Supporting Information

An Asymmetric Intramolecular Conjugate Addition nitro-Mannich route to *cis*-2-aryl-3-nitrotetrahydroquinolines

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General Experimental

Unless otherwise stated, all reactions were carried out under an atmosphere of nitrogen. All glassware was flame dried under a stream of nitrogen before use. Cooling to 0 °C was effected using an ice-water bath. Reactions were monitored by thin layer chromatography (TLC) using Polygram Sil G/UV_{254} 0.25 mm silica gel precoated plastic plates with fluorescent indicator. Sheets were visualised using ultraviolet light (254 nm), ninhydrin or $KMnO_4$, as appropriate. Flash chromatography was performed using Fluorochem silica gel 60, 35-70 μ. The liquid phase was analytical grade 40-60 petroleum ether (pet. Ether) and ethyl acetate (EtOAc) unless otherwise stated.

Removal of solvents (*in vacuo*) was achieved using a Vacuubrand diaphragm pump or house vacuum and Büchi rotary evaporators.

All NMR data was collected using a Bruker AMX 300 MHz, Bruker AVANCE III 400 MHz, Bruker AVANCE 500 MHz or Bruker AVANCE III 600 MHz. Data was manipulated directly using Bruker XwinNMR (version 2.6) or TopSpin (version 2.1) or Mnova (version 9.1.0). Reference values for residual solvents were taken as δ = 7.27 ($CDCl_3$) and 2.51 ppm (DMSO-*d*6) for ^{1}H NMR; δ = 77.16 ppm ($CDCl_3$) for ^{13}C NMR. Multiplicities for coupled signals were denoted as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad, apt. = apparent and dd = double doublet *etc.* Coupling constants (*J*) are given in Hz and are uncorrected. Where appropriate, COSY, DEPT,

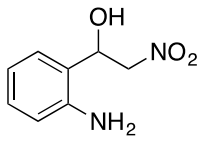
HMBC, HMQC and NOE experiments were carried out to aid assignment. Mass spectroscopy data was collected on a Thermo Finnigan Mat900xp (EI/CI) VG-70se (FAB) and Waters LCT Premier XE (ES) instruments. Infrared data was collected using a Perkin-Elmer 1600 FTIR machine as a thin film unless otherwise stated. Elemental analysis was performed on an Exeter Analytical Inc. EA440 horizontal load analyser. Melting points are uncorrected and were recorded on a Stuart Scientific SMP3 system. Optical rotations were obtained using a Jasco DIP370 digital polarimeter and are reported in deg cm^2 g^{-1}. Chiral HPLC was performed using a Chiralcel OD 25 cm analytical column. Samples were dissolved in solutions of MeCN to concentrations of 2.0 mg/mL.

Purification of Solvents and Reagents:

Commercial solvents and reagents were used as supplied or purified in accordance with standard procedures, as described below. THF, Et_2O and Toluene were obtained from solvent towers, where the degassed solvent was passed through a 7 micron filter under 4 bar pressure.

2-vinylaniline[1] and 4-chloro-2-vinylaniline[2] and 2-nitro-1-(2-nitrophenyl)ethan-1-ol[3] were synthesised by literature procedures. Hantzsch ester **11** and thiourea **12** were synthesised according to a previous report.[4] Racemic samples were made using racemic catalyst **12**.

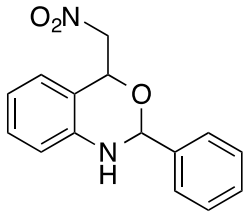
8 1-(2-aminophenyl)-2-nitroethan-1-ol



A suspension of nitroalcohol **7** (4.98g, 23.5 mmol) and Pd/C (2.49 g, 10% wt on carbon, 10 mol%) & Pearlman's catalyst (823 mg, 20% wt on carbon, 5 mol%) in DCM (35 mL) and EtOAc (35 mL) were stirred under a H_2 balloon for 5 hours. The reaction mixture was filtered through a pad of Celite, washed with DCM (3 x 20 mL) and concentrated *in vacuo*. Purification by recrystallisation ($CHCl_3$) afforded arylamine **8** as white crystals (3.29 g, 77%); mp 90-91°C; R_f = 0.43 (2% MeOH/DCM); IR ν_{max} (neat) 3356 (O-H), 1610 (N-H), 1544 (N-O); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.15 (1 H, dd, *J* = 7.5, 1.0

Hz), 7.01 (1 H, td, *J* = 7.3, 1.5 Hz), 6.68 (1 H, d, *J* = 8.0 Hz), 6.58 (1 H, td, *J* = 7.5, 1.0 Hz), 6.08 (1 H, d, *J* = 4.5 Hz), 5.31 (1 H, dt, *J* = 9.9, 4.0 Hz), 5.07 (2 H, s), 4.76 (1 H, dd, *J* = 9.0, 3.5 Hz), 4.58 (1 H, dd, *J* = 12.4, 9.9 Hz); ^{13}C NMR (DMSO-d_6, 151 MHz) δ 145.82, 128.54, 127.06, 123.16, 116.53, 115.93, 79.42, 68.08; m/z (EI) 182 (100%, $M^{+\cdot}$); HRMS $C_8H_{10}N_2O_3$ calcd. 182.0686, found 182.0685.

9 4-(nitromethyl)-2-phenyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazine **(crude)**

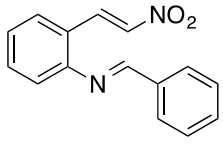


^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67-5.72 (m, 2H, CH_2NO_2), 5.72 (s, 1H, OC*H*PhNH), 5.92 (dd, *J* = 9.3, 3.1 Hz, 1H, OC*H*Ar). *Remaining signals could not be resolved.*

General Procedure A

To a suspension of aminostyrene (2.00 mmol) in DCE (10 mL) was added aldehyde (2 mmol) and AcOH (6 mmol). The reaction mixture was left to stir for 48 hours at room temperature. The solution was concentrated *in vacuo*. The residues were dissolved in DCE (6 mL) before $AgNO_2$ (6.00 mmol), 4Å molecular sieves (600 mg) and TEMPO (0.30 mmol) were added. The reaction was stirred for 2 hours at 65 °C in air, filtered through a pad of Celite and concentrated *in vacuo* to give the crude nitrostyrene, which was purified by column chromatography.

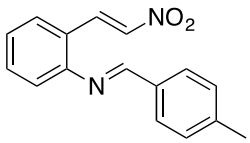
10a (*E*)-*N*-(2-((*E*)-2-nitrovinyl)phenyl)-1-phenylmethanimine



Brown oil (489 mg, 97%); R_f = 0.25 (8:2 Hexane:Et_2O); IR ν_{max} (neat) 1623 (C=N), 1509 (N-O), 1332 (N-O), 964 (C-H) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.44 (1H, s), 8.44 (1H, d, *J* = 13.9 Hz), 7.97 (2H, dd, *J* = 7.7, 1.6 Hz), 7.75 (1H, d, *J* = 13.7 Hz), 7.50 - 7.60 (5H, m), 7.31 (1H, td, *J* = 7.6, 1.1 Hz), 7.10

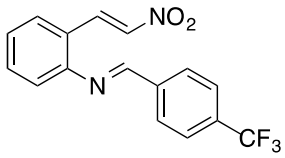
(1H, dd, *J* = 8.0, 0.9 Hz); ^{13}C NMR (CDCl$_3$, 126 MHz) δ 161.4, 152.3, 138.5, 136.3, 135.6, 133.0, 132.2, 130.0, 129.2, 129.0, 126.4, 124.4, 119.1; m/z (EI) 206 (100%, M$^+$-NO$_2$); HRMS $C_{15}H_{12}N_2O_2$ calcd. 252.0893, found 252.0895.

10b (*E*)-*N*-(2-((*E*)-2-nitrovinyl)phenyl)-1-(*p*-tolyl)methanimine



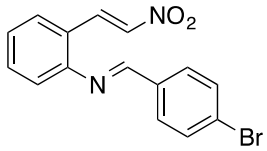
Yellow oil (500 mg, 94%); R$_f$ = 0.29 (8:2 Hexane:Et$_2$O); IR ν$_{max}$ (neat) 1503 (N-O), 1370 (C-H), 1334 (N-O), 965 (C-H) cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.42 (1H, d, *J* = 13.6 Hz), 8.39 (1H, s), 7.86 (2H, d, *J* = 8.0 Hz), 7.76 (1H, d, *J* = 13.6 Hz), 7.58 (1H, dd, *J* = 7.7, 1.1 Hz), 7.51 (1H, td, *J* = 7.7, 1.3 Hz), 7.35 (2H, d, *J* = 7.9 Hz), 7.30 (1H, td, *J* = 7.6, 1.0 Hz), 7.08 (1H, d, *J* = 7.9 Hz), 2.47 (3H, s); ^{13}C NMR (CDCl$_3$, 126 MHz) δ 161.3, 152.6, 143.0, 138.6, 136.5, 133.1, 133.0, 130.2, 129.8, 129.2, 126.1, 124.4, 119.2, 21.7; m/z (EI) 220 (100%, M$^+$-NO$_2$); HRMS $C_{16}H_{14}N_2O_2$ calcd. 266.1055, found 266.1050.

10c(*E*)-*N*-(2-((*E*)-2-nitrovinyl)phenyl)-1-(4-(trifluoromethyl)phenyl)methanimine



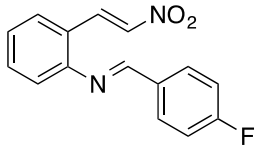
Yellow solid (608 mg, 95%); m.p. 65-67 °C; R$_f$ = 0.30 (8:2 pet. Ether:EtOAc); IR ν$_{max}$ (neat) 1625 (C=N), 1505 (N-O), 1335 (N-O) cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.49 (1H, s), 8.44 (1H, d, *J* = 13.7 Hz), 8.07 (2H, d, *J* = 8.0 Hz), 7.78 (2H, d, *J* = 8.1 Hz), 7.68 (1H, d, *J* = 13.7 Hz), 7.60 (1H, dd, *J* = 7.8, 1.4 Hz), 7.54 (1H, td, *J* = 7.7, 1.4 Hz), 7.35 (1H, td, *J* = 7.6, 1.1 Hz), 7.12 (1H, dd, *J* = 8.0, 1.1 Hz); ^{13}C NMR (151 MHz, CDCl$_3$) δ 159.9, 151.4, 138.6 (d, *J* = 11.9 Hz), 138.5, 136.0, 133.61 (1C, q, *J* = 32.5 Hz), 133.2, 129.8, 129.4, 127.1, 126.1 (1C, q, *J* = 3.7 Hz), 124.7, 122.9, 121.1, 119.0; ^{19}F NMR (282 MHz, CDCl$_3$) δ -62.95 (3F, s); m/z (CI) 321 (100%, M+H$^+$), 274 (60%, M-NO$_2^+$); HRMS $C_{16}H_{12}F_3N_2O_2$ calcd. 321.0851, found 321.0859.

10d (*E*)-1-(4-bromophenyl)-*N*-(2-((*E*)-2-nitrovinyl)phenyl)methanimine



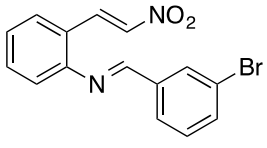
Yellow wax (652 mg, 44%); R_f = 0.3 (9:1 pet. Ether:EtOAc); IR ν_{max} (neat) 1621 (C=N), 1559 (N-O) cm^{-1}; ^1H NMR ($CDCl_3$ 600 MHz) δ 8.43 (1 H, d, *J* = 13.9 Hz), 8.39 (1 H, s), 7.83 (2 H, d, *J* = 7.9 Hz), 7.66-7.73 (3 H, m), 7.59 (1 H, d, *J* = 7.9 Hz), 7.52 (1 H, t), 7.33 (1 H, t, *J* = 7.5 Hz), 7.09 (1 H, d, *J* = 7.9 Hz, Ar*H*); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 160.1, 151.9, 138.5, 136.1, 134.3, 133.1, 132.4, 130.5, 129.9, 127.0, 126.7, 124.5, 119.0; m/z (ESI+) 331 (100%, $M+H^+$); HRMS $C_{16}H_{12}BrN_2O_2$ calcd. 331.0082, found 331.0060.

10e (*E*)-1-(4-fluorophenyl)-*N*-(2-((*E*)-2-nitrovinyl)phenyl)methanimine



Yellow wax (760 mg, 94%); R_f = 0.30 (9:1 pet. Ether:EtOAc); IR ν_{max} (neat) 1626 (C=N), 1505 (N-O), 1332 (N-O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, *J* = 13.7 Hz, 1H), 8.39 (s, 1H), 7.93-8.00 (m, 2H), 7.71 (d, *J* = 13.7 Hz, 1H), 7.57-7.60 (m, 1H), 7.48-7.55 (m, 1H), 7.31 (td, *J* = 7.6, 1.2 Hz, 1H), 7.16-7.28 (m, 2H), 7.07 (dd, *J* = 7.9, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$ 126 MHz) δ 160.1, 152.2, 138.6, 136.4, 135.1, 133.2, 132.3, 131.4, 130.0, 126.5, 124.6, 119.2, 116.5; ^{19}F ($CDCl_3$, 282 MHz) 106.30; m/z (CI) 271 (100%, $M+H^+$); HRMS $C_{15}H_{12}FN_2O_2$ calcd. 271.0883, found 271.0893

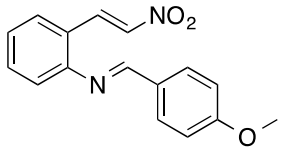
10f (*E*)-1-(3-bromophenyl)-*N*-(2-((*E*)-2-nitrovinyl)phenyl)methanimine



Yellow solid (629 mg, 95%); m.p. 105-107 °C; R_f = 0.30 (8:2 pet. Ether:Et_2O); IR ν_{max} (neat) 3107 (C-H), 1614 (C=N), 1503 (N-O), 1334 (N-O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.43 (1H, d, *J* = 13.7 Hz), 8.37 (1H, s), 8.09 (1H, s), 7.90 (1H, d, *J* = 7.6 Hz), 7.68 (1H, d, *J* = 1.1 Hz), 7.68 (1H, d, *J* = 13.7 Hz), 7.60

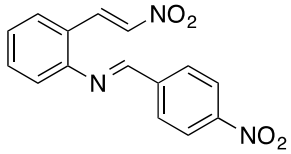
(1H, d, *J* = 7.7 Hz), 7.50-7.56 (1H, m), 7.40-7.43 (1H, m), 7.39-7.45 (1H, m), 7.33 (1H, t, *J* = 7.6 Hz), 7.07 (1H, d, *J* = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 159.9, 151.7, 138.5, 137.5, 136.0, 135.0, 133.0, 132.0, 130.6, 129.7, 127.6, 126.8, 124.5, 123.2, 119.0; m/z (CI) 331 (100%, $M+H^+$), 286 (45%, $M-NO_2^+$); HRMS $C_{15}H_{12}BrN_2O_2$ calcd. 331.0082, found 331.0079.

10g (*E*)-1-(4-methoxyphenyl)-*N*-(2-((*E*)-2-nitrovinyl)phenyl)methanimine



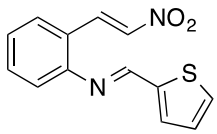
Yellow solid (288 mg, 51%); m.p. 108-110 °C; R_f = 0.36 (8:2 pet. Ether:EtOAc); IR ν_{max} (neat) 1681 (C=N), 1509 (N-O), 1333 (N-O), 1253 (C-O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.43 (1H, d, *J* = 13.7 Hz) 8.35 (1H, s), 7.92 (1H, d, *J* = 8.8 Hz), 7.77 (1H, d, *J* = 13.7 Hz), 7.57 (1H, d, *J* = 8.7 Hz), 7.51 (1H, t, *J* = 7.0 Hz), 7.29 (1H, d, *J* = 6.8 Hz), 7.07 (1H, d, *J* = 7.9 Hz), 7.05 (2H, d, *J* = 8.8 Hz), 3.91 (3H, s); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 162.9, 160.6, 152.7, 138.5, 136.6, 133.0, 131.0, 130.2, 128.6, 125.9, 124.3, 119.2, 114.5, 55.5; m/z (CI) 283 (100%, $M+H^+$), 236 (31%, $M-NO_2^+$); HRMS $C_{16}H_{15}N_2O_3$ calcd. 283.1084, found 283.1082.

10h (*E*)-1-(4-nitrophenyl)-*N*-(2-((*E*)-2-nitrovinyl)phenyl)methanimine



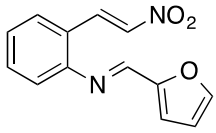
Yellow solid (487 mg, 82%); m.p. 131-133 °C; R_f = 0.38 (7:3 Hexane:EtOAc); IR ν_{max} (neat) 1630 (C=N), 1523 (N-O), 1333 (N-O) cm^{-1} ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.56 (1H, s), 8.49 (1H, d, *J* = 13.6 Hz), 8.40 (2H, d, *J* = 8.7 Hz), 8.15 (2H, d, *J* = 8.7 Hz), 7.68 (1H, d, *J* = 13.9 Hz), 7.64 (1H, d, *J* = 7.5 Hz), 7.57 (1H, t, *J* = 7.7 Hz), 7.39 (1H, t, *J* = 7.5 Hz), 7.15 (1 H, d, *J* = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 158.9, 151.0, 149.7, 140.7, 138.5, 135.7, 133.1, 129.8, 129.5, 127.5, 124.9, 124.3, 118.8; m/z (EI) 251 (100%, $M-NO_2^+$), 204 (72%, $M-N_2O_2H^+$); HRMS $C_{15}H_{11}N_3O_4$ calcd. 297.0750, found 297.0751.

10i (*E*)-*N*-(2-((*E*)-2-nitrovinyl)phenyl)-1-(thiophen-2-yl)methanimine



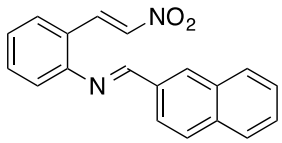
Red oil (444 mg, 86%); R_f = 0.30 (9:1 pet. Ether:EtOAc); IR ν_{max} (neat) 2920 (C-H), 1626 (C=N), 1510 (N-O), 1334 (N-O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.52 (1 H, s), 8.33 (1 H, d, *J* = 13.7 Hz), 7.80 (1 H, d, *J* = 13.7 Hz), 7.59 (1 H, d, *J* = 5.0 Hz), 7.55 (1 H, d, *J* = 3.6 Hz), 7.53 (1 H, d, *J* = 7.7 Hz), 7.45-7.50 (1 H, m), 7.23-7.33 (2 H, m), 7.17 (1 H, dd, *J* = 4.9, 3.8 Hz), 7.08 (1 H, d, *J* = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 153.8, 151.5, 142.3, 138.9, 136.3, 133.2, 132.8, 131.9, 130.7, 128.1, 126.4, 124.4, 118.9; m/z (CI) 259 (100%, $M+H^+$), 212 (39%, $M-NO_2^+$); HRMS $C_{13}H_{11}N_2O_2S$ calcd. 259.0541, found 259.0539.

10j (*E*)-1-(furan-2-yl)-*N*-(2-((*E*)-2-nitrovinyl)phenyl)methanimine



Brown oil (426 mg, 88%); R_f = 0.14 (8:2 pet. Ether:Et_2O); IR ν_{max} (neat) 1614 (C=N), 1505 (N-O), 1335 (N-O) cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 8.39 (1H, d, *J* = 13.6 Hz), 8.24 (1H, s), 7.82 (1H, d, *J* = 13.6 Hz), 7.70 (1H, dd, *J* = 1.1, 0.4 Hz), 7.57 (1H, dd, *J* = 7.7, 1.4 Hz), 7.50 (1H, td, *J* = 7.7, 1.5 Hz), 7.30 (1H, td, *J* = 7.5, 1.0 Hz), 7.10 (1H, dd, *J* = 3.5, 0.4 Hz), 7.07 (1H, dd, *J* = 7.9, 1.0 Hz), 6.63 (1H, dd, *J* = 3.5, 1.7 Hz); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.0, 151.8, 148.8, 146.6, 138.7, 136.4, 132.9, 130.3, 126.4, 124.5, 118.9, 117.4, 112.6; m/z (EI) 243 (100%, $M+H^+$), 196 (58%, $M-NO_2^+$); HRMS $C_{13}H_{10}N_2O_3$ calcd. 243.0770, found 243.0763.

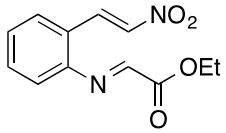
10k (*E*)-1-(naphthalen-2-yl)-*N*-(2-((*E*)-2-nitrovinyl)phenyl)methanimine



Brown solid (462 mg, 73%); m.p. 105-107 °C; R_f = 0.40 (6:4 pet. Ether:Et_2O); IR ν_{max} (neat) 1613 (C=N), 1507 (N-O), 1333 (N-O) cm^{-1}; ^1H NMR ($CDCl_3$, 600

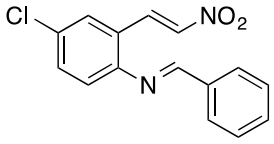
MHz) δ 8.59 (1 H, s), 8.50 (1 H, d, *J* = 13.6 Hz), 8.22-8.26 (2 H, m), 7.96-8.00 (2 H, m), 7.93 (1 H, d, *J* = 7.9 Hz), 7.79 (1 H, d, *J* = 13.6 Hz), 7.57-7.63 (3 H, m), 7.55 (1 H, td, *J* = 7.7, 1.4 Hz), 7.33 (1 H, td, *J* = 7.6, 0.9 Hz), 7.15 (1 H, dd, *J* = 8.0, 1.1 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 161.4, 152.3, 138.5, 136.4, 135.4, 133.4, 133.0, 133.0, 132.3, 130.0, 129.1, 128.9, 128.1, 128.0, 126.9, 126.4, 124.5, 123.6, 119.1; m/z (CI) 303 (100%, $M+H^+$), 256 (34%, $M-NO_2^+$); HRMS $C_{19}H_{15}N_2O_2$ calcd. 303.1134, found 303.1133.

10l ethyl (*E*)-2-((2-((*E*)-2-nitrovinyl)phenyl)imino)acetate



Red oil (150 mg, 15%); R_f = 0.32 (7:3 pet. Ether:EtOAc); IR ν_{max} (neat) 1713 (C=O), 1625 (C=N), 1503 (N-O) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (1H, d, *J* = 13.8 Hz), 7.85 (1H, d, *J* = 1.1 Hz), 7.78 (1H, d, *J* = 13.6 Hz), 7.59 (1H, d, *J* = 7.7 Hz), 7.51 (1H, t, *J* = 7.7 Hz), 7.39 (1H, t, *J* = 7.6 Hz, 1H), 7.05 (1H, d, *J* = 7.9 Hz), 4.43 (2H, q, *J* = 7.1 Hz), 1.43 (3H, t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7, 152.6, 149.0, 139.6, 135.3, 132.9, 130.6, 128.8, 125.2, 118.5, 62.5, 14.2; m/z (ESI+) 247 (100%, $M-H^+$); HRMS $C_{12}H_{12}N_2O_4$ calcd. 247.0719, found 247.0725.

