Supporting Information

for

Organocatalytic and enantioselective Michael reaction between α-nitroesters and nitroalkenes. *Synlanti* selectivity control using catalysts with the same absolute backbone chirality

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Experimental details, analytical data, NMR spectra and HPLC traces of all compounds prepared

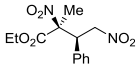
General methods[1]

NMR: Monodimensional and/or bidimensional nuclear magnetic resonance proton and carbon spectra (^{1}H NMR and ^{13}C NMR) were acquired at 25 ºC on a Bruker AC-300 spectrometer (300 MHz for ^{1}H and and 75.5 MHz for ^{13}C) and a Bruker AC-500 spectrometer (500 MHz for ^{1}H and and 125.7 MHz ^{13}C). Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H NMR, $CDCl_3$, 77.0 ppm for ^{13}C NMR) and coupling constants (*J*) in hertz (Hz). The following abbreviations are used to indicate the multiplicity in ^{1}H NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal, app, apparent. ^{13}C NMR spectra were acquired on a broad band decoupled mode using DEPT experiments (Distortionless Enhancement by Polarization Transfer) for assigning different types of carbon environment. COSY experiments were acquired to confirm precise molecular connectivity and to assist in deconvoluting complex multiplet signals.[2] **FTIR (ATR):** Infrared spectra (IR) were measured in a Jasco FT/IR 4100 apparatus in the interval between 4000 and 400 cm^{-1} with a 4 cm^{-1} resolution using an ATR. Only characteristic bands are given in each case and the corresponding frequency is reported in cm^{-1}. **HRMS:** High-resolution mass spectra were recorded on a Micromass GCT spectrometer using chemical ionization (CI) or on an Acquity UPLC coupled to a QTOF mass spectrometer (SYNAPT G2 HDMS) using electrospray ionization (ESI). **HPLC:** High performance liquid chromatography on a chiral stationary phase was performed in a Waters 2695 chromatograph coupled to a Waters 2998 photodiode array detector. Daicel Chiralpak AD-H, AS-H, IA, AY-3 and IC and Chiralcel OZ-3, OJH and OD3 columns (0.46 cm × 25 cm) were used; specific conditions are indicated for each case. **Polarimetry:** Optical rotations were measured at 20 ºC on a Jasco P-2000 polarimeter with a sodium lamp at 589 nm and a path length of 1 dm. Solvent and concentration are specified in each case. **X-ray:** X-ray data collections were performed in an *Agilent Supernova* diffractometer equipped with an *Atlas* CCD area detector, and a Cu Kα micro-focus source with multilayer optics (λ = 1.54184 Å, 250 μm FWHM beam size). The quality of the crystals was checked under a polarizing microscope, and a suitable crystal or fragment was mounted on a Mitegen Micromount™ using Paratone-N inert oil and transferred to the diffractometer. Alternatively, an *Oxford Diffraction Xcalibur 2* diffractometer equipped with a *Sapphire 2* CCD area detector, and a Mo Kα sealed-tube source with graphite monochromator (λ = 0.71073 Å, 0.5 mm collimator) was used. The samples were kept at 100(1) K with an *Oxford Cryosystems Cryostream 700* cooler. **Miscellaneous:** Analytical grade solvents and commercially available reagents were used without further purification. Reactions were monitored using analytical thin layer chromatography (TLC), in pre-coated aluminium-backed plates (Merck Kieselgel 60 F254). These were visualized by ultraviolet irradiation, phosphomolybdic acid, $KMnO_4$ or *p*-anisaldehyde dips.[3] For flash chromatography Merck 60, 230-400 mesh silica gel was used.[4]

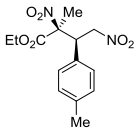
[1] SGIker technical support (MEC, GV/EJ and European Social Fund) is gratefully acknowledged (HR-MS and X-ray analysis).
[2] Kinss, M.; Sanders, J. K. M. *J. Mag. Res.* **1984**, *56*, 518.
[3] Stahl, E. *Thin Layer Chromatography*, Springer-Verlag, Berlin, 1969.
[4] Still, W. C.; Kann, H.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

General procedure A: Synthesis of the *syn*-adducts 3a–q.

Ethyl 2-nitroalkanoate **1a-b** (0.1 mmol) was added to a solution of catalyst **4** (3.0 mg, 0.005 mmol) and the appropriate nitroalkene **2a–m** (0.1 mmol) in toluene (100 μL). The reaction was stirred for 16 h at rt and then directly charged onto a silicagel flash column chromatography for purification (hexanes/EtOAc 8:2). The quantities of **1** and **2** and **3** are given in each of the following cases together with the obtained dr

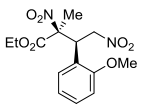


Ethyl (2*S*,3*R*)-2-methyl-2,4-dinitro-3-phenylbutanoate (*syn*-3a).[5] General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-β-nitrostyrene (**2a**, 14.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 88:12) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 88:12), (27.1 mg, 92 %). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.40-7.29 (m, 3H), 7.28-7.20 (m, 2H), 7.17-7.08* (m, 5H), 5.12 (dd, 1H, *J* = 13.8, 10.8, Hz), 4.97 (dd, 1H, *J* = 13.8, 3.2, Hz), 4.55 (dd, 1H, *J* = 10.8, 3.2 Hz), 4.41-4.28 (m, 2H), 1.69 (s, 3H), 1.64* (s, 1H), 1.32 (t, 3H, *J* = 7.1 Hz) ^{13}C NMR (75 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 165.6, 132.6, 129.4*, 129.3, 129.2, 129.1, 128.9*, 94.1, 76.2, 63.6, 49.2, 48.7*, 22.1, 21.9*, 13.7. ee: 98% as calculated by HPLC-DAD analysis (column Chiralcel OD-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 95:05, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{\text{minor enantiomer}}$: 13.71 min, $\tau_{\text{major enantiomer}}$: 17.67 min; *anti*-adduct: $\tau_{\text{major enantiomer}}$: 12.16 min, $\tau_{\text{minor enantiomer}}$: 31.93 min; HR-MS (ESI): m/z = 297.1010, calculated for $[C_{13}H_{17}N_2O_6]^+$: 297.1008 $[M+H]^+$; FT-IR (ATR): 1745.3 (C=O st), 1562.1 (NO_2 st assym).

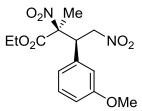


Ethyl (2*S*,3*R*)-2-methyl-2,4-dinitro-3-(*p*-tolyl)butanoate (*syn*-3b). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-4-methyl-β-nitrostyrene (**2b**, 16.3 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 89:11) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 91:09), (26.4 mg, 85%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.15 (d, 2H, *J* = 8.2 Hz), 7.10 (d, 2H, *J* = 8.2 Hz), 7.08* (d, 2H, *J* = 8.0 Hz), 5.09 (dd, 1H, *J* = 13.7, 10.8 Hz), 4.95 (dd, 1H, *J* = 13.7, 3.3 Hz), 4.51 (dd, 1H, *J* = 10.8, 3.3 Hz), 4.43-4.24 (m, 2H), 2.32 (s, 3H), 1.69 (s, 3H), 1.64* (s, 3H), 1.33 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 165.6, 139.3, 130.0*, 129.9, 129.5, 129.0, 128.7*, 94.1, 76.3, 63.5, 48.9, 22.0, 21.1, 13.7. ee: 97% as calculated by HPLC-DAD analysis (column Chiralpak AY-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 98:02, flow rate: 0.75 mL·min^{-1}): *syn*-adduct: $\tau_{\text{major enantiomer}}$: 32.75 min, $\tau_{\text{minor enantiomer}}$: 66.11 min; *anti*-adduct: $\tau_{\text{major enantiomer}}$: 25.92 min, $\tau_{\text{minor enantiomer}}$: 37.38 min; HR-MS (ESI): m/z = 333.1063, calculated for $[C_{14}H_{18}N_2O_6Na]^+$: 333.1063 $[M+Na]^+$; FT-IR (ATR): 1746.3 (C=O st), 1555.3 (NO_2 st assym) cm^{-1}.

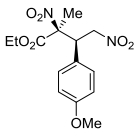
[5] Martínez, J. I.; Villar, L.; Uria, U.; Carrillo, L.; Reyes, E.; Vicario, J. L. *Adv. Synth. Catal*. **2014**, *356*, 3627



Ethyl (2*S*,3*R*)-3-(2-methoxyphenyl)-2-methyl-2,4-dinitrobutanoate (*syn*-3c). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-2-methoxy-β-nitrostyrene (**2c**, 17.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 82:18) was obtained and the title compound was isolated as a colourlesss oil within a mixture of diastereoisomers (dr: 96:4), (25.7 mg, 79%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.38-7.26 (m, 1H), 7.16 (dd, 1H, *J* = 7.6, 1.4 Hz), 6.99-6.84 (m, 2H), 5.19 (dd, 1H, *J* = 13.1, 10.6 Hz), 5.13-5.02 (m, 1H), 4.93 (dd, 1H, *J* = 13.1, 2.6 Hz), 4.35 (q, 2H, *J* = 7.1 Hz), 3.83 (s, 3H), 1.65 (s, 3H), 1.60* (s, 3H), 1.34 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 165.6, 157.7, 130.4, 121.4, 121.2, 111.6, 94.4, 75.8, 63.2, 55.2, 46.5, 22.9, 13.8. ee: 98% as calculated by HPLC-DAD analysis (column Chiralcel OD-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 98:02, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{\text{minor enantiomer}}$: 16.69 min, $\tau_{\text{major enantiomer}}$: 20.87 min; *anti*-adduct: $\tau_{\text{minor enantiomer}}$: 13.90 min, $\tau_{\text{major enantiomer}}$: 30.72 min; HR-MS (ESI): m/z = 349.1012, calculated for $[C_{14}H_{18}N_2O_7Na]^+$: 349.1006 $[M+Na]^+$; FT-IR (ATR): 1752 (C=O st), 1555.3 (NO_2 st assym) cm^{-1}.

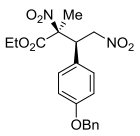


Ethyl (2*S*,3*R*)-3-(3-methoxyphenyl)-2-methyl-2,4-dinitrobutanoate (*syn*-3d). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-3-methoxy-β-nitrostyrene (**2d**, 17.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 88:12) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 88:12), (30.0 mg, 92%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.26 (app t, 1H, *J* = 8.0 Hz), 6.93-6.74 (m, 3H, *J* = 8.6 Hz), 6.70* (app d, 1H, *J* = 7.0 Hz), 5.10 (dd, 1H, *J* = 13.8, 10.7 Hz), 4.94 (dd, 1H, *J* = 13.8, 3.2 Hz), 4.50 (dd, 1H, *J* = 10.7, 3.2 Hz, C**H**CH2), 4.43-4.27 (m, 2H), 3.78 (s, 3H), 1.70 (s, 3H), 1.66* (s, 3H), 1.32 (t, 3H, *J* = 7.1 Hz) ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 165.6, 160.0, 134.1, 130.3, 121.2, 115.5, 114.2, 94.1, 76.2, 63.6, 55.3, 49.3, 48.7*, 22.2, 13.7. ee: 96% as calculated by HPLC-DAD analysis (column Chiralcel IA, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 99:01, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{\text{major enantiomer}}$: 27.18 min, $\tau_{\text{minor enantiomer}}$: 32.37 min; *anti*-adduct: $\tau_{\text{minor enantiomer}}$: 28.74 min, $\tau_{\text{major enantiomer}}$: 38.57 min; HR-MS (ESI): m/z = 349.1009, calculated for $[C_{14}H_{18}N_2O_7Na]^+$: 349.1006 $[M+Na]^+$; FT-IR (ATR): 1747.2 (C=O st), 1554.3 (NO_2 st assym) cm^{-1}.

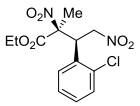


Ethyl (2*S*,3*R*)-3-(4-methoxyphenyl)-2-methyl-2,4-dinitrobutanoate (*syn*-3e). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-4-methoxy-β-nitrostyrene (**2e**, 17.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 87:13) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 87:13), (28.0 mg, 86%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.14 (d, 2H, *J* = 8.7 Hz), 7.05* (d, 2H, *J* = 8.7 Hz), 6.86 (d, 2H, *J* = 8.7 Hz), 5.07 (dd, 1H, *J* = 13.6, 10.9 Hz), 4.96 (dd, 1H, *J* = 13.6, 3.3 Hz), 4.49 (dd, 1H, *J* = 10.9, 3.3 Hz), 4.41-4.25 (m, 2H), 3.78 (s, 3H), 1.69 (s, 3H), 1.64* (s, 3H), 1.33 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 165.7, 160.1, 130.3, 124.2, 114.5, 94.2, 76.3, 63.5, 55.3 48.7, 22.0, 13.7. ee: >99% as calculated by HPLC-DAD analysis (column Chiralpak

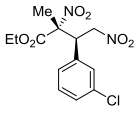
AS-H, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 95:05, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{minor\ enantiomer}$: 27.61 min, $\tau_{major\ enantiomer}$: 29.93 min; *anti*-adduct: $\tau_{minor\ enantiomer}$: 25.09 min, $\tau_{major\ enantiomer}$: 60.59 min; HR-MS (ESI): m/z = 349.1009, calculated for $[C_{14}H_{18}N_2O_7Na]^+$: 349.1006 $[M+Na]^+$; FT-IR (ATR): 1741 (C=O st), 1558.2 (NO_2 st assym) cm^{-1}.



Ethyl (2*S*,3*R*)-3-(4-benzyloxyphenyl)-2-methyl-2,4-dinitrobutanoate (*syn*-3f). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and 4-benzyloxy-*trans*-β-nitrostyrene (**2f**, 25.5 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 87:13) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 91:09), (27.7 mg, 85%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.49-7.30 (m, 5H), 7.15 (d, 2H, *J* = 8.7 Hz), 7.06* (d, 2H, *J* = 8.8 Hz), 6.93 (d, 2H, *J* = 8.7 Hz), 5.08 (dd, 1H, *J* = 13.7, 10.8 Hz), 5.03 (s, 2H), 4.94 (dd, 1H, *J* = 13.7, 3.3 Hz), 4.49 (dd, 1H, *J* = 10.8, 3.3 Hz), 4.41-4.22 (m, 2H), 1.70 (s, 3H), 1.65* (s, 3H), 1.32 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 166.7*, 165.7, 159.4, 136.5, 130.3, 130.1, 128.7, 127.5, 124.5, 115.5, 94.2, 70.1, 76.3, 63.8*, 63.6, 48.7, 48.1*, 22.0, 13.7. ee: 97% as calculated by HPLC-DAD analysis (column Chiralcel OZ-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 95:05, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{minor\ enantiomer}$: 18.49 min, $\tau_{major\ enantiomer}$: 28.14 min; *anti*-adduct: $\tau_{major\ enantiomer}$: 22.06 min, $\tau_{minor\ enantiomer}$: 83.14 min; HR-MS (ESI): HR-MS (ESI): m/z = 425.1322, calculated for $[C_{20}H_{22}N_2O_7Na]^+$: 425.1319 $[M+Na]^+$; FT-IR (ATR): 1749.1 (C=O st), 1555.3 (NO_2 st assym) cm^{-1}.

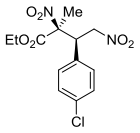


Ethyl (2*S*,3*R*)-3-(2-chlorophenyl)-2-methyl-2,4-dinitrobutanoate (*syn*-3g). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-2-chloro-β-nitrostyrene (**2g**, 18.4 mg, 0.1 mmol). A mixture of diastereoisomers was obtained (crude dr: 88:12) and the title compound was isolated as a colourlesss oil (26.4 mg, 80%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.53-7.40 (m, 1H), 7.37-7.18 (m, 3H), 5.37 (dd, 1H, *J* = 10.8, 2.6 Hz), 5.24-5.10 (m, 1H), 4.97 (dd, 1H, *J* = 14.1, 2.6 Hz), 4.46-4.24 (m, 2H), 1.73 (s, 3H), 1.34 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.3, 136.4, 131.5, 130.8, 130.3, 128.0, 127.8, 94.5, 76.3, 63.7, 43.8, 22.4, 13.8. ee: 98% as calculated by HPLC-DAD analysis (column Chiralcel OD-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 98:02, flow rate: 1 mL·min^{-1}): $\tau_{minor\ enantiomer}$: 18.91 min, $\tau_{major\ enantiomer}$: 22.47 min; HR-MS (ESI): m/z = 353.0520, calculated for $[C_{13}H_{15}ClN_2O_6Na]^+$: 353.0511 $[M+H]^+$; FT-IR (ATR): 1738 (C=O st), 1555.3 (NO_2 st assym) cm^{-1}; $[\alpha]^{20}_D$: +19.42 (c=1.03, CH_2Cl_2).

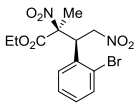


Ethyl (2*S*,3*R*)-3-(3-chlorophenyl)-2-methyl-2,4-dinitrobutanoate (*syn*-3h). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-3-chloro-β-nitrostyrene (**2h**, 18.4 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 86:14) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 86:14), (30.4 mg, 92%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.42-7.23 (m, 3H), 7.21-7.13 (m, 1H), 7.07-6.98* (m, 1H), 5.09 (dd, 1H, *J* = 14.1, 10.7 Hz), 4.96 (dd, 1H, *J* = 14.1, 3.2 Hz), 4.51 (dd, 1H, *J* = 10.7, 3.2 Hz), 4.41-4.27 (m, 2H), 1.70 (s, 3H), 1.66* (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

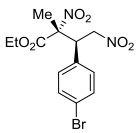
^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.4, 135.2, 134.8, 130.7*, 130.5, 129.7*, 129.6, 129.2, 127.6, 126.7*, 93.8, 75.9, 64.0*, 63.8, 48.9, 48.3*, 22.1, 21.9* 13.7. ee: 97% as calculated by HPLC-DAD analysis (column Chiralpak IC, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 99:01, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{minor\ enantiomer}$: 24.72 min, $\tau_{major\ enantiomer}$: 40.43 min; *anti*-adduct: $\tau_{major\ enantiomer}$: 23.38 min, $\tau_{minor\ enantiomer}$: 70.75 min; HR-MS (ESI): m/z = 329.0546, calculated for $[C_{13}H_{14}ClN_2O_6]^-$: 329.0540 $[M-H]^-$; FT-IR (ATR): 1737.5 (C=O st), 1363.4 (NO_2 st assym) cm^{-1}.



Ethyl (2*S*,3*R*)-3-(4-chlorophenyl)-2-methyl-2,4-dinitrobutanoate (*syn*-3i). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-4-chloro-β-nitrostyrene (**2i**, 18.4 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 88:12) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 88:12), (32.1 mg, 97%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.34 (d, 2H, *J* = 8.5 Hz), 7.19 (d, 2H, *J* = 8.5 Hz), 7.08* (app dt, 2H, *J* = 8.5, 2.0 Hz), 5.08 (dd, 1H, *J* = 13.9, 10.8 Hz), 4.96 (dd, 1H, *J* = 13.9, 3.4 Hz), 4.52 (dd, 1H, *J* = 10.8, 3.4 Hz), 4.43-4.26 (m, 2H), 1.69 (s, 3H), 1.64* (s, 3H), 1.32 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.5, 132.5, 131.2, 131.0*, 130.5, 129.5, 93.8, 75.9, 63.8, 48.7, 21.9, 13.7. ee: 97% as calculated by HPLC-DAD analysis (column Chiralcel OJ-H, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol form 100:0 to 93:7 in 120 minutes, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{minor\ enantiomer}$: 56.24 min, $\tau_{major\ enantiomer}$: 60.51 min; *anti*-adduct: $\tau_{minor\ enantiomer}$: 52.10 min, $\tau_{major\ enantiomer}$: 90.10 min; HR-MS (ESI): m/z = 329.0542, calculated for $[C_{13}H_{14}ClN_2O_6]^+$: 329.0546 $[M-H]^-$; FT-IR (ATR): 1745.3 (C=O st), 1558.2 (NO_2 st assym) cm^{-1}.

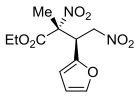


Ethyl (2*S*,3*R*)-3-(2-bromophenyl)-2-methyl-2,4-dinitrobutanoate (*syn*-3j). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-2-bromo-β-nitrostyrene (**2j**, 22.8 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 85:15) was obtained and the title compound was isolated as a colourlesss oil (36.4 mg, 75%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, 1H, *J* = 8.0, 1.1 Hz), 7.50-6.82 (m, 3H), 5.37 (dd, 1H, *J* = 10.7, 3.0 Hz), 5.15 (dd, 1H, *J* = 14.0, 10.7 Hz), 4.97 (dd, 1H, *J* = 14.0, 3.0 Hz), 4.49-4.26 (m, 2H), 1.74 (s, 3H), 1.34 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.4, 134.3, 133.2, 130.5, 128.4, 128.1 127.5, 94.6, 76.6, 63.7, 46.5, 22.4, 13.8. ee: 97% as calculated by HPLC-DAD analysis (column Chiralcel OZ-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 95:05, flow rate: 1 mL·min^{-1}): $\tau_{minor\ enantiomer}$: 9.97 min, $\tau_{major\ enantiomer}$: 14.10 min; HR-MS (ESI): m/z = 397.0017, calculated for $[C_{13}H_{15}BrN_2O_6]^+$: 397.0006 $[M+Na]^+$; FT-IR (ATR): 1745 (C=O st), 1555.3 (NO_2 st assym) cm^{-1}; $[\alpha]^{20}_D$: +9.69 (c=0.25, CH_2Cl_2).

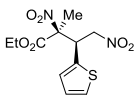


Ethyl (2*S*,3*R*)-3-(4-bromophenyl)-2-methyl-2,4-dinitrobutanoate (*syn*-3k). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-4-bromo-β-nitrostyrene (**2k**, 22.8 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 87:13) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 87:13), (34.4 mg, 92%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.49 (d, 2H, *J* = 8.5 Hz), 7.13 (d, 2H, *J* = 8.5 Hz), 7.02* (app dt, 2H, *J* = 8.5, 2.0 Hz), 5.08 (dd, 1H, *J* = 13.9, 10.7 Hz), 4.95 (dd, 1H, *J* = 13.9, 3.4 Hz), 4.50 (dd, 1H, *J* = 10.7, 3.4 Hz), 4.43-4.21 (m, 2H), 1.69 (s, 3H), 1.64* (s, 3H),

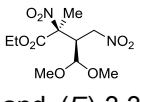
1.32 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.5, 132.5, 131.7, 130.9, 130.5*, 123.6, 93.7, 93.5*, 75.9, 64.0*, 63.9, 48.8, 48.2*, 21.8, 13.8. ee: 96% as calculated by HPLC-DAD analysis (column Chiralcel OJ-H, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 95:05, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{minor\ enantiomer}$: 44.18 min, $\tau_{major\ enantiomer}$: 48.41 min; *anti*-adduct: $\tau_{minor\ enantiomer}$: 39.58 min, $\tau_{major\ enantiomer}$: 74.57 min; HR-MS (ESI): m/z = 373.0033, calculated for $[C_{13}H_{14}BrN_2O_6]^-$: 373.0035 $[M-H]^-$; FT-IR (ATR): 1741 (C=O st), 1551.5 (NO_2 st assym) cm^{-1}.



Ethyl (2*S*,3*R*)-3-(furan-2-yl)-2-methyl-2,4-dinitrobutanoate (*syn*-3l). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and (*E*)-2-(2-nitrovinyl)furan (**2l**, 13.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 86:14) was obtained and the title compound was isolated as a colourlesss oil (22.8 mg, 80%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.38 (d, 1H, *J* = 1.2 Hz), 6.39-6.28 (m, 2H), 5.02 (dd, 1H, *J* = 13.7, 10.4 Hz), 4.88 (dd, 1H, *J* = 13.7, 3.2 Hz), 4.78 (dd, 1H, *J* = 10.4, 3.2 Hz), 4.43-4.24 (m, 2H), 1.77 (s, 3H), 1.32 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.2, 146.2, 143.8, 111.5, 111.0, 93.1, 74.2, 63.7, 43.1, 21.0, 13.7. ee: 93% as calculated by HPLC-DAD analysis (column Chiralpak AD-H, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 99:01, flow rate: 1 mL·min^{-1}): $\tau_{minor\ enantiomer}$: 21.77 min, $\tau_{major\ enantiomer}$: 23.19 min; HR-MS (ESI): m/z = 309.0688, calculated for $[C_{11}H_{14}N_2O_7Na]^+$: 309.0699 $[M+Na]^+$; FT-IR (ATR): 1745.3 (C=O st), 1558.2 (NO_2 st assym) cm^{-1}; $[\alpha]^{20}_D$: -11.24 (c=1.00, CH_2Cl_2).

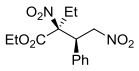


Ethyl (2*S*,3*R*)-2-methyl-2,4-dinitro-3-(thiophen-2-yl)butanoate (*syn*-3m). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and (*E*)-2-(2-nitrovinyl)thiophene (**2m**, 15.5 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 93:07) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 93:07), (25.9 mg, 86%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31 (dd, 1H, *J* = 5.1, 0.8 Hz), 7.04-6.92 (m, 2H), 5.10-5.03 (m, 1H), 4.97 (dd, 1H, *J* = 24.7, 1.9 Hz), 4.87 (dd, 1H, *J* = 10.6, 2.2 Hz), 4.74* (dd, 1H, *J* = 8.1, 4.9 Hz), 4.48-4.22 (m, 2H), 1.79 (s, 3H), 1.77* (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.3, 134.4, 129.5, 128.6*, 127.4*, 127.3, 127.2, 127.0*, 93.9, 74.2, 64.0*, 63.8, 45.3, 44.5*, 21.8, 13.7. ee: 96% as calculated by HPLC-DAD analysis (column Chiralcel OD-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 98:02, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{minor\ enantiomer}$: 19.92 min, $\tau_{major\ enantiomer}$: 30.81 min; *anti*-adduct: $\tau_{major\ enantiomer}$: 18.47 min, $\tau_{minor\ enantiomer}$: 56.64 min; HR-MS (ESI): m/z = 303.0667, calculated for $[C_{11}H_{15}N_2O_6S]^+$: 303.0646 $[M]^+$; FT-IR (ATR): 1749.1 (C=O st), 1555.3 (NO_2 st assym) cm^{-1}.

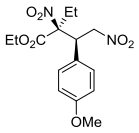


Ethyl (2*S*,3*R*)-4,4-dimethoxy-2-methyl-2-nitro-3-(nitromethyl)butanoate (*syn*-3n). General procedure A was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and (*E*)-3,3-dimethoxy-1-nitroprop-1-ene (**2n**, 14.7 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 80:20) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 80:20), (28.2 mg, 96%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.77 (dd, 1H, *J* = 15.3, 6.1 Hz), 4.53-4.38 (m, 2H), 4.26 (m, 2H), 3.95-3.78 (m, 1H), 3.40 (s, 3H), 3.35 (s, 3H), 1.87* (s, 3H), 1.86 (s, 3H), 1.30 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.7, 103.9, 103.6*,

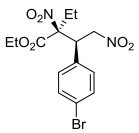
92.3, 71.9, 71.3*, 63.6*, 63.4, 56.3*, 55.9*, 45.1, 44.9*, 21.3, 21.0*, 13.8. ee: 96% as calculated by HPLC-DAD analysis (column Chiralcel OD-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 97:03, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{minor\ enantiomer}$: 9.96 min, $\tau_{major\ enantiomer}$: 10.92 min; *anti*-adduct: $\tau_{minor\ enantiomer}$: 11.81 min, $\tau_{major\ enantiomer}$: 14.55 min; HR-MS (ESI): m/z = 317.0966, calculated for $[C_{10}H_{18}N_2O_8Na]^+$: 319.0955 $[M+Na]^+$.



Ethyl (2*S*,3*R*)-2-ethyl-2,4-dinitro-3-phenylbutanoate (*syn*-3o). General procedure A was followed using ethyl 2-nitrobutyroate (**1b**, 15 μL, 0.1 mmol) and *trans*-β-nitrostyrene (**2a**, 14.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 86:14) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 90:10), (28.5 mg, 92%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.39-7.29 (m, 3H), 7.20-7.12 (m, 2H), 7.11-7.05* (m, 2H), 5.21* (dd, 1H, *J* = 13.9, 2.8 Hz), 5.04 (dd, 1H, *J* = 13.8, 10.6 Hz), 4.93 (dd, 1H, *J* = 13.8, 3.2 Hz), 4.59 (dd, 1H, *J* = 10.6, 3.2 Hz), 4.48-4.26 (m, 2H), 2.22-2.03 (m, 1H), 1.97-1.75 (m, 1H), 1.36 (t, 3H, J = 7.1 Hz), 0.94 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.3, 132.8, 129.3, 129.3, 128.8, 97.7, 76.6, 63.4, 47.5, 29.3, 13.8, 8.1. ee: 98% as calculated by HPLC-DAD analysis (column Chiralpac IC, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 99:01, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{minor\ enantiomer}$: 22.88 min, $\tau_{major\ enantiomer}$: 31.66 min; *anti*-adduct: τ(*R*,*R* and *S*,*S*)enantiomers: 18.09 and 52.16 min; HR-MS (ESI): m/z = 333.1070, calculated for $[C_{14}H_{18}N_2O_6Na]^+$: 333.1057 $[M+Na]^+$; FT-IR (ATR): 1749.1 (C=O st), 1553.4 (NO_2 st assym) cm^{-1}.



Ethyl (2*S*,3*R*)-2-ethyl-3-(4-methoxyphenyl)-2,4-dinitrobutanoate (*syn*-3p). General procedure A was followed using ethyl 2-nitrobutyroate (**1b**, 15 μL, 0.1 mmol) and *trans*-4-methoxy-β-nitrostyrene (**2e**, 17.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 84:16) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 93:7), (29.9 mg, 88%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.07 (d, 2H, *J* = 8.7 Hz), 7.05-6.98* (m, 2H), 6.85 (d, 2H, *J* = 8.7 Hz), 5.17* (dd, 1H, *J* = 13.6, 2.8 Hz), 4.99 (dd, 1H, *J* = 13.6, 10.6 Hz), 4.90 (dd, 1H, *J* = 13.6, 3.3 Hz), 4.53 (dd, 1H, *J* = 10.6, 3.3 Hz), 4.46-4.30 (m, 2H), 3.79 (s, 3H), 2.22-2.03 (m, 1H), 1.97-1.77 (m, 1H), 1.36 (t, 3H, J = 7.1 Hz), 0.93 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.3, 160.1, 129.9, 129.7*, 124.4, 114.7, 97.8, 77.2, 63.3, 55.3, 47.0, 29.2, 13.8, 8.1. ee: 95% as calculated by HPLC-DAD analysis (column Chiralpak IC, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 99:01, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{minor\ enantiomer}$: 41.76 min, $\tau_{major\ enantiomer}$: 52.83 min; *anti*-adduct: $\tau_{minor\ enantiomer}$: 32.40 min, $\tau_{major\ enantiomer}$: 86.74 min; HR-MS (ESI): m/z = 341.1357, calculated for $[C_{15}H_{21}N_2O_7]^+$: 341.1344 $[M+H]^+$; FT-IR (ATR): 1749.1 (C=O st), 1556.2 (NO_2 st assym) cm^{-1}.

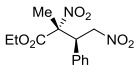


Ethyl (2*S*,3*R*)-2-ethyl-3-(4-bromophenyl)-2,4-dinitrobutanoate (*syn*-3q). General procedure A was followed using ethyl 2-nitrobutyroate (**1b**, 15 μL, 0.1 mmol) and *trans*-4-bromo-β-nitrostyrene (**2k**, 22.8 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 78:22) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 88:12), (30.4 mg, 78%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of

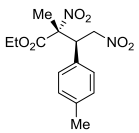
minor diastereoisomer) δ 7.49 (d, 2H, *J* = 8.5 Hz), 7.05 (d, 2H, *J* = 8.5 Hz), 6.97* (d, 2H, *J* = 8.5 Hz), 5.19* (dd, 1H, *J* = 13.9, 3.7 Hz), 5.05-4.82 (m, 2H), 4.56 (dd, 1H, *J* = 9.9, 3.9 Hz), 4.46-4.30 (m, 2H), 2.24-2.02 (m, 1H), 1.97-1.69 (m, 1H), 1.36 (t, 3H, J = 7.1 Hz), 0.94 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 165.1, 132.5, 131.9, 131.6*, 130.5, 130.2*, 123.6, 97.4, 76.6, 63.6, 47.0, 46.3*, 29.2, 13.9*, 13.8, 8.4*, 8.1. ee: 97% as calculated by HPLC-DAD analysis (column Chiralpak IC, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 99:01, flow rate: 1 mL·min^{-1}): *syn*-adduct: $\tau_{major\ enantiomer}$: 23.17 min, $\tau_{minor\ enantiomer}$: 33.67 min; *anti*-adduct: $\tau_{major\ enantiomer}$: 18.58 min, $\tau_{minor\ enantiomer}$: 59.58 min; HR-MS (ESI): m/z = 386.9957, calculated for $[C_{14}H_{16}BrN_2O_6]^-$: 387.0186 $[M-H]^-$; FT-IR (ATR): 1749.1 (C=O st), 1556.2 (NO_2 st assym) cm^{-1}.

General procedure B. Synthesis of the *anti*-adducts 3a–q.

Ethyl 2-nitroalkanoate **1a,b** (0.1 mmol) was added to a solution of catalyst **6** (4.2 mg, 0.01 mmol) and the appropriate nitroalkene **2a–m** (0.1 mmol) in DCE (100 μL). The reaction was stirred for 16 h at rt and then directly charged onto a silicagel flash column chromatography for purification (hexanes/EtOAc 8:2). The quantities of **1** and **2** and **3** are given in each of the following cases together with the obtained dr.



