Merging Chiral Organocatalysts: Enantio- and Diastereoselective Direct Vinylogous Mannich Reaction of Alkylimines

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Supplementary Information

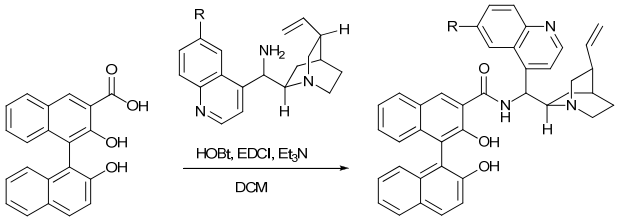
Table of Contents

1. General methods;

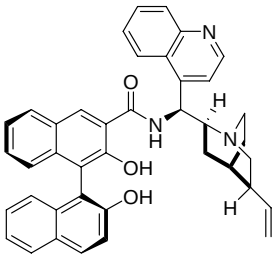
NMR spectra were recorded with tetramethylsilane as the internal standard. TLC was performed on glass-backed silica plates. Column chromatography was performed using silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 50 MHz or 100 MHz (Bruker Avance). Chemical shifts are reported in ppm downfield from $CDCl_3$ (δ = 7.27 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0 ppm) for ^{13}C NMR spectroscopy. Coupling constants are given in Hz. Optical rotations were measured at 589 nm at 20 ºC. Enantiomeric excess was determined by HPLC analysis on Chiralpak IC, AD and Chiralcel OD columns. Commercial grade solvents were dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997). All other chemicals were used without purification as commercially available. *N*-Sulfonyl alkylimines were prepared according to the reported procedure.[1]

2. Synthesis of new catalysts

Bifunctional catalyst **1a** and **1c** have been previously reported, and **1b, 1d**–**1f** were prepared via the same procedures.[2]

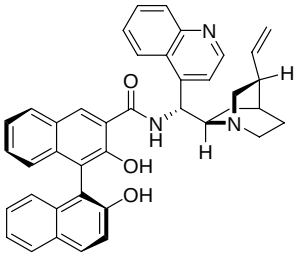


A mixture of 1,1′-binaphthyl-2,2′-dihydroxy-3-carboxylic acid (127 mg, 0.38 mmol), 9-amine-9-deoxyepicinchona alkaloid (0.38 mmol), EDCI (110 mg, 0.58 mmol), HOBt (63 mg, 0.47 mmol) and Et_3N (81 μL, 0.58 mmol) in DCM (4 mL) was stirred at room temperature for 12 h. Then the reaction mixture was diluted with EtOAc, washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/acetone = 3:1) to afford the pure amide as a yellow solid.

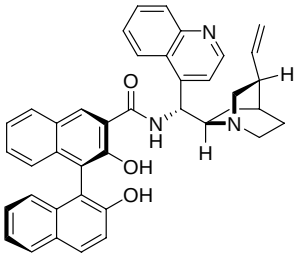


1b 35% yield; yellow solid; $[\alpha]_D^{20}$ = -111.0 (*c* = 1.00 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (d, *J* = 4.8 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 8.32 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.88-7.86 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.74-7.70 (m, 1H), 7.66 (t, *J* = 6.8 Hz, 1H), 7.51 (d, *J* = 4.4 Hz,

1H), 7.34-7.24 (m, 4H), 7.17-7.13 (m, 1H), 7.11-7.09 (m, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.78-5.71 (m, 1H), 5.61 (br s, 1H), 5.04-4.98 (m, 2H), 3.33-3.27 (m, 2H), 2.95 (br s, 1H), 2.81-2.76 (m, 3H), 2.35 (s, 1H), 2.04 (s, 2H), 1.71 (d, *J* = 2.4 Hz, 4H), 1.45 (t, *J* = 1H), 1.08-1.02 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.5, 154.7, 151.8, 150.0, 148.5, 145.9, 140.8, 136.4, 133.5, 130.5, 130.1, 129.6, 129.4, 129.2, 128.1, 127.2, 127.1, 126.5, 124.8, 124.7, 124.2, 123.3, 123.2, 119.4, 118.0, 115.2, 115.0, 114.1, 60.0, 55.7, 41.0, 39.3, 29.7, 27.5, 27.2, 26.0, 22.6, 14.1 ppm; ESI-HRMS: calcd. for $C_{40}H_{36}N_3O_3$+H 606.2757, found 606.2785.

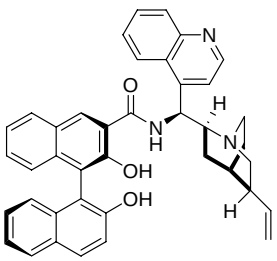


1d 37% yield; yellow solid; $[\alpha]_D^{20}$ = +36.5 (*c* = 1.42 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 4.4 Hz, 1H), 8.38 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.88-7.83 (m, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 4.4 Hz, 1H), 7.36-7.29 (m, 4H), 7.23-7.18 (m, 1H), 7.12-7.06 (m, 2H), 5.98-5.89 (m, 1H), 5.64 (br s, 1H), 5.30-5.20 (m, 2H), 3.74 (s, 2H), 3.35 (br s, 1H), 3.12-3.03 (m, 4H), 2.58 (br s, 1H), 2.43-2.36 (m, 1H), 2.19-2.18 (m, 1H), 1.65-1.49 (m, 3H), 1.44-1.39 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.7, 154.8, 151.9, 150.0, 139.4, 133.6, 130.5, 130.1, 129.7, 129.3, 128.2, 127.0, 126.4, 124.8, 124.7, 124.3, 123.2, 123.0, 118.1, 115.6, 63.7, 49.3, 46.9, 38.6, 29.7, 27.1, 26.1, 25.3 ppm; ESI-HRMS: calcd. for $C_{40}H_{36}N_3O_3$+H 606.2757, found 606.2789.



1e 29% yield; yellow solid; $[\alpha]_D^{20}$ = +58.5 (*c* = 0.81 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.85 (d, *J* = 4.4, 1H), 8.47 (d, *J* = 7.6 Hz, 1H), 8.20 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.84-7.81 (m, 2H), 7.66-7.60 (m, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.32-7.27 (m, 3H), 7.15 (t, *J* = 3.6 Hz, 1H), 7.09-7.07 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.98-5.89 (m, 1H), 5.59 (br s, 1H), 5.20-5.13 (m, 2H), 3.76-3.61 (m, 1H), 3.05 (br s, 1H), 2.98-2.93 (m, 4H), 2.34-2.33 (m, 1H), 2.17 (s, 2H), 1.71 (s, 1H), 1.68-1.50 (m, 2H), 1.41-1.30 (m, 1H), 1.08-1.04 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 166.7, 153.6, 152.2, 149.6, 146.3, 146.1, 139.9, 136.2, 133.7, 130.2, 130.1, 129.8, 129.4, 129.1, 128.9, 128.1, 127.2, 127.0, 126.5, 124.9, 124.8, 124.1, 123.3, 116.7, 116.3, 115.2, 113.6, 59.7, 49.2, 47.0, 30.0, 30.7, 27.2, 26.5, 25.6, 22.6 ppm; ESI-HRMS: calcd. for $C_{40}H_{36}N_3O_3$+H 606.2757, found 606.2766.

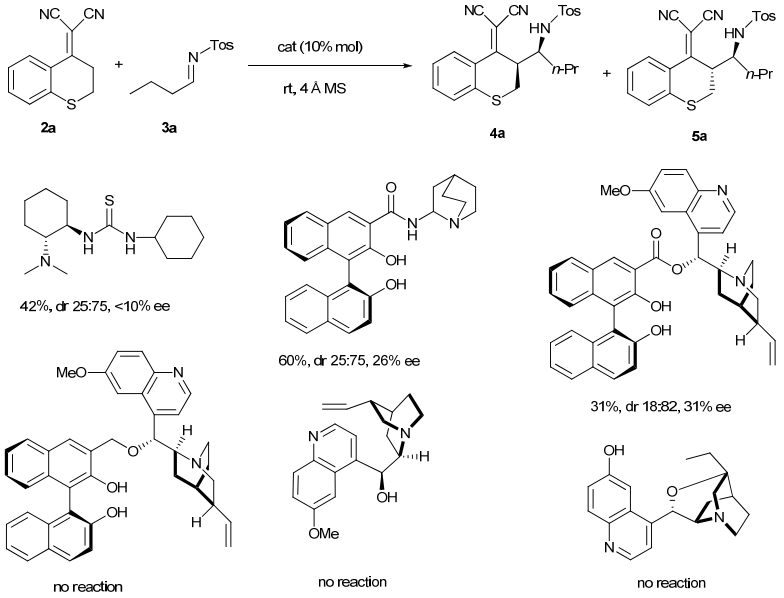
1f 24% yield; yellow solid; $[\alpha]_D^{20}$ = -40.8 (*c* = 0.80 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81, (d, *J* = 4.4 Hz, 1H), 8.41 (d, *J* = 8.8 Hz, 1H), 8.34 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.91-7.83



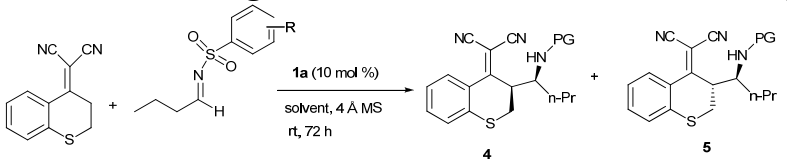
(m, 3H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 4.4 Hz, 1H), 7.43-7.27 (m, 4H), 7.21 (t, *J* = 6.8 Hz, 1H), 7.14-7.06 (m, 2H), 5.75-5.66 (m, 1H), 5.56 (br s, 1H), 5.02-4.95 (m, 2H), 3.37-3.31 (m, 2H), 3.20 (br s, 1H), 2.88-2.78 (m, 4H), 2.64 (br s, 1H), 2.36 (s, 1H), 1.73-1.68 (m, 3H), 1.50-1.42 (m, 1H), 1.07-1.02 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 189.6, 155.1, 152.3, 150.0, 146.5, 145.9, 140.5, 136.7, 133.6, 130.5, 130.2, 129.8, 129.5, 129.3, 128.3, 127.3, 127.1, 126.6, 125.0, 124.7, 124.3, 123.3, 123.2, 119.5, 116.5, 117.8, 115.8, 115.3, 114.4, 60.1, 55.7, 41.1, 39.2, 29.6, 27.5, 27.3, 25.9 ppm; ESI-HRMS: calcd. for $C_{40}H_{36}N_3O_3$+H 606.2757, found 606.2720.

3. More screening studies

3.1 Initial catalyst screenings



3.2 More screening studies of the AVM reaction of α,α-dicyanoolefin and alkylimine



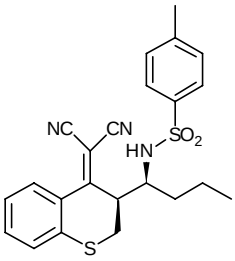
entry	R	solvent	yield (%)	dr (**4**:**5**)	ee (%)
1	4-Me	THF	93	27:73	<5/-
2	4-Me	DCM	88	57:43	87/-
3	4-Me	*m*-xylene	97	70:30	93/-
4	4-Me	C_6H_5F	81	73:27	92/-
5	4-Me	mesitylene	88	79:21	93/-
6	4-MeO	mesitylene	84	35:65	86/-
7	2,4-Me_2	mesitylene	75	86:14	93/-
8	2,4,6-Me_3	mesitylene	/	/	/
9[a]	2,4-Me_2	mesitylene	73	15:85	-/–58

[a] SBADC **1d** was used.

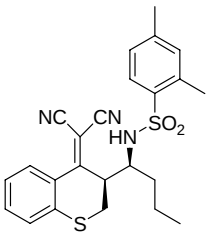
4. General procedure for AVM of α,α-dicyanoolefins and alkylimines

4.1 Asymmetric *syn*-stereoselective AVM reaction

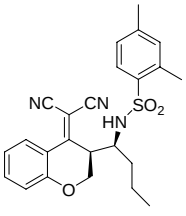
α,α-Dicyanoolefin **2** (0.1 mmol), alkylimine **3** (0.12 mmol), catalyst **1a** or **1e** (0.01 mmol) and 4 Å MS (30 mg) in dry mesitylene (0.4 mL) were stirred at room temperature (25 °C). After completion, the reaction mixture was subjected to flash chromatography to give *syn*-adduct **4**.



4a 70% yield; R_f = 0.1 (petroleum ether/EtOAc = 20:1); $[\alpha]_D^{20}$ = +33.4 (*c* = 0.50 in EtOH); 69:31 dr, 90% ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 21.73 min, t (minor) = 8.74 min]; ^{1}H NMR (400 MHz, $CDCl_3$) (major isomer): δ = 7.75 (t, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 8.4 Hz, 1H), 7.43-7.37 (m, 1H), 7.31-7.24 (m, 3H), 7.22-7.17 (m, 1H), 4.58 (d, *J* = 9.2 Hz, 1H), 3.74-3.62 (m, 1H), 3.60-3.43 (m, 1H), 3.19 (dd, *J* = 3.6, 13.6 Hz, 1H), 3.09 (dd, *J* = 4.4, 14.0 Hz, 1H), 2.44 (s, 3H), 1.49-1.39 (m, 1H), 1.12-0.85 (m, 3H), 0.63 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.0, 143.9, 137.9, 133.6, 133.5, 131.5, 130.1, 129.7, 127.4, 127.0, 126.8, 125.1, 125.0, 112.9, 53.2, 45.7, 36.0, 28.0, 21.5, 18.2, 13.5 ppm; SI-HRMS: calcd. for $C_{23}H_{23}N_3O_2S_2$+Na 460.1129, found 460.1132.

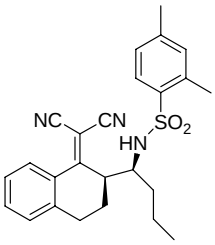


4b 98% yield; R_f = 0.1 (petroleum ether/EtOAc = 20:1); $[\alpha]_D^{20}$ = +204.5 (*c* = 1.01 in EtOH); 81:19 dr, 97% ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 15.88 min, t (minor) = 10.29 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.87 (m, 1H), 7.74 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.42-7.38 (m, 1H), 7.22-7.17 (m, 2H), 7.13-7.11 (m, 2H), 4.55-4.52 (m, 1H), 3.65 (qd, *J* = 4.0, 9.2 Hz, 1H), 3.46-3.41 (m, 1H), 3.17 (dd, *J* = 4.0, 13.6 Hz, 1H), 2.94 (dd, *J* = 4.0, 13.6 Hz, 1H), 2.59 (s, 3H), 2.39 (s, 3H), 1.35-1.02 (m, 2H), 0.91-0.83 (m, 2H), 0.65 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.0, 143.8, 138.4, 136.3, 136.0, 133.7, 133.2, 130.1, 129.6, 127.3, 126.9, 125.0, 124.8, 112.9, 112.7, 83.2, 53.1, 45.3, 36.0, 28.1, 21.3, 20.5, 18.2, 13.4 ppm; ESI-HRMS: calcd. for $C_{24}H_{25}N_3O_2S_2$+Na 474.1286, found 474.1277.

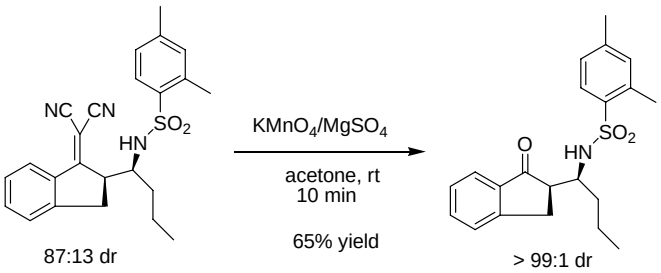


4c 92 yield; R_f = 0.1 (petroleum ether/EtOAc = 20:1); $[\alpha]_D^{20}$ = +6.4 (*c* = 0.62 in EtOH); 51:49 dr, 89% ee, determined by HPLC analysis [Daicel chiralcel AD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 16.64 min, t

(minor) = 25.24 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63-7.61 (m, 1H), 7.48-7.44 (m, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 0.8 Hz, 1H), 7.06 (d, *J* = 1.2 Hz, 1H), 6.95-6.87 (m, 2H), 4.63 (d, *J* = 10.0 Hz, 1H), 4.48 (dd, *J* = 1.6, 12.4 Hz, 1H), 4.17 (dd, *J* = 2.4, 12.8 Hz, 1H), 3.68-3.54 (m, 1H), 3.04-3.01 (m, 1H), 2.62 (s, 3H), 2.43 (s, 3H), 1.87-1.79 (m, 1H), 1.67-1.59 (m, 1H), 1.50-1.36 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.4, 156.0, 143.5, 136.6, 135.8, 133.5, 129.4, 128.9, 128.2, 127.5, 127.1, 121.6, 117.9, 113.9, 113.3, 66.3, 54.0, 44.3, 35.7, 25.4, 21.3, 18.8, 17.5, 13.9 ppm; ESI-HRMS: calcd. for $C_{24}H_{25}N_3O_3S$+H 436.1695, found 436.1667.



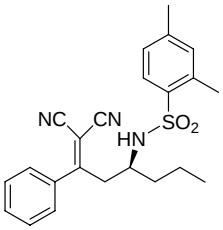
4d 89% yield; R_f = 0.1 (petroleum ether/EtOAc = 15:1); $[\alpha]_D^{20}$ = +99.7 (*c* = 1.00 in EtOH); 86:14 dr, 95% ee, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 19.43 min, t (minor) = 12.58 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (t, *J* = 7.2 Hz, 2H), 7.51-7.47 (m, 1H), 7.31 (t, *J* = 3.2 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.51 (d, *J* = 10.0 Hz, 1H), 3.53-3.46 (m, 1H), 3.28-3.23 (m, 1H), 3.02-2.94 (m, 1H), 2.69-2.63 (m, 1H), 2.51 (s, 3H), 2.39 (s, 3H), 1.98 (q, *J* = 6.0 Hz, 2H), 1.28-1.20 (m, 2H), 0.89-0.84 (m, 2H), 0.64 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.6, 143.8, 140.6, 136.4, 136.1, 133.6, 133.3, 129.5, 129.2, 129.0, 128.3, 126.9, 126.8, 126.6, 113.3, 113.2, 81.7, 54.3, 47.0, 38.5, 25.3, 23.2, 21.3, 20.5, 16.3, 13.6 ppm; ESI-HRMS: calcd. for $C_{25}H_{27}N_3O_2S$+Na 456.1722, found 156.1709.



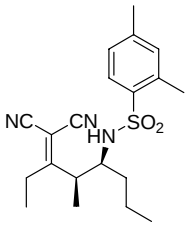
4e 87% yield, 87:13 dr (by ^{1}H NMR analysis); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.41-7.35 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.14-7.10 (m, 1H), 6.96 (s, 1H), 4.52 (d, *J* = 5.6 Hz, 1H), 4.03-3.97 (m, 1H), 3.45 (d, *J* = 8.0 Hz, 1H), 3.15 (dd, *J* = 7.6 Hz, 18.0 Hz, 1H), 2.97 (d, *J* = 18.0 Hz, 1H), 2.65 (s, 3H), 2.34 (s, 3H), 1.93-1.84 (m, 1H), 1.73-1.64 (m, 1H), 1.55-1.38 (m, 2H), 1.01 (t, *J* = 7.6 Hz, 3H) ppm.

90% ee, determined by HPLC analysis after conversion to β-amino ketone derivative; $[\alpha]_D^{20}$ = -1.01 (*c* = 0.80 in EtOH); [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 15.75 min, t (minor) = 27.30 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.0

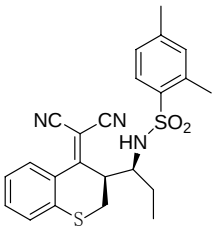
Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.61-7.57 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 5.81 (d, *J* = 10.0 Hz, 1H), 3.63-3.56 (m, 1H), 3.13 (dd, *J* = 8.4, 18.0 Hz, 1H), 2.74 (dd, *J* = 4.0, 17.6 Hz, 1H), 2.62-2.58 (m, 4H), 2.35 (s, 3H), 1.50-1.41 (m, 1H), 1.30-1.14 (m, 3H), 0.76 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.3, 153.6, 143.2, 137.1, 137.0, 136.1, 135.3, 133.2, 129.5, 127.6, 126.6, 126.5, 123.7, 54.8, 49.4, 32.8, 30.1, 21.3, 20.1, 19.2, 13.5 ppm; ESI-HRMS: calcd. for $C_{21}H_{25}NO_3S$+H 394.1453, found 394.1459.



4f 83% yield; R_f = 0.1 (petroleum ether/EtOAc = 20:1); $[\alpha]_D^{20}$ = +7.1 (*c* = 1.04 in EtOH); 63% ee, determined by HPLC analysis [Daicel chiralcel AD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 9.59 min, t (minor) = 8.51 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.0 Hz, 1H), 7.59-7.54 (m, 1H), 7.50-7.46 (m, 2H), 7.32-7.29 (m, 2H), 7.15 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 4.48 (d, *J* = 8.4 Hz, 1H), 3.26-3.20 (m, 1H), 3.10-3.04 (m, 2H), 2.58 (s, 3H), 2.39 (s, 3H), 1.32-1.17 (m, 3H), 1.06-0.97 (m, 1H), 0.61 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.6, 143.7, 136.9, 135.1, 133.7, 133.4, 132.4, 129.7, 129.2, 127.8, 126.7, 112.6, 112.3, 68.3, 52.5, 43.4, 37.2, 21.2, 20.3, 16.3, 13.1 ppm; ESI-HRMS: calcd. for $C_{23}H_{25}N_3O_2S$+Na 421.1481, found 421.1475.

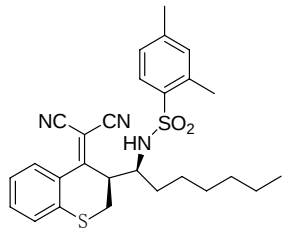


58% yield, for pure **4g**; R_f = 0.1 (petroleum ether/EtOAc = 20:1); $[\alpha]_D^{20}$ = +6.95 (*c* = 0.70 in EtOH); 96% ee, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 10.92 min, t (minor) = 9.95 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.82 (m, 1H), 7.15-7.12 (m, 2H), 4.32 (d, *J* = 9.6 Hz, 1H), 3.42-3.38 (m, 1H), 3.05-3.00 (m, 1H), 2.60 (s, 3H), 2.55-2.47 (m, 2H), 2.39 (s, 3H), 1.27-1.18 (m, 5H), 1.15 (d, *J* = 6.8 Hz, 3H), 1.06-0.89 (m, 2H), 0.72 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.4, 143.6, 136.3, 136.0, 133.3, 129.3, 127.0, 111.7, 111.5, 87.0, 57.0, 46.1, 36.7, 26.4, 21.3, 20.5, 16.4, 14.2, 13.8, 13.6 ppm; ESI-HRMS: calcd. for $C_{20}H_{27}N_3O_2S$+H 374.1902, found 374.1885.

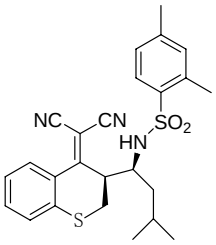


4h 95% yield, 82:18 dr (by ^{1}H NMR analysis); R_f = 0.1 (petroleum ether/EtOAc = 20:1); $[\alpha]_D^{20}$ = +65.9 (*c* = 0.43 in EtOH); 97% ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 12.51 min, t (minor) = 8.84 min]; ^{1}H NMR (400 MHz, $CDCl_3$):

δ = 7.88 (t, *J* = 4.4 Hz, 1H), 7.76-7.74 (m, 1H), 7.43-7.39 (m, 1H), 7.21-7.16 (m, 2H), 7.13 (s, 2H), 4.48 (d, *J* = 9.6 Hz, 1H), 3.63 (qd, *J* = 4.8, 9.2 Hz, 1H), 3.45-3.40 (m, 1H), 3.20 (dd, *J* = 4.0, 13.6 Hz, 1H), 2.97 (dd, *J* = 4.0, 13.6 Hz, 1H), 2.61 (s, 3H), 2.40 (s, 3H), 1.36-1.26 (m, 2H), 0.80 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.8, 143.9, 138.4, 136.3, 135.9, 133.7, 133.2, 130.1, 129.7, 127.3, 127.0, 125.9, 125.0, 112.9, 112.7, 83.3, 54.4, 44.9, 28.1, 26.7, 21.3, 20.5, 9.4 ppm; ESI-HRMS: calcd. for $C_{23}H_{23}N_3O_2S_2$+Na 460.1129, found 460.1144.

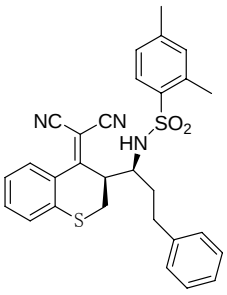


4i 92% yield; R_f = 0.1 (petroleum ether/EtOAc = 20:1); $[\alpha]_D^{20}$ = +86.5 (*c* = 1.04 in EtOH); 91:9 dr, 86% ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 13.11 min, t (minor) = 11.21 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88-7.86 (m, 1H), 7.74 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.42-7.35 (m, 1H), 7.23-7.15 (m, 2H), 7.12 (d, *J* = 4.8 Hz, 2H), 4.53 (d, *J* = 9.6 Hz, 1H), 3.63 (qd, *J* = 4.0, 8.8 Hz, 1H), 3.47-3.42 (m, 1H), 3.20 (dd, *J* = 4.0, 13.6 Hz, 1H), 3.06 (dd, *J* = 4.0, 13.6 Hz, 1H), 2.59 (s, 3H), 2.38 (s, 3H), 1.35-1.24 (m, 2H), 1.17-1.04 (m, 2H), 1.00-0.90 (m, 3H), 0.89-0.83 (m, 3H), 0.81 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.9, 143.6, 138.4, 133.6, 133.2, 131.2, 130.1, 129.6, 129.1, 127.3, 126.9, 126.0, 124.9, 112.7, 112.6, 53.4, 45.5, 33.7, 31.3, 26.5, 26.0, 24.8, 22.3, 21.2, 20.5 13.9 ppm; ESI-HRMS: calcd. for $C_{25}H_{25}N_3O_2S_2$+Na 516.1755, found 516.1741.

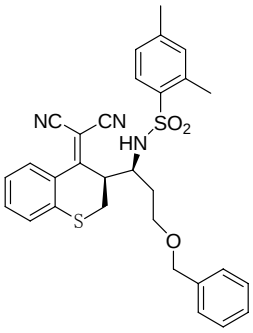


4j 97% yield; R_f = 0.1 (petroleum ether/EtOAc = 20:1); $[\alpha]_D^{20}$ = +263.3 (*c* = 2.02 in EtOH); 84:16 dr, 97% ee, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 31.32 min, t (minor) = 11.97 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.21-7.14 (m, 2H), 7.12 (s, 1H), 4.50 (d, *J* = 8.8 Hz, 1H), 3.67-3.60 (m, 1H), 3.49-3.45 (m, 1H), 3.16 (dd, *J* = 4.0, 13.6 Hz, 1H), 2.94 (dd, *J* = 4.4, 13.6 Hz, 1H), 2.59 (s, 3H), 2.38 (s, 3H), 1.45-1.31 (m, 2H), 0.88-0.83 (m, 1H), 0.66 (d, *J* = 6.8 Hz, 3H), 0.32 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.4, 143.8, 136.4, 136.3, 133.6, 133.2, 131.4, 130.2, 129.5, 127.3, 126.6, 126.5, 126.2, 124.9, 112.9, 112.7, 63.1, 52.2, 46.0, 43.7, 26.1, 24.0, 23.2, 21.1, 20.7, 20.4 ppm; ESI-HRMS: calcd. for $C_{25}H_{27}N_3O_2S_2$+K 504.1182, found 504.1186.

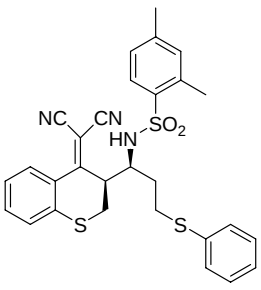
4k 84% yield; R_f = 0.1 (petroleum ether/EtOAc = 20:1); $[\alpha]_D^{20}$ = +45.9 (*c* = 0.70 in EtOH); 82:18 dr, 96% ee, determined by HPLC analysis [Daicel chiralcel AD, *n*-hexane/*i*-PrOH = 80/20, 1.0



mL/min, λ = 254 nm, t (major) = 8.96 min, t (minor) = 15.54 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.90 (m, 1H), 7.67 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.40-7.36 (m, 1H), 7.20-7.11 (m, 7H), 6.84-6.82 (m, 2H), 4.69 (d, *J* = 9.2 Hz, 1H), 3.68 (qd, *J* = 4.0, 9.2 Hz, 1H), 3.58-3.54 (m, 1H), 3.22 (dd, *J* = 4.0, 13.6 Hz, 1H), 3.03 (dd, *J* = 4.0, 13.6 Hz, 1H), 2.63 (s, 3H), 2.55-2.48 (m, 1H), 2.39 (s, 3H), 2.29-2.22 (m, 1H), 1.72-1.62 (m, 1H), 1.55-1.46 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.7, 143.9, 140.0, 138.2, 136.3, 138.2, 133.7, 133.3, 131.1, 130.0, 129.6, 128.5, 128.2, 128.0, 127.2, 127.0, 126.2, 125.0, 112.8, 112.7, 83.1, 53.4, 44.9, 35.3, 31.3, 28,1, 21.3, 20.5 ppm; ESI-HRMS: calcd. for $C_{29}H_{27}N_3O_2S_2$+Na 536.1442, found 536.1415.



4l 89% yield; R_f = 0.1 (petroleum ether/EtOAc = 20:1); $[\alpha]_D^{20}$ = +86.3 (*c* = 0.96 in EtOH); 90:10 dr, 97% ee, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 48.35 min, t (minor) = 42.14 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.39-7.32 (m, 4H), 7.29-7.26 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.07-7.04 (m, 2H), 5.83 (d, *J* = 9.2 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H), 4.41 (d, *J* = 11.6 Hz, 1H), 3.76-3.72 (m, 1H), 3.61-3.52 (m, 3H), 3.23 (t, *J* = 2.4 Hz, 2H), 2.48 (s, 3H), 2.36 (s, 3H), 1.66-1.60 (m, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.1, 143.7, 136.6, 137.3, 136.7, 135.7, 133.7, 133.2, 131.4, 129.7, 128.6, 128.2, 128.0, 127.0, 126.8, 125.5, 124.7, 112.8, 112.6, 83.6, 73.5, 66.5, 51.5, 43.6, 31.8, 26.6, 21.3, 20.3 ppm; ESI-HRMS: calcd. for $C_{30}H_{30}N_3O_3S_2$+H 544.1729, found 544.1727.

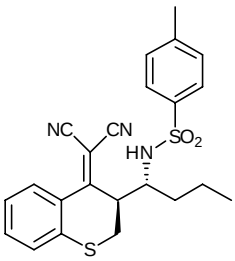


4m 86% yield, 88:12 dr (by ^{1}H NMR analysis); R_f = 0.1 (petroleum ether/EtOAc = 15:1); $[\alpha]_D^{20}$ = +27.5 (*c* = 0.76 in EtOH); 94% ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 17.04 min, t (major) = 49.33 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.6 Hz, 1H), 7.40-7.35 (m, 2H), 7.29-7.22 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.13-7.06 (m, 4H), 7.03 (t, *J* = 8.0 Hz, 1H), 4.85 (d, *J* = 9.2 Hz, 1H), 3.77 (qd, *J* = 2.8, 9.6 Hz, 1H), 3.49-3.45 (m, 1H), 3.19 (dd, *J* = 3.6, 13.6 Hz, 1H), 2.98 (dd, *J* = 3.6, 13.6 Hz, 1H), 2.78-2.72 (m, 1H), 2.59 (s, 3H), 2.49-2.42 (m, 1H), 2.37 (s, 3H), 1.77-1.68 (m, 1H), 1.49-1.42 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.5, 144.6, 138.5, 136.7, 136.5, 135.4, 134.3, 133.8, 130.6, 130.4, 130.0, 129.5, 127.6, 127.1, 125.5, 113.2, 113.1, 53.1, 45.2, 33.8, 30.1, 28.6, 21.8, 21.0 ppm; ESI-HRMS: calcd.

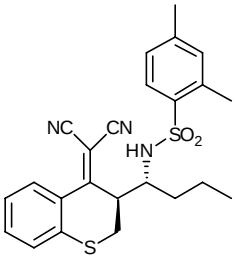
for $C_{29}H_{27}N_3O_2S_3$+Na 568.1163, found 568.1162.

4.2 Asymmetric *anti*-stereoselective AVM reaction.

α,α-Dicyanoolefin **2** (0.1 mmol), alkylimine **3** (0.12 mmol), catalyst **1f** or **1d** (0.01 mmol) and 4 Å MS (30 mg) in dry mesitylene (0.2 mL) were stirred at room temperature (25 °C). After completion, the reaction mixture was subjected to flash chromatography to give *anti*-adduct **5** or **6**.

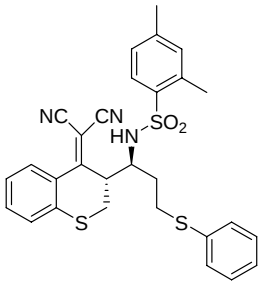


5a 50% yield; R_f = 0.1 (petroleum ether/EtOAc = 20:1); $[\alpha]_D^{20}$ = +26.6 (*c* = 0.60 in EtOH); 80:20 dr, 61% ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 7.88 min, t (minor) = 12.78 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.4 Hz, 3H), 7.41-7.39 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 4.72 (t, *J* = 8.8 Hz, 1H), 3.69-3.62 (m, 1H), 3.51-3.47 (m, 1H), 3.41 (dd, *J* = 3.6, 14.4 Hz, 1H), 2.94 (dd, *J* = 4.4, 14.0 Hz, 1H), 2.45 (s, 3H), 1.60-1.52 (m, 1H), 1.49-1.42 (m, 1H), 1.33-1.25 (m, 1H), 1.20-1.13 (m, 1H), 0.81 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.1, 143.7, 138.1, 137.4, 133.5, 131.5, 129.7, 127.1, 126.8, 126.3, 125.0, 113.4, 83.6, 54.6, 44.8, 34.8, 28.3, 21.5, 17.6, 13.8 ppm; ESI-HRMS: calcd. for $C_{23}H_{23}N_3NaO_2S_2$+Na 460.1129, found 460.1124.

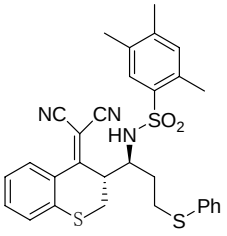


5b 73% yield; R_f = 0.1 (petroleum ether/EtOAc = 20:1); $[\alpha]_D^{20}$ = +65.7 (*c* = 0.50 in EtOH); 85:15 dr, 58% ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 7.76 min, t (minor) = 11.06 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.0 Hz, 1H), 7.36-7.32 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.19-7.16 (m, 2H), 7.01-6.96 (t, *J* = 8.4 Hz, 2H), 4.67 (d, *J* = 10.0 Hz, 1H), 3.70-3.62 (m, 1H), 3.47-3.38 (m, 2H), 2.95 (dd, *J* = 4.0, 14.0 Hz, 1H), 2.59 (s, 3H), 2.42 (s, 3H), 1.72-1.65 (m, 1H), 1.57-1.48 (m, 1H), 1.43-1.21 (m, 2H), 0.59 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.1, 143.7, 137.3, 136.6, 136.1, 133.4, 133.3, 131.1, 129.1, 127.3, 127.0, 125.7, 124.8, 113.4, 54.5, 44.0, 35.2, 28.3, 21.3, 20.2, 17.2, 13.9 ppm; ESI-HRMS: calcd. for $C_{24}H_{25}N_3NaO_2S_2$+Na 474.1286, found 474.1278.