10m (*E*)-*N*-(4-chloro-2-((*E*)-2-nitrovinyl)phenyl)-1-phenylmethanimine

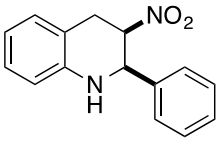


Yellow solid (534 mg, 93%); m.p. 128-130 °C; R_f = 0.28 (9:1 pet. Ether:EtOAc); IR ν_{max} (neat) 3110 (C-H), 1615 (C=N), 1576 (C=C), 1508 (N-O), 1332 (N-O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.43 (1 H, s), 8.37 (1 H, d, *J* = 13.6 Hz), 7.96 (1 H, dd, *J* = 8.2, 1.3 Hz), 7.72 (1 H, d, *J* = 13.7 Hz), 7.53 - 7.60 (5 H, m), 7.48 (1 H, dd, *J* = 8.5, 2.3 Hz), 7.06 (1 H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 162.0, 150.6, 135.4, 139.3, 135.1, 132.8, 132.6, 132.0, 129.4, 129.4, 129.2, 126.0, 120.5,; m/z (ESI+) 287 (100%, $M+H^+$); HRMS $C_{15}H_{12}ClN_2O_2$ calcd. 287.0587, found 287.0597.

General procedure B

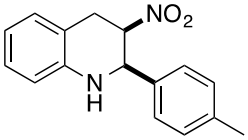
To a solution of nitrostyrene (0.1 mmol) and Hantzsch ester **11** (0.1 mmol) in PhMe (1 mL) was added catalyst **12** (5 mol%, 5.00 μmol) and the reaction mixture was stirred for 18 hours at 0 °C. The solution was concentrated *in vacuo* to give the crude tetrahydroquinoline. Purification by column chromatography (9:1 Hexane:EtOAc or 1:1 Hexane:DCM) gave the pure tetrahydroquinoline.

13a (2*R*,3*R*)-3-nitro-2-phenyl-1,2,3,4-tetrahydroquinoline



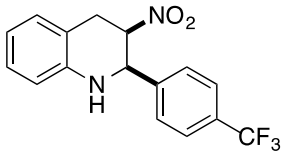
Yellow Solid (32 mg, 93%); m.p. 136-137 °C; Enantiomeric excess 97%; $[\alpha]_D^{20}$= 85.9 (c 0.17, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) 7.30-7.35 (3H, m), 7.20-7.23 (2H, m), 7.13 (1H, t, *J* = 7.5 Hz), 7.09 (1H, d, *J* = 7.5 Hz), 6.78 (1H, td, *J* = 7.4, 0.9 Hz), 6.67 (1H, d, *J* = 7.9 Hz) 5.14 (1H, ddd, *J* = 8.7, 4.7, 4.7 Hz), 5.09 (1H, d, *J* = 4.1 Hz), 4.25-4.59 (1H, br.s.), 3.30 (1H, d, *J* = 8.7 Hz), 3.26 (1H, d, *J* = 5.3 Hz); HPLC analysis: Daicel Chiralpak OD, hexane/*iso*-propanol = 1:1, flow rate = 1.0 mL/min, λ = 254 nm, retention time 12.9 min (major) and 19.9 (minor). ^{1}H NMR data are consistent with literature data.[5]

13b (2*R*,3*R*)-3-nitro-2-(*p*-tolyl)-1,2,3,4-tetrahydroquinoline



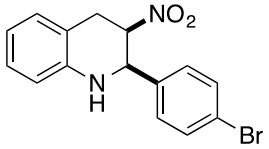
Yellow Solid (27 mg, 100%); m.p. 142-144 °C; Enantiomeric excess 98%; $[\alpha]_D^{20}$= 93.6 (c 0.33, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.21 (1H, dd, *J* = 5.0, 1.2 Hz), 7.10-7.14 (1H, m), 7.07-7.10 (1H, m), 6.94 (1H, dd, *J* = 5.1, 3.6 Hz), 6.88 - 6.91 (1H, m), 6.80 (1H, td, *J* = 7.5, 1.1 Hz), 6.65 (1H, dd, *J* = 8.0, 1.1 Hz), 5.47 (1H, d, *J* = 4.2 Hz), 5.09 (1H, ddd, *J* = 10.0, 5.4, 4.2 Hz), 4.52 (1H, s), 3.38 (1H, dd, *J* = 16.5, 10.3 Hz), 3.27 (1H, dd, *J* = 16.5, 5.5 Hz); HPLC analysis (Daicel Chiralpak OD, Hexane/*iso*-propanol 50:50, flow rate 1 mL/min, λ = 254 nm): retention time t_r, (major) = 18.0 min, t_r (minor) = 30.6 min. ^{1}H NMR data are consistent with literature data.[5]

13c (2*R*,3*R*)-3-nitro-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinoline



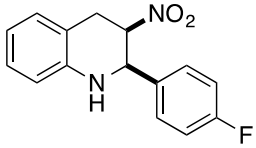
Yellow Solid (31 mg, 95%); m.p. 140-142 °C; Enantiomeric excess >99%; $[\alpha]_D^{20}$= 78.0 (c 0.38, $CHCl_3$); NMR ($CDCl_3$, 600 MHz) δ 7.57 (2H, d, *J* = 8.0 Hz), 7.33 (2H, d, *J* = 8.1 Hz), 7.07-7.18 (2H, m), 6.80 (1H, t, *J* = 7.5 Hz), 6.68 (1H, d, *J* = 8.1 Hz), 5.09-5.29 (2H, m), 4.42 (1H, s), 3.26 (2H, d, *J* = 7.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.76 (3F, s); HPLC analysis: Daicel Chiralpak OD, hexane/*iso*-propanol = 1:1, flow rate = 1.0 mL/min, λ = 254 nm, retention time 17.1 min (major) and 26.4 (minor). ^{1}H NMR data are consistent with literature data.[5]

13d (2*R*,3*R*)-2-(4-bromophenyl)-3-nitro-1,2,3,4-tetrahydroquinoline



Yellow solid (33 mg, 99%); m.p. 151-153 °C; Enantiomeric excess 98%; $[\alpha]_D^{20}$= 74.7 (c 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40-7.45 (2H, m), 7.12 (1H, t, *J* = 7.7 Hz), 7.06-7.09 (2H, m), 6.78 (1H, t, *J* = 7.4 Hz), 6.66 (1H, d, *J* = 8.0 Hz), 5.11 (1H, dt, *J* = 8.5, 4.8 Hz), 5.07 (1H, s), 4.37 (1H, s), 3.18-3.29 (2H, m); HPLC analysis: Daicel Chiralpak OD, hexane/*iso*-propanol = 1:1, flow rate = 1.0 mL/min, λ = 254 nm, retention time 19.9 min (major) and 34.3 (minor). ^{1}H NMR data are consistent with literature data.[5]

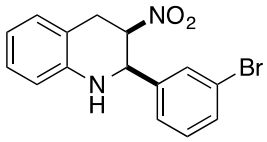
13e (2*R*,3*R*)-2-(4-fluorophenyl)-3-nitro-1,2,3,4-tetrahydroquinoline



Yellow solid (27 mg, 100%); m.p. 148-150 °C; Enantiomeric excess >99%; $[\alpha]_D^{20}$= 84.1 (c 0.15, $CHCl_3$); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.18 (2H, dd, *J* = 7.7, 4.7 Hz), 7.13 (1H, t, *J* = 7.7 Hz), 7.09 (1H, d, *J* = 7.6 Hz), 7.00 (2H, td, *J* = 8.6, 1.6 Hz), 6.79 (1H, t, *J* = 7.5 Hz), 6.65 (1H, d, *J* = 8.0 Hz), 5.05-5.13 (2H, m), 4.38 (1H, s), 3.15-3.32 (3H, m); ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.87 (1F, s); HPLC analysis: Daicel Chiralpak OD, hexane/*iso*-propranol =

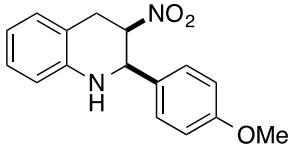
1:1, flow rate = 1.0 mL/min, λ = 254 nm, retention time 16.4 min (major) and 28.0 (minor). ^{1}H NMR data are consistent with literature data.[5]

13f (2*R*,3*R*)-2-(3-bromophenyl)-3-nitro-1,2,3,4-tetrahydroquinoline



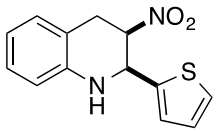
Yellow Solid (31 mg, 100%); m.p. 112-113 °C; Enantiomeric excess 96%; $[\alpha]_D^{20}$= 75.1 (c 0.2, $CHCl_3$); IR ν_{max} (neat) 3389, 1540, 1475, 1368; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.18-7.47 (1 H, d, *J* = 7.5 Hz), 7.38 (1 H, s), 7.22 (1 H, m), 7.12-7.18 (2 H, m), 7.10 (1 H, d, *J* = 7.5 Hz), 6.81 (1 H, t, *J* = 7.5 Hz), 6.67 (1 H, d, *J* = 7.9 Hz), 5.11 (1 H, ddd, *J* = 8.3, 5.3, 4.1 Hz), 5.03 (1 H, d, *J* = 3.8 Hz), 4.25 (1 H, br. s), 3.30 (1 H, dd, *J* = 16.6, 7.9 Hz), 3.25 (1 H, dd, *J* = 16.9, 5.6 Hz); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 142.2, 140.6, 132.0, 130.3, 129.9, 129.6, 128.0, 125.4, 122.8, 118.8, 115.9, 114.1, 82.3, 56.6, 27.6; m/z (CI) 286 (100%, M-NO_2); HRMS (CI) calcd. for $C_{15}H_{14}BrN_2O_2$: 333.0239, found 333.0225; HPLC analysis: Daicel Chiralpak OD, hexane/*iso*-propranol = 1:1, flow rate = 1.0 mL/min, λ = 254 nm, retention time 15.7 min (major) and 28.6 (minor).

13g (2*R*,3*R*)-2-(4-methoxyphenyl)-3-nitro-1,2,3,4-tetrahydroquinoline



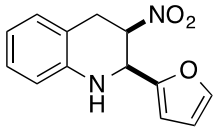
Yellow solid (28 mg, 97%); m.p. 144-146°C; Enantiomeric excess >99%; $[\alpha]_D^{20}$= 67.9 (c 0.34 , $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06-7.15 (4H, m), 6.83 (1H, d, *J* = 8.7 Hz), 6.74-6.79 (1H, m), 6.64 (1H, d, *J* = 8.0 Hz), 5.09 (1H, ddd, *J* = 8.9, 4.4 Hz), 5.03 (1H, d, *J* = 4.1 Hz), 4.35 (1H, s), 3.78 (3H, s), 3.29 (1H, dd, *J* = 16.7, 8.5 Hz), 3.22 (1H, dd, *J* = 16.6, 5.3 Hz); HPLC analysis: Daicel Chiralpak OD, hexane/*iso*-propranol = 1:1, flow rate = 1.0 mL/min, λ = 254 nm, retention time 17.9 min (major) and 31.0 (minor). ^{1}H NMR data are consistent with literature data.[5]

13i (2*S*,3*R*)-3-nitro-2-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoline



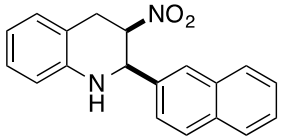
Red oil (39 mg, 97%); Enantiomeric excess 99%; $[\alpha]_D^{20}$= 46.0 (c 0.15, $CHCl_3$); IR ν_{max} (neat) 3398, 1545, 1369; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11-7.14 (1H, m), 7.08-7.10 (1H, m), 6.94 (1H, dd, *J* = 5.1, 3.6 Hz), 6.88-6.91 (1H, m), 6.80 (1H, td, *J* = 7.5, 1.1 Hz), 6.65 (1H, dd, *J* = 8.0, 1.1 Hz), 5.47 (1H, d, *J* = 4.2 Hz), 5.09 (1H, ddd, *J* = 10.0, 5.4, 4.2 Hz), 4.52 (1H, s), 3.38 (1H, dd, *J* = 16.5, 10.3 Hz), 3.27 (1H, dd, *J* = 16.5, 5.5 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.7, 140.8, 129.8, 128.2, 127.2, 126.1, 125.9, 119.1, 116.3, 114.7, 82.2, 53.3, 27.1; m/z (ESI+) 211 (100%, $M+H^+$); HRMS (ESI+) calcd. for $C_{13}H_{13}N_2O_2S$: 261.0698, found 261.0703; HPLC analysis: Daicel Chiralpak OD, hexane/*iso*-propanol = 1:1, flow rate = 1.0 mL/min, λ = 254 nm, retention time 18.0 min (major) and 30.6 (minor).

13j (2*S*,3*R*)-2-(furan-2-yl)-3-nitro-1,2,3,4-tetrahydroquinoline



Brown oil (17 mg, 88%); Enantiomeric excess 88%; $[\alpha]_D^{20}$= 89.4 (c 0.62, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35 (1 H, s), 7.05-7.13 (2 H, m), 6.79 (1 H, t, *J* = 7.5 Hz), 6.66 (1 H, d, *J* = 8.0 Hz), 6.31 (1 H, m, *J* = 3.1, 1.7 Hz), 6.20-6.23 (1 H, m), 5.23 (1 H, d, *J* = 3.6 Hz), 5.11 (6 H, ddd, *J* = 9.3, 5.2, 3.9 Hz), 4.35 (1 H, br. s.), 3.38 (1 H, dd, *J* = 16.6, 9.5 Hz), 3.28 (1 H, dd, *J* = 16.6, 5.5 Hz); HPLC analysis: Daicel Chiralpak OD, hexane/*iso*-propanol = 1:1, flow rate = 1.0 mL/min, λ = 254 nm, retention time 9.20 min (major) and 13.2 (minor). ^{1}H NMR data are consistent with literature data.[5]

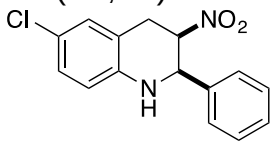
13k (2*R*,3*R*)-2-(naphthalen-2-yl)-3-nitro-1,2,3,4-tetrahydroquinoline



Brown oil (31 mg, 100%); Enantiomeric excess 98%; $[\alpha]_D^{20}$= 63.6 (c 0.38, $CHCl_3$); IR ν_{max} (neat) 2919, 1563, 1508, 1334; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.76-7.86 (3 H, m), 7.71 (1 H, s), 7.46-7.52 (2 H, m), 7.32 (1 H, dd, *J* = 8.5, 1.6 Hz), 7.17 (1 H, t, *J* = 7.6 Hz), 7.12 (1 H, d, *J* = 7.4 Hz), 6.82 (1 H, t, *J* = 7.4

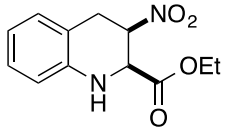
Hz), 6.72 (1 H, d, *J* = 7.9 Hz), 5.24 (1 H, d, *J* = 3.6 Hz), 5.20-5.24 (1 H,), 4.49 (1 H, br. s), 3.36 (1 H, dd, *J* = 16.9, 8.0 Hz), 3.28 (1 H, dd, *J* = 16.8, 5.0 Hz); HRMS (CI) calcd. for $C_{19}H_{17}N_2O_2$: 305.1290, found 305.1289; HPLC analysis: Daicel Chiralpak OD, hexane/*iso*-propanol = 1:1, flow rate = 1.0 mL/min, λ = 254 nm, retention time 23.1 min (major) and 43.1 (minor). ^{1}H NMR data are consistent with literature data.[5]

13l (2*R*,3*R*)-6-chloro-3-nitro-2-phenyl-1,2,3,4-tetrahydroquinoline



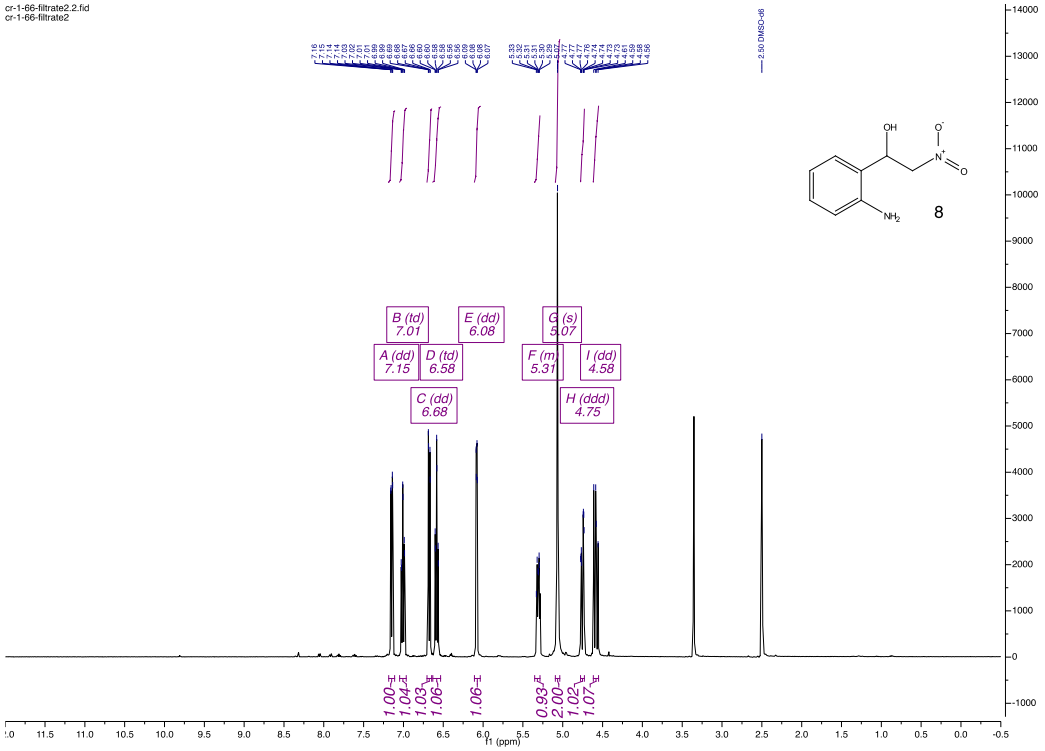
Yellow wax (32 mg, 93%); Enantiomeric excess 93%; $[\alpha]_D^{20}$= 65.2 (c 0.2, $CHCl_3$); IR ν_{max} (neat) 3385, 1547, 1368; ^{1}H NMR ($CDCl_3$, 600 MHz) 7.32-7.36 (3H, m), 7.17-7.23 (2H, m), 7.07-7.09 (2H, m), 6.58-6.61 (1H, m), 5.11 (1H, ddd, J = 7.8, 5.3, 4.0 Hz), 5.05 (1H, d, *J* = 3.8 Hz), 4.41 (1H, br. s), 3.28 (1H, dd, *J* = 16.9, 7.7 Hz), 3.22 (1H, dd, *J* = 16.8, 5.5 Hz),. ^{13}C NMR ($CDCl_3$, 151 MHz) δ 141.3, 137.8, 129.1, 129.0, 128.9, 127.9, 126.7, 123.0, 117.6, 115.1, 82.1, 57.1, 27.7; m/z (EI) 288 (100%, $M^{+\cdot}$); HRMS (CI) calcd. for $C_{15}H_{14}ClN_2O_2$: 288.0666, found 288.0660; HPLC analysis: Daicel Chiralpak OD, hexane/*iso*-propanol = 1:1, flow rate = 1.0 mL/min, λ = 254 nm, retention time 8.3 min (major) and 21.0 (minor).

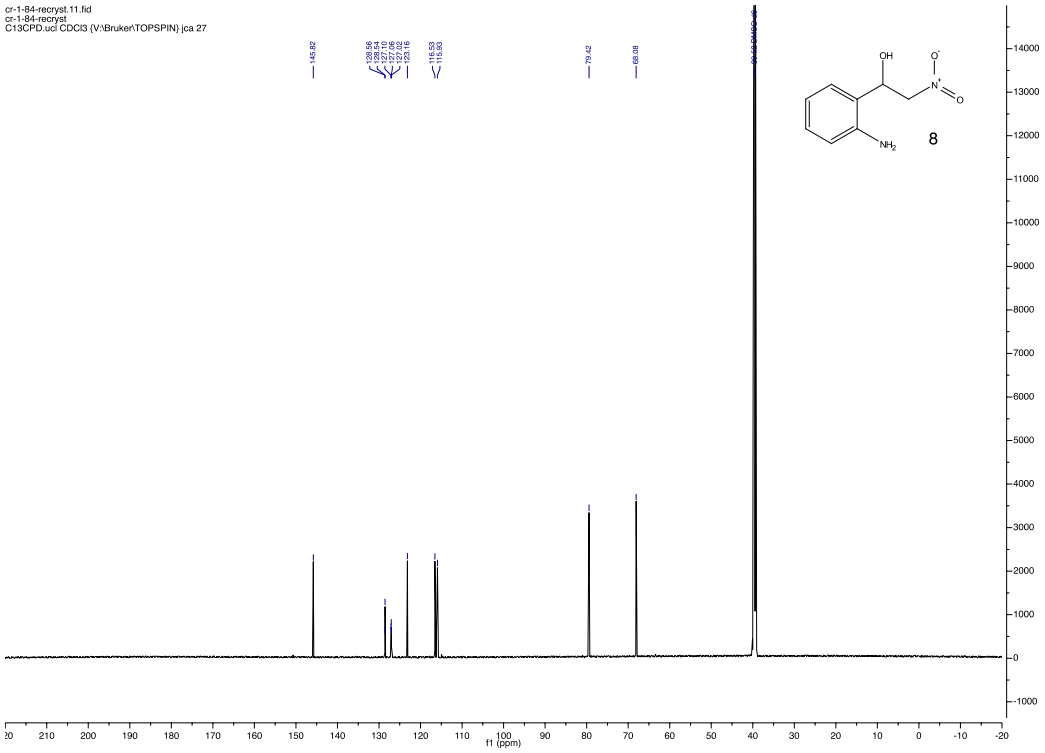
13m ethyl (2*S*,3*R*)-3-nitro-1,2,3,4-tetrahydroquinoline-2-carboxylate