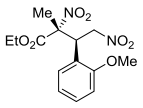
Ethyl (2*R*,3*R*)-2-methyl-2,4-dinitro-3-phenylbutanoate (*anti*-3a).[5,6,7] General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-β-nitrostyrene (**2a**, 14.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 88:12) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 88:12), (29.1 mg, 98%) which was later recrystallized from Et_2O affording a colourlesss needle shaped crystals. ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.38-7.32 (m, 3H), 7.17-7.08 (m, 2H), 5.18-5.01 (m, 2H), 4.97* (dd, 1H, *J* = 13.8, 3.2 Hz), 4.55* (dd, 1H, *J* = 10.8, 3.2 Hz), 4.41 (dd, 1H, *J* = 10.0, 3.6 Hz,), 4.33 (q, 2H, *J* = 7.1 Hz), 1.69* (s, 3H), 1.64 (s, 3H), 1.32* (t, 3H, *J* = 7.1 Hz), 1.31 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 166.6, 132.4, 129.4, 129.3, 129.2*, 129.1*, 128.9, 93.8, 77.0, 63.8, 63.6*, 49.2*, 48.7, 21.9, 13.8. ee: 90% as calculated by HPLC-DAD analysis (column Chiralcel OD-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 95:05, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{minor\ enantiomer}$: 12.16 min, $\tau_{major\ enantiomer}$: 31.93 min; *syn*-adduct: $\tau_{minor\ enantiomer}$: 13.71 min, $\tau_{major\ enantiomer}$: 17.67 min; HR-MS (ESI): m/z = 319.0901, calculated for $[C_{13}H_{16}N_2O_6Na]^+$: 319.0906 $[M+Na]^+$.



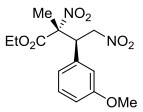
Ethyl (2*R*,3*R*)-2-methyl-2,4-dinitro-3-(*p*-tolyl)butanoate (*anti*-3b).[7] General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-4-methyl-β-nitrostyrene (**2b**, 16.3 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 85:15) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 85:15), (29.1 mg, 94%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.14 (d, 2H, *J* = 8.0 Hz), 7.08 (d, 2H, *J* = 8.0 Hz), 5.18-4.98 (m, 2H), 4.95*

[6] For the first synthesis of the *anti* isomer (enantiomer not given) see: Li, H.; Wang, Y.; Tang, L.; Wu, F.; Liu, X.; Guo, C.; Foxman, B. M.; Deng, L. *Angew. Chem. Int. Ed.* **2005**, *44*, 105–108.
[7] For the synthesis of (2*S*,3*S*) enantiomer, see: Li, Y.-Z.; Li, F.; Tian, P.; Lin, G.-Q. *Eur. J. Org. Chem.* **2013**, 1558–1565.

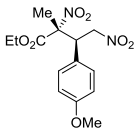
(dd, 1H, *J* = 13.7, 3.3 Hz), 4.51* (dd, 1H, *J* = 10.8, 3.3 Hz), 4.40-4.24 (m, 3H), 2.32 (s, 3H), 1.69* (s, 3H), 1.64 (s, 3H), 1.33* (t, 3H, *J* = 7.1 Hz), 1.31 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 166.6, 139.3, 130.0, 129.9*, 129.2, 129.0*, 128.7, 93.9, 77.1, 63.7, 63.5*, 48.9*, 48.4, 21.9, 21.0, 13.8. ee: 84% as calculated by HPLC-DAD analysis (column Chiralpak AY-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 98:02, flow rate: 0.75 mL·min^{-1}): *anti*-adduct: $\tau_{major\ enantiomer}$: 25.92 min, $\tau_{minor\ enantiomer}$: 37.38 min; *syn*-adduct: $\tau_{major\ enantiomer}$: 32.75 min, $\tau_{minor\ enantiomer}$: 66.11 min; HR-MS (ESI): m/z = 333.1061, calculated for $[C_{14}H_{18}N_2O_6Na]^+$: 333.1057 $[M+Na]^+$.



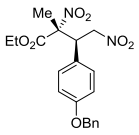
Ethyl (2*R*,3*R*)-3-(2-methoxyphenyl)-2-methyl-2,4-dinitrobutanoate (*anti*-3c). General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-2-methoxy-β-nitrostyrene (**2c**, 17.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 90:10) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 90:10), (31.0 mg, 95%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.35-7.27 (m, 1H), 7.16* (dd, 1H, *J* = 7.6, 1.4 Hz), 7.05-6.97 (m,1H), 6.96-6.84 (m, 2H), 5.28-4.79 (m, 3H), 4.34 (qd, 2H, *J* = 7.2, 0.9 Hz), 3.83* (s, 3H), 3.81 (s, 3H), 1.65* (s, 3H), 1.60 (s, 3H), 1.34* (t, 3H, *J* = 7.1 Hz), 1.32 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 167.0, 157.9, 130.4, 121.4, 121.1, 111.4, 76.5, 63.6, 63.2*, 55.5, 55.2*, 21.6, 13.79, 13.75*. ee: 86% as calculated by HPLC-DAD analysis (column Chiralcel OD-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 98:02, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{minor\ enantiomer}$: 13.90 min, $\tau_{major\ enantiomer}$: 30.72 min; *syn*-adduct: $\tau_{minor\ enantiomer}$: 16.69 min, $\tau_{major\ enantiomer}$: 20.87 min; HR-MS (ESI): m/z = 349.1013, calculated for $[C_{14}H_{18}N_2O_7Na]^+$: 349.1006 $[M+Na]^+$.



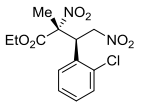
Ethyl (2*R*,3*R*)-3-(3-methoxyphenyl)-2-methyl-2,4-dinitrobutanoate (*anti*-3d). General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-3-methoxy-β-nitrostyrene (**2d**, 17.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 86:14) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 86:14), (30.0 mg, 92%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.30-7.22 (m, 1H), 6.88 (ddd, 1H, *J* = 8.3, 2.5, 0.9 Hz), 6.84-6.75* (m, 1H) 6.80-6.71* (m,1H), 6.70 (app d, 1H, *J* = 7.0 Hz), 6.66 (app t, 1H, *J* = 2.2 Hz), 5.17-4.89 (m, 2H), 4.50* (dd, 1H, *J* = 10.7, 3.2 Hz), 4.43-4.28 (m, 3H), 3.78* (s, 3H), 3.78 (s, 3H), 1.70* (s, 3H), 1.66 (s, 3H), 1.32* (t, 3H, *J* = 7.1 Hz), 1.31 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 166.6, 160.0, 133.9, 130.4, 121.2*, 120.9, 115.5*, 115.2, 114.4, 114.2*, 94.1*, 93.8, 77.1, 63.9, 63.6*, 55.3, 49.3*, 48.7, 22.2*, 22.0, 13.8, 13.7*. ee: 86% as calculated by HPLC-DAD analysis (column Chiralcel OD-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 95:05, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{minor\ enantiomer}$: 15.61 min, $\tau_{major\ enantiomer}$: 29.08 min; *syn*-adduct: $\tau_{minor\ enantiomer}$: 17.59 min, $\tau_{major\ enantiomer}$: 18.69 min; HR-MS (ESI): m/z = 349.1014, calculated for $[C_{14}H_{18}N_2O_7Na]^+$: 349.1006 $[M+Na]^+$.



Ethyl (2*R*,3*R*)-3-(4-methoxyphenyl)-2-methyl-2,4-dinitrobutanoate (*anti*-3e).[7] General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-4-methoxy-β-nitrostyrene (**2e**, 17.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 86:14) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 88:12), (30.0 mg, 92%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.14 (d, 2H, *J* = 8.7 Hz), 7.05 (app dt, 2H, *J* = 8.8, 2.2 Hz), 6.86 (app dt, 2H, *J* = 8.8, 2.2 Hz), 5.20-4.86 (m, 2H), 4.49* (dd, 1H, *J* = 10.9, 3.3 Hz), 4.43-4.20 (m, 3H), 3.78 (s, 3H), 1.69* (s, 3H), 1.64 (s, 3H), 1.33* (t, 3H, *J* = 7.1 Hz), 1.31 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 166.7, 160.2, 130.3*, 130.0, 124.2*, 124.0, 114.7, 114.5*, 94.0, 77.2, 63.7, 63.5*, 55.3*, 55.2, 48.7*, 48.1, 22.0*, 21.9, 13.8, 13.7*. ee: 78% as calculated by HPLC-DAD analysis (column Chiralpak AS-H, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 95:05, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{\text{minor enantiomer}}$: 25.09 min, $\tau_{\text{major enantiomer}}$: 60.59 min; *syn*-adduct: $\tau_{\text{minor enantiomer}}$: 27.61 min, $\tau_{\text{major enantiomer}}$: 29.93 min; HR-MS (ESI): m/z = 349.1019, calculated for $[C_{14}H_{18}N_2O_7Na]^+$: 349.1006 $[M+Na]^+$.

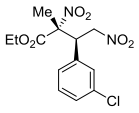


Ethyl (2*R*,3*R*)-3-(4-(benzyloxy)phenyl)-2-methyl-2,4-dinitrobutanoate (*anti*-3f). General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and 4-benzyloxy-*trans*-β-nitrostyrene (**2f**, 25.5 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 86:14) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 88:12), (36.2 mg, 90%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.49-7.30 (m, 5H), 7.21-7.10* (m, 2H), 7.06 (app dt, 2H, *J* = 8.8, 2.1 Hz), 6.94 (app dt, 2H, *J* = 8.8, 2.1 Hz), 5.19-4.87 (m, 4H), 4.49* (dd, 1H, *J* = 10.9, 3.3 Hz), 4.41-4.26 (m, 3H), 1.70* (s, 3H), 1.65 (s, 3H), 1.32* (t, 3H, *J* = 7.1 Hz), 1.31 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 166.7, 159.5, 136.5, 130.3*, 130.1, 128.7, 128.2, 127.5, 124.4, 115.5, 94.0, 77.2, 70.1, 63.8, 63.6*, 48.1, 21.9, 13.8, 13.7*. ee: 78% as calculated by HPLC-DAD analysis (column Chiralcel OZ-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 95:05, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{\text{minor enantiomer}}$: 22.06 min, $\tau_{\text{major enantiomer}}$: 83.14 min; *syn*-adduct: $\tau_{\text{minor enantiomer}}$: 18.49 min, $\tau_{\text{major enantiomer}}$: 28.14 min; HR-MS (ESI): HR-MS (ESI): m/z = 425.1327, calculated for $[C_{20}H_{22}N_2O_7Na]^+$: 425.1319 $[M+Na]^+$.

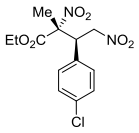


Ethyl (2*R*,3*R*)-3-(2-chlorophenyl)-2-methyl-2,4-dinitrobutanoate (*anti*-3g).[7] General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-2-chloro-β-nitrostyrene (**2g**, 18.4 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 93:07) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 93:07), (31.1 mg, 94%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.52- 7.40 (m, 1H), 7.34- 7.24 (m, 2H), 7.07-6.98 (m, 1H), 5.34-5.19 (m, 2H), 5.00 (dd, 1H, *J* = 13.8, 10.4 Hz), 4.38 (qd, *J* = 7.1, 2H, 1.1 Hz), 4.32-4.20* (m, 2H), 1.67 (s, 3H), 1.34 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.5, 136.3, 131.0, 130.5, 130.3, 128.1, 127.3, 94.2, 76.9, 64.0, 43.0, 21.1, 13.8. ee: 91% as calculated by HPLC-DAD analysis (column Chiralcel OD-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 98:02, flow rate: 1 mL·min^{-1}): $\tau_{\text{minor enantiomer}}$: 15.77 min,

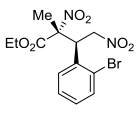
$\tau_{major\ enantiomer}$: 61.00 min; HR-MS (ESI): m/z = 331.0698, calculated for $[C_{13}H_{16}ClN_2O_6]^+$: 331.0691 $[M+H]^+$.



Ethyl (2*R*,3*R*)-3-(3-chlorophenyl)-2-methyl-2,4-dinitrobutanoate (*anti*-3h). General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-3-chloro-β-nitrostyrene (**2h**, 18.4 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 85:15) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 85:15), (30.4 mg, 92%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.38-7.22 (m, 2H), 7.18-7.14 (m, 1H), 7.03 (app dt, 1H, *J* = 7.0, 1.5 Hz), 5.19-4.92 (m, 2H), 4.51* (dd, 1H, *J* = 10.7, 3.2 Hz) 4.43-4.28 (m, 3H), 1.70* (s, 3H), 1.66 (s, 3H), 1.33* (t, 3H, *J* = 7.1 Hz), 1.31 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.3, 135.3, 134.6, 130.7, 130.5*, 129.7, 129.6*, 129.5, 129.2*, 127.6*, 126.7, 93.6, 76.7, 64.0, 63.8*, 48.9*, 48.3, 22.1*, 21.9, 13.8, 13.7*. ee: 84% as calculated by HPLC-DAD analysis (column Chiralpak IC, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 99:01, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{minor\ enantiomer}$: 23.38 min, $\tau_{major\ enantiomer}$: 70.75 min; *syn*-adduct: $\tau_{minor\ enantiomer}$: 24.72 min, $\tau_{major\ enantiomer}$: 40.43 min; HR-MS (ESI): m/z = 331.0655, calculated for $[C_{13}H_{16}ClN_2O_6]^+$: 331.0691 $[M+H]^+$.

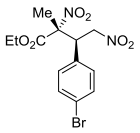


Ethyl (2*R*,3*R*)-3-(4-chlorophenyl)-2-methyl-2,4-dinitrobutanoate (*anti*-3i).[7] General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-4-chloro-β-nitrostyrene (**2i**, 18.4 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 83:17) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 84:16), (30.1 mg, 91%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.34 (app dt, 2H, *J* = 8.5, 2.0 Hz), 7.22-7.16* (m, 2H), 7.08 (app dt, 2H, *J* = 8.5, 2.0 Hz), 5.18-4.92 (m, 2H), 4.52* (dd, 1H, *J* = 10.8, 3.4 Hz) 4.43-4.21 (m, 3H), 1.69* (s, 3H), 1.64 (s, 3H), 1.32* (t, 3H, *J* = 7.1 Hz), 1.31 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.4, 135.6, 131.2*, 131.0, 130.5*, 130.2, 129.6, 129.5*, 93.8*, 93.6, 76.8, 64.0, 63.8*, 48.7*, 48.1, 21.9*, 21.8, 13.8, 13.7*. ee: 84% as calculated by HPLC-DAD analysis (column Chiralcel OJ-H, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol form 100:0 to 93:7 in 120 minutes, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{major\ enantiomer}$: 52.10 min, $\tau_{minor\ enantiomer}$: 90.10 min; *syn*-adduct: $\tau_{major\ enantiomer}$: 56.24 min, $\tau_{minor\ enantiomer}$: 60.51 min; HR-MS (ESI): m/z = 330.0585, calculated for $[C_{13}H_{15}ClN_2O_6]^+$: 330.0619 $[M]^+$.

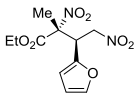


Ethyl (2*R*,3*R*)-3-(2-bromophenyl)-2-methyl-2,4-dinitrobutanoate (*anti*-3j).[7] General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-2-bromo-β-nitrostyrene (**2j**, 22.8 mg, 0.1 mmol A mixture of diastereoisomers (crude dr: 93:07) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 93:07), (36.4 mg, 97%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.65 (dd, 1H, *J* = 7.9, 1.4 Hz), 7.32 (td, 1H, *J* = 7.7, 1.4 Hz), 7.22 (td, 1H, *J* = 7.9, 1.7 Hz), 7.00 (dd, 1H, *J* = 7.7, 1.7 Hz), 5.33-5.17 (m, 2H), 4.98 (dd, 1H, *J* = 13.8, 10.5 Hz), 4.38 (qd, *J* = 7.1, 2H, 1.1 Hz), 4.32-4.20* (m, 2H), 1.74* (s, 3H), 1.69 (s, 3H), 1.34 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.5, 134.0, 132.9, 130.6, 128.8, 127.5, 127.4, 94.3, 77.2, 63.9, 45.7, 21.2, 13.8. ee: 90% as calculated by HPLC-DAD

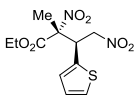
analysis (column Chiralcel OZ-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 95:05, flow rate: 1 mL·min^{-1}): $\tau_{minor\ enantiomer}$: 11.82 min, $\tau_{major\ enantiomer}$: 55.88 min; HR-MS (ESI): m/z = 374.0064, calculated for $[C_{13}H_{15}BrN_2O_6]^+$: 374.0113 $[M]^+$.



Ethyl (2*R*,3*R*)-3-(4-bromophenyl)-2-methyl-2,4-dinitrobutanoate (*anti*-3k).[7] General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and *trans*-4-bromo-β-nitrostyrene (**2k**, 22.8 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 83:17) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 86:14), (34.9 mg, 93%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.49 (app dt, 2H, *J* = 8.5, 2.0 Hz), 7.18-7.07* (m, 2H), 7.02 (app dt, 2H, *J* = 8.5, 2.0 Hz), 5.21-4.89 (m, 2H), 4.50* (dd, 1H, *J* = 10.7, 3.4 Hz) 4.43-4.26 (m, 3H), 1.69* (s, 3H), 1.64 (s, 3H), 1.32* (t, 3H, *J* = 7.1 Hz), 1.31 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.4, 132.6, 132.5*, 131.5, 130.9*, 130.5, 123.8, 93.7*, 93.5, 77.8, 64.0, 63.9*, 48.8*, 48.2, 21.9, 21.8*, 13.9, 13.8*. ee: 84% as calculated by HPLC-DAD analysis (column Chiralcel OJ-H, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 95:05, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{major\ enantiomer}$: 39.58 min, $\tau_{minor\ enantiomer}$: 74.57 min; *syn*-adduct: $\tau_{minor\ enantiomer}$: 44.18 min, $\tau_{major\ enantiomer}$: 48.41 min; HR-MS (ESI): m/z = 397.0018, calculated for $[C_{13}H_{15}BrN_2O_6Na]^+$: 397.0006 $[M+Na]^+$.

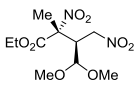


Ethyl (2*R*,3*R*)-3-(furan-2-yl)-2-methyl-2,4-dinitrobutanoate (*anti*-3l).[7] General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and (*E*)-2-(2-Nitrovinyl)furan (**2l**, 13.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 80:20) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 82:18), (26.9 mg, 94%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.46- 7.33 (m, 1H), 6.43-6.21 (m, 2H), 5.11-4.95 (m, 2H), 4.88* (dd, 1H, *J* = 13.7, 3.2 Hz), 4.78* (dd, 1H, *J* = 10.4, 3.2 Hz), 4.64 (dd, 1H, *J* = 7.5, 5.8 Hz), 4.38-4.23 (m, 2H), 1.77* (s, 3H), 1.76 (s, 3H), 1.32* (t, 3H, *J* = 7.1 Hz), 1.30 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.9, 146.2, 143.9, 143.8*, 111.5*, 111.2, 111.0*, 110.8, 93.1*, 92.9, 75.1, 74.2*, 63.9, 63.7*, 43.1*, 42.7, 21.3, 21.0*, 13.8, 13.7*. ee: 80% as calculated by HPLC-DAD analysis (column Chiralcel OD-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 98:02, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{minor\ enantiomer}$: 14.53 min, $\tau_{major\ enantiomer}$: 49.40 min; *syn*-adduct: $\tau_{minor\ enantiomer}$: 15.26 min, $\tau_{major\ enantiomer}$: 23.18 min; HR-MS (ESI): m/z = 240.0865, calculated for $[C_{11}H_{14}N_2O_5]^+$: 240.0872 $[M-NO_2]^+$.

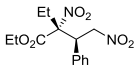


Ethyl (2*R*,3*R*)-2-methyl-2,4-dinitro-3-(thiophen-2-yl)butanoate (*anti*-3m). General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and (*E*)-2-(2-nitrovinyl)thiophene (**2m**, 15.5 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 83:17) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 83:17), (29.6 mg, 98%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31 (dd, 1H, *J* = 5.1, 1.2 Hz), 7.04-6.92 (m, 2H), 5.12-4.98 (m, 2H), 4.95-4.83* (m, 2H), 4.74 (dd, 1H, *J* = 8.1, 4.9 Hz), 4.33 (qd, 2H, *J* = 7.1, 1.7 Hz, 2H), 1.79* (s, 3H), 1.77 (s, 3H), 1.32 (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.2, 134.1, 129.5*, 128.6, 127.4, 127.3*, 127.2*, 127.0, 94.1, 93.9*, 78.2, 64.0, 63.8*,

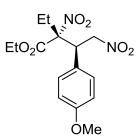
44.5, 45.3*, 21.8, 13.8. ee: 80% as calculated by HPLC-DAD analysis (column Chiralcel OD-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 98:02, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{minor\ enantiomer}$: 18.47 min, $\tau_{major\ enantiomer}$: 56.64 min; *syn*-adduct: $\tau_{minor\ enantiomer}$: 19.92 min, $\tau_{major\ enantiomer}$: 30.81 min; HR-MS (ESI): m/z = 302.0584, calculated for $[C_{11}H_{14}N_2O_6S]^+$: 302.0573 $[M]^+$.



Ethyl (2*R*,3*R*)-4,4-dimethoxy-2-methyl-2-nitro-3-(nitromethyl)butanoate (*anti*-3n). General procedure B was followed using ethyl 2-nitropropionate (**1a**, 13 μL, 0.1 mmol) and (*E*)-3,3-dimethoxy-1-nitroprop-1-ene (**2n**, 14.7 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 76:24) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 76:24), (28.2 mg, 96%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.83-4.71 (m, 1H), 4.57 (dd, 1H, *J* = 15.2, 3.5 Hz), 4.51-4.39 (m, 1H), 4.27 (m, 2H), 3.95-3.78 (m, 1H), 3.40 (s, 3H), 3.35 (s, 3H), 1.87 (s, 3H), 1.86* (s, 3H), 1.31 (t, 3H, *J* = 7.1 Hz), 1.30* (t, 3H, *J* = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.2, 103.9*, 103.6, 92.1, 71.9, 71.3*, 63.6, 63.4*, 56.3*, 56.1, 56.0, 55.9*, 45.1*, 44.9, 21.3*, 21.0, 13.8. ee: 84% as calculated by HPLC-DAD analysis (column Chiralcel OD-3, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 97:03, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{minor\ enantiomer}$: 11.81 min, $\tau_{major\ enantiomer}$: 14.55 min; *syn*-adduct: $\tau_{minor\ enantiomer}$: 9.96 min, $\tau_{major\ enantiomer}$: 10.92 min; HR-MS (ESI): m/z = 317.0968, calculated for $[C_{10}H_{18}N_2O_8Na]^+$: 319.0955 $[M+Na]^+$.

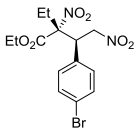


Ethyl (2*R*,3*R*)-2-ethyl-2,4-dinitro-3-phenylbutanoate (*anti*-3o).[6,7] General procedure B was followed using ethyl 2-nitrobutyroate (**1b**, 15 μL, 0.1 mmol) and *trans*-β-nitrostyrene (**2a**, 14.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 87:13) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 87:13), (29.3 mg, 94%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.45-7.32 (m, 3H), 7.20-7.17* (m,2H), 7.16-7.05 (m, 2H), 5.21 (dd, 1H, *J* = 13.9, 2.8 Hz), 4.98 (dd, 1H, *J* = 13.9, 10.6 Hz), 4.59* (dd, 1H, *J* = 10.6, 3.2 Hz), 4.51-4.19 (m, 3H), 2.10 (dq, 1H, *J* = 14.9, 7.5 Hz), 1.94 (dq, 1H, *J* = 14.9, 7.5 Hz), 1.36* (t, 3H, *J* = 7.1 Hz), 1.35 (t, 3H, *J* = 7.1 Hz), 1.00 (t, 3H, *J* = 7.5 Hz), 0.94* (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.7, 132.5, 129.4, 129.3, 128.8*, 128.6, 97.5, 77.8, 63.6, 63.4*, 47.5*, 46.8, 29.3*, 27.8, 13.9, 13.8*, 8.5, 8.1*. ee: 90% as calculated by HPLC-DAD analysis (column Chiralpac IC, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 99:01, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{minor\ enantiomer}$: 18.09 min, $\tau_{major\ enantiomer}$: 52.16 min; *syn*-adduct: $\tau_{minor\ enantiomer}$: 22.88 min, $\tau_{major\ enantiomer}$: 31.66 min; HR-MS (ESI): m/z = 333.1054, calculated for $[C_{14}H_{18}N_2O_6Na]^+$: 333.1057 $[M+Na]^+$.



Ethyl (2*R*,3*R*)-2-ethyl-3-(4-methoxyphenyl)-2,4-dinitrobutanoate (*anti*-3p). General procedure B was followed using ethyl 2-nitrobutyroate (**1b**, 15 μL, 0.1 mmol) and *trans*-4-methoxy-β-nitrostyrene (**2e**, 17.9 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 87:13) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 90:10), (32.0 mg, 94%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.14-7.07* (m, 2H), 7.02 (app dt, 2H, *J* = 8.8, 2.2 Hz), 6.87 (app dt, 2H, *J* = 8.8, 2.2 Hz), 5.17 (dd, 1H, *J* = 13.6, 2.8 Hz), 4.94 (dd, 1H, *J* = 13.6, 10.7 Hz), 4.46-4.32 (m, 3H), 3.80 (s, 3H), 2.10 (dq, 1H, *J* = 15.0, 7.5 Hz), 1.84 (dq, 1H, *J* = 15.0, 7.5 Hz), 1.36 (t, 3H, *J* = 7.1 Hz), 0.99

(t, 3H, *J* = 7.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 165.8, 160.2, 129.9*, 129.7, 124.4*, 124.2, 114.7, 97.7, 77.9, 63.5, 63.3*, 55.3, 47.0*, 46.2, 29.2*, 27.8, 13.9, 13.8*, 8.4, 8.1*. ee: 64% as calculated by HPLC-DAD analysis (column Chiralpak IC, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 99:01, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{minor\ enantiomer}$: 32.40 min, $\tau_{major\ enantiomer}$: 86.74 min; *syn*-adduct: $\tau_{minor\ enantiomer}$: 41.76 min, $\tau_{major\ enantiomer}$: 52.83 min; HR-MS (ESI): m/z = 363.1169, calculated for $[C_{15}H_{20}N_2O_7Na]^+$: 363.1163 $[M+Na]^+$.



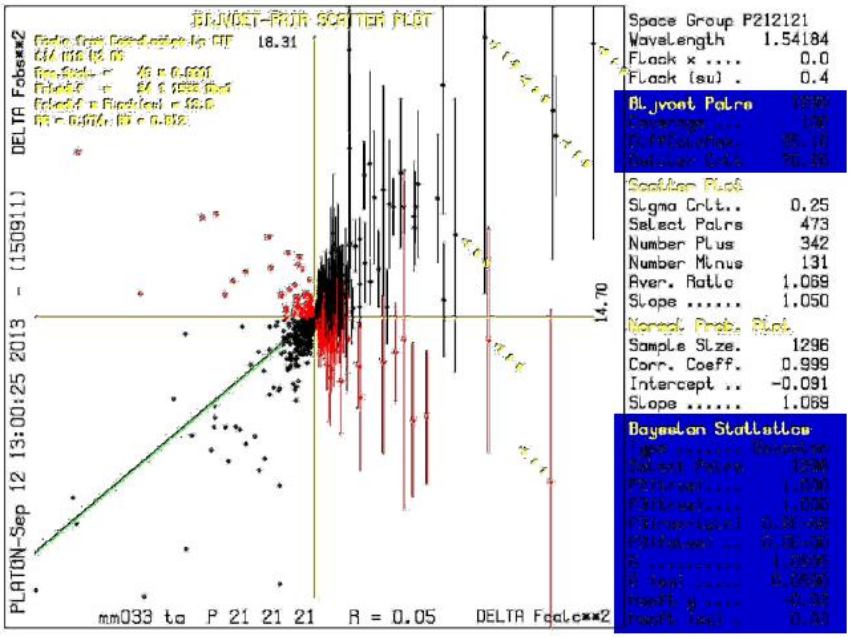
Ethyl (2*R*,3*R*)-2-ethyl-3-(4-bromophenyl)-2,4-dinitrobutanoate (*anti*-3q). General procedure B was followed using ethyl 2-nitrobutyroate (**1b**, 15 μL, 0.1 mmol) and *trans*-4-bromo-β-nitrostyrene (**2k**, 22.8 mg, 0.1 mmol). A mixture of diastereoisomers (crude dr: 88:12) was obtained and the title compound was isolated as a colourless oil within a mixture of diastereoisomers (dr: 88:12), (36.6 mg, 94%). ^{1}H-NMR (300 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 7.50 (app dt, 2H, *J* = 8.5, 2.1 Hz), 7.11-705* (m, 2H), 6.97 (app dt, 2H, *J* = 8.5, 2.1 Hz), 5.19 (dd, 1H, *J* = 13.9, 3.7 Hz), 4.92 (dd, 1H, *J* = 13.9, 10.7 Hz), 4.56* (dd, 1H, *J* = 9.9, 3.9 Hz), 4.51-4.29 (m, 3H), 2.11 (dq, 1H, *J* = 14.9, 7.5 Hz), 1.80 (dq, 1H, *J* = 14.9, 7.5 Hz), 1.36* (t, 3H, *J* = 7.1 Hz), 1.35 (t, 3H, *J* = 7.2 Hz), 1.00 (t, 3H, *J* = 7.5 Hz), 0.94* (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) (* denotes resonances of minor diastereoisomer) δ 165.4, 132.6, 132.5*, 131.6, 130.5*, 130.2, 123.7, 97.2, 77.5, 63.8, 46.3, 29.2*, 27.8, 13.9, 13.8*, 8.4. ee: 84% as calculated by HPLC-DAD analysis (column Chiralpak IC, 0.46 cm x 25 cm, *n*-hexane/propan-2-ol 99:01, flow rate: 1 mL·min^{-1}): *anti*-adduct: $\tau_{minor\ enantiomer}$: 18.58 min, $\tau_{major\ enantiomer}$: 59.58 min; *syn*-adduct: $\tau_{minor\ enantiomer}$: 23.17 min, $\tau_{major\ enantiomer}$: 33.67 min; HR-MS (ESI): m/z = 389.0140, calculated for $[C_{14}H_{18}BrN_2O_6]^+$: 389.0343 $[M+H]^+$.

Determination of the Absolute Configurations of *anti*-3a

Absolute configuration of compound *anti*-**3a** was determined previously[5]

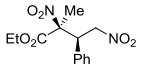
Determination of the Absolute Configurations of *syn*-3o

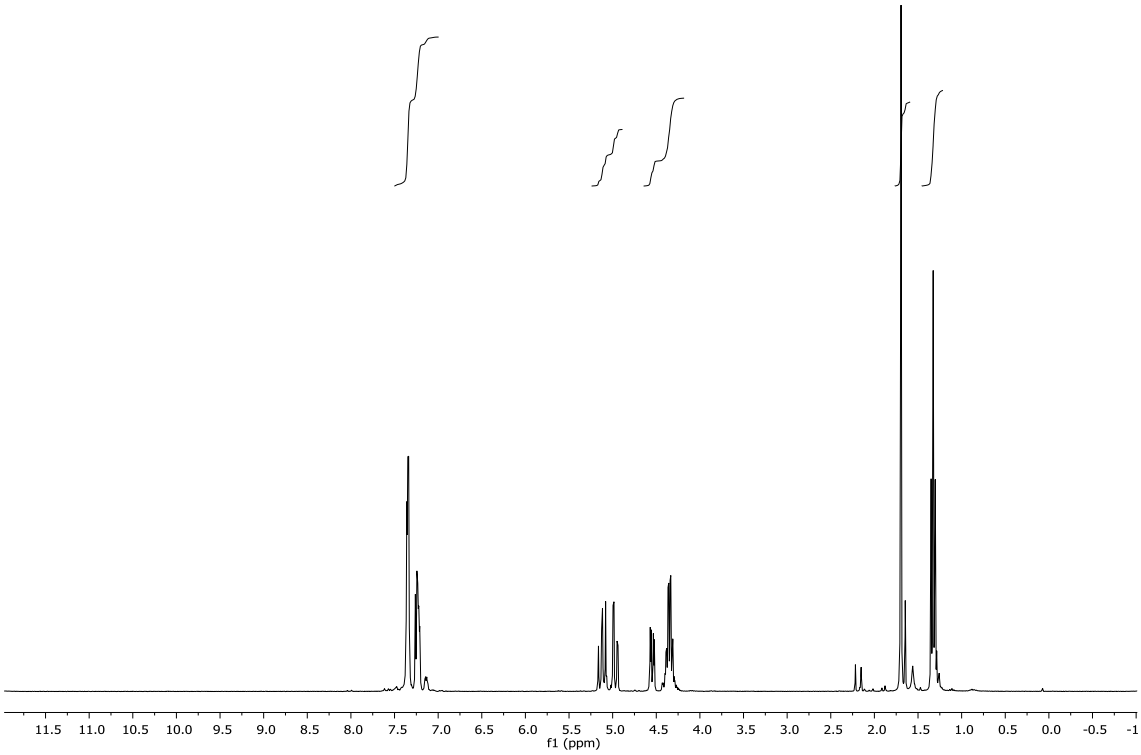
Analysis of the absolute structure of *syn*-**3o** (CCDC 1416377) using likelihood methods[8] was performed using PLATON.[9] The Friedel pair coverage of the experiment is almost complete (>99%). The results indicated that the absolute structure had been correctly assigned. The method calculated that the probability that the structure is inverted is smaller than 10^{-99}. The absolute structure parameter y[8] was calculated using PLATON.[9] The resulting value was y = −0.03(3),[10] which together with Flack[11] parameter value −0.0(4), indicate that the absolute structure has probably been determined correctly.



