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Supplementary Information

Chemoenzymatic Resolution of β-Azidophenylethanols by *Candida antarctica* and their Application for the Synthesis of Chiral Benzotriazoles

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Preparation of α-azido ketones **5-8**

A mixture of the appropriate α-haloacetophenones **1**-**5** (14.00 mmol) and sodium azide (1.82 g, 28.00 mmol) in acetone (250 mL) was stirred at room temperature until completed. The mixture was poured into water and extracted with EtOAc (3 × 30 mL), and the organic layer was dried ($MgSO_4$), concentrated under reduced pressure and purified by column chromatography.

2-Azido-1-phenylethanone (**6**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.57 (s, 2H); 7.48-7.68 (m, 3H); 7.90-7.95 (m, 2H); IR (KBr) ν/cm^{-1} 2103 (N_3), 1695 (C=O).

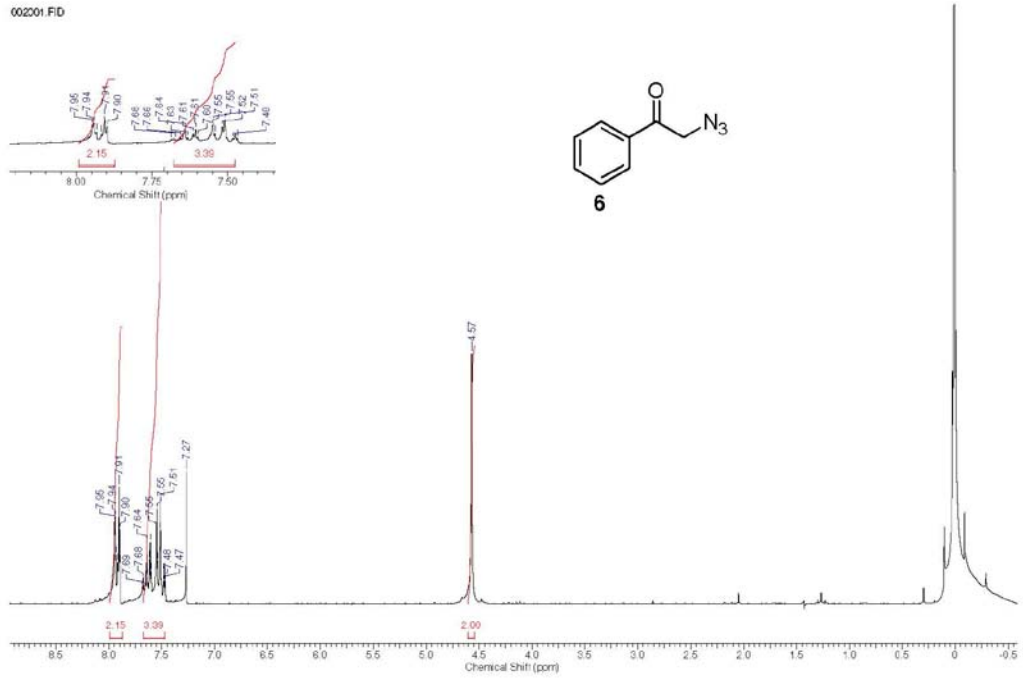

Figure S1. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 2-azido-1-phenyletanone (**6**).

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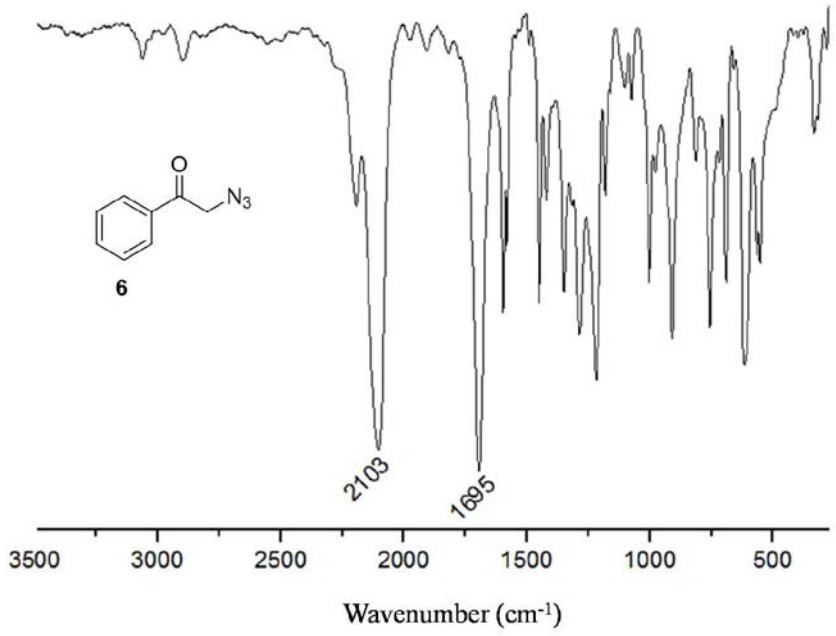

Figure S2. IR spectrum (KBr) of 2-azido-1-phenylethanone (**6**).

2-Azido-1-(4-methoxyphenyl)ethanone (**7**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.89 (s, 3H); 4.51 (s, 2H); 6.97 (d, 2H, *J* 8.0 Hz); 7.90 (d, 2H, *J* 8.0 Hz); IR (KBr) ν/cm^{-1} 2120 (N_3), 1684 (C=O).

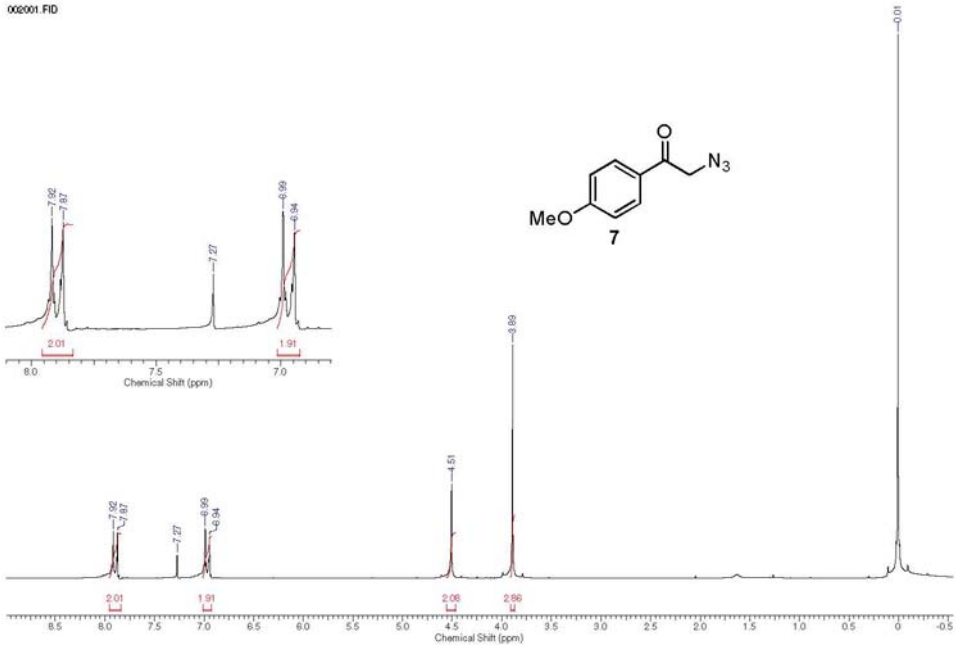

Figure S3. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 2-azido-1-(4-methoxyphenyl)ethanone (**7**).

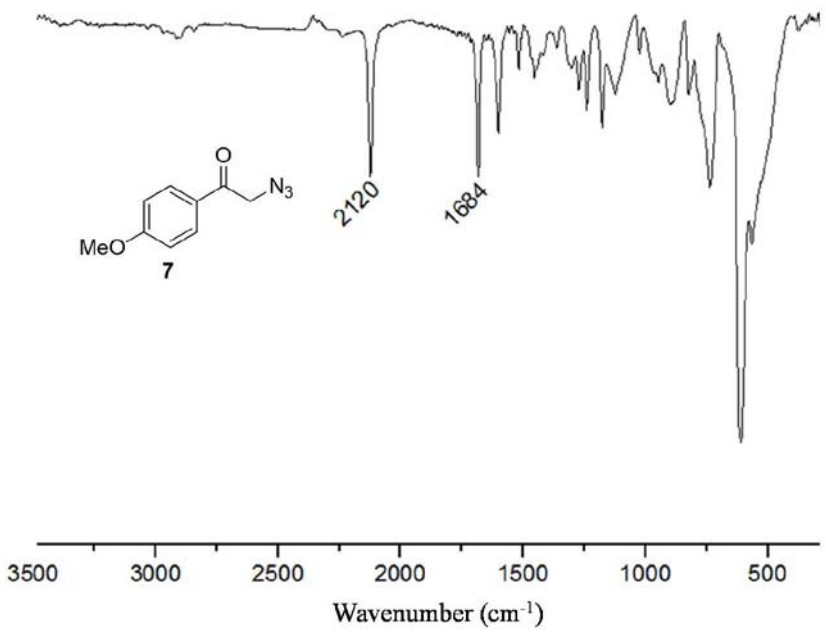

Figure S4. IR spectrum (KBr) of 2-azido-1-(4-methoxyphenyl)ethanone (**7**).

2-Azido-1-(4-bromophenyl)ethanone (**8**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (s, 2H); 7.66 (d, 2H, *J* 8.0 Hz); 7.79 (d, 2H, *J* 8.0 Hz); IR (KBr) ν/cm^{-1} 2102 (N_3), 1690 (C=O).

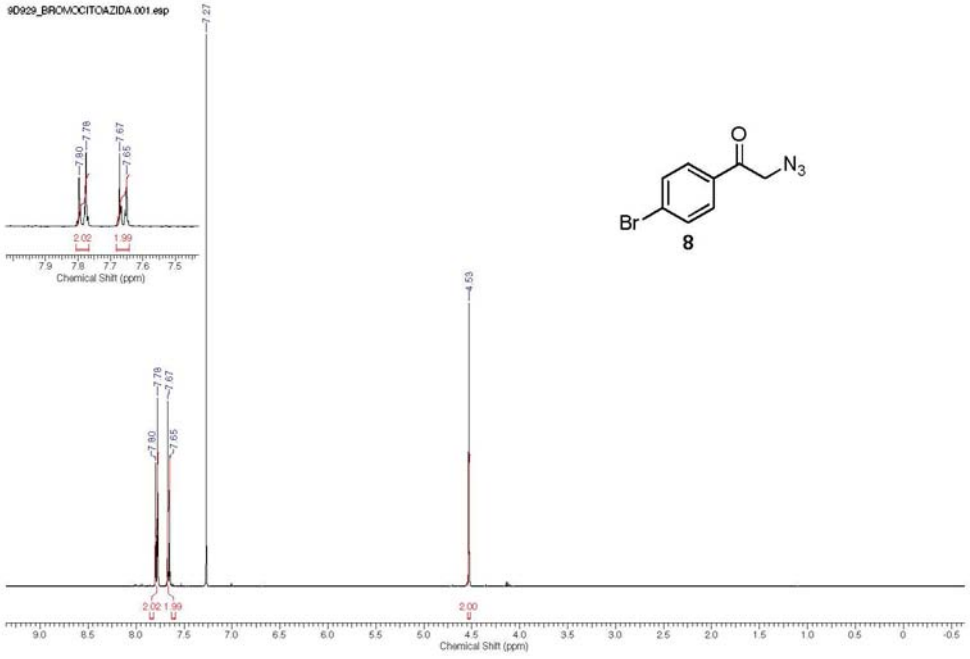

Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-azido-1-(4-bromophenyl)ethanone (**8**).

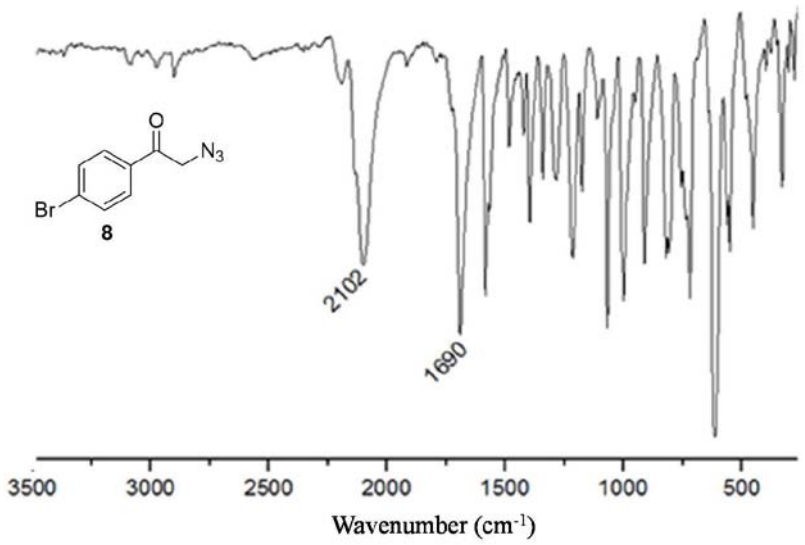

Figure S6. IR spectrum (KBr) of 2-azido-1-(4-bromophenyl)ethanone (**8**).

2-Azido-1-(4-chlorophenyl)ethanone (**9**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (s, 2H); 7.42 (d, 2H, *J* 8.0 Hz); 8.80 (d, 2H, *J* 8.0 Hz); IR (KBr) ν/cm^{-1} 2101 (N_3), 1657 (C=O).

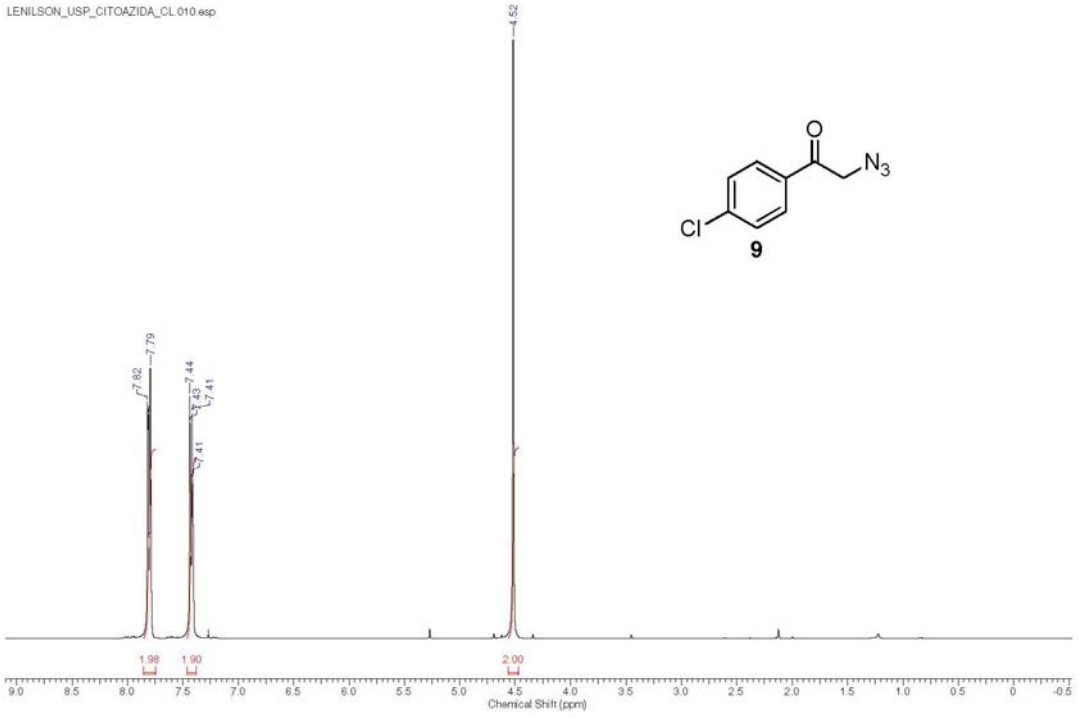

Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-azido-1-(4-chlorophenyl)ethanone (**9**).