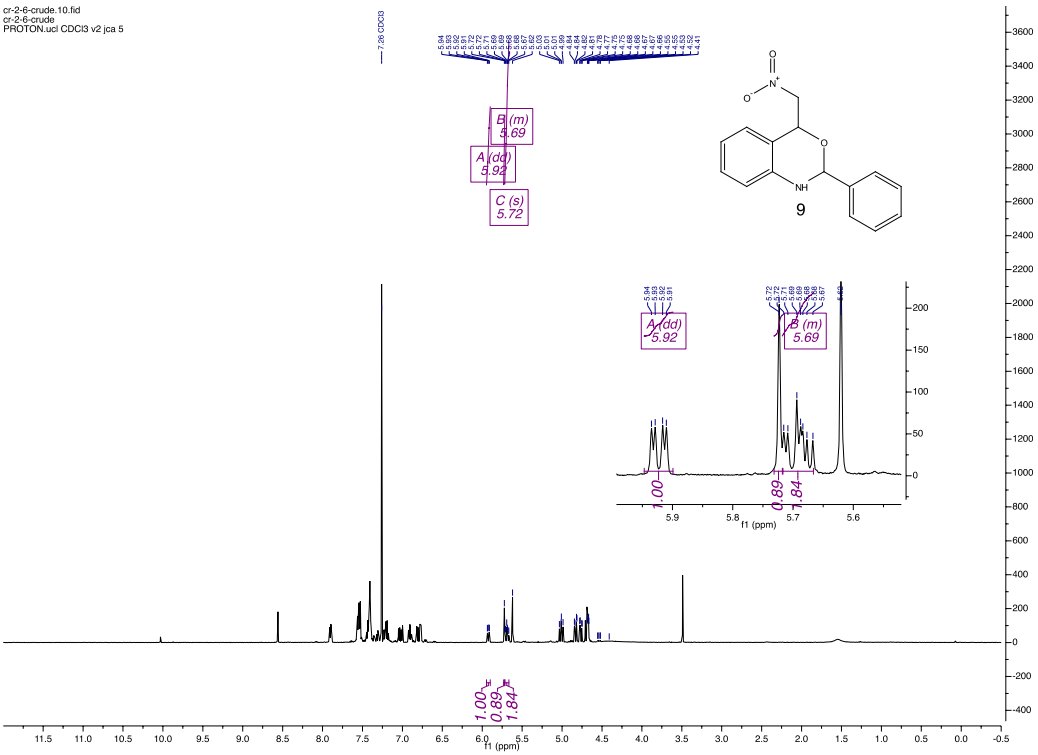


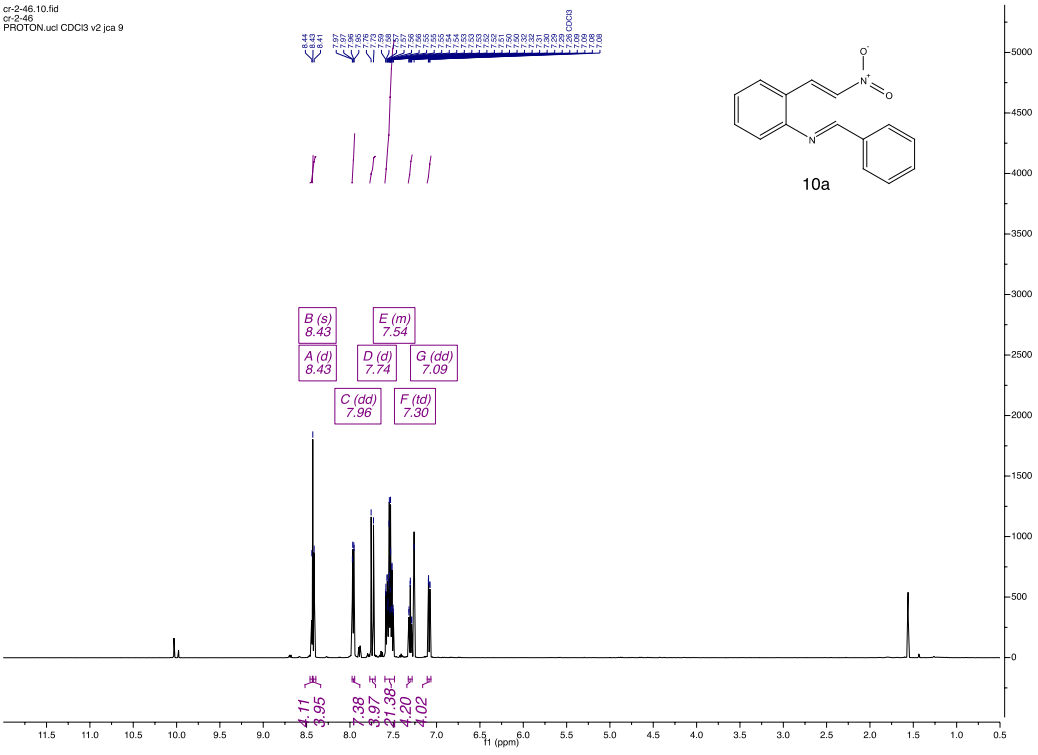
White solid (22 mg, 88%); m.p. 35 °C (dec); IR ν_{max} (neat) 3386, 1723, 1555; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02-7.08 (2H, m), 6.74 (1H, t, *J* = 7.4 Hz), 6.64 (1H, d, *J* = 8.0 Hz), 5.28-5.32 (1H, m), 4.60 (1H, s), 4.28-4.42 (3H, m), 3.67 (1H, dd, *J* = 17.5, 3.2 Hz), 3.37 (1H, dd, *J* = 17.4, 5.2 Hz), 1.33 (3H, td, *J* = 7.2, 1.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 141.5, 129.5, 128.1, 119.2, 115.7, 115.2, 78.5, 62.6, 55.6, 30.4, 14.2; m/z (ESI+) 251 (100%, $M+H^+$); HRMS (ESI) calcd. for $C_{12}H_{15}N_2O_4$: 251.1032, found 251.1037.

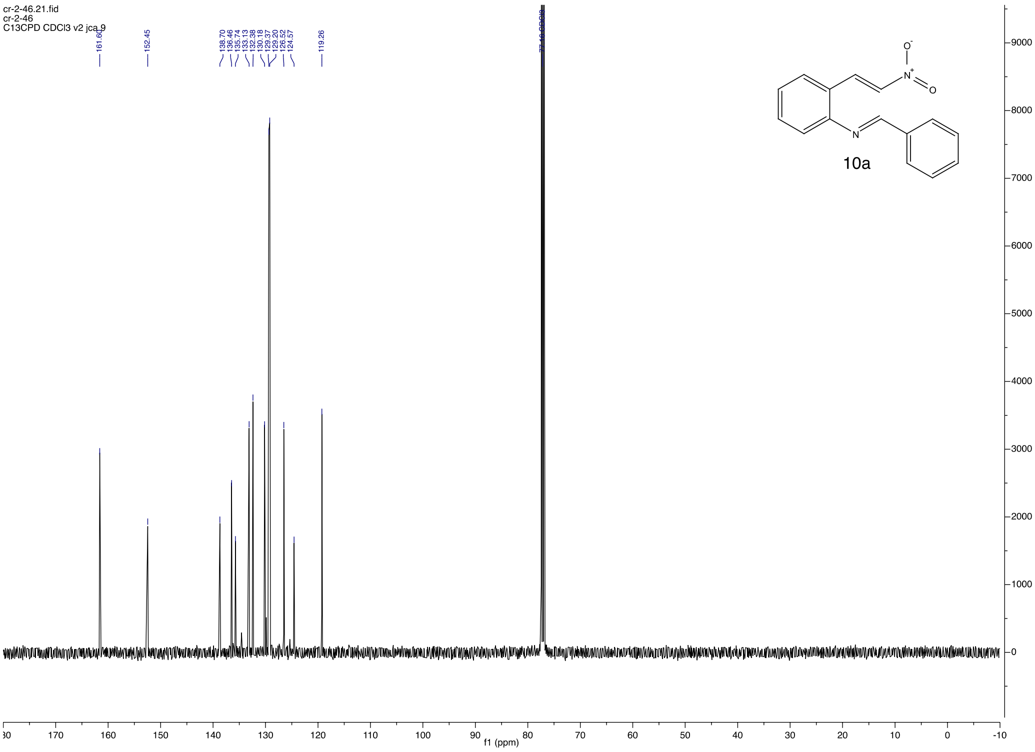
Spectra and HPLC Traces

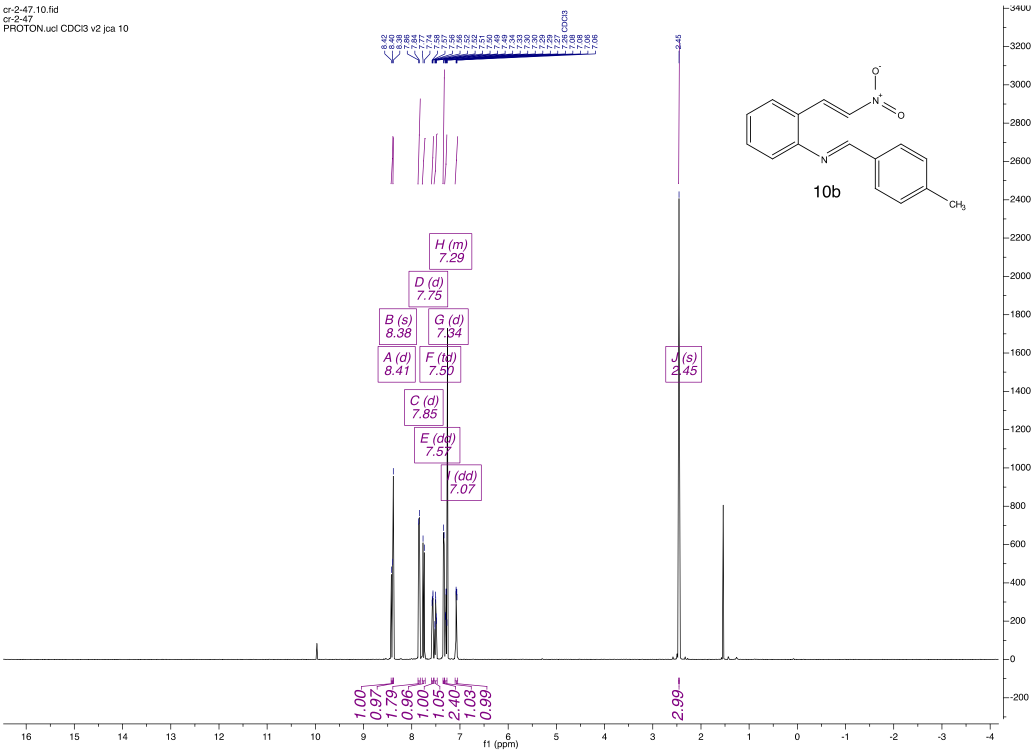


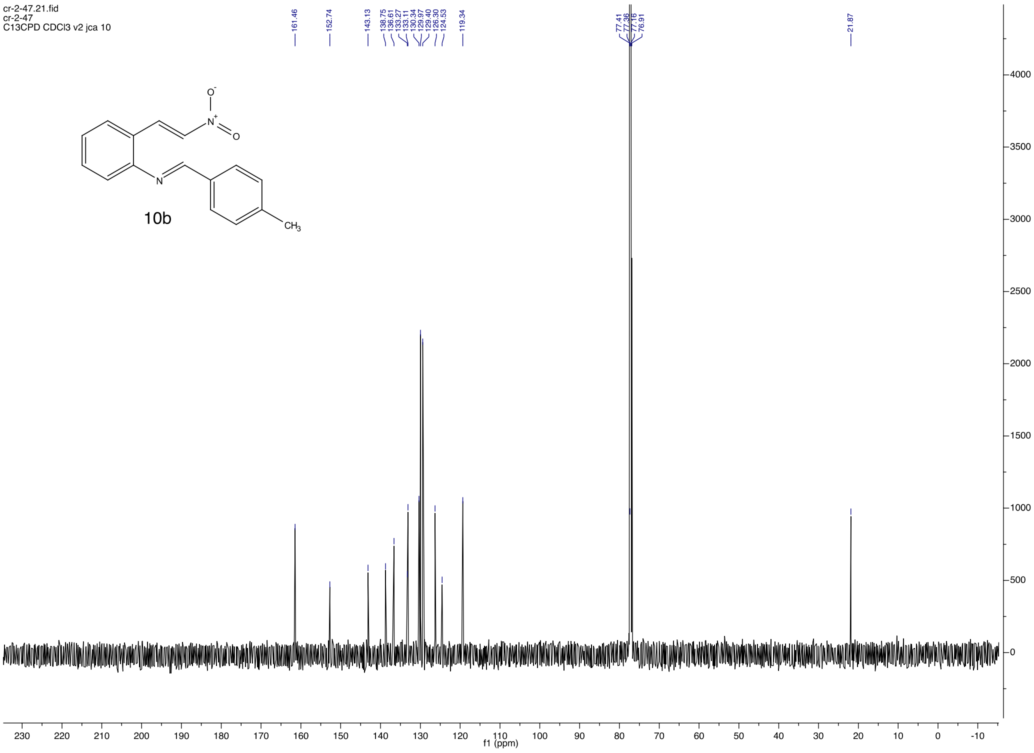


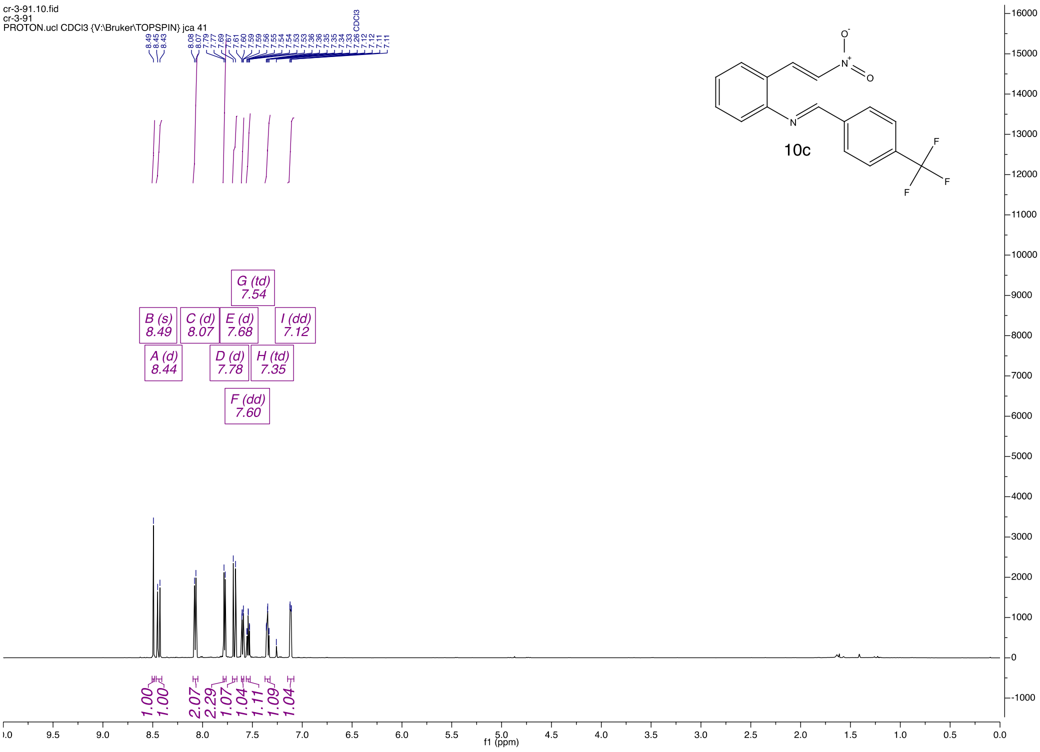

cr-2-6-crude.10.fid
cr-2-6-crude
PROTON.ucl CDCl3 v2 jca 5
B (m) 5.69
A (dd) 5.92
C (s) 5.72
9
1.00
0.89
1.84
f1 (ppm)

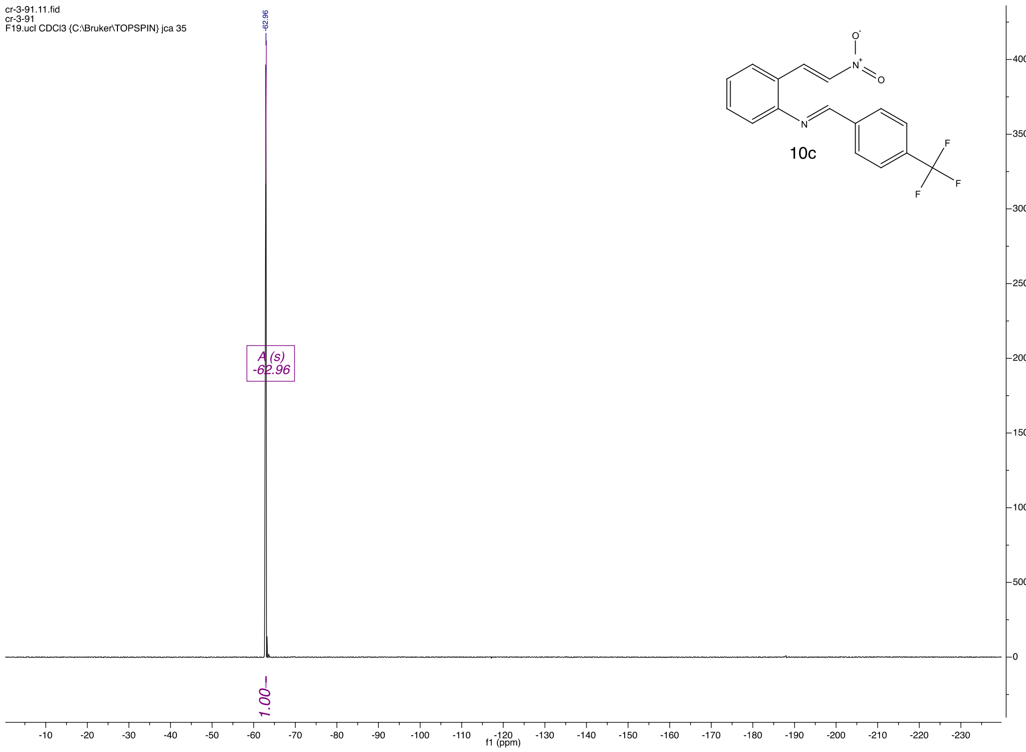

cr-2-46.10.fid
cr-2-46
PROTON.ucl CDCl3 v2 jca 9
B (s) 8.43
E (m) 7.54
A (d) 8.43
D (d) 7.74
G (dd) 7.09
C (dd) 7.96
F (td) 7.30
10a
4.11
3.95
7.38
1.97
1.38
4.20
4.02
f1 (ppm)


cr-2-46.21.fid
cr-2-46
C13CPD CDCl3 v2 jca 9
152.45
138.70
136.46
135.74
133.13
132.38
130.18
129.37
129.20
126.52
124.57
119.26
10a
f1 (ppm)

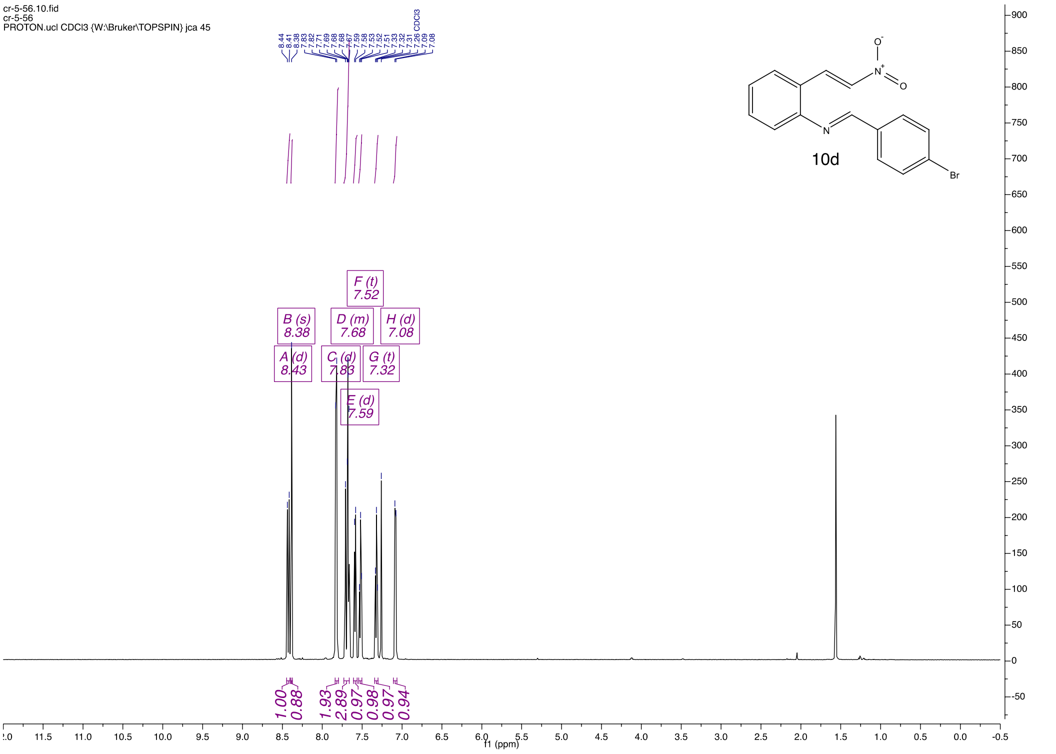

cr-2-47.10.fid
cr-2-47
PROTON.ucl CDCl3 v2 jca 10
CDCl3
2.45
10b
CH_3
H (m) 7.29
D (d) 7.75
B (s) 8.38
G (d) 7.34
A (d) 8.41
F (td) 7.50
J (s) 2.45
C (d) 7.85
E (dd) 7.57
I (dd) 7.07
1.00
0.97
1.79
0.96
1.00
1.05
2.40
1.03
0.99
2.99
f1 (ppm)


cr-2-47.21.fid
cr-2-47
C13CPD CDCl3 v2 jca 10
10b
f1 (ppm)

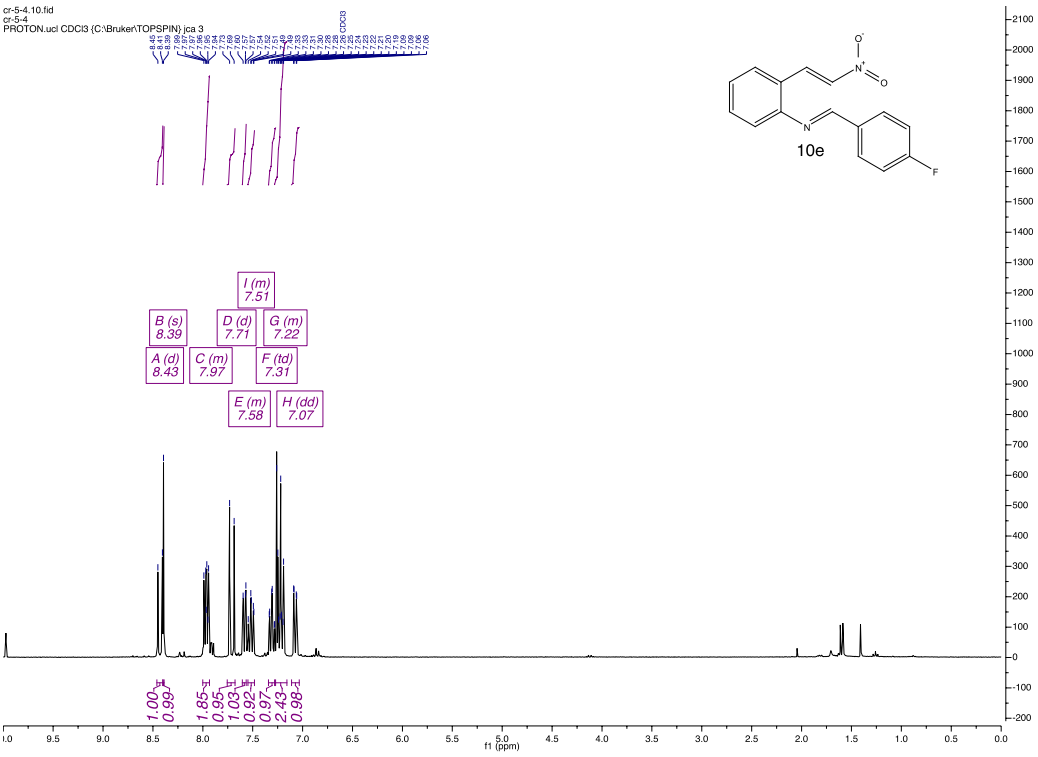

cr-3-91.10.fid
cr-3-91
PROTON.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 41
10c
f1 (ppm)

