Electronic Supplementary Material (ESI) for Chemical Science

Supporting Information

Organocatalytic enantioselective construction of nitrocyclohexanes containing multiple chiral centres via a cascade reaction

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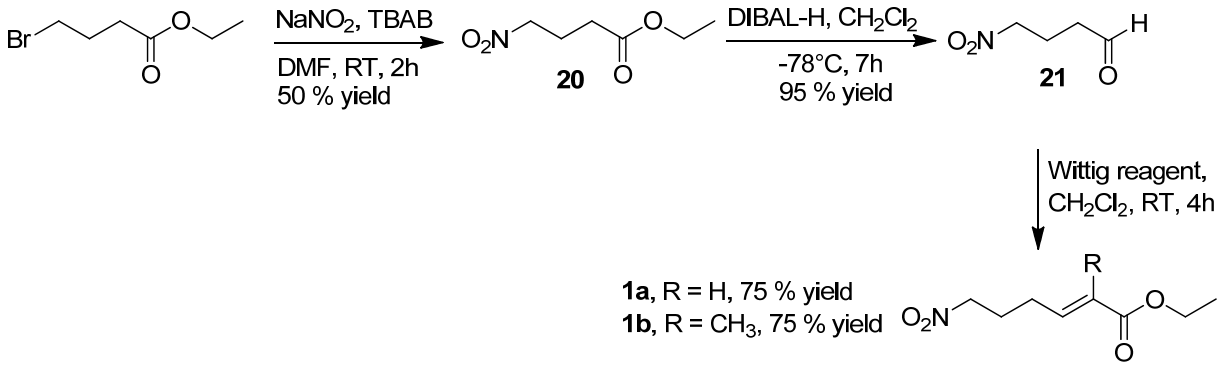
General

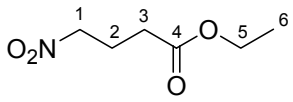
^{1}H NMR spectra were recorded in deuterated chloroform ($CDCl_3$) using a Bruker DPX 400 (400 MHz) or a Bruker Avance III 400 (400 MHz) or a Bruker Avance II^{+} 500 (500 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million using the abbreviations: s, singlet; d, doublet; dd, double doublet; ddd, double doublet doublet; dddd, double doublet doublet doublet; dddt, double doublet doublet triplet; t, triplet; tt, triplet triplet; q, quartet; m, multiplet and the coupling constants *J* are quoted in Hz. ^{13}C NMR spectra were recorded at 100 MHz on a DPX 400 or Avance III 400 or 125 MHz on a Avance II^{+} 500 in deuterated chloroform ($CDCl_3$). Infrared spectra were recorded on a Perkin-Elmer FT-IR spectrometer as a thin film. The absorptions are quoted in wavenumbers (cm^{-1}). Mass spectrometry data was recorded on a Thermo Scientific LTQ Orbitrap XL using electrospray ionisation (ESI) conditions. Specific optical rotations ($[\alpha]_D$) were recorded at the sodium D line in chloroform and are quoted in units of 10^{-1} deg cm^2 g^{-1}. Solution concentrations (c) are given in the units of 10^{-2} g mL^{-1}. Readings were taken using a Perkin-Elmer 341 polarimeter. Melting points were determined on a Stuart SMP3 melting point apparatus and are uncorrected. Thin layer chromatography (tlc) was performed on Merck aluminium backed plates coated with 0.2 mm silica gel $60F_{254}$. The spots were visualised using UV light (254 nm) and then permanent staining by solutions of potassium permanganate. Column chromatography was carried out using silica gel 60Å (35-70 μm). HPLC analysis was determined on an Agilent Technologies 1200 Series HPLC, using a ratio of hexanes and propan-2-ol as the elutent, using either a Chiralpak AD-H column (0.46 cm ø X 25 cm) or a Chrialcel OD column (0.46 cm ø X 25 cm), detection by UV at 210 nm or 254 nm. X-ray data was collected on a Oxford Gemini S-ultra defractometer using Kα (λ = 1.54180 Å) radiation. Anhydrous solvents were supplied as Sureseal® bottles by Aldrich. All reagents were supplied by Aldrich, Fisher and Acros and were used as supplied unless otherwise stated. Compound numbering within this supporting information continues from the manuscript.

Starting material preparation



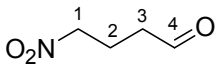
Scheme 1: Synthesis of **1a** and **1b**

Ethyl 4-nitrobutyrate, 20



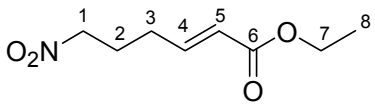
To a solution of ethyl 4-bromobutyrate **1** (8g, 41.03 mmol) in dimethyl formamide (300 mL) was added sodium nitrite (4.25g, 61.54 mmol) and tetrabutylammonium bromide (2.64g, 8.21 mmol) at 20 ^{o}C. After 3 hours, cold water (200 mL) was added and the aqueous phase extracted with diethyl ether (3 x 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification by column chromatography (silica gel, diethyl ether/hexane, 3/17) afforded the title compound as a light yellow oil (3.3g, 20.5 mmol, 50 %). IR (cm^{-1}) 1728 (s), 1550 (s), 1375 (s), 1176 (s), 1027 (m), 798 (m); ^{1}H NMR (400 MHz, $CDCl_3$) 1.27 (3H, t, *J* 7.2, H-6), 2.32 (2H, m, H-2), 2.47 (2H, m, H-3), 4.16 (2H, q, *J* 7.2, H-5), 4.48 (2H, t, 6.4, H-1); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (C-6), 22.3 (C-2), 30.4 (C-3), 60.8 (C-5), 74.3 (C-1), 171.8 (C-4). HRMS required for $C_6H_{11}O_4NNa$ is 184.0580, found 184.0576.

4-nitrobutanal, 21



To a solution of ethyl 4-nitrobutyrate **2** (3g, 18.63 mmol) in dichloromethane (160mL) at -78 °C was added DIBAL-H (26mL, 26.09 mmol, 1M solution in hexane). After 7.5 h the reaction was quenched with aqueous hydrochloric acid (1N, 100 mL) and the aqueous phase was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford the title compound as light yellow oil which was used without further purification. IR (cm^{-1}) 2842 (w), 1719 (s), 1545 (s), 1434 (m), 1382 (m), 1186 (m), 1097 (m); ^{1}H NMR (400 MHz, $CDCl_3$) 2.32 (2H, m, H-2), 2.67 (2H, t, *J* 6.8, H-3), 4.46 (2H, t, *J* 6.7, H-1), 9.8 (1H, s, H-4); ^{13}C NMR (100 MHz, $CDCl_3$) 19.6 (C-2), 40.0 (C-3), 74.2 (C-1), 199.7 (C-4).

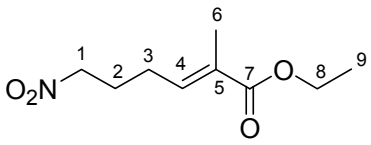
(*E*)-Ethyl 6-nitrohex-2-enoate, 1a



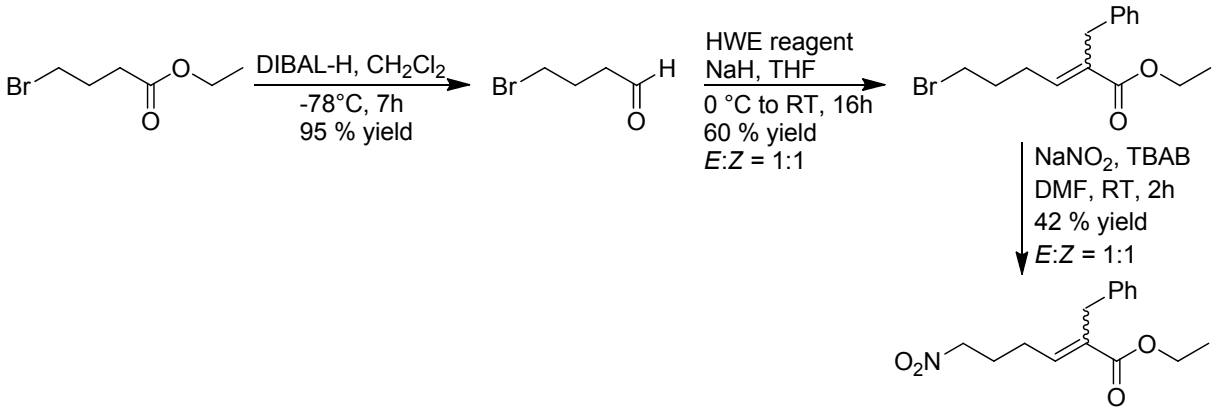
To a solution of crude 4-nitrobutanal **3** (1.89 g, 16.15 mmol) in dichloromethane (42 mL) was added (carbethoxymethylene)triphenylphosphorane (3.87 g, 10.68 mmol) in one portion. After 4h, saturated ammonium chloride (15 mL) and water (100 mL) were added and extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification by column chromatography (silica gel, diethyl ether/hexane, 1/4) afforded the title compound as a colorless oil (2.26g, 75%, 12.09 mmol). IR (cm^{-1}) 1725 (s), 1612 (w), 1553 (s), 1515 (m), 1462 (m), 1372 (m), 1252 (s), 1182 (m), 1031 (m), 832 (m); ^{1}H NMR (400 MHz, $CDCl_3$) 1.29 (3H, t, *J* 7.1, H-8), 2.19 (2H, m, H-2), 2.35 (2H, m, H-3), 4.20 (2H, q, *J* 7.1, H-7),

4.41 (2H, t, *J* 6.8, H-1), 5.88 (1H, dt, *J* 15.6, 1.5, H-5), 6.89 (1H, dt, *J* 15.6, 1.5, H-4); ^{13}C NMR (100 MHz, $CDCl_3$) 14.2 (C-8), 25.5 (C-2), 28.5 (C-3), 60.4 (C-7), 74.4 (C-1), 123.3 (C-5), 145.3 (C-4), 166.0 (C-6); HRMS required for $C_8H_{14}O_4N$ is 188.0917, found 188.0917.

(*E*)-Ethyl 2-methyl-6-nitrohex-2-enoate, 1b

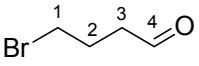


To a solution of crude 4-nitrobutanal **3** (1.1 g, 9.4 mmol) in dichloromethane (50 mL) was added in one portion of (carbethoxyethylidene)triphenylphosphorane (3.75 g, 10.34 mmol). After 4h, saturated ammonium chloride (15 mL) and water (100 mL) were added and extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification by column chromatography (silica gel, diethyl ether/hexane, 1/4) afforded the title compound as colorless oil (1.4g, 75%, 7.05 mmol). IR (cm^{-1}) 1704 (s), 1651 (m), 1549 (s), 1435 (m), 1382 (m), 1367 (m), 1259 (s), 1129 (s); ^{1}H NMR (400 MHz, $CDCl_3$) 1.30 (3H, t, *J* 7.16, H-9), 1.83 (3H, s, H-6), 2.18 (2H, m, H-2), 2.31 (2H, m, H-3), 4.20 (2H, q, *J* 7.12, H-8), 4.41 (2H, t, *J* 6.74, H-1), 6.68 (1H, t, *J* 7.38, H-4); ^{13}C NMR (100 MHz, $CDCl_3$) 12.4 (C-6), 14.2 (C-9), 25.1 (C-3), 26.2 (C-2), 60.6 (C-8), 74.7 (C-1), 130.0 (C-5), 138.2 (C-4), 167.6 (C-7); HRMS required for $C_9H_{16}O_4N$ is 202.1074, found 202.1073.



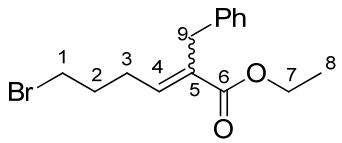
Scheme 2: Synthesis of Ethyl 2-benzyl-6-nitrohex-2-enoate

4-bromobutanal



To a solution of ethyl 4-bromobutyrate **2** (2 g, 10.25 mmol) in DCM (150 ml) at -78° C was added DIBAL-H (15 ml,15.38 mmol, 1M solution in hexane). After 9 h the reaction was quenched with aqueous hydrochloric acid (1N, 100 ml) and the aqueous phase was extracted with DCM (2*20 ml). The combined organic layers were dried and concentrated to afford the title compound as light yellow oil which was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) 2.19 (2H, m, H-2), 2.68 (2H, t, *J* 6.7, H-3), 3.45 (2H, t, *J* 6.4, H-1), 9.81 (1H, s, H-4); ^{13}C NMR (100 MHz, $CDCl_3$) 24.9 (C-2), 32.7 (C-1), 30.4 (C-3), 200.8 (C-4).

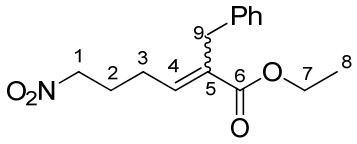
Ethyl 2-benzyl-6-bromohex-2-enoate



To a solution of triethy 2-benzyl-2-phosphonoacetate (1.99 g, 6.36 mmol) in THF (20 ml) at 0° C was added NaH (254 mg, 6.36 mmol) and stirred at this temperature for half an hour. Now, 4-bromobutanal (0.8 g, 5.30 mmol) in 6 ml of THF was added slowly into the reaction mixture and left stirring slowly to RT for 16h. It was then quenched with satd.NH_4Cl and

the aqueous phase was extracted with diethyl ether (3*25 ml). The combined organic layers were dried and concentrated. Purification by column chromatography (silica gel, 10 % diethyl ether/ hexane) afforded the title compound as colorless oil (1 g, 60%, 3.22 mmol, *E*/*Z* ratio 1:1). Analytical data of *E* isomer: IR (cm^{-1}) 1710 (s), 1451 (w), 1231 (s), 1190 (s), 699 (s); ^{1}H NMR (400 MHz, $CDCl_3$) 1.22 (3H, t, *J* 7.1, H-8), 2.00 (2H, m, H-2), 2.46 (2H, m, H-3), 3.39 (3H, t, *J* 6.5, H-1), 3.71 (2H, s, H-9), 4.15 (2H, q, *J 7.1*, H-7), 6.86 (1H, t, *J 7.5*, H-4), 7.21 (5H, m, H-aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) 14.2 (C-8), 27.3 (C-3), 31.5 (C-2), 32.4 (C-9), 32.9 (C-1), 60.7 (C-7), 126.0, 128.2, 128.3, 132.6 (C-5), 139.6, 141.3 (C-4), 167.4 (C-6); HRMS required for $C_{15}H_{19}O_2{}^{81}BrNa$ is 335.0440, found 335.0436. Analytical data of *Z* isomer: IR (cm^{-1}) ; ^{1}H NMR (400 MHz, $CDCl_3$) 1.20 (3H, t, *J* 7.1, H-8), 1.99 (2H, m, H-2), 2.62 (2H, m, H-3), 3.39 (3H, t, *J* 6.8, H-1), 3.58 (2H, s, H-9), 4.13 (2H, q, *J 7.1*, H-7), 5.87 (1H, t, *J 7.6*, H-4), 7.22 (5H, m, H-aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) 14.2 (C-8), 28.3 (C-3), 32.4 (C-2), 33.0 (C-1), 40.4 (C-9), 60.3 (C-7), 126.2, 128.3, 128.8, 132.9 (C-5), 139.3, 140.9 (C-4), 167.3 (C-6); HRMS required for $C_{15}H_{19}O_2BrNa$ is 333.0461, found 333.0461.

Ethyl 2-benzyl-6-nitrohex-2-enoate

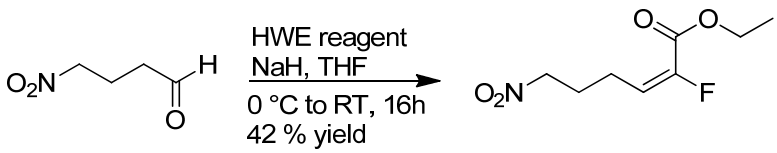


To a solution Ethyl 2-benzyl-6-bromohex-2-enoate (1 g, 3.22 mmol) in DMF (40 ml) was added sodium nitrite (333 mg, 4.82 mmol) and TBAB (207 mg, 0.64 mmol) at RT. After 26 hours, cold water was added and extracted with diethyl ether (25 ml), The aqueous phase was extracted with diethyl ether again (2*25 ml). The combined organic layers were dried over anhy. $MgSO_4$, filtered and concentrated. Purification by column chromatography (silica gel, 15

% diethyl ether/ hexane) afforded the title compound as colorless oils, E isomer (190 mg, 21%, 0.69 mmol) and Z isomer (185 mg, 21%, 0.67 mmol).

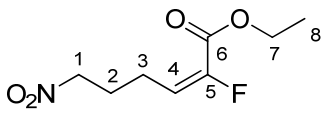
Analytical data of *E* isomer: IR (cm^{-1}) 1704(s), 1579(s), 1379(m), 1263 (m), 1189 (m), 736 (s); ^{1}H NMR (400 MHz, $CDCl_3$) 1.23 (3H, t, *J* 7.1, H-8), 2.13 (2H, m, H-2), 2.37 (2H, m, H-3), 3.68 (2H, s, H-9), 4.16 (2H, q, *J 7.1*, H-7), 4.33 (3H, t, *J* 6.8, H-1), 6.84 (1H, t, *J 7.5*, H-4), 7.21 (5H, m, H-aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (C-8), 25.5 (C-3), 26.2 (C-2), 32.4 (C-9), 60.8 (C-7), 74.6 (C-1), 126.2, 128.1, 128.4, 133.3(C-5), 139.3, 140.0 (C-4), 167.2 (C-6); HRMS required for $C_{15}H_{20}O_4N$ is 278.1387, found 278.1388.

Analytical data of *Z* isomer: IR (cm^{-1}) 1708(s), 1549(s), 1379(m), 1221 (m), 1191 (m), 736 (w), 699 (m); ^{1}H NMR (400 MHz, $CDCl_3$) 1.20 (3H, t, *J* 7.2, H-8), 2.14 (2H, m, H-2), 2.57 (2H, m, H-3), 3.59 (2H, s, H-9), 4.13 (2H, q, *J 7.1*, H-7), 4.38 (3H, t, *J* 7.1, H-1), 5.83 (1H, t, *J 7.6*, H-4), 7.23 (5H, m, H-aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (C-8), 26.1 (C-3), 26.8 (C-2), 40.8 (C-9), 60.4 (C-7), 74.8 (C-1), 126.3, 128.4, 128.8, 133.9(C-5), 138.9, 139.5 (C-4), 167.0 (C-6); HRMS required for $C_{15}H_{20}O_4N$ is 278.1387, found 278.1387.



Scheme 3: Synthesis of (*E*)-Ethyl 2-fluoro-6-nitrohex-2-enoate

(*E*)-Ethyl 2-fluoro-6-nitrohex-2-enoate

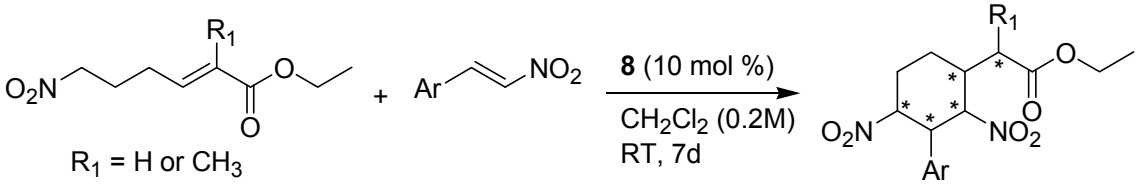


To a solution of triethy 2-fluorol-2-phosphonoacetate (0.807 g, 3.33 mmol) in THF (10 ml) at 0° C was added NaH (103 mg, 2.56 mmol) and stirred at this temperature for half an hour. Now, 4-nitrobutanal (0.3 g, 2.56 mmol) in 3 ml of THF was added slowly into the reaction

mixture and left stirring slowly to RT for 7h. It was then quenched with satd.NH_4Cl and the aqueous phase was extracted with diethyl ether (3*25 ml). The combined organic layers were dried and concentrated. Purification by column chromatography (silica gel, 10 % diethyl ether/ hexane) afforded the title compound as colorless oil (0.22 g, 42%, 1.07 mmol). IR (cm^{-1}) 1708(s), 1549(s), 1379(m), 1221 (m), 1191 (m), 736 (w), 699 (m); ^1H NMR (400 MHz, $CDCl_3$) 1.35 (3H, t, *J* 7.2, H-8), 2.18 (2H, m, H-2), 2.65 (2H, m, H-3), 4.3 (2H, q, *J 7.1*, H-7), 4.42 (2H, t, *J* 6.9, H-1), 5.89 (1H, dt, *J 20.5, 8.4,* H-4); ^{13}C NMR (100 MHz, $CDCl_3$) 14.0 (C-8), 22.3 (J_{C-F} *5.7*, C-3), 26.5 (J_{C-F} *2.8,* C-2), 61.7 (C-7), 74.5 (C-1), 120.1 (J_{C-F} *19.6,* C-4), 148.2 (J_{C-F} *253.9,* C-5), 160.6 (J_{C-F} *35.3,* C-6); ^{19}F NMR (376 MHz, $CDCl_3$) -119.4 (dd, *J 20.4*, 5.2); HRMS required for $C_8H_{12}O_4NFNa$ is 228.0643, found 228.0644. Assignment as '*E*' was achieved by comparison of the 3-bond coupling constants with the corresponding *Z*-ester. See : *Structure Elucidation by Modern NMR*; Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W.; Springer-Verlag: New York, 1989.

General organocatalysis reaction: General procedure A

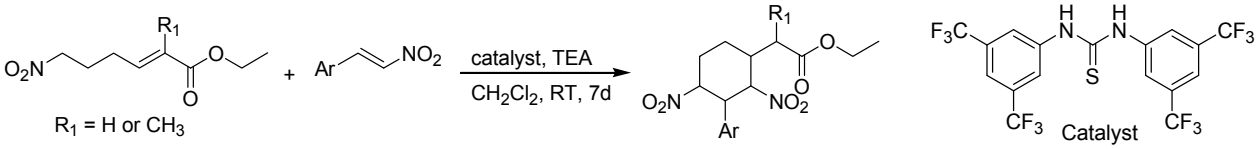
To a solution of the nitro-α,β-unsaturated ester (1 eq.) in solvent (0.2 M concentration), was added nitroalkene (1.1 eq.) and bifunctional organocatalyst **8** (0.1 eq.). The resulting solution was stirred for 7 days, concentrated under reduced pressure and purified by column chromatography (silica gel, Ethyl acetate/hexane 1/4).



Scheme 4: General organocatalysis reaction

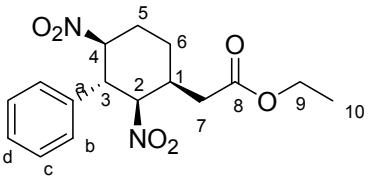
General racemic reaction

To a solution of the nitro-α,β-unsaturated ester (1 eq.) in solvent (0.2 M concentration), was added nitroalkene (1.1 eq.), catalyst (0.1 eq.) and triethylamine (0.1 eq.). The resulting solution was stirred for 7 days, concentrated under reduced pressure and purified by column chromatography (silica gel, Ethyl acetate/hexane 1/4).



Scheme 5: General racemic reaction

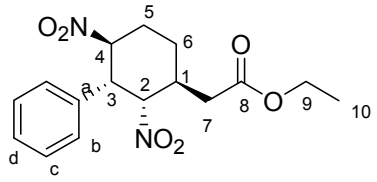
(+)-Ethyl (2*R*,4*S*-dinitro-3*R*-phenyl-1*S*-cyclohexyl) acetate, 3a



Following the general procedure A, in dichloromethane (4 mL), (*E*)-Ethyl 6-nitrohex-2-enoate (150 mg, 0.80 mmol) gave a yellow oil after purification (200 mg, 0.5952 mmol, 74 %). A colourless crystal was obtained after recrystallisation with dichloromethane and hexane. M.Pt. = 110-111 ºC. Enantiomeric excess was determined by HPLC analysis (20 ºC). [Chiralcel OD column (0.46 cm ø X 25 cm) 2-propanol/hexane= 2.5/97.5; flow rate = 1 mL/min; detection wavelength = 210 nm] tR 67.06 min. $[\alpha]_D^{20}$ +25.6 (*c* = 0.5, $CHCl_3$); IR (cm^{-1}) 1730 (s), 1550 (s), 1455 (m), 1372 (m), 1339 (w), 1182 (m), 1032 (m), 761 (w); ^{1}H NMR (400 MHz, $CDCl_3$) 1.26 (3H, t, *J* 7.1, H-10), 1.86 (1H, dddd, *J* 18.5, 14.4, 4.4, 4.2, H-6α), 2.20 (3H, m, H-5 and H-6β), 2.64 (1H, dd, *J* 17.2, 6.1, H-7), 2.70 (1H, dd, *J* 16.7, 8.7, H-7), 3.21 (1H, m, H-1), 3.90 (1H, dd, *J* 11.9, 11.9, H-3), 4.16 (2H, m, H-9), 4.69 (1H, ddd, *J* 16.4, 11.6, 4.8, H-4), 5.06 (1H, dd, *J* 12.2, 4.8, H-2), 7.27 (5H, m, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$)

14.1 (C-10), 25.7 (C-5), 26.4 (C-6), 31.7 (C-7), 33.6 (C-1), 44.8 (C-3), 61.1 (C-9), 89.3 (C-4 and C-2), 127.8 (C-d), 128.9 (C-b), 129.2 (C-c), 134.0 (C-a), 170.6 (C-8). HRMS required for $C_{16}H_{20}O_6N_2Na$ is 359.1214, found 359.1210.

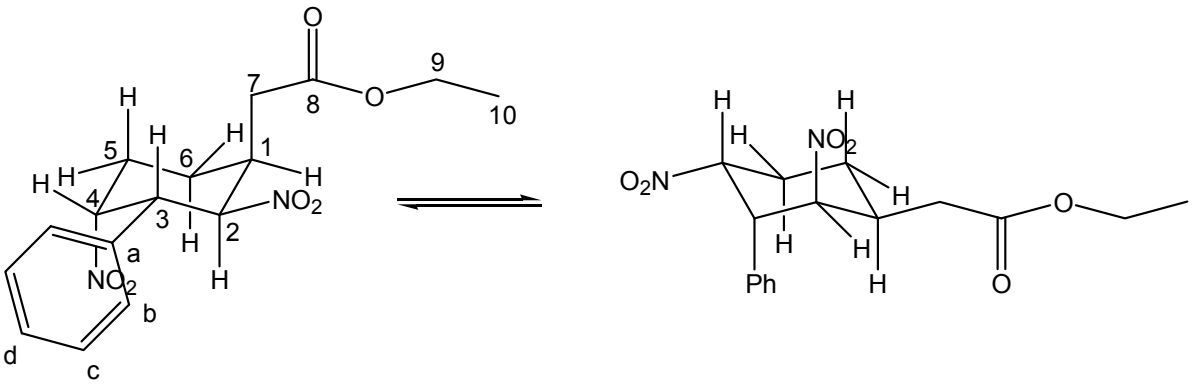
(+)-Ethyl (2*S*,4*S*-dinitro-3*R*-phenyl-1*S*-cyclohexyl) acetate, 10



M.Pt. = 153-154° C. $[\alpha]_D^{20}$ +44.8 (*c* = 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 1.31 (3H, t, *J* 7.2, H-10), 1.80 (1H, m, H-6), 2.16 (1H, m, H-5), 2.34 (1H, m, H-6), 2.51 (1H, dddd, *J* 12.8, 8.7, 4.3, 4.3, H-5), 2.66 (1H, dd, *J* 15.8, 7.4, H-7), 2.74 (1H, dd, *J* 15.8, 7.9, H-7), 2.91 (1H, m, H-1), 3.79 (1H, dd, *J* 11.5, 4.6, H-3), 4.23 (2H, q, J 7.1, H-9), 5.01 (1H, dd, *J* 4.4, 2.1, H-2), 5.84 (1H, ddd, *J* 16.1, 11.3, 4.8, H-4), 7.28 (5H, m, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.2 (C-10), 23.5 (C-6), 26.4 (C-5), 34.0 (C-1), 36.2 (C-7), 43.6 (C-3), 61.4 (C-9), 83.2 (C-4), 91.2 (C-2), 127.5, 128.8, 129.3, 133.8, 170.5 (C-8).

Determination of other diastereomers using NMR

Ethyl (2*R*,4*R*-dinitro-3*R*-phenyl-1*S*-cyclohexyl) acetate, 9



^{1}H NMR (500 MHz, $CDCl_3$) 1.24 (3H, t, *J* 7), 1.82 (1H, m, H-6α), 2.20 (2H, m, H-5), 2.24 (1H, m, H-6β), 2.47 (2H, m, H-7), 3.25 (1H, dddt, *J* 5, 5, 5, 5, H-1α), 3.86 (1H, dd, *J* 12, 5, H-3β), 4.13 (2H, q, *J* 7, H-9), 5.13 (1H, ddd, *J* 4, 4, 4, H-4β), 5.91 (1H, dd, *J* 12, 5, H-2α), 7.20 (2H, d, *J* 8, H-b) 7.29 (3H, m, H-c,d); ^{13}C NMR (125 MHz, $CDCl_3$) 14.0 (C-10), 23.5 (C-6), 24.1 (C-5), 32.5 (C-7), 33.2 (C-1), 42.8 (C-3), 61.0 (C-9), 85.3 (C-2), 86.7 (C-4), 127.6 (C-b), 127.8 (C-d), 129.3 (C-c), 134.5 (C-a), 170.7 (C-8).

In the major conformation, two groups are axial - the 4-nitro and 1-methlynic ester groups; while two groups are equatorial (2-nitro and 3-phenyl).

Methylenic ester substituent at C-1 is axial, because H-1α is clearly equatorial as shown by 3 small equatorial-axial and equatorial-equatorial couplings ($^{3}J_{HH}$ = 5, 5 and 5) to H-2α, H-6α and H-6β.

Nitro ester substituent at C-2 is equatorial, because H-2α is clearly axial as shown by 1 large axial-axial coupling ($^{3}J_{HH}$ = 12) to H-3β (there is also a small axial-equatorial (5 Hz) coupling to H-1α).

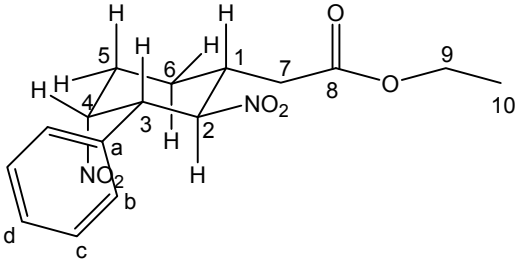
Phenyl substituent at C-3 is equatorial, because H-3β is clearly axial as shown by 1 large axial-axial coupling ($^{3}J_{HH}$ = 12) to H-2α (there is also a small axial-equatorial (5 Hz) coupling to H-4β).

Nitro substituent at C-4 is axial, because H-4β is clearly equatorial as shown by 3 small equatorial-axial and equatorial-equatorial couplings ($^{3}J_{HH}$ = 4, 4 and 4) to H-3β, H-5α and H-5β.

In the minor conformation, the cyclohexane ring flips, placing the 2-nitro and 3-phenyl groups axial, while the 4-nitro and 1-methlynic ester groups become equatorial. Evidence that this ring flipping occurs on the NMR timescale is seen for the line

broadening of C-d (127.8 ppm), C-4 (86.7 ppm), C-2 (85.3 ppm), C-1 (33.2 ppm) and C-7 (32.5 ppm) in ^{13}C NMR.

Ethyl (2*R*,4*R*-dinitro-3*R*-phenyl-1*R*-cyclohexyl) acetate, 11



^{1}H NMR (500 MHz, $CDCl_3$) 1.24 (3H, t, *J* 7), 1.87 (1H, m, H-6α), 2.01 (1H, m, H-6β), 2.11 (1H, m, H-5β), 2.31 (1H, m, H-5α), 2.45 (1H, m, H-7b), 2.50 (1H, m, H-7a), 2.58 (1H, dddt, *J* 12, 12, 5, 5, H-1β), 3.68 (1H, dd, *J* 12, 5, H-3β), 4.13 (2H, q, *J* 7, H-9), 5.04 (1H, ddd, *J* 4, 4, 2, H-4β), 5.77 (1H, dd, *J* 12, 12, H-2α), 7.21 (2H, d, *J* 8, H-b), 7.29 (3H, m, H-c,d); ^{13}C NMR (125 MHz, $CDCl_3$) 14.2 (C-10), 24.5 (C-6), 28.9 (C-5), 37.0 (C-7), 38.2 (C-1), 48.3 (C-3), 60.8 (C-9), 87.7 (C-4), 87.8 (C-2), 127.9 (C-b), 128.8 (C-d), 129.0 (C-c), 133.7 (C-a), 170.6 (C-8).

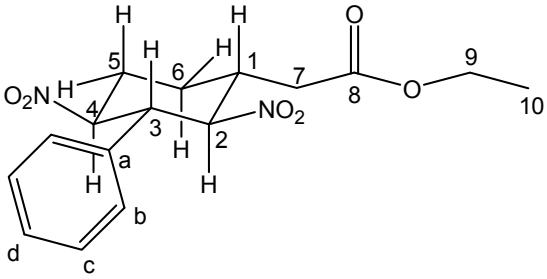
Methylenic ester substituent at C-1 is equatorial, because H-1β is clearly axial as shown by 2 large axial-axial couplings ($^3J_{HH}$ = 12 and 12) to H-2α and H-6α.

Nitro ester substituent at C-2 is equatorial, because H-2α is clearly axial as shown by 2 large axial-axial couplings ($^3J_{HH}$ = 12 and 12) to H-1β and H-3β.

Phenyl substituent at C-3 is equatorial, because H-3β is clearly axial as shown by 1 large axial-axial coupling ($^3J_{HH}$ = 12) to H-2α (small axial-equatorial coupling of $^3J_{HH}$ = 4 to H-4β).

Nitro substituent at C-4 is axial, because H-4β only shows 3 small equatorial-axial and equatorial-equatorial couplings ($^3J_{HH}$ = 4, 4 and 4) to H-3α, H-5α and H-5β.

Ethyl (2*R*,4*S*-dinitro-3*R*-phenyl-1*R*-cyclohexyl) acetate, 12



^{1}H NMR (500 MHz, $CDCl_3$) 1.24 (3H, t, *J* 7), 1.54 (1H, dddd, *J* 13, 13, 12, 5, H-6α), 2.19-2.16 (2H, m, H-5β, H-6β), 2.28 (1H, dd, *J* 16, 6, H-7b), 2.41 (2H, m, H-5α and H-7a), 2.62 (1H, dddt, *J* 12, 12, 5, 5, H-1β), 3.82 (1H, dd, *J* 12, 12, H-3β), 4.13 (2H, q, *J* 7, H-9), 4.77 (1H, dd, *J* 12, 12, H-2α), 4.80 (1H, ddd, *J* 12, 12, 4, H-4α), 7.20 (2H, d, *J* 8, H-b), 7.29 (3H, m, H-c,d); ^{13}C NMR (125 MHz, $CDCl_3$) 14.1 (C-10), 27.0 (C-6), 30.6 (C-5), 36.0 (C-7), 37.8 (C-1), 50.6 (C-3), 60.9 (C-9), 88.0 (C-4), 92.2 (C-2), 127.4 (C-b), 129.2 (C-d), 129.3 (C-c), 133.5 (C-a), 170.3 (C-8).

