7.5 Hz, J_2 = 1.1 Hz, 1H, Ar-H), 7.16 (td, J_1 = 7.4 Hz, J_2 = 1.0 Hz, 1H, Ar-H), 7.00 (dt, J_1 = 8.9 Hz, J_2 = 2.3 Hz, 2H, Ar-H), 6.12-5.93 (m, 2H, CH=CH), 4.87-4.64 (m, 3H, NCH₂ + CH), 3.58 (dd, J_1 = 16.7 Hz, J_2 = 2.0 Hz, 1H, one proton of Ar-CH₂), 3.27 (dd, J_1 = 16.4 Hz, J_2 = 3.2 Hz, 1H, one proton of Ar-CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 198.7, 141.9, 135.4, 134.2, 132.0, 129.6, 128.0, 127.0, 121.6, 120.8, 120.3, 119.2, 117.9, 109.2, 100.6, 41.9, 39.9, 39.4; IR (neat) ν (cm⁻¹) 3045, 2818, 2716, 1712, 1485, 1472, 1458, 1404, 1370, 1318, 1292, 1243, 1170, 1072, 1010; MS (70 eV, EI) *m/z* (%) 367 (M⁺(⁸¹Br), 8.47), 365 (M⁺(⁷⁹Br), 8.81), 167 (100); HRMS calcd for C₂₀H₁₆⁷⁹BrNO [M⁺]: 365.0415, Found: 365.0417.

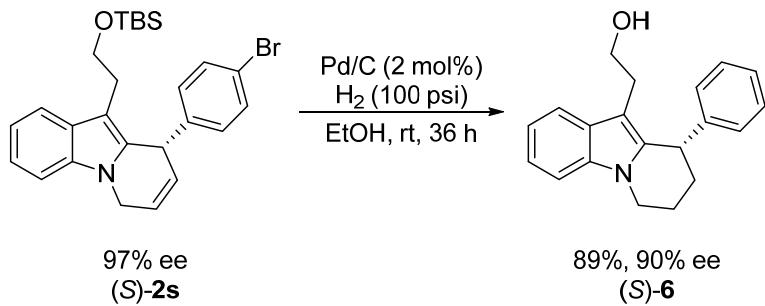
8.4 Synthesis of 9-(4-bromophenyl)-6,9-dihdropyrido[1,2-*a*]indole-10-acetaldehyde *rac*-**5**⁸⁻⁹ (jf-3-133, jf-3-134)



Following the preparation of (*S*)-**5**, the reaction of *rac*-**2s** (96.0 mg, 0.2 mmol), V_{MeOH}/V_{DCM} = 3/1 (4 mL), and HCl (30 µL) for 40 min at room temperature afforded the crude product. Then the reaction of the crude product, acetonitrile (4 mL), and IBX (0.1683 g, 0.6 mmol) for 2 h at 60 °C afforded *rac*-**5** (0.0571 g, 78%) [eluent: petroleum ether/ethyl acetate = 10/1] as an oil: ¹H NMR (300 MHz, CDCl₃) δ 9.27 (t, *J* = 2.4 Hz, 1H, CHO), 7.47 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.38 (d, *J* = 8.4 Hz, 3H, Ar-H), 7.26 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.17 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.01 (d, *J* = 8.1 Hz, 2H, Ar-H), 6.13-5.93 (m, 2H, CH=CH), 4.88-4.63 (m, 3H, NCH₂ + CH), 3.59 (dd, *J*₁ = 16.4 Hz, *J*₂ = 1.7 Hz, 1H, one proton of Ar-CH₂), 3.28 (dd, *J*₁ = 16.5 Hz, *J*₂ = 3.3 Hz, 1H, one proton of Ar-CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 198.7, 141.9, 135.4, 134.2, 132.0, 129.6, 128.0, 127.1, 121.6, 120.9, 120.4, 119.2, 117.9, 109.2, 100.7, 42.0, 39.9, 39.4; IR (neat) ν (cm⁻¹) 3045, 2860, 2837, 2730, 1723, 1488, 1471, 1456, 1411, 1372, 1309, 1244, 1178, 1168, 1071, 1011; MS (70 ev, EI) *m/z* (%) 367 (M⁺(⁸¹Br), 53.50), 365 (M⁺(⁷⁹Br), 45.56), 336 (100); HRMS calcd for C₂₀H₁₆⁷⁹BrNO [M⁺]: 365.0415, Found: 365.0413.

8.5 Synthesis of (*S*)-9-phenyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-10-ethanol

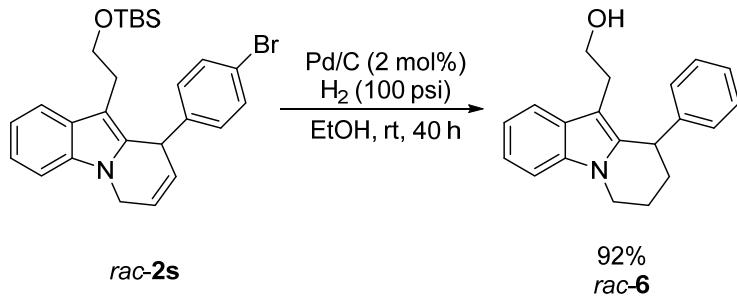
(S)-6 (jf-3-121)



To a conical flask were added (*S*)-**2s** (96.2 mg, 0.2 mmol), Pd/C (10% on C, dry, 4.4 mg, 0.04 mmol), and EtOH (1 mL) sequentially. The conical flask was placed in an autoclave and charged with H₂ (100 psi) with stirring at room temperature for 36 h.

After filtration through a short column of silica gel eluted with EtOAc (5 mL \times 4) and evaporation, the crude product was then purified by column chromatography on silica gel to afford (*S*)-**6** (0.0519 g, 89%) [eluent: petroleum ether/ethyl acetate = 5/1] as a liquid: 90% ee (HPLC conditions: Chiralcel OZ-H column, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 214 nm, t_R (major) = 16.3 min, t_R (minor) = 27.6 min); $[\alpha]_D^{20}$ = -38.0 (c = 1.00, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.57 (d, J = 8.1 Hz, 1H, Ar-H), 7.34 (d, J = 7.8 Hz, 1H, Ar-H), 7.29-7.09 (m, 5H, Ar-H), 7.05 (d, J = 6.9 Hz, 2H, Ar-H), 4.52 (t, J = 4.8 Hz, 1H, Ar-CH), 4.28 (dt, J_1 = 11.7 Hz, J_2 = 4.8 Hz, 1H, one proton of OCH₂), 4.02-3.89 (m, 1H, one proton of OCH₂), 3.65-3.46 (m, 2H, Ar-CH₂), 2.82-2.52 (m, 2H, NCH₂), 2.31-2.17 (m, 1H, one proton of CH₂), 2.15-1.99 (m, 2H, CH₂), 1.97-1.84 (m, 1H, one proton of CH₂) 1.25 (brs, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 144.9, 136.1, 135.6, 128.3, 128.0, 126.4, 120.8, 119.5, 118.3, 108.9, 106.9, 62.4, 42.4, 38.8, 30.6, 27.6, 19.0; IR (neat) ν (cm⁻¹) 3390, 3057, 3025, 2943, 2865, 1601, 1590, 1490, 1462, 1449, 1362, 1322, 1256, 1241, 1203, 1156, 1034, 1013; MS (70 ev, EI) m/z (%) 292 (M⁺+1, 5.83), 291 (M⁺, 28.55), 260 (100); HRMS calcd for C₂₀H₂₁NO [M⁺]: 291.1623, Found: 291.1621.

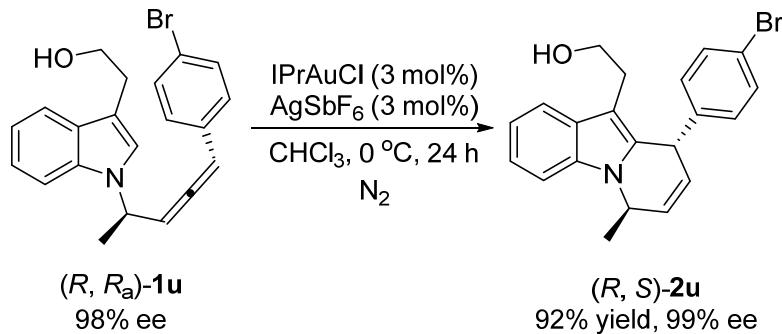
8.6 Synthesis of 9-phenyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-10-ethanol *rac*-**6** (jf-3-125)



Following the preparation of (*S*)-**6**, the reaction of *rac*-**2s** (94.8 mg, 0.2 mmol), Pd/C (10% on C, dry, 4.2 mg, 0.04 mmol), EtOH (1 mL), and H₂ (100 psi) for 40 h at room temperature afforded *rac*-**6** (0.0524 g, 92%) [eluent: petroleum ether/ethyl acetate = 4/1] as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.57 (d, J = 7.8 Hz, 1H, Ar-H), 7.34 (d, J = 7.8 Hz, 1H, Ar-H), 7.29-7.09 (m, 5H, Ar-H), 7.05 (d, J = 6.6 Hz, 2H, Ar-H), 4.52 (t, J = 4.8 Hz, 1H, Ar-CH), 4.28 (dt, J_1 = 11.7 Hz, J_2 = 4.8 Hz, 1H,

one proton of OCH_2), 4.02-3.89 (m, 1H, one proton of OCH_2), 3.65-3.46 (m, 2H, Ar- CH_2), 2.82-2.52 (m, 2H, NCH_2), 2.31-2.17 (m, 1H, one proton of CH_2), 2.15-1.99 (m, 2H, CH_2), 1.97-1.84 (m, 1H, one proton of CH_2) 1.25 (brs, 1H, OH); ^{13}C NMR (75 MHz, CDCl_3) δ 144.9, 136.1, 135.7, 128.3, 128.0, 126.4, 120.8, 119.5, 118.3, 108.9, 106.9, 62.5, 42.4, 38.8, 30.6, 27.6, 19.0; IR (neat) ν (cm^{-1}) 3390, 3056, 3025, 2943, 2866, 1601, 1491, 1462, 1449, 1362, 1322, 1256, 1241, 1203, 1156, 1034, 1013; MS (70 ev, EI) m/z (%) 292 (M^++1 , 7.33), 291 (M^+ , 32.13), 260 (100); HRMS calcd for $\text{C}_{20}\text{H}_{21}\text{NO} [\text{M}^+]$: 291.1623, Found: 291.1624.

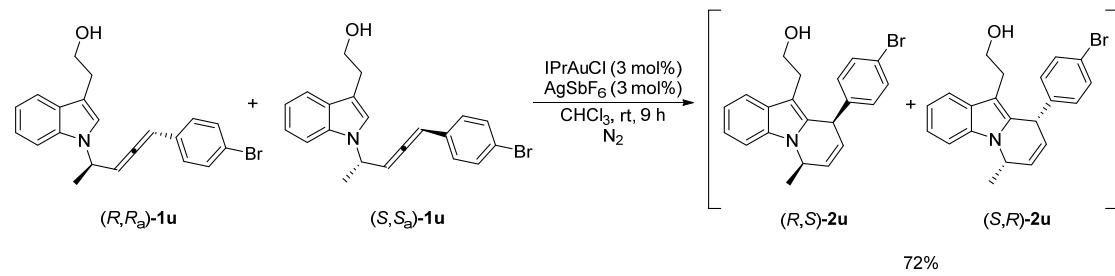
8.7 Synthesis of (*R, S*)-2-(9-(4-bromophenyl)-6-methyl-6,9-dihydropyrido[1,2-*a*]indol-10-yl)ethanol (*R, S*)-2u (jf-5-119)



Typical Procedure VI: To an oven-dried Schlenk tube were added IPrAuCl (0.0195 g, weighed in a glove box, 0.03 mmol, 95%), AgSbF₆ (0.0106 g, weighed in a glove box, 0.03 mmol, 98%), (*R, R_a*)-1u (0.3720 g, 1 mmol), and CHCl₃ (25 mL) under nitrogen atmosphere sequentially. The reaction was complete after being stirred at 0 °C for 24 h as monitored by TLC. After filtration through a short column of silica gel (3 cm × 2 cm) [eluent: ethyl acetate (8 mL × 4)] and evaporation, the crude product was purified by column chromatography on silica gel to afford (*R, S*)-2u (0.3434 g, 92%) [eluent: petroleum ether/ethyl acetate = 5/1] as a foamy solid: m.p. 57.1-59.2 °C (without recrystallization); 99% ee (HPLC conditions: Chiralcel IA-H column, *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, λ = 254 nm, t_R (major) = 18.5 min, t_R (minor) = 21.2 min); $[\alpha]_D^{20} = -270.8$ ($c = 0.975$, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.56 (d, J = 7.8 Hz, 1H, Ar-H), 7.45-7.32 (m, 3H, Ar-H), 7.25-7.17 (m, 1H, Ar-H), 7.16-7.08 (m, 1H, Ar-H), 7.01-6.94 (m, 2H, Ar-H), 5.98 (ddd, J_1 = 10.2 Hz, J_2 = 3.8

Hz, J_3 = 2.3 Hz, 1H, =CH), 5.80 (ddd, J_1 = 10.2 Hz, J_2 = 3.4 Hz, J_3 = 1.6 Hz, 1H, =CH), 5.18-5.06 (m, 1H, CH), 4.83 (q, J = 2.7 Hz, 1H, NCH), 3.60-3.30 (m, 2H, OCH₂), 2.78-2.62 (m, 1H, one proton of CH₂), 2.54-2.39 (m, 1H, one proton of CH₂), 1.53 (d, J = 6.6 Hz, 3H, CH₃), 1.30 (s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 143.2, 134.4, 133.0, 131.7, 129.8, 128.8, 126.0, 125.7, 120.9, 120.4, 119.4, 118.5, 110.5, 107.2, 62.2, 47.8, 40.2, 27.9, 22.0; IR (neat) ν (cm⁻¹) 3390, 3042, 2963, 2929, 2873, 1486, 1460, 1403, 1353, 1316, 1239, 1169, 1099, 1038, 1011; MS (70 ev, EI) *m/z* (%) 383 (M⁺(⁸¹Br), 37.29), 381 (M⁺(⁷⁹Br), 36.80), 350 (100); HRMS calcd for C₂₁H₂₀NO⁷⁹Br [M⁺]: 381.0728, Found: 381.0728.

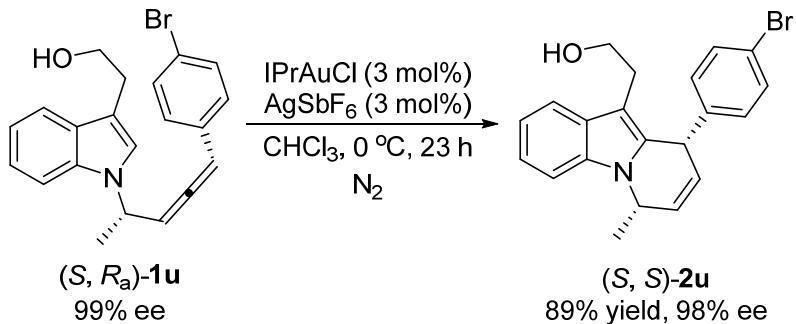
8.8 Synthesis of (*R,S*)-2-(9-(4-bromophenyl)-6-methyl-6,9-dihydropyrido[1,2-*a*]indol-10-yl)ethanol (*R,S*)-2u, and (*S,R*)-2-(9-(4-bromophenyl)-6-methyl-6,9-dihydropyrido[1,2-*a*]indol-10-yl)ethanol (*S,R*)-2u (jf-5-120-2)



Following **Typical Procedure VI**, the reaction of IPrAuCl (0.0038 g, 0.006 mmol, 95%), AgSbF₆ (0.0020 g, 0.006 mmol, 98%), ((*R, R_a*)-**1u** + (*S, S_a*)-**1u**) (0.0745 g, 0.2 mmol), and CHCl₃ (5 mL) for 9 h at room temperature afforded ((*R, S*)-**2u** + (*S, R*)-**2u**) (0.0534 g, 72%) [eluent: petroleum ether/diethyl ether = 2/1 (300 mL) to 1/1 (300 mL)] as an oil: ¹H NMR (300 MHz, CDCl₃) δ 7.56 (d, J = 8.1 Hz, 1H, Ar-H), 7.46-7.32 (m, 3H, Ar-H), 7.27-7.17 (m, 1H, Ar-H), 7.16-7.08 (m, 1H, Ar-H), 7.03-6.93 (m, 2H, Ar-H), 6.05-5.92 (m, 1H, =CH), 5.87-5.73 (m, 1H, =CH), 5.20-5.05 (m, 1H, CH), 4.91-4.75 (m, 1H, NCH), 3.60-3.31 (m, 2H, OCH₂), 2.76-2.62 (m, 1H, one proton of CH₂), 2.55-2.40 (m, 1H, one proton of CH₂), 1.53 (d, J = 6.3 Hz, 3H, CH₃), 1.28 (s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 143.2, 134.4, 133.1, 131.8, 129.8, 128.9, 126.1, 125.8, 120.9, 120.5, 119.5, 118.5, 110.5, 107.3, 62.3, 47.9, 40.3,

27.9, 22.0; IR (neat) ν (cm^{-1}) 3396, 3040, 2968, 2928, 2877, 1485, 1460, 1403, 1352, 1316, 1285, 1238, 1167, 1098, 1071, 1039, 1011; MS (70 ev, EI) m/z (%) 383 ($M^+(^{81}\text{Br})$, 35.18), 381 ($M^+(^{79}\text{Br})$, 34.96), 350 (100); HRMS calcd for $C_{21}\text{H}_{20}\text{NO}^{79}\text{Br}$ [M^+]: 381.0728, Found: 381.0728.

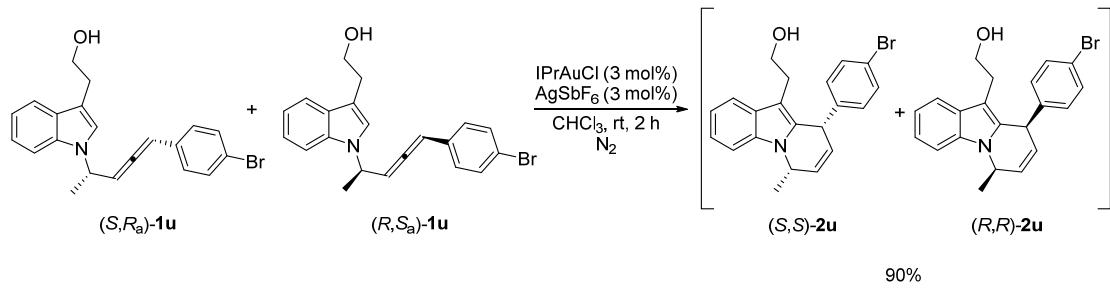
8.9 Synthesis of (*S, S*)-2-(9-(4-bromophenyl)-6-methyl-6,9-dihydropyrido[1,2-*a*]indol-10-yl)ethanol (*S, S*)-2u (jf-5-123)



Following **Typical Procedure VI**, the reaction of IPrAuCl (0.0195 g, 0.03 mmol, 95%), AgSbF₆ (0.0106 g, 0.03 mmol, 98%), (*S, R_a*)-**1u** (0.3740 g, 1 mmol), and CHCl₃ (25 mL) for 23 h at 0 °C afforded (*S, S*)-**2u** (0.3321 g, 89%) [eluent: petroleum ether/diethyl ether = 2/1 (300 mL) to 1/1 (300 mL)] as a foamy solid: m.p. 55.9-58.1 °C (without recrystallization); 98% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, λ = 254 nm, t_R (major) = 49.6 min, t_R (minor) = 22.0 min); $[\alpha]_D^{20} = -103.8$ ($c = 0.900$, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.46-7.31 (m, 3H, Ar-H), 7.27-7.18 (m, 1H, Ar-H), 7.18-7.09 (m, 1H, Ar-H), 7.07-6.95 (m, 2H, Ar-H), 6.14-5.82 (m, 2H, CH=CH), 5.08-4.80 (m, 2H, CH + NCH), 3.68-3.40 (m, 2H, OCH₂), 2.87-2.60 (m, 2H, CH₂), 1.66 (d, $J = 6.6$ Hz, 3H, CH₃), 1.43 (s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 142.4, 134.6, 132.8, 131.9, 129.3, 128.3, 126.5, 126.0, 121.0, 120.4, 119.5, 118.5, 109.8, 106.4, 62.3, 48.2, 39.7, 27.7, 22.6; IR (neat) ν (cm^{-1}) 3391, 3044, 2973, 2929, 2873, 1666, 1609, 1586, 1562, 1486, 1462, 1427, 1403, 1353, 1317, 1292, 1265, 1240, 1170, 1071, 1039, 1010; MS (70 ev, EI) m/z (%) 384 ($M^+(^{81}\text{Br}) + 1$, 6.10), 383 ($M^+(^{81}\text{Br})$, 31.52), 382 ($M^+(^{79}\text{Br}) + 1$, 8.06), 381 ($M^+(^{79}\text{Br})$, 29.99), 350 (100); HRMS calcd for $C_{21}\text{H}_{20}\text{NO}^{79}\text{Br}$ [M^+]: 381.0728, Found: 381.0729.

8.10 Synthesis of (*S,S*)-2-(9-(4-bromophenyl)-6-methyl-6,9-dihydropyrido[1,2-*a*]

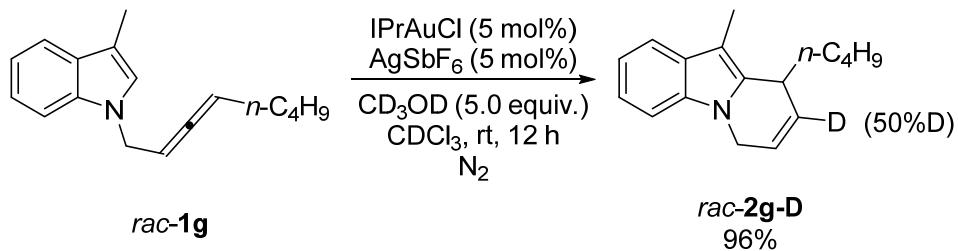
indol-10-yl)ethanol (*S,S*)-2u** and (*R,R*)-**2-(9-(4-bromophenyl)-6-methyl-6,9-dihydropyrido[1,2-*a*]indol-10-yl)ethanol (*R,R*)-**2u** (jf-5-124)****



Following **Typical Procedure VI**, the reaction of IPrAuCl (0.0038 g, 0.006 mmol, 95%), AgSbF₆ (0.0020 g, 0.006 mmol, 98%), ((S,R_a)-**1u** + (R,S_a)-**1u**) (0.0771 g, 0.2 mmol), and CHCl₃ (5 mL) for 2 h at room temperature afforded ((S,S)-**1u** + (R,R)-**2u**) (0.0693 g, 90%) [eluent: petroleum ether/diethyl ether = 2/1 (300 mL) to 1/1 (300 mL)] as a foamy solid: m.p. 48.9–51.0 °C (without recrystallization); ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.45–7.33 (m, 3H, Ar-H), 7.27–7.18 (m, 1H, Ar-H), 7.18–7.10 (m, 1H, Ar-H), 7.07–6.95 (m, 2H, Ar-H), 6.08–5.90 (m, 2H, CH=CH), 5.08–4.83 (m, 2H, CH + NCH), 3.68–3.41 (m, 2H, OCH₂), 2.87–2.60 (m, 2H, CH₂), 1.66 (d, *J* = 6.6 Hz, 3H, CH₃), 1.35 (s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 142.5, 134.6, 132.8, 131.9, 129.3, 128.3, 126.6, 126.1, 121.0, 120.5, 119.5, 118.5, 109.8, 106.4, 62.4, 48.2, 39.7, 27.7, 22.7; IR (neat) *v* (cm⁻¹) 3391, 3042, 2926, 2870, 2853, 1486, 1461, 1425, 1403, 1353, 1317, 1292, 1264, 1240, 1170, 1099, 1071, 1039, 1010; MS (70 ev, EI) *m/z* (%) 384 (M⁺(⁸¹Br) + 1, 8.43), 383 (M⁺(⁸¹Br), 35.81), 382 (M⁺(⁷⁹Br) + 1, 8.80), 381 (M⁺(⁷⁹Br), 34.47), 350 (100); HRMS calcd for C₂₁H₂₀NO⁷⁹Br [M⁺]: 381.0728, Found: 381.0732.

9. Deuterium-labeling experiment and Parallel reactions

9.1 Preparation of 9-butyl-10-methyl-6,9-dihydropyrido[1,2-*a*]indole-8-*D* *rac*-**2g-D**. (jf-3-170)

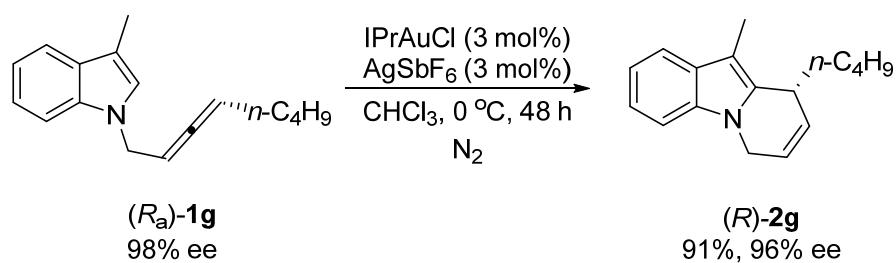


To a oven-dried Schlenk tube were added IPrAuCl (0.0165 g, weighed in a glove box, 0.025 mmol, 95%), AgSbF₆ (0.0088 g, weighed in a glove box, 0.025 mmol, 98%), *rac*-**1g** (0.1194 g, 0.5 mmol), CDCl₃ (2.5 mL), and CD₃OD (104 µL, d = 0.888 g/mL, 92.4 mg, 2.5 mmol, 99%) under nitrogen atmosphere sequentially. The resulting mixture was stirred at room temperature for 12 h and complete as monitored by TLC. After transferred to a pear-shaped bottle with DCM and evaporated, the crude product was then purified by column chromatography on silica gel to afford *rac*-**2g-D** (0.1155 g, 96%, 50% D) [eluent: petroleum ether] as a powder solid: ¹H NMR (300 MHz, CDCl₃) δ 7.54 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.23 (t, *J* = 6.5 Hz, 1H, Ar-H), 7.20-7.07 (m, 2H, Ar-H), 6.09-5.97 (m, 1.5H, =CH × 1.5), 4.63-4.45 (m, 2H, NCH₂), 3.83-3.64 (m, 1H, CH), 2.30 (s, 3H, CH₃), 1.83-1.65 (m, 2H, CH₂), 1.37-1.18 (m, 3H, CH₂ + one proton of CH₂), 1.17-1.00 (m, 1H, one proton of CH₂), 0.83 (t, *J* = 6.9 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 135.2, 133.9, 128.8, 127.4 (t, *J*_{C-D} = 24.5), 120.7, 120.2, 119.0, 117.8, 108.4, 104.1, 41.9, 35.5, 33.2, 27.5, 22.7, 14.0, 8.8; ¹³C NMR (75 MHz, CDCl₃) the following signals are discernible for *rac*-**2g** δ 127.7, 120.5, 33.1; IR (neat) ν (cm⁻¹) 3044, 2956, 2929, 2858, 1657, 1615, 1568, 1471, 1462, 1425, 1384, 1369, 1313, 1239, 1195, 1169, 1123, 1056, 1012; MS (70 ev, EI) *m/z* (%) 241 (M⁺ + 1, 2.41), 240 (M⁺, 16.74), 182 (100); HRMS calcd for C₁₇H₂₀DN [M⁺]: 240.1737, Found: 240.1737.

9.2 Parallel reactions

Synthesis of (*R*)-9-butyl-10-methyl-6,9-dihydropyrido[1,2-*a*]indole (*R*)-**2g**

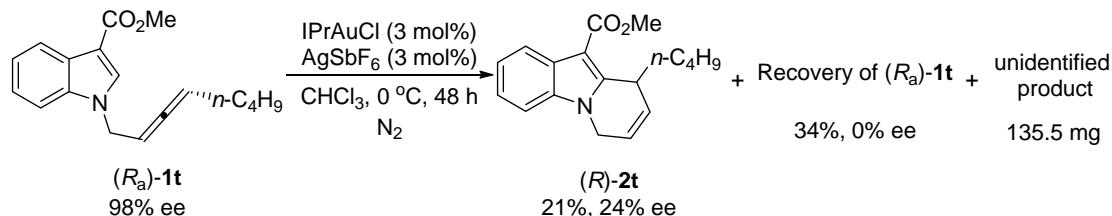
(jf-5-026)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0105 g, 0.03 mmol, 98%), (*R*_a)-**1g** (0.2363 g, 1 mmol), and CHCl₃

(25 mL) for 48 h at 0 °C afforded (*R*)-**2g** (0.2153 g, 91%) [eluent: petroleum ether/ethyl acetate = 100/1] as a powder solid: 96% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 100/1, 0.4 mL/min, λ = 254 nm, t_R (major) = 17.3 min, t_R (minor) = 18.3 min); ^1H NMR (300 MHz, CDCl₃) δ 7.55 (d, J = 7.5 Hz, 1H, Ar-H), 7.26 (d, J = 6.6 Hz, 1H, Ar-H), 7.20-7.07 (m, 2H, Ar-H), 6.16-5.95 (m, 2H, =CH × 2), 4.64-4.50 (m, 2H, NCH₂), 3.85-3.65 (m, 1H, CH), 2.30 (s, 3H, CH₃), 1.88-1.65 (m, 2H, CH₂), 1.39-1.00 (m, 4H, CH₂ × 2), 0.83 (t, J = 7.1 Hz, 3H, CH₃).

Synthesis of methyl (*R*)-9-butyl-6,9-dihydropyrido[1,2-*a*]indole-10-carboxylate (*R*)-**2t** (jf-5-025)



Following **Typical Procedure IV**, the reaction of IPrAuCl (0.0196 g, 0.03 mmol, 95%), AgSbF₆ (0.0106 g, 0.03 mmol, 98%), (Ra)-**1t** (0.2857 g, 1 mmol), and CHCl₃ (25 mL) for 48 h at 0 °C afforded (*R*)-**2t** (0.0593 g, 21%), recovery of (Ra)-**1t** (0.0970 g, 34%), and unidentified product (135.5 mg) [eluent: petroleum ether/ ethyl acetate = 15/1 (450 mL) to 10/1 (200 mL)].

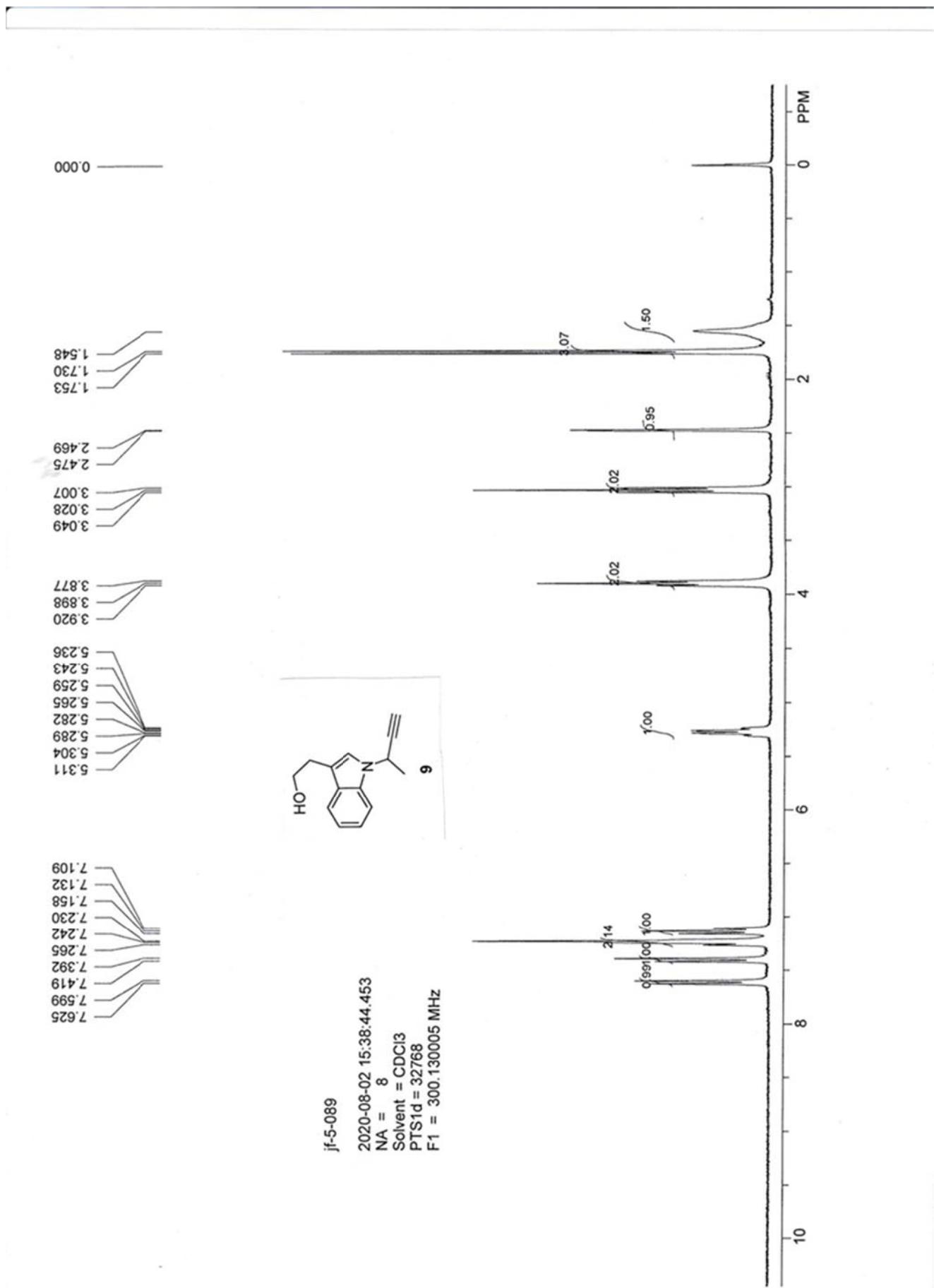
(*R*)-**2t** as a liquid: 24% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, λ = 214 nm, t_R (major) = 8.4 min, t_R (minor) = 9.8 min); ^1H NMR (300 MHz, CDCl₃) δ 8.16 (d, J = 7.2 Hz, 1H, Ar-H), 7.37-7.14 (m, 3H, Ar-H), 6.21-5.90 (m, 2H, =CH × 2), 4.73-4.45 (m, 2H, NCH₂), 4.41-4.25 (m, 1H, CH), 3.93 (s, 3H, OCH₃), 1.99-1.77 (m, 2H, CH₂), 1.45-1.18 (m, 3H, CH₂ + one proton of CH₂), 1.13-0.96 (m, 1H, one proton of CH₂), 0.83 (t, J = 7.2 Hz, 3H, CH₃).

Recovery of (Ra)-**1t** as a liquid: 0% ee (HPLC conditions: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, λ = 214 nm, t_R (major) = 26.7 min, t_R (minor) = 25.8 min); ^1H NMR (300 MHz, CDCl₃) δ 8.22-8.09 (m, 1H, Ar-H), 7.85 (s, 1H, Ar-H), 7.42-7.32 (m, 1H, Ar-H), 7.31-7.15 (m, 2H, Ar-H), 5.34-5.16 (m, 2H, CH=C=CH), 4.70 (dd, J_1 = 6.0 Hz, J_2 = 2.4 Hz, 2H, NCH₂), 3.90 (s, 3H, OCH₃),

2.00-1.84 (m, 2H, CH₂), 1.35-1.15 (m, 4H, CH₂ × 2), 0.85 (t, *J* = 6.3 Hz, 3H, CH₃).

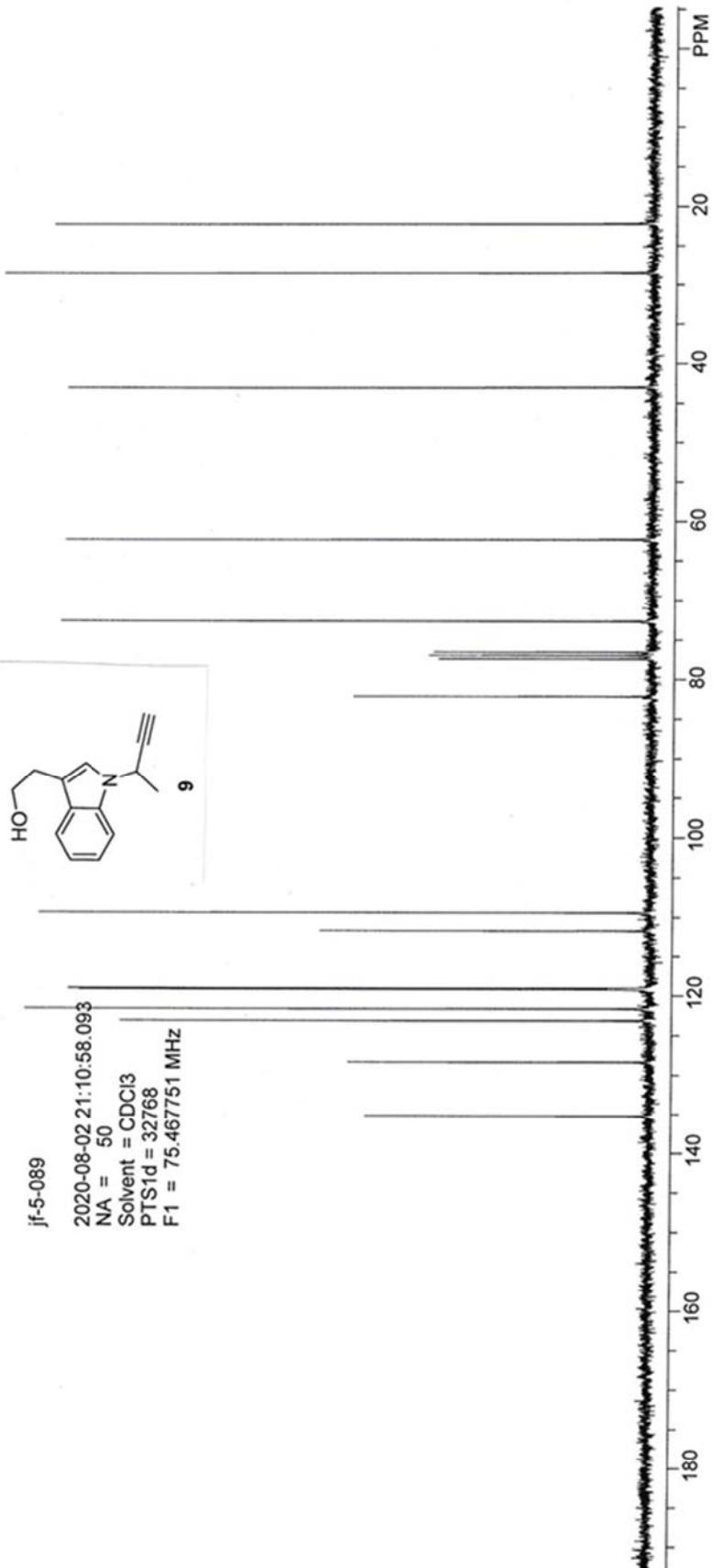
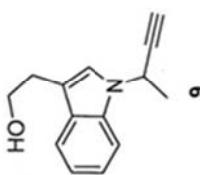
10. References

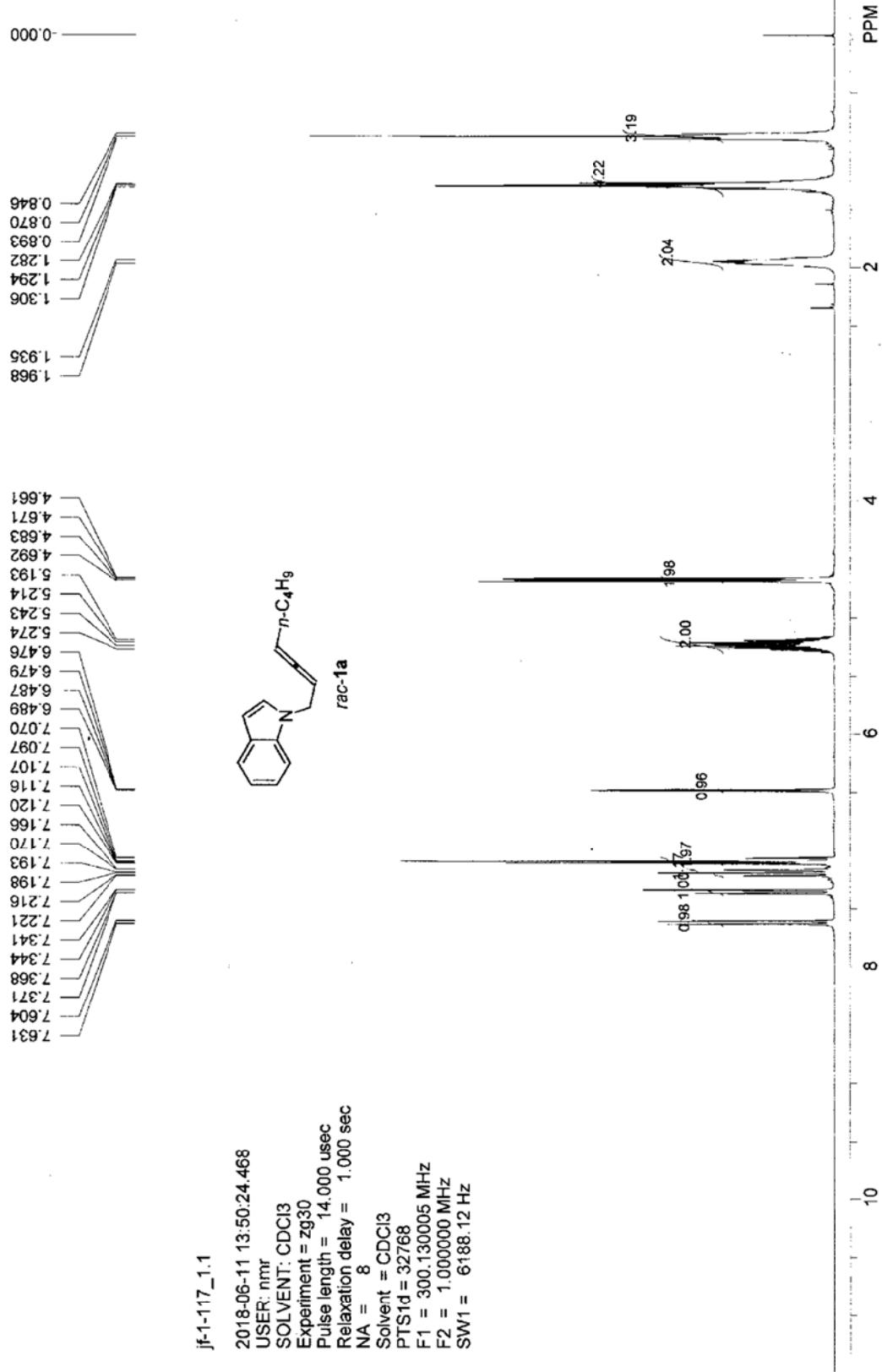
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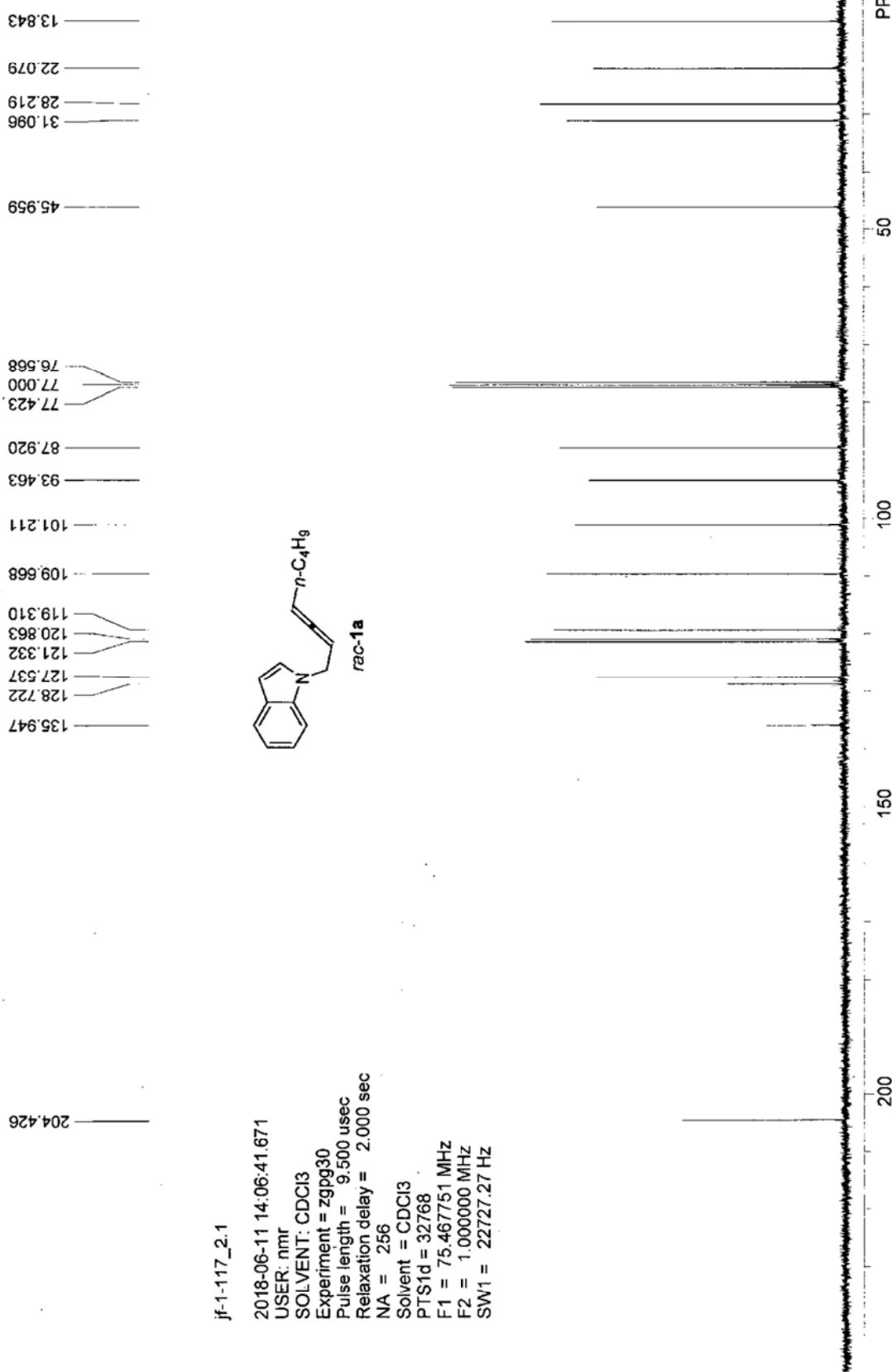


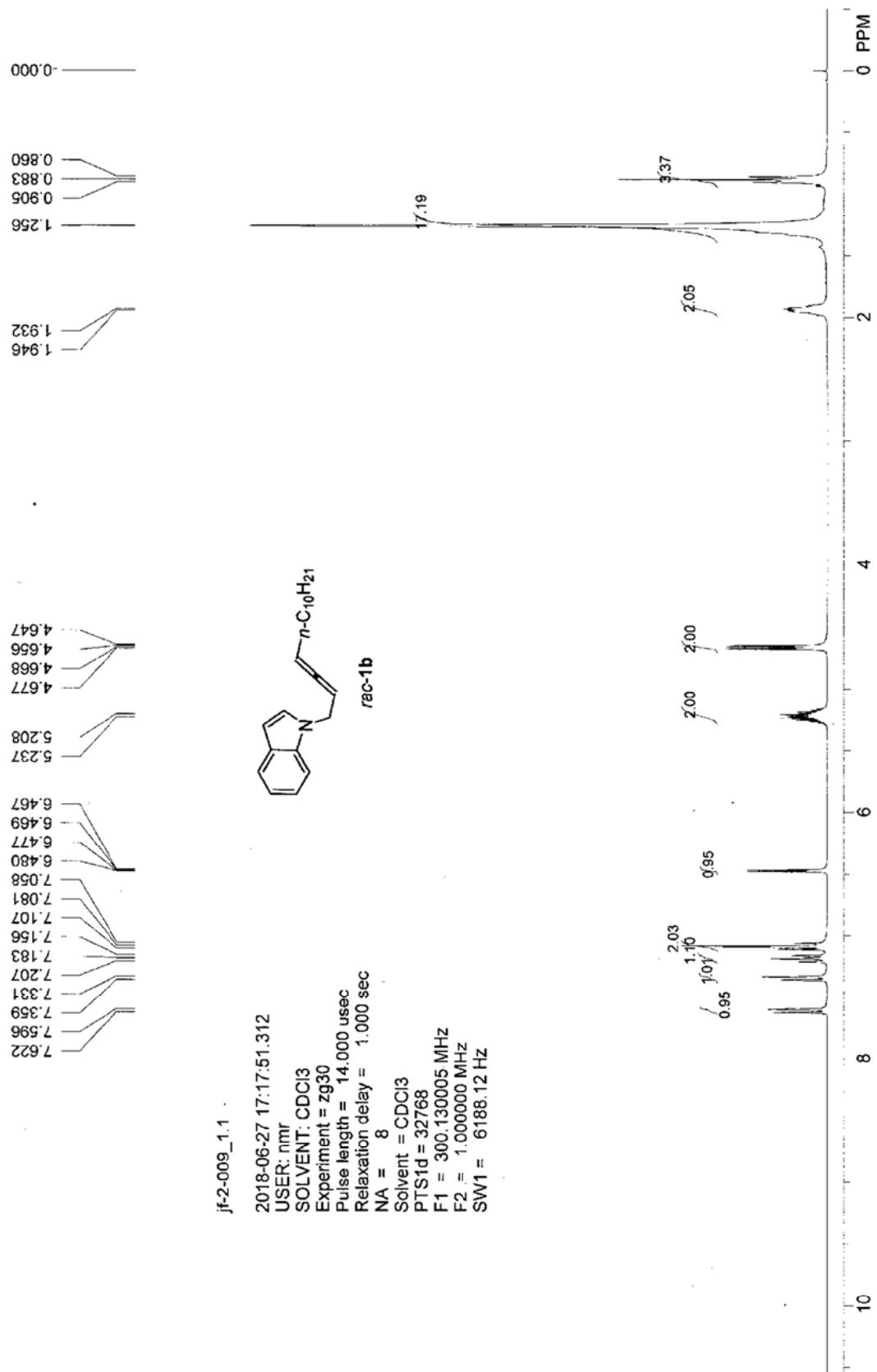
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121.645
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if-5-089
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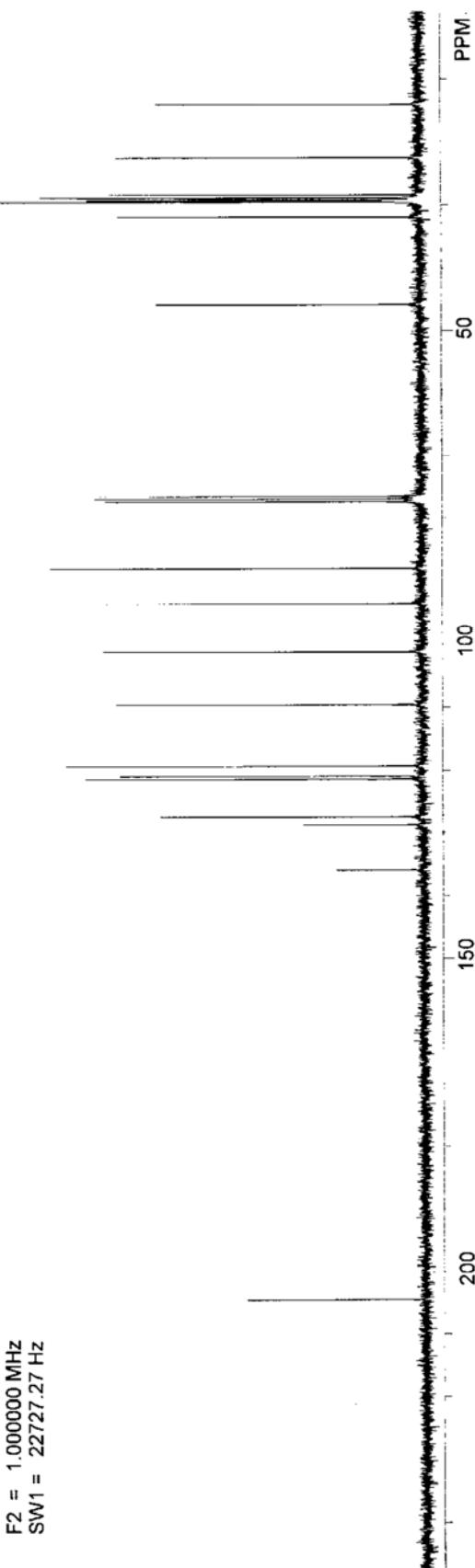
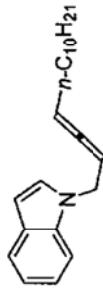
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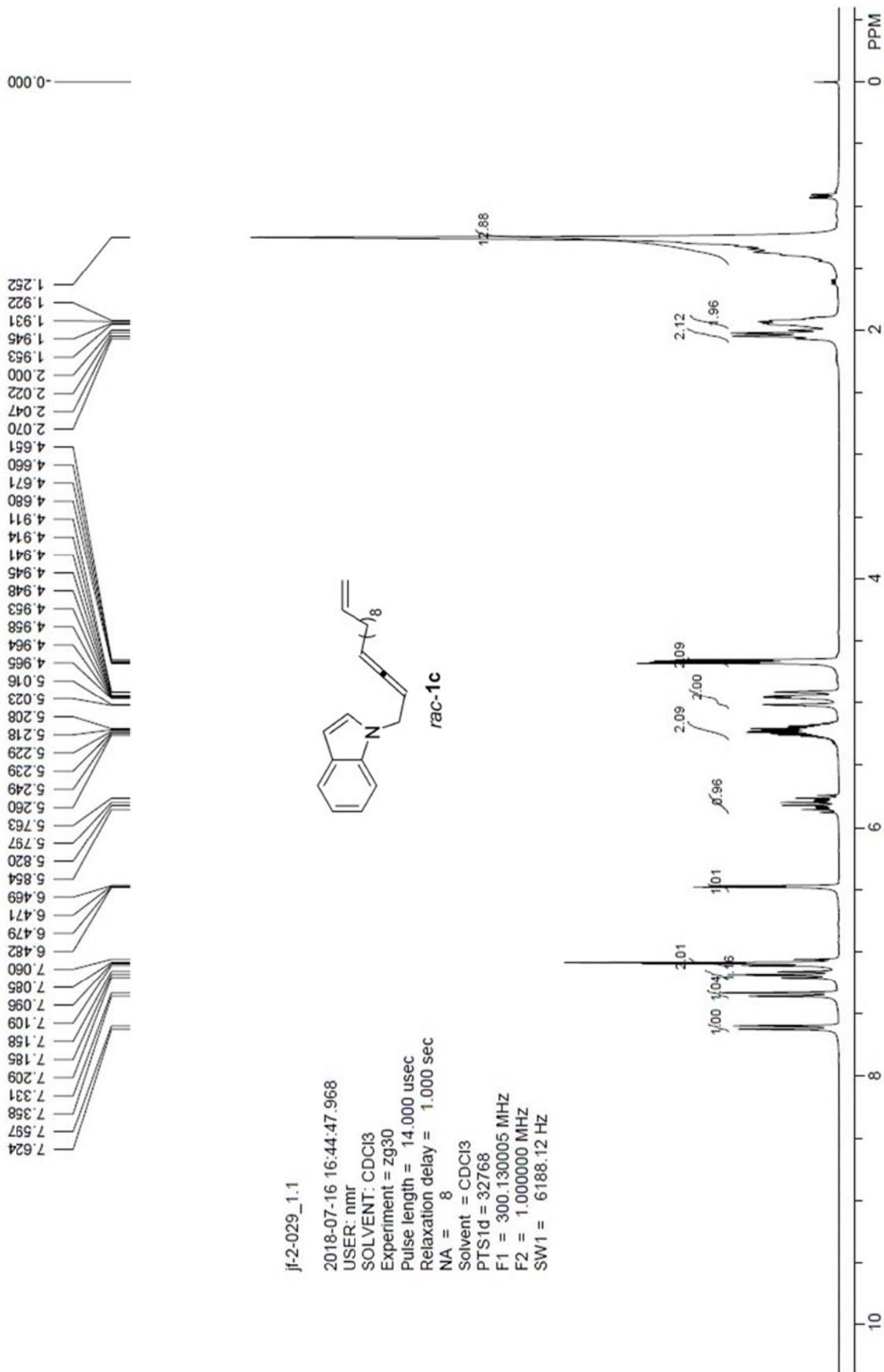
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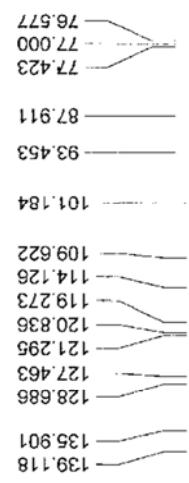
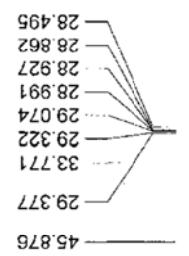
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jf-2-009_2.1

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jj-2-029_2.1

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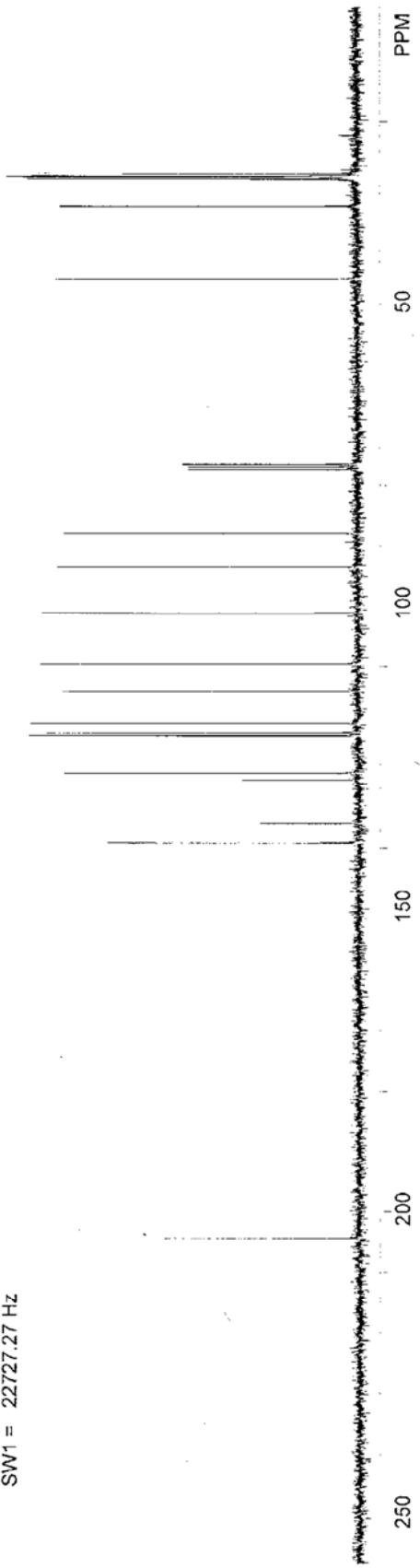
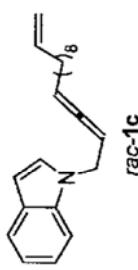
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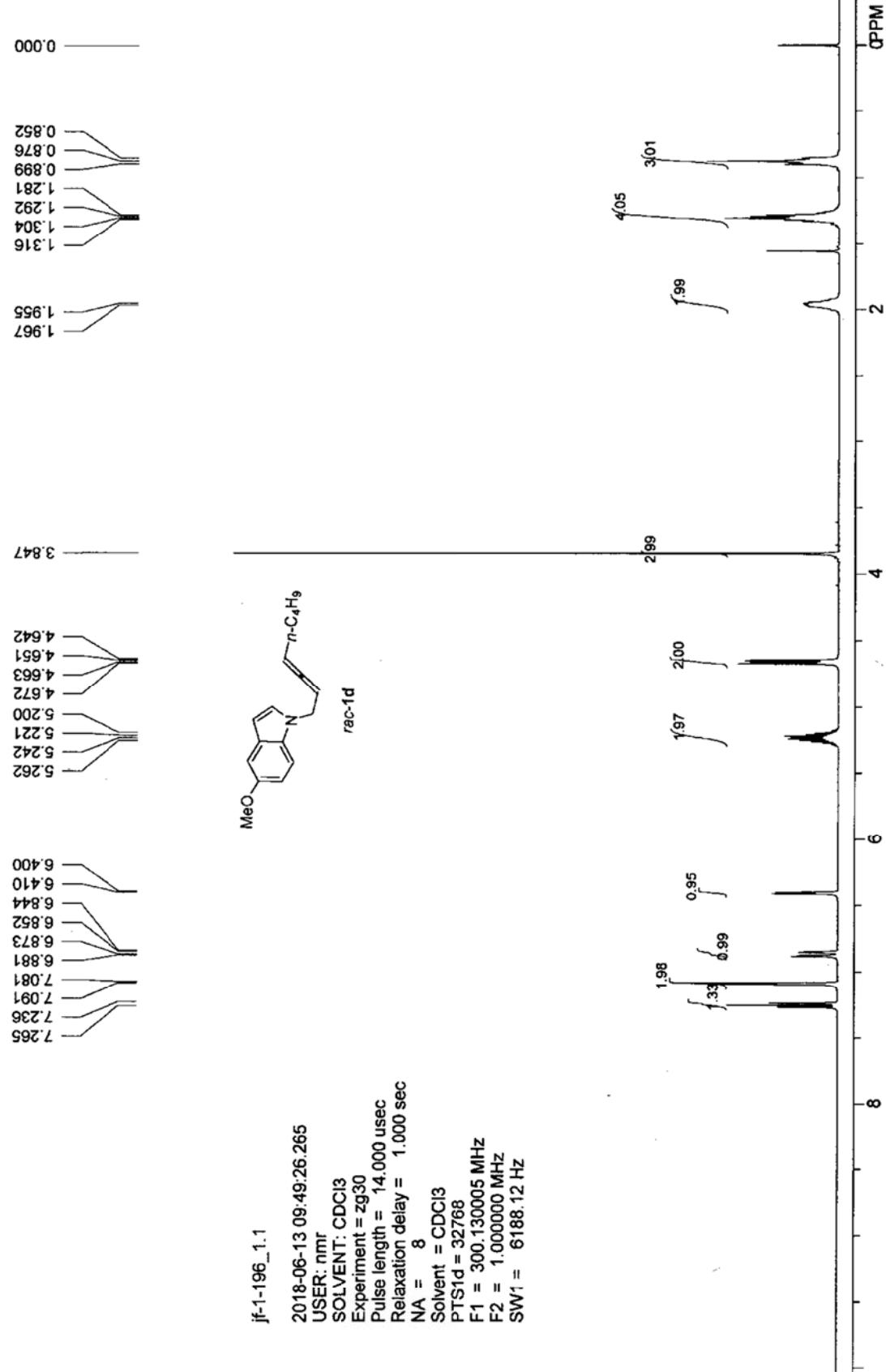
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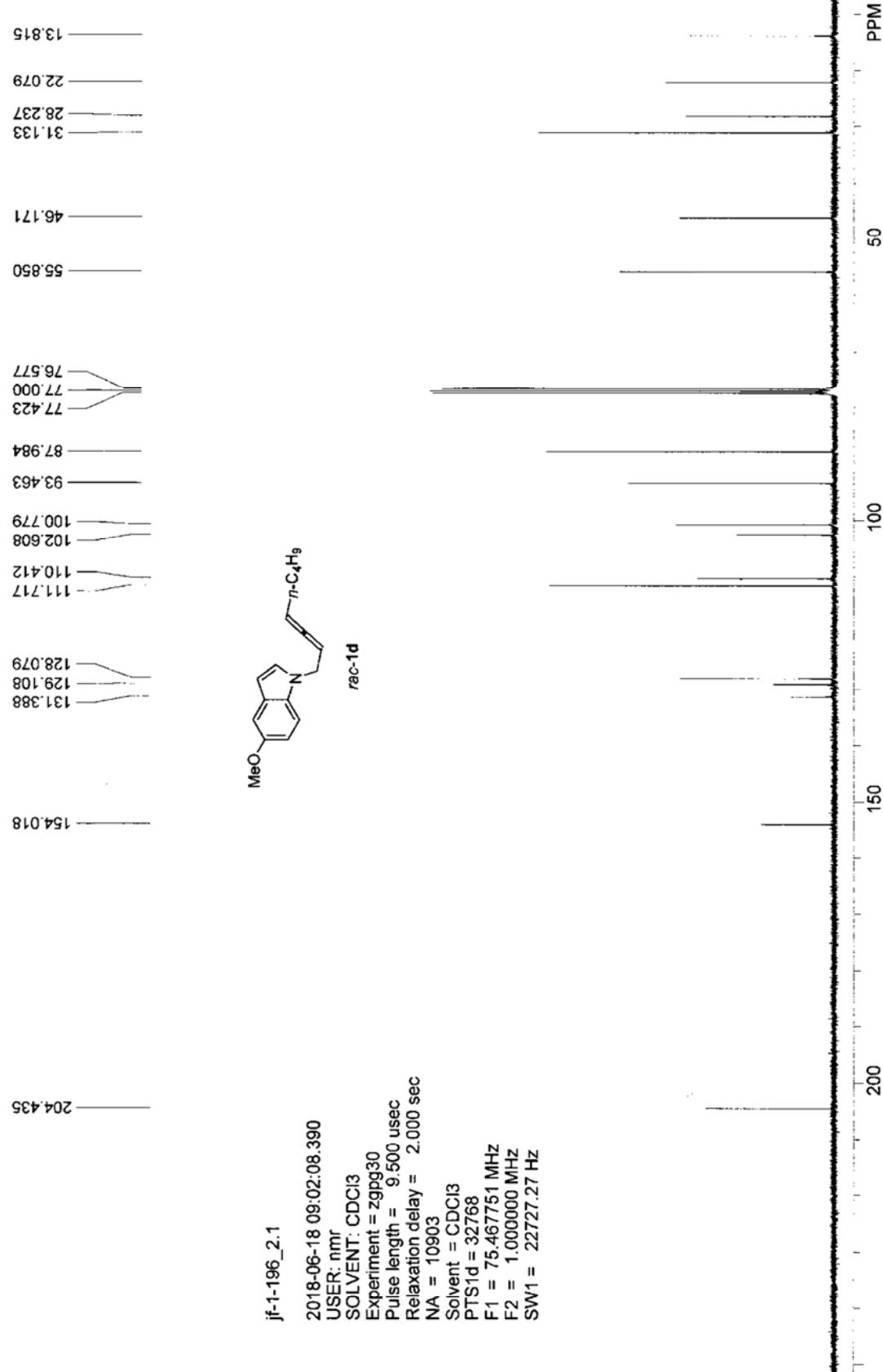
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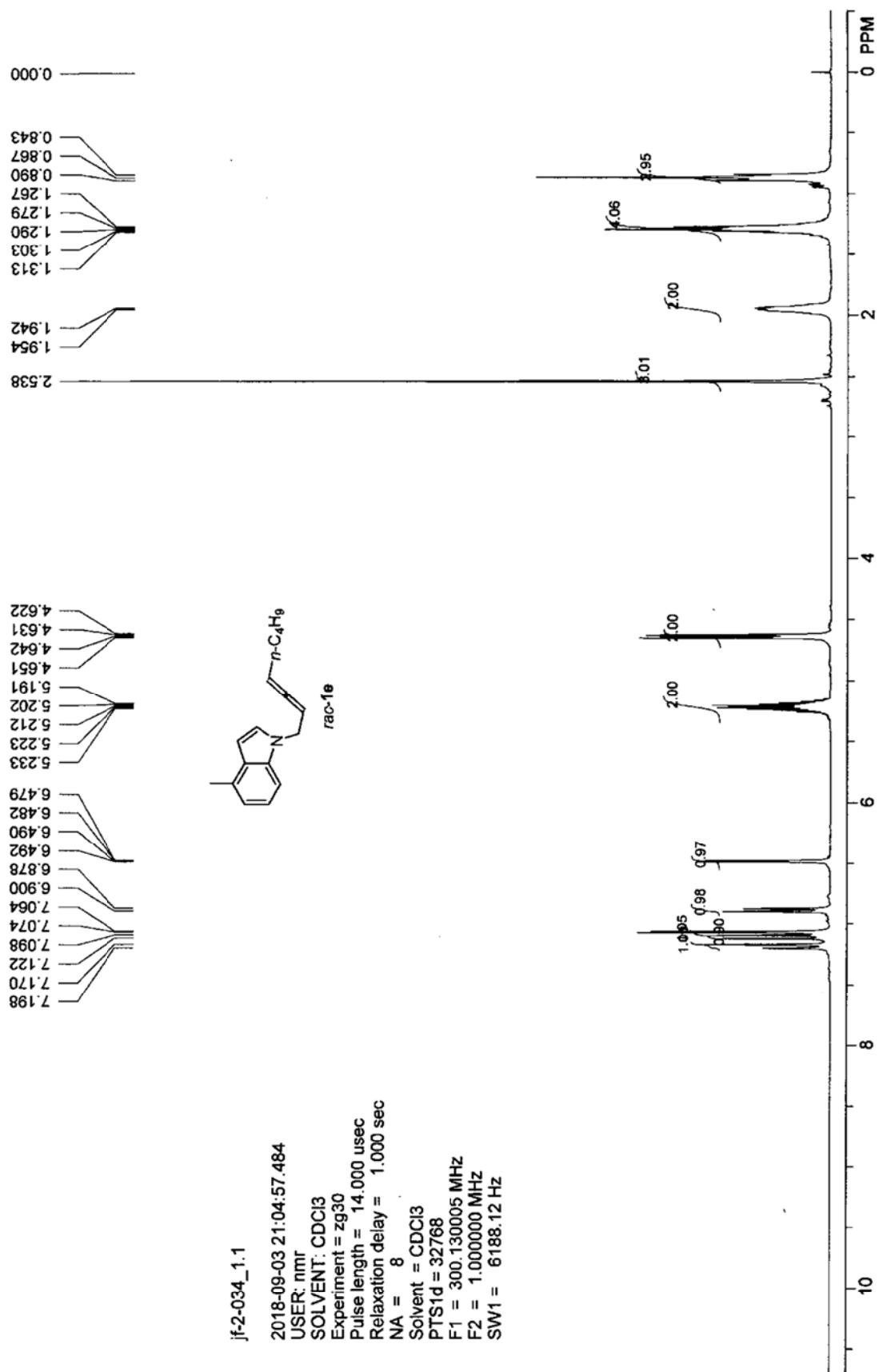
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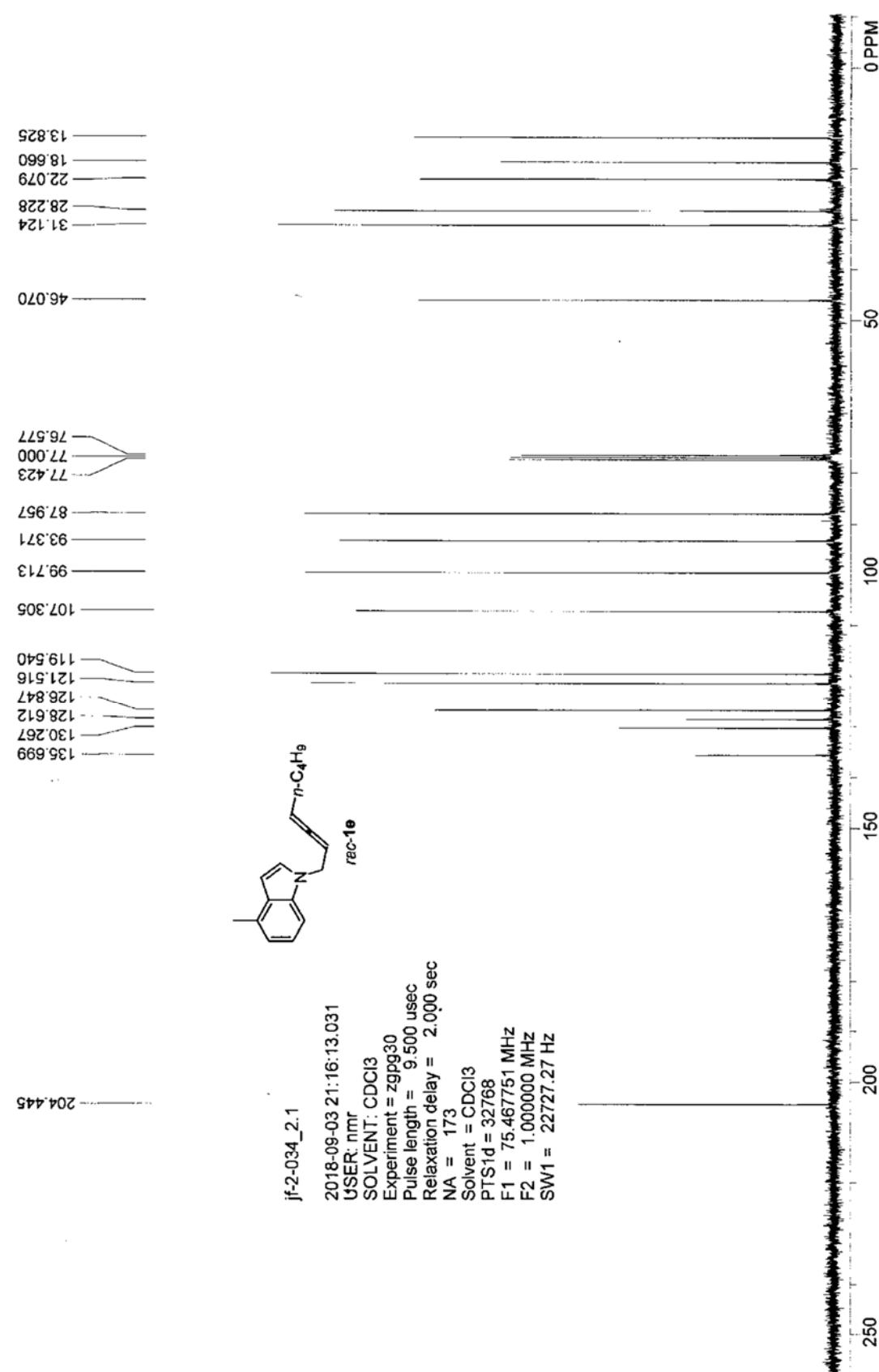
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SW2 = 1000.00 Hz

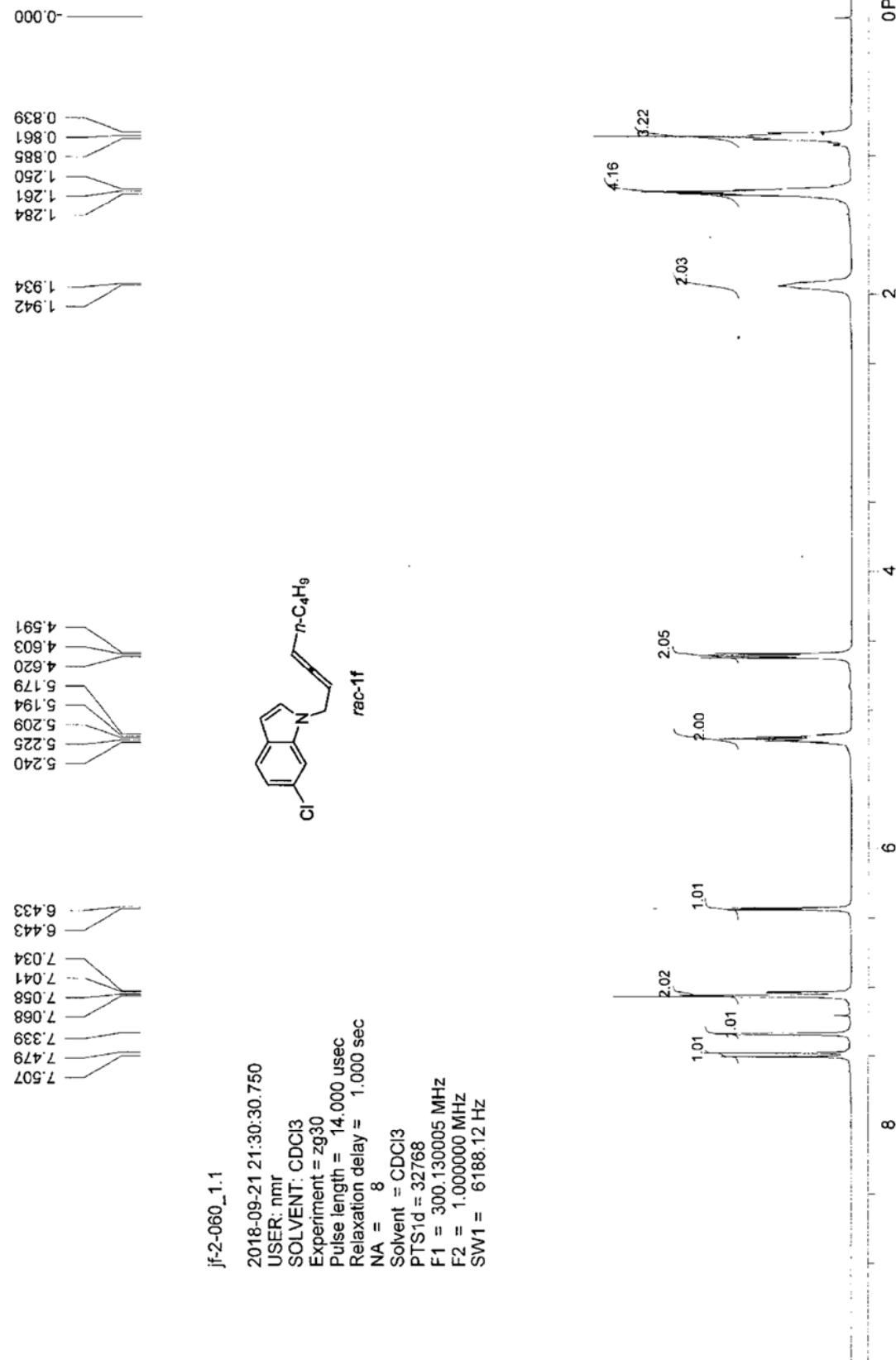


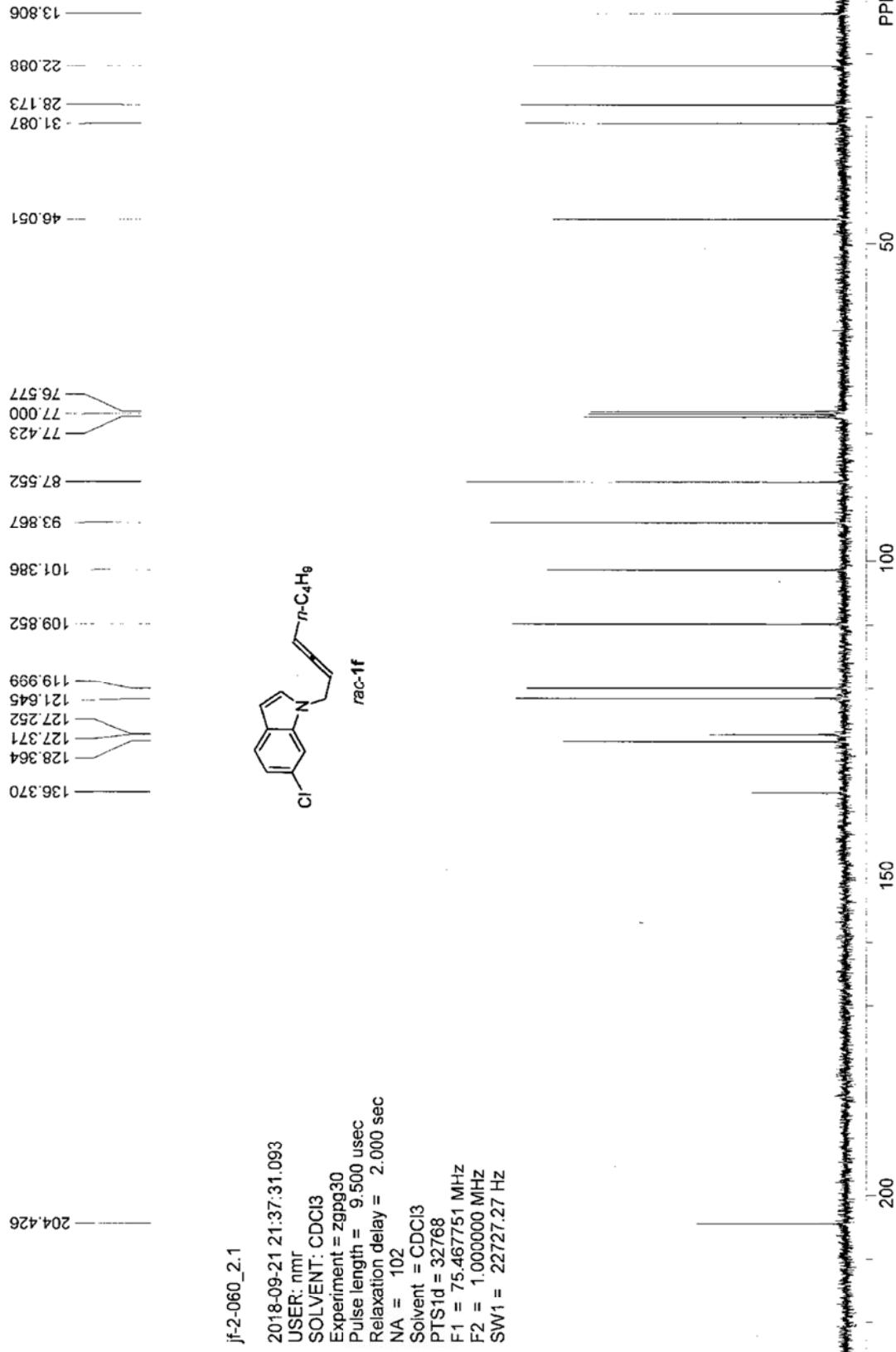


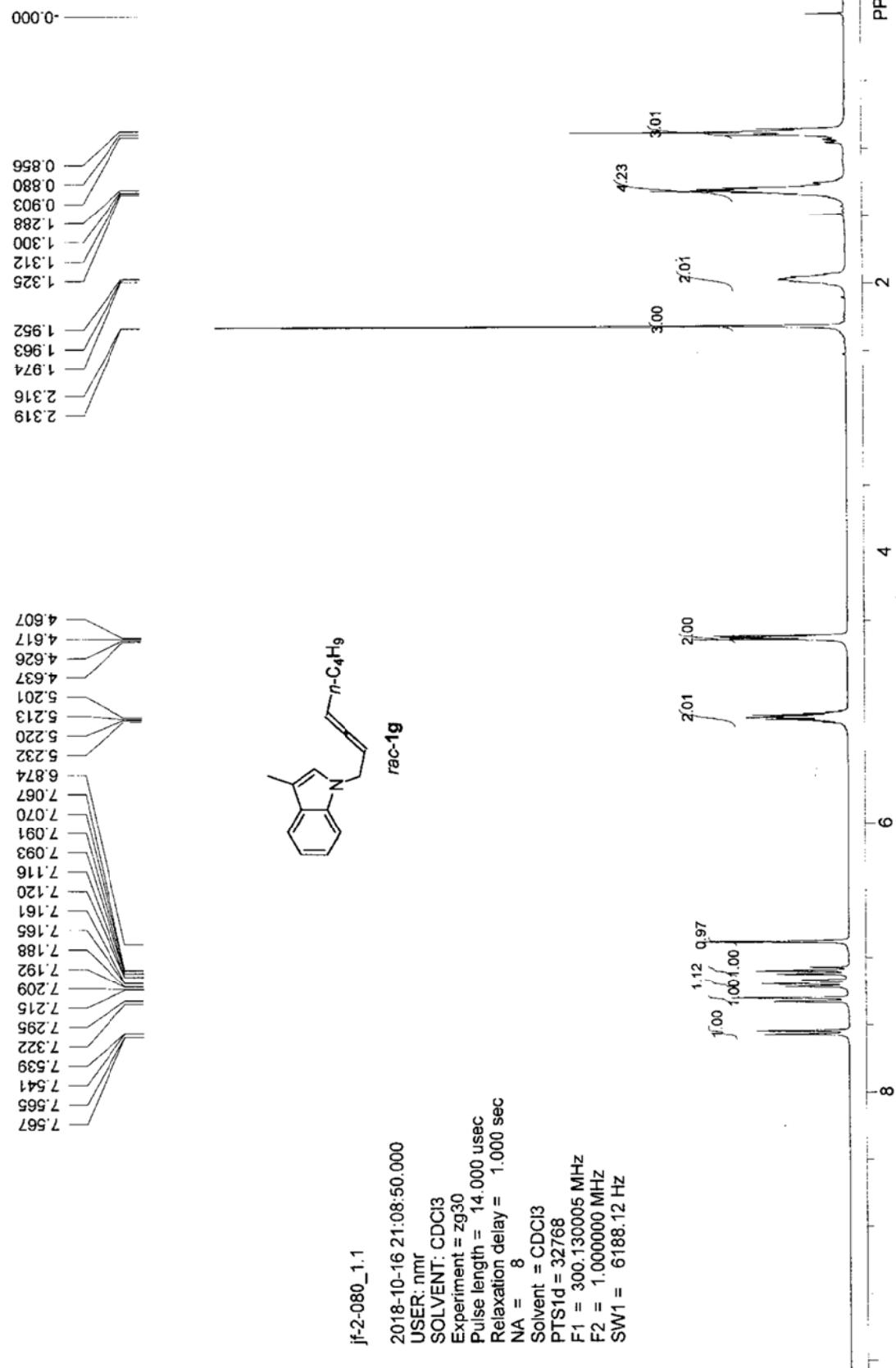




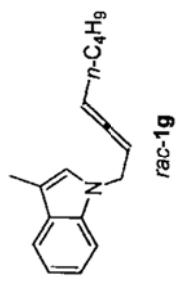




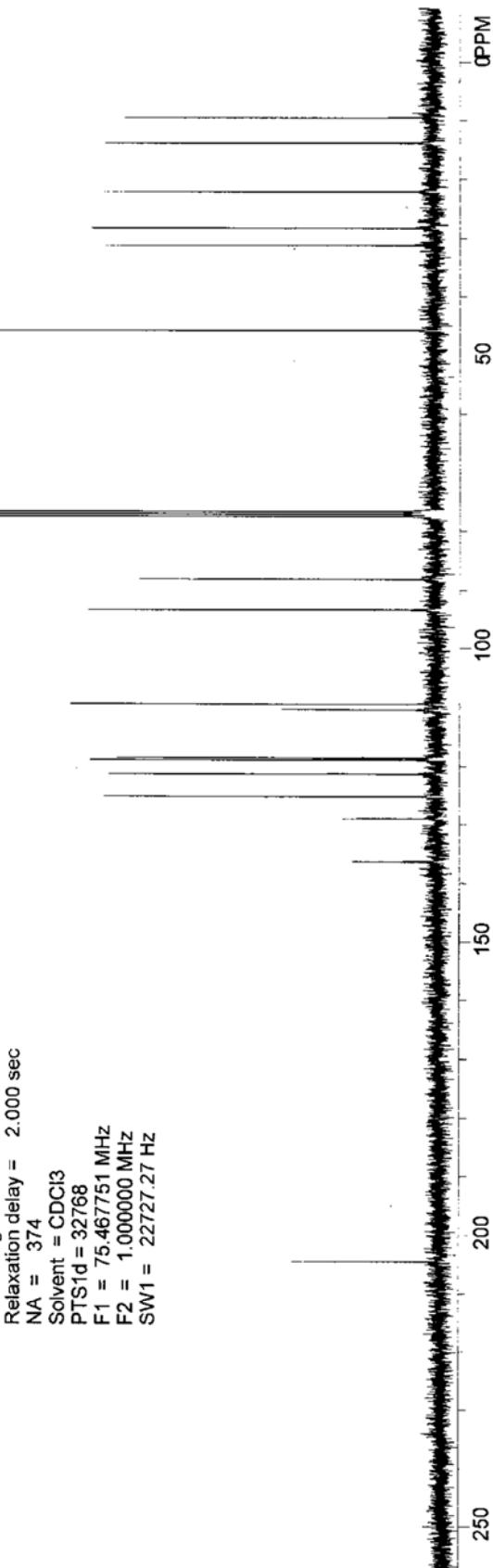




204.417
 136.278
 128.961
 125.184
 121.295
 118.952
 118.593
 110.431
 109.475
 93.270
 88.104
 77.423
 77.000
 76.577
 45.748
 31.170
 28.283
 22.106
 13.880
 9.569



jf-2-080_2.1
 2018-10-17 15:23:11.171
 USER: nmr
 SOLVENT: CDCl₃
 Experiment = zgppg30
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 374
 Solvent = CDCl₃
 PTS1d = 32768
 F1 = 75.467751 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz



-0.000

1.314

1.331

1.348

1.368

1.387

1.701

1.720

1.737

1.949

1.959

1.967

2.318

3.487

3.504

4.617

4.624

4.633

4.640

5.178

5.193

5.239

5.254

5.262

6.872

7.075

7.092

7.111

7.168

7.189

7.206

7.289

7.309

7.542

7.561

JF-2-149_1.1
JF-2-149,

2018-12-24 11:24:28.046

USFER: nmr1u

SOLVENT: CDCl₃

Experiment = zg30

Pulse length = 15.000 usec

Relaxation delay = 1.000 sec

NA = 16

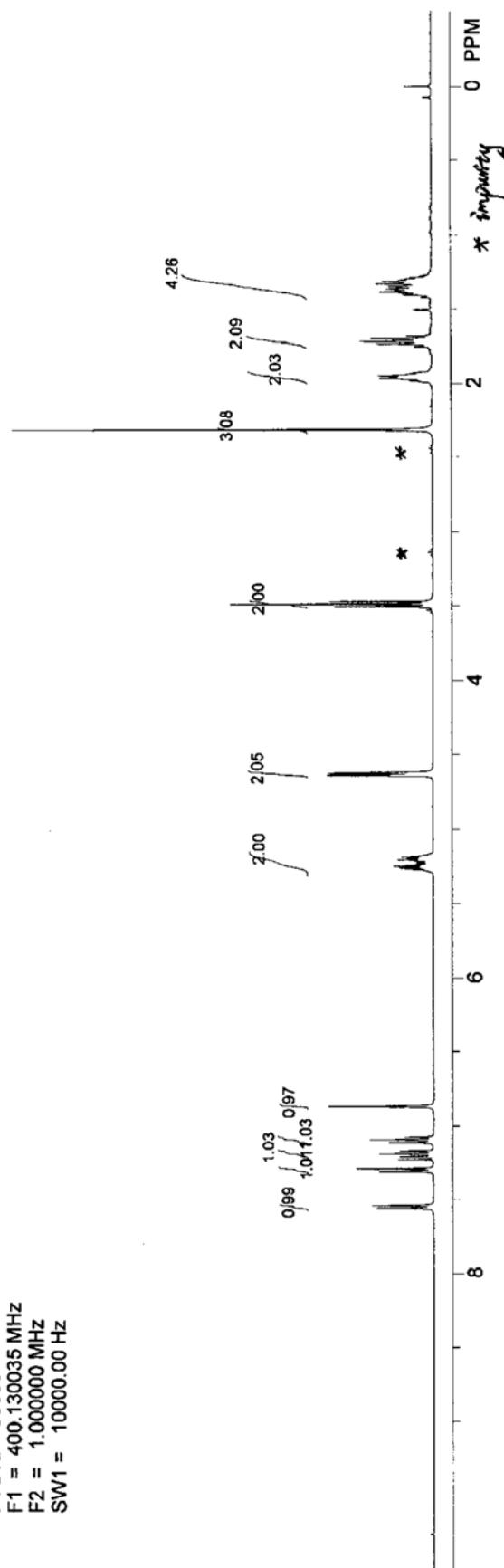
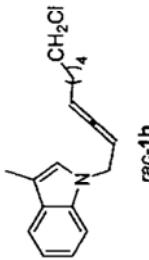
Solvent = CDCl₃

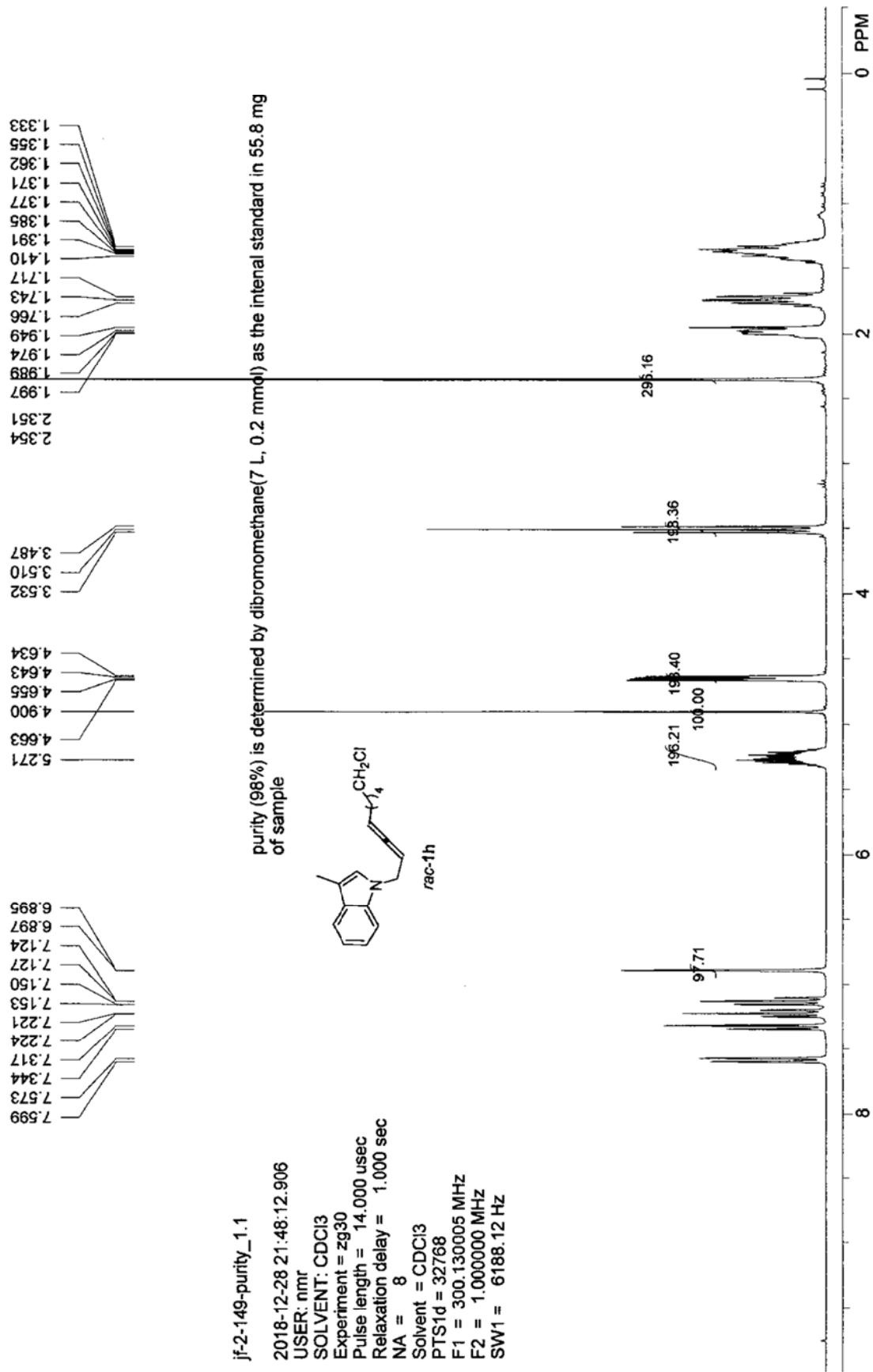
PTTS1d = 65536

F1 = 400.130035 MHz

F2 = 1.000000 MHz

SW1 = 10000.00 Hz

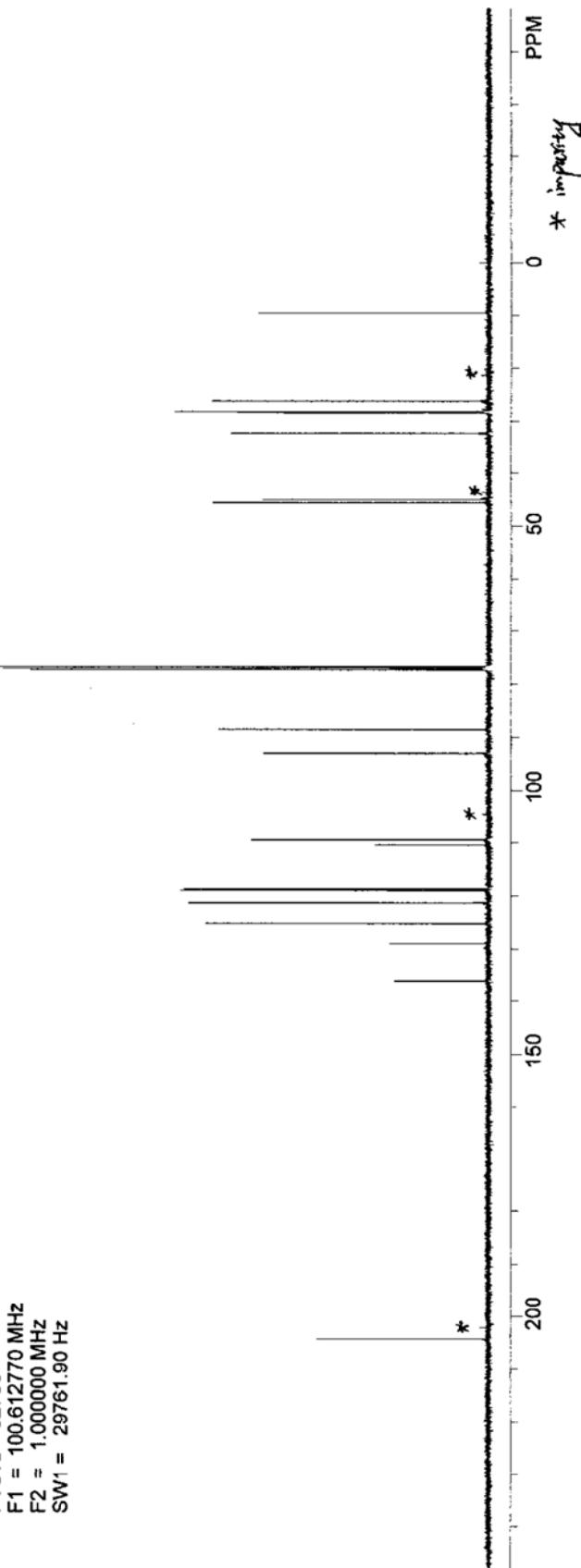
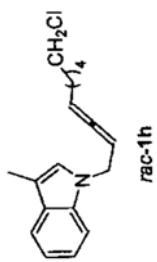


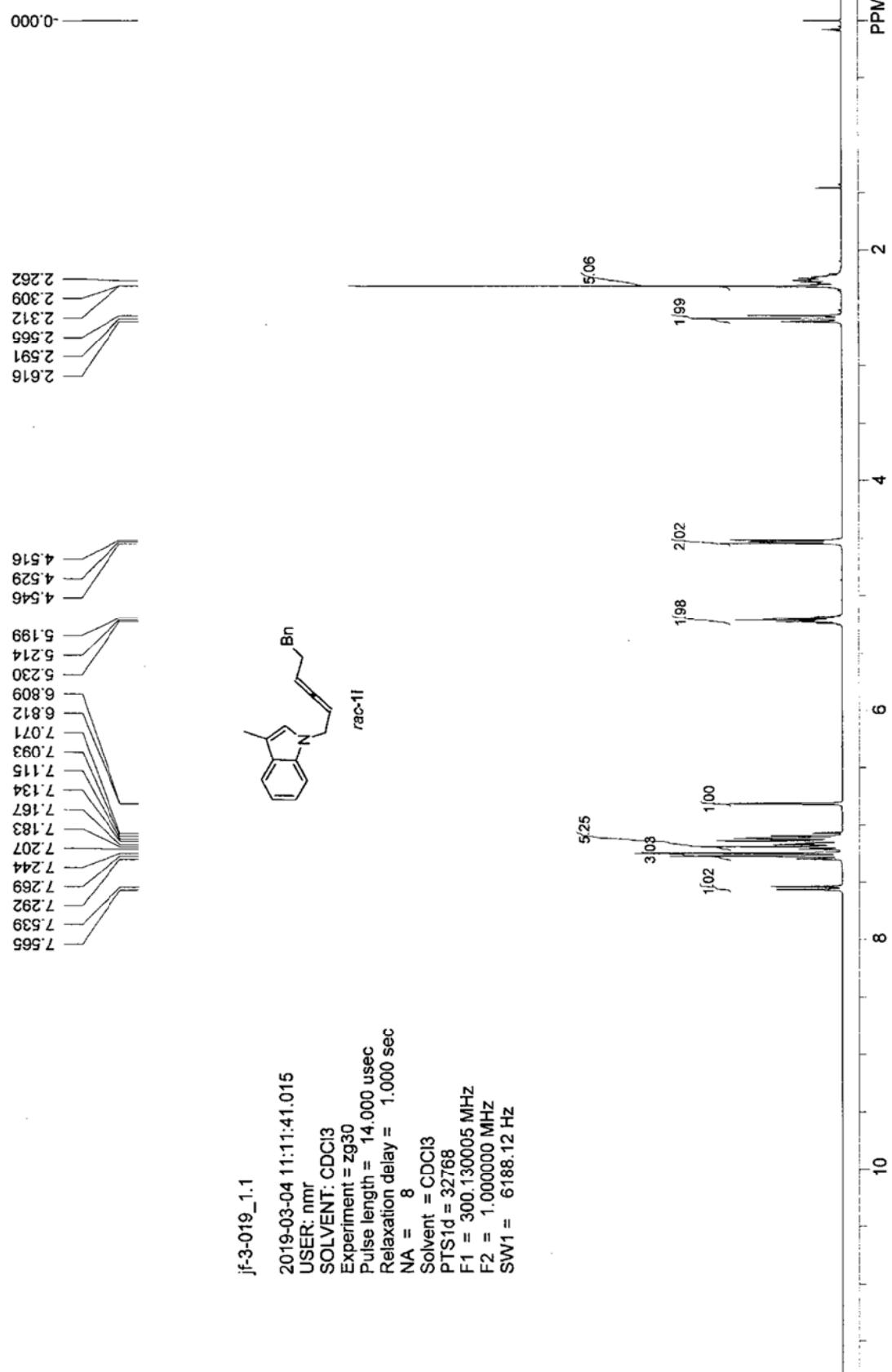


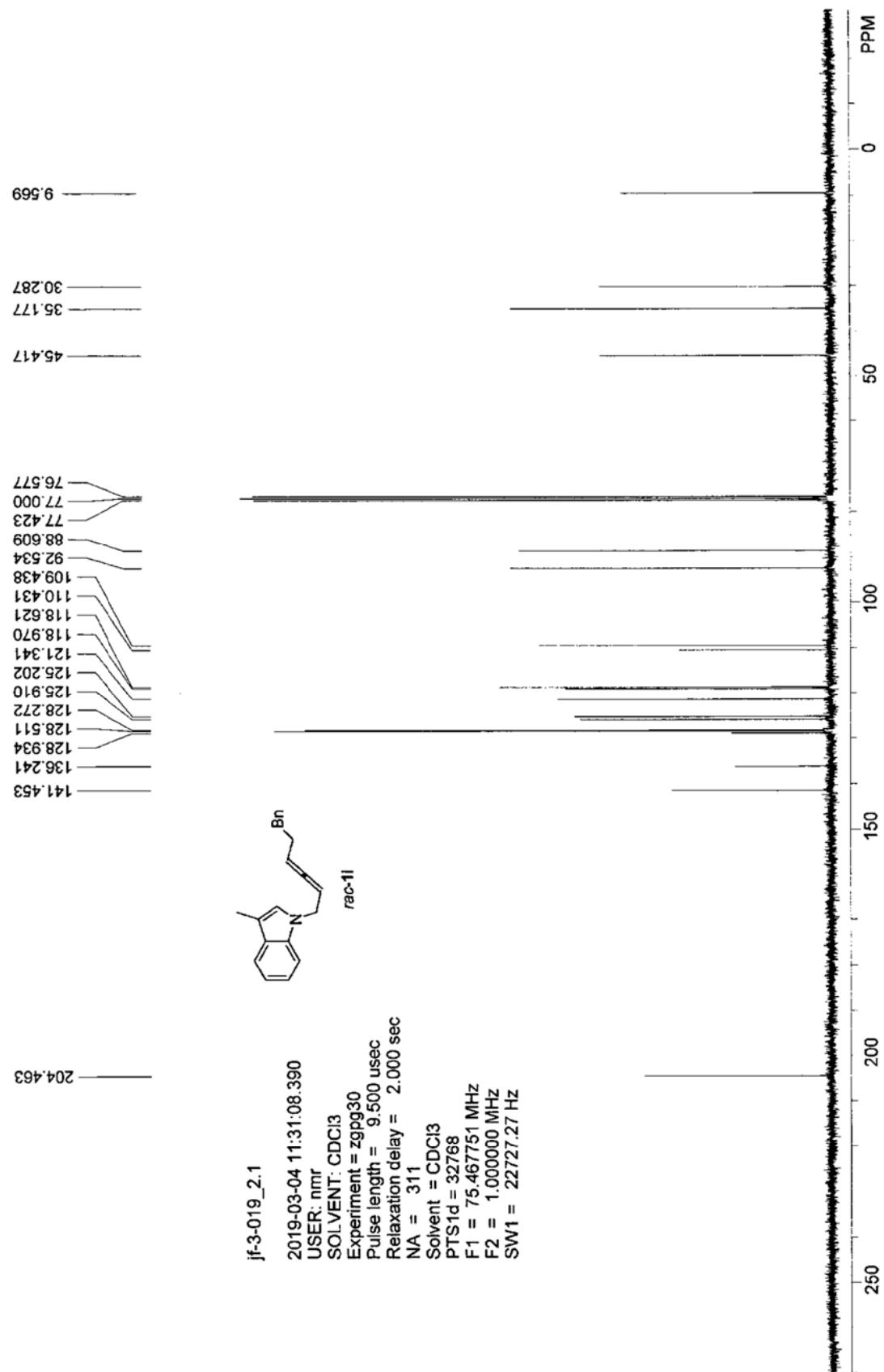
204.365
 136.263
 128.950
 125.194
 121.303
 118.955
 118.612
 110.441
 109.448
 92.989
 88.412
 77.316
 76.684
 45.572
 44.967
 32.364
 28.318
 28.138
 26.206
 9.575

jF-2-149_2.1

2018-12-24 11:48:38.334
 USER: nimusu
 SOLVENT: CDCl₃
 Experiment = zgpg30
 Pulse length = 10.000 usec
 Relaxation delay = 1.500 sec
 NA = 512
 Solvent = CDCl₃
 PTS1d = 32/68
 F1 = 100.612770 MHz
 F2 = 1.000000 MHz
 SW1 = 29761.90 Hz







0.000

0.824
0.848
0.871
1.247
1.259
1.269
1.372
1.393
1.413
1.848
2.318

4.634
4.655
5.027
5.033
5.220
5.241
5.262
5.280
6.888
7.070
7.095
7.119
7.168
7.193
7.217
7.304
7.331
7.542
7.567

jf-3-092_1.1

2019-05-09 21:28:56.484

USER: nmr

SOLVENT: CDCl₃

Experiment = zg30

Pulse length = 14.000 usec

Relaxation delay = 1.000 sec

NA = 8

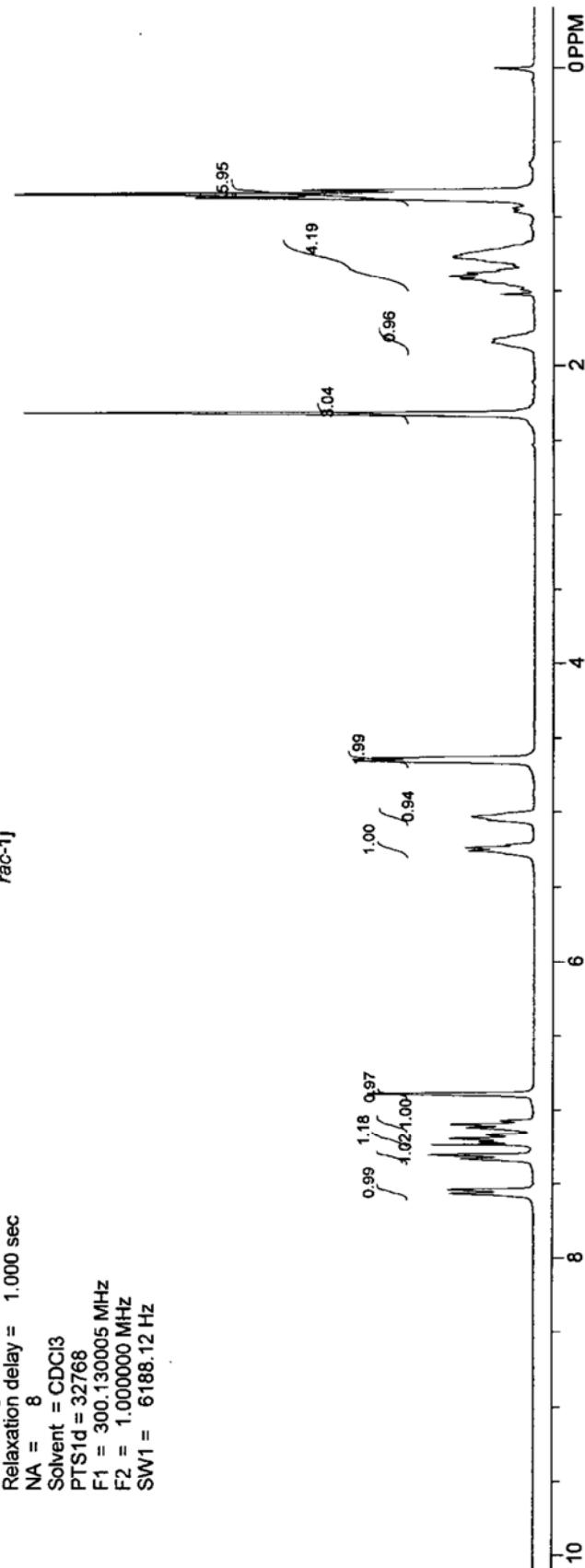
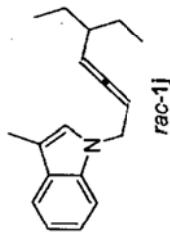
Solvent = CDCl₃

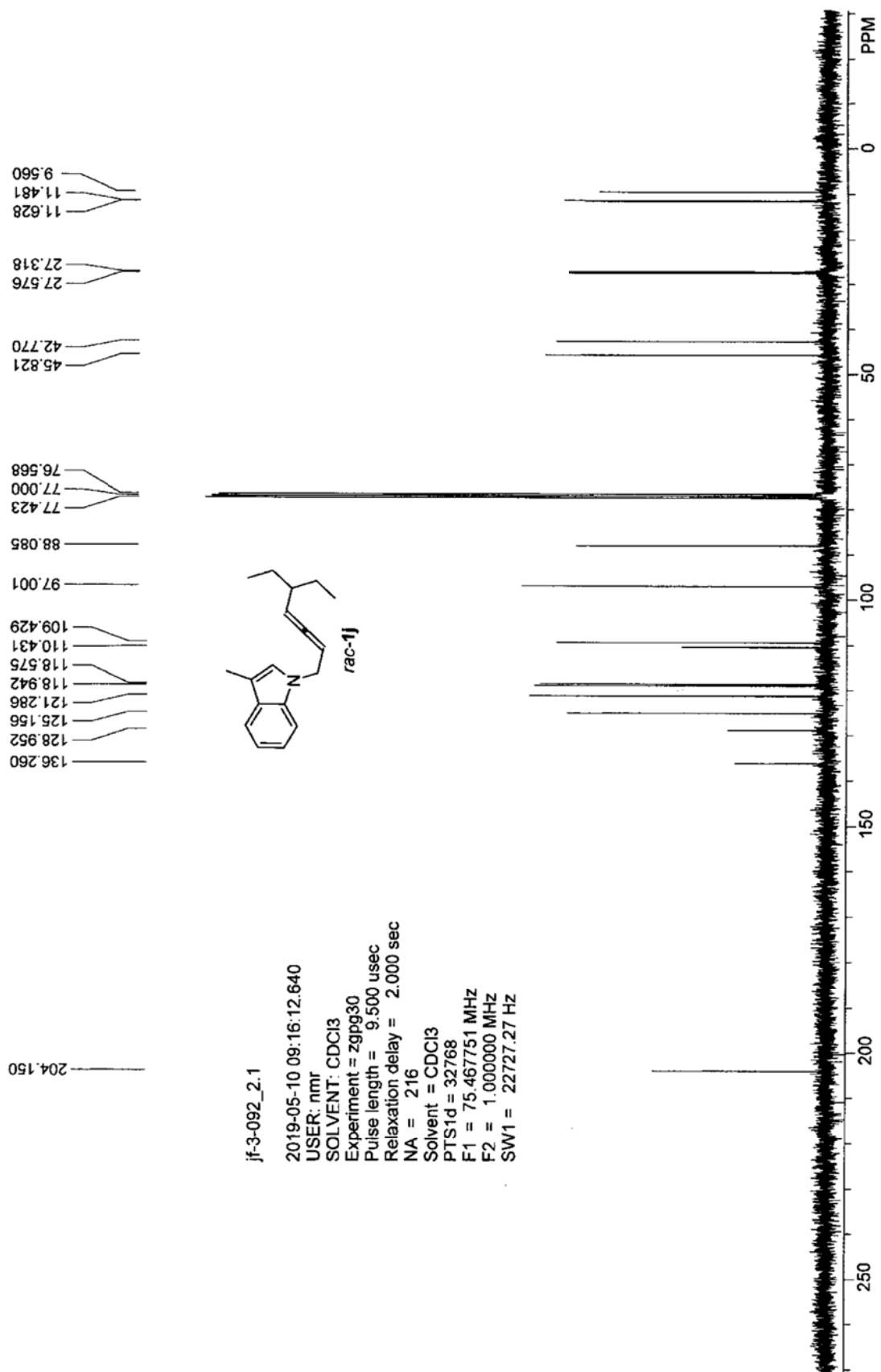
PTSID = 32768

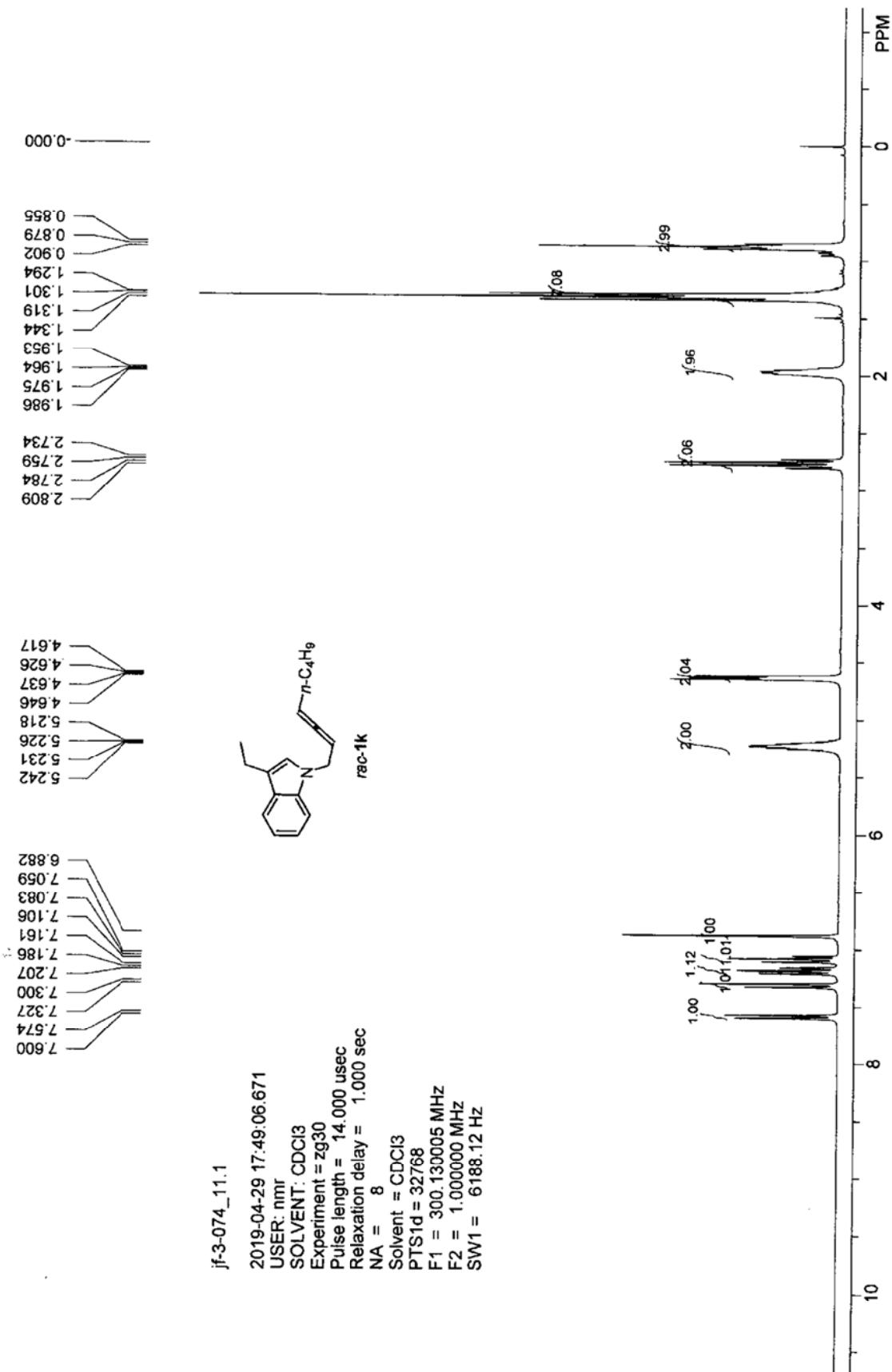
F1 = 300.130005 MHz

F2 = 1.000000 MHz

SW1 = 6188.12 Hz







204.399

136.388

93.270

88.122

77.423

77.000

76.577

31.142

28.265

22.116

18.283

14.542

13.871

jf-3-074_2.1

2019-04-29 17:17:10.171

USER: nmr

SOLVENT: CDCl₃

Experiment = zgpp30

Pulse length = 9.500 usec

Relaxation delay = 2.000 sec

NA = 297

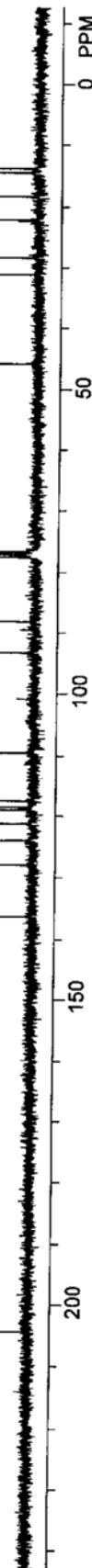
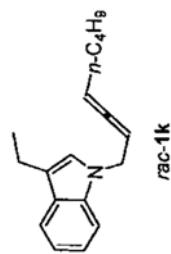
Solvent = CDCl₃

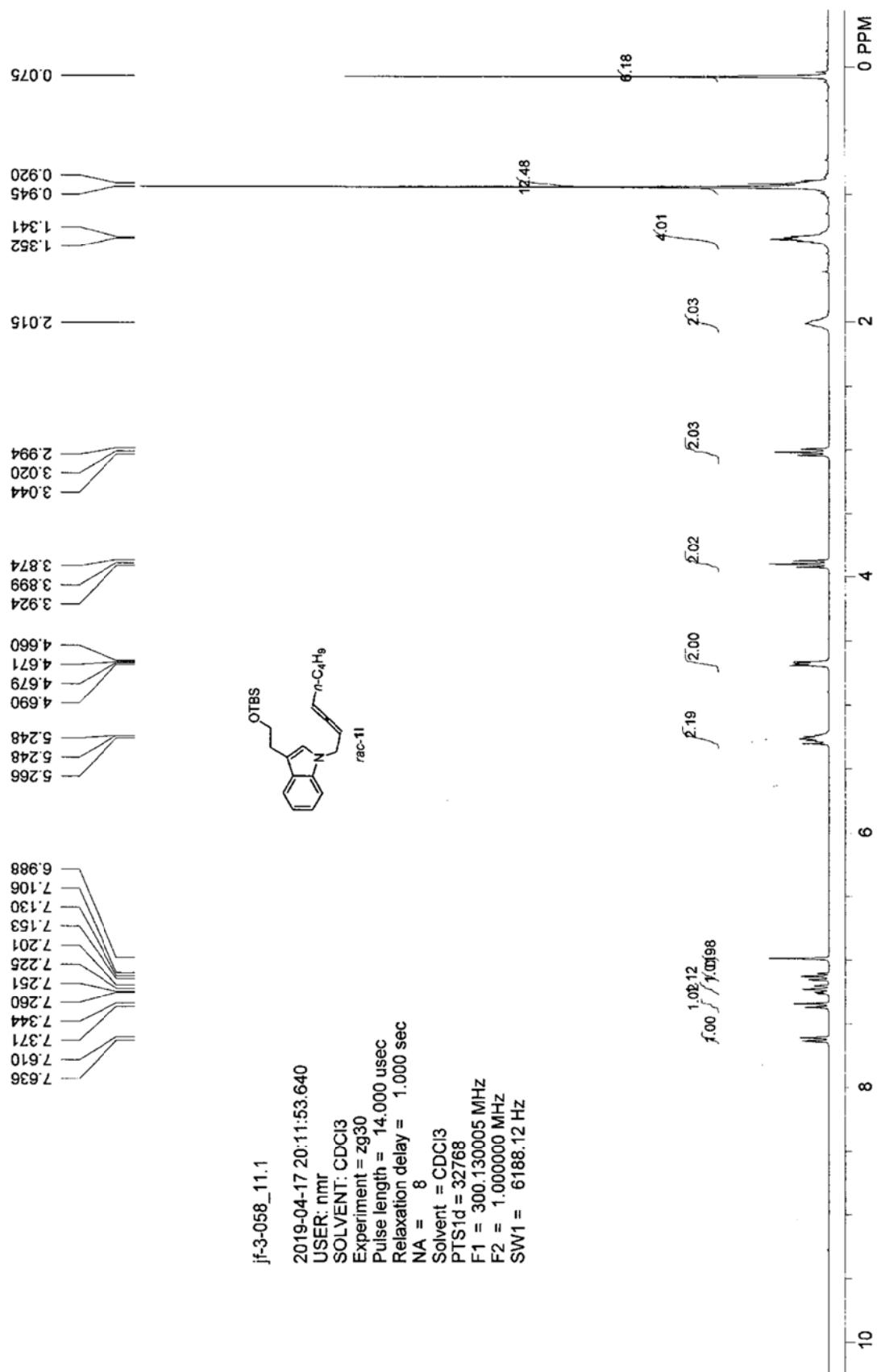
PTS1d = 32768

F1 = 75.46751 MHz

F2 = 1.000000 MHz

SW1 = 22727.27 Hz





-5.294

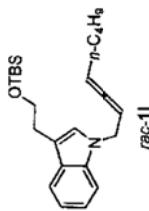
13.871
18.375
22.097
25.976
28.256
28.982
31.151

45.821

63.975
76.577
77.000
77.423
88.003
93.306

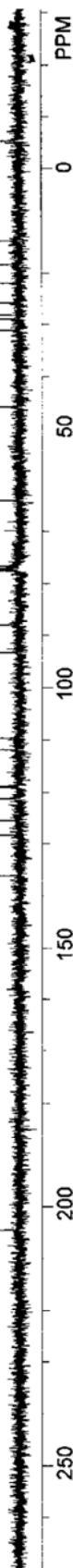
109.594
111.782
118.749
118.988
121.305
125.597
128.391
136.149

-204.435



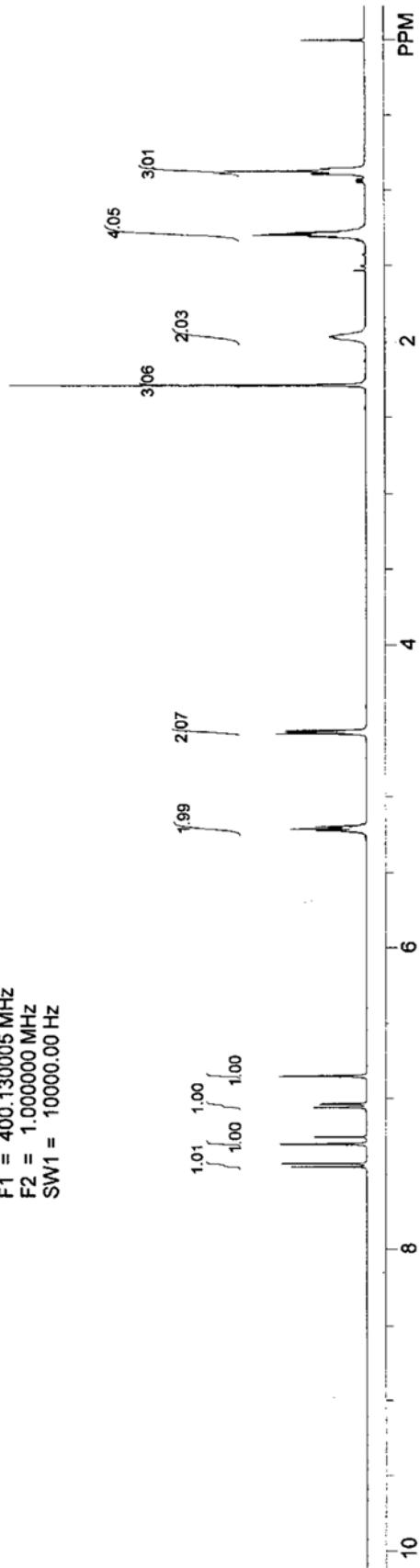
jf-3-058_2.1

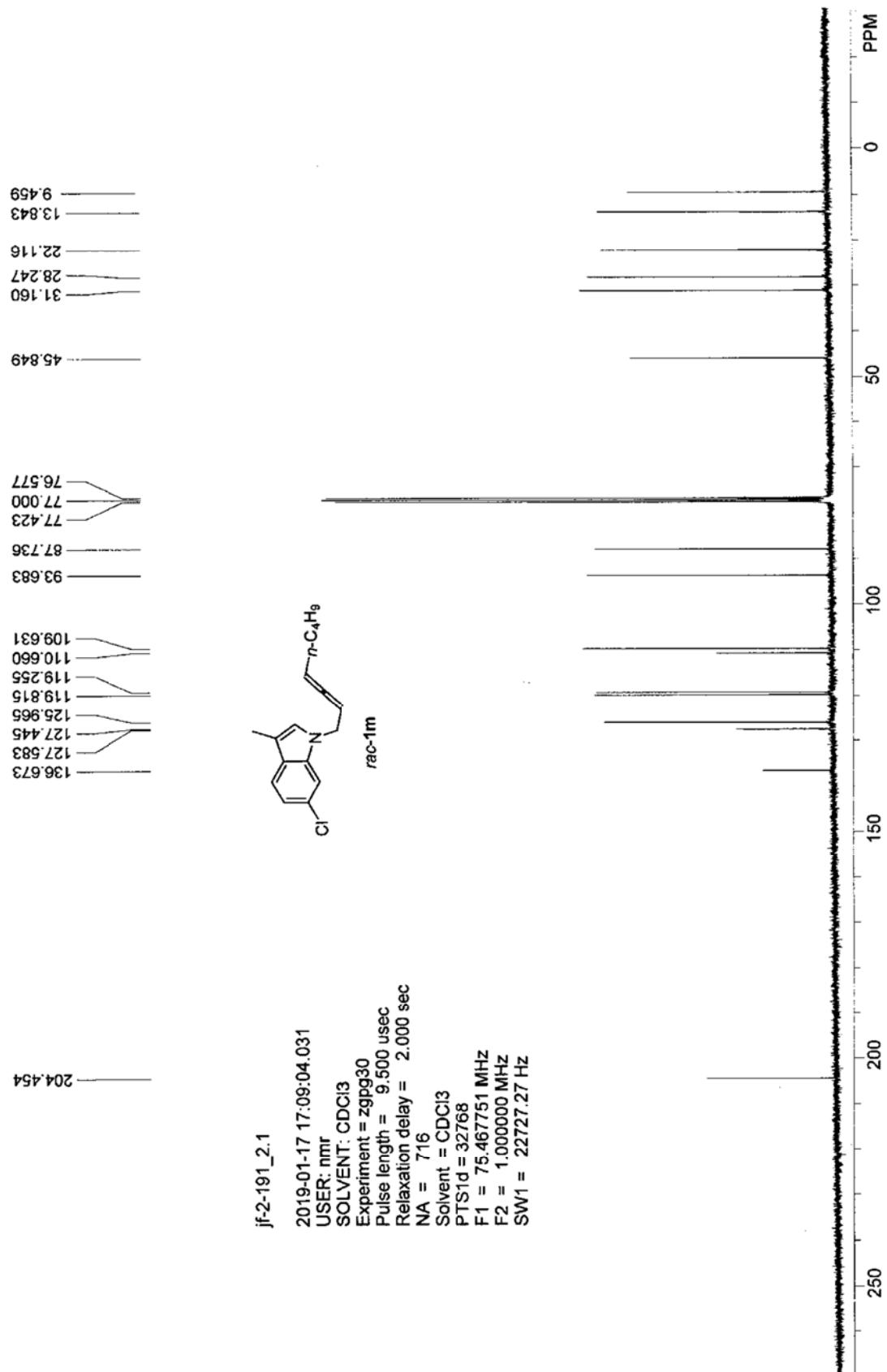
2019-04-17 20:06:42.578
USER: nmr
SOLVENT: CDCl₃
Experiment = zgppg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 104
Solvent = CDCl₃
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