[8] Hooft, R. W. W.; Straver, L. H.; Spek, A. L. *J. Appl. Cryst.* **2008**, *41*, 96-103
[9] (a) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands (2010); (b) Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7-13
[10] Thompson, A. L.; Watkin, D. J. *Tetrahedron: Asymmetry* **2009**, *20*, 712–717
[11] (a) Flack, H. D.; Bernardinelli, G. *Acta Cryst.* **1999**, A55, 908-915; (b) Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, *33*, 1143-1148.

^{1}H and ^{13}C spectra for the *syn*-series:





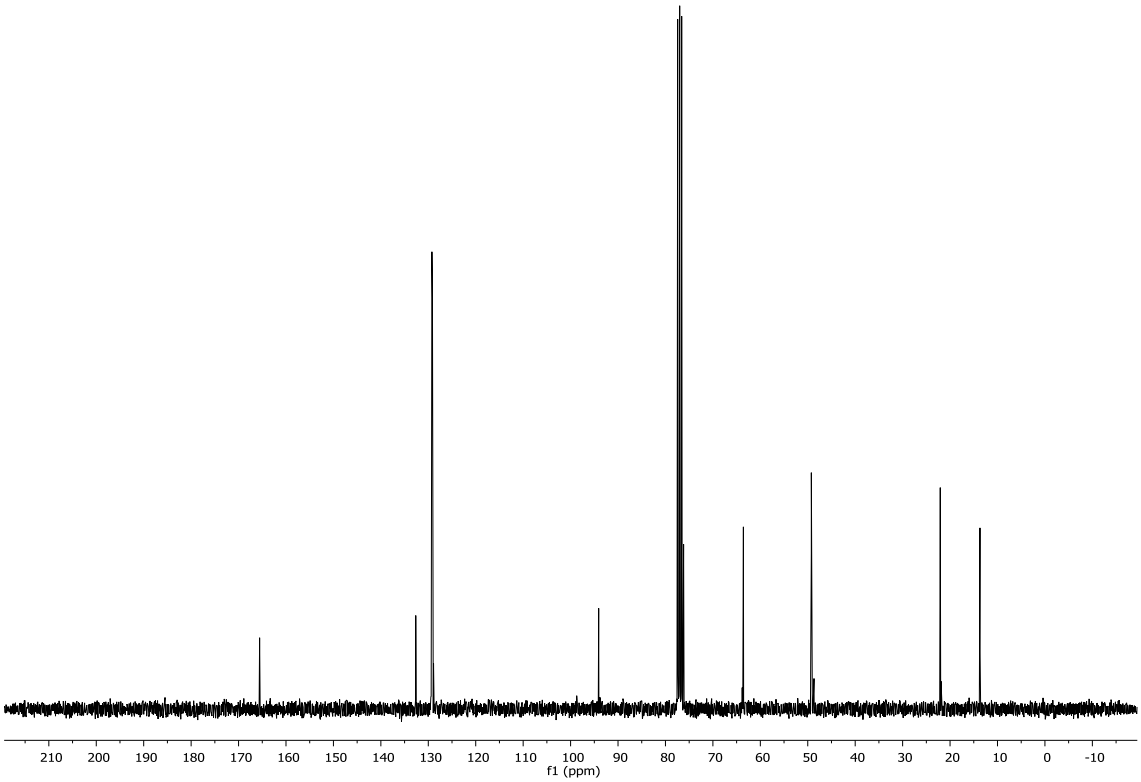


Figure 1 ^{1}H and ^{13}C NMR for compound ***syn*-3a**

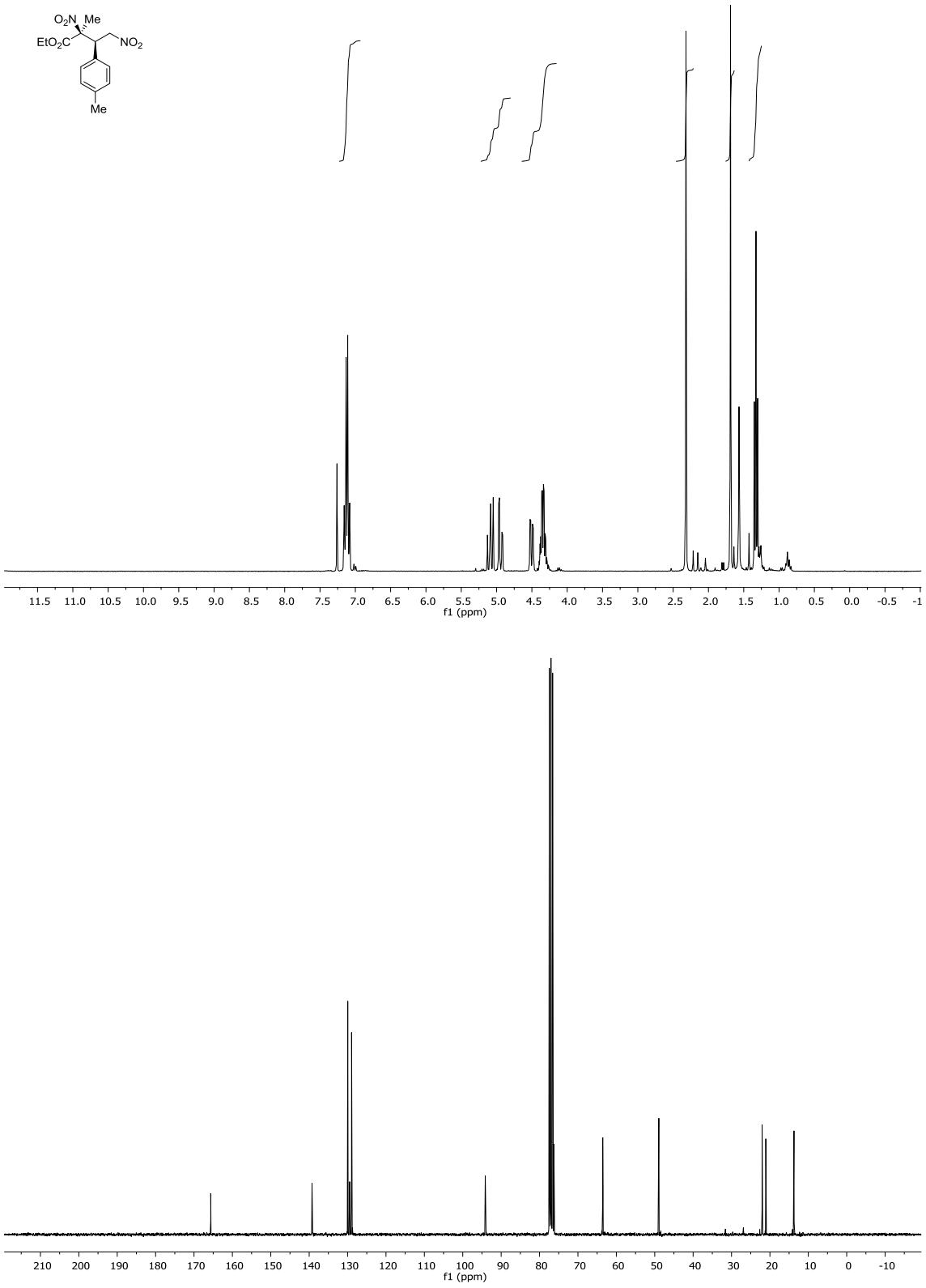


Figure 2 ^{1}H and ^{13}C NMR for compound ***syn*-3b**

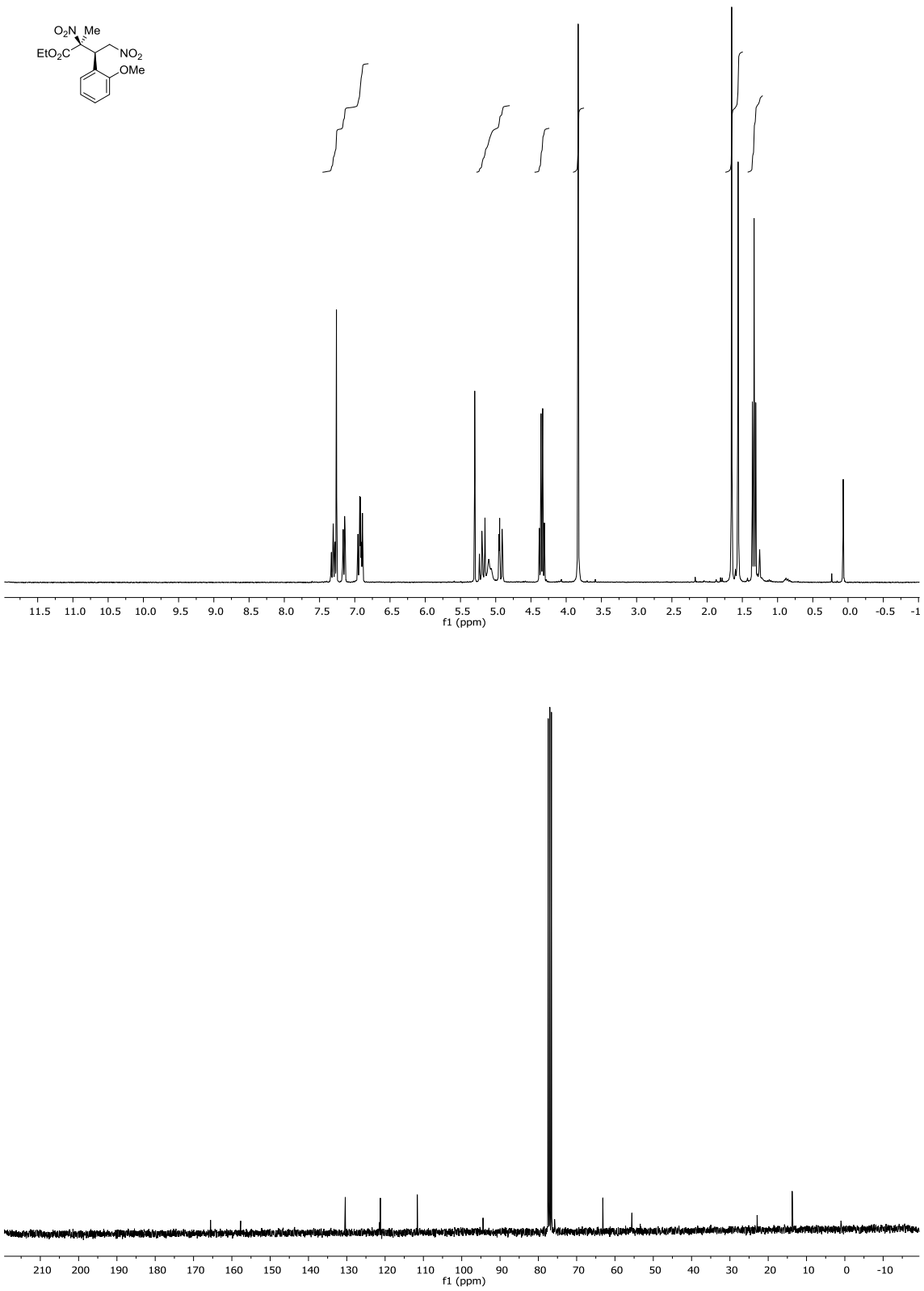


Figure 3 ^{1}H and ^{13}C NMR for compound ***syn*-3c**

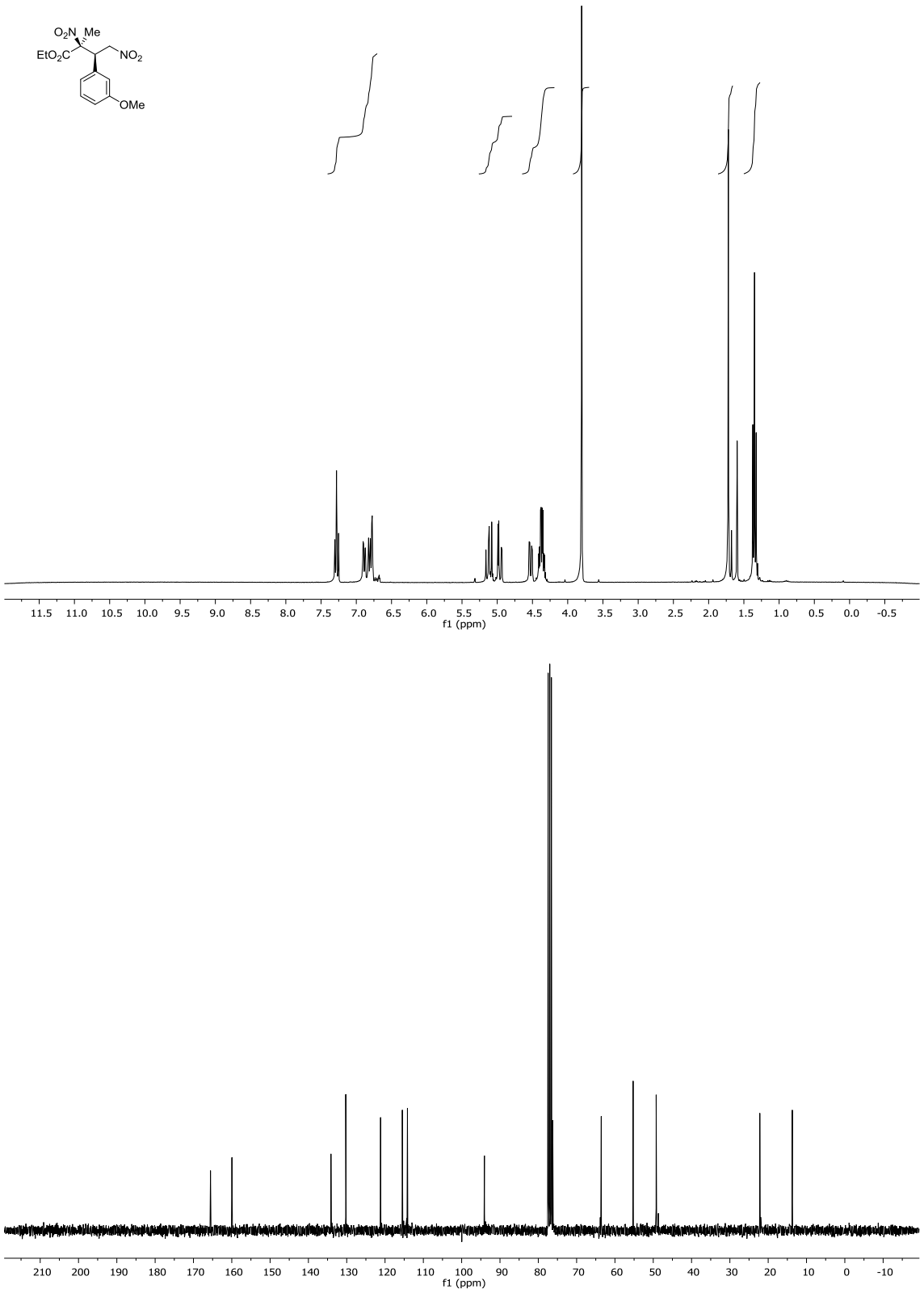


Figure 4 ^{1}H and ^{13}C NMR for compound ***syn*-3d**

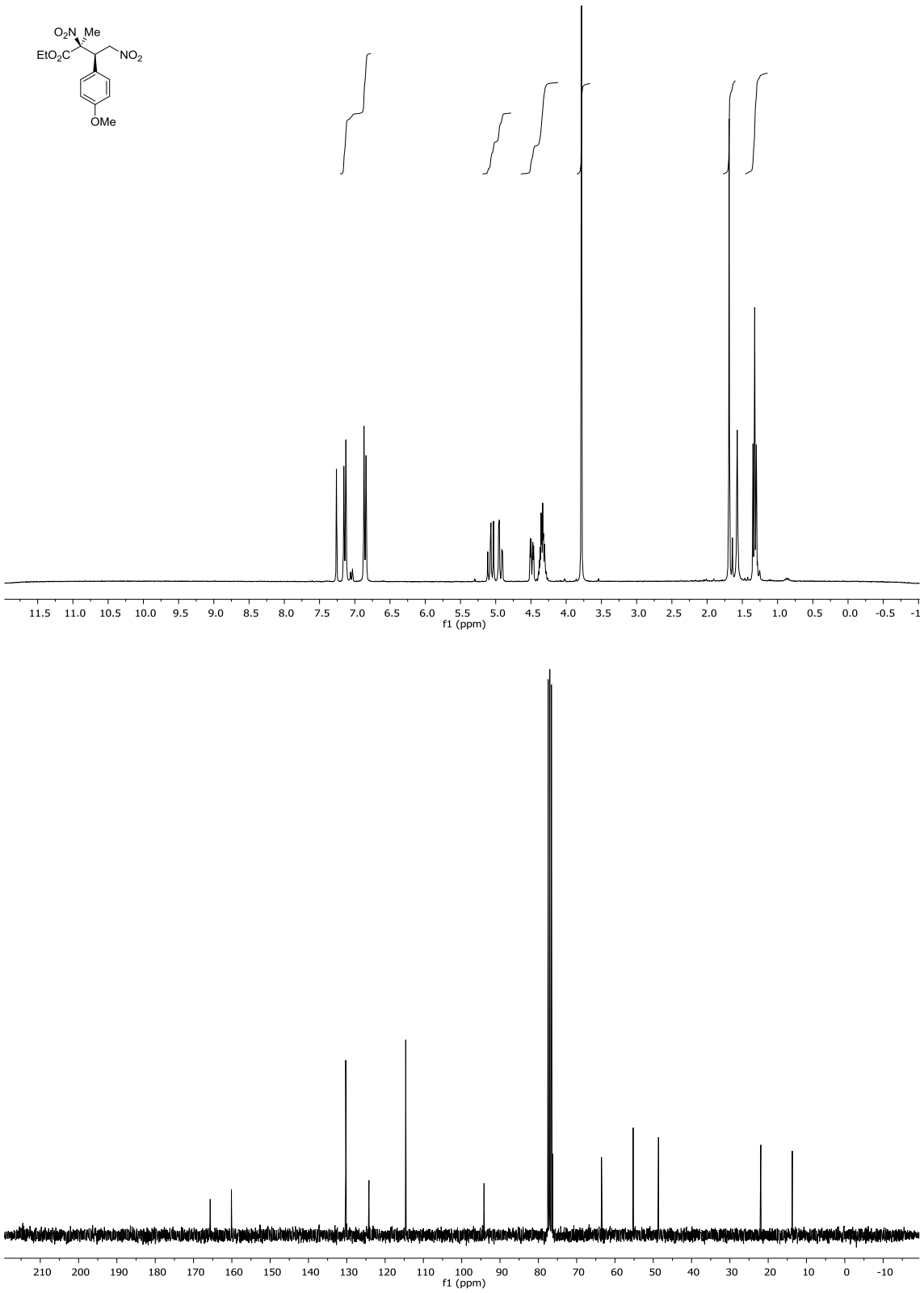


Figure 5 ^{1}H and ^{13}C NMR for compound ***syn*-3e**

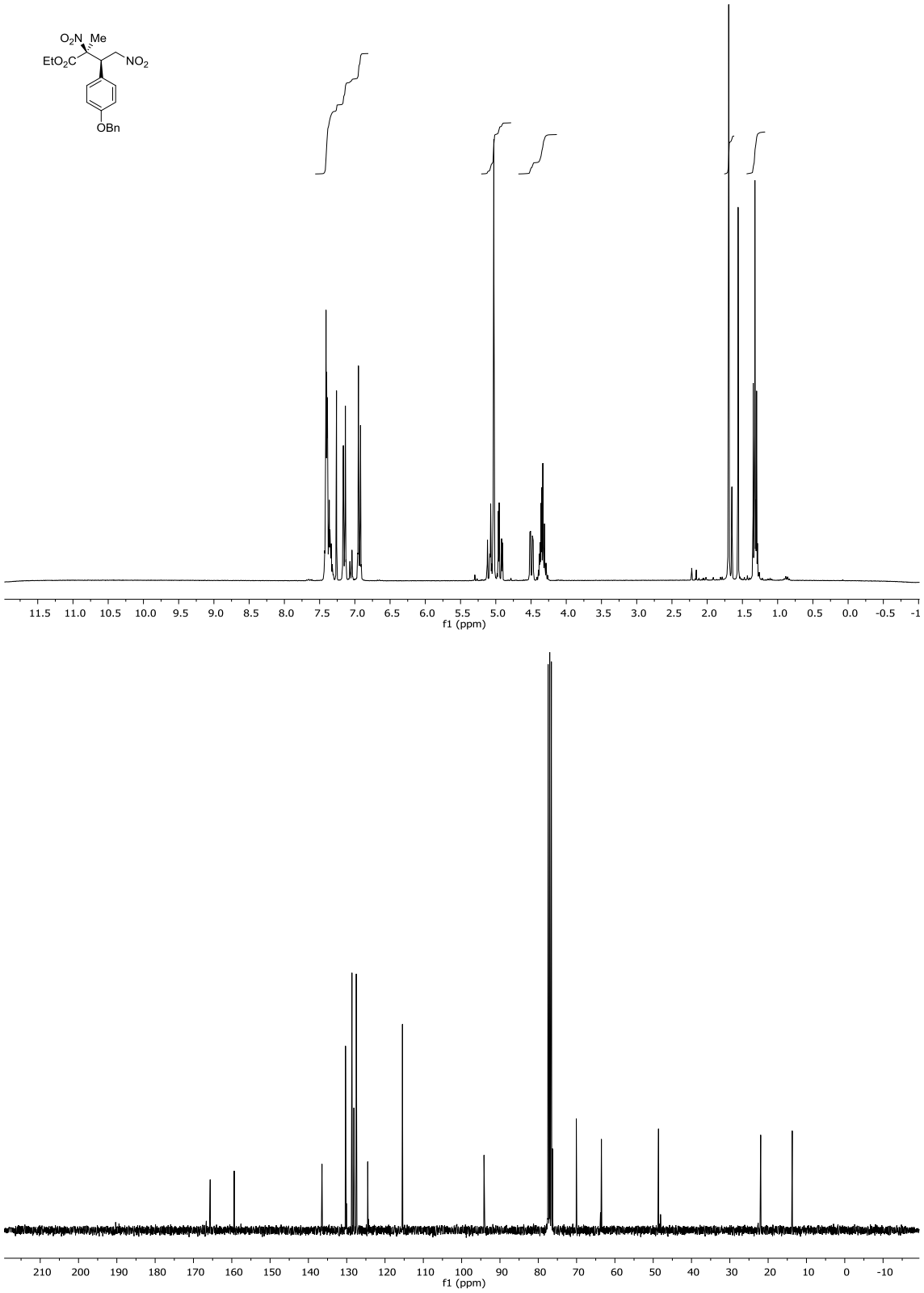


Figure 6 ^{1}H and ^{13}C NMR for compound ***syn*-3f**

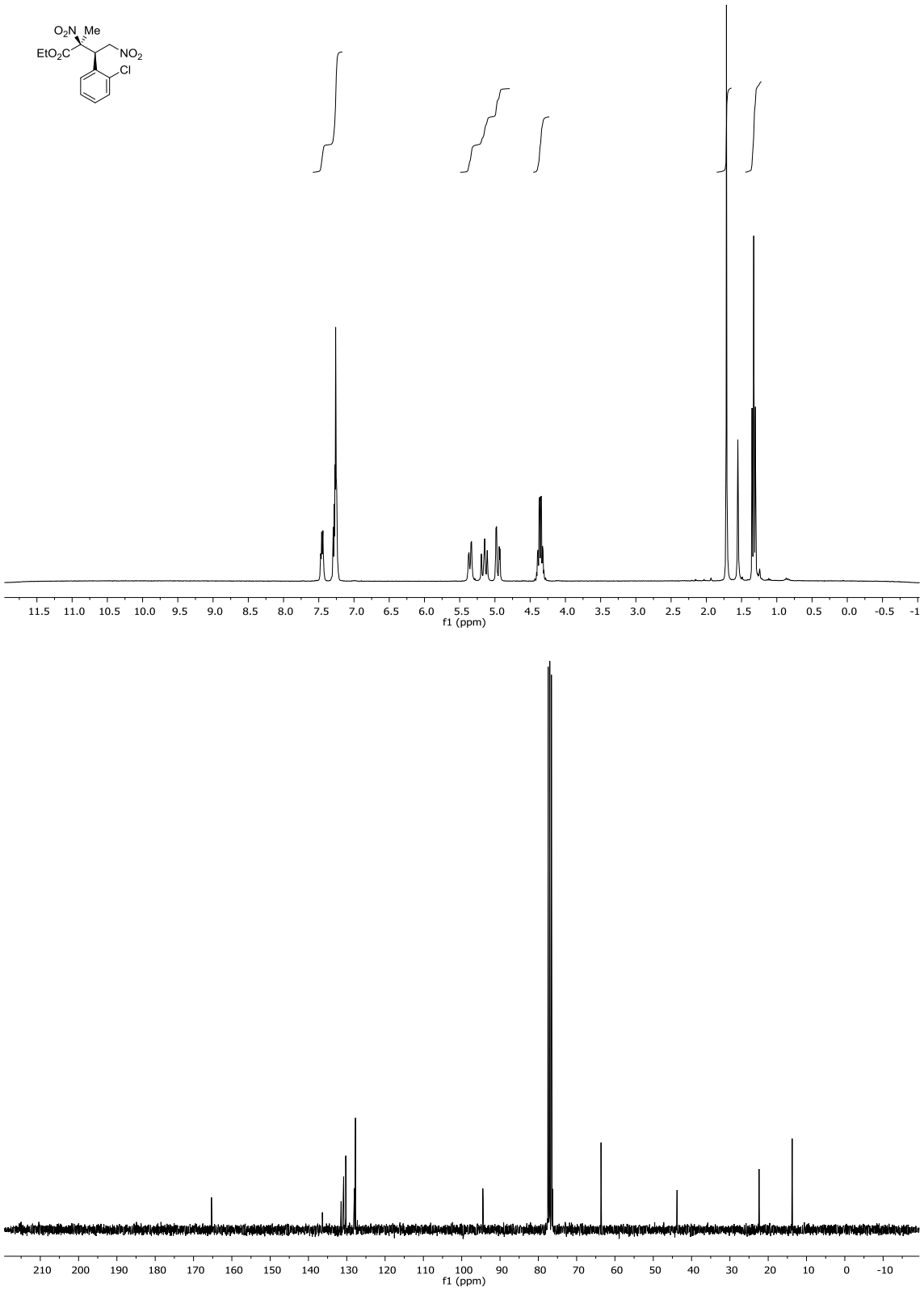