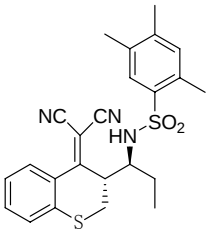
5m 67% yield, 87:13 dr (by ^{1}H NMR analysis); R_f = 0.1 (petroleum ether/EtOAc = 15:1); $[\alpha]_D^{20}$ = -67.9 (*c* = 0.81 in EtOH); 52% ee, determined by HPLC analysis [Daicel chiralcel AD,



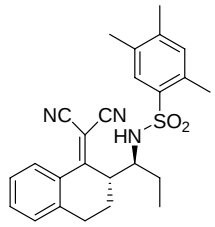
n-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 6.90 min, t (minor) = 8.11 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.0 Hz, 1H), 7.38-7.33 (m, 2H), 7.32-7.29 (m, 2H), 7.27-7.21 (m, 3H), 7.18 (dd, *J* = 0.8, 8.0 Hz, 2H), 7.03-6.97 (m, 2H), 4.79 (d, *J* = 10.4 Hz, 1H), 3.81 (qd, *J* = 3.2, 10.0 Hz, 1H), 3.56-3.51 (m, 1H), 3.35 (dd, *J* = 3.6, 14.4 Hz, 1H), 2.99-2.92 (m, 1H), 2.82-2.73 (m, 2H), 2.58 (s, 3H), 2.42 (s, 3H), 2.08-2.00 (m, 1H), 1.81-1.72 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.8, 142.8, 136.3, 135.4, 134.9, 134.0, 132.4, 130.1, 128.7, 128.1, 127.3, 126.2, 126.1, 125.6, 125.2, 124.0, 112.2, 111.8, 82.5, 53.2, 44.2, 31.5, 28.4, 27.3, 20.3, 19.5 ppm; ESI-HRMS: calcd. for $C_{29}H_{27}N_3O_2S_3$+H 546.1344, found 546.1349.



6a 70% yield, 84:16 dr (by ^{1}H NMR analysis); R_f = 0.1 (petroleum ether/EtOAc = 15:1); $[\alpha]_D^{20}$ = -50.5 (*c* = 0.60 in EtOH); 83% ee, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 15.93 min, t (minor) = 11.24 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (s, 1H), 7.35 (s, 1H), 7.33-7.30 (m, 4H), 7.19-7.14 (m, 4H), 6.96-6.93 (m, 1H), 4.68 (d, *J* = 9.6 Hz, 1H), 3.84-3.79 (m, 1H), 3.54-3.49 (m, 1H), 3.34 (dd, *J* = 3.6, 14.0 Hz, 1H), 3.04-2.98 (m, 1H), 2.85-2.78 (m, 2H), 2.54 (s, 3H), 2.32 (s, 3H), 2.22 (s, 3H), 2.12 (m, 1H), 1.83-1.74 (m, 1H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.8, 142.4, 137.3, 136.0, 135.5, 134.6, 133.9, 133.2, 130.9, 130.6, 129.8, 127.3, 127.0, 125.5, 124.7, 124.5, 113.3, 112.9, 83.0, 55.2, 43.2, 28.1, 25.8, 19.9, 19.7, 19.1, 8.0 ppm; ESI-HRMS: calcd. for $C_{30}H_{29}N_3O_2S_3$+H 560.1500, found 560.1493.



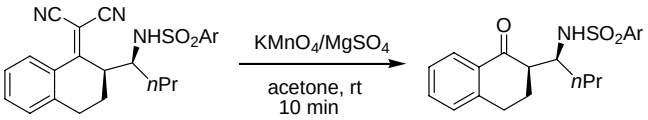
6b 73% yield, 84:16 dr (by ^{1}H NMR analysis); R_f = 0.1 (petroleum ether/EtOAc = 15:1); $[\alpha]_D^{20}$ = -157.1 (*c* = 1.05 in EtOH); 73% ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 9.83 min, t (minor) = 6.68 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.30 (m, 2H), 7.19-7.15 (m, 3H), 6.91-6.87 (m, 1H), 4.59 (d, *J* = 10.4 Hz, 1H), 3.66-3.63 (m, 1H), 3.44-3.37 (m, 2H), 2.94 (dd, *J* = 4.4, 14.4 Hz, 1H), 2.57 (s, 3H), 2.33 (s, 3H), 2.18 (s, 3H), 1.95-1.88 (m, 1H), 1.68-1.61 (m, 1H), 1.00 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.8, 142.4, 137.3, 136.0, 135.5, 134.6, 133.9, 133.2, 130.9, 129.9, 127.3, 127.0, 124.5, 113.3, 112.9, 55.2, 43.2, 28.1, 25.8, 19.9, 19.6, 19.1, 8.0 ppm; ESI-HRMS: calcd. for $C_{24}H_{25}N_3O_2S_2$+H 452.1466, found 452.1472.



6c 60% yield, 85:15 dr (by ^{1}H NMR analysis); R_f = 0.1 (petroleum ether/EtOAc = 15:1); $[\alpha]_D^{20}$ = -17.5 (*c* = 0.59 in EtOH); 77% ee, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 16.79 min, t (minor) = 10.57 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.39 (m, 1H), 7.33 (s, 1H), 7.23 (t, *J* = 7.2 Hz, 2H), 7.19 (s, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 4.55 (d, *J* = 10.4 Hz, 1H), 3.46-3.38 (m, 1H), 3.34-3.29 (m, 1H), 2.93-2.79 (m, 2H), 2.61 (s, 3H), 2.35 (s, 3H), 2.18 (s, 3H), 2.12-2.04 (m, 1H), 2.02-1.95 (m, 1H), 1.93-1.84 (m, 1H), 1.64-1.53 (m, 1H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.1, 139.5, 136.0, 135.5, 134.5, 134.0, 133.2, 129.9, 129.1, 128.9, 127,3, 126.6, 126.4, 100.8, 56.1, 45.7, 25.9, 25.1, 24.9, 20.0, 19.6, 19.1, 8.1 ppm; ESI-HRMS: calcd. for $C_{25}H_{27}N_3O_2S$+H 434.1902, found 434.1908.

4.3. Synthetic transformations of the AVM adducts

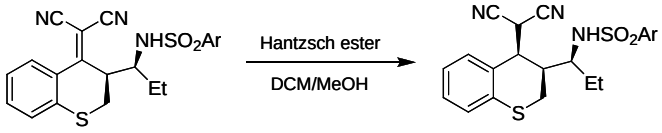
Synthesis of β-amino compound 7



4d 95% ee, dr 86:14 Ar = 2,4-$Me_2C_6H_3$ **7** 95% ee, dr >99:1

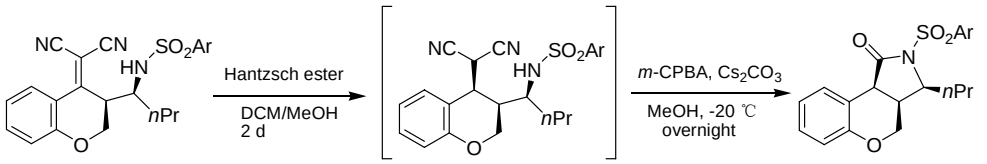
A flask equipped with a magnetic bar was charged with **4d** (43 mg, 0.10 mmol), $KMnO_4$ (0.25 mmol) and anhydrous $MgSO_4$ (0.20 mmol). Then acetone (1 mL) and water (one drop) was added and the mixture was stirred at room temperature for 10 min. The mixture was concentrated and flash chromatograph on silica gel (PE/AcOEt = 20:1) gave diastereomerically pure **7** as a white solid (29 mg, 76% yield). R_f = 0.1 (petroleum ether/EtOAc = 30:1); $[\alpha]_D^{20}$ = -11.2 (*c* = 0.90, EtOH); 95% ee, determined by HPLC analysis [Daicel chiralpak AD, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 10.62 min, t (minor) = 12.27 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 6.8 Hz, 1H), 7.86 (t, *J* = 4.0 Hz, 1H), 7.48-7.44 (m, 1H), 7.29 (t, *J* = 4.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 3.2 Hz, 2H), 4.88 (d, *J* = 8.8 Hz, 1H), 3.71-3.64 (m, 1H), 2.99-2.93 (m, 1H), 2.81-2.76 (m, 1H), 2.59 (s, 3H), 2.35 (s, 3H), 2.11-2.05 (m, 1H), 2.02-1.92 (m, 1H), 1.55-1.51 (m, 1H), 1.42-1.33 (m, 1H), 1.26-1.03 (m, 2H), 0.72 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 198.7, 143.8, 143.2, 136.6, 135.8, 133.5, 133.1, 132.7, 129.6, 128.7, 127.2, 126.7, 126.6, 54.6, 51.5, 35.4, 28.3, 25.7, 21.2, 20.4, 19.4, 13.5 ppm; ESI-HRMS: calcd. for $C_{22}H_{27}NO_3S$+Na 408.1609, found 408.1610.

Synthesis of δ-amino compound 8



Hantzsch ester (158 mg, 0.6 mmol) was added to a stirred solution of diastereomerically pure **4h** (44 mg, 0.1 mmol) in DCM/EtOH (1:1, 2 mL). The solution was stirred at 50 °C and monitor by TLC. After 48 h, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/AcOEt = 20:1) to give the reduced product **8** (42 mg, 95%) as a solid. R_f = 0.1 (petroleum ether/EtOAc = 13:1); $[\alpha]_D^{20}$ = -6.6 (*c* = 0.28 in EtOH); 98% ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 34.54 min, t (minor) = 22.19 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.8 Hz, 1H), 7.27-7.25 (m, 1H), 7.24-7.21 (m, 2H), 7.16-7.12 (m, 3H), 4.61 (d, *J* = 9.6 Hz, 1H), 4.55 (d, *J* = 7.2 Hz, 1H), 3.68-3.60 (m, 1H), 3.44 (d, *J* = 7.2 Hz, 1H), 3.33 (dd, *J* = 4.0, 13.2 Hz, 1H), 2.96 (t, *J* = 12.8 Hz, 1H), 2.59 (s, 3H), 2.39 (s, 3H), 2.27-2.21 (m, 1H), 1.58-1.48 (m, 1H), 1.45-1.37 (m, 1H), 0.68 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1, 136.3, 134.0, 133.3, 132.6, 132.0, 131.1, 130.1, 129.7, 129.6, 127.2, 127.1, 112.6, 111.5, 56.3, 43.4, 40.8, 25.9, 24.2, 22.4, 21.2, 20.4, 8.5 ppm; ESI-HRMS: calcd. for $C_{23}H_{26}N_3O_2S_2$+H 440.1466, found 440.1470.

Synthesis of γ-amino compound 9



Compound **4c** was reduced via the same procedure as above. Then the intermediate was directly used in the next step. *m*-CPBA (23 mg, 0.15 mmol) and Cs_2CO_3 (34 mg, 0.105 mmol) were added to a solution of the obtained intermediate (44 mg, 0.1 mmol) in methanol (1.5 mL) at -20 °C for 8 h. Then the solvent was concentrated and flash chromatograph on silica gel (PE/AcoEt = 30:1) gave the product **9** (15 mg, 37% yield for steps). R_f = 0.1 (petroleum ether/EtOAc = 30:1); $[\alpha]_D^{20}$ = -3.7 (*c* = 0.70, EtOH); 90% ee, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 7.36 min, t (minor) = 7.96 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 6.8 Hz, 1H), 7.19-7.15 (m, 2H), 7.10 (s, 1H), 6.93 (td, *J* =1.2, 7.6 Hz, 1H), 6.84 (dd, *J* = 0.8, 8.0 Hz, 1H), 4.55-4.50 (m, 1H), 4.32 (dd, *J* = 4.0, 11.6 Hz, 1H), 3.89 (dd, *J* = 8.8, 12.0 Hz, 1H), 3.61 (d, *J* = 8.0 Hz, 1H), 2.99-2.92

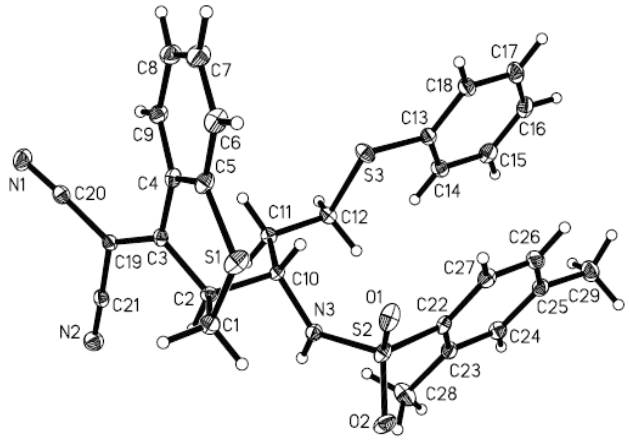
(m, 1H), 2.60 (s, 3H), 2.37 (s, 3H), 1.65-1.49 (m, 4H), 1.02 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.6, 154.2, 144.8, 137.6, 134.4, 133.2, 131.3, 130.5, 128.8, 127.0, 121.5, 116.8, 115.8, 63.0, 61.5, 42.0, 32.7, 32.0, 21.4, 20.3, 19.3, 14.2, 14.0 ppm; ESI-HRMS: calcd. for $C_{22}H_{25}NO_4S$+K 438.1141, found 438.1148.

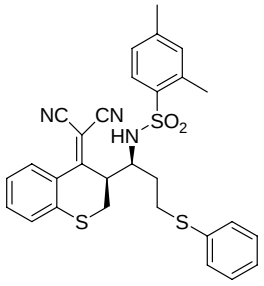
Reference:

1. T. Ooi, Y. Uematsu and K. Maruoka, *J. Am. Chem. Soc*., 2006, **128**, 2548.
2. H.-L. Cui, J. Peng, X. Feng, W. Du, K. Jiang and Y.-C. Chen, *Chem.–Eur. J.* 2009, **15**, 1574.

5. Crystal data for *syn*-4m and *anti*-5m

Crystal data and structure refinement for *syn*-4m



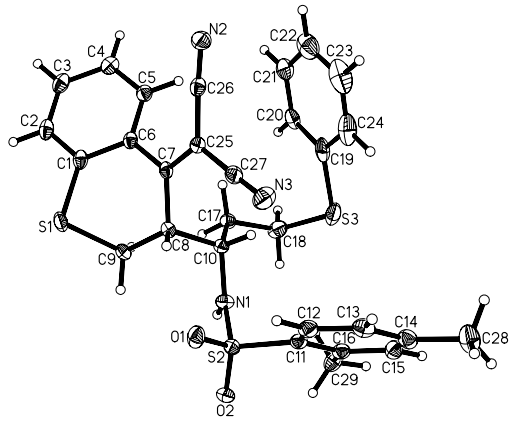


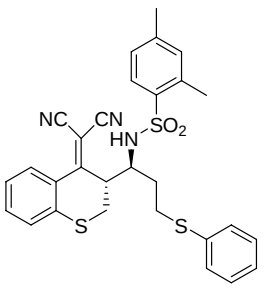
4m

Identification code	***syn*-4m**
Empirical formula	C29 H27 N3 O2 S3
Formula weight	545.72
Temperature	113(2) K
Wavelength	0.71070 A
Crystal system, space group	Monoclinic, P 1 21 1
Unit cell dimensions	a = 7.2498(8) A alpha = 90 deg. b = 13.0008(15) A beta = 90.274(3) deg. c = 14.4114(18) A gamma = 90 deg.
Volume	1358.3(3) A^3
Z, Calculated density	2, 1.334 Mg/m^3

Absorption coefficient	0.305 mm^-1
F(000)	572
Crystal size	0.14 x 0.12 x 0.10 mm
Theta range for data collection	3.13 to 27.48 deg.
Limiting indices	-9<=h<=9, -15<=k<=16, -18<=l<=18
Reflections collected / unique	16640 / 6100 [R(int) = 0.0516]
Completeness to theta = 27.48	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.970 and 0.942
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6100 / 1 / 340
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0863
R indices (all data)	R1 = 0.0471, wR2 = 0.0909
Absolute structure parameter	0.00(5)
Largest diff. peak and hole	0.194 and -0.305 e.A^-3

Crystal data and structure refinement for *anti*-5m



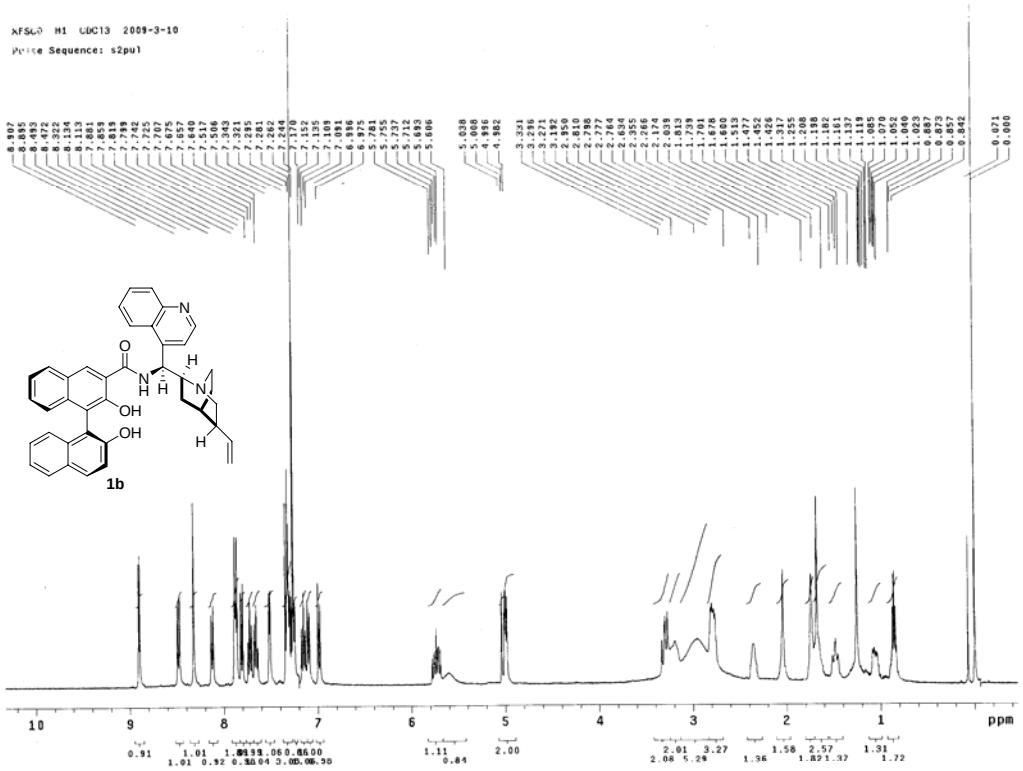


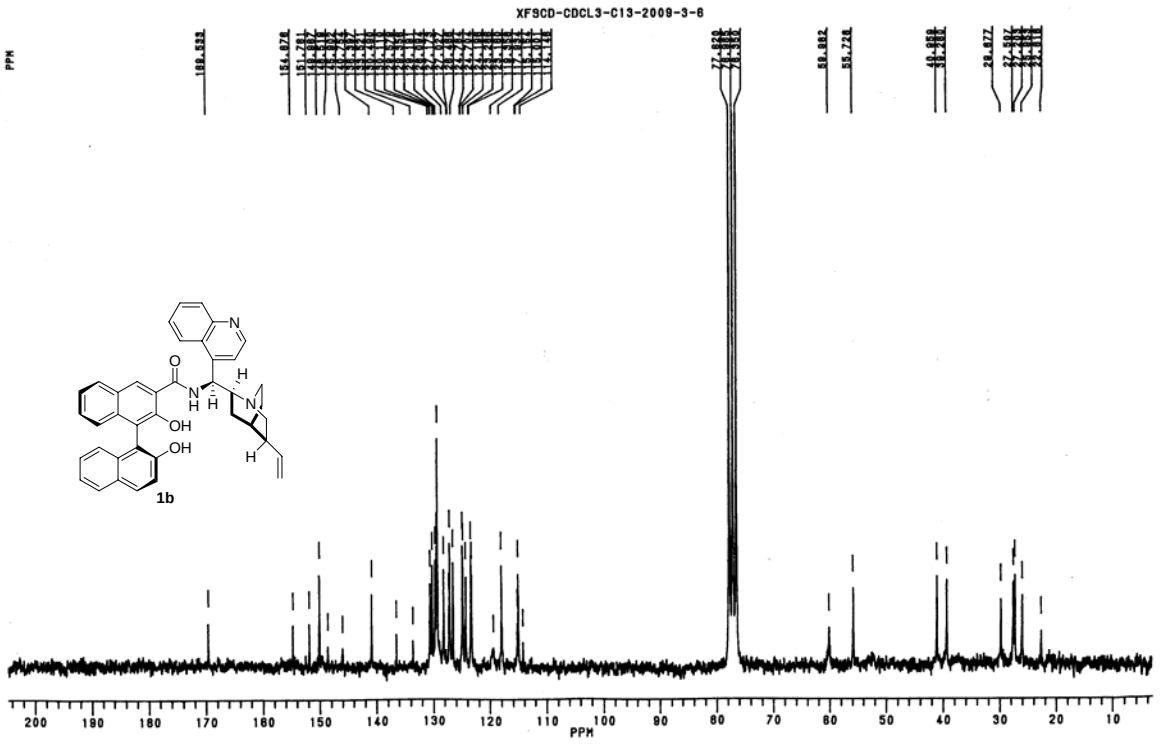
5m

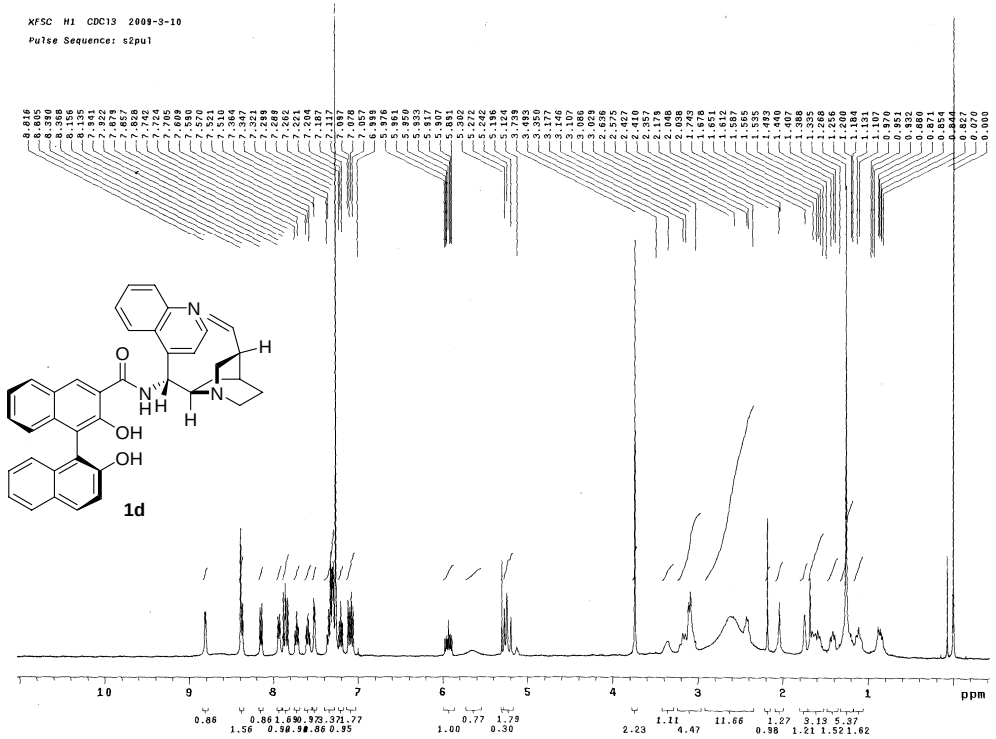
Identification code	***anti*-5m**

Empirical formula	C29 H27 N3 O2 S3
Formula weight	545.72
Temperature	93(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 9.2353(10) A alpha = 90 deg. b = 16.2177(18) A beta = 90 deg. c = 17.641(2) A gamma = 90 deg.
Volume	2642.2(5) A^3
Z, Calculated density	4, 1.372 Mg/m^3
Absorption coefficient	0.313 mm^-1
F(000)	1144
Crystal size	0.40 x 0.40 x 0.27 mm
Theta range for data collection	3.19 to 27.48 deg.
Limiting indices	-11<=h<=11, -21<=k<=16, -22<=l<=22
Reflections collected / unique	21830 / 6032 [R(int) = 0.0302]
Completeness to theta = 27.48	99.7 %
Absorption correction	Empirical
Max. and min. transmission	0.9210 and 0.8849
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6032 / 0 / 340
Goodness-of-fit on F^2	1.000
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0716
R indices (all data)	R1 = 0.0319, wR2 = 0.0726
Absolute structure parameter	-0.03(4)
Largest diff. peak and hole	0.280 and -0.249 e.A^-3

6. NMR spectra and HPLC chromatograms



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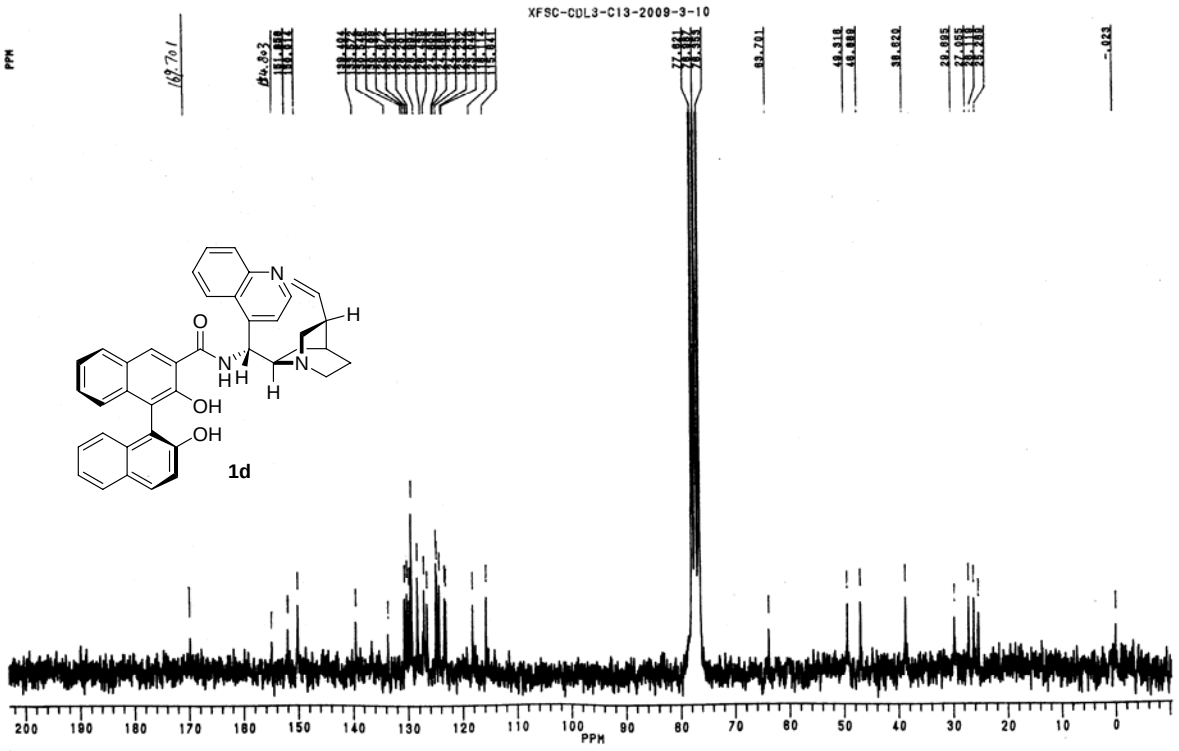
Pulse Sequence: s2pul
1d
ppm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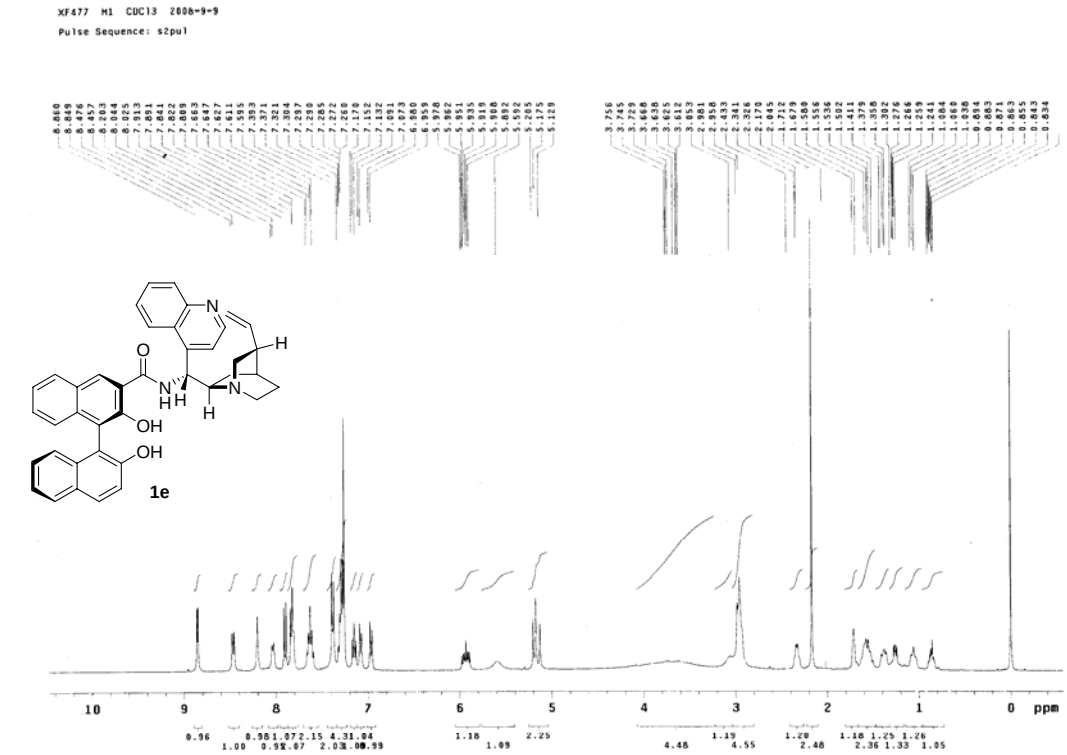
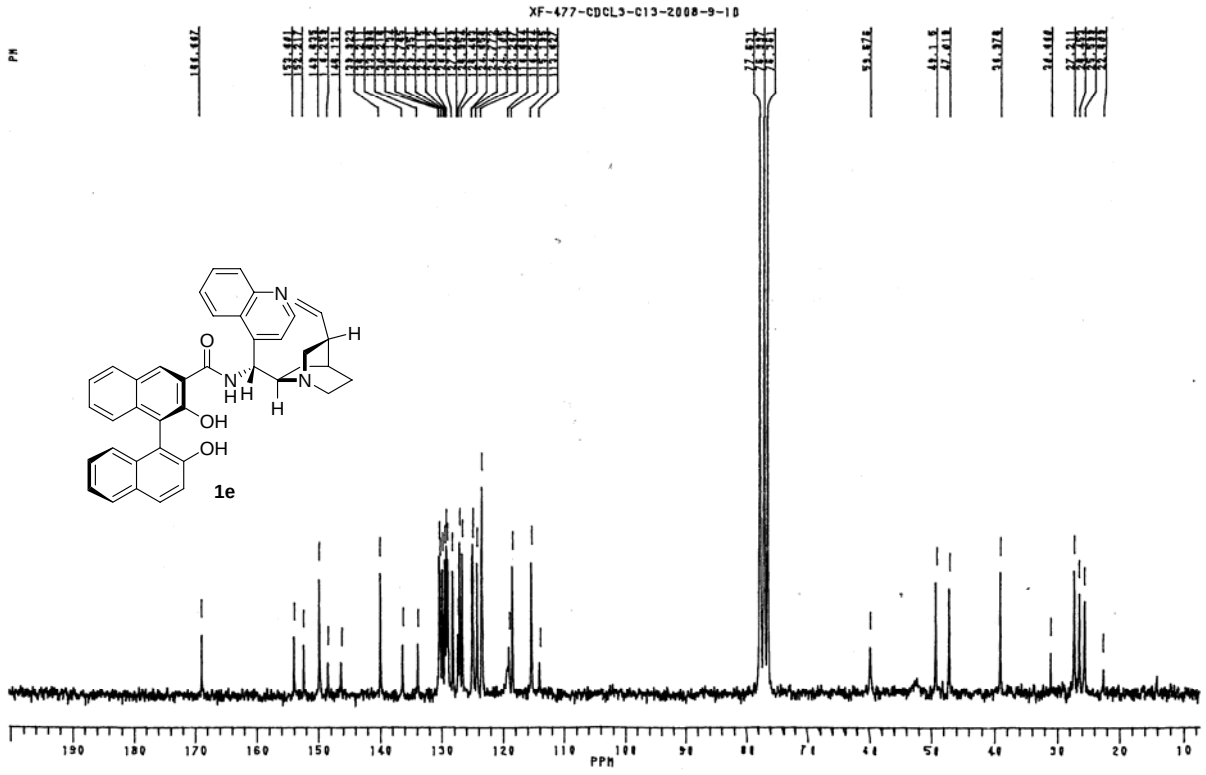
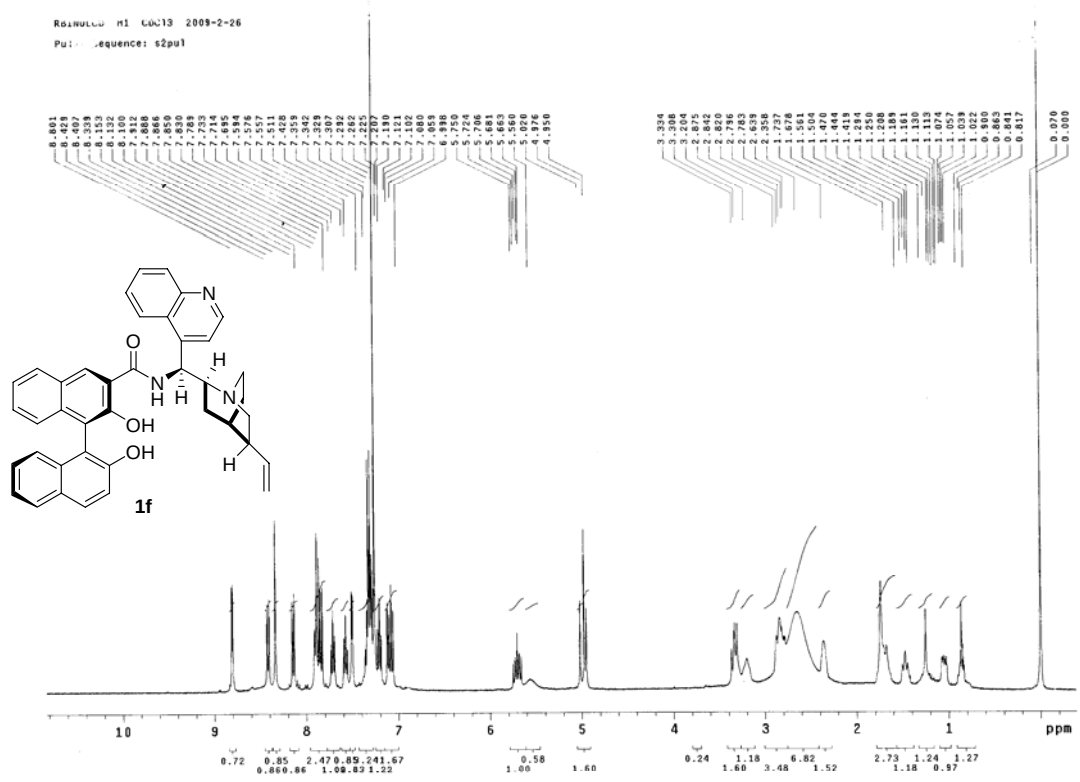
1d
PPM