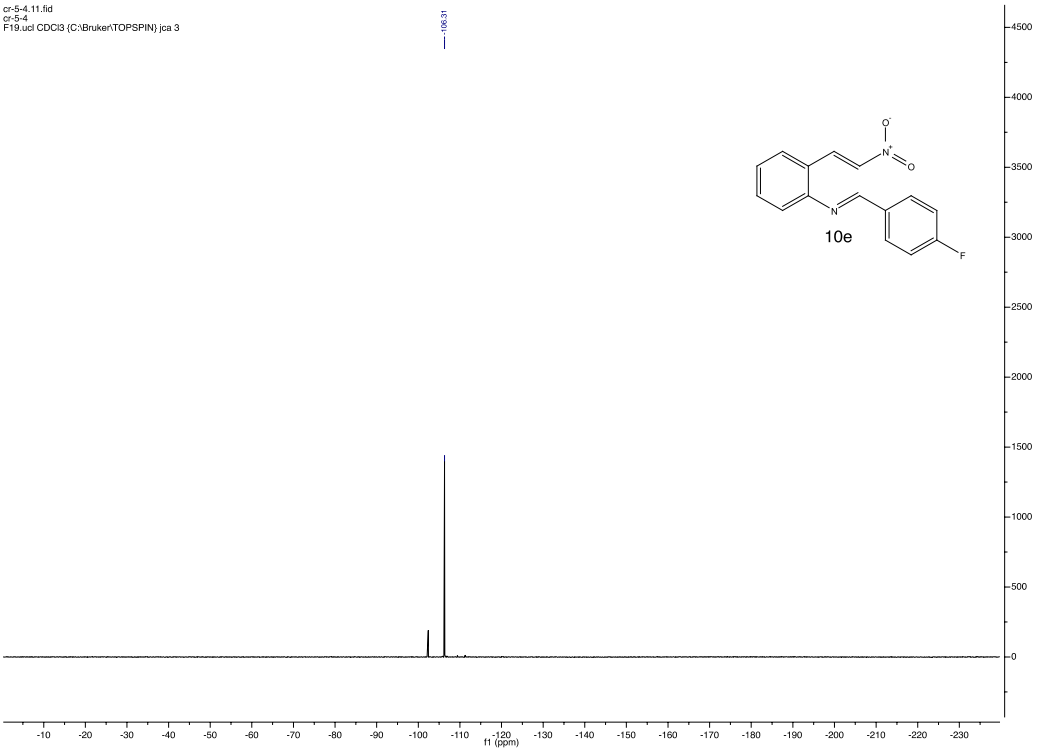

cr-3-91.11.fid
cr-3-91
F19.ucl CDCl3 {C:\Bruker\TOPSPIN} jca 35
-62.96
A (s)
-62.96
1.00
10c
f1 (ppm)

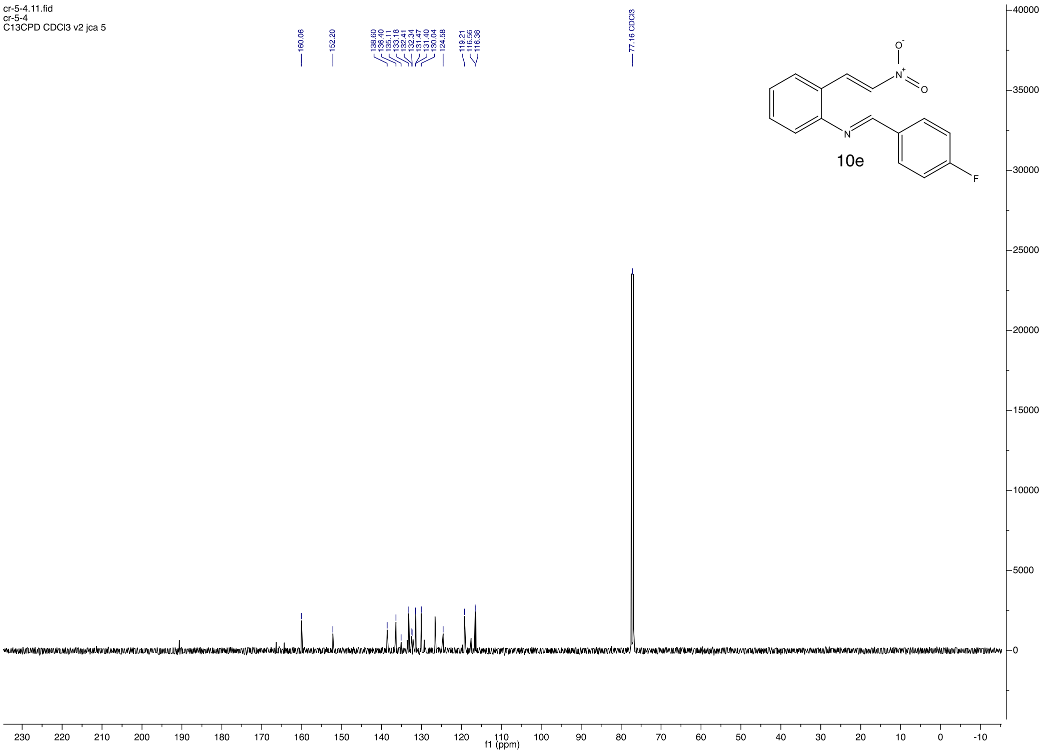

cr-3-91.12.fid
cr-3-91
C13CPD.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 41
159.90
151.45
77.16 CDCl3
10c
f1 (ppm)

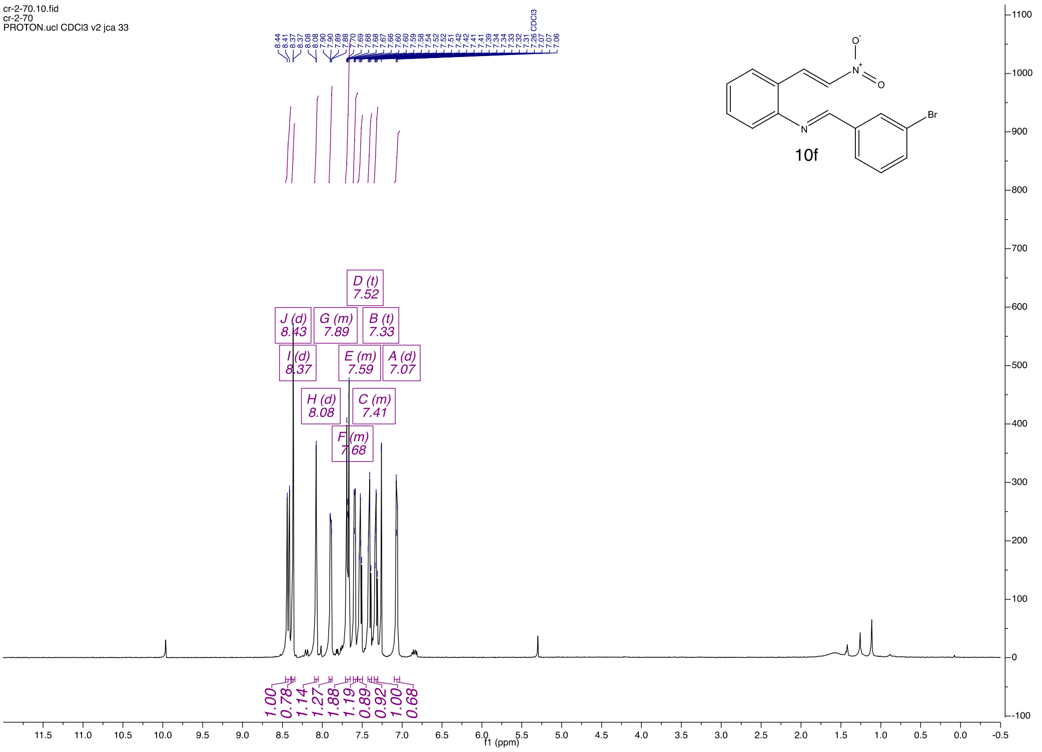

cr-5-56.10.fid
cr-5-56
PROTON.ucl CDCl3 {W:\Bruker\TOPSPIN} jca 45
10d
Br
A (d) 8.43
B (s) 8.38
C (d) 7.83
D (m) 7.68
E (d) 7.59
F (t) 7.52
G (t) 7.32
H (d) 7.08
f1 (ppm)

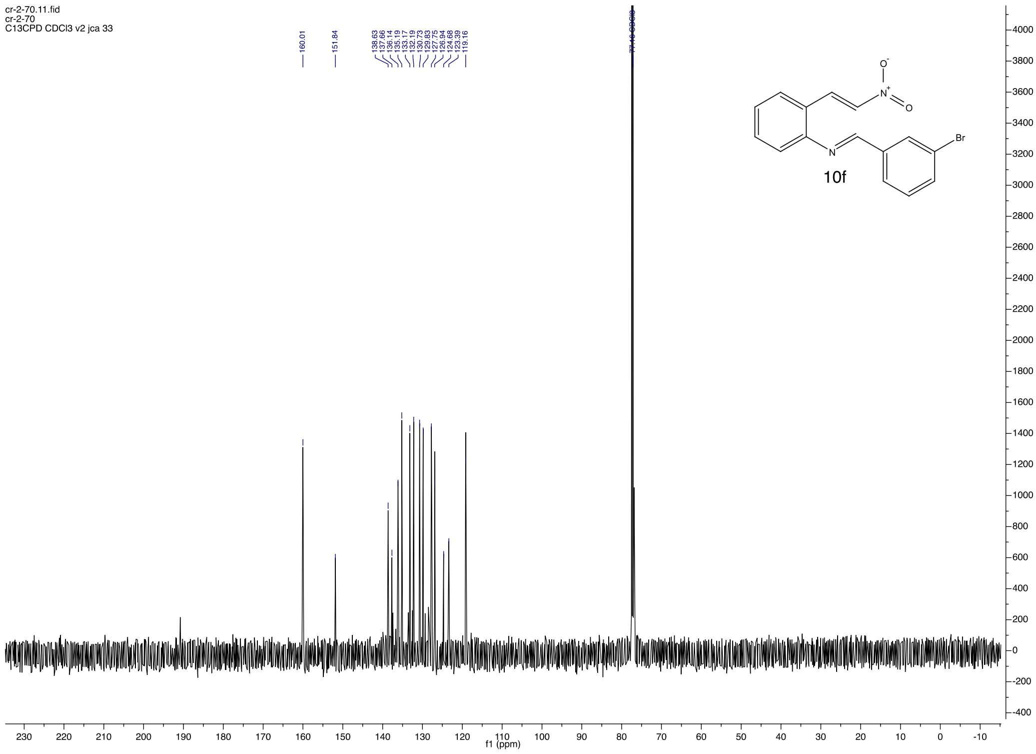

cr-5-56.12.fid
cr-5-56
C13CPD.ucl CDCl3 {W:\Bruker\TOPSPIN} jca 45
160.28
151.98
119.13
10d
Br
f1 (ppm)


cr-5-4.10.fid
cr-5-4
PROTON.ucl CDCl3 {C:\Bruker\TOPSPIN} jca 3
CDCl3
10e
I (m) 7.51
B (s) 8.39
D (d) 7.71
G (m) 7.22
A (d) 8.43
C (m) 7.97
F (td) 7.31
E (m) 7.58
H (dd) 7.07
1.00
0.99
1.85
0.95
1.03
0.92
0.97
2.43
0.98
f1 (ppm)

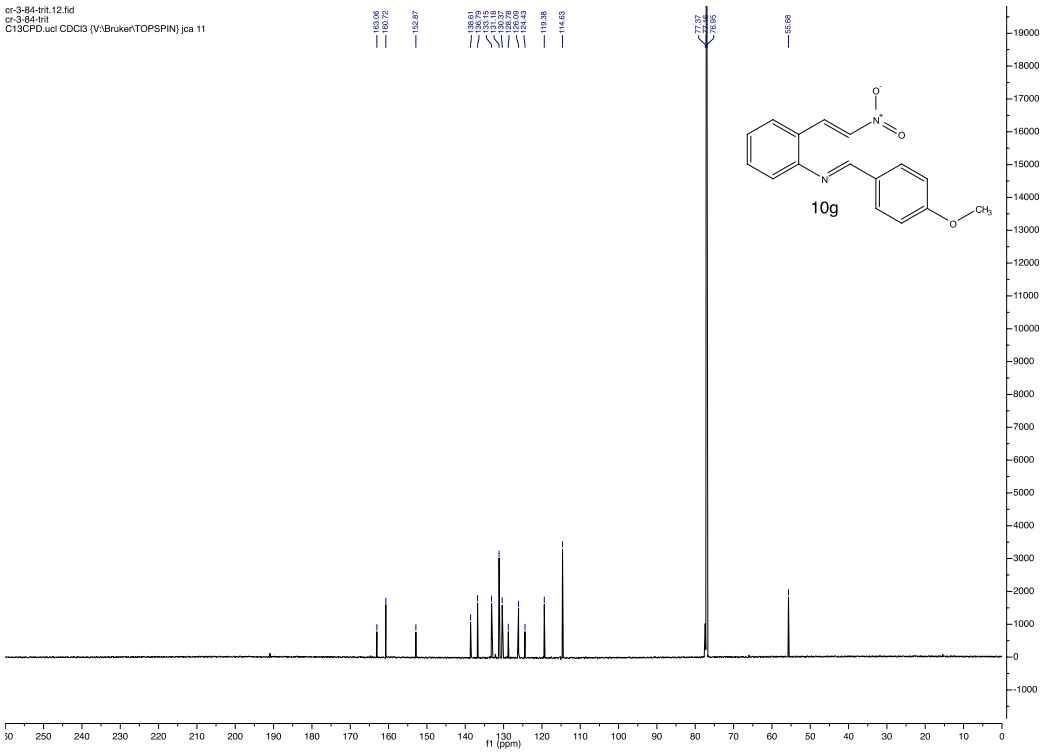

cr-5-4.11.fid
cr-5-4
F19.ucl CDCl3 {C:\Bruker\TOPSPIN} jca 3
-106.31
10e
f1 (ppm)

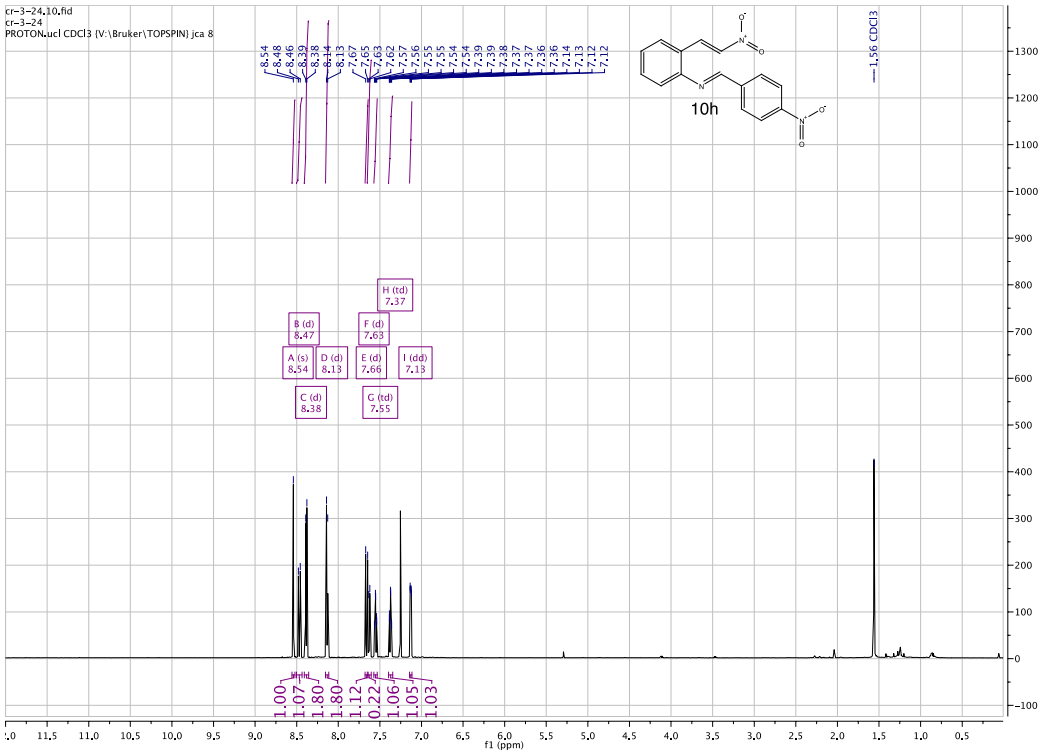

cr-5-4.11.fid
cr-5-4
C13CPD CDCl3 v2 jca 5
160.06
152.20
138.60
136.40
135.11
133.18
132.41
132.34
131.47
131.40
130.04
124.58
119.21
116.56
116.38
77.16 CDCl3
10e
f1 (ppm)

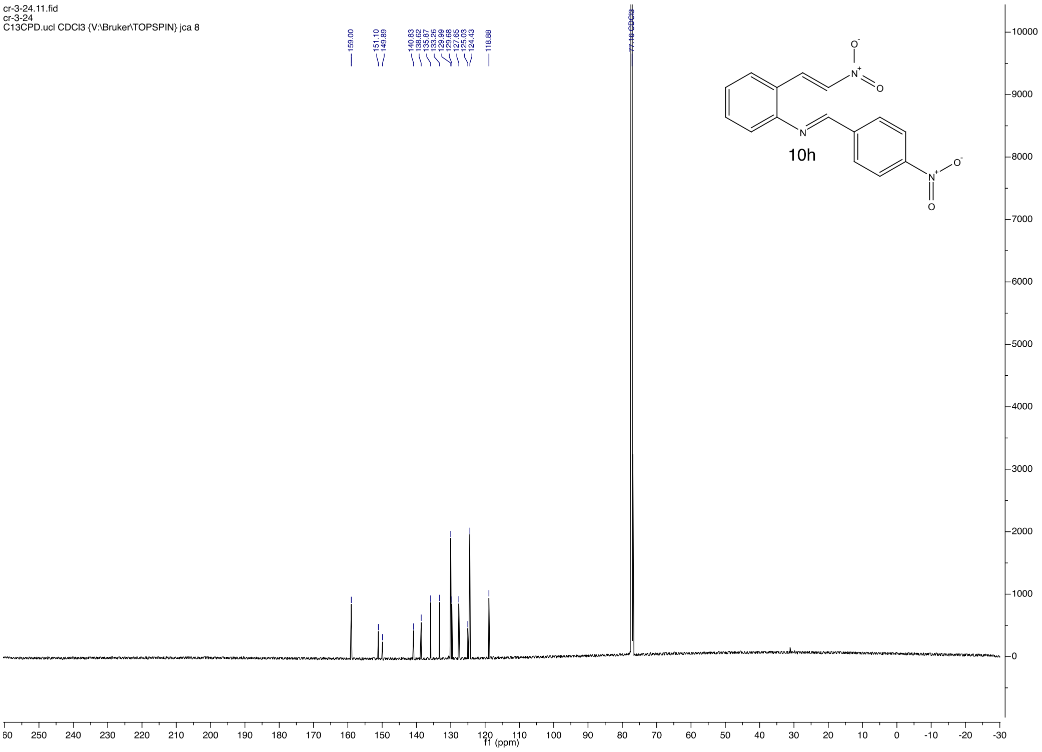

cr-2-70.10.fid
cr-2-70
PROTON.ucl CDCl3 v2 jca 33
10f
J (d) 8.43
I (d) 8.37
H (d) 8.08
G (m) 7.89
F (m) 7.68
E (m) 7.59
D (t) 7.52
C (m) 7.41
B (t) 7.33
A (d) 7.07
f1 (ppm)

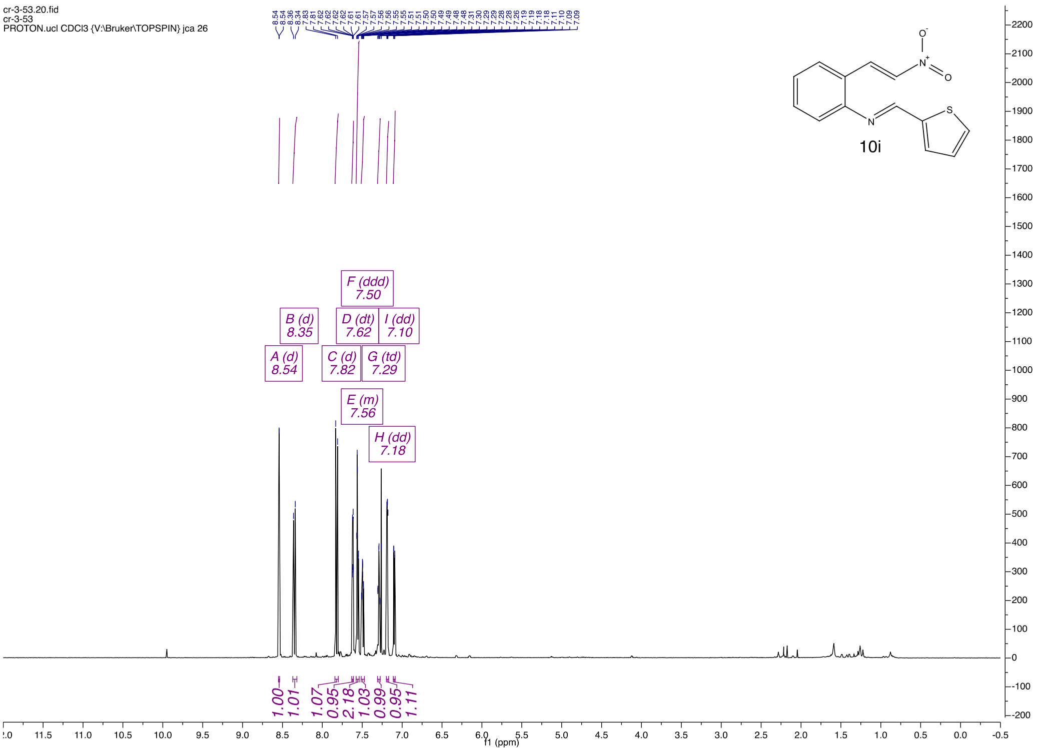

cr-2-70.11.fid
cr-2-70
C13CPD CDCl3 v2 jca 33
10f
f1 (ppm)

