A highly enantioselective catalytic Strecker reaction of cyclic (*Z*)-aldimines

You-Dong Shao[a] and Shi-Kai Tian*[a,b]

[a] Joint Laboratory of Green Synthetic Chemistry, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China
[b] Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China

Supporting information

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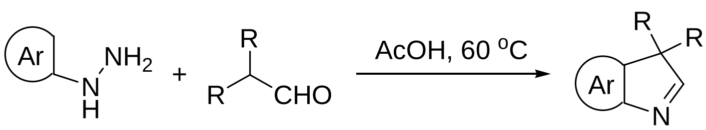
General information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT (400 MHz and 100 MHz, respectively) using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High resolution mass spectra were recorded on a LC-TOF spectrometer (Micromass). ESI-MS data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. High pressure liquid chromatography (HPLC) analyses were performed on a Hewlett-Packard 1200 Series instrument equipped with an isostatic pump, using a chiral stationary phase column (Daicel Co. CHIRALPAK), and the UV detection was monitored at 254 nm. The chiral HPLC methods were calibrated with the corresponding racemic mixtures. Optical rotations were measured on a Perkin-Elmer 343 Polarimeter with a sodium lamp at λ = 589 nm and reported as $[\alpha]_D^{T\,^\circ C}$ (c = g/100 mL, solvent). Melting points were uncorrected.

Toluene and ethyl ether were distilled over sodium/benzophenone. Dichloromethane, chloroform, and 1,2-dichloroethane were distilled over calcium hydride. Ethyl acetate and acetonitrile were dried over aluminum oxide prior to use. Methanol was distilled over sodium. Chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, Alfa Aesar, and AstaTech Pharmaceutical Co., and used as received. Cinchona alkaloid-derived thiourea catalysts were prepared according to known procedures.[1]

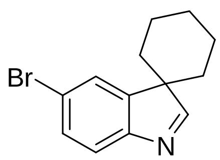
Preparation of cyclic (*Z*)-aldimines

3*H*-Indoles **1a-b**, **1e**, and **1h**[2] and 2*H*-benzo[*b*][1,4]thiazines **1m-n**[3] are known compounds, and they were prepared according to literature procedures. New 3*H*-indoles were prepared as shown below.[2]



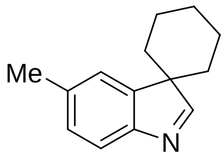
1a-l

To a solution of the aldehyde (2.0 mmol) in acetic acid (20 mL) was added the arylhydrazine (2.0 mmol). The mixture was heated at 60 °C for 0.5-2 h, cooled to room temperature, and concentrated under reduced pressure. The residue was dissolved in ethyl acetate (30 mL), and washed with ice-cold saturated aqueous sodium bicarbonate. The organic layer was dried over anhydrous sodium sulfate, and concentrated. The residue was subjected to column chromatography on silica gel, using ethyl acetate/petroleum ether (1:20 to 1:5) as eluent, to give a 3*H*-indole.



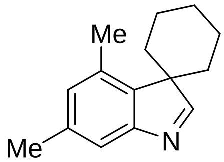
1c

1c was obtained in 54% yield. Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.52-7.48 (m, 1H), 7.32-7.28 (m, 1H), 7.15-7.10 (m, 1H), 1.94-1.55 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 152.6, 146.5, 131.2, 127.5, 121.2, 115.1, 59.8, 31.7, 25.5, 23.9; HRMS (EI) calcd for $C_{13}H_{14}BrN$ (M) 263.0310, found 263.0311.



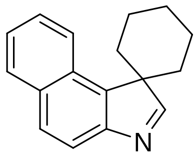
1d

1d was obtained in 55% yield. Yollowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.53-7.49 (m, 1H), 7.18 (s, 1H), 7.15-7.12 (m, 1H), 2.41 (s, 3H), 1.94-1.54 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 152.6, 145.0, 135.8, 128.4, 123.1, 120.8, 57.7, 32.0, 25.7, 24.1, 21.7; HRMS (EI) calcd for $C_{14}H_{17}N$ (M) 199.1361, found 199.1358.



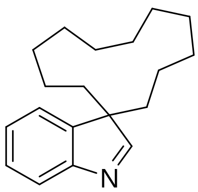
1f

1f was obtained in 63% yield. Yollowish solid, m.p. 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.30 (s, 1H), 6.83 (s, 1H), 2.44 (s, 3H), 2.36 (s, 3H), 2.28-2.18 (m, 2H), 2.00-1.88 (m, 3H), 1.77-1.70 (m, 2H), 1.50-1.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 154.8, 138.7, 137.7, 132.7, 129.5, 119.7, 58.7, 29.8, 25.9, 25.0, 21.3, 18.1; HRMS (EI) calcd for $C_{15}H_{19}N$ (M) 213.1517, found 213.1520.



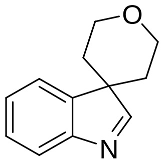
1g

1g was obtained in 70% yield. Brown solid, m.p. 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.13-8.09 (m, 1H), 7.98-7.95 (m, 1H), 7.90-7.85 (m, 2H), 7.58-7.54 (m, 1H), 7.49-7.45 (m, 1H), 2.46-2.37 (m, 2H), 2.11-2.00 (m, 3H), 1.92-1.78 (m, 2H), 1.65-1.56 (m, 1H), 1.53-1.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 151.1, 138.1, 133.0, 129.7, 129.1, 128.6, 126.2, 124.8, 123.0, 120.6, 60.0, 31.7, 25.9, 25.1; HRMS (EI) calcd for $C_{17}H_{17}N$ (M) 235.1361, found 235.1342.



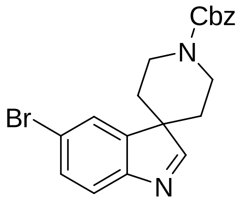
1i

1i was obtained in 47% yield. Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.65-7.61 (m, 1H), 7.37-7.30 (m, 2H), 7.22-7.17 (m, 1H), 1.76-1.41 (m, 22H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 154.6, 144.3, 127.6, 125.5, 123.0, 121.2, 60.1, 28.0, 26.7, 26.1, 22.7, 22.1, 21.0; HRMS (EI) calcd for $C_{19}H_{27}N$ (M) 269.2143, found 269.2149.



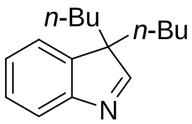
1j

1j was obtained in 51% yield. Yollowish solid, m.p. 112-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.70-7.67 (m, 1H), 7.52-7.44 (m, 1H), 7.41-7.36 (m, 1H), 7.32-7.28 (m, 1H), 4.17-4.10 (m, 2H), 3.96-3.88 (m, 2H), 2.02-1.94 (m, 2H), 1.68-1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 154.3, 143.1, 128.3, 126.5, 122.2, 121.5, 65.5, 55.0, 31.1; HRMS (EI) calcd for $C_{12}H_{13}NO$ (M) 187.0997, found 187.0983.



1k

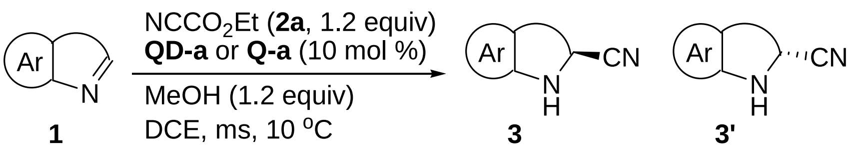
1k was obtained in 67% yield. Brown solid, m.p. 56-57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.57-7.50 (m, 3H), 7.42-7.31 (m, 5H), 5.20 (s, 2H), 4.13-4.07 (m, 2H), 3.60-3.51 (m, 2H), 1.86-1.79 (m, 2H), 1.71-1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 155.5, 153.1, 144.8, 136.6, 131.7, 128.7, 128.4, 128.2, 125.9, 123.0, 120.7, 67.6, 56.4, 42.0, 30.6; HRMS (EI) calcd for $C_{20}H_{19}N_2O_2Br$ (M) 398.0630, found 398.0638.

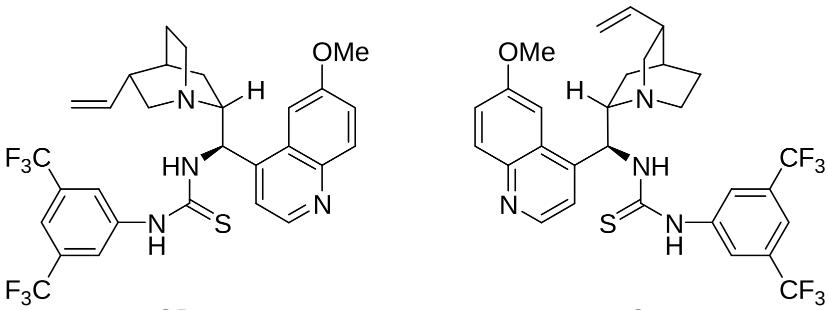


1l

1l was obtained in 32% yield. Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.63-7.60 (m, 1H), 7.35-7.28 (m, 1H), 7.26-7.23 (m, 2H), 1.91-1.74 (m, 4H), 1.25-1.11 (m, 4H), 1.05-0.94 (m, 2H), 0.88-0.78 (m, 2H), 0.77 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 155.8, 142.6, 127.6, 126.0, 121.9, 121.1, 62.2, 35.2, 26.6, 23.2, 13.9; HRMS (EI) calcd for $C_{16}H_{23}N$ (M) 229.1830, found 229.1801.

General procedure for the catalytic asymmetric Strecker reaction of cyclic (*Z*)-aldimines

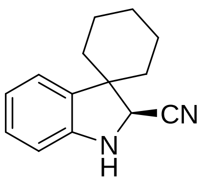




To a flame dried reaction vial equipped with a magnetic stirring bar were added powdered 3 Å molecular sieves (20.0 mg). The molecular sieves were thermally activated under vacuum for 30 min, and cooled to 10 °C under nitrogen. To the reaction vial were added cyclic (*Z*)-aldimine **1** (0.10 mmol), catalyst **QD-a** or **Q-a** (5.9 mg, 0.010 mmol), 1,2-dichloroethane (1.0 mL), ethyl cyanoformate (**2a**, 12.0 mg, 0.12 mmol), and methanol (3.8 mg, 0.12 mmol). The resulting mixture was stirred at 10 °C for a period as specified in Table 2, and directly charged onto silica gel. Product **3** or **3'** was isolated using petroleum ether/ethyl acetate (20/1~3/1) as eluent.

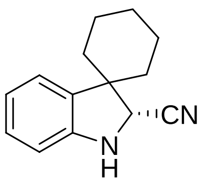
The absolute configuration of 2-cyanoindoline **3b** and 3-cyano-3,4-dihydro-2*H*-benzo[*b*][1,4]thiazine **3m** was determined to be *S* and *R*, respectively, by single-crystal X-ray analysis, and that of the rest products was determined by analogy.

Analytical data for the products



3a

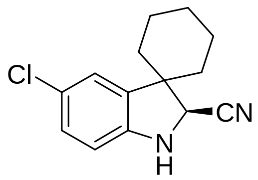
3a was obtained as a white solid in 99% yield and 96% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Hypersil + Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (major) = 25.1 min, t_r (minor) = 32.8 min]. m.p. 82-84 °C; $[\alpha]_D^{25}$ = +169.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.07 (m, 2H), 6.87-6.82 (m, 1H), 6.72-6.68 (m, 1H), 4.47 (s, 1H), 4.13 (br., s, 1H), 2.20-2.14 (m, 1H), 2.02-1.72 (m, 5H), 1.51-1.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 135.1, 128.4, 123.0, 120.6, 119.6, 110.6, 57.2, 49.9, 35.6, 33.0, 25.5, 23.3, 23.2; HRMS (EI) calcd for $C_{14}H_{16}N_2$ (M) 212.1313, found 212.1316.



3a'

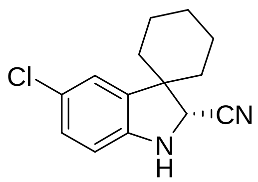
3a' was obtained as a white solid in 99% yield and 97% ee from a reaction catalyzed by **Q-a**.

The ee value was determined by chiral stationary phase HPLC analysis [Hypersil + Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (minor) = 23.8 min, t_r (major) = 30.1 min]. $[\alpha]_D^{25}$ = -171.4 (c = 1.0, $CHCl_3$).



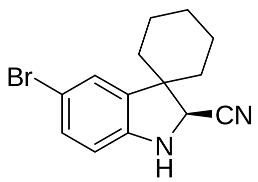
3b

3b was obtained as a white solid in 73% yield and 97% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Hypersil + Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (major) = 13.6 min, t_r (minor) = 18.3 min]. m.p. 101-102 °C; $[\alpha]_D^{25}$ = +152.5 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07-7.02 (m, 2H), 6.63-6.60 (m, 1H), 4.49 (s, 1H), 2.19-2.14 (m, 1H), 1.97-1.73 (m, 5H), 1.49-1.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 137.0, 128.2, 125.3, 123.4, 119.1, 111.4, 57.5, 50.0, 35.4, 32.8, 25.3, 23.1, 23.0; HRMS (EI) calcd for $C_{14}H_{15}N_2Cl$ (M) 246.0924, found 246.0941.



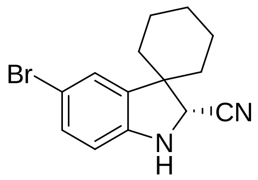
3b'

3b' was obtained as a white solid in 80% yield and 97% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Hypersil + Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (minor) = 13.6 min, t_r (major) = 17.4 min]. $[\alpha]_D^{25}$ = -153.2 (c = 1.0, $CHCl_3$).



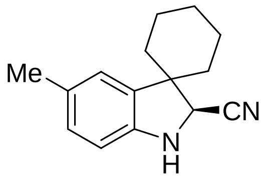
3c

3c was obtained as a white solid in 83% yield and 98% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (major) = 13.8 min, t_r (minor) = 18.9 min]. m.p. 97-98 °C; $[\alpha]_D^{25}$ = +149.5 (c = 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.17 (m, 2H), 6.58-6.54 (m, 1H), 4.48 (s, 1H), 2.18-2.13 (m, 1H), 1.96-1.70 (m, 5H), 1.49-1.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 137.5, 131.1, 126.2, 119.1, 112.4, 112.0, 57.4, 50.0, 35.5, 32.8, 25.3, 23.1, 23.0; HRMS (EI) calcd for $C_{14}H_{15}N_2Br$ (M) 290.0419, found 290.0426.



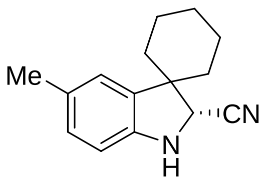
3c'

3c’ was obtained as a white solid in 90% yield and 96% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (minor) = 12.0 min, t_r (major) = 15.8 min]. $[\alpha]_D^{25}$ = -142.8 (c = 1.1, $CHCl_3$).



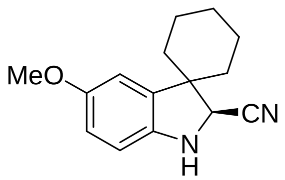
3d

3d was obtained as a white solid in 99% yield and 97% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (major) = 12.5 min, t_r (minor) = 14.2 min]. m.p. 92-94 ^oC; $[\alpha]_D^{25}$ = +168.6 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.91-6.88 (m, 2H), 6.61-6.58 (m, 1H), 4.45 (s, 1H), 2.28 (s, 3H), 2.18-2.13 (m, 1H), 2.00-1.71 (m, 5H), 1.50-1.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 135.4, 130.0, 128.8, 123.6, 119.7, 110.5, 57.4, 49.9, 35.5, 33.0, 25.5, 23.3, 23.2, 21.1; HRMS (EI) calcd for $C_{15}H_{18}N_2$ (M) 226.1470, found 226.1477.



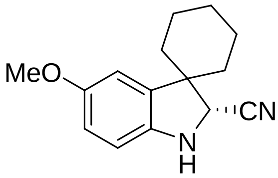
3d'

3d’ was obtained as a white solid in 99% yield and 98% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (minor) = 12.4 min, t_r (major) = 14.1 min]. $[\alpha]_D^{25}$ = -170.6 (c = 1.0, $CHCl_3$).



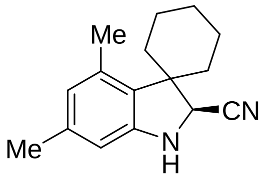
3e

3e was obtained as a white solid in 99% yield and 97% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak AD, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (minor) = 14.6 min, t_r (major) = 18.5 min]. m.p. 92-93 °C; $[\alpha]_D^{25}$ = +196.1 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.71-6.60 (m, 3H), 4.46 (s, 1H), 3.97 (br., s, 1H), 3.76 (s, 3H), 2.19-2.13 (m, 1H), 1.97-1.70 (m, 5H), 1.49-1.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 140.8, 136.9, 119.7, 113.0, 111.2, 110.0, 57.7, 56.0, 50.1, 35.3, 32.9, 25.4, 23.3, 23.1; HRMS (EI) calcd for $C_{15}H_{18}N_2O$ (M) 242.1419, found 242.1422.



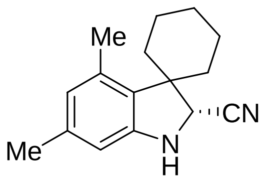
3e'

3e' was obtained as a white solid in 99% yield and 97% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak AD, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (major) = 14.9 min, t_r (minor) = 18.1 min]. $[\alpha]_D^{25}$ = -194.3 (c = 1.0, $CHCl_3$).



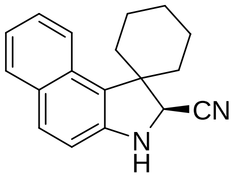
3f

3f was obtained as a white solid in 99% yield and 98% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (major) = 15.3 min, t_r (minor) = 18.0 min]. m.p. 77-79 °C; $[\alpha]_D^{25}$ = +173.1 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.41 (s, 1H), 6.37 (s, 1H), 4.53 (s, 1H), 2.40-2.25 (m, 5H), 2.22 (s, 3H), 1.87-1.72 (m, 4H), 1.63-1.54 (m, 1H), 1.46-1.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 138.2, 134.0, 128.5, 124.8, 120.2, 109.5, 56.4, 51.5, 32.9, 31.8, 25.5, 23.6, 23.3, 21.2, 19.5; HRMS (EI) calcd for $C_{16}H_{20}N_2$ (M) 240.1626, found 240.1655.



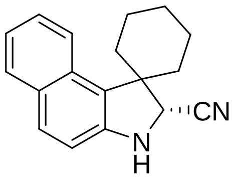
3f'

3f' was obtained as a white solid in 99% yield and 97% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (minor) = 15.2 min, t_r (major) = 17.9 min]. $[\alpha]_D^{25}$ = -167.3 (c = 1.0, $CHCl_3$).



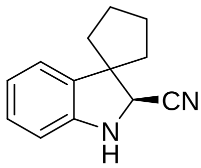
3g

3g was obtained as a white solid in 99% yield and 95% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Hypersil + Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (major) = 19.7 min, t_r (minor) = 28.4 min]. m.p. 160-161 °C; $[\alpha]_D^{25}$ = +283.0 (c = 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4, Hz, 1H), 7.80-7.76 (m, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.45-7.40 (m, 1H), 7.28-7.23 (m, 1H), 7.00 (d, J = 8.8 Hz, 1H), 4.72 (s, 1H), 4.27 (br., s, 1H), 2.86-2.76 (m, 1H), 2.49-2.43 (m, 1H), 2.04-1.80 (m, 5H), 1.53-1.43 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 130.6, 130.5, 130.3, 129.9, 126.6, 124.0, 122.5, 121.5, 120.1, 113.1, 57.0, 52.9, 33.5, 32.6, 25.6, 23.8, 23.4; HRMS (EI) calcd for $C_{18}H_{18}N_2$ (M) 262.1470, found 262.1485.



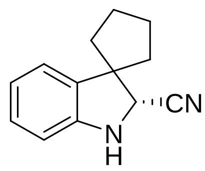
3g'

3g’ was obtained as a white solid in 99% yield and 97% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Hypersil + Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (minor) = 19.9 min, t_r (major) = 28.6 min]. $[\alpha]_D^{25}$ = -304.4 (c = 0.4, $CHCl_3$).



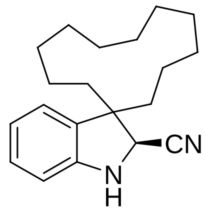
3h

3h was obtained as a yellowish oil in 93% yield and 92% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (major) = 9.9 min, t_r (minor) = 17.8 min]. $[\alpha]_D^{25}$ = +159.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.05 (m, 2H), 6.87-6.83 (m, 1H), 6.70 (d, J = 8.0 Hz, 1H), 4.29 (s, 1H), 2.32-2.25 (m, 1H), 2.06-1.74 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 134.9, 128.2, 122.5, 120.9, 119.3, 110.5, 60.2, 56.7, 39.7, 36.1, 25.0, 24.9; HRMS (EI) calcd for $C_{13}H_{14}N_2$ (M) 198.1157, found 198.1176.



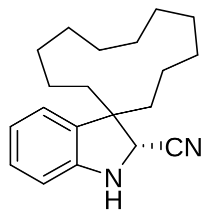
3h'

3h' was obtained as a yellowish oil in 83% yield and 98% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (minor) = 9.3 min, t_r (major) = 15.9 min]. $[\alpha]_D^{25}$ = -171.6 (c = 1.0, $CHCl_3$).



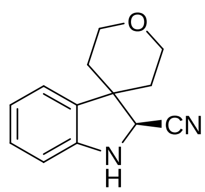
3i

3i was obtained as a white solid in 99% yield and 93% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (major) = 10.0 min, t_r (minor) = 13.0 min]. m.p. 119-120 ^oC; $[\alpha]_D^{25}$ = +100.2 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.11-7.06 (m, 1H), 7.05-7.02 (m, 1H), 6.83-6.79 (m, 1H), 6.69 (d, J = 7.6 Hz, 1H), 4.22 (s, 1H), 2.00-1.87 (m, 3H), 1.61-1.31 (m, 19H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 133.9, 128.2, 124.2, 120.1, 119.3, 110.6, 59.8, 51.7, 31.3, 28.6, 26.5, 26.4, 26.2, 22.7, 22.6, 22.2, 22.1, 19.4, 19.3; HRMS (EI) calcd for $C_{20}H_{28}N_2$ (M) 296.2252, found 296.2259.



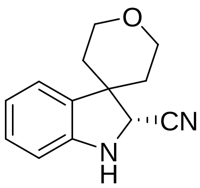
3i'

3i' was obtained as a white solid in 99% yield and 94% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (minor) = 10.0 min, t_r (major) = 13.0 min]. $[\alpha]_D^{25}$ = -104.9 (c = 1.0, $CHCl_3$).



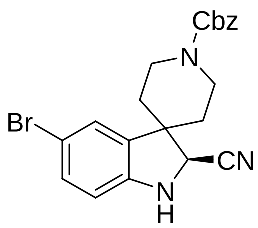
3j

3j was obtained as a white solid in 99% yield and 91% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Hypersil + Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (major) = 21.8 min, t_r (minor) = 27.6 min]. m.p. 217-218 °C; $[\alpha]_D^{25}$ = +146.5 (c = 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.17 (d, J = 7.6 Hz, 1H), 7.08-7.02 (m, 1H), 6.75-6.69 (m, 1H), 6.67-6.63 (m, 2H), 4.91 (s, 1H), 3.97-3.91 (m, 1H), 3.76-3.64 (m, 2H), 3.53-3.45 (m, 1H), 2.28-2.20 (m, 1H), 1.90-1.82 (m, 1H), 1.67-1.60 (m, 1H), 1.55-1.47 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.4, 133.8, 128.2, 122.7, 119.8, 118.9, 109.7, 63.8, 63.6, 56.1, 46.7, 34.9, 32.2; HRMS (EI) calcd for $C_{13}H_{12}N_2O$ (M) 214.1106, found 214.1112.



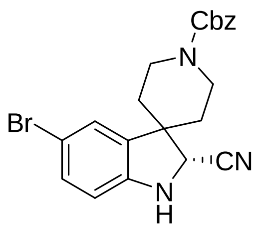
3j'

3j' was obtained as a white solid in 99% yield and 98% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Hypersil + Chiralpak IC, isopropanol/hexane (10:90), 1.0 mL/min, λ = 254 nm, t_r (minor) = 22.7 min, t_r (major) = 28.5 min]. $[\alpha]_D^{25}$ = -166.7 (c = 0.2, $CHCl_3$).



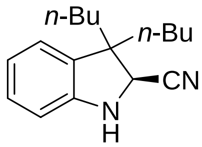
3k

3k was obtained as a white solid in 85% yield and 97% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (20:80), 1.0 mL/min, λ = 254 nm, t_r (major) = 17.9 min, t_r (minor) = 22.6 min]. m.p. 67-69 °C; $[\alpha]_D^{25}$ = +145.5 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.30 (m, 5H), 7.22 (dd, J = 8.4, 2.0 Hz, 1H), 7.17 (d, J = 2.0 Hz, 1H), 6.59 (d, J = 8.4 Hz, 1H), 5.17 (s, 2H), 4.49 (s, 1H), 4.20-4.15 (m, 1H), 4.08-4.04 (m, 1H), 3.17-3.07 (m, 2H), 2.20-2.06 (m, 2H), 1.84-1.80 (m, 1H), 1.65-1.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 146.3, 136.6, 135.3, 131.8, 128.7, 128.3, 128.1, 126.3, 118.3, 112.6, 112.2, 67.5, 56.8, 48.3, 41.1, 40.9, 34.5, 32.0; HRMS (EI) calcd for $C_{21}H_{20}N_3O_2Br$ (M) 425.0739, found 425.0772.



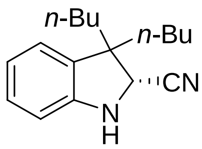
3k'

3k' was obtained as a white solid in 79% yield and 97% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (20:80), 1.0 mL/min, λ = 254 nm, t_r (minor) = 18.0 min, t_r (major) = 22.4 min]. $[\alpha]_D^{25}$ = -146.8 (c = 1.0, $CHCl_3$).



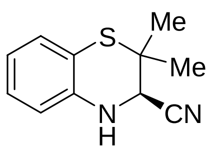
3l

3l was obtained as a yellowish oil in 98% yield and 96% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak AD, isopropanol/hexane (2:98), 1.0 mL/min, λ = 254 nm, t_r (major) = 12.2 min, t_r (minor) = 17.2 min]. $[\alpha]_D^{25}$ = +169.7 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.06 (m, 1H), 7.00 (d, J = 7.2 Hz, 1H), 6.86-6.80 (m, 1H), 6.68 (d, J = 7.6 Hz, 1H), 4.37 (d, J = 2.8 Hz, 1H), 4.11 (br., s, 1H), 2.01-1.92 (m, 1H), 1.84-1.61 (m, 3H), 1.45-1.11 (m, 8H), 1.00-0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 133.1, 128.3, 123.9, 120.2, 119.0, 110.4, 58.8, 52.4, 36.8, 35.5, 26.3, 26.2, 23.3, 23.2, 14.1; HRMS (EI) calcd for $C_{17}H_{24}N_2$ (M) 256.1939, found 256.1959.



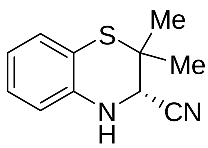
3l'

3l' was obtained as a yellowish oil in 95% yield and 98% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak AD, isopropanol/hexane (2:98), 1.0 mL/min, λ = 254 nm, t_r (minor) = 12.1 min, t_r (major) = 17.1 min]. $[\alpha]_D^{25}$ = -177.9 (c = 1.0, $CHCl_3$).



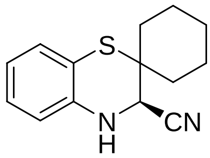
3m

3m was obtained as a white solid in 90% yield and 94% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Hypersil + Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (major) = 20.0 min, t_r (minor) = 23.0 min]. m.p. 120-121 °C; $[\alpha]_D^{25}$ = +179.5 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02-6.94 (m, 2H), 6.80-6.74 (m, 1H), 6.60 (dd, J = 8.0, 1.2 Hz, 1H), 4.20 (s, 1H), 1.57 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 127.9, 126.1, 120.4, 117.7, 116.0, 115.9, 54.3, 40.8, 27.8, 26.3; HRMS (EI) calcd for $C_{11}H_{12}N_2S$ (M) 204.0721, found 204.0726.



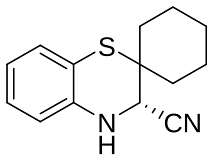
3m'

3m’ was obtained as a white solid in 98% yield and 97% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Hypersil + Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (minor) = 20.3 min, t_r (major) = 23.5 min]. $[\alpha]_D^{25}$ = -186.6 (c = 1.0, $CHCl_3$).



3n

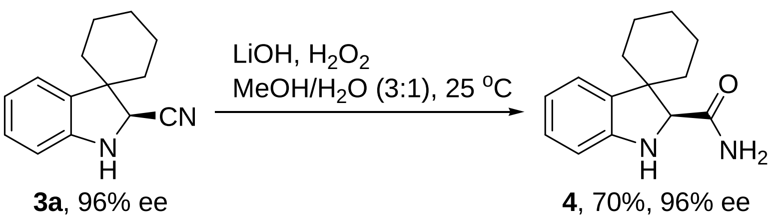
3n was obtained as a white solid in 99% yield and 94% ee from a reaction catalyzed by **QD-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (major) = 18.2 min, t_r (minor) = 20.1 min]. m.p. 121-122 ^oC; $[\alpha]_D^{25}$ = +224.3 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (dd, J = 8.0, 1.2 Hz,, 1H), 7.00-6.93 (m, 1H), 6.78-6.73 (m, 1H), 6.58-6.55 (m, 1H), 4.40 (br., s, 1H), 4.26 (s, 1H), 2.09-2.01 (m, 1H), 1.92-1.46 (m, 8H), 1.37-1.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 127.9, 125.8, 120.2, 117.7, 115.8, 115.5, 53.7, 45.5, 35.1, 34.8, 25.6, 21.6, 21.5; HRMS (EI) calcd for $C_{14}H_{16}N_2S$ (M) 244.1034, found 244.1035.



3n'

3n’ was obtained as a white solid in 99% yield and 97% ee from a reaction catalyzed by **Q-a**. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak IC, isopropanol/hexane (5:95), 1.0 mL/min, λ = 254 nm, t_r (minor) = 18.1 min, t_r (major) = 19.9 min]. $[\alpha]_D^{25}$ = -233.6 (c = 1.0, $CHCl_3$).

Transformation of compound 3a[4]



To a solution of compound **3a** (96% ee, 21.2 mg, 0.10 mmol) in methanol (1.0 mL) at room temperature were added $LiOH{\cdot}H_2O$ (8.4 mg, 0.20 mmol), aqueous H_2O_2 (30 wt%, 48 µL, 0.50

mmol), and water (0.30 mL). The mixture was stirred for 1 h, added water (5 mL), and extracted with ethyl acetate (4 × 10 mL). The organic phases were combined, washed with brine, dried over anhydrous sodium sulfate, and concentrated. The residue was subjected to column chromatography on silica gel, using petroleum ether/ethyl acetate (5/1~1/1) as eluent, to give compound **4** (16.2 mg, 70%) as a white solid. The ee value was determined by chiral stationary phase HPLC analysis [Chiralpak AD, isopropanol/hexane (15:85), 1.0 mL/min, λ = 254 nm, t_r (minor) = 7.4 min, t_r (major) = 15.8 min]. m.p. 165-166 °C; $[\alpha]_D^{25}$ = -112.0 (c = 0.15, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.6 Hz, 1H), 7.13-7.08 (m, 1H), 6.86-6.81 (m, 1H), 6.79 (br., s, 1H), 6.73 (d, J = 7.6 Hz, 1H), 5.61 (br., s, 1H), 4.04 (s, 1H), 2.05-1.40 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 148.0, 136.9, 127.7, 125.2, 120.1, 110.5, 73.1, 48.8, 36.8, 32.4, 25.4, 22.7, 21.5; HRMS (ESI) calcd for $C_{14}H_{19}N_2O^+$ $(M+H)^+$ 231.14919, found 231.14835.

