Supplementary Material (ESI) for Chemical Communications

Aminocatalytic Asymmetric Inverse-Electron-Demand Aza-Diels–Alder Reaction of *N*-Ts-1-aza-1,3-butadienes Based on Coumarin Cores

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Supplementary Information

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1. General methods

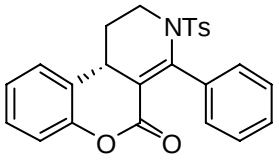
NMR data were obtained for ^{1}H at 400 MHz, and for ^{13}C at 50, 75 or 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI HRMS was recorded on a Bruker Apex-2. In each case, enantiomeric ratio was determined by HPLC analysis on chiral column in comparison with authentic racemate, using a Daicel Chiralpak OD-H Column (250 x 4.6 mm), Chiralpak AD-H Column (250 x 4.6 mm), Chiralpak AS-H Column (250 x 4.6 mm) or Chiralpak IC Column (250 x 4.6 mm). UV detection was monitored at 220 nm or 254 nm. Optical rotation data were examined in $CHCl_3$ solution at 20 °C. Column chromatography was performed on silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates. UV light and I_2 were used to visualize products. All chemicals were used without purification as commercially available unless otherwise noted. The *N*-Ts-1-aza-1,3-butadienes were prepared from the corresponding ketone and $TsNH_2$ according to the literature procedures.[1] The secondary amine catalysts were also synthesized according to the literature procedures.[2]

(1) (*a*) F. Sandrinelli, S. Perrio and P. Belsin. *J. Org. Chem.,* 1997, **62**, 8626; (*b*) B. Han, J.-L. Li, C. Ma, S.-J. Zhang and Y.-C. Chen, *Angew. Chem., Int. Ed.,* 2008, **47**, 9971; (*c*) B. Han, Z.-Q. He, J.-L. Li, R. Li, K. Jiang, T.-Y. Liu and Y.-C. Chen, *Angew. Chem., Int. Ed.,* 2009, **48**, 5474.
(2) (*a*) M. Marigo, T. C. Wabnitz, D. Fielenbach and K. A. Jørgensen, *Angew. Chem., Int. Ed.,* 2005, **44**, 794; (*b*) Y. Hayashi, H. Gotoh, T. Hayashi and M. Shoji, *Angew. Chem., Int. Ed.,* 2005, **44**, 4212; (*c*) Y.-K. Liu, C. Ma, J K. iang, T.-Y. Liu and Y.-C. Chen, *Org. Lett.,* 2009, **11**, 2848.

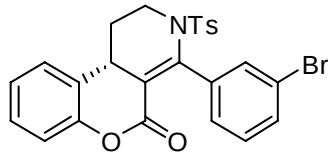
2. General procedure for the aza-Diels–Alder reaction of acetaldehyde

The reaction was carried out with acetaldehyde (25 μL, 0.4 mmol) and *N*-Ts-1-aza-1,3-butadiene **2** (0.1 mmol) in the presence of catalyst **1f** (12.4 mg, 0.02 mmol), benzoic acid (2.4 mg, 0.02 mmol) in tetrahydrofuran (1.0 mL) at about 5 °C for 12–24 h. After the reaction completed, the mixture was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to afford the aza-Diels-Alder adduct **3**. To an anhydrous dichloromethane solution of the adduct **3** was added triethyl silane (34.8 mg, 0.3 mmol) and $BF_3.Et_2O$ (36 μL, 0.3 mmol) in one portion. The reaction mixture was stirred at 0 °C for 5 min and then at room temperature until the reaction completed (monitored by TLC). The reaction was quenched with aqueous $NaHCO_3$, extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography (petroleum

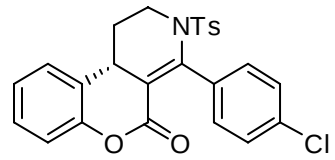
ether/ethyl acetate = 10:1) to give the final product **4**.



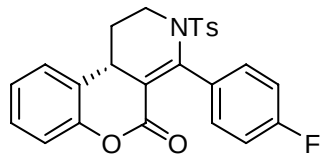
4a was obtained in 79% yield for two steps and the enantiomeric excess was determined to be 95% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 13.68 min, t_{minor} = 17.50 min. $[\alpha]_D^{20}$ -268.2 (*c* = 1.70 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.28 (m, 2H), 7.23-7.21 (m, 2H), 7.18-7.12 (m, 4H), 7.10-7.05 (m, 5H), 4.61 (dt, *J* = 14.0 Hz, *J* = 3.2 Hz, 1H), 3.85 (t, *J* = 8.8 Hz, 1H), 3.56 (t, *J* = 12.4 Hz, 1H), 2.54-2.48 (m, 1H), 2.37 (s, 3H), 1.97-1.88 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 151.2, 149.6, 143.9, 137.1, 134.4, 129.6, 129.4, 129.3, 128.5, 127.6, 127.1, 125.7, 124.6, 124.4, 116.6, 111.8, 46.1, 33.8, 24.6, 21.5 ppm; ESI HRMS: calcd. for $C_{25}H_{21}NO_4S$+H 432.1270, found 432.1275.



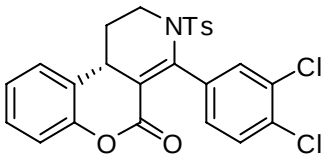
4b was obtained in 91% yield for two steps and the enantiomeric excess was determined to be 92% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{minor} = 13.10 min, t_{major} = 15.65 min. $[\alpha]_D^{20}$ -154.3 (*c* = 0.70 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 7.2 Hz, 1H), 7.34-7.30 (m, 1H), 7.23-7.17 (m, 4H), 7.15-6.97 (m, 6H), 4.66 (br s, 1H), 3.87 (dd, *J* = 10.0 Hz, *J* = 8.0 Hz, 1H), 3.62-3.50 (m, 1H), 2.59-2.56 (m, 1H), 2.41 (s, 3H), 2.10-2.01 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.1, 151.2, 147.9, 144.4, 137.2, 136.1, 132.3, 132.2, 129.6, 129.2, 128.9, 128.6, 126.9, 125.3, 124.7, 121.5, 116.8, 112.5, 46.1, 34.0, 25.0, 21.6 ppm; ESI HRMS: calcd. for $C_{25}H_{20}BrNO_4S$+H 510.0375, found 510.0381.



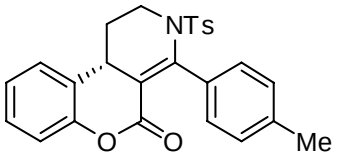
4c was obtained in 82% yield for two steps and the enantiomeric excess was determined to be 90% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 9.78 min, t_{minor} = 12.47 min. $[\alpha]_D^{20}$ -250.5 (*c* = 1.10 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.29 (m, 1H), 7.26-7.24 (m, 2H), 7.19-7.06 (m, 7H), 7.01-6.99 (m, 2H), 4.61 (dt, *J* = 13.6 Hz, *J* = 3.2 Hz, 1H), 3.86 (dd, *J* = 10.4 Hz, *J* = 8.0 Hz, 1H), 3.61-3.54 (m, 1H), 2.56-2.50 (m, 1H), 2.40 (s, 3H), 1.99-1.90 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.4, 151.2, 148.4, 144.3, 137.1, 135.5, 132.9, 131.0, 129.5, 128.6, 127.9, 127.1, 125.4, 124.6, 116.7, 112.4, 46.1, 33.9, 24.6, 21.6 ppm; ESI HRMS: calcd. for $C_{25}H_{21}ClNO_4S$+H 466.0880, found 466.0879.



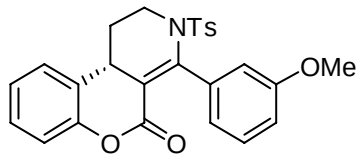
4d was obtained in 81% yield for two steps and the enantiomeric excess was determined to be 89% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 9.71 min, t_{minor} = 14.06 min. $[\alpha]_D^{20}$ -203.7 (*c* = 0.70 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.29 (m, 1H), 7.26-7.23 (m, 2H), 7.18-7.12 (m, 4H), 7.08-7.03 (m, 3H), 6.86-6.82 (m, 2H), 4.61 (dt, *J* = 13.6 Hz, *J* = 3.2 Hz, 1H), 3.86 (t, *J* = 9.2 Hz, 1H), 3.58 (t, *J* = 12.4 Hz, 1H), 2.55-2.50 (m, 1H), 2.39 (s, 3H), 1.99-1.89 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.8, 163.5, 160.9, 151.2, 148.6, 144.2, 137.2, 131.7, 131.5, 130.4, 129.5, 128.6, 127.1, 125.6, 124.6, 116.7, 115.0, 114.6, 112.1, 46.1, 33.9, 24.7, 21.5 ppm; ESI HRMS: calcd. for $C_{25}H_{21}FNO_4S$+H 450.1175, found 450.1179.



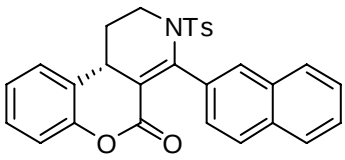
4e was obtained in 79% yield for two steps and the enantiomeric excess was determined to be 87% by HPLC analysis on Chiralpak AD column (15% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 46.84 min, t_{minor} = 53.69 min. $[\alpha]_D^{20}$ -212.7 (*c* = 1.10 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.29 (m, 2H), 7.25-7.21 (m, 2H), 7.18-7.14 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.94 (br s, 1H), 4.64 (br s, 1H), 3.88 (dd, *J* = 10.0 Hz, *J* = 7.6 Hz, 1H), 3.60-3.54 (m, 1H), 2.58-2.57 (m, 1H), 2.41 (s, 3H), 2.07-2.02 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.1, 151.1, 147.1, 144.7, 137.0, 134.1, 133.6, 131.8, 131.3, 129.7, 129.6, 129.5, 128.7, 126.9, 125.1, 124.8, 124.7, 116.8, 112.9, 46.0, 33.9, 24.8, 21.6 ppm; ESI HRMS: calcd. for $C_{25}H_{19}Cl_2NO_4S$+H 500.0490, found 500.0498.



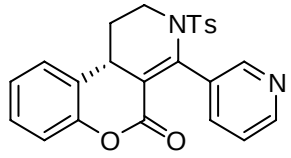
4f was obtained in 84% yield for two steps and the enantiomeric excess was determined to be 88% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{major} = 12.18 min, t_{minor} = 14.74 min. $[\alpha]_D^{20}$ -202.5 (*c* = 1.15 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.25 (m, 3H), 7.16-7.05 (m, 5H), 6.98 (br s, 4H), 4.59 (dt, *J* = 13.6 Hz, *J* = 3.2 Hz, 1H), 3.83 (dd, *J* = 10.4 Hz, *J* = 8.0 Hz, 1H), 3.59-3.52 (m, 1H), 2.51-2.44 (m, 1H), 2.38 (s, 3H), 2.33 (s, 3H), 1.92-1.83 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.8, 151.3, 149.7, 143.9, 139.4, 137.1, 131.6, 129.5, 129.3, 128.4, 127.2, 125.8, 124.5, 124.3, 116.6, 111.5, 46.1, 33.9, 24.5, 21.5 ppm; ESI HRMS: calcd. for $C_{26}H_{23}NO_4S$+H 446.1426, found 446.1432.



4g was obtained in 86% yield for two steps and the enantiomeric excess was determined to be 84% by HPLC analysis on Chiralpak AS column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 18.59 min, t_{minor} = 28.53 min. $[\alpha]_D^{20}$ -163.7 (*c* = 1.15 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.29 (m, 1H), 7.25-7.23 (m, 2H), 7.18-7.06 (m, 6H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 6.0 Hz, 1H), 6.50 (br s, 1H), 4.64 (d, *J* = 13.2 Hz, 1H), 3.86 (dd, *J* = 10.4 Hz, *J* = 8.0 Hz, 1H), 3.62 (s, 3H), 3.59-3.53 (m, 1H), 2.57-2.52 (m, 1H), 2.37 (s, 3H), 2.05-1.92 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.5, 158.8, 151.3, 149.3, 143.9, 137.4, 135.5, 129.4, 128.7, 128.5, 127.2, 125.7, 124.7, 124.5, 122.5, 116.7, 115.3, 115.0, 111.9, 54.9, 46.2, 34.0, 24.9, 21.5 ppm; ESI HRMS: calcd. for $C_{26}H_{23}NO_4S$+H 462.1375, found 462.1369.

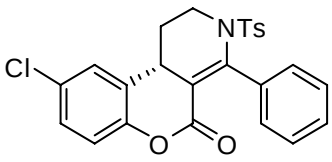


4h was obtained in 87% yield for two steps and the enantiomeric excess was determined to be 89% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{minor} = 17.28 min, t_{major} = 20.77 min. $[\alpha]_D^{20}$ -215.4 (*c* = 1.30 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.48-7.31 (m, 5H), 7.25-7.17 (m, 3H), 7.11-7.08 (m, 3H), 6.84 (d, *J* = 7.6 Hz, 2H), 4.79-4.68 (m, 1H), 3.93 (dd, *J* = 10.4 Hz, *J* = 8.0 Hz, 1H), 3.65 (t, *J* = 12.4 Hz, 1H), 2.62-2.59 (m, 1H), 2.23 (s, 3H), 2.12-2.04 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.5, 151.4, 149.9, 143.9, 137.7, 133.6, 132.4, 131.6, 129.5, 129.2, 128.6, 128.4, 127.7, 127.4, 127.2, 127.0, 126.8, 125.7, 124.7, 124.6, 116.7, 112.0, 46.2, 34.1, 25.1, 21.4 ppm; ESI HRMS: calcd. for $C_{29}H_{23}NO_4S$+H 482.1426, found 482.1420.

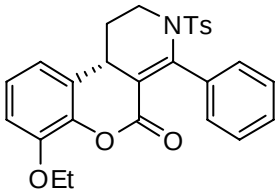


4i was obtained in 75% yield for two steps and the enantiomeric excess was determined to be 90% by HPLC analysis on Chiralpak OD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 18.16 min, t_{minor} = 21.10 min. $[\alpha]_D^{20}$ -190.0 (*c* = 0.40 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 4.8 Hz, 1H), 8.22 (s, 1H), 7.52 (d, *J* = 7.6 Hz,, 1H), 7.34-7.24 (m, 3H), 7.19-7.15 (m, 5H), 7.07 (d, *J* = 8.0 Hz, 1H), 4.56 (dt, *J* = 13.6 Hz, *J* = 3.6 Hz, 1H), 3.89 (dd, *J* = 10.0 Hz, *J* = 7.6 Hz, 1H), 3.64 (t, *J* = 12.0 Hz, 1H), 2.57-2.54 (m, 1H), 2.39 (s, 3H), 2.04-1.97 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.1, 154.4, 151.2, 150.0, 149.5, 146.5, 144.6, 137.4, 136.7, 131.0, 129.8, 128.7, 127.0, 125.2, 124.7, 124.6, 122.5, 116.8, 113.2, 46.0, 33.9, 24.5, 21.6

ppm; ESI HRMS: calcd. for $C_{24}H_{20}N_2O_4S$+H 433.1222, found 433.1229.

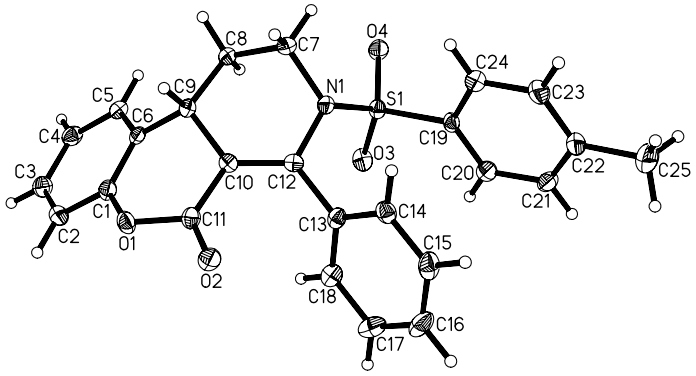


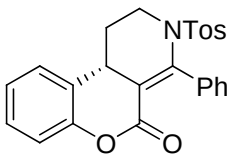
4j was obtained in 89% yield for two steps and the enantiomeric excess was determined to be 91% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 11.29 min, t_{minor} = 16.37 min. $[\alpha]_D^{20}$ -251.0 (*c* = 1.65 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (t, *J* = 7.6 Hz, 1H), 7.28-7.24 (m, 3H), 7.20-7.17 (m, 2H), 7.13-7.05 (m, 5H), 7.00 (d, *J* = 8.4 Hz, 1H), 4.60 (dt, *J* = 14.0 Hz, *J* = 3.2 Hz, 1H), 3.82 (t, *J* = 9.2 Hz, 1H), 3.56 (t, *J* = 12.4 Hz, 1H), 2.49-2.42 (m, 1H), 2.40 (s, 3H), 1.88-1.78 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.1, 150.4, 149.9, 144.3, 137.0, 134.3, 129.6, 129.5, 128.5, 127.7, 127.6, 127.2, 124.8, 118.0, 110.8, 46.0, 33.8, 24.3, 21.6 ppm; ESI HRMS: calcd. for $C_{25}H_{20}ClNO_4S$+H 466.0880, found 466.0887.



4k was obtained in 86% yield for two steps and the enantiomeric excess was determined to be 90% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 10.13 min, t_{minor} = 14.40 min. $[\alpha]_D^{20}$ -242.4 (*c* = 0.70 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.28 (m, 1H), 7.24-7.22 (m, 2H), 7.18-7.15 (m, 2H), 7.12-7.04 (m, 5H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 4.58 (dt, *J* = 14.0 Hz, *J* = 3.2 Hz, 1H), 4.15-4.08 (m, 2H), 3.84 (dd, *J* = 10.4 Hz, *J* = 8.0 Hz, 1H), 3.57 (t, *J* = 12.4 Hz, 1H), 2.51-2.44 (m, 1H), 2.38 (s, 3H), 1.98-1.89 (m, 1H) , 1.45 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.0, 149.4, 146.8, 143.9, 137.3, 134.5, 129.8, 129.4, 129.2, 129.0, 127.6, 127.2, 126.8, 124.3, 116.0, 113.1, 111.9, 64.9, 46.2, 34.1, 24.8, 21.5, 14.8 ppm; ESI HRMS: calcd. for $C_{27}H_{25}NO_5S$+H 476.1532, found 476.1538.

3. Crystal data and structure refinement for enantiopure 4a





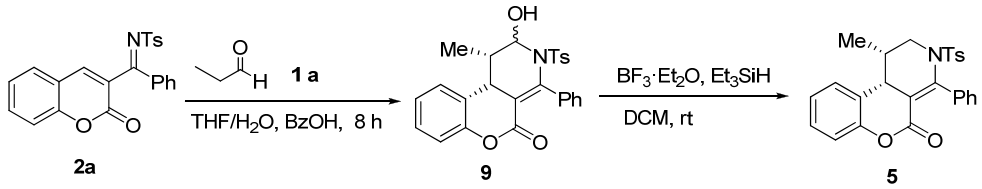
4a

Identification code	**4a**
Empirical formula	C25 H21 N O4 S
Formula weight	431.49
Temperature	93(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 8.7886(13) A alpha = 90 deg. b = 12.2877(19) A beta = 90 deg. c = 19.835(3) A gamma = 90 deg.
Volume	2142.0(6) A^3
Z, Calculated density	4, 1.338 Mg/m^3
Absorption coefficient	0.183 mm^-1
F(000)	904
Crystal size	0.33 x 0.23 x 0.20 mm
Theta range for data collection	3.03 to 27.47 deg.
Limiting indices	-11<=h<=11, -15<=k<=13, -25<=l<=25
Reflections collected / unique	17503 / 4904 [R(int) = 0.0303]
Completeness to theta = 27.47	99.8 %
Absorption correction	Empirical
Max. and min. transmission	0.9642 and 0.9414
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	4904 / 0 / 281
Goodness-of-fit on F^2	0.998
Final R indices [I>2sigma(I)]	R1 = 0.0334, wR2 = 0.0738
R indices (all data)	R1 = 0.0355, wR2 = 0.0751
Absolute structure parameter	-0.02(5)
Largest diff. peak and hole	0.226 and -0.302 e.A^-3

4. Aza-Diels–Alder reaction (ADAR) of other types of aldehydes

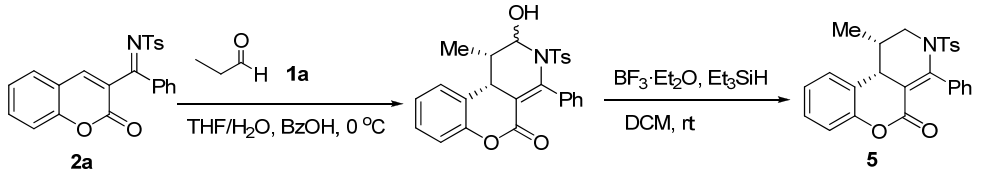
4.1 Procedure for the synthesis of compound 5 via ADAR with propionaldehyde



The reaction was carried out with *N*-Ts-1-aza-1,3-butadiene **2a** (40.3 mg, 0.1 mmol) and propionaldehyde (17.4 mg, 0.3 mmol) in the presence of catalyst **1a** (6.2 mg, 20 mol%) and benzoic acid (2.4 mg, 20 mol%) in a mixture of THF (1.0 mL) and water (0.1 mL) at 0 °C for about 8 h. Then the reaction mixture was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to give the intermediate hemiaminal **9**. To an anhydrous dichloromethane solution of the hemiaminal **9** was added triethyl silane (34.8 mg, 0.3 mmol) and $BF_3.Et_2O$ (36 μL, 0.3 mmol) in one portion. The reaction mixture was stirred at 0 °C for 5 min and then at room temperature for about 10 min. After the reaction was complete, the reaction was quenched with aqueous $NaHCO_3$, extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product **5** in 90% yield (40 mg) for two steps and the enantiomeric excess was determined to be 95% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 8.58 min, t_{minor} = 13.79 min. $[\alpha]_D^{20}$ -210.6 (*c* = 0.85 in $CHCl_3$); The diastereomeric ratio (85:15) was determined by ^1H NMR analysis. Major diastereomer: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.29 (m, 2H), 7.26-7.24 (m, 3H), 7.16-7.12 (m, 3H), 7.10-7.06 (m, 5H), 4.37 (dd, *J* = 13.2 Hz, *J* = 4.0 Hz, 1H), 3.34 (d, *J* = 9.2 Hz, 1H), 3.24 (dd, *J* = 13.2 Hz, *J* = 11.6 Hz, 1H), 2.38 (s, 3H), 2.19-2.12 (m, 1H), 1.28 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 151.7, 148.4, 143.9, 136.8, 134.1, 129.6, 129.5, 129.4, 129.3, 128.3, 128.0, 127.5, 127.1, 126.0, 124.4, 123.8, 117.0, 113.5,

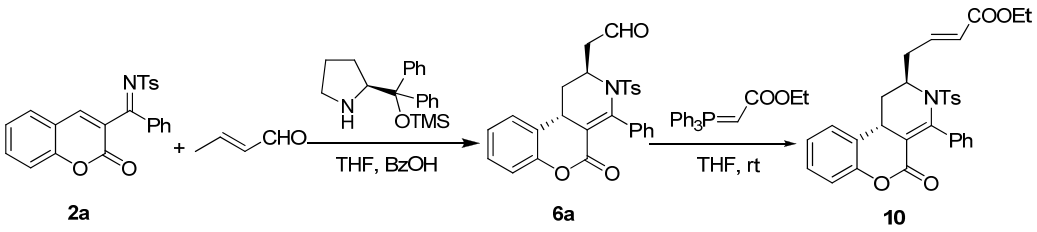
52.4, 40.7, 28.7, 21.5, 18.8 ppm; ESI HRMS: calcd. for $C_{26}H_{23}NO_4S$+H 446.1426, found 446.1420. *Its relative configuration has been established by NOE analysis.*

Since the unexpected *cis*-configuration for compound **5** was observed, we investigated the diastereoselectivity at various reaction times. As shown in the following scheme, the dr ratios did not change, which indicated that the relative configuration was generated in the cyclization process and the product's configuration did not epimerize under the catalytic conditions. Currently we have no clear accounts for the observed stereocontrol.



Time	2 h	4 h	8 h	24 h	48 h
Yield:	76%	83%	90%	91%	90%
dr	83:17	89:11	85:15	82:18	85:15

4.2 Procedure for the synthesis of compound 6 via dienamine catalysis

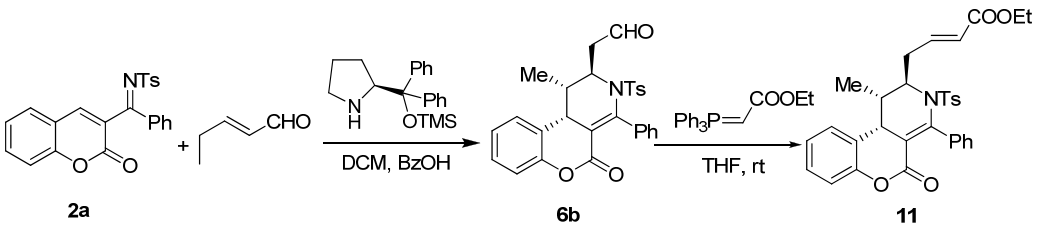


The reaction was carried out with *N*-Ts-1-aza-1,3-butadiene **2a** (40.3 mg, 0.1 mmol) and crotonaldehyde (21 mg, 0.3 mmol) in the presence of catalyst **1a** (6.2 mg, 20 mol %), benzoic acid (2.4 mg, 20 mol %) in tetrahydrofuran (1.0 mL) at 0 °C for about 12 h. Then the mixture was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to give the adduct **6a** in 90% yield (42.5 mg) and the enantiomeric excess was determined after conversion to its derivative **10**.

The chiral product **6a**: $[\alpha]_D^{20}$ -93.3 (c = 1.20 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s, 1H), 7.34-7.26 (m, 3H), 7.23-7.21 (m, 3H), 7.17-7.14 (m, 1H), 7.09-7.05 (m, 5H), 6.80 (br s, 1H), 5.45-5.44 (m, 1H), 3.72 (dd, J = 11.2 Hz, J = 8.0 Hz, 1H), 3.04 (dd, J = 17.6 Hz, J = 8.8 Hz, 1H), 2.77 (dd, J = 17.6 Hz, J = 5.2 Hz, 1H), 2.53-2.47 (m, 1H), 2.36 (s, 3H), 2.04-1.98 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 198.6, 163.1, 151.3, 147.1, 144.2, 136.5, 134.6, 129.9, 129.4, 128.7, 128.0, 127.5, 125.2, 124.6, 116.7, 111.8, 48.9, 45.1, 30.0, 27.7, 21.5 ppm; ESI HRMS: calcd. for $C_{27}H_{23}NO_5S$+Na 496.1195, found 496.1171.

To the tetrahydrofuran solution of the adduct **6a** was added $Ph_3PCHCOOEt$ (41.8 mg, 0.12

mmol) in one portion, and the reaction mixture was stirred at room temperature for 2 h. Then the solution was concentrated and the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the derivative **10** in 70% yield and the enantiomeric excess was determined to be 68% by HPLC analysis on Chiralpak OD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 15.35 min, t_{minor} = 24.34 min. $[\alpha]_D^{20}$ -71.0 (*c* = 0.60 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.29 (m, 3H), 7.24-7.22 (m, 1H), 7.20-7.15 (m, 3H), 7.12-7.06 (m, 3H), 7.04-6.96 (m, 3H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.01 (d, *J* = 15.6 Hz, 1H), 5.05-4.99 (m, 1H), 4.28-4.21 (m, 2H), 3.77 (dd, *J* = 11.6 Hz, *J* = 7.6 Hz, 1H), 2.81-2.73 (m, 1H), 2.58-2.47 (m, 2H), 2.36 (s, 3H), 2.06-1.99 (m, 1H), 1.33 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.7, 163.2, 151.3, 147.1, 144.0, 143.4, 136.7, 134.6, 130.1, 129.4, 129.3, 128.6, 128.1, 127.4, 125.3, 125.0, 124.6, 116.7, 111.4, 60.5, 53.6, 34.0, 29.8, 27.6, 21.5, 14.3 ppm; ESI HRMS: calcd. for $C_{31}H_{29}NO_6S$+H 544.1794, found 544.1785. *Its relative configuration has been established by NOE analysis.*



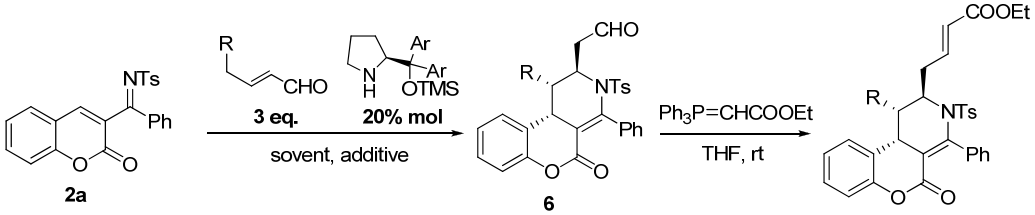
The reaction was carried out with *N*-Ts-1-aza-1,3-butadiene **2a** (40.3 mg, 0.1 mmol) and penten-2-al (25 mg, 0.3 mmol) in the presence of catalyst **1a** (6.2 mg, 20 mol %), benzoic acid (2.4 mg, 20 mol %) in dichloromethane (1.0 mL) at 25 °C for 24 h. Then the reaction mixture was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to give the adduct **6b** in 62% yield (30.2 mg) and the enantiomeric excess was determined after conversion to its derivative **11**.