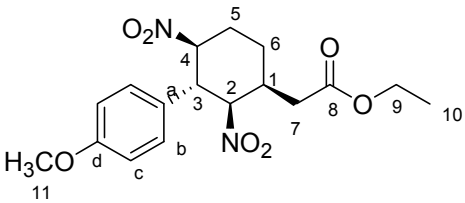
Methylenic ester substituent at C-1 is equatorial, because H-1β is clearly axial as shown by 2 large axial-axial couplings ($^3J_{HH}$ = 12 and 12) to H-2α and H-6α.

Nitro ester substituent at C-2 is equatorial, because H-2α is clearly axial as shown by 2 large axial-axial couplings ($^3J_{HH}$ = 12 and 12) to H-1β and H-3β.

Phenyl substituent at C-3 is equatorial, because H-3β is clearly axial as shown by 2 large axial-axial couplings ($^3J_{HH}$ = 12 and 12) to H-2α and H-4α.

Nitro substituent at C-4 is equatorial, because H-4α is clearly axial as shown by 2 large axial-axial couplings ($^3J_{HH}$ = 12 and 12) to H-3β and H-5β.

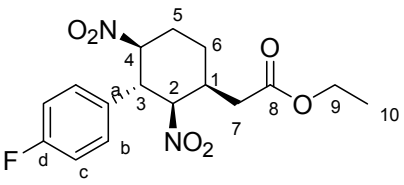
(+)-Ethyl [3*R*-(4'-methoxy-phenyl)-2*R*,4*S*-dinitro-1*S*-cyclohexyl] acetate, 3b



Following the general procedure A, in dichloromethane (4 mL), (*E*)-Ethyl 6-nitrohex-2-enoate (150 mg, 0.80 mmol) gave a yellow oil after

purification (200 mg, 0.5464 mmol, 68%). An off white crystal was obtained after recrystallisation with dichloromethane and hexane. M.Pt. = 157-158 ºC. Enantiomeric excess was determined by HPLC analysis (20 ºC). [Chiralpak AD-H column (0.46 cm ø X 25 cm) 2-propanol/hexane= 1.5/48.5; flow rate = 1 mL/min; detection wavelength = 210 nm] tR 98.89 min, tR 109.47. $[\alpha]_D^{20}$ +21.6 (*c* = 0.5, $CHCl_3$); IR (cm^{-1}) 1730 (s), 1612 (w), 1551 (s), 1515 (s), 1371 (m), 1250 (s), 1181 (m), 1030 (s), 732 (s); ^{1}H NMR (400 MHz, $CDCl_3$) 1.26 (3H, t, *J* 7.1, H-10), 1.86 (1H, dddd, *J* 18.6, 14.2, 4.2, 4.2, H-6α), 2.21 (3H, m, H-5 and H-6β), 2.64 (1H, dd, *J* 16.8, 6.1, H-7), 2.69 (1H, dd, *J* 16.7, 8.3, H-7), 3.19 (1H, m, H-1), 3.75 (3H, s, H-11), 3.85 (1H, dd, *J* 11.9, 11.9, H-3), 4.16 (2H, m, H-9), 4.65 (1H, ddd, *J* 16.4, 11.6, 4.8, H-4), 4.93 (1H, dd, *J* 12.3, 4.8, H-2), 6.82 (2H, d, *J* 8.8, H-c), 7.13 (2H, d, *J* 8.7, H-b); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (C-10), 25.7 (C-5), 26.4 (C-6), 31.7 (C-7), 33.6 (C-1), 44.1 (C-3), 55.2 (C-11), 61.1 (C-9), 89.4 (C-4), 89.5 (C-2), 114.6 (C-c), 125.7 (C-a), 128.9 (C-b), 159.8 (C-d), 170.6 (C-8). HRMS required for $C_{17}H_{12}O_7N_2Na$ is 389.1319, found 389.1322.

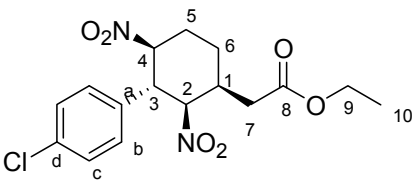
(+)-Ethyl [3*R*-(4'-fluoro-phenyl)-2*R*,4*S*-dinitro-1*S*-cyclohexyl] acetate, 3c



Following the general procedure A, in dichloromethane (4 mL), (*E*)-Ethyl 6-nitrohex-2-enoate (150 mg, 0.80 mmol) gave a yellow oil after purification (190 mg, 0.5367 mmol, 67%). A colourless crystal was obtained after recrystallisation with dichloromethane and hexane. M.Pt. = 148-149 ºC. Enantiomeric excess was determined by HPLC analysis (20 ºC). [Chiralcel OD column (0.46 cm ø X 25 cm) 2-propanol/hexane= 5/45; flow rate = 0.5 mL/min; detection wavelength = 210

nm] tR 49.83 min; tR 61.07 min. $[\alpha]_D^{20}$ +19.2 (*c* = 0.5, $CHCl_3$); IR (cm^{-1}) 1727 (s), 1606 (w), 1548 (s), 1511 (s), 1370 (s), 1226 (m), 833 (m); ^1H NMR (400 MHz, $CDCl_3$) 1.27 (3H, t, *J* 7.1, H-10), 1.87 (1H, dddd, *J* 18.5, 14.3, 4.2, 4.2, H-6α), 2.22 (3H, m, H-5 and H-6β), 2.64 (1H, dd, *J* 16.5, 5.4, H-7), 2.69 (1H, dd, *J* 16.6, 8.5, H-7), 3.21 (1H, m, H-1), 3.91 (1H, dd, *J* 11.9, 11.9, H-3), 4.16 (2H, m, H-9), 4.79 (1H, ddd, *J* 16.3, 11.7, 4.7, H-4), 4.94 (1H, dd, *J* 12.3, 4.8, H-2), 7.01 (2H, dd, J_{HH} = 8.6 (aromatic AB), $^3J_{HF}$ = 8.6, H-c), 7.22 (2H, dd, J_{HH} = 8.8 (aromatic AB), $^4J_{HF}$ = 5.1, H-b); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (C-10), 25.7 (C-5), 25.4 (C-6), 31.7 (C-7), 33.6 (C-1), 44.2 (C-3), 61.2 (C-9), 89.2 (C-4), 89.3 (C-2), 116.2, 116.4(C-c), 129.6, 129.6 (C-b), 129.8, 129.8 (C-a), 161.5, 163.9 (C-d), 170.5 (C-8). ^{19}F NMR (376 MHz, $CDCl_3$) -112.2 (tt, *J* 13.2, 4.4). HRMS required for $C_{16}H_{19}O_6N_2FNa$ is 377.1119, found 377.1124.

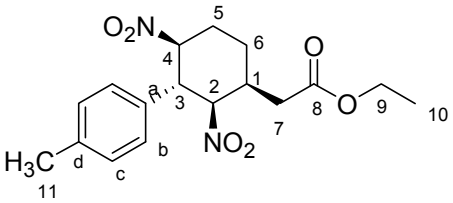
(+)-Ethyl [3*R*-(4'-chloro-phenyl)-2*R*,4*S*-dinitro-1*S*-cyclohexyl] acetate, 3d



Following the general procedure A, in dichloromethane (4 mL), (*E*)-Ethyl 6-nitrohex-2-enoate (150 mg, 0.80 mmol) gave a yellow oil after purification (182 mg, 0.4908 mmol, 61%). A colourless crystal was obtained after recrystallisation with dichloromethane and hexane. M. Pt. = 182-183 ºC. Enantiomeric excess was determined by HPLC analysis (20 ºC). [Chiralpak AD-H column (0.46 cm ø X 25 cm) 2-propanol/hexane= 2.5/47.5; flow rate = 1 mL/min; detection wavelength = 210 nm] tR 50.33 min; tR 60.12 min. $[\alpha]_D^{20}$ +25.6 (*c* = 0.5, $CHCl_3$); IR (cm^{-1}) 1728 (s), 1548 (s), 1494 (m), 1370 (m), 1182 (s), 1092 (m), 824 (s), 735 (s); ^1H NMR (400 MHz, $CDCl_3$) 1.27 (3H, t, *J* 7.2, H-10), 1.87 (1H, dddd, *J* 18.5, 14.4, 4.2, 4.2, H-6α), 2.23 (3H,

m, H-5 and H-6β), 2.62 (1H, dd, *J* 16.8, 5.5, H-7), 2.69 (1H, dd, *J* 16.6, 8.8, H-7), 3.22 (1H, m, H-1), 3.90 (1H, dd, *J* 11.9, 11.9, H-3), 4.16 (2H, m, H-9), 4.65 (1H, ddd, *J* 16.2, 11.6, 4.7, H-4), 4.93 (1H, dd, *J* 12.3, 4.8, H-2), 7.18 (2H, d, *J* 8.5, H-b), 7.3 (2H, d, *J* 8.6, H-c); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (C-10), 25.7 (C-5), 26.4 (C-6), 31.6 (C-7), 33.6 (C-1), 44.3 (C-3), 61.2 (C-9), 89.0 (C-4), 89.1 (C-2), 129.2 (C-b), 129.5 (C-c), 132.6 (C-d), 134.9 (C-a), 170.5 C-8). HRMS required for $C_{16}H_{19}O_6N_2ClNa$ is 393.0824, found 393.0828.

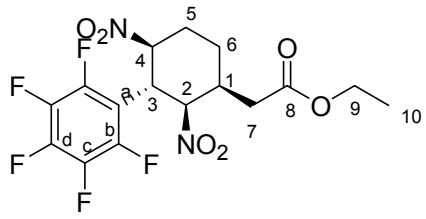
(+)-Ethyl [3*R*-(4'-methyl-phenyl)-2*R*,4*S*-dinitro-1*S*-cyclohexyl] acetate, 3e



Following the general procedure A, in dichloromethane (4 mL), (*E*)-Ethyl 6-nitrohex-2-enoate (150 mg, 0.80 mmol) gave a yellow oil after purification (196 mg, 0.56 mmol, 70%). A colourless crystal was obtained after recrystallisation with dichloromethane and hexane. M.Pt. = 166-167 ºC. Enantiomeric excess was determined by HPLC analysis (20 ºC). [Chiralpak AD-H column (0.46 cm ø X 25 cm) 2-propanol/hexane= 2/48; flow rate = 0.75 mL/min; detection wavelength = 210 nm] tR 52.01 min. $[\alpha]_D^{20}$ +22.4 (*c* = 0.5, $CHCl_3$); IR (cm^{-1}) 1731 (s), 1552 (s), 1454 (w), 1371 (m), 1182 (m), 1033 (m); ^{1}H NMR (400 MHz, $CDCl_3$) 1.26 (3H, t, *J* 7.1, H-10), 1.86 (1H, dddd, *J* 18.5, 14.3, 4.3, 4.2, H-6α), 2.20 (3H, m, H-5 and H-6β), 2.27 (3H, s, H-11), 2.64 (1H, dd, *J* 16.5, 5.5, H-7), 2.69 (1H, dd, *J* 16.6, 8.5, H-7), 3.19 (1H, m, H-1), 3.86 (1H, dd, *J* 11.9, 11.9, H-3), 4.15 (2H, m, H-9), 4.67 (1H, ddd, *J* 16.4, 11.6, 4.9, H-4), 4.96 (1H, dd, *J* 12.3, 4.7, H-2), 7.10 (4H, m, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (C-10), 21.0 (C-11), 25.7 (C-5), 26.4 (C-6), 31.7 (C-7), 33.6 (C-1), 44.4 (C-

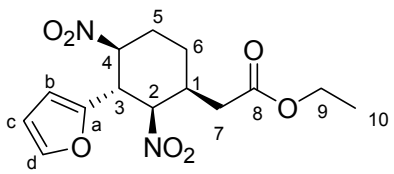
3), 61.1 (C-9), 89.3 (C-4), 89.4 (C-2), 127.6 (C-b), 129.8 (C-c), 130.9 (C-d), 138.7 (C-a), 170.7 (C-8). HRMS required for $C_{17}H_{12}O_6N_2Na$ is 373.1370, found 373.1374.

Ethyl [3-pentafluoro-phenyl)-2,4-dinitro-1-cyclohexyl] acetate, 3f



Following the general procedure A, in dichloromethane (4 mL), (*E*)-Ethyl 6-nitrohex-2-enoate (150 mg, 0.80 mmol) gave a yellow oil after purification (96 mg, 0.2253 mmol, 28%). Enantiomeric excess was determined by HPLC analysis (20 ºC). [Chiralcel OD column (0.46 cm ø X 25 cm) 2-propanol/hexane= 2/48; flow rate = 1 mL/min; detection wavelength = 210 nm] tR 31.77 min. IR (cm^{-1}) 1732 (s), 1656 (w), 1556 (s), 1524 (s), 1504 (s), 1370 (m), 1186 (s), 1105 (s), 1020 (s), 986 (s), 731 (s); ^{1}H NMR (500 MHz, $CDCl_3$) 1.27 (3H, t, *J* 7.2, H-10), 1.93 (1H, m, H-6α), 2.30 (3H, m, H-5 and H-6β), 2.51 (1H, dd, *J* 16.8, 4.6, H-7), 2.69 (1H, dd, *J* 16.6, 9.8, H-7), 3.29 (1H, m, H-1), 4.17 (2H, m, H-9), 4.37 (1H, dd, *J* 11.9, 11.9, H-3), 4.91 (1H, ddd, *J* 16.2, 11.7, 4.5, H-4), 5.15 (1H, dd, *J* 12.2, 4.8, H-2); ^{13}C NMR (125 MHz, $CDCl_3$) 14.1 (C-10), 25.8 (C-5), 25.9 (C-6), 30.9 (C-7), 34.0 (C-1), 35.8 (C-3), 61.4 (C-9), 85.3 (C-4), 86.3 (C-2), 170.3 (C-8). HRMS required for $C_{16}H_{15}O_6N_2F_5Na$ is 449.0742, found 449.0734.

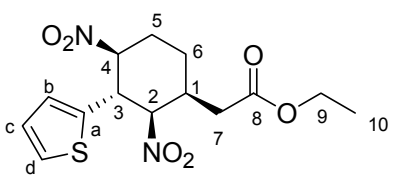
(+)-Ethyl (3*R*-furan-2'-yl-2*R*,4*S*-dinitro-1*S*-cyclohexyl) acetate, 3g



Following the general procedure A, in dichloromethane (4 mL), (*E*)-Ethyl 6-nitrohex-2-enoate (150 mg, 0.80 mmol) gave a yellow oil after

purification (173 mg, 0.5307 mmol, 66 %). An off white crystal was obtained after recrystallisation with dichloromethane and hexane. M.Pt. = 120-121 ºC. Enantiomeric excess was determined by HPLC analysis (20 ºC). [Chiralpak AD-H column (0.46 cm ø X 25 cm) 2-propanol/hexane= 1/49; flow rate = 1 mL/min; detection wavelength = 210 nm] tR 53.53 min. $[\alpha]_D^{20}$ +9.6 (*c* = 0.5, $CHCl_3$); IR (cm^{-1}) 1729 (s), 1552 (s), 1455 (w), 1370 (m), 1182 (s), 1098 (m), 1014 (s), 739 (s); ^1H NMR (400 MHz, $CDCl_3$) 1.26 (3H, t, *J* 7.1, H-10), 1.83 (1H, dddd, *J* 18.4, 14.3, 4, 4, H-6α), 2.21 (3H, m, H-5 and H-6β), 2.54 (1H, dd, *J* 16.8, 5.4, H-7), 2.62 (1H, dd, *J* 16.6, 8.9, H-7), 3.19 (1H, m, H-1), 4.16 (3H, m, H-3 and H-9), 4.79 (1H, ddd, *J* 16, 11.6, 4.6, H-4), 5.06 (1H, dd, *J* 11.8, 4.8, H-2), 6.24 (1H, dd, *J* 3.3, 0.6,H-b), 6.27 (1H, dd, *J* 3.3, 1.9, H-c), 7.33 (1H, dd, *J* 1.8, 0.7, H-d); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (C-10), 25.2 (C-5), 25.9 (C-6), 31.7 (C-7), 33.3 (C-1), 38.8 (C-3), 61.2 (C-9), 86.5 (C-4), 86.8 (C-2), 110.3 (C-b), 110.8 (C-c), 143.2 (C-d), 147.2 (C-a), 170.5 (C-8). HRMS required for $C_{14}H_{18}O_7N_2Na$ is 349.1006, found 349.1001.

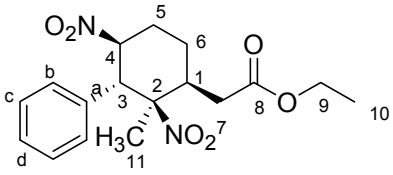
(+)-Ethyl (2*R*,4*S*-dinitro-3*R*-thiophen-2'-yl-1*S*-cyclohexyl) acetate, 3h



Following the general procedure A, in dichloromethane (4 mL), (*E*)-Ethyl 6-nitrohex-2-enoate (150 mg, 0.80 mmol) gave a yellow oil after purification (214 mg, 0.6257 mmol, 78%). An off white crystal was obtained after recrystallisation with dichloromethane and hexane. M.Pt. = 143-144 ºC. Enantiomeric excess was determined by HPLC analysis (20 ºC). [Chiralpak AD-H column (0.46 cm ø X 25 cm) 2-propanol/hexane= 1.5/48.5; flow rate = 1 mL/min; detection wavelength =

210 nm] tR 63.50 min. $[\alpha]_D^{20}$ +19.6 (*c* = 0.5, $CHCl_3$); IR (cm^{-1}) 1728 (s), 1551 (s), 1456 (w), 1371 (m), 1186 (s), 1095 (m), 1030 (s), 705 (s); ^1H NMR (400 MHz, $CDCl_3$) 1.26 (3H, t, *J* 7.1, H-10), 1.87 (1H, dddd, *J* 18.5, 14.5, 4.1, 4.1, H-6α), 2.22 (3H, m, H-5 and H-6β), 2.61 (1H, dd, *J* 16.8, 6.2, H-7), 2.66 (1H, dd, *J* 16.6, 8.2, H-7), 3.21 (1H, m, H-1), 4.16 (2H, m, H-9), 4.29 (1H, dd, *J* 11.6, 11.6, H-3), 4.68 (1H, ddd, *J* 16.1, 11.6, 4.6, H-4), 4.92 (1H, dd, *J* 12, 4.8, H-2), 6.91 (1H, dd, *J* 5.1, 3.6,H-c), 6.96 (1H, dd, *J* 3.6, 1, H-b), 7.23 (1H, dd, *J* 5.1, 0.8, H-d); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (C-10), 25.8 (C-5), 26.2 (C-6), 31.7 (C-7), 33.7 (C-1), 40.5 (C-3), 61.2 (C-9), 90.0 (C-4), 90.2 (C-2), 125.8 (C-d), 127.3 (C-c), 127.8 (C-b), 136.6 (C-a), 170.5 (C-8). HRMS required for $C_{14}H_{18}O_6N_2NaS$ is 365.0778, found 365.0771.

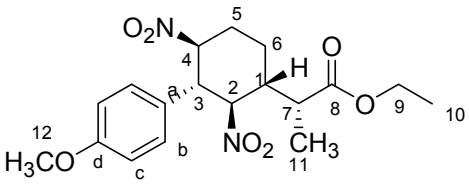
(-)-Ethyl [2*R*-methyl-2*R*,4*S*-dinitro-3*R*-phenyl-1*S*-cyclohexyl] acetate, 3i



Following the general procedure A, in dichloromethane (4 mL), (*E*)-Ethyl 6-nitrohex-2-enoate (150 mg, 0.80 mmol) gave a yellow oil after purification (12 mg, 0.03428 mmol, 4%). A colourless crystal was obtained after recrystallisation with dichloromethane and hexane. M.Pt. = 133-134 ºC. Enantiomeric excess was determined by HPLC analysis (20 ºC). [Chiralpak AD-H column (0.46 cm ø X 25 cm) 2-propanol/hexane= 2/48; flow rate = 1 mL/min; detection wavelength = 210 nm] tR 25.36 min. $[\alpha]_D^{20}$ -38.7 (*c* = 0.3, $CHCl_3$); IR (cm^{-1}) 1730 (s), 1542 (s), 1454 (w), 1374 (m), 1189 (s), 1032 (m), 704 (s); ^1H NMR (400 MHz, $CDCl_3$) 1.27 (3H, t, *J* 7.1, H-10), 1.76 (3H, s, H-11), 2.02 (2H, m, H-6), 2.30 (2H, m, H-5), 2.60 (1H, dd, J 15.5, 4.4, H-7), 2.74 (2H, m, H-1 and H-7), 4.16 (2H, m, H-9), 4.36 (1H, d, *J* 12.1, H-3), 5.05 (1H,

ddd, *J* 17.0, 12.0, 5.0, H-4), 7.26 (5H, m, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (C-10), 21.5 (C-11), 24.8 (C-6), 26.3 (C-5), 33.9 (C-7), 40.8 (C-1), 46.9 (C-3), 61.1 (C-9), 87.5 (C-4), 93.2 (C-2), 128.5 (C-d), 128.6 (C-b), 130.2 (C-c), 132.5 (C-a), 170.8 (C-8). HRMS required for $C_{17}H_{12}O_6N_2Na$ is 373.1370, found 373.1355.

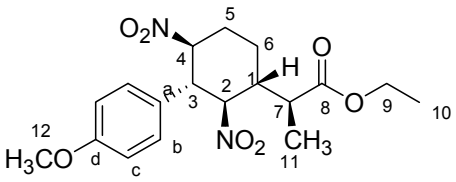
(+)-Ethyl 2(*R*)-[3(*R*)-(4'-methoxy-phenyl)-2(*R*),4(*S*)-dinitro-1(*R*)cyclohexyl] propanoate, 13



Following the general procedure A, in dichloromethane (4 mL), (E)-Ethyl 2-methyl-6-nitrohex-2-enoate (160 mg, 0.80 mmol) gave a yellow oil after purification (90 mg, 0.2368 mmol, 30%). A colourless crystal was obtained after recrystallisation with dichloromethane and hexane. M.Pt. = 162-163 ºC. Enantiomeric excess was determined by HPLC analysis (20 ºC). [Chiralpak AD-H column (0.46 cm ø X 25 cm) 2-propanol/hexane= 3/97; flow rate = 1 mL/min; detection wavelength = 210 nm] tR 40.26 min, 46.88 min. $[\alpha]_D^{20}$ +30.4 (*c* = 0.5, $CHCl_3$); IR (cm^{-1}) 1712 (s), 1655 (m), 1547 (s), 1435 (m), 1368 (m), 1268 (s), 1197 (s), 1160 (s), 1039 (s), 980 (m), 848 (m), 706 (m); ^{1}H NMR (400 MHz, $CDCl_3$) 1.25 (3H, d, *J* 7.3, H-11), 1.28 (3H, t, *J* 7.1, H-10), 1.73 (1H, m, H-6), 2.14 (2H, m, H-5 and H-6), 2.31 (1H, m, H-1), 2.48 (2H, m, H-5 and H-7), 3.75 (4H, m, H-3 and H-12), 4.18 (2H, m, H-9), 4.74 (1H, ddd, *J* 15.7, 11.9, 4.0, H-4), 5.02 (1H, dd, *J* 11.3, 11.3, H-2), 6.82 (2H, d, *J* 8.7, H-c), 7.10 (2H, d, *J* 8.6, H-b); ^{13}C NMR (100 MHz, $CDCl_3$) 14.2 (C-10), 15.2 (C-11), 22.1 (C-6), 30.8 (C-5), 38.6 (C-7), 44.4 (C-1), 50.6 (C-3), 55.1 (C-12), 60.8 (C-9), 88.3 (C-4), 91.7 (C-2), 114.6 (C-c), 125.3

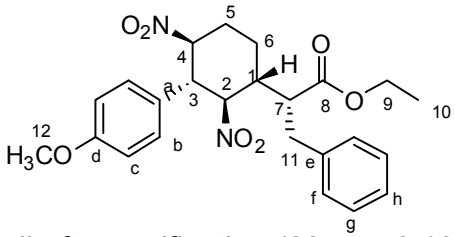
(C-a), 128.8 (C-b), 159.9 (C-d), 173.0 (C-8). HRMS required for $C_{18}H_{24}O_7N_2Na$ is 403.1476, found 403.1472. And this analytical data is for minor diastereo isomer.

Ethyl 2(*R*)-[3(*R*)-(4'-methoxy-phenyl)-2(*R*),4(*S*)-dinitro-1(*R*)cyclohexyl] propanoate,



^{1}H NMR (400 MHz, $CDCl_3$) 1.18 (3H, d, *J* 7.2, H-11)1.27 (3H, t, *J* 7.1, H-10), 1.50 (1H, m, H-6), 2.11 (2H, m, H-5 and H-6), 2.46 (2H, m, H-5 and H-7), 2.31 (1H, dddd, *J* 15.3, 12.0, 3.3, 3.3, H-1), 3.75 (3H, s, H-12), 3.82 (1H, dd, *J* 11.1, 11.1, H-3), 4.16 (2H, q, *J* 7.1, H-9), 4.62 (1H, dd, *J* 11.4, 11.4, H-2), 4.71 (1H, ddd, *J* 16.0, 11.9, 4.1, H-4), 6.83 (2H, d, *J* 8.8, H-c), 7.12 (2H, d, *J* 8.7, H-b); ^{13}C NMR (100 MHz, $CDCl_3$) 9.8(C-11), 14.2 (C-10), 22.5 (C-6), 30.4 (C-5), 39.2 (C-7), 42.3 (C-1), 50.3 (C-3), 55.2 (C-12), 61.1 (C-9), 88.2 (C-4), 91.1 (C-2), 114.7 (C-c), 125.1 (C-a), 128.9 (C-b), 159.9 (C-d), 173.3 (C-8).

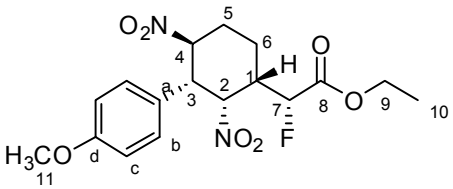
Ethyl 2(*R*)-[3(*R*)-(4'-methoxy-phenyl)-2(*R*),4(*S*)-dinitro-1(*R*)cyclohexyl]-3-phenylpropanoate 14



Following the general procedure A, in dichloromethane (4 mL), (E)-Ethyl 2-methyl-6-nitrohex-2-enoate (180 mg, 0.65 mmol) gave a yellow oil after purification (82 mg, 0.18 mmol, 28%). Enantiomeric excess was determined by HPLC analysis (20 ºC). [Chiralpak AD-H column (0.46 cm ø X 25 cm) 2-propanol/hexane= 2.5/47.5; flow rate = 1 mL/min; detection wavelength = 210 nm] tR 42.96 min, 48.65 min. IR (cm^{-1}) 1727 (s), 1612 (m), 1553 (s), 1515 (m), 1372 (m), 1252

(s), 1181 (s), 1119 (m), 1030 (s), 832 (m), 700 (m); ^{1}H NMR (400 MHz, $CDCl_3$) 1.12 (3H, t, *J* 7, H-10), 1.65 (1H, dddd, *J* 12, 12, 12, 3, H-6β), 2.14 (2H, m, H-5α and H-6α), 2.49 (1H, dddd, *J* 12, 3, 3, 3, H-5β), 2.63 (1H, dd, *J* 11, 3, H-7), 2.71 (1H, dddd, *J* 13, 11, 3, 3, H-1), 2.98 (2H, dd, *J* 13, 11, H-11), 3.76 (3H, s, H-12), 3.81 (1H, dd, *J* 11, 11, H-3), 4.05 (2H, q, *J* 7, H-9), 4.72 (1H, m, H-4), 4.77 (1H, dd, *J* 12, 12, H-9), 6.84 (2H, d, *J* 8, H-c), 7.11 (2H, d, *J* 8, H-b), 7.15 (2H, d, *J* 8, H-f), 7.19 (1H, m, H-h),7.25 (2H, dd, *J* 8, 8, H-g); ^{13}C NMR (100 MHz, $CDCl_3$) 14.0 (C-10), 23.4 (C-6), 30.6 (C-5), 31.7 (C-11), 42.8 (C-1), 48.0 (C-7), 50.4 (C-3), 55.2 (C-12), 61.1 (C-9), 88.2 (C-4), 91.0 (C-2), 114.7 (C-c), 125.1 (C-a), 126.7 (C-h), 128.4 (C-g), 129.0 (C-b), 129.1 (C-f), 138.4 (C-e), 160.1 (C-d), 172.4 (C-8). Stereochemsitry of C-7 assigned by analogy to compound **13**.

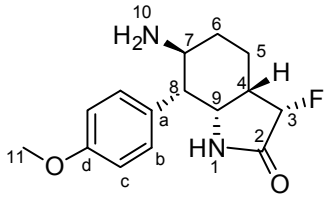
(+)-Ethyl 2(*R*)-fluoro-[3*R*-(4'-methoxy-phenyl)-2*R*,4*S*-dinitro-1*S*-cyclohexyl] acetate 15



Following the general procedure A, in dichloromethane (4 mL), (*E*)-Ethyl 6-nitrohex-2-enoate (175 mg, 0.85 mmol) gave a yellow oil after purification (99 mg, 0.2571 mmol, 30%). An off white crystal was obtained after recrystallisation with dichloromethane and hexane. M.Pt. = 173-174 ºC. Enantiomeric excess was determined by HPLC analysis (20 ºC). [Chiralpak AD-H column (0.46 cm ø X 25 cm) 2-propanol/hexane= 2.5/47.5; flow rate = 1 mL/min; detection wavelength = 210 nm] tR 53.60 min, tR 66.27. $[\alpha]_D^{20}$ +60.6 (*c* = 0.35, $CHCl_3$); IR (cm^{-1}) 1731 (s), 1612 (w), 1551 (s), 1514 (s), 1377 (m), 1289 (m), 1247 (s), 1025 (s), 798 (s), 731 (s); ^{1}H NMR (400 MHz, $CDCl_3$) 1.34 (3H, t, *J* 7.2, H-10), 1.86 (1H, dddd, *J* 14, 4, 4, 4, H-6α), 2.11

(1H, dddd, *J* 14, 14, 14, 4, H-5β), 2.29 (1H, dddd, *J* 14, 14, 14, 4, H-6β), 2.69 (1H, dddd, *J* 14, 7, 4, 4, H-1), 2.72 (1H, m, H-5α), 3.63 (1H, dd, *J* 12, 4, H-3), 3.76 (3H, s, H-11), 4.32 (2H, m, H-9), 4.69 (1H, dd, $^{2}J_{HF}$ 48, J_{HH} 7, H-7), 5.16 (1H, dd, *J* 4, 4, H-2), 5.78 (1H, ddd, *J* 12, 12, 5, H-4), 6.84 (2H, d, *J* 8.7, H-b), 7.10 (2H, d, *J* 8.7, H-c); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (C-10), 20.7 (d, $^{3}J_{CF}$ 5, C-6), 30.6 (C-5), 42.1 (d, $^{2}J_{CF}$ 22, C-1), 47.5 (C-3), 55.3 (C-11), 62.6 (C-9), 83.1 (C-4), 87.7 (d, $^{3}J_{CF}$ 2, C-2), 88.7 (d, $^{1}J_{CF}$ 189, C-7), 114.9 (C-c), 125.1 (C-a), 128.4 (C-b), 160.0 (C-d), 167.4 (d, $^{2}J_{CF}$ 22, C-8). ^{19}F NMR (376 MHz, $CDCl_3$) -118.9. HRMS required for $C_{17}H_{21}O_7N_2FNa$ is 407.1225, found 407.1220.

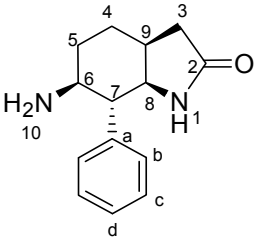
(3*S*, 3a*S*, 6*S*, 7*R*, 7aR)-6-amino-3-fluoro-7-(4'-methoxyphenyl-hexahydro-1H-indol-2(3H)-one



To a solution of (+)-Ethyl 2(R)-fluoro-[3R-(4'-methoxy-phenyl)-2R,4S-dinitro-1S-cyclohexyl] acetate, (24 mg, 0.0623 mmol) in ethanol (2mL) was added Raney Nickel (1 spatula). It was then stirred under an atmosphere of hydrogen (1 atm) at RT. After stirring for 24h, the mixture was filtered through a pad of celite and washed with ethanol, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude is pure enough for analytical data. IR (cm^{-1}) 3286 (br), 2926 (m), 1717 (s), 1611(m), 1512 (s), 1446 (w), 1245 (s), 1110 (m), 835 (w), 731 (s); ^{1}H NMR (400 MHz, $CDCl_3$) 1.34 (1H, dddd, *J* 11, 11, 11, 3, H-6β), 1.61 (1H, dddd, *J* 14, 14, 14, 3, H-5α), 1.89 (1H, dddd, *J* 14, 6, 3, 3, H-5β), 2.04 (1H, dd, *J* 13, 3, 3, 3, H-6α), 2.62 (1H, dd, *J* 11, 4, H-8), 2.82 (1H, dddd, *J* 12, 6, 6, 6, H-4), 3.29 (1H, ddd, *J* 10, 10, 3, H-7), 3.69 (1H, dd, *J* 4, 4, H-9),

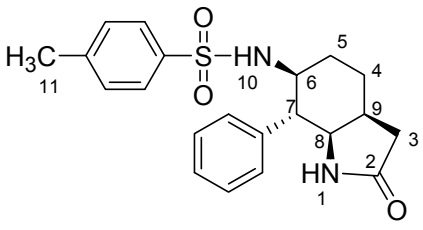
3.81 (3H, s, H-11), 5.10 (1H, dd, $^{2}J_{HF}$ 51, J_{HH} 7, H-3), 7.05 (5H, m, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$) 19.9 (d, $^{3}J_{HF}$ 10, C-5), 32.6 (C-6), 39.9 (d, $^{2}J_{HF}$ 16, C-4), 47.0 (C-10), 51.9 (C-8), 53.6 (d, $^{3}J_{HF}$ 4, C-9), 90.8 (d, $^{1}J_{HF}$ 198, C-3), 115.1 (C-c), 129.0 (C-b), 159.2 (C-d), 171.7 (d, $^{2}J_{HF}$ 24, C-2).