XF477 H1 CDCl3 2008-9-9
Pulse Sequence: s2pul
1e
ppm


XF-477-CDCL3-C13-2008-9-10
1e
PPM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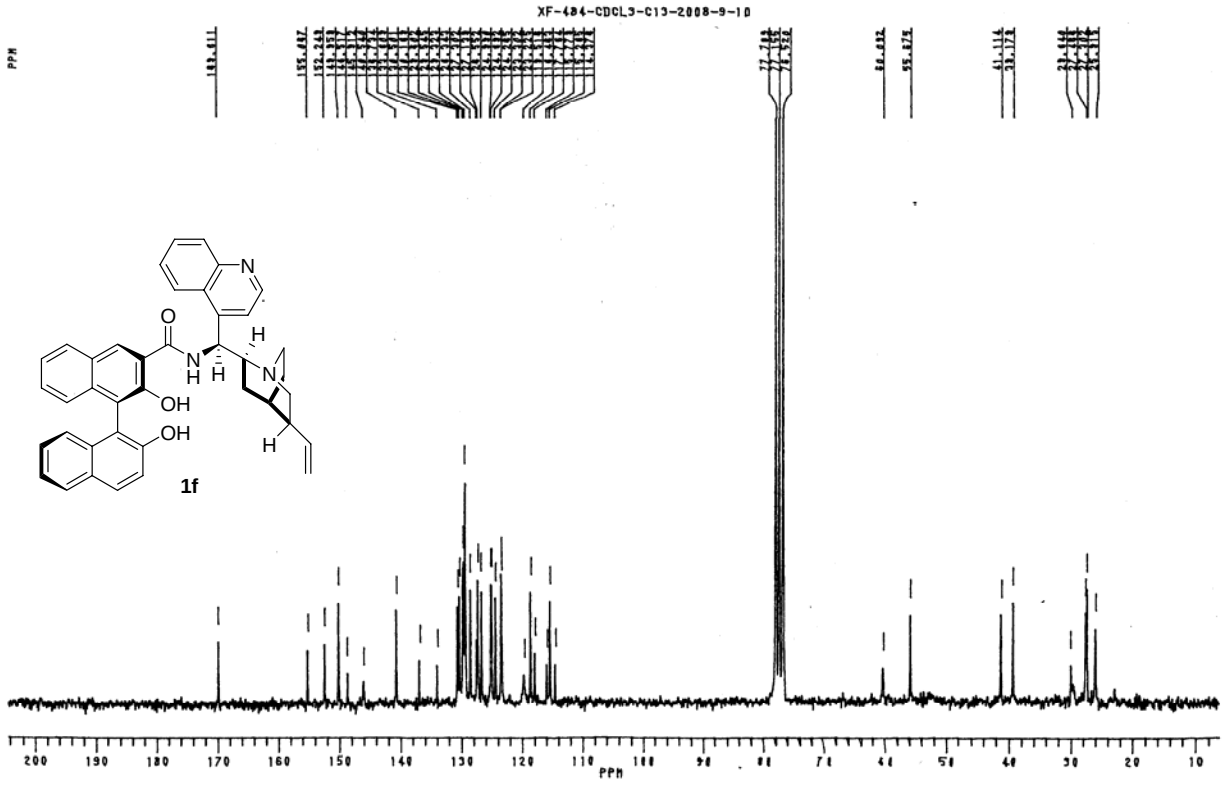
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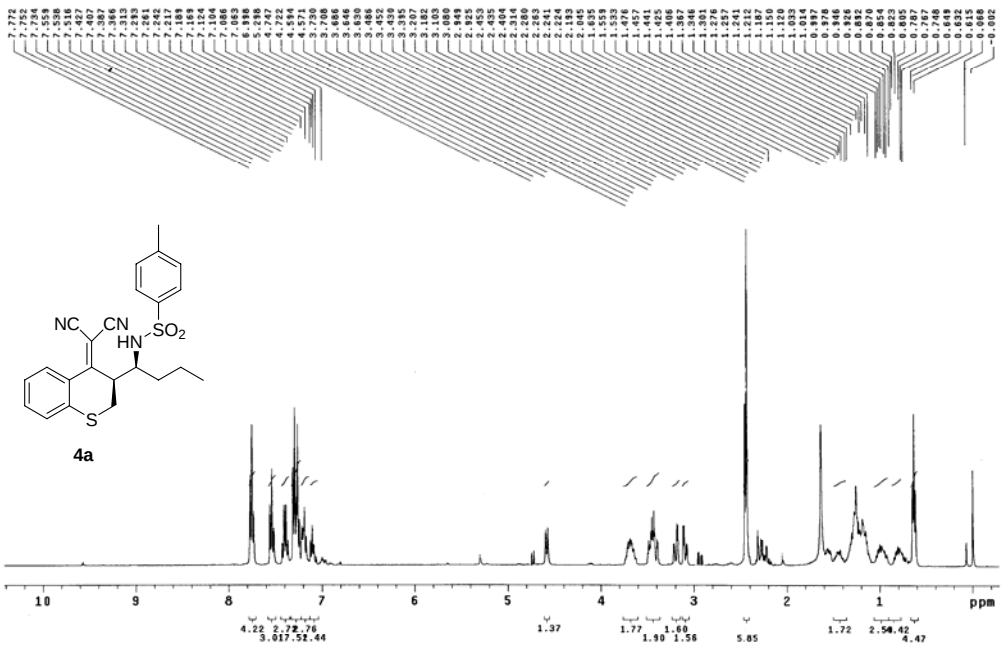
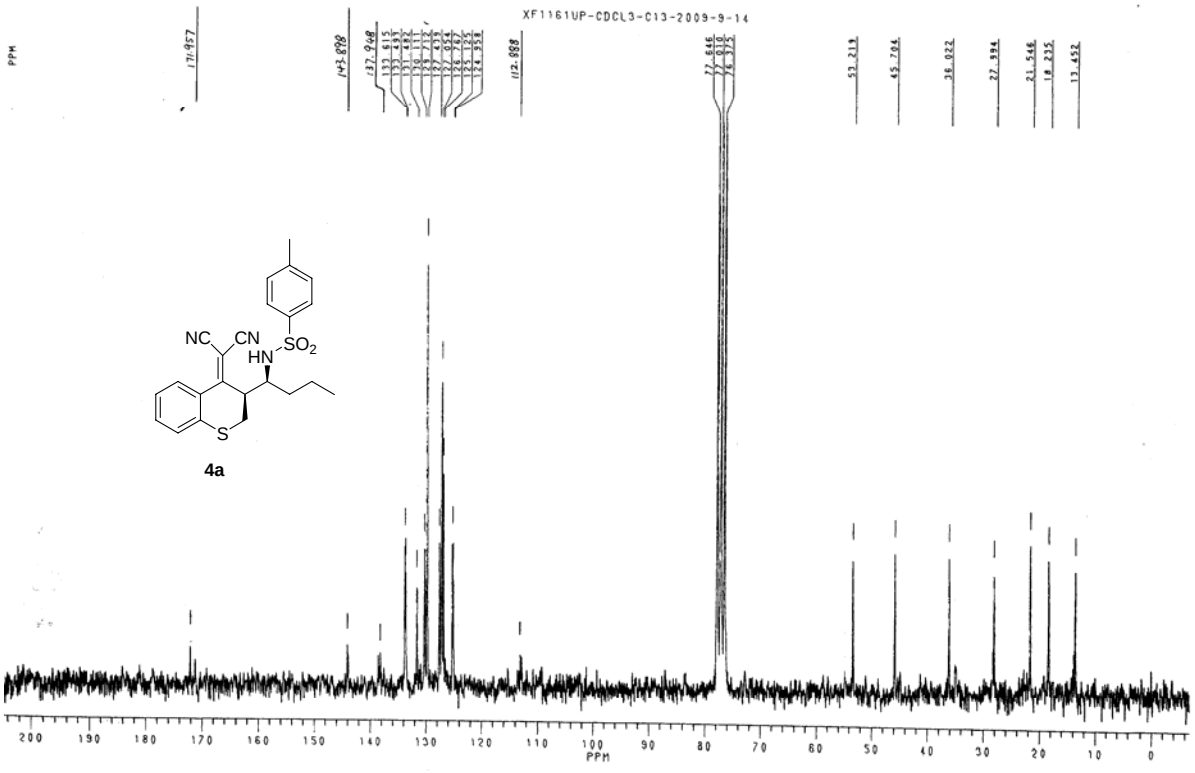

NC
CN
HN
SO2
S
4a
10
9
8
7
6
5
4
3
2
1
ppm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CN
HN
SO2
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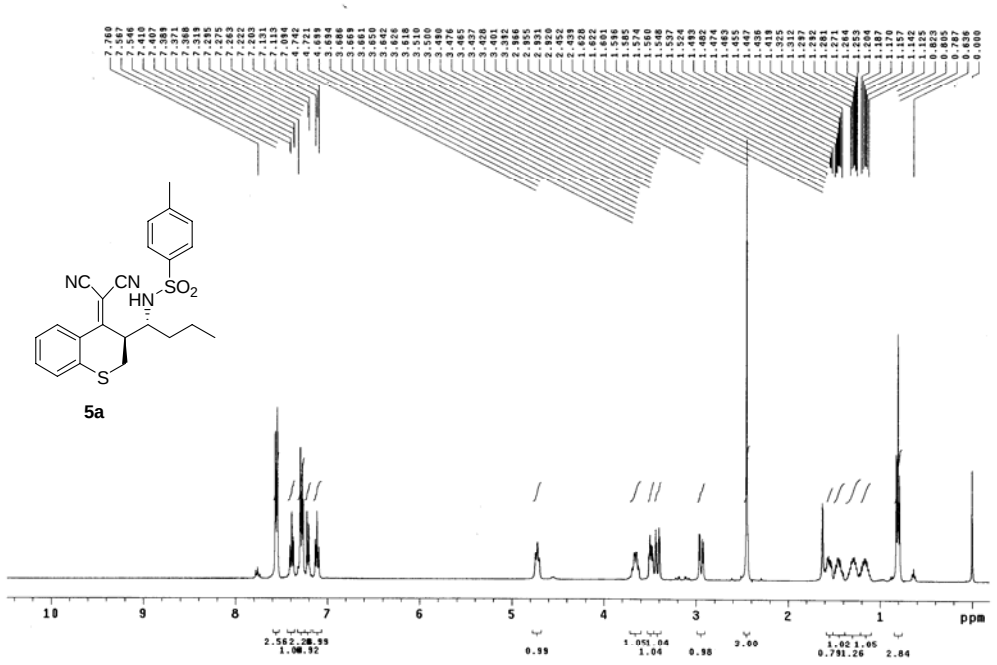
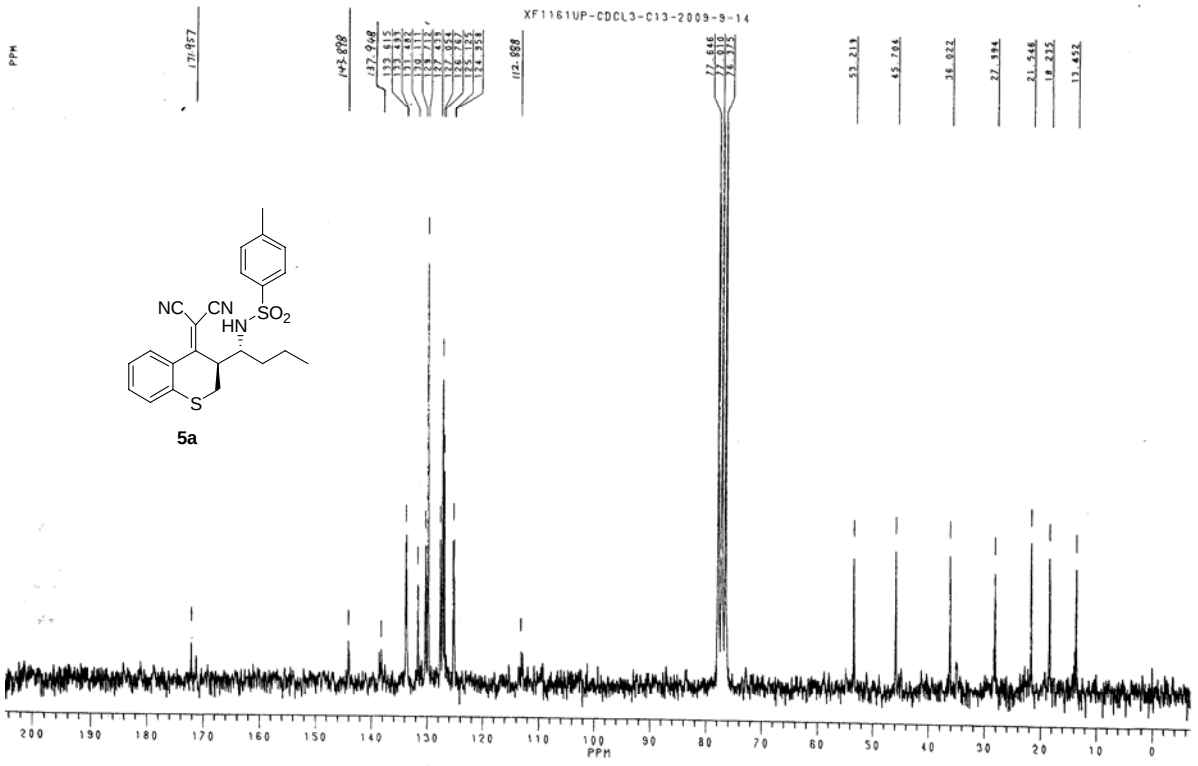
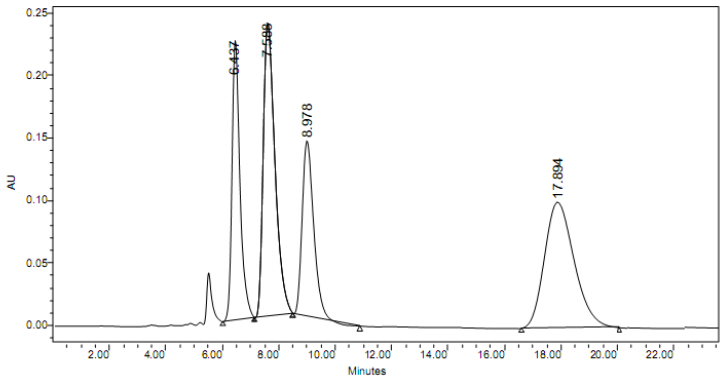
4a
PPM

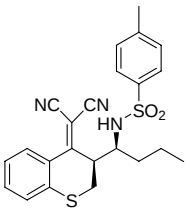


5a



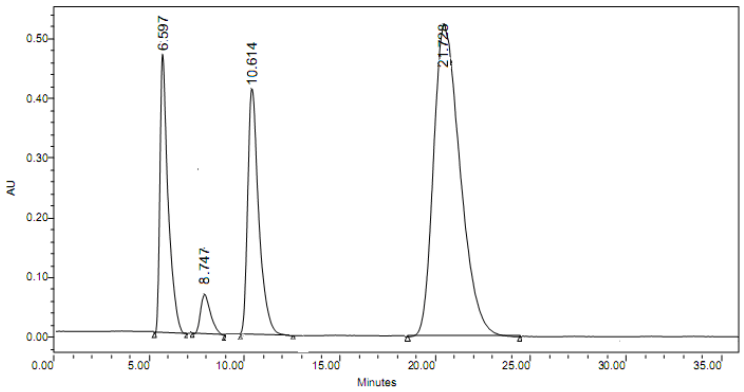
5a

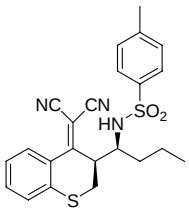




rac-4a and 5a

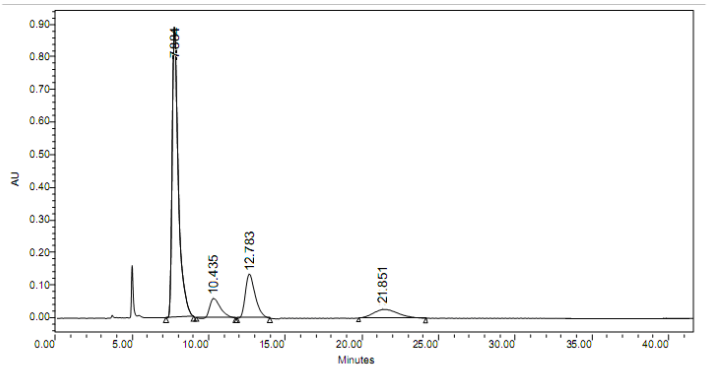
	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	6.437	4393556	19.45	223860	32.01
2	7.588	6786328	30.05	234790	33.57
3	8.978	4033748	17.86	140036	20.02
4	17.894	7371276	32.64	100638	14.39

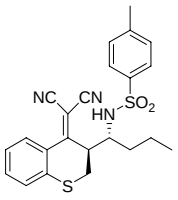




4a

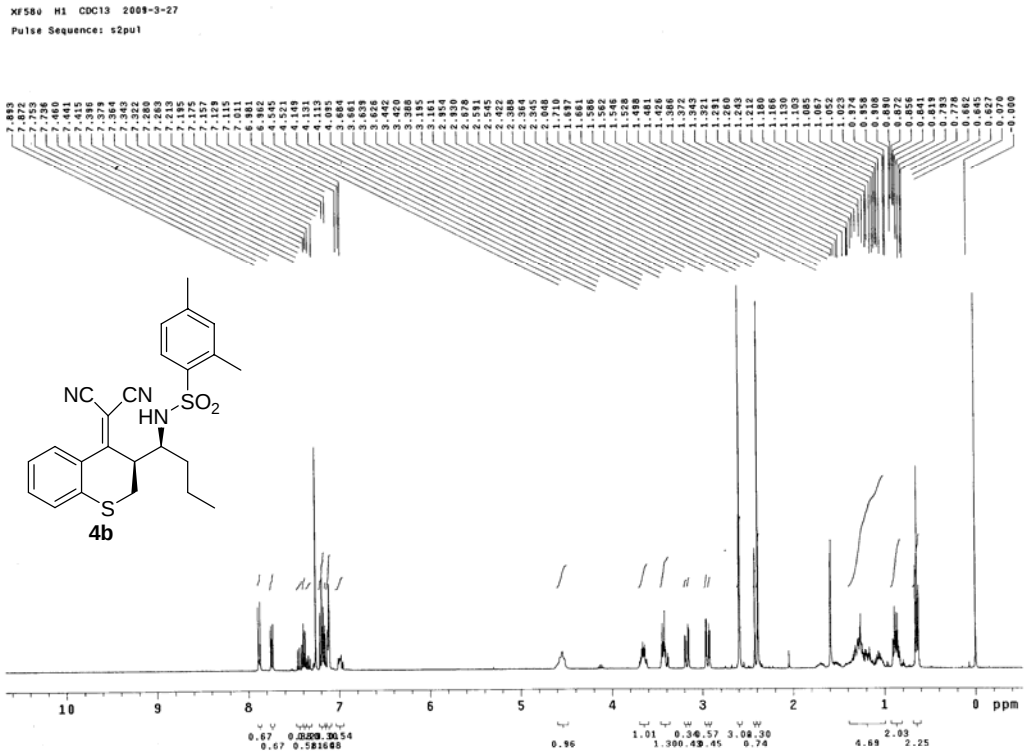
	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	6.597	13955777	14.32	468044	31.80
2	8.747	2467804	3.24	66759	4.54
3	10.614	16616319	17.18	411856	27.99
4	21.728	50949316	65.26	524985	35.67

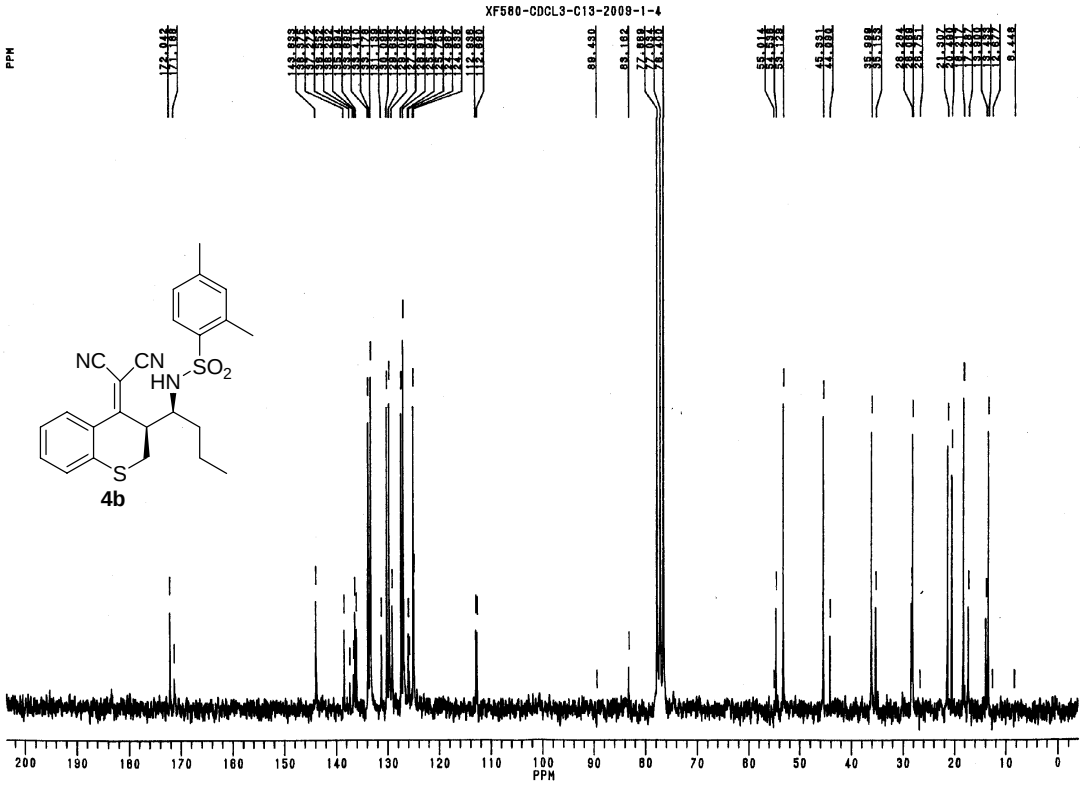


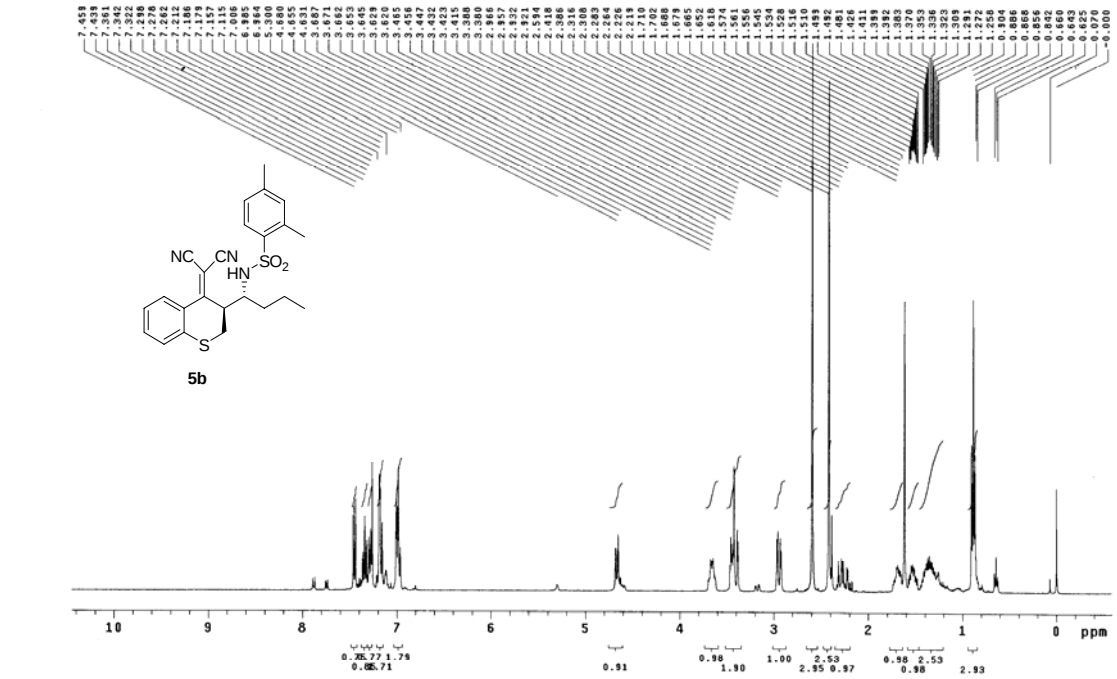


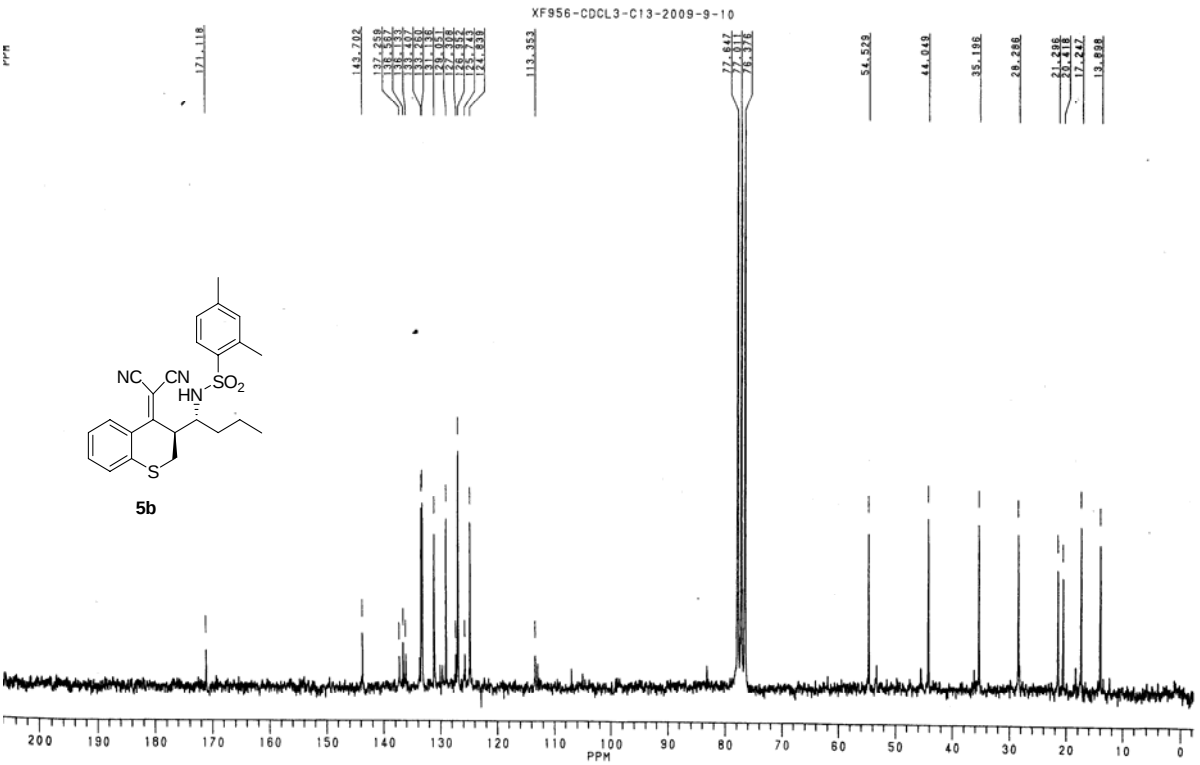
5a

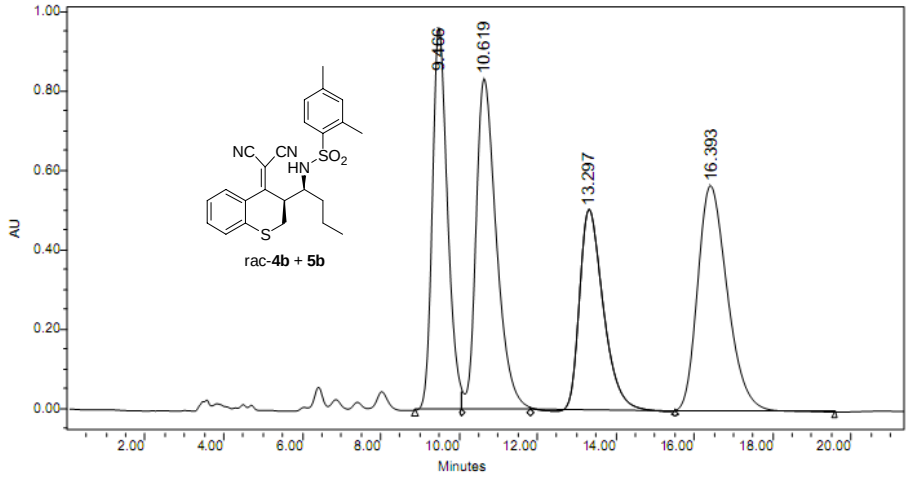
	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	7.884	25219446	64.66	891187	80.13
2	10.435	3003744	10.06	59416	5.34
3	12.783	6103173	15.38	135368	12.17
4	21.851	2945300	9.90	26182	2.35


XF580 H1 CDCl3 2009-3-27
Pulse Sequence: s2pul
NC
CN
HN
SO2
S
4b
ppm

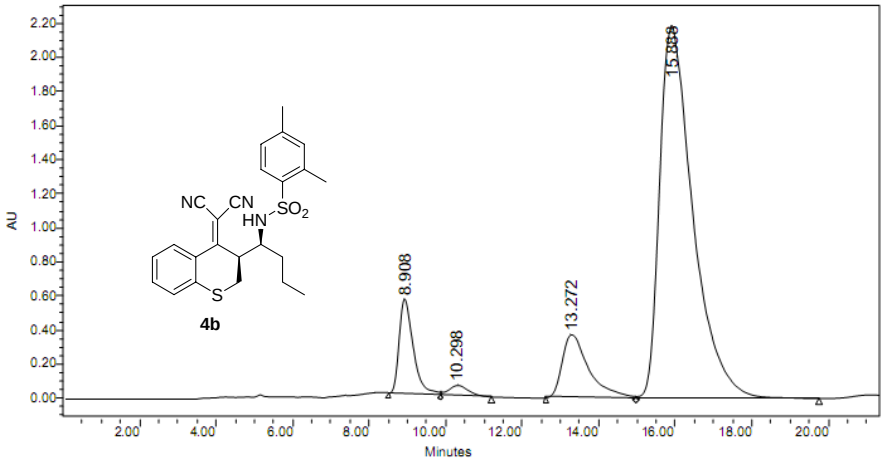

XF580-CDCL3-C13-2009-1-4
PPM
NC
CN
HN
SO2
S
4b
PPM


NC
CN
HN
SO2
S
5b
ppm

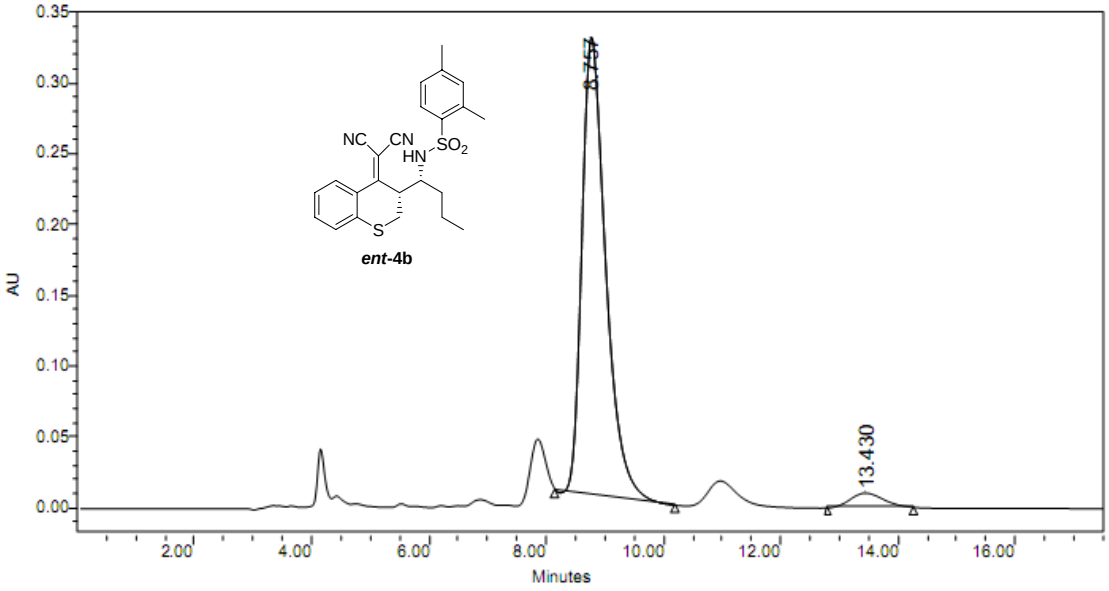

XF956-CDCL3-C13-2009-9-10
NC
CN
HN
SO2
S
5b
PPM



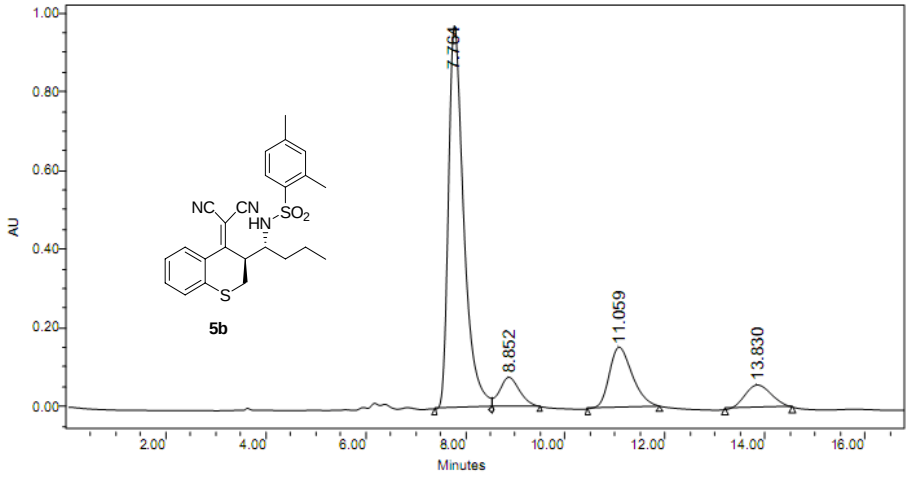
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.466	25985380	22.04	963513	33.52
2	10.619	30344882	28.08	835498	29.06
3	13.297	21679110	22.06	507375	17.65
4	16.393	30064889	27.82	568459	19.77