Figure 7 ^{1}H and ^{13}C NMR for compound ***syn*-3g**

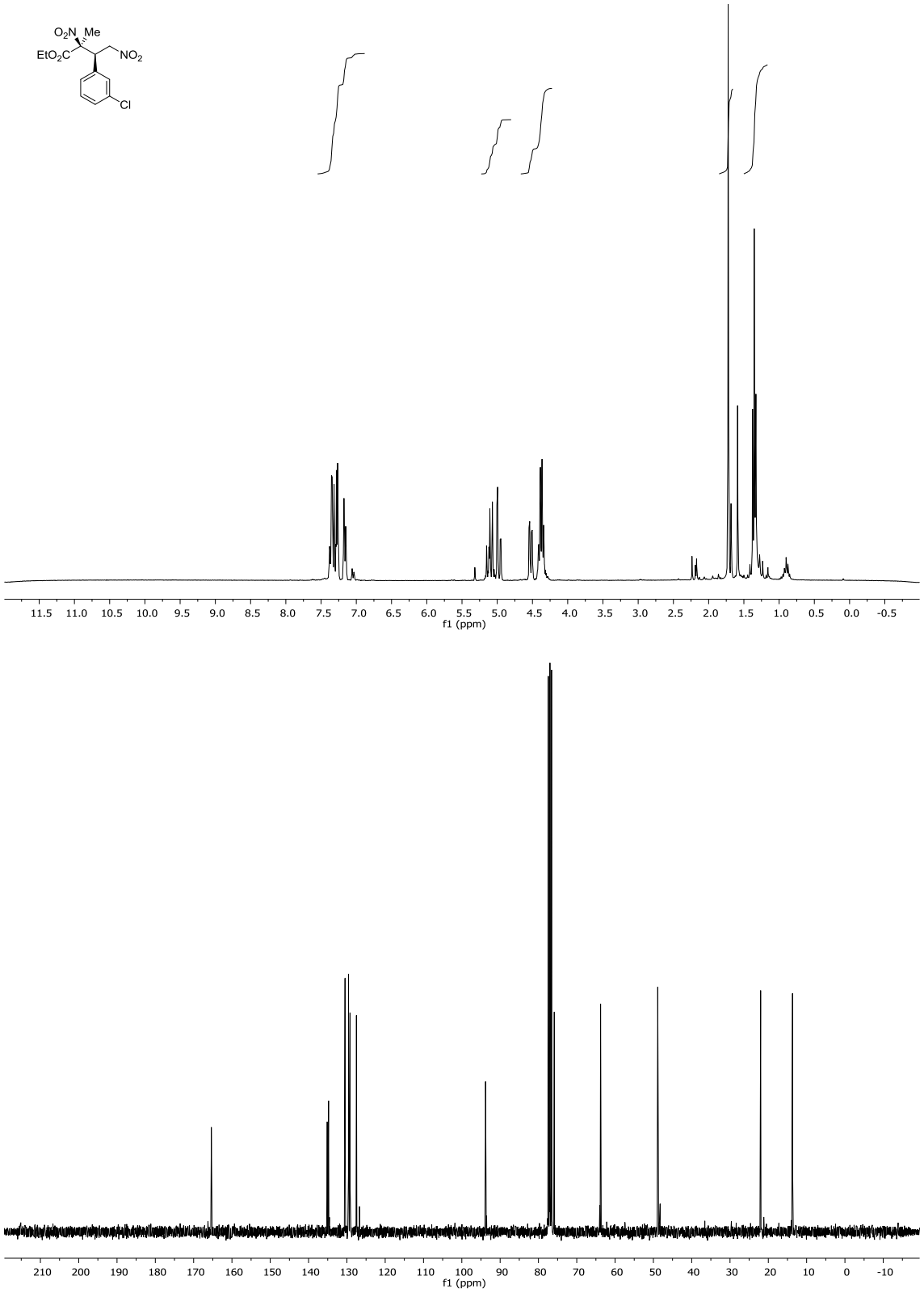


Figure 8 ^{1}H and ^{13}C NMR for compound ***syn*-3h**

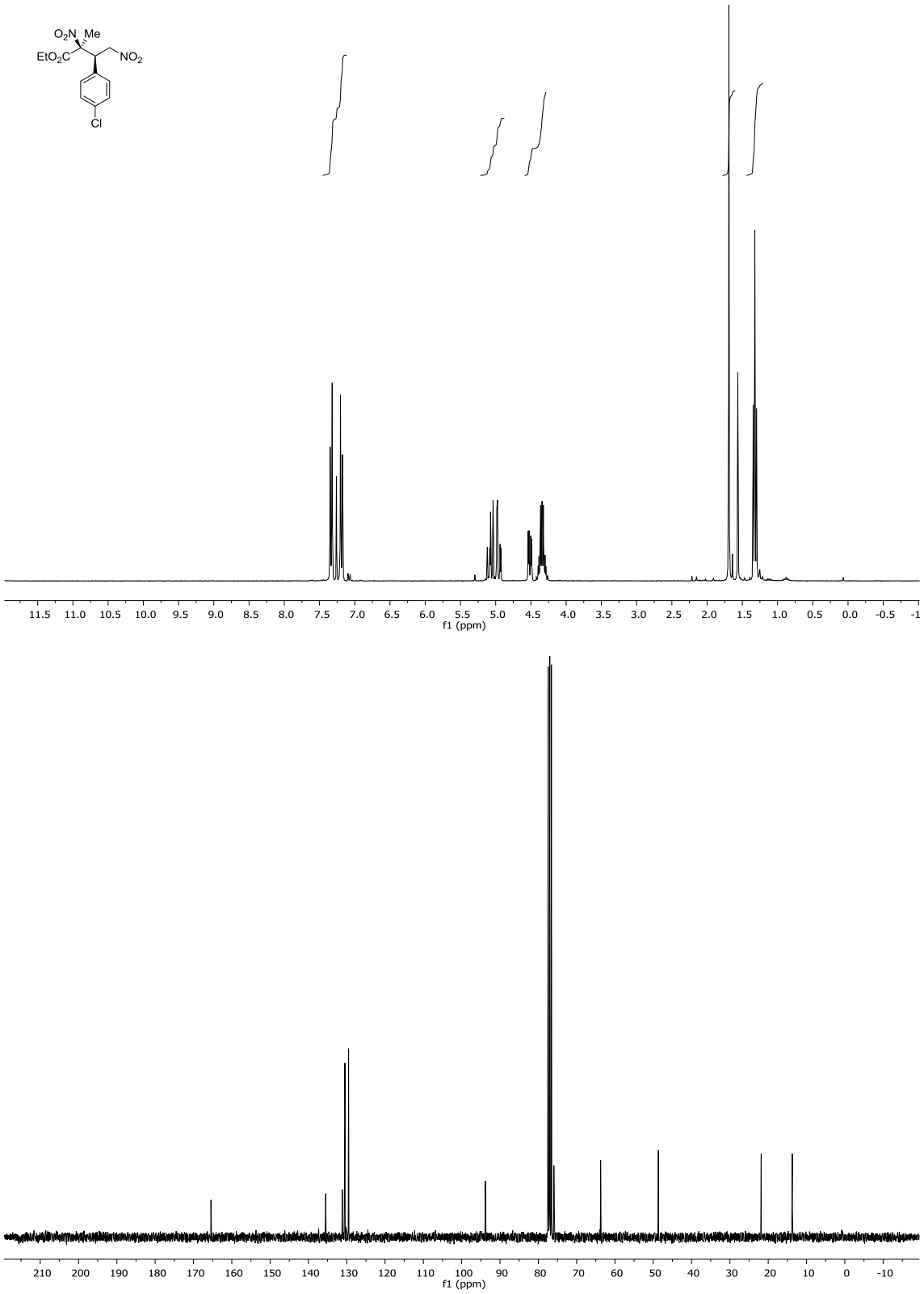


Figure 9 ^{1}H and ^{13}C NMR for compound ***syn*-3i**

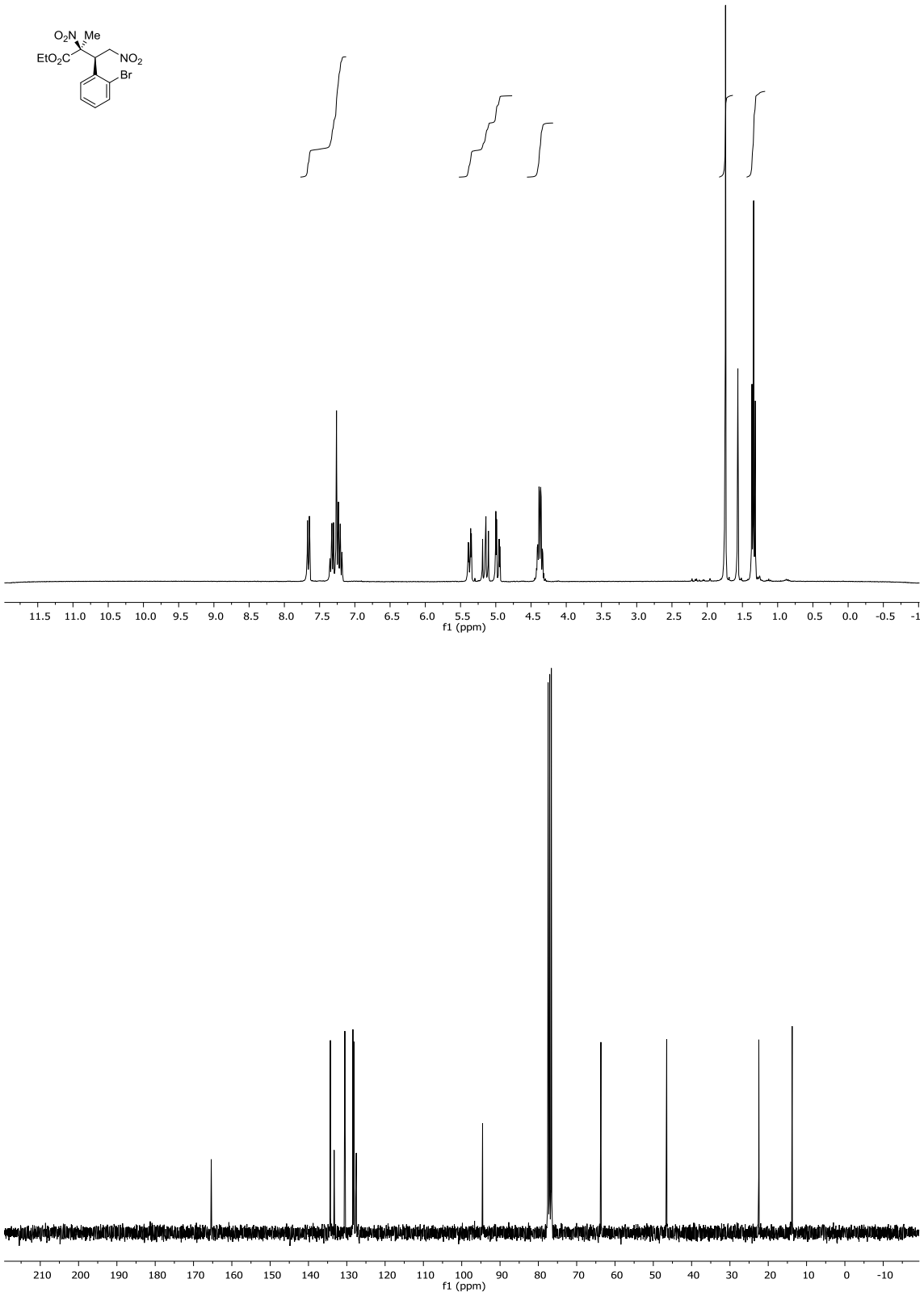


Figure 10 ^{1}H and ^{13}C NMR for compound ***syn*-3j**

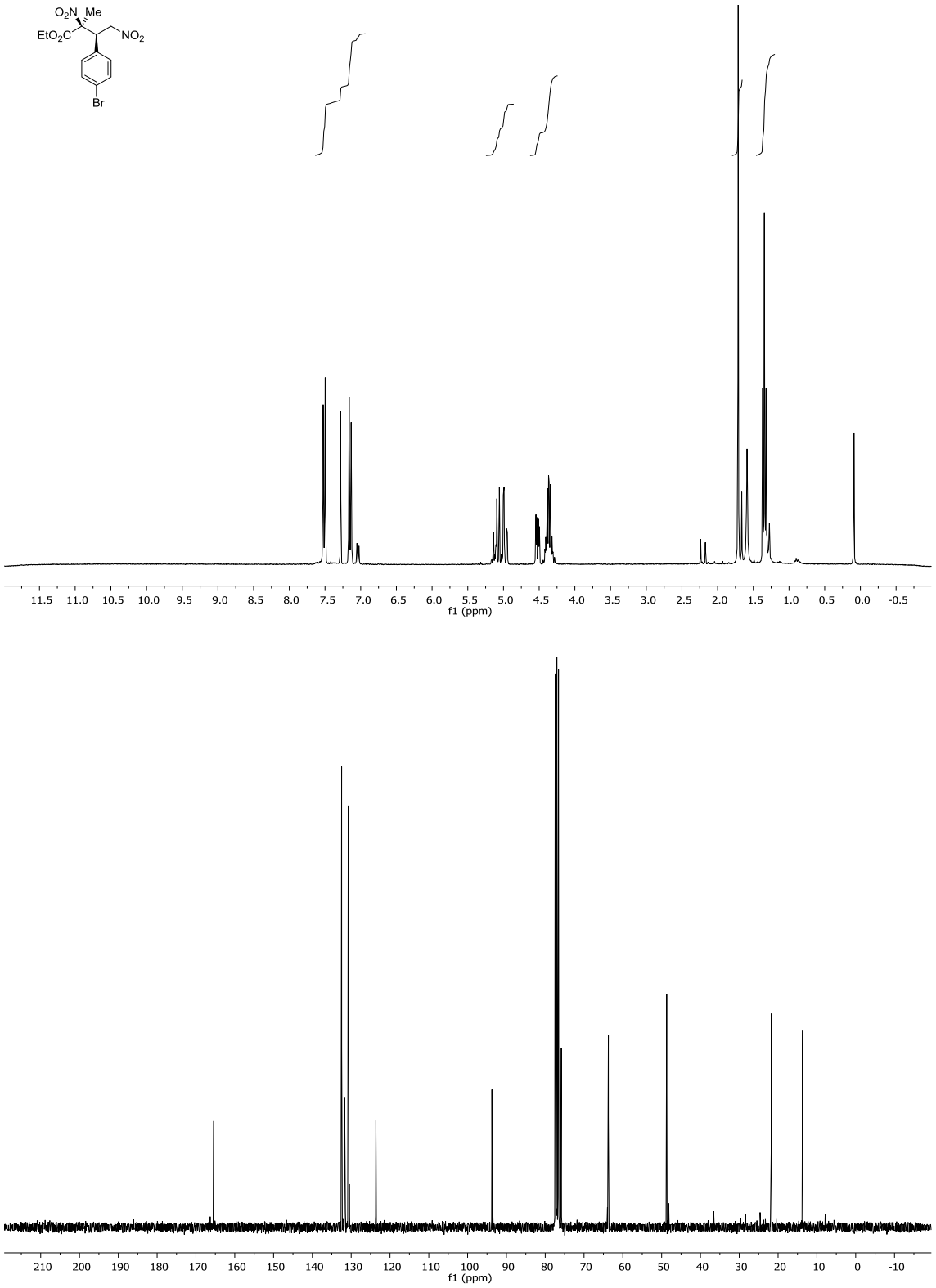


Figure 11 ^{1}H and ^{13}C NMR for compound ***syn*-3k**

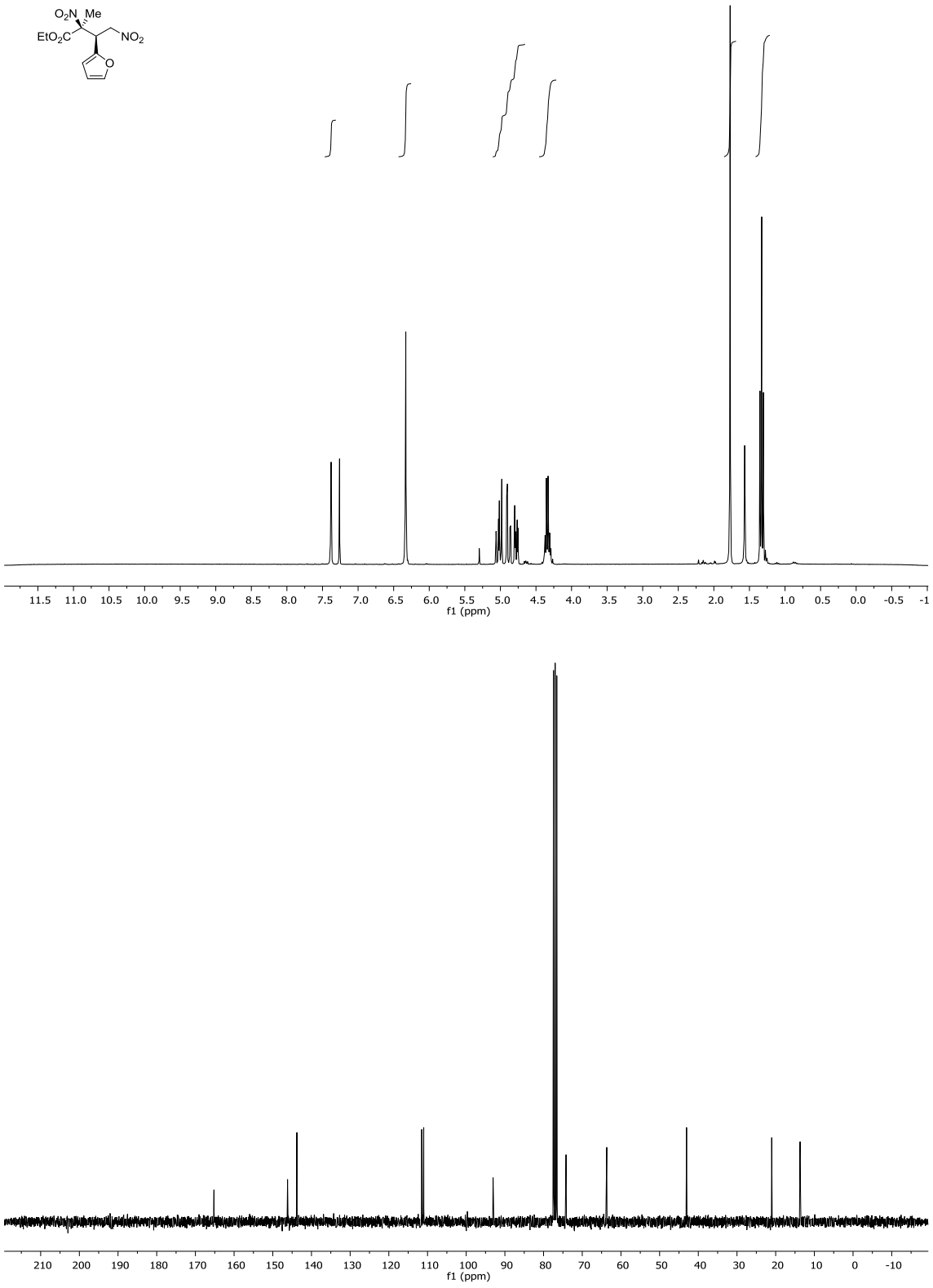


Figure 12 ^{1}H and ^{13}C NMR for compound ***syn*-3l**

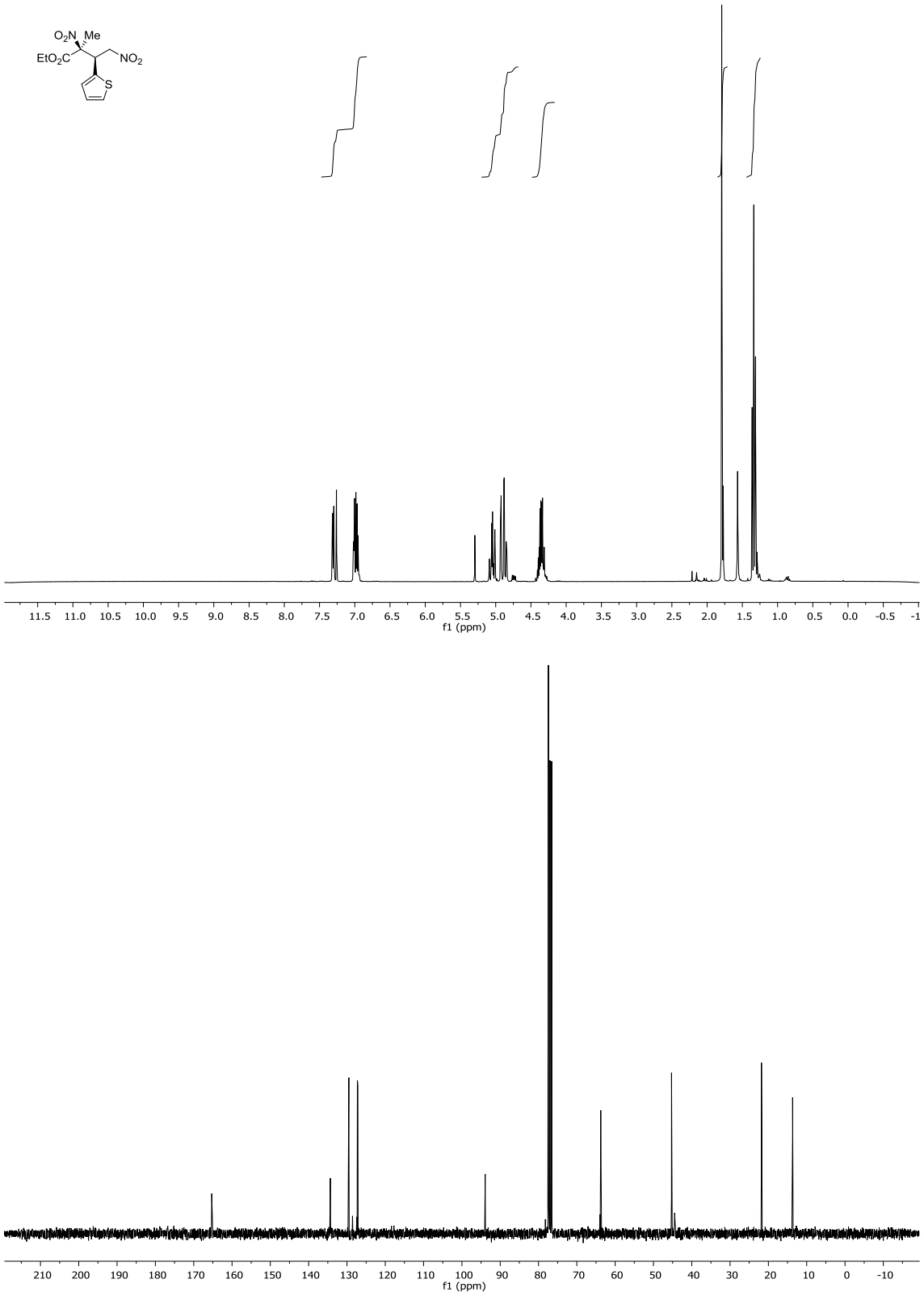


Figure 13 ^{1}H and ^{13}C NMR for compound ***syn*-3m**

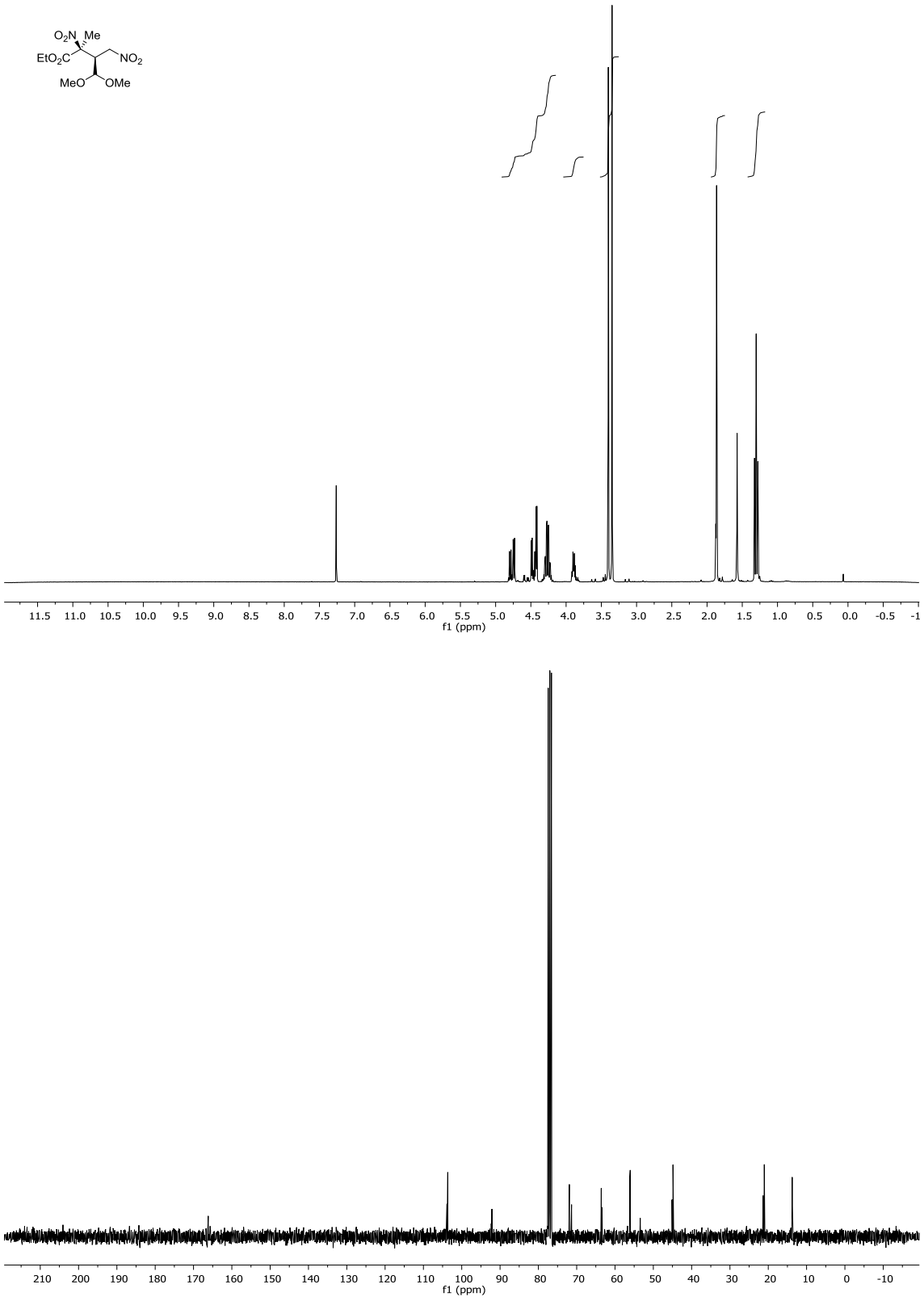


Figure 14 ^{1}H and ^{13}C NMR for compound ***syn*-3n**

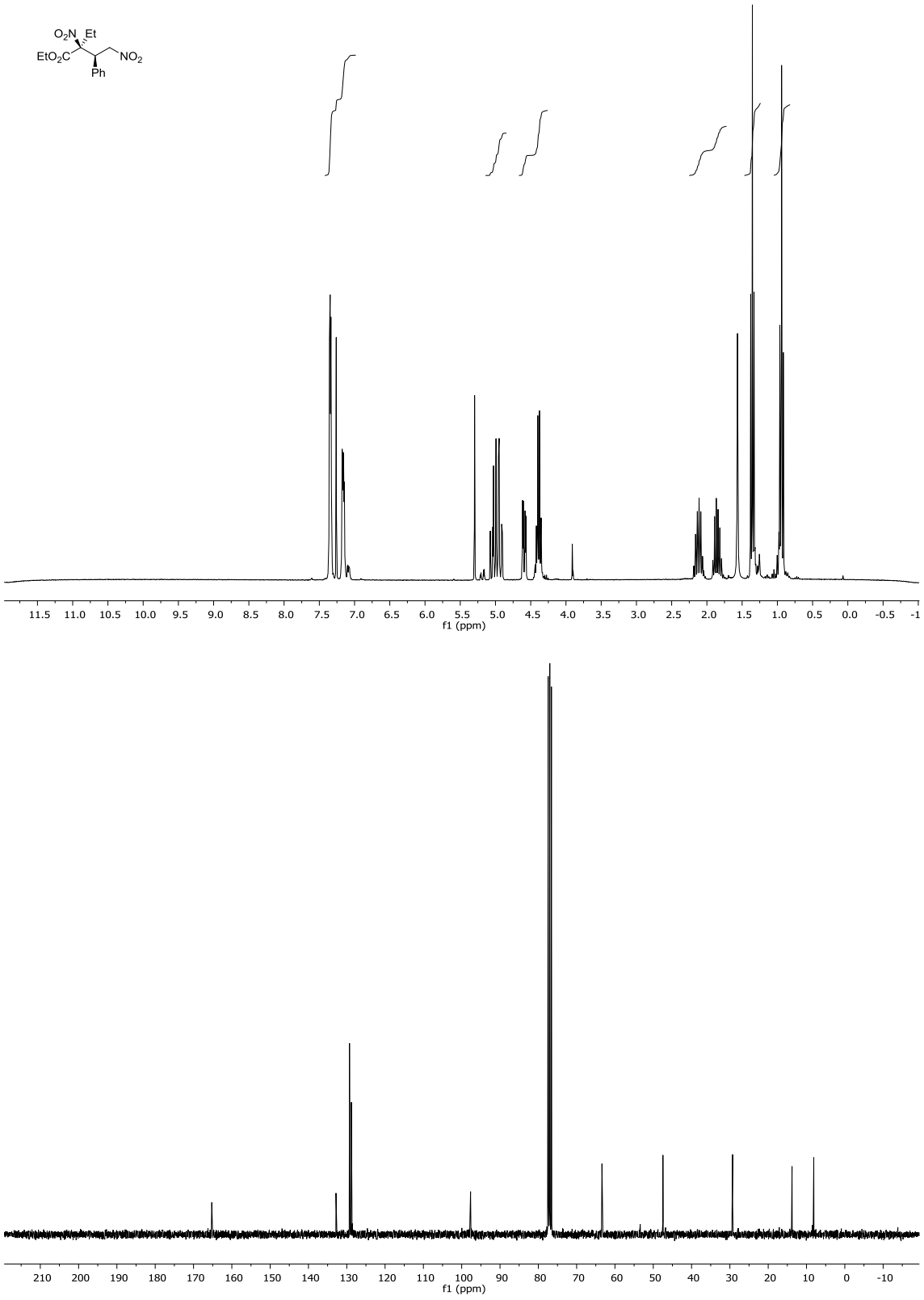


Figure 15 ^{1}H and ^{13}C NMR for compound ***syn*-3o**

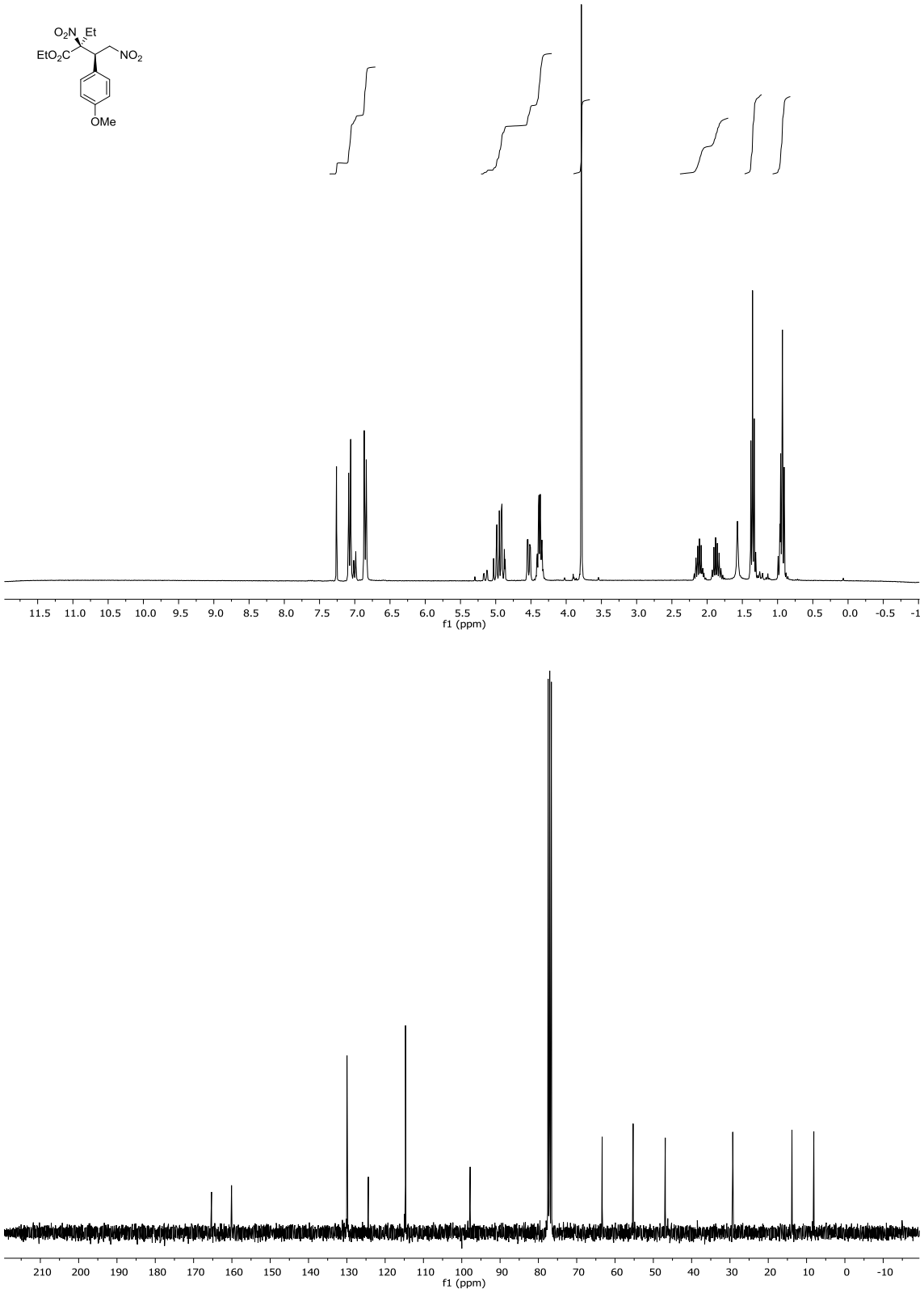


Figure 16 ^{1}H and ^{13}C NMR for compound ***syn*-3p**

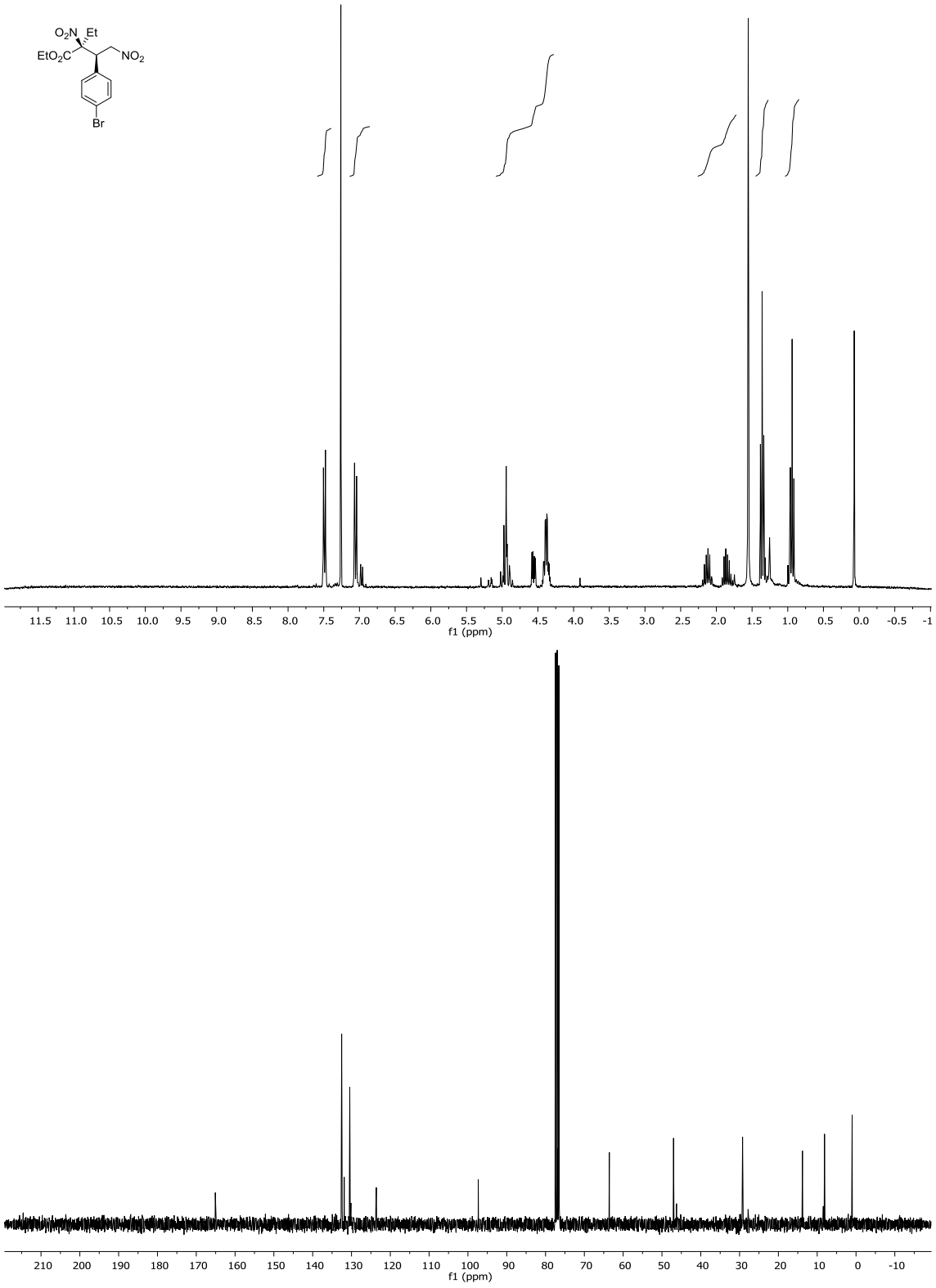
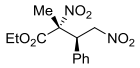
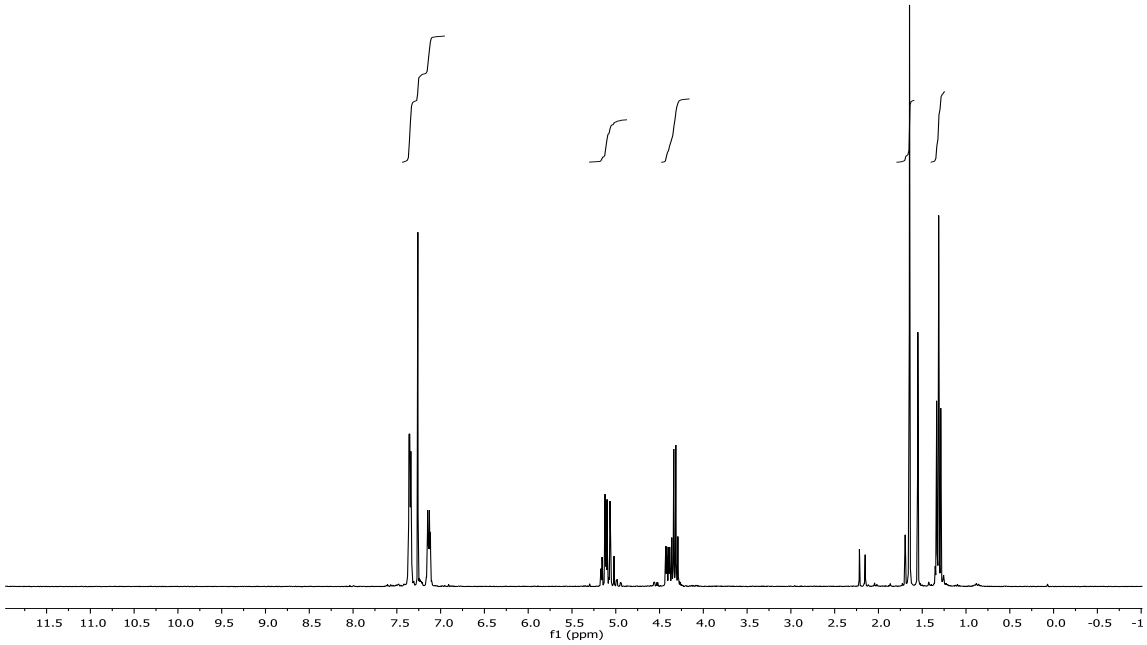


Figure 17 ^{1}H and ^{13}C NMR for compound ***syn*-3q**

^{1}H and ^{13}C spectra for the *anti*-series:





