Supporting Information
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Construction of polycyclic fused pyrrolidines with three contiguous stereocentres via Michael addition of vinyl malononitriles with nitrostyrenes using L-Proline derived thiourea

Manjunatha Vishwanath , Muthuraj Prakash, Poopathy Vinayagam, Venkitasamy Kesavan*

List of content

I. General Remarks:

All reactions were carried out in an oven dried flask. Solvents used for reactions and column chromatography were commercial grade and distilled prior to use. Toluene and THF were dried over sodium/benzophenone, CH_2Cl_2 and $CHCl_3$ over CaH_2. Solvents for HPLC bought as analytical grade and used without further purification. TLC was performed on pre-coated Merck silica gel aluminium plates with 60_F254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60-100 mesh. ^{1}H-NMR and ^{13}C-NMR were recorded on a Bruker AV 500 MHz using CD_3OD-d_4 and $CDCl_3$ as solvent and multiplicity indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet) bs (broad singlet). Coupling constants J were reported in Hertz. High resolution mass spectra were obtained by ESI using Thermo scientific Orbitrap Elite mass spectrometer. IR spectra were recorded on a Perkin Elmer FT/IR-420 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). The enantiomeric excess is obtained by HPLC analysis using a chiral stationary phase column (CHIRALPAK ADH, CHIRALCELL OD-H and Phenomenex Amylose-2. All the physical and spectroscopic data of **3a - d**, **3aa – ah**, **3ba**, **3bh** and **7a** were in complete agreement with the reported literature.

II. General procedure for asymmetric vinylogous Michael addition of vinyl malononitriles to nitrostyrene
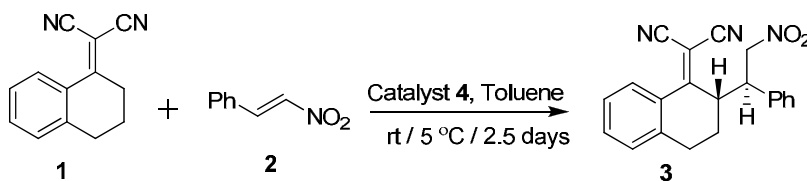
To a stirred solution of **4** (0.92 mg, 0.002mmol, 5 mol %) and vinyl malanonitriles **1** (0.1 mmol) in Toluene (1 mL), nitrostyrene **2** (0.12 mmol) was added. The solution was stirred at ambient temperature for mentioned days. After the reaction was completed (monitored by TLC), the resulting mixture was concentrated under reduced pressure and the residue was purified through column chromatography on silica gel to give the product **3.**

2-((S)-2-((R)-2-nitro-1-phenylethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile 3a:

General experimental procedure I was followed to prepare the Michael addtion product **3a**. The desired product was obtained as white solid 28.5 mg (0.083mmol) with 83% yield; 91% ee determined by HPLC on AS column, 30% 2-propanol/hexane, 1.0ml/min, UV 254nm, t_{minor}=13.3 min, t_{major}=20.4 min.

2-((S)-3-((R)-2-nitro-1-phenylethyl)chroman-4 ylidene)malononitrile 3b:

General experimental procedure I was followed to prepare the Michael addtion product **3b**. The desired product was obtained as white solid 27.9 mg (0.081mmol) with 81% yield; 95% ee was determined by HPLC on AS column, 30% 2-propanol/hexane, 1.0ml/min, UV 254nm, t_{minor} = 15.14 min, t_{major} = 17.3mmin; $[\alpha]_D^{25}$ −172.3° (c 0.15, $CHCl_3$).

2-((S)-3-((R)-2-nitro-1-phenylethyl)thiochroman-4-ylidene)malononitrile 3c:

General experimental procedure I was followed to prepare the Michael addtion product **3a**. The desired product was obtained as white solid 28.9 mg (0.080mmol) with 80% yield; 90% ee was determined by HPLC on AS column, 35% 2-propanol/hexane, 1.0ml/min, Uv 254nm, t_{minor} = 15.78 min, t_{major} = 31.04min.

2-((S)-2-((R)-2-nitro-1-phenylethyl)cyclohexylidene)malononitrile 3d:

General experimental procedure I was followed to prepare the Michael addtion product **3a**. The desired product was obtained as white solid 16.5 mg (0.056mmol) with 56% yield; 28% ee was determined by HPLC on AS column, 30% 2-propanol/hexane, 1.0ml/min, Uv 254nm, t_{minor} = 7.3 min, t_{major} = 9.3 min.

2-((S)-2-((R)-1-(2-fluorophenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile 3aa:

General experimental procedure I was followed to prepare the Michael addtion product **3a**. The desired product was obtained as white solid 28.9 mg (0.080mmol) with 80% yield; 85% ee was determined by HPLC on AS column, 35% 2-propanol/hexane, 1.0ml/min, Uv 254nm, t_{minor} = 19.6 min, t_{major} = 23.3 min.

2-((S)-2-((R)-1-(2-chlorophenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile 3ab:

General experimental procedure I was followed to prepare the Michael addtion product **3a**. The desired product was obtained as white solid 29.4 mg (0.078 mmol) with 78 % yield; 90% ee was determined by HPLC on AS column, 35% 2-propanol/hexane, 1.0ml/min, Uv 254nm, t_{minor} = 8.1 min, t_{major} = 10.1 min.

2-((S)-2-((R)-1-(2-bromophenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile 3ac:

General experimental procedure I was followed to prepare the Michael addtion product **3a**. The desired product was obtained as white solid 35 mg (0.083mmol) with 93% yield; 86% ee was determined by HPLC on AS column, 35% 2-propanol/hexane, 1.0ml/min, Uv 254nm, t_{minor} = 19.0 min, t_{major} = 19.9 min.

2-((S)-2-((R)-1-(3-chlorophenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile 3ad:

General experimental procedure I was followed to prepare the Michael addtion product **3a**. The desired product was obtained as white solid 30.5 mg (0.081mmol) with 81% yield; 88% ee was determined by HPLC on AS column, 35% 2-propanol/hexane, 1.0ml/min, Uv 254nm, t_{minor} = 10.3 min, t_{major} = 15.8 min.

2-((S)-2-((R)-1-(3-methoxyphenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile 3ae:

General experimental procedure I was followed to prepare the Michael addtion product **3a**. The desired product was obtained as white solid 28.0mg (0.075mmol) with 75% yield; 84% ee was determined by HPLC on AS column, 35% 2-propanol/hexane, 1.0ml/min, Uv 254nm, t_{minor} = 29.5 min, t_{major} = 27.11 min.

2-((S)-2-((R)-1-(4-chlorophenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile 3af:

General experimental procedure I was followed to prepare the Michael addtion product **3a**. The desired product was obtained as white solid 27.1 mg (0.072mmol) with 72% yield; 88% ee was determined by HPLC on AS column, 30% 2-propanol/hexane, 1.0ml/min, UV 254nm, t_{minor}=13.5 min, t_{major}=18.6min.

2-((S)-2-((R)-1-(4-bromophenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile 3ag:

General experimental procedure I was followed to prepare the Michael addtion product **3a**. The desired product was obtained as white solid 30.4 (0.072mmol) with 72% yield; 92% ee was determined by HPLC on AS column, 30% 2-propanol/hexane, 1.0ml/min, UV 254nm, t_{minor}= 14.0 min, t_{major}=19.4 min.

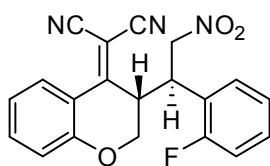### 2-((S)-2-((R)-1-(4-fluorophenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile 3ah:

General experimental procedure I was followed to prepare the Michael addtion product **3a**. The desired product was obtained as white solid 29.2 mg (0.081mmol) with 81% yield; 87% ee was determined by HPLC on AS column, 30% 2-propanol/hexane, 1.0ml/min, UV 254nm, t_{minor}=16.8 min, t_{major}=25.4 min.

2-((S)-3-((R)-1-(4-methoxyphenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile 3bh:

General experimental procedure I was followed to prepare the Michael addtion product **3a**. The desired product was obtained as white solid 28.5 mg (0.076mmol) with 76% yield. 91% ee was determined by HPLC on AS column, 80% 2-propanol/hexane, 1.0ml/min, UV 254nm, t_{minor}=10.2 min, t_{major}=13.2 min.

2-((S)-3-((R)-1-(2-fluorophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile

General experimental procedure **II** was followed to prepare the Michael/hemiketalization product **3bb**. The desired product was obtained as white solid with 75% yield , mp: 183-185°C; ^{1}H NMR (500MHz, CDCl$_3$) δ (ppm) 8.27 (dd, J = 1.5, 8.0 Hz, 1H), 7.63 (td, J = 1.5, 6.0 Hz, 1H), 7.44-7.38 (m, 1H), 7.29-7.22 (m, 2H), 7.19- 7.19 (m, 3H), 7.16 (dd, J = 1.5, 10Hz, 1H), 5.02 (t, J = 7.5 Hz, 1H), 4.57 (dd, J = 10.5, 18.5 Hz, 1H), 4.16 (dd, J = 3.5, 12.5 Hz, 2H), 3.58(d, J = 8.5 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 165.0, 155.9, 137.6, 131.1, 127.9, 125.3, 122.4, 118.4, 116.8, 116.6, 114.8, 112.8, 79.4, 76.3,

66.8, 59.5; HRMS (ESI) calcd for $C_{20}H_{14}FN_3O_3$ [M+H]$^+$: 386.0911, found: 386.0922; IR (KBr): ν 3457, 2928, 2230, 1560, 1542, 1487, 1447, 1378, 1082, 1014, 832, 760 cm^{-1}; 86% ee was determined by HPLC on ADH column, 10/90% 2-propanol/hexane, 1.0mL/min, UV 254nm, t_{minor}= 19.1 min, t_{major} = 21.8 min.

2-((S)-3-((R)-1-(3-chlorophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile:
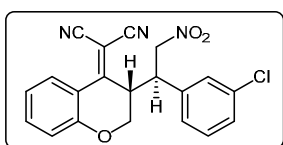
General experimental procedure **II** was followed to prepare the Michael addition product **3bc.** The desired product was obtained as white solid with 82% yield, mp: 187-189°C; ^{1}H NMR (500MHz, CDCl$_3$) δ = 8.28 (dd, J = 1.6, 8.2 Hz, 1 H), 7.65 (ddd, J = 1.4, 7.2, 8.4 Hz, 1 H), 7.44 - 7.38 (m, 2 H), 7.36 - 7.31 (m, 1 H), 7.27 - 7.23 (m, 1 H), 7.18 (dt, J = 1.3, 7.7 Hz, 1 H), 7.10 (dd, J = 1.1, 8.4 Hz, 1 H), 4.85 (dd, J = 10.4, 13.2 Hz, 1 H), 4.52 (dd, J = 5.2, 13.1 Hz, 1 H), 4.18 (dd, J = 2.4, 12.5 Hz, 1 H), 4.09 (dd, J = 1.7, 12.5 Hz, 1 H), 3.73 (dt, J = 5.2, 11.0 Hz, 1 H), 3.32 (td, J = 1.9, 11.3 Hz, 1 H); ^{13}C NMR (126MHz, CDCl$_3$) δ = 164.7, 156.0, 137.8, 137.5, 135.6, 131.0, 130.0, 129.4, 128.4, 127.9, 122.6, 118.6, 114.8, 113.0, 112.6, 79.2, 77.1, 66.5, 43.2, 42.7. HRMS (ESI) calcd for $C_{20}H_{14}ClN_3O_3$ [M+H]$^+$: 380.0796, found: 386.0809; IR (KBr): ν 3470, 2225, 1572, 1556, 1497, 1363, 1094, 1010, 827, 784, 736; 88% ee was determined by HPLC on ODH column, 10/90% 2-propanol/hexane, 1.0mL/min, UV 254nm, t_{minor} = 18.3 min, t_{major} = 20.8 min.
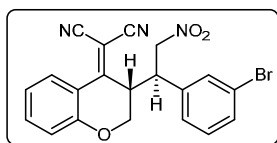
2-((S)-3-((R)-1-(4-chlorophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile:

General experimental procedure **II** was followed to prepare the Michael addtion product **3bd.**
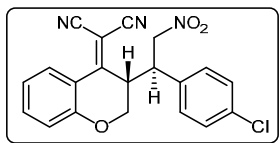
The desired product was obtained as white solid with 80% yield, mp: 177-179 °C; ^{1}H NMR (500MHz, CDCl$_3$) δ = 8.28 (dd, J = 1.6, 8.2 Hz, 1 H), 7.64 (ddd, J = 1.4, 7.2, 8.4 Hz, 1 H), 7.46 - 7.41 (m, 2 H), 7.29 (d, J = 8.5 Hz, 2 H), 7.21 - 7.15 (m, 1 H), 7.09 (dd, J = 0.9, 8.5 Hz, 1 H), 4.84 (dd, J = 10.7, 12.9 Hz, 1 H), 4.51 (dd, J = 5.2, 13.1 Hz, 1 H), 4.23 - 4.12 (m, 1 H), 4.12 - 4.03 (m, 1 H), 3.74 (dt, J = 5.0, 11.0 Hz, 1 H), 3.29 (td, J = 1.9, 11.4 Hz, 1 H).^{13}C NMR (125 MHz, CDCl$_3$) δ = 164.8, 156.0, 137.8, 135.2, 135.1, 133.9, 129.9, 129.5, 127.9, 122.6, 118.6, 114.8, 113.1, 112.7, 79.1, 77.2, 66.5, 43.0. HRMS (ESI) calcd for $C_{20}H_{14}ClN_3O_3$ [M+H]$^+$: 380.0796, found: 386.0802. IR (KBr): ν 3468, 2235, 1580, 1560, 1499, 1365, 1097, 1015, 829, 784, 735 cm^{-1}; 93% ee was determined by HPLC on AS column, 15/85% 2-propanol/hexane, 1.0mL/min, UV 254nm, t_{minor}= 29.5 min, t_{major} = 32.3 min.
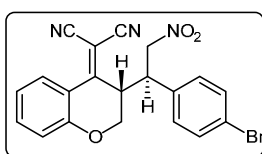
2-((S)-3-((R)-1-(3-bromophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile:

General experimental procedure **II** was followed to prepare the Michael addition product **3be.** The desired product was obtained as white solid with 79% yield, mp: 182-185 °C; ^{1}H NMR (500MHz, CDCl$_3$) δ = 8.28 (dd, J = 1.6, 8.2 Hz, 1 H), 7.64 (ddd, J = 1.4, 7.2, 8.4 Hz, 1 H), 7.55 (qd, J = 1.1, 7.9 Hz, 1 H), 7.48 (t, J = 1.7 Hz, 1 H), 7.37 - 7.32 (m, 1 H), 7.30 (t, J = 1.4 Hz, 1 H), 7.18 (ddd, J = 0.9, 7.3, 8.2 Hz, 1 H), 7.10 (dd, J = 1.1, 8.4 Hz, 1 H), 4.84 (dd, J = 10.6, 13.1 Hz, 1 H), 4.52 (dd, J = 5.0, 13.2 Hz, 1 H), 4.18 (dd, J = 2.4, 12.5 Hz, 1 H), 4.09 (dd, J = 1.7, 12.5 Hz, 1 H), 3.72 (dt, J = 5.2, 11.0 Hz, 1 H), 3.32 (td, J = 2.0, 11.4 Hz, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ = 164.7, 156.0, 137.8, 137.8, 132.4, 131.3, 131.2, 127.9, 126.6, 123.7, 122.6, 118.6, 114.8, 113.0, 112.6, 79.2, 77.1, 66.5, 43.1, 42. HRMS (ESI)

calcd for $C_{20}H_{14}BrN_3O_3$ [M+Na]$^+$: 446.0110, found: 446.0121; IR (KBr): 3468, 2928, 2232, 1585, 1561, 1494, 1437, 1375, 1094, 1015, 830, 768, 738, 641; 87% ee was determined by HPLC on ODH column, 20/80% 2-propanol/hexane, 1.0mL/min, UV 254nm, t_{minor} = 17.6 min, t_{major} = 21.9 min.