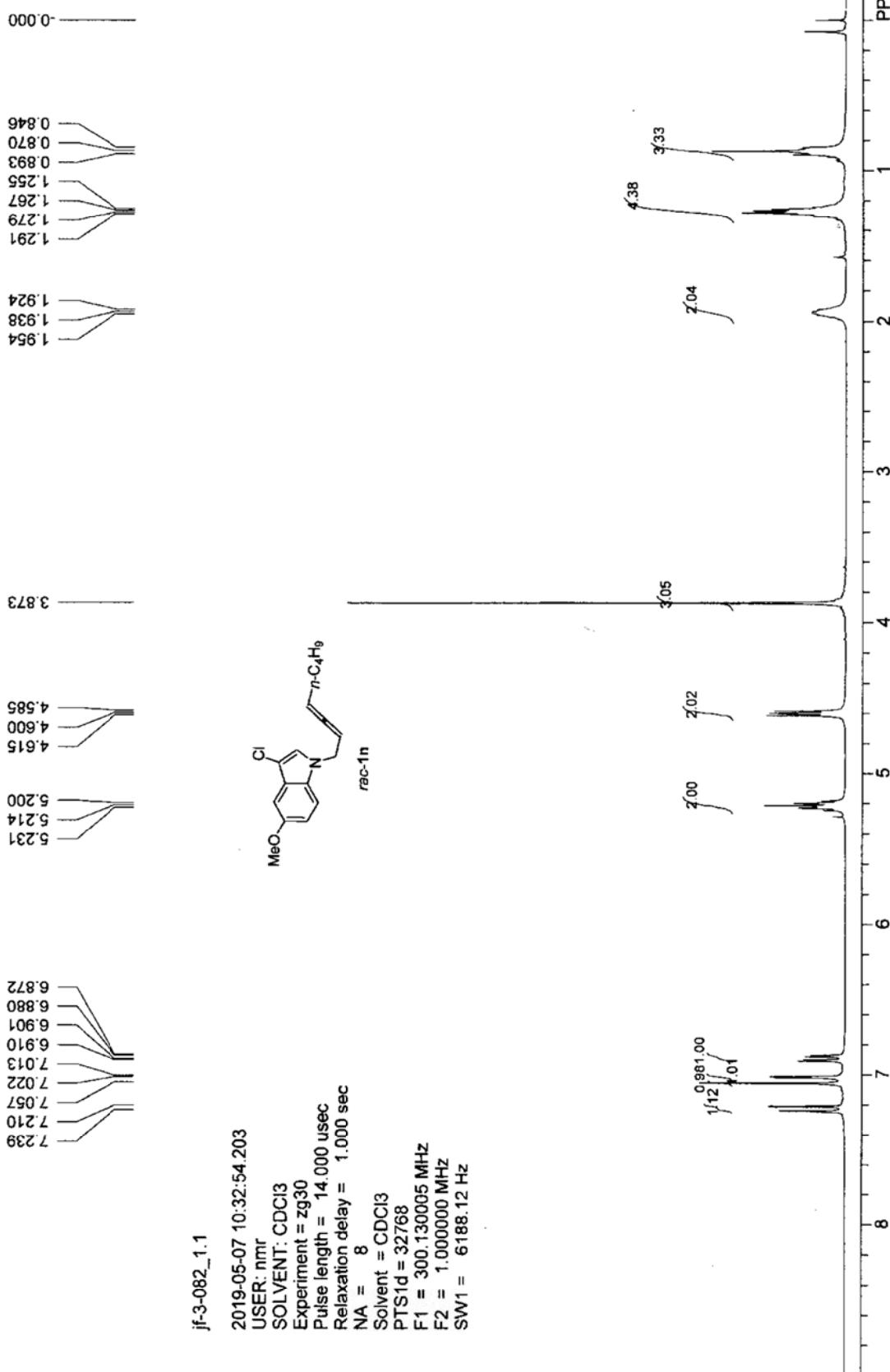


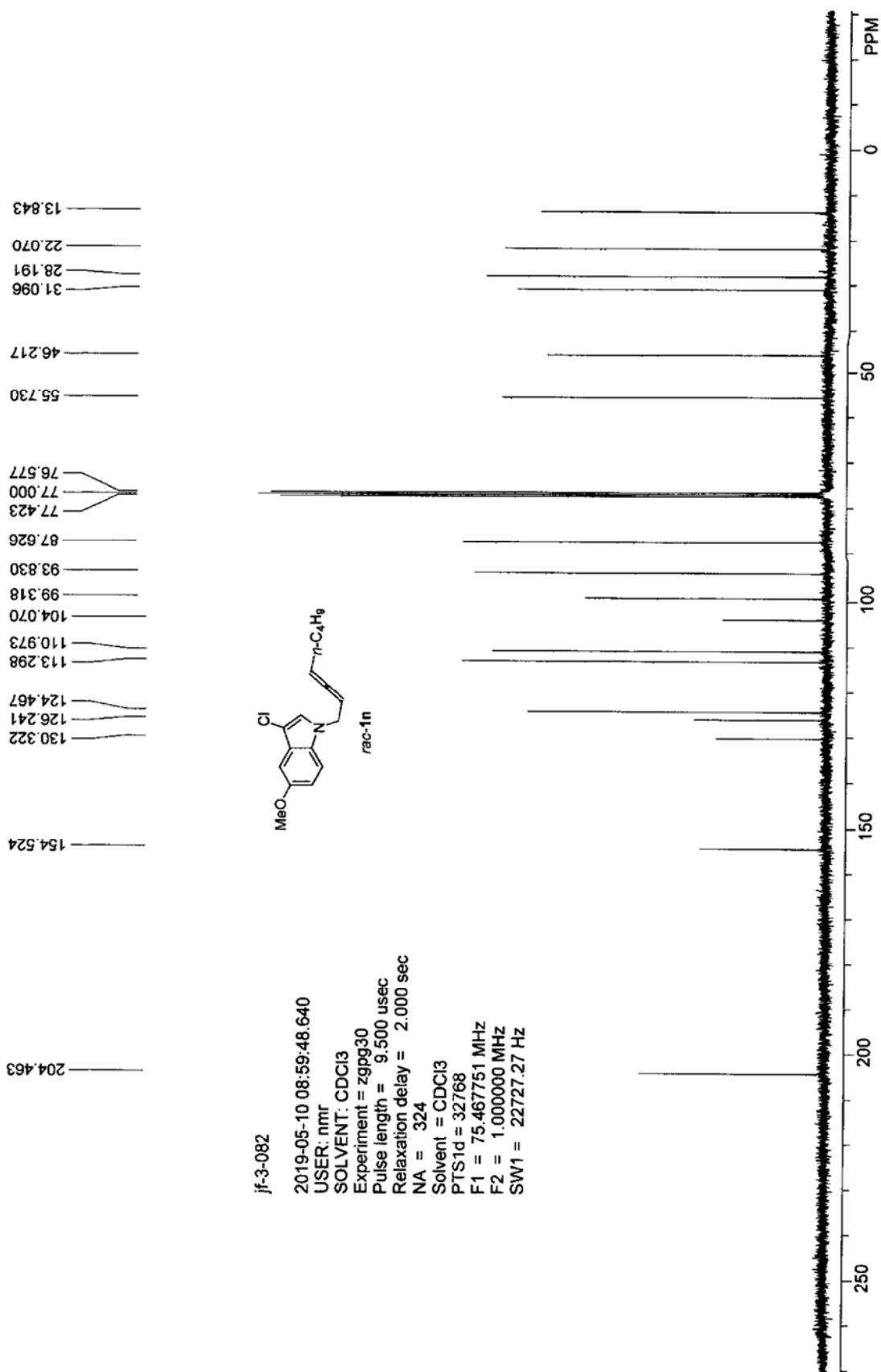


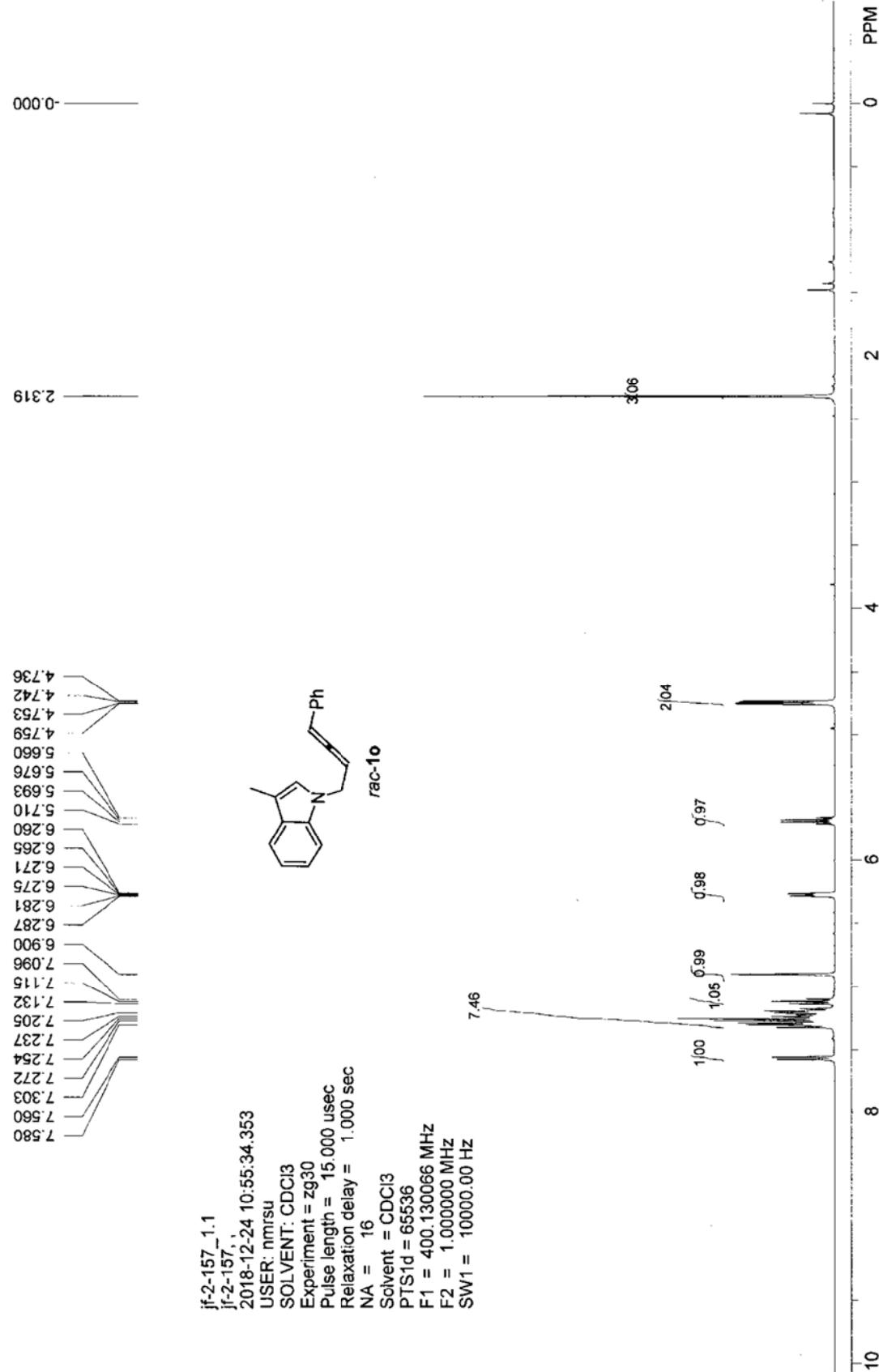
Cc1ccccc1C[C@H](CCCC)n
rac-1m
 Jf-2-191_1.1
 Jf-2-191_1
 2019-01-21 16:02:22.935
 USER: nmrisu
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 15.000 usec
 Relaxation delay = 1.000 sec
 NA = 16
 Solvent = CDCl3
 PTS1d = 65536
 F1 = 400.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 10000.00 Hz

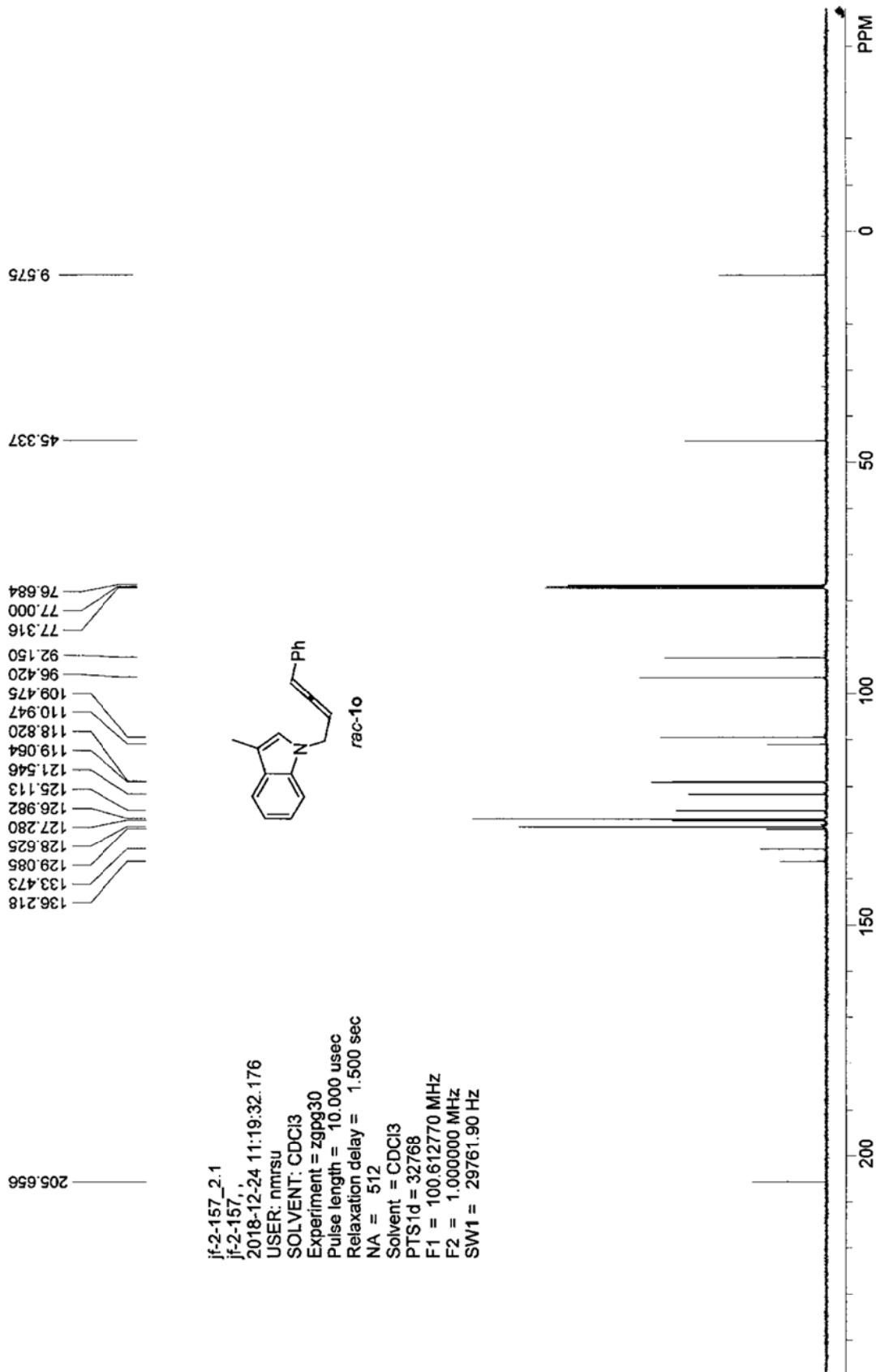


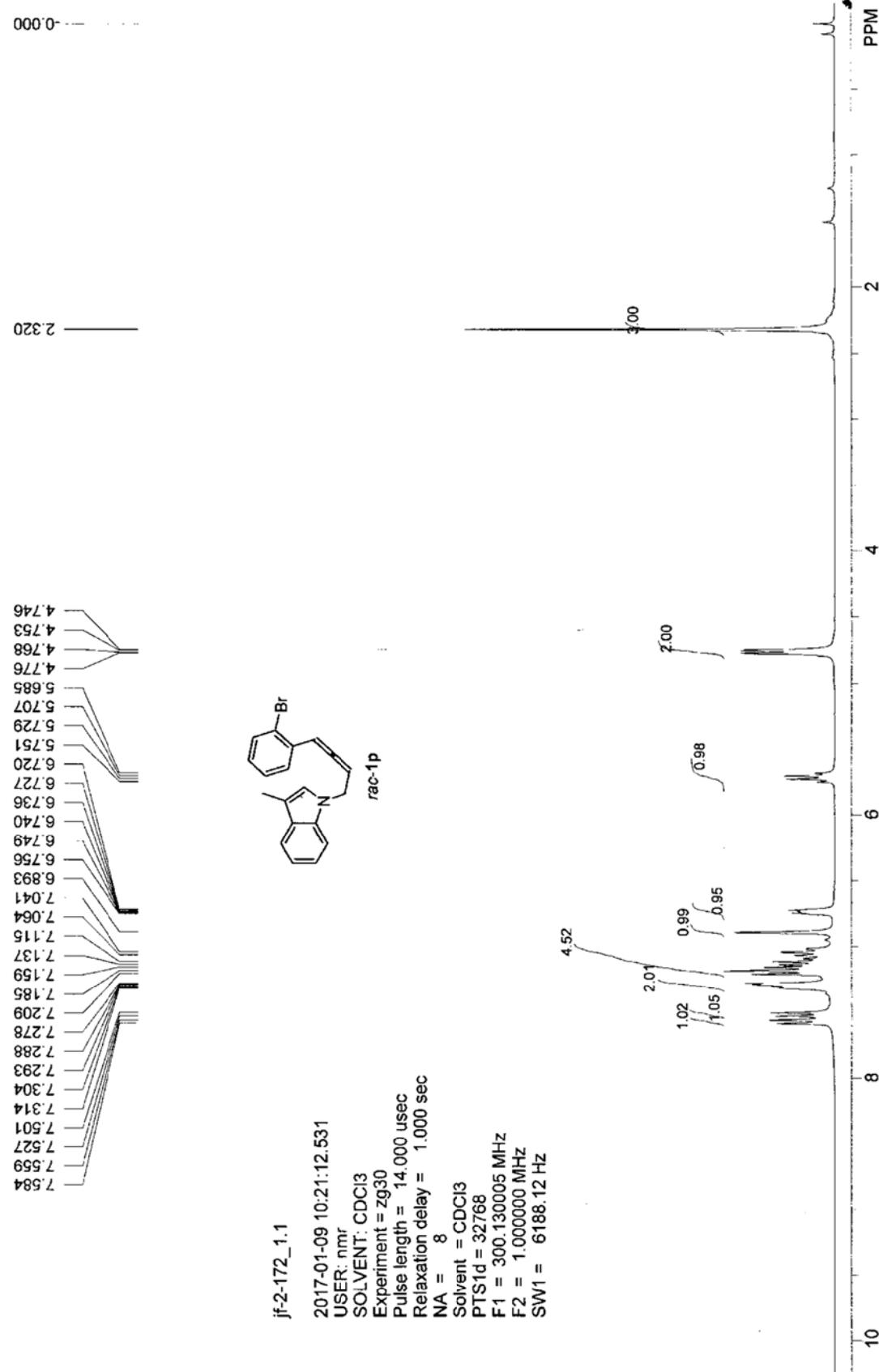




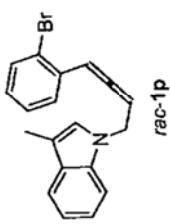








jf2-172
2017-01-09 10:37:11.781
USER: nmr
SOLVENT: CDCl₃
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 251
Solvent = CDCl₃
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

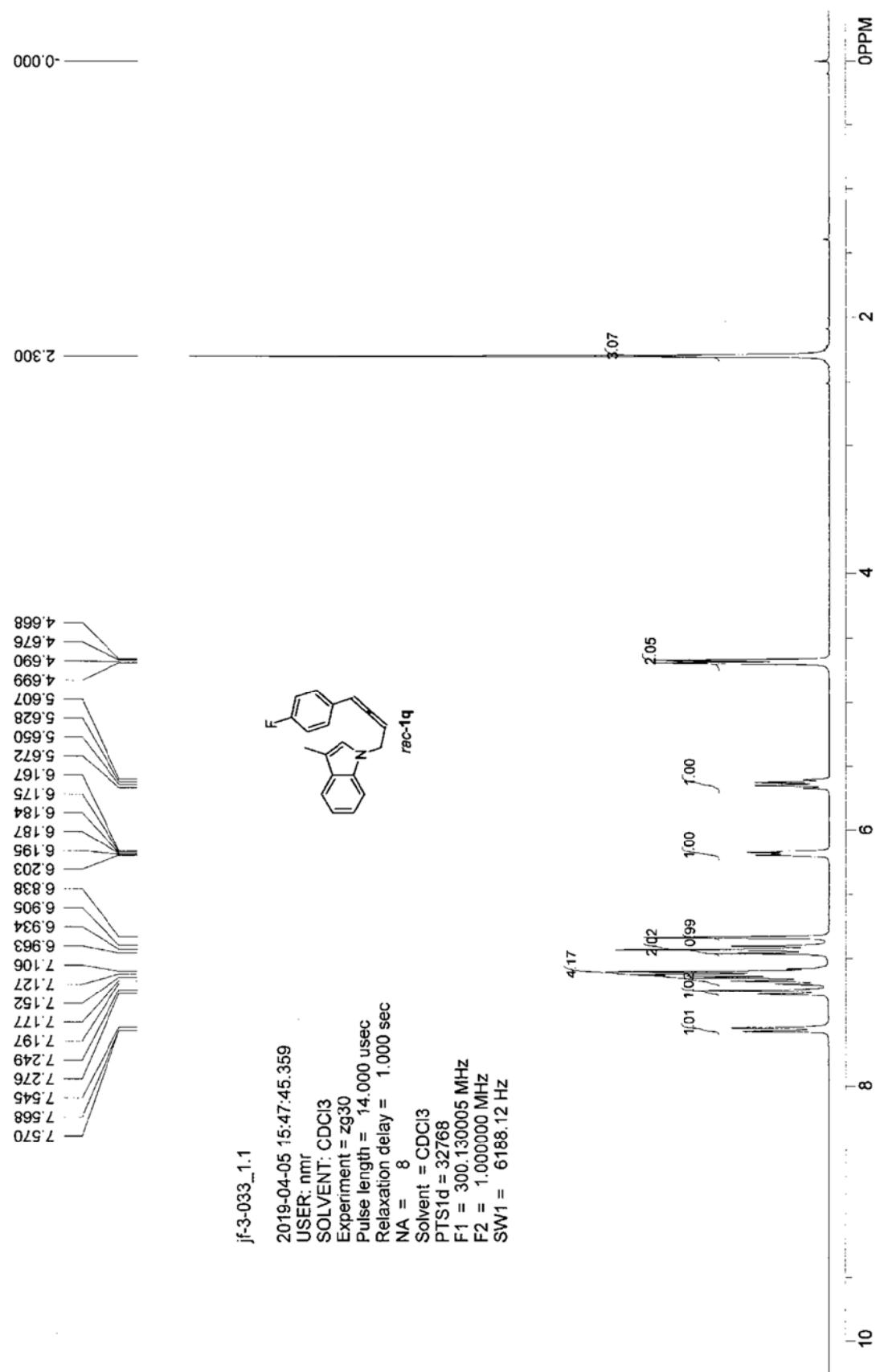


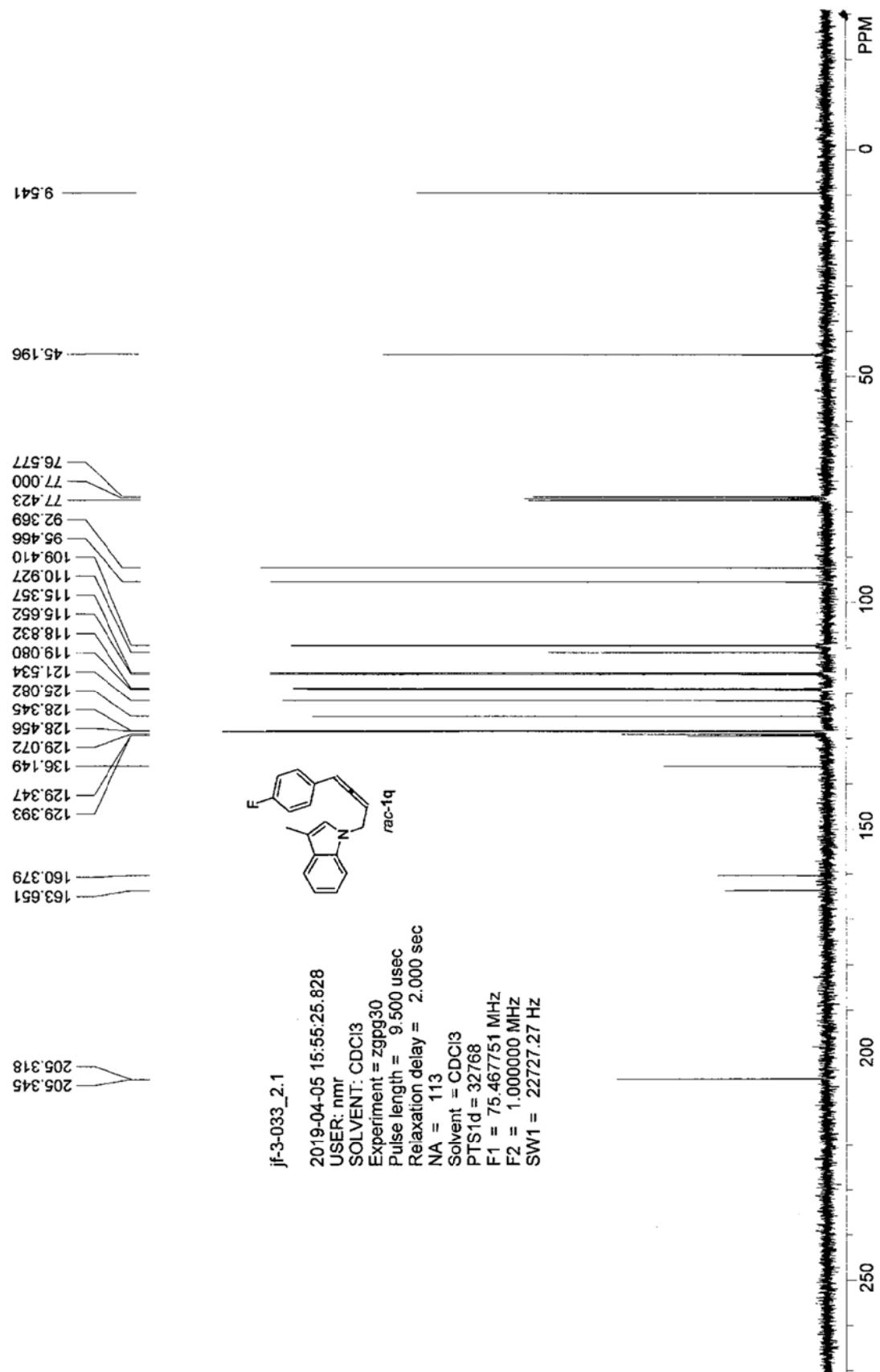
9.578

45.058

136.159
132.987
132.951
129.099
128.649
128.557
127.408
125.092
122.564
121.599
119.108
118.869
111.065
109.420
95.521
92.387
77.423
77.000
76.577



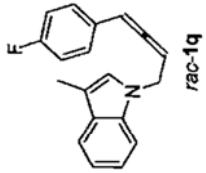




jf-3-033_4.1

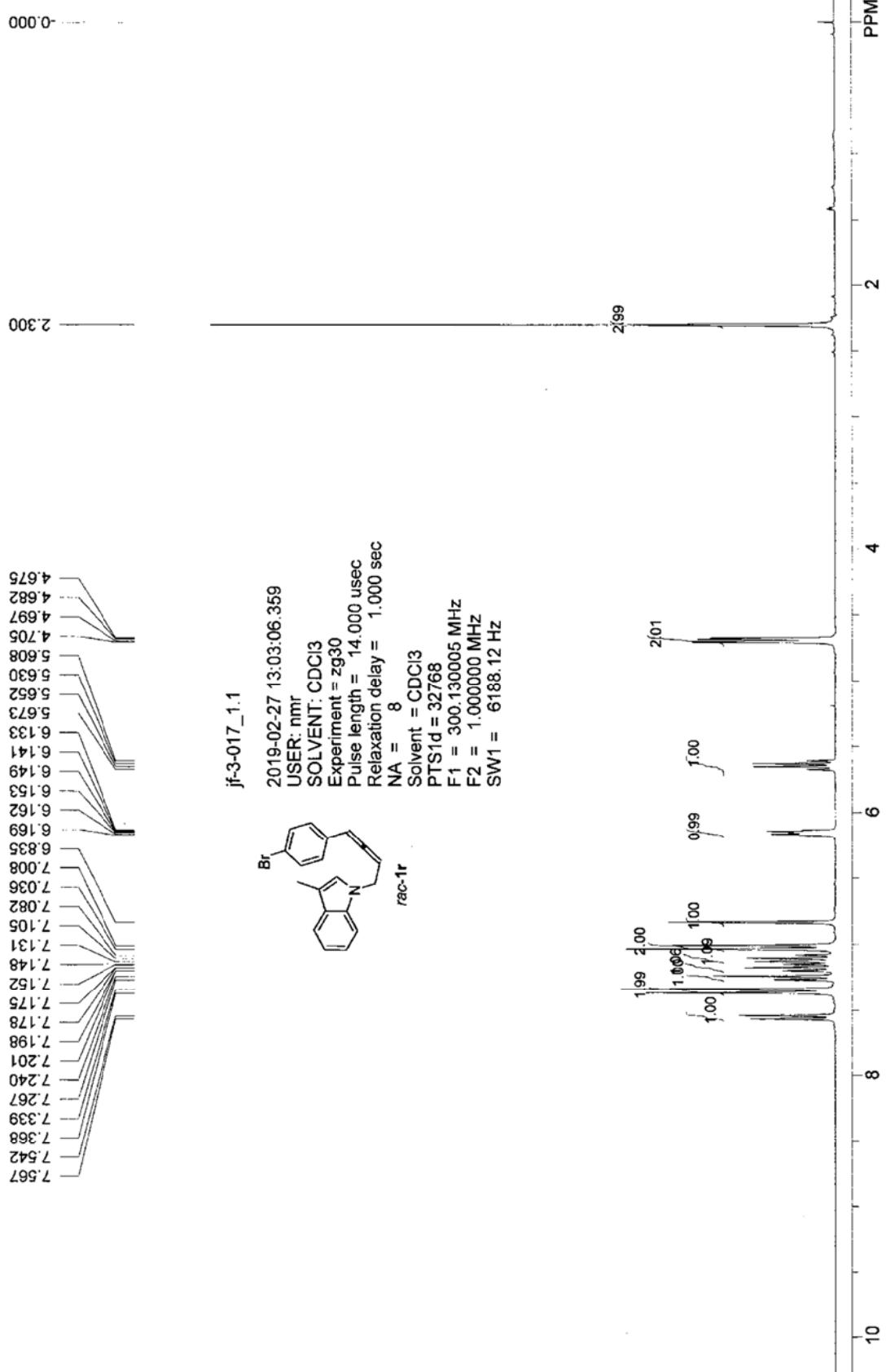
2019-04-06 09:22:32.859
USER: nmr
SOLVENT: CDCl₃
Experiment = zgfhgqn
Pulse length = 13.500 usec
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl₃
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz
SW1 = 66964.29 Hz

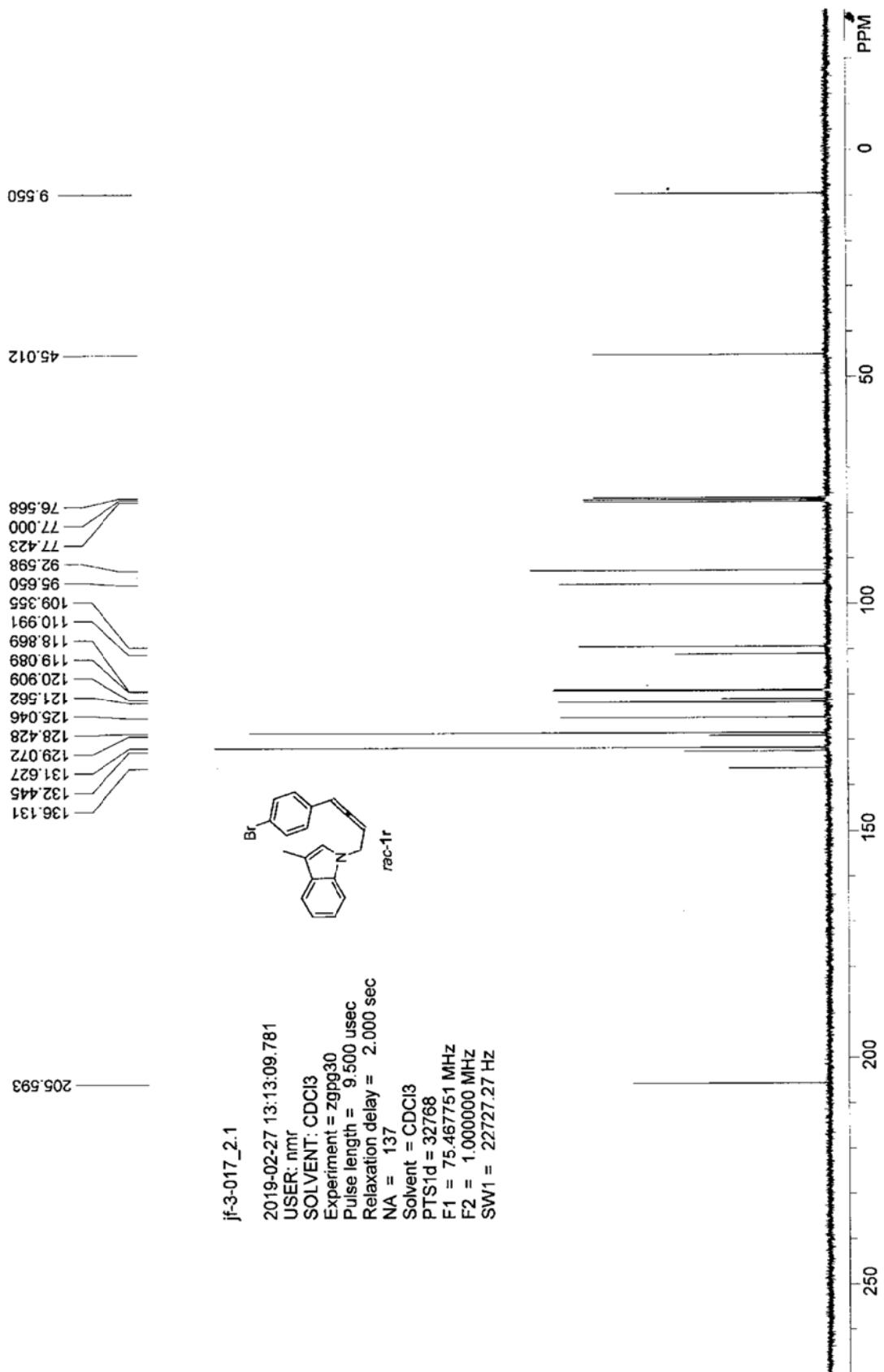
-115215

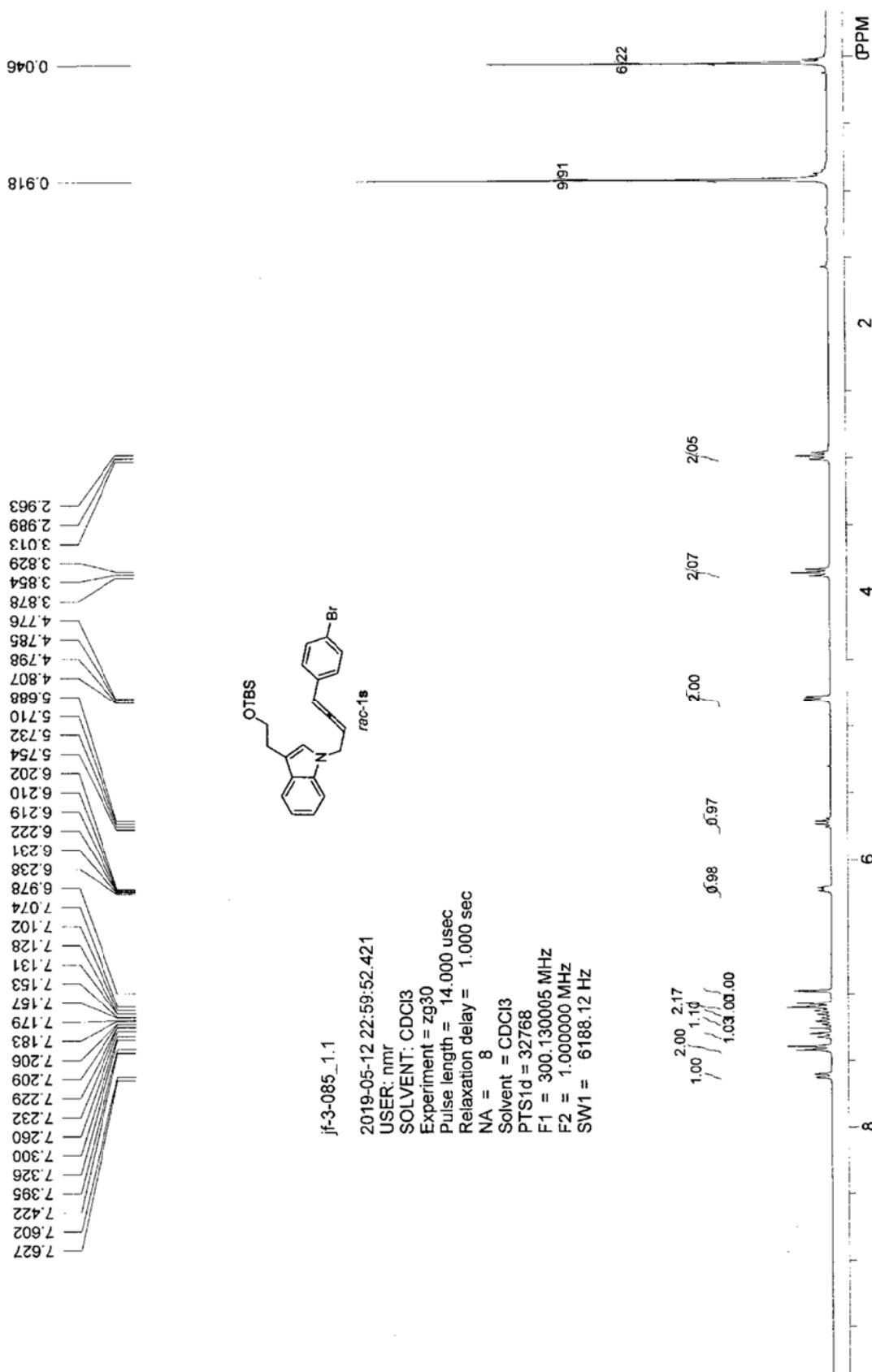


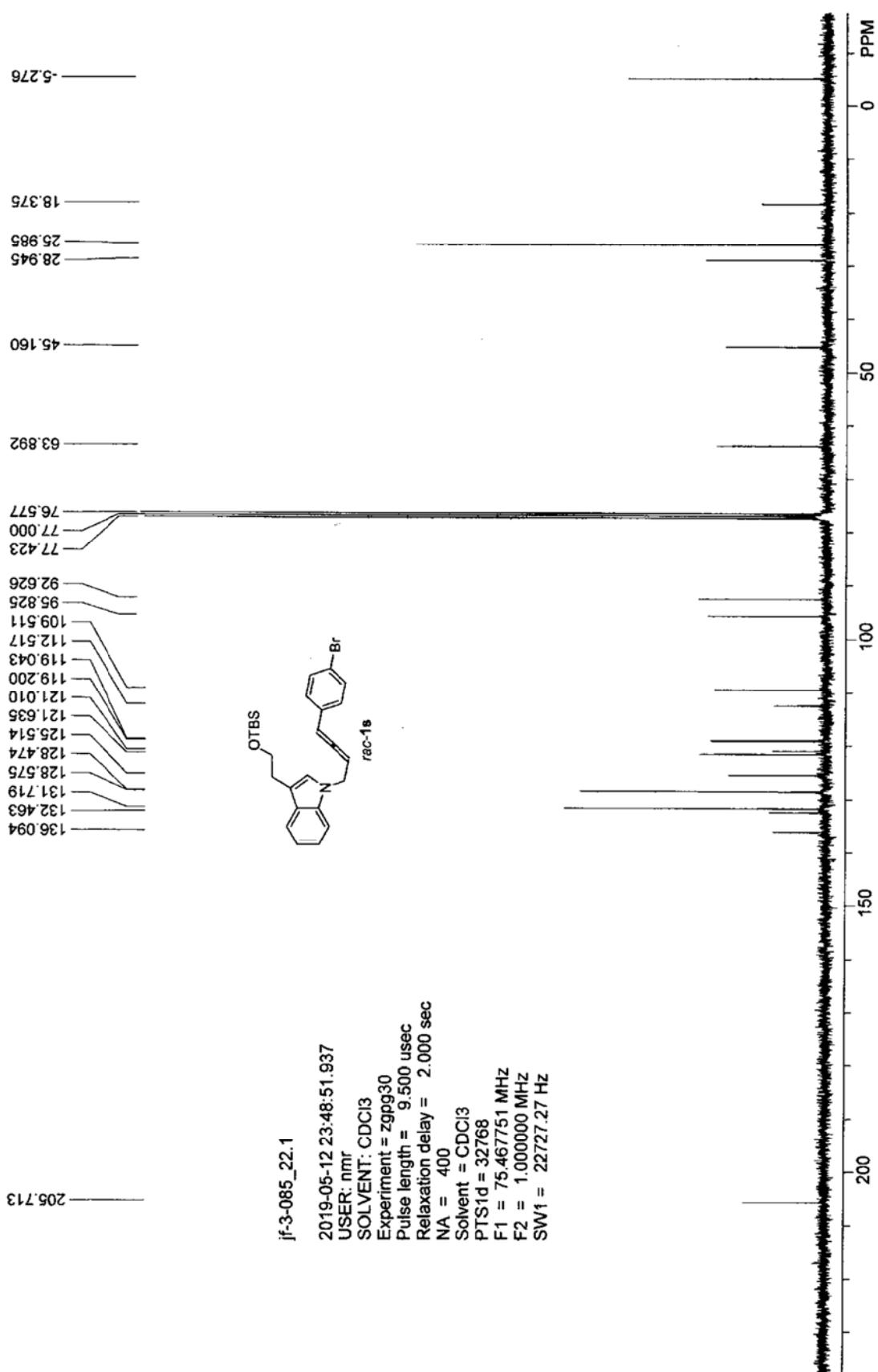
0.000-









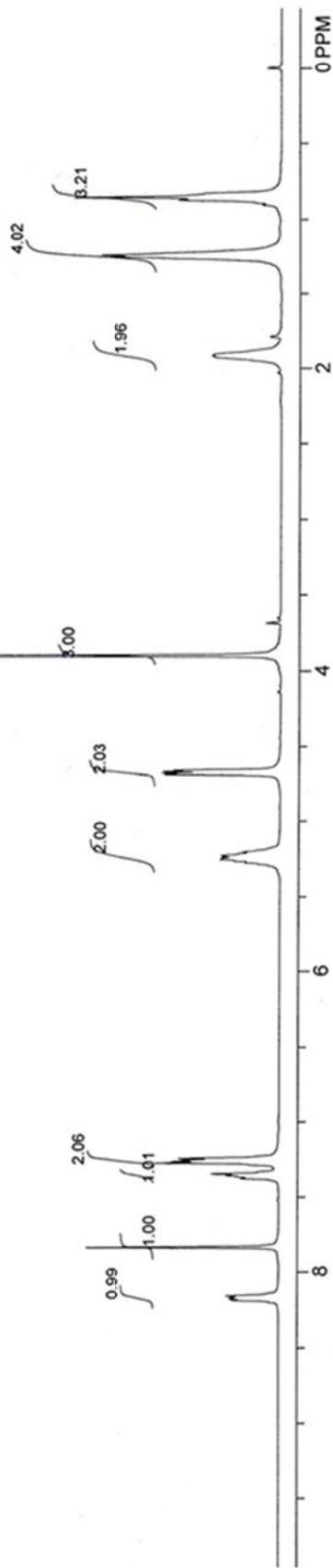


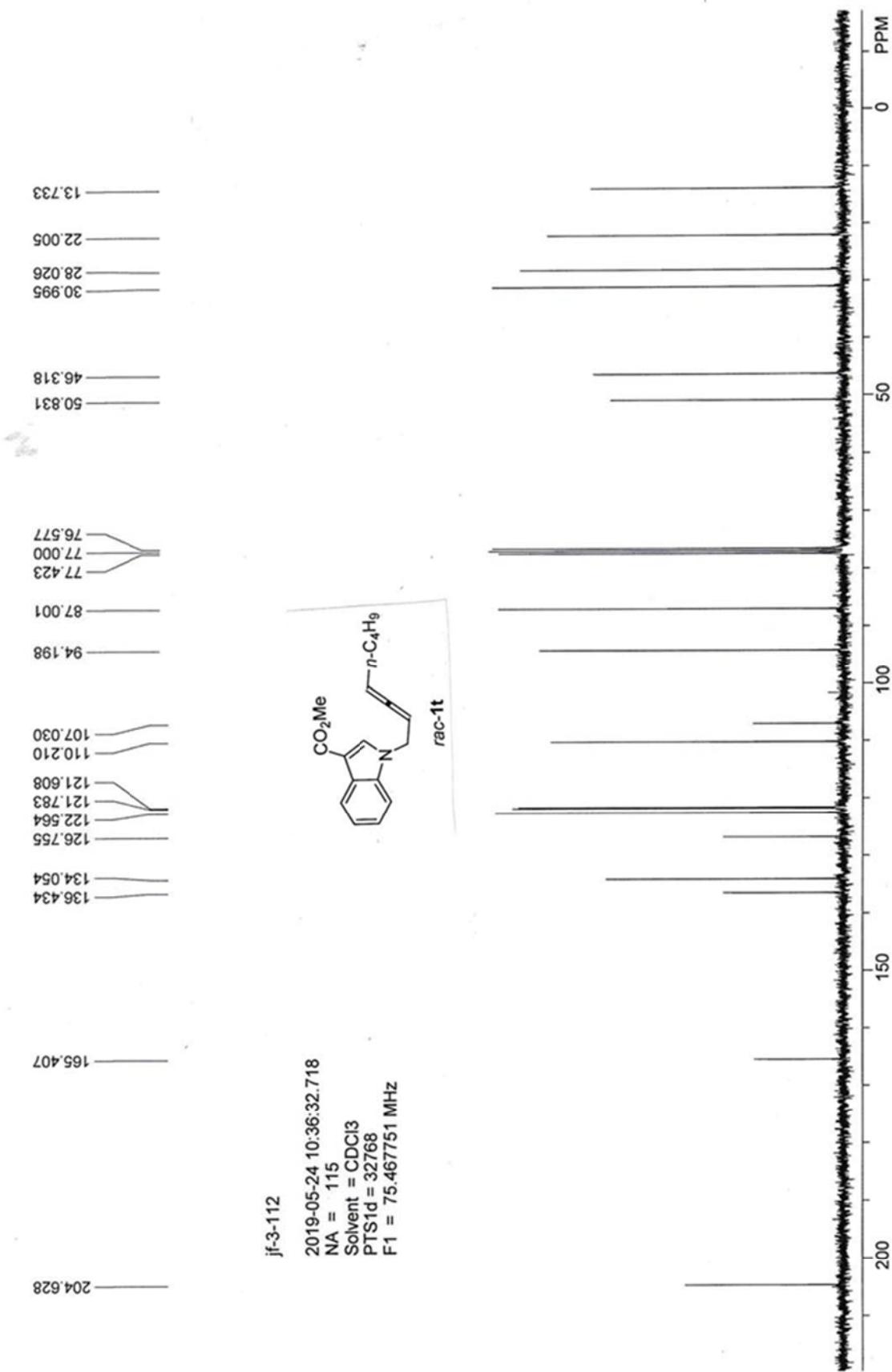
0.000
 0.827
 0.849
 0.869
 1.236
 1.248
 1.905
 1.914
 3.897
 5.274
 5.225
 5.253
 5.203
 4.690
 4.680
 4.670
 4.661

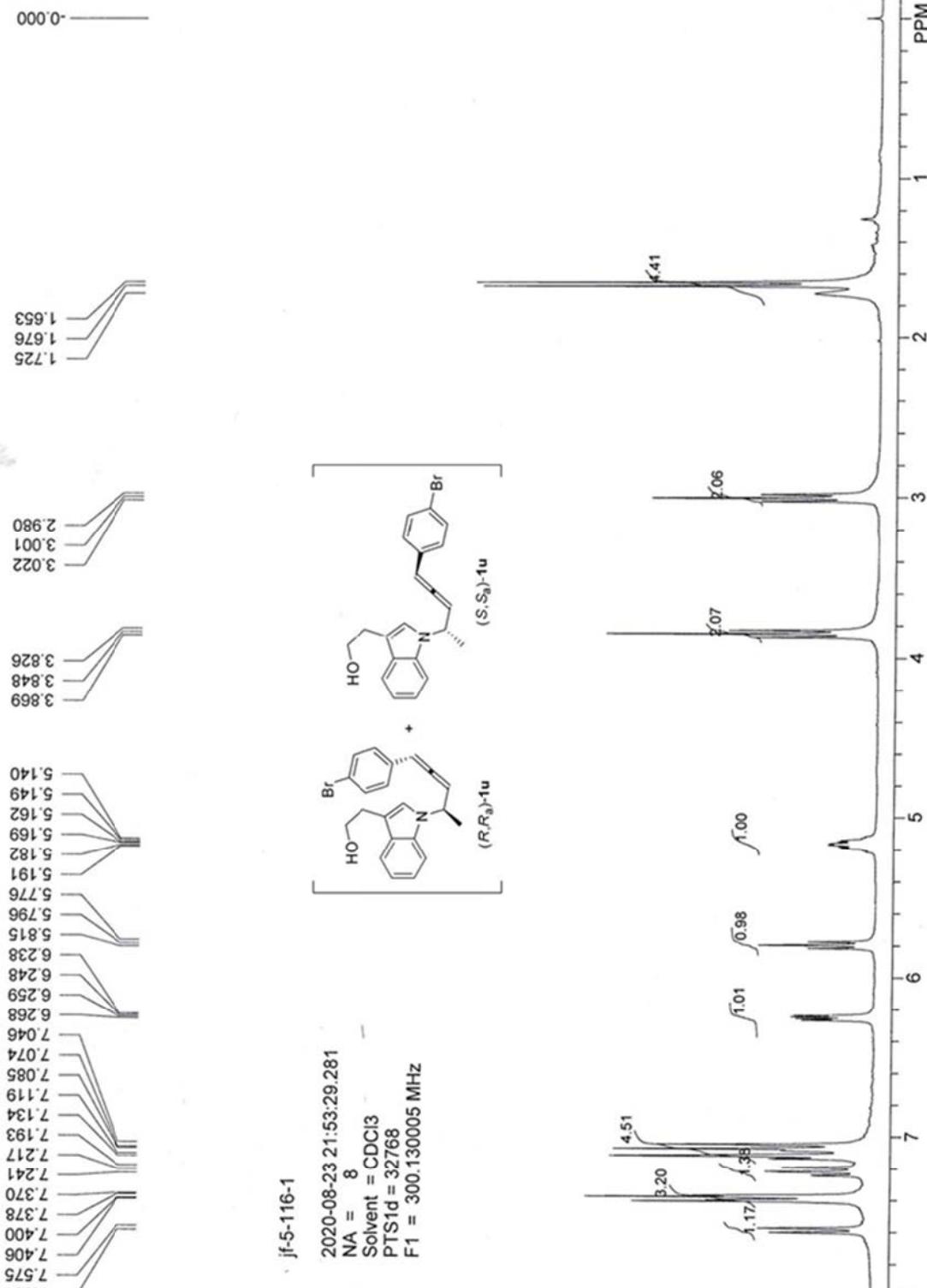
jf-3-112
 2019-05-24 10:28:38.515
 NA = 8
 Solvent = CDCl₃
 PTS1d = 32768
 F1 = 300.130005 MHz

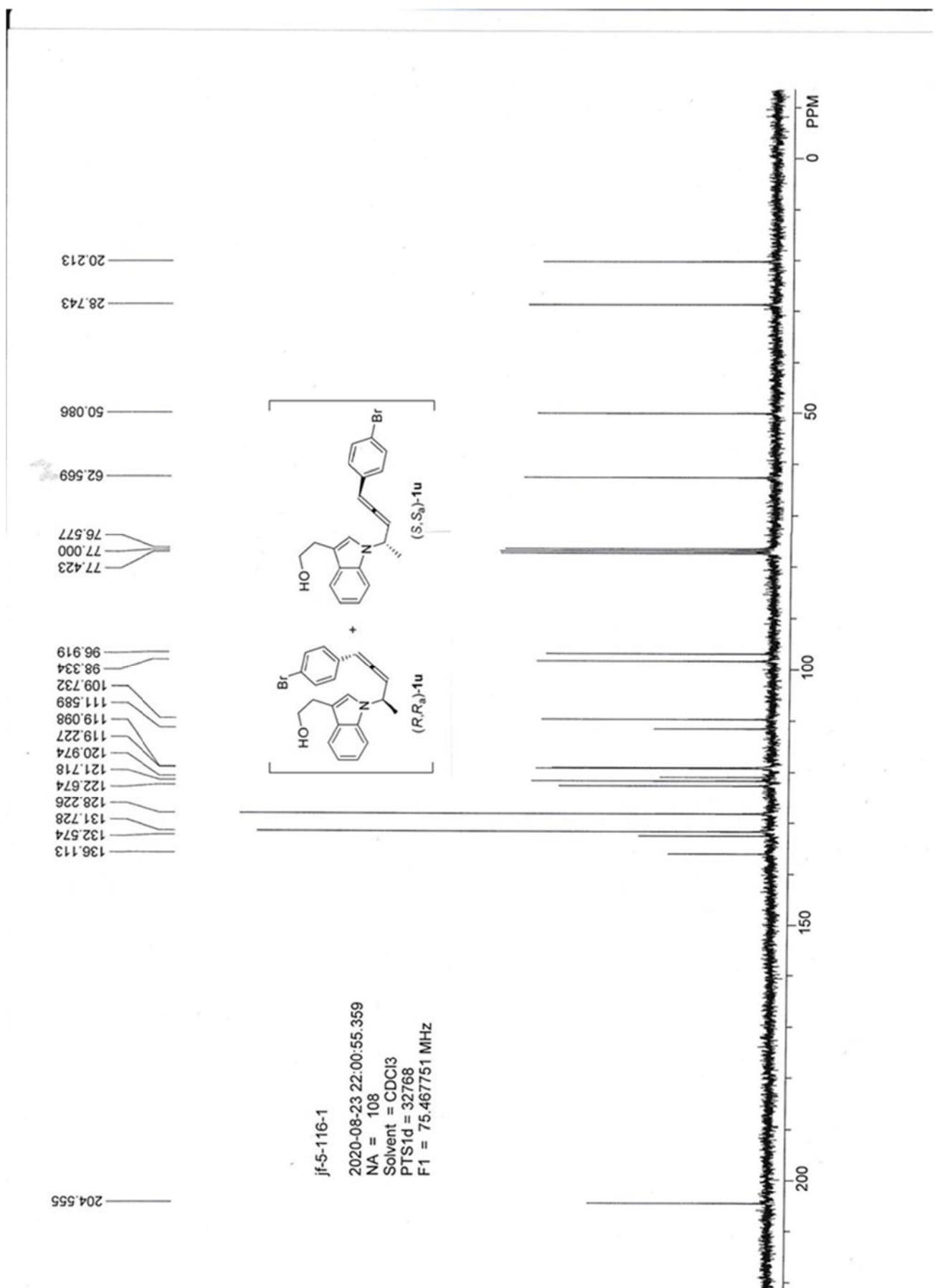
C=CCn1c(C(=O)O)c2ccccc21

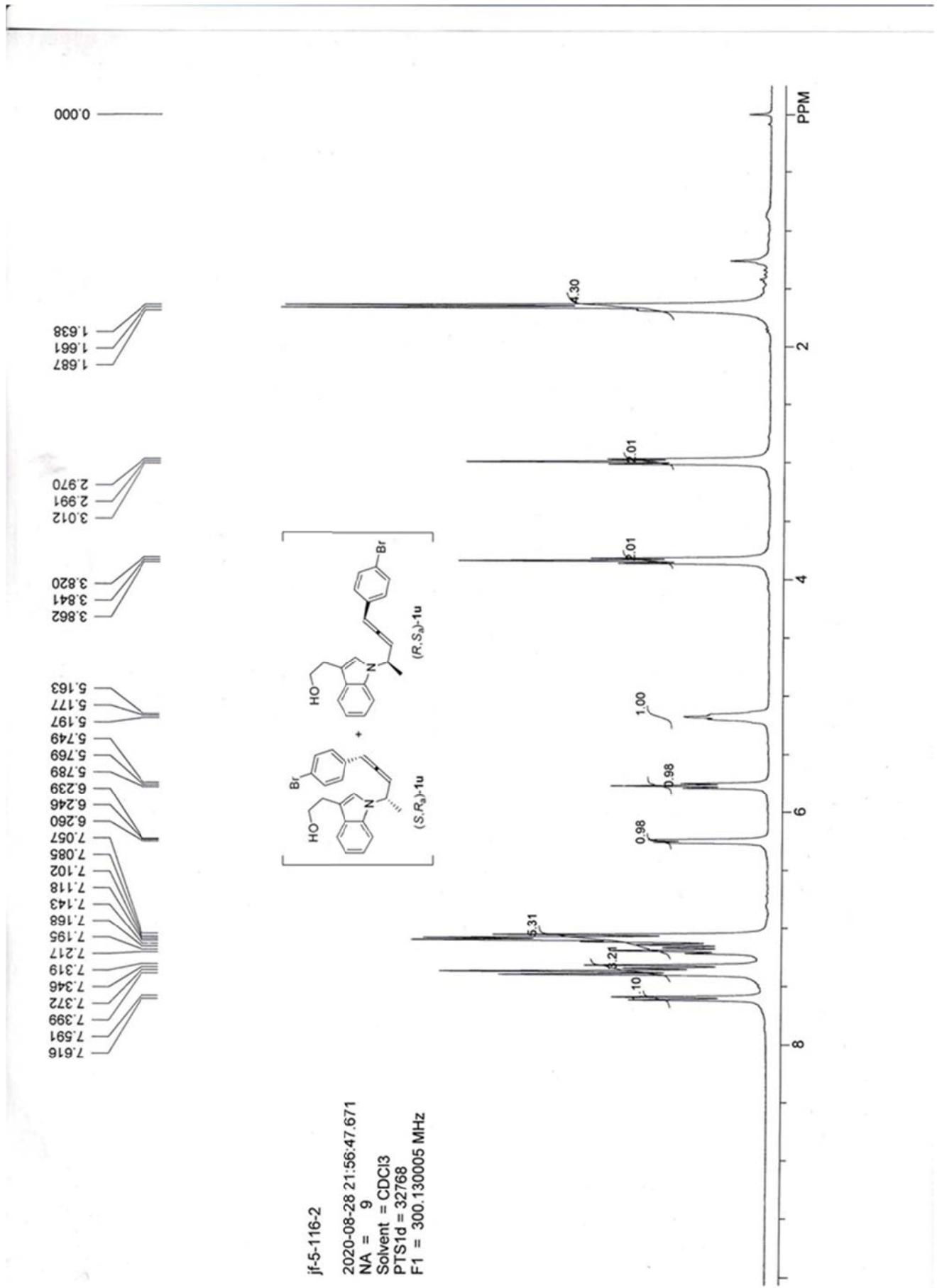
rac-1t

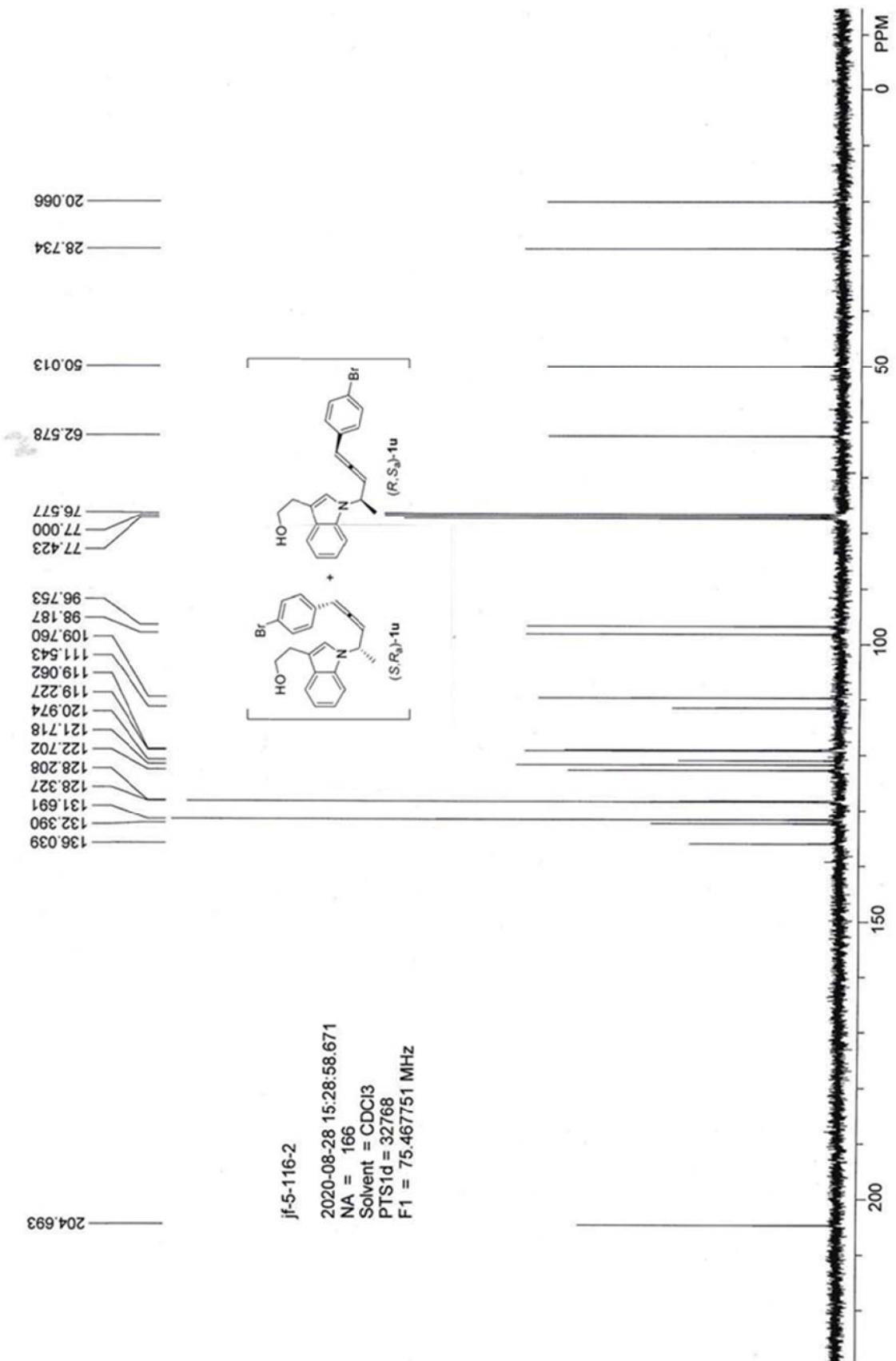


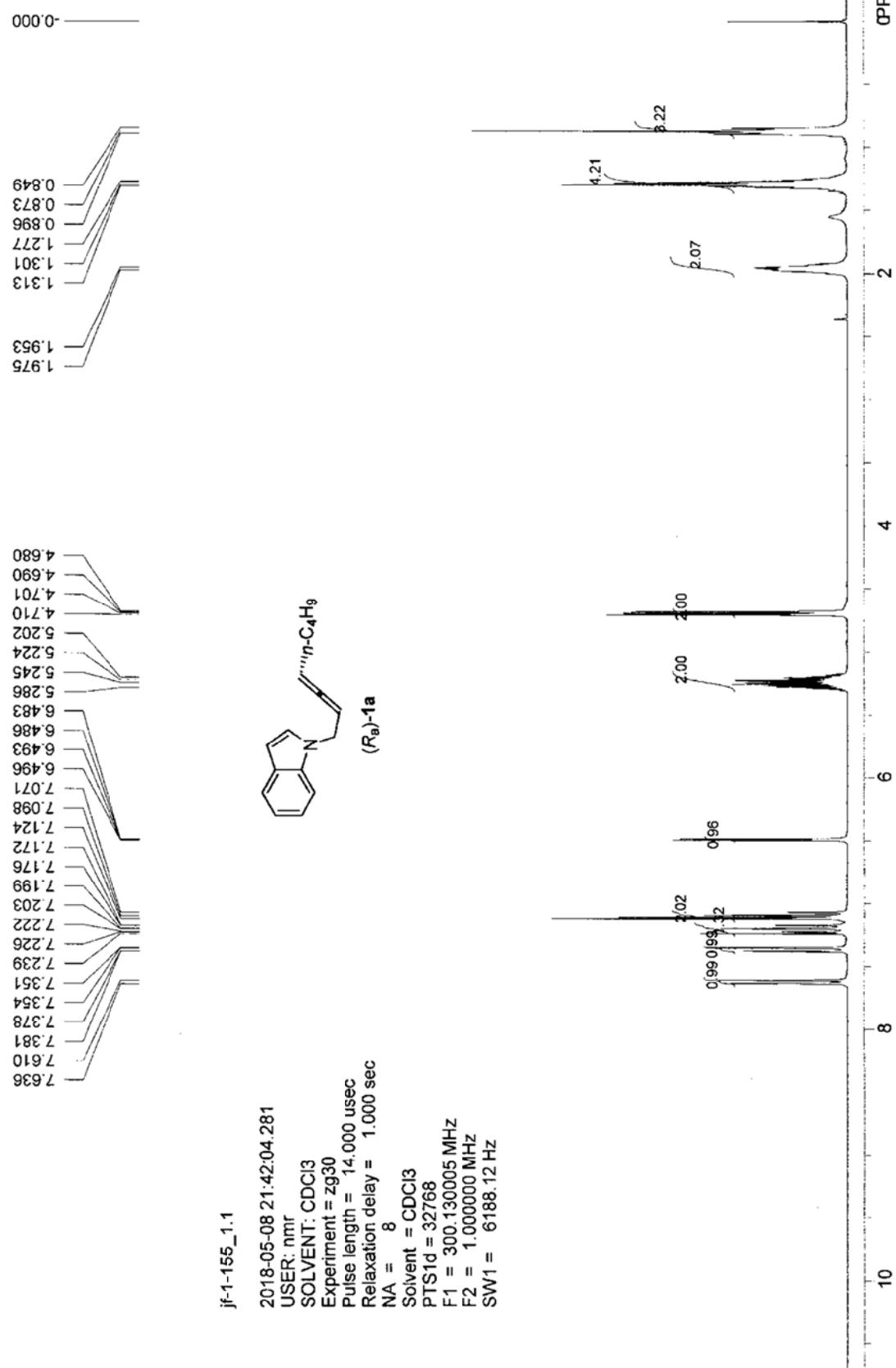


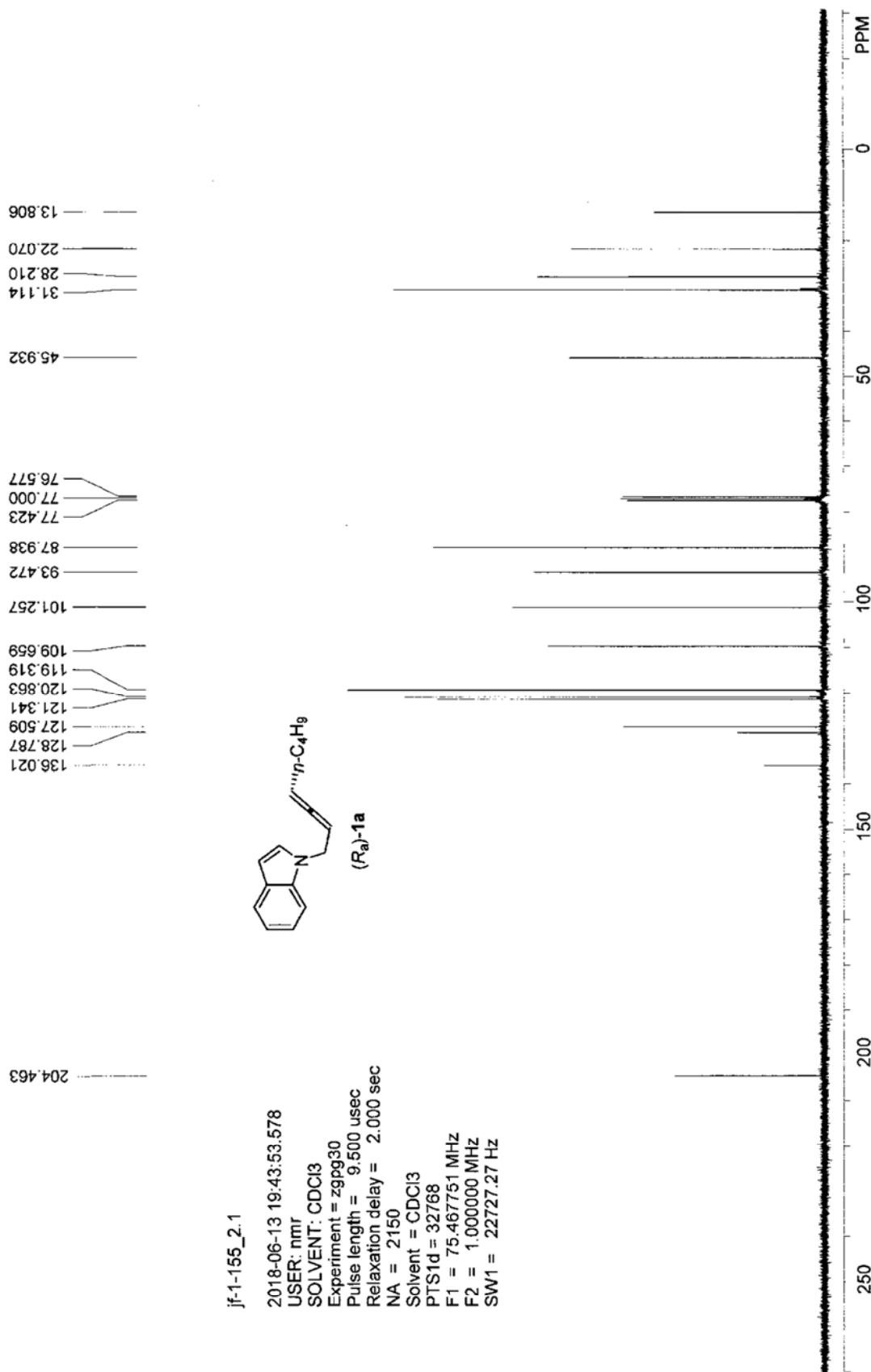










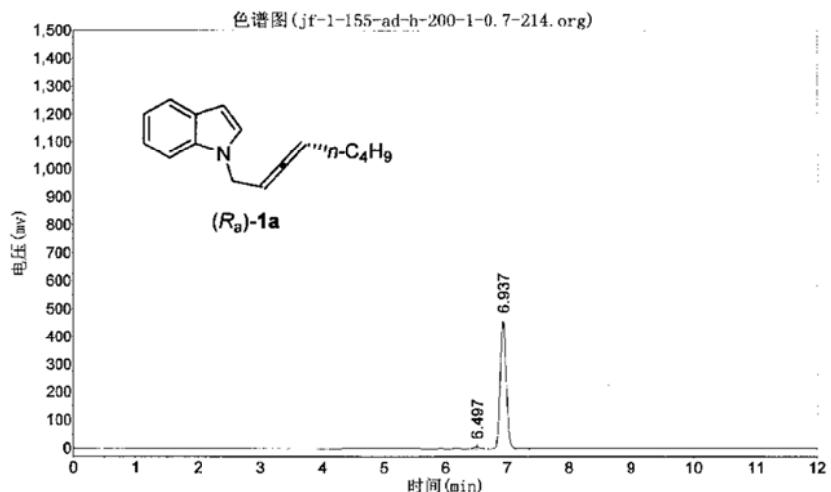


jf-1-155-ad-h-200-1-0.7-214

实验时间: 2018-05-18, 11:23:52
谱图文件:D:\zhuguangjióng\jf\20180518\jf-1-155-ad-h-200-1-0.7-214.org

报告时间: 2018-05-18, 15:32:01

实验内容简介:



分析结果表

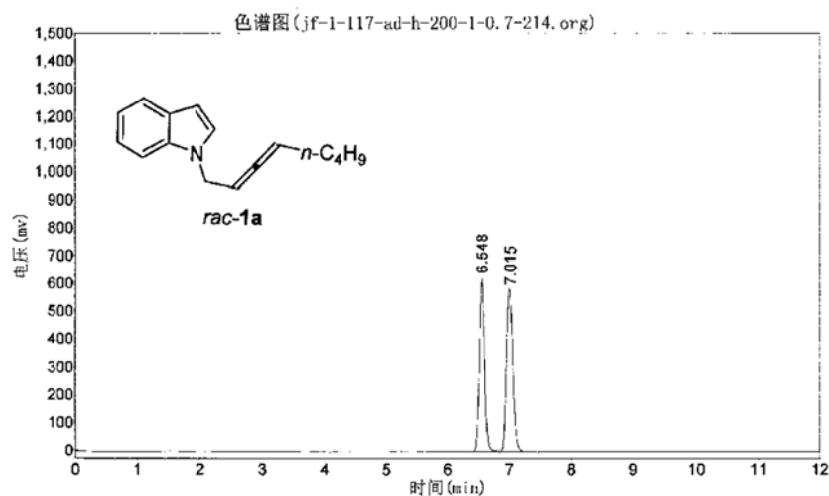
峰号	峰名	保留时间	峰高	峰面积	含量
1		6.497	6550.627	40616.551	1.2829
2		6.937	458458.469	3125256.500	98.7170
总计			465009.096	3165873.051	100.0000

jf-1-117-ad-h-200-1-0.7-214

实验时间: 2018-05-18, 10:54:14
谱图文件:D:\zhuguangjióng\jf\20180518\jf-1-117-ad-h-200-1-0.7-214.org

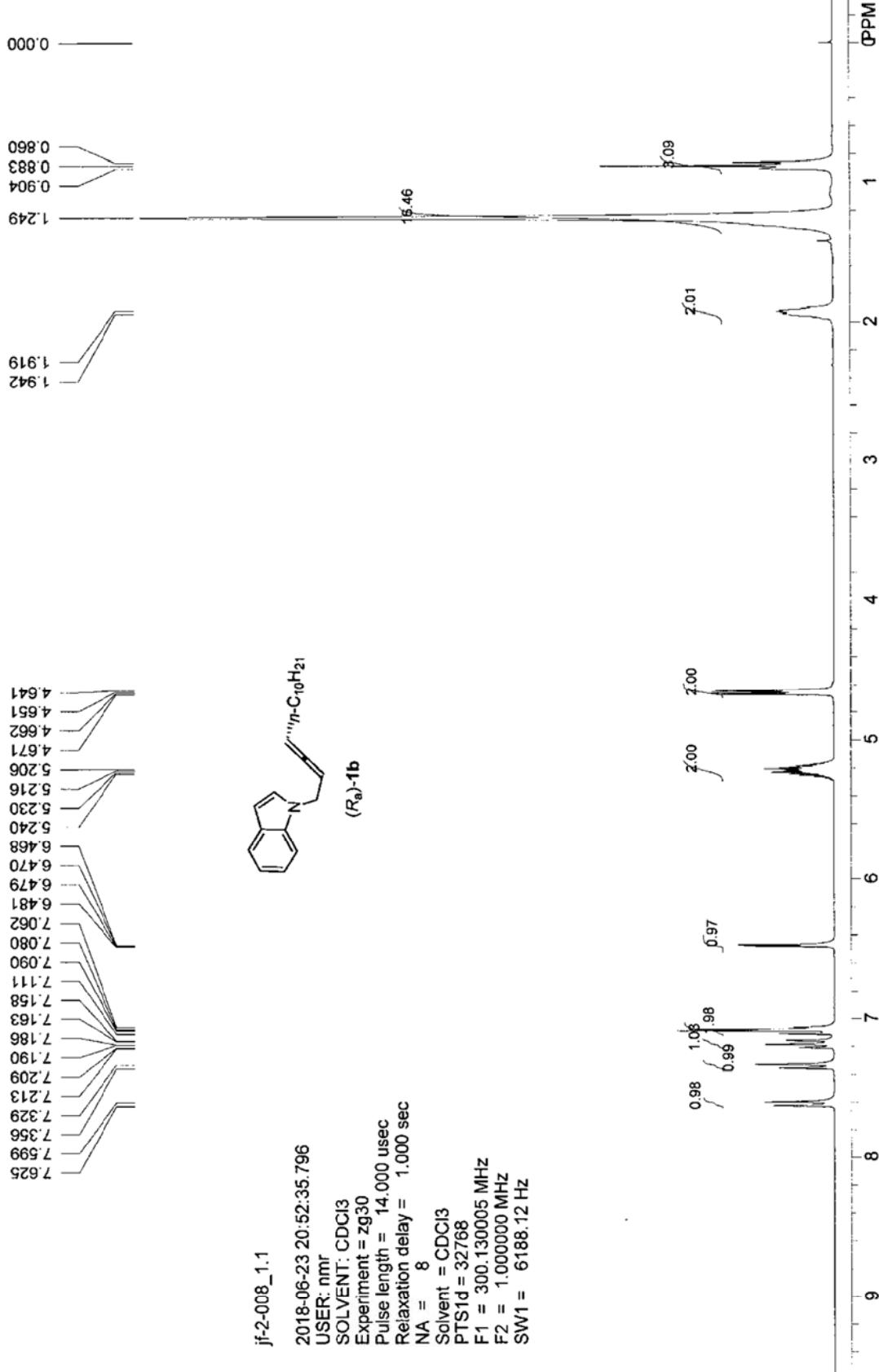
报告时间: 2018-05-1

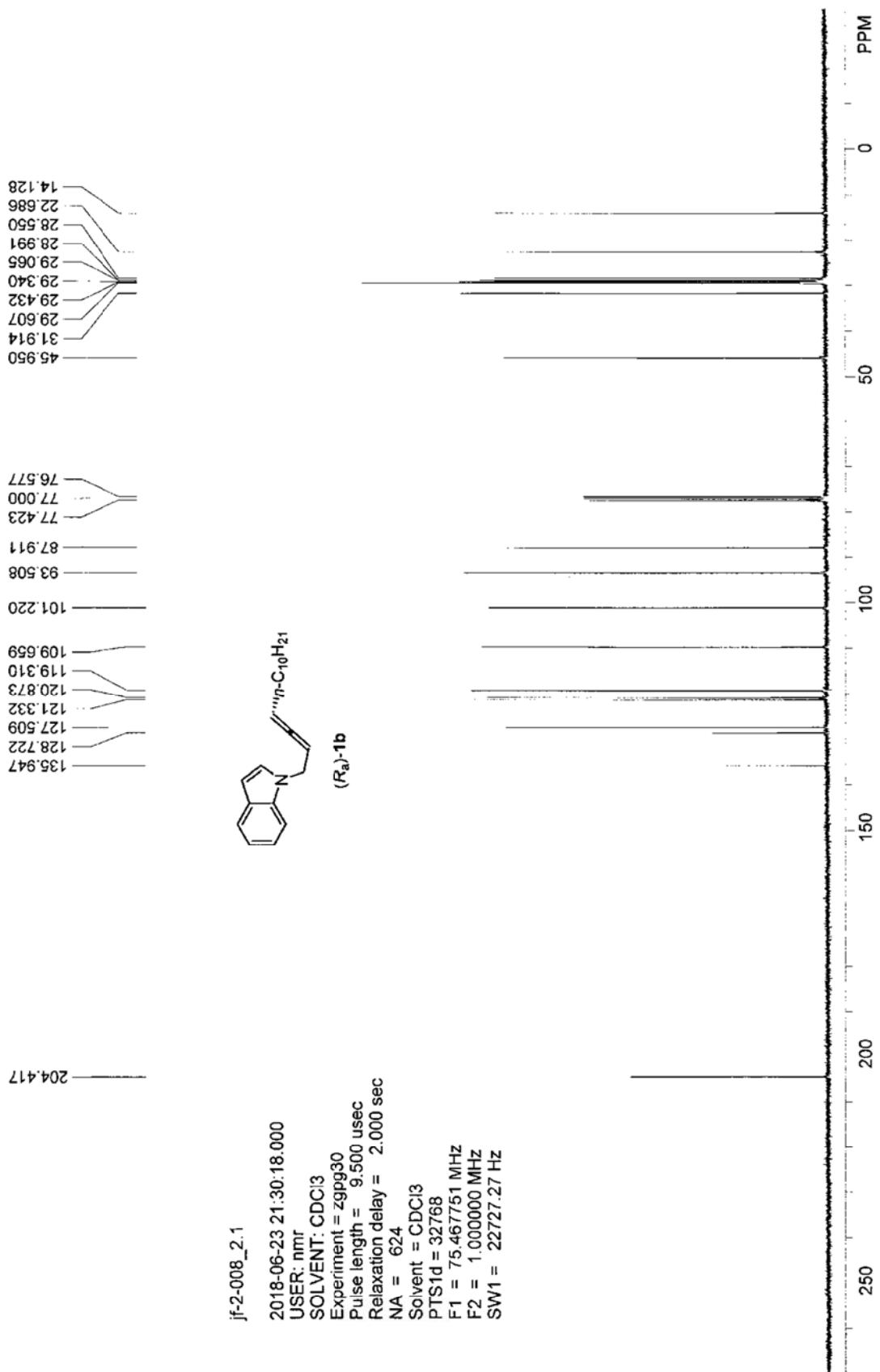
实验内容简介:



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		6.548	600066.250	3953276.250	48.1530
2		7.015	584220.375	4256541.500	51.8470
总计			1184286.625	8209817.750	100.0000



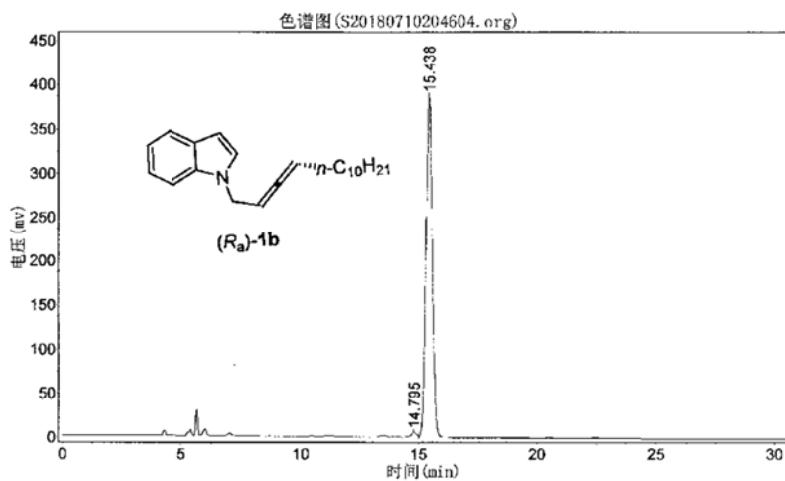


jf-2-008

实验时间: 2018-07-10, 20:46:04
截图文件:D:\浙大智达\N2000\样品\S20180710204604.org
方法文件:D:\浙大智达\N2000\d.jx.mtd

实验者: jf
报告时间: 2018-07-10, 21:19:16
积分方法: 面积归一法

实验内容简介:
od-il, n-hexane/i-PrOH = 200/1, 0.7, 214



分析结果表

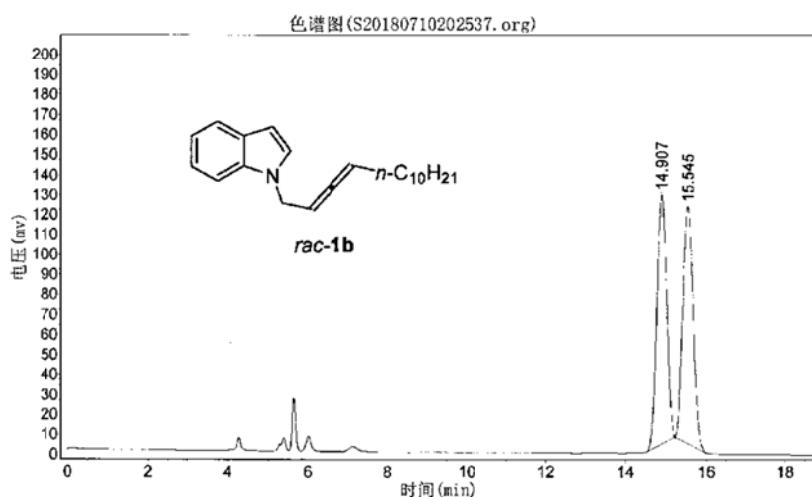
峰号	峰名	保留时间	峰高	峰面积	含量
1		14.795	5025.257	82230.117	1.1333
2		15.438	386057.656	7173386.000	98.8667
总计			391082.914	7255616.117	100.0000

jf-2-009

实验时间: 2018-07-10, 20:25:37
谱图文件:D:\浙大智达\N2000\样品\S20180710202537.org
方法文件:D:\浙大智达\N2000\djx.mtd

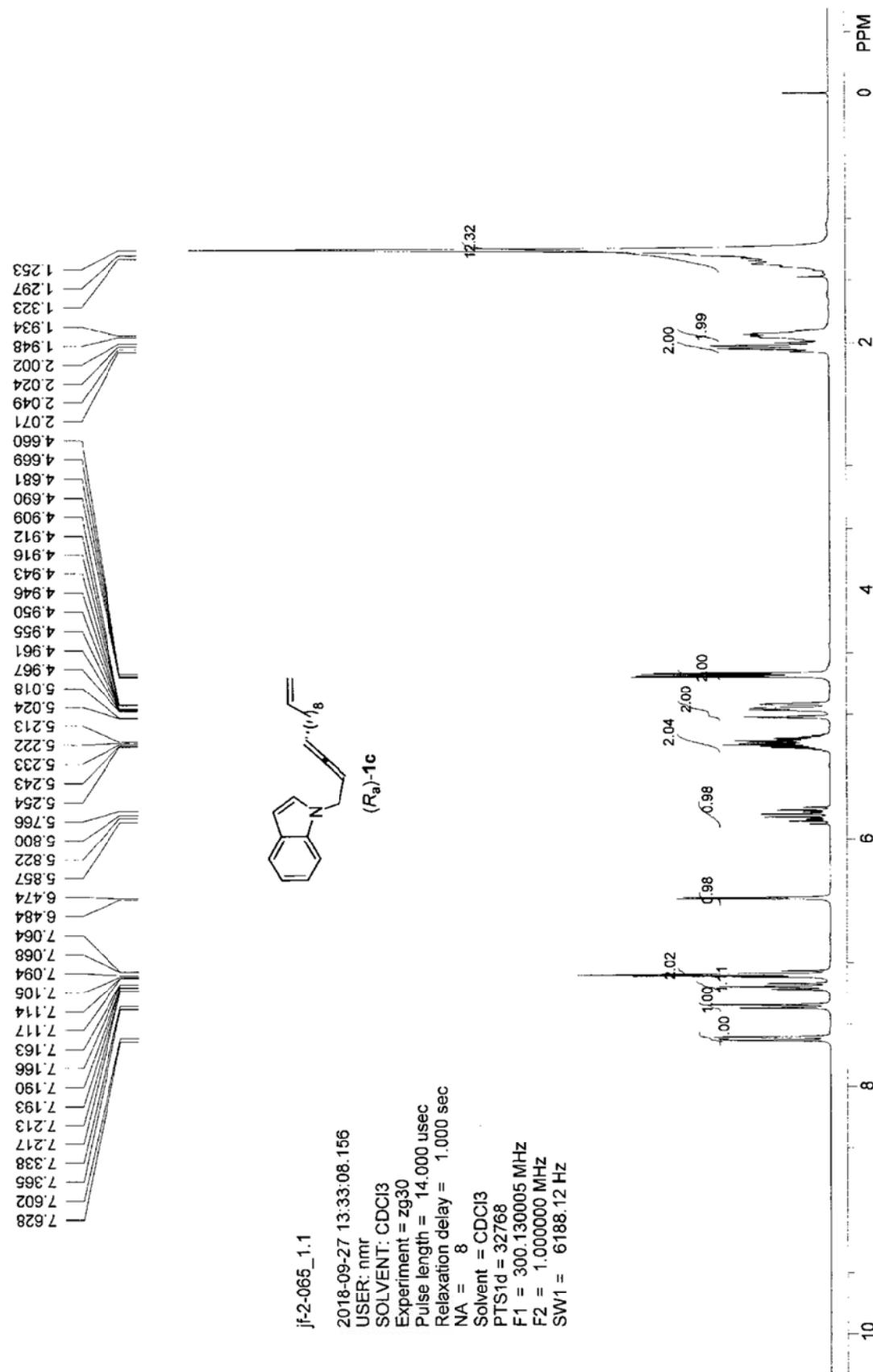
实验者: jf
报告时间: 2018-07-10, 20:48:32
积分方法: 面积归一法

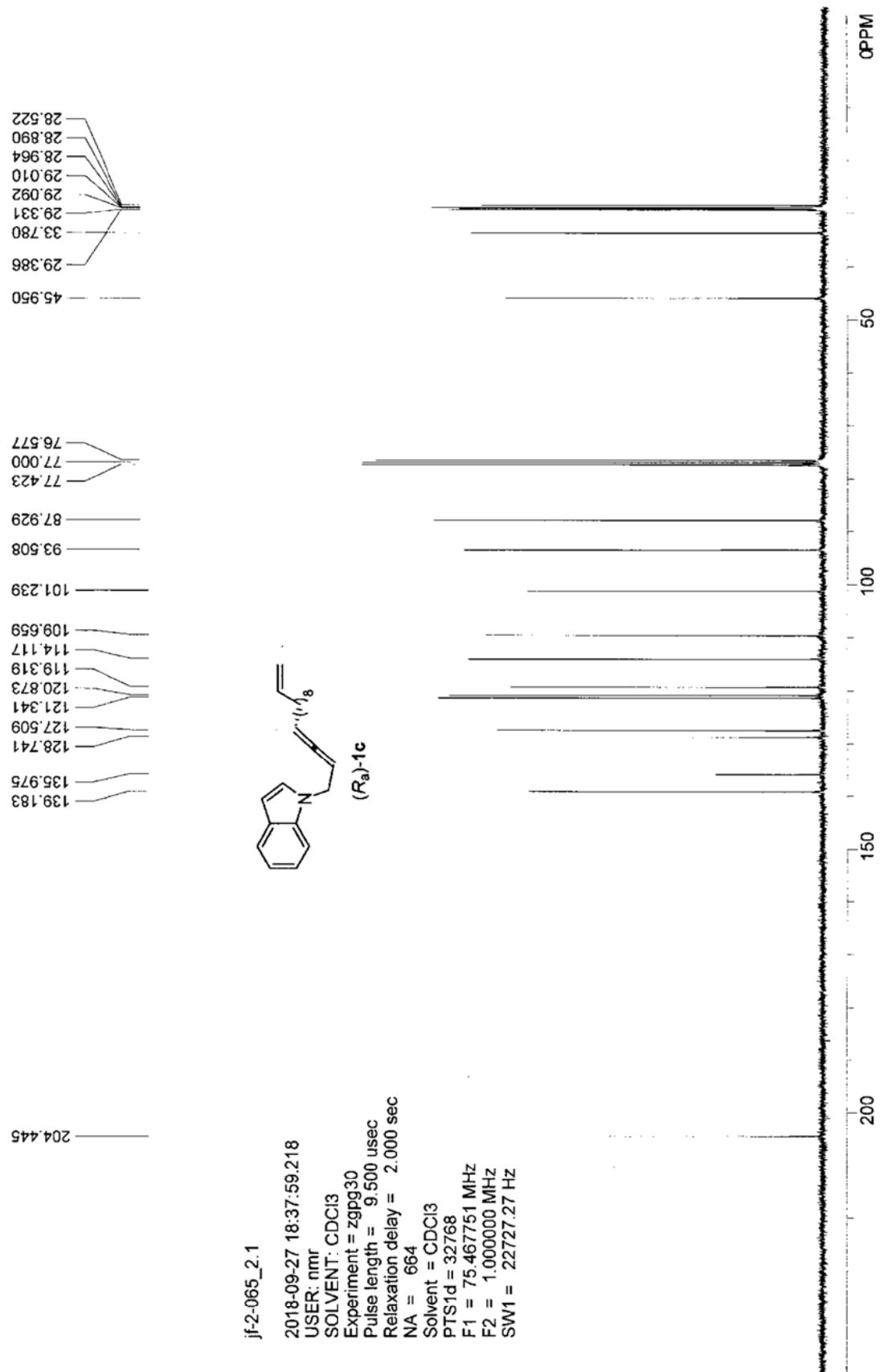
实验内容简介:
od-H, n-hexane/i-PrOH = 200/1, 0.7, 214



分析结果表

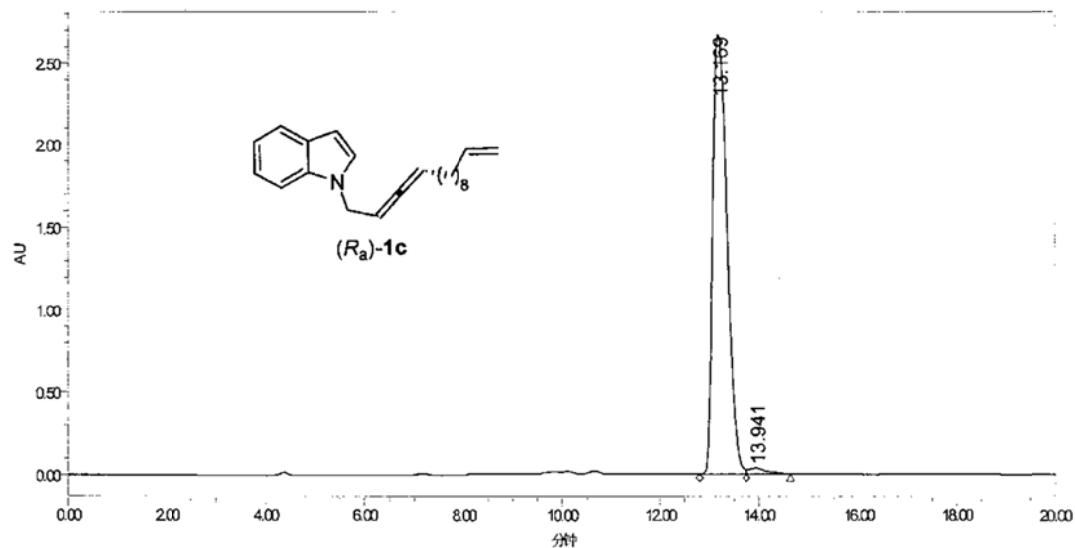
峰号	峰名	保留时间	峰高	峰面积	含量
1		14.907	124962.844	2110827.000	50.0497
2		15.545	118739.664	2106637.500	49.9503
总计			243702.508	4217464.500	100.0000





SAMPLE INFORMATION

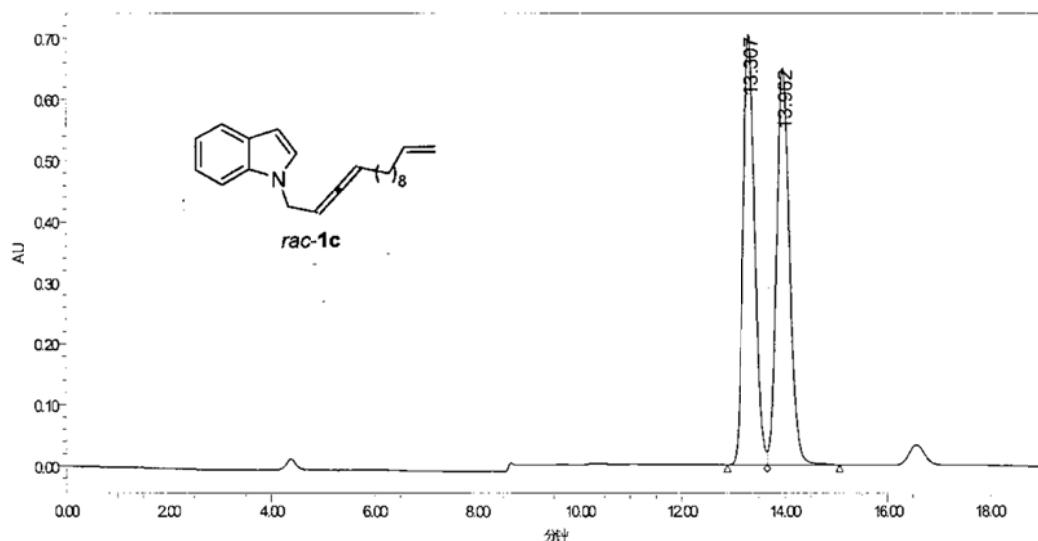
Sample Name:	jf2-065-q-h-100-1-1-214	Acquired By:	Breeze
Sample Type:	未知	Date Acquired:	2018/9/29 18:25:36 CST
Vial:	999	Acq. Method:	zg1001
Injection #:	58	Date Processed:	2018/9/29 19:23:10 CST
Injection Volume:	10.00 μ l	Channel Name:	W2489 ChA
Run Time:	20.00 Minutes	Channel Desc.:	W2489 ChA 214nm
Column Type:		Sample Set Name:	



	RT (min)	Area (msec)	% Area	Height (mm)	% Height
1	13.168	53680404	98.23	2574198	98.63
2	13.941	934888	1.77	37035	1.37

SAMPLE INFORMATION

Sample Name:	jf-207-q-h-100-1-1-214	Acquired By:	Breeze
Sample Type:	未知	Date Acquired:	2018/9/29 18:05:36 CST
Vial:	999	Acq Method:	zj1001
Injection #:	57	Date Processed:	2018/9/29 19:22:54 CST
Injection Volume:	10.00 μ l	Channel Name:	W2489 ChA
Run Time:	80.00 Minutes	Channel Desc.:	W2489 ChA.214nm
Column Type:		Sample Set Name:	



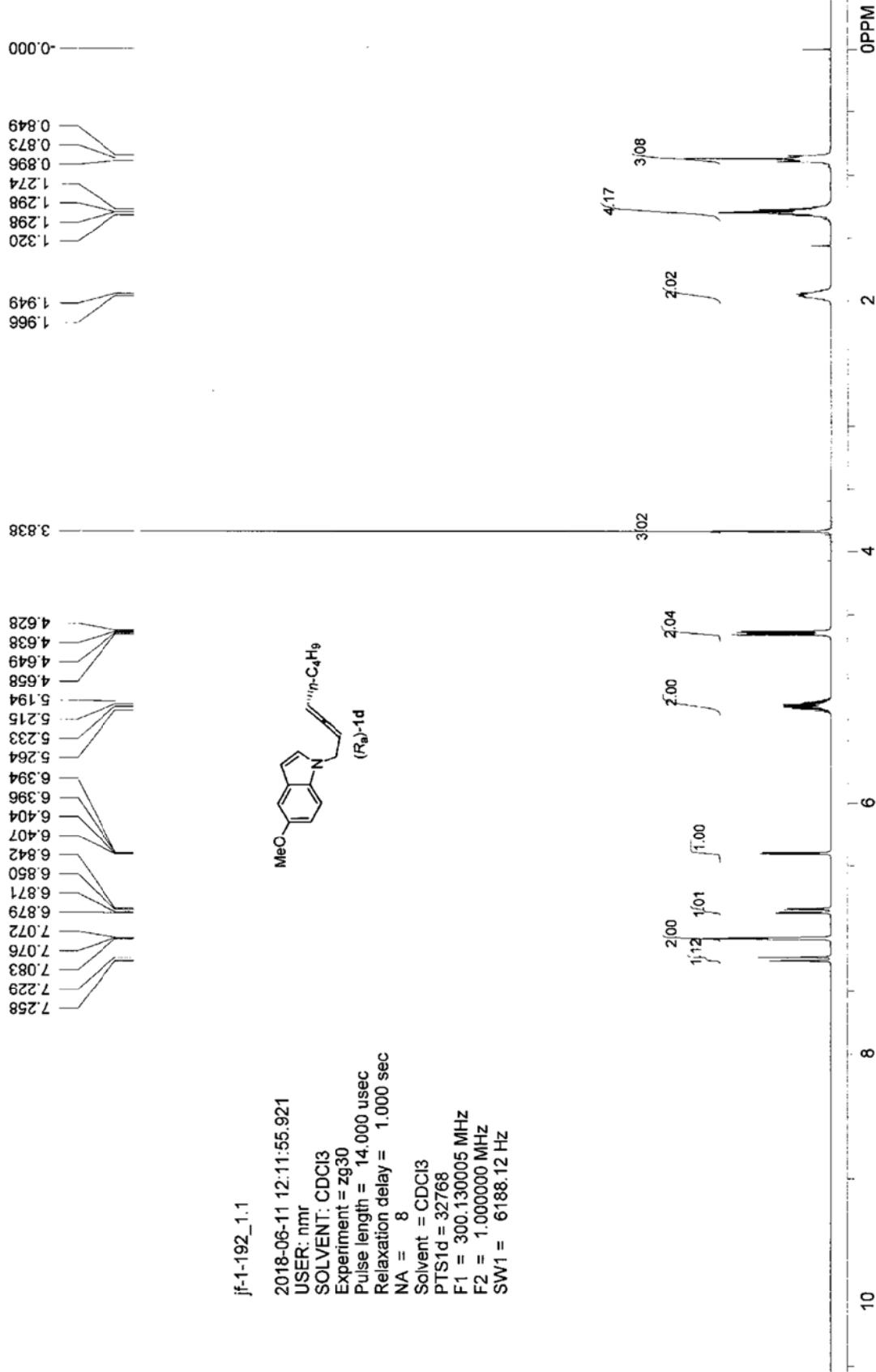
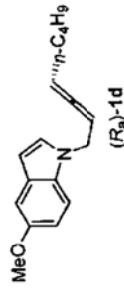
	RT (min)	Area (msec)	% Area	Height (m)	% Height
1	13.307	11026414	49.66	708177	52.04
2	13.962	11181078	50.35	660682	47.95

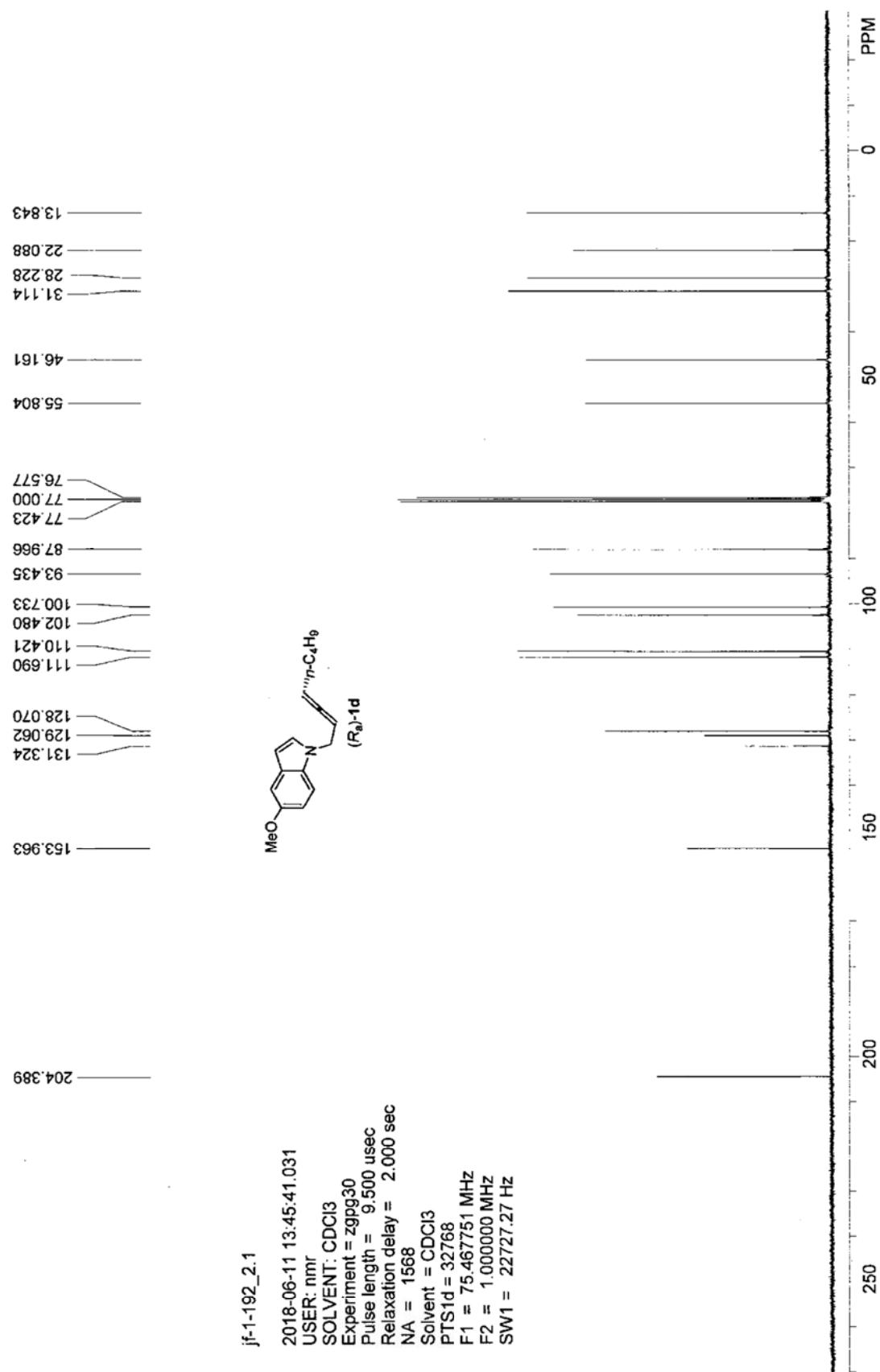
if-1-192_1.1

```

2018-06-11 12:11:55.921
USER: rnmf
SOLVENT: CDC13
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDC13
RTS1d = 32768
F1 = 300.130000 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz

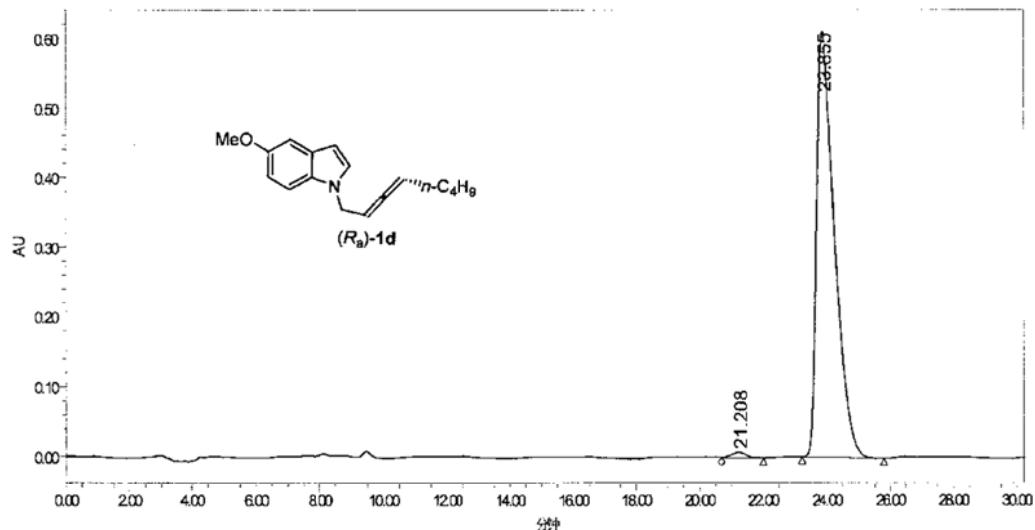
```





SAMPLE INFORMATION

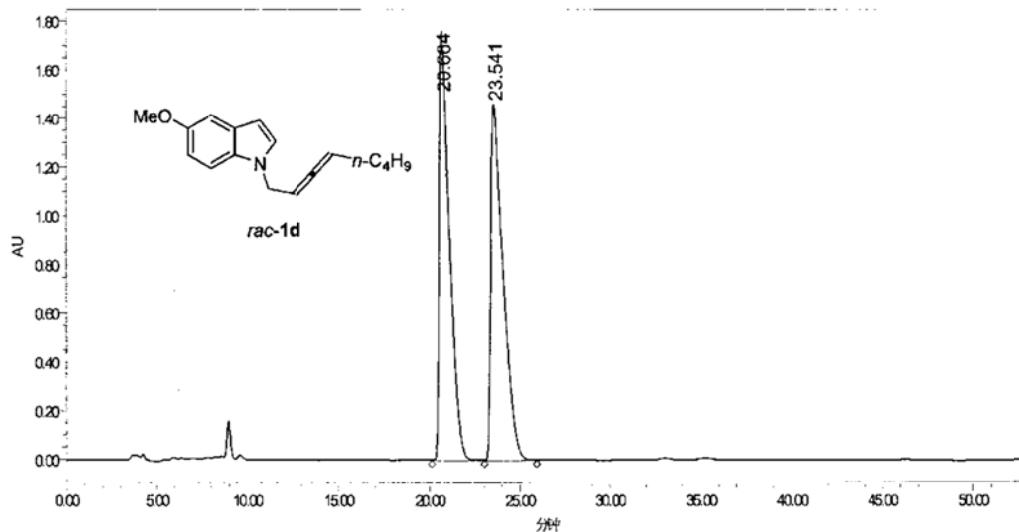
Sample Name:	jf1-192-qjh-955-1214	Acquired By:	Breeze
Sample Type:	未知	Date Acquired:	2018/6/22 11:07:05 CST
Vial:	999	Acq. Method:	zg55
Injection #:	27	Date Processed:	2018/6/22 14:52:48 CST
Injection Volume:	10.00 μ l	Channel Name:	W2489 ChA
Run Time:	35.00 Minutes	Channel Desc.:	W2489 ChA.214nm
Column Type:		Sample Set Name:	



	RT (min)	Area (#sec)	% Area	Height (#)	% Height
1	21.208	282123	1.15	8222	1.33
2	23.855	2429422	98.85	611693	98.67

SAMPLE INFORMATION

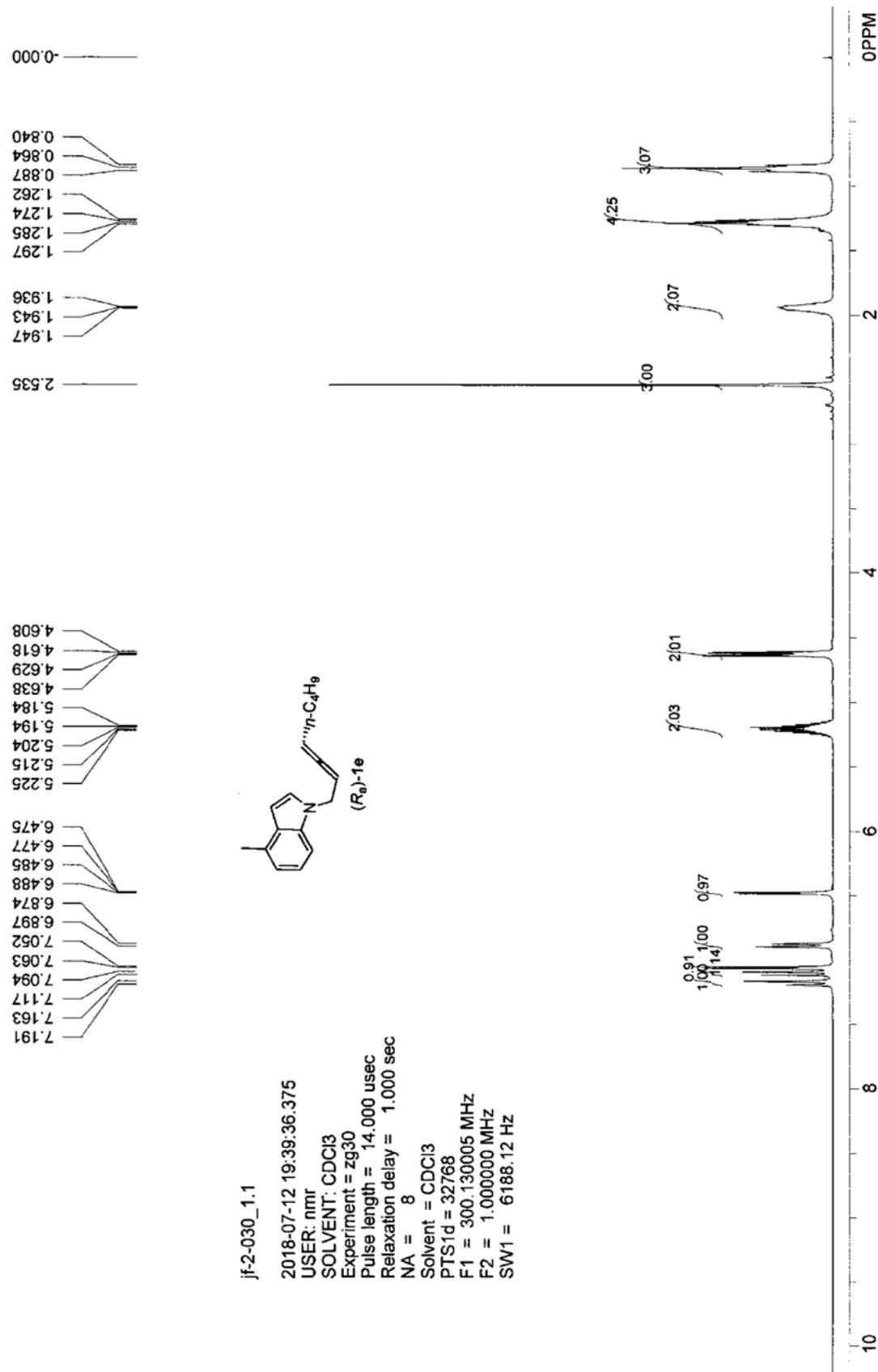
Sample Name:	jf1-196-q-h-955-1-214	Acquired By:	Breeze
Sample Type:	未知	Date Acquired:	2018/6/22 10:11:45 CST
Vial:	999	Acq. Method:	zg95
Injection #:	26	Date Processed:	2018/6/22 14:52:36 CST
Injection Volume:	10.00 μ l	Channel Name:	W2489 ChA
Run Time:	75.00 Minutes	Channel Desc.:	W2489 ChA,214nm
Column Type:		Sample Set Name:	

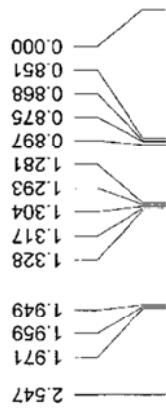
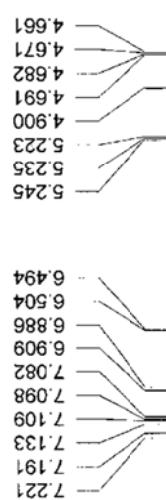


	RT (min)	Area (吸光度)	%Area	Height (峰高)	% Height
1	20.664	70746576	49.99	1761612	54.62
2	23.541	70761906	50.01	1463673	45.36

if-2-030_1.1

2018-07-12 19:39:36.375
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14.000 us
 Relaxation delay = 1.0000
 NA = 8
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz





jf2-030-chundu_11

2018-09-05 15:05:16.187

USER: nmr

SOLVENT: CDCl₃

Experiment = zg30

Pulse length = 14.000 usec

Relaxation delay = 1.000 sec

NA = 8

Solvent = CDCl₃

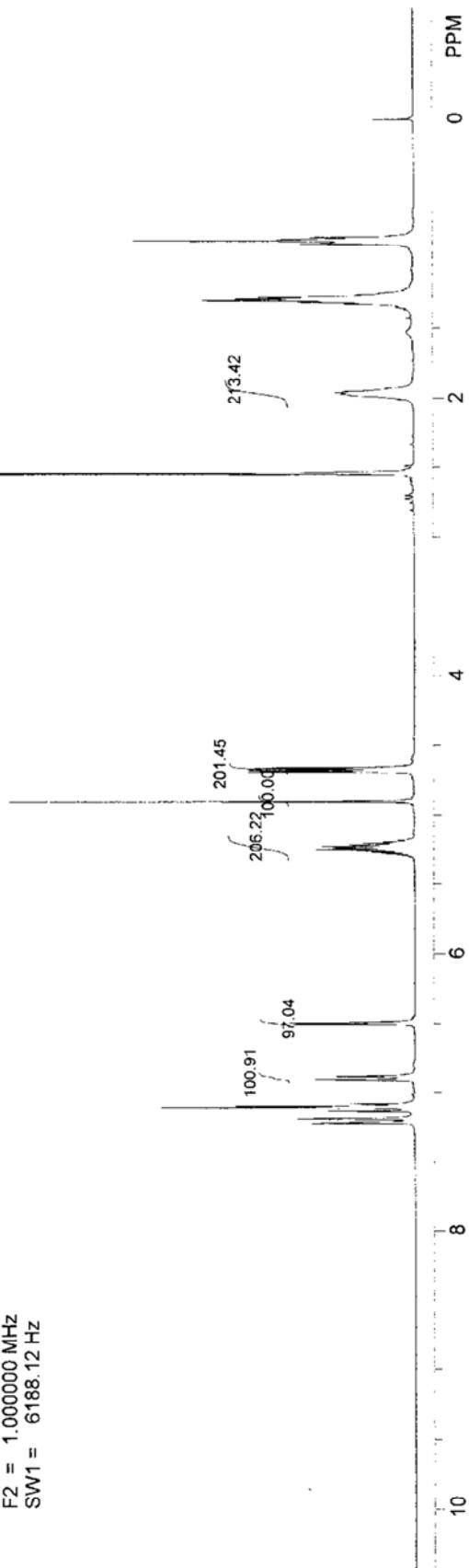
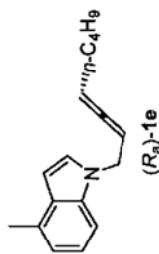
PTS1d = 32768

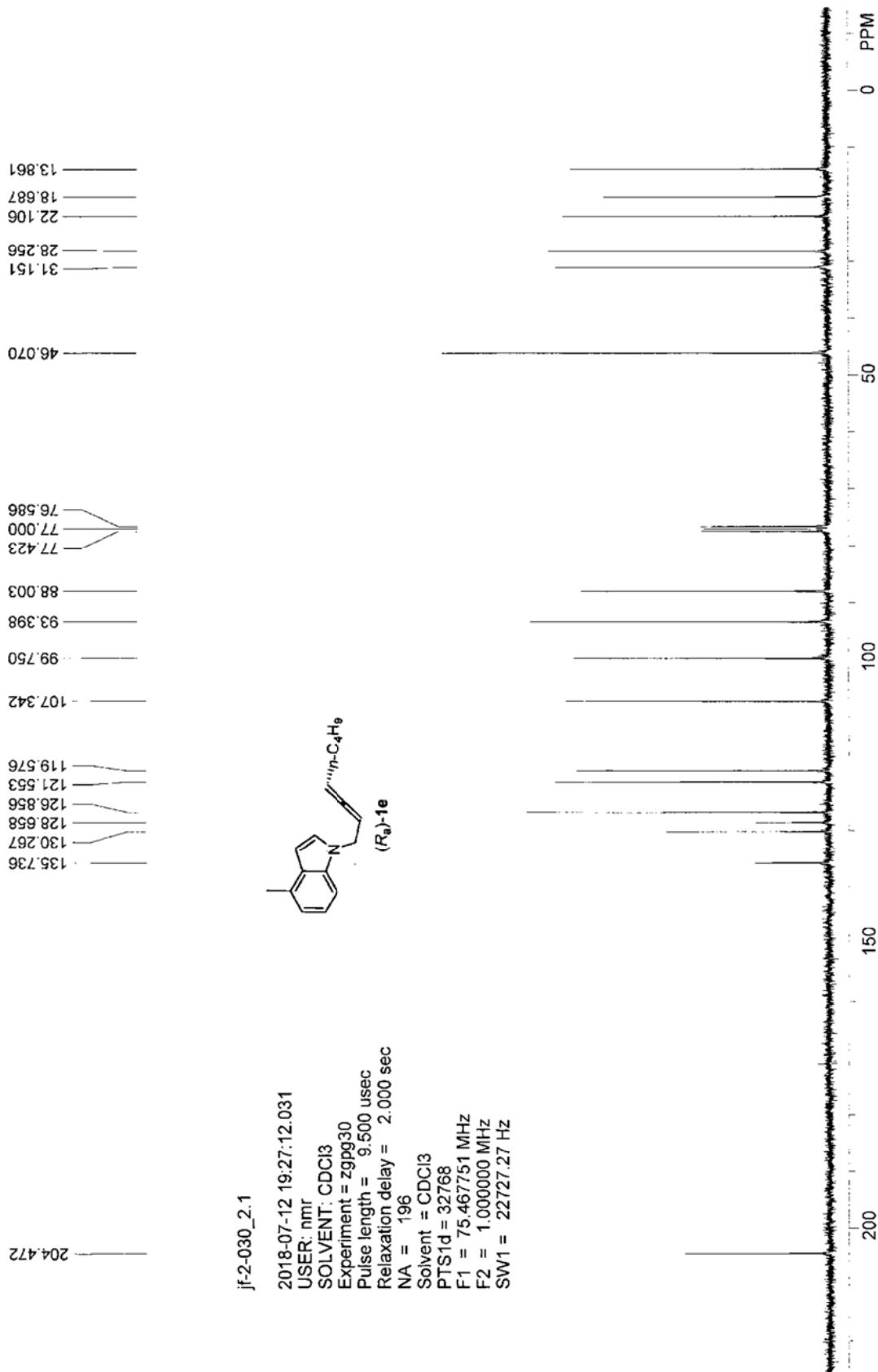
F1 = 300.130005 MHz

F2 = 1.000000 MHz

SW1 = 6188.12 Hz

Purity (97%) is determined by dibromomethane
(14 μ , 0.4 mmol) as the internal standard in 96.0 mg
of sample



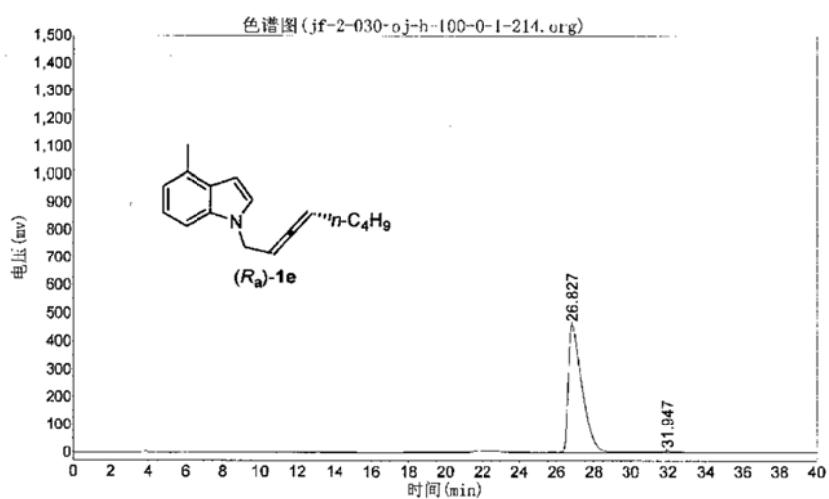


jf-2-030-oj-h-100-0-1-214

实验时间: 2018-09-11, 13:59:20
谱图文件:D:\zhuguangjiong\jf\20180911\jf-2-030-oj-h-100-0-1-
214.org

报告时间: 2018-09-11, 17:27:22

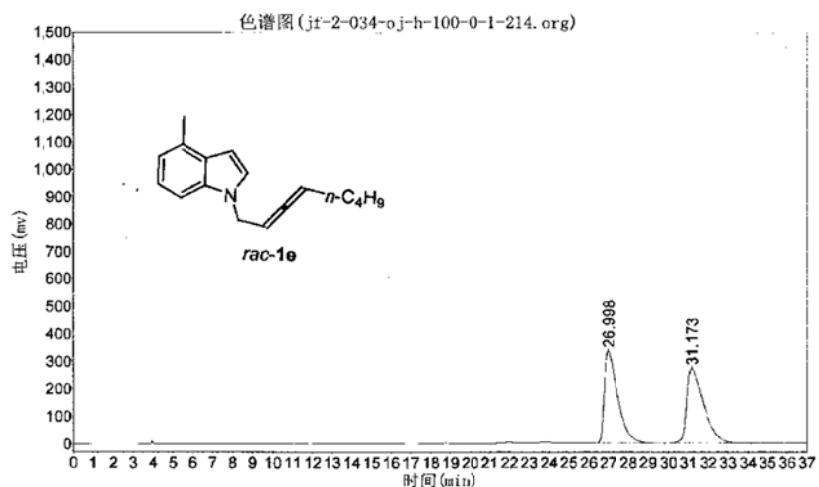
实验内容简介:



jf-2-034-o j-h-100-0-1-214

实验时间: 2018-09-11, 13:18:32
报告时间: 2018-09-11, 17:28:08
谱图文件:D:\zhuguangjiong\jf\20180911\jf-2-034-o j-h-100-0-1-
214.org

实验内容简介:

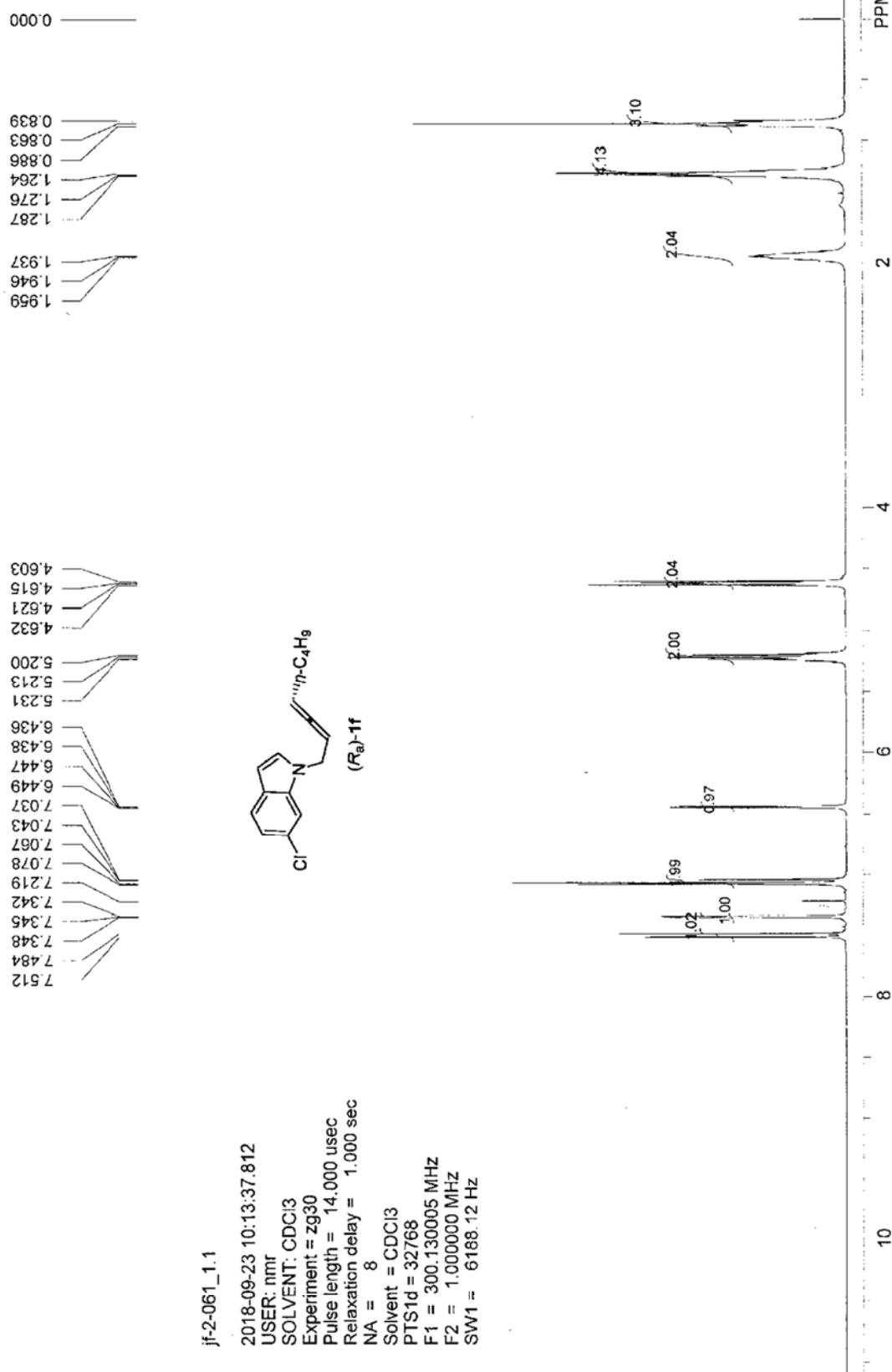
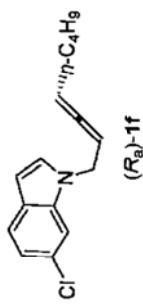


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		26.998	337095.250	16141427.000	50.0089
2		31.173	272200.156	16135701.000	49.9911
总计			609295.406	32277128.000	100.0000

if-2-061_1.1

2018-09-23 10:13:37.812
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14.000 us
 Relaxation delay = 1.000 s
 NA = 8
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz



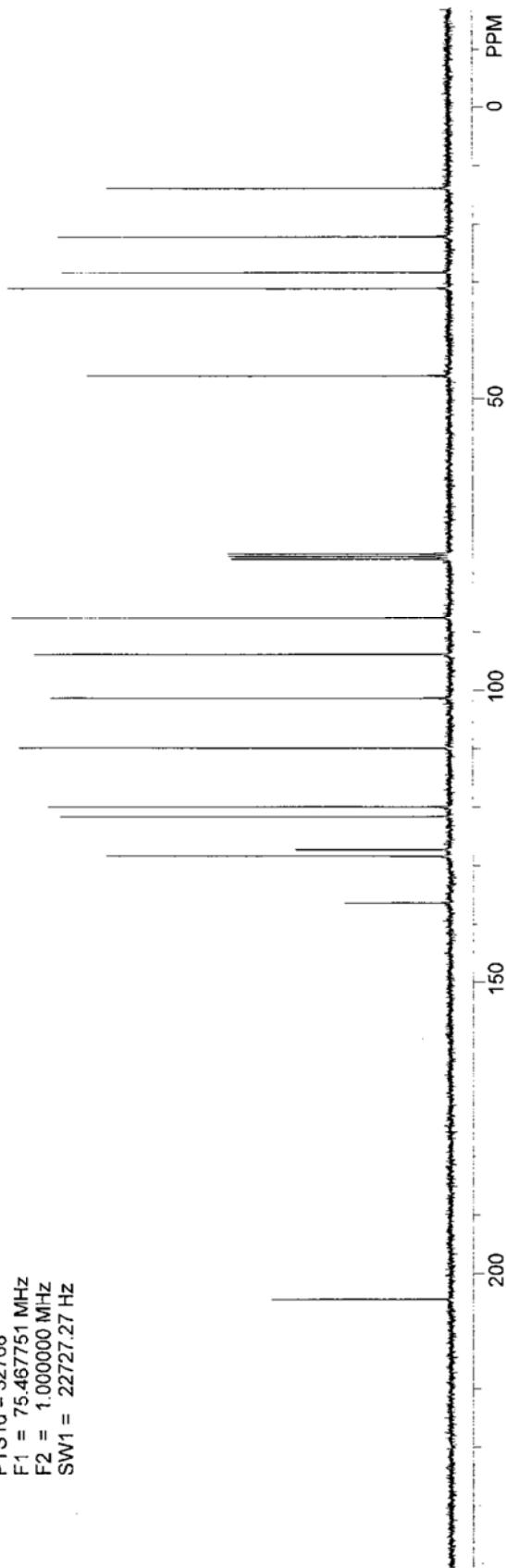
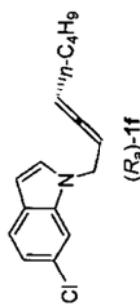
204.426