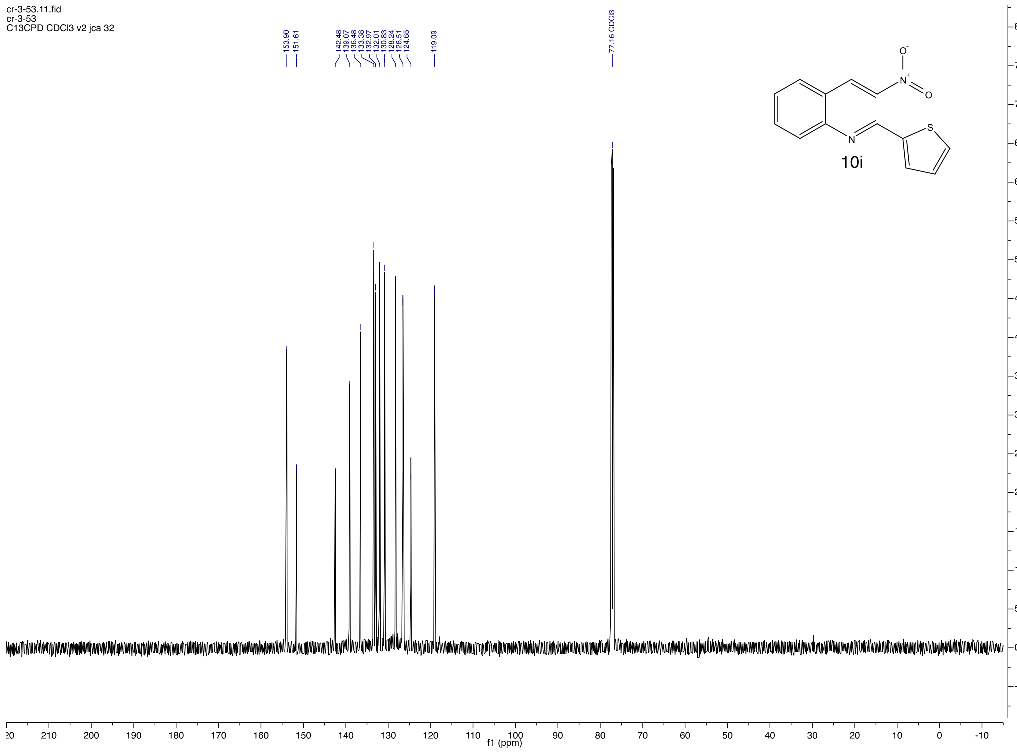

cr-3-84-trit.10.fid
cr-3-84-trit
PROTON.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 11
10g
A (d) 8.42
B (s) 8.34
C (m) 7.91
D (d) 7.77
E (dd) 7.56
F (td) 7.50
G (m) 7.28
H (dd) 7.06
I (m) 7.04
J (s) 3.90
f1 (ppm)

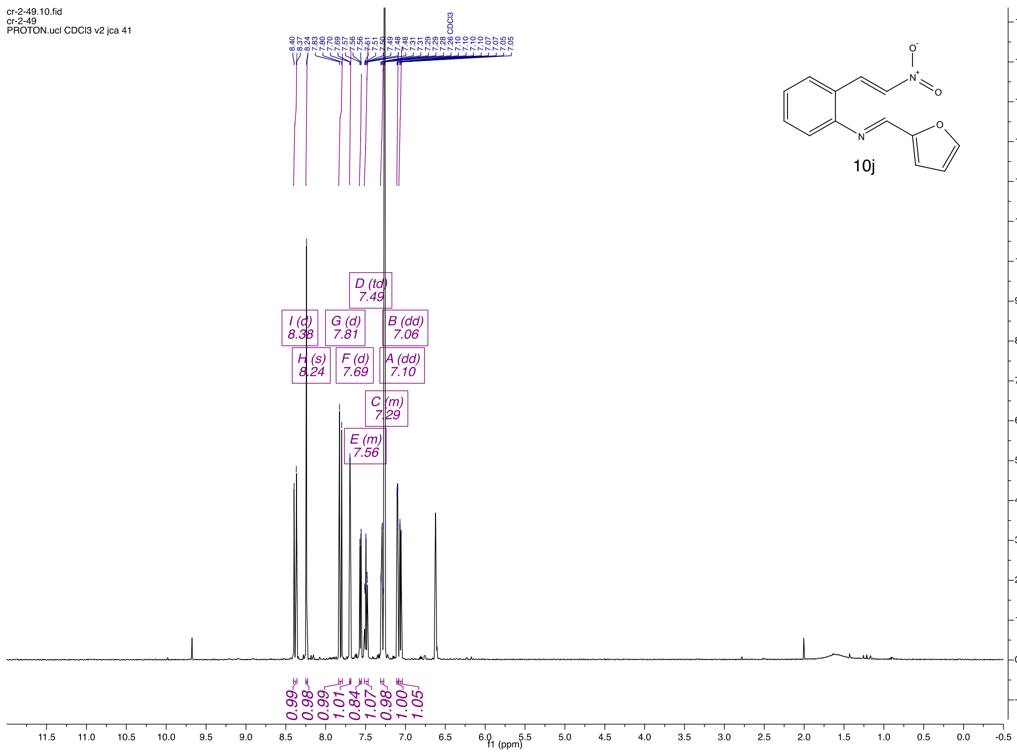

cr-3-84-trit.12.fid
cr-3-84-trit
C13CPD.ucl CDCl3 (V:\Bruker\TOPSPIN) jca 11
163.06
160.72
152.87
138.61
136.79
133.15
131.18
130.57
128.79
126.09
124.43
119.38
114.63
77.37
77.04
76.85
55.68
10g
f1 (ppm)


cr-3-24.10.fid
cr-3-24
PROTON.ucl CDCl3 (V:\Bruker\TOPSPIN) jca 8
8.54
8.48
8.46
8.39
8.38
8.14
8.13
7.67
7.65
7.63
7.62
7.57
7.56
7.55
7.55
7.54
7.54
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.14
7.13
7.12
7.12
1.56 CDCl3
10h
H (td) 7.37
B (d) 8.47
F (d) 7.63
A (s) 8.54
D (d) 8.13
E (d) 7.66
I (dd) 7.13
C (d) 8.38
G (td) 7.55
1.00
1.07
1.80
1.80
1.12
0.22
1.06
1.05
1.03
f1 (ppm)

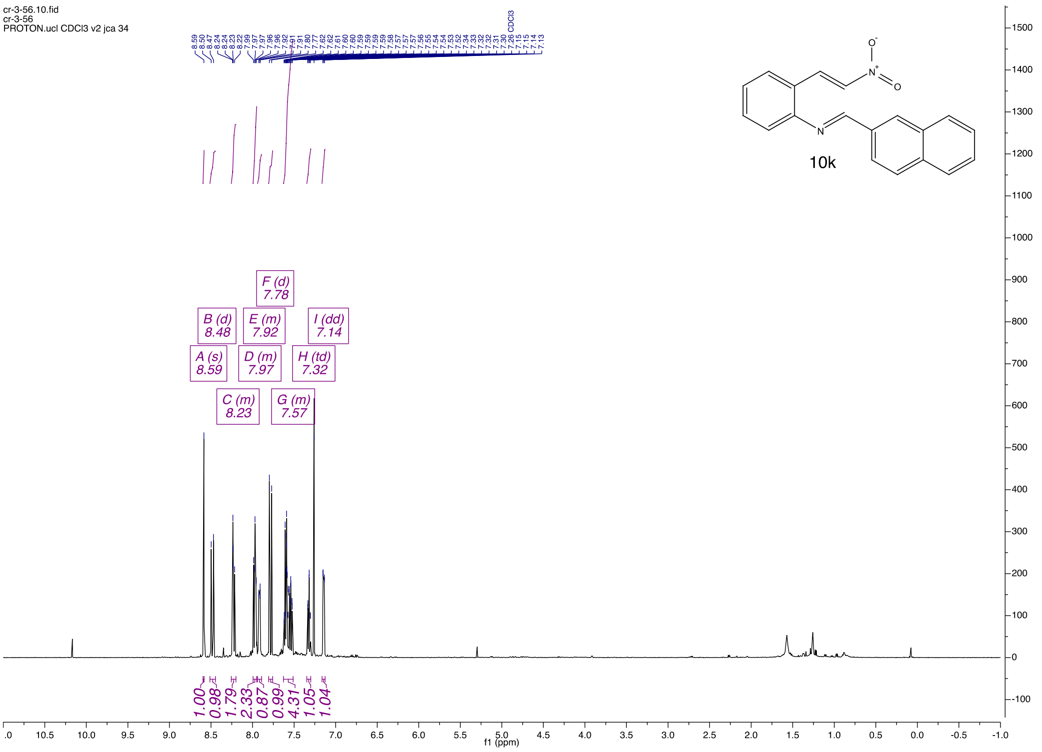

cr-3-24.11.fid
cr-3-24
C13CPD.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 8
159.00
151.10
149.89
140.83
138.62
135.87
133.26
129.99
129.68
127.65
125.03
124.43
118.88
77.16 CDCl3
10h
f1 (ppm)

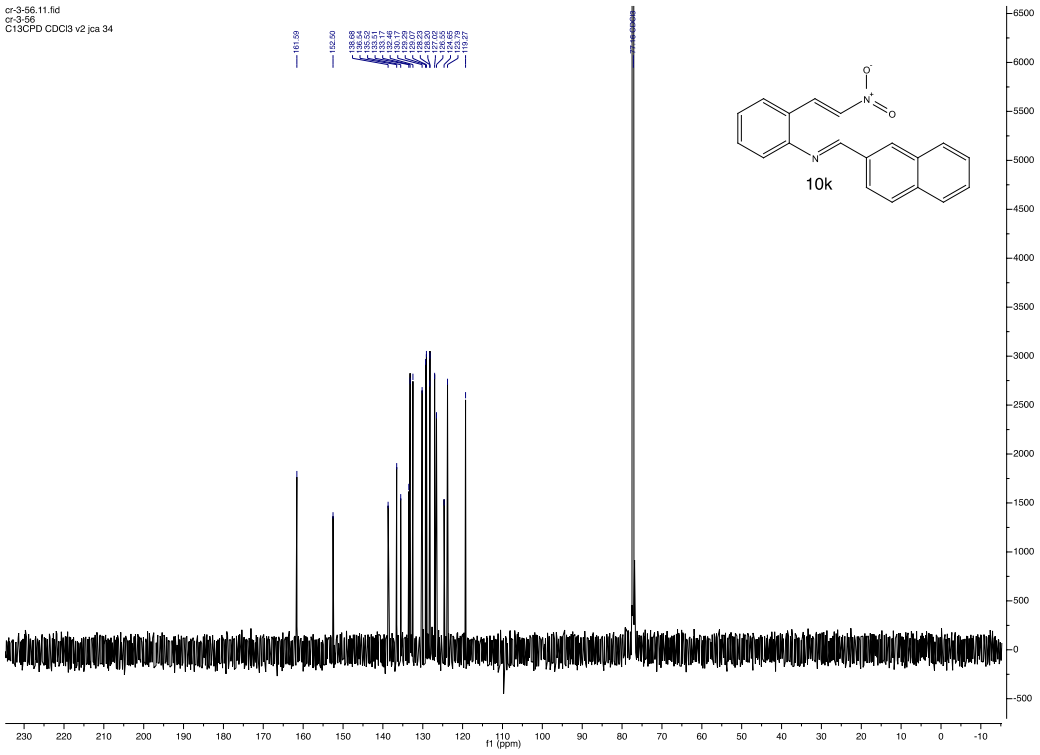

cr-3-53.20.fid
cr-3-53
PROTON.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 26
10i
A (d) 8.54
B (d) 8.35
C (d) 7.82
D (dt) 7.62
E (m) 7.56
F (ddd) 7.50
G (td) 7.29
H (dd) 7.18
I (dd) 7.10
1.00
1.01
1.07
0.95
2.18
1.03
0.99
0.95
1.11
f1 (ppm)

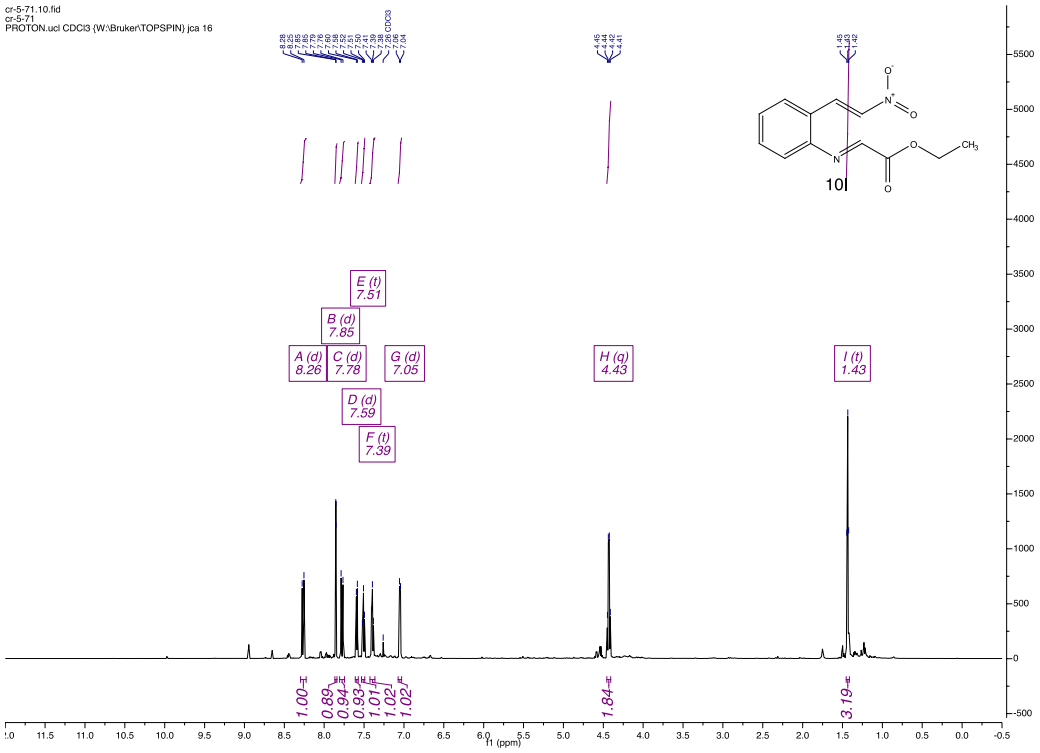

cr-3-53.11.fid
cr-3-53
C13CPD CDCl3 v2 jca 32
153.90
151.61
142.48
139.07
136.48
133.38
132.97
132.01
130.83
128.24
126.51
124.65
119.09
77.16 CDCl3
10i
f1 (ppm)

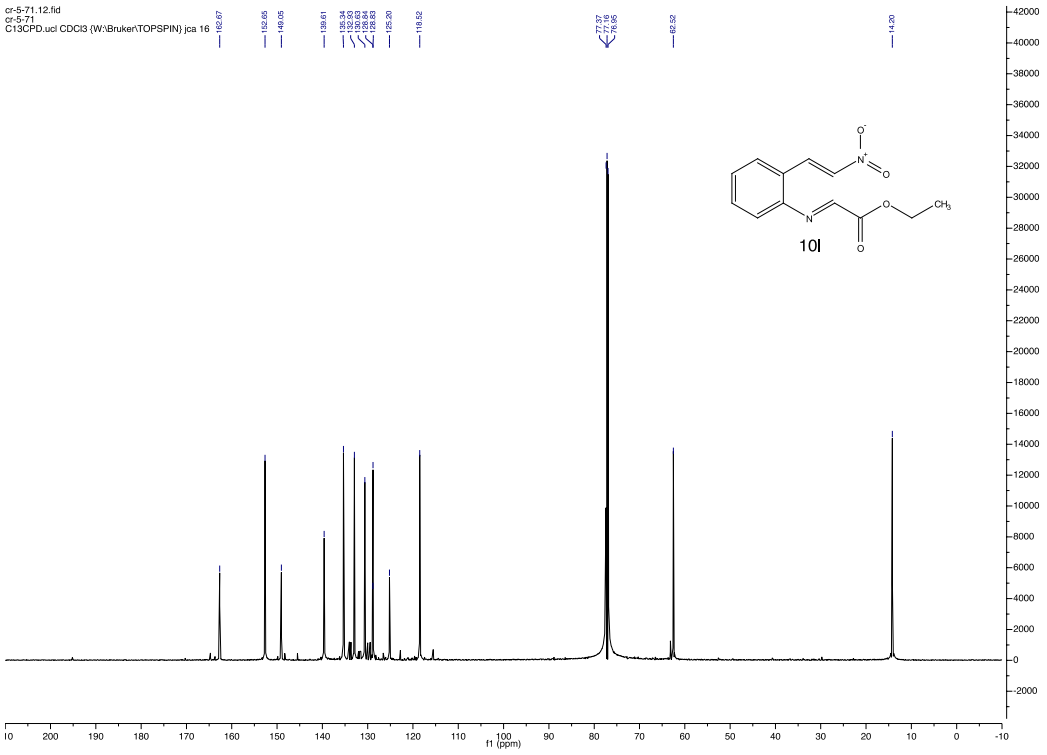

cr-2-49.10.fid
cr-2-49
PROTON.ucl CDCl3 v2 jca 41
10j
I (d) 8.38
H (s) 8.24
G (d) 7.81
F (d) 7.69
E (m) 7.56
D (td) 7.49
C (m) 7.29
B (dd) 7.06
A (dd) 7.10
0.99
0.98
0.99
1.01
0.84
1.07
0.98
1.00
1.05
f1 (ppm)

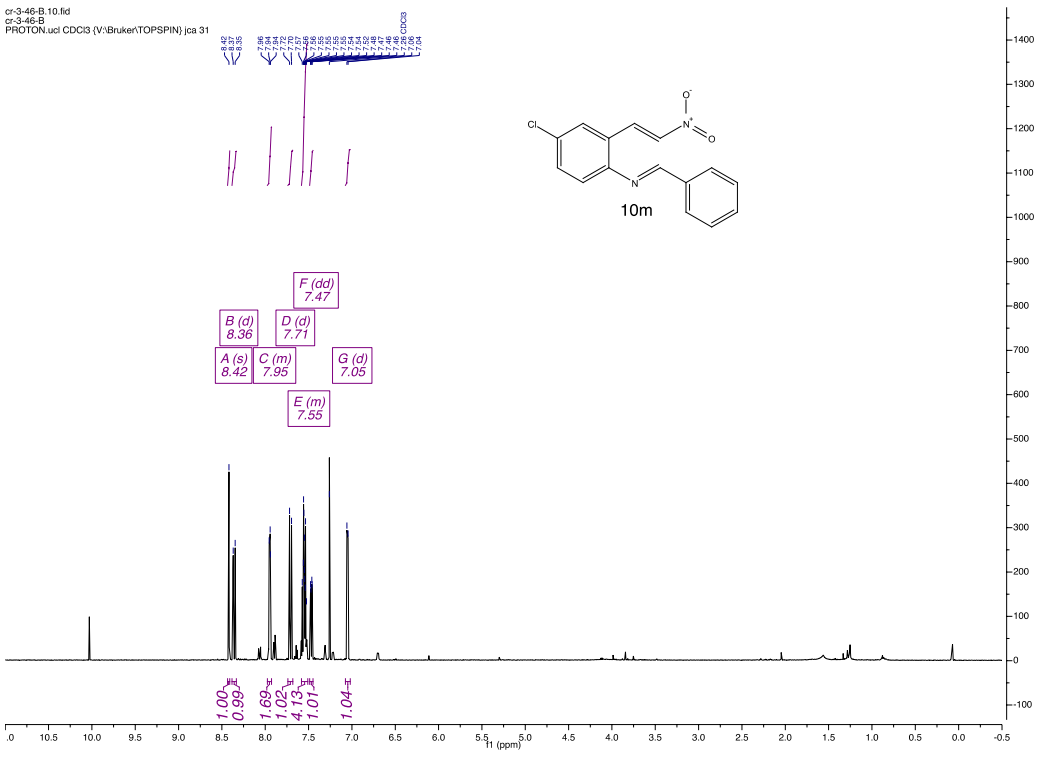

cr-2-49.12.fid
cr-2-49
C13CPD.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 39
152.20
151.98
148.91
146.75
138.87
136.51
133.08
130.51
126.51
124.63
119.08
117.55
112.71
10j
f1 (ppm)

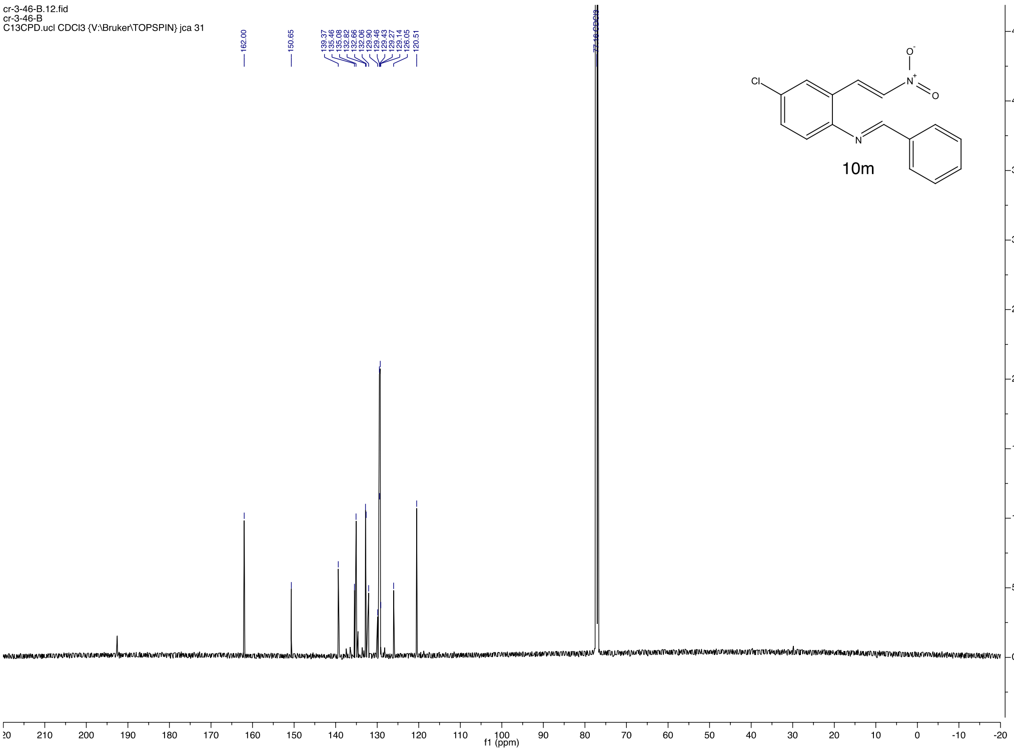

cr-3-56.10.fid
cr-3-56
PROTON.ucl CDCl3 v2 jca 34
10k
A (s) 8.59
B (d) 8.48
C (m) 8.23
D (m) 7.97
E (m) 7.92
F (d) 7.78
G (m) 7.57
H (td) 7.32
I (dd) 7.14
1.00
0.98
1.79
2.33
0.87
0.99
4.31
1.05
1.04
f1 (ppm)