References

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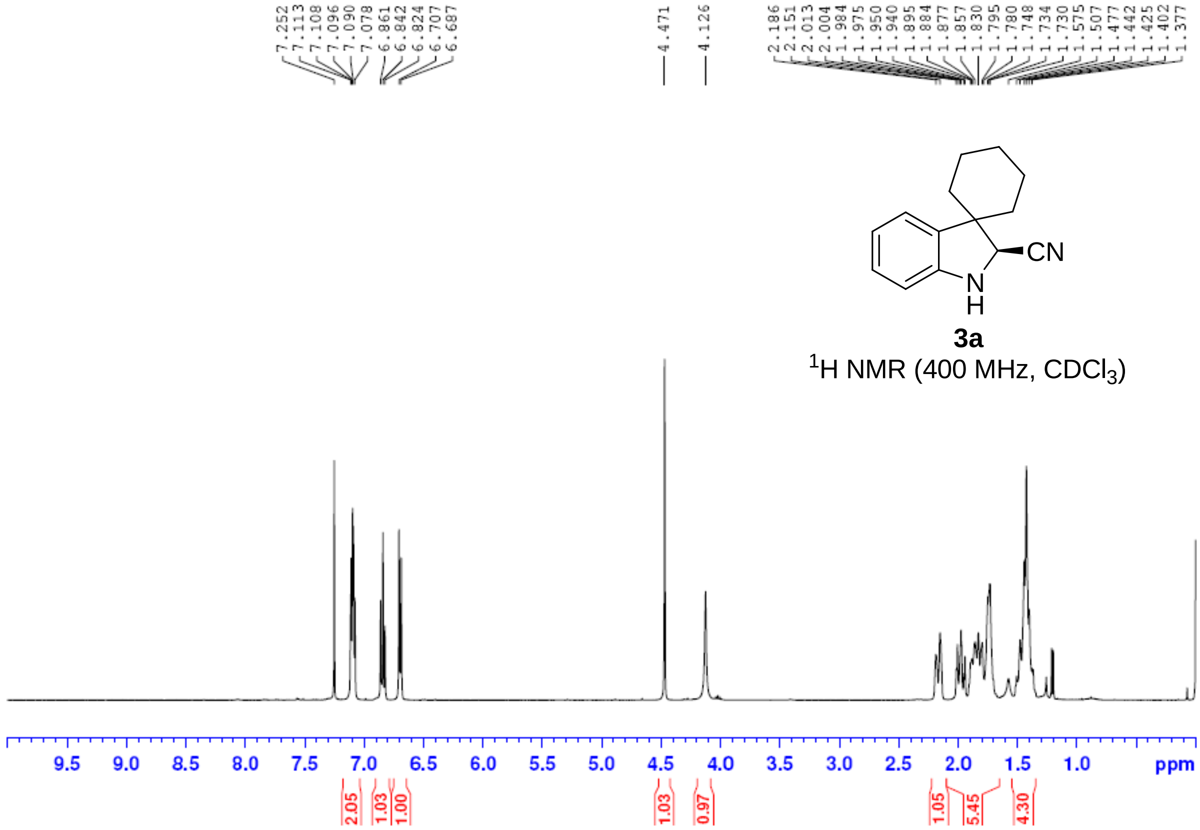
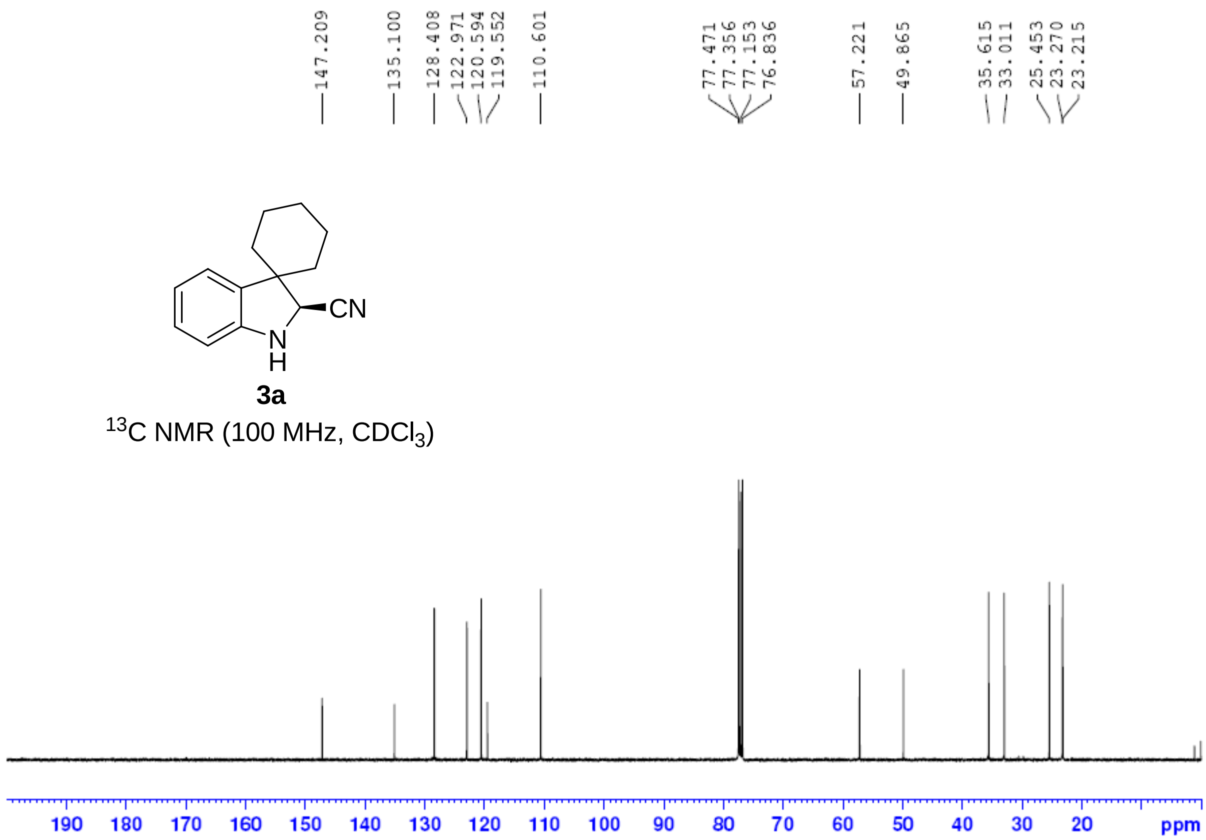
3 M. Watzke, K. Schulz, K. Johannes, P. Ullrich and J. Martens, *Eur. J. Org. Chem.*, 2008, 3859.

4 K. Funabashi, H. Ratni, M. Kanai and M. Shibasaki, *J. Am. Chem. Soc.*, 2001, **123**, 10784.



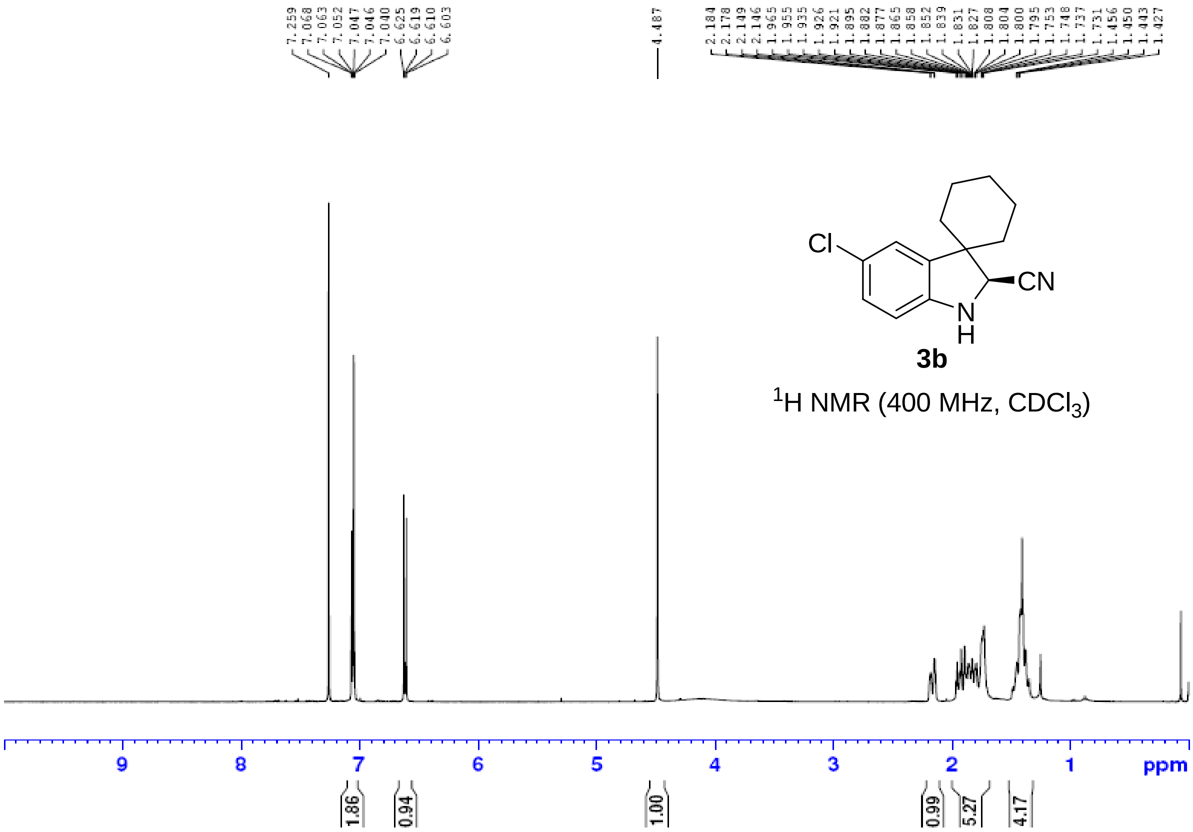
3a

^{1}H NMR (400 MHz, $CDCl_3$)



3a

^{13}C NMR (100 MHz, $CDCl_3$)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Cl
CN
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H
3b
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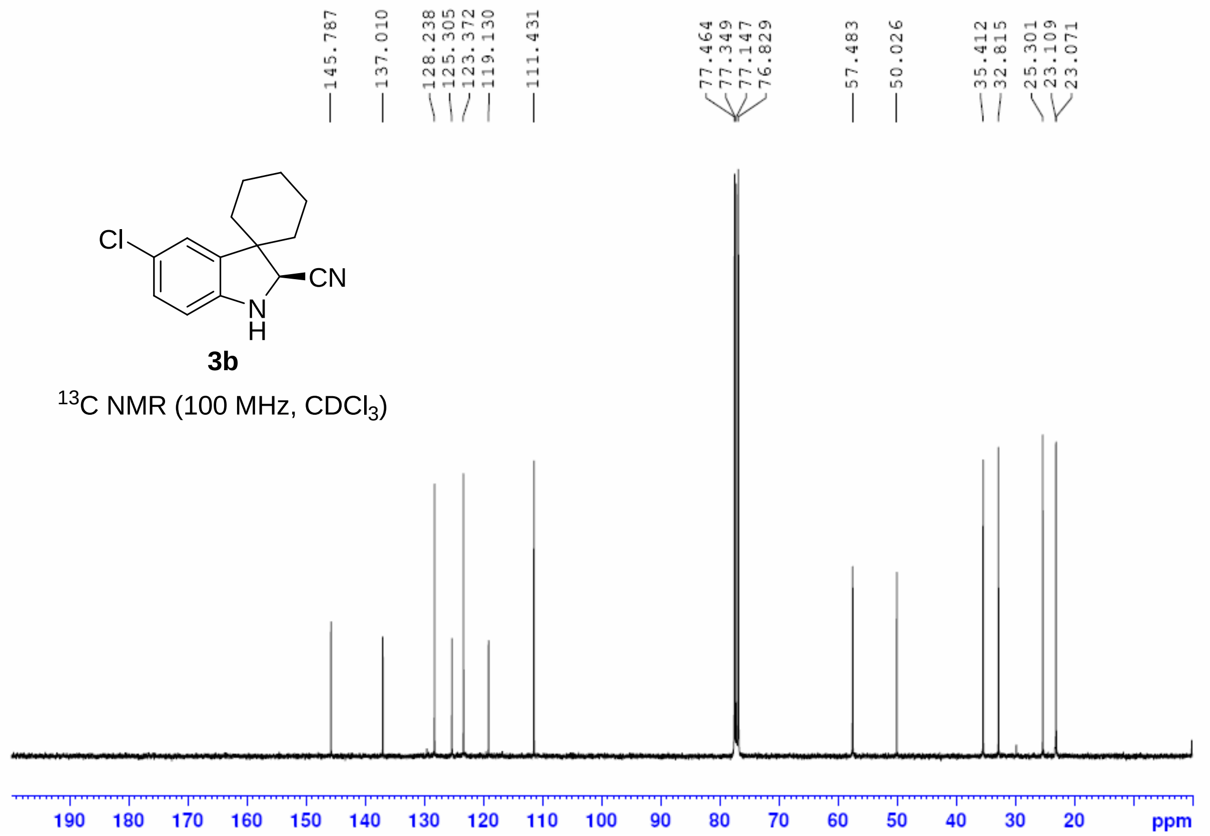
4.17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H
3b
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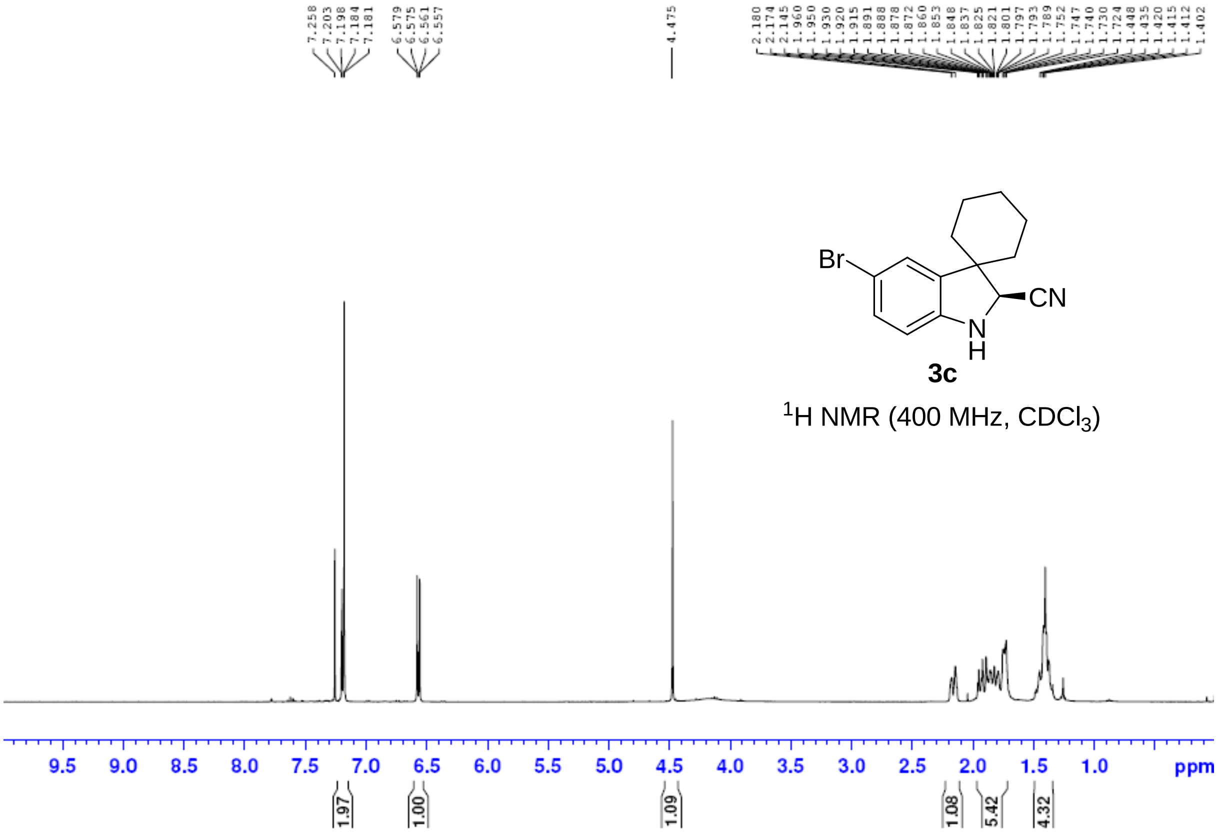
20
ppm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7.5
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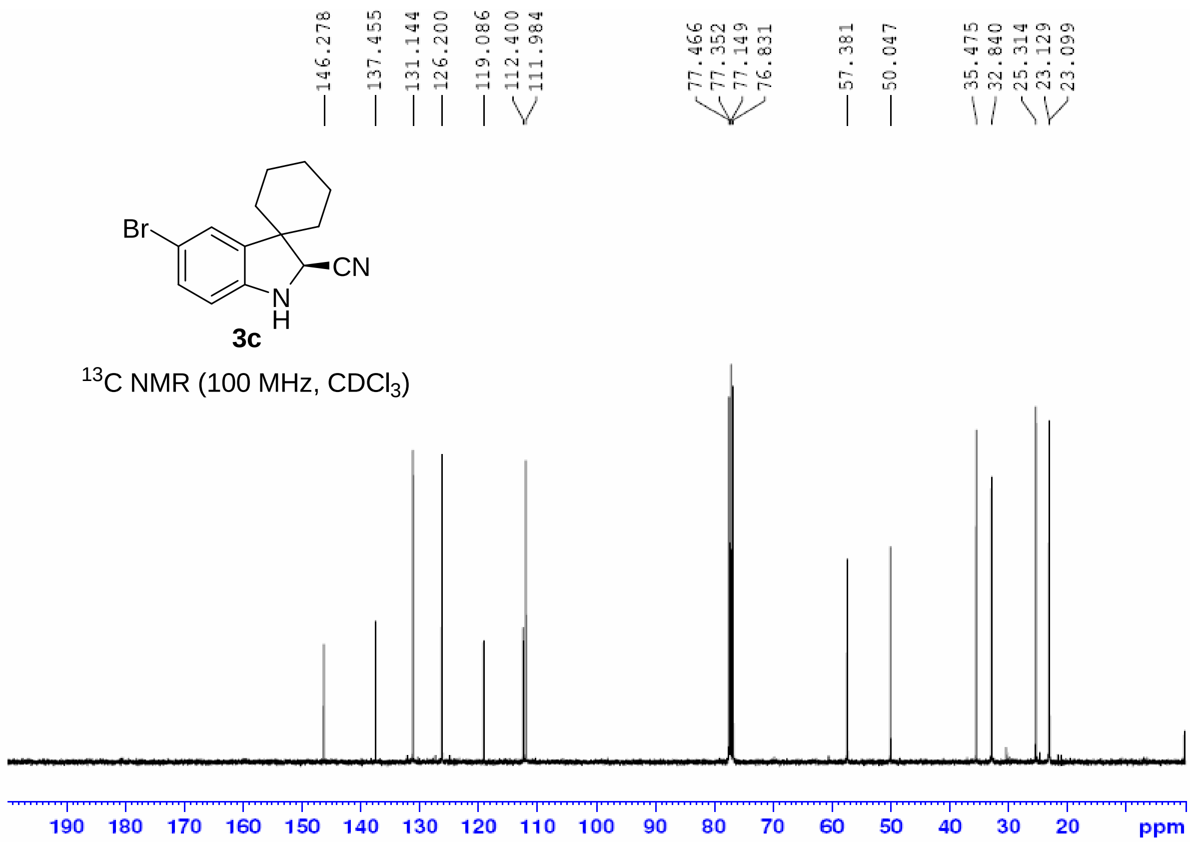
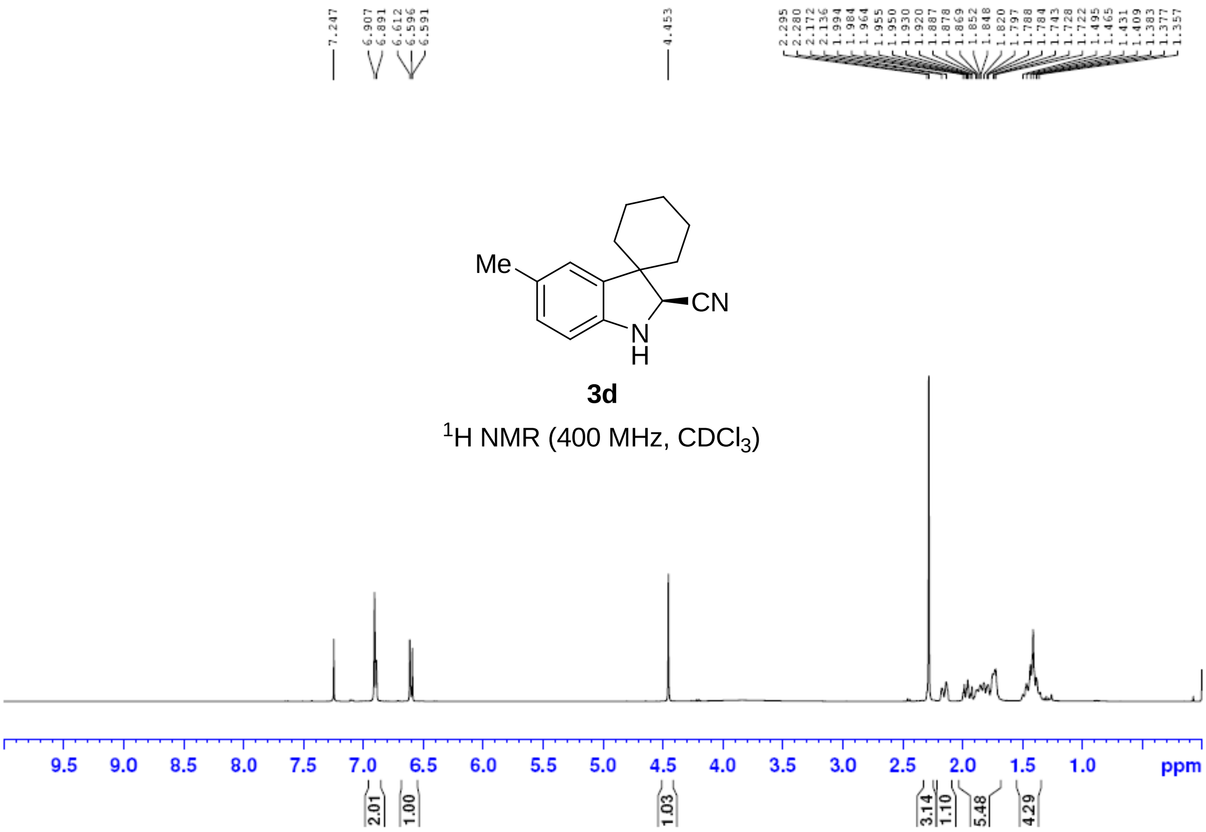
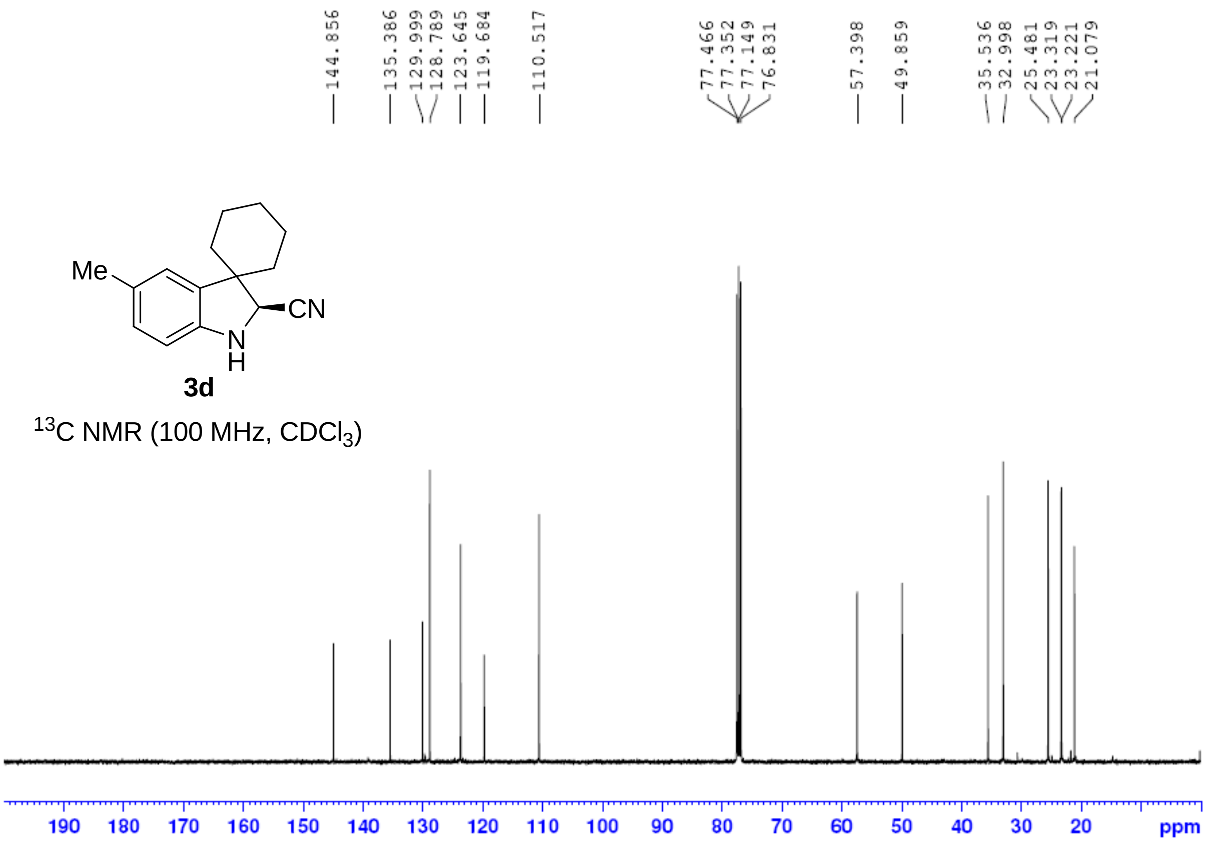
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.97
1.00
1.09
1.08
5.42
4.32


146.278
137.455
131.144
126.200
119.086
112.400
111.984
77.466
77.352
77.149
76.831
57.381
50.047
35.475
32.840
25.314
23.129
23.099
Br
CN
N
H
3c
^{13}C NMR (100 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



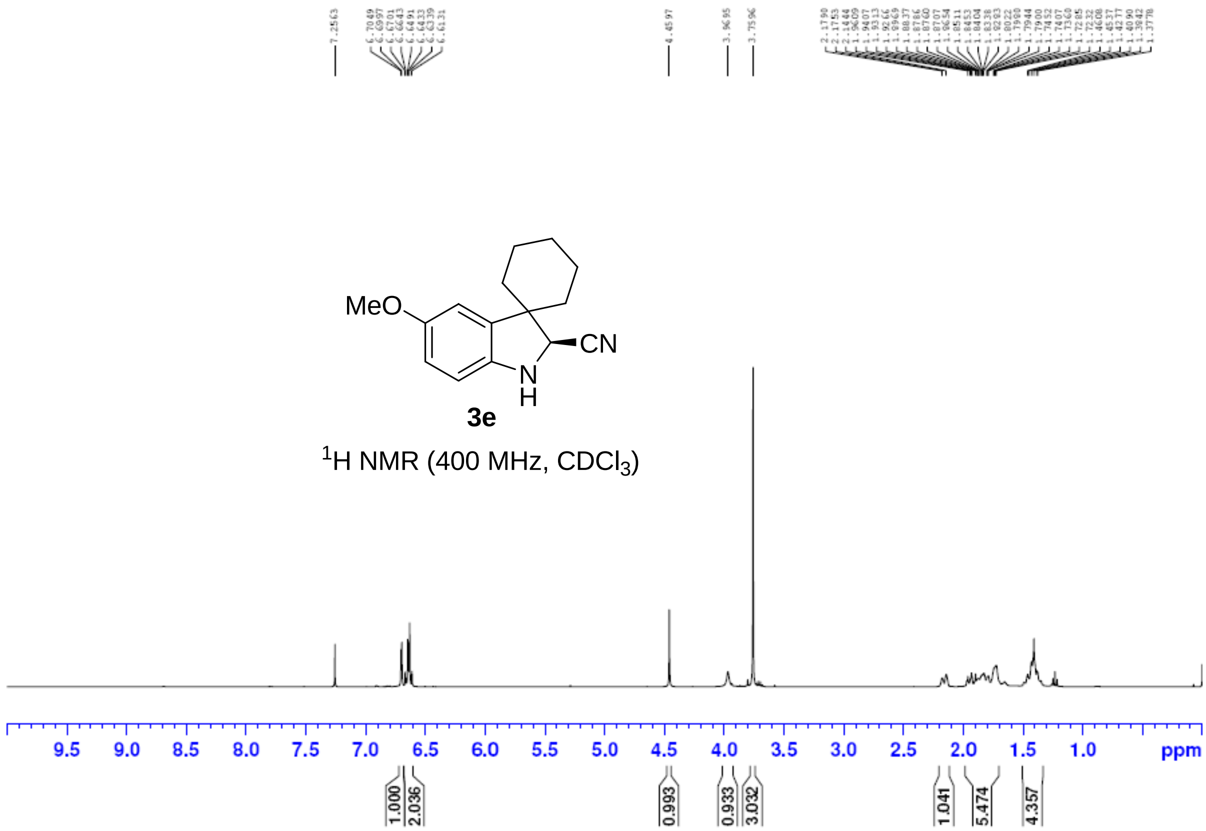
3d

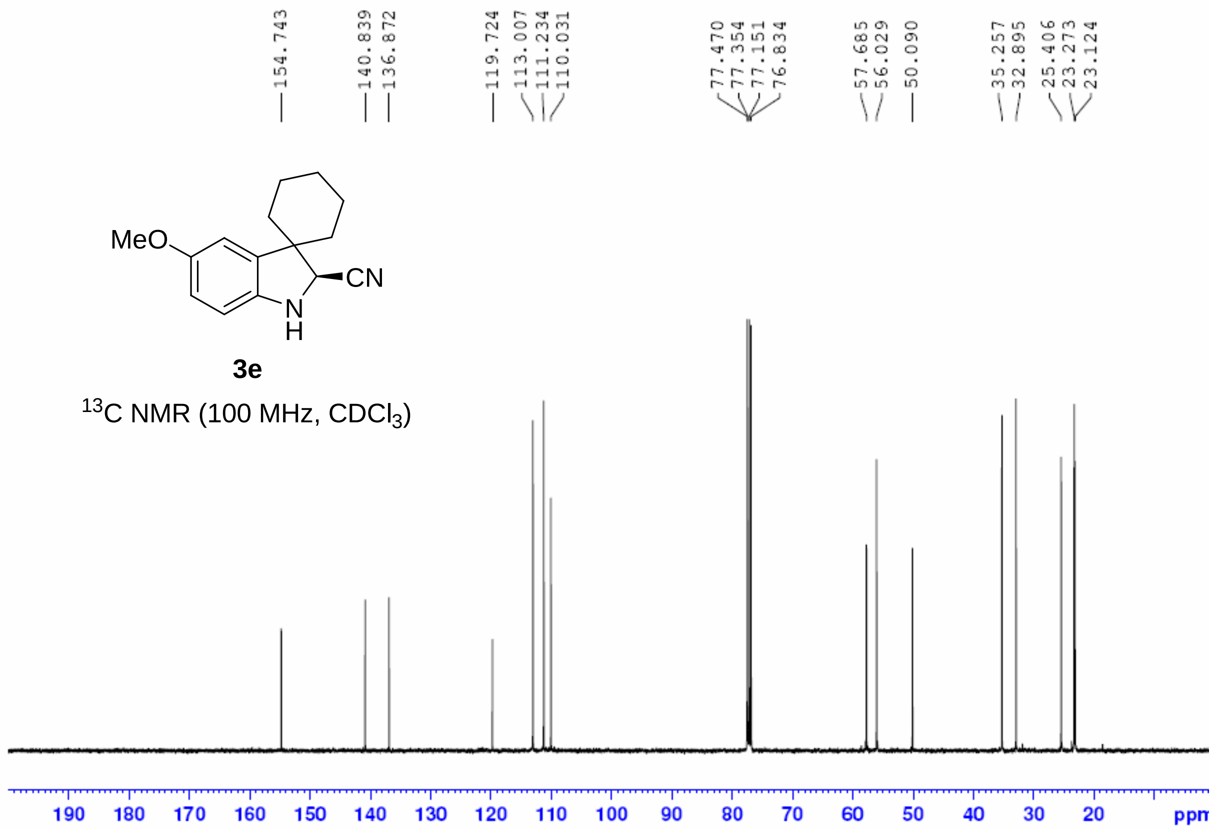
^{1}H NMR (400 MHz, $CDCl_3$)

