Supporting information

Chiral modification of copper exchanged zeolite-y with cinchonidine and its Application in asymmetric Henry reaction

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Characterization data for the nitro-aldol products.

1. 2-nitro-1-phenylethanol

Determined by Chiral HPLC, acetonitrile:ethanol(70:30), 1 mL/min, major enantiomer (*S*) *r.t* = 12.8, minor enantiomer (*R*) *r.t* = 18.2), absolute stereochemistry assigned by comparison of the retention times in HPLC with the standard. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.46-7.36 (m, 5H), 5.42 (d, 1 H), 4.63-4.43 (m, 2 H), 2.88(br, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 70.6, 81.1, 126.7, 128.9, 129.0, 138.5. IR (KBr film, cm^{-1}): ν = 3535, 3032, 2920, 1554, 1495, 1453, 1418, 1379, 1290, 1212, 1066, 895, 764, 702, 608.

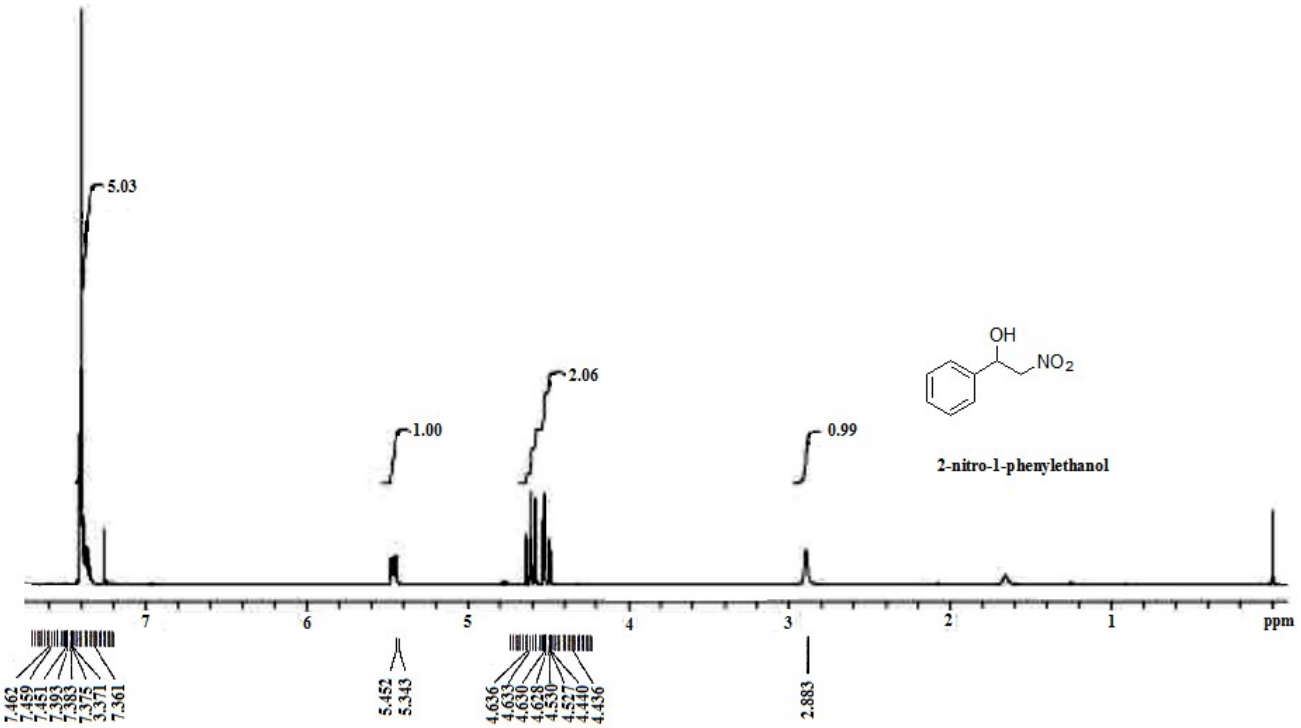

Figure S1. ^{1}H NMR spectra of 2-nitro-1-phenylethanol

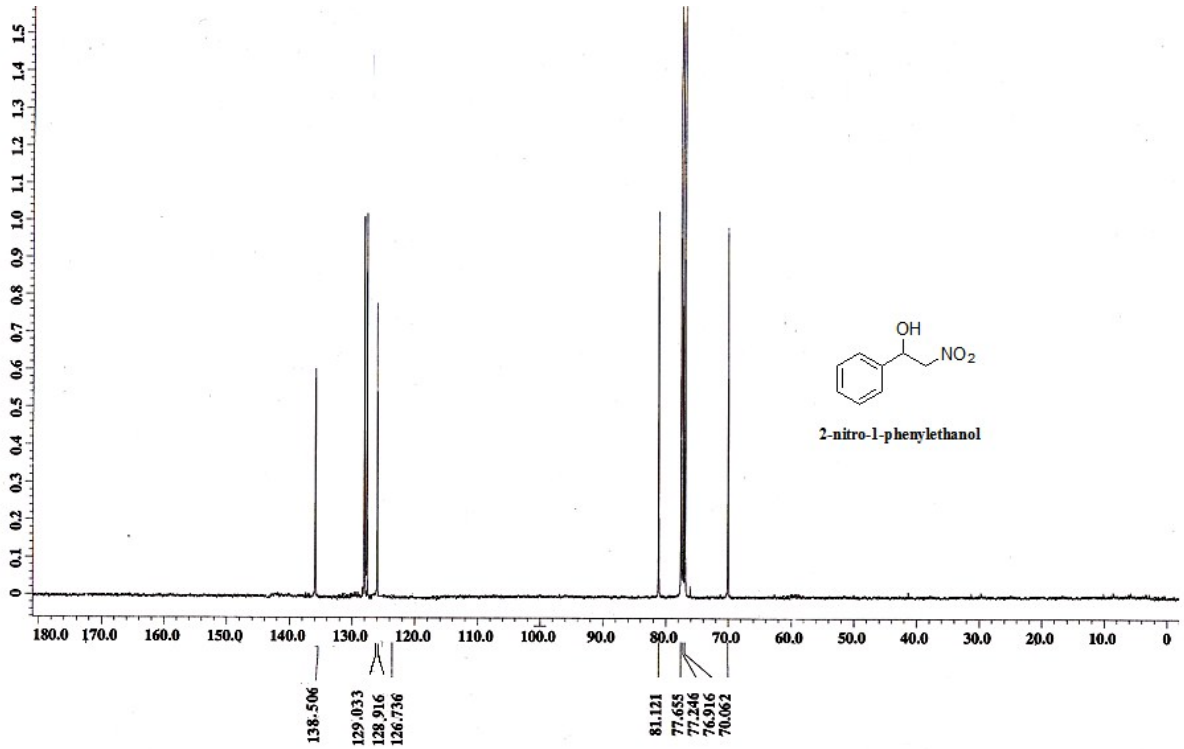

Figure S2. ^{13}C NMR spectra of 2-nitro-1-phenylethanol

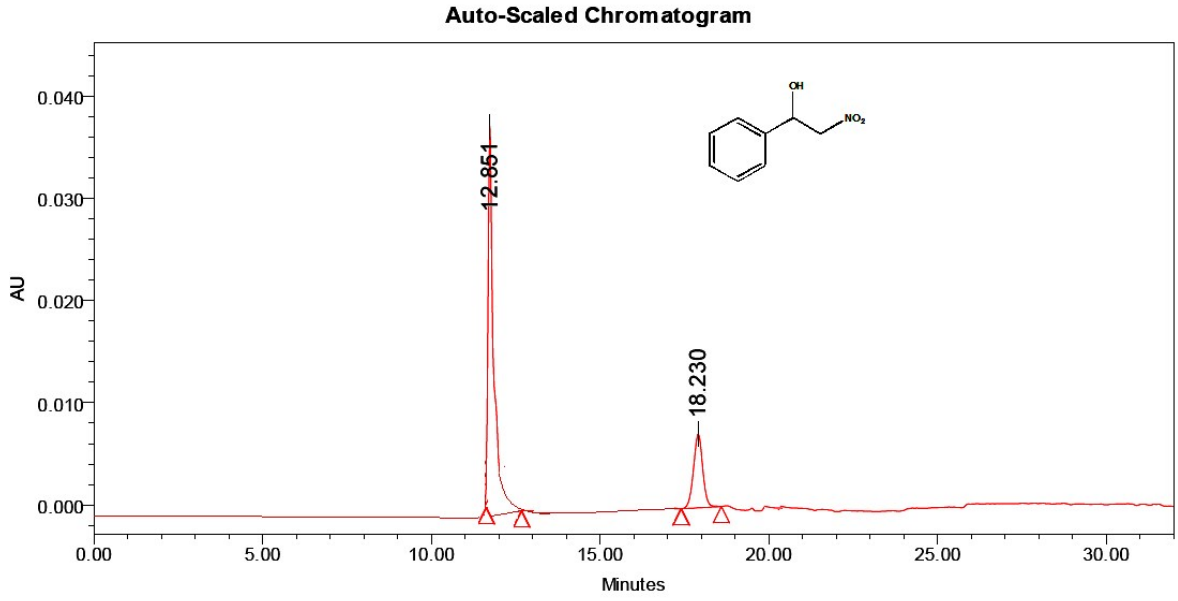

Figure S3. HPLC analysis of 2-nitro-1-phenylethanol

2. (*S*)-(+) 2-nitro-1-(4-nitrophenyl) ethanol

Determined by Chiral HPLC, acetonitrile:ethanol(70:30), 1 mL/min, major enantiomer (*S*) *r.t* = 33.21, minor enantiomer (*R*) *r.t* = 28.24), absolute stereochemistry assigned by comparison of the retention times in HPLC with the standard. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d,

2H), 7.63 (d, 2H), 5.62-5.52 (m, 1H), 4.61-4.54 (m, 2H), 3.25 ppm (br s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 70.04, 80.12, 124.03, 127.01, 145.9, 147.9. IR (KBr film, cm^{-1}): ν = 3401, 2919, 1555, 1416, 1382, 1349, 1086, 856, 754, 727, 697.