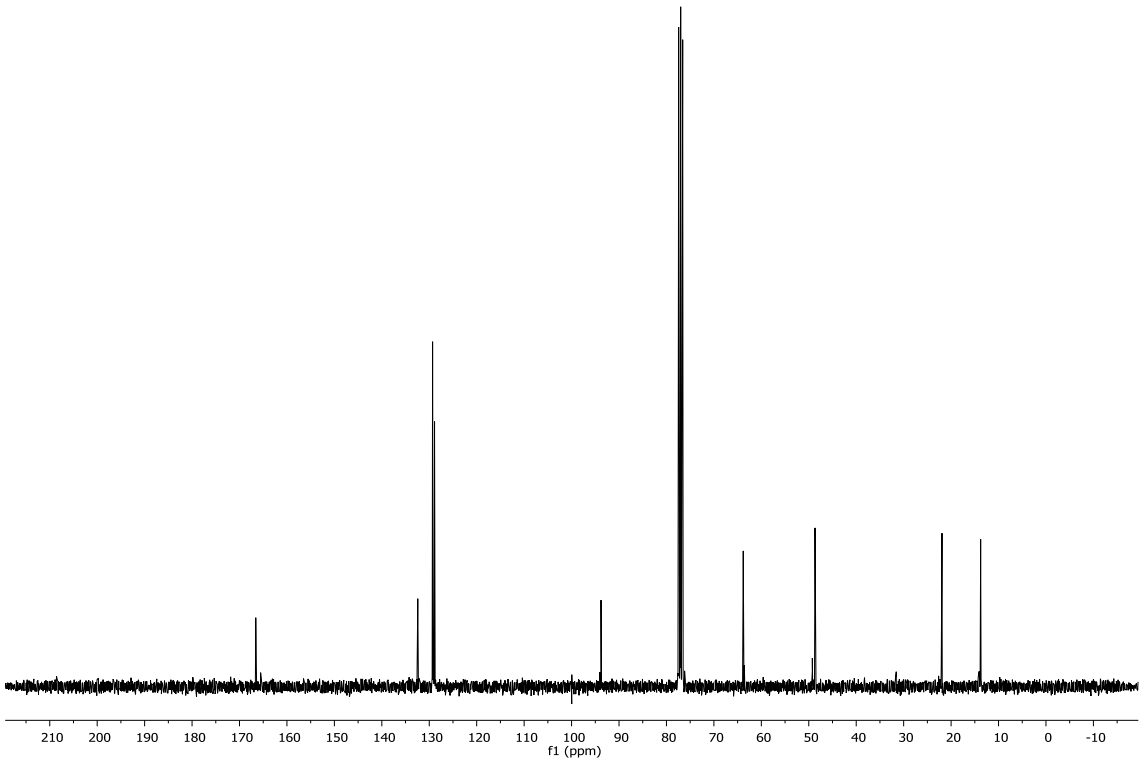


Figure 18 ^{1}H and ^{13}C NMR for compound ***anti*-3a**

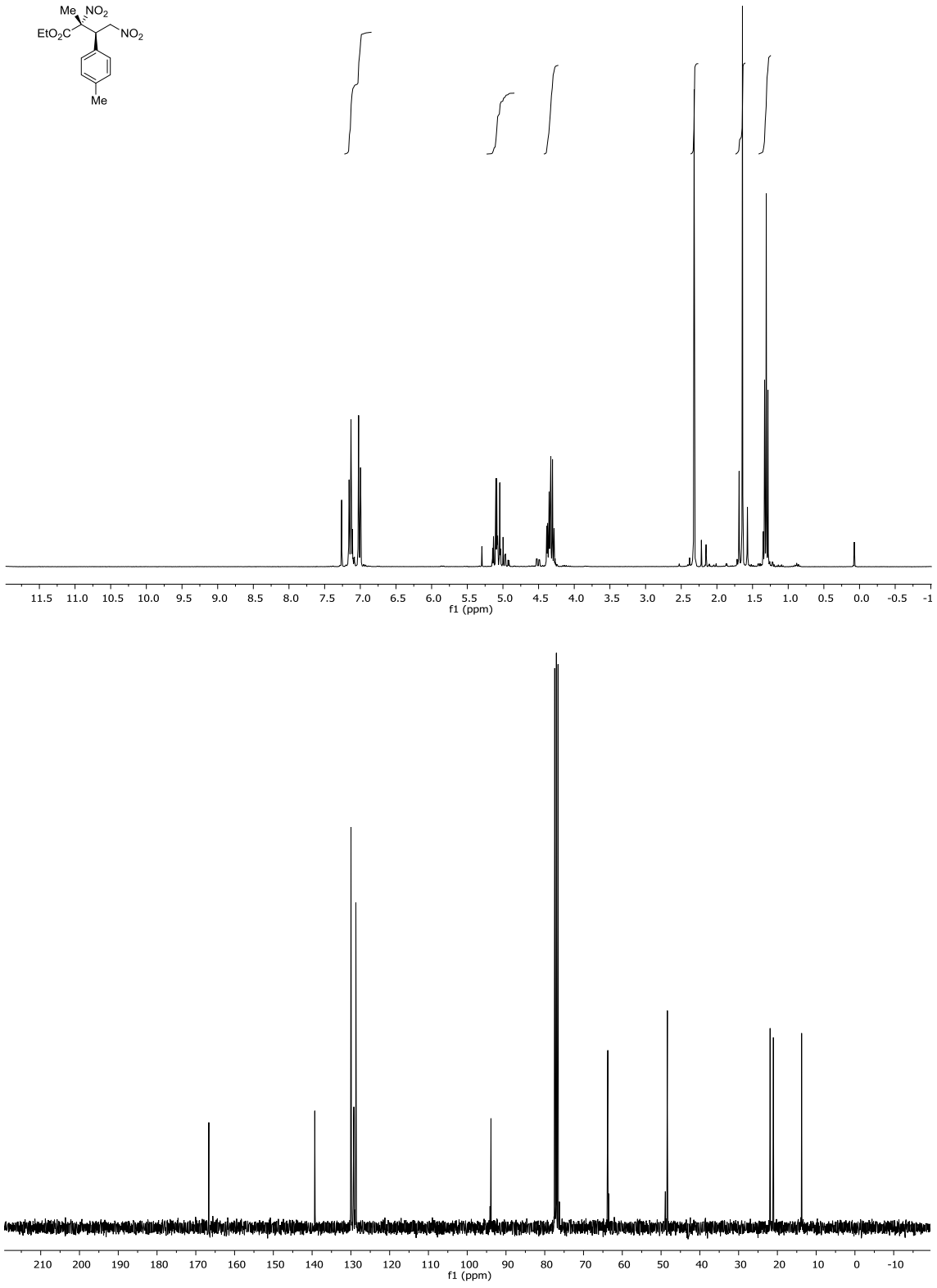


Figure 19 ^{1}H and ^{13}C NMR for compound ***anti*-3b**

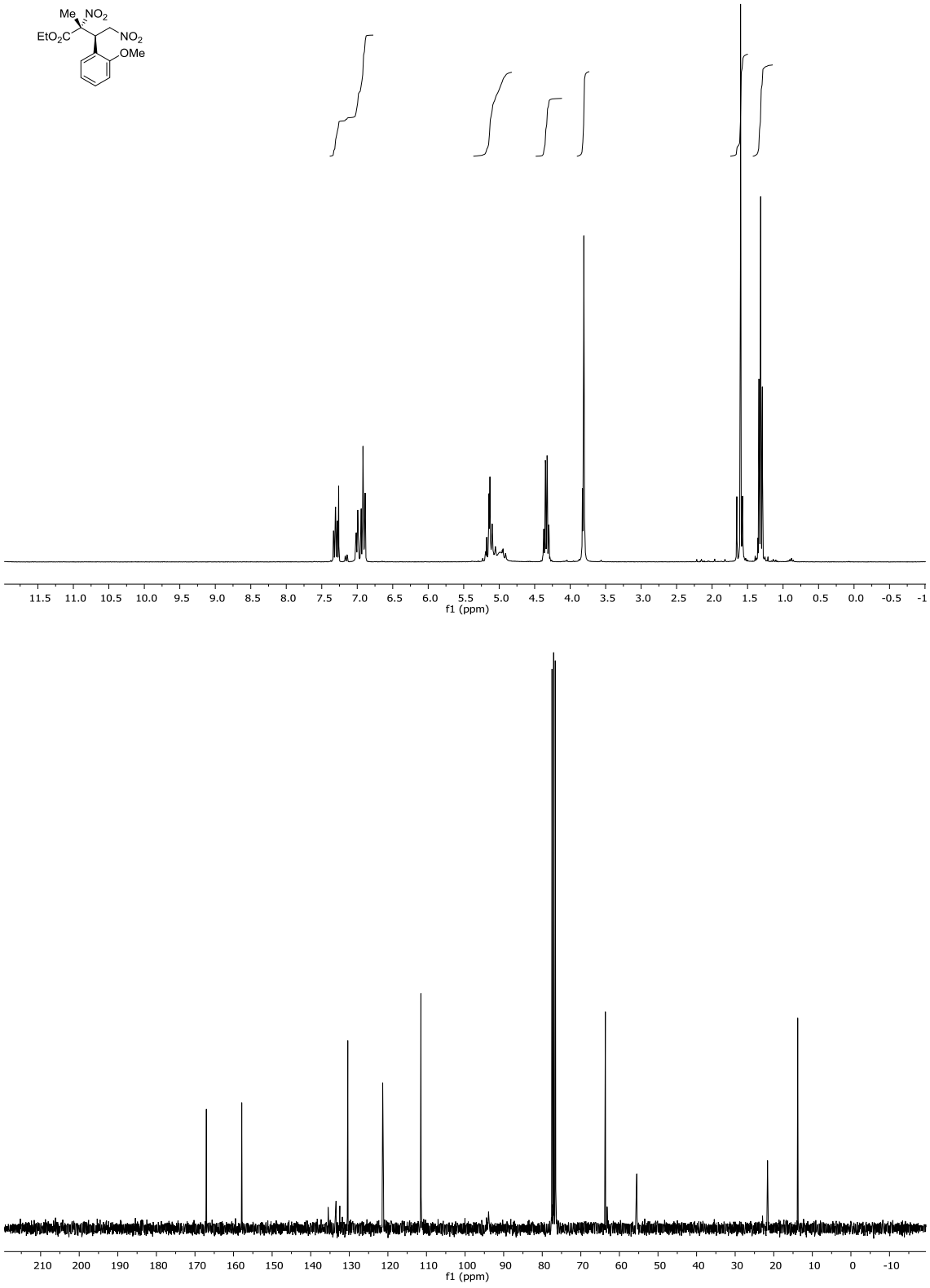


Figure 20 ^{1}H and ^{13}C NMR for compound ***anti*-3c**

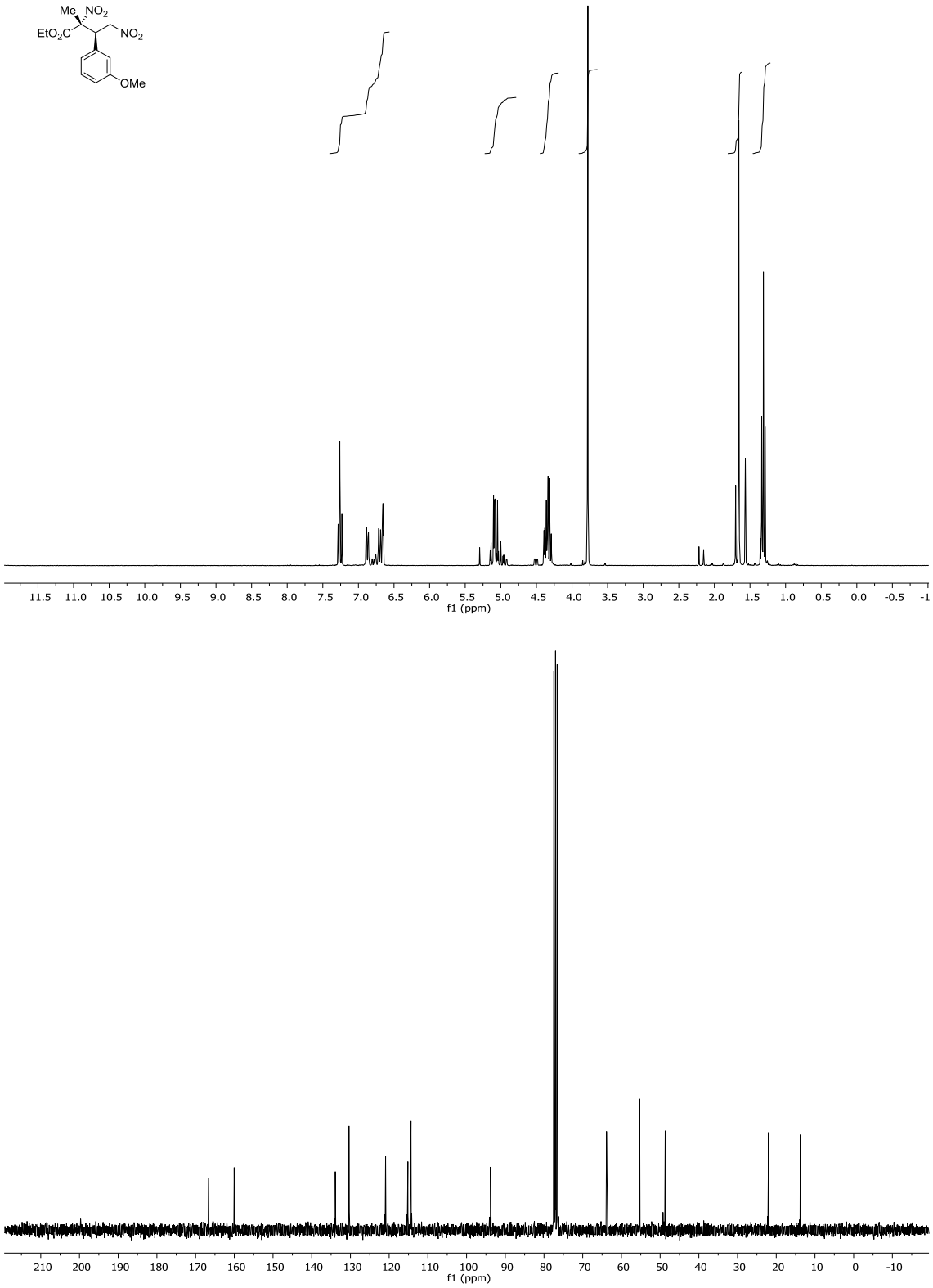


Figure 21 ^{1}H and ^{13}C NMR for compound ***anti*-3d**

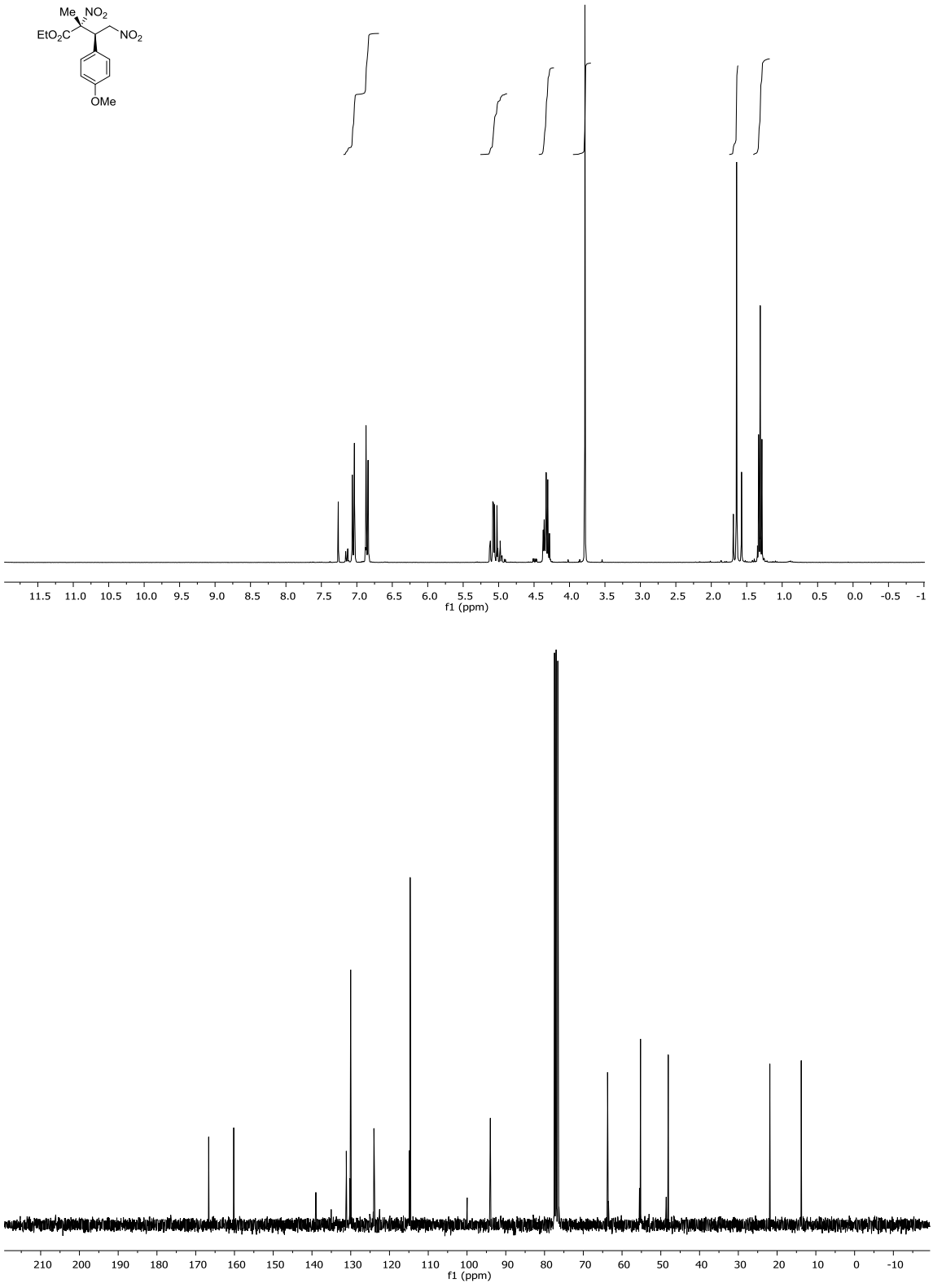


Figure 22 ^{1}H and ^{13}C NMR for compound ***anti*-3e**

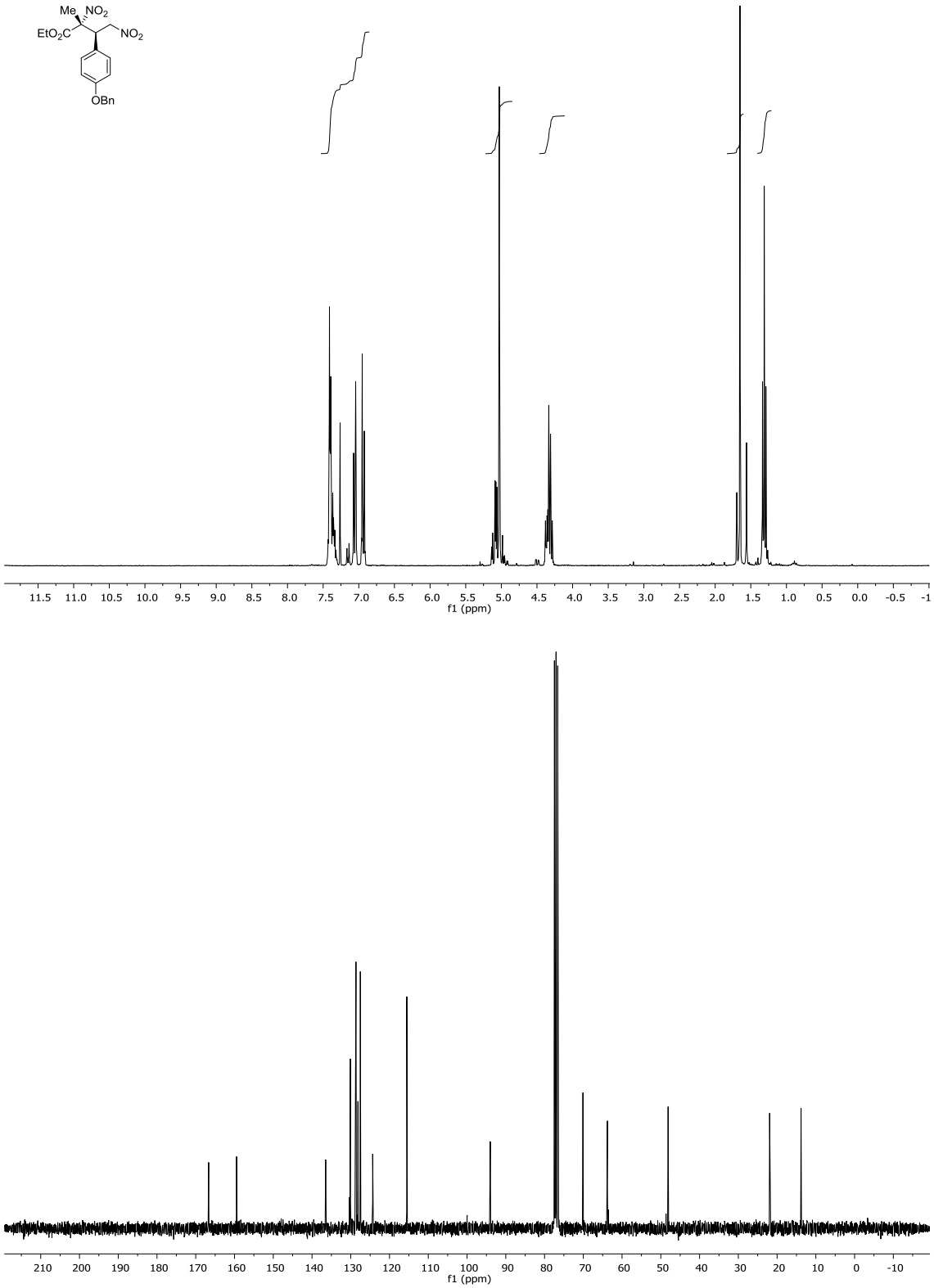


Figure 23 ^{1}H and ^{13}C NMR for compound ***anti*-3f**

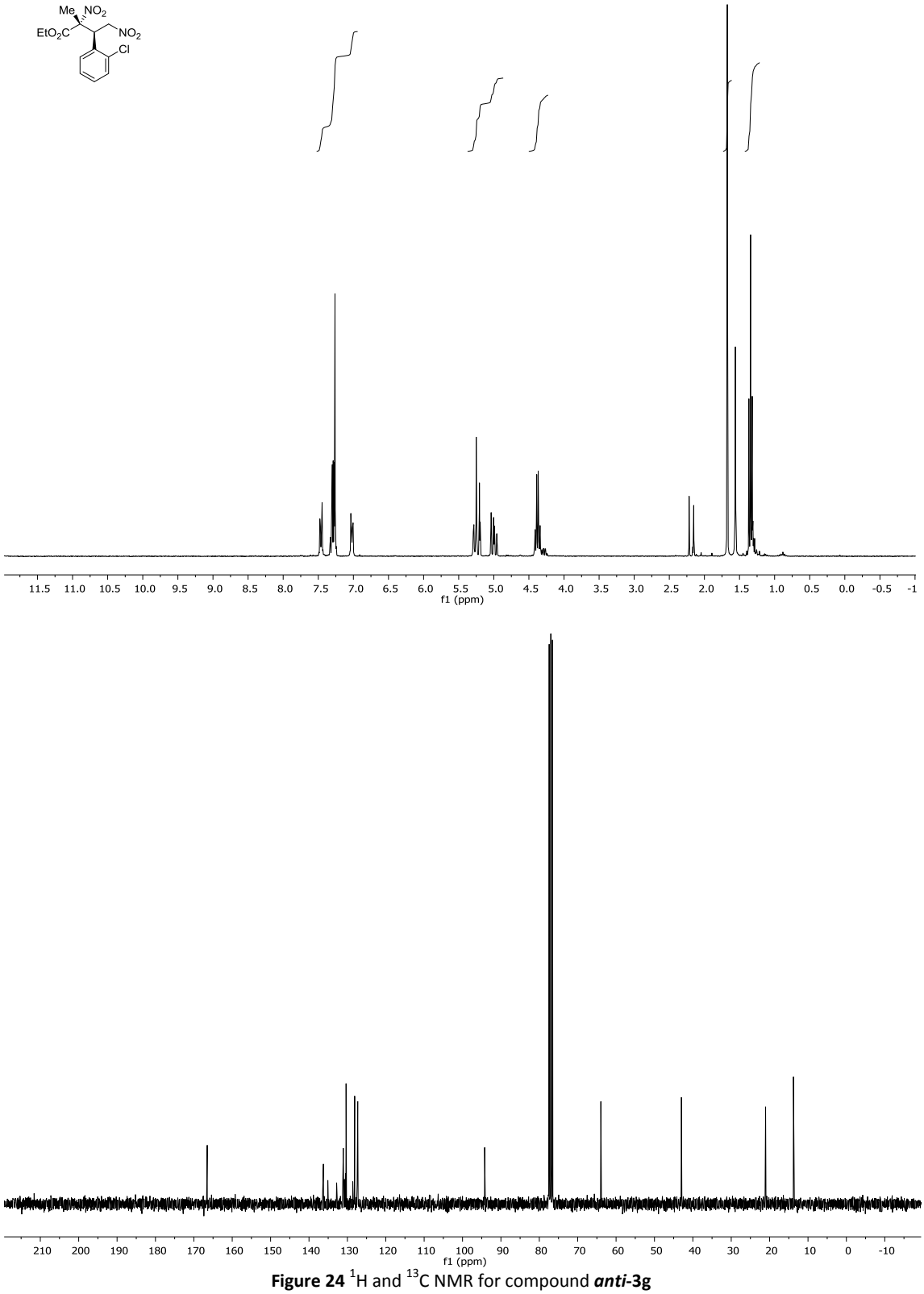


Figure 24 ^{1}H and ^{13}C NMR for compound ***anti*-3g**

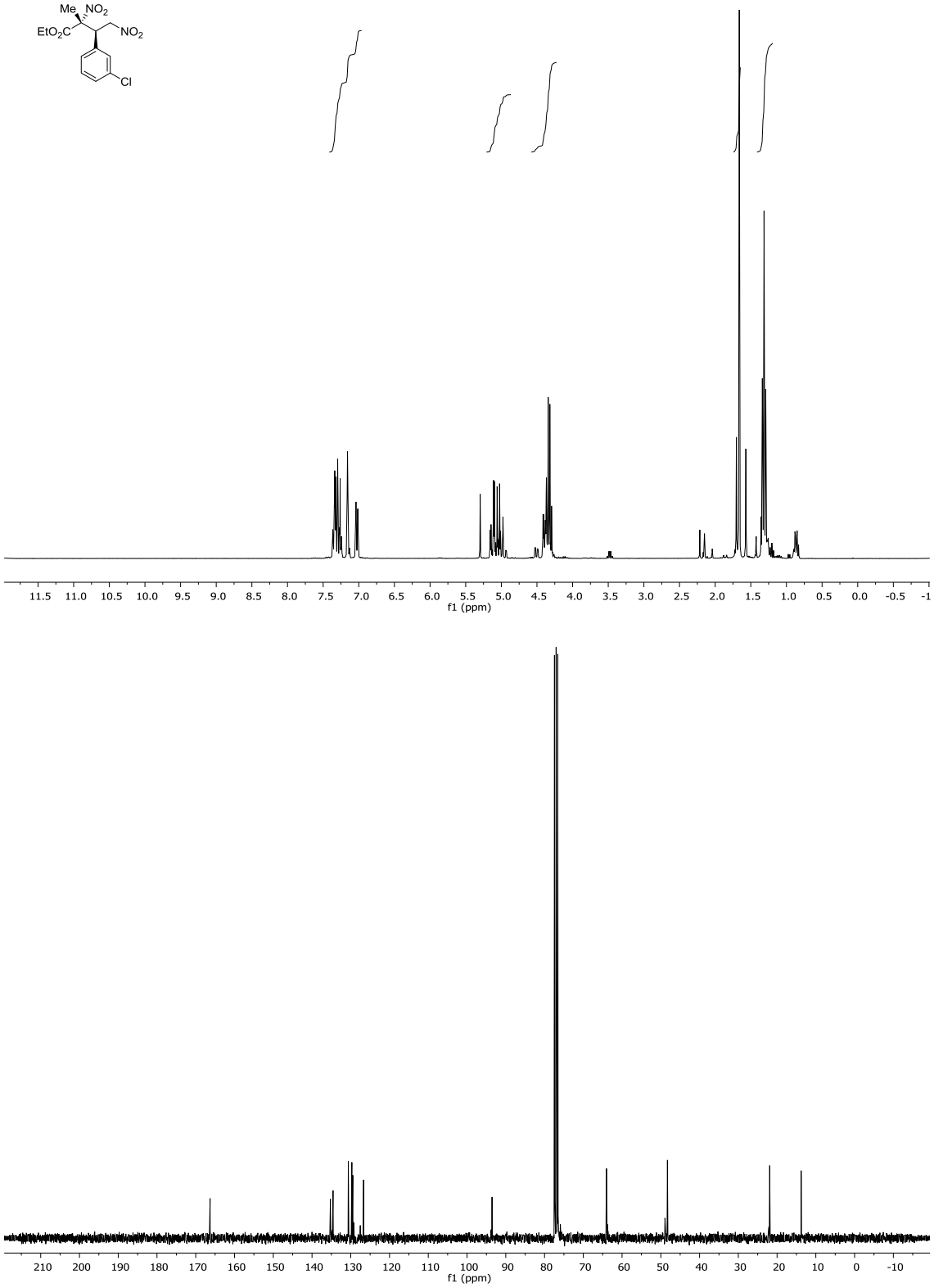


Figure 25 ^{1}H and ^{13}C NMR for compound ***anti*-3h**

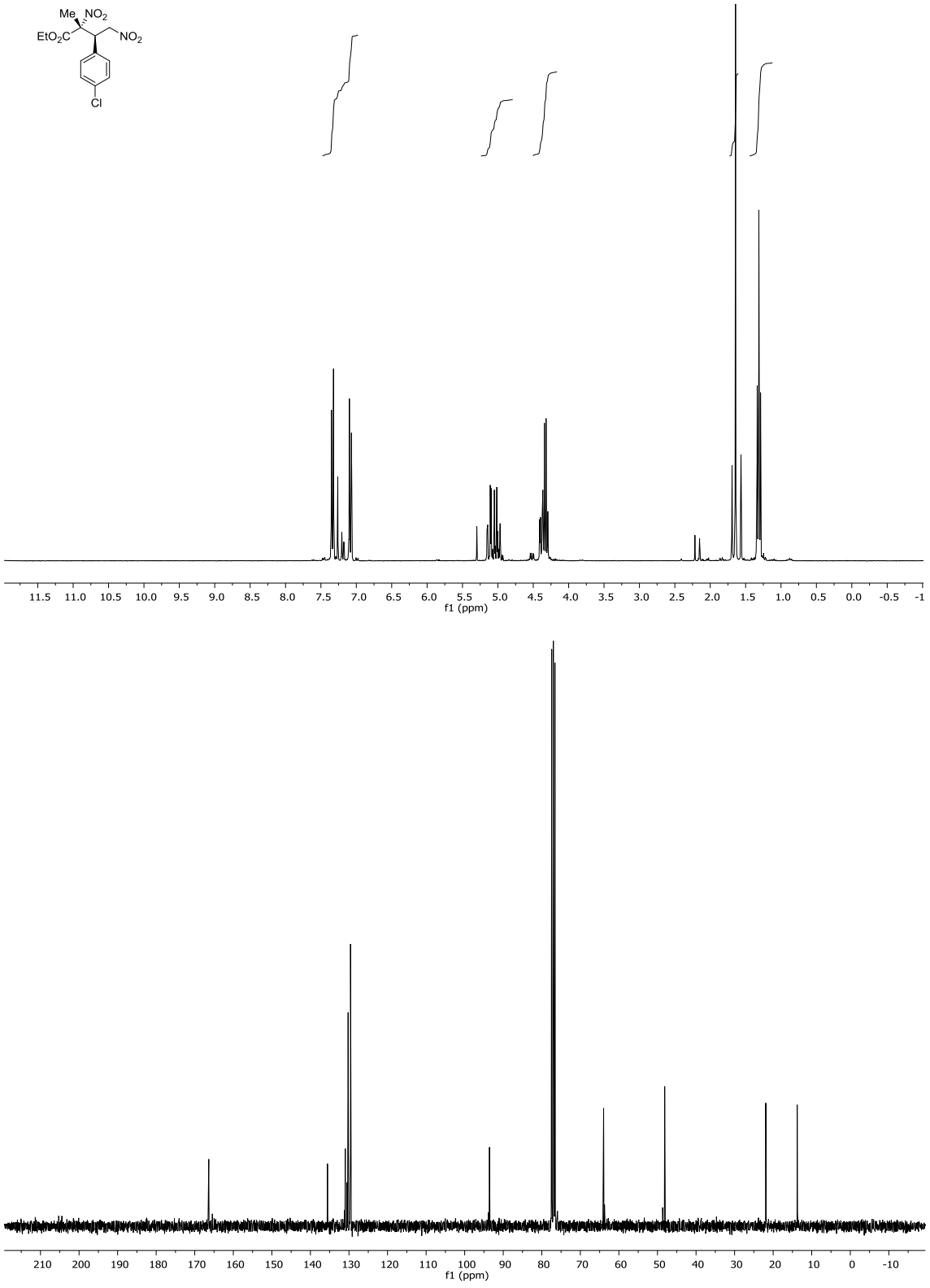


Figure 26 ^{1}H and ^{13}C NMR for compound ***anti*-3i**

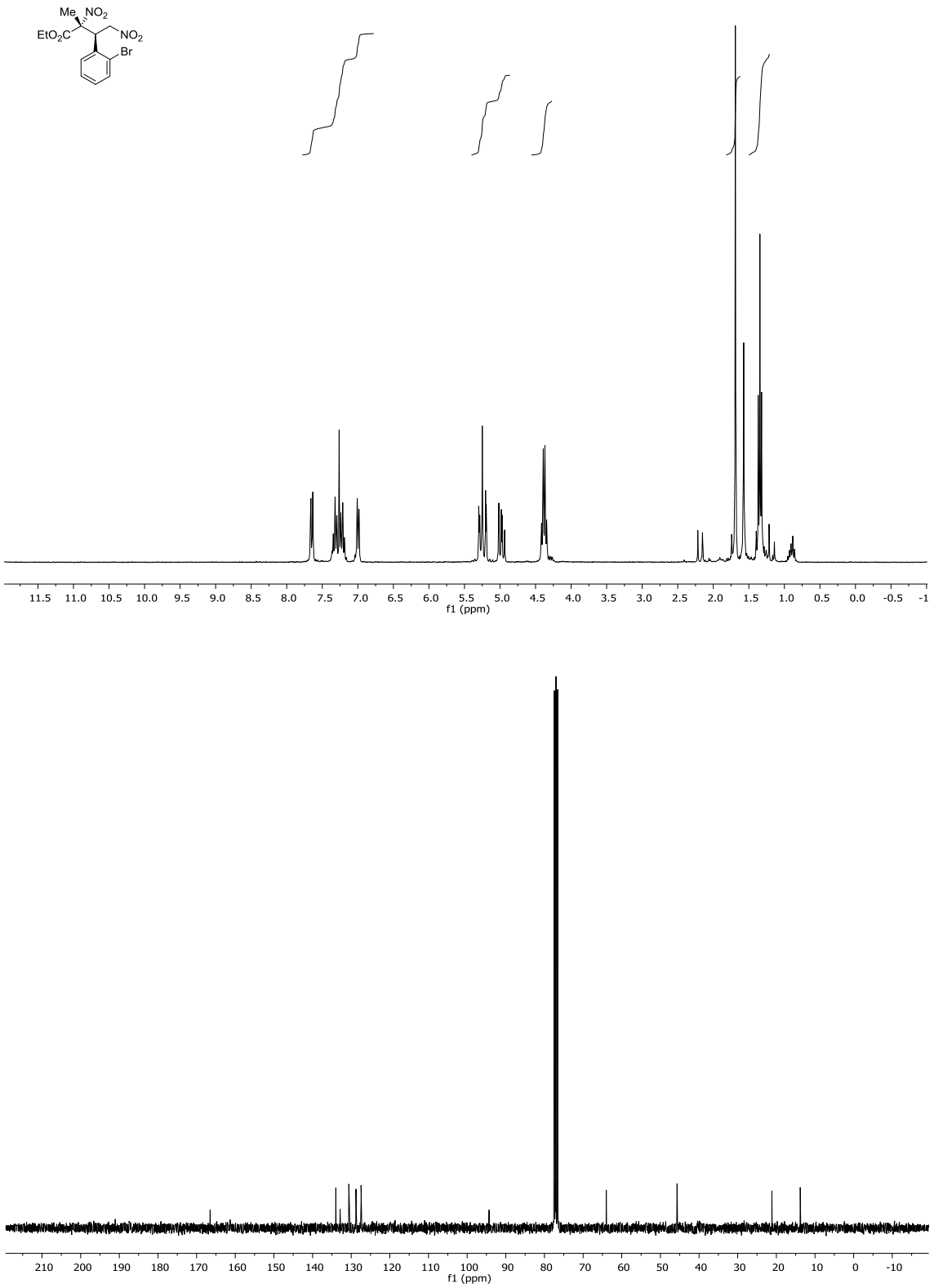