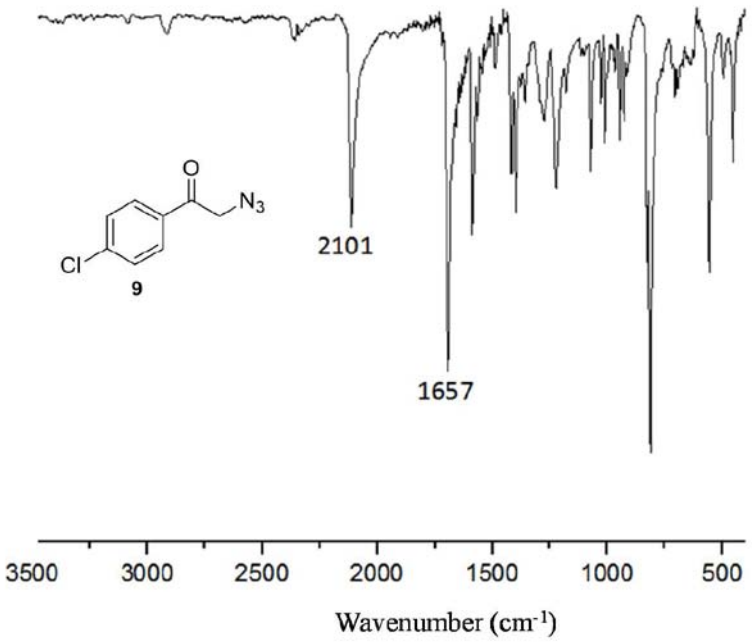

Figure S8. IR spectrum (KBr) of 2-azido-1-(4-chlorophenyl)ethanone (**9**).

2-Azido-1-(4-nitrophenyl)ethanone (**10**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (s, 2H); 8.08 (d, 2H, *J* 8.0 Hz); 8.31 (d, 2H, *J* 8.0 Hz); IR (KBr) ν/cm^{-1} 2105 (N_3), 1706 (C=O), 1554, 1349.

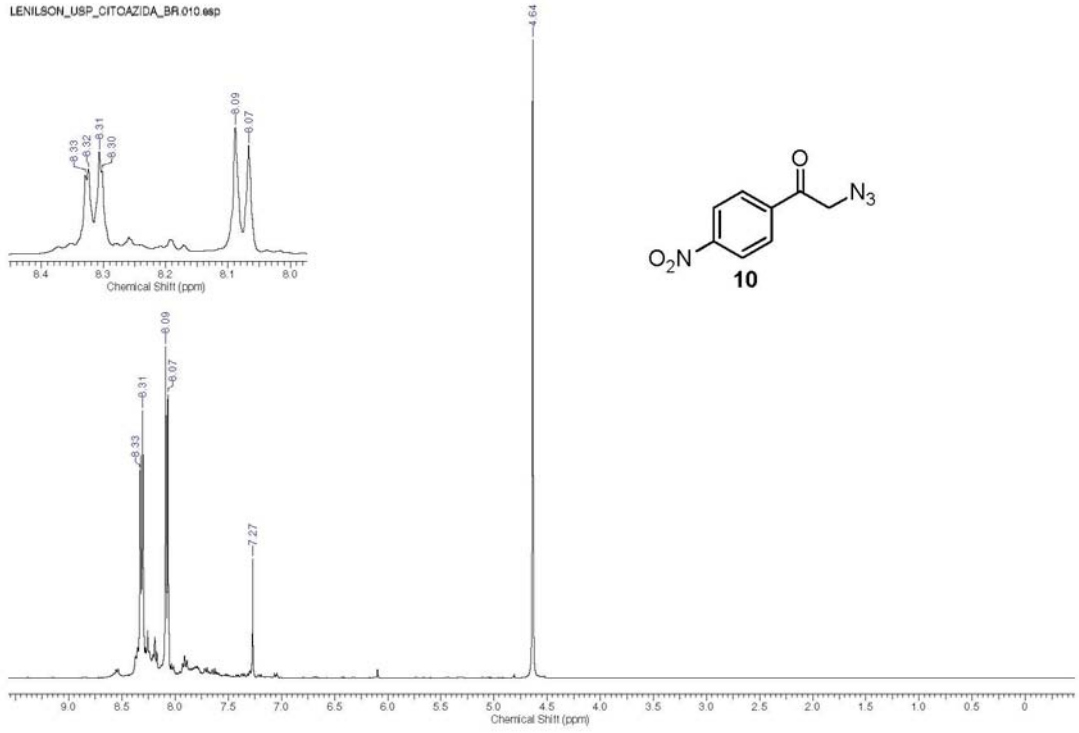

Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-azido-1-(4-nitrophenyl)ethanone (**10**)

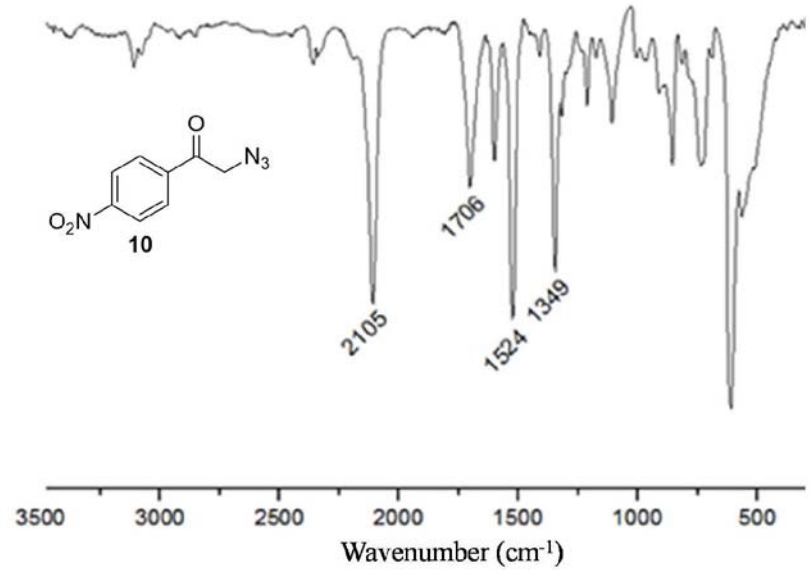

Figure S10. IR spectrum (KBr) of 2-azido-1-(4-nitrophenyl)ethanone (**10**).

Preparation of (±)-β-azidophenylethanols **11-15**

The ketones **6**-**10** (5 mmol), $NaBH_4$ (5.5 mmol) and methanol (10 mL) were added to a 25 mL flask equipped with a magnetic stirrer. The mixtures were stirred for 1 h at 0 °C. Next, the reactions were quenched by the addition of water (5 mL), the methanol was removed under vacuum and the residue was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$ and then filtered. The organic solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to produce racemic β-azidophenylethanols **11**-**15**.

2-Azido-1-phenylethanol (**11**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.49 (s, 1H); 3.35-3.52 (m, 2H); 4.84 (dd, 1H, *J* 8.0, 4.0 Hz); 7.35 (m, 5H); ^{13}C RMN (50 MHz, $CDCl_3$) δ 58.0, 73.3, 125.9, 128.6, 140.5; IR (KBr) ν/cm^{-1} 3400 (OH), 2103 (N_3).

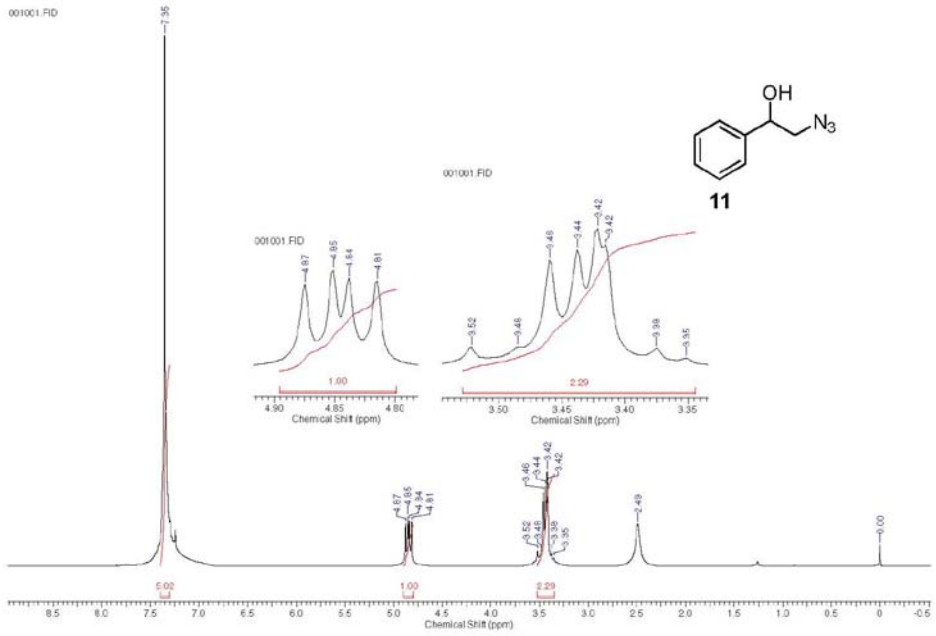

Figure S11. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 2-azido-1-phenylethanol (**11**).

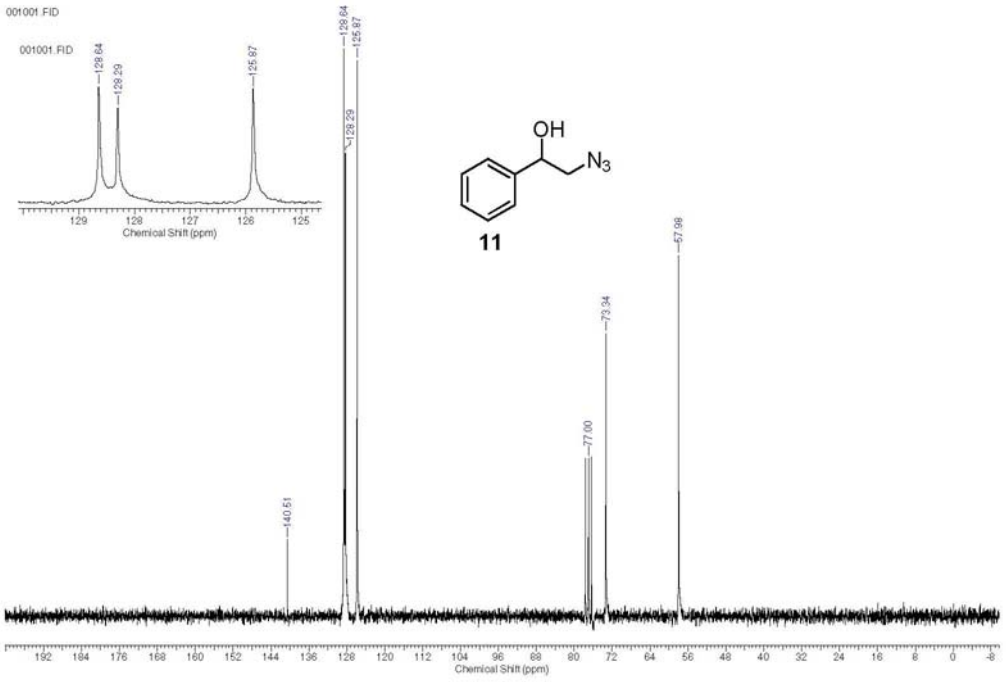

Figure S12. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of 2-azido-1-phenylethanol (**11**).

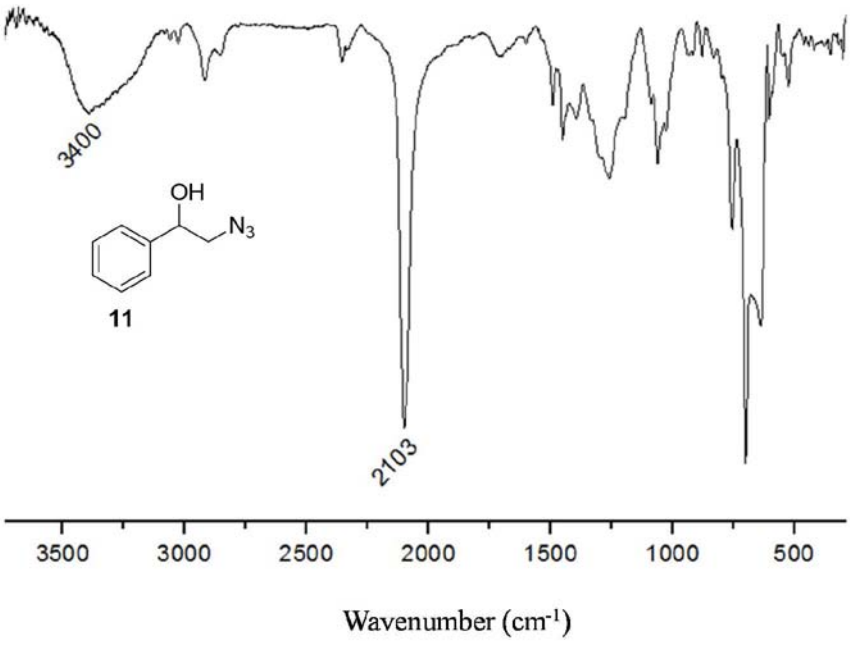

Figure S13. IR spectrum (KBr) of 2-azido-1-phenylethanol (**11**).

2-Azido-1-(4-methoxyphenyl)ethanol (**12**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.19 (s, 1H); 3.36-3.54 (m, 3H); 3.82 (s, 3H); 4.84 (dd, 1H, *J* 8.0, 4.0 Hz); 6.90 (d, 2H, *J* 8.0 Hz); 7.30 (d, 2H, *J* 8.0 Hz); ^{13}C RMN (50 MHz, $CDCl_3$) δ 55.0, 57.6, 72.6, 113.8, 127.0, 132.7, 159.2; IR (KBr) ν/cm^{-1} 3418 (OH), 2103 (N_3).

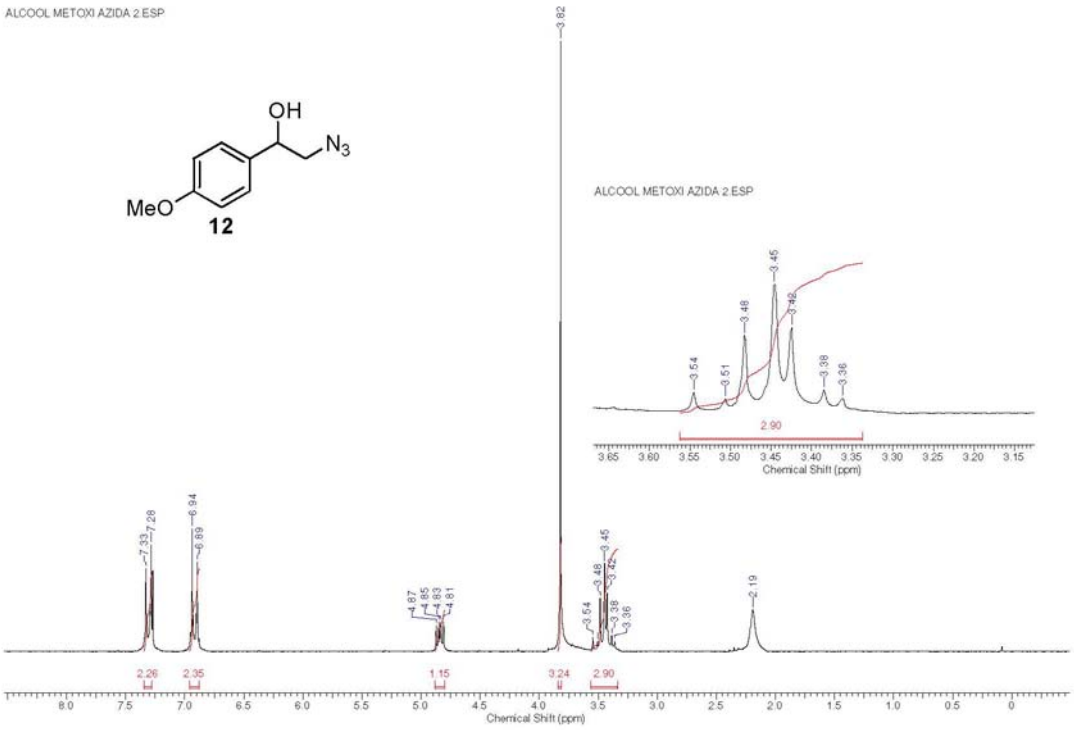

Figure S14. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 2-azido-1-(4-methoxyphenyl)ethanol (**12**).