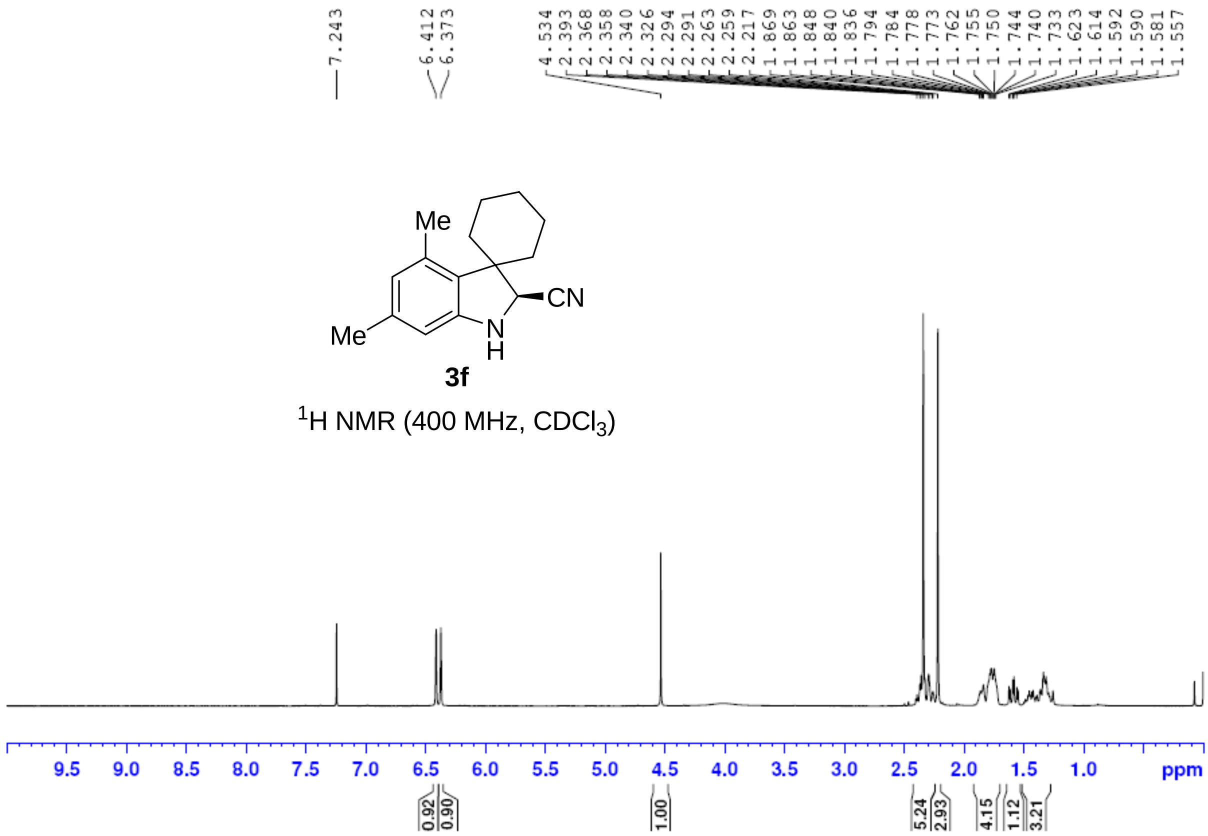


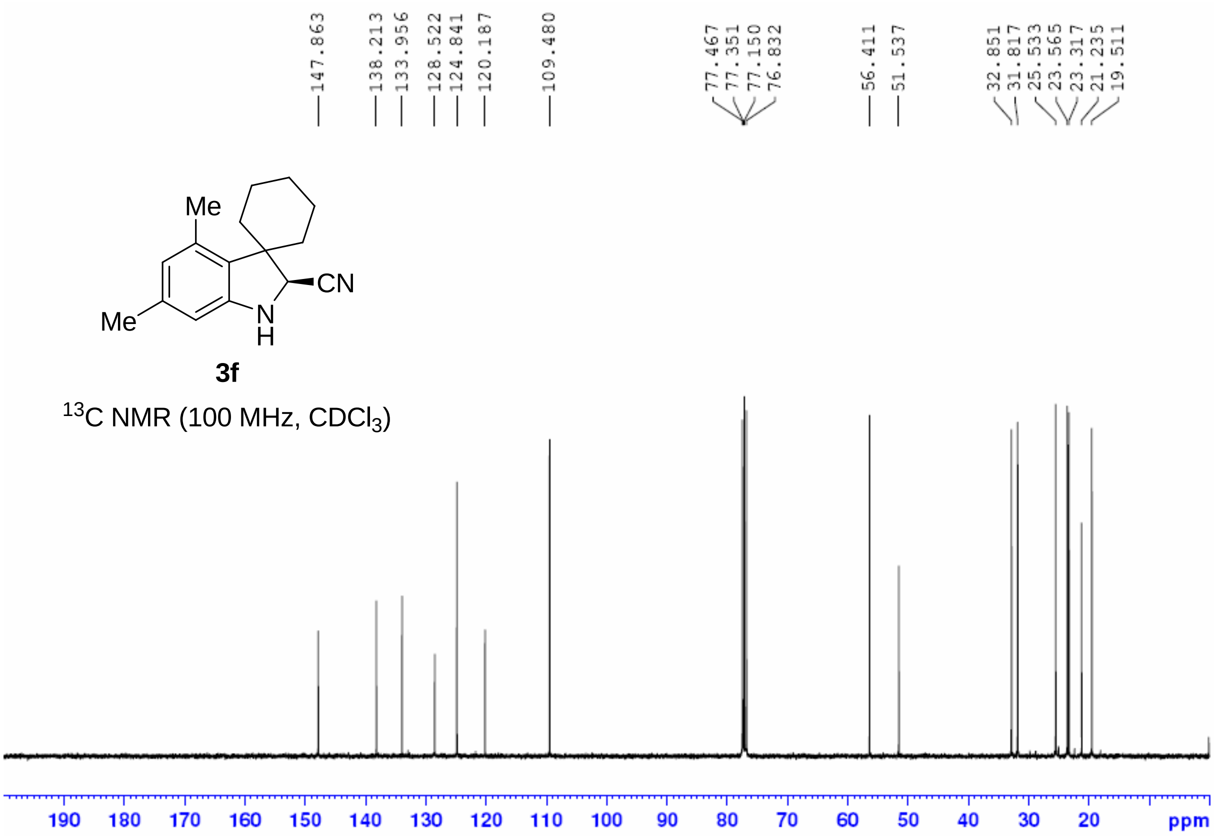
3d

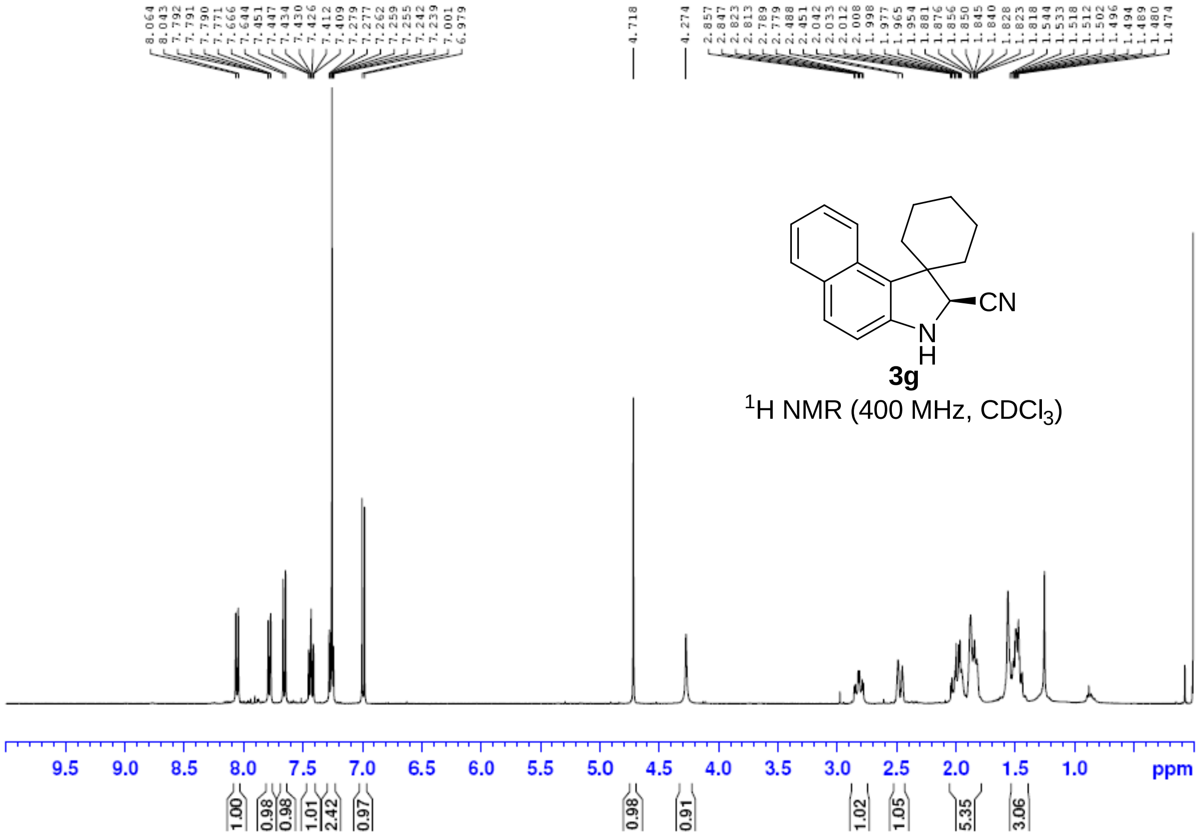
^{13}C NMR (100 MHz, $CDCl_3$)

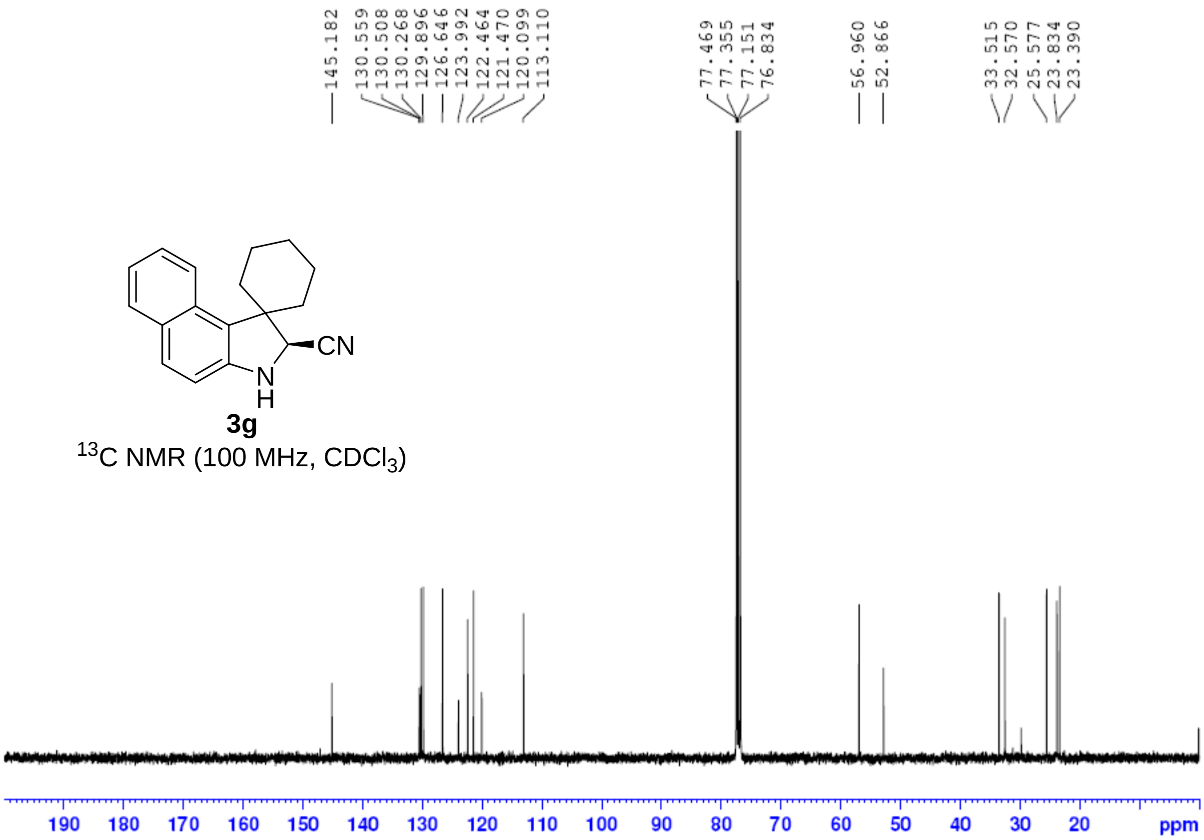

MeO
CN
N
H
3e
^{1}H NMR (400 MHz, $CDCl_3$)
ppm

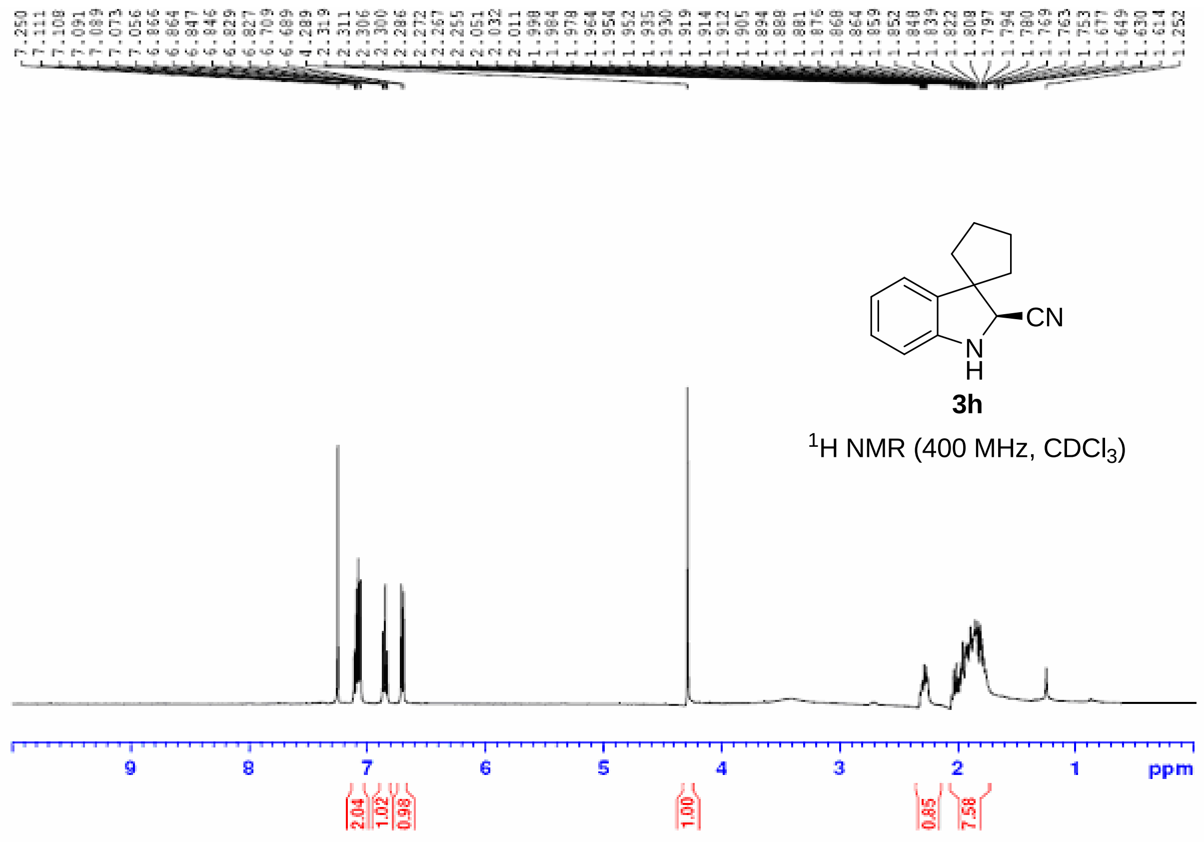

154.743
140.839
136.872
119.724
113.007
111.234
110.031
77.470
77.354
77.151
76.834
57.685
56.029
50.090
35.257
32.895
25.406
23.273
23.124
MeO
CN
N
H
3e
^{13}C NMR (100 MHz, $CDCl_3$)
ppm

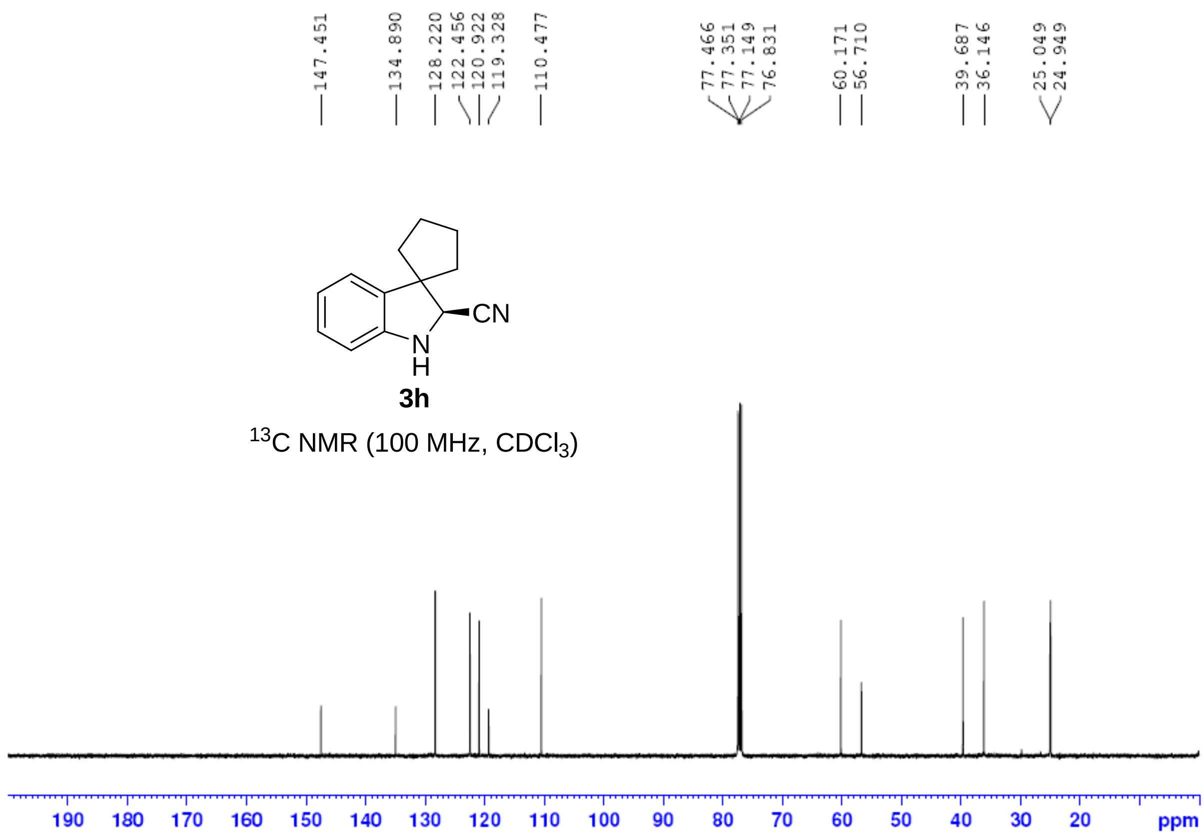

7.243
6.412
6.373
4.534
2.393
2.368
2.358
2.340
2.326
2.294
2.291
2.263
2.259
2.217
1.869
1.863
1.848
1.840
1.836
1.794
1.784
1.778
1.773
1.762
1.755
1.750
1.744
1.740
1.733
1.623
1.614
1.592
1.590
1.581
1.557
Me
CN
Me
N
H
3f
1H NMR (400 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.92
0.90
1.00
5.24
2.93
4.15
1.12
3.21

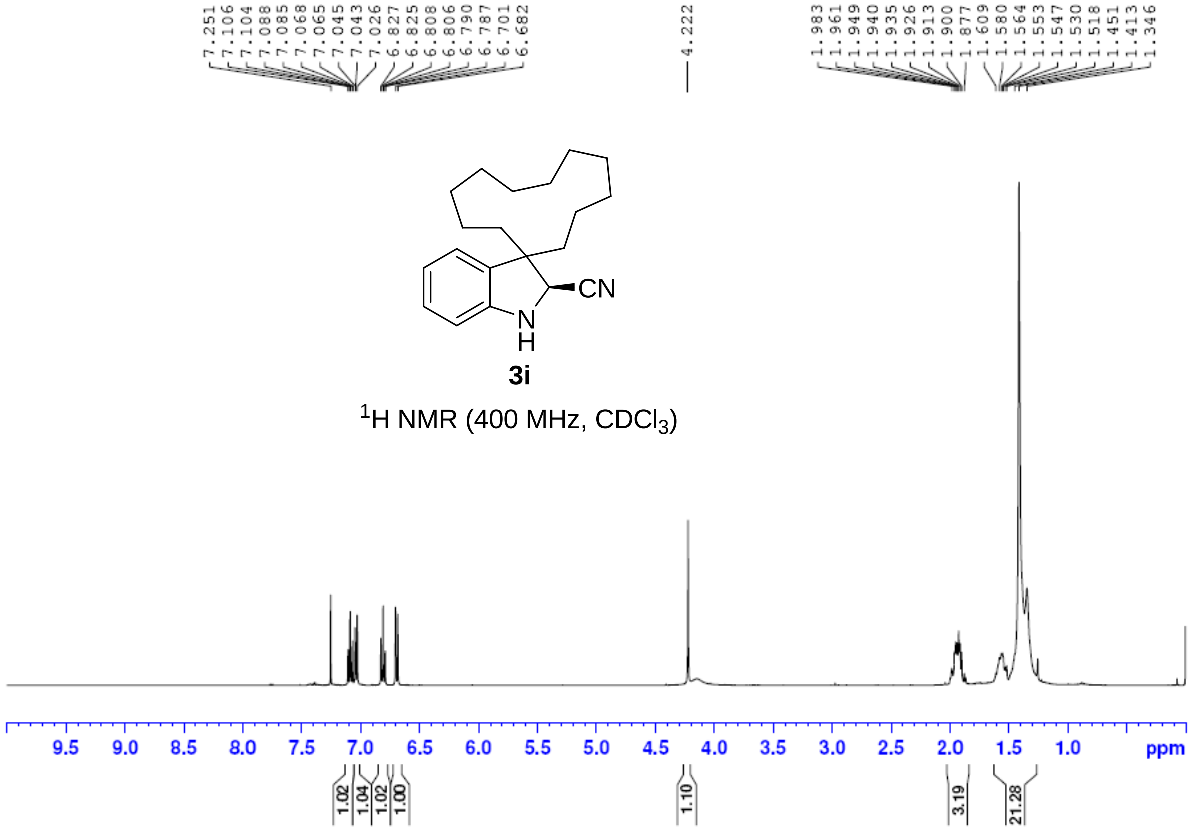

147.863
138.213
133.956
128.522
124.841
120.187
109.480
77.467
77.351
77.150
76.832
56.411
51.537
32.851
31.817
25.533
23.565
23.317
21.235
19.511
Me
CN
Me
N
H
3f
13C NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

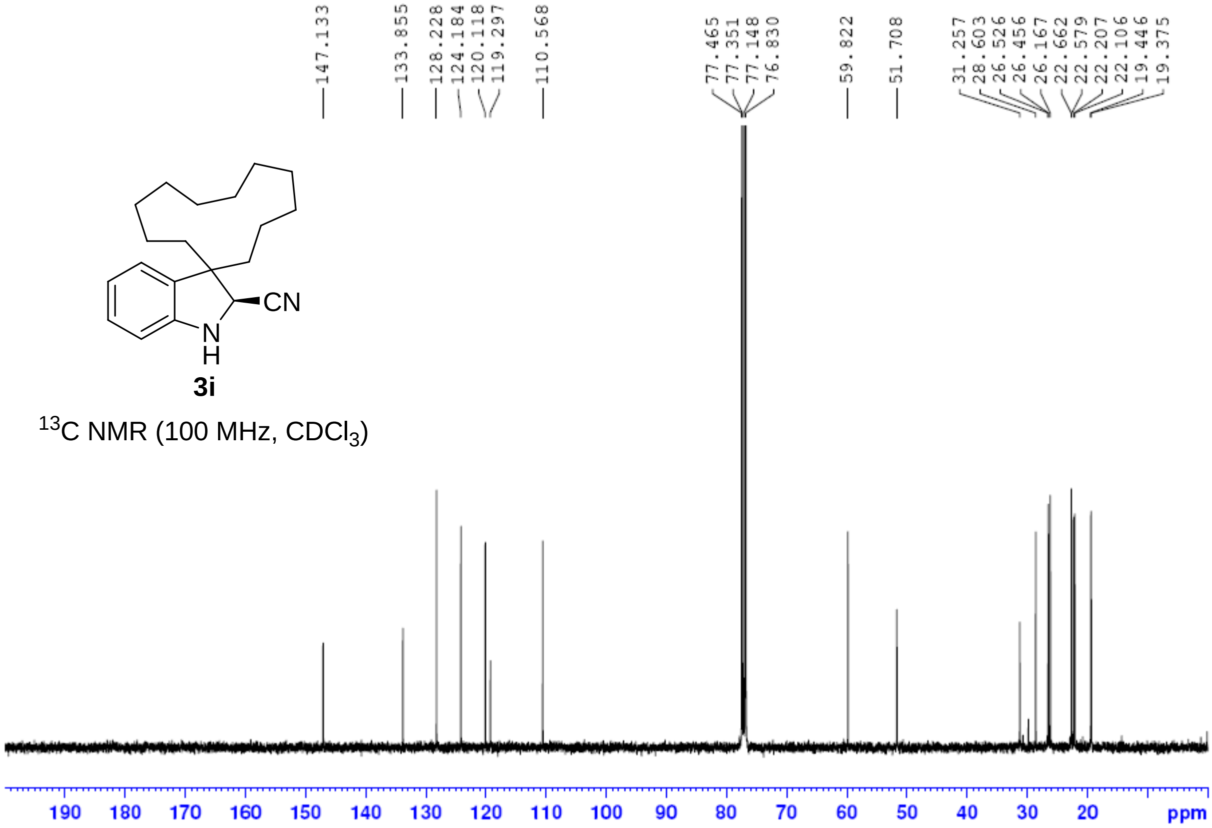

8.064
8.043
7.792
7.790
7.771
7.666
7.644
7.451
7.447
7.434
7.430
7.426
7.412
7.409
7.279
7.277
7.262
7.259
7.255
7.242
7.239
7.001
6.979
4.718
4.274
2.857
2.847
2.823
2.813
2.789
2.779
2.488
2.451
2.042
2.033
2.012
2.008
1.998
1.977
1.965
1.954
1.881
1.876
1.856
1.850
1.845
1.840
1.828
1.823
1.818
1.544
1.533
1.518
1.512
1.502
1.496
1.494
1.489
1.480
1.474
CN
N
H
3g
1H NMR (400 MHz, CDCl3)
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 ppm
1.00
0.98
0.98
1.01
2.42
0.97
0.98
0.91
1.02
1.05
5.35
3.06

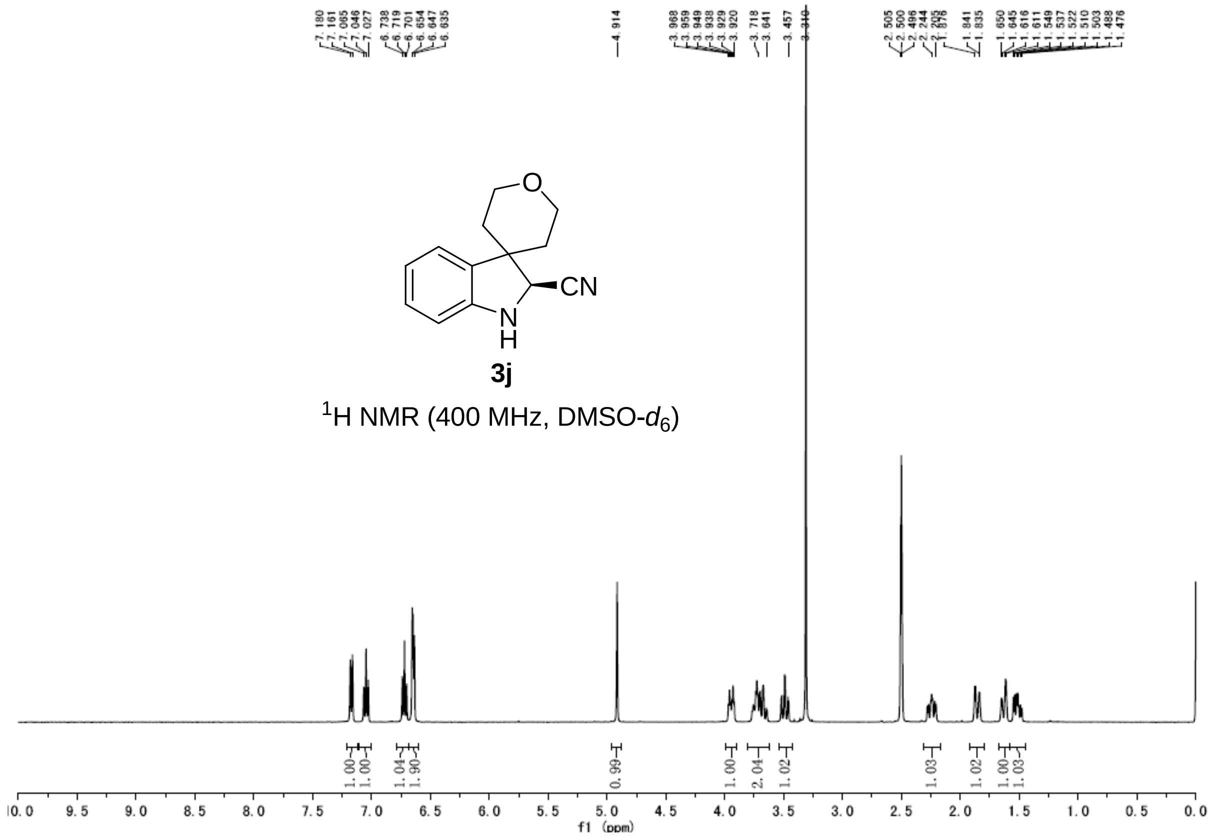

145.182
130.559
130.508
130.268
129.896
126.646
123.992
122.464
121.470
120.099
113.110
77.469
77.355
77.151
76.834
56.960
52.866
33.515
32.570
25.577
23.834
23.390
CN
N
H
3g
13C NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

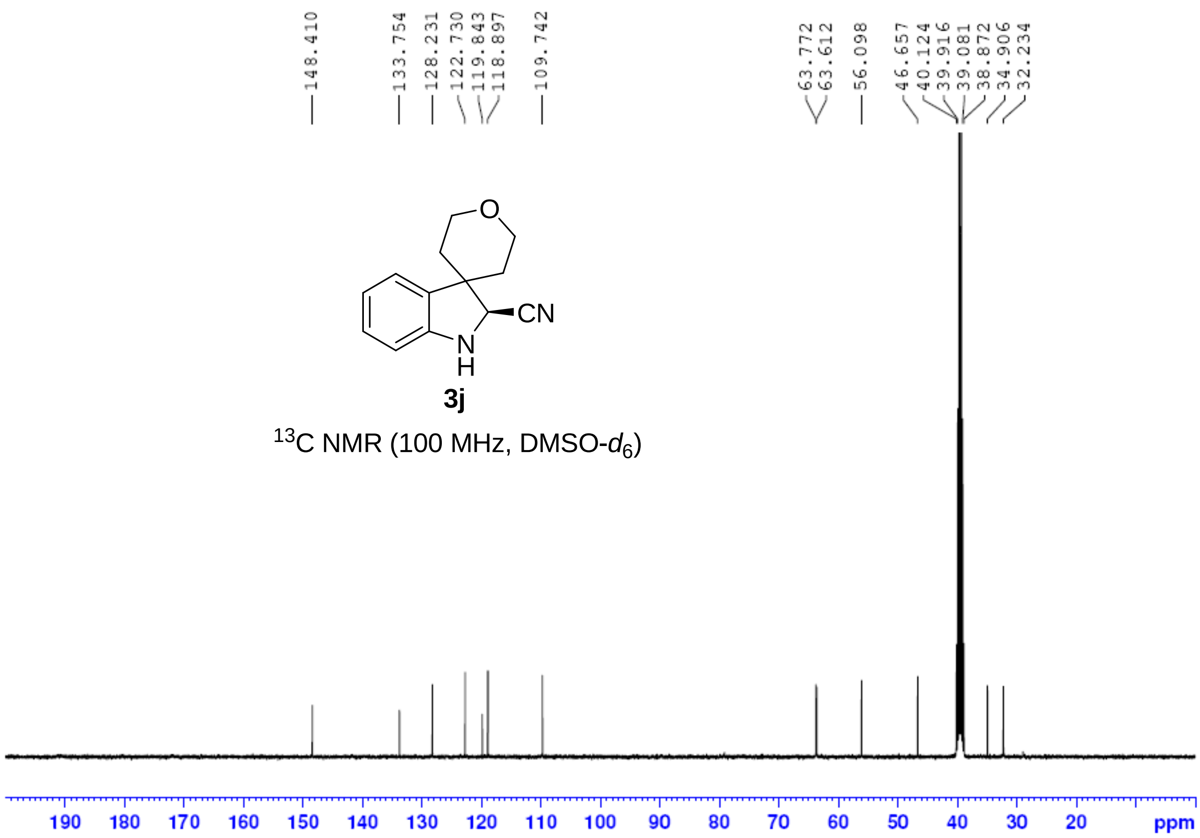

7.250
7.111
7.108
7.091
7.089
7.073
7.056
6.866
6.864
6.847
6.846
6.829
6.827
6.709
6.689
4.289
2.319
2.311
2.306
2.300
2.286
2.272
2.267
2.255
2.051
2.032
2.011
1.990
1.984
1.978
1.964
1.954
1.952
1.935
1.930
1.919
1.914
1.912
1.905
1.894
1.888
1.881
1.876
1.868
1.864
1.859
1.852
1.840
1.839
1.822
1.808
1.797
1.794
1.780
1.769
1.763
1.753
1.677
1.649
1.630
1.614
1.252
CN
N
H
3h
^{1}H NMR (400 MHz, $CDCl_3$)
9
8
7
6
5
4
3
2
1
ppm
2.04
1.02
0.98
1.00
0.85
7.58