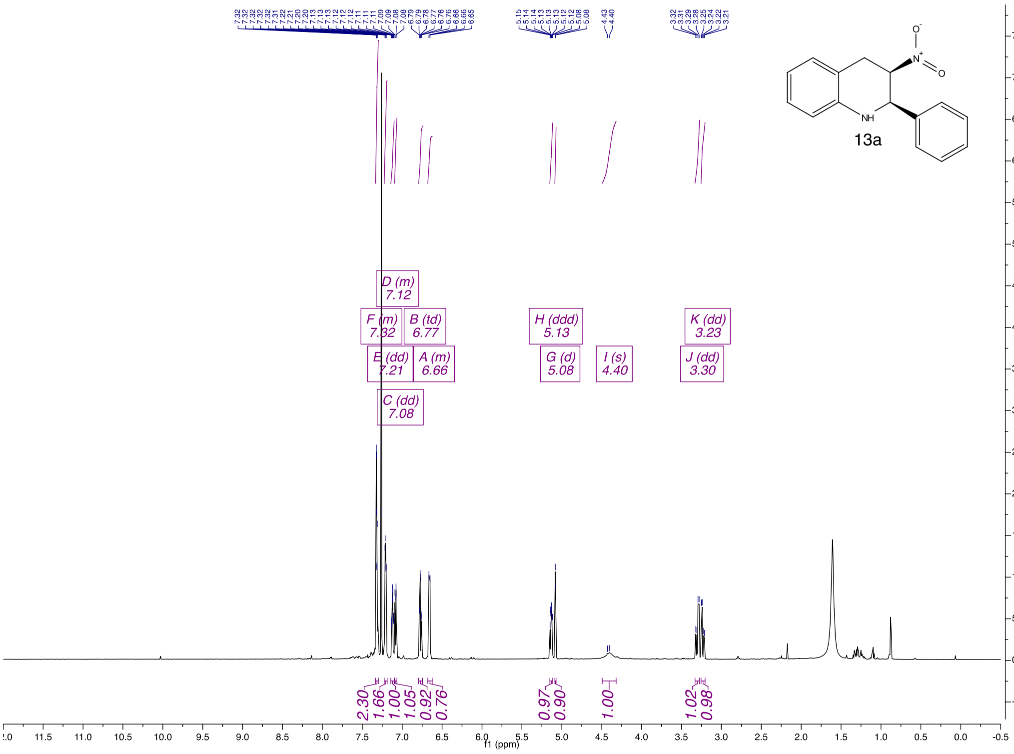

cr-3-56.11.fid
cr-3-56
C13CPD CDCl3 v2 jca 34
10k
f1 (ppm)

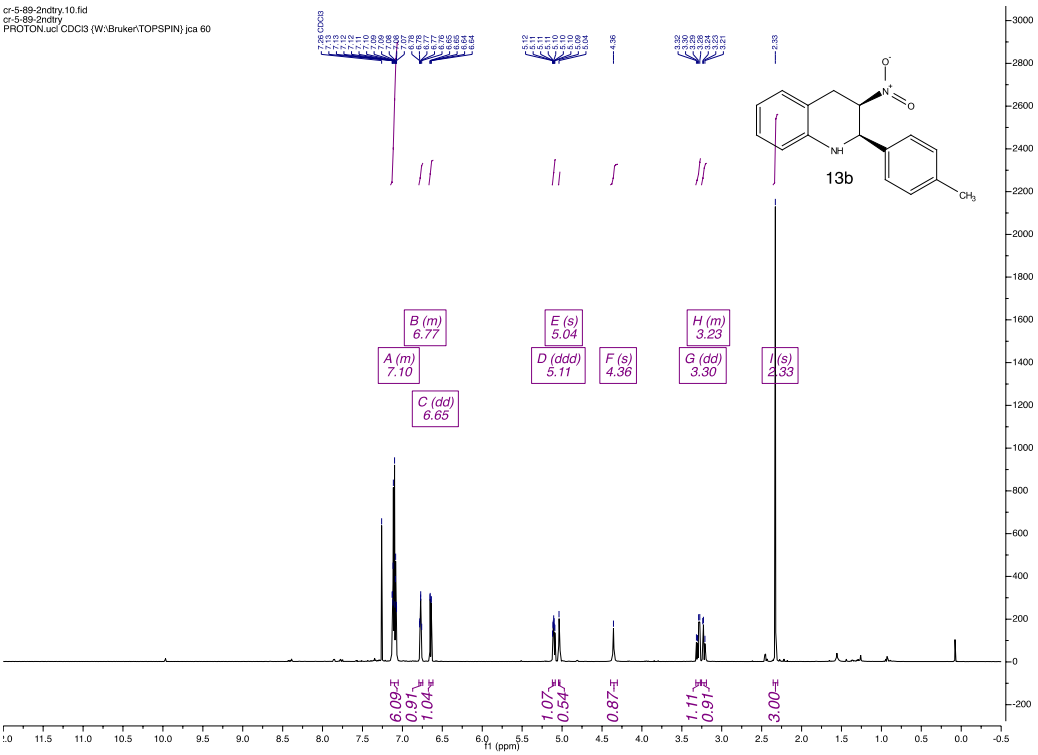

cr-5-71.10.fid
cr-5-71
PROTON.ucl CDCl3 {W:\Bruker\TOPSPIN} jca 16
10l
E (t) 7.51
B (d) 7.85
A (d) 8.26
C (d) 7.78
G (d) 7.05
D (d) 7.59
F (t) 7.39
H (q) 4.43
I (t) 1.43
1.00
0.89
0.94
0.93
1.01
1.02
1.02
1.84
3.19
f1 (ppm)

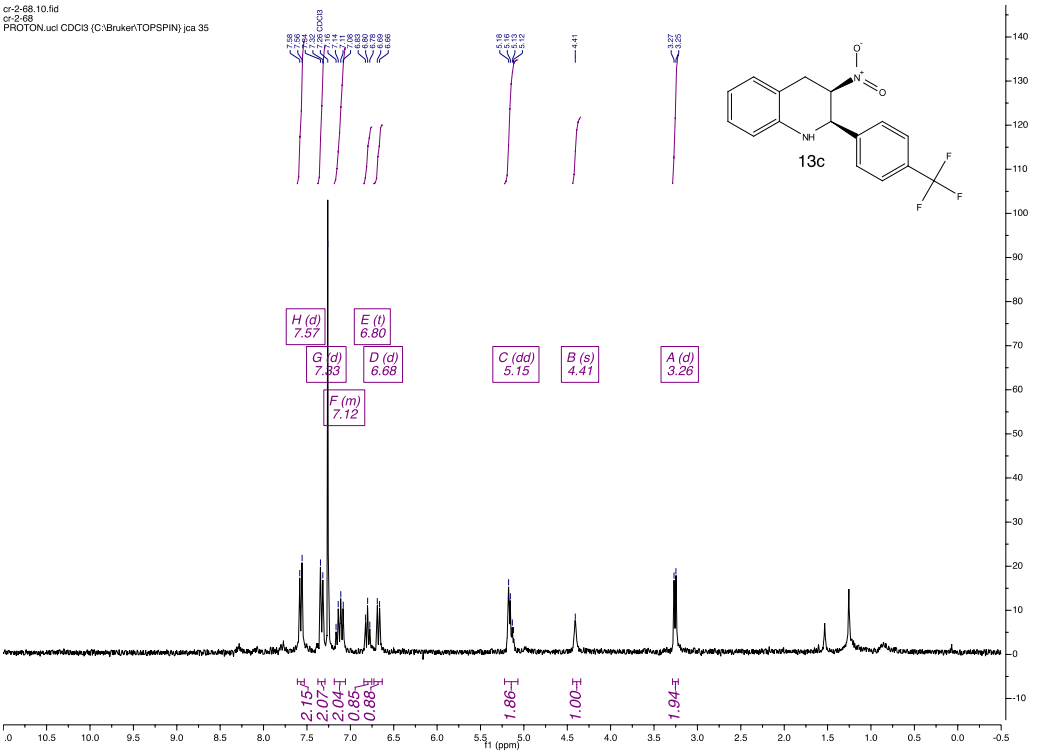

cr-5-71.12.fid
cr-5-71
C13CPD.ucl CDCl3 {W:\Bruker\TOPSPIN} jca 16
162.67
152.65
149.05
139.61
135.34
131.03
130.63
128.84
128.66
125.20
118.52
77.37
77.16
76.95
62.52
14.20
10l
f1 (ppm)

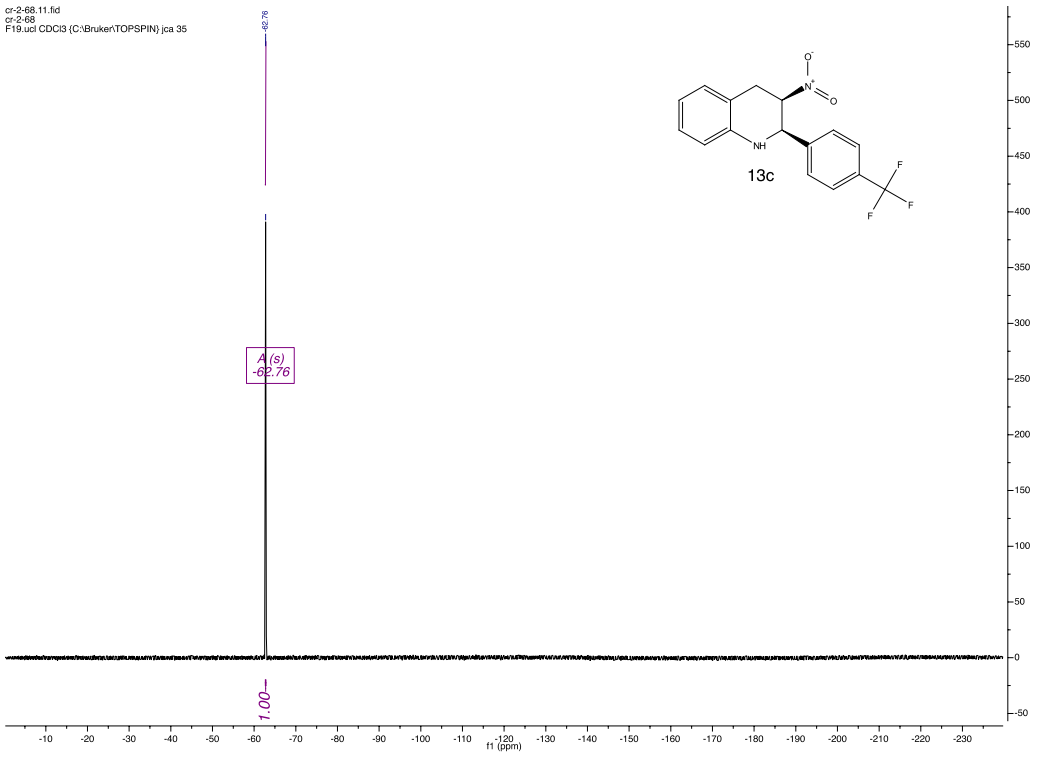

cr-3-46-B.10.fid
cr-3-46-B
PROTON.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 31
8.42
8.36
8.35
7.96
7.94
7.72
7.57
7.56
7.55
7.54
7.53
7.52
7.47
7.46
7.26 CDCl3
7.05
7.04
10m
F (dd) 7.47
B (d) 8.36
D (d) 7.71
A (s) 8.42
C (m) 7.95
G (d) 7.05
E (m) 7.55
1.00
0.99
1.69
1.02
4.13
1.01
1.04
f1 (ppm)


cr-3-46-B.12.fid
cr-3-46-B
C13CPD.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 31
10m
f1 (ppm)

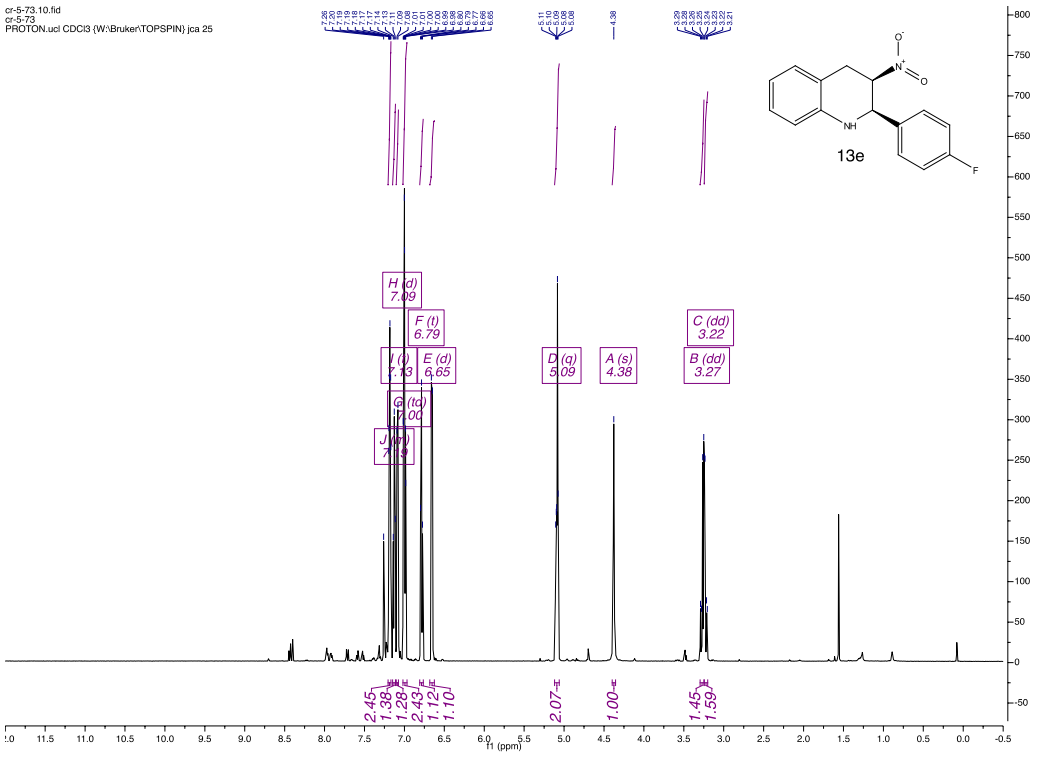

13a
D (m) 7.12
F (m) 7.32
B (td) 6.77
E (dd) 7.21
A (m) 6.66
C (dd) 7.08
H (ddd) 5.13
G (d) 5.08
I (s) 4.40
K (dd) 3.23
J (dd) 3.30
f1 (ppm)

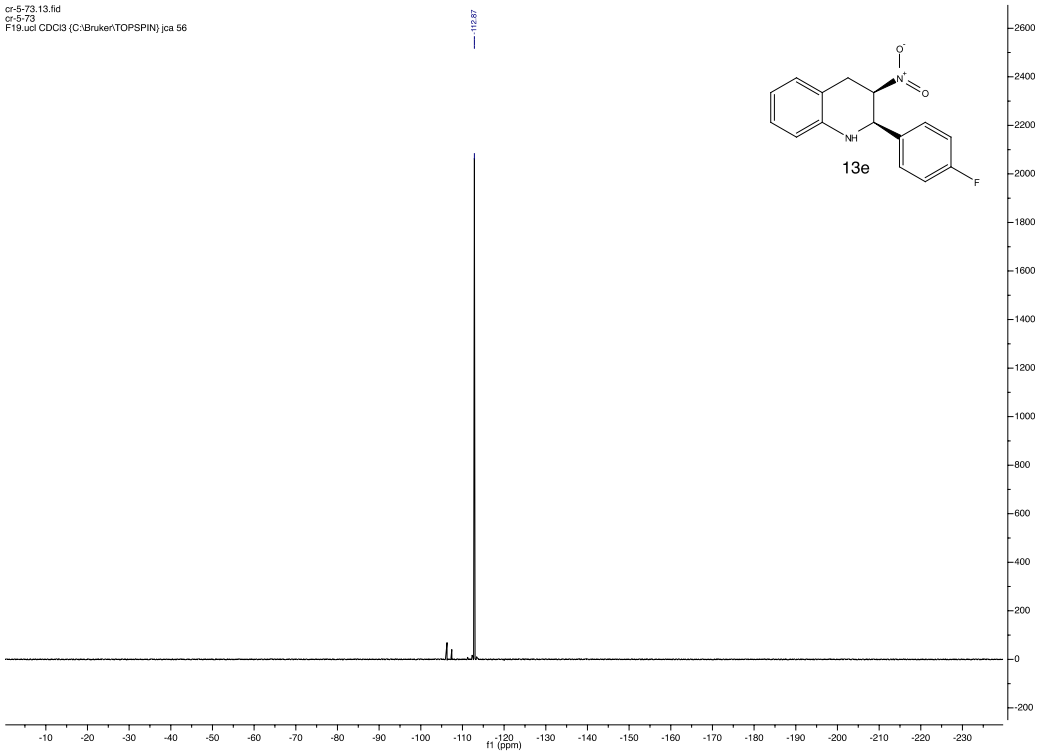

cr-5-89-2ndtry.10.fid
cr-5-89-2ndtry
PROTON.ucl CDCl3 {W:\Bruker\TOPSPIN} jca 60
B (m) 6.77
A (m) 7.10
C (dd) 6.65
E (s) 5.04
D (ddd) 5.11
F (s) 4.36
H (m) 3.23
G (dd) 3.30
I (s) 2.33
6.09
0.91
1.04
1.07
0.54
0.87
1.11
0.91
3.00
13b
f1 (ppm)

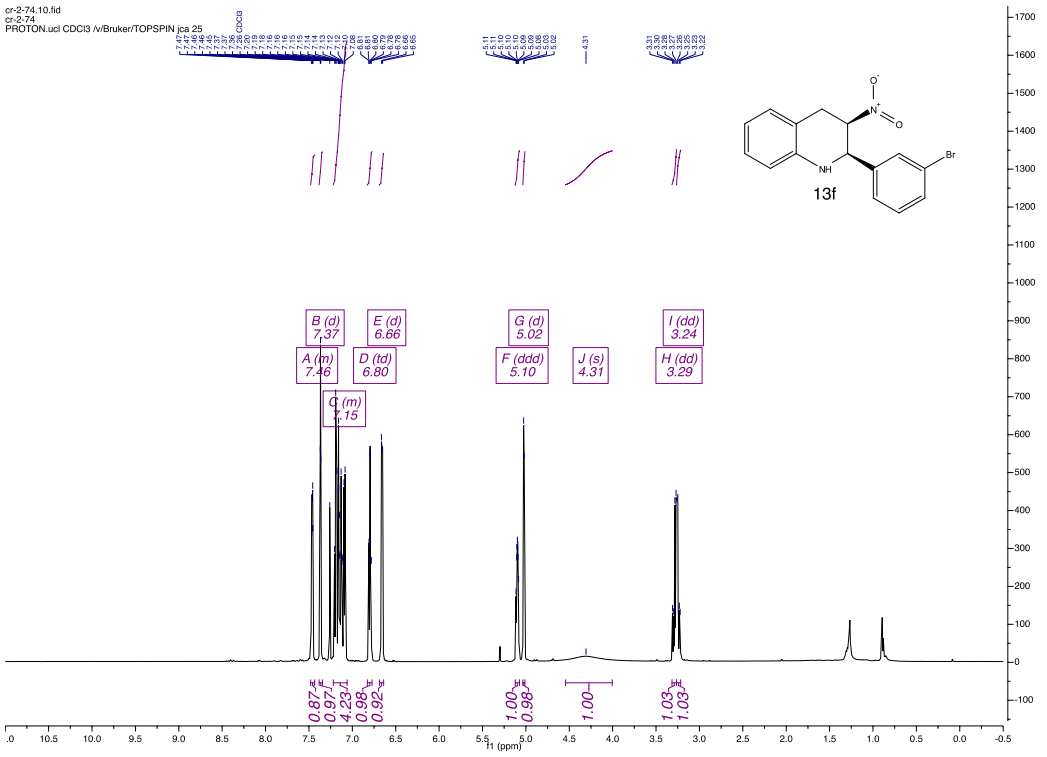

cr-2-68.10.fid
cr-2-68
PROTON.ucl CDCl3 {C:\Bruker\TOPSPIN} jca 35
H (d) 7.57
E (t) 6.80
G (d) 7.33
D (d) 6.68
F (m) 7.12
C (dd) 5.15
B (s) 4.41
A (d) 3.26
2.15
2.07
2.04
0.85
0.88
1.86
1.00
1.94
13c
f1 (ppm)


cr-2-68.11.fid
cr-2-68
F19.ucl CDCl3 (C:\Bruker\TOPSPIN) jca 35
-62.76
A (s)
-62.76
1.00
13c
f1 (ppm)


cr-5-65.10.fid
cr-5-65
PROTON.ucl CDCl3 (W:\Bruker\TOPSPIN) jca 6
13d
Br
E (m)
7.43
B (t)
6.78
G (d)
5.07
D (t)
7.12
A (d)
6.66
F (m)
5.11
H (m)
3.25
C (m)
7.08
2.31
1.14
3.07
1.04
1.00
1.16
1.09
2.41
f1 (ppm)

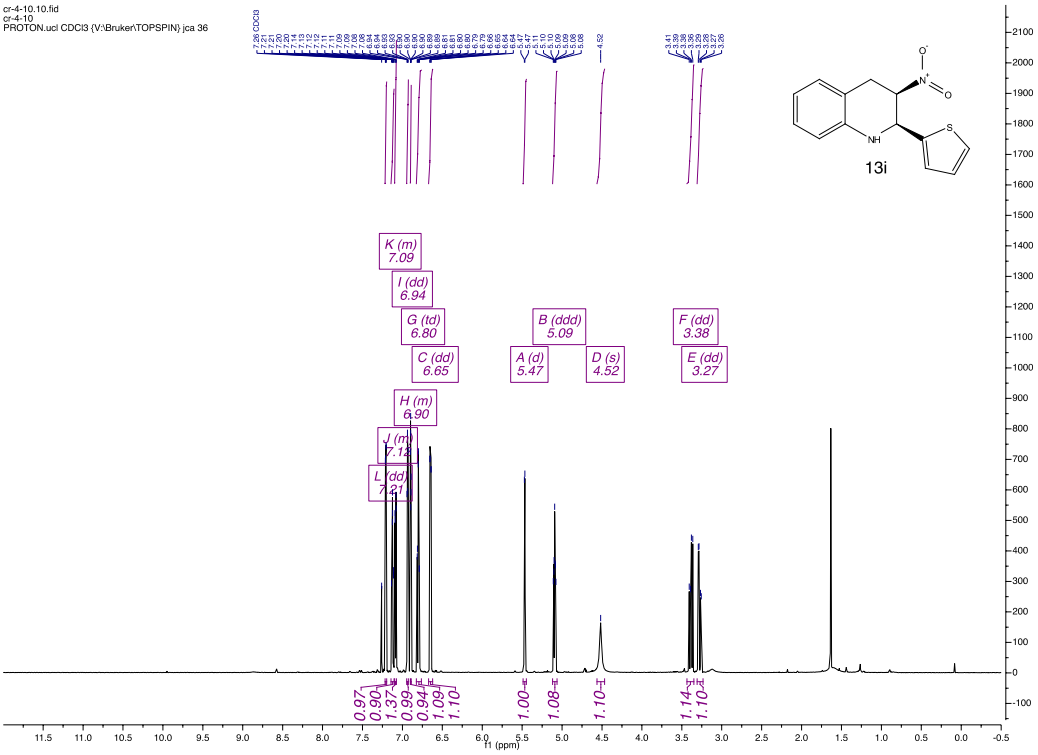

cr-5-73.10.fid
cr-5-73
PROTON.ucl CDCl3 {W:\Bruker\TOPSPIN} jca 25
H (d) 7.09
F (t) 6.79
I (t) 7.13
E (d) 6.65
G (td) 7.00
J (dd) 7.18
D (q) 5.09
A (s) 4.38
C (dd) 3.22
B (dd) 3.27
2.45
1.38
1.28
2.43
1.12
1.10
2.07
1.00
1.45
1.59
13e
f1 (ppm)

