Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. Z52175

© Wiley-VCH 2003

69451 Weinheim, Germany

Catalytic Enantioselective Conjugate Reduction of β,β-Disubstituted Nitroalkenes

Constantin Czekelius and Erick M. Carreira

Experimental Section

All reactions were carried out in dried glassware under an atmosphere of argon. Toluene was dried by passage over alumina (activated at 350 °C under nitrogen atmosphere for 12 h) and degassed by three freeze–pump–thaw–cycles. PMHS was purchased from Fluka and used without further purification. Phenylsilane was purchased from Gelest and used without further purification. (*S*)-*p*-tol-BINAP and (*S*)-(*R*)-JOSIPHOS were purchased from Strem and stored in a glove box. Copper (I) *t*-butoxide was prepared according to literature procedures[5b], sublimed three times under high vacuum, and stored in a glove box.

Evaporation of organic solutions was achieved by rotary evaporation with a water bath temperature below 40 °C. Product purification by flash column chromatography (FC) was accomplished using silica gel 60 (32-63 μm particle size) at 0.1 – 0.3 bar pressure. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} glass plates. Visualization was achieved by either fluorescence quenching or by staining with aqueous potassium permanganate solution.

NMR spectra were recorded at room temperature on a Varian Mercury operating at 300 MHz (^{1}H) and 75 MHz (^{13}C) respectively.

Residual protio solvent signals are internally referenced. Chemical shift δ is referred in terms of ppm, coupling constants are given in Hz. Following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, q = quartett, m = multiplet or unresolved, br = broad signal. NOE-measurements were obtained from the NMR-Service at ETH Zurich. Infrared spectra were recorded on a Perkin-Elmer Spektrum RX I FT-IR System and reported in cm^{-1}. Samples were prepared in thin film technique. Combustion analysis was performed by the Mikroelementaranalytisches Laboratorium at ETH Zurich. Mass spectra were obtained from the MS service of the University of Fribourg/Switzerland. Enantiomeric ratios were determined with a Merck Hitachi LaChrom D-7000 HPLC using Chiracel OD-H or Chiracel AD-H (2-Methyl-3-nitro-propan-1-ol) columns, a Knauer differential refractometer, and hexane/isopropanol as eluents. Racemic reference samples were prepared by nitroolefin reduction with sodium borohydride in MeOH/THF.

Nitroolefins were prepared by literature procedures.[9,10]

(*E*)-2-Phenyl-1-nitro-1-propene:[10b]

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.45 (m, 5H, arom. *H*), 7.31 (m, 1H, C1-*H*), 2.65 (m, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 149.8, 138.1, 136.1, 130.2, 128.9, 126.7, 18.6. IR (film): ν = 1623, 1576, 1514, 1445, 1375, 1340, 1257, 921, 835, 765, 738, 696, 609 cm^{-1}.

(*E*)-2-(4-Chloro-phenyl)-1-nitro-1-propene:[10b]

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.40 (m, 4H, arom. *H*), 7.28 (q, *J* = 1.6 Hz, 1H, C1-*H*), 2.62 (d, *J* = 1.6 Hz, 3H, Me). ^{13}C NMR (75 MHz, [D_6]DMSO, 25 °C): δ = 147.0, 136.7, 136.0, 135.0, 128.9, 128.7, 17.7. IR (film): ν = 3106, 1622, 1591, 1515, 1490, 1435, 1402, 1374, 1342, 1255, 1097, 1012, 921, 823, 756 cm^{-1}.

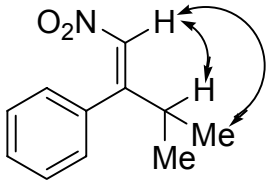
(*E*)-2-(4-Methoxy-phenyl)-1-nitro-1-propene:[9c]

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.43 (d, *J* = 8.1 Hz, 2H, arom. *H*), 7.33 (s, 1H, C1-*H*), 6.94 (d, *J* = 8.1 Hz, 2H, arom. *H*), 3.85 (s, 3H, OMe), 2.64 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.4, 149.6, 135.0, 130.1, 128.3, 114.3, 55.5, 18.4. IR (film): ν = 3107, 2966, 2937, 2841, 1602, 1571, 1513, 1462, 1374, 1335, 1295, 1252, 1184, 1029, 921, 827, 786 cm^{-1}.