136.370
128.364
127.371
127.252
121.654
119.990
109.852
101.386
93.867
87.552
77.423
77.000
76.577

46.042
31.087
28.173
22.097
13.815

f2-061_2.1

2018-09-23 09:55:05.234
USER: nmr
SOLVENT: CDCl₃
Experiment = zgpp30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 300
Solvent = CDCl₃
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

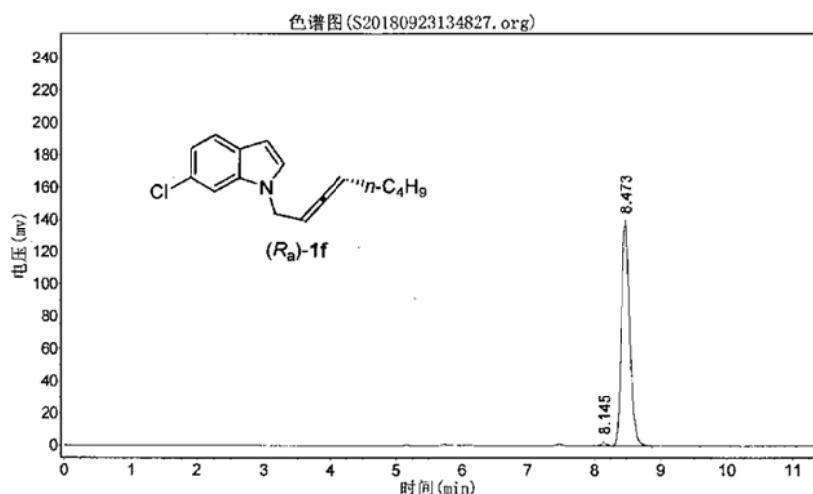


jf-2-061

实验时间: 2018-09-23, 13:48:27
谱图文件:D:\浙大智达\N2000\样品\S20180923134827.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2018-09-23, 14:01:30
积分方法: 面积归一法

实验内容简介:
od-II, n-hexane/i-PrOH = 20/1, 0. 6, 254



分析结果表

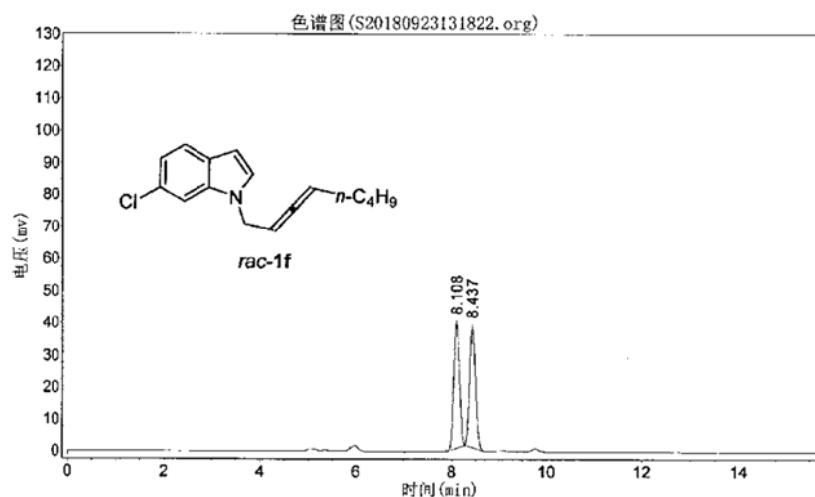
峰号	峰名	保留时间	峰高	峰面积	含量
1		8.145	1300.869	10567.610	0.8316
2		8.473	137773.656	1260234.875	99.1684
总计			139074.525	1270802.485	100.0000

jf-2-060

实验时间: 2018-09-23, 13:18:22
谱图文件:D:\浙大智达\N2000\样品\S20180923131822.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2018-09-23, 13:52:21
积分方法: 面积归一法

实验内容简介:
od-l, n-hexane/i-PrOH = 20/1, 0.6, 254



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.108	38811.453	324656.031	49.7408
2		8.437	37423.965	328039.188	50.2592
总计			76235.418	652695.219	100.0000

-----0.000

0.899
0.882
0.864

1.314
1.297

1.984
1.978
1.962

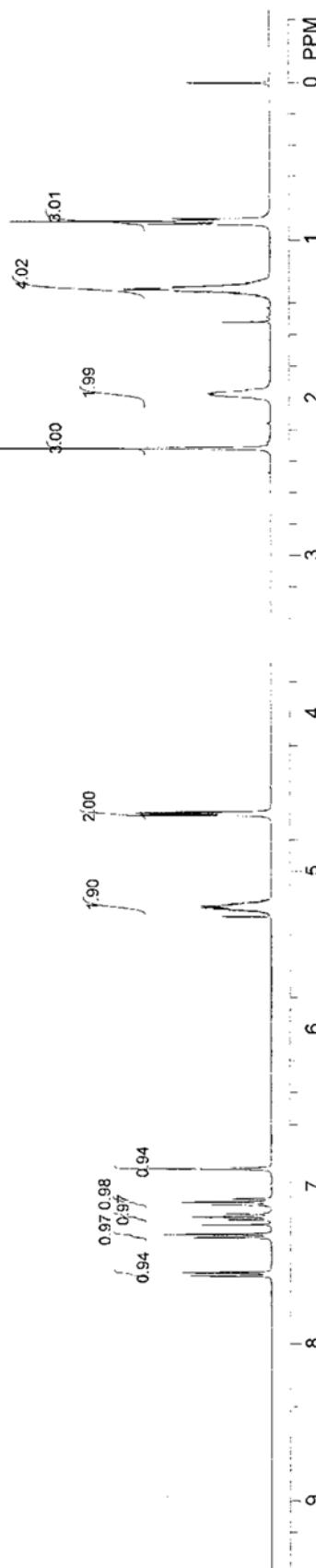
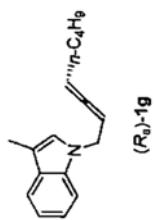
2.320

4.644
4.636
4.628
4.621

5.236
5.216
5.200

7.564
7.545
7.322
7.302
7.240
7.207
7.189
7.171
7.113
7.093
7.076
6.884

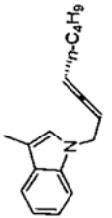
if-2-81.1.1
2018-10-13 05:20:47.221
USER: nmrsu
SOLVENT: CDCl₃
Experiment = zg30
Pulse length = 15.000 usec
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl₃
PTSD = 655536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
SW1 = 10000.00 Hz



— 204.417

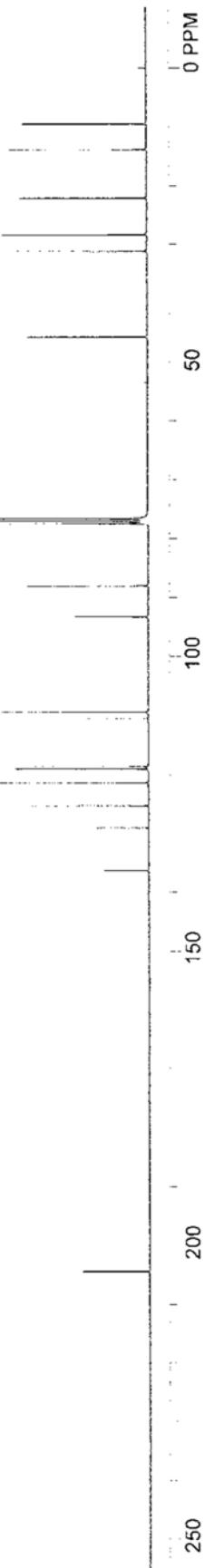
jf2-081_2.1

2018-10-17 09:43:52.156
USER: nmr
SOLVENT: CDCl₃
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 11560
Solvent = CDCl₃
PTS1d = 327688
F1 = 75.467751 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz



— 136.269
— 128.952
— 125.183
— 121.295
— 118.942
— 118.593
— 110.431
— 109.475
— 93.270
— 88.095
— 77.423
— 77.000
— 76.577

— 45.748
— 31.170
— 28.283
— 22.097
— 13.871
— 9.569

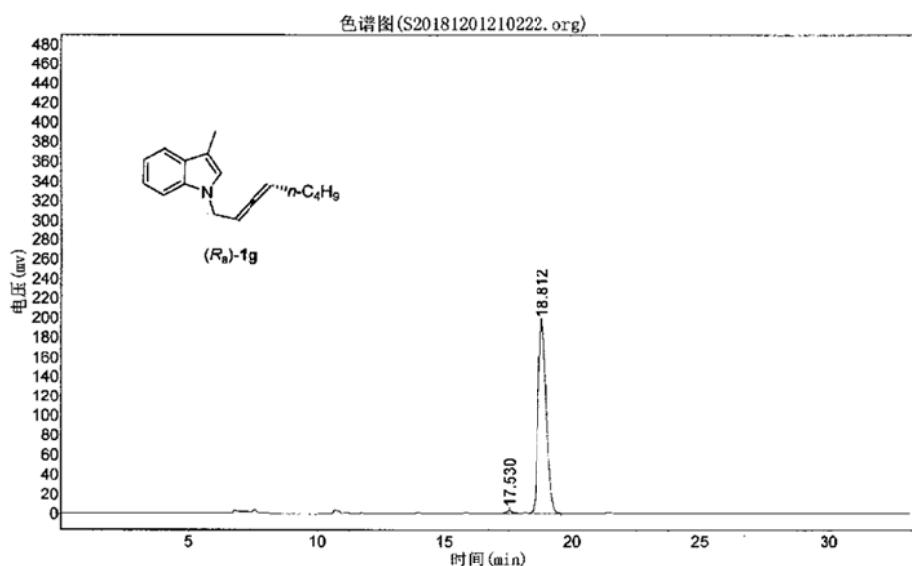


jf-2-081

实验时间: 2018-12-01, 21:02:22
谱图文件:D:\浙大智达\N2000\样品\S20181201210222.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-03-26, 13:06:21
积分方法: 面积归一法

实验内容简介:
od-L, n-hexane/i-PrOH = 100/1, 0.5, 214



分析结果表

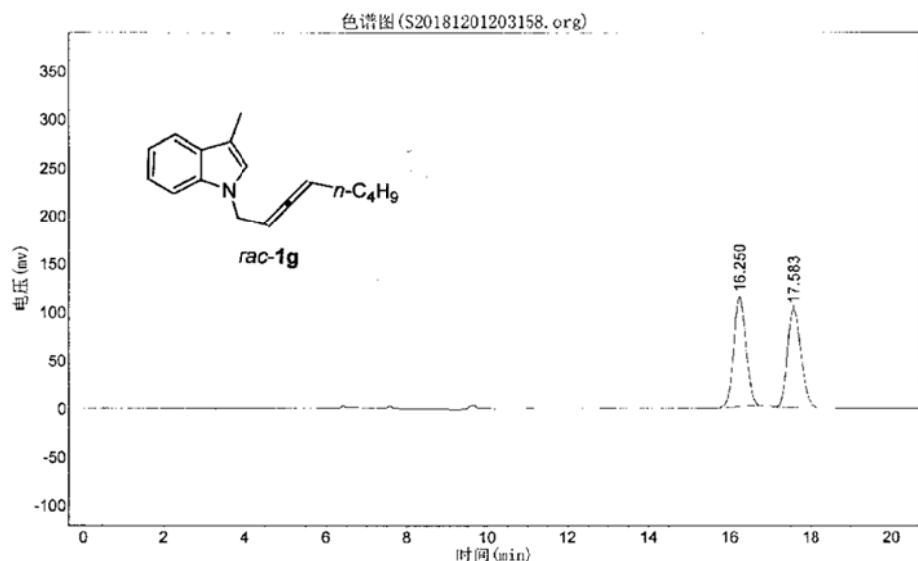
峰号	峰名	保留时间	峰高	峰面积	含量
1		17.530	1894.339	36207.355	0.8110
2		18.812	194880.563	4428530.500	99.1890
总计			196774.901	4464737.855	100.0000

jf-2-080

实验时间: 2018-12-01, 20:31:58
谱图文件:D:\浙大智达\N2000\样品\S20181201203158.org
方法文件:D:\浙大智达\N2000\dxjx.mtd

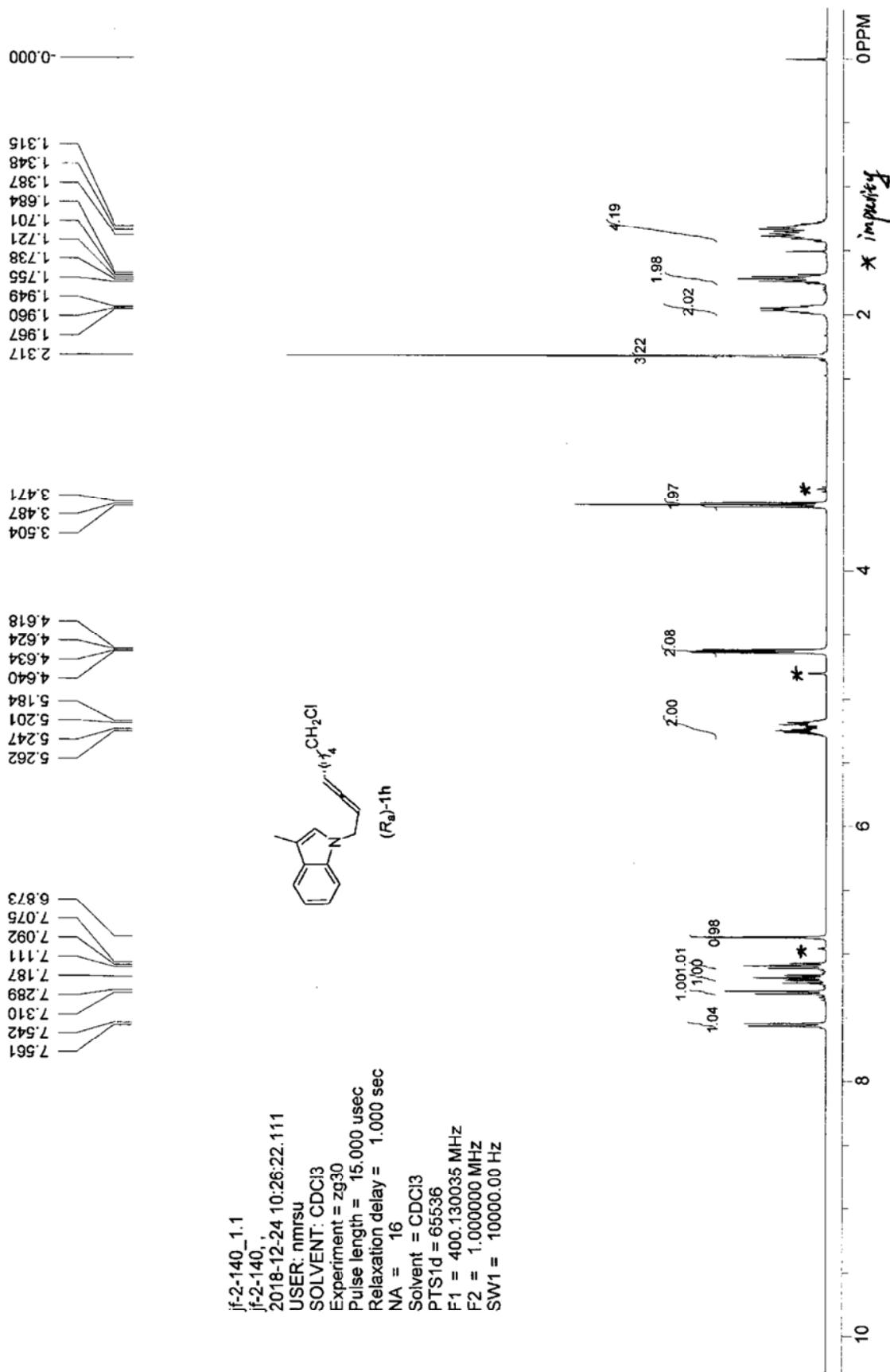
实验者: jf
报告时间: 2018-12-01, 20:57:49
积分方法: 面积归一法

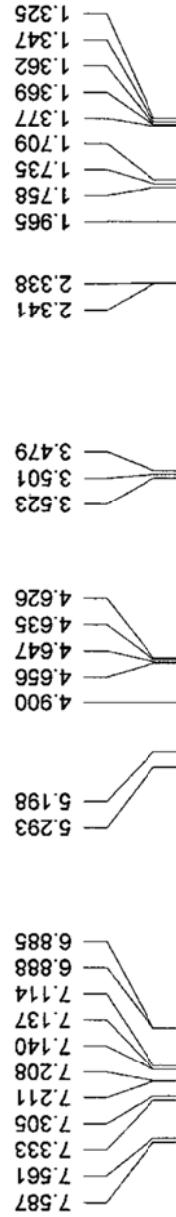
实验内容简介:
OD-II, n-hexane/i-PrOH = 100/1, 0.5, 214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.250	113337.664	2361383.500	50.0570
2		17.583	102322.461	2356004.250	49.9430
总计			215660.125	4717387.750	100.0000





2018-12-28 21:01:39.468

USER: nmr

SOLVENT: CDCl₃

Experiment = zg30

Pulse length = 14.000 usec

Relaxation delay = 1.000 sec

NA = 8

Solvent = CDCl₃

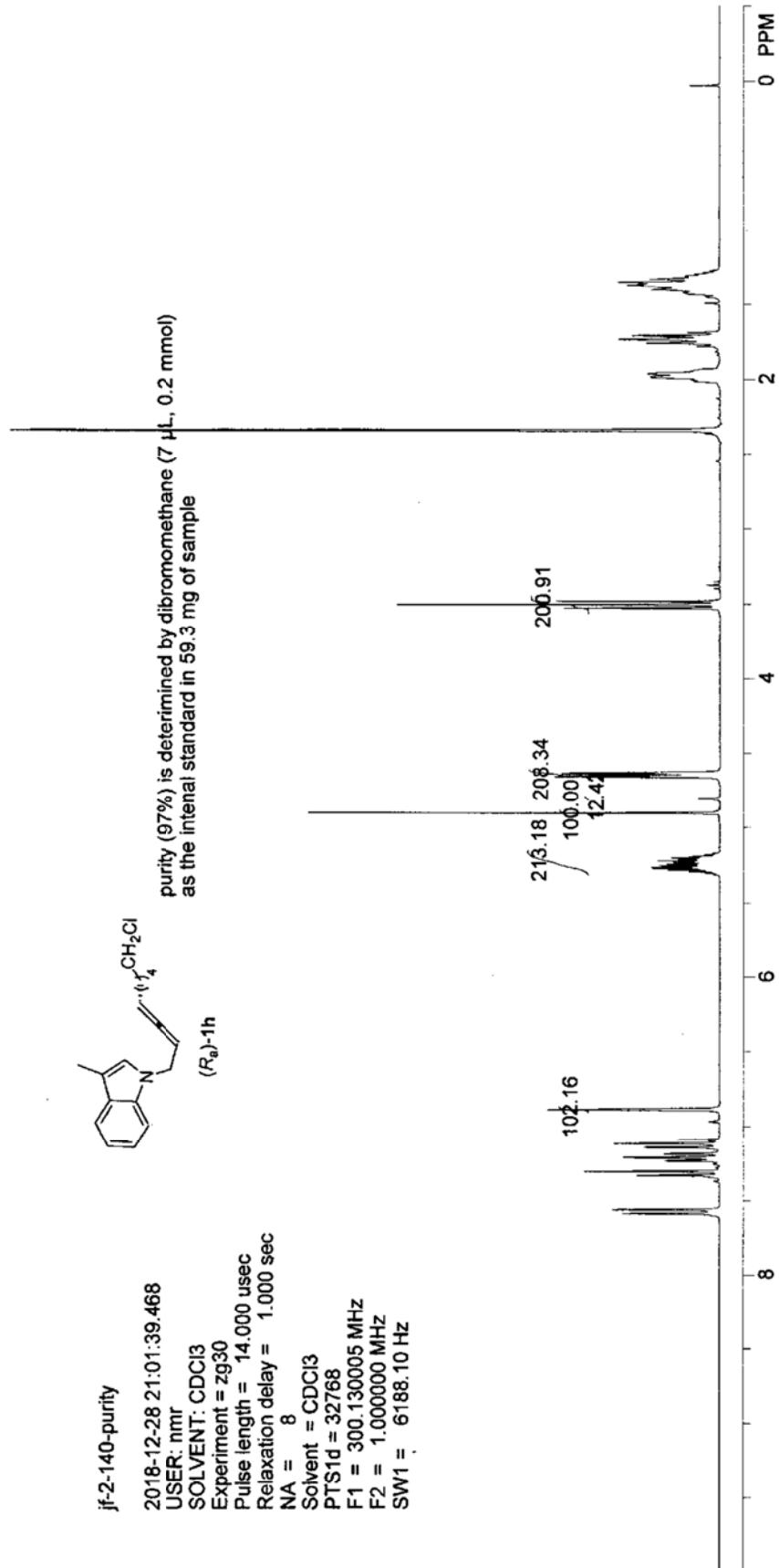
PTS1d = 32768

F1 = 300.130005 MHz

F2 = 1.000000 MHz

SW1 = 6188.10 Hz

purity (97%) is determined by dibromomethane (7 μ L, 0.2 mmol)
as the internal standard in 59.3 mg of sample



9.575

26.206
28.138
28.318
32.354

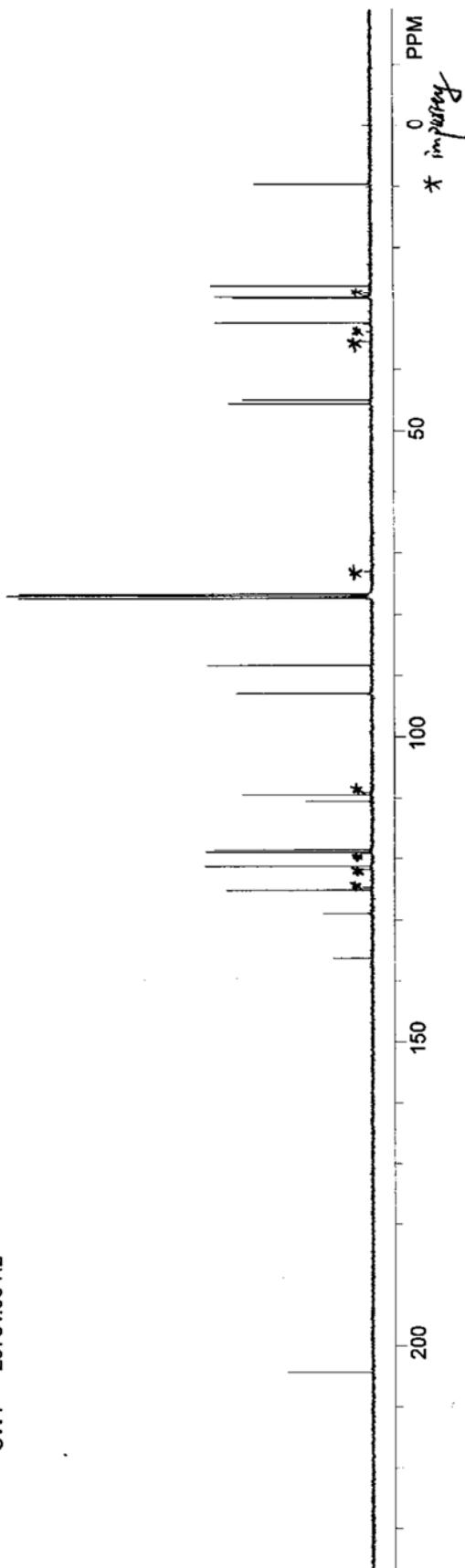
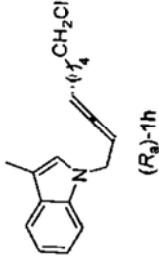
44.967
45.572

76.684
77.000
77.316
88.412
92.989

109.439
110.441
118.612
118.955
121.303
125.194
128.941
136.263

204.365

jf-2-140_2.1
jf-2-140,
2018-12-24 10:50:21.697
USER: nmrstu
SOLVENT: CDCl₃
Experiment = zgpg30
Pulse length = 10.000 ussec
Relaxation delay = 1.500 sec
NA = 512
Solvent = CDCl₃
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
SW1 = 2976190 Hz

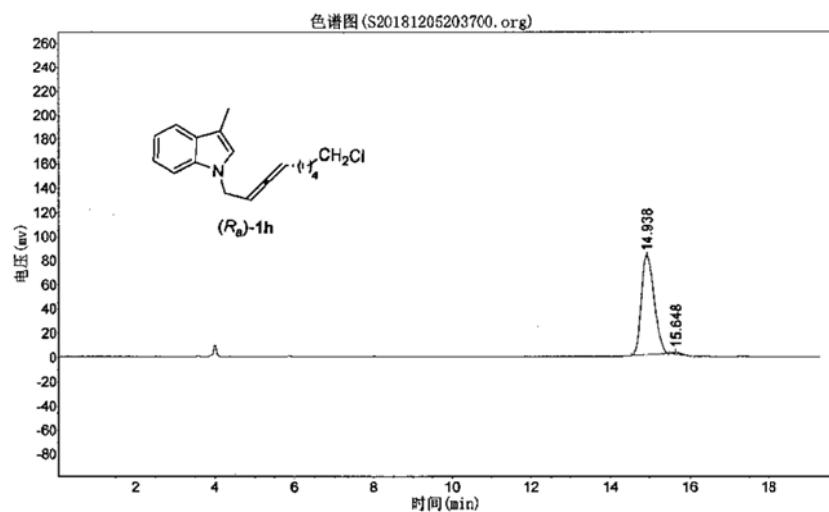


jf-2-140

实验时间: 2018-12-05, 20:37:00
谱图文件:D:\浙大智达\N2000\样品\S20181205203700.org
方法文件:D:\浙大智达\N2000\djx.atd

实验者: jf
报告时间: 2018-12-05, 21:59:55
积分方法: 面积归一法

实验内容简介:
od-H, n-hexane/i-PrOH = 100/1, 1.0, 254



分析结果表

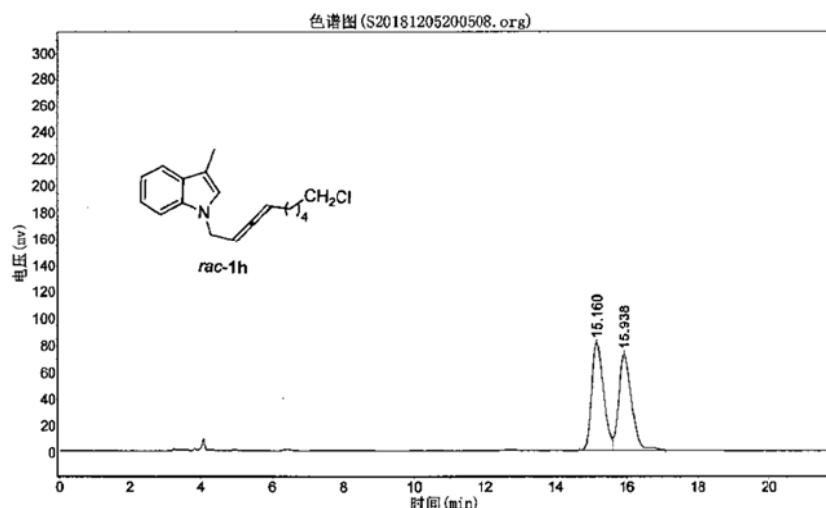
峰号	峰名	保留时间	峰高	峰面积	含量
1		14.938	81651.016	1794848.500	98.9537
2		15.648	1267.406	18978.699	1.0463
总计			82918.422	1813827.199	100.0000

jf-2-149

实验时间: 2018-12-05, 20:05:08
谱图文件:D:\浙大智达\N2000\样品\S20181205200508.org
方法文件:D:\浙大智达\N2000\djx.atd

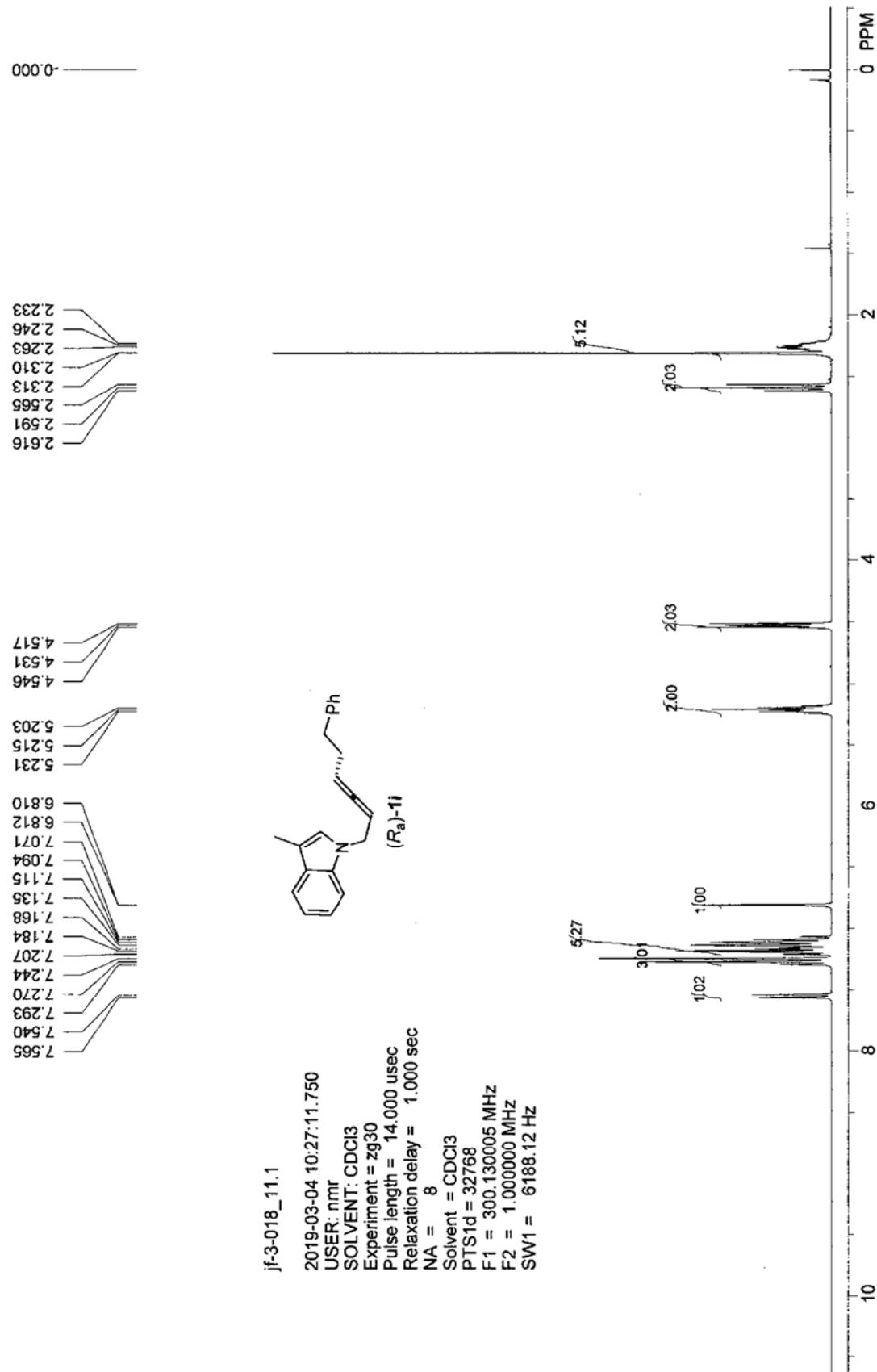
实验者: jf
报告时间: 2018-12-05, 21:53:33
积分方法: 面积归一法

实验内容简介:
od-H, n-hexane/i-PrOH = 100/1, 1.0, 254



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		15.160	80705.750	1870816.875	49.5970
2		15.938	72716.227	1901219.000	50.4030
总计			153421.977	3772035.875	100.0000



204.435

141.425

136.232

128.434

128.934

125.183

121.323

118.951

118.611

110.394

109.420

92.516

88.600

77.423

76.577

77.000

35.150

30.269

9.560

jf-3-018_2.1

2019-03-04 08:51:23.437

USER: nmr

SOLVENT: CDCl₃

Experiment = zgpg30

Pulse length = 9.500 usec

Relaxation delay = 2.000 sec

NA = 11503

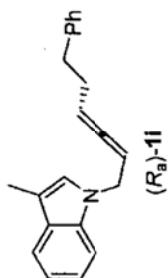
Solvent = CDCl₃

PTSDid = 32768

F1 = 75.467751 MHz

F2 = 1.000000 MHz

SW1 = 22727.27 Hz

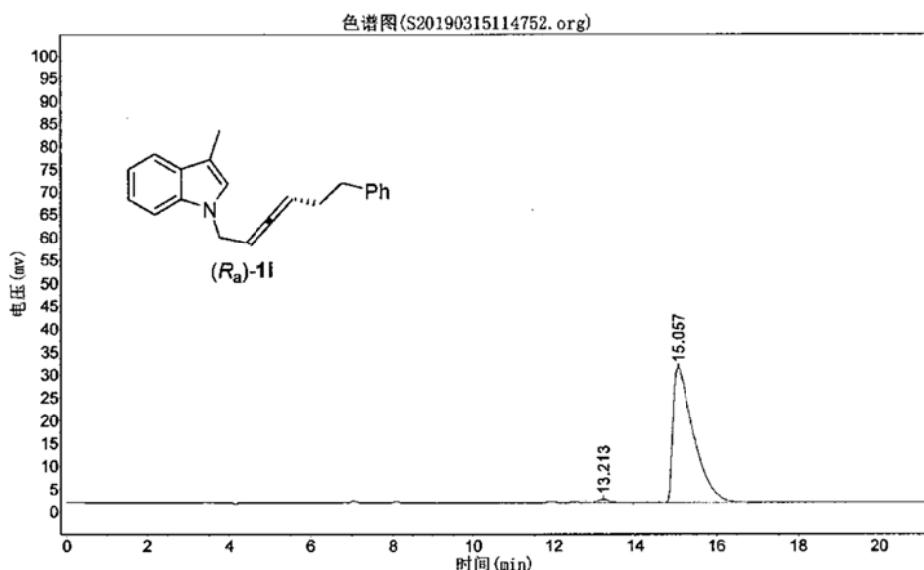


jf-3-018

实验时间: 2019-03-15, 11:47:52
谱图文件:D:\浙大智达\N2000\样品\S20190315114752.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-03-15, 13:12:51
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 90/10, 0.7, 254



分析结果表

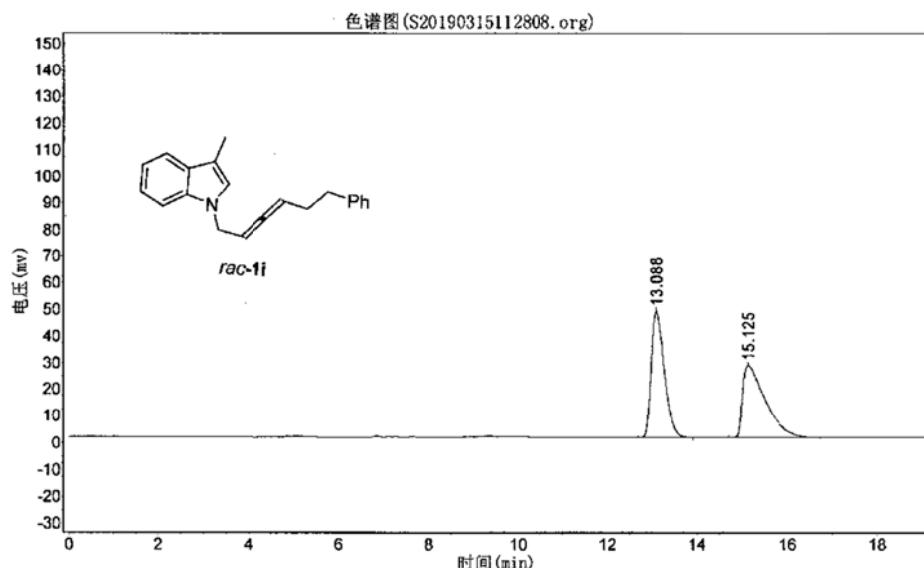
峰号	峰名	保留时间	峰高	峰面积	含量
1		13.213	799.362	15104.655	1.4136
2		15.057	29589.570	1053417.750	98.5864
总计			30388.932	1068522.405	100.0000

jf-3-019

实验时间: 2019-03-15, 11:28:08
谱图文件:D:\浙大智达\N2000\样品\S20190315112808.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-03-15, 13:08:30
积分方法: 面积归一法

实验内容简介:
cd, n-hexane/i-PrOH = 90/10, 0.7, 254

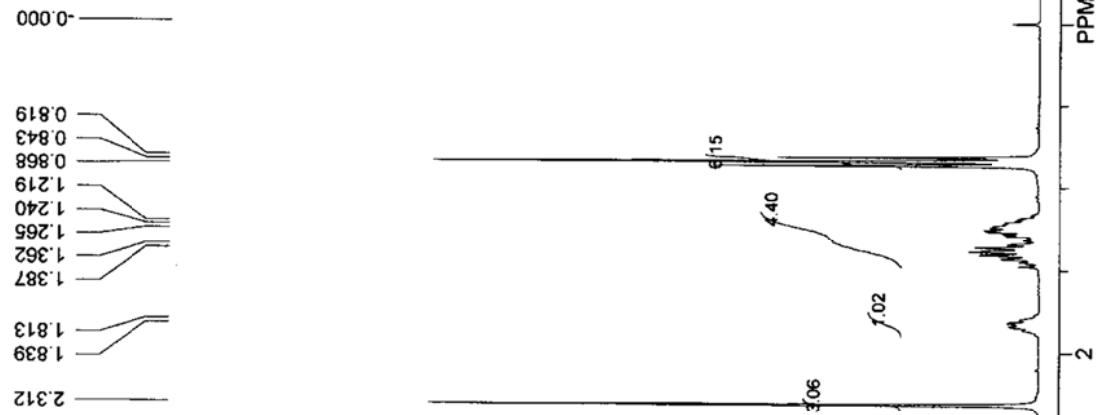
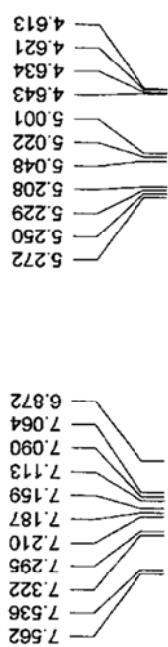
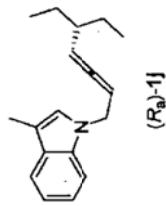


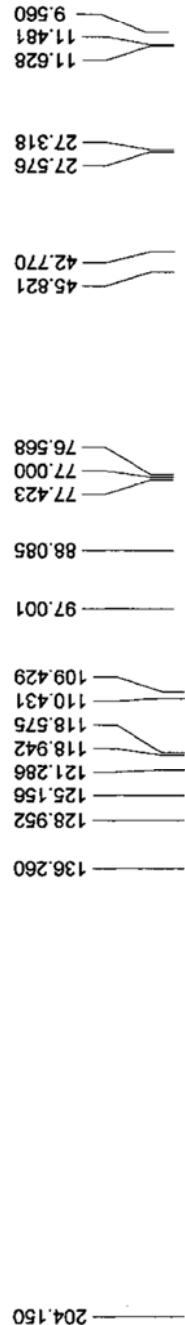
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		13.088	47537.207	942730.313	50.0716
2		15.125	27094.576	940032.500	49.9284
总计			74631.783	1882762.813	100.0000

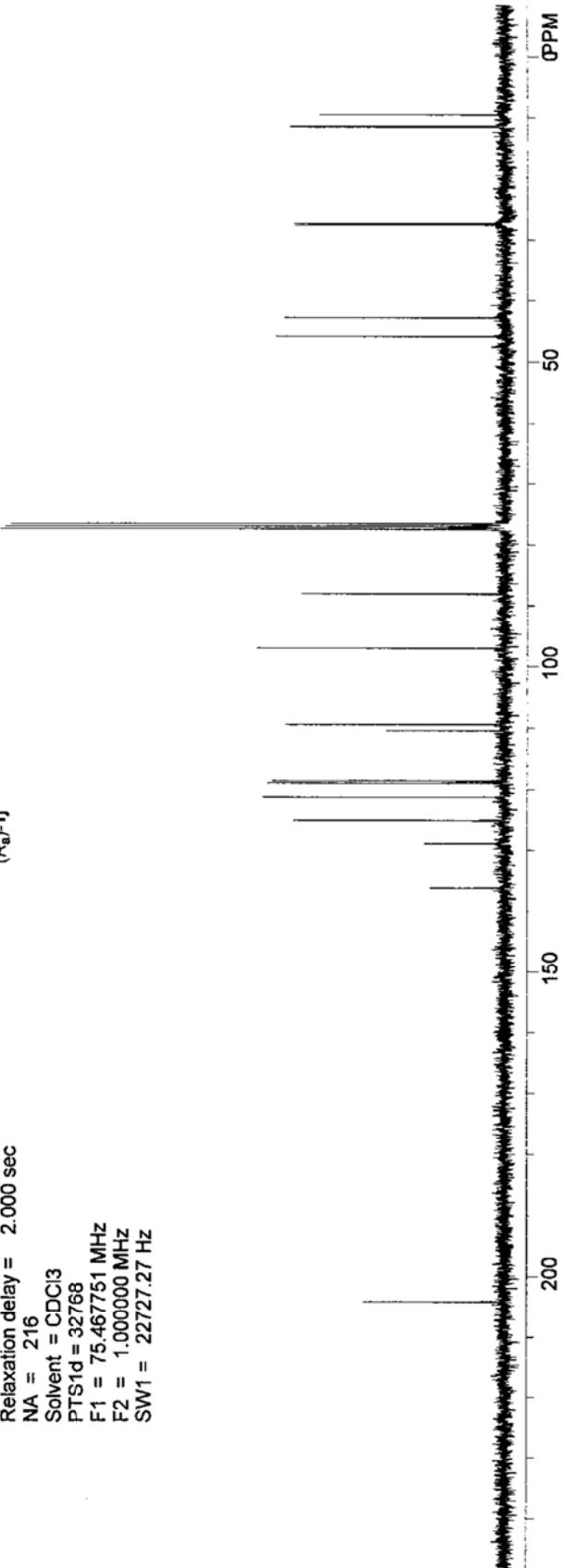
jf-3-093_1.1

2019-05-10 14:28:36.781
USER: nmr
SOLVENT: CDCl₃
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl₃
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz





2019-05-11 09:16:12.640
 USER: nmr
 SOLVENT: CDCl₃
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 216
 Solvent = CDCl₃
 PTS1d = 322768
 F1 = 75.467751 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

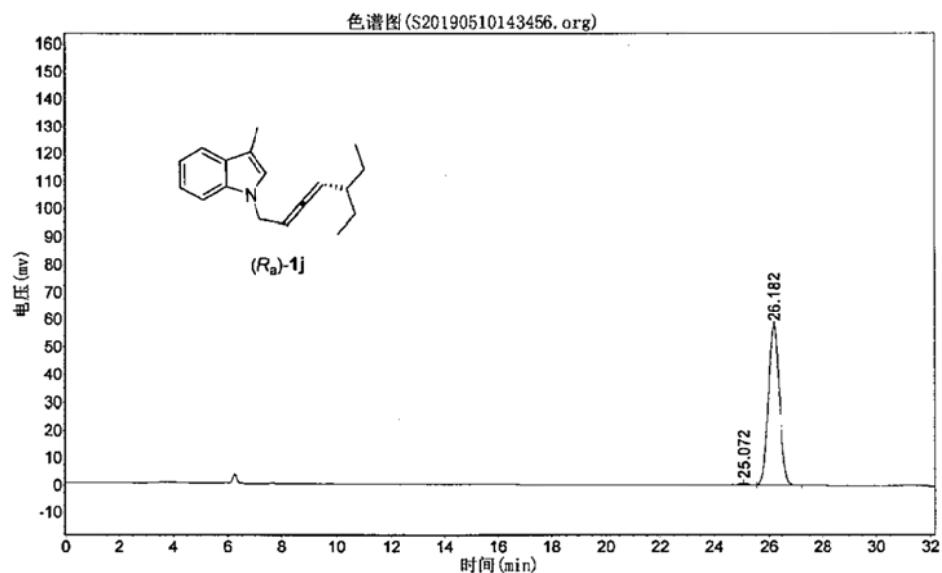


jf-3-093

实验时间: 2019-05-10, 14:34:56
谱图文件:D:\浙大智达\N2000\样品\S20190510143456.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-05-10, 15:08:51
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 200/1, 0.5, 214



分析结果表

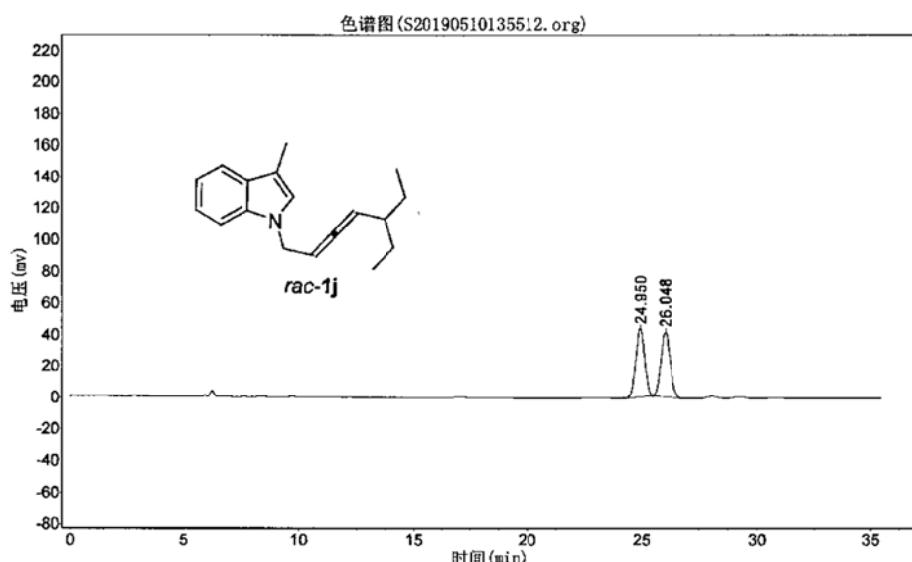
峰号	峰名	保留时间	峰高	峰面积	含量
1		25.072	735.653	18265.891	1.0860
2		26.182	57452.762	1663650.875	98.9140
总计			58188.415	1681916.766	100.0000

jf-3-092

实验时间: 2019-05-10, 13:55:12
谱图文件:D:\浙大智达\N2000\样品\S20190510135512.org
方法文件:D:\浙大智达\N2000\djx.mtd

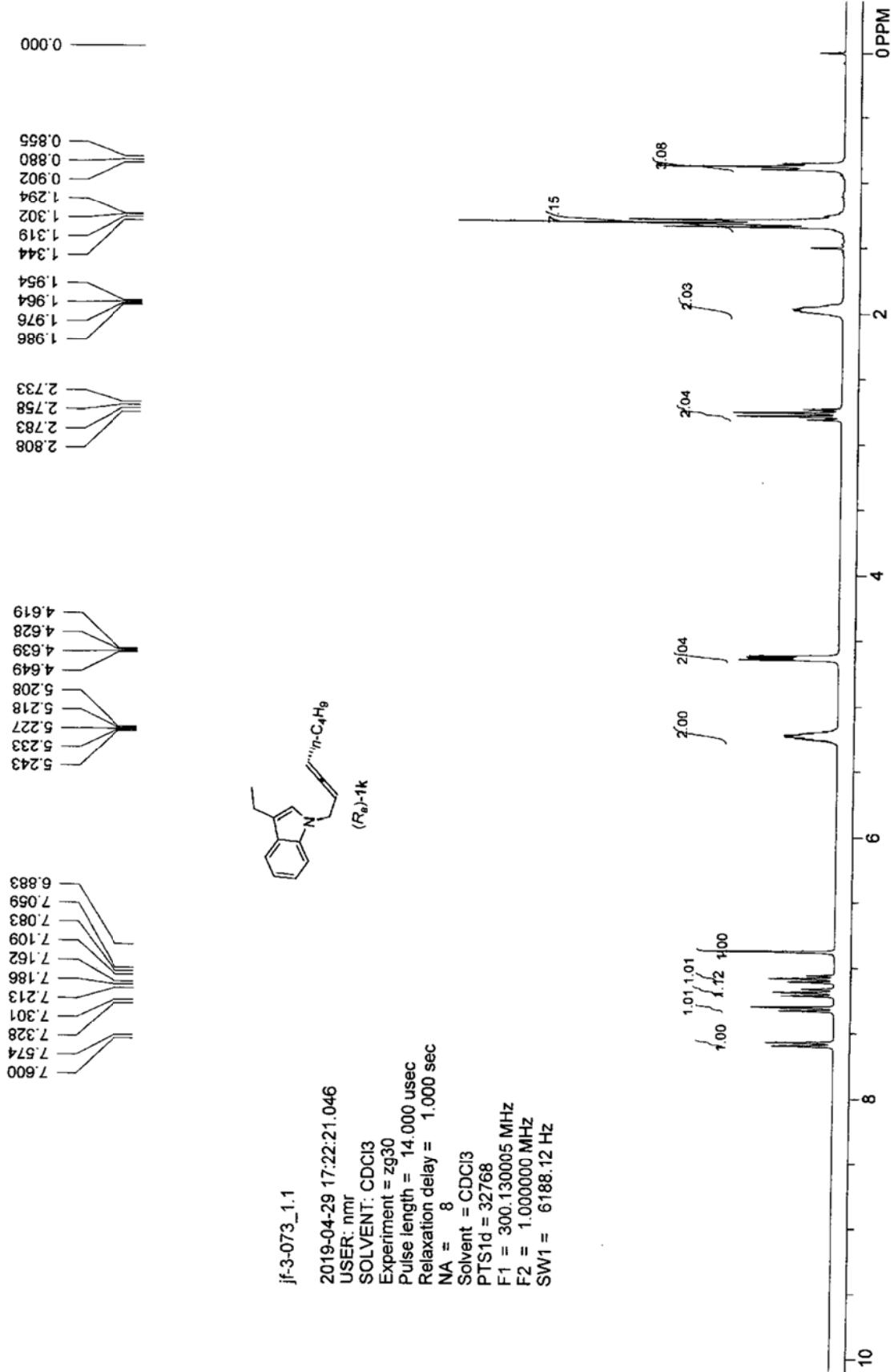
实验者: jf
报告时间: 2019-05-10, 15:06:57
积分方法: 面积归一法

实验内容简介:
od,n-hexane/i-PrOH = 200/1, 0.5, 214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		24.950	43364.660	1165965.375	50.0998
2		26.048	41332.988	1161318.250	49.9002
总计			84697.648	2327283.625	100.0000



204.408

136.388

128.097
124.053
121.314
119.043
118.547
117.573
109.557

93.279
88.122

77.423
77.000
76.577

45.785

31.151
28.274
22.116
18.283
14.551
13.880

jf-3-073_2.1

2019-04-29 17:45:03.062

USER: nmr

SOLVENT: CDCl₃

Experiment = zgpp30

Pulse length = 9.500 usec

Relaxation delay = 2.000 sec

NA = 364

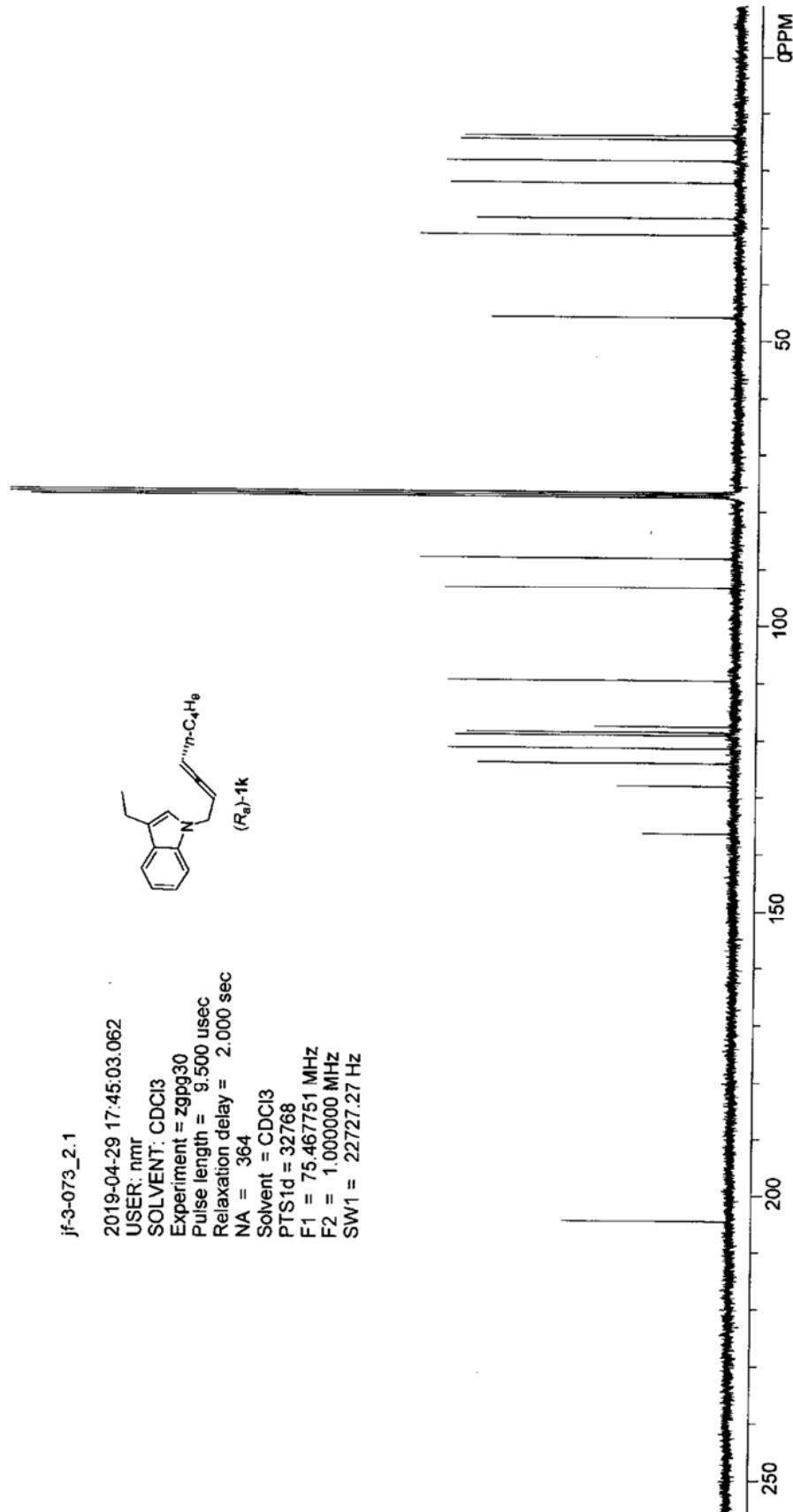
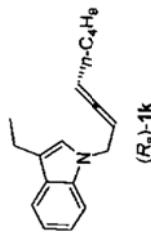
Solvent = CDCl₃

PTS1d = 32768

F1 = 75.467751 MHz

F2 = 1.000000 MHz

SW1 = 227/27.27 Hz

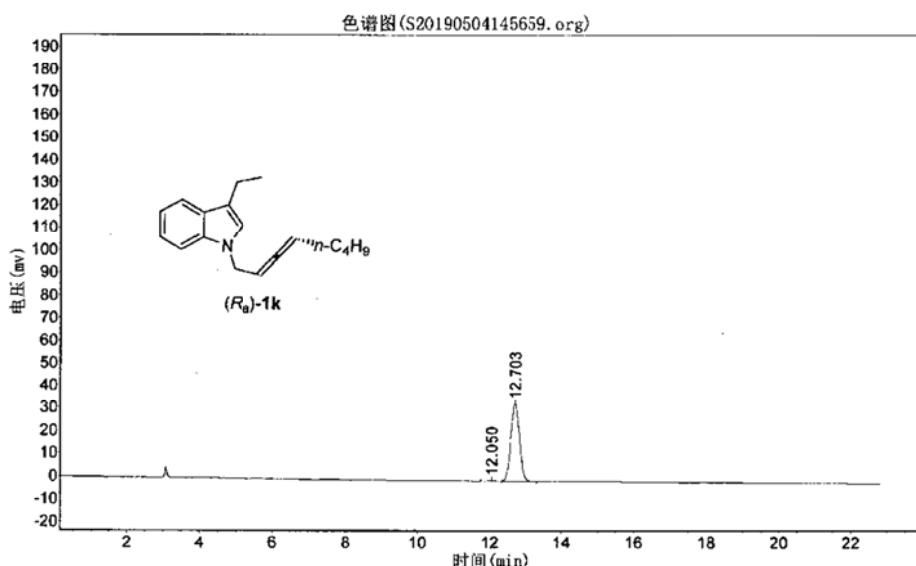


jf-3-073

实验时间: 2019-05-04, 14:56:59
谱图文件:D:\浙大智达\N2000\样品\S20190504145659.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-05-04, 17:58:38
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 200/1, 1.0, 214



分析结果表

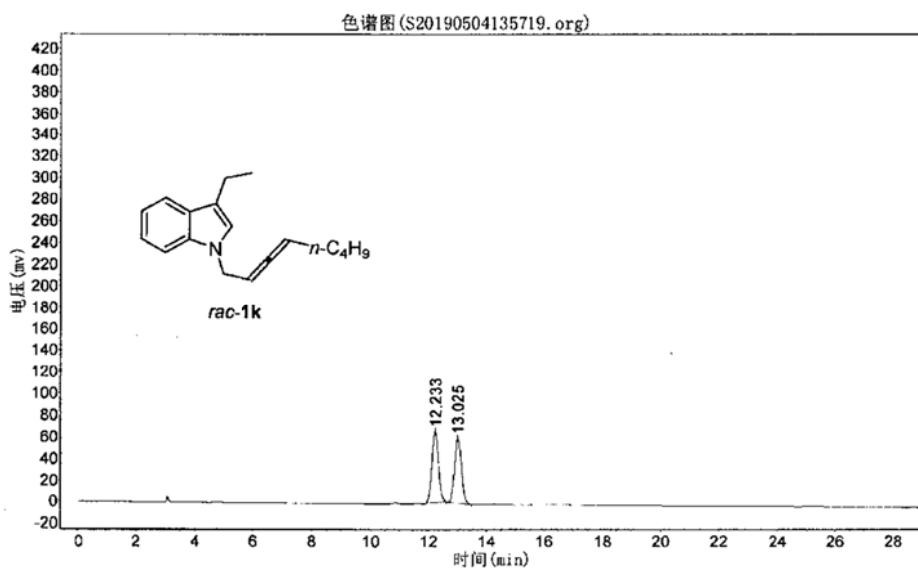
峰号	峰名	保留时间	峰高	峰面积	含量
1		12.050	219.680	2907.099	0.5185
2		12.703	33962.777	557729.563	99.4815
总计			34182.458	560636.661	100.0000

jf-3-074

实验时间: 2019-05-04, 13:57:19
谱图文件:D:\浙大智达\N2000\样品\S20190504135719.org
方法文件:D:\浙大智达\N2000\djx.mtd

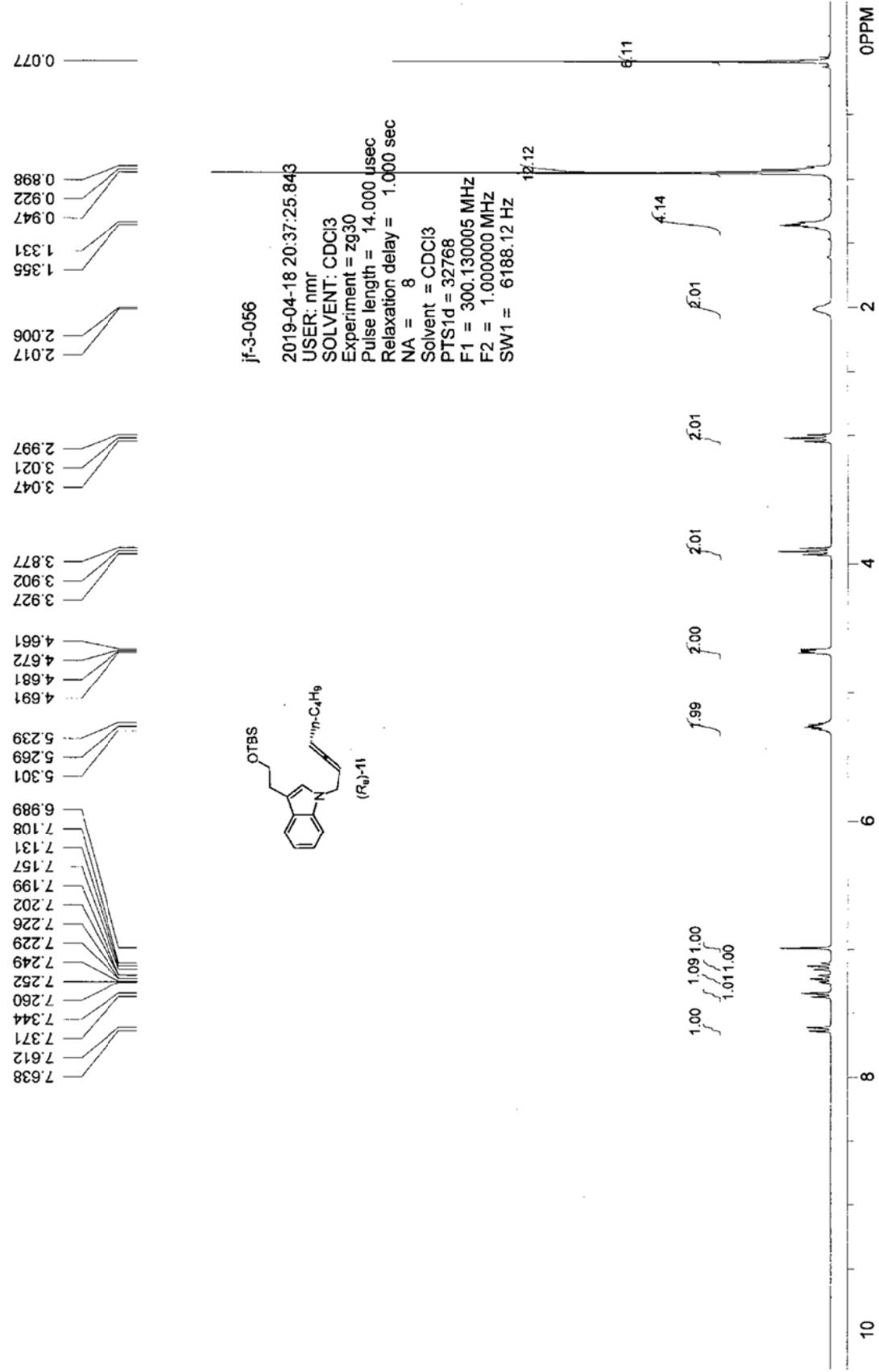
实验者: jf
报告时间: 2019-05-04, 15:00:46
积分方法: 面积归一法

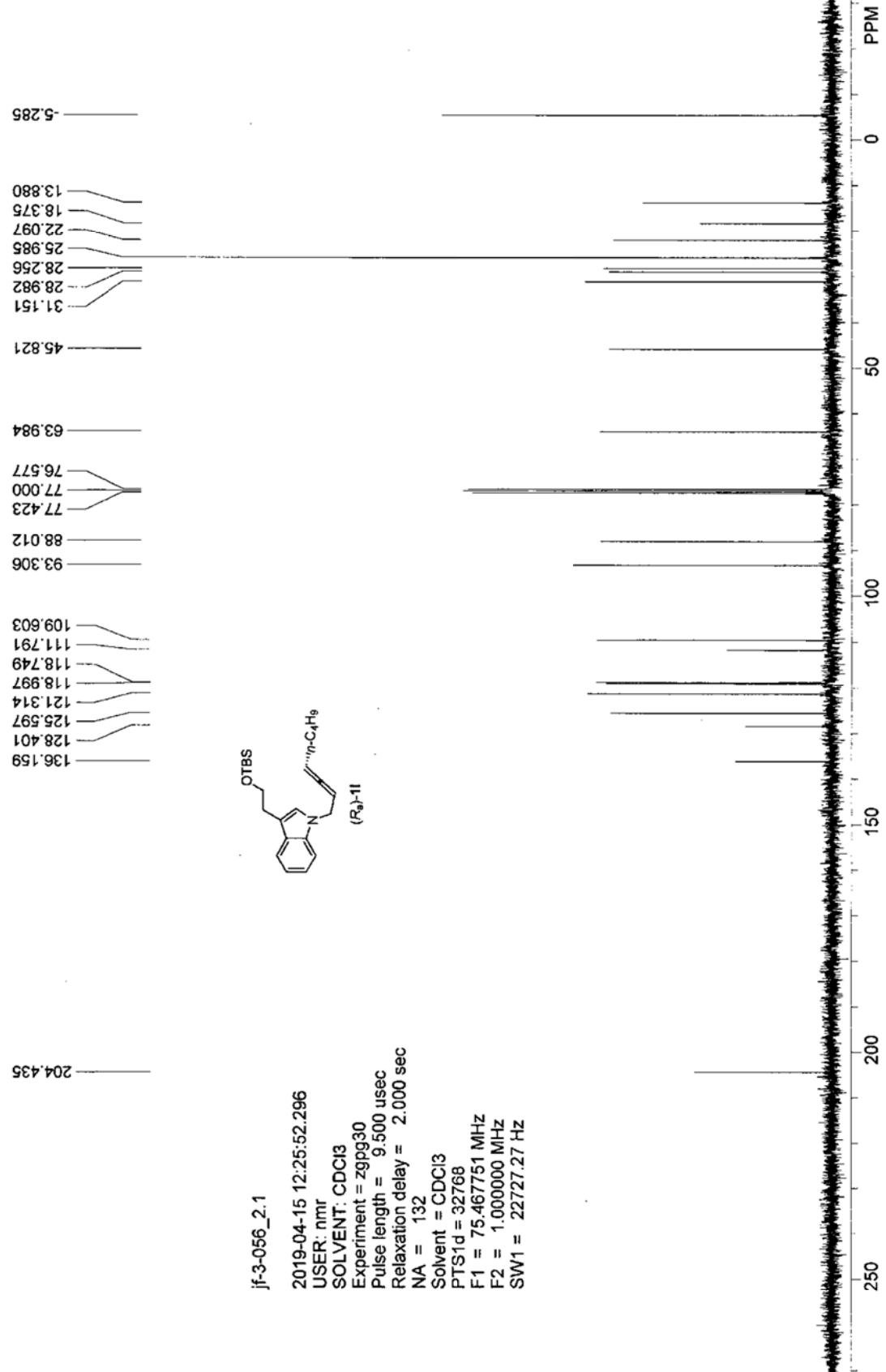
实验内容简介:
od, n-hexane/i-PrOH = 200/1, 1.0, 214



分析结果表

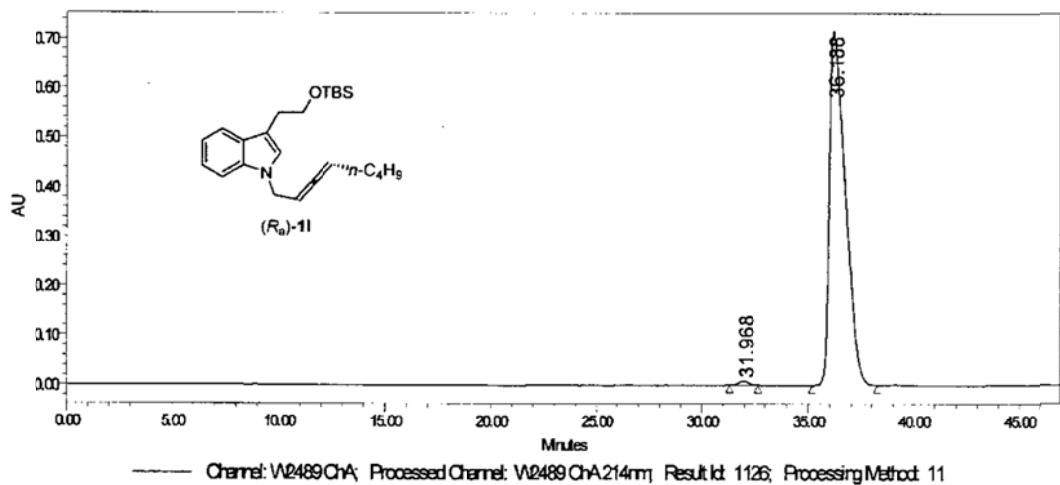
峰号	峰名	保留时间	峰高	峰面积	含量
1		12.233	65802.266	1037234.250	50.6075
2		13.025	60332.977	1012333.000	49.3925
总计			126135.242	2049567.250	100.0000





SAMPLE INFORMATION

Sample Name:	JF-3-056-B-100-0-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	ZGU100
Vial:	1	Acq. Method Set:	111
Injection#:	9	Processing Method:	W2489 ChA
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA.214nm
Run Time:	50.0 Minutes	Proc. Chrl. Descr.:	W2489 ChA.214nm
Date Acquired:	4/28/2019 6:37:46 PM EDT		
Date Processed:	4/29/2019 9:18:04 PM EDT		



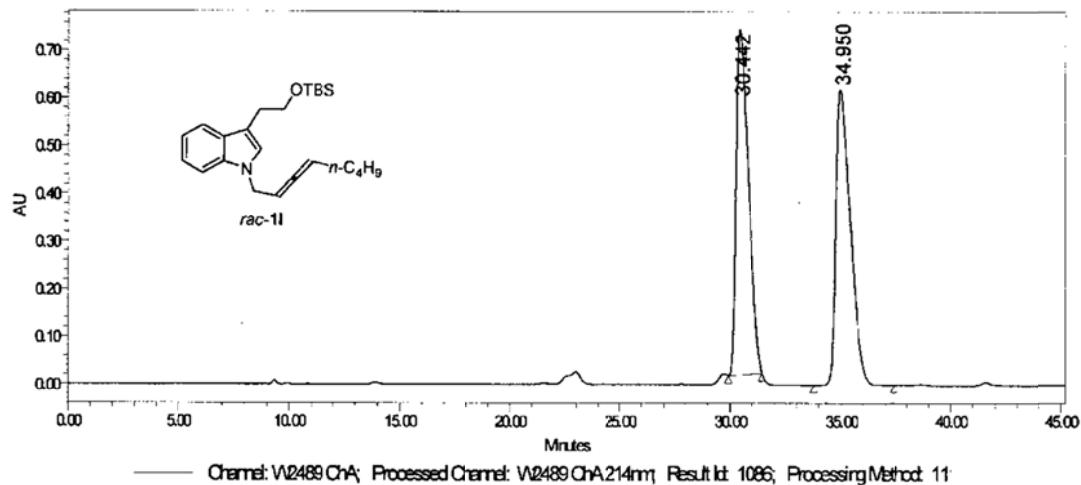
Processed Channel Descr.: W2489 ChA.214nm

	Processed Channel Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	31.968	289640	0.78	8363
2	W2489 ChA.214nm	36.188	36976617	99.22	716510

Reported by User: System
 Report Method: Injection Summary Report
 Report Method ID: 1029 1029
 Page: 1 of 1

Project Name: HPLC_1525
 Date Printed:
 4/29/2019
 9:20:05 PM America/New_York

SAMPLE INFORMATION			
Sample Name:	JF-3-058-B-100-0-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	ZGJ100
Vial:	1	Acq. Method Set:	111
Injection#:	8	Processing Method:	W2489 ChA
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA.214nm
Run Time:	60.0 Minutes	Proc. Chrl. Descr.:	W2489 ChA.214nm
Date Acquired:	4/28/2019 5:50:55 PM EDT		
Date Processed:	4/28/2019 7:23:32 PM EDT		

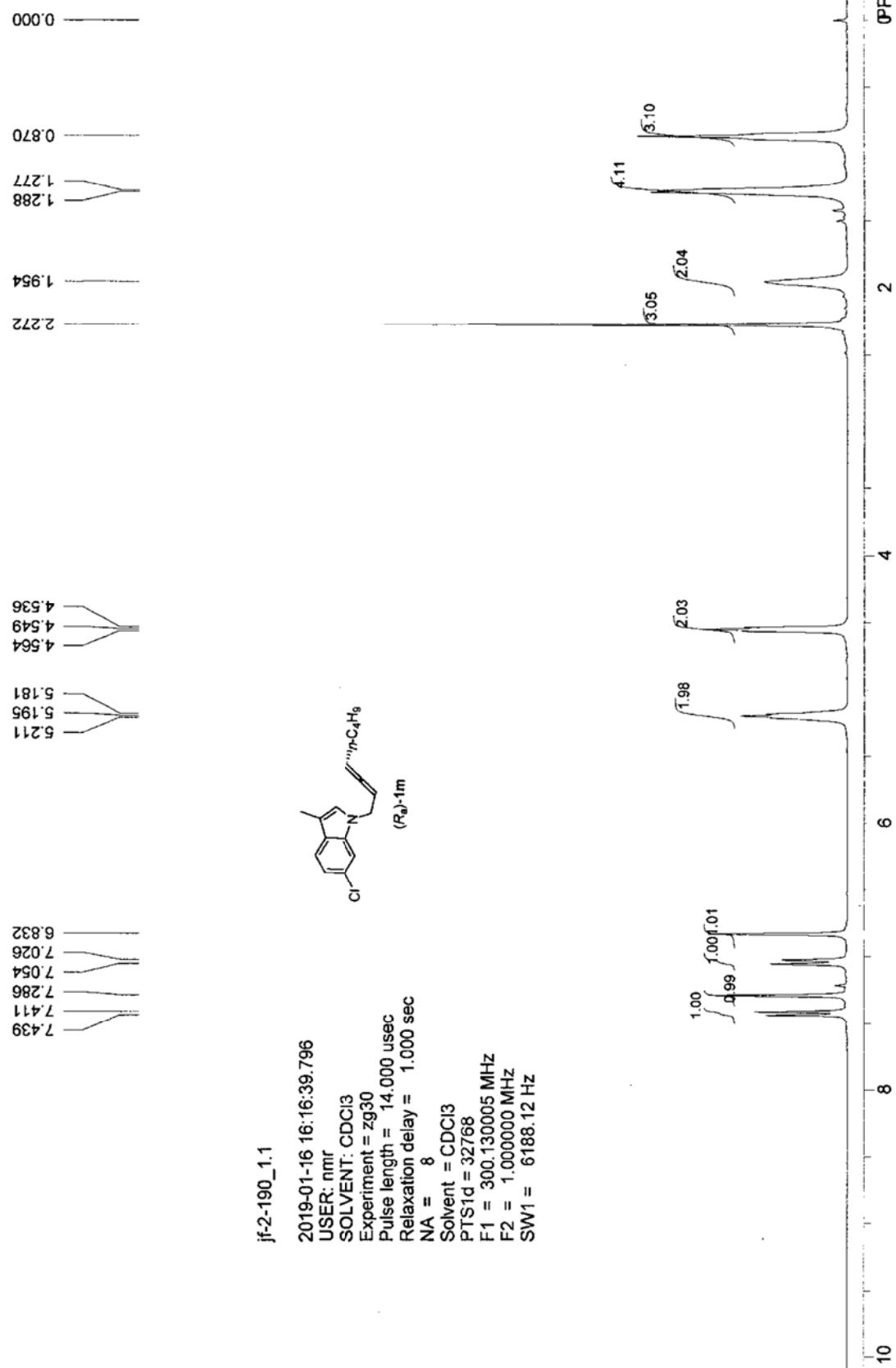


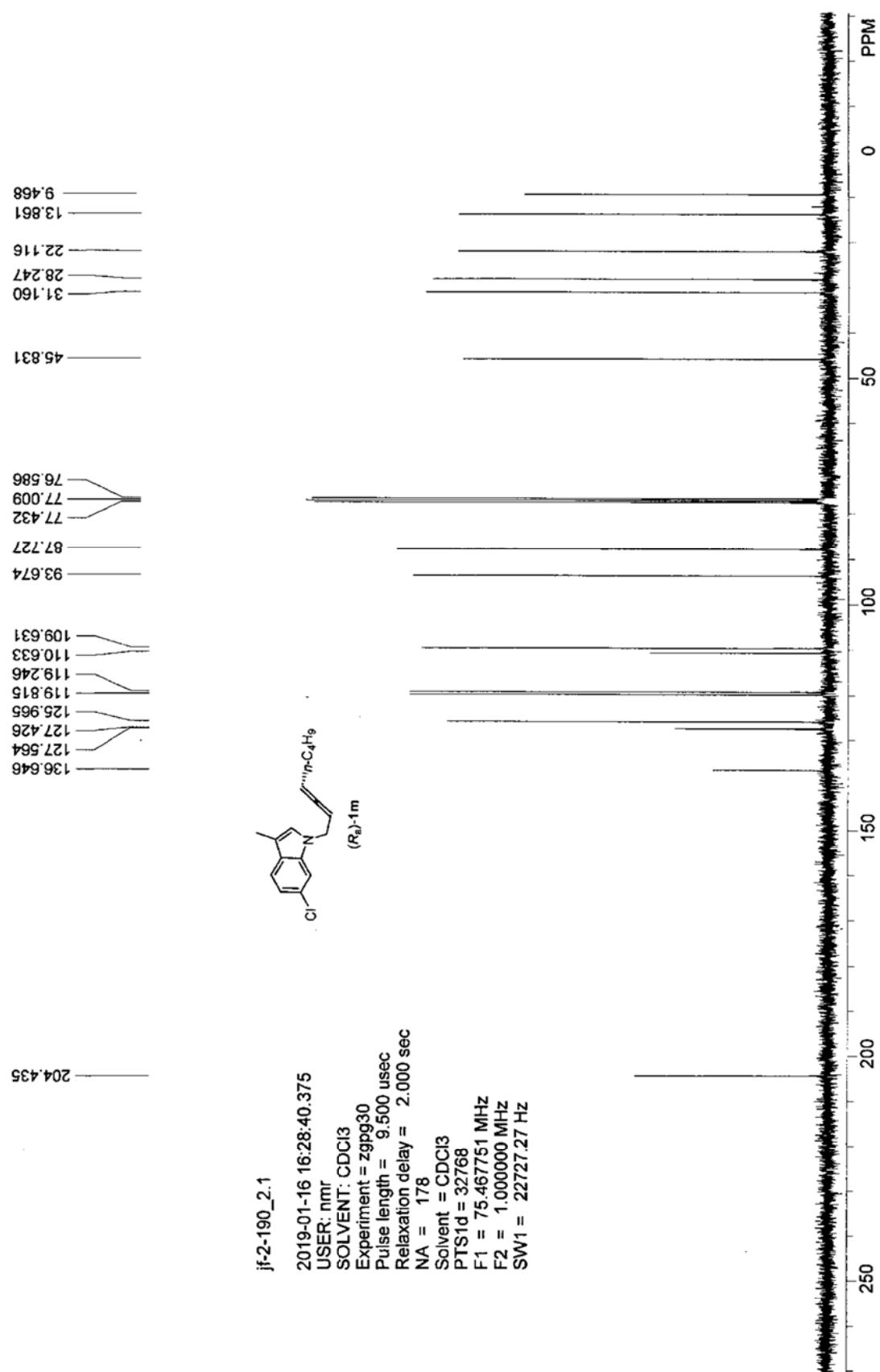
Processed Channel Descr.: W2489 ChA.214nm

	Processed Channel Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	30.442	28669025	50.35	726520
2	W2489 ChA.214nm	34.950	28273083	49.65	621392

Reported by User: System
Report Method: Injection Summary Report
Report Method ID: 1029 1029
Page: 1 of 1

Project Name: HPLC_1525
Date Printed: 4/29/2019
9:18:20 PM America/New_York



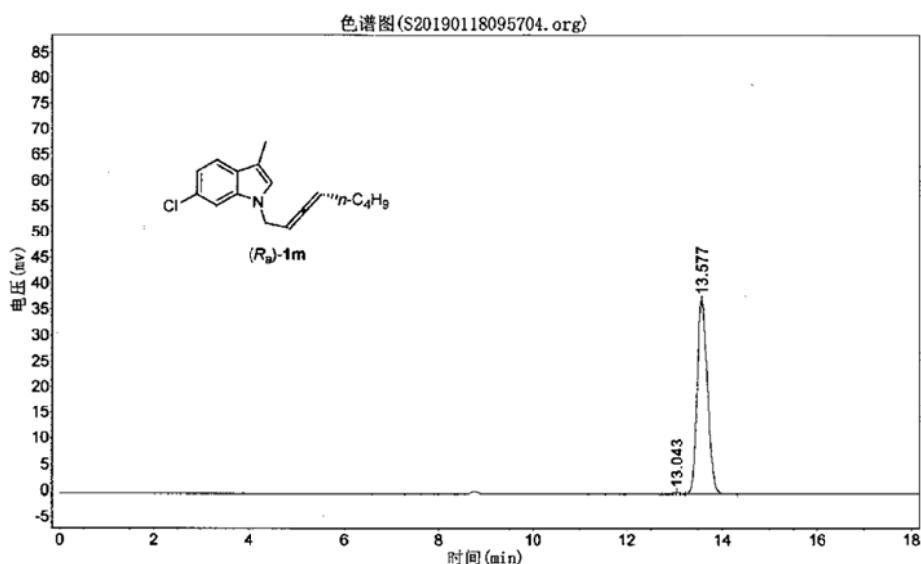


jf-2-190

实验时间: 2019-01-18, 9:57:04
谱图文件:D:\浙大智达\N2000\样品\S20190118095704.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-01-18, 10:32:24
积分方法: 面积归一法

实验内容简介:
OD, n-hexane/i-PrOH = 100/1, 0.5, 254



分析结果表

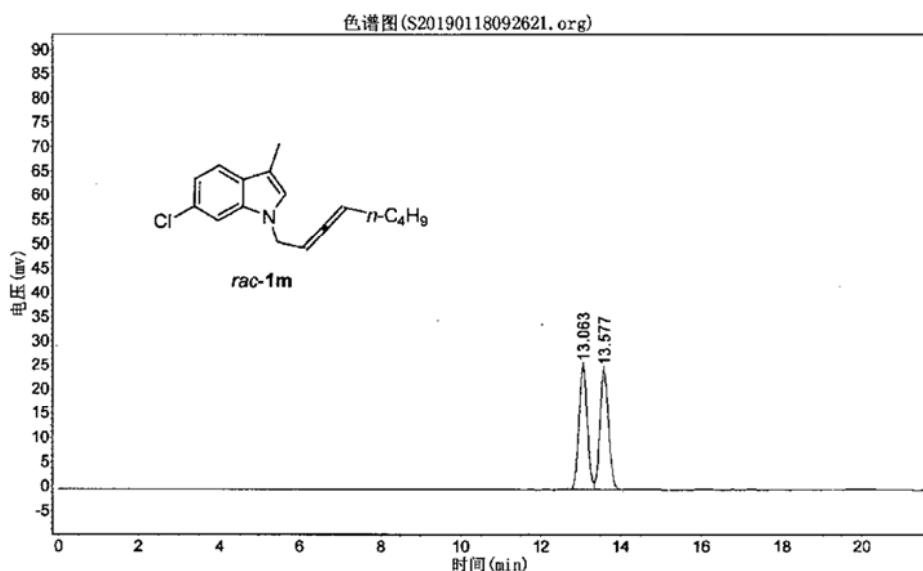
峰号	峰名	保留时间	峰高	峰面积	含量
1		13.043	320.753	4455.119	0.7924
2		13.577	37554.258	557744.813	99.2076
总计			37875.011	562199.931	100.0000

jf-2-191

实验时间: 2019-01-18, 9:26:21
谱图文件:D:\浙大智达\N2000\样品\S20190118092621.org
方法文件:D:\浙大智达\N2000\djx.mtd

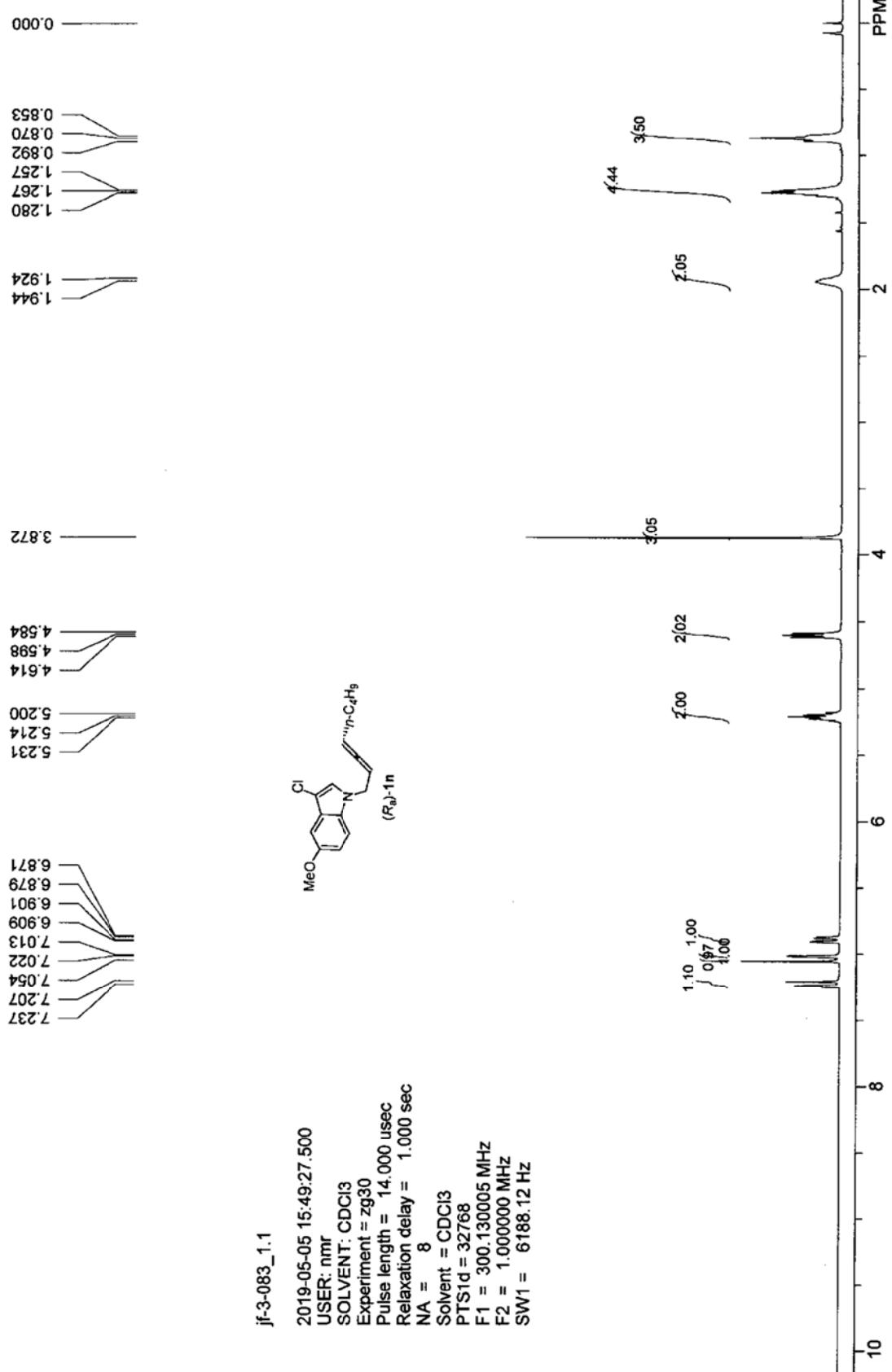
实验者: jf
报告时间: 2019-01-18, 10:36:36
积分方法: 面积归一法

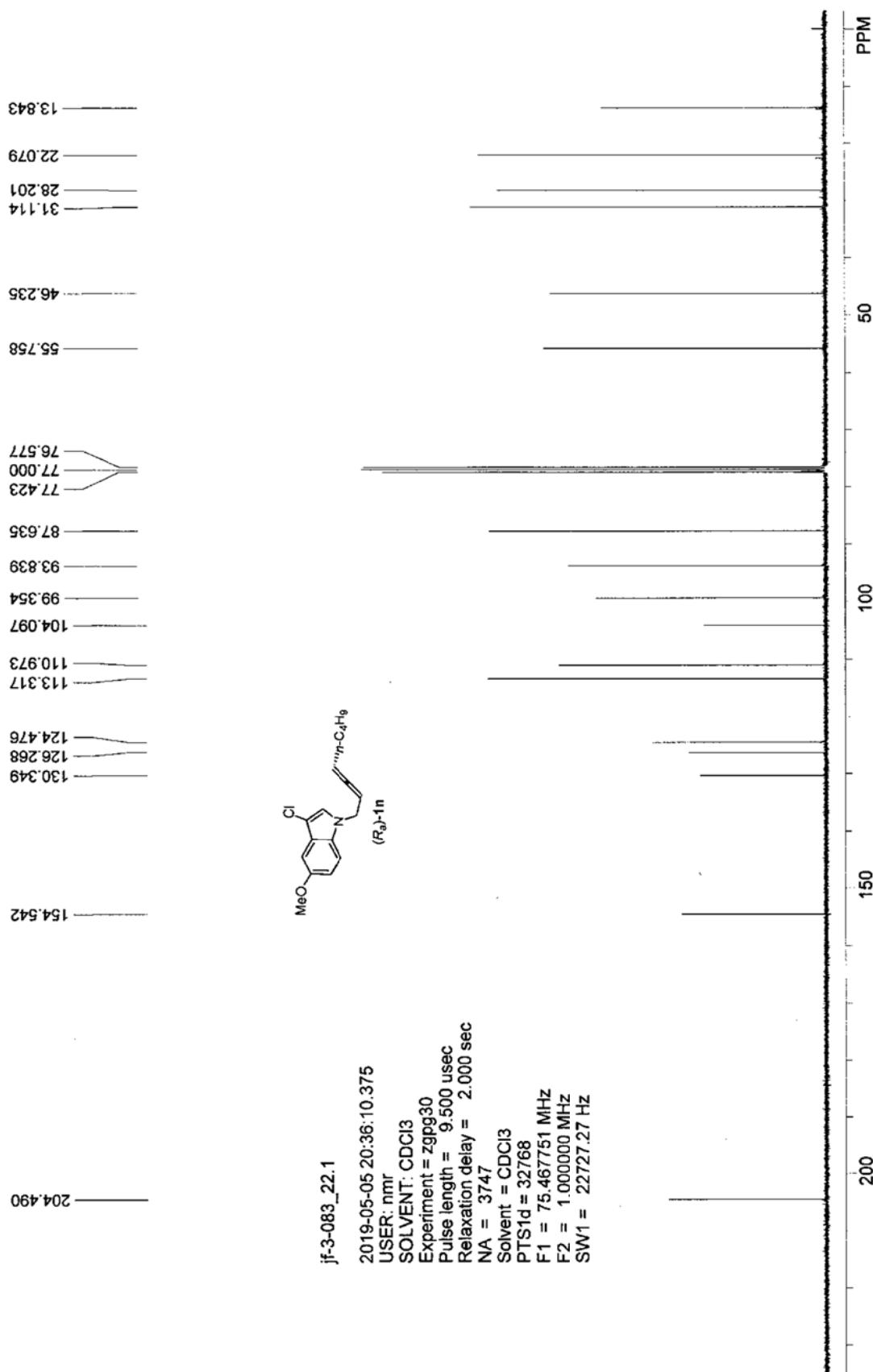
实验内容简介:
od, n-hexane/i-PrOH = 100/1, 0.5, 254



分析结果表

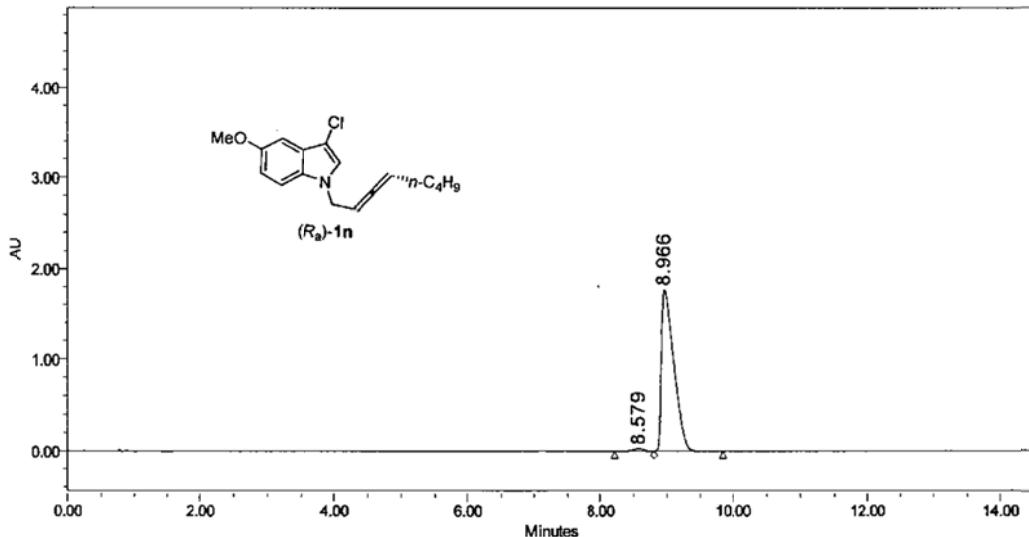
峰号	峰名	保留时间	峰高	峰面积	含量
1		13.063	25586.842	361937.313	49.6575
2		13.577	24708.260	366930.469	50.3425
总计			50295.102	728867.781	100.0000





SAMPLE INFORMATION

Sample Name:	jf-3-083	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1:F.4	Acq. Method Set:	upc_pda_2019m
Injection #:	1	Processing Method	TEST
Injection Volume:	1.00 ul	Channel Name:	PDA Ch2 214nm@4.8nm
Run Time:	50.0 Minutes	Proc. Chnl. Descr.:	PDA Ch2 214nm@4.8nm
Date Acquired:	6/18/2019 1:27:51 PM CST		
Date Processed:	6/20/2019 1:10:44 PM CST		

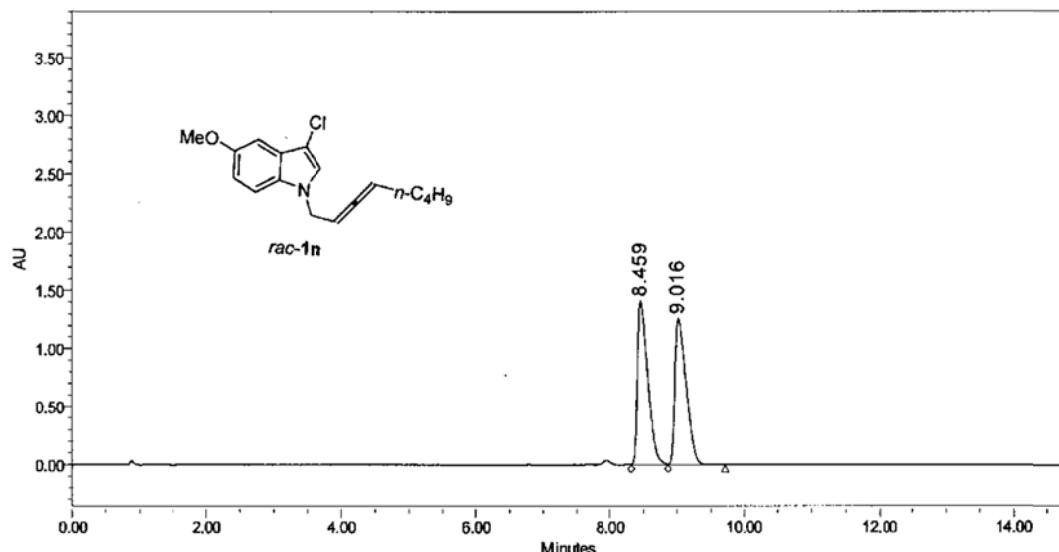


	RT	Peak Type	Height	Width (sec)	Area	% Area
1	8.579	Unknown	28229	35.500	275604	1.20
2	8.966	Unknown	1774506	61.800	22673777	98.80

Reported by User: System
Report Method: Default Individual Report
Report Method ID: 13742
Page: 1 of 1

Project Name: TEST
Date Printed: 6/20/2019
1:13:33 PM PRC

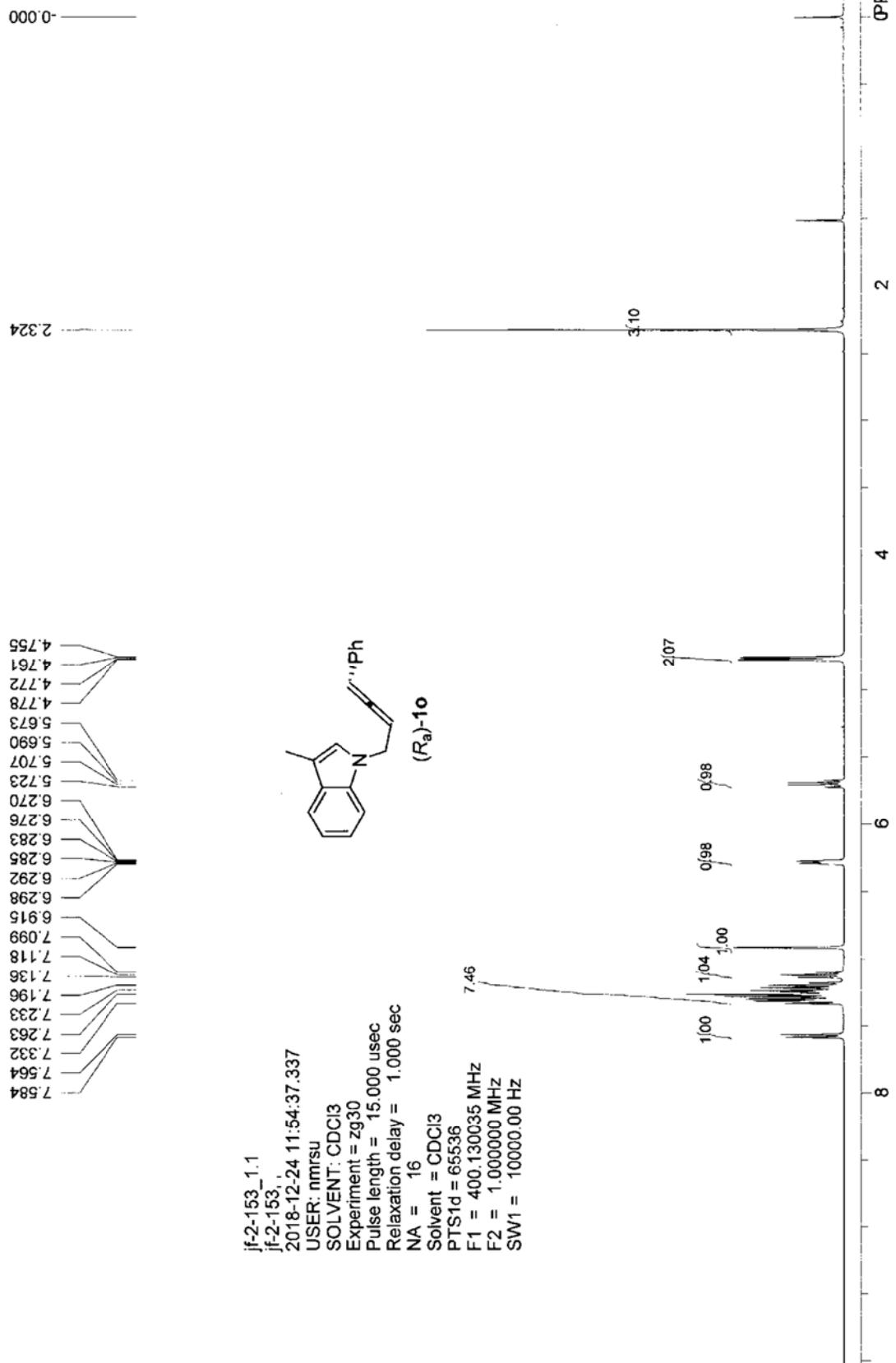
SAMPLE INFORMATION	
Sample Name:	jf-3-082-rac-oj-3-98-2
Sample Type:	Unknown
Vial:	1:F,2
Injection #:	1
Injection Volume:	1.00 ul
Run Time:	50.0 Minutes
Acquired By:	System
Sample Set Name:	
Acq. Method Set:	upc_pda_2019m
Processing Method	TEST
Channel Name:	PDA Ch2 214nm@4.8nm
Proc. Chnl. Descr.:	PDA Ch2 214nm@4.8nm
Date Acquired:	6/18/2019 1:11:48 PM CST
Date Processed:	6/20/2019 1:09:40 PM CST

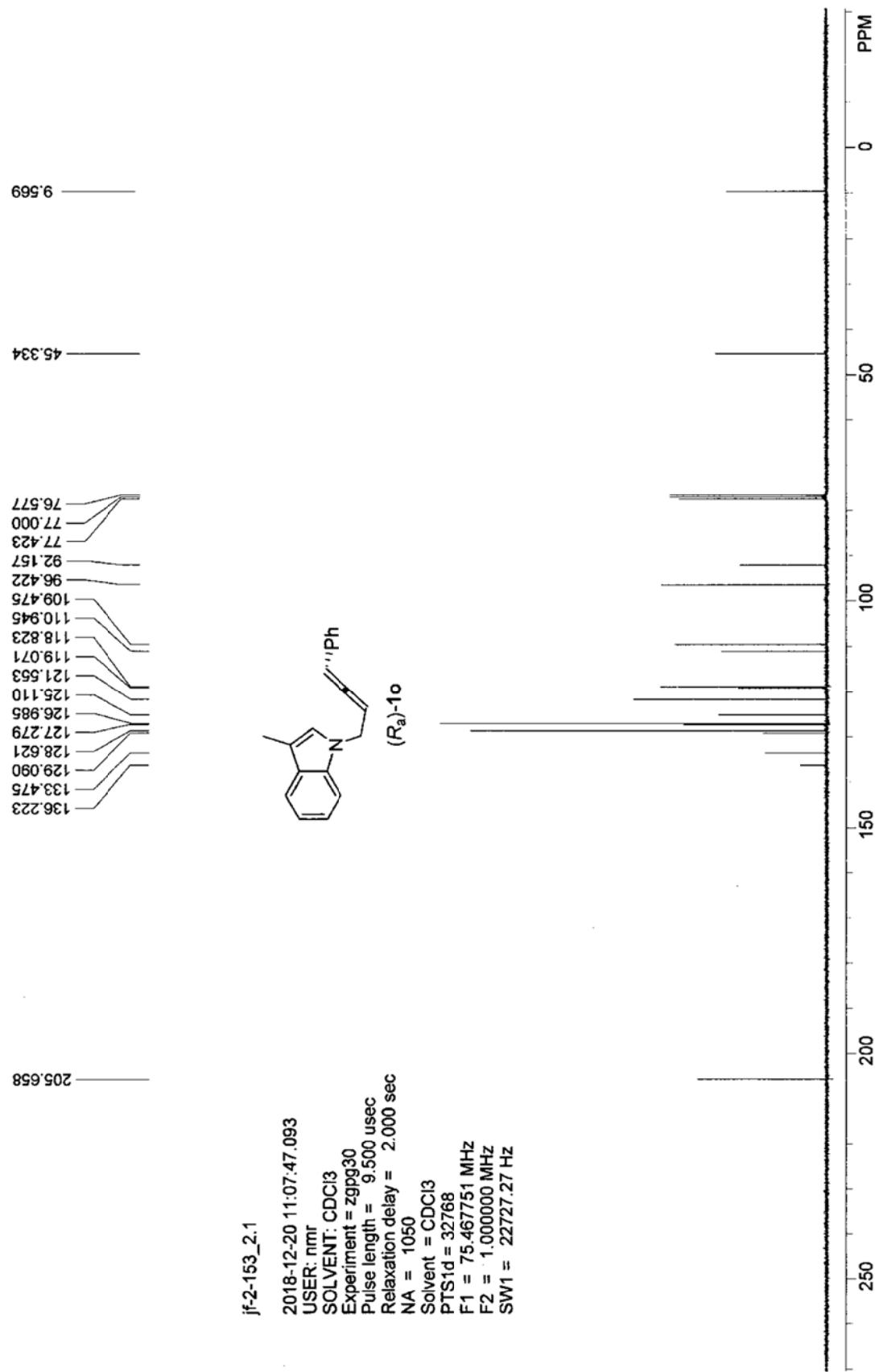


	RT	Peak Type	Height	Width (sec)	Area	% Area
1	8.459	Unknown	1419057	32.600	15111263	50.53
2	9.016	Unknown	1267336	51.150	14793421	49.47

Reported by User: System
 Report Method: Default Individual Report
 Report Method ID: 13742
 Page: 1 of 1

Project Name: TEST
 Date Printed:
 6/20/2019
 1:13:47 PM PRC



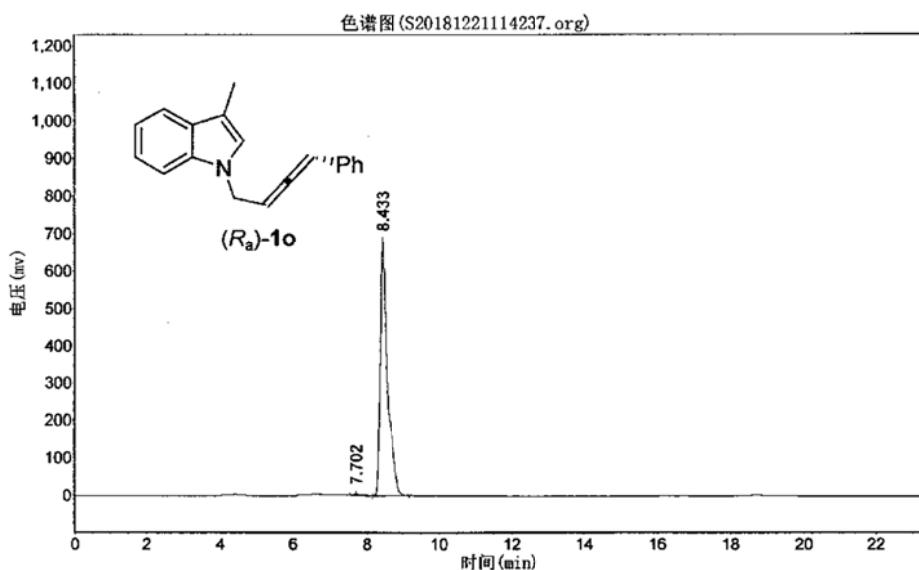


jf-2-153

实验时间: 2018-12-21, 11:42:37
谱图文件:D:\浙大智达\N2000\样品\S20181221114237.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2018-12-21, 12:38:55
积分方法: 面积归一法

实验内容简介:
AD, r-hexane/i-PrOH = 99/1, 0.7, 214



分析结果表

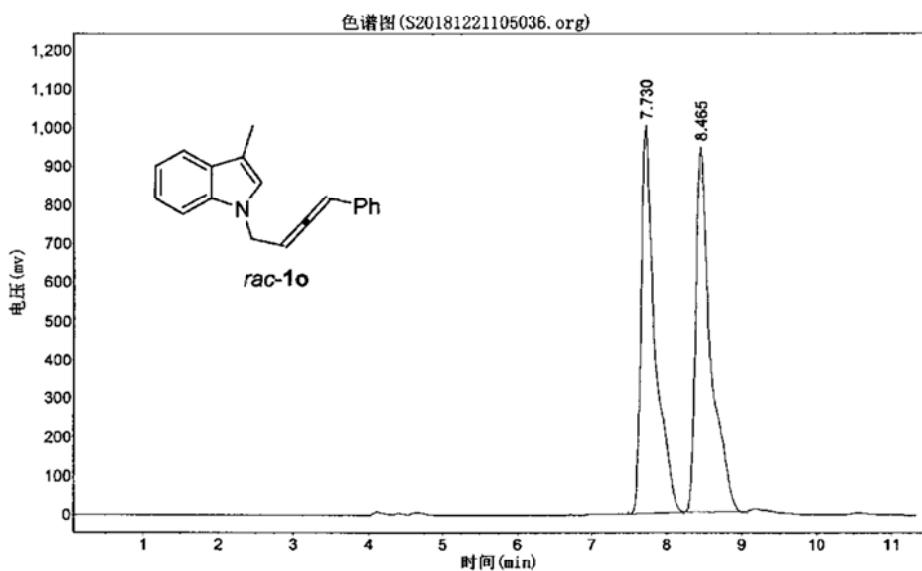
峰号	峰名	保留时间	峰高	峰面积	含量
1		7.702	3376.311	44261.047	0.4620
2		8.433	681389.188	9536051.000	99.5380
总计			684765.498	9580312.047	100.0000

jf-2-157

实验时间: 2018-12-21, 10:50:36
谱图文件:D:\浙大智达\N2000\样品\S20181221105036.org
方法文件:D:\浙大智达\N2000\djx.mtd

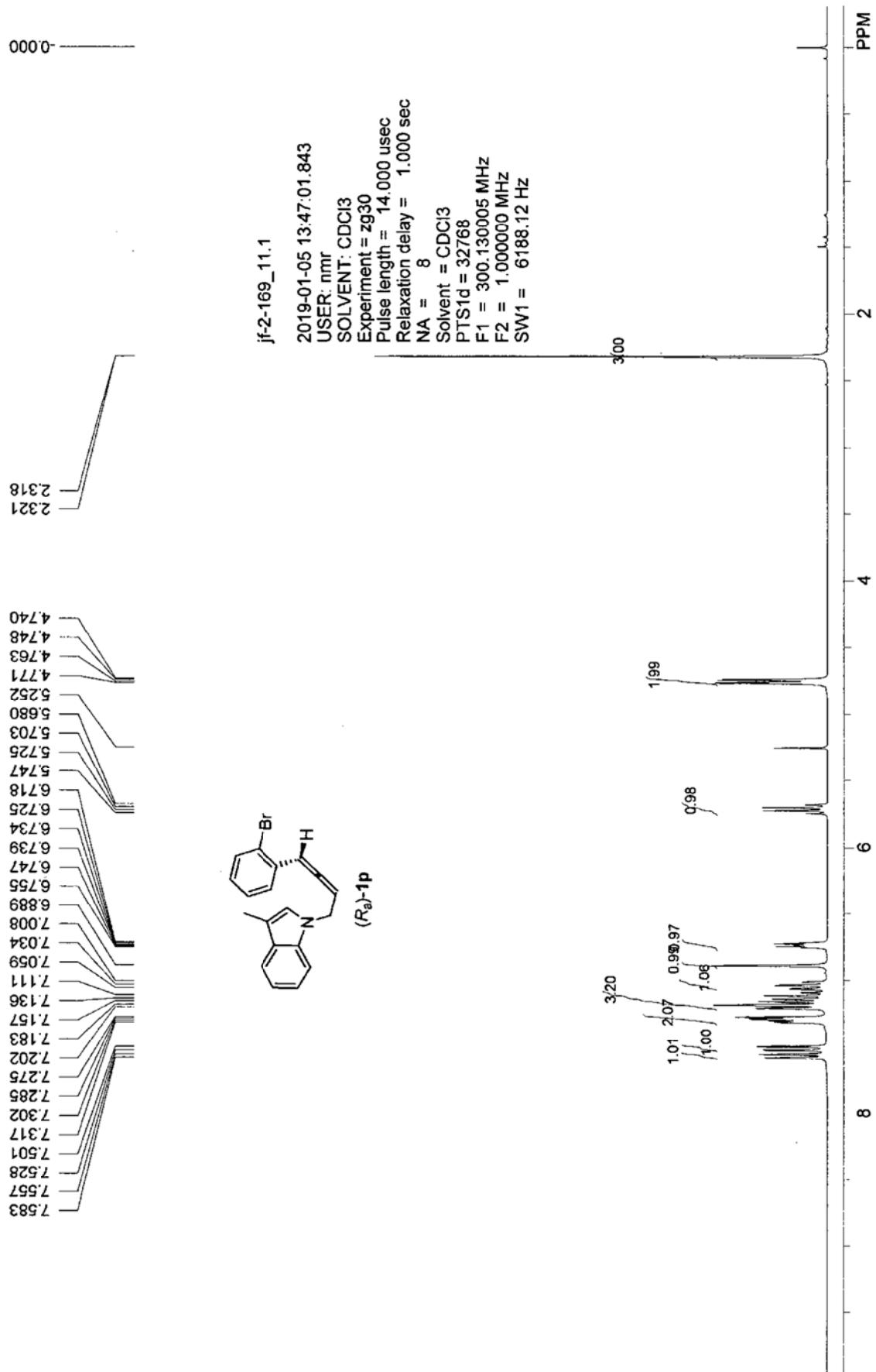
实验者: jf
报告时间: 2018-12-21, 12:35:15
积分方法: 面积归一法

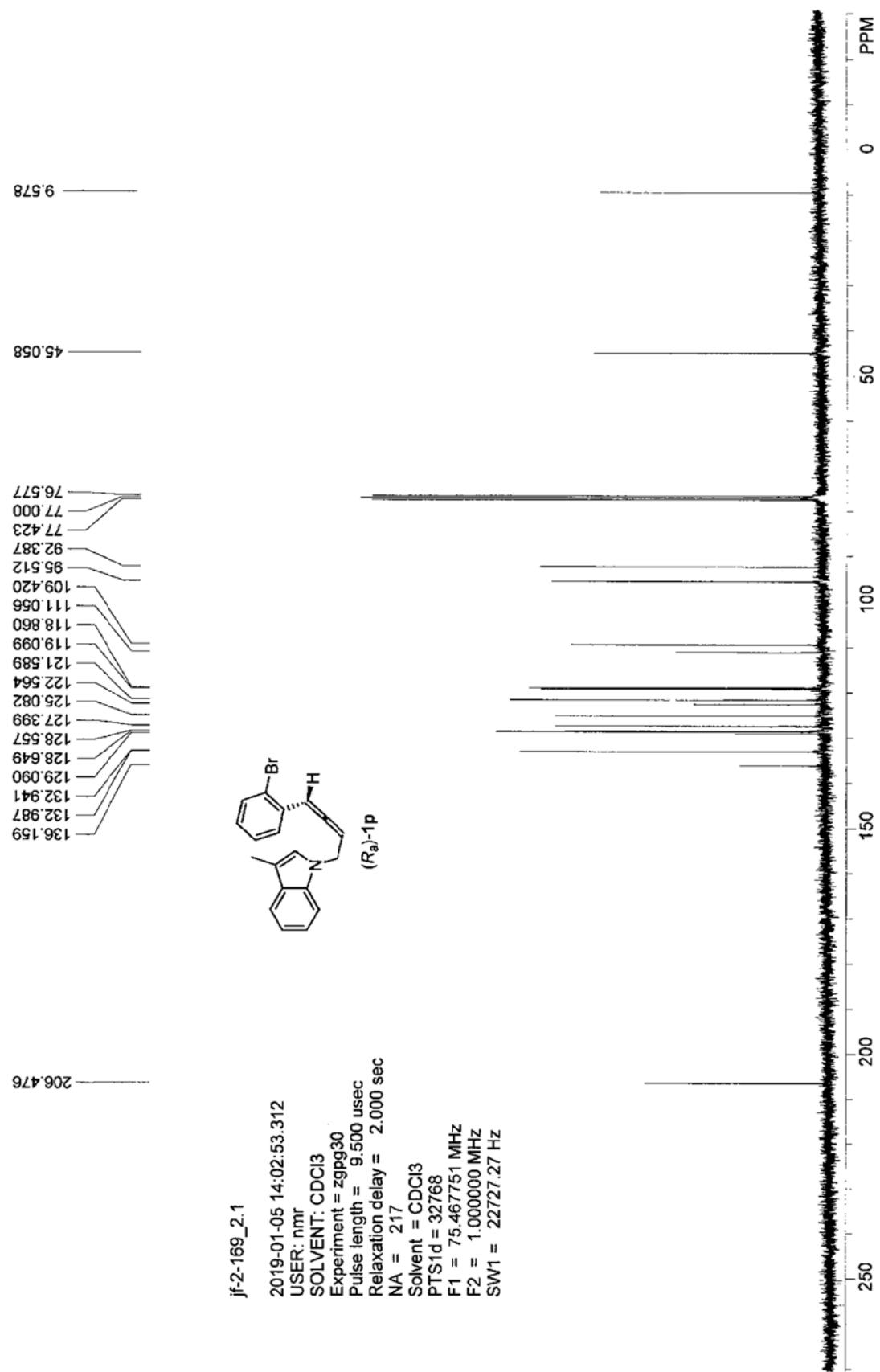
实验内容简介:
AD, n-hexane/i-PrOH = 99/1, 0.7, 214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		7.730	994593.875	12781228.000	49.8731
2		8.465	935218.875	12846270.000	50.1269
总计			1929812.750	25627498.000	100.0000



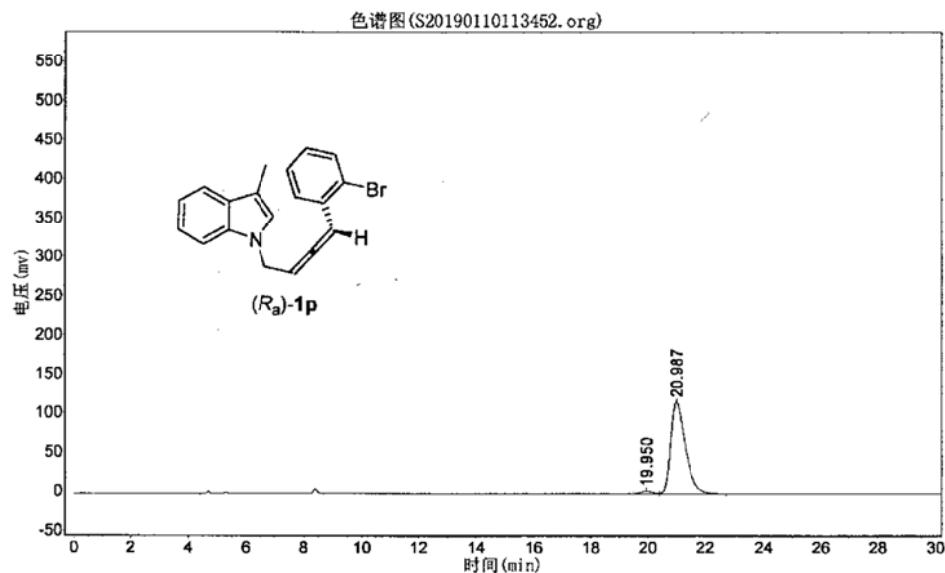


jf-2-169

实验时间: 2019-01-10, 11:34:52
谱图文件:D:\浙大智达\N2000\样品\S20190110113452.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-01-10, 12:29:42
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 90/10, 0.7, 254



分析结果表

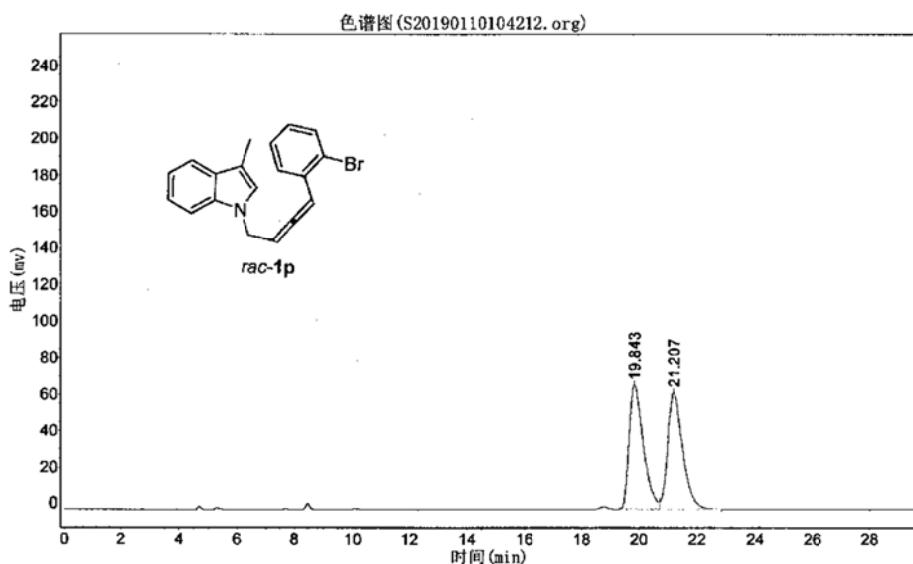
峰号	峰名	保留时间	峰高	峰面积	含量
1		19.950	2718.615	86753.391	2.0472
2		20.987	116535.891	4150971.000	97.9528
总计			119254.506	4237724.391	100.0000

jf-2-172

实验时间: 2019-01-10, 10:42:12
谱图文件:D:\浙大智达\N2000\样品\S20190110104212.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-01-10, 12:31:31
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 90/10, 0.7, 254



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		19.843	68290.195	2334392.250	49.6334
2		21.207	64551.098	2368880.500	50.3666
总计			132841.293	4703272.750	100.0000

0.000

2.322
2.319
4.741
4.749
4.763
4.771
5.661
5.683
5.705
5.727
6.219
6.228
6.236
6.240
6.249
6.257
6.897
6.900
6.943
6.972
6.972
7.001
7.095
7.118
7.144
7.159
7.176
7.189
7.193
7.205
7.230
7.284
7.310
7.562
7.587

jf-3-031_1.1

2019-04-05 14:19:36.796

USER: nmr

SOLVENT: CDCl₃

Experiment = zg30

Pulse length = 14.000 usec

Relaxation delay = 1.000 sec

NA = 8

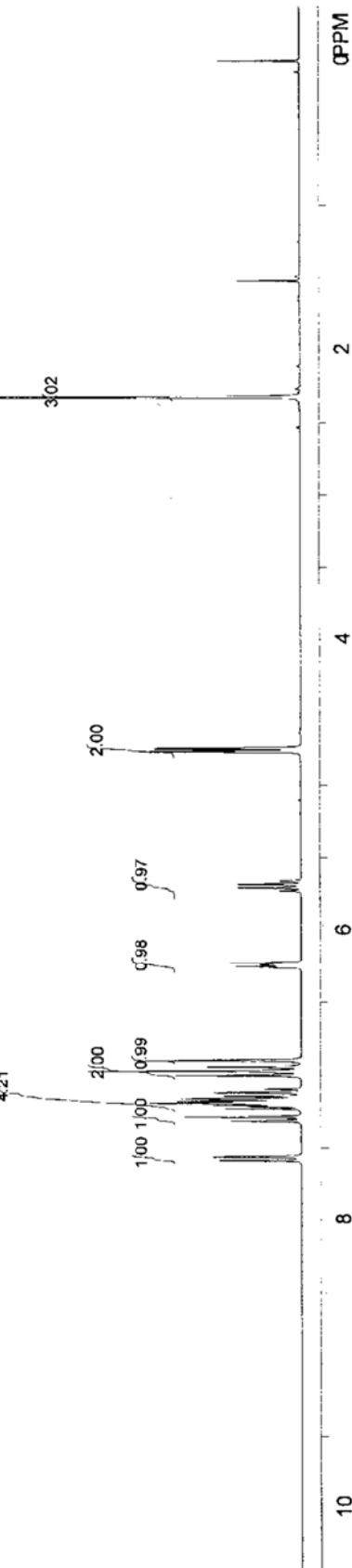
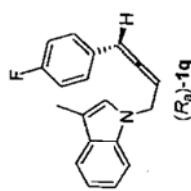
Solvent = CDCl₃

PTS1d = 32768

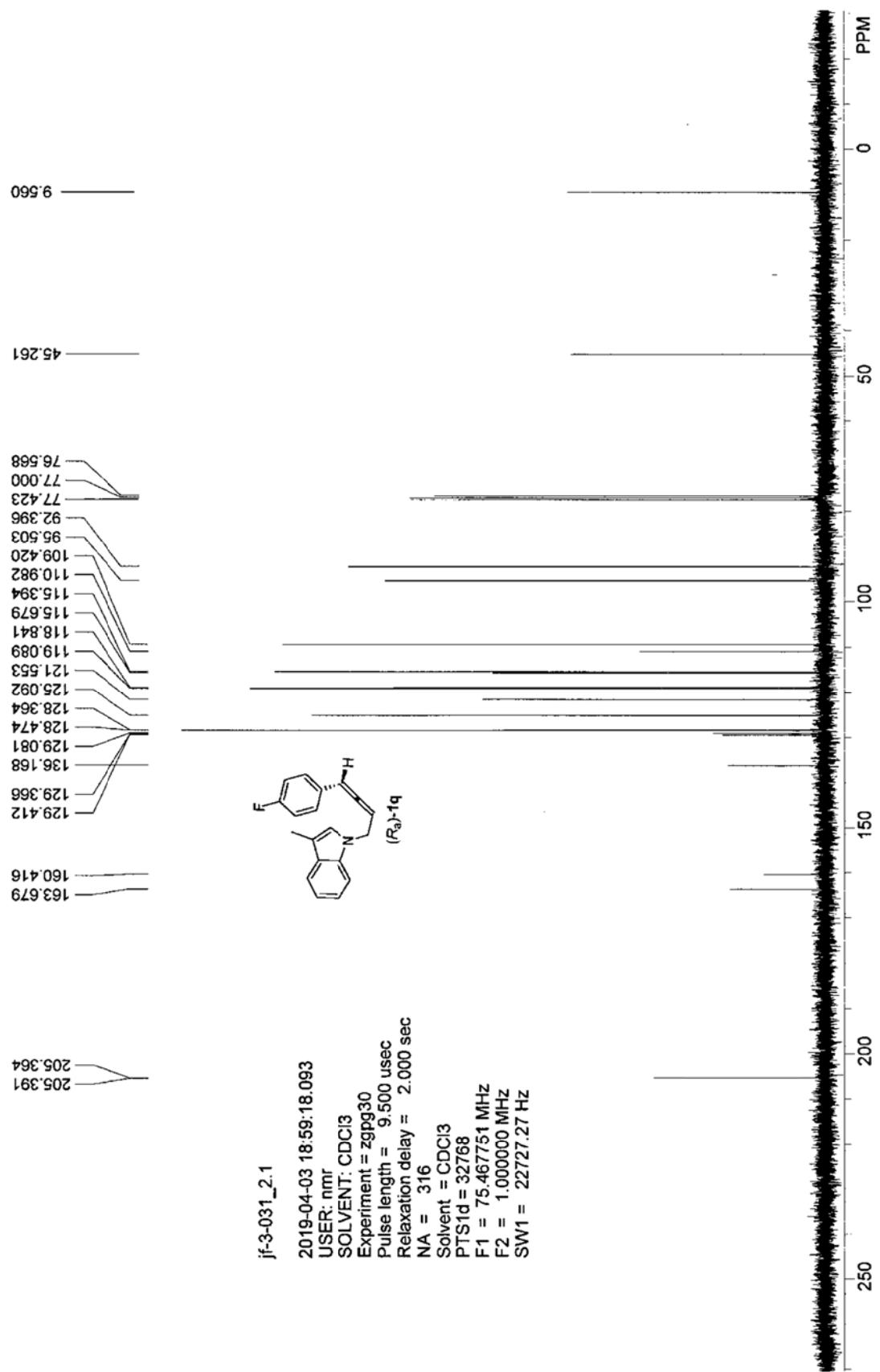
F1 = 300.130005 MHz

F2 = 1.000000 MHz

SW1 = 6188.12 Hz

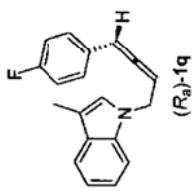


10



0.000

-115.204



Jf-3-031_4.1

2019-04-15 09:16:27.296

USER: nmr

SOLVENT: CDCl₃

Experiment = zgffigian

Pulse length = 13.500 usec

Relaxation delay = 1.000 sec

NA = 16

Solvent = CDCl₃

PTS1d = 65536

F1 = 282.404358 MHz

F2 = 1.000000 MHz

SW1 = 66984.29 Hz

PPM

-200

-150

-100

-50

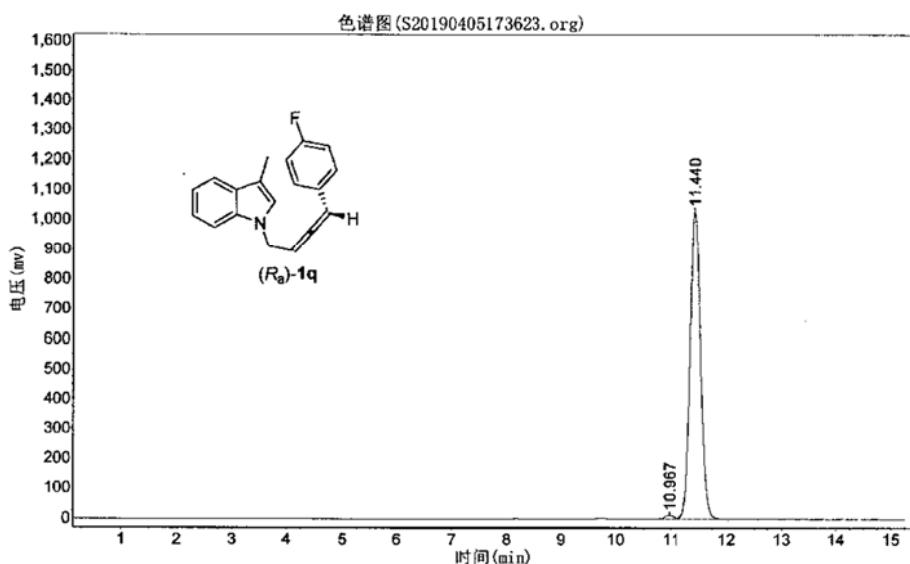
0

jf-3-031

实验时间: 2019-04-05, 17:36:23
谱图文件:D:\浙大智达\N2000\样品\S20190405173623.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-04-05, 17:53:40
积分方法: 面积归一法