6-Amino-7-phenyl-octahydro-indol-2-one,



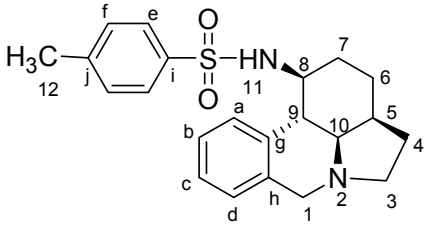
To a solution of (+)-Ethyl (2*R*,4*S*-dinitro-3*R*-phenyl-1*S*-cyclohexyl) acetate, **3a** (135 mg, 0.4 mmol) in ethanol (5mL) was added Raney Nickel (1 spatula). It was then stirred under an atmosphere of hydrogen (1 atm) at RT. After stirring for 24h, the mixture was filtered through a pad of celite and washed with ethanol, dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification by column chromatography (silica gel, methanol/ dichloromethane,1/4) afforded the title compound as a yellow oil (83 mg, 0.36 mmol, 90%). IR (cm^{-1}) 3206 (br), 2924 (m), 1683 (s), 1599 (w), 1451 (w), 1343 (m), 1263 (w), 1058 (m), 702 (s); ^{1}H NMR (400 MHz, $CDCl_3$) 1.36 (2H, br s, H-10), 1.40 (1H, m, H-5), 1.88 (3H, m, H-4 and 5), 2.18 (1H, dd, *J* 8.2, 8.2, H-3), 2.22 (1H, dd, *J* 10.5, 10.5, H-7), 2.42 (1H, dd, *J* 16.5, 12.7, H-3), 2.73 (1H, m, H-9), 2.93 (1H, tdd, *J* 13.8, 10.8, 3.1, H-6), 3.53 (1H, ddd, *J* 10.1, 7.0, 9.2, H-6), 5.58 (1H, s, H-1), 7.28 (5H, m, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$) 24.2 (C-4), 29.9 (C-5), 33.19 (C-3), 34.8 (C-9), 51.6 (C-6), 57.6 (C-7), 60.1 (C-8), 127.5 (C-d), 128.5 (C-b), 129.1 (C-c), 139.8 (C-a), 177.3 (C-2). HRMS required for $C_{14}H_{19}ON_2$ is 231.1492, found 231.1491.

4-methyl-*N*-(2-oxo-7-phenyl-octahydro-indol-6-yl)benzenesulfonamide, 16



To a solution of 6-Amino-7-phenyl-octahydro-indol-2-one (76 mg, 0.33 mmol) in anhydrous dichloromethane (10 mL) was added anhydrous triethylamine (0.11 mL, 0.79 mmol, 2.4 eq.) and tosyl chloride (76 mg, 0.40 mmol, 1.2 eq.) at 0 °C and allowed to RT and stirred for 3 days. After removal of dichloromethane, it was loaded onto column and eluted with 10 % methanol/dichloromethane to obtain pure 4-methyl-*N*-(2-oxo-7-phenyl-octahydro-indol-6-yl)benzenesulfonamide as an off white semi solid (108mg, 0.28 mmol, 85 %). IR (cm^{-1}) 3270 (br), 2926 (m), 1675 (s), 1599 (w), 1451 (m), 1422 (m), 1318 (m), 1152 (s), 1091 (s), 813 (m), 732 (s), 700 (s), 671(s); ^{1}H NMR (400 MHz, $CDCl_3$) 1.50-1.83 (3H, m, H-4 and 5), 2.09-2.37 (4H, m, H-3, 5 and 7), 2.40 (3H, s, H11), 2.59-2.67 (1H, m, H-9), 3.16-3.24 (1H, m, H-6), 3.44 (1H, dd, *J* 9.5, 7.3, H-8), 5.28-5.31 (1H, m, H-10), 5.77 (1H, s, H-1), 6.83 (2H, d, *J* 7.3, aromatic H), 7.05-7.17 (5H, m, aromatic H), 7.33 (2H, d, *J* 8.0, aromatic H); ^{13}C NMR (100 MHz, $CDCl_3$) 21.4 (C-12), 23.7 (C-4), 29.0 (C-5), 33.2 (C-3), 34.1 (C-9), 53.7 (C-7), 54.1 (C-6), 60.4 (C-8), 126.8, 127.4, 128.3, 128.9, 129.4, 137.3, 138.1, 142.8, 177.5 (C-2). HRMS required for $C_{21}H_{25}O_3N_2S$ is 385.1580, found 385.1582.

4-Methyl-*N*-(1,2,3,3a,4,5,11b,11c-octahydro-7*H*-pyrrolo[3,2,1-*de*]phenanthridin-1-yl)-benzenesulfonamide, 18

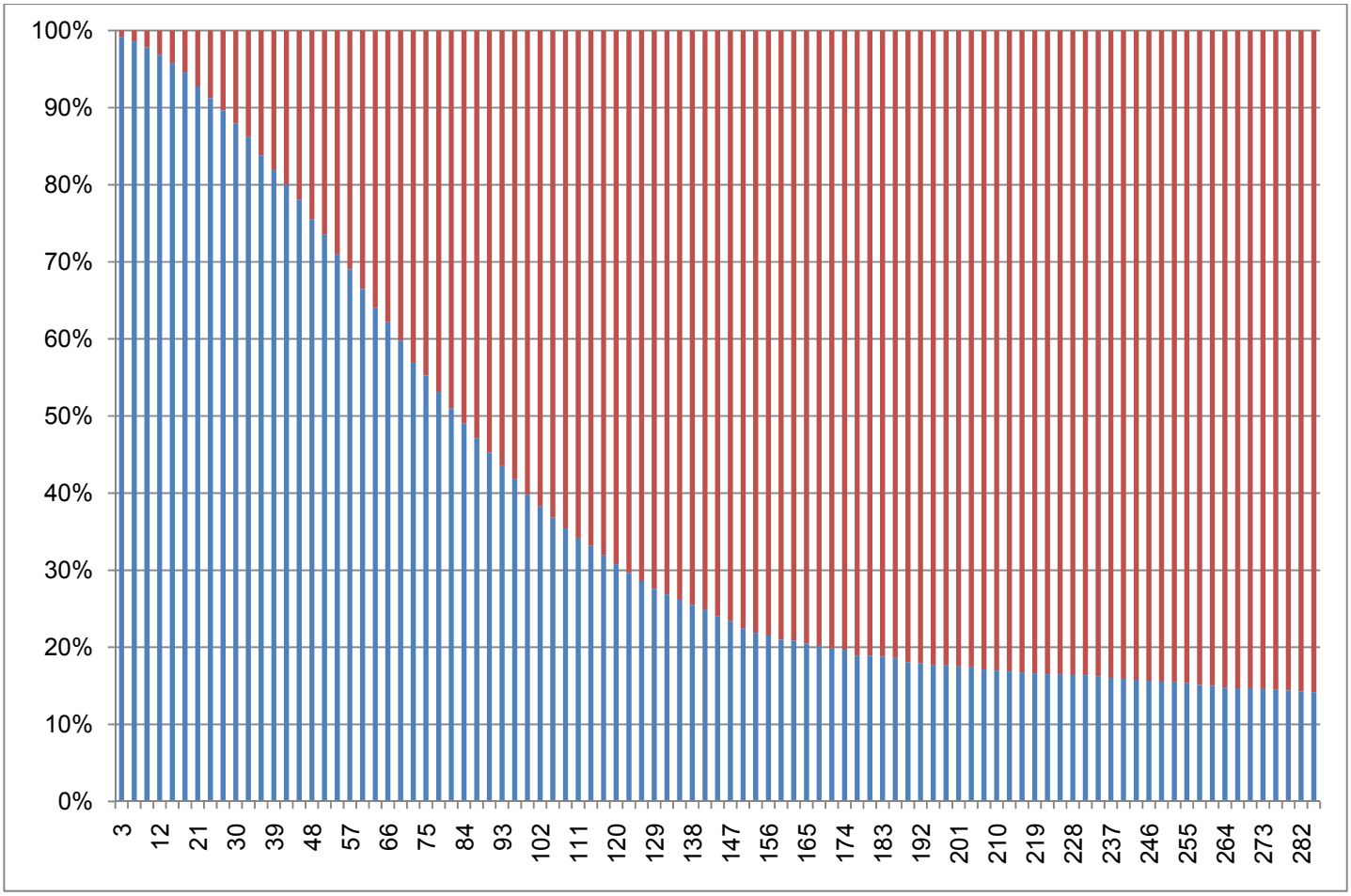


To a solution of 4-methyl-*N*-(2-oxo-7-phenyl-octahydro-indol-6-yl)benzenesulfonamide, **16** (150 mg, 0.39 mmol) in anhydrous THF (5 mL) was added lithium aluminium hydride powder (30 mg, 0.78 mmol, 2 eq.) at 0 °C. The mixture was then heated at reflux for 6h. After this time, the reaction mixture was quenched with ethyl acetate and then passed through a pad of celite, which was washed thoroughly with ethyl acetate. The combined filtrates were concentrated under reduced pressure. To the crude residue (58 mg, 0.16 mmol) was added conc. HCl (5 mL) and 37 % aq. formaldehyde solution (0.1 mL). The resulting was heated at 50 °C for 21h. After this time, water (10 mL) was added and extracted with dichloromethane (3 x 25 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a brown oil which was purified by column chromatography (silica gel, 10 % methanol/ dichloromethane) to afford the title compound as a yellow oil (36 mg, 0.09 mmol, 60%). IR (cm^{-1}) 2924 (br), 2873 (m), 1598 (m), 1457 (m), 1333 (s), 1156 (s), 1089 (m), 1021 (m), 919 (s), 732 (m), 663 (s); ^1H NMR (400 MHz, $CDCl_3$) 1.72-1.90 (5H, m, H-4,6 and 11), 2.18 (3H, s, H-12), 2.24-2.38 (4H, m, H-5,7 and 9), 2.90-3.04 (3H, m, H-8 and 3), 3.55 (1H, dd, *J* 10.2 ,6.8, H-10), 4.11 (1H, d, *J* 15.9, H-1), 4.42 (1H, d, *J* 15.9, H-1), 6.50 (1H, d, *J* 7.4, H-d), 6.81 (1H, t, *J* 7.4, H-c), 6.87 (1H, d, *J* 8, H-f), 7.02 (1H, t, *J* 7.5, H-b), 7.13 (1H, d, *J* 7.6, H-a), 7.25 (1H, d, *J* 8.1, H-e); ^{13}C NMR (100 MHz, $CDCl_3$) 21.3 (C-12), 24.1 (C-6), 28.5 (C-4), 29.6 (C-7), 37.9 (C-5), 43.0 (C-9), 44.7 (C-3), 46.1 (C-1), 58.7 (C-8), 59.1 (C-10), 123.8 (C-

a), 125.7 (C-c), 125.9 (C-d), 127.2 (C-e), 127.5 (C-b), 129.0 (C-f), 135.8 (C-h), 136.3 (C-i), 136.6 (C-j), 142.8 (C-g); HRMS required for $C_{22}H_{27}O_2N_2S$ is 383.1788, found 383.1788.

Days Optimisation Using NMR (500 MHz)

To a solution of the nitro-α,β-unsaturated ester (40 mg, 0.21 mmol) in 1mL of CD_2Cl_2 was added nitro alkene (35 mg, 0.24 mmol) and bifunctional organocatalyst **C** (12.7 mg, 0.02 mmol). This solution was then transferred to NMR tube and was monitored at 3 hours intervals in 500 MHz NMR for 12 days and the proportions of starting material:product determined by measurement of the relative quantities as determined from integrals at 5.74-5.81 ppm for starting material (1H) and 4.92-4.98 ppm for product (1H).

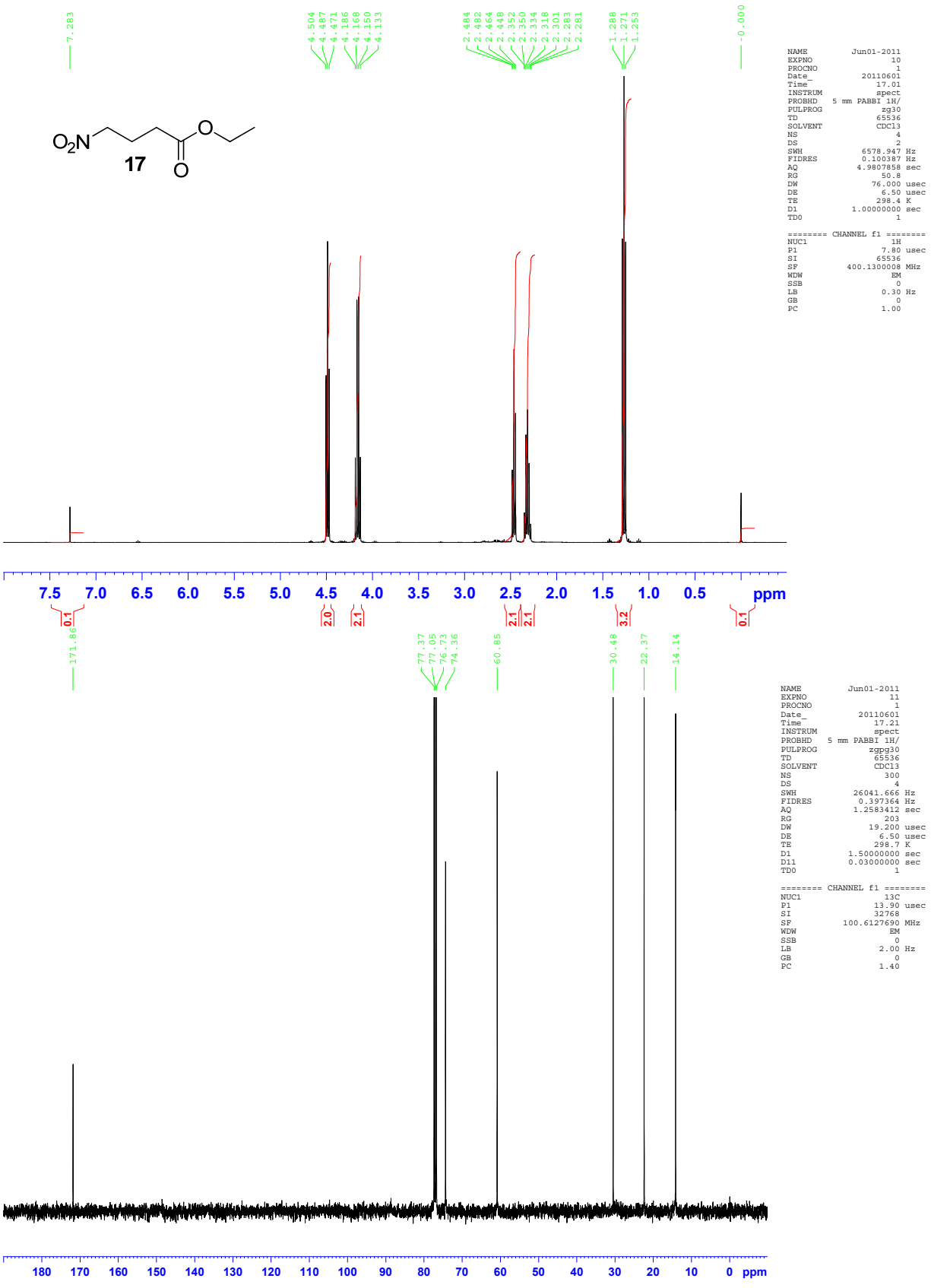


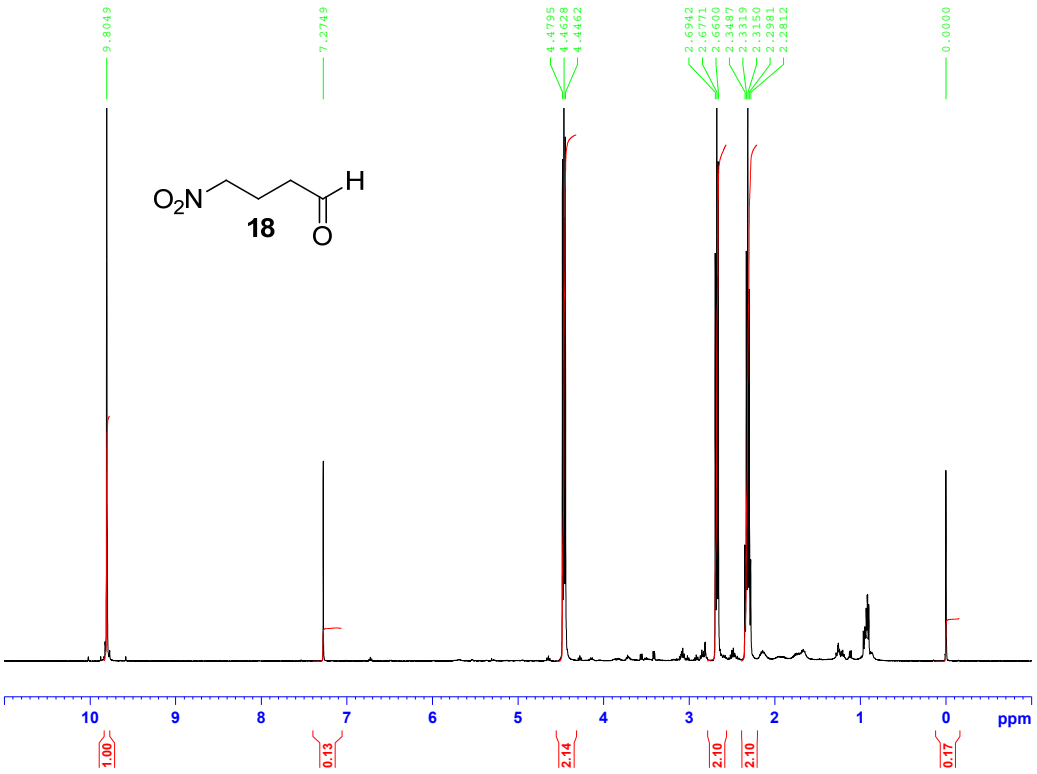
X-axis – Time in hours

Y-axis – Percentage of material

- Starting material

- Product



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Current Data Parameters
NAME                  Aug19-2010
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20100819
Time                       12.22
INSTRUM                    spect
PROBHD    5 mm PABBO BB/
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                             8
DS                             2
SWH                     8278.146 Hz
FIDRES                  0.126314 Hz
AQ                      3.9584243 sec
RG                         203.2
DW                        60.400 usec
DE                         6.00 usec
TE                        297.2 K
D1                    1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         1H
P1                        11.88 usec
PL1                       -3.30 dB
SFO1                399.9024695 MHz

F2 - Processing parameters
SI                         32768
SF                  399.8999991 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
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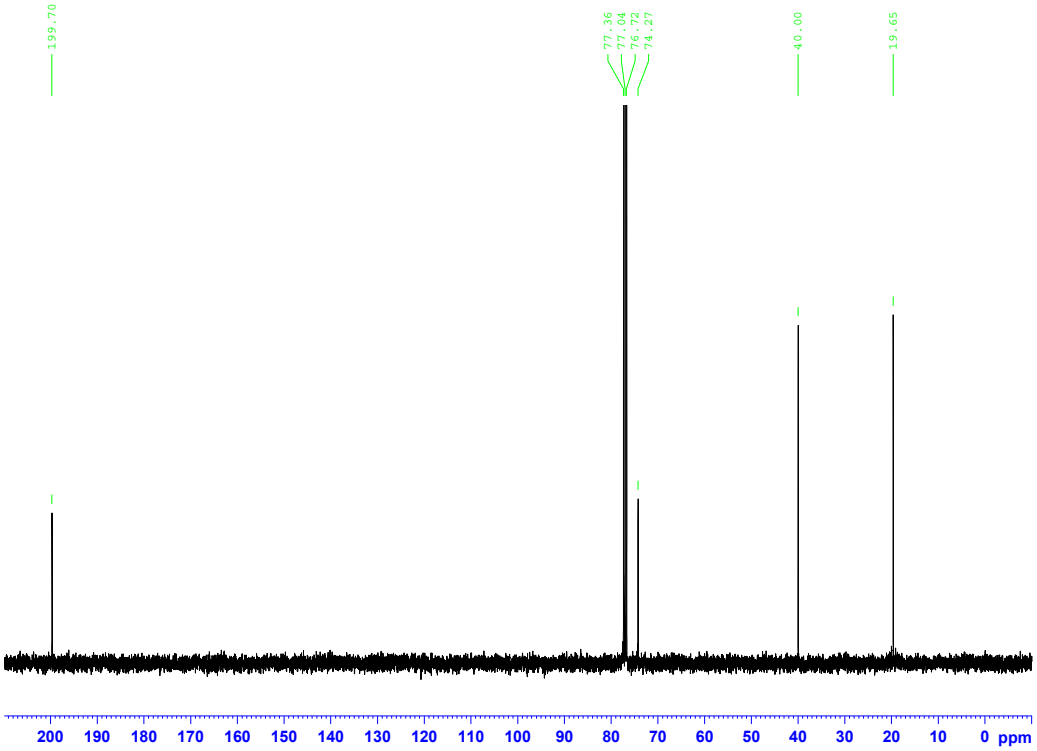


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Current Data Parameters
NAME                  Aug19-2010
EXPNO                         11
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20100819
Time                       12.30
INSTRUM                    spect
PROBHD    5 mm PABBO BB/
PULPROG                 zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                           128
DS                             4
SWH                    23980.814 Hz
FIDRES                  0.365918 Hz
AQ                      1.3664756 sec
RG                        1149.4
DW                        20.850 usec
DE                         6.00 usec
TE                        298.2 K
D1                    1.50000000 sec
d11                   0.03000000 sec
DELTA                 1.39999998 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                         8.00 usec
PL1                       -2.10 dB
SFO1               100.5649905 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                     80.00 usec
PL2                       -3.30 dB
PL12                      13.60 dB
PL13                      13.60 dB
SFO2               399.9015996 MHz

F2 - Processing parameters
SI                         32768
SF                 100.5549350 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
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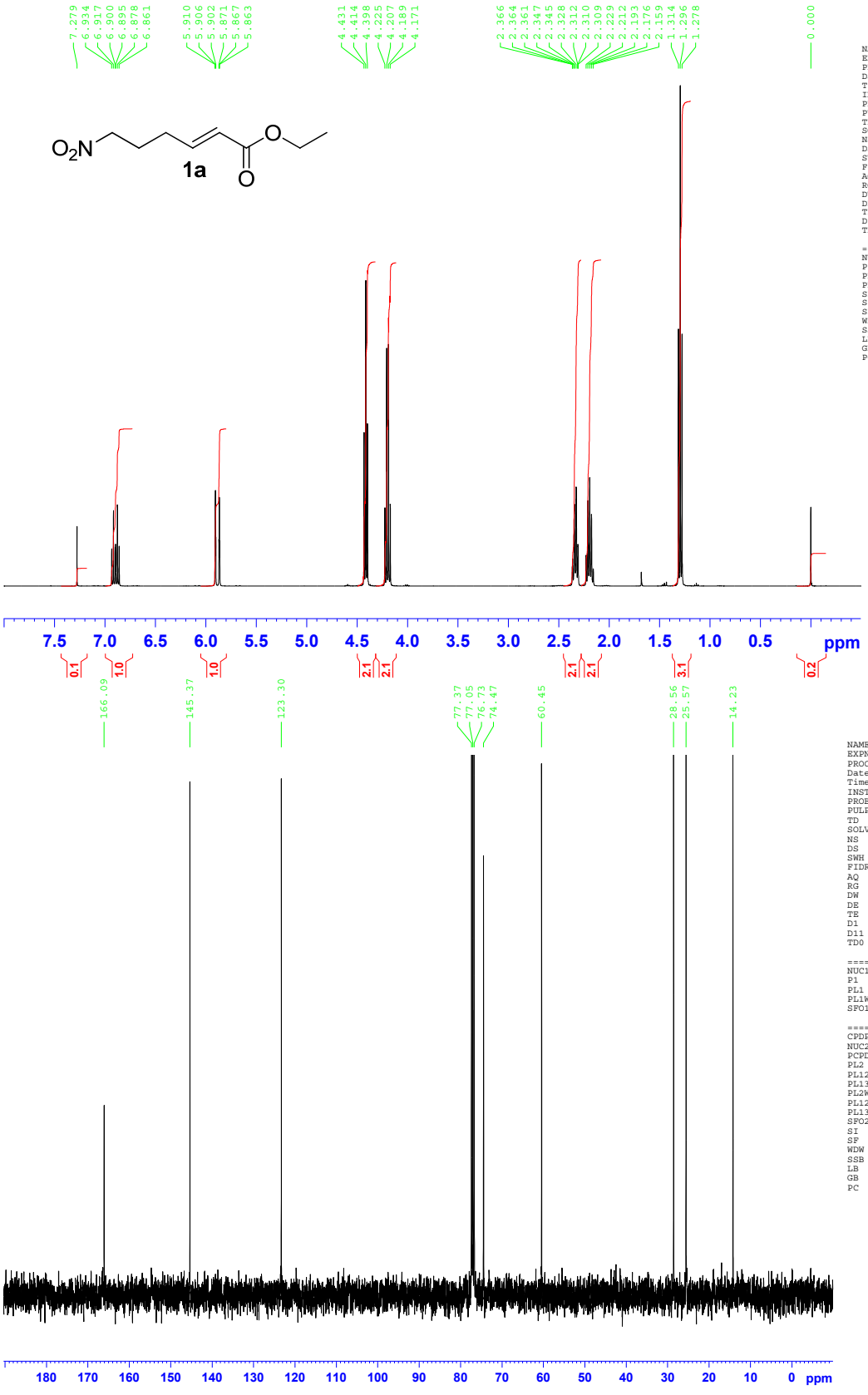


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EXPNO                   10
PROCNO                   1
Date_             20101213
Time                 19.12
INSTRUM              spect
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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                       4
DS                       2
SWH               6578.947 Hz
FIDRES               0.100387 Hz
AQ                4.9807858 sec
RG                      64
DW                   76.000 usec
DE                    6.50 usec
TE                  295.8 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.80 usec
PL1                  0.00 dB
PL1W            12.55943203 W
SFO1           400.1324804 MHz
SI                    65536
SF             400.1300021 MHz
WDW                     EM
SSB                      0
LB                   0.30 Hz
GB                       0
PC                   1.00
```

```
NAME            Dec13-2010
EXPNO                   11
PROCNO                   1
Date_             20101213
Time                 19.19
INSTRUM              spect
PROBHD   5 mm PABBI 1H/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     128
DS                       4
SWH              26041.666 Hz
FIDRES               0.397364 Hz
AQ                1.2583412 sec
RG                     203
DW                   19.200 usec
DE                    6.50 usec
TE                  296.0 K
D1                1.50000000 sec
D11               0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   13.90 usec
PL1                  -3.70 dB
PL1W            90.09307861 W
SFO1           100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 20.22 dB
PL13                 24.00 dB
PL2W            12.55943203 W
PL12W            0.11939058 W
PL13W            0.05000000 W
SFO2           400.1316005 MHz
SI                    32768
SF             100.6127690 MHz
WDW                     EM
SSB                      0
LB                   2.00 Hz
GB                       0
PC                   1.40
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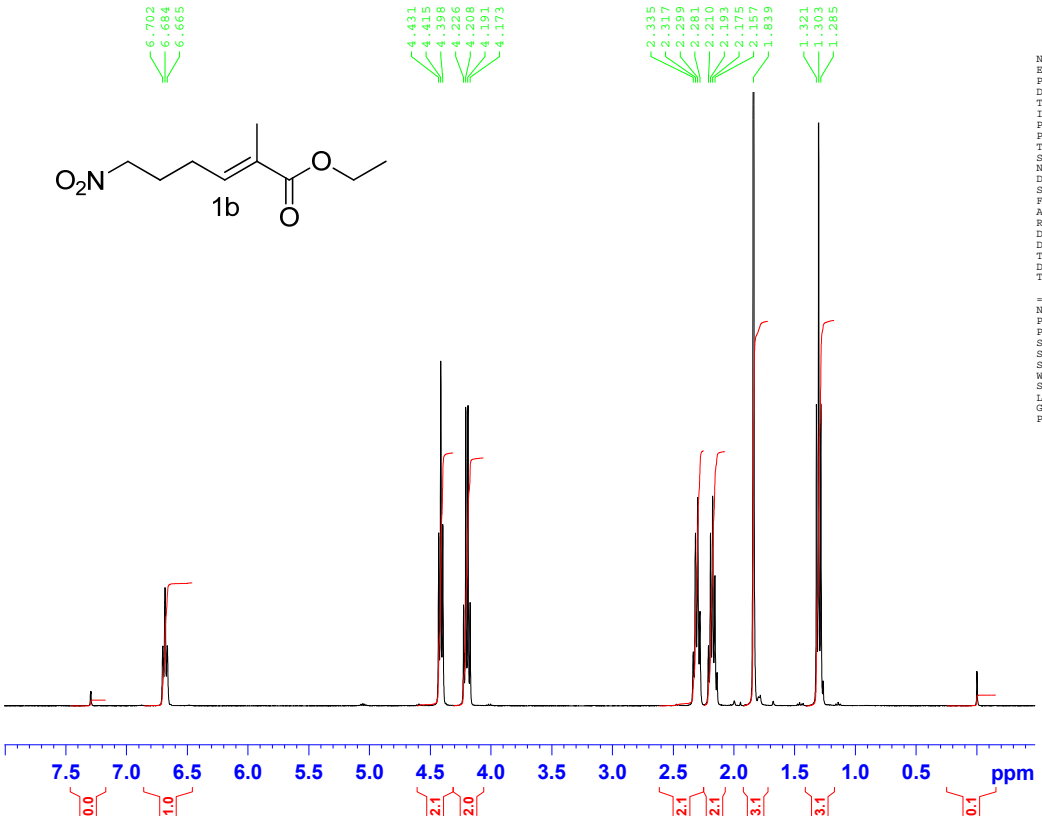


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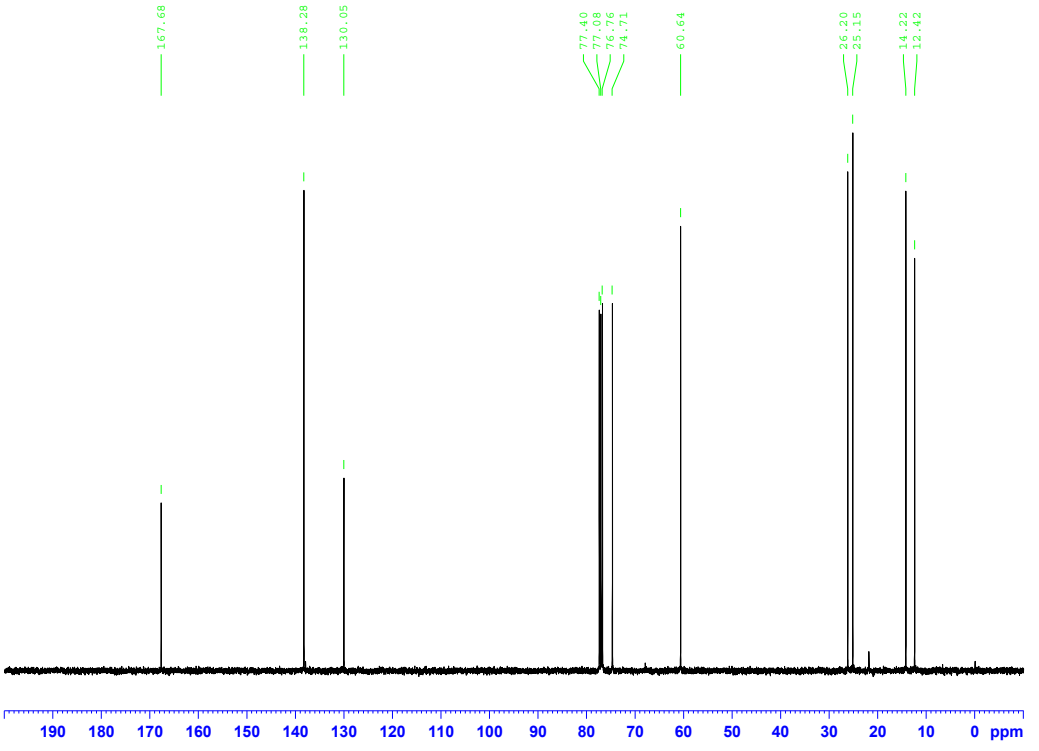
NAME            Feb04-2011
EXPNO                   10
PROCNO                   1
Date_             20110205
Time                 11.25
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                    50.8
DW                  60.400 usec
DE                   6.00 usec
TE                  297.2 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.88 usec
PL1                  -3.30 dB
SFO1          399.9024695 MHz
SI                   32768
SF            399.8999907 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

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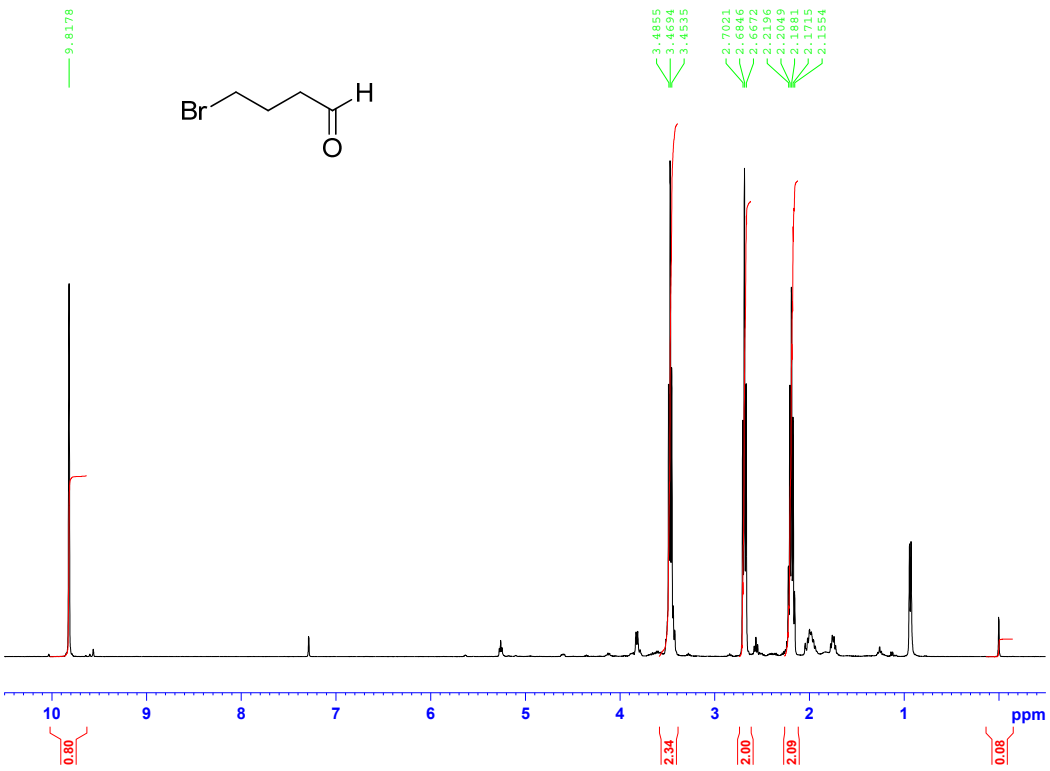
Current Data Parameters
NAME            Feb04-2011
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110205
Time                 11.46
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     400
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ                1.3664756 sec
RG                   1149.4
DW                  20.850 usec
DE                   6.00 usec
TE                  298.2 K
D1                1.50000000 sec
d11               0.03000000 sec
DELTA             1.39999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                  -2.10 dB
SFO1          100.5649905 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -3.30 dB
PL12                 13.60 dB
PL13                 13.60 dB
SFO2          399.9015996 MHz

