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Electronic supporting information

A novel C-5' substituted cinchona alkaloid-derived catalyst promotes additions of alkyl thiols to nitroolefins with excellent enantioselectivity

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1.0 General

Proton Nuclear Magnetic Resonance spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ (unless otherwise stated) referenced relative to residual $CHCl_3$ (δ = 7.26 ppm). Chemical shifts are reported in ppm and coupling constants in Hertz. Carbon NMR spectra were recorded on the same instrument (100 MHz) with total proton decoupling. Fluorine NMR spectra were recorded at 350 MHz. HSQC, TOCSY and NOE NMR experiments were used to aid assignment of NMR resonances when required. Mass spectra were recorded by electron impact ionization, chemical ionisation, in ES positive or ES negative modes for electron spray mass spectroscopy. All melting points were determined using a standard melting point apparatus and are uncorrected. $[\alpha]_D$ values are given in 10^{-1} deg cm^2g^{-1}. Flash chromatography was carried out using silica gel, particle size 0.04-0.063 mm. TLC analysis was performed on precoated $60F_{254}$ slides, and visualized by UV irradiation, $KMnO_4$ staining. *Tert*-butyl benzylmercaptan, *para*-methoxybenzylmercaptan, *trans*-β-nitrostyrene, 2-((*E*)-2-nitrovinyl)thiophene, 2-nitrobenzaldehyde and hydrocinnamaldehyde were sourced commercially. All reactions were carried out under a protective argon atmosphere. The starting material used in the synthesis of the cinchona alkaloid derivative **12** was prepared according to the literature.[1]

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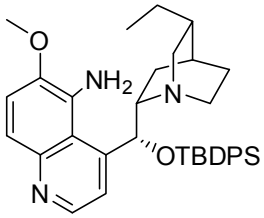
2.0 Synthesis of catalyst

2.1 4-((*R*)-((2*S*,4*S*,8*R*)-8-Ethylquinuclidin-2-yl)(tertbutyldiphenylsilyloxy)methyl)-6-methoxyquinolin-5-amine



5'-aminoquinine[1] (1.50 g, 4.40 mmol) was dissolved in freshly distilled DMF (8.0 mL). DMAP (55.10 mg, 0.44 mmol) was added and triethylamine (3.1 mL, 22.20 mmol) was injected *via* syringe. The obtained mixture was cooled to 0 °C and *tert*-butylchlorodiphenylsilane (1.4 mL, 5.28 mmol) was finally added dropwise *via* syringe. The reaction was then allowed to warm to room temperature and was stirred for 18 h. Diethyl ether (30 mL) was added and the resulting solution was washed with water (4 × 100 mL). The organic layer was separated, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (100% EtOAc -> 8:2 EtOAc:methanol) to give the expected silyl protected amino derivative (1.82 g, 71%) as a yellow solid. mp 179 °C-180 °C (decomposition 131 °C). $[\alpha]_D^{22}$ -114 (*c* 0.4 in $CHCl_3$). ν_{max}/cm^{-1}: 3325, 2933, 1798, 1551, 1454, 1378, 1277, 1182, 1124, 1042, 999, 842, 700. δ_H (400 MHz, $CDCl_3$): 8.41 (d, J 3.8, 1H), 7.79 (m, 2H), 7.58-7.43 (m, 5H), 7.36-7.30 (m, 1H), 7.25 (d, J 7.6, 2H), 7.11 (app. t, 2H), 6.56 (d, J 3.8, 1H), 5.99 (s, NH_2), 4.69 (d, J 10.0, 1H), 4.06 (s, 3H), 3.99 (app q, 1H), 2.79 (dd, J 9.2, 13.2, 1H), 2.31 (app t, 2H), 2.11-2.03 (m, 1H), 2.00-1.89 (m, 1H), 1.89 (br. s, 1H), 1.45-1.13 (m, 6H), 1.00 (s, 9H), 0.83 (t, J 7.2, 3H). δ_C (100 MHz, $CDCl_3$): 147.1, 145.7 (q), 142.8 (q), 135.9, 135.7, 132.2 (q), 131.6 (q), 131.4 (q), 129.9, 129.5, 127.5, 126.9, 126.8 (q), 122.0, 118.5, 116.9 (q), 114.4, 79.5, 59.4, 57.1, 56.1, 40.8, 37.2, 27.9, 27.2, 26.7, 24.9, 24.8, 18.9 (q), 11.9. HRMS (*m/z* -ES): Found: 580.3340 (M^+ + H. $C_{36}H_{46}N_3O_2Si$ Requires: 580.3359)

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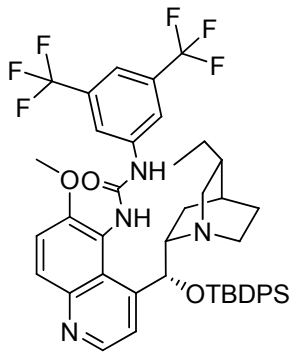
2.2 1-(3,5-*Bis*(trifluoromethyl)phenyl)-3-(4-((*R*)-((2*S*,4*S*,8*R*)-8-ethylquinuclidin-2-yl)(tertbutyldiphenylsilyloxy)methyl)-6-methoxyquinolin-5-yl)urea (12)



The amino derivative described above (1 g, 1.72 mmol) was dissolved in freshly distilled CH_2Cl_2 (5.0 mL) under an Ar atmosphere. The obtained solution was cooled to 0 °C and 3,5-*bis*(trifluoromethyl)phenyl isocyanate (350 µL, 2.00 mmol) was added dropwise over 10 min *via* syringe. The reaction was stirred for 18 h at 0 °C. Finally, the crude mixture was charged directly onto a flash chromatography column for purification (100% EtOAc -> 10/0.4 EtOAc-methanol) to give **12** as a cream solid (848 mg, 59%). mp 98-103 °C. $[\alpha]_D^{22}$ -55 (*c* 0.3 in $CHCl_3$). ν_{max}/cm^{-1}: 3264, 2932, 2861, 1686, 1542, 1471, 1429, 1384, 1276, 1175, 1129, 1110, 1026, 863, 701. δ_H (600 MHz, $CDCl_3$): 0.46 (t, J 6.9, 3H), 0.91-1.23 (m, 15H), 1.58 (app. br s, 1H), 1.93 (app. d, 1H), 2.18 (m, 1H), 2.31 (app. dd, 1H), 2.39-2.48 (m, 1H), 2.71 (dd, J 13.2, 9.6, 1H), 3.48 (app. dd, 1H), 4.02 (s, 3H), 4.85 (d, J 10.8, 1H), 6.73 (d, J 4.6, 1H), 6.88 (br s, NH), 7.09 (app. t, 2H), 7.15 (d, J 6.6, 2H), 7.30 (t, J 7.2, 1H), 7.48 (app. t, 2H), 7.50-7.55 (m, 2H), 7.65 (d, J 9.3, 1H), 7.78 (d, J 6.6, 2H), 7.97 (s, 2H), 8.15 (d, J 9.3, 1H), 8.53 (d, J 4.6, 1H), 9.31 (br s, NH). δ_C (100 MHz, $CDCl_3$): 171.4 (q), 153.1 (q), 152.7 (q), 147.9, 146.0 (q), 140.7 (q), 136.3, 135.8, 132.1 (q, J 33.0), 131.9 (q), 131.6 (q), 131.2, 130.4, 130.1, 127.9, 127.3, 125.1, 124.2 (q), 123.0 (q, J 275), 118.7 (q), 118.4, 117.0, 115.8, 81.07, 60.7, 57.9, 57.1, 41.0, 37.5, 28.4, 27.4, 27.0, 26.1, 25.1, 19.2 (q), 11.4. δ_F (350 MHz, $CDCl_3$): -63.4. HRMS (*m/z*-MALDI): Found: 835.3334 (M^+ + H. $C_{45}H_{49}F_6N_4O_3Si$. Requires: 835.3400)

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3. Asymmetric Michael addition procedures

3.1 Procedure A

A reaction vessel containing a stirring bar was flushed with argon, charged with the quinine-based cinchona alkaloid catalyst **12** (16.7 mg, 0.02 mmol) and trans-β-nitrostyrene (30 mg, 0.20 mmol). Anhydrous CH_2Cl_2 (10.0 mL, 0.02 M) was added *via* syringe followed by styrene (23 µL, 0.20 mmol) used as an internal standard. The vial was then cooled to -78 °C. After stirring for 20 min at this temperature, *tert*-butylbenzylmercaptan (37 µL, 0.20 mmol) was added dropwise to the reaction medium *via* syringe. The resulting solution was stirred at -78 °C for 20 h. The obtained solution was analysed by ^{1}H-NMR spectroscopy. The product was then directly purified by flash chromatography.

3.2 Procedure B

A reaction vessel containing a stirring bar was flushed with argon, charged with the quinine-based cinchona alkaloid catalyst **12** (25.06 mg, 0.03 mmol) and 1-methoxy-4-((*E*)-2-nitrovinyl)benzene (26.87 mg, 0.15 mmol). Anhydrous CH_2Cl_2 (15.0 mL, 0.010 M) was added *via* syringe. The vial was then cooled to -78 °C. After stirring for 20 min at this temperature, *tert*-butylbenzylmercaptan (28 µL, 0.15 mmol) was added dropwise to the reaction medium *via* syringe. The resulting solution was stirred at -78 °C for 68 h. The product was then directly purified by flash chromatography.

3.3 Procedure C

A reaction vessel containing a stirring bar was flushed with argon, charged with the quinine-based cinchona alkaloid catalyst **12** (25.06 mg, 0.03 mmol) and 1-chloro-3-((*E*)-2-nitrovinyl)benzene (27.54 mg, 0.15 mmol). Anhydrous CH_2Cl_2 (22.5 mL, 0.007 M) was added *via* syringe. The vial was then cooled to -78 °C. After stirring for 20 min at this temperature, *tert*-butylbenzylmercaptan (28 µL, 0.15 mmol) was added dropwise to the reaction medium *via* syringe. The resulting solution was stirred at -78 °C for 68 h. The product was then directly purified by flash chromatography.

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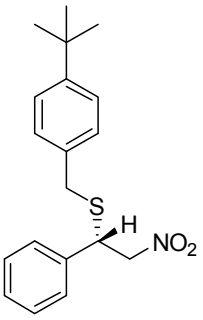
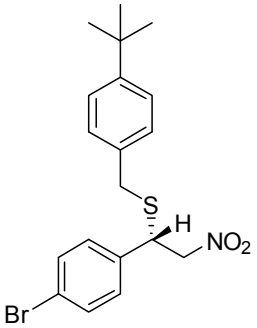
4. Characterisation data

4.1 (*S*)-(4-tert-butylbenzyl)(2-nitro-1-phenylethyl)sulfane (4a)



The Michael adduct was prepared according to procedure A using the quinine-based cinchona alkaloid catalyst **12** (16.7 mg, 0.02 mmol), trans-β-nitrostyrene (30 mg, 0.20 mmol), *tert*-butylbenzylmercaptan (37 µL, 0.20 mmol), CH_2Cl_2 (10.0 mL, 0.02 M) and styrene (23 µL, 0.20 mmol) as an internal standard. After purification of the crude material by flash chromatography (9:1 hexane:EtOAc) the product was obtained as a yellow oil (63.17 mg, 96%)**.** mp 42-45 °C. $[\alpha]_D^{22}$ +135 (*c* 0.2 in $CHCl_3$). The enantiomeric excess was determined by CSP-HPLC analysis using a Chiralcel AS column (4.6 mm x 25 cm); *n*-hexane/IPA 99/1; 1 mL/min; λ = 220 nm. t_R (major) = 7.85 min; t_R (minor) = 10.85 min; 92% *ee*. The absolute configuration of **(*S*)-4a** was established by crystal structure. ν_{max}/cm^{-1}: 2965, 1551, 1426, 1374, 1266, 1190, 905, 836, 751, 697. δ_H (400 MHz, $CDCl_3$): 7.44-7.27 (m, 7H), 7.21 (d, J 8.4, 2H), 4.77-4.66 (m, 2H), 4.47 (dd, J 9.2, 6.8, 1H), 3.70 (d, J 13.6, 1H), 3.61 (d, J 13.6, 1H), 1.36 (s, 9H). δ_C (100 MHz, $CDCl_3$): 150.2 (q), 137.1 (q), 133.8 (q), 129.0, 128.6, 128.5, 127.8, 125.7, 79.1, 46.0, 35.7, 34.6 (q), 31.3. HRMS (*m/z* -ES): Found: 329.1442 ($M^{+\cdot}$. $[C_{19}H_{23}NO_2S]^{+\cdot}$ Requires: 329.1450).

4.2 (*S*)-(4-*tert*-butylbenzyl)(1-(4-bromophenyl)-2-nitroethyl)sulfane (13)



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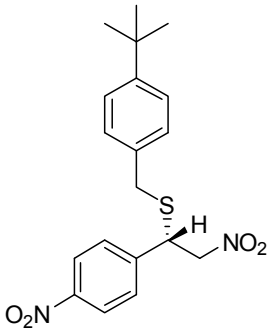
The Michael adduct was prepared according to procedure A using the quinine-based cinchona alkaloid catalyst **12** (12.53 mg, 0.015 mmol), 1-bromo-4-((*E*)-2-nitrovinyl)benzene (34.20 mg, 0.15 mmol), *tert*-butylbenzylmercaptan (28 µL, 0.15 mmol) and CH_2Cl_2 (7.5 mL, 0.02 M). After purification of the crude material by flash chromatography (CH_2Cl_2), the product was obtained as a yellow oil (58.30 mg, 96%). $[\alpha]_D^{22}$ +152 (*c* 0.4 in $CHCl_3$). The enantiomeric excess was determined by CSP-HPLC analysis using a Chiralcel AD-H column (4.6 mm x 25 cm); *n*-hexane/IPA 95/5; 1 mL/min; λ = 220 nm. t_R (minor) = 7.36 min; t_R (major) = 8.49 min; 90% *ee*. The absolute configuration of **(*S*)-13** was established by analogy with **(*S*)-4a**. ν_{max}/cm^{-1}: 2961, 1552, 1488, 1373, 1268, 1107, 1073, 1010, 825, 713. δ_H (400 MHz, $CDCl_3$): 7.46 (d, J 8.4, 2H), 7.33 (d, J 8.4, 2H), 7.20-7.10 (m, 4H), 4.64 (app. d, 2H), 4.38 (app. t, 1H), 3.67 (d, J 13.6, 1H), 3.57 (d, J 13.6, 1H), 1.32 (s, 9H). δ_C (100 MHz, $CDCl_3$): 150.7 (q), 136.4 (q), 133.5 (q), 132.2, 129.5, 128.6, 125.7, 122.4 (q), 78.8, 45.4, 35.8, 34.6 (q), 31.3.

4.3 (*S*)-(4-*tert*-butylbenzyl)(2-nitro-1-(4-nitrophenyl)ethyl)sulfane (14)



The Michael adduct was prepared according to procedure B using the quinine-based cinchona alkaloid catalyst **12** (12.53 mg, 0.015 mmol), 1-nitro-4-((*E*)-2-nitrovinyl)benzene (12.5 mg, 0.06 mmol), *tert*-butylbenzylmercaptan (12 µL, 0.06 mmol) and CH_2Cl_2 (6.4 mL, 0.01 M). After purification of the crude material by flash chromatography (CH_2Cl_2), the product was obtained as a yellow oil (23.62 mg, 98%). $[\alpha]_D^{22}$ +175 (*c* 0.3 in $CHCl_3$). The enantiomeric excess was determined by CSP-HPLC analysis using a Chiralcel AD-H column (4.6 mm x 25 cm); *n*-hexane/IPA 90/10; 1 mL/min; λ = 220 nm. t_R (minor) = 13.12 min; t_R (minor) = 16.73 min; 85% *ee*. The absolute configuration of **(*S*)-14** was established by analogy with **(*S*)-4a**. ν_{max} (film)/cm^{-1}: 2962, 2867, 1553, 1519, 1344, 1268, 1108, 857, 832, 696. δ_H (400 MHz, $CDCl_3$): 8.20 (d, J 8.4, 2H), 7.44 (d, J 8.4, 2H), 7.36 (d, J 8.0, 2H), 7.18 (d, J 8.0, 2H), 4.73

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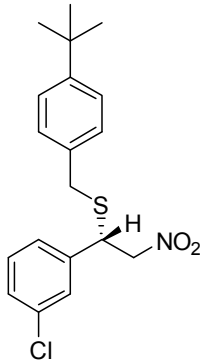
(app. d, 2H), 4.52 (app. t, 1H), 3.75 (d, J 13.6, 1H), 3.65 (d, J 13.6, 1H), 1.35 (s, 9H); δ_C (100 MHz, $CDCl_3$): 150.5 (q), 147.3 (q), 144.4 (q), 132.6 (q), 128.4, 128.1, 125.3, 123.7, 77.9, 44.7, 35.6, 34.1 (q), 30.9.

4.4 (*S*)-(4-*tert*-butylbenzyl)(1-(3-chlorophenyl)-2-nitroethyl)sulfane (15)



The Michael adduct was prepared according to procedure C using the quinine-based cinchona alkaloid catalyst **12** (25.06 mg, 0.03 mmol), 1-chloro-3-((*E*)-2-nitrovinyl)benzene (27.54 mg, 0.15 mmol), *tert*-butylbenzylmercaptan (28 µL, 0.15 mmol) and CH_2Cl_2 (22.5 mL, 0.007 M). After purification of the crude material by flash chromatography (9:1 hexane:CH_2Cl_2), the product was obtained as a white solid (45.74 mg, 84%). mp 62-64 °C. $[\alpha]_D^{22}$ +158 (*c* 0.4 in $CHCl_3$). The enantiomeric excess was determined by CSP-HPLC analysis using a Chiralcel OD-H column (4.6 mm x 25 cm); *n*-hexane/IPA 90/10; 1 mL/min; λ = 220 nm. t_R (minor) = 10.08 min; t_R (major) = 15.43 min; 91% *ee*. The absolute configuration of **(*S*)-15** was established by analogy with **(*S*)-4a**. ν_{max}/cm^{-1}: 2965, 2911, 1556, 1474, 1429, 1376, 1235, 1194, 1083, 831, 786, 693. δ_H (400 MHz, $CDCl_3$): 7.37 (d, J 8.0, 2H), 7.33-7.26 (m, 3H), 7.23-7.15 (m, 3H), 4.68 (m, 2H), 4.41 (dd, J 8.8, 6.8, 1H), 3.71 (d, J 13.6, 1H), 3.62 (d, J 13.6, 1H), 1.36 (s, 9H). δ_C (100 MHz, $CDCl_3$): 150.2 (q), 138.9 (q), 134.4 (q), 133.0 (q), 129.9, 128.2, 128.1, 127.6, 125.5, 125.3, 78.3, 44.9, 35.4, 34.1 (q), 30.9. HRMS (*m/z* -ES): Found: 363.1069 ($M^{+\cdot}$. $[C_{19}H_{22}NO_2SCl]^{+\cdot}$ Requires: 363.1060).

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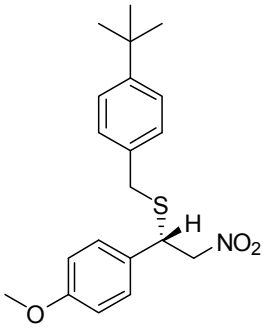
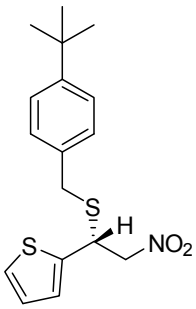
4.5 (*S*)-(4-*tert*-butylbenzyl)(1-(4-methoxyphenyl)-2-nitroethyl)sulfane (16)



The Michael adduct was prepared according to procedure B using the quinine-based cinchona alkaloid catalyst **12** (25.06 mg, 0.03 mmol), 1-methoxy-4-((*E*)-2-nitrovinyl)benzene (26.87 mg, 0.15 mmol), *tert*-butylbenzylmercaptan (28 µL, 0.15 mmol) and CH_2Cl_2 (15.0 mL, 0.01 M). After purification of the crude material by flash chromatography (CH_2Cl_2), the product was obtained as a yellow oil (52.06 mg, 97%). $[\alpha]_D^{22}$ +187 (*c* 0.2 in $CHCl_3$). The enantiomeric excess was determined by CSP-HPLC analysis using a Chiralcel AD-H column (4.6 mm x 25 cm); *n*-hexane/IPA 99/1; 0.8 mL/min; λ = 220 nm. t_R (minor) = 26.72 min; t_R (major) = 31.32 min; 90% *ee*. The absolute configuration of **(*S*)-16** was established by analogy with **(*S*)-4a**. ν_{max}/cm^{-1}: 2960, 1610, 1552, 1511, 1374, 1249, 1177, 1111, 1032, 832, 675. δ_H (400 MHz, $CDCl_3$): 7.36 (d, J 8.4, 2H), 7.27-7.17 (m, 4H), 6.89 (d, J 8.8, 2H), 4.74-4.61 (m, 2H), 4.43 (dd, J 8.8, 6.8, 1H), 3.83 (s, 3H), 3.67 (d, J 13.6, 1H), 3.59 (d, J 13.6, 1H), 1.35 (s, 9H). δ_C (100 MHz, $CDCl_3$): 159.1 (q), 150.0 (q), 140.0 (q), 133.4 (q), 128.5, 128.1, 125.2, 113.9, 78.8, 54.8, 45.2, 35.1, 34.1 (q), 30.9.