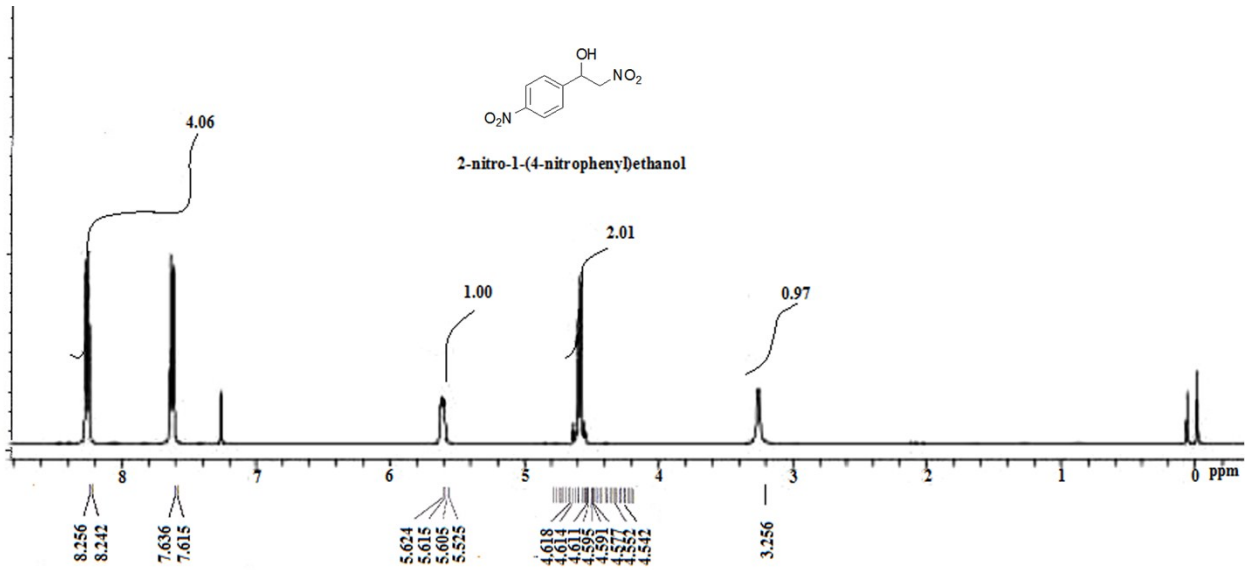

Figure S4. 1H NMR spectra of (*S*)-(+) 2-nitro-1-(4-nitrophenyl) ethanol

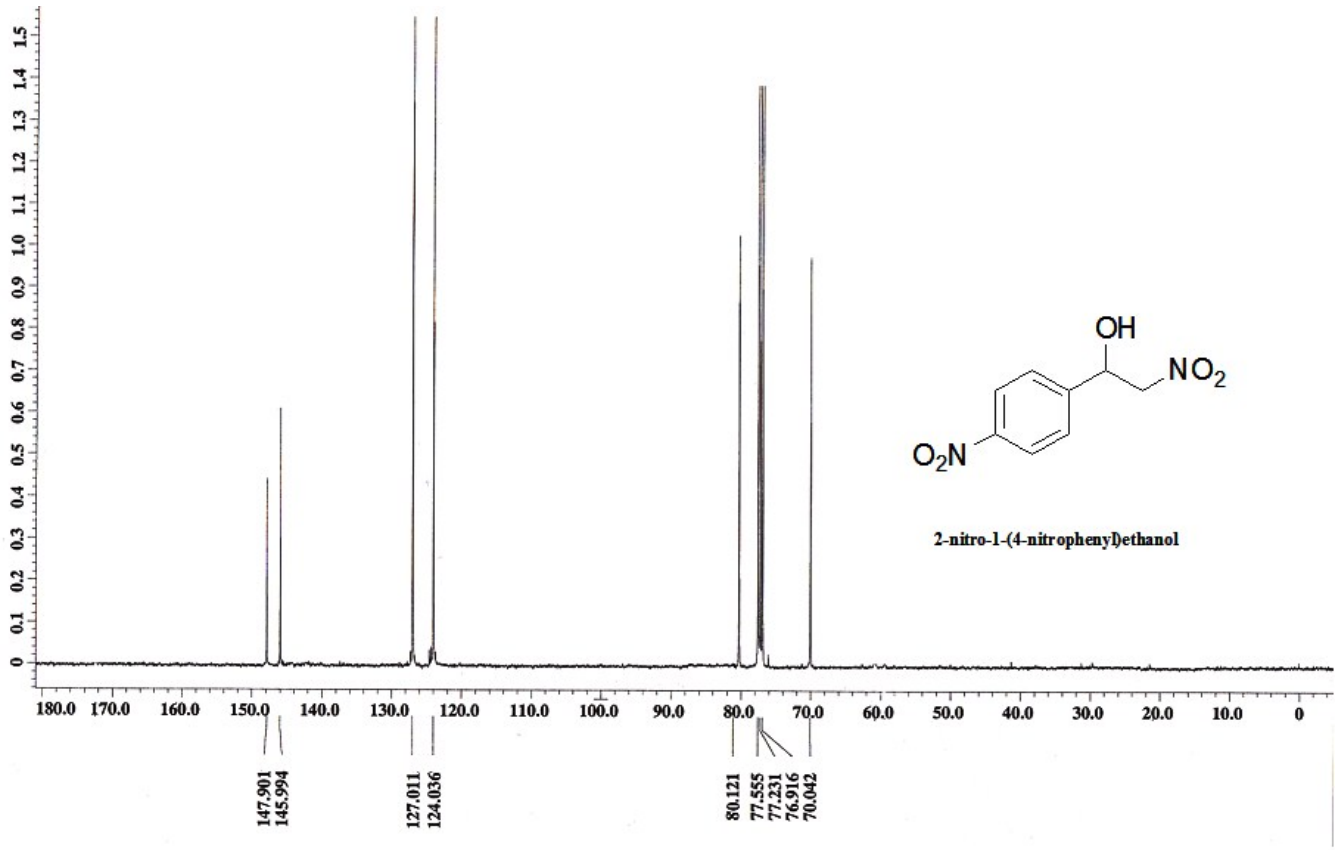

Figure S5. ^{13}C NMR spectra of (*S*)-(+) 2-nitro-1-(4-nitrophenyl) ethanol

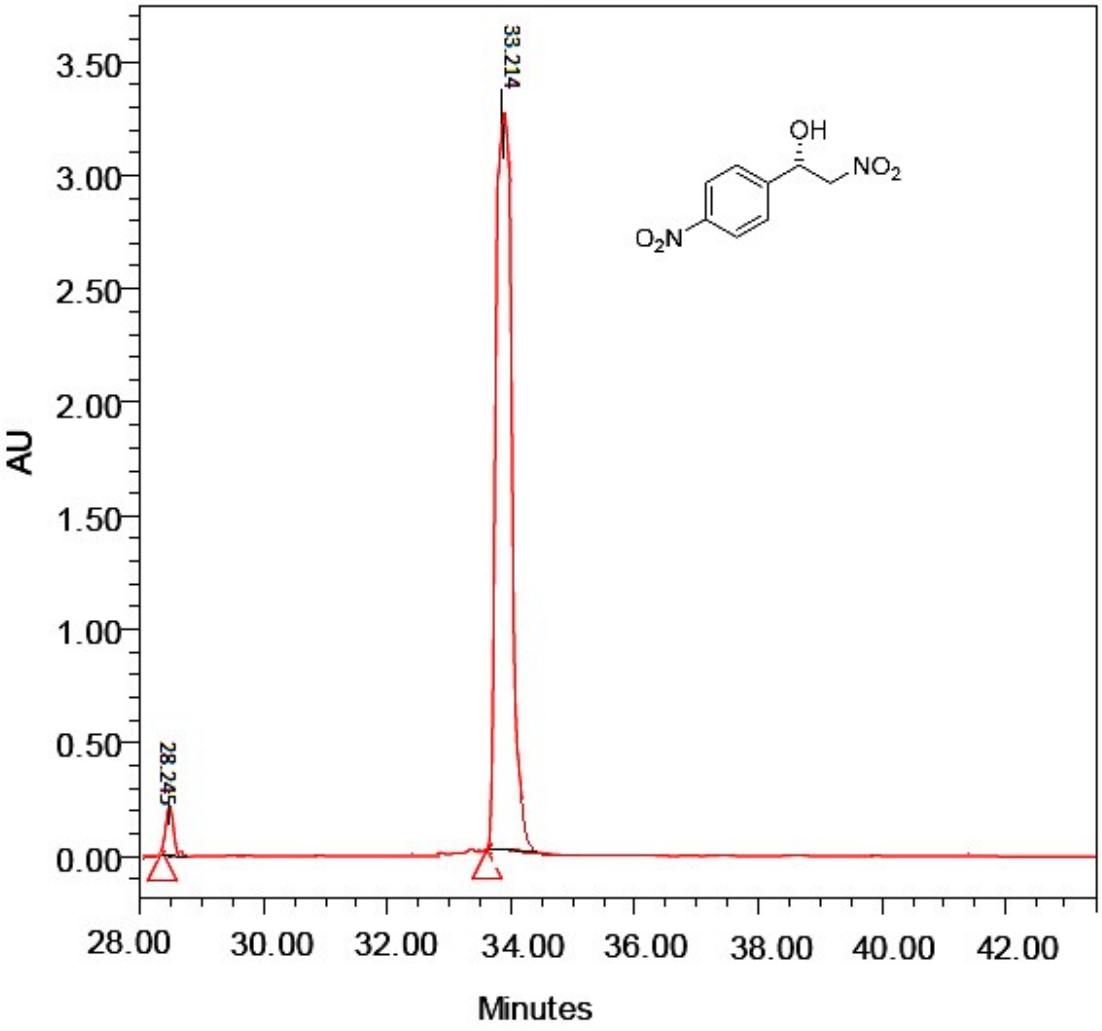

Figure S6. HPLC analysis of (*S*)-(+) 2-nitro-1-(4-nitrophenyl) ethanol

3. (*S*)-(−) 2-nitro-1-(2-nitrophenyl) ethanol

Determined by Chiral HPLC, (acetonitrile:ethanol(70:30), 1 mL/min, major enantiomer (*S*) *r.t* = 18.50, minor enantiomer (*R*) *r.t* = 13.23), absolute stereochemistry assigned by comparison of the retention times in HPLC with the standard. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, 1H), 7.96 (d, 1H), 7.76-7.73 (m, 1H), 7.57-7.53 (m, 1H) 6.05-6.03 (m, 1H), 4.89(dd, 1H), 4.59 (dd, 1H), 3.28 ppm (br s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 66.7, 81.1, 124.7, 128.0, 129.0, 134.4, 134.5, 147.9. IR (KBr film, cm^{-1}): ν = 3537, 1587, 1533, 1422, 1380, 1365, 1091, 1071, 866.