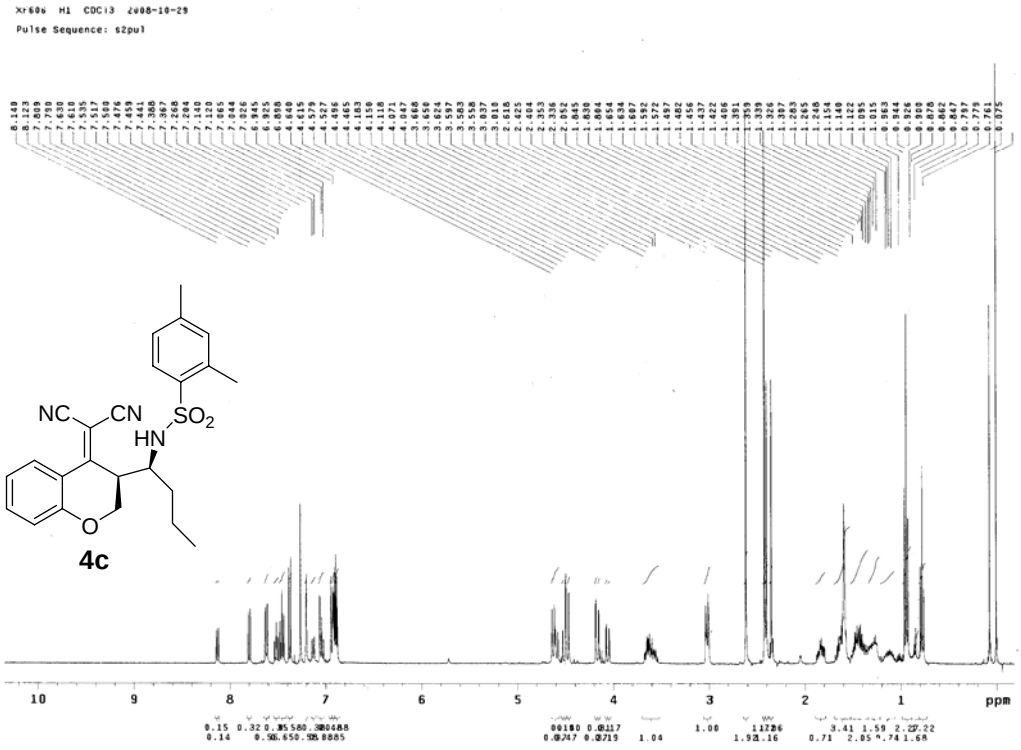
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.908	14207719	8.55	555325	17.51
2	10.298	2134831	1.28	59591	1.88
3	13.272	18026249	10.84	370101	11.67
4	15.888	131866866	79.33	2186792	68.94



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.757	9122835	95.72	323618	96.92
2	13.430	407626	4.28	10287	3.08



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	7.764	20806395	67.67	973549	77.04
2	8.852	2158702	7.16	76573	6.06
3	11.059	4957213	17.73	153988	12.19
4	13.830	2242872	7.44	59636	4.72


Xr606 H1 CDCl3 2008-10-29
Pulse Sequence: s2pul
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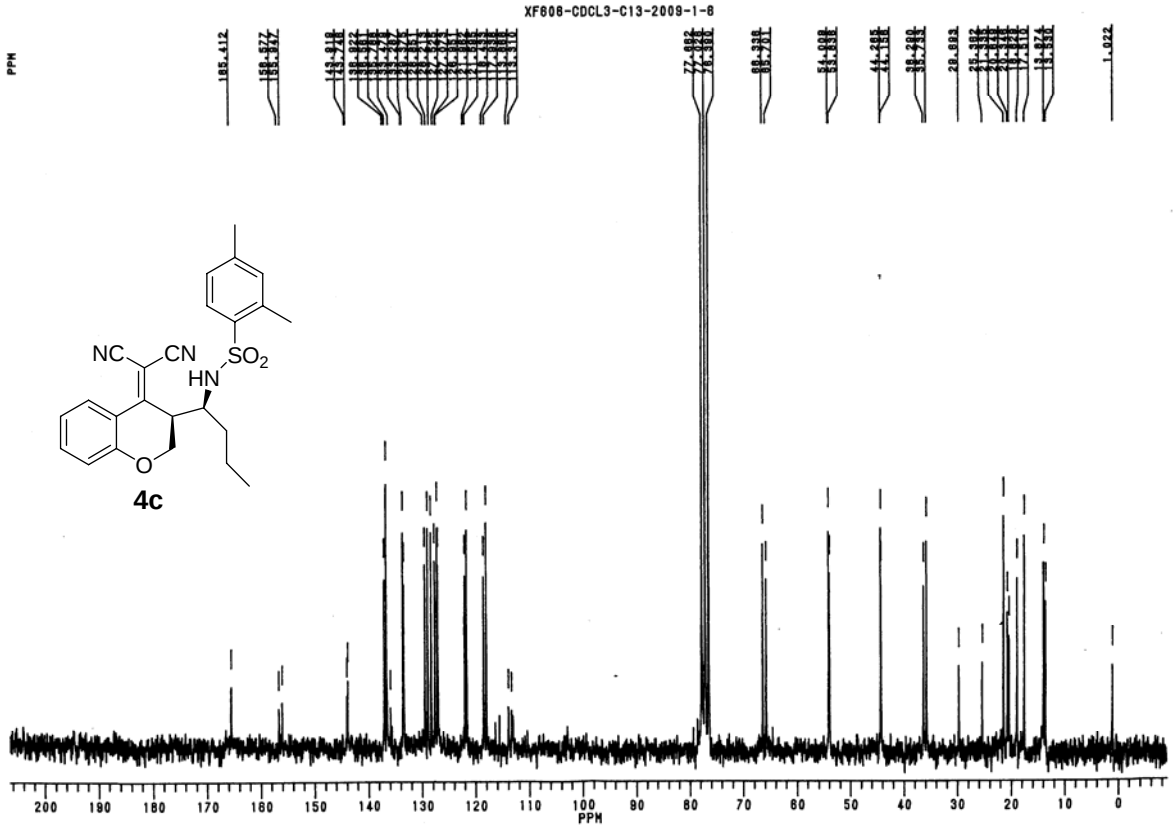
CN
SO2
HN
O
4c
10
9
8
7
6
5
4
3
2
1
ppm


XF608-CDCL3-C13-2009-1-8
PPM
NC
CN
SO2
HN
O
4c
200
190
180
170
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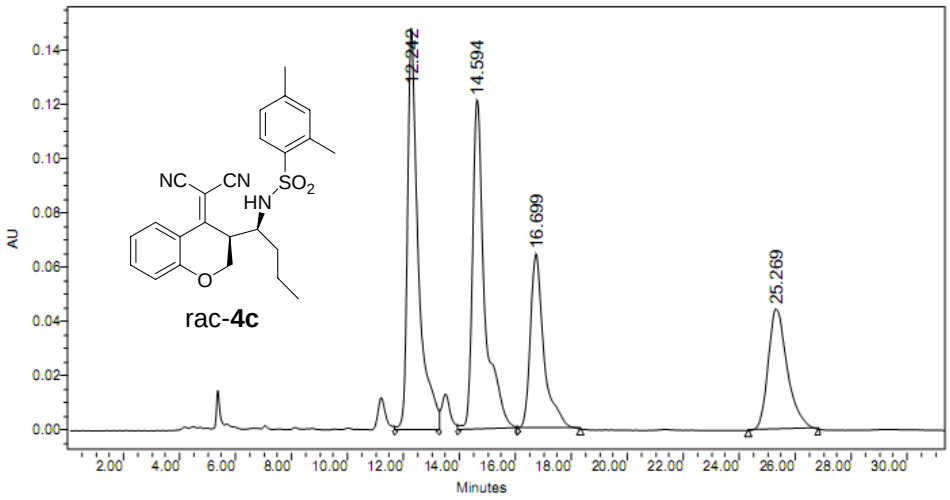
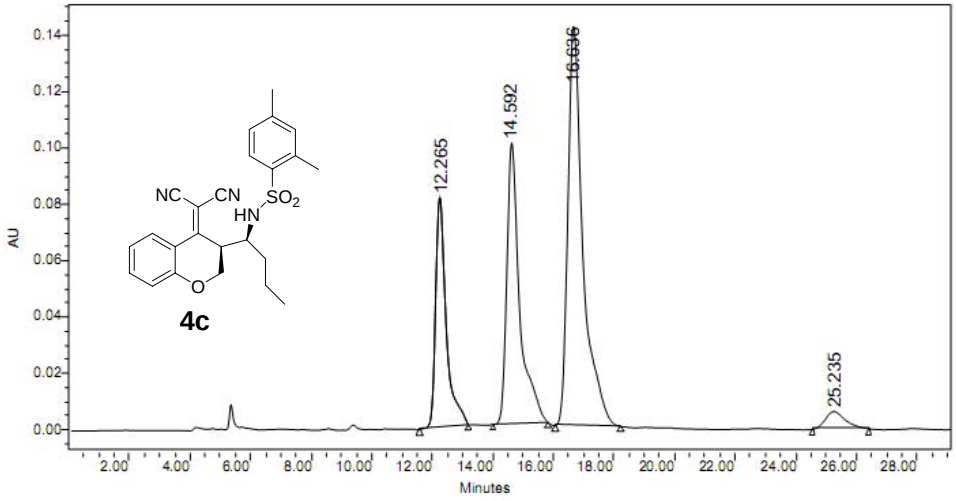
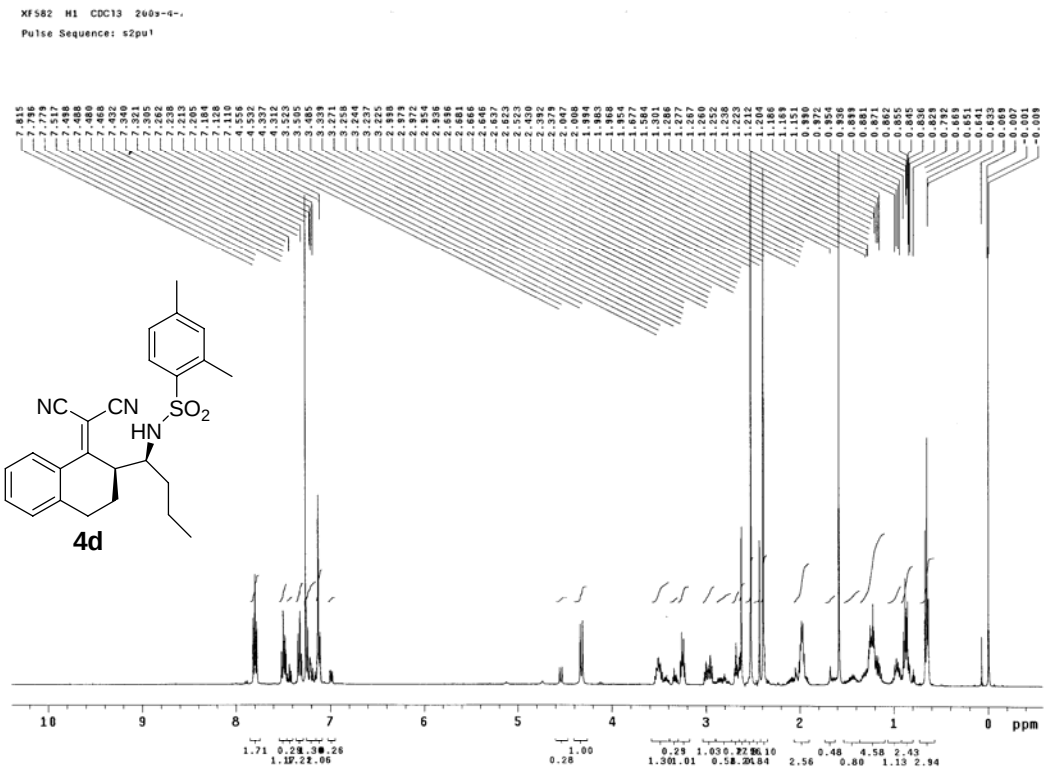
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PPM

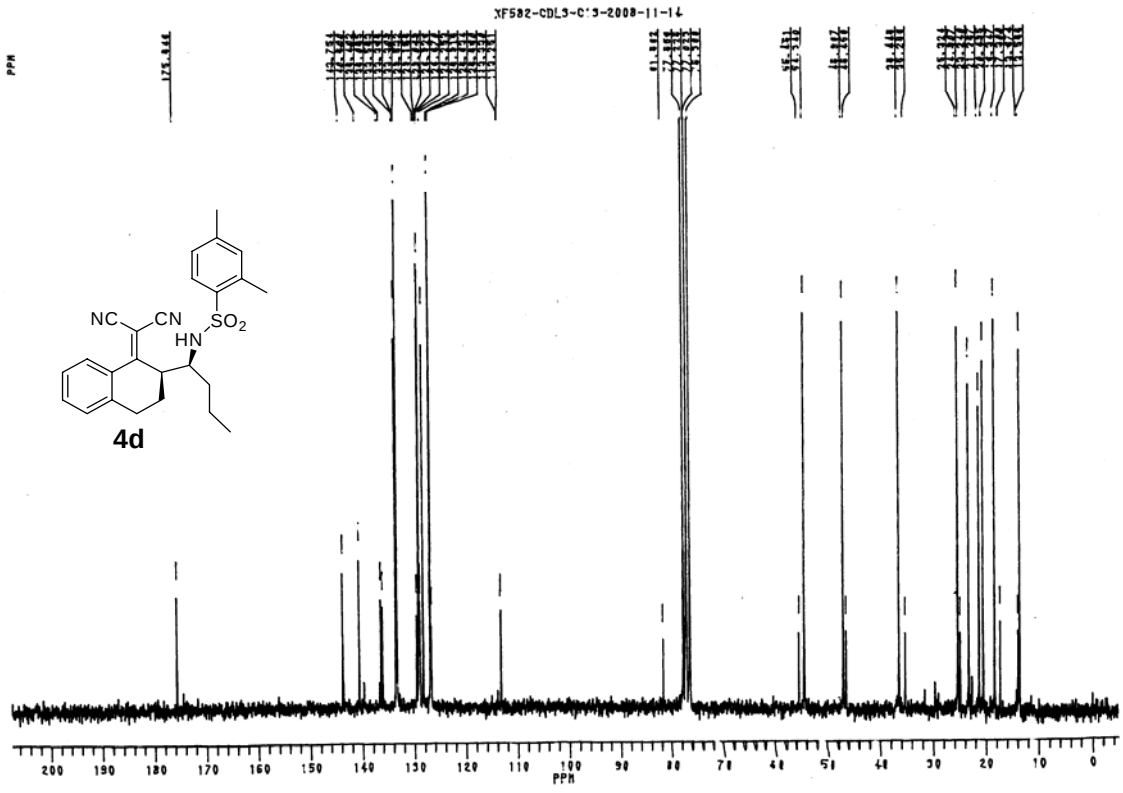


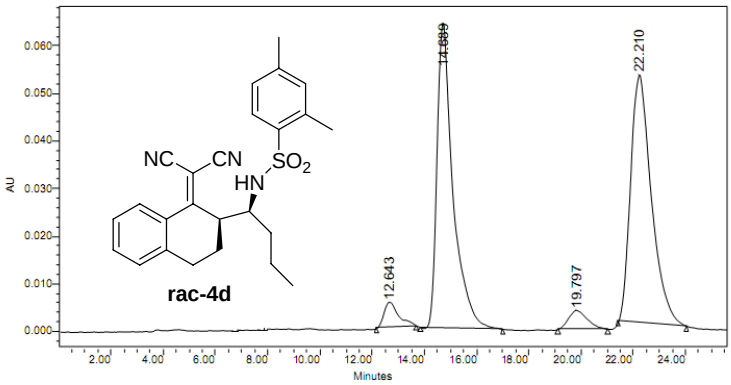
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.242	3981125	32.98	148441	39.10
2	14.594	3728473	30.89	121744	32.07
3	16.699	2216094	18.36	64768	17.06
4	25.269	2145298	17.77	44647	11.76



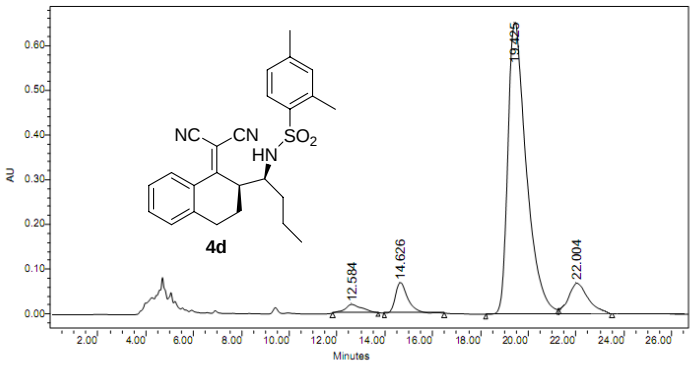
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.265	1991557	19.62	81657	24.80
2	14.592	2954249	29.11	99724	30.28
3	16.636	4917155	48.45	141704	43.03
4	25.235	286367	2.82	6236	1.89


XF582 H1 CDCl3 2009-4-.
Pulse Sequence: s2pul
NC
CN
SO2
HN
4d
ppm

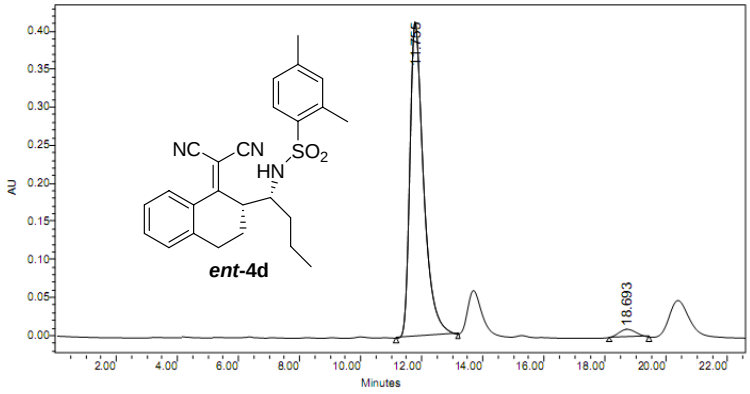

XF582-CDL3-C'3-2009-11-14
PPM
NC
CN
SO2
HN
4d
PPM



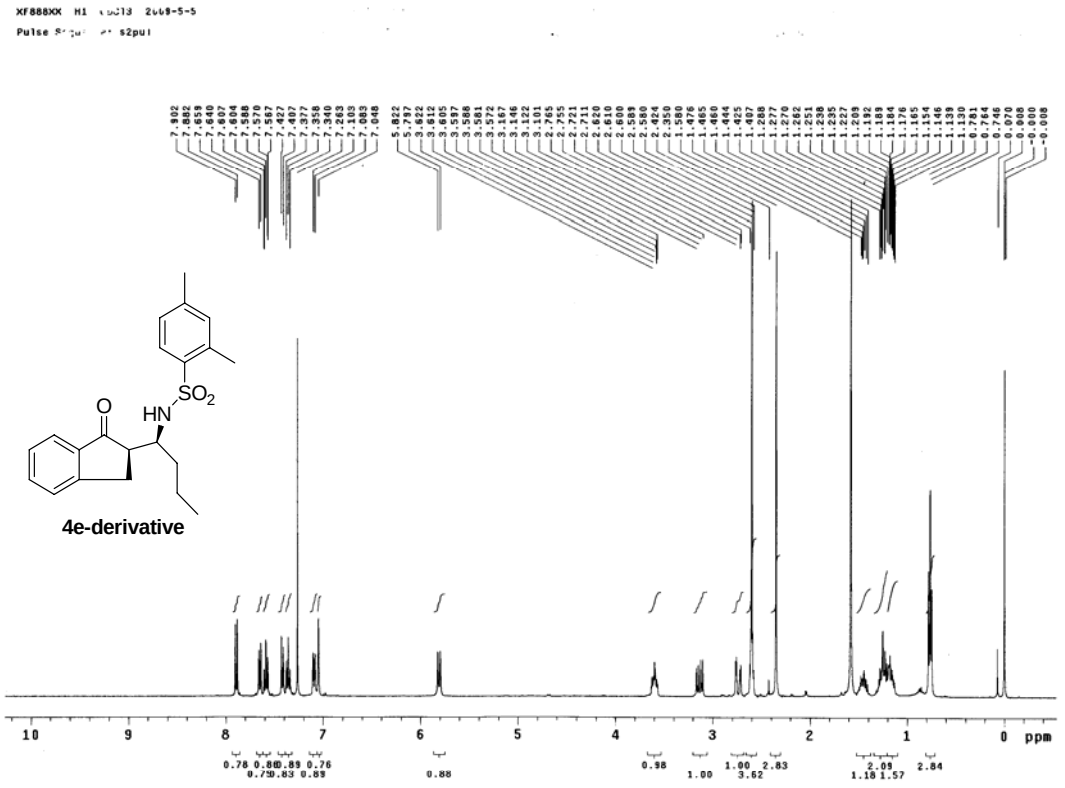
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.643	210803	3.51	5328	4.25
2	14.689	2717284	46.20	64081	51.06
3	19.797	197677	3.29	3962	3.16
4	22.210	2886394	47.01	52121	41.53

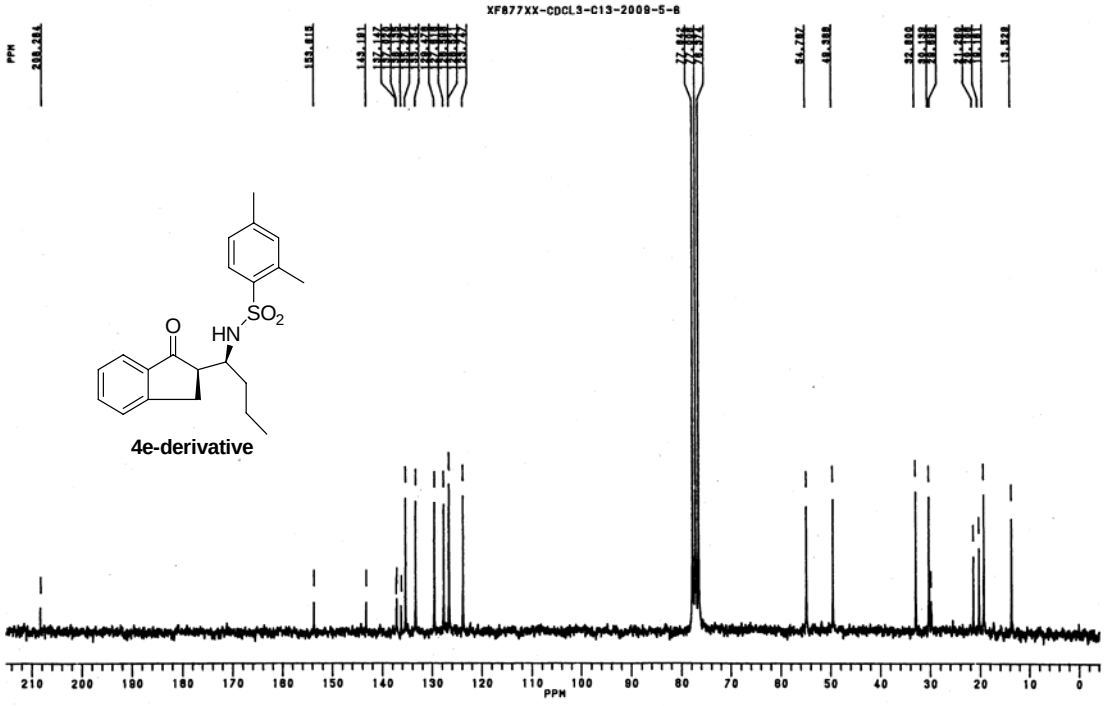


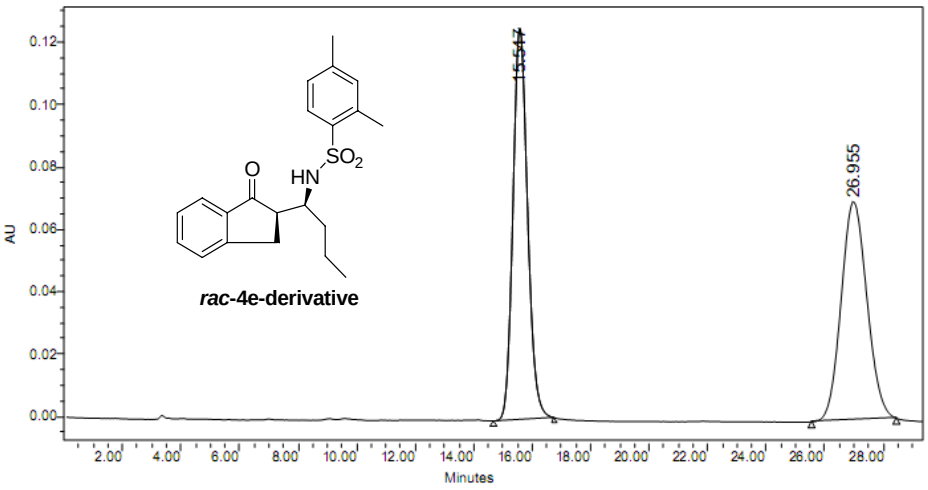
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.584	929878	2.23	18701	2.33
2	14.626	2501484	6.00	68192	8.51
3	19.425	35086004	84.12	652737	81.47
4	22.004	3193962	7.66	61581	7.69



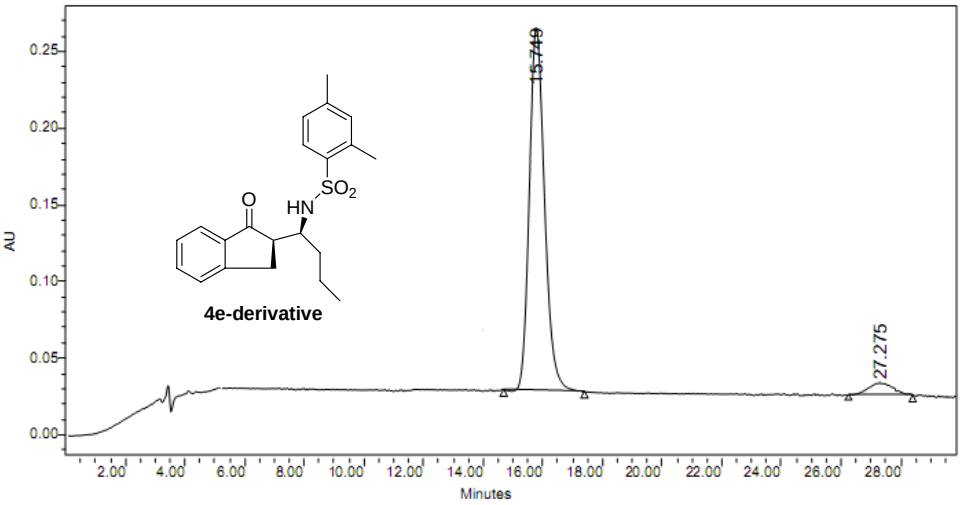
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.755	12956078	97.00	414075	97.56
2	18.693	401388	3.00	10340	2.44


4e-derivative

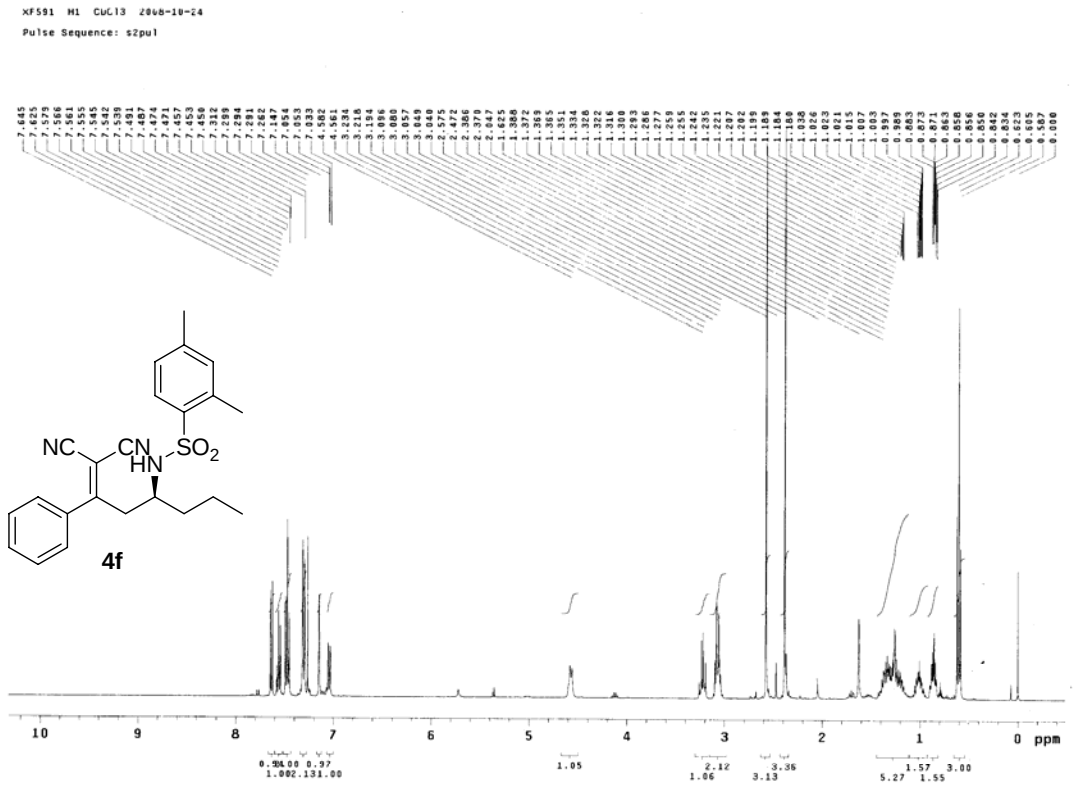

4e-derivative

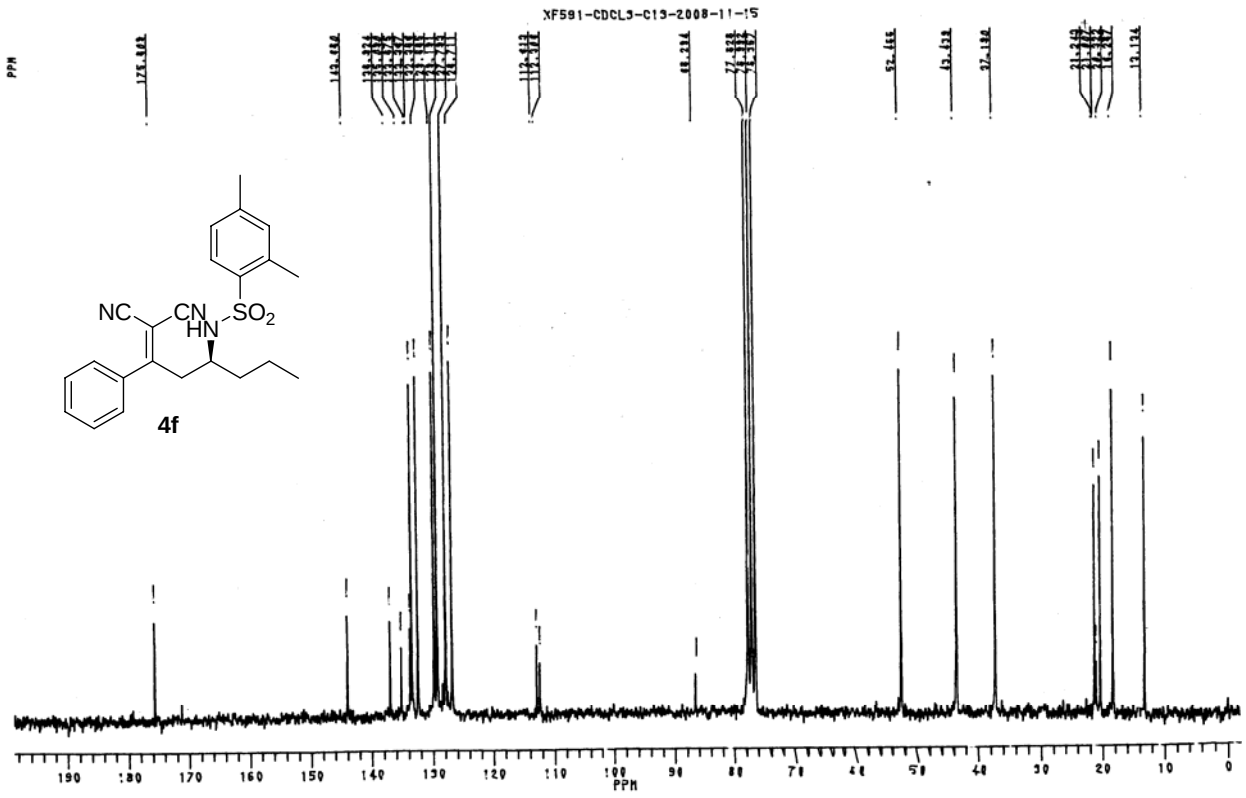


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.547	4358687	50.32	125582	64.18
2	26.955	4302487	49.68	70077	35.82



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.749	8407549	94.73	236609	96.78
2	27.275	467469	5.27	7865	3.22


XF591 H1 CDCl3 2008-10-24
Pulse Sequence: s2pul
NC
CN
HN
SO2
4f
10
9
8
7
6
5
4
3
2
1
0 ppm