The diastereomeric ratio (88:12) of the chiral product **6b** was determined by ^{1}H NMR analysis. Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s, 1H), 7.36-7.26 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.18-7.12 (m, 4H), 7.06-6.94 (m, 3H), 6.72 (d, *J* = 7.6 Hz, 1H), 5.20-5.16 (m, 1H), 3.25 (d, *J* = 10.0 Hz, 1H), 2.88-2.73 (m, 2H), 2.54-2.43 (m, 1H), 2.36 (s, 3H), 1.34 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 198.9, 163.9, 151.8, 145.6, 144.2, 136.6, 134.0, 130.1, 129.6, 129.3, 128.9, 128.5, 128.1, 127.6, 126.9, 125.6, 124.8, 124.0, 117.1, 114.7, 54.2, 40.8, 37.9, 32.1, 21.5, 18.6 ppm; ESI HRMS: calcd. for $C_{28}H_{25}NO_5S$+Na 510.1351, found 510.1324.

To the tetrahydrofuran solution of the adduct **6b** was added $Ph_3PCHCOOEt$ (41.8 mg, 0.12 mmol) in one portion, and the reaction mixture was stirred at room temperature for 2 h. Then the solution was concentrated and the crude product was purified by column chromatography

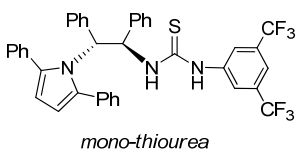
(petroleum ether/ethyl acetate = 10:1) to give the derivative **11** in 67% yield and the enantiomeric excess was determined to be 50% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{minor} = 12.38 min, t_{major} = 38.21 min. $[\alpha]_D^{20}$ -62.9 (*c* = 0.85 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.31 (m, 1H), 7.29-7.24 (m, 2H), 7.19-7.17 (m, 3H), 7.15-7.12 (m, 2H), 7.04-6.99 (m, 3H), 6.97-6.95 (m, 2H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.01 (d, *J* = 15.6 Hz, 1H), 4.72-4.67 (m, 1H), 4.31-4.18 (m, 2H), 3.30 (d, *J* = 10.4 Hz, 1H), 2.64-2.48 (m, 3H), 2.36 (s, 3H), 1.40 (d, *J* = 6.4 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.7, 164.1, 151.9, 145.7, 144.7, 144.0, 136.6, 134.1, 130.3, 129.5, 129.3, 129.1, 128.4, 128.1, 127.5, 127.4, 125.8, 124.8, 124.7, 124.0, 117.1, 114.4, 60.4, 59.4, 37.8, 32.6, 28.9, 21.5, 18.7, 14.3 ppm; ESI HRMS: calcd. for $C_{32}H_{31}NO_6S$+Na 580.1770, found 580.1789. *Its relative configuration has been established by NOE analysis.*

We have explored more reaction conditions in order to improve the enantioselectivity. The results were summarized in the following table. However, we could not obtain satisfying data yet. The stereocontrol in ADAR via dienamine catalysis still needs more investigation.

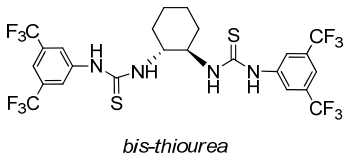


entry	R	catalyst	solvent	additive	T	yield[a] (%)	dr	ee[b] (%)
1	H	**1a**	THF	BzOH	rt	90	>99:1	51
2	H	**1c**	THF	BzOH	rt	<10	>99:1	/
3	H	**1f**	THF	BzOH	rt	70	>99:1	40
4	Me	**1a**	THF	BzOH	rt	64	85:15	43
5	Me	**1a**	DMSO	BzOH	rt	70	80:20	20
6	Me	**1a**	dioxane	BzOH	rt	68	89:11	29
7	Me	**1a**	THF	BzOH	0 °C	<10	/	/
8	Me	**1f**	THF	BzOH	rt	<10	/	/
9	Me	**1a**	DCM	BzOH	rt	62	88:12	50
10	Me	**1a**	DCM	*mono-thiourea*	rt	72	92:8	39
11	Me	**1a**	DCM	*bis-thiourea*	rt	66	93:7	37
12	Me	**1f**	DCM	*mono-thiourea*	rt	<10	/	/
13	Me	**1a**	DCM	*mono-thiourea*	0 °C	<10	/	/
14	Me	**1a**	DCM	*VANOL-Acid*	rt	70	90:10	38
15	Me	**1a(*R*)**	DCM	*VANOL-acid*	rt	62	85:15	-52

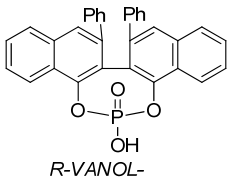
[a] Isolated yield of product **6.** [b] The ee value was determined after conversion to the α,β-unsaturated ester**.**



mono-thiourea

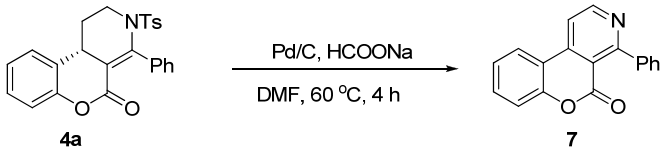


bis-thiourea



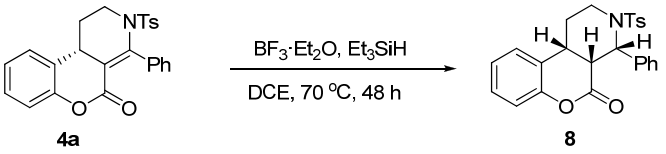
R-VANOL-phosphoric acid

5. Synthetic transformation of product 4a



4a **7**

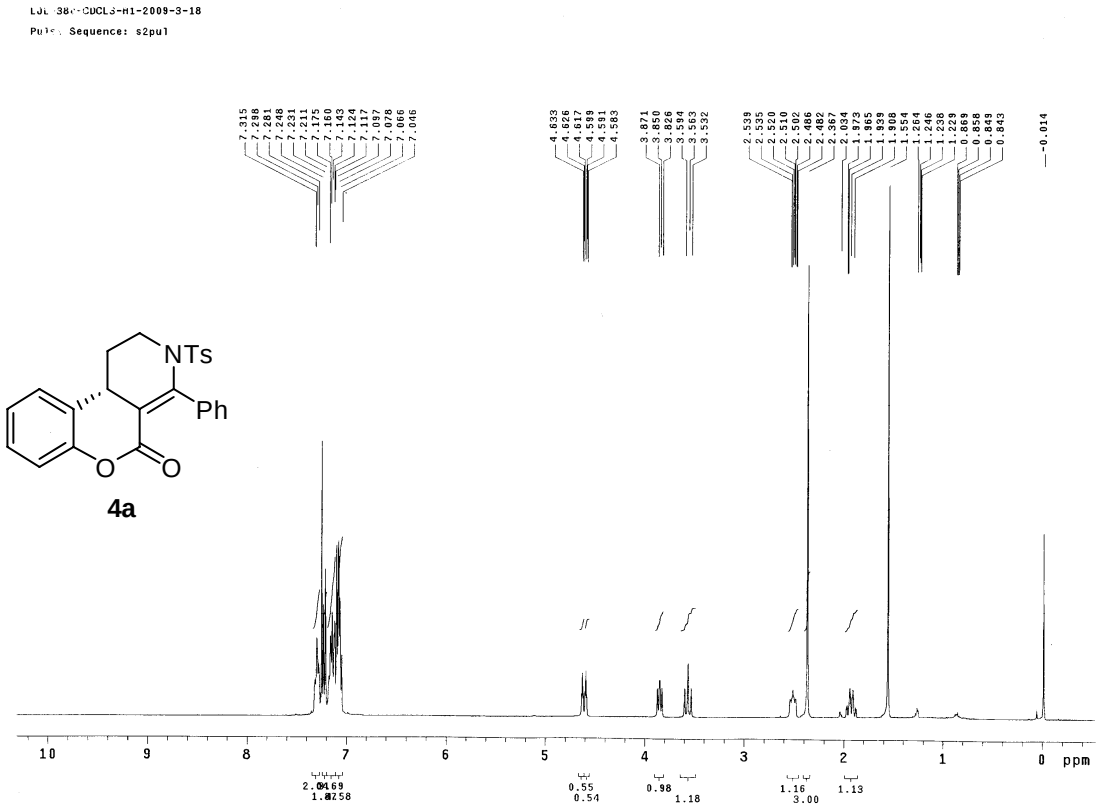
To a DMF solution of the product **4a** (30 mg, 0.07 mmol) was added Pd/C (9 mg) and sodium formate (23 mg, 0.35 mmol) at room temperature. The mixture was stirred at 60 °C for 4 h. Then the reaction was quenched with water and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to afford product **7** in 79% yield (15 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.96 (d, *J* = 5.6 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 5.2 Hz, 1H), 7.64-7.59 (m, 1H), 7.57-7.54 (m, 2H), 7.49-7.47 (m, 3H), 7.43-7.38 (m, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 164.5, 152.8, 152.4, 143.6, 140.6, 132.9, 128.9, 128.7, 128.0, 124.7, 123.8, 117.8, 116.2, 114.1 ppm; ESI HRMS: calcd. for $C_{18}H_{11}NO_2$+Na 296.0687, found 296.0699.

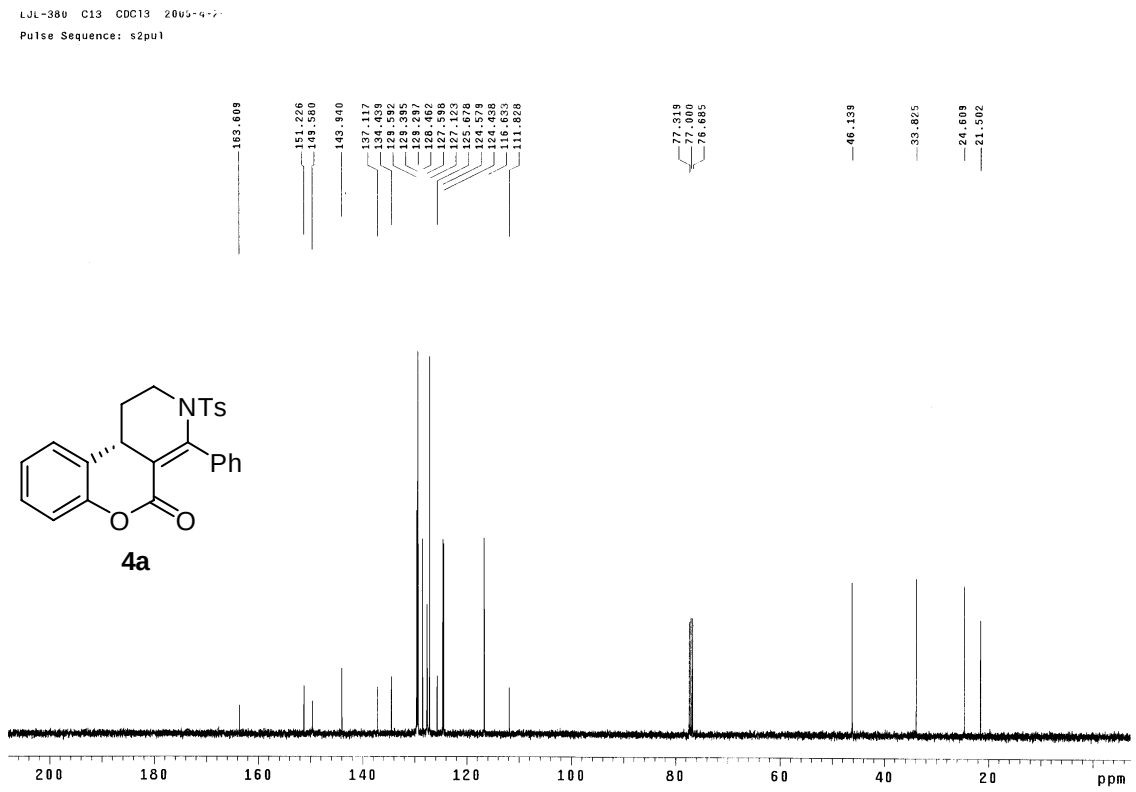


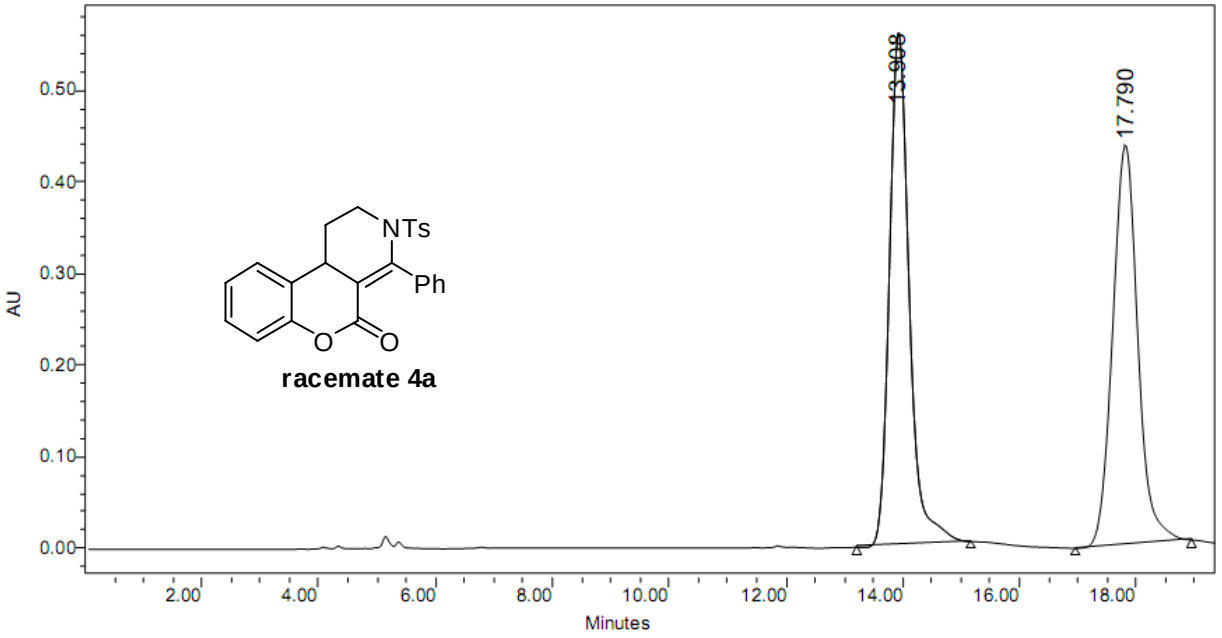
4a **8**

To a dichloroethane solution of the product **4a** (30 mg, 0.07 mmol) was added triethyl silane (16.2 mg, 0.14 mmol) and $BF_3.Et_2O$ (17 μL, 0.14 mmol) under the protection of argon atmosphere at room temperature. Then, the reaction was carried out at 70 °C for 24 h, and the same amount of triethyl silane and $BF_3 \cdot Et_2O$ were added again and the mixture was stirred at 70 °C for additional 24 h. The reaction was quenched with aqueous $NaHCO_3$, extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford chiral piperidine derivative **8** in 48% yield (14.5 mg) and the enantiomeric excess was determined to be 95% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{minor} = 13.67 min, t_{major} = 19.14 min. $[\alpha]_D^{20}$ -148.4 (*c* = 0.45 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.0 Hz, 2H), 7.30-7.28 (m, 3H), 7.26-7.21 (m, 3H), 7.19-7.12 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.54 (d, *J* = 7.2 Hz, 1H), 3.73-3.70 (m, 2H), 2.86-2.80 (m, 2H), 2.73-2.67 (m, 1H), 2.37 (s, 3H), 1.79-1.73 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.5, 150.6, 143.3, 139.9, 136.9, 129.6, 128.7, 128.3, 127.7, 127.6, 127.2, 126.3, 124.9, 124.7, 116.7, 57.3, 46.9, 40.9, 31.9, 26.0, 21.5 ppm; ESI HRMS: calcd. for $C_{25}H_{23}NO_4S$+Na 456.1245, found 456.1246. *Its relative configuration has been established by NOE analysis.*

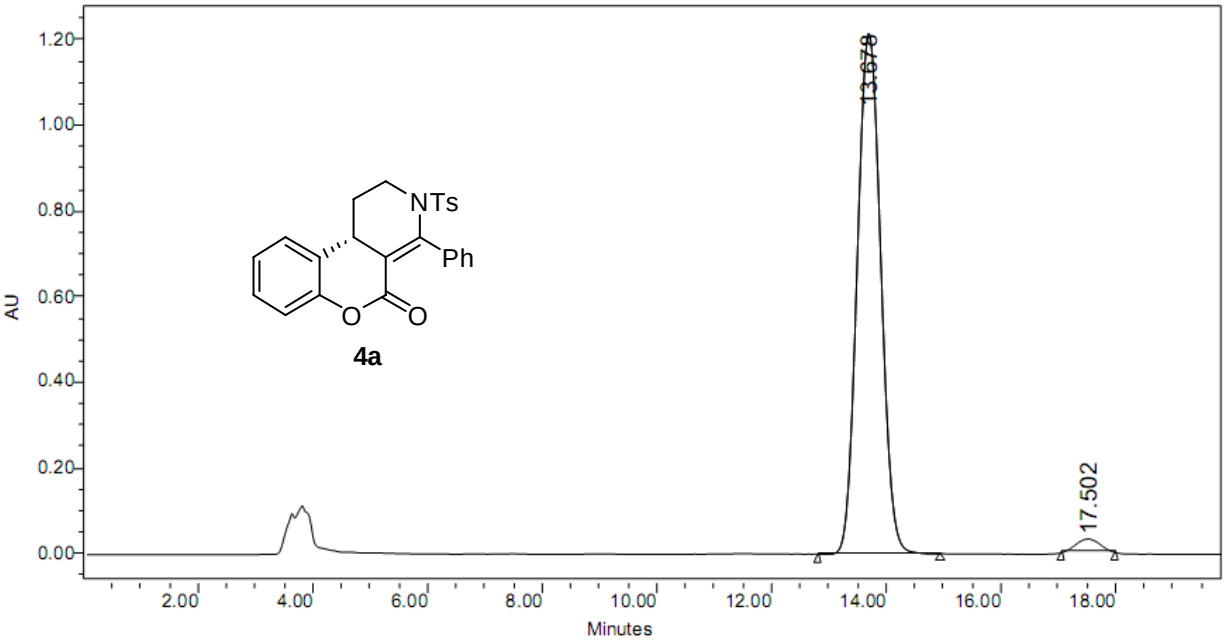
6. NMR spectra and HPLC chromatograms







	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.908	13179015	50.24	560436	56.21
2	17.790	13050765	49.76	436615	43.79



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
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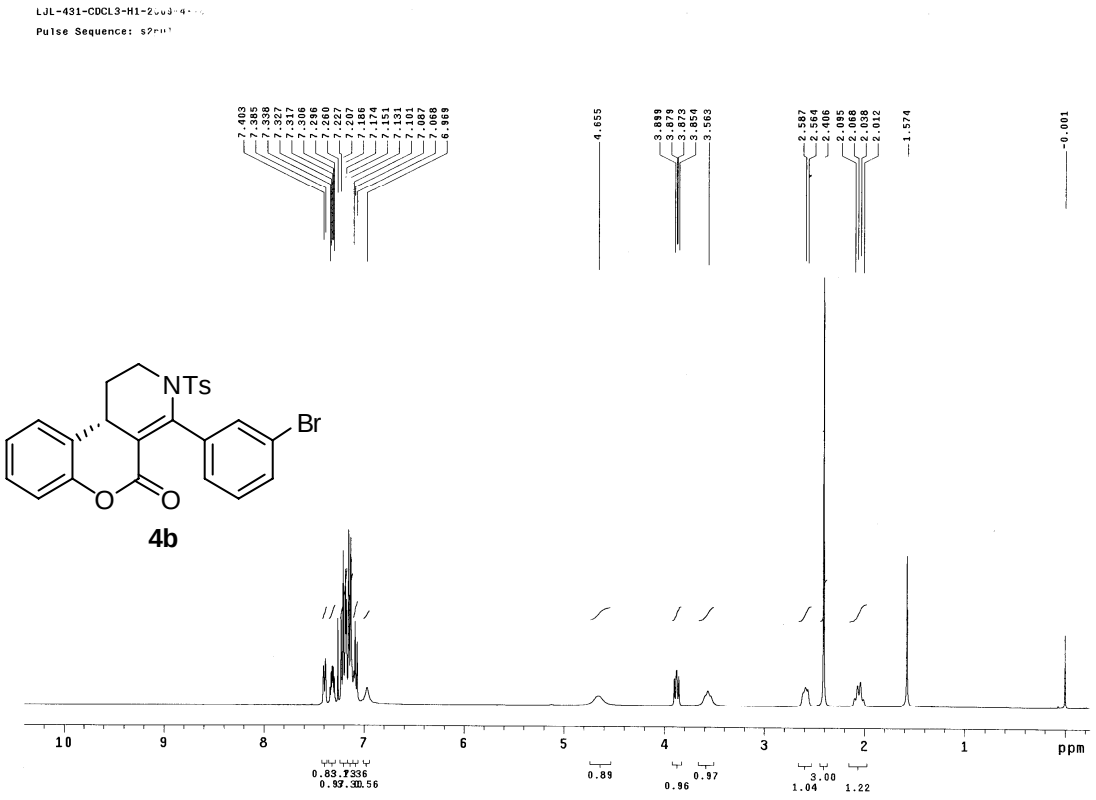
2	17.502	933246	2.63	31866	2.56


Pulse Sequence: s2pul
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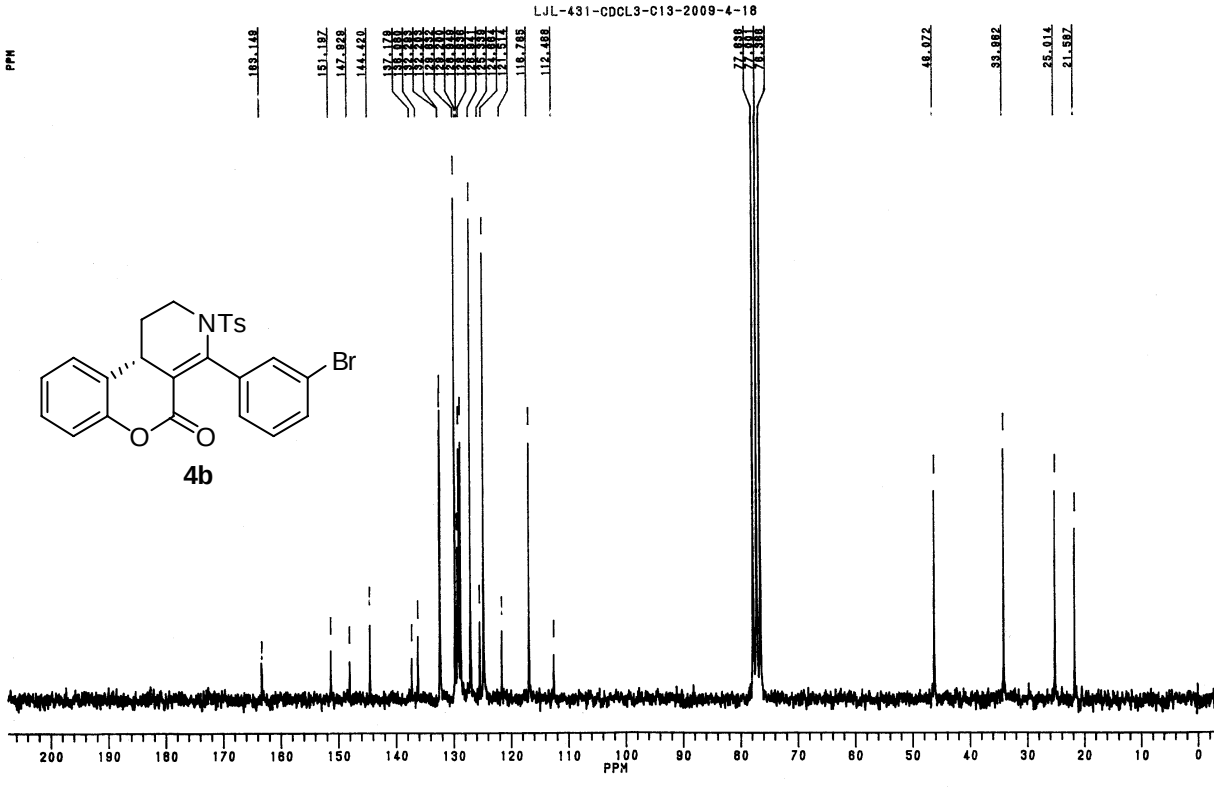
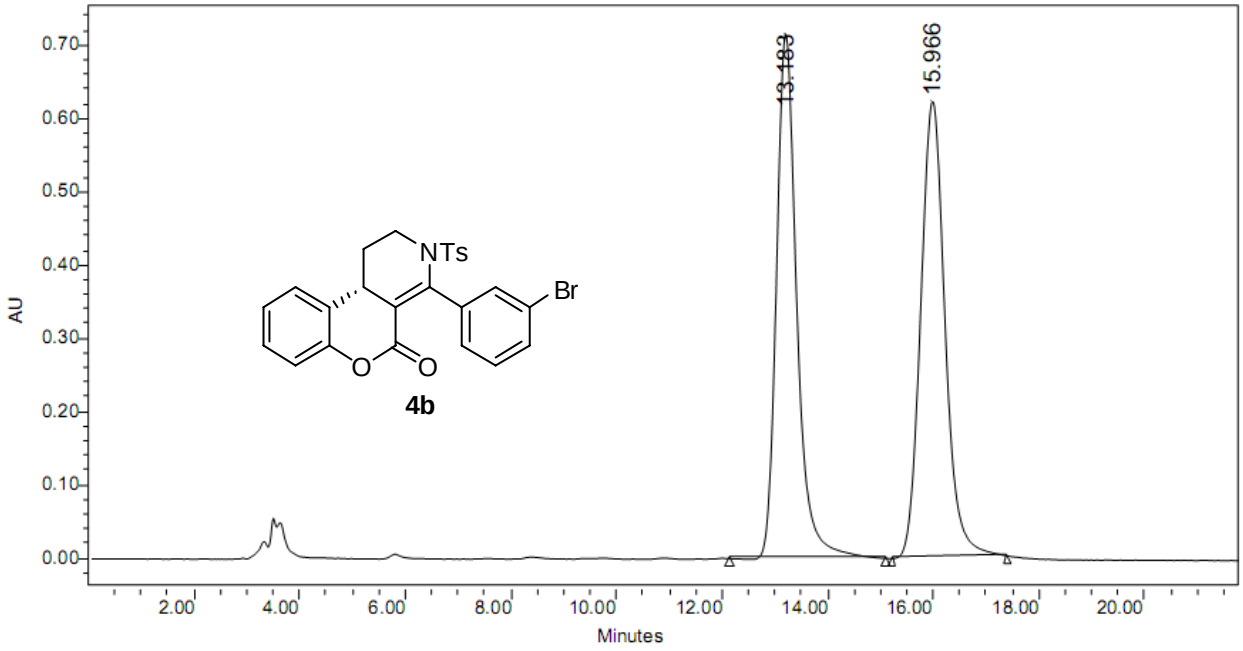
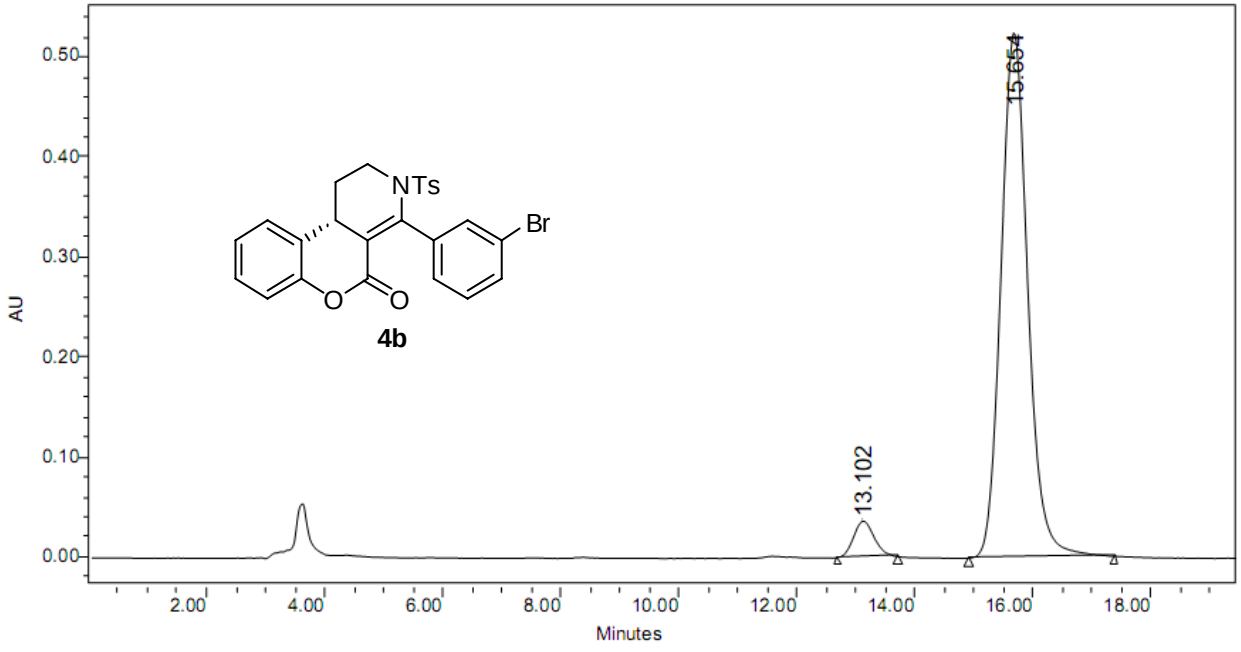
7.385
7.338
7.327
7.317
7.306
7.298
7.260
7.227
7.207
7.186
7.174
7.151
7.131
7.101
7.087
7.068
6.969
4.655
3.899
3.879
3.873
3.854
3.563
2.587
2.564
2.406
2.095
2.068
2.038
2.012
1.574
0.001
NTs
Br
O
O
4b
10
9
8
7
6
5
4
3
2
1
ppm
0.83
7.33
0.97
3.00
0.56
0.89
0.96
0.97
3.00
1.04
1.22