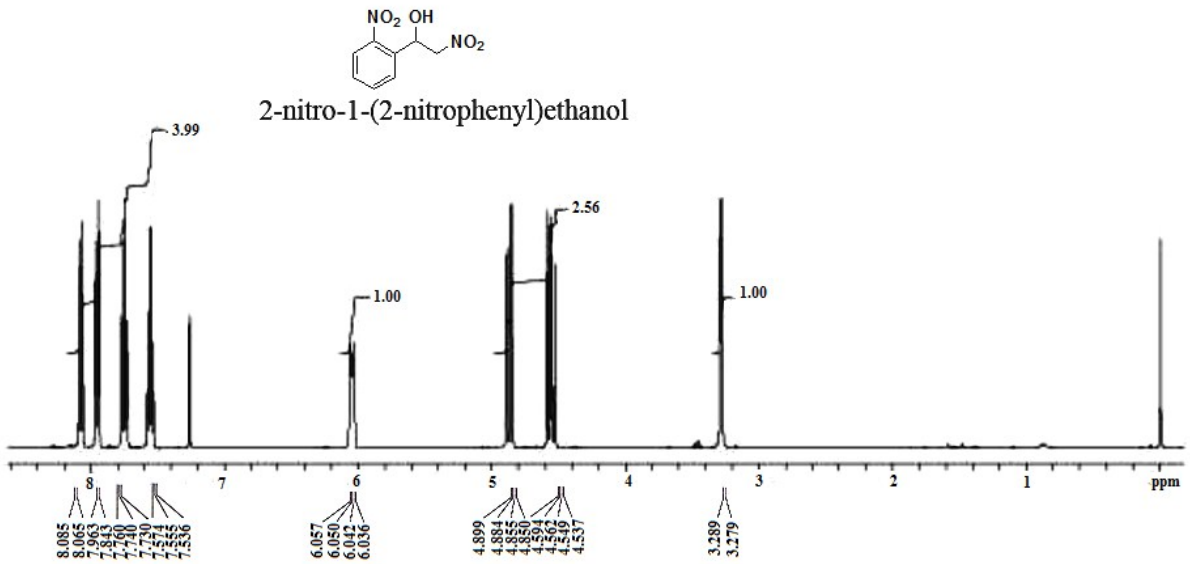

Figure S7. [1]H NMR spectra of (*S*)-(−) 2-nitro-1-(2-nitrophenyl) ethanol

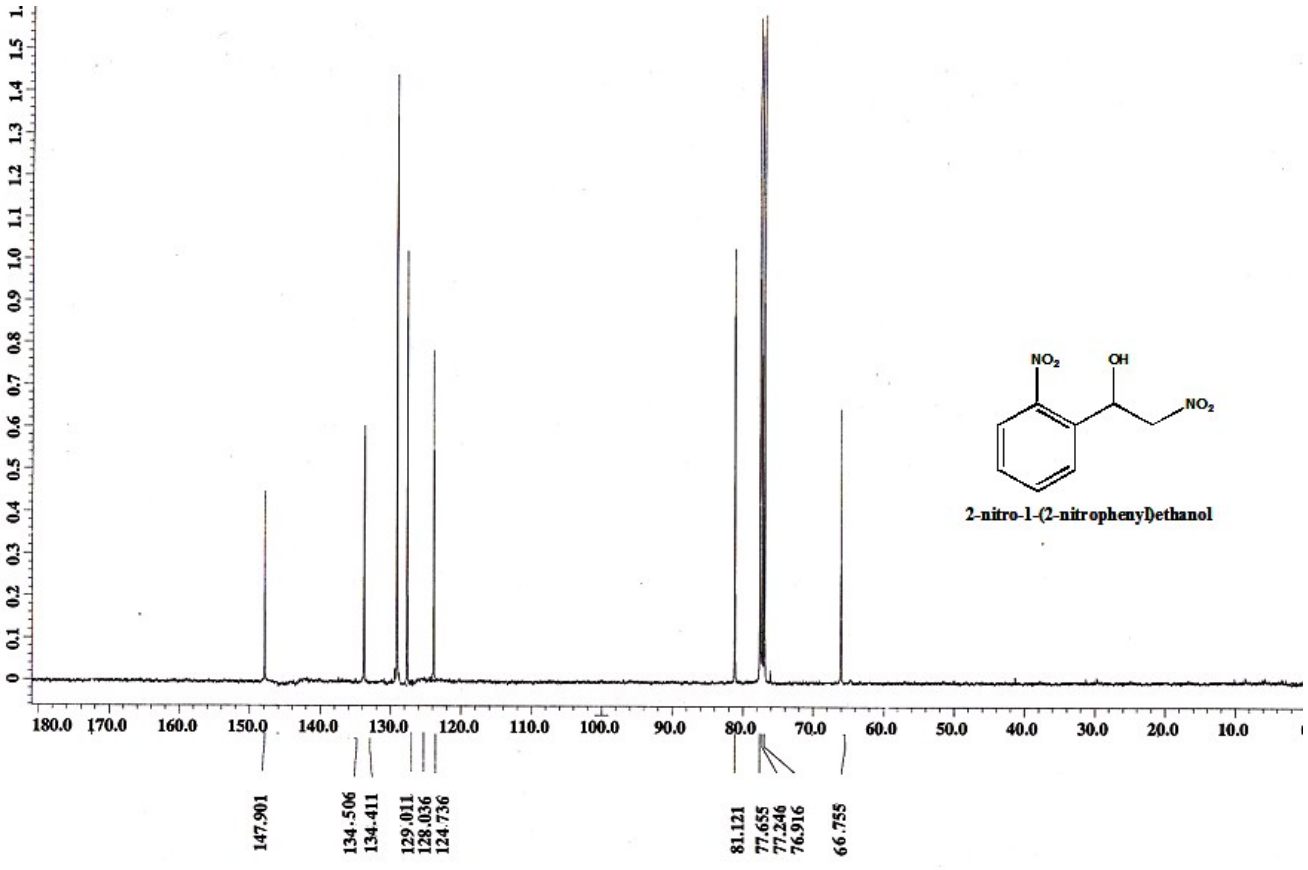

Figure S8. [13]C NMR spectra of (*S*)-(−) 2-nitro-1-(2-nitrophenyl) ethanol

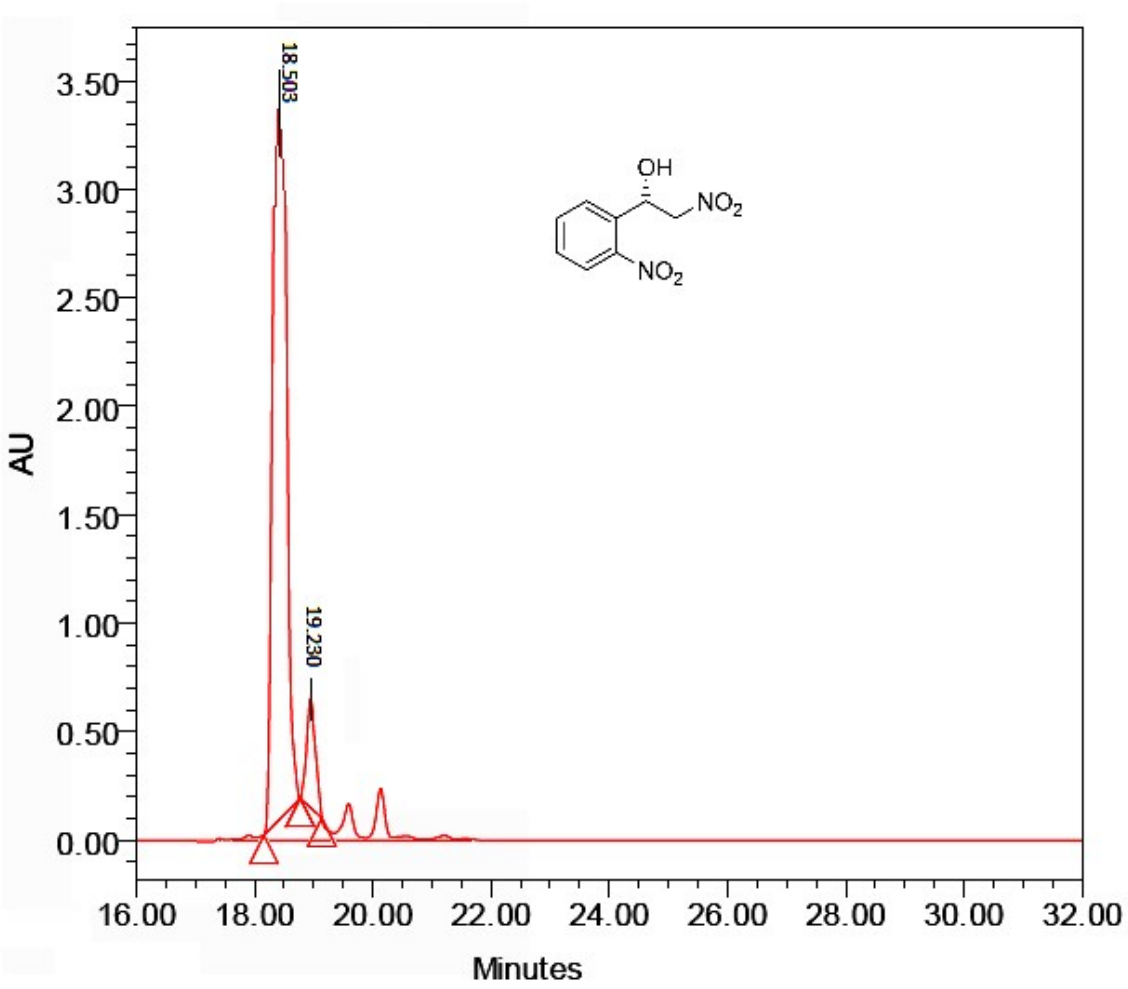

Figure S9. HPLC analysis of (*S*)-(−) 2-nitro-1-(2-nitrophenyl) ethanol

4. (*S*) - 4-(1-hydroxy-2-nitroethyl) phenol

Determined by Chiral HPLC, acetonitrile:ethanol(70:30), 1 mL/min, major enantiomer (*S*) *r.t* = 13.61, minor enantiomer (*R*) *r.t* = 12.50), absolute stereochemistry assigned by comparison of the retention times in HPLC with the standard. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.53 (d, 2H), 6.41(dd, 2H), 5.3(m, 1H), 5.05 (br, 1H), 4.32-4.02 (m, 2H), 3.08 (br, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 70.0, 81.1, 116.1, 129.1, 132.5, 156.5. IR (KBr film, cm-1): *v* = 3348, 2923, 2852, 1675, 1601, 1553, 1515, 1495, 1449, 1378, 1261, 1219, 1157, 1108, 1042, 910, 838, 734, 698.