XF591-CDCL3-C13-2008-11-15
PPM
NC
CN
HN
SO2
4f
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140
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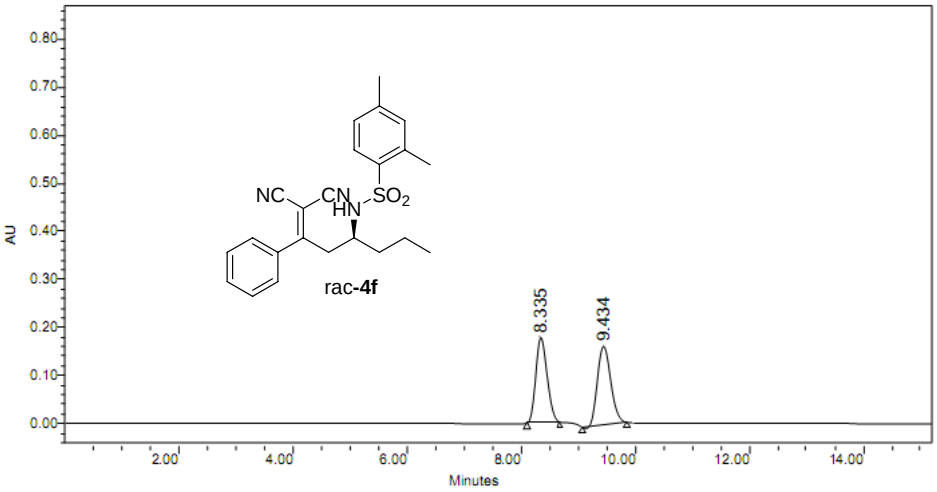
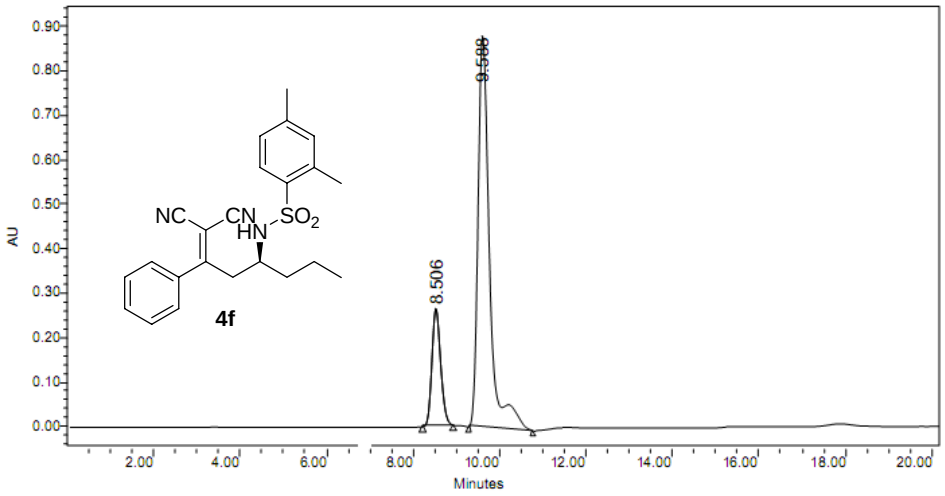
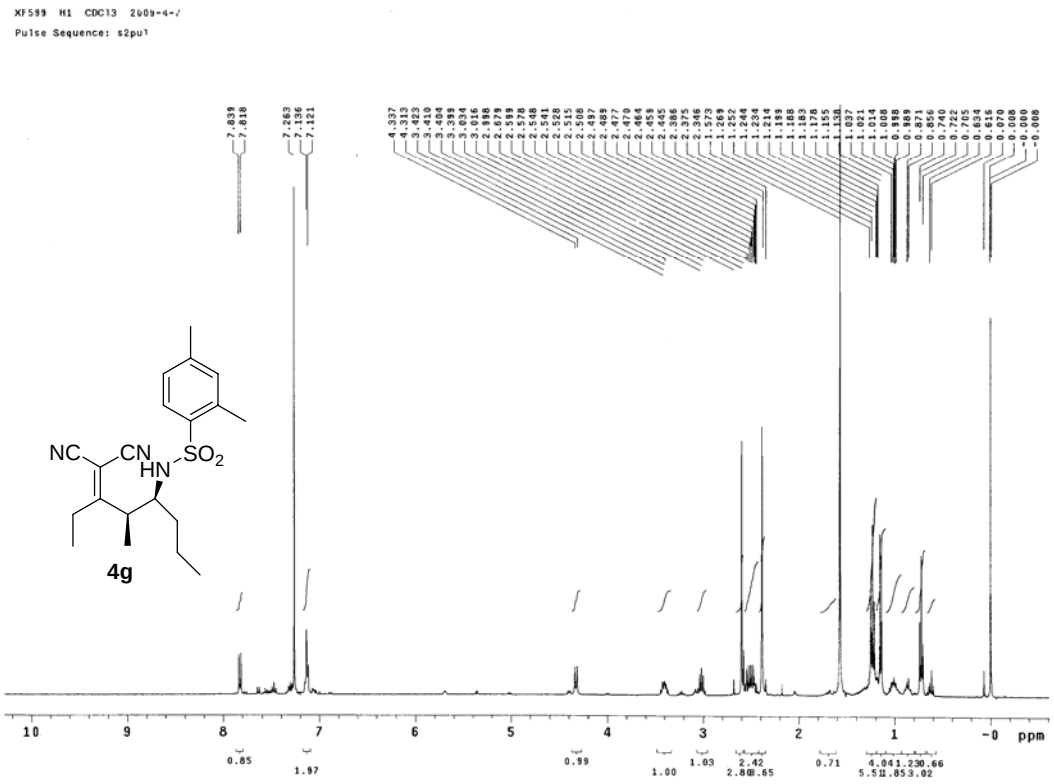
70
60
50
40
30
20
10
0

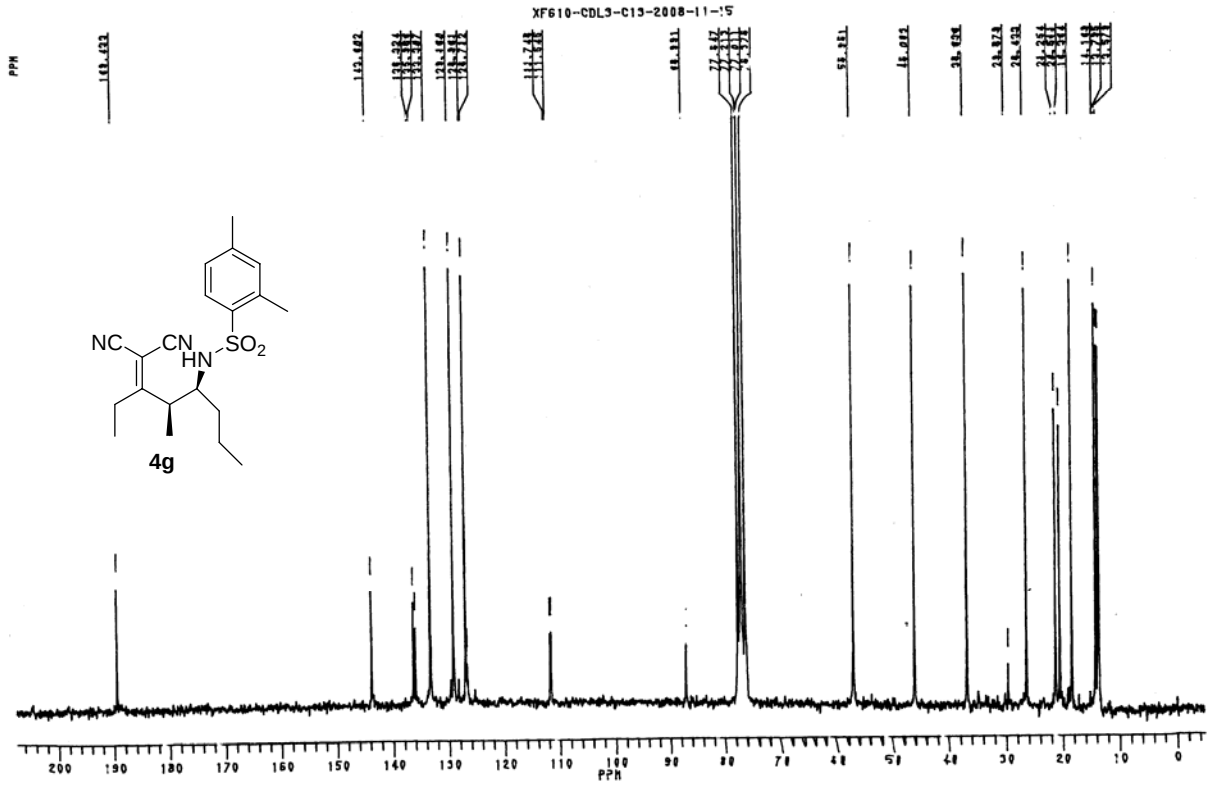


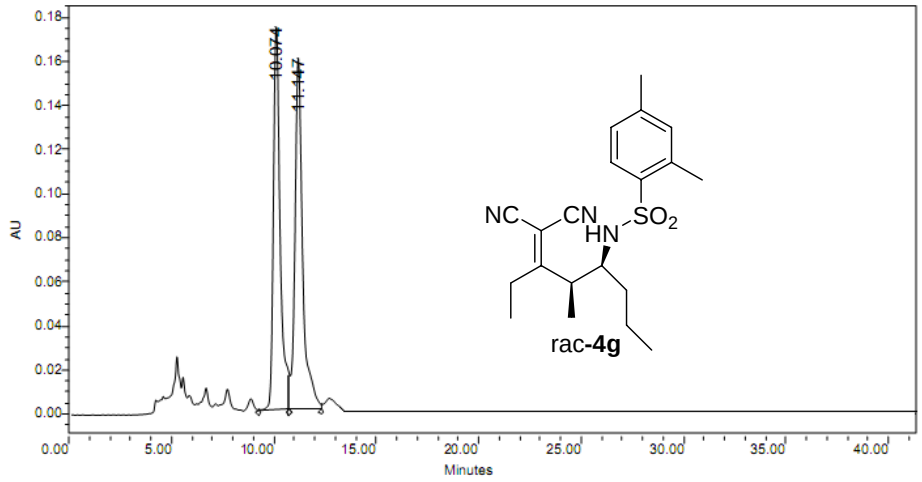
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.335	2453081	51.55	178337	51.97
2	9.434	2706169	48.45	164815	48.03



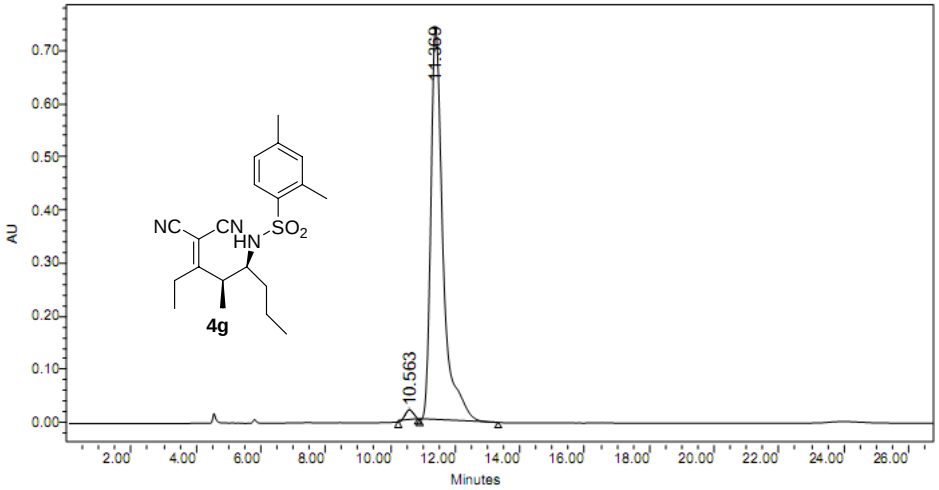
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.506	3730503	18.64	264730	23.11
2	9.588	16278329	81.36	880998	76.89


XF599 H1 CDCl3 2009-4-7
Pulse Sequence: s2pul
NC
CN
HN
SO2
4g
ppm

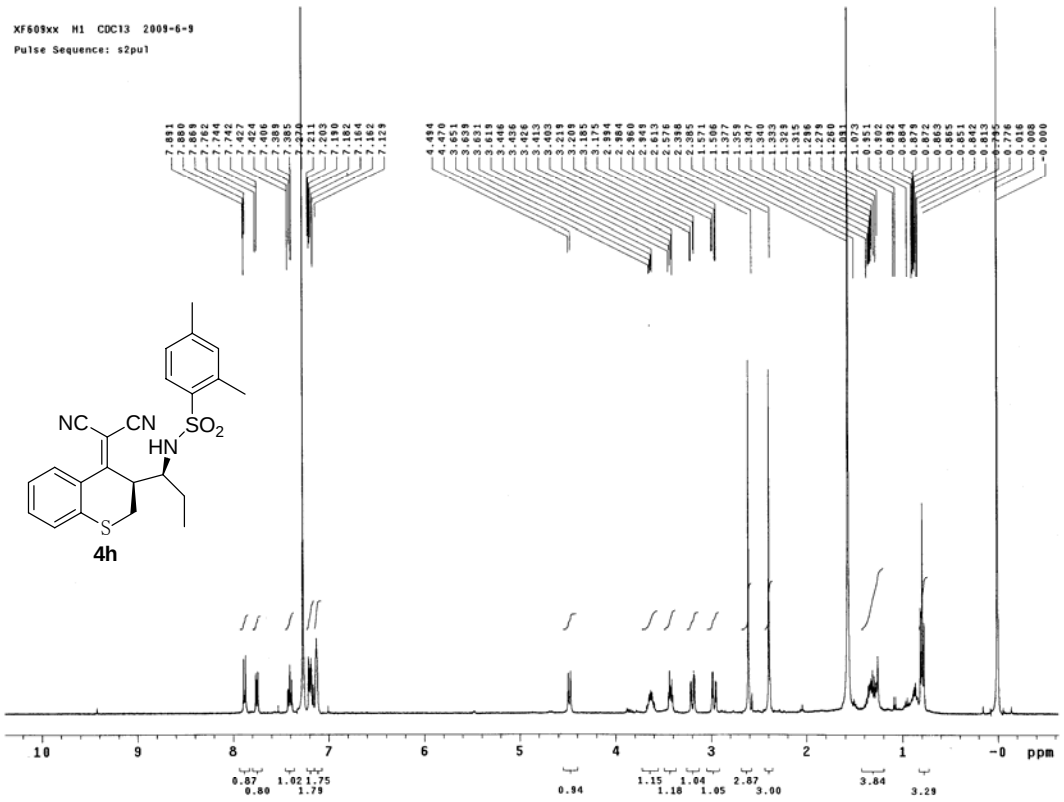

XF610-CDL3-C13-2008-11-15
PPM
NC
CN
HN
SO2
4g

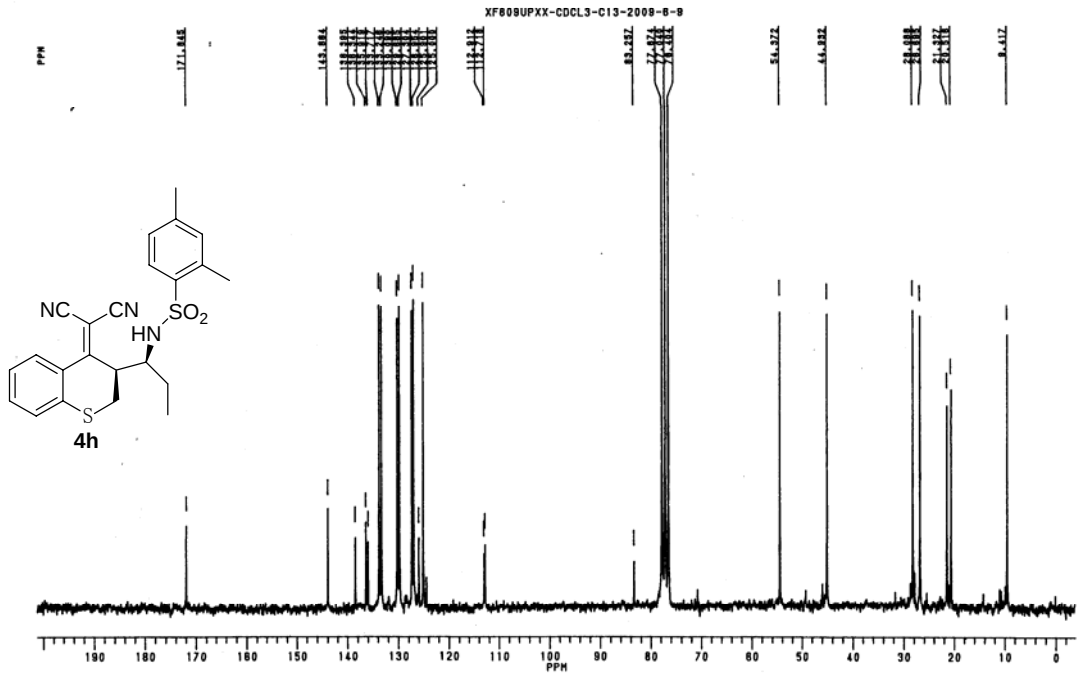


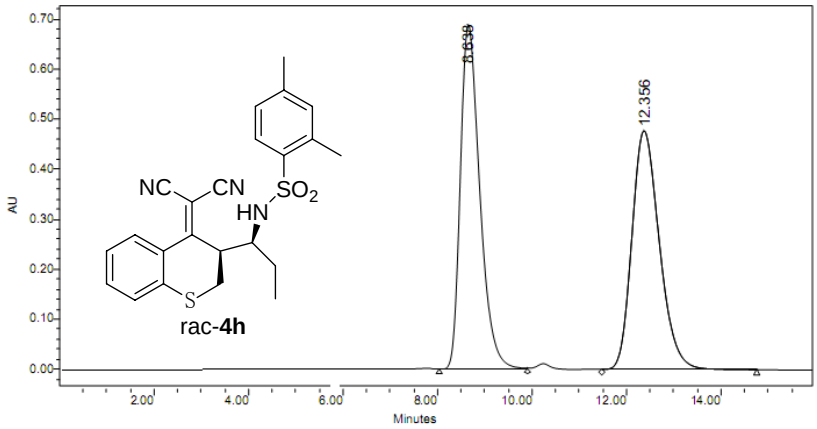
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.074	4066877	49.44	174157	46.04
2	11.147	4160968	50.56	159586	42.19



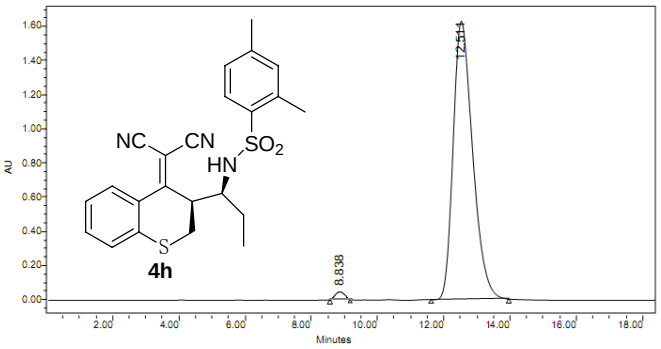
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.563	363459	1.84	20151	2.64
2	11.369	19430224	98.16	741905	97.36


XF609xx H1 CDCl3 2009-6-9
Pulse Sequence: s2pul
NC
CN
SO2
HN
S
4h
ppm

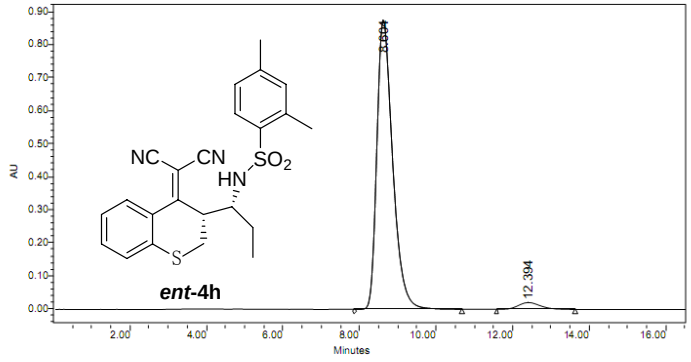

XF609UPXX-CDCL3-C13-2009-6-9
PPM
NC
CN
SO2
HN
S
4h



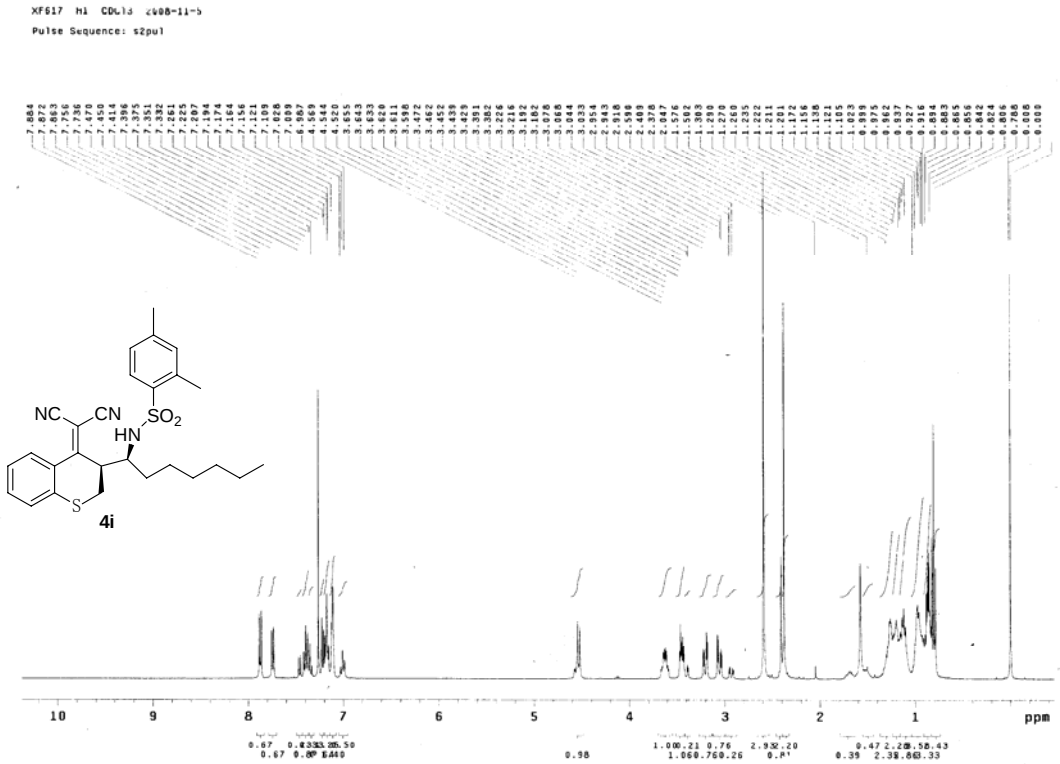
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.638	19664883	50.50	689165	59.09
2	12.356	19275793	49.50	477125	40.91

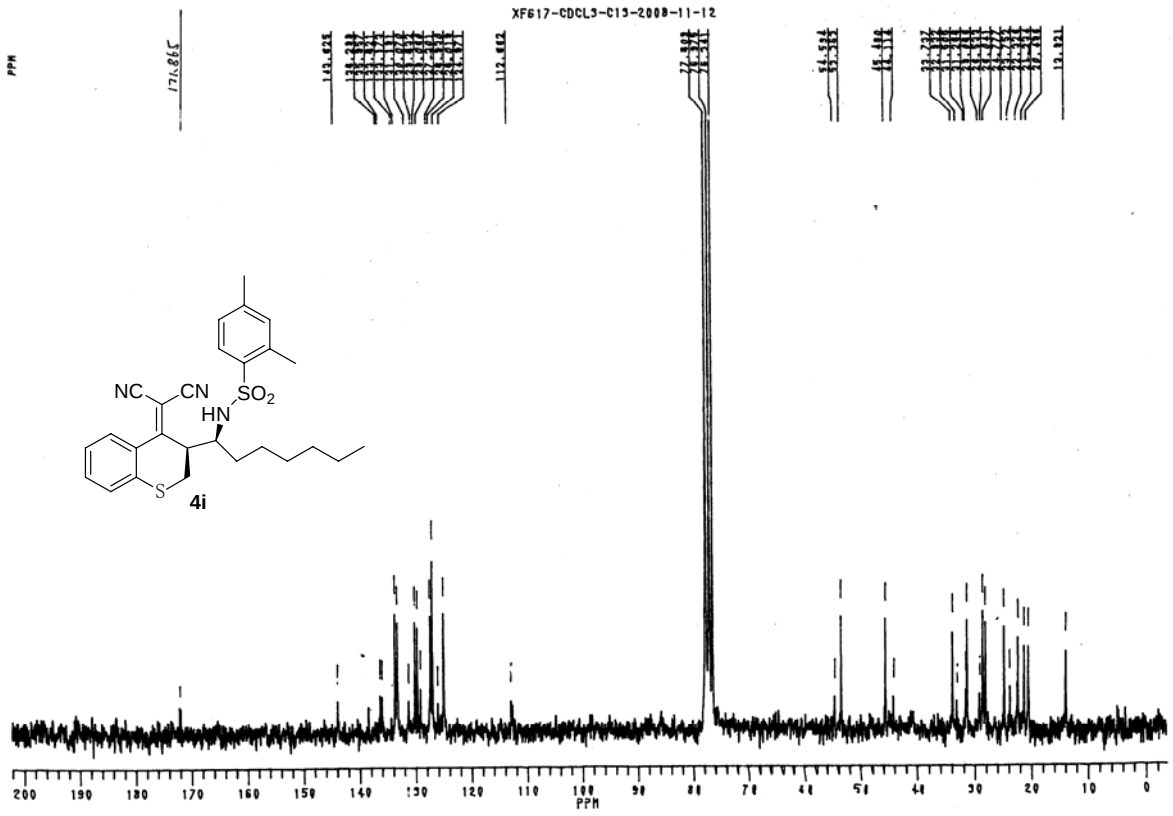


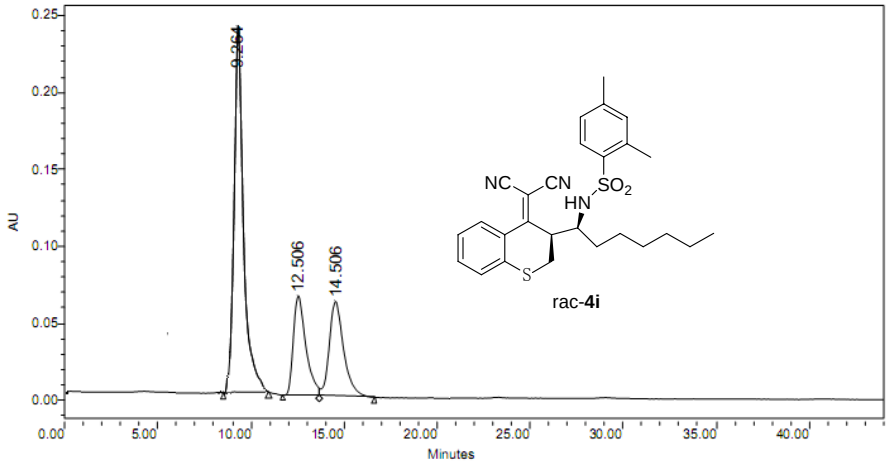
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.838	1571918	1.31	62143	3.67
2	12.511	66577040	98.69	1629047	96.33



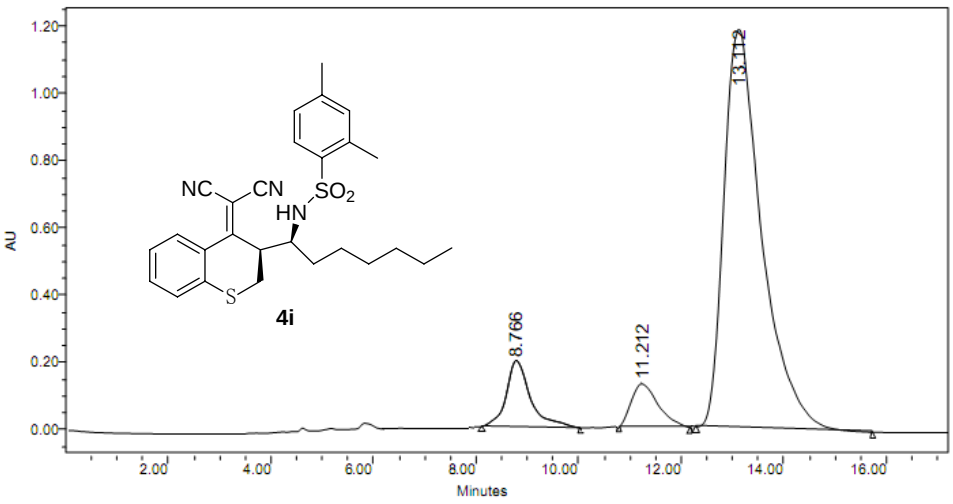
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.604	25106722	96.80	876352	97.70
2	12.394	828715	3.20	20648	2.30


Pulse Sequence: s2pul
NC
CN
SO2
HN
S
4i
10
9
8
7
6
5
4
3
2
1
ppm

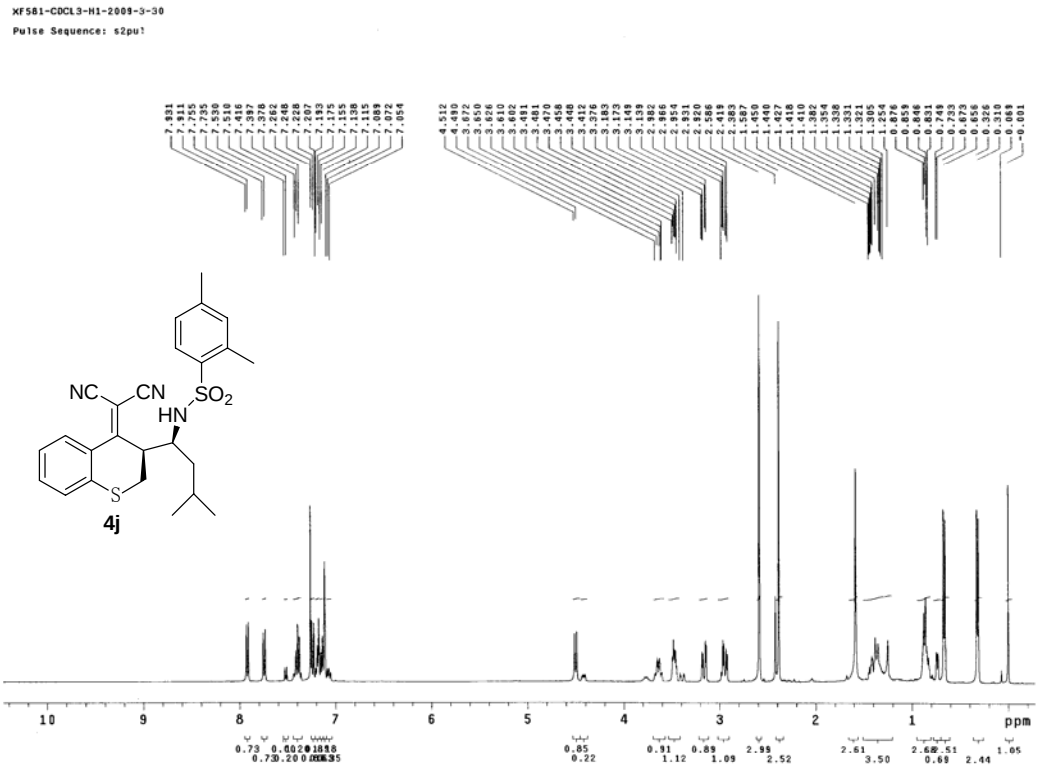

XF617-CDCL3-C13-2008-11-12
NC
CN
SO2
HN
S
4i
PPM

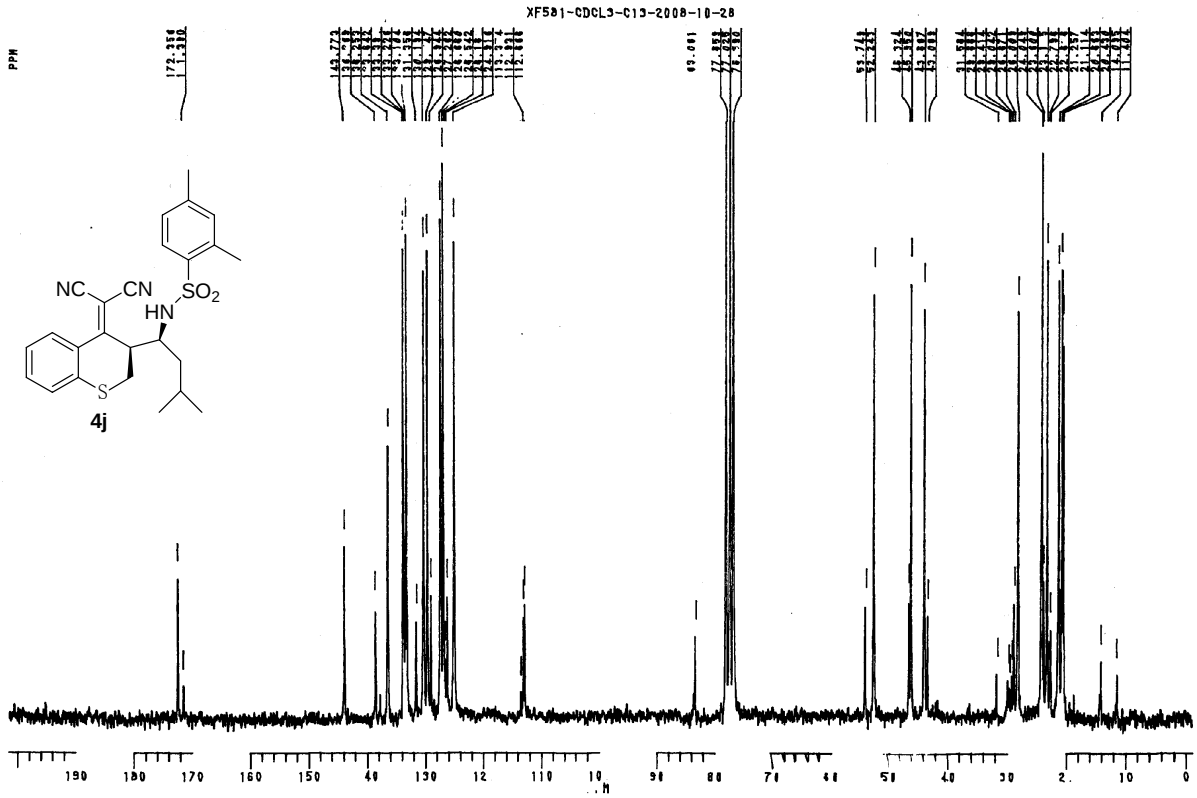


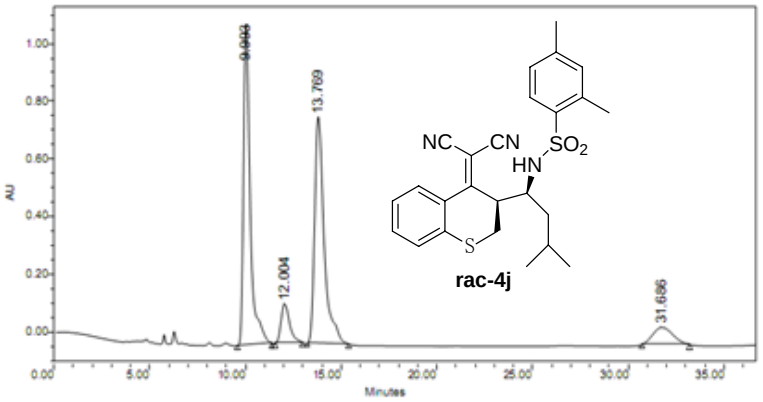
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.264	7634880	54.32	230362	64.50
2	12.506	3070984	21.85	64972	18.19
3	14.506	3348398	23.82	61828	17.31



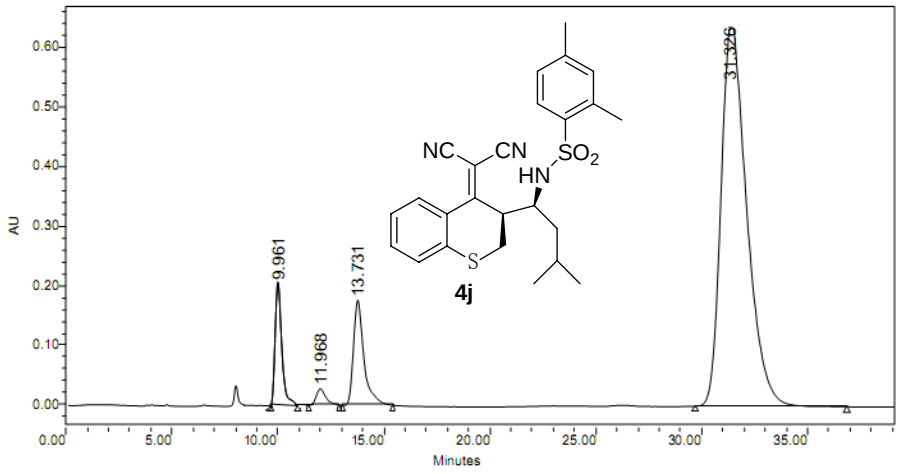
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.766	6508044	9.01	197451	13.06
2	11.212	4717726	6.54	128240	8.49
3	13.112	60957355	84.45	1185659	78.45