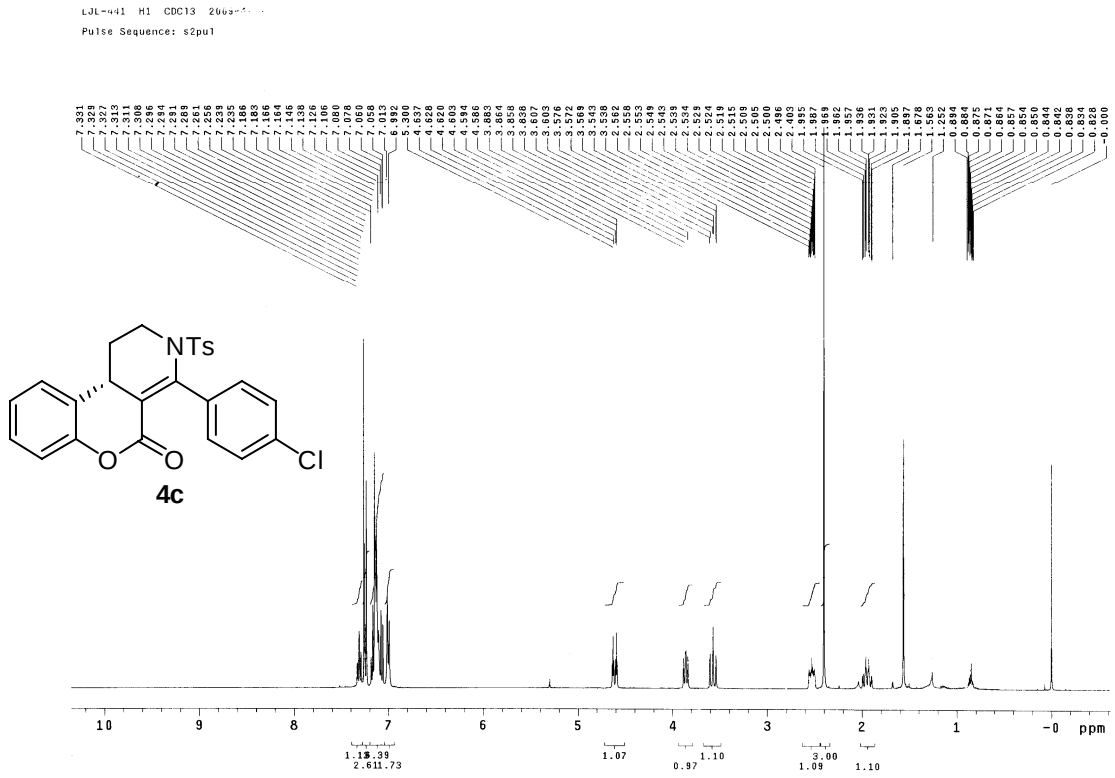

LJL-431-CDCL3-C13-2009-4-18
PPM
183.149
151.197
147.928
144.420
118.785
112.488
49.072
33.982
25.014
21.582
NTs
Br
O
O
4b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PPM

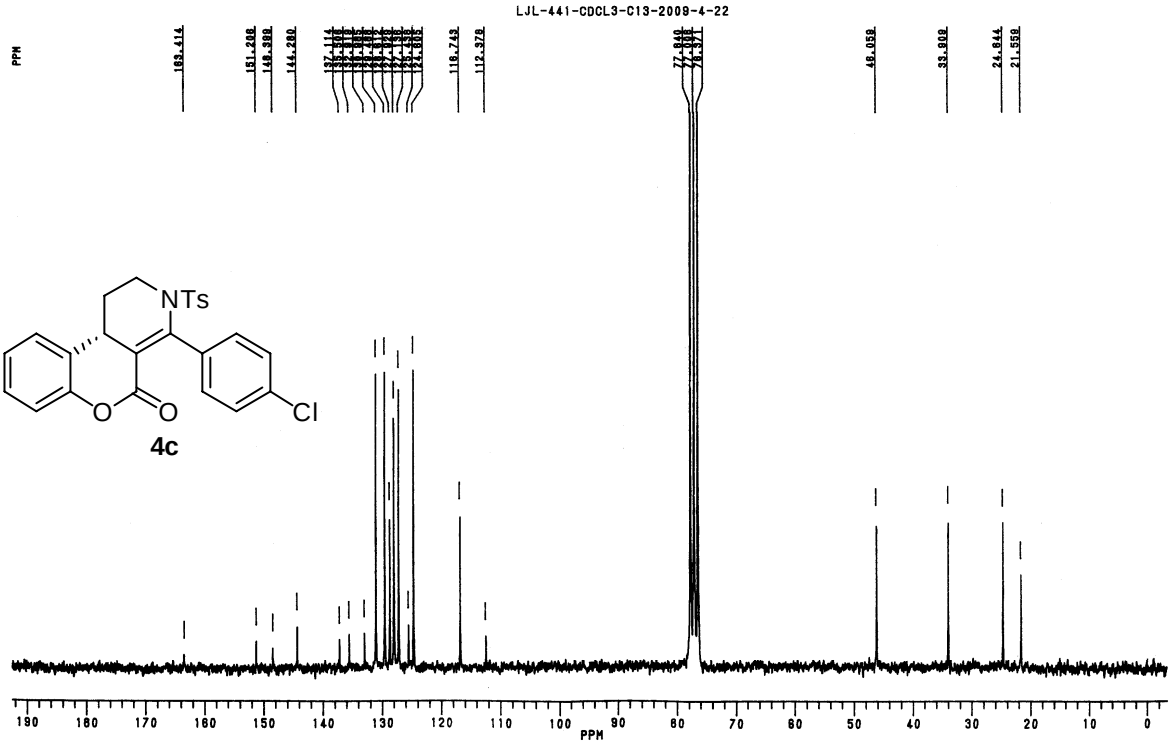


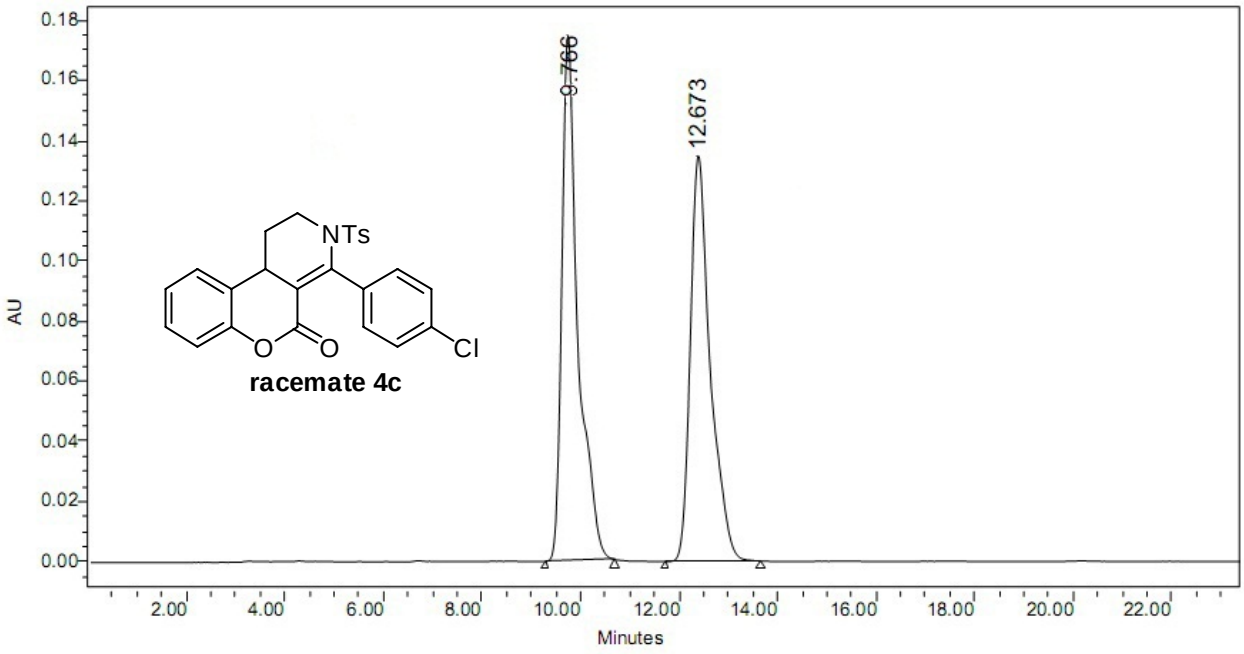
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.183	19202964	49.03	716465	53.49
2	15.966	19961595	50.97	623032	46.51



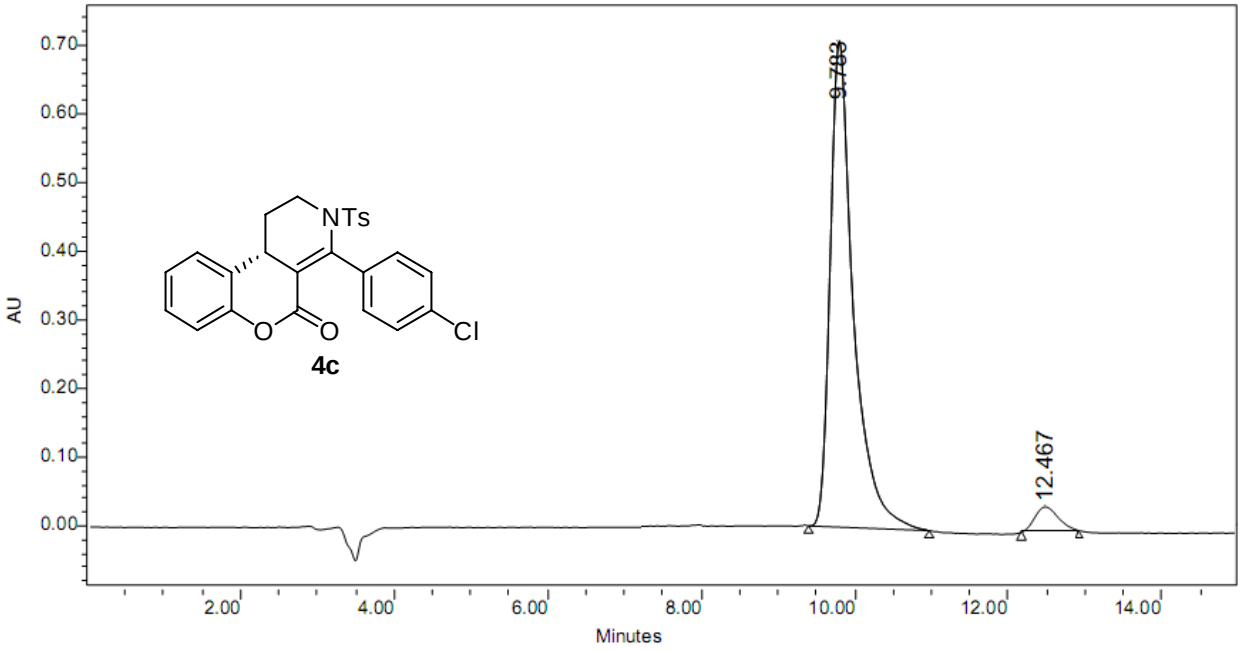
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.102	656147	3.81	31303	5.63
2	15.654	16552325	96.19	524616	94.37


Pulse Sequence: s2pul
NTs
O
O
Cl
4c
ppm

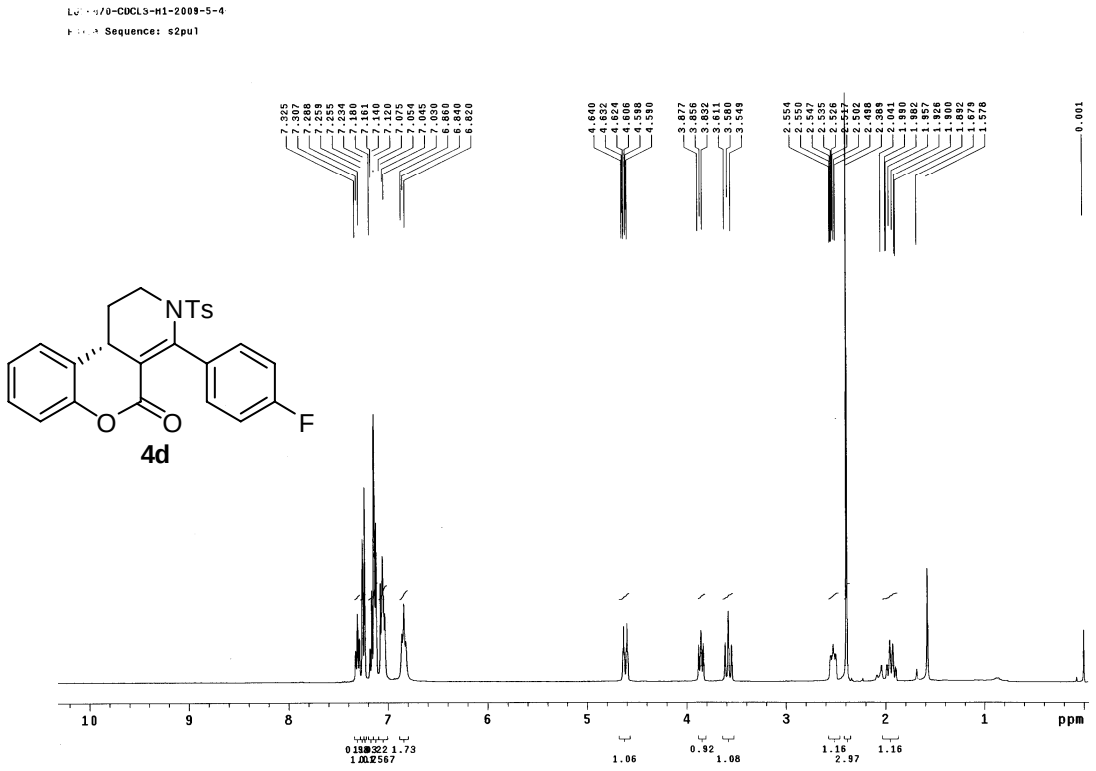

LJL-441-CDCL3-C13-2009-4-22
PPM
NTs
O
O
Cl
4c

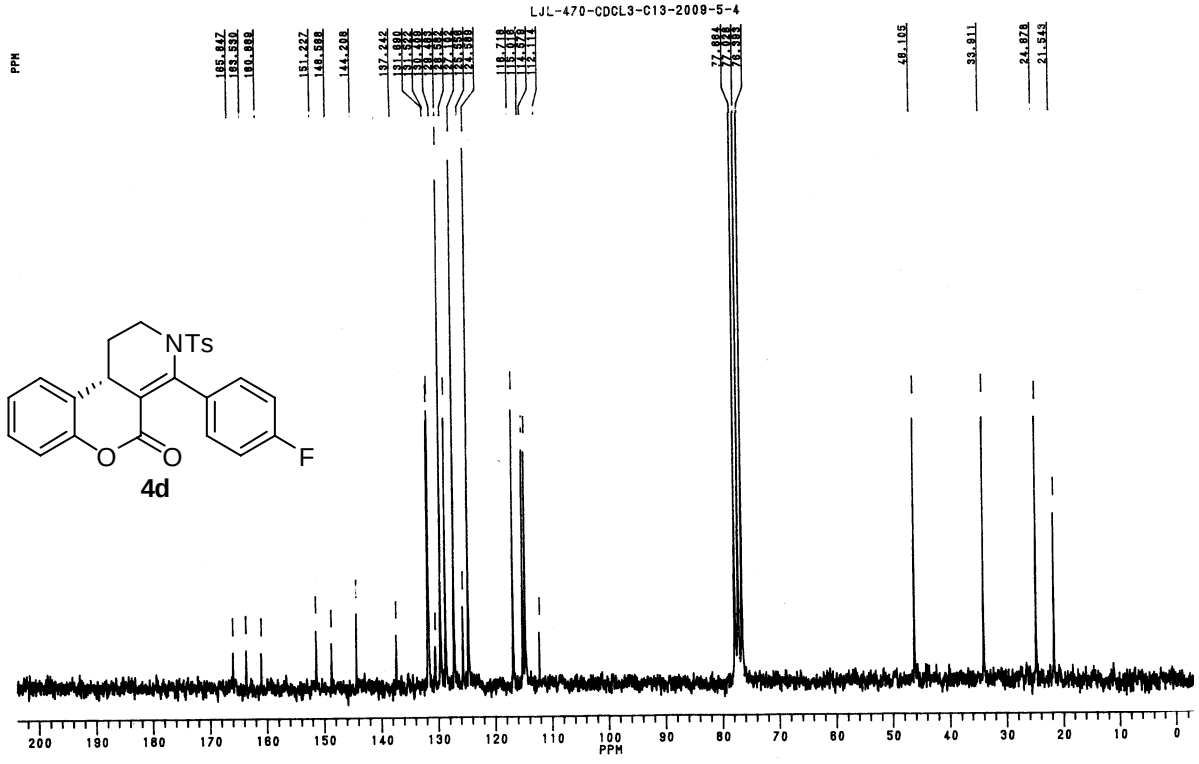


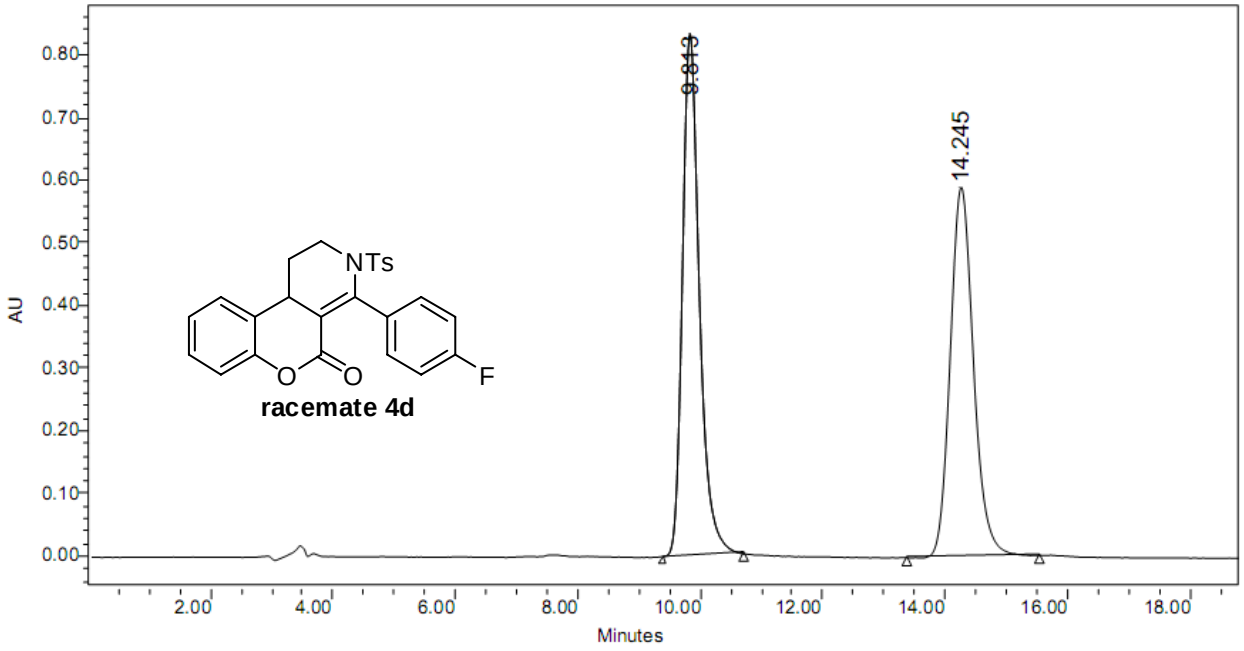
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.766	3970212	51.15	174860	56.43
2	12.673	3791426	48.85	135009	43.57



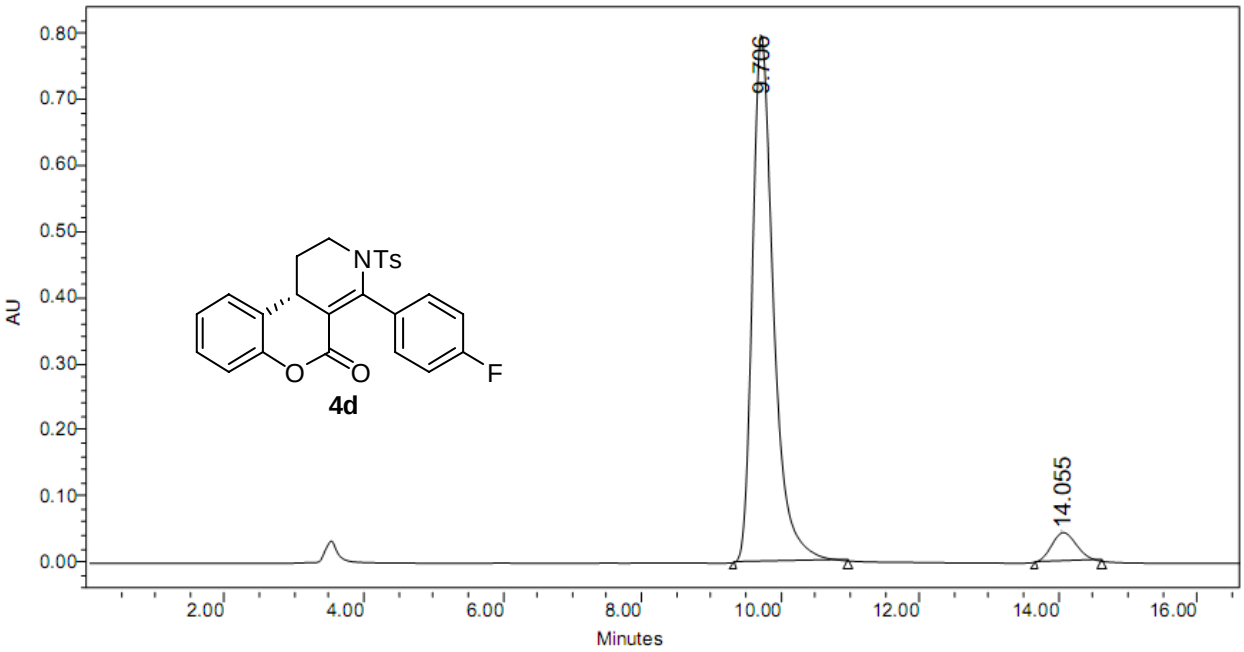
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.783	14926935	95.15	708414	95.21
2	12.467	760237	4.85	35644	4.79


Sequence: s2pul
NTs
O
O
F
4d
ppm
1.06
0.92
1.08
1.16
2.97
1.16

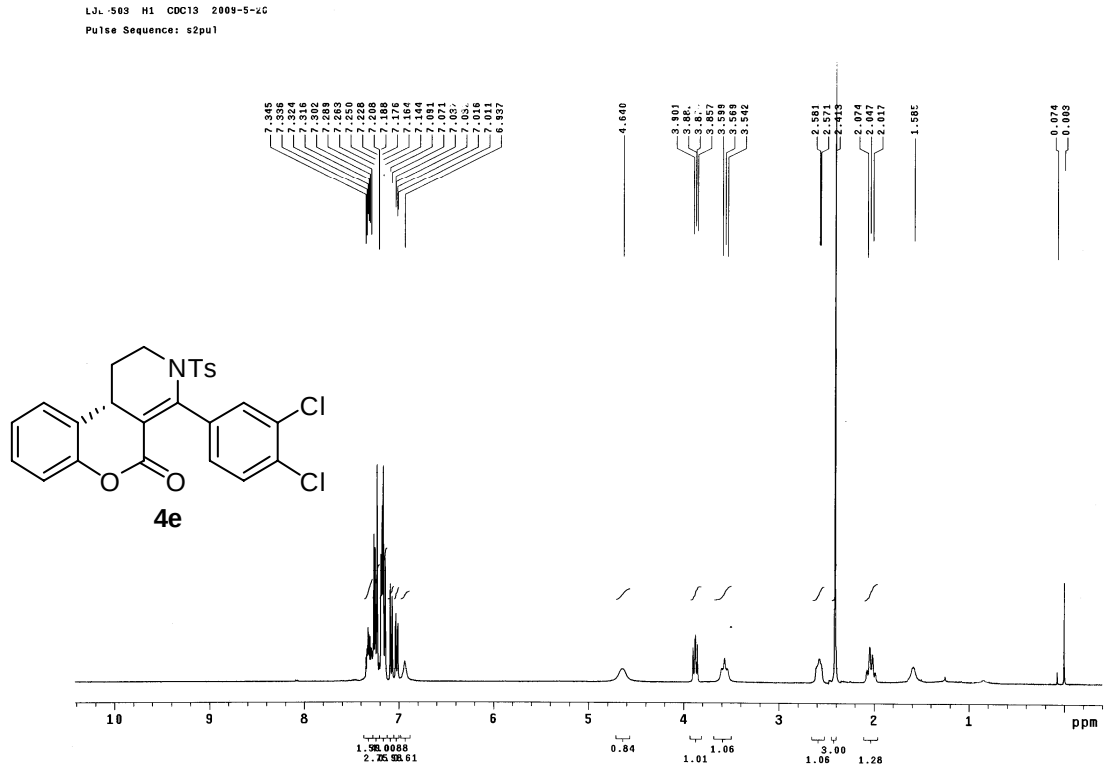

LJL-470-CDCL3-C13-2009-5-4
PPM
NTs
O
O
F
4d
PPM

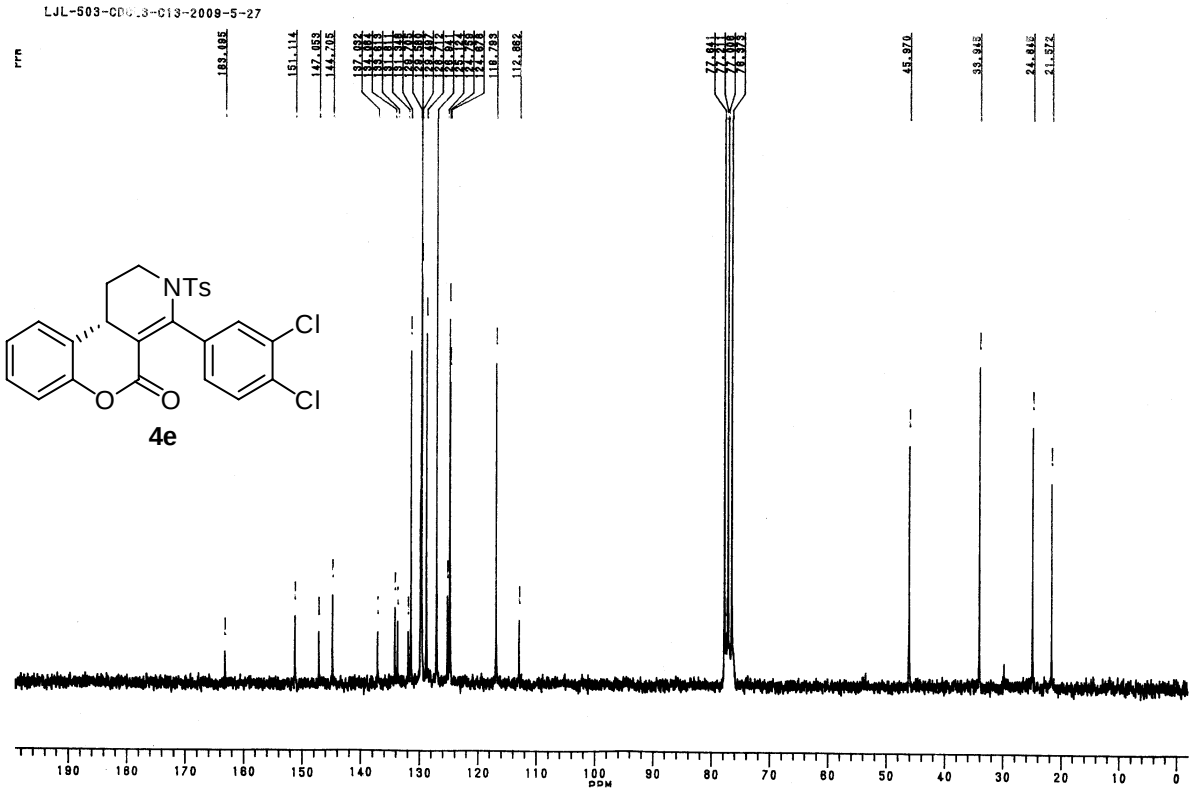


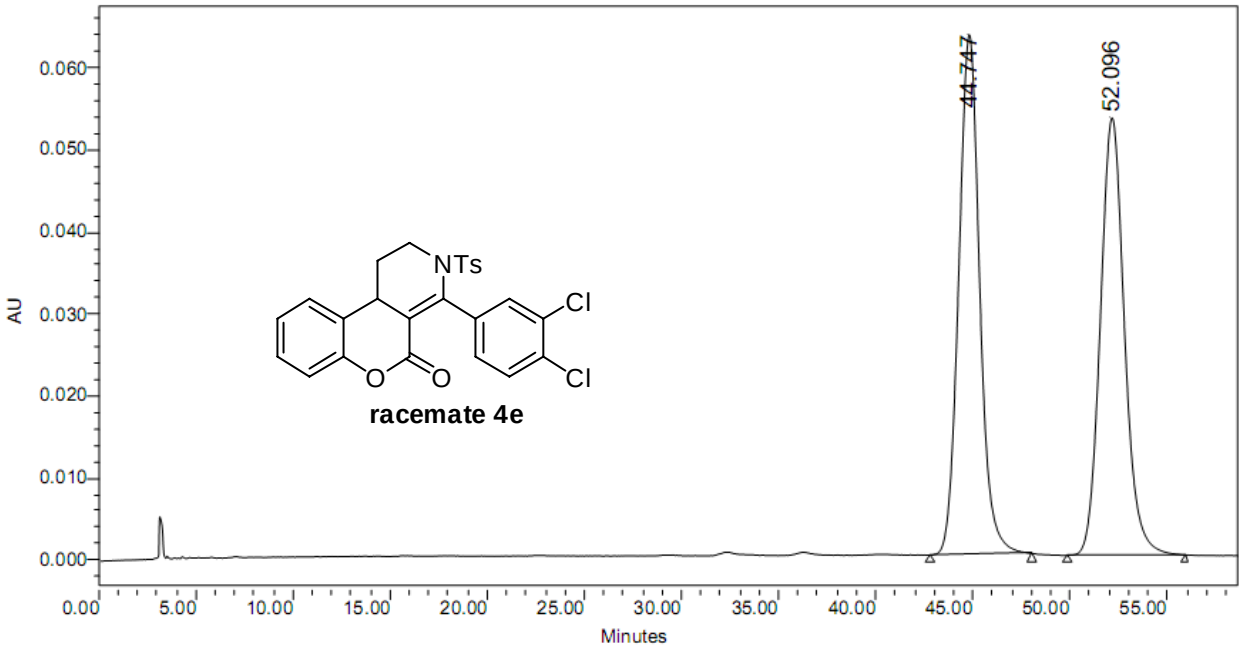
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.813	16039161	50.61	833282	58.53
2	14.245	15655168	49.39	590317	41.47