(*Z*)-3-Methyl-2-phenyl-1-nitro-1-butene:[9c]

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.34-7.43 (m, 3H, arom. *H*), 7.07-7.14 (m, 2H, arom. *H*), 7.00 (d, *J* = 1.3 Hz, 1H, C1-*H*), 2.72 (dm, *J* = 6.9, 1.3 Hz, 1H, C3-*H*), 1.13 (d, *J* = 6.9 Hz, 6H, C3*Me*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 157.5, 135.9, 134.4, 128.2, 128.2, 126.5, 35.8, 20.8. IR (film): ν = 2970, 2934, 2876, 1636, 1524, 1467, 1444,

1344, 779, 746, 701 cm^{-1}. Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32 Found: C, 69.10; H, 6.65; N, 7.14.

NOE: 

(*E*)-2-Phenyl-1-nitro-1-pentene:[9c, 10b]

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.43 (m, 5H, arom. *H*), 7.20 (m, 1H, C1-*H*), 3.01 (m, 2H, C3-H_2), 1.53 (m, 2H, C4-*H*), 0.97 (t, *J* = 7.5 Hz, 3H, *Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.2, 137.2, 136.0, 130.0, 128.9, 127.0, 33.1, 21.9, 14.2. IR (film): ν = 2964, 2934, 2874, 1614, 1575, 1518, 1444, 1339, 934, 838, 770, 744, 697 cm^{-1}.

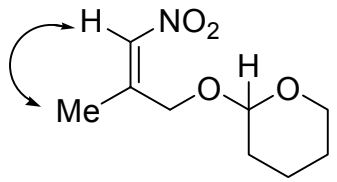
(*E*)-3-Hydroxy-2,3-dimethyl-1-nitro-1-butene:[9d]

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.35 (m, 1H, C1-*H*), 2.17 (d, *J* = 1.6 Hz, 3H, C2-*Me*), 2.10 (br s, 1H, O*H*), 1.42 (s, 6H, C3-Me_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 156.9, 134.9, 73.4, 28.4, 15.3. IR (film): ν = 3459, 2983, 2937, 1634, 1516, 1468, 1348, 1233, 1184, 1116, 966, 935, 866, 846, 717 cm^{-1}. Anal. Calcd for $C_6H_{11}NO_3$: C, 49.65; H, 7.64; N, 9.65. Found: C, 49.69; H, 7.83; N, 9.89.

(*Z*)-*O*-Tetrahydropyranyl-2-methyl-3-nitro-prop-2-en-1-ol:[9e]

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.94 (m, 1H, C3-*H*), 4.91 (m, 1H, C1-H^1), 4.73 (m, 1H, C1-H^2), 4.62 (m, 1H, C1'-*H*), 3.81 (m, 1H, C6'-H^1), 3.53 (m, 1H, C6'-H^2), 2.04 (m, 3H, C2-*Me*), 1.67-1.87 (m, 3H, THP), 1.49-1.66 (m, 3H, THP). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.1, 133.9, 98.9, 66.4, 62.6, 30.5, 25.3, 19.6, 18.6. IR (film): ν = 2945, 2871, 1733, 1635, 1518, 1442, 1354, 1317, 1202, 1125, 1077, 1034, 975, 908, 871, 818 cm^{-1}.