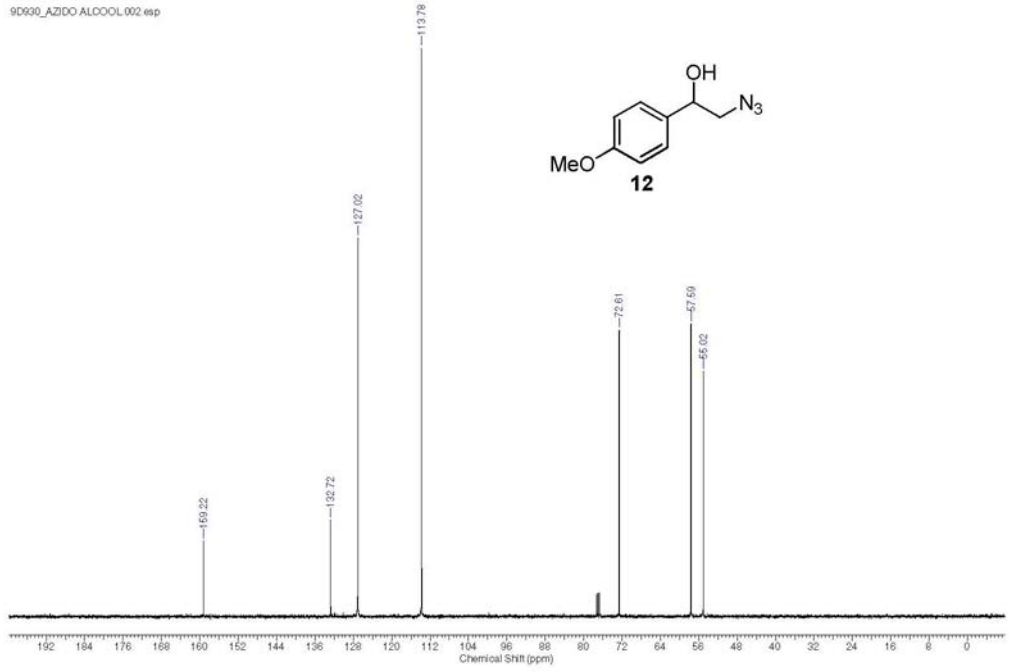

Figure S15. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of 2-azido-1-(4-methoxyphenyl)ethanol (**12**).

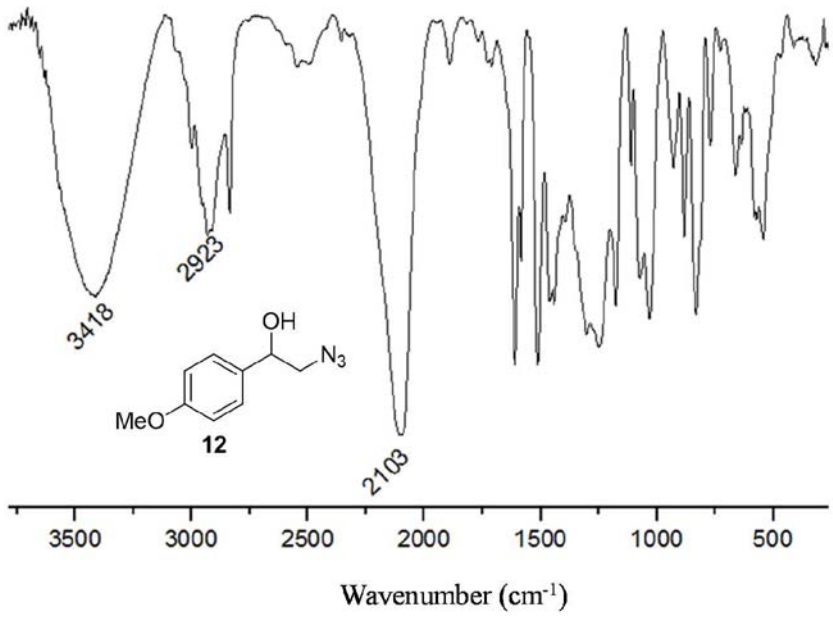

Figure S16. IR spectrum (KBr) of 2-azido-1-(4-methoxyphenyl)ethanol (**12**).

2-Azido-1-(4-bromophenyl)ethanol (**13**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.45 (d, 2H, *J* 6.0 Hz); 4.85 (dd, 1H, *J* 12.0, 6.0 Hz); 7.26 (d, 2H, *J* 8.0 Hz); 7.50 (d, 2H, *J* 8.0 Hz); ^{13}C RMN (50 MHz, $CDCl_3$) δ 57.9, 72.7, 122.2, 127.6, 131.8, 139.4, 159.4; IR (KBr) ν/cm^{-1} 3406 (OH), 2103 (N_3).

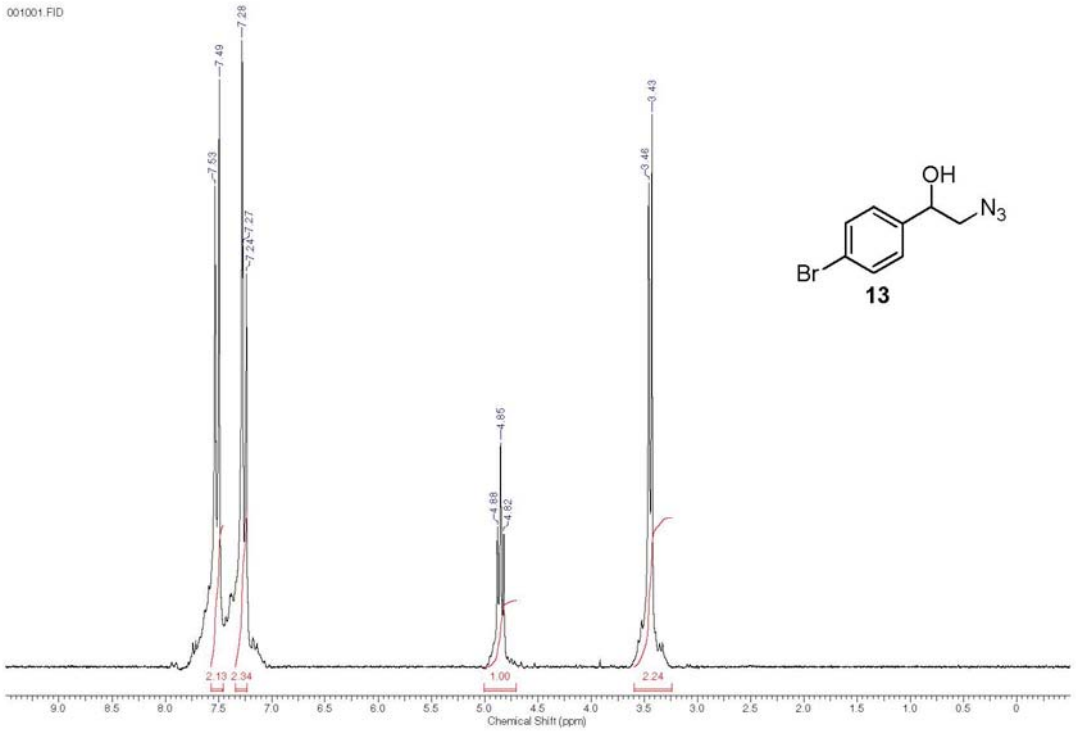

Figure S17. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 2-azido-1-(4-bromophenyl)ethanol (**13**).

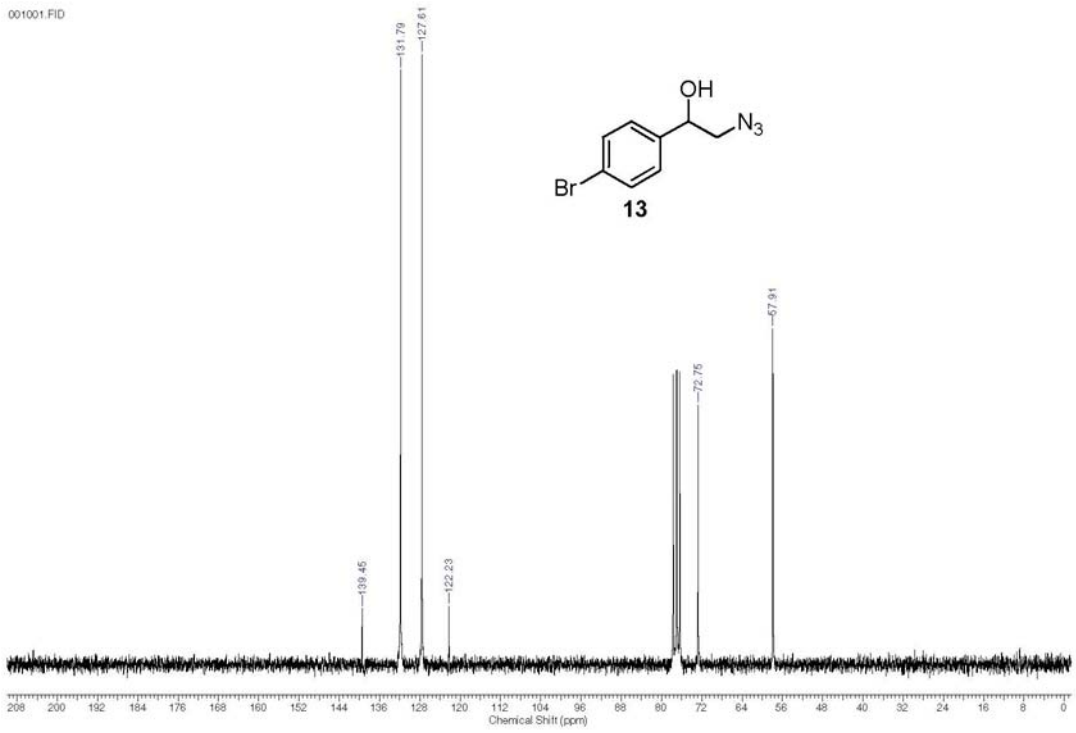

Figure S18. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) 2-azido-1-(4-bromophenyl)ethanol (**13**).

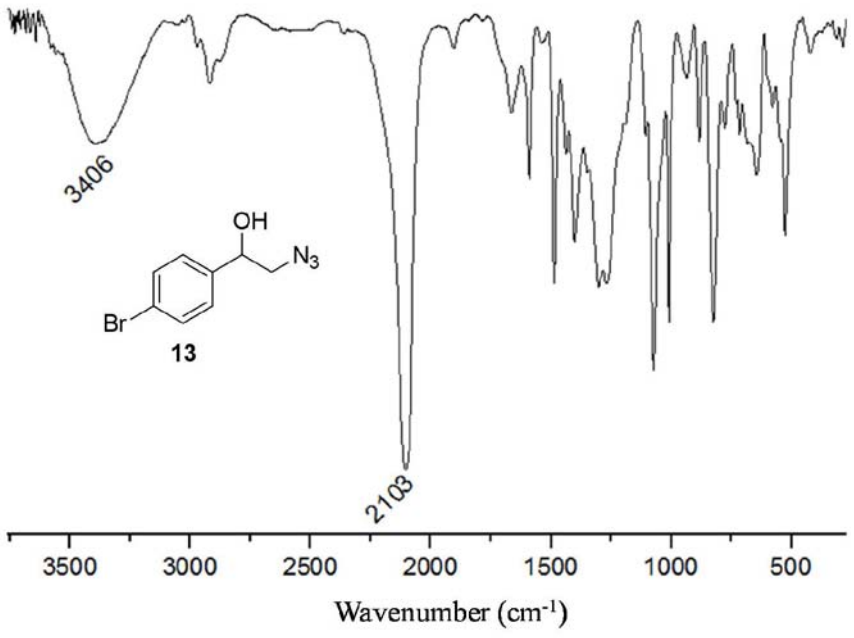

Figure S19. IR spectrum (KBr) of 2-azido-1-(4-bromophenyl)ethanol (**13**).

2-Azido-1-(4-clorophenyl)ethanol (**14**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.67 (s, 1H); 3.40-3.46 (m, 2H); 4.45 (dd, 2H, *J* 8.0, 4,0 Hz); 7.30 (d, 2H, *J* 8.0 Hz); 7.35 (d, 2H, *J* 8.0 Hz); ^{13}C RMN (50 MHz, $CDCl_3$) δ 57.9, 72.5, 127.2, 128.8, 134.1, 139.0; IR (KBr) ν/cm^{-1} 3418 (OH), 2103 (N_3).

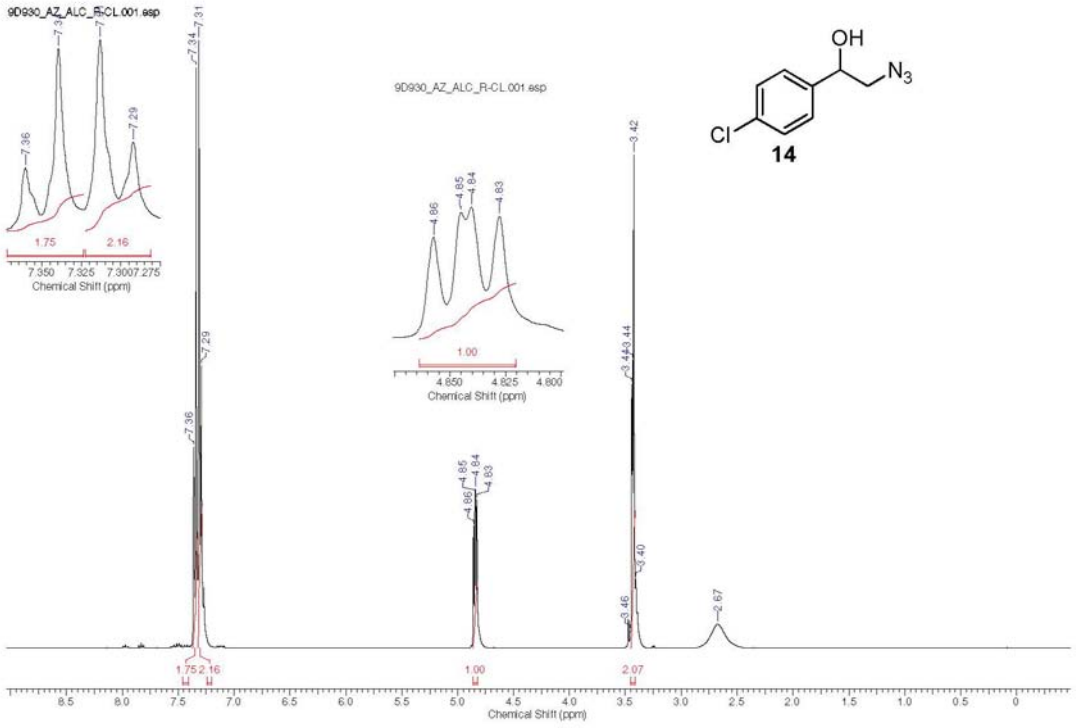

Figure S20. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) 2-azido-1-(4-chlorophenyl)ethanol (**14**).

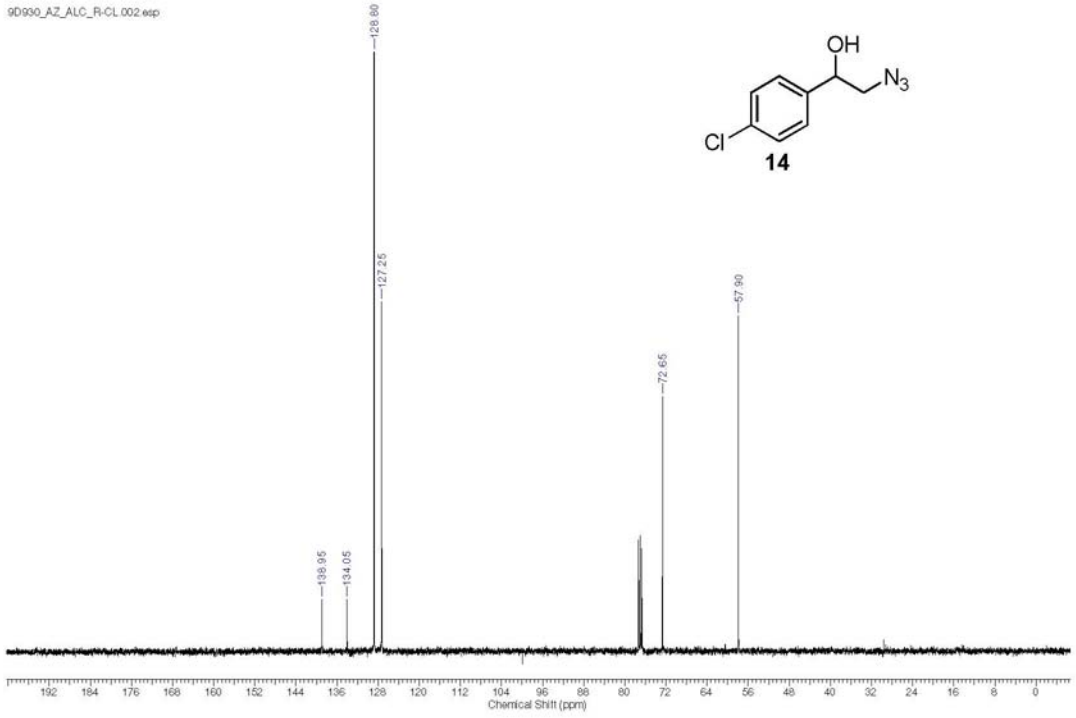

Figure S21. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) 2-azido-1-(4-chlorophenyl)ethanol (**14**).