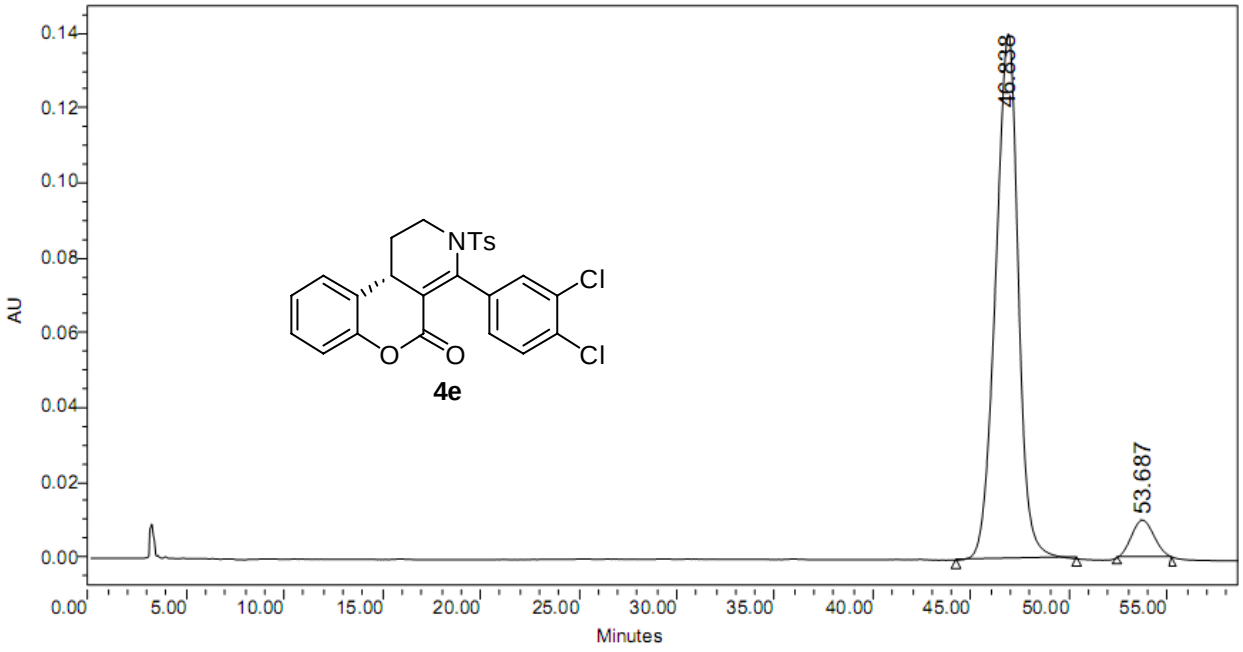
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.706	16855357	94.34	797790	94.98
2	14.055	1011868	5.66	42160	5.02


Pulse Sequence: s2pul
NTs
Cl
Cl
O
O
4e
ppm

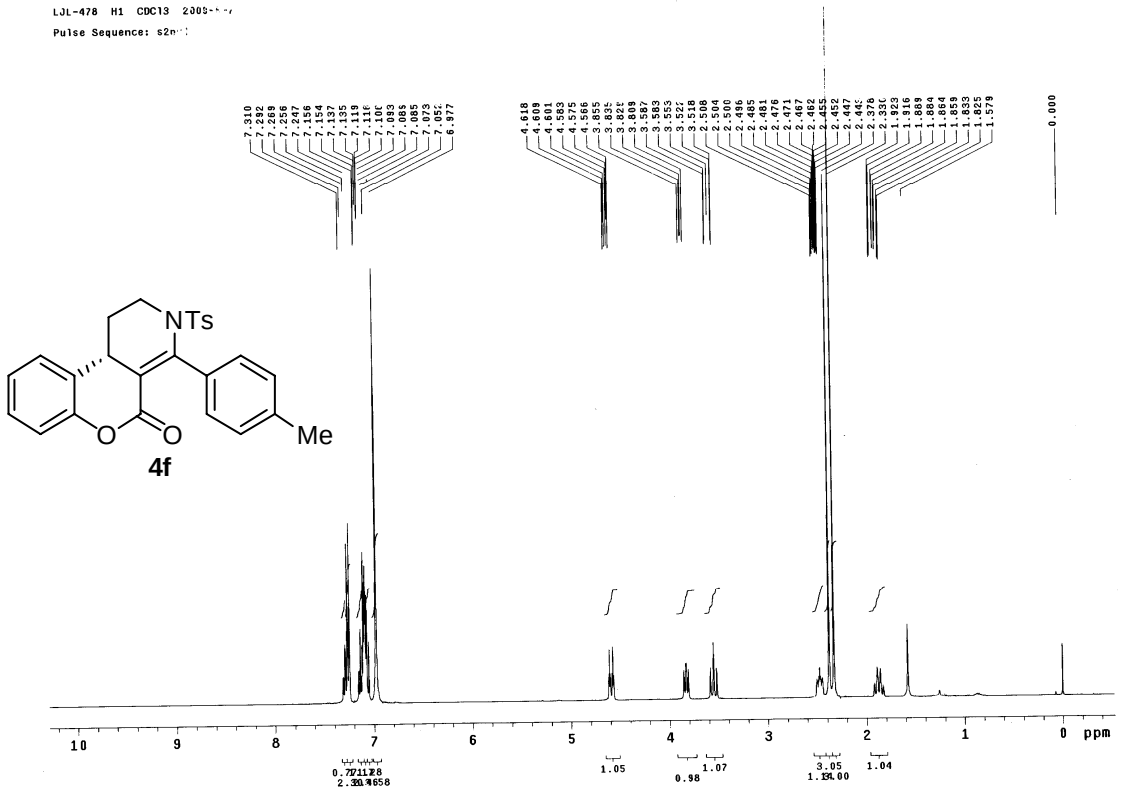

NTs
Cl
Cl
O
O
4e
ppm

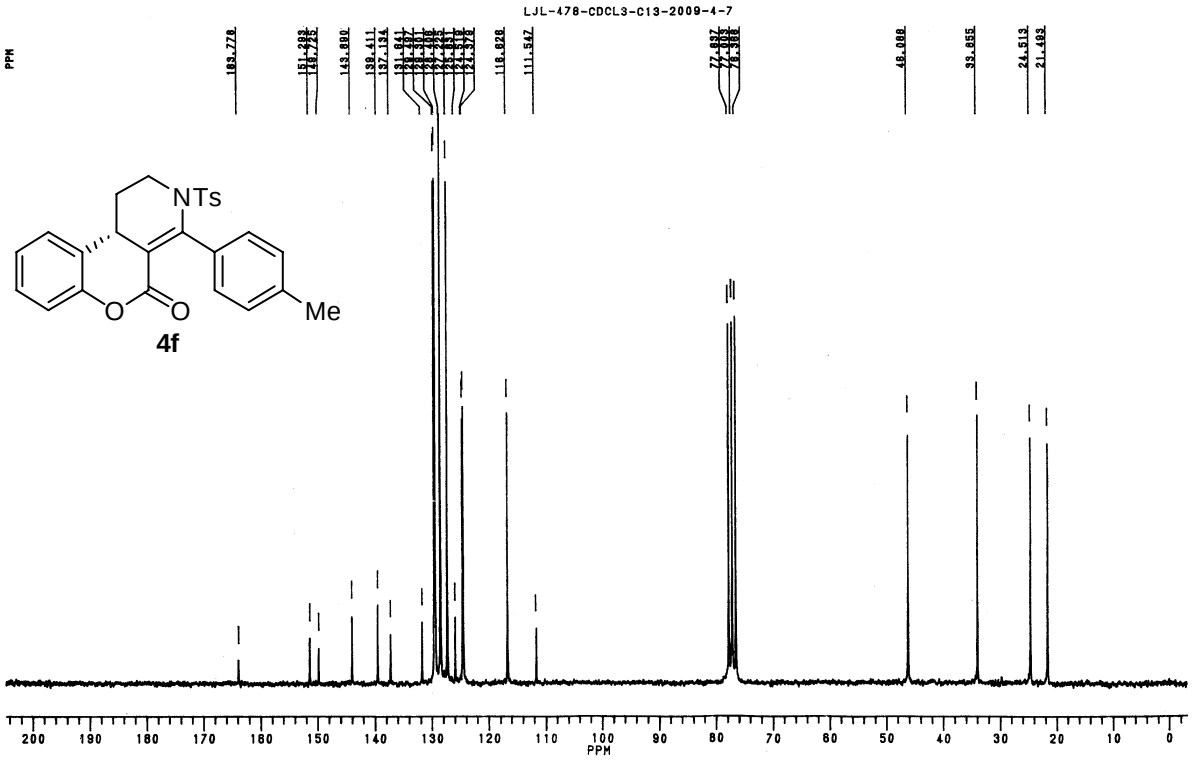


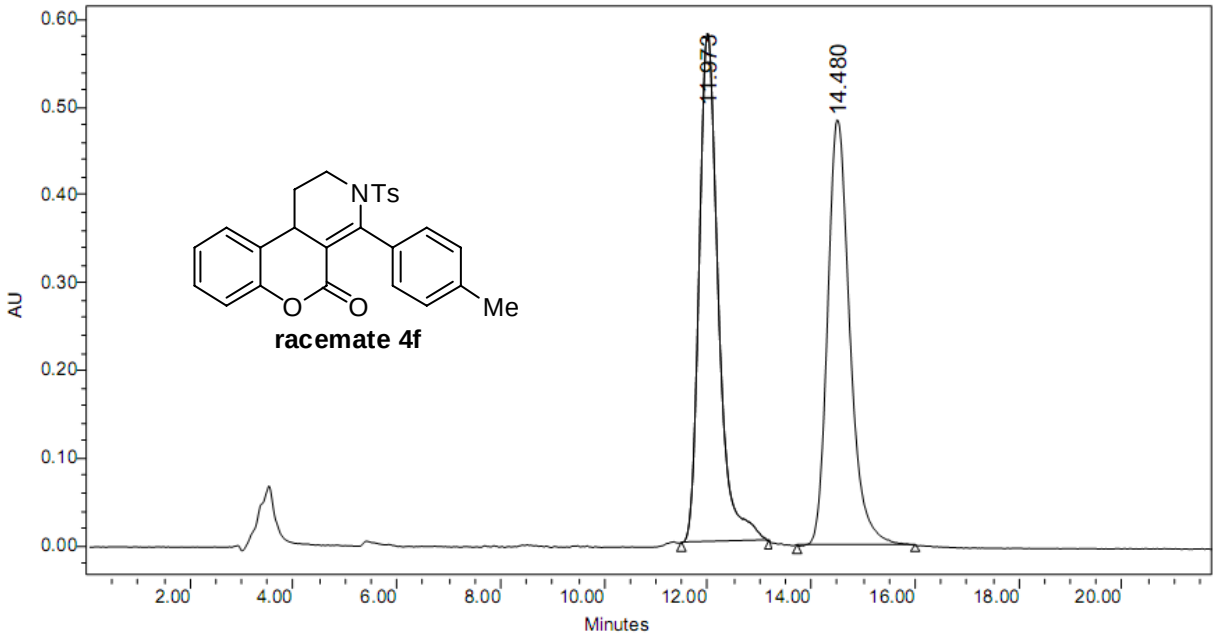
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	44.747	4749758	50.88	63401	54.31
2	52.096	4585583	49.12	53334	45.69



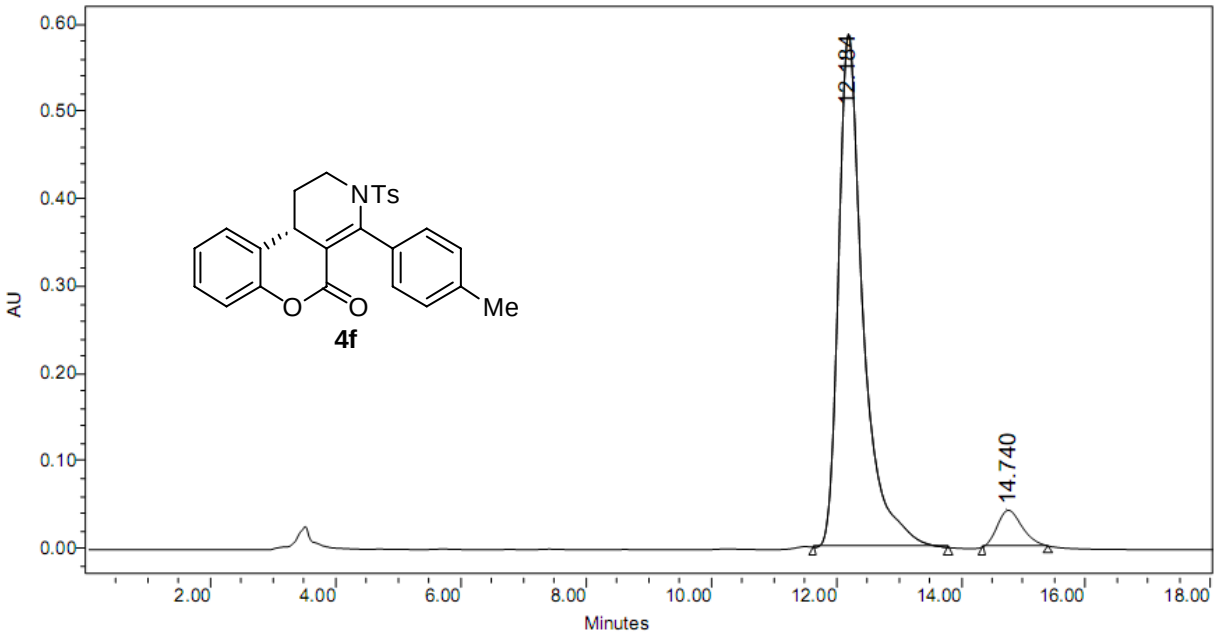
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	46.838	11315497	93.45	140465	93.40
2	53.687	793684	6.55	9920	6.60


LJL-478 H1 CDCl3
Pulse Sequence:
NTs
O
O
Me
4f
ppm
1.05
1.07
0.98
3.05
1.04

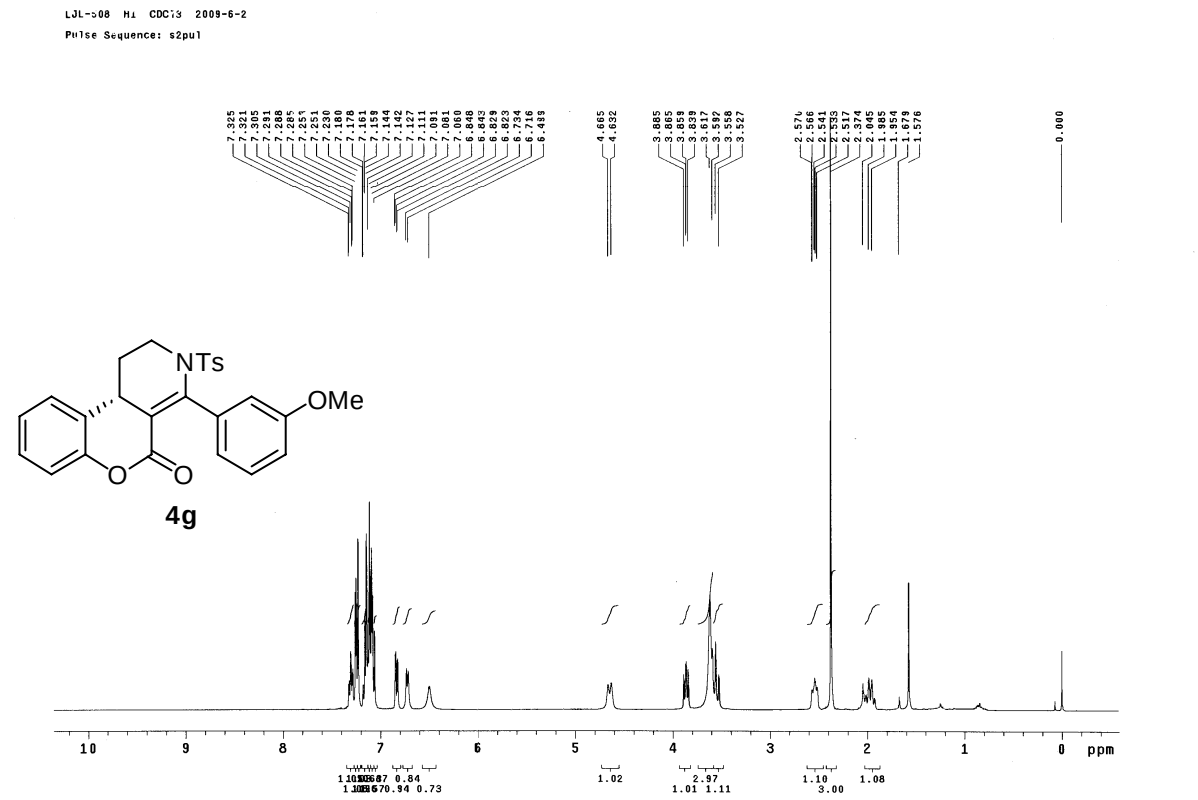

LJL-478-CDCL3-C13-2009-4-7
PPM
NTs
O
O
Me
4f

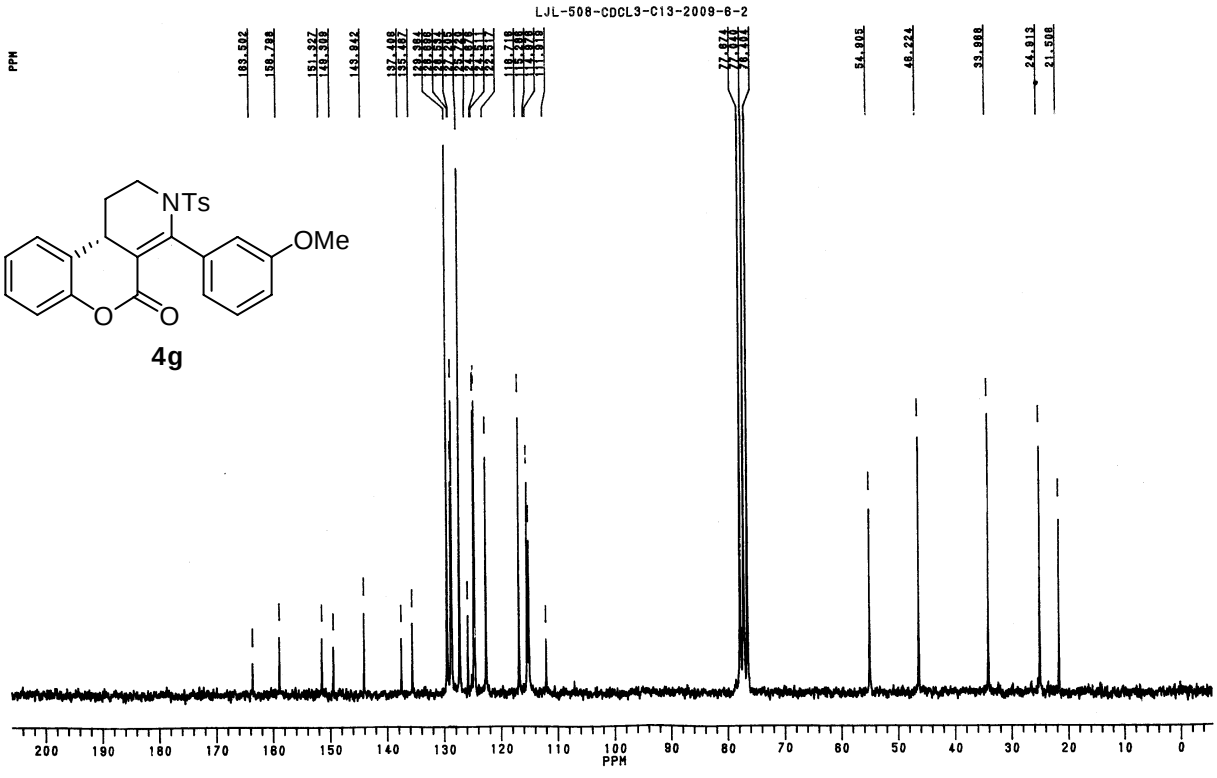


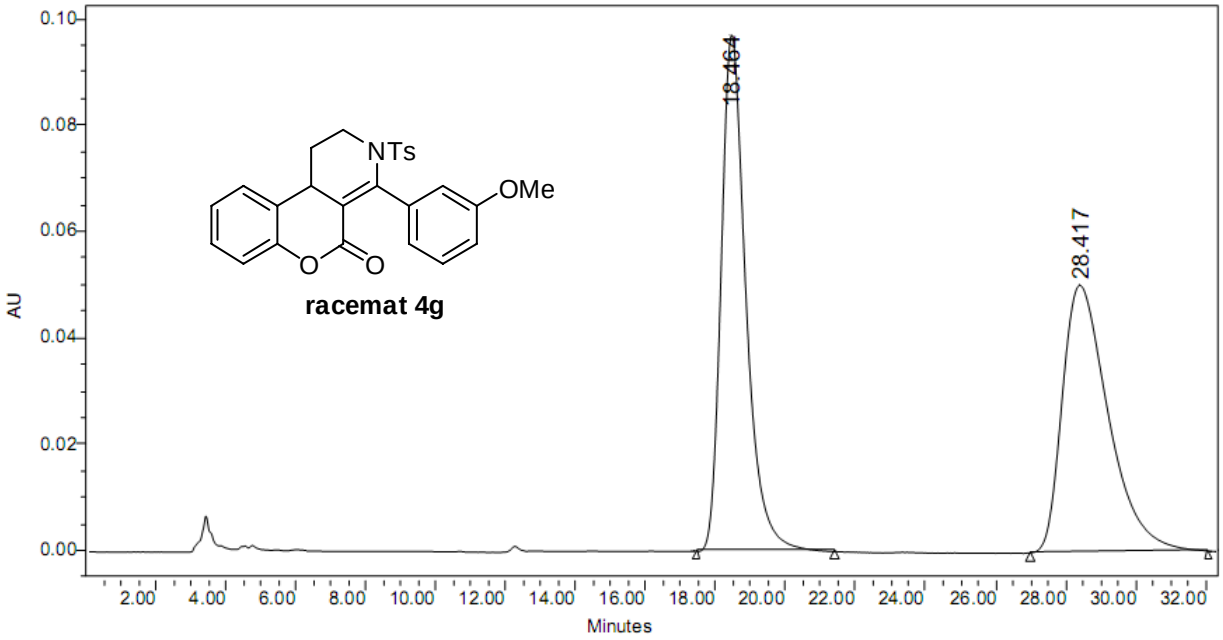
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.973	14969489	50.81	580902	54.50
2	14.480	14490042	49.19	484911	45.50



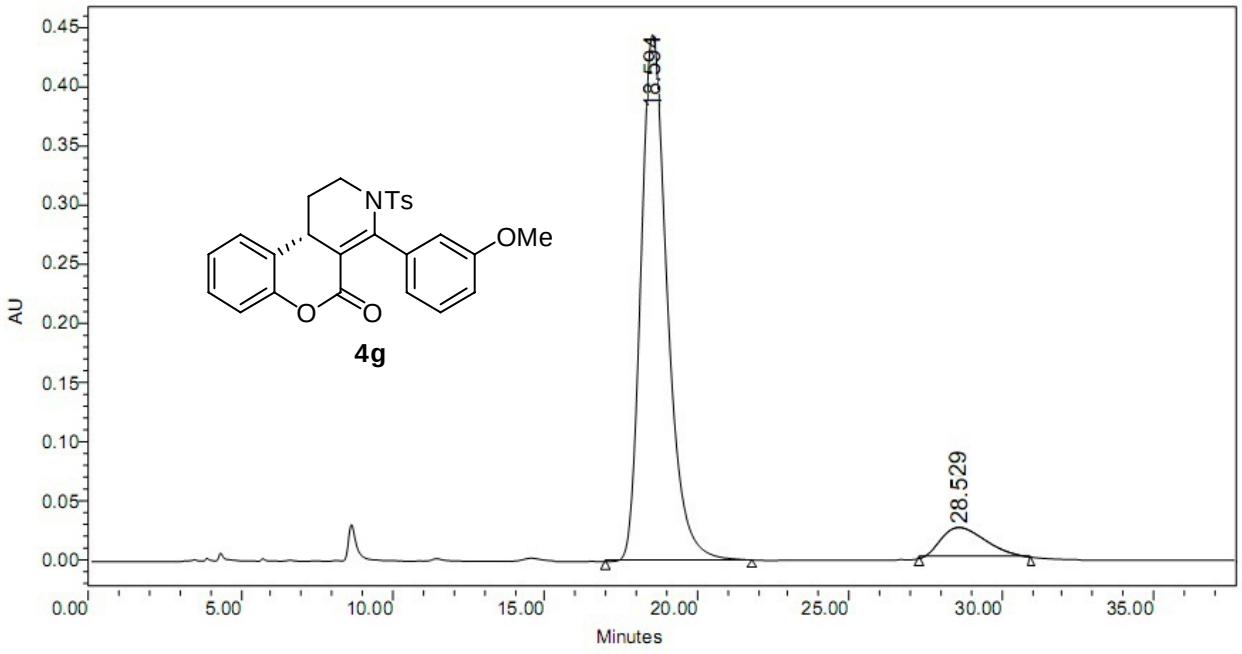
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.184	16151911	93.93	587189	93.65
2	14.740	1042888	6.07	39815	6.35