4.6 (*R*)-2-(1-(4-*tert*-butylbenzylthio)-2-nitroethyl)thiophene (17)



The Michael adduct was prepared according to procedure A using the quinine-based cinchona alkaloid catalyst **12** (12.53 mg, 0.015 mmol), 2-((*E*)-2-nitrovinyl)thiophene (23.28 mg, 0.15

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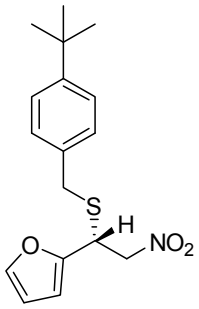
mmol), *tert*-butylbenzylmercaptan (28 μL, 0.15 mmol) and CH_2Cl_2 (7.5 mL, 0.02 M). After purification of the crude material by flash chromatography (CH_2Cl_2), the product was obtained as a yellow solid (46.77 mg, 93%). mp 60-62 °C. $[\alpha]_D^{22}$ +164 (*c* 0.4 in $CHCl_3$). The enantiomeric excess was determined by CSP-HPLC analysis using a Chiralcel AD-H column (4.6 mm x 25 cm); *n*-hexane/IPA 99/1; 1 mL/min; λ = 220 nm. t_R (min) = 14.89 min; t_R (major) = 16.55 min; 92% *ee*. The absolute configuration of **(*R*)-17** was established by analogy with **(*S*)-4a**. ν_{max}/cm^{-1}: 2965, 1551, 1425, 1374, 1268, 1107, 1044, 838, 712, 663. δ_H (400 MHz, $CDCl_3$): 7.43-7.31 (m, 3H), 7.21 (d, J 8.0, 2H), 6.97 (app. s, 2H), 4.84-4.64 (m, 3H), 3.76 (d, J 13.4, 1H), 3.69 (d, J 13.4, 1H), 1.34 (s, 9H). δ_C (100 MHz, $CDCl_3$): 150.2 (q), 140.6 (q), 133.1 (q), 128.2, 126.5, 126.3, 125.7, 125.2, 79.2, 40.8, 35.2, 34.1 (q), 30.9.

4.7 (*R*)-2-(1-(4-*tert*-butylbenzylthio)-2-nitroethyl)furan (18)



The Michael adduct was prepared according to procedure B using the quinine-based cinchona alkaloid catalyst **12** (25.06 mg, 0.03 mmol), 2-((*E*)-nitrovinyl)furan (20.87 mg, 0.15 mmol), *tert*-butylbenzylmercaptan (28 μL, 0.15 mmol) and CH_2Cl_2 (15.0 mL, 0.01 M). After purification of the crude material by flash chromatography (CH_2Cl_2), the product was obtained as a clear yellow solid (47.62 mg, 99%). mp 64-66 °C. $[\alpha]_D^{22}$ +139 (*c* 0.4 in $CHCl_3$). The enantiomeric excess was determined by CSP-HPLC analysis using a Chiralcel AD-H column (4.6 mm x 25 cm); *n*-hexane/IPA 99/1; 1 mL/min; λ = 220 nm. t_R (minor) = 15.15 min; t_R (major) = 17.33 min; 90% *ee*. The absolute configuration of **(*R*)-18** was established by analogy with **(*S*)-4a**. ν_{max}/cm^{-1}: 2966, 1552, 1427, 1373, 1185, 1150, 1015, 965, 838, 808, 751, 695. δ_H (400 MHz, $CDCl_3$): 7.43 (dd, J 1.8, 0.6, 1H), 7.38 (d, J 8.4, 2H), 7.25 (d, J 8.4, 2H), 6.36 (dd, J 3.2, 1.8, 1H), 6.28 (d, J 3.2, 1H), 4.82 (dd, J 15.2, 11.2, 1H), 4.68-4.58 (m, 2H), 3.78 (d, J 13.6, 1H), 3.72 (d, J 13.6, 1H), 1.35 (s, 9H). δ_C (100 MHz, $CDCl_3$): 150.2 (q), 149.1 (q), 142.6 (q), 133.2, 128.1, 125.3, 110.2, 108.1, 76.2, 38.8, 35.1, 34.1 (q), 30.9.

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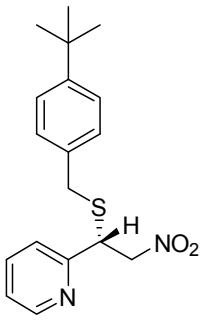
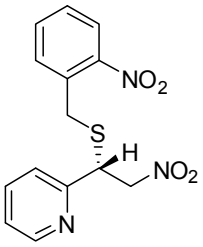
4.8 (*R*)-3-(1-(4-*tert*-butylbenzylthio)-2-nitroethyl)pyridine (19)



The Michael adduct was prepared according to procedure A using the quinine-based cinchona alkaloid catalyst **12** (12.53 mg, 0.015 mmol), 3-((*E*)-2-nitrovinyl)pyridine (22.51 mg, 0.15 mmol), *tert*-butylbenzylmercaptan (28 μL, 0.15 mmol) and CH_2Cl_2 (7.5 mL, 0.02 M). After purification of the crude material by flash chromatography (8:2 -> 5:5 Hexane:CH_2Cl_2) the product was obtained as a dark yellow oil (44.97 mg, 91%). $[\alpha]_D^{22}$ -15 (*c* 0.2 in $CHCl_3$). The enantiomeric excess was determined by CSP-HPLC analysis using a Chiralcel OD-H column (4.6 mm x 25 cm); *n*-hexane/IPA 99/1; 0.8 mL/min; λ = 220 nm. t_R (major) = 29.97 min; t_R (minor) = 39.81 min; 96% *ee*. The absolute configuration of **(*R*)-19** was established by analogy with **(*S*)-4a**. ν_{max}/cm^{-1}: 2959, 1686, 1553, 1470, 1386, 1277, 1176, 1132, 1110, 1027, 864, 731, 702, 681. δ_H (400 MHz, $CDCl_3$): 8.54 (d, J 4.4, 1H), 7.65 (dt, J 7.6, 1.6, 1H), 7.36 (d, J 8.4, 2H), 7.27-7.17 (m, 4H), 5.28 (dd, J 13.6, 9.2, 1H), 4.75 (dd, J 13.6, 5.6, 1H), 4.59 (dd, J 9.2, 5.6, 1H), 3.78 (d, J 13.2, 1H), 3.68 (d, J 13.2, 1H), 1.34 (s, 9H). δ_C (100 MHz, $CDCl_3$): 156.5 (q), 150.1 (q), 148.8, 136.5, 133.5 (q), 128.2, 125.2, 123.0, 122.3, 76.2, 45.6, 34.8, 34.1 (q), 30.9.

4.9 (*R*)-2-(2-nitro-1-(2-nitrobenzylthio)ethyl)pyridine (20)



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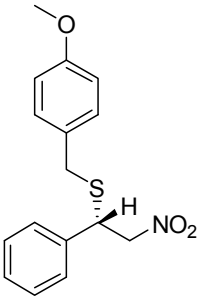
2-Nitrobenzyl ethanethiolate (144 mg, 0.68 mmol) was dissolved in freshly degassed methanol (3.0 ml). Acetyl chloride (153 µl, 2.15 mmol) was added *via* syringe at room temperature under an argon atmosphere and the obtained solution was allowed to stir at room temperature for 18 h. The solvent was then evaporated *in vacuo*. The obtained thiol was used in the next step without the need of further purification.

The Michael adduct was prepared according to procedure A using the quinine-based cinchona alkaloid catalyst **12** (11.88 mg, 0.01 mmol), 3-((*E*)-2-nitrovinyl)pyridine (21.34 mg, 0.14 mmol), (2-nitrophenyl)methanethiol (24.05 mg, 0.14 mmol) and CH_2Cl_2 (7.0 mL, 0.02 M). After purification of the crude material by flash chromatography (CH_2Cl_2) the product was obtained as a clear yellow oil (36.42 mg, 82%). $[\alpha]_D^{22}$ +24 (*c* 0.2 in $CHCl_3$). The enantiomeric excess was determined by CSP-HPLC analysis using a Chiralcel AD-H column (4.6 mm x 25 cm); n-hexane/IPA 95/5; 1 mL/min; λ□= 220 nm. t_R (minor) = 46.52 min; t_R (major) = 49.35 min; 93% ee. The absolute configuration of **(*R*)-20** was established by analogy with **(*S*)-4a**. ν_{max}/cm^{-1}: 2930, 1731, 1553, 1522, 1342, 1242, 1173, 1044, 858, 786, 751, 696. δ_H (400 MHz, $CDCl_3$): 8.52 (d, J 4.7, 1H), 8.00 (dd, J 8.0, 0.8, 1H), 7.67 (td, J 7.4, 1.6, 1H), 7.56 (td, J 7.4, 0.8, 1H), 7.45 (app t, 1H), 7.39 (d, J 7.4, 1H), 7.32 (d, J 7.4, 1H), 7.22 (dd, J 7.4, 4.7, 1H), 5.28 (dd, J 13.8, 8.8, 1 H), 4.79 (dd, J 13.8, 6.0, 1H), 4.66 (dd, J 8.8, 6.0, 1H), 4.12 (d, J 13.6, 1H), 4.04 (d, J 13.6, 1H). δ_C (100 MHz, $CDCl_3$): 155.9 (q), 148.7, 148.1 (q), 136.8, 132.9, 132.7 (q), 131.5, 128.2, 125.1, 123.1, 122.6, 76.1, 46.0, 31.7;

4.10 (*S*)-(4-methoxybenzyl)(2-nitro-1-phenylethyl)sulfane (21)



The Michael adduct was prepared according to procedure A using the quinine-based cinchona alkaloid catalyst **12** (16.7 mg, 0.02 mmol), nitrostyrene (30 mg, 0.2 mmol), 4-methoxy-α-toluenethiol (28 µL, 0.2 mmol) and CH_2Cl_2 (10.0 mL, 0.02 M). After purification of the crude material by flash chromatography (CH_2Cl_2), the product was obtained as a yellow oil (59.50

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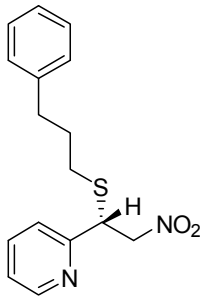
mg, 98%). $[\alpha]_D^{22}$ +55 (*c* 0.4 in $CHCl_3$). The enantiomeric excess was determined by CSP-HPLC analysis using a Chiralcel AD-H column (4.6 mm x 25 cm); n-hexane/IPA 99/1; 0.8 mL/min; λ□= 220 nm. t_R (minor) = 28.65 min; t_R (minor) = 31.50 min; 90% ee. The absolute configuration of **(*S*)-21** was established by analogy with **(*S*)-4a**. ν_{max}/cm^{-1}: 2914, 2836, 1609, 1551, 1510, 1374, 1243, 1174, 1030, 830, 747, 698. δ_H (400 MHz, $CDCl_3$): 7.43-7.23 (m, 5H), 7.19 (d, J 8.4, 2H), 6.88 (d, J 8.4, 2H), 4.79-4.63 (m, 2H), 4.43 (dd, J 8.8, 7.2, 1H), 3.84 (s, 3H), 3.67 (d, J 13.6, 1H), 3.58 (d, J 13.6, 1H). δ_C (100 MHz, $CDCl_3$): 158.5 (q), 136.7 (q), 129.6, 128.6, 128.3 (q), 128.0, 127.3, 113.6, 78.7, 54.9, 45.4, 35.0.

4.11 (*R*)-2-(2-nitro-1-(3-phenylpropylthio)ethyl)pyridine (22)



3-Phenylpropyl ethanethiolate (300 mg, 1.54 mmol) was dissolved in freshly degassed methanol (3.0 ml). Acetyl chloride (175 µl, 2.46 mmol) was added *via* syringe at room temperature under an argon atmosphere and the obtained solution was allowed to stir at room temperature for 18 h. The solvent was then evaporated *in vacuo*. The obtained thiol was used in the next step without the need of further purification.

The Michael adduct was prepared according to procedure B using the quinine-based cinchona alkaloid catalyst **12** (25.84 mg, 0.03 mmol), 3-((*E*)-2-nitrovinyl)pyridine (23.21 mg, 0.16 mmol), 3-phenylpropane-1-thiol (23 µL, 0.16 mmol) and CH_2Cl_2 (15.5 mL, 0.01 M). After purification of the crude material by flash chromatography (CH_2Cl_2) the product was obtained as a clear yellow oil (26.27 mg, 56%). $[\alpha]_D^{22}$ +34 (*c* 0.2 in $CHCl_3$). The enantiomeric excess was determined by CSP-HPLC analysis using a Chiralcel AD-H column (4.6 mm x 25 cm); n-hexane/IPA 95/5; 1 mL/min; λ□= 220 nm. t_R (minor) = 16.09 min; t_R (major) = 17.27 min; 94% ee. The absolute configuration of **(*R*)-22** was established by analogy with **(*S*)-4a**. ν_{max}/cm^{-1}: 2923, 1702, 1589, 1550, 1471, 1434, 1375, 1294, 1076, 949, 744, 699. δ_H (400 MHz, $(CD_3)_2CO$): 8.48 (d, J 4.4, 1H), 7.82 (td, J 7.6, 1.6, 1H), 7.58 (d, J 7.6, 1H), 7.33-7.14

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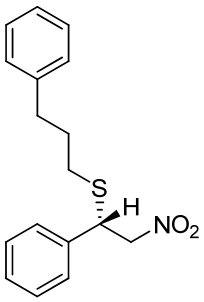
(m, 6H), 5.39 (dd, J 14.0, 9.2, 1H), 5.07 (dd, J 14.0, 6.0, 1H), 4.80 (dd, J 9.2, 6.0, 1H), 2.75-2.62 (m, 3H), 2.59-2.50 (m, 1H), 1.90-1.76 (m, 2H). δ_C (100 MHz, $(CD_3)_2CO$): 157.2 (q), 148.3, 141.0 (q), 136.7, 127.9, 127.8, 125.4, 123.1, 122.3, 75.9, 45.3, 33.9, 30.9, 29.0.

4.12 (*S*)-2-nitro-1-phenylethyl)(3-phenylpropyl)sulfane (23)



3-Phenylpropyl ethanethiolate (300 mg, 1.54 mmol) was dissolved in freshly degassed methanol (3.0 ml). Acetyl chloride (175 µl, 2.46 mmol) was added *via* syringe at room temperature under an argon atmosphere and the obtained solution was allowed to stir at room temperature for 18 h. The solvent was then evaporated *in vacuo.* The obtained thiol was used in the next step without the need of further purification.

The Michael adduct was prepared according to procedure B using the quinine-based cinchona alkaloid catalyst **12** (33.42 mg, 0.04 mmol), trans-*β*-nitrostyrene (30 mg, 0.20 mmol), 3-phenylpropane-1-thiol (30 µL, 0.20 mmol) and CH_2Cl_2 (20 mL, 0.01 M). After purification of the crude material by flash chromatography (CH_2Cl_2) the product was obtained as a yellow oil (46.31 mg, 77%). $[\alpha]_D^{22}$ +71 (*c* 0.2 in $CHCl_3$). The enantiomeric excess was determined by CSP-HPLC analysis using a Chiralcel AD-H column (4.6 mm x 25 cm); n-hexane/IPA 99/1; 1 mL/min; λ□= 220 nm. t_R (minor) = 15.11 min; t_R (major) = 16.57 min; 89% ee. The absolute configuration of **(*S*)-23** was established by analogy with **(*S*)-4a**. ν_{max}/cm^{-1}: 2921, 1634, 1552, 1495, 1452, 1342, 1260, 1200, 1078, 966, 745, 697. δ_H (400 MHz, $CDCl_3$): 7.63-6.90 (m, 10H), 4.76 (app. d, 2H), 4.56 (app. t, 1H), 2.69-2.64 (m, 2H), 2.47 (t, J 7.2, 2H), 1.91-1.81 (m, 2H). δ_C (100 MHz, $CDCl_3$): 141.0 (q), 137.4 (q), 129.1, 128.5, 128.4, 128.4, 127.6, 126.1, 79.3, 46.5, 34.5, 30.9, 30.7.

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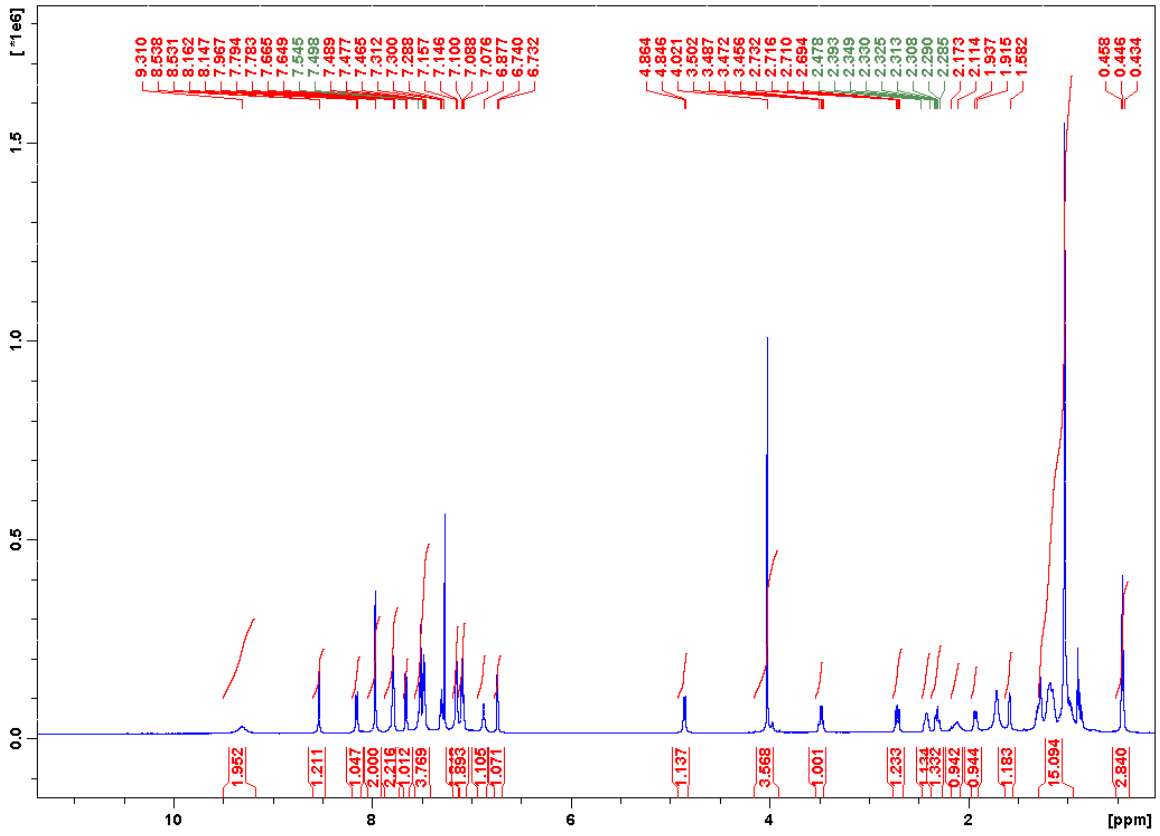
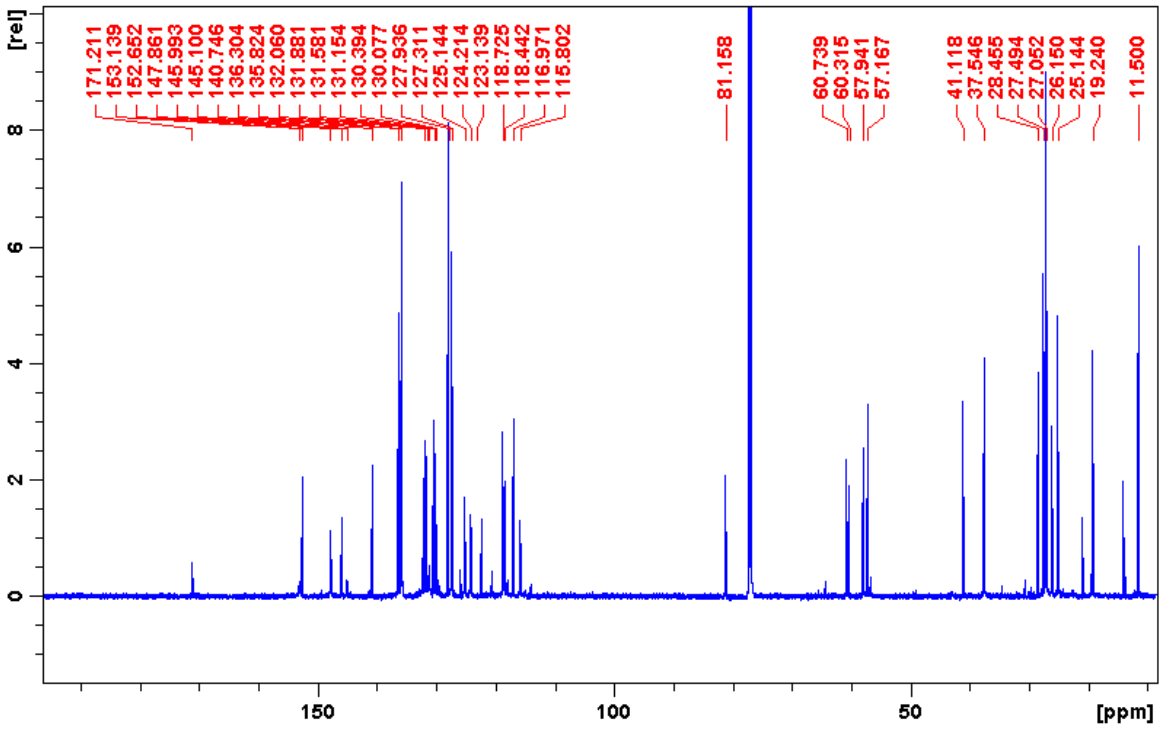
5.0 NMR Spectra