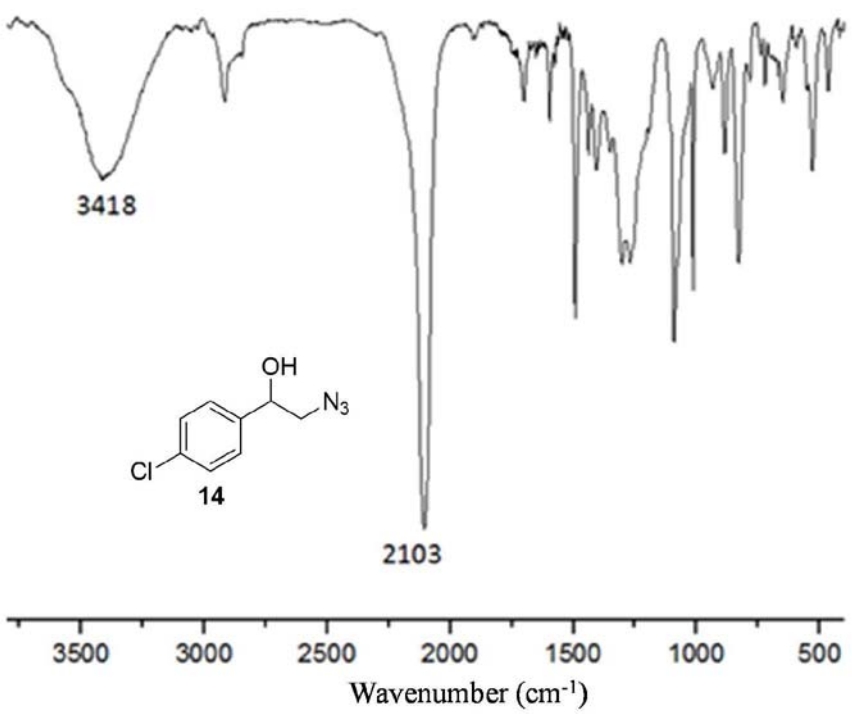

Figure S22. IR spectrum (KBr) of 2-azido-1-(4-chlorophenyl)ethanol (**14**).

2-Azido-1-(4-nitrophenyl)ethanol (**15**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.95 (s, 1H); 3.39-3.47 (m, 2H); 4.97 (dd, 1H, *J* 8.0, 4.0 Hz); 7.51 (d, 2H, *J* 8.0 Hz); 8.08 (d, 2H, *J* 8.0 Hz); ^{13}C RMN (100 MHz, $CDCl_3$) δ 57.1, 72.0, 123.3, 126.6, 147.0, 148.0; IR (KBr) ν/cm^{-1} 3401 (OH), 2108 (N_3).

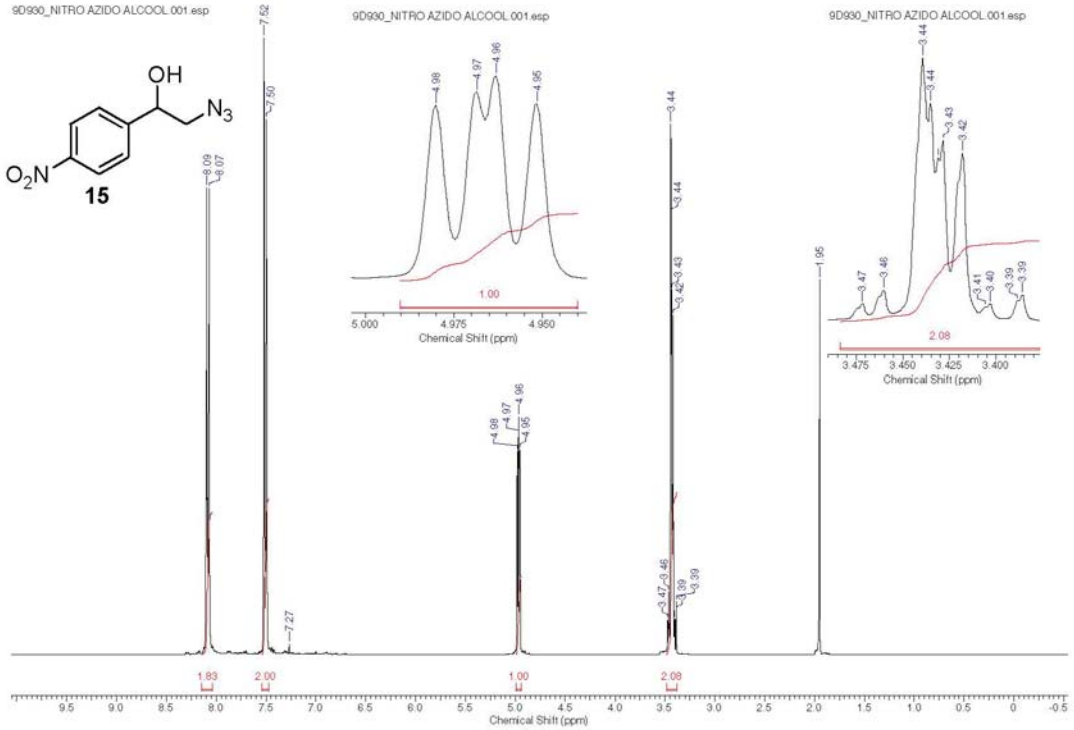

Figure S23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-azido-1-(4-nitrophenyl)ethanol (**15**).

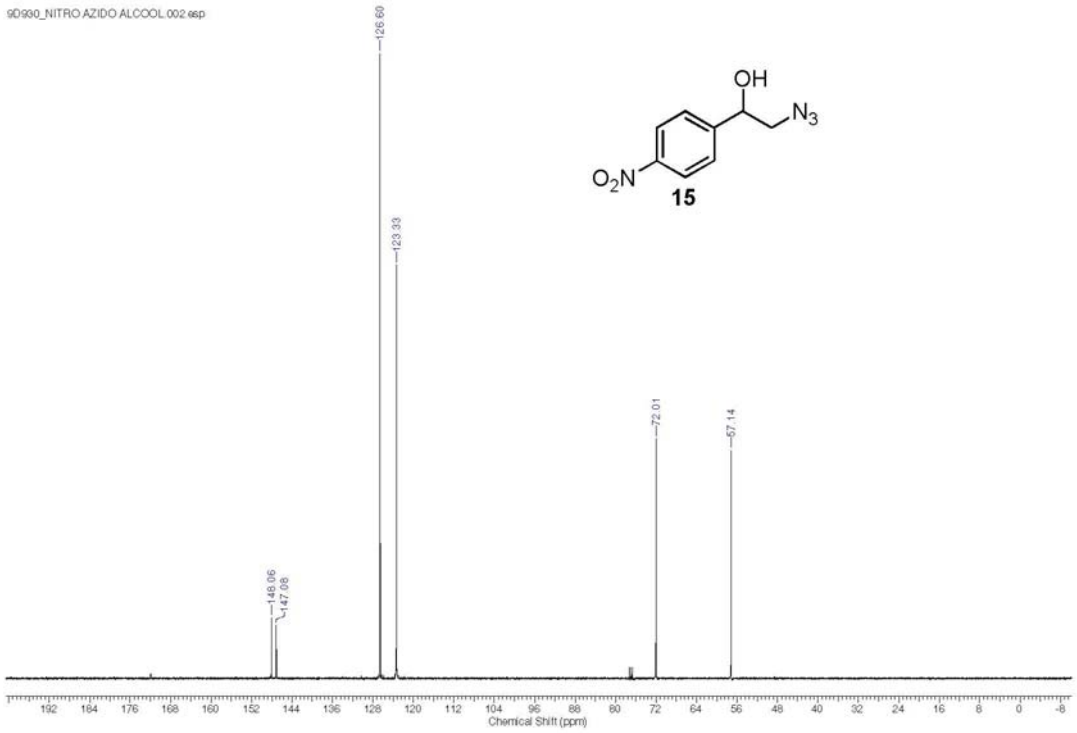

Figure S24. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) 2-azido-1-(4-nitrophenyl)ethanol (**15**).

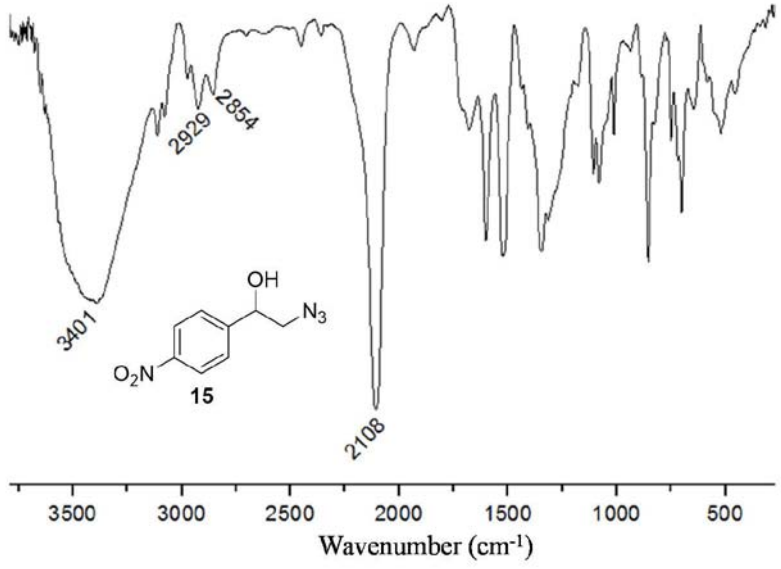

Figure S25. IR spectrum (KBr) of 2-azido-1-(4-nitrophenyl)ethanol (**15**).

Preparation of (±)-β-azidophenylethyl acetates **16**-**20**

(±)-β-Azidophenylethanols **11**-**15** (3.0 mmol), pyridine (0.5 mL, 6.2 mmol) and Ac_2O (0.5 mL, 5.3 mmol) were added to a 25 mL flask equipped with a magnetic stirrer. The mixture was stirred for 24 h at room temperature. The reactions were quenched by the addition of 10% HCl (2 mL), and the organic phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$ and then filtered. The organic solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to give racemic acetates **16**-**20** in good to high yields.

2-Azido-1-phenylethyl acetate (**16**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16 (s, 3H); 3.44 (dd, 1H, *J* 8.0, 4.0 Hz); 3.64 (dd, 1H, *J* 12.0, 8.0 Hz); 5.94 (dd, 1H, *J* 8.0, 4.0 Hz); 7.37 (m, 5H); ^{13}C RMN (100 MHz, $CDCl_3$) δ 20.7, 54.8, 74.3, 126.2, 128.4, 136.9, 169.4; IR (KBr) ν/cm^{-1} 2101 (N_3), 1752 (C=O), 1230 (C−O).

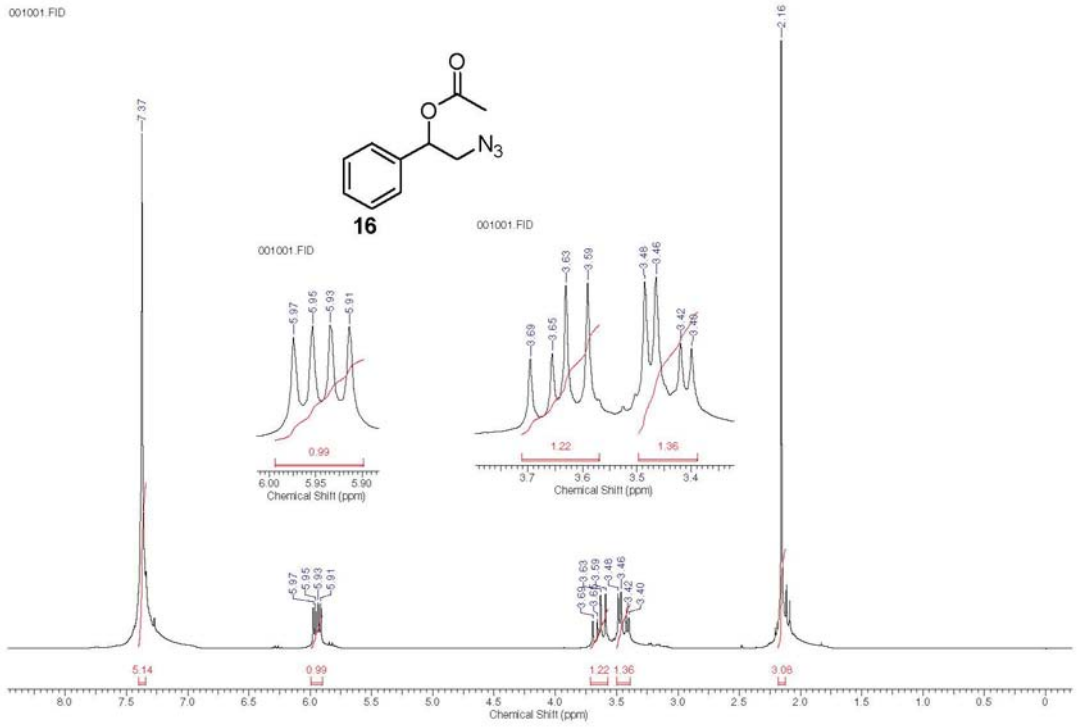

Figure S26. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-azido-1-phenylethyl acetate (**16**).

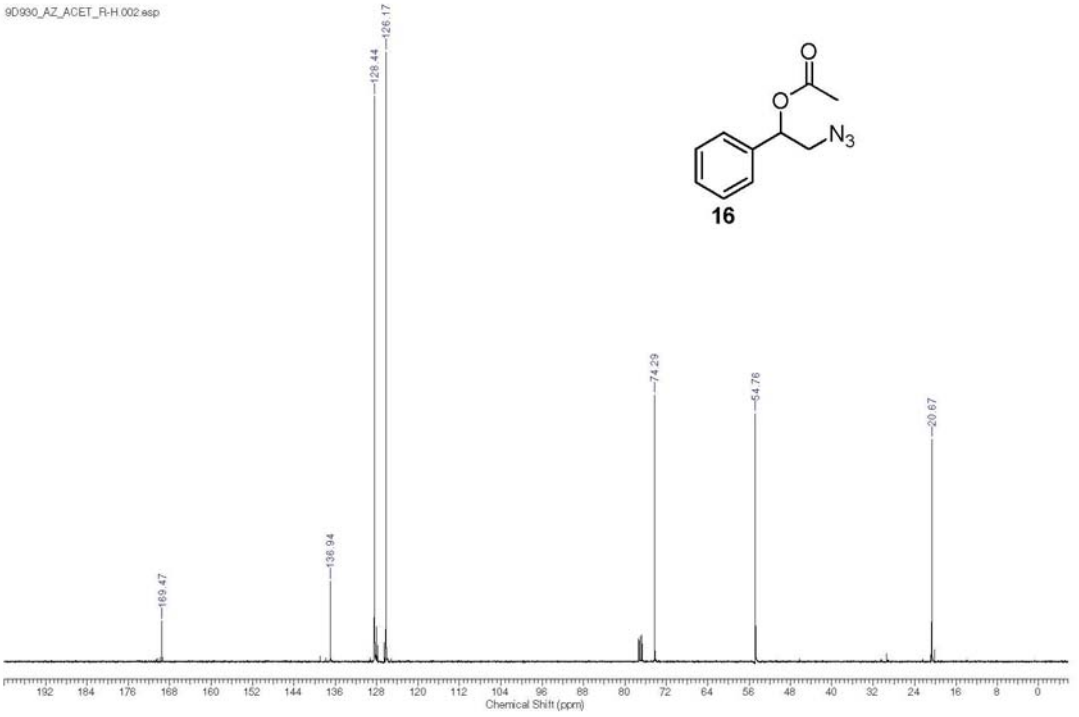

Figure S27. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 2-azido-1-phenylethyl acetate (**16**).