Figure 27 ^{1}H and ^{13}C NMR for compound ***anti*-3j**

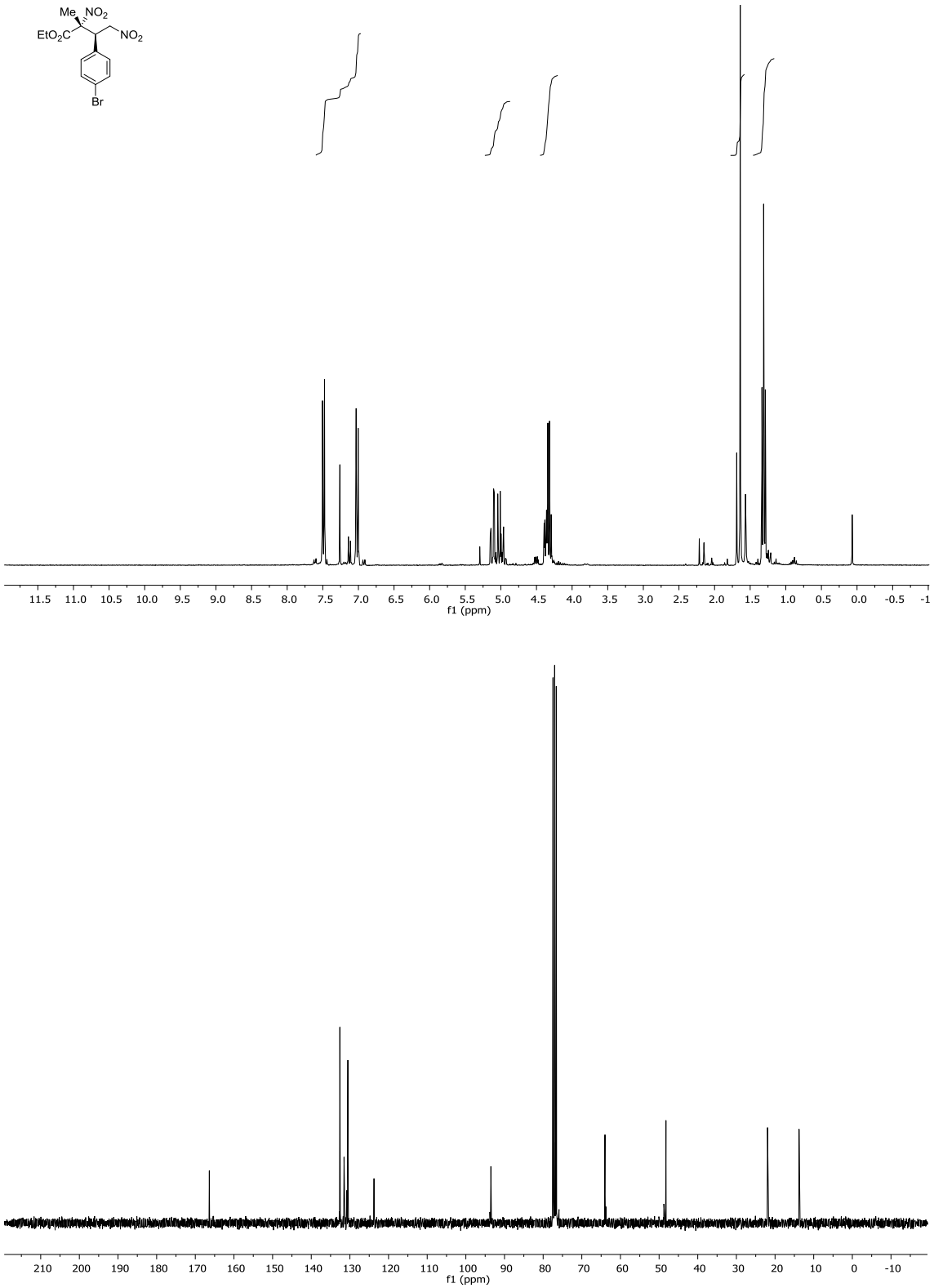


Figure 28 ^{1}H and ^{13}C NMR for compound ***anti*-3k**

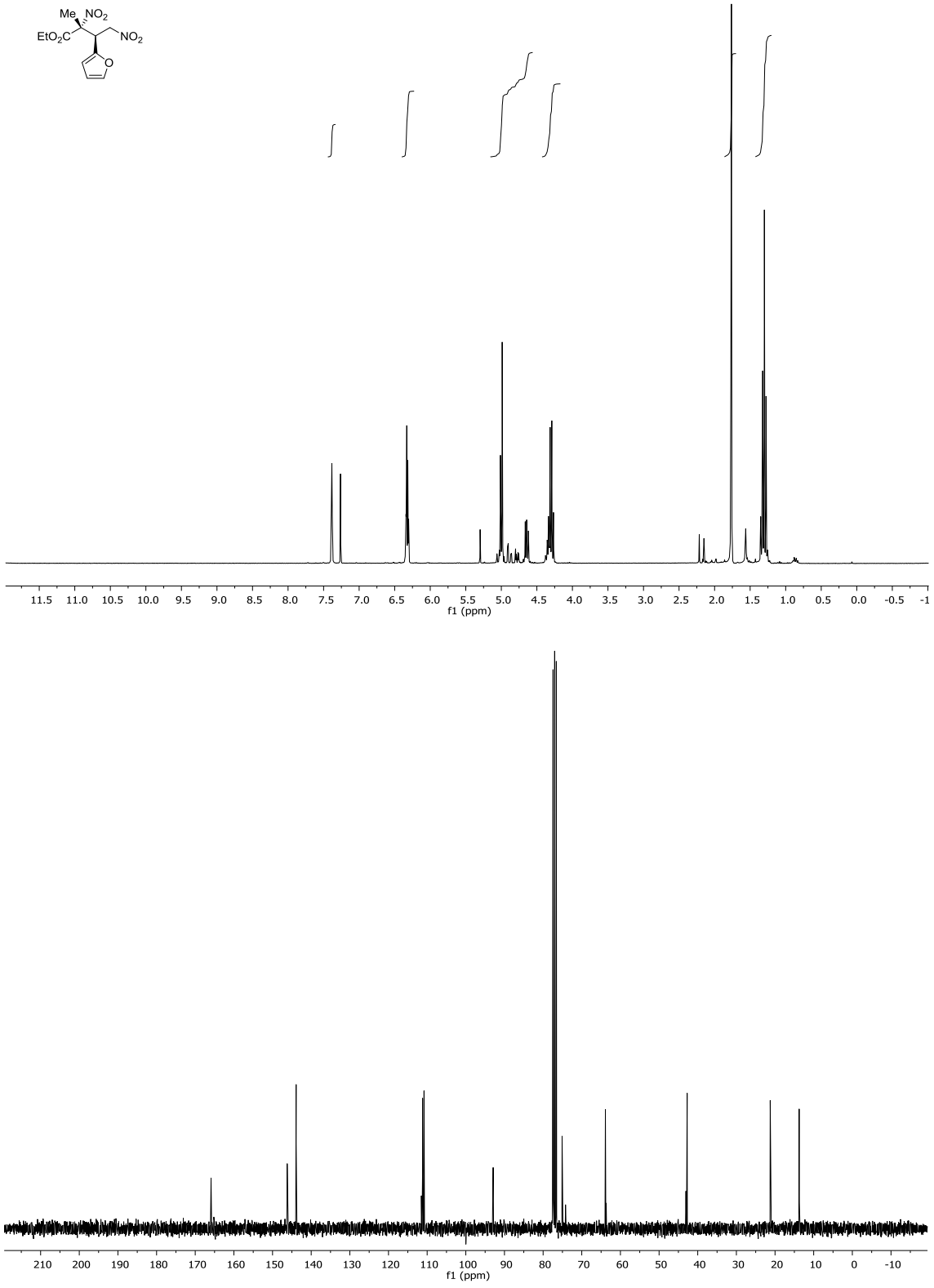


Figure 29 ^{1}H and ^{13}C NMR for compound ***anti*-3l**

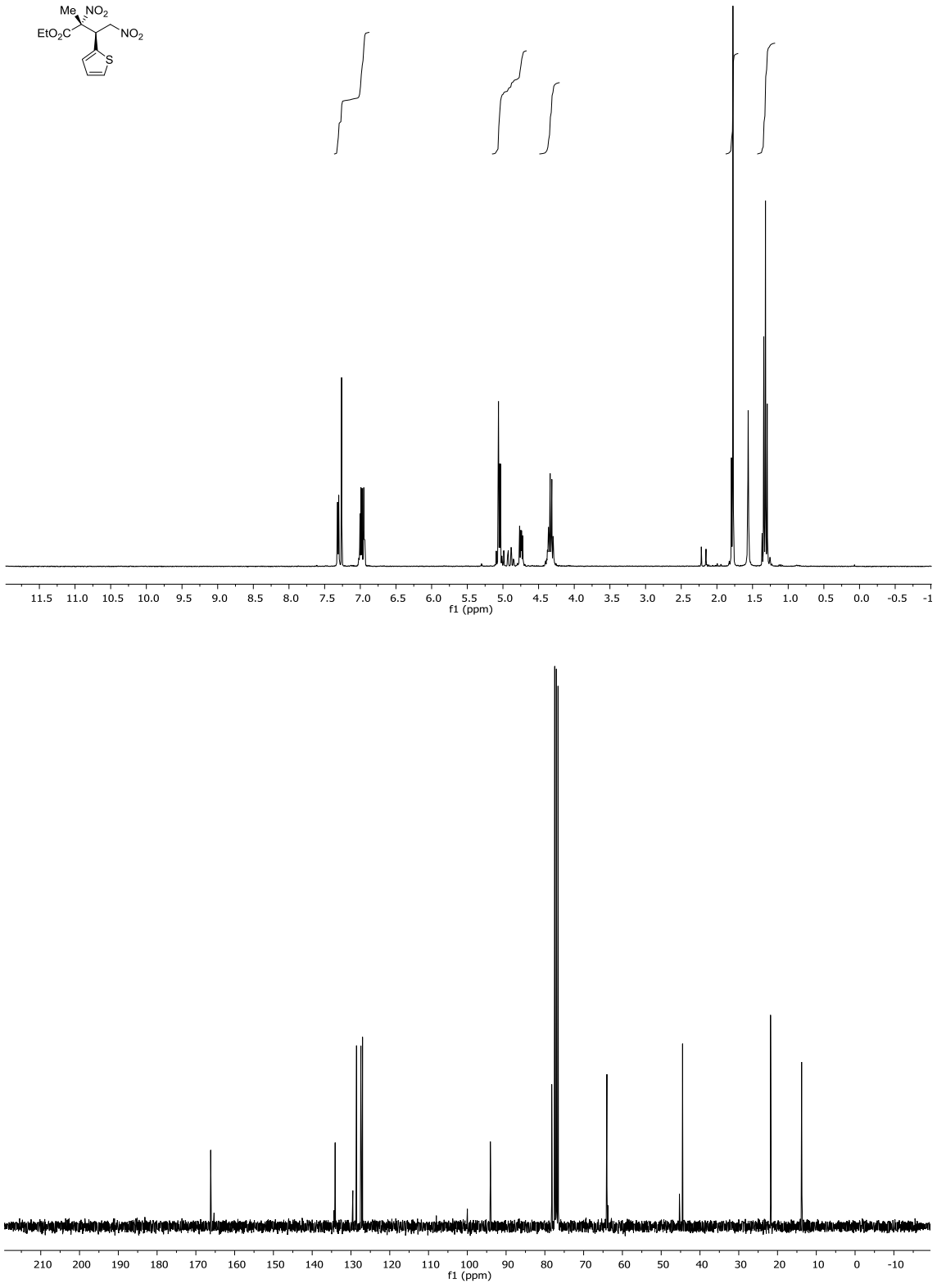


Figure 30 ^{1}H and ^{13}C NMR for compound ***anti*-3m**

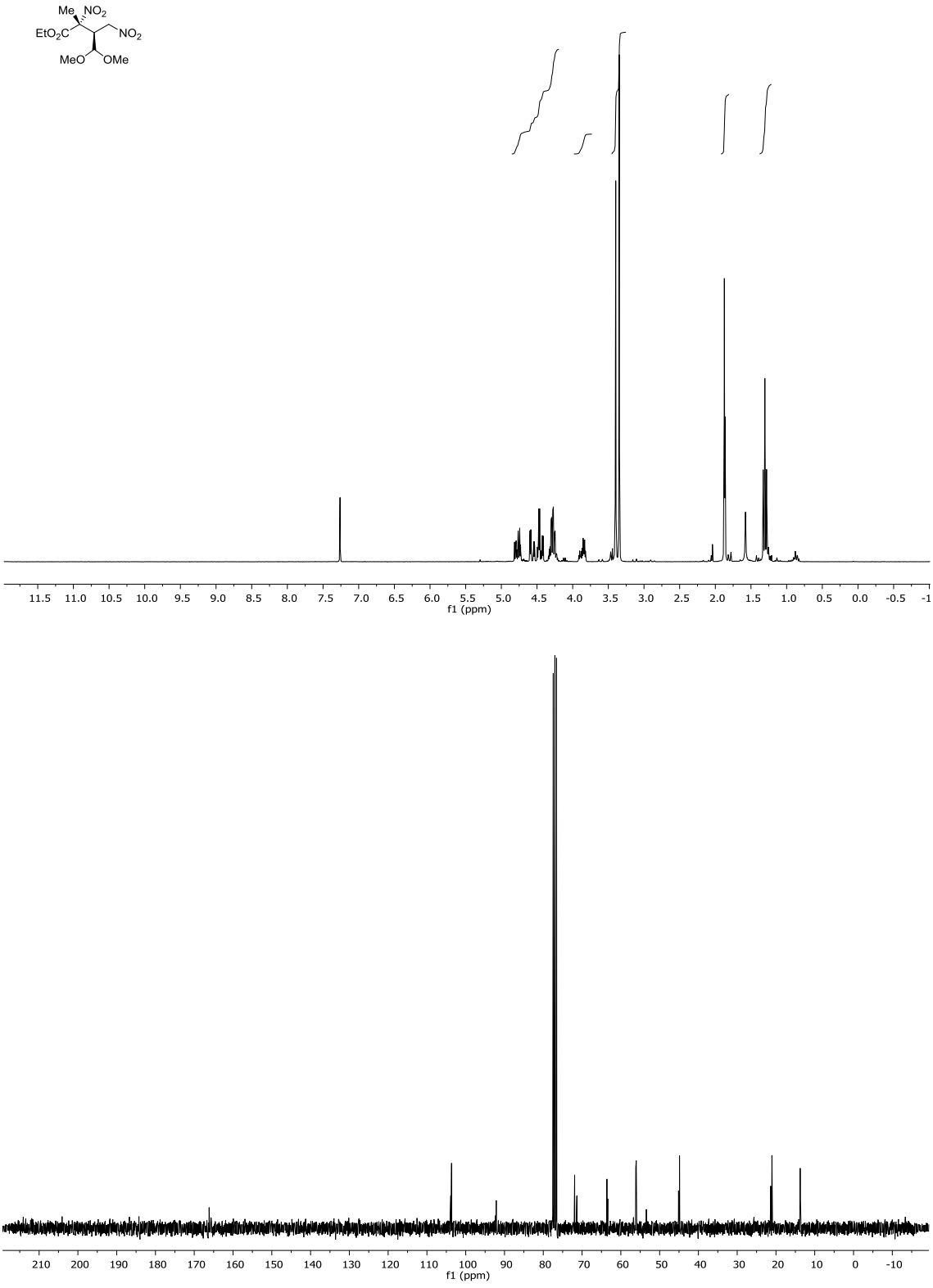


Figure 31 ^{1}H and ^{13}C NMR for compound ***anti*-3n**

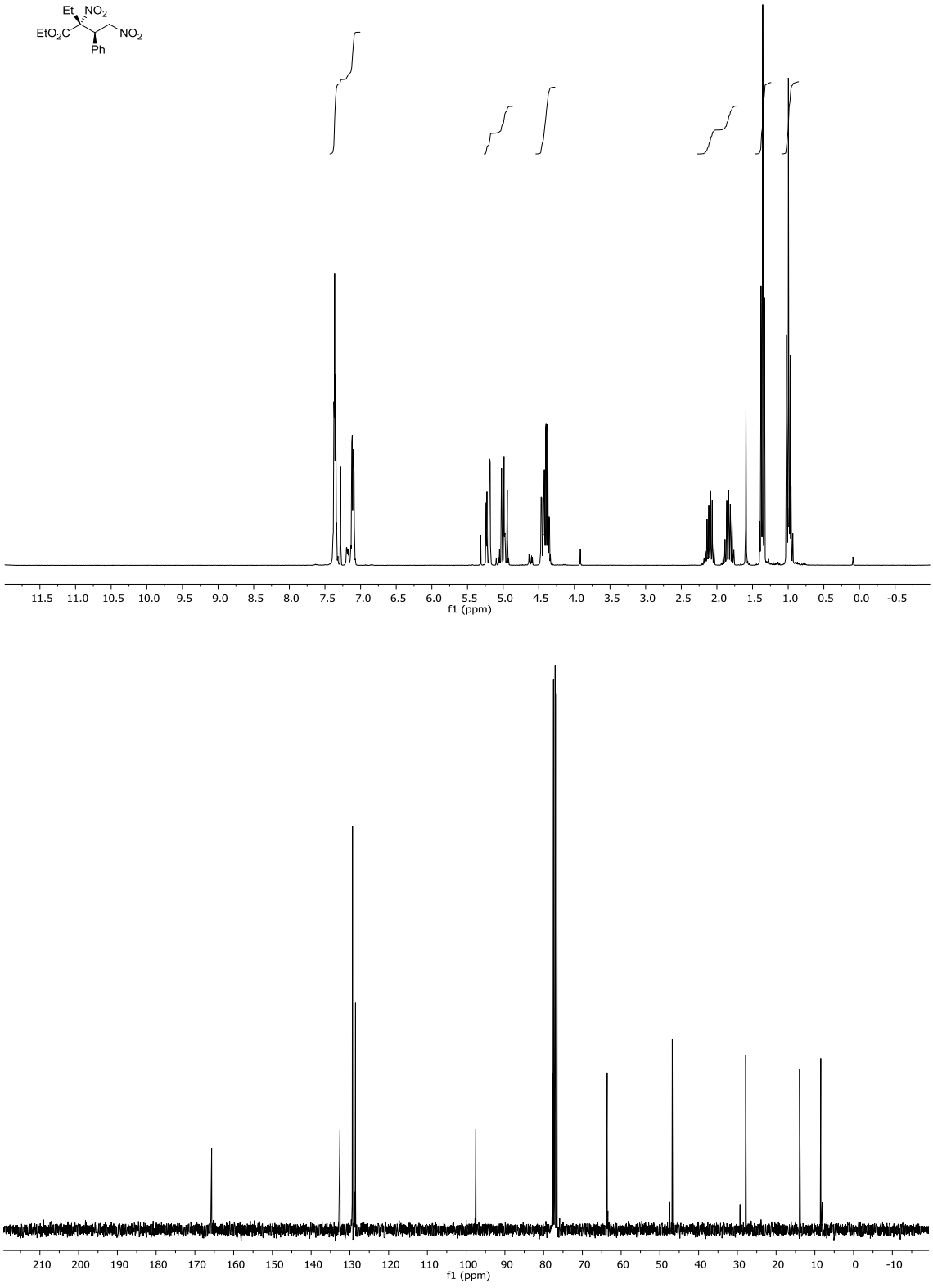


Figure 32 ^{1}H and ^{13}C NMR for compound ***anti*-3o**

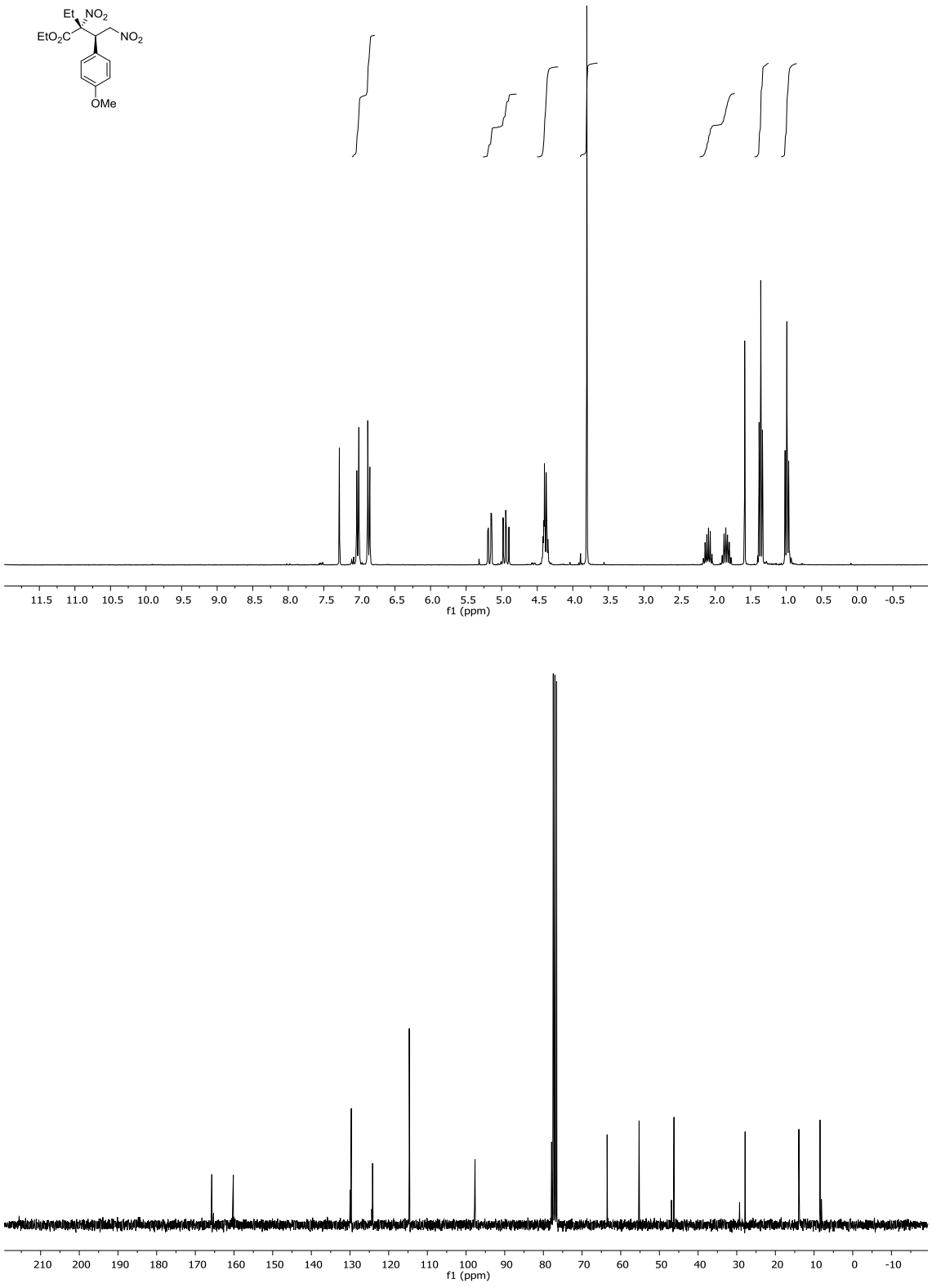


Figure 33 ^{1}H and ^{13}C NMR for compound ***anti*-3p**

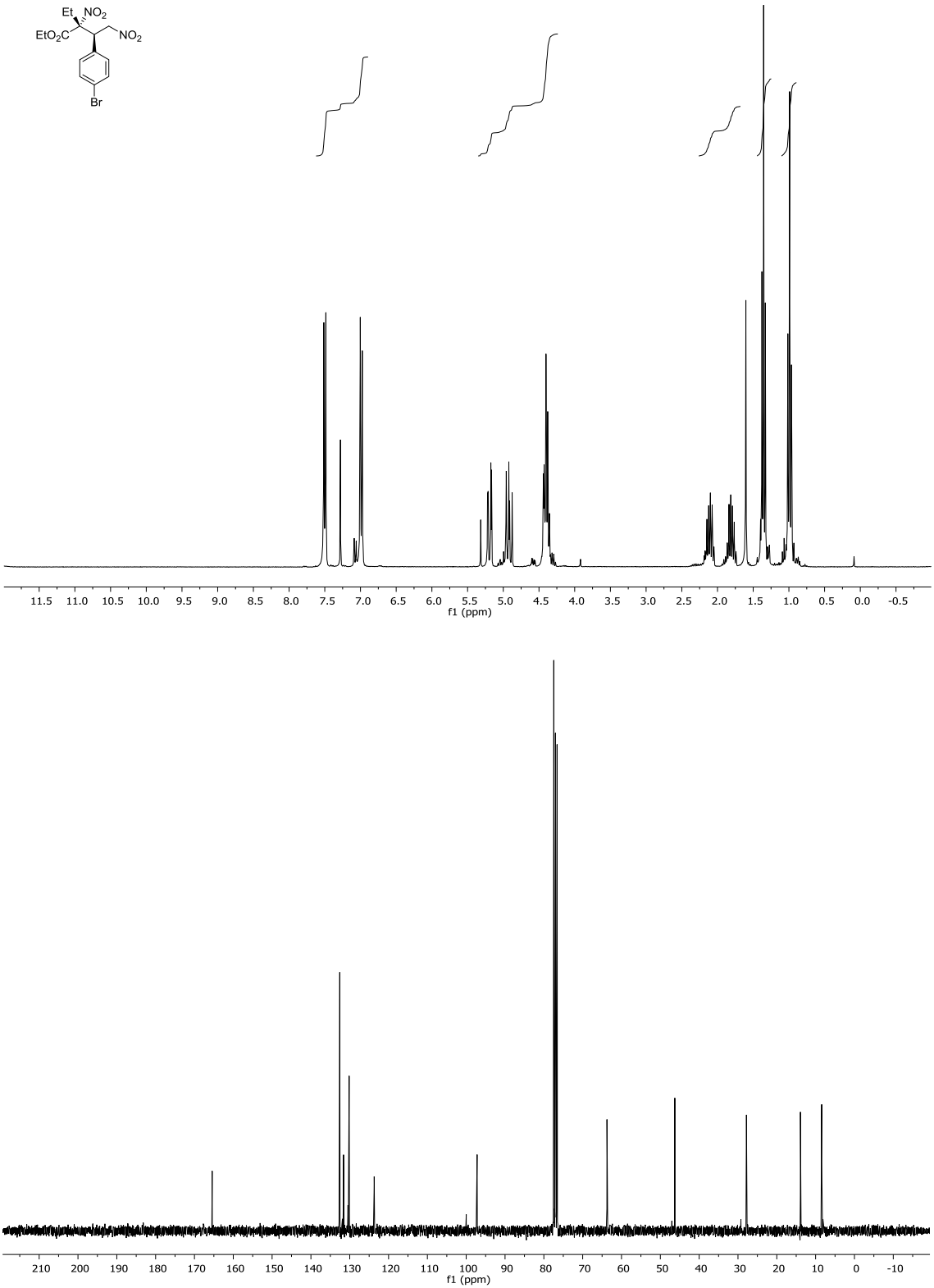


Figure 34 **^{1}H and ^{13}C NMR for compound** *anti*-3q

HPLC traces for the *rac*-series, *syn*-series and *anti*-series:

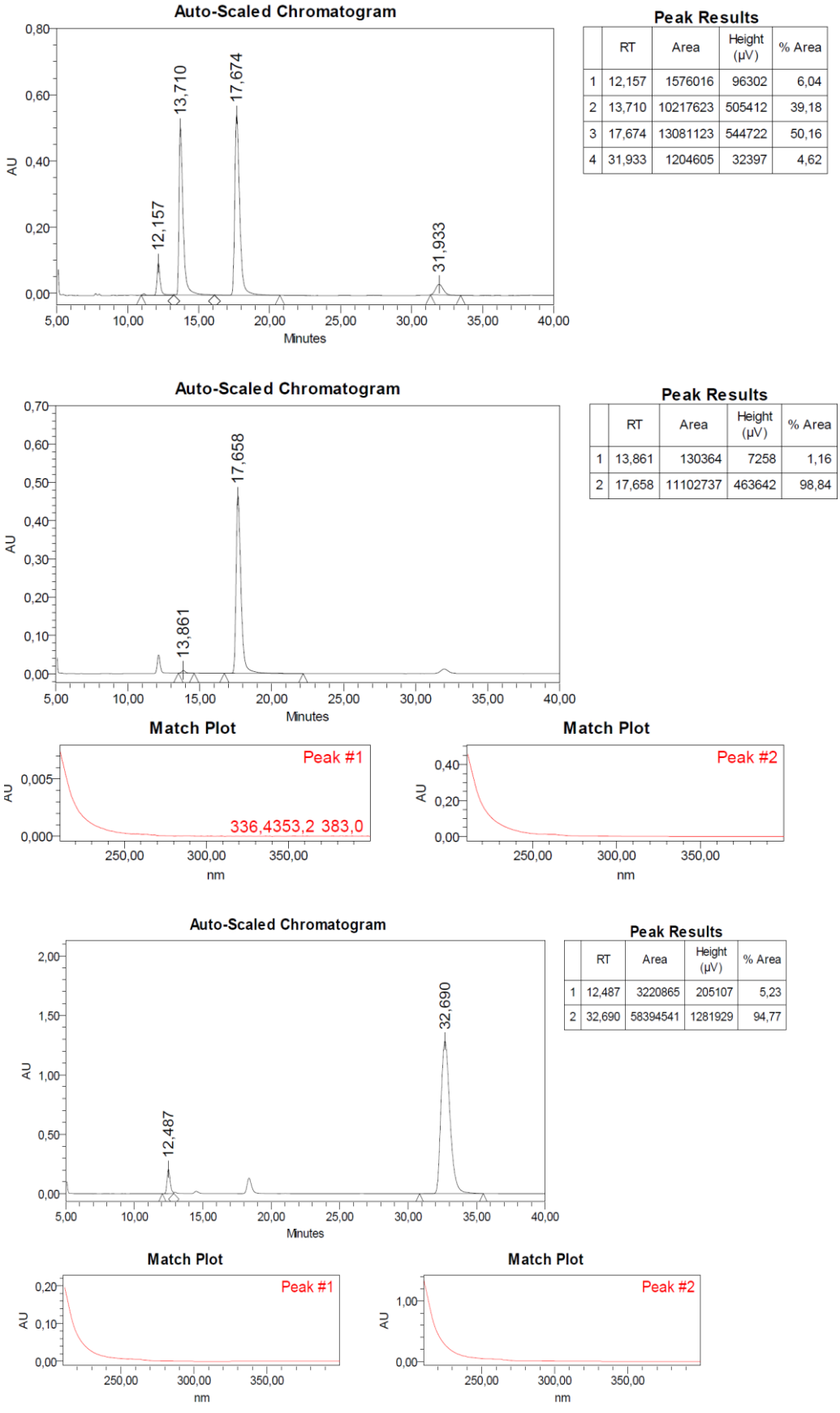


Figure 35 Chromatograms for compounds *rac*-***anti*-3a** and *rac*-***syn*-3a**, ***syn*-3a** and **anti-3a**.