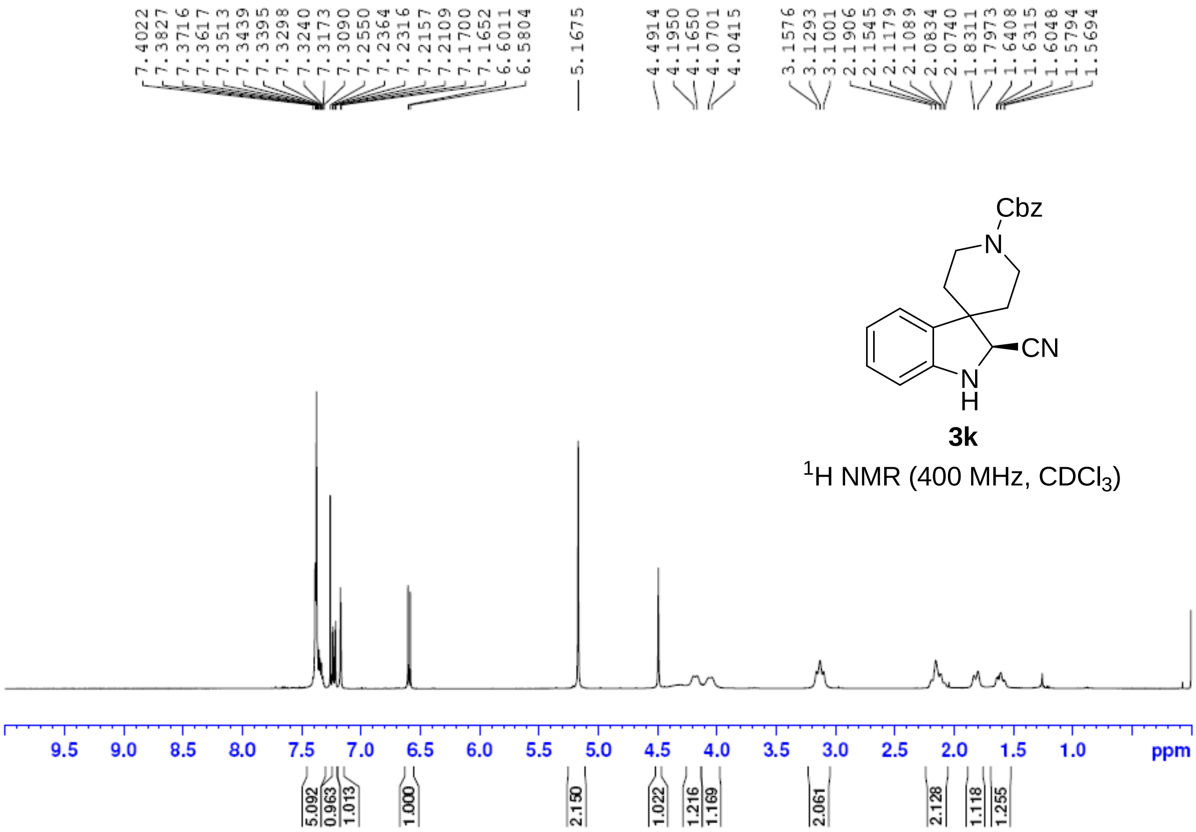

147.451
134.890
128.220
122.456
120.922
119.328
110.477
77.466
77.351
77.149
76.831
60.171
56.710
39.687
36.146
25.049
24.949
CN
N
H
3h
^{13}C NMR (100 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

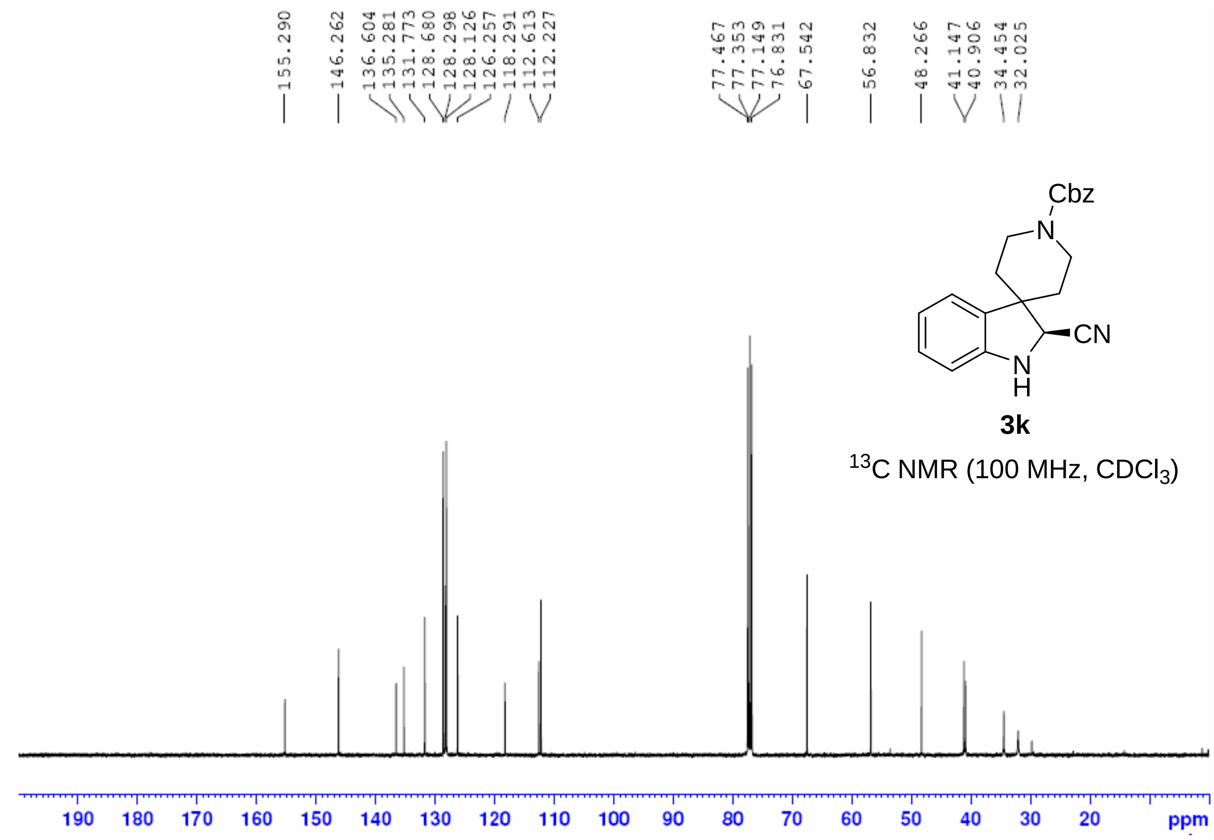

7.251 7.106 7.104 7.088 7.085 7.068 7.065 7.045 7.043 7.026 6.827 6.825 6.808 6.806 6.790 6.787 6.701 6.682
4.222
1.983 1.961 1.949 1.940 1.935 1.926 1.913 1.900 1.877 1.609 1.580 1.564 1.553 1.547 1.530 1.518 1.451 1.413 1.346
CN
N
H
3i
^{1}H NMR (400 MHz, $CDCl_3$)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.02 1.04 1.02 1.00
1.10
3.19
21.28

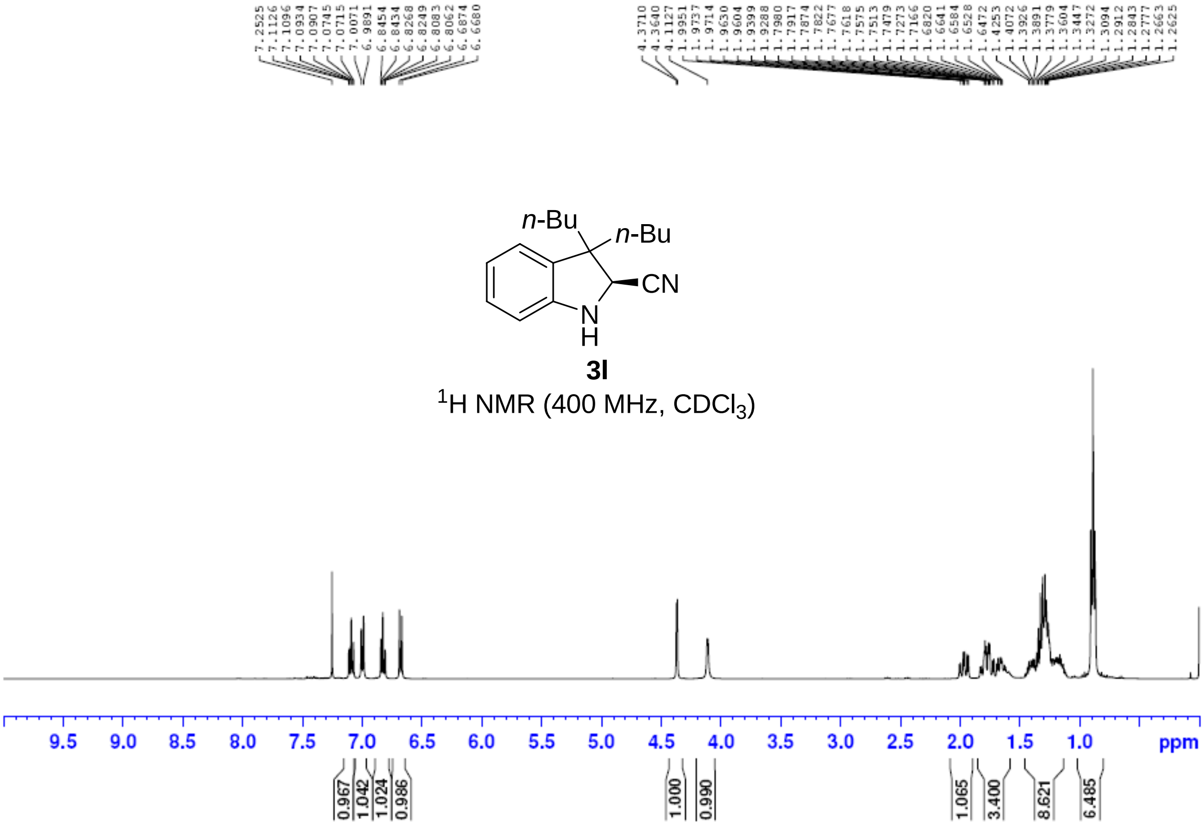

147.133
133.855 128.228 124.184 120.118 119.297
110.568
77.465 77.351 77.148 76.830
59.822
51.708
31.257 28.603 26.526 26.456 26.167 22.662 22.579 22.207 22.106 19.446 19.375
CN
N
H
3i
^{13}C NMR (100 MHz, $CDCl_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


CN
N
H
O
3j
1H NMR (400 MHz, DMSO-d6)
1.00
1.00
1.04
1.90
0.99
1.00
2.04
1.02
1.03
1.02
1.00
1.03
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)


148.410
133.754
128.231
122.730
119.843
118.897
109.742
63.772
63.612
56.098
46.657
40.124
39.916
39.081
38.872
34.906
32.234
CN
N
H
O
3j
13C NMR (100 MHz, DMSO-d6)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

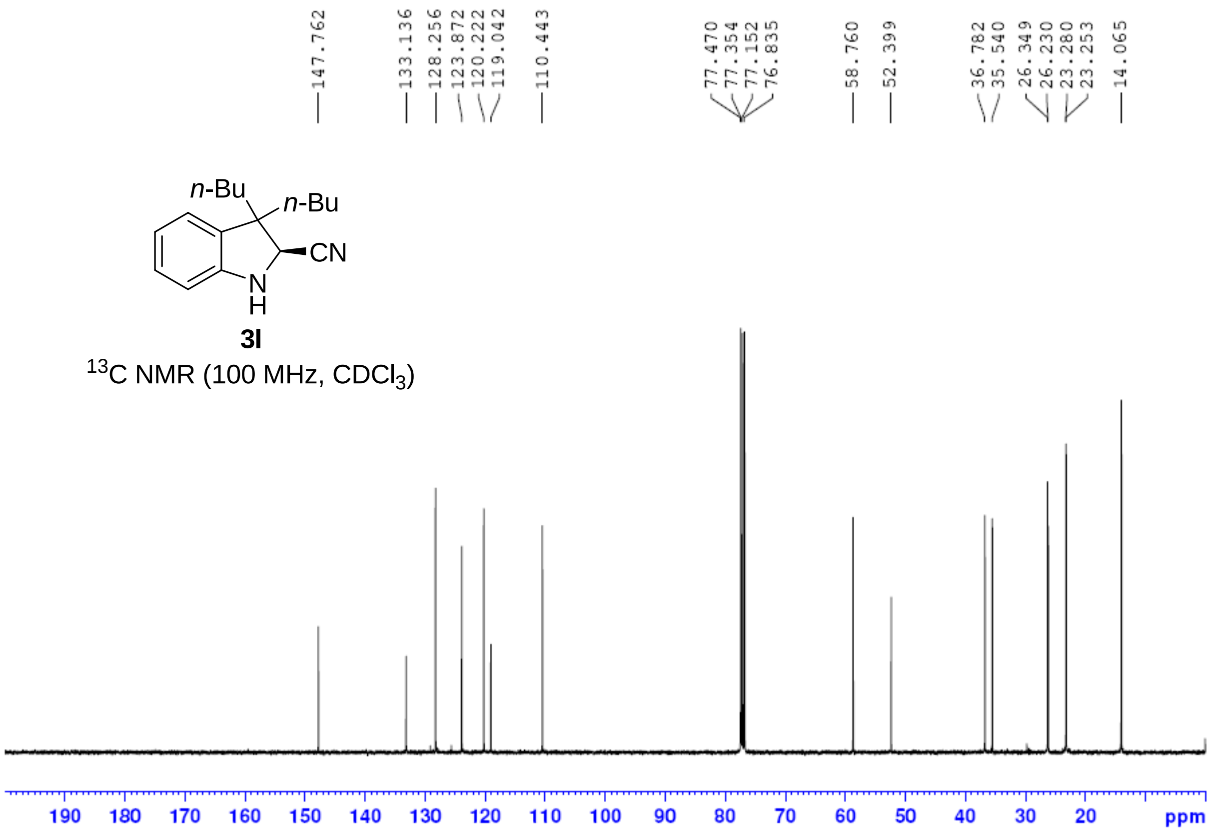

Cbz
N
CN
N
H
3k
^{1}H NMR (400 MHz, $CDCl_3$)
ppm


Cbz
N
CN
N
H
3k
^{13}C NMR (100 MHz, $CDCl_3$)
ppm



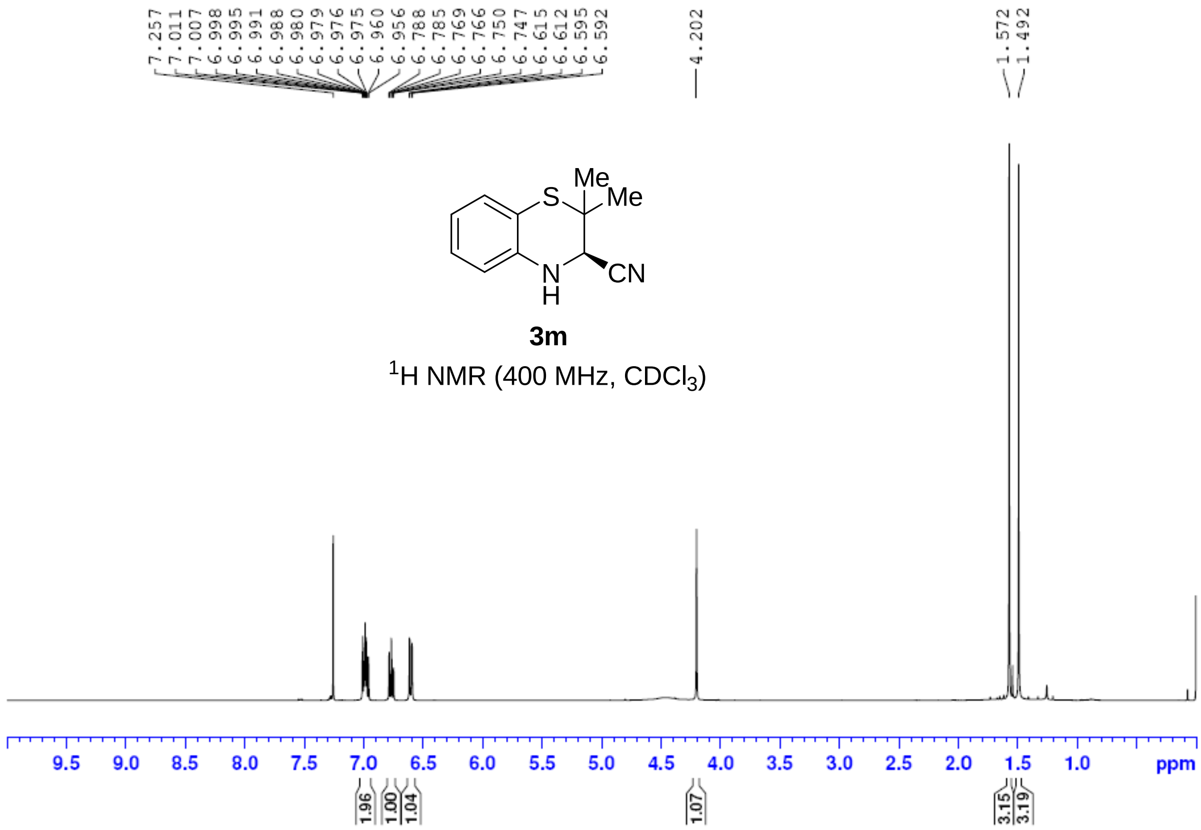
3l

^{1}H NMR (400 MHz, $CDCl_3$)



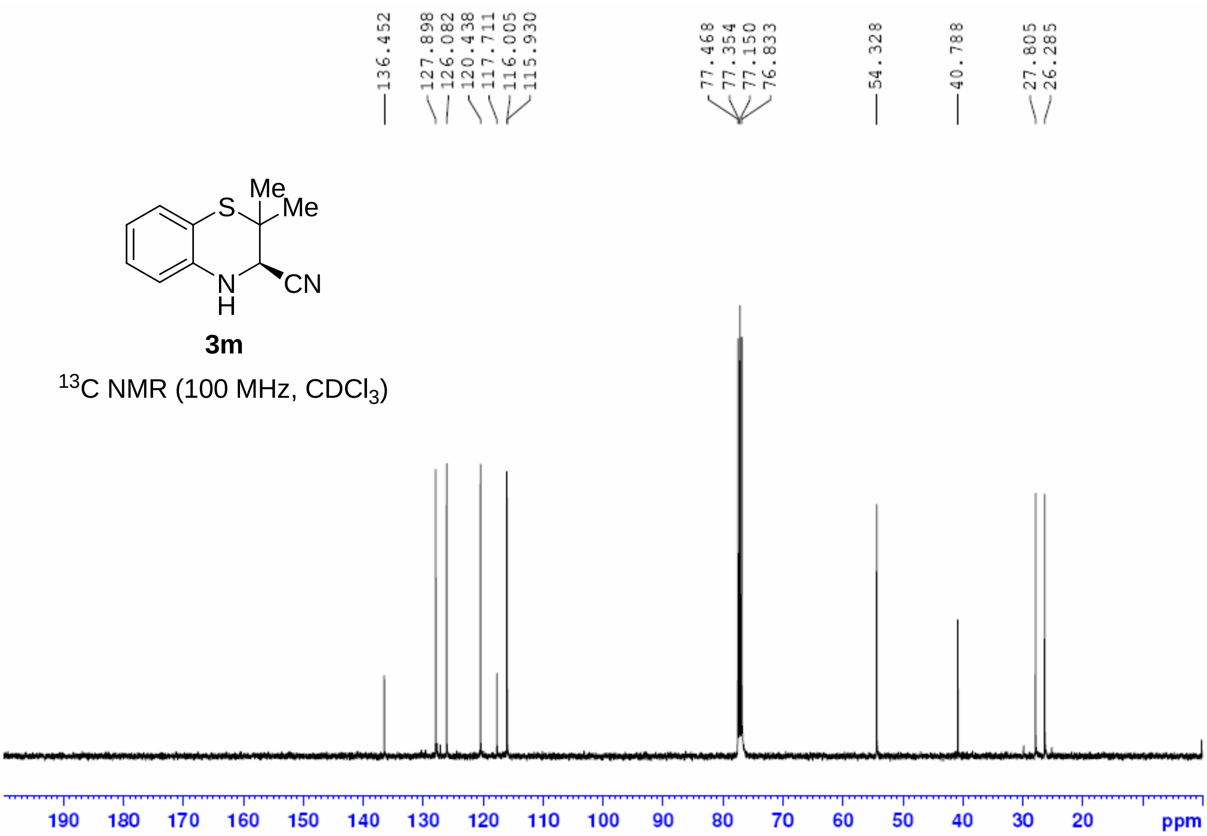
3l

^{13}C NMR (100 MHz, $CDCl_3$)



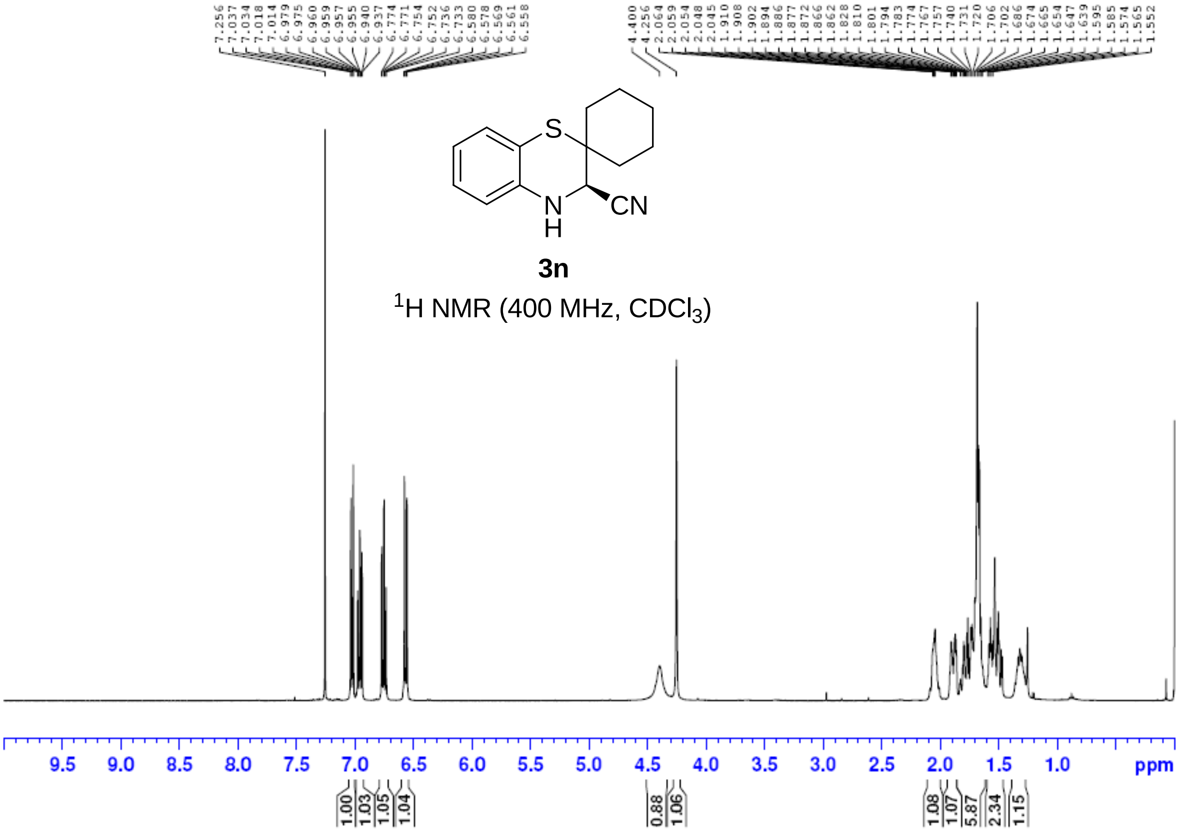
3m

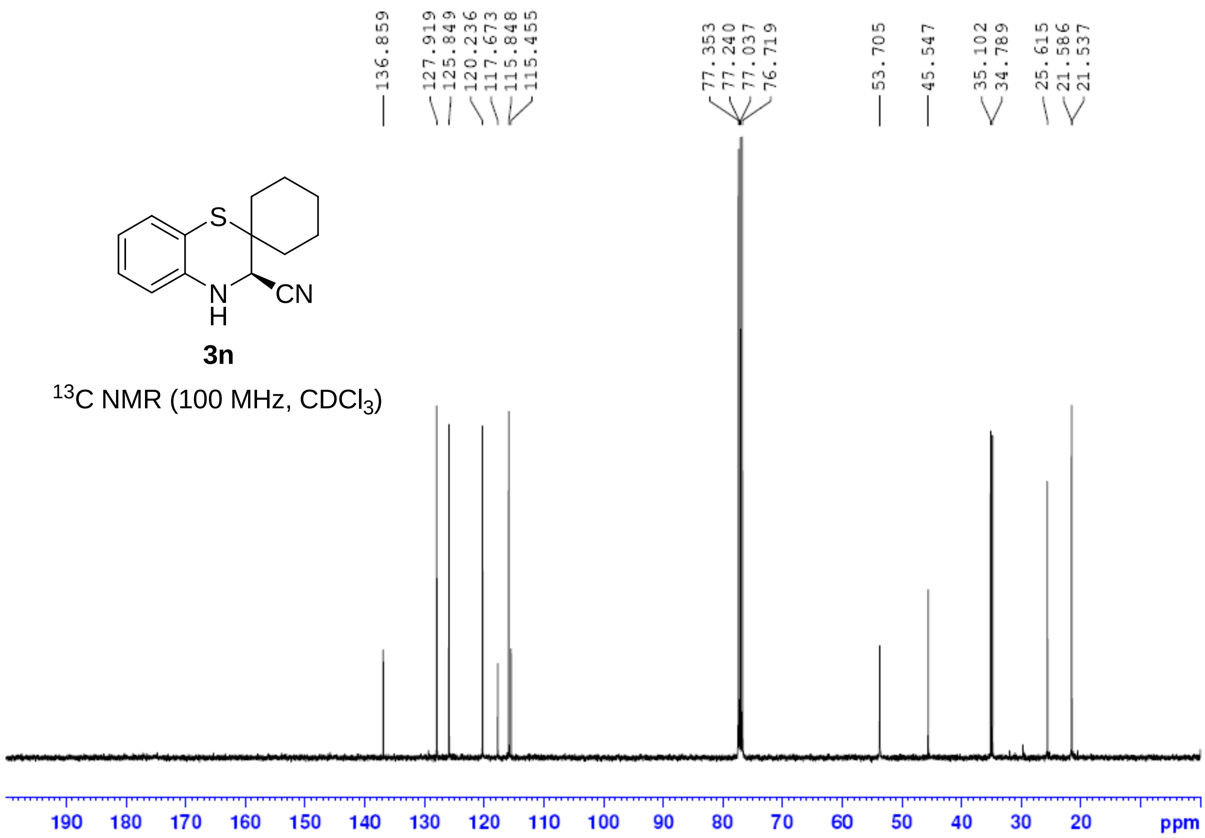
^1H NMR (400 MHz, $CDCl_3$)

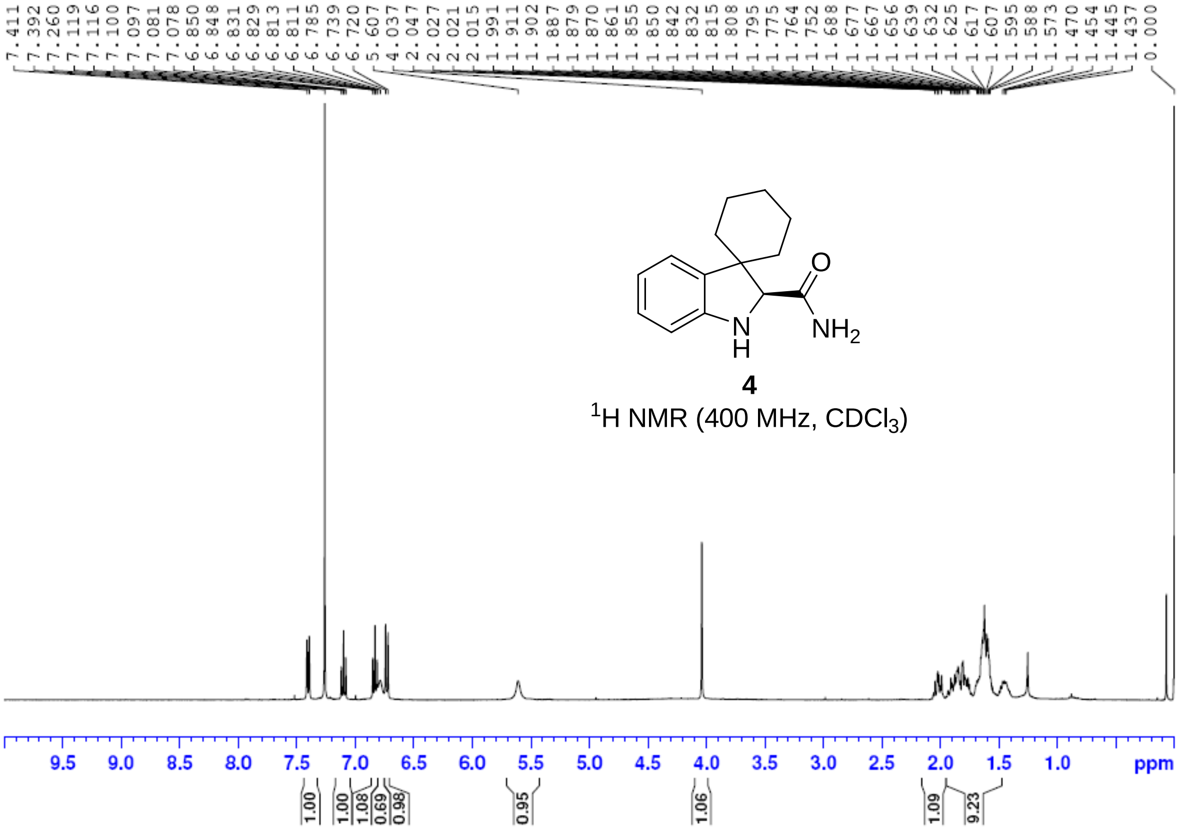


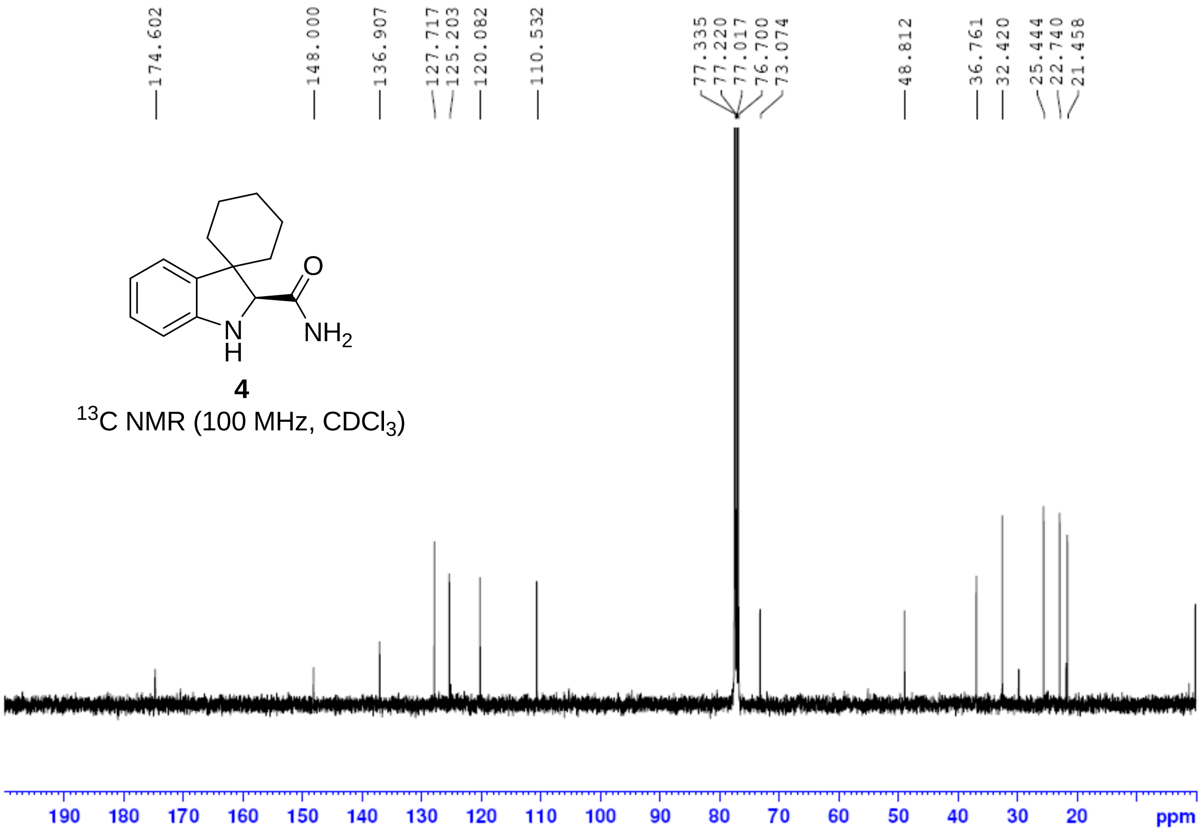
3m

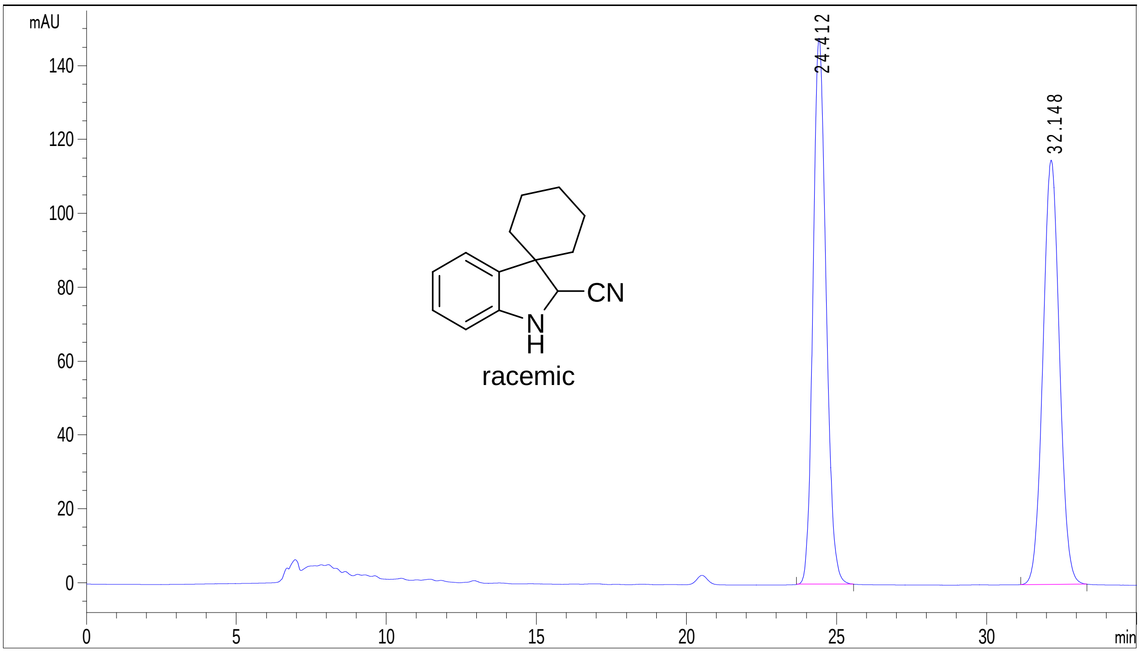
^{13}C NMR (100 MHz, $CDCl_3$)