LJL-508 H1 CDCl3 2009-6-2
Pulse Sequence: s2pul
NTs
OMe
O
O
4g
ppm

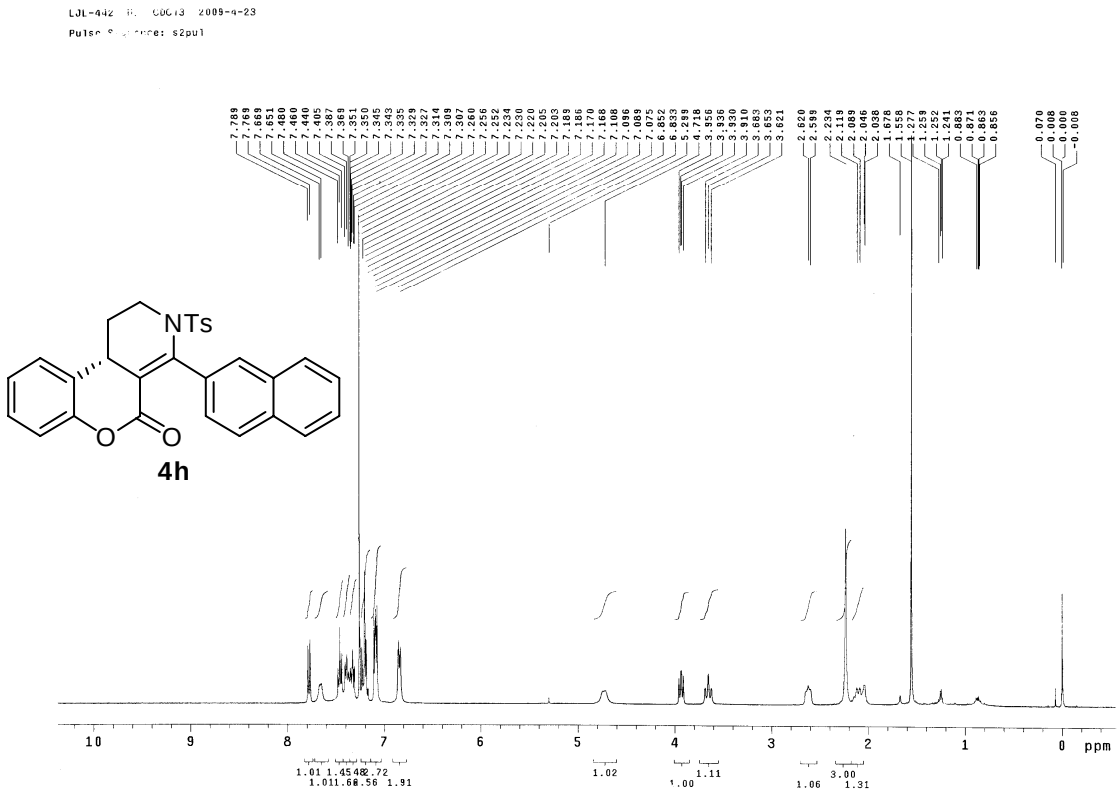

LJL-508-CDCL3-C13-2009-6-2
PPM
NTs
OMe
O
O
4g
PPM

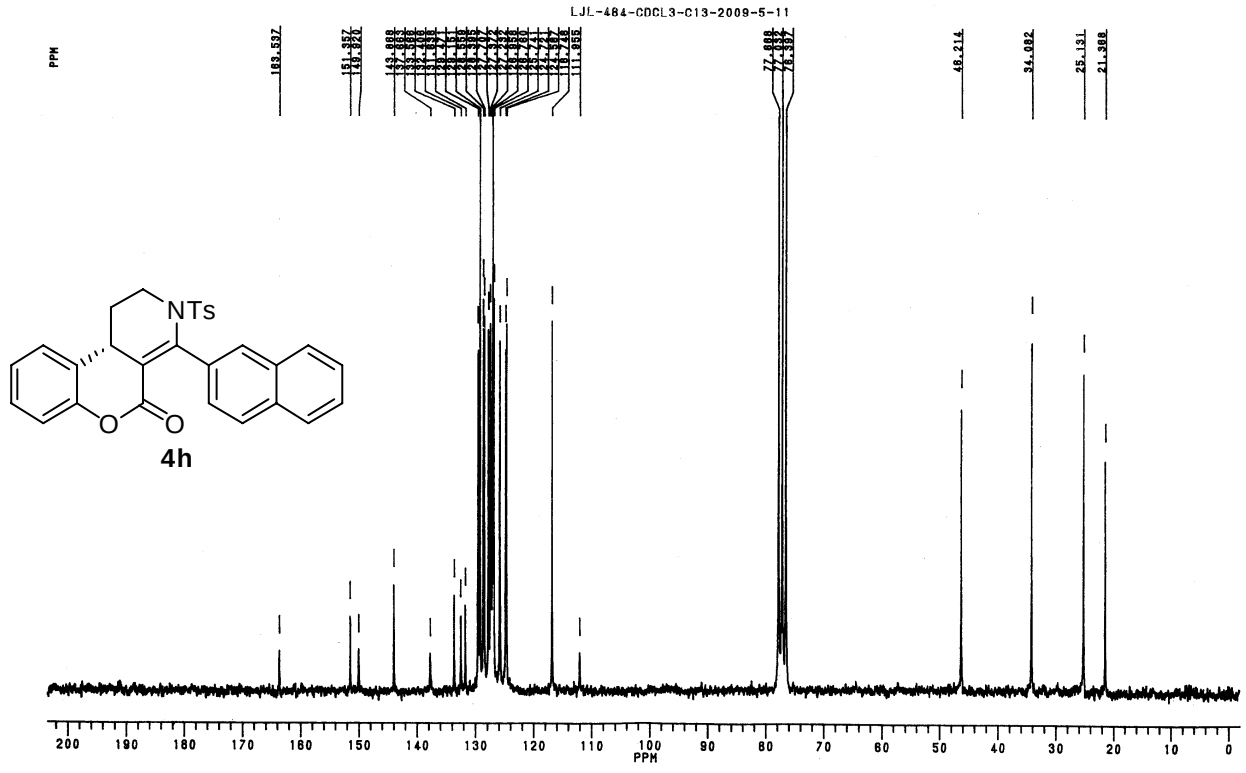


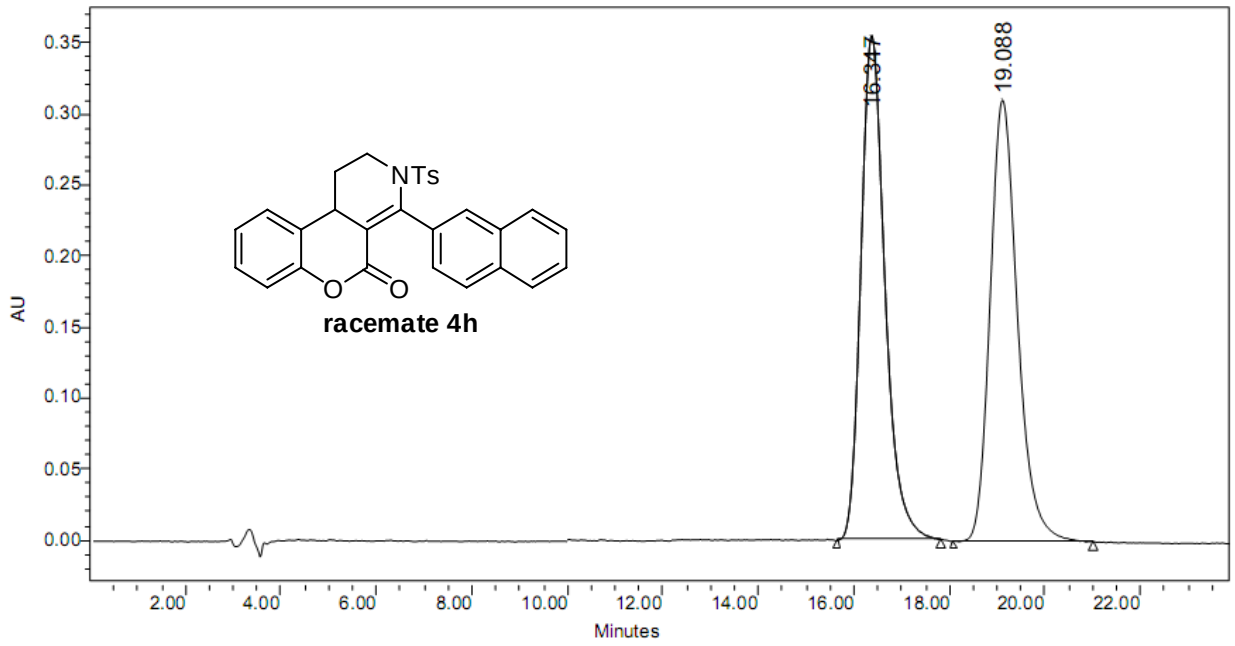
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	18.464	4782083	50.96	97088	65.91
2	28.417	4601445	49.04	50215	34.09



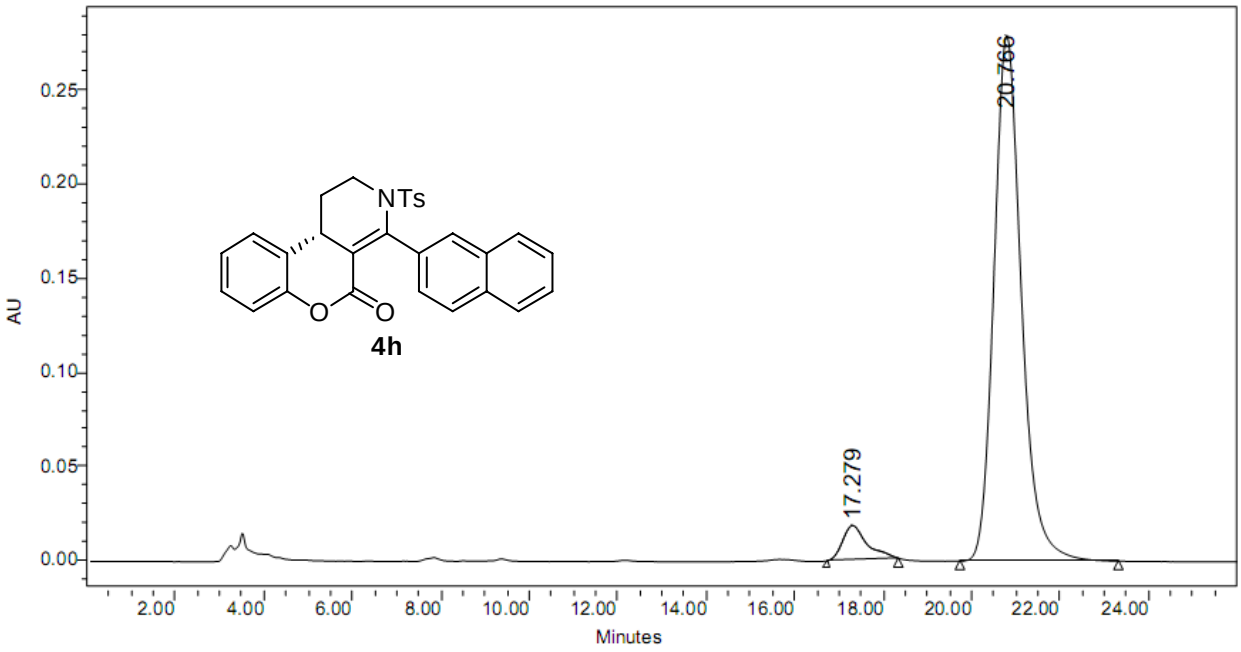
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	18.594	26727969	92.03	444313	94.91
2	28.529	2313727	7.97	23847	5.09


NTs
O
O
4h
ppm

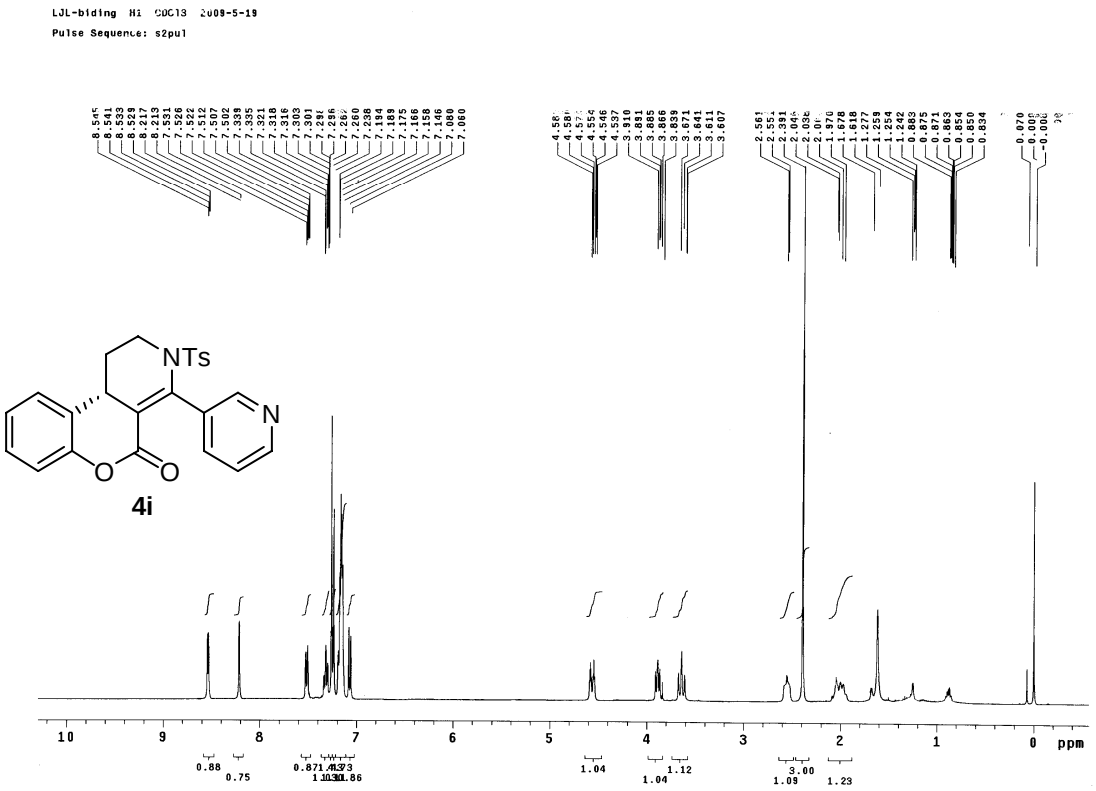

LJL-484-CDCL3-C13-2009-5-11
PPM
NTs
O
O
4h
PPM

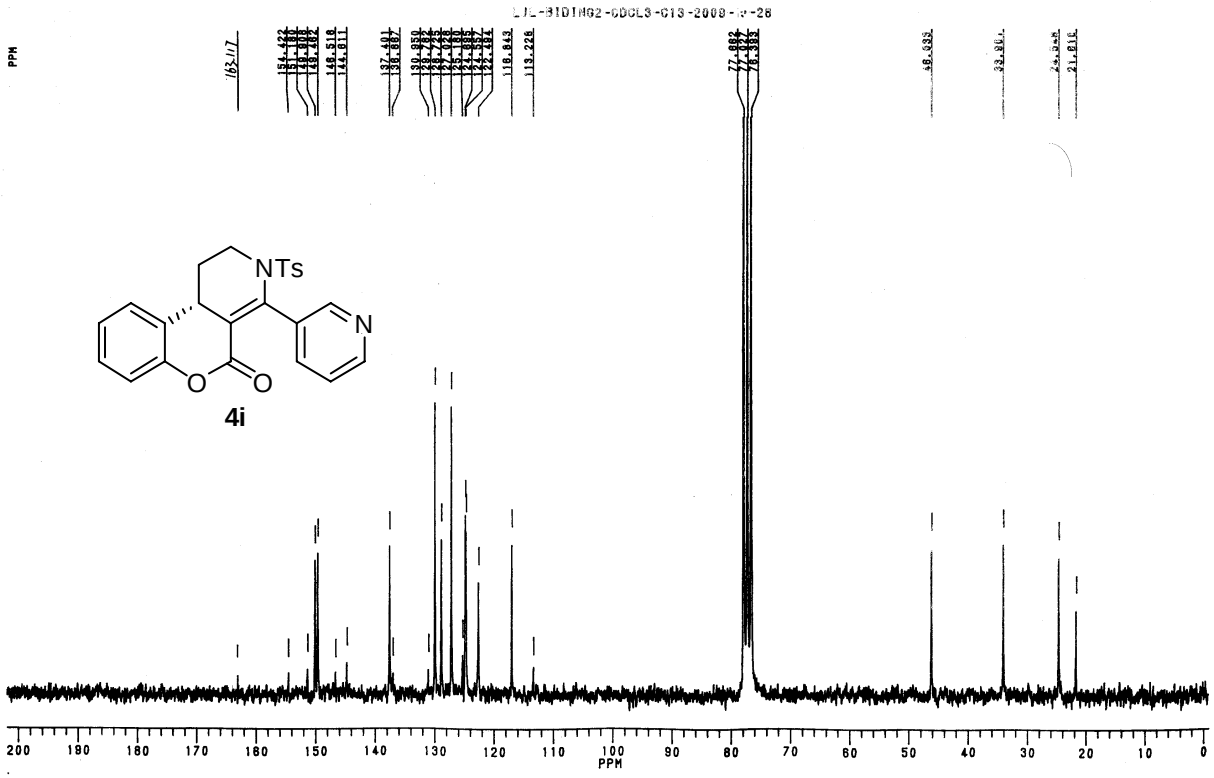


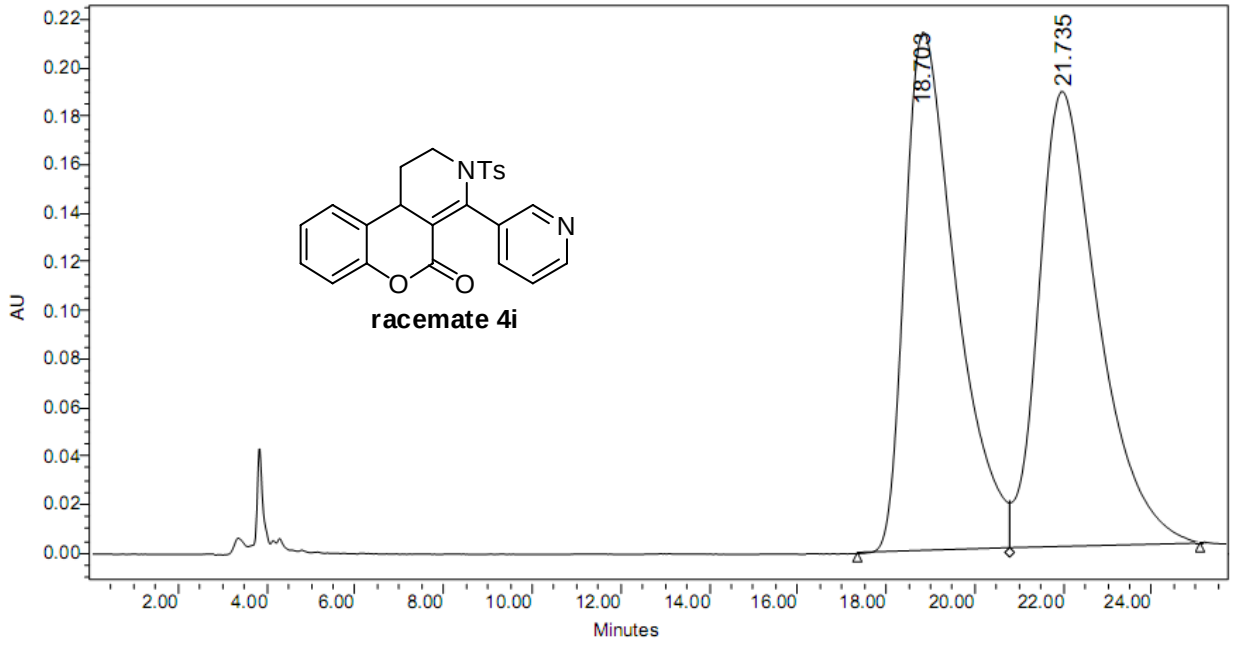
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	16.347	12458249	50.11	355486	53.36
2	19.088	12403297	49.89	310754	46.64



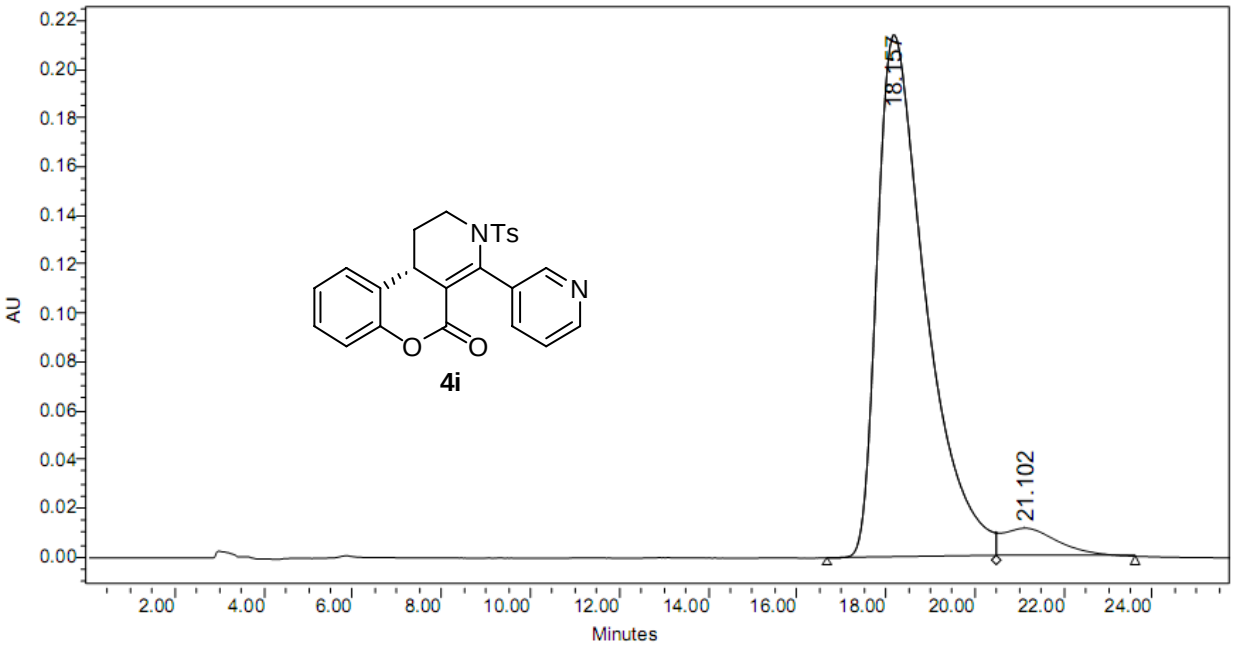
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	17.279	713067	5.59	18334	6.15
2	20.766	12042373	94.41	279674	93.85


LJL-biding H1 CDCl3 2009-5-19
Pulse Sequence: s2pul
NTs
N
O
O
4i
ppm

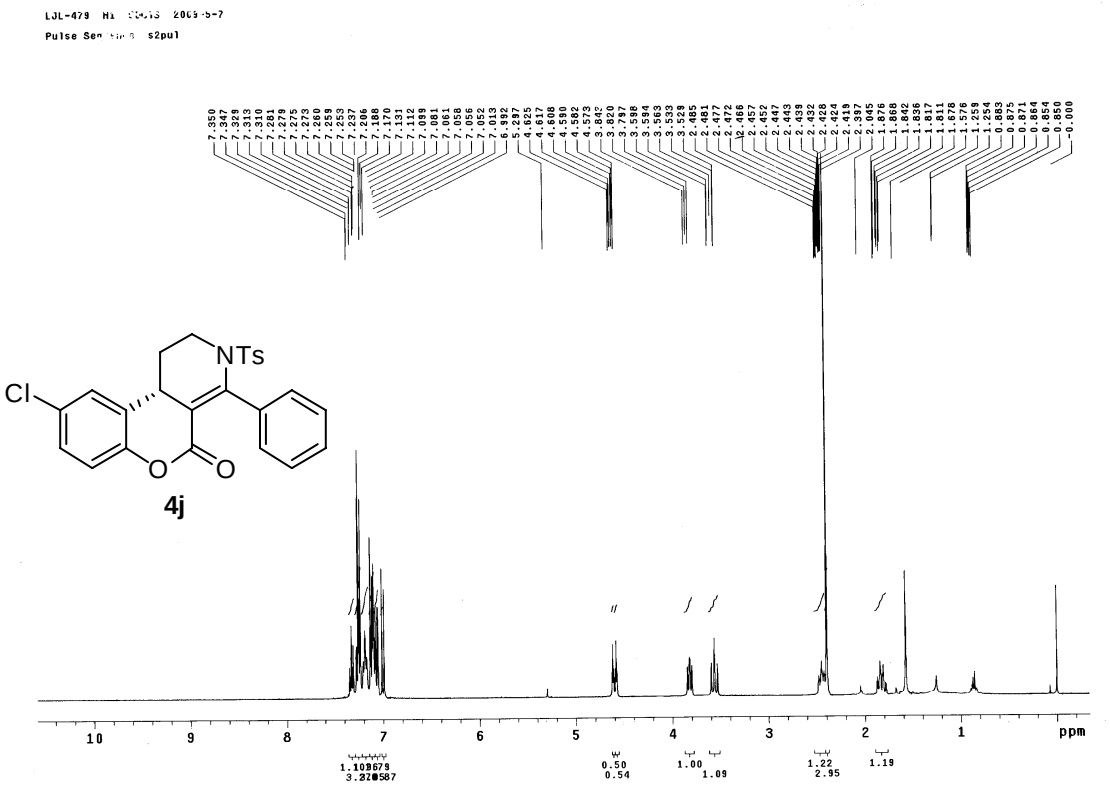

NTs
N
O
O
4i
PPM

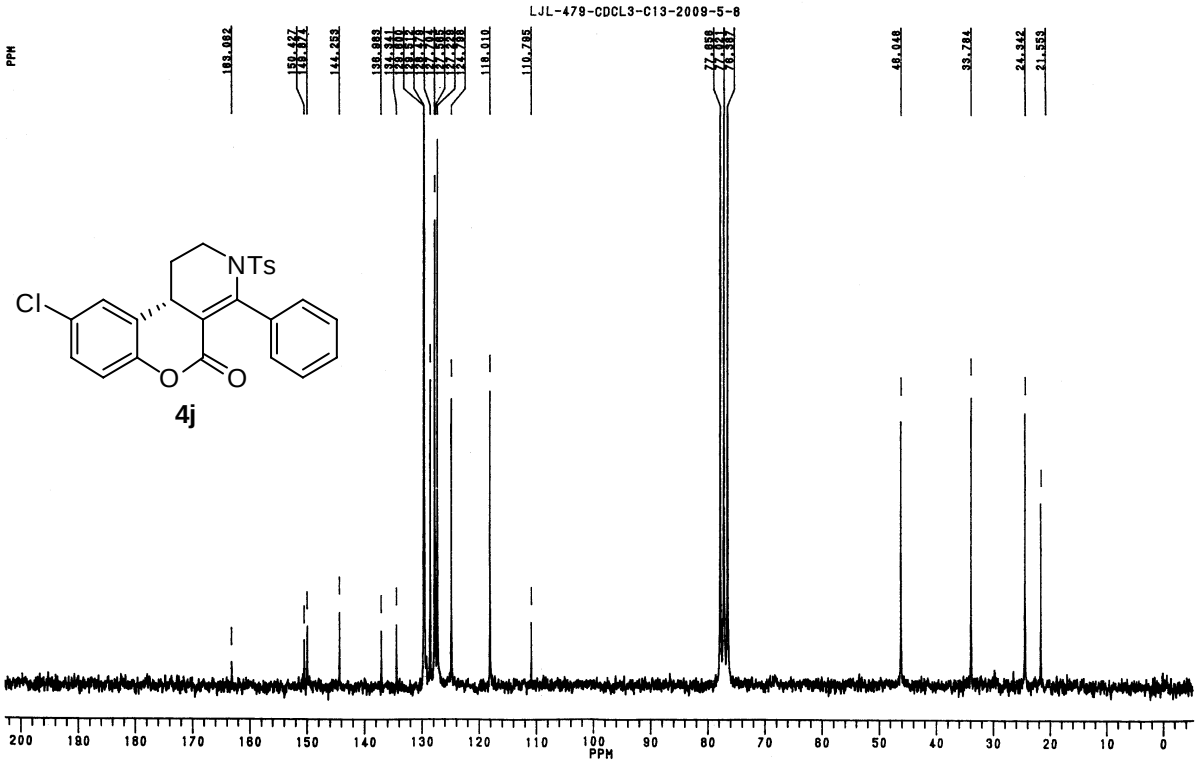


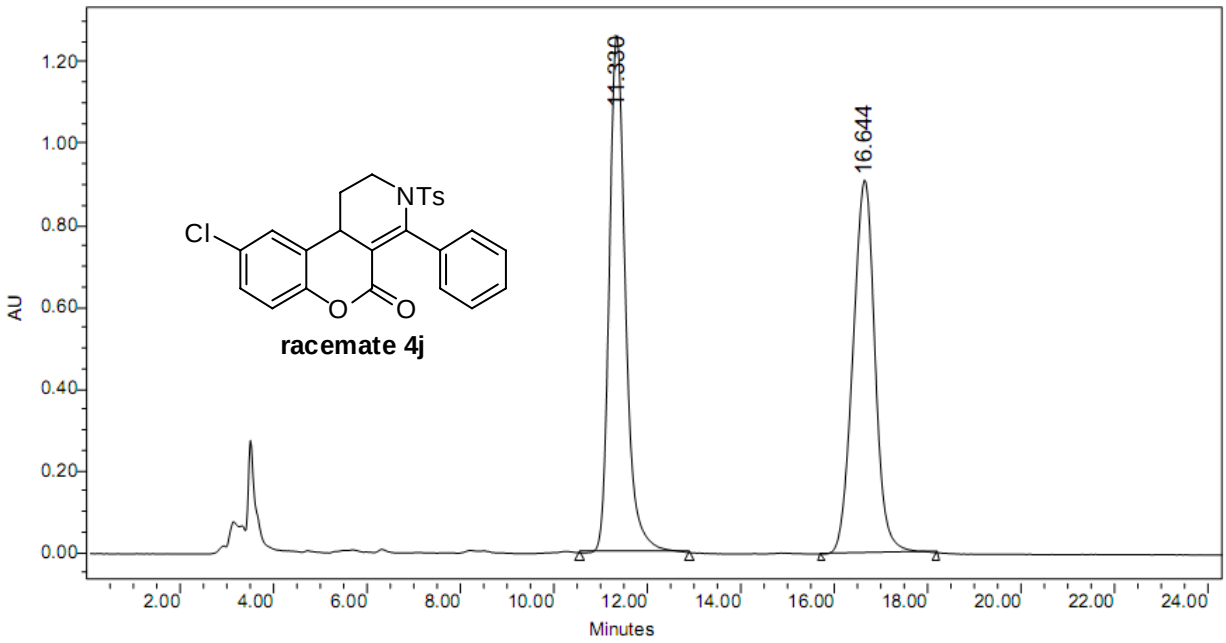
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	18.703	21925280	49.33	280743	53.23
2	21.735	22516599	50.67	246670	46.77