2-((S)-3-((R)-1-(4-bromophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile


General experimental procedure **II** was followed to prepare the Michael addition product **3bf.** The desired product was obtained as white solid with 83% yield, mp: 178-180 °C; ^{1}H NMR (500MHz, CDCl$_3$) δ = 8.28 (dd, J = 1.3, 8.2 Hz, 1 H), 7.64 (ddd, J = 1.6, 7.1, 8.4 Hz, 1 H), 7.62 - 7.56 (m, 2 H), 7.26 - 7.20 (m, 2 H), 7.20 - 7.15 (m, 1 H), 7.09 (dd, J = 0.9, 8.5 Hz, 1 H), 4.84 (dd, J = 10.7, 12.9 Hz, 1 H), 4.51 (dd, J = 5.0, 12.9 Hz, 1 H), 4.16 (dd, J = 2.4, 12.5 Hz, 1 H), 4.12 - 4.05 (m, 1 H), 3.73 (dt, J = 5.0, 11.0 Hz, 1 H), 3.29 (td, J = 2.0, 11.4 Hz, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ = 164.8, 156.0, 137.8, 134.4, 132.9, 129.7, 127.9, 123.3, 122.6, 118.6, 114.8, 113.1, 112.7, 79.1, 77.2, 66.5, 43.0, 42.7. HRMS (ESI) calcd for $C_{20}H_{14}BrN_3O_3$[M+Na]$^+$: 446.0110, found: 446.0121; IR (KBr): v 3466, 2929, 2234, 1587, 1564, 1497, 1439, 1379, 1095, 1017, 832, 770, 740, 641 cm^{-1}; 86% ee was determined by HPLC on ODH column, 10/90% 2-propanol/hexane, 1.0mL/min, UV 254nm, t_{minor} = 12.6 min, t_{major} = 18.6 min.

2-(2-(1-(4-Methylphenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile.
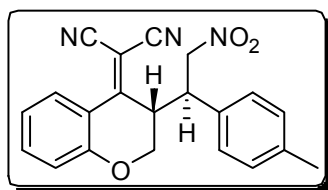
General experimental procedure **II** was followed to prepare the Michael addition product **3bg.** The desired product was obtained as white solid with 81% yield mp: 183-185°C; ^{1}H NMR (500MHz, CDCl$_3$) δ (ppm) 8.26 (dd, J = 1.0, 8.0 Hz, 1H), 7.63 (td, J = 7.5, 0.5 Hz, 1H), 7.29-7.26 (m, 4H), 7.17 (td, J = 1, 7.0 Hz, 1H), 7.07 (dd, J = 1.0, 8.5 Hz, 1H), 4.84 (dd, J = 2.5, 13.0 Hz, 1H), 4.49 (dd, J = 5.5, 12.5Hz, 1H), 4.12- 4.11 (m, 2H), 3.69 (dt, J = 3, 11.5 Hz, 1H), 3.30 (dd, J = 2, 13.5Hz, 1H; ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 174.4, 166.0, 156.1, 139. 9, 137.7, 132.2, 131.7, 130.3, 127.9, 122.4, 114.9, 78.9, 77.3, 66.6, 43.3, 43.1, 21.1; HRMS (ESI) calcd for $C_{21}H_{17}N_3O_3$ [M+H]$^+$: 360.1342, found: 360.1331; IR (KBr): 3468, 2230, 1574, 1559, 1515, 1378, 1260, 1180, 1037, 828, 775, 751 cm-1; 90% ee was determined by HPLC on ADH column, 15/85% 2-propanol/hexane, 1.0mL/min, UV 254nm, t_{minor} = 21.5 min, t_{major} = 26.4 min.
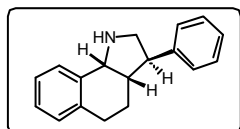
(R)-3-((R)-2-nitro-1-phenylethyl)chroman-4-one:
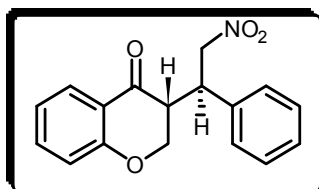
To a stirred solution of **3ba** (1 equiv) in acetone and water as solvent , KMnO$_4$ (2 equiv) was added. The solution was stirred at ambient temperature for 4h. After the reaction was completed (monitored by TLC), the resulting mixture was concentrated under reduced pressure and the residue was purified through column chromatography on silica gel to give the product **7b.**The desired product **7b** was obtained as white solid with 67% yield; mp: 155-157°C; ^{1}H NMR (500MHz, CDCl$_3$) δ = 7.95 (dd, J = 1.9, 7.9 Hz, 1 H), 7.56 (ddd, J = 1.7, 7.1, 8.5 Hz, 1 H), 7.44 - 7.40 (m, 2 H), 7.38 - 7.34 (m, 1 H), 7.33 - 7.30 (m, 2 H), 7.13 - 7.08 (m, 1 H), 7.04 - 7.00 (m, 1 H), 4.96 (dd, J = 5.0, 13.2 Hz, 1 H), 4.82 (dd, J = 10.6, 13.4 Hz, 1 H), 4.28

(dd, J = 3.5, 11.7 Hz, 1 H), 4.04 (dd, J = 5.2, 11.8 Hz, 1 H), 3.95 (dt, J = 4.7, 10.9 Hz, 1 H), 2.84 - 2.78 (m, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ = 192.8, 161.4, 136.7, 136.3, 129.4, 128.5, 128.0, 127.7, 122.0, 120.0, 117.9, 78.5, 68.7, 48.6, 41.2; HRMS (ESI) calcd for C$_{17}$H$_{15}$NO$_4$ [M+H]$^+$: 298.1074, found: 298.1087; IR (KBr): 3467, 2228, 1779, 1575, 1560, 1525, 1381, 1265, 1182, 1034, 820, 770 cm^{-1};

(3R,3aS,9bR)-3-phenyl-2,3,3a,4,5,9b-hexahydro-1H-benzo[g]indole:
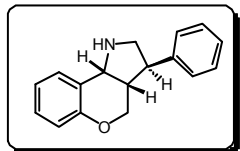

To a stirred solution of **7a** (1 equiv) in acetic acid as solvent, Zn dust (10 equiv) was added. The solution was stirred at ambient temperature for 8h. After the reaction was completed (monitored by TLC), the resulting mixture was concentrated under reduced pressure and the residue was purified through column chromatography on silica gel to give the product **8a.** The desired product was obtained as pasty solid with 61% yield; ^{1}H NMR (500MHz, CDCl$_3$) δ = 7.47 (d, J = 7.3 Hz, 1 H), 7.37 - 7.29 (m, 4 H), 7.25 - 7.10 (m, 4 H), 4.45 (d, J = 8.2 Hz, 1 H), 3.49 (dd, J = 6.8, 10.6 Hz, 1 H), 3.09 - 3.04 (m, 1 H), 3.04 - 2.98 (m, 1 H), 2.84 - 2.77 (m, 1 H), 2.64 (ddd, J = 4.1, 9.1, 15.8 Hz, 1 H), 2.55 - 2.45 (m, 1 H), 1.95 - 1.88 (m, 1 H), 1.60 (dtd, J = 4.1, 8.8, 13.2 Hz, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ = 144.5, 138.4, 138.2, 129.7, 128.9, 128.4, 127.9, 126.7, 126.5, 126.4, 59.7, 55.1, 52.6, 46.9, 28.3, 26.7; HRMS (ESI) calcd for C$_{18}$H$_{19}$N [M+Na]$^+$: 298.1074, found: 298.1087; IR (KBr): 3625, 3650, 2230, 1625, 1556, 1378, 1271, 1185, 1037, 838, 779 cm^{-1};85% ee was determined by HPLC on phenomenex Amylose 2 column, 20/80% 2-propanol/hexane, 1.0mL/min, UV 254nm, t_{minor}= 19.6 min, t_{major} = 22.3 min.

### (3R,3aS,9bR)-3-phenyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole:

To a stirred solution of **7b** (1 equiv) in acetic acid as solvent, Zn dust (10 equiv) was added. The solution was stirred at ambient temperature for 8h. After the reaction was completed (monitored by TLC), the resulting mixture was concentrated under reduced pressure and the residue was purified through column chromatography on silica gel to give the product **8b.** The desired product **8b** was obtained as pasty solid with 64% yield; ^{1}H NMR (500MHz, DMSO-d$_6$) δ = 7.40 (dd, J = 1.6, 7.6 Hz, 1 H), 7.36 - 7.30 (m, 4 H), 7.25 - 7.20 (m, 1 H), 7.18 - 7.12 (m, 1 H), 6.94 (dt, J = 1.3, 7.4 Hz, 1 H), 6.84 (dd, J = 1.3, 8.2 Hz, 1 H), 4.23 - 4.12 (m, 2 H), 3.67 (dd, J = 9.8, 10.7 Hz, 1 H), 3.31 (dd, J = 7.9, 10.7 Hz, 1 H), 2.88 (d, J = 5.4 Hz, 1 H), 2.77 (dd, J = 8.7, 10.6 Hz, 1 H), 2.43 (tdd, J = 5.1, 6.9, 9.8 Hz, 1 H); ^{13}C NMR (125 MHz, DMSO-d$_6$) δ = 155.1, 144.4, 131.1, 129.0, 128.3, 128.0, 126.7, 125.1, 121.2, 116.9, 66.0, 56.3, 55.3, 48.3, 45.8; HRMS (ESI) calcd for C$_{17}$H$_{17}$NO [M+H]$^+$: 252.1383, found: 252.1370; IR (KBr): 3628, 3655, 2235, 1628, 1558, 1374, 1275, 1182, 1039, 845, 740 cm^{-1} ; 75% ee was determined by HPLC on ODH column, 30/70% 2-propanol/hexane, 1.0mL/min, UV 254nm, t_{minor}= 49.6 min, t_{major} = 59.0 min.
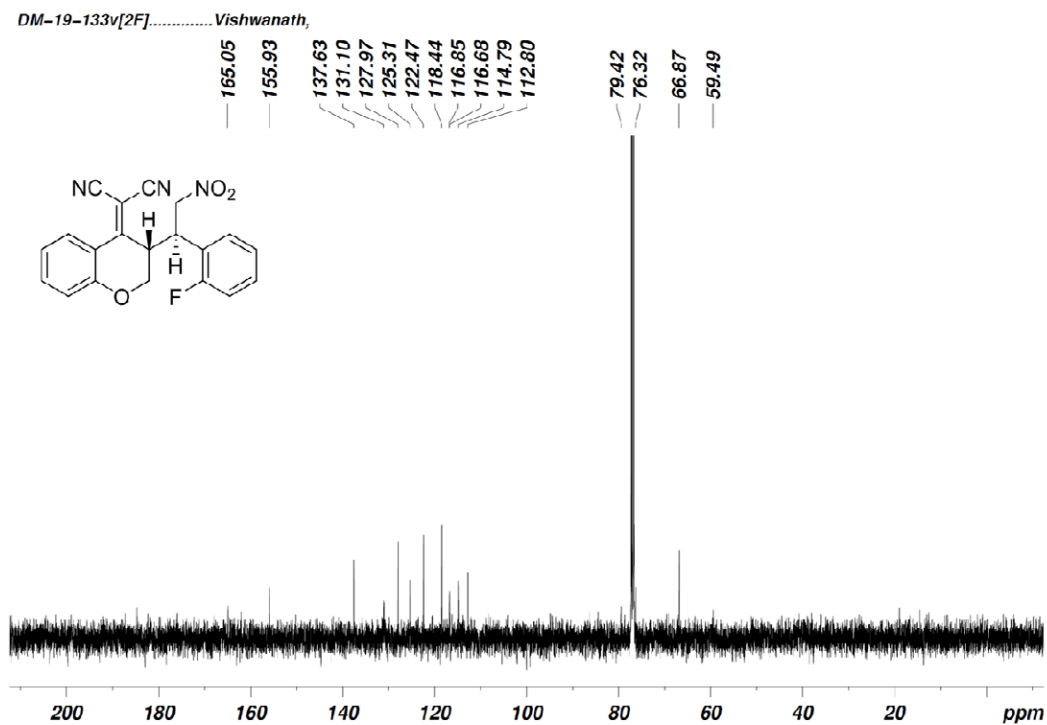
References:

1) D. Xue, Y.-C. Chen, Q.-W. Wang, L.-F. Cun, J. Zhu, J.-G. Deng, Org. Lett. **2005**, 7, 5293-5296;

2) T. B. Poulsen, M. Bell, K. A. Jorgensen, Org. Biomol. Chem. **2006**, 4, 63-70.

