Organocatalytic Asymmetric [4+2] Formal Cycloadditions of Cyclohexenylidenemalononitriles and Enals to Construct Chiral Bicyclo[2.2.2]octanes

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Supplementary Information

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1. General methods

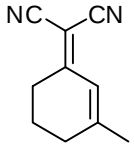
NMR data were obtained for ^{1}H at 400 MHz, and for ^{13}C at 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2. In each case, enantiomeric ratio was determined by HPLC analysis on a chiral column in comparison with authentic racemate, using a Daicel Chiralpak AD-H Column (250 × 4.6 mm) or Chiralpak OD Column (250 × 4.6 mm), Chiralpak IB Column (250 × 4.6 mm), Chiralpak IC Column (250 × 4.6 mm). UV detection was monitored at 220 nm or 254 nm. Optical rotation was 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 secondary amines **1** were synthesized according to the literature procedures.[1]

1. (*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, K. Jiang, T.-Y. Liu and Y.-C. Chen, *Org. Lett.*, 2009, **11**, 2848; (*d*) C. Ma, Z.-J. Jia, J.-X. Liu, Q.-Q. Zhou, L. Dong, Y.-C. Chen, *Angew. Chem.*, *Int. Ed.*, 2013, **52**, 948.

2. General procedure for the preparation of cyclohexenylidenemalononitriles

The cyclohexenylidenemalononitriles **2a**–**2e** were prepared from the corresponding 3-substituted 2-cyclohexenones and malononitrile. *The desired condensation product could not be obtained from simple 2-cyclohexenone*.

A solution of 3-methyl-2-cyclohexenone (2.2 g, 20 mmol), malononitrile (1.3 g, 20 mmol), anhydrous ammonium acetate (0.3 g, 2 mmol) and acetic acid (1.1 mL, 20 mmol) in toluene (20 mL) was refluxed under a Dean-Stark trap for 48 h at 120 °C. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to give the cyclohexenylidenemalononitrile **2a** (2.3 g, 73% yield).



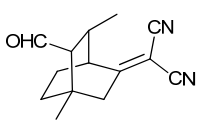
2-(3-Methylcyclohex-2-en-1-ylidene)malononitrile 2a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.62 (d, *J* = 1.6 Hz, 1H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.33 (t, *J* = 6.0 Hz, 2H), 2.06 (s,

3H), 1.88 (quint, J = 6.4 Hz, 2H) ppm.

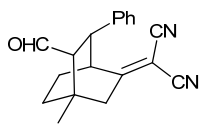
3. General procedure for asymmetric [4+2] formal cycloadditions

Conditions A: The reaction was conducted with cyclohexenylidenemalononitrile **2** (0.1 mmol) and *a*,*β*-unsaturated aldehyde **3** (0.15 mmol) in the presence of *α*,*α*-diphenylprolinol *O*-TES ether **1b** (0.02 mmol), *N*,*N*-diisopropylethylamine (DIPEA, 0.02 mmol) in MeCN (1 mL) at room temperature. After completion (monitored by TLC analysis), the solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the bicyclo[2.2.2]octanes **4a**, **4c** and **4d**.

Conditions B: The reaction was conducted with cyclohexenylidenemalononitrile **2** (0.1 mmol) and *a*,*β*-unsaturated aldehydes **3** (0.15 mmol) in the presence of *α*,*α*-diphenylprolinol *O*-TMS ether **1a** (0.02 mmol), benzoic acid (0.02 mmol) in MeCN (1 mL) at room temperature. After completion (monitored by TLC analysis), the solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the bicyclo[2.2.2]octanes **4b** and **4e**–**4q**.

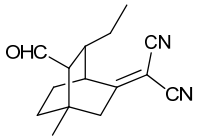


2-((1*S*,4*S*,5*R*)-5-Formyl-4,6-dimethylbicyclo[2.2.2]octan-2-ylidene)malononitrile (4a) was obtained in 84% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 97% by HPLC analysis on Chiralpak OD column (5% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 25.53 min, t_{minor} = 29.33 min; $[\alpha]_D^{20}$ = -15.3 (c = 0.6 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.87 (d, J = 2.4 Hz, 1H), 2.98-2.97 (m, 1H), 2.62-2.56 (m, 2H), 2.47 (d, J = 20.4 Hz, 1H), 2.00-1.89 (m, 2H), 1.74-1.59 (m, 2H), 1.33-1.27 (m, 1H), 1.22 (s, 3H), 0.92 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.9, 187.0, 111.1, 111.0, 83.6, 61.9, 44.7, 42.2, 34.5, 31.6, 27.0, 24.7, 24.0, 20.9 ppm; ESI HRMS: calcd. for $C_{14}H_{16}N_2O$+MeOH+Na^+283.1417, found 283.1420.

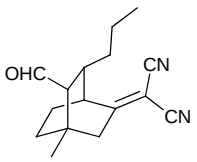


2-((1*S*,4*S*,5*R*)-5-Formyl-4-methyl-6-phenylbicyclo[2.2.2]octan-2-ylidene)malononitrile (4b) was obtained in 90% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 98% by HPLC analysis on Chiralpak OD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 14.07 min, t_{minor} = 22.66 min; $[\alpha]_D^{20}$ = +44.1 (c = 1.8 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ =

9.93 (d, *J* = 1.6 Hz, 1H), 7.35-7.26(m, 3H), 7.02 (d, *J* = 7.2 Hz, 2H), 3.88 (dd, *J* = 7.2 Hz, *J* = 1.6 Hz, 1H), 3.24-3.23 (m, 1H), 2.83-2.74 (m, 2H), 2.58 (d, *J* = 20.4 Hz, 1H), 2.20-2.13 (m, 1H), 1.79-1.67 (m, 2H), 1.41-1.34 (m, 1H), 1.35 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.6, 185.8, 141.1, 129.0, 127.5, 126.8, 111.0, 110.5, 83.7, 59.5, 45.0, 43.0, 42.3, 34.7, 27.1, 25.5, 24.0 ppm; ESI HRMS: calcd. for $C_{19}H_{18}N_2O$+MeOH+Na^+ 345.1573, found 345.1576.

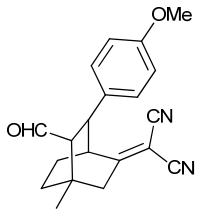


2-((1*S*,4*S*,5*R*,6*S*)-6-Ethyl-5-formyl-4-methylbicyclo[2.2.2]octan-2-ylidene)malononitrile (4c) was obtained in 73% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 91% by HPLC analysis on Chiralpak OD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 7.06 min, t_{minor} = 8.40 min; $[\alpha]_D^{20}$ = -21.6 (*c* = 1.3 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.88 (d, *J* = 2.0 Hz, 1H), 3.14-3.12 (m, 1H), 2.56 (dd, *J* = 20.4 Hz, *J* = 2.4 Hz, 1H), 2.46 (d, *J* = 20.4 Hz, 1H), 2.39-2.37 (m, 1H), 1.96-1.92 (m, 1H), 1.71-1.57 (m, 2H), 1.31-1.22 (m, 3H), 1.22 (s, 3H), 1.13-1.09 (m, 1H), 0.89 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.2, 187.4, 111.2, 111.0, 83.4, 60.6, 44.8, 40.3, 38.8, 34.6, 28.8, 27.4, 24.9, 24.1, 11.5 ppm; ESI HRMS: calcd. for $C_{15}H_{18}N_2O$-H^+ 241.1346, found 241.1341.

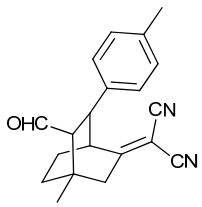


2-((1*S*,4*S*,5*R*,6*S*)-5-Formyl-4-methyl-6-propylbicyclo[2.2.2]octan-2-ylidene)malononitrile (4d) was obtained in 76% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 93% by HPLC analysis on Chiralpak IC column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 26.70 min, t_{minor} = 31.71 min; $[\alpha]_D^{20}$ = -11.4 (*c* = 0.45 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.88 (d, *J* = 2.4 Hz, 1H), 3.09-3.09 (m, 1H), 2.56 (dd, *J* = 20.8 Hz, *J* = 2.4 Hz, 1H), 2.49-2.44 (m, 2H), 1.97-1.93 (m, 2H), 1.71-1.59 (m, 2H), 1.31-1.19 (m, 4H), 1.21 (s, 3H), 1.05-1.01 (m, 1H), 0.89 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.3, 187.4, 111.1, 111.0, 83.3, 60.8, 44.8, 40.4, 38.0, 36.7, 34.6, 27.4, 24.9, 24.1, 20.0, 13.8 ppm; ESI HRMS: calcd. for $C_{16}H_{20}N_2O$-H^+ 255.1503, found 255.1501.

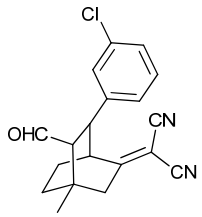
2-((1*S*,4*S*,5*R*)-5-Formyl-6-(4-methoxyphenyl)-4-methylbicyclo[2.2.2]octan-2-ylidene)malononitrile (4e) was obtained in 94% yield. After reduction, the enantiomeric excess of the corresponding



alcohol was determined to be 95% by HPLC analysis on Chiralpak OD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 20.26 min, t_{minor} = 8.44 min; $[\alpha]_D^{20}$ = +13.4 (*c* = 1.2 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.90 (d, *J* = 1.2 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.80-3.78 (m, 1H), 3.78 (s, 3H), 3.19 (d, *J* = 2.4 Hz, 1H), 2.77 (dd, *J* = 20.8 Hz, *J* = 2.4 Hz, 1H), 2.70 (d, *J* = 6.4 Hz, 1H), 2.57 (d, *J* = 20.8 Hz, 1H), 2.17-2.05 (m, 1H), 1.77-1.65 (m, 2H), 1.38-1.26 (m, 1H), 1.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.7, 186.0, 158.7, 133.1, 127.9, 114.3, 111.0, 110.7, 83.7, 59.8, 55.2, 45.0, 43.3, 41.6, 34.7, 27.0, 25.5, 24.0 ppm; ESI HRMS: calcd. for $C_{20}H_{20}N_2O_2$+MeOH+Na^+ 375.1679, found 375.1689.

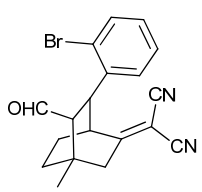


2-((1*S*,4*S*,5*R*)-5-Formyl-4-methyl-6-(p-tolyl)bicyclo[2.2.2]octan-2-ylidene)malononitrile (4f) was obtained in 83% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 95% by HPLC analysis on Chiralpak OD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 14.04 min, t_{minor} = 7.18 min; $[\alpha]_D^{20}$ = +21.3 (*c* = 0.43 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.91 (d, *J* = 1.2 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 3.82 (dd, *J* = 7.2 Hz, *J* = 1.6 Hz, 1H), 3.22-3.20 (m, 1H), 2.77 (dd, *J* = 20.8 Hz, *J* = 2.4 Hz, 1H), 2.72 (d, *J* = 6.8 Hz, 1H), 2.57 (d, *J* = 20.4 Hz, 1H), 2.32 (s, 3H), 2.15-2.14 (m, 1H), 1.74-1.69 (m, 2H), 1.37-1.32 (m, 1H), 1.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.6, 186.0, 138.1, 137.2, 129.7, 126.6, 111.0, 110.6, 83.7, 59.7, 45.1, 43.1, 42.0, 34.7, 27.1, 25.6, 24.1, 20.9 ppm; ESI HRMS: calcd. for $C_{20}H_{20}N_2O$+MeOH+Na^+ 359.1730, found 359.1734.

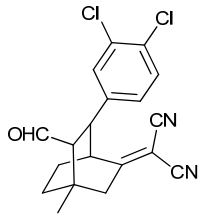


2-((1*S*,4*S*,5*R*)-6-(3-Chlorophenyl)-5-formyl-4-methylbicyclo[2.2.2]octan-2-ylidene)malononitrile (4g) was obtained in 91% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 94% by HPLC analysis on Chiralpak AD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 5.70 min, t_{minor} = 7.60 min; $[\alpha]_D^{20}$ = +28.6 (*c* = 1.3 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.92 (d, *J* = 1.2 Hz, 1H), 7.29-7.23 (m, 2H), 7.03 (s, 1H), 6.92-6.89 (m, 1H), 3.87 (dd, *J* = 6.8 Hz, *J* = 1.6 Hz, 1H), 3.22-3.21 (m, 1H), 2.79 (dd, *J* = 20.4 Hz, *J* = 2.4 Hz, 1H), 2.69 (d, *J* = 7.2 Hz, 1H), 2.59 (d, *J* = 20.4 Hz, 1H), 2.18-2.12 (m, 1H), 1.78-1.61 (m, 2H), 1.41-1.33 (m, 1H), 1.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.1, 185.1, 143.2, 134.9, 130.3,

127.8, 127.3, 124.8, 110.8, 110.5, 84.0, 59.5, 45.0, 42.6, 41.8, 34.8, 27.0, 25.6, 24.0 ppm; ESI HRMS: calcd. for $C_{19}H_{17}ClN_2O$+MeOH+Na^+ 379.1184 (Cl^{35}) and 381.1155 (Cl^{37}), found 379.1187 and 381.1160.

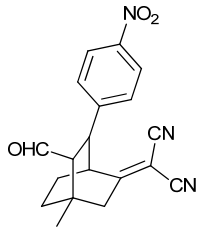


2-((1*S*,4*S*,5*R*)-6-(2-Bromophenyl)-5-formyl-4-methylbicyclo[2.2.2]octan-2-ylidene)malononitrile (4h) was obtained in 87% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 94% by HPLC analysis on Chiralpak OD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 10.14 min, t_{minor} = 8.47 min; $[\alpha]_D^{20}$ = +10.4 (*c* = 1.4 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.88 (d, *J* = 1.2 Hz, 1H), 7.64-7.62 (m, 1H), 7.33-7.29 (m, 1H), 7.18-7.14 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 4.44 (dd, *J* = 7.2 Hz, *J* = 1.6 Hz, 1H), 3.19 (d, *J* = 2.0 Hz, 1H), 2.81 (dd, *J* = 20.4 Hz, *J* = 1.6 Hz, 1H), 2.74 (d, *J* = 7.2 Hz, 1H), 2.58 (d, *J* = 20.4 Hz, 1H), 2.30-2.22 (m, 1H), 1.81-1.74 (m, 2H), 1.43-1.35 (m, 1H), 1.35 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.8, 184.6, 138.9, 134.0, 129.2, 127.7, 126.4, 125.5, 110.9, 110.1, 84.1, 57.9, 44.9, 42.0, 41.6, 34.8, 27.1, 24.7, 24.2 ppm; ESI HRMS: calcd. for $C_{19}H_{17}BrN_2O$+MeOH+Na^+ 423.0679 (Br^{79}) and 425.0659 (Br^{81}), found 423.0681 and 425.0664.

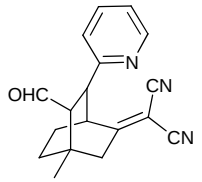


2-((1*S*,4*S*,5*R*)-6-(3,4-Dichlorophenyl)-5-formyl-4-methylbicyclo[2.2.2]octan-2-ylidene)malononitrile (4i) was obtained in 85% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 96% by HPLC analysis on Chiralpak AD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 10.09 min, t_{minor} = 11.38 min; $[\alpha]_D^{20}$ = +17.9 (*c* = 2.1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.93 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 2.0 Hz, 1H), 6.86 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 3.87-3.85 (m, 1H), 3.23 (d, *J* = 2.4 Hz, 1H), 2.79 (dd, *J* = 20.8 Hz, *J* = 2.4 Hz, 1H), 2.65-2.58 (m, 2H), 2.18-2.12 (m, 1H), 1.78-1.61 (2H), 1.42-1.34 (m, 1H), 1.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.9, 184.7, 141.4, 133.2, 131.8, 131.0, 129.2, 125.9, 110.7, 110.4, 84.2, 59.8, 45.0, 42.4, 41.2, 34.9, 27.0, 25.6, 24.2 ppm; ESI HRMS: calcd. for $C_{19}H_{16}Cl_2N_2O$+MeOH+Na^+ 413.0794 (Cl^{35}) and 415.0764 (Cl^{37}), found 413.0793 and 415.0766.

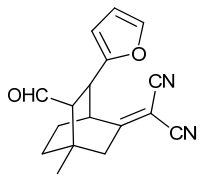
2-((1*S*,4*S*,5*R*)-5-Formyl-4-methyl-6-(4-nitrophenyl)bicyclo[2.2.2]octan-2-ylidene)malononitrile (4j) was obtained in 90% yield. After reduction, the enantiomeric excess of the corresponding



alcohol was determined to be 92% by HPLC analysis on Chiralpak AD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 16.21 min, t_{minor} = 14.95 min; $[\alpha]_D^{20}$ = +14.0 (*c* = 0.94 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.95 (s, 1H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 4.05 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 3.26-3.25 (m, 1H), 2.85 (dd, *J* = 20.8 Hz, *J* = 2.4 Hz, 1H), 2.73 (d, *J* = 6.8 Hz, 1H), 2.65 (d, *J* = 20.8 Hz, 1H), 2.23-2.16 (m, 1H), 1.82-1.74 (m, 1H), 1.72-1.64 (m, 1H), 1.46-1.38 (m, 1H), 1.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184, 148.5, 147.1, 127.9, 124.3, 110.6, 110.4, 84.3, 59.6, 45.0, 42.3, 41.7, 34.9, 27.0, 25.6, 24.0 ppm; ESI HRMS: calcd. for $C_{19}H_{17}N_3O_3$+MeOH+Na^+ 390.1424, found 390.1430.

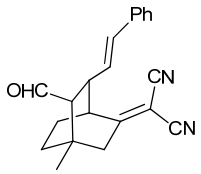


2-((1*S*,4*S*,5*R*)-5-Formyl-4-methyl-6-(pyridin-2-yl)bicyclo[2.2.2]octan-2-ylidene)malononitrile (4k) was obtained in 94% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 84% by HPLC analysis on Chiralpak IC column (10% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 16.48 min, t_{minor} = 19.72 min; $[\alpha]_D^{20}$ = +9.3 (*c* = 0.56 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.94 (s, 1H), 8.54 (dd, *J* = 4.8 Hz, *J* = 1.6 Hz, 1H), 8.37 (d, *J* = 2.0 Hz, 1H), 7.36-7.26 (m, 2H), 3.94-3.93 (m, 1H), 3.21-3.20 (m, 1H), 2.83 (dd, *J* = 20.8 Hz, *J* = 2.4 Hz, 1H), 2.71 (d, *J* = 6.8 Hz, 1H), 2.64 (d, *J* = 20.8 Hz, 1H), 2.22-2.16 (m, 1H), 1.81-1.65 (m, 2H), 1.43-1.39 (m, 1H), 1.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.8, 184.6, 149.1, 148.6, 136.7, 134.2, 123.7, 110.7, 110.4, 84.3, 59.5, 45.1, 42.5, 39.8, 34.8, 27.0, 25.6, 24.0 ppm; ESI HRMS: calcd. for $C_{18}H_{17}N_3O$+MeOH+H^+ 324.1707, found 324.1705.

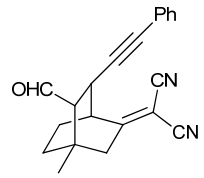


2-((1*S*,4*S*,5*R*)-5-Formyl-6-(furan-2-yl)-4-methylbicyclo[2.2.2]octan-2-ylidene) malononitrile (4l) was obtained in 93% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 94% by HPLC analysis on Chiralpak OD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 8.80 min, t_{minor} = 12.15 min; $[\alpha]_D^{20}$ = +45.5 (*c* = 1.4 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.95 (s, 1H), 7.32 (d, *J* = 1.6 Hz, 1H), 6.29-6.28 (m, 1H), 6.05 (d, *J* = 2.8 Hz, 1H), 3.96 (dd, *J* = 6.0 Hz, *J* = 2.0 Hz, 1H), 3.41-3.40 (m, 1H), 2.78-2.72 (m, 2H), 2.52 (d, *J* = 20.4 Hz,1H), 2.08-2.03 (m, 1H), 1.76-1.69 (m, 1H), 1.67-1.60 (m, 1H), 1.38-1.29 (m, 1H), 1.34 (s, 3H) ppm; ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 201.1, 185.7, 153.8, 142.3, 111.0, 110.7, 110.4, 105.8, 83.4, 57.6, 44.6, 40.6, 35.5, 34.6, 27.2, 24.4, 24.0 ppm; ESI HRMS: calcd. for $C_{17}H_{16}N_2O_2$+MeOH+Na^+ 335.1366, found 335.1374.

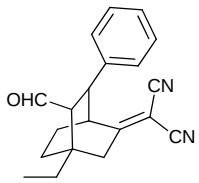


2-((1*S*,4*S*,5*R*)-5-Formyl-4-methyl-6-((E)-styryl)bicyclo[2.2.2]octan-2-ylidene) malononitrile (4m) was obtained in 79% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 92% by HPLC analysis on Chiralpak OD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 6.35 min, t_{minor} = 7.15 min; $[\alpha]_D^{20}$ = -20.6 (*c* = 1.1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.93 (d, *J* = 1.2 Hz, 1H), 7.31-7.23 (m, 5H), 6.43 (d, *J* = 15.6 Hz, 1H), 5.78 (dd, *J* = 16.0 Hz, *J* = 7.6 Hz, 1H), 3.43 (t, *J* = 6.8 Hz, 1H), 3.22 (d, *J* = 2.4 Hz, 1H), 2.67 (dd, *J* = 20.4 Hz, *J* = 2.0 Hz, 1H) 2.52 (d, *J* = 20.4 Hz, 1H), 2.36 (d, *J* = 6.0 Hz, 1H), 2.05-2.02 (m, 1H), 1.73-1.62 (m, 2H), 1.35-1.26 (m, 1H), 1.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 186.2, 136.0, 132.0, 129.0, 128.6, 128.0, 126.4, 111.0, 111.0, 83.6, 59.7, 44.9, 41.4, 39.5, 34.6, 27.2, 24.6, 24.0 ppm; ESI HRMS: calcd. for $C_{21}H_{20}N_2O$+MeOH+Na^+ 371.1730, found 371.1738.

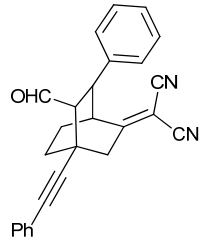


2-((1S,4S,5R,6S)-5-Formyl-4-methyl-6-(phenylethynyl)bicyclo[2.2.2]octan-2-ylidene)malononitrile (4n) was obtained in 83% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 94% by HPLC analysis on Chiralpak OD column (30% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 9.76 min, t_{minor} = 15.11 min; $[\alpha]_D^{20}$ = 18.6 (*c* = 0.58 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.97 (s, 1H), 7.38-7.26 (m, 5H), 3.79 (dd, *J* = 5.2 Hz, *J* = 2.8 Hz, 1H) 3.40-3.39 (m, 1H), 2.82 (dd, *J* = 20.4 Hz, *J* = 2.8 Hz, 1H), 2.71 (d, *J* = 4.8 Hz, 1H) 2.54 (d, *J* = 20.4 Hz, 1H) 2.01-1.92 (m, 1H), 1.77-1.69 (m, 1H), 1.57-1.48 (m, 1H), 1.34 (s, 3H), 1.33-1.24 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 186.2, 136.0, 132.0, 129.0, 128.6, 128.0, 126.4, 111.0, 111.0, 83.6, 59.7, 44.9, 41.4, 39.5, 34.6, 27.2, 24.6, 24.0 ppm; ESI HRMS: calcd. for $C_{21}H_{18}N_2O$+MeOH+Na^+ 369.1573, found 369.1573.

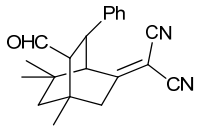
2-((1*S*,4*S*,5*R*)-4-Ethyl-5-formyl-6-phenylbicyclo[2.2.2]octan-2-ylidene)malononitrile (4o) was obtained in 84% yield. After reduction, the enantiomeric excess of the corresponding alcohol was



determined to be 91% by HPLC analysis on Chiralpak OD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 19.25 min, t_{minor} = 28.50 min; $[\alpha]_D^{20}$ = +30.5 (*c* = 1.1 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.91 (d, *J* = 1.6 Hz, 1H), 7.35-7.25 (m, 3H), 7.03 (d, *J* = 7.2 Hz, 2H), 3.88-3.86 (m, 1H), 3.24 (d, *J* = 2.4 Hz, 1H), 2.89-2.81 (m, 2H), 2.54 (d, *J* = 20.4 Hz, 1H), 2.22-2.15 (m, 1H), 1.80-1.71 (m, 2H), 1.68-1.1.52 (m, 2H), 1.46-1.39 (m ,1H), 1.09 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.5, 186.3, 141.2, 129.1, 127.6, 126.8, 111.1, 110.6, 83.9, 56.9, 43.1, 42.3, 41.1, 38.3, 29.6, 26.0, 25.5, 8.2 ppm; ESI HRMS: calcd. for $C_{20}H_{20}N_2O$+MeOH+Na^+ 359.1730, found 359.1731.



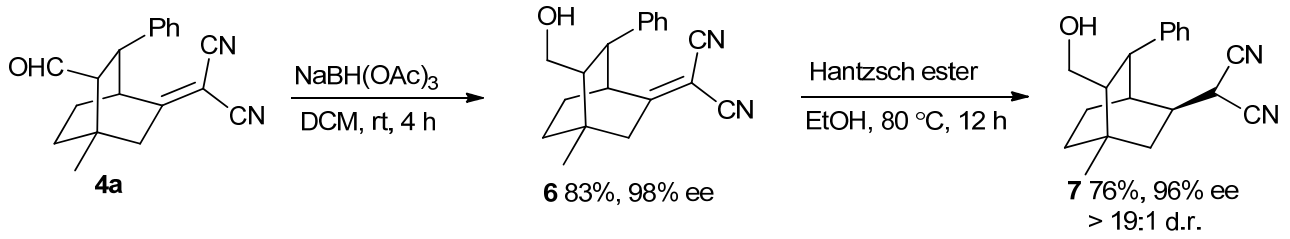
2-((1*S*,4*R*,5*R*)-5-Formyl-6-phenyl-4-(phenylethynyl)bicyclo[2.2.2]octan-2-ylidene)malononitrile (4p) was obtained in 82% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 86% by HPLC analysis on Chiralpak OD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 17.31 min, t_{minor} = 24.01 min; $[\alpha]_D^{20}$ = +10.8 (*c* = 0.51 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 10.21 (s, 1H), 7.44-7.26 (m, 8H), 7.08-7.06 (m, 2H), 4.01 (d, *J* = 6.4 Hz, 1H), 3.29-3.24 (m, 2H), 3.14-3.08 (m, 2H), 2.19-2.13 (m, 1H), 1.98-1.92 (m, 1H), 1.88-1.75 (m 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.0, 183.1, 140.7, 131.7, 129.2, 128.9, 128.5, 127.7, 126.8, 121.7, 110.8, 110.3, 88.0, 86.4, 84.5, 57.9, 43.7, 42.6, 41.0, 32.1, 27.2, 24.9 ppm; ESI HRMS: calcd. for $C_{26}H_{20}N_2O$+MeOH+Na^+ 431.1730, found 431.1734.



2-((1*R*,4*S*,5*R*,6*S*)-5-Formyl-4,7,7-trimethyl-6-phenylbicyclo[2.2.2]octan-2-ylidene)malononitrile (4q) was obtained in 78% yield. After reduction, the enantiomeric excess of the corresponding alcohol was determined to be 92% by HPLC analysis on Chiralpak OD column (10% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 9.19 min, t_{minor} = 9.92 min; $[\alpha]_D^{20}$ = +27.1 (*c* = 0.87 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.90 (s, 1H), 7.35-7.26 (m, 3H), 7.03 (d, *J* = 6.8 Hz, 2H), 4.22-4.20 (m, 1H), 2.79-2.68 (m, 3H), 2.51 (d, *J* = 20.8 Hz, 1H), 1.46 (dd, *J* = 14.4 Hz, *J* = 2.8 Hz, 1H), 1.35 (s, 3H), 1.35 (s, 3H), 1.15 (dd, *J* = 18.0 Hz, *J* = 5.0 Hz, 1H), 0.92 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.3, 184.7, 140.6, 129.0, 127.6, 127.2, 110.9, 110.5, 85.4, 58.2, 56.0, 43.8, 43.2, 38.1, 36.1, 33.0, 31.6, 28.6,

24.1 ppm; ESI HRMS: calcd. for $C_{21}H_{22}N_2O$+MeOH+Na^+ 373.1886, found 373.1894.

4. Procedure for regio- and diastereoselective reduction of 4a

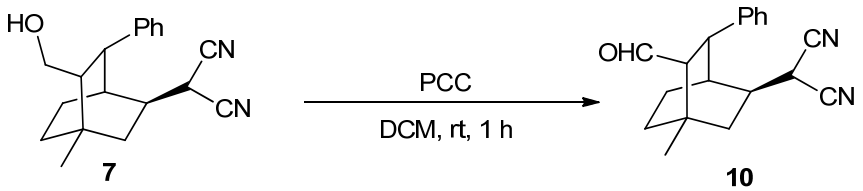


To a solution of bicyclo[2.2.2]octane **4a** (0.1 mmol) in DCM (1 mL) was added $NaBH(OAc)_3$ (0.15 mmol). After stirred for 4 h at room temperature, the reaction was quenched by water (1 mL) and the organic phase was separated and dried by anhydrous Na_2SO_4. Then, the solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the alcohol **6** in 83% yield and the enantiomeric excess was determined to be 98% by HPLC analysis on Chiralpak OD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 14.07 min, t_{minor} = 22.66 min; $[\alpha]_D^{20}$ = +35.8 (*c* = 0.89 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.24 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 2H), 3.78 (dd, *J* = 10.8 Hz, *J* = 5.2 Hz, 1H), 3.68 (dd, *J* = 10.8 Hz, *J* = 6.0 Hz, 1H), 3.10 (d, *J* = 8.0 Hz, 1H), 3.05-3.03 (m, 1H), 2.66 (d, *J* = 20.4 Hz, 1H), 2.52 (d, *J* = 20.4 Hz, 1H), 2.13-1.94 (m, 2H), 1.79-1.68 (m, 2H), 1.30-1.24 (m, 1H), 1.13 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187, 142.4, 129.0, 127.3, 127.2, 111.3, 110.7, 83.1, 62.7, 49.0, 48.3, 46.0, 44.8, 33.3, 26.8, 26.1, 24.2 ppm; ESI HRMS: calcd. for $C_{19}H_{20}N_2O$+Na^+ 315.1468, found 315.1474.

A mixture of alcohol **6** (0.1 mmol) and Hantzsch ester (0.15 mmol) in ethanol (1 mL) was stirred at 80 °C for 12 h. Then the solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the product **7** in 76% yield. The enantiomeric excess was determined to be 96% by HPLC analysis on Chiralpak OD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 220 nm, t_{major} = 12.25 min, t_{minor} = 19.87 min; $[\alpha]_D^{20}$ = -90.4 (*c* = 2.4 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.37 (m, 4H), 7.30-7.26 (m, 1H), 3.91 (dd, *J* = 10.8 Hz, *J* = 5.2 Hz, 1H), 3.57 (dd, *J* = 10.4 Hz, *J* = 7.6 Hz, 1H), 3.02 (d, *J* = 4.4 Hz, 1H), 2.85 (d, *J* = 12.4 Hz, 1H), 2.43-2.41 (m, 1H), 2.35-2.24 (m, 2H), 1.94-1.86 (m, 2H), 1.78-1.65 (m, 2H) 1.38-1.19 (m, 3H), 1.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 129.3, 112.3, 112.0, 64.5, 45.3, 44.9, 41.1, 39.3, 35.4, 31.7, 29.3, 26.9, 26.9, 25.6 ppm; ESI HRMS:

calcd. for. $C_{19}H_{22}N_2O$+Na^+ 317.1624, found 317.1629.

Since some typical peaks of compound **7** overlapped, a simple synthetic transformation was applied to oxidate the hydroxy group to the corresponding aldehyde **10**, whose relative configuration could be established by NOE analysis.

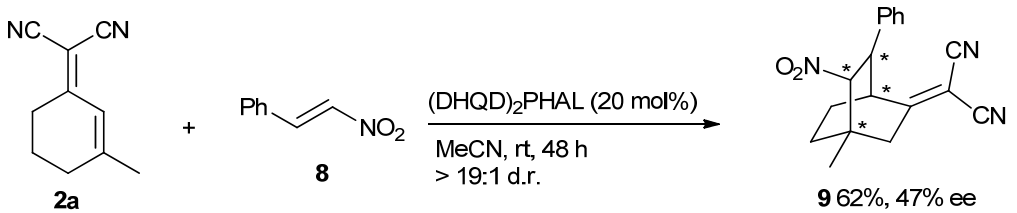


7 **10**

PCC (0.15 mmol) was added to the solution of alcohol **7** (0.1 mmol) in DCM (1 mL) at room temperature. After stirred for 1 h at rt, 30 mg silica gel was added and the mixture was filtrated. The filtrate was concentrated under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the aldehyde **10** in 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.92 (d, *J* = 2.0 Hz, 1H), 7.42-7.29 (m, 5H), 3.78-3.76 (m, 1H), 3.04-3.02 (m, 1H), 2.74 (d, *J* = 12.0 Hz, 1H), 2.56-2.54 (m, 1H), 2.35 (dd, *J* = 19.6 Hz, *J* = 10.8 Hz, 1H), 1.96-1.86 (m, 2H), 1.81-1.73 (m, 1H), 1.65-1.59 (m, 1H), 1.47-1.32 (m, 2H), 1.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.5, 140.8, 129.5, 127.6, 126.9, 112.1, 112.0, 56.0, 40.2, 39.1, 38.9, 34.2, 33.3, 28.5, 27.6, 26.7, 25.2 ppm; ESI HRMS: calcd. for $C_{19}H_{20}N_2O$+MeOH+Na^+ 347.1730, found 347.1733.