XF581-CDCL3-H1-2009-3-30
Pulse Sequence: s2pul
NC
CN
SO2
HN
S
4j
ppm

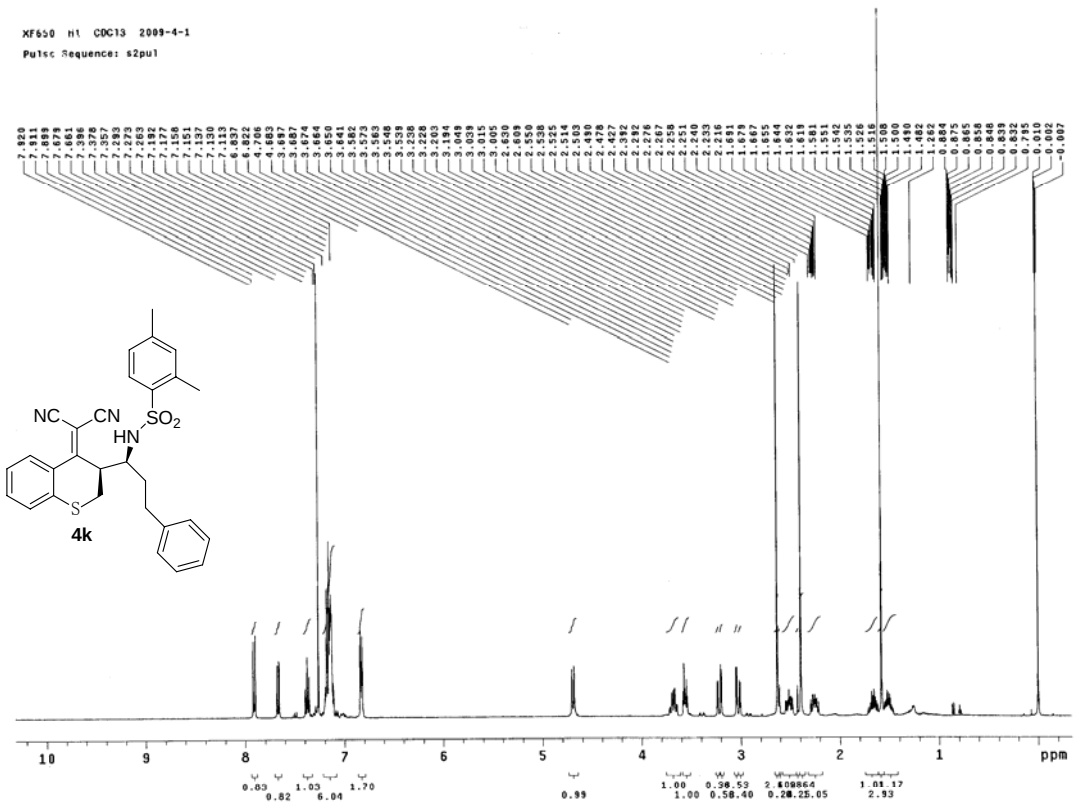

XF581-CDCL3-C13-2008-10-28
PPM
NC
CN
SO2
HN
S
4j

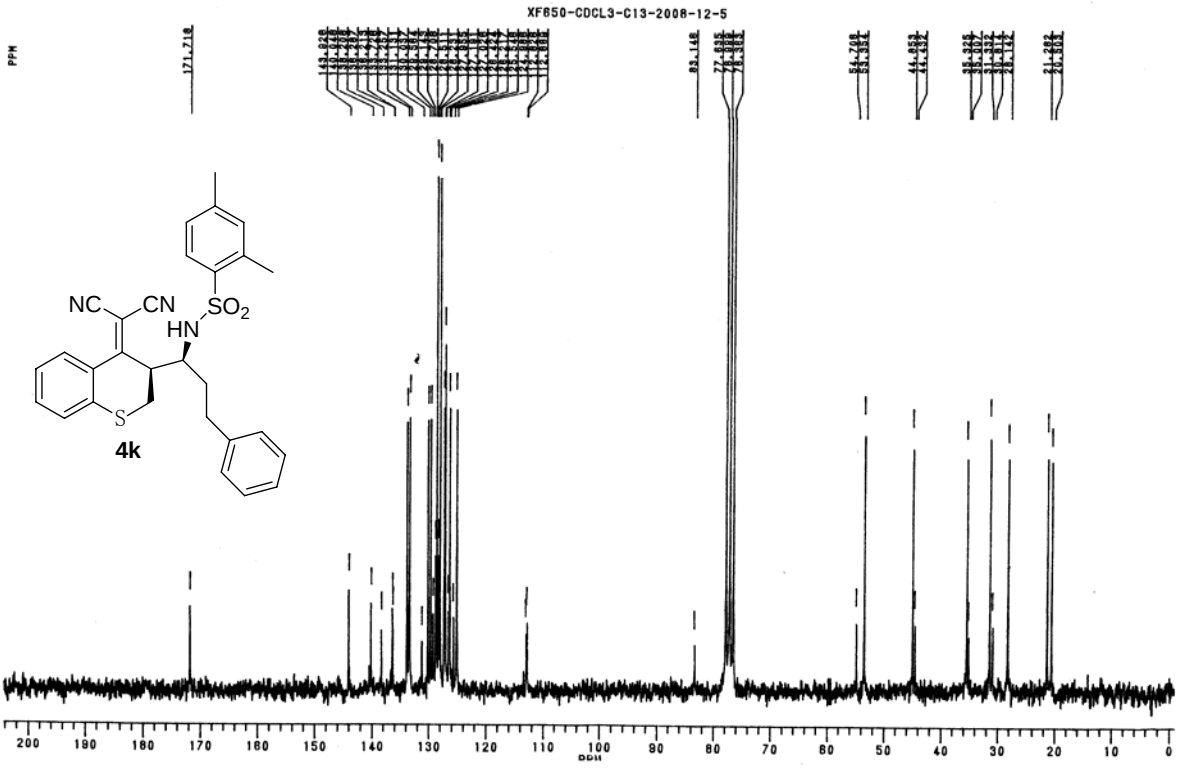


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.993	26974343	43.08	1114396	53.20
2	12.004	4310770	6.88	137231	6.55
3	13.769	27037055	43.18	783924	37.42
4	31.686	4291110	6.85	59365	2.83



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.961	4611163	7.04	207492	19.78
2	11.968	864707	1.32	27525	2.62
3	13.731	6119735	9.35	176580	16.83
4	31.326	53860683	82.28	637366	60.76


XF650 H1 CDCl3 2009-4-1
Pulse Sequence: s2pul
NC
CN
SO2
HN
S
4k
10
9
8
7
6
5
4
3
2
1
ppm


XF650-CDCL3-C13-2008-12-5
PPM
171.718
83.148
77.000
NC
CN
SO2
HN
S
4k
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190
180
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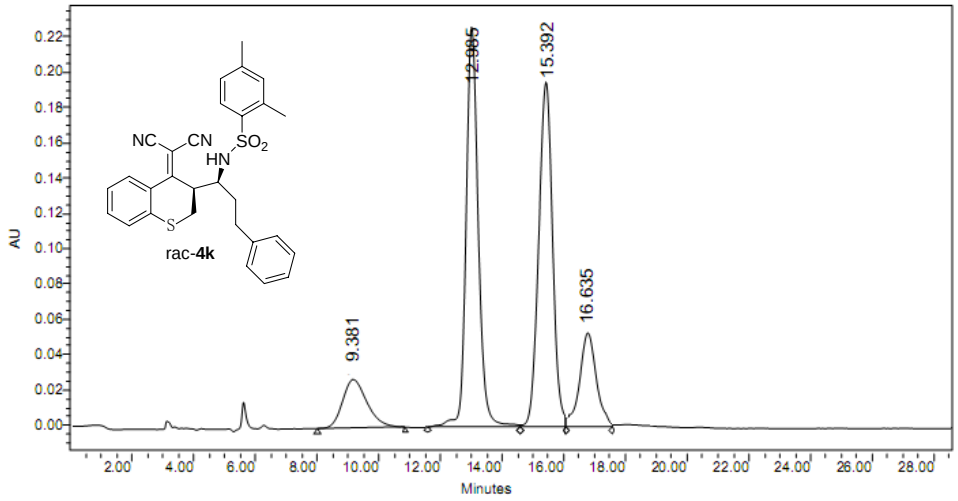
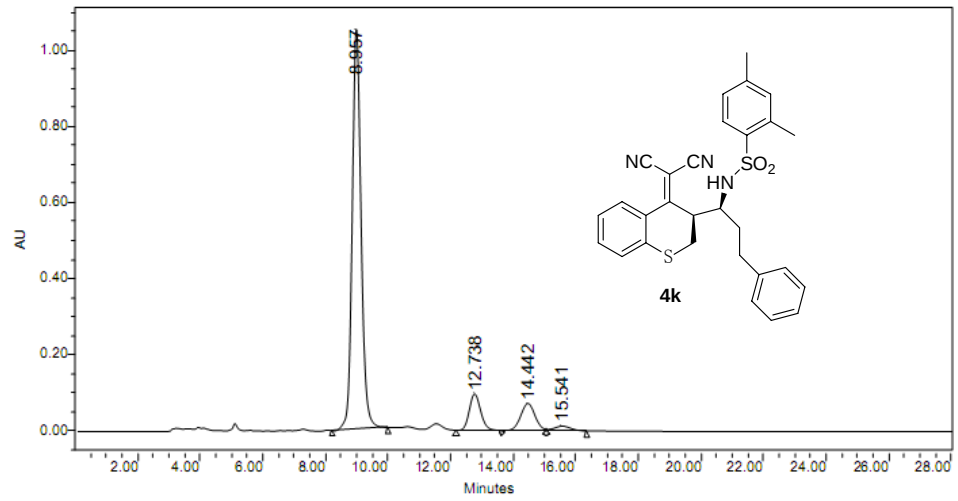
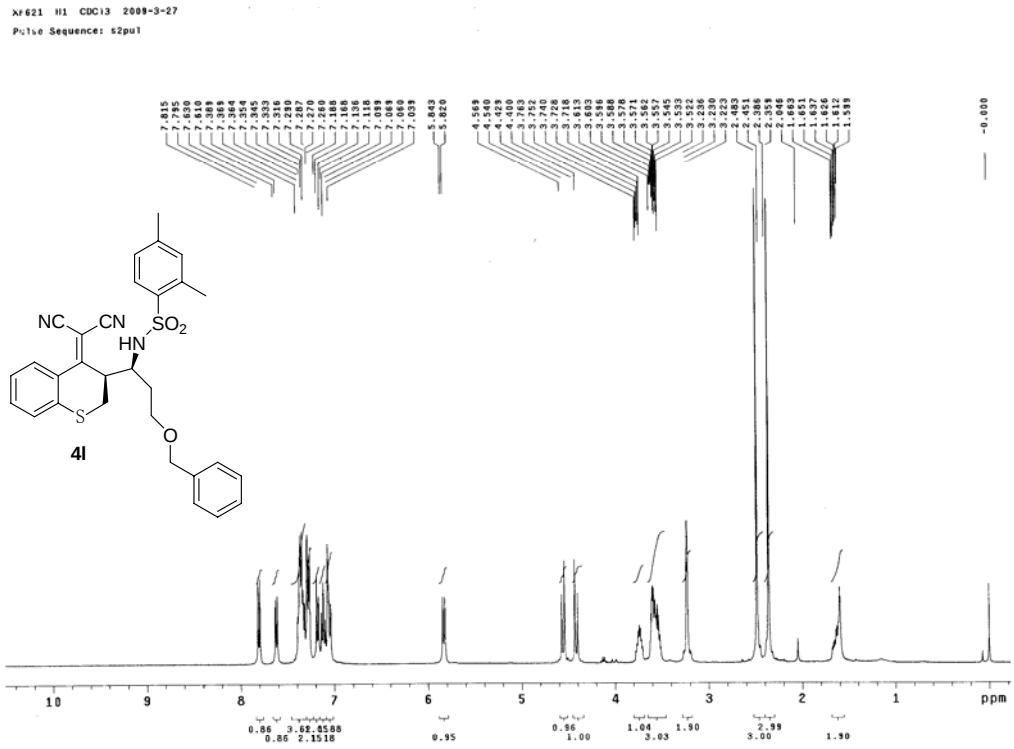
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

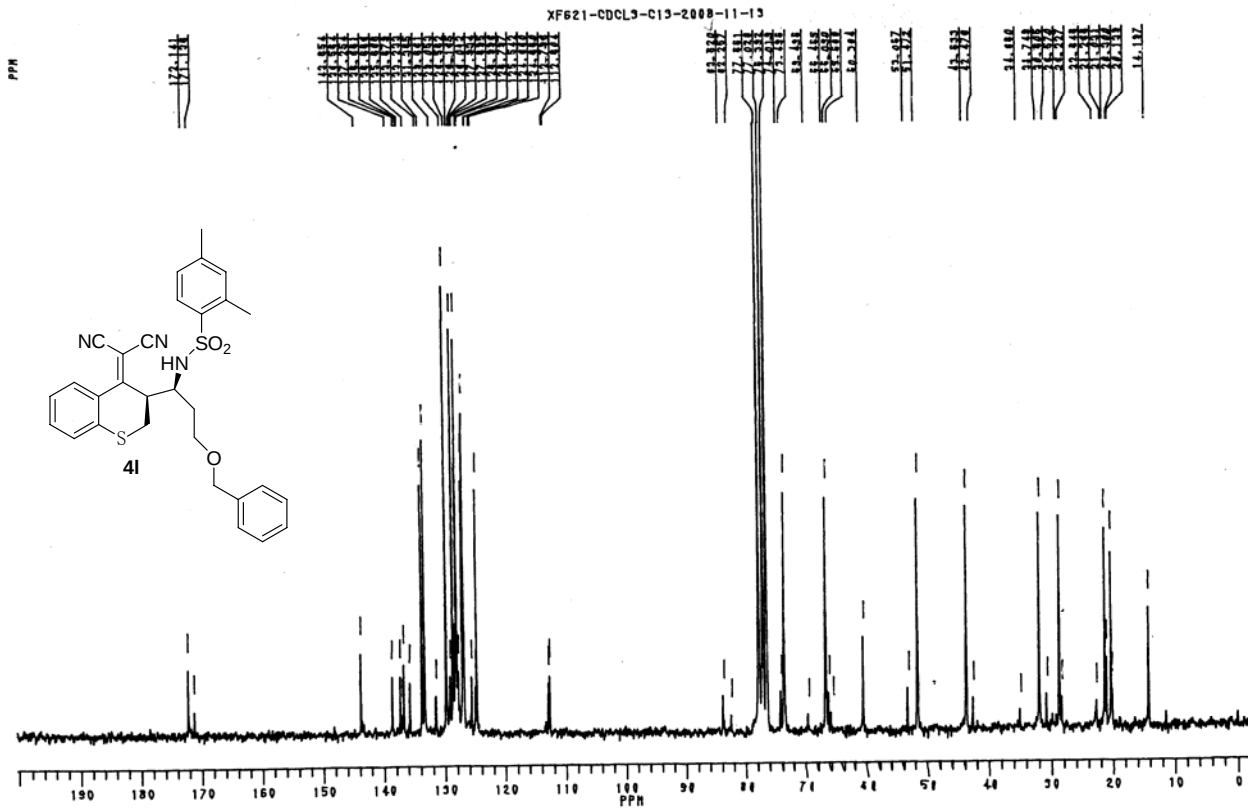


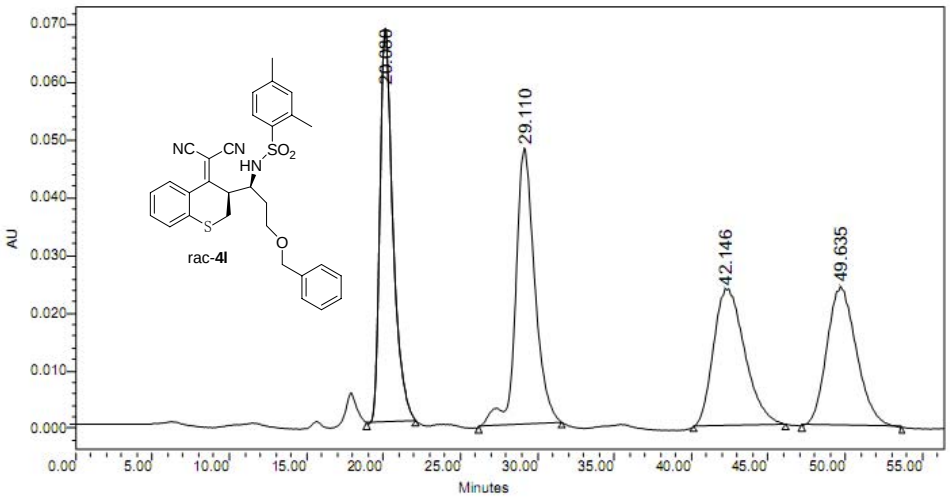
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.381	1491556	9.87	51923	10.28
2	12.985	6276642	40.61	226804	44.88
3	15.392	6147718	39.78	195668	38.72
4	16.635	1167488	9.74	30914	6.12



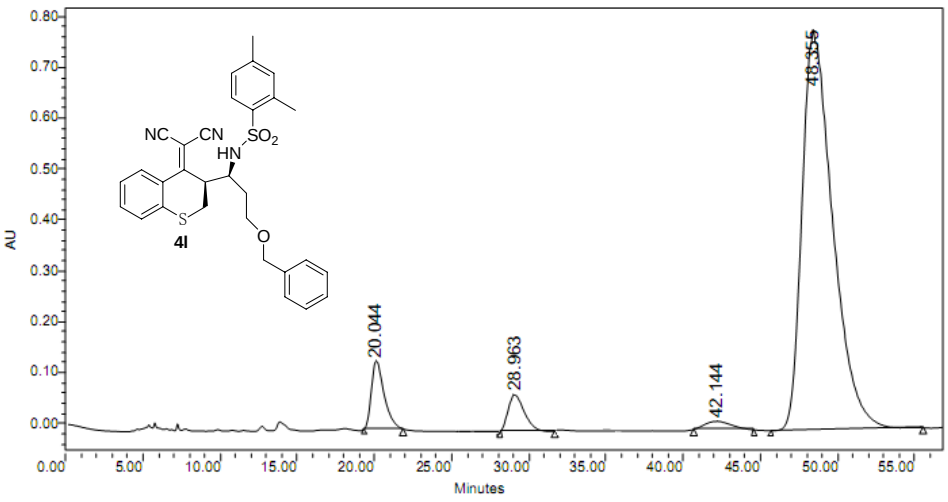
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.957	20685122	80.00	1054512	85.42
2	12.738	2436255	9.42	96044	7.78
3	14.442	2287944	8.85	71617	5.80
4	15.541	446968	1.73	12267	0.99


XF621 H1 CDCl3 2009-3-27
Pulse Sequence: s2pul
NC
CN
SO2
HN
S
O
4l
ppm

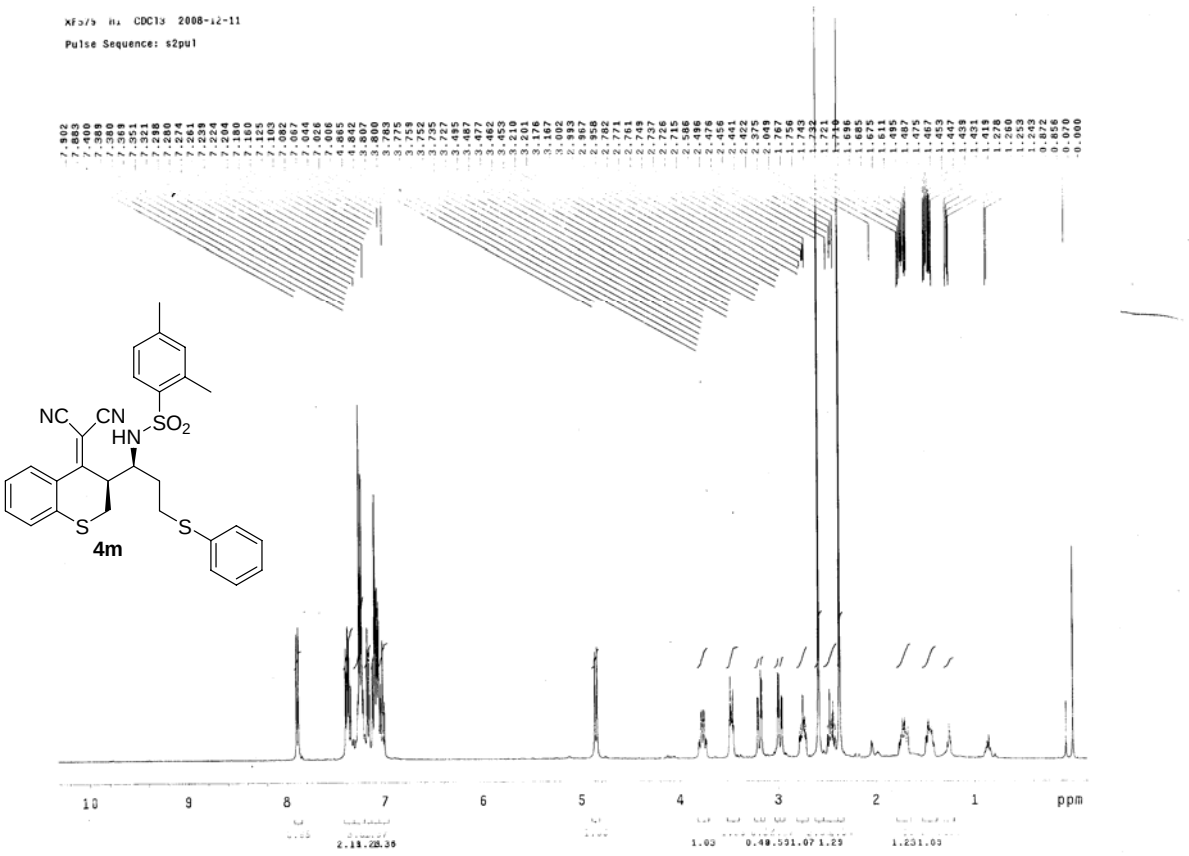

XF621-CDCL3-C13-2008-11-13
PPM
NC
CN
SO2
HN
S
O
4l

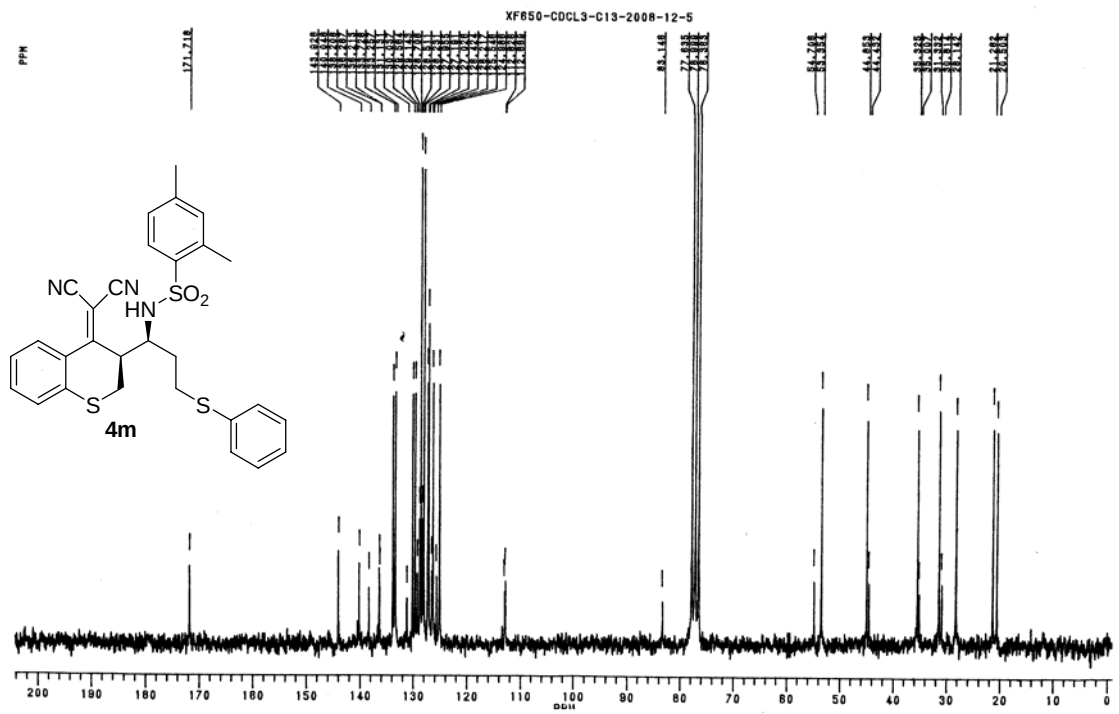


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	20.080	4035133	27.29	68348	41.60
2	29.110	4159647	28.13	47930	29.18
3	42.146	3348648	22.65	23772	14.47
4	49.635	3243466	21.93	24232	14.75



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	20.044	7666885	6.21	132244	13.13
2	28.963	5300806	4.29	72152	7.17
3	42.144	1922562	1.56	16209	1.61
4	48.355	108553710	87.94	786225	78.09


Pulse Sequence: s2pul
NC
CN
HN
SO2
S
S
4m
10
9
8
7
6
5
4
3
2
1
ppm


XF650-CDCL3-C13-2008-12-5
PPM
NC
CN
HN
SO2
S
S
4m
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190
180
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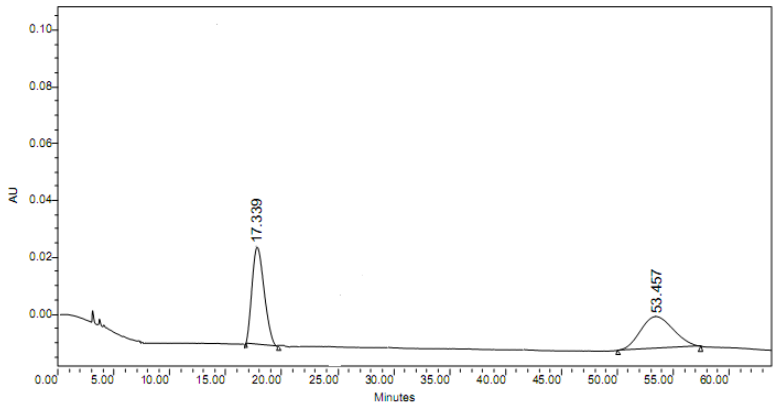
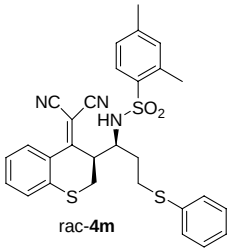
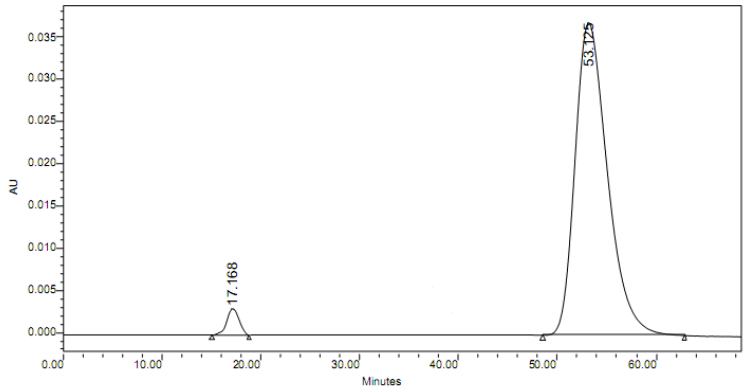
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

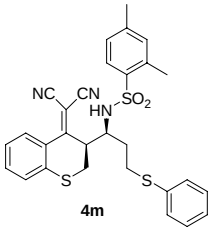




rac-**4m**

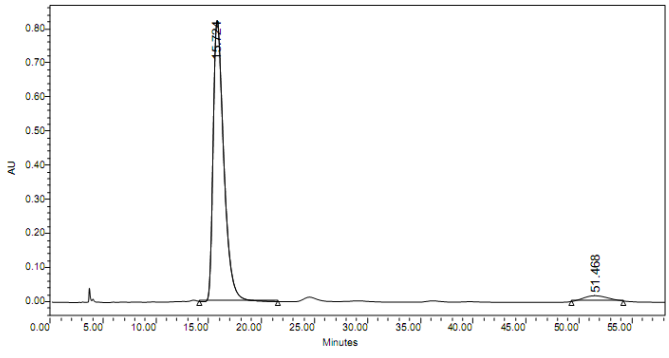
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	17.339	2575461	50.52	34141	14.94
2	53.457	2294797	49.48	11243	4.92

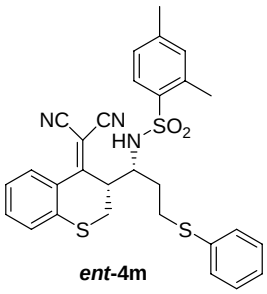




4m

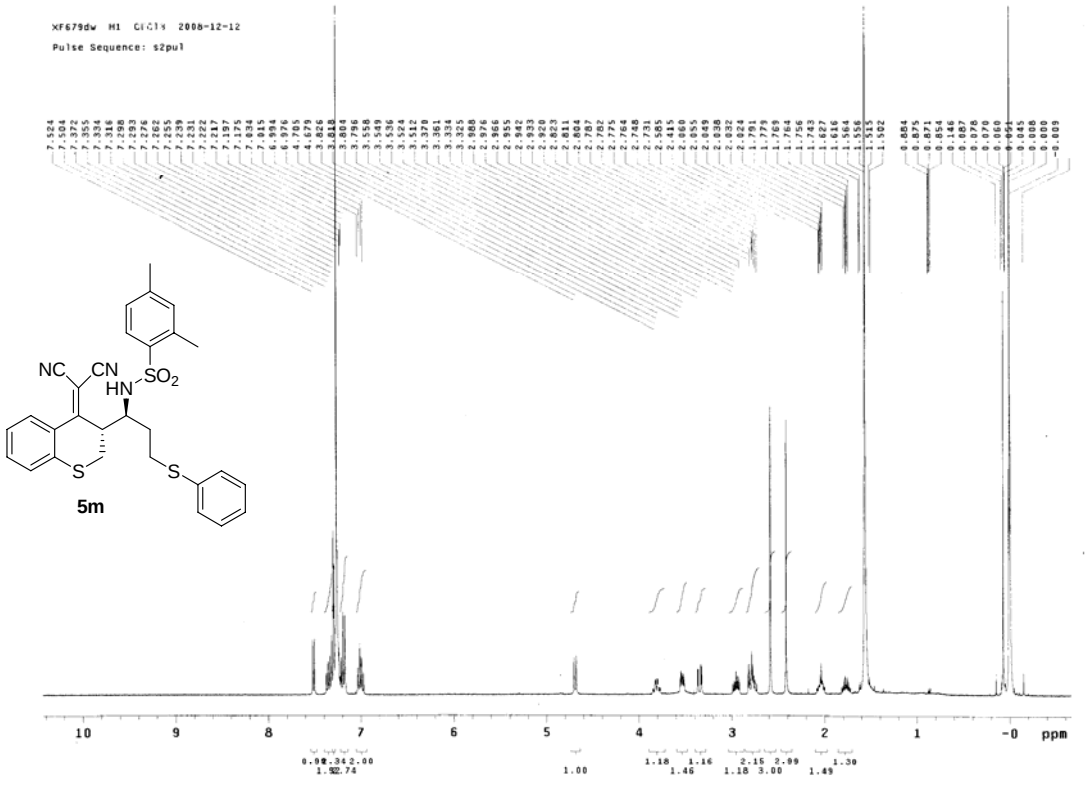
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	17.168	279909	3.21	3158	7.86
2	53.125	8436983	96.79	37033	92.14

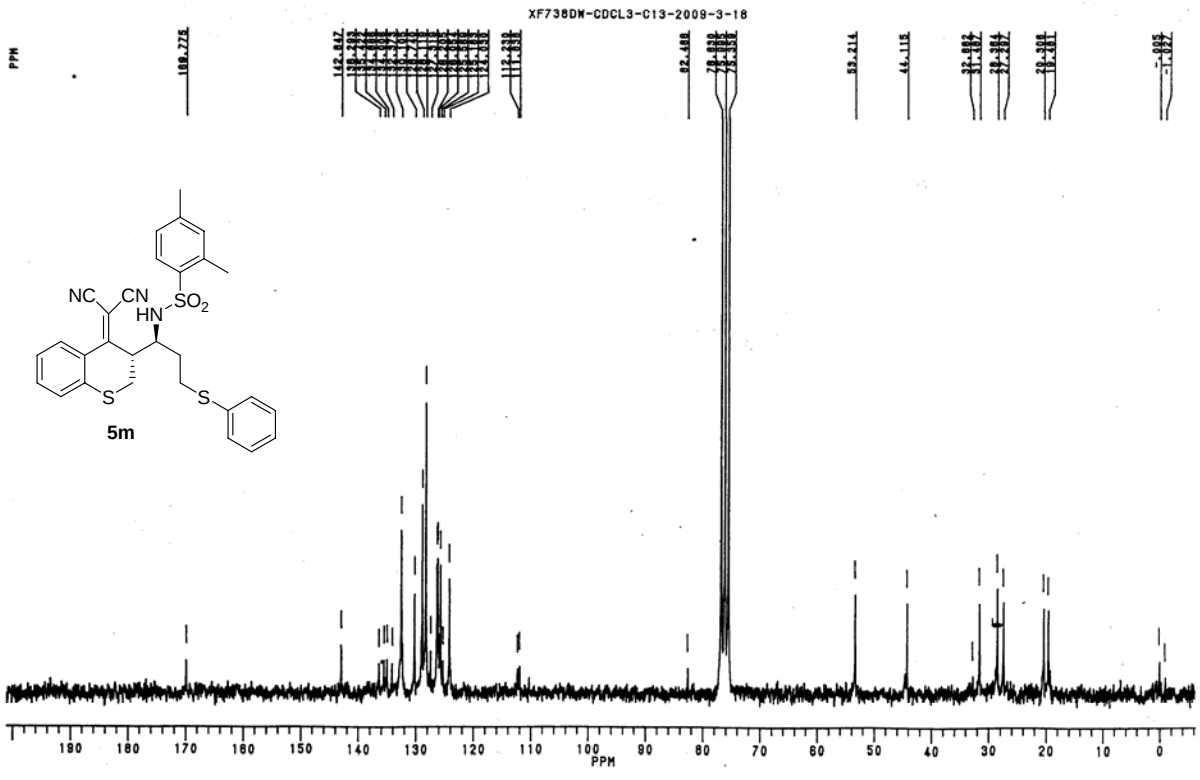


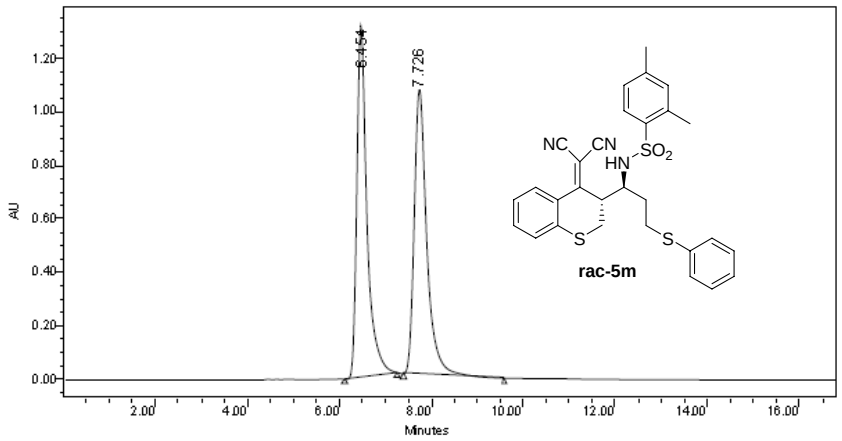


***ent*-4m**

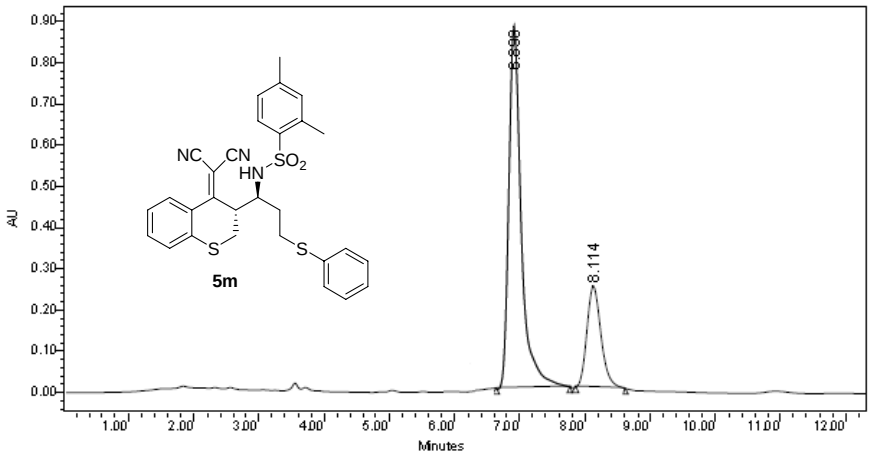
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.724	57870667	95.78	823939	98.09
2	51.468	2550329	4.22	16062	1.91