实验内容简介:
ia, n-hexane/i-PrOH = 100/1, 0.5, 254

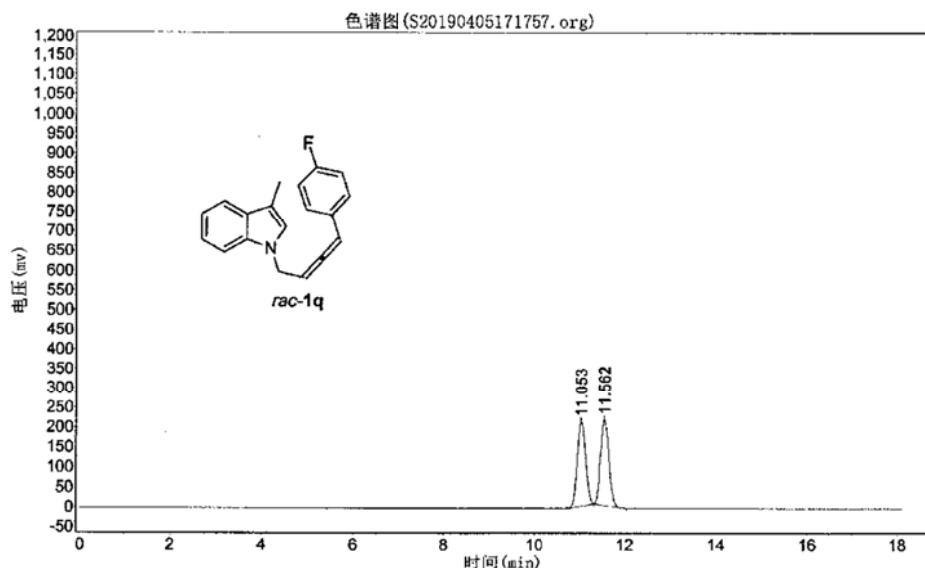


jf-3-033

实验时间: 2019-04-05, 17:17:57
谱图文件:D:\浙大智达\N2000\样品\S20190405171757.org
方法文件:D:\浙大智达\N2000\djx.mtd

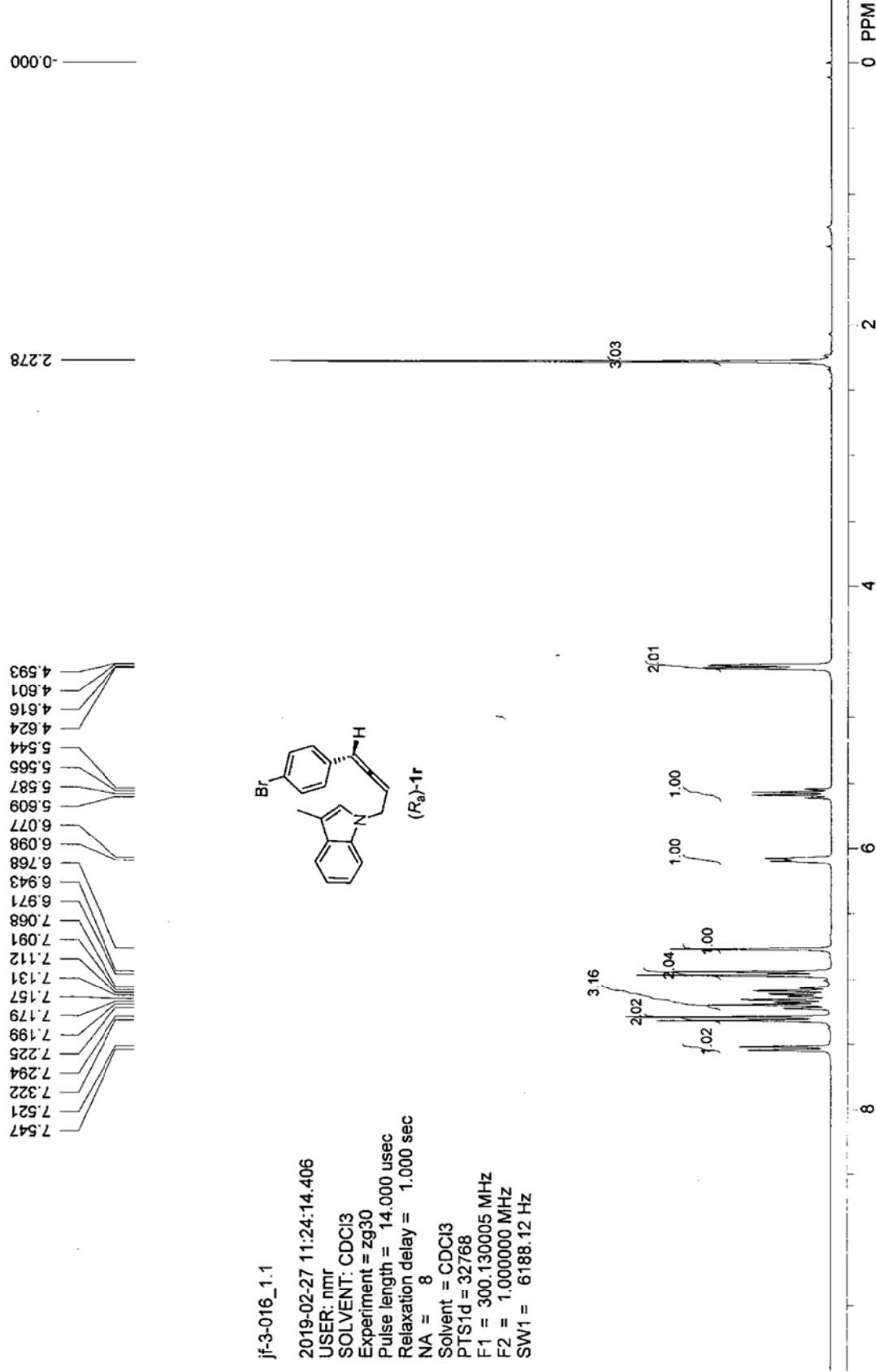
实验者: jf
报告时间: 2019-04-05, 17:39:39
积分方法: 面积归一法

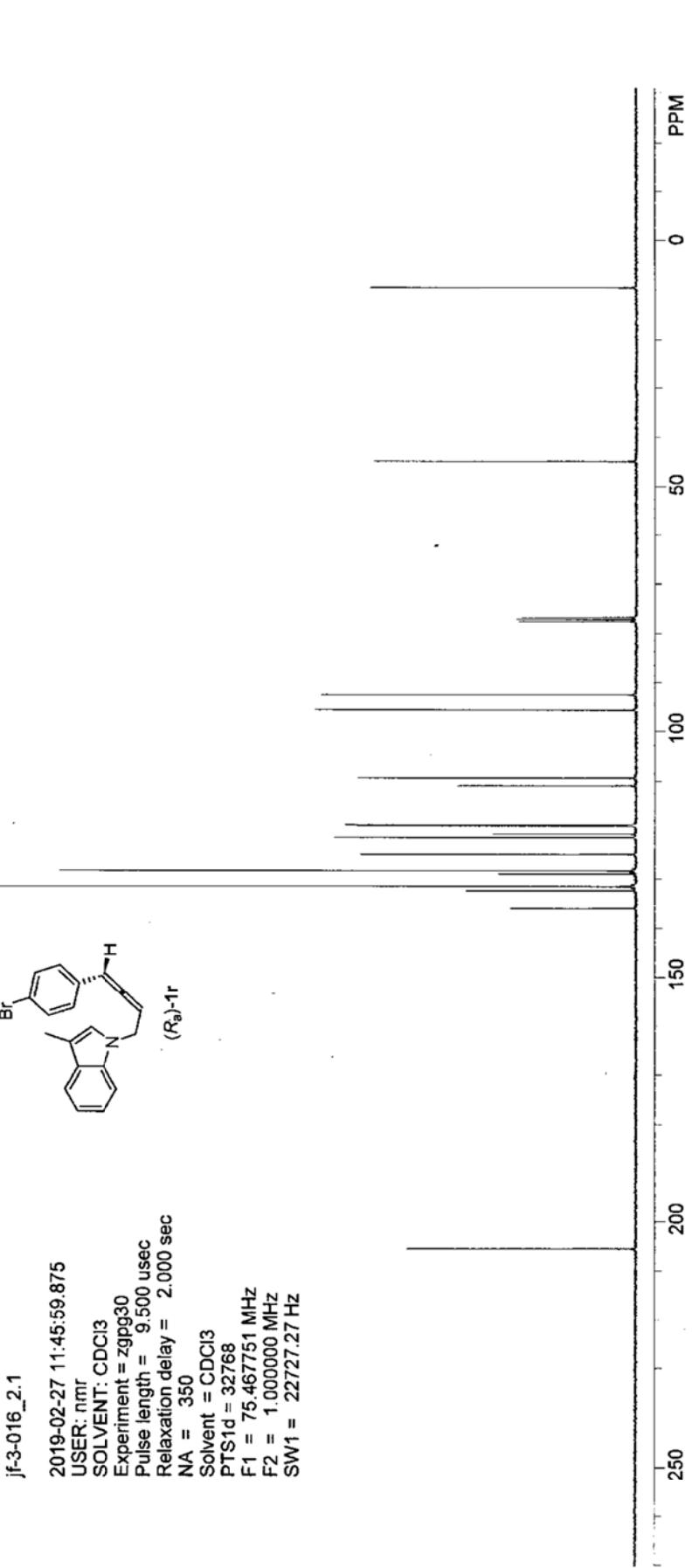
实验内容简介:
ia, n-hexane/i-PrOH = 100/1, 0.5, 254



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		11.053	212771.875	2700423.000	49.5927
2		11.562	215981.672	2744780.500	50.4073
总计			428753.547	5445203.500	100.0000



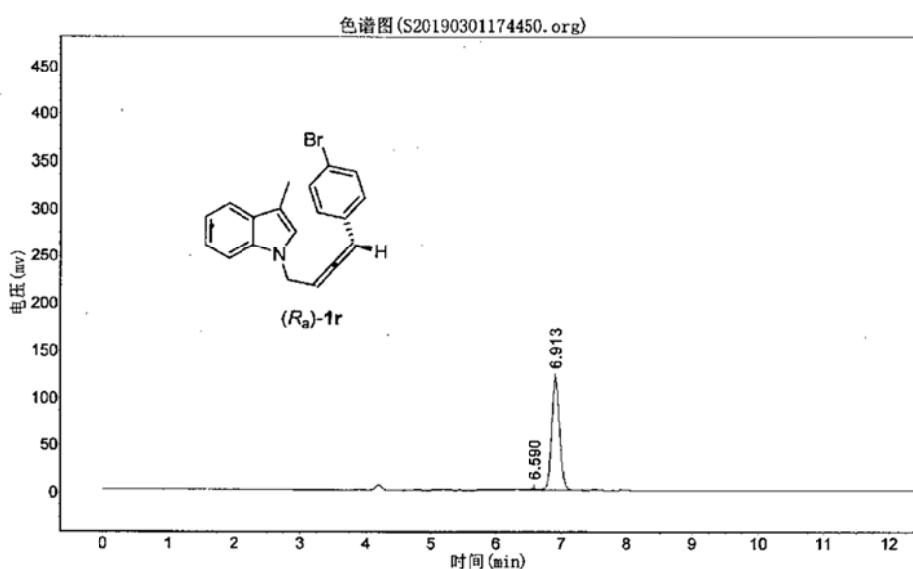


jf-3-016

实验时间: 2019-03-01, 17:44:50
谱图文件:D:\浙大智达\N2000\样品\S20190301174450.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-03-01, 18:03:59
积分方法: 面积归一法

实验内容简介:
ia, n-hexane/i-PrOH = 95/5, 0.7, 214



分析结果表

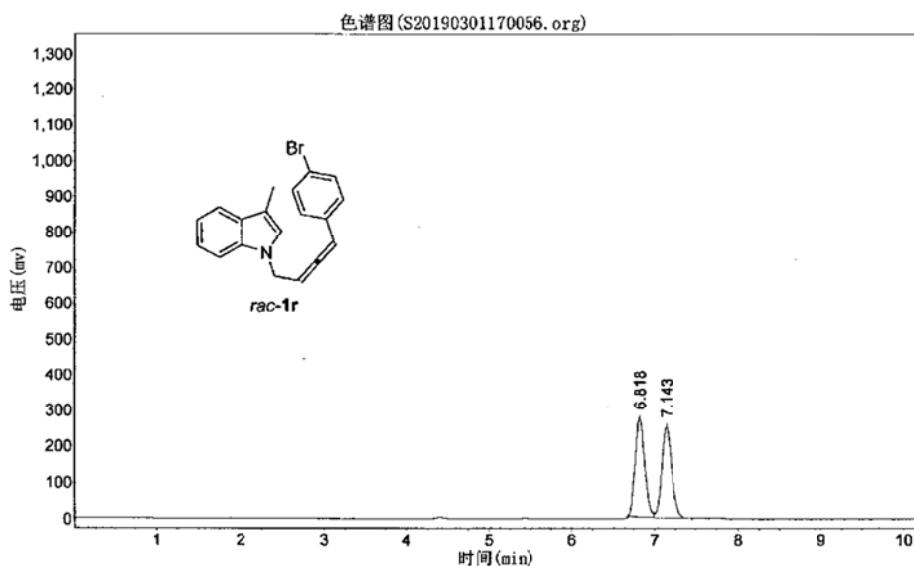
峰号	峰名	保留时间	峰高	峰面积	含量
1		6.590	1009.766	8176.603	0.8267
2		6.913	118586.102	980940.563	99.1733
总计			119595.867	989117.165	100.0000

jf-3-017

实验时间: 2019-03-01, 17:00:56
谱图文件:D:\浙大智达\N2000\样品\S20190301170056.org
方法文件:D:\浙大智达\N2000\djx.mtd

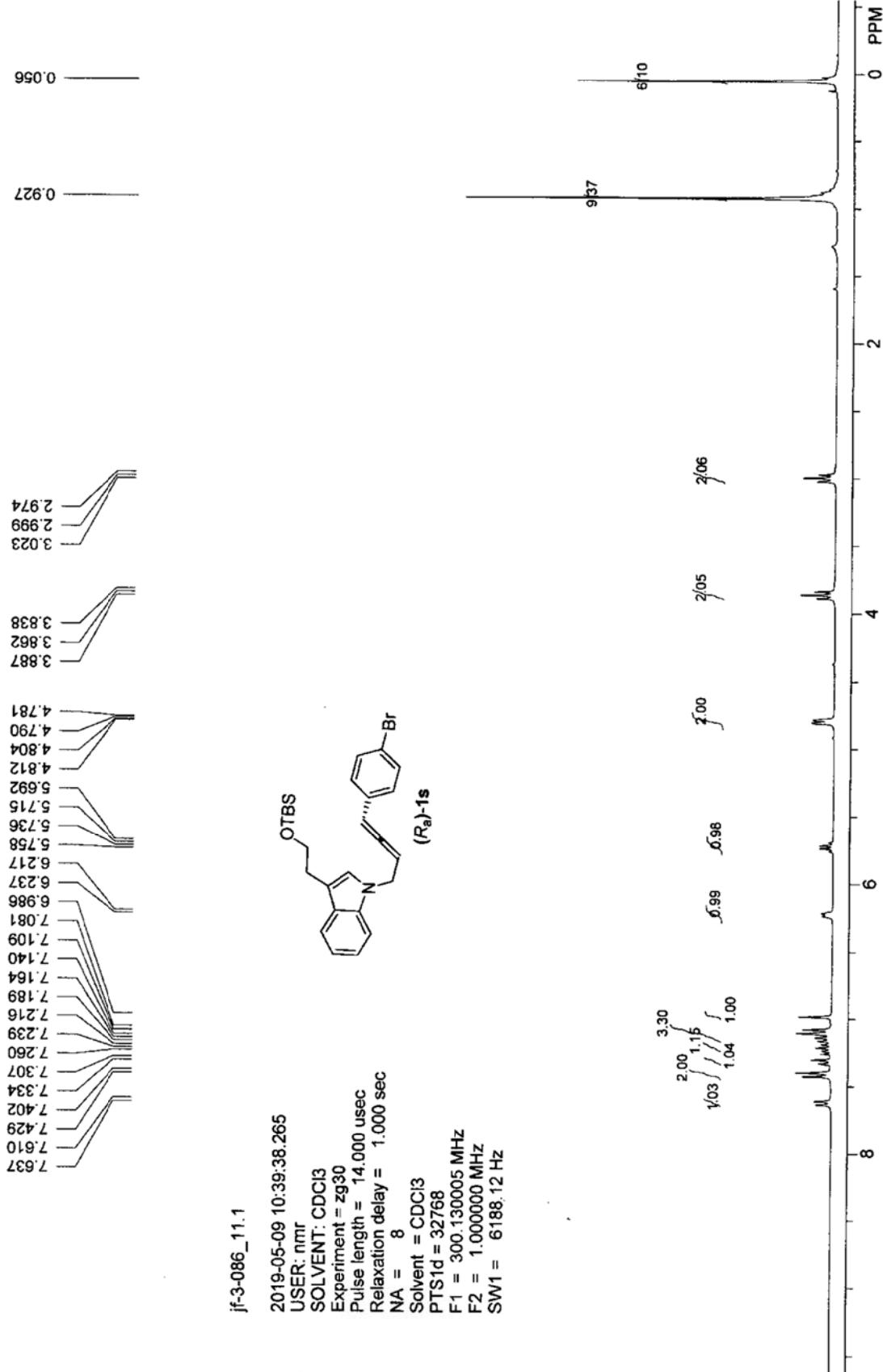
实验者: jf
报告时间: 2019-03-01, 17:38:23
积分方法: 面积归一法

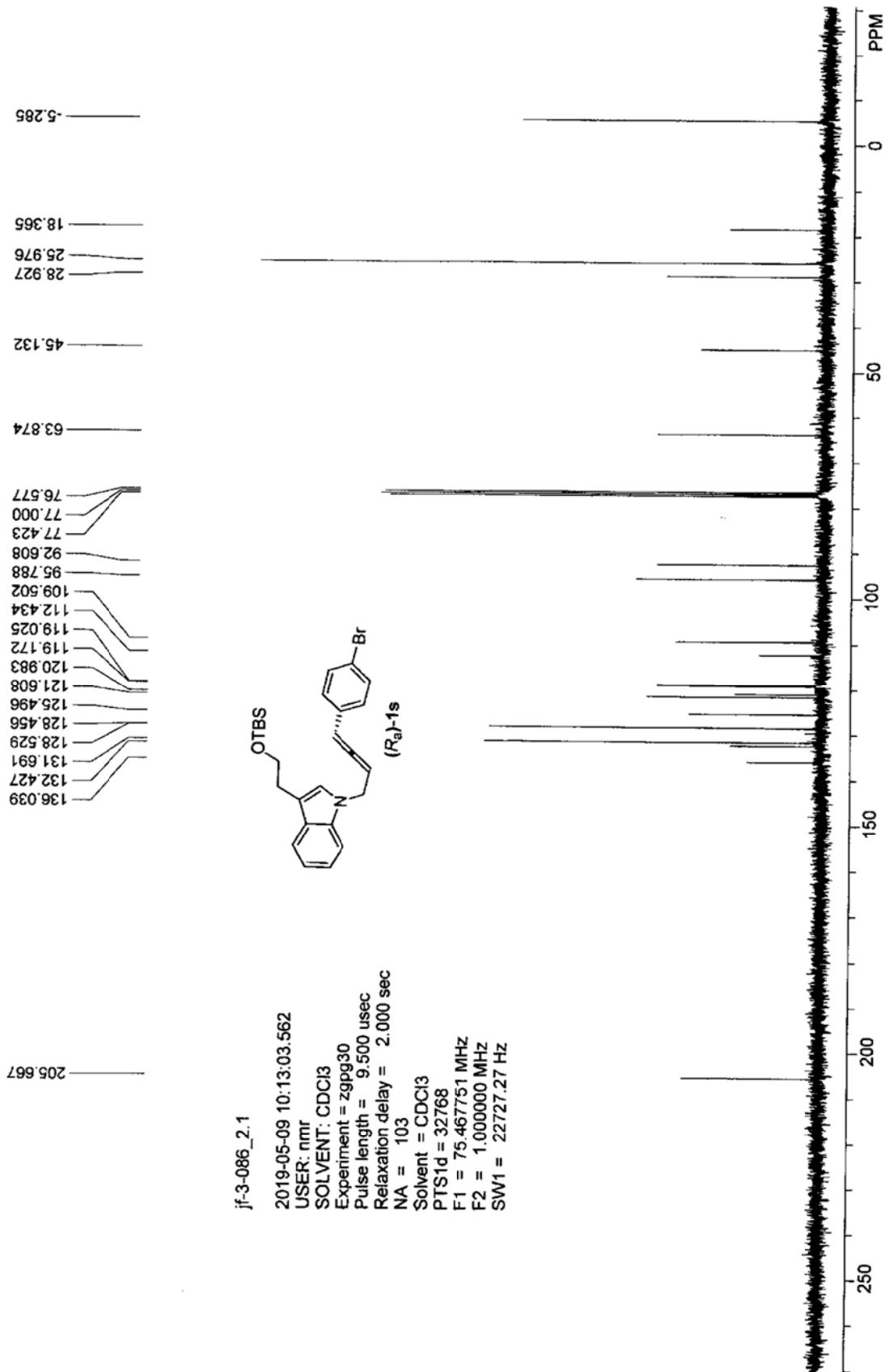
实验内容简介:
ia, n-hexane/i-PrOH = 95/5, 0.7, 214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		6.818	270851.531	2150464.500	50.7985
2		7.143	250713.391	2082854.750	49.2015
总计			521564.922	4233319.250	100.0000



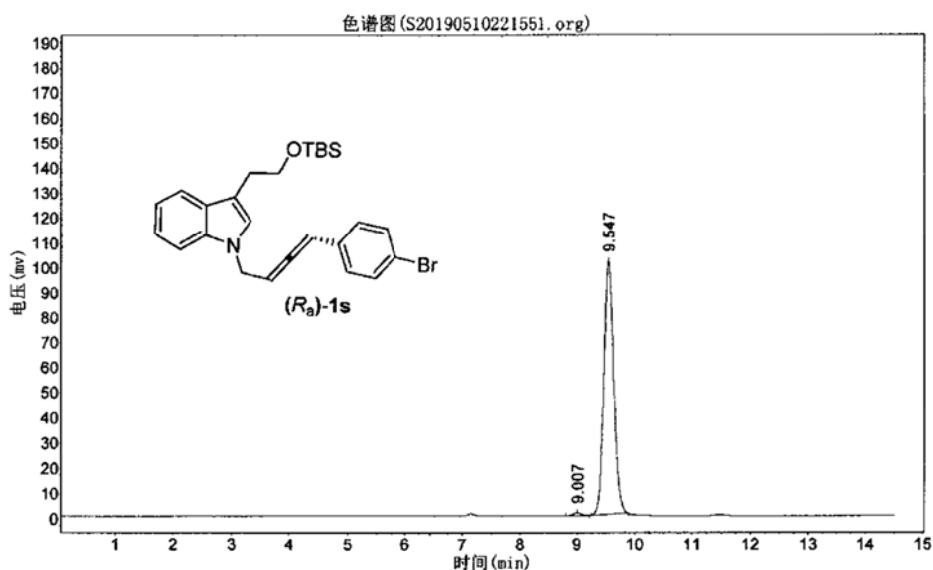


jf-3-086

实验时间: 2019-05-10, 22:15:51
谱图文件:D:\浙大智达\N2000\样品\S20190510221551.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-05-10, 22:33:51
积分方法: 面积归一法

实验内容简介:
1a, n-hexane/i-PrOH = 200/1, 0.7, 254



分析结果表

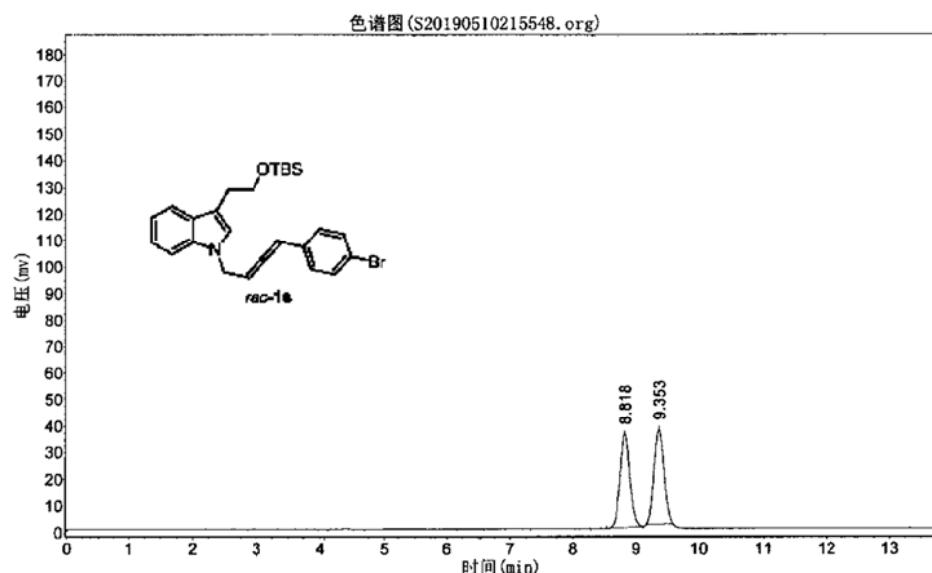
峰号	峰名	保留时间	峰高	峰面积	含量
1		9.007	864.045	8699.901	0.7097
2		9.547	100842.844	1217236.375	99.2903
总计			101706.889	1225936.276	100.0000

jf-3-085

实验时间: 2019-05-10, 21:55:48
谱图文件:D:\浙大智达\N2000\样品\S20190510215548.org
方法文件:D:\浙大智达\N2000\djx.mtd

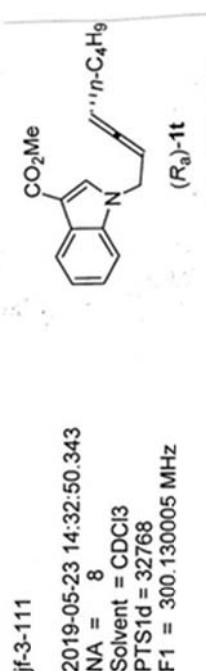
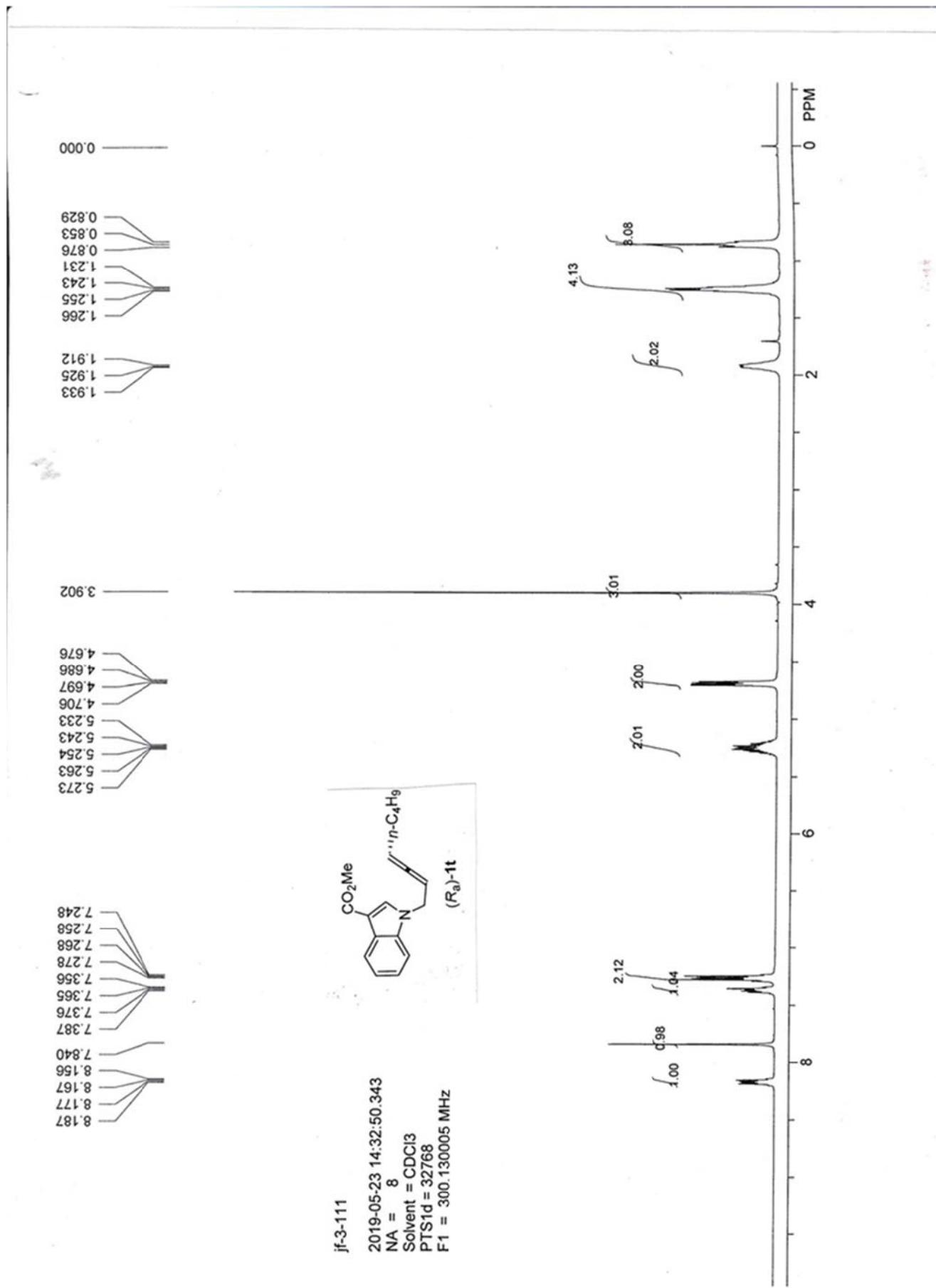
实验者: jf
报告时间: 2019-05-10, 22:12:48
积分方法: 面积归一法

实验内容简介:
ia, n-hexane/i-PrOH = 200/1, 0.7, 254

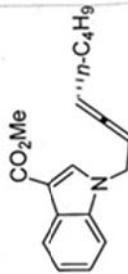


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.818	34930.078	382395.313	49.6410
2		9.353	35449.820	387926.844	50.3590
总计			70379.898	770322.156	100.0000

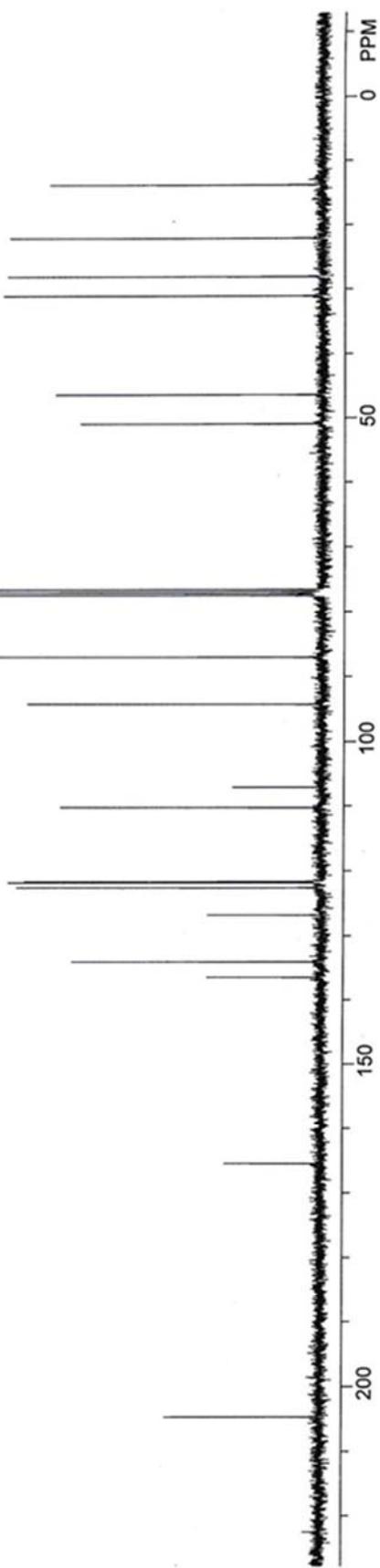


13.760
22.033
28.054
31.023
46.373
50.868
76.577
77.000
77.423
87.019
94.235
107.076
110.238
121.654
121.819
122.601
126.783
134.072
136.471
165.444
204.684



jf-3-111

2019-05-23 14:46:02.593
NA = 202
Solvent = CDCl₃
PTS1d = 32768
F1 = 75.467751 MHz

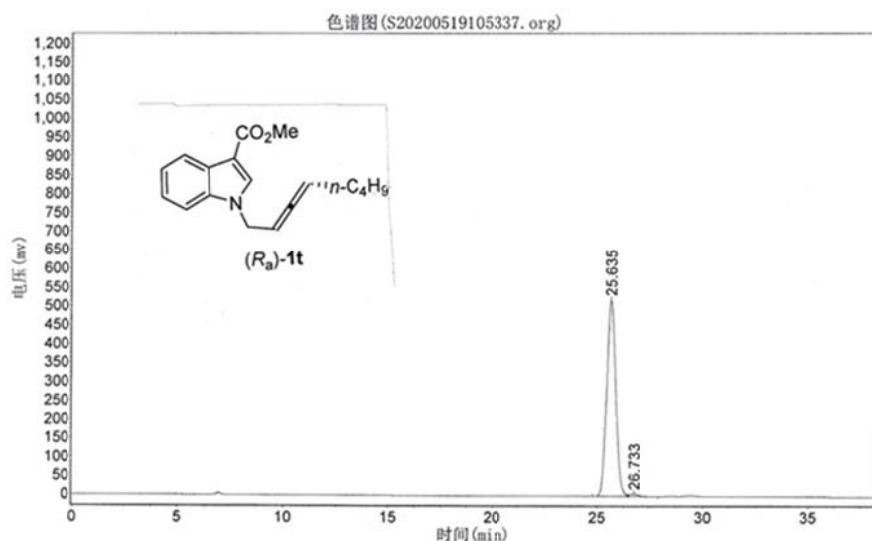


jf-3-111

实验时间: 2020-05-19, 10:53:37
谱图文件:D:\浙大智达\N2000\样品\S20200519105337.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-05-19, 12:33:40
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 90/10, 0.5, 214

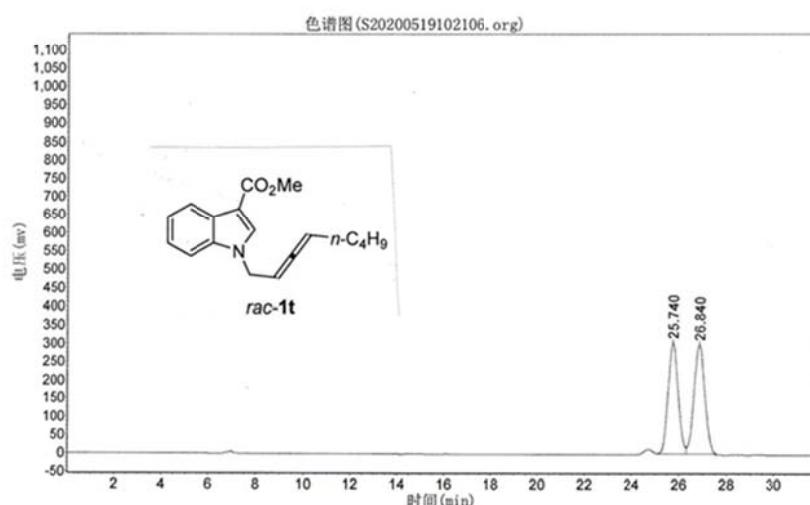


jf-3-112

实验时间: 2020-05-19, 10:21:06
谱图文件:D:\浙大智达\N2000\样品\S20200519102106.org
方法文件:D:\浙大智达\N2000\djx.mtd

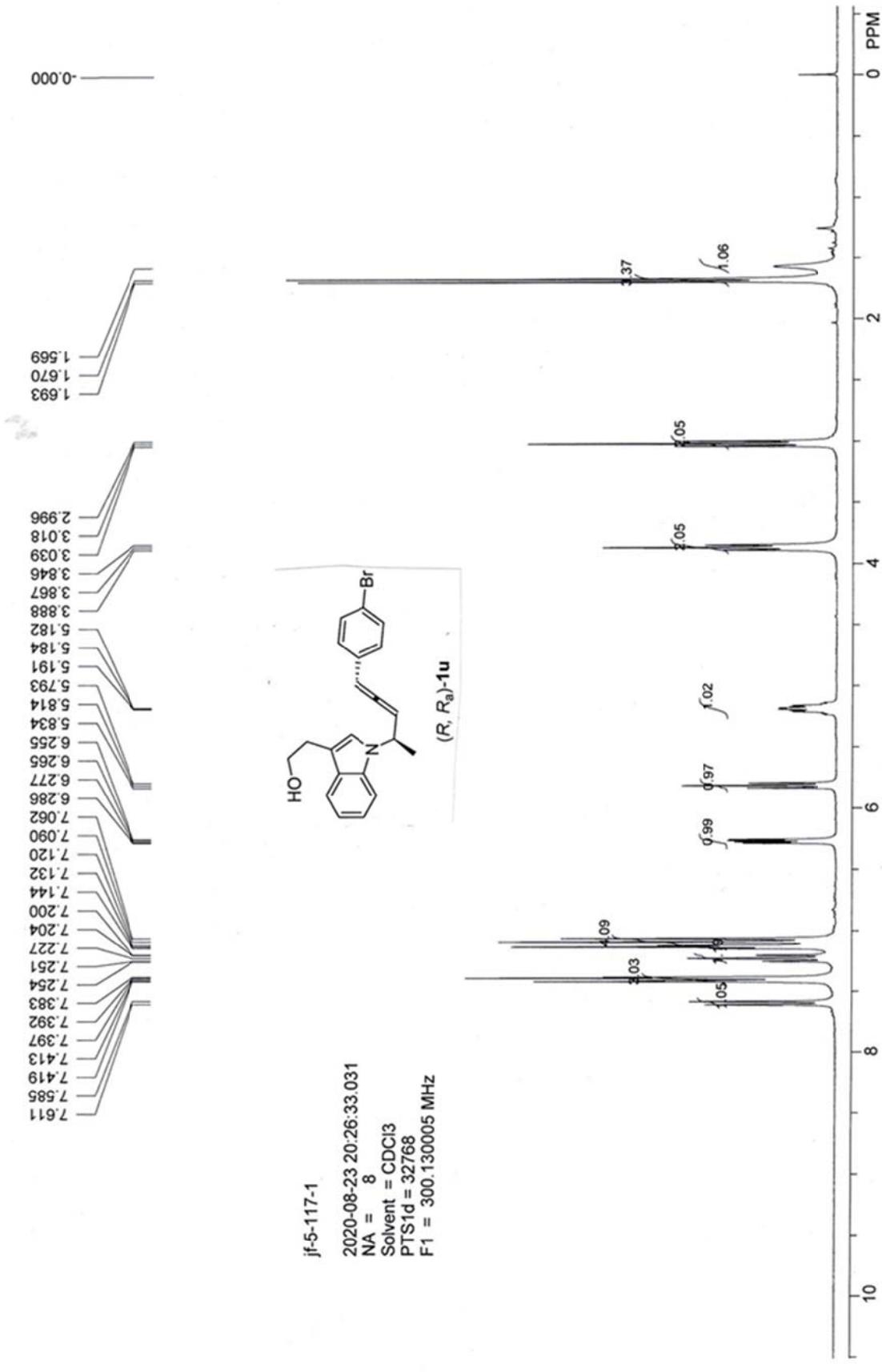
实验者: jf
报告时间: 2020-05-19, 12:40:43
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 90/10, 0.5, 214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		25.740	302774.969	8816655.000	48.5545
2		26.840	298169.438	9373410.000	51.4455
总计			600944.406	18220065.000	100.0000

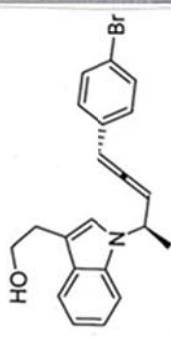


jf-5-117-1

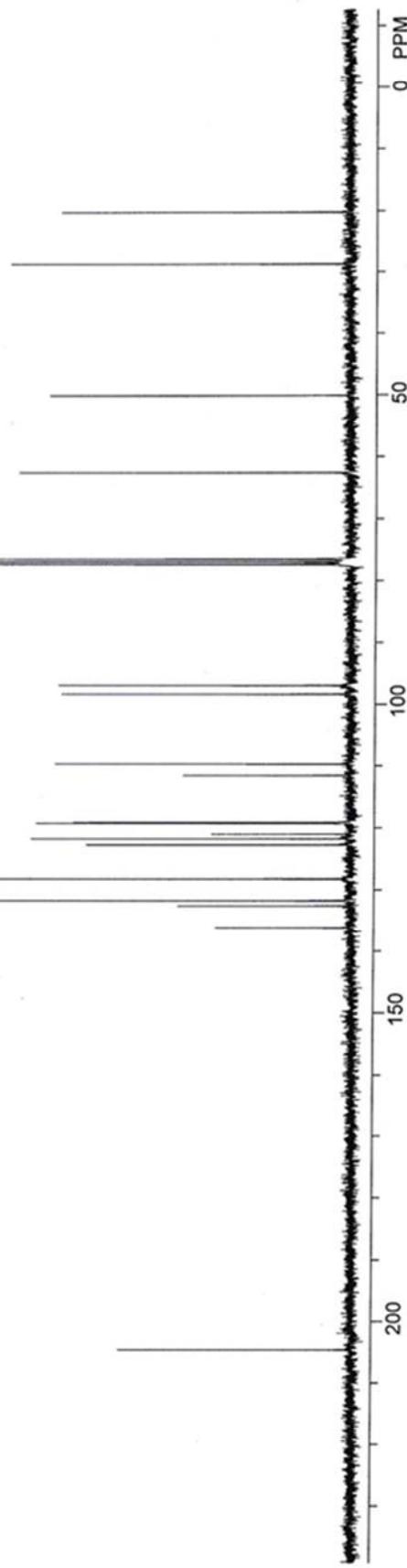
2020-08-23 20:26:33.031
NA = 8
Solvent = CDCl₃
PTS1d = 32768
F1 = 300.130005 MHz

204.610
132.610
131.783
128.254
122.729
121.773
121.020
119.144
119.282
111.607
109.760
98.371
96.974
77.423
77.000
76.577
62.615
50.132
28.789
20.259

jf-5-117-1
2020-08-23 20:50:21.265
NA = 389
Solvent = CDCl₃
PTSD = 32768
F1 = 75.467751 MHz



(R, R)-1u

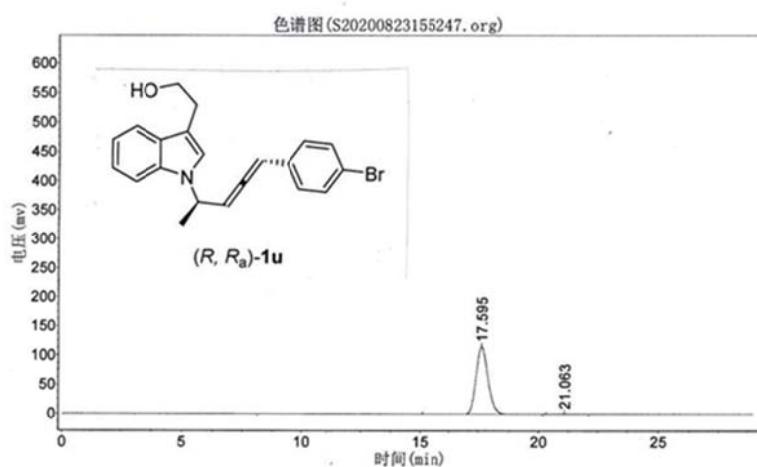


jf-5-117-1

实验时间: 2020-08-23, 15:52:47
谱图文件:D:\浙大智达\N2000\样品\S20200823155247.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-08-23, 18:28:43
积分方法: 面积归一法

实验内容简介:
OD-H, n-hexane/i-PrOH = 90/10, 1.0, 254



分析结果表

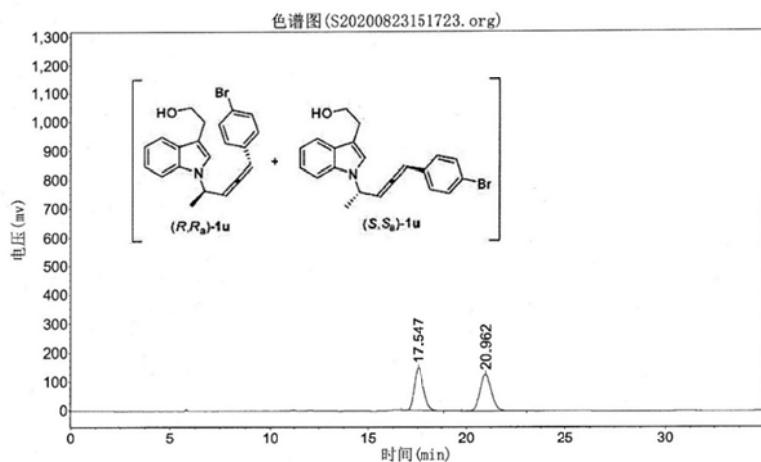
峰号	峰名	保留时间	峰高	峰面积	含量
1		17.595	114882.648	4000157.500	99.1567
2		21.063	872.019	34020.348	0.8433
总计			115754.668	4034177.848	100.0000

jf-5-116-1

实验时间: 2020-08-23, 15:17:23
 谱图文件:D:\浙大智达\N2000\样品\S20200823151723.org
 方法文件:D:\浙大智达\N2000\djx.mtd

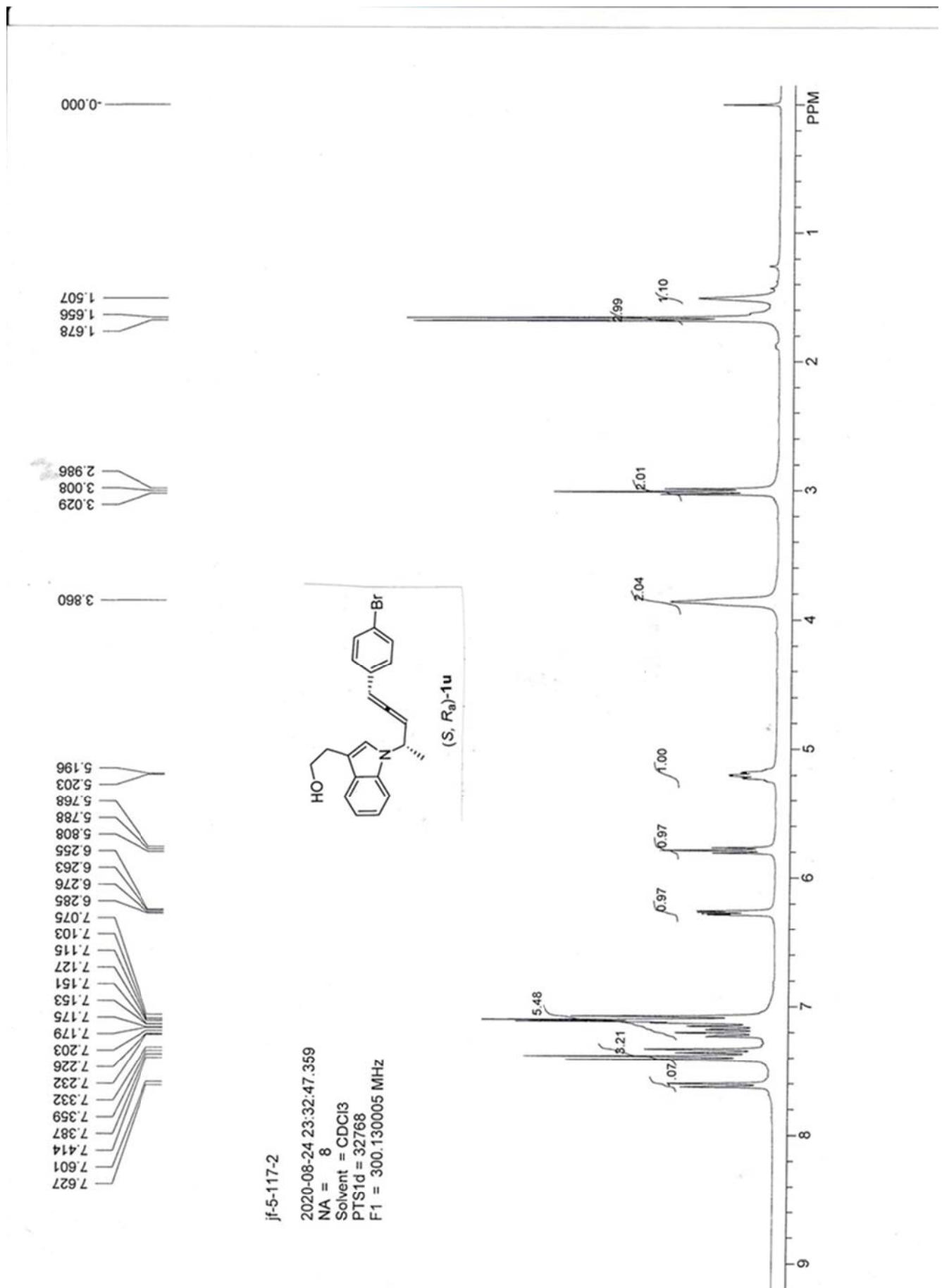
实验者: jf
 报告时间: 2020-08-23, 18:30:20
 积分方法: 面积归一法

实验内容简介:
 $\text{OD-H, n-hexane/i-PrOH} = 90/10, 1.0, 254$

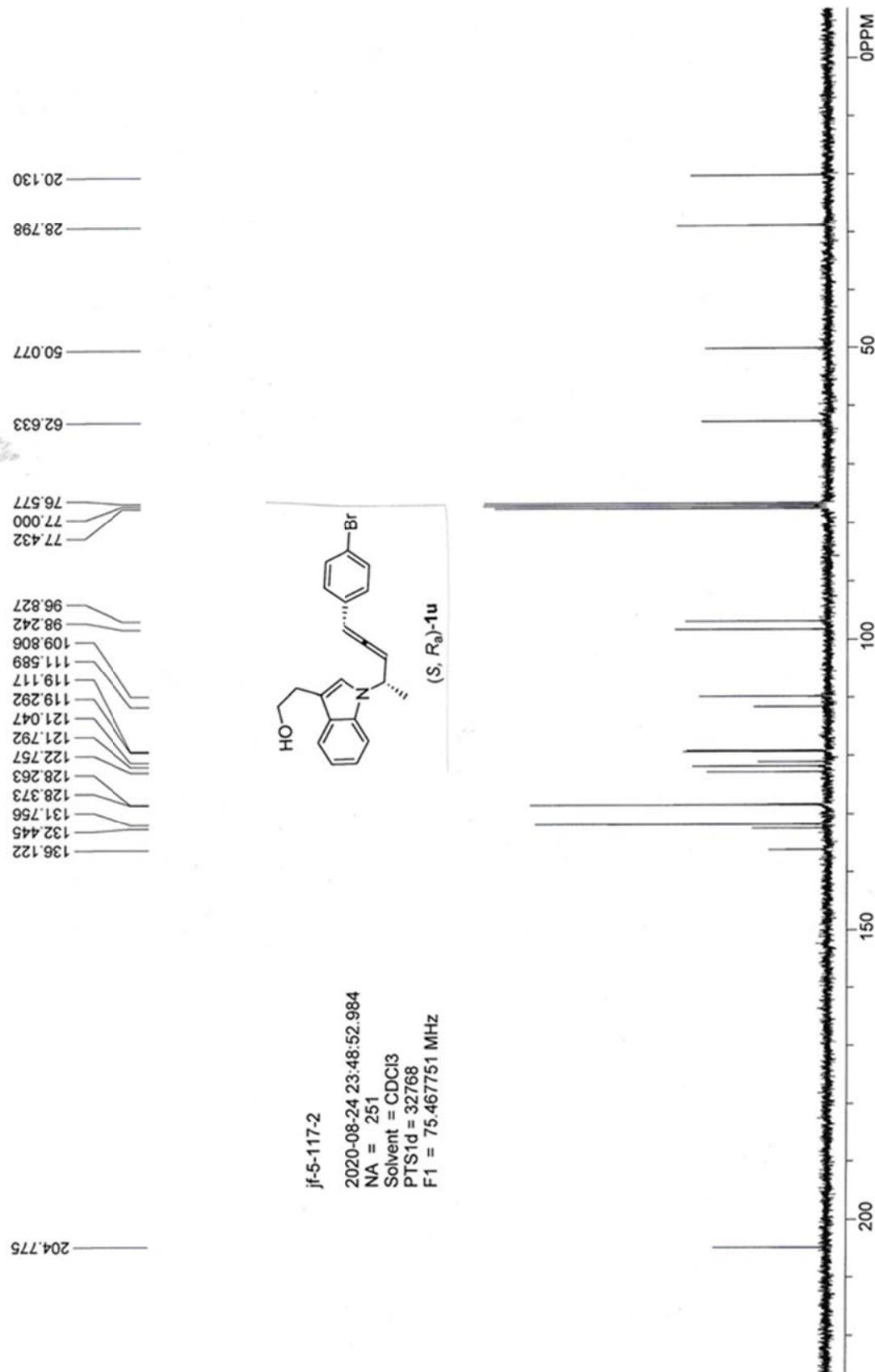


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		17.547	146482.031	4955288.000	49.5083
2		20.962	126074.859	5053708.000	50.4917
总计			272556.891	10008996.000	100.0000



J



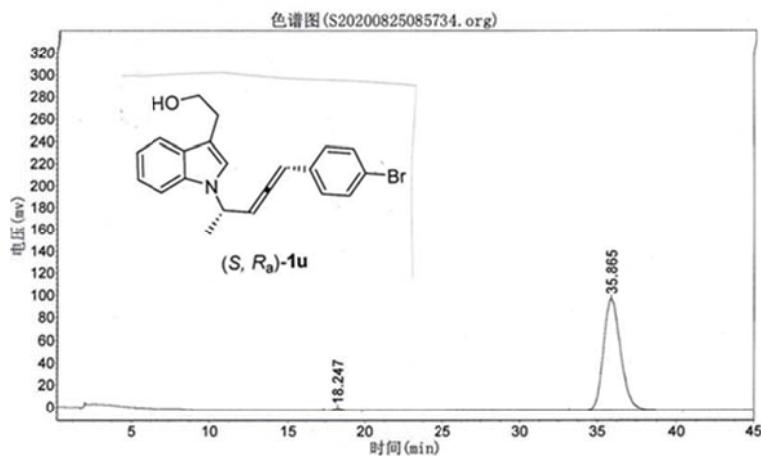
Jf-5-117-2
2020-08-24 23:48:52.984
NA = 251
Solvent = CDCl₃
PTS1d = 32/68
F1 = 75.467751 MHz

jf-5-117-2

实验时间：2020-08-25, 8:57:34
谱图文件:D:\浙大智达\N2000\样品\S20200825085734.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者：jf
报告时间：2020-08-25, 9:44:43
积分方法：面积归一法

实验内容简介：
od-H, n-hexane/i-PrOH = 90/10, 1.0, 254

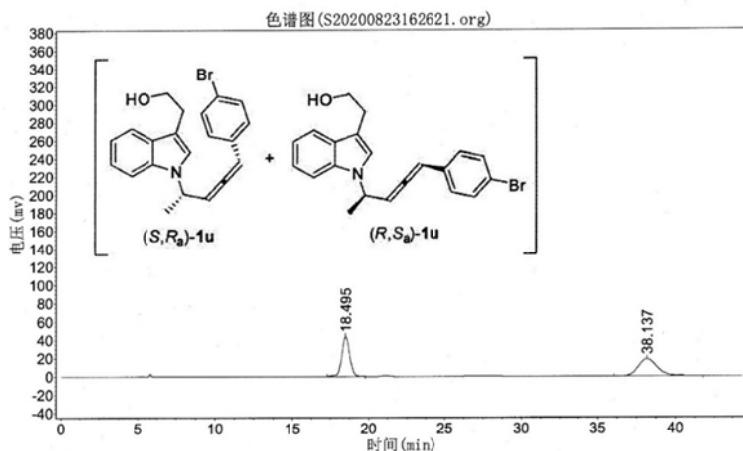


jf-5-116-2

实验时间: 2020-08-23, 16:26:21
谱图文件:D:\浙大智达\N2000\样品\S20200823162621.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-08-23, 18:23:57
积分方法: 面积归一法

实验内容简介:
OD-H, n-hexane/i-PrOH = 90/10, 1.0, 254

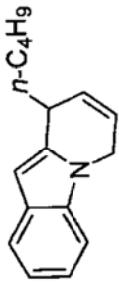


分析结果表

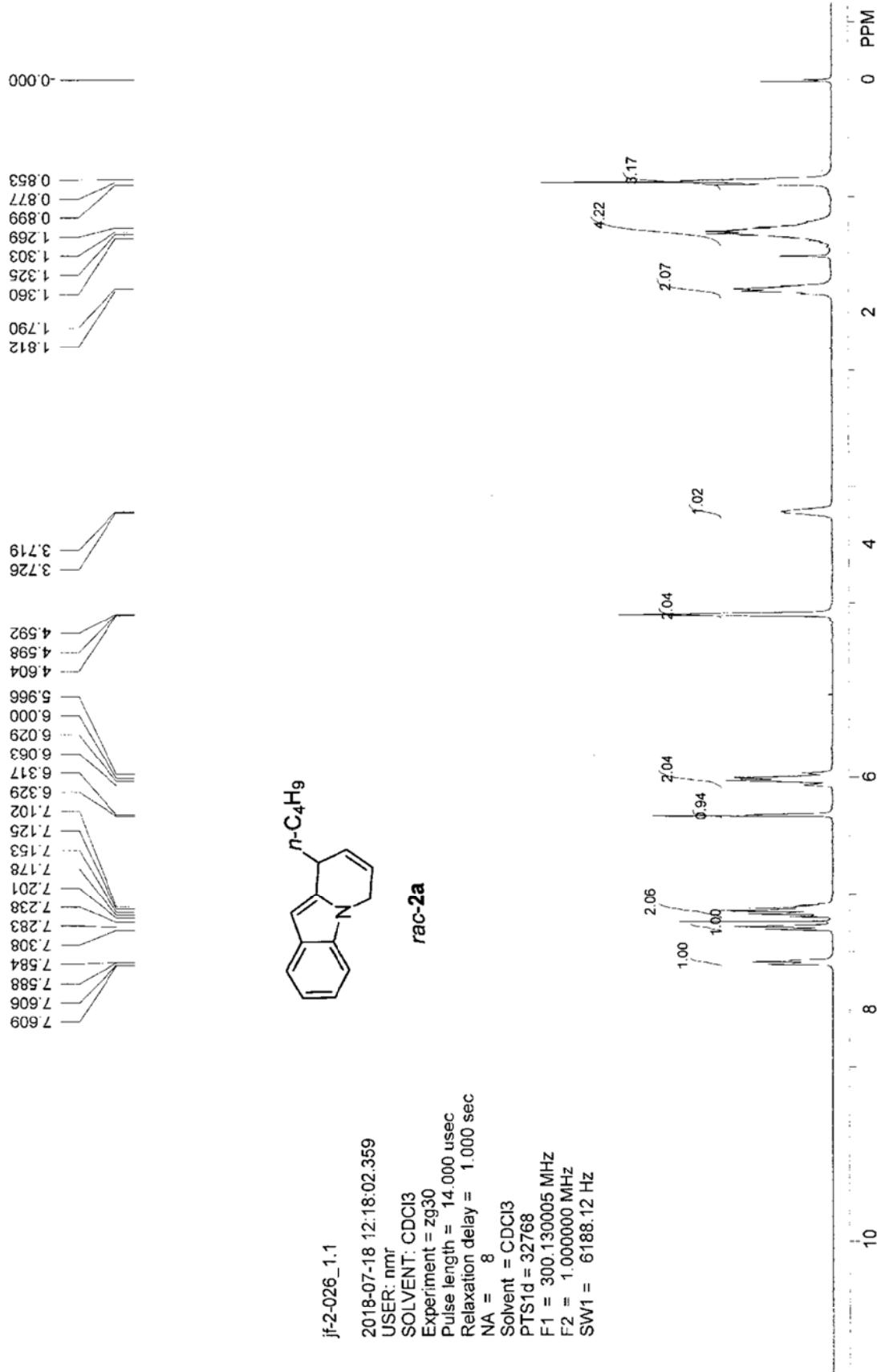
峰号	峰名	保留时间	峰高	峰面积	含量
1		18.495	43026.918	1562052.125	50.1923
2		38.137	18605.803	1550085.500	49.8077
总计			61632.721	3112137.625	100.0000

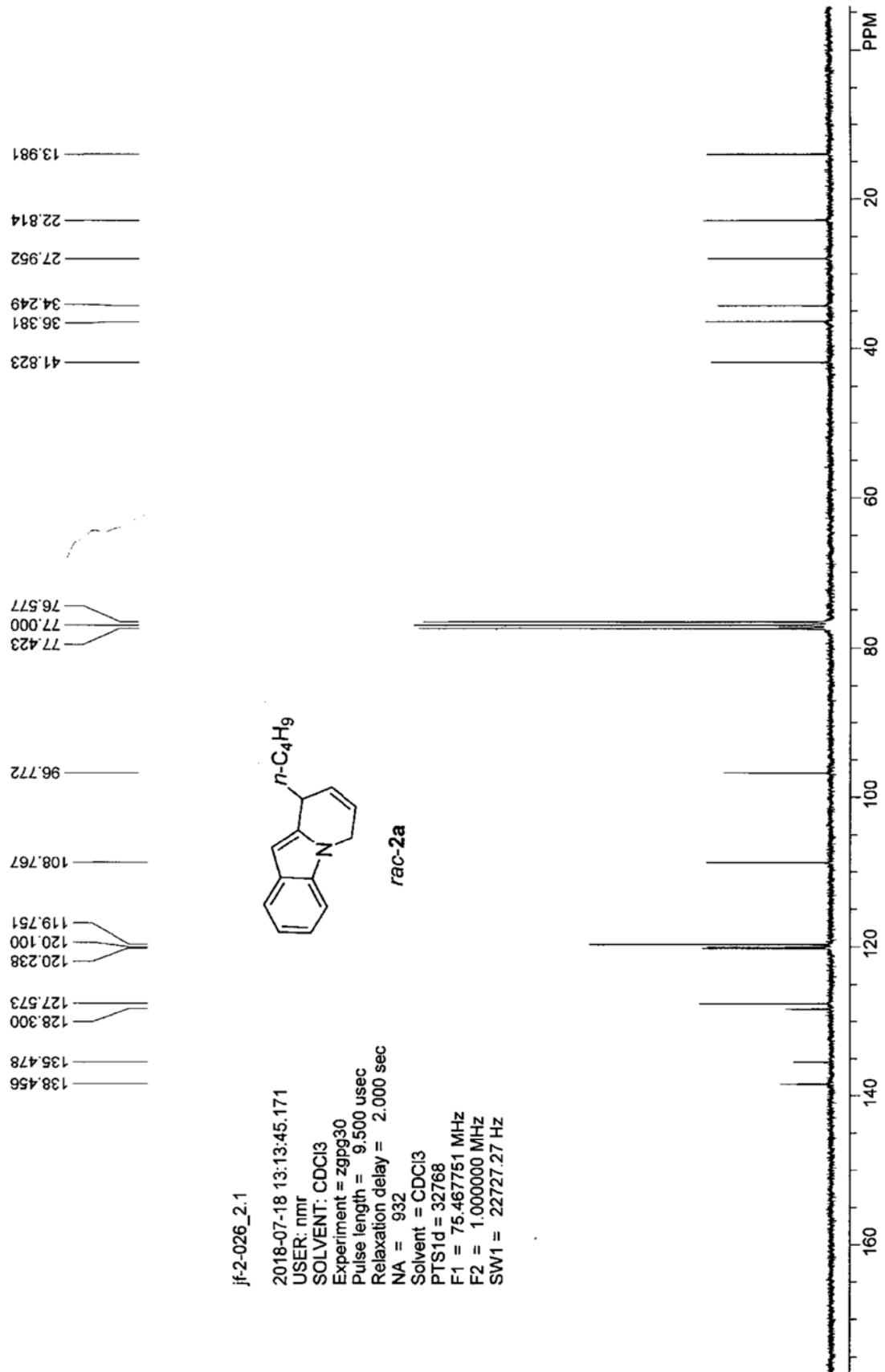
if-2-026_1.1

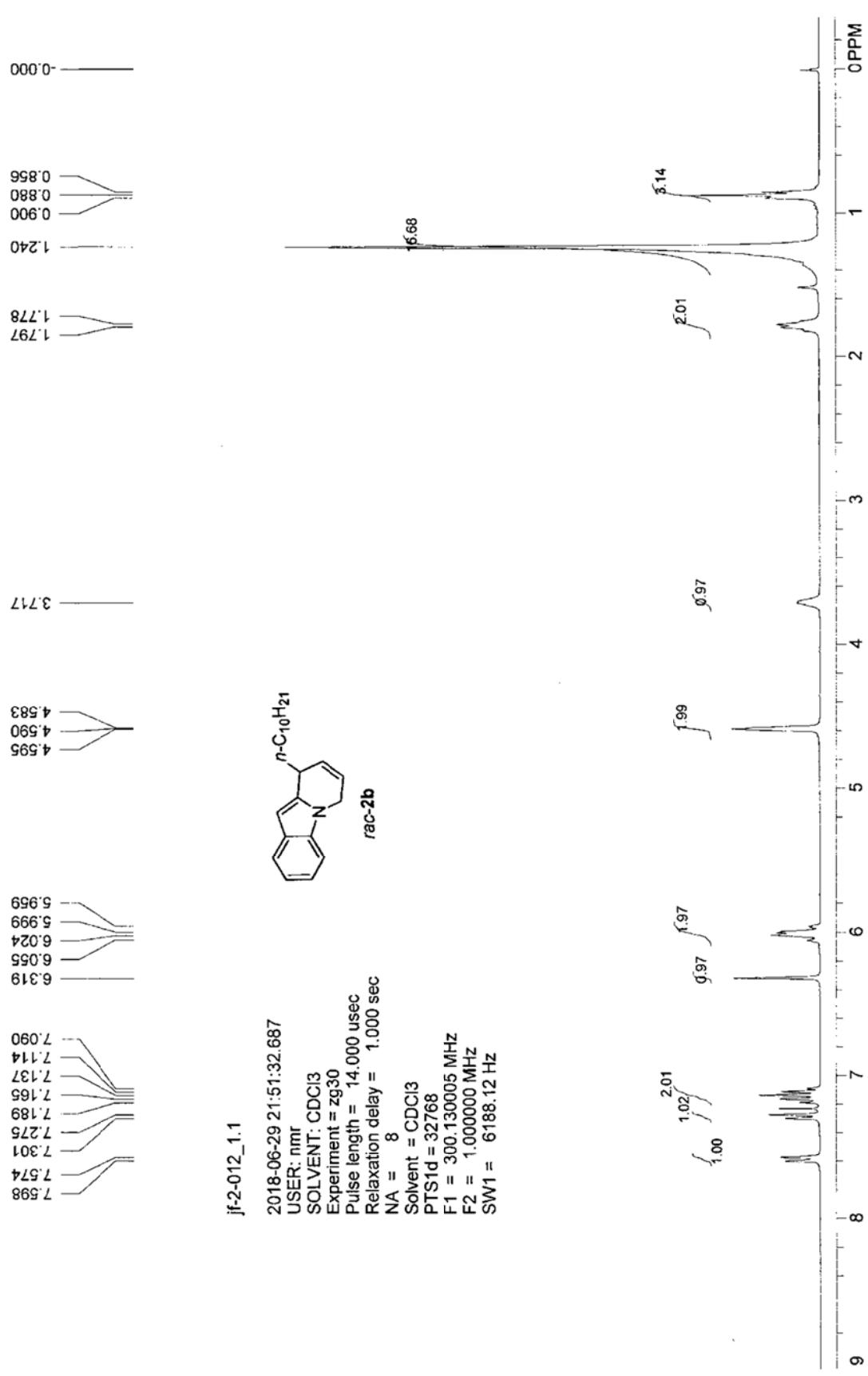
2018-07-18 12:18:02.359
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14.000 us
 Relaxation delay = 1.000
 NA = 8
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

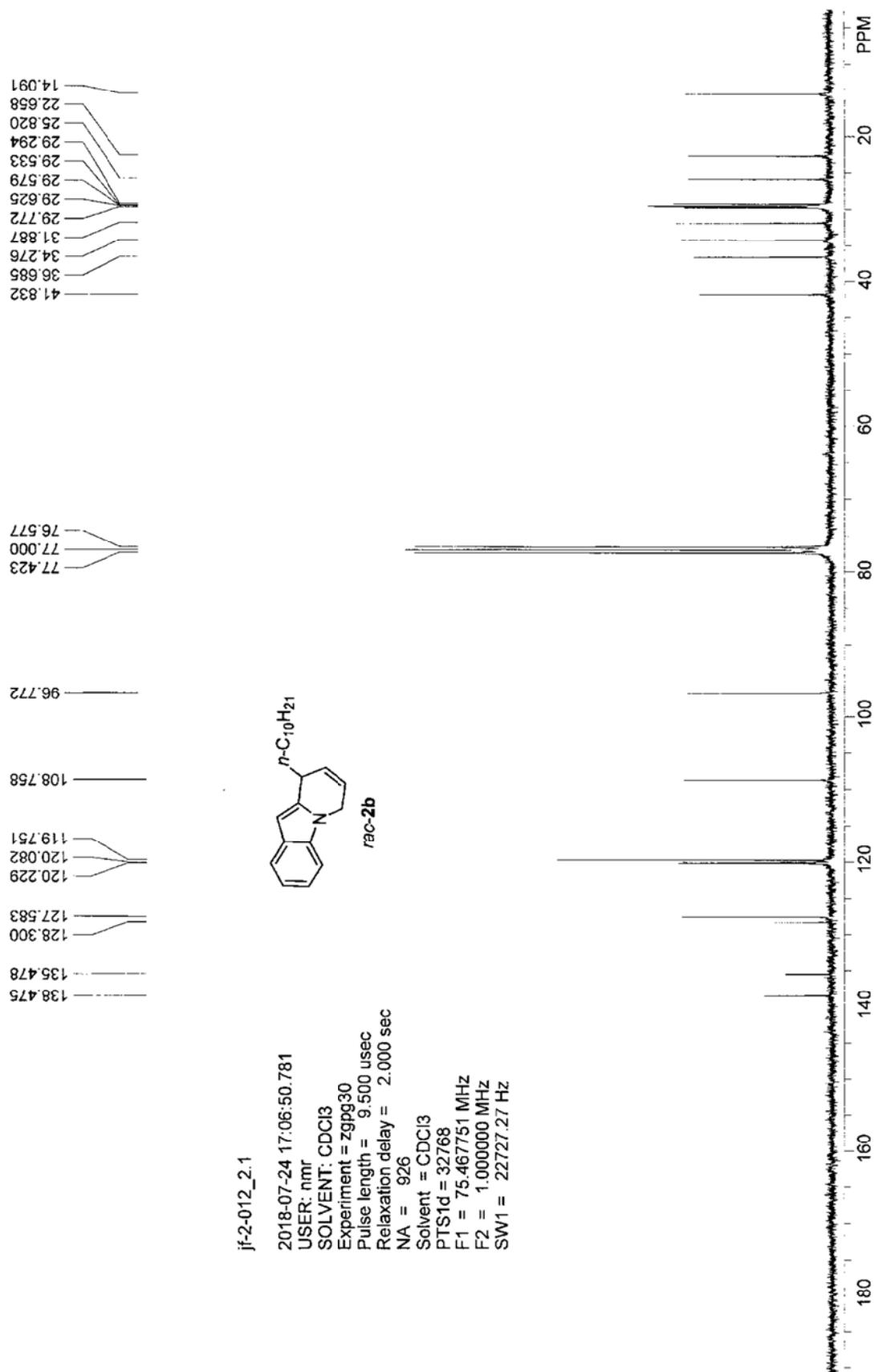


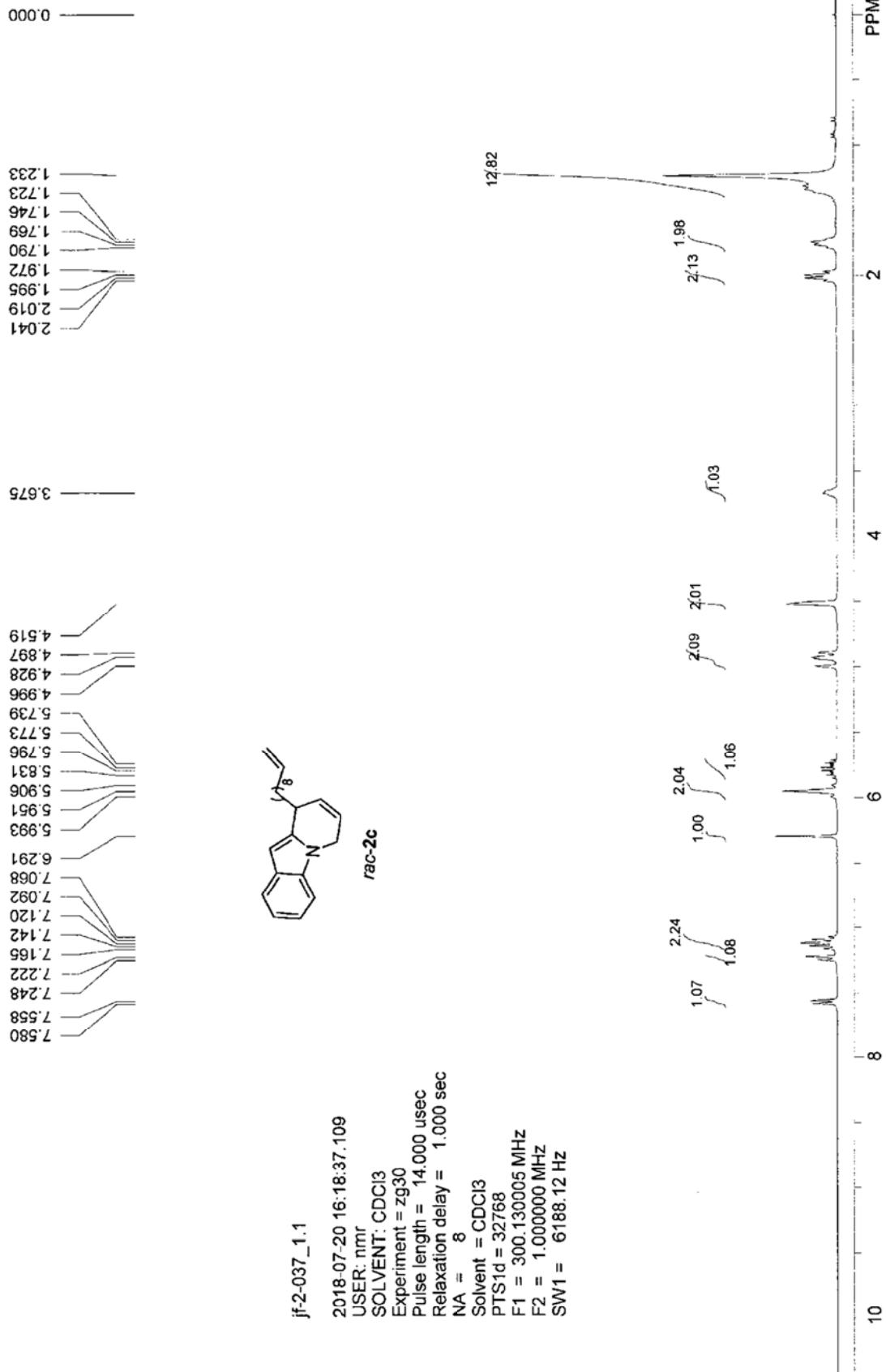
rac-2a

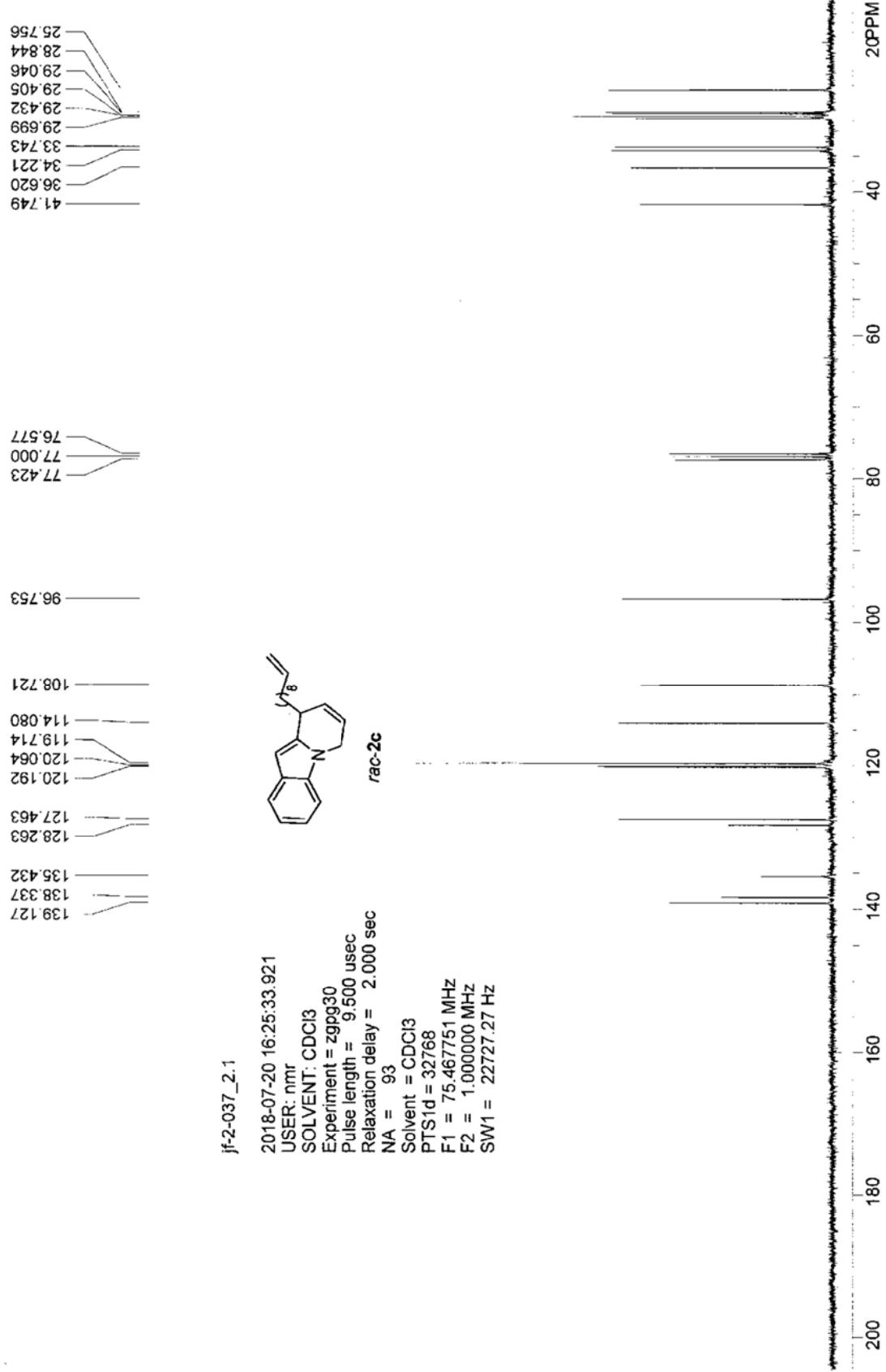






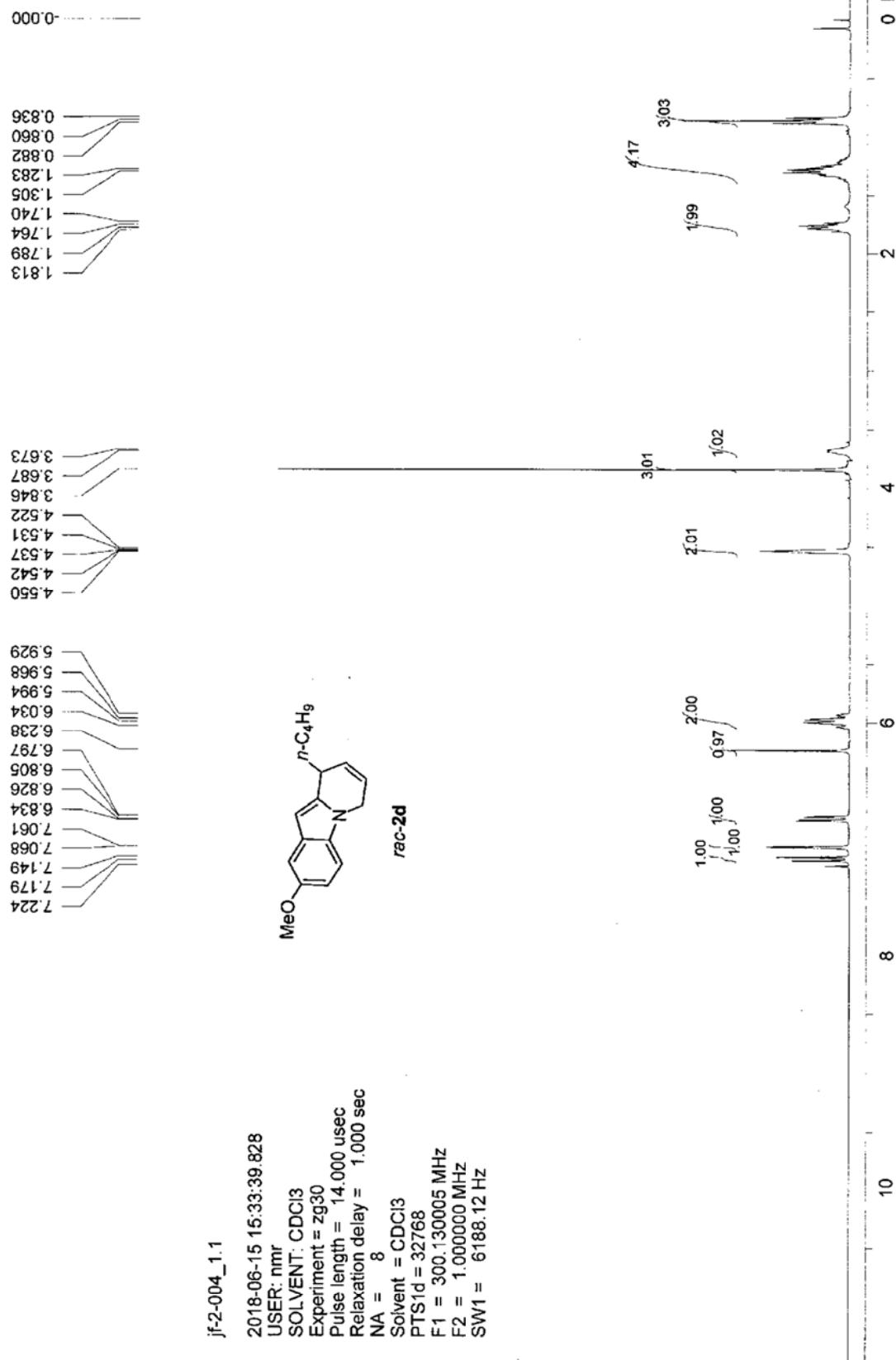
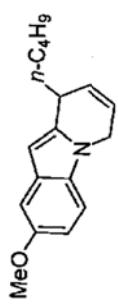






jf2-004_1.i

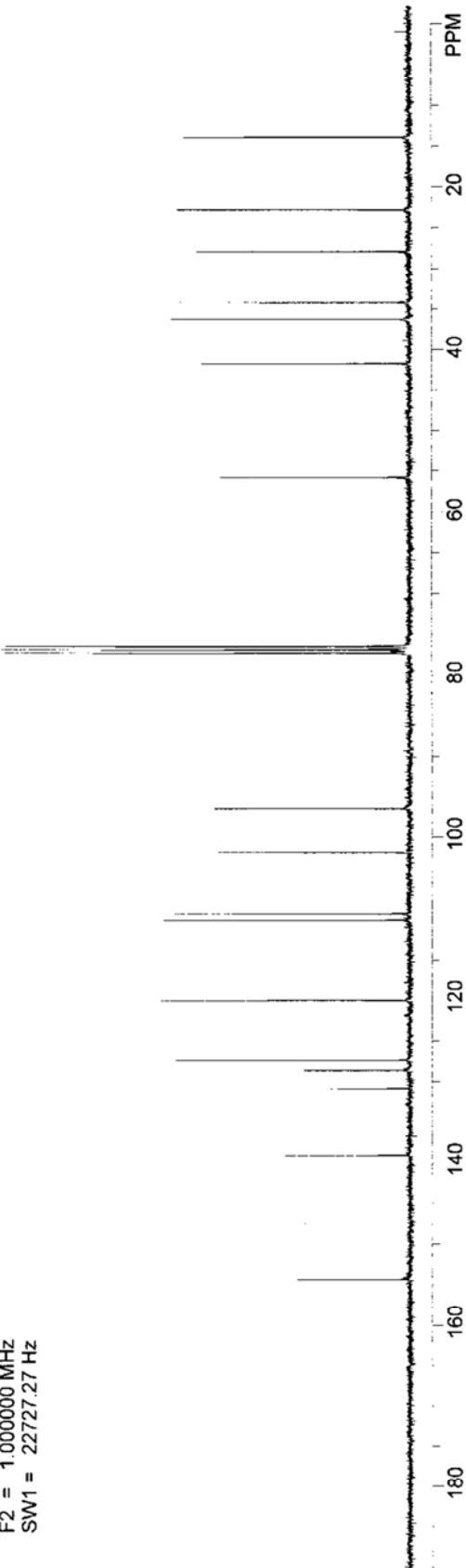
2018-06-15 15:33:39.828
USER: nmr
SOLVENT: CDCl₃
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl₃
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz

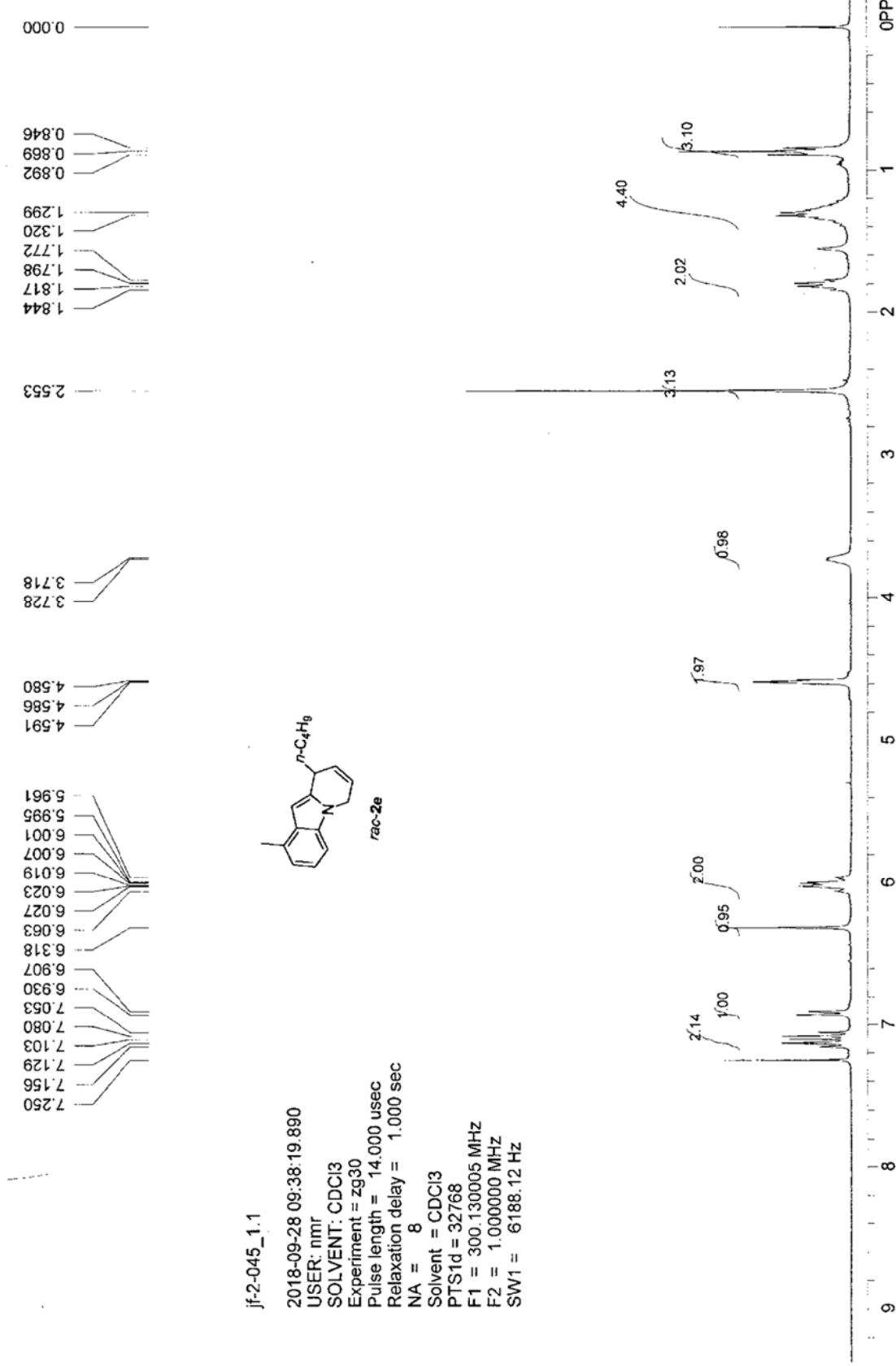


jf-2-004_2.1
 154.349
 139.082
 130.827
 128.603
 127.399
 120.091
 110.146
 109.364
 101.882
 96.441
 77.423
 77.000
 76.577
 55.896
 41.823
 36.308
 34.258
 27.916
 22.805
 13.981

2018-06-15 16:14:50.218
 USER: nmr
 SOLVENT: CDCl₃
 Experiment = zgppg30
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 671
 Solvent = CDCl₃
 PTS1d = 32768
 F1 = 75.467751 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz
 rac-2d

Cn1ccccc1Cc2ccccc2O



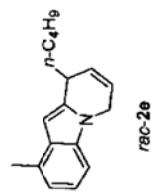




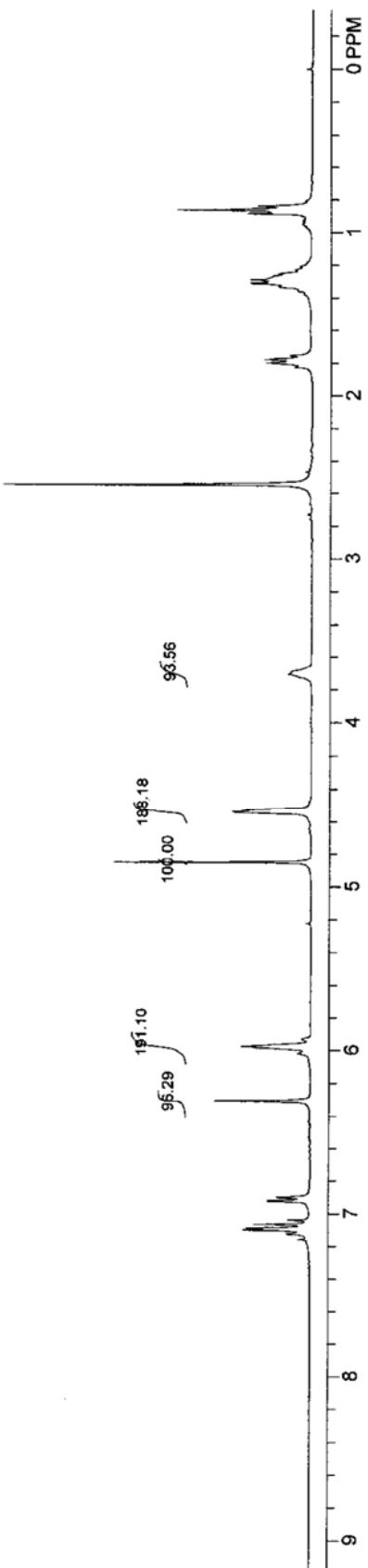
jf2-045chundu_1.1

2018-09-28 11:26:17.062

USER: nmr
SOLVENT: CDCl₃
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl₃
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz

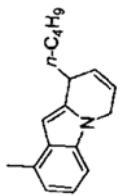


purity (96%) is determined by dibromomethane (8 μ l, 0.229 mmol) as
the internal standard in 54.9 mg of sample



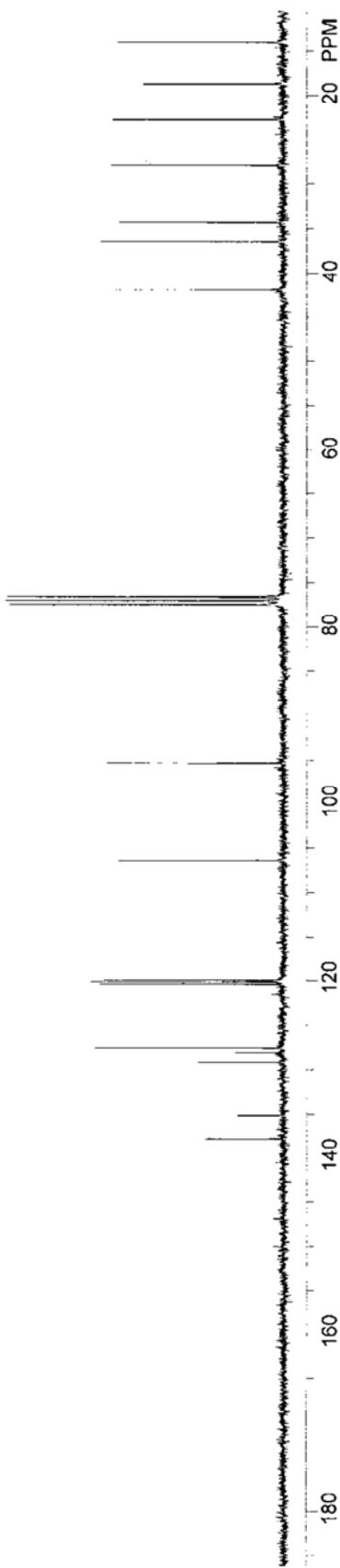
jf-2-045_2-1

2018-09-06 23:03:06.062
USER: nmr
SOLVENT: CDCl₃
Experiment = zgppg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 231
Solvent = CDCl₃
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.0000000 MHz
SW1 = 22727.27 Hz



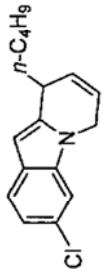
137.850
135.147
129.191
128.088
127.555
120.422
120.156
119.981
95.301
106.405
77.423
77.000
76.577

41.942
36.464
34.286
27.952
22.833
18.742
13.990

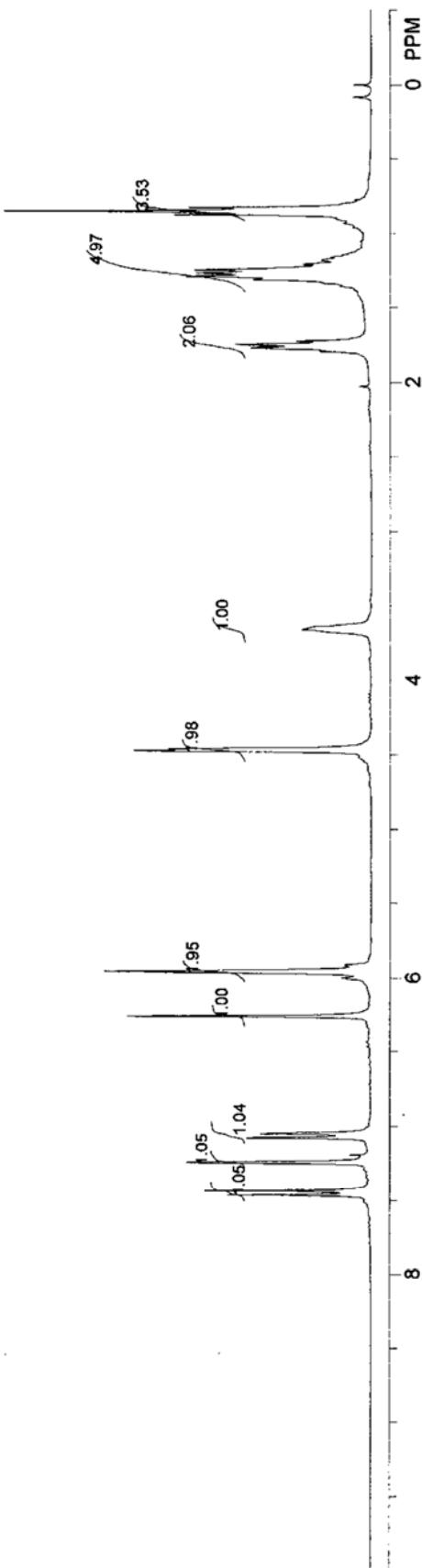
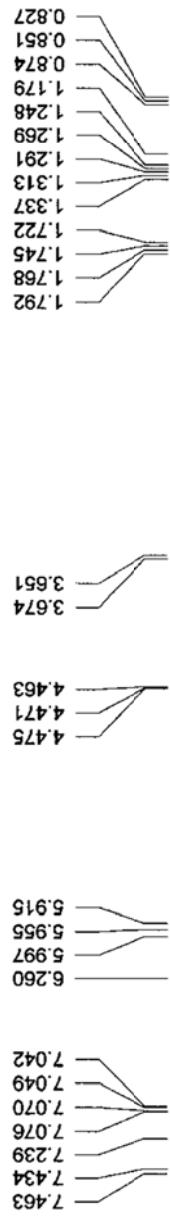


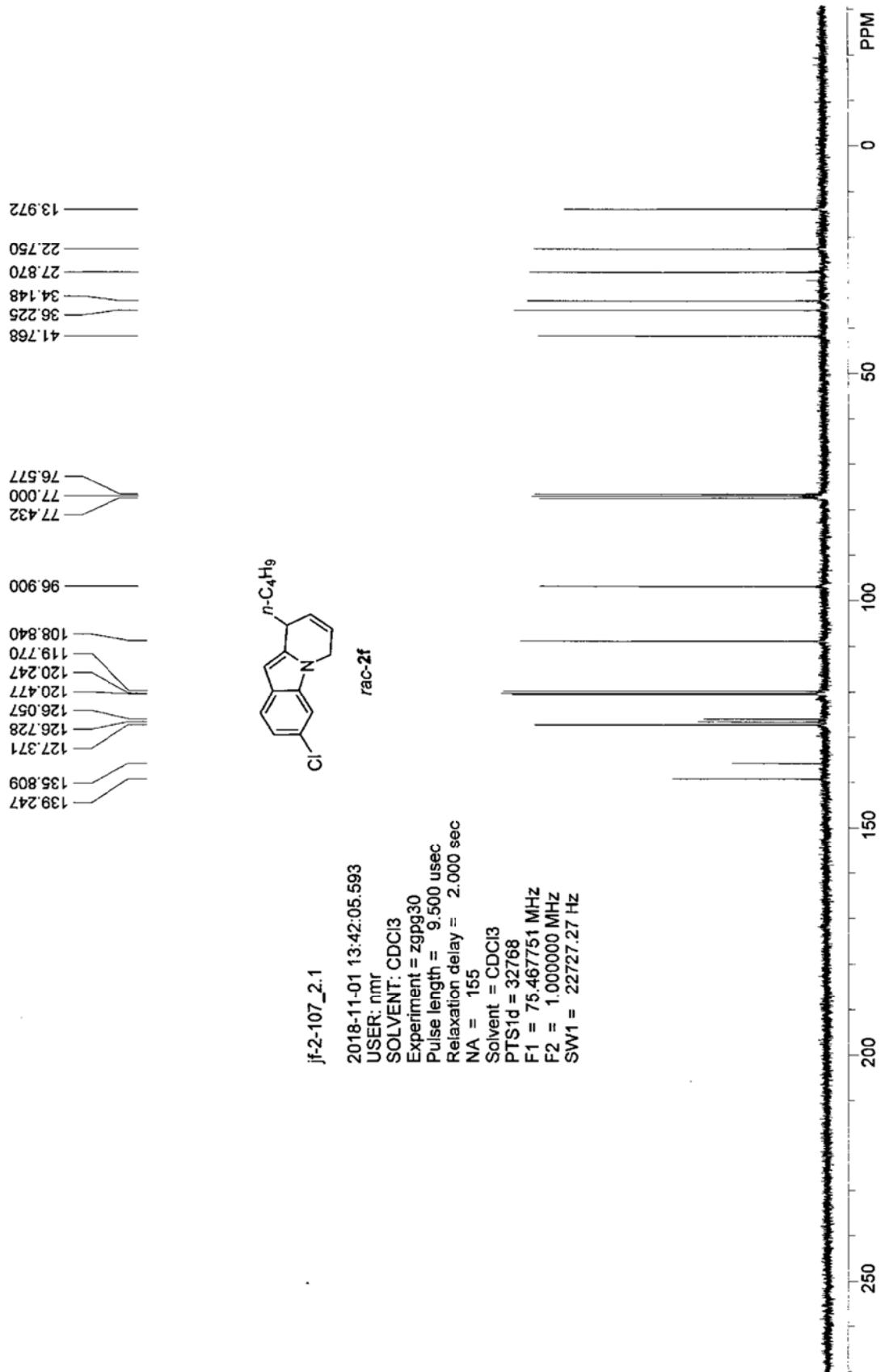
f-2-107

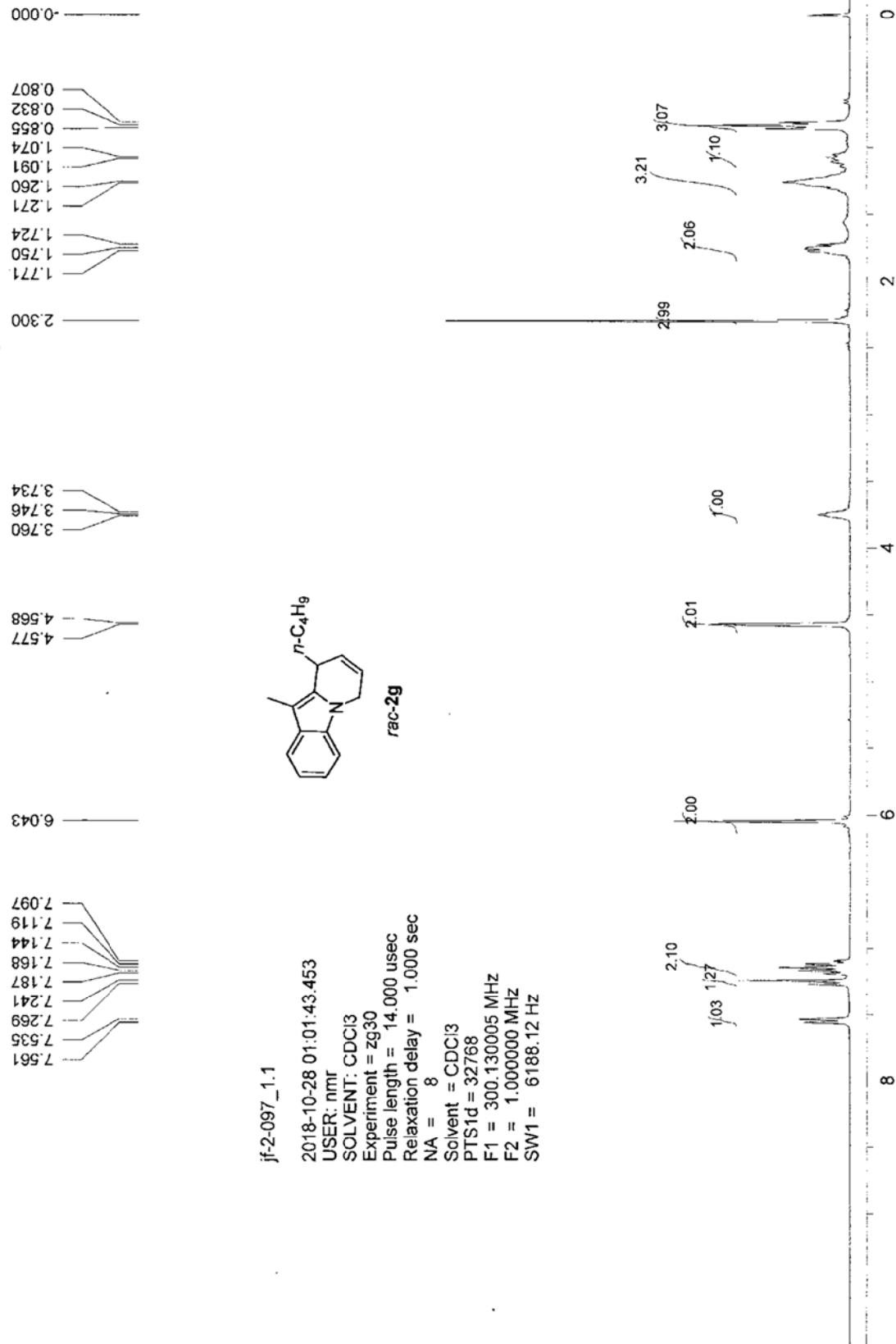
2018-11-0113:31:01.953
 USER: rmfr
 SOLVENT: CDCl₃
 Experiment = zg30
 Pulse length = 14.000 usec
 Relaxation delay = 1.000 sec
 NA = 8
 Solvent = CDCl₃
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz

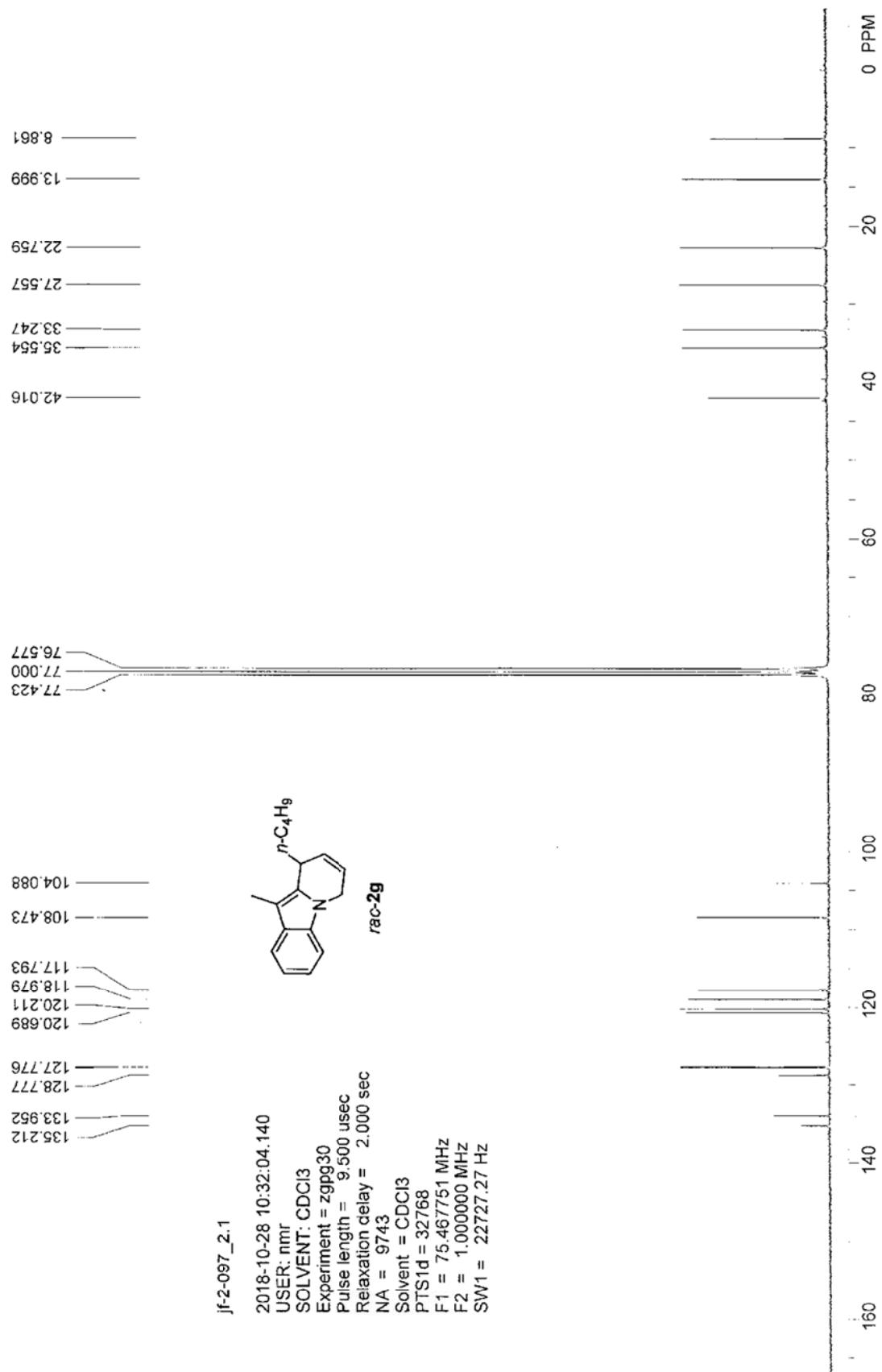


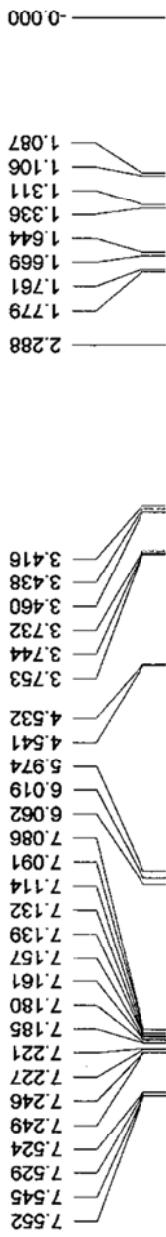
rac-2f





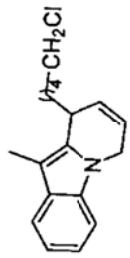




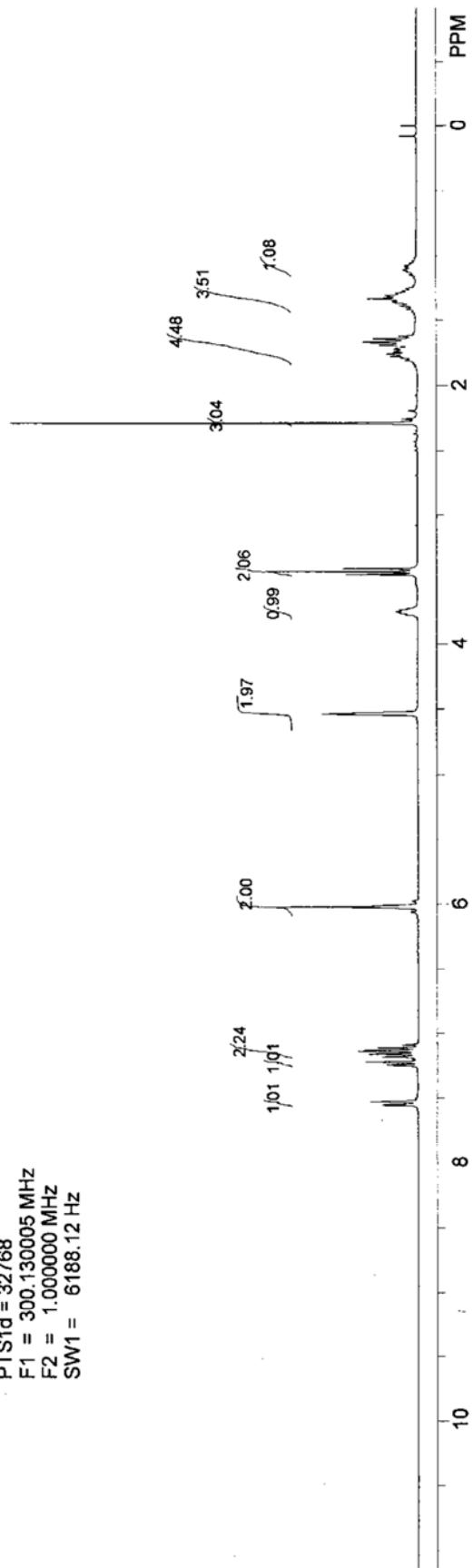


jf-2-152_1.1

2018-12-08 16:58:23.765
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg30
 Pulse length = 14.000 us
 Relaxation delay = 1.000
 NA = 8
 Solvent = CDCl3
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz



rac-2h



jf-2-152_2.1

2018-12-08 17:05:33.562

USER: nmr

SOLVENT: CDCl₃

Experiment = zgpg30

Pulse length = 9.500 usec

Relaxation delay = 2.000 sec

NA = 105

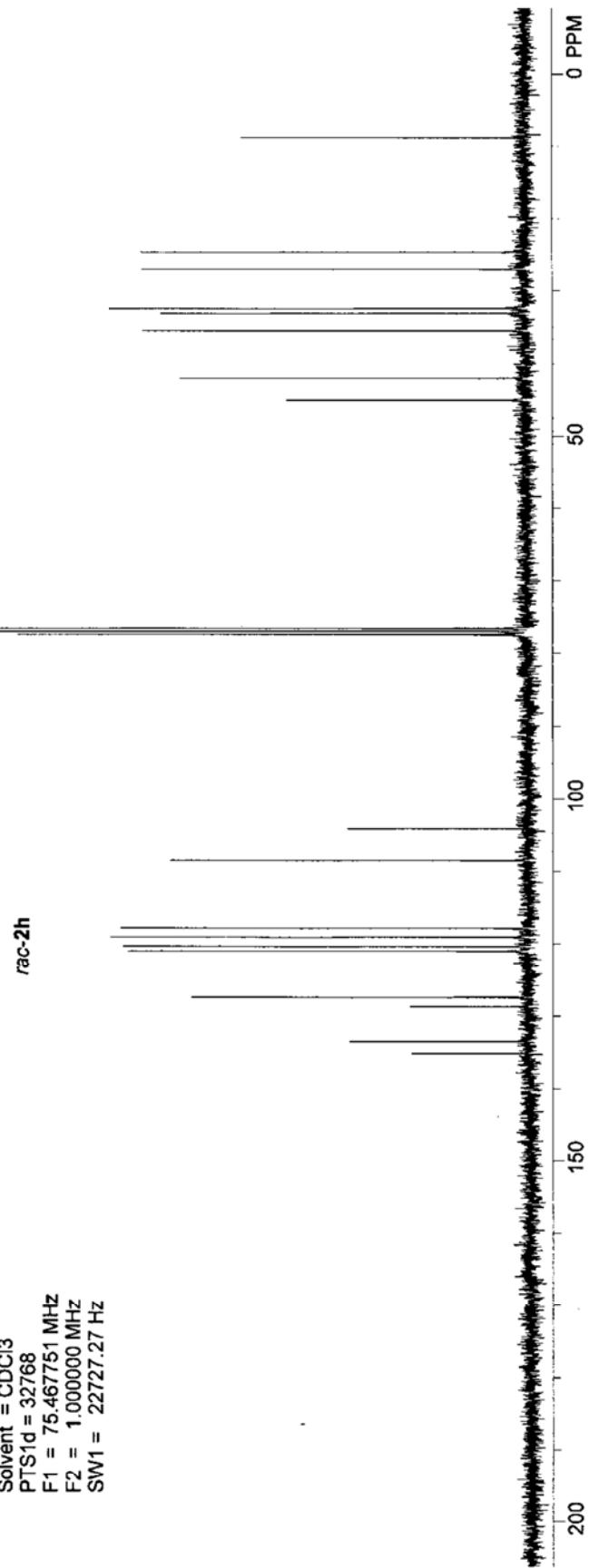
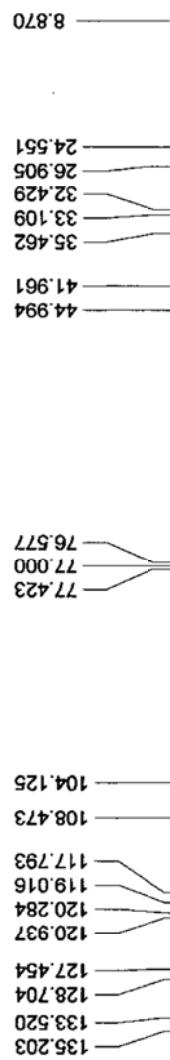
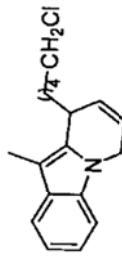
Solvent = CDCl₃

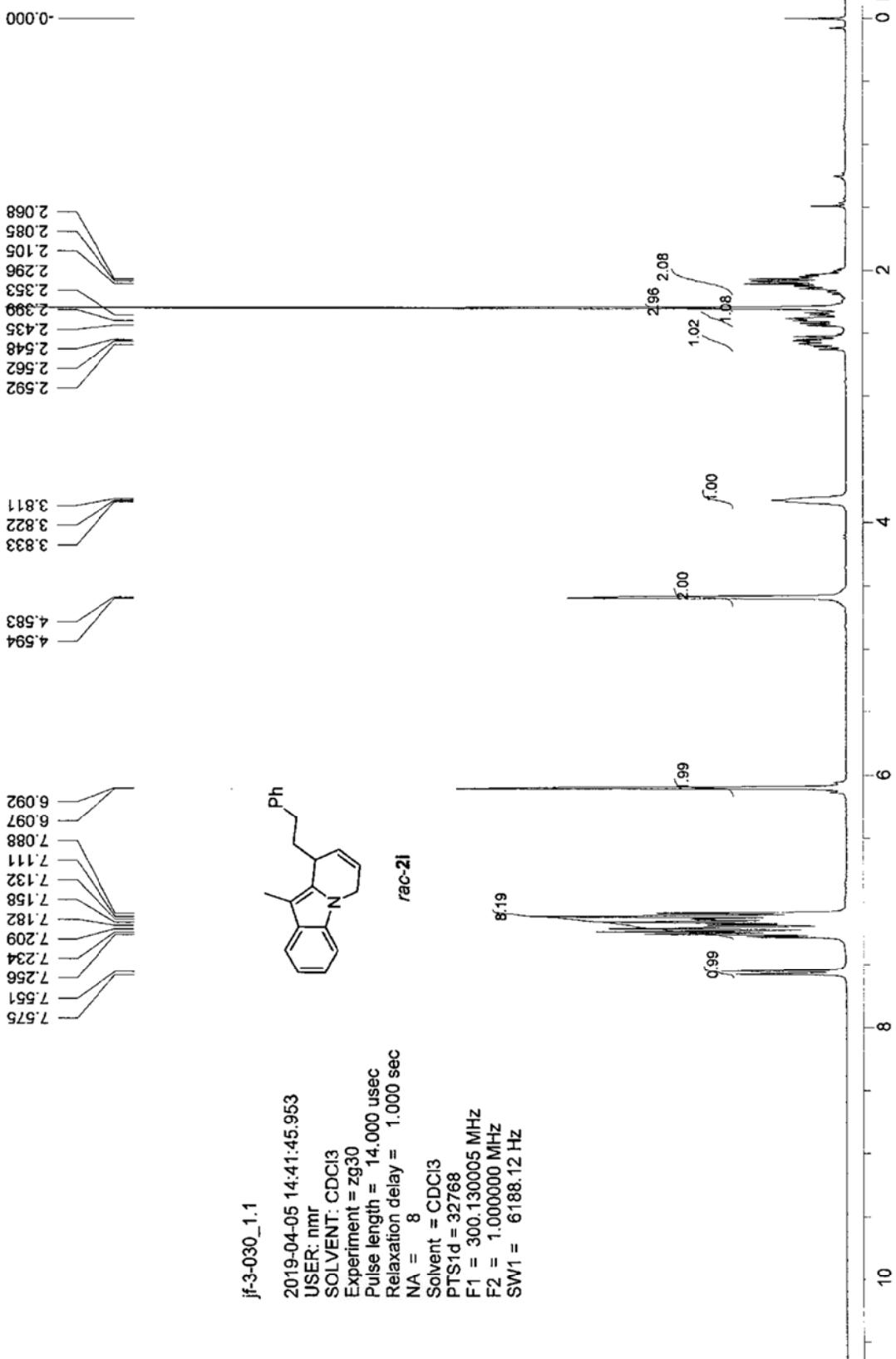
PTS1d = 32768

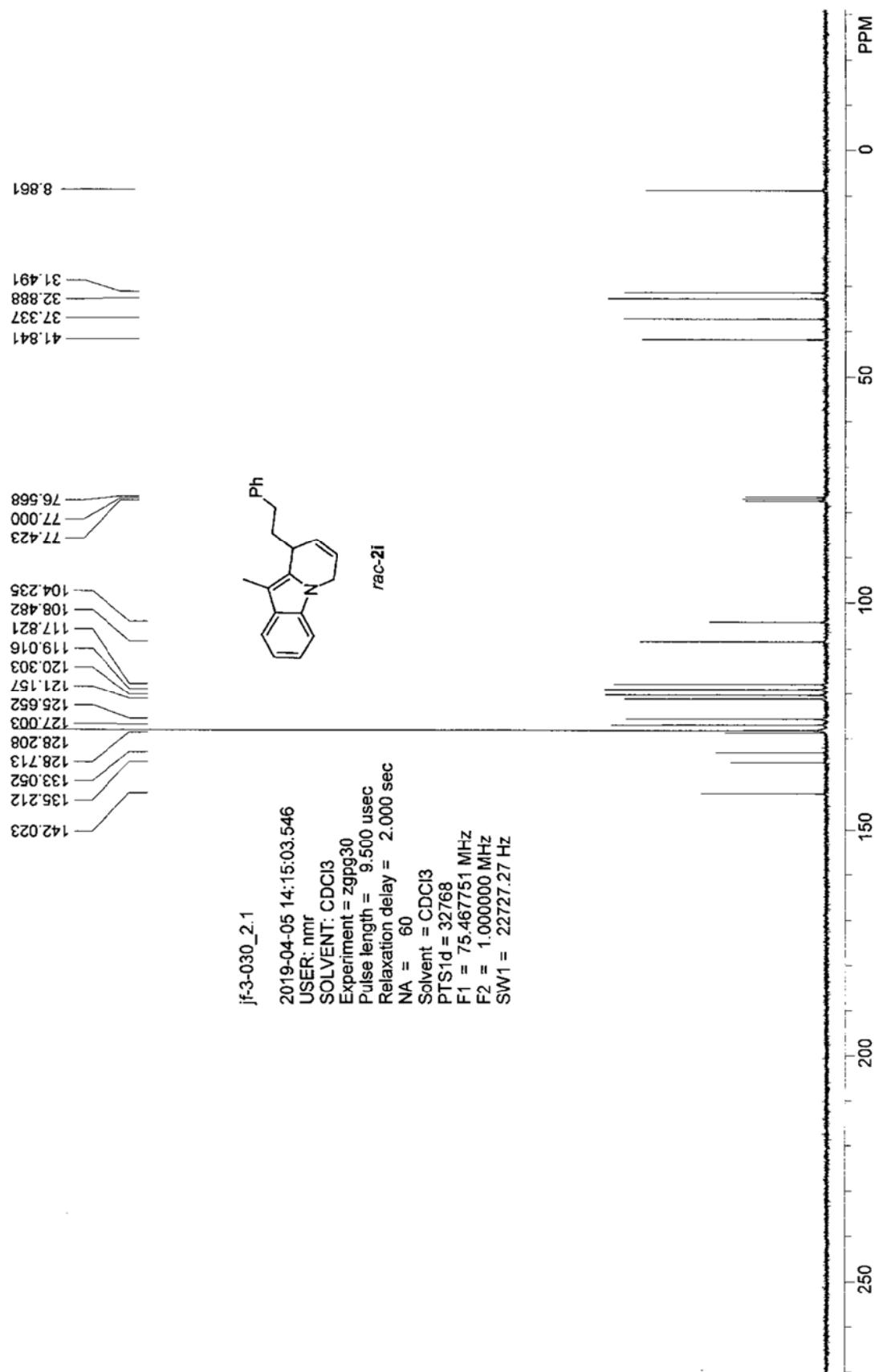
F1 = 75.467751 MHz

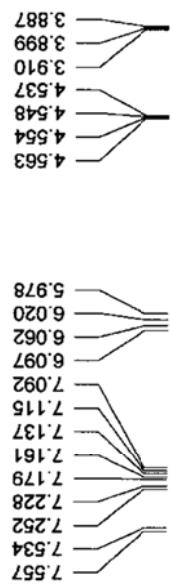
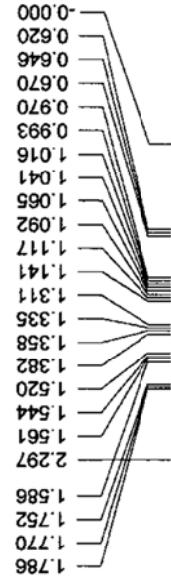
F2 = 1.000000 MHz

SW1 = 22727.27 Hz









JF-3-094_111.1

2019-05-14 22:46:47.125

USER: nmr

SOLVENT: CDCl₃

Experiment = zg30

Pulse length = 14.000 usec

Relaxation delay = 1.000 sec

NA = 8

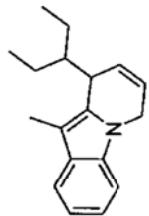
Solvent = CDCl₃

PTS1d = 32768

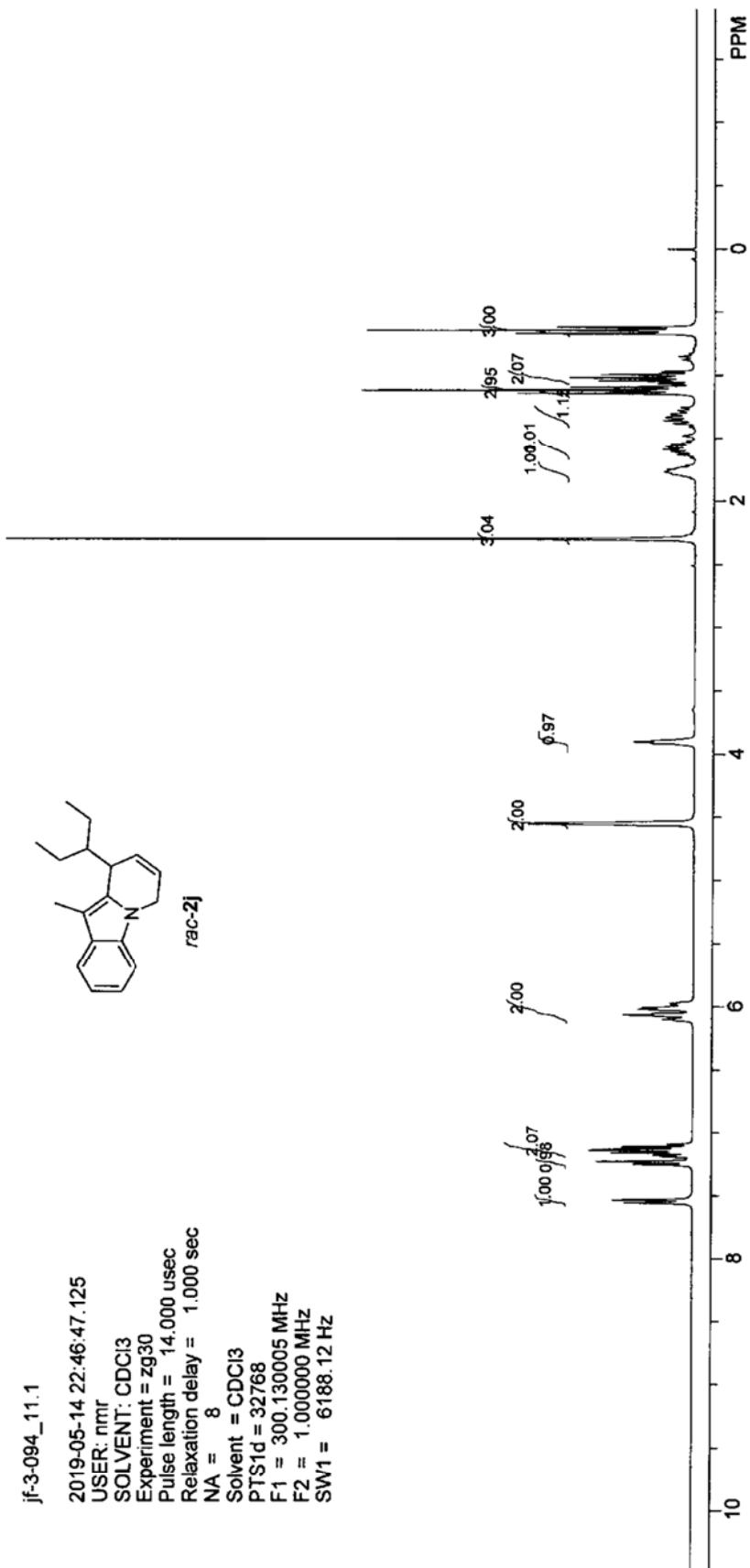
F1 = 300.130005 MHz

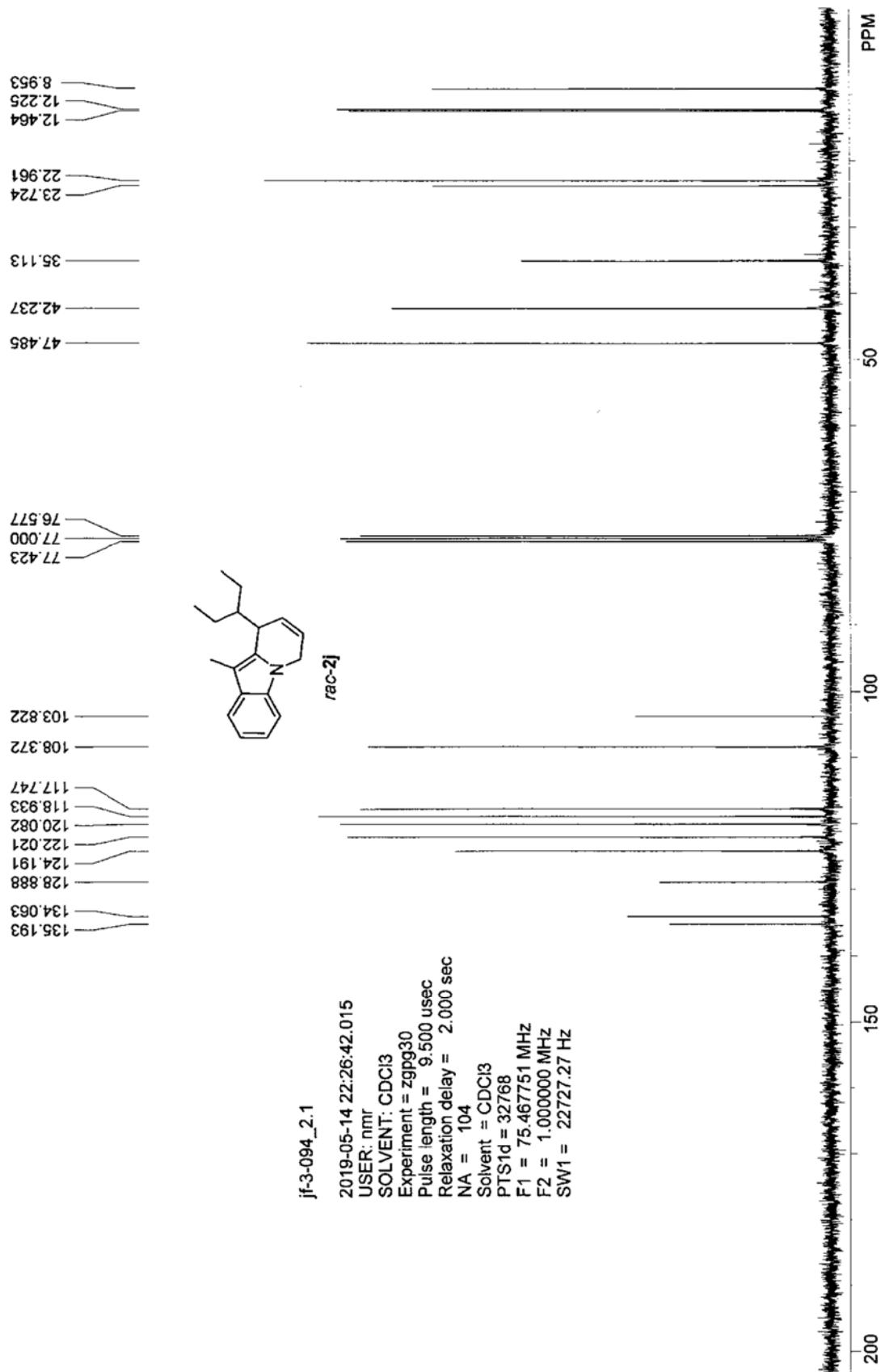
F2 = 1.000000 MHz

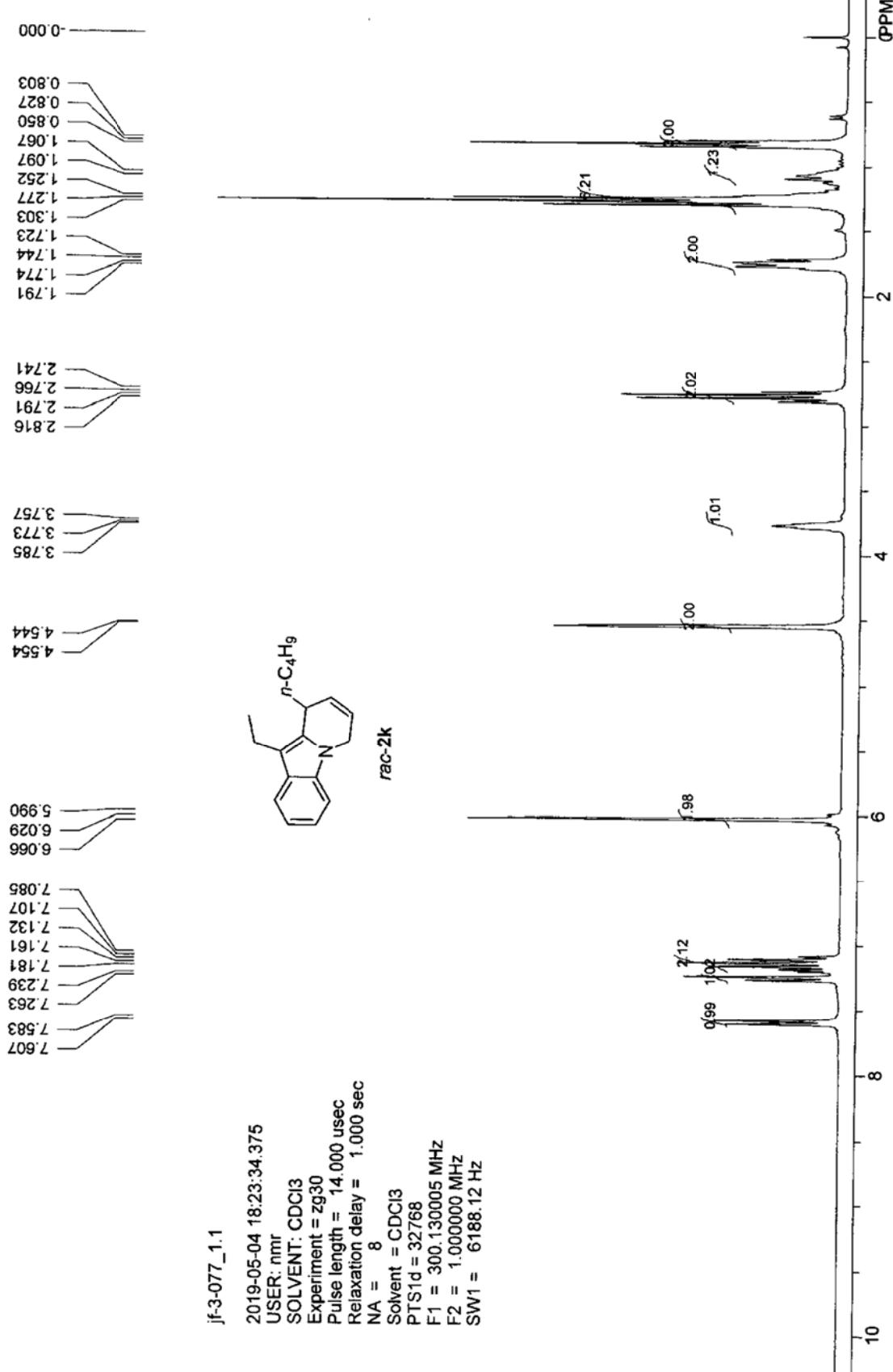
SW1 = 6188.12 Hz



[rac-2j]