5. Procedure for asymmetric [4+2] formal cycloaddition of cyclohexenylidenemalononitrile 2a and nitroolefin 8

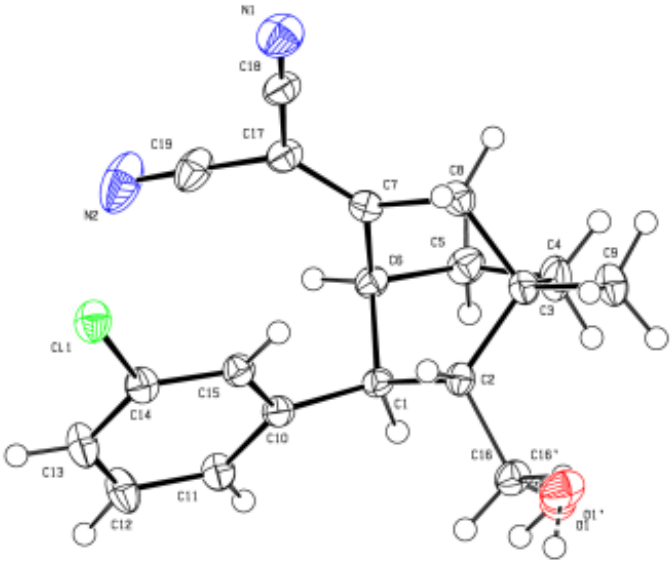


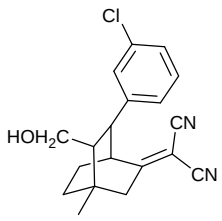
2a **8** **9** 62%, 47% ee

The reaction was conducted with cyclohexenylidenemalononitrile **2a** (0.1 mmol) and nitroolefin **8** in the presence of $(DHQD)_2PHAL$ (hydroquinidine 1,4-phthalazinediyl diether, 0.02 mmol) in MeCN (1 mL) at room temperature. After 48 h, the solvent were removed under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the nitro-containing bicyclo[2.2.2]octane **9** in 62% yield and the enantiomeric excess was

determined to be 47% by HPLC analysis on Chiralpak AD column (20% 2-propanol/*n*-hexane, 1 mL/min), UV 254 nm, t_{major} = 10.63 min, t_{minor} = 12.80 min; $[\alpha]_D^{20}$ = -53.6 (*c* = 1.3 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.33 (m, 3H), 7.02 (d, *J* = 6.8 Hz, 2H), 4.75 (dd, *J* = 6.8 Hz, *J* = 1.6 Hz, 1H), 4.03 (dd, *J* = 6.8 Hz, *J* = 1.6 Hz, 1H), 3.35 (dd, *J* = 5.2 Hz, *J* = 3.2 Hz, 1H), 2.73-2.71 (m, 2H), 2.46-2.39 (m, 1H), 2.16-2.09 (m, 1H), 1.88-1.81 (m, 1H), 1.44-1.37 (m, 1H), 1.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.8, 138.6, 129.5, 128.4, 126.4, 110.6, 110.3, 94.6, 84.7, 47.7, 42.7, 42.5, 35.9, 25.6, 24.7, 22.9 ppm; ESI HRMS: calcd. for $C_{18}H_{17}N_3O_2$+Na^+ 330.1213, found 330.1207.

6. Crystal data and structure refinement for enantiopure alcohol of 4g



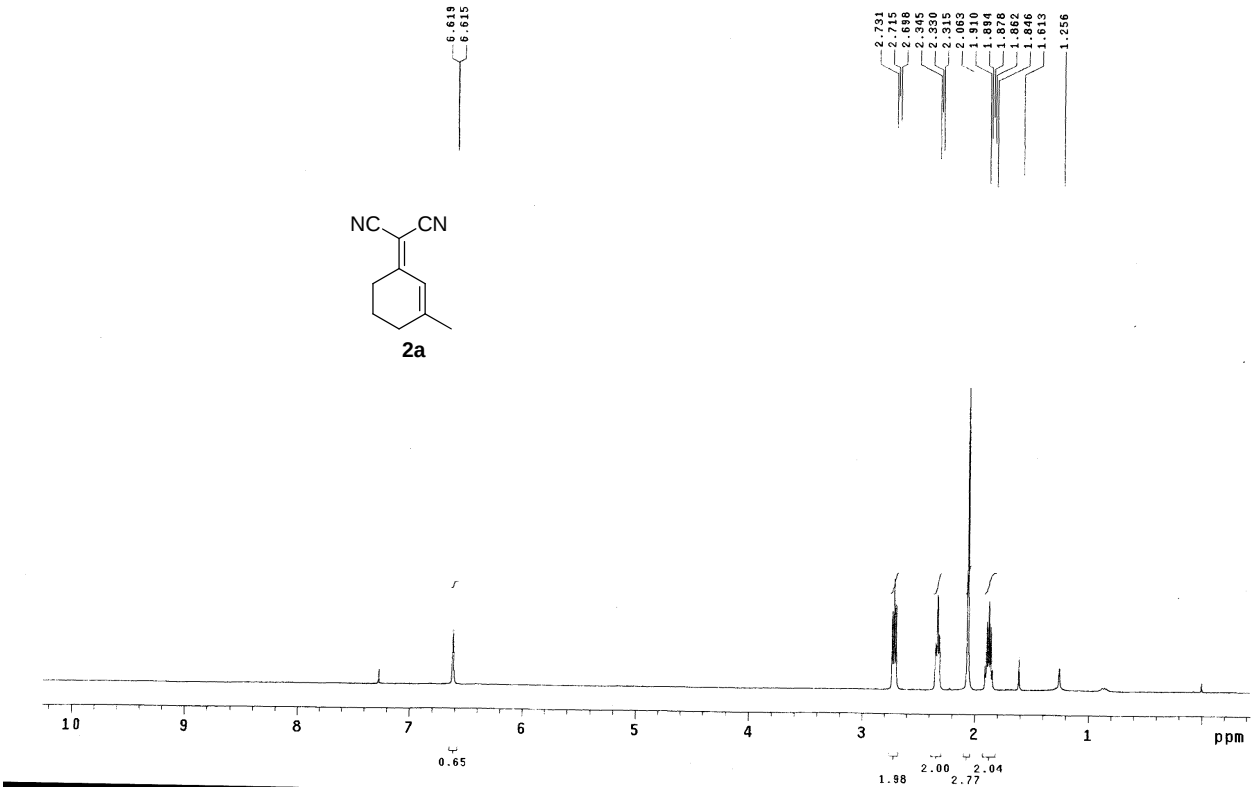


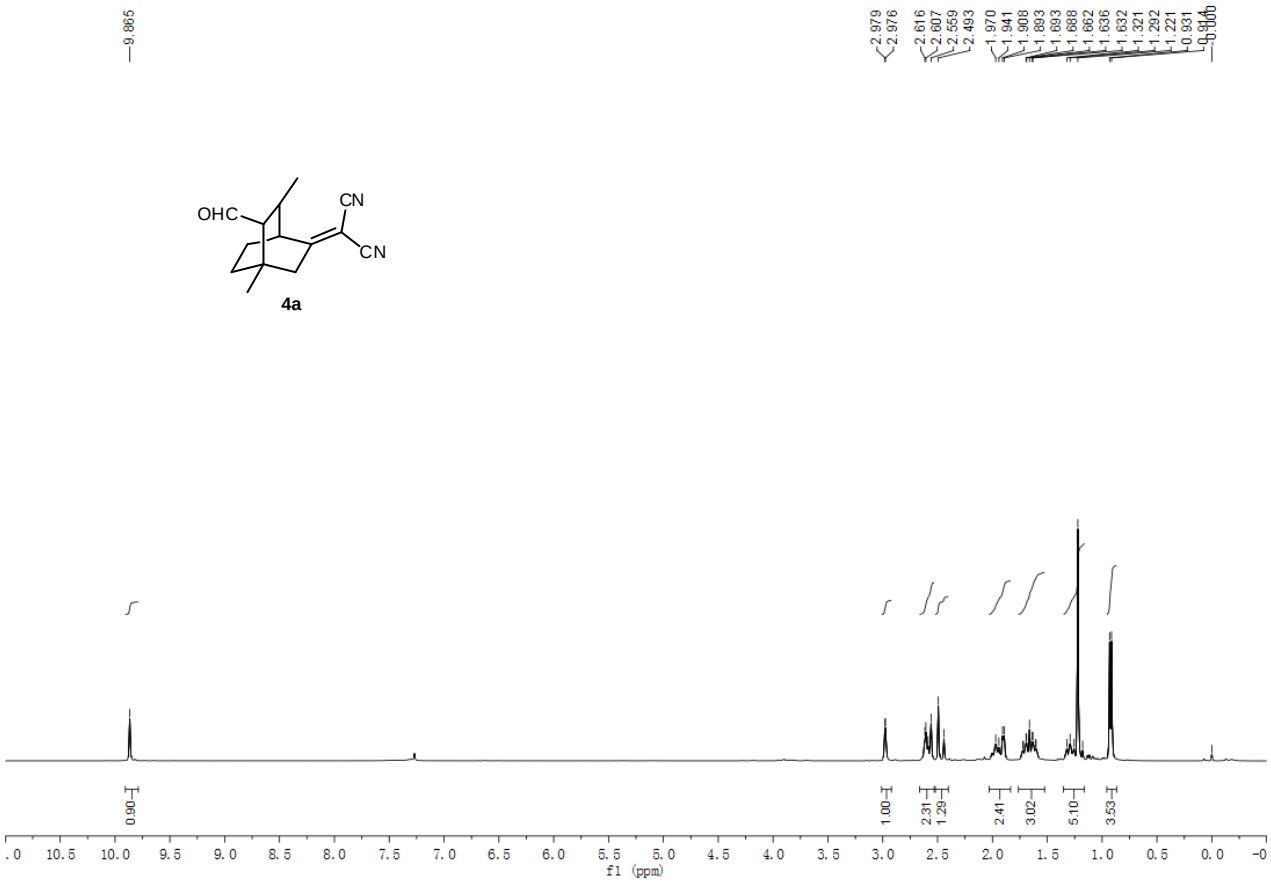
alcohol of **4g**

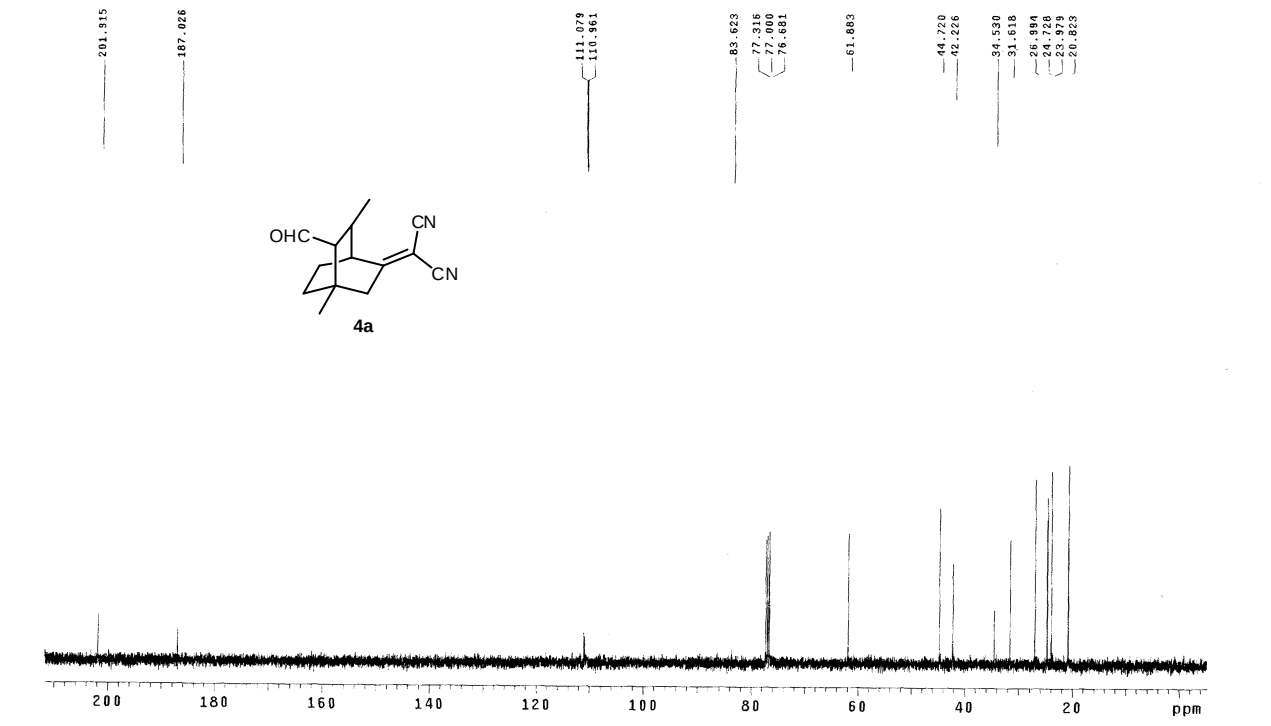
Identification code	**4g**
Empirical formula	C19 H19 Cl N2 O
Formula weight	326.81
Temperature	143(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 7.2494(19) A alpha = 90 deg. b = 13.352(4) A beta = 90 deg.

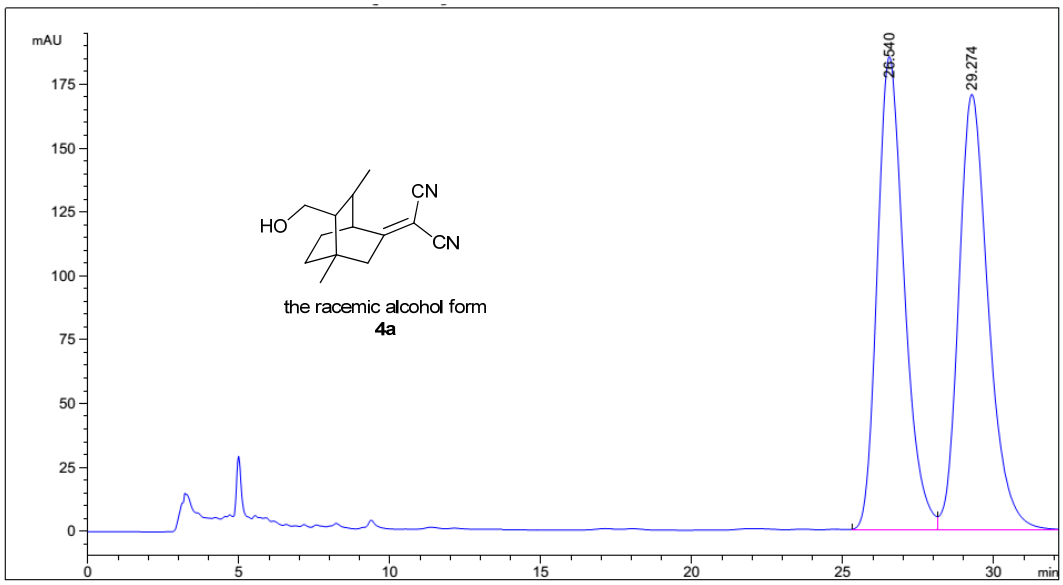
	c = 16.888(5) A gamma = 90 deg.
Volume	1634.7(7) A^3
Z, Calculated density	4, 1.328 Mg/m^3
Absorption coefficient	0.240 mm^-1
F(000)	688
Crystal size	0.51 x 0.50 x 0.50 mm
Theta range for data collection	3.06 to 31.53 deg.
Limiting indices	-10<=h<=10, -19<=k<=15, -24<=l<=24
Reflections collected / unique	16028 / 5405 [R(int) = 0.0622]
Completeness to theta = 31.53	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8895 and 0.8875
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5405 / 0 / 222
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0579, wR2 = 0.1405
R indices (all data)	R1 = 0.0652, wR2 = 0.1455
Absolute structure parameter	0.10(8)
Extinction coefficient	0.024(3)
Largest diff. peak and hole	0.283 and -0.271 e.A^-3

7. NMR spectra and HPLC chromatograms

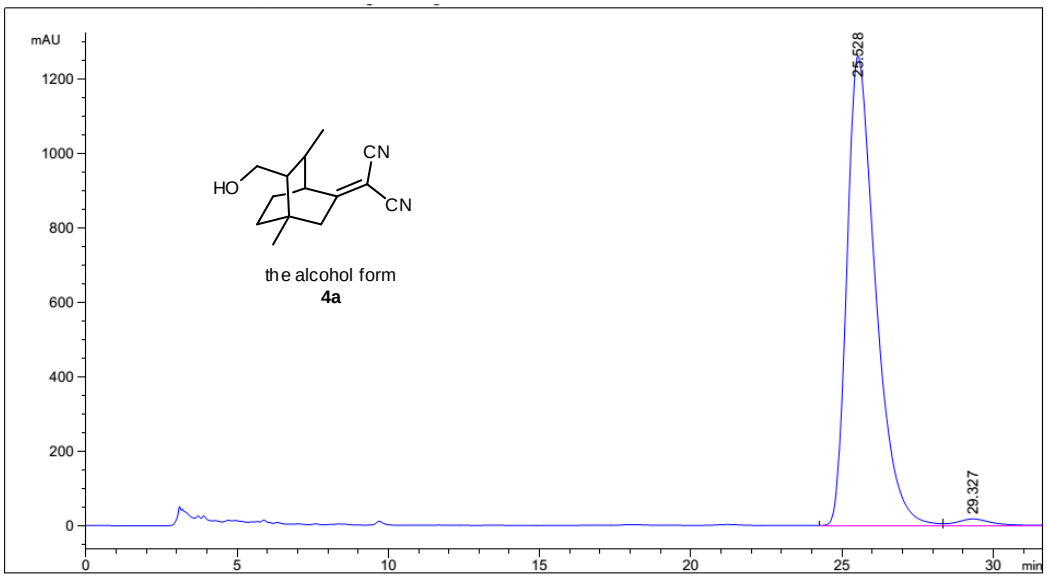



9.865
2.979
2.976
2.616
2.607
2.559
2.493
1.970
1.941
1.908
1.893
1.693
1.688
1.662
1.636
1.632
1.321
1.292
1.221
0.931
0.900
OHC
CN
CN
4a
0.90
1.00
2.31
1.29
2.41
3.02
5.10
3.53
f1 (ppm)

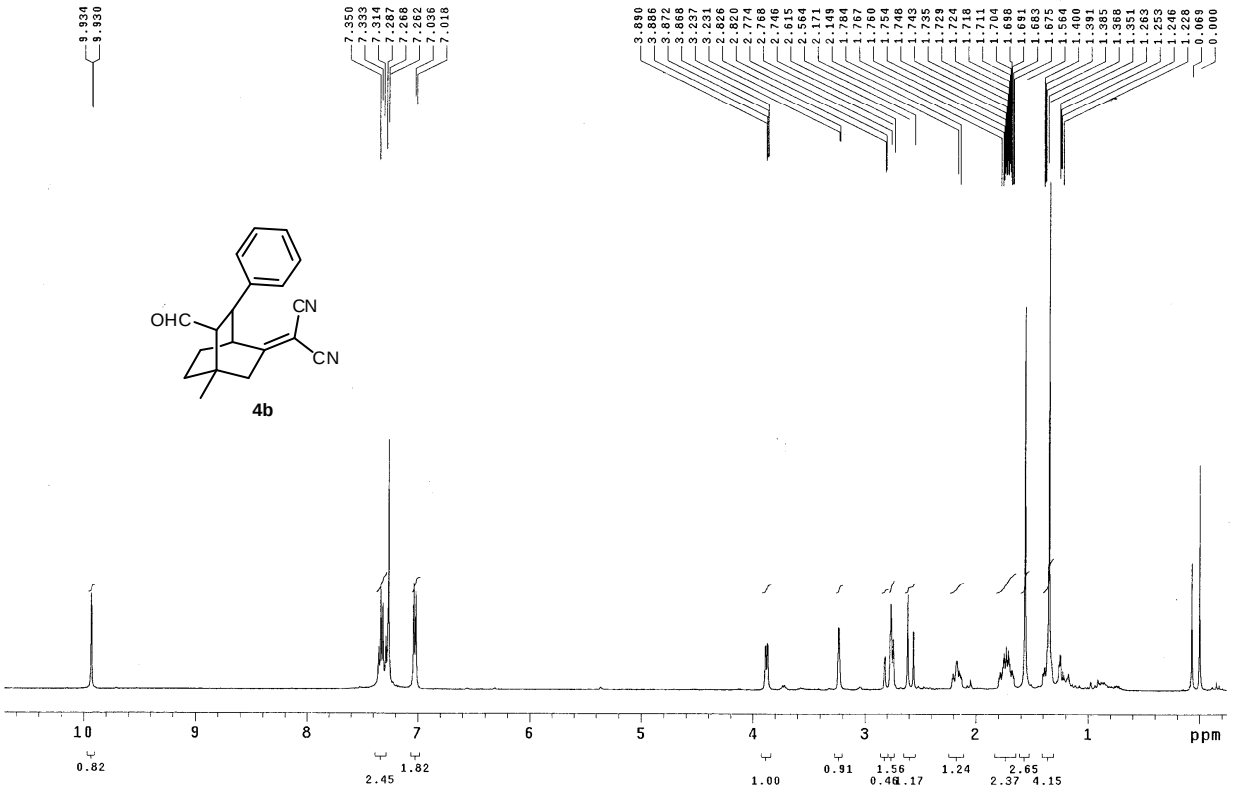

201.915
187.026
111.079
110.961
83.623
77.316
77.000
76.681
61.883
44.720
42.226
34.530
31.618
26.994
24.728
23.779
20.823
OHC
CN
CN
4a
ppm

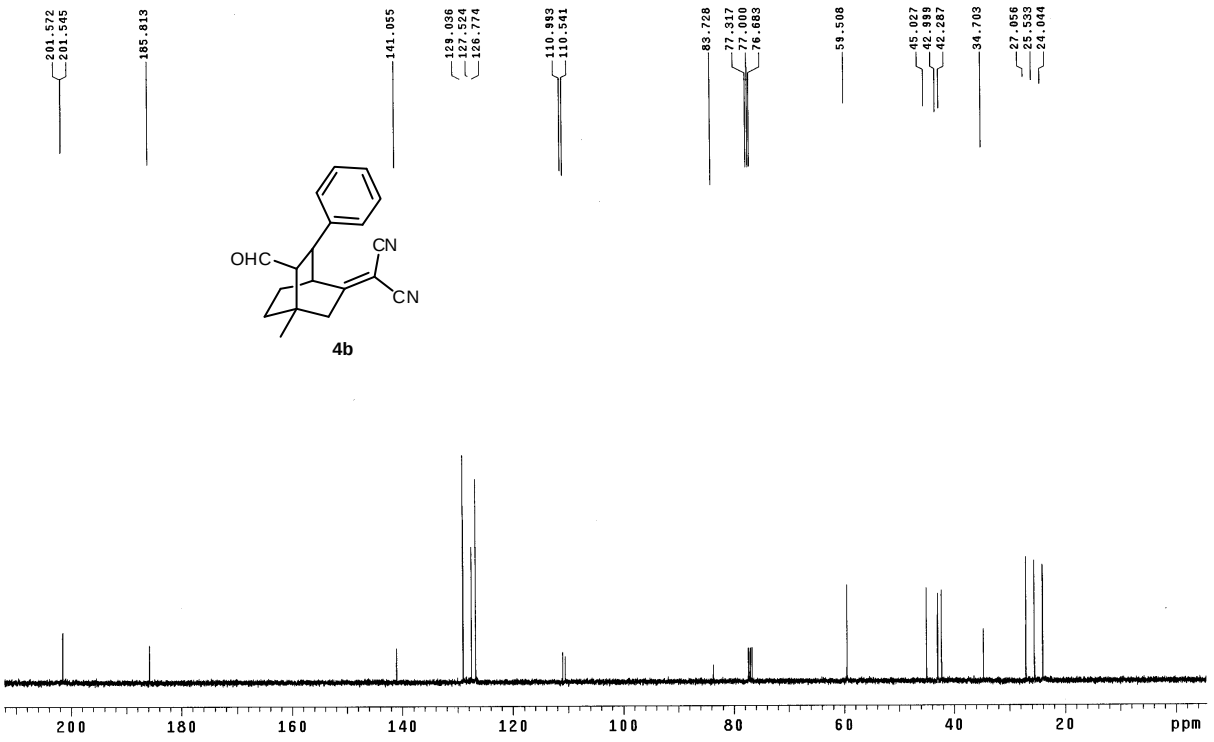


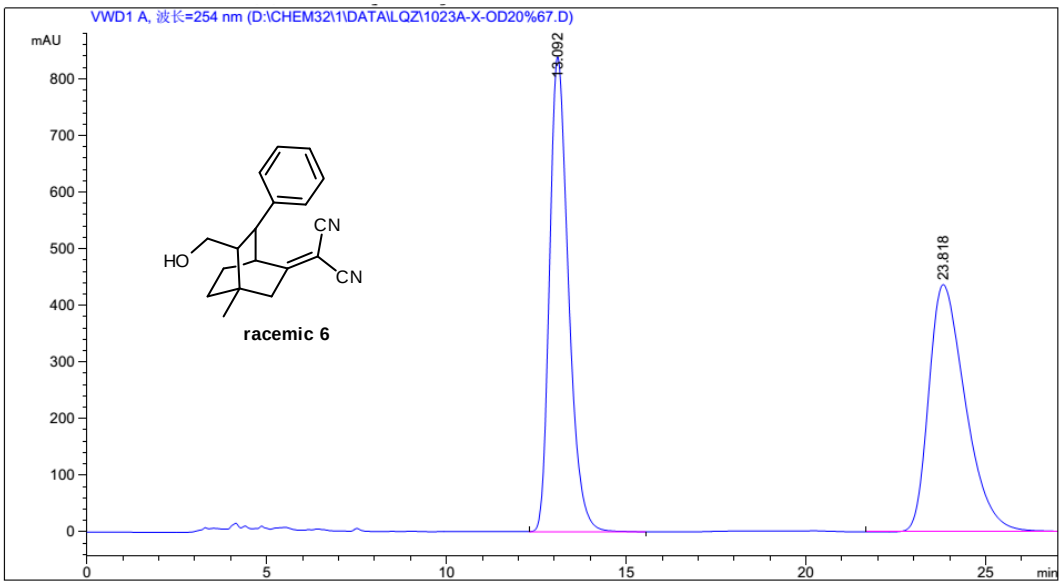
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.540	BV	0.9554	1.14649e4	185.13612	49.7521
2	29.274	VBA	1.0432	1.15791e4	170.39453	50.2479



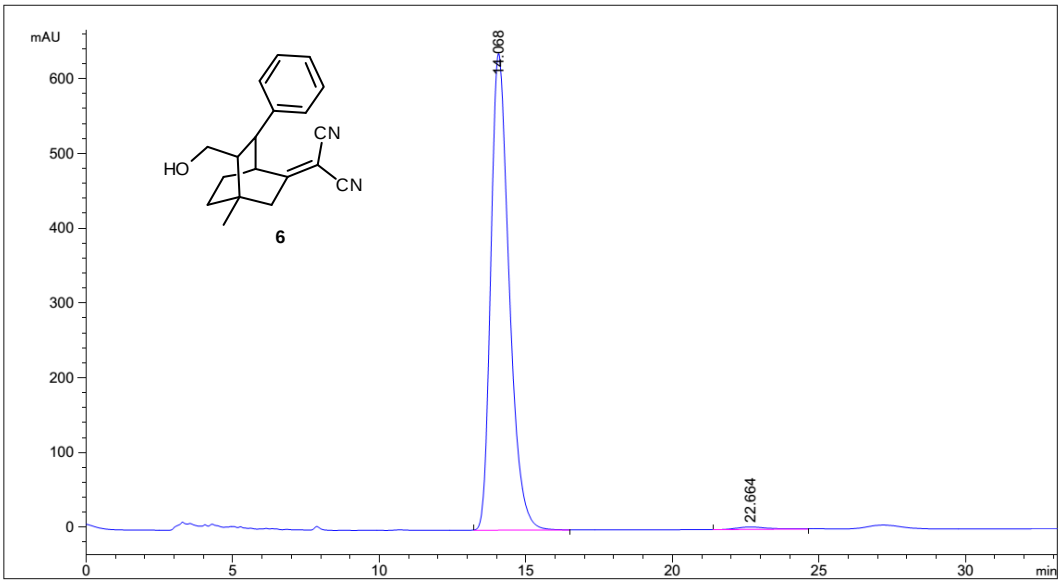
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.528	BV	0.9923	8.25961e4	1259.34399	98.3172
2	29.327	VBA	1.1595	1413.69324	17.80094	1.6828


9.834
9.830
7.350
7.333
7.314
7.287
7.268
7.262
7.036
7.018
3.890
3.886
3.872
3.868
3.237
3.231
2.826
2.820
2.774
2.768
2.746
2.615
2.564
2.171
2.149
1.784
1.767
1.760
1.754
1.748
1.743
1.735
1.729
1.724
1.718
1.711
1.704
1.698
1.691
1.683
1.675
1.564
1.400
1.391
1.385
1.368
1.351
1.263
1.253
1.246
1.228
0.069
0.000
OHC
CN
CN
4b
10
9
8
7
6
5
4
3
2
1
ppm
0.82
2.45
1.82
1.00
0.91
1.56
0.46
1.17
1.24
2.65
2.37
4.15

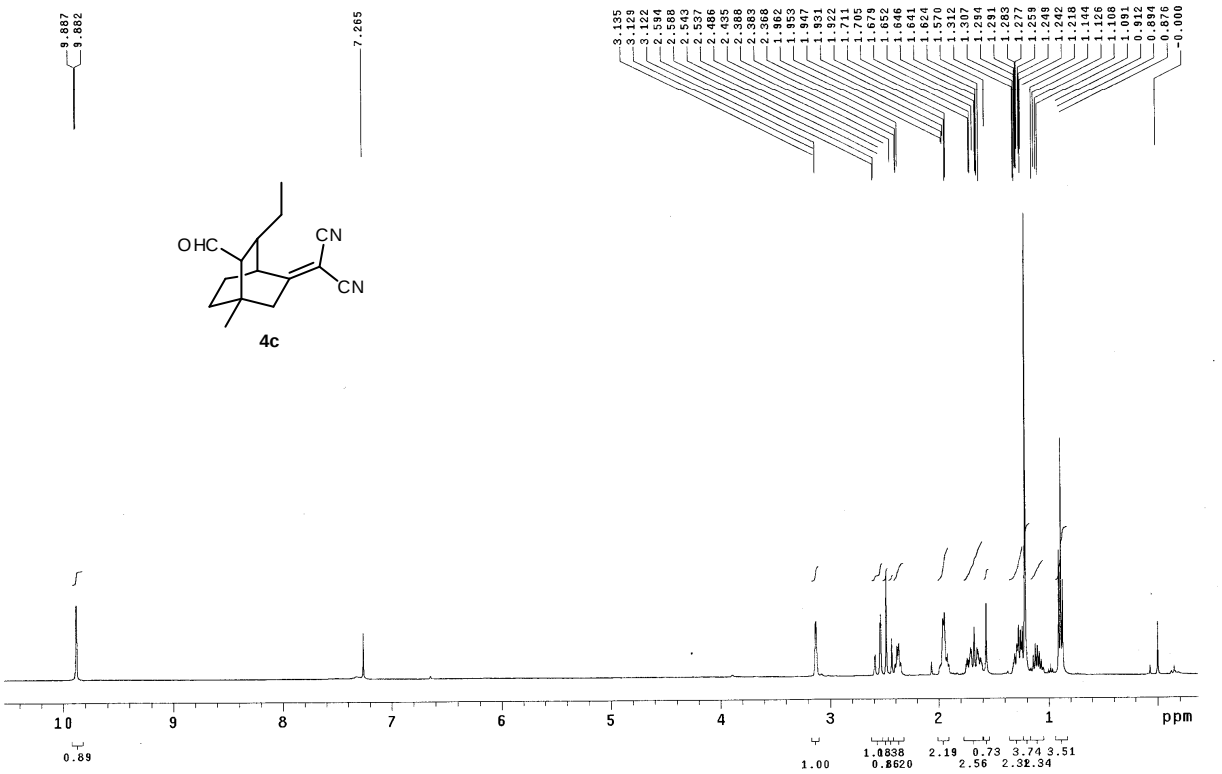

201.572
201.545
185.813
141.055
129.036
127.524
126.774
110.993
110.541
83.728
77.317
77.000
76.683
59.508
45.027
42.999
42.287
34.703
27.056
25.533
24.044
OHC
CN
CN
4b
200
180
160
140
120
100
80
60
40
20
ppm