F2 - Processing parameters
SI                   32768
SF            100.5549350 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```




```
NAME            May11-2011
EXPNO                   30
PROCNO                   1
Date_             20110512
Time                 2.45
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                    128
DW                 60.400 usec
DE                  6.00 usec
TE                 297.2 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 11.88 usec
PL1                -3.30 dB
SFO1          399.9024695 MHz
SI                  32768
SF            399.8999944 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
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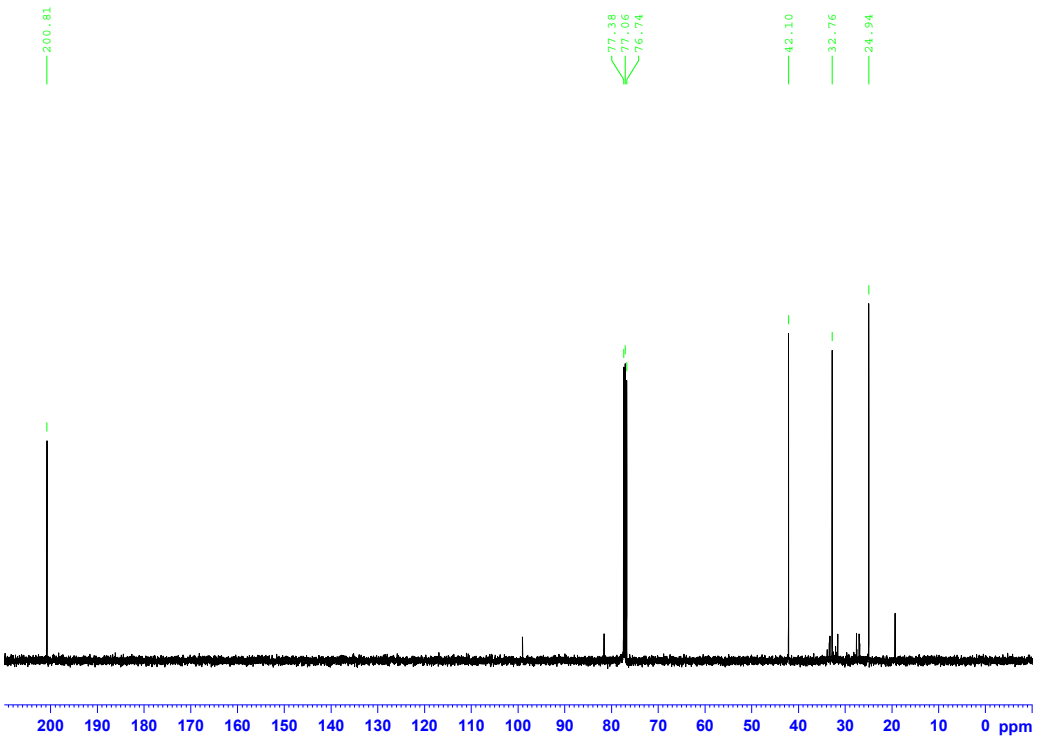


```
NAME            May11-2011
EXPNO                   32
PROCNO                   1
Date_             20110512
Time                 2.57
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                 5160.6
DW                 20.850 usec
DE                  6.00 usec
TE                 298.2 K
D1              1.50000000 sec
d11             0.03000000 sec
DELTA           1.39999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                  8.00 usec
PL1                -2.10 dB
SFO1          100.5649905 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -3.30 dB
PL12               13.60 dB
PL13               13.60 dB
SFO2          399.9015996 MHz
SI                  32768
SF            100.5549350 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
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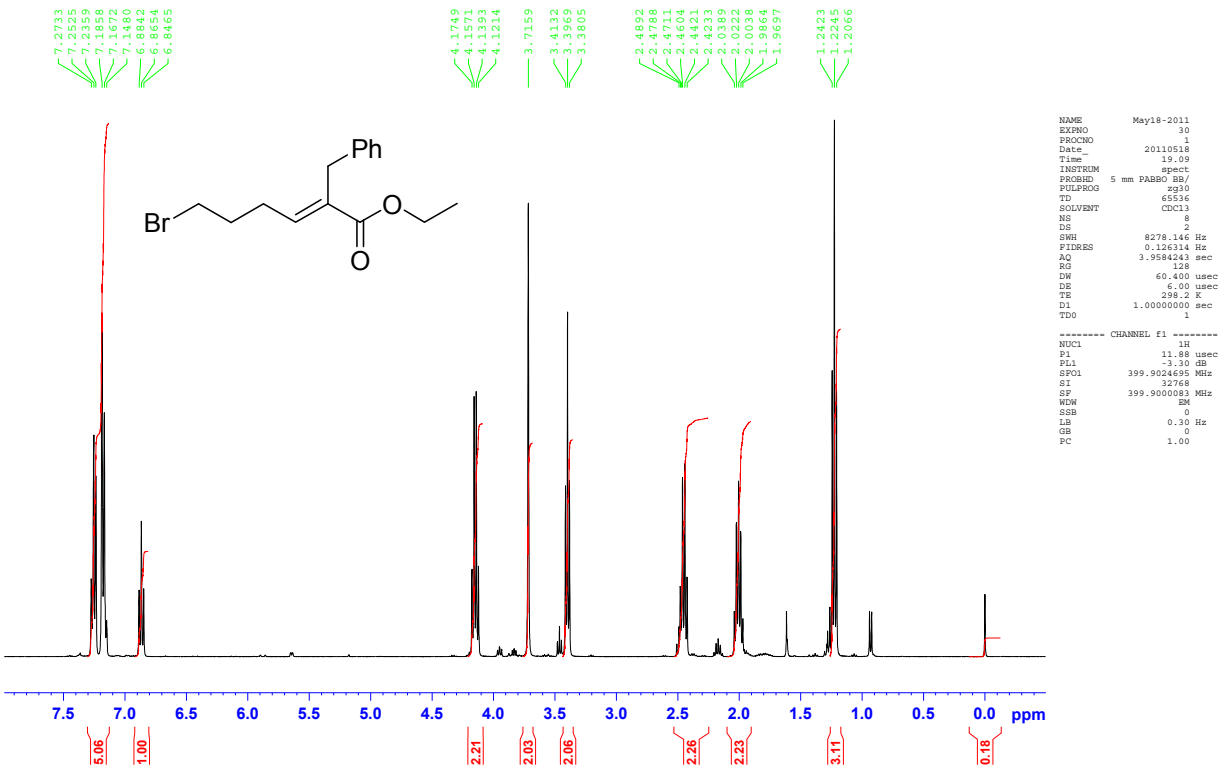
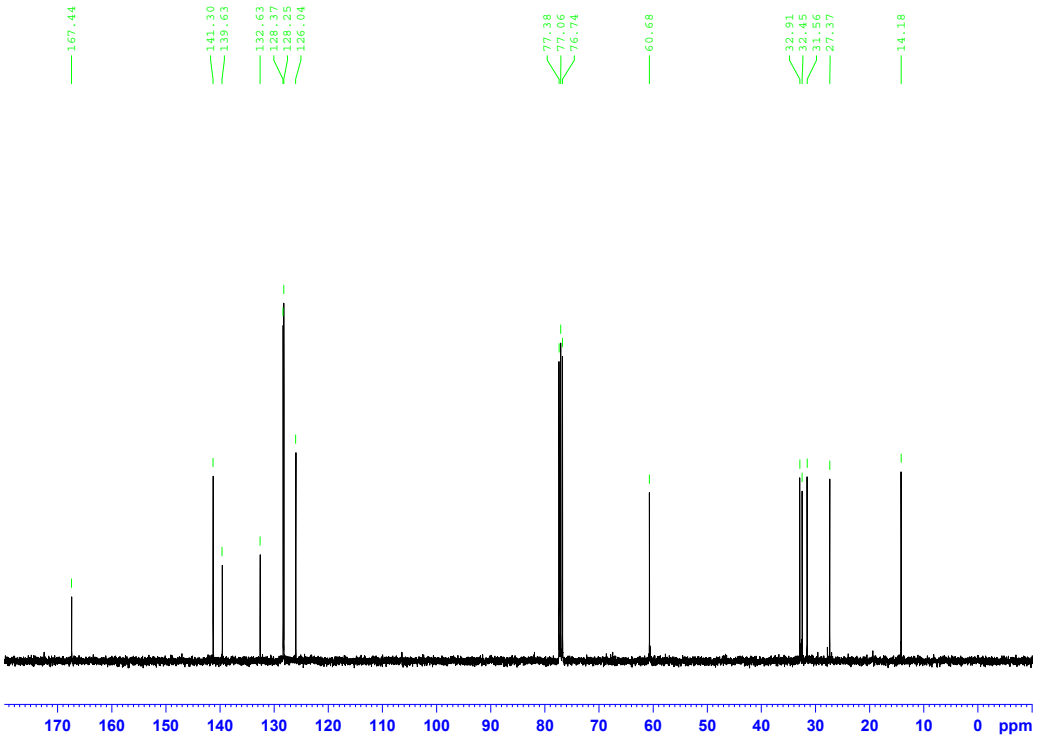



```
NAME            May18-2011
EXPNO                   30
PROCNO                   1
Date_             20110518
Time_                19.09
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                       8
DS                       2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                     128
DW                60.400 usec
DE                 6.00 usec
TE                298.2 K
D1             1.00000000 sec
TD0                      1

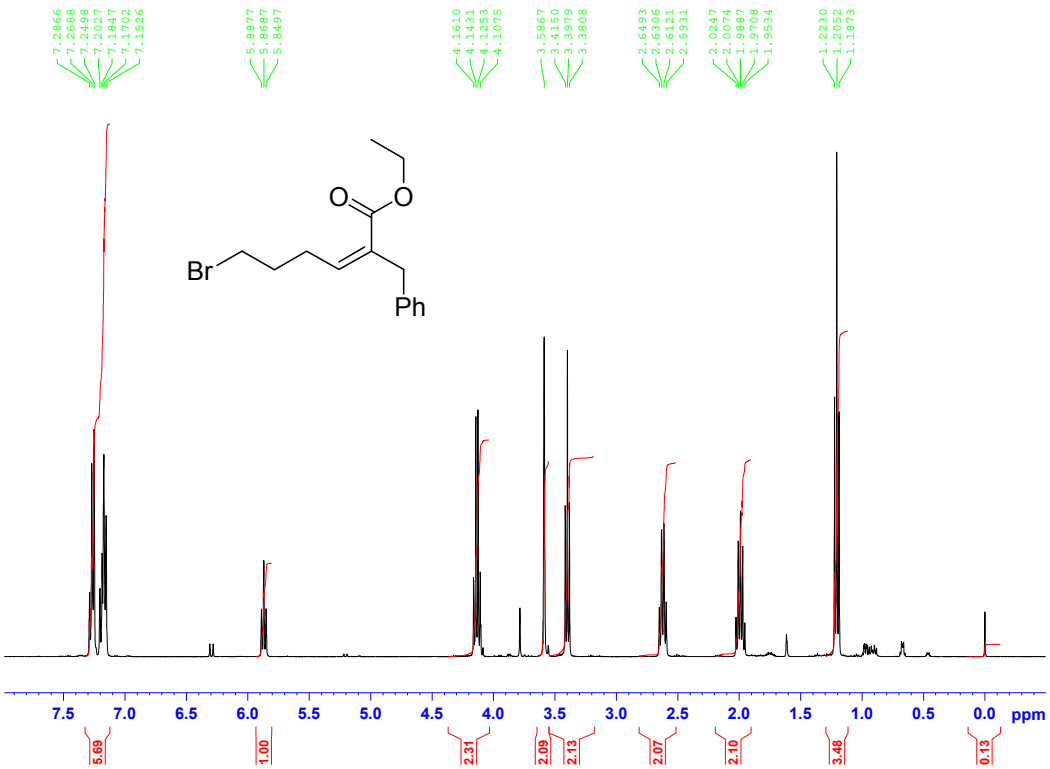
======== CHANNEL f1 ========
NUC1                   1H
P1                 11.88 usec
PL1                -3.30 dB
SFO1          399.9024695 MHz
SI                   32768
SF            399.9000083 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```




```
NAME            May18-2011
EXPNO                   31
PROCNO                   1
Date_             20110518
Time_                19.17
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     128
DS                       4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                    8192
DW                20.850 usec
DE                 6.00 usec
TE                299.2 K
D1             1.50000000 sec
d11            0.03000000 sec
DELTA          1.39999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                  13C
P1                  8.00 usec
PL1                -2.10 dB
SFO1          100.5649905 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -3.30 dB
PL12               13.60 dB
PL13               13.60 dB
SFO2          399.9015996 MHz
SI                   32768
SF            100.5549350 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```




```
NAME            May18-2011
EXPNO                   20
PROCNO                   1
Date_             20110518
Time                 18.34
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                       8
DS                       2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                    80.6
DW                60.400 usec
DE                 6.00 usec
TE                298.2 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  11.88 usec
PL1                 -3.30 dB
SFO1          399.9024695 MHz
SI                   32768
SF            399.9000103 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
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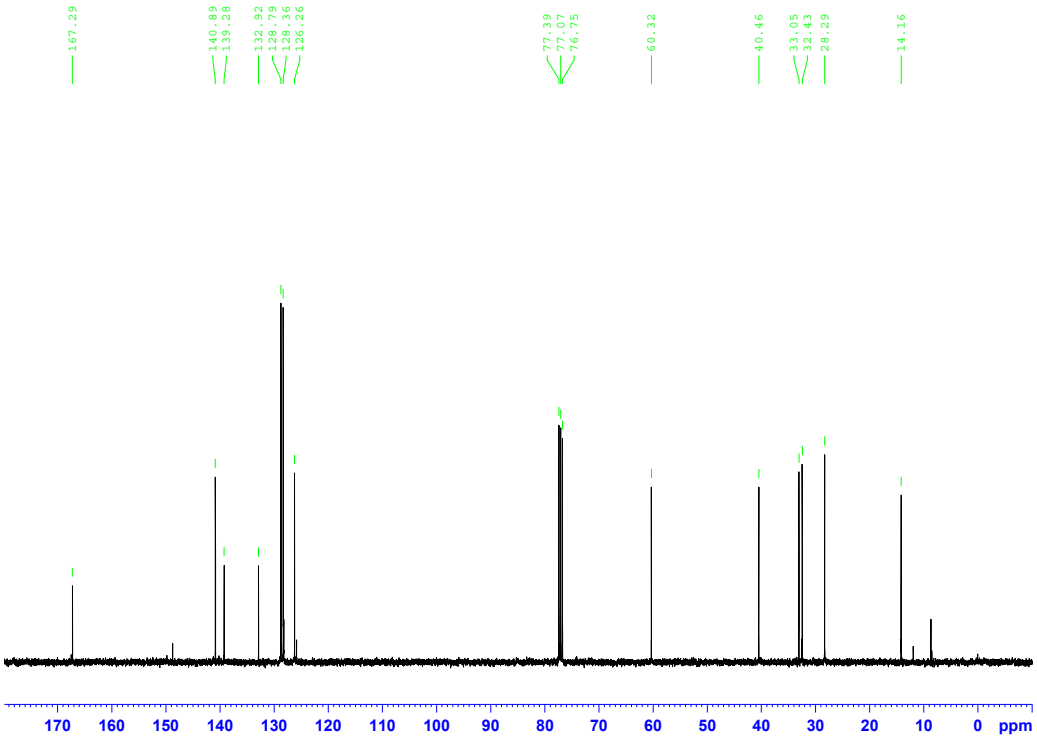
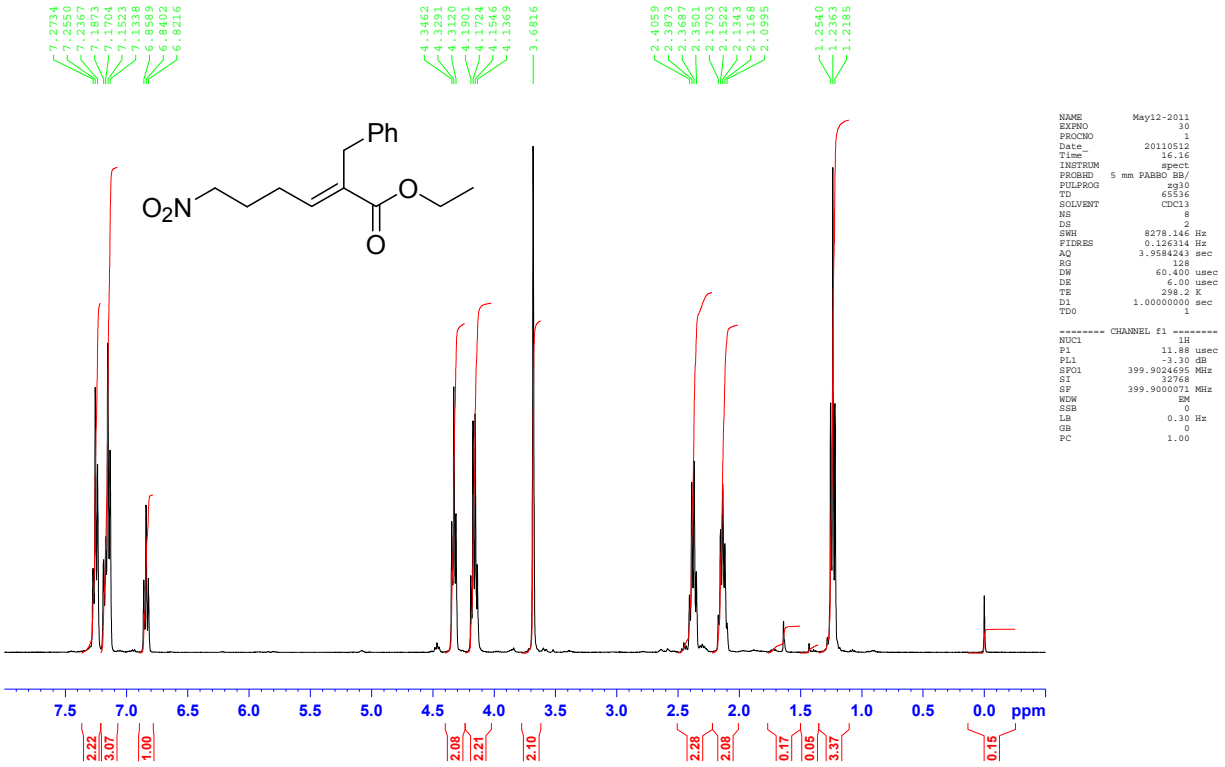



```
NAME            May18-2011
EXPNO                   21
PROCNO                   1
Date_             20110518
Time                 18.42
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     128
DS                       4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                   16384
DW                20.850 usec
DE                 6.00 usec
TE                299.2 K
D1             1.50000000 sec
d11            0.03000000 sec
DELTA          1.39999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  8.00 usec
PL1                 -2.10 dB
SFO1          100.5649905 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2              80.00 usec
PL2                 -3.30 dB
PL12                13.60 dB
PL13                13.60 dB
SFO2          399.9015996 MHz
SI                   32768
SF            100.5549350 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    1.40
```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7.2367
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7.1704
7.1523
7.1338
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6.8402
6.8216
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4.3291
4.3120
4.1901
4.1724
4.1546
4.1369
3.6816
2.4059
2.3873
2.3687
2.3501
2.1703
2.1522
2.1343
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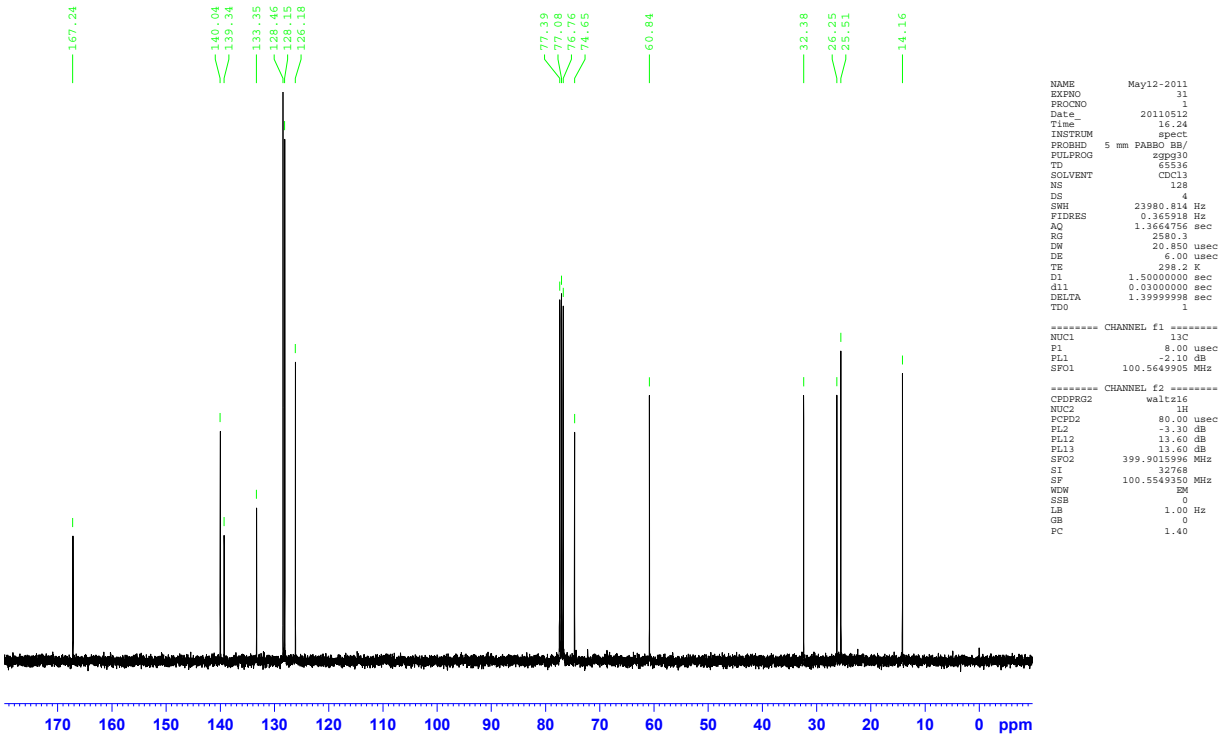
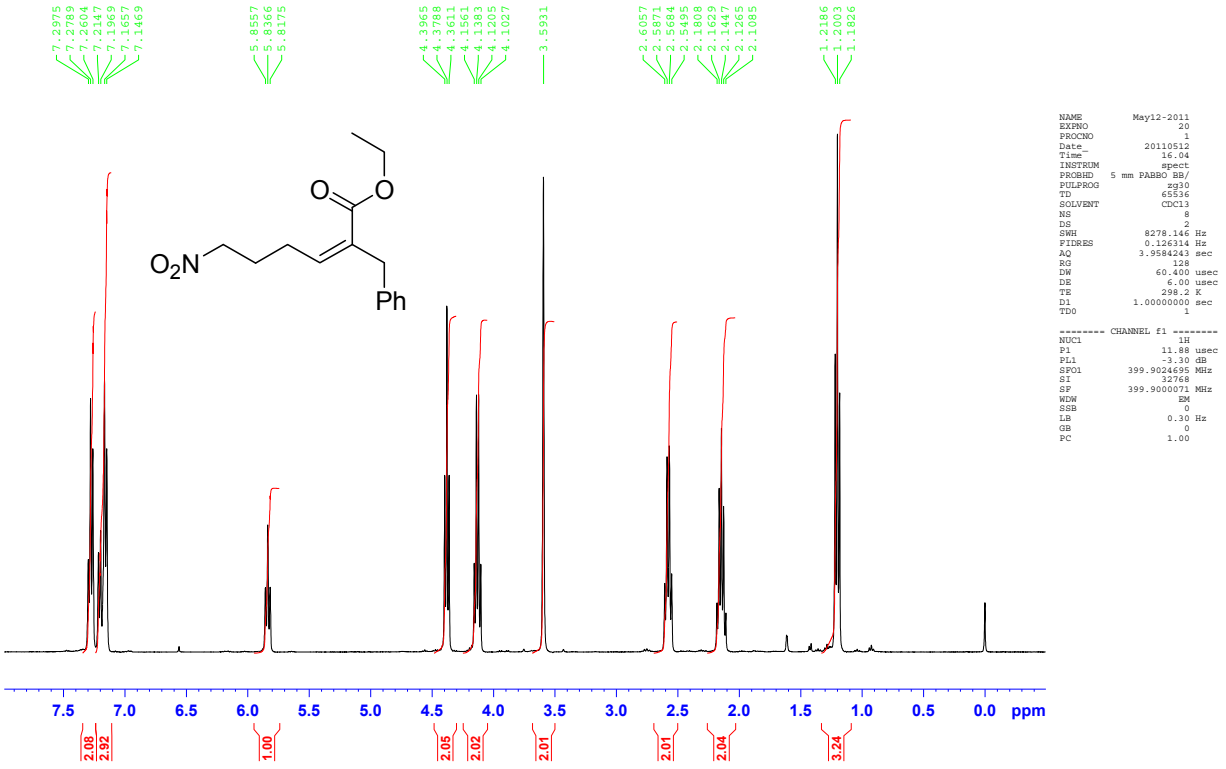
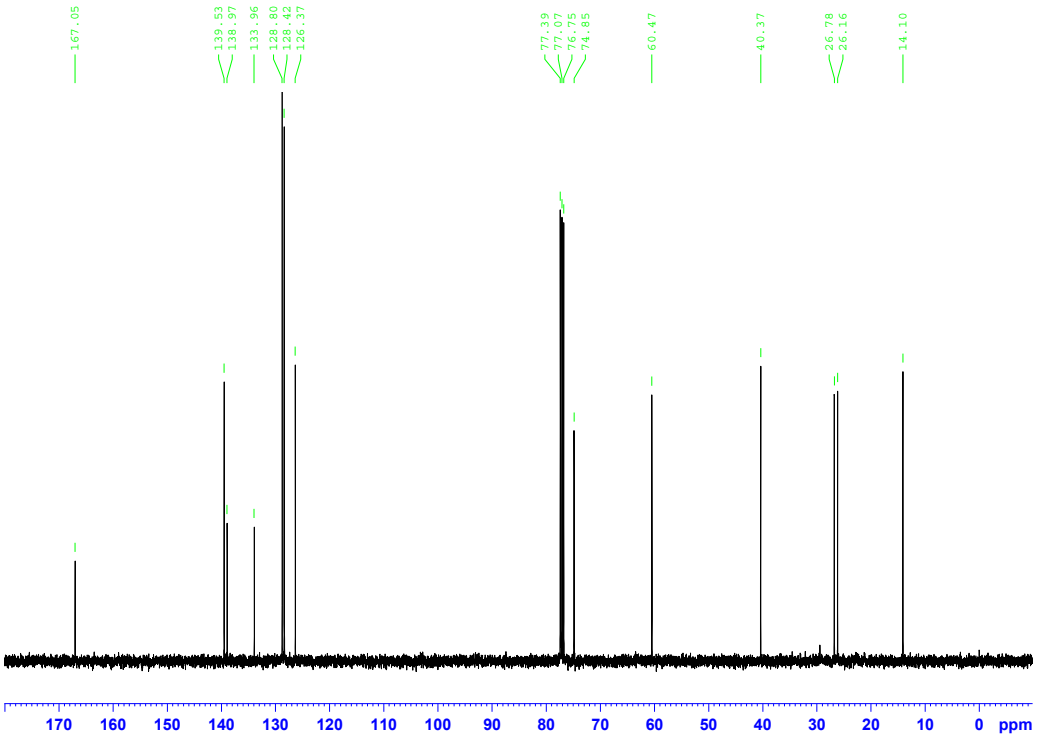
1.2363
1.2185
Ph
O2N
O
O
NAME May12-2011
EXPNO 30
PROCNO 1
Date_ 20110512
Time 16.16
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 128
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.88 usec
PL1 -3.30 dB
SFO1 399.9026695 MHz
SI 32768
SF 399.9000071 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.22
3.07
1.00
2.08
2.21
2.10
2.28
2.08
0.17
0.05
3.37
0.15


167.24
140.04
139.34
133.35
128.46
128.15
126.18
77.39
77.08
76.76
74.65
60.84
32.38
26.25
25.51
14.16
NAME May12-2011
EXPNO 31
PROCNO 1
Date_ 20110512
Time 16.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 2580.3
DW 20.850 usec
DE 6.00 usec
TE 298.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 -2.10 dB
SFO1 100.5649905 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.30 dB
PL12 13.60 dB
PL13 13.60 dB
SFO2 399.9015996 MHz
SI 32768
SF 100.5549350 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm




```
NAME            May12-2011
EXPNO                   20
PROCNO                   1
Date_             20110512
Time                 16.04
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                    128
DW                 60.400 usec
DE                  6.00 usec
TE                298.2 K
D1              1.00000000 sec
TD0                     1

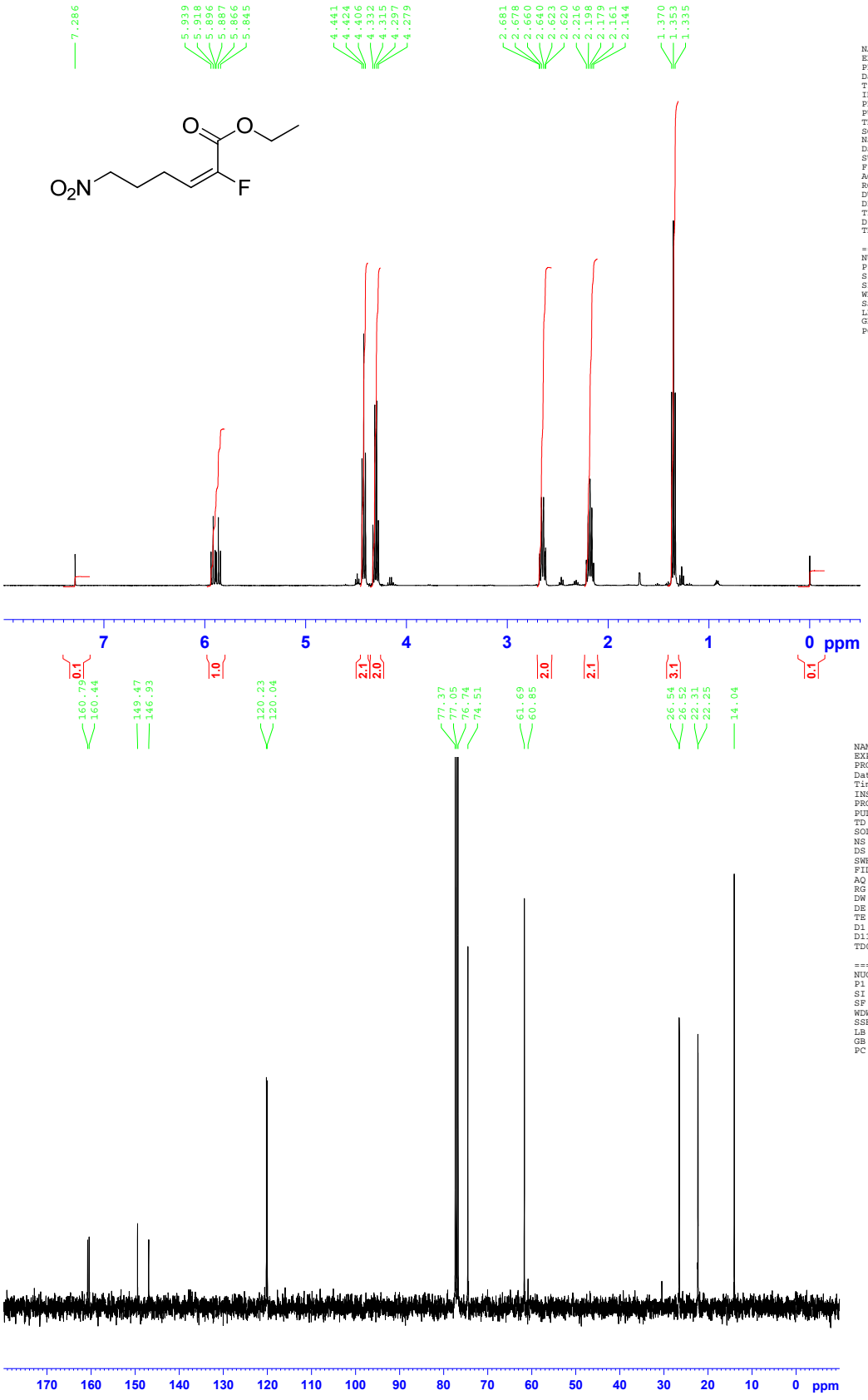
======== CHANNEL f1 ========
NUC1                  1H
P1                 11.88 usec
PL1                -3.30 dB
SFO1          399.9026695 MHz
SI                  32768
SF            399.9000071 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