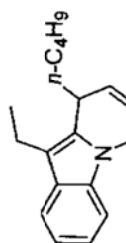




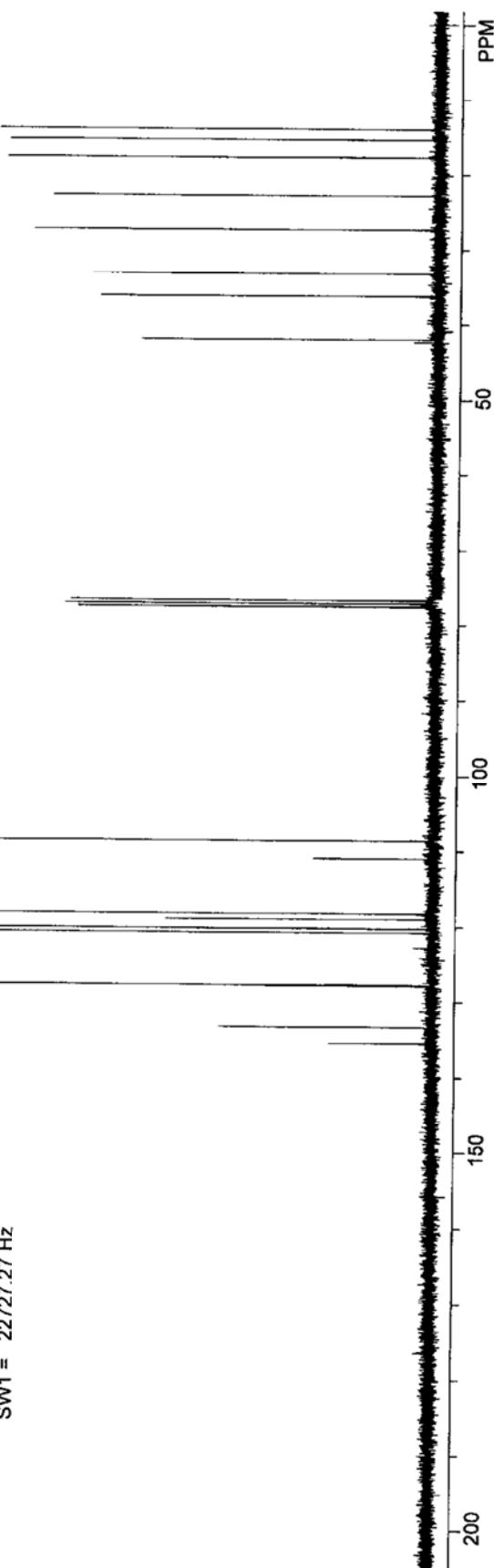


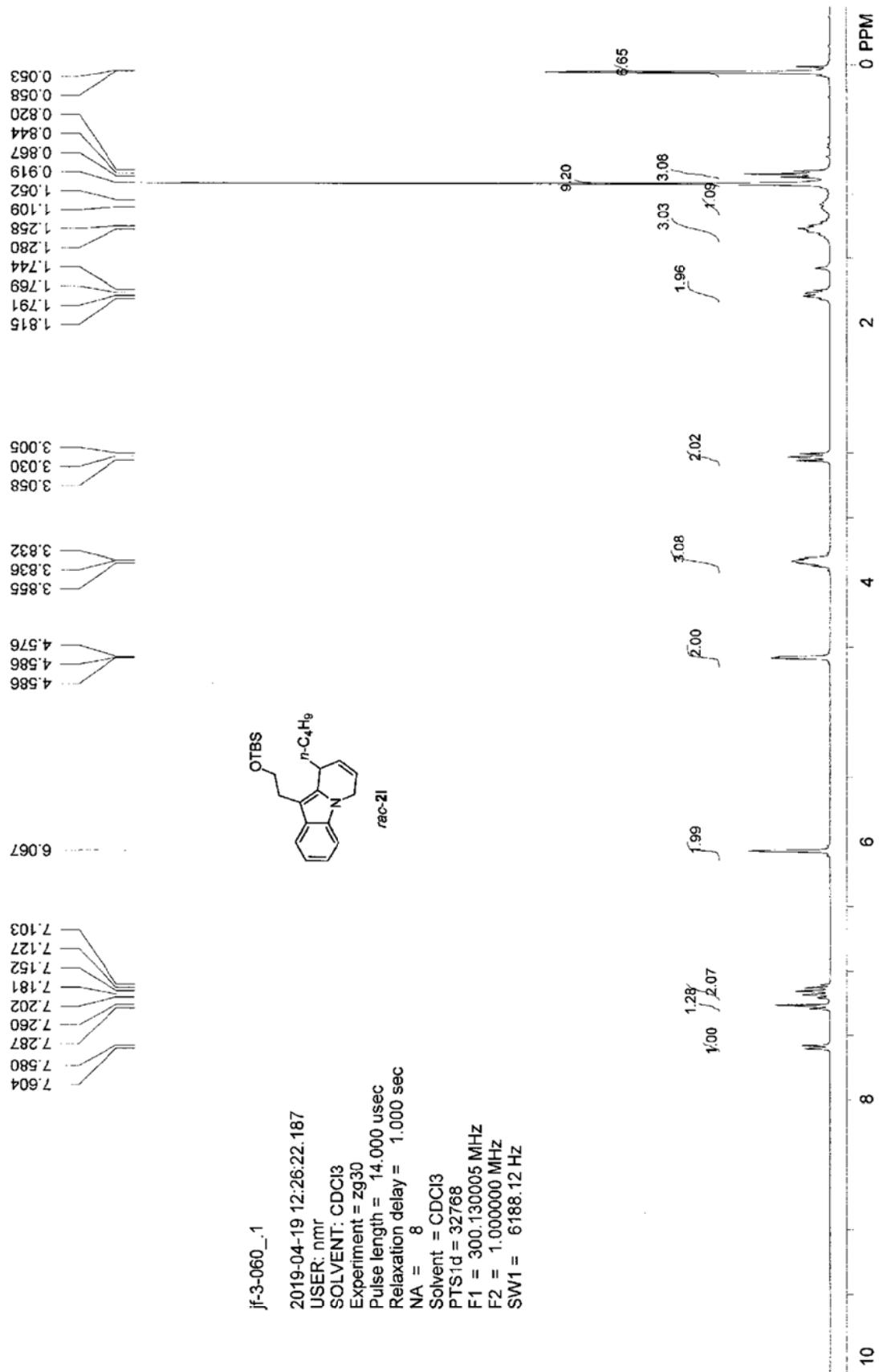
jf-3-077_2.1

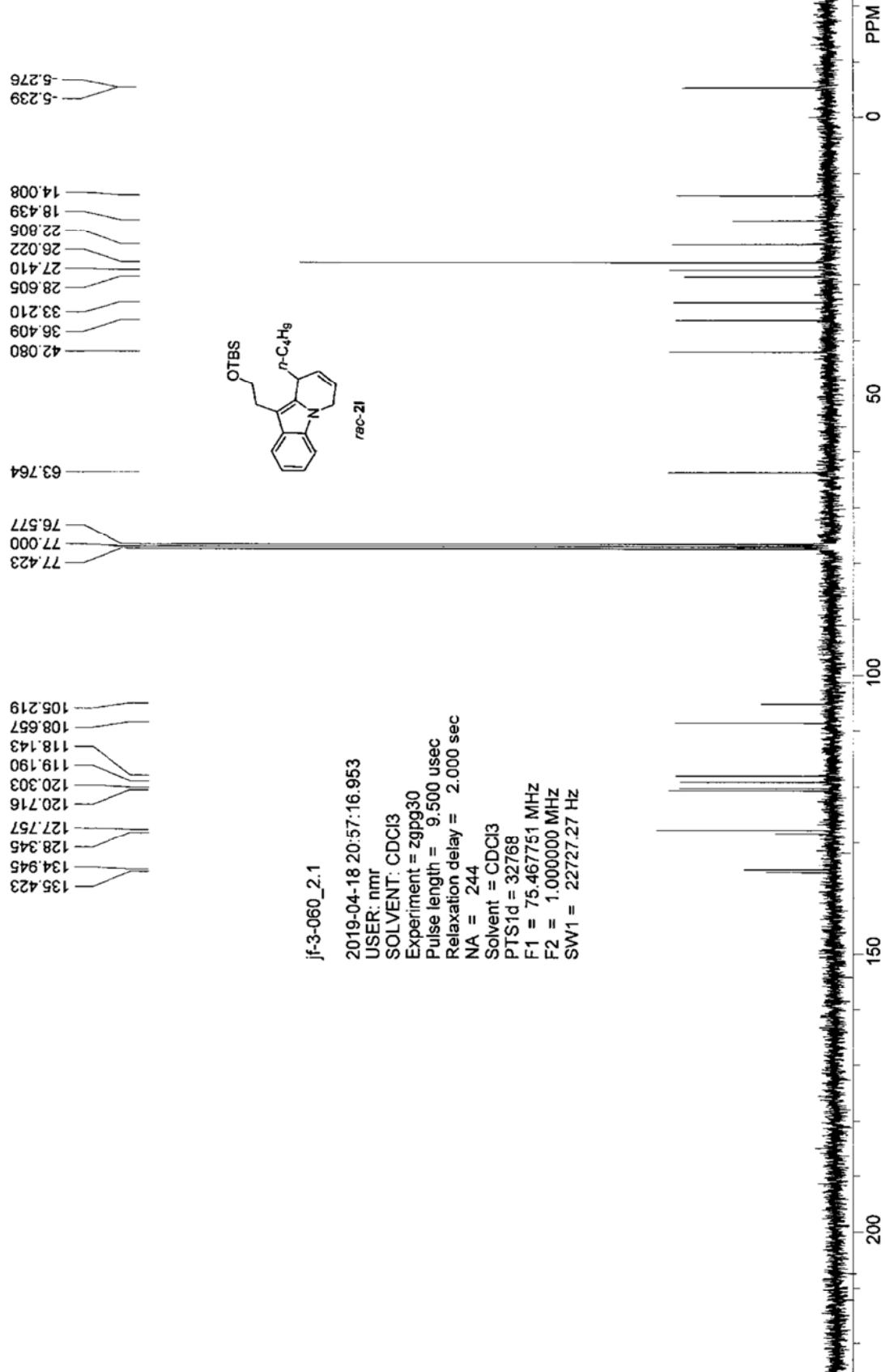
2019-05-04 19:04:07.359
USER: nmr
SOLVENT: CDCl₃
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 657
Solvent = CDCl₃
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

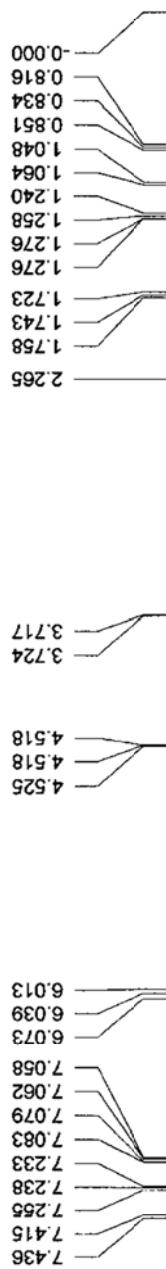


135.460
133.318
127.904
127.766
120.716
118.951
118.192
110.991
108.620
rac-2k
77.432
77.000
76.577
42.007
36.253
33.201
27.327
22.796
17.740
15.378
13.990

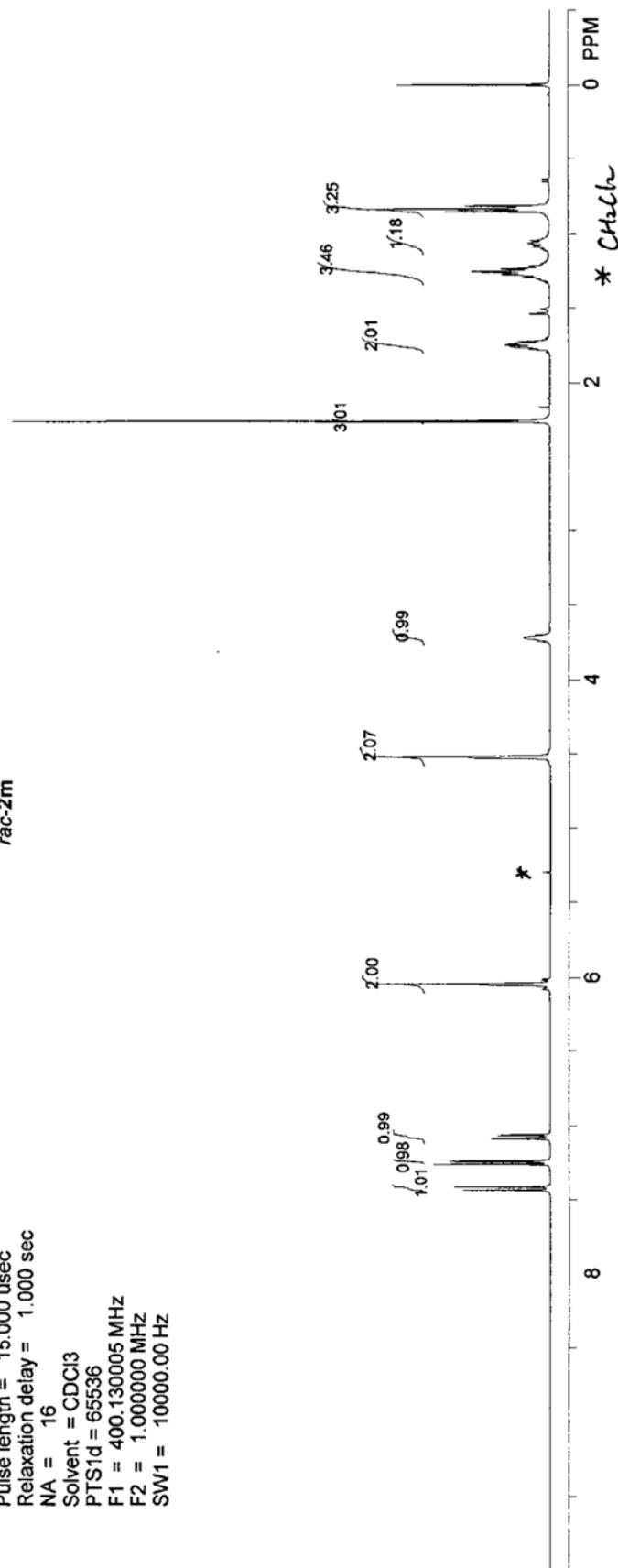
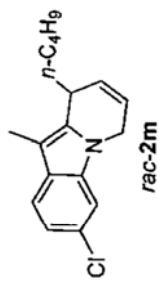


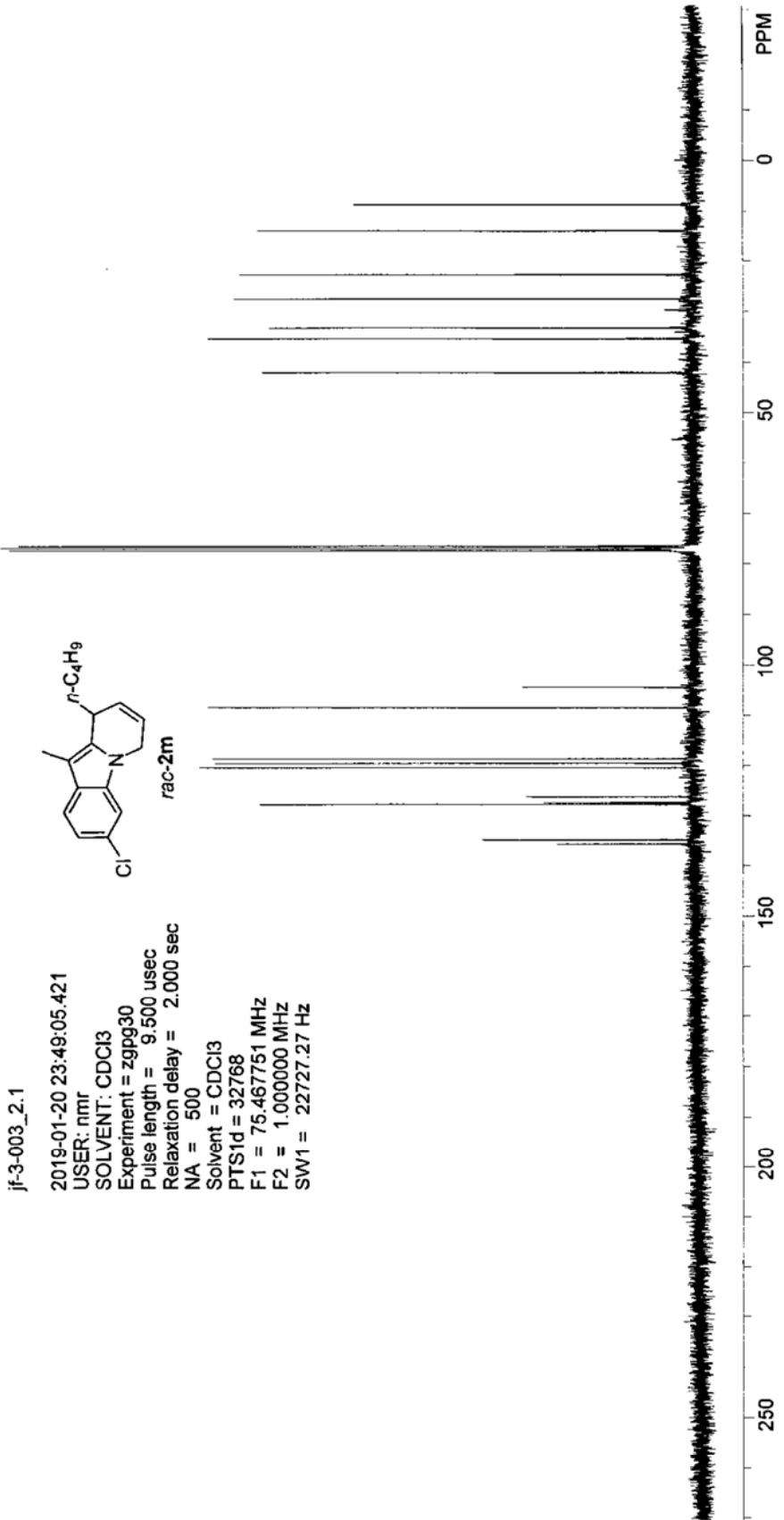


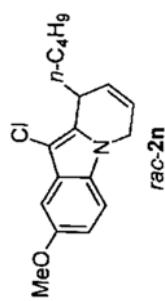
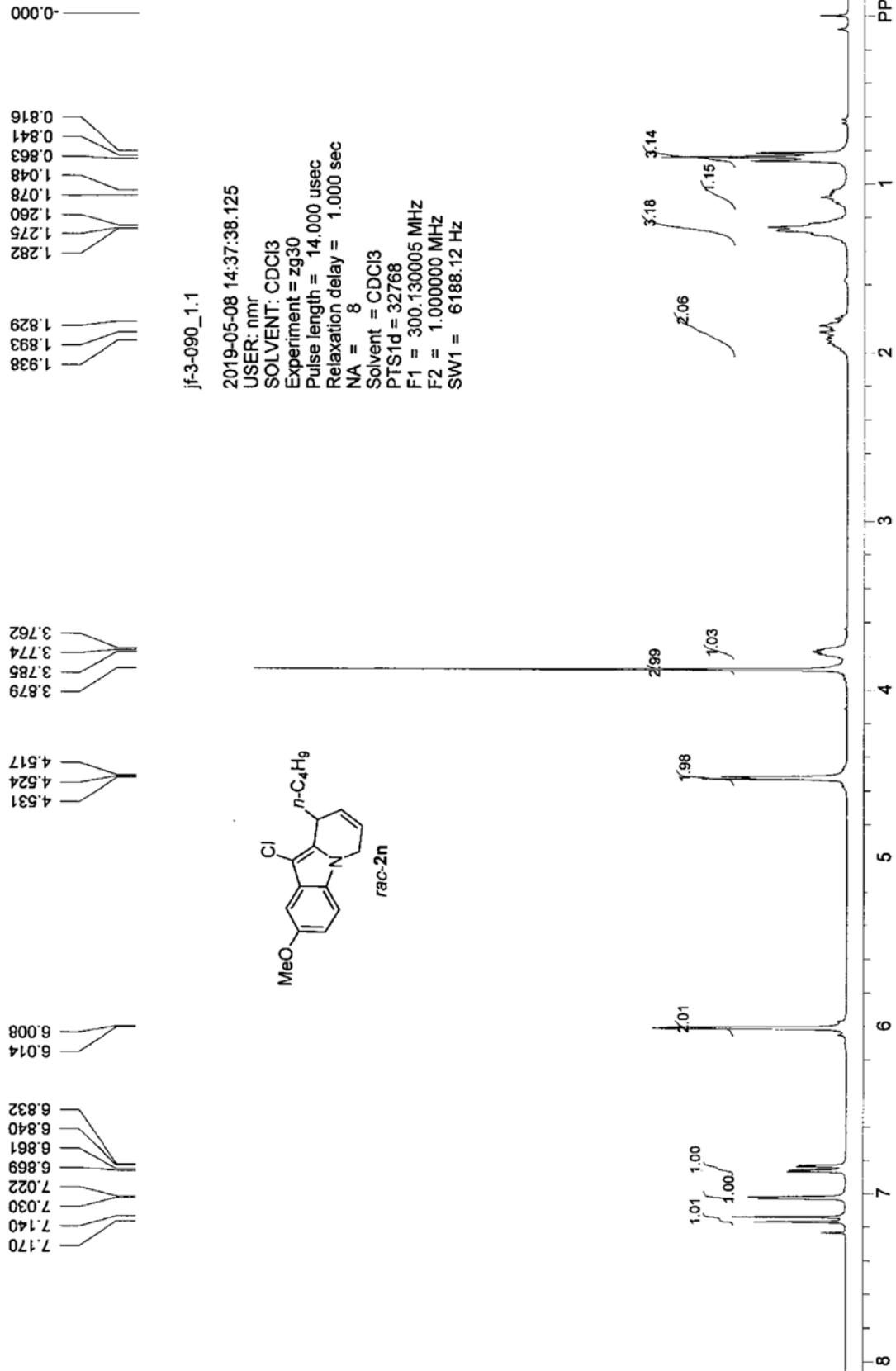


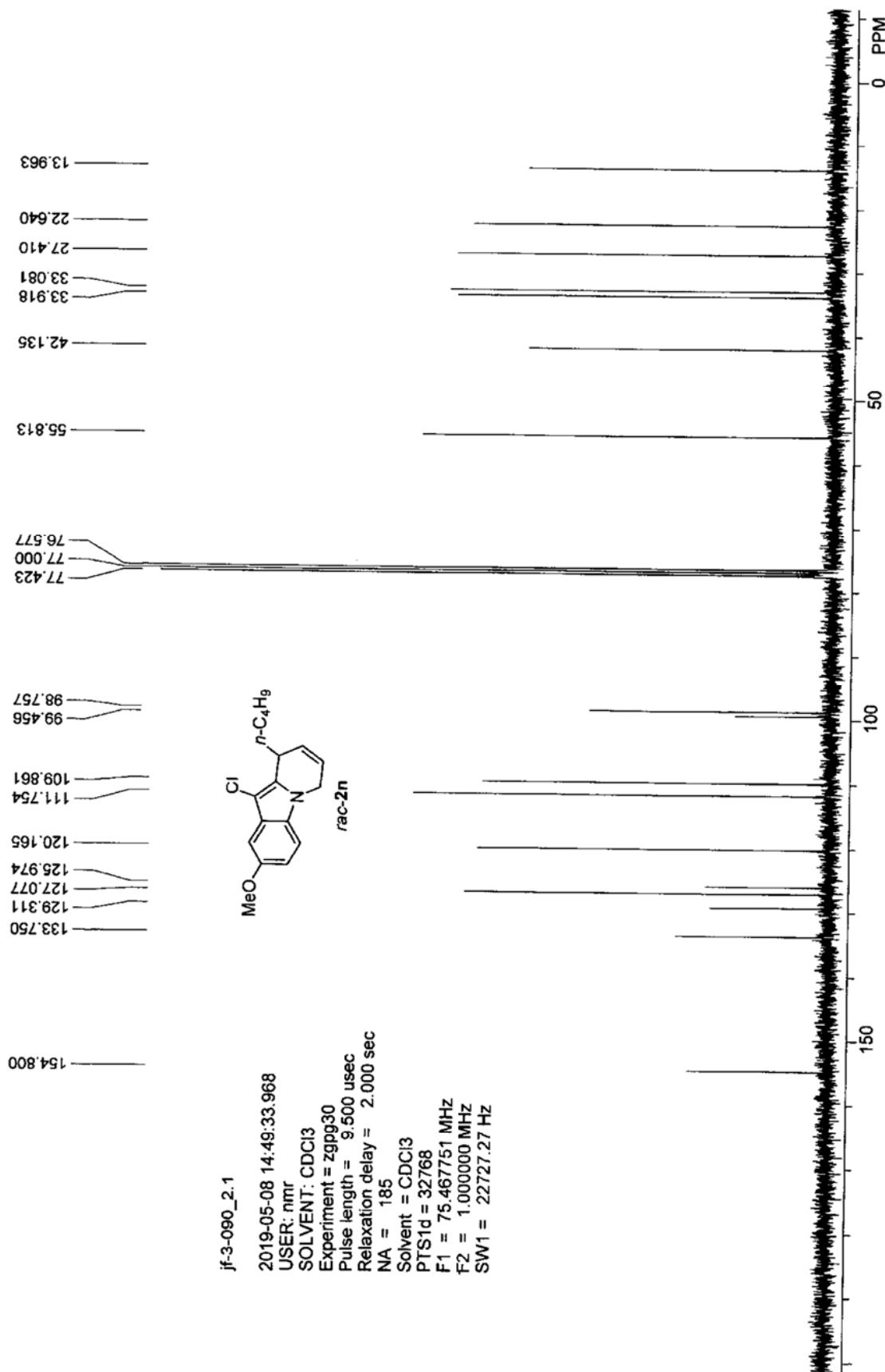


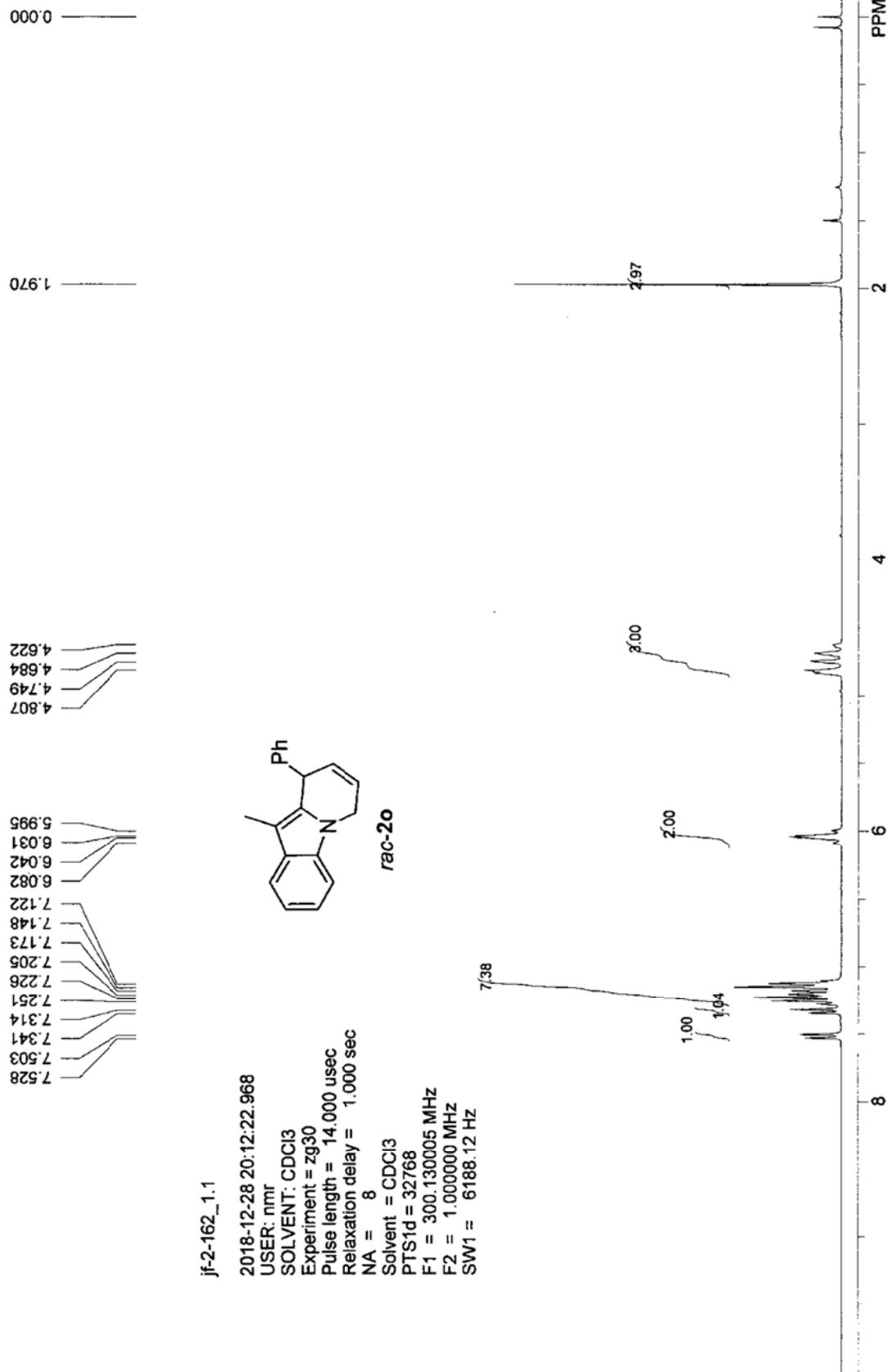
jf3-003_1.1
jf3-003_,
2019-01-21 16:12:10.386
USER: nmrsu
SOLVENT: CDCl₃
Experiment = zg30
Pulse length = 15.000 usec
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl₃
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
SW1 = 10000.00 Hz

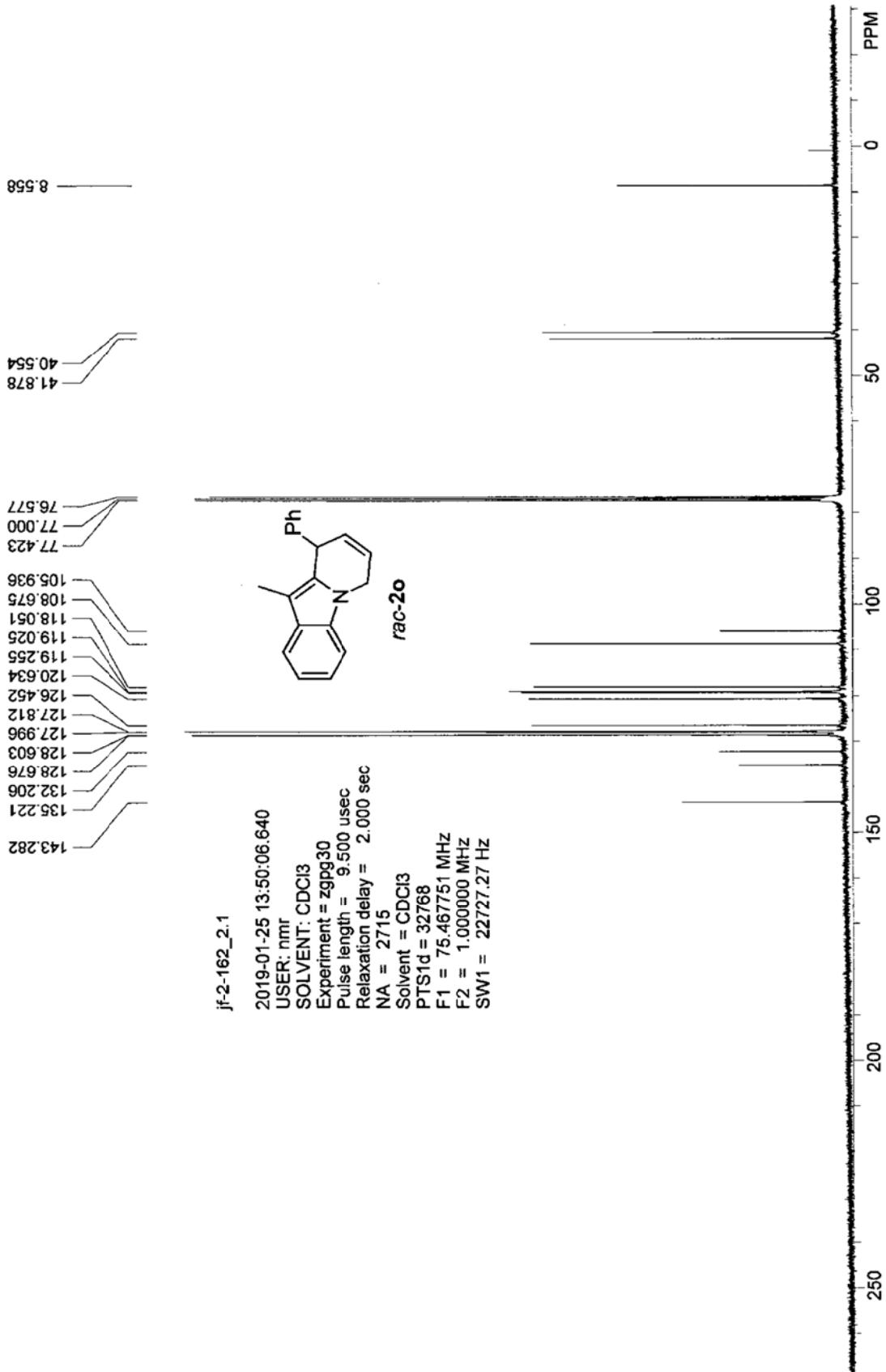


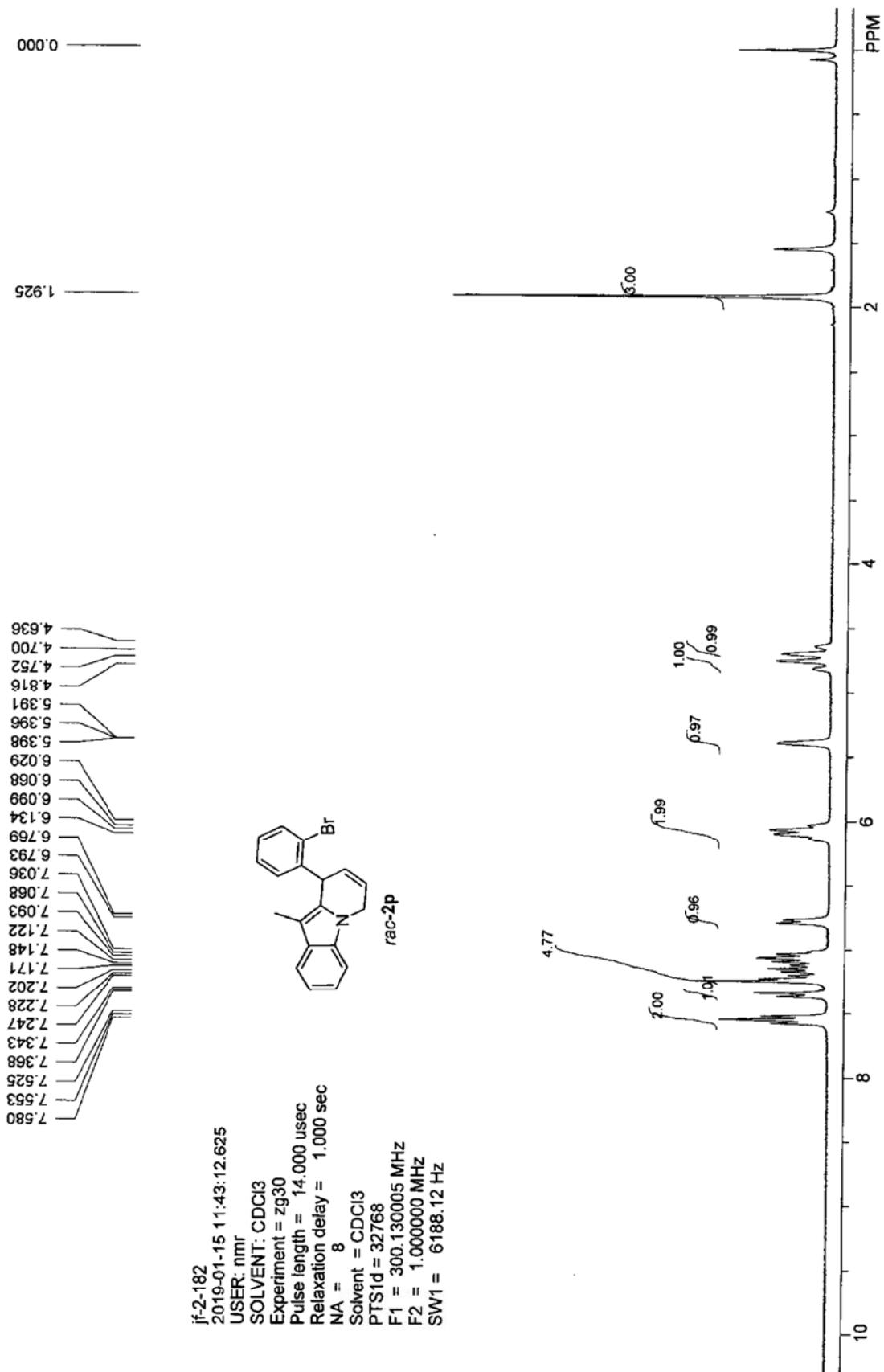


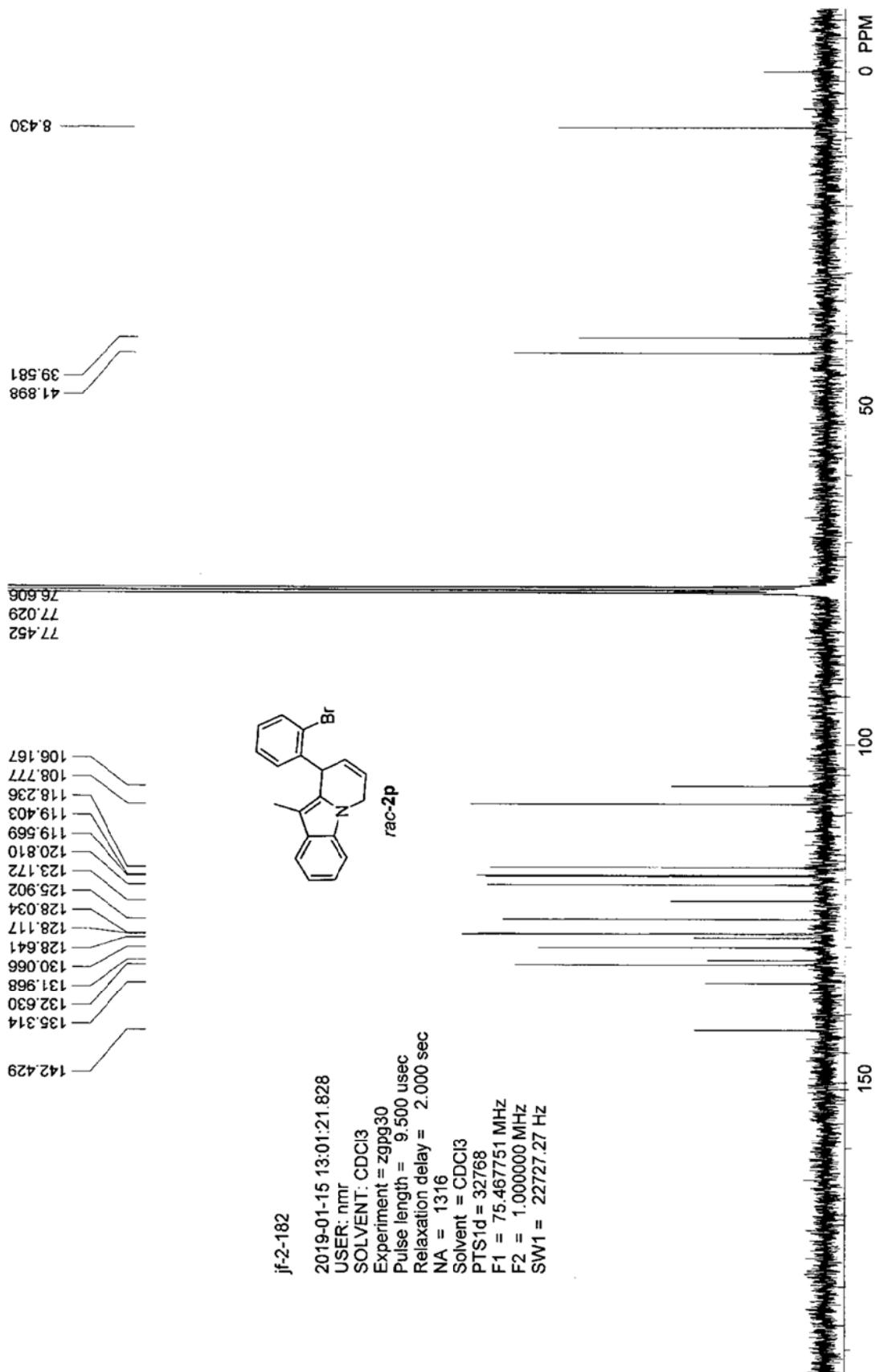


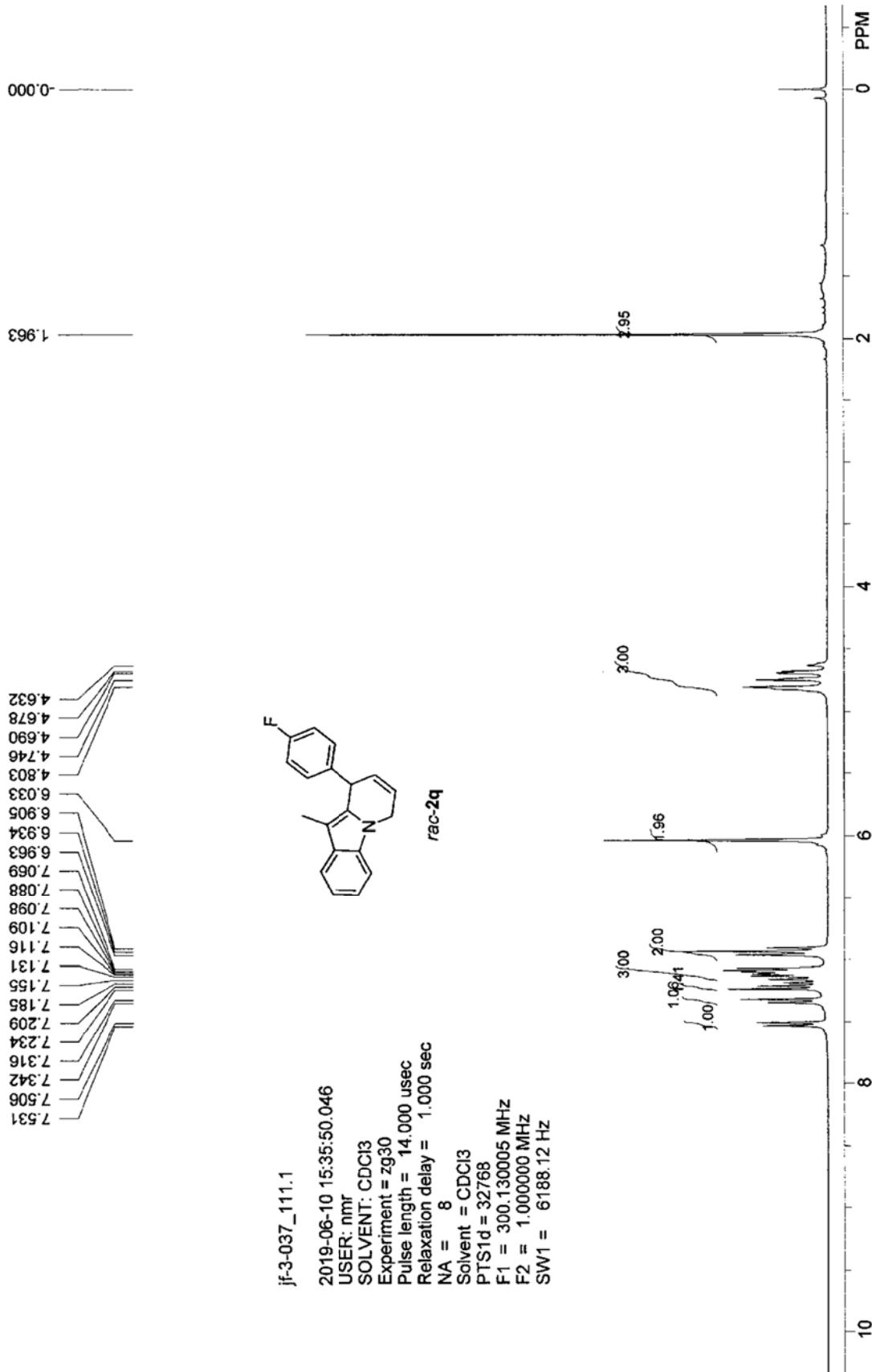












jf-3-037_

2019-04-12 13:13:54.656

USER: nmr

SOLVENT: CDCl₃

Experiment = zgpg30

Pulse length = 9.500 usec

Relaxation delay = 2.000 sec

NA = 193

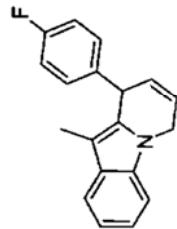
Solvent = CDCl₃

PTS1d = 32768

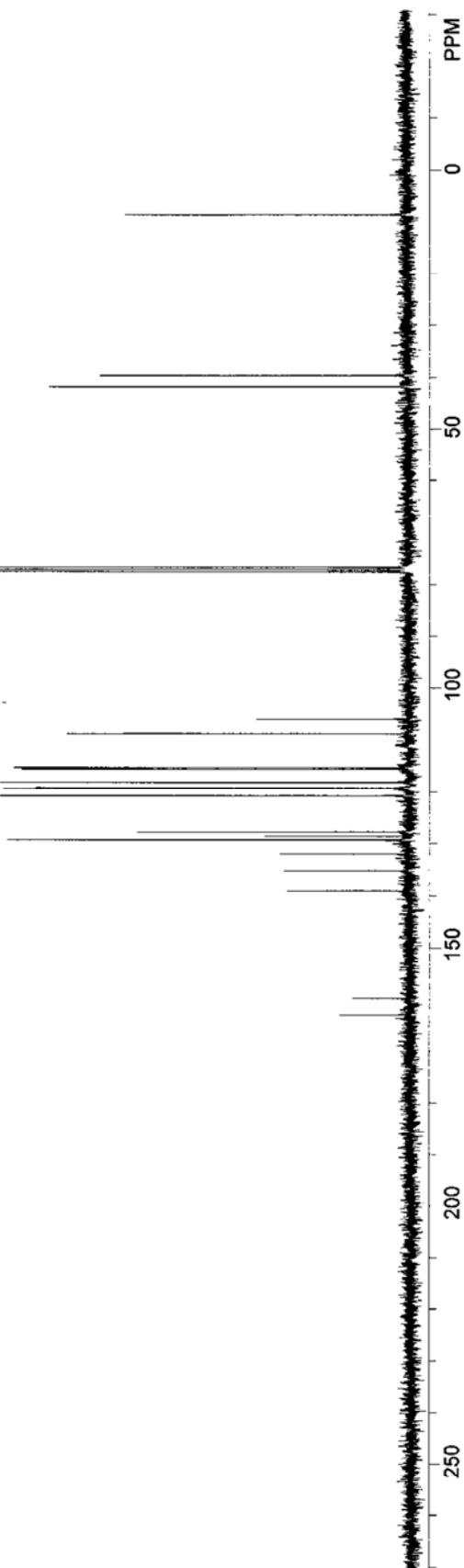
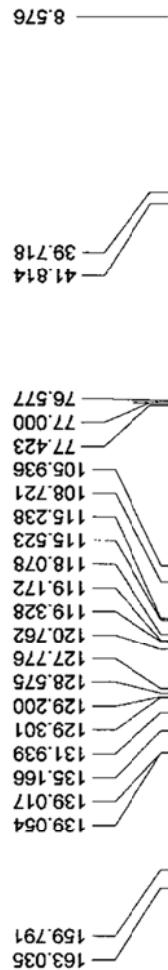
F1 = 75.467751 MHz

F2 = 1.000000 MHz

SW1 = 22727.27 Hz



rac-2q



PPM

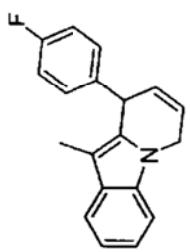
-150

-100

-50

0

rac-2q



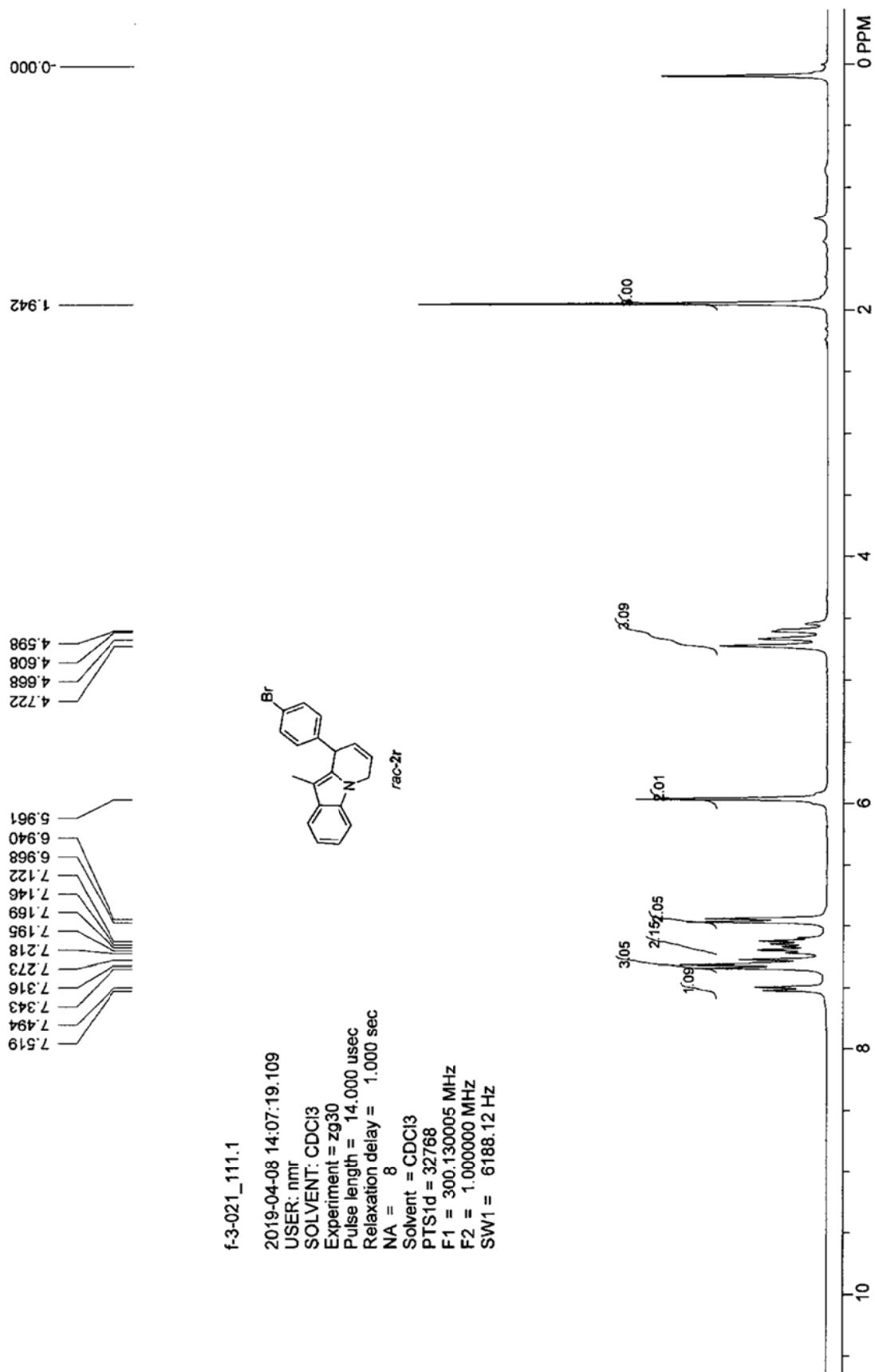
jf-3-037_4.1

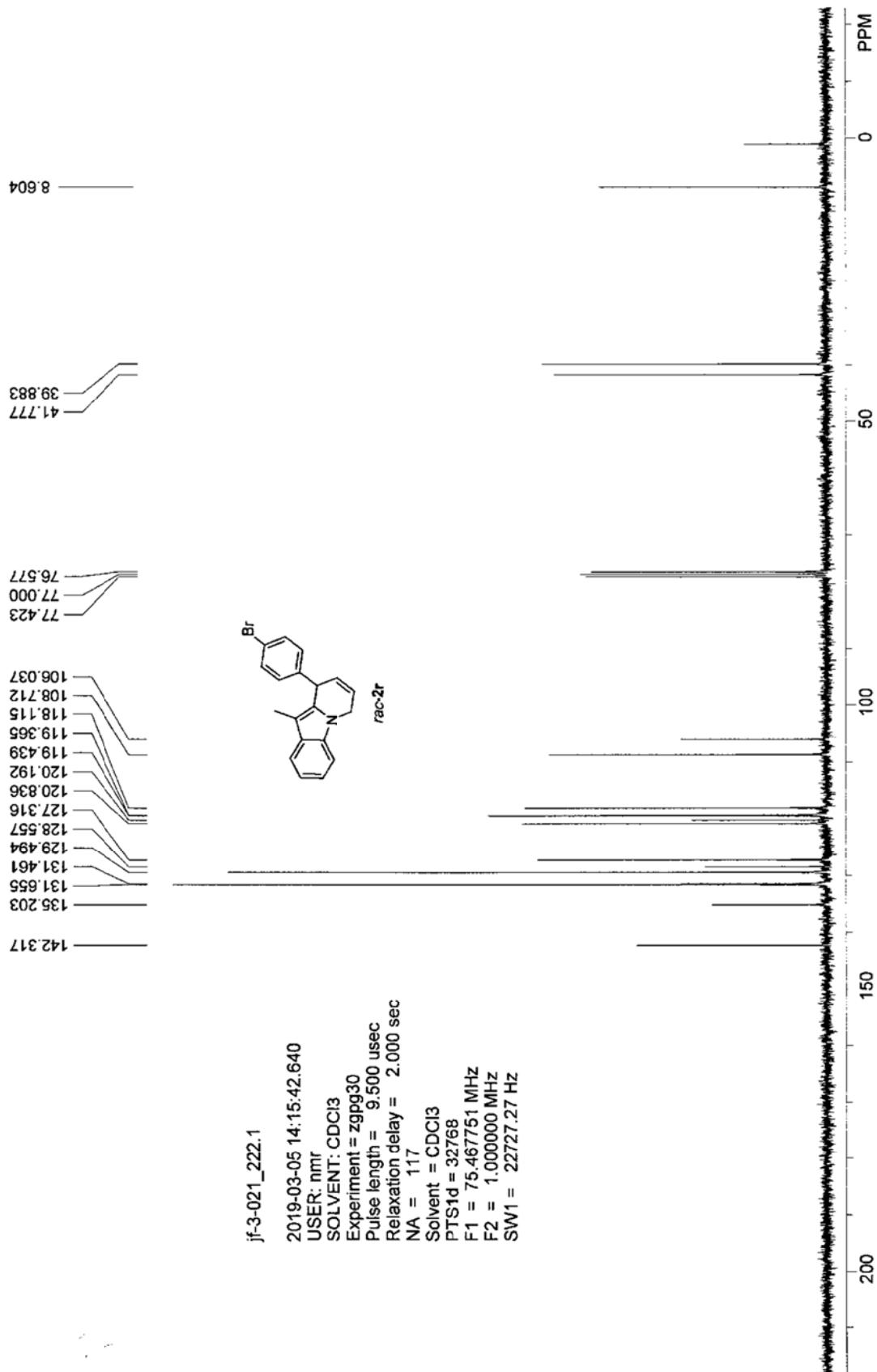
2019-04-16 08:52:10.125
USER: nmr
SOLVENT: CDCl₃
Experiment = zgfhgqn
Pulse length = 13.500 usec
Relaxation delay = 1.000 sec
NA = 2
Solvent = CDCl₃
PTS1d = 65536
F1 = 282.404368 MHz
F2 = 1.000000 MHz
SW1 = 66964.29 Hz

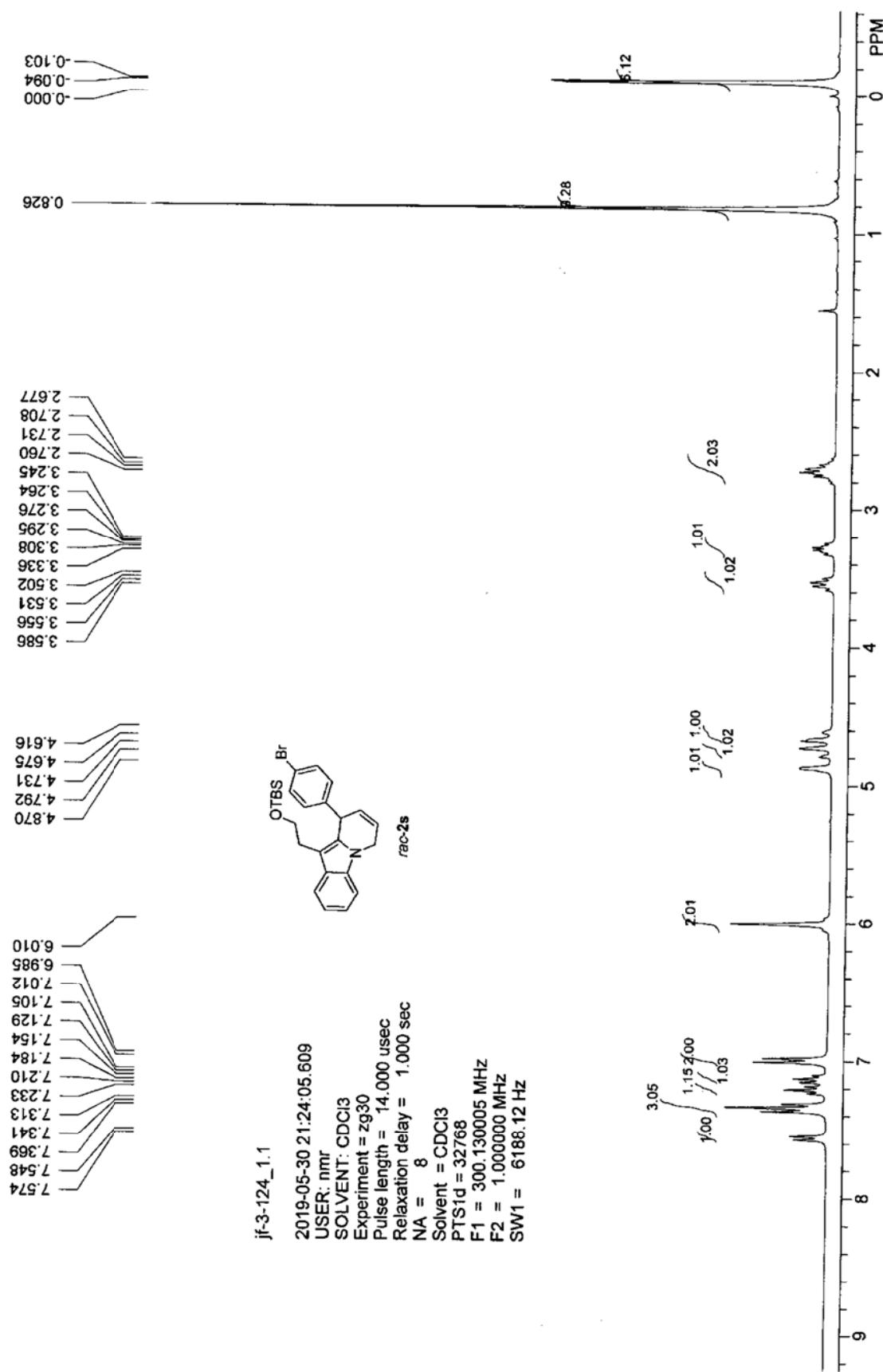
0.000

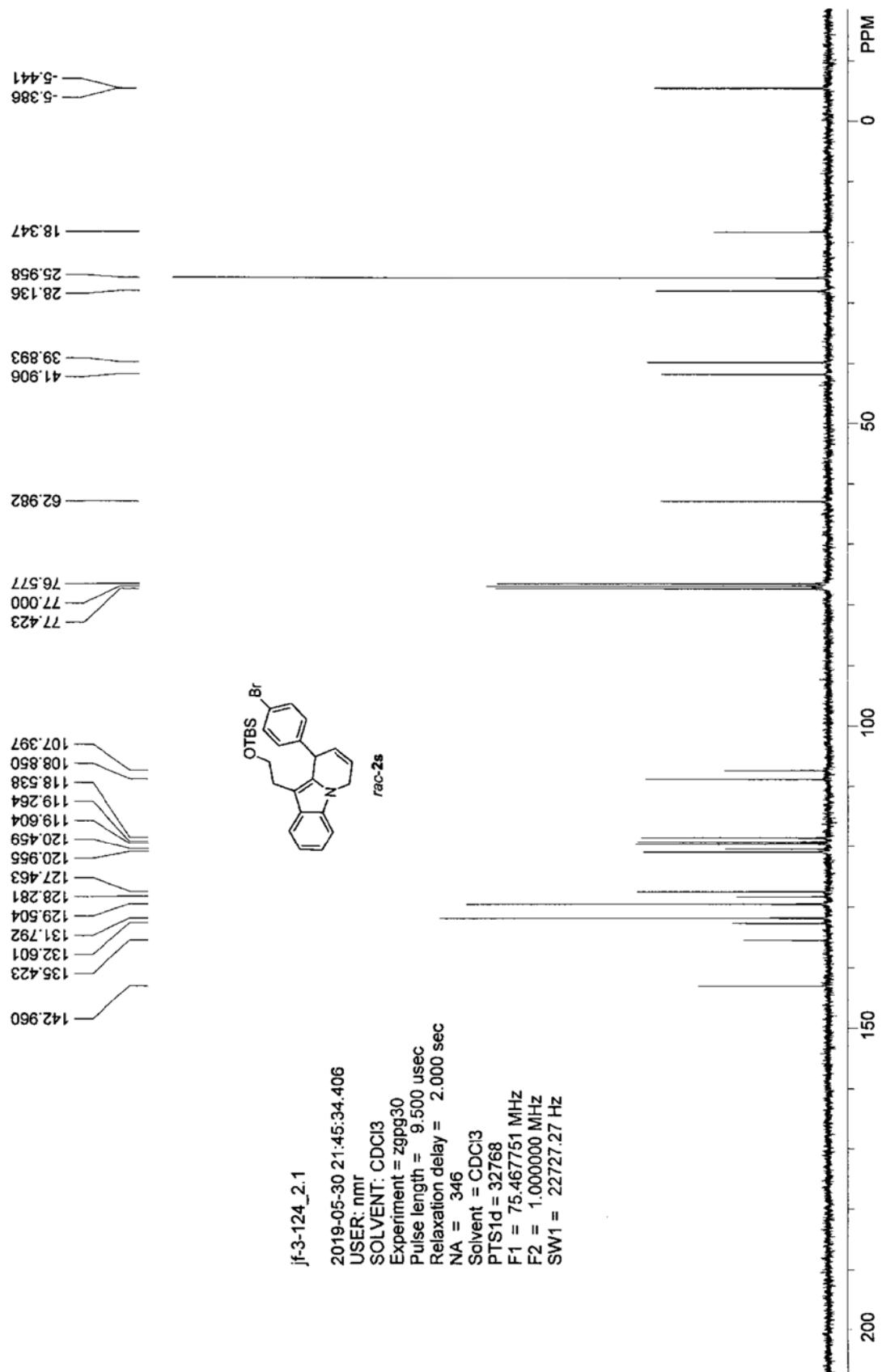
f-3-021_111.1

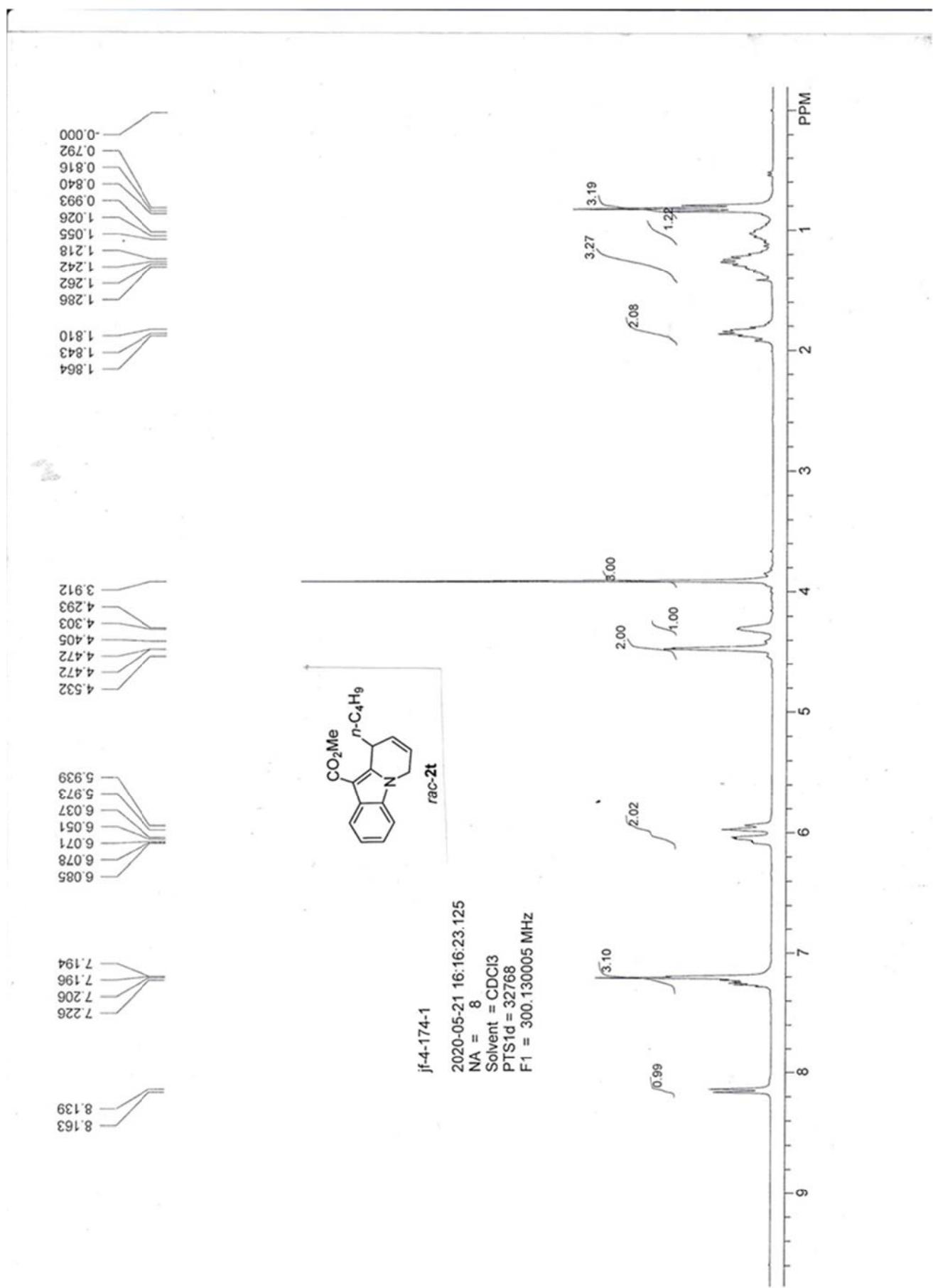
2019-04-08 14:07:19.109
 USER: nmr
 SOLVENT: CDCl₃
 Experiment = zg30
 Pulse length = 14.000 us
 Relaxation delay = 1.0000
 NA = 8
 Solvent = CDCl₃
 PTS Id = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz



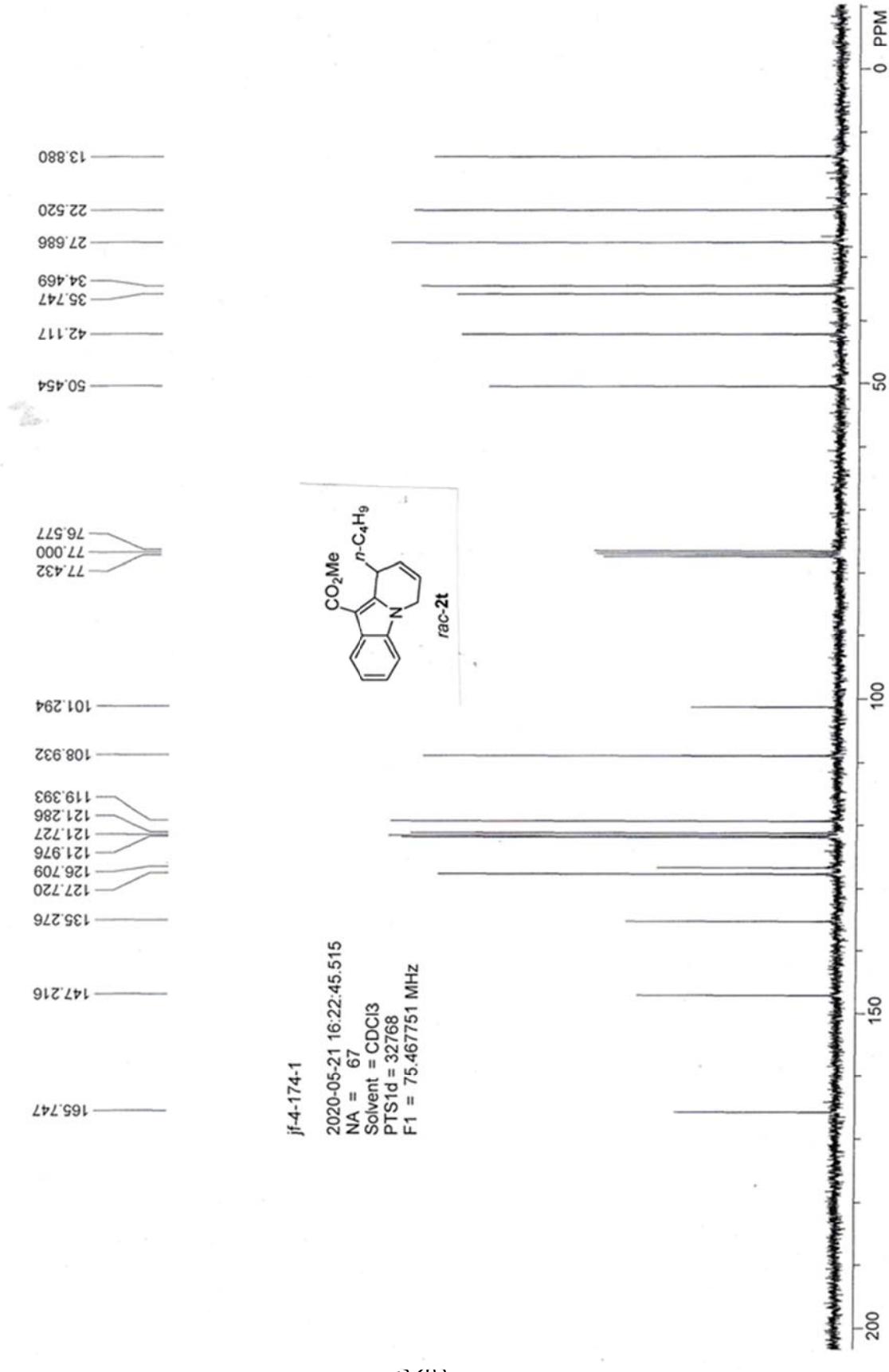


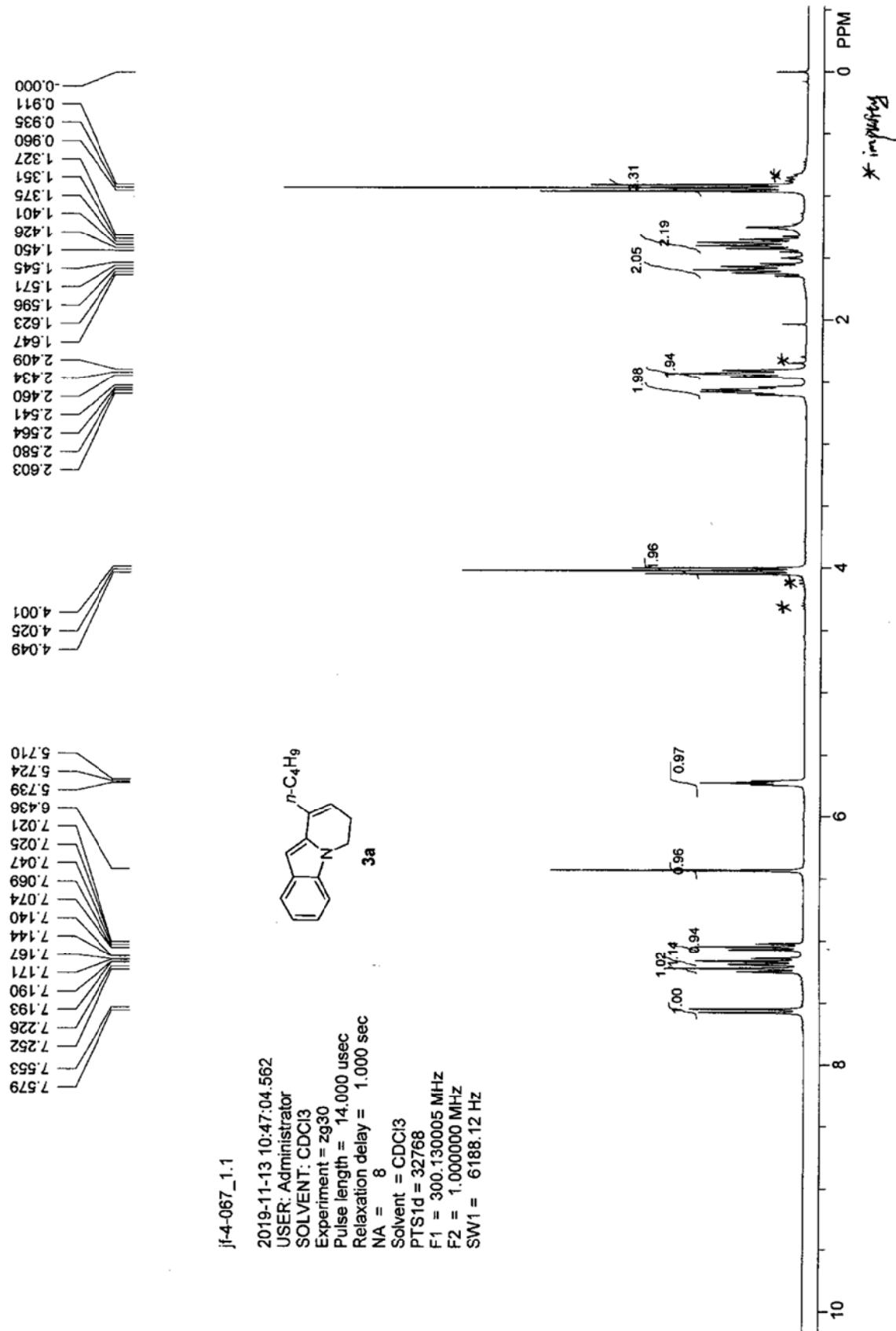


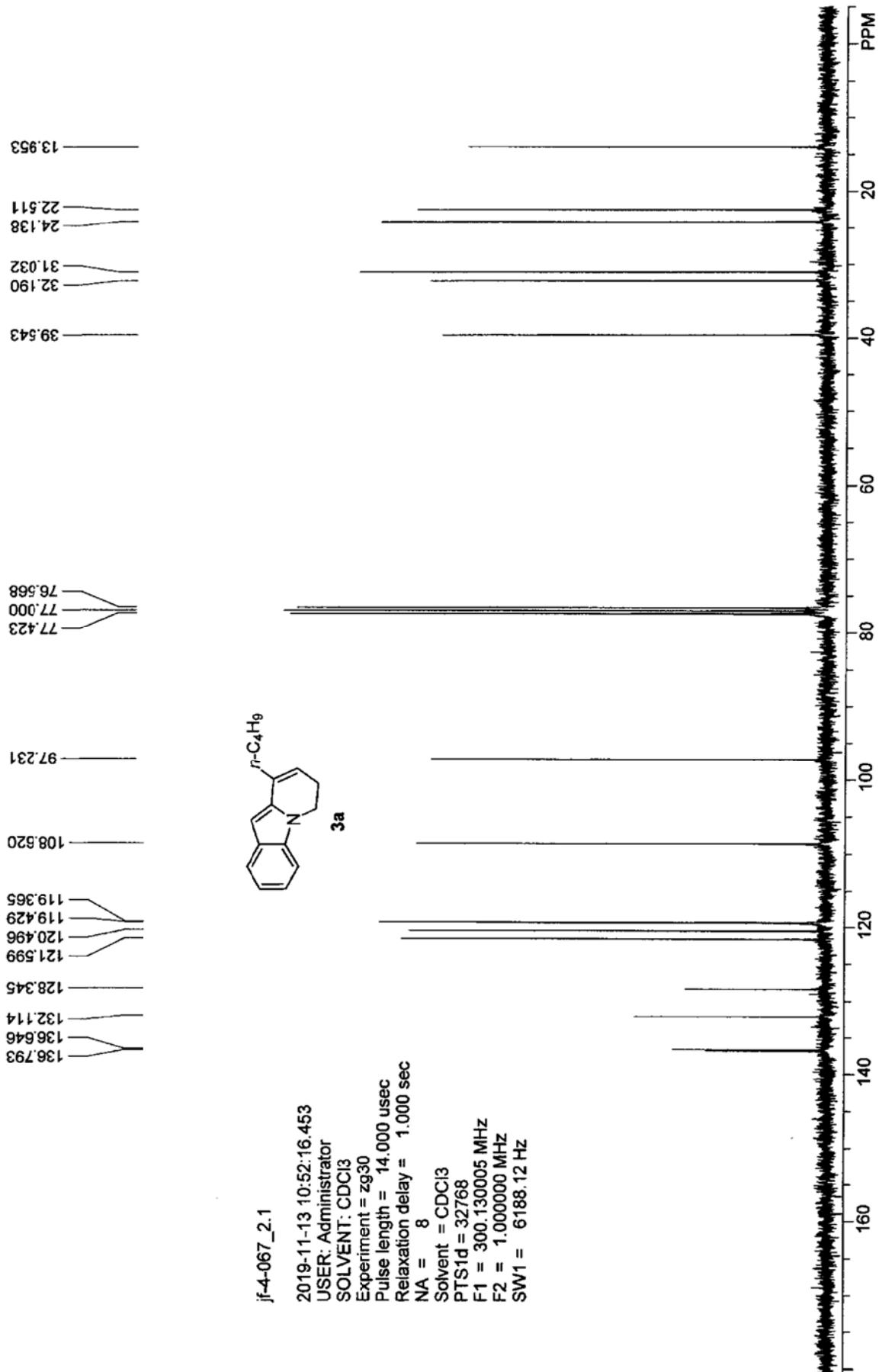


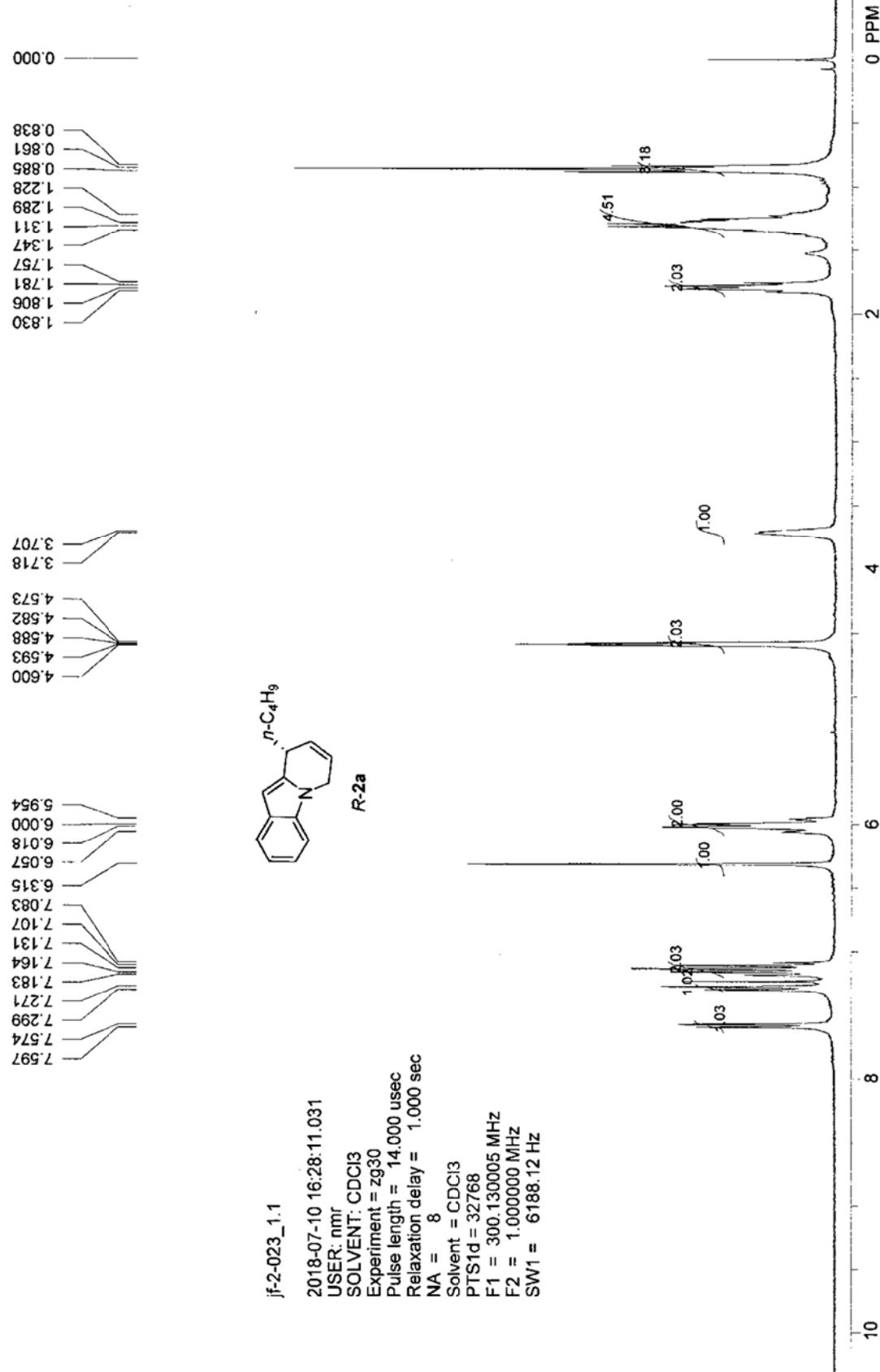


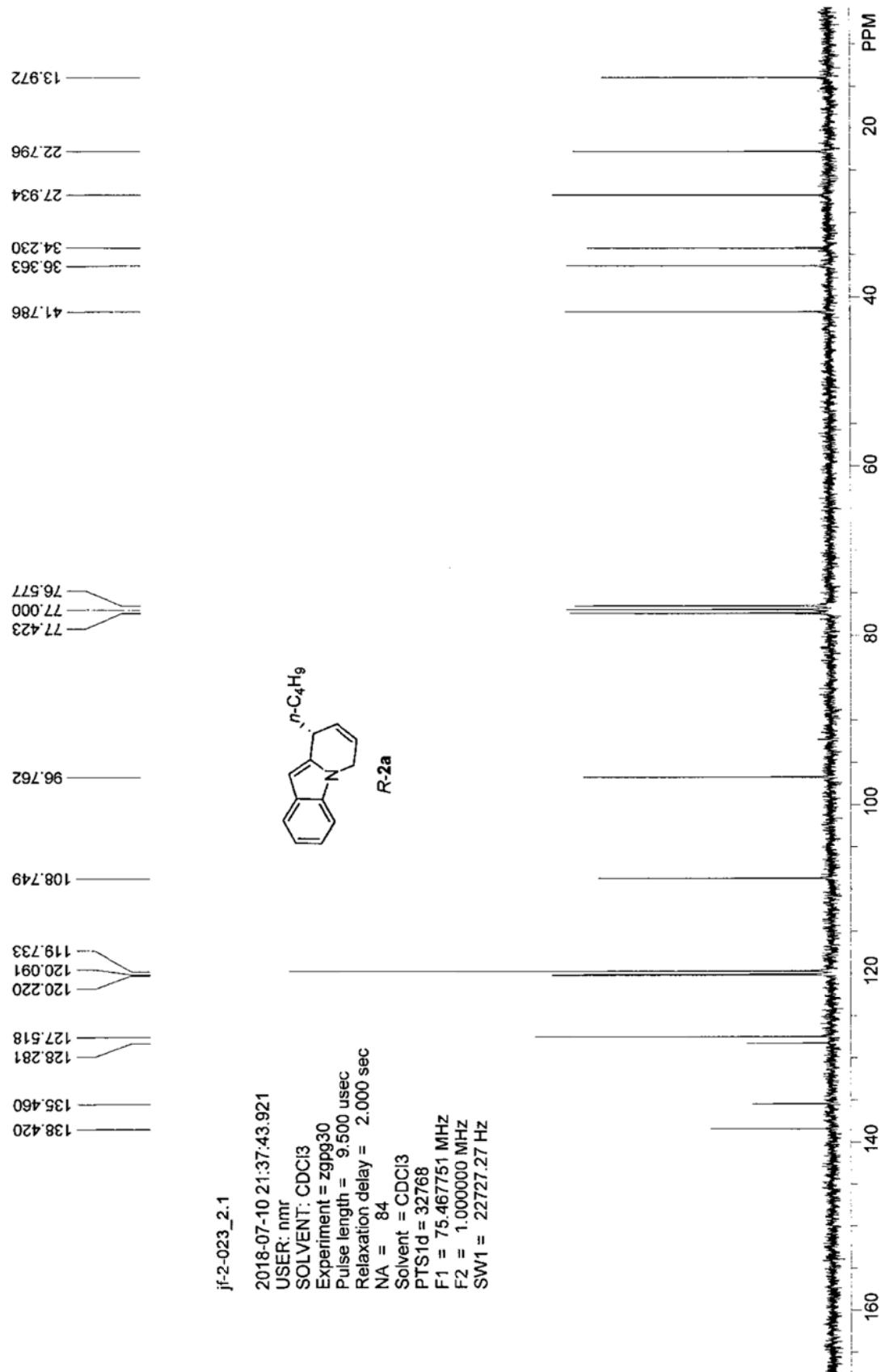
LUL









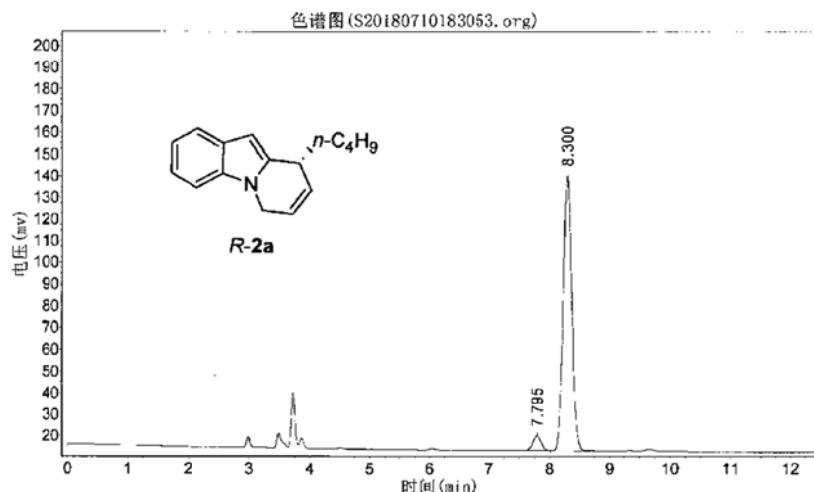


jf-2-023

实验时间: 2018-07-10, 18:30:53
谱图文件:D:\浙大智达\N2000\样品\S20180710183053.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jj'
报告时间: 2018-07-10, 20:22:38
积分方法: 面积归一法

实验内容简介:
od-II, n-hexane/i-PrOH = 100/1, 1, 214



分析结果表

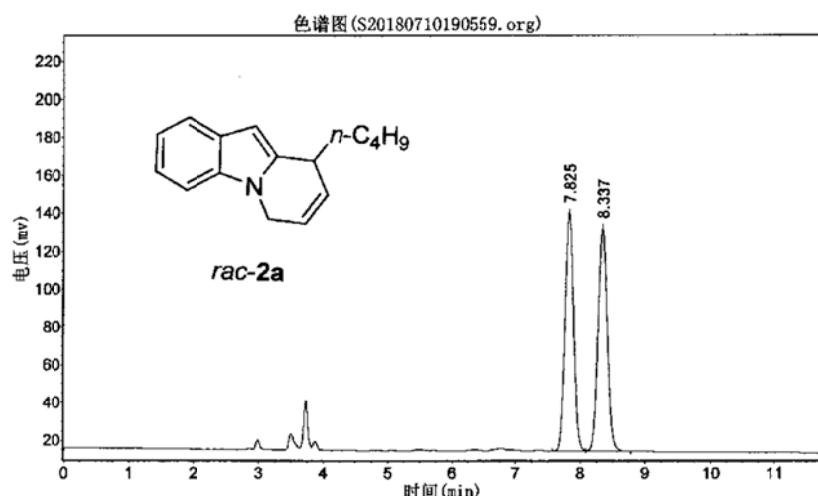
峰号	峰名	保留时间	峰高	峰面积	含量
1		7.795	6932.048	65231.785	4.9002
2		8.300	127378.266	1265982.375	95.0998
总计			134310.314	1331214.160	100.0000

jf-2-026

实验时间: 2018-07-10, 19:05:59
谱图文件:D:\浙大智达\N2000\样品\S20180710190559.org
方法文件:D:\浙大智达\N2000\djx.mtd

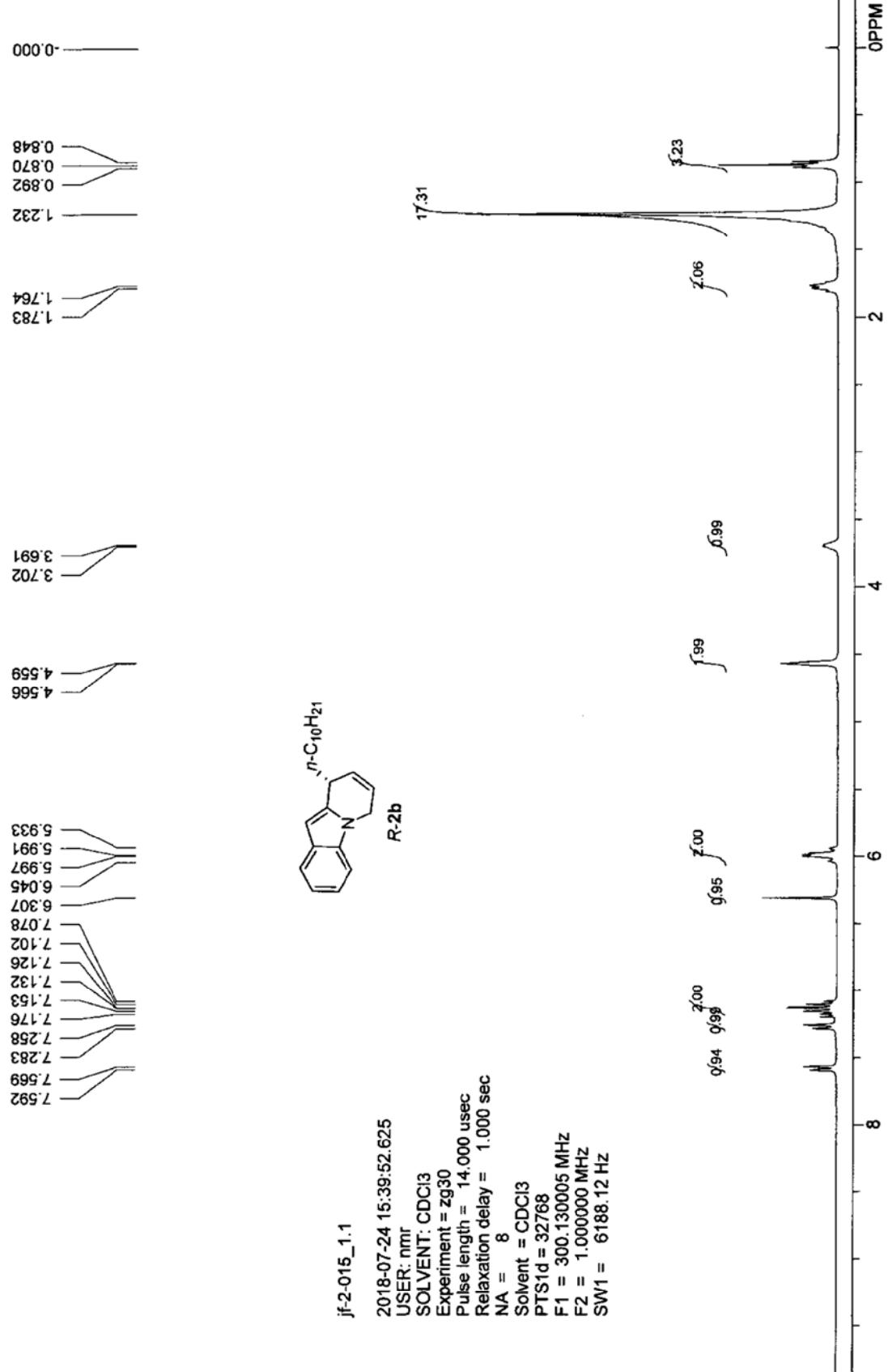
实验者: jf
报告时间: 2018-07-10, 20:25:19
积分方法: 面积归一法

实验内容简介:
od-³H, n-hexane/i-PrOH = 100/1, 1, 214



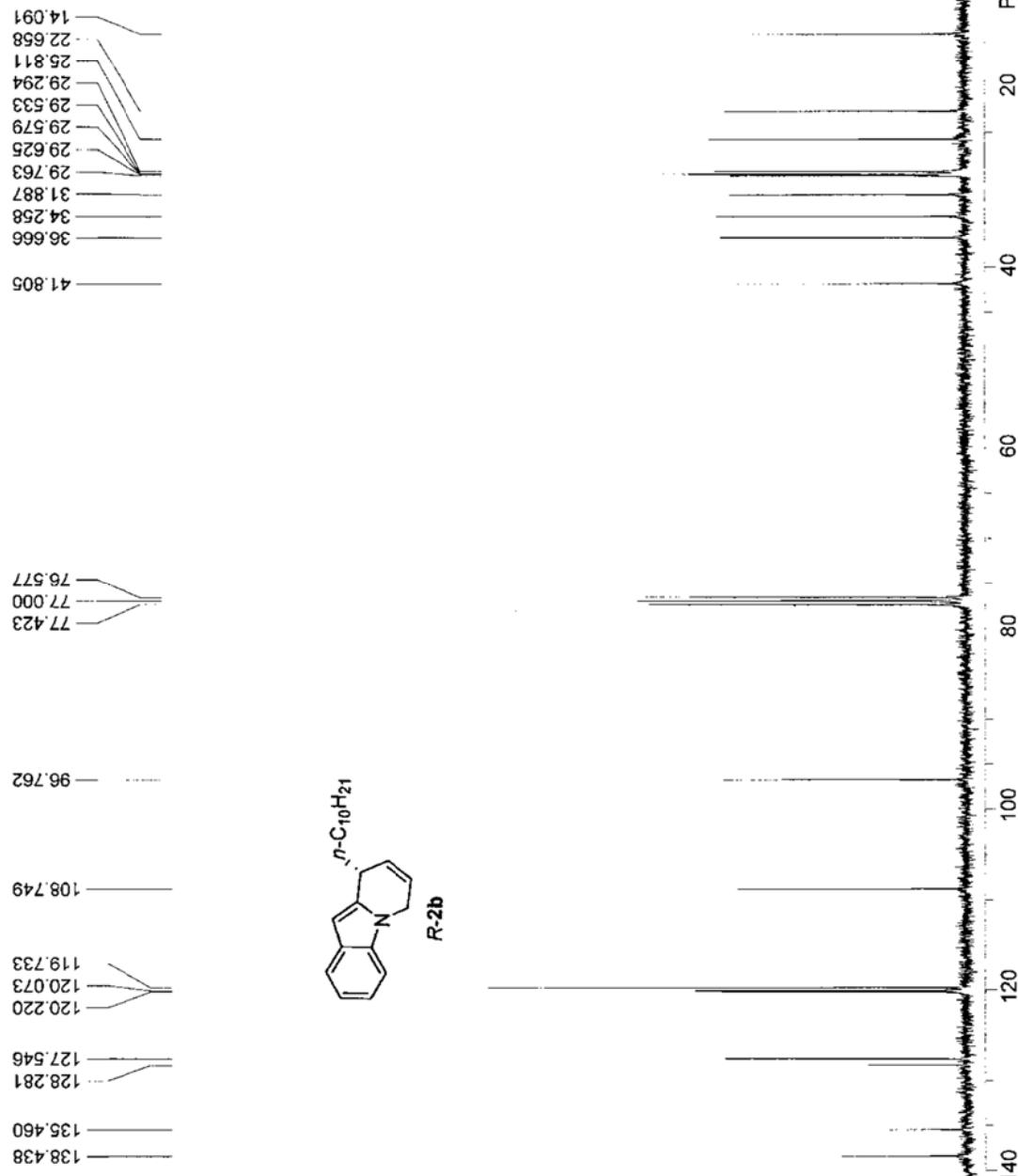
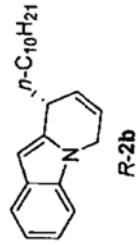
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		7.825	126056.820	1159691.750	49.7334
2		8.337	117834.695	1172125.375	50.2666
总计			243891.516	2331817.125	100.0000



jf2-015_2.1

2018-07-24 15:54:39.421
USER: nmr
SOLVENT: CDCl₃
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 145
Solvent = CDCl₃
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

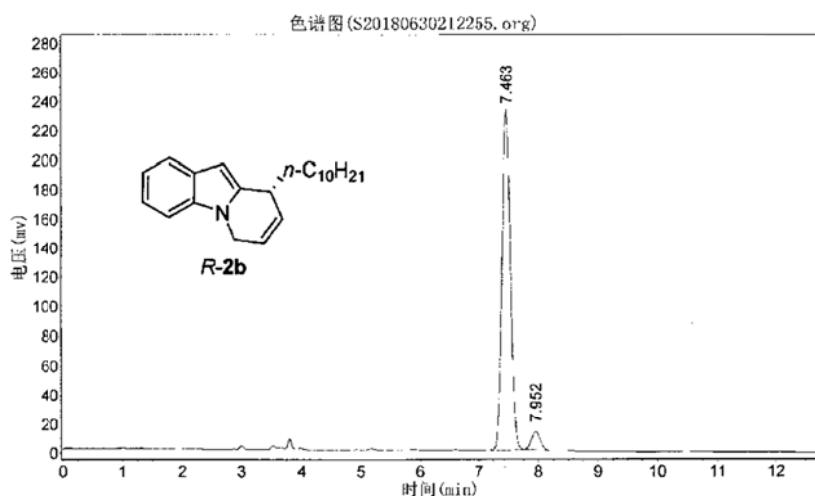


jf-2-015

实验时间: 2018-06-30, 21:22:55
谱图文件:D:\浙大智达\N2000\样品\S20180630212255.org
方法文件:D:\浙大智达\N2000\d.jx.mtd

实验者: jf
报告时间: 2018-06-30, 21:38:04
积分方法: 面积归一法

实验内容简介:
OD-H, n-hexane/i-PrOH = 100/1, 1.0, 214

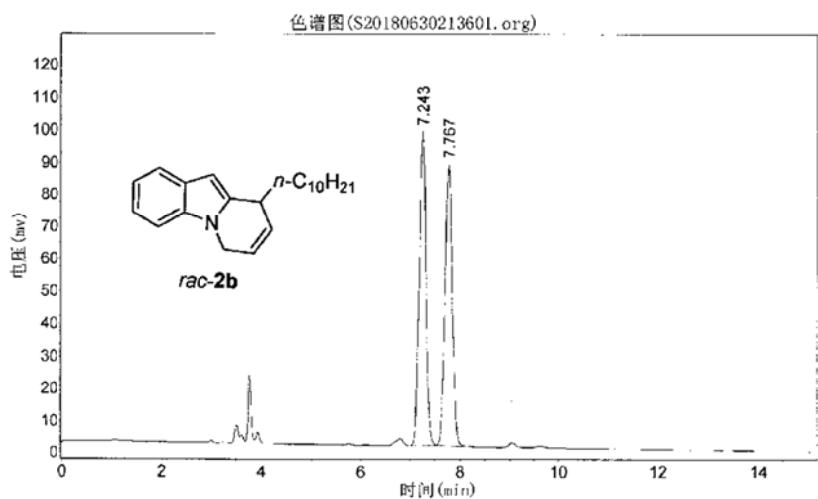


jf-2-012

实验时间: 2018-06-30, 21:36:01
谱图文件:D:\浙大智达\N2000\样品\S20180630213601.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2018-06-30, 21:52:50
积分方法: 面积归一法

实验内容简介:
OD-H, n-hexane/i-PrOH = 100/1, 1.0, 214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		7.243	96253.953	914269.875	50.4090
2		7.767	86400.266	899433.438	49.5910
总计			182654.219	1813703.313	100.0000

-0.000

1.240
1.363
1.745
1.766
1.791
1.813
1.981
2.004
2.029
2.051

3.699
3.711
4.4571
4.4578
4.4583
4.4898
4.4905
4.4932
4.4948
5.004
5.010
5.264
5.752
5.786
5.809
5.843
5.984
5.990
6.009
6.013
6.311
7.088
7.112
7.137
7.163
7.183
7.268
7.294
7.596
7.574

jf-2-066_1

2018-09-29 22:09:29.406

USER: nmr

SOLVENT: CDCl₃

Experiment = zg30

Pulse length = 14.000 usec

Relaxation delay = 1.000 sec

NA = 8

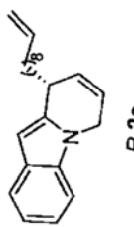
Solvent = CDCl₃

PTS1d = 32768

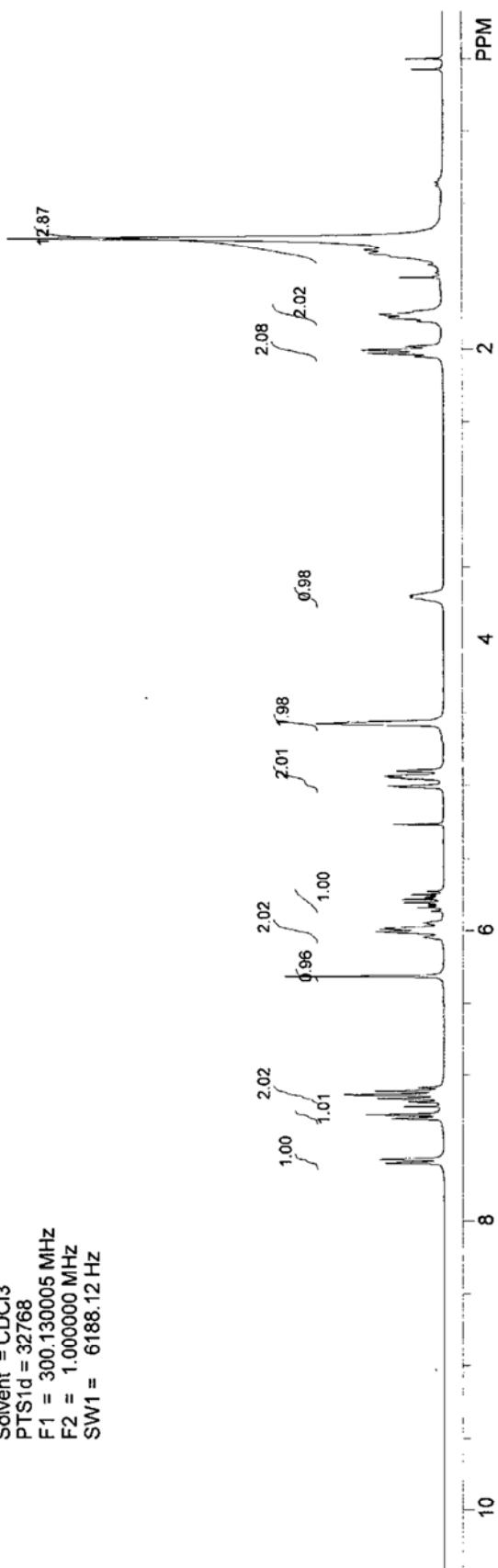
F1 = 300.130005 MHz

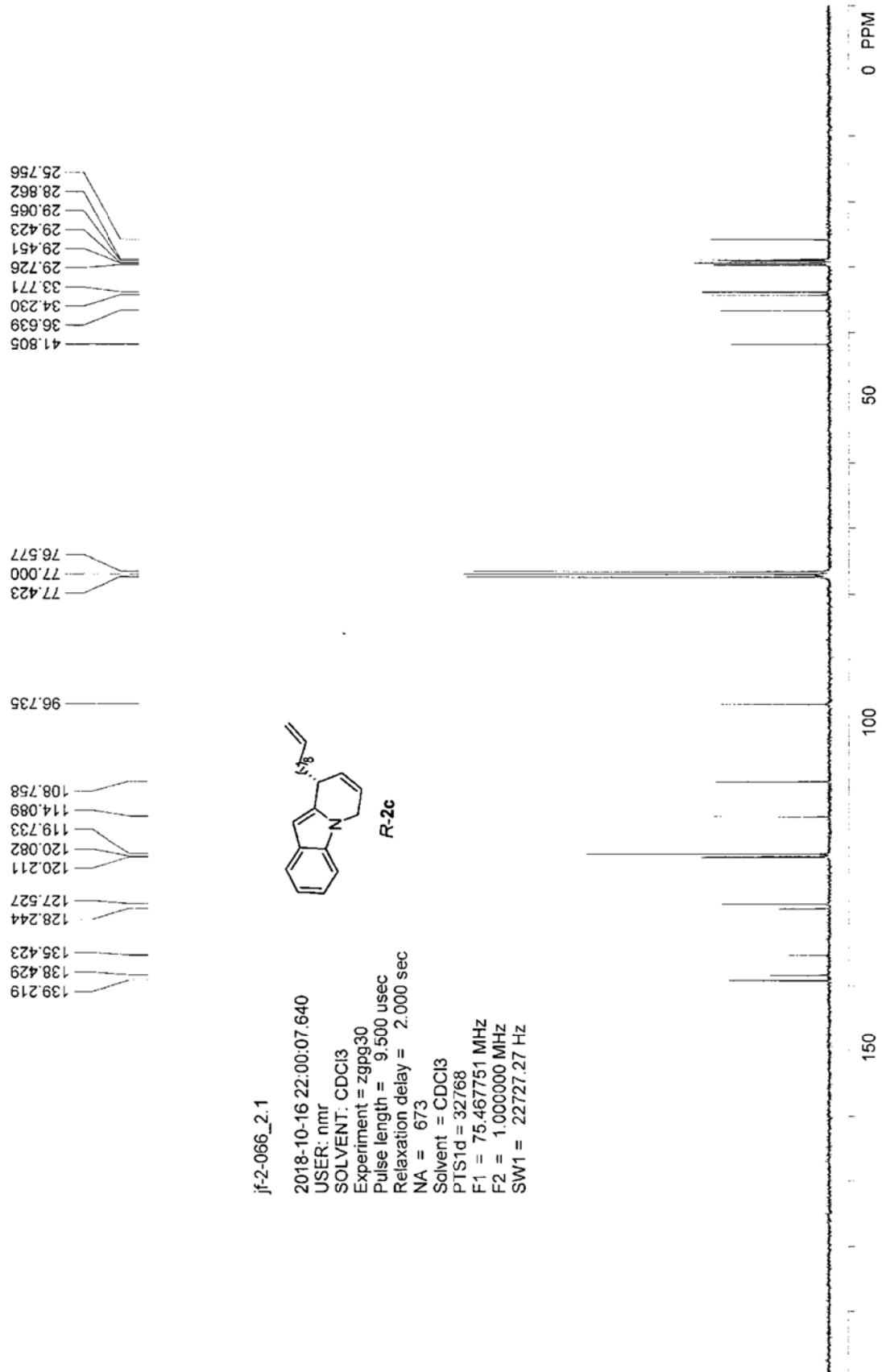
F2 = 1.000000 MHz

SW1 = 6188.12 Hz



R-2c



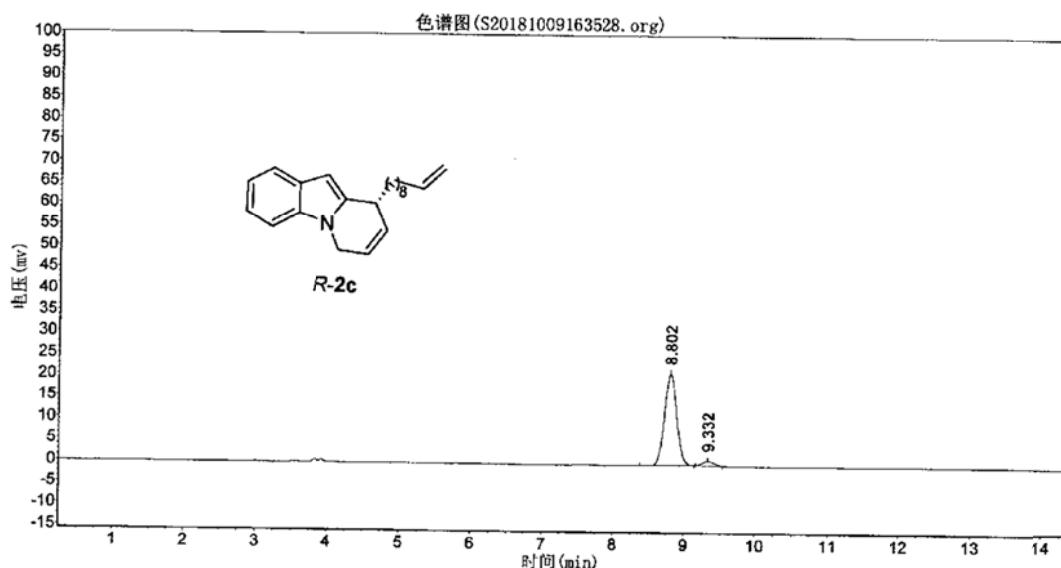


jf-2-066

实验时间: 2018-10-09, 16:35:28
谱图文件:D:\浙大智达\N2000\样品\S20181009163528.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-11-13, 15:21:41
积分方法: 面积归一法

实验内容简介:
od-H, n-hexane/i-PrOH = 100/1, 1.0, 214



分析结果表

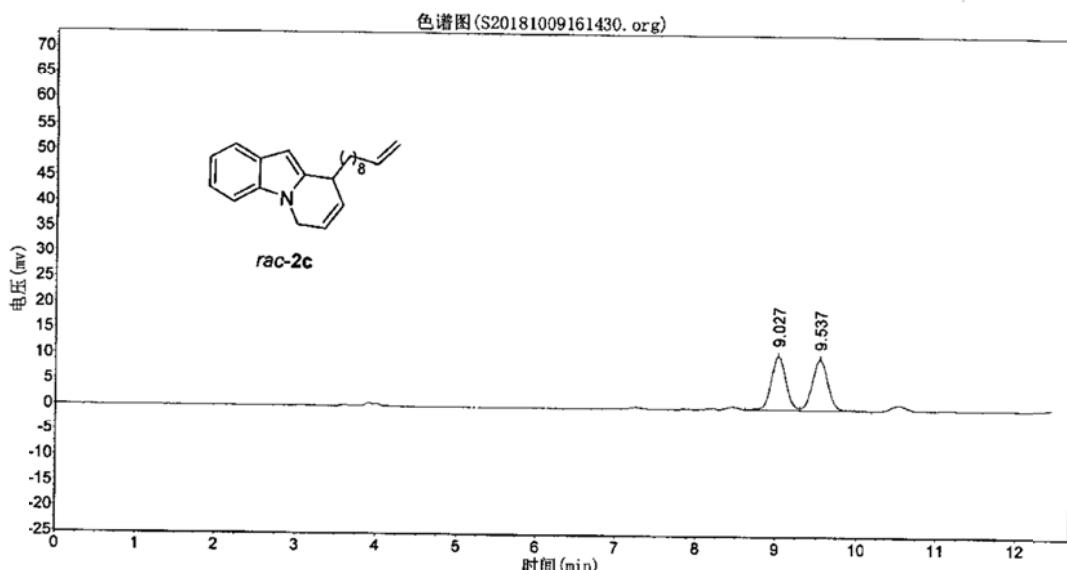
峰号	峰名	保留时间	峰高	峰面积	含量
1		8.802	21281.363	255511.766	95.8335
2		9.332	986.432	11108.700	4.1665
总计			22267.796	266620.466	100.0000

jf-2-037

实验时间: 2018-10-09, 16:14:30
谱图文件:D:\浙大智达\N2000\样品\S20181009161430.org
方法文件:D:\浙大智达\N2000\djx.mtd

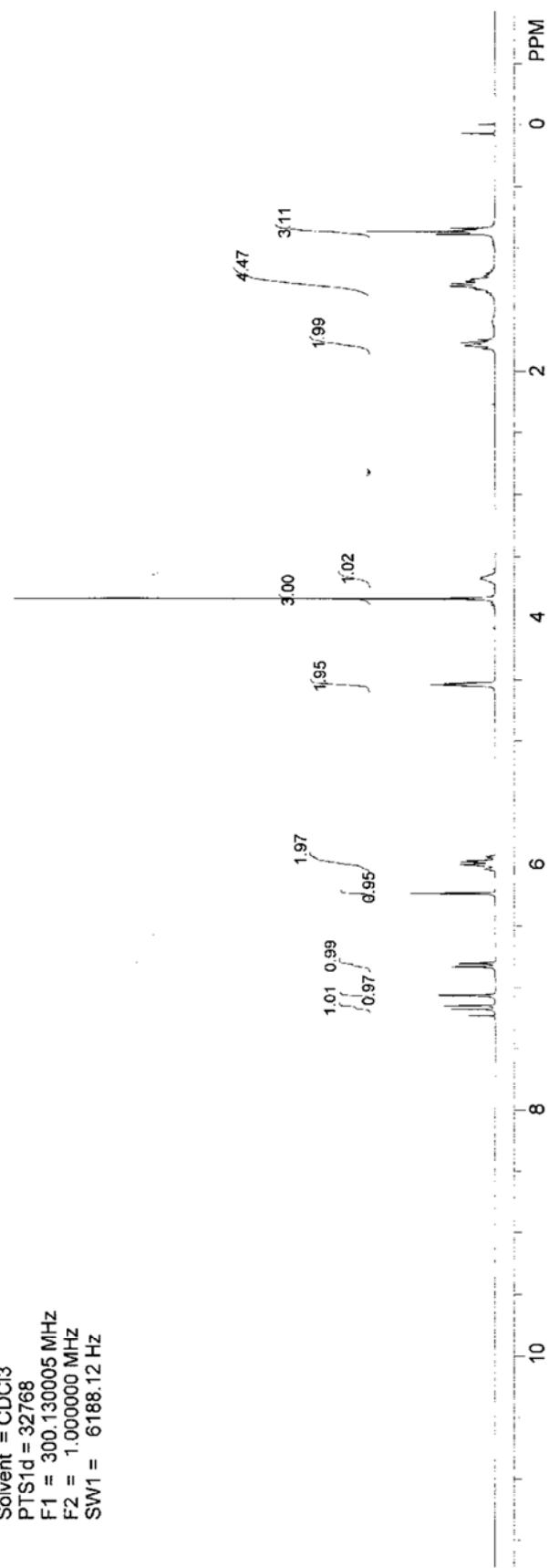
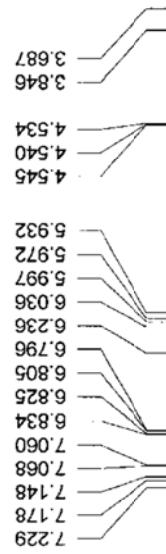
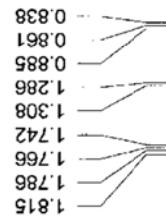
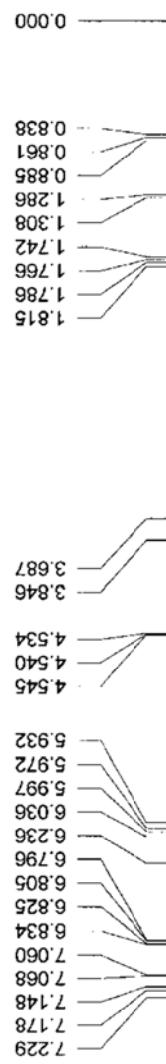
实验者: Jf
报告时间: 2019-11-13, 15:25:18
积分方法: 面积归一法

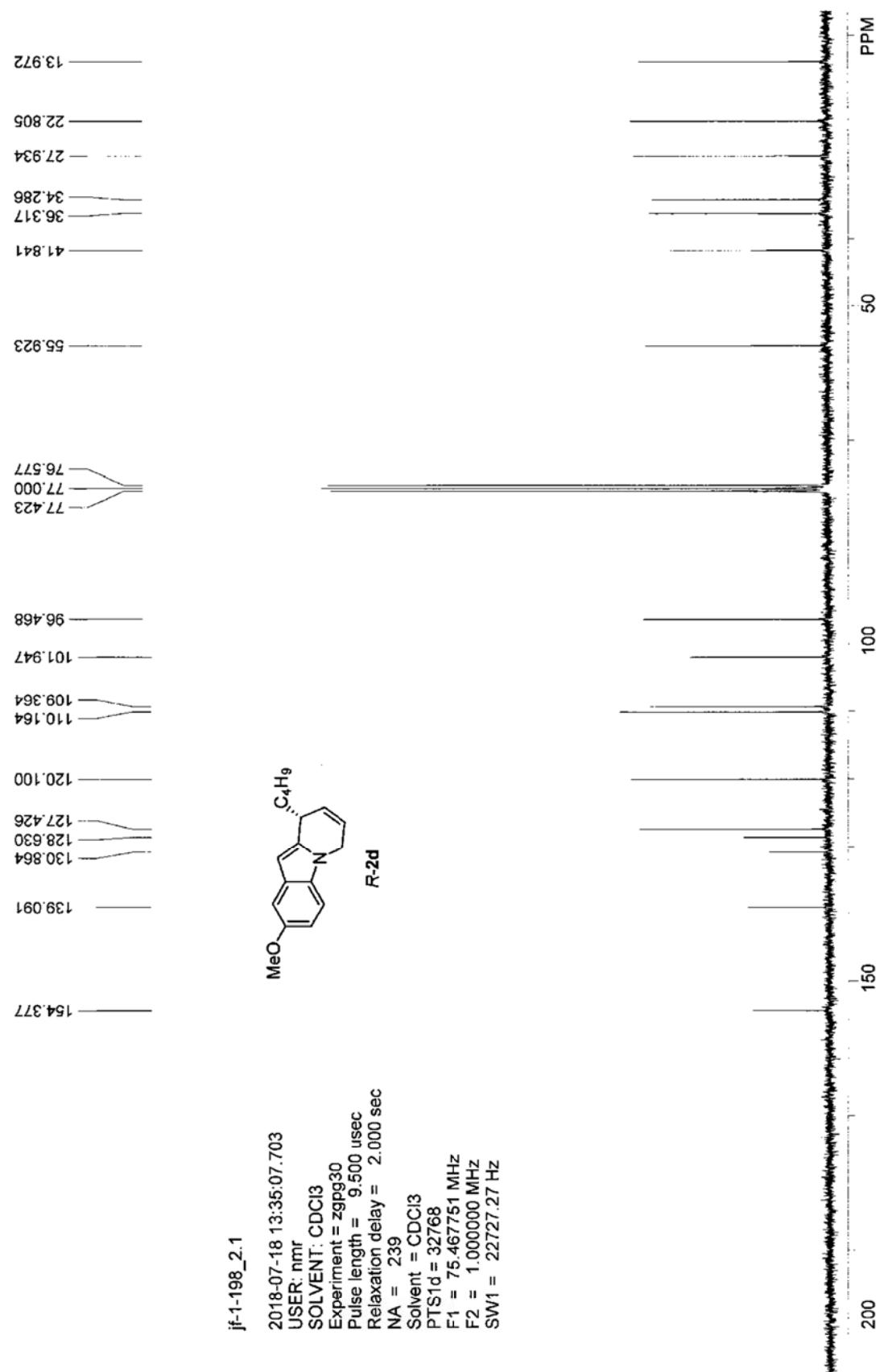
实验内容简介:
od-H, n-hexane/i-PrOH = 100/1, 1.0, 214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		9.027	10504.213	131674.938	49.6421
2		9.537	9912.612	133573.734	50.3579
总计			20416.825	265248.672	100.0000

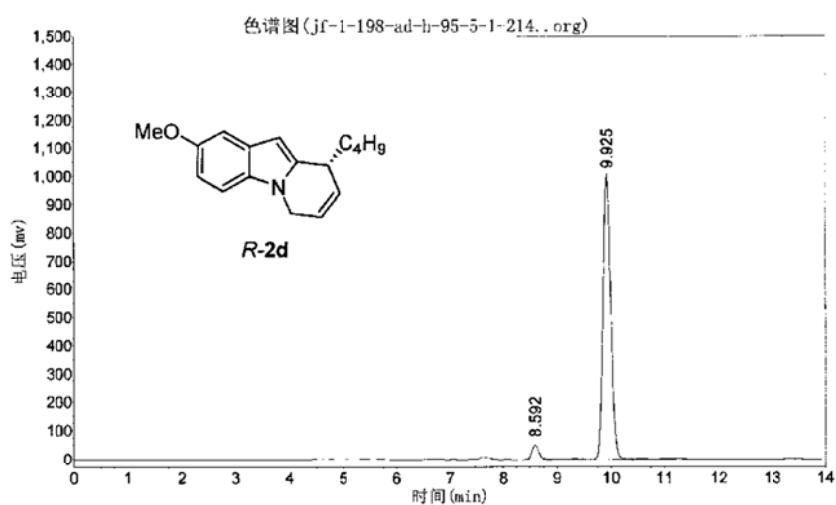




jf-1-198-ad-h-95-5-1-214

实验时间: 2018-06-21, 12:30:06
报告时间: 2018-06-21, 18:29:25
谱图文件:D:\zhuguangjiong\jf\20180621\jf-1-198-ad-h-95-5-1-
214..org