XF679dw H1 CDCl3 2008-12-12
Pulse Sequence: s2pul
NC
CN
HN
SO2
S
S
5m
10
9
8
7
6
5
4
3
2
1
-0
ppm

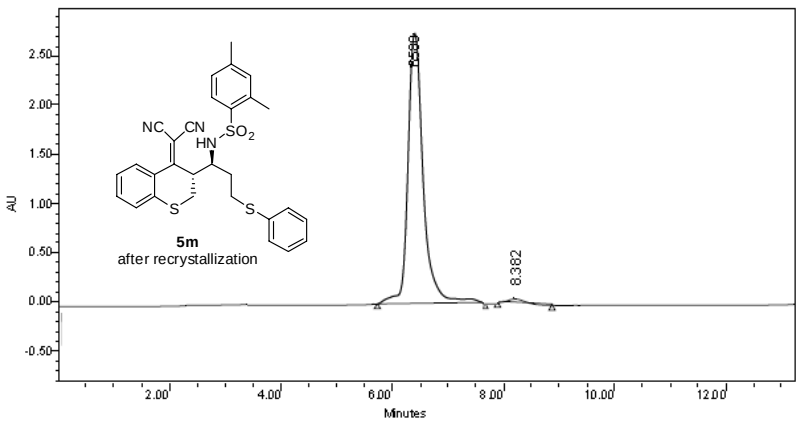

XF736DW-CDCL3-C13-2009-3-18
PPM
NC
CN
HN
SO2
S
S
5m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PPM



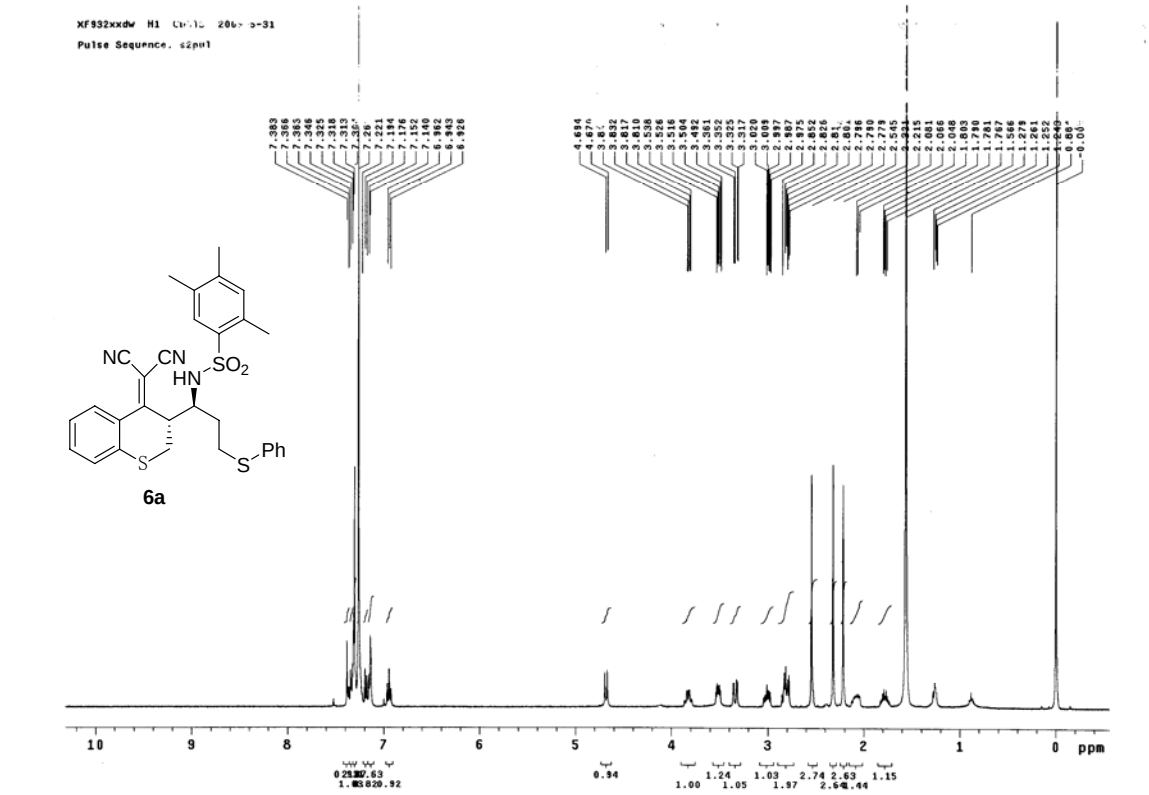
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.454	20161004	49.96	1315004	55.27
2	7.726	20196074	50.04	1064126	44.73

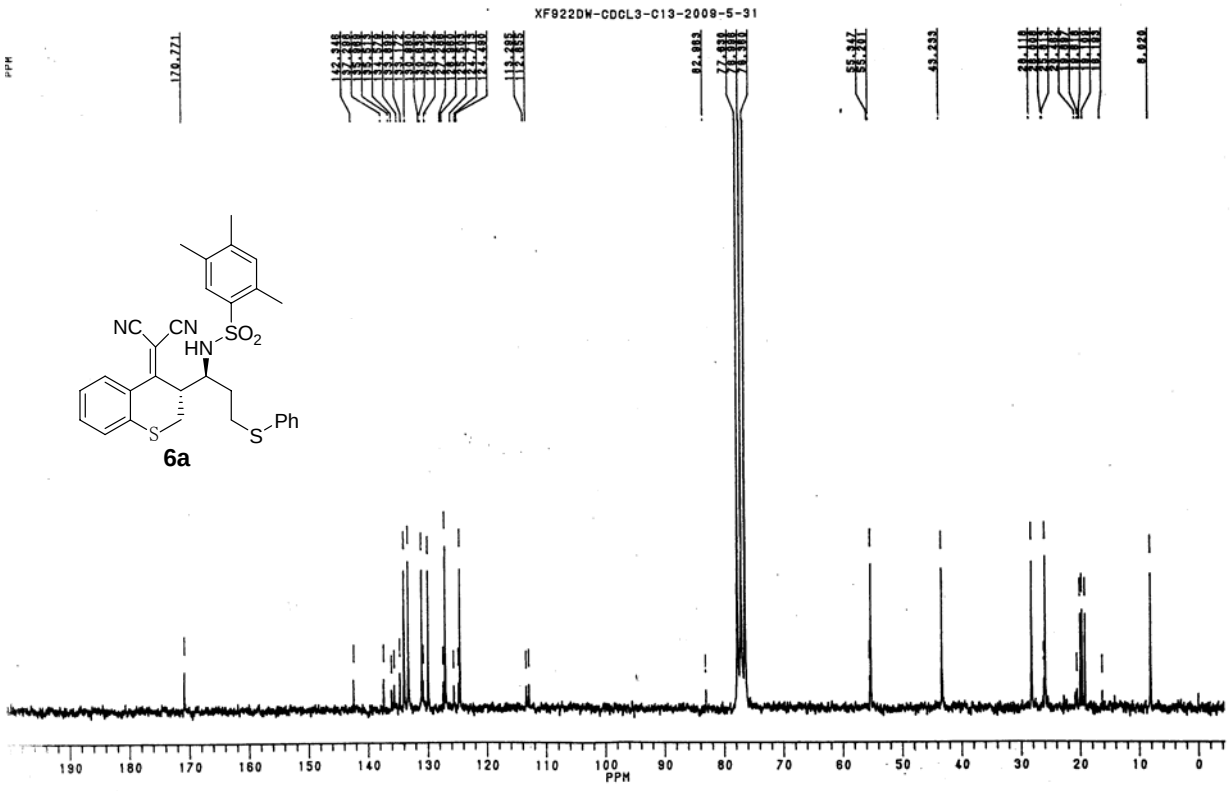


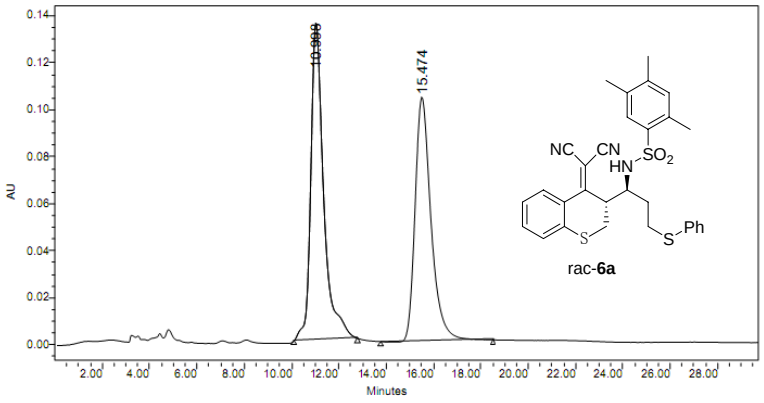
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.898	11736084	75.92	879265	78.12
2	8.114	3723044	24.08	246298	21.88



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.580	52879545	98.31	2746561	98.41
2	8.382	907251	1.69	44318	1.59

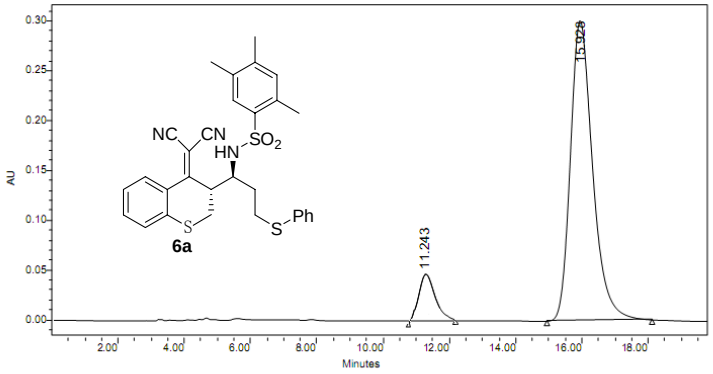

Pulse Sequence. s2pul
NC
CN
HN
SO2
S
Ph
6a
10
9
8
7
6
5
4
3
2
1
0
ppm


XF922DW-CDCL3-C13-2009-5-31
PPM
NC
CN
HN
SO2
S
Ph
6a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PPM



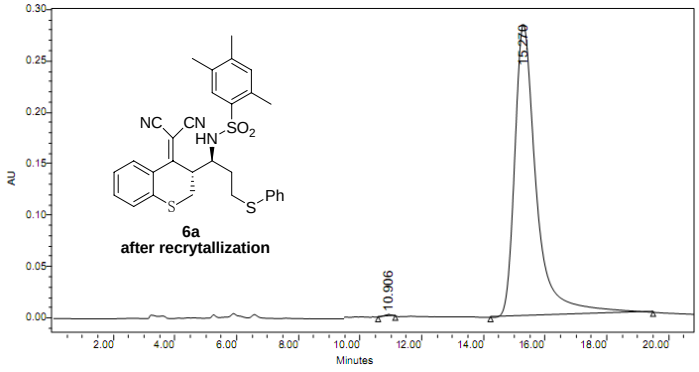
rac-**6a**

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.998	5092625	51.16	134644	56.50
2	15.474	4860838	48.84	103660	43.50



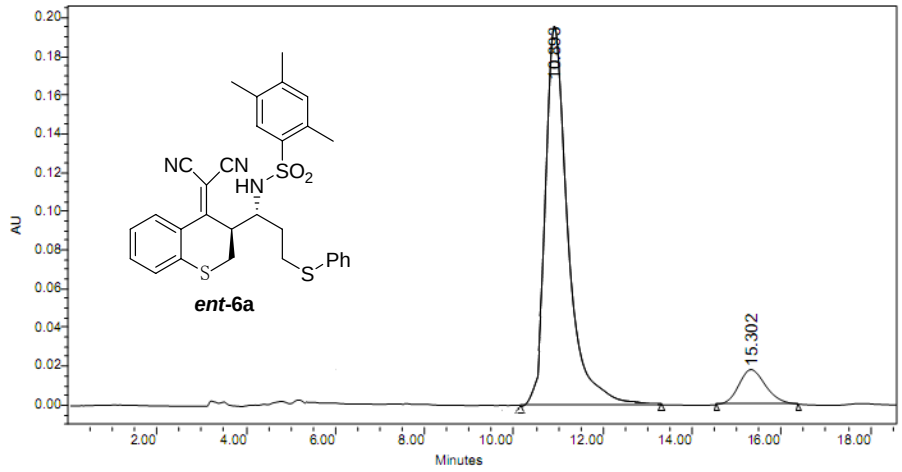
6a

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.243	1340318	8.70	42270	12.32
2	15.928	14072018	91.30	300904	87.68

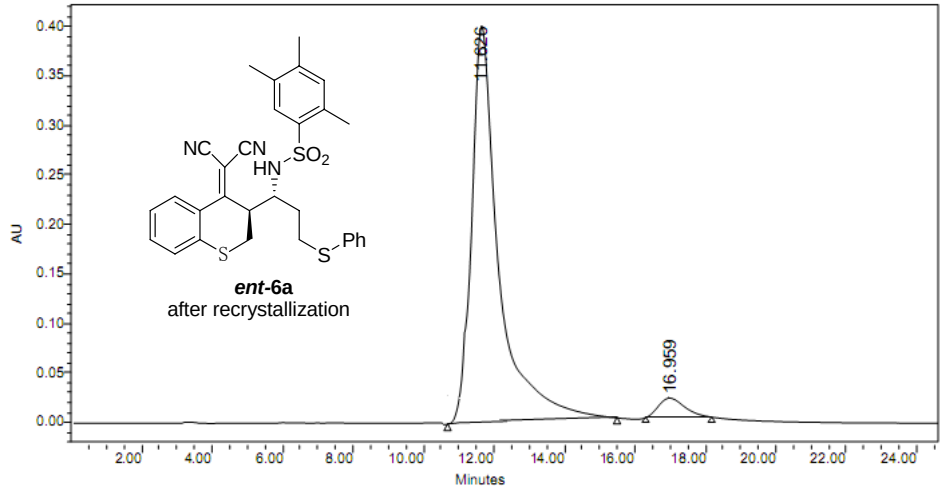


6a
after recrytallization

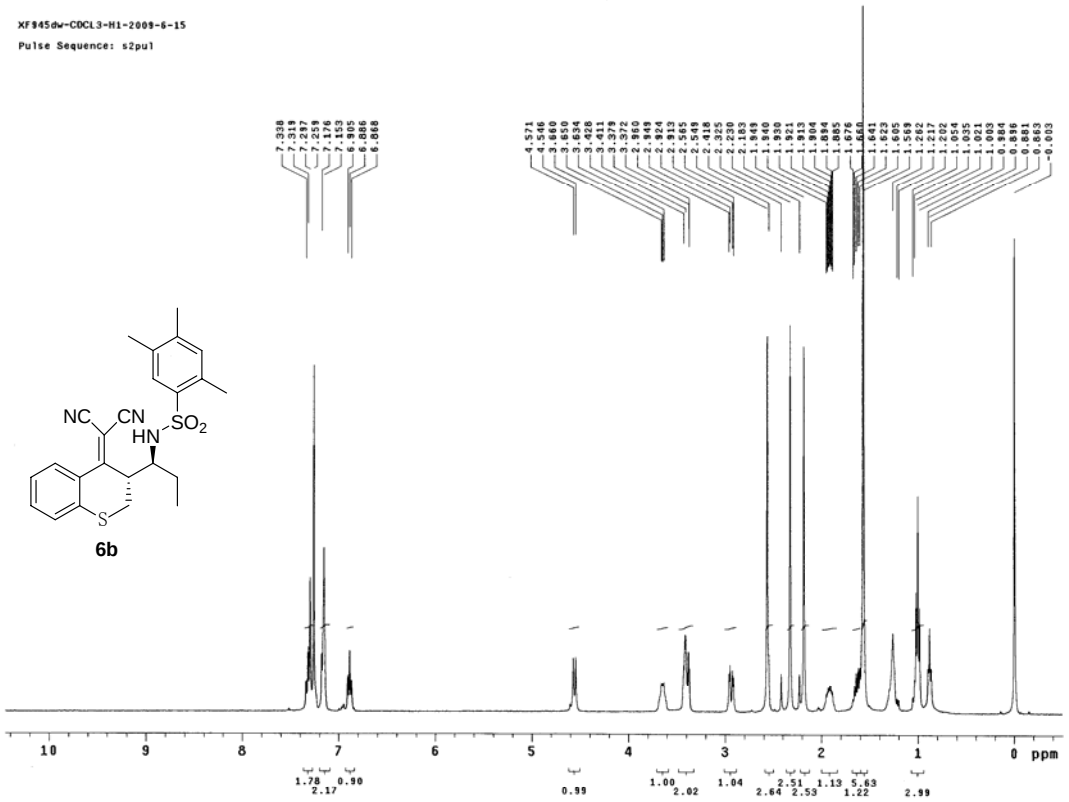
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.906	36275	0.26	1864	0.65
2	15.270	13981865	99.74	284231	99.35

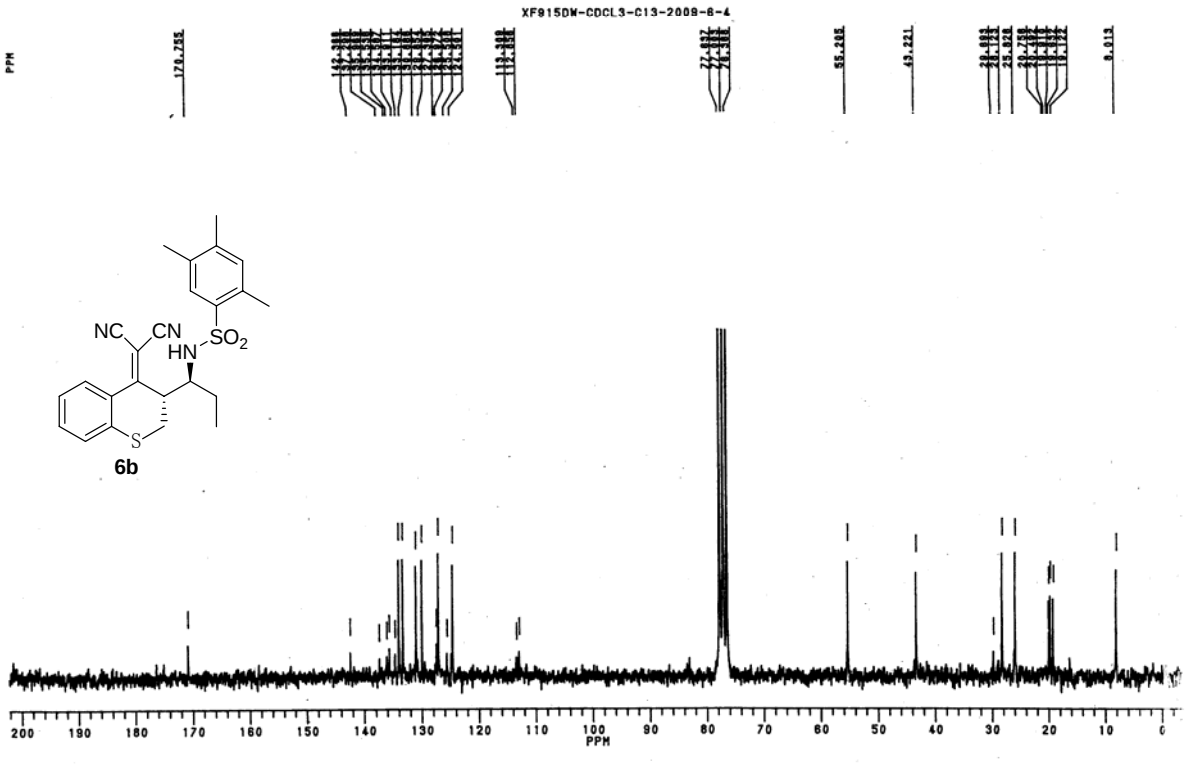


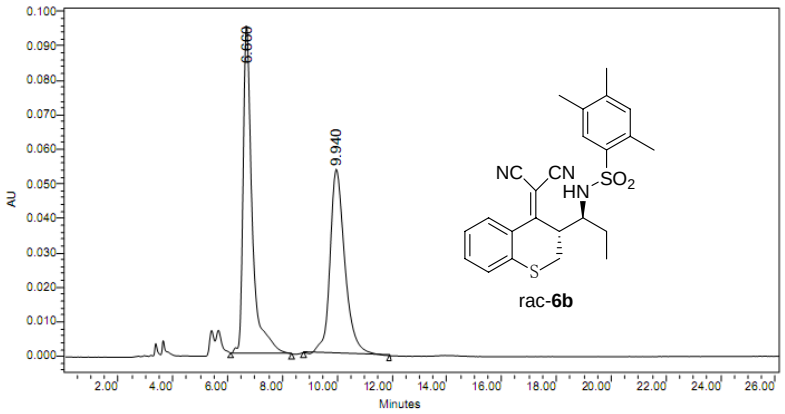
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.893	7327534	90.64	195438	91.58
2	15.302	756818	9.36	17968	8.42



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.626	22822569	96.84	399778	95.91
2	16.959	745746	3.16	17061	4.09

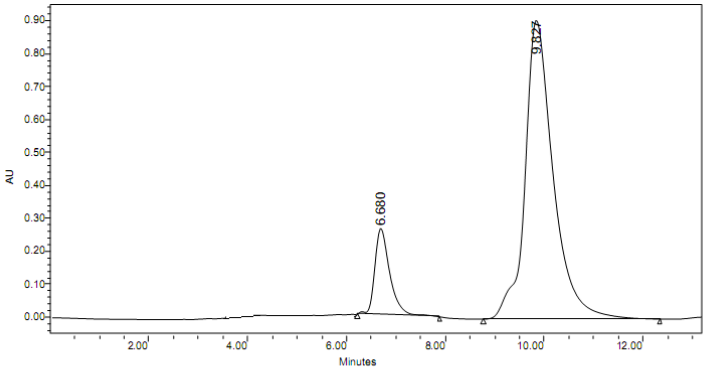

XF945dw-CDCL3-H1-2009-6-15
Pulse Sequence: s2pul
NC
CN
HN
SO2
S
6b
ppm

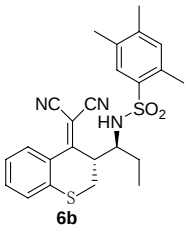

XF915DW-CDCL3-C13-2009-6-4
PPM
NC
CN
HN
SO2
S
6b
PPM



rac-**6b**

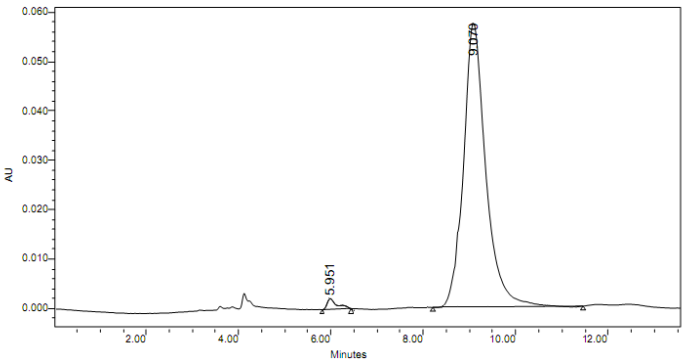
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.660	2194065	51.95	95015	64.01
2	9.940	2029149	48.05	53429	35.99

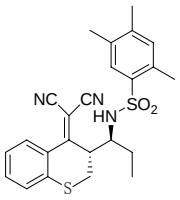




6b

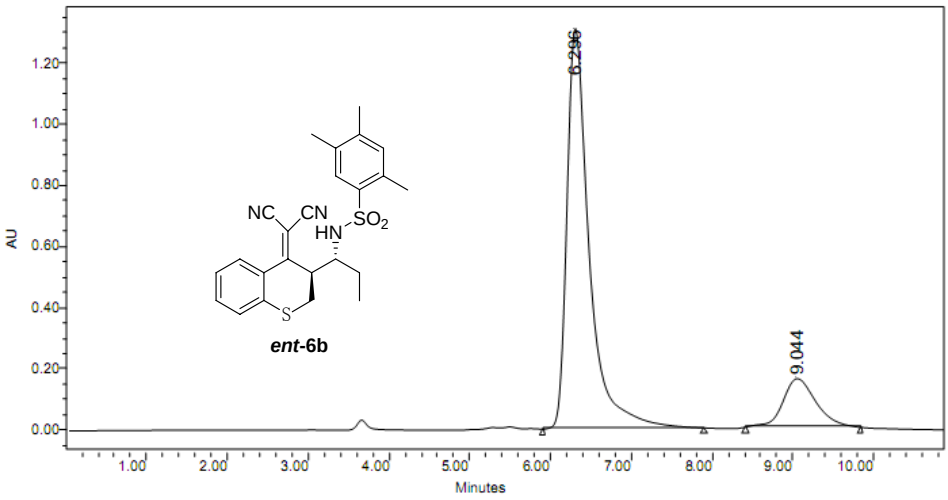
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.680	5602410	13.45	261840	22.42
2	9.827	36061467	86.55	906224	77.58



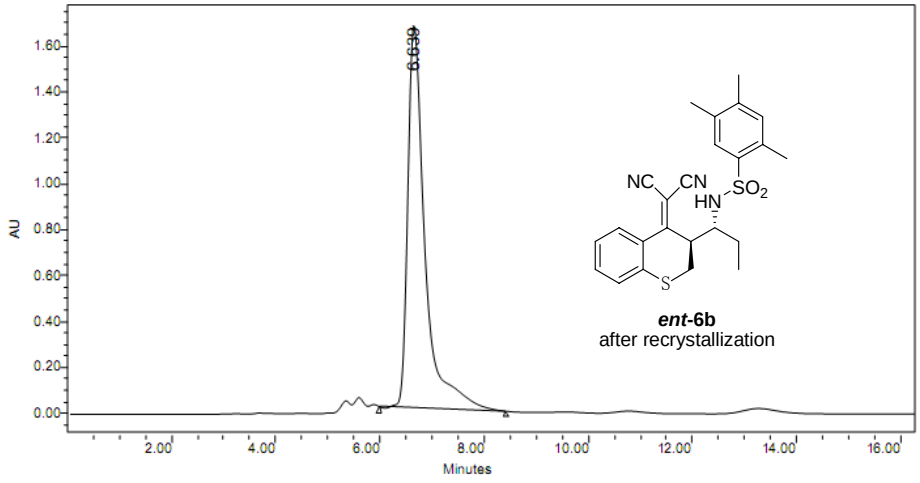


6b
after recrystallization

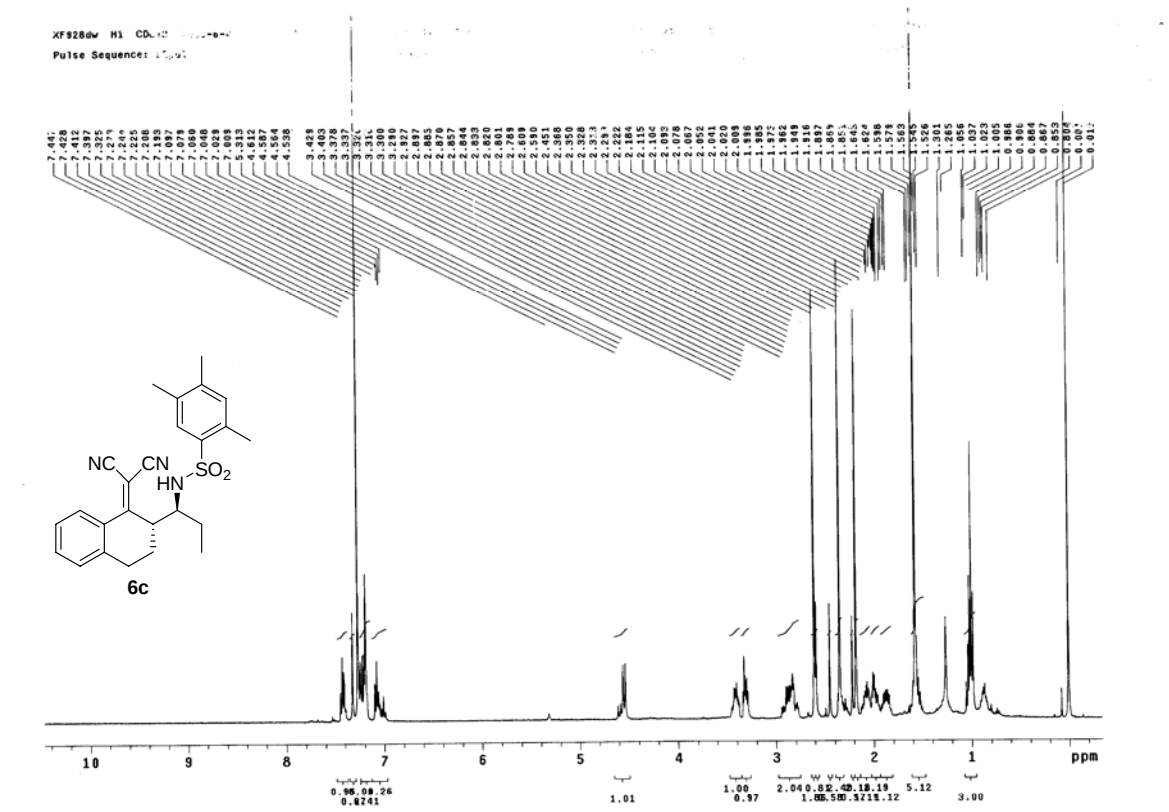
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	5.951	35184	1.65	2235	3.74
2	9.070	2094533	98.35	57486	96.26

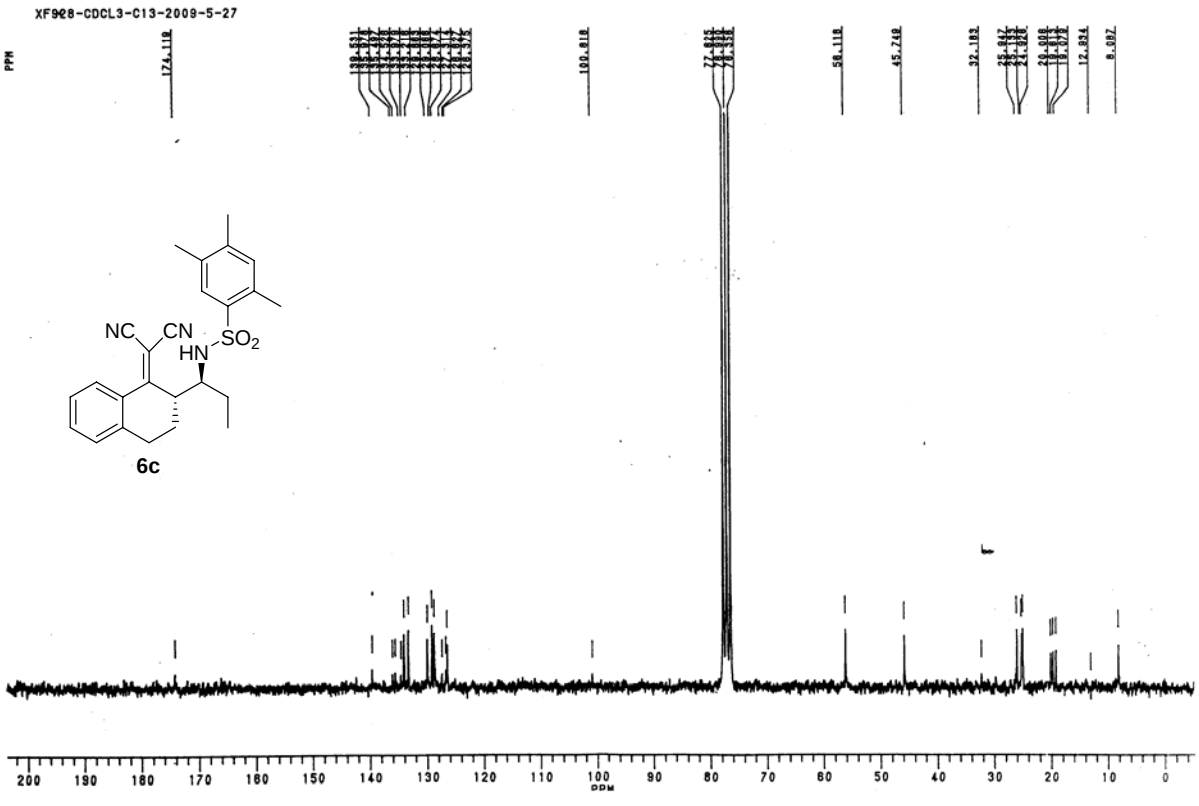


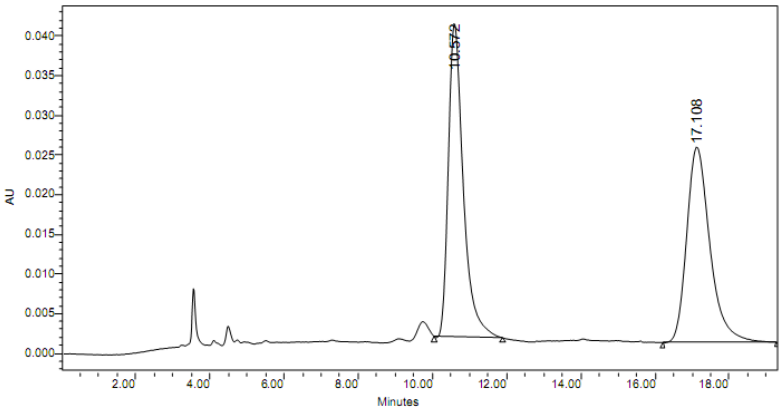
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.296	25201943	84.77	1310874	89.21
2	9.044	4528993	15.23	158521	10.79

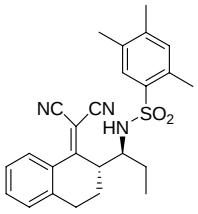


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	6.639	38352376	100.00	1665692	100.00