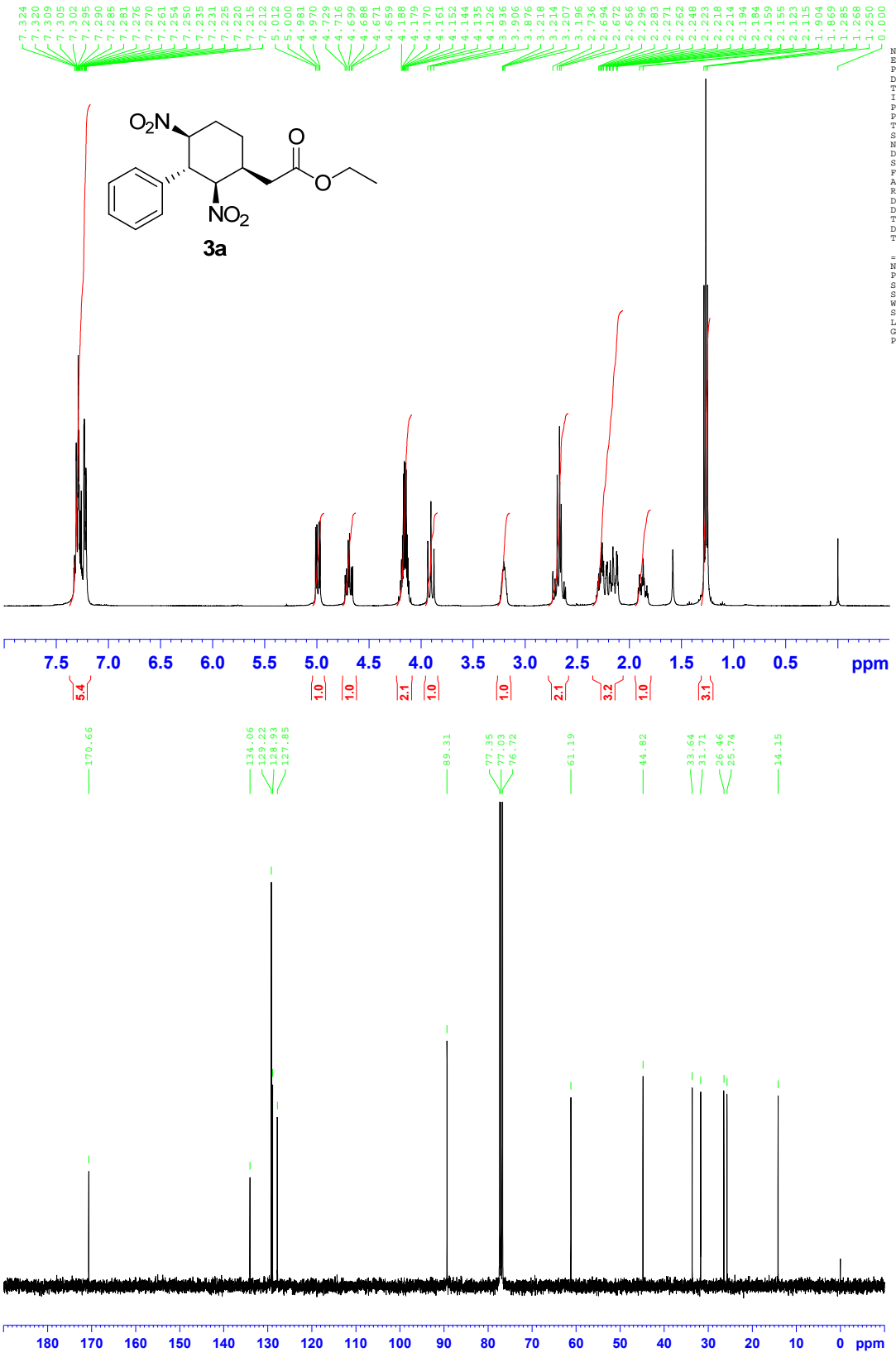


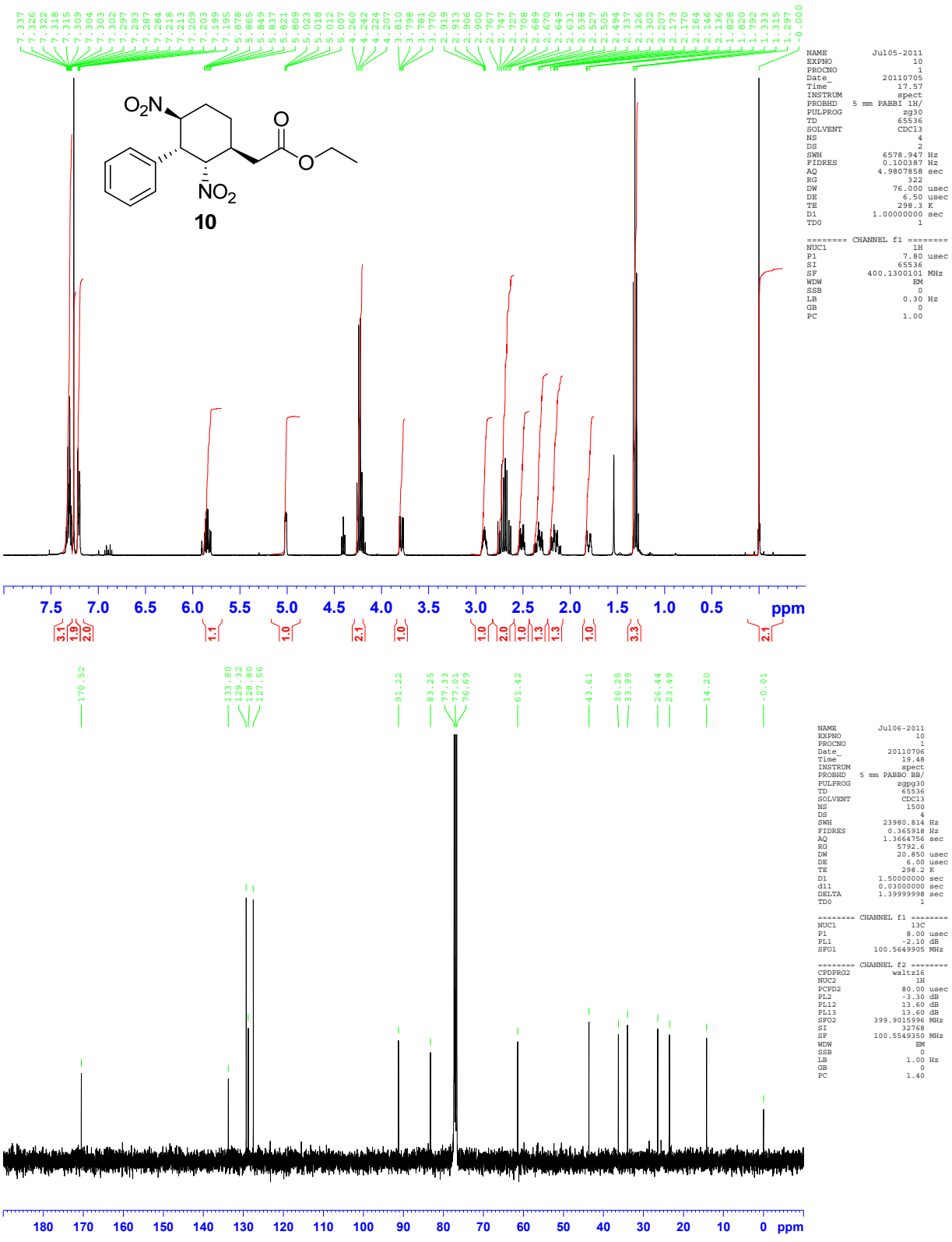

```
NAME            May12-2011
EXPNO                   21
PROCNO                   1
Date_             20110512
Time                 16.12
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      4
SWH              23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                 1149.4
DW                 20.850 usec
DE                  6.00 usec
TE                298.2 K
D1              1.50000000 sec
d11             0.03000000 sec
DELTA           1.39999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  8.00 usec
PL1                -2.10 dB
SFO1         100.5649905 MHz

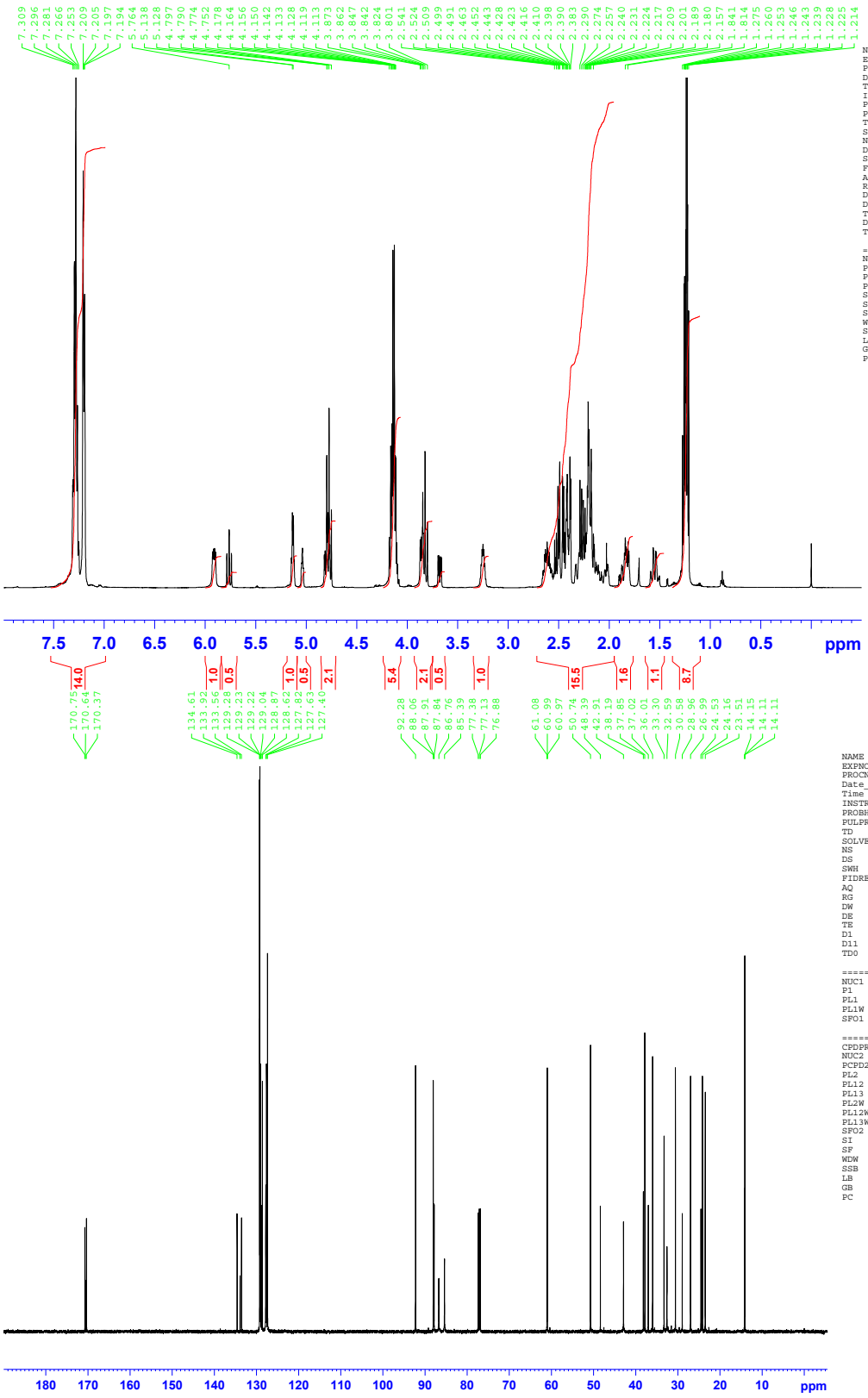
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.30 dB
PL12               13.60 dB
PL13               13.60 dB
SFO2          399.9015996 MHz
SI                  32768
SF           100.5549350 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

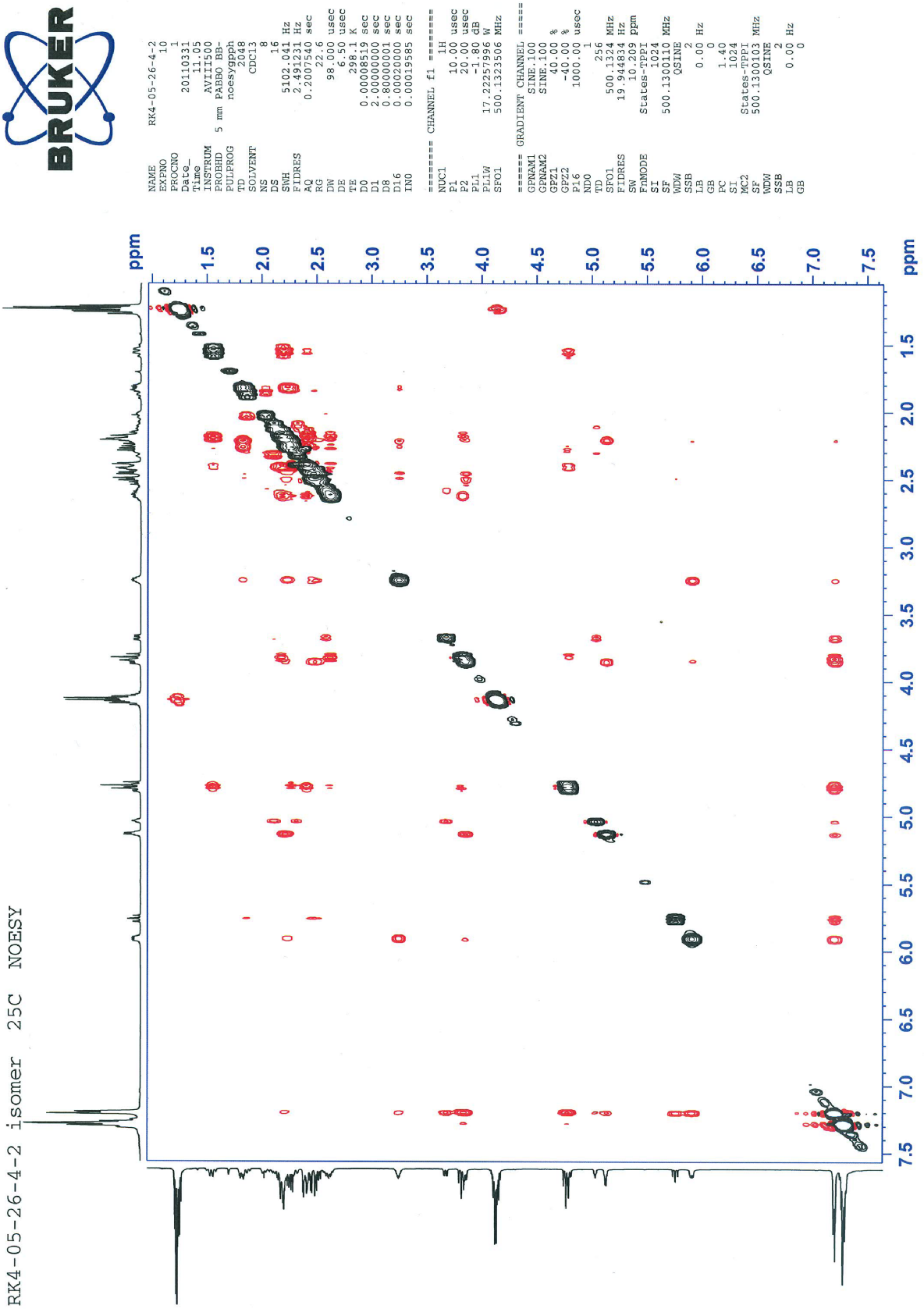


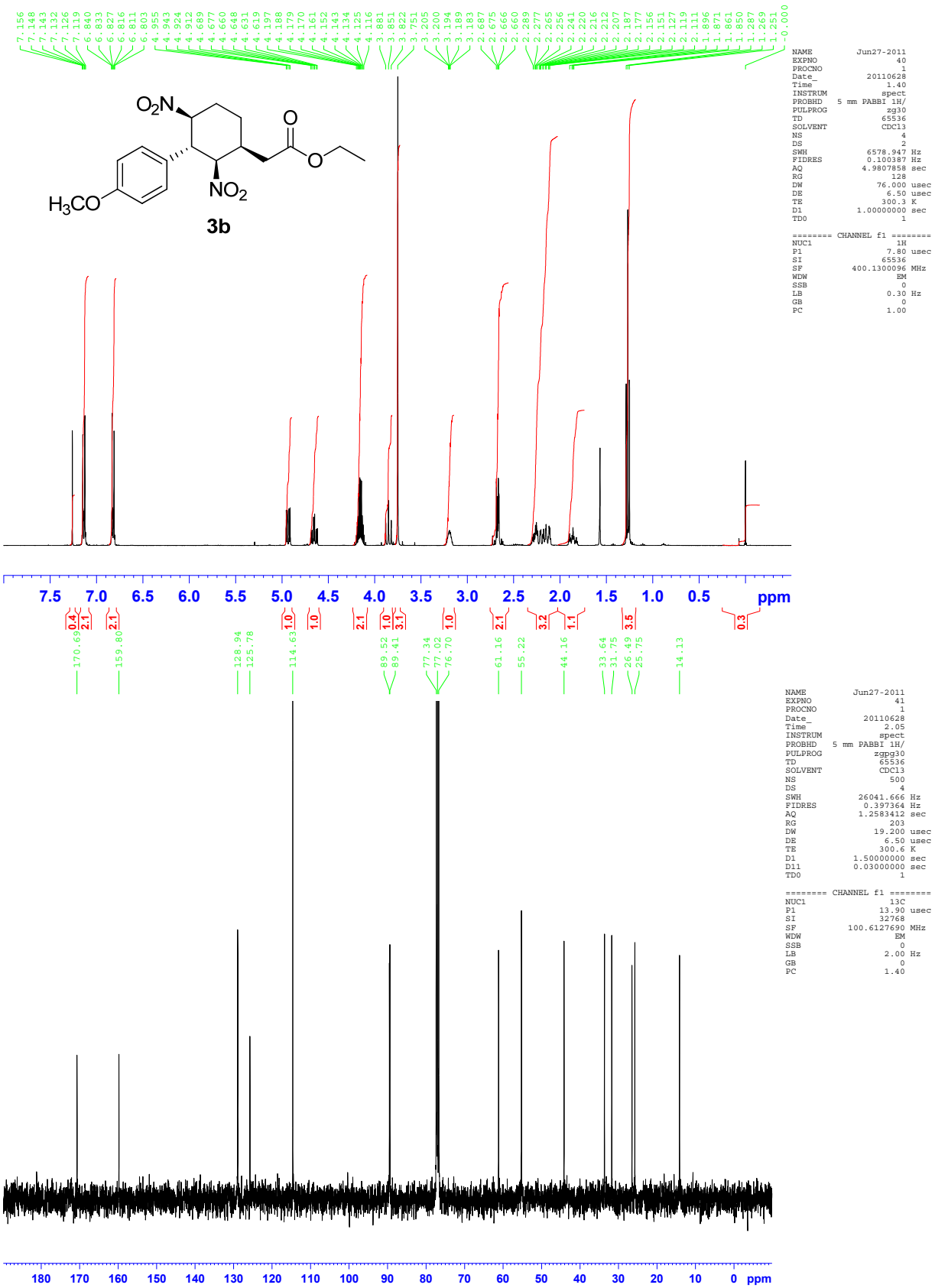

7.324 7.320 7.309 7.305 7.302 7.295 7.290 7.285 7.281 7.276 7.270 7.261 7.254 7.250 7.235 7.231 7.225 7.220 7.215 7.212 5.012 5.000 4.981 4.970 4.729 4.716 4.699 4.688 4.671 4.659 4.188 4.179 4.170 4.161 4.152 4.144 4.135 4.126 3.936 3.906 3.876 3.218 3.214 3.207 3.196 2.736 2.694 2.672 2.656 2.296 2.283 2.271 2.262 2.248 2.223 2.218 2.214 2.194 2.184 2.159 2.155 2.123 2.115 1.904 1.869 1.285 1.268 1.250 0.000
O2N
NO2
O
O
3a
NAME Jun27-2011
EXPNO 30
PROCNO 1
Date_ 20110628
Time 1.07
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 12
DS 2
SWH 6578.947 Hz
FIDRES 0.100387 Hz
AQ 4.9807858 sec
RG 80.6
DW 76.000 usec
DE 6.50 usec
TE 300.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.80 usec
SI 65536
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.4 1.0 1.0 2.1 1.0 1.0 2.1 3.2 1.0 3.1
170.66 134.06 129.22 128.93 127.85 89.31 77.35 77.03 76.72 61.19 44.82 33.64 31.71 26.46 25.74 14.15
NAME Apr17-2011
EXPNO 11
PROCNO 1
Date_ 20110417
Time 21.59
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 5792.6
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 -2.10 dB
SFO1 100.5649905 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.30 dB
PL12 13.60 dB
PL13 13.60 dB
SFO2 399.9015996 MHz
SI 32768
SF 100.5549344 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

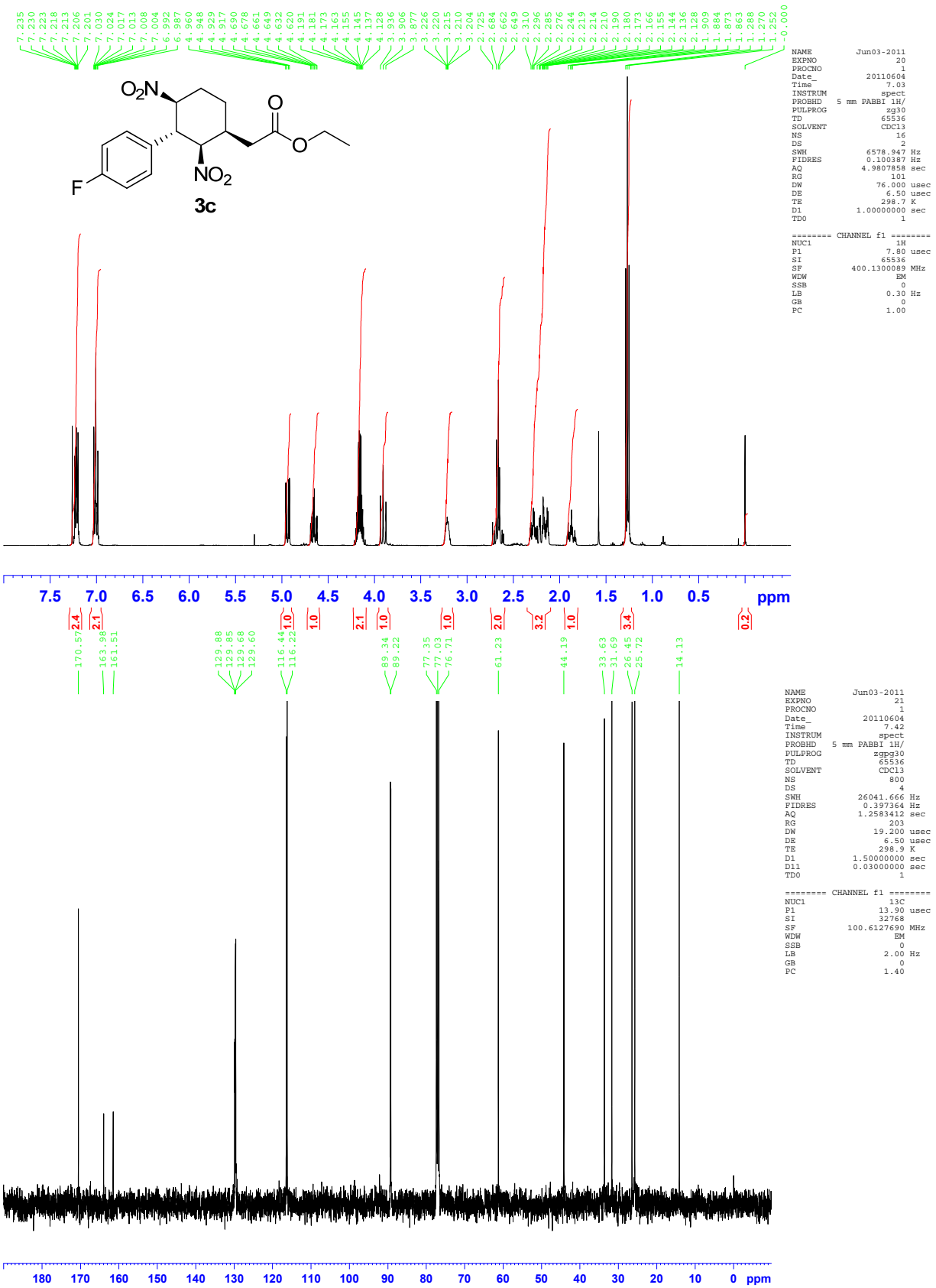

7.337
7.326
7.322
7.318
7.315
7.309
7.304
7.303
7.302
7.297
7.293
7.287
7.284
7.218
7.213
7.209
7.203
7.199
7.195
5.878
5.865
5.849
5.837
5.821
5.809
5.023
5.018
5.012
5.007
4.260
4.242
4.224
4.207
3.810
3.798
3.781
3.770
2.919
2.913
2.906
2.900
2.767
2.747
2.727
2.708
2.689
2.670
2.649
2.631
2.538
2.527
2.505
2.494
2.337
2.326
2.302
2.207
2.173
2.170
2.164
2.146
2.136
1.828
1.820
1.792
1.333
1.315
1.297
0.000
O2N
NO2
O
O
10
NAME Jul05-2011
EXPNO 10
PROCNO 1
Date_ 20110705
Time 17.57
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 6578.947 Hz
FIDRES 0.100387 Hz
AQ 4.9807858 sec
RG 322
DW 76.000 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.80 usec
SI 65536
SF 400.1300101 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.1 1.9 2.0 1.1 1.0 2.1 1.0 1.0 2.0 1.0 1.3 1.3 1.0 3.3 2.1
170.52
133.80
129.32
128.80
127.56
91.22
83.25
77.33
77.01
76.69
61.42
43.61
36.25
33.99
26.44
23.49
14.20
-0.01
NAME Jul06-2011
EXPNO 10
PROCNO 1
Date_ 20110706
Time 19.48
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1500
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 5792.6
DW 20.850 usec
DE 6.00 usec
TE 298.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 -2.10 dB
SFO1 100.5649905 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.30 dB
PL12 13.60 dB
PL13 13.60 dB
SFO2 399.9015996 MHz
SI 32768
SF 100.5549350 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

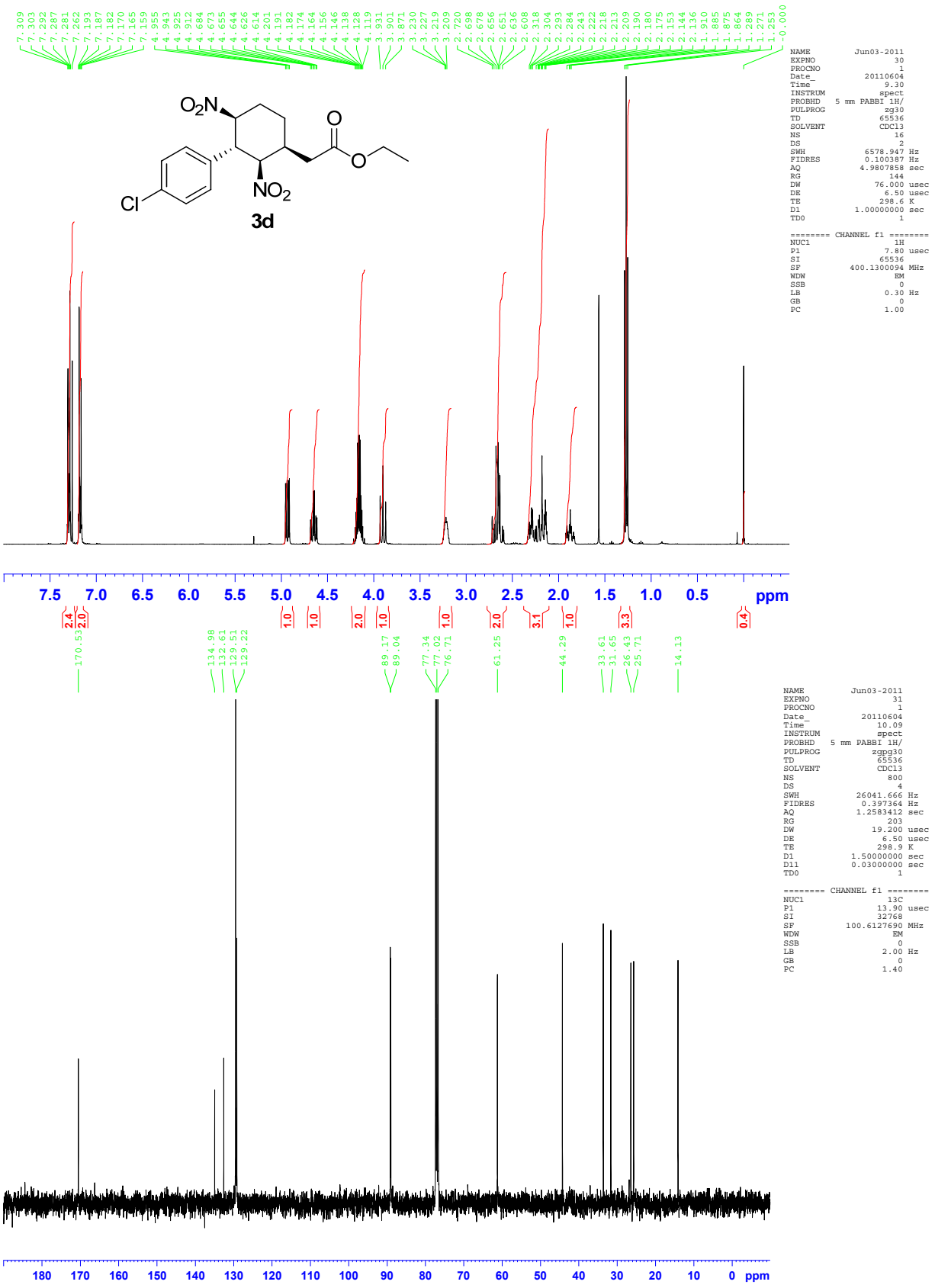
^{1}H, ^{13}C and NOESY of mixtures of **9**, **11** and **12**

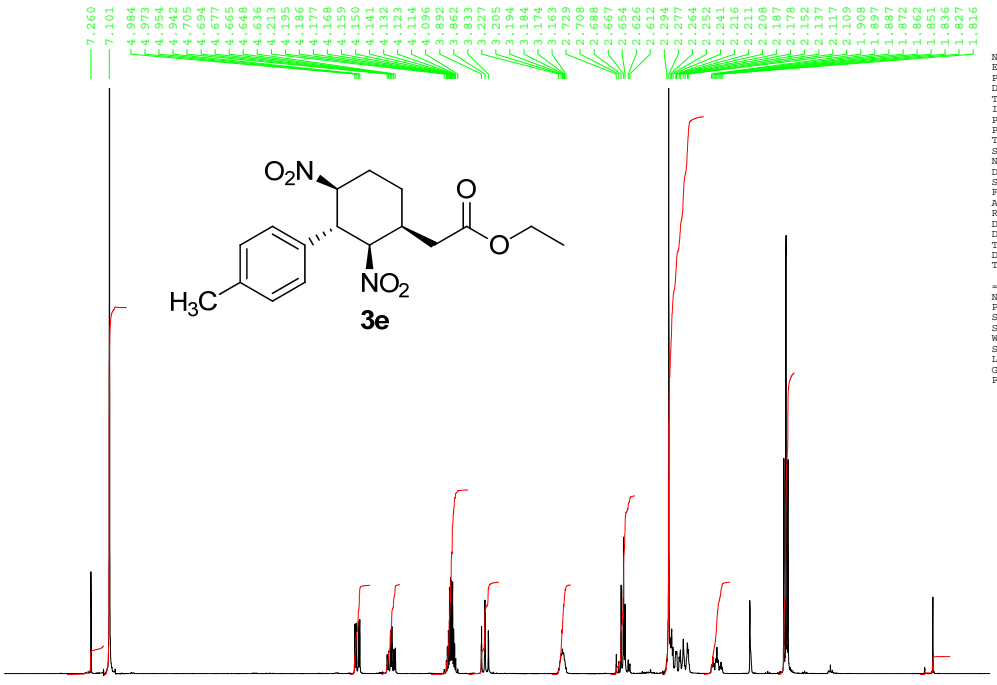


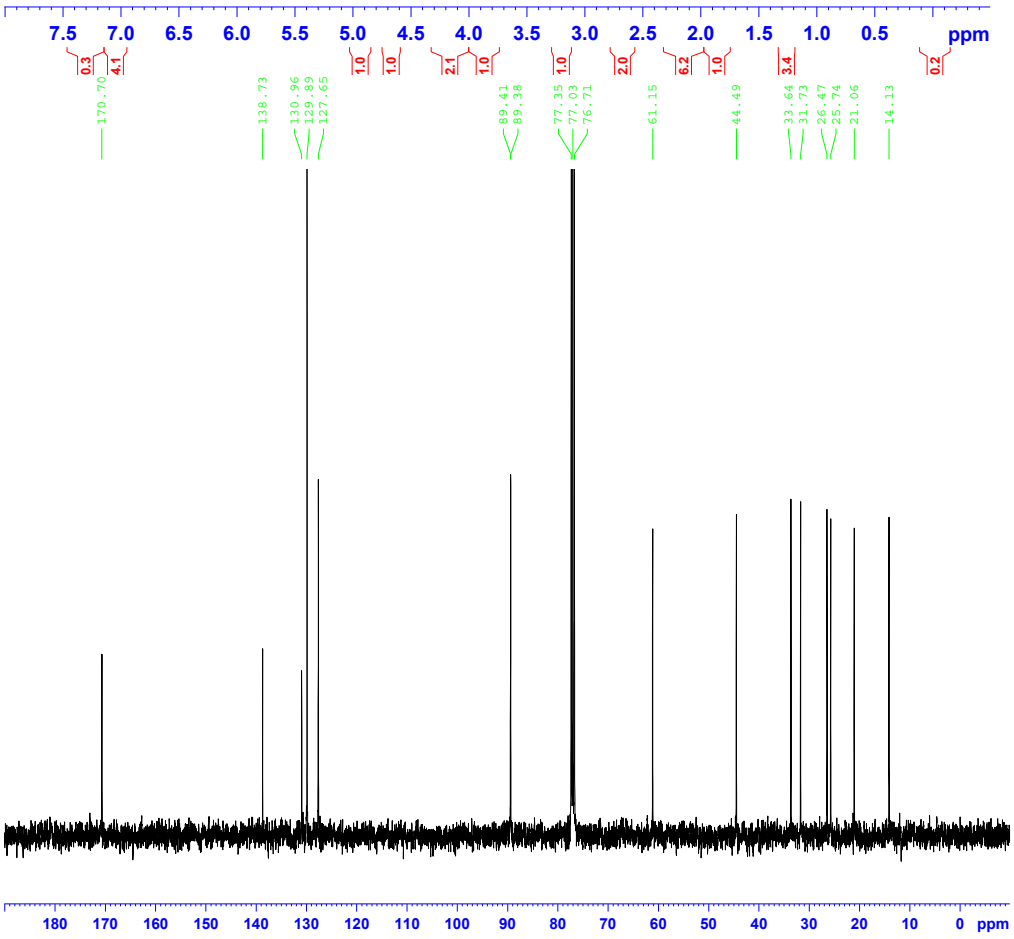

BRUKER
NAME RK4-05-26-4-2
EXPNO 10
PROCNO 1
Date_ 20110331
Time 11.05
INSTRUM AVIII500
PROBHD 5 mm PABBO BB-
PULPROG noesygpph
TD 2048
SOLVENT CDC13
NS 8
DS 16
SWH 5102.041 Hz
FIDRES 2.491231 Hz
AQ 0.2007540 sec
RG 22.6
DW 98.000 usec
DE 6.50 usec
TE 298.1 K
D0 0.00000819 sec
D1 2.00000000 sec
D8 0.80000001 sec
D16 0.00020000 sec
IN0 0.00019585 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
P2 20.00 usec
PL1 -1.80 dB
PLW1 17.22257996 W
SFO1 500.1323506 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 40.00 %
GPZ2 -40.00 %
P16 1000.00 usec
ND0 1
TD 256
SFO1 500.1324 MHz
FIDRES 19.944834 Hz
SW 10.209 ppm
FnMODE States-TPPI
SI 1024
SF 500.1300110 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.40
SI 1024
MC2 States-TPPI
SF 500.1300103 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
RK4-05-26-4-2 isomer 25C NOESY
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

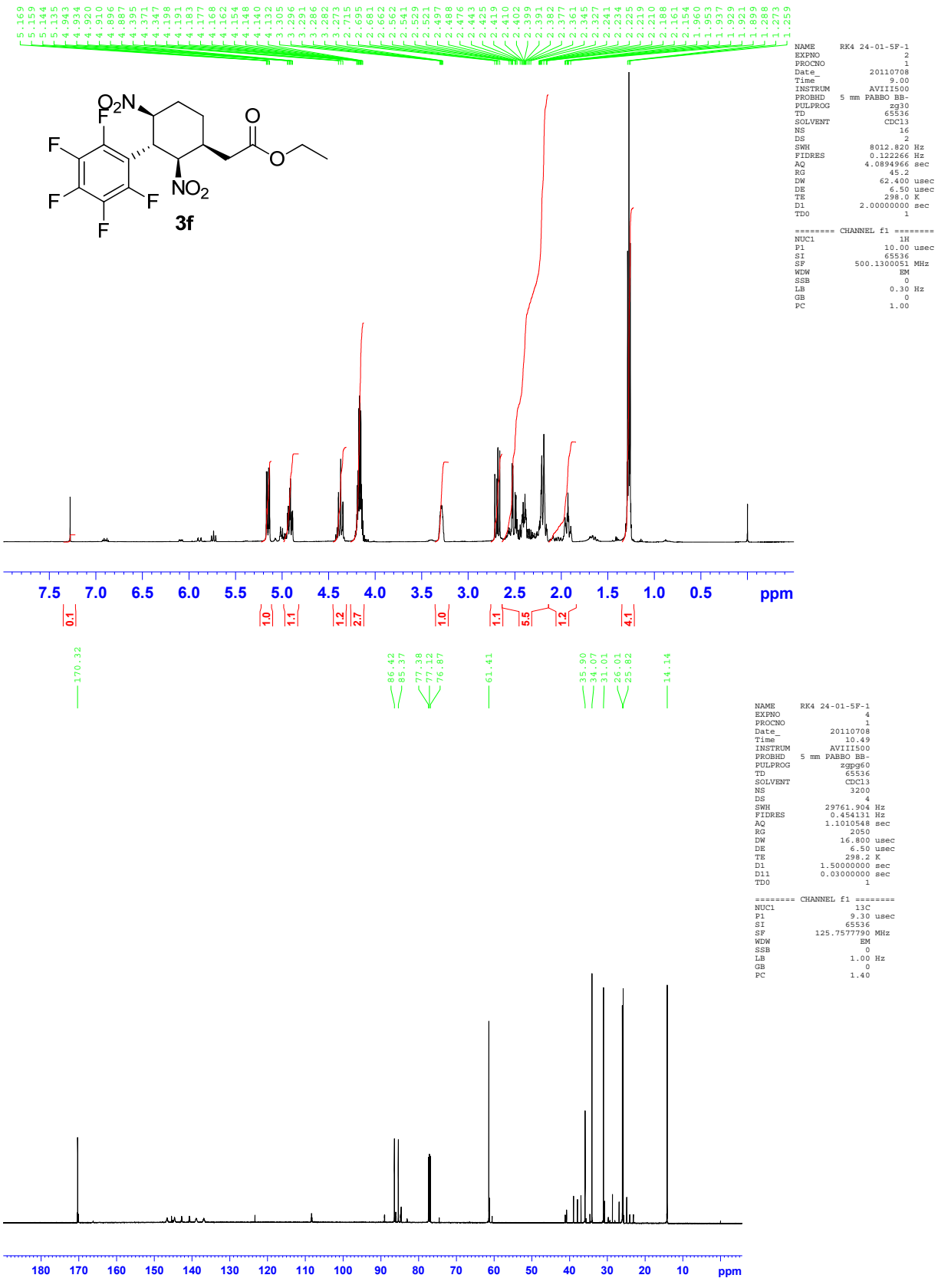