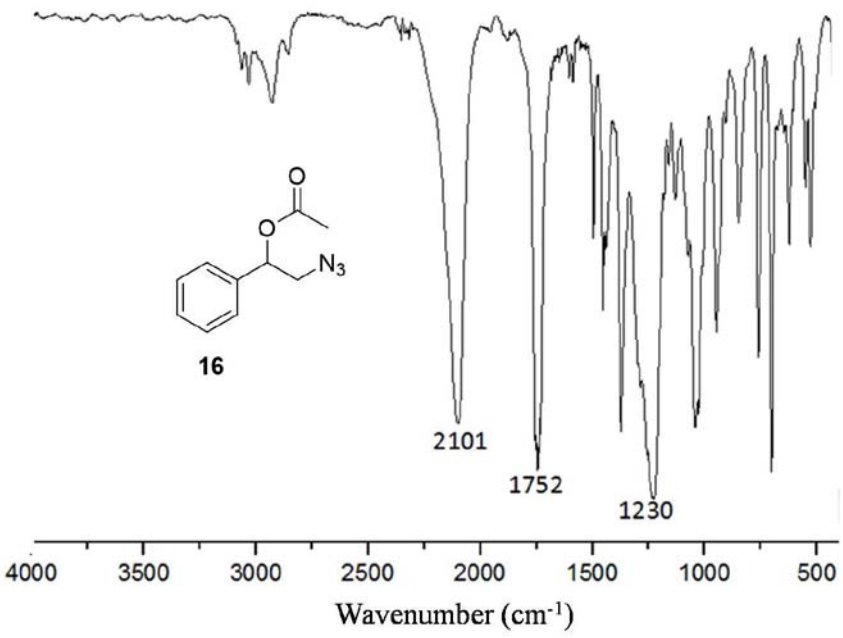

Figure S28. IR spectrum (KBr) of 2-azido-1-phenylethyl acetate (**16**).

2-Azido-1-(4-methoxyphenyl)ethyl acetate (**17**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.04 (s, 1H); 3.32 (dd, 1H, *J* 14.0, 4.0 Hz); 3,54 (dd, 1H, *J* 14.0 e 8.0 Hz); 5,79 (dd, 1H, *J* 80 4.0 Hz); 6.81 (d, 1H, *J* 10.0 Hz); 7,20 (d, 2H, *J* 8.0 Hz); ^{13}C RMN (100 MHz, $CDCl_3$) δ 21.1, 54.9, 55.2, 74.2, 114.1, 127.9, 129.1, 159.9, 169.9; IR (KBr) ν/cm^{-1} 2101 (C-N_3), 1737 (C=O), 1242 (C–0).

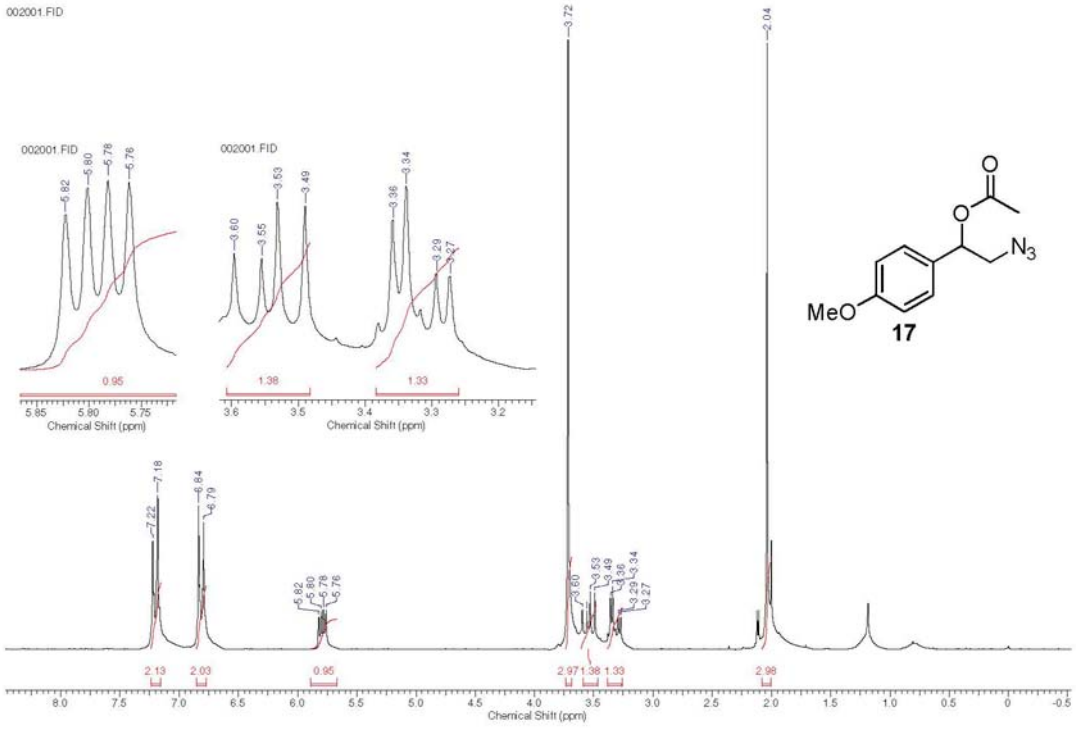

Figure S29. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-azido-1-(4-methoxyphenyl)ethyl acetate (**17**).

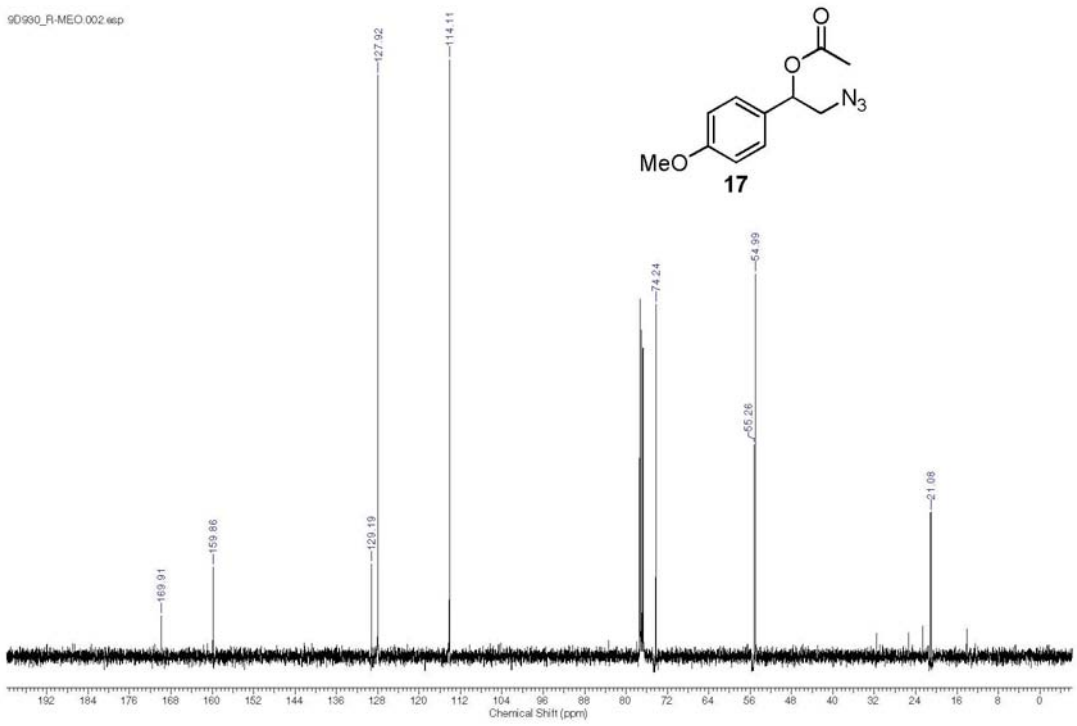

Figure S30. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 2-azido-1-(4-methoxyphenyl)ethyl acetate (**17**).

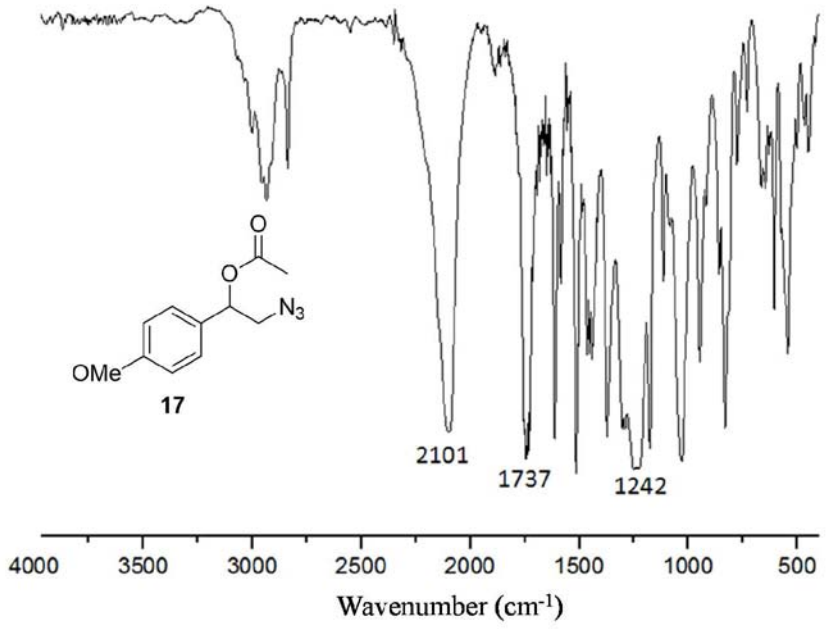

Figure S31. IR spectrum (KBr) of 2-azido-1-(4-methoxyphenyl)ethyl acetate (**17**).

2-Azido-1-(4-bromophenyl)ethyl acetate (**18**): ^{13}C RMN (100 MHz, $CDCl_3$) δ 20.6, 54.5, 73.8, 122.5, 127.9, 131.6, 135.8, 169.8; IR (KBr) ν/cm^{-1} 2103 (N_3), 1741 (C=O), 1215 (C–O).

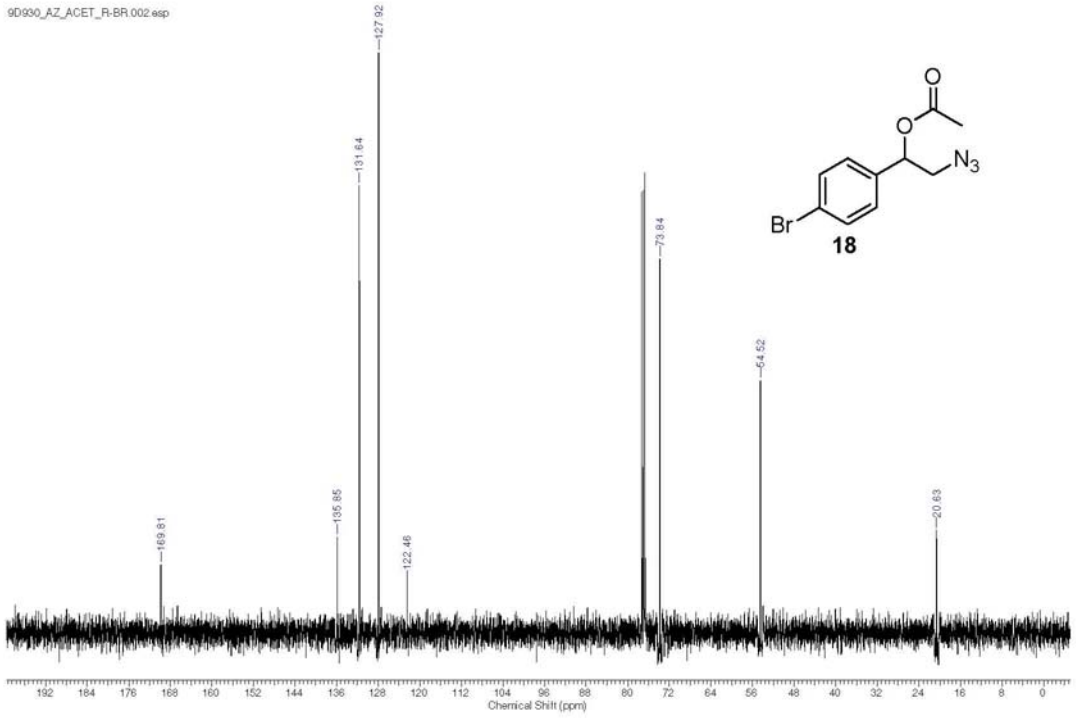

Figure S32. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 2-azido-1-(4-bromophenyl)ethyl acetate (**18**).

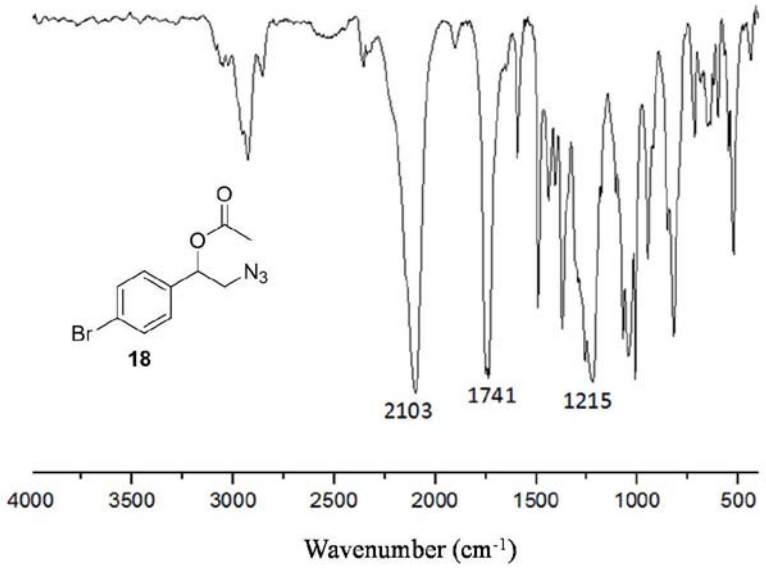

Figure S33. IR spectrum (KBr) of 2-azido-1-(4-bromophenyl)ethyl acetate (**18**).

2-Azido-1-(4-chlorophenyl)ethyl acetate (**19**): ^{13}C RMN (100 MHz, $CDCl_3$) δ 21.0, 54.9, 73.9, 127.9, 129.0, 134.7, 135.6, 169.8; IR (KBr) ν/cm^{-1} 2101 (N_3), 1747 (C=O), 1224 (C–O).