3) Zhou, L.-H.; Wang, N.; Chen, G.-N.; Yang, Q.; Yang, S.-Y.; Zhang, W.; Zhang, Y.; Yu, X.-Q. Journal of Molecular Catalysis B: Enzymatic 2014, 109, 170-177
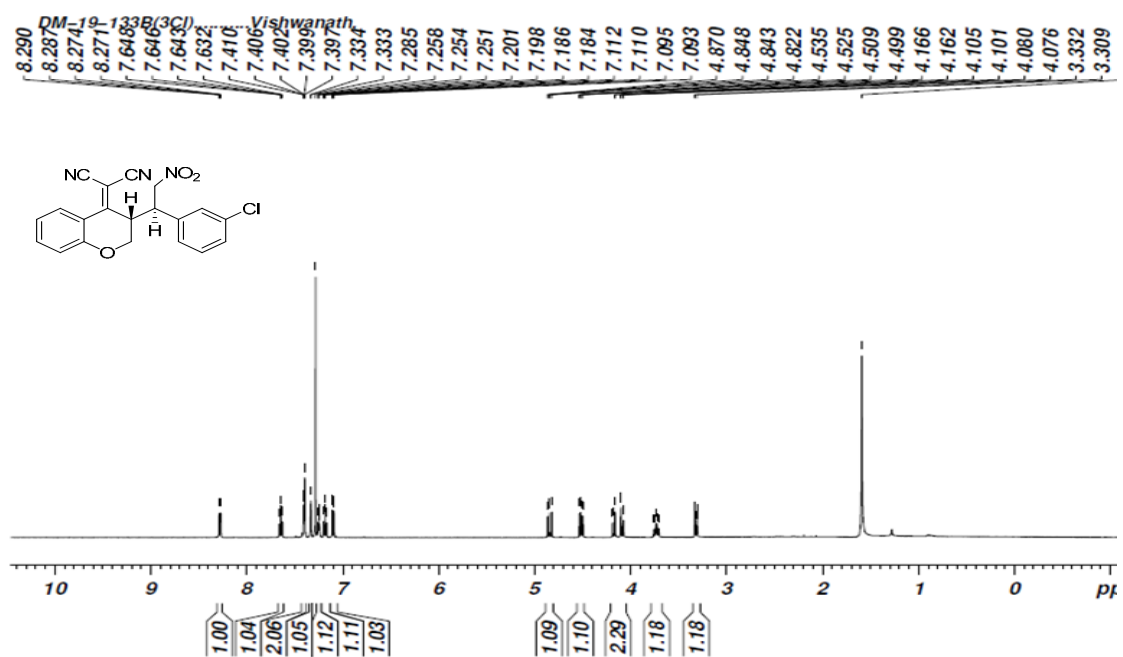
^{1}H NMR of 2-(2-(1-(2-fluorophenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile
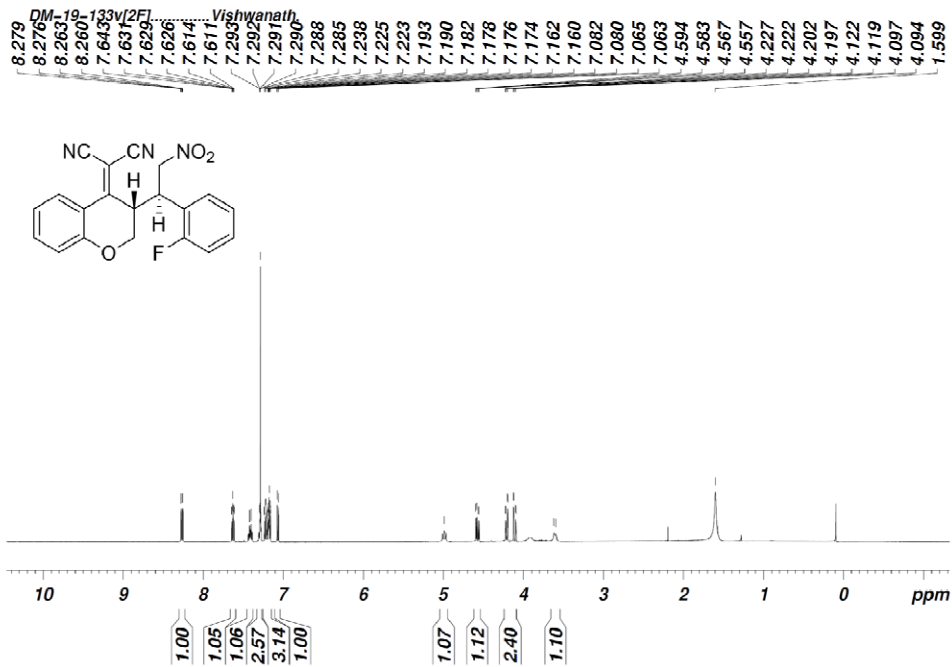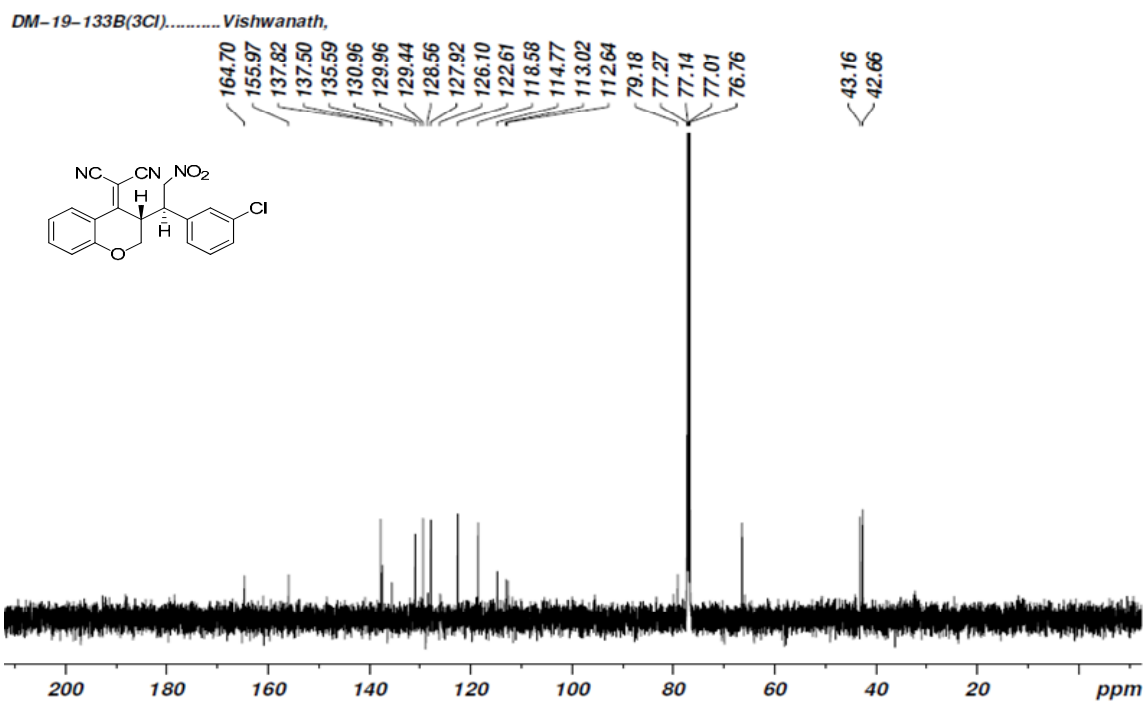

^{13}C NMR of 2-(2-(1-(4-fluorophenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile

¹H NMR of 2-(3-(1-(3-Chlorophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile.

8.290, 8.287, 8.274, 8.271, 7.648, 7.646, 7.643, 7.632, 7.410, 7.406, 7.402, 7.399, 7.397, 7.334, 7.333, 7.285, 7.258, 7.254, 7.251, 7.201, 7.198, 7.186, 7.184, 7.112, 7.110, 7.095, 7.093, 4.870, 4.848, 4.843, 4.822, 4.535, 4.525, 4.509, 4.499, 4.166, 4.162, 4.105, 4.101, 4.080, 4.076, 3.332, 3.309

1.00, 1.04, 2.06, 1.05, 1.12, 1.11, 1.03, 1.09, 1.10, 2.29, 1.18, 1.18

¹³C NMR of 2-(3-(1-(3-Chlorophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile.

164.70, 155.97, 137.82, 137.50, 135.59, 130.96, 129.96, 129.44, 128.56, 127.92, 126.10, 122.61, 118.58, 114.77, 113.02, 112.64, 79.18, 77.27, 77.14, 77.01, 76.76, 43.16, 42.66

^{1}H NMR of 2-(3-(1-(4-chlorophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile.

8.289
8.287
8.273
8.270
7.643
7.641
7.638
7.626
7.623
7.443
7.426
7.301
7.285
7.196
7.194
7.180
7.165
7.163
7.096
7.094
7.079
7.077
4.862
4.840
4.836
4.814
4.527
4.516
4.500
4.490
4.179
4.174
4.154
4.149
4.085
4.082
4.060
4.057
3.743
3.733
3.305
3.302
3.279

1.00 1.04 1.97 2.38 1.03 1.04 | 1.08 1.06 2.17 1.08 1.08

^{13}C NMR of 2-(3-(1-(4-chlorophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile.

164.83
155.99
137.81
135.14
133.88
129.91
129.46
127.93
122.59
118.56
114.78
113.06
112.68
79.10
77.29
77.24
77.04
76.78
66.45
42.96
42.76

¹H NMR of 2-(3-(1-(3-bromophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile.

8.287, 8.285, 8.271, 8.268, 7.649, 7.642, 7.562, 7.561, 7.546, 7.545, 7.543, 7.488, 7.485, 7.481, 7.358, 7.342, 7.327, 7.306, 7.303, 7.301, 7.285, 7.184, 7.182, 7.181, 7.111, 7.109, 7.095, 7.093, 4.864, 4.843, 4.838, 4.816, 4.534, 4.523, 4.507, 4.497, 4.166, 4.161, 4.105, 4.102, 4.080, 3.328, 3.306

0.99, 1.02, 0.97, 1.05, 1.02, 1.48, 1.08, 1.03

1.10, 1.11, 2.28, 1.14, 1.15

¹³C NMR of 2-(3-(1-(3-bromophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile.

164.70, 155.96, 137.81, 137.77, 132.38, 131.33, 131.19, 127.92, 126.50, 123.68, 122.60, 118.58, 114.77, 113.02, 112.65, 79.18, 77.27, 77.14, 77.02, 76.76, 66.47, 43.11, 42.67

¹H NMR of 2-(3-(1-(4-bromophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile.

8.290, 8.287, 8.274, 8.271, 7.643, 7.641, 7.638, 7.627, 7.624, 7.598, 7.595, 7.585, 7.582, 7.285, 7.240, 7.226, 7.223, 7.197, 7.195, 7.183, 7.181, 7.164, 7.095, 7.093, 7.078, 7.076, 4.860, 4.839, 4.834, 4.813, 4.524, 4.513, 4.498, 4.487, 4.175, 4.154, 4.150, 4.088, 4.084, 4.063, 4.059, 3.300, 3.277, 1.604

1.00 1.07 2.04 2.12 1.12 1.09   1.10 1.09 2.21 1.07 1.07

¹³C NMR of 2-(3-(1-(4-bromophenyl)-2-nitroethyl)chroman-4-ylidene)malononitrile.

164.78, 155.98, 137.81, 134.42, 132.88, 129.75, 127.92, 123.25, 122.60, 118.56, 114.78, 113.05, 112.65, 79.11, 77.28, 77.16, 77.02, 76.77, 66.45, 43.03, 42.71
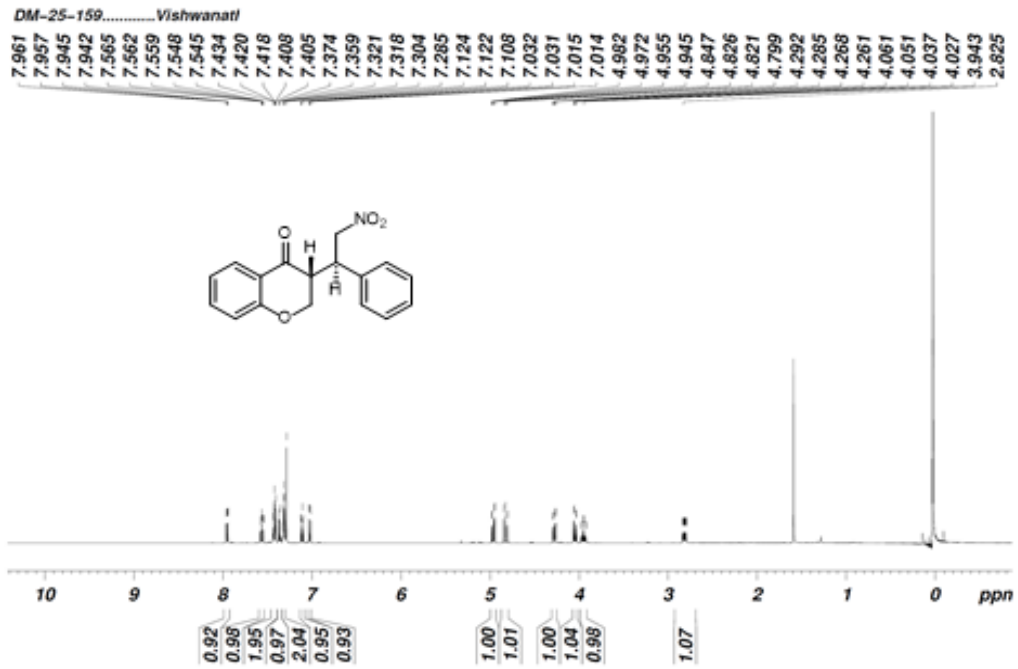
¹H NMR of 2-(2-(1-(4-Methylphenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile
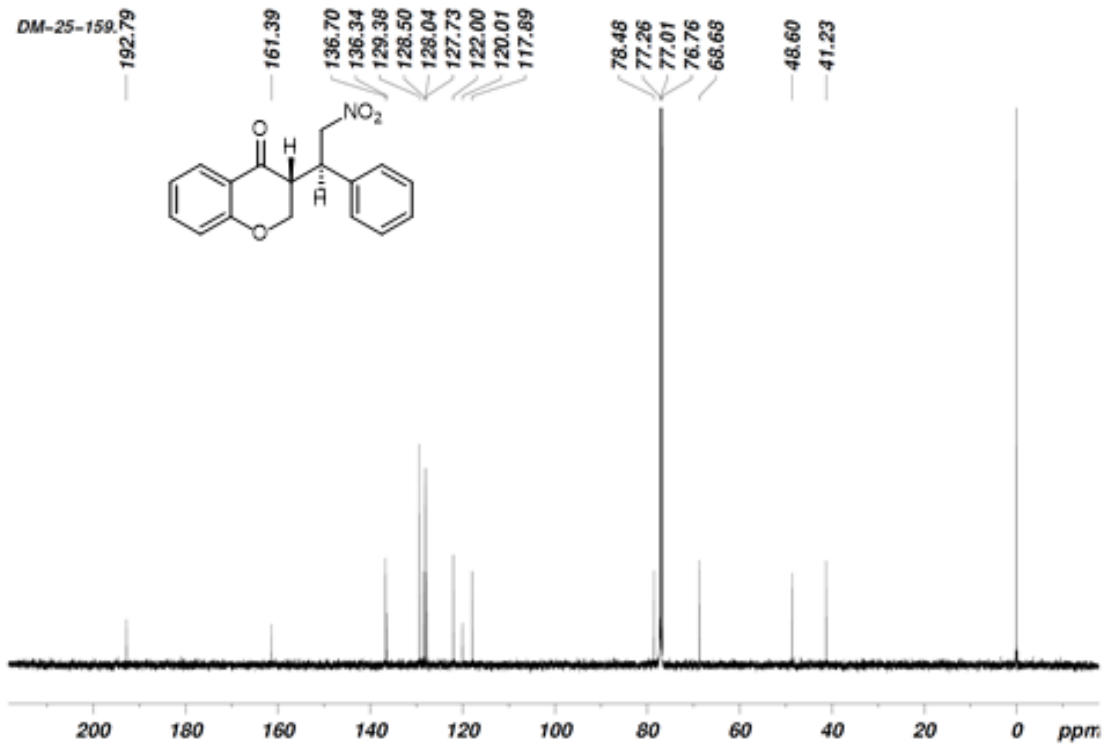