^{1}H NMR spectrum (600 MHz, $CDCl_3$) of the quinine-derived catalyst (**12**)



^{13}C NMR spectrum (150 MHz, $CDCl_3$) of the quinine-derived catalyst (**12**)



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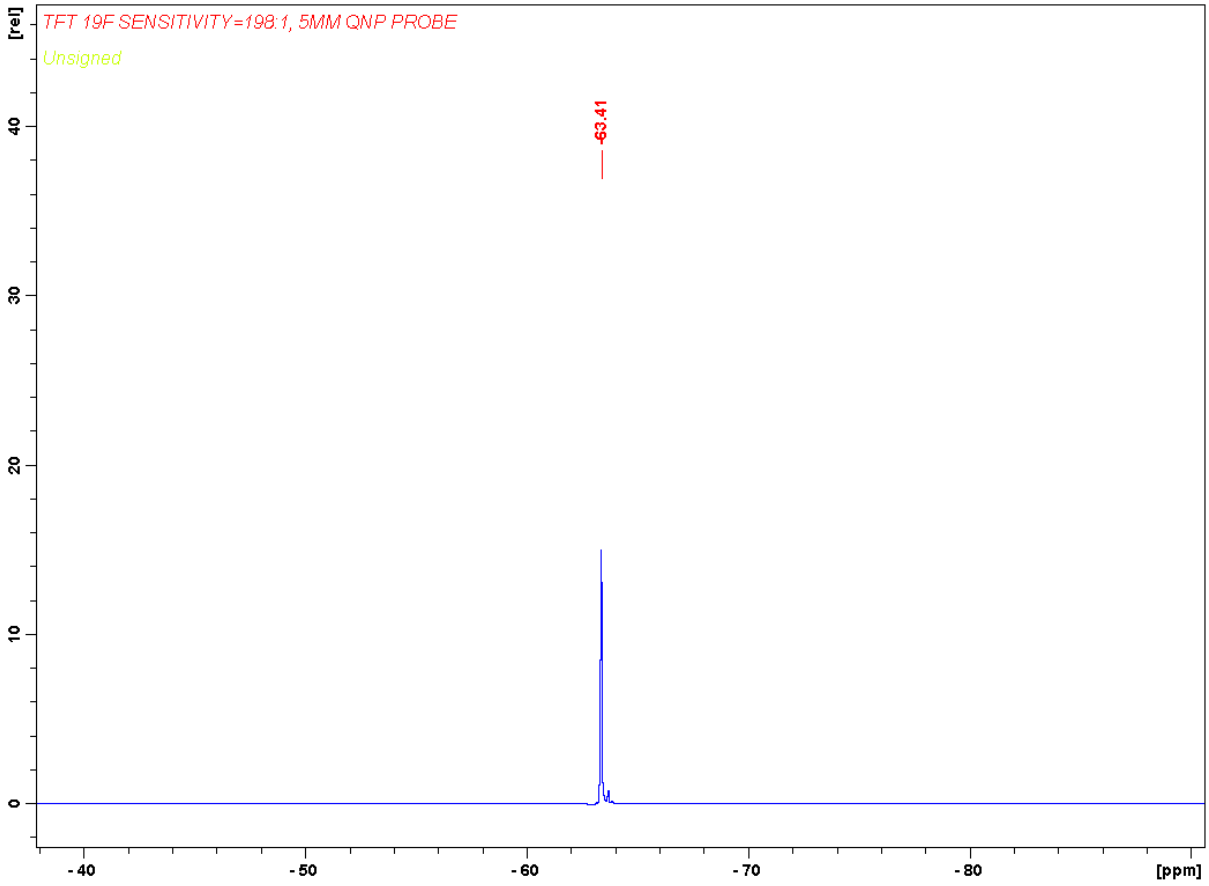
^{19}F NMR spectrum (350 MHz, $CDCl_3$) of the quinine-derived catalyst (**12**)



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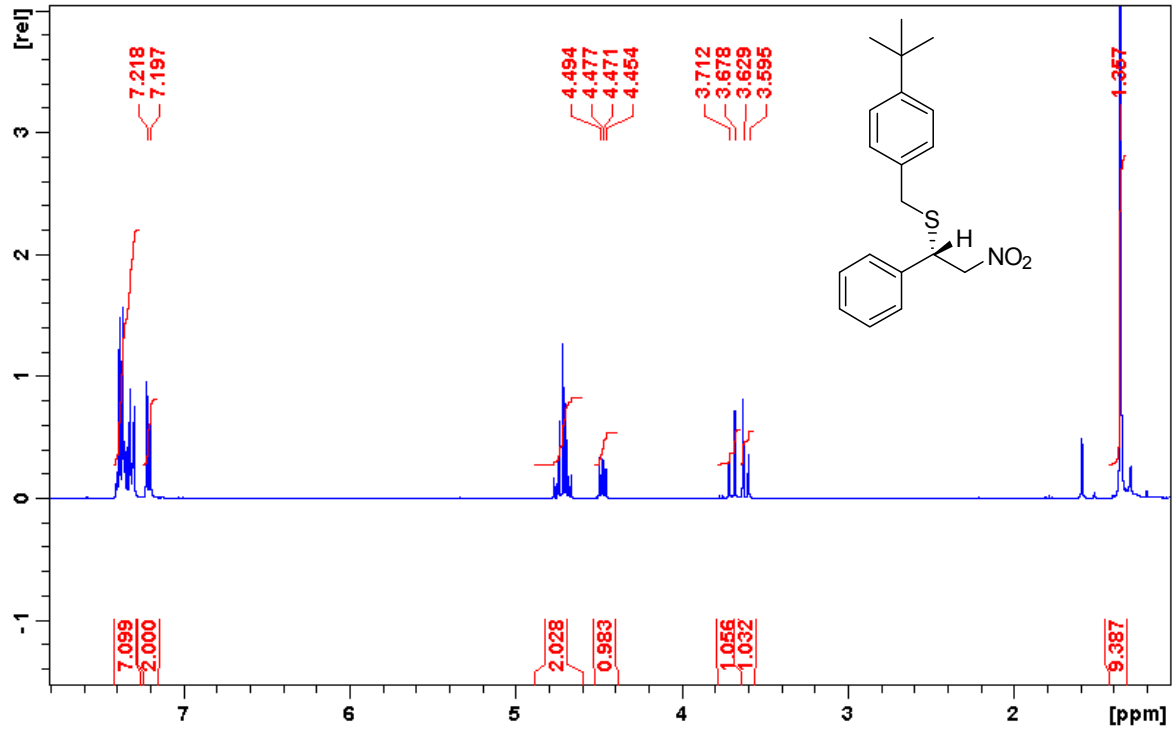
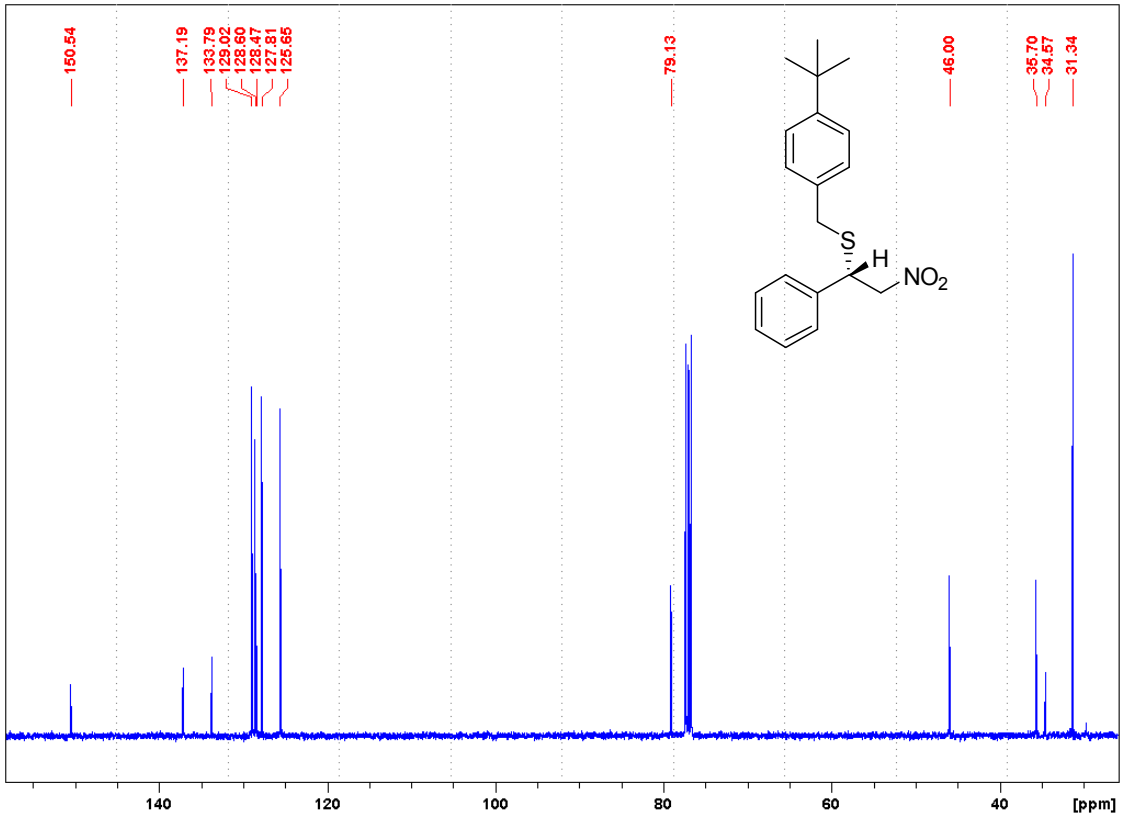
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (4-tert-butylbenzyl)(2-nitro-1-phenylethyl)sulfane (**4a**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of nitrostyrene(4-tert-butylbenzyl)(2-nitro-1-phenylethyl)sulfane (**4a**)



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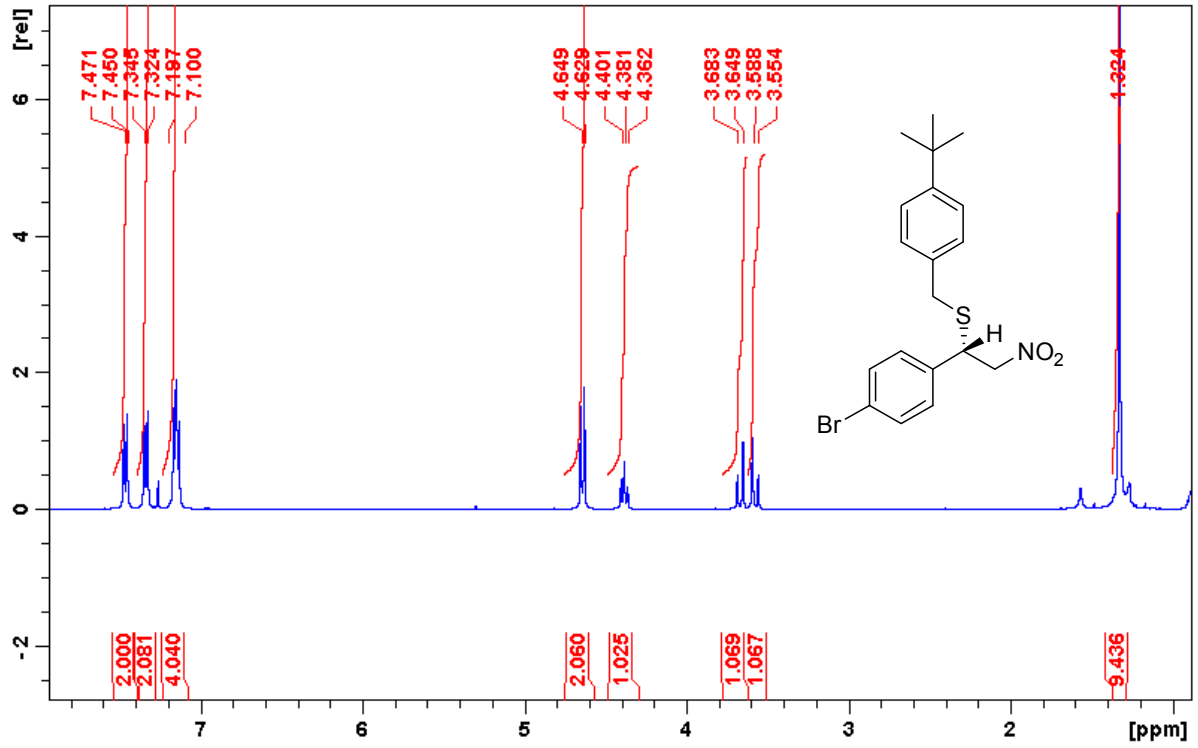
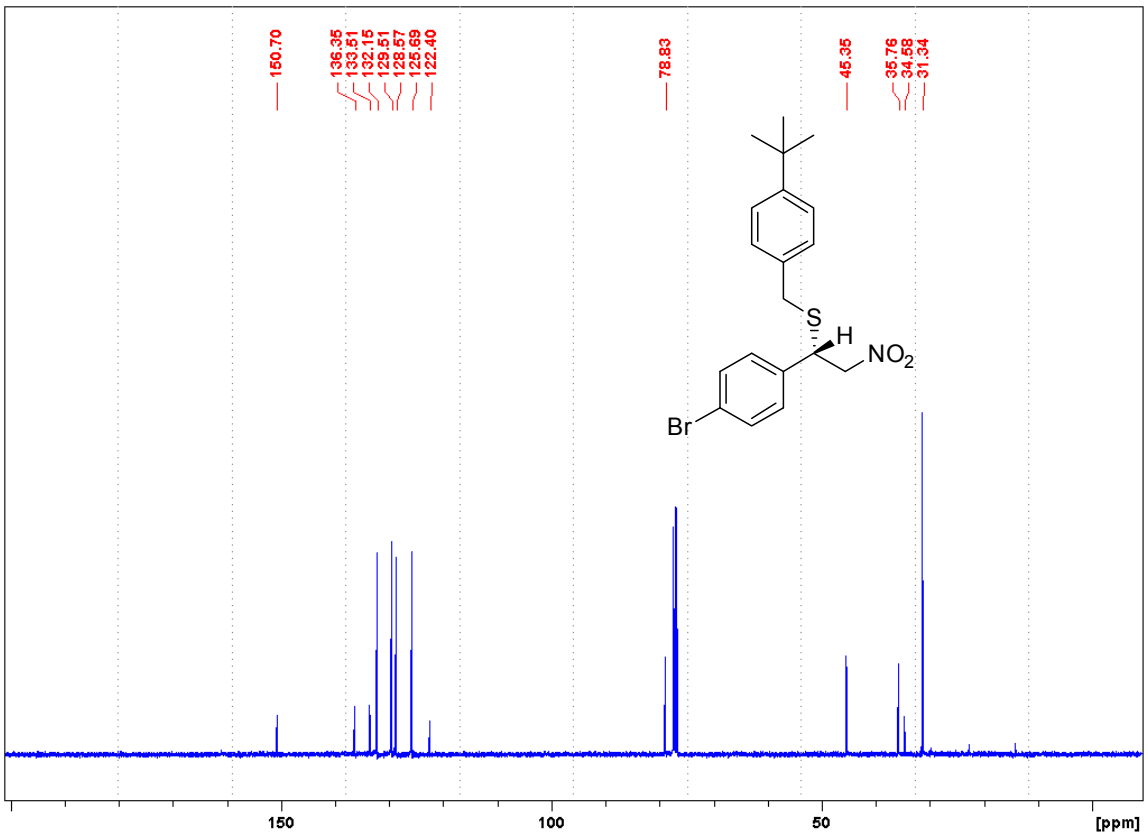
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (4-tert-butylbenzyl)(1-(4-bromophenyl)-2-nitroethyl)sulfane (**13**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (4-tert-butylbenzyl)(1-(4-bromophenyl)-2-nitroethyl)sulfane (**13**)



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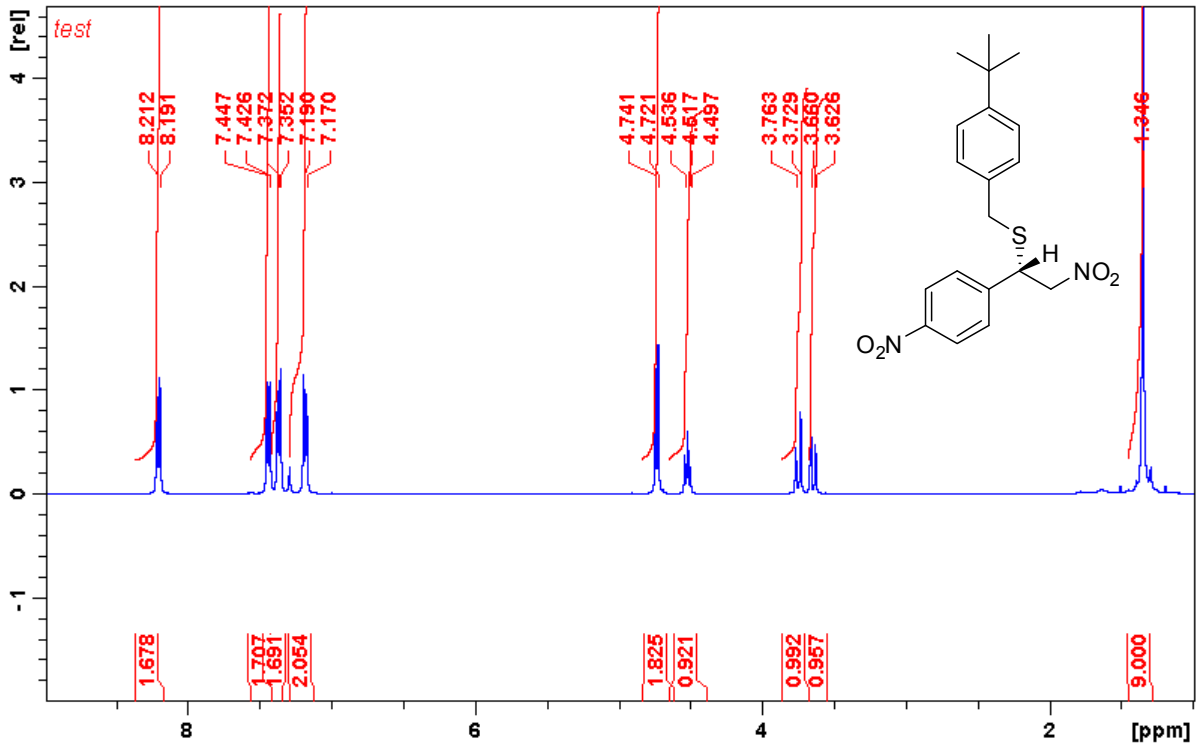
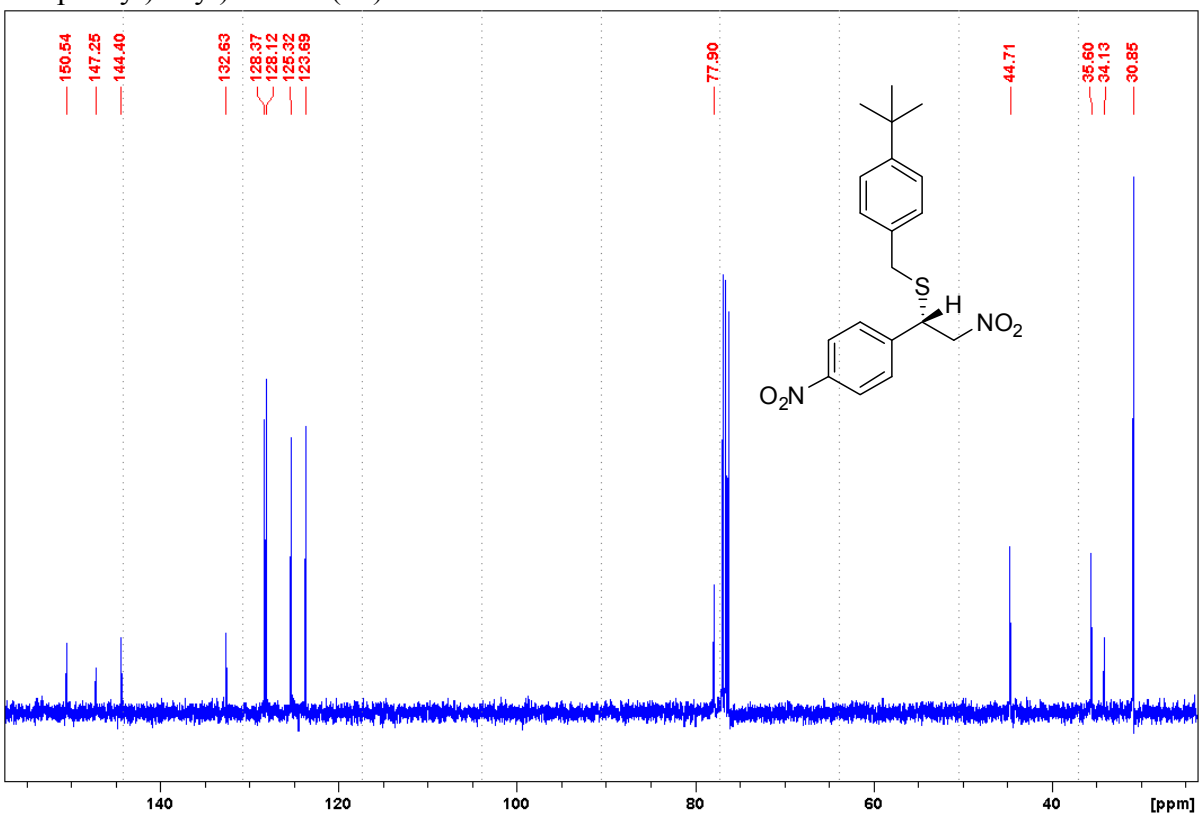
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (4-tert-butylbenzyl)(2-nitro-1-(4-nitrophenyl)ethyl)sulfane (**14**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (4-tert-butylbenzyl)(2-nitro-1-(4-nitrophenyl)ethyl)sulfane (**14**)