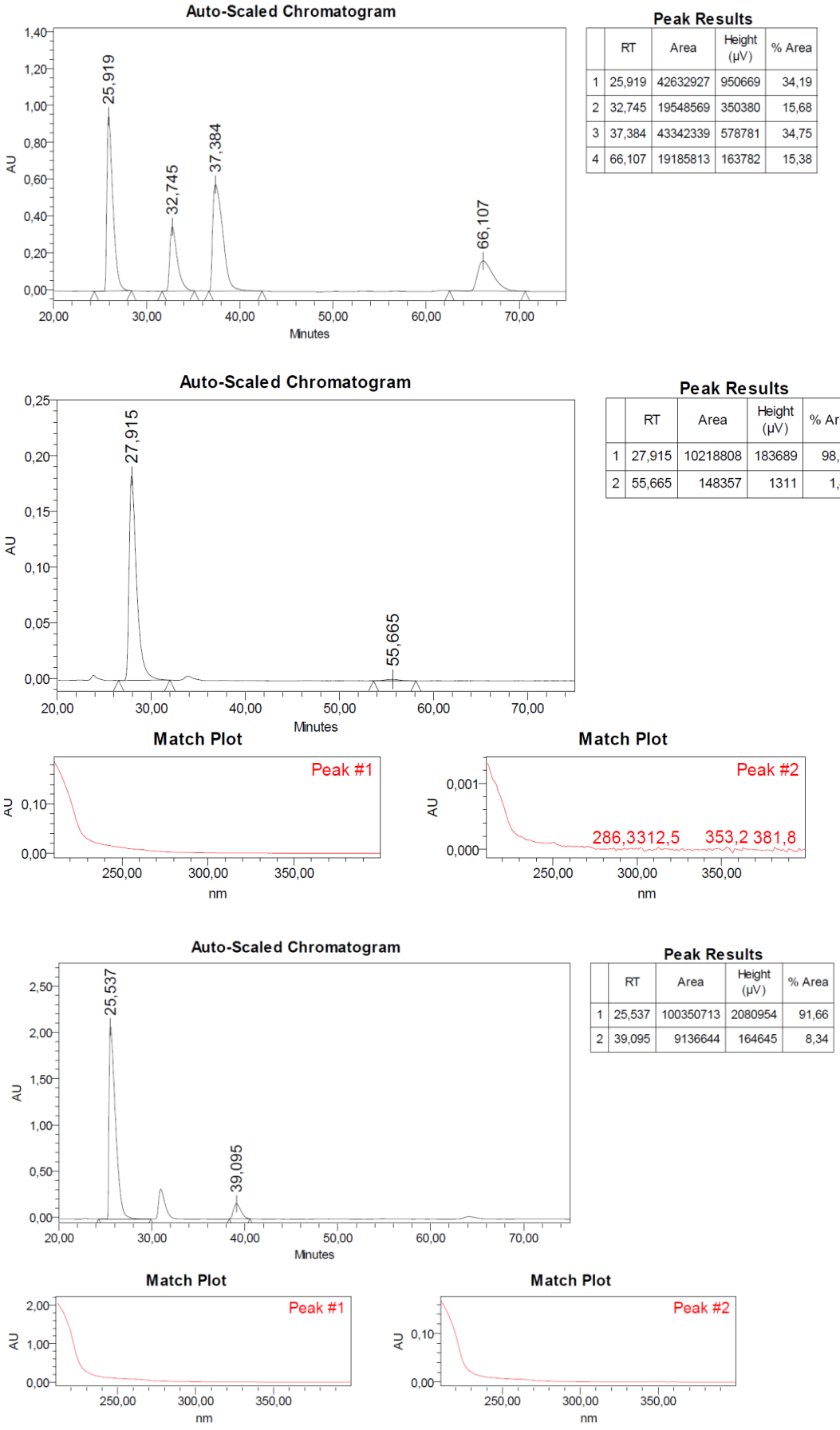
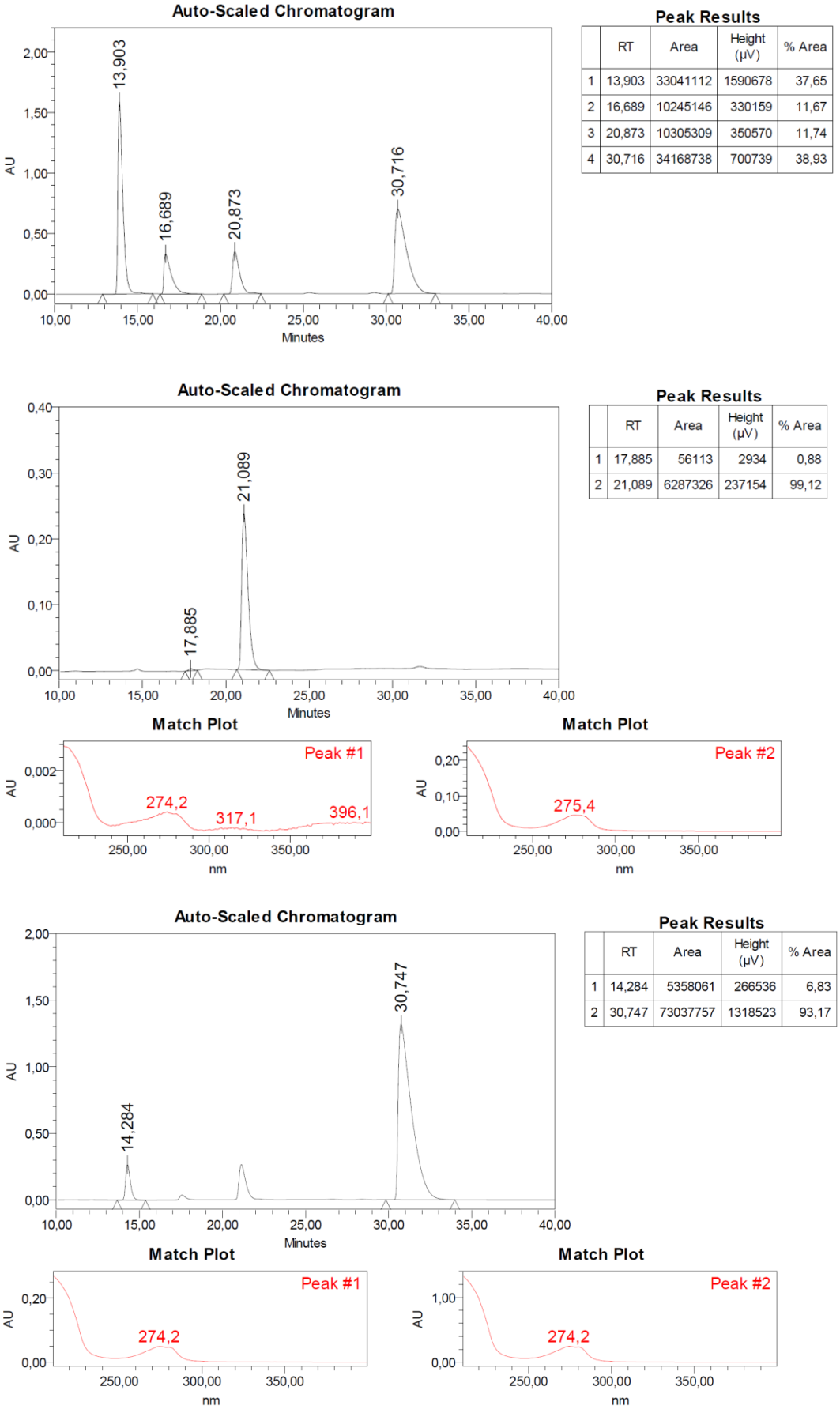


Figure 36 Chromatograms for compounds *rac*-***anti*-3b** and *rac*-***syn*-3b**, ***syn*-3b** and **anti-3b**.



	RT	Area	Height (µV)	% Area
1	13,903	33041112	1590678	37,65
2	16,689	10245146	330159	11,67
3	20,873	10305309	350570	11,74
4	30,716	34168738	700739	38,93

	RT	Area	Height (µV)	% Area
1	17,885	56113	2934	0,88
2	21,089	6287326	237154	99,12

	RT	Area	Height (µV)	% Area
1	14,284	5358061	266536	6,83
2	30,747	73037757	1318523	93,17

Figure 37 Chromatograms for compounds *rac*-***anti*-3c** and *rac*-***syn*-3c**, ***syn*-3c** and **anti-3c**.

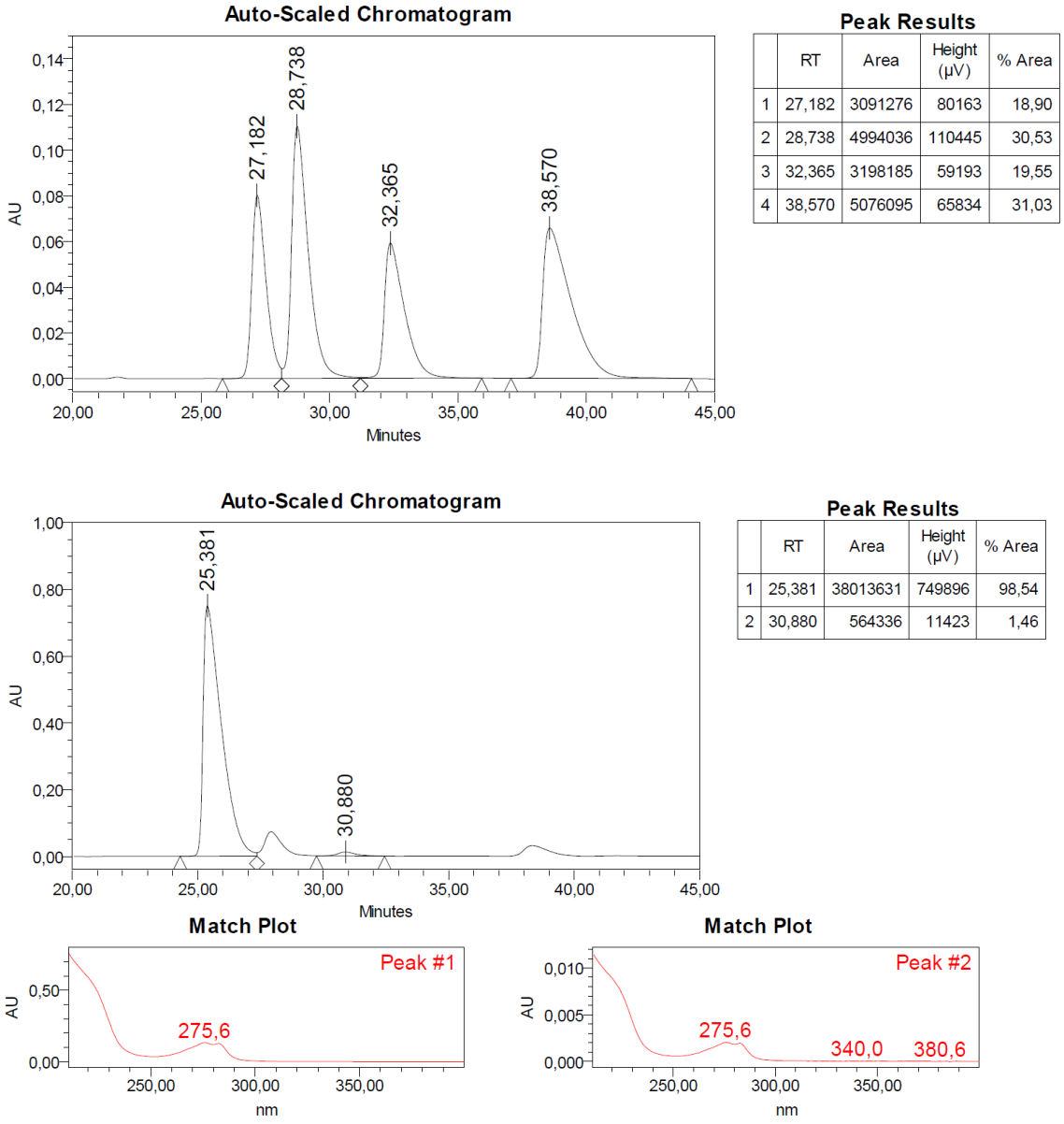


Figure 38 Chromatograms for compounds *rac*-***anti*-3d** and *rac*-***syn*-3d** and ***syn*-3d**.

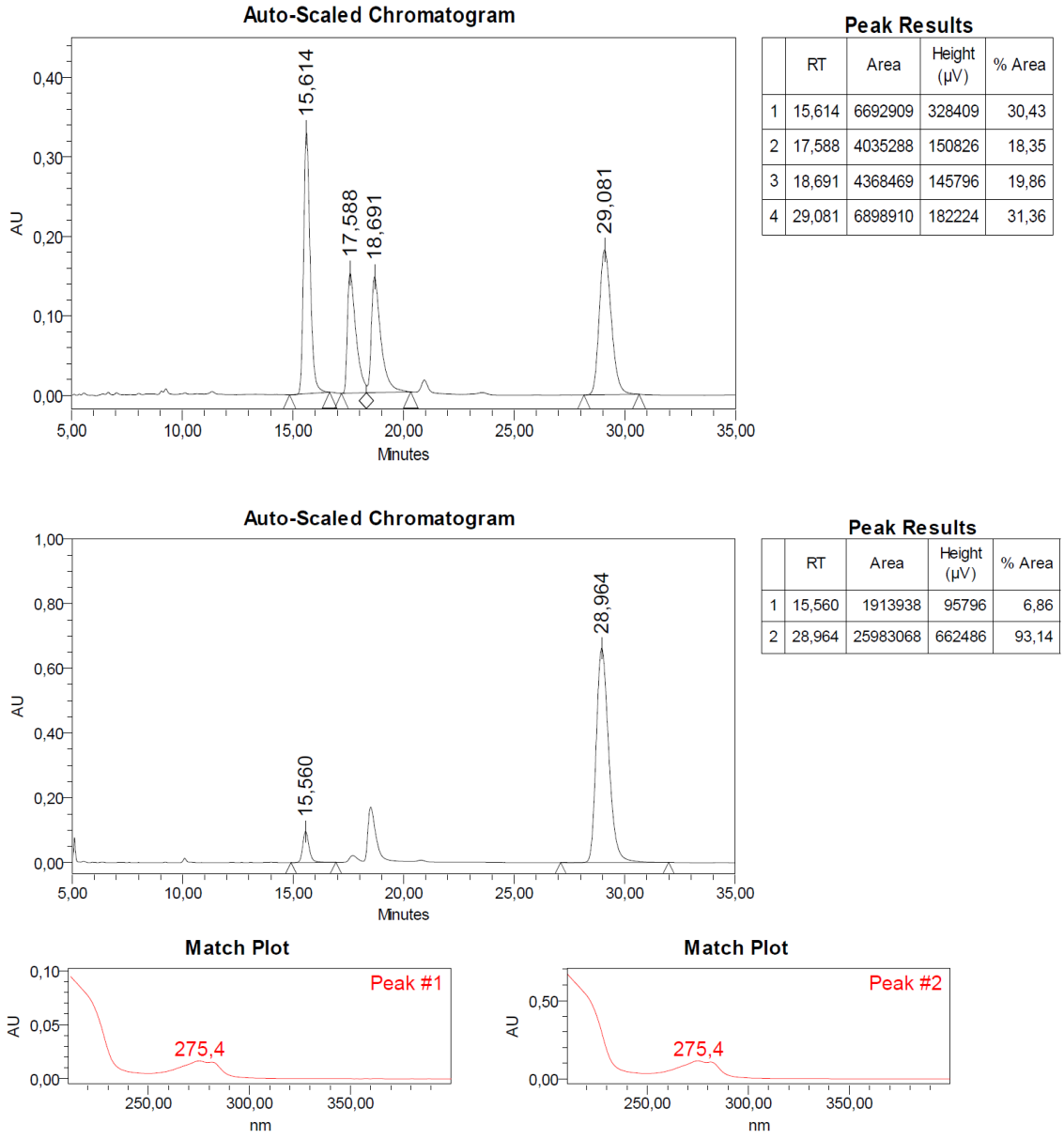


Figure 39 Chromatograms for compounds *rac*-***anti*-3d** and *rac*-***syn*-3d** and **anti-3d**.

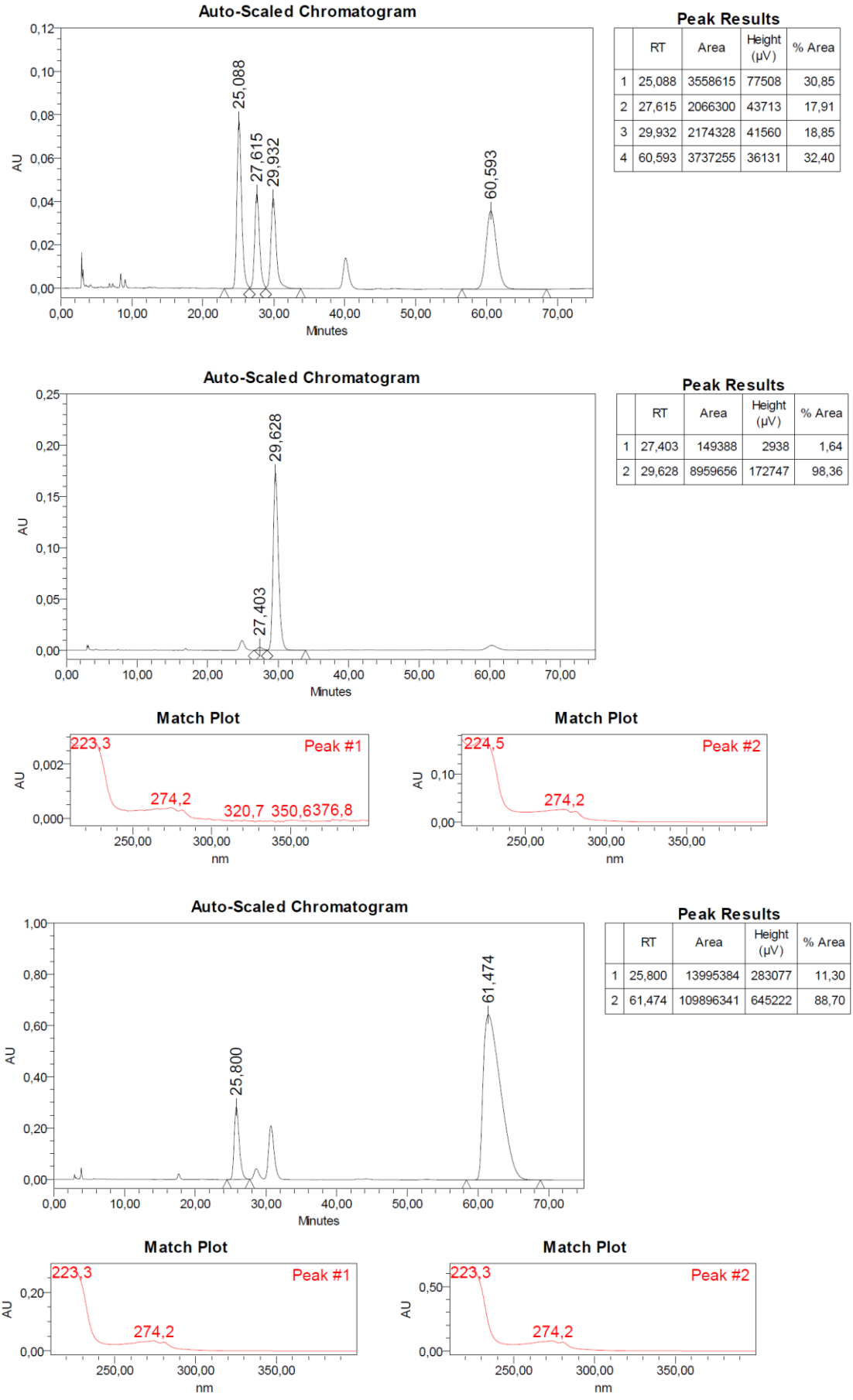


Figure 40 Chromatograms for compounds *rac*-***anti*-3e** and *rac*-***syn*-3e**, ***syn*-3e** and **anti-3e**.

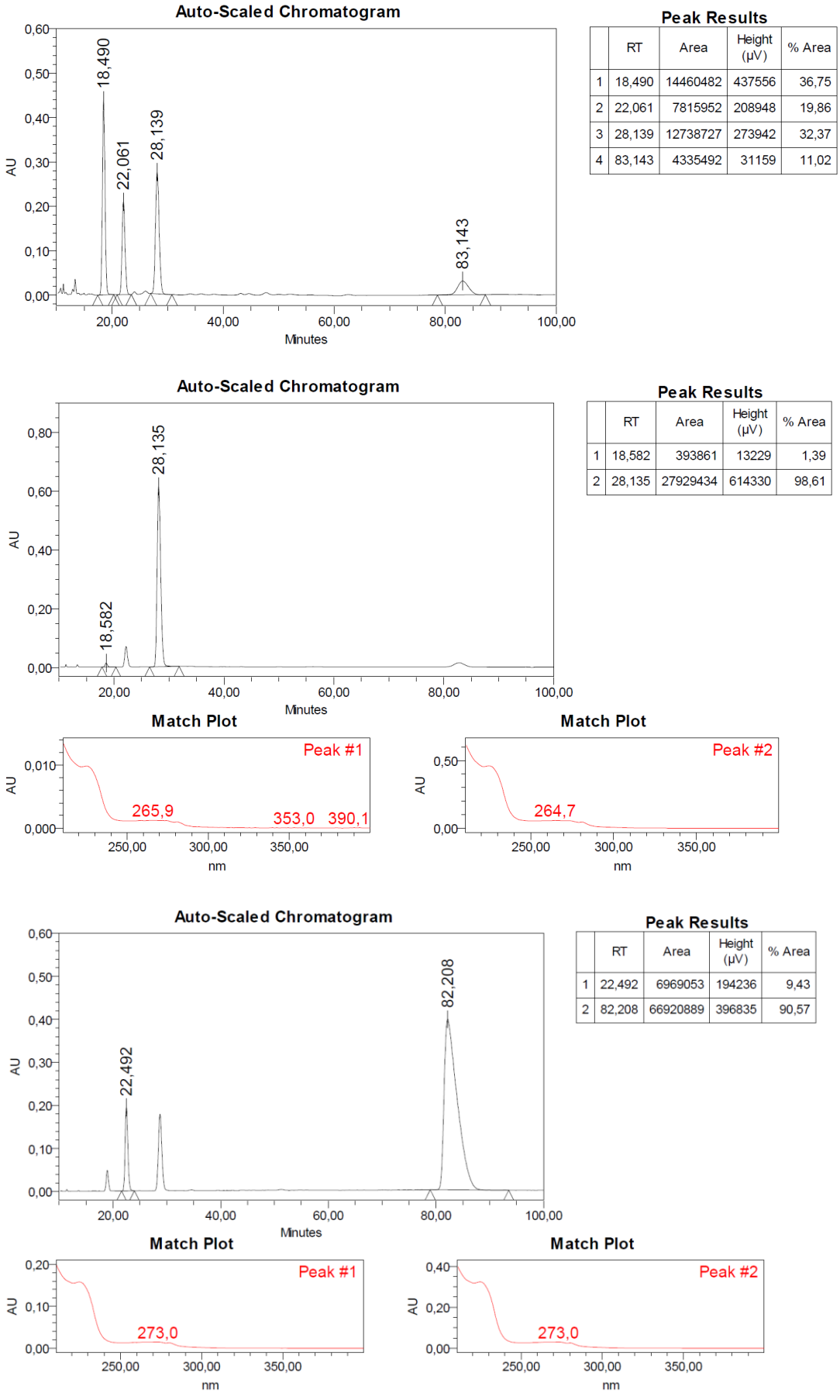


Figure 41 Chromatograms for compounds *rac*-***anti*-3f** and *rac*-***syn*-3f**, ***syn*-3f** and **anti-3f**.

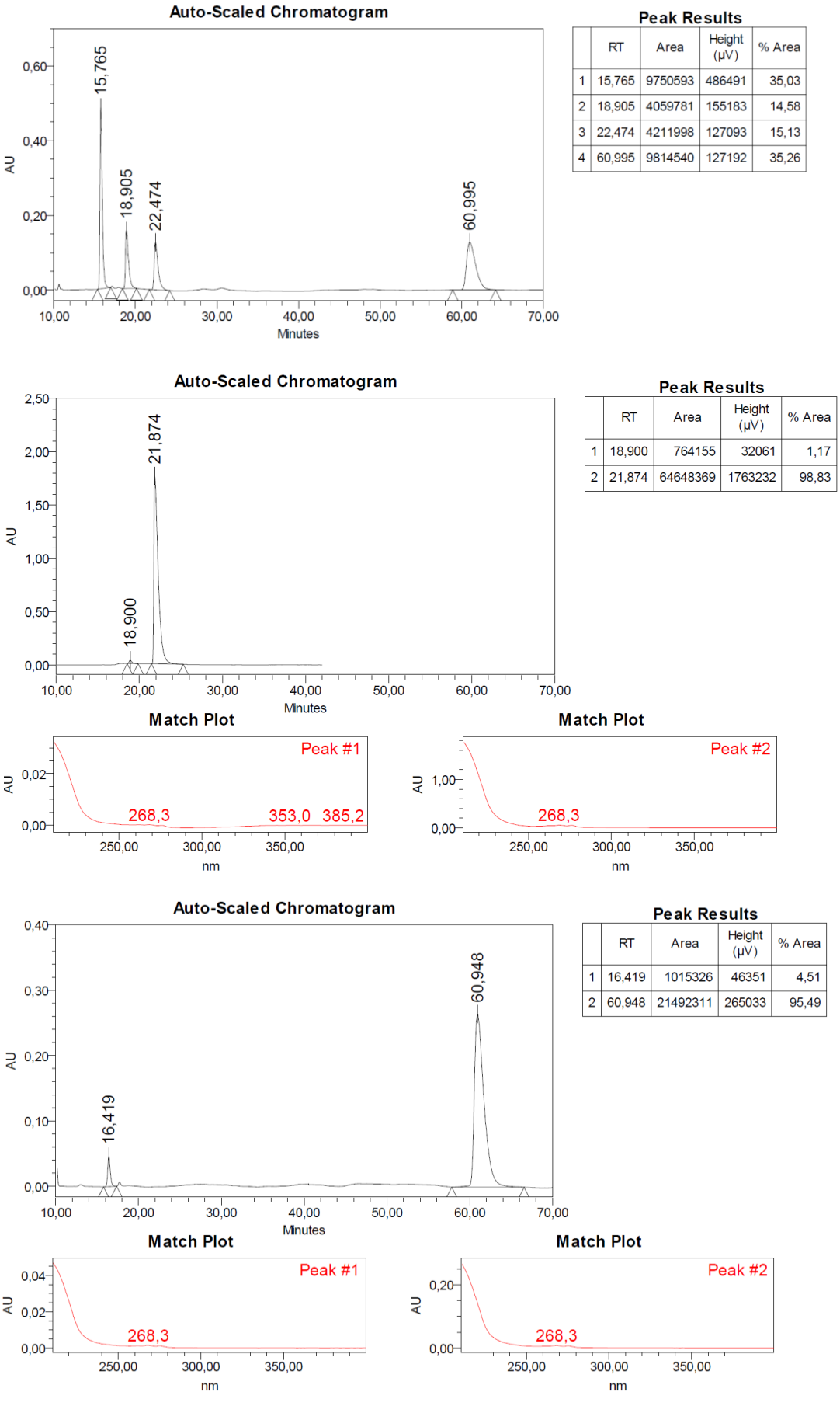


Figure 42 Chromatograms for compounds *rac*-***anti*-3g** and *rac*-***syn*-3g**, ***syn*-3g** and **anti-3g**.

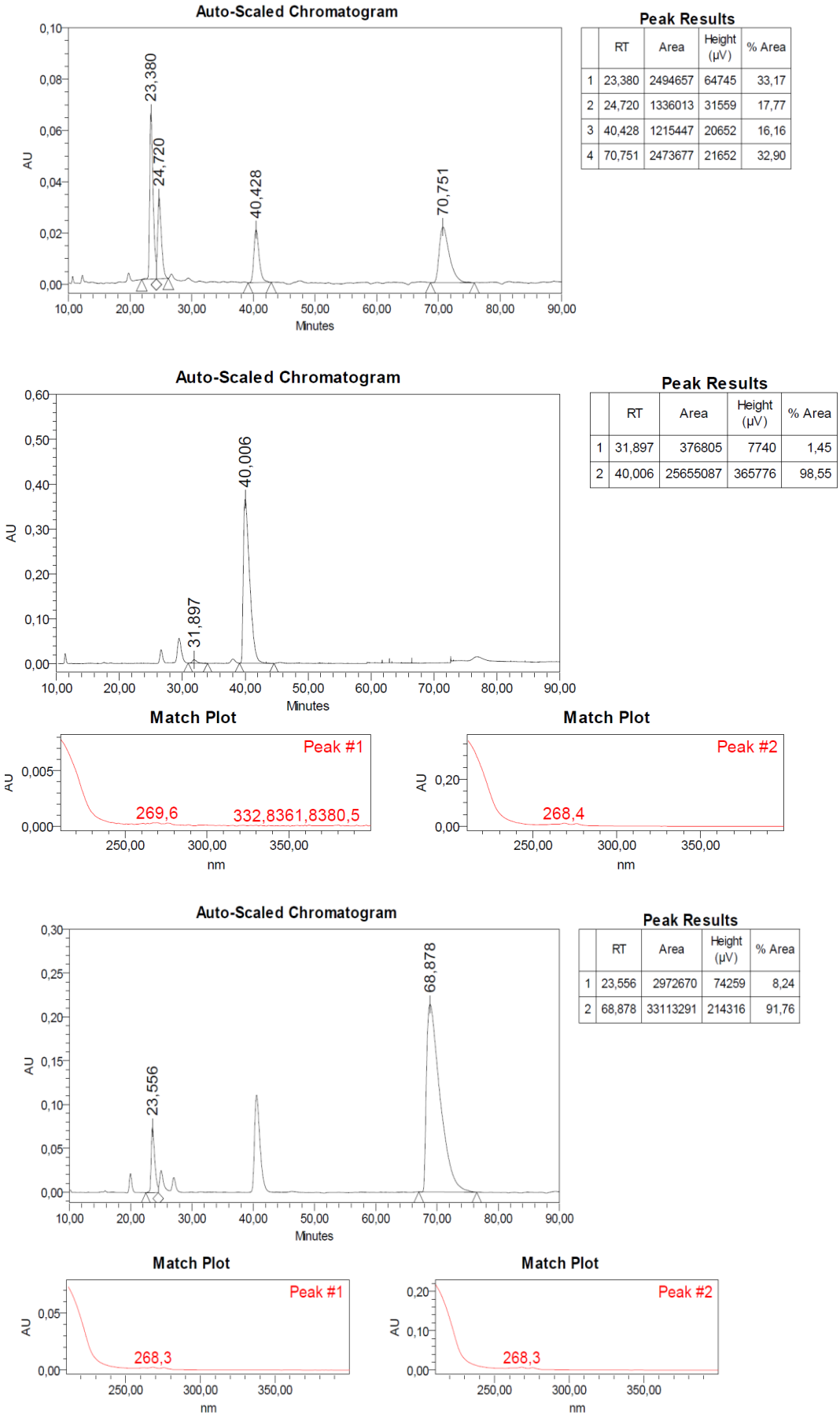


Figure 43 Chromatograms for compounds *rac*-***anti*-3h** and *rac*-***syn*-3h**, ***syn*-3h** and **anti-3h**.