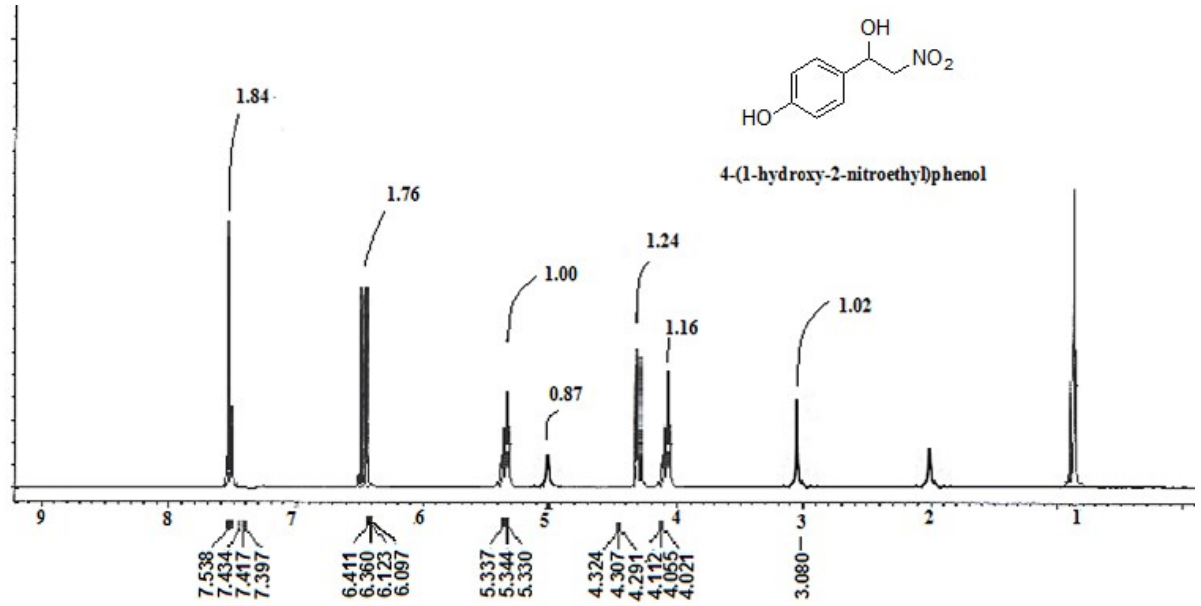

Figure S10. ^{1}H NMR spectra of (*S*) - 4-(1-hydroxy-2-nitroethyl) phenol

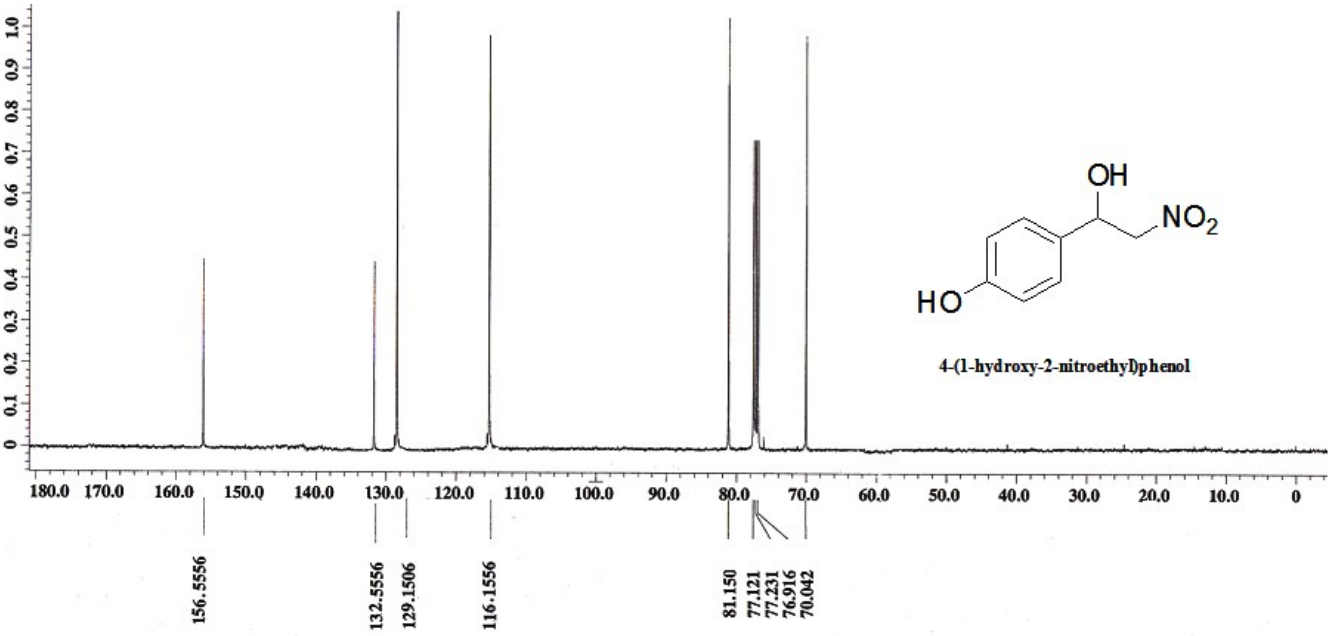

Figure S11. ^{13}C NMR spectra of (*S*) - 4-(1-hydroxy-2-nitroethyl) phenol

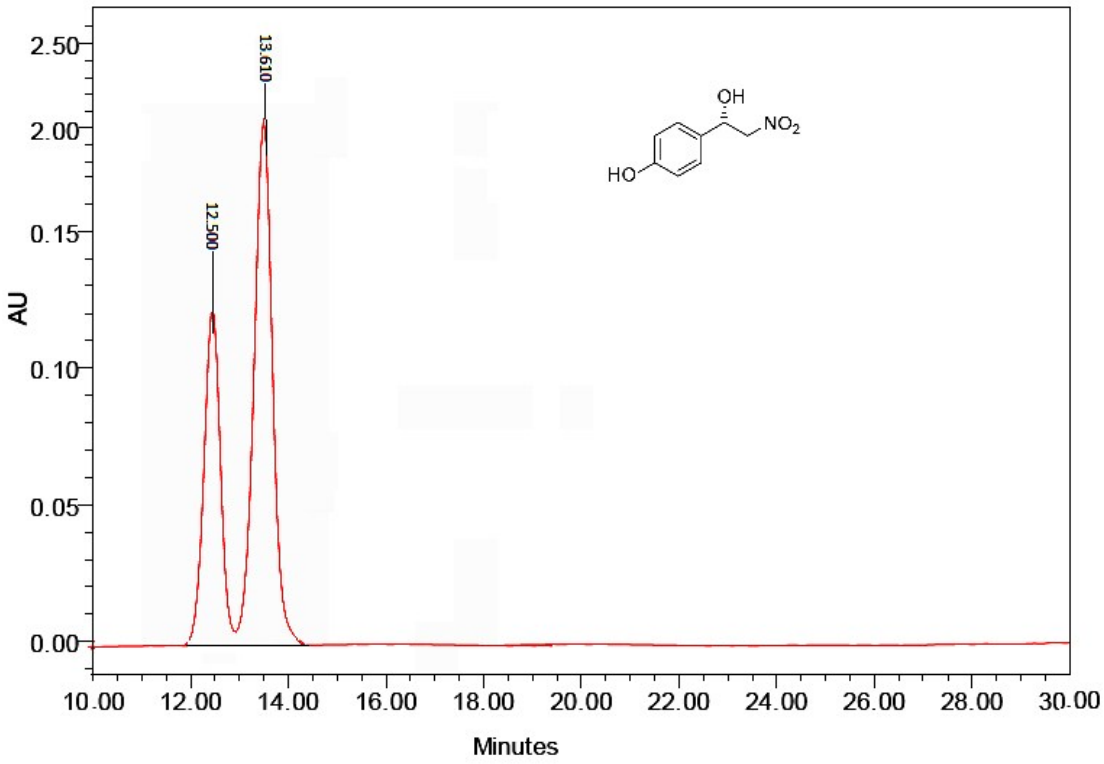

Figure S12. HPLC analysis of (*S*) - 4-(1-hydroxy-2-nitroethyl) phenol

5. (*S*)-(+) 2-nitro-1-p-tolyl ethanol

Determined by Chiral HPLC, acetonitrile:ethanol(70:30), 1 mL/min, major enantiomer (*S*) *r.t* = 16.23, minor enantiomer (*R*) *r.t* = 12.51), absolute stereochemistry assigned by comparison of the retention times in HPLC with the standard. ^{1}H NMR (400 MHz, CDCl3): δ = 7.29 (m, 2H), 7.24 (d, 2H), 5.45-5.33 (m, 1H), 4.59(dd, 2H), 2.88 (br s, 1H), 2.38 ppm (s, 3H). ^{13}C NMR($CDCl_3$ 100 MHz, ppm): δ = 21.0, 71.0, 81.1, 124.5, 129.0, 135.5, 136.1. IR (KBr film, cm^{-1}): v = 3548, 3028, 2924, 1555, 1516, 1418, 1378, 1287, 1208, 1077, 910, 819, 734.