3b
ppm
ppm

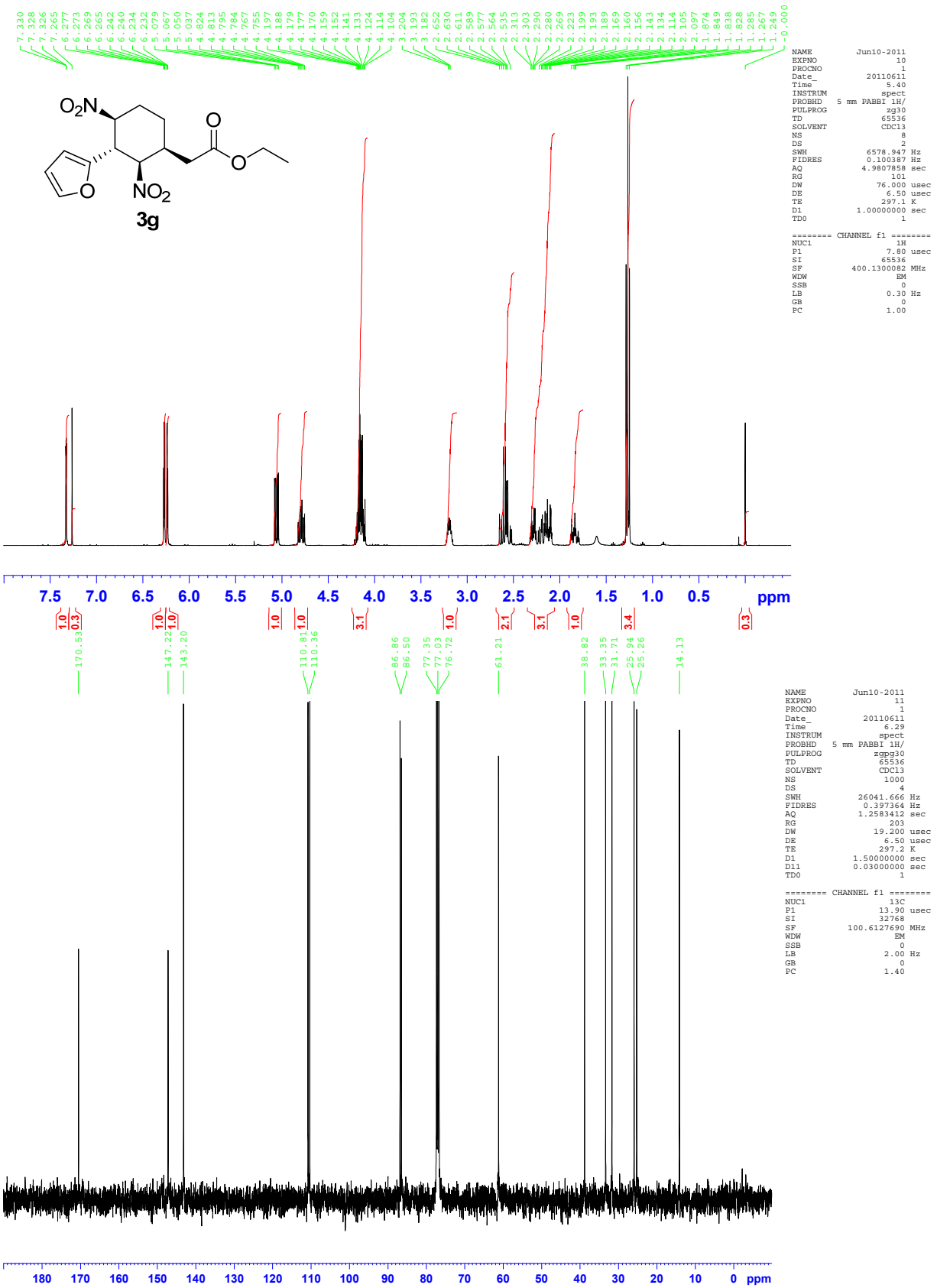

3c
ppm
ppm

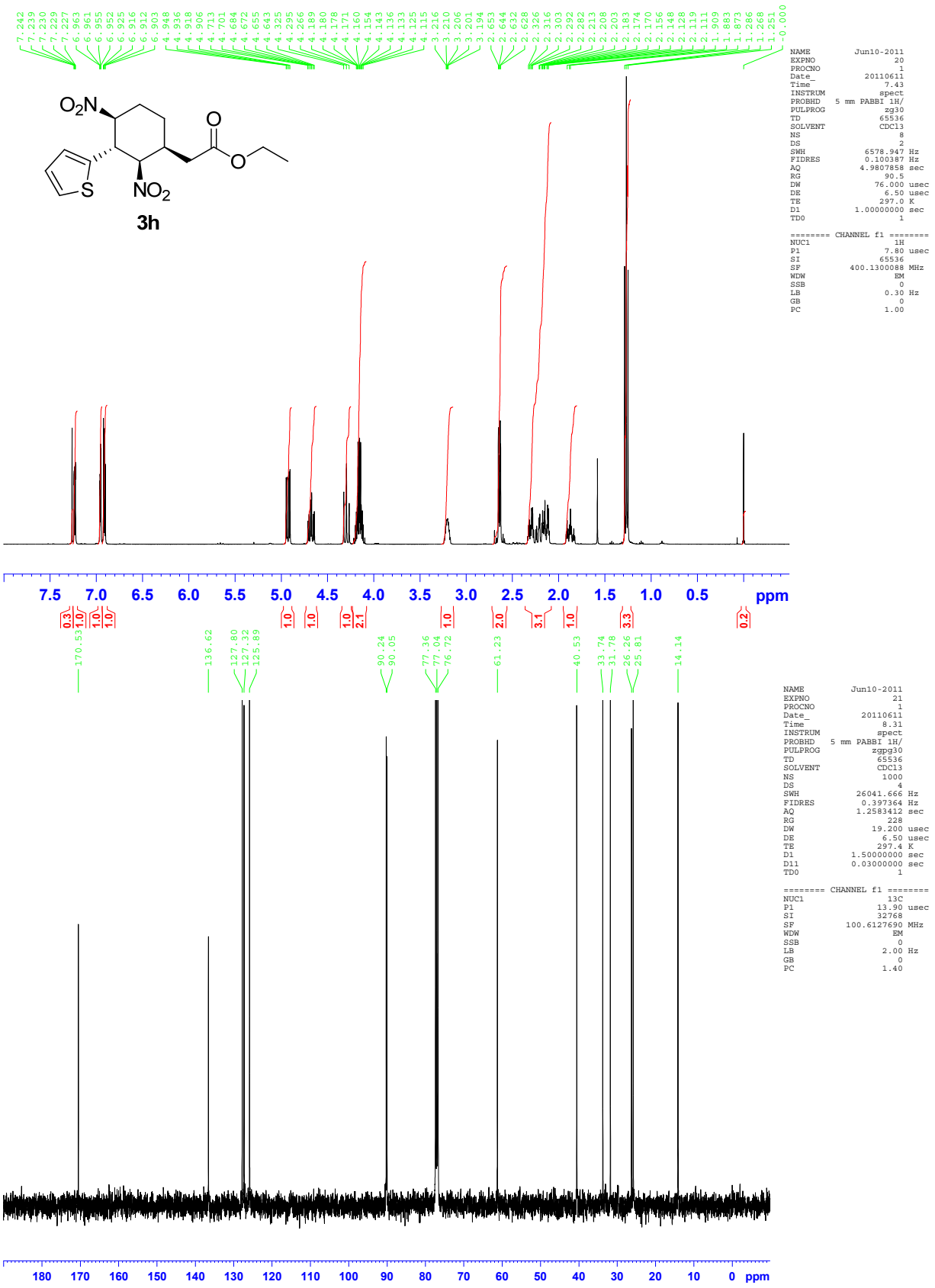

3d
ppm
ppm

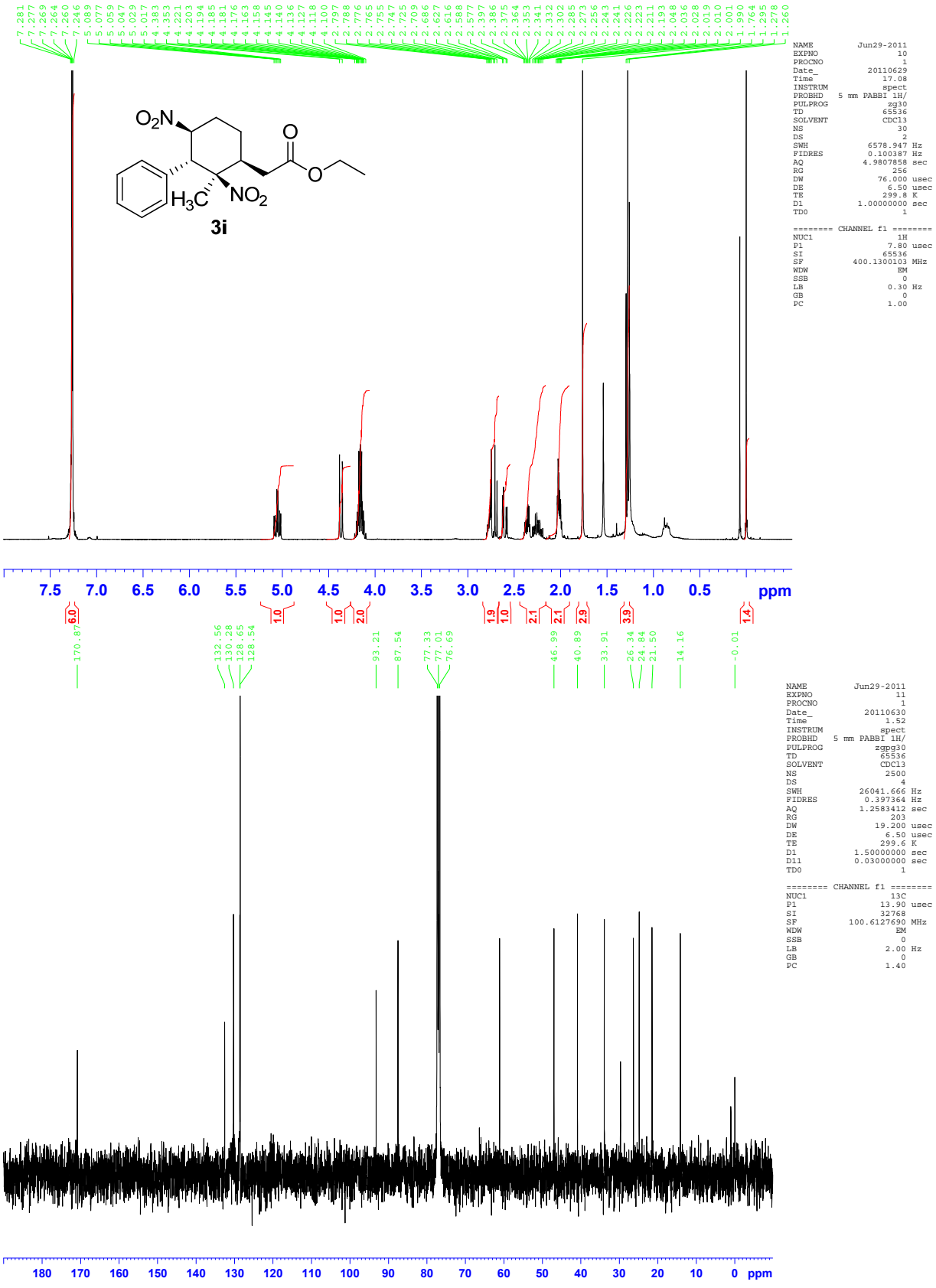

7.260
7.101
4.984
4.973
4.954
4.942
4.705
4.694
4.677
4.665
4.648
4.636
4.213
4.195
4.186
4.177
4.168
4.159
4.150
4.141
4.132
4.123
4.114
4.096
3.892
3.862
3.833
3.227
3.205
3.194
3.184
3.174
3.163
2.729
2.708
2.688
2.667
2.654
2.626
2.612
2.294
2.277
2.264
2.252
2.241
2.216
2.211
2.208
2.187
2.178
2.152
2.137
2.117
2.109
1.908
1.897
1.887
1.872
1.862
1.851
1.836
1.827
1.816
O2N
O
O
NO2
H3C
3e
NAME Jun27-2011
EXPNO 50
PROCNO 1
Date_ 20110628
Time 3.04
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 6578.947 Hz
FIDRES 0.100387 Hz
AQ 4.9807858 sec
RG 90.5
DW 76.000 usec
DE 6.50 usec
TE 300.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.80 usec
SI 65536
SF 400.1300103 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.3 4.1 1.0 1.0 2.1 1.0 1.0 2.0 6.2 1.0 3.4 0.2

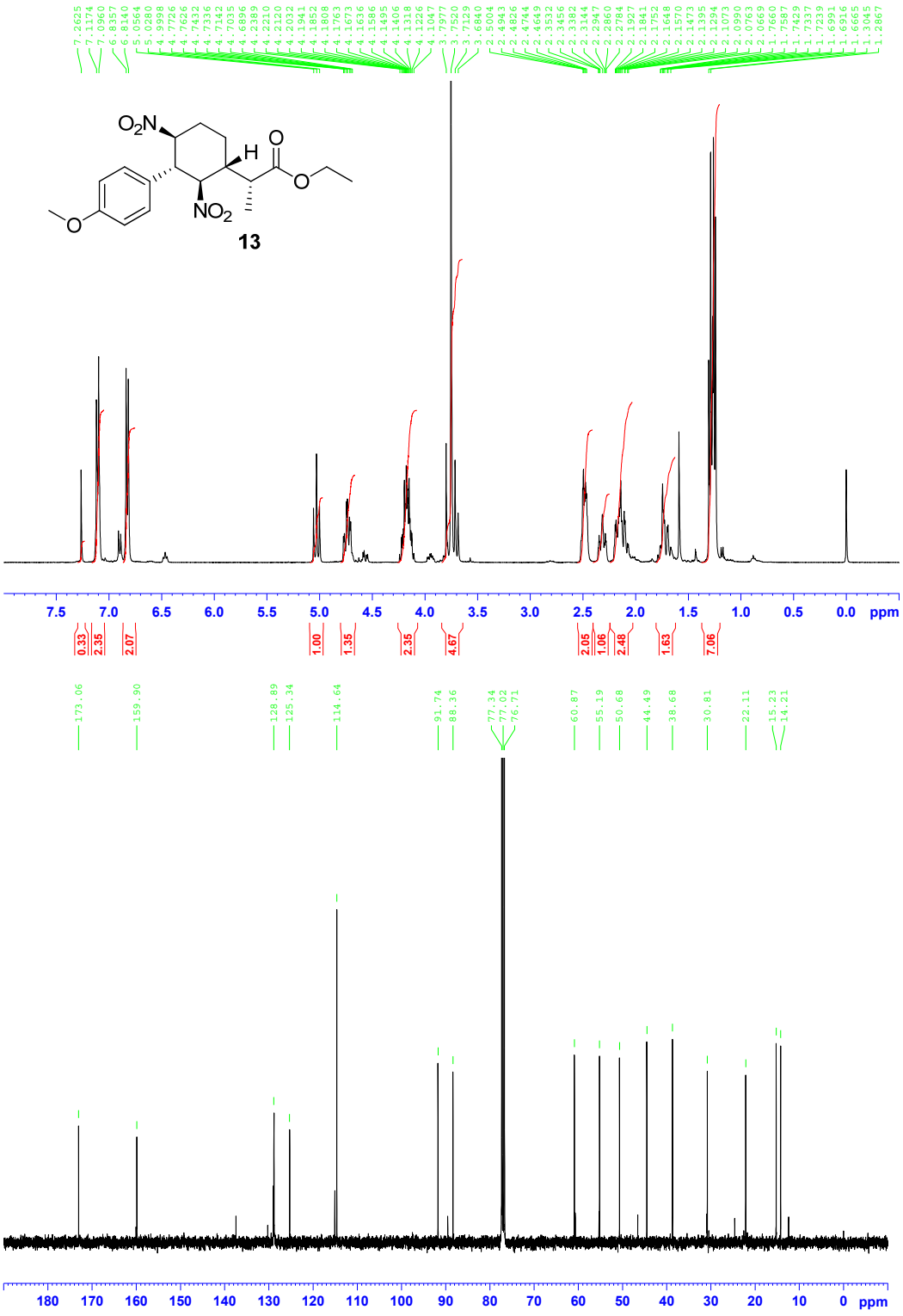

170.70
138.73
130.96
129.89
127.65
89.41
89.38
77.35
77.03
76.71
61.15
44.49
33.64
31.73
26.47
25.74
21.06
14.13
NAME Jun27-2011
EXPNO 51
PROCNO 1
Date_ 20110628
Time 3.29
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 4
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2583412 sec
RG 203
DW 19.200 usec
DE 6.50 usec
TE 300.3 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 13.90 usec
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


3f
ppm
ppm


7.330
7.328
7.326
7.265
6.277
6.273
6.269
6.265
6.242
6.240
6.234
6.232
5.079
5.067
5.050
5.037
4.824
4.813
4.795
4.784
4.767
4.755
4.197
4.188
4.179
4.177
4.170
4.159
4.152
4.141
4.133
4.124
4.114
4.104
3.204
3.193
3.182
2.652
2.630
2.611
2.589
2.577
2.564
2.535
2.313
2.303
2.290
2.280
2.269
2.223
2.199
2.193
2.189
2.169
2.160
2.156
2.143
2.134
2.114
2.105
2.097
1.874
1.849
1.838
1.828
1.285
1.267
1.249
0.000
O2N
O
O
O
NO2
3g
NAME Jun10-2011
EXPNO 10
PROCNO 1
Date_ 20110611
Time 5.40
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6578.947 Hz
FIDRES 0.100387 Hz
AQ 4.9807858 sec
RG 101
DW 76.000 usec
DE 6.50 usec
TE 297.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.80 usec
SI 65536
SF 400.1300082 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.0 0.3 1.0 1.0 1.0 1.0 3.1 1.0 2.1 3.1 1.0 3.4 0.3
170.53
147.22
143.20
110.81
110.36
86.86
86.50
77.35
77.03
76.72
61.21
38.82
33.35
31.71
25.94
25.26
14.13
NAME Jun10-2011
EXPNO 11
PROCNO 1
Date_ 20110611
Time 6.29
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1000
DS 4
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2583412 sec
RG 203
DW 19.200 usec
DE 6.50 usec
TE 297.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 13.90 usec
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


3h
ppm
ppm

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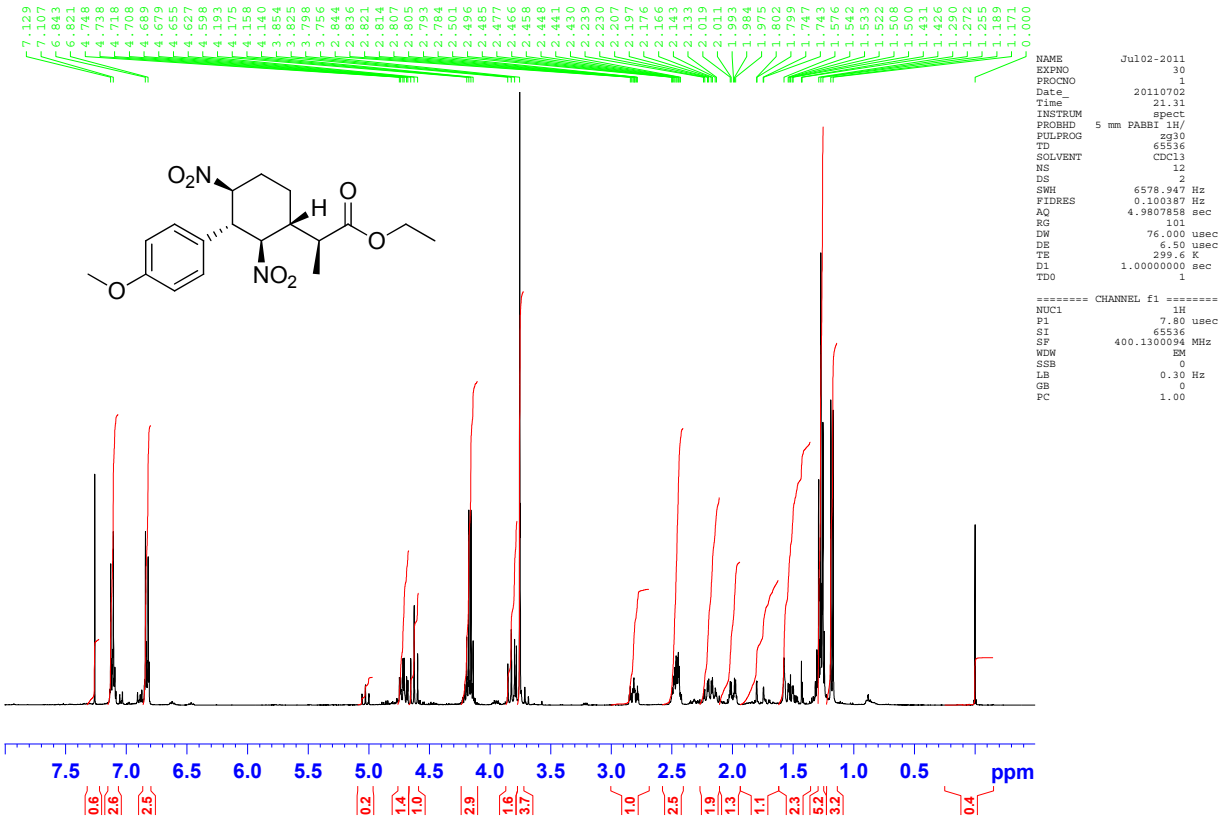
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O2N
H
O
O
O
NO2
NAME Jul02-2011
EXPNO 30
PROCNO 1
Date_ 20110702
Time 21.31
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PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 12
DS 2
SWH 6578.947 Hz
FIDRES 0.100387 Hz
AQ 4.9807858 sec
RG 101
DW 76.000 usec
DE 6.50 usec
TE 299.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.80 usec
SI 65536
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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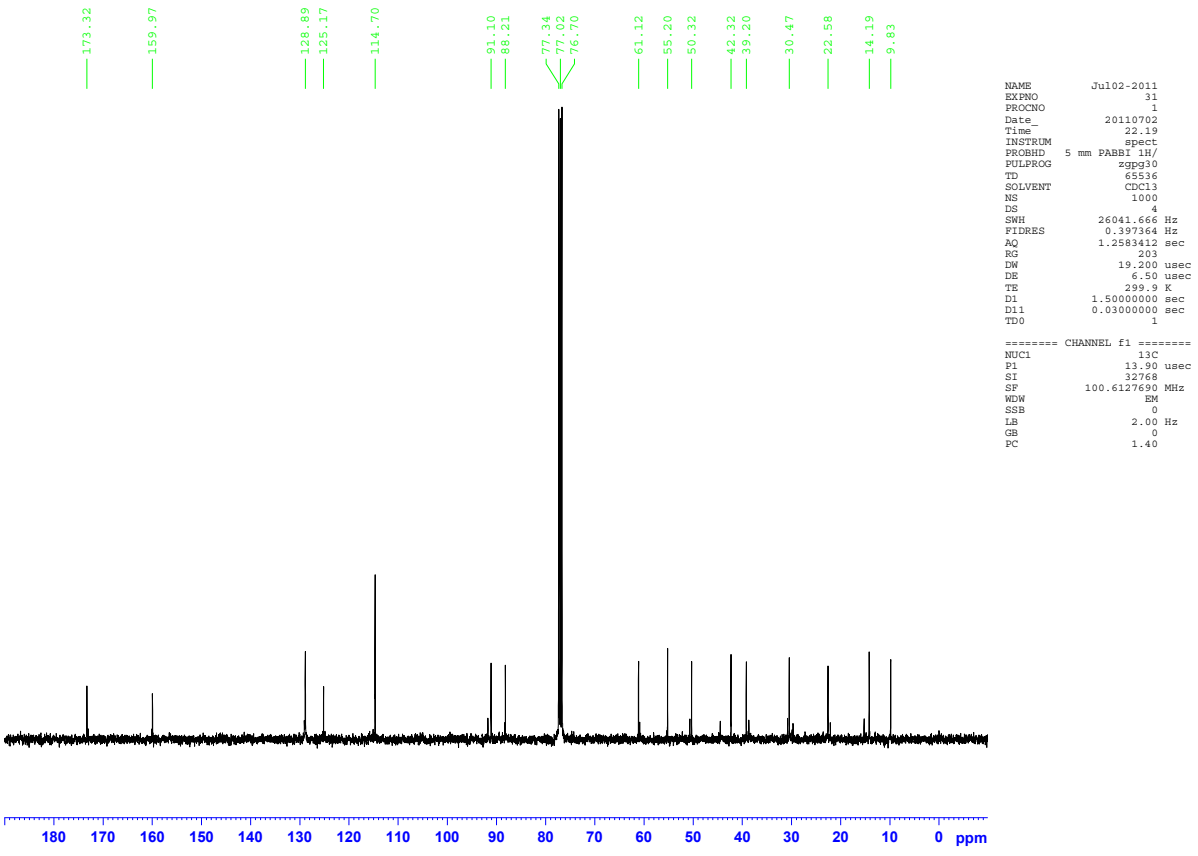
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NAME Jul02-2011
EXPNO 31
PROCNO 1
Date_ 20110702
Time 22.19
INSTRUM spect
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1000
DS 4
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2583412 sec
RG 203
DW 19.200 usec
DE 6.50 usec
TE 299.9 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 13.90 usec
SI 32768
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WDW EM
SSB 0
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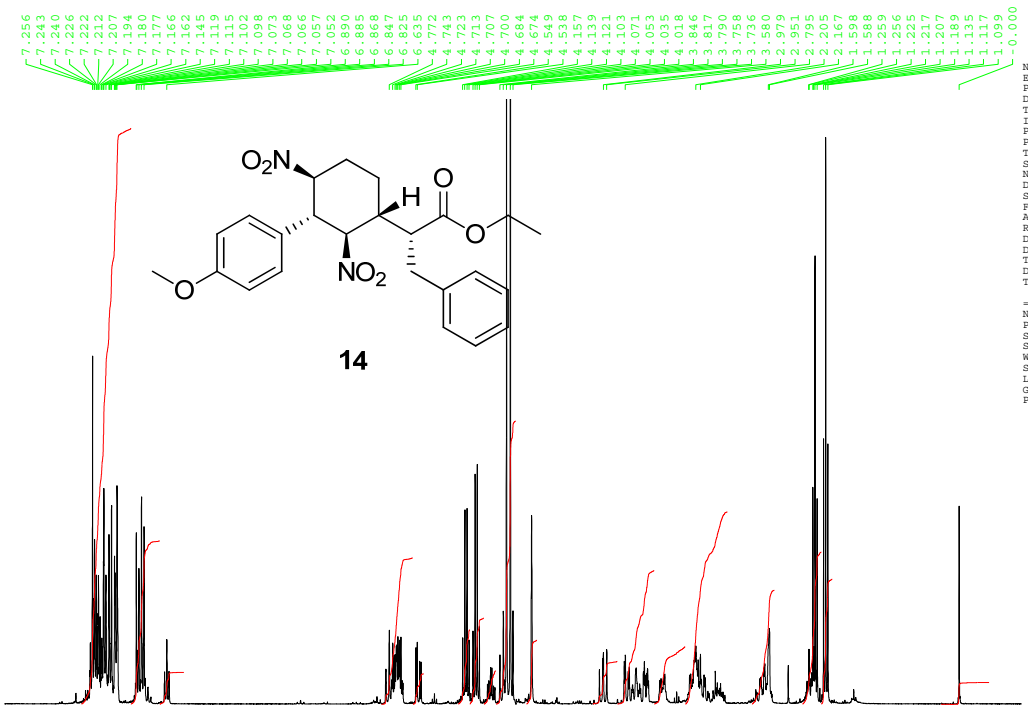
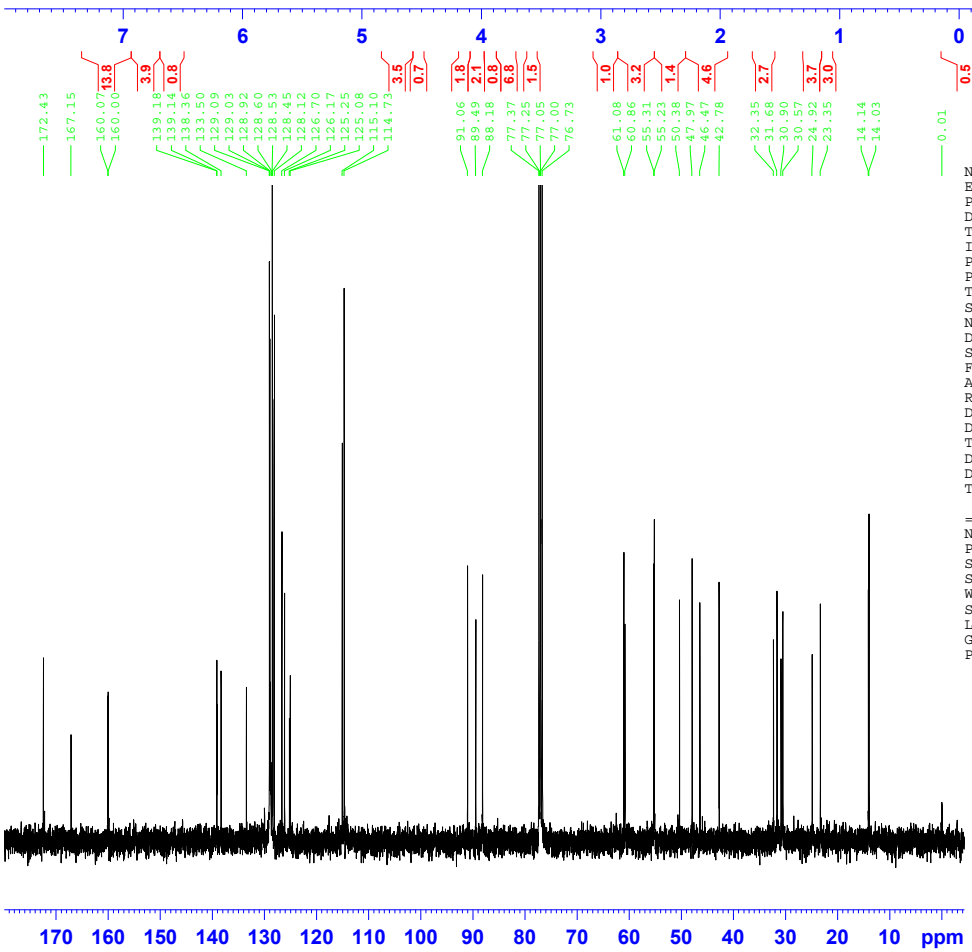

14
ppm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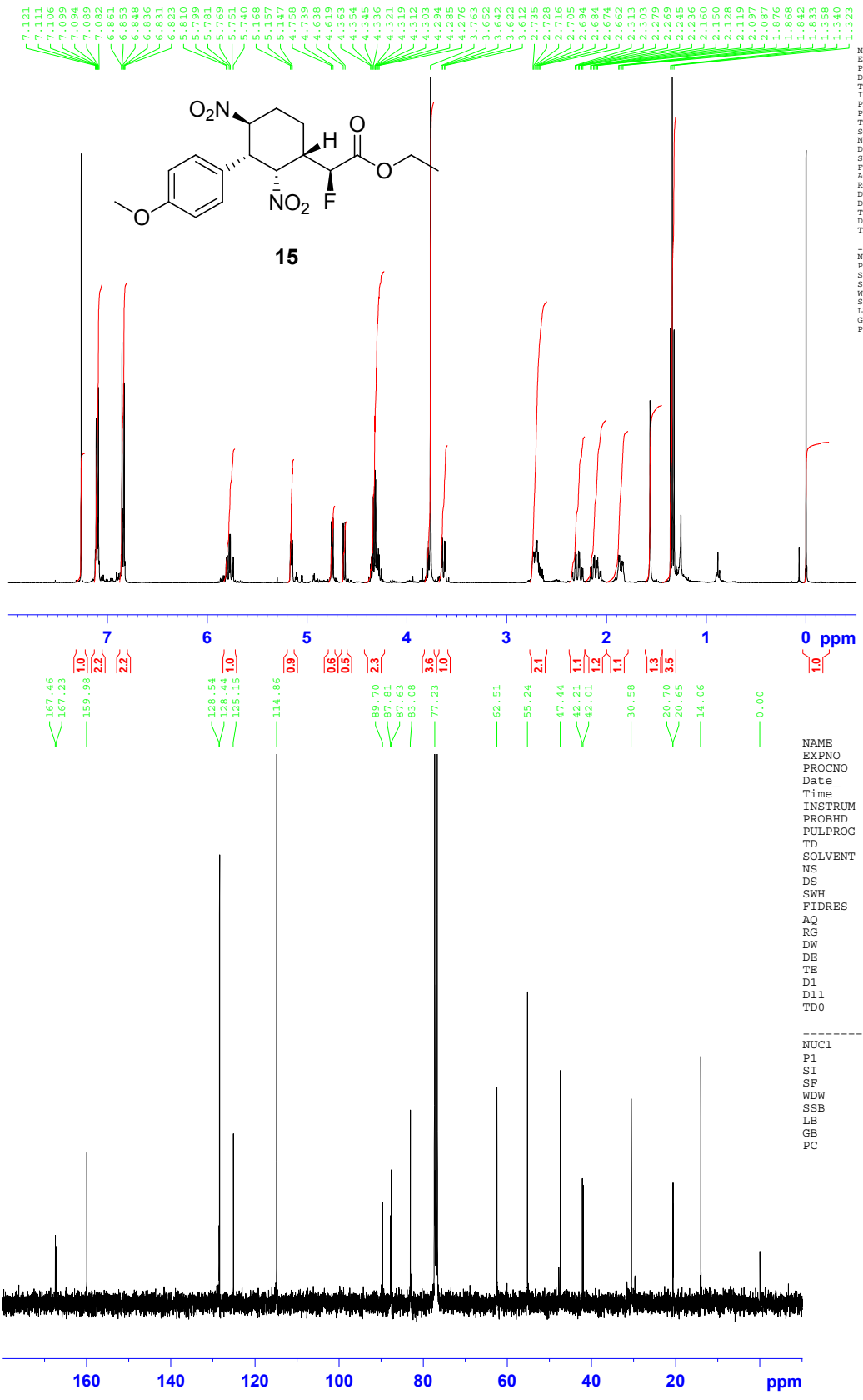
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NAME Oct07-2011
EXPNO 10
PROCNO 1
Date_ 20111007
Time_ 21.04
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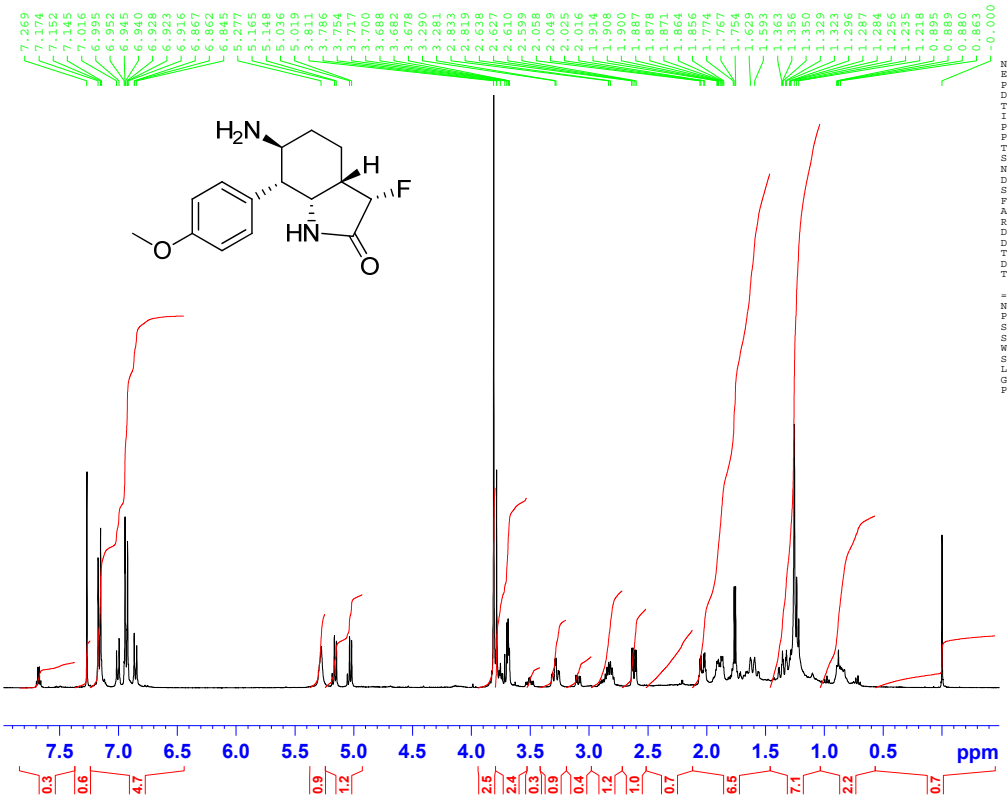
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6578.947 Hz
FIDRES 0.100387 Hz
AQ 4.9807858 sec
RG 181
DW 76.000 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.80 usec
SI 65536
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NAME Oct07-2011
EXPNO 14
PROCNO 1
Date_ 20111008
Time 2.17
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4000
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 181
DW 20.800 usec
DE 6.50 usec
TE 296.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 13.90 usec
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40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7.116