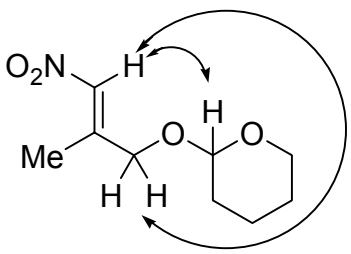
NOE:



(*E*)-*O*-Tetrahydropyranyl-2-methyl-3-nitro-prop-2-en-1-ol:[9e]

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.20 (m, 1H, C3-*H*), 4.65 (m, 1H, C1'-*H*), 4.32 (m, 1H, C1-H^1), 4.20 (m, 1H, C1-H^2), 3.78 (m, 1H, C6'-H^1), 3.52 (m, 1H, C6'-H^2), 2.15 (m, 3H, C2-*Me*), 1.51-1.87 (m, 6H, THP). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 148.7, 134.6, 98.2, 68.3, 62.1, 30.2, 25.2, 16.1, 15.7. IR (film): ν = 2945, 2871, 1652, 1517, 1442, 1376, 1343, 1202, 1185, 1130, 1080, 1037, 1022, 970, 906, 871, 830, 817 cm^{-1}.

NOE:



(*E*)-2-Methyl-3-nitro-prop-2-en-1-ol:[9e]

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.23 (m, 1H, C3-*H*), 4.26 (s, 2H, C1-H_2), 2.67 (s, 1H, O*H*), 2.13 (m, 3H, C2-*Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 151.7, 134.3, 64.8, 15.5. IR (film): ν = 3427, 3122, 2924, 2856, 1652, 1514, 1441, 1348, 1180, 1080, 1039, 966, 929, 829 cm^{-1}.

(*E*)-2-(Pyridin-2-yl)-1-nitro-1-propene:[9c]

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.68 (ddd, *J* = 4.7, 1.9, 0.9 Hz, 1H, arom. *H*), 7.88 (q, *J* = 1.6 Hz, 1H, C1-*H*), 7.79(ddd, *J* = 7.8, 1.9 Hz, 1H, arom. *H*), 7.56 (m, 1H, arom. *H*), 7.36 (ddd, *J* = 7.8, 5.0, 1.2 Hz arom. *H*), 2.66 (d, *J* = 1.6 Hz, *Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.4, 149.7, 146.1, 138.4, 137.0, 124.6, 121.8, 16.0. IR (film): ν = 3113, 3057, 1630, 1583, 1570, 1556, 1515, 1467, 1433, 1375, 1343, 1158, 1101, 1048, 992, 924, 849, 784 cm^{-1}. Anal. Calcd for $C_8H_8N_2O_2$: C, 58.53; H, 4.91; N, 17.06 Found: C, 58.46; H, 4.94; N, 16.98.

(*E*)-2-(Furan-2-yl)-1-nitro-1-propene:[9c]

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.67 (m, 1H, C1-*H*), 7.54 (m, 1H, arom. *H*), 6.90 (d, *J* = 3.7 Hz, 1H, arom. *H*), 6.55 (m, 1H, arom. *H*), 2.55 (m, 3H, *Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 150.5, 145.5,

136.6, 132.9, 115.8, 112.8, 14.9. IR (film): ν = 3117, 1610, 1563, 1504, 1393, 1343, 1324, 1266, 1226, 1161, 1030, 946, 884, 821, 755, 690 cm^{-1}. Anal. Calcd for $C_7H_7NO_3$: C, 54.90; H, 4.61; N, 9.15 Found: C, 54.91; H, 4.77; N, 8.99.

(*E*)-2-(Thiophen-2-yl)-1-nitro-1-propene:[9c]

^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.57 (q, *J* = 1.3 Hz, 1H, C1-*H*), 7.46-7.50 (m, 2H, arom. *H*), 7.13 (dd, *J* = 5.0, 3.7 Hz, 1H, arom. *H*), 2.70 (d, *J* = 1.3 Hz, 3H, *Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 142.8, 140.4, 133.6, 129.5, 129.1, 128.5, 18.0. IR (film): ν = 3108, 1600, 1504, 1423, 1378, 1355, 1334, 1318, 1251, 1061, 905, 856, 818, 712 cm^{-1}. Anal. Calcd for $C_7H_7NO_2S$: C, 49.69; H, 4.17; N, 8.28 Found: C, 49.94; H, 4.37; N, 8.24.