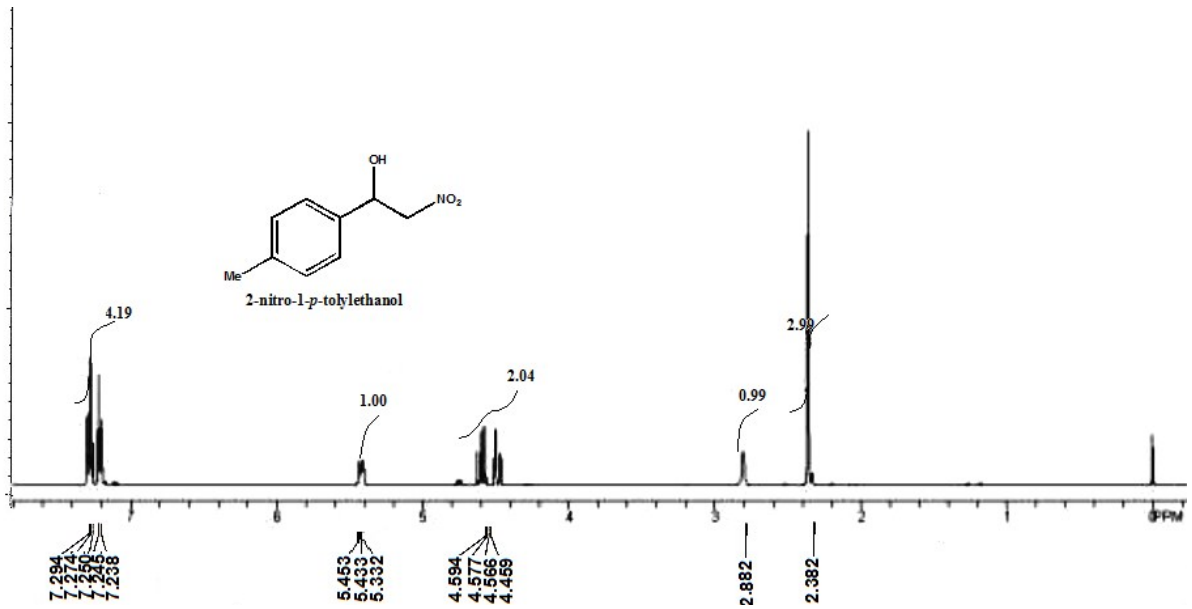

Figure S13. ^{1}H NMR spectra of (*S*)-(+) 2-nitro-1-p-tolyl ethanol

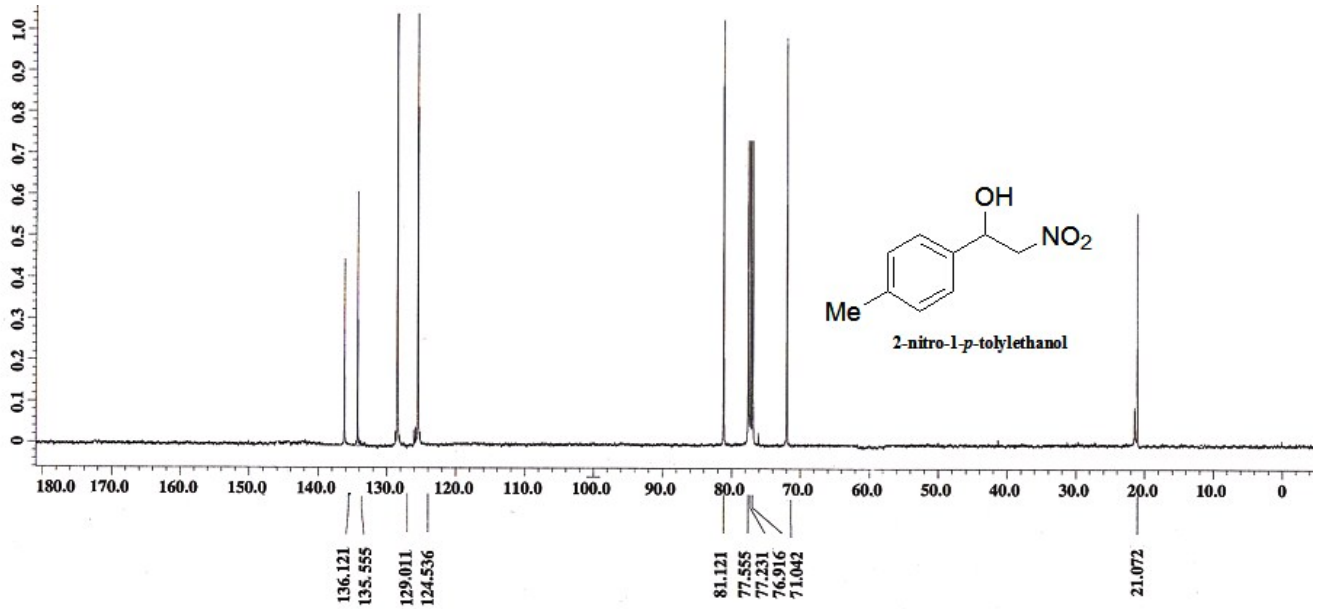

Figure S14. ^{13}C NMR spectra of (*S*)-(+) 2-nitro-1-p-tolyl ethanol

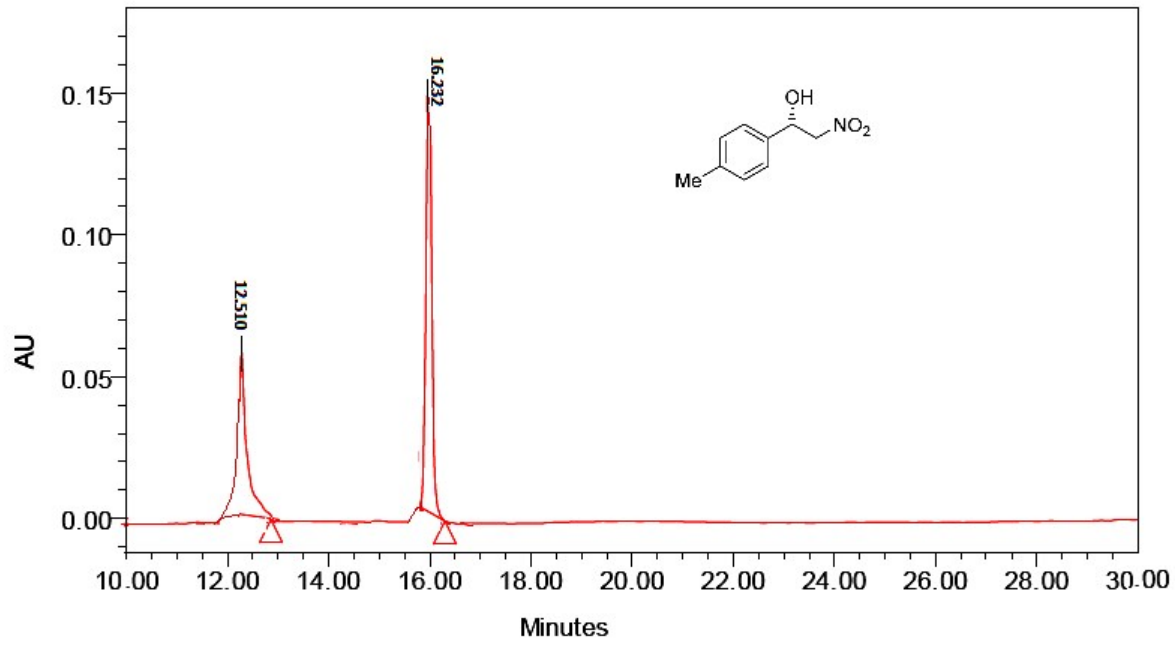

Figure S15. HPLC analysis of (*S*)-(+) 2-nitro-1-p-tolyl ethanol

6. (*S*) - 1-(naphthalen-6-yl)-2-nitroethanol

Determined by Chiral HPLC, acetonitrile:ethanol(70:30), 1 mL/min, major enantiomer (*S*) *r.t* = 23.12, minor enantiomer (*R*) *r.t* = 16.54), absolute stereochemistry assigned by comparison of the retention times in HPLC with the standard. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 (d, 1H) 7.73-7.64 (m. 2H) , 7.51-7.54 (d, 1H) 7.50-7.27 (m, 3H) 6.92- 6.58 (m, 1H), 4.54-4.11 (m, 2H), 2.78 (br, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 70.0, 81.1, 122.2, 123.8, 125.5, 126.05, 126.09, 128.2, 128.3, 128.5, 131.6, 133.7. IR (KBr film, cm^{-1}): ν = 3558, 3062, 2922, 1552, 1513, 1418, 1378, 1277, 1204, 1097, 911, 802, 780, 738, 650, 622.