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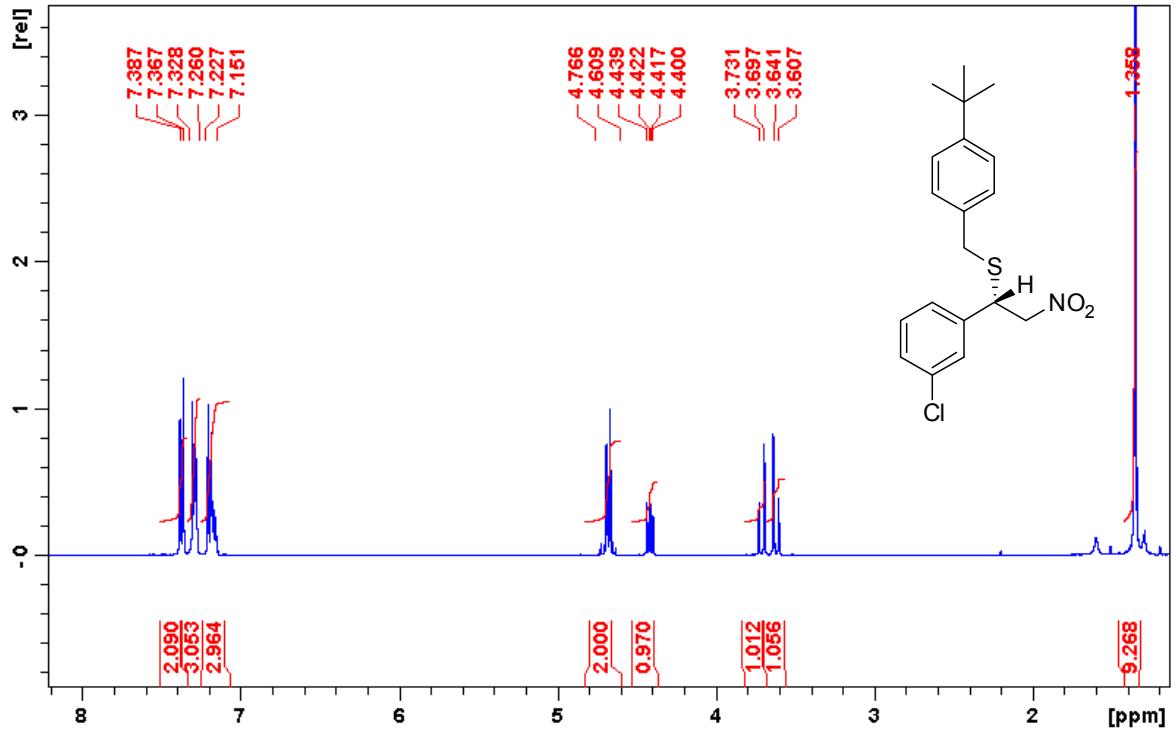
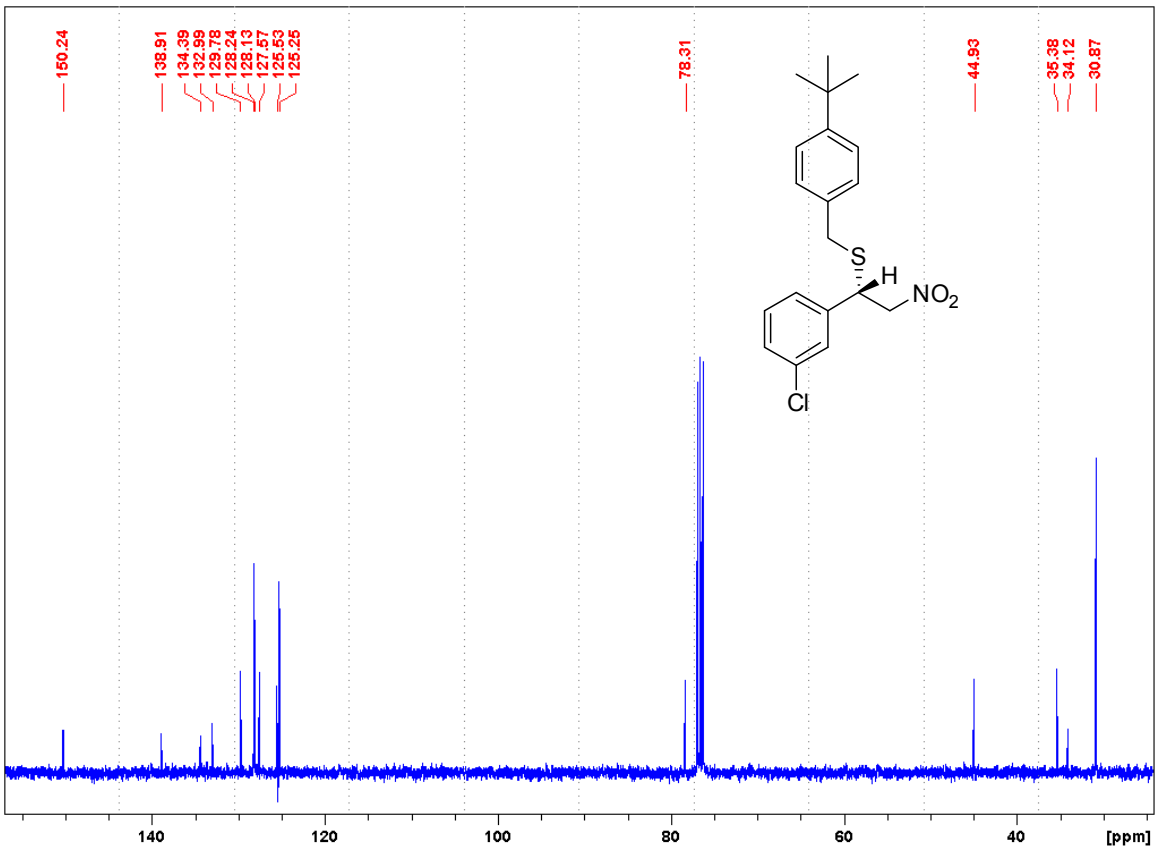
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (4-tert-butylbenzyl)(1-(3-chlorophenyl)-2-nitroethyl)sulfane (**15**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (4-tert-butylbenzyl)(1-(3-chlorophenyl)-2-nitroethyl)sulfane (**15**)



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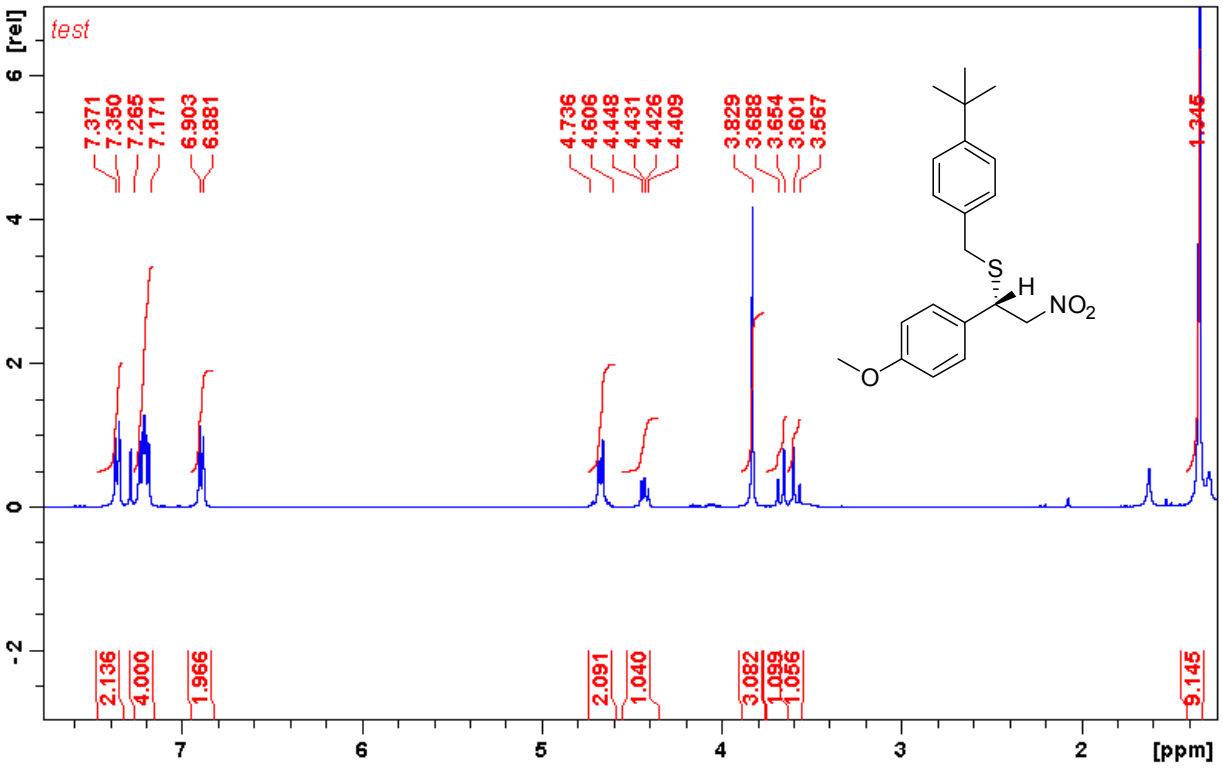
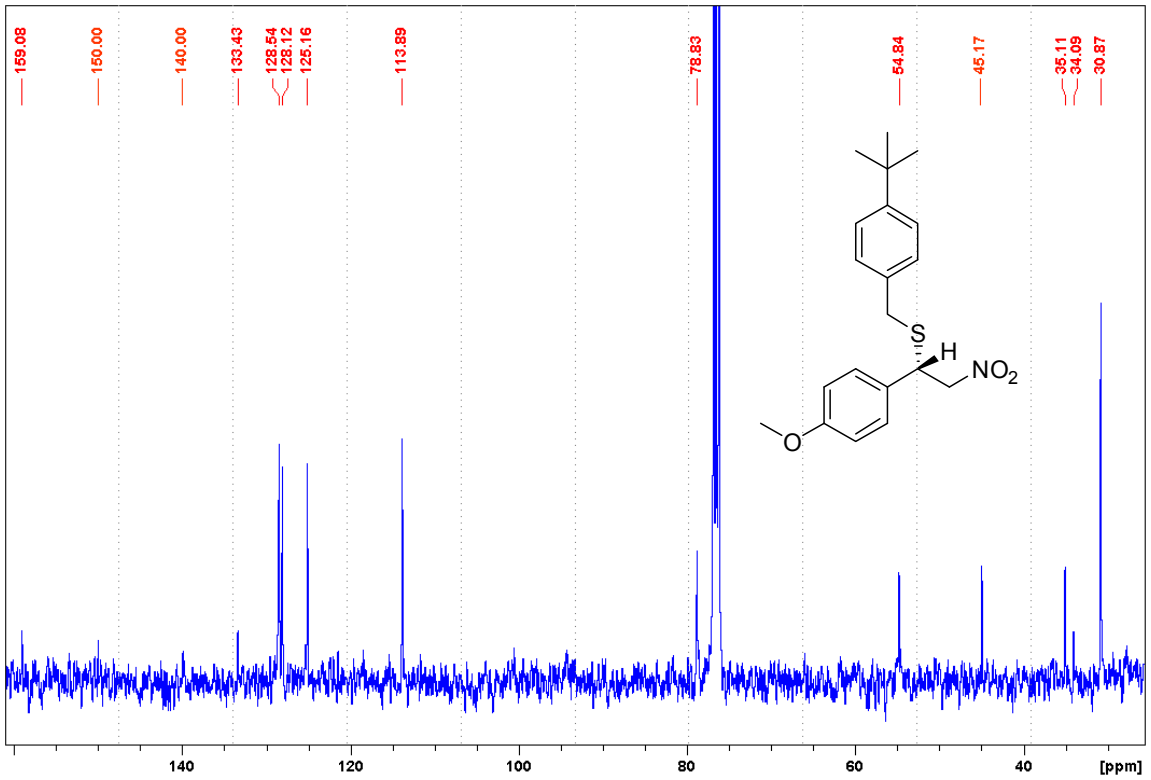
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (4-tert-butylbenzyl)(1-(4-methoxyphenyl)-2-nitroethyl)sulfane (**16**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (4-tert-butylbenzyl)(1-(4-methoxyphenyl)-2-nitroethyl)sulfane (**16**)



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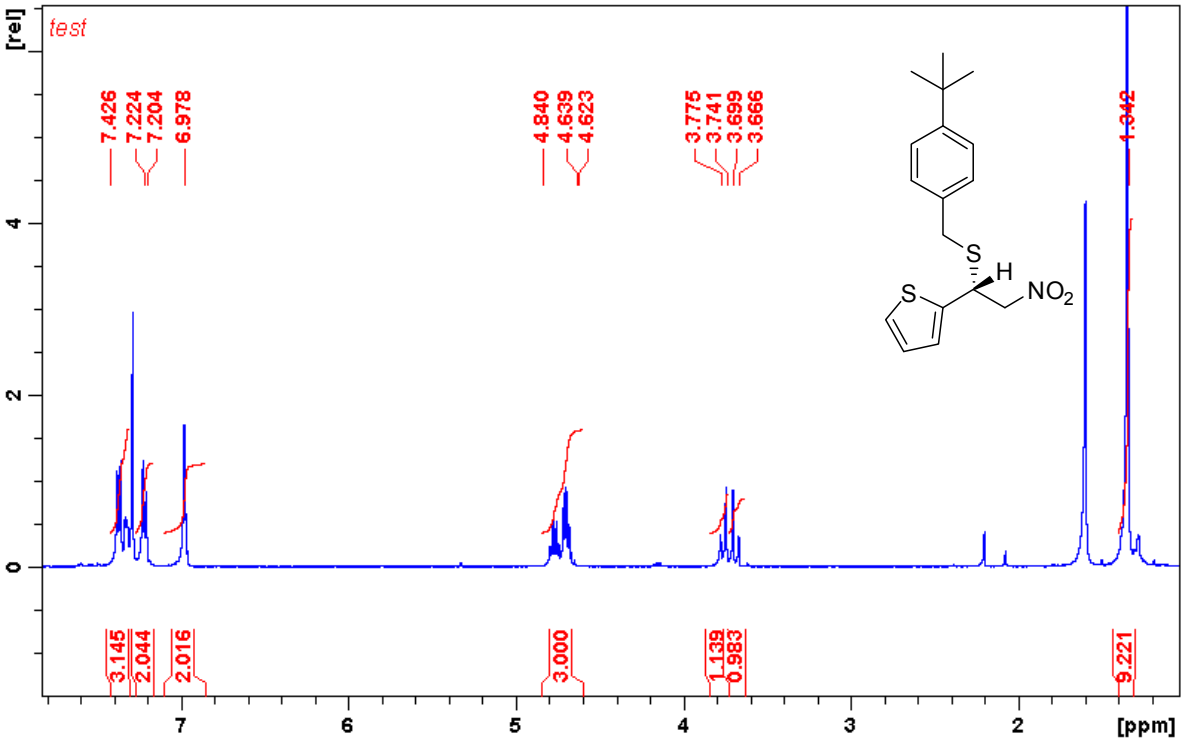
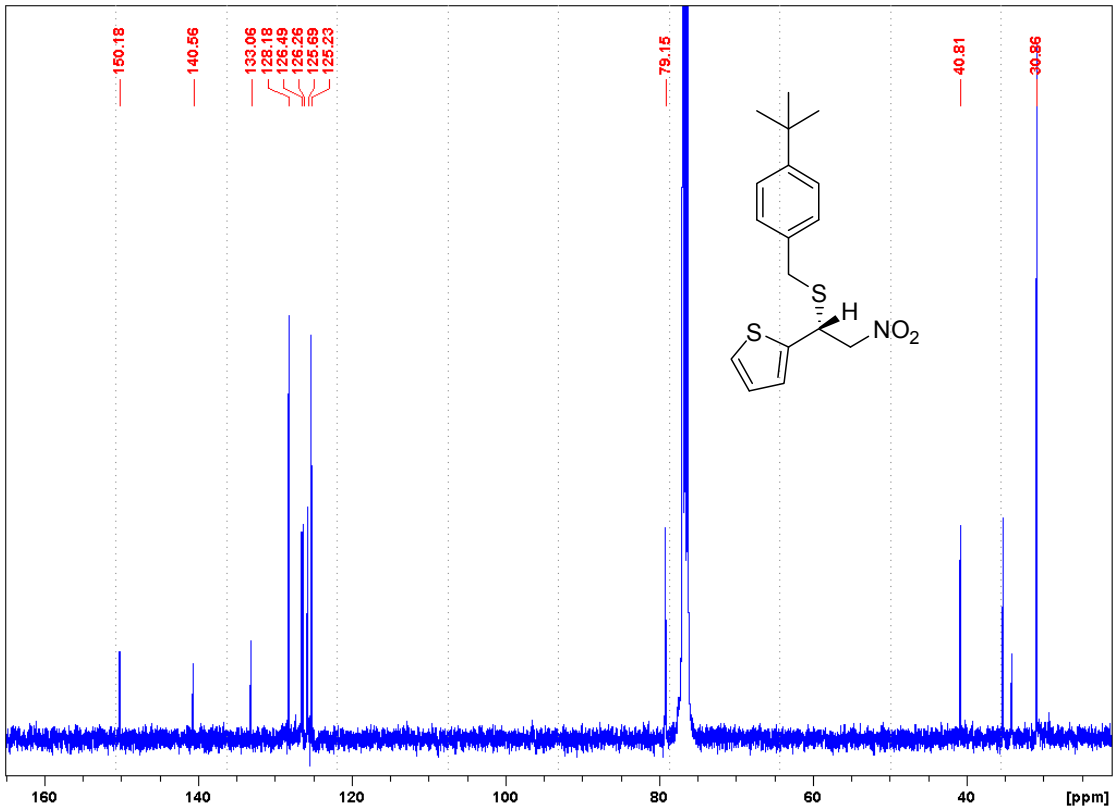
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-(1-(4-tert-butylbenzylthio)-2-nitroethyl)thiophene (**17**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 2-(1-(4-tert-butylbenzylthio)-2-nitroethyl)thiophene (**17**)