General procedure for the reduction of nitroolefins using PMHS

In a 10 mL Schlenk-flask copper(I)-*t*-butoxide (6.8 mg, 50 μmol) and (*S*)-*p*-tolBINAP (37.3 mg, 55 μmol) were dissolved in toluene (6 mL). After stirring for 30 min at RT PMHS (90 μL, 1.50 mmol) was added to the yellow solution turning the color to deep red. Stirring was continued for 15 min. The nitroolefin (1.00 mmol) was added and the mixture stirred at RT for 18h. Sat. NH_4Cl solution (20 mL) was added and the mixture extracted with ether (2 x 30 mL). After drying over

sodium sulfate, the solvent was evaporated. Flash chromatography (hexane: EtOAc) provided the product as a colorless oil.

General procedure for the reduction of nitroolefins using phenylsilane and PMHS

In a 10 mL Schlenck–flask copper(I)-*t*-butoxide (6.8 mg, 50 µmol) and the ligand (55 µmol) were dissolved in toluene (5 mL). After stirring for 30 min at RT 100 µL (1.0 µmol of complex) of this solution were taken and mixed with toluene (4.9 mL). PMHS (6 µL, 0.10 mmol) was added followed by phenylsilane (150 µL, 1.20 mmol) and water (22 µL, 1.20 mmol). After stirring for 5 min the nitroolefin (1.00 mmol) was added with vigorous stirring. The dark mixture turned yellow and gas evolution was observed. After stirring for 24 h, TBAF solution (4 mL, 1.0 M in THF, 4.0 mmol) was added and stirring was continued for 3 h. Water (20 mL) was added and the mixture extracted with ether (2 x 30 mL). After drying over sodium sulfate, the solvent was evaporated. Flash chromatography (hexane: EtOAc) provided the product as a colorless oil.

2-Phenyl-1-nitro-propane:

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.34 (m, 2H, arom. *H*), 7.25 (m, 3H, arom. *H*), 4.58 (dd, *J* = 12.1, 7.5 Hz, 1H, C1-*H*^{1}), 4.49 (dd, *J* = 12.1, 8.1 Hz, 1H, C1-*H*^{2}), 3.64 (m, 1H, C2-*H*), 1.39 (d, *J* = 6.8 Hz, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 140.7, 128.8, 127.4,

126.8, 81.8, 38.7, 18.8. IR (film): ν = 3032, 2974, 2934, 1604, 1556, 1496, 1454, 1432, 1384, 1332, 1204, 1211, 1022, 765, 701 cm^{-1}.

2-(4-Chloro-phenyl)-1-nitro-propane:

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.31 (m, 2H, arom. *H*), 7.16 (m, 2H, arom. *H*), 4.52 (dd, *J* = 15.8, 7.8 Hz, 1H, C1-H^1), 4.48 (dd, *J* = 15.8, 7.8 Hz, 1H, C1-H^2), 3.62 (m, 1H, C2-*H*), 1.36 (d, *J* = 7.2 Hz, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 139.2, 133.2, 129.0, 128.2, 81.5, 38.1, 18.8. IR (film): ν = 2974, 1553, 1495, 1381, 1094, 1014, 829, 738 cm^{-1}.

2-(4-Methoxy-phenyl)-1-nitro-propane:

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.15 (m, 2H, arom. *H*), 6.87 (m, 2H, arom. *H*), 4.51 (dd, *J* = 11.8, 7.5 Hz, 1H, C1-H^1), 4.45 (dd, *J* = 11.8, 8.1 Hz, 1H, C1-H^2), 3.79 (s, 3H, OMe), 3.59 (m, 1H, C2-*H*), 1.36 (d, 3H, *J* = 7.2 Hz, Me). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 158.7, 132.7, 127.8, 114.2, 82.1, 55.3, 38.0, 18.9. IR (film): ν = 2968, 1613, 1551, 1515, 1459, 1382, 1300, 1250, 1181, 1123, 1025, 832, 772 cm^{-1}.