XF928dw H1
Pulse Sequence:
NC
CN
HN
SO2
6c
10
9
8
7
6
5
4
3
2
1
ppm

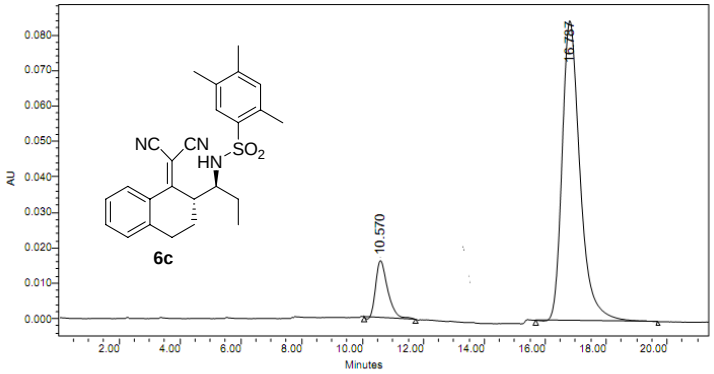

XF928-CDCL3-C13-2009-5-27
PPM
NC
CN
HN
SO2
6c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PPM





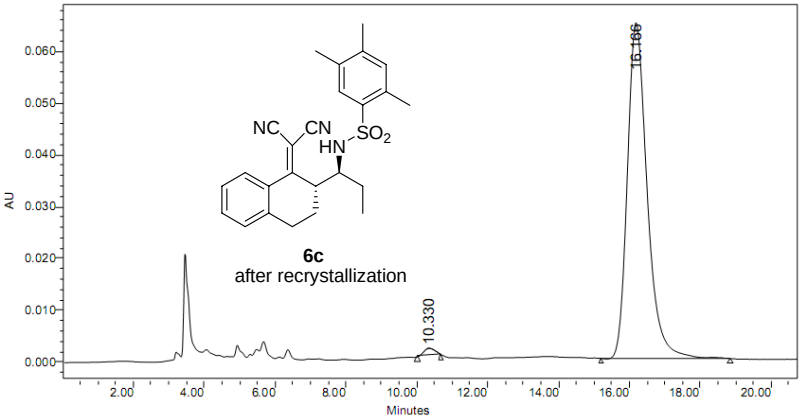
rac-6c

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.572	1110421	50.80	39553	61.62
2	17.108	1075280	49.20	24637	38.38



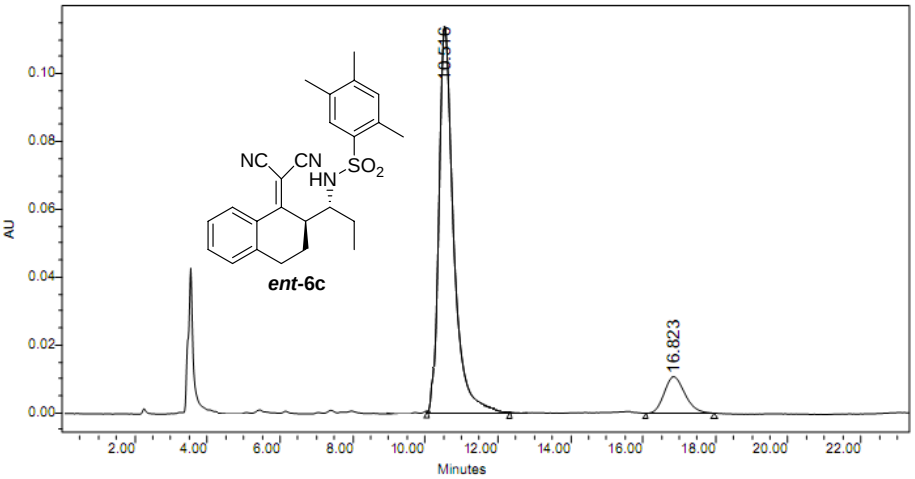
6c

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.570	451487	11.54	16252	16.13
2	16.787	3462491	88.46	84533	83.87

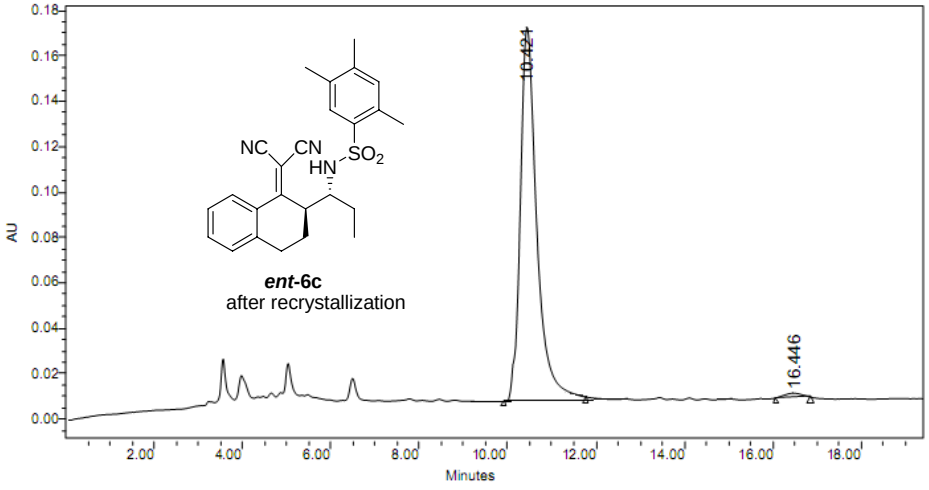


6c
after recrystallization

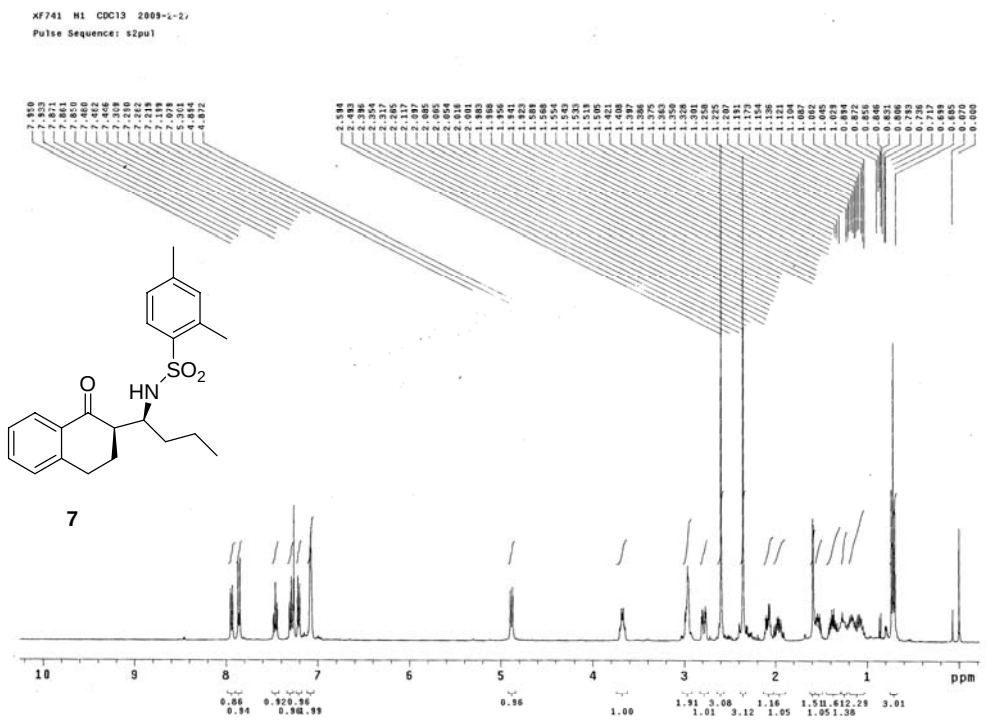
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.330	32978	1.29	1483	2.23
2	16.166	2525338	98.71	64880	97.77

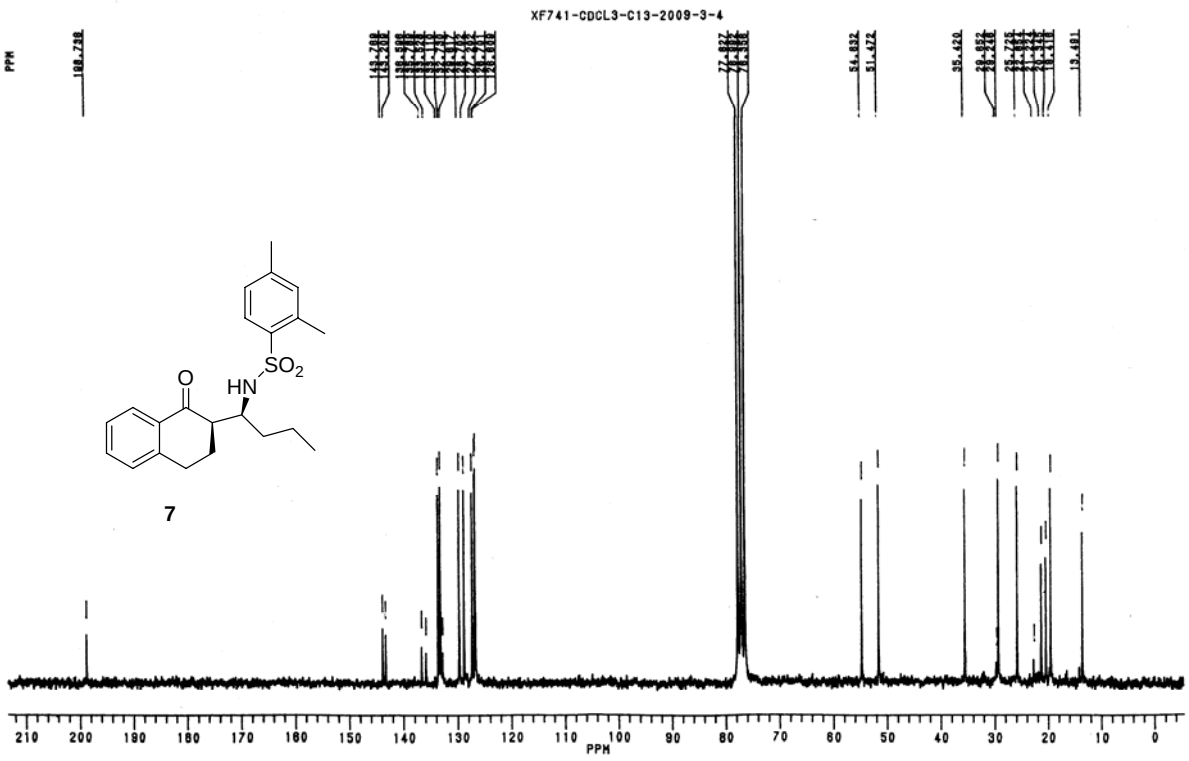


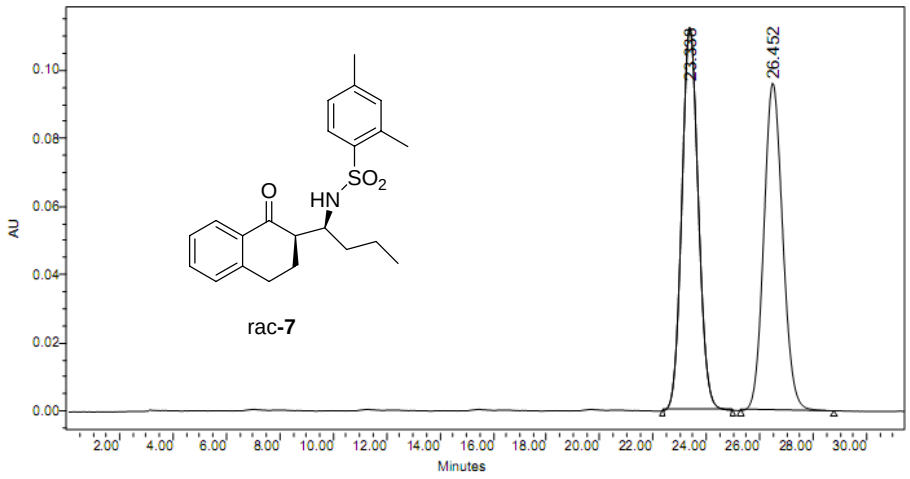
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.516	2845476	86.89	109730	91.05
2	16.823	429397	13.11	10791	8.95



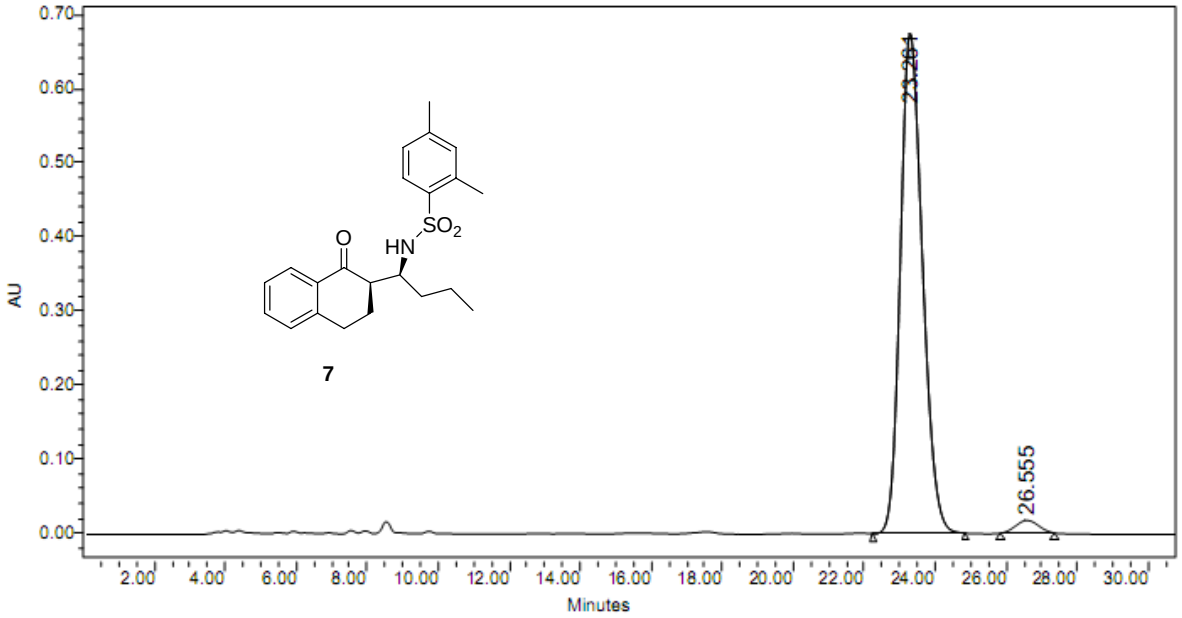
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.421	3862867	98.71	159603	98.84
2	16.446	50651	1.29	1876	1.16


XF741 H1 CDCl3 2009-3-2
Pulse Sequence: s2pul
O
HN
SO2
7
ppm

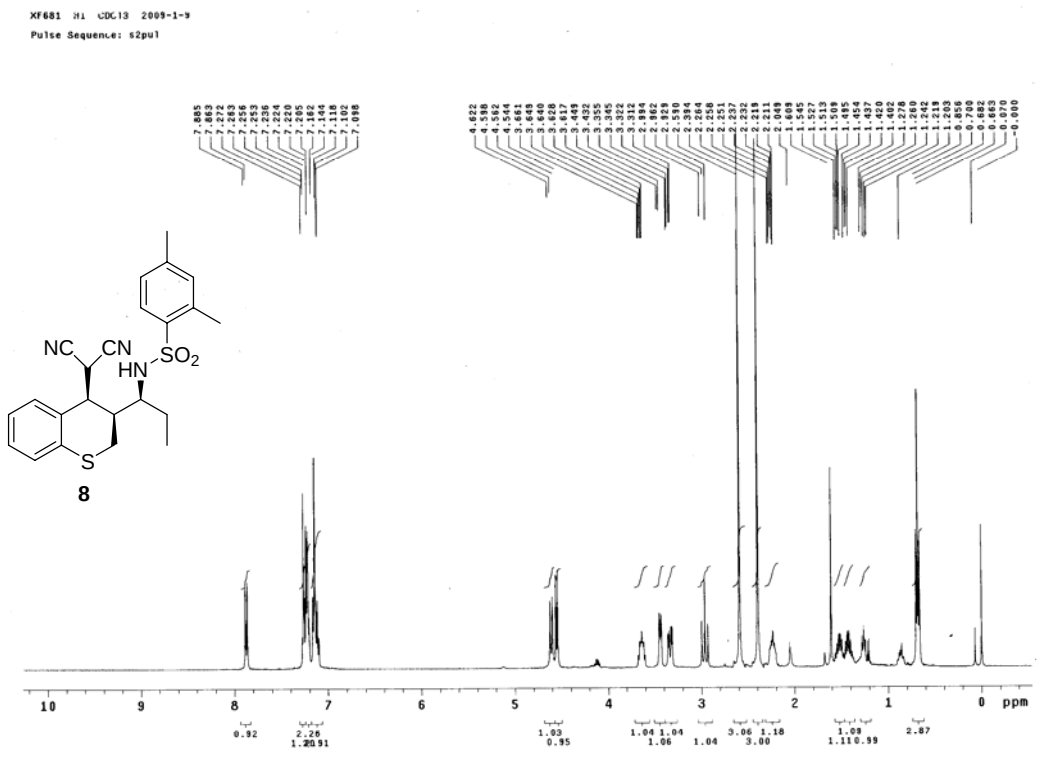

XF741-CDCL3-C13-2009-3-4
PPM
O
HN
SO2
7
PPM



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	23.338	4826448	50.51	112316	53.93
2	26.452	4728047	49.49	95956	46.07



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	23.261	29231360	97.45	674980	97.52
2	26.555	763889	2.55	17156	2.48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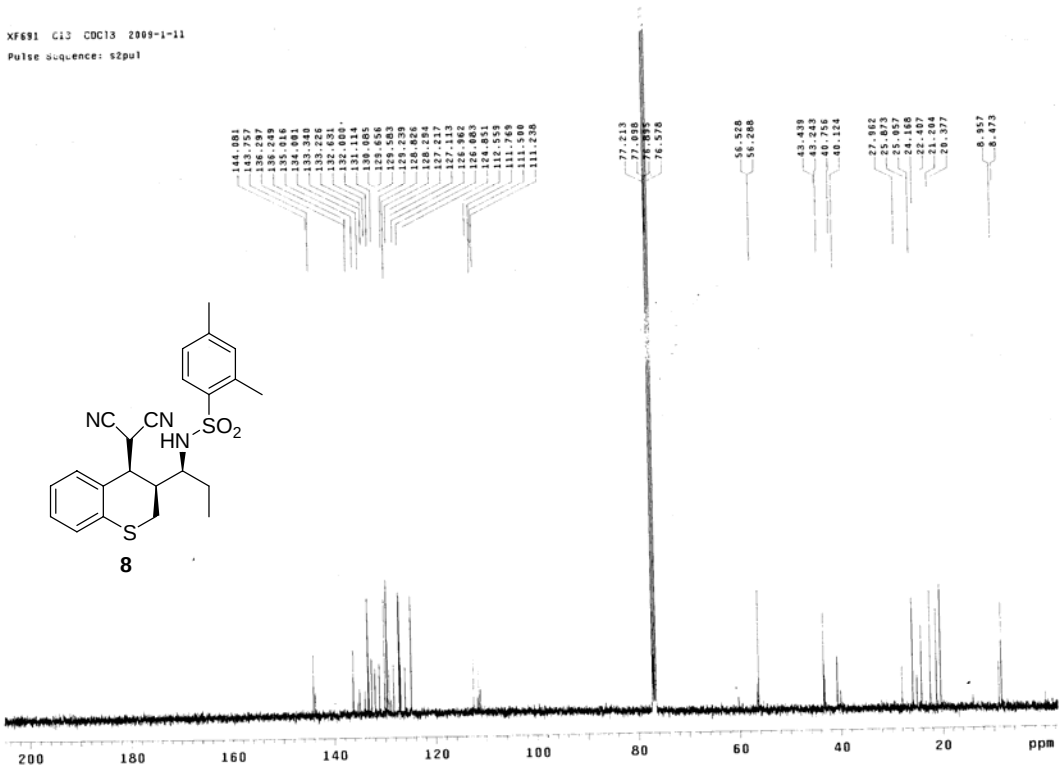
CN
HN
SO2
S
8
ppm


XF691 C13 CDCl3 2009-1-11
Pulse Sequence: s2pul
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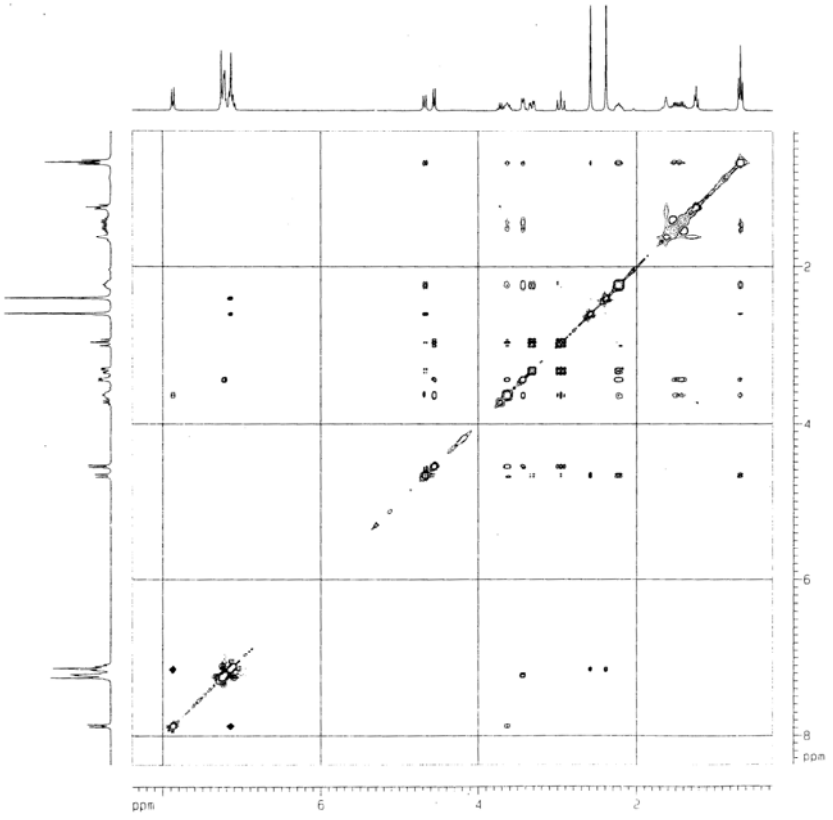
HN
SO2
S
8
ppm


ppm
6
4
2
ppm


XF-681
Current Data Parameters
NAME cyc-2009-06-1
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090217
Time 18.12
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG noesygpt
TD 1024
SOLVENT CDCl3
NS 32
DS 4
SWH 2436.647 Hz
FIDRES 2.379538 Hz
AQ 0.2101748 sec
RG 362
DW 205.200 usec
DE 6.00 usec
TE 300.0 K
D0 0.00000300 sec
D1 2.00000000 sec
D8 1.00000000 sec
IN0 0.00041640 sec
MCREST 0.00000000 sec
MCWRK 1.00000000 sec
STSCNT 256
======== CHANNEL f1 ========
NUC1 1H
P1 7.80 usec
PL1 -2.00 dB
SFO1 300.1313094 MHz
F1 - Acquisition parameters
ND0 1
TD 512
SFO1 300.1313 MHz
FIDRES 4.759077 Hz
SW 8.159 ppm
FnMODE States-TPPI
F2 - Processing parameters
SI 1024
SF 300.1300124 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 States-TPPI
SF 300.1300124 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
2D NMR plot parameters
CX2 15.00 cm
CY1 15.00 cm
F2PLO 6.381 ppm
F2LO 2515.30 Hz
F2PH1 0.252 ppm
F2H1 78.65 Hz
F1PLO 6.381 ppm
F1LO 2515.30 Hz
F1PH1 0.252 ppm
F1H1 78.65 Hz
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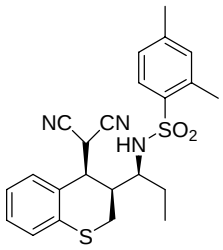
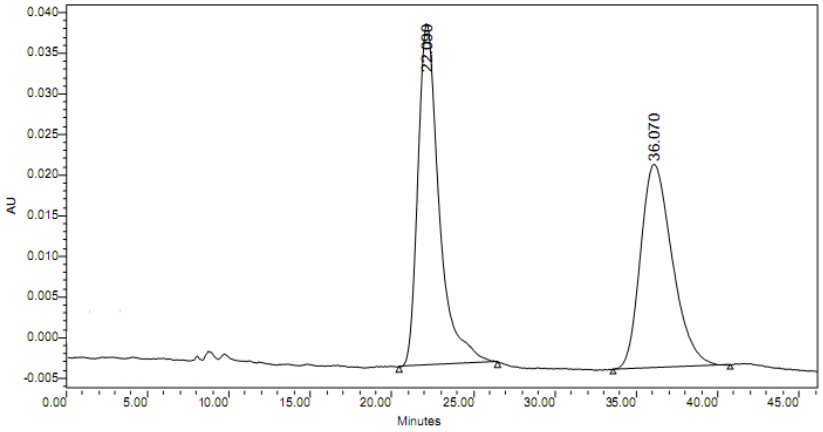
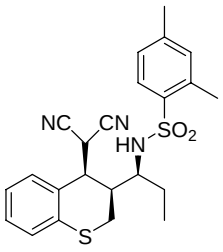
F1HZCM 162.44315 Hz/cm


NC
CN
HN
SO2
S

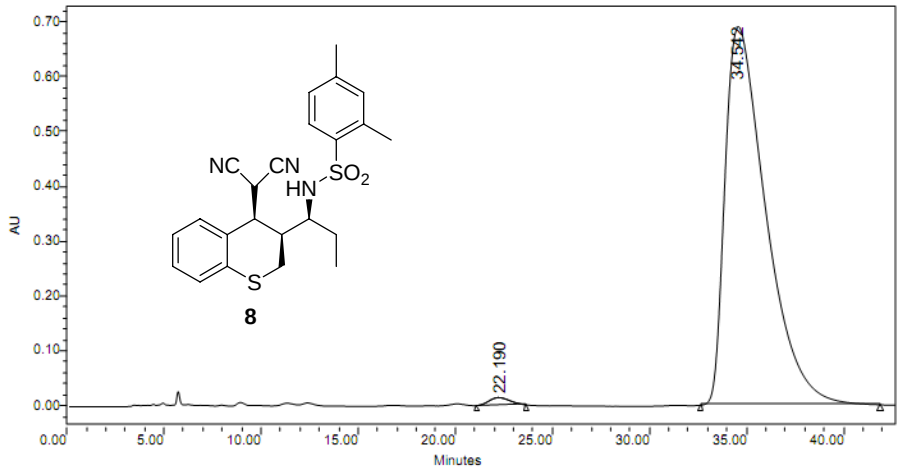
8





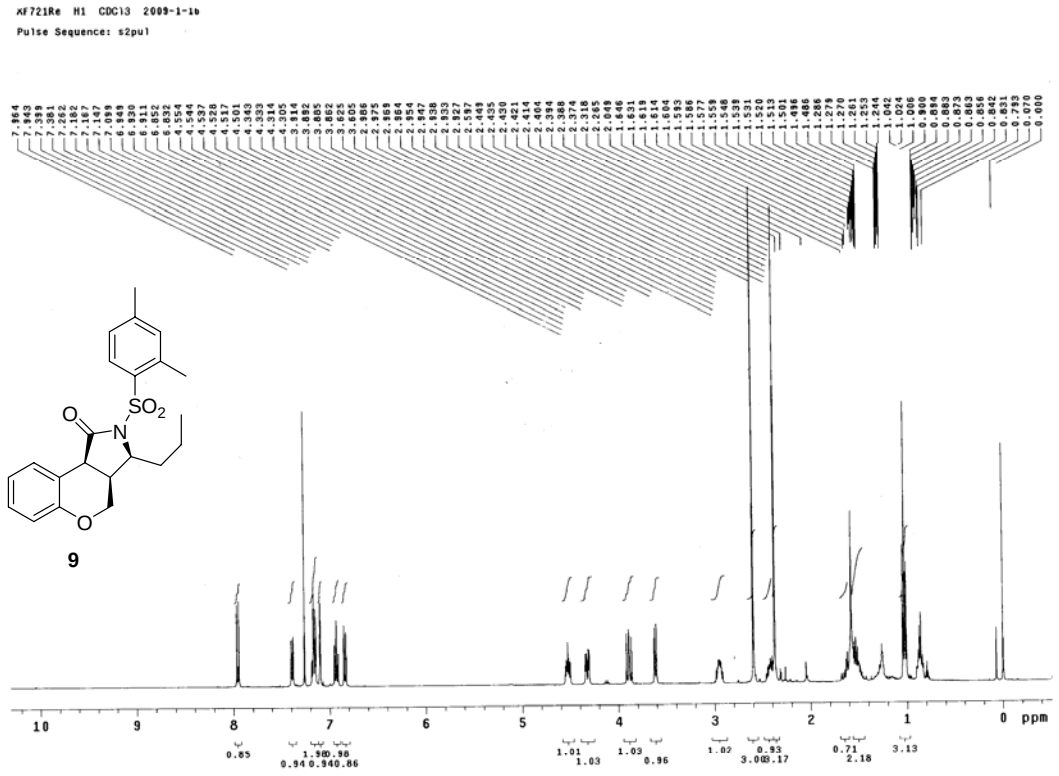
rac-**8**

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	22.090	3829451	51.91	42101	62.68
2	36.070	3408440	48.09	25071	37.32



8

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	22.190	1053796	1.03	13999	1.99
2	34.542	100949388	98.97	689665	98.01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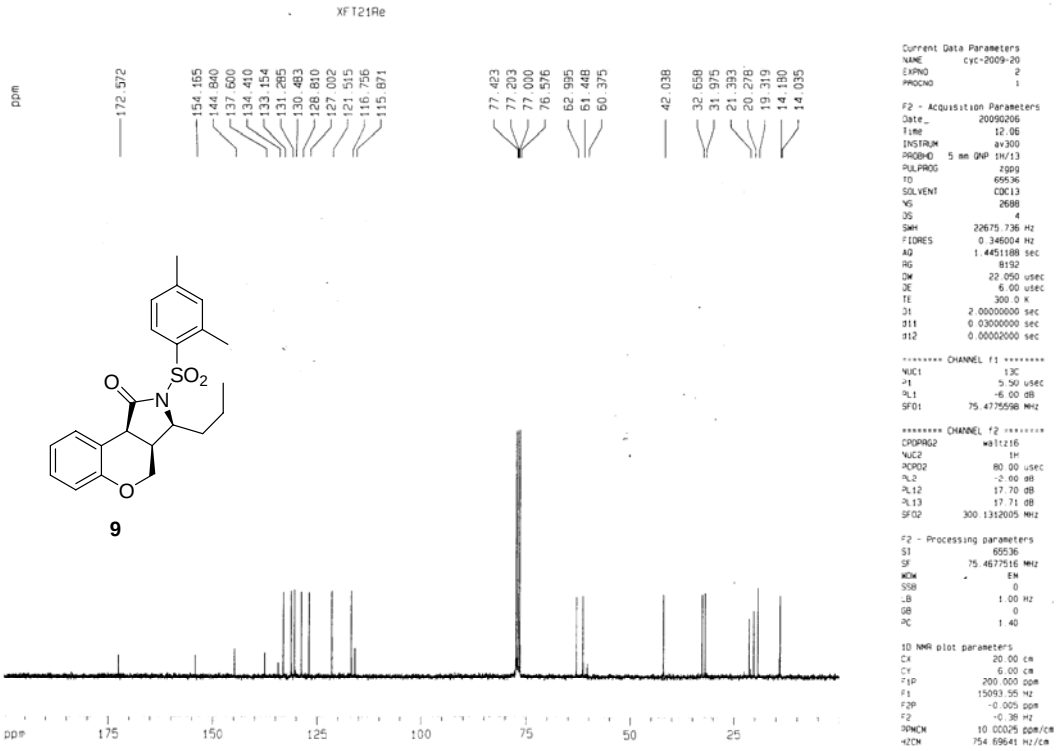
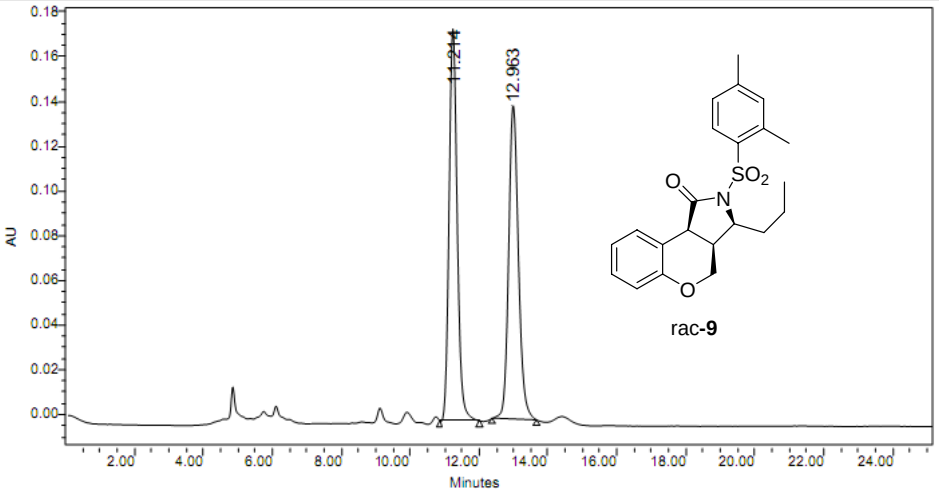
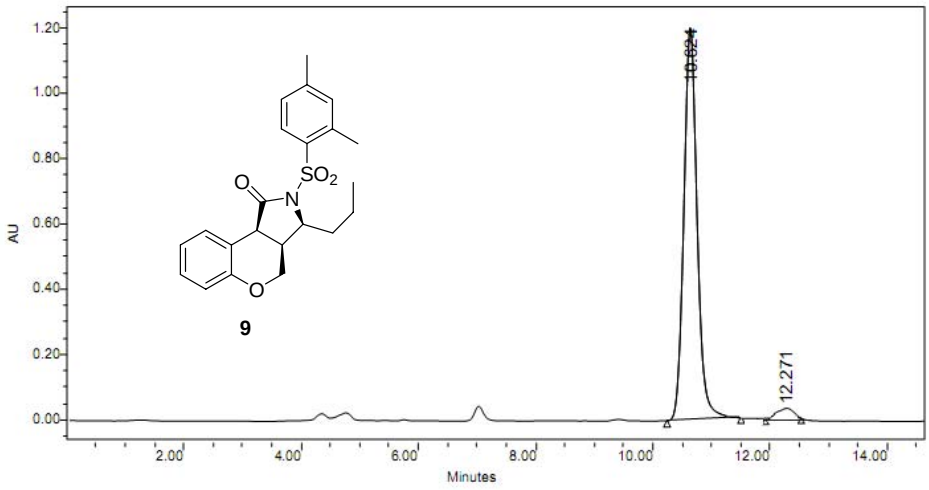
Pulse Sequence: s2pul
9
ppm


XFT21Re
9
ppm



rac-**9**

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.214	2877115	51.06	175306	55.58
2	12.963	2757425	48.94	140078	44.42



9

	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.624	18891552	95.01	1204179	98.16
2	12.271	383296	4.99	22609	1.84