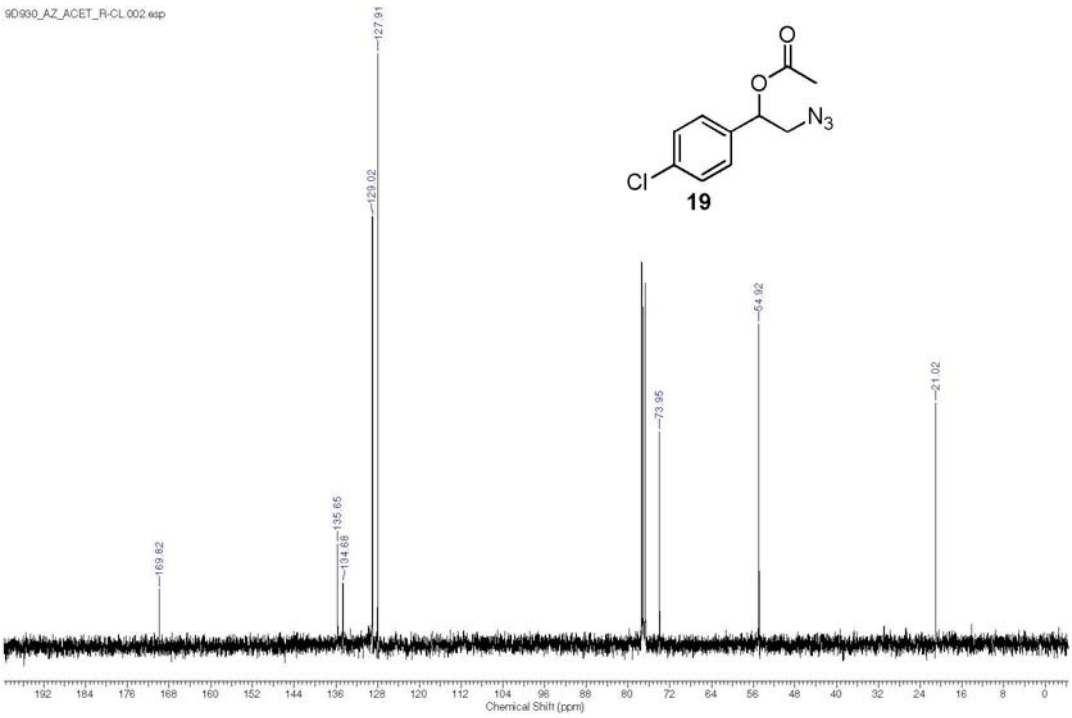

Figure S34. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 2-azido-1-(4-chlorophenyl)ethyl acetate (**19**).

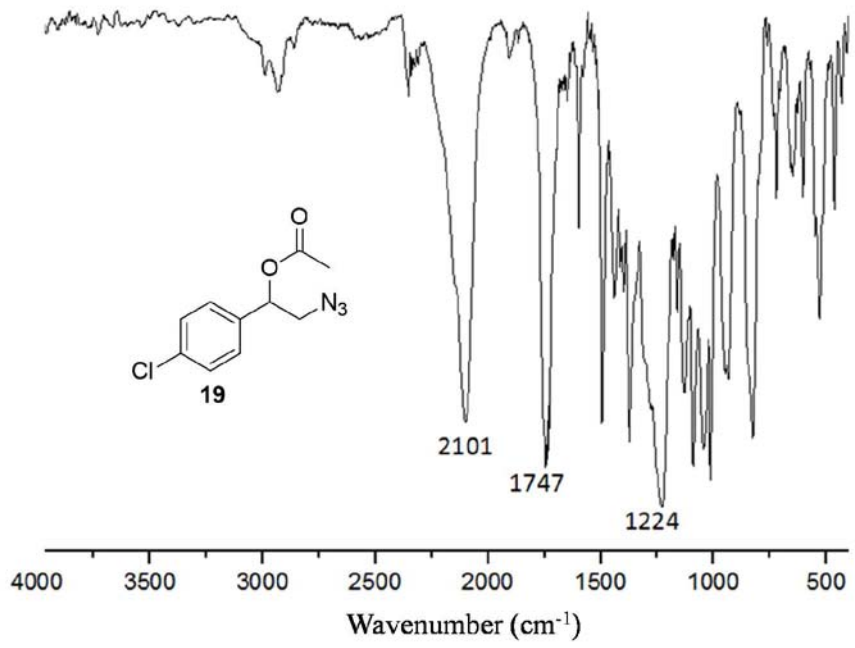

Figure S35. IR spectrum (KBr) of 2-azido-1-(4-chlorophenyl)ethyl acetate (**19**).

Kinetic resolution of (±)-azidophenylethanols **11**-**15** by immobilized CALB

HPLC grade hexane (10 mL), vinyl acetate (1 mL), immobilized CALB (100 mg, 10,000 propyl laurate units *per* g), and the appropriate (±)-azidophenylethanols **11**-**15** (1.20, 1.0, 0.8, 1.0, 0.9 mmol, respectively) were added to 50 mL Erlenmeyer flasks. These flasks was sealed using a rubber stopper, and the reaction mixture was stirred in orbital shaker at 32 °C and 130 rpm. After the reaction proceeds to completion the immobilized lipase was filtered off. The filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane/EtOAc (8:2) as eluent yielding the alcohols **11**-**15** and acetates **16**-**20**.

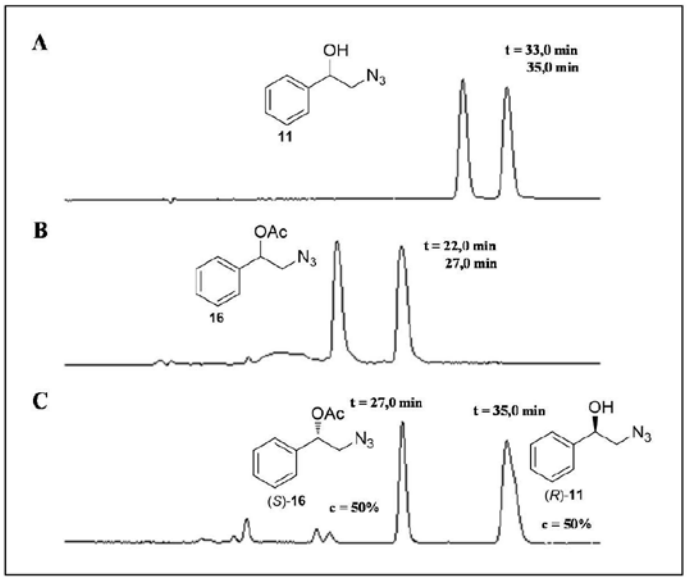

Figure S36. Chiral analyses obtained by HPLC chromatograms. (A) Racemic alcohol (±)-**11**. (B) Racemic acetate (±)-**16**. (C) Chromatograms of the kinetic resolution of rac-**11** by lipase CALB (5 days).

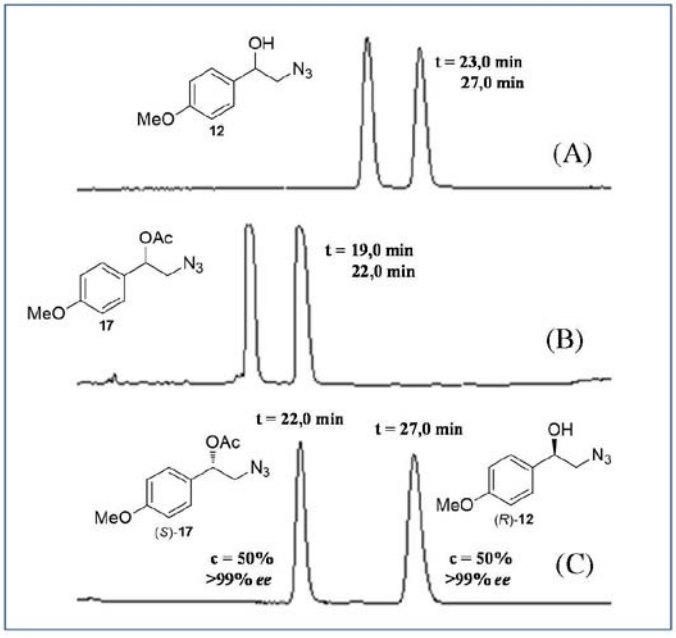

Figure S37. Chiral analyses obtained by HPLC chromatograms. (A) Racemic alcohol (±)-**12**. (B) Racemic acetate (±)-**17**. (B) Chromatograms of the kinetic resolution of rac-**12** by lipase CALB (5 days).

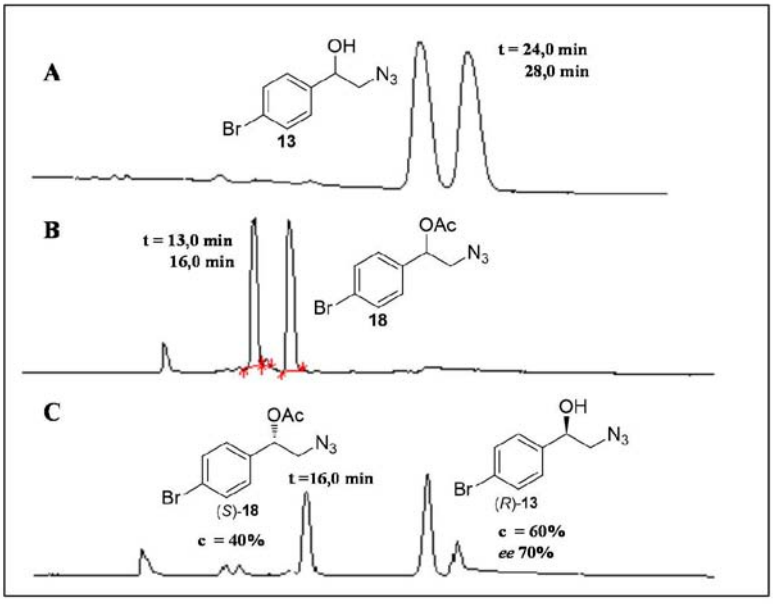

Figure S38. Chiral analyses obtained by HPLC chromatograms. (A) Racemic alcohol (±)-**13**. (B) Racemic acetate (±)-**18**. (C) Chromatograms of the kinetic resolution of rac-**13** by lipase CALB (10 days).

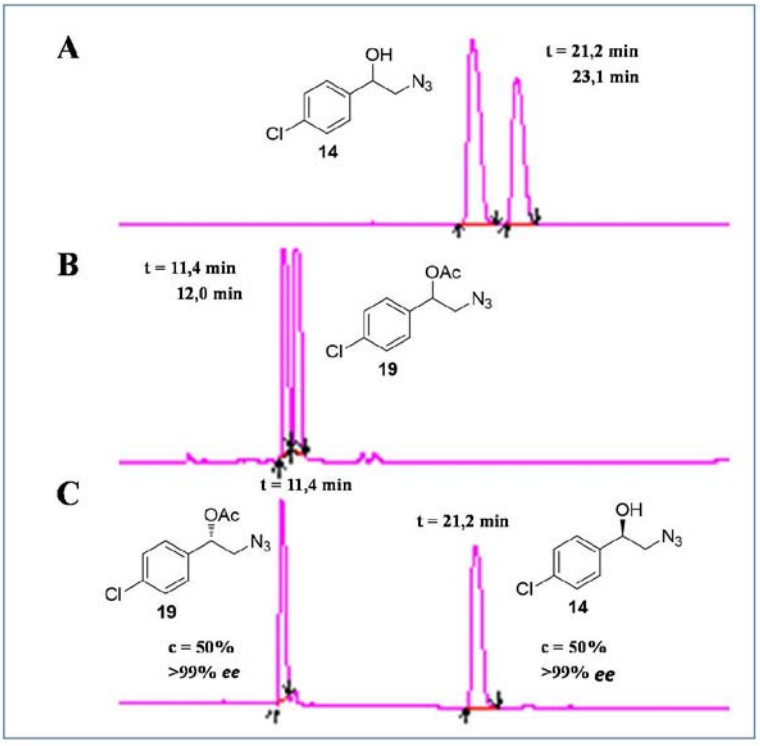

Figure S39. Chiral analyses obtained by HPLC chromatograms. (A) Racemic alcohol (±)-**14**. (B) Racemic acetate (±)-**19**. (C) Chromatograms of the kinetic resolution of rac-**14** by lipase CALB (10 days).

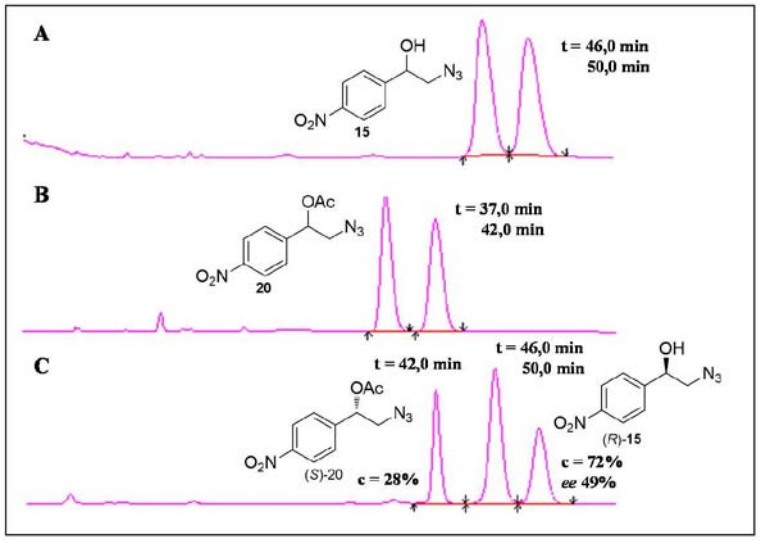

Figure S40. Chiral analyses obtained by HPLC chromatograms. (A) Racemic alcohol (±)-**15**. (B) Racemic acetate (±)-**20**. (C) Chromatograms of the kinetic resolution of rac-**15** by lipase CALB (7 days).

Preparation of chiral triazole compounds **21**-**25** by click chemistry reaction

(*R*)-β-azidophenylethanols **11**-**15** (1.0 mmol), 2-(trimethylsilyl)phenyl triflate (1.5 mmol, 0.45 g), acetonitrile (5 mL) and CsF (3 mmol, 0.46 g) were added to a vial (10 mL). The vial was sealed using a cap, and the reaction mixture was stirred for 18-24 h at room temperature. Afterward, a solution of $NaHCO_3$ 10% (5 mL) was added to the mixture, which was extracted with EtOAc (3 × 10 mL). The organic phase was dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel, using a 7:3 mixture of hexane/EtOAc as eluent, yielding the desired products **21**-**25**.

Assignment of absolute configuration and characterization data of the benzotriazoles **21**-**25**

(–)-(*R*)-2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-phenylethanol (21): $[\alpha]_D^{25}$ –20.5 (*c* 1.20, $CHCl_3$, > 99% ee); mp 130-131 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 4.73 (dd, *J* 12.0, 8.0, 1H, CH_2), 4.82 (dd, *J* 12.0, 4.0, 1H, CH_2), 5.36 (dd, *J* 8.0, 4.0, 1H, CHOH), 7.28-7.30 (m, 1H, Bt-H*), 7.36-7.39 (m, 2H, Ph-H), 7.41-7.45 (m, 3H, 2Ar-H and 1Bt-H), 7.50 (dt, *J* 8.5, 0.9, 1H, Bt-H), 7.91 (dt, 1H, *J* 8.5, 0.9, 1H, Bt-H); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 55.3, 73.1, 109.8, 119.5, 123.8, 125.5, 126.0, 127.3, 128.4, 133.8, 140.5, 145.5; IR (KBr) ν/cm^{-1} 3218, 2941, 2894, 2850, 1594, 1492, 1451, 1426, 1275, 1233, 1189, 1158, 1124, 1071, 1029, 883, 749, 746, 699, 586, 525, 484. HRMS (FTMS + pESI) *m/z* calcd. for $C_{14}H_{14}N_3O$ $[M]^+$ 240.1131, found 240.1134; *Bt-H: benzotriazole hydrogens.

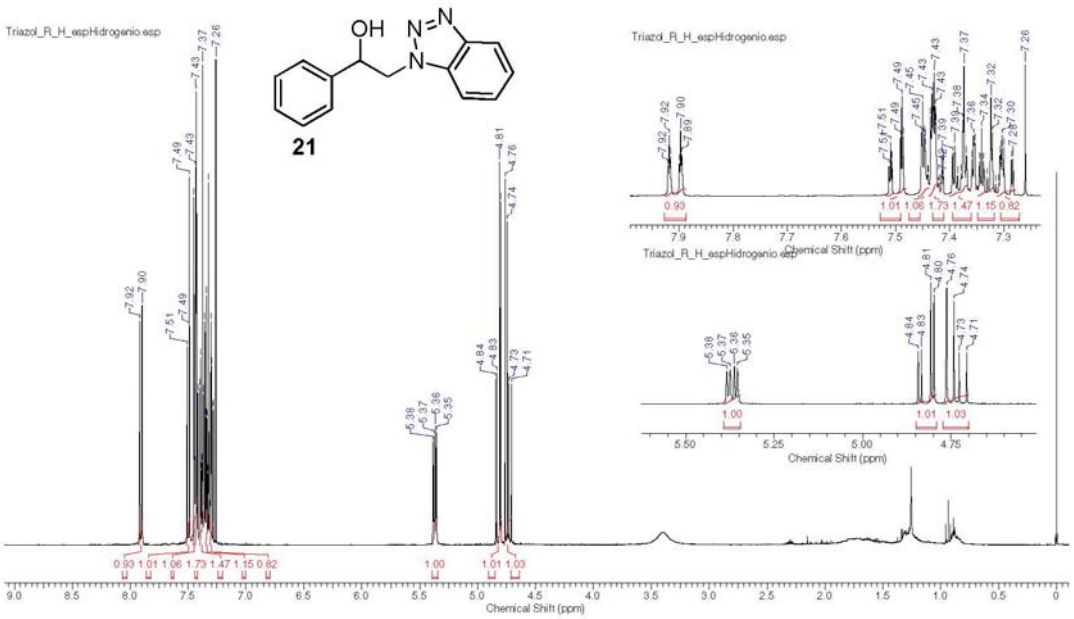

Figure S41. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-phenylethanol (**21**).