3n
1H NMR (400 MHz, CDCl3)
ppm

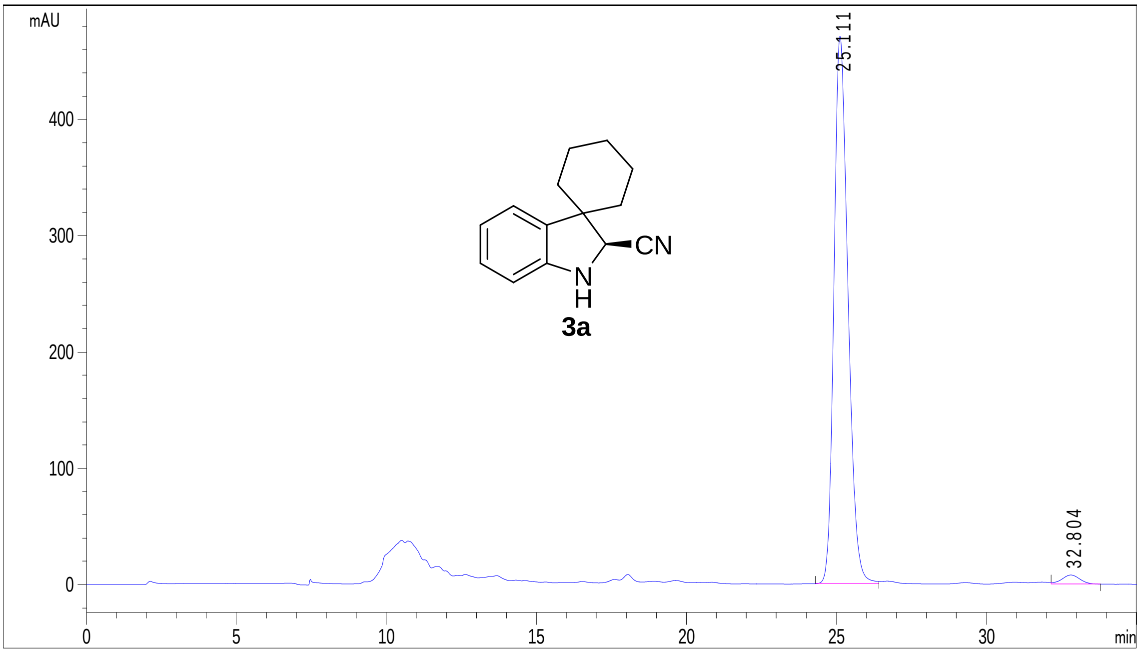

3n
13C NMR (100 MHz, CDCl3)
136.859
127.919
125.849
120.236
117.673
115.848
115.455
77.353
77.240
77.037
76.719
53.705
45.547
35.102
34.789
25.615
21.586
21.537
ppm


4
^{1}H NMR (400 MHz, CDCl$_3$)

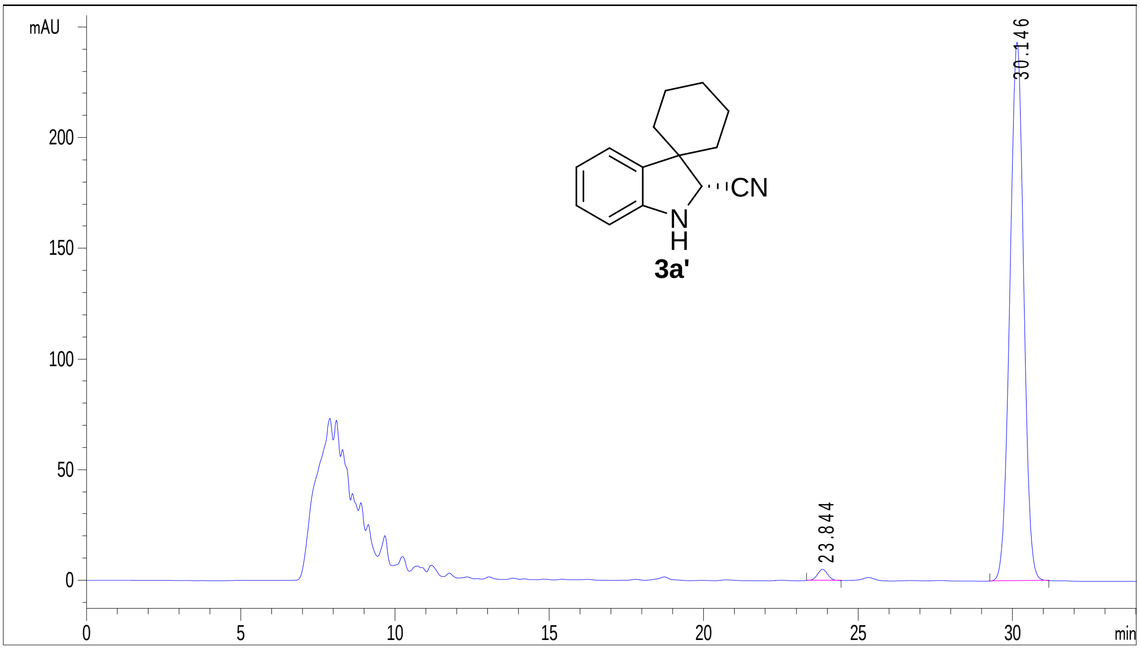

4
^{13}C NMR (100 MHz, CDCl$_3$)



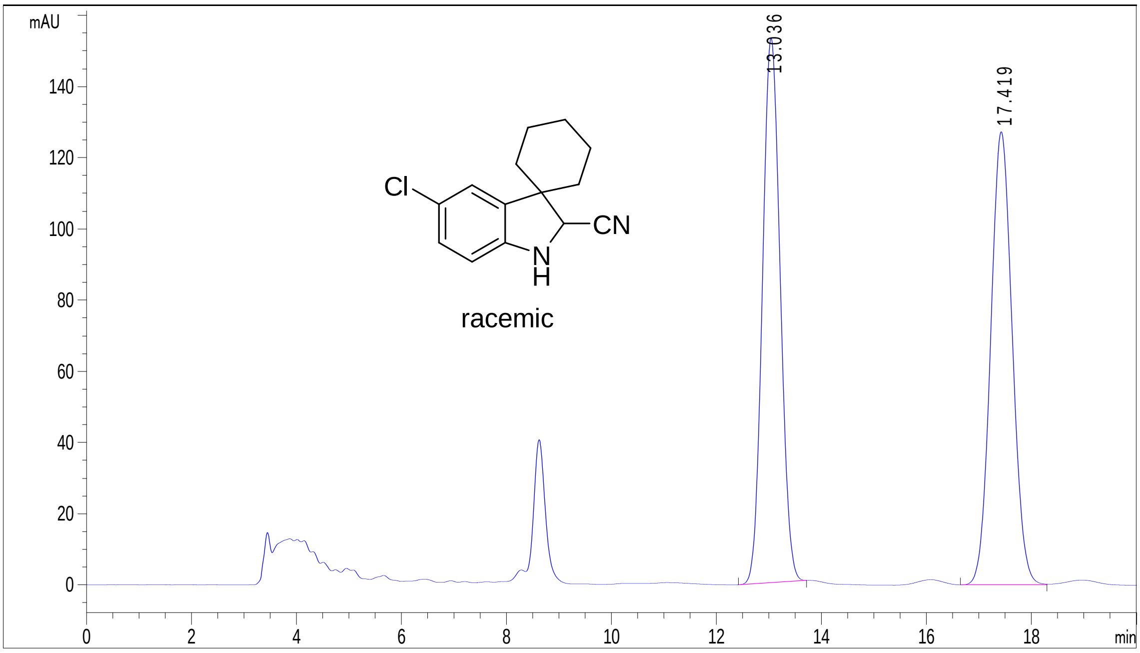
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	24.412	4472.1	148	0.4676	0.809	50.327
2	32.148	4413.9	115	0.5965	0.947	49.673



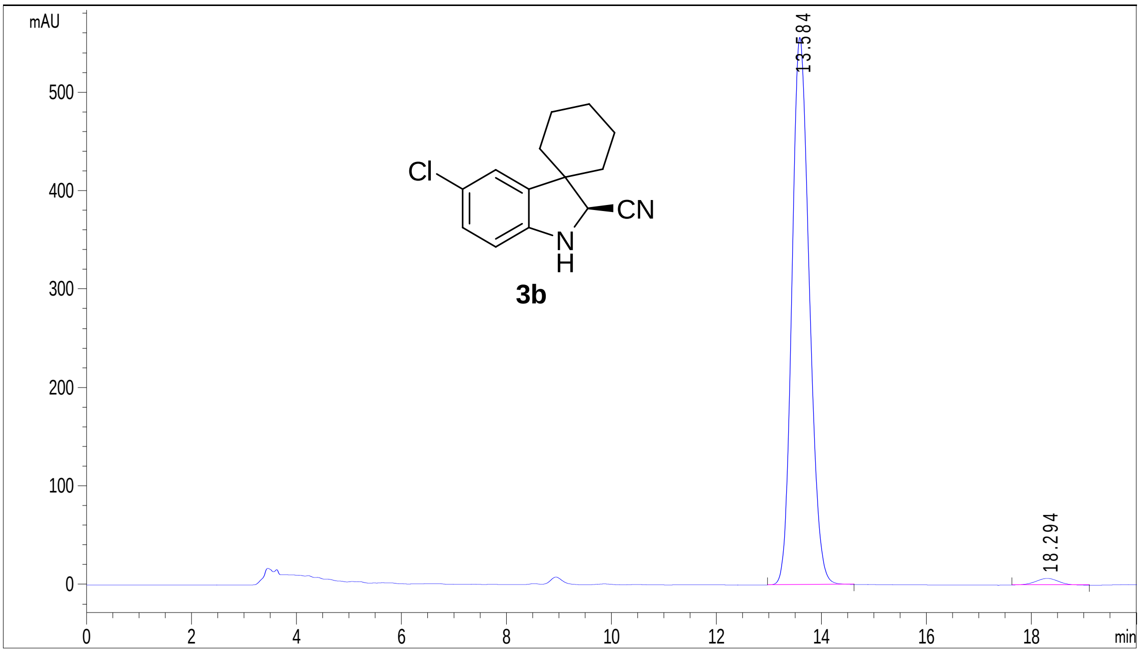
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	25.111	15279.4	470.9	0.5008	0.715	97.900
2	32.804	327.7	7.8	0.6366	0.991	2.100



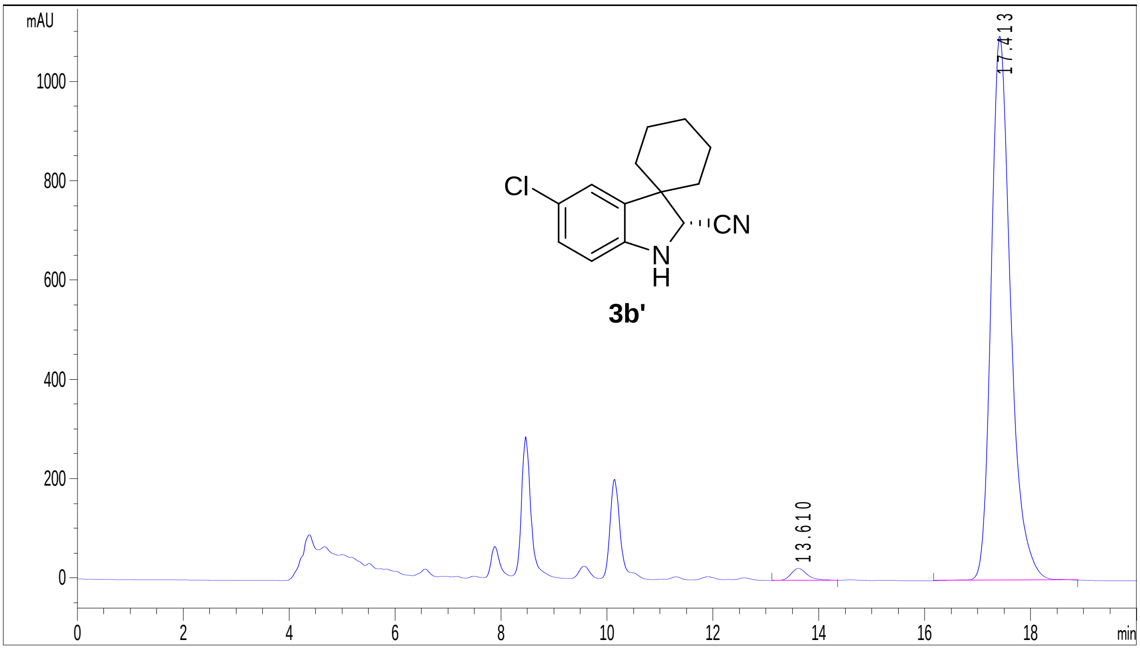
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	23.844	119.1	5.1	0.3607	0.991	1.547
2	30.146	7578.6	243.4	0.487	1.038	98.453



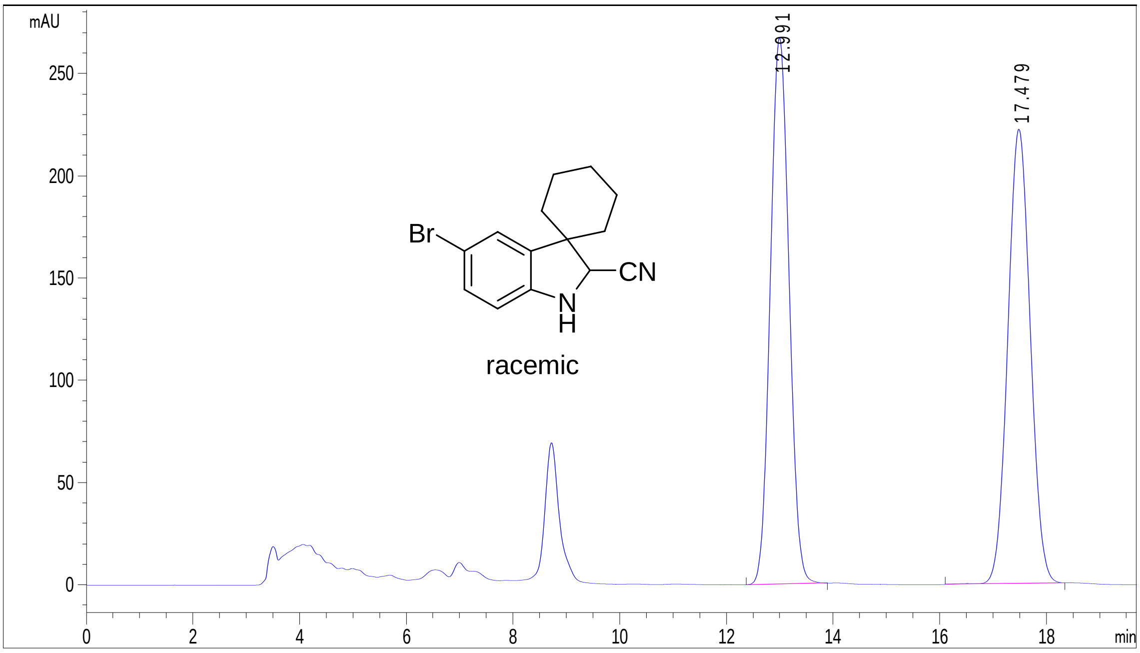
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.036	3591.1	153	0.3685	0.905	49.654
2	17.419	3641.1	127.4	0.4457	0.917	50.346



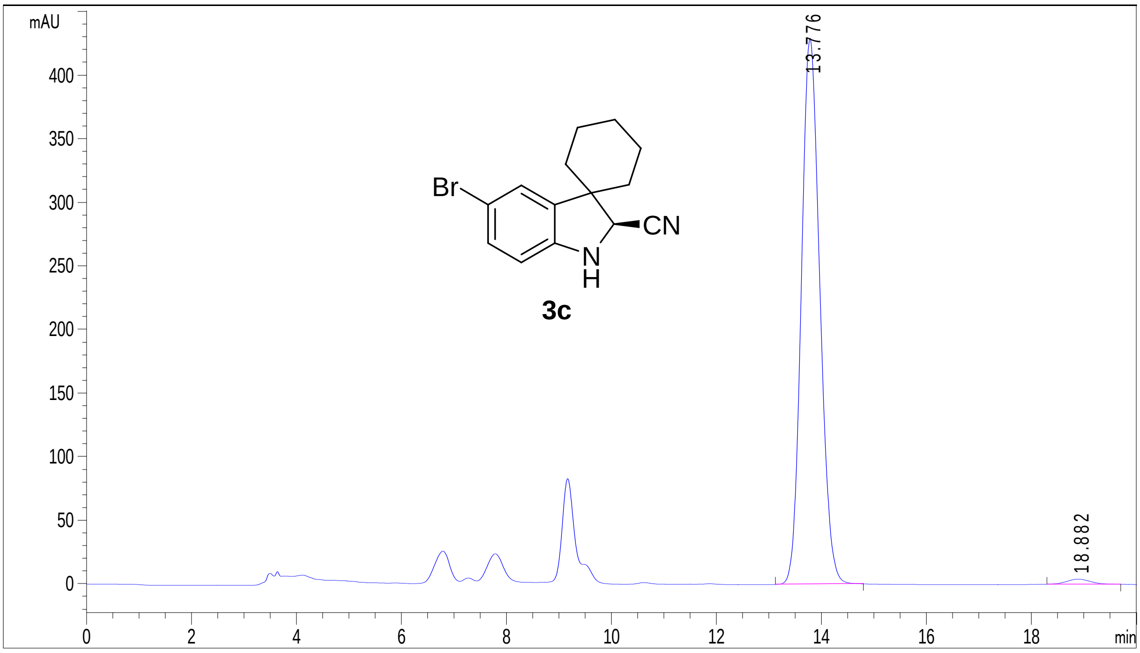
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.584	12826.5	556.2	0.3579	0.787	98.406
2	18.294	207.7	6.8	0.4688	1.005	1.594



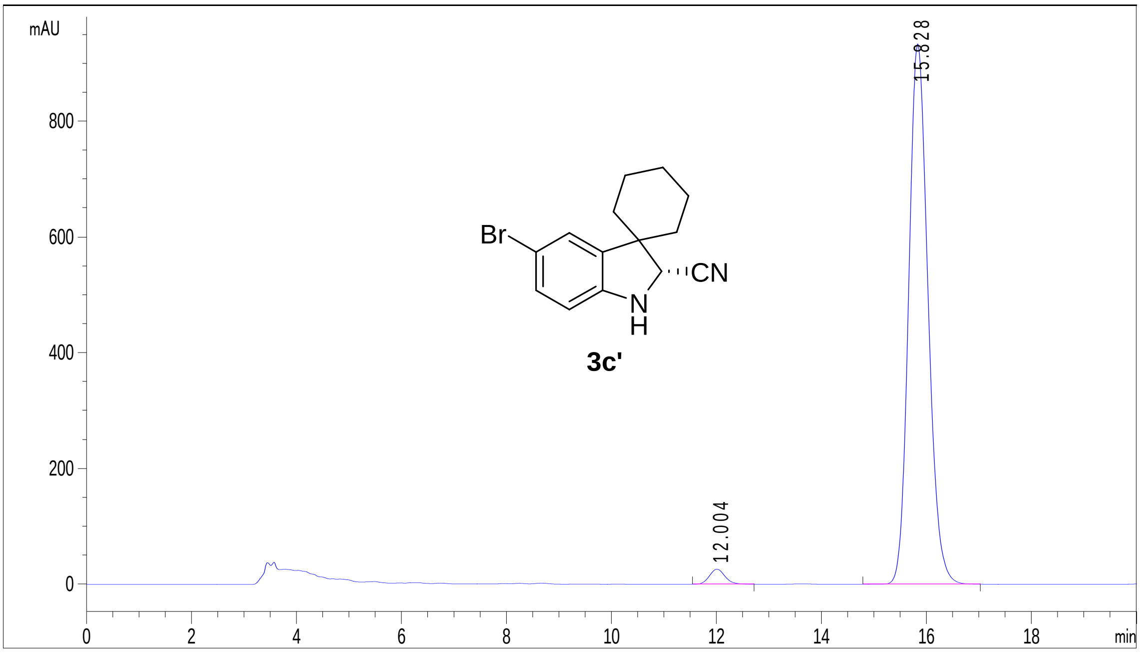
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.61	492.4	25	0.3287	0.846	1.715
2	17.413	28225.4	1096.1	0.3922	0.734	98.285



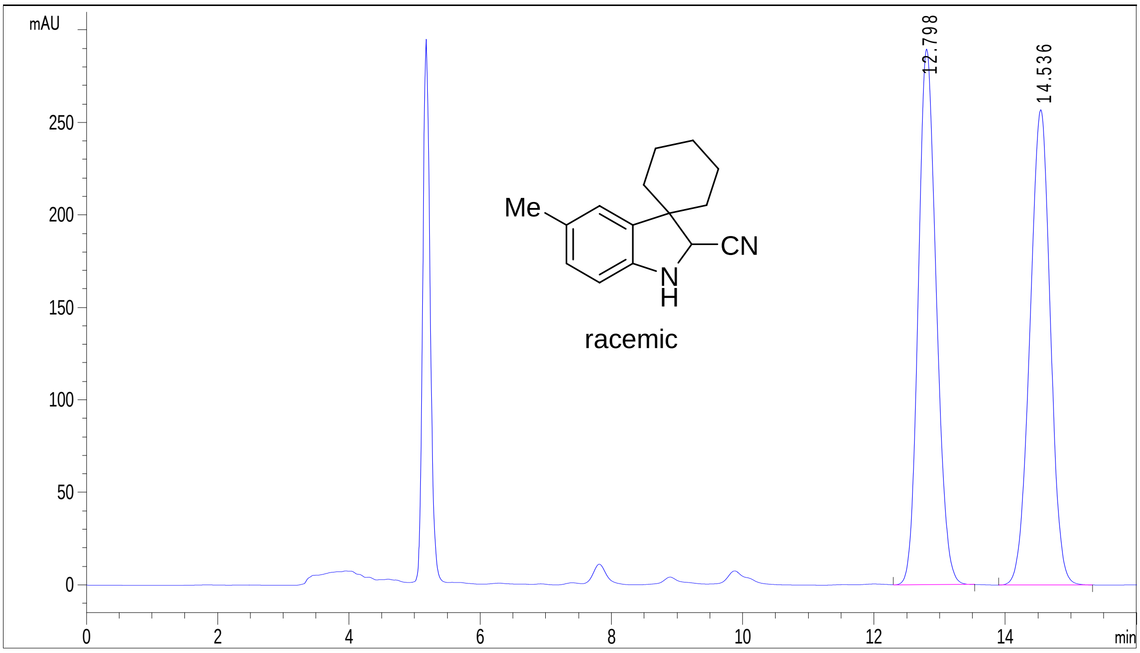
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.991	6524.8	267.4	0.3852	0.917	50.091
2	17.479	6501.1	222.2	0.4578	0.935	49.909



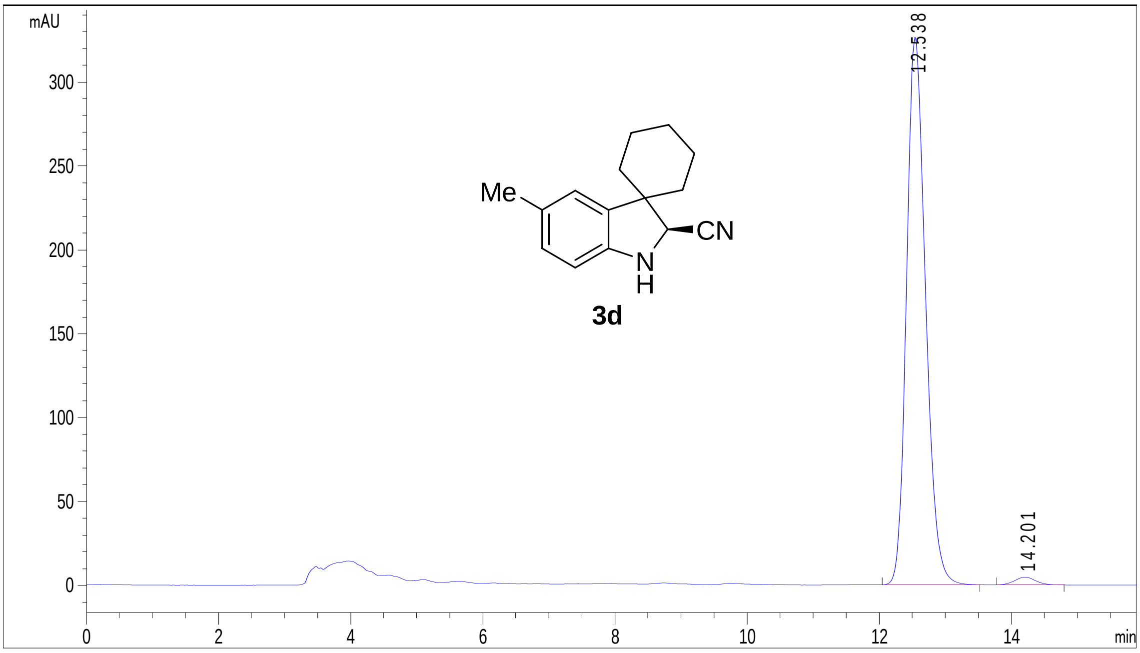
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.776	10497.5	429.6	0.3797	0.83	98.775
2	18.882	130.2	4.1	0.4864	0.892	1.225



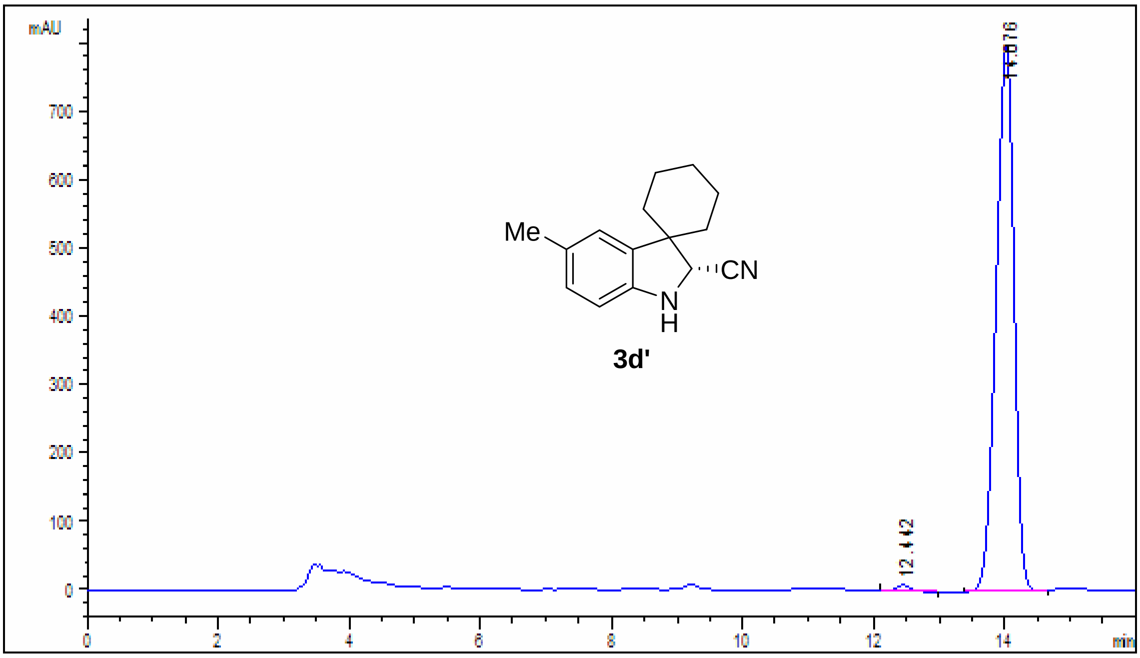
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.004	544.4	26.1	0.3234	0.878	2.234
2	15.828	23828.7	933.8	0.3953	0.822	97.766



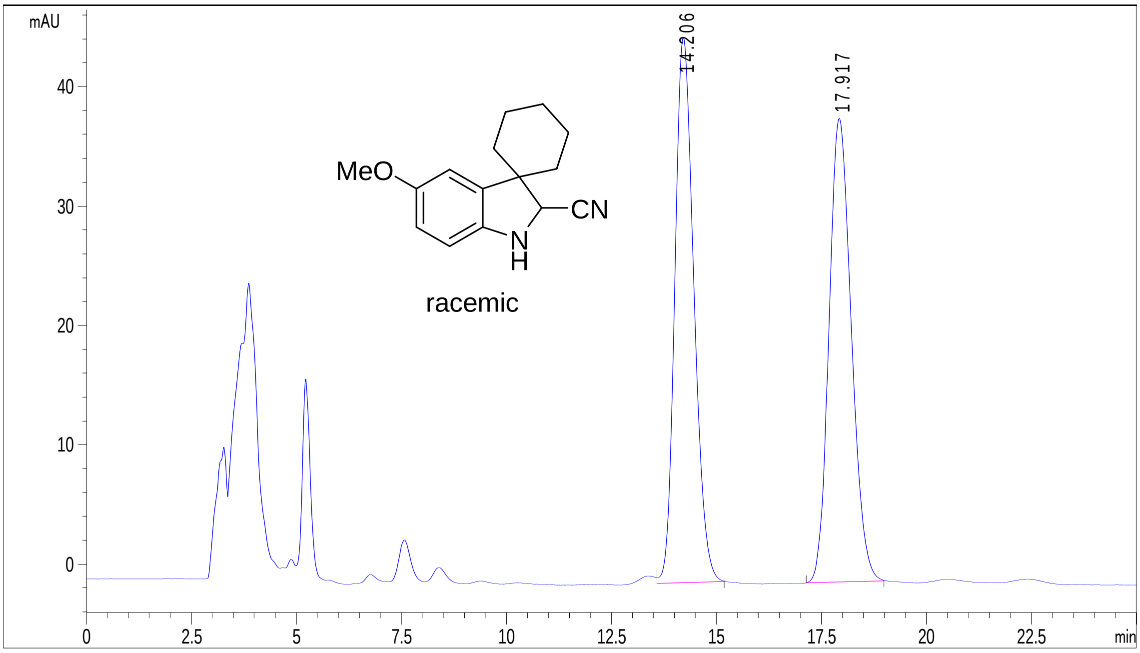
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.798	5562.9	289.7	0.2968	0.808	49.956
2	14.536	5572.8	257	0.3374	1.057	50.044