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6.945
6.940
6.928
6.923
6.916
6.867
6.862
6.845
5.277
5.165
5.148
5.036
5.019
3.811
3.786
3.754
3.717
3.700
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2.016
1.914
1.908
1.900
1.887
1.878
1.871
1.864
1.856
1.774
1.767
1.754
1.629
1.593
1.363
1.356
1.350
1.329
1.323
1.296
1.287
1.284
1.256
1.235
1.218
0.895
0.889
0.880
0.863
0.000
H2N
H
F
HN
O
O
NAME Oct12-2011
EXPNO 10
PROCNO 1
Date_ 20111012
Time 18.37
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PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6578.947 Hz
FIDRES 0.100387 Hz
AQ 4.9807858 sec
RG 114
DW 76.000 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.80 usec
SI 65536
SF 400.1300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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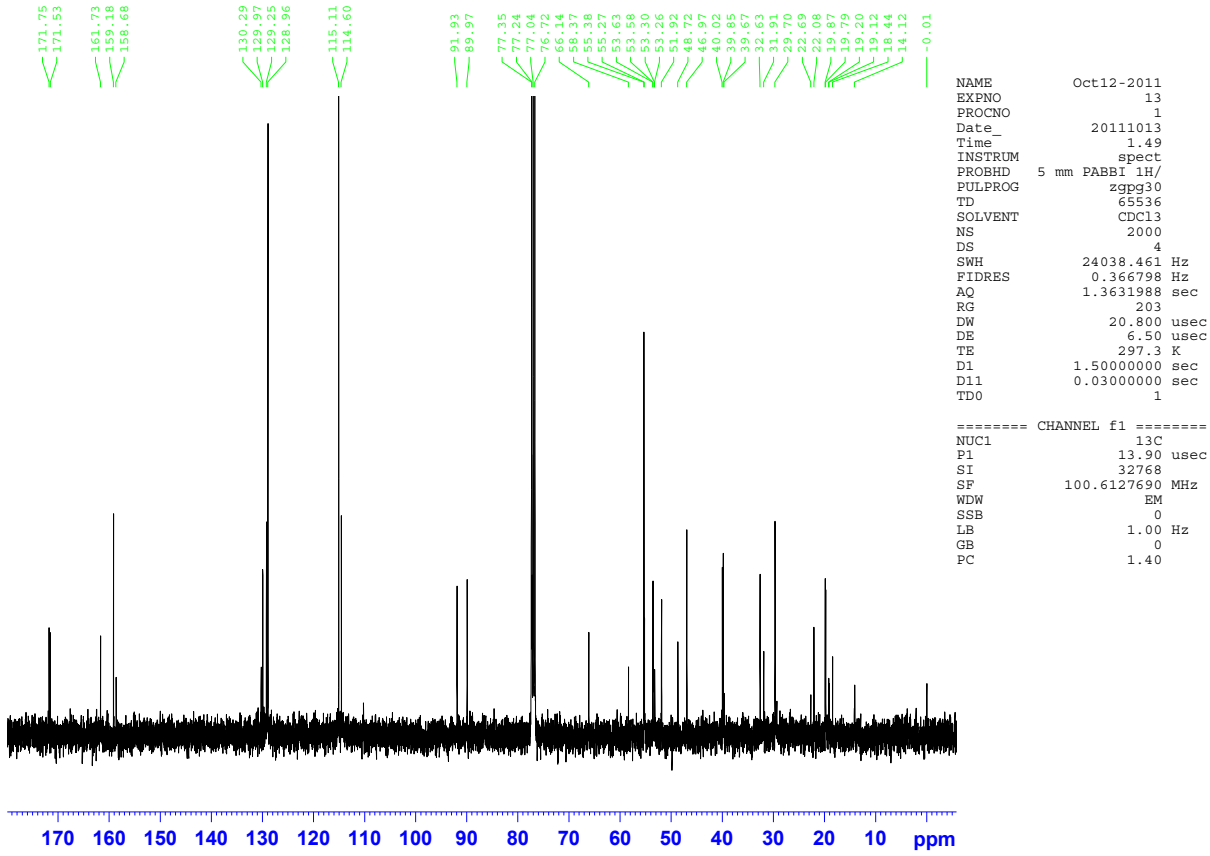
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129.97
129.25
128.96
115.11
114.60
91.93
89.97
77.35
77.24
77.04
76.72
66.14
58.37
55.38
55.27
53.63
53.58
53.30
53.26
51.92
48.72
46.97
40.02
39.85
39.67
32.63
31.91
29.70
22.69
22.08
19.87
19.79
19.20
19.12
18.44
14.12
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NAME Oct12-2011
EXPNO 13
PROCNO 1
Date_ 20111013
Time 1.49
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PROBHD 5 mm PABBI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2000
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 297.3 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 13.90 usec
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
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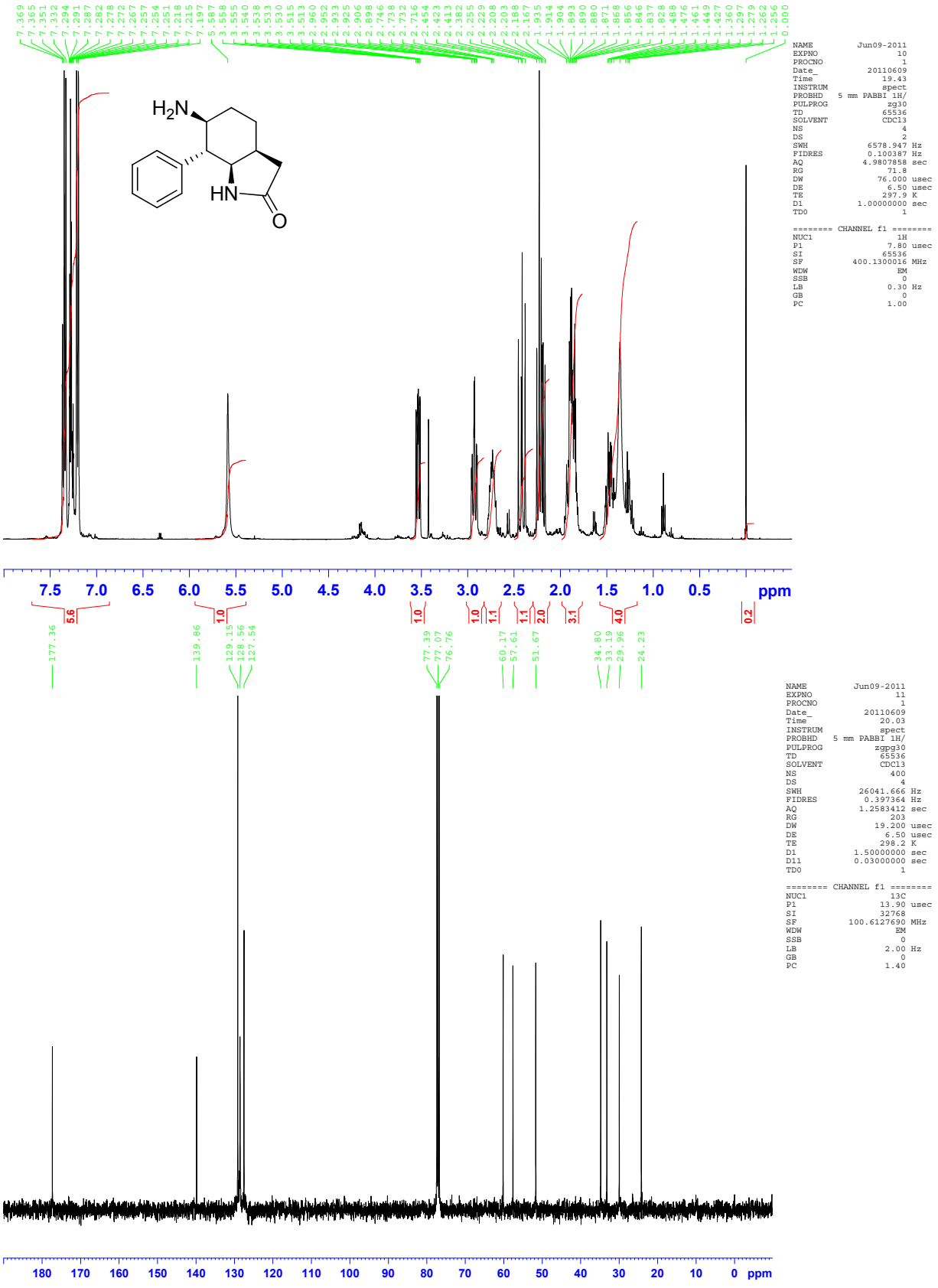
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7.215
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3.540
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3.515
3.513
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2.933
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2.382
2.255
2.229
2.208
2.203
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2.167
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1.914
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1.837
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1.461
1.449
1.427
1.360
1.297
1.279
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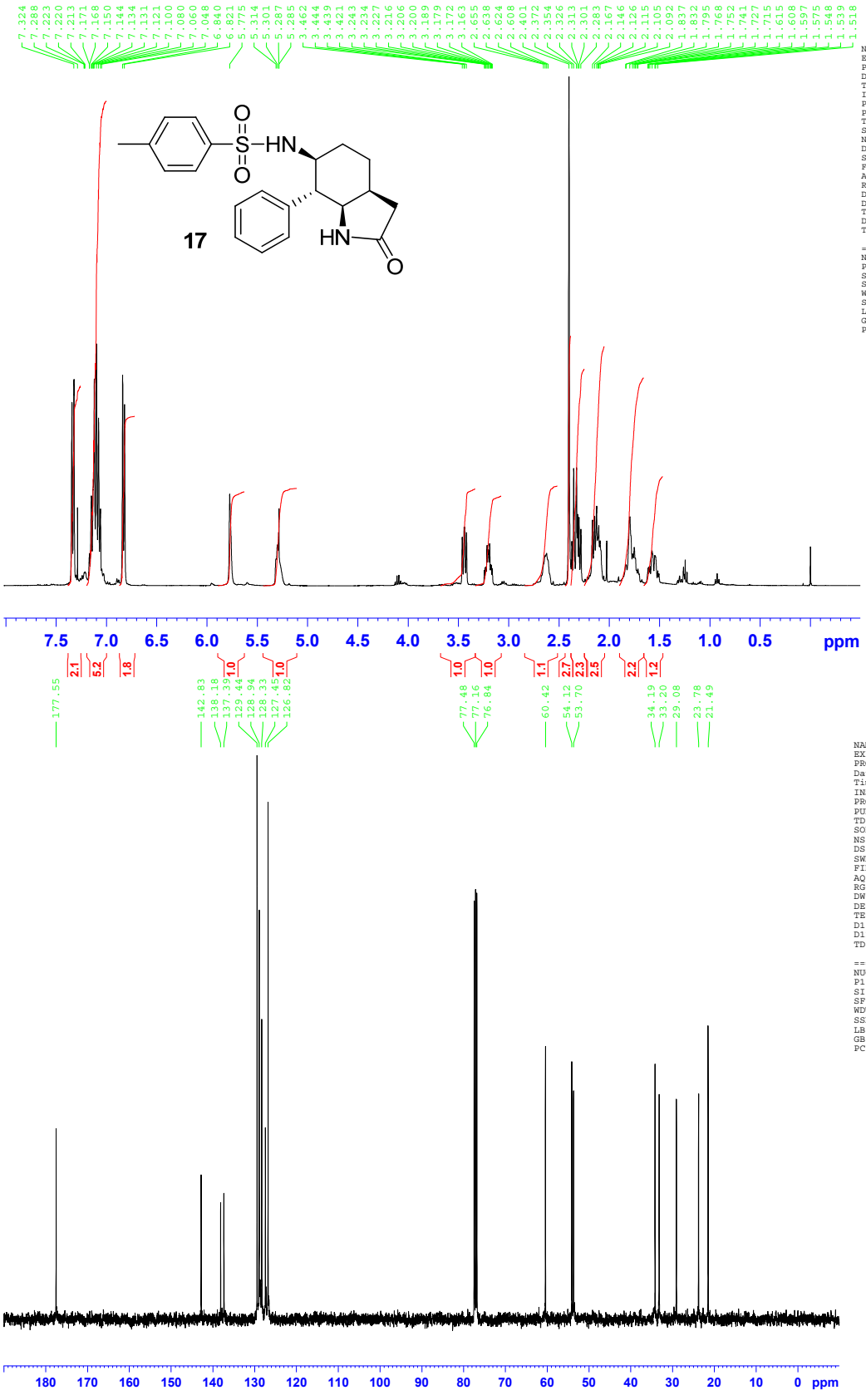
1.256
0.000
H2N
HN
O
NAME Jun09-2011
EXPNO 10
PROCNO 1
Date_ 20110609
Time 19.43
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 6578.947 Hz
FIDRES 0.100387 Hz
AQ 4.9807858 sec
RG 71.8
DW 76.000 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.80 usec
SI 65536
SF 400.1300016 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.6
1.0
1.0
1.1
1.1
2.0
3.1
4.0
0.2
177.36
139.86
129.15
128.56
127.54
77.39
77.07
76.76
60.17
57.61
51.67
34.80
33.19
29.96
24.23
NAME Jun09-2011
EXPNO 11
PROCNO 1
Date_ 20110609
Time 20.03
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2583412 sec
RG 203
DW 19.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 13.90 usec
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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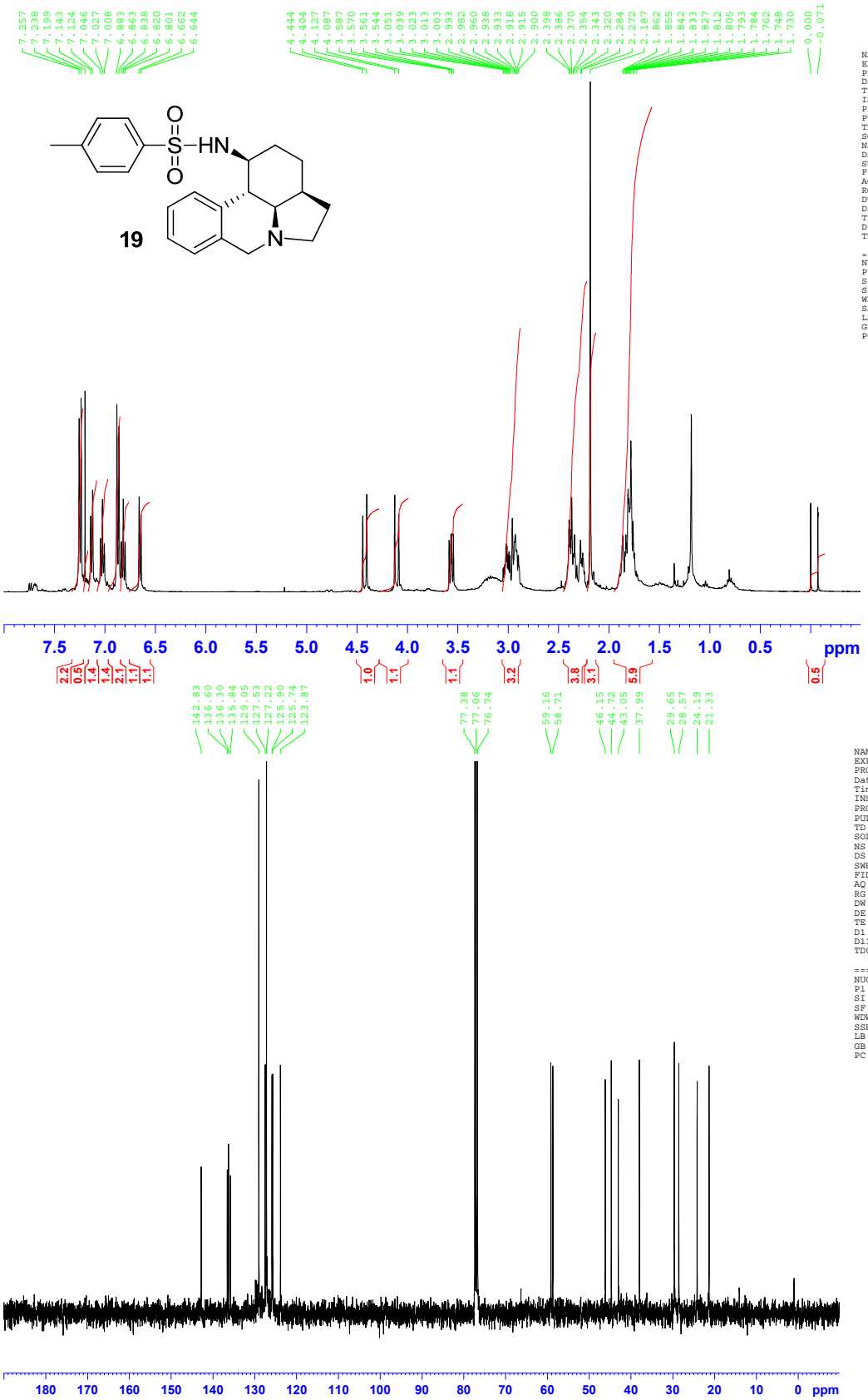
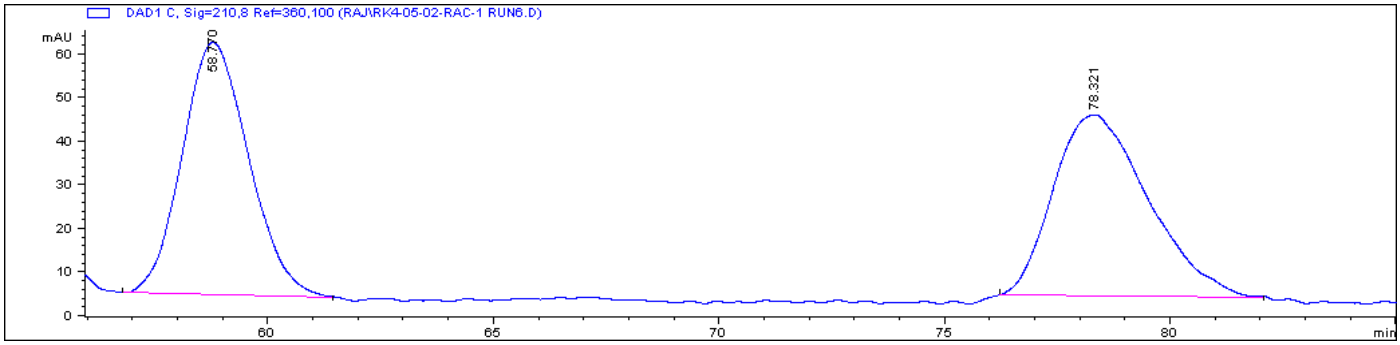

19
ppm
ppm

HPLC profiles

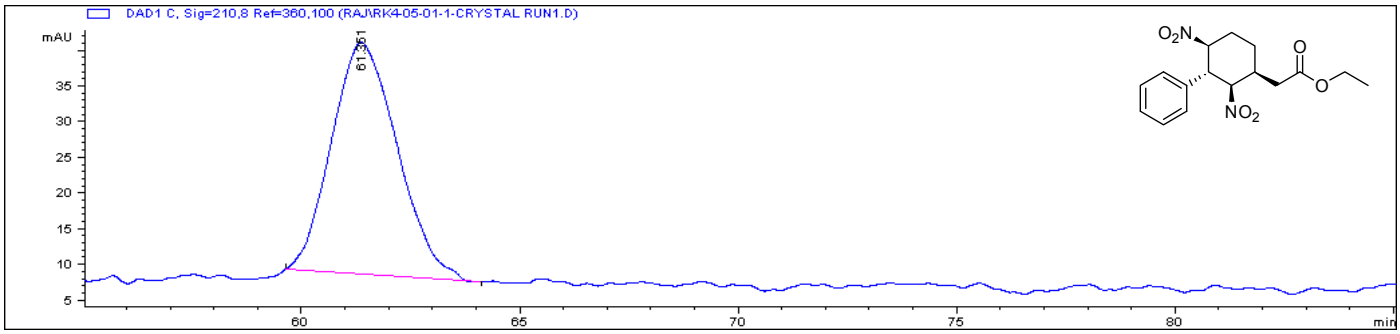
Racemic **3a**



Time	Area	Height	Width	Area%	Symmetry
58.77	5954.9	57.9	1.4976	49.49	0.837
78.32	6077.2	41.6	1.7805	50.51	0.754

2.5% IPA in Hexane 1mL/min OD

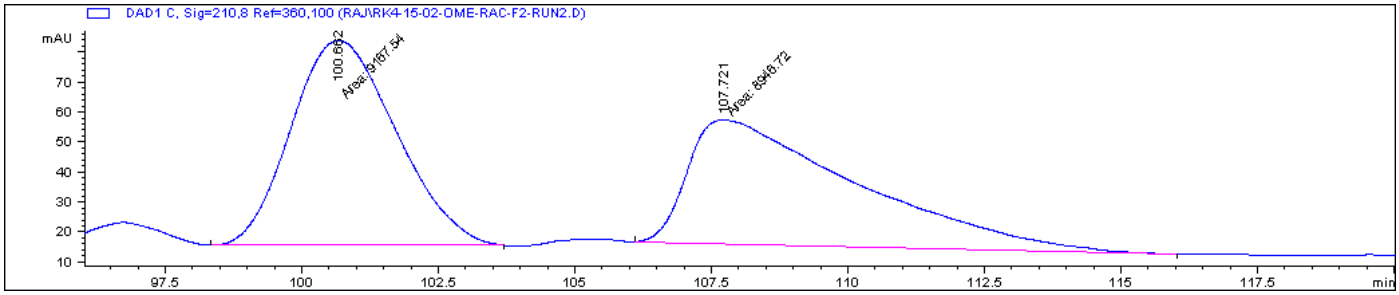
Enantio enriched **3a**



Time	Area	Height	Width	Area%	Symmetry
61.351	3411.3	32.6	1.3891	100	0.788

2.5% IPA in Hexane 1mL/min OD

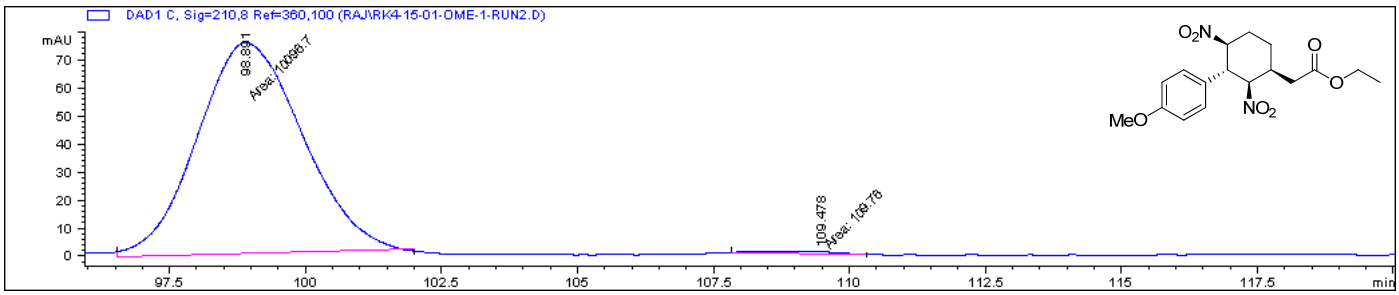
Racemic **3b**



Time	Area	Height	Width	Area%	Symmetry
100.66	9167.5	68.4	2.2339	50.61	0.809
107.72	8946.7	41.5	3.5956	49.39	0.264

3% IPA in Hexane 1mL/min AD-H

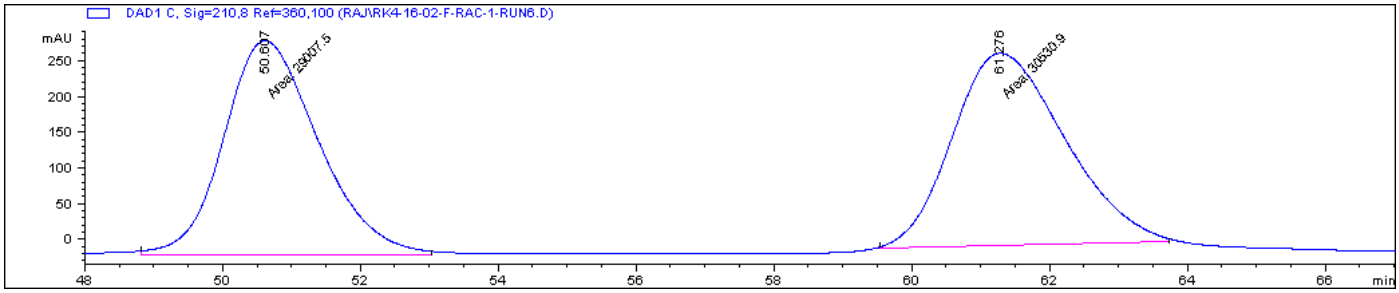
Enantio enriched **3b**



Time	Area	Height	Width	Area%	Symmetry
98.89	10096.7	75.1	2.2402	98.925	1.853
109.47	109.8	1	1.7744	1.075	1.947

3% IPA in Hexane 1mL/min AD-H

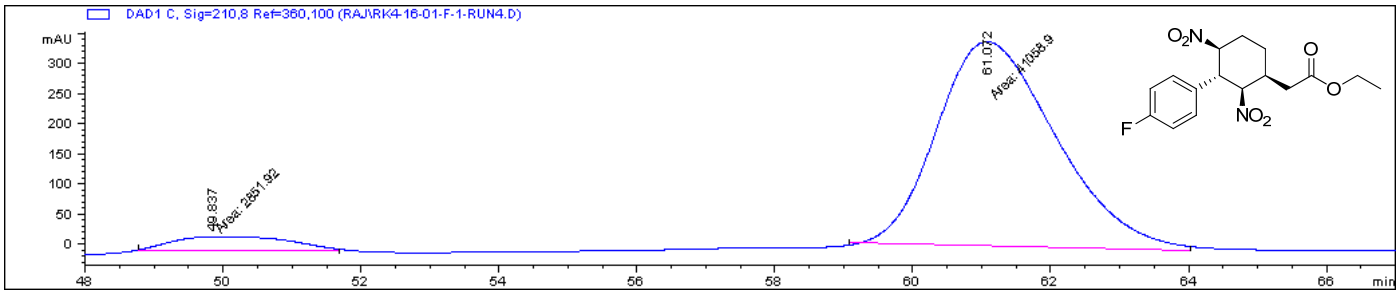
Racemic **3c**



Time	Area	Height	Width	Area%	Symmetry
50.60	29007.5	301.1	1.6056	48.721	0.758
61.27	30530.9	269.2	1.8904	51.279	0.734

10% IPA in Hexane 0.5mL/min OD

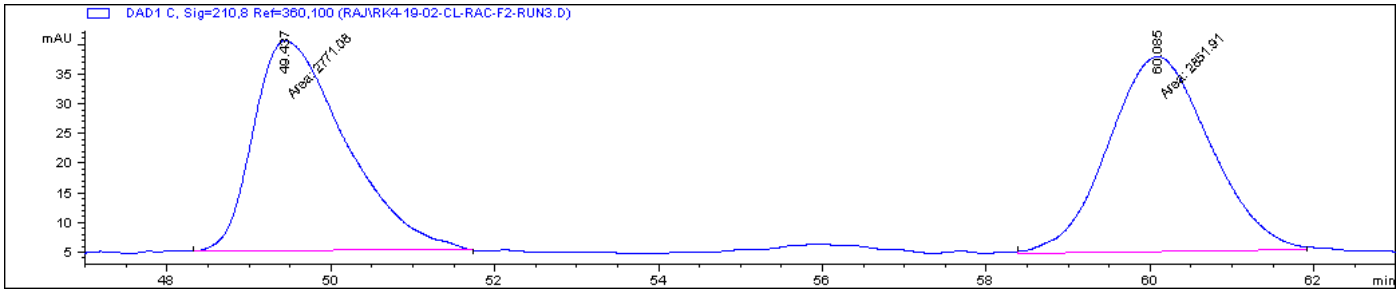
Enantio enriched **3c**



Time	Area	Height	Width	Area%	Symmetry
49.83	2851.9	23.3	2.0413	6.495	0.528
61.07	41058.9	340.6	2.0089	93.505	0.706

10% IPA in Hexane 0.5mL/min OD

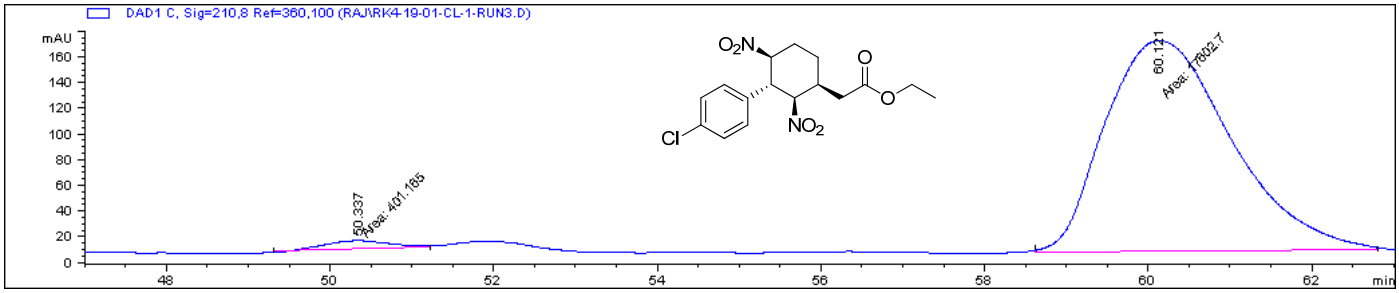
Racemic **3d**



Time	Area	Height	Width	Area%	Symmetry
49.43	2771.1	35.5	1.3005	49.281	0.525
60.08	2851.9	32.9	1.4432	50.719	0.922

5% IPA in Hexane 1mL/min AD-H

Enantio enriched **3d**

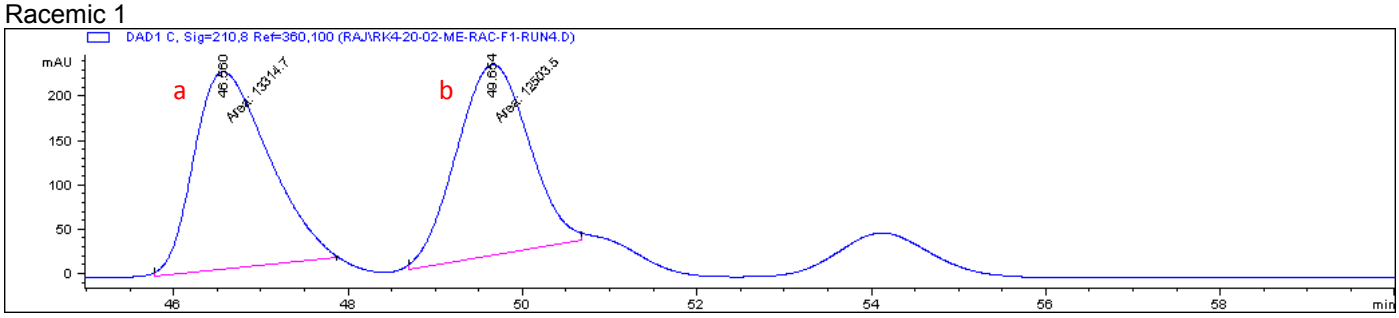


Time	Area	Height	Width	Area%	Symmetry
50.33	401.2	6.9	0.9752	2.228	1.002
60.12	17602.7	164.2	1.7865	97.772	0.717

5% IPA in Hexane 1mL/min AD-H

Racemic **3e**