3-Methyl-2-phenyl-1-nitro-butane:

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.22-7.34 (m, 3H, arom. *H*), 7.12-7.17 (m, 2H, arom. *H*), 4.77 (dd, *J* = 12.5, 5.9 Hz, 1H, C1-*H*^{1}), 4.64 (dd, *J* = 12.1, 10.0 Hz, 1H, C1-*H*^{2}), 3.23 (m, 1H, C2-*H*), 1.96 (m, 1H, C3-*H*), 1.01 (d, *J* = 6.9 Hz, 3H, C3*Me*^{1}), 0.81 (d, *J* = 6.9 Hz, 3H, C3*Me*^{2}). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 138.5, 128.5, 128.0, 127.3, 79.1, 51.1, 31.4, 20.7, 20.3. IR (film): ν = 3032, 2965, 1556, 1496, 1455, 1435, 1381, 755, 702 cm^{-1}. Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.40; H, 7.72; N, 7.23.

2-Phenyl-1-nitro-pentane:

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.23-7.37 (m, 3H, arom. *H*), 7.17-7.22 (m, 2H, arom. *H*), 4.58 (dd, *J* = 12.1, 7.8 Hz, 1H, C1-*H*^{1}), 4.53 (dd, *J* = 12.1, 8.1 Hz, 1H, C1-*H*^{2}), 3.47 (m, 2H, C2-*H*), 1.67 (m, 2H, C3-H_2), 1.22 (m, 2H, C4-H_2), 0.88 (t, *J* = 7.2 Hz, 3H, *Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 139.4, 128.8, 127.4, 127.4, 81.0, 44.2, 35.2, 20.2, 13.9. IR (film): ν = 3032, 2961, 2934, 2874, 1553, 1496, 1455, 1431, 1380, 763, 701 cm^{-1}.

3-Hydroxy-2,3-dimethyl-1-nitro-butane:

(TBAF-workup was omitted)

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.77 (dd, *J* = 12.1, 4.4 Hz, 1H, C1-*H*^{1}), 4.17 (dd, *J* = 12.1, 9.7 Hz, 1H, C1-*H*^{2}), 2.44 (m, 1H, C2-*H*), 1.31 (s, 3H, C3-*Me*^{1}), 1.25 (s, 1H, O*H*), 1.17 (s, 3H, C3-*Me*^{2}), 1.03 (d, *J* = 6.9 Hz, 3H, C2-*Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 78.6, 43.3, 29.3, 25.0, 13.7. IR (film): ν = 3402, 2977, 2924, 2855, 1552, 1463, 1435, 1379, 1227, 1154, 1095, 952, 899 cm^{-1}. HRMS (ESI, MeOH/KOAc) *m/e*: Calcd for ($M+K^+$) $C_6H_{13}NO_3K$ 186.05270, found 186.05278. Anal. Calcd for $C_6H_{13}NO_3$: C, 48.97; H, 8.90; N, 9.52. Found: C, 49.12; H, 8.83; N, 9.44.

***O*-Tetrahydropyranyl-2-methyl-3-nitro-propan-1-ol (mixture of diastereomers):**

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.56 (m, 4H), 4.29 (dd, *J* = 12.1, 7.8 Hz, 1H), 4.25 (dd, *J* = 12.1, 7.8 Hz, 1H), 3.80 (m, 3H), 3.62 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.52 (m, 2H), 3.41 (dd, *J* = 10.0, 4.7 Hz, 1H), 3.24 (dd, *J* = 10.0, 7.5 Hz, 1H), 2.65 (m, 2H), 1.62-1.86 (m, 4H), 1.46-1.62 (m, 8 H), 1.06 (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 99.2, 98.6, 79.0, 69.4, 68.9, 62.2, 62.2, 34.5, 33.3, 33.2, 30.4, 25.3, 19.3, 19.2, 14.5, 14.5. IR (film): ν = 2944, 2875, 1552, 1456, 1436, 1383, 1354, 1202, 1124,

1078, 1065, 1035, 975, 904, 870, 815 cm^{-1}. Anal. Calcd for $C_9H_{17}NO_4$: C, 53.19; H, 8.43; N, 6.89. Found: C, 53.35; H, 8.39; N, 6.87.