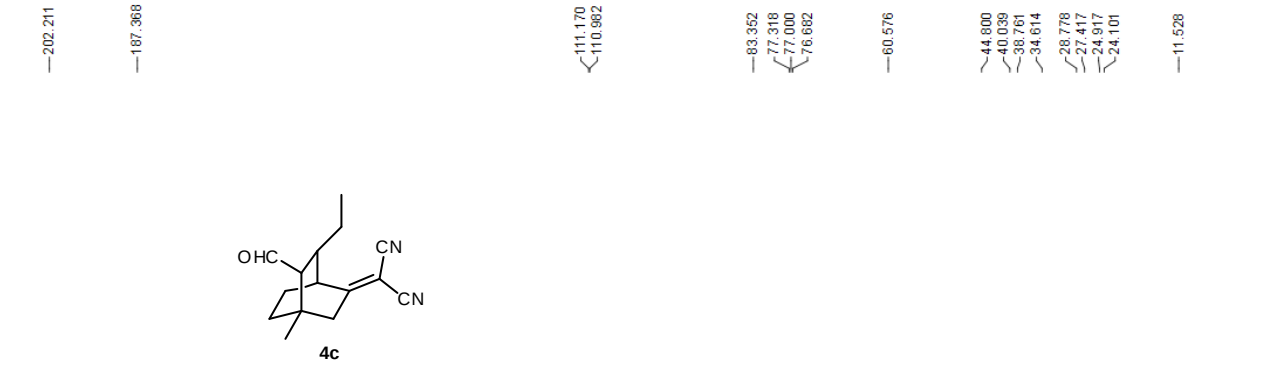


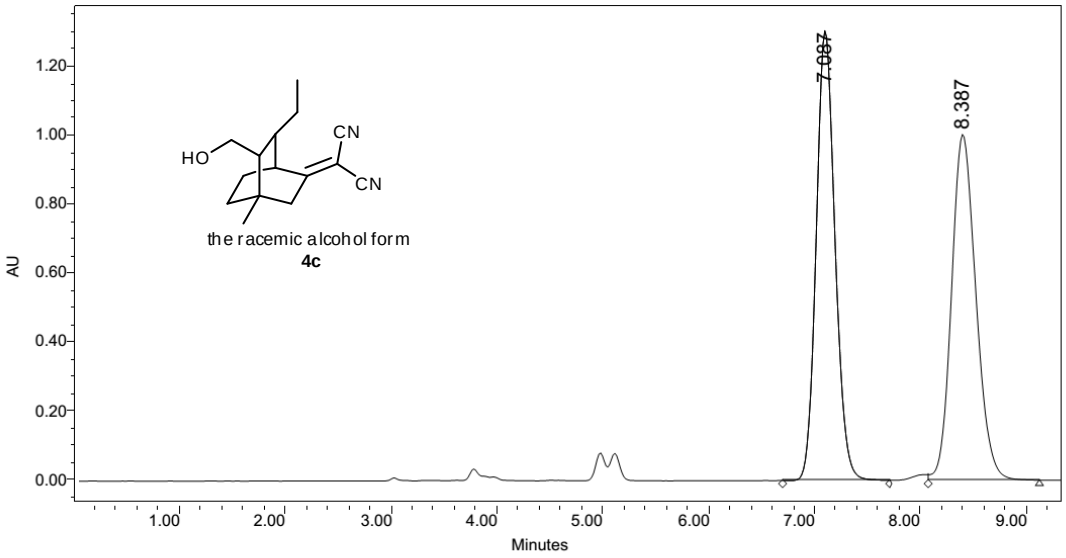
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.092	BB	0.5602	3.06356e4	838.46545	49.7354
2	23.818	VBA	1.0895	3.09616e4	436.53714	50.2646



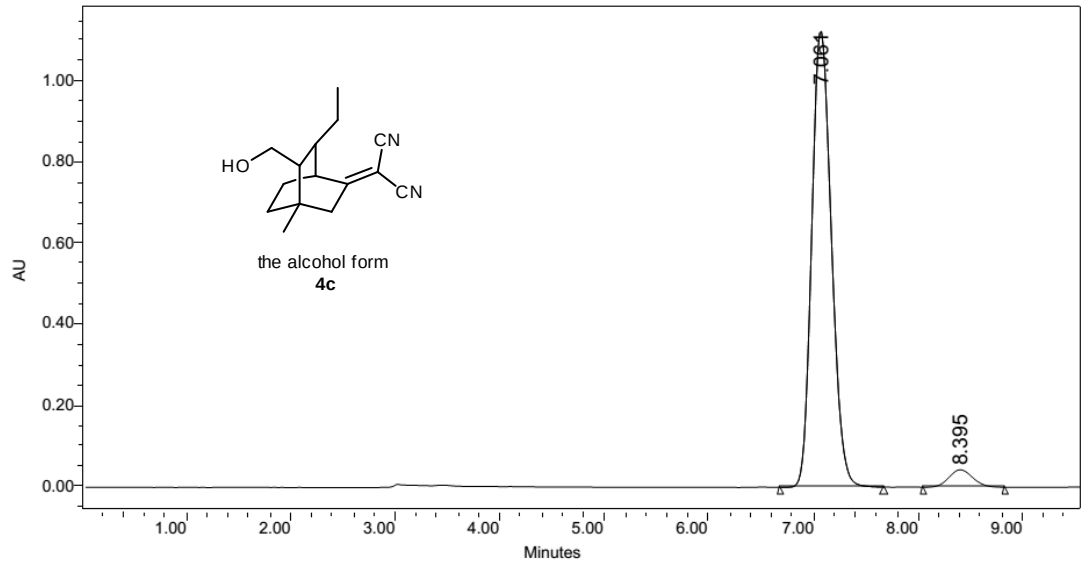
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.068	BB	0.6703	2.77171e4	637.55310	99.0948
2	22.664	BB	1.1555	253.19107	3.26379	0.9052


9.887
9.882
7.265
3.135
3.129
3.122
2.594
2.588
2.543
2.537
2.486
2.435
2.388
2.368
1.962
1.953
1.947
1.931
1.922
1.711
1.705
1.679
1.652
1.646
1.641
1.624
1.570
1.312
1.307
1.294
1.291
1.283
1.277
1.259
1.248
1.242
1.218
1.144
1.126
1.108
1.091
0.912
0.894
0.876
-0.000
OHC
CN
CN
4c
10
9
8
7
6
5
4
3
2
1
ppm
0.89
1.00
1.08
0.86
2.19
0.73
3.74
3.51
2.56
2.32
2.34

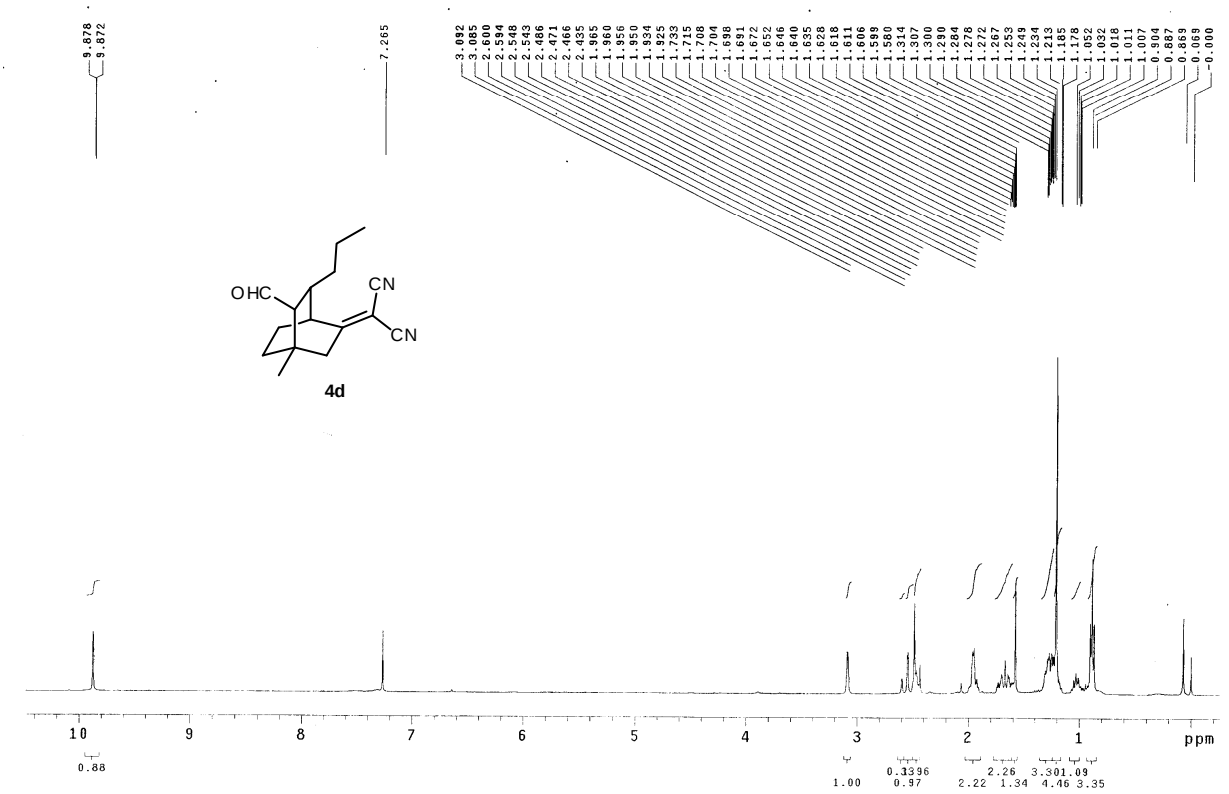

202.211
187.368
111.170
110.982
83.352
77.318
77.000
76.682
60.576
44.800
40.039
38.761
34.614
28.778
27.417
24.917
24.101
11.528
OHC
CN
CN
4c
f1 (ppm)



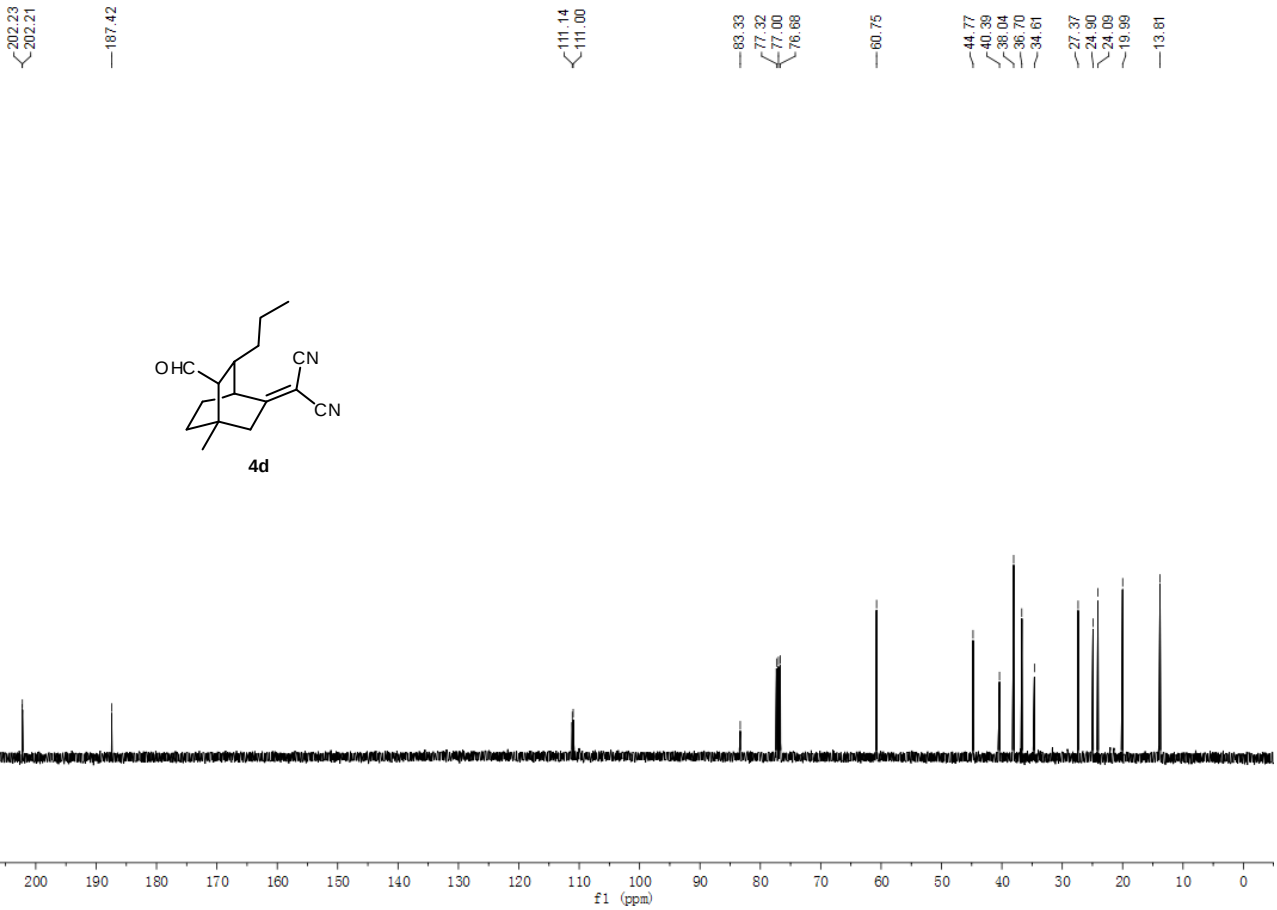
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	7.087	16115038	50.08	1306607	56.52
2	8.387	16065068	49.92	1004959	43.48



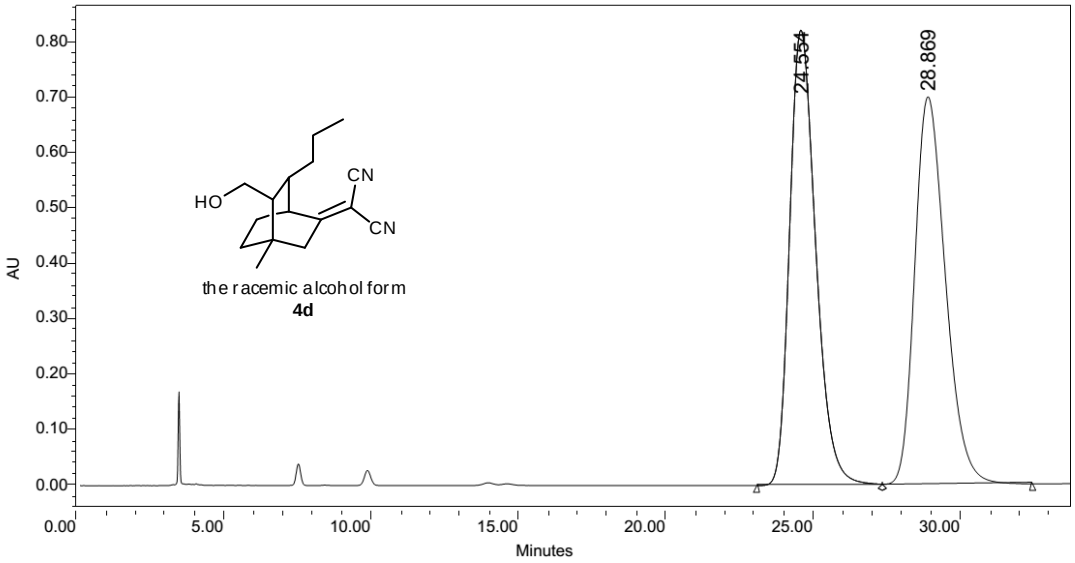
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	7.061	14702674	95.56	1126352	96.31
2	8.395	683400	4.44	43144	3.69


9.878
9.872
7.265
3.092
3.085
2.600
2.594
2.548
2.543
2.486
2.471
2.466
2.435
1.965
1.960
1.956
1.950
1.934
1.925
1.733
1.715
1.708
1.704
1.698
1.691
1.672
1.652
1.646
1.640
1.635
1.628
1.618
1.611
1.606
1.599
1.580
1.314
1.307
1.300
1.290
1.284
1.278
1.272
1.267
1.253
1.249
1.234
1.213
1.185
1.178
1.052
1.032
1.018
1.011
1.007
0.904
0.887
0.869
0.069
-0.000
OHC
CN
CN
10
9
8
7
6
5
4
3
2
1
ppm
0.88
1.00
0.97
2.22
1.34
4.46
3.35

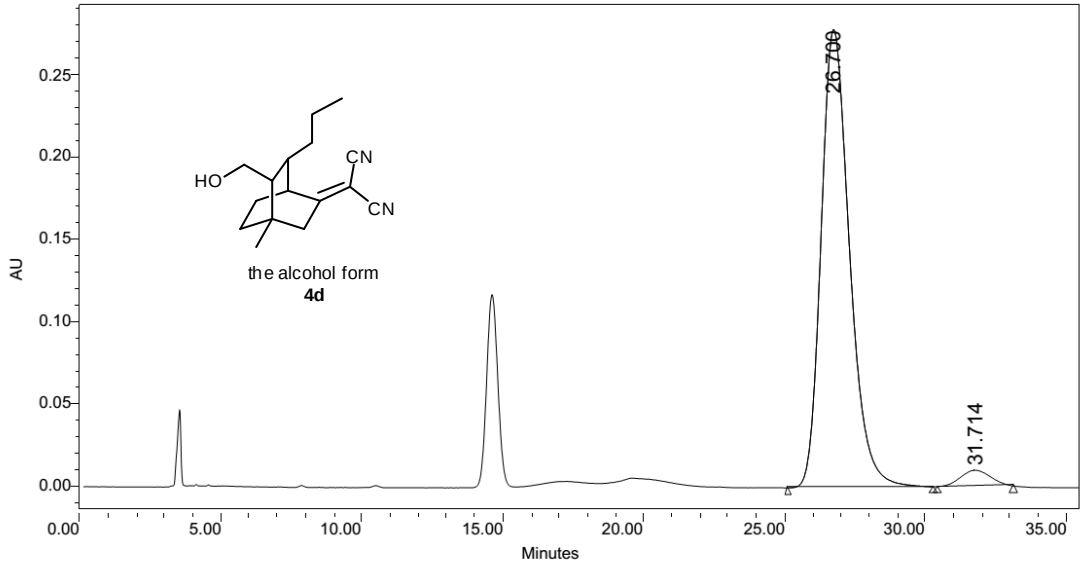
4d


202.23
202.21
187.42
111.14
111.00
83.33
77.32
77.00
76.68
60.75
44.77
40.39
38.04
36.70
34.61
27.37
24.90
24.09
19.99
13.81
OHC
CN
CN
f1 (ppm)

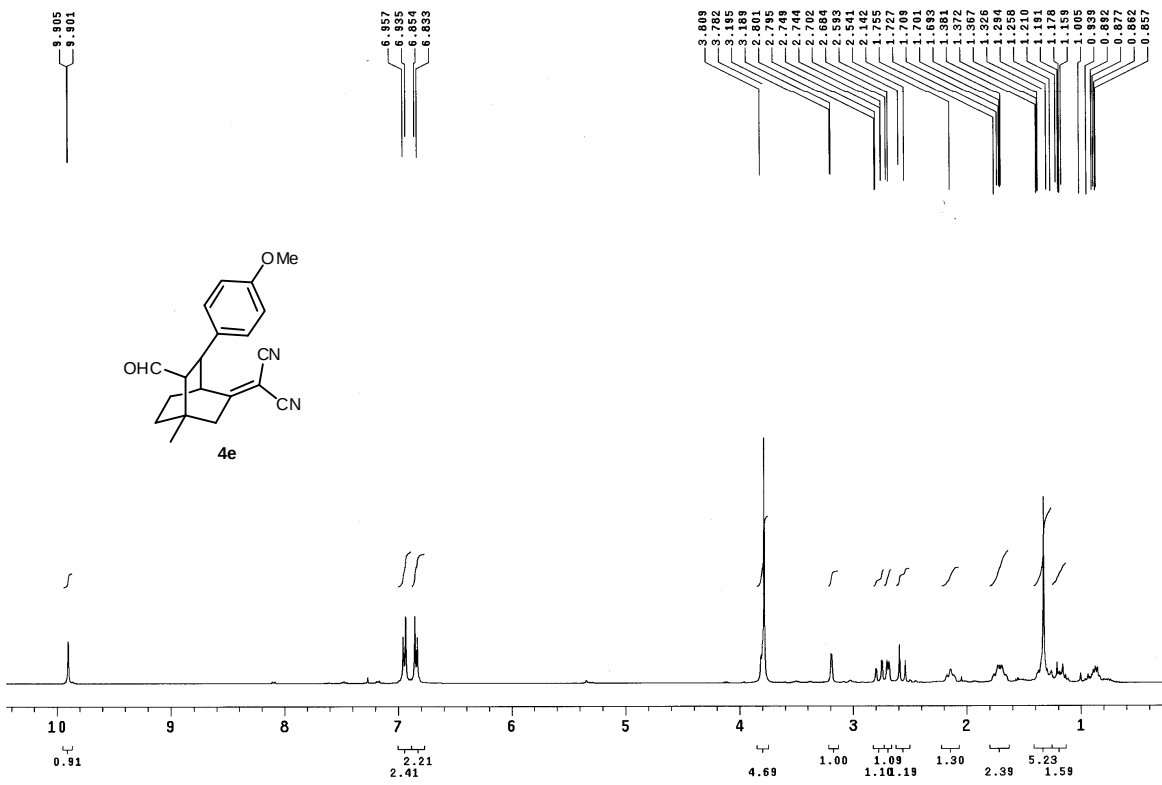
4d

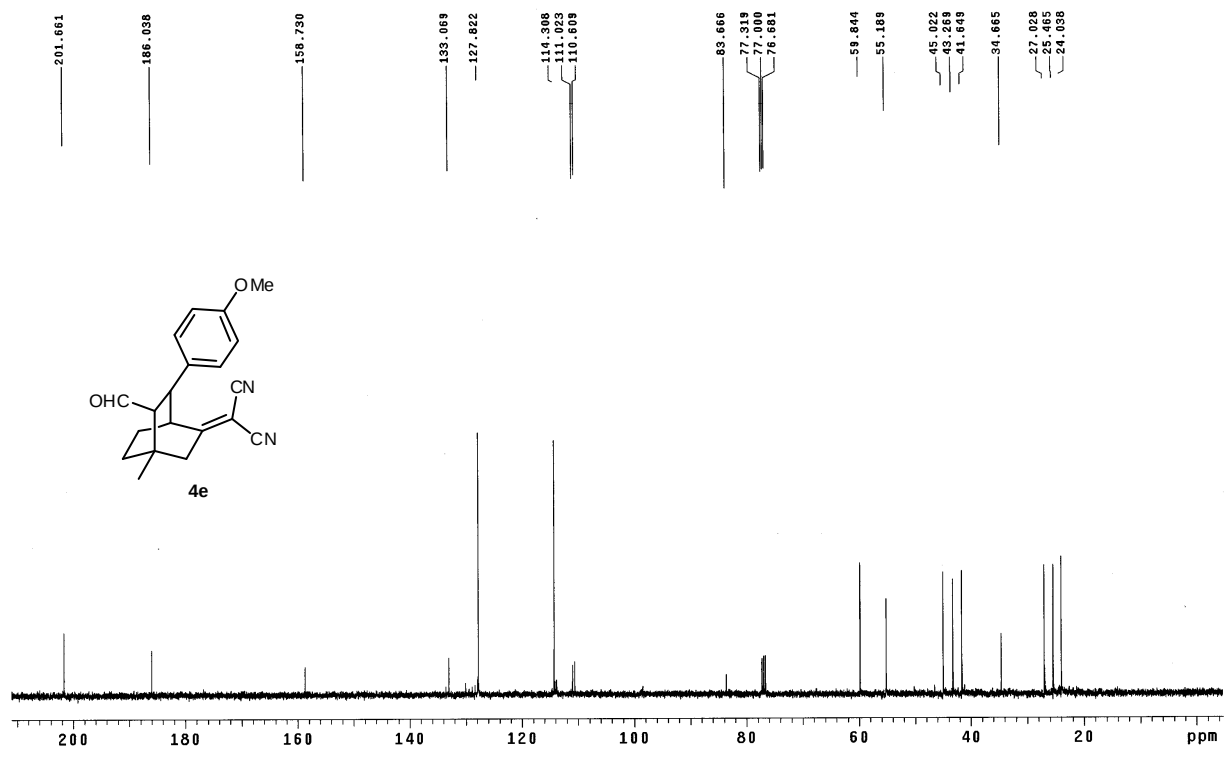


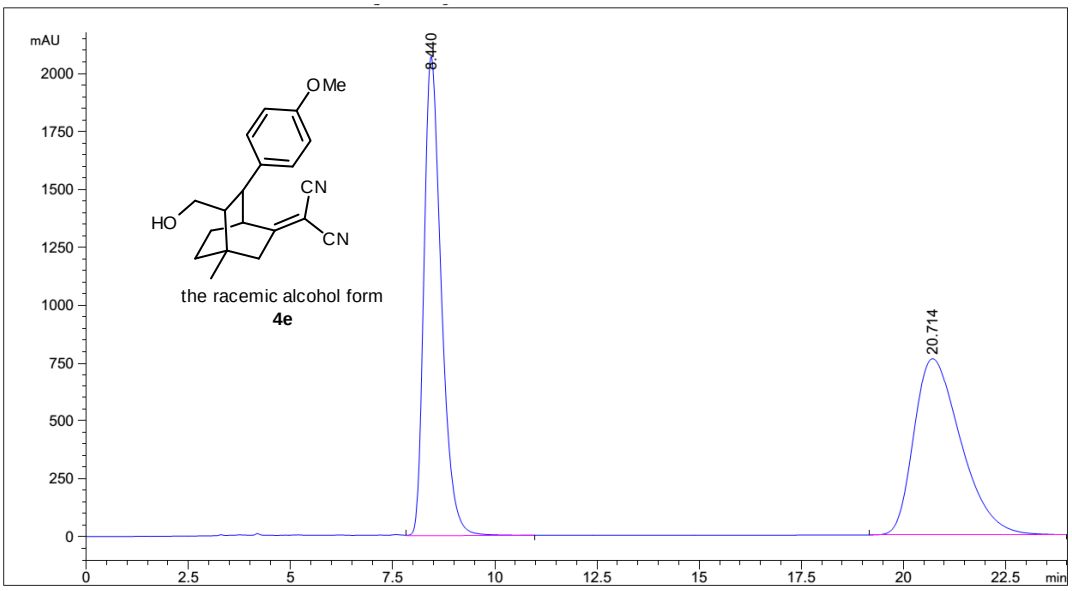
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	24.554	50564833	49.89	821856	54.01
2	28.869	50791968	50.11	699951	45.99



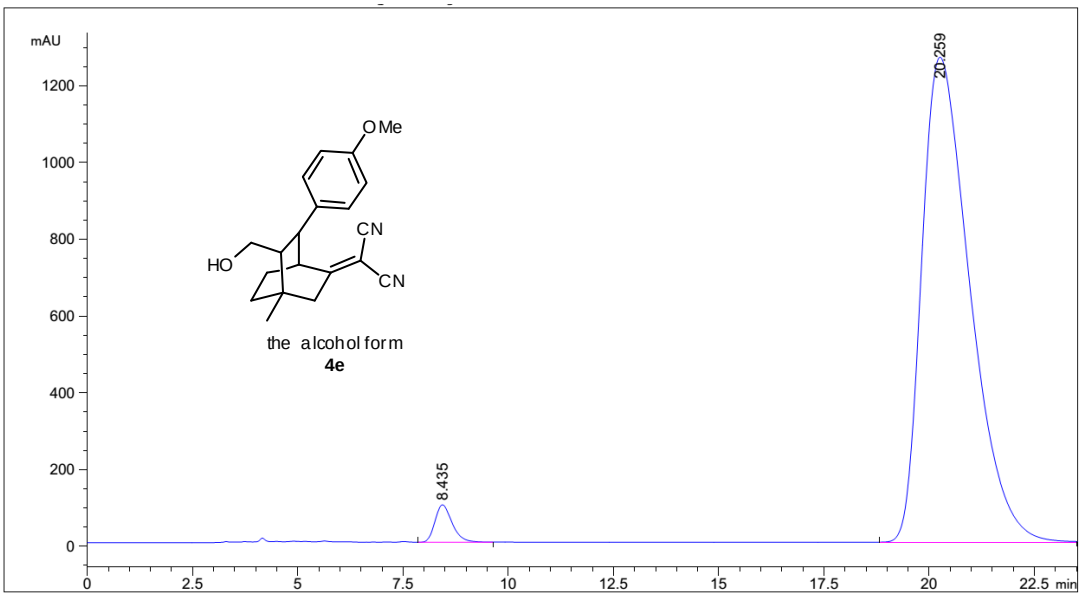
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	26.700	19525827	96.40	278969	96.60
2	31.714	729004	3.60	9805	3.40


9.905
9.901
6.857
6.855
6.854
6.853
3.809
3.782
3.185
3.169
2.801
2.795
2.749
2.744
2.702
2.684
2.593
2.541
2.142
1.755
1.727
1.709
1.701
1.693
1.381
1.372
1.357
1.326
1.284
1.258
1.210
1.181
1.178
1.159
1.005
0.939
0.892
0.877
0.862
0.857
OMe
CN
OHC
CN
4e
10
9
8
7
6
5
4
3
2
1
ppm
0.91
2.21
2.41
4.69
1.00
1.09
1.10
1.19
1.30
2.39
5.23
1.59

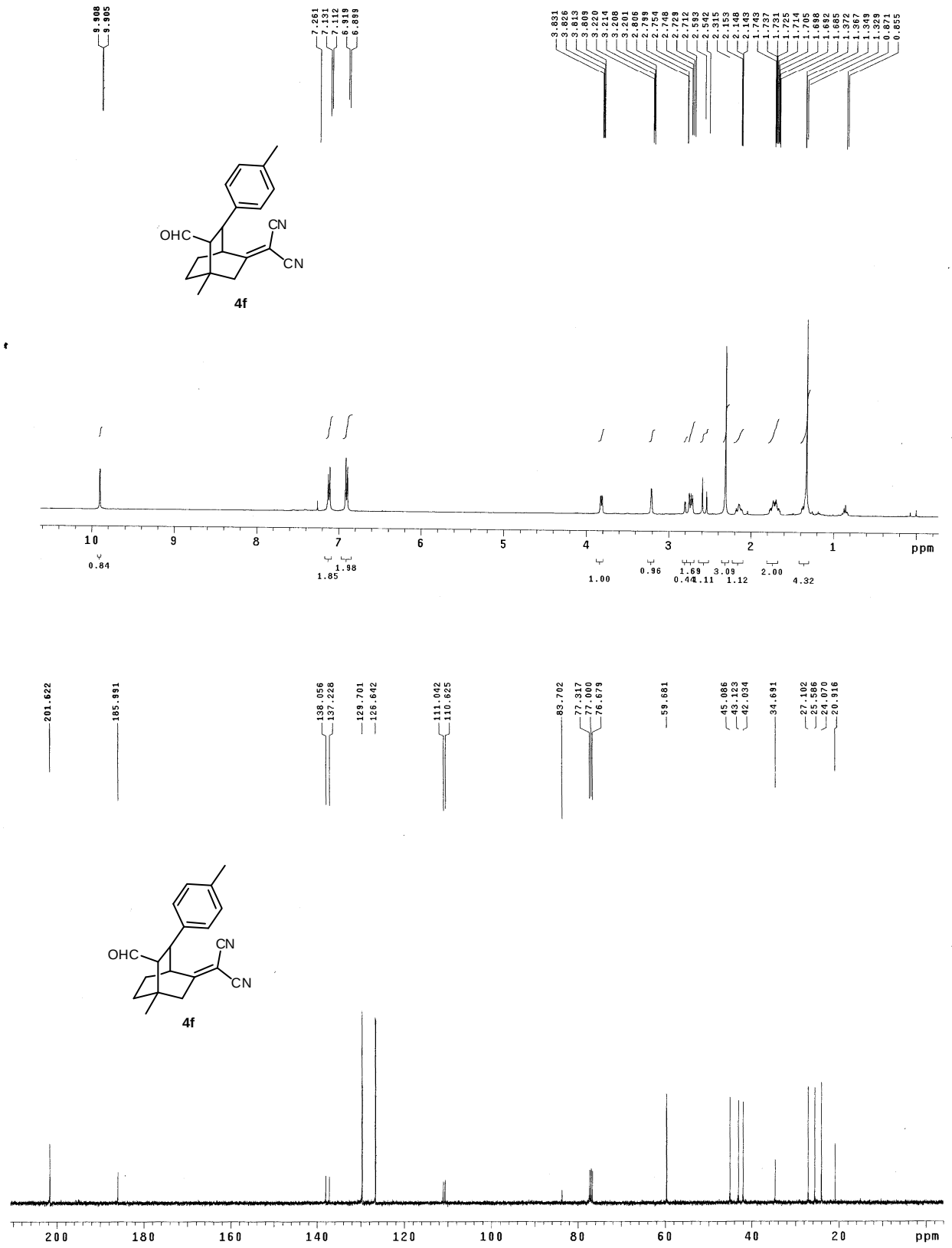

201.661
166.038
158.730
133.069
127.822
114.308
111.023
110.609
83.666
77.319
77.000
76.681
59.844
55.189
45.022
43.269
41.649
34.665
27.028
25.465
24.038
OMe
CN
OHC
CN
4e
200
180
160
140
120
100
80
60
40
20
ppm