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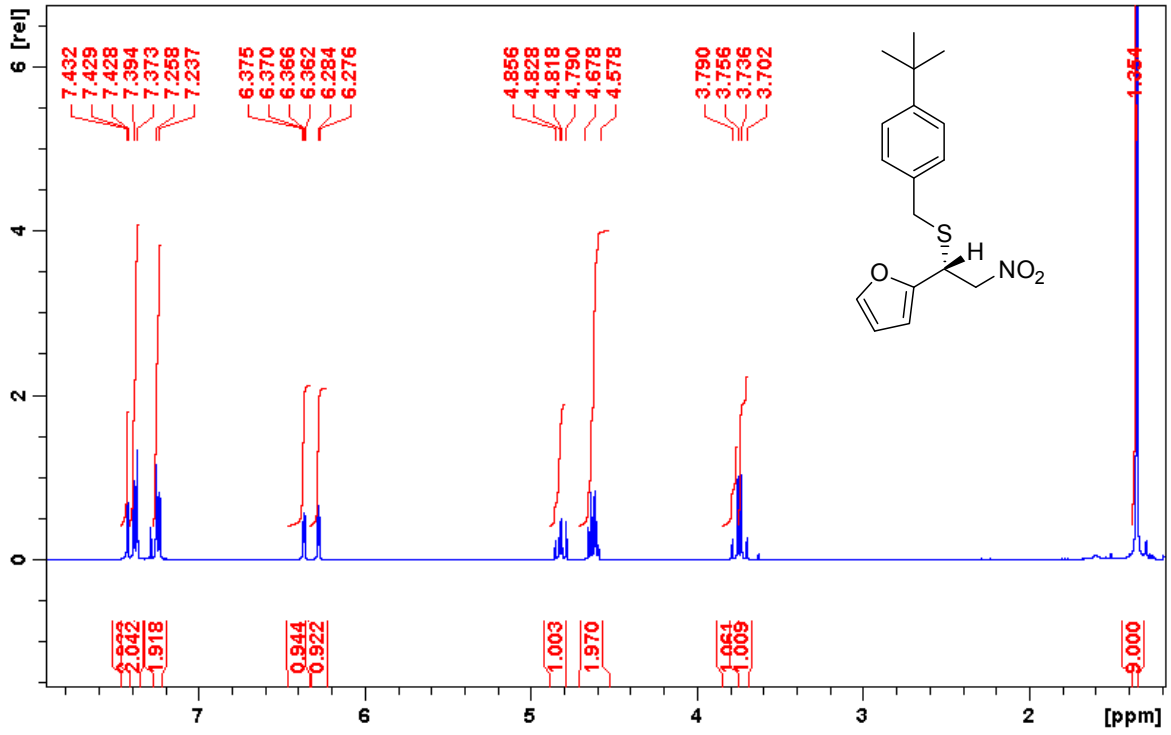
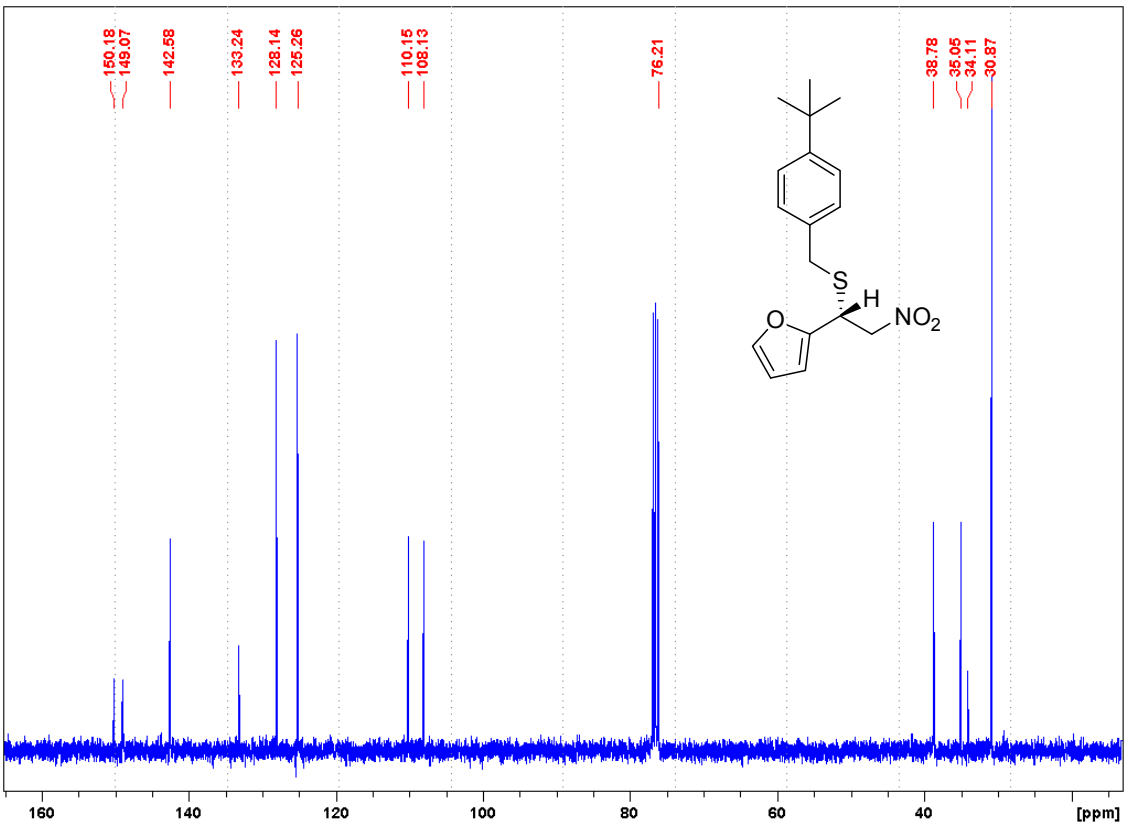
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-(1-(4-tert-butylbenzylthio)-2-nitroethyl)furane (**18**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 2-(1-(4-tert-butylbenzylthio)-2-nitroethyl)furane (**18**)



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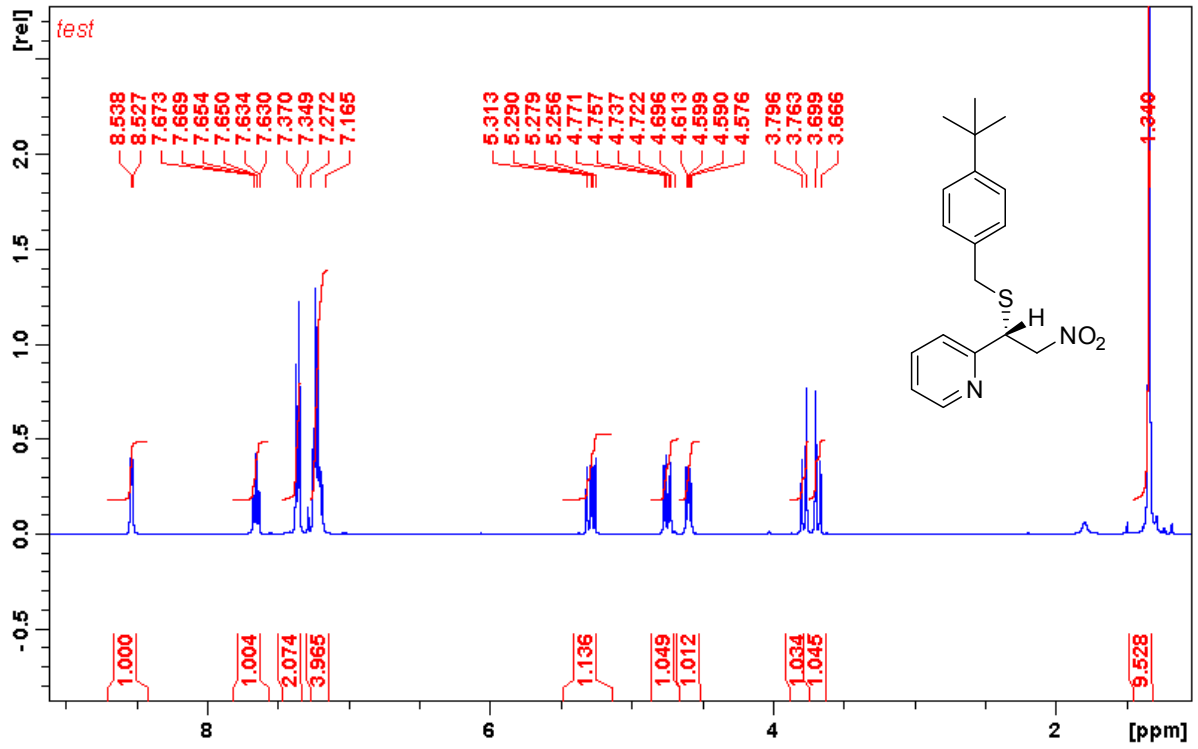
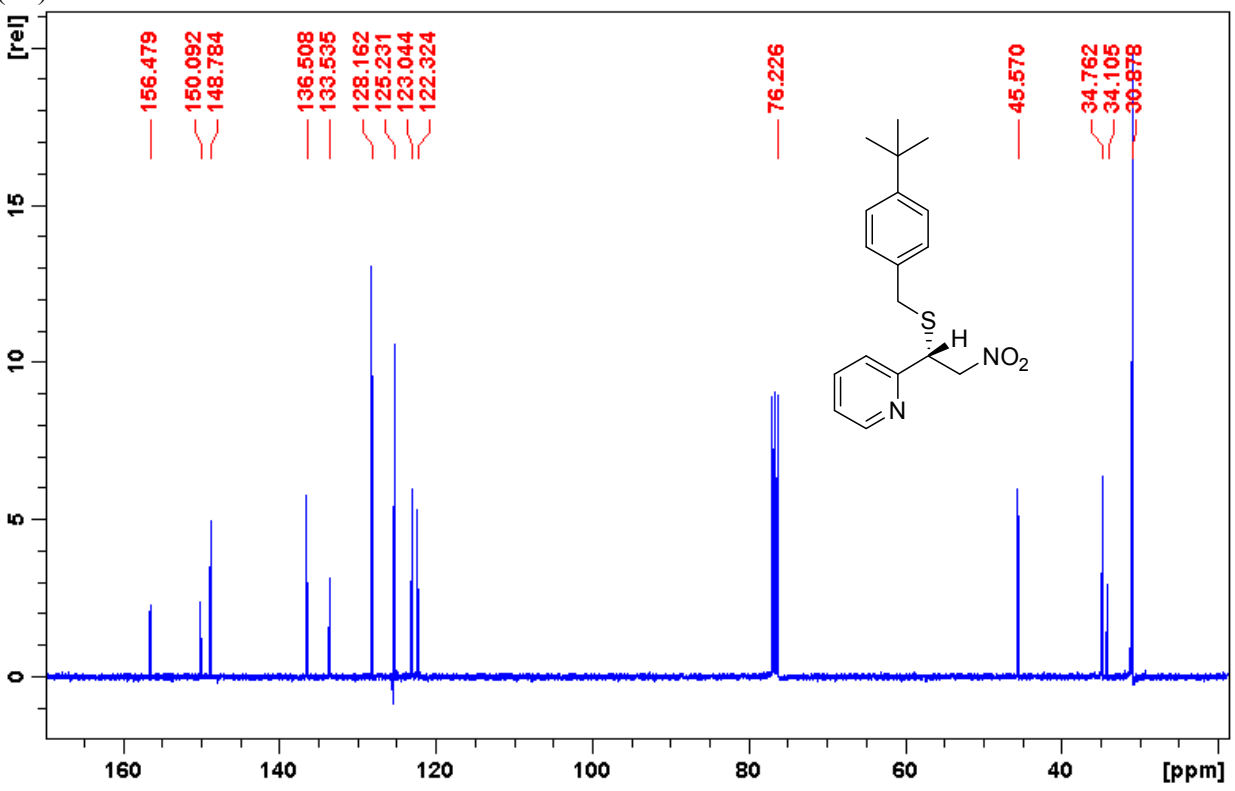
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-(1-(4-tert-butylbenzylthio)-2-nitroethyl)pyridine (**19**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3-(1-(4-tert-butylbenzylthio)-2-nitroethyl)pyridine (**19**)



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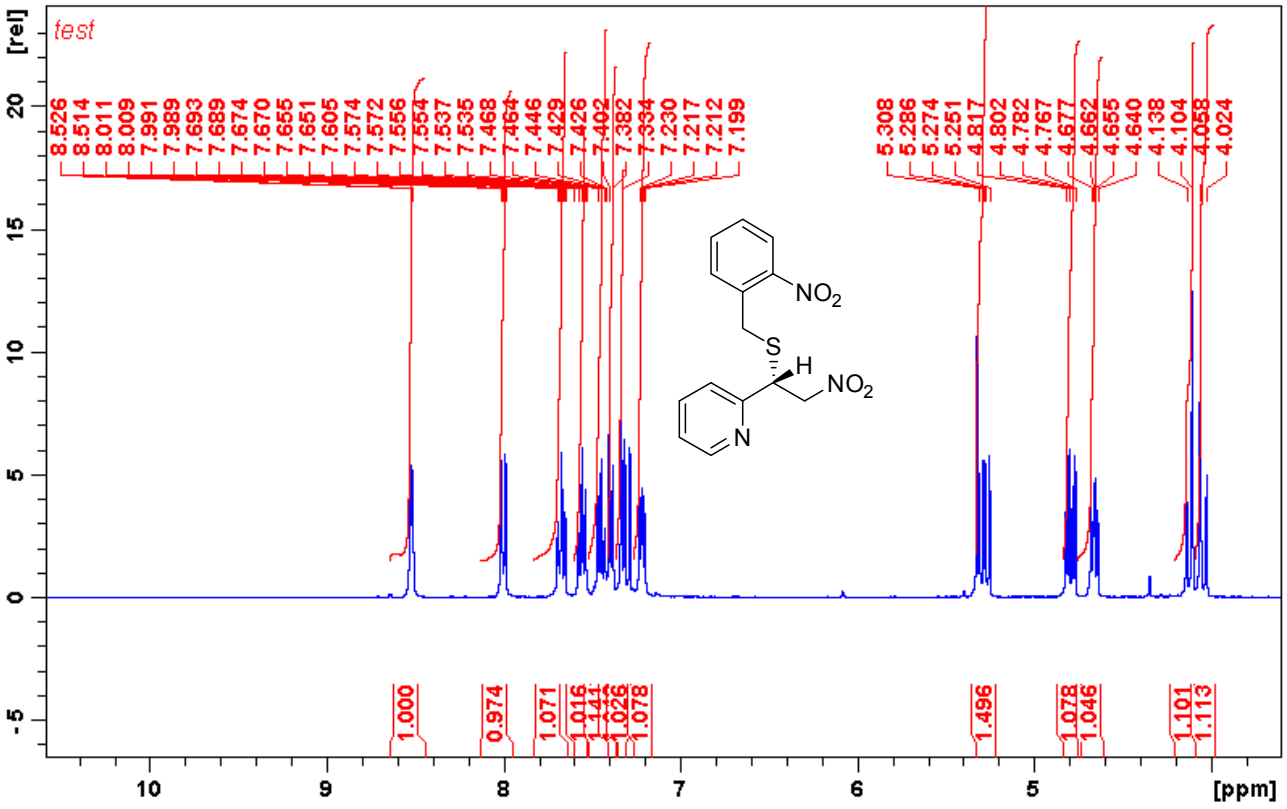
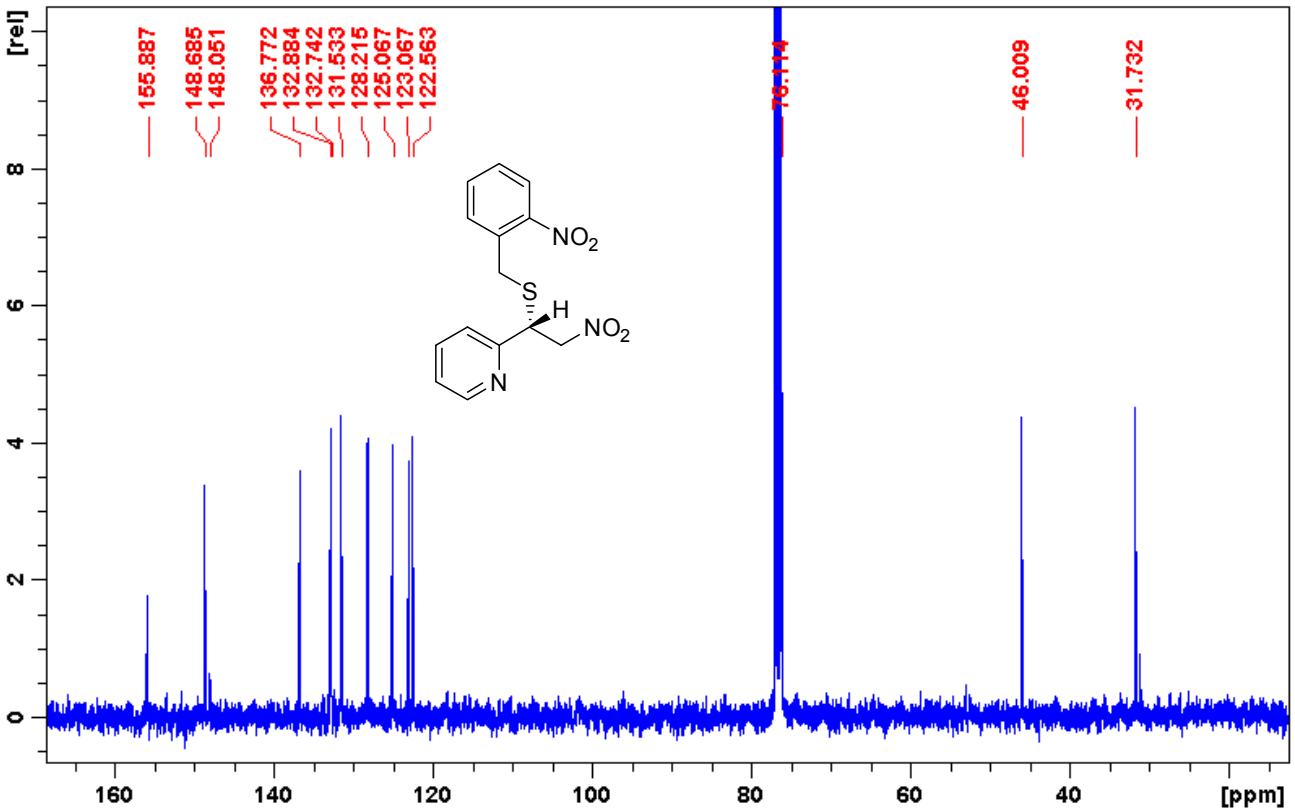
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-(1-(2-nitrobenzylthio)-2-nitroethyl)pyridine (**20**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 2-(1-(2-nitrobenzylthio)-2-nitroethyl)pyridine (**20**)