¹³C NMR of 2-(2-(1-(4-Methylphenyl)-2-nitroethyl)-3,4-dihydronaphthalen-1(2H)-ylidene)malononitrile
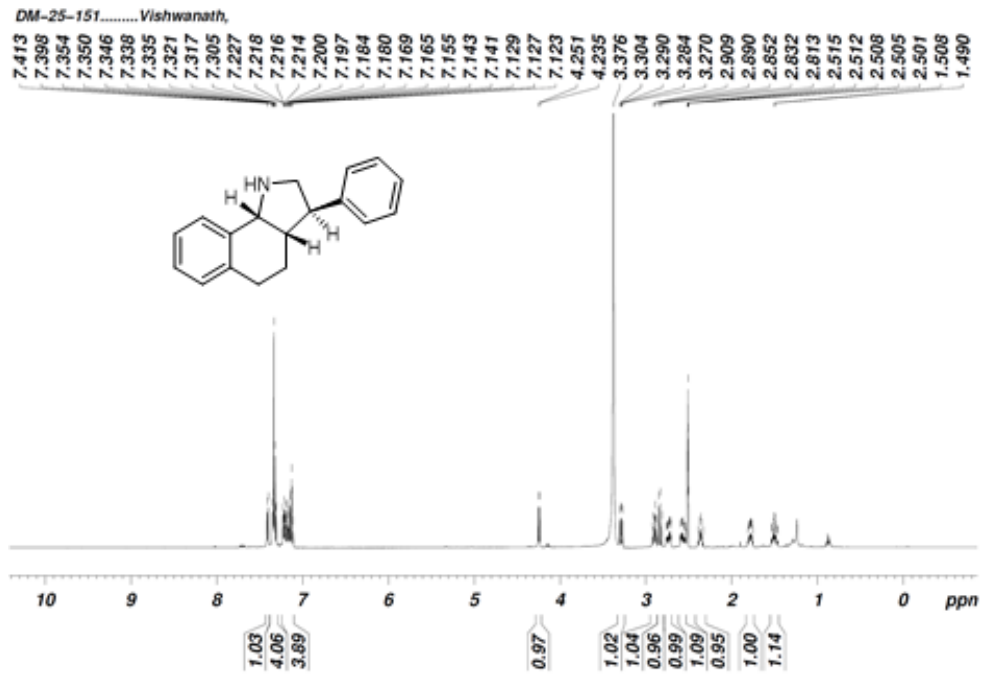
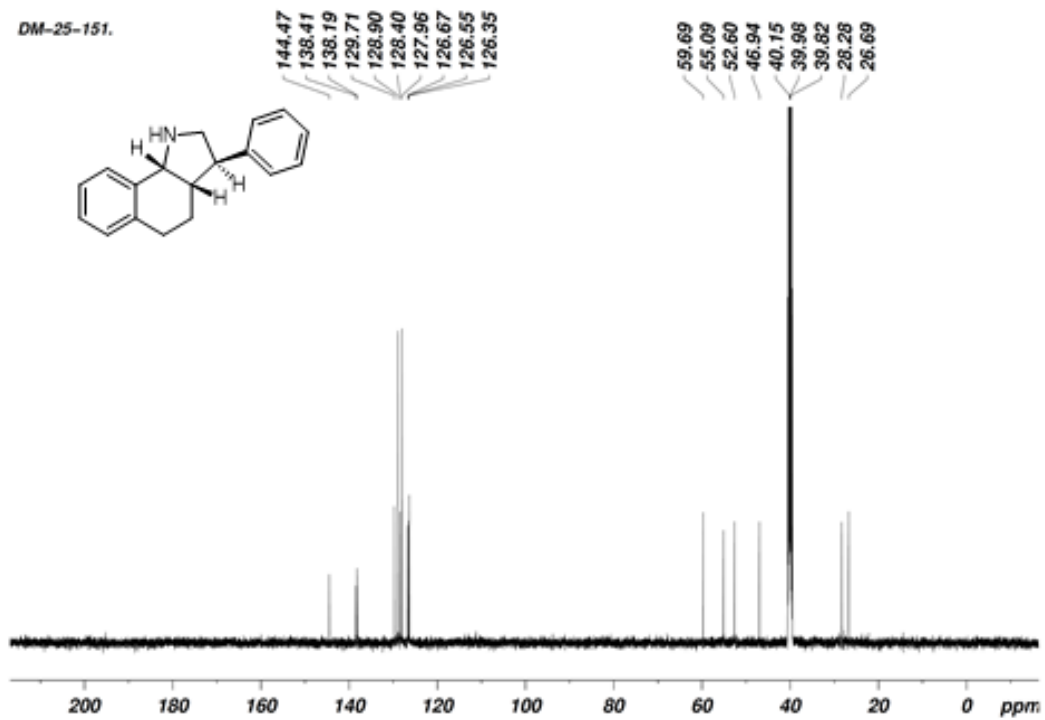# ^{1}H NMR of (R)-3-((R)-2-nitro-1-phenylethyl)chroman-4-one.

7.961, 7.957, 7.945, 7.942, 7.565, 7.562, 7.559, 7.548, 7.545, 7.434, 7.420, 7.418, 7.408, 7.405, 7.374, 7.359, 7.321, 7.318, 7.304, 7.285, 7.124, 7.122, 7.108, 7.032, 7.031, 7.015, 7.014, 4.962, 4.972, 4.955, 4.945, 4.847, 4.826, 4.821, 4.799, 4.292, 4.285, 4.268, 4.261, 4.061, 4.051, 4.037, 4.027, 3.943, 2.825

0.92 0.98 1.95 0.97 2.04 0.95 0.93   1.00 1.01   1.00 1.04 0.98   1.07

^{13}C NMR of (R)-3-((R)-2-nitro-1-phenylethyl)chroman-4-one

192.79 — 161.39 — 136.70, 136.34, 129.38, 128.50, 128.04, 127.73, 122.00, 120.01, 117.89 — 78.48, 77.26, 77.01, 76.76, 68.68 — 48.60, 41.23

¹H NMR of (3R,3aS,9bR)-3-phenyl-2,3,3a,4,5,9b-hexahydro-1H-benzo[g]indole.

DM-25-151.........Vishwanath,

7.413 7.398 7.354 7.350 7.346 7.338 7.335 7.321 7.317 7.305 7.227 7.218 7.216 7.214 7.200 7.197 7.184 7.180 7.169 7.165 7.155 7.143 7.141 7.129 7.127 7.123 4.251 4.235 3.376 3.304 3.290 3.284 3.270 2.909 2.890 2.852 2.832 2.813 2.515 2.512 2.508 2.505 2.501 1.508 1.490

1.03 4.06 3.89   0.97   1.02 1.04 0.96 0.99 1.09 0.95 1.00 1.14

¹³C NMR of (3R,3aS,9bR)-3-phenyl-2,3,3a,4,5,9b-hexahydro-1H-benzo[g]indole.

DM-25-151.

144.47 138.41 138.19 129.71 128.90 128.40 127.96 126.67 126.55 126.35   59.69 55.09 52.60 46.94 40.15 39.98 39.82 28.28 26.69
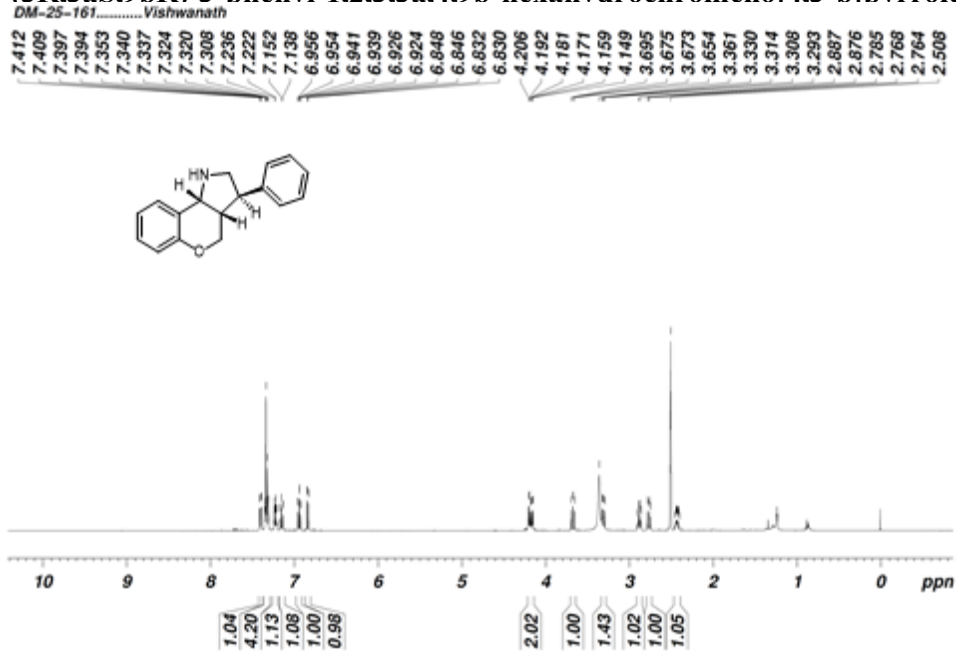
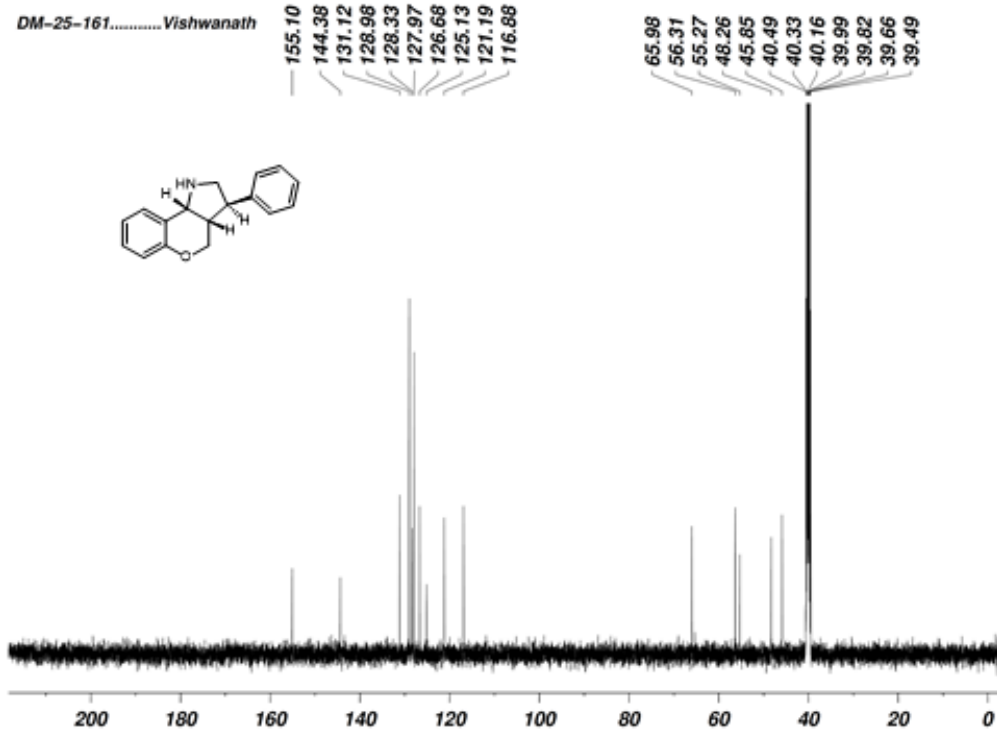**NOESY spectrum of (3R,3aS,9bR)-3-phenyl-2,3,3a,4,5,9b-hexahydro-1H-benzo[g]indole.**
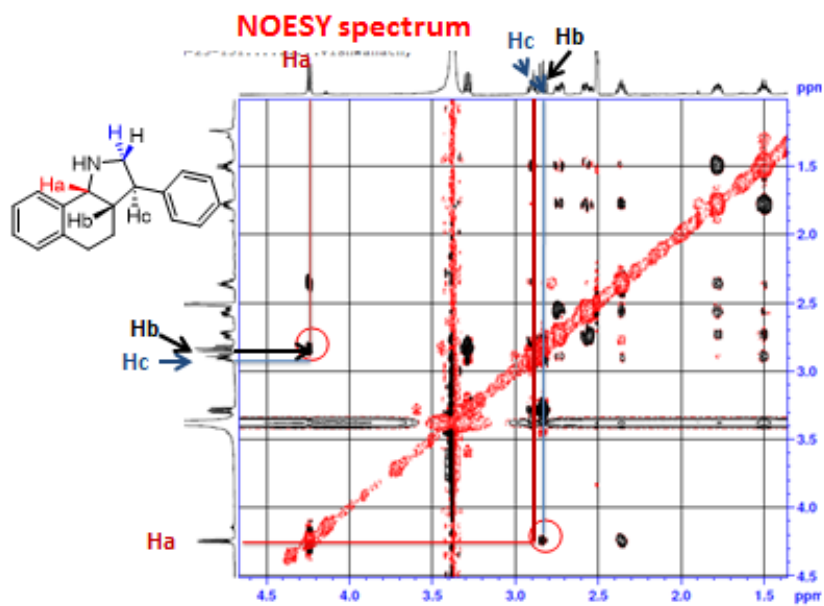
NOESY spectum shows no spatial interactions between **Ha** and **Hc**, which indicates those protons are in "anti" configuration in cyclised product.
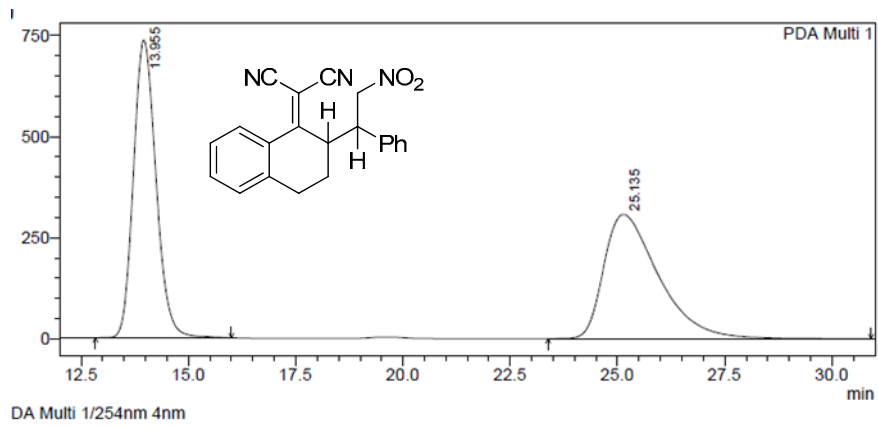
¹H NMR of (3R,3aS,9bR)-3-phenyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole

DM–25–161...........Vishwanath

7.412, 7.409, 7.397, 7.394, 7.353, 7.340, 7.337, 7.324, 7.320, 7.308, 7.236, 7.222, 7.152, 7.138, 6.956, 6.954, 6.941, 6.939, 6.926, 6.924, 6.848, 6.846, 6.832, 6.830, 4.206, 4.192, 4.181, 4.171, 4.159, 4.149, 3.695, 3.675, 3.673, 3.654, 3.361, 3.330, 3.314, 3.308, 3.293, 2.887, 2.876, 2.785, 2.768, 2.764, 2.508

10   9   8   7   6   5   4   3   2   1   0   ppn

1.04 4.20 1.13 1.08 1.00 0.98   2.02 1.00 1.43 1.02 1.00 1.05

¹³C NMR of (3R,3aS,9bR)-3-phenyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole.