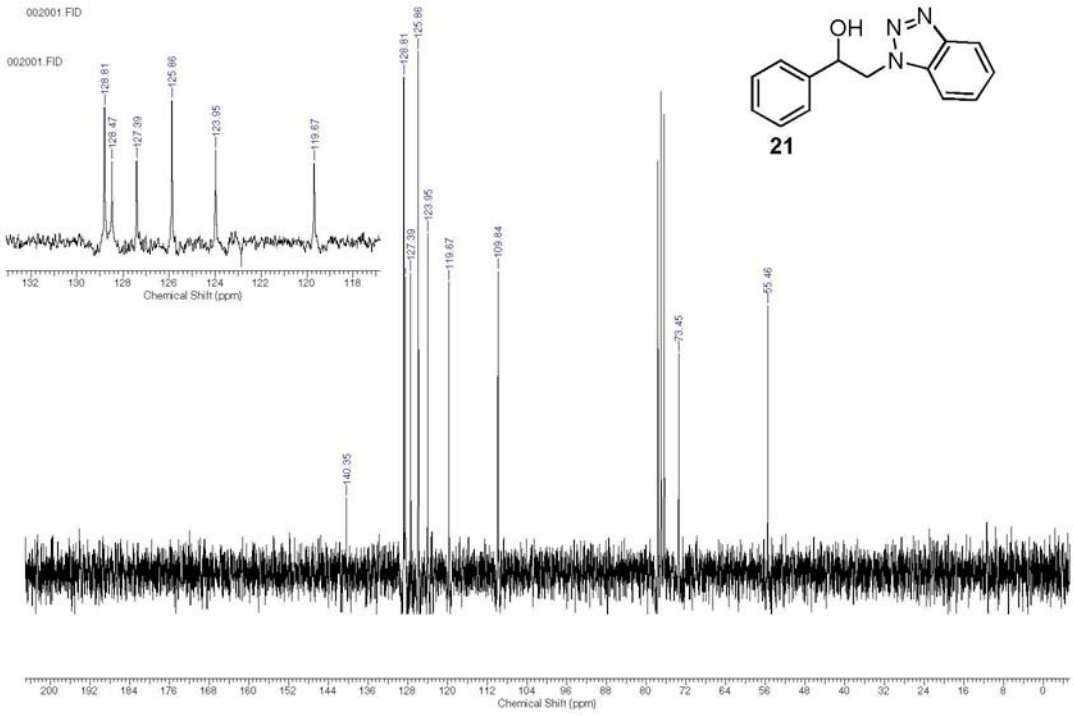

Figure S42. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-phenylethanol (**21**).

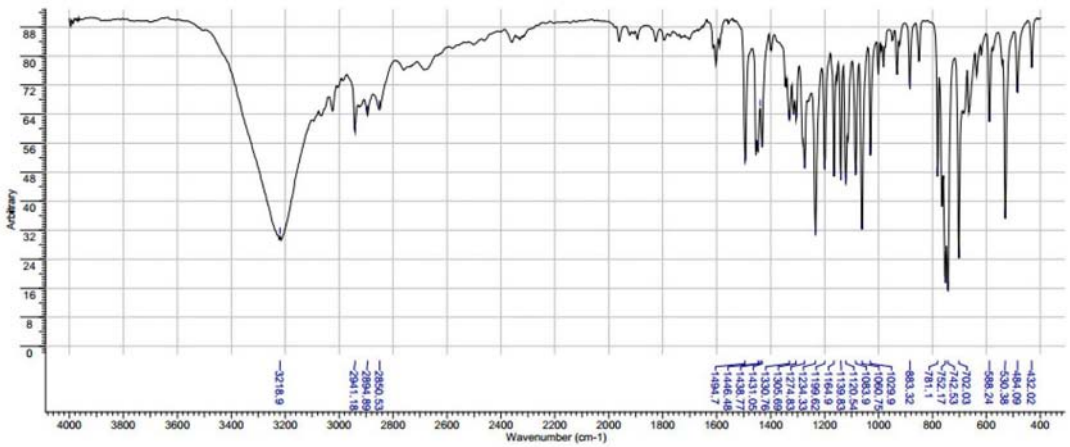

Figure S43. IR spectrum (KBr) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-phenylethanol (**21**).

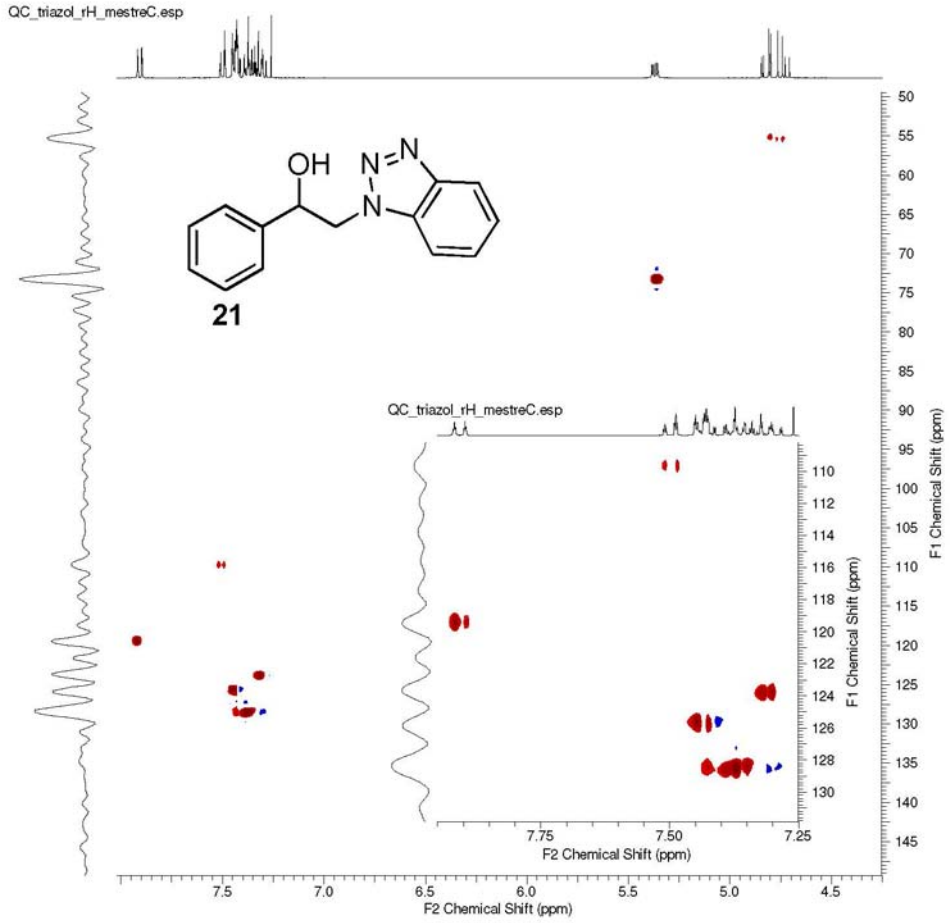

Figure S44. 2D RMN HSQC spectra of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-phenylethanol (**21**).

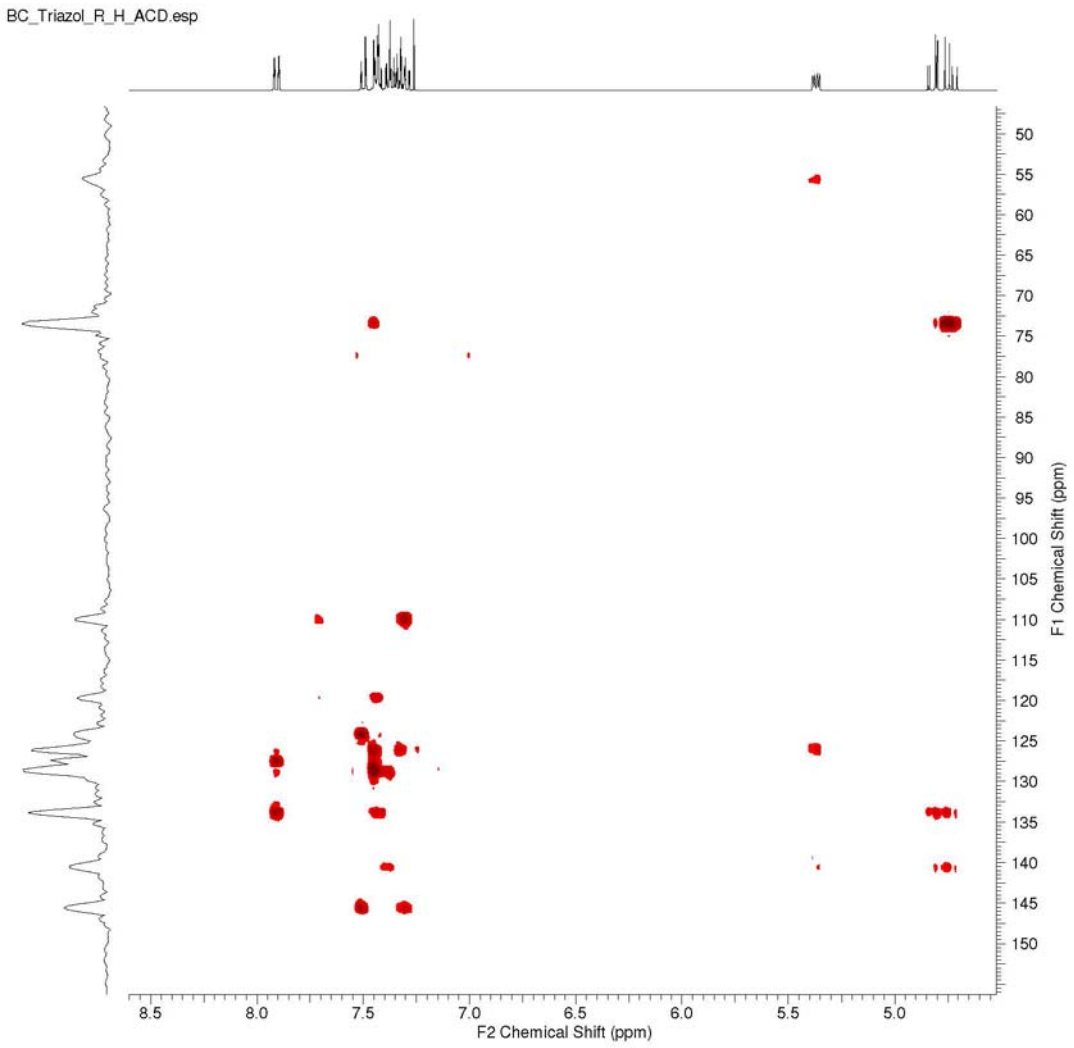

Figure S45. 2D RMN HMBC spectra of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-phenylethanol (**21**).

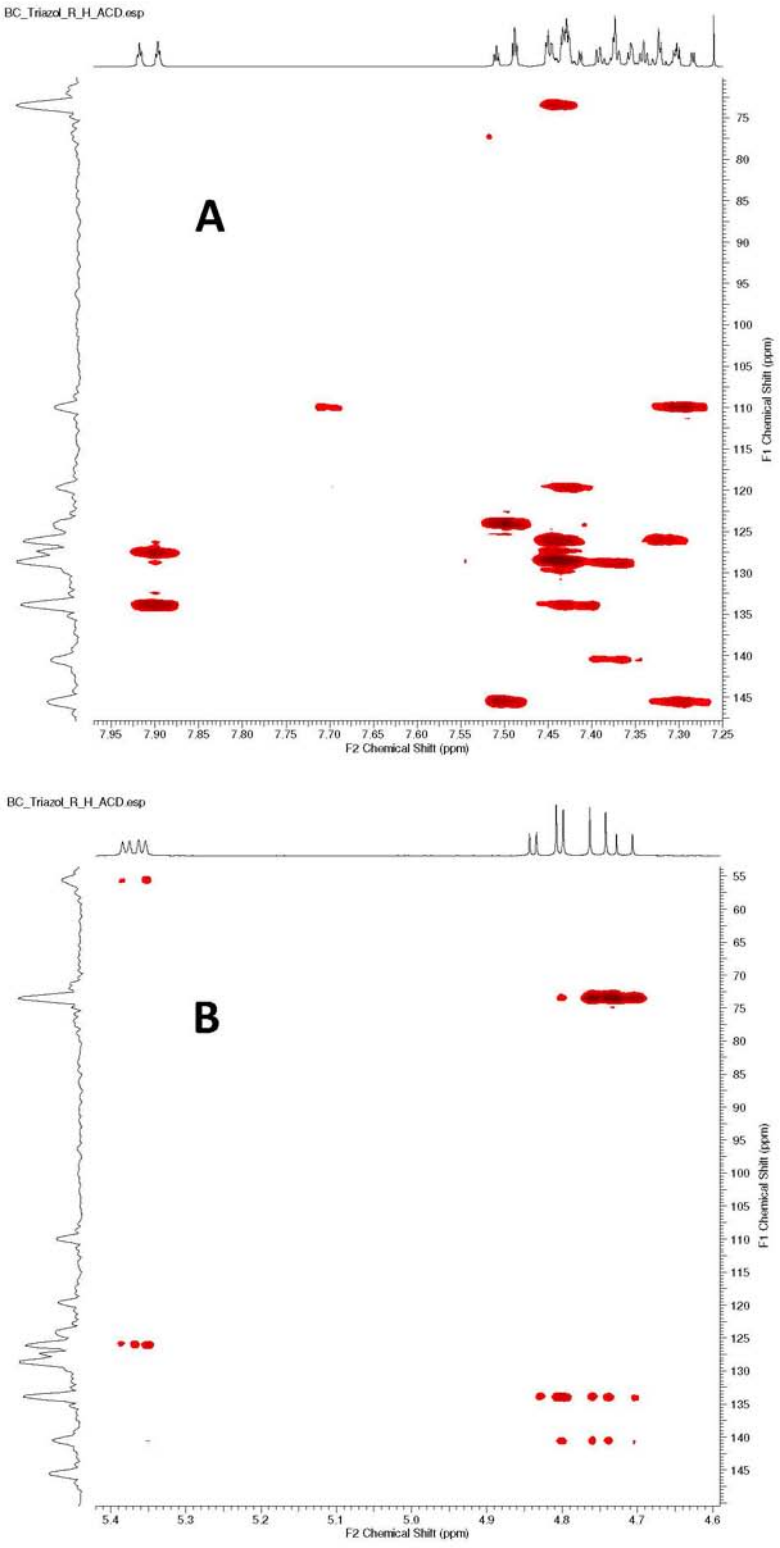

Figure S46. A, B. (Extension) 2D RMN HMBC of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-phenylethanol (**21**).