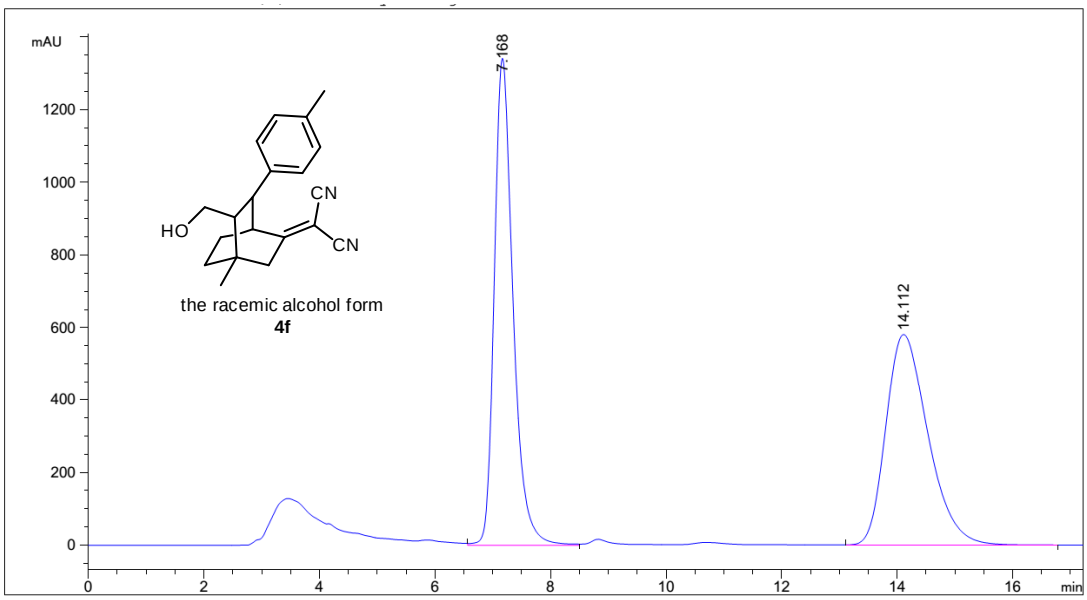


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.440	VB	0.4488	6.09301e4	2066.88184	49.9668
2	20.714	BBA	1.2357	6.10111e4	763.04572	50.0332

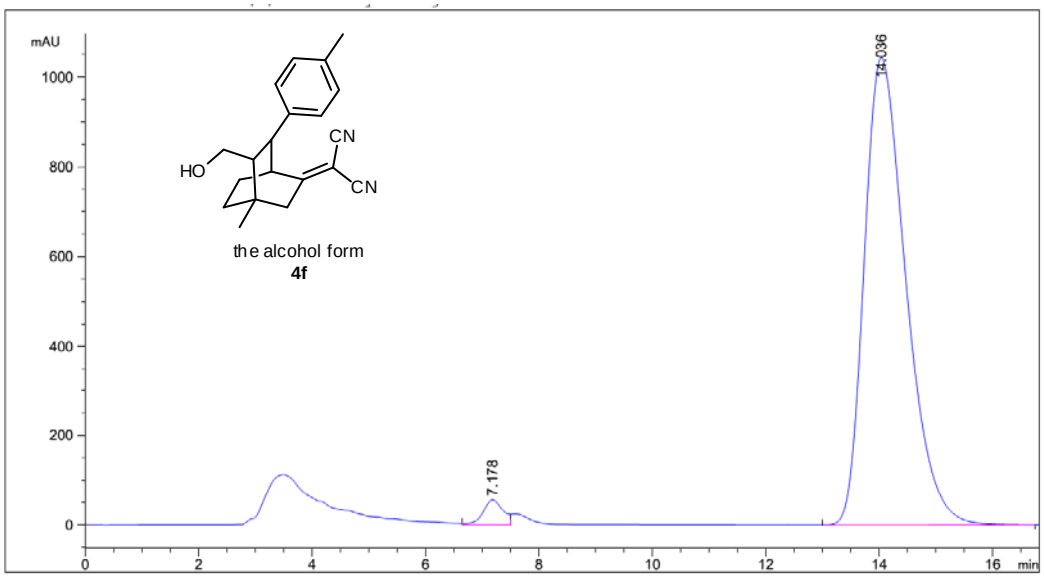


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.435	VB	0.4384	2797.36377	97.84207	2.7091
2	20.259	BBA	1.2243	1.00460e5	1263.97815	97.2909

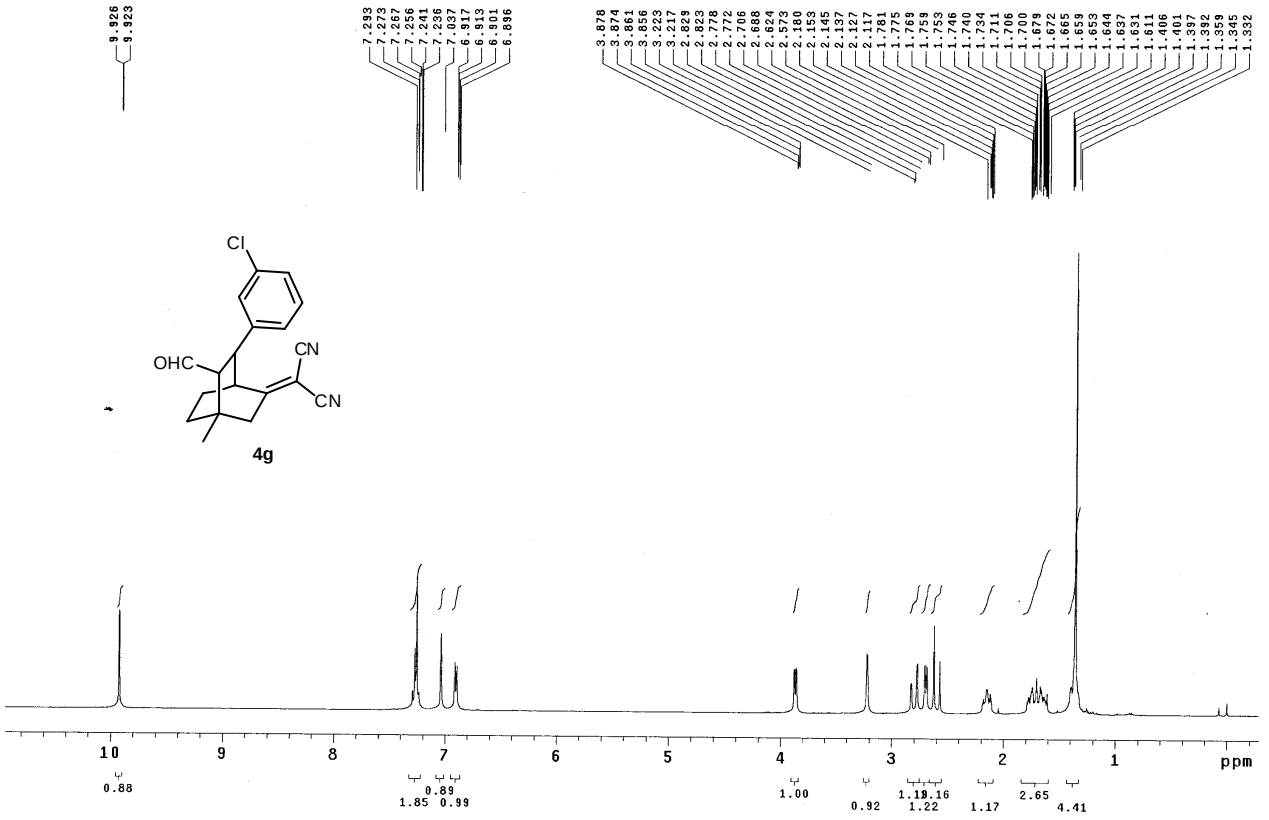

9.308
9.305
7.261
7.131
7.112
6.919
6.899
3.831
3.826
3.813
3.809
3.220
3.214
3.208
3.201
2.806
2.799
2.754
2.748
2.729
2.712
2.593
2.542
2.315
2.153
2.146
2.143
1.743
1.737
1.731
1.725
1.714
1.705
1.698
1.692
1.685
1.372
1.367
1.349
1.329
0.871
0.855
OHC
CN
CN
4f
10
9
8
7
6
5
4
3
2
1
ppm
0.84
1.85
1.98
1.00
0.96
1.69
0.44
1.11
3.09
1.12
2.00
4.32
201.622
185.991
138.056
137.228
129.701
126.642
111.042
110.625
83.702
77.317
77.000
76.679
59.681
45.086
43.123
42.034
34.691
27.102
25.586
24.070
20.916
OHC
CN
CN
4f
200
180
160
140
120
100
80
60
40
20
ppm

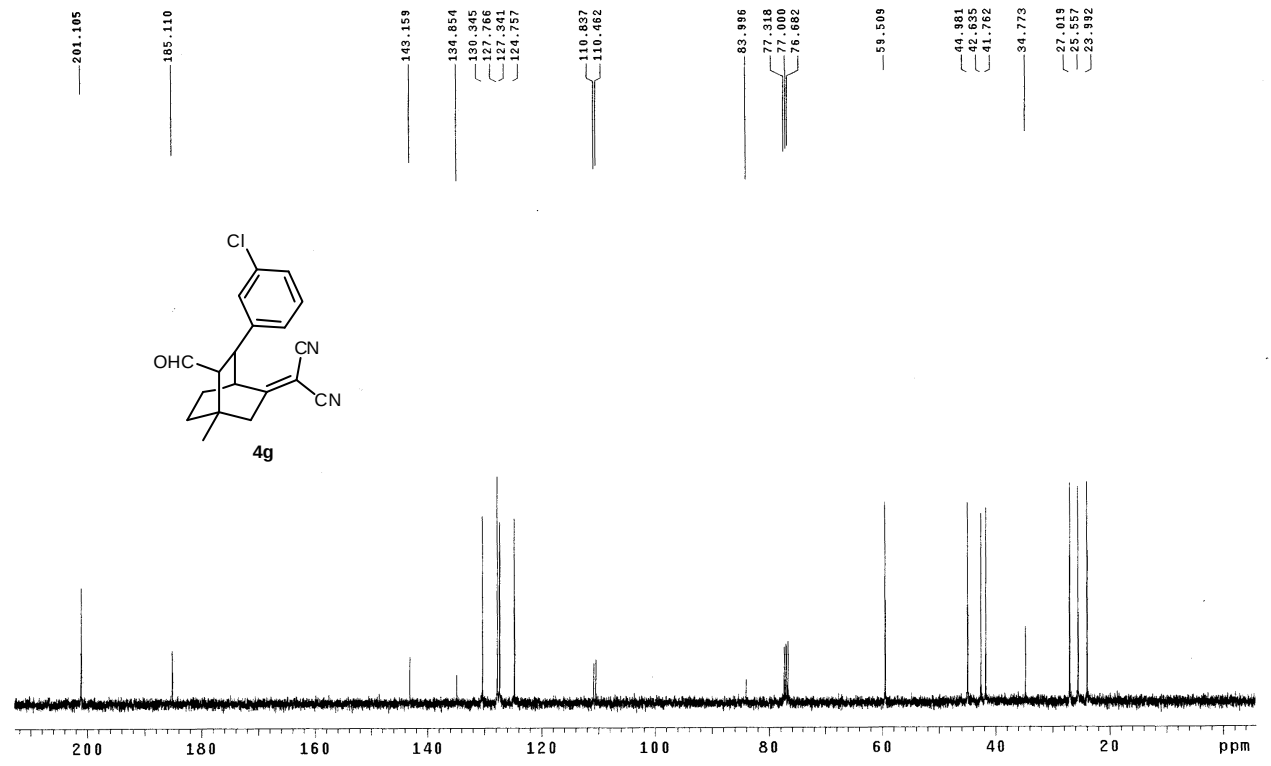


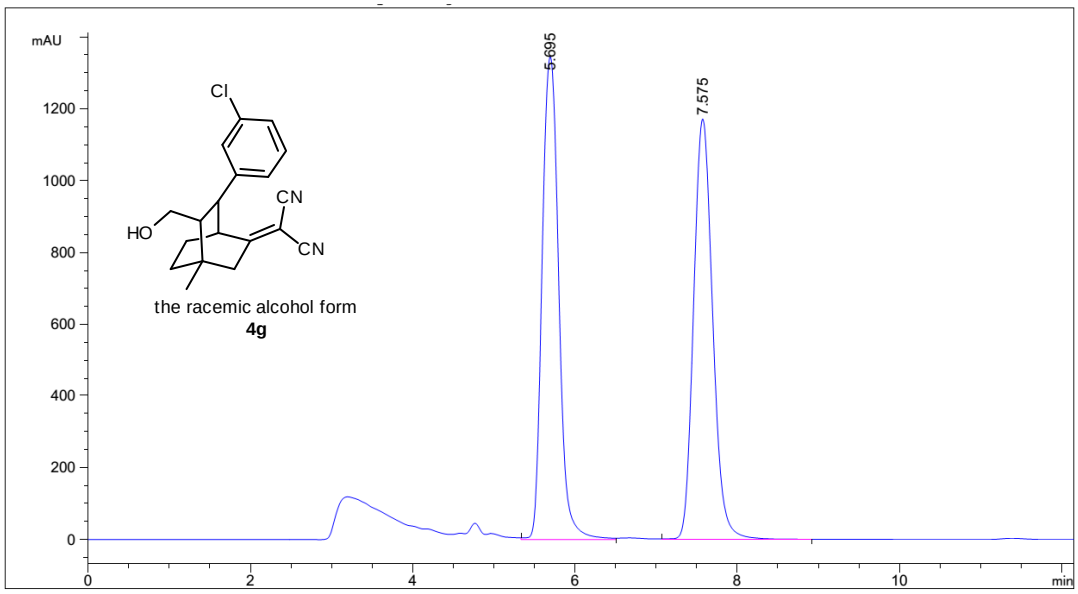
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.168	VV	0.3444	3.01849e4	1339.48206	50.7208
2	14.112	BB	0.7813	2.93269e4	580.76318	49.2792



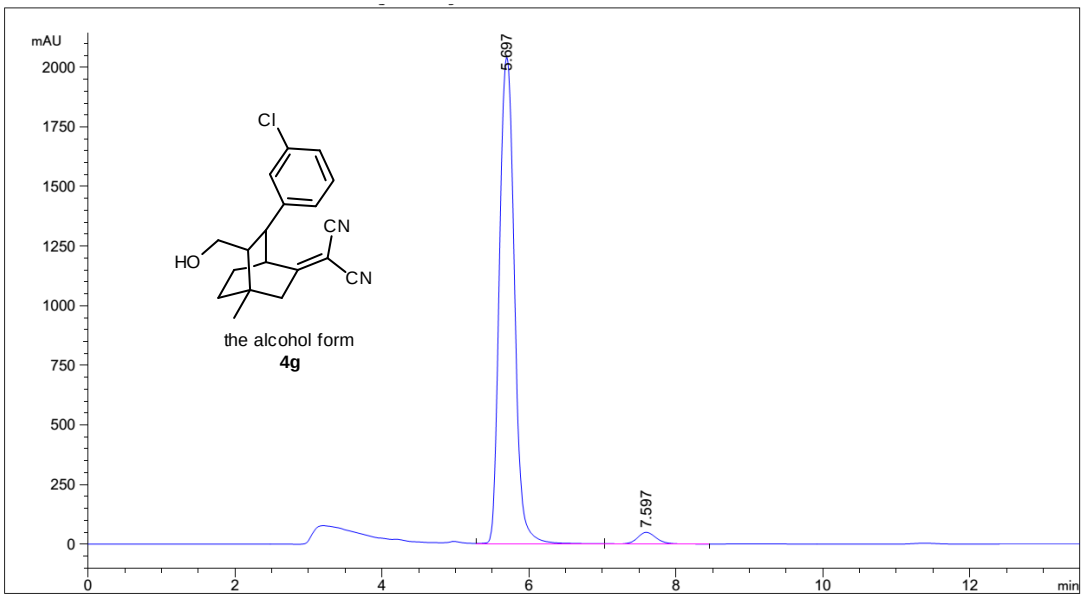
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.178	VV	0.3619	1360.31458	55.46121	2.5016
2	14.036	BB	0.7854	5.30182e4	1042.76135	97.4984


9.926
9.923
7.293
7.273
7.267
7.256
7.241
7.236
7.037
6.917
6.913
6.901
6.896
3.878
3.874
3.861
3.856
3.223
3.217
2.829
2.823
2.778
2.772
2.706
2.688
2.624
2.573
2.180
2.153
2.145
2.137
2.127
2.117
1.781
1.775
1.769
1.759
1.753
1.746
1.740
1.734
1.711
1.706
1.700
1.679
1.672
1.665
1.659
1.653
1.644
1.637
1.631
1.611
1.406
1.401
1.397
1.392
1.359
1.345
1.332
Cl
OHC
CN
CN
4g
10
9
8
7
6
5
4
3
2
1
ppm
0.88
0.89
1.85
0.99
1.00
0.92
1.19
1.16
1.22
1.17
2.65
4.41

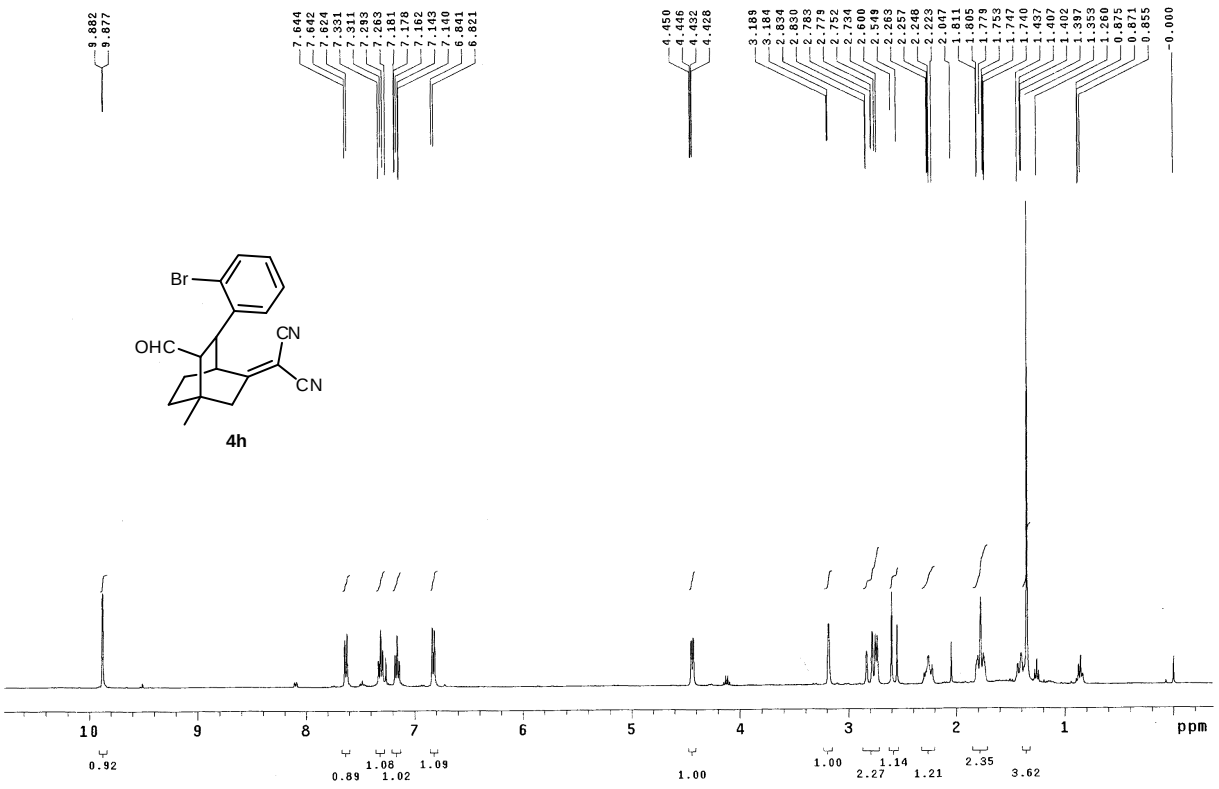

201.105
185.110
143.159
134.854
130.345
127.766
127.341
124.757
110.837
110.462
83.996
77.318
77.000
76.682
59.509
44.981
42.635
41.762
34.773
27.019
25.557
23.992
Cl
OHC
CN
CN
4g
200
180
160
140
120
100
80
60
40
20
ppm



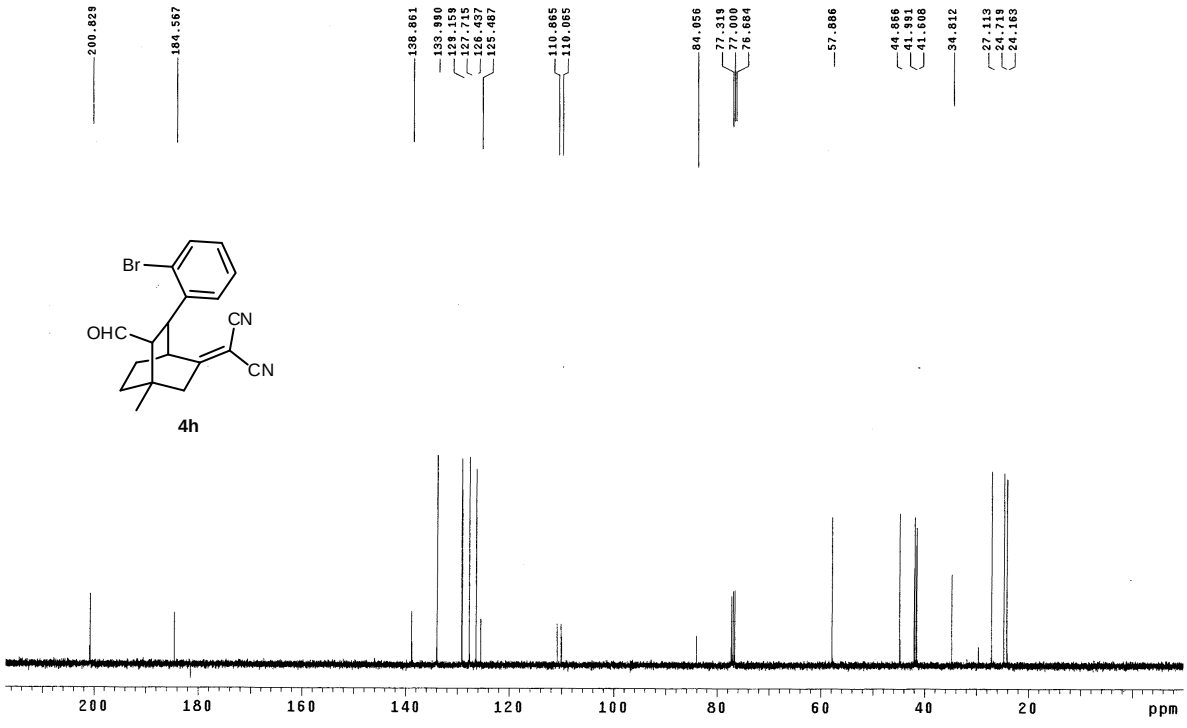
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.695	VV	0.2297	1.90592e4	1342.36780	49.9902
2	7.575	VB	0.2601	1.90666e4	1169.37610	50.0098



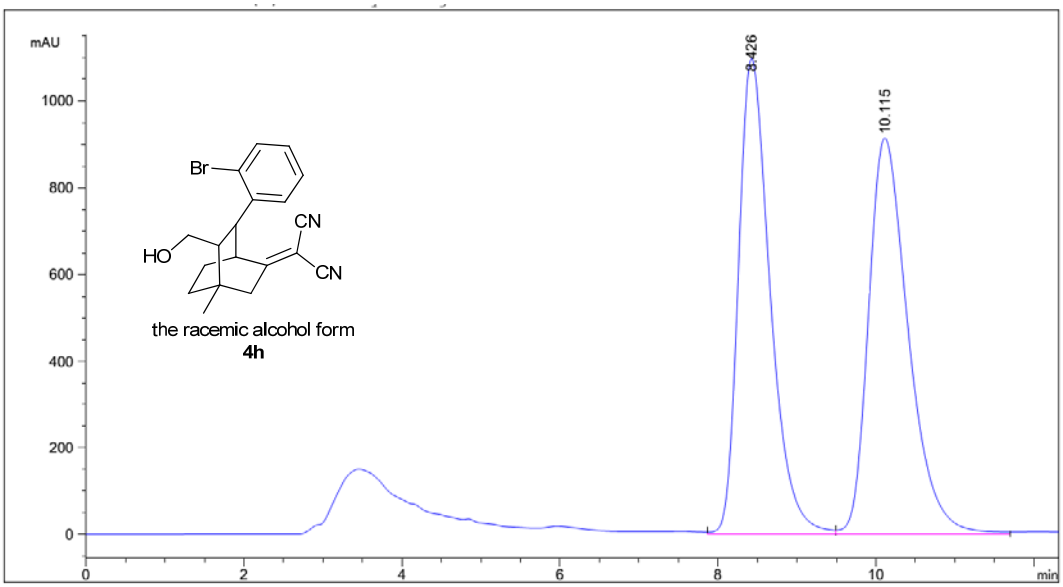
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.697	VV	0.2299	2.89930e4	2039.22522	96.8512
2	7.597	VB	0.2915	942.61377	49.61486	3.1488


9.882
9.877
7.644
7.642
7.624
7.331
7.311
7.293
7.263
7.181
7.178
7.162
7.143
7.140
6.841
6.821
4.450
4.446
4.432
4.428
3.189
3.184
2.834
2.830
2.783
2.779
2.752
2.734
2.600
2.549
2.263
2.257
2.248
2.243
2.047
2.011
1.805
1.779
1.753
1.747
1.740
1.437
1.407
1.402
1.397
1.353
1.260
0.875
0.871
0.855
-0.000
Br
OHC
CN
CN
10
9
8
7
6
5
4
3
2
1
ppm
0.92
0.89
1.08
1.02
1.09
1.00
1.00
1.14
2.27
1.21
2.35
3.62

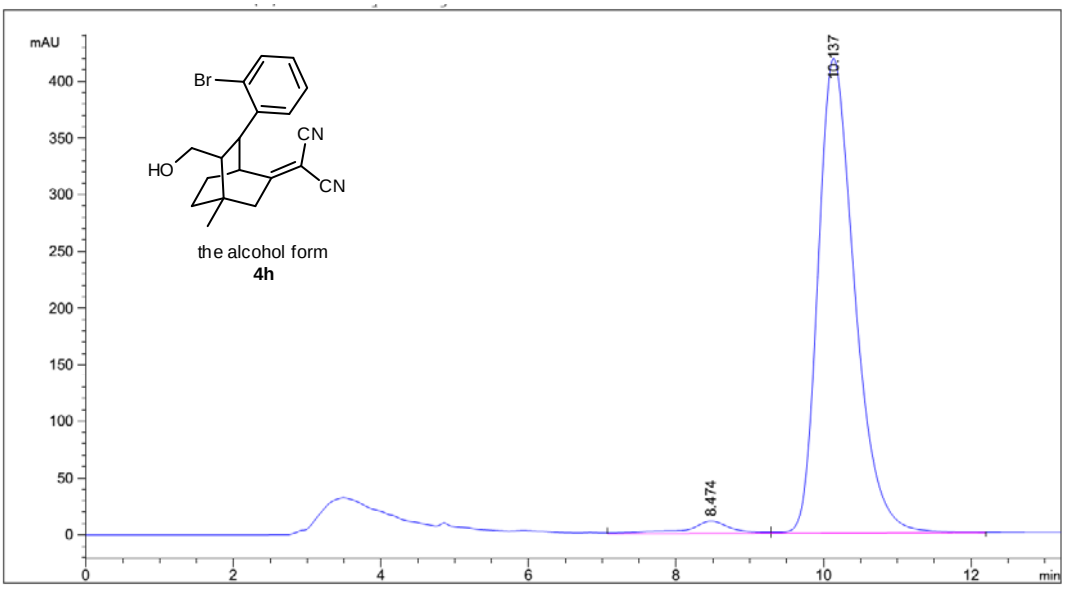
4h


200.829
184.567
138.861
133.990
129.159
127.715
126.437
125.487
110.865
110.065
84.056
77.319
77.000
76.684
57.886
44.866
41.991
41.608
34.812
27.113
24.719
24.163
Br
OHC
CN
CN
200
180
160
140
120
100
80
60
40
20
ppm

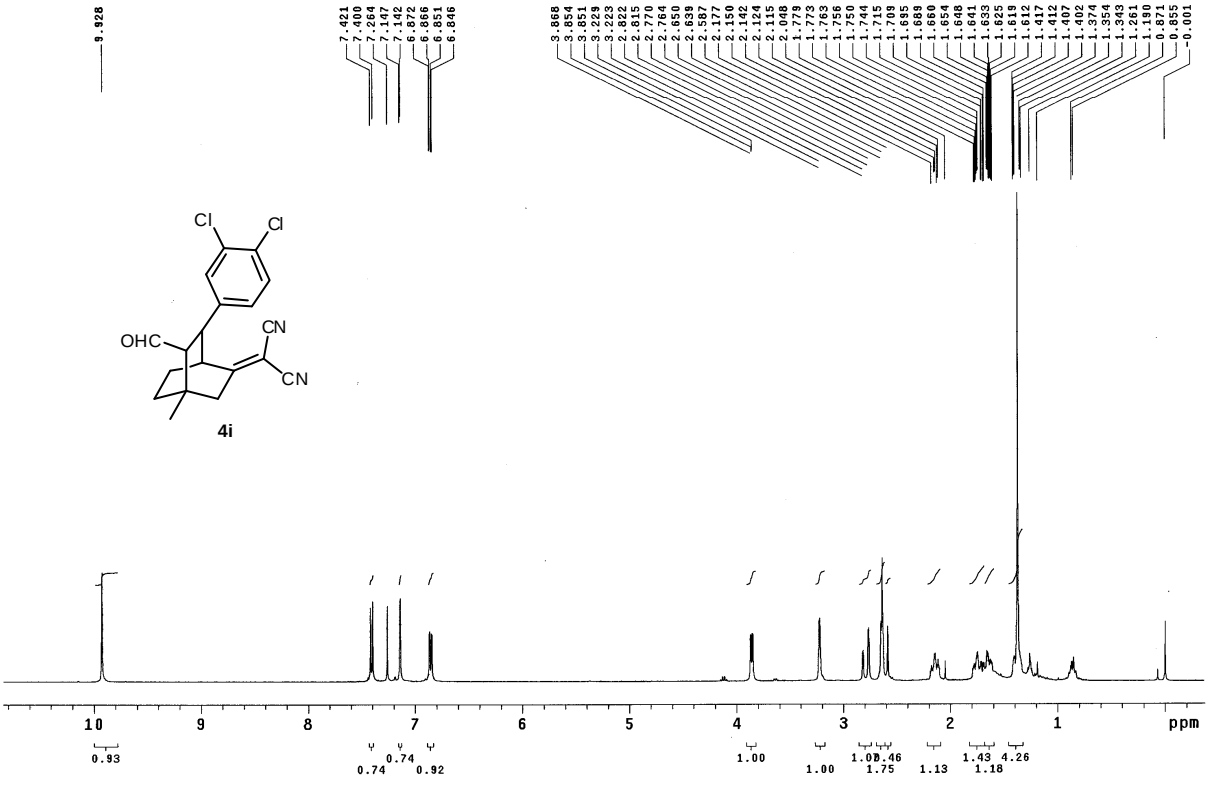
4h

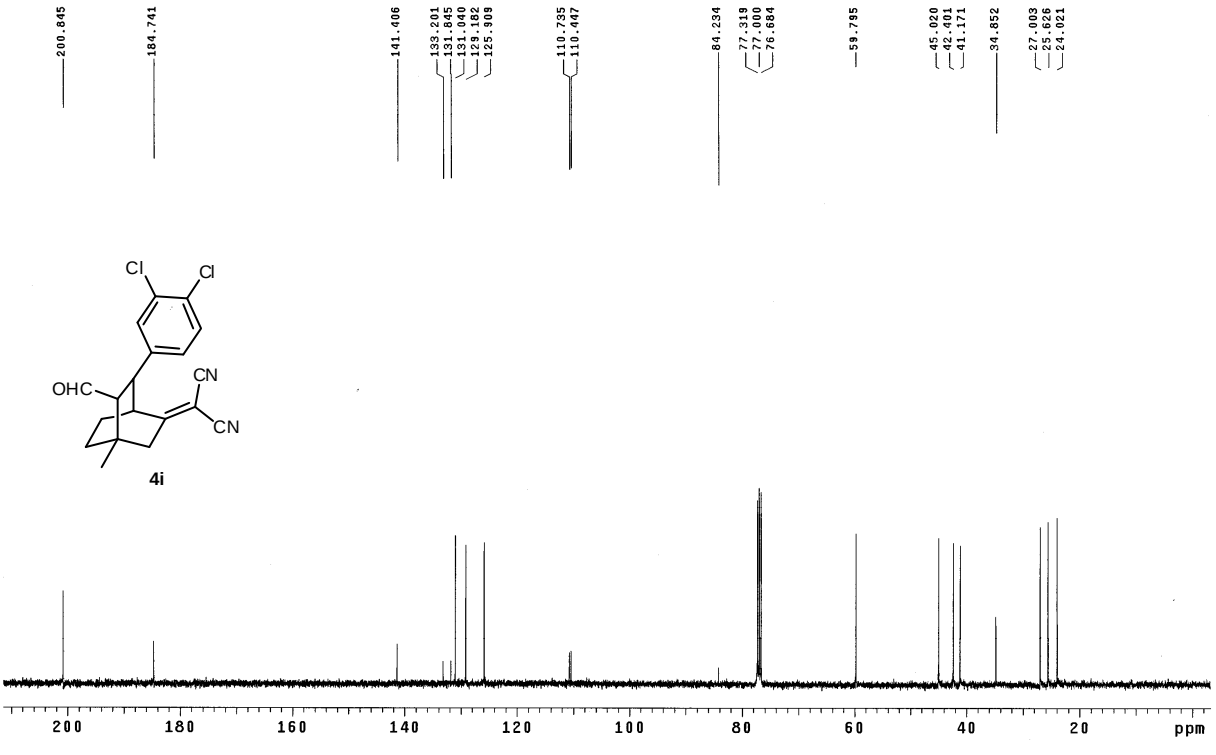


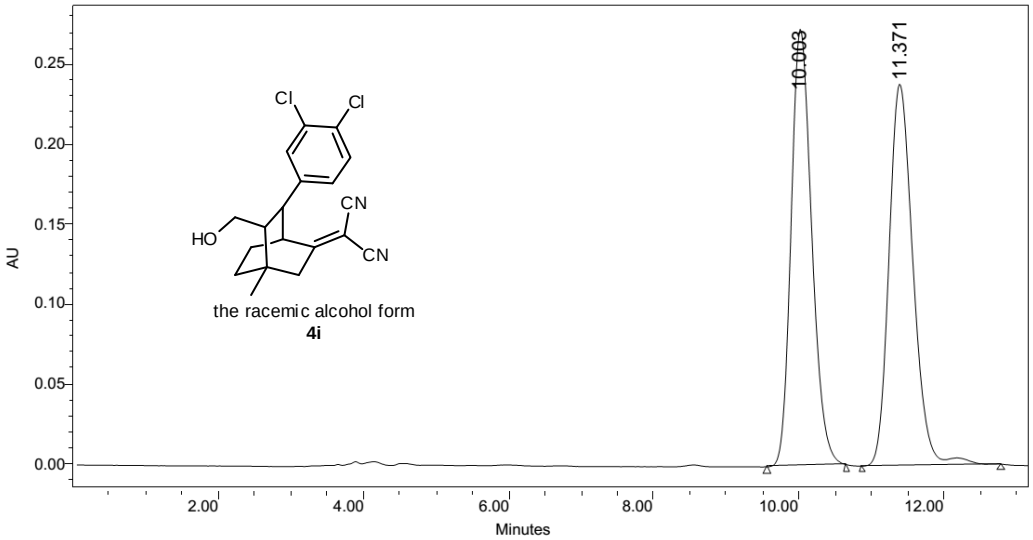
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.426	VV	0.4240	3.05647e4	1097.35803	48.8988
2	10.115	VV	0.5358	3.19413e4	914.05096	51.1012