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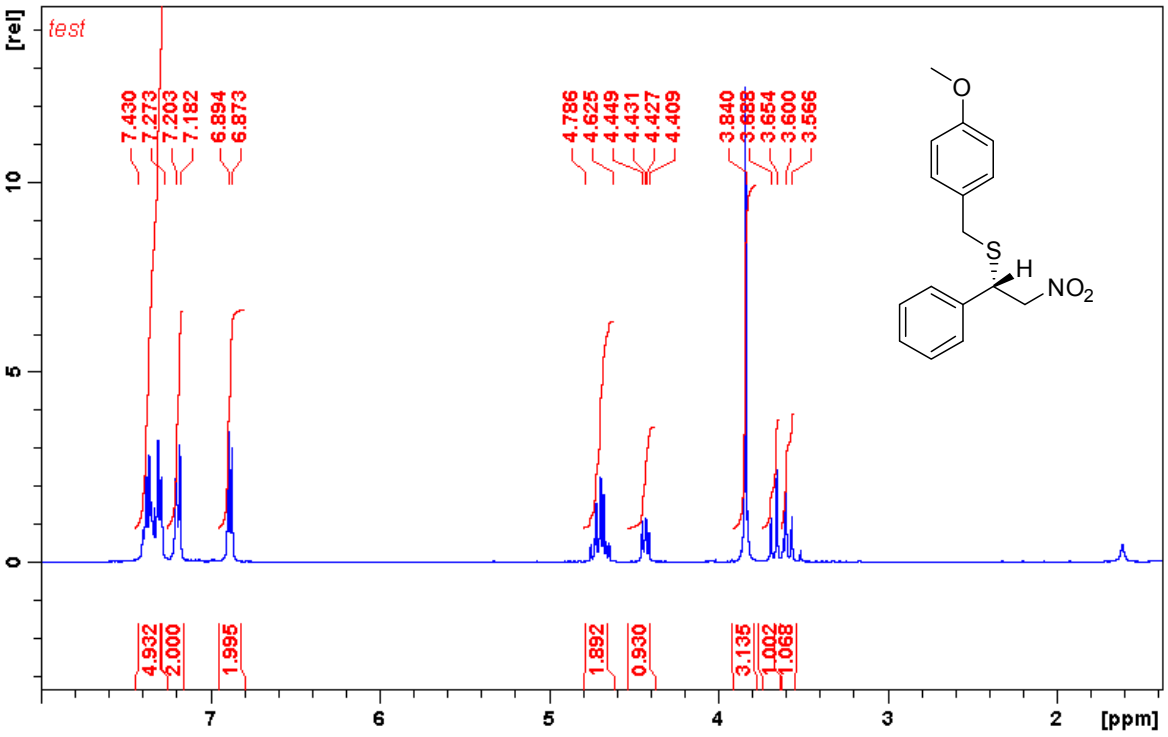
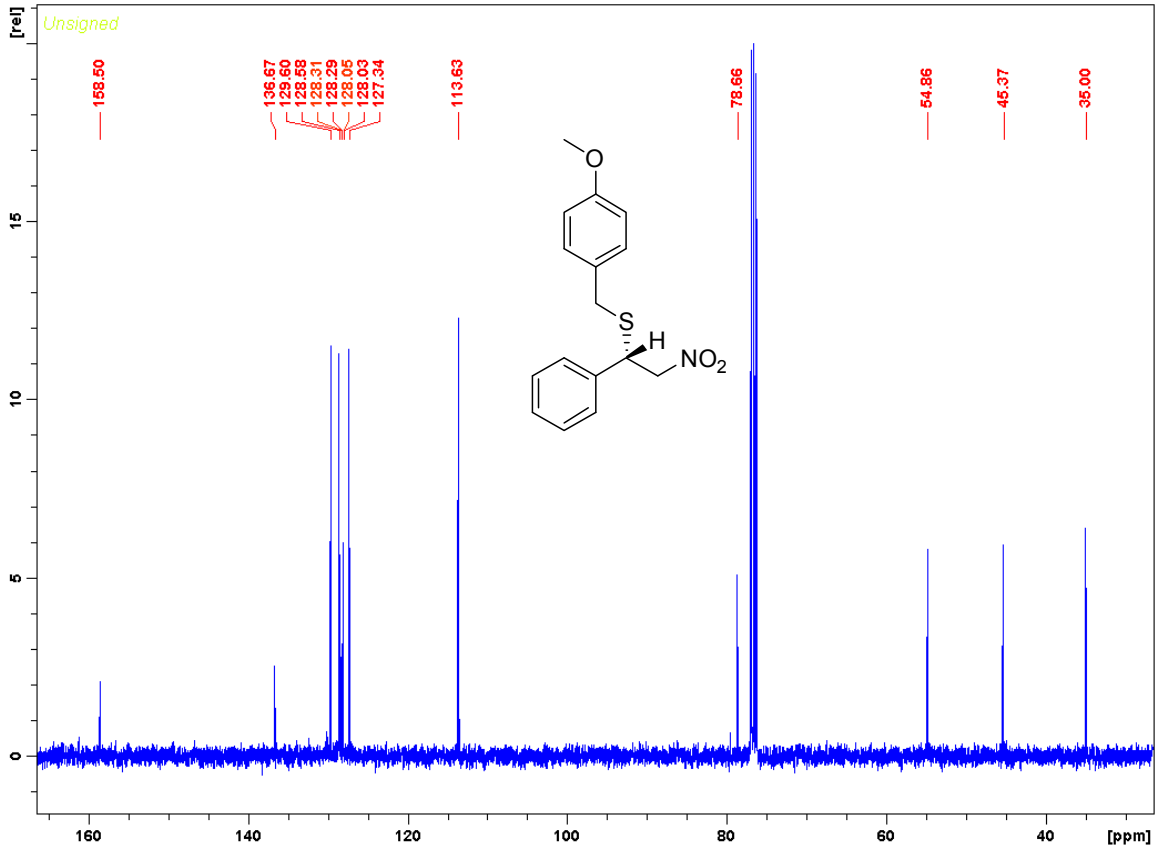
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (4-methoxybenzyl)(2-nitro-1-phenylethyl)sulfane (**21**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (4-methoxybenzyl)(2-nitro-1-phenylethyl)sulfane (**21**)



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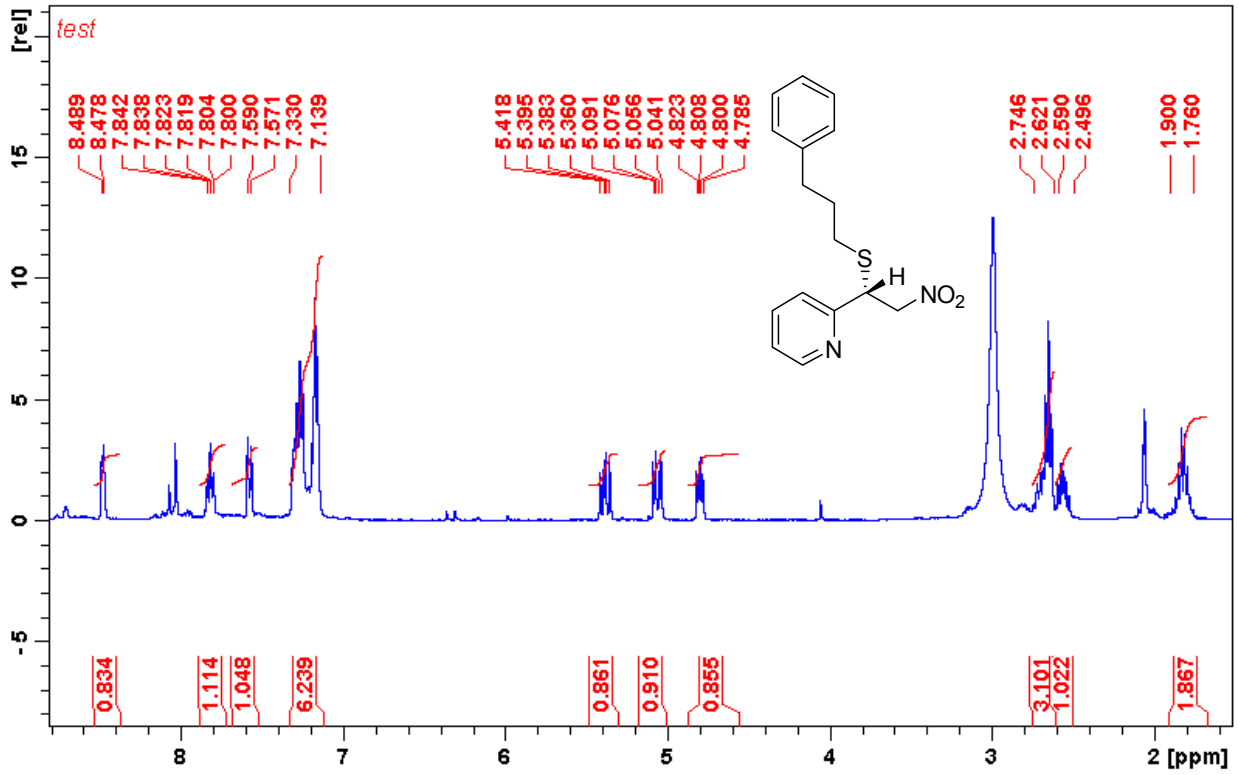
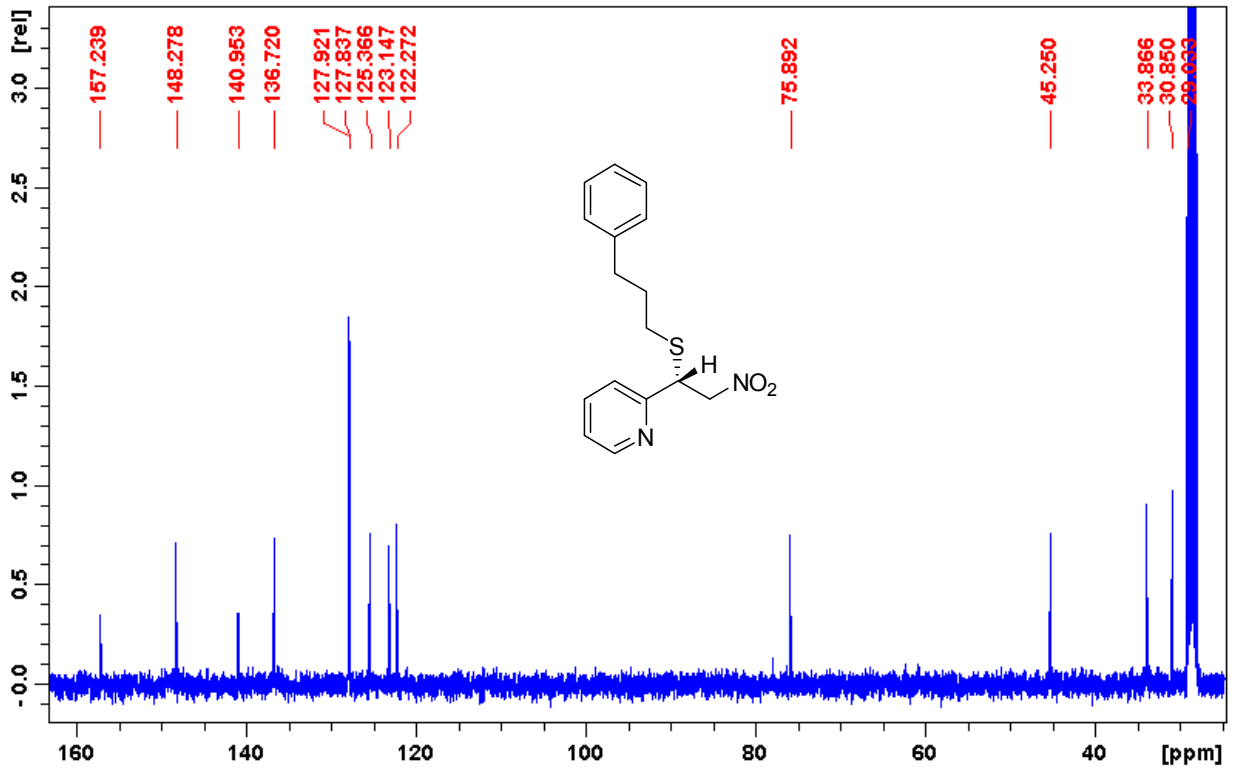
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of (2-nitro-1-phenylethyl)(3-phenylpropyl)sulfane (**22**)



^{13}C NMR spectrum (100 MHz, $(CD_3)_2CO$) of (2-nitro-1-phenylethyl)(3-phenylpropyl)sulfane (**22**)



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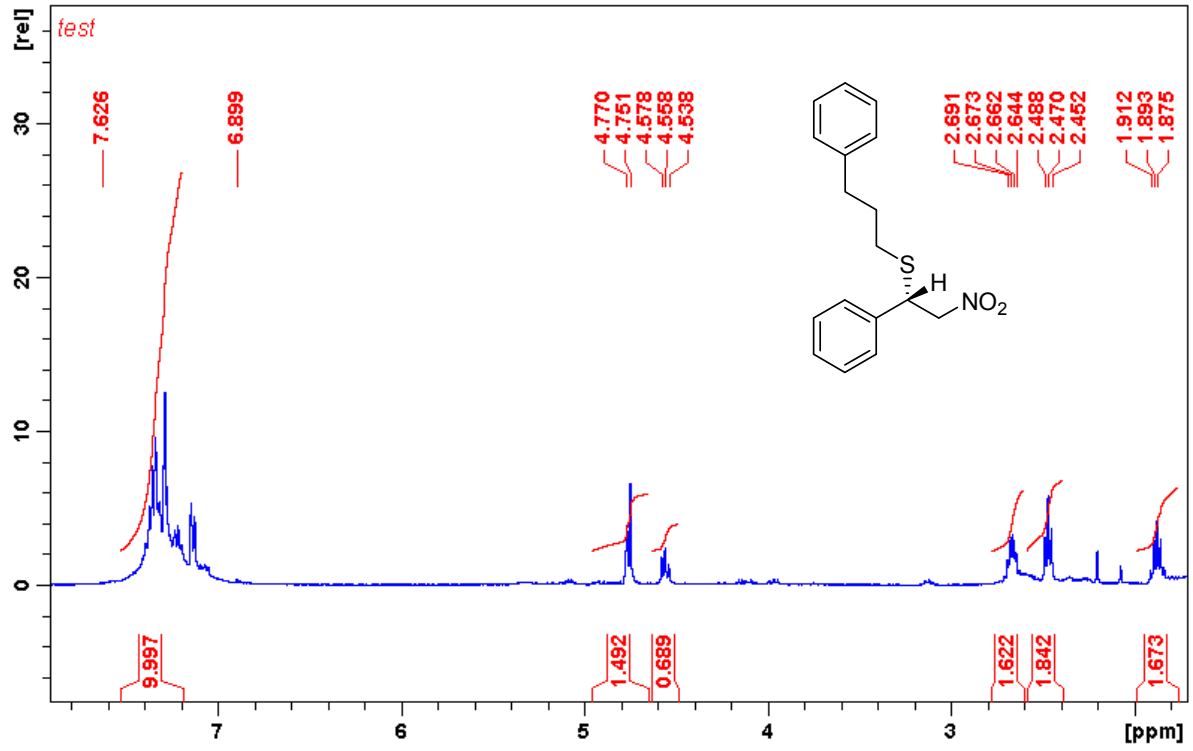
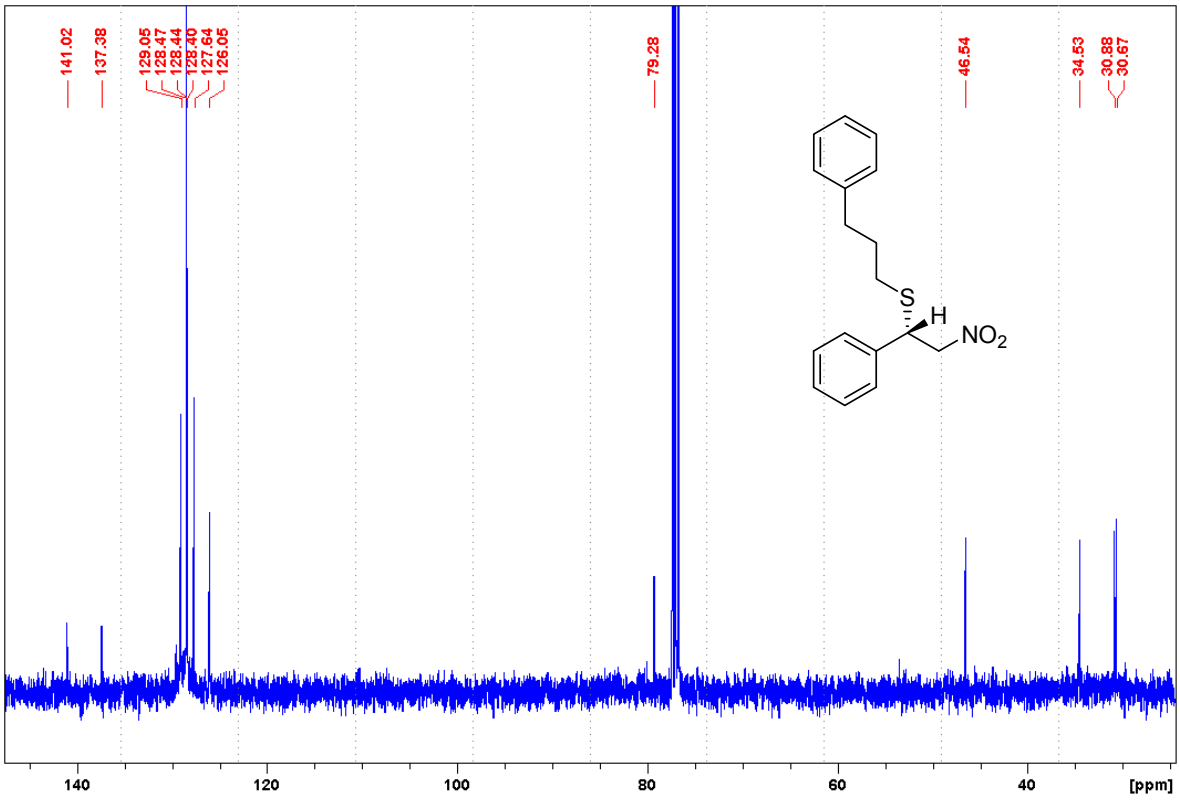
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*S*)-2-nitro-1-phenylethyl)(3-phenylpropyl)sulfane (**23**)



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*S*)-2-nitro-1-phenylethyl)(3-phenylpropyl)sulfane (**23**)



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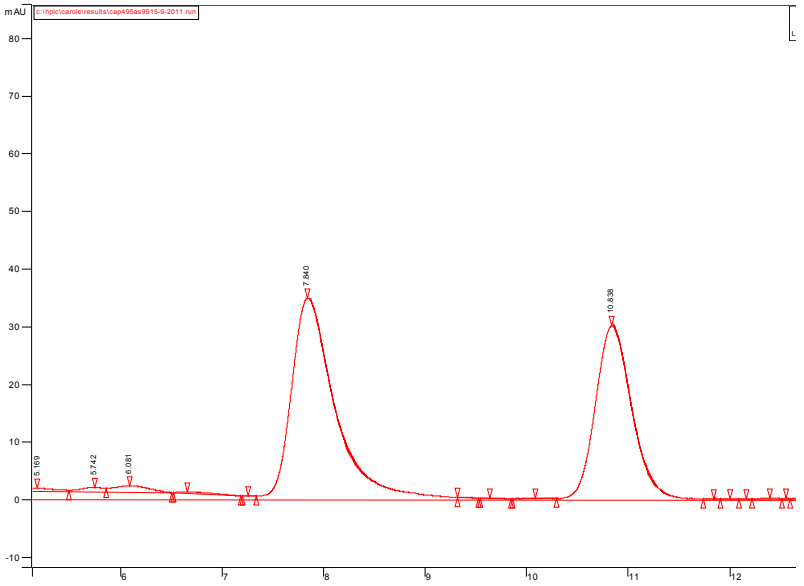
6.0 HPLC conditions and chromatograms

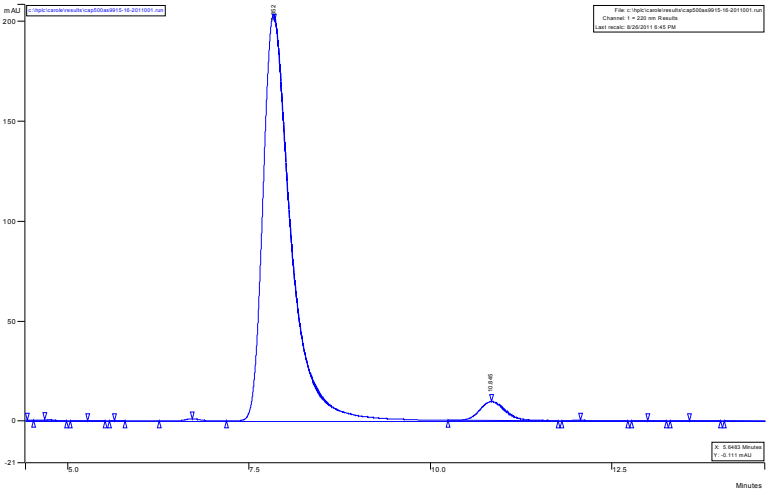
6. 1 (4-tert-butylbenzyl)(2-nitro-1-phenylethyl)sulfane (4a)

Chiralcel AS (4.6 mm x 25 cm), hexane/IPA: 99/1, 1 mL min^{-1}, RT, UV detection at 220 nm.