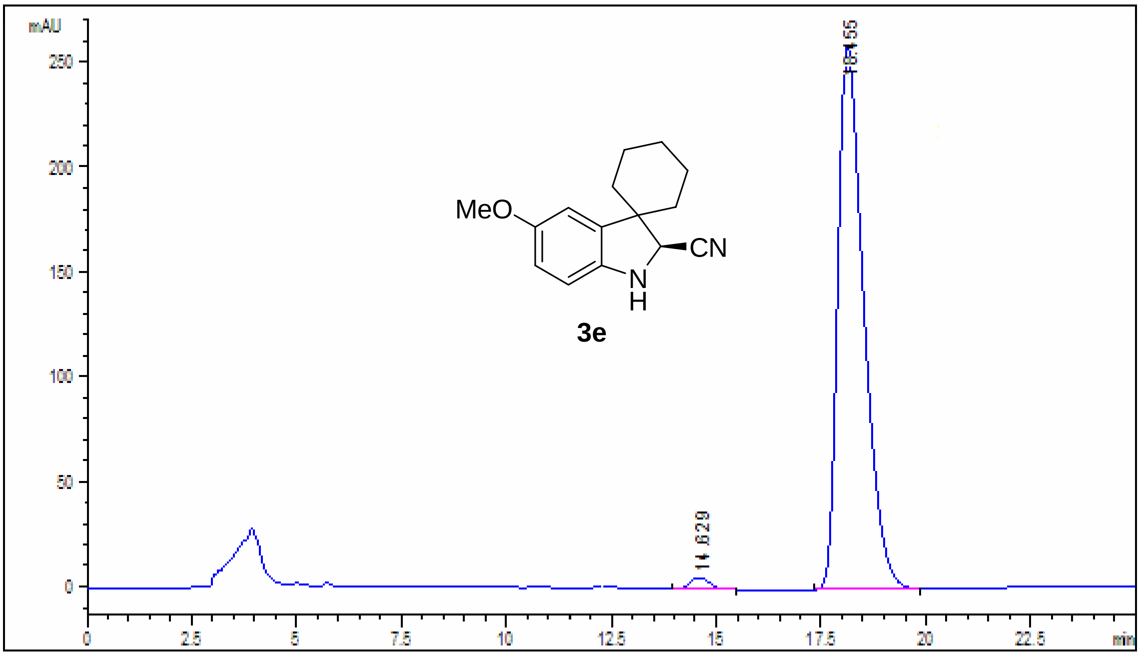
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.538	6533.2	326.3	0.3093	0.758	98.457
2	14.201	102.4	4.6	0.3429	0.907	1.543



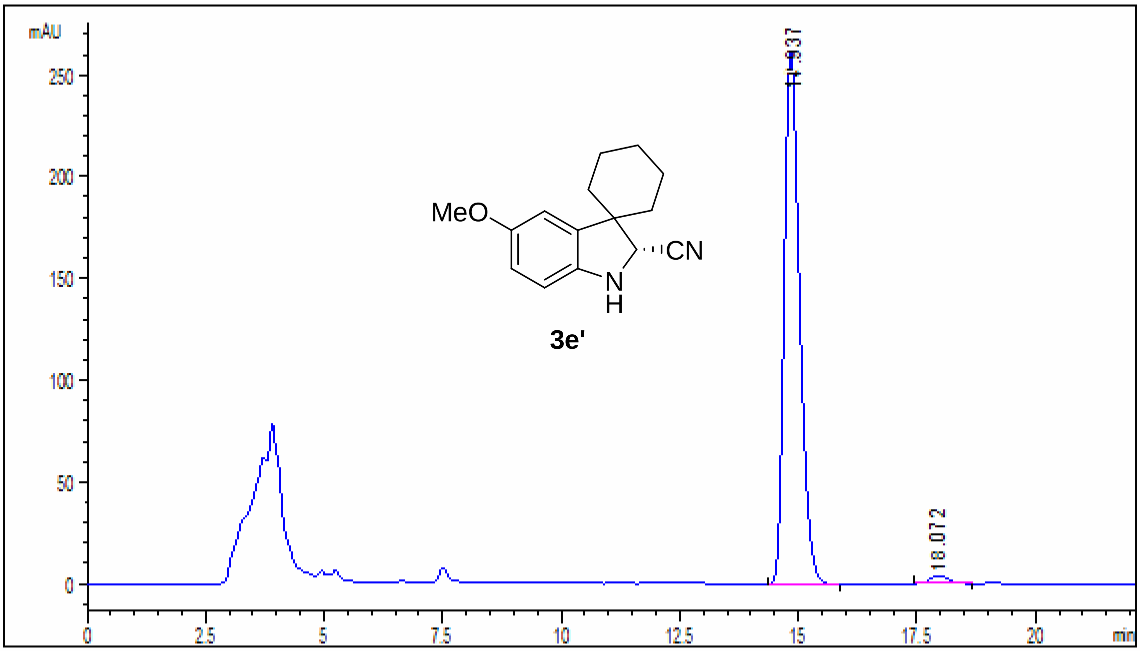
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.442	163.5	9.7	0.2586	0.957	1.064
2	14.076	15195.9	797.5	0.2966	1.271	98.936



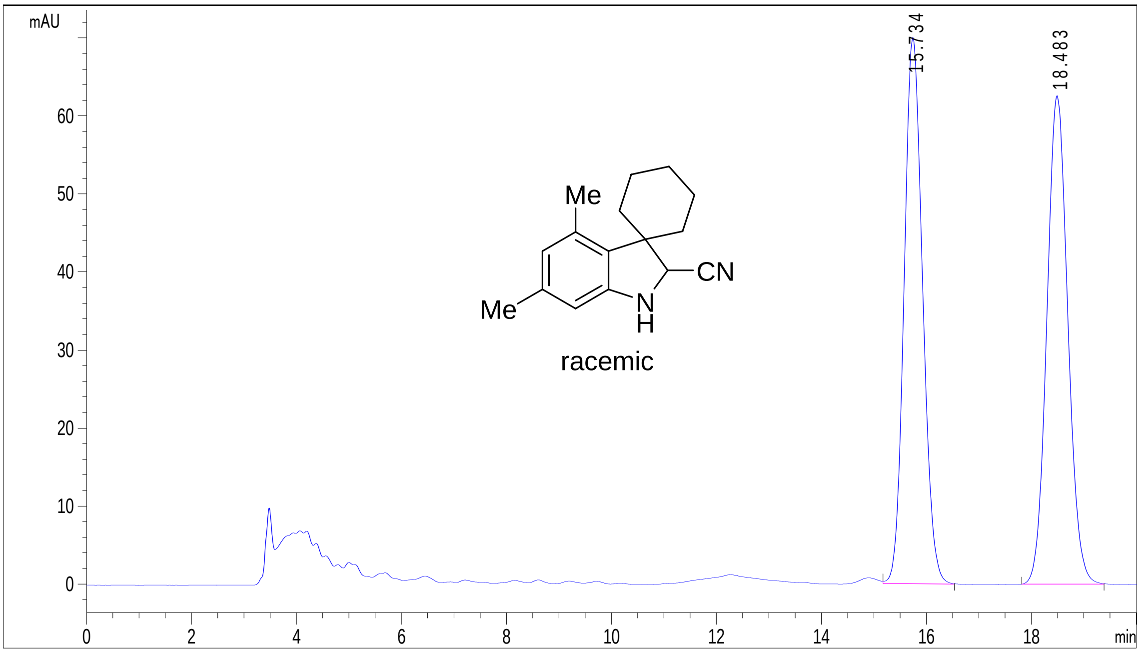
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.206	1442.7	45.7	0.4875	0.758	50.103
2	17.917	1436.8	38.9	0.574	0.8	49.897



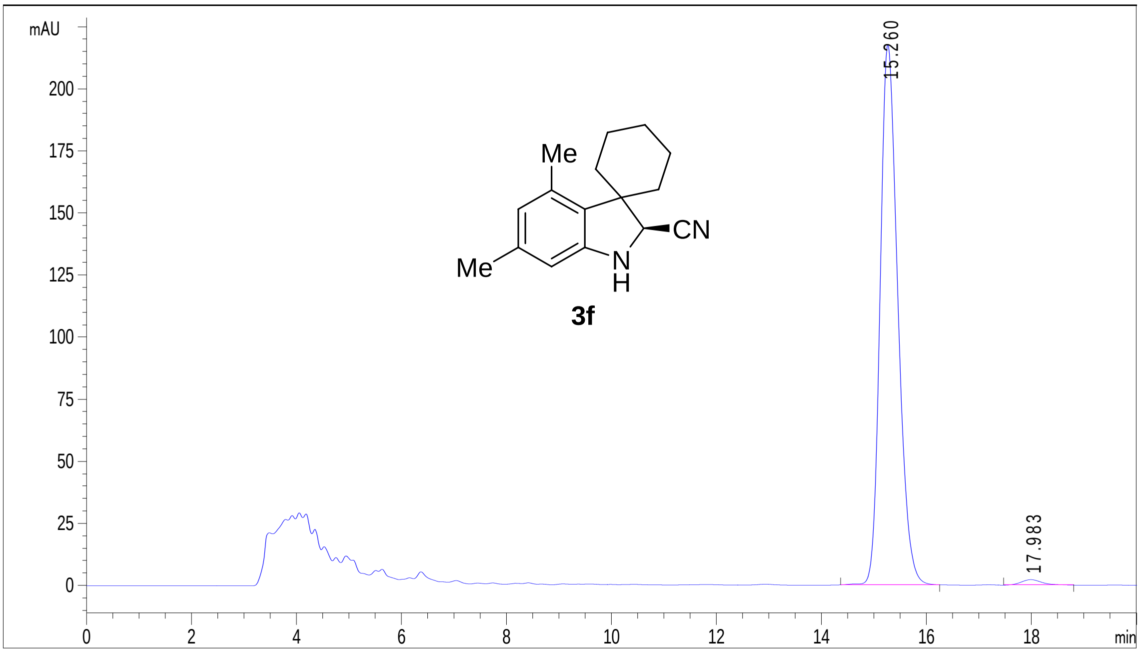
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.629	185.4	5.6	0.5175	0.858	1.638
2	18.455	11136.2	259.7	0.6518	0.555	98.362



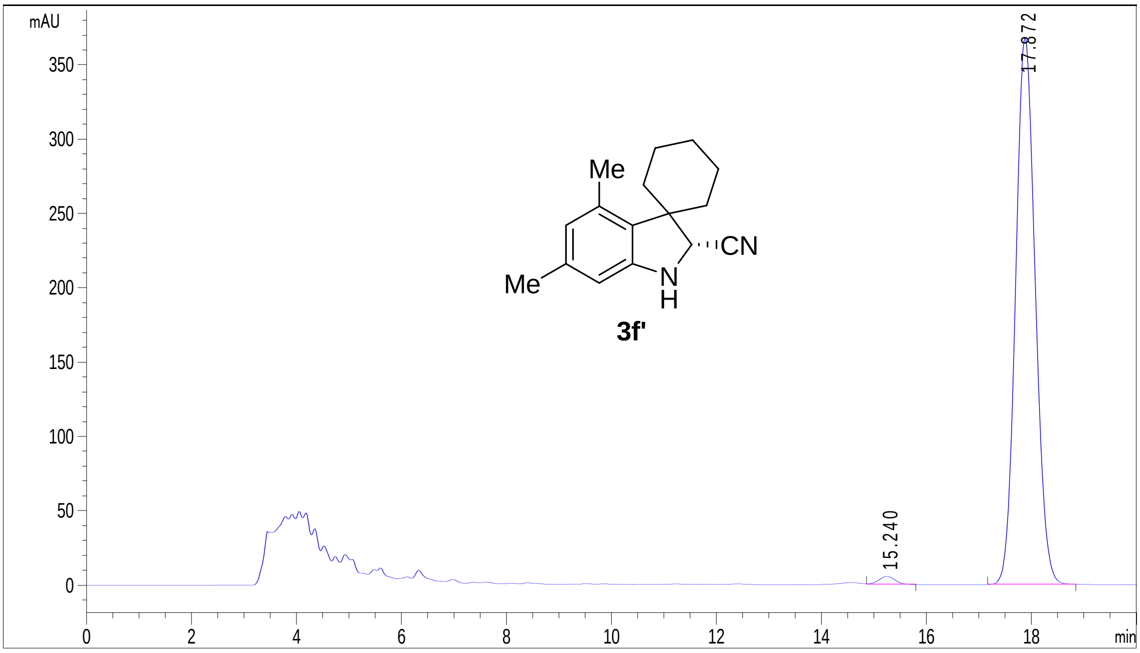
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.937	5974.5	262.4	0.3501	0.673	98.233
2	18.072	107.5	4	0.4189	0.887	1.767



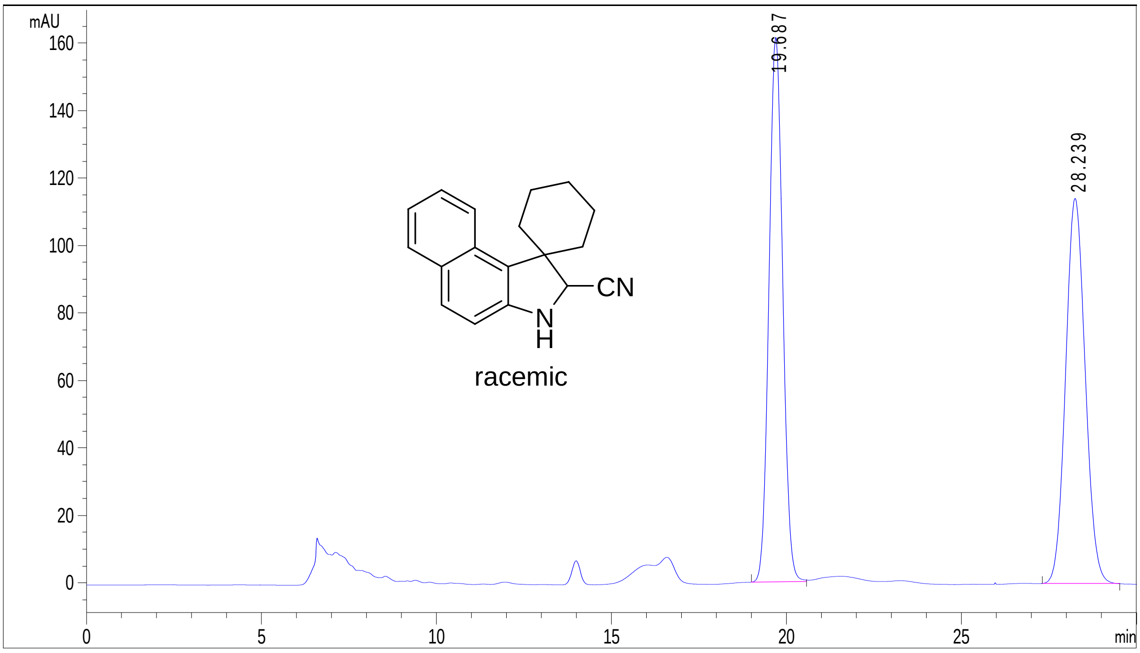
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.734	1719.8	70.1	0.3808	0.845	49.702
2	18.483	1740.4	62.7	0.4302	0.908	50.298



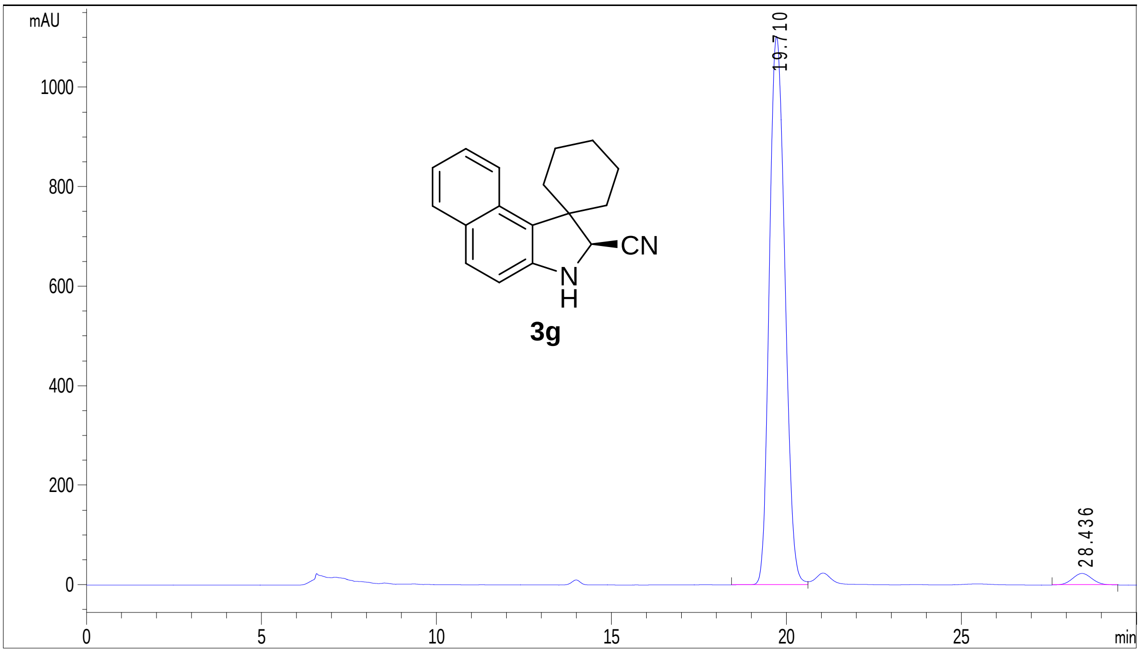
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.26	5081.7	217.6	0.3598	0.734	98.795
2	17.983	62	2.2	0.4259	0.784	1.205



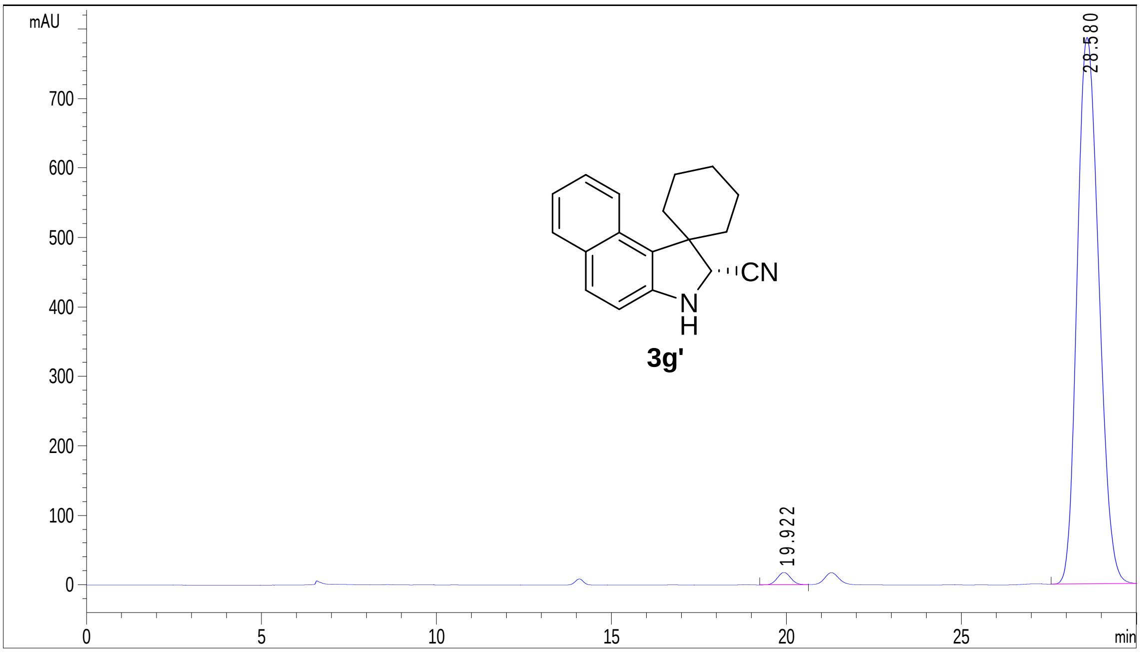
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.24	124.4	5.5	0.3455	0.982	1.284
2	17.872	9562.8	368.1	0.405	0.877	98.716



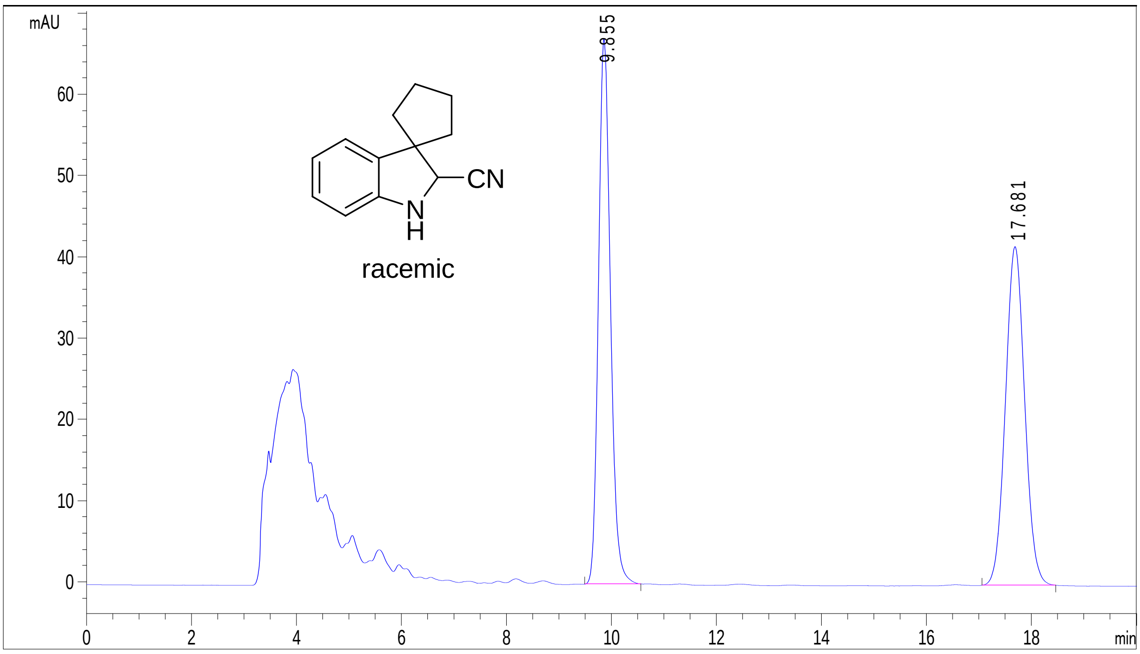
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	19.687	4391.7	161.5	0.425	0.917	49.695
2	28.239	4445.6	114.3	0.6053	0.894	50.305



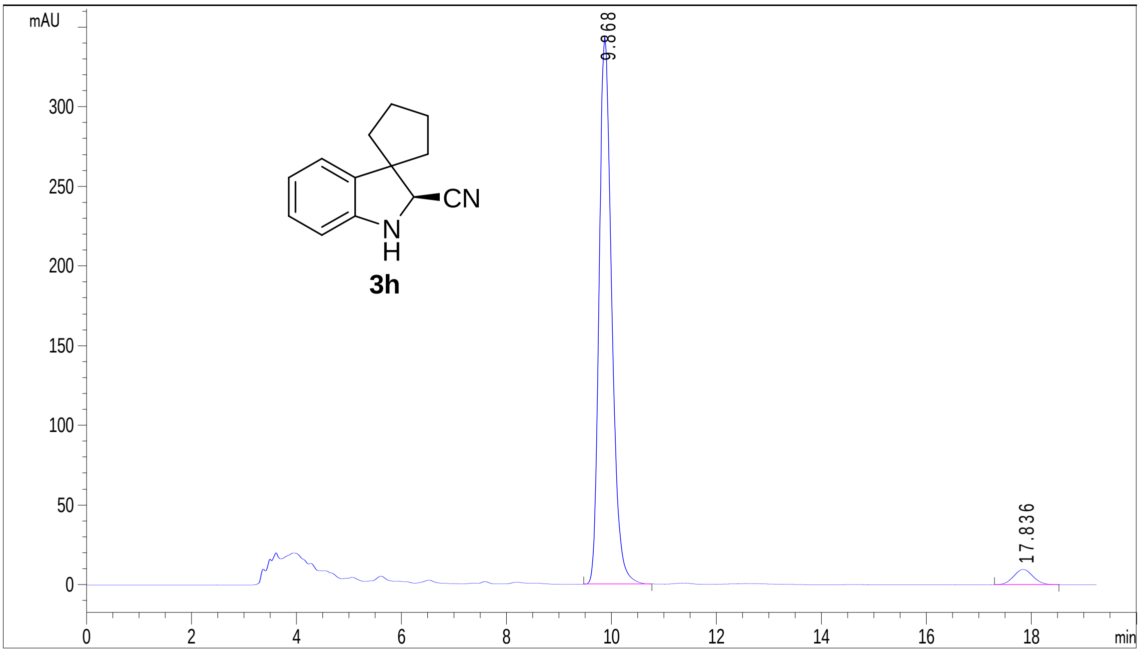
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	19.71	34101.7	1102.5	0.4977	0.808	97.408
2	28.436	907.3	23.3	0.6082	0.929	2.592



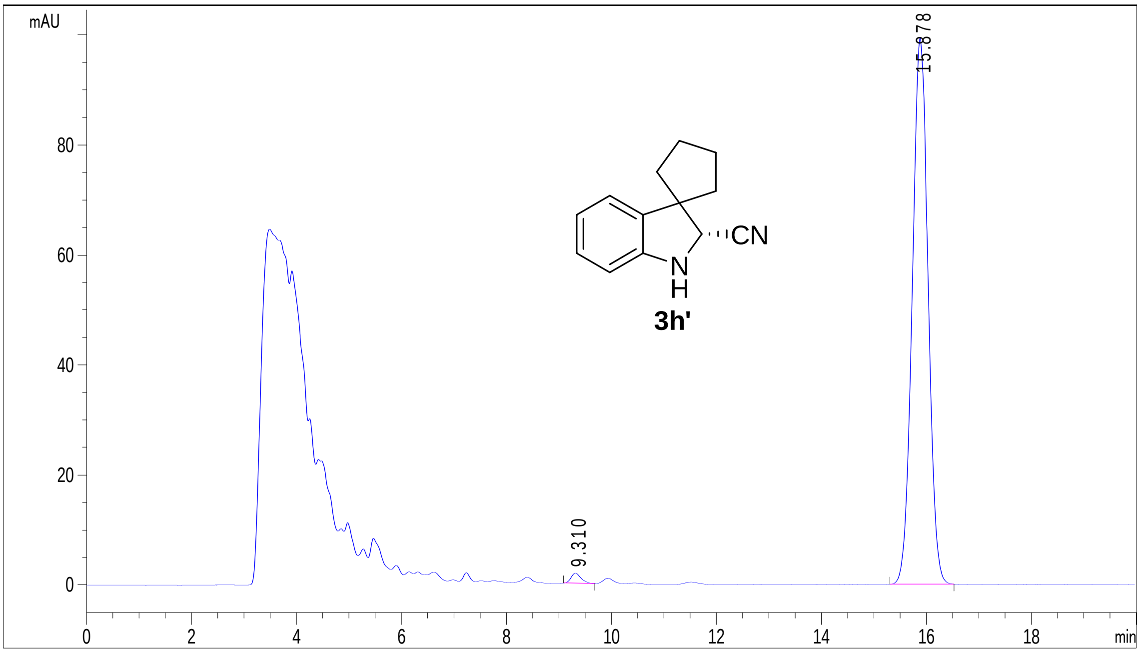
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	19.922	490.5	17.9	0.4237	0.919	1.422
2	28.58	34008.6	787.4	0.6859	0.79	98.578



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.855	1060.4	67.1	0.2455	0.813	49.925
2	17.681	1063.6	41.7	0.395	0.945	50.075

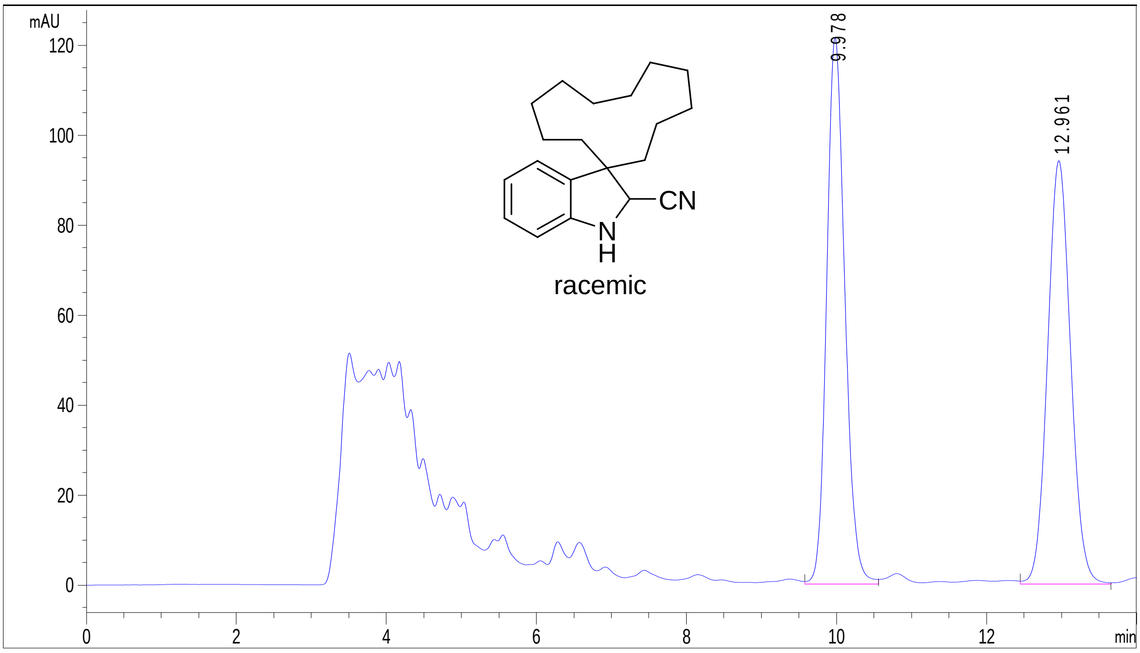


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.868	5715.5	344	0.2579	0.734	95.799
2	17.836	250.7	9.7	0.4002	0.931	4.201

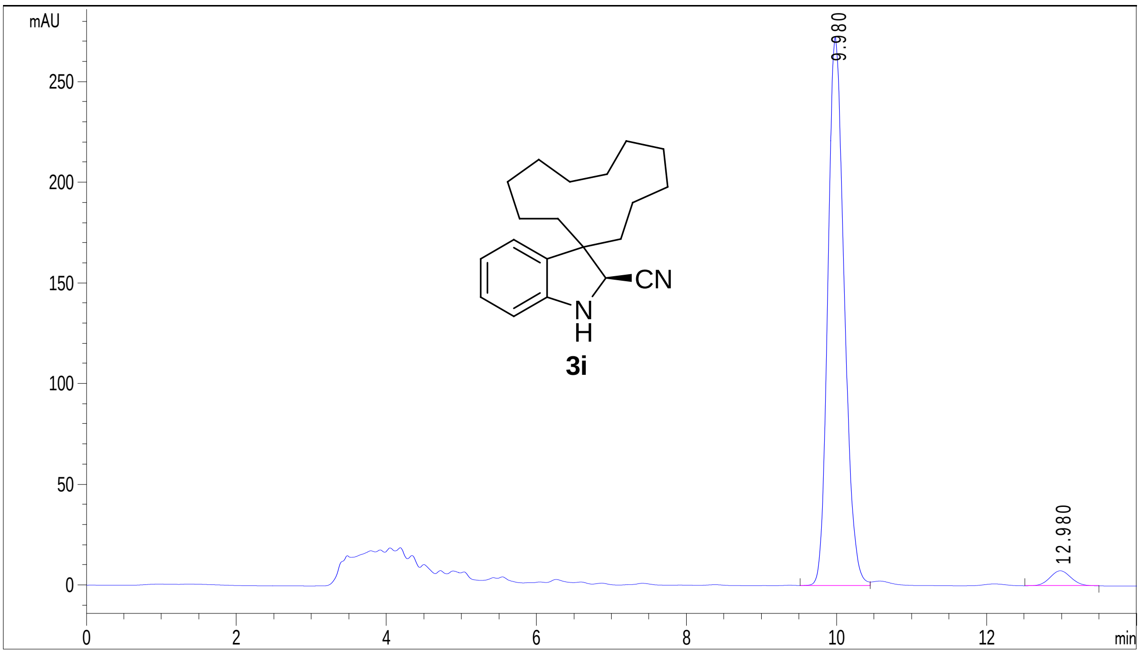


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.31	25.4	1.9	0.2007	0.748	1.207
2	15.878	2077.1	99.5	0.3251	0.99	98.793