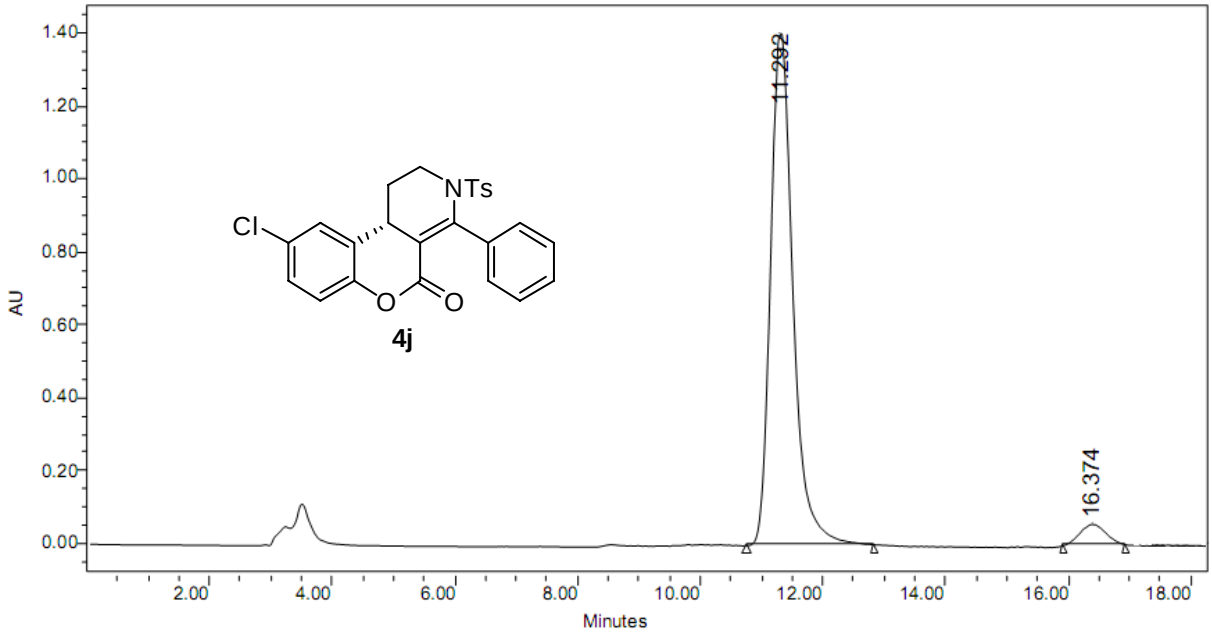
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	18.157	16493907	94.83	214474	94.79
2	21.102	899676	5.17	11788	5.21


NTs
Cl
O
O
4j
ppm

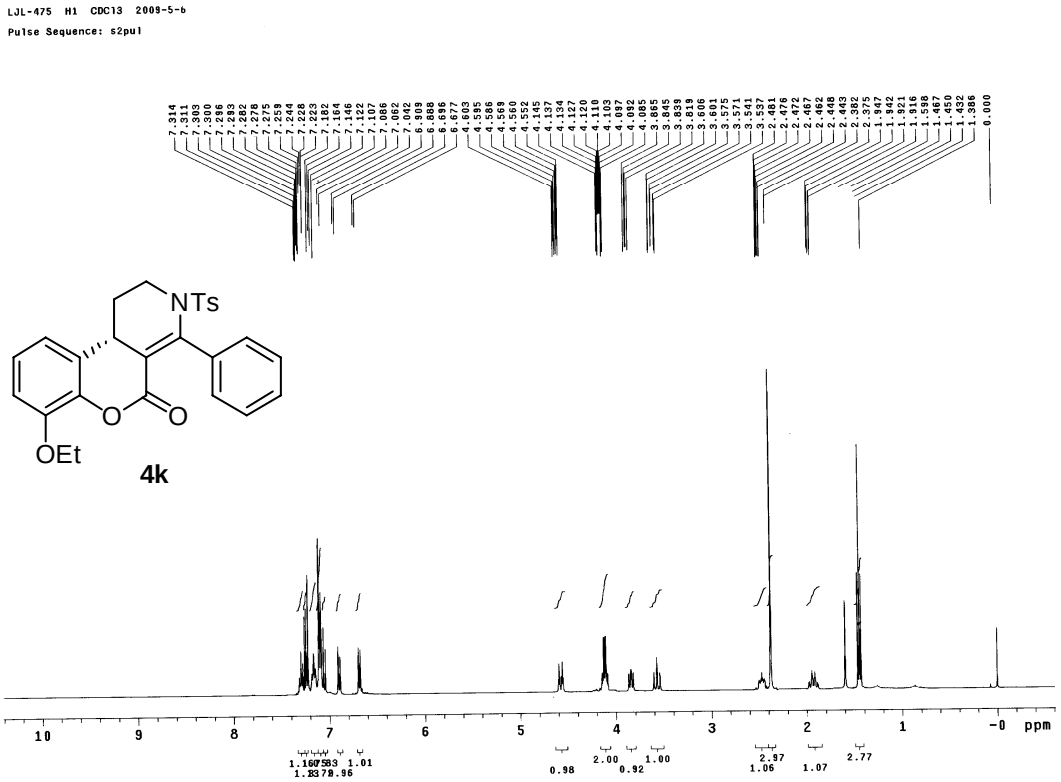

LJL-479-CDCL3-C13-2009-5-8
PPM
NTs
Cl
O
O
4j
PPM

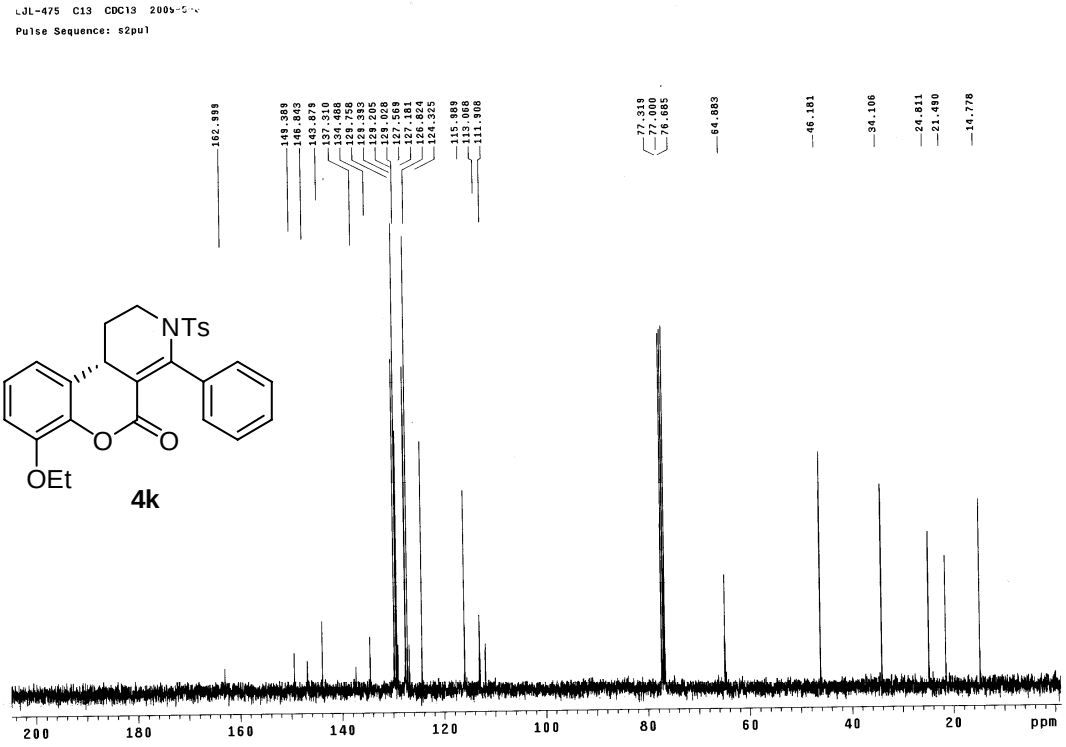


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.330	30699009	50.51	1265882	58.11
2	16.644	30080568	49.49	912371	41.89



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.292	35800790	95.50	1407442	96.10
2	16.374	1687653	4.50	57116	3.90


LJL-475 H1 CDCl3 2009-5-6
Pulse Sequence: s2pul
NTs
O
O
OEt
4k
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.16
1.83
1.00
1.01
0.96
0.98
2.00
0.92
1.00
2.87
1.06
1.07
2.77


LJL-475 C13 CDCl3
Pulse Sequence: s2pul
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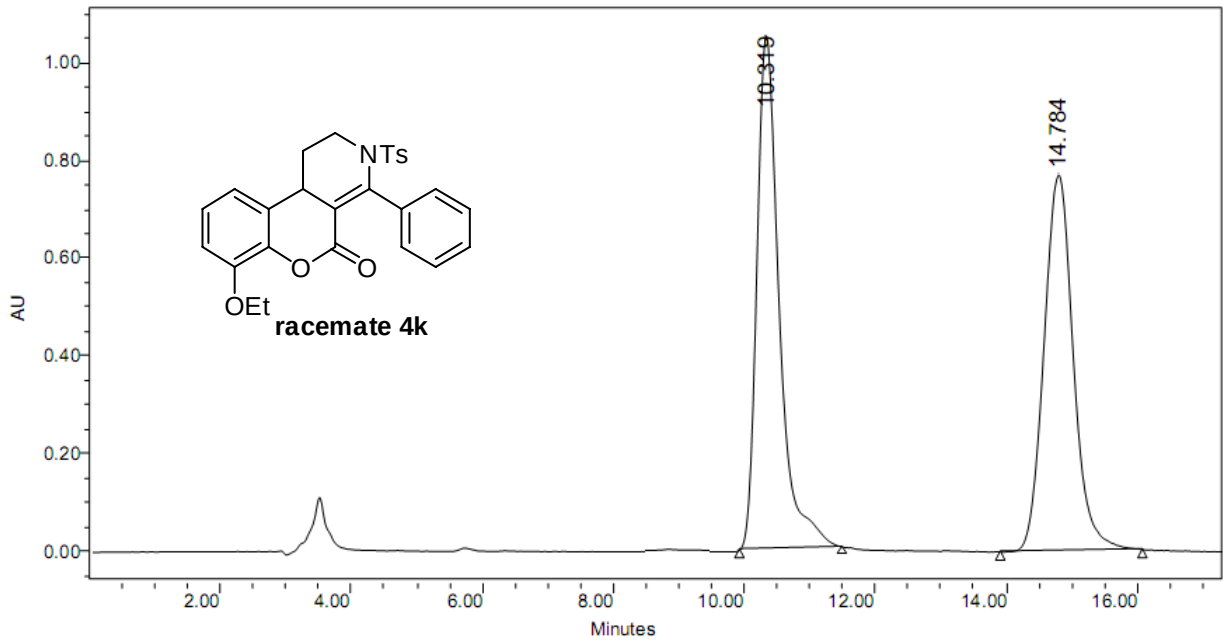
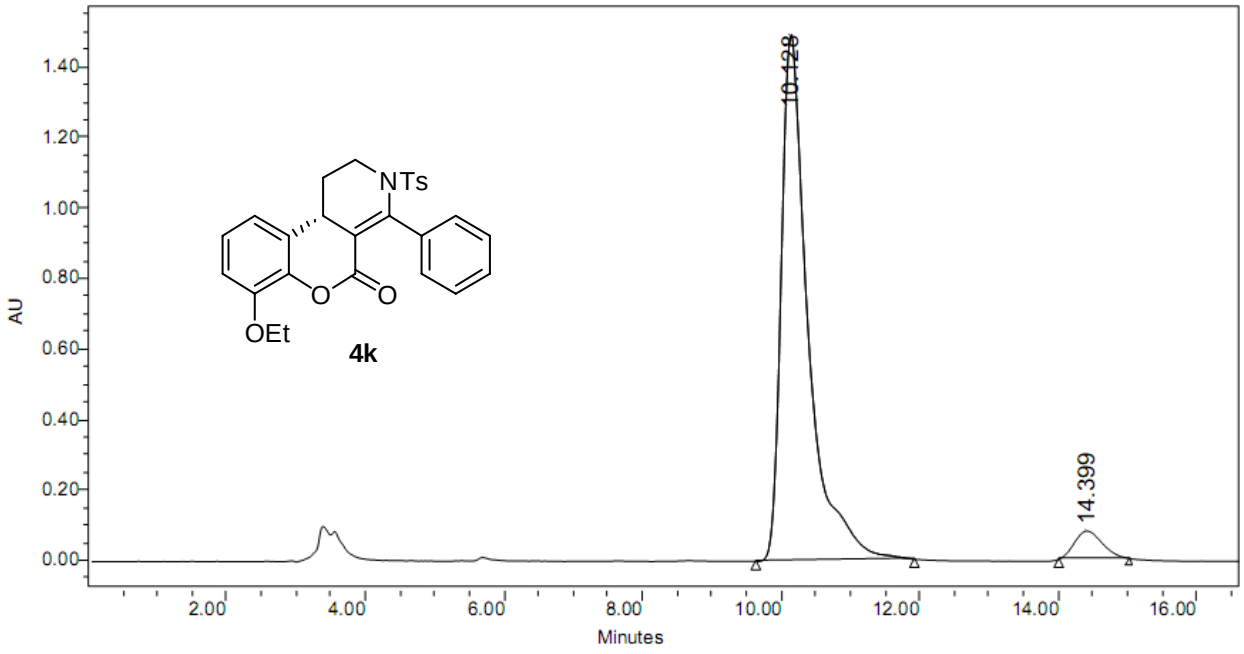
O
O
OEt
4k
200
180
160
140
120
100
80
60
40
20
ppm

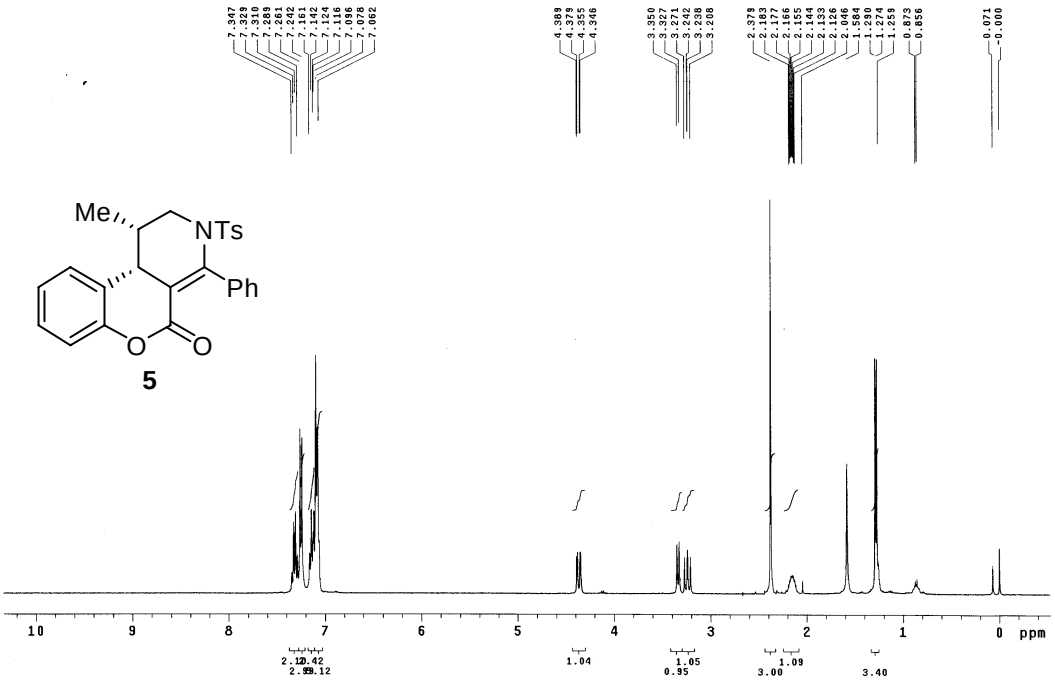


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.319	24917675	50.99	1051452	57.72
2	14.784	23949491	49.01	770290	42.28

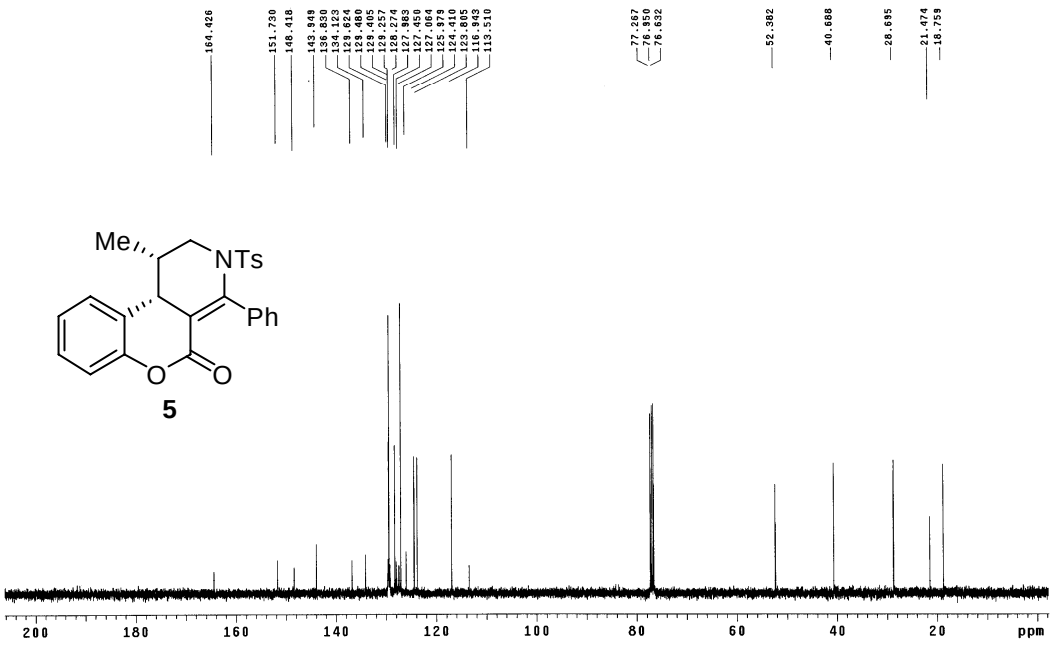


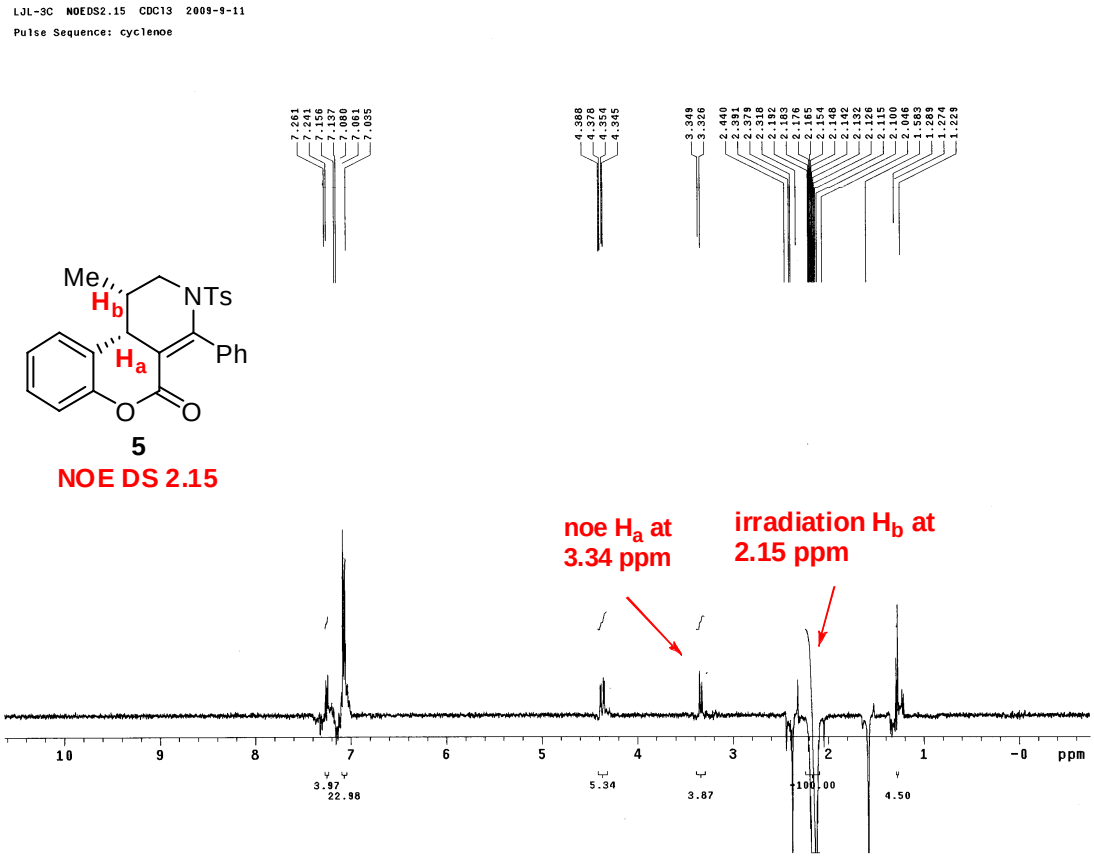
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.128	40300679	94.80	1493121	94.99
2	14.399	2208404	5.20	78778	5.01

LJL-3C H1 CDCl3 2009-9-11
Pulse Sequence: s2pul



LJL-3C-CDCL3-C13-2009-9-12
Pulse Sequence: s2pul




LJL-3C NOEDS2.15 CDCl3 2009-9-11
Pulse Sequence: cyclenoe
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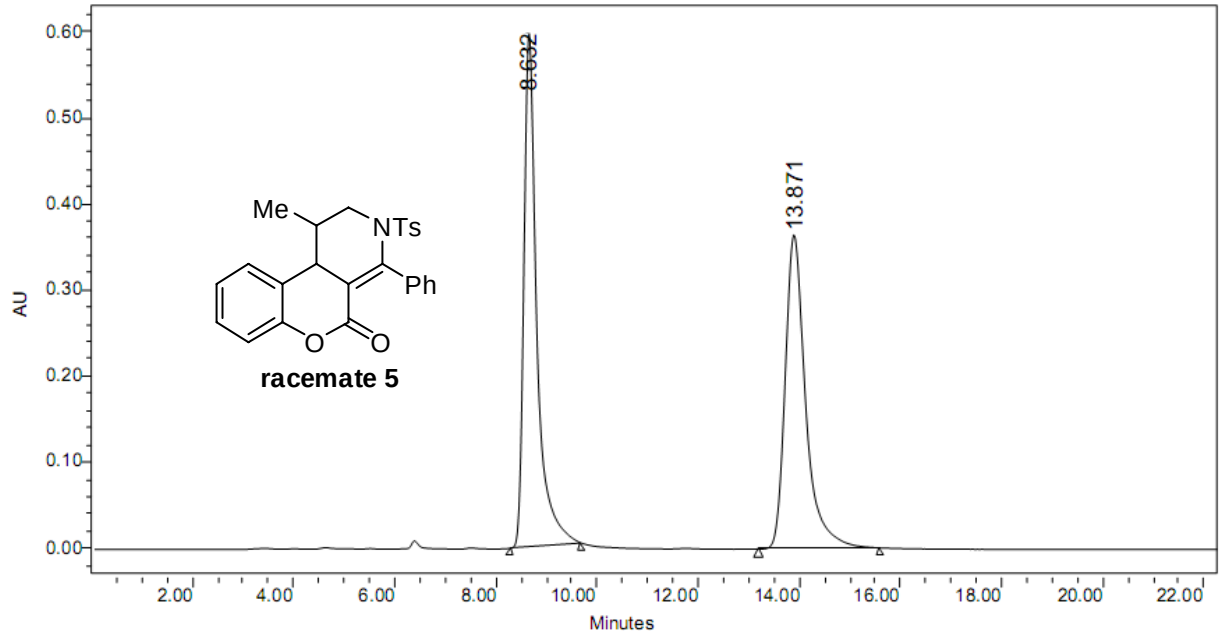
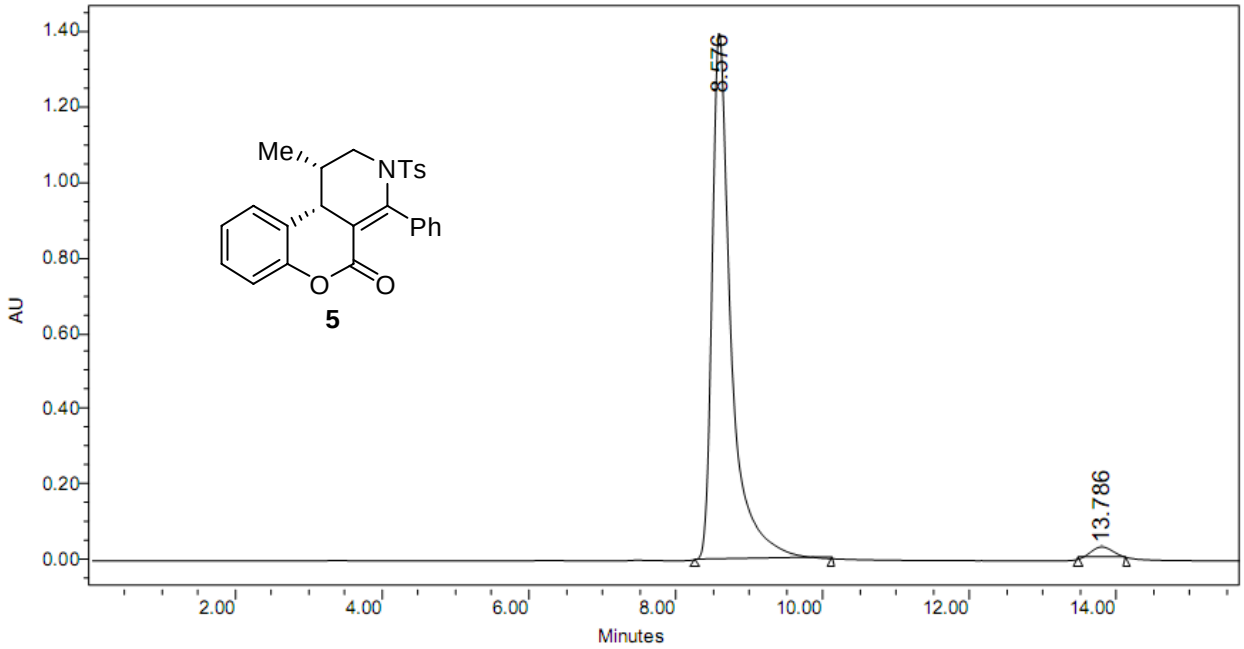
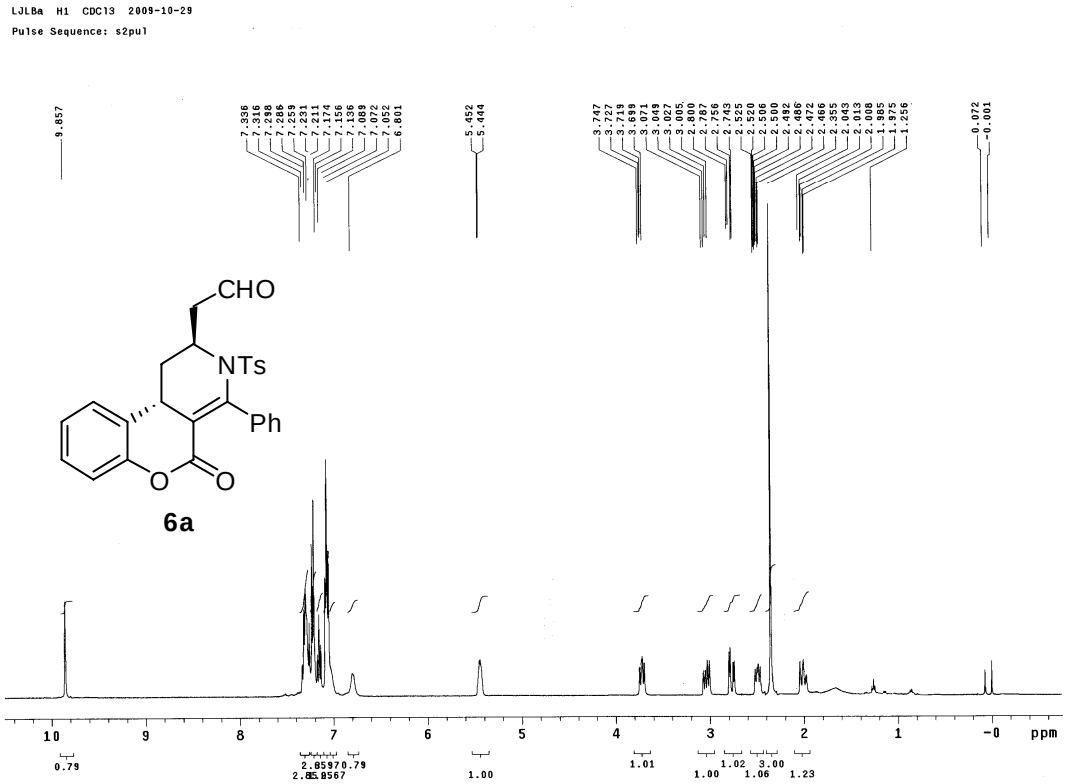
7.241
7.156
7.137
7.080
7.061
7.035
4.388
4.378
4.354
4.345
3.349
3.326
2.440
2.391
2.379
2.318
2.182
2.165
2.176
2.165
2.154
2.148
2.142
2.132
2.126
2.115
2.100
2.046
1.583
1.289
1.274
1.229
Me
Hb
NTs
Ha
Ph
O
O
5
NOE DS 2.15
noe Ha at 3.34 ppm
irradiation Hb at 2.15 ppm
10
9
8
7
6
5
4
3
2
1
-0
ppm
3.97
22.98
5.34
3.87
-100.00
4.50