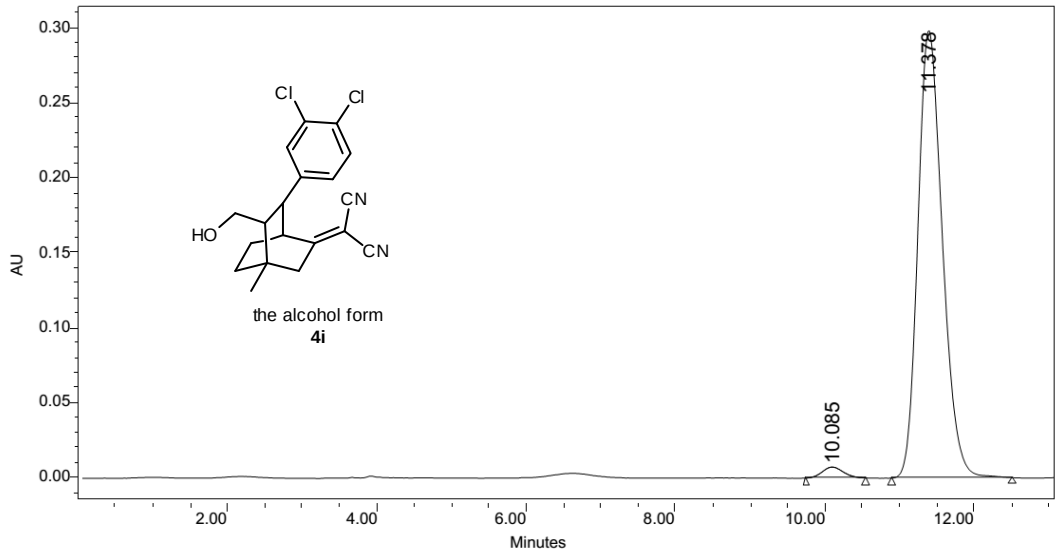
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.474	VV	0.5864	461.44046	11.04608	3.1035
2	10.137	VB	0.5299	1.44069e4	418.33609	96.8965


9.928
7.421
7.400
7.264
7.147
7.142
6.872
6.866
6.851
6.846
3.868
3.854
3.851
3.229
3.223
2.822
2.815
2.770
2.764
2.650
2.639
2.587
2.177
2.150
2.142
2.124
2.115
2.046
1.779
1.773
1.763
1.756
1.750
1.744
1.715
1.709
1.695
1.688
1.660
1.654
1.648
1.641
1.633
1.625
1.619
1.612
1.417
1.412
1.407
1.402
1.374
1.354
1.343
1.261
1.190
0.871
0.855
0.001
Cl
Cl
OHC
CN
CN
4i
10
9
8
7
6
5
4
3
2
1
ppm
0.93
0.74
0.74
0.92
1.00
1.00
1.00
0.46
1.75
1.13
1.43
4.26
1.18

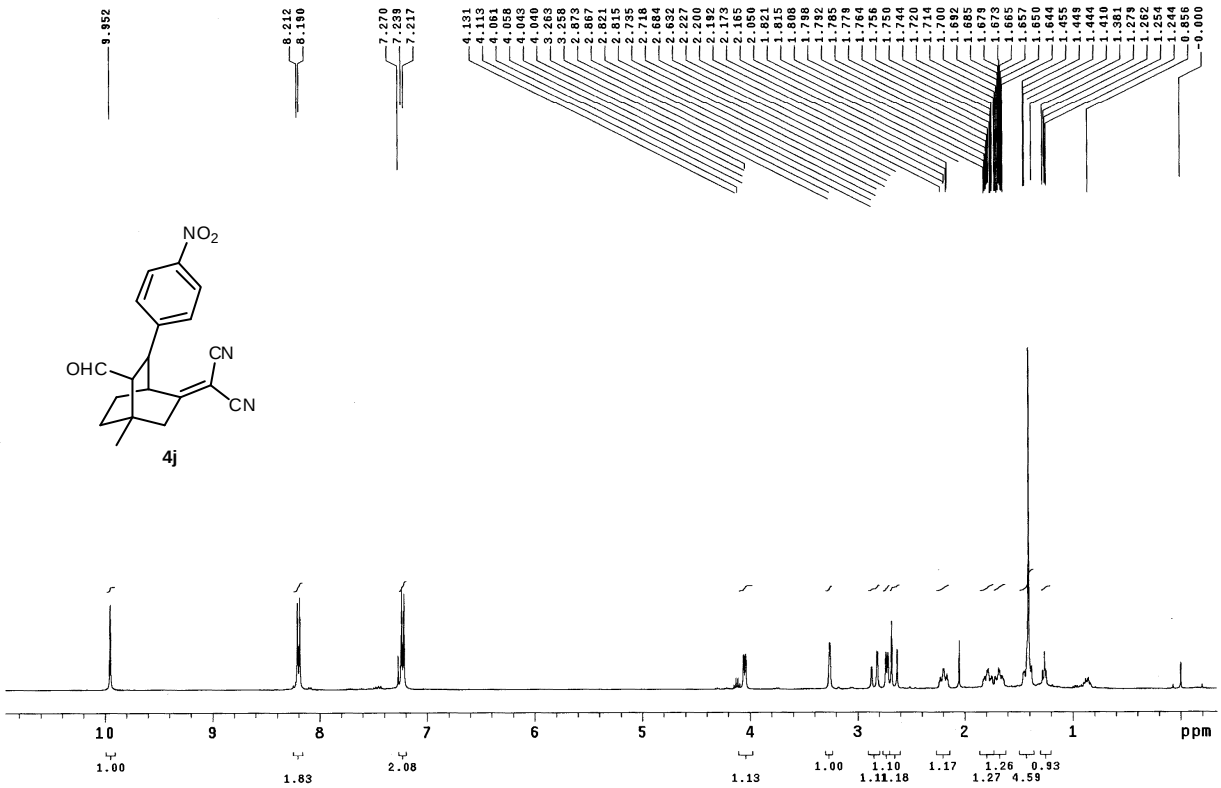

200.845
184.741
141.406
133.201
131.845
131.040
129.182
125.909
110.735
110.447
84.234
77.318
77.000
76.684
59.795
45.020
42.401
41.171
34.852
27.003
25.626
24.021
Cl
Cl
OHC
CN
CN
4i
200
180
160
140
120
100
80
60
40
20
ppm

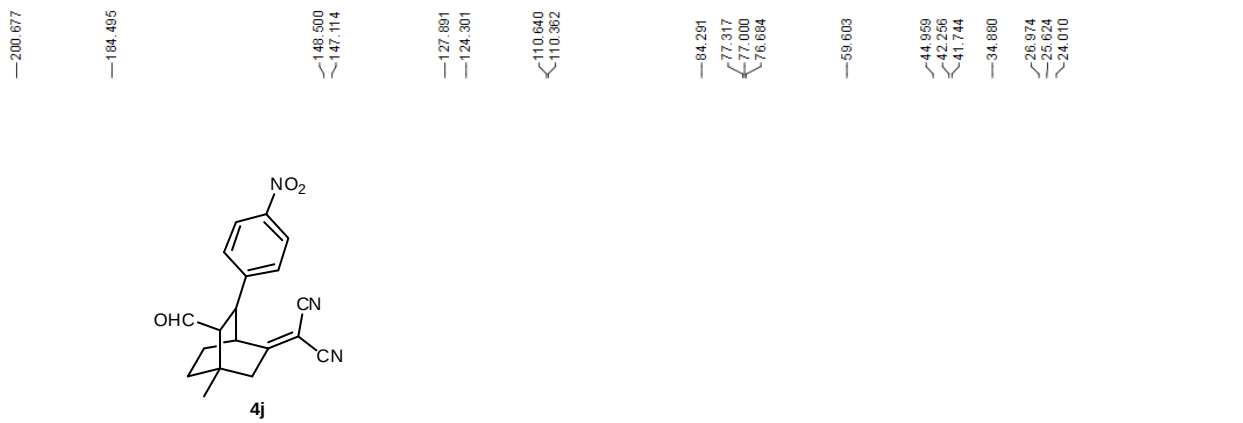


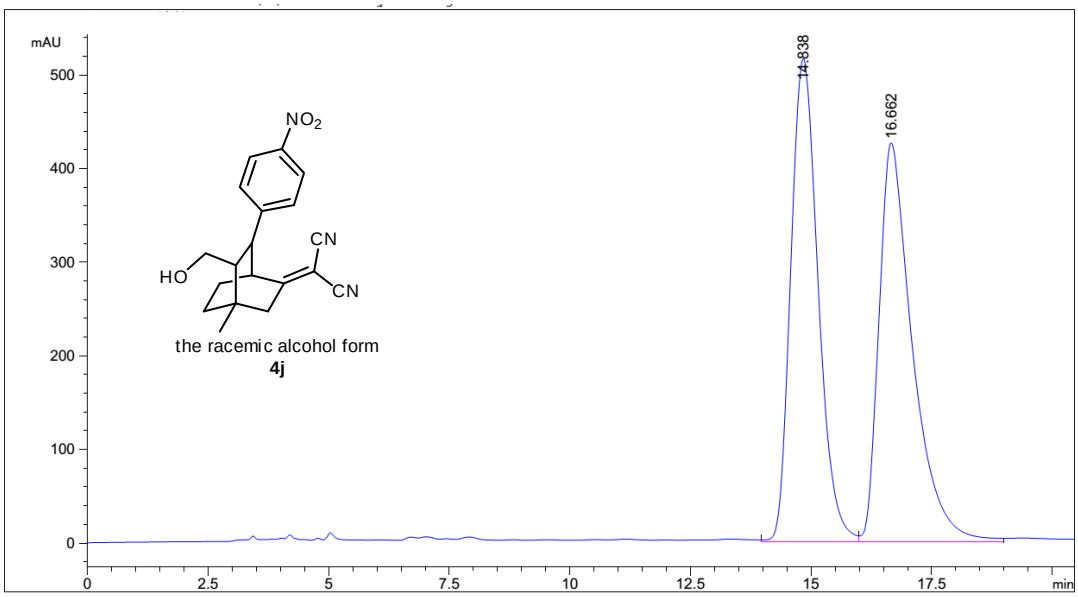
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.003	5395991	49.58	273179	53.38
2	11.371	5486543	50.42	238549	46.62



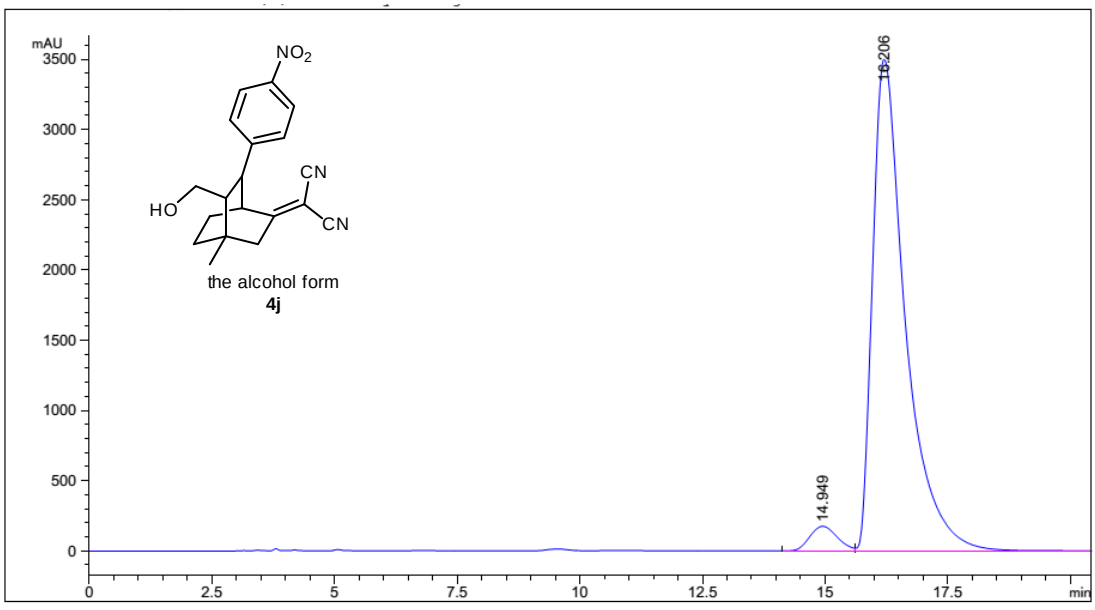
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	10.085	143413	2.07	7324	2.39
2	11.378	6799468	97.93	298540	97.61


9.952
8.212
8.190
7.270
7.239
7.217
4.131
4.113
4.061
4.058
4.043
4.040
3.263
3.258
2.873
2.867
2.821
2.815
2.735
2.718
2.684
2.632
2.227
2.200
2.192
2.173
2.165
2.050
1.821
1.815
1.808
1.798
1.792
1.785
1.775
1.764
1.756
1.750
1.744
1.720
1.714
1.700
1.692
1.685
1.679
1.673
1.665
1.657
1.650
1.644
1.455
1.449
1.444
1.410
1.381
1.279
1.262
1.254
1.244
0.856
-0.000
NO2
CN
OHC
CN
4j
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.83
2.08
1.13
1.00
1.10
1.11
1.18
1.17
1.26
1.27
0.93
4.59

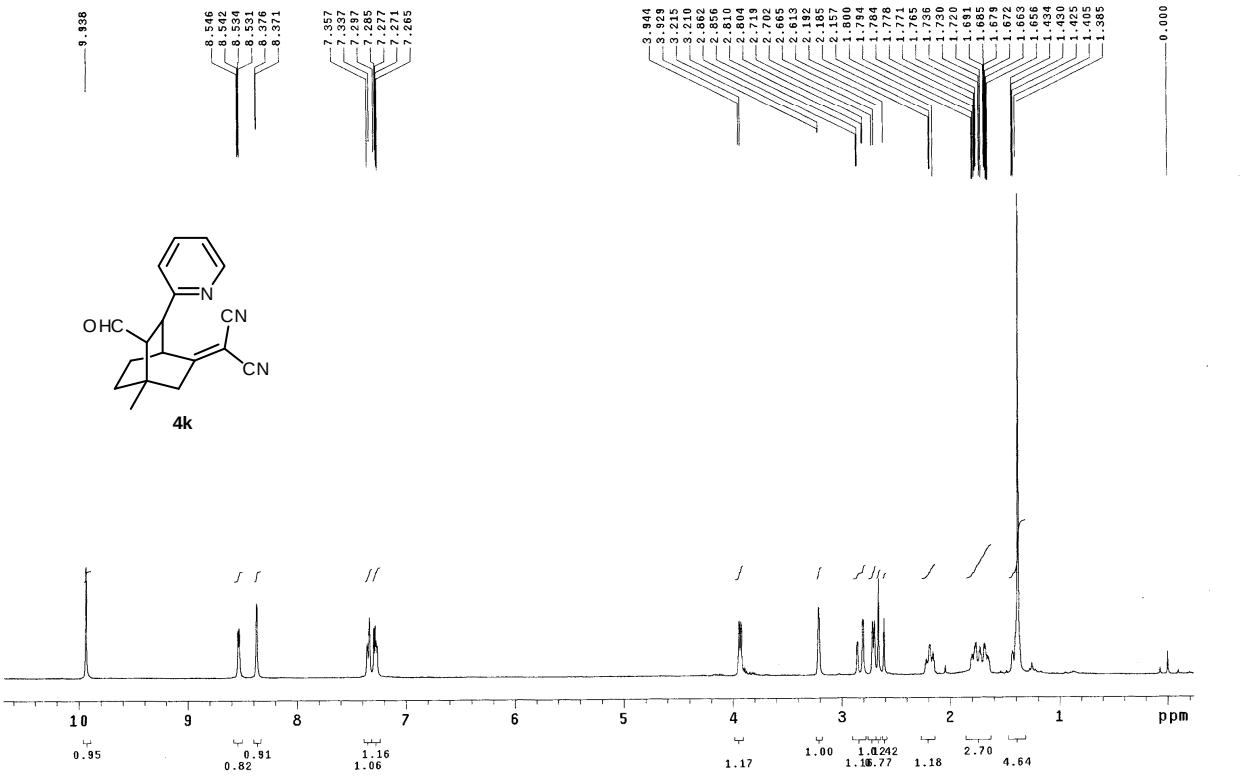

200.677
184.495
148.500
147.114
127.891
124.301
110.640
110.362
84.291
77.317
77.000
76.684
59.603
44.959
42.256
41.744
34.880
26.974
25.624
24.010
NO2
CN
OHC
CN
4j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

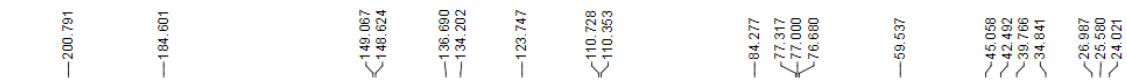


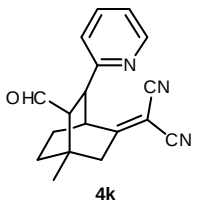
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.838	VV	0.6171	2.03335e4	515.88580	49.7454
2	16.662	VV	0.7084	2.05417e4	425.82550	50.2546

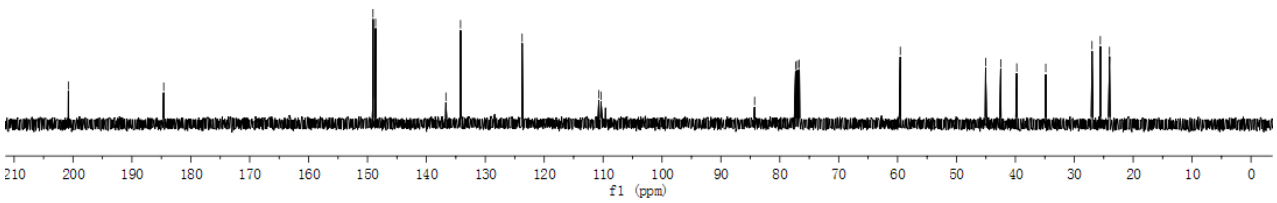


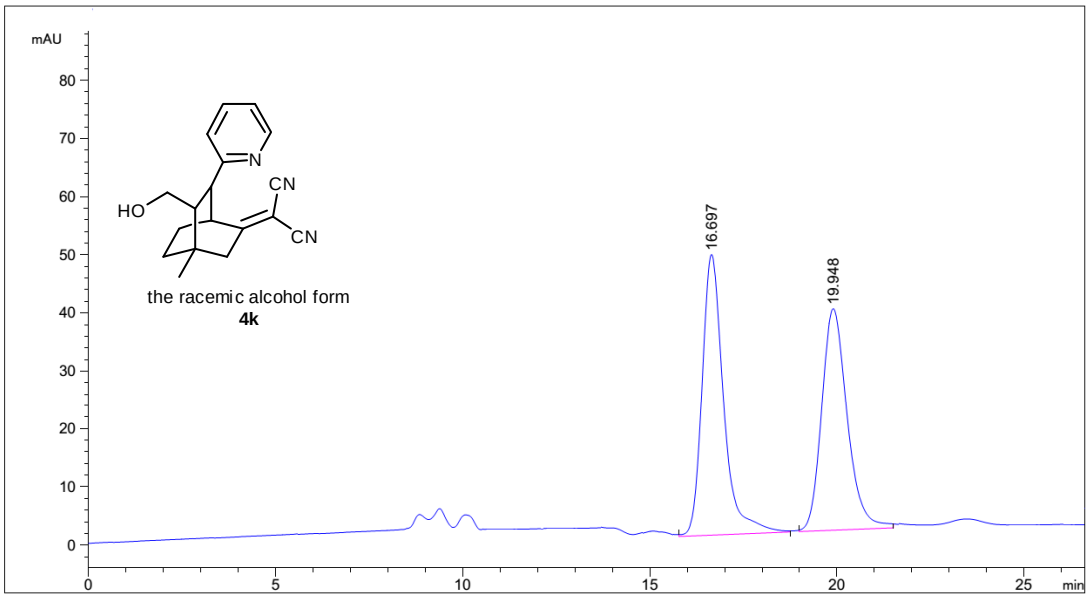
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.949	BV	0.6146	6907.70557	176.21121	4.0712
2	16.206	VBA	0.6881	1.62767e5	3500.51123	95.9288


9.938
8.546
8.542
8.534
8.531
8.376
8.371
7.357
7.337
7.297
7.285
7.277
7.271
7.265
3.944
3.929
3.215
3.210
2.862
2.856
2.810
2.804
2.713
2.702
2.665
2.613
2.192
2.185
2.157
1.800
1.794
1.784
1.778
1.771
1.765
1.736
1.730
1.720
1.691
1.685
1.679
1.672
1.663
1.656
1.434
1.430
1.425
1.405
1.385
0.000
N
OHC
CN
CN
4k
10
9
8
7
6
5
4
3
2
1
ppm
0.95
0.91
0.82
1.16
1.06
1.17
1.00
1.18
2.70
4.64

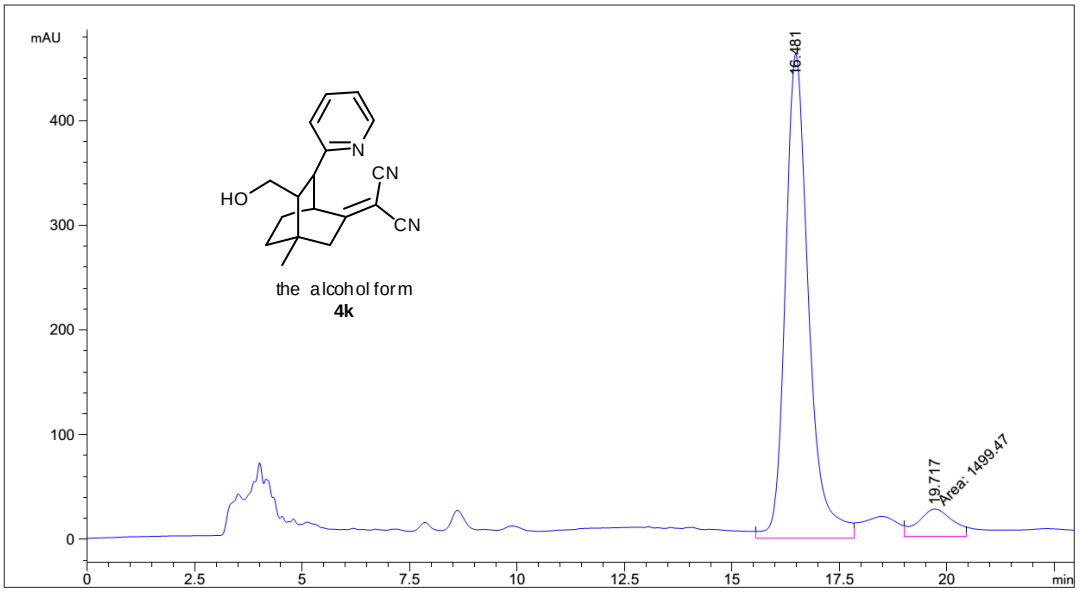

200.791
184.601
149.067
148.624
136.690
134.202
123.747
110.728
110.353
84.277
77.317
77.000
76.680
59.537
45.058
42.492
39.766
34.841
26.987
25.580
24.021


N
OHC
CN
CN
4k

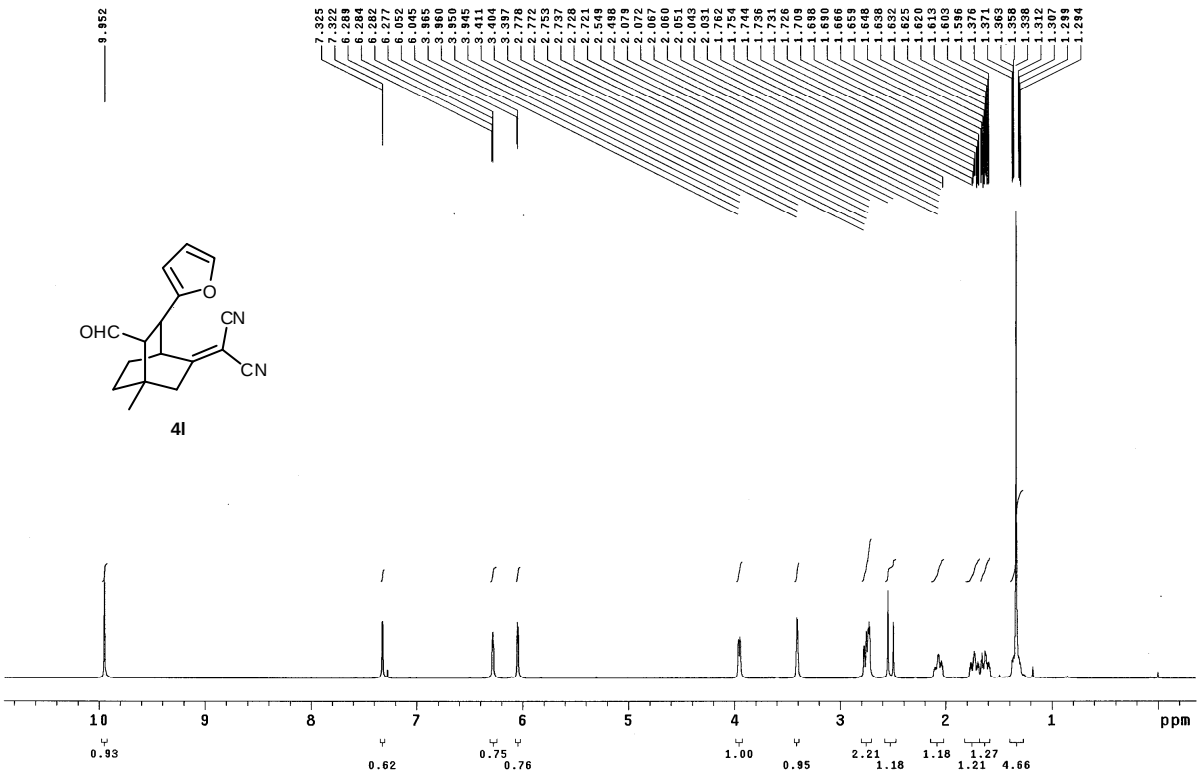

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



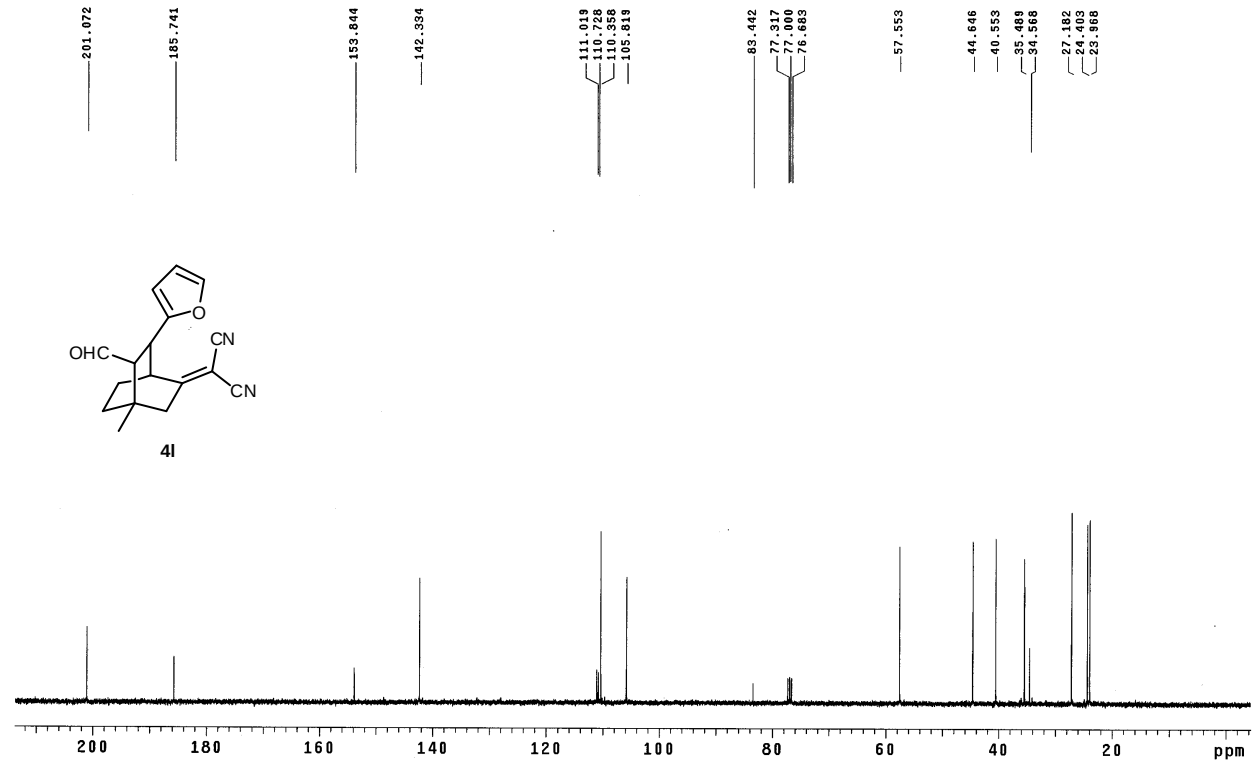
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.697	VB	0.6058	1930.58850	48.32963	51.6377
2	19.948	BB	0.7212	1808.12939	38.19479	48.3623