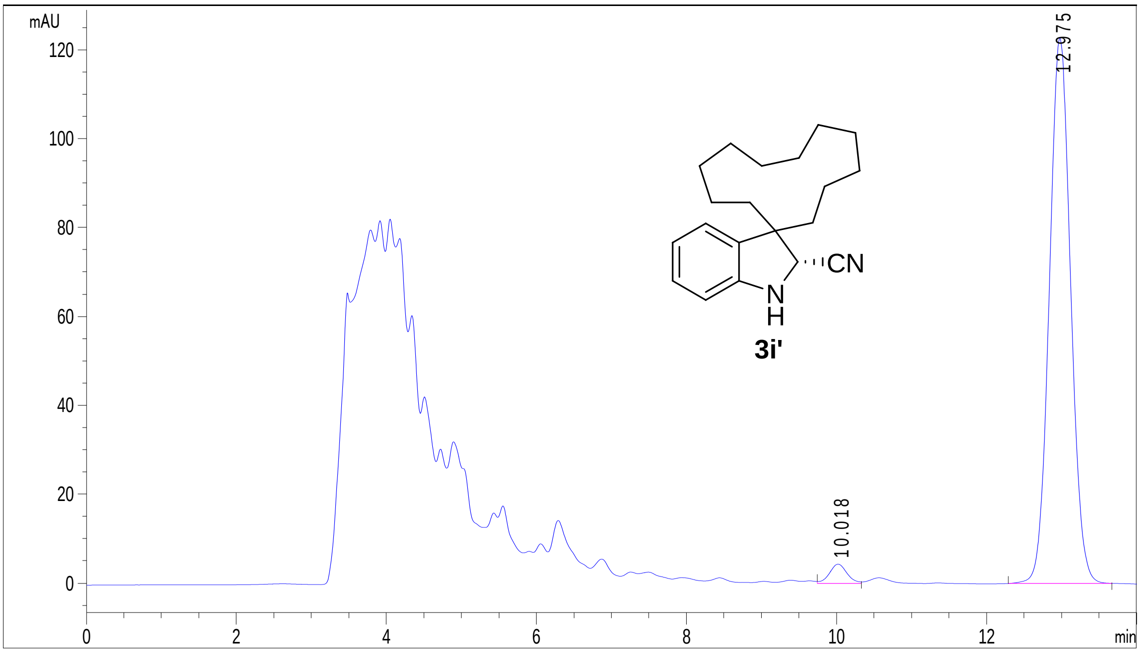
Electronic Supplementary Material (ESI) for Chemical Communications



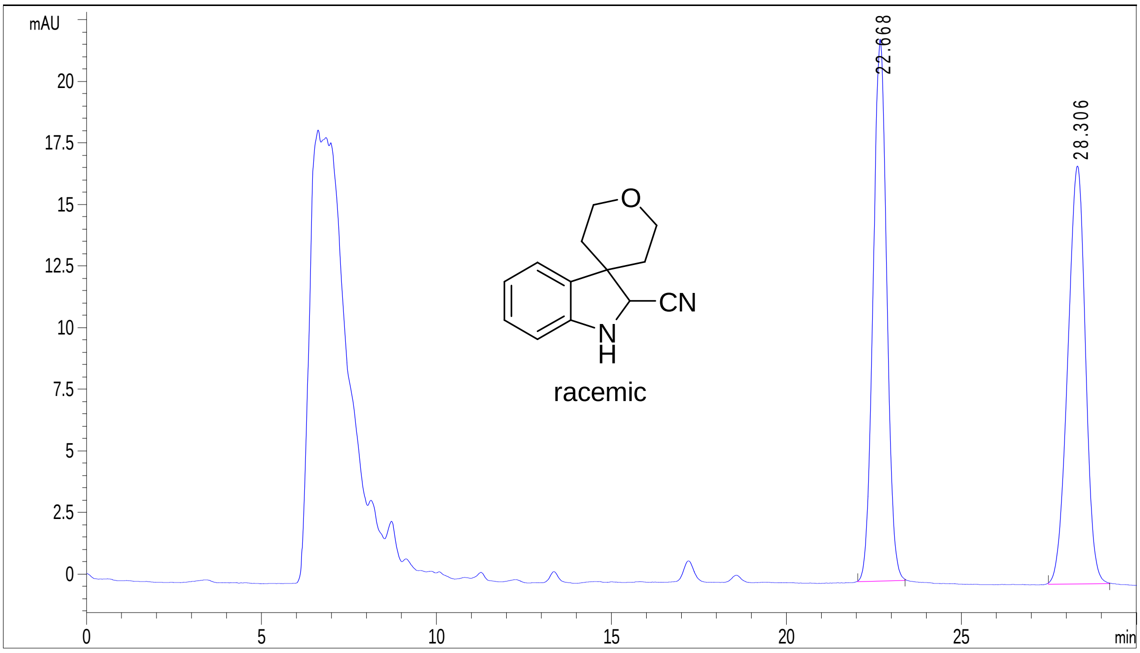
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.978	2053.3	121.6	0.2611	0.807	50.525
2	12.961	2010.6	94.1	0.3322	0.913	49.475



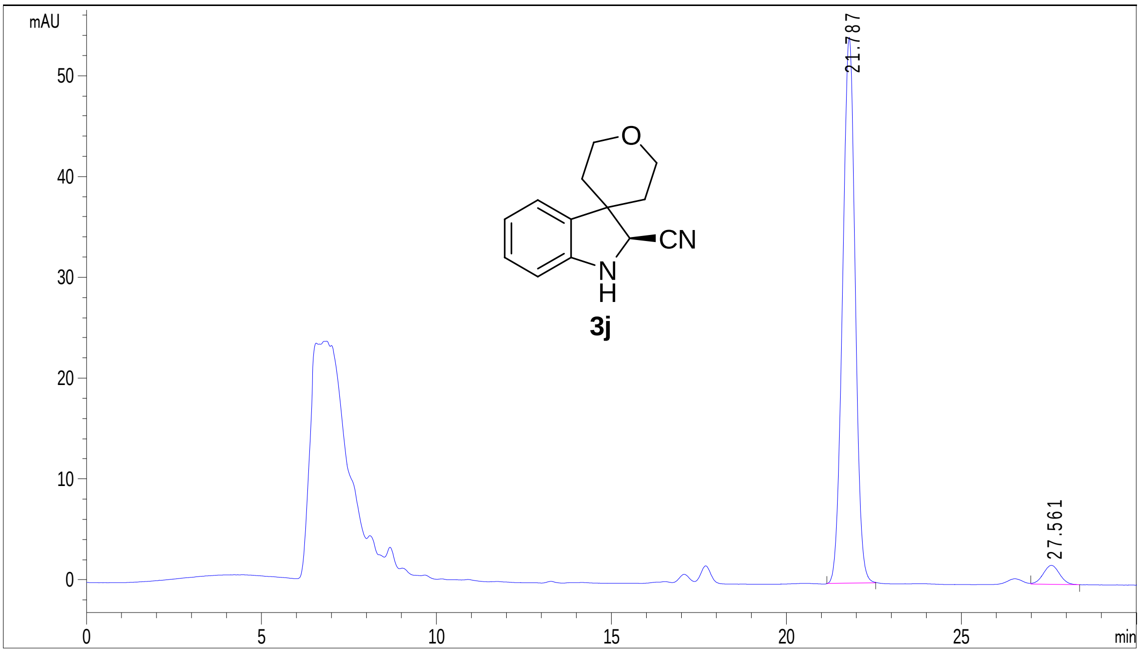
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.98	4142.8	272.7	0.2355	0.775	96.559
2	12.98	147.6	7.5	0.3065	0.925	3.441



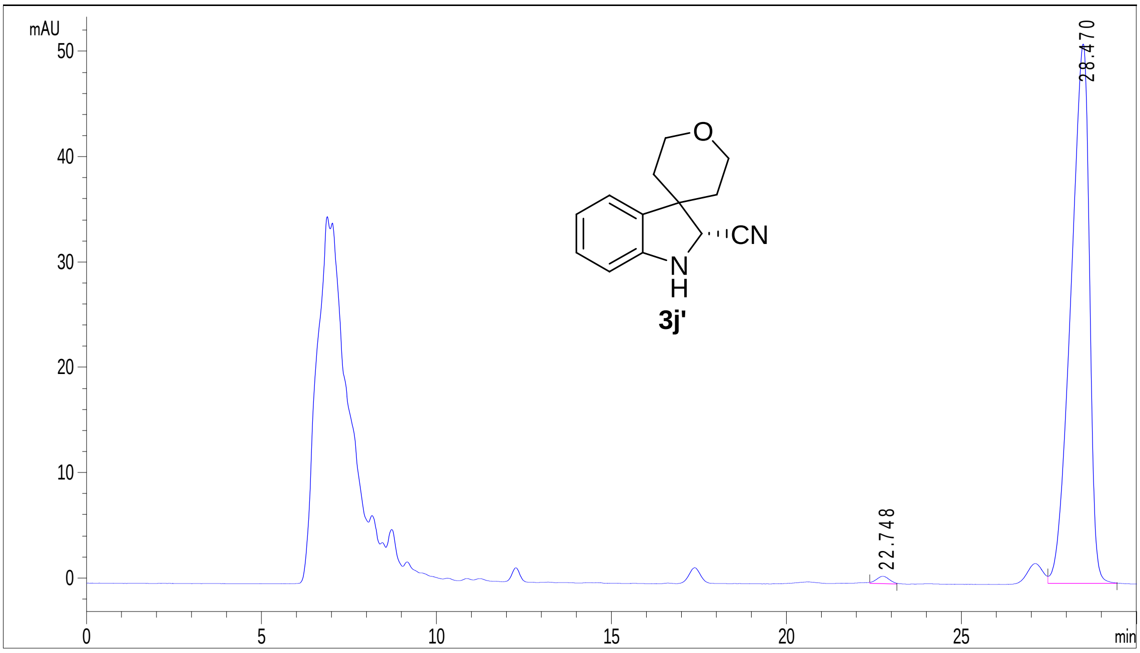
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.018	73.5	4.4	0.2517	0.928	2.931
2	12.975	2432.6	123	0.308	0.946	97.069



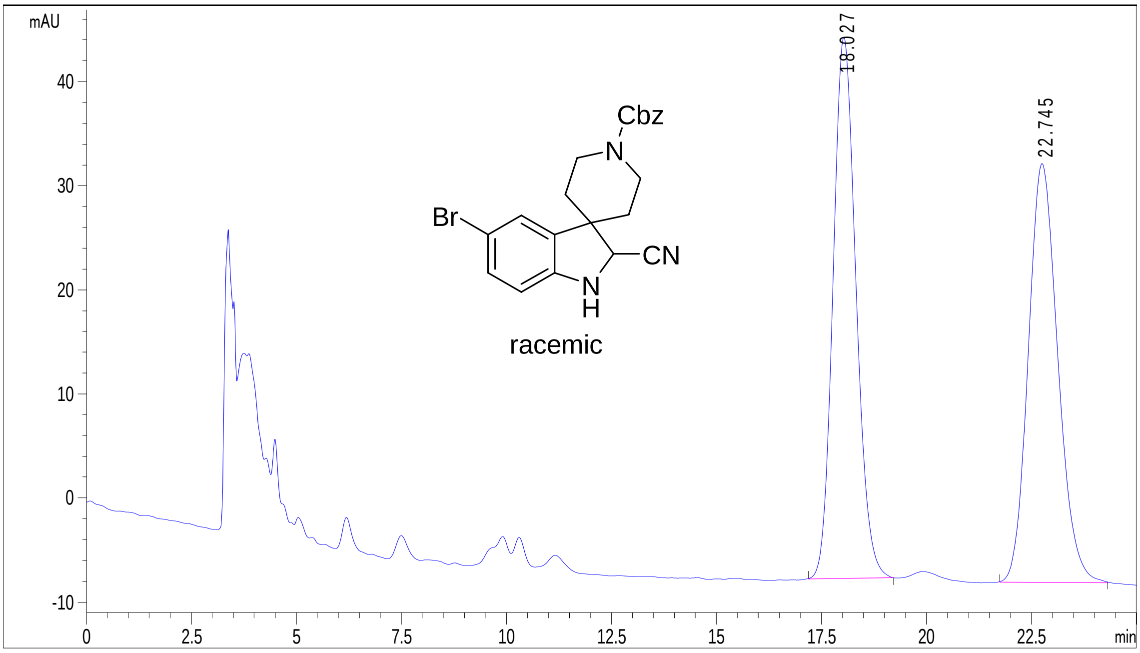
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	22.668	598.4	22	0.4221	0.997	50.107
2	28.306	595.8	17	0.5437	1.153	49.893



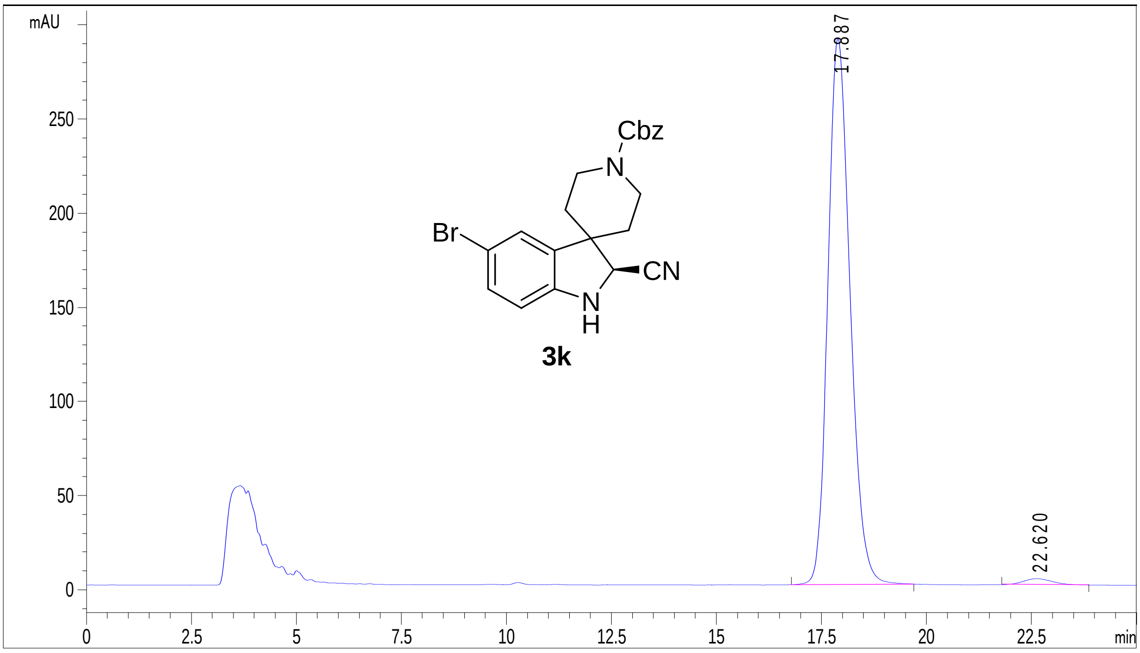
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	21.787	1357.1	54.2	0.3913	1.063	95.622
2	27.561	62.1	1.9	0.4975	0.962	4.378



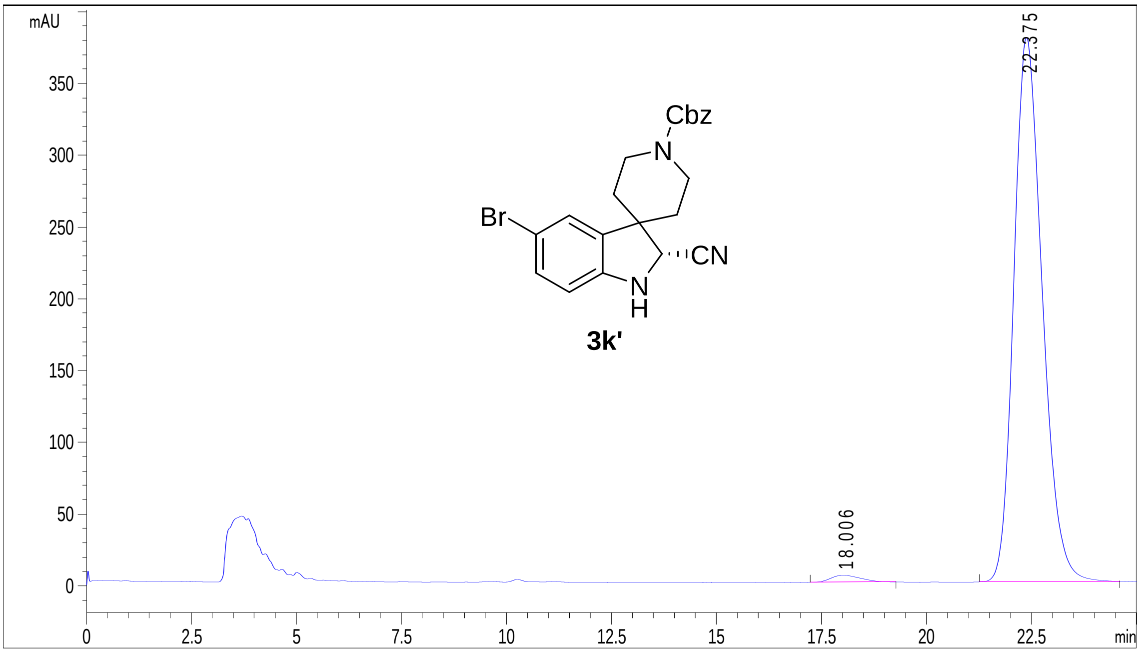
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	22.748	18.6	7.2E-1	0.4335	0.929	0.980
2	28.47	1884.9	51.2	0.5617	1.882	99.020



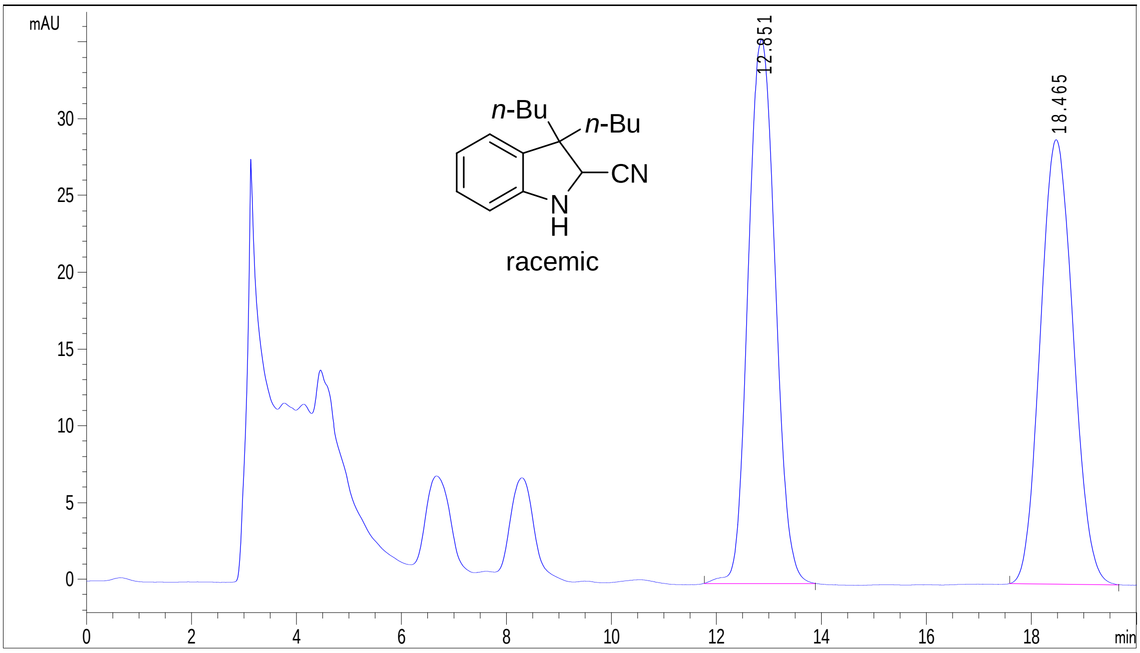
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	18.027	1978.7	52	0.5895	0.837	50.132
2	22.745	1968.3	40.2	0.7554	0.826	49.868



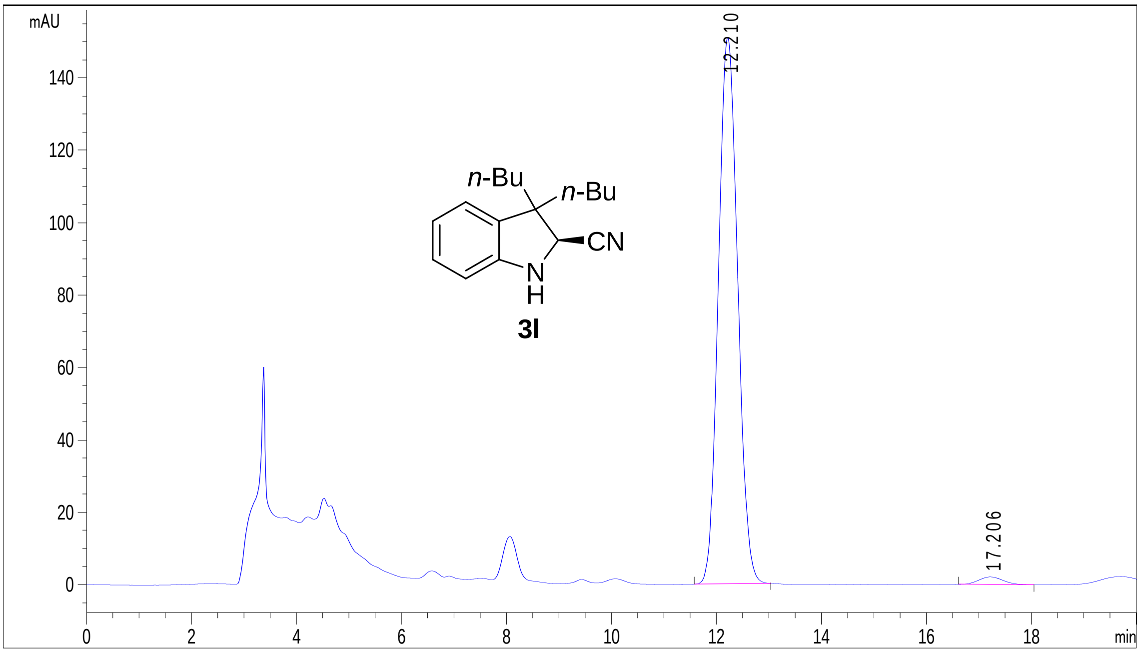
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	17.887	10641.1	290.3	0.5674	0.784	98.543
2	22.62	157.4	3.3	0.6665	0.831	1.457



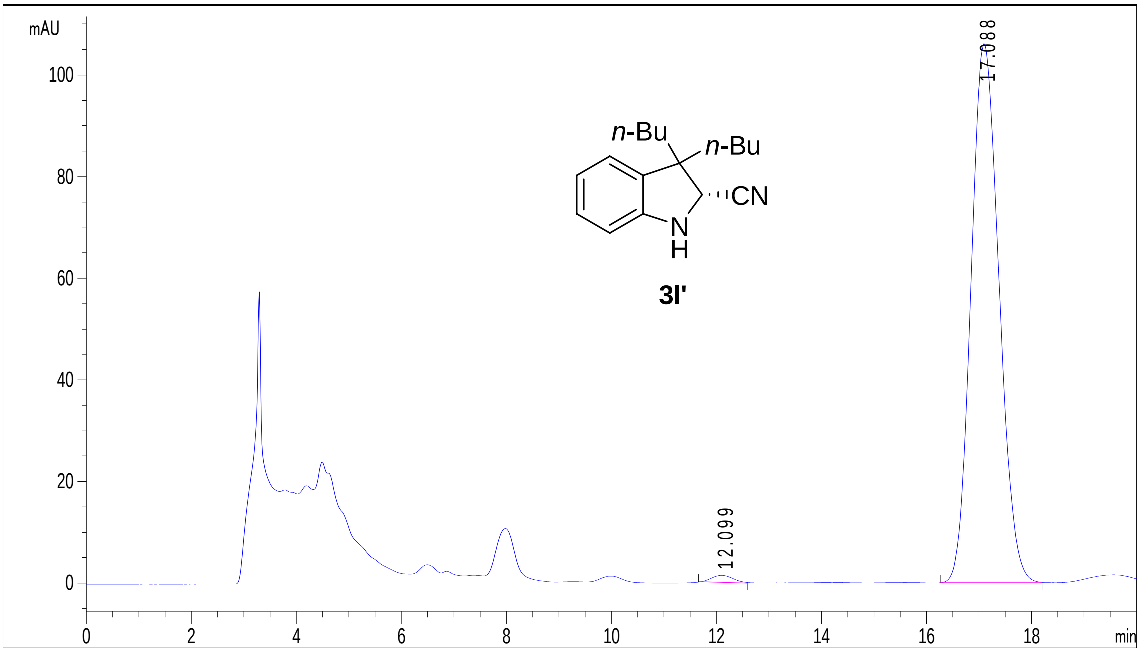
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	18.006	240.8	4.9	0.7233	0.657	1.333
2	22.375	17821	379.2	0.7274	0.754	98.667



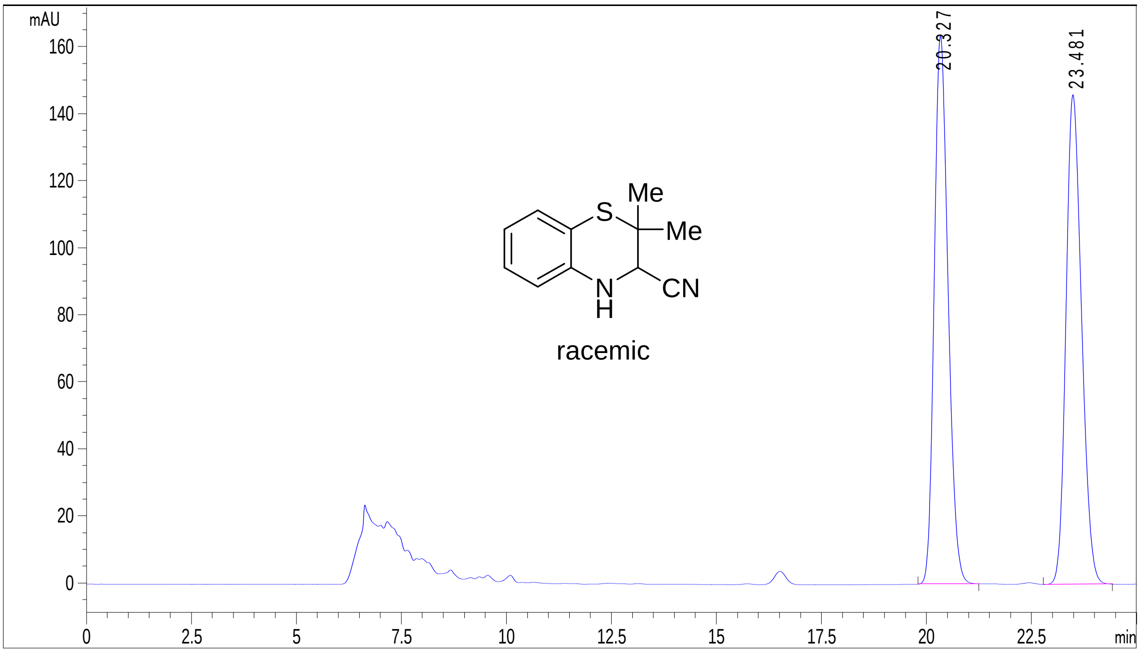
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.851	1277.2	35.5	0.5742	0.909	50.276
2	18.465	1263.1	29	0.6877	0.887	49.724



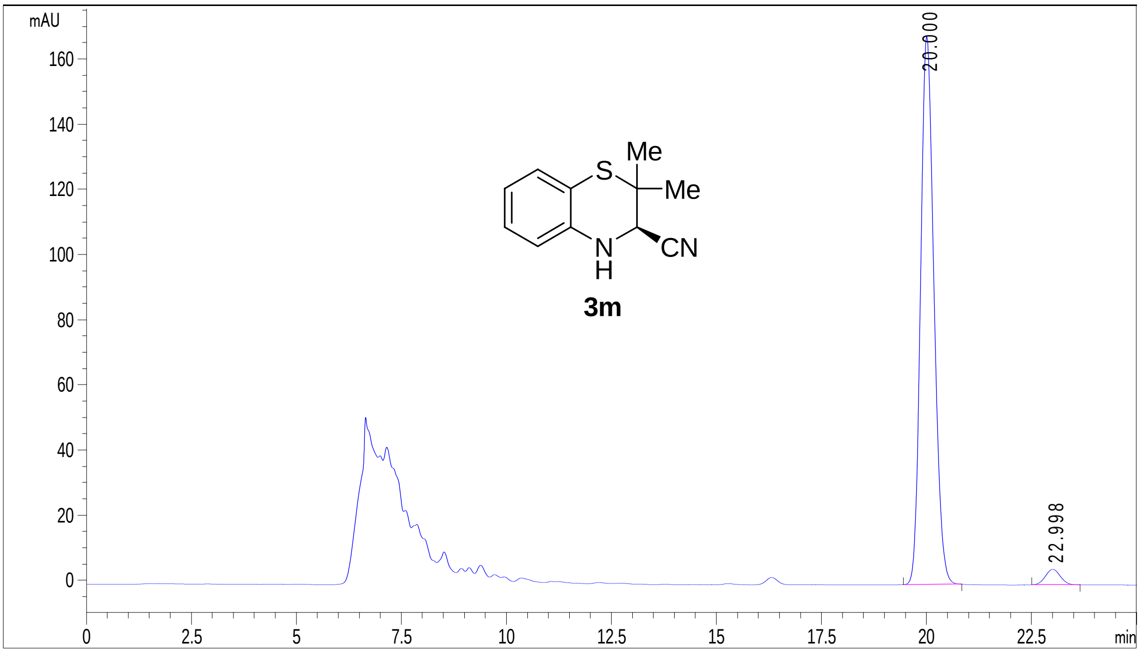
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.21	3856.9	151	0.4013	0.891	98.204
2	17.206	70.5	2.1	0.4958	0.868	1.796



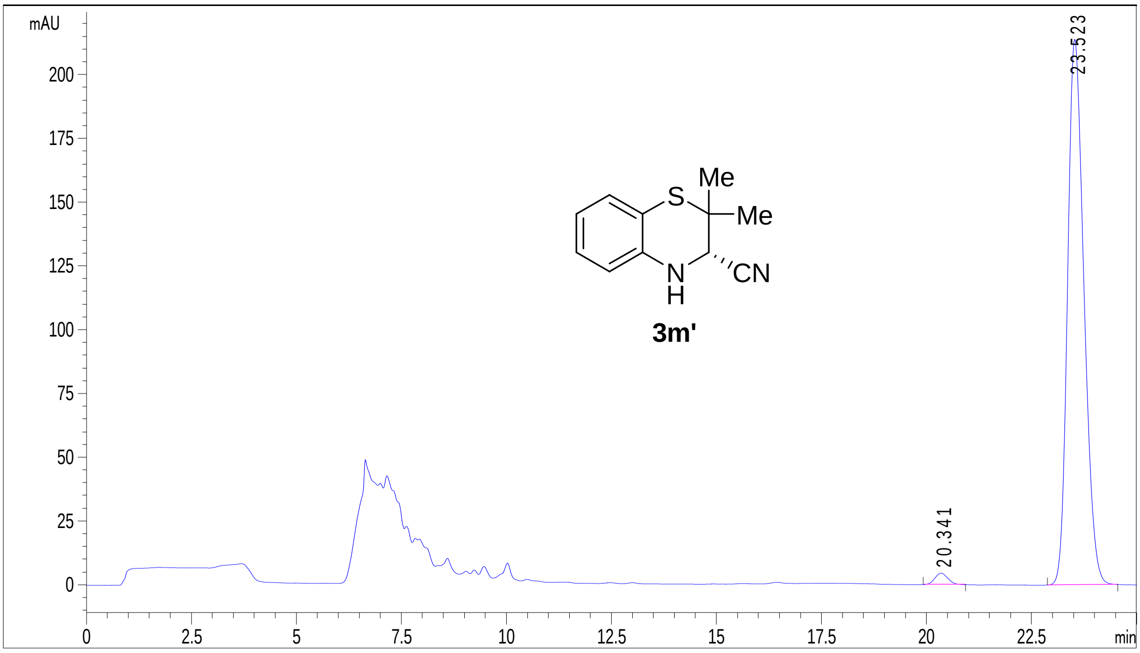
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.099	43.3	1.5	0.4958	0.812	1.091
2	17.088	3929.7	106.1	0.5806	0.831	98.756



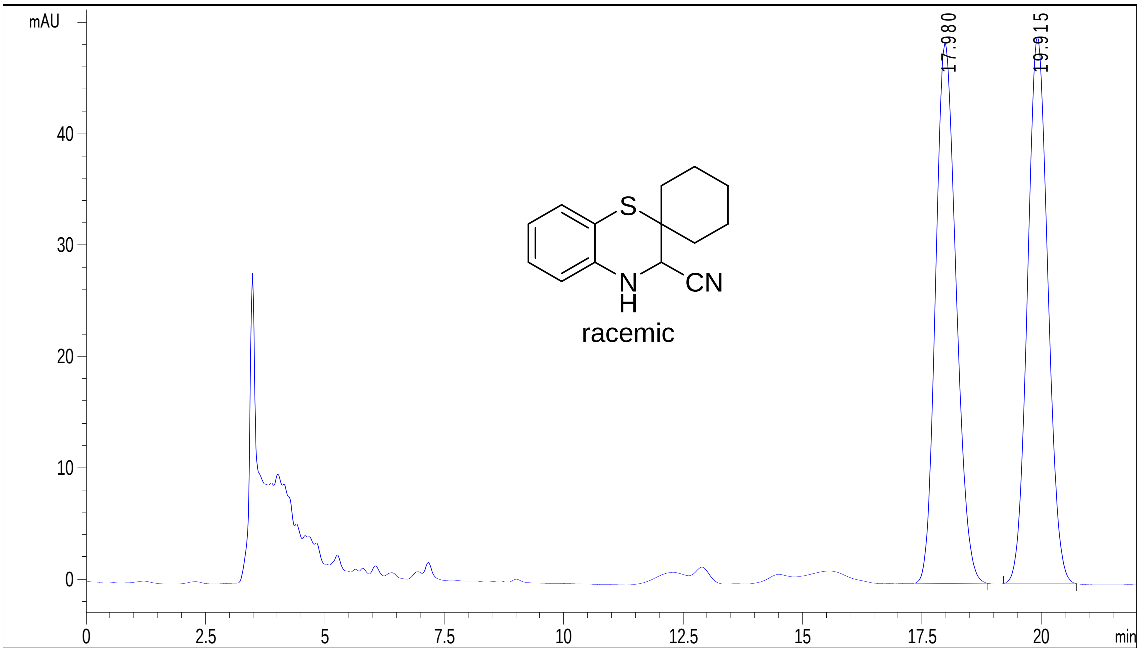
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	20.327	3742.7	163.8	0.354	0.773	49.798
2	23.481	3773.1	146	0.4004	0.767	50.202