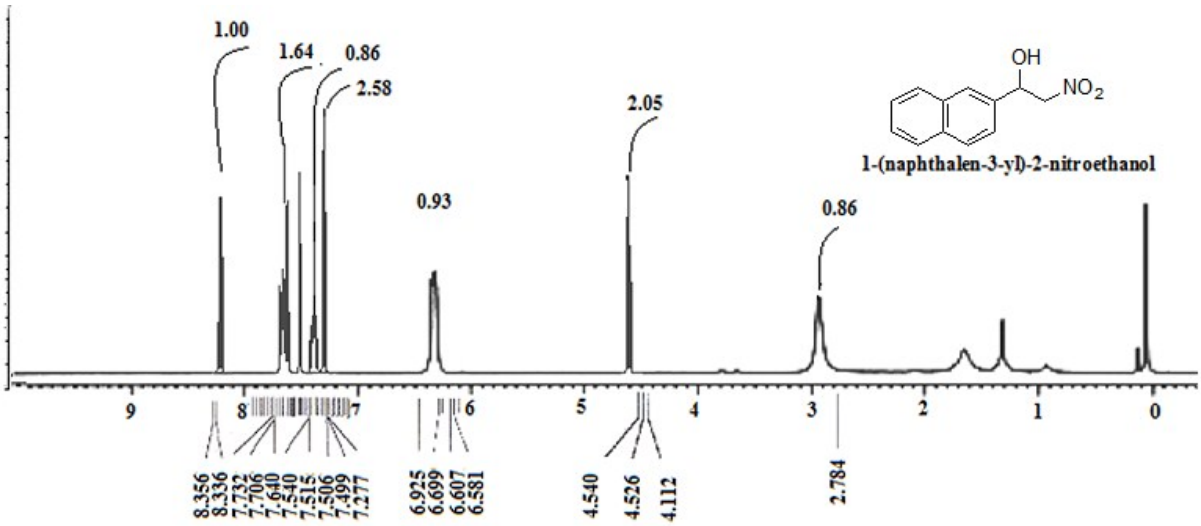

Figure S16. ^{1}H NMR spectra of (*S*) - 1-(naphthalen-6-yl)-2-nitroethanol

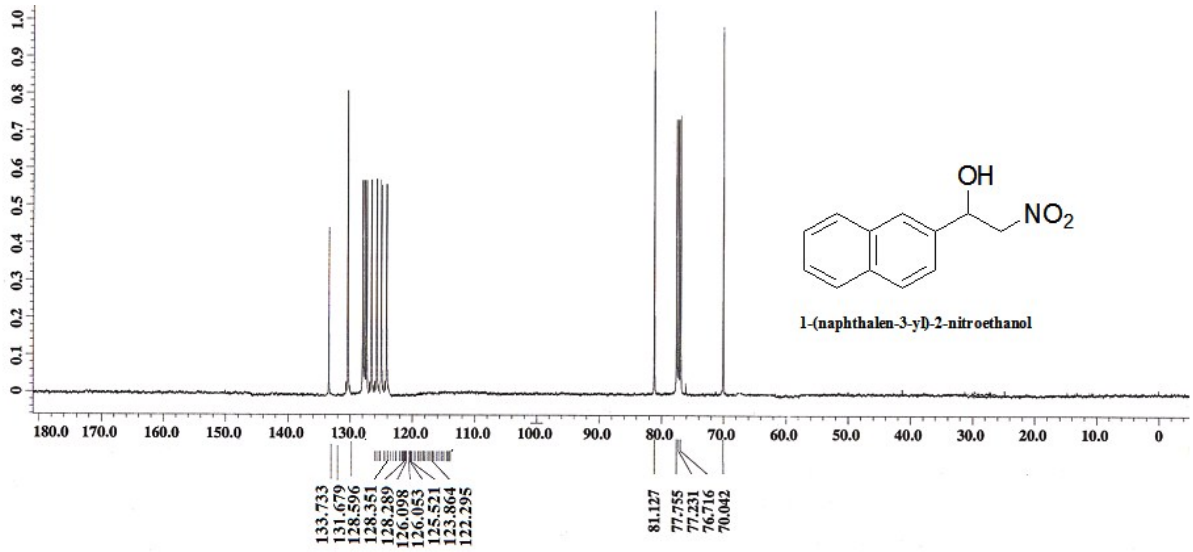

Figure S17. ^{13}C NMR spectra of (*S*) - 1-(naphthalen-6-yl)-2-nitroethanol

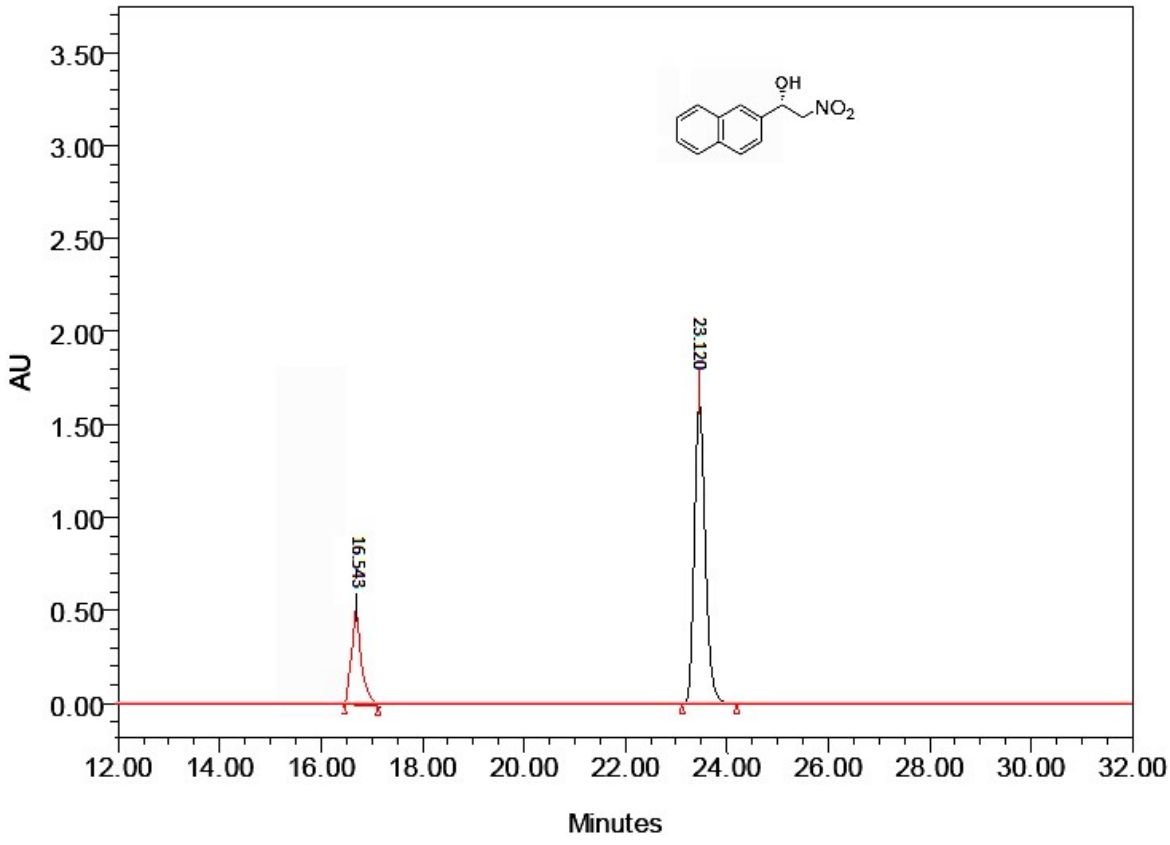

Figure S18. HPLC analysis of (*S*) - 1-(naphthalen-6-yl)-2-nitroethanol

Complete reference of Gaussian 09 programme. M. C. Frisch, et al. Gaussian 09, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009. Gaussian 09, Revision ***A.1***, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.