Peak No	Result	Ret. Time (min)
1	9.6800	7.840
2	7.1484	10.838



Peak No	Result	Ret. Time (min)
1	91.5865	7.852
2	3.7594	10.845



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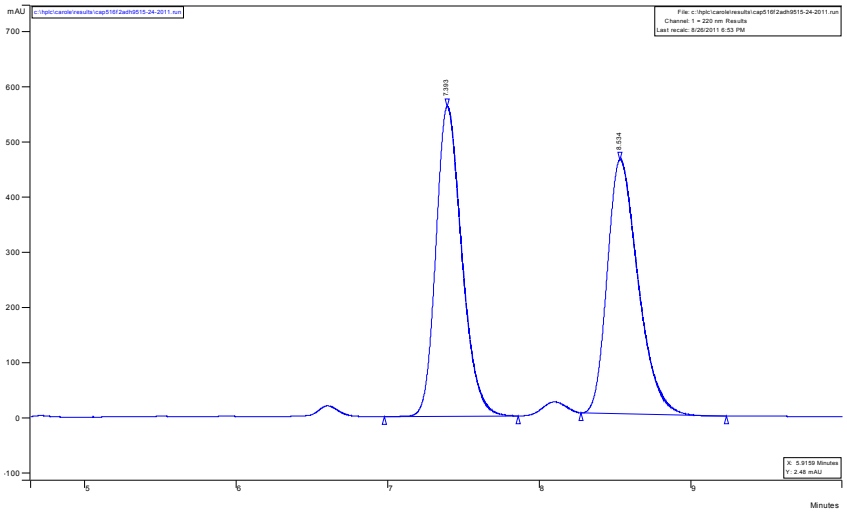
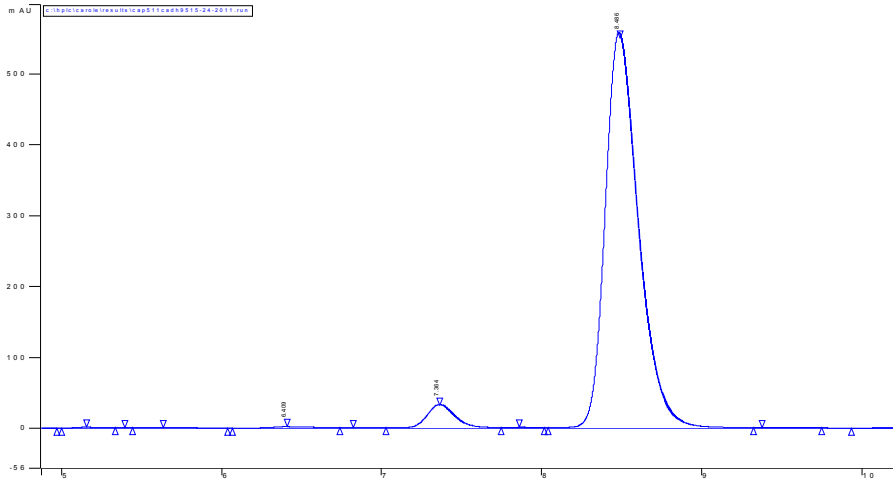
6.2 (4-tert-butylbenzyl)(1-(4-bromophenyl)-2-nitroethyl)sulfane (13)

Chiralcel OD-H (4.6 mm x 25 cm), hexane/IPA: 98/2, 0.8 mL min^{-1}, RT, UV detection at 220 nm.

Peak No	Result	Ret. Time (min)
1	31.6890	7.393
2	31.0313	8.534



Peak No	Result	Ret. Time (min)
1	4.7713	7.364
2	92.5823	8.486



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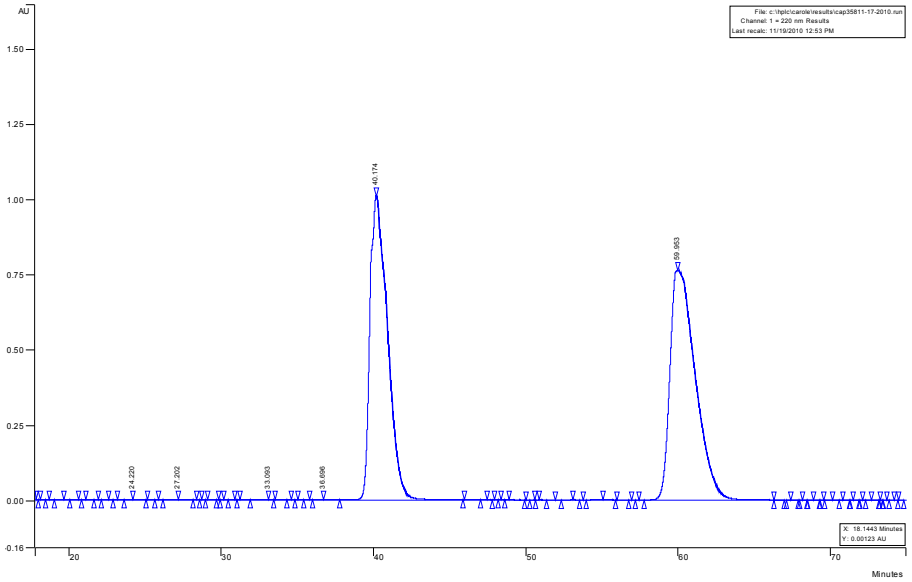
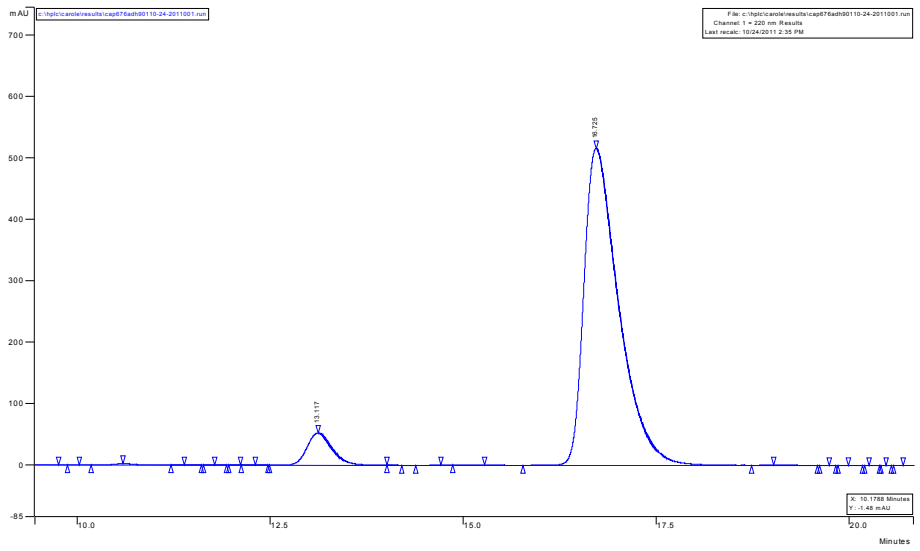
6.3 (4-tert-butylbenzyl)(2-nitro-1-(4-nitrophenyl)ethyl)sulfane (14)

Chiralcel AD-H (4.6 mm x 25 cm), hexane/IPA: 90/10, 1 mL min^{-1}, RT, UV detection at 220 nm.

Peak No	Result	Ret. Time (min)
1	49.7541	13.545
2	50.2459	17.523



Peak No	Result	Ret. Time (min)
1	5.2719	13.117
2	71.2159	16.725



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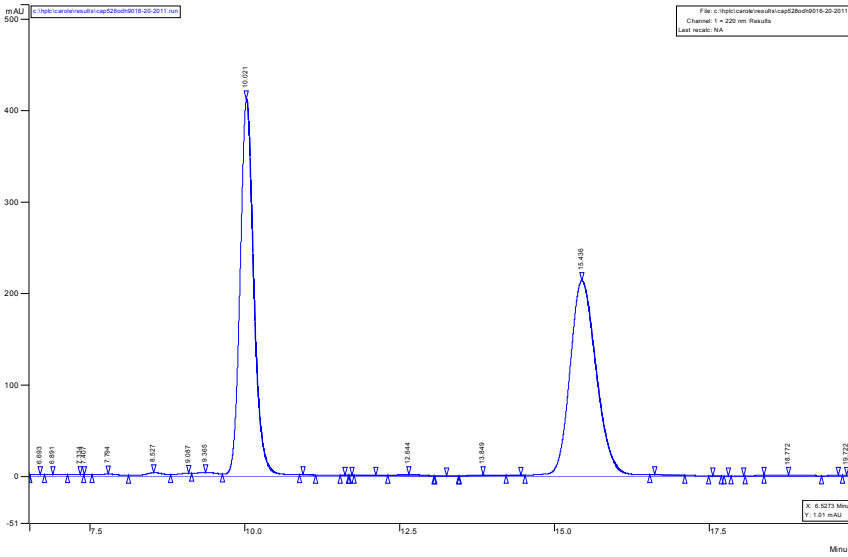
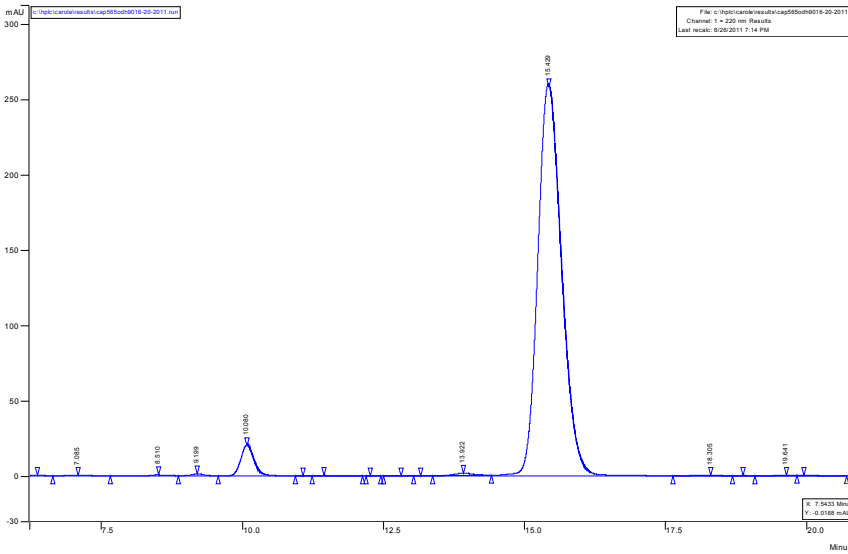
6.4 (4-tert-butylbenzyl)(1-(3-chlorophenyl)-2-nitroethyl)sulfane (15)

Chiralcel OD-H (4.6 mm x 25 cm), hexane/IPA: 90/10, 1 mL min^{-1}, RT, UV detection at 220 nm.

Peak No	Result	Ret. Time (min)
1	41.9457	10.021
2	41.5103	15.438



Peak No	Result	Ret. Time (min)
1	4.4548	10.080
2	91.6170	15.429



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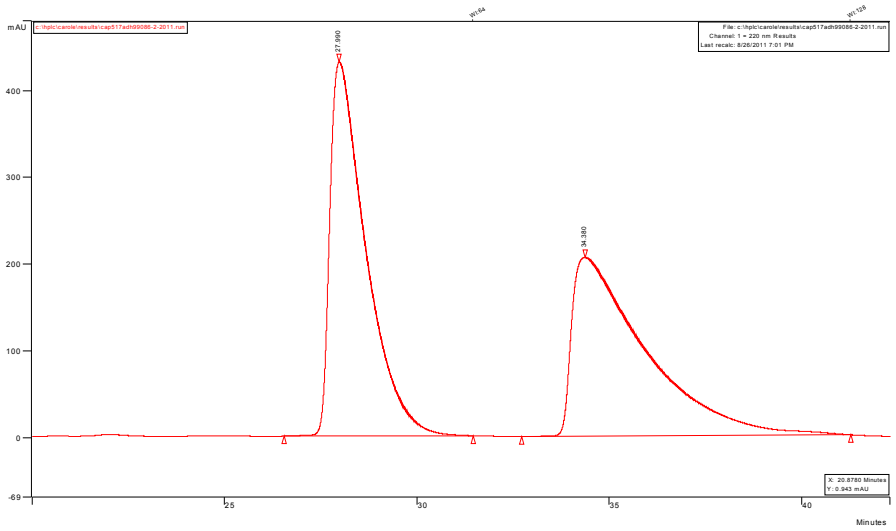
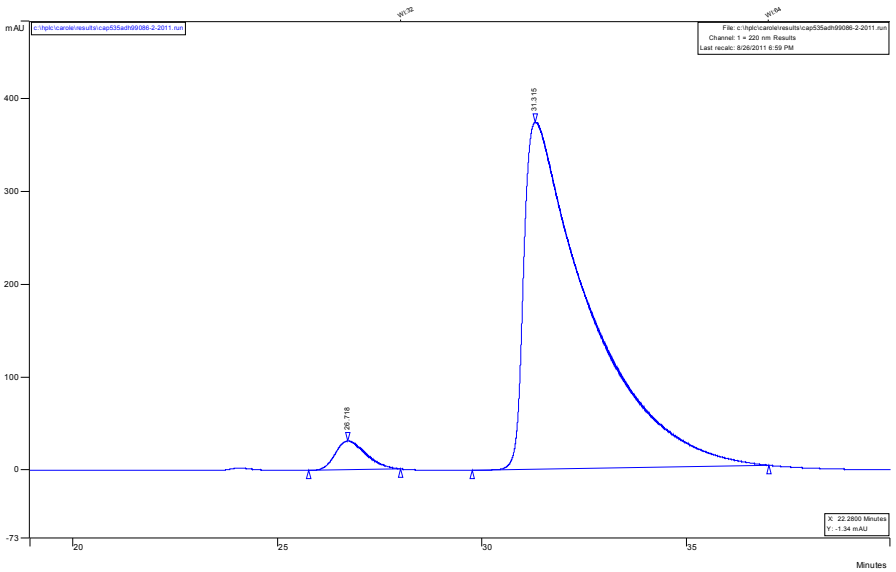
6.5 (4-tert-butylbenzyl)(1-(4-methoxyphenyl)-2-nitroethyl)sulfane (16)

Chiralcel AD-H (4.6 mm x 25 cm), hexane/IPA: 99/1, 0.8 mL min^{-1}, RT, UV detection at 220 nm.

Peak No	Result	Ret. Time (min)
1	3.1626	27.990
2	3.1014	34.380



Peak No	Result	Ret. Time (min)
1	3.6801	26.718
2	94.0283	31.315



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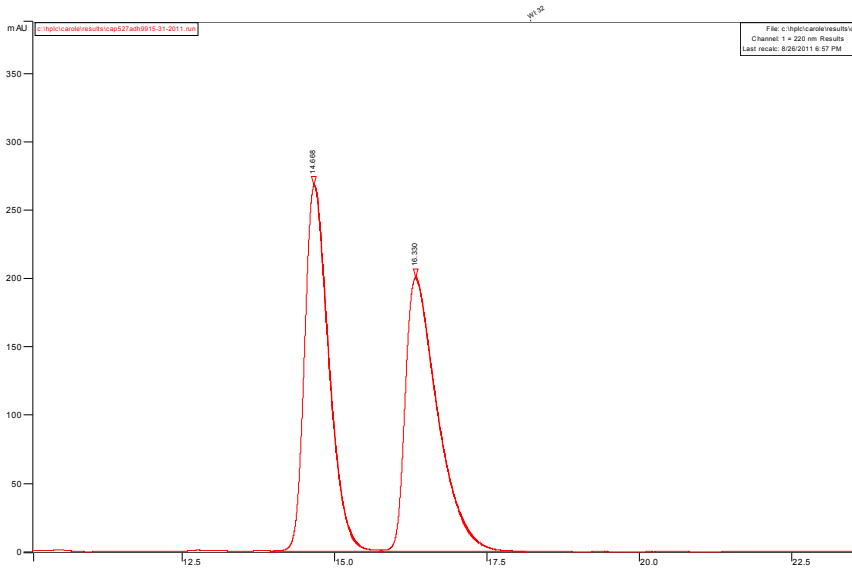
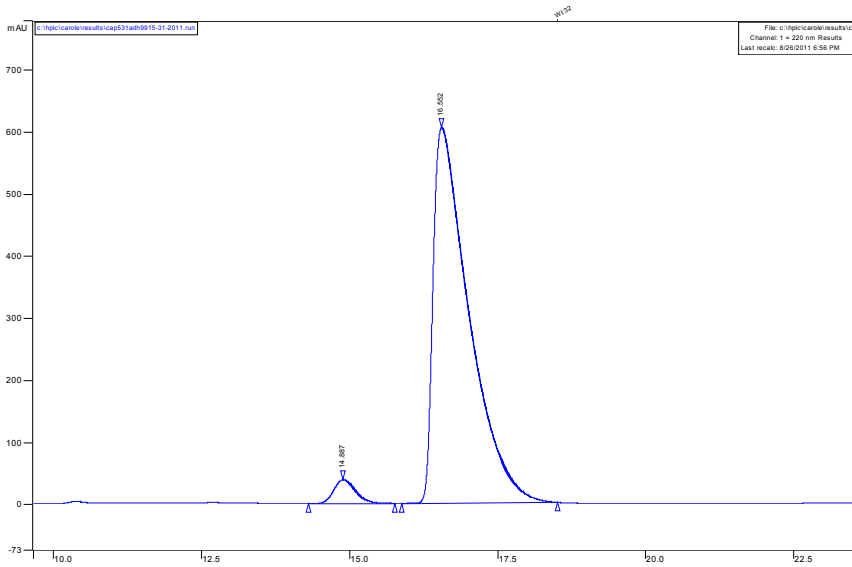
6.6 2-(1-(4-tert-butylbenzylthio)-2-nitroethyl)thiophene (17)

Chiralcel AD-H (4.6 mm x 25 cm), hexane/IPA: 99/1, 1 mL min^{-1}, RT, UV detection at 220 nm.

Peak No	Result	Ret. Time (min)
1	28.6455	14.668
2	28.5375	16.330



Peak No	Result	Ret. Time (min)
1	3.7050	14.887
2	94.1917	16.552



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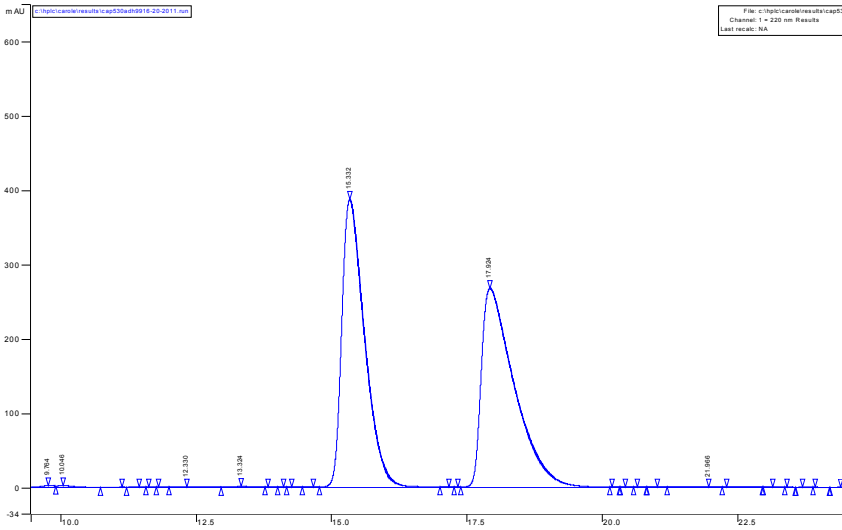
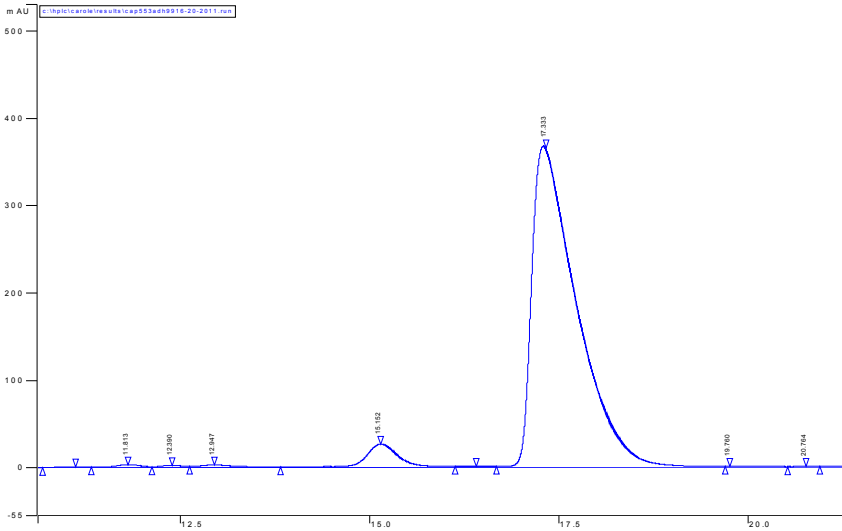
6.7 2-(1-(4-tert-butylbenzylthio)-2-nitroethyl)furane (18)

Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 99/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm.