2-Methyl-3-nitro-propan-1-ol:

(TBAF-workup was omitted)

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.56 (dd, *J* = 11.8, 6.2 Hz, 1H, C3-*H*^{1}), 4.32 (dd, *J* = 12.1, 7.2 Hz, 1H, C3-*H*^{2}), 3.71 (dd, *J* = 10.9, 4.7 Hz, 1H, C1-*H*^{1}), 3.53 (dd, *J* = 11.2, 7.0 Hz, 1H, C1-*H*^{2}), 2.53 (m, 1H, C2-*H*), 1.04 (d, *J* = 6.9 Hz, 3H, C2-*Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 78.5, 64.5, 35.2, 14.2. IR (film): ν = 3368, 2971, 2939, 2883, 1551, 1462, 1435, 1384, 1208, 1095, 1041, 995, 948, 898 cm^{-1}. Anal. Calcd for $C_4H_9NO_3$: C, 40.33; H, 7.62; N, 11.76. Found: C, 40.45; H, 7.37; N, 11.86.

2-(Pyridin-2-yl)-1-nitro-propane:

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.54 (m, 1H, arom. *H*), 7.64 (ddd, *J* = 7.8, 1.9 Hz, 1H, arom. *H*), 7.14-7.24 (m, 2H, arom. *H*), 4.95 (dd, *J* = 12.8, 8.1 Hz, 1H, C1-*H*^{1}), 4.59 (dd, *J* = 12.8, 6.8 Hz, 1H, C1-*H*^{2}), 3.75 (m, 1H, C2-*H*), 1.37 (d, *J* = 6.8 Hz, 3H, *Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 160.2, 149.3, 136.7, 122.3, 122.1, 79.6, 39.8, 18.4. IR (film): ν = 2976, 1593, 1551, 1475, 1436, 1382, 1151, 1033, 993, 788, 750 cm^{-1}. HRMS (ESI, MeOH) *m/e*: Calcd for ($M+H^+$) $C_8H_{11}N_2O_2$ 167.0815, found 167.0815.

2-(Furan-2-yl)-1-nitro-propane:

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.35 (dd, *J* = 1.9, 0.6 Hz, 1H, arom. *H*), 6.31 (dd, *J* = 3.4, 1.9 Hz, 1H, arom. *H*), 6.13 (m, 1H, arom. *H*), 4.67 (dd, *J* = 12.1, 6.5 Hz, 1H, C1-*H*^{1}), 4.43 (dd, *J* = 12.1, 8.1 Hz, 1H, C1-*H*^{2}), 3.74 (m, 1H, C2-*H*), 1.38 (d, *J* = 7.2 Hz, 3H, *Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.7, 141.9, 110.2, 105.9, 79.5, 32.5, 16.2. IR (film): ν = 2982, 1555, 1508, 1433, 1378, 1150, 1013, 739 cm^{-1}. Anal. Calcd for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.30; H, 6.12; N, 8.77.

2-(Thiophen-2-yl)-1-nitro-propane:

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.22 (dd, *J* = 5.3, 1.2 Hz, 1H, arom. *H*), 6.96 (dd, *J* = 5.3, 3.4, 1H, arom. *H*), 6.90 (m, 1H, arom. *H*), 4.58 (dd, *J* = 12.1, 7.2 Hz, 1H, C1-*H*^{1}), 4.48 (dd, *J* = 12.1, 8.1 Hz, 1H, C1-*H*^{2}), 3.97 (m, 1H, C2-*H*), 1.47 (d, *J* = 6.9 Hz, 3H, *Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 143.8, 126.9, 124.4, 124.2, 82.1, 34.2, 19.8. IR (film): ν = 2973, 1552, 1455, 1430, 1384, 1240, 1113, 1040, 850, 772, 702 cm^{-1}. Anal. Calcd for $C_7H_9NO_2S$: C, 49.10; H, 5.30; N, 8.18. Found: C, 49.28; H, 5.37; N, 8.30.