DM–25–161...........Vishwanath

155.10 144.38 131.12 128.98 128.33 127.97 126.68 125.13 121.19 116.88   65.98 56.31 55.27 48.26 45.85 40.49 40.33 40.16 39.99 39.82 39.66 39.49

200   180   160   140   120   100   80   60   40   20   0

HPLC profile for table3, entry 1

DA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.955	26947195	735911	49.599	70.545
2	25.135	27383159	307271	50.401	29.455
Total		54330354	1043181	100.000	100.000

A Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm
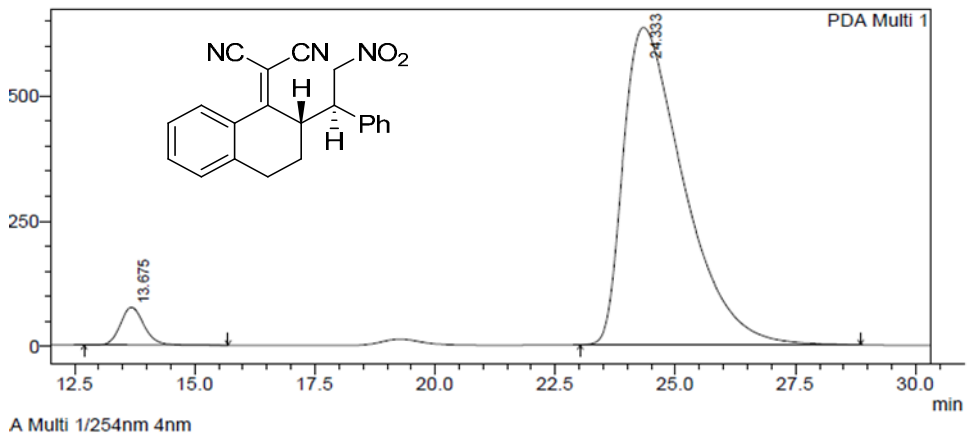
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.675	2569671	75341	4.419	10.609
2	24.333	55575036	634836	95.581	89.391
Total		58144707	710176	100.000	100.000

HPLC profile for table3, entry 2

PDA Multi 1

)A Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.081	9015261	151860	49.881	46.087
2	17.564	9058285	177646	50.119	53.913
Total		18073545	329505	100.000	100.000

PDA Multi 1

A Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.141	2168839	36067	2.366	1.938
2	17.587	89482351	1824522	97.634	98.062
Total		91651190	1860589	100.000	100.000

HPLC profile for table3, entry 3

et.A Ch1/310nm

PeakTable

Detector A Ch1 310nm
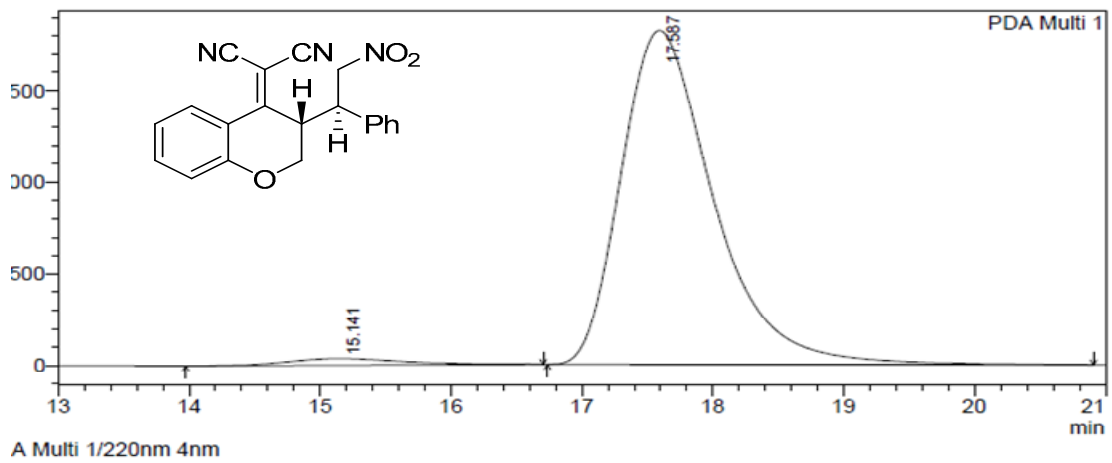
Peak#	Ret. Time	Area	Height	Area %
1	11.574	1261592	49068	50.309
2	20.659	1246085	22342	49.691
Total		2507677	71411	100.000

Height %
68.713
31.287
100.000

et.A Ch1/310nm

PeakTable

Detector A Ch1 310nm
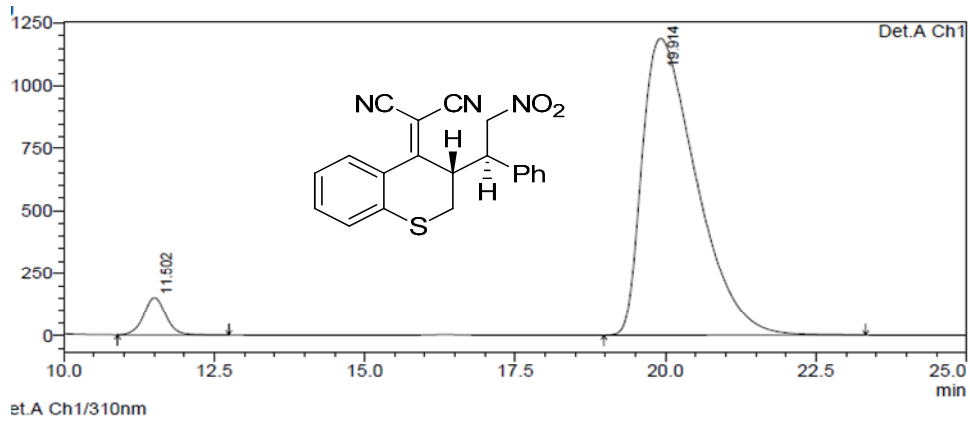
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.502	3806054	149489	4.875	11.178
2	19.914	74274536	1187841	95.125	88.822
Total		78080590	1337330	100.000	100.000

\
HPLC profile for table3, entry 4

et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm
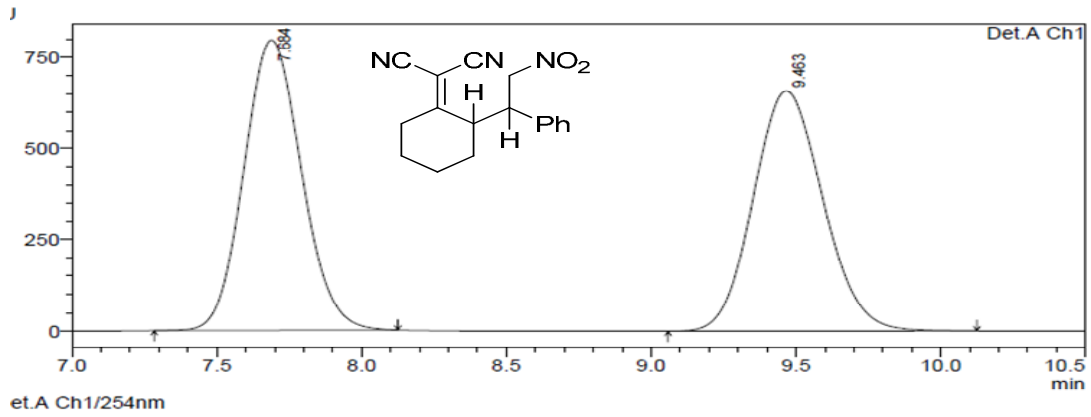
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.684	11007789	795532	50.086	54.779
2	9.463	10970056	656736	49.914	45.221
Total		21977845	1452267	100.000	100.000

et.A Ch1/254nm

PeakTable
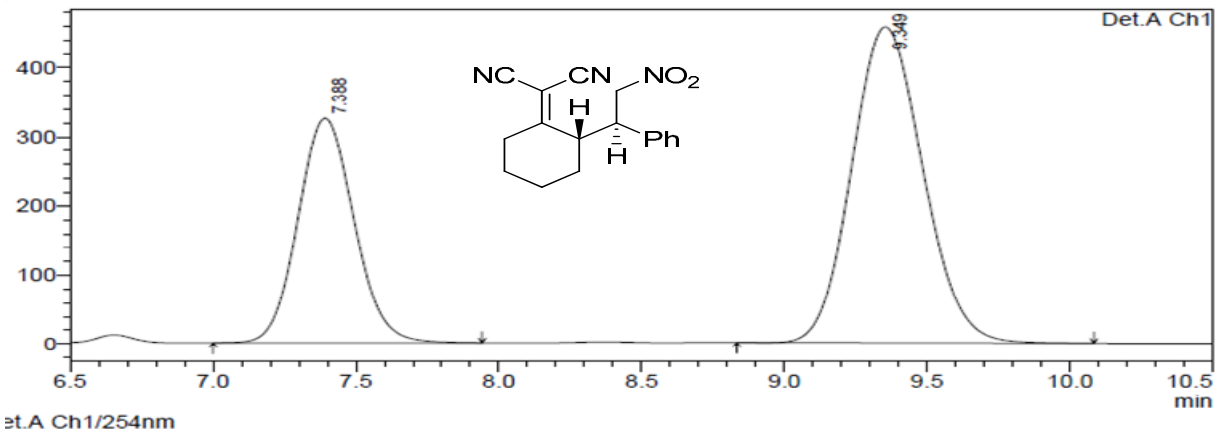
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.388	4470846	325709	35.990	41.577
2	9.349	7951607	457681	64.010	58.423
Total		12422452	783390	100.000	100.000

HPLC profile for table 4, entry 1
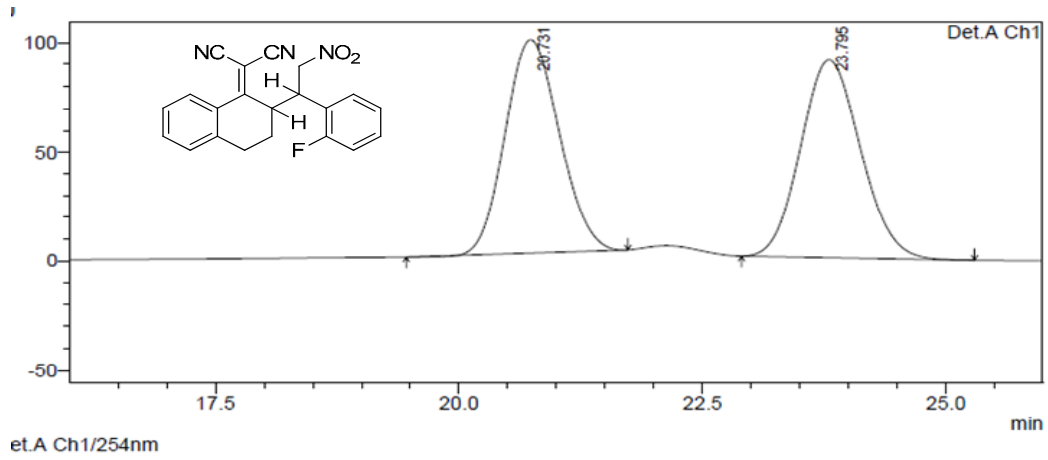
et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.731	3785151	97609	49.380	51.954
2	23.795	3880135	90265	50.620	48.046
Total		7665286	187874	100.000	100.000
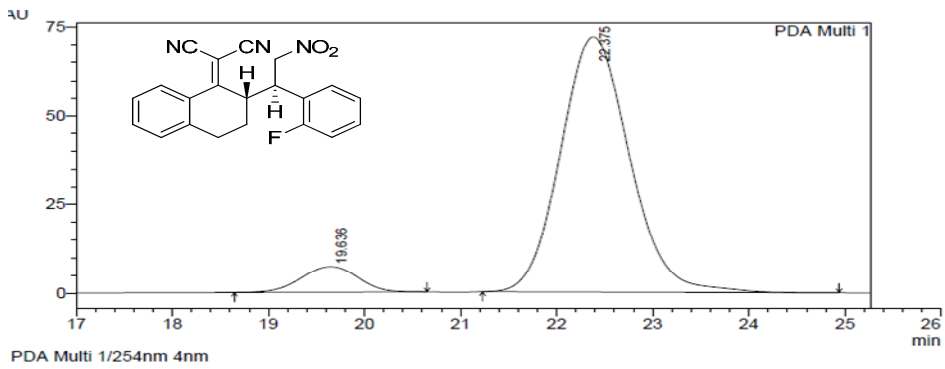
PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.636	289704	7079	7.480	8.968
2	22.375	3583401	71856	92.520	91.032
Total		3873105	78936	100.000	100.000