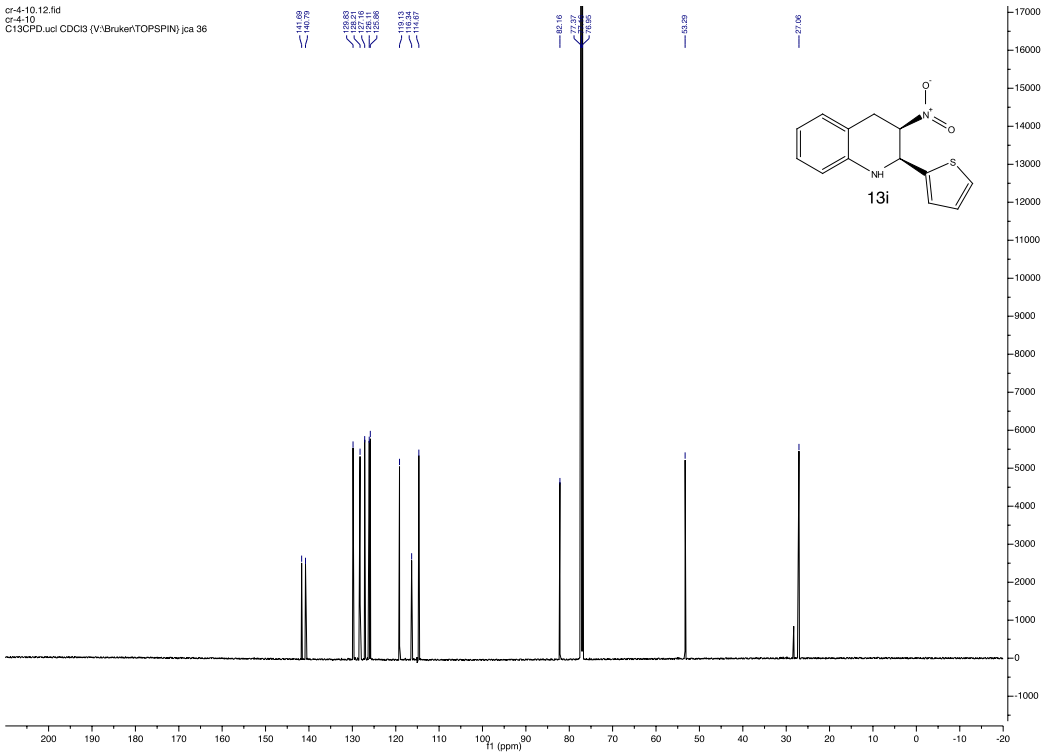

cr-5-73.13.fid
cr-5-73
F19.ucl CDCl3 {C:\Bruker\TOPSPIN} jca 56
-112.87
13e
f1 (ppm)

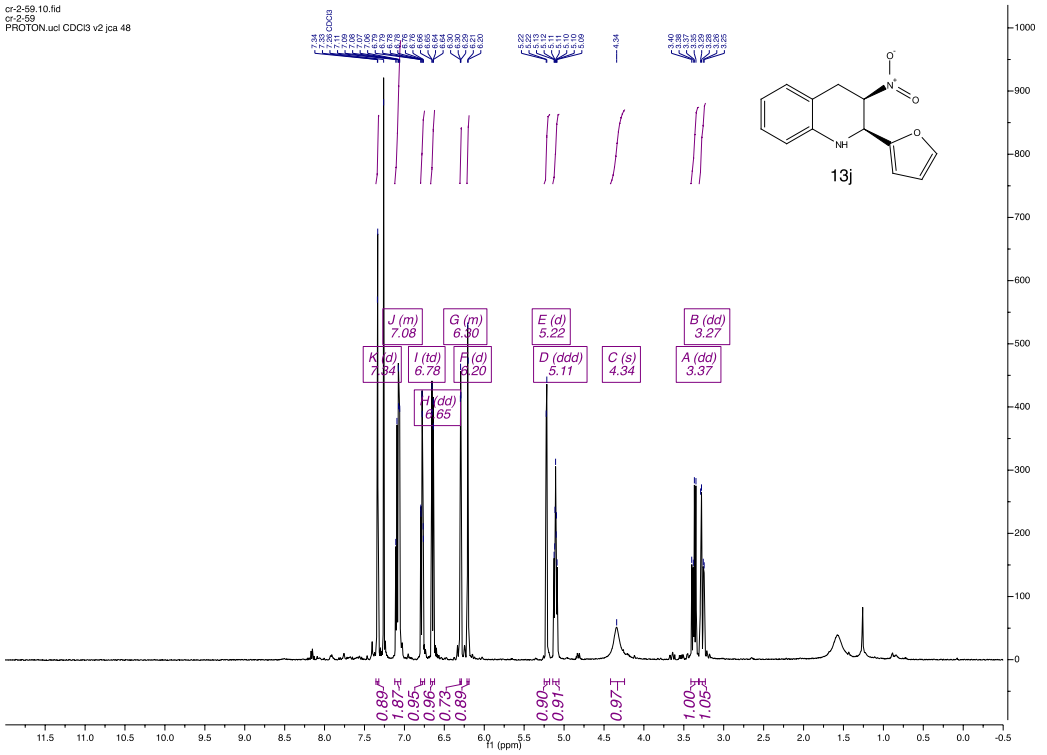

cr-2-74.10.fid
cr-2-74
PROTON.ucl CDCl3 /v/Bruker/TOPSPIN jca 25
B (d) 7.37
E (d) 6.66
G (d) 5.02
I (dd) 3.24
A (m) 7.46
D (td) 6.80
F (ddd) 5.10
J (s) 4.31
H (dd) 3.29
C (m) 7.15
0.87
0.97
4.23
0.98
0.92
1.00
0.98
1.00
1.03
1.03
f1 (ppm)
13f

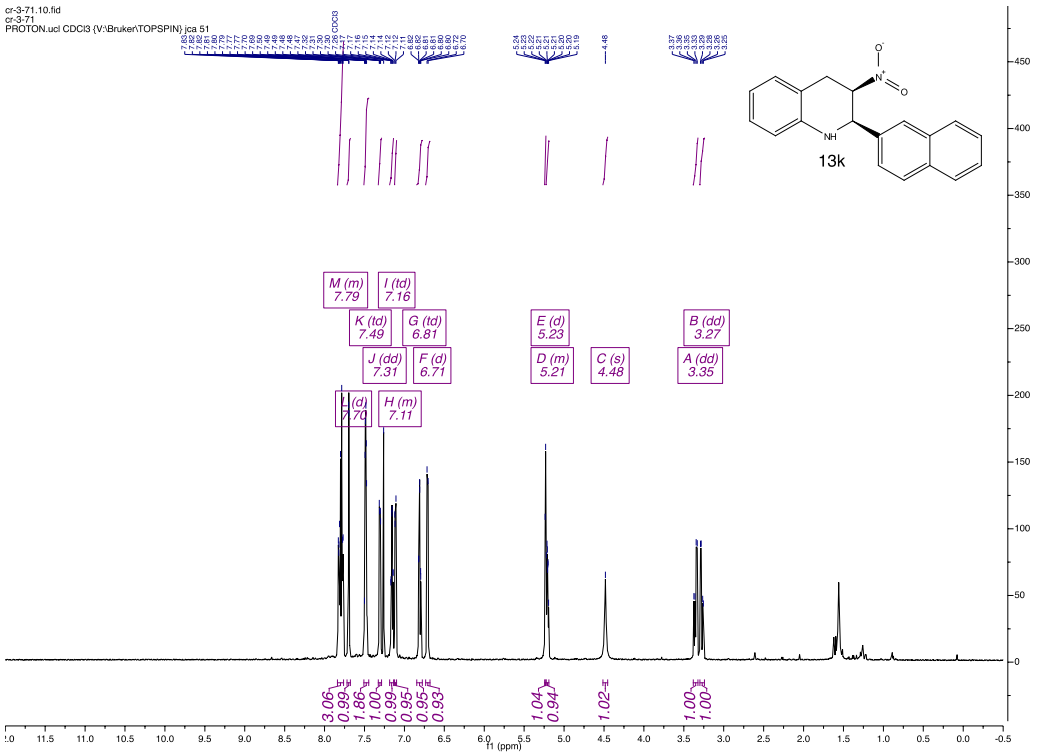

cr-2-74.11.fid
cr-2-74
C13CPD.ucl CDCl3 /v/Bruker/TOPSPIN jca 25
f1 (ppm)
13f

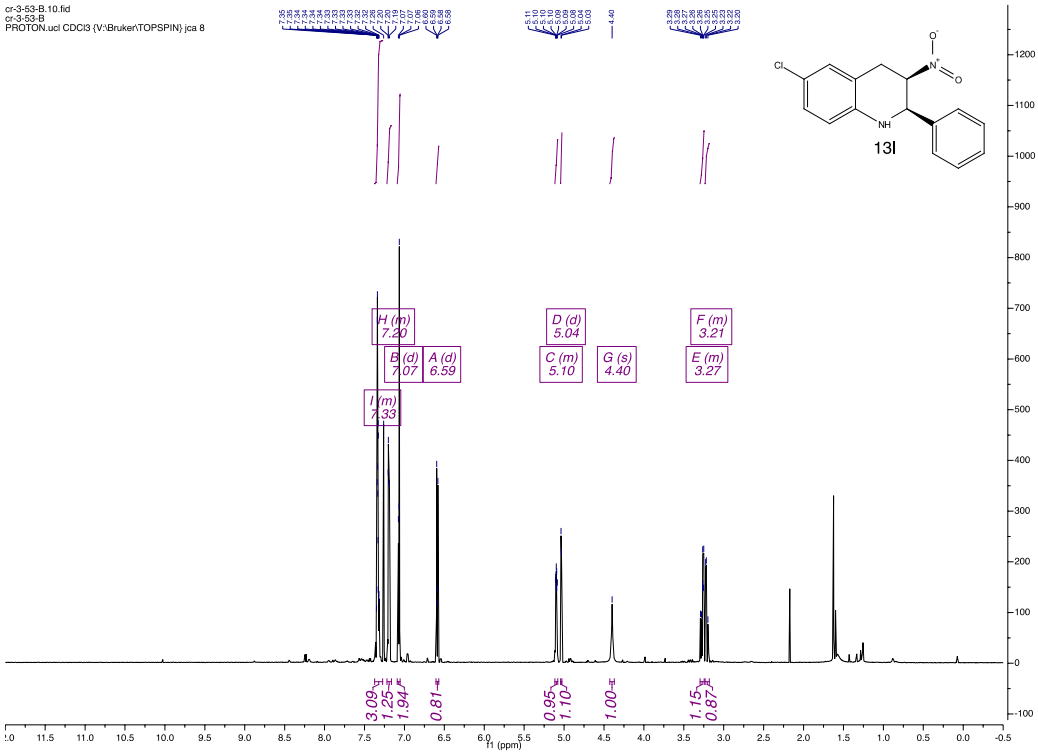

cr-4-34-trit.10.fid
cr-4-34-trit
PROTON.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 50
13g
H (m) 7.11
F (m) 6.77
E (d) 6.64
G (m) 6.83
D (dt) 5.09
C (d) 5.03
B (s) 4.35
A (s) 3.78
J (dd) 3.22
I (dd) 3.29
f1 (ppm)

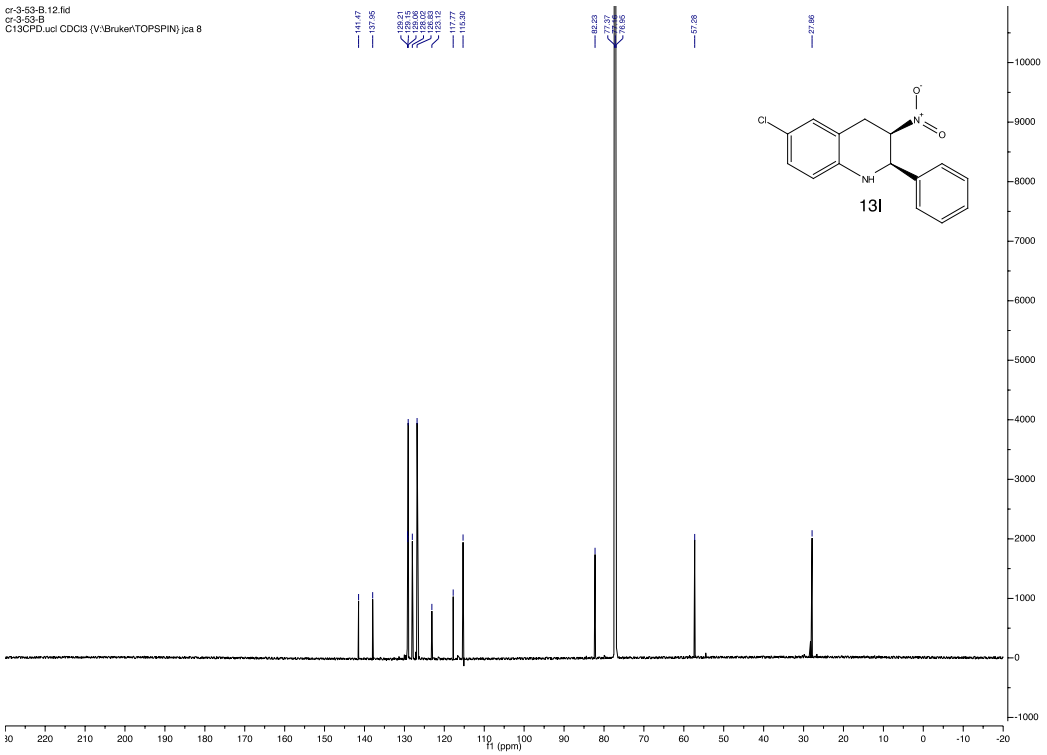

cr-4-10.10.fid
cr-4-10
PROTON.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 36
13i
K (m) 7.09
I (dd) 6.94
G (td) 6.80
C (dd) 6.65
H (m) 6.90
J (m) 7.13
L (dd) 7.21
B (ddd) 5.09
A (d) 5.47
D (s) 4.52
F (dd) 3.38
E (dd) 3.27
f1 (ppm)

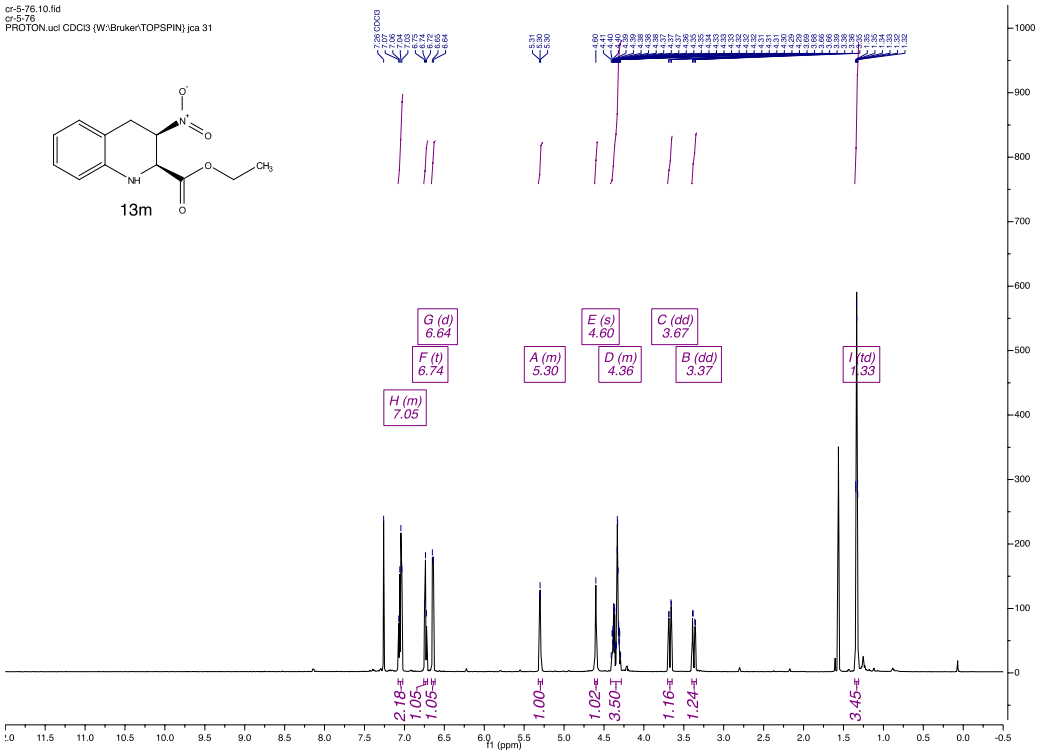

cr-4-10.12.fid
cr-4-10
C13CPD.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 36
141.69
140.79
129.83
128.21
127.15
126.11
125.66
119.13
116.34
114.67
82.16
77.32
77.07
76.85
53.29
27.06
13i
f1 (ppm)

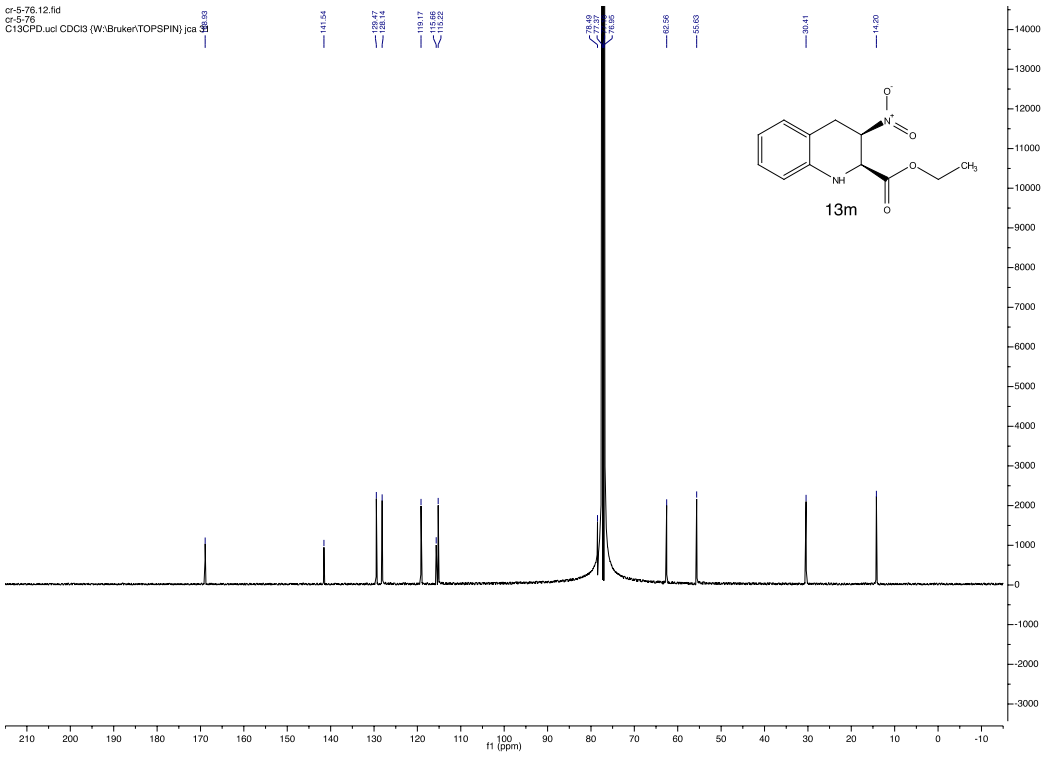

cr-2-59.10.fid
cr-2-59
PROTON.ucl CDCl3 v2 jca 48
CDCl3
4.34
13j
J (m) 7.08
G (m) 6.30
E (d) 5.22
B (dd) 3.27
K (d) 7.34
I (td) 6.78
F (d) 6.20
D (ddd) 5.11
C (s) 4.34
A (dd) 3.37
H (dd) 6.65
0.89
1.87
0.95
0.96
0.73
0.69
0.90
0.91
0.97
1.00
1.05
f1 (ppm)


cr-3-71.10.fid
cr-3-71
PROTON.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 51
13k
M (m) 7.79
I (td) 7.16
K (td) 7.49
G (td) 6.81
J (dd) 7.31
F (d) 6.71
L (d) 7.70
H (m) 7.11
E (d) 5.23
D (m) 5.21
C (s) 4.48
B (dd) 3.27
A (dd) 3.35
3.06
0.99
1.86
1.00
0.99
0.95
0.95
0.93
1.04
0.94
1.02
1.00
1.00
f1 (ppm)

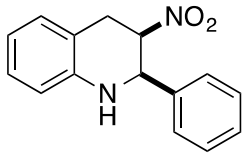

cr-3-53-B.10.fid
cr-3-53-B
PROTON.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 8
13l
H (m) 7.20
B (d) 7.07
A (d) 6.59
I (m) 7.33
D (d) 5.04
C (m) 5.10
G (s) 4.40
F (m) 3.21
E (m) 3.27
3.09
1.25
1.94
0.81
0.95
1.10
1.00
1.15
0.87
f1 (ppm)


cr-3-53-B.12.fid
cr-3-53-B
C13CPD.ucl CDCl3 {V:\Bruker\TOPSPIN} jca 8
141.47
137.95
129.21
129.15
128.93
128.02
125.63
123.12
117.77
115.30
82.23
77.37
77.05
76.85
57.28
27.86
Cl
O
N
O
NH
13l
f1 (ppm)


cr-5-76.10.fid
cr-5-76
PROTON.ucl CDCl3 {W:\Bruker\TOPSPIN} jca 31
7.26 CDCl3
7.07
7.06
7.05
6.75
6.74
6.65
6.64
5.31
5.30
4.60
4.41
4.40
4.39
4.38
4.37
4.36
4.35
4.34
4.33
4.32
4.31
4.30
4.29
4.28
3.68
3.67
3.66
3.38
3.37
1.35
1.34
1.33
1.32
O
N
O
NH
O
O
CH3
13m
G (d) 6.64
F (t) 6.74
H (m) 7.05
A (m) 5.30
E (s) 4.60
D (m) 4.36
C (dd) 3.67
B (dd) 3.37
I (td) 1.33
2.18
1.05
1.05
1.00
1.02
3.50
1.16
1.24
3.45
f1 (ppm)

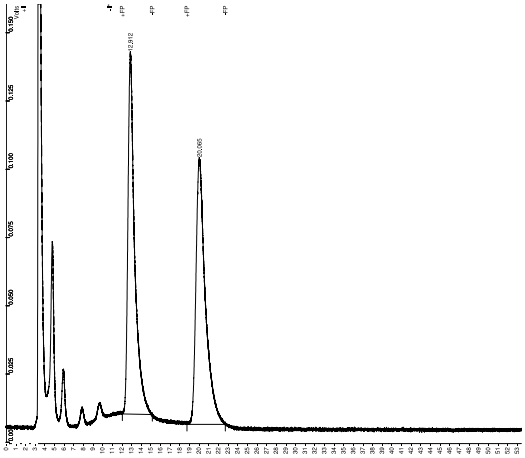

cr-5-76.12.fid
cr-5-76
C13CPD.ucl CDCl3 {W:\Bruker\TOPSPIN} jca 3
169.93
141.54
129.47
128.14
119.17
115.66
115.22
79.49
77.37
77.05
76.86
62.56
55.63
30.41
14.20
13m
f1 (ppm)

HPLC Traces:



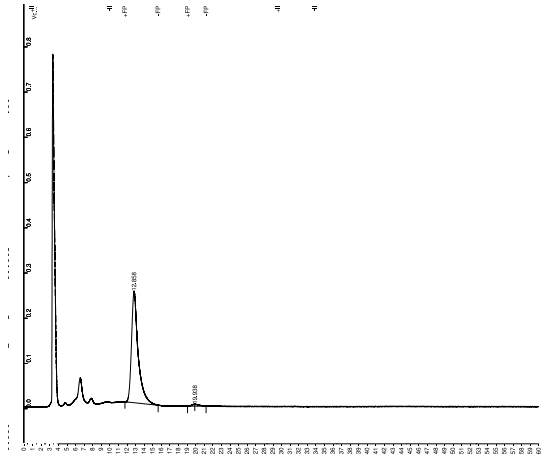
13a

Racemic:



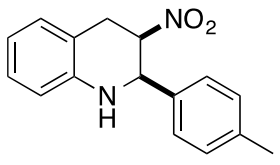
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.3966	12.912	0.000	6450071	BB	39.3	
2		50.6034	20.065	0.000	6607659	BB	56.9	
	Totals:	100.0000		0.000	13057730			

Enantioselective:



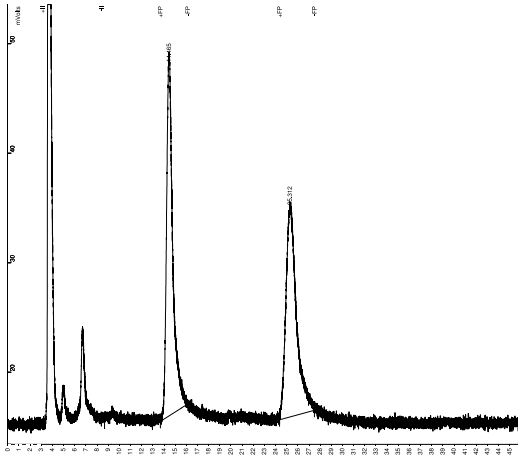
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		98.3046	12.858	0.000	13255282	BB	43.4	
2		1.6954	19.938	0.000	228608	BB	44.7	
	Totals:	100.0000		0.000	13483890			

Shows 97% ee.