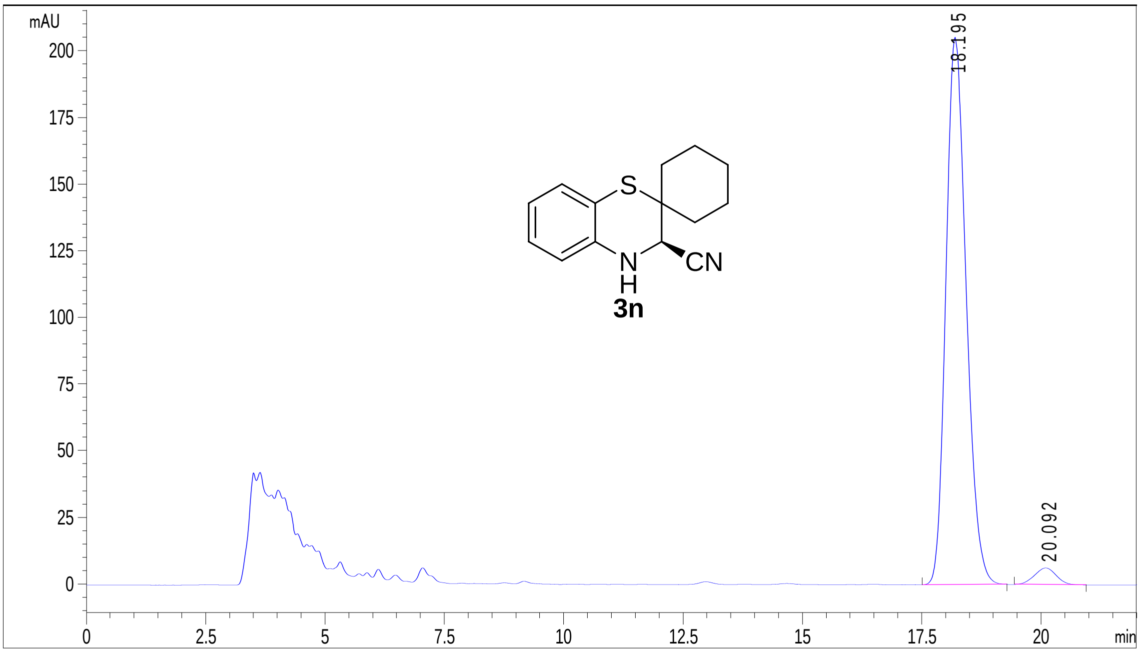
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	20	3721.7	168.3	0.3439	0.803	96.879
2	22.998	119.9	4.8	0.3845	0.928	3.121



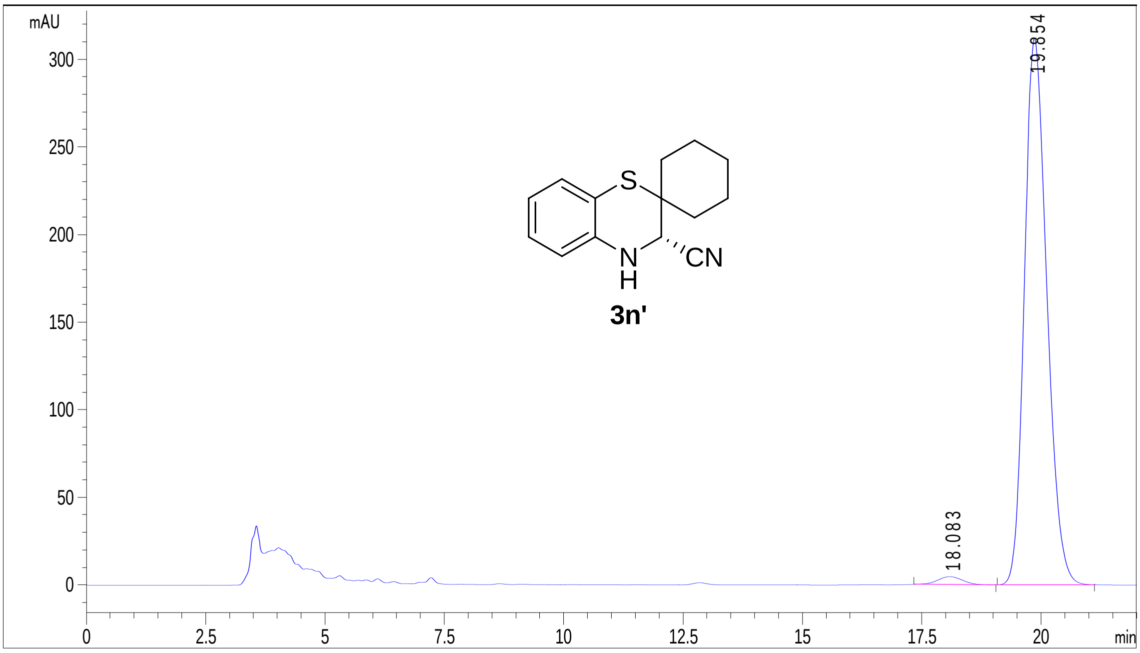
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	20.341	100.1	4.6	0.3426	0.867	1.701
2	23.523	5787.4	214	0.4175	0.726	98.299



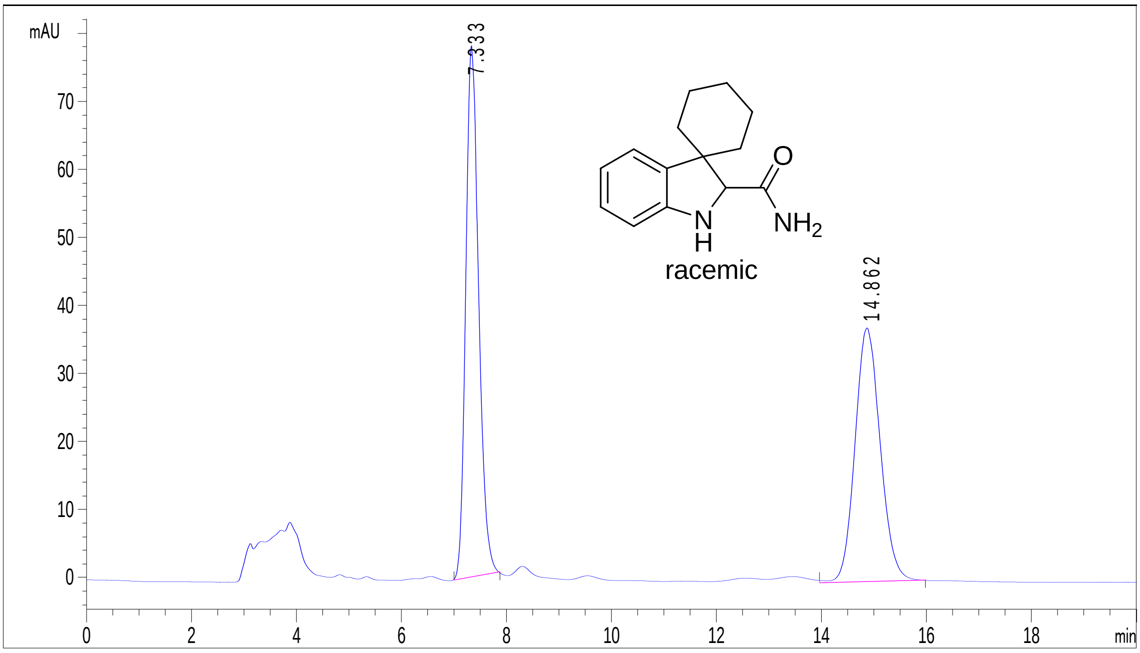
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	17.98	1457	48.5	0.4682	0.802	49.934
2	19.915	1460.8	49.1	0.4634	0.91	50.066



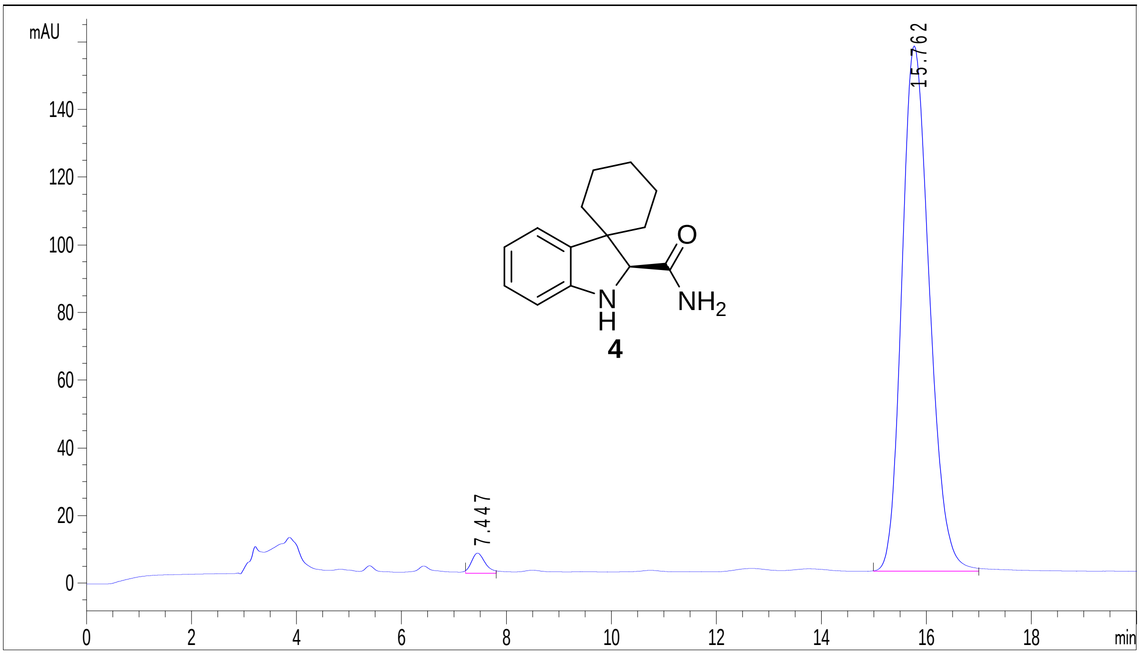
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	18.195	6058.5	205.4	0.4562	0.784	96.794
2	20.092	200.7	6.3	0.4925	1.044	3.206



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	18.083	169.6	4.6	0.5766	0.98	1.641
2	19.854	10166.5	312.1	0.5053	0.757	98.359

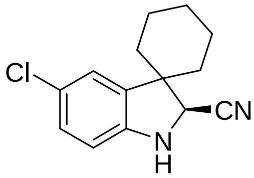


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	7.333	1332.9	78.1	0.2843	0.786	51.761
2	14.862	1242.2	37.3	0.5552	0.878	48.239



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	7.447	115.2	6.1	0.3124	0.766	1.991
2	15.762	5671.9	155.3	0.6088	0.783	98.009

The crystal data of compound **3b** have been deposited in CCDC with number 837035.



3b

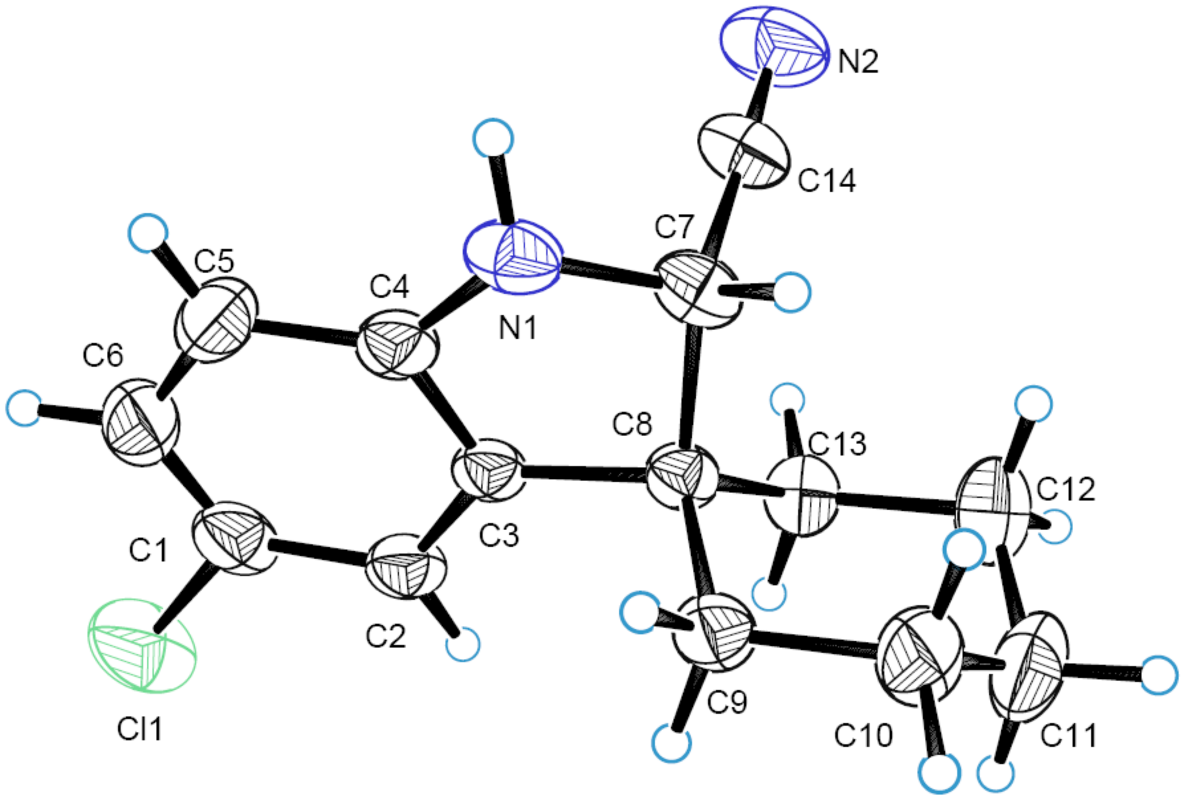


Table 1 Crystal data and structure refinement for 110726

Identification code	110726
Empirical formula	$C_{14}H_{15}ClN_2$
Formula weight	246.73
Temperature	291(2)
Crystal system	Monoclinic
Space group	$P2_1$
a/Å, b/Å, c/Å	7.2479(3), 7.0711(4), 13.0826(6)
α /°, β /°, γ /°,	90.00, 98.024(5), 90.00
Volume/Å^3	663.93(6)
Z	2
ρ_{calc}mg/mm^3	1.234
m/mm^{-1}	0.267
F(000)	260
Crystal size	0.42 × 0.36 × 0.31
Theta range for data collection	3.15 to 26.37°
Index ranges	-9 ≤ h ≤ 9, -8 ≤ k ≤ 8, -16 ≤ l ≤ 13
Reflections collected	6023
Independent reflections	2686[R(int) = 0.0243]
Data/restraints/parameters	2686/2/158
Goodness-of-fit on F^2	1.024
Final R indexes [I>2 σ (I)]	R_1 = 0.0460, wR_2 = 0.0895
Final R indexes [all data]	R_1 = 0.0640, wR_2 = 0.0981
Largest diff. peak/hole	0.231/-0.272

Table 2 Atomic Coordinates (Å×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 110726. $U_{eq}$is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	12948.5(11)	2115.1(19)	5499.4(6)	107.8(4)
N1	8674(3)	-1218(3)	1808.7(17)	56.1(6)
C3	9339(3)	1177(3)	2972.5(17)	41.8(5)
C8	7666(3)	1857(3)	2226.3(16)	41.4(5)
C7	7822(4)	472(4)	1310.1(18)	48.8(6)
C9	5868(3)	1420(4)	2686.2(18)	54.1(7)
C4	9850(3)	-620(4)	2690.3(19)	48.8(6)
N2	9890(4)	1769(4)	-16.1(19)	79(7)
C2	10257(3)	2027(4)	3845.3(17)	52.2(6)
C5	11274(4)	-1601(4)	3273(3)	67.7(8)
C10	4113(3)	2106(5)	2008(2)	73(9)
C14	8982(4)	1244(4)	564.5(19)	56.6(7)
C13	7728(4)	3949(4)	1936(2)	53(6)
C1	11712(4)	1045(5)	4412(2)	65.6(8)
C12	5967(4)	4573(5)	1236(3)	73.8(9)
C6	12215(4)	-724(5)	4143(2)	74(9)
C11	4245(4)	4182(6)	1741(3)	88.9(11)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 110726. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	63.1(4)	193.1(11)	61.2(4)	-14(6)	-12.1(4)	-10.7(6)
N1	78.8(16)	43.5(13)	50(13)	-6.6(11)	22.6(12)	-6.9(11)
C3	38.2(11)	51.1(14)	38.4(11)	0.8(11)	13.5(10)	-1.9(10)
C8	37.1(11)	48.8(14)	38.9(11)	-3(11)	7.1(9)	-4.5(11)
C7	52.4(15)	53.8(15)	41.1(13)	-2.1(11)	10.4(11)	-15.9(12)
C9	42.5(12)	72.1(18)	49.2(13)	6.3(13)	11.9(11)	-0.2(12)
C4	50.5(14)	52.6(16)	47.4(15)	5.7(12)	21.8(12)	0.6(12)
N2	110.6(19)	73.6(19)	60.5(14)	3.4(13)	38.9(14)	-8.6(15)
C2	42.2(12)	70.5(17)	45.2(12)	-7.7(13)	10.6(10)	-2.3(13)
C5	68(19)	62.5(19)	79(2)	20.8(16)	32.1(17)	22.3(15)
C10	38.3(13)	108(3)	72(17)	14.3(19)	6.9(12)	-0.9(16)
C14	73.2(18)	58.6(16)	40(12)	-2.8(13)	15.2(13)	-10.5(14)
C13	53(15)	47.3(15)	57.3(16)	0(13)	3(12)	-3.3(12)
C1	40.2(14)	112(3)	45.3(14)	2.5(17)	8.6(12)	-2.3(16)
C12	70.8(19)	61.4(18)	84(2)	17.1(16)	-6.2(17)	4.3(15)
C6	48.9(16)	110(3)	65(2)	26(2)	15.7(15)	19.7(18)
C11	54.3(19)	110(3)	99(3)	21(2)	-1(17)	27(2)

Table 4 Bond Lengths for 110726.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C1	1.745(3)	C9	C10	1.525(3)
N1	C4	1.400(3)	C4	C5	1.382(4)
N1	C7	1.457(3)	N2	C14	1.135(3)
C3	C2	1.377(3)	C2	C1	1.388(4)
C3	C4	1.388(3)	C5	C6	1.389(4)
C3	C8	1.524(3)	C10	C11	1.515(5)
C8	C13	1.529(4)	C13	C12	1.529(4)
C8	C9	1.541(3)	C1	C6	1.363(4)
C8	C7	1.564(3)	C12	C11	1.516(4)
C7	C14	1.478(4)			

Table 5 Bond Angles for 110726.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C4	N1	C7	107.0(2)	C5	C4	C3	121.3(2)
C2	C3	C4	120.3(2)	C5	C4	N1	128.7(3)
C2	C3	C8	130.0(2)	C3	C4	N1	110.0(2)
C4	C3	C8	109.65(19)	C3	C2	C1	117.9(3)
C3	C8	C13	114.55(18)	C4	C5	C6	118.2(3)
C3	C8	C9	109.08(18)	C11	C10	C9	111.6(2)
C13	C8	C9	110.3(2)	N2	C14	C7	177.4(3)
C3	C8	C7	99.04(18)	C12	C13	C8	112.1(2)
C13	C8	C7	114.07(19)	C6	C1	C2	122.2(3)
C9	C8	C7	109.21(19)	C6	C1	Cl1	118.9(2)
N1	C7	C14	110.7(2)	C2	C1	Cl1	118.9(3)
N1	C7	C8	104.01(18)	C11	C12	C13	110.8(2)
C14	C7	C8	112.52(19)	C1	C6	C5	120.2(3)
C10	C9	C8	113.0(2)	C10	C11	C12	111.1(3)

Table 6 Hydrogen Bonds for 110726.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	N2	0.871(17)	2.200(19)	3.048(3)	164(3)

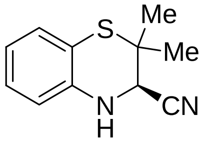
Table 7 Torsion Angles for 110726.

A	B	C	D	Angle/•
C2	C3	C8	C13	42.8(3)
C4	C3	C8	C13	-140.6(2)
C2	C3	C8	C9	-81.4(3)
C4	C3	C8	C9	95.3(2)
C2	C3	C8	C7	164.6(2)
C4	C3	C8	C7	-18.8(2)
C4	N1	C7	C14	89.5(2)
C4	N1	C7	C8	-31.6(3)
C3	C8	C7	N1	29.6(2)
C13	C8	C7	N1	151.8(2)
C9	C8	C7	N1	-84.3(2)
C3	C8	C7	C14	-90.3(2)
C13	C8	C7	C14	31.9(3)
C9	C8	C7	C14	155.8(2)
C3	C8	C9	C10	178.2(2)
C13	C8	C9	C10	51.6(3)
C7	C8	C9	C10	-74.6(3)
C2	C3	C4	C5	0.3(3)
C8	C3	C4	C5	-176.7(2)
C2	C3	C4	N1	177.4(2)
C8	C3	C4	N1	0.4(3)
C7	N1	C4	C5	-162.9(3)
C7	N1	C4	C3	20.2(3)
C4	C3	C2	C1	1.1(3)
C8	C3	C2	C1	177.4(2)
C3	C4	C5	C6	-1.3(4)
N1	C4	C5	C6	-177.9(3)
C8	C9	C10	C11	-53.2(3)
N1	C7	C14	N2	35(6)

Table 8 Hydrogen Atom Coordinates ($Å\times10^4$) and Isotropic Displacement Parameters ($Å^2\times10^3$) for 110726.

Atom	*x*	*y*	*z*	U(eq)
H7	6576	171	955	59
H9A	5778	65	2784	65
H9B	5941	2014	3359	65
H2	9913	3222	4049	63
H5	11594	-2814	3088	81
H10A	3925	1368	1377	88
H10B	3045	1910	2367	88
H13A	7873	4706	2561	64
H13B	8803	4174	1587	64
H12B	6041	5915	1093	89
H12A	5876	3900	585	89
H6	13191	-1346	4544	89
H11B	4291	4934	2364	107
H11A	3144	4550	1275	107
H1	9110(4)	-1990(3)	1378(18)	66(9)

The crystal data of compound **3m** have been deposited in CCDC with number 832628.



3m

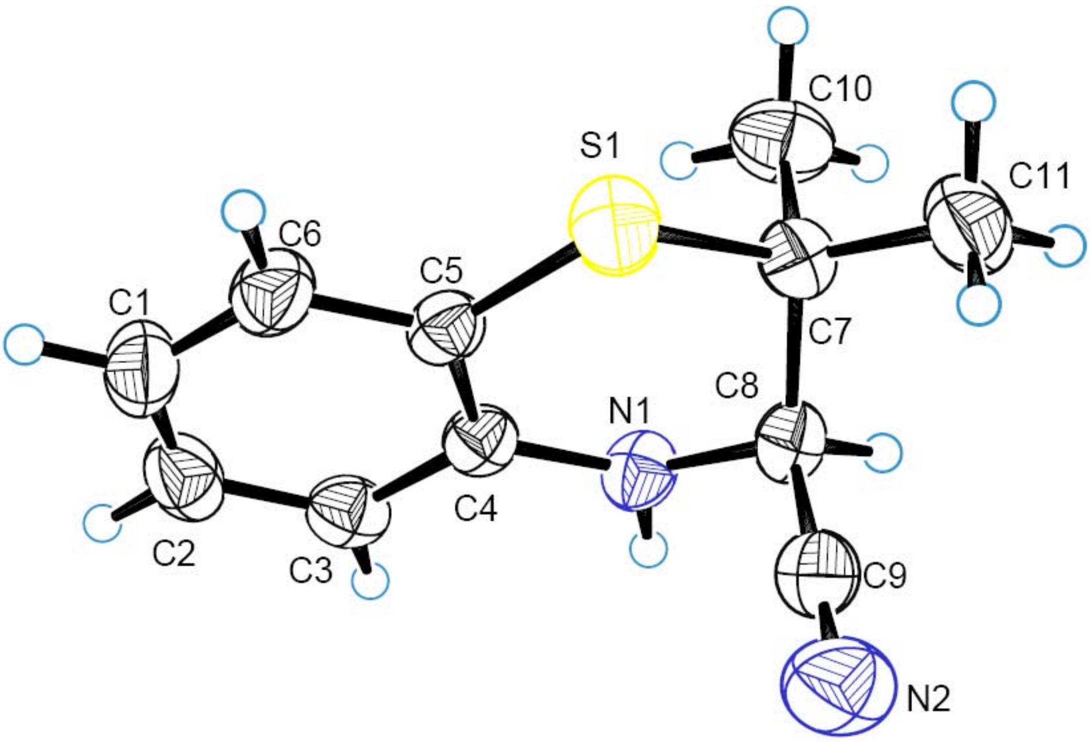


Table 1 Crystal data and structure refinement for syd110701

Identification code	syd110701
Empirical formula	$C_{11}H_{12}SN_2$
Formula weight	204.29
Temperature	291(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å, b/Å, c/Å	5.9323(3), 10.0252(8), 18.0127(16)
α /°, β /°, γ /°,	90.00, 90.00, 90.00
Volume/Å^3	1071.26(14)
Z	4
ρ_{calc}mg/mm^3	1.267
m/mm^{-1}	0.263
F(000)	432
Crystal size	0.42 × 0.36 × 0.32
Theta range for data collection	3.62 to 26.37°
Index ranges	$-7 \leq h \leq 7, -12 \leq k \leq 12, -22 \leq l \leq 22$
Reflections collected	9400
Independent reflections	2199[R(int) = 0.0294]
Data/restraints/parameters	2199/1/133
Goodness-of-fit on F^2	1.045
Final R indexes [I>2 σ (I)]	$R_1 = 0.0317$, $wR_2 = 0.0754$
Final R indexes [all data]	$R_1 = 0.0366$, $wR_2 = 0.0783$
Largest diff. peak/hole	0.156/-0.154

Table 2 Atomic Coordinates (Å×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for syd110701. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	5799.9(7)	10069.2(5)	8442.3(3)	53.65(15)
N2	7588(4)	11426.4(18)	10337.5(11)	72.3(5)
C6	5458(3)	7397(19)	8621.1(11)	50.6(5)
N1	10454(3)	9376.2(15)	9149.4(9)	43.8(4)
C4	8943(3)	8331.5(16)	9066.8(9)	37.4(4)
C7	8385(3)	11058.9(17)	8418.2(11)	44.4(4)
C1	6101(4)	6142(2)	8848.3(11)	59.1(5)
C3	9565(3)	7052.1(17)	9299.2(10)	45.6(4)
C5	6840(3)	8498.7(16)	8723.1(9)	39.4(4)
C2	8169(4)	5969.8(19)	9184(11)	55.8(5)
C10	9794(4)	10736(2)	7734.5(12)	63.9(6)
C8	9750(3)	10754.9(16)	9123.6(10)	42.7(4)
C9	8497(3)	11144.4(18)	9802.6(11)	50.4(4)
C11	7622(4)	12520.1(19)	8413.7(13)	62.6(6)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for syd110701. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	38.4(2)	51.6(2)	71(3)	5.4(2)	-11.1(2)	2.3(2)
N2	90.8(14)	70.4(12)	55.7(11)	-4.7(10)	10.8(10)	18.6(11)
C6	47.1(10)	57(11)	47.7(11)	-4.3(8)	1(8)	-13.1(9)
N1	34.9(7)	44(8)	52.5(10)	-2.9(7)	-7.6(7)	0.7(6)
C4	37.8(8)	40(8)	34.5(9)	-4.2(7)	4.8(7)	2(7)
C7	44.7(9)	42.1(8)	46.4(10)	2.7(8)	2.3(8)	-0.8(7)
C1	71.6(14)	48.3(10)	57.4(12)	-5.2(9)	12.4(11)	-19.2(10)
C3	49.8(10)	48.2(10)	38.7(10)	-1.3(7)	5.1(8)	8.9(8)
C5	39.5(9)	42.5(9)	36.1(9)	-4.7(7)	1.5(7)	-2.2(7)
C2	78.1(13)	38.2(9)	51.2(12)	1.8(9)	15.4(11)	4.1(9)
C10	66.1(13)	78.7(14)	47(12)	2.7(10)	10(10)	7.4(11)
C8	41.4(9)	38.8(9)	47.9(11)	-3.7(7)	0.5(8)	-4.8(7)
C9	58(11)	43.2(9)	50.1(11)	-1.5(8)	-1.3(9)	2.9(8)
C11	78.4(15)	45.3(10)	64.1(14)	9.7(10)	2.7(12)	5.6(10)

Table 4 Bond Lengths for syd110701.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C5	1.7650(17)	C4	C5	1.403(2)
S1	C7	1.8272(18)	C7	C10	1.523(3)
N2	C9	1.140(3)	C7	C11	1.533(2)
C6	C1	1.377(3)	C7	C8	1.537(2)
C6	C5	1.388(2)	C1	C2	1.379(3)
N1	C4	1.386(2)	C3	C2	1.381(3)
N1	C8	1.445(2)	C8	C9	1.484(3)
C4	C3	1.399(2)			

Table 5 Bond Angles for syd110701.

Atom	Atom	Atom	Angle/•	Atom	Atom	Atom	Angle/•
C5	S1	C7	101.41(8)	C8	C7	S1	108.35(12)
C1	C6	C5	121.61(19)	C6	C1	C2	119.42(19)
C4	N1	C8	122.19(13)	C2	C3	C4	121.16(18)
N1	C4	C3	119.35(15)	C6	C5	C4	119.26(16)
N1	C4	C5	122.13(15)	C6	C5	S1	117.74(14)
C3	C4	C5	118.44(16)	C4	C5	S1	122.95(13)
C10	C7	C11	111.17(17)	C1	C2	C3	120.09(18)
C10	C7	C8	109.70(15)	N1	C8	C9	111.72(16)
C11	C7	C8	110.45(16)	N1	C8	C7	111.63(14)
C10	C7	S1	111.35(14)	C9	C8	C7	111.43(15)
C11	C7	S1	105.73(13)	N2	C9	C8	177.8(2)

Table 6 Torsion Angles for syd110701.

A	B	C	D	Angle/•
C8	N1	C4	C3	-162.15(16)
C8	N1	C4	C5	21.1(3)
C5	S1	C7	C10	75.93(15)
C5	S1	C7	C11	-163.22(14)
C5	S1	C7	C8	-44.80(13)
C5	C6	C1	C2	-0.1(3)
N1	C4	C3	C2	-175.84(16)
C5	C4	C3	C2	1.1(3)
C1	C6	C5	C4	-0.1(3)
C1	C6	C5	S1	-177.65(15)
N1	C4	C5	C6	176.46(16)
C3	C4	C5	C6	-0.4(2)
N1	C4	C5	S1	-6.1(2)
C3	C4	C5	S1	177.07(13)
C7	S1	C5	C6	-163.75(14)
C7	S1	C5	C4	18.79(16)
C6	C1	C2	C3	0.8(3)
C4	C3	C2	C1	-1.3(3)
C4	N1	C8	C9	72.7(2)
C4	N1	C8	C7	-52.8(2)
C10	C7	C8	N1	-58.26(19)
C11	C7	C8	N1	178.86(16)
S1	C7	C8	N1	63.49(15)
C10	C7	C8	C9	176.06(17)
C11	C7	C8	C9	53.18(19)
S1	C7	C8	C9	-62.19(16)
N1	C8	C9	N2	49(6)
C7	C8	C9	N2	175(100)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for syd110701.

Atom	*x*	*y*	*z*	U(eq)
H6	4063	7509	8394	61
H1	5149	5417	8776	71
H3	10944	6928	9535	55
H2	8625	5124	9333	67
H10B	10172	9805	7736	96
H10C	11151	11257	7742	96
H10A	8946	10941	7295	96
H8	11118	11301	9105	51
H11B	8920	13092	8425	94
H11C	6701	12690	8841	94
H11A	6768	12694	7971	94
H4	11560(3)	9241(19)	9437(10)	54(6)