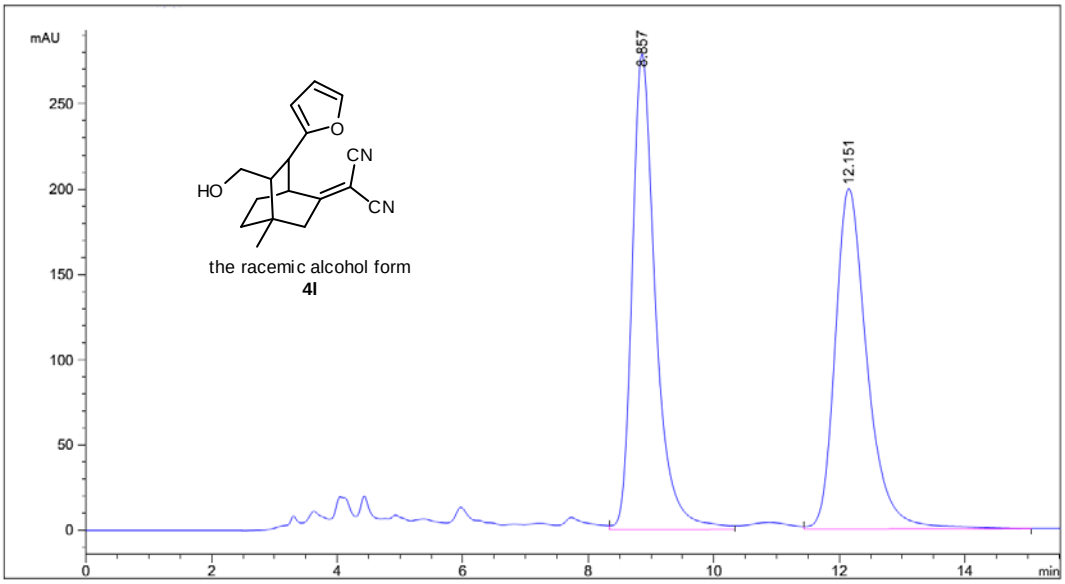
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.481	VV	0.5676	1.74194e4	462.42593	92.0742
2	19.717	MM	0.9400	1499.46558	26.58686	7.9258


9.952
7.325
7.322
6.289
6.284
6.282
6.277
6.052
6.045
3.965
3.960
3.950
3.945
3.411
3.404
3.397
2.778
2.772
2.753
2.737
2.728
2.721
2.549
2.498
2.079
2.072
2.067
2.060
2.051
2.043
2.031
1.762
1.754
1.744
1.736
1.731
1.726
1.709
1.698
1.690
1.680
1.655
1.648
1.638
1.632
1.625
1.620
1.613
1.603
1.596
1.376
1.371
1.363
1.358
1.338
1.312
1.307
1.298
1.294
O
CN
OHC
CN
10
9
8
7
6
5
4
3
2
1
ppm
0.93
0.62
0.75
0.76
1.00
0.95
2.21
1.18
1.18
1.27
1.21
4.66

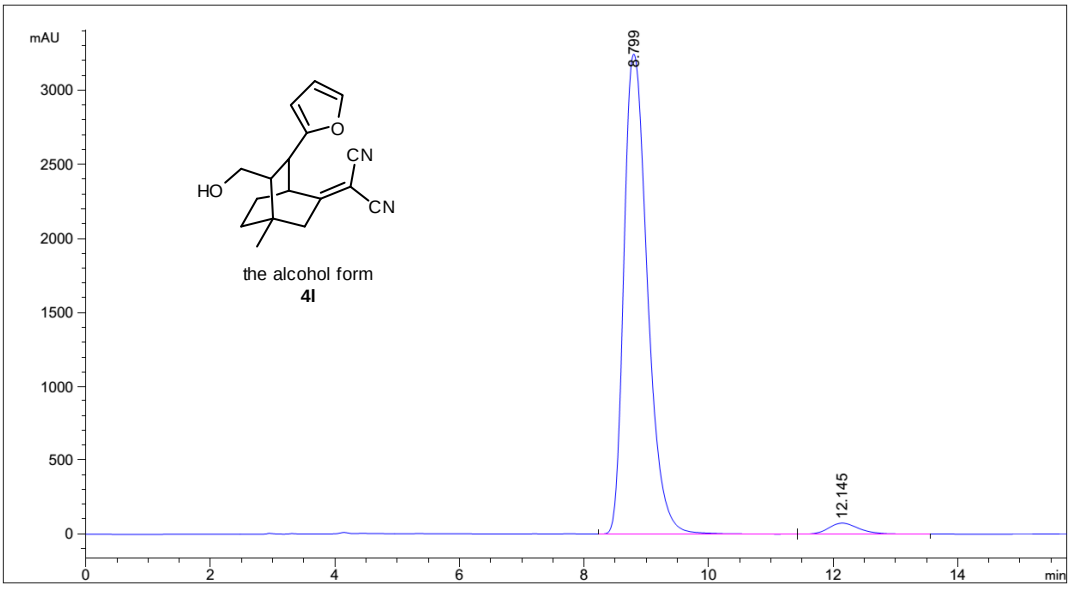
4l


201.072
185.741
153.844
142.334
111.019
110.728
110.358
105.819
83.442
77.317
77.000
76.683
57.553
44.646
40.553
35.489
34.568
27.182
24.403
23.968
O
CN
OHC
CN
200
180
160
140
120
100
80
60
40
20
ppm

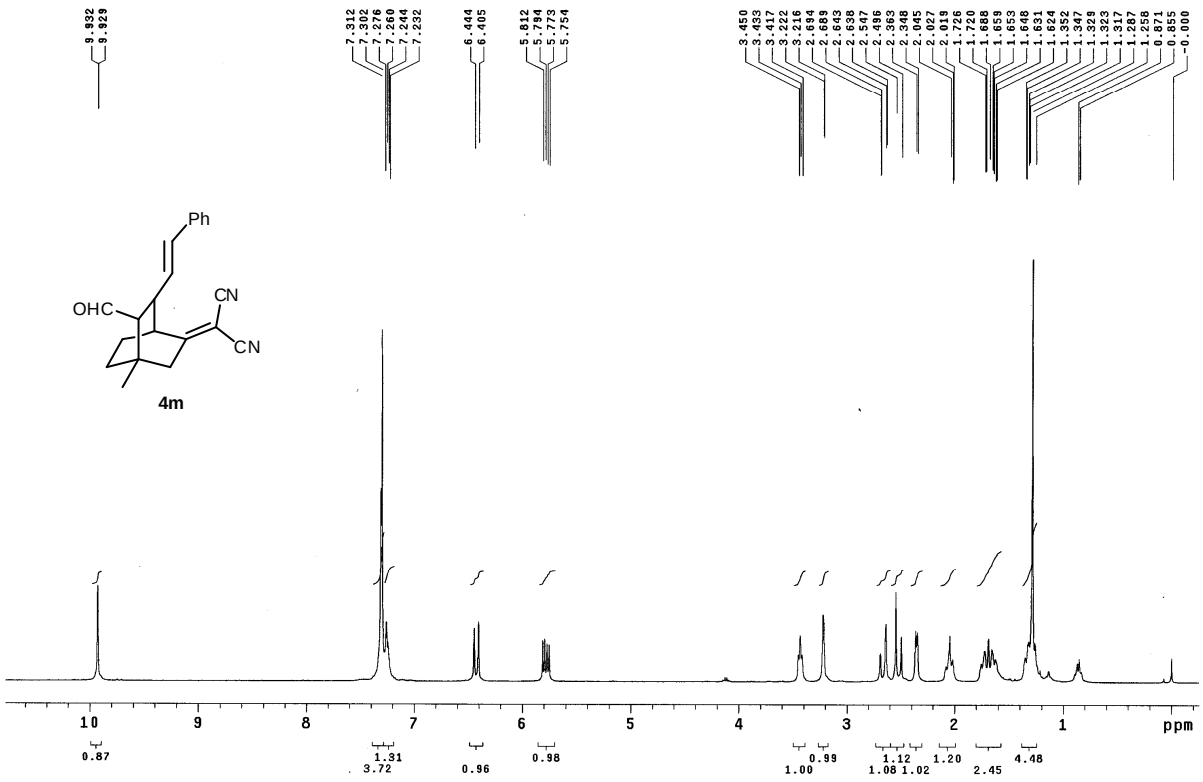
4l

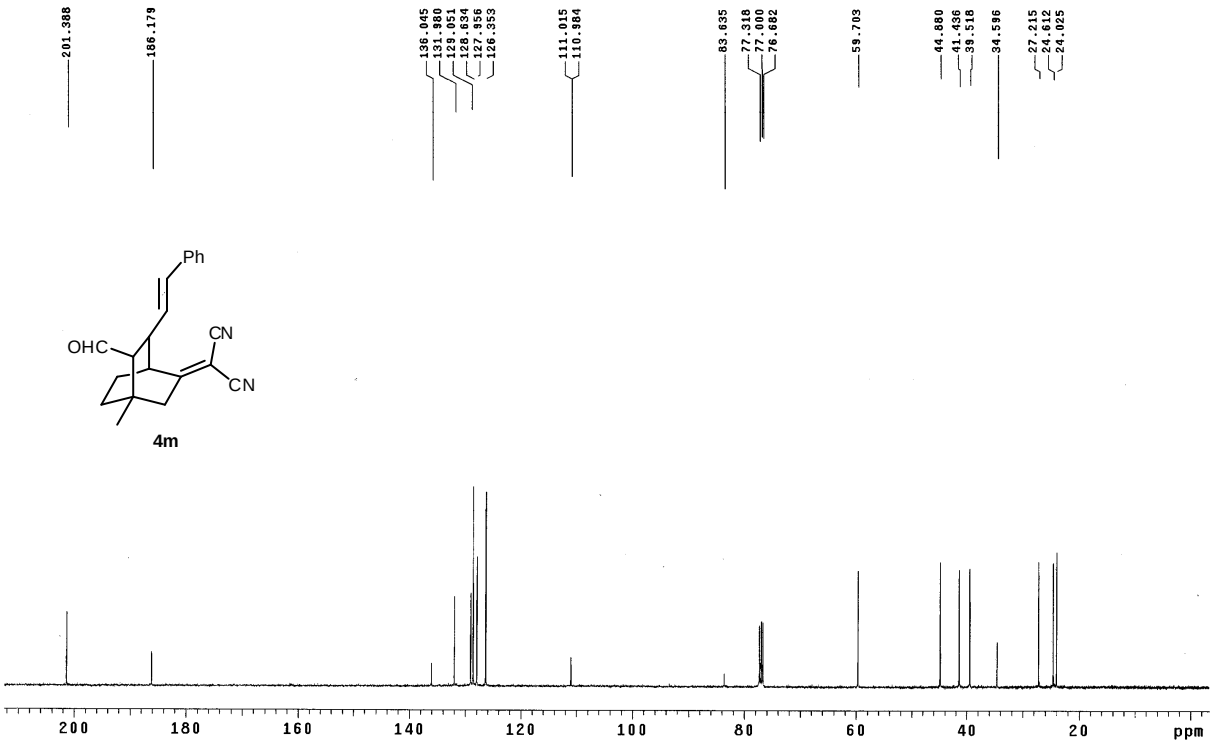


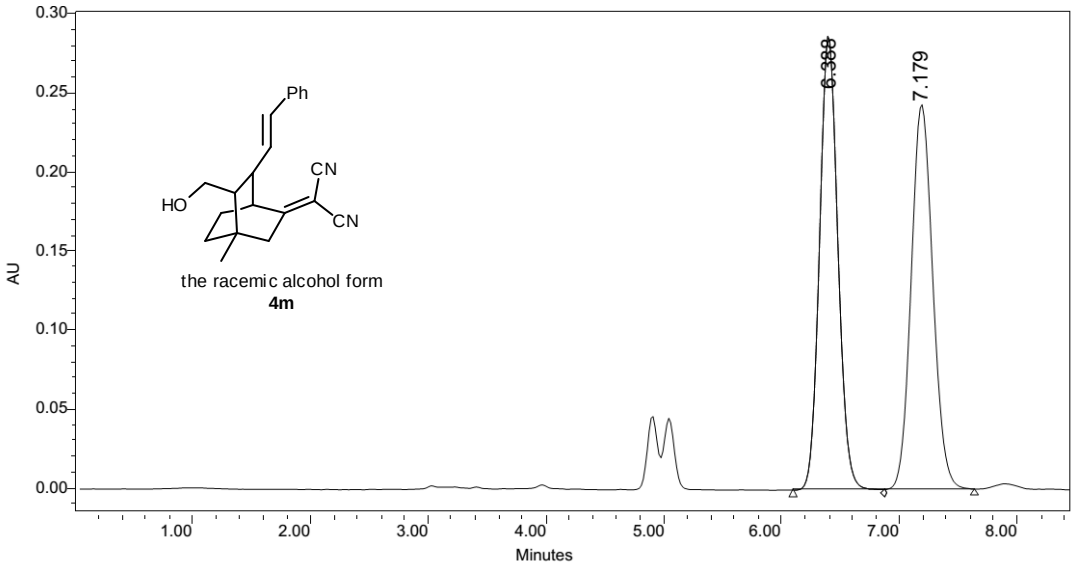
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.857	VV	0.3897	7218.44482	278.52066	50.4851
2	12.151	VB	0.5419	7079.72900	199.63078	49.5149



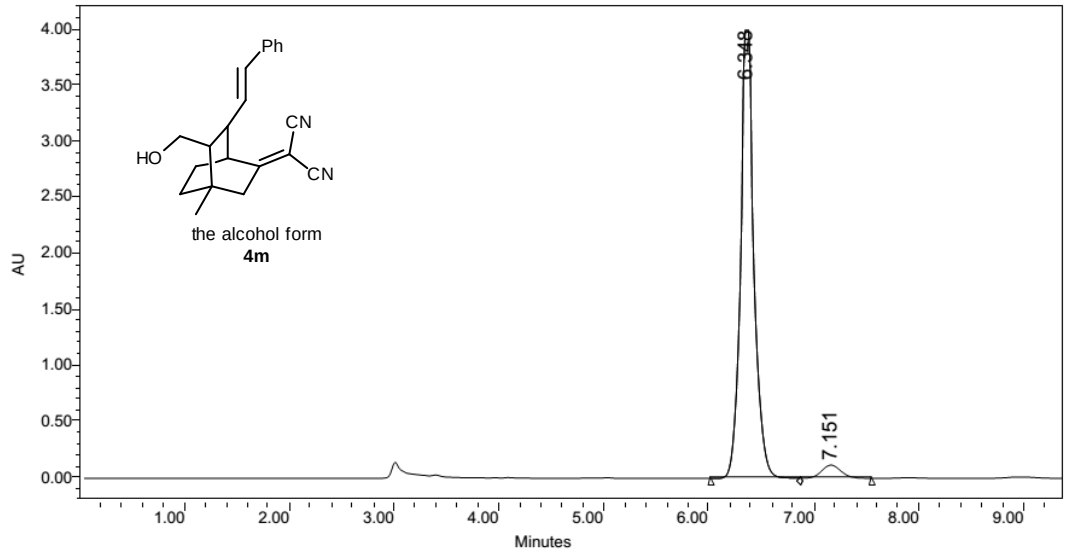
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.799	VV	0.4054	8.52341e4	3245.43091	97.0739
2	12.145	VB	0.5213	2569.17773	75.12193	2.9261


9.832
9.829
7.312
7.302
7.276
7.260
7.244
7.232
6.444
6.405
5.812
5.794
5.773
5.754
3.450
3.433
3.417
3.222
3.216
2.694
2.689
2.643
2.638
2.547
2.496
2.363
2.348
2.045
2.027
2.019
1.726
1.720
1.688
1.659
1.653
1.648
1.631
1.624
1.352
1.347
1.329
1.323
1.317
1.287
1.258
0.871
0.855
-0.000
Ph
CN
OHC
CN
4m
10
9
8
7
6
5
4
3
2
1
ppm
0.87
1.31
3.72
0.96
0.98
1.00
0.99
1.12
1.08
1.02
1.20
2.45
4.48

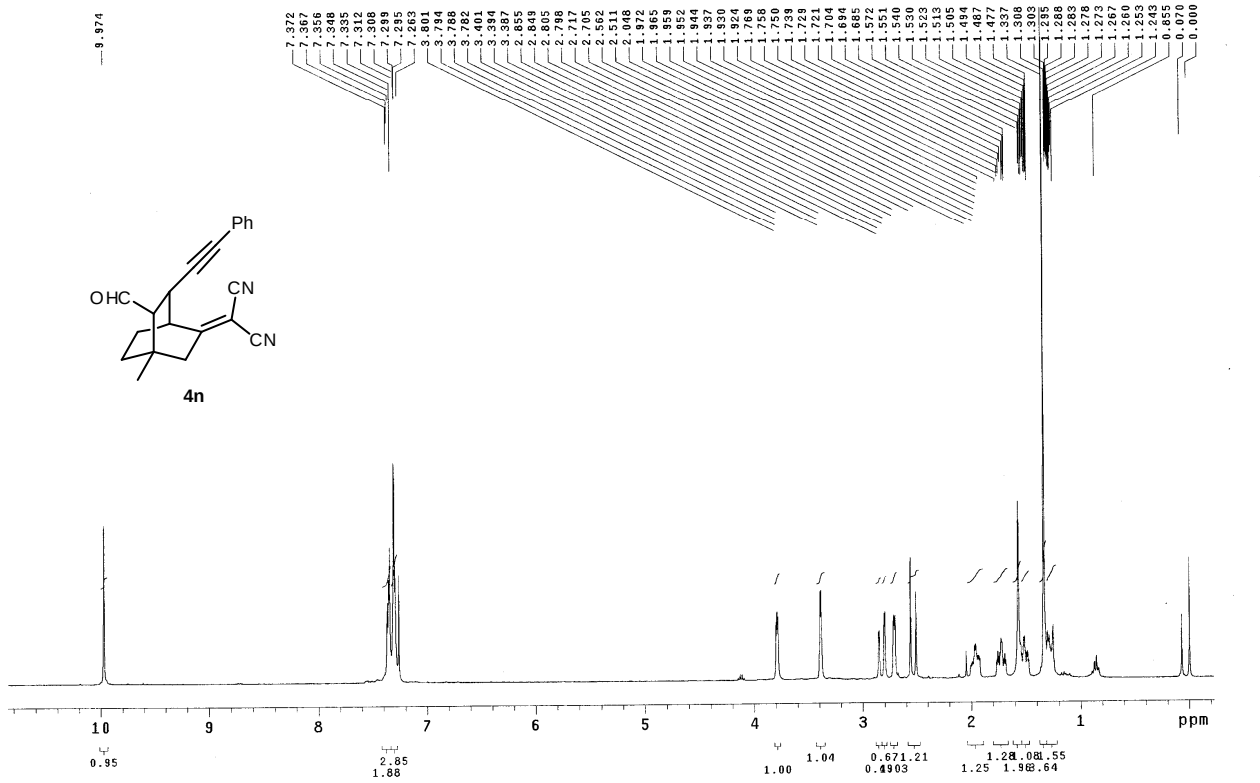

201.388
186.179
136.045
131.980
129.051
128.634
127.956
126.353
111.015
110.984
83.635
77.318
77.000
76.682
59.703
44.880
41.436
39.518
34.596
27.215
24.612
24.025
Ph
CN
OHC
CN
4m
200
180
160
140
120
100
80
60
40
20
ppm



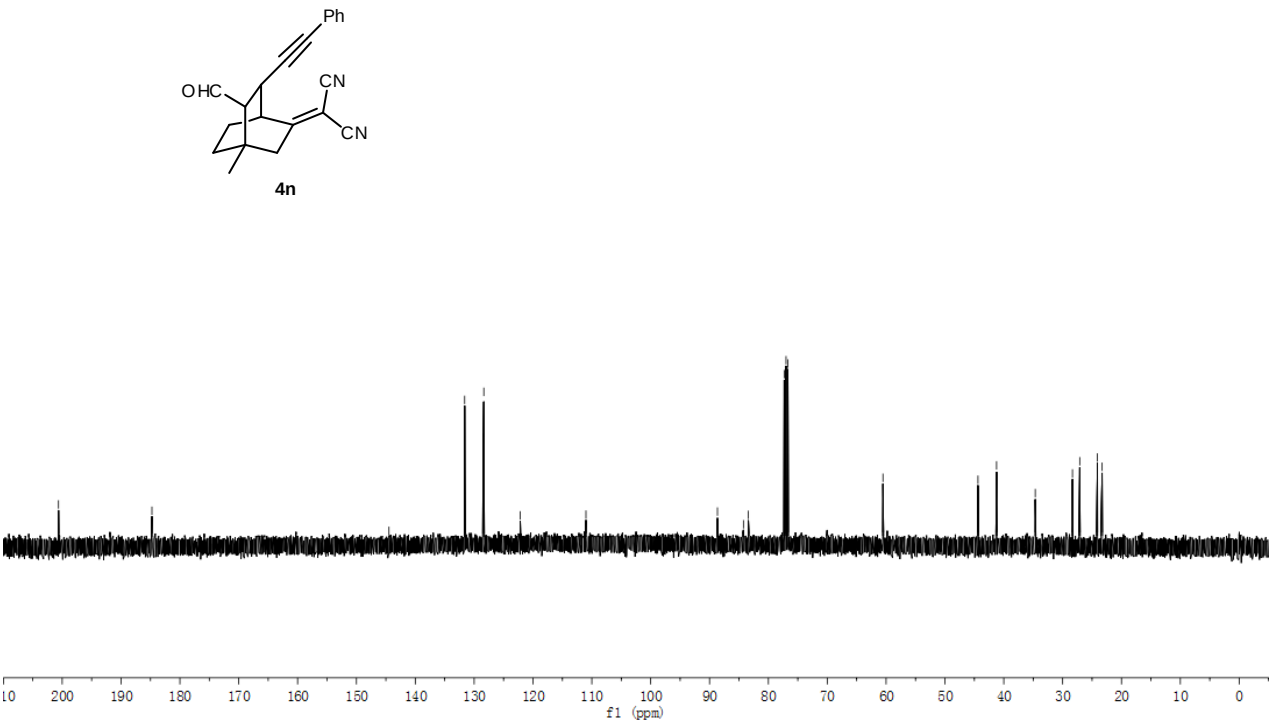
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	6.388	3108836	49.97	287390	54.12
2	7.179	3113018	50.03	243617	45.88



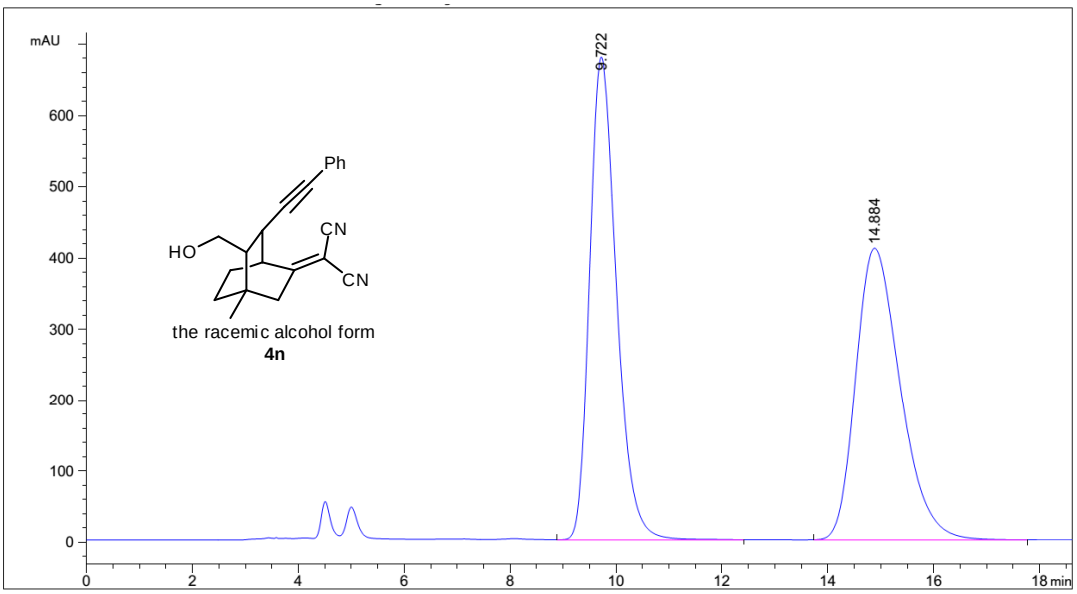
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	6.348	35725940	95.87	4171091	97.24
2	7.151	1537867	4.13	118589	2.76


9.974
7.372
7.367
7.356
7.348
7.335
7.312
7.308
7.299
7.295
7.263
3.801
3.794
3.788
3.782
3.401
3.394
3.387
2.855
2.848
2.805
2.798
2.717
2.705
2.562
2.511
2.048
1.972
1.965
1.959
1.952
1.944
1.937
1.930
1.924
1.769
1.758
1.750
1.739
1.728
1.721
1.704
1.694
1.685
1.572
1.551
1.540
1.530
1.523
1.513
1.505
1.494
1.487
1.477
1.337
1.308
1.303
1.295
1.288
1.283
1.278
1.273
1.267
1.260
1.253
1.243
0.855
0.070
0.000
Ph
OHC
CN
CN
10
9
8
7
6
5
4
3
2
1
ppm
0.95
2.85
1.88
1.00
1.04
0.67
1.21
0.49
03
1.25
1.28
1.08
1.55
1.96
3.64

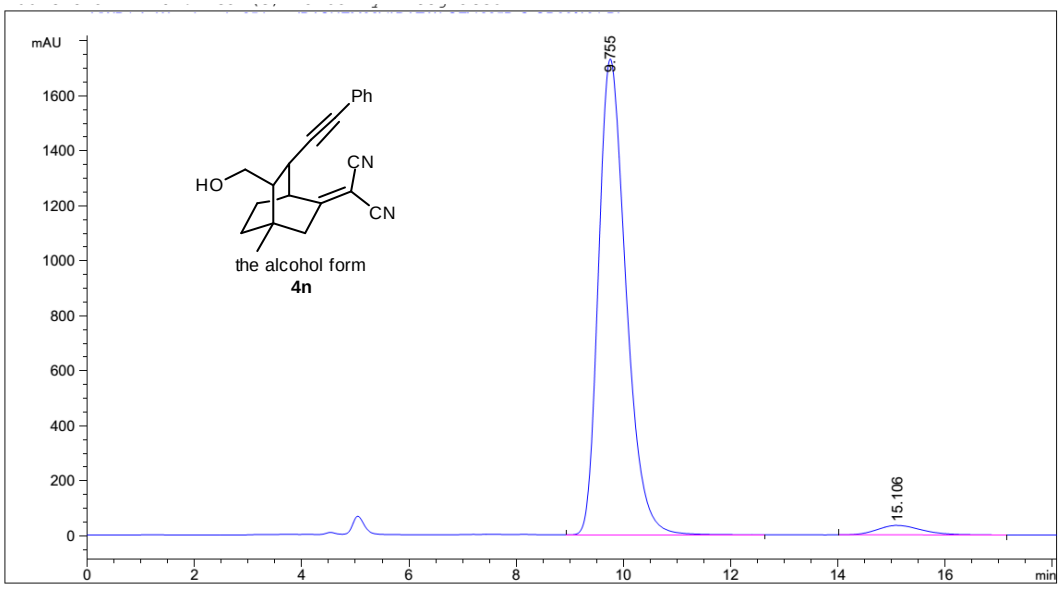
4n


200.627
184.755
144.475
131.611
128.472
128.359
122.156
111.003
88.655
84.241
83.394
77.316
77.000
76.681
60.533
44.385
41.225
34.653
28.331
27.095
24.083
23.287
Ph
OHC
CN
CN
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

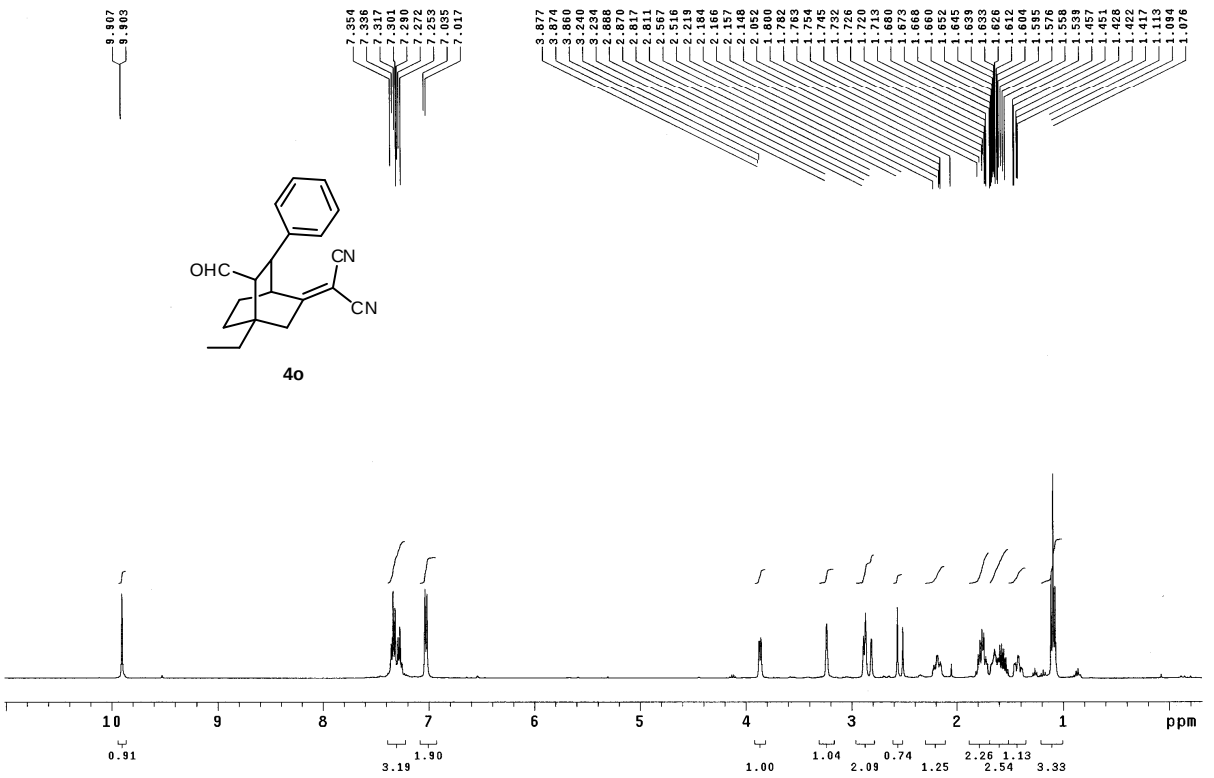
4n

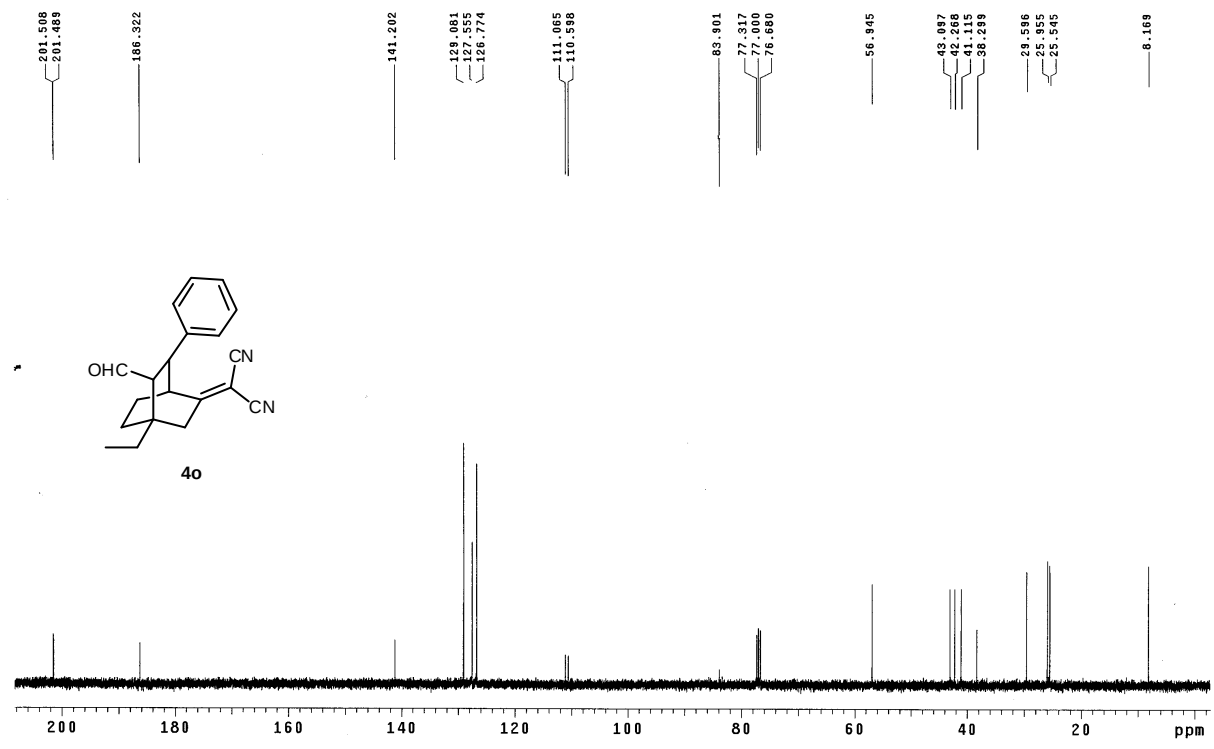


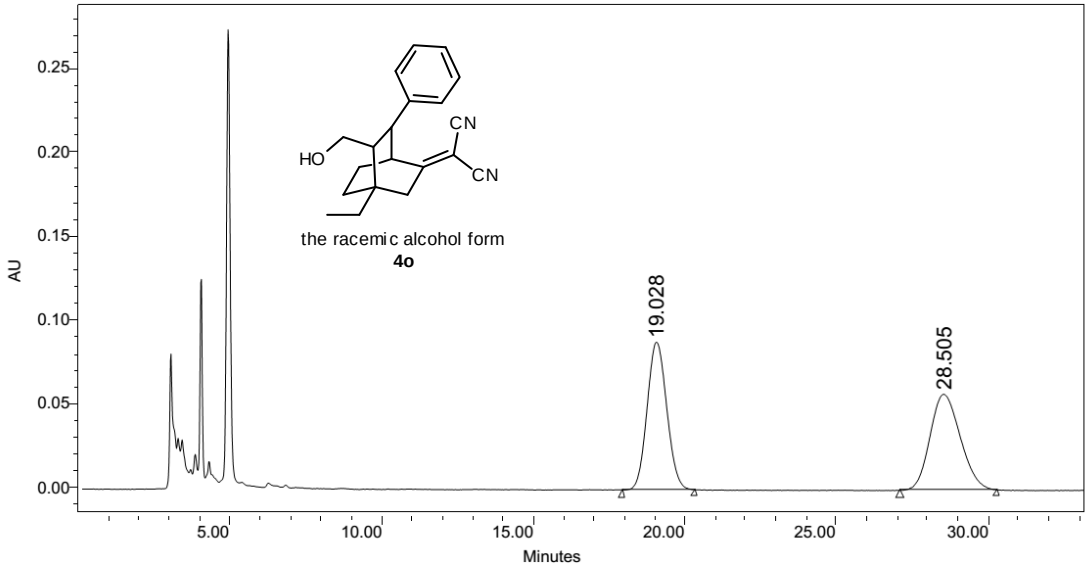
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.722	VB	0.5389	2.38853e4	678.40619	49.9173
2	14.884	BB	0.9025	2.39645e4	410.44202	50.0827