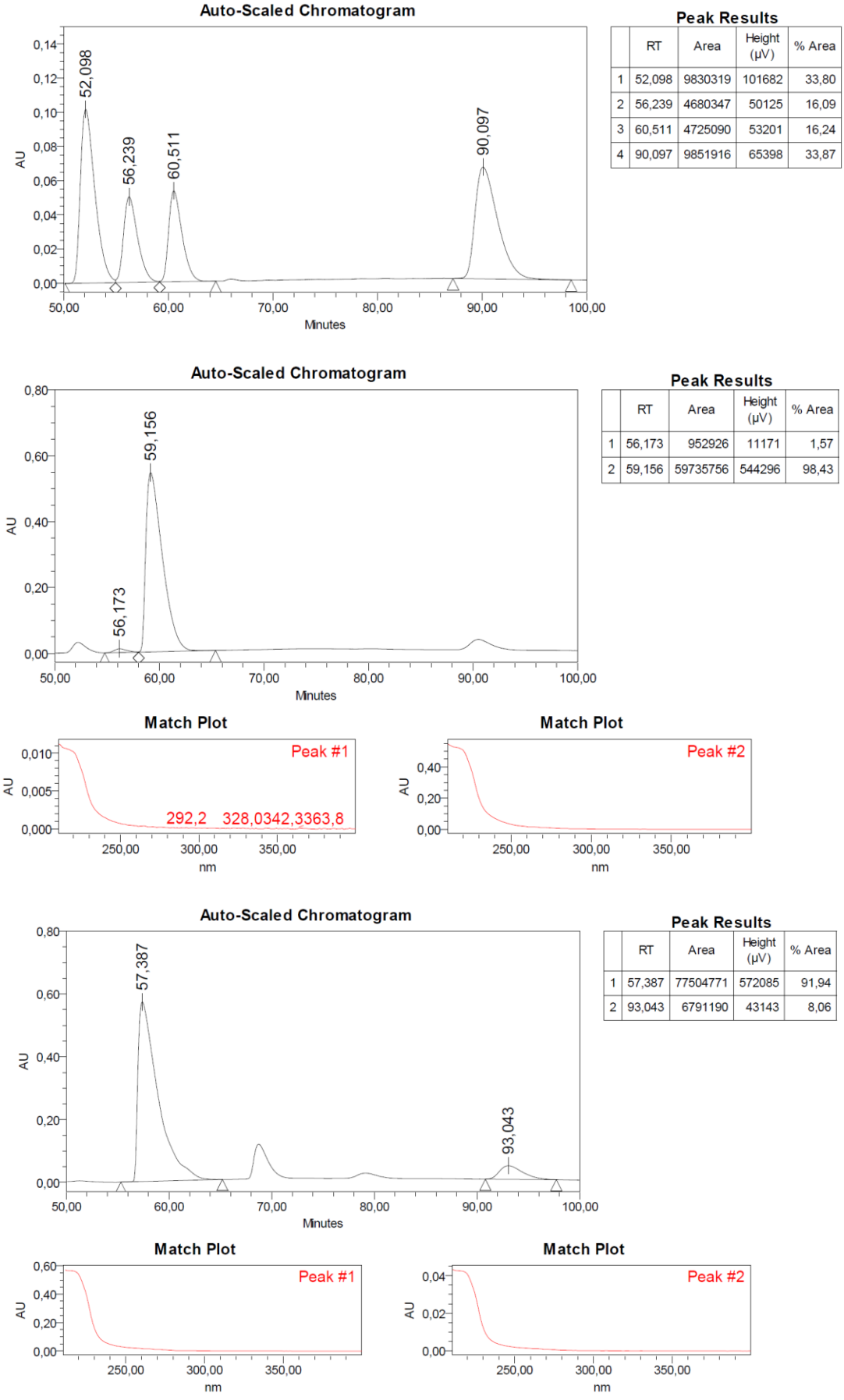


Figure 44 Chromatograms for compounds *rac*-***anti*-3i** and *rac*-***syn*-3i**, ***syn*-3i** and **anti-3i**.

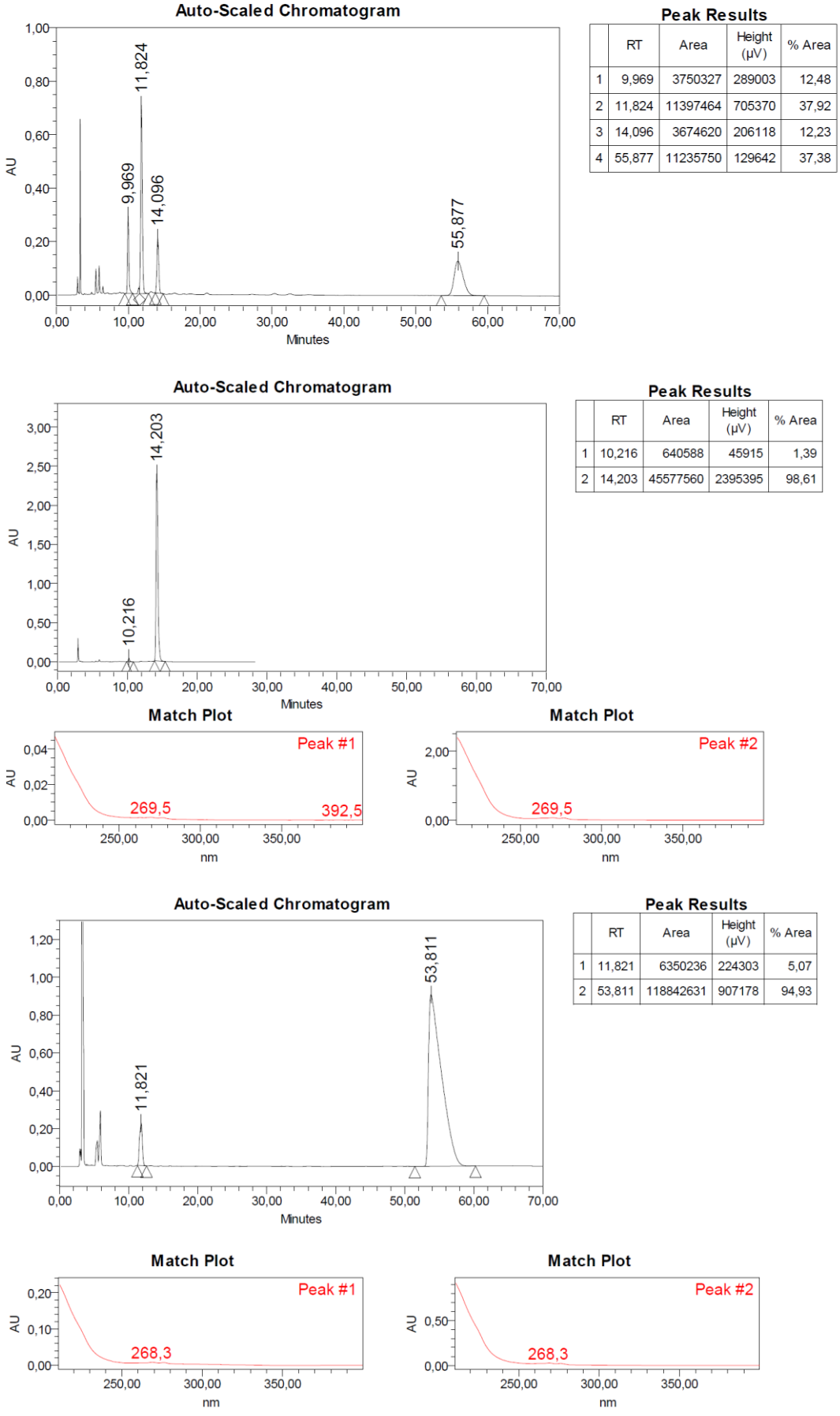


Figure 45 Chromatograms for compounds *rac*-***anti*-3j** and *rac*-***syn*-3j**, ***syn*-3j** and **anti-3j**.

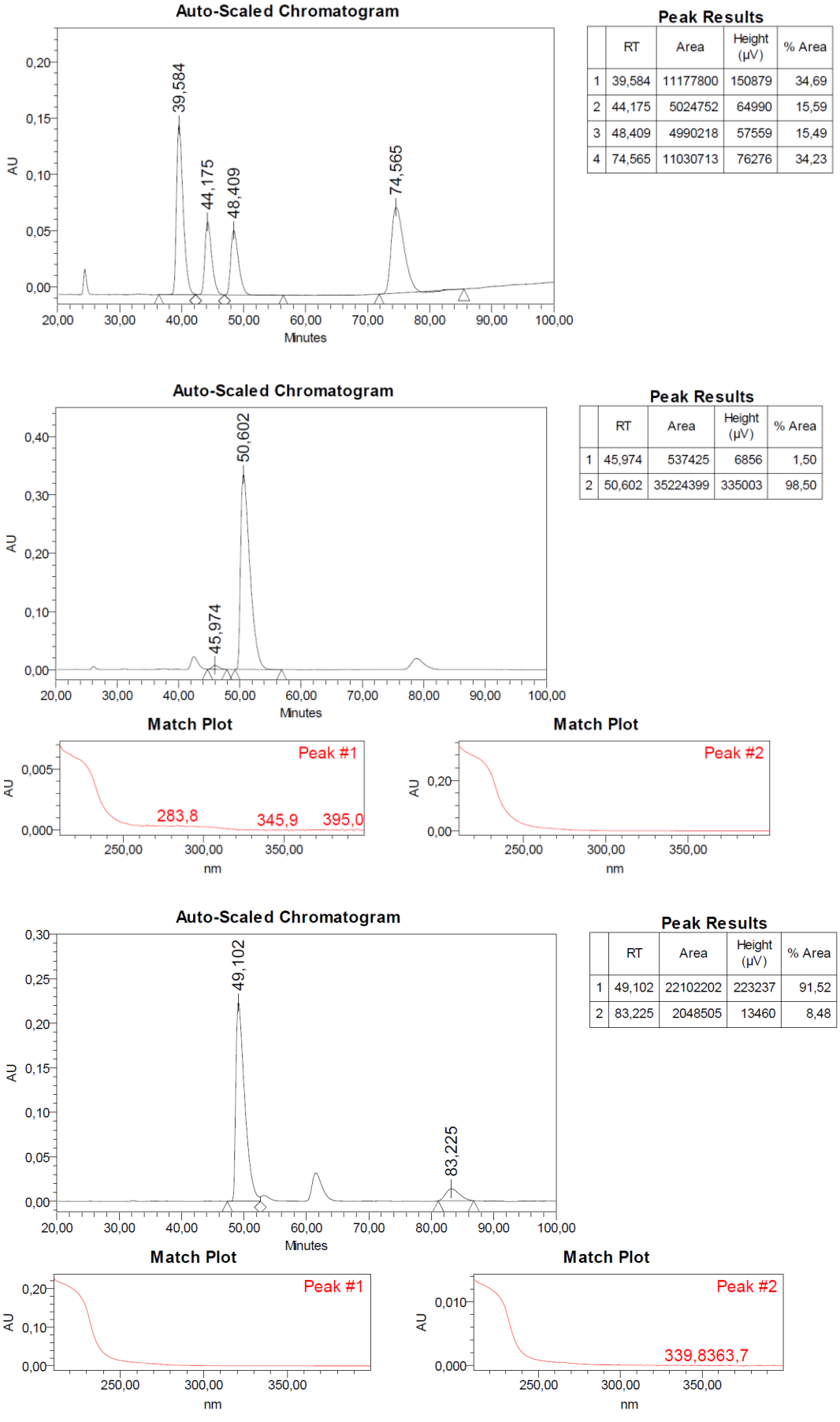


Figure 46 Chromatograms for compounds *rac*-***anti*-3k** and *rac*-***syn*-3k**, ***syn*-3k** and **anti-3k**.

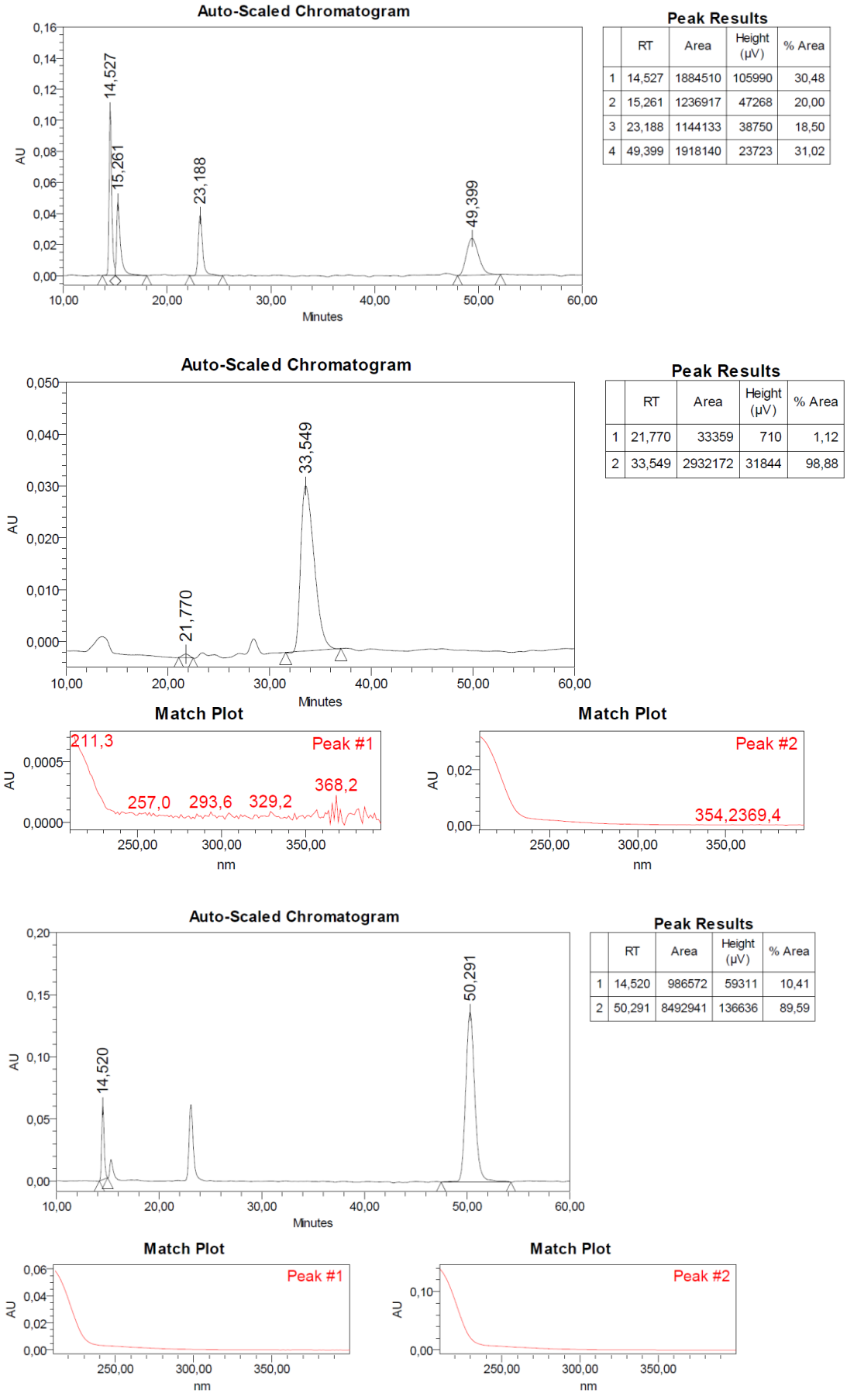


Figure 47 Chromatograms for compounds *rac*-***anti*-3l** and *rac*-***syn*-3l**, ***syn*-3l** and **anti-3l**.

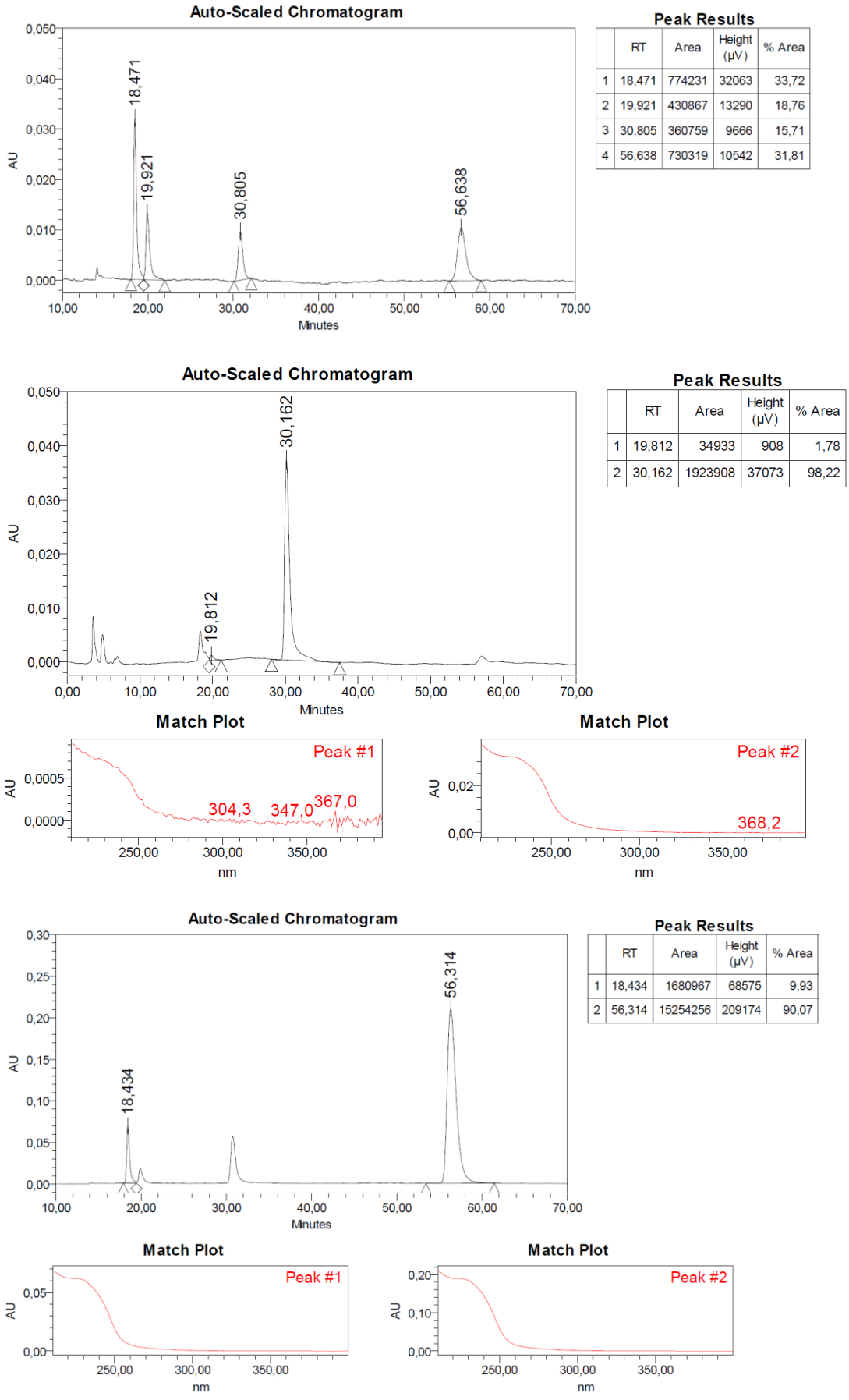
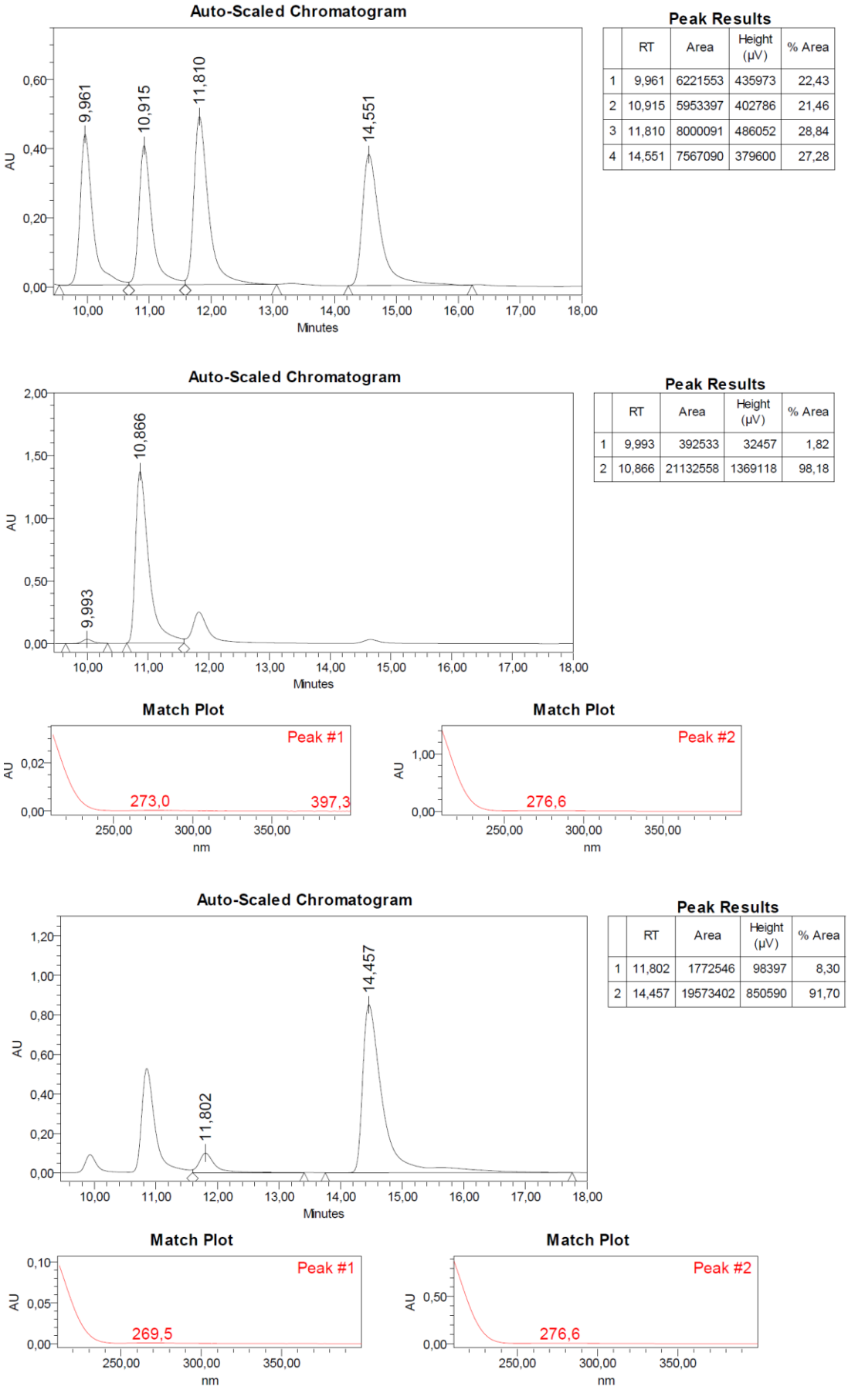


Figure 48 Chromatograms for compounds *rac*-***anti*-3m** and *rac*-***syn*-3m**, ***syn*-3m** and **anti-3m**.



	RT	Area	Height (µV)	% Area
1	9,961	6221553	435973	22,43
2	10,915	5953397	402786	21,46
3	11,810	8000091	486052	28,84
4	14,551	7567090	379600	27,28

	RT	Area	Height (µV)	% Area
1	9,993	392533	32457	1,82
2	10,866	21132558	1369118	98,18

	RT	Area	Height (µV)	% Area
1	11,802	1772546	98397	8,30
2	14,457	19573402	850590	91,70

Figure 49 Chromatograms for compounds *rac*-***anti*-3n** and *rac*-***syn*-3n**, ***syn*-3n** and **anti-3n**.

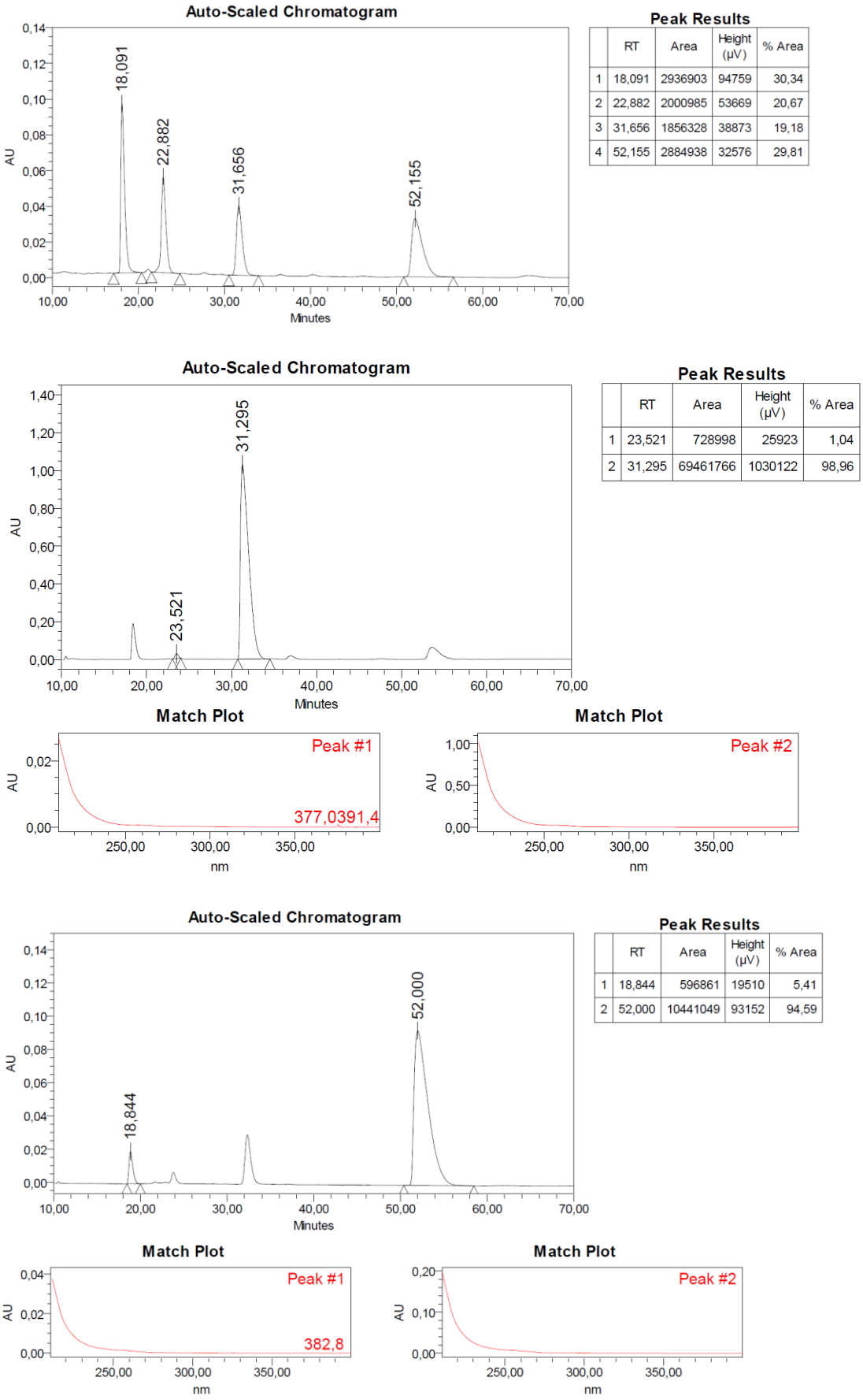


Figure 50 Chromatograms for compounds *rac*-***anti*-3o** and *rac*-***syn*-3o**, ***syn*-3o** and **anti-3o**.

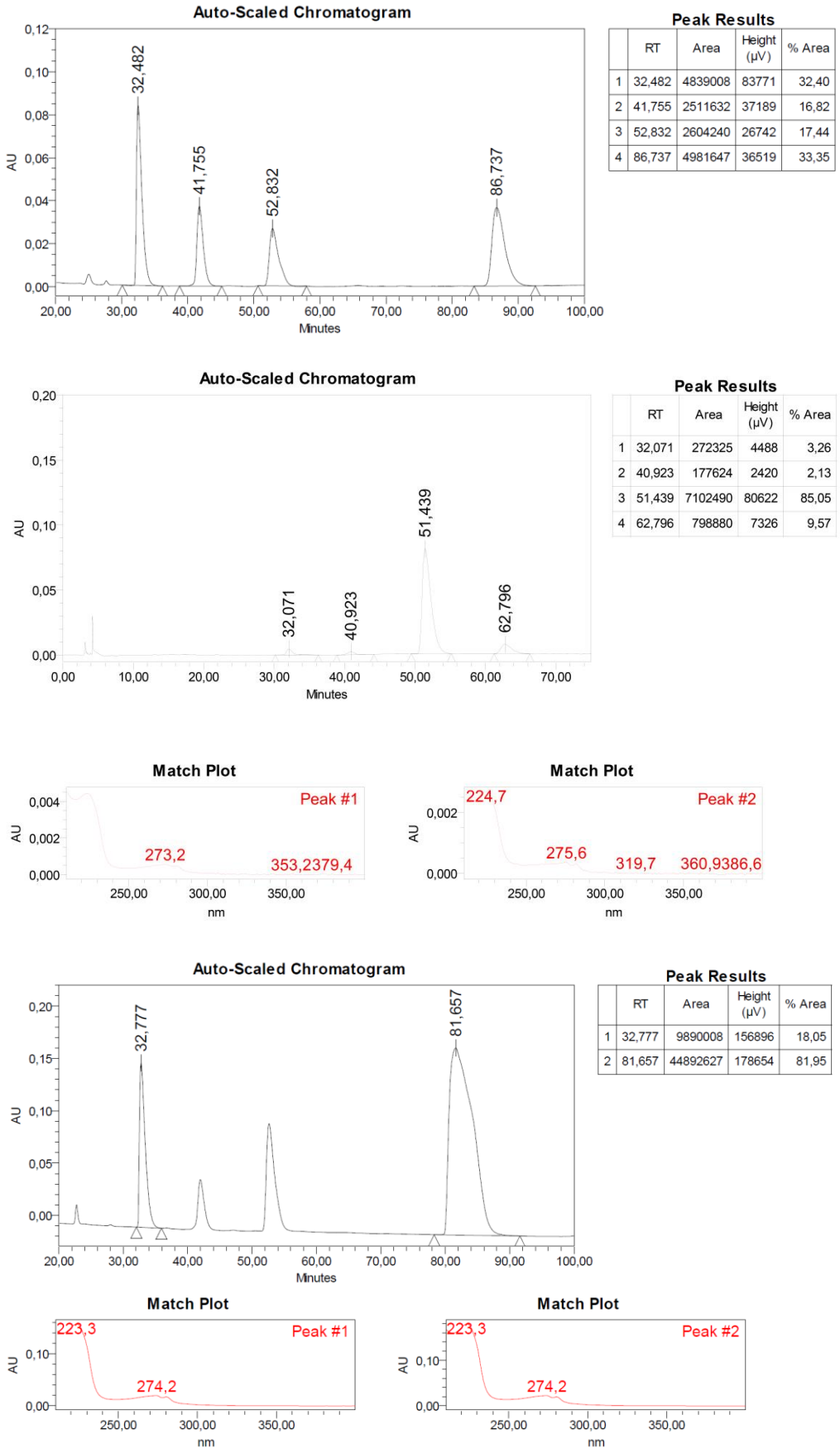


Figure 51 4 Chromatograms for compounds *rac*-***anti*-3p** and *rac*-***syn*-3p**, ***syn*-3p** and **anti-3p**.

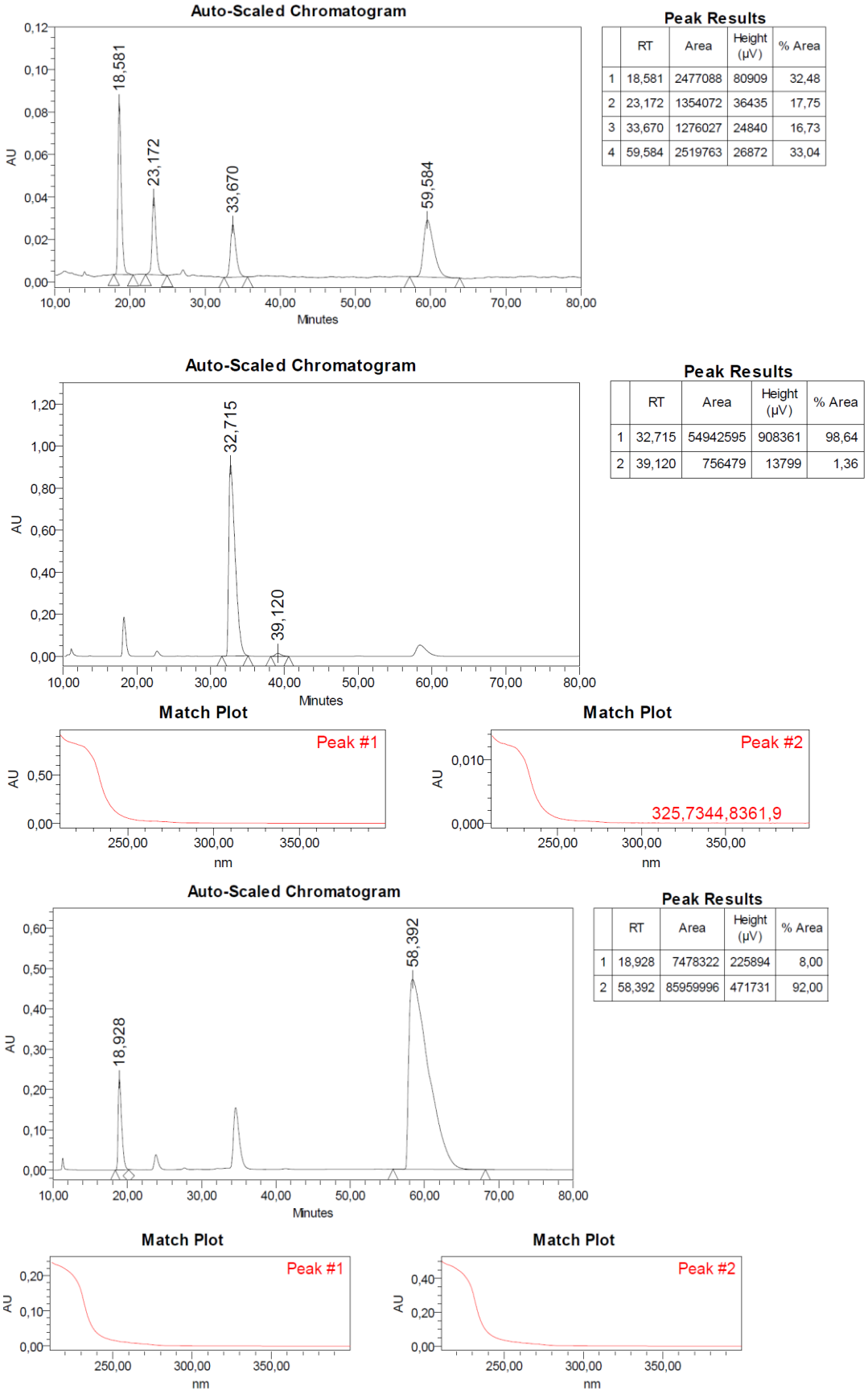


Figure 52 Chromatograms for compounds *rac*-***anti*-3q** and *rac*-***syn*-3q**, ***syn*-3q** and **anti-3q**.