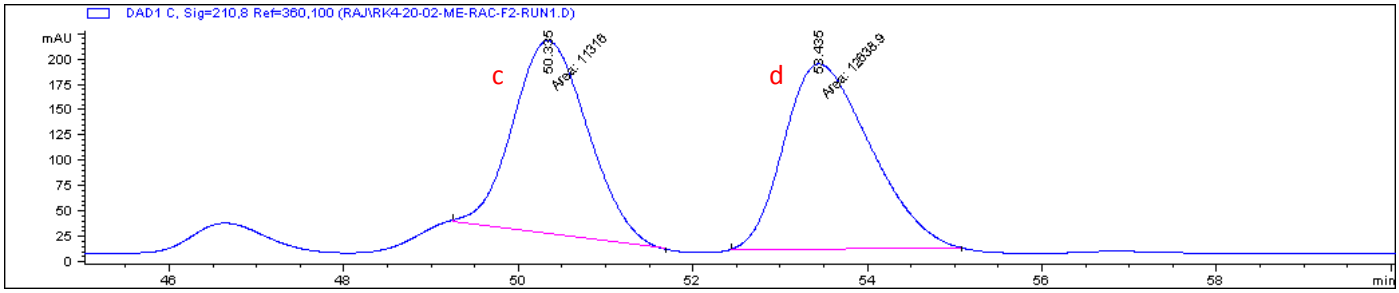
Racemic 1



Time	Area	Height	Width	Area%	Symmetry
46.56	13314.7	223.5	0.9927	51.571	0.627
49.65	12503.5	215.9	0.9653	48.429	1.004

4% IPA in Hexane 0.75mL/min AD-H

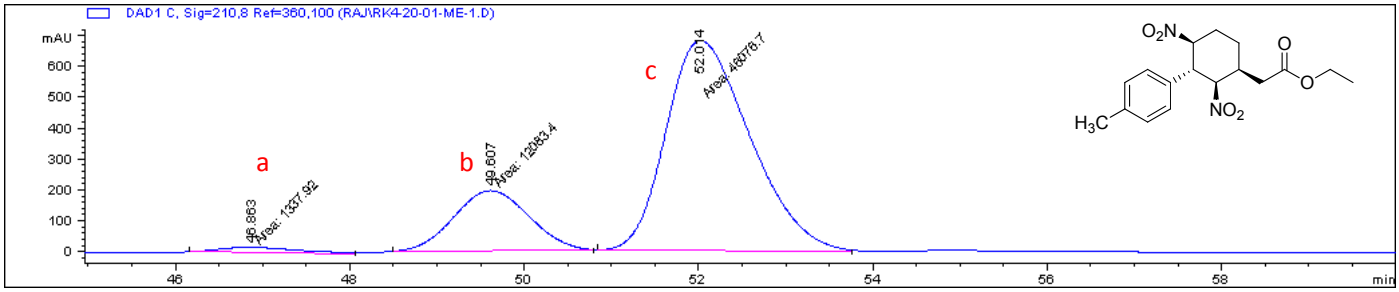
Racemic 2



Time	Area	Height	Width	Area%	Symmetry
50.33	11316	190.1	0.9919	47.239	0.844
53.43	12638.9	183	1.1509	52.761	0.663

4% IPA in Hexane 0.75mL/min AD-H

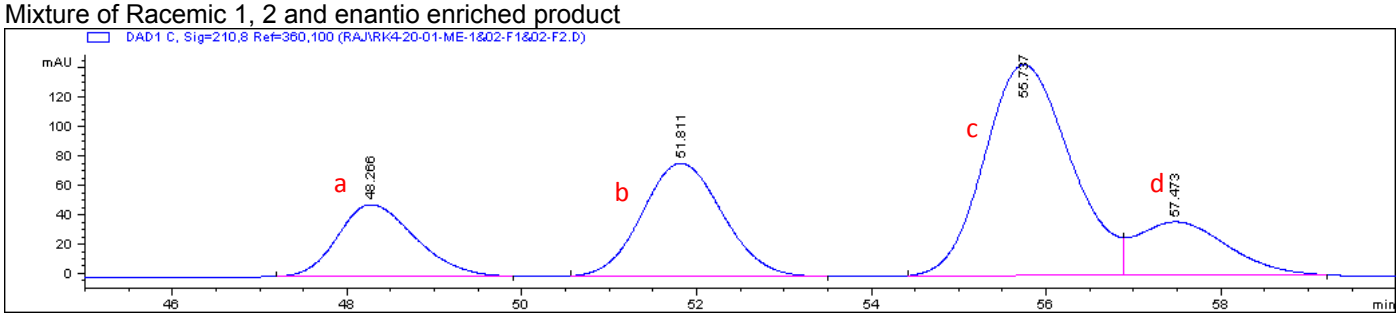
Enantio enriched **3e**



Time	Area	Height	Width	Area%	Symmetry
46.86	1337.9	19.1	1.1663	2.249	0.551
49.60	12083.4	197.8	1.018	20.309	0.947
52.01	46076.7	683.2	1.124	77.442	0.674

4% IPA in Hexane 0.75mL/min AD-H

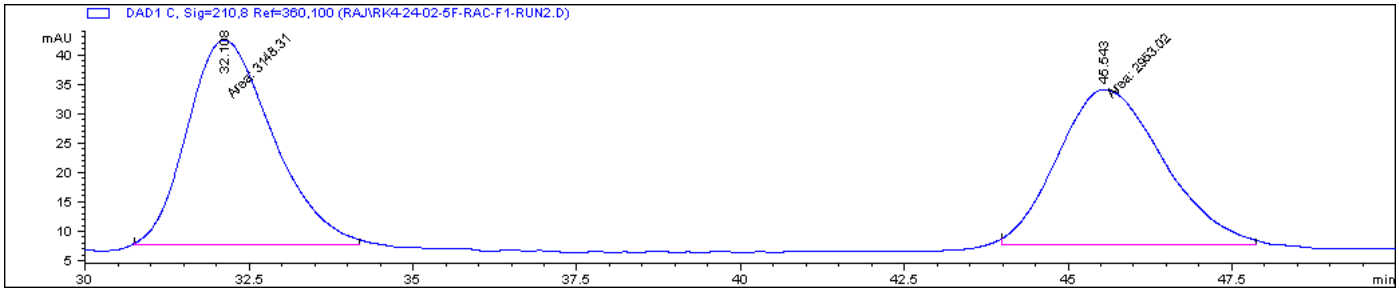
Mixture of Racemic 1, 2 and enantio enriched product



Time	Area	Height	Width	Area%	Symmetry
48.26	3050.2	49.2	0.958	17.754	0.723
51.811	4966.5	77.2	1.0007	24.023	0.901
55.73	9970.8	144.2	1.0666	48.229	0.811
57.47	2686.2	37	1.0954	12.993	0.665

4% IPA in Hexane 0.75mL/min AD-H

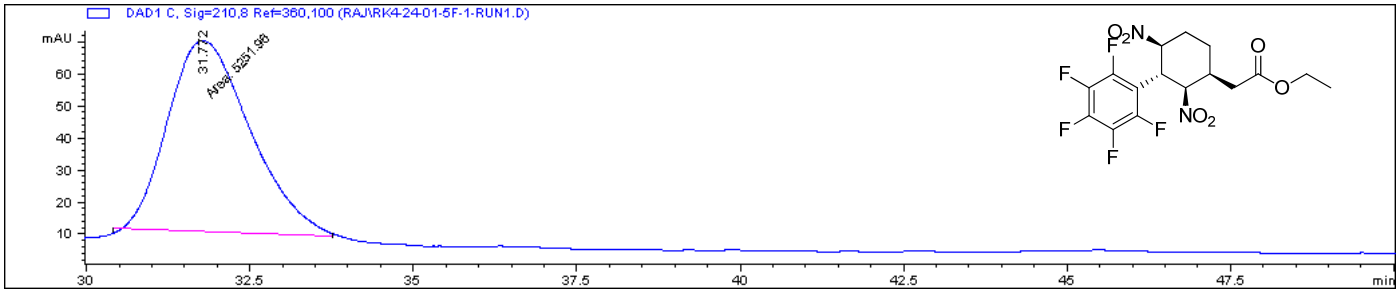
Racemic **3f**



Time	Area	Height	Width	Area%	Symmetry
32.10	3148.3	34.7	1.5105	51.6	0.736
45.54	2953	26.4	1.8616	48.4	0.777

4% IPA in Hexane 1mL/min OD

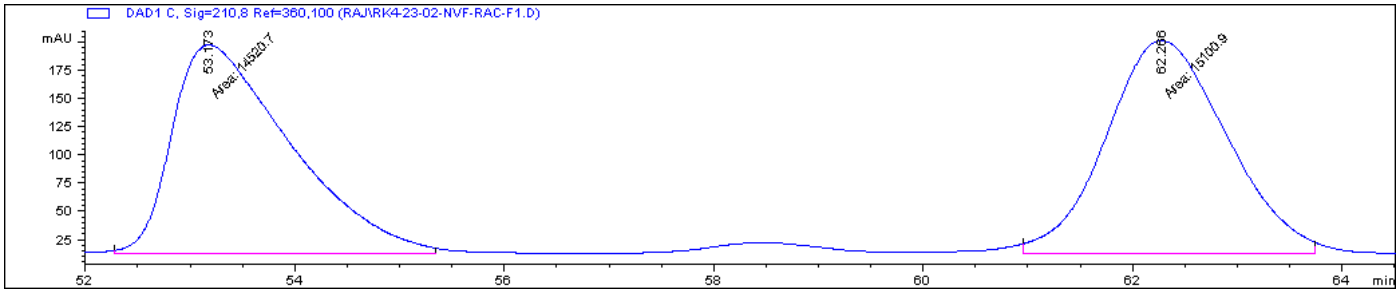
Enantio enriched **3f**



Time	Area	Height	Width	Area%	Symmetry
31.77	5252	59.7	1.4657	100	0.709

4% IPA in Hexane 1mL/min OD

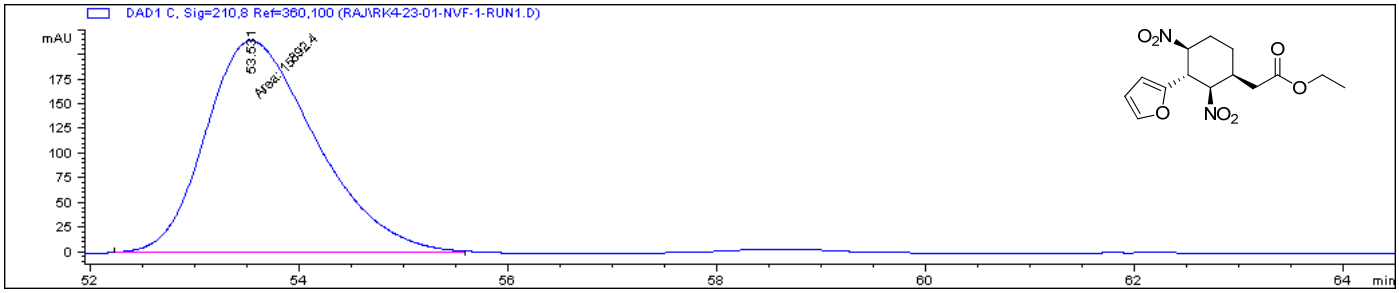
Racemic **3g**



Time	Area	Height	Width	Area%	Symmetry	
53.17	14520.7		185.3	1.3061	49.021	0.445
62.26	15100.9		189	1.3316	50.979	0.835

2% IPA in Hexane 1mL/min AD-H

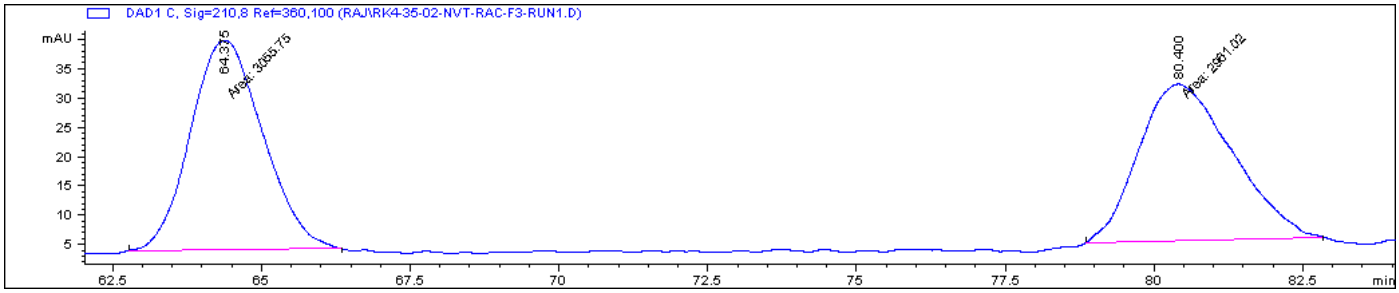
Enantio enriched **3g**



Time	Area	Height	Width	Area%	Symmetry	
53.53	15892.4		215.2	1.2308	100	0.681

2% IPA in Hexane 1mL/min AD-H

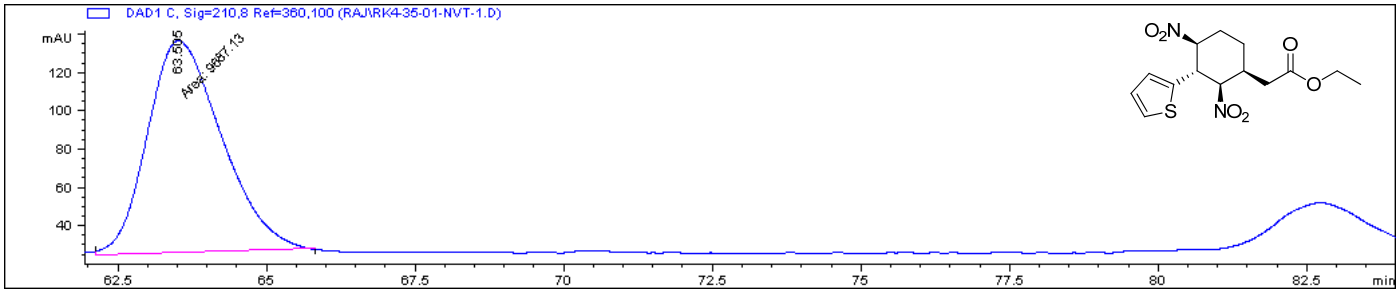
Racemic **3h**



Time	Area	Height	Width	Area%	Symmetry
64.37	3055.7	35.9	1.4197	50.787	0.881
80.4	2961	26.9	1.8338	49.213	0.726

3% IPA in Hexane 1mL/min AD-H

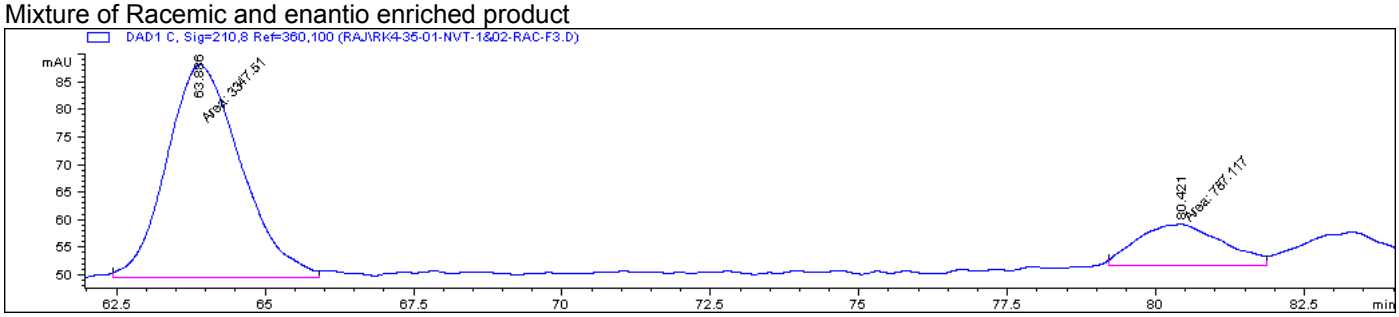
Enantio enriched **3h**



Time	Area	Height	Width	Area%	Symmetry
63.50	9687.1	111	1.4539	100	0.704

3% IPA in Hexane 1mL/min AD-H

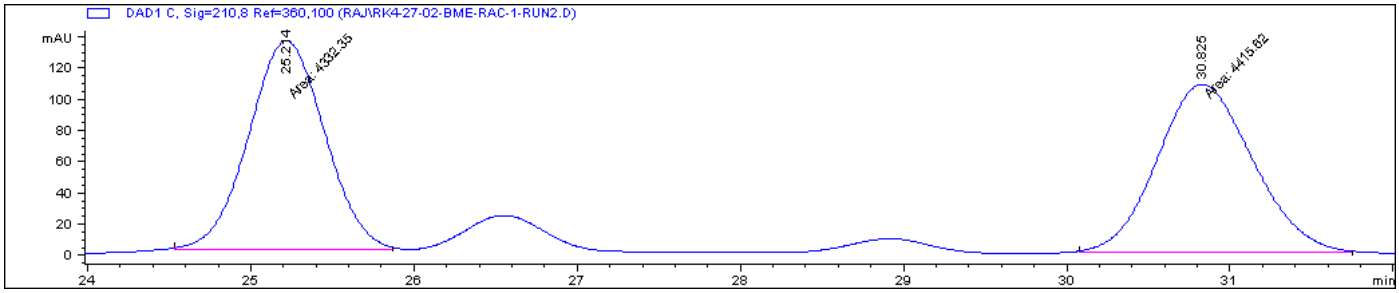
Mixture of Racemic and enantio enriched product



Time	Area	Height	Width	Area%	Symmetry
63.886	3347.5	38.6	1.4444	80.963	0.776
80.42	787.1	7.7	1.7076	19.037	0.999

3% IPA in Hexane 1mL/min AD-H

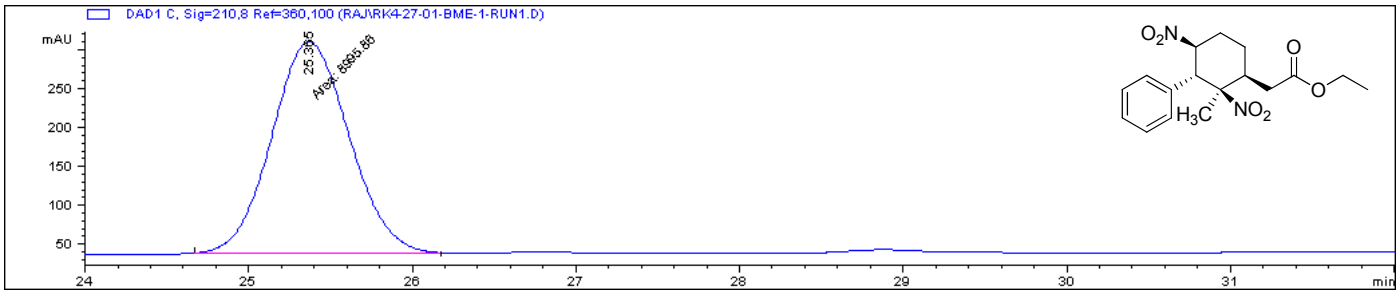
Racemic **3i**



Time	Area	Height	Width	Area%	Symmetry
25.21	4332.3	133.9	0.5393	49.524	0.969
30.825	4415.6	108.2	0.6805	50.476	0.865

4% IPA in Hexane 1mL/min AD-H

Enantio enriched **3i**

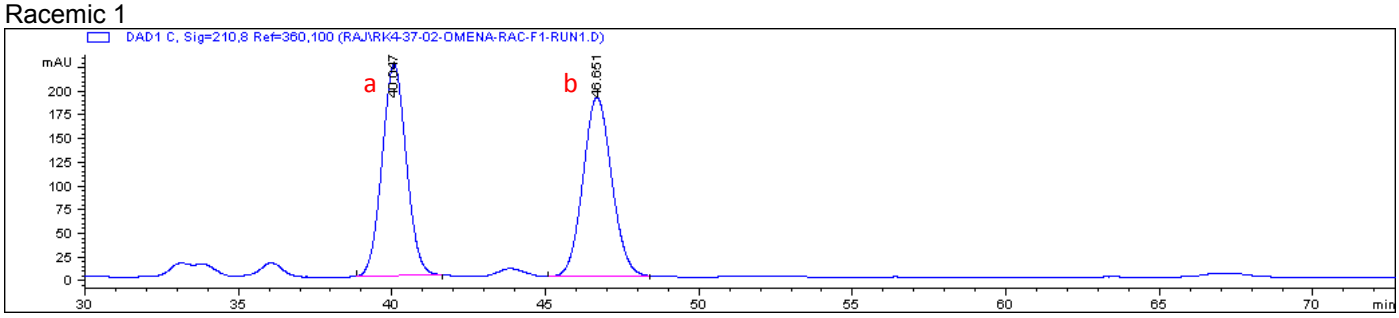


Time	Area	Height	Width	Area%	Symmetry
25.365	8995.9	272.6	0.5501	100	0.903

4% IPA in Hexane 1mL/min AD-H

Racemic **13**

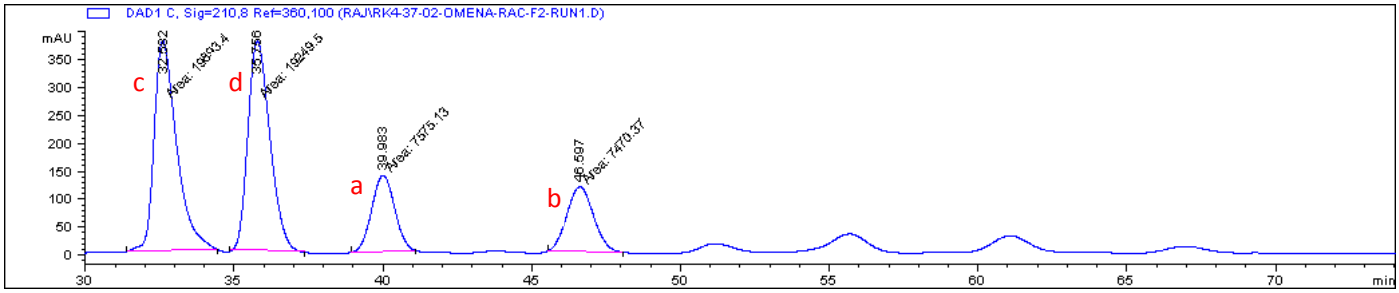
Racemic 1



Time	Area	Height	Width	Area%	Symmetry
40.04	12375.6	223.4	0.8622	50.081	0.938
46.65	12335.5	189.2	1.0007	49.919	0.894

3% IPA in Hexane 1mL/min AD-H

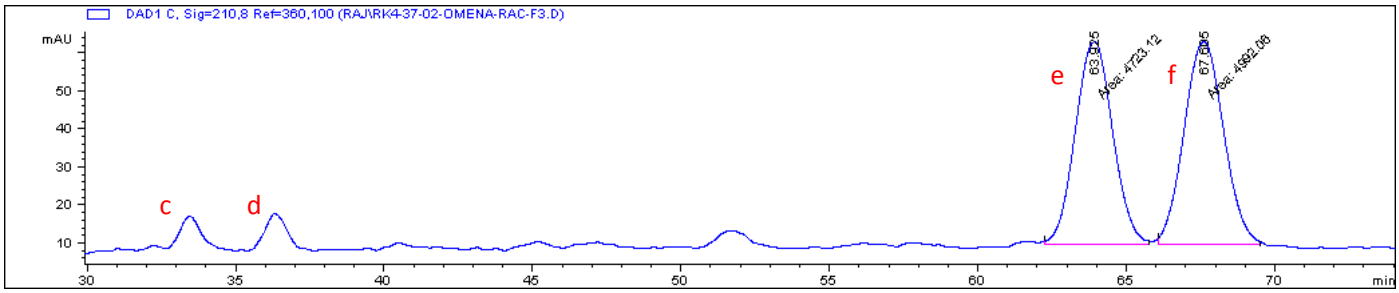
Racemic 2



Time	Area	Height	Width	Area%	Symmetry
32.58	19893.4	376.7	0.8801	36.712	0.61
35.75	19249.5	374.9	0.8558	35.523	0.713
39.98	7575.1	138.6	0.9107	13.979	0.959
46.59	7470.4	117.4	1.0609	13.786	0.888

3% IPA in Hexane 1mL/min AD-H

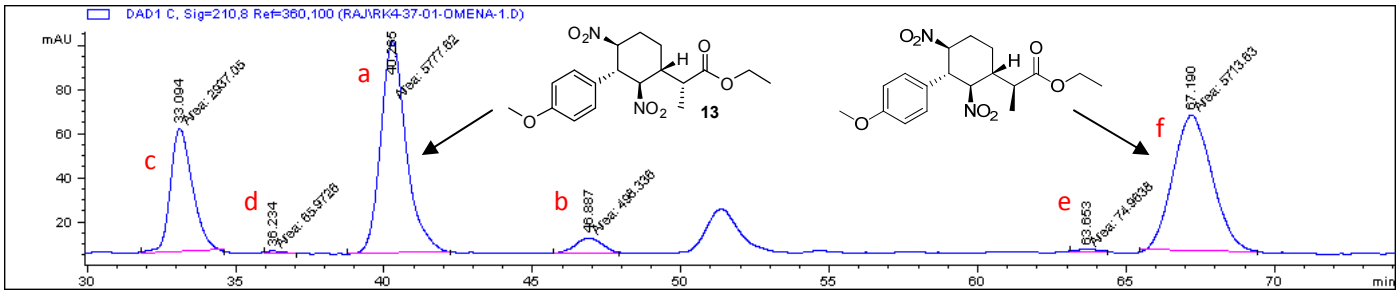
Racemic 3



Time	Area	Height	Width	Area%	Symmetry
63.92	4723.1	53.5	1.4714	48.616	1.054
67.60	4992.1	53.5	1.5541	51.384	0.997

3% IPA in Hexane 1mL/min AD-H

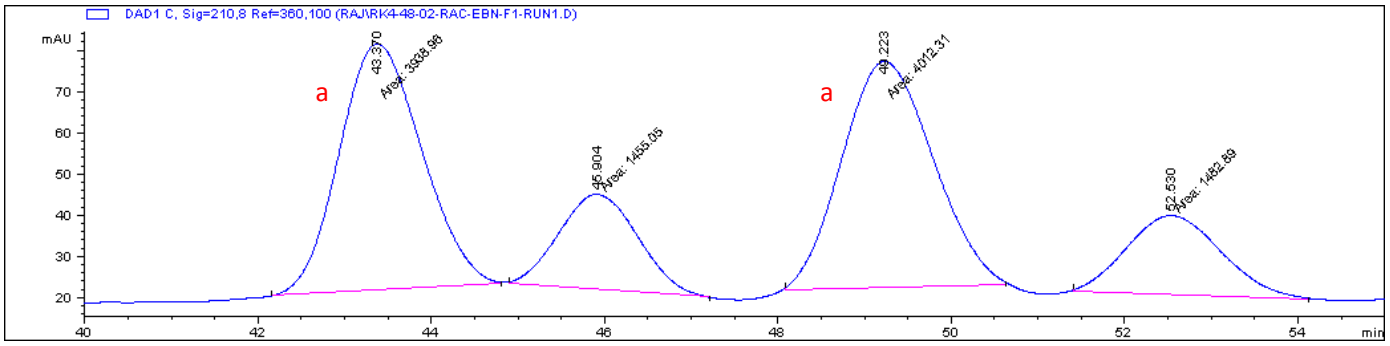
Enantio enriched **13**



Time	Area	Height	Width	Area%	Symmetry
33.09	2937.1	56.2	0.8716	19.493	0.727
36.23	66	1.6	0.6844	0.438	0.469
40.26	5777.6	96	1.0034	38.345	0.826
46.88	498.3	7.3	1.1305	3.307	1.025
63.65	75	1.4	0.9186	0.498	0.845
67.19	5713.6	61.9	1.5383	37.92	0.89

3% IPA in Hexane 1mL/min AD-H

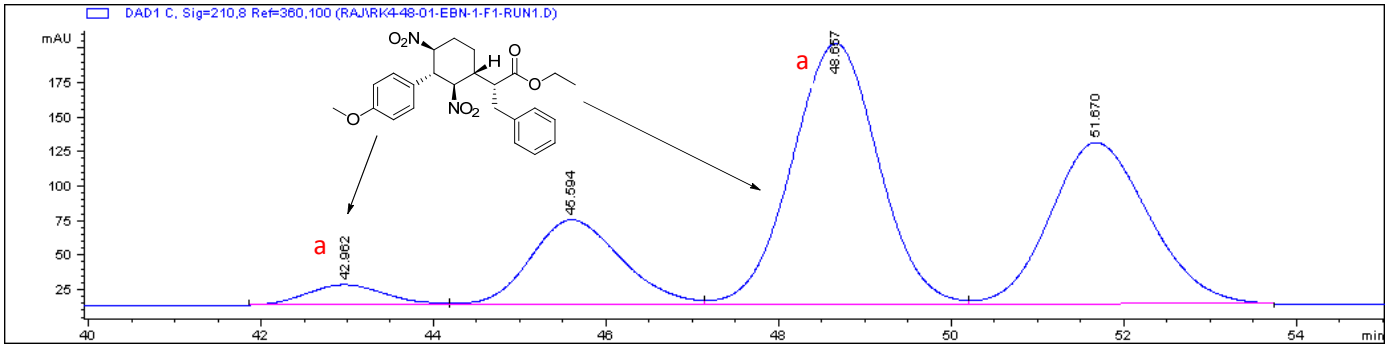
Racemic **14**



Time	Area	Height	Width	Area%	Symmetry
43.37	3939	59.7	1.0997	36.173	0.839
45.90	1455.1	23	1.0526	13.362	0.852
49.22	4012.3	55	1.2165	36.847	0.859
52.53	1482.9	19.4	1.2758	13.618	0.836

5% IPA in Hexane 1mL/min AD-H
RK4-48-02-Rac-EBn-f1

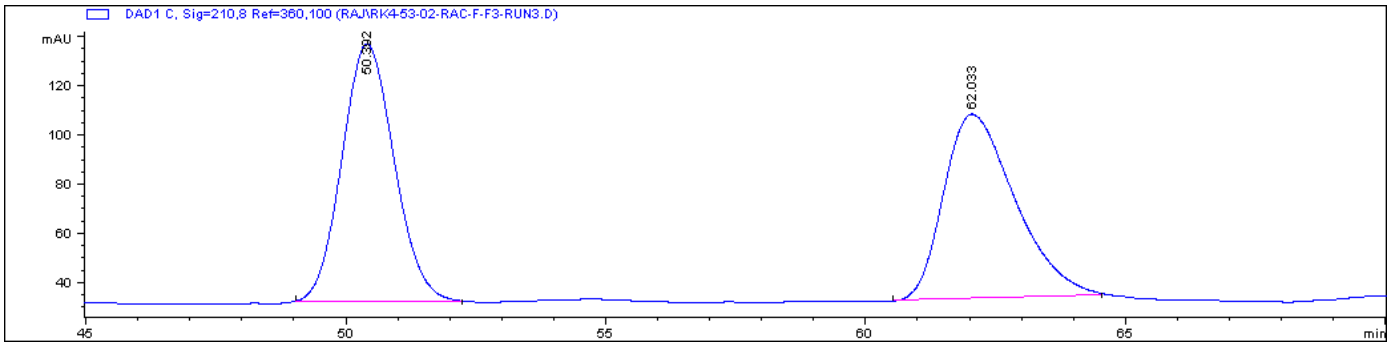
Enantio enriched **14**



Time	Area	Height	Width	Area%	Symmetry
42.96	946.1	14.7	0.8715	3.378	0.887
45.59	4523.8	61.6	1.1245	16.15	0.796
48.65	13184.2	189.3	1.0887	47.066	1.004
51.67	9357.8	117.2	1.2155	33.406	0.831

5% IPA in Hexane 1mL/min AD-H
RK4-48-01-EBn-1-f1

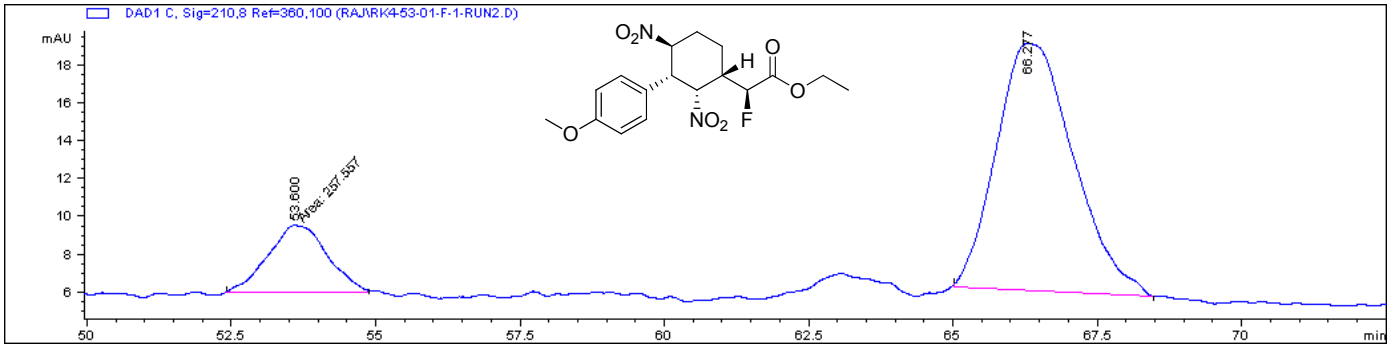
Racemic **16**



Time	Area	Height	Width	Area%	Symmetry
50.39	7359.2	104.9	1.0883	50.639	0.883
62.03	7173.3	75	1.4292	49.361	0.624

5% IPA in Hexane 1mL/min AD-H
RK4-53-02-Rac-F-f3. Run3

Enantio enriched **16**



Time	Area	Height	Width	Area%	Symmetry
53.6	257.6	3.6	1.2016	17.459	0.857
66.27	1217.6	13.1	1.192	82.541	0.638

5% IPA in Hexane 1mL/min AD-H
RK4-53-01-F-1. Run2

The authors would like to thank Amelia Lucy Cobb (Age 4¾) for modeling her finger in the graphical abstract.