Peak No	Result	Ret. Time (min)
1	41.5742	15.332
2	41.8771	17.924



Peak No	Result	Ret. Time (min)
1	4.6180	15.152
2	86.0601	17.333



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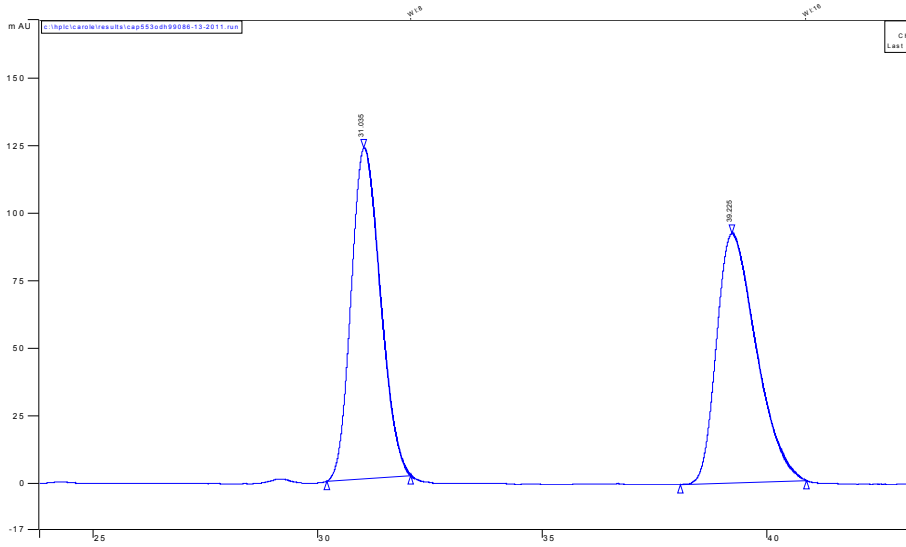
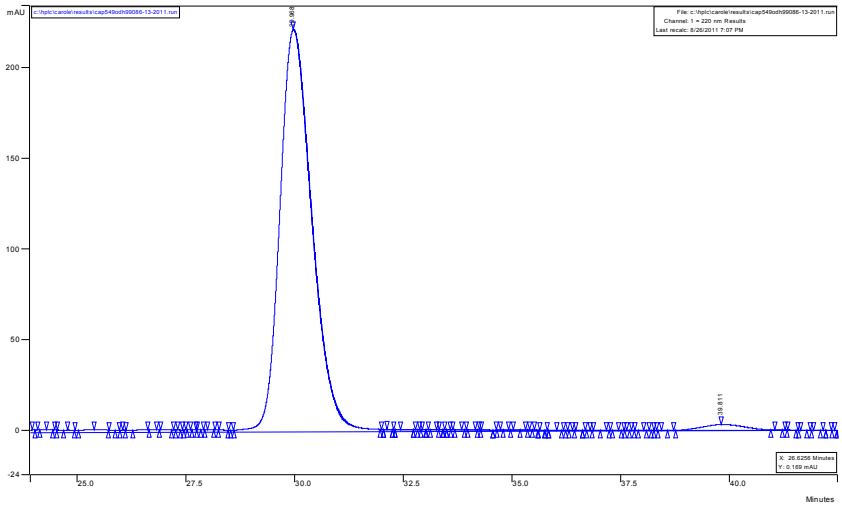
6.8 3-(1-(4-tert-butylbenzylthio)-2-nitroethyl)pyridine (19)

Chiralcel OD-H (4.6 mm x 25 cm), hexane/IPA: 99/1, 0.8 mL min^{-1}, RT, UV detection at 220 nm.

Peak No	Result	Ret. Time (min)
1	49.2944	31.035
2	50.3004	39.225



Peak No	Result	Ret. Time (min)
1	98.1437	29.968
2	1.8563	39.811



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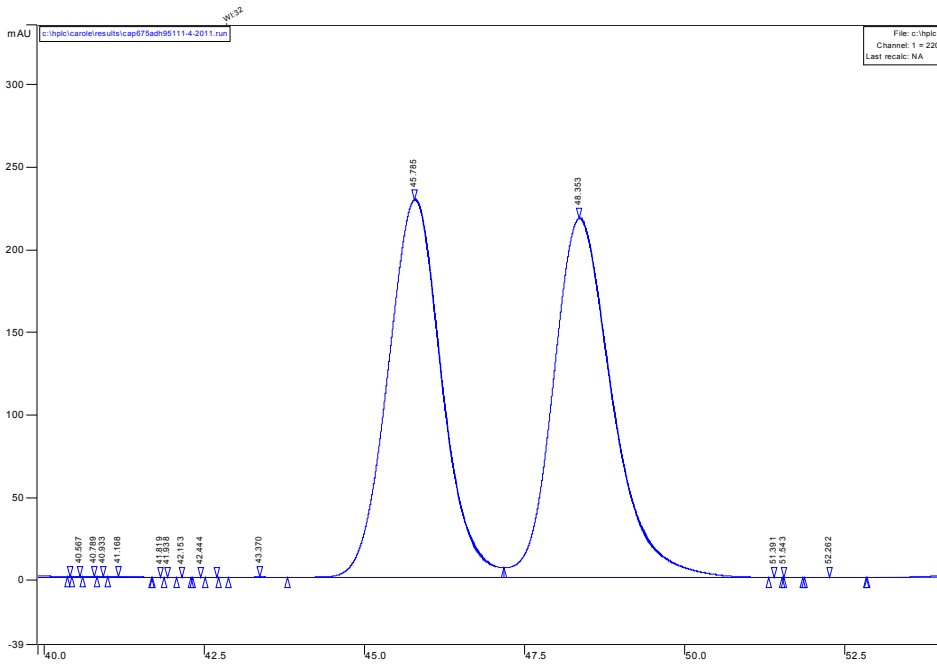
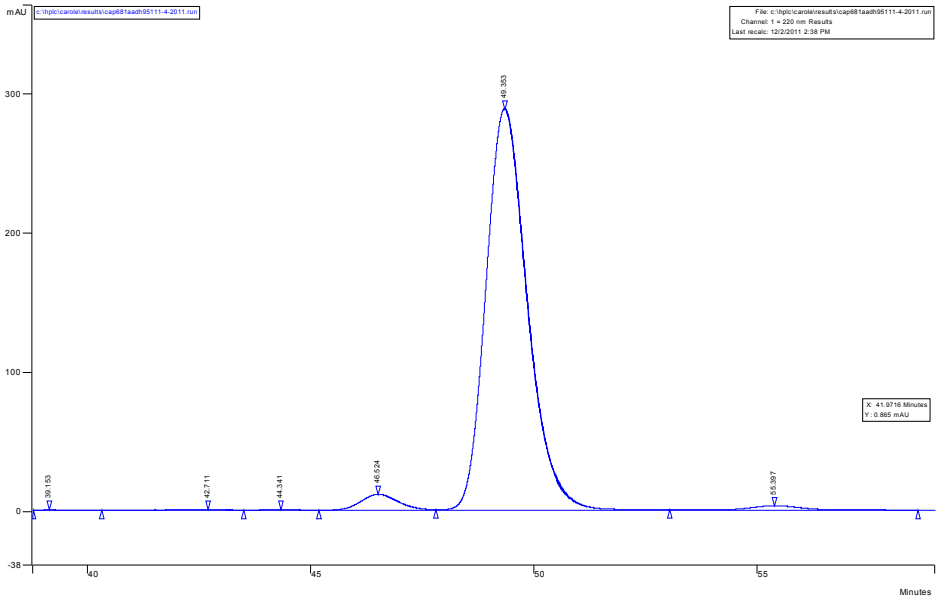
6.9 (*R*)-2-(2-nitro-1-(2-nitrobenzylthio)ethyl)pyridine (20)

Chiralcel AD-H (4.6 mm x 25 cm), hexane/IPA: 99/1, 1 mL min^{-1}, RT, UV detection at 220 nm.

Peak No	Result	Ret. Time (min)
1	22.764	45.785
2	23.656	48.353



Peak No	Result	Ret. Time (min)
1	1.638	46.524
2	44.311	49.353



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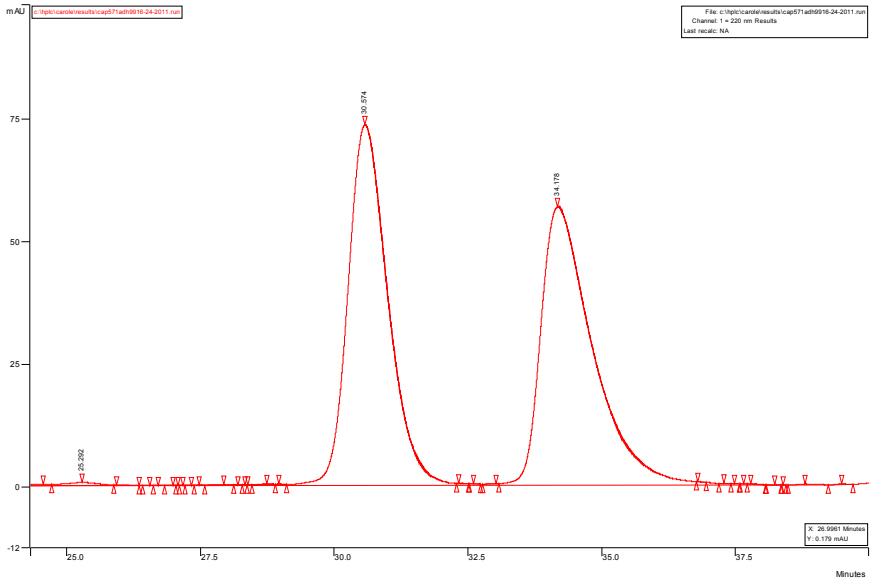
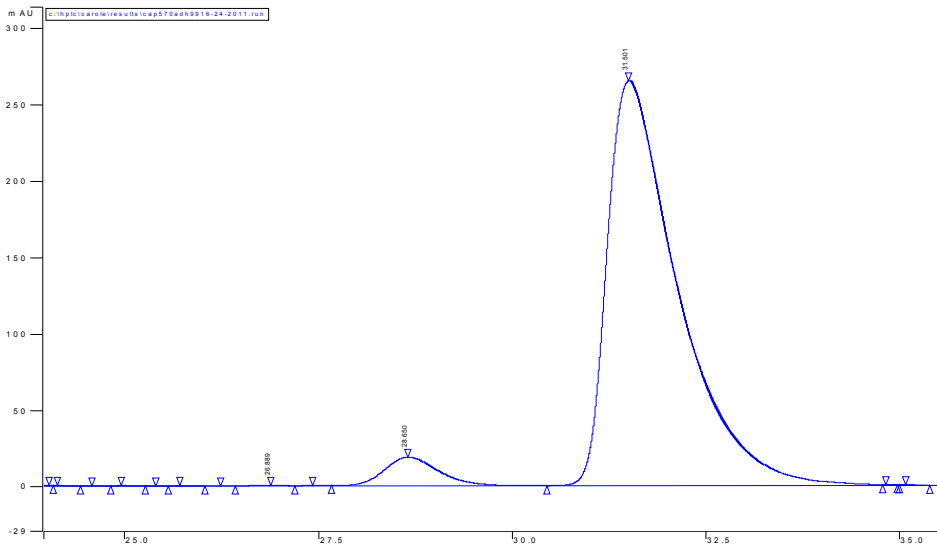
6.10 (4-methoxybenzyl)(2-nitro-1-phenylethyl)sulfane (21)

Chiralcel AD-H (4.6 mm x 25 cm), hexane/IPA: 99/1, 1 mL min^{-1}, RT, UV detection at 220 nm.

Peak No	Result	Ret. Time (min)
1	32.9344	30.574
2	32.9632	34.178



Peak No	Result	Ret. Time (min)
1	2.2776	28.650
2	41.6149	31.501



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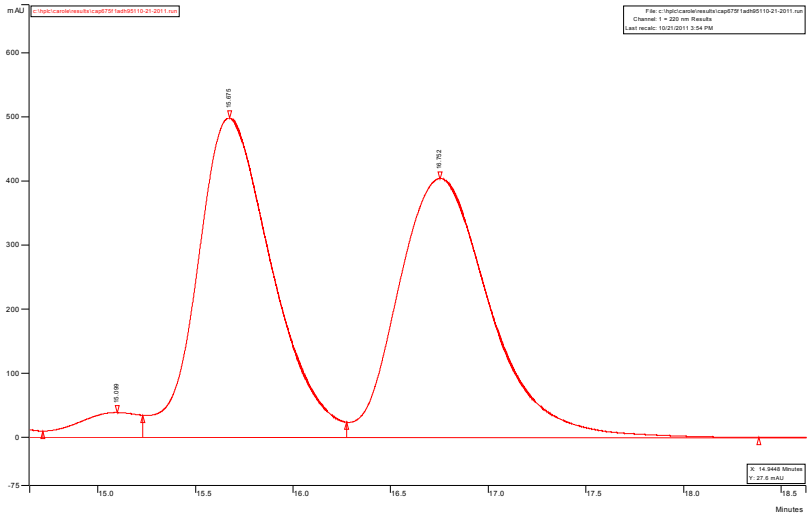
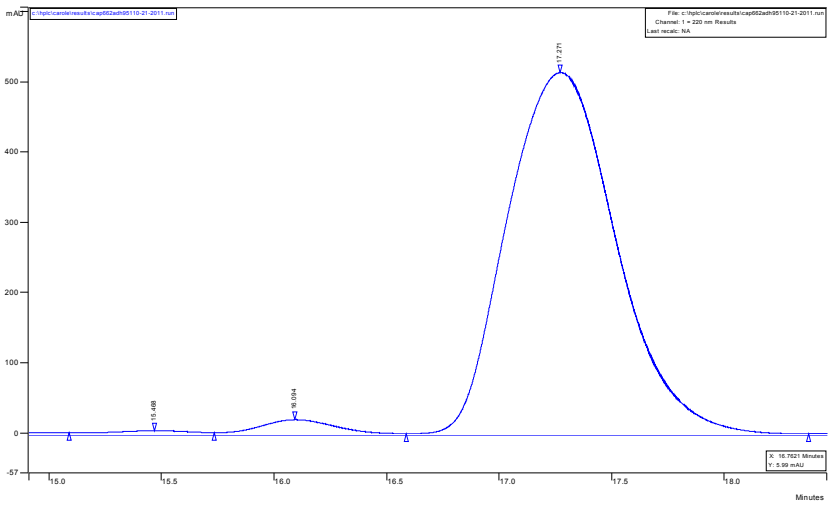
6.11 (*R*)-2-(2-nitro-1-(3-phenylpropylthio)ethyl)pyridine (22)

Chiralcel AD-H (4.6 mm x 25 cm), hexane/IPA: 99/1, 1 mL min^{-1}, RT, UV detection at 220 nm.

Peak No	Result	Ret. Time (min)
1	26.5455	15.675
2	26.4615	16.752



Peak No	Result	Ret. Time (min)
1	1.7760	16.09
2	58.0266	17.27



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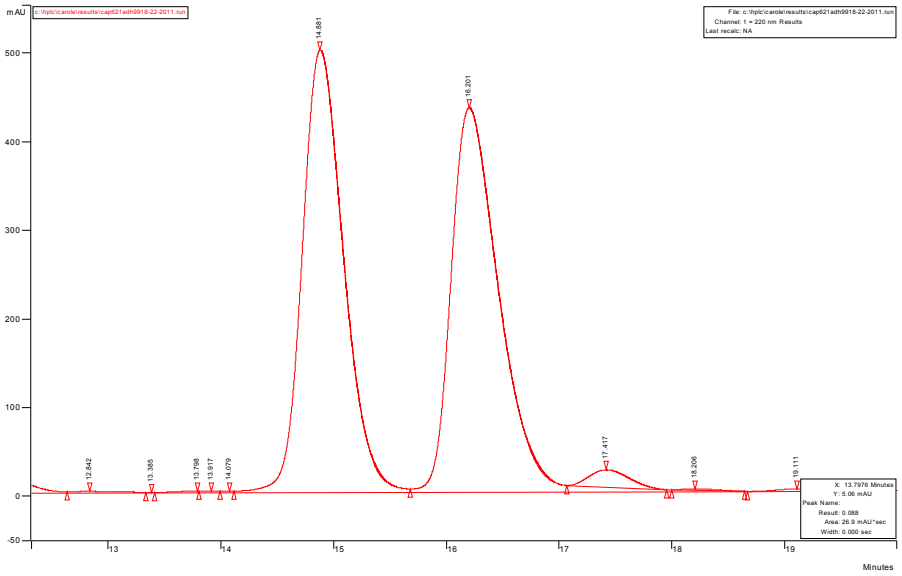
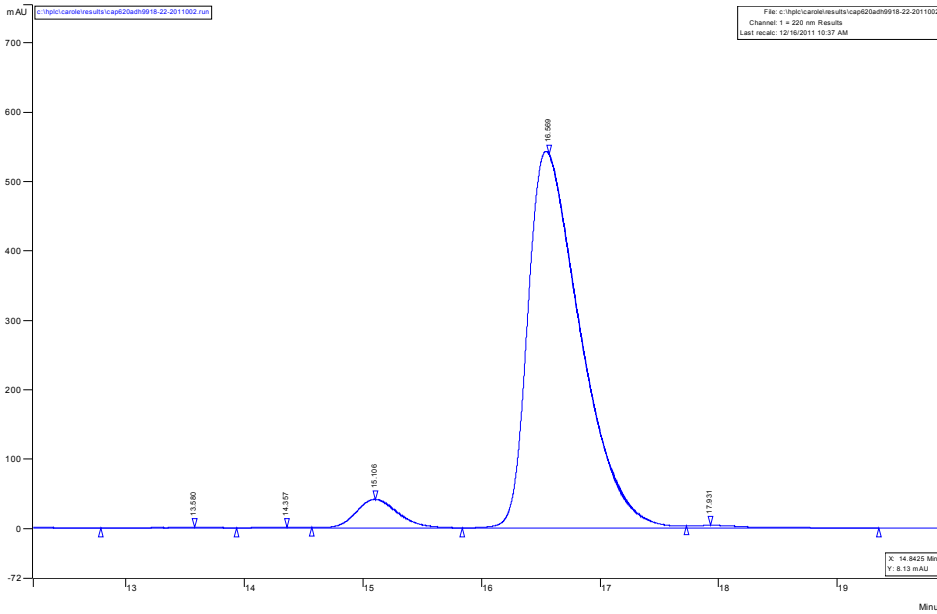
6.12 (*S*)-2-nitro-1-phenylethyl)(3-phenylpropyl)sulfane (23)

Peak No	Result	Ret. Time (min)
1	41.8012	14.881
2	42.5944	16.201



Peak No	Result	Ret. Time (min)
1	3.148	15.106
2	52.715	16.569



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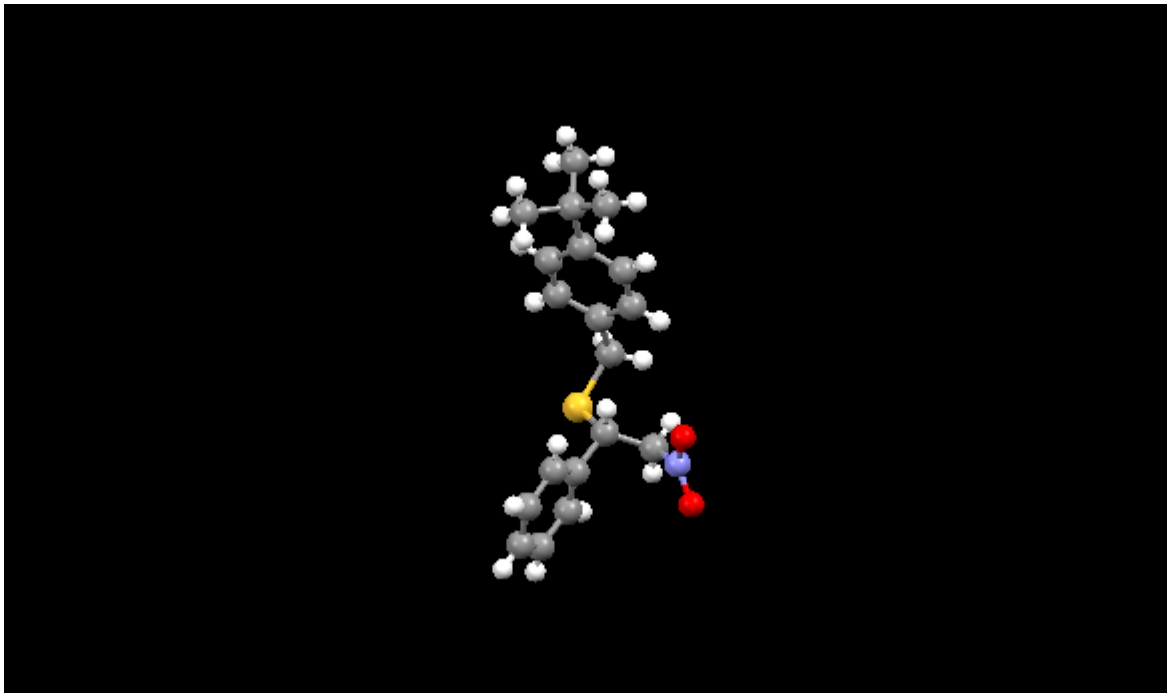
7.0 Crystal structure

The structure have been deposited in the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 859316

7. 1 (*S*)-(4-tert-butylbenzyl)(2-nitro-1-phenylethyl)sulfane (4a)



Formula: $C_{19}H_{23}NO_2S$

Space group: P 2_1 2_1 2_1

Cell lengths: a 8.4220(17) b 10.230(2) c 20.787(4)

Cell angles: α 90.00 β 90.00 γ 90.00

Cell volume: 1790.95

Z, Z': 4, 0

R-factor: 6.39

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8.0 References

1. C. Palacio and S. J. Connon, *Org. Lett.* 2011, **13**, 1298-1301.