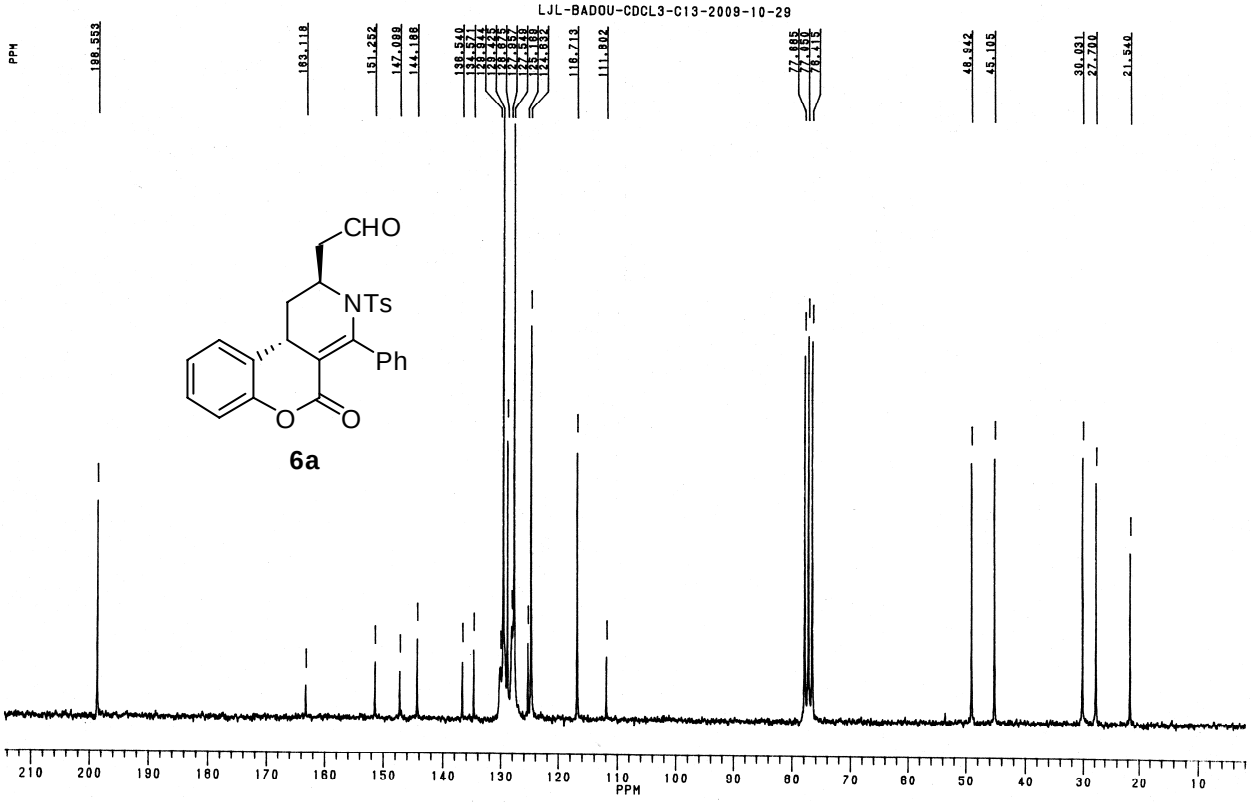


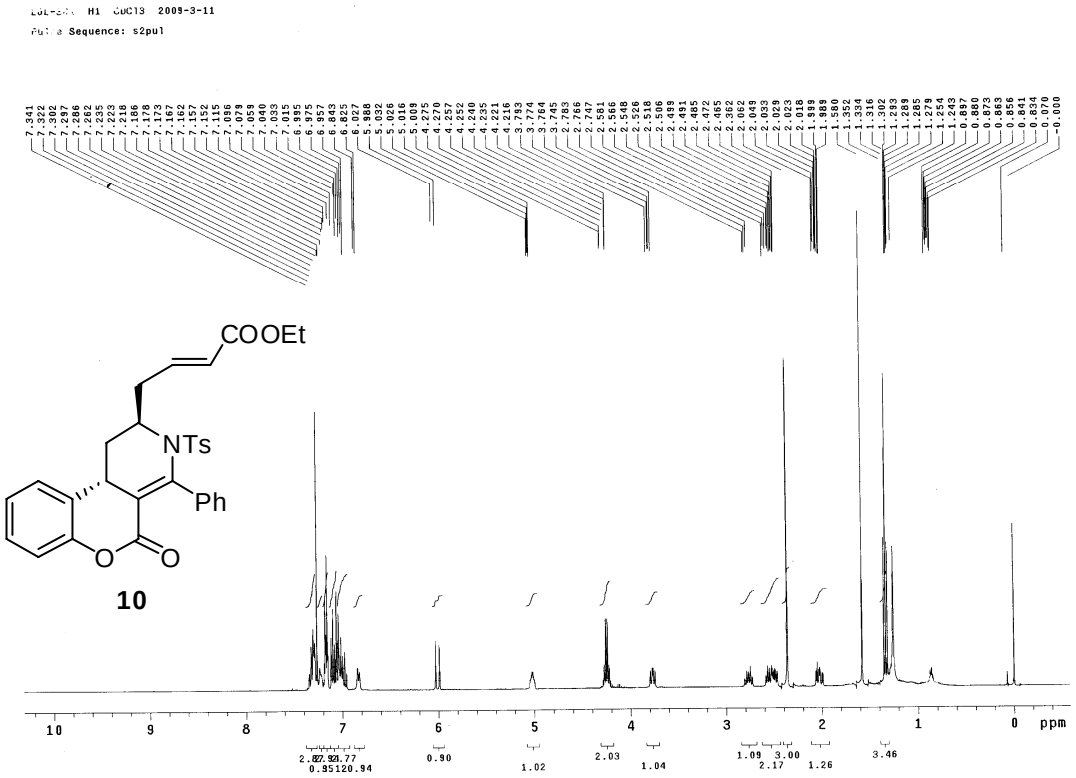
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.632	10594235	50.84	596441	62.08
2	13.871	10243257	49.16	364334	37.92

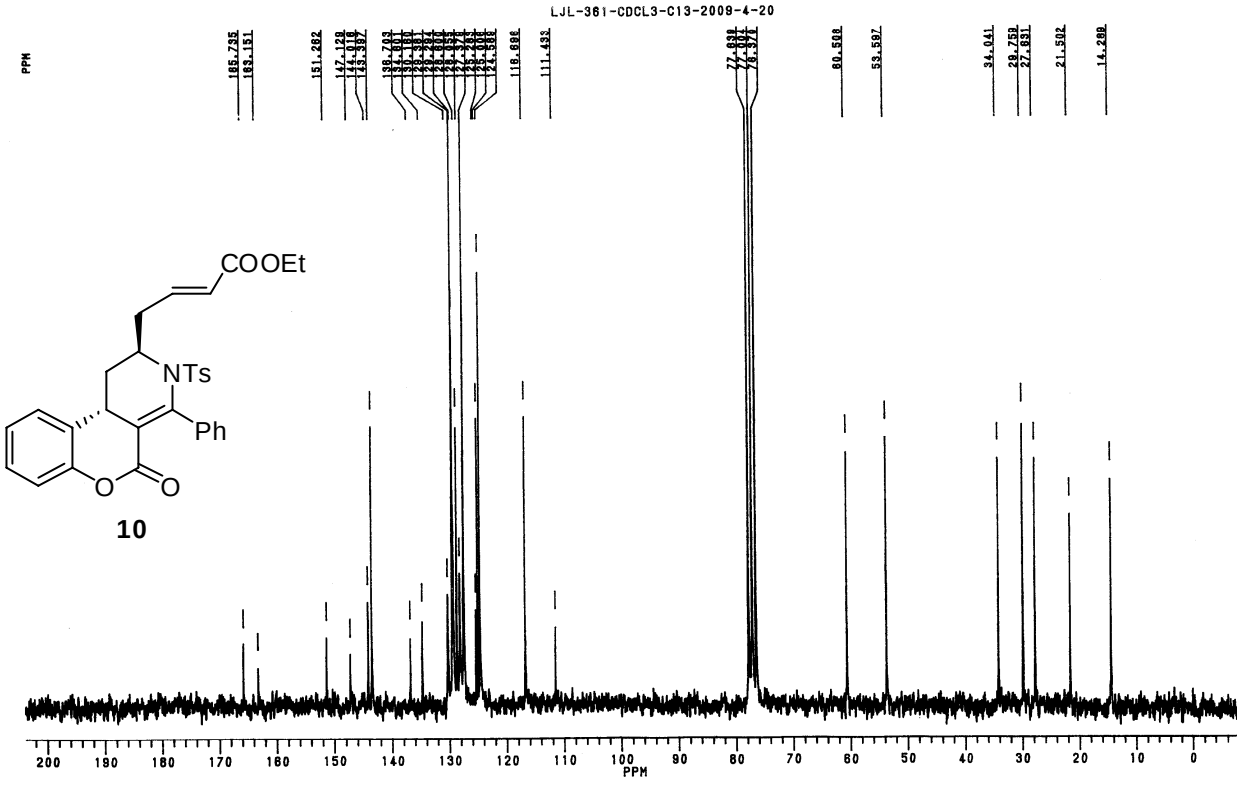


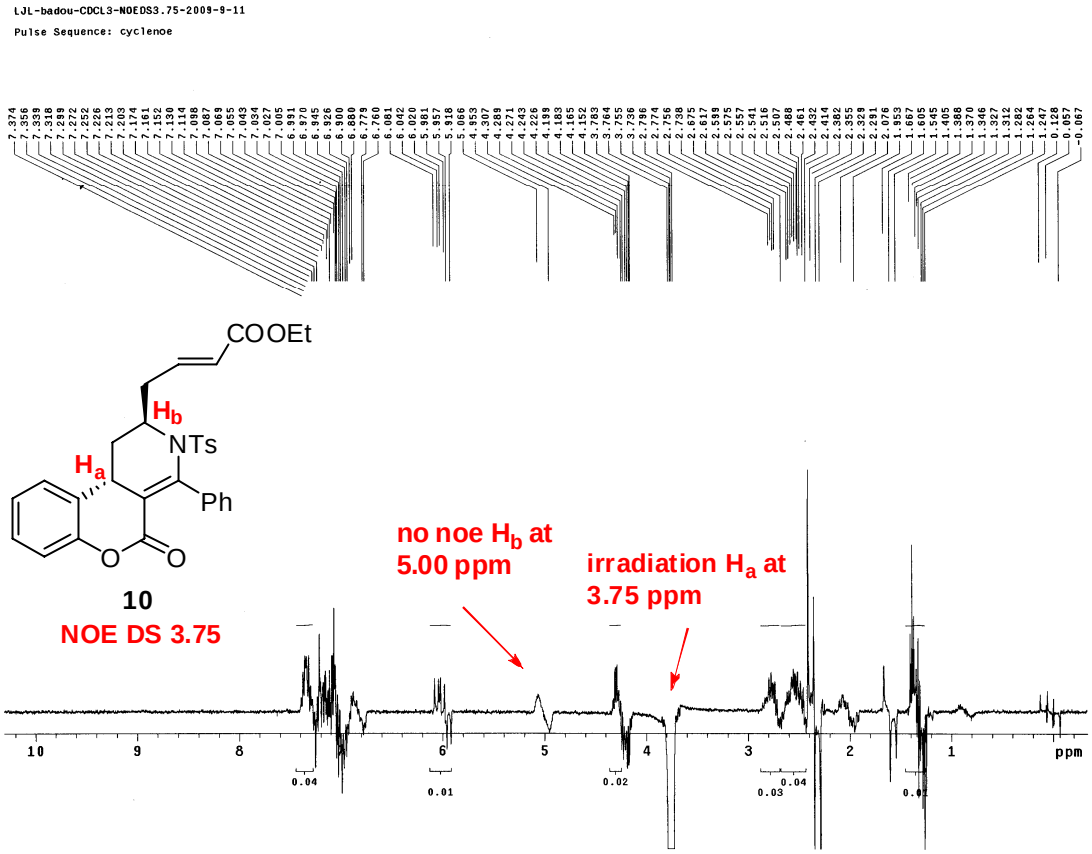
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.576	25071859	97.59	1394430	97.89
2	13.786	619785	2.41	30107	2.11

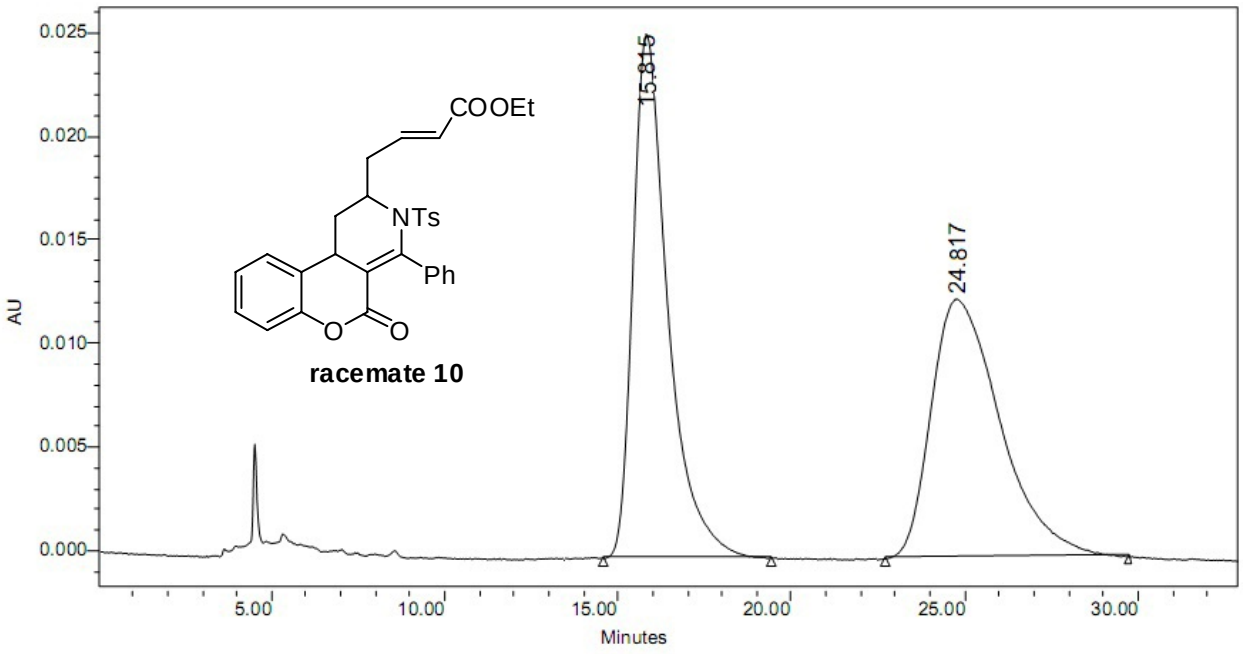

LJLBa H1 CDCl3 2009-10-29
Pulse Sequence: s2pul
CHO
NTs
Ph
O
O
6a
ppm


LJL-BADOU-CDCL3-C13-2009-10-29
PPM
CHO
NTs
Ph
O
O
6a
PPM

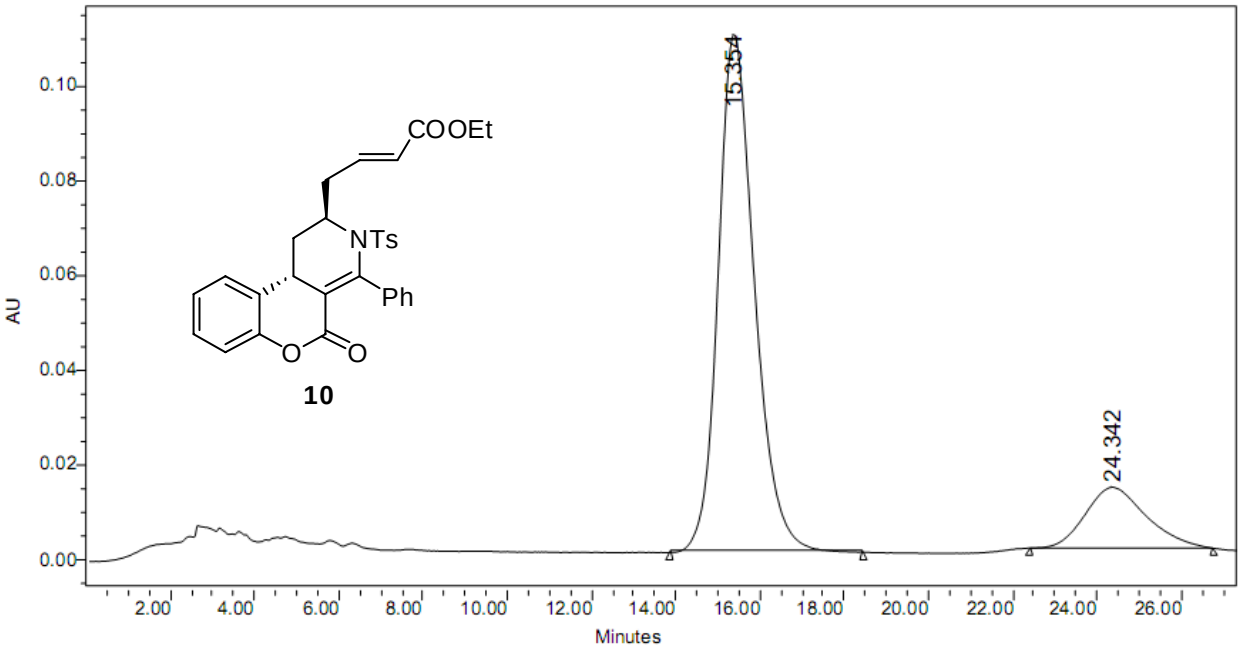

COOEt
NTs
Ph
O
O
10
ppm


COOEt
NTs
Ph
O
O
10
PPM

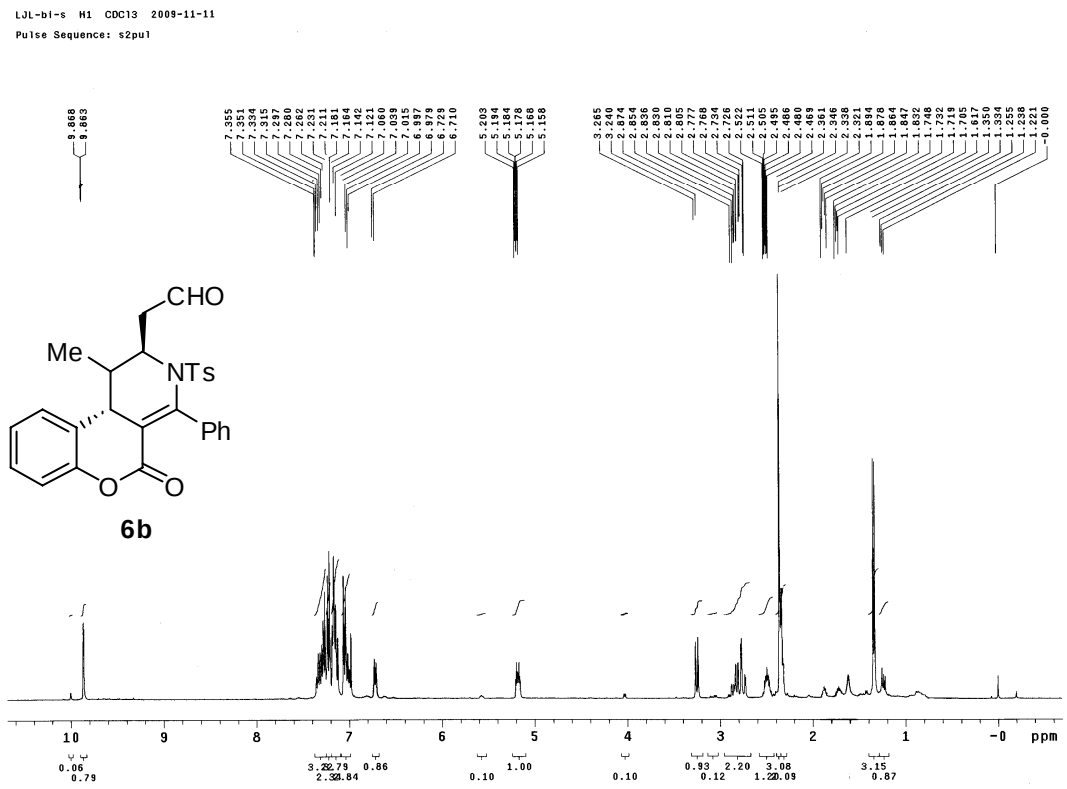

LJL-badou-CDCL3-NOEDS3.75-2009-9-11
Pulse Sequence: cyclenoe
COOEt
Hb
NTs
Ha
Ph
O
O
10
NOE DS 3.75
no noe Hb at 5.00 ppm
irradiation Ha at 3.75 ppm
10
9
8
6
5
4
3
2
1
ppm
0.04
0.01
0.02
0.03
0.04

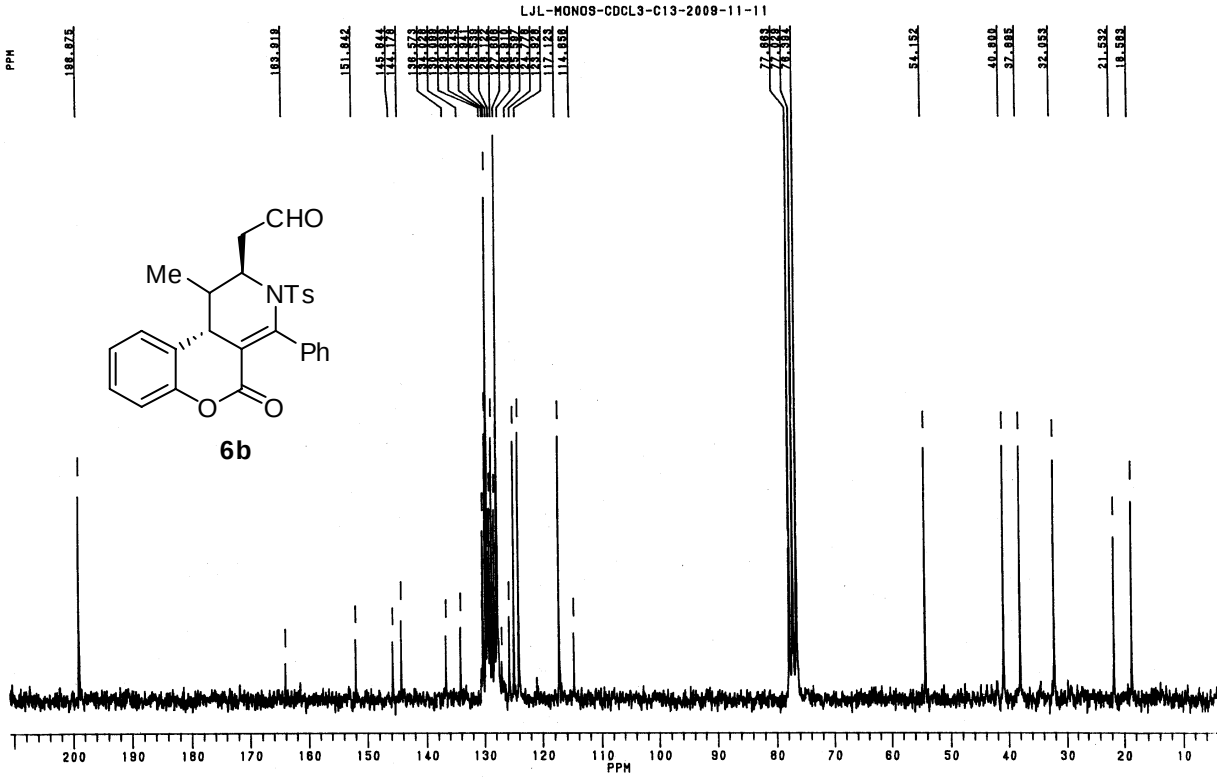


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.815	1767317	50.46	25249	66.92
2	24.817	1735389	49.54	12482	33.08

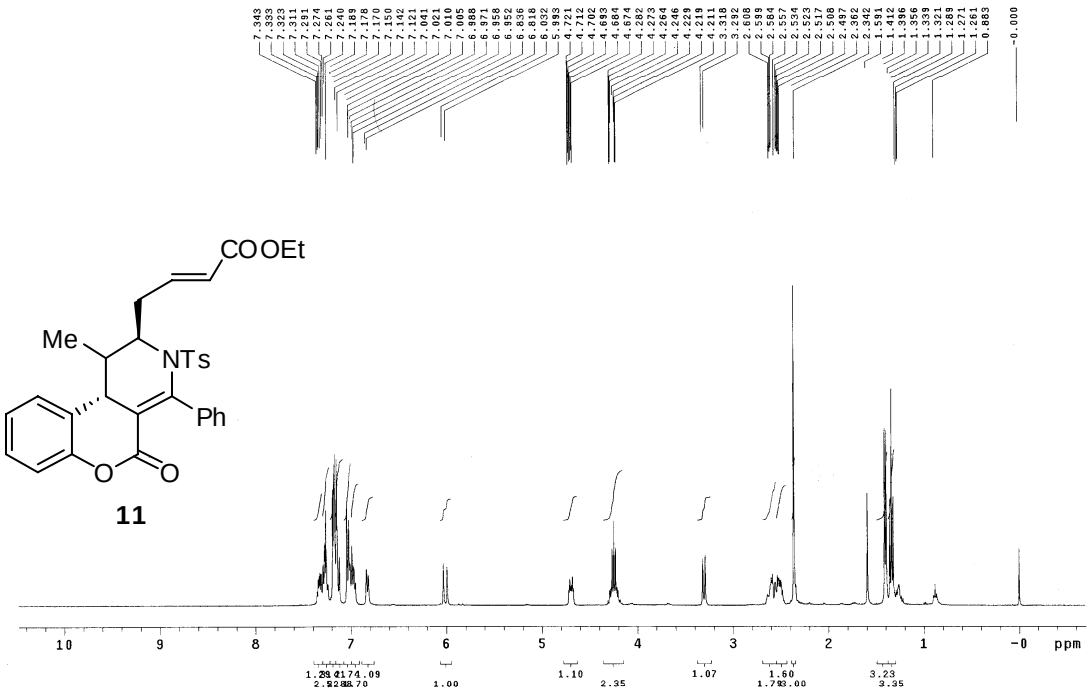


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.354	6566646	84.09	109101	89.63
2	24.342	1242150	15.91	12622	10.37

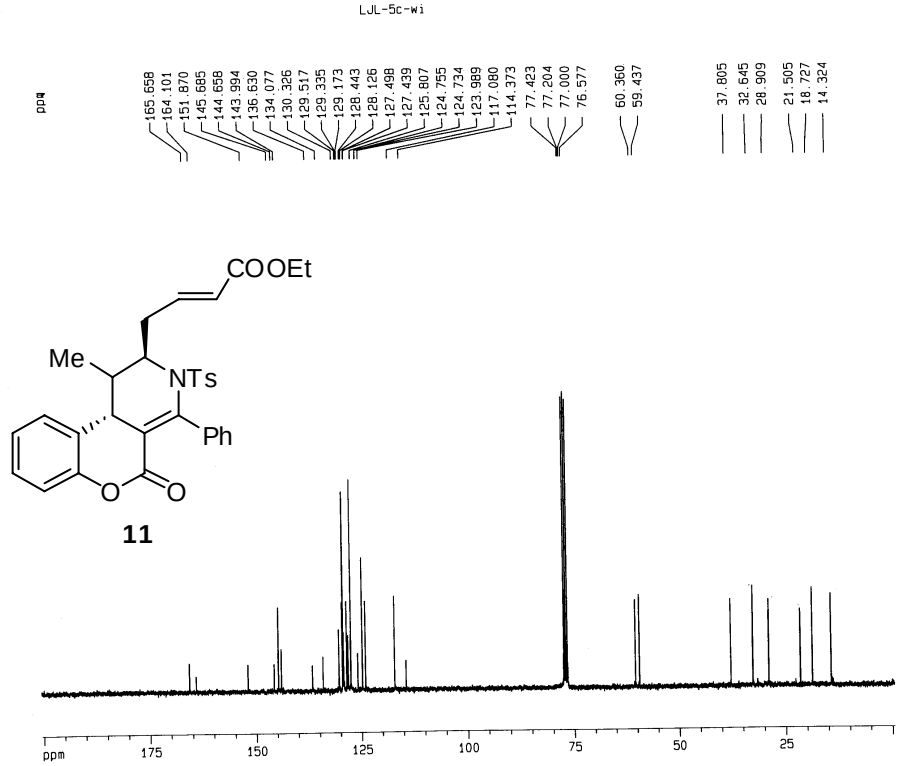

LJL-bi-s H1 CDCl3 2009-11-11
Pulse Sequence: s2pul
CHO
Me
NTs
Ph
O
O
6b
ppm


LJL-MONOS-CDCL3-C13-2009-11-11
PPM
CHO
Me
NTs
Ph
O
O
6b

LJL-5CWI H1 CDCl3 2009-11-20
Pulse Sequence: s2pul



LJL-5c-Wi



Current Data Parameters
NAME cyc-2009-78
EXPNO 2
PROCNO 1

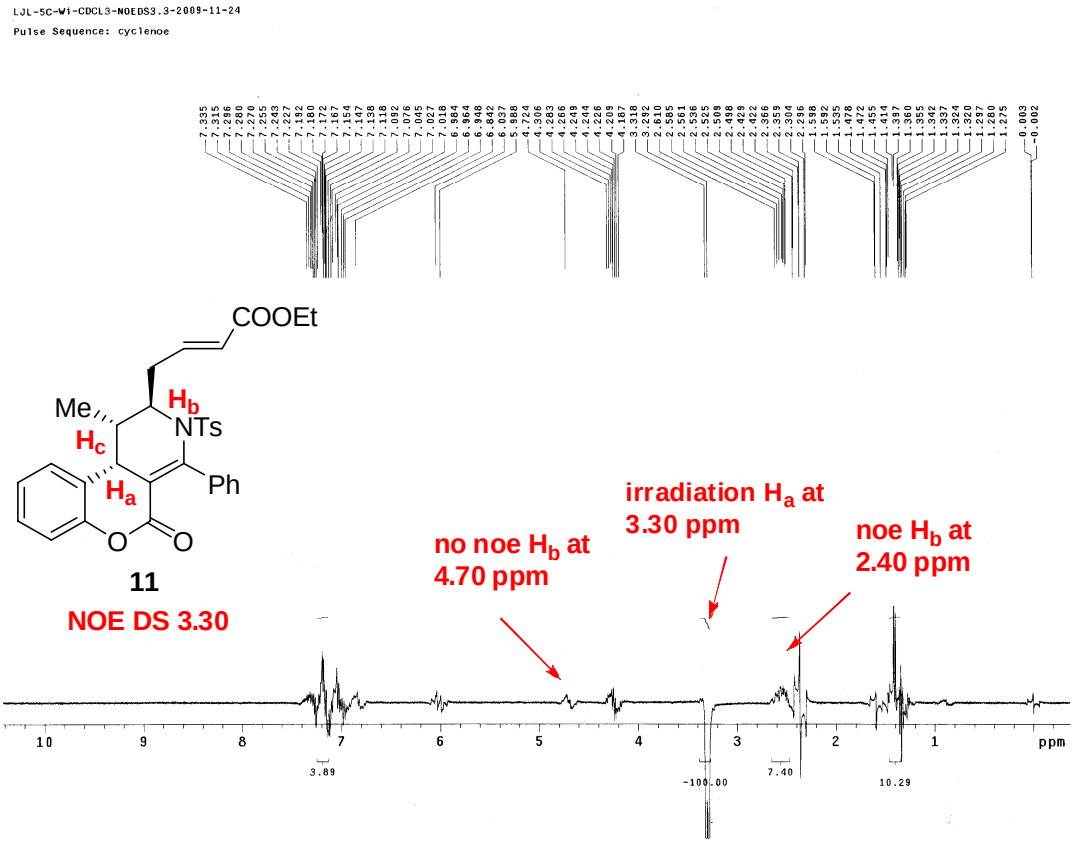
F2 - Acquisition Parameters
Date_ 20091125
Time 13.21
INSTRUM av300
PROBHD 5 mm GNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 294.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