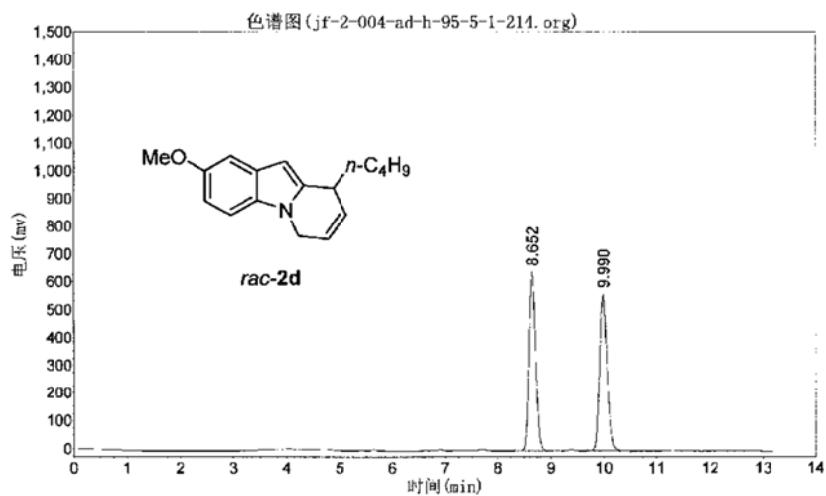
实验内容简介:



jf-2-004-ad-h-95-5-1-214

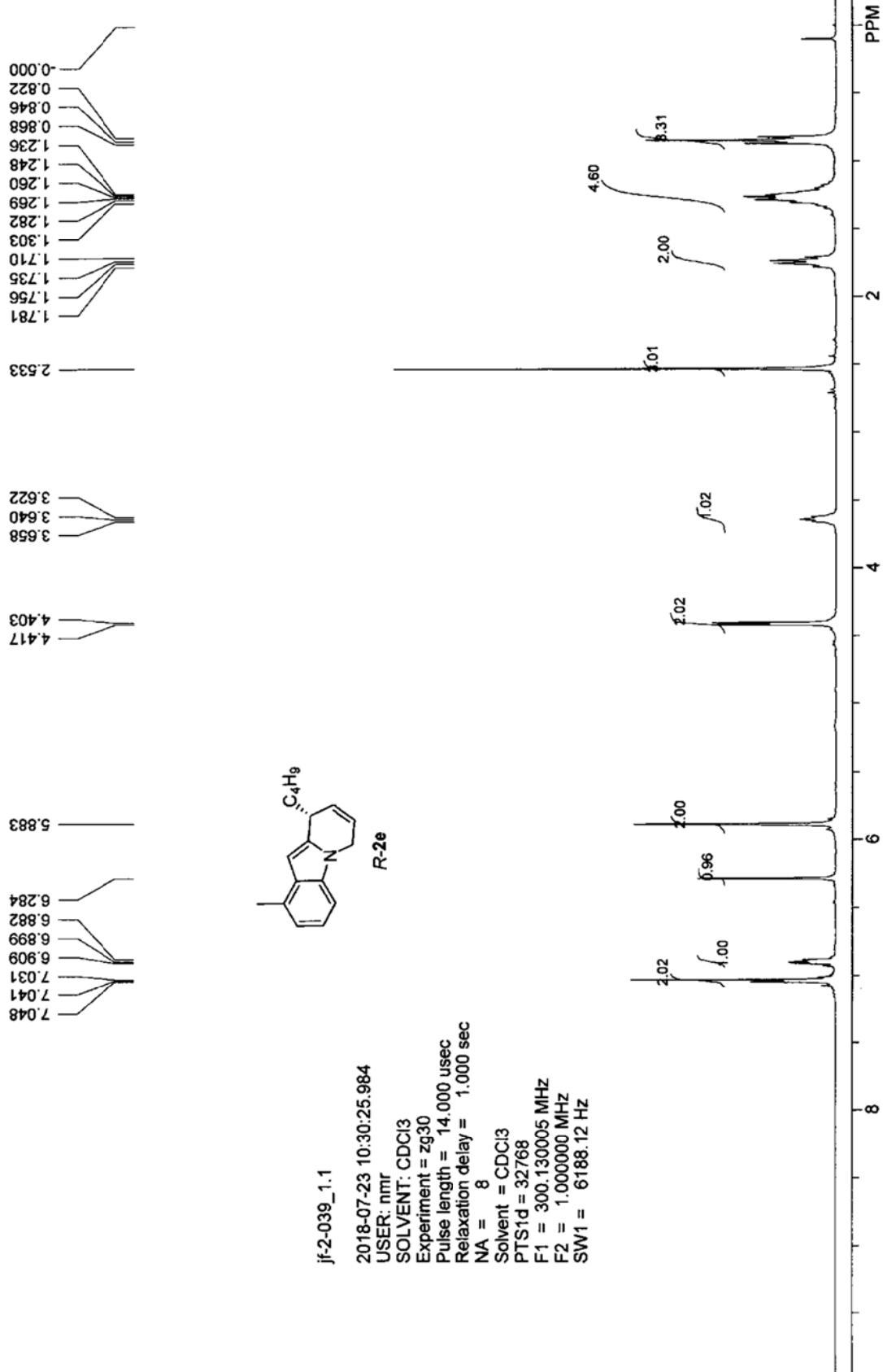
实验时间: 2018-06-21 11:24:11
报告时间: 2018-06-21 18:30:38
谱图文件:D:\zhuguangjiong\jf\20180621\jf-2-004-ad-h-95-5-1-
214.org

实验内容简介:



分析结果表

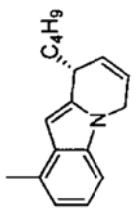
峰号	峰名	保留时间	峰高	峰面积	含量
1		8.652	637217.875	5573784.500	50.2454
2		9.990	557189.375	5519331.500	49.7546
总计			1194407.250	11093116.000	100.0000





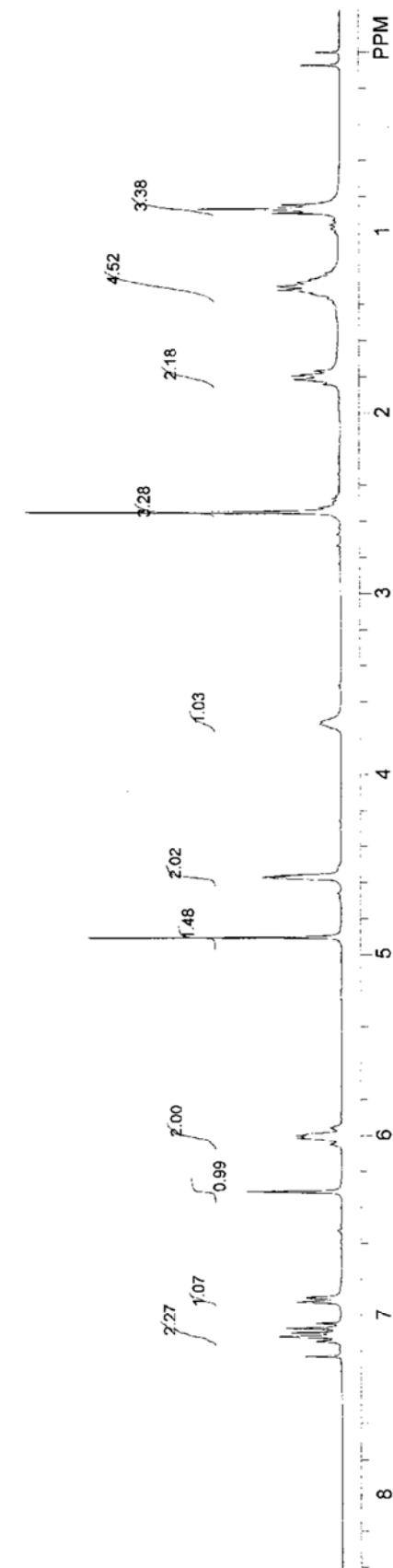
jif-2-039chundu_1.1

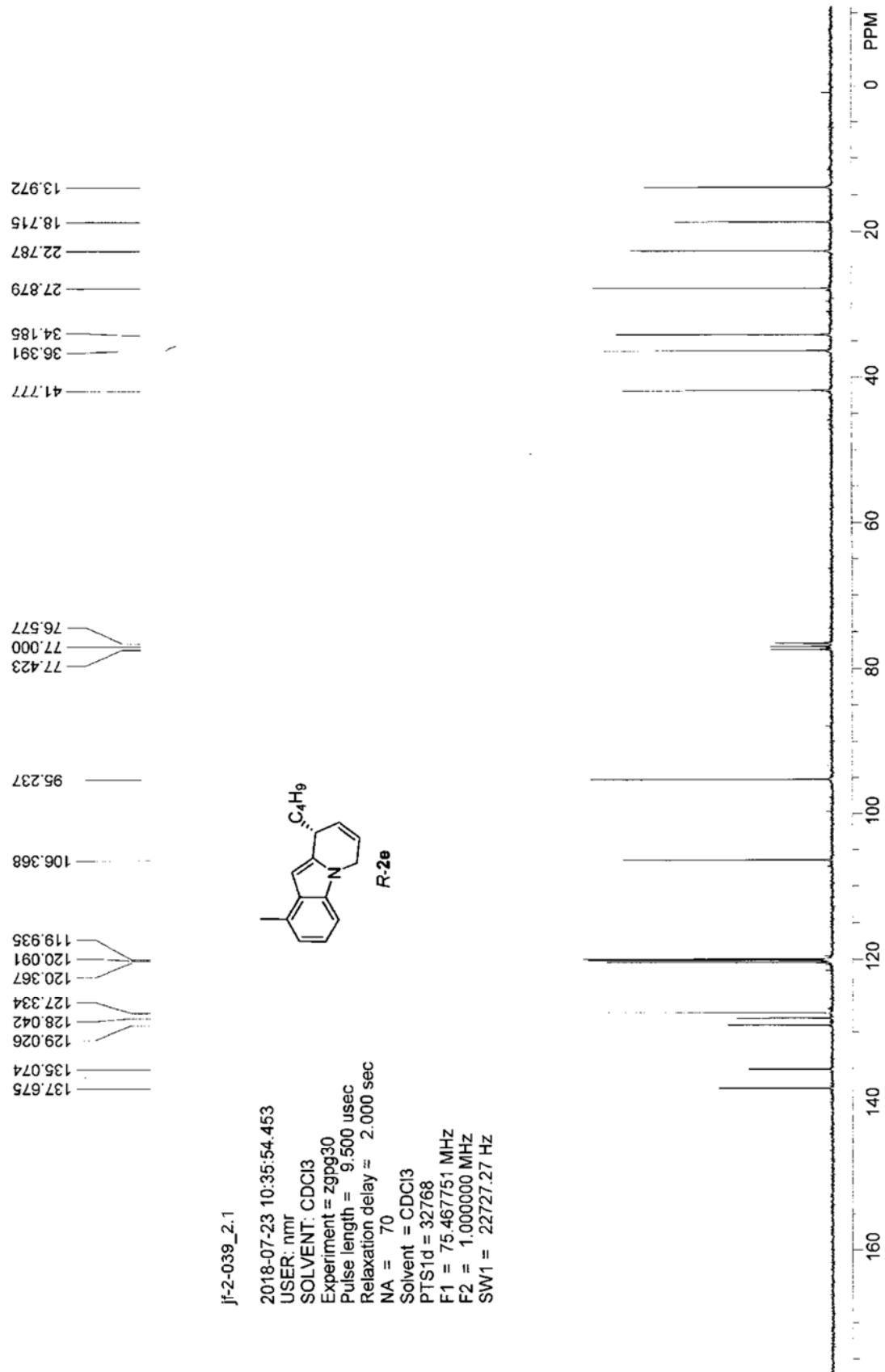
2018-09-02 14:08:11.828
 USER: nmr
 SOLVENT: CDCl₃
 Experiment = zg30
 Pulse length = 14.000 us
 Relaxation delay = 1.0000
 NA = 8
 Solvent = CDCl₃
 PTS1d = 32768
 F1 = 300.130005 MHz
 F2 = 1.000000 MHz
 SW1 = 6188.12 Hz



R-2e

Purity (91%) is determined by dibromomethane ($10 \mu\text{l}$, 0.29 mmol) as the internal standard in 50.8 mg of sample





jf-2-039-o j-h-95-5-0.6-214

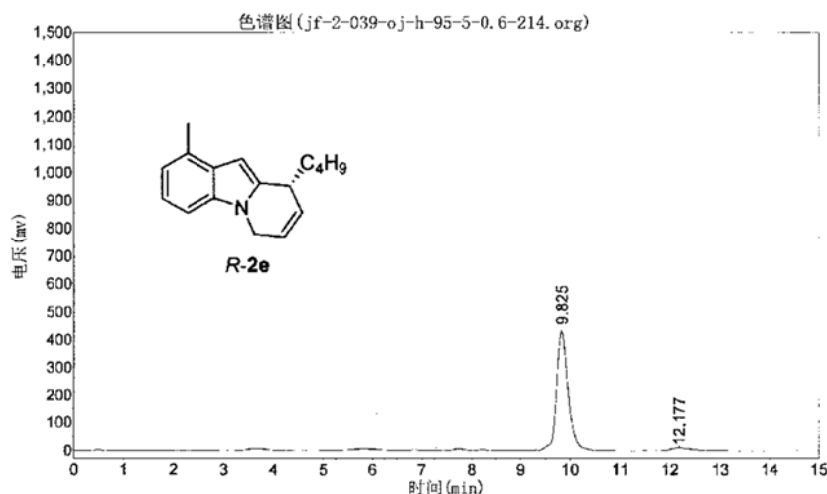
实验时间: 2018-07-23, 17:35:11

报告时间: 2018-07-23, 18:57:18

谱图文件:D:\zhuguangjiong\jf\20180723\jf-2-039-o j-h-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		9.825	429159.875	7128186.000	94.8342
2		12.177	10283.476	388289.844	5.1658
总计			439443.351	7516475.844	100.0000

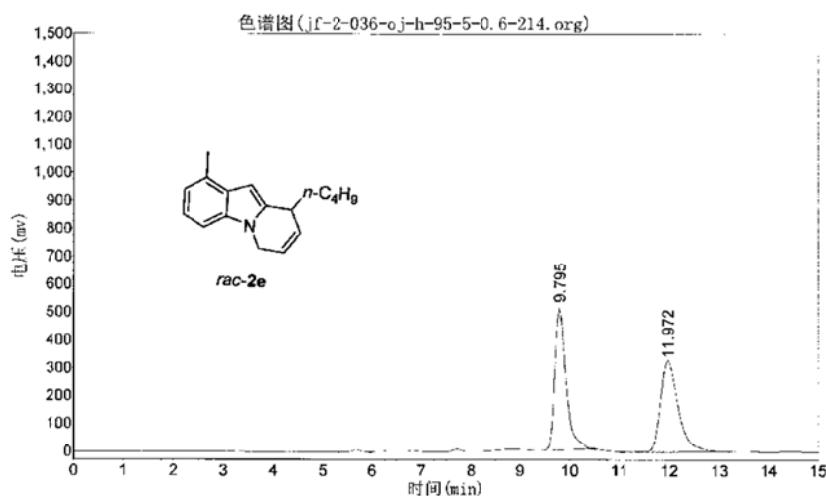
jf-2-036-oj-h-95-5-0.6-214

实验时间: 2018-07-23, 17:03:03

谱图文件:D:\zhuguangjióng\jf\20180723\jf-2-036-oj-h-95-5-0.6-214.org

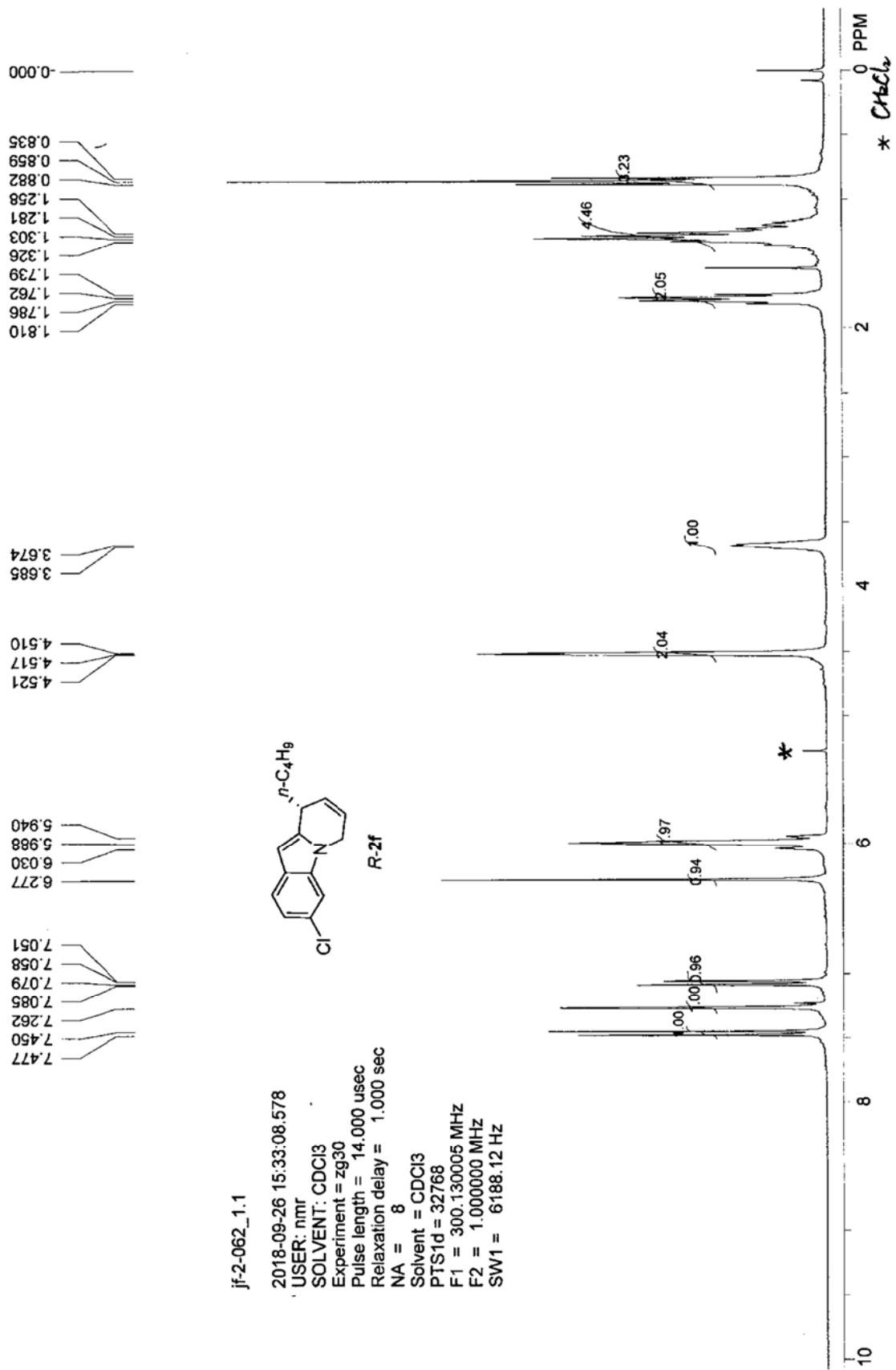
报告时间: 2018-07-23, 18:56:23

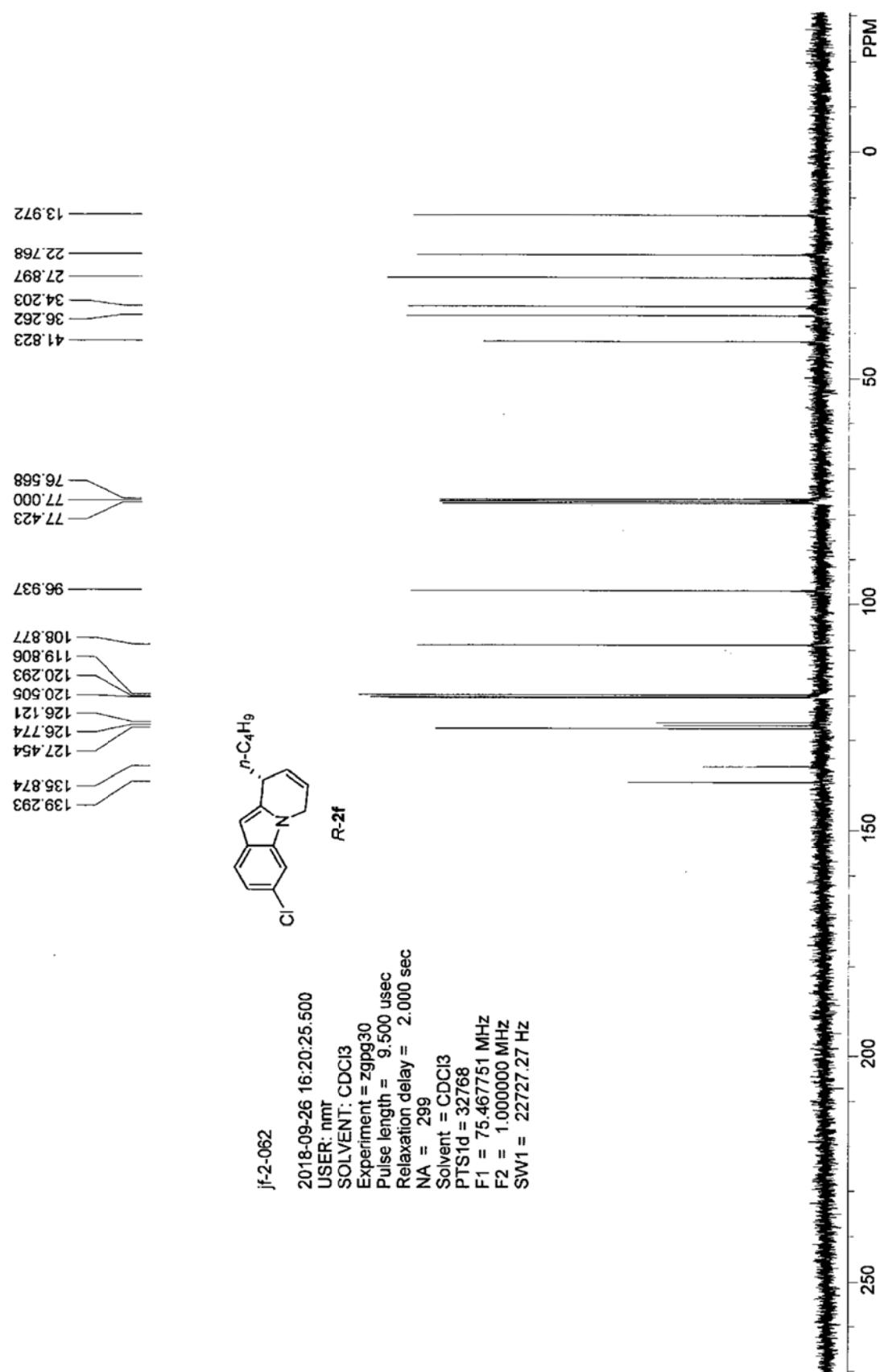
实验内容简介:



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		9.795	500864.156	7928337.500	50.0015
2		11.972	326163.969	7927857.000	49.9985
总计			827028.125	15856194.500	100.0000



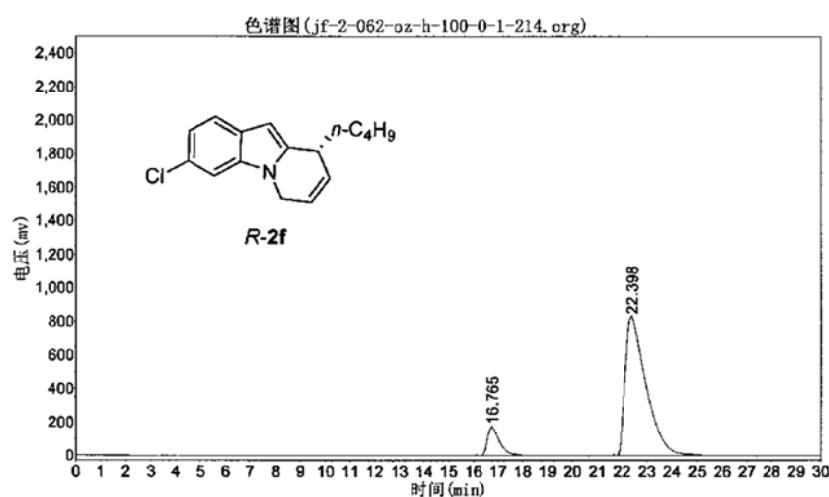


jf-2-062-oz-h-100-0-1-214

实验时间: 2018-09-29, 16:01:09
谱图文件:D:\zhuguangjiong\jf\20180929\jf-2-062-oz-h-100-0-1-214.org

报告时间: 2018-09-29, 18:22:17

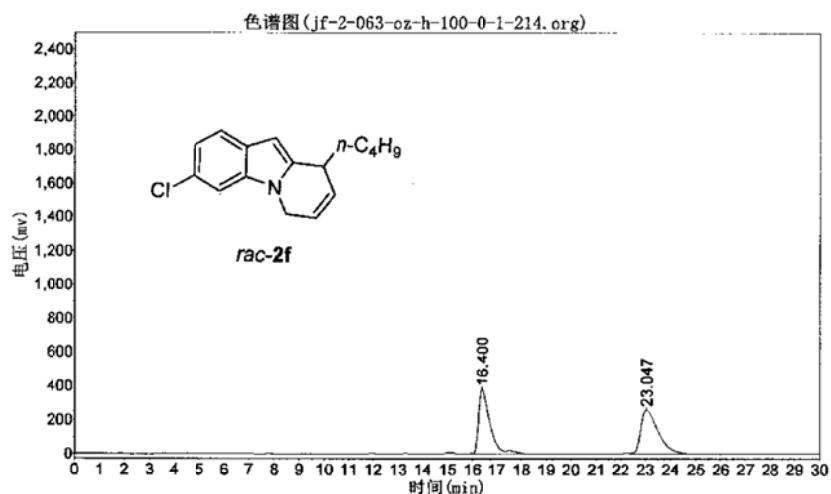
实验内容简介:



jf-2-063-oz-h-100-0-1-214

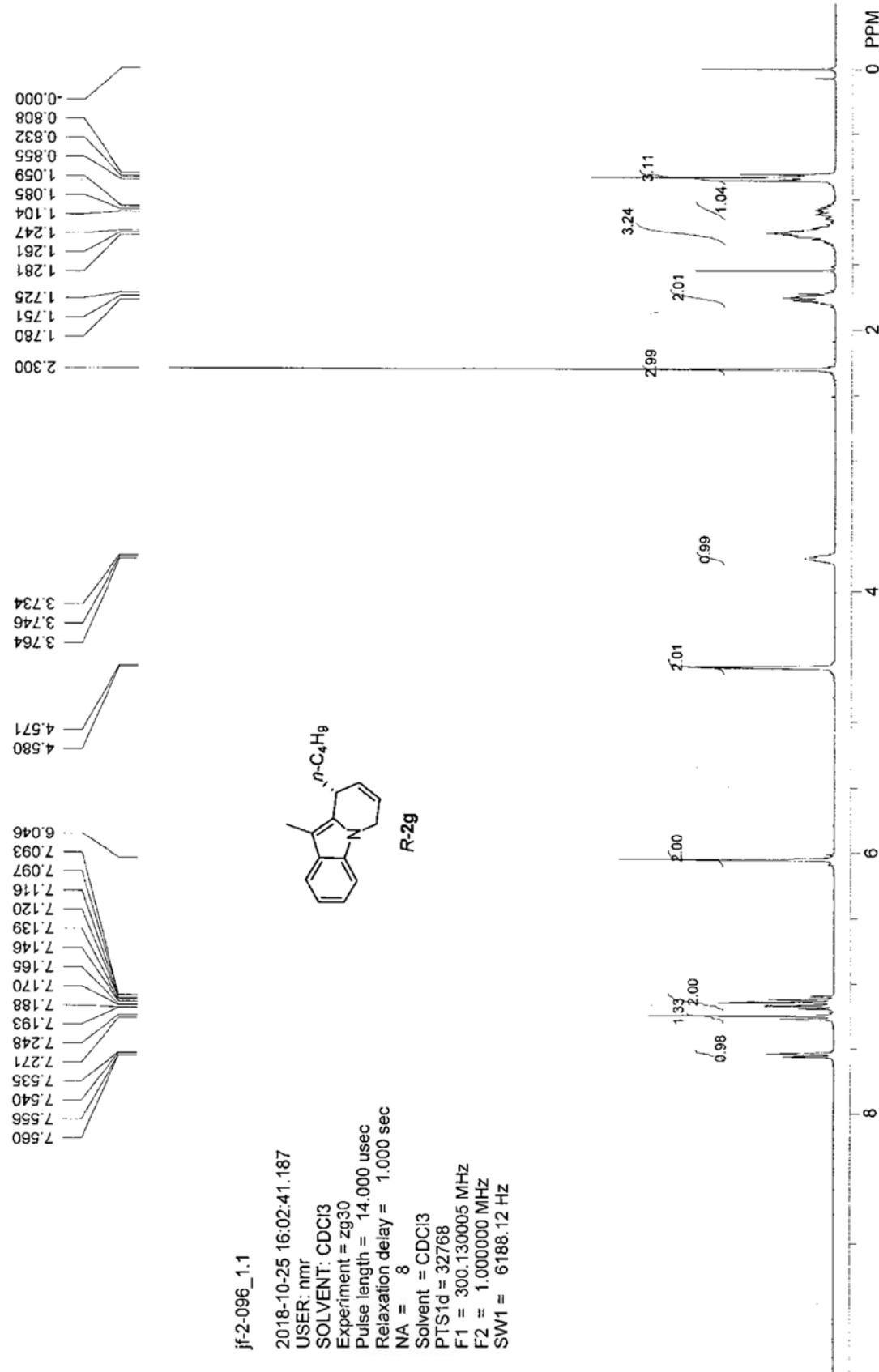
实验时间: 2018-09-29, 15:26:45
报告时间: 2018-09-29, 18:21:41
谱图文件:D:\zhuguangjiong\jf\20180929\jf-2-063-oz-h-100-0-1-
214.org

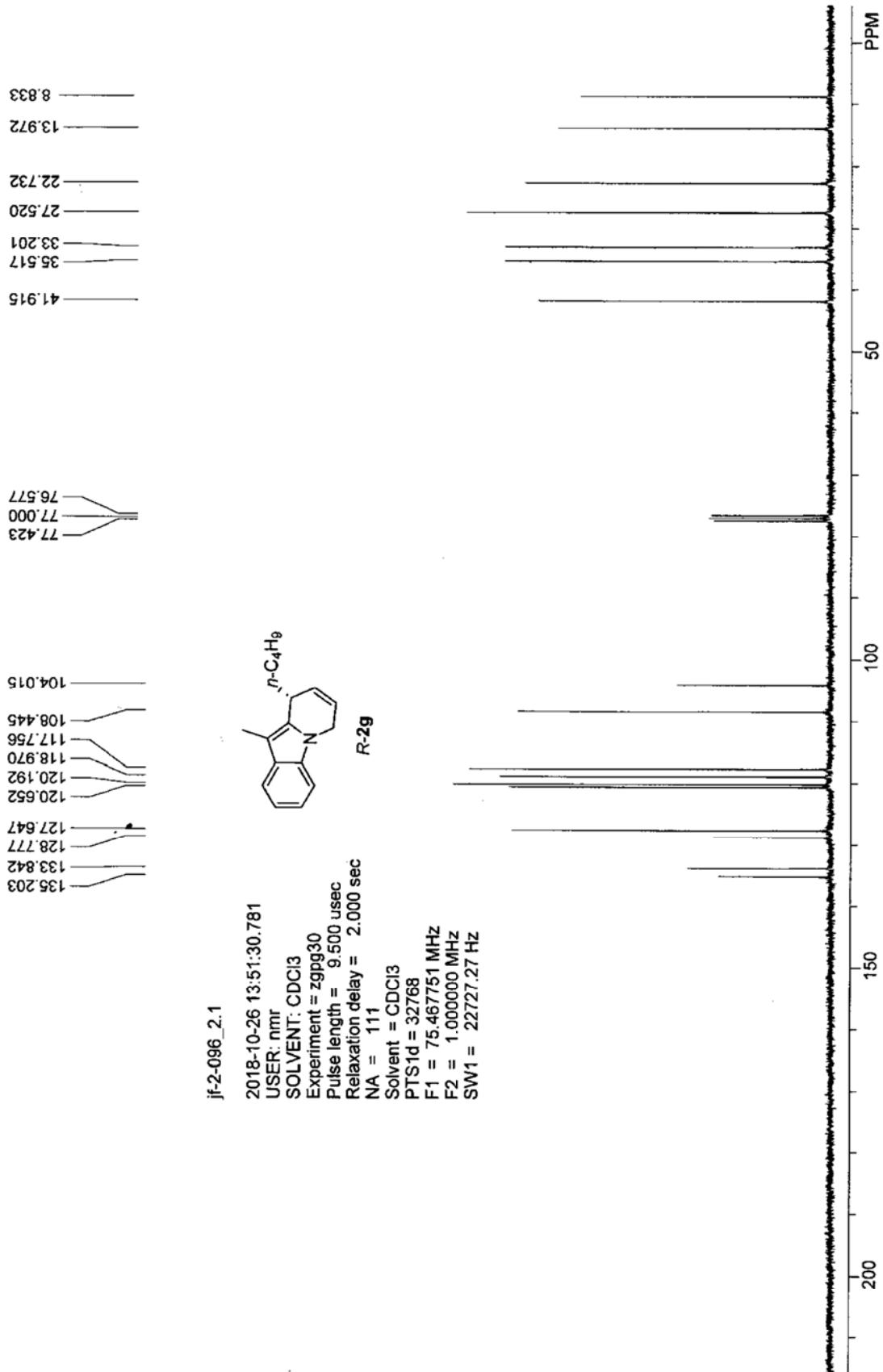
实验内容简介:



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.400	382431.438	12647115.000	50.0486
2		23.047	261258.469	12622542.000	49.9514
总计			643689.906	25269657.000	100.0000



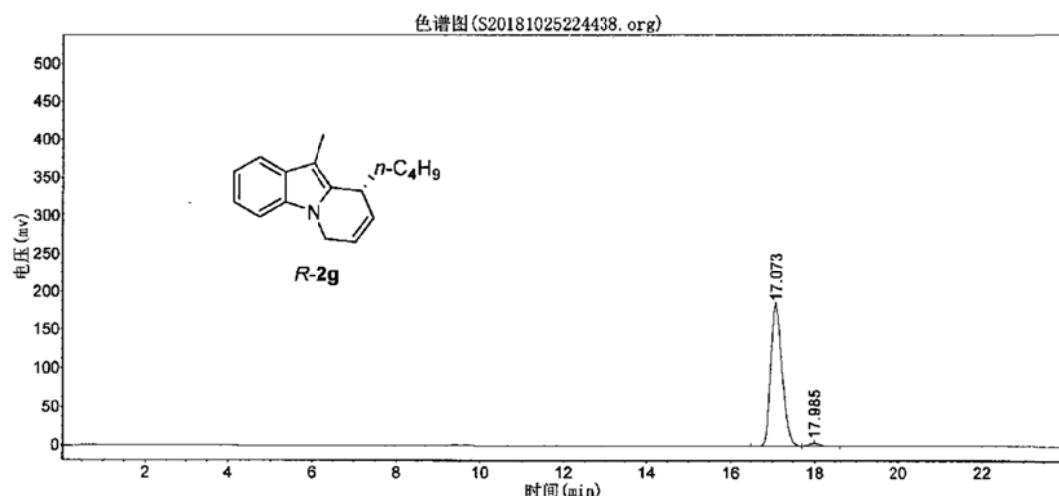


jf-2-096

实验时间: 2018-10-25, 22:44:38
谱图文件:D:\浙大智达\N2000\样品\S20181025224438.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-11-13, 21:41:11
积分方法: 面积归一法

实验内容简介:
od-l, n-hexane/i-PrOH = 100/1, 0. 4, 254



分析结果表

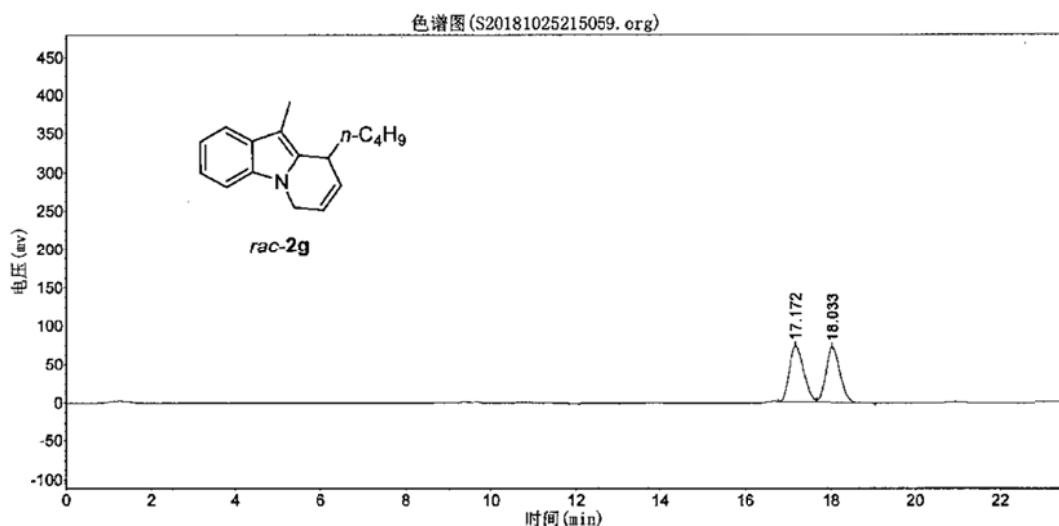
峰号	峰名	保留时间	峰高	峰面积	含量
1		17.073	182440.531	3464835.250	98.1705
2		17.985	3529.913	64571.457	1.8295
总计			185970.445	3529406.707	100.0000

jf-2-097

实验时间: 2018-10-25, 21:50:59
谱图文件:D:\浙大智达\N2000\样品\S20181025215059.org
方法文件:D:\浙大智达\N2000\djx.mtd

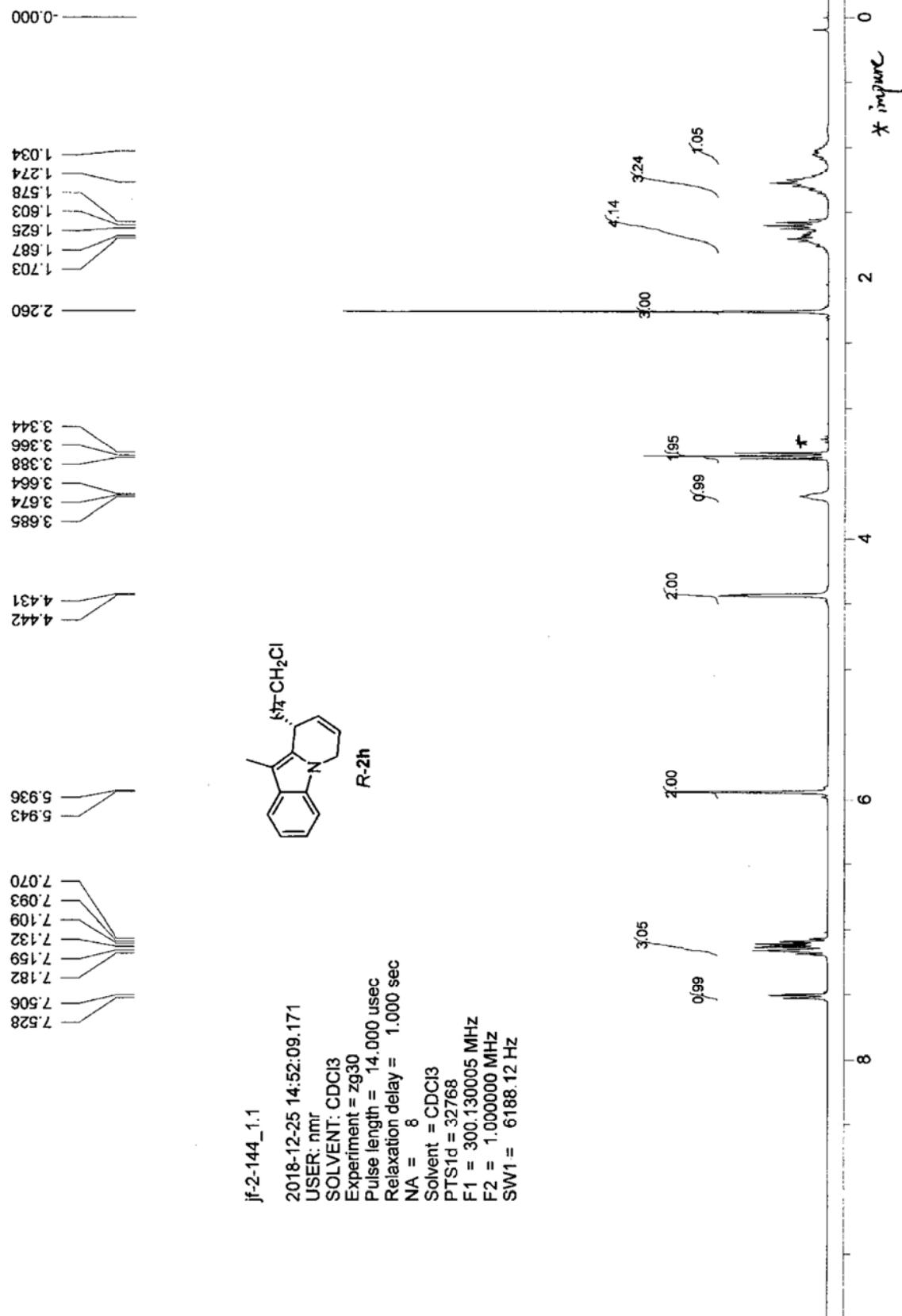
实验者: jf
报告时间: 2019-11-13, 21:45:25
积分方法: 面积归一法

实验内容简介:
od-II, n-hexane/i-PrOH = 100/1, 0. 4, 254

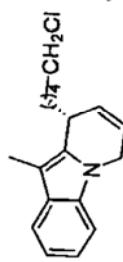


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		17.172	73097.867	1658753.500	49.7618
2		18.033	72283.656	1674633.625	50.2382
总计			145381.523	3333387.125	100.0000

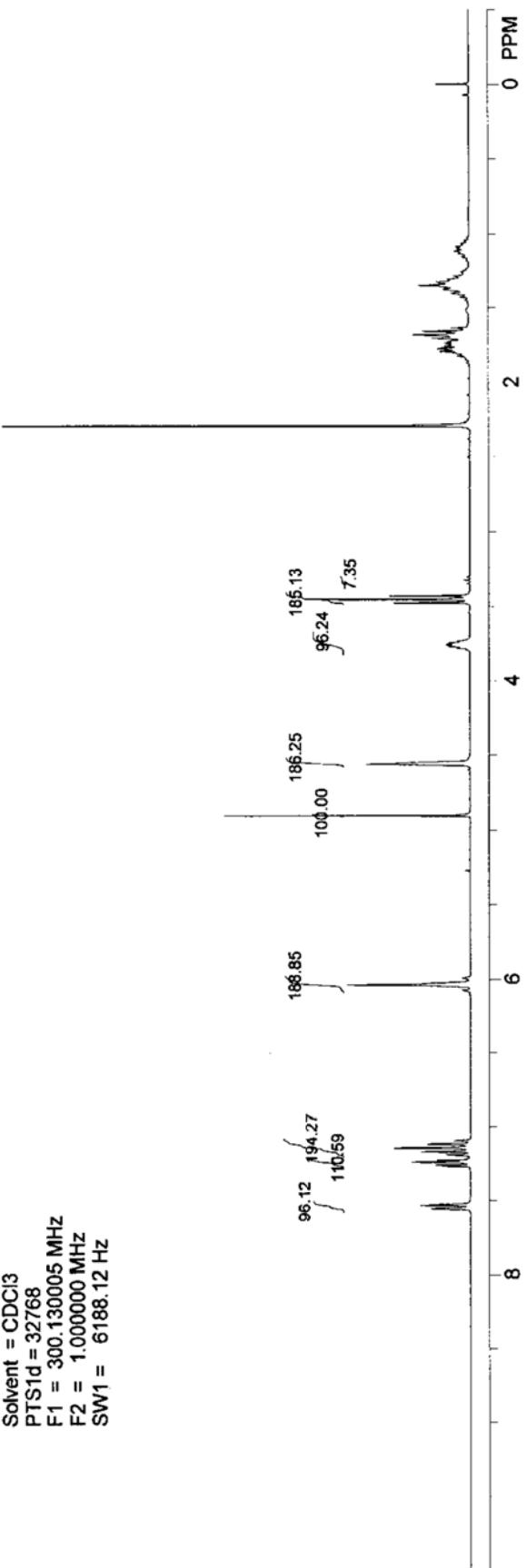
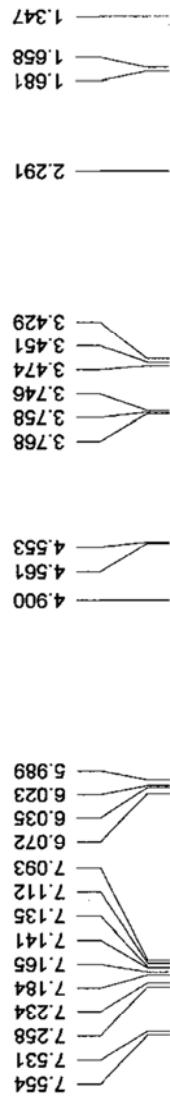


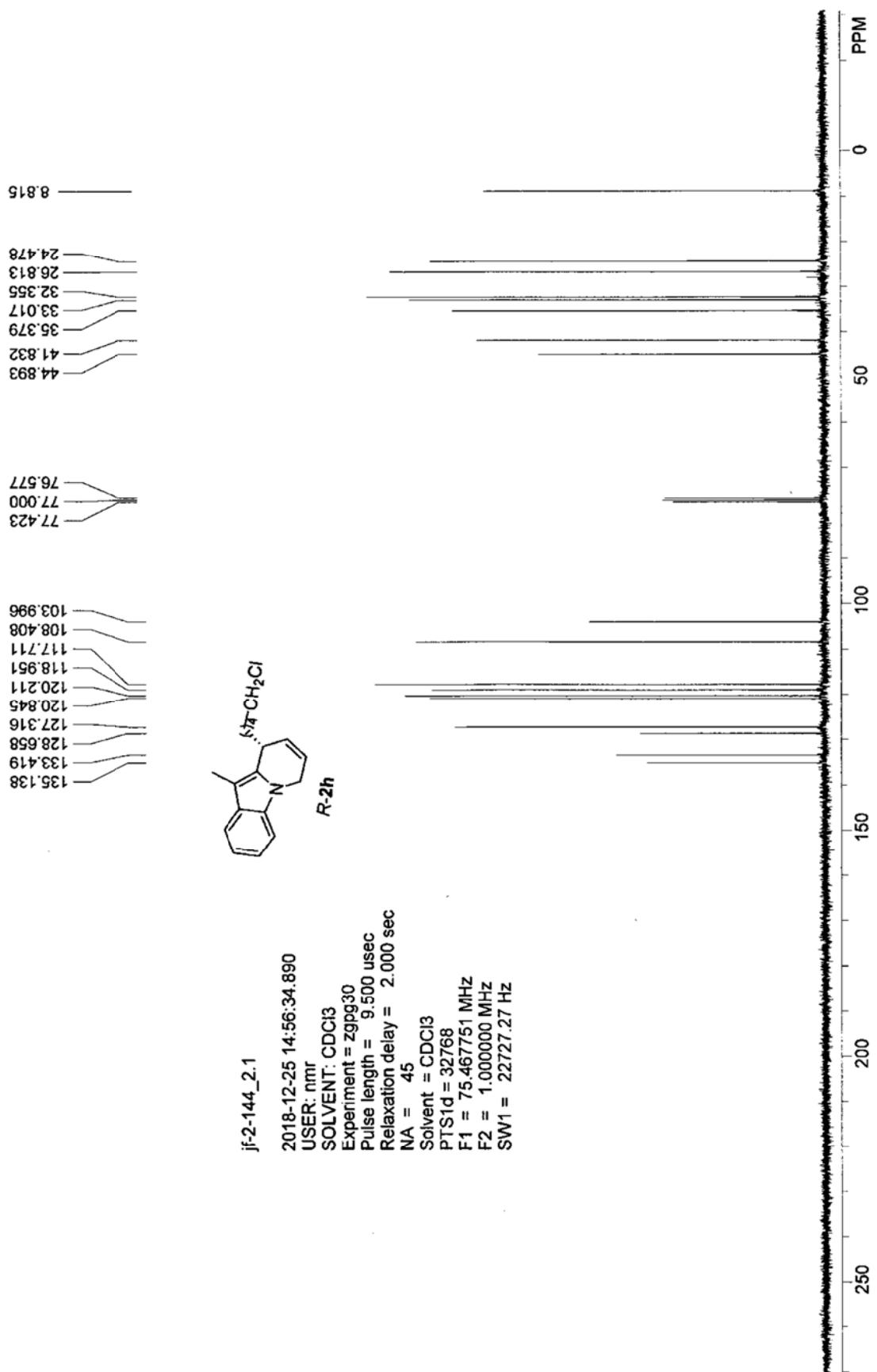
jf-2-144-purity



2018-12-28 21:54:41.546
USER: nmr
SOLVENT: CDCl₃
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl₃
PTStId = 322768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz

purity (96%) is determined by dibromomethane(7 μ L, 0.2 mmol) as the internal standard in 55.8 mg of sample



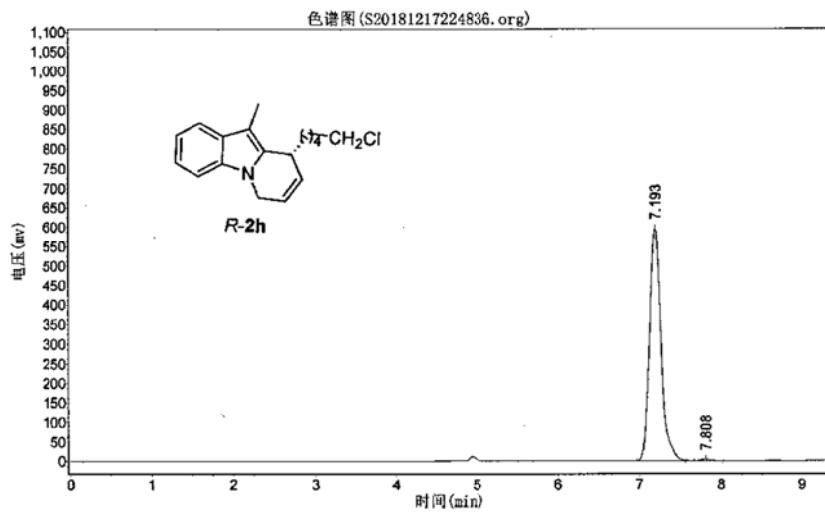


jf-2-144

实验时间: 2018-12-17, 22:48:36
谱图文件:D:\浙大智达\N2000\样品\S20181217224836.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2018-12-17, 23:03:30
积分方法: 面积归一法

实验内容简介:
IA, n-hexane/i-PrOH = 100/1, 0.7, 254



分析结果表

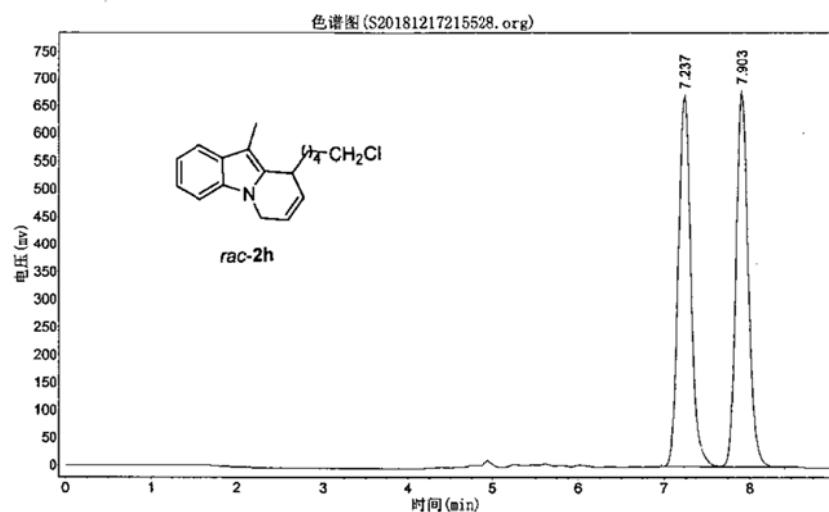
峰号	峰名	保留时间	峰高	峰面积	含量
1		7.193	596055.250	5739957.000	99.2745
2		7.808	4944.250	41945.203	0.7255
总计			600999.500	5781902.203	100.0000

jf-2-152

实验时间: 2018-12-17, 21:55:28
谱图文件:D:\浙大智达\N2000\样品\S20181217215528.org
方法文件:D:\浙大智达\N2000\djx.mtd

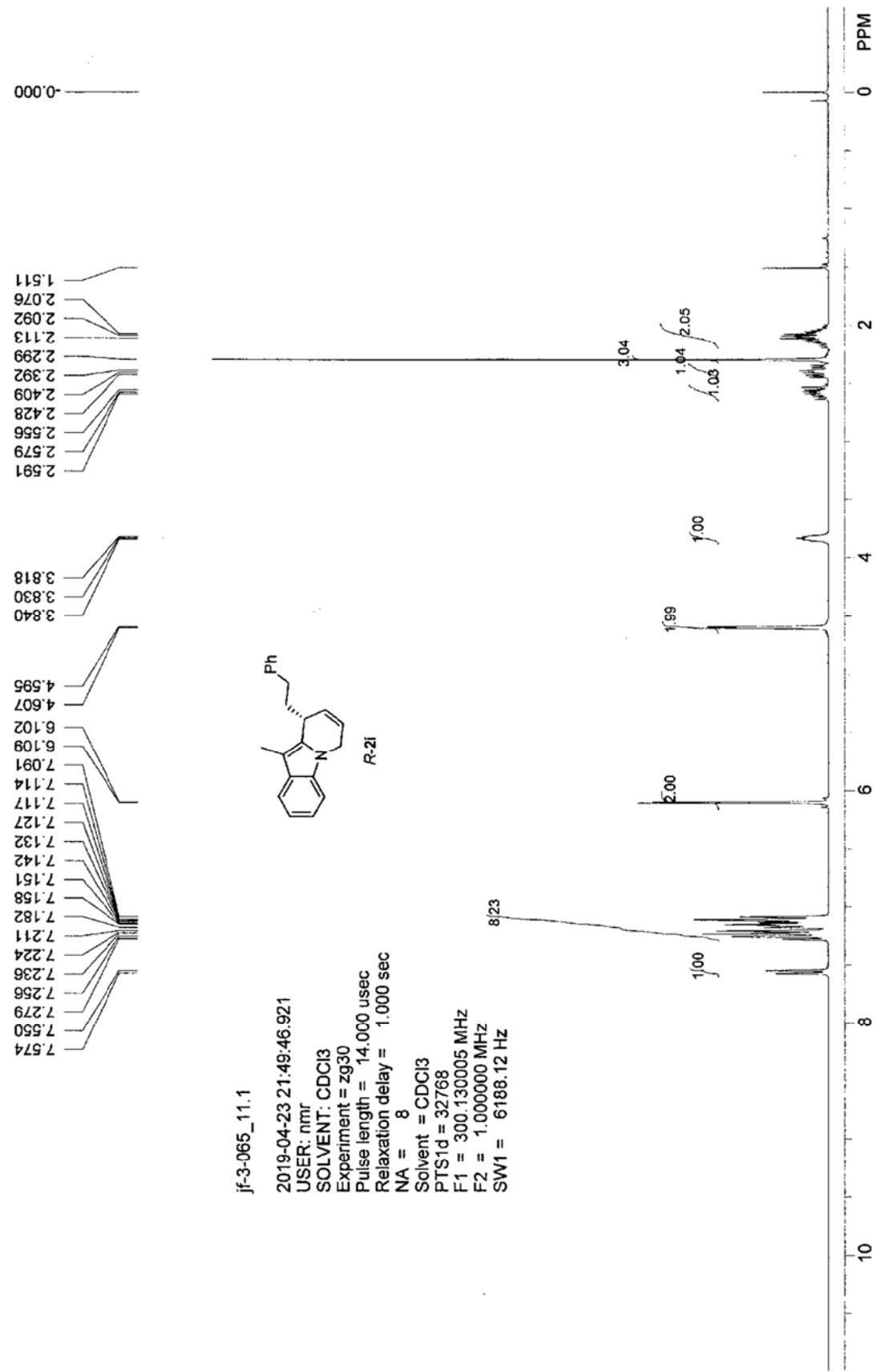
实验者: jf
报告时间: 2018-12-17, 23:05:57
积分方法: 面积归一法

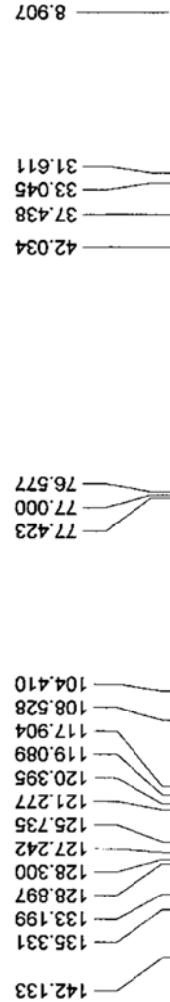
实验内容简介:
IA, n-hexane/i-PrOH = 100/1, 0.7, 254



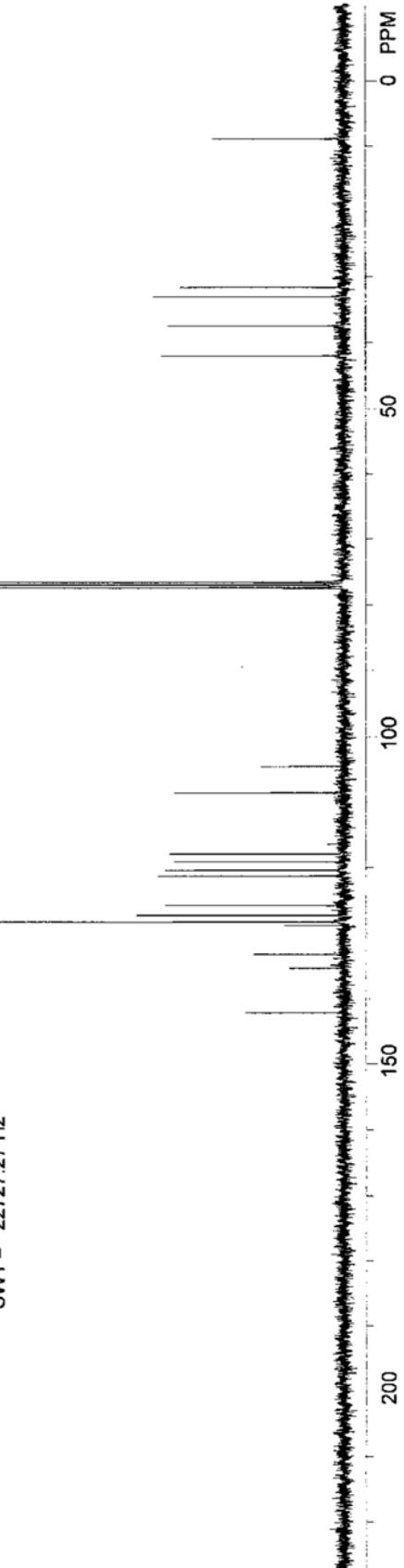
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		7.237	666976.375	6778395.000	50.4837
2		7.903	675224.625	6648491.000	49.5163
总计			1342201.000	13426886.000	100.0000





jf-3-065_2.1
2019-04-23 21:39:02.218
USER: nmr
SOLVENT: CDCl₃
Experiment = zg9930
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 111
Solvent = CDCl₃
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz

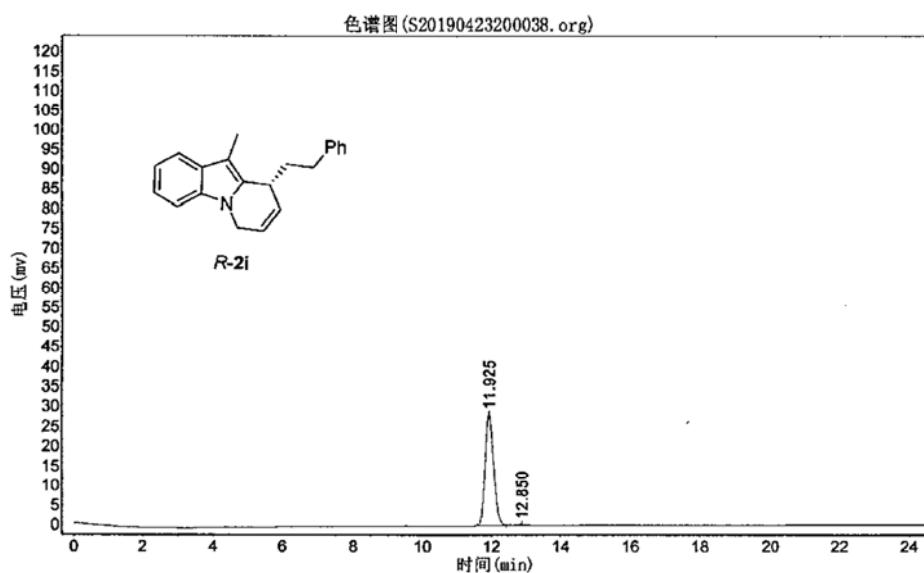


jf-3-065

实验时间: 2019-04-23, 20:00:38
谱图文件:D:\浙大智达\N2000\样品\S20190423200038.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-04-23, 21:55:15
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 95/5, 0.7, 254



分析结果表

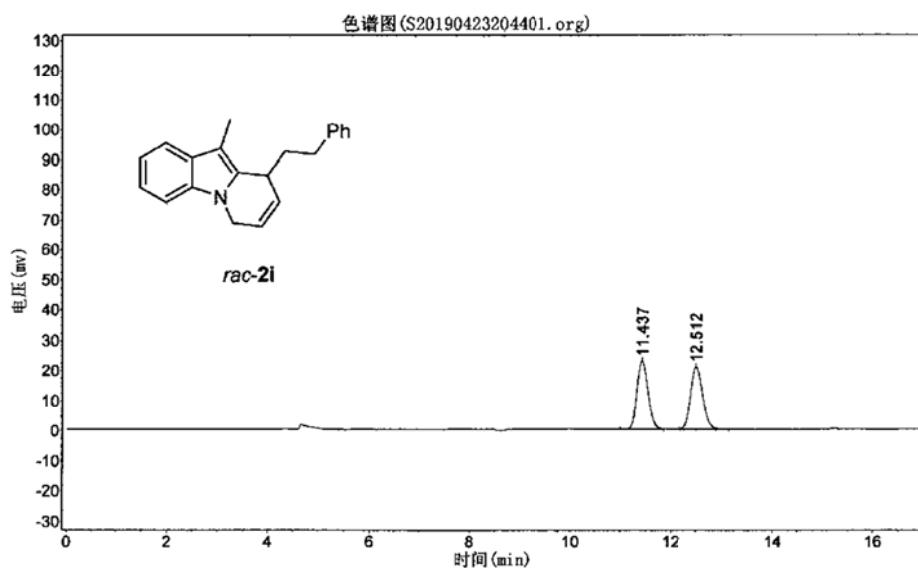
峰号	峰名	保留时间	峰高	峰面积	含量
1		11.925	28254.723	480391.094	99.0361
2		12.850	305.214	4675.650	0.9639
总计			28559.936	485066.744	100.0000

jf-3-030

实验时间: 2019-04-23, 20:44:01
谱图文件:D:\浙大智达\N2000\样品\S20190423204401.org
方法文件:D:\浙大智达\N2000\djx.mtd

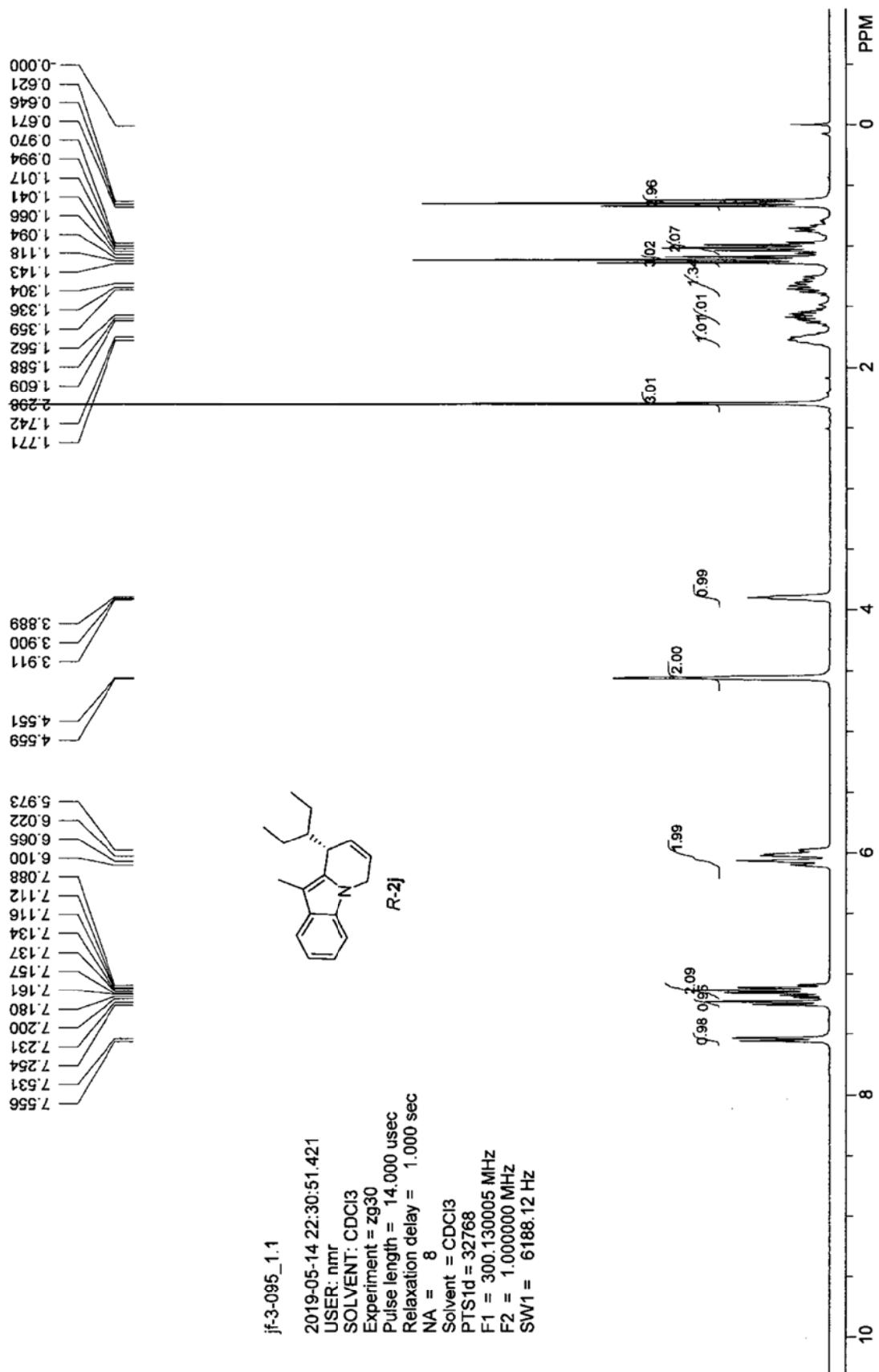
实验者: 30
报告时间: 2019-04-23, 21:57:54
积分方法: 面积归一法

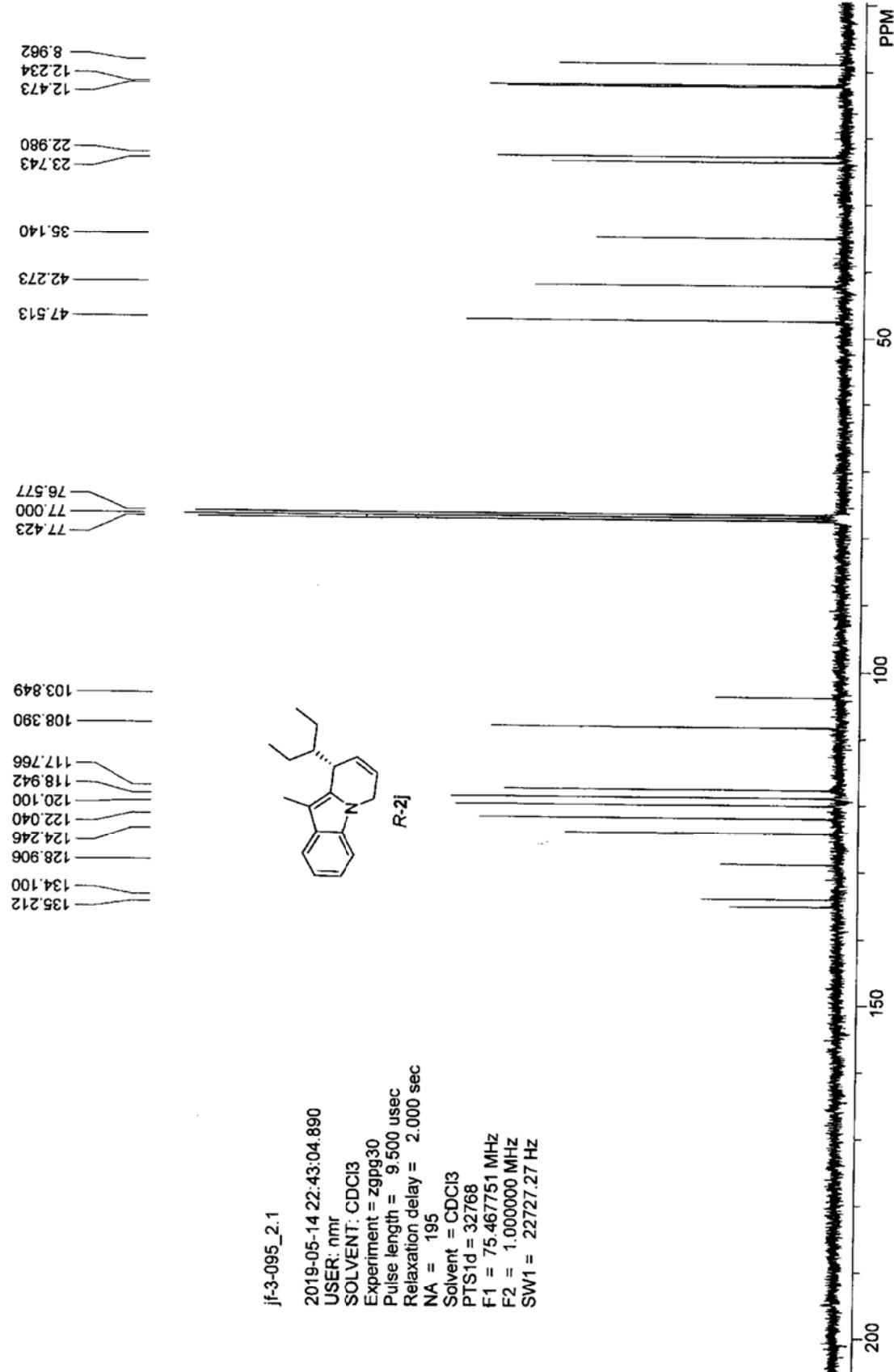
实验内容简介:
od, n-hexane/i-PrOH = 95/5, 0.7, 254



分析结果表

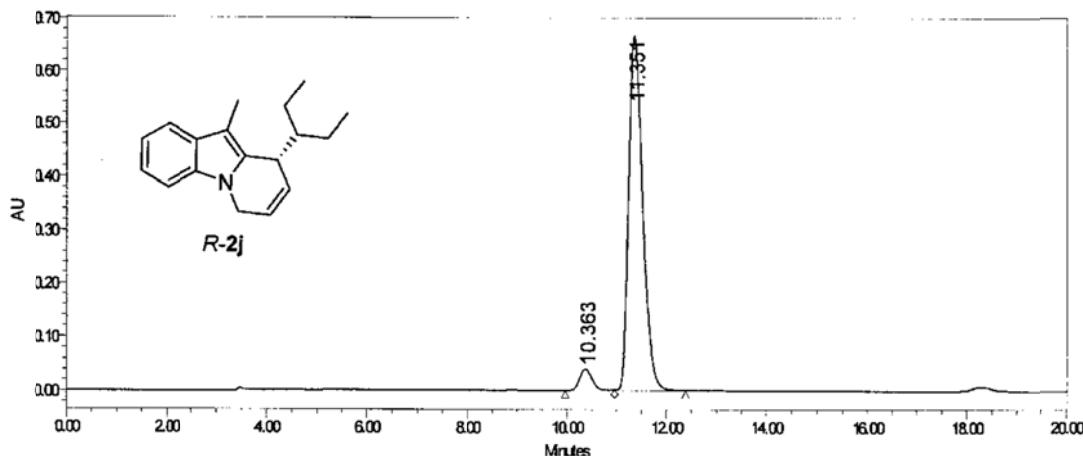
峰号	峰名	保留时间	峰高	峰面积	含量
1		11.437	22686.373	339313.313	50.1361
2		12.512	20679.621	337470.688	49.8639
总计			43365.994	676784.000	100.0000





SAMPLE INFORMATION

Sample Name:	JF3-095-az-100-0-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Aq. Method Set:	ZGJ100
Injection#:	11	Processing Method:	111
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA
Run Time:	20.0 Minutes	Proc. Chrl. Descr.:	W2489 ChA.214nm
Date Acquired:	5/22/2019 7:38:31 PM EDT		
Date Processed:	5/22/2019 10:24:36 PM EDT		



—— Channel: W2489 ChA; Processed Channel: W2489 ChA.214nm; Result Id: 1404; ProcessingMethod: 11

Processed Channel Descr.: W2489 ChA.214nm

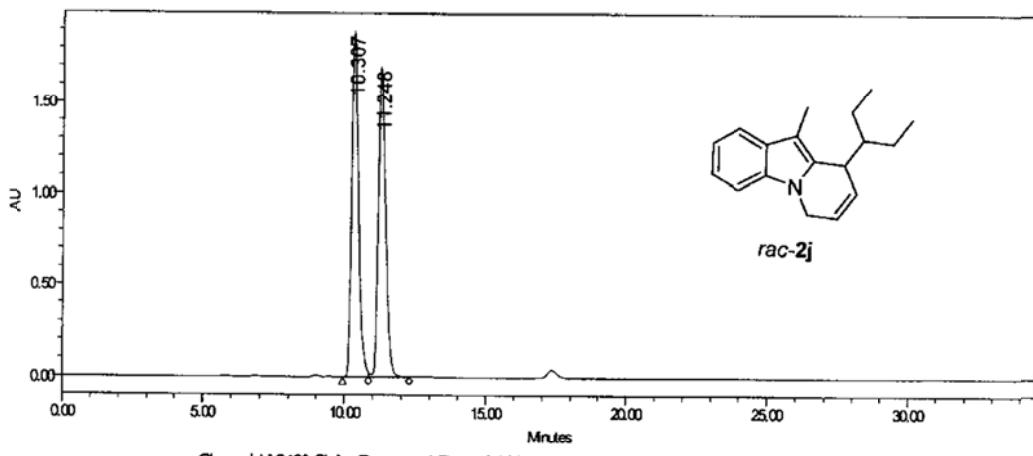
	Processed Channel Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	10.363	707155	5.20	41008
2	W2489 ChA.214nm	11.351	12904436	94.80	667098

Reported by User: System
Report Method: Injection Summary Report
Report Method ID: 1029 1029
Page: 1 of 1

Project Name: HPLC_1525
Date Printed:
5/22/2019
10:25:55 PM America/New_York

SAMPLE INFORMATION

Sample Name:	jF3-094-az-100-0-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	ZGJ100
Injection #:	9	Processing Method:	111
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Ctrl. Descr.:	W2489 ChA.214nm
Date Acquired:	5/22/2019 6:38:53 PM EDT		
Date Processed:	5/22/2019 10:25:10 PM EDT		

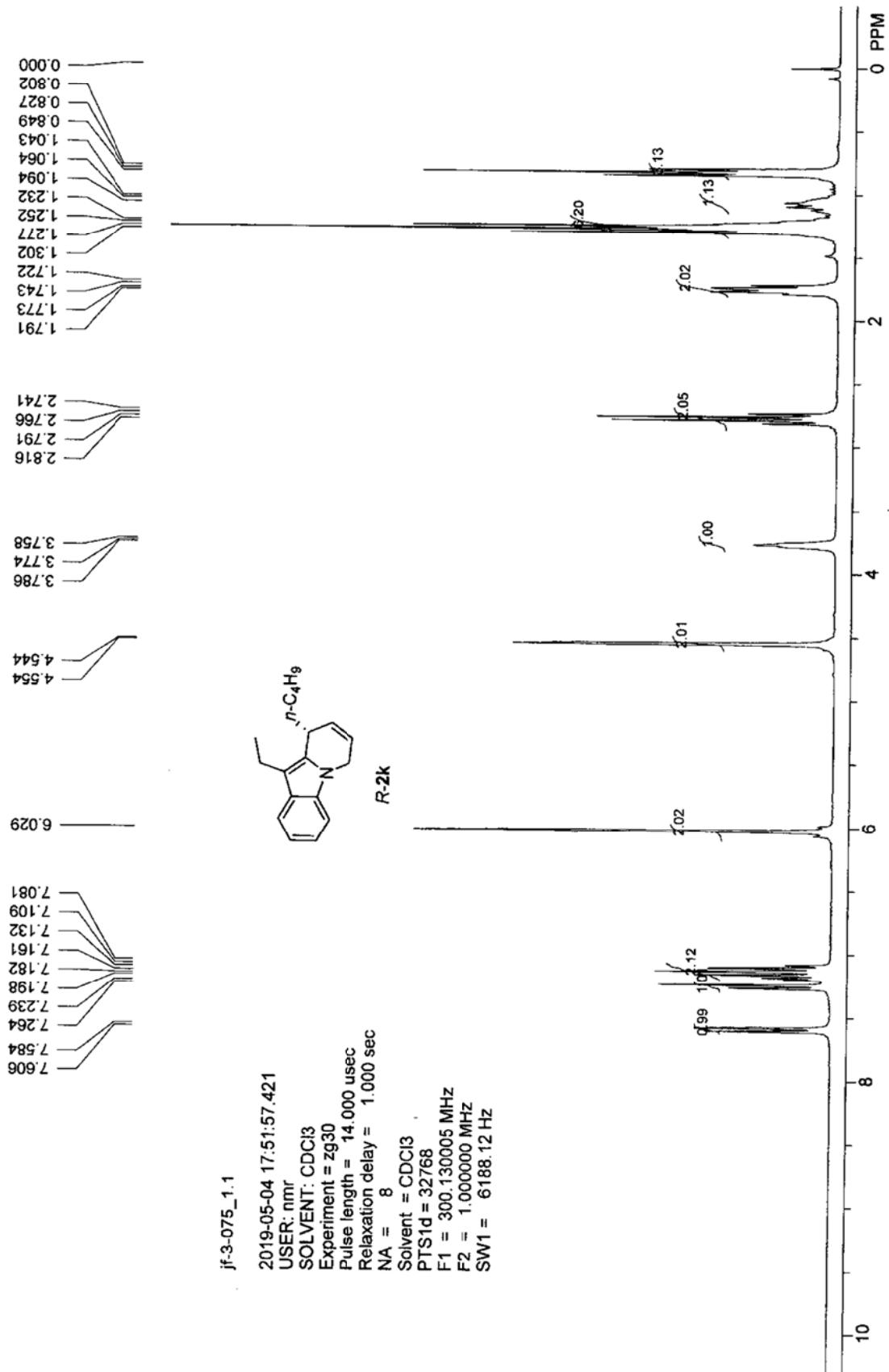


Processed Channel Descr.: W2489 ChA.214nm

	Processed Channel Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	10.307	31444767	50.85	1901440
2	W2489 ChA.214nm	11.248	30394358	49.15	1699535

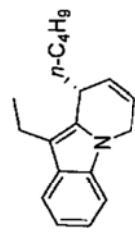
Reported by User: System
 Report Method: Injection Summary Report
 Report Method ID: 1029 1029
 Page: 1 of 1

Project Name: HPLC_1525
 Date Printed:
 5/22/2019
 10:25:24 PM America/New_York

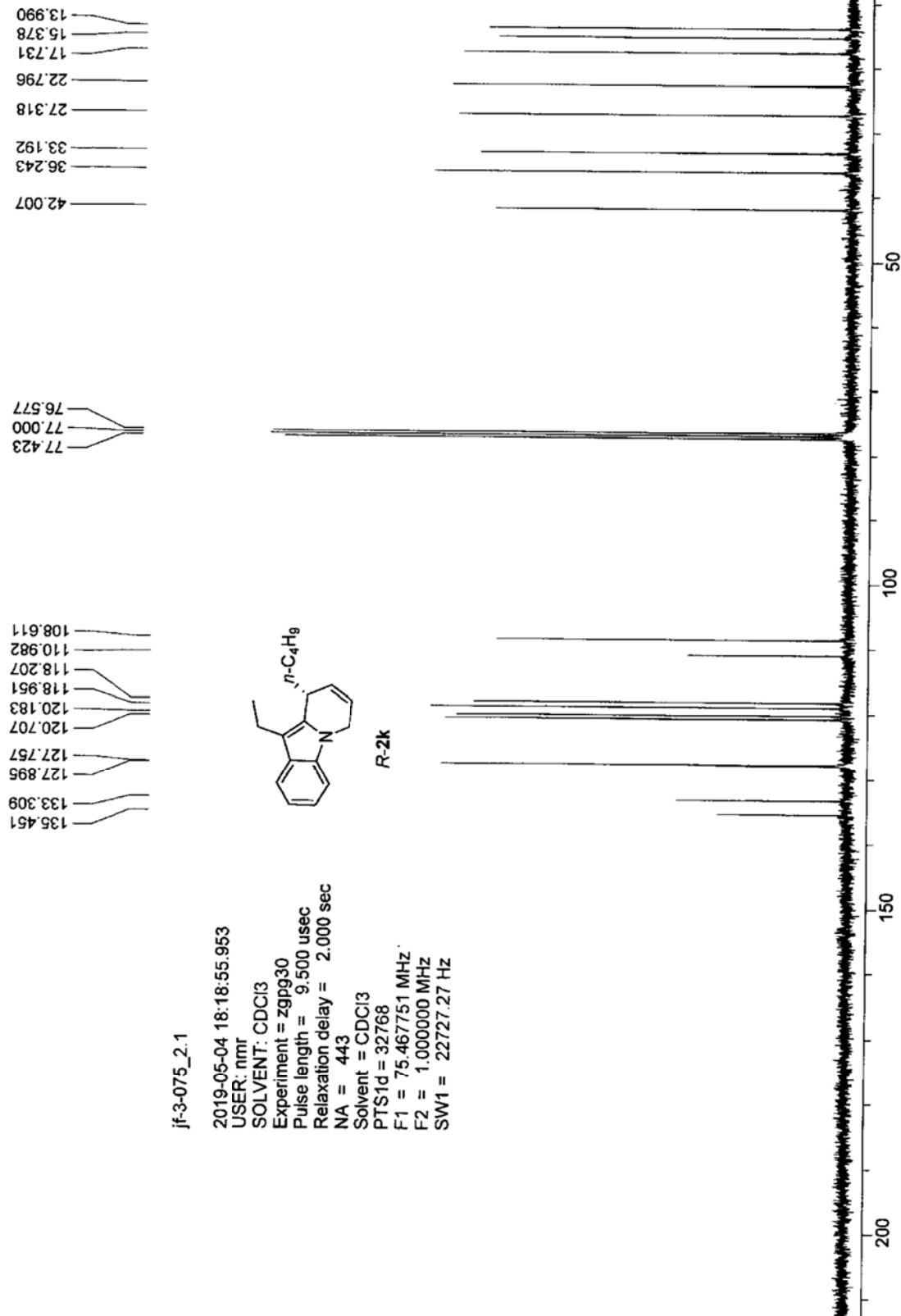


jj-3-075_2.1

2019-05-04 18:18:55.953
USER: nmr
SOLVENT: CDCl₃
Experiment = zgpg30
Pulse length = 9.500 usec
Relaxation delay = 2.000 sec
NA = 443
Solvent = CDCl₃
PTS1d = 32768
F1 = 75.467751 MHz
F2 = 1.000000 MHz
SW1 = 22727.27 Hz



R-2k

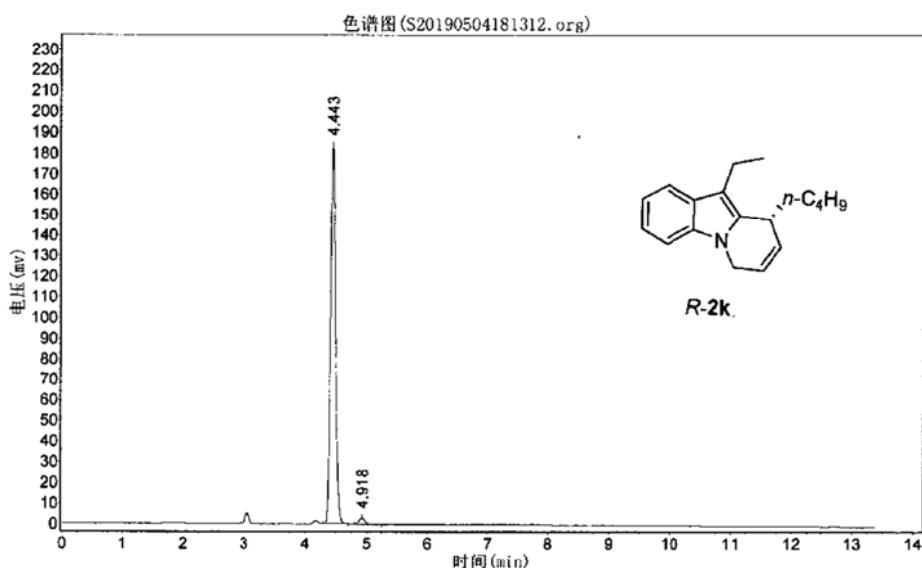


jf-3-075

实验时间：2019-05-04, 18:13:12
谱图文件:D:\浙大智达\N2000\样品\S20190504181312.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者：jf
报告时间：2019-05-04, 18:28:03
积分方法：面积归一法

实验内容简介：
od,n-hexane/i-PrOH = 95/5, l. 0, 214



分析结果表

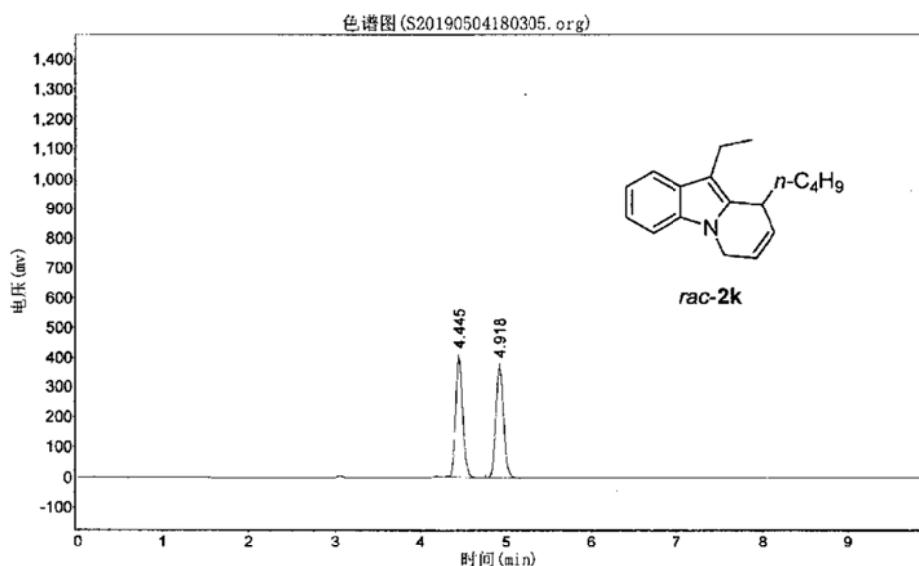
峰号	峰名	保留时间	峰高	峰面积	含量
1		4.443	183596.484	1026928.625	98.2911
2		4.918	2916.195	17853.949	1.7089
总计			186512.679	1044782.574	100.0000

jf-3-077

实验时间: 2019-05-04, 18:03:05
谱图文件:D:\浙大智达\N2000\样品\S20190504180305.org
方法文件:D:\浙大智达\N2000\djx.mtd

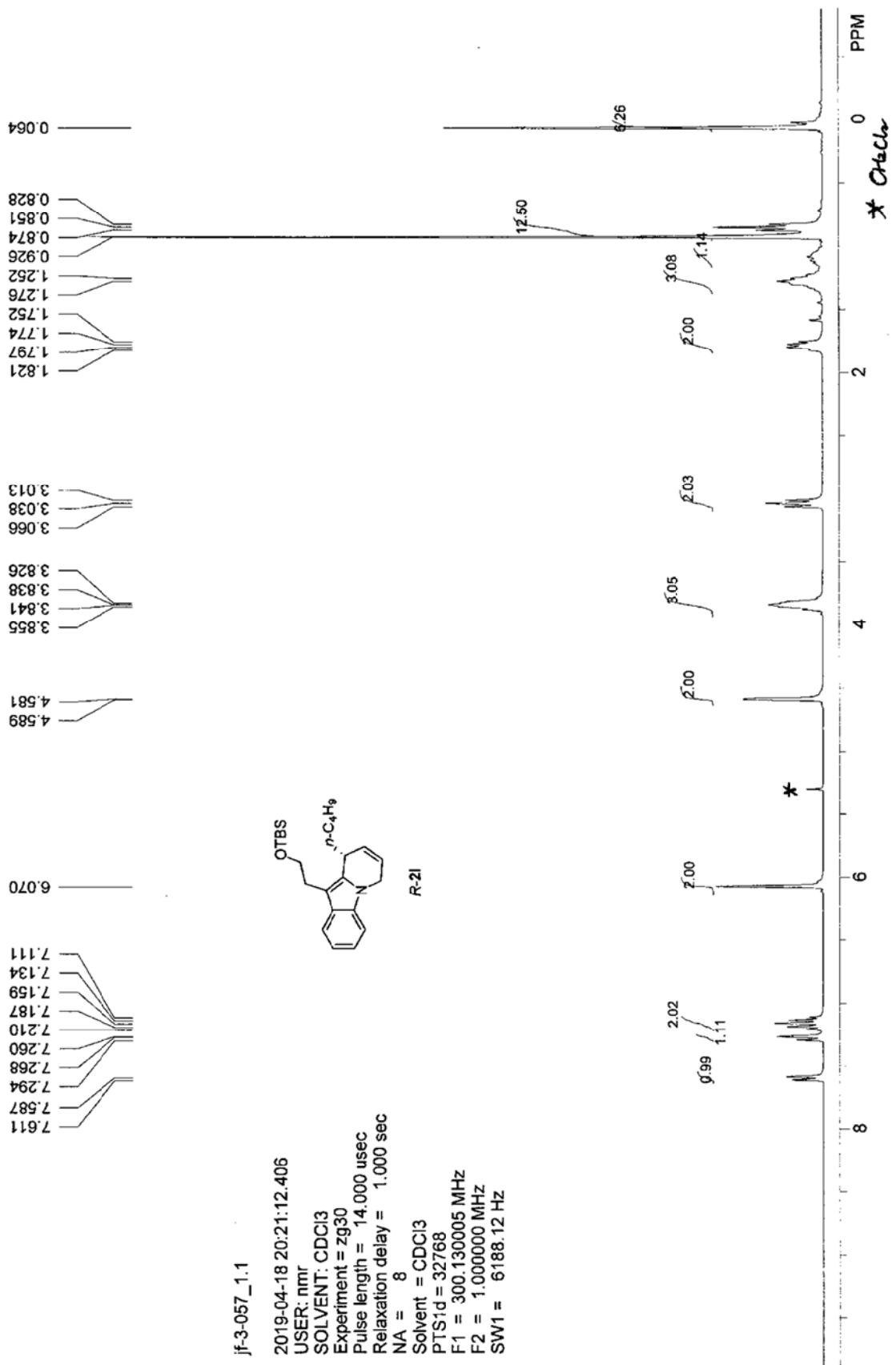
实验者: jf
报告时间: 2019-05-04, 18:15:20
积分方法: 面积归一法

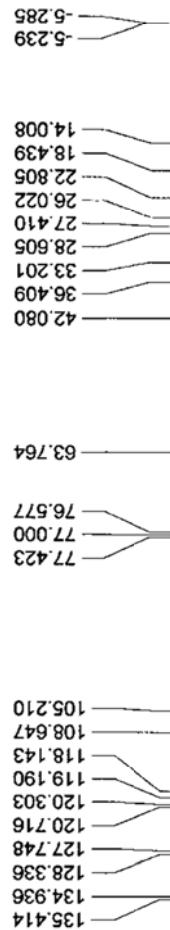
实验内容简介:
od, n-hexane/i-PrOH = 95/5, 1.0, 214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		4.445	397677.344	2287410.000	49.8355
2		4.918	370122.875	2302510.750	50.1645
总计			767800.219	4589920.750	100.0000





jf-3-057_2.1

2019-04-18 20:32:43.531

USER: nmr

SOLVENT: CDCl₃

Experiment = zgppg30

Pulse length = 9.500 usec

Relaxation delay = 2.000 sec

NA = 178

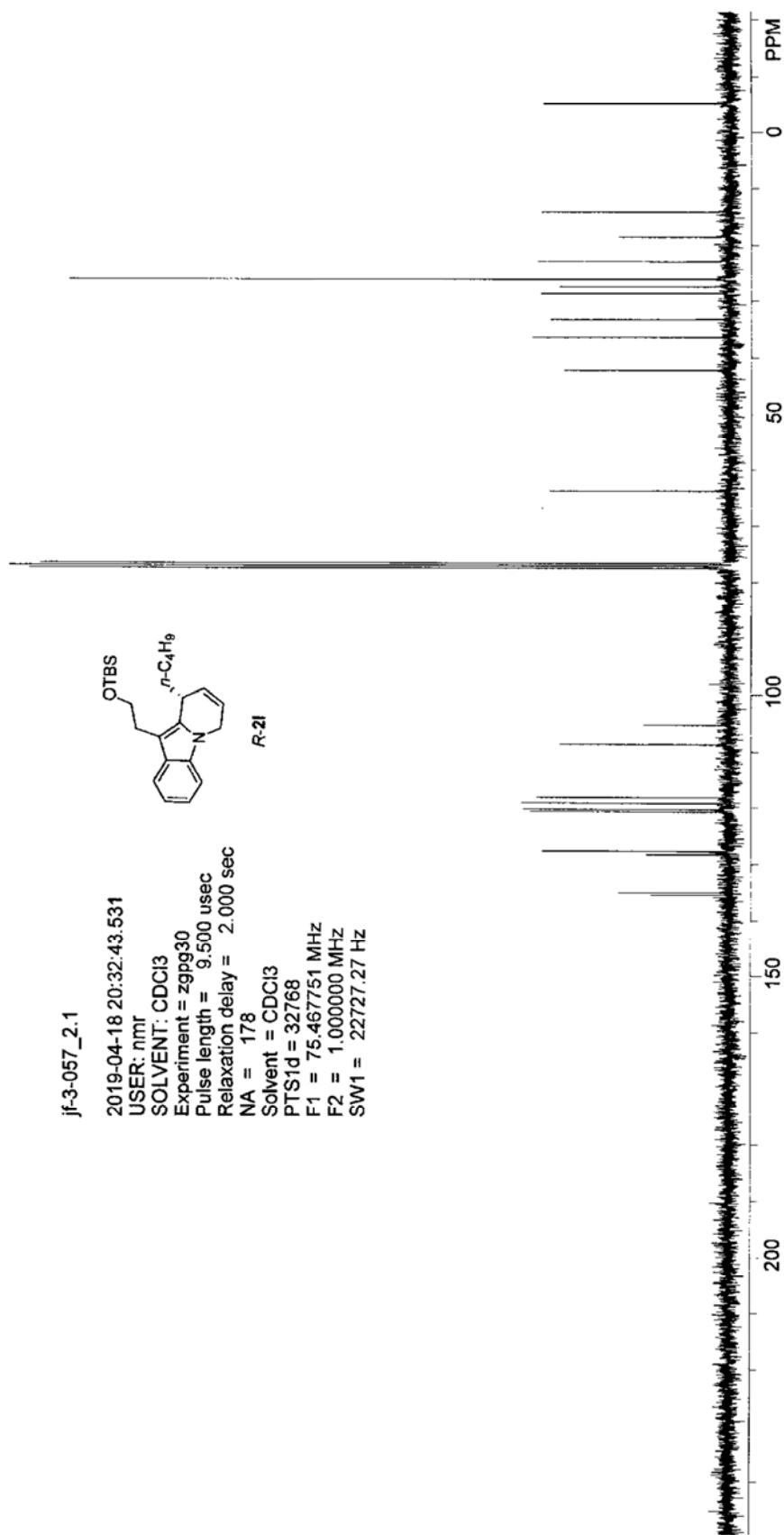
Solvent = CDCl₃

PTS1d = 32768

F1 = 75.467751 MHz

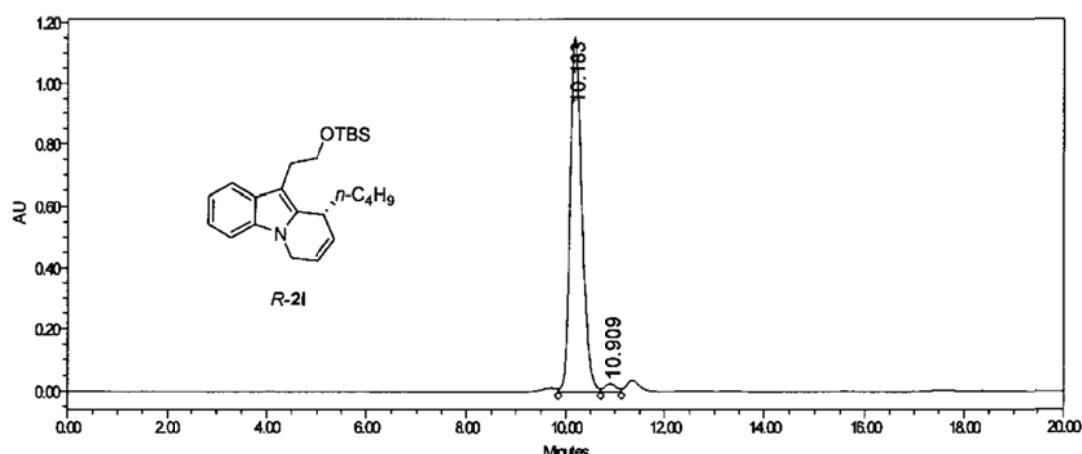
F2 = 1.000000 MHz

SW1 = 22727.27 Hz



SAMPLE INFORMATION

Sample Name:	JF-3-057-F-100-0-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	ZGJ100
Injection#:	19	Processing Method:	111
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA.214nm
Date Acquired:	4/29/2019 8:45:46 PM EDT		
Date Processed:	4/29/2019 9:17:04 PM EDT		



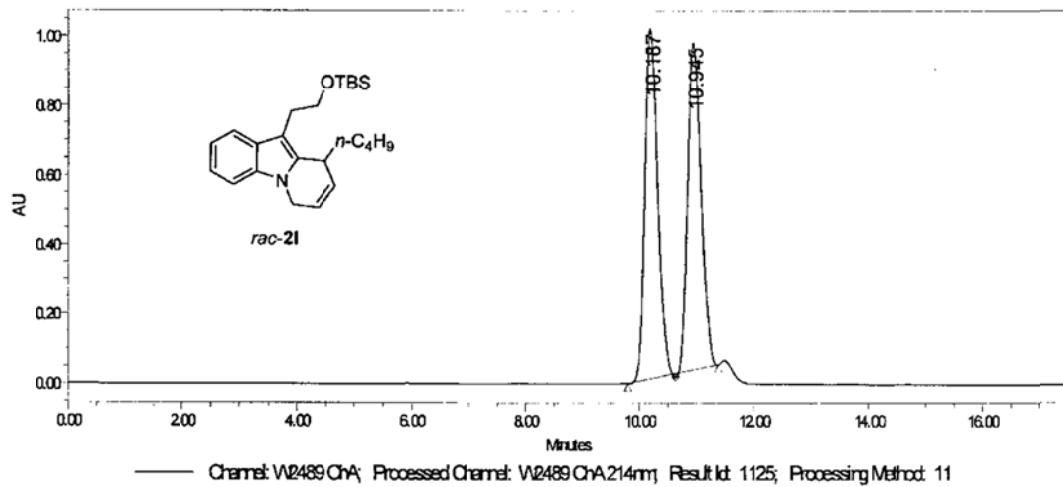
Processed Channel Descr.: W2489 ChA.214nm

	Processed Chnl Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	10.183	18787915	97.80	1154771
2	W2489 ChA.214nm	10.909	423601	2.20	25318

Reported by User: System
 Report Method: Injection Summary Report
 Report Method ID: 1029 1029
 Page: 1 of 1

Project Name: HPLC_1525
 Date Printed: 4/29/2019
 9:19:26 PM America/New_York

SAMPLE INFORMATION			
Sample Name:	JF-3-060-F-100-0-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	ZGJ100
Injection#:	18	Processing Method:	111
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA
Run Time:	200.0 Minutes	Proc. Ctrl. Descr.:	W2489 ChA.214nm
Date Acquired:	4/29/2019 8:26:52 PM EDT		
Date Processed:	4/29/2019 9:17:34 PM EDT		



Processed Channel Descr.: W2489 ChA.214nm

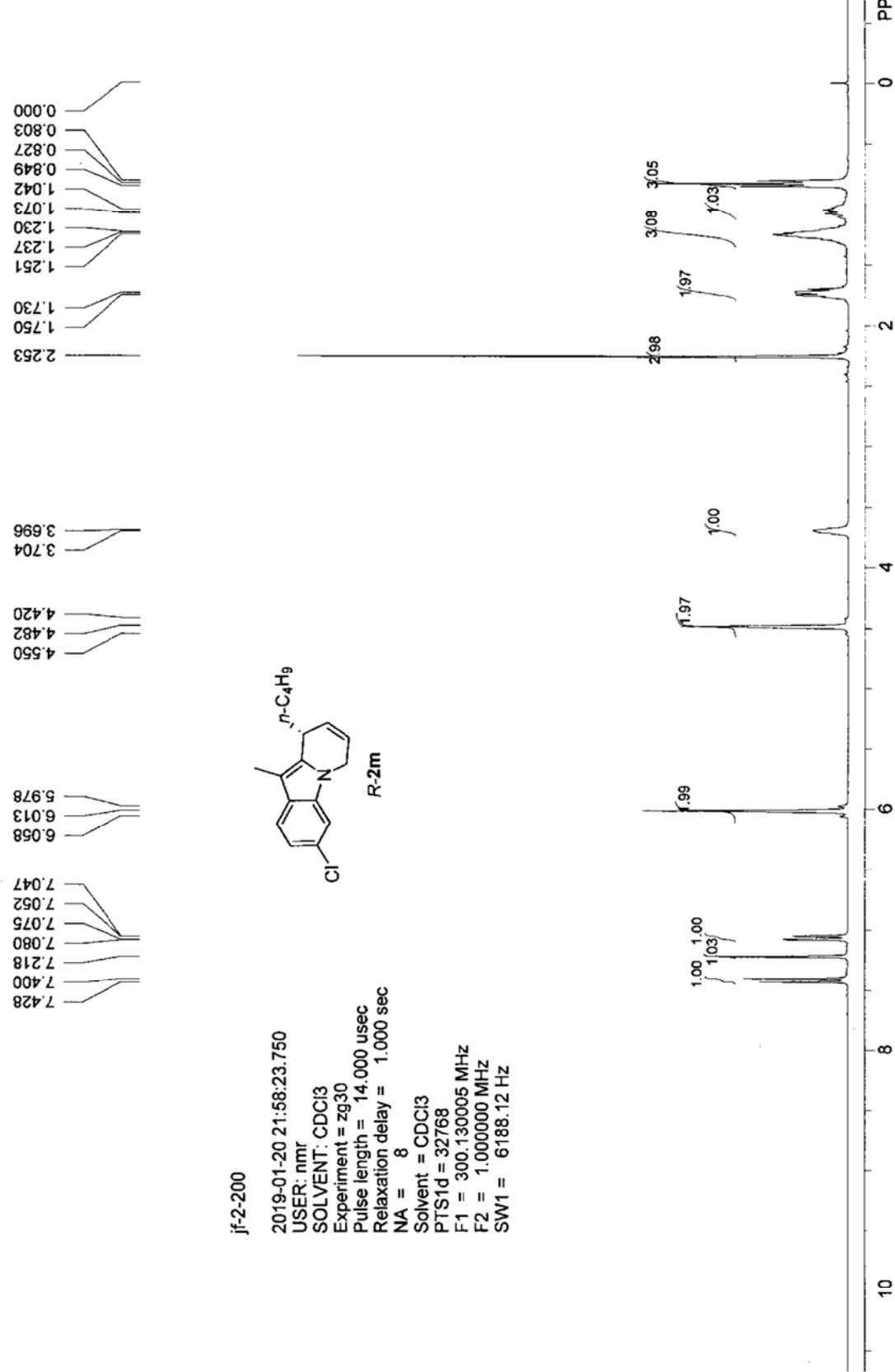
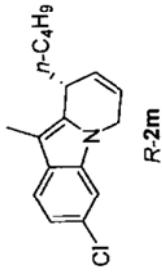
	Processed Channel Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	10.187	15777055	50.06	1009220
2	W2489 ChA.214nm	10.945	15738033	49.94	942521

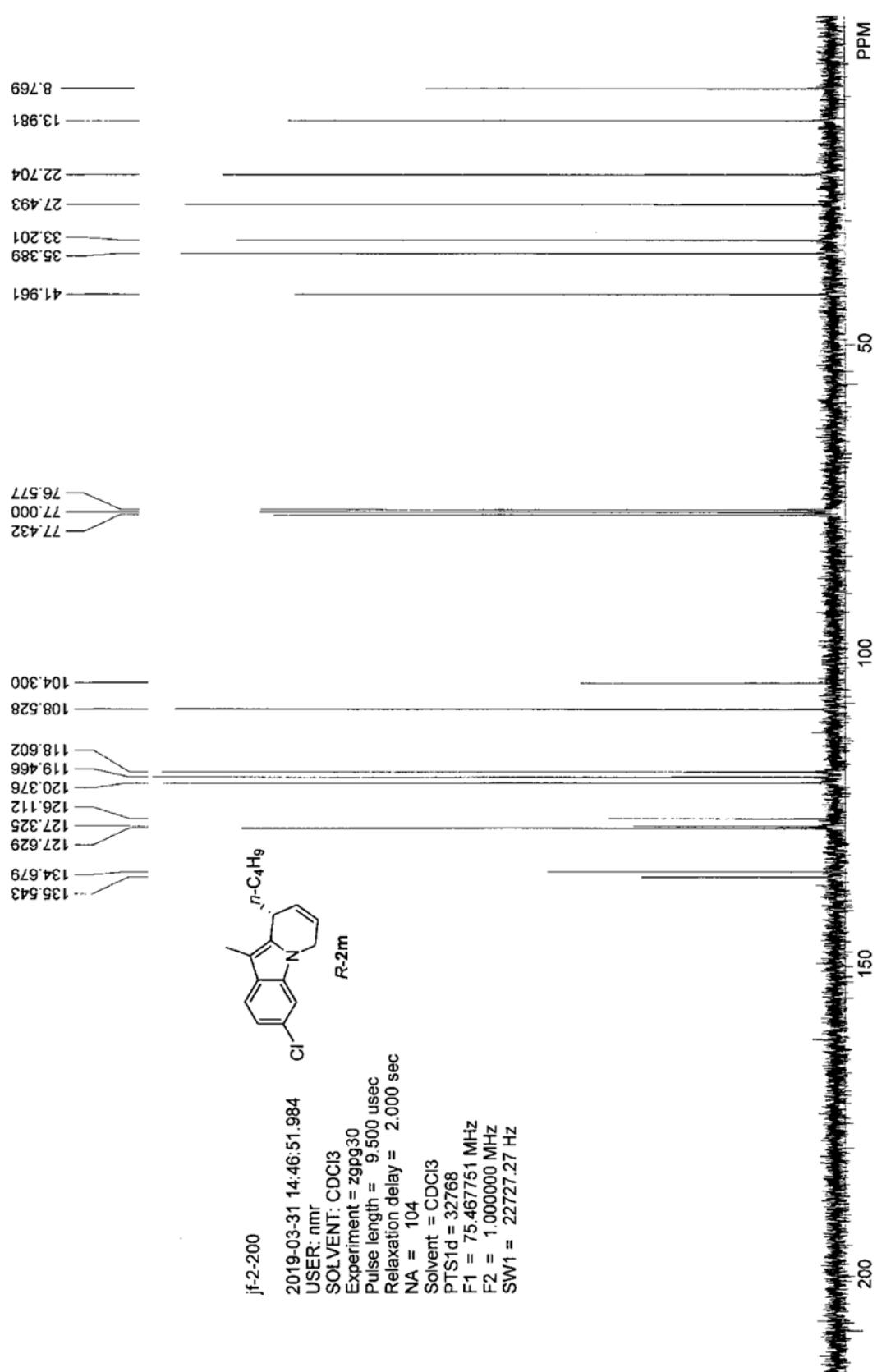
Reported by User: System
Report Method: InjectionSummary Report
Report Method ID: 1029 1029
Page: 1 of 1

Project Name: HPLC_1525
Date Printed: 4/29/2019
9:19:48 PM America/New_York

jf-2-200

2019-01-20 21:58:23.750
USER: nmr
SOLVENT: CDCl₃
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl₃
FTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz



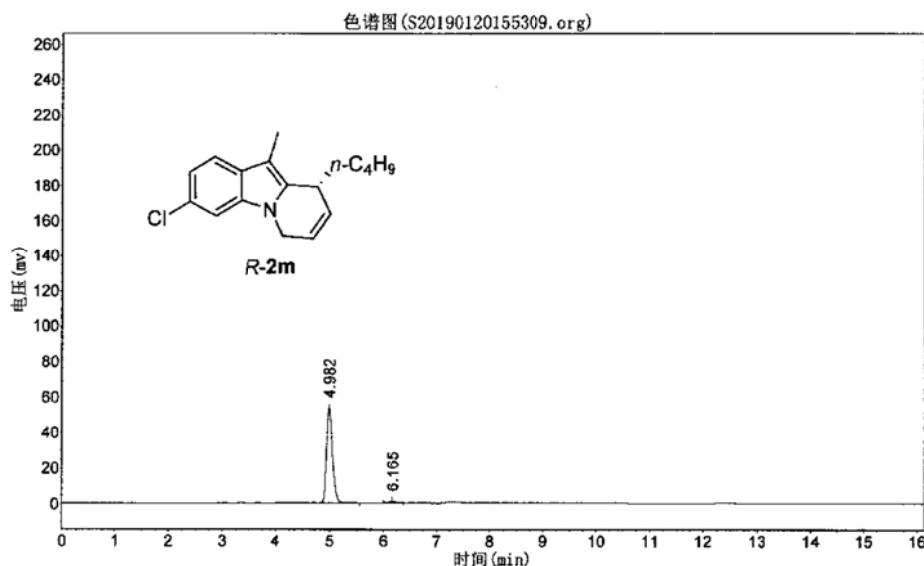


jf-2-200

实验时间: 2019-01-20, 15:53:09
谱图文件:D:\浙大智达\N2000\样品\S20190120155309.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-11-13, 21:55:03
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 100/1, 1.0, 254



分析结果表

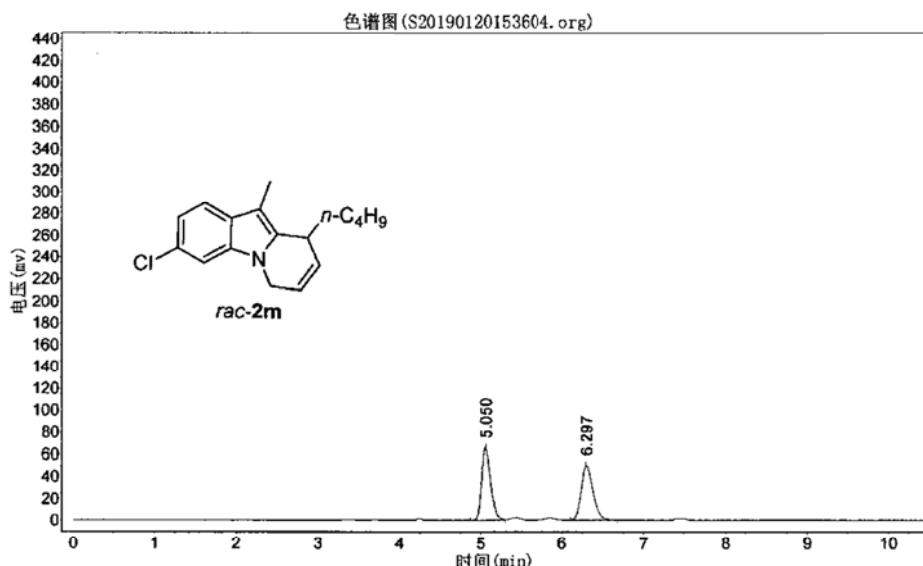
峰号	峰名	保留时间	峰高	峰面积	含量
1		4.982	53587.926	410560.844	97.3700
2		6.165	1151.276	11089.398	2.6300
总计			54739.202	421650.242	100.0000

jf-3-003

实验时间: 2019-01-20, 15:36:04
谱图文件:D:\浙大智达\N2000\样品\S20190120153604.org
方法文件:D:\浙大智达\N2000\djx.mtd

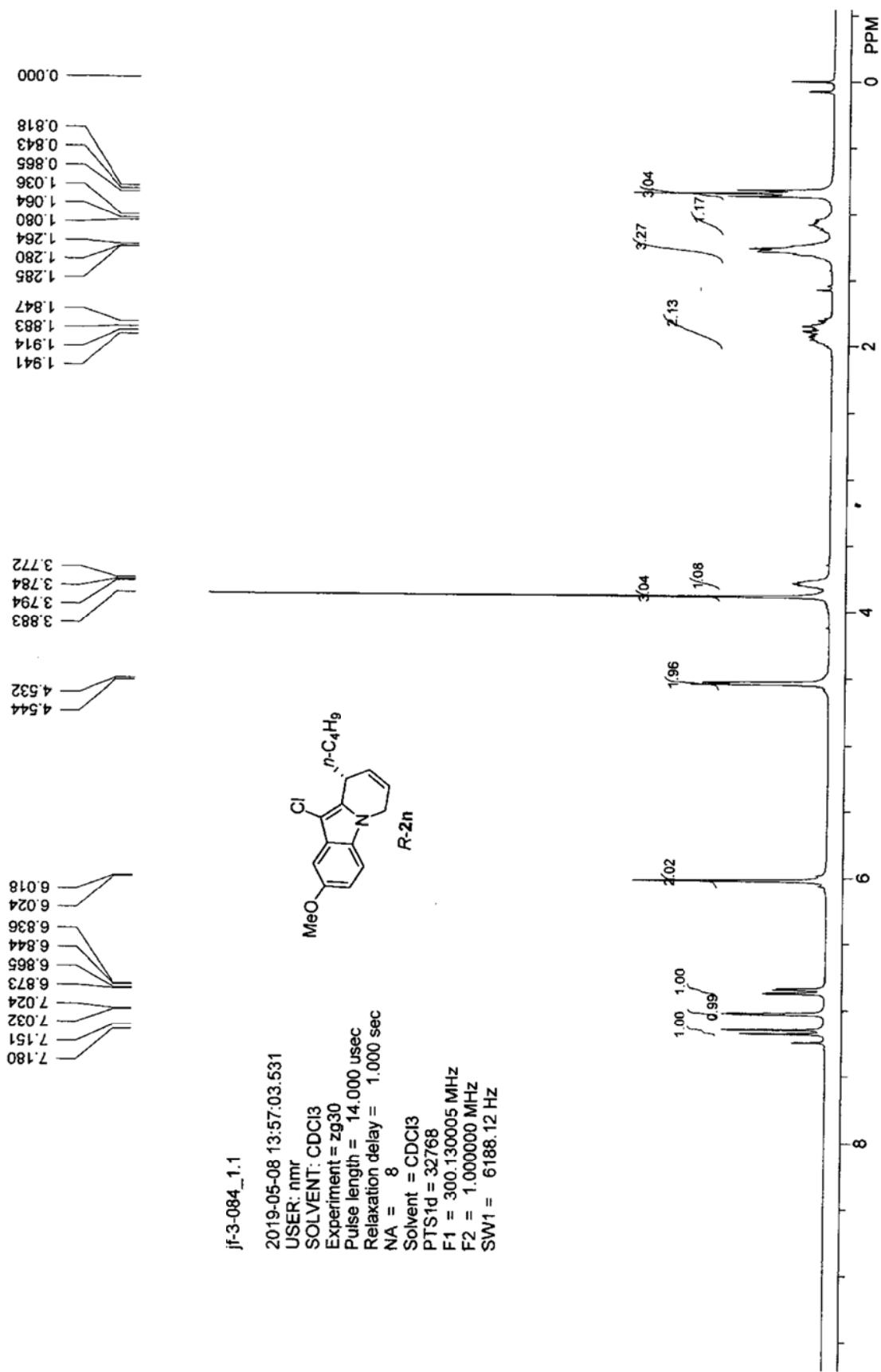
实验者: jf
报告时间: 2019-01-20, 15:49:02
积分方法: 面积归一法

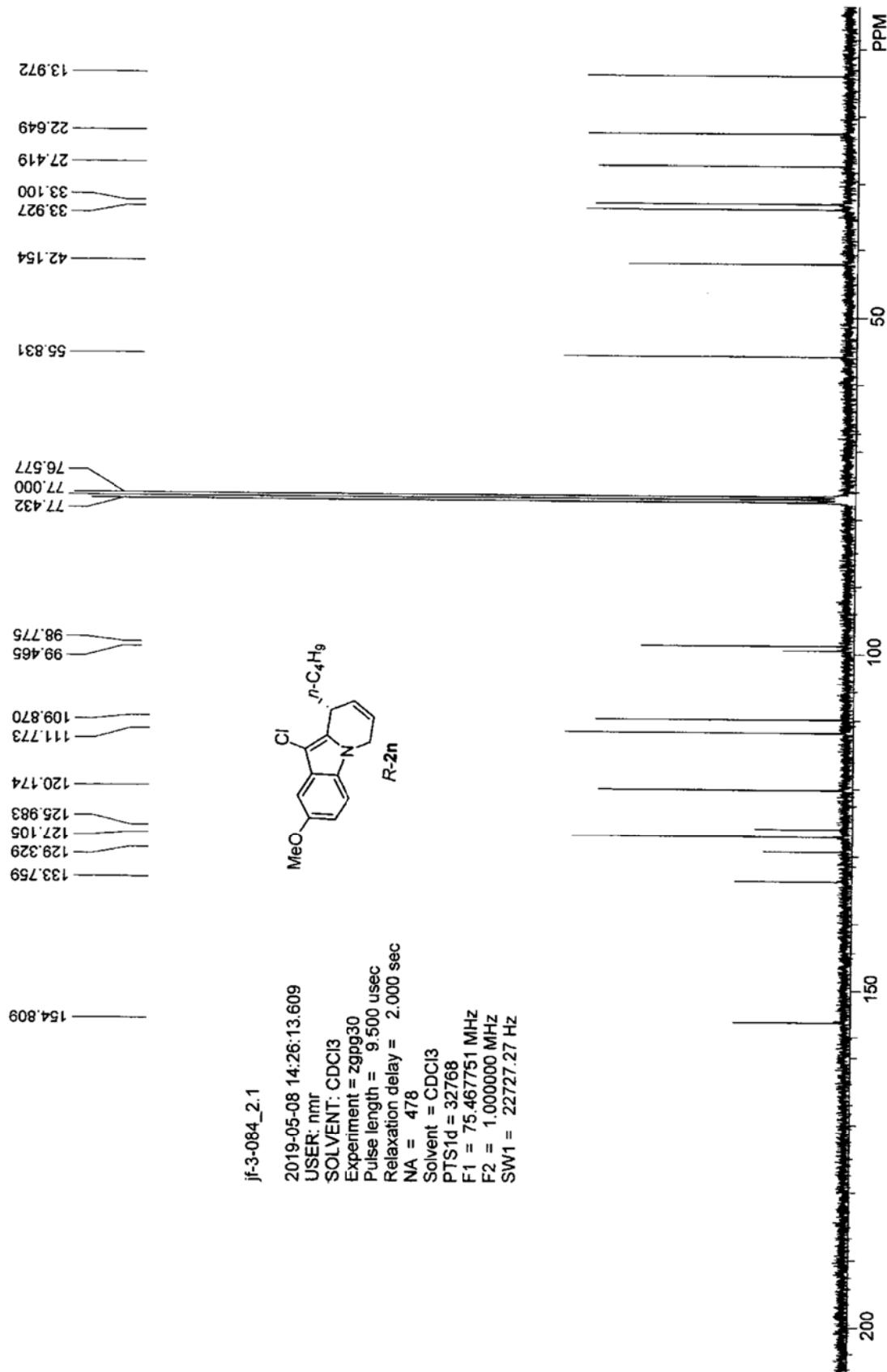
实验内容简介:
od, n-hexane/i-PrOH = 100/1, 1.0, 254



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		5.050	65469.352	495104.719	50.0374
2		6.297	49762.418	494365.250	49.9626
总计			115231.770	989469.969	100.0000



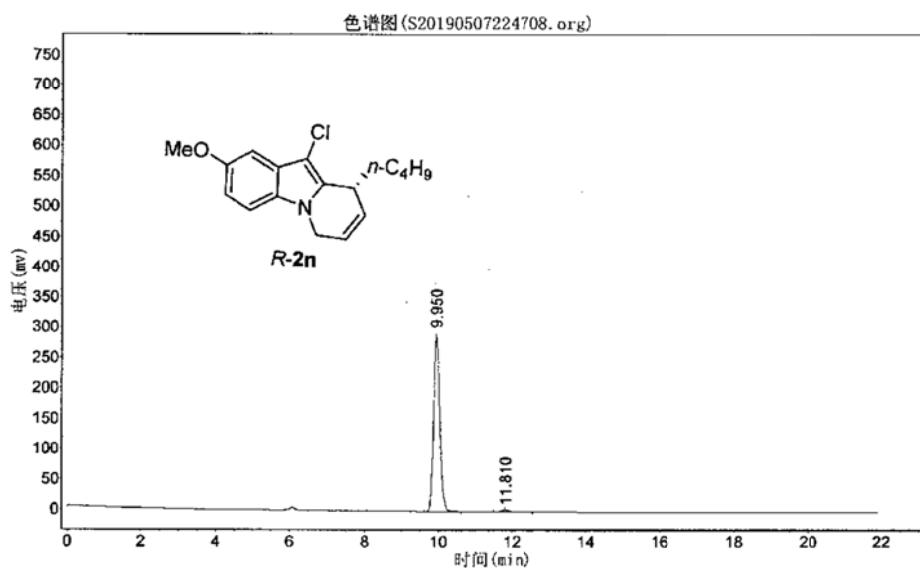


jf-3-084

实验时间: 2019-05-07, 22:47:08
谱图文件:D:\浙大智达\N2000\样品\S20190507224708.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-05-07, 23:11:06
积分方法: 面积归一法

实验内容简介:
od. n-hexane/i-PrOH = 95/5, 0.5, 214

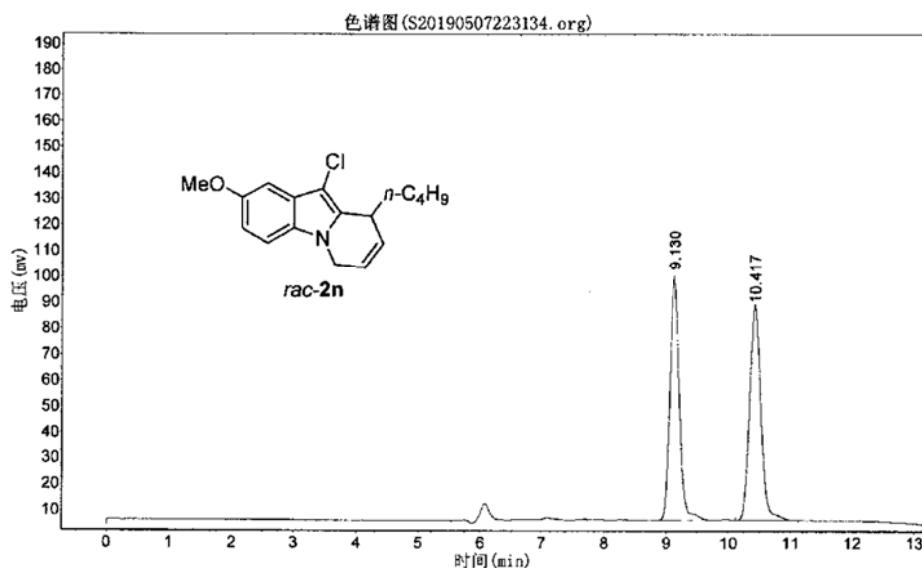


jf-3-090

实验时间: 2019-05-07, 22:31:34
谱图文件:D:\浙大智达\N2000\样品\S20190507223134.org
方法文件:D:\浙大智达\N2000\djx.mtd

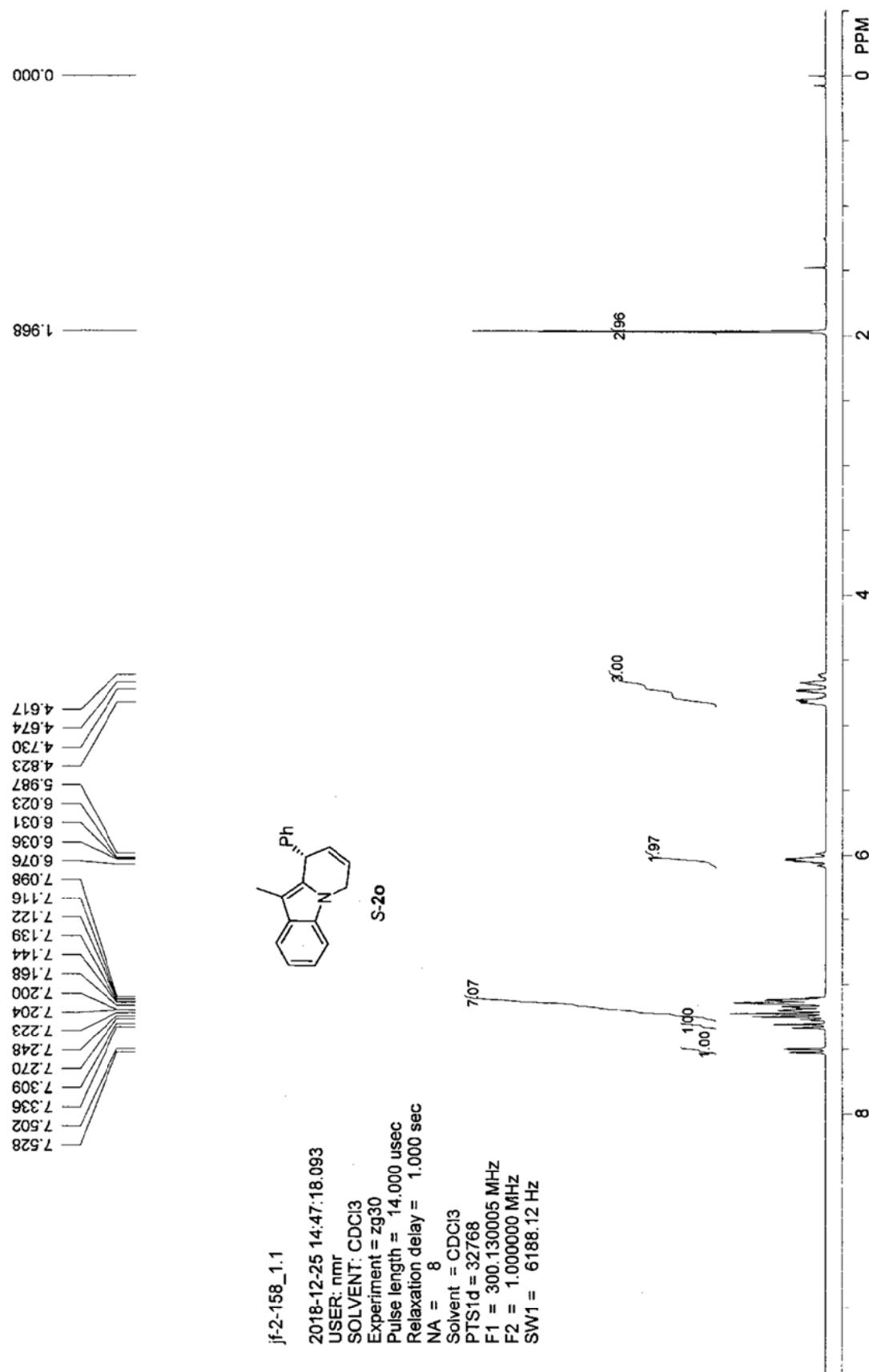
实验者: jf
报告时间: 2019-05-07, 22:51:43
积分方法:面积归一法

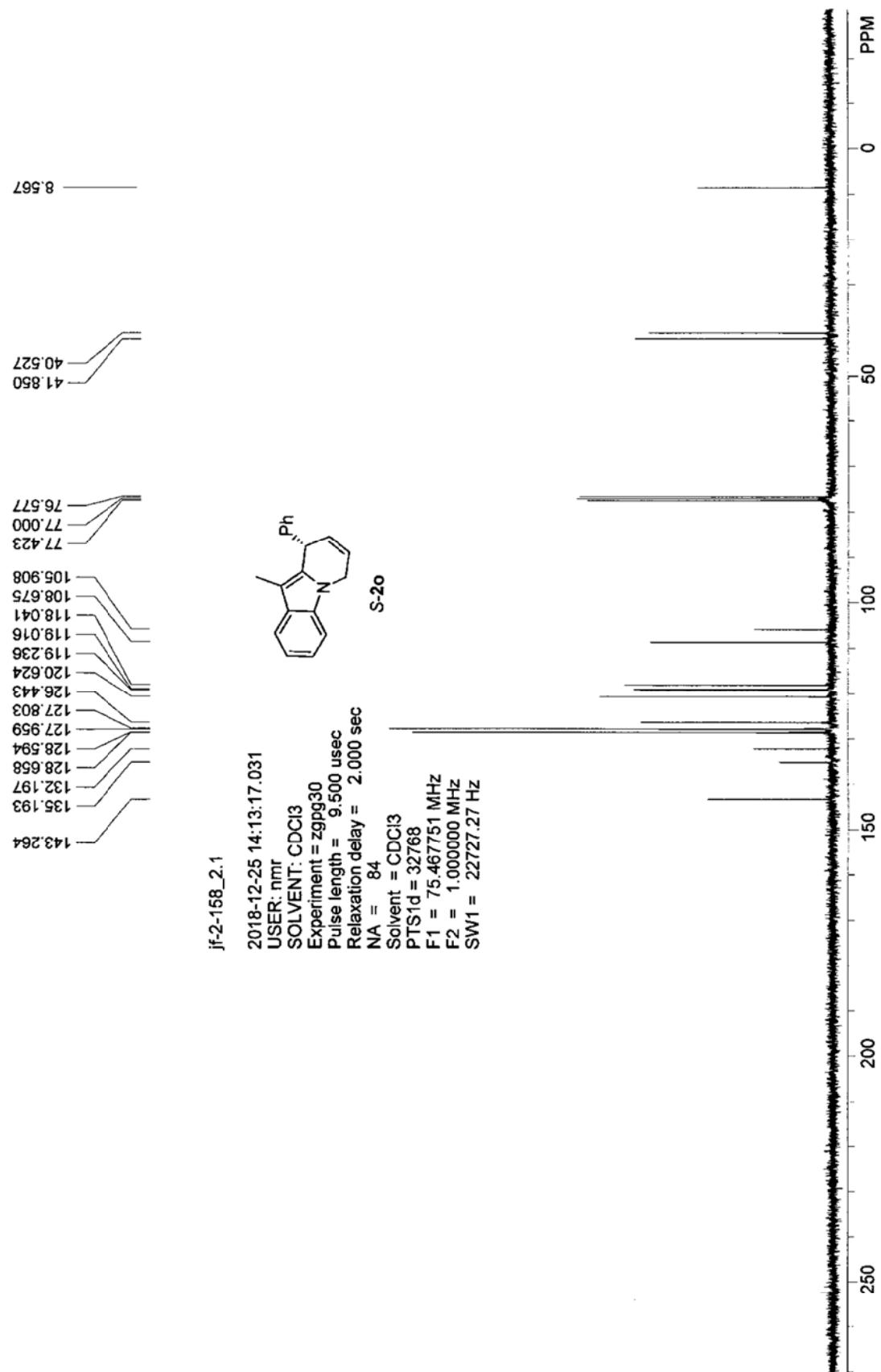
实验内容简介:
od,n-hexane/i-ProOH = 95/5, 0.5, 214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		9.130	92939.141	1034501.688	50.0649
2		10.417	81985.625	1031818.250	49.9351
总计			174924.766	2066319.938	100.0000