HPLC profile for table 4, entry 2

Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm
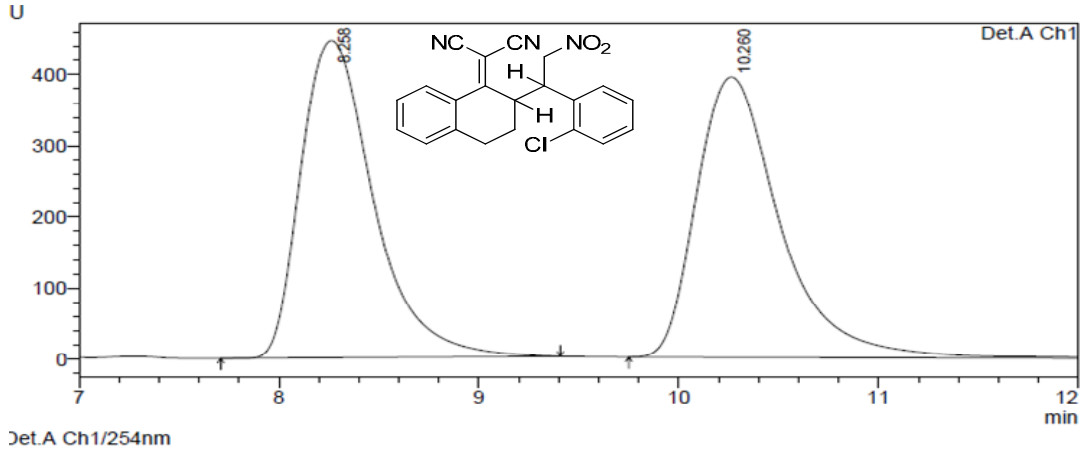
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.258	11288799	446150	49.533	53.127
2	10.260	11501444	393635	50.467	46.873
Total		22790243	839784	100.000	100.000

et.A Ch1/254nm

PeakTable
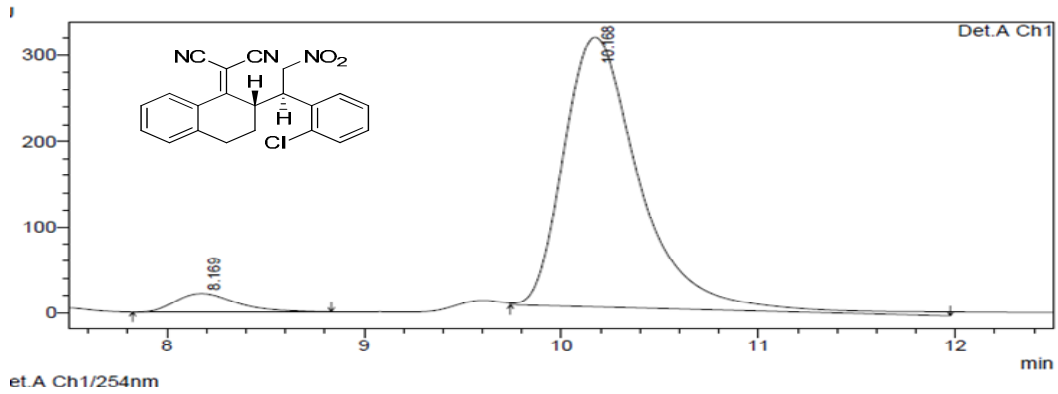
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.169	464727	21637	5.208	6.442
2	10.168	8458352	314233	94.792	93.558
3	14.933	0	0	0.000	0.000
Total		8923080	335871	100.000	100.000

HPLC profile for table 4, entry 3
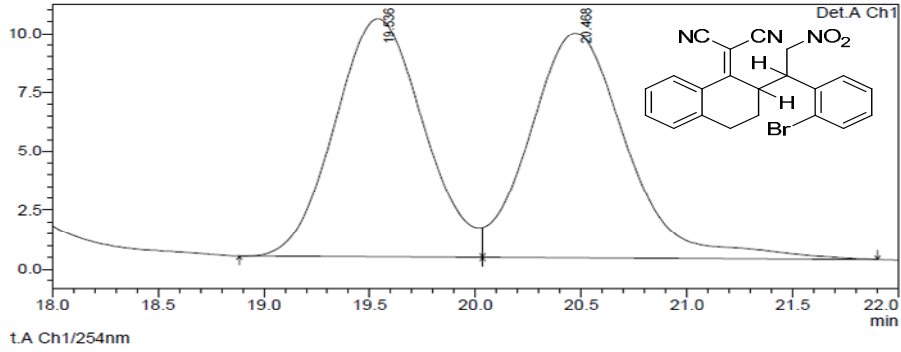
t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.536	294078	10079	49.235	51.411
2	20.468	303213	9526	50.765	48.589
Total		597291	19604	100.000	100.000
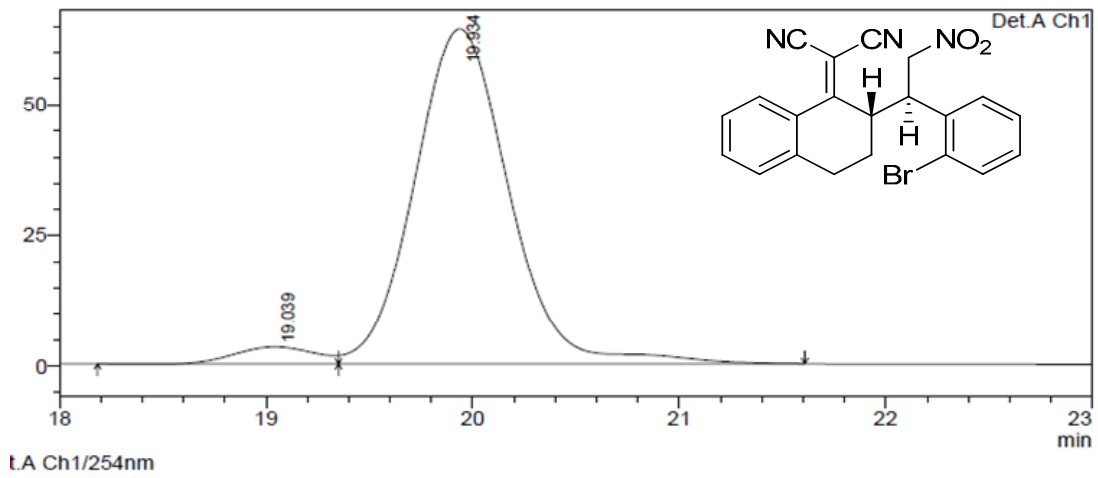
t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.039	83939	3156	3.965	4.696
2	19.934	2033259	64049	96.035	95.304
Total		2117199	67205	100.000	100.000

HPLC profile for table 4, entry 4
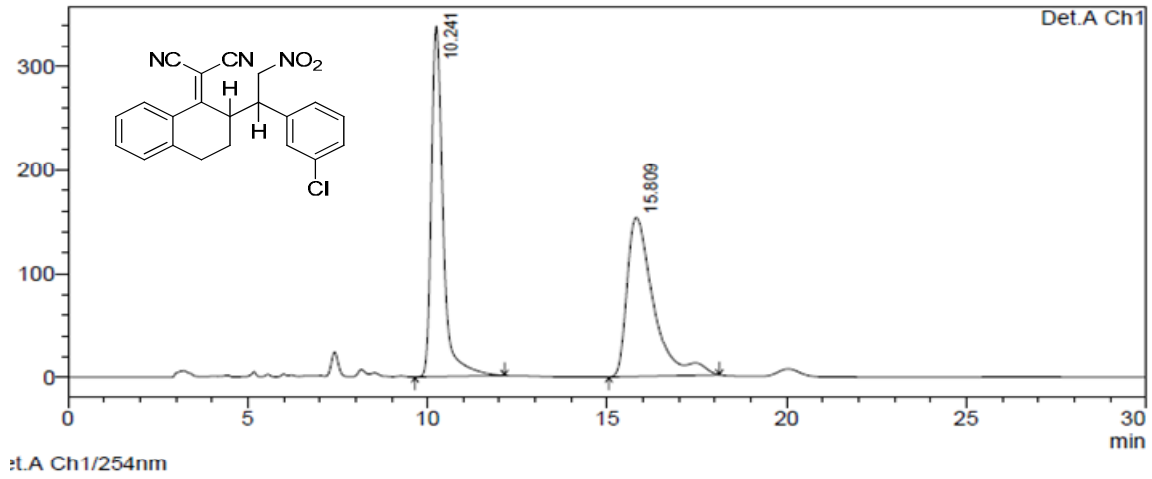
et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.241	7678770	338919	49.292	68.827
2	15.809	7899399	153502	50.708	31.173
Total		15578168	492421	100.000	100.000
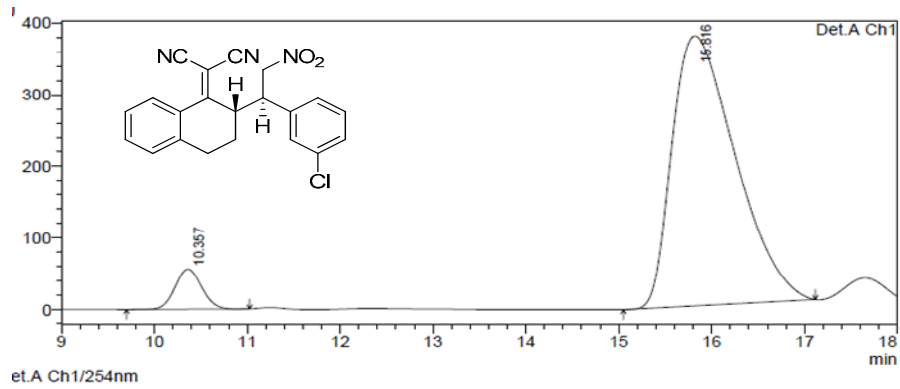
et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.357	1097625	55457	5.789	12.821
2	15.816	17861565	377079	94.211	87.179
Total		18959190	432537	100.000	100.000

HPLC profile for table 4, entry 5

A Ch1/254nm

PeakTable

Detector A Ch1 254nm
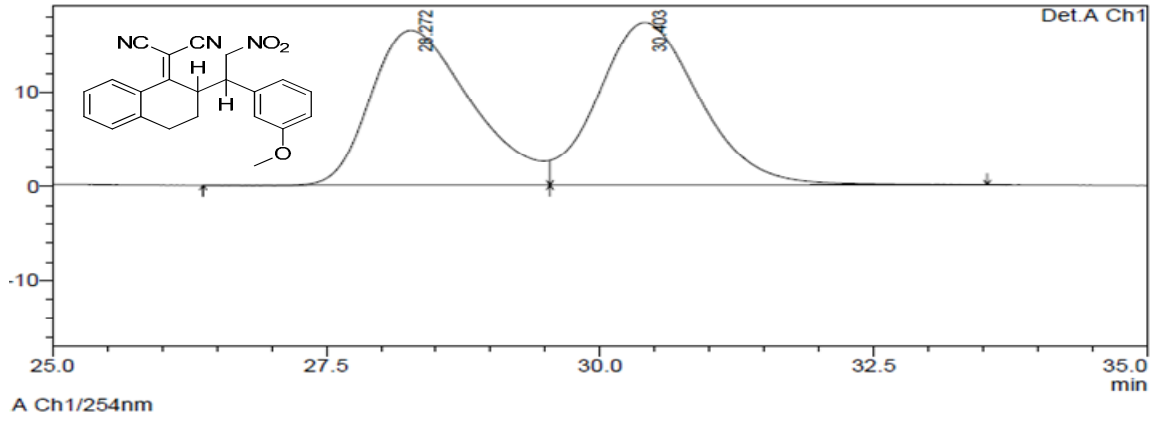
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.272	1050746	16429	48.566	48.791
2	30.403	1112818	17242	51.434	51.209
Total		2163564	33671	100.000	100.000

et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm
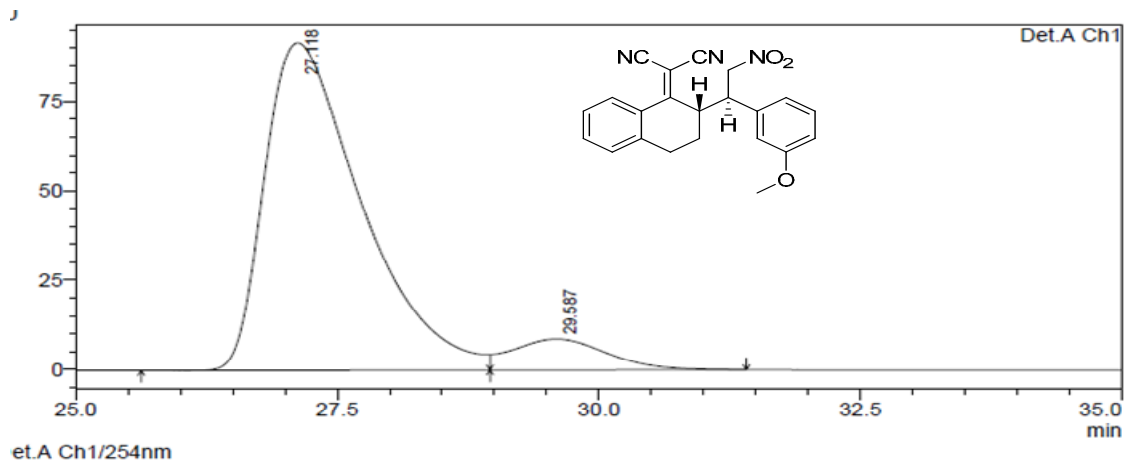
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.118	5895994	91631	91.538	91.357
2	29.587	545072	8669	8.462	8.643
Total		6441065	100300	100.000	100.000