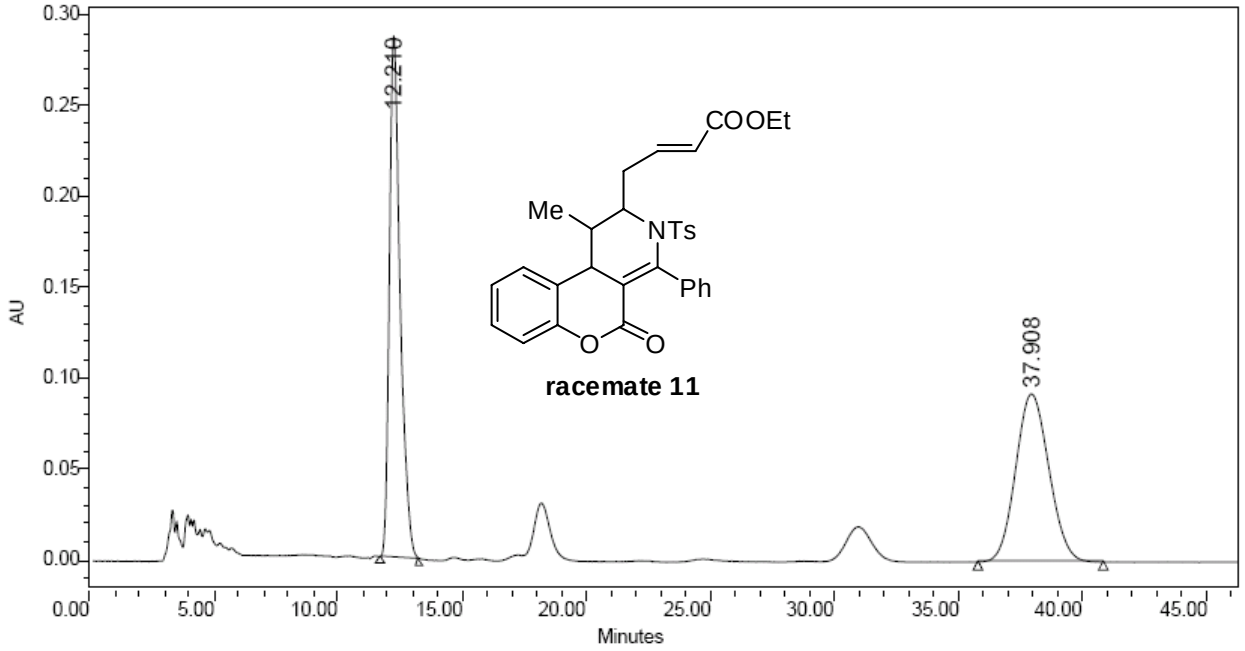
======== CHANNEL f1 ========
NUC1 13C
P1 10.50 usec
PL1 -0.81 dB
SFO1 75.4775598 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.10 dB
PL12 17.74 dB
PL13 17.74 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 65536
SF 75.4677531 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

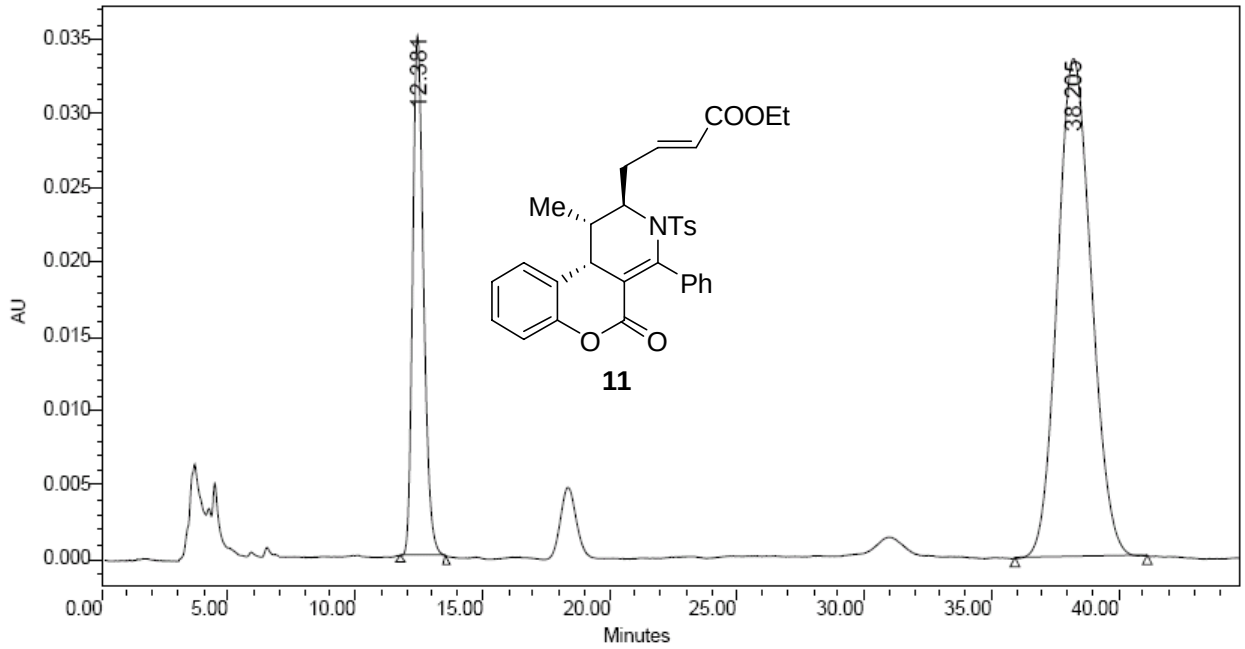
1D NMR plot parameters
CX 20.00 cm
CY 7.00 cm
F1P 200.500 ppm
F1 15131.28 Hz
F2P -0.500 ppm
F2 -37.73 Hz
PPMCM 10.05000 ppm/cm
HZCM 758.45087 Hz/cm


LJL-5C-W1-CDCL3-NOEDS3.3-2009-11-24
Pulse Sequence: cyclenoe
COOEt
Me
Hb
NTs
Hc
Ha
Ph
O
O
11
NOE DS 3.30
irradiation Ha at 3.30 ppm
no noe Hb at 4.70 ppm
noe Hb at 2.40 ppm
10
9
8
7
6
5
4
3
2
1
ppm
3.89
-100.00
7.40
10.29



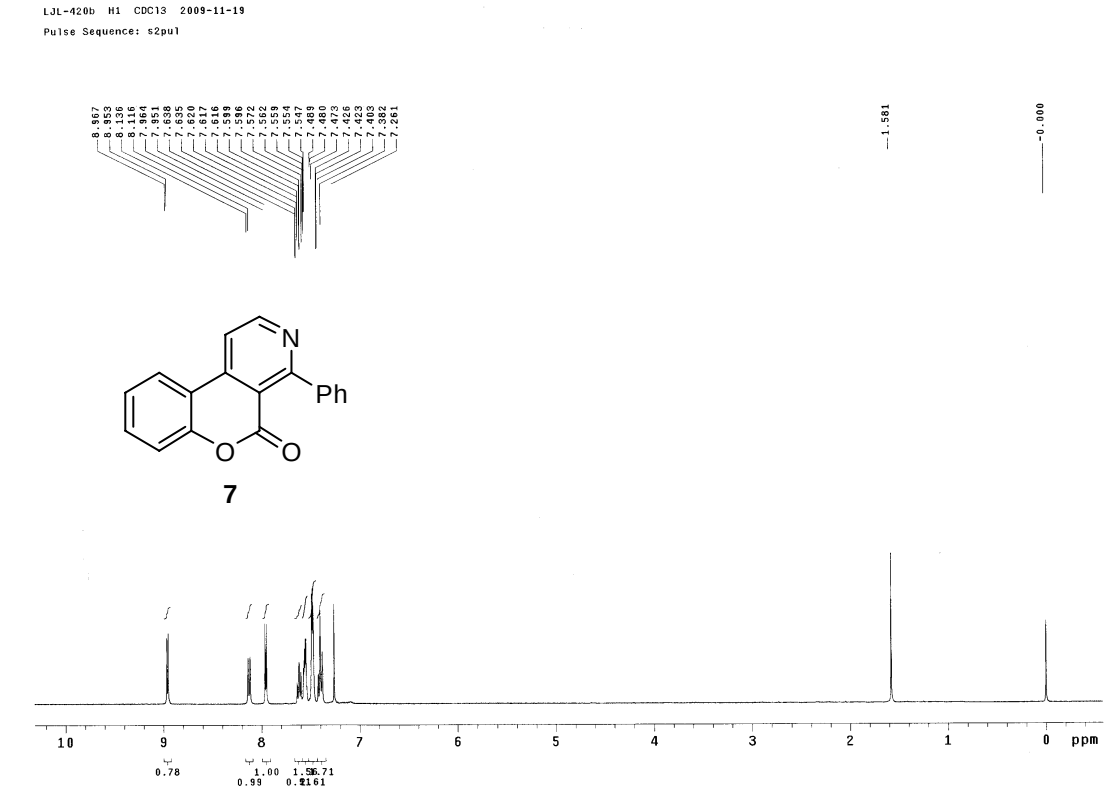
racemate 11

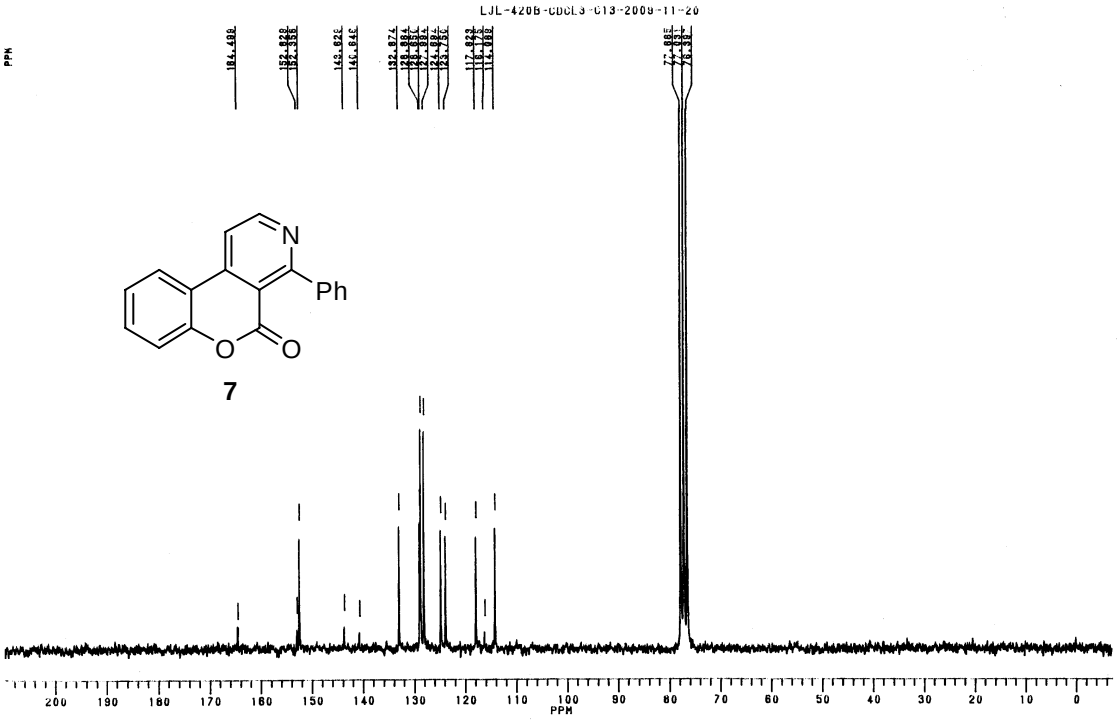
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	12.210	8648677	50.04	286943	75.64
2	37.908	8635192	49.96	92418	24.36

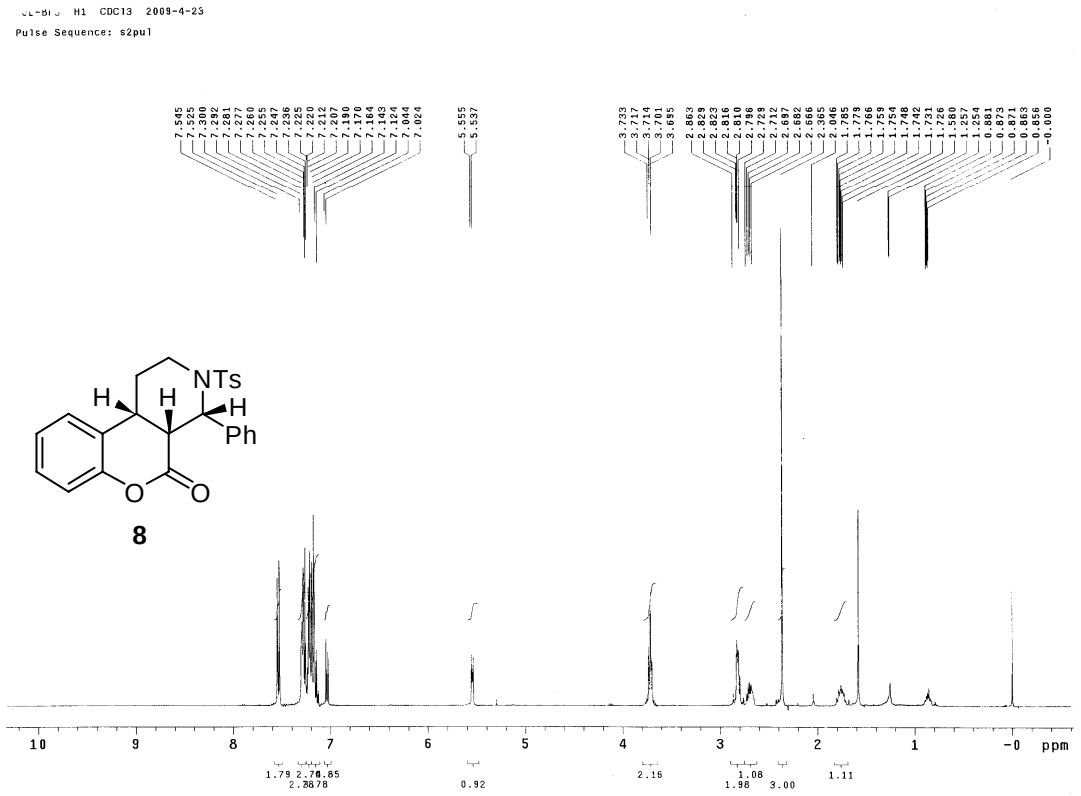


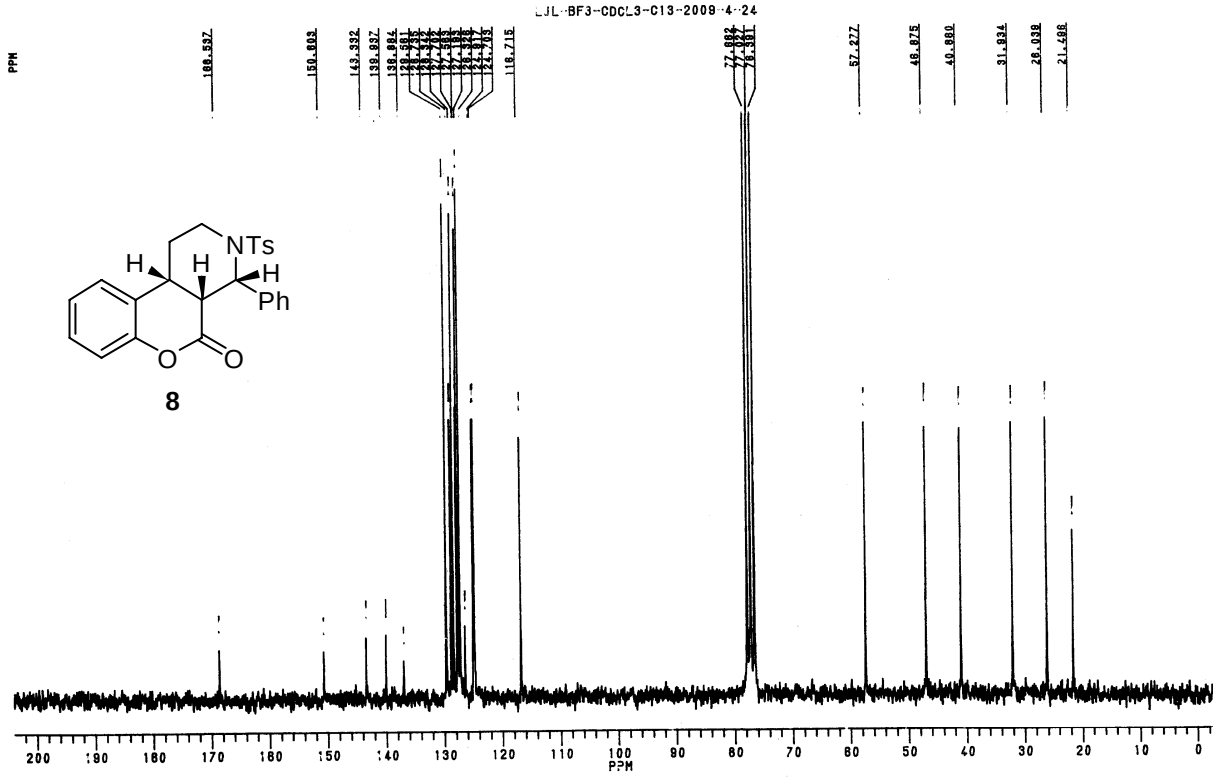
11

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	12.381	1045401	25.00	35048	51.06
2	38.205	3136416	75.00	33593	48.94

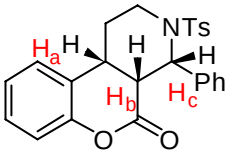

LJL-420b H1 CDCl3 2009-11-19
Pulse Sequence: s2pul
8.967
8.953
8.136
8.116
7.964
7.951
7.638
7.635
7.620
7.617
7.616
7.599
7.596
7.572
7.562
7.559
7.554
7.547
7.489
7.480
7.473
7.426
7.423
7.408
7.382
7.261
1.581
0.000
N
Ph
O
O
7
10
9
8
7
6
5
4
3
2
1
0
ppm
0.78
1.00
0.99
1.56
0.71
0.91
2.61


LJL-420b-CDCl3-C13-2009-11-20
PPM
N
Ph
O
O
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PPM

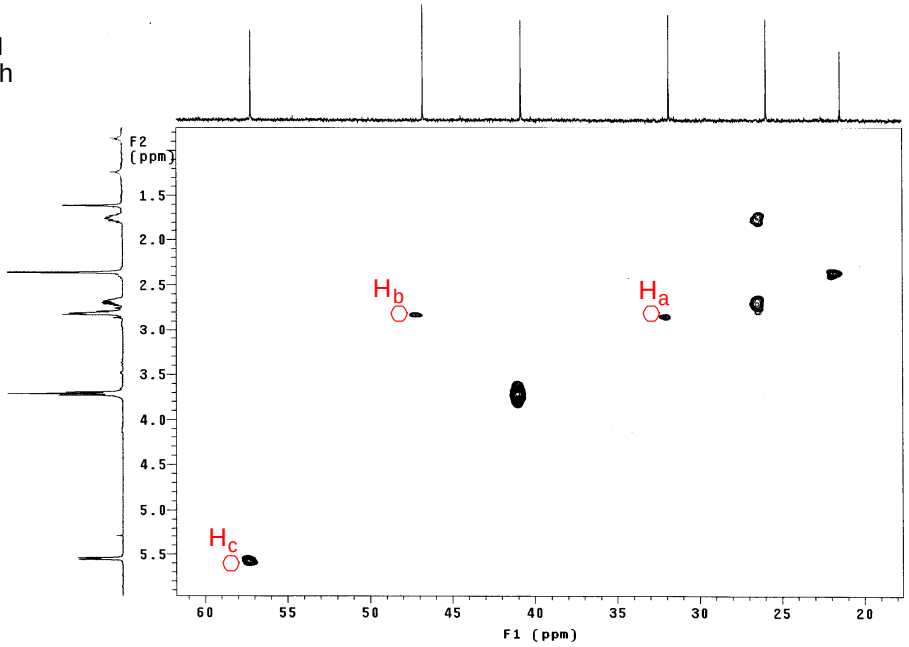

Pulse Sequence: s2pul
NTs
H
H
H
Ph
O
O
8
ppm
1.79
2.76
2.85
2.8878
0.92
2.15
1.08
1.98
3.00
1.11


PPM
NTs
H
H
H
Ph
O
O
8
PPM

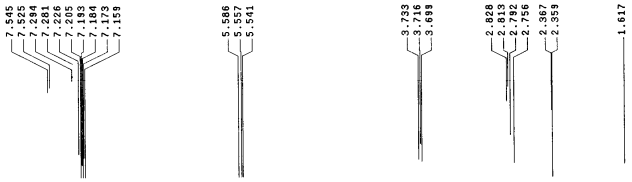
LJL-0908-CDCL3-gHMQC-2009-9-10
Pulse Sequence: gHMQC

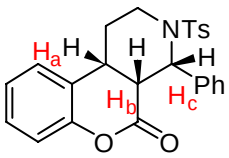


8



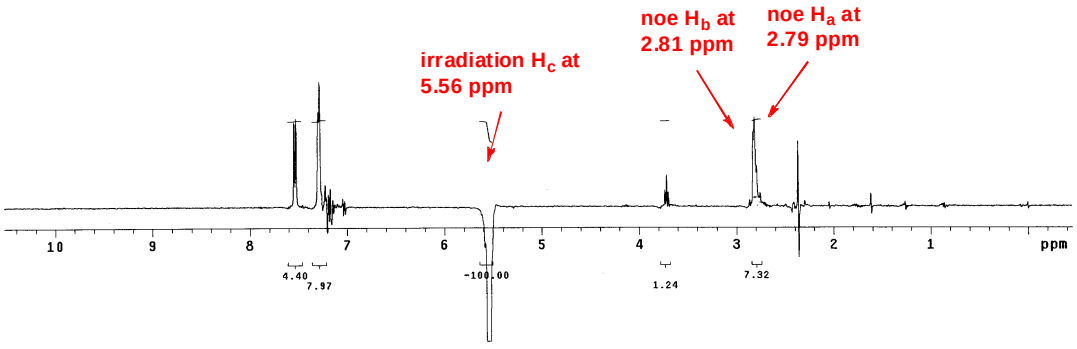
LJL-0908-CDCL3-NOEDS5.555-2009-9-8
Pulse Sequence: cyclenoe

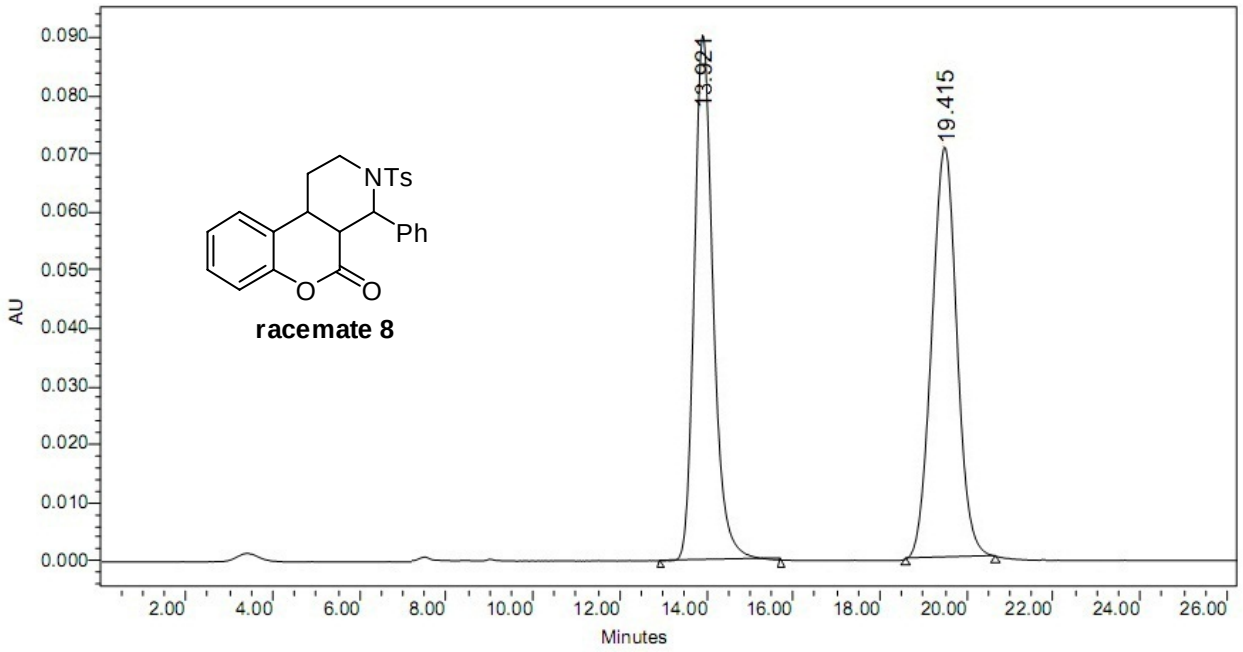




8

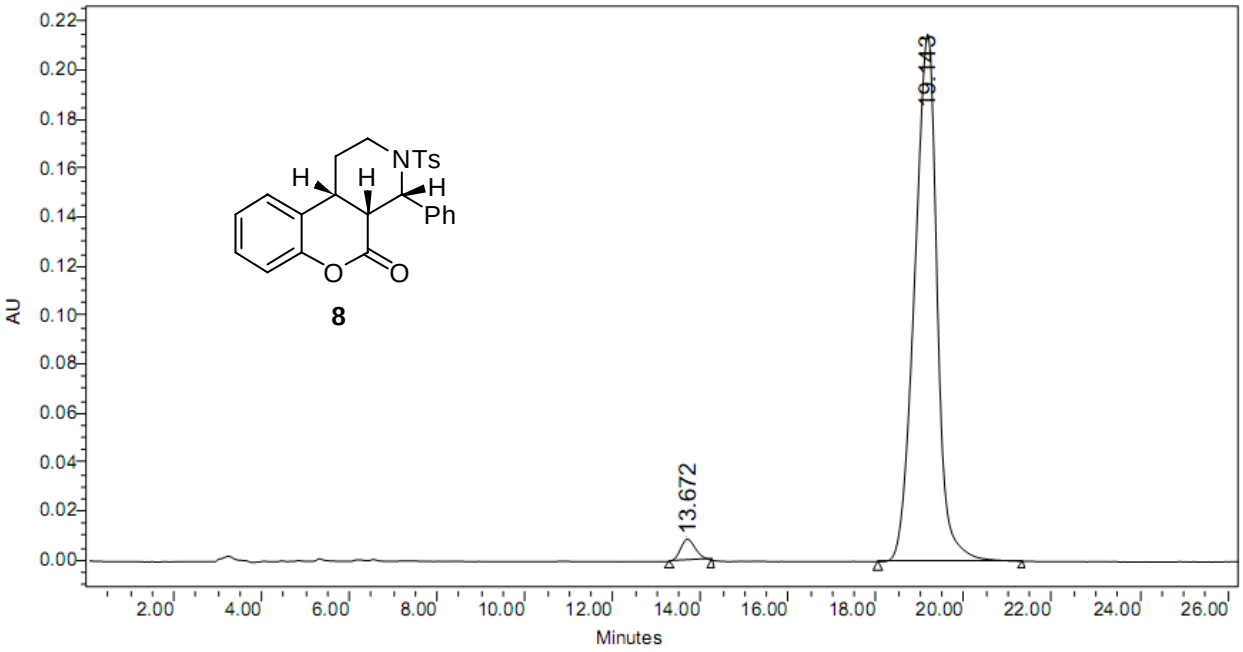
NOE DS 5.56





racemate 8

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.921	2740175	49.10	90428	56.15
2	19.415	2840769	50.90	70625	43.85



8

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.672	211166	2.68	8797	3.92
2	19.143	7666006	97.32	215333	96.08