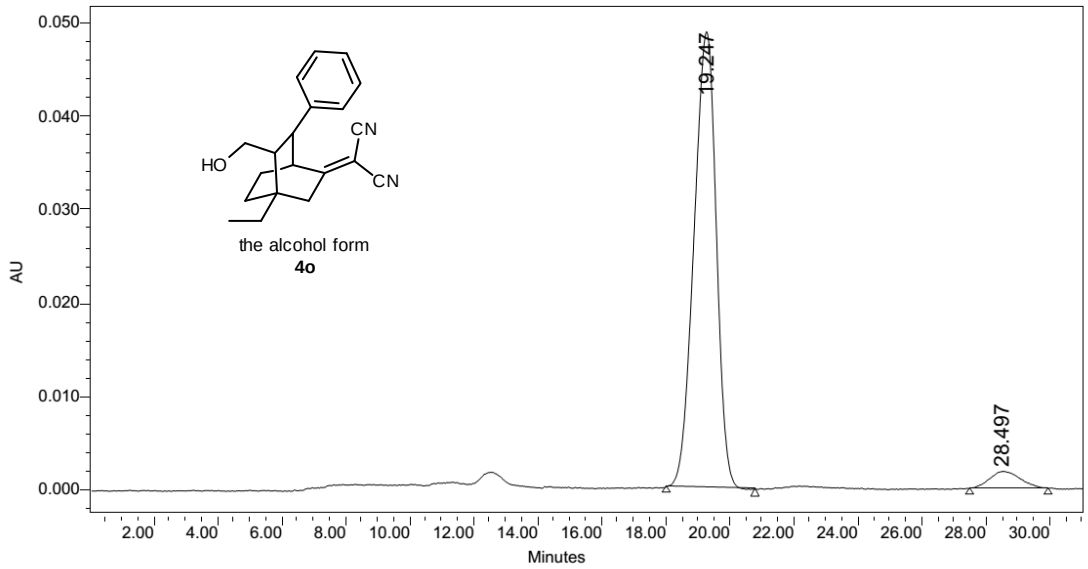
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.755	VB	0.5486	6.14883e4	1730.18323	96.8671
2	15.106	BB	0.8924	1988.69312	34.57166	3.1329


9.907
9.903
7.354
7.336
7.317
7.301
7.290
7.272
7.253
7.035
7.017
3.877
3.874
3.860
3.240
3.234
2.888
2.870
2.817
2.811
2.567
2.516
2.219
2.184
2.166
2.157
2.148
2.052
1.800
1.782
1.763
1.754
1.745
1.732
1.726
1.720
1.713
1.680
1.673
1.668
1.660
1.652
1.645
1.639
1.633
1.626
1.612
1.604
1.595
1.576
1.558
1.539
1.457
1.451
1.428
1.422
1.417
1.113
1.094
1.076
OHC
CN
CN
4o
10
9
8
7
6
5
4
3
2
1
ppm
0.91
3.19
1.90
1.00
1.04
2.09
0.74
1.25
2.26
1.13
2.54
3.33

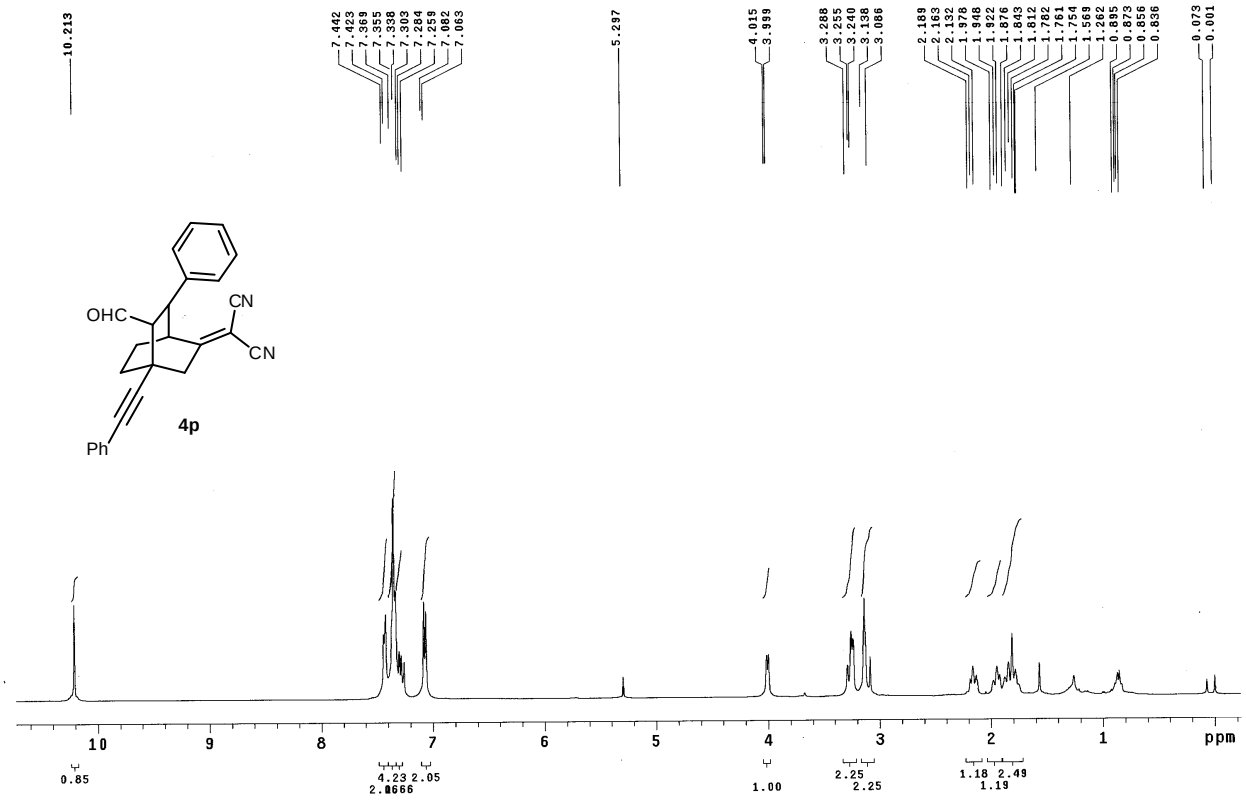

201.508
201.489
186.322
141.202
129.081
127.555
126.774
111.065
110.598
83.901
77.317
77.000
76.680
56.845
43.097
42.268
41.115
38.299
29.596
25.955
25.545
8.169
OHC
CN
CN
4o
200
180
160
140
120
100
80
60
40
20
ppm

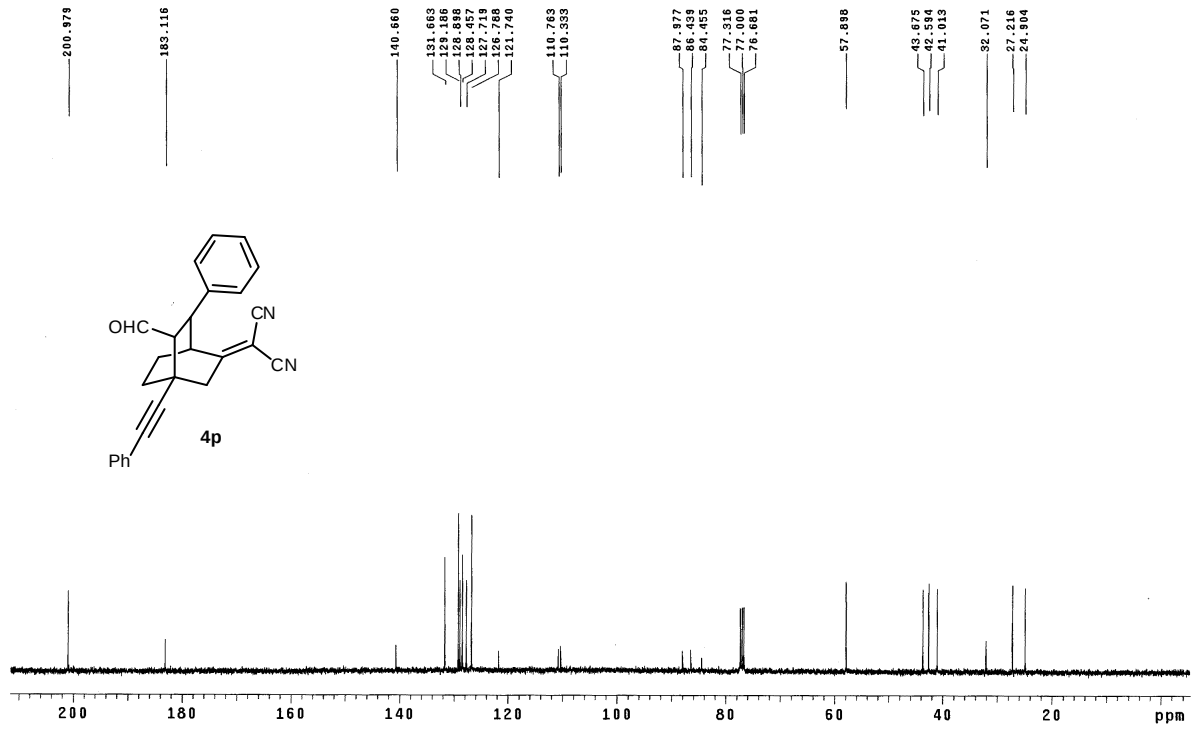


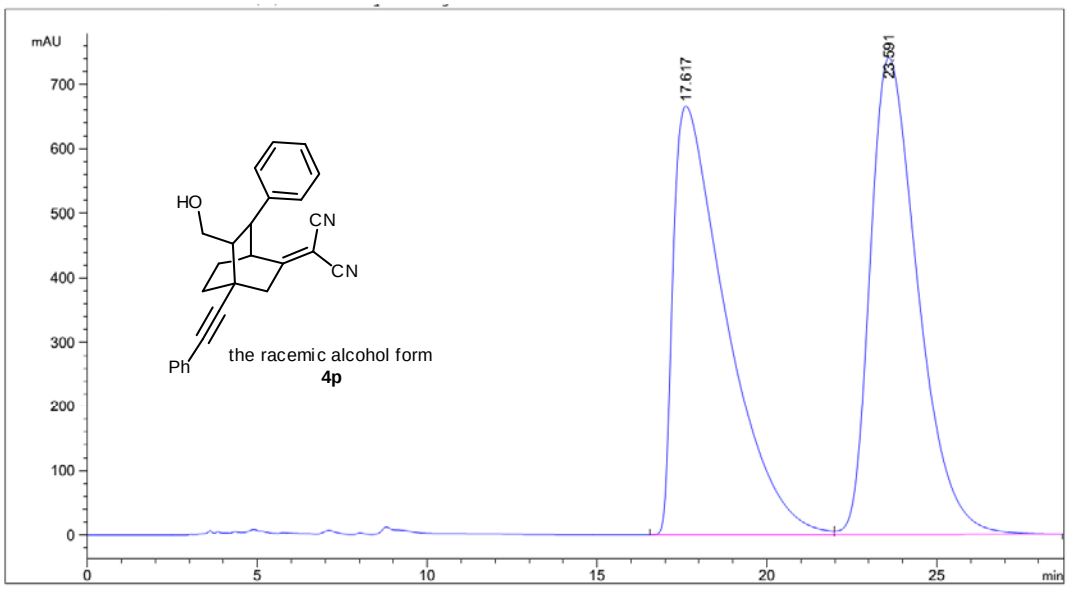
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	19.028	3971639	50.02	88006	60.63
2	28.505	3967968	49.98	57142	39.37



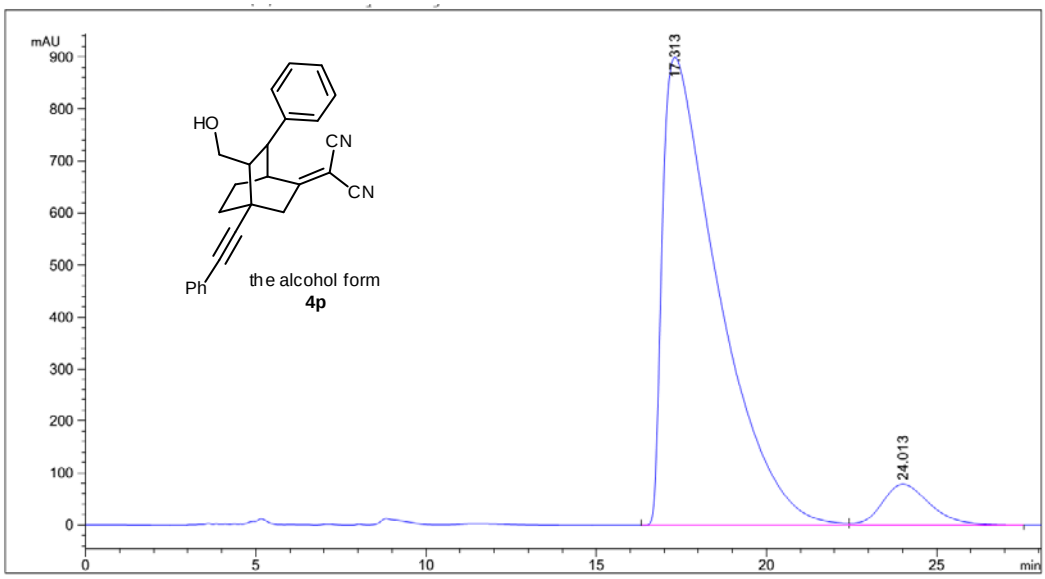
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	19.247	2359080	95.23	48876	96.49
2	28.497	118104	4.77	1780	3.51


10.213
7.442
7.423
7.369
7.355
7.338
7.303
7.284
7.259
7.082
7.063
5.297
4.015
3.999
3.288
3.255
3.240
3.138
3.086
2.189
2.163
2.132
1.978
1.948
1.922
1.876
1.843
1.812
1.782
1.761
1.754
1.568
1.282
0.885
0.873
0.856
0.836
0.073
0.001
OHC
CN
CN
Ph
4p
10
9
8
7
6
5
4
3
2
1
ppm
0.85
4.23
2.05
1.00
2.25
2.25
1.18
2.49
1.19

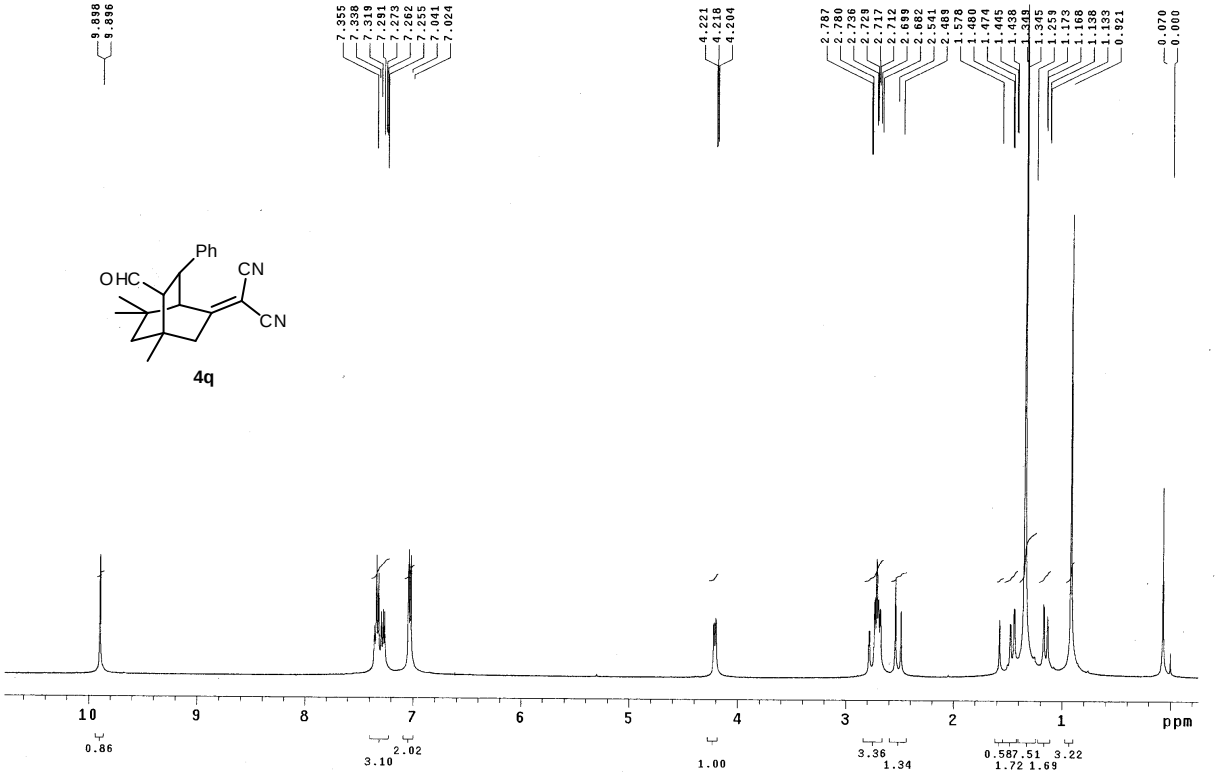

200.979
183.116
140.660
131.663
129.186
128.898
128.457
127.719
126.788
121.740
110.763
110.333
87.977
86.439
84.455
77.316
77.000
76.681
57.898
43.675
42.594
41.013
32.071
27.216
24.904
OHC
CN
CN
Ph
4p
200
180
160
140
120
100
80
60
40
20
ppm

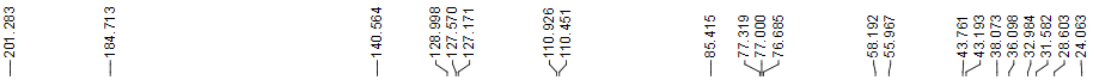


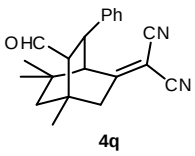
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.617	BV	1.5892	7.20520e4	665.51752	49.9377
2	23.591	VB	1.5056	7.22318e4	740.07532	50.0623

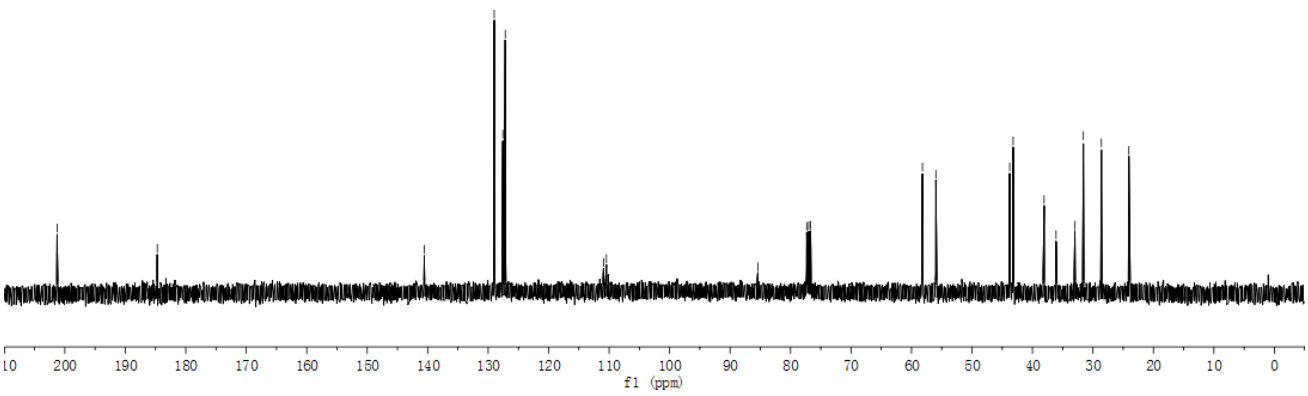


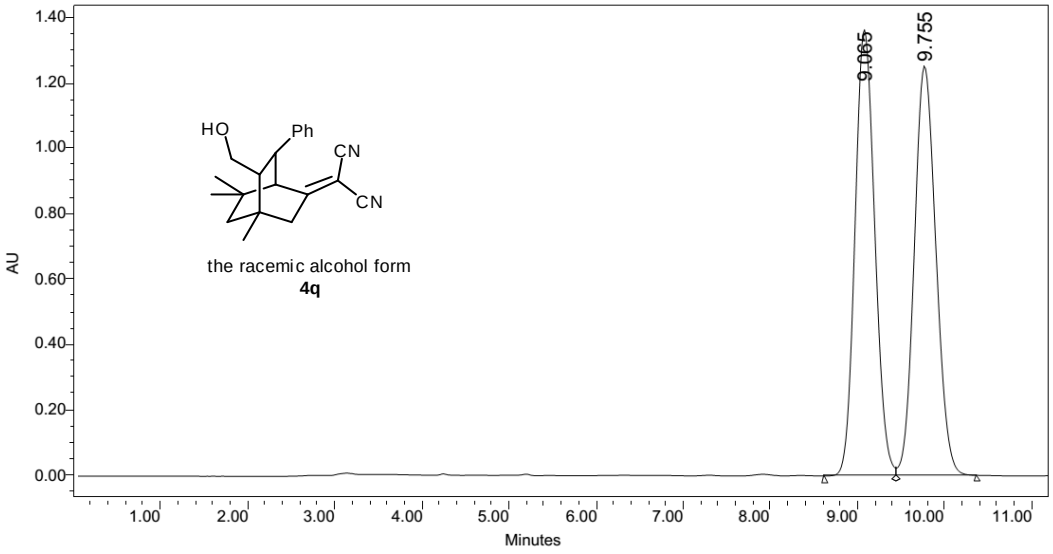
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.313	BV	1.6570	1.02612e5	899.53992	93.0029
2	24.013	VB	1.5007	7720.04492	78.63197	6.9971


9.898
9.896
7.355
7.338
7.319
7.291
7.273
7.262
7.255
7.041
7.024
4.221
4.218
4.204
2.787
2.780
2.736
2.729
2.717
2.712
2.689
2.682
2.541
2.489
1.578
1.480
1.474
1.445
1.438
1.349
1.345
1.259
1.173
1.168
1.138
1.133
0.921
0.070
0.000
Ph
OHC
CN
CN
4q
10
9
8
7
6
5
4
3
2
1
ppm
0.86
3.10
2.02
1.00
3.36
1.34
0.587.51
1.72
1.69
3.22

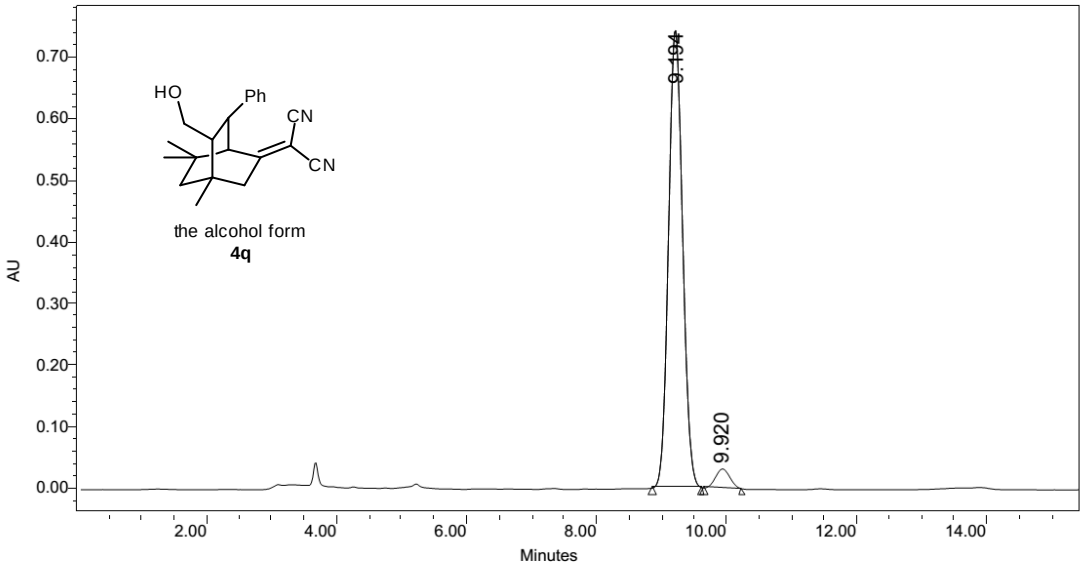

201.283
184.713
140.564
128.998
127.570
127.171
110.926
110.451
85.415
77.319
77.000
76.685
58.192
55.967
43.761
43.193
38.073
36.098
32.984
31.582
28.603
24.063


Ph
OHC
CN
CN
4q

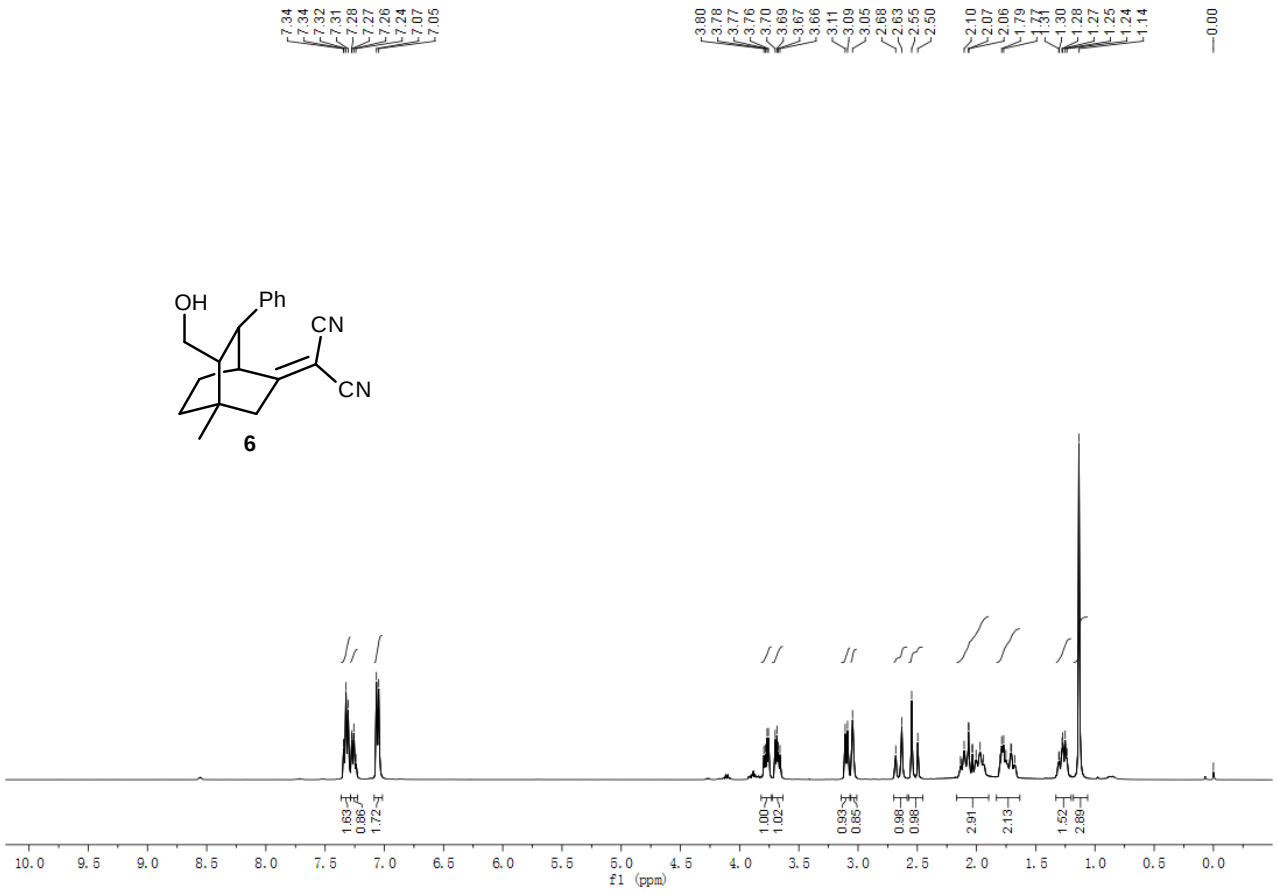

10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

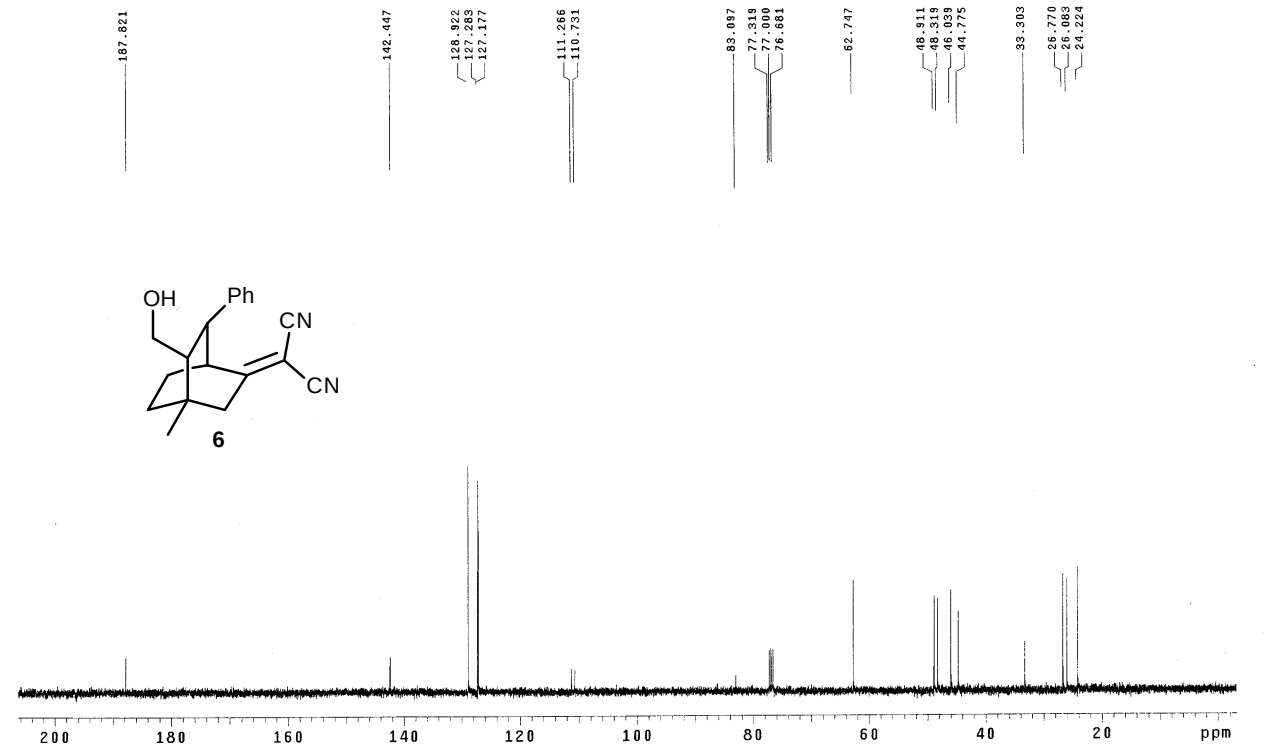


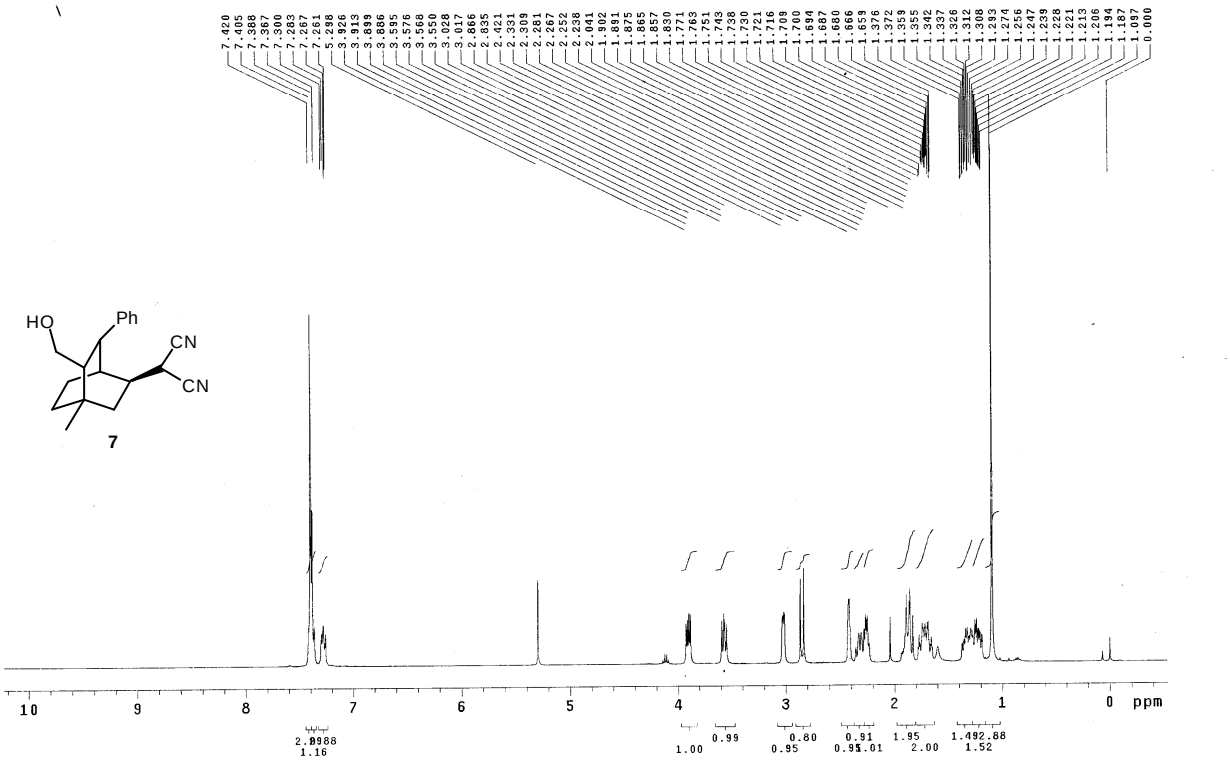
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	9.065	21477507	49.87	1363631	52.14
2	9.755	21592192	50.13	1251481	47.86