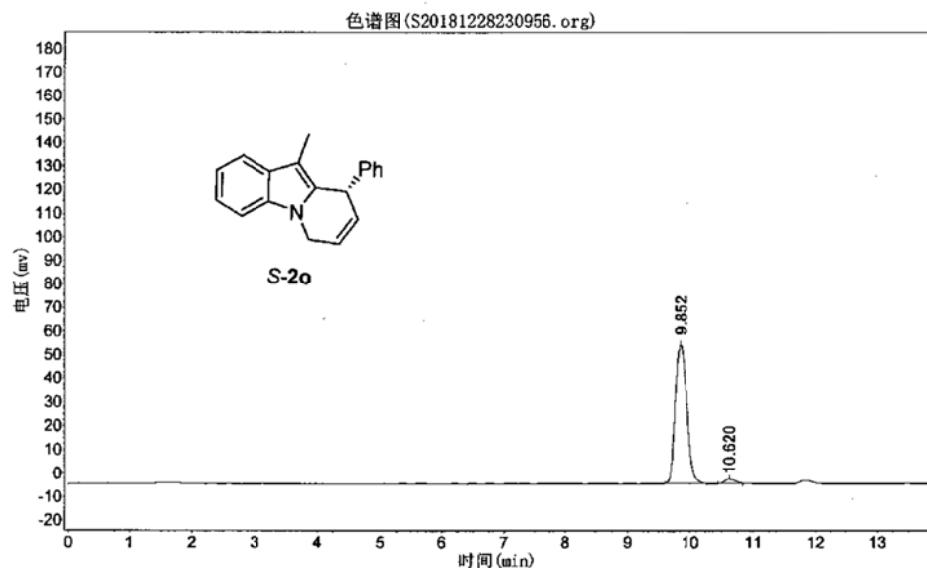


jf-2-158

实验时间: 2018-12-28, 23:09:56
谱图文件:D:\浙大智达\N2000\样品\S20181228230956.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2018-12-28, 23:39:39
积分方法: 面积归一法

实验内容简介:
1a, n-hexane/i-PrOH = 100/1, 0.7, 254



分析结果表

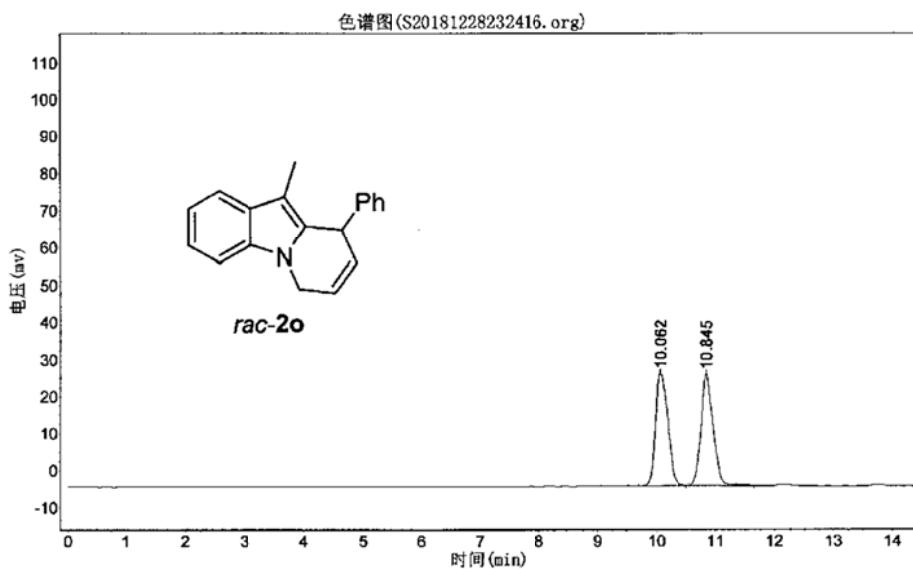
峰号	峰名	保留时间	峰高	峰面积	含量
1		9.852	58514.051	761684.063	97.5062
2		10.620	1683.175	19481.045	2.4938
总计			60197.225	781165.107	100.0000

jf-2-162

实验时间: 2018-12-28, 23:24:16
谱图文件:D:\浙大智达\N2000\样品\S20181228232416.org
方法文件:D:\浙大智达\N2000\djx.mtd

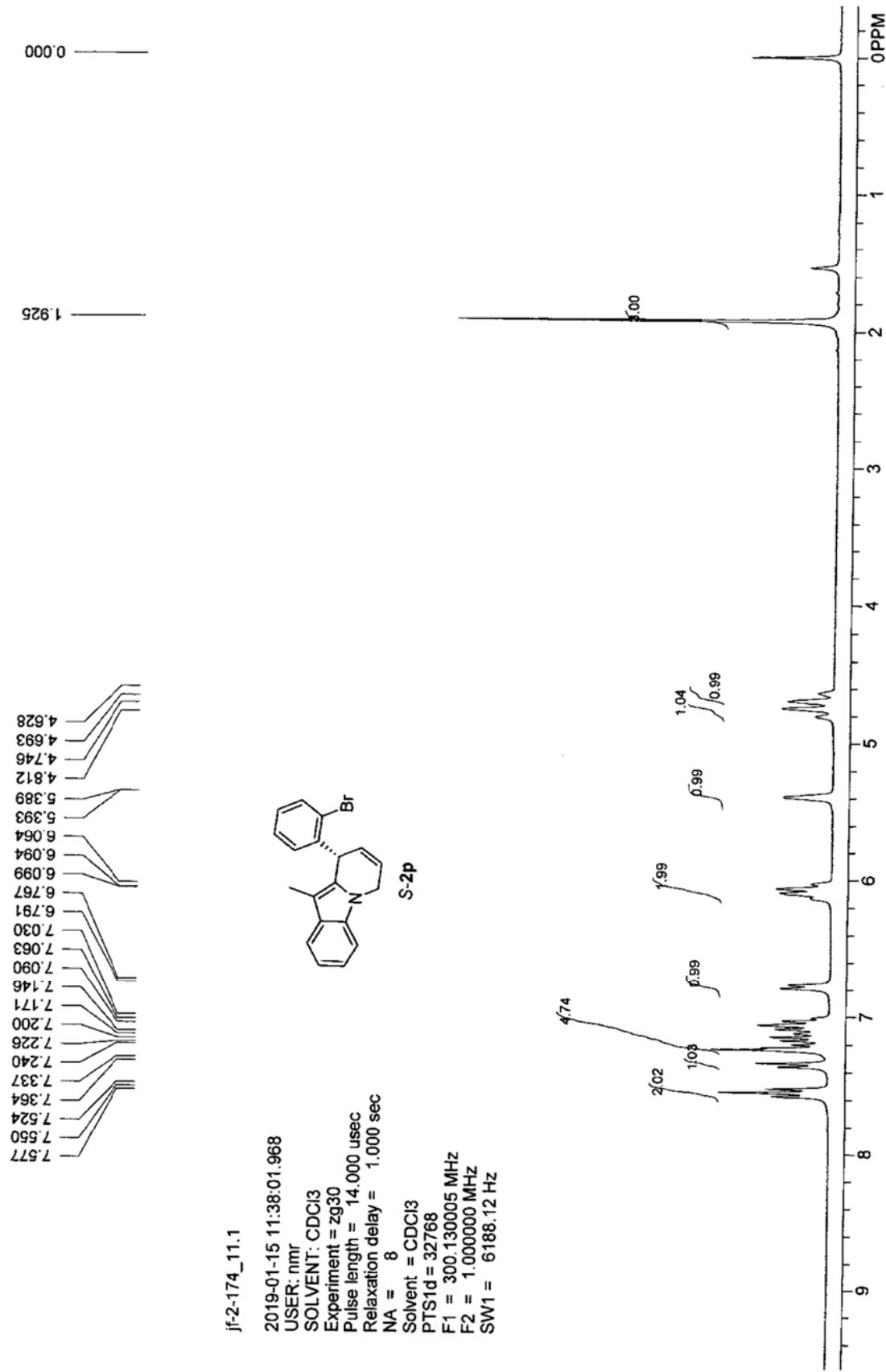
实验者: jf
报告时间: 2018-12-28, 23:42:28
积分方法: 面积归一法

实验内容简介:
ia, n-hexane/i-PrOH = 100/1, 0.7, 254

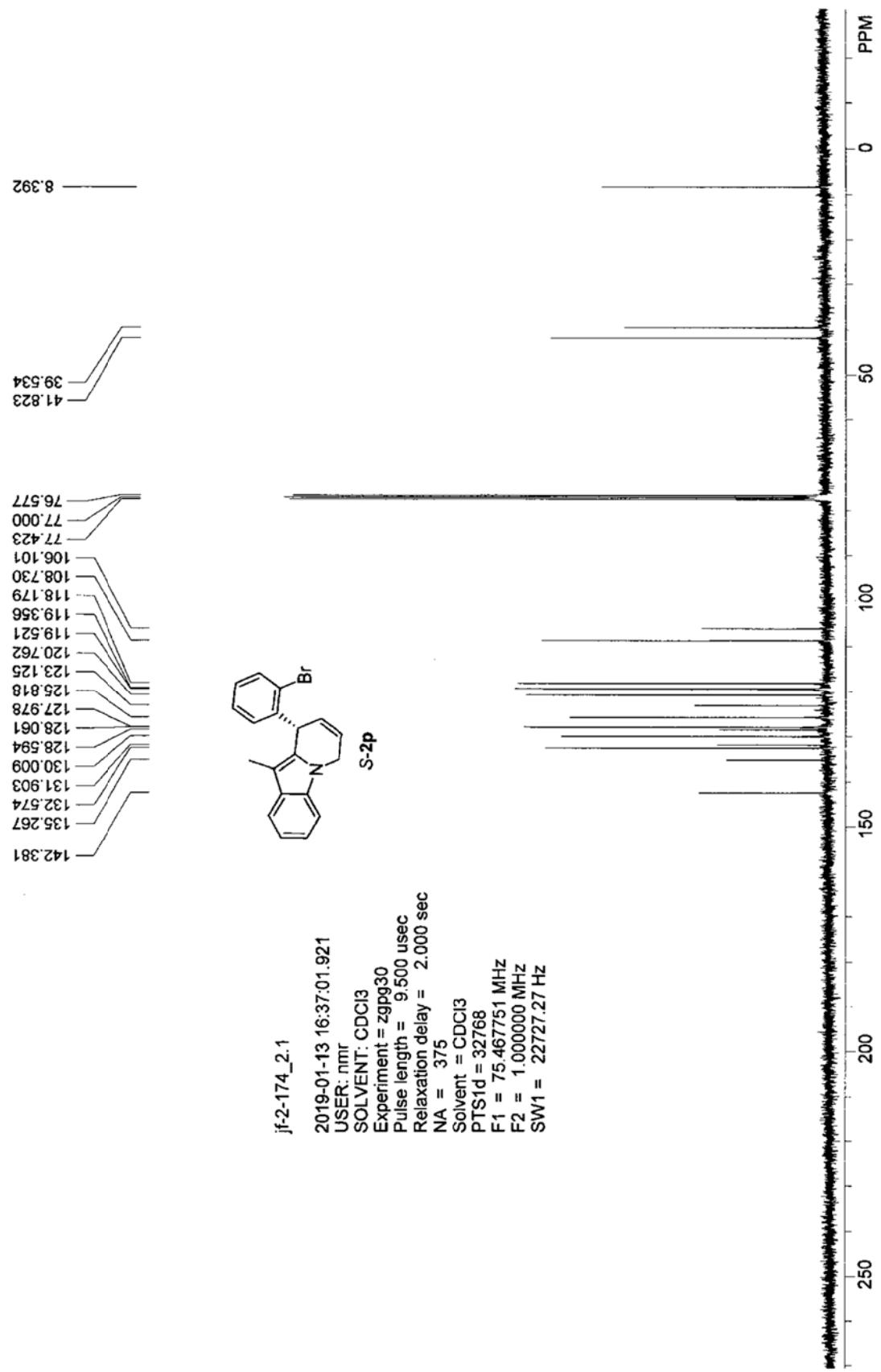


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		10.062	30378.490	436356.813	50.7925
2		10.845	30080.557	422739.313	49.2075
总计			60459.047	859096.125	100.0000



if-2-174 11,1

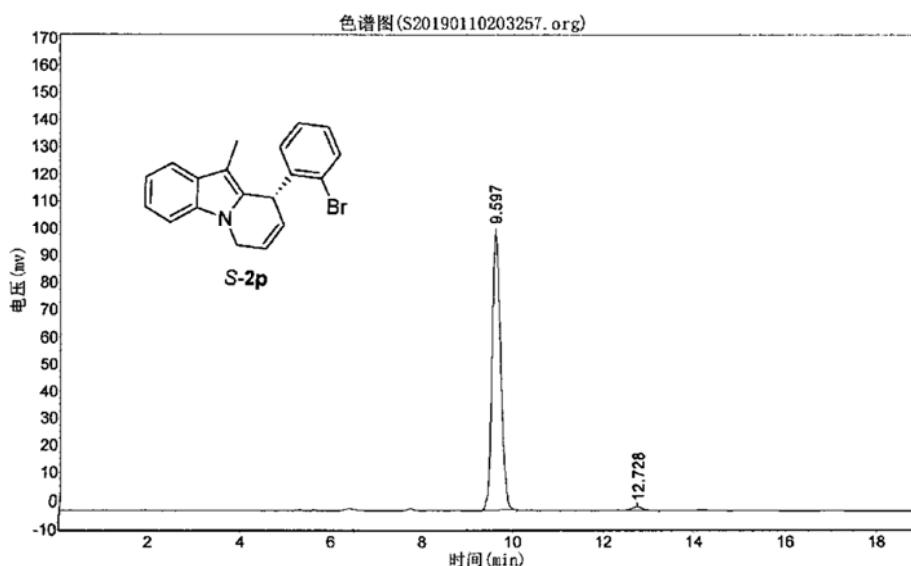


jf-2-174

实验时间: 2019-01-10, 20:32:57
谱图文件:D:\浙大智达\N2000\样品\S20190110203257.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-01-10, 20:54:25
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 90/10, 0.7, 254



分析结果表

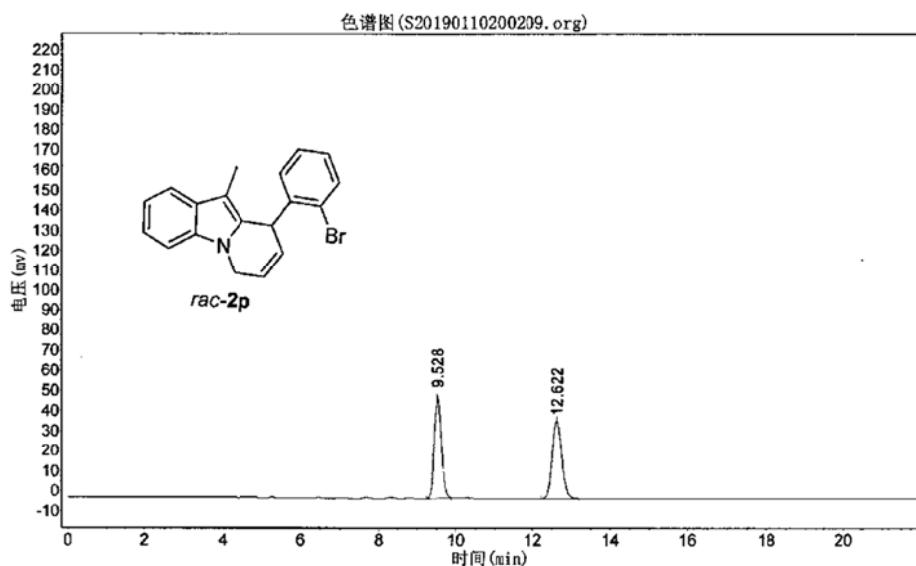
峰号	峰名	保留时间	峰高	峰面积	含量
1		9.597	101252.500	1324026.875	98.2498
2		12.728	1328.548	23586.201	1.7502
总计			102581.048	1347613.076	100.0000

jf-2-182

实验时间：2019-01-10, 20:02:09
谱图文件:D:\浙大智达\N2000\样品\S20190110200209.org
方法文件:D:\浙大智达\N2000\djx.mtd

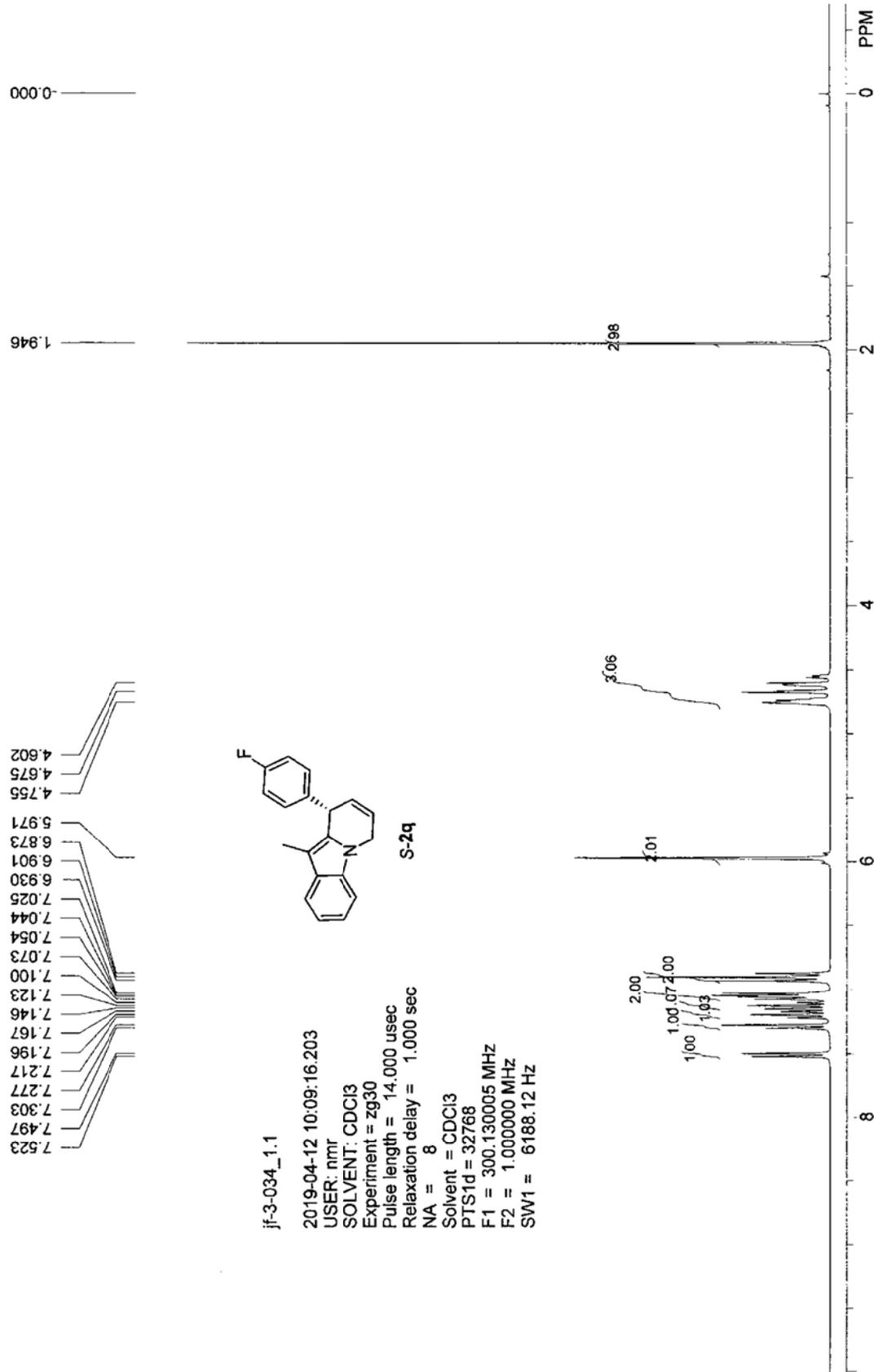
实验者：jf
报告时间：2019-01-10, 20:27:13
积分方法：面积归一法

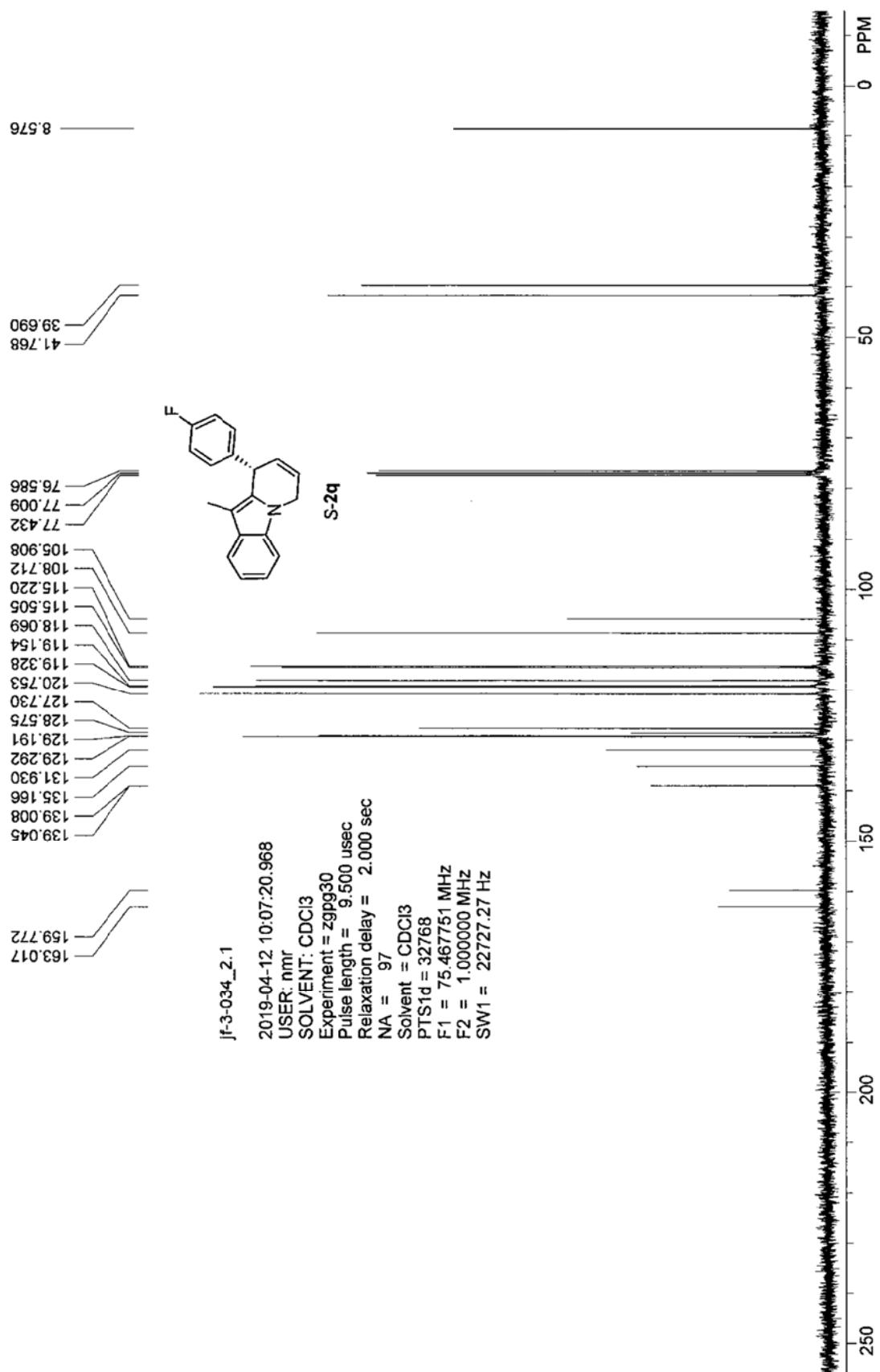
实验内容简介：
od,n-hexane/i-PrOH = 90/10, 0.7, 254



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		9.528	50245.449	648797.000	49.2446
2		12.622	38988.070	668702.875	50.7554
总计			89233.520	1317499.875	100.0000

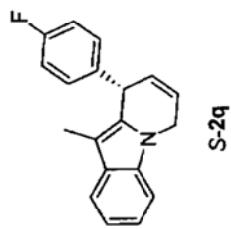






jf-3-034_4.1

2019-04-15 09:25:50.906
USER: nmr
SOLVENT: CDCl₃
Experiment = zgfhgqn
Pulse length = 13.500 usec
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl₃
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz
SW1 = 66964.29 Hz

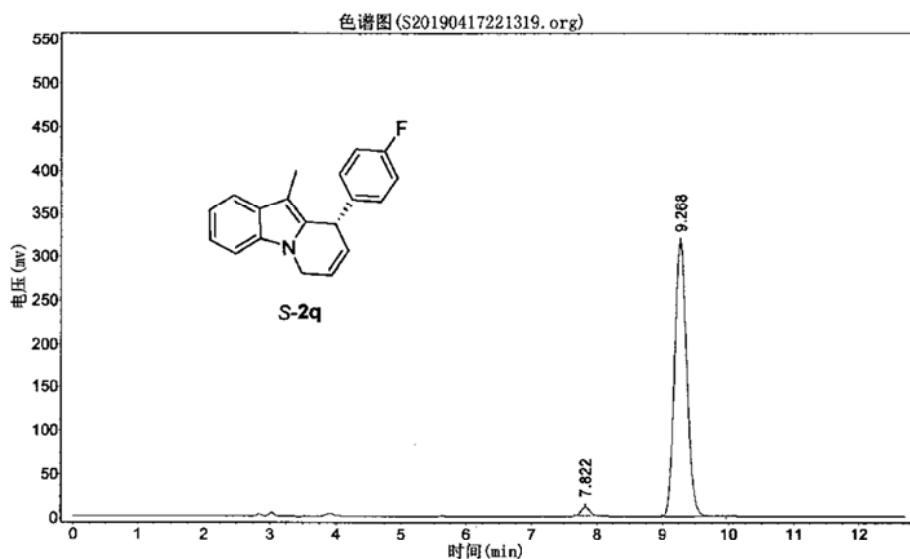


jf-3-034

实验时间: 2019-04-17, 22:13:19
谱图文件:D:\浙大智达\N2000\样品\S20190417221319.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-04-17, 22:29:21
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 95/5, 1. 0, 214

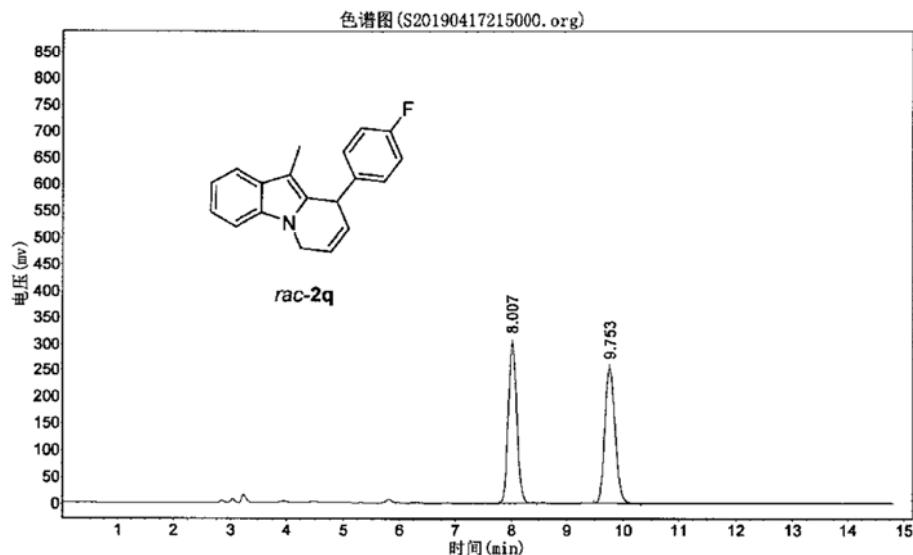


jf-3-037

实验时间: 2019-04-17, 21:50:00
谱图文件:D:\浙大智达\N2000\样品\S20190417215000.org
方法文件:D:\浙大智达\N2000\djx.mtd

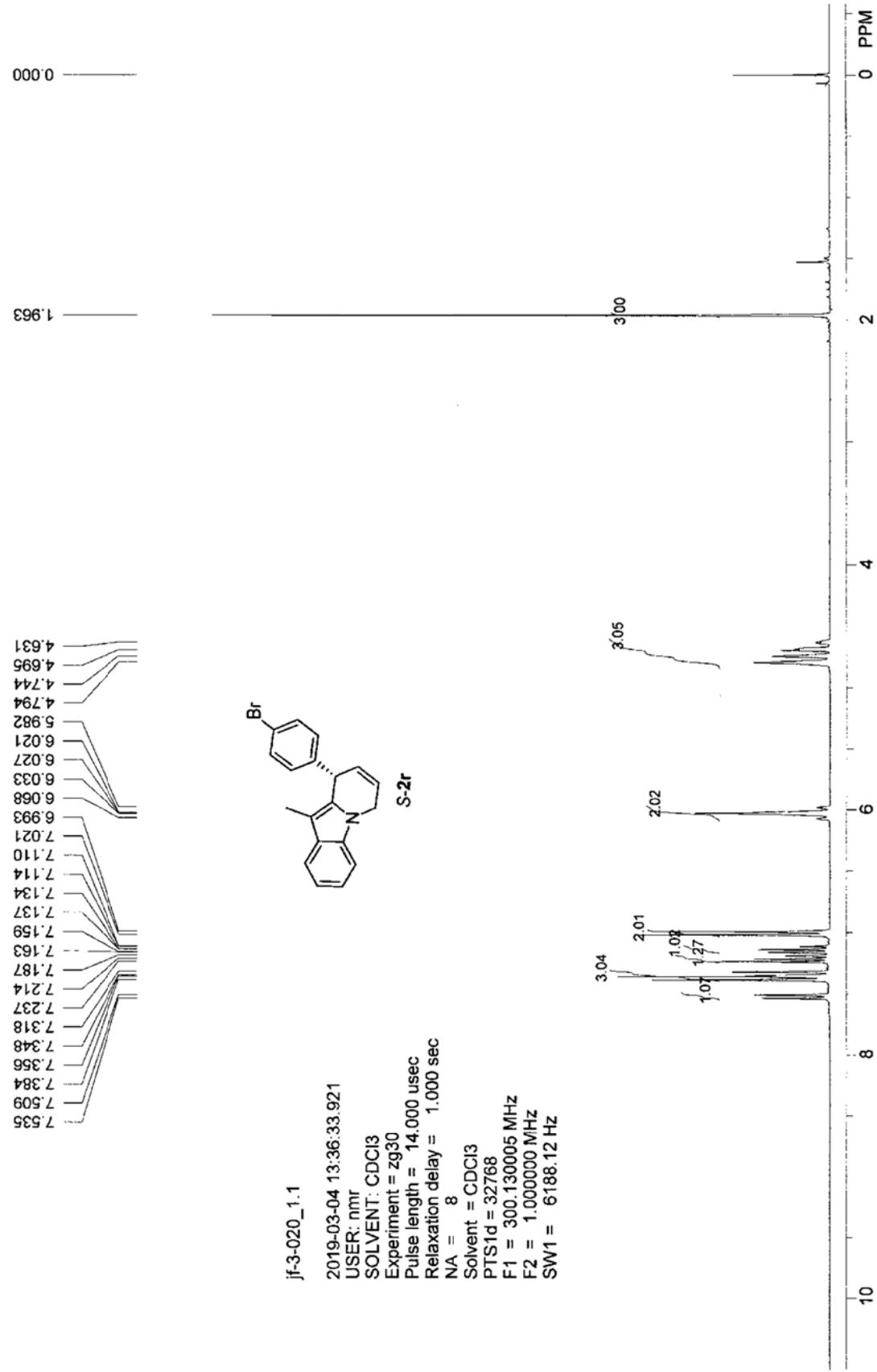
实验者: jf
报告时间: 2019-04-17, 22:07:14
积分方法: 面积归一法

实验内容简介:
OD:n-hexane/i-PrOH = 95/5, 1.0, 214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.007	300605.156	3133754.750	49.3676
2		9.753	251914.344	3214042.000	50.6324
总计			552519.500	6347796.750	100.0000



8.613

41.860
39.975

77.423
77.000
76.577

142.372
135.258
131.710
131.507
129.540
128.603
127.435
120.873
120.257
119.503
119.402
118.152
108.730
106.138

Jf-3-020_2.1

2019-03-04 14:37:21.718

USER: nmr

SOLVENT: CDCl₃

Experiment = zgpp30

Pulse length = 9.500 usec

Relaxation delay = 2.000 sec

NA = 1025

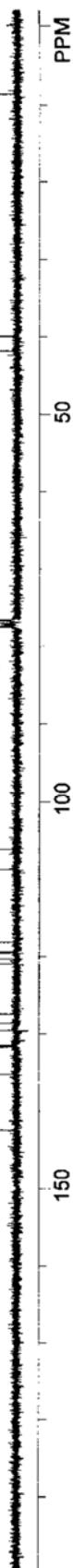
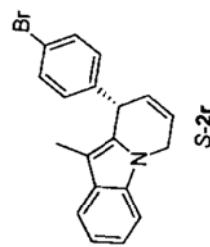
Solvent = CDCl₃

PTSwd = 32768

F1 = 75.467751 MHz

F2 = 1.000000 MHz

SW1 = 22727.27 Hz

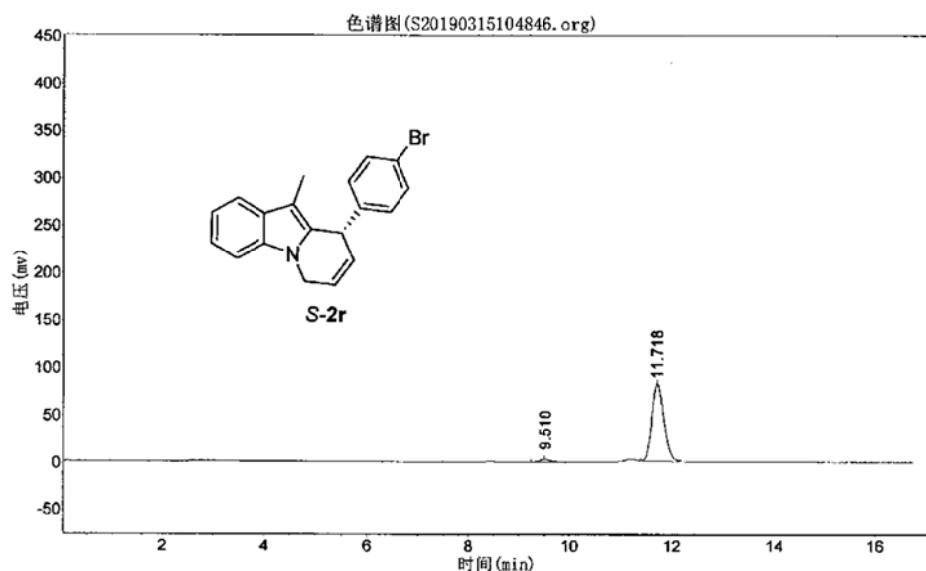


jf-3-020

实验时间: 2019-03-15, 10:48:46
谱图文件:D:\浙大智达\N2000\样品\S20190315104846.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-03-15, 11:10:36
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 90/10, 0.7, 254



分析结果表

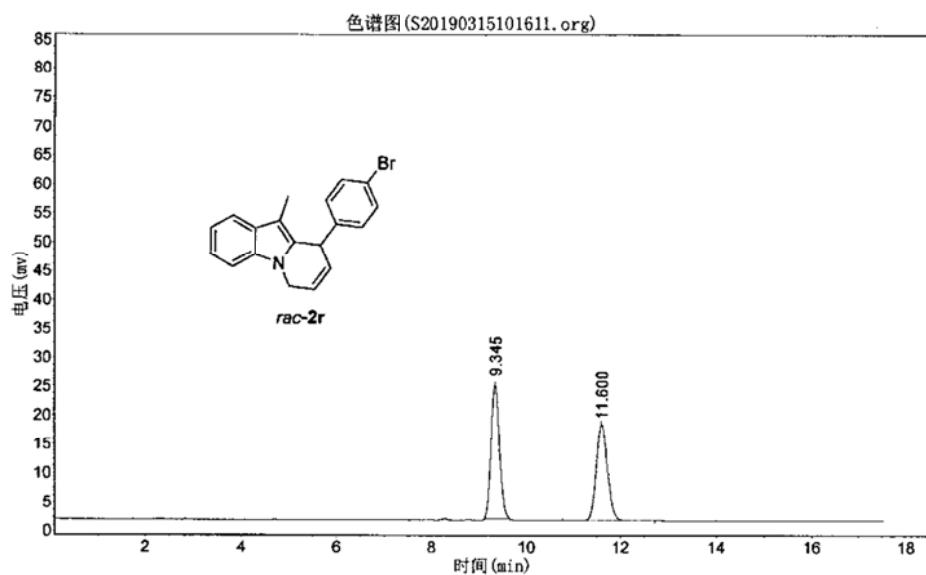
峰号	峰名	保留时间	峰高	峰面积	含量
1		9.510	2047.599	25743.447	1.9239
2		11.718	81314.156	1312318.500	98.0761
总计			83361.755	1338061.947	100.0000

jf-3-021

实验时间: 2019-03-15, 10:16:11
谱图文件:D:\浙大智达\N2000\样品\S20190315101611.org
方法文件:D:\浙大智达\N2000\djx.mtd

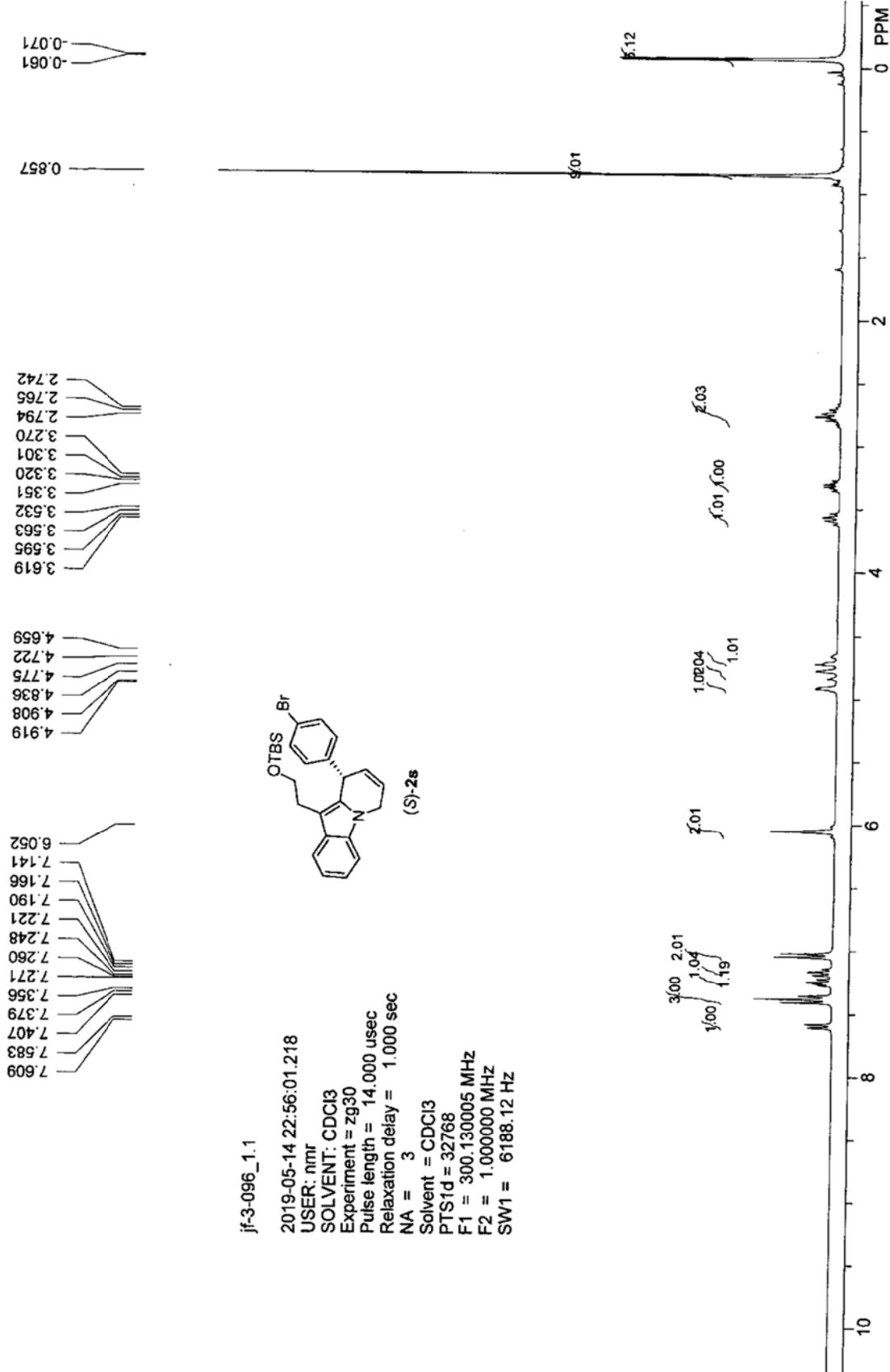
实验者: jf
报告时间: 2019-03-15, 10:43:18
积分方法: 面积归一法

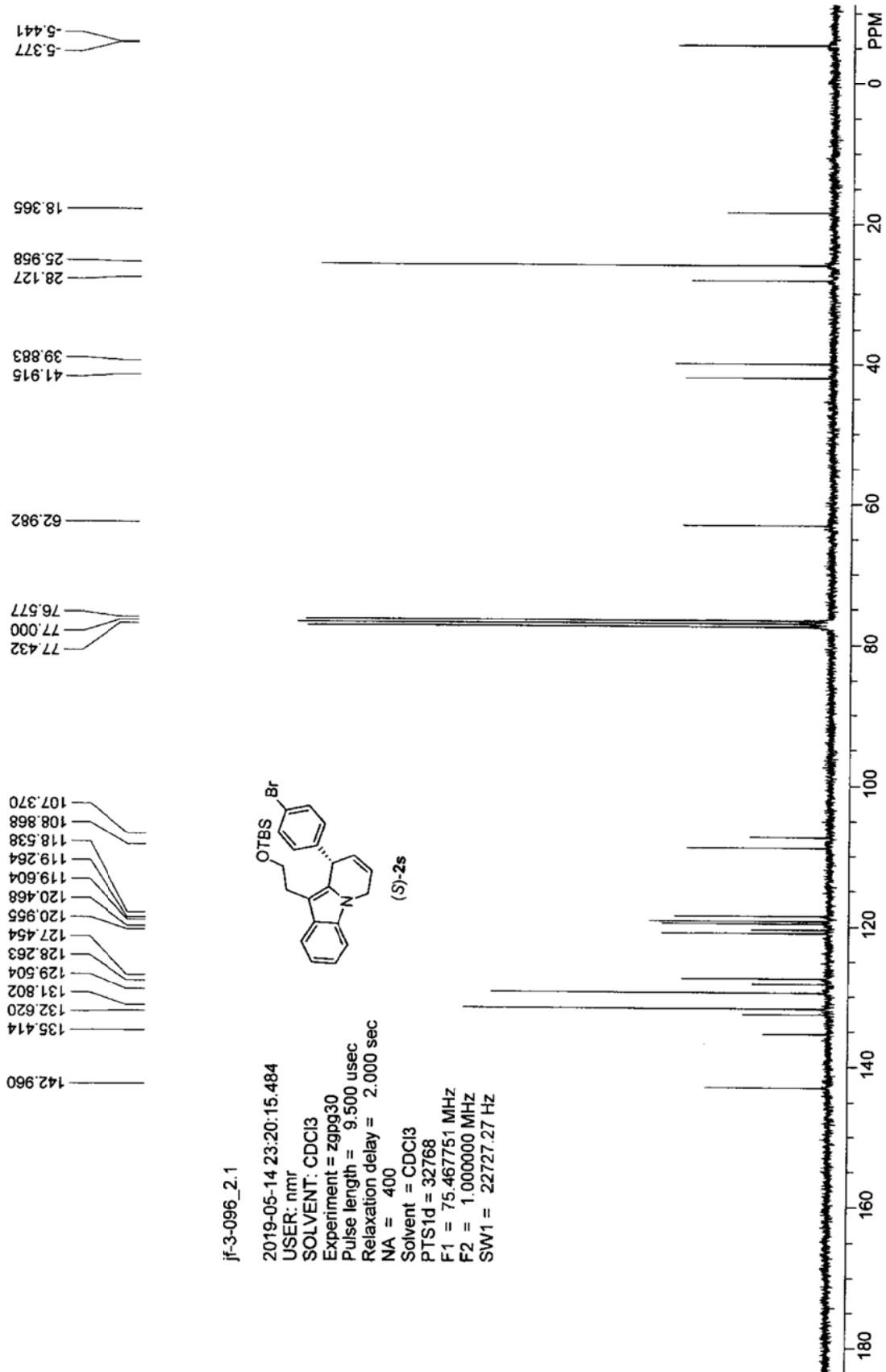
实验内容简介:
od, n-hexane/i-PrOH = 90/10, 0.7, 254



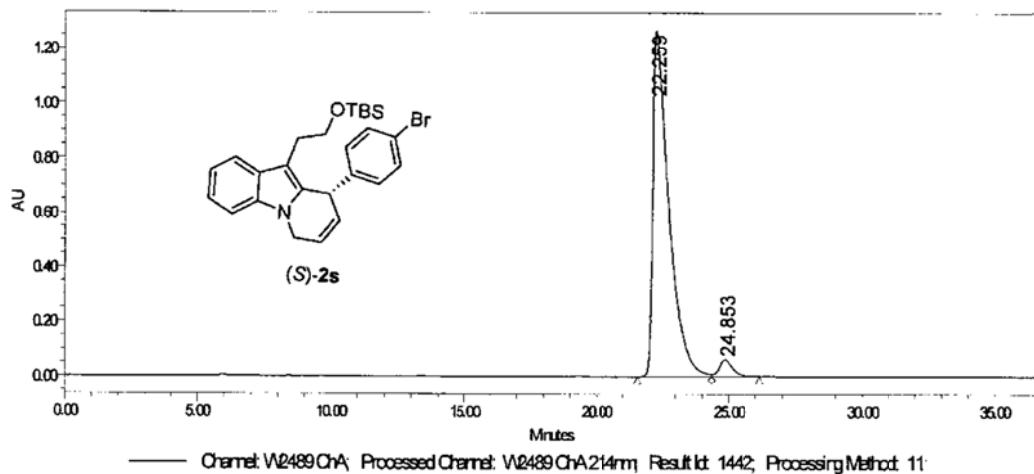
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		9.345	22995.117	285223.875	50.8220
2		11.600	16691.217	275997.781	49.1780
总计			39686.334	561221.656	100.0000





SAMPLE INFORMATION			
Sample Name:	JF3-096-JF1000-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	ZG100
Injection #:	23	Processing Method:	111
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA.214nm
Date Acquired:	5/24/2019 6:51:06 PM EDT		
Date Processed:	5/24/2019 9:41:15 PM EDT		



—— Channel: W2489 ChA; Processed Channel: W2489 ChA.214nm; Result Id: 1442; Processing Method: 11;

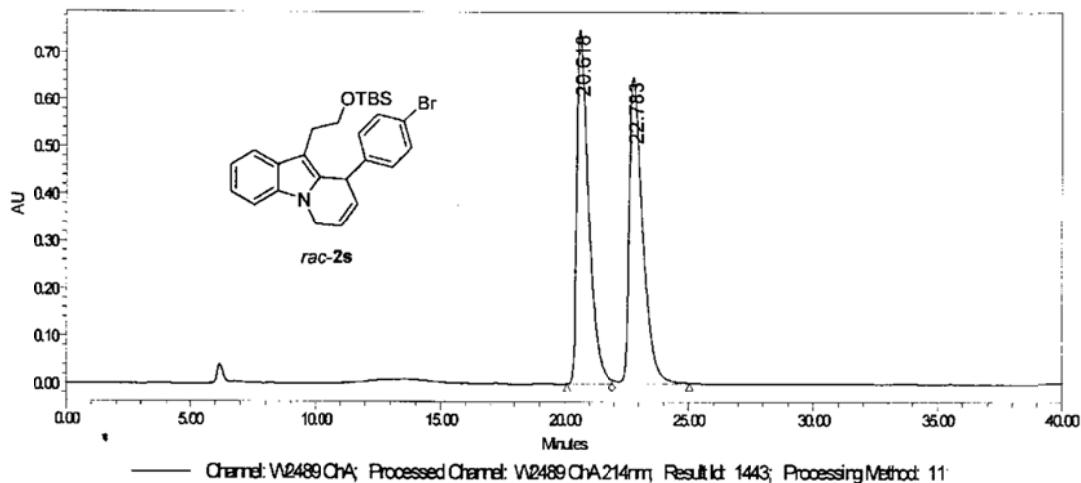
Processed Channel Descr.: W2489 ChA.214nm

	Processed Channel Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	22.258	52849065	96.00	1271914
2	W2489 ChA.214nm	24.853	2201217	4.00	62267

Reported by User: System
 Report Method: InjectionSummary Report
 Report Method ID: 1029 1029
 Page: 1 of 1

Project Name: HPLC_1525
 Date Printed:
 5/24/2019
 9:42:01 PM America/New_York

SAMPLE INFORMATION			
Sample Name:	jf3-097-f-100-0-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	ZGJ100
Injection #:	24	Processing Method:	111
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chrt. Descr.:	W2489 ChA.214nm
Date Acquired:	5/24/2019 7:26:33 PM EDT		
Date Processed:	5/24/2019 9:41:49 PM EDT		

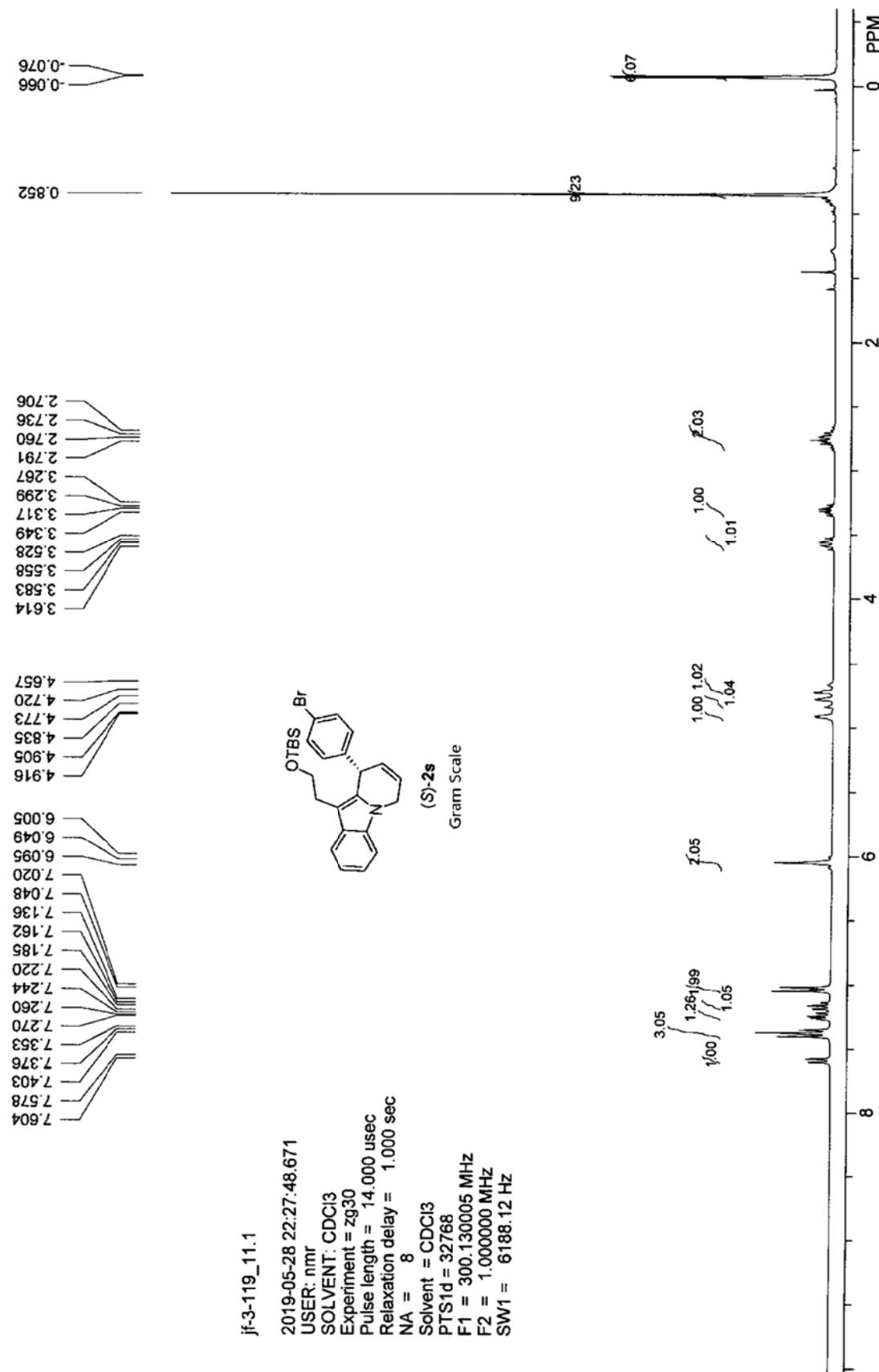


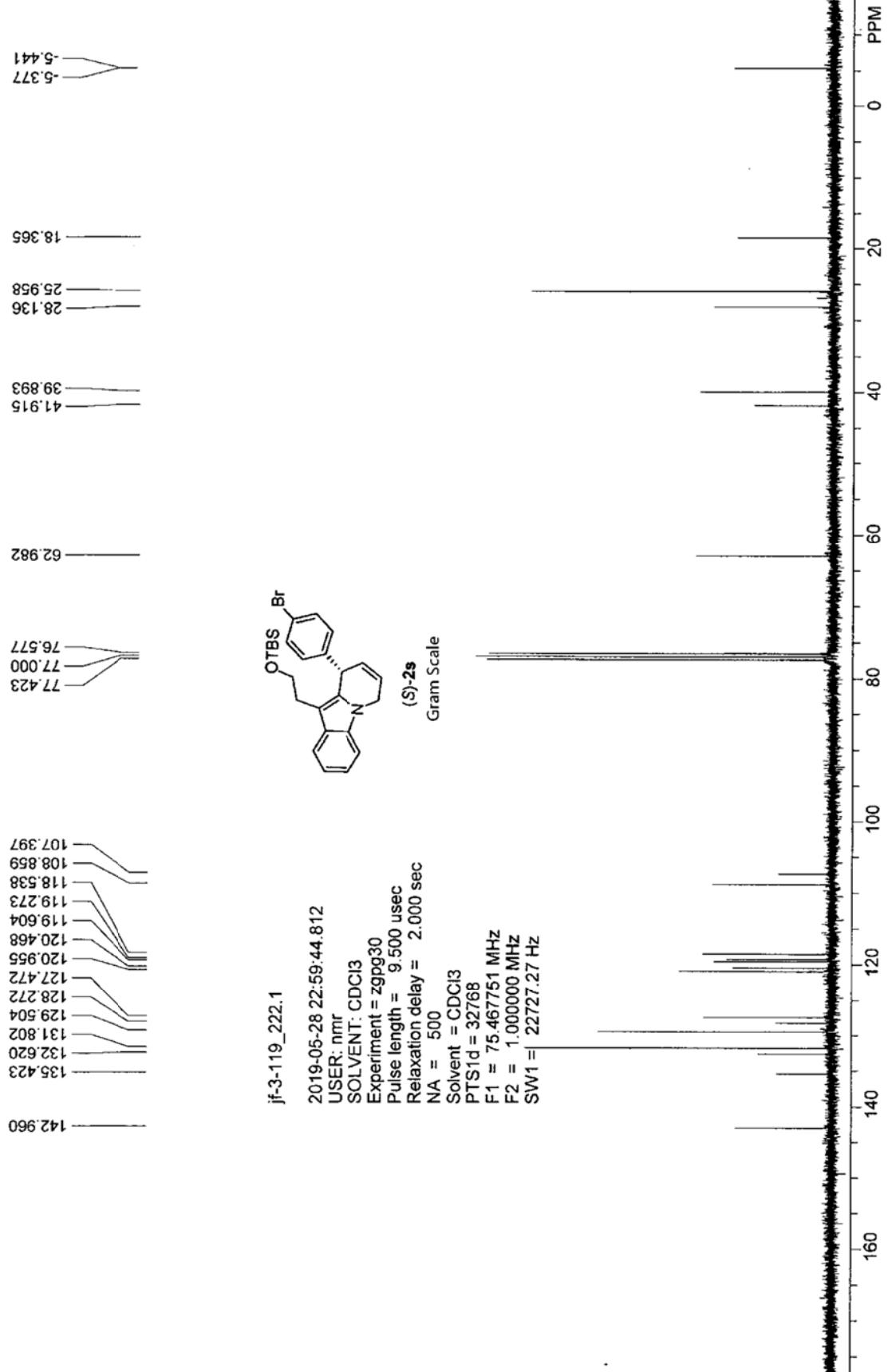
Processed Channel Descr.: W2489 ChA.214nm

	Processed Channel Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	20.618	24579324	50.49	749950
2	W2489 ChA.214nm	22.783	24098763	49.51	646916

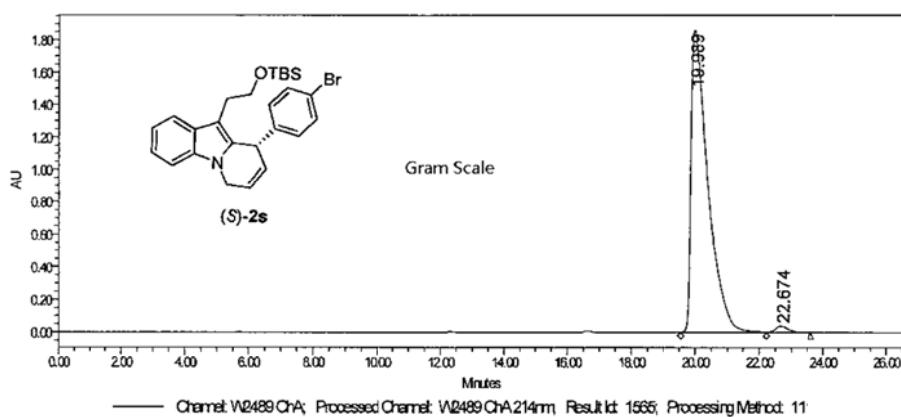
Reported by User: System
Report Method: Injection Summary Report
Report Method ID: 1029 1029
Page: 1 of 1

Project Name: HPLC_1525
Date Printed:
5/24/2019
9:42:36 PM America/New York





SAMPLE INFORMATION			
Sample Name:	JF3-119-JF100-0-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	ZGJ100
Injection #:	29	Processing Method:	111
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Ctrl. Descr.:	W2489 ChA.214nm
Date Acquired:	5/30/2019 7:04:54 PM EDT		
Date Processed:	5/30/2019 8:29:01 PM EDT		



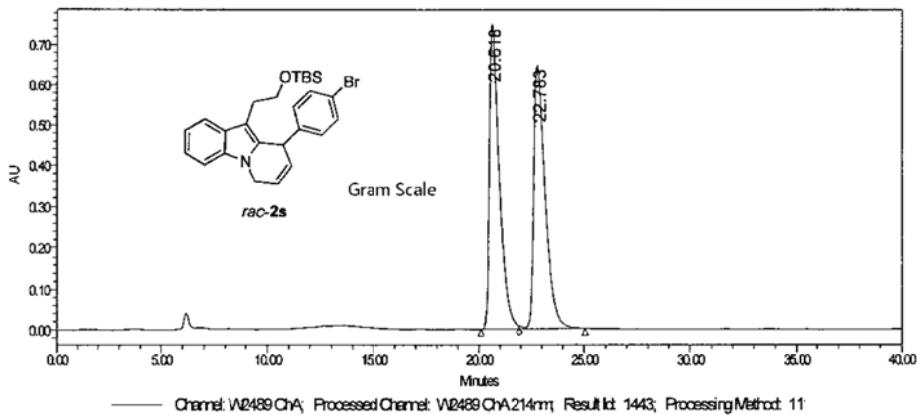
Processed Channel Descr.: W2489 ChA.214nm

	Processed Channel Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	19.989	68903629	98.43	1863150
2	W2489 ChA.214nm	22.674	1086606	1.57	39090

Reported by User: System
Report Method: InjectionSummaryReport
Report Method ID: 1029 1029
Page: 1 of 1

Project Name: HPLC_1525
Date Printed:
5/30/2019
8:29:37 PM America/New_York

SAMPLE INFORMATION			
Sample Name:	jf-3-097-if-100-0-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	ZGI100
Injection#:	24	Processing Method:	111
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chrl. Descr.:	W2489 ChA.214nm
Date Acquired:	5/24/2019 7:28:33 PM EDT		
Date Processed:	5/24/2019 9:41:49 PM EDT		



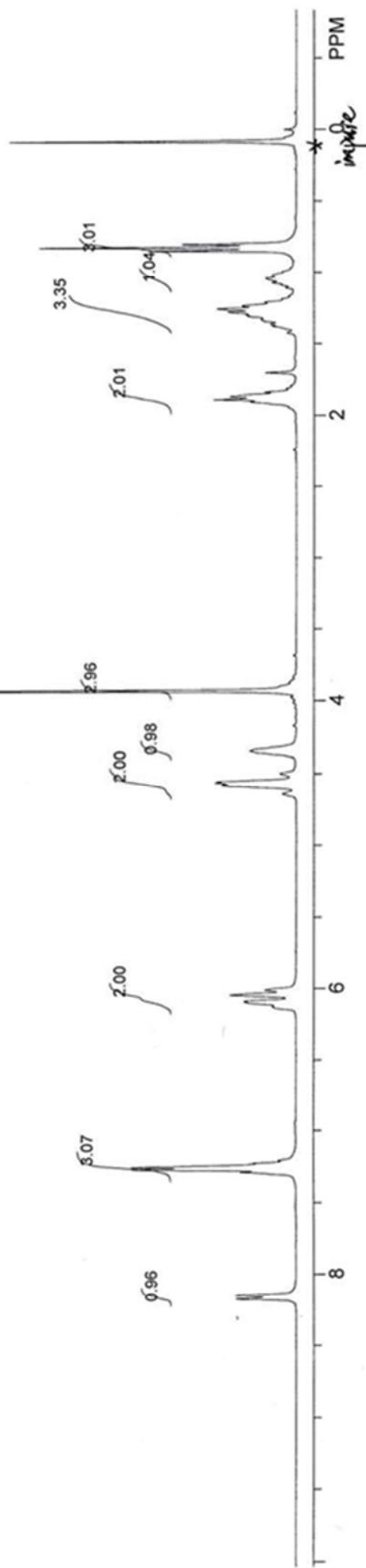
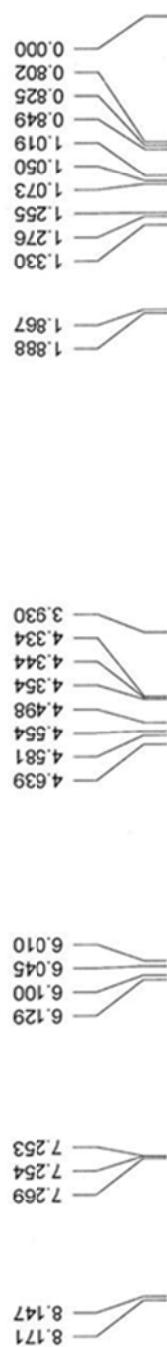
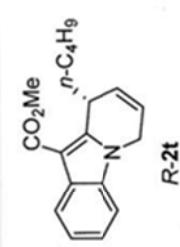
Processed Channel Descr.: W2489 ChA.214nm

	Processed Channel Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	20.618	24579324	50.49	749950
2	W2489 ChA.214nm	22.783	24098763	49.51	646916

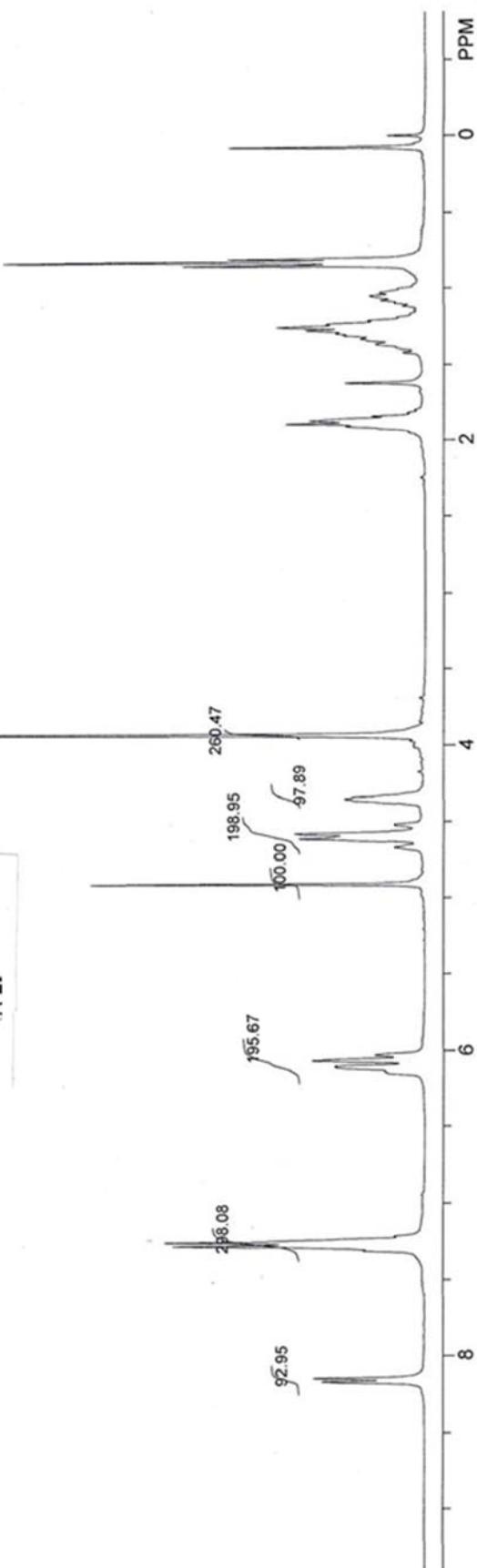
Reported by User: System
 Report Method: Injection Summary Report
 Report Method ID: 1029 1029
 Page: 1 of 1

Project Name: HPLC_1525
 Date Printed:
 5/24/2019
 9:42:36 PM America/New_York

jf4-173-1
2020-05-27 15:00:00.218
NA = 8
Solvent = CDCl₃
PTS1d = 32768
F1 = 300.130005 MHz

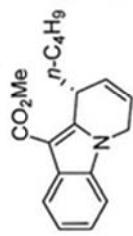


8.146
8.111
6.063
6.029
6.145
4.910
4.871
4.612
4.584
4.578
4.520
4.361
4.352
4.342
3.933
1.893
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1.225
1.081
1.051
1.033
0.851
0.827
0.804
0.766
0.000

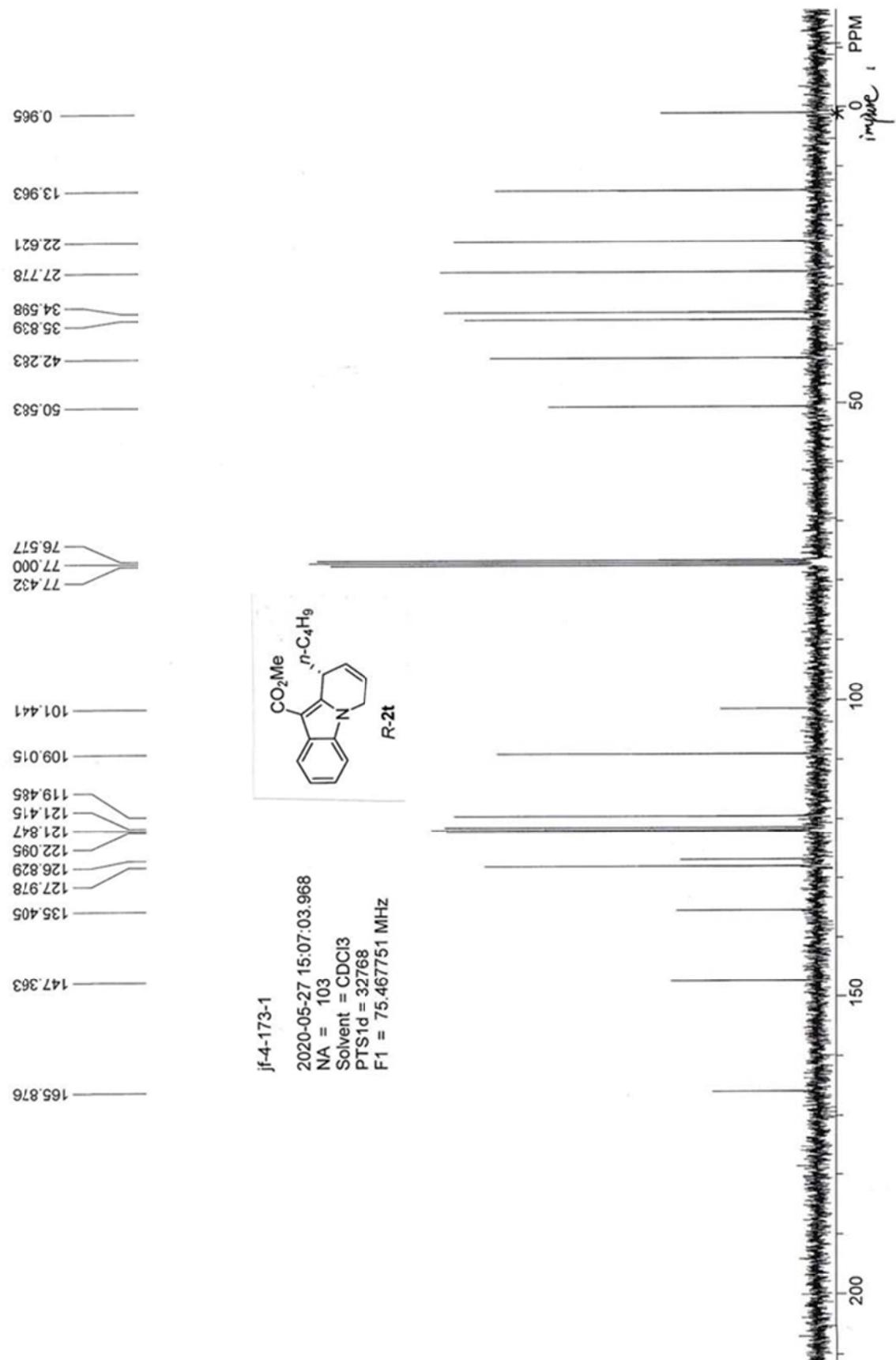


jf-4-173-1-purity

2020-06-01 14:59:15.687
NA = 8
Solvent = CDCl₃
PTS1d = 32768
F1 = 300.130005 MHz



R-2t

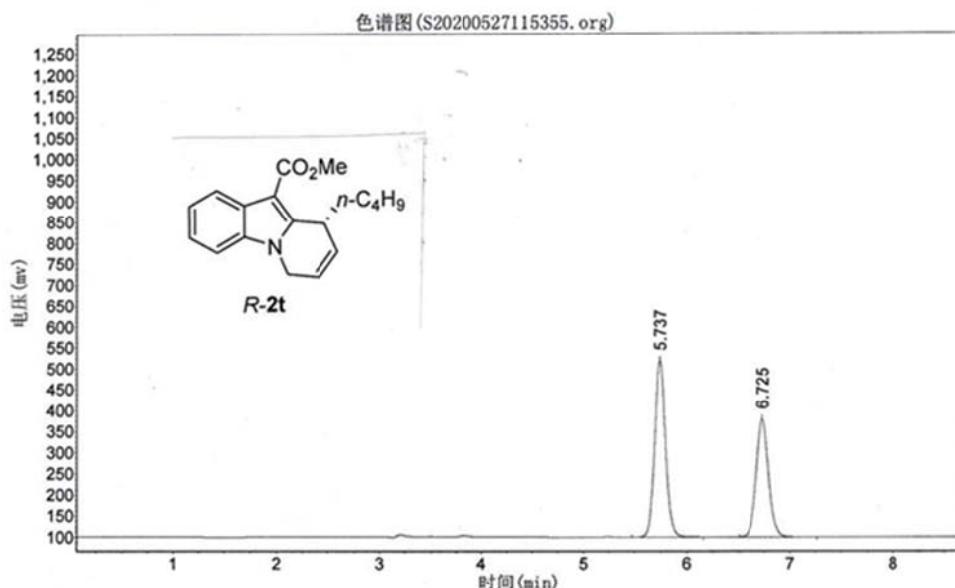


jf-4-173-1

实验时间: 2020-05-27, 11:53:55
谱图文件:D:\浙大智达\N2000\样品\S20200527115355.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-05-27, 12:03:48
积分方法: 面积归一法

实验内容简介:
ia, n-hexane/i-PrOH = 90/10, 0.7, 214



分析结果表

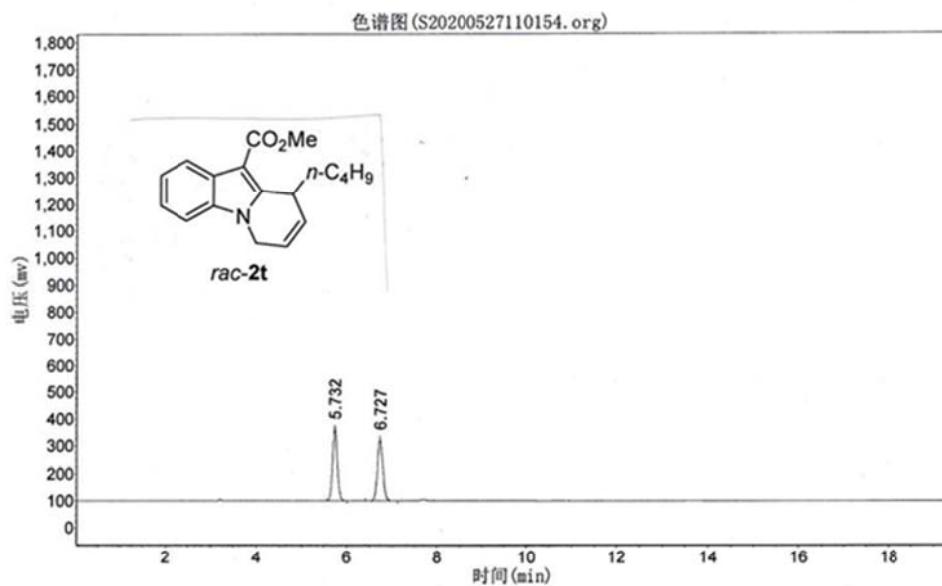
峰号	峰名	保留时间	峰高	峰面积	含量
1		5.737	418210.844	3019584.500	56.5661
2		6.725	278275.625	2318564.500	43.4339
总计			696486.469	5338149.000	100.0000

jf-4-174-1

实验时间: 2020-05-27, 11:01:54
谱图文件:D:\浙大智达\N2000\样品\S20200527110154.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-05-27, 11:56:20
积分方法: 面积归一法

实验内容简介:
ia, n-hexane/i-PrOH = 90/10, 0.7, 214

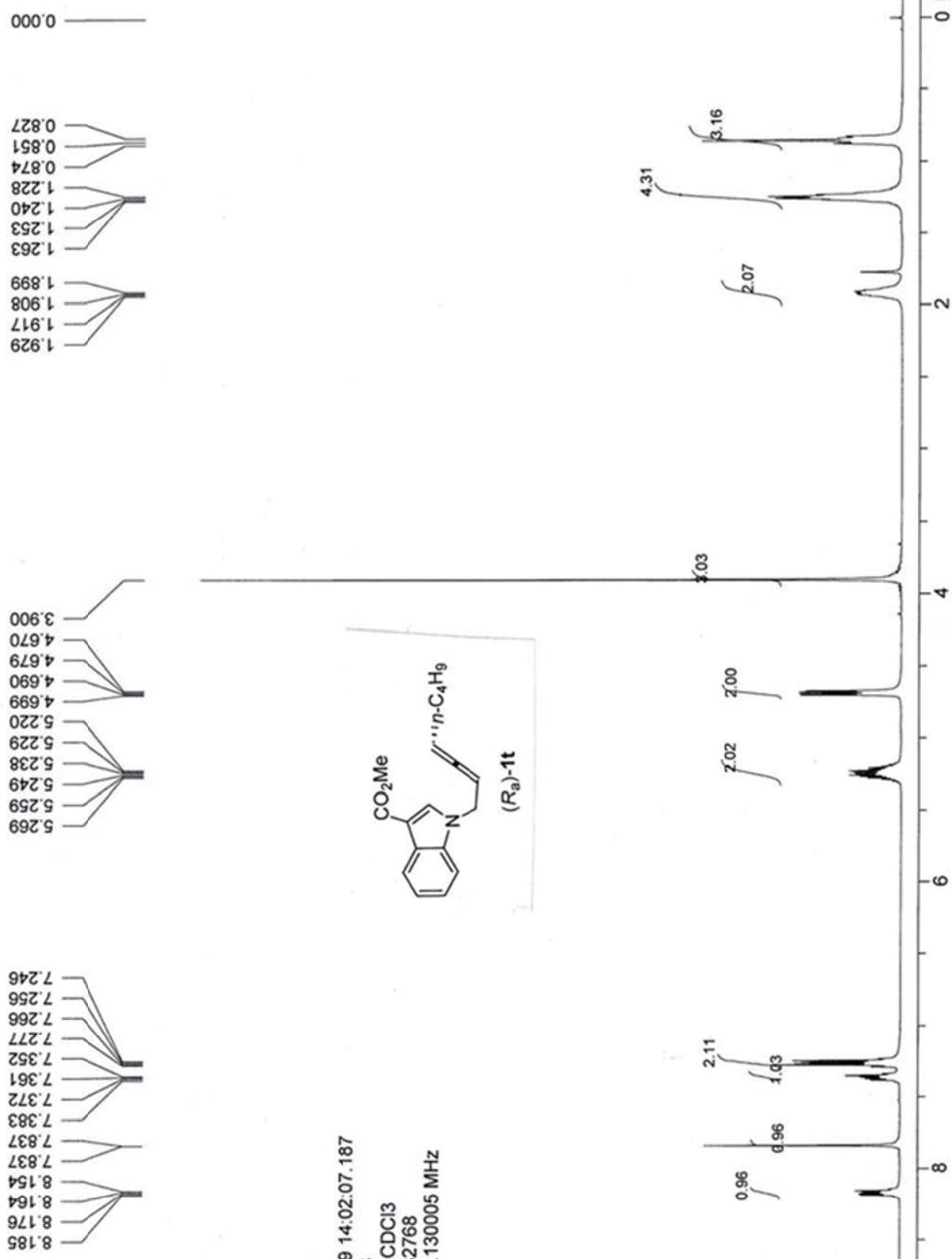
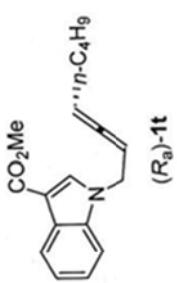


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		5.732	261362.781	1918391.375	50.5729
2		6.727	222631.875	1874928.000	49.4271
总计			483994.656	3793319.375	100.0000

jf4-173-2

2020-05-29 14:02:07.187
NA = 8
Solvent = CDCl₃
PTS1d = 32768
F1 = 300.130005 MHz

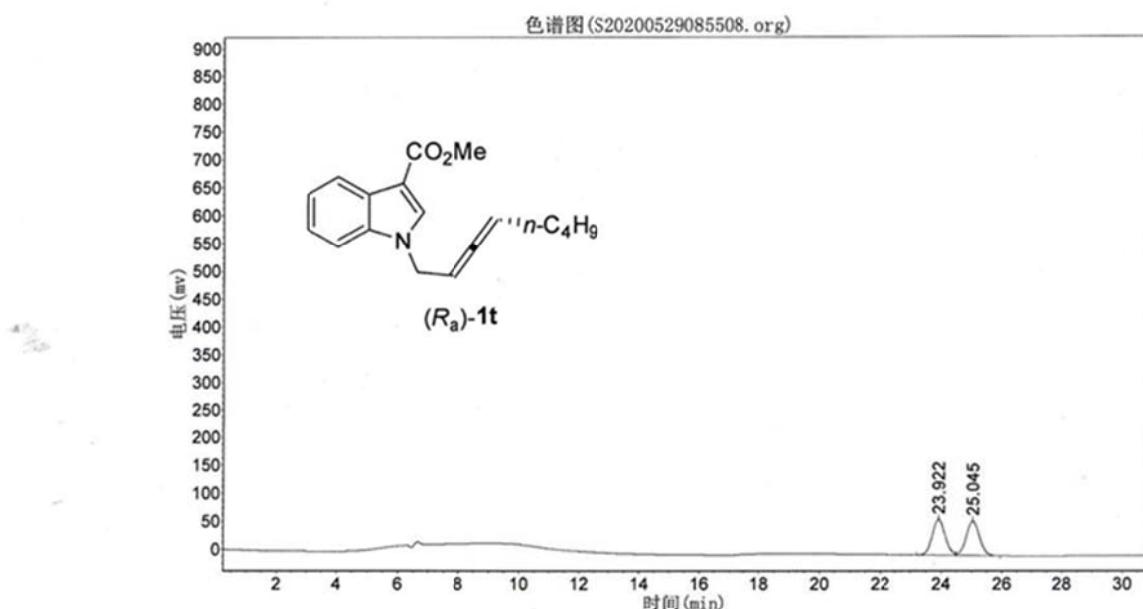


jf-4-173-2

实验时间: 2020-05-29, 8:55:08
谱图文件:D:\浙大智达\N2000\样品\S20200529085508.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-05-29, 9:27:59
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 90/10, 0.5, 214

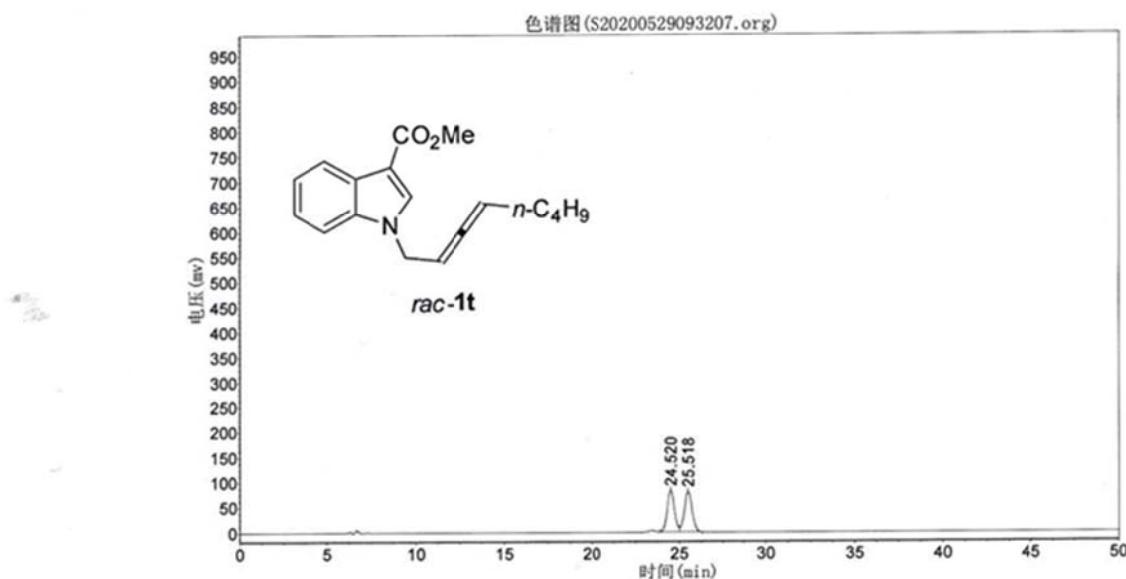


jf-3-112

实验时间: 2020-05-29, 9:32:07
谱图文件:D:\浙大智达\N2000\样品\S20200529093207.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-09-13, 18:38:28
积分方法: 面积归一法

实验内容简介:
od, n-hexane/i-PrOH = 90/10, 0.5, 214

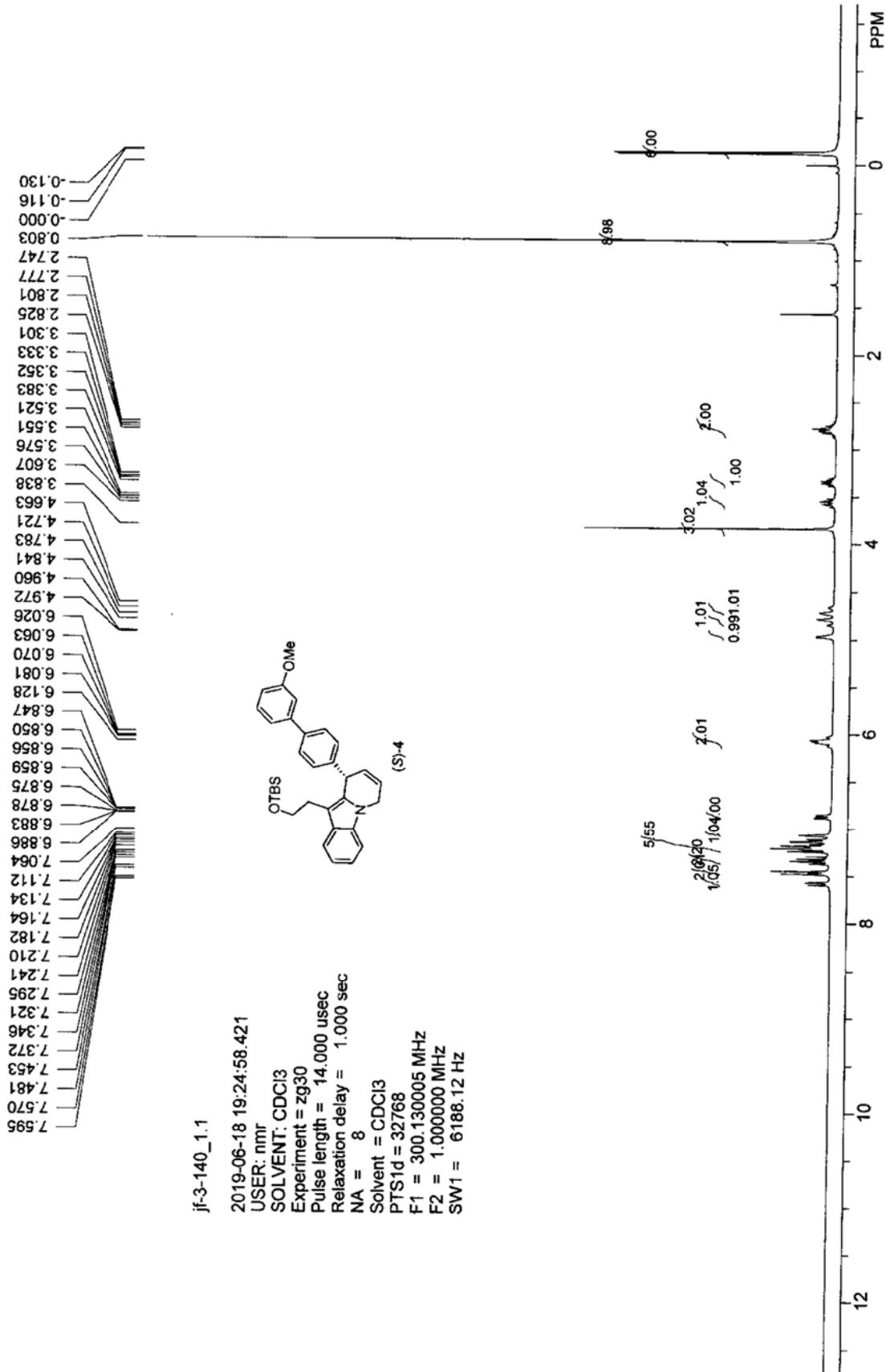
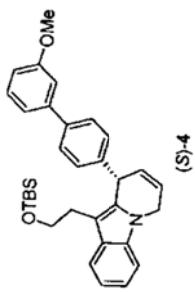


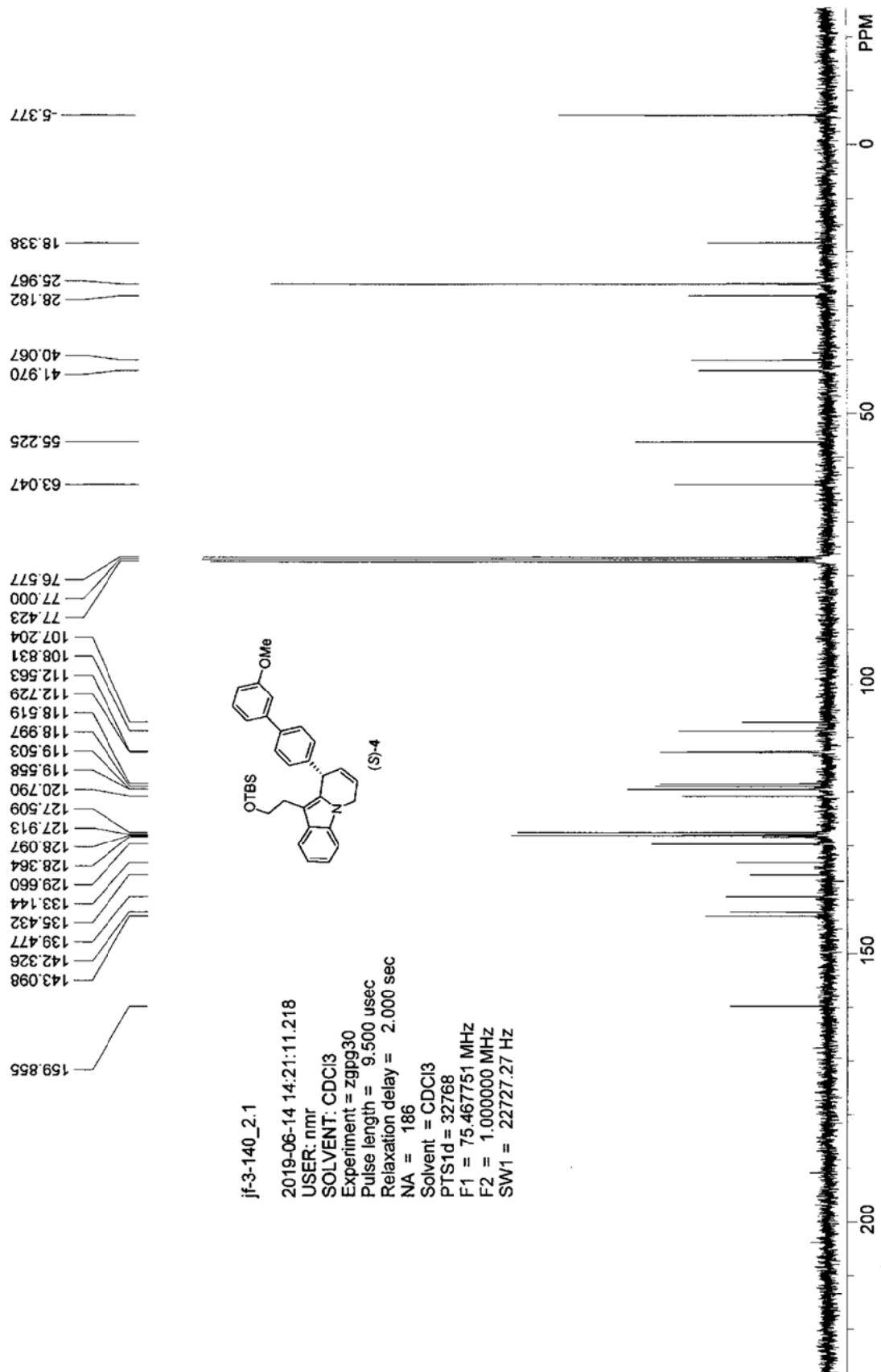
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		24.520	81369.563	2359160.000	49.0409
2		25.518	79835.367	2451435.000	50.9591
总计			161204.930	4810595.000	100.0000

jf-3-140_1.1

2019-06-18 19:24:58.421
USER: nmr
SOLVENT: CDCl3
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl3
PTSId = 32768
F1 = -300.130005 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz



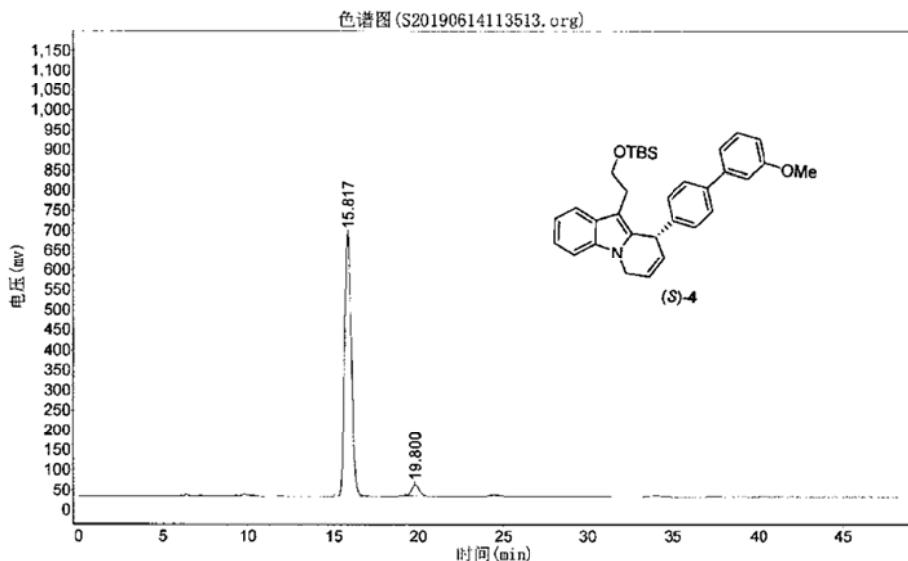


jf-3-140

实验时间: 2019-06-14, 11:35:13
谱图文件:D:\浙大智达\N2000\样品\S20190614113513.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-06-14, 12:28:14
积分方法: 面积归一法

实验内容简介:
ia, n hexane/i-PrOH = 100/1, 0.5, 214



分析结果表

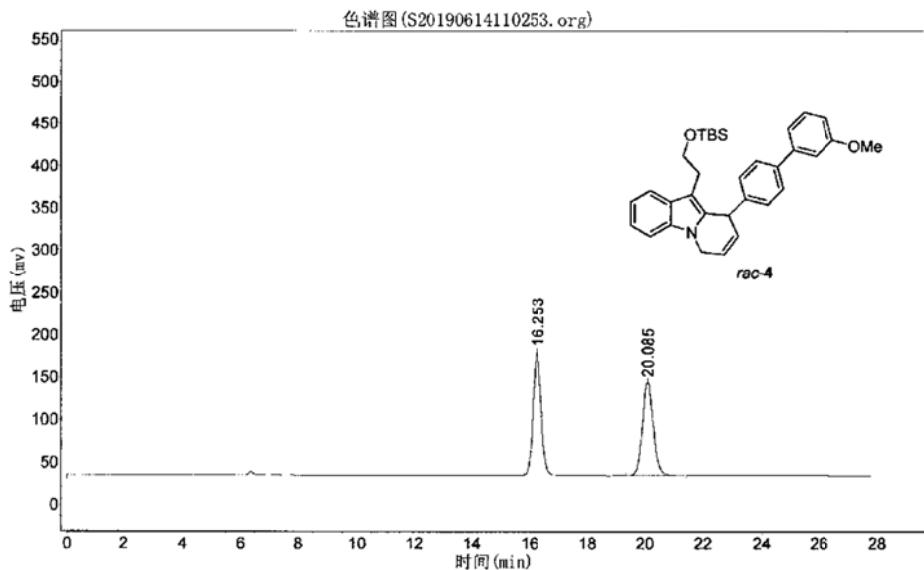
峰号	峰名	保留时间	峰高	峰面积	含量
1		15.817	657689.063	18151676.000	95.3860
2		19.800	27621.441	878027.188	4.6140
总计			685310.504	19029703.188	100.0000

jf-3-139

实验时间: 2019-06-14, 11:02:53
谱图文件:D:\浙大智达\N2000\样品\S20190614110253.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2019-06-14, 11:37:39
积分方法: 面积归一法

实验内容简介:
1a, n-hexane/i-PrOH = 100/1, 0.5, 214

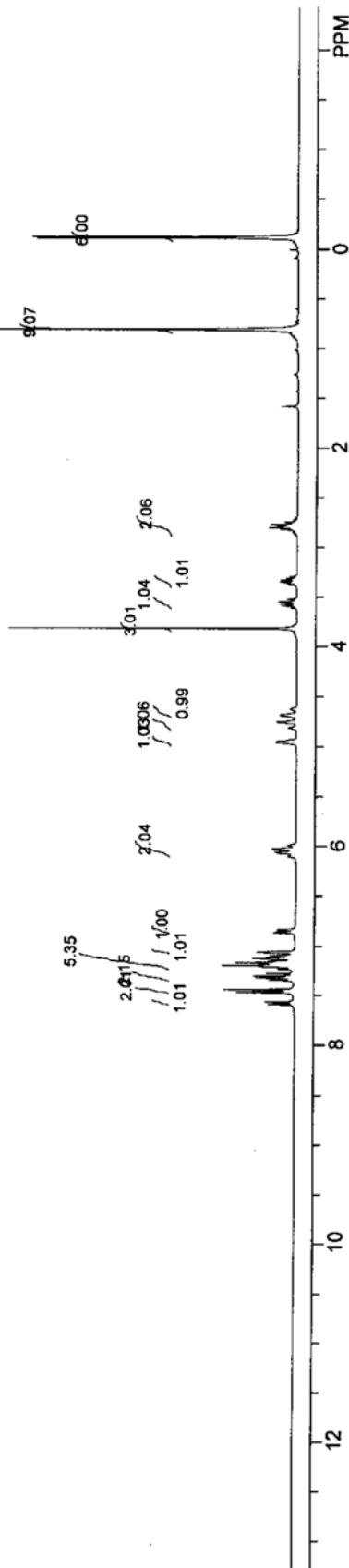
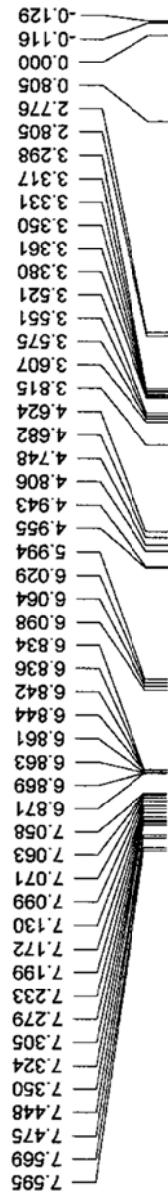
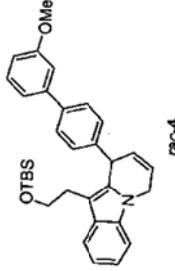


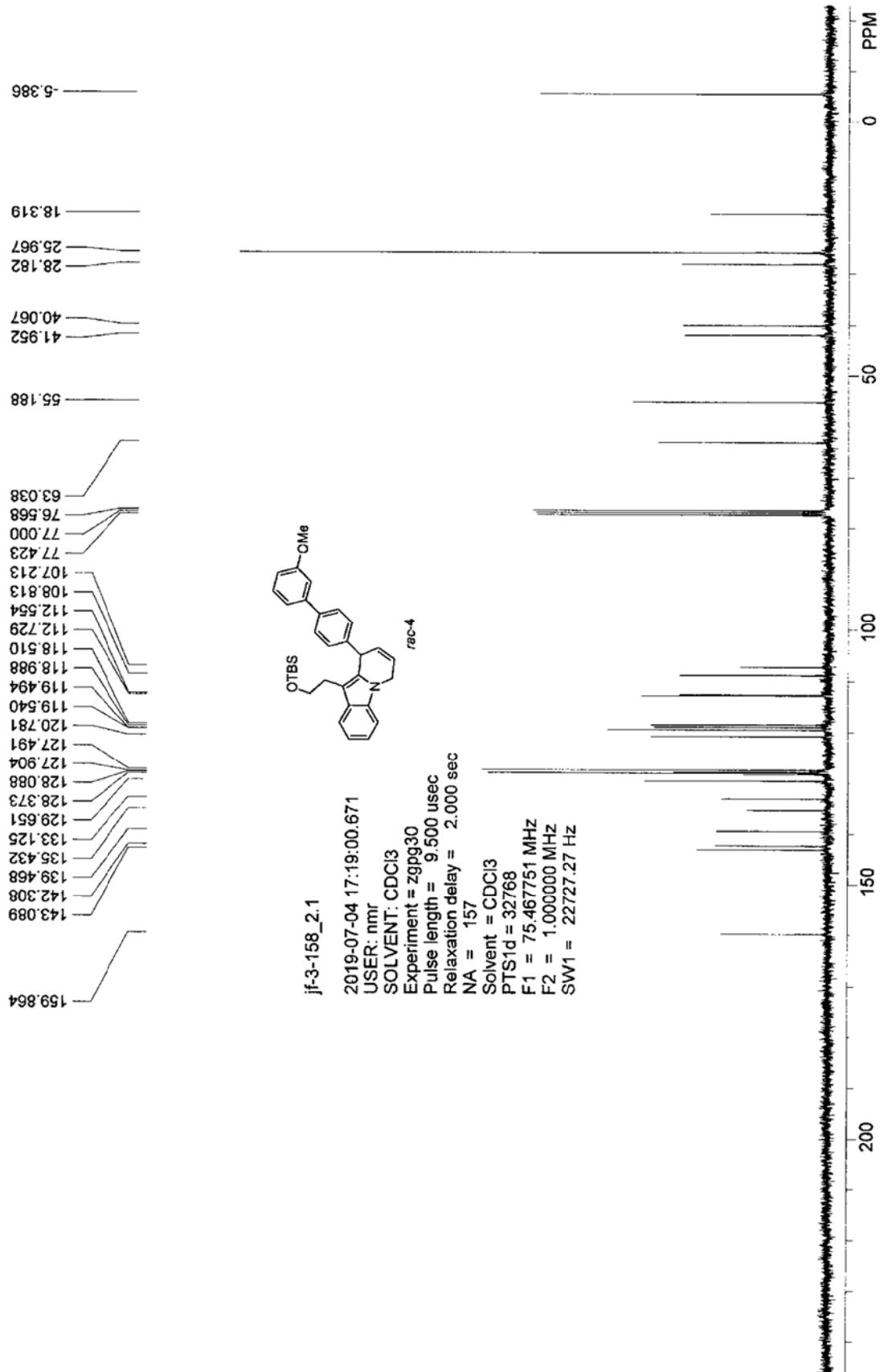
分析结果表

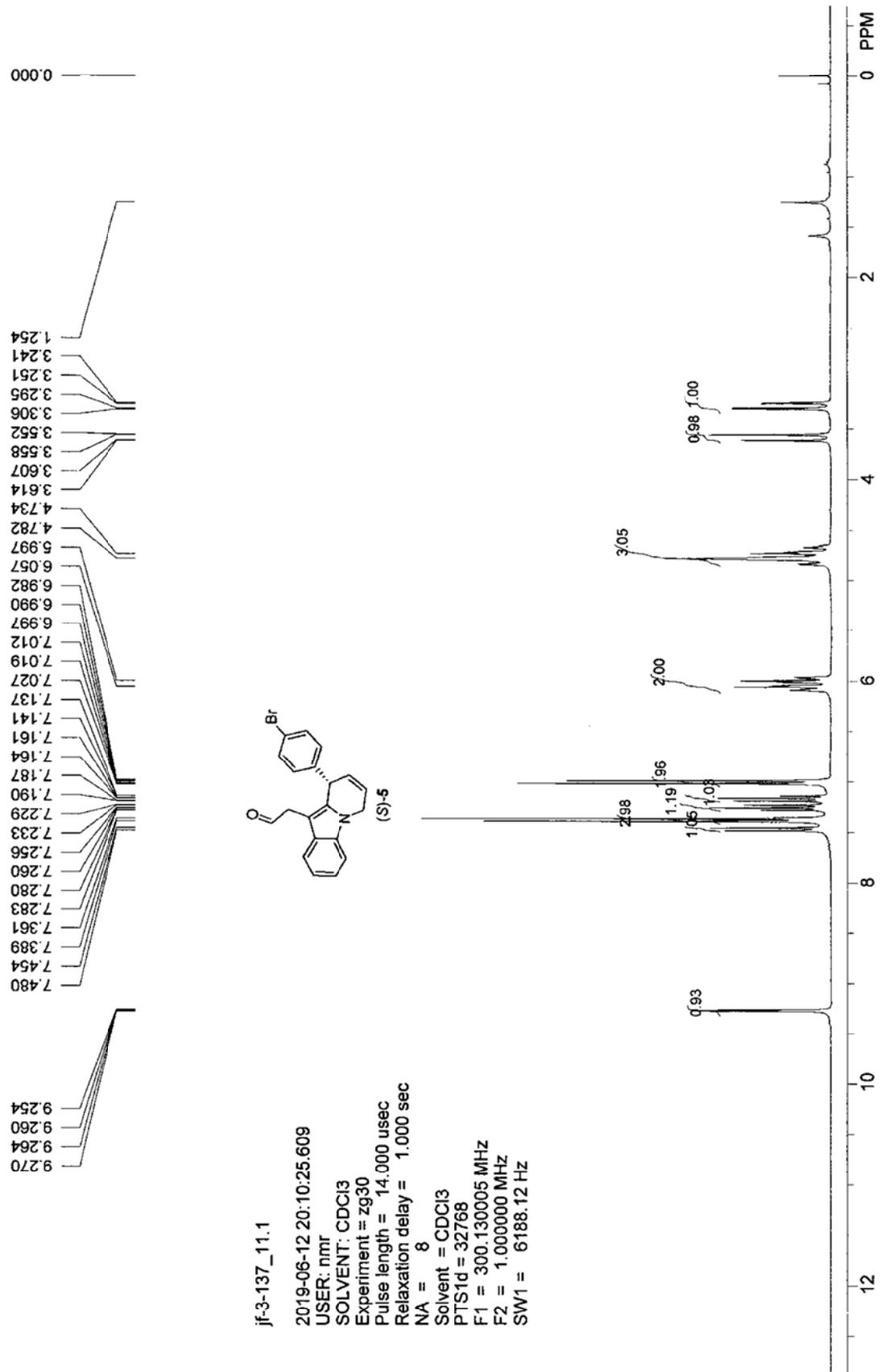
峰号	峰名	保留时间	峰高	峰面积	含量
1		16.253	145316.078	2903197.250	50.4508
2		20.085	109694.234	2851317.500	49.5492
总计			255010.313	5754514.750	100.0000

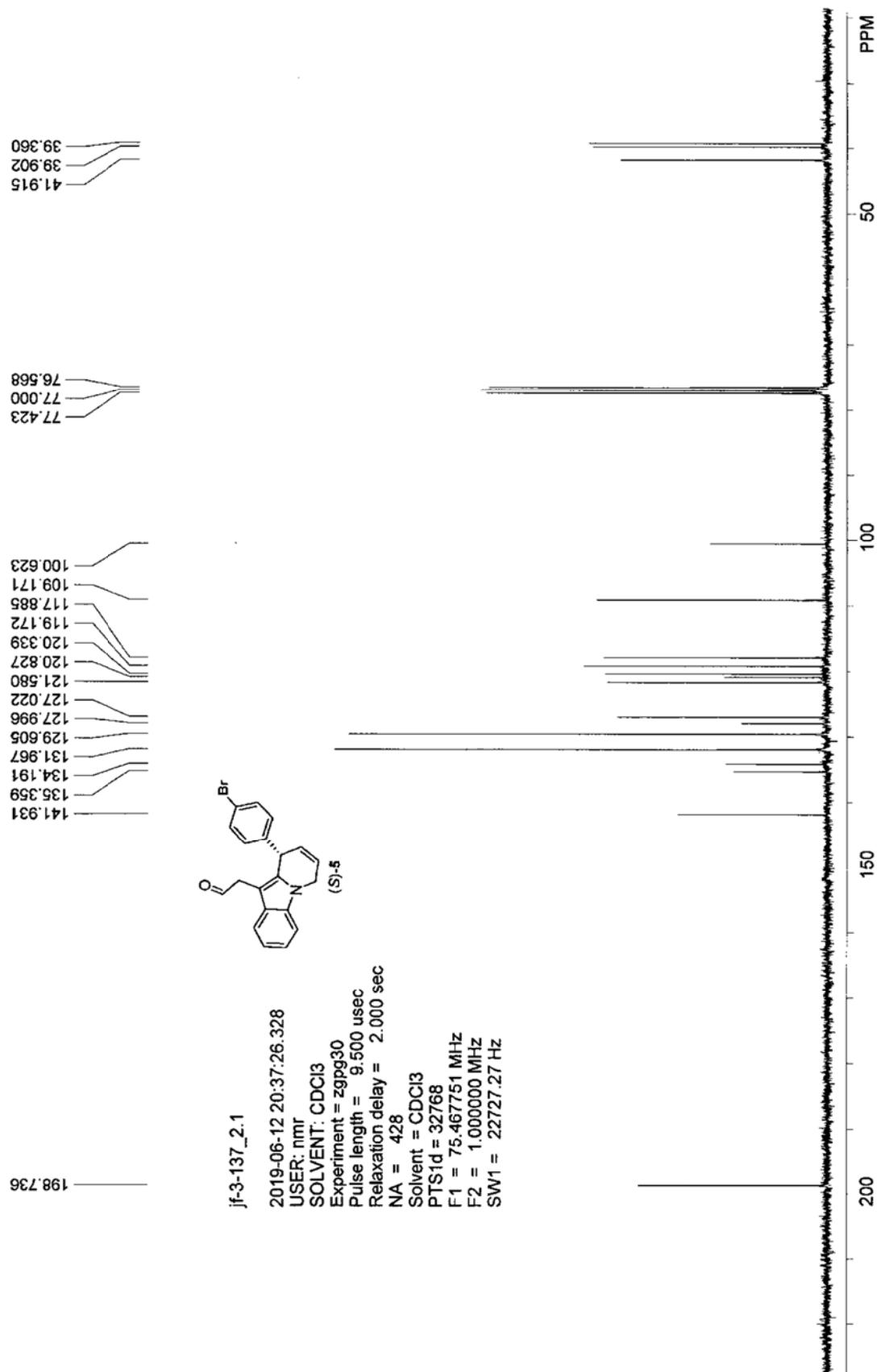
jf-3-158

2019-07-04 17:08:48.406
USER: nmr
SOLVENT: CDCl₃
Experiment = zg30
Pulse length = 14.000 usec
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl₃
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz



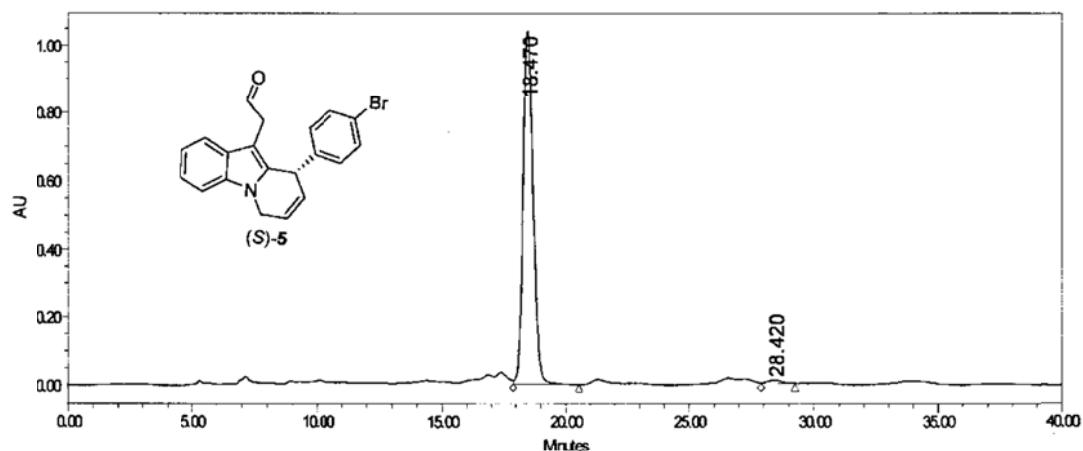






SAMPLE INFORMATION

Sample Name:	jf-3-137- <i>o</i> -h95-5-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq Method Set:	zg95
Injection#:	13	Processing Method:	111
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Ctrl. Descr.:	W2489 ChA.214nm
Date Acquired:	6/14/2019 4:32:51 PM EDT		
Date Processed:	6/14/2019 8:45:42 PM EDT		



—— Channel: W2489 ChA; Processed Channel: W2489 ChA.214nm; Result Id: 1707; Processing Method: 11

Processed Channel Descr.: W2489 ChA.214nm

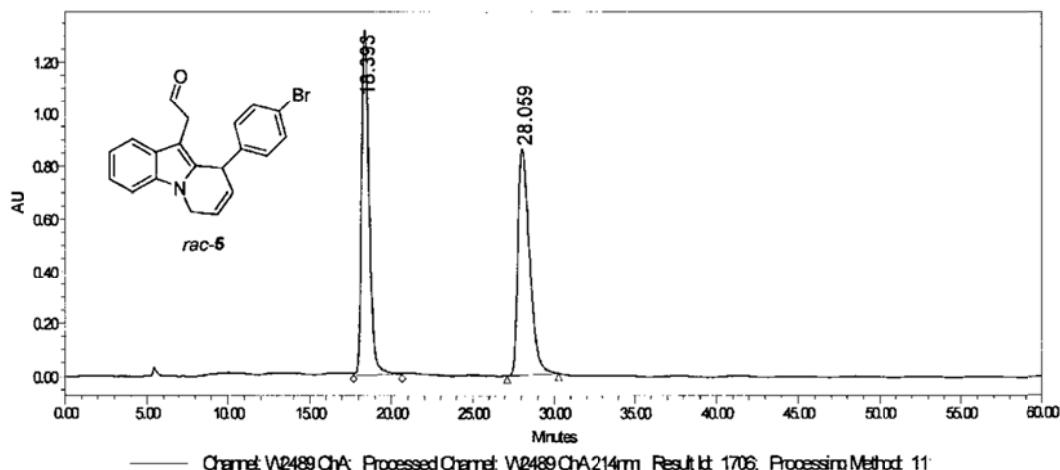
	Processed Channel Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	18.470	28897983	98.62	1038615
2	W2489 ChA.214nm	28.420	403798	1.38	9848

Reported by User: System
Report Method: Injection Summary Report
Report Method ID: 1029 1029
Page: 1 of 1

Project Name: HPLC_1525
Date Printed:
6/14/2019
8:47:15 PM America/New_York

SAMPLE INFORMATION

Sample Name:	jf3-134-az-h95-5-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	zpj95
Injection#:	12	Processing Method:	111
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chrl. Descr.:	W2489 ChA.214nm
Date Acquired:	6/14/2019 2:20:21 PM EDT		
Date Processed:	6/14/2019 8:43:49 PM EDT		

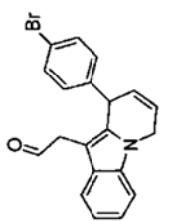
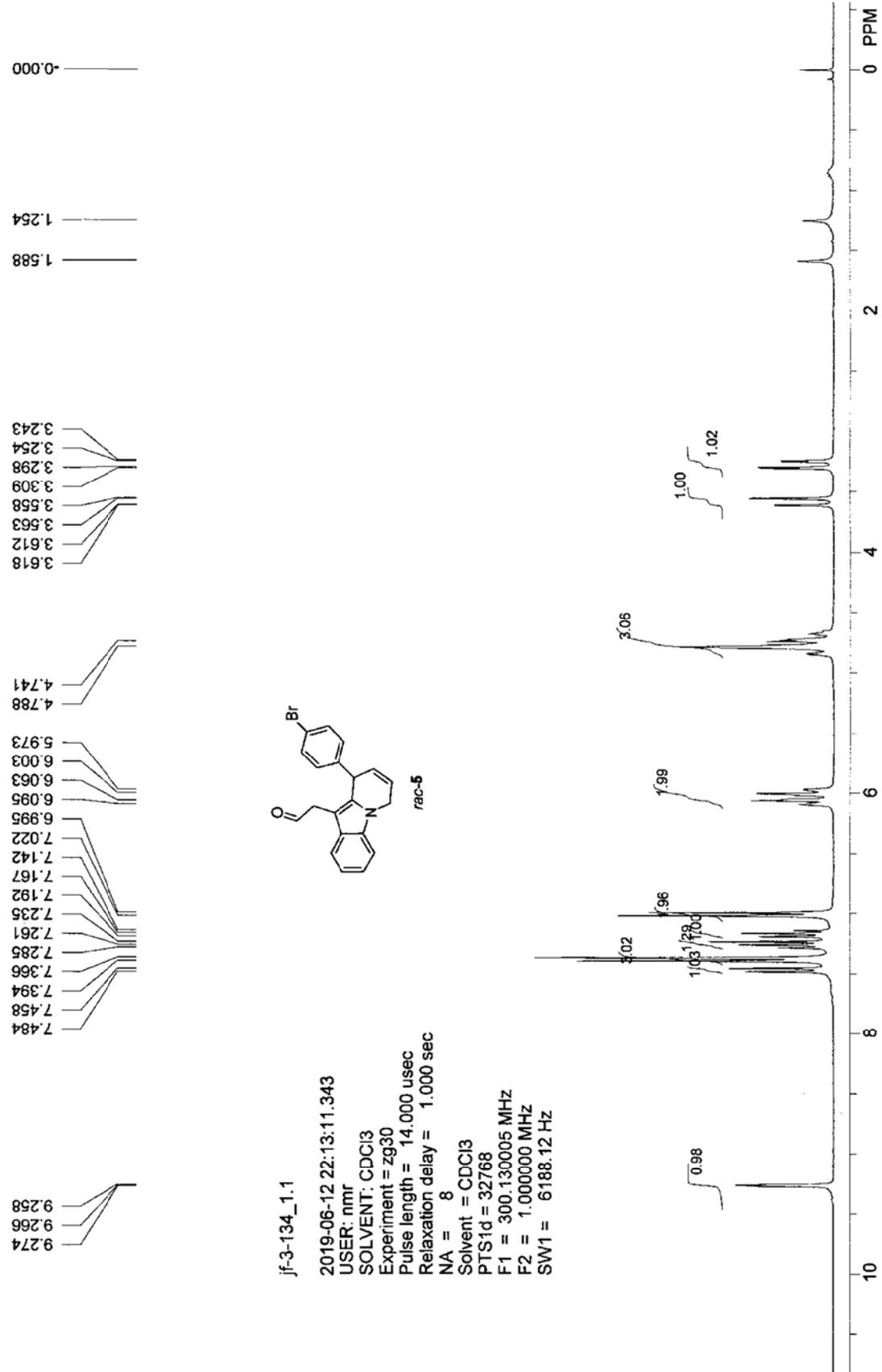


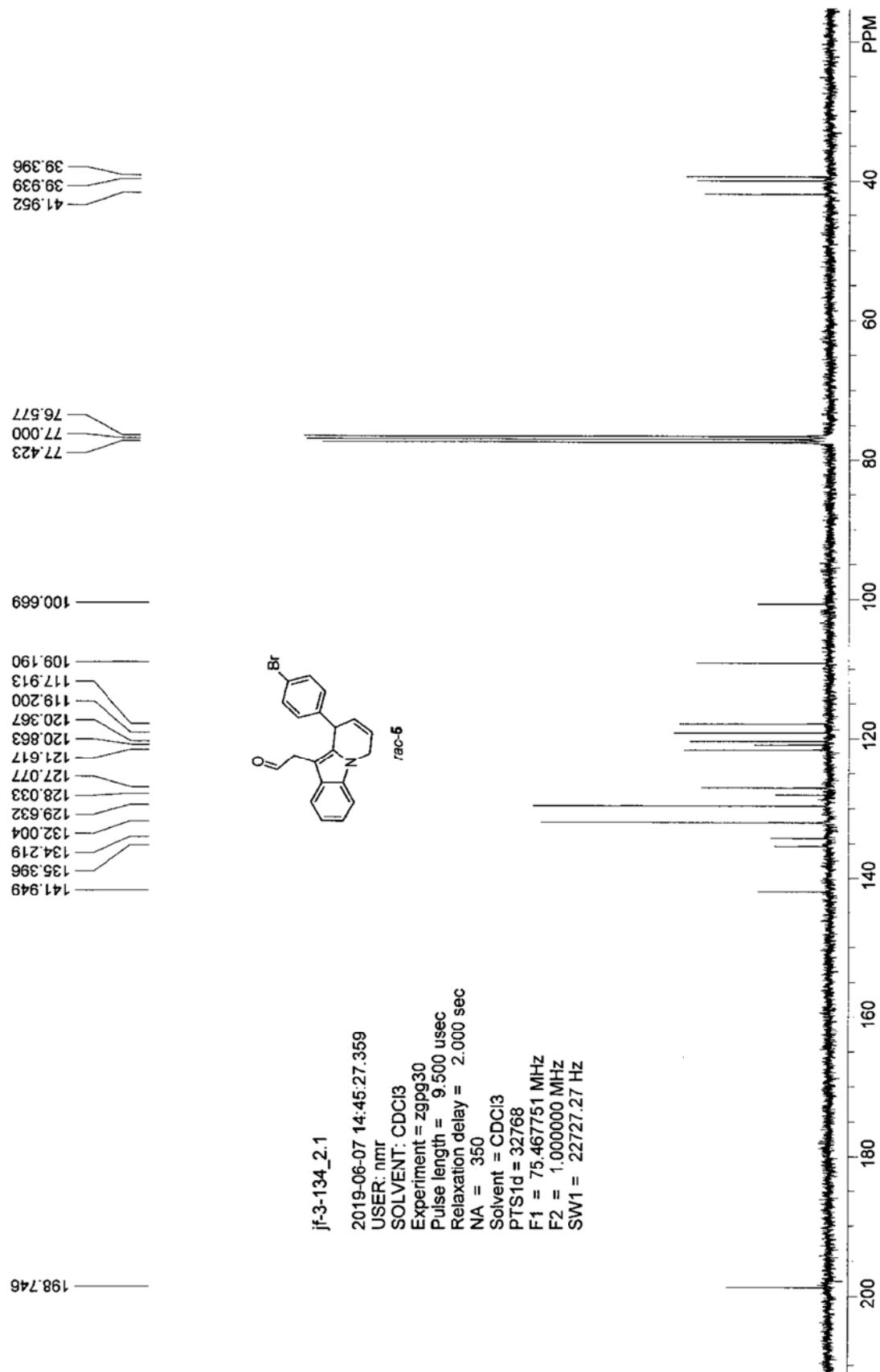
Processed Channel Descr.: W2489 ChA.214nm

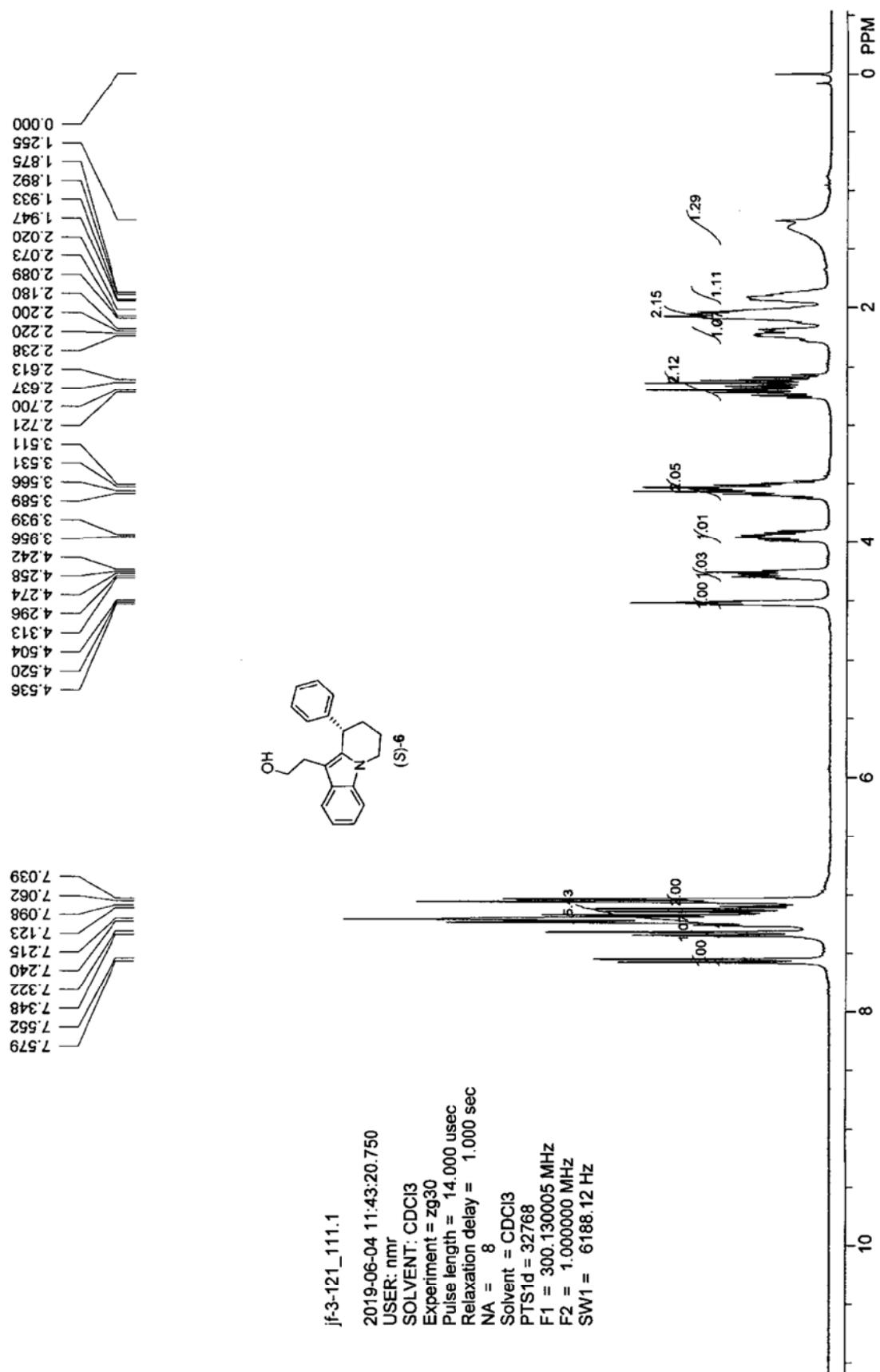
	Processed Chrmel Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	18.393	42378585	49.84	1319321
2	W2489 ChA.214nm	28.059	42655462	50.16	860473

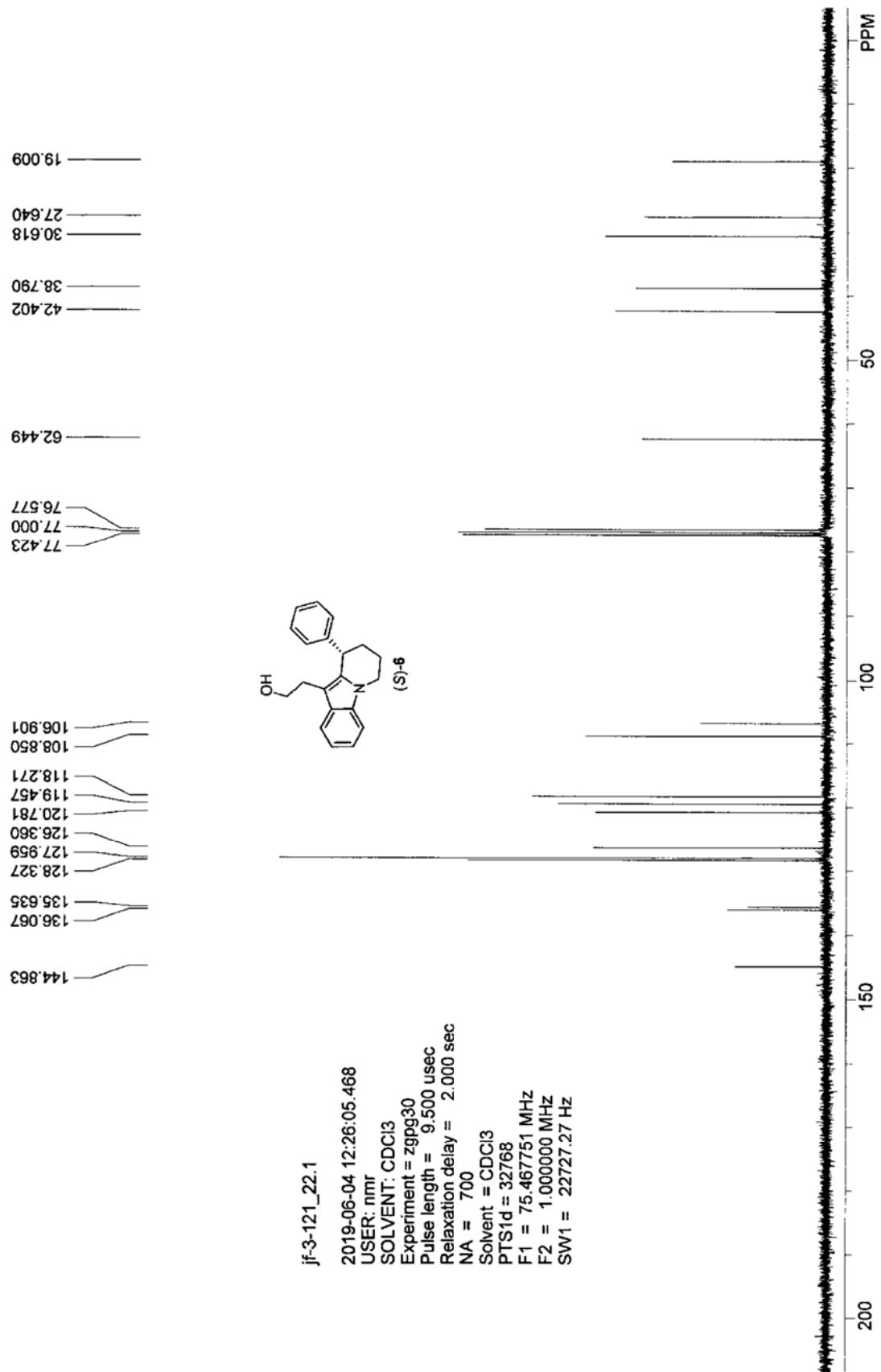
Reported by User: System
Report Method: InjectionSummary Report
Report Method ID: 1029 1029
Page: 1 of 1