HPLC profile for table 4, entry 6

Det.A Ch1

Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm
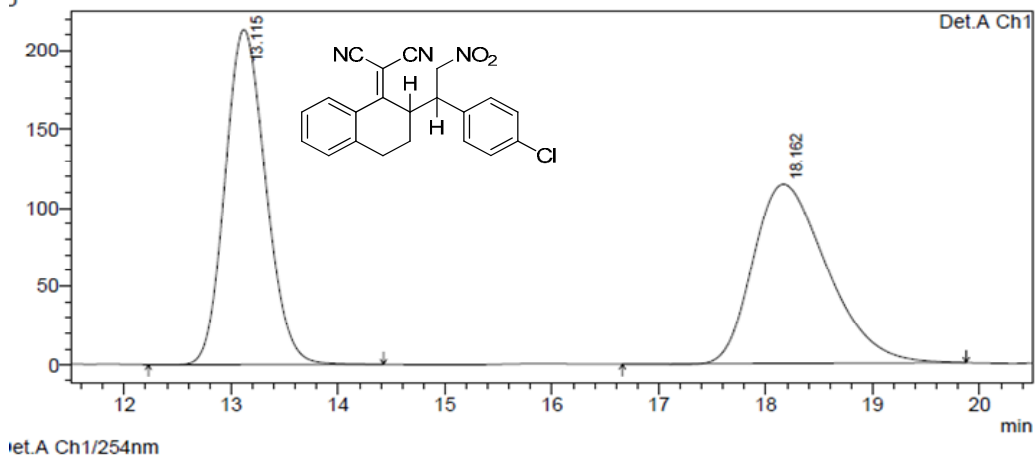
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.115	5624880	212978	50.629	65.124
2	18.162	5485166	114057	49.371	34.876
Total		11110045	327034	100.000	100.000

Det.A Ch1

et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm
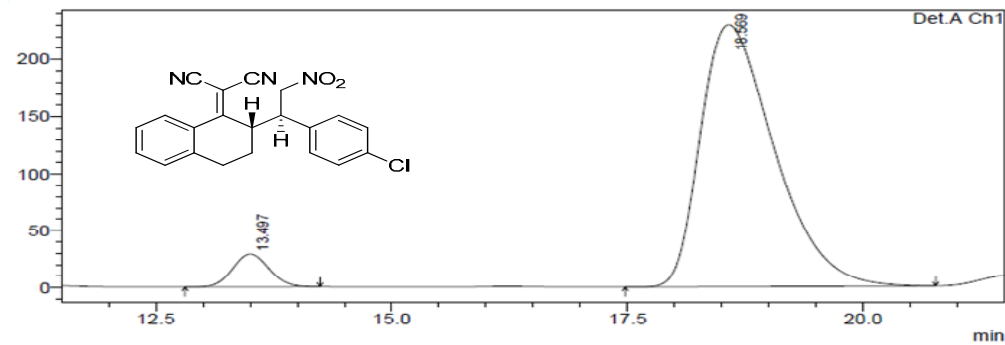
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.497	769089	28600	5.796	11.091
2	18.569	12499451	229261	94.204	88.909
Total		13268540	257861	100.000	100.000

HPLC profile for table 4, entry 7

et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.157	2371480	82770	50.399	64.002
2	19.751	2333973	46554	49.601	35.998
Total		4705453	129324	100.000	100.000

et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm
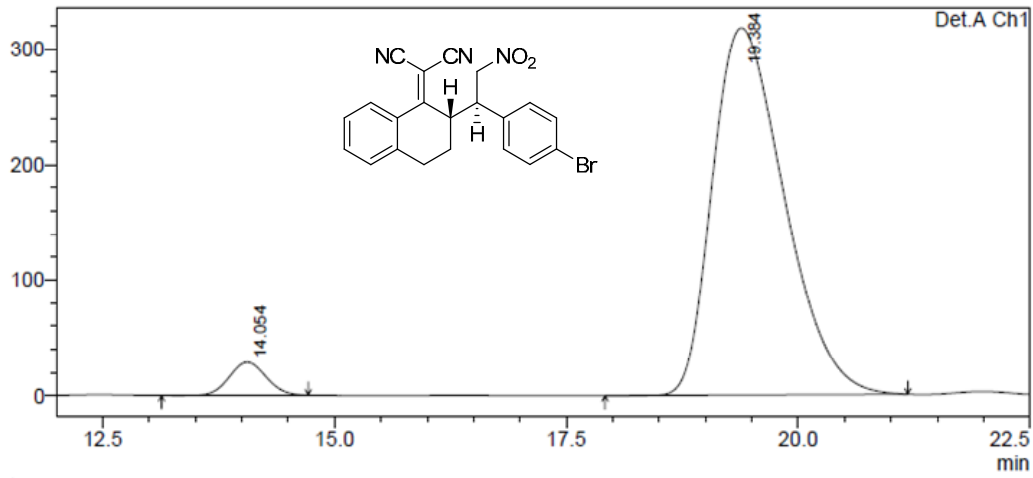
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.054	781132	28397	4.364	8.213
2	19.384	17117417	317366	95.636	91.787
Total		17898550	345763	100.000	100.000

HPLC profile for table 4, entry 8

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.157	2371480	82770	50.399	64.002
2	19.751	2333973	46554	49.601	35.998
Total		4705453	129324	100.000	100.000

et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.054	781132	28397	4.364	8.213
2	19.384	17117417	317366	95.636	91.787
Total		17898550	345763	100.000	100.000

HPLC profile for table 5, entry 1

PDA Multi 1

ЭA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.081	9015261	151860	49.881	46.087
2	17.564	9058285	177646	50.119	53.913
Total		18073545	329505	100.000	100.000

PDA Multi 1

A Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.141	2168839	36067	2.366	1.938
2	17.587	89482351	1824522	97.634	98.062
Total		91651190	1860589	100.000	100.000

HPLC profile for table 5, entry 2

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.361	3382550	100386	50.075	52.415
2	20.971	3372374	91134	49.925	47.585
Total		6754924	191519	100.000	100.000
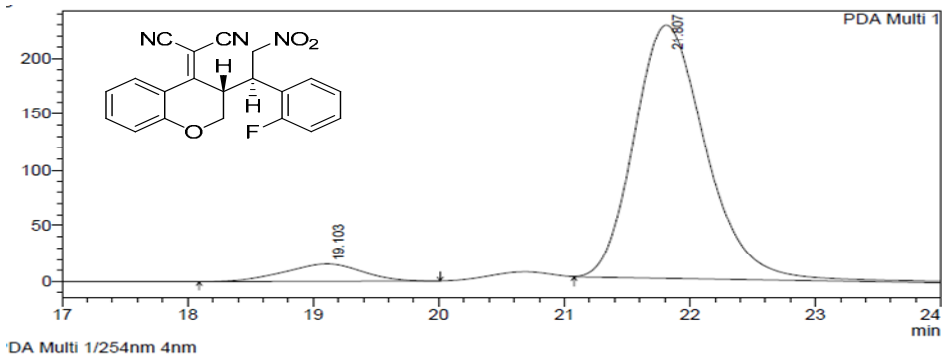
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.103	662258	15482	6.821	6.384
2	21.807	9046242	227034	93.179	93.616
Total		9708500	242516	100.000	100.000

HPLC profile for table 5, entry 3

DA Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm
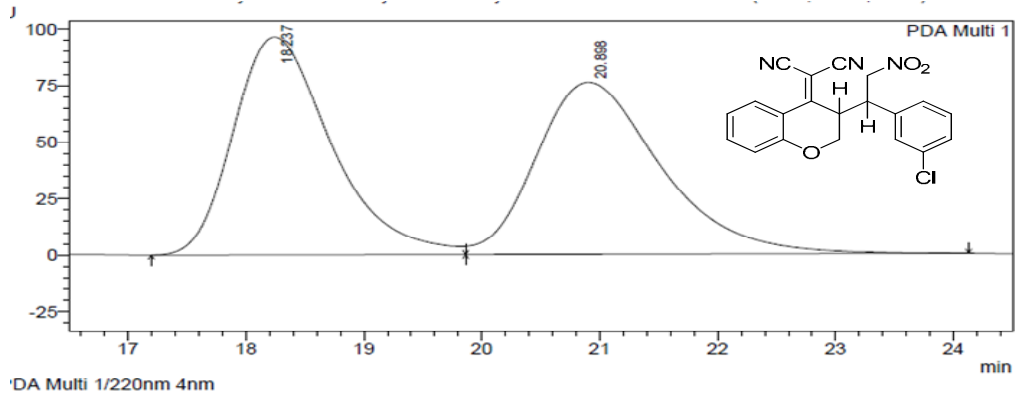
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.237	5589148	96384	49.918	55.944
2	20.898	5607447	75903	50.082	44.056
Total		11196595	172287	100.000	100.000

A Multi 1/220nm 4nm

PeakTable

PDA Ch1 220nm 4nm
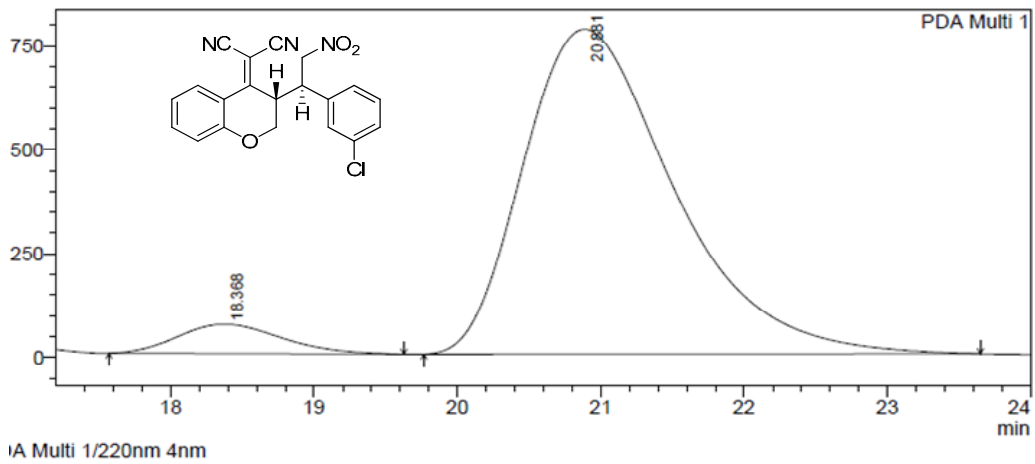
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.368	3519944	69919	5.814	8.201
2	20.881	57027713	782674	94.186	91.799
Total		60547657	852593	100.000	100.000

HPLC profile for table 5, entry 4

et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm
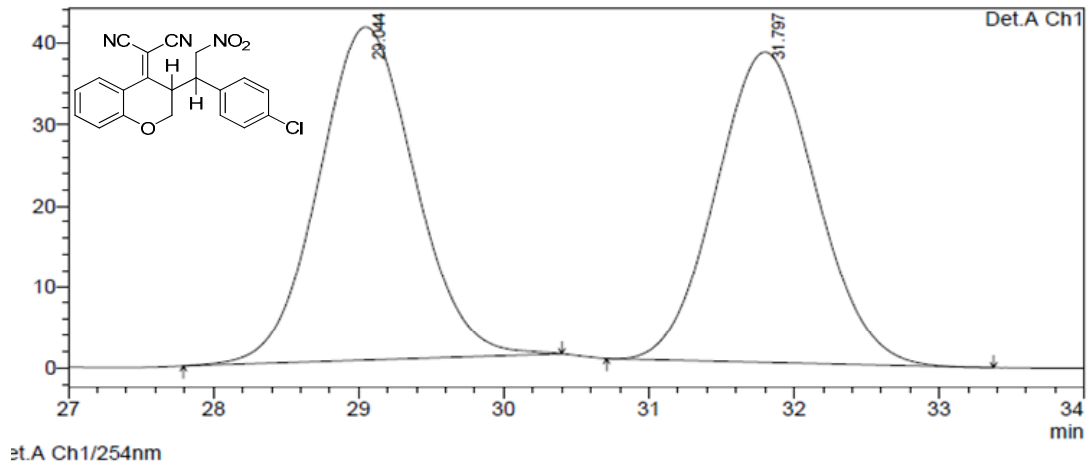
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.044	1893763	41025	50.683	51.835
2	31.797	1842691	38121	49.317	48.165
Total		3736454	79146	100.000	100.000

et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm
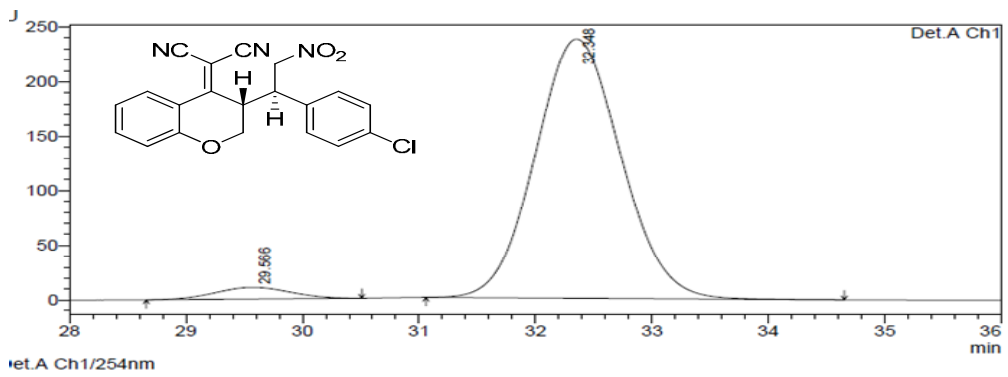
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.566	475140	10639	3.767	4.294
2	32.348	12138613	237148	96.233	95.706
Total		12613754	247787	100.000	100.000

HPLC profile for table 5, entry 5

et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm
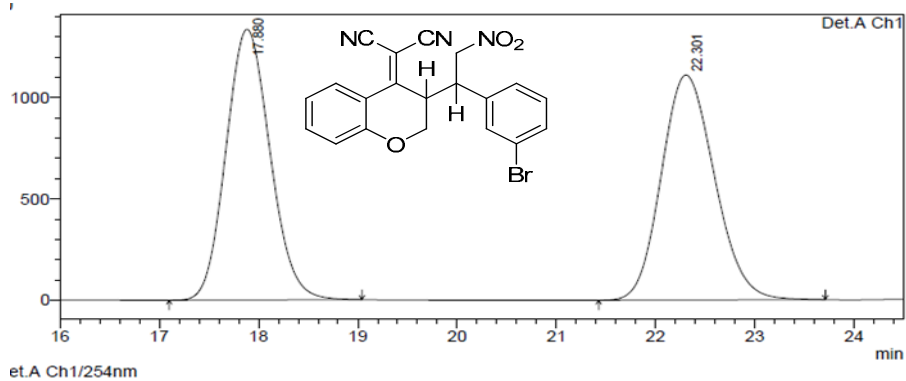
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.880	41183161	1334860	49.888	54.610
2	22.301	41368840	1109496	50.112	45.390
Total		82552002	2444356	100.000	100.000

et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm
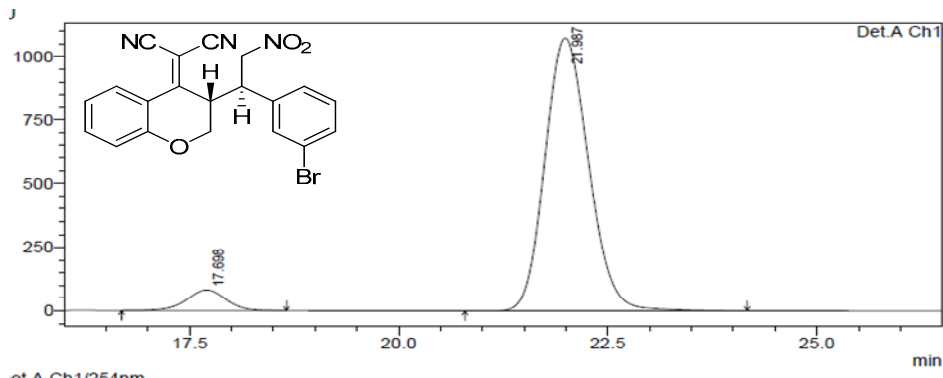
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.698	2679378	81398	6.429	7.048
2	21.987	38998718	1073432	93.571	92.952
Total		41678096	1154830	100.000	100.000