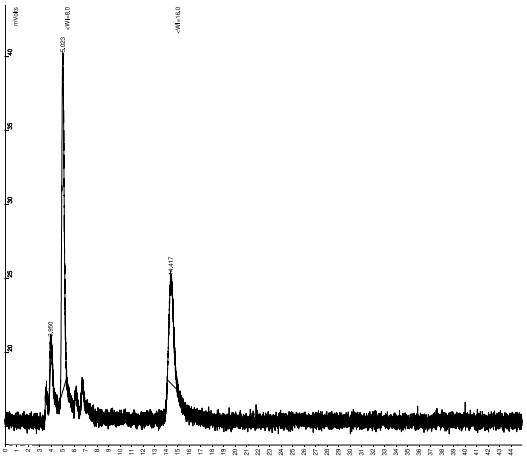
13b

Racemic:

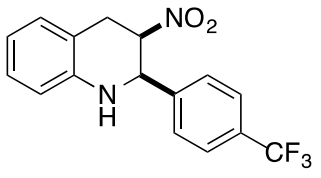


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.1781	14.465	0.000	1291861	BB	32.1	
2		49.8219	25.312	0.000	1282690	BB	55.7	
	Totals:	100.0000		0.000	2574551			

Enantioselective:

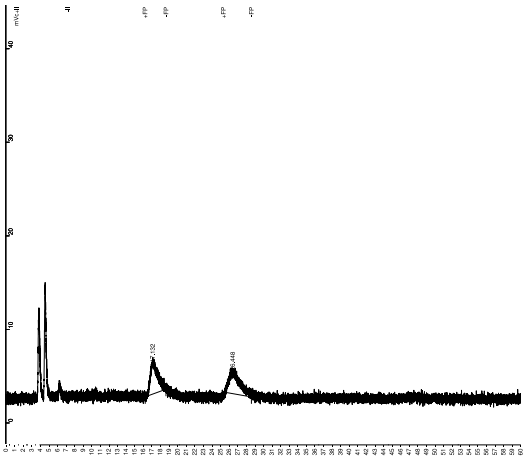


Shows >99% ee.



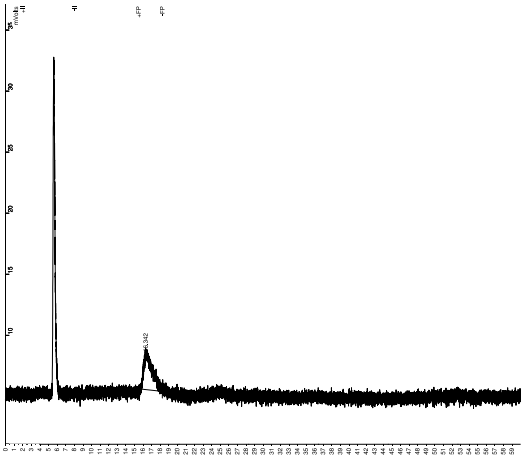
13c

Racemic:



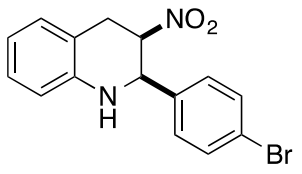
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.4734	17.132	0.000	208456	BB	42.6	
2		50.5266	26.448	0.000	212894	BB	38.0	
	Totals:	100.0000		0.000	421350			

Enantioselective:



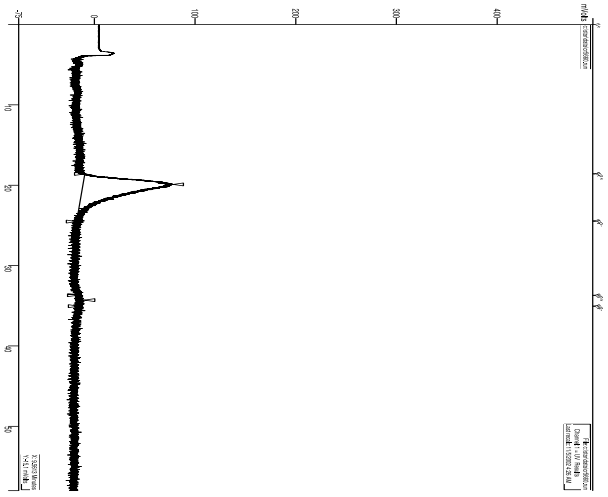
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		100.0000	16.342	0.000	211160	BB	39.7	
	Totals:	100.0000		0.000	211160			

Shows >99% ee.



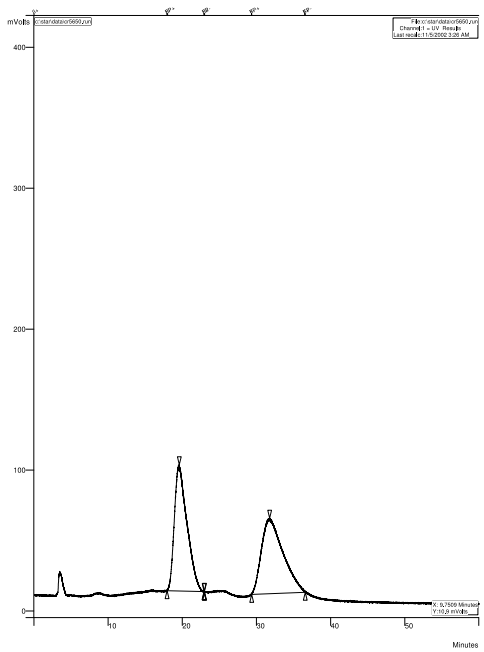
13d

Enantioselective:



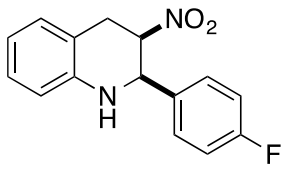
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		99.0992	19.898	0.000	10870178	BB	98.7	
2		0.9008	34.295	0.000	98809	BB	0.2	
	Totals:	100.0000		0.000	10968987			

Racemic:



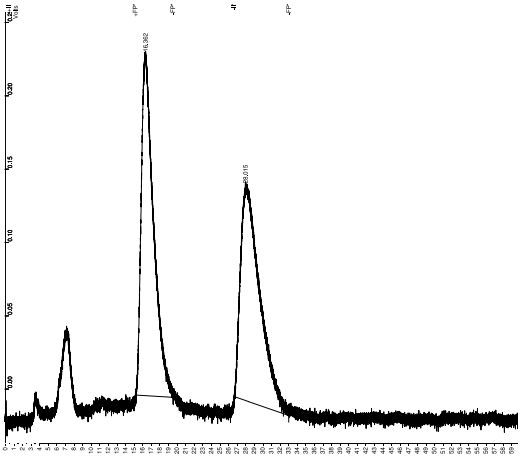
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.4552	19.598	0.000	10520790	BB	110.3	
2		50.5448	31.785	0.000	10752580	BB	189.8	
	Totals:	100.0000		0.000	21273370			

Shows 98% ee.



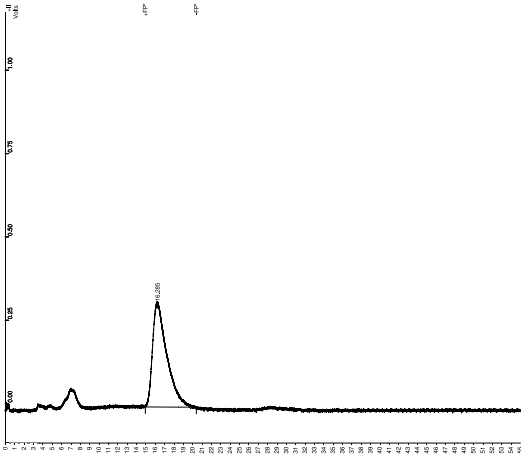
13e

Racemic:



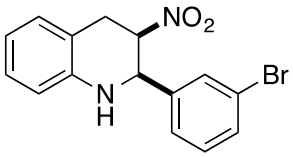
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.0784	16.362	0.000	23251024	BB	87.3	
2		49.9216	28.015	0.000	23178204	BB	134.0	
	Totals:	100.0000		0.000	46429228			

Enantioselective:



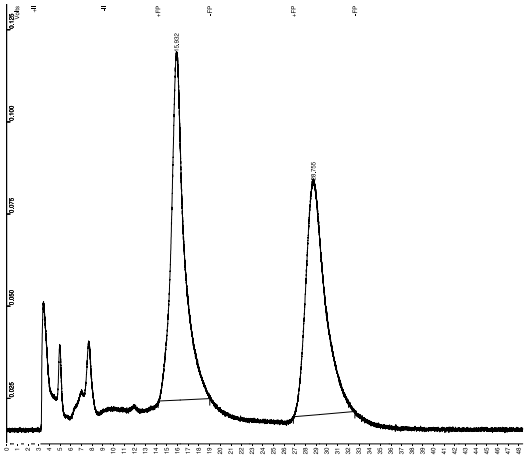
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		100.0000	16.285	0.000	33193842	BB	91.9	
	Totals:	100.0000		0.000	33193842			

Shows >99% ee.



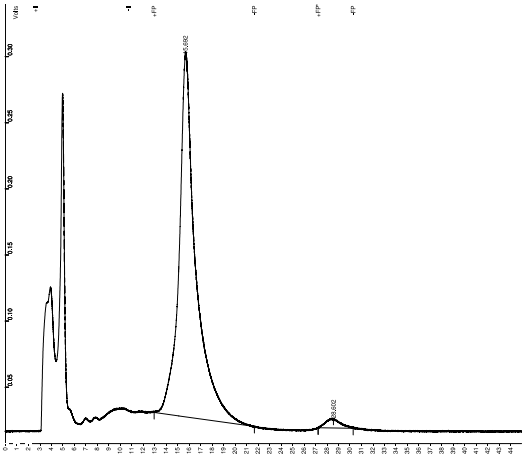
13f

Racemic:



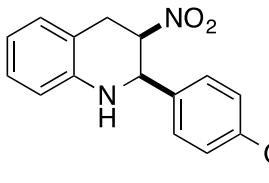
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.0963	15.932	0.000	8081304	BB	64.2	
2		49.9037	28.755	0.000	8050225	BB	109.6	
	Totals:	100.0000		0.000	16131529			

Enantioselective:



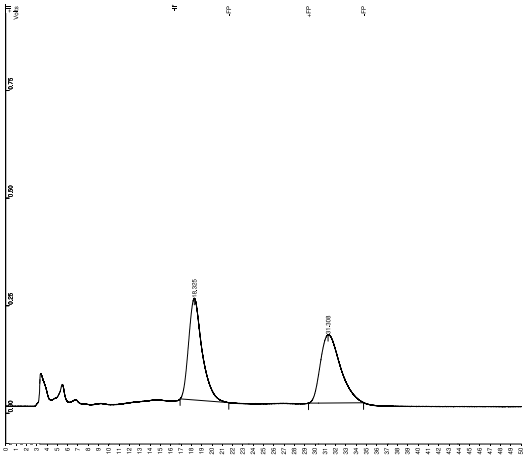
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		97.8058	15.692	0.000	27887674	BB	69.8	
2		2.1942	28.602	0.000	625645	BB	72.3	
	Totals:	100.0000		0.000	28513319			

Shows 96% ee.



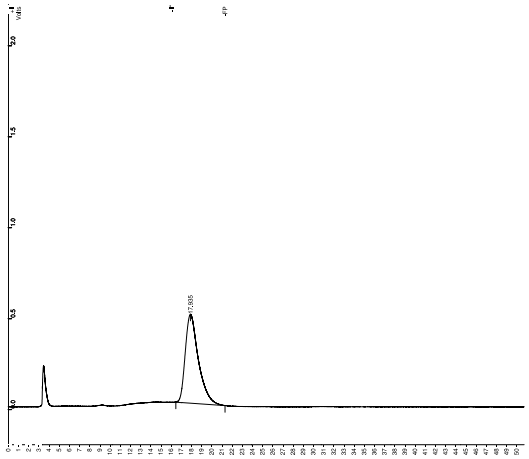
13g

Racemic:



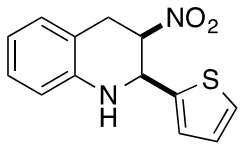
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.0659	18.325	0.000	21389380	BB	79.2	
2		49.9341	31.308	0.000	21333044	BB	125.3	
Totals:		100.0000		0.000	42722424			

Enantioselective:



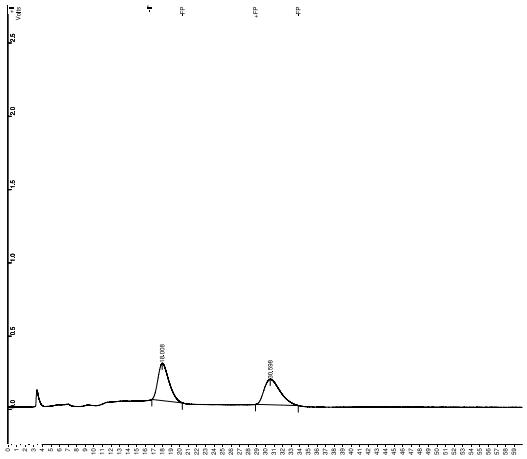
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		99.9135	17.935	0.000	43756116	BB	78.7	
2		0.0865	30.978	0.000	37882	BB	0.5	
Totals:		100.0000		0.000	43793998			

Shows >99% ee.



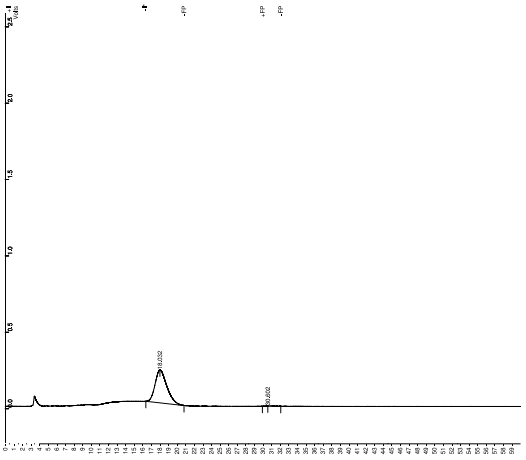
13i

Racemic:



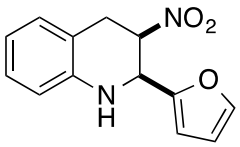
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.0545	18.008	0.000	22622934	BB	79.7	
2		49.9455	30.598	0.000	22573630	BB	119.1	
	Totals:	100.0000		0.000	45196564			

Enantioselective:

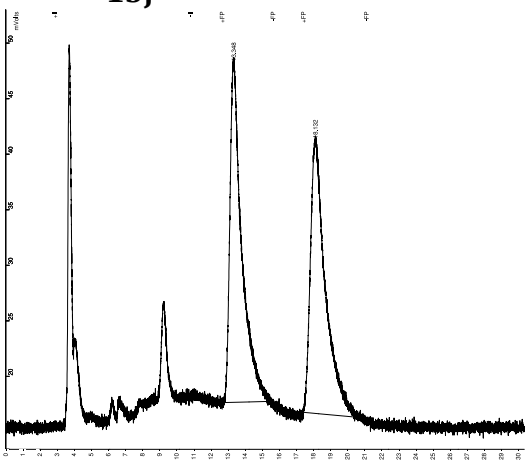


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		99.3196	18.032	0.000	20423136	BB	82.5	
2		0.6804	30.602	0.000	139920	BB	41.6	
	Totals:	100.0000		0.000	20563056			

Shows 99% ee.



13j

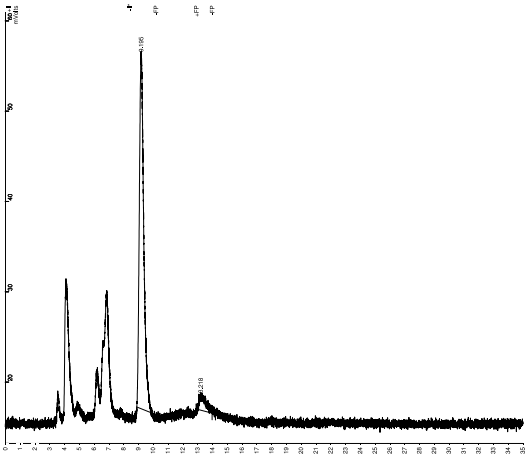


Racemic:

Calculation Type: Percent

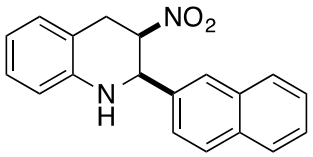
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.7915	13.348	0.000	1489284	BB	37.9	
2		50.2085	18.132	0.000	1501757	BB	48.1	
	Totals:	100.0000		0.000	2991041			

Enantioselective:



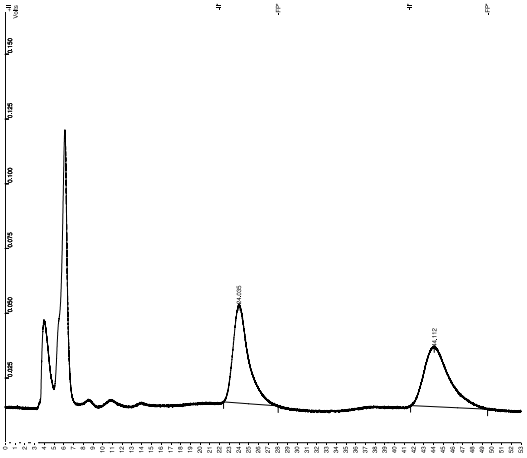
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		93.9264	9.195	0.000	816852	BB	18.4	
2		6.0736	13.218	0.000	52820	BB	2.2	
	Totals:	100.0000		0.000	869672			

Shows 88% ee.



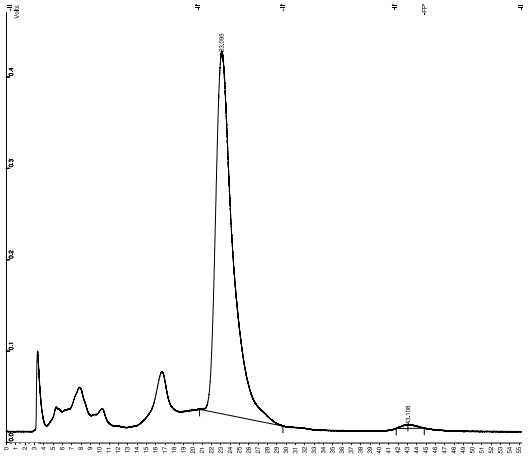
13k

Racemic:



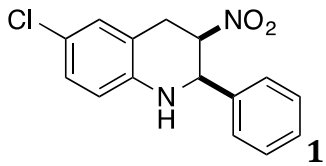
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.9874	24.035	0.000	4162485	BB	90.7	
2		50.0127	44.112	0.000	4164592	BB	153.6	
	Totals:	100.0001		0.000	8327077			

Enantioselective:



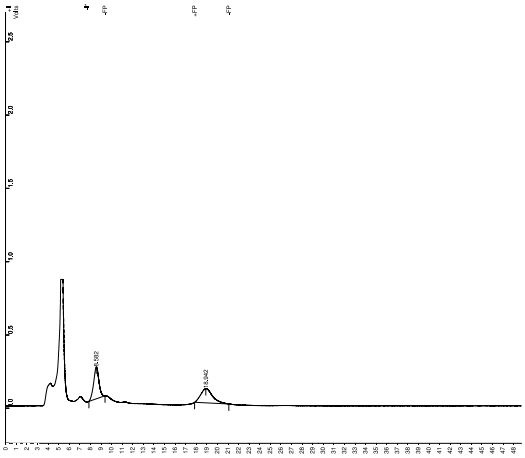
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		99.1646	23.095	0.000	50486400	BB	104.4	
2		0.8354	43.108	0.000	425335	BB	93.7	
	Totals:	100.0000		0.000	50911735			

Shows 98% ee.



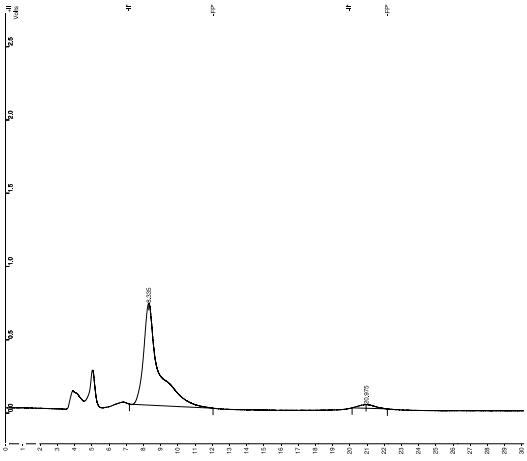
13l

Racemic:



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.0143	8.535	0.000	685099	BB	20.3	
2		50.9857	21.278	0.000	712655	BB	49.8	
	Totals:	100.0000		0.000	1397754			

Enantioselective:



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Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		96.4190	8.335	0.000	42631440	BB	37.8	
2		3.5810	20.975	0.000	1583313	BB	56.5	
	Totals:	100.0000		0.000	44214753			

Shows 93% ee.

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