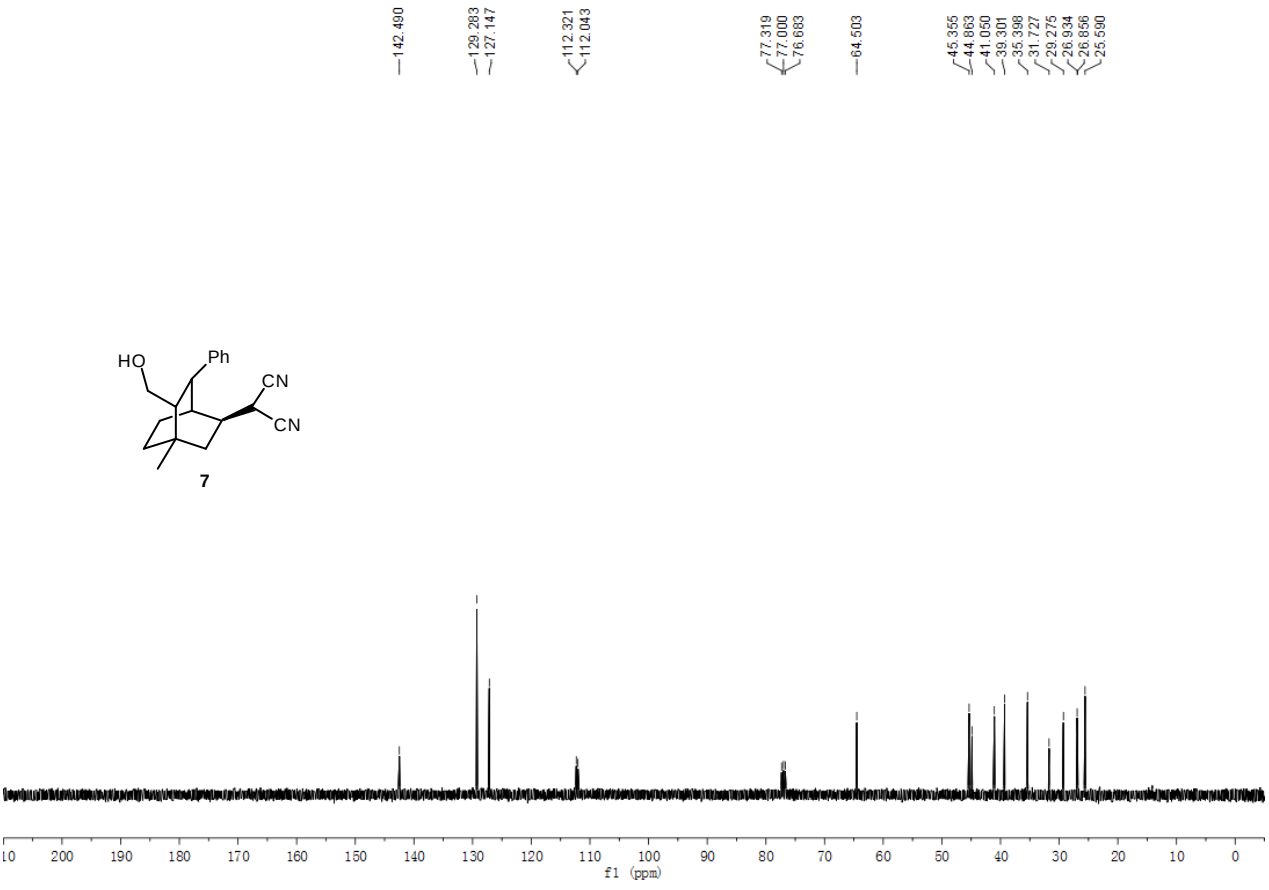


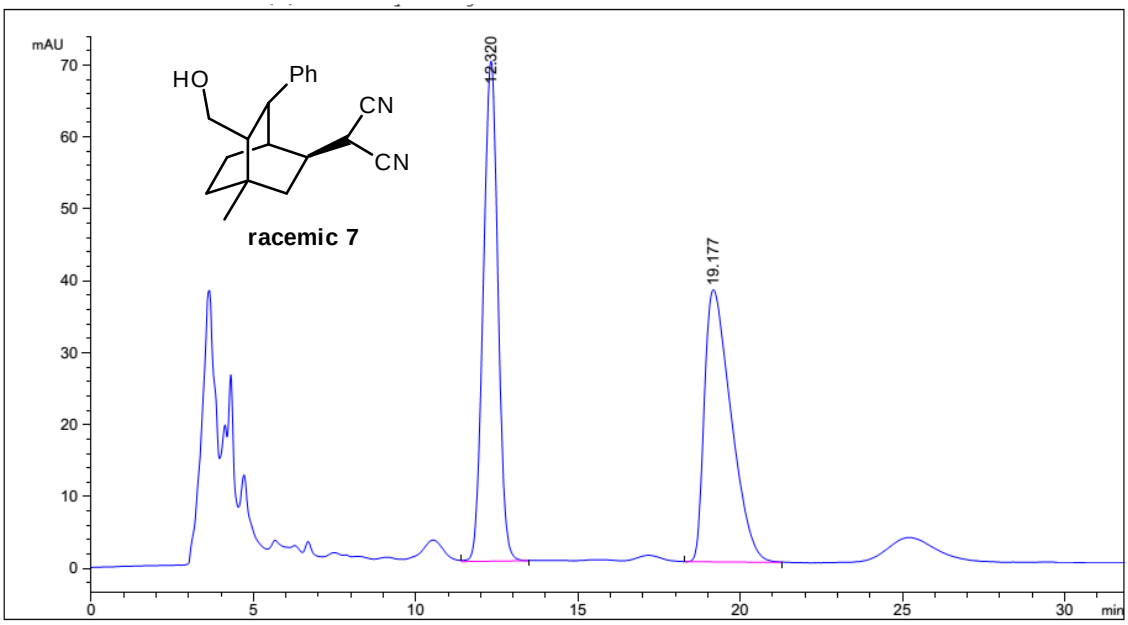
	RT (min)	Area (*sec)	% Area	Height ( )	% Height
1	9.194	11173064	95.83	743129	95.93
2	9.920	486181	4.17	31547	4.07


7.34
7.34
7.32
7.31
7.28
7.27
7.26
7.24
7.07
7.05
3.80
3.78
3.77
3.76
3.70
3.69
3.67
3.66
3.11
3.09
3.05
2.68
2.63
2.55
2.50
2.10
2.07
2.06
1.79
1.77
1.31
1.30
1.28
1.27
1.25
1.24
1.14
0.00
OH
Ph
CN
CN
6
1.63
0.86
1.72
1.00
1.02
0.93
0.85
0.98
0.98
2.91
2.13
1.52
2.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

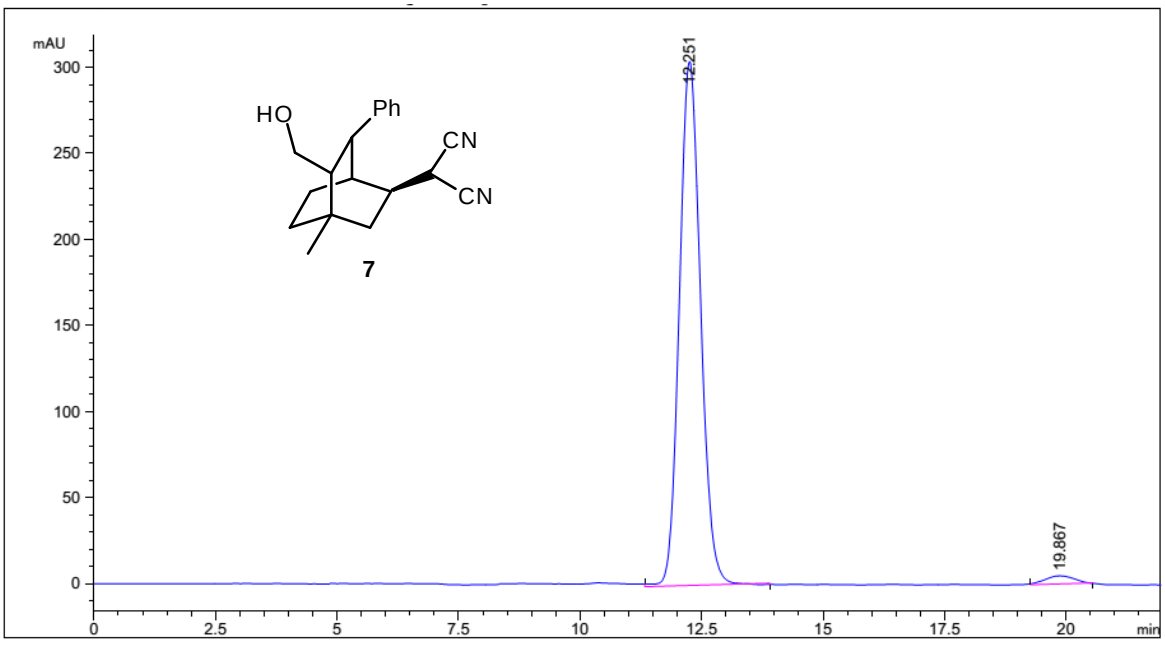

187.821
142.447
128.922
127.283
127.177
111.266
110.731
83.097
77.319
77.000
76.681
62.747
48.911
48.319
46.039
44.775
33.303
26.770
26.083
24.224
OH
Ph
CN
CN
6
200 180 160 140 120 100 80 60 40 20 ppm


HO
Ph
CN
CN
7
ppm

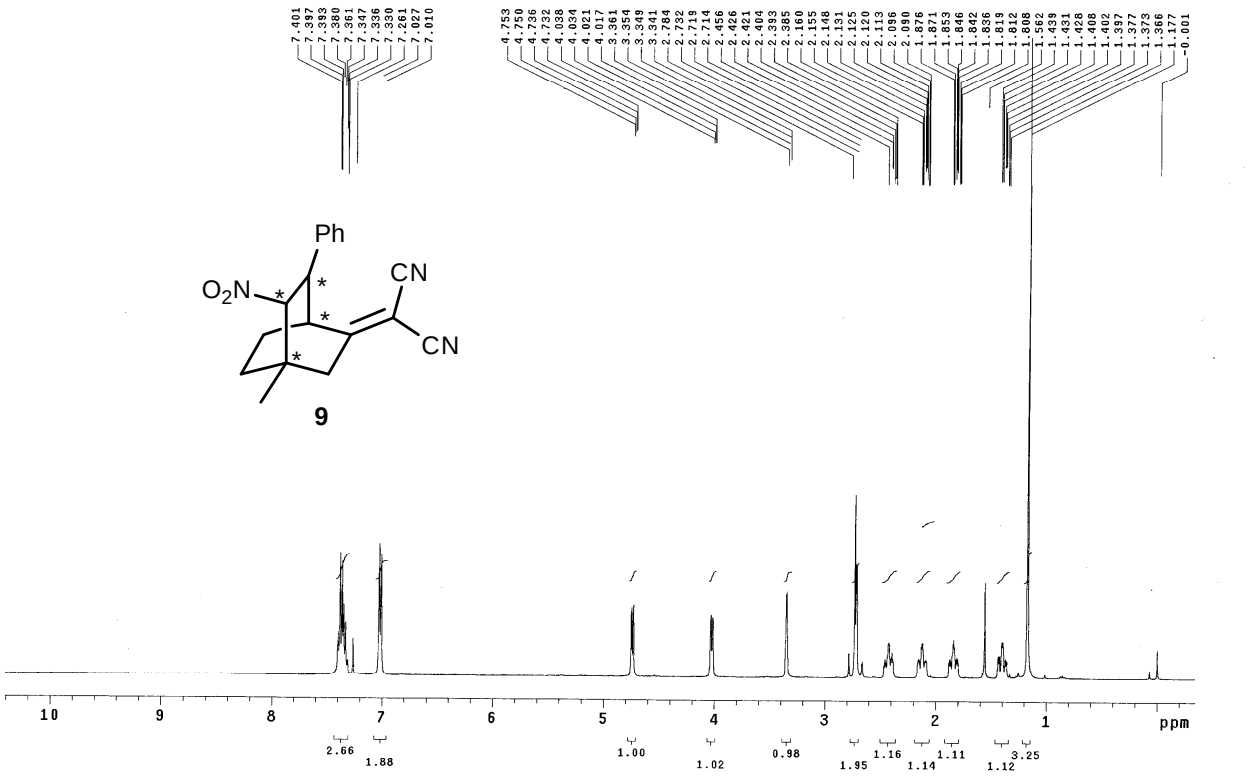

HO
Ph
CN
CN
7
f1 (ppm)

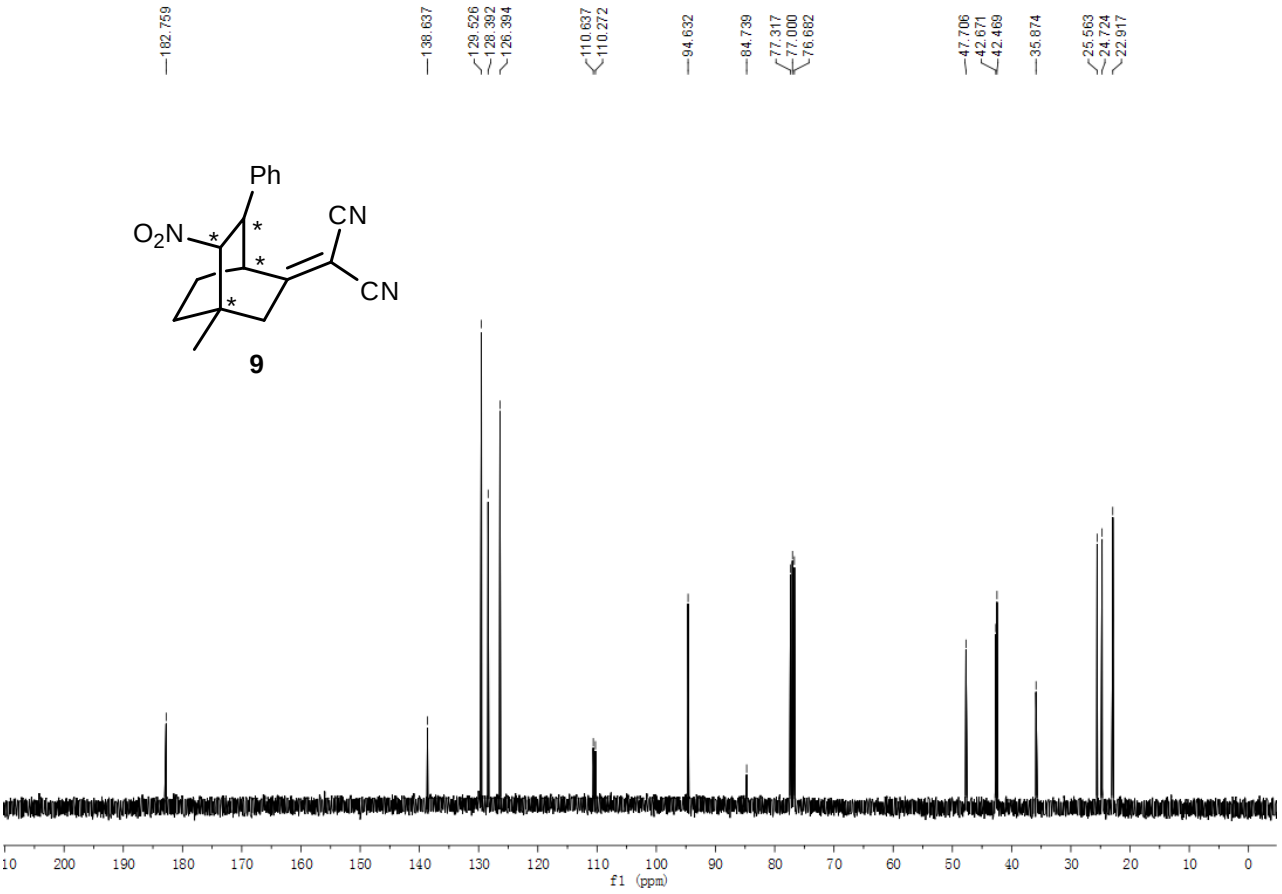


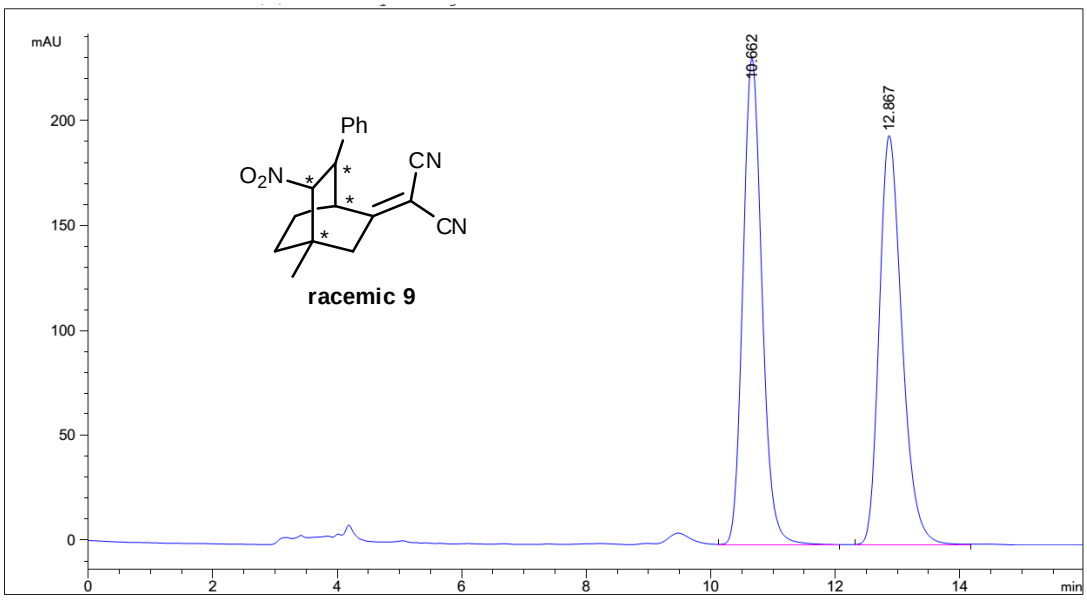
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.320	VB	0.4953	2187.13257	69.49327	50.2974
2	19.177	VB	0.8821	2161.26929	37.82491	49.7026



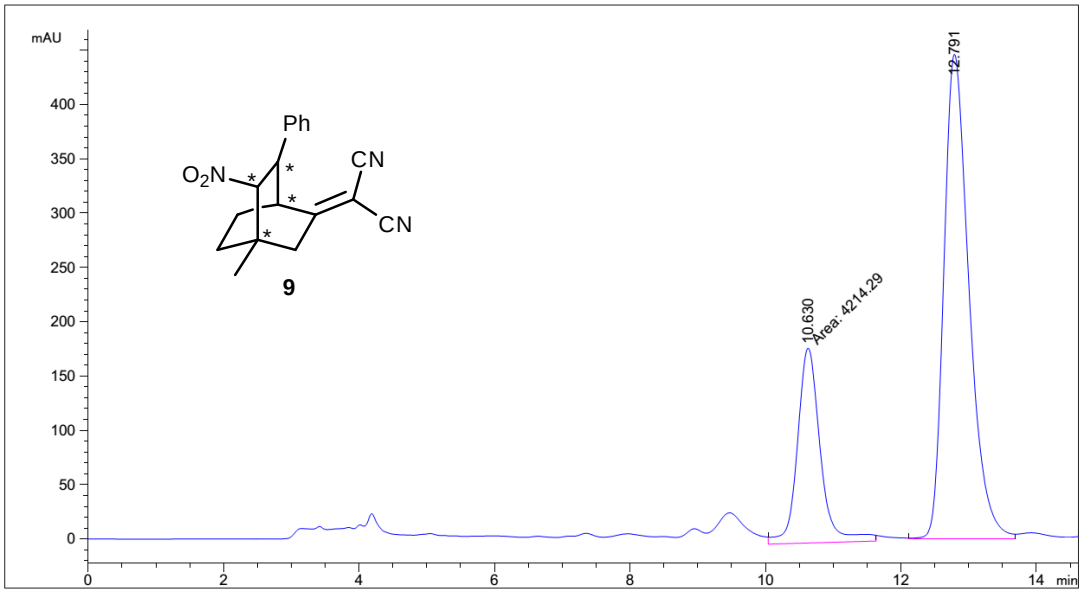
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.251	MM	0.5035	9200.94629	304.55545	97.9628
2	19.867	MM	0.6846	191.33849	4.65794	2.0372


7.401
7.397
7.393
7.380
7.361
7.347
7.336
7.280
7.261
7.027
7.010
4.753
4.750
4.736
4.732
4.038
4.034
4.021
4.017
3.354
3.349
3.341
2.784
2.732
2.719
2.714
2.456
2.426
2.421
2.404
2.393
2.385
2.160
2.155
2.148
2.131
2.125
2.120
2.113
2.096
2.090
1.876
1.871
1.853
1.846
1.842
1.836
1.819
1.812
1.808
1.562
1.439
1.431
1.428
1.408
1.402
1.397
1.377
1.373
1.366
1.177
-0.001
Ph
O2N
CN
CN
9
10
9
8
7
6
5
4
3
2
1
ppm
2.66
1.88
1.00
1.02
0.98
1.95
1.16
1.14
1.11
1.12
3.25

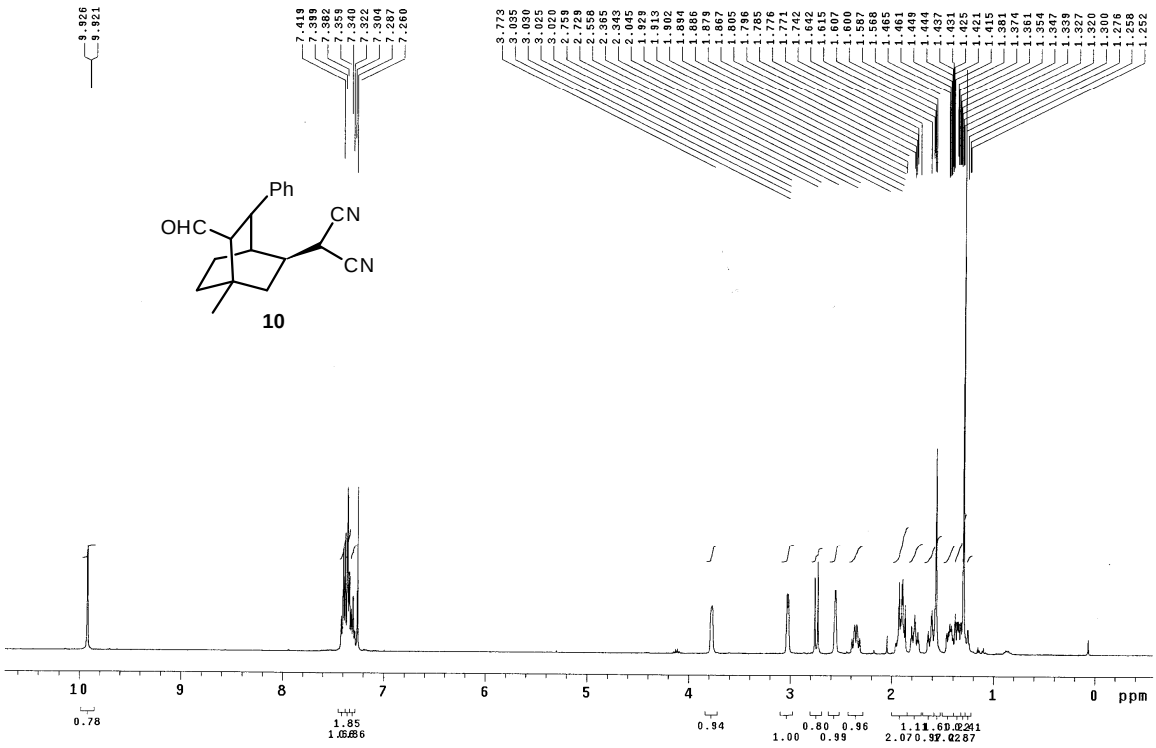

182.759
138.637
129.526
128.392
126.394
110.637
110.272
94.632
84.739
77.317
77.000
76.682
47.706
42.671
42.469
35.874
25.563
24.724
22.917
Ph
O2N
CN
CN
9
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

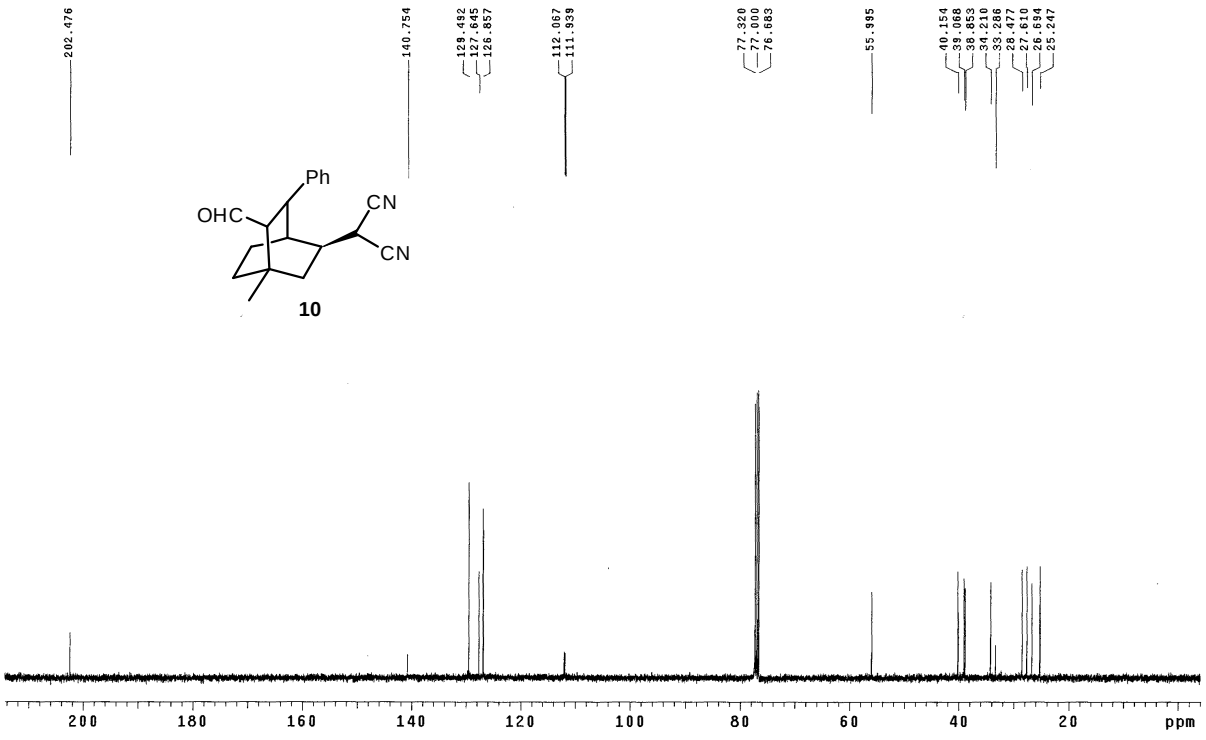


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.662	VB	0.3296	4924.30176	231.62505	49.9151
2	12.867	BB	0.3888	4941.05078	194.98373	50.0849



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.630	MM	0.3912	4214.29004	179.52557	26.7791
2	12.791	VV	0.3945	1.15229e4	446.12006	73.2209


Ph
OHC
CN
CN
10
ppm


Ph
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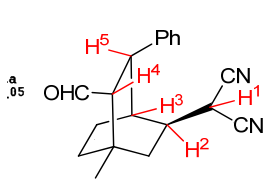
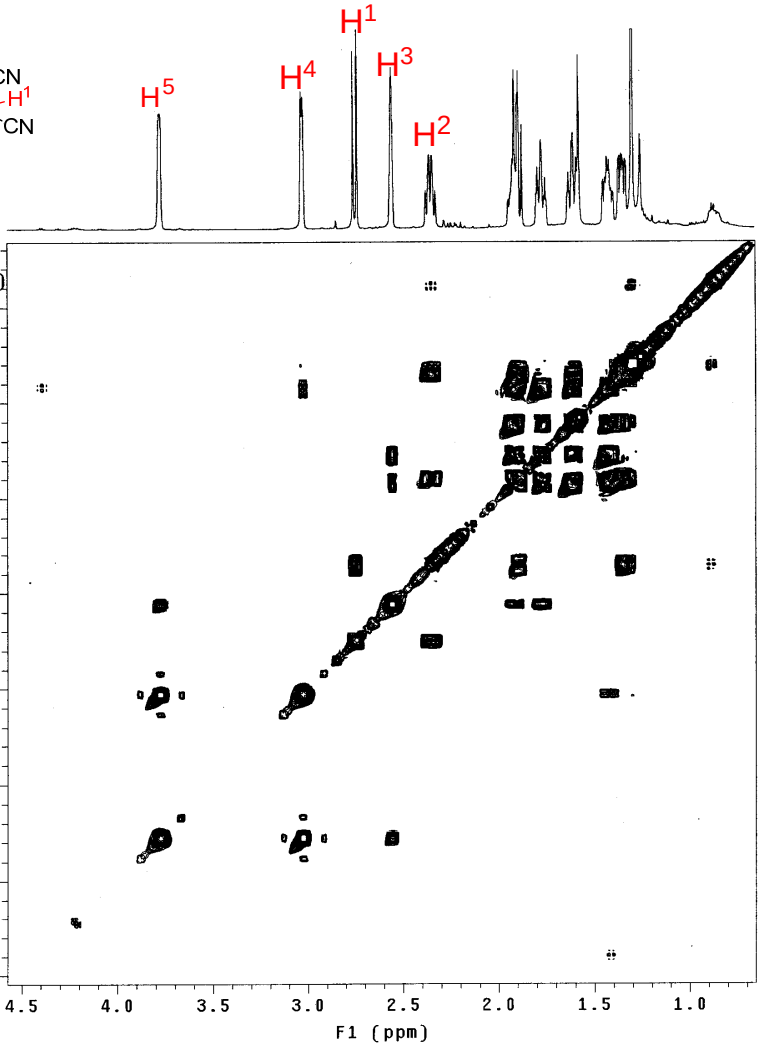
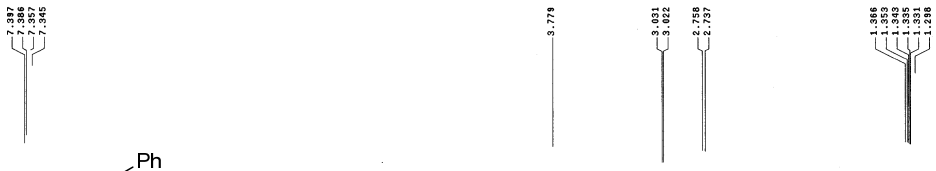
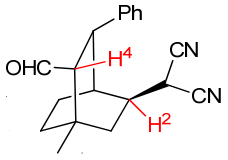
CN
CN
10
ppm



gCOSY of **10**







NOEDS of **10**