HPLC profile for table 5, entry 6

IA Multi 1/254nm 4nm
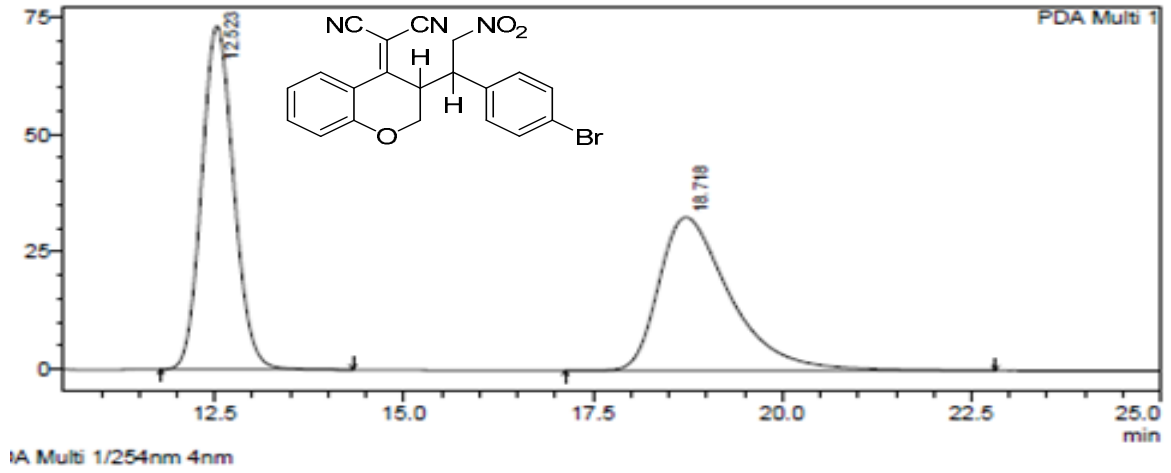
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.523	2154083	73118	50.258	69.154
2	18.718	2131933	32614	49.742	30.846
Total		4286016	105732	100.000	100.000

DA Multi 1/254nm 4nm
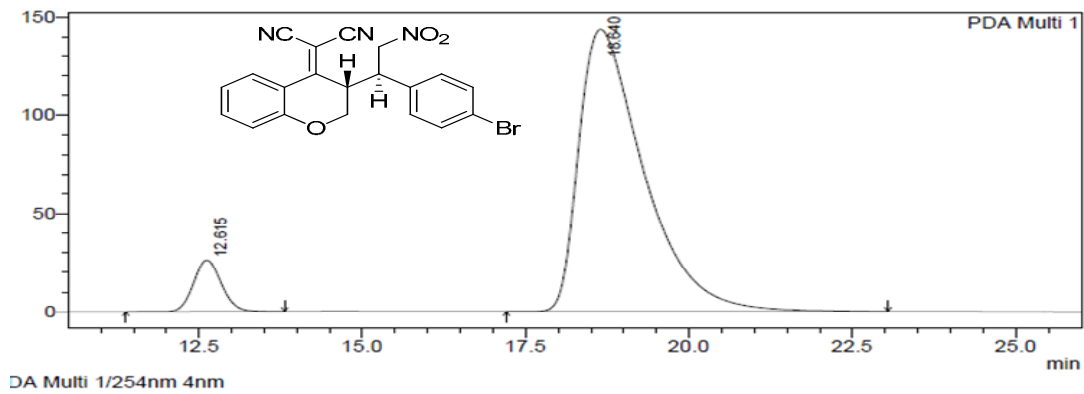
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.615	774877	25984	7.263	15.334
2	18.640	9894663	143472	92.737	84.666
Total		10669539	169455	100.000	100.000

HPLC profile for table 5, entry 7

DA Multi 1/254nm 4nm
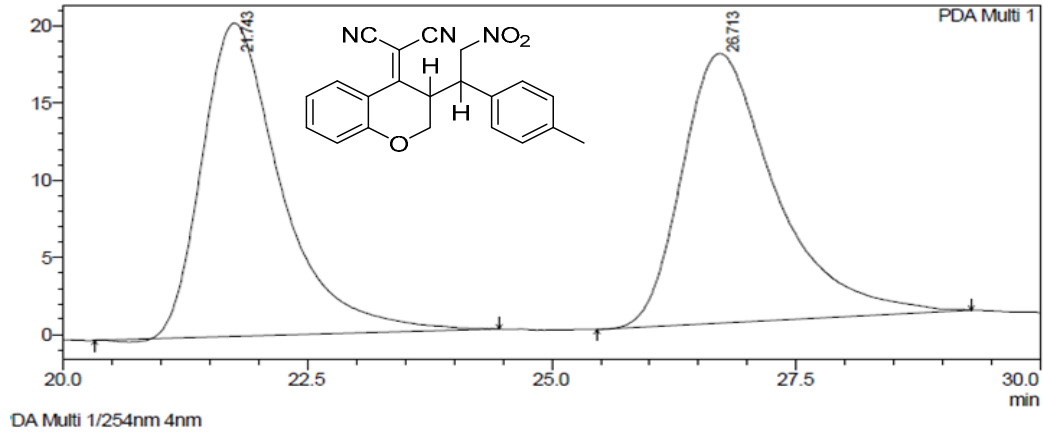
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	21.743	1146070	20286	49.465
2	26.713	1170878	17472	50.535
Total		2316948	37758	100.000

Height %
53.727
46.273
100.000

DA Multi 1/254nm 4nm
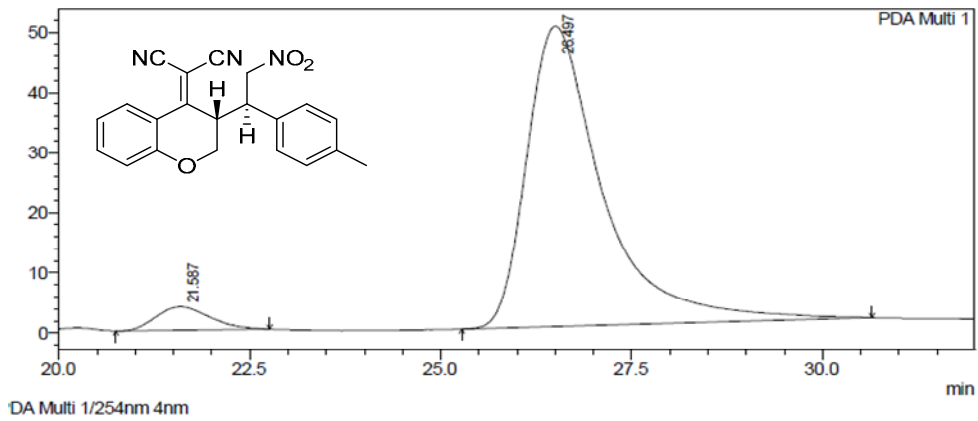
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.587	190903	3889	5.209	7.228
2	26.497	3473651	49914	94.791	92.772
Total		3664554	53803	100.000	100.000

HPLC profile for table 5, entry 8

DA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm
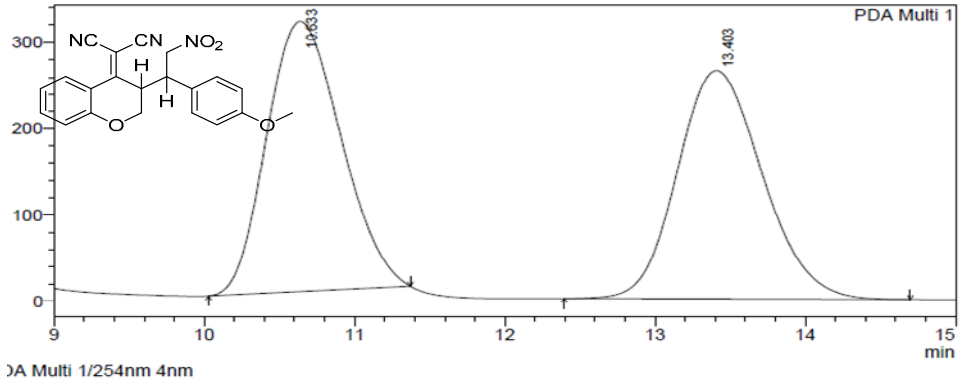
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.633	10796471	313123	50.829	54.145
2	13.403	10444326	265186	49.171	45.855
Total		21240797	578309	100.000	100.000

DA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm
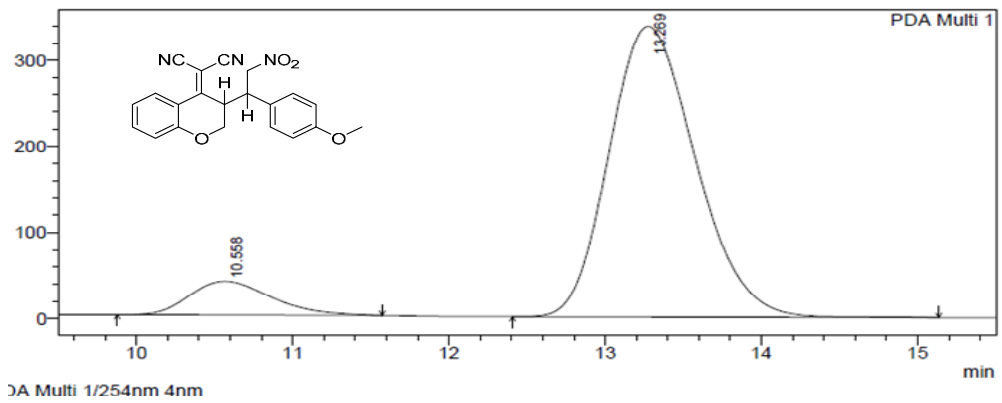
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.558	1416199	39060	9.831	10.357
2	13.269	12988798	338071	90.169	89.643
Total		14404997	377131	100.000	100.000

HPLC profile for Scheme 2, entry 8a

1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.361	3382550	100386	50.075	52.415
2	20.971	3372374	91134	49.925	47.585
Total		6754924	191519	100.000	100.000

1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm
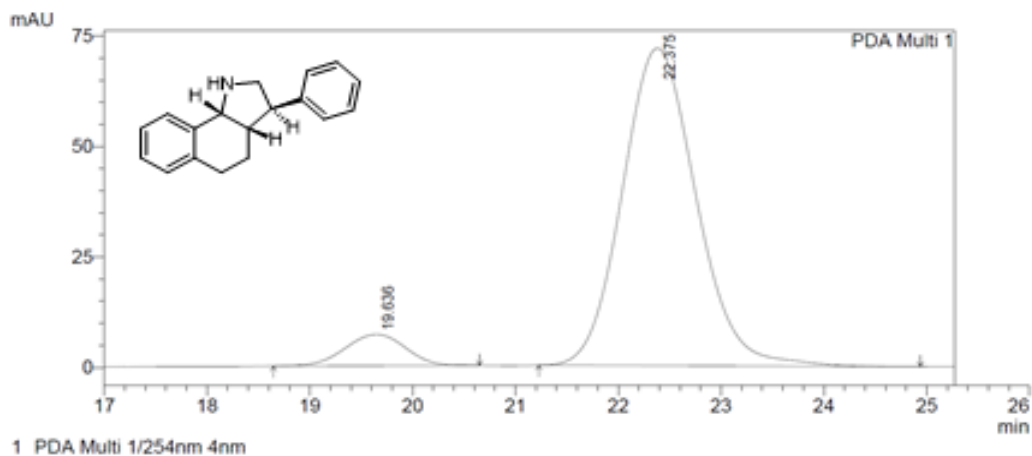
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.636	289704	7079	7.480	8.968
2	22.375	3583401	71856	92.520	91.032
Total		3873105	78936	100.000	100.000

HPLC profile for Scheme 2, entry 8b

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	51.864	36557083	383877	51.339	53.730
2	61.375	34649864	330580	48.661	46.270
Total		71206947	714457	100.000	100.000

1 PDA Multi 3/254nm 4nm

PeakTable

PDA Ch3 254nm 4nm
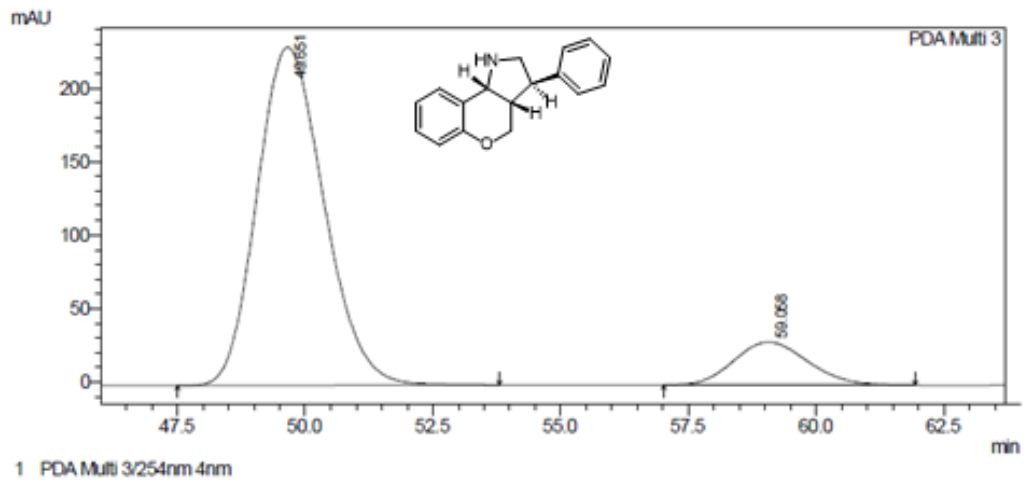
Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.651	20982936	230042	87.569	88.691
2	59.058	2978791	29334	12.431	11.309
Total		23961727	259376	100.000	100.000