Project Name: HPLC_1525
Date Printed: 6/14/2019
8:46:59 PM America/New_York



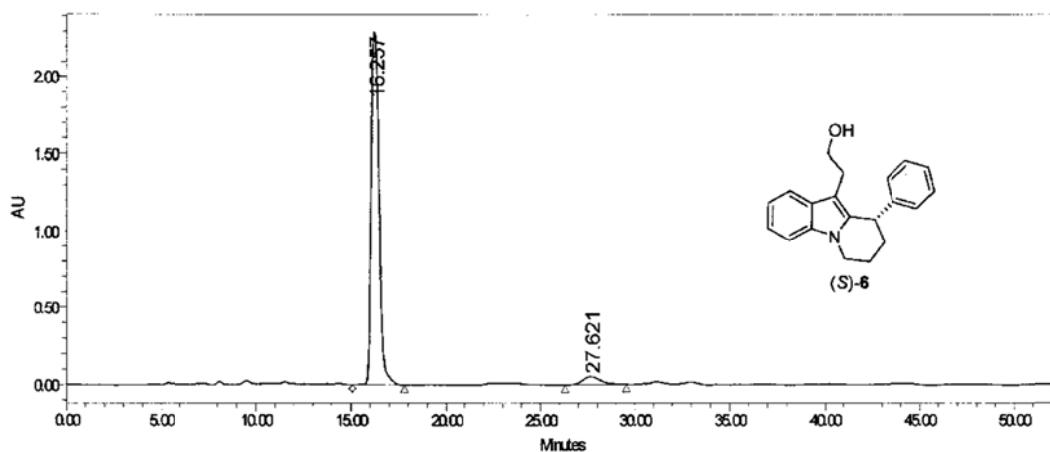






SAMPLE INFORMATION

Sample Name:	jf3-121-02-h95-5-1-214	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	zpj05
Injection #:	11	Processing Method:	111
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chrt. Desc.:	W2489 ChA.214nm
Date Acquired:	6/14/2019 1:23:00 PM EDT		
Date Processed:	6/14/2019 8:43:28 PM EDT		



Processed Channel Descr.: W2489 ChA.214nm

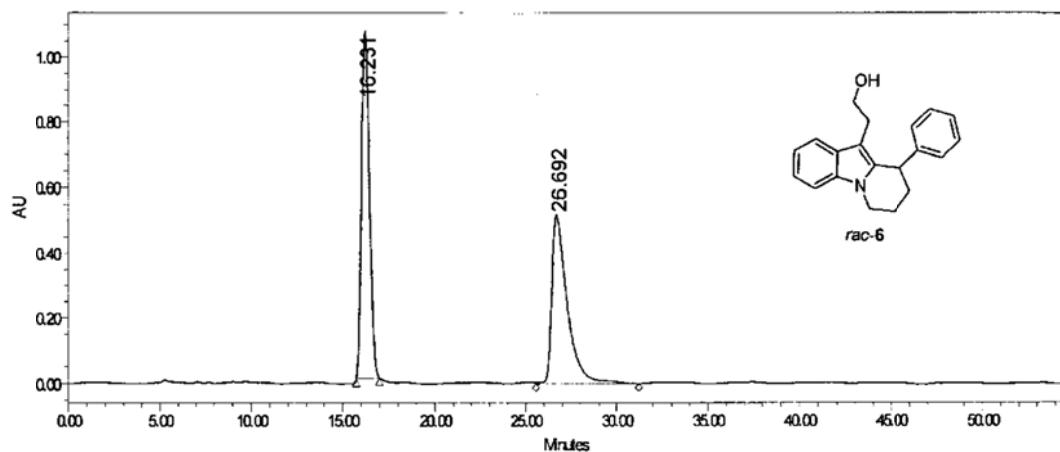
	Processed Channel Descr.	RT	Area	%Area	Height
1	W2489 ChA.214nm	16.257	66283184	94.95	2298893
2	W2489 ChA.214nm	27.621	3523081	5.05	52275

Reported by User: System
Report Method: Injection Summary Report
Report Method ID: 1029 1029
Page: 1 of 1

Project Name: HPLC_1525
Date Printed: 6/14/2019
8:46:30 PM America/New_York

SAMPLE INFORMATION

Sample Name:	jF3-125-az-h95-5-1-214	Acquired By:	
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	zpj95
Injection#:	10	Processing Method:	111
Injection Volume:	10.00 μ L	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Ctrl. Descr.:	W2489 ChA214nm
Date Acquired:	6/14/2019 12:26:53 PM EDT		
Date Processed:	6/14/2019 8:42:53 PM EDT		

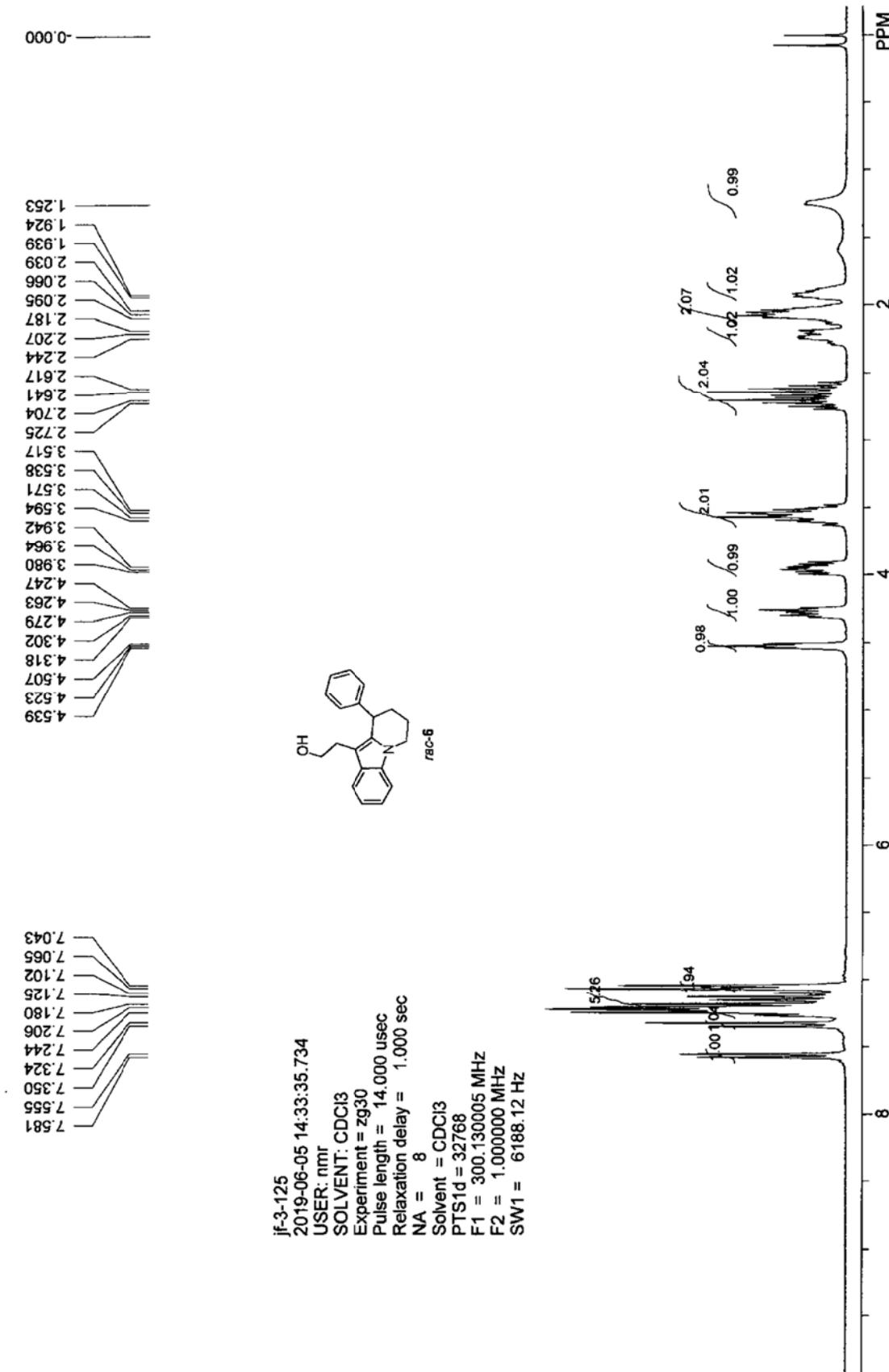


Processed Channel Descr.: W2489 ChA214nm

	Processed Channel Descr.	RT	Area	%Area	Height
1	W2489 ChA214nm	16.231	31414739	50.76	1064852
2	W2489 ChA214nm	26.692	30472914	49.24	518554

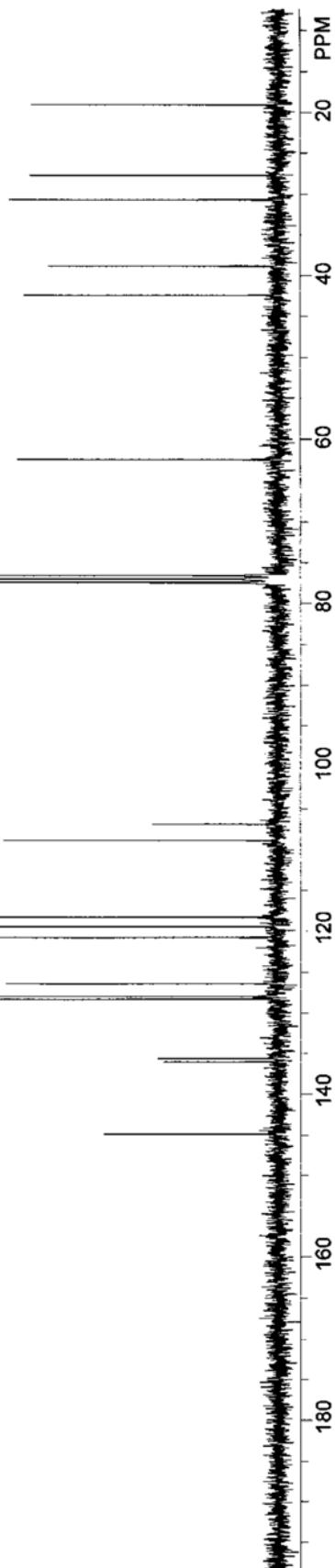
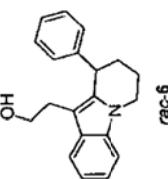
Reported by User: System
 Report Method: Injection Summary Report
 Report Method ID: 1029 1029
 Page: 1 of 1

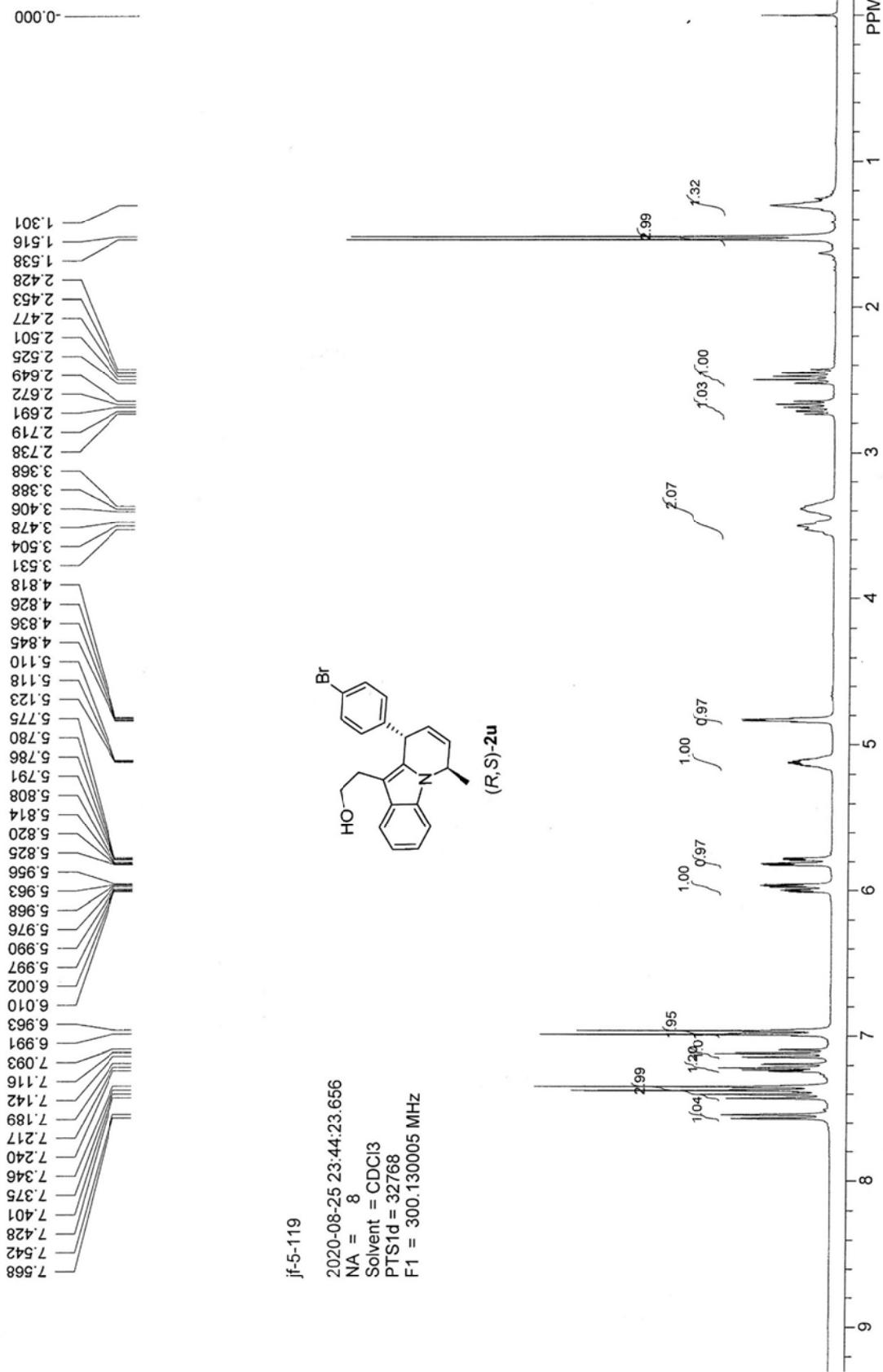
Project Name: HPLC_1525
 Date Printed: 6/14/2019 8:45:57 PM America/New_York



jf-3-125_22.1
 2019-06-05 14:43:56.593
 USER: nmr
 SOLVENT: CDCl₃
 Experiment = zgpg30
 Pulse length = 9.500 usec
 Relaxation delay = 2.000 sec
 NA = 157
 Solvent = CDCl₃
 PTS Id = 32768
 F1 = 75.467751 MHz
 F2 = 1.000000 MHz
 SW1 = 22727.27 Hz

jf-3-125_22.1

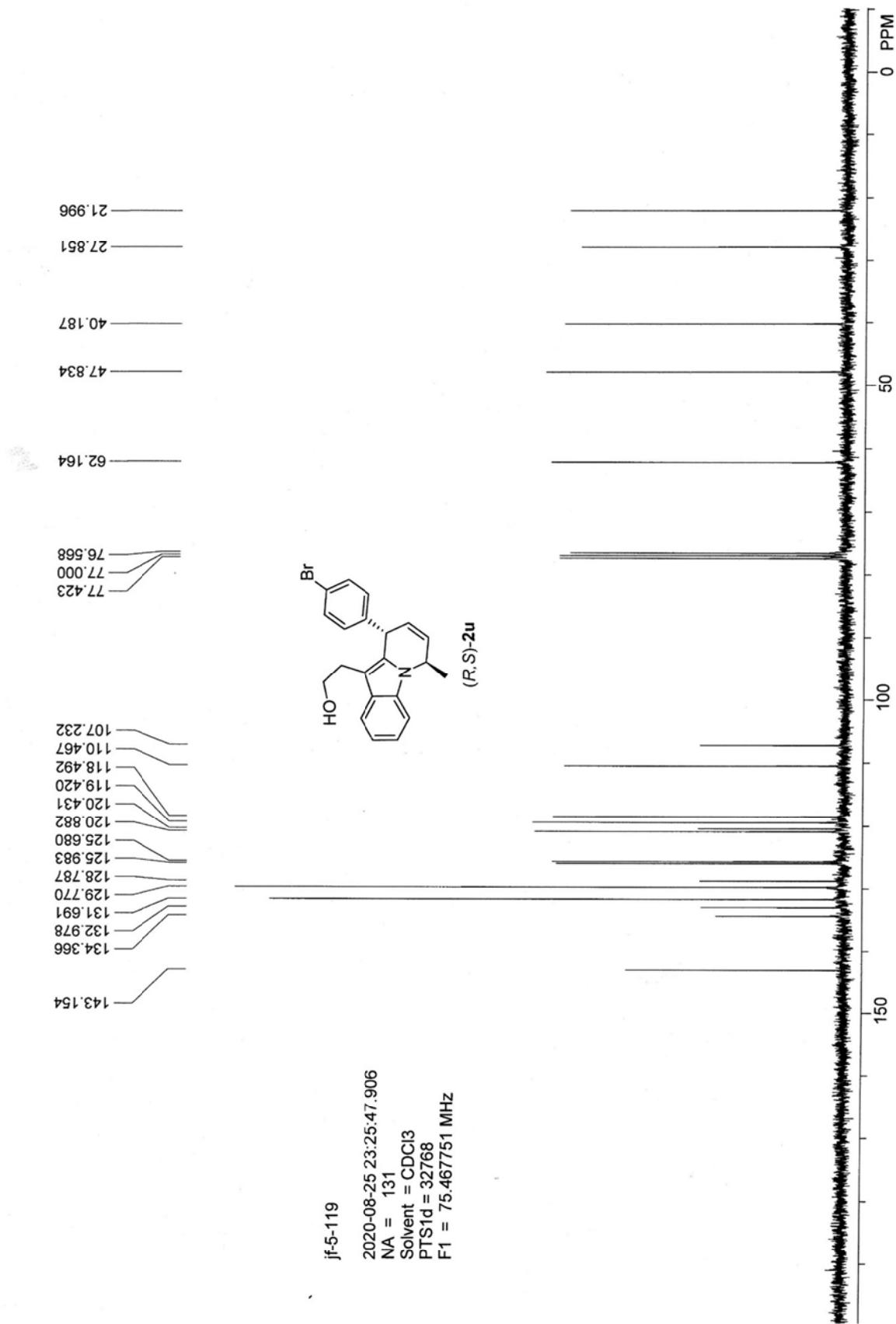




if-5-119

2020-08-25 23:44:23.656
NA = 8
Solvent = CDCI3
PTS1d = 32768
F1 = 300.130005 MHz

三〇

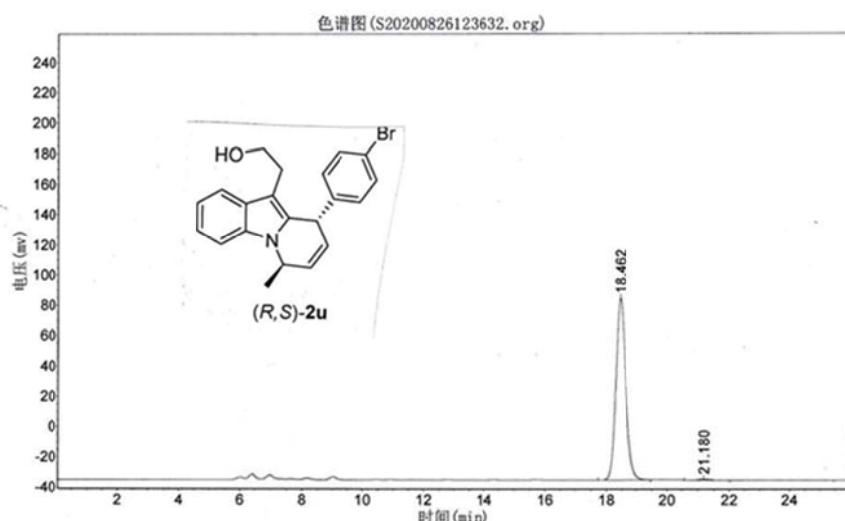


jf-5-119

实验时间: 2020-08-26, 12:36:32
谱图文件:D:\浙大智达\N2000\样品\S20200826123632.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-08-26, 13:09:59
积分方法: 面积归一法

实验内容简介:
ia-h, n-hexane/i-PrOH = 90/10, 0.5, 254



分析结果表

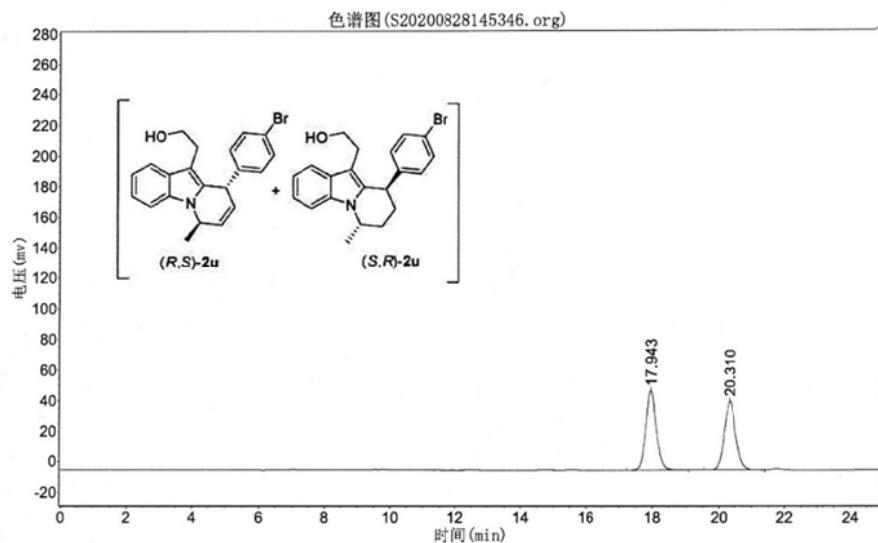
峰号	峰名	保留时间	峰高	峰面积	含量
1		18.462	119845.000	2755509.500	99.3952
2		21.180	753.668	16767.461	0.6048
总计			120598.668	2772276.961	100.0000

jf-5-120-2

实验时间: 2020-08-28, 14:53:46
谱图文件:D:\浙大智达\N2000\样品\S20200828145346.org
方法文件:D:\浙大智达\N2000\djx.mtd

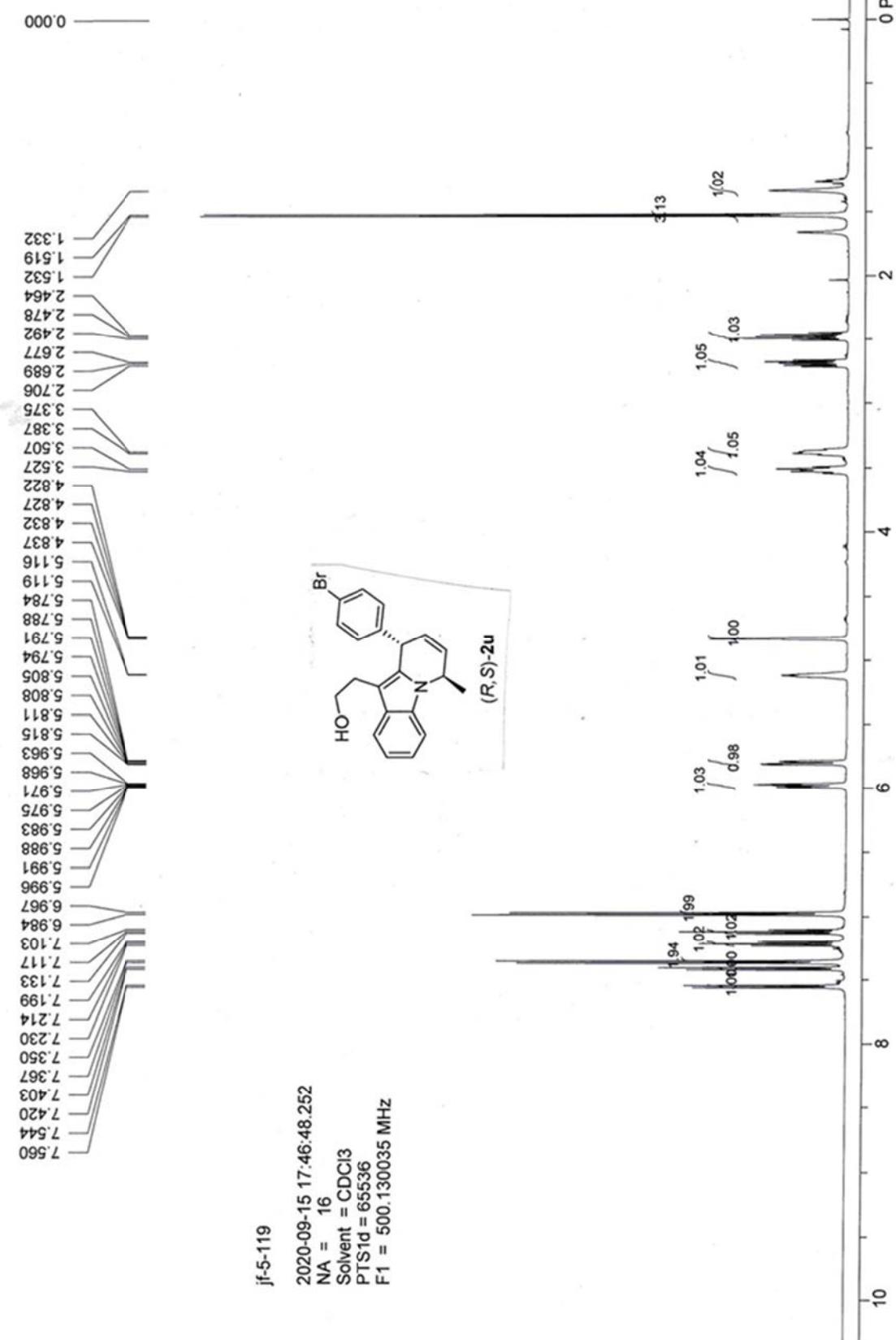
实验者: jf
报告时间: 2020-08-28, 15:27:38
积分方法: 面积归一法

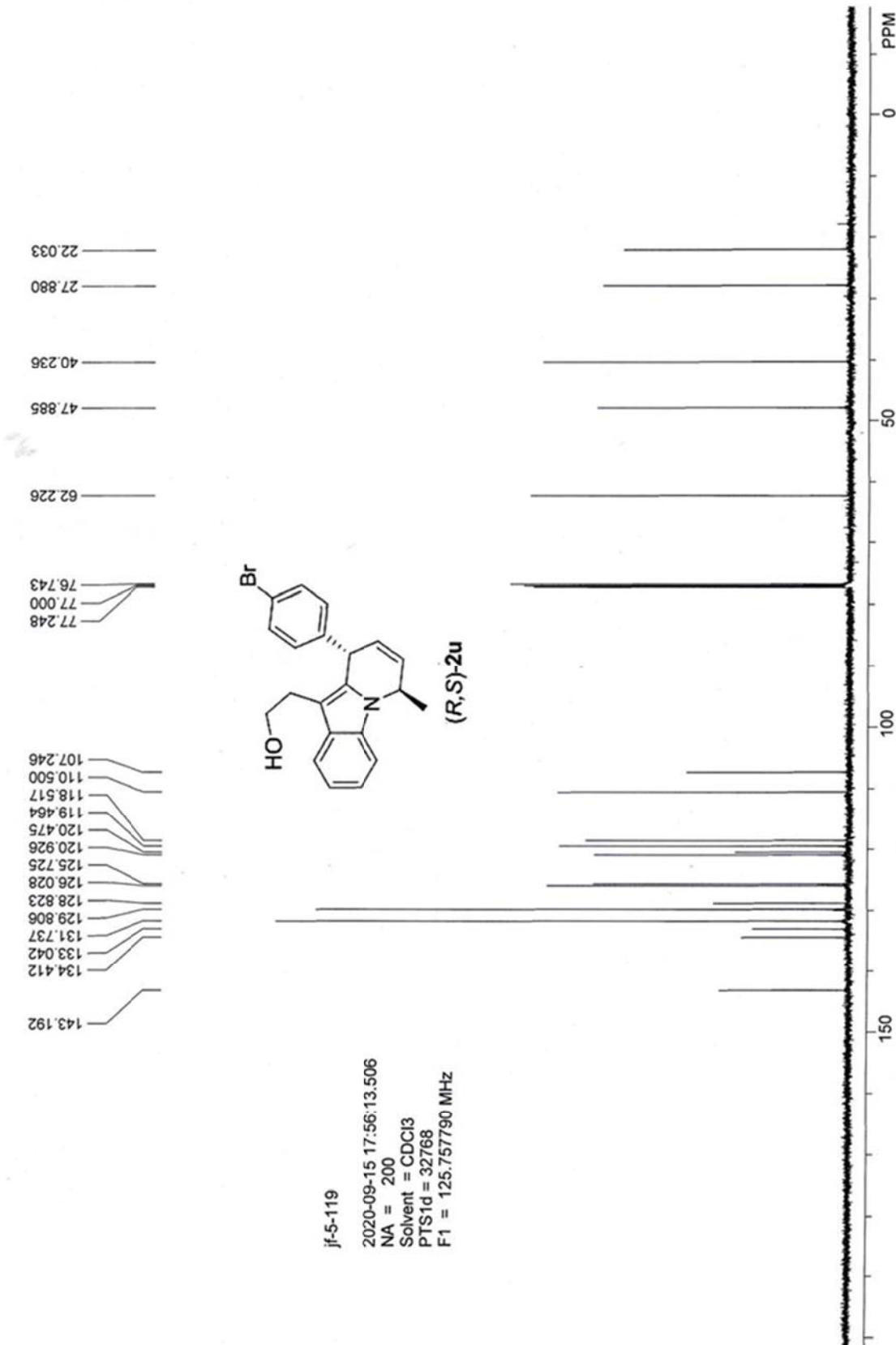
实验内容简介:
ia-h, n-hexane/i-PrOH = 90/10, 0.5, 254

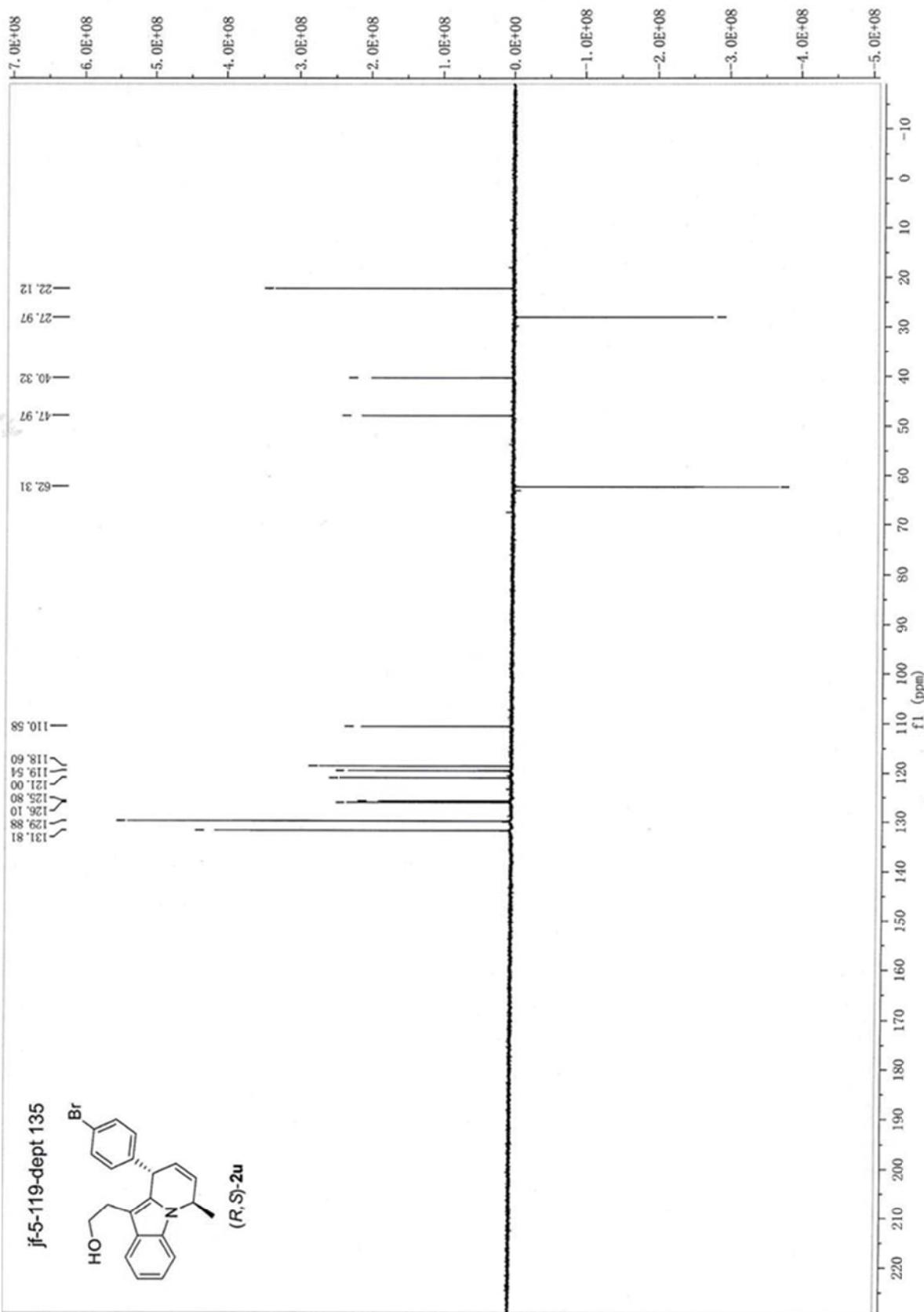


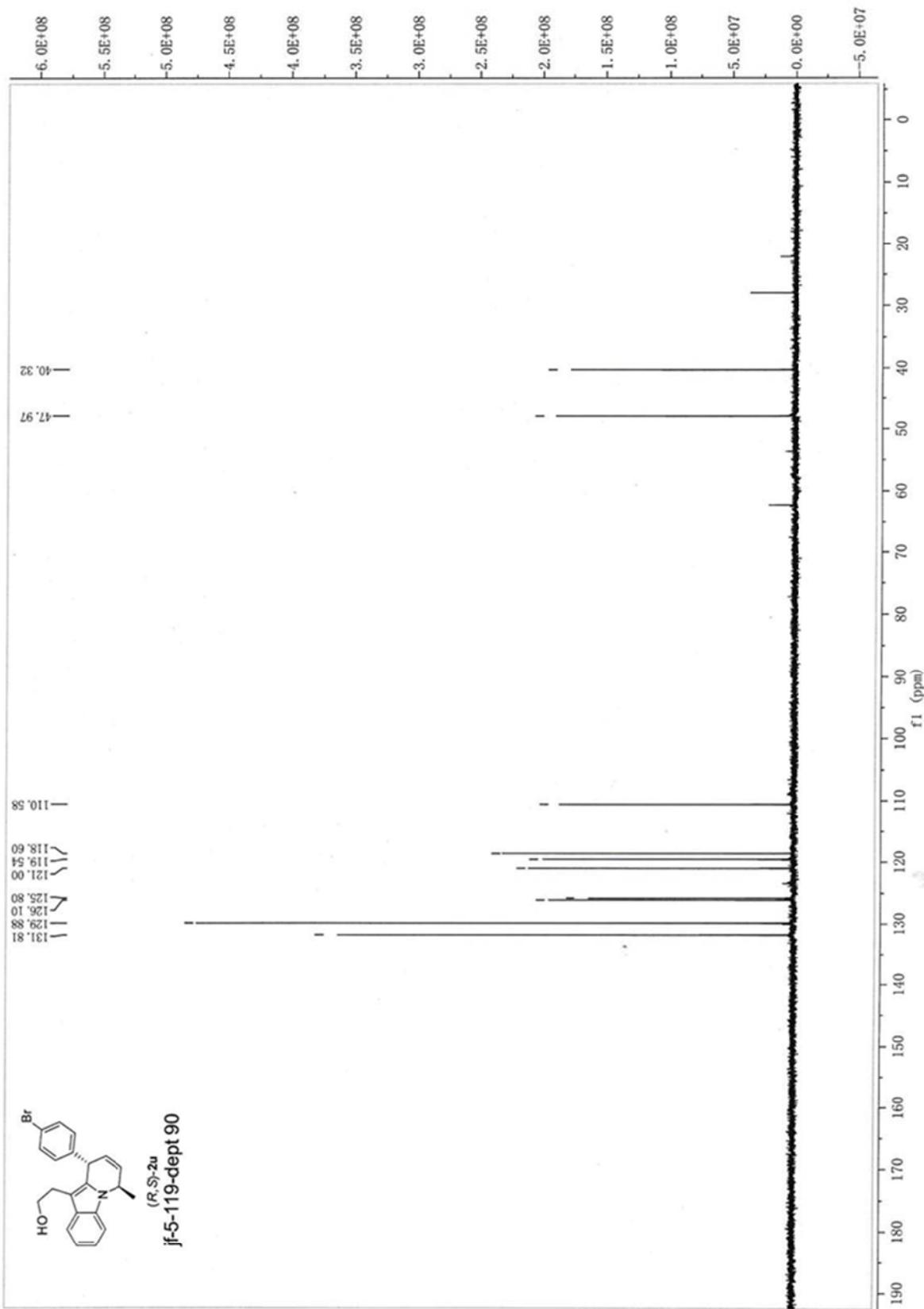
分析结果表

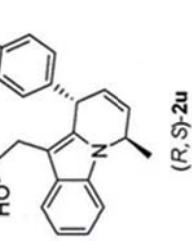
峰号	峰名	保留时间	峰高	峰面积	含量
1		17.943	52239.355	1145330.000	50.5363
2		20.310	45460.883	1121022.375	49.4637
总计			97700.238	2266352.375	100.0000



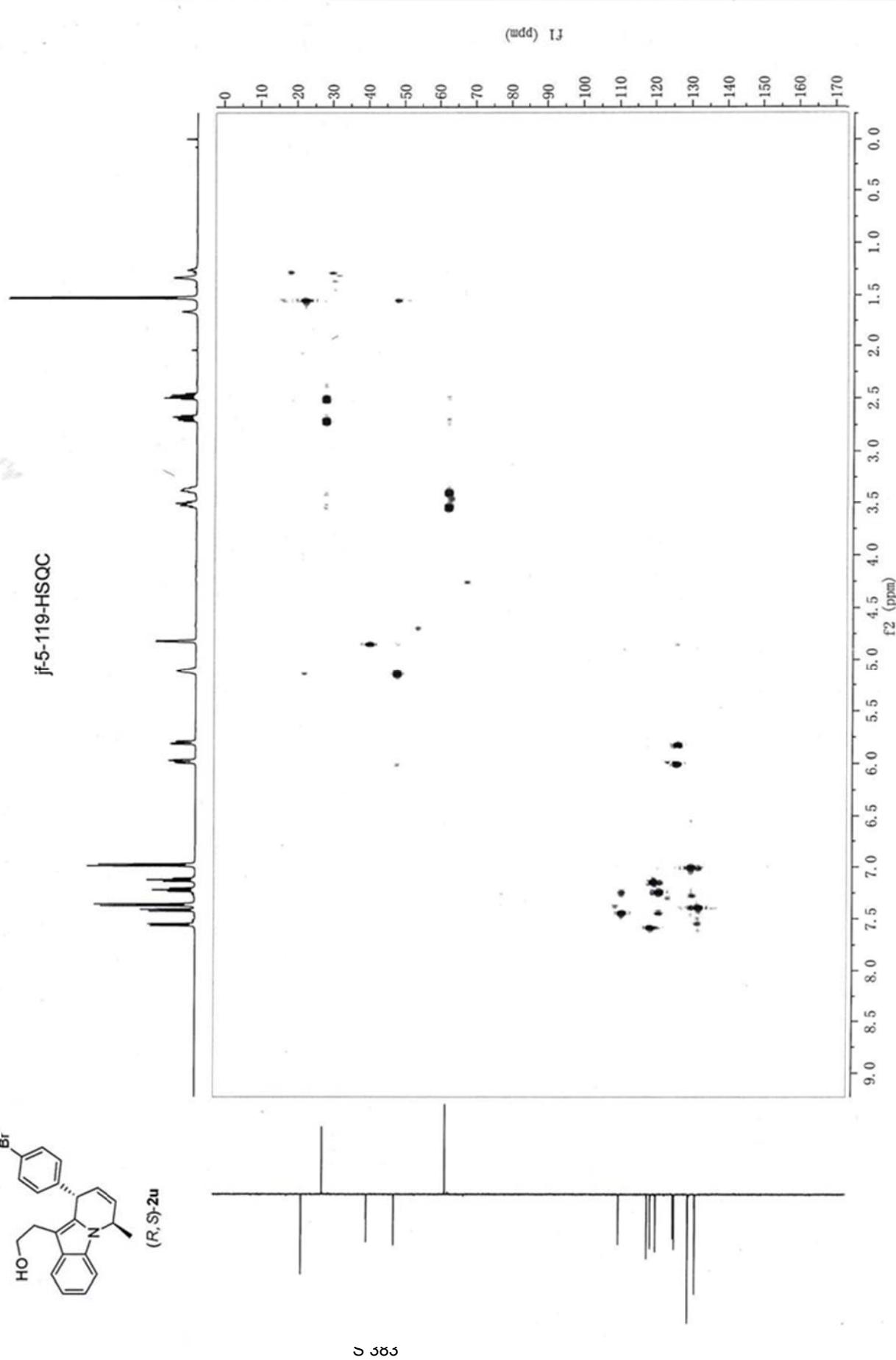


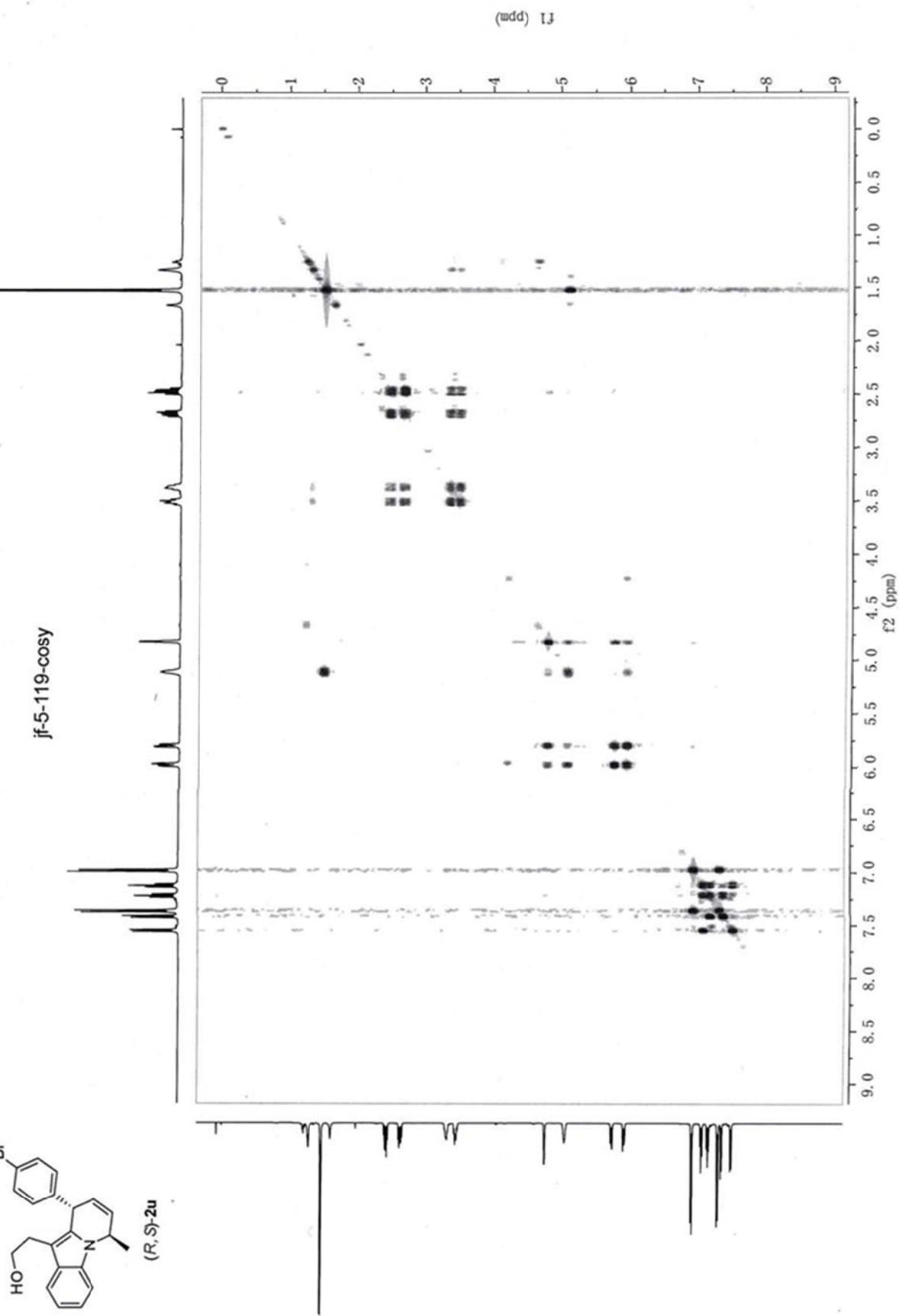




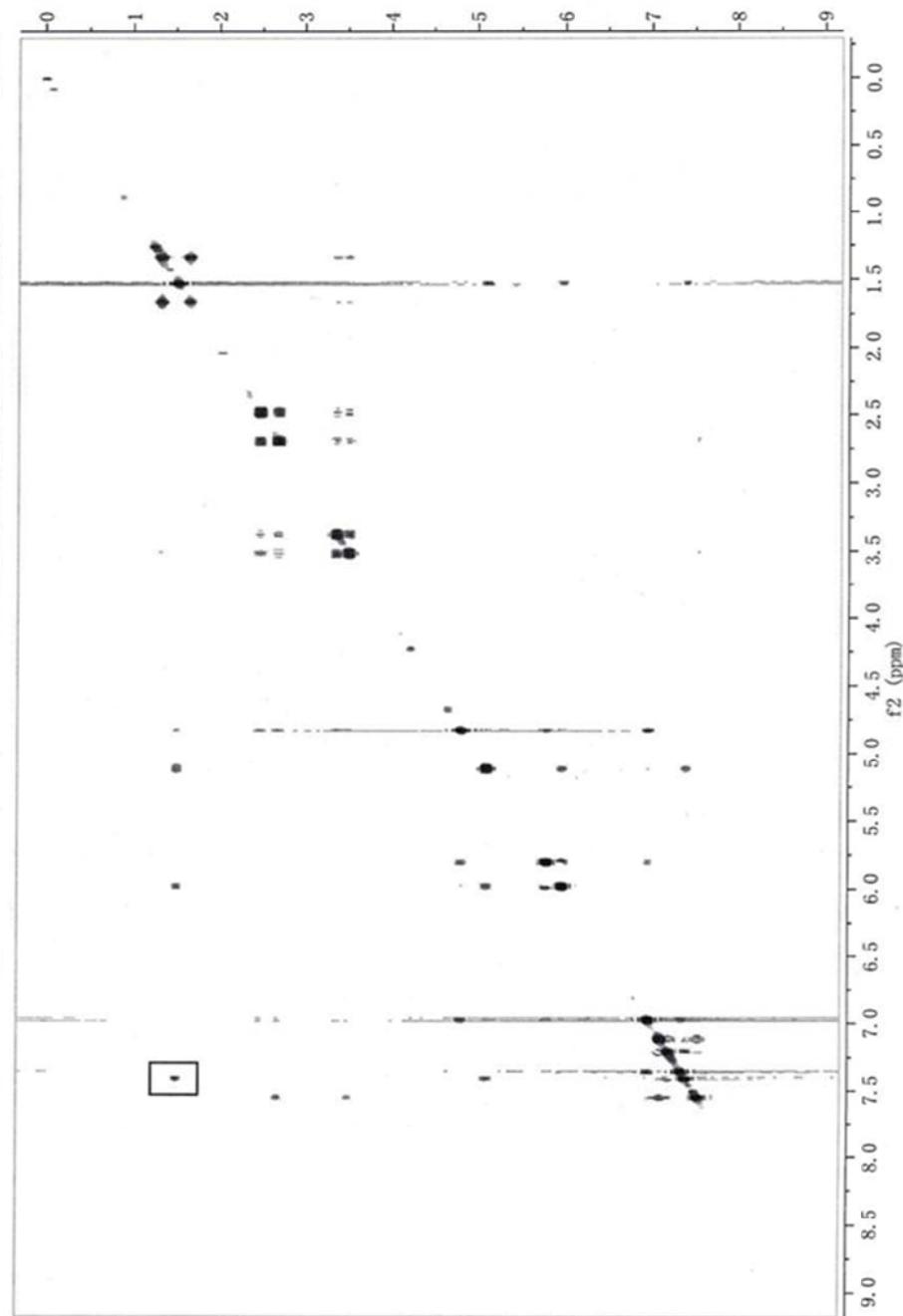
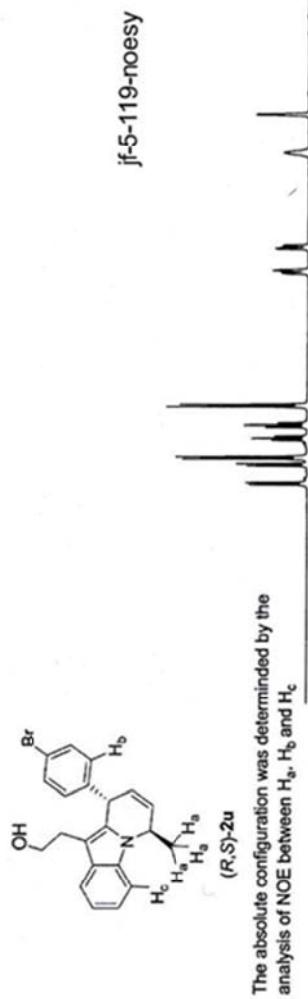


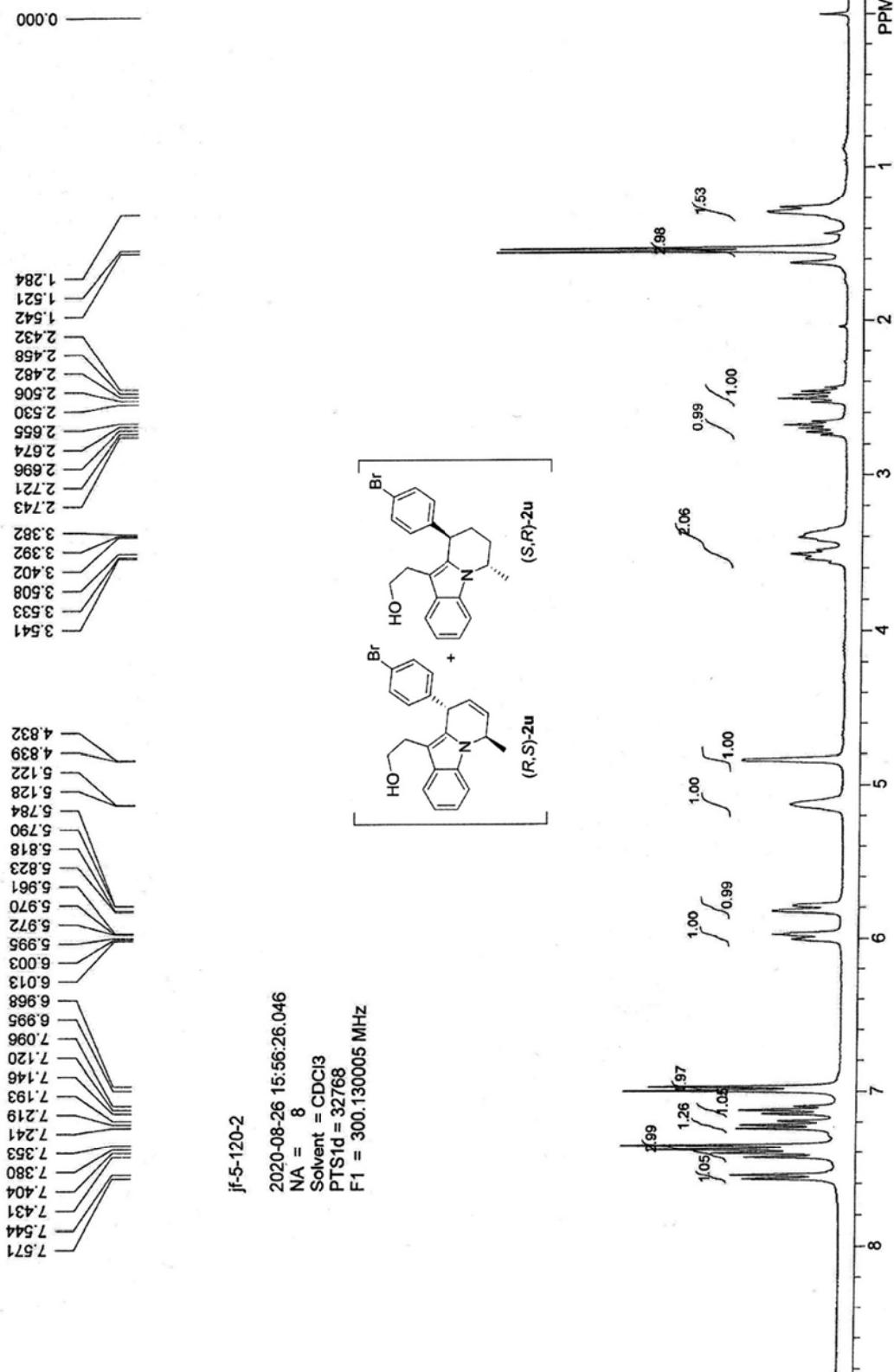
$\text{f}^{\text{f}}\text{-119-HSQC}$





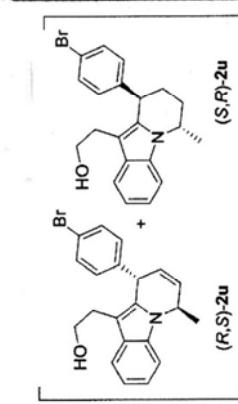
(wdd) IJ



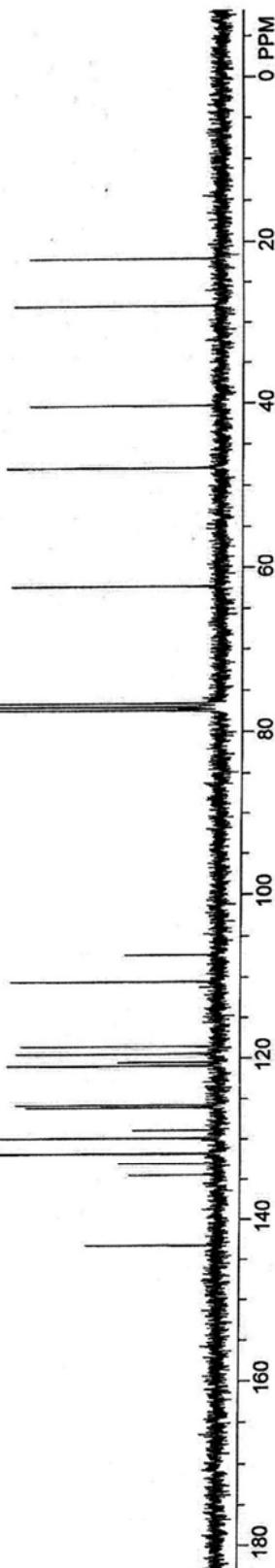


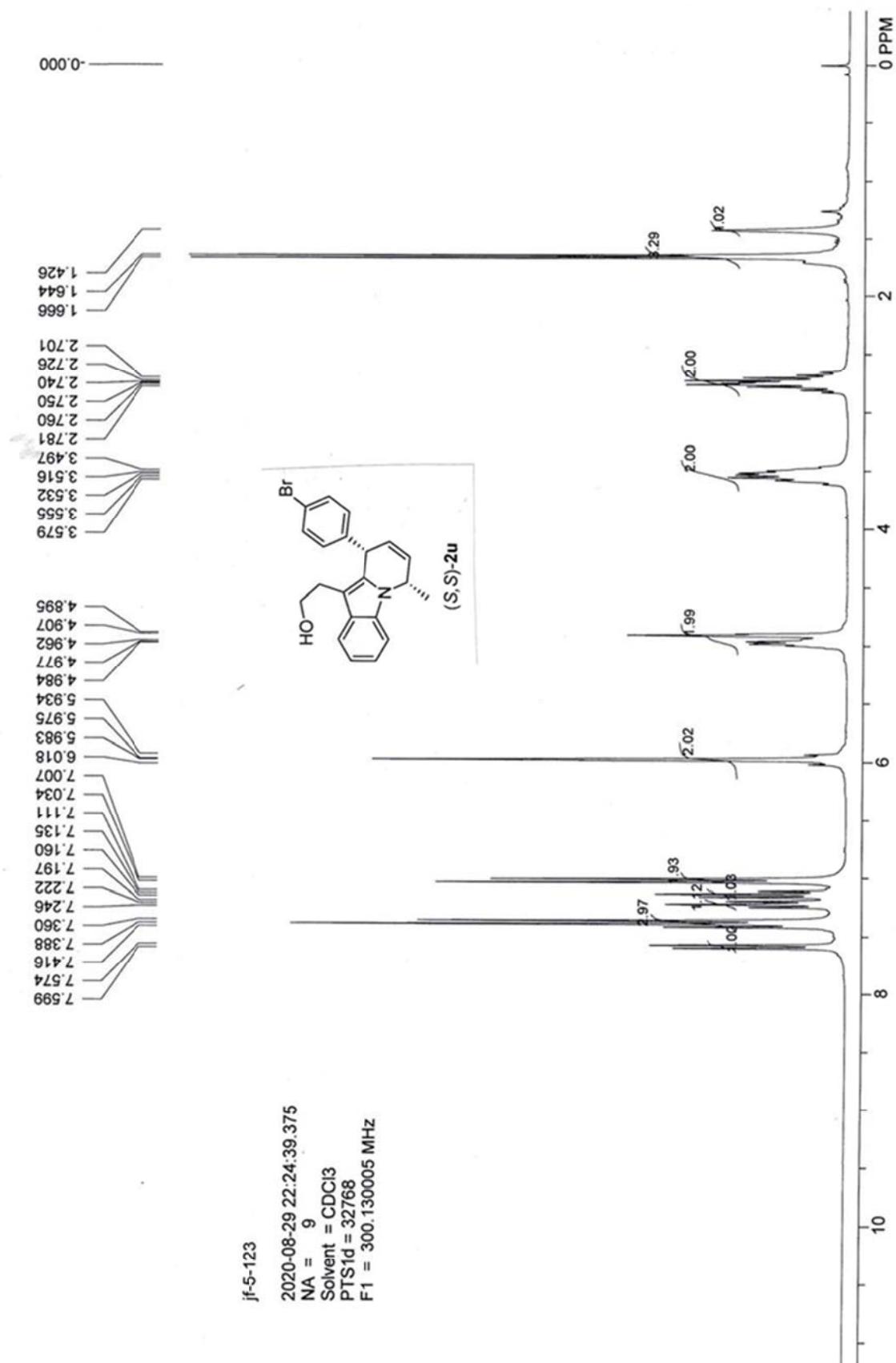
jf-5-120-2

2020-08-26 16:15:54.250
NA = 311
Solvent = CDCl₃
PT51d = 32768
F1 = 75.467751 MHz

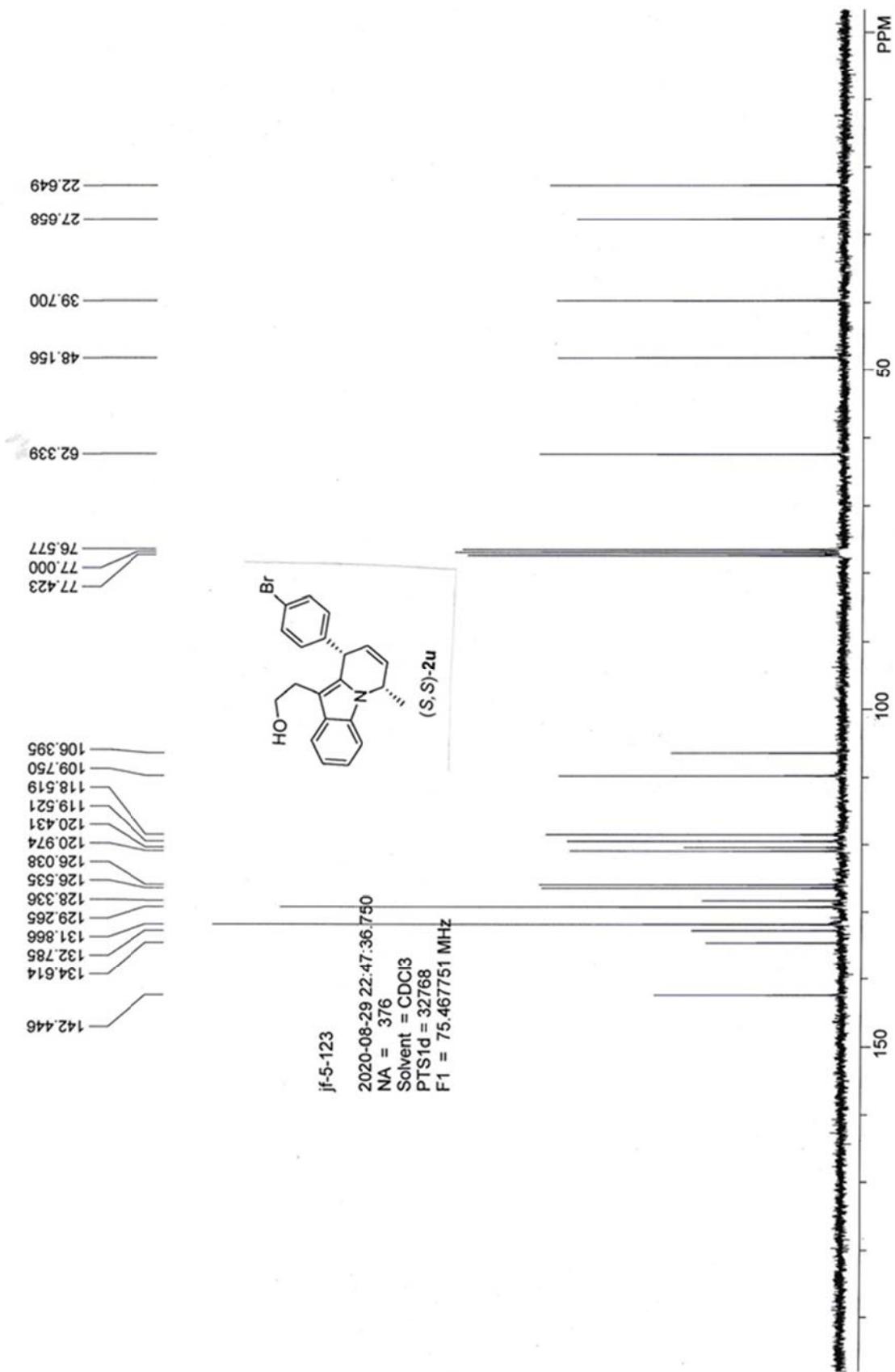


143.209
133.061
131.765
129.825
128.860
126.057
125.753
120.946
120.514
118.547
110.513
107.278
77.000
76.577
62.266
47.908
40.269
27.916
22.042





Jf-5-123
2020-08-29 22:24:39.375
NA = 9
Solvent = CDCl3
PTSid = 32768
F1 = 300.130005 MHz



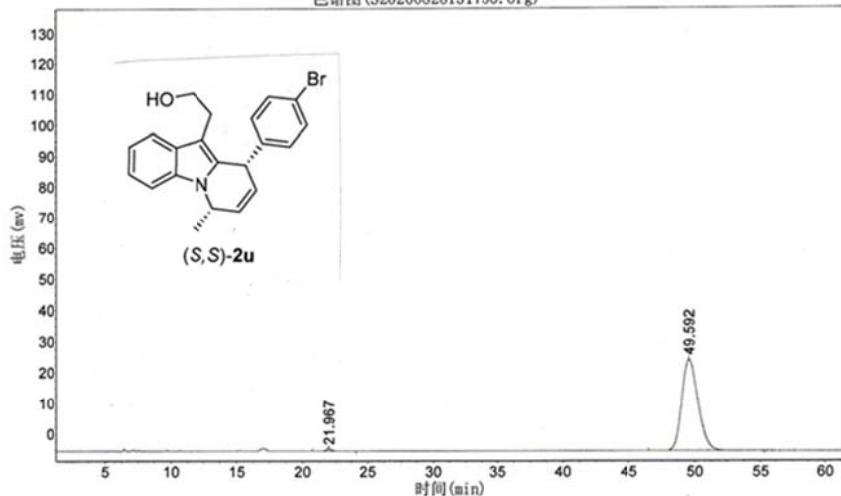
jf-5-123

实验时间: 2020-08-28, 13:17:56
谱图文件:D:\浙大智达\N2000\样品\S20200828131756.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-08-28, 14:25:15
积分方法: 面积归一法

实验内容简介:
od-h, n-hexane/i-PrOH = 90/10 0.5, 254

色谱图(S20200828131756.org)



分析结果表

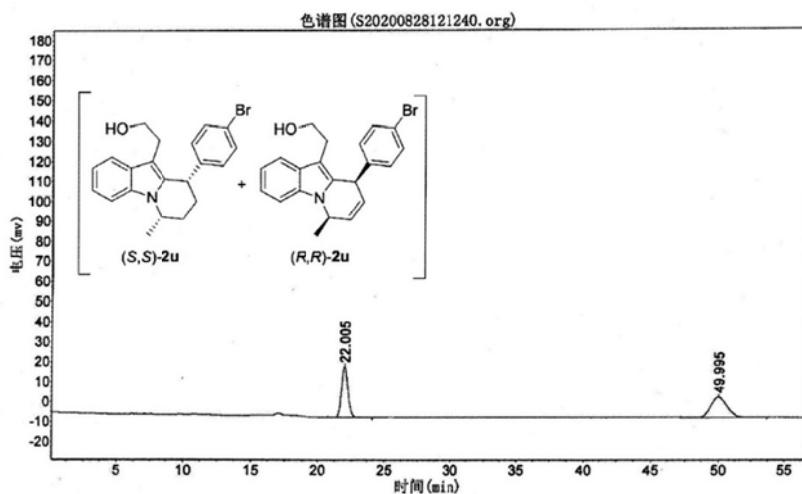
峰号	峰名	保留时间	峰高	峰面积	含量
1		21.967	625.189	21345.367	0.8380
2		49.592	29620.104	2525772.750	99.1620
总计			30245.293	2547118.117	100.0000

jf-5-124

实验时间: 2020-08-28, 12:12:40
谱图文件:D:\浙大普达\N2000\样品\S20200828121240.org
方法文件:D:\浙大普达\N2000\djx.mtd

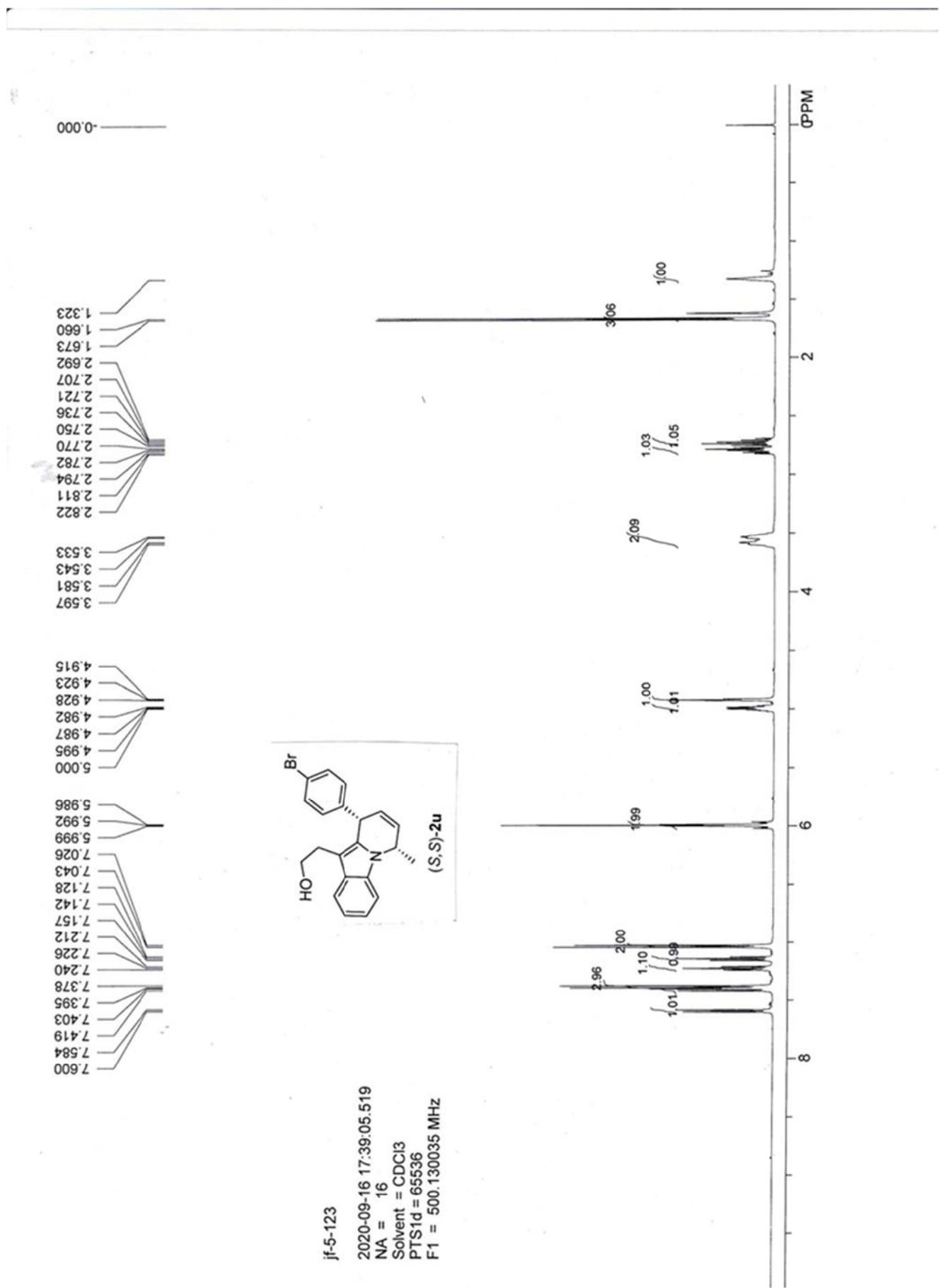
实验者: jf
报告时间: 2020-08-28, 13:11:09
积分方法: 面积归一法

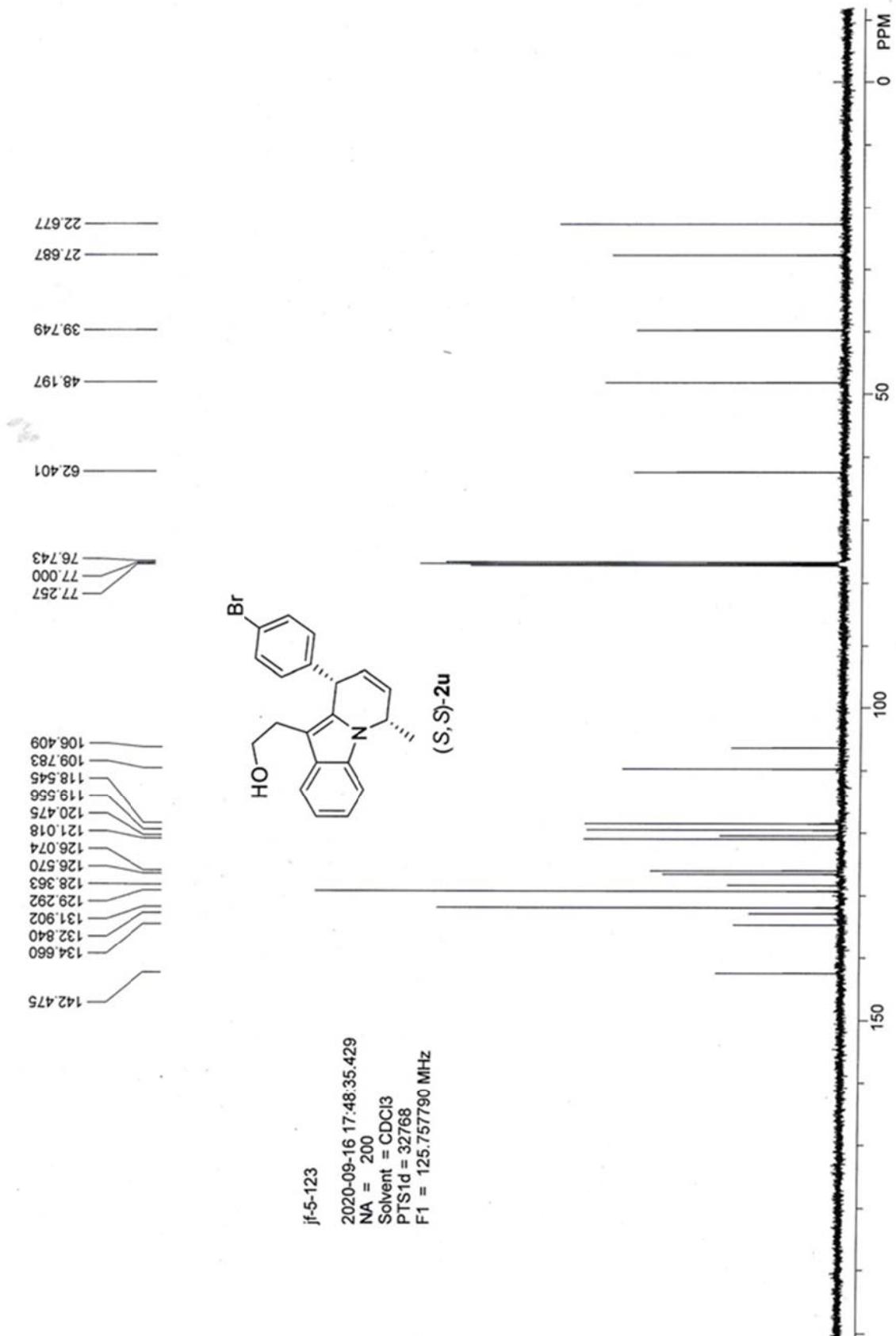
实验内容简介:
od-h, n-hexane/i-PrOH = 90/10, 0.5, 254

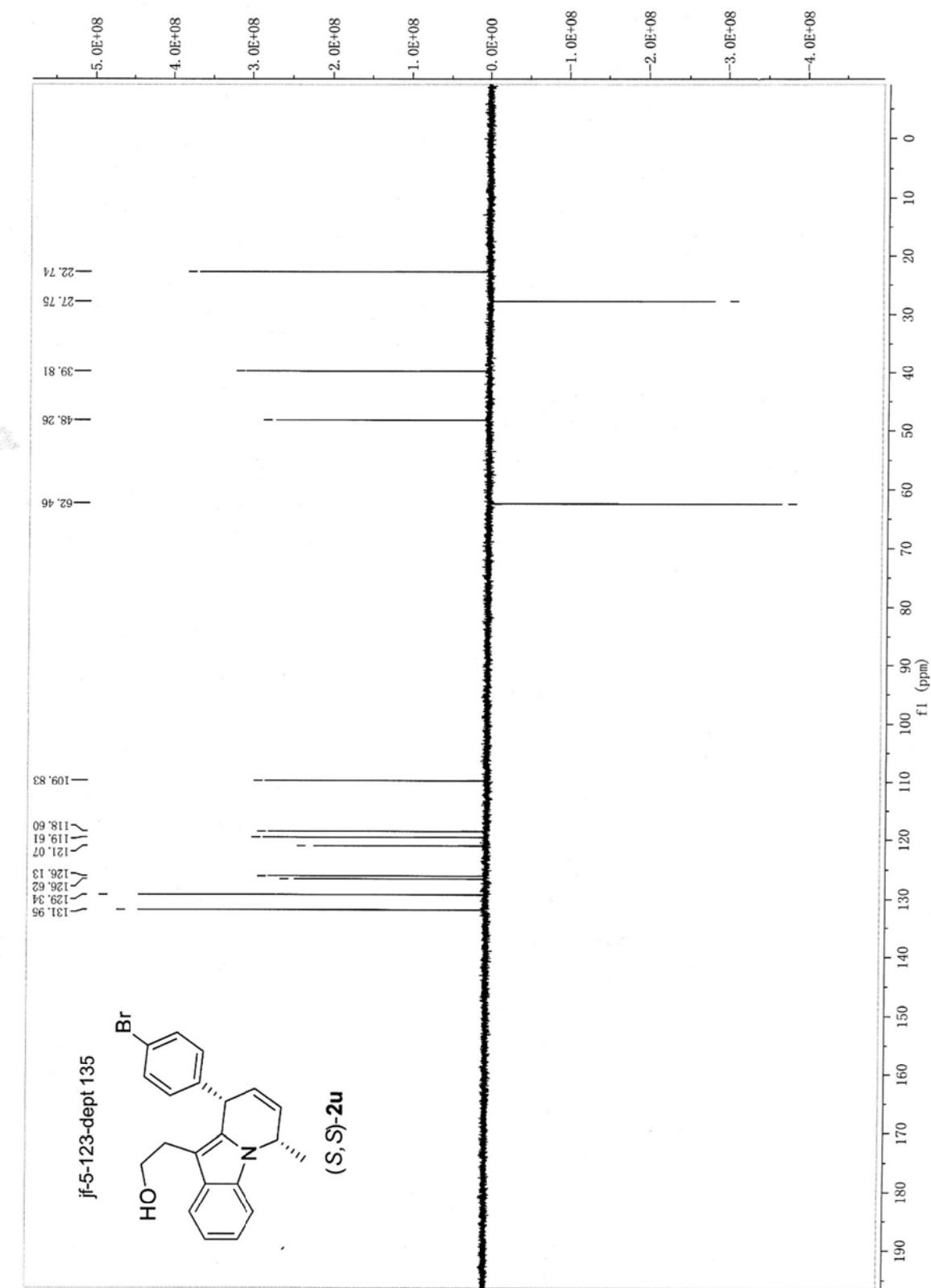


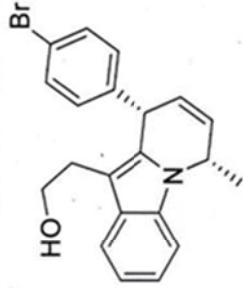
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		22.005	25665.793	865941.125	49.6035
2		49.995	10280.941	879785.125	50.3965
总计			35946.734	1745726.250	100.0000

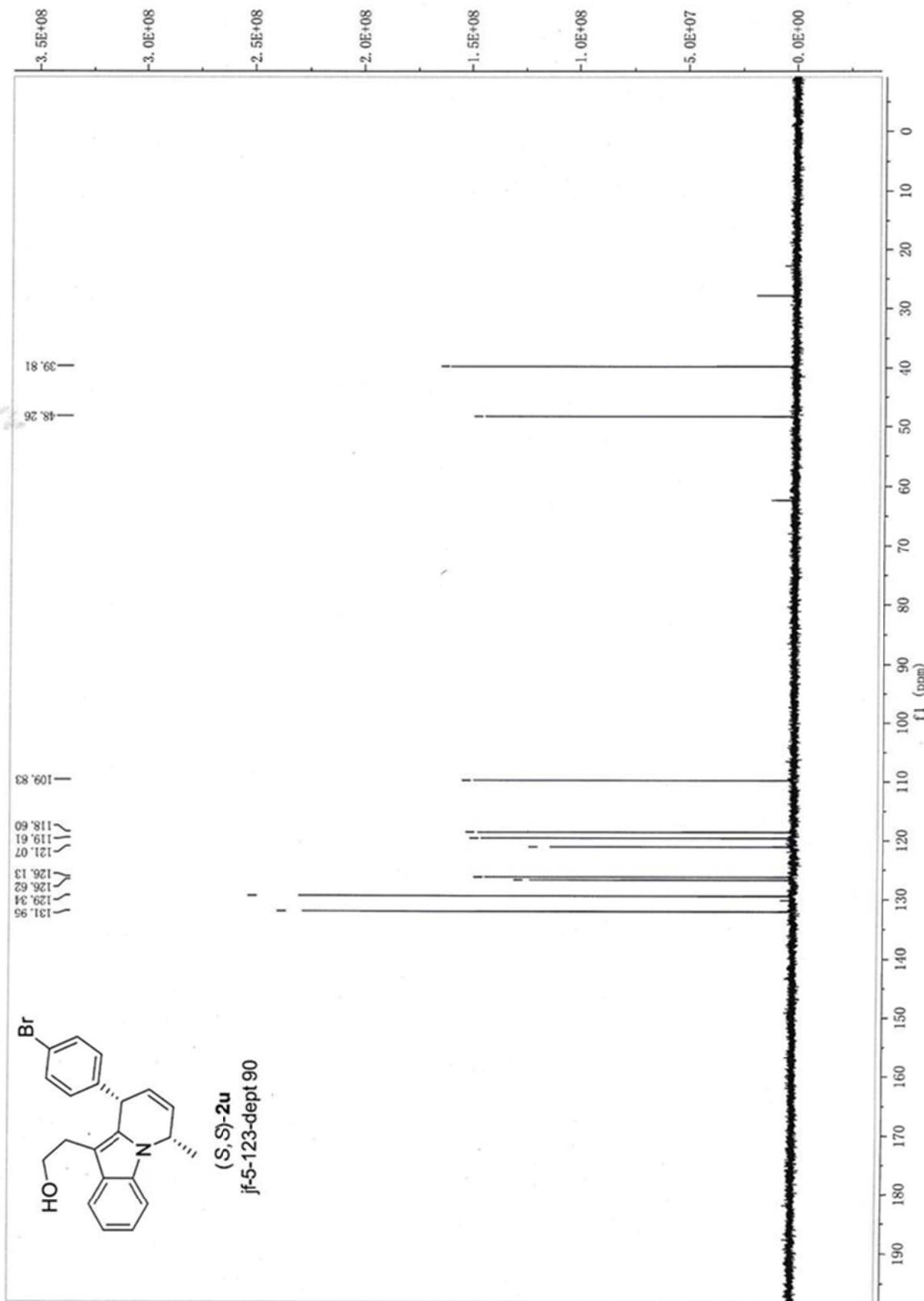


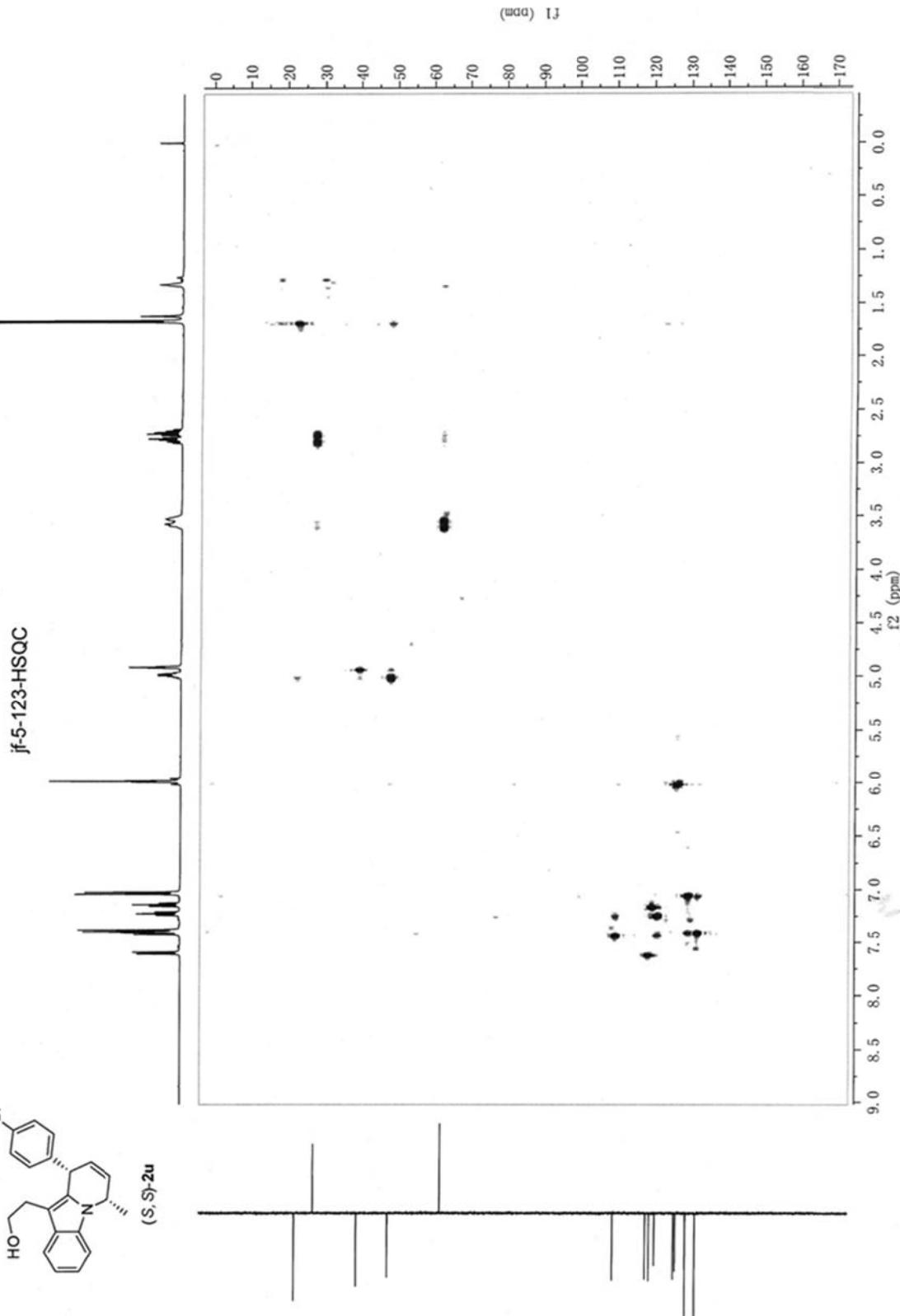


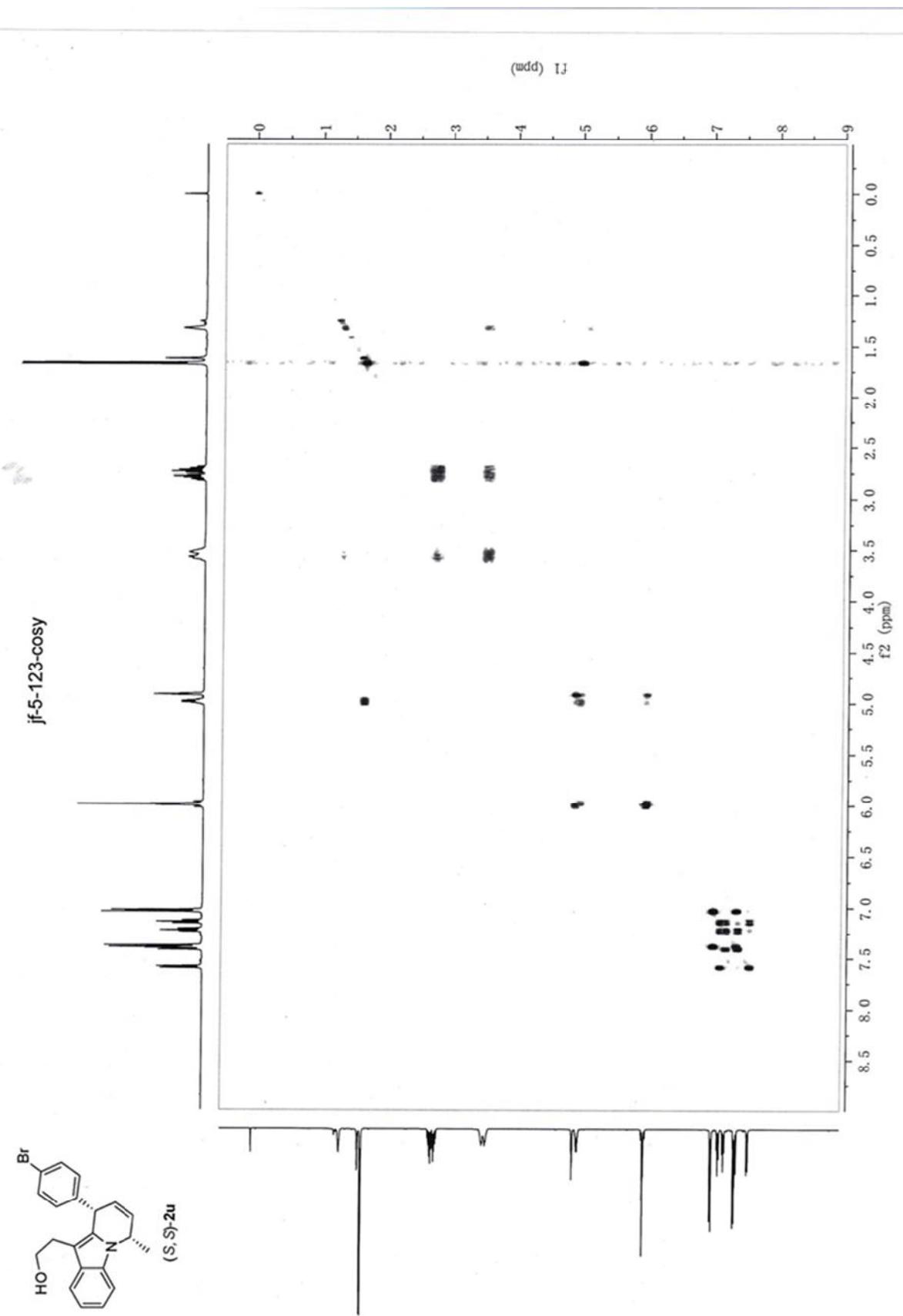


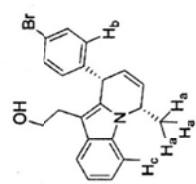


(*S,S*)-**2u**
jf-5-123-dept 90



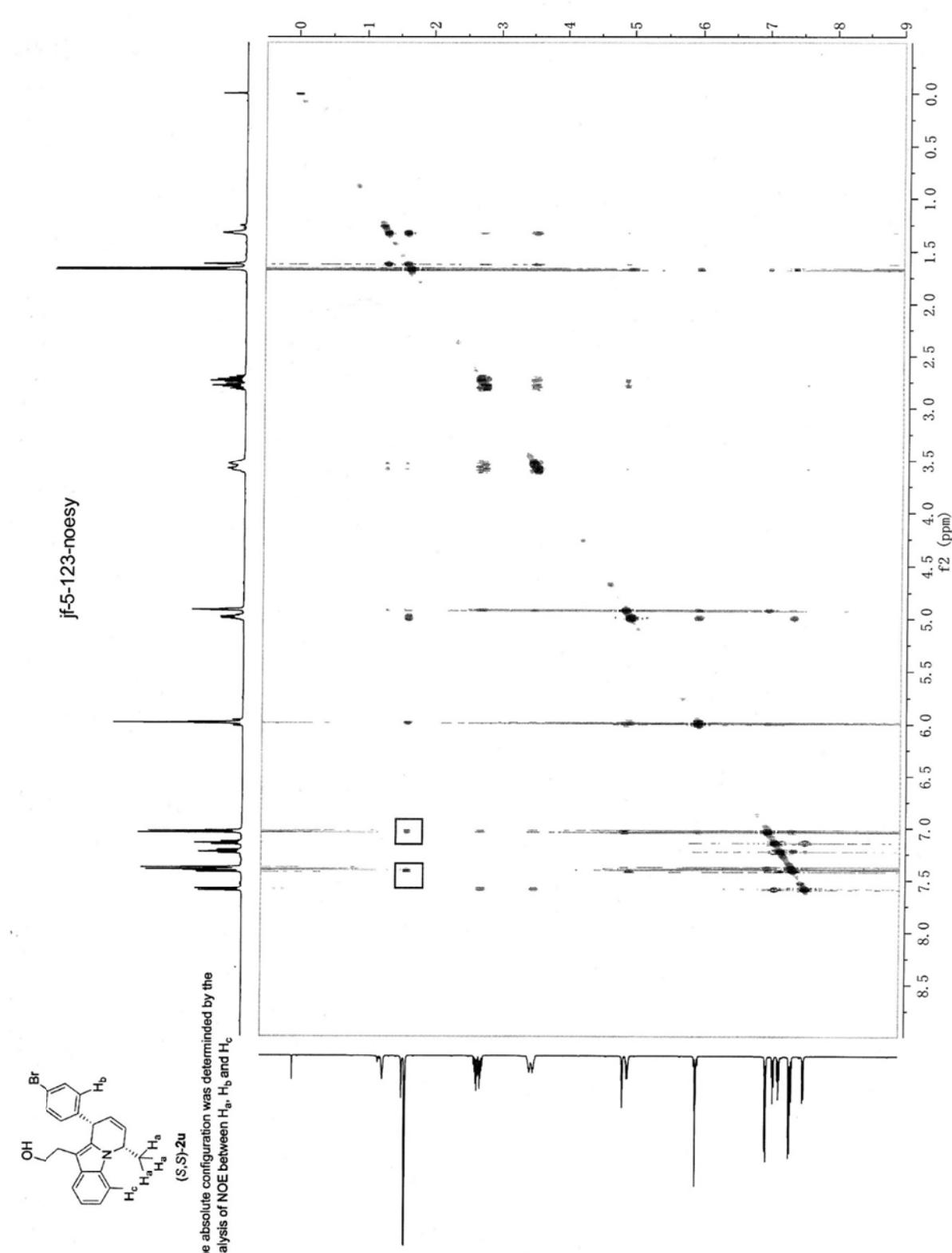


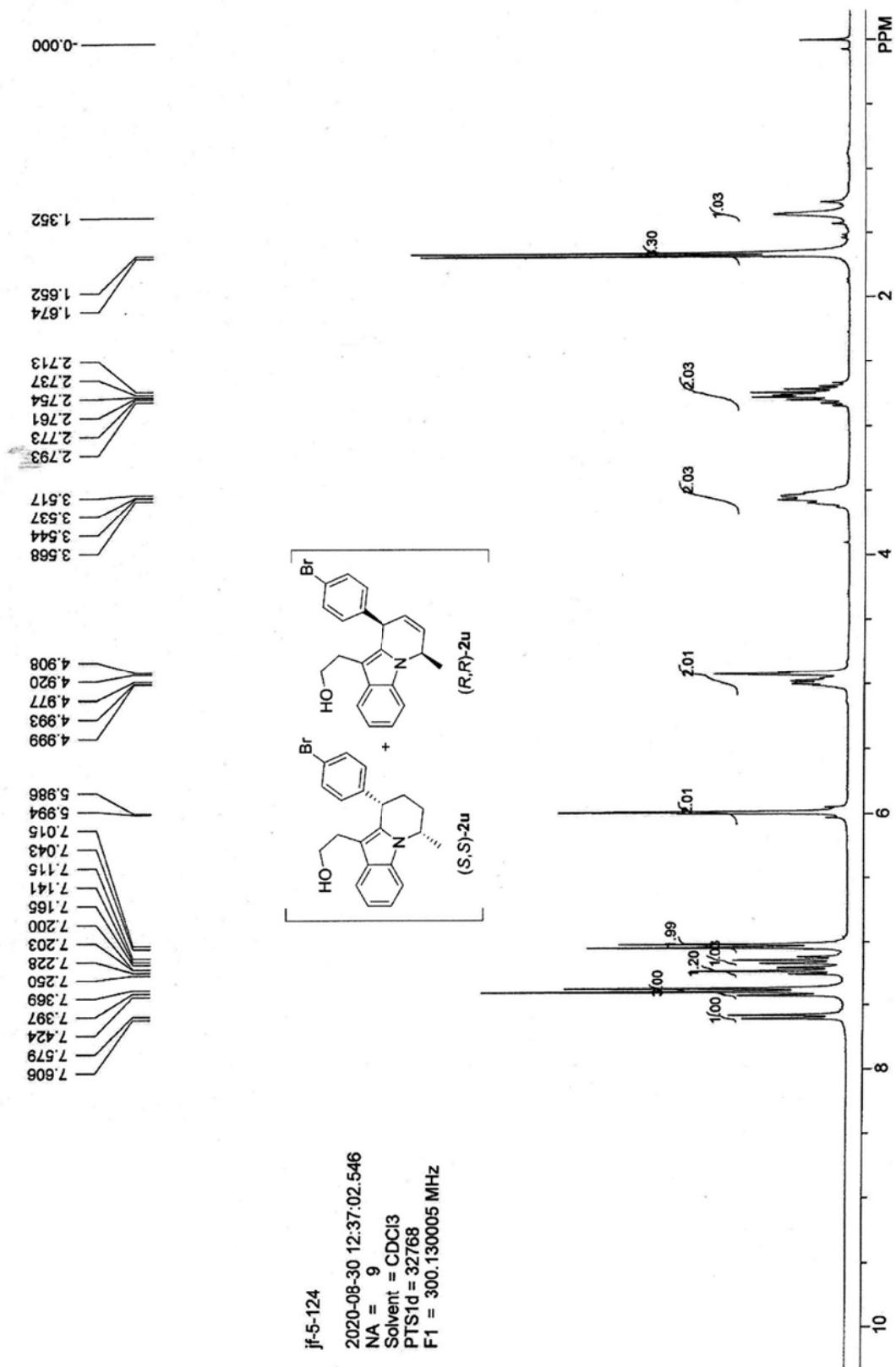




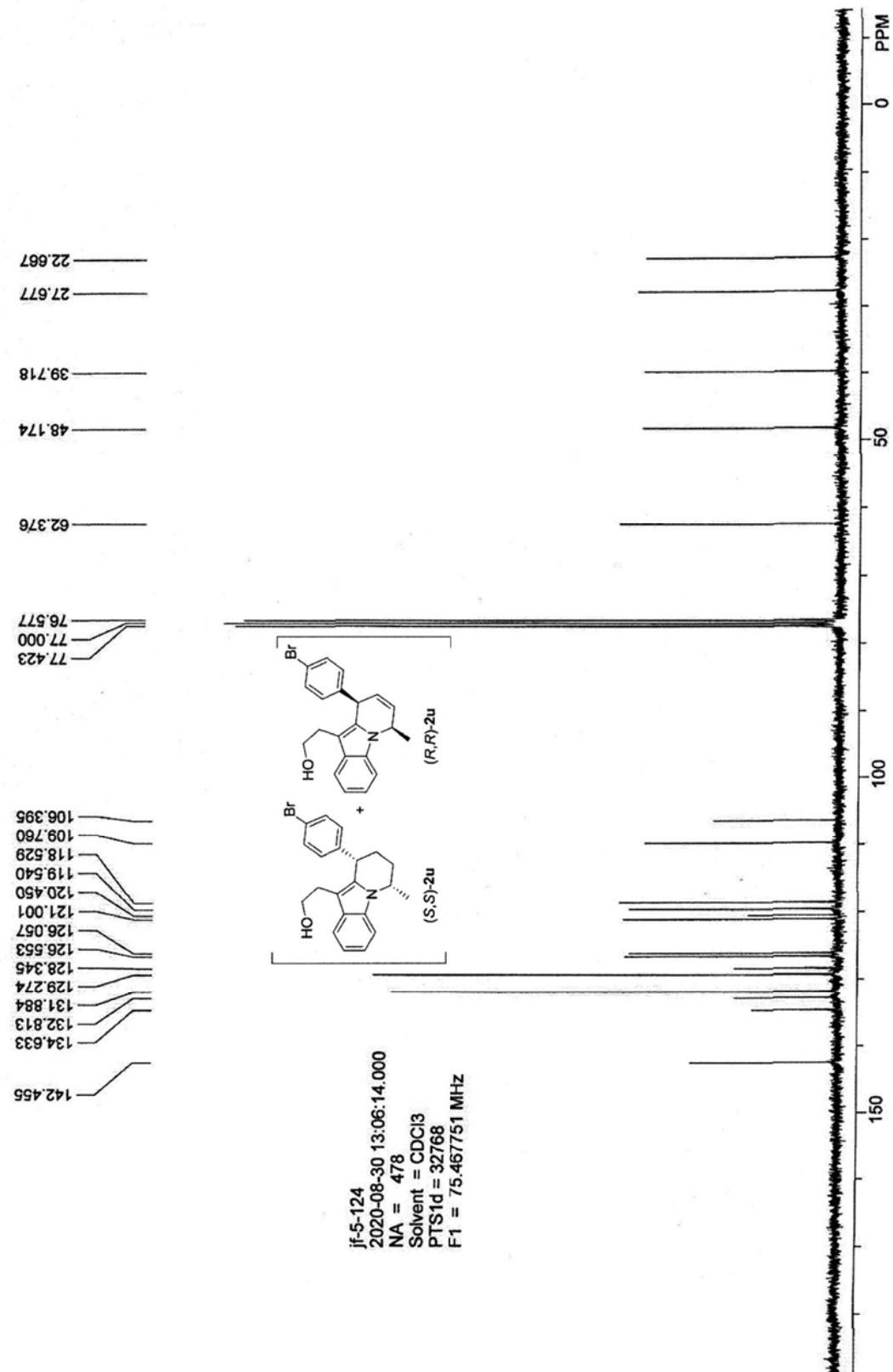
The absolute configuration was determined by the analysis of NOE between H_b , H_c and H_c

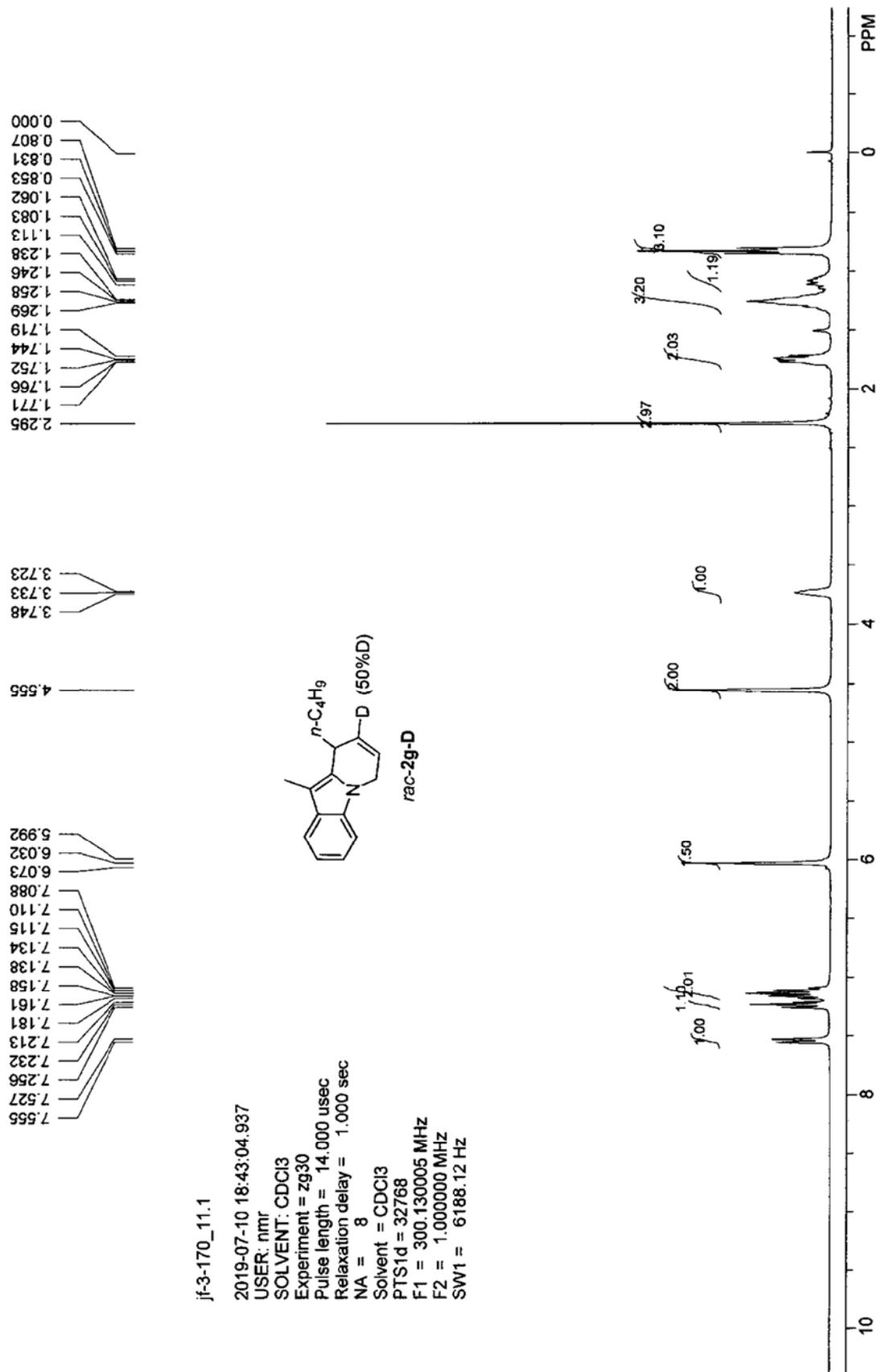
jf-5-123-noesy

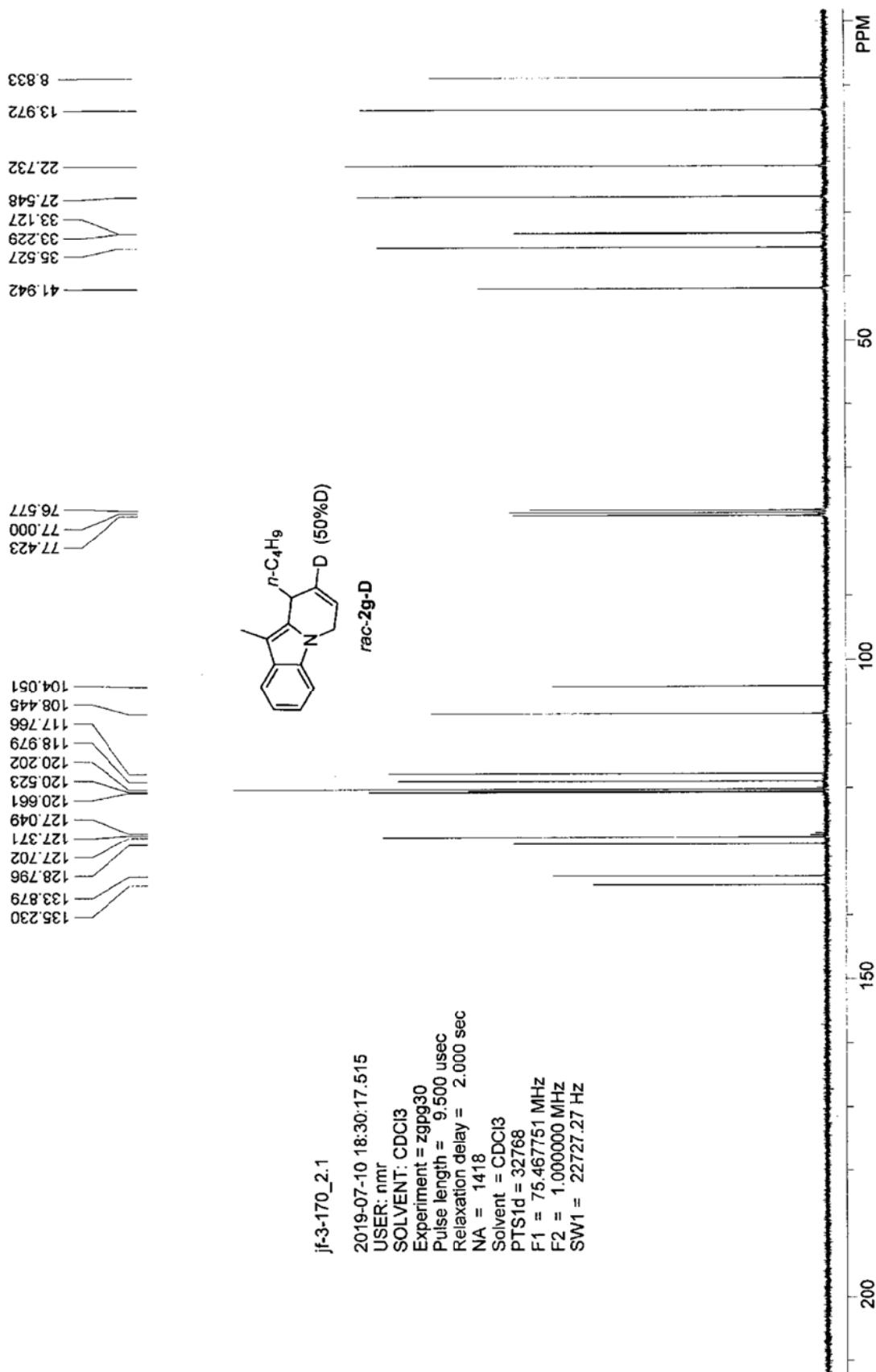


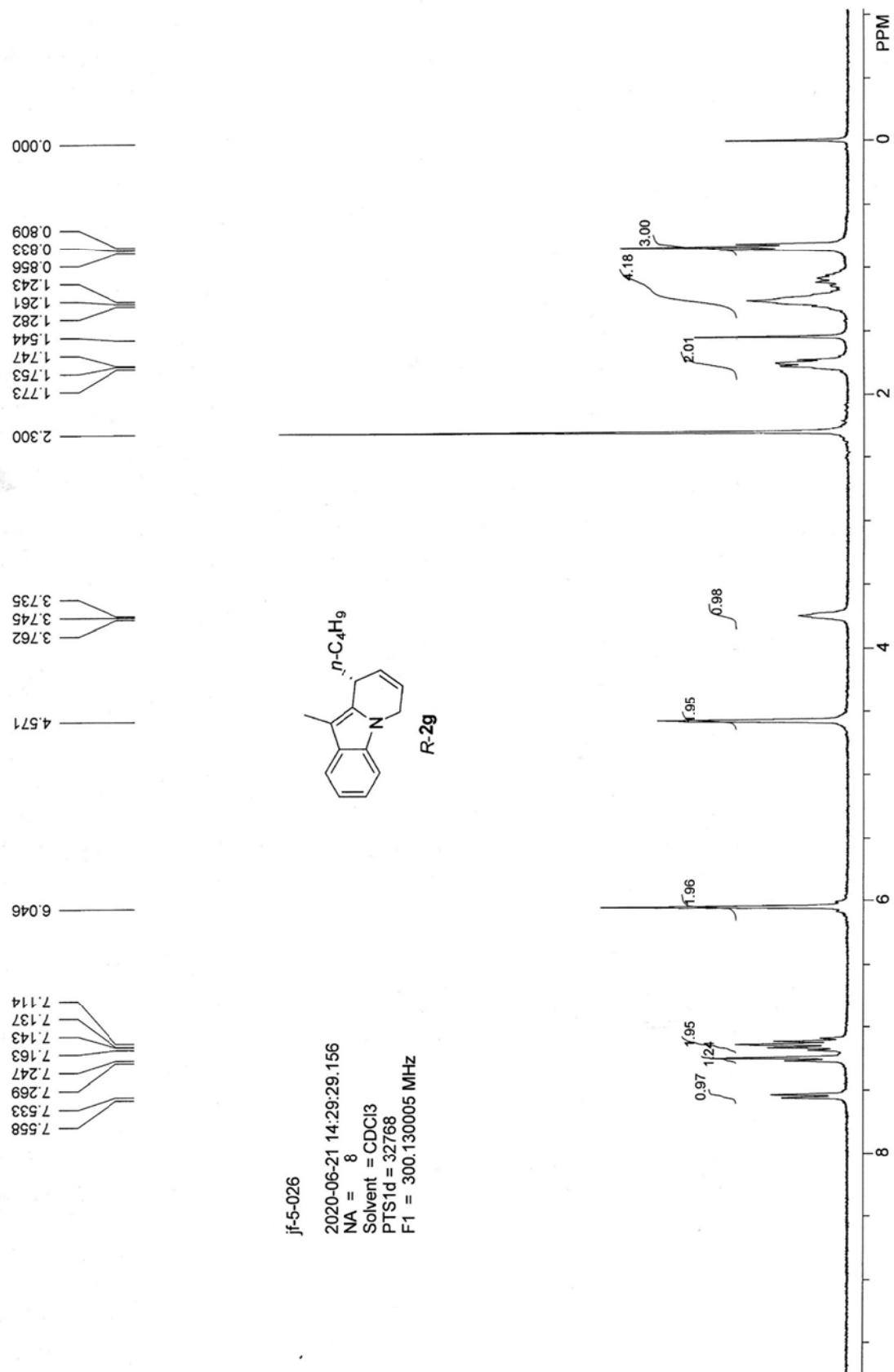


if-5-124
2020-08-30 12:37:02.546
NA = 9
Solvent = CDCl3
PT51d = 32768
F1 = 300.130005 MHz







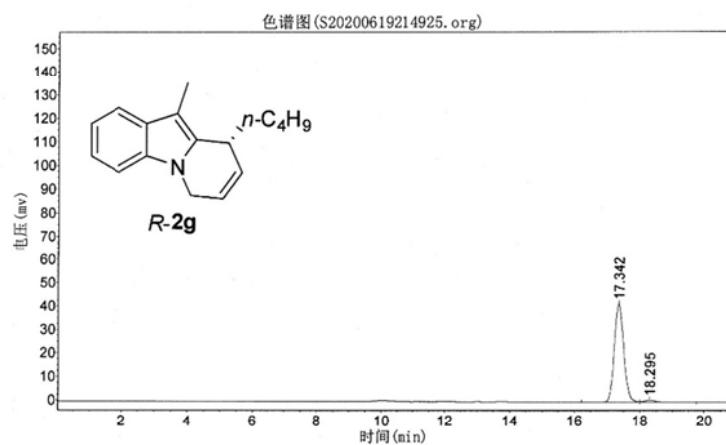


jf-5-026

实验时间: 2020-06-19, 21:49:25
谱图文件:D:\浙大智达\N2000\样品\S20200619214925.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-10-07. 13:10:59
积分方法: 面积归一法

实验内容简介:
od-H, n-hexane/i-PrOH = 100/1, 0.4, 254



分析结果表

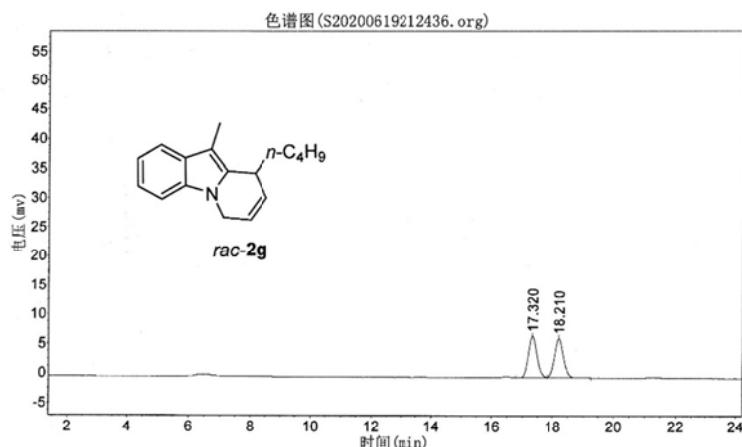
峰号	峰名	保留时间	峰高	峰面积	含量
1		17.342	41500.578	823340.188	97.8554
2		18.295	814.613	18043.951	2.1446
总计			42315.191	841384.139	100.0000

jf-2-097-0619

实验时间: 2020-06-19, 21:24:36
谱图文件:D:\浙大智达\N2000\样品\S20200619212436.org
方法文件:D:\浙大智达\N2000\djx.mtd

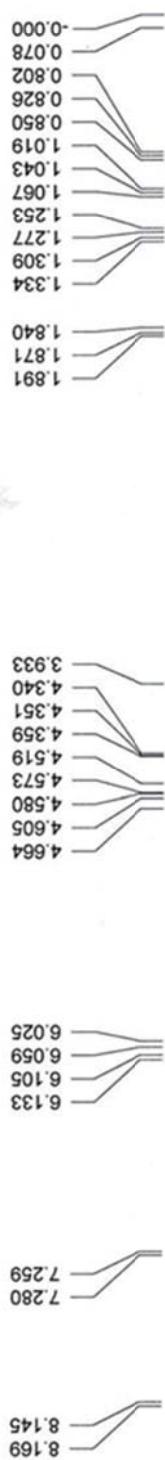
实验者: jf
报告时间: 2020-06-19, 22:08:54
积分方法: 面积归一法

实验内容简介:
OD-H, n-hexane/i-PrOH = 100/1, 0.4, 254



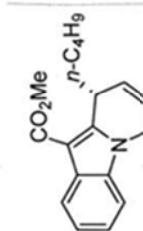
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		17.320	6929. 225	138574. 953	50. 7164
2		18.210	6519. 636	134659. 922	49. 2836
总计			13448. 860	273234. 875	100. 0000

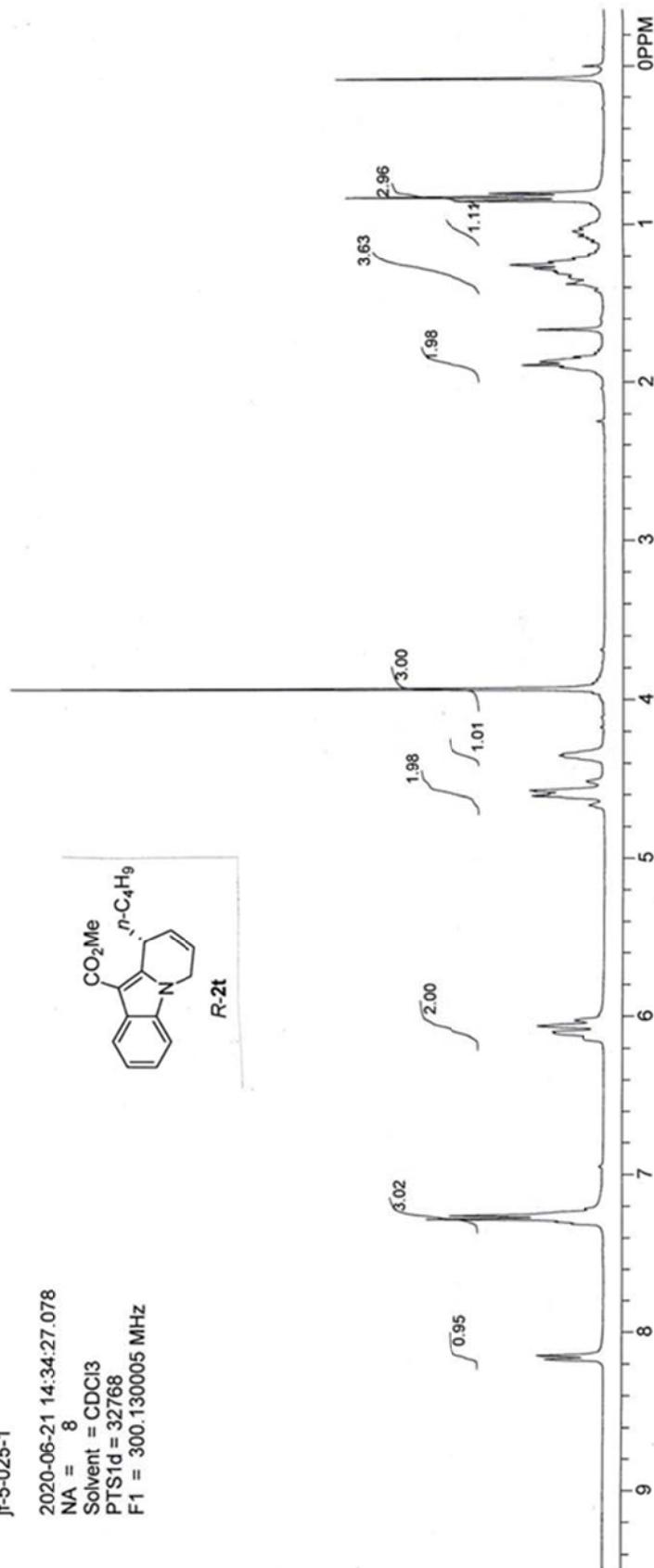


Jf-5-025-1

2020-06-21 14:34:27.078
 NA = 8
 Solvent = CDCl₃
 P1/T1d = 32/768
 F1 = 300.1330005 MHz



R-2t

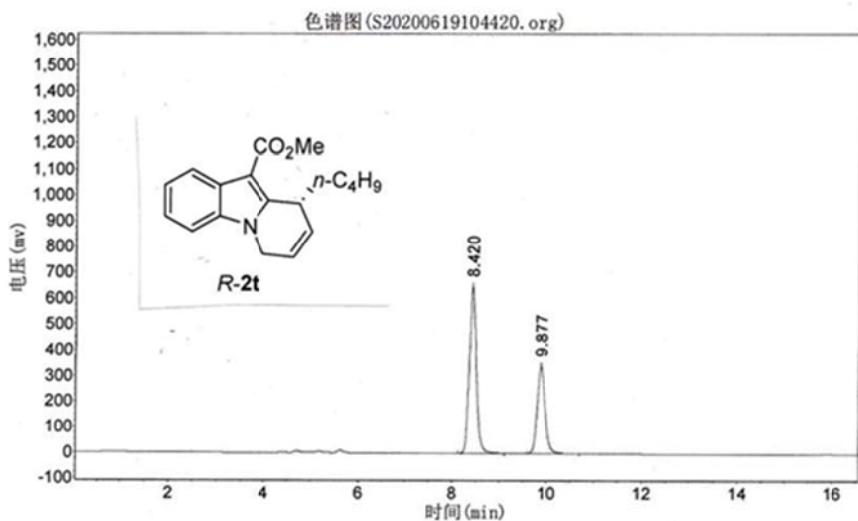


jf-5-025-1

实验时间: 2020-06-19, 10:44:20
谱图文件:D:\浙大智达\N2000\样品\S20200619104420.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-06-19, 11:03:19
积分方法: 面积归一法

实验内容简介:
OD-H, n-hexane/i-PrOH = 90/10, 0.7, 214



分析结果表

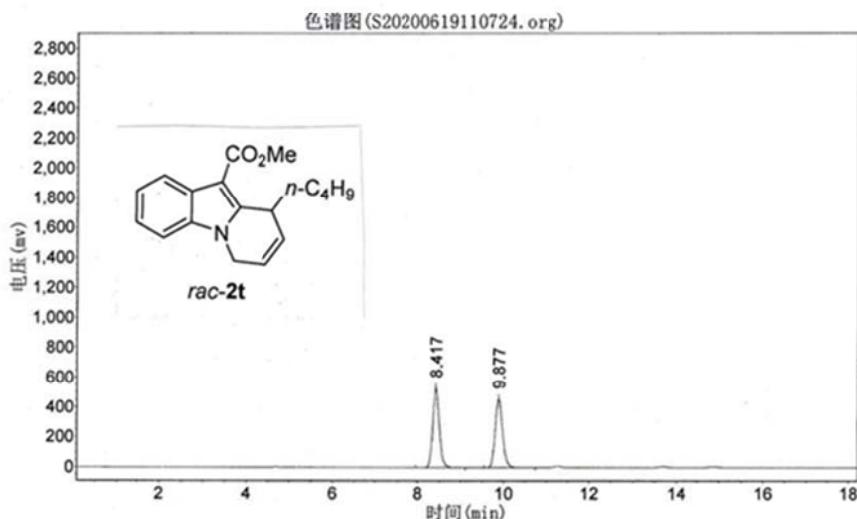
峰号	峰名	保留时间	峰高	峰面积	含量
1		8.420	646405.625	6669780.500	62.1773
2		9.877	340081.563	4057247.500	37.8227
总计			986487.188	10727028.000	100.0000

jf-4-174-1

实验时间: 2020-06-19, 11:07:24
谱图文件:D:\浙大智达\N2000\样品\S20200619110724.org
方法文件:D:\浙大智达\N2000\djx.mtd

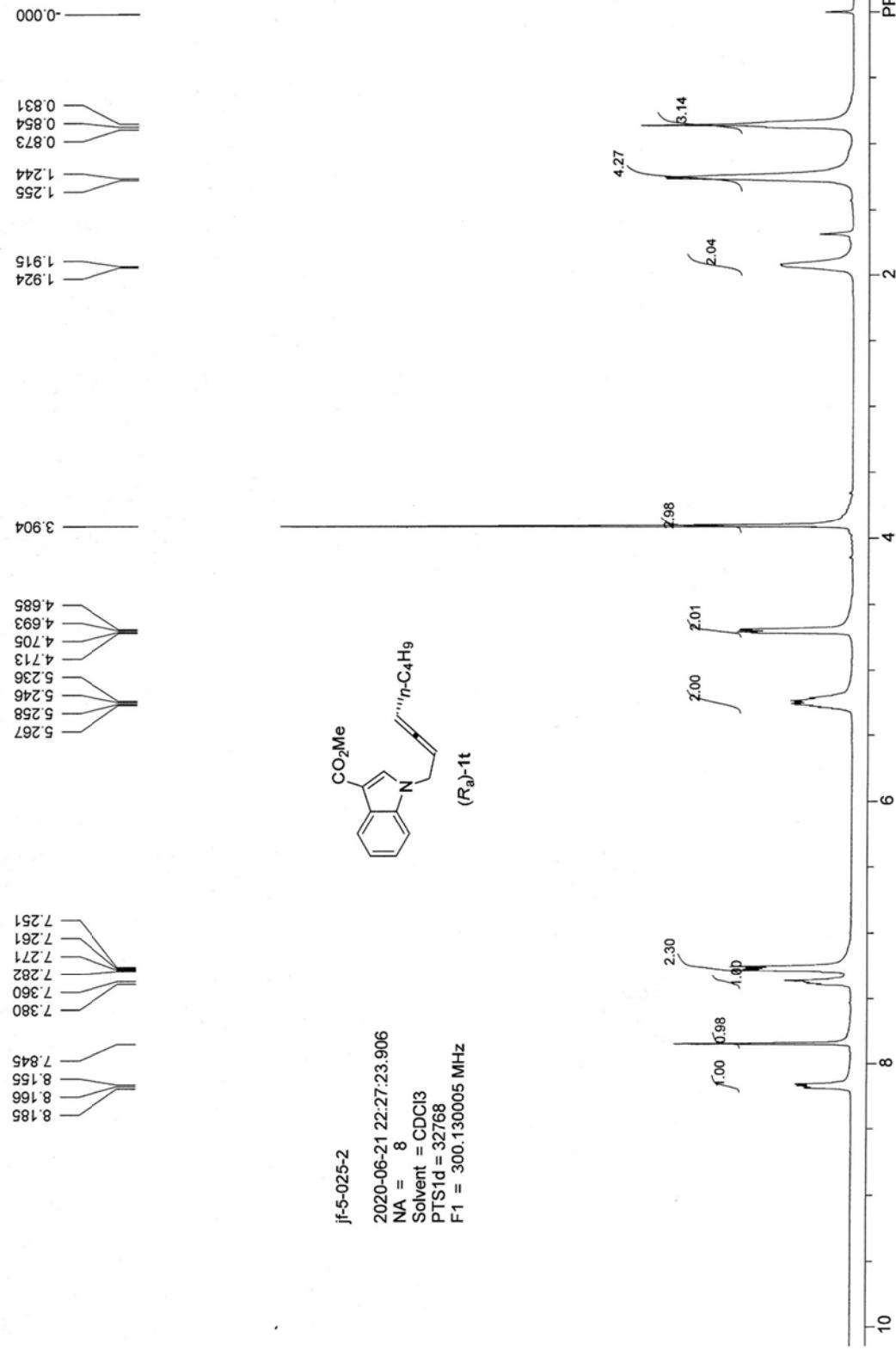
实验者: jf
报告时间: 2020-06-19, 11:32:11
积分方法: 面积归一法

实验内容简介:
OD-H, n-hexane/i-PrOH = 90/10, 0.7, 214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		8.417	529681.625	5579407.000	50.5149
2		9.877	455515.313	5465655.500	49.4851
总计			985196.938	11045062.500	100.0000

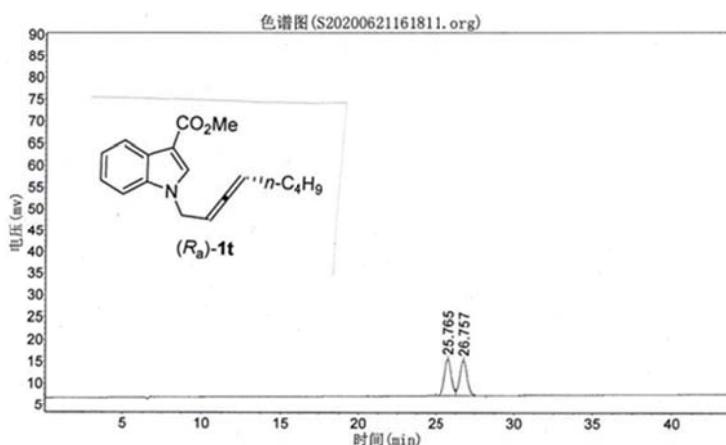


jf-5-025-2

实验时间: 2020-06-21, 16:18:11
谱图文件:D:\浙大智达\N2000\样品\S20200621161811.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-06-21, 17:07:06
积分方法: 面积归一法

实验内容简介:
OD-H, n-hexane/i-PrOH = 90/10, 0.5, 214



分析结果表

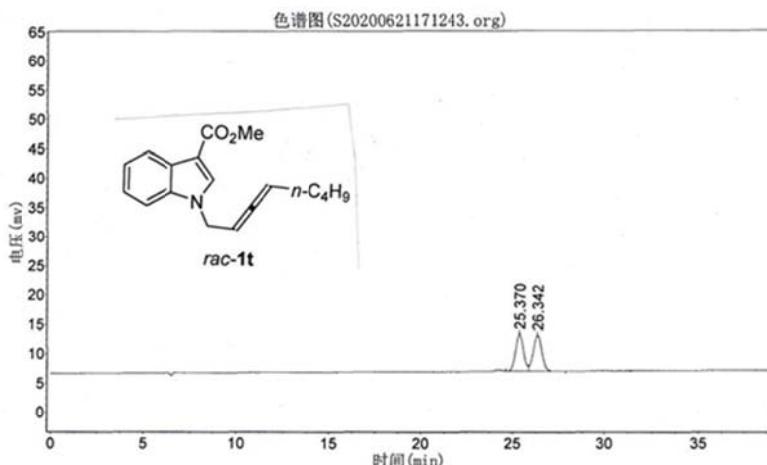
峰号	峰名	保留时间	峰高	峰面积	含量
1		25.765	8295.294	254018.875	49.7509
2		26.757	7942.925	256562.656	50.2491
总计			16238.219	510581.531	100.0000

jf-3-112

实验时间: 2020-06-21, 17:12:43
谱图文件:D:\浙大智达\N2000\样品\S20200621171243.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者: jf
报告时间: 2020-06-21, 18:10:14
积分方法: 面积归一法

实验内容简介:
OD-H, n-hexane/i-PrOH = 90/10, 0.5, 214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		25.370	6233.678	186407.172	48.7367
2		26.342	6127.121	196070.625	51.2633
总计			12360.798	382477.797	100.0000