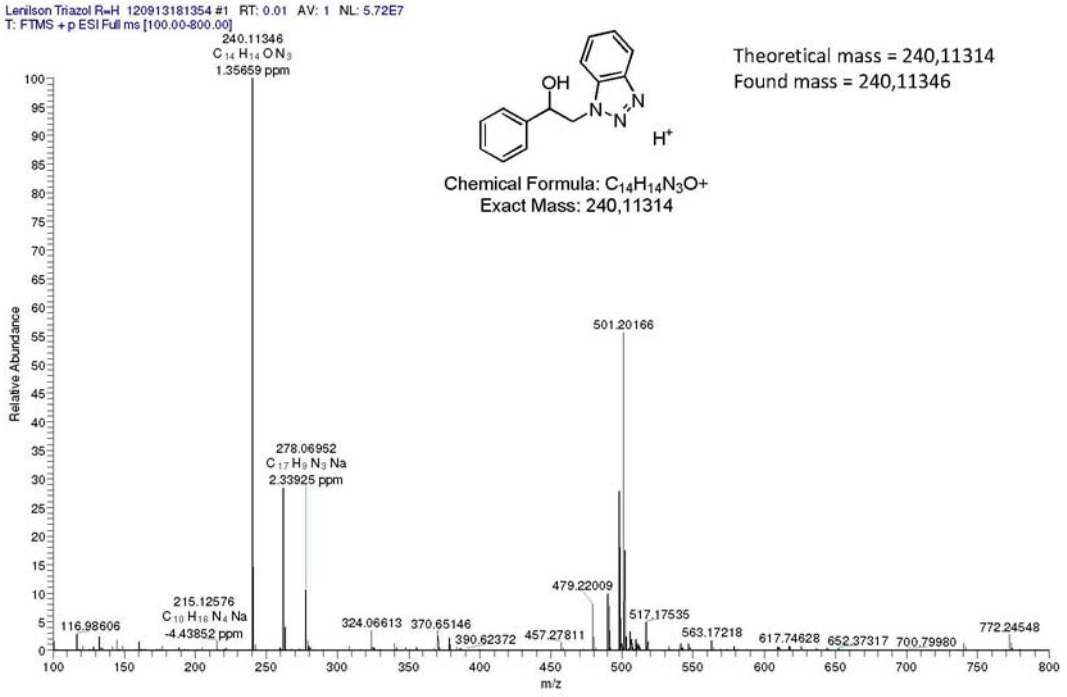

Figure S47. HRMS spectrum of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-phenylethanol (**21**).

(–)-(*R*)-2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-(4-methoxyphenyl)ethanol (**22**): $[\alpha]_D^{25}$ –43.3 (*c* 1.50, $CHCl_3$; > 99% ee); mp 136-137 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 3.76 (s, 3H, OCH_3), 4.68 (dd, *J* 14.3, 8.0, 1H, CH_2), 4.73 (dd, *J* 14.3, 4.2, 1H, CH_2), 5.27 (dd, *J* 8.0, 4.2, 1H, CHOH), 6.84 (d, *J* 8.5, 2H, Ar-H), 7.23 (d, *J* 8.4, 2H, Bt-H*), 7.30 (d, *J* 8.5, 2H, Ar-H), 7.38 (d, *J* 8.4, 1H, Bt-H), 7.49 (d, *J* 8.4, 1H, Bt-H), 7.76 (d, *J* 8.4, 1H, Bt-H); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 55.2, 55.5, 72.7, 110.0, 114.0, 119.2, 123.9, 127.0, 127.2, 132.6, 133.6, 145.1, 159.4; IR (KBr) ν/cm^{-1} 3281, 2926, 2839, 1610, 1581, 1510, 1446, 1311, 1263, 1190, 1132, 1003. 932, 926, 708. HRMS (FTMS + pESI) *m/z* calcd. for $C_{15}H_{16}N_3O_2$ $[M]^+$ 270.1237, found: 270.1243; *Bt-H: benzotriazole hydrogens.

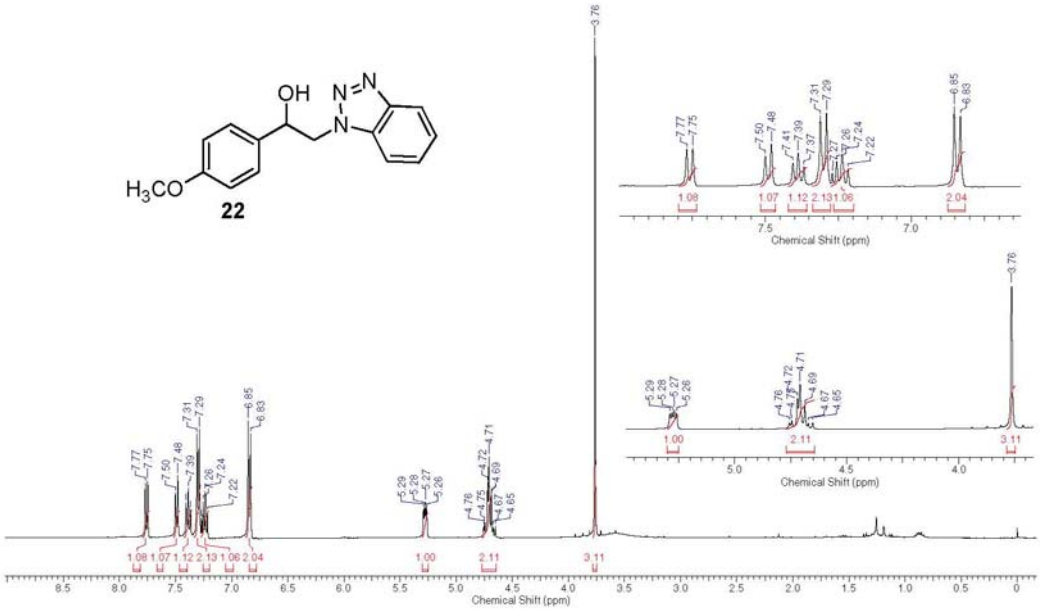

Figure S48. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-methoxyphenyl)ethanol (**22**).

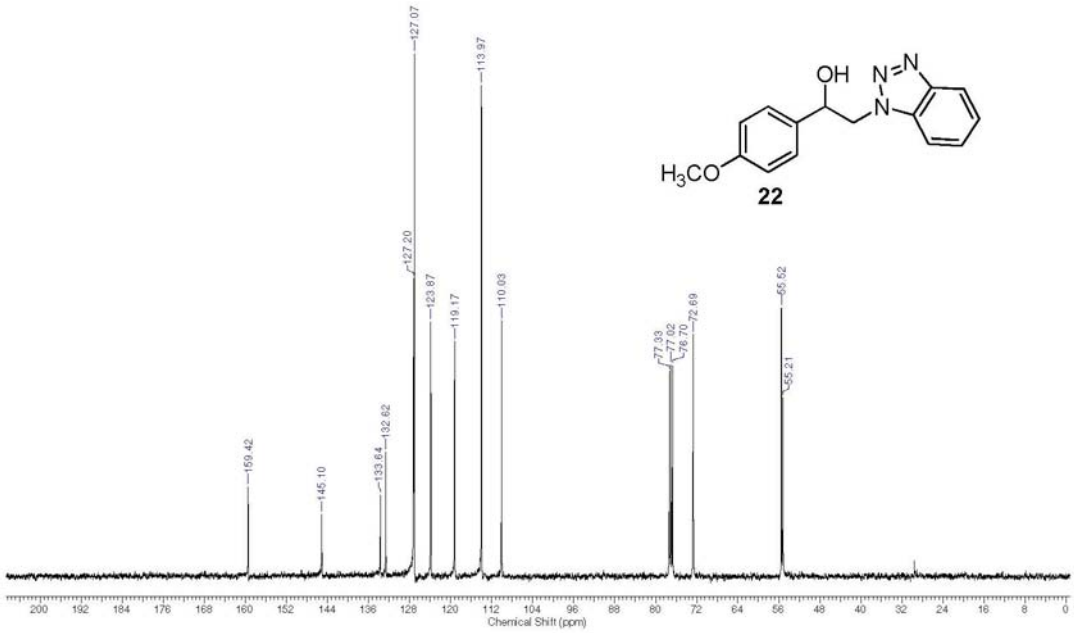

Figure S49. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-methoxyphenyl)ethanol (**22**).

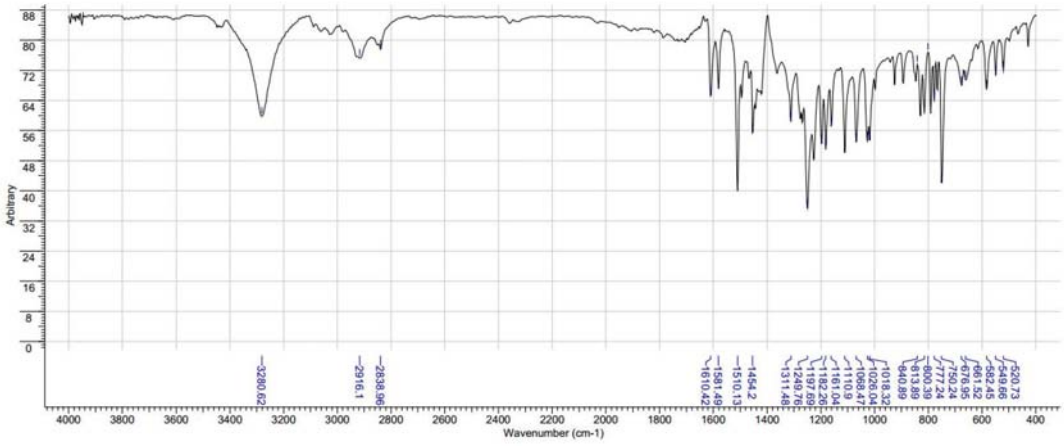

Figure S50. IR spectrum (KBr) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-methoxyphenyl)ethanol (**22**).

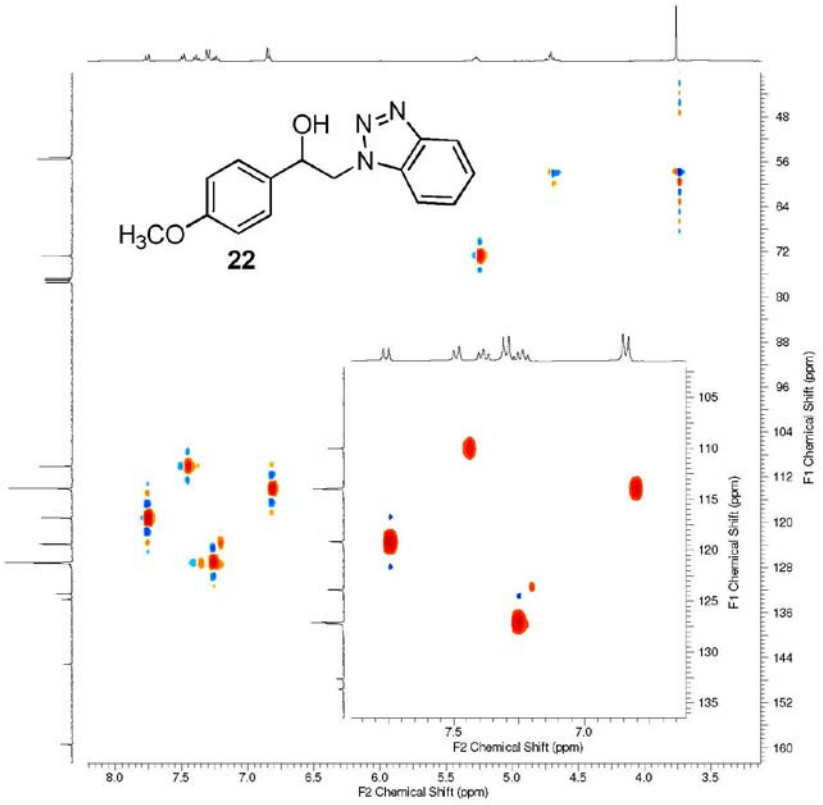

Figure S51. 2D RMN HSQC spectra of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-methoxyphenyl)ethanol (**22**).

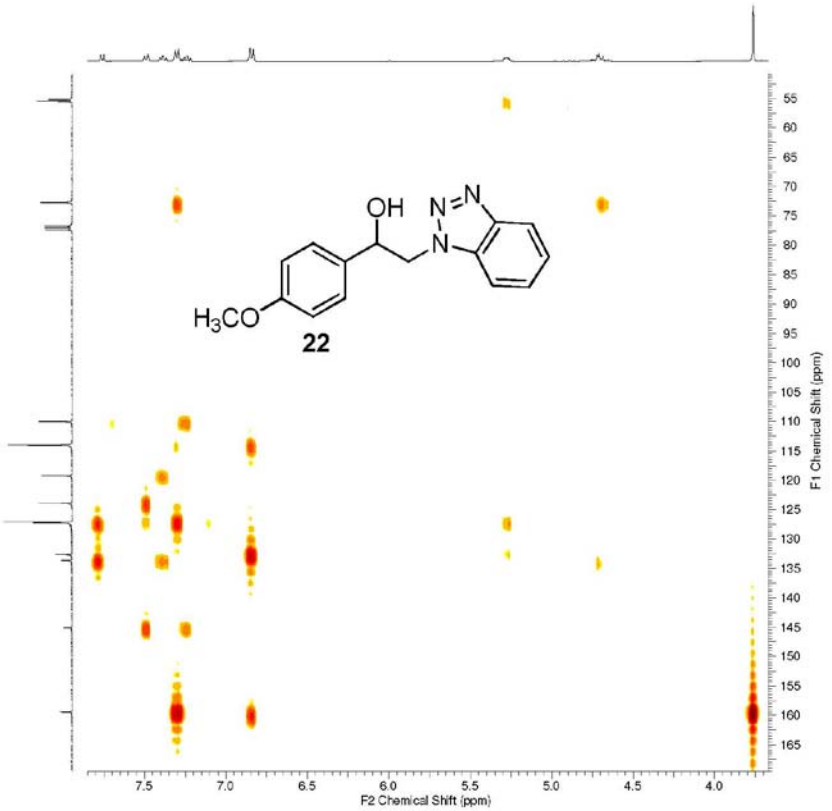

Figure S52. 2D RMN HMBC of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-methoxyphenyl)ethanol (**22**).

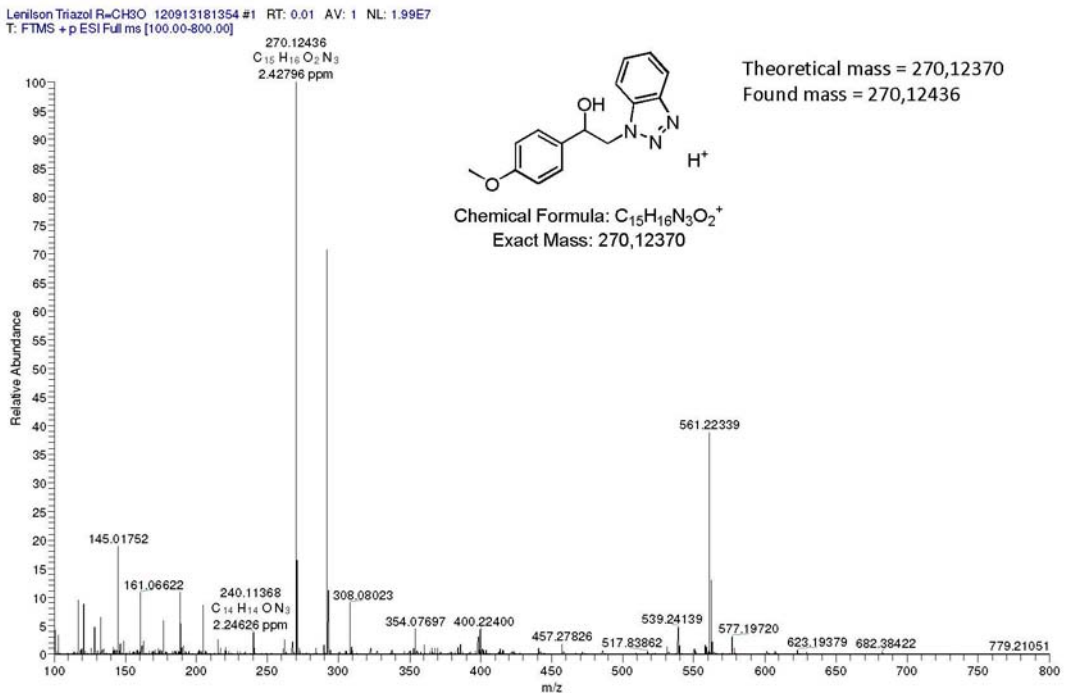

Figure S53. HRMS spectrum of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-methoxyphenyl)ethanol (**22**).

(–)-(*R*)-2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-(4-bromophenyl)ethanol (**23**): $[\alpha]_D^{25}$ –6.8 (*c* 0.90, $CHCl_3$, 70% ee); mp 165-166 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 4.68 (dd, *J* 16.0, 8.0, 1H, CH_2), 4.82 (dd, 1H, *J* 16.0, 4.0, 1H, CH_2), 5.41 (dd, *J* 8.0, 4.0, 1H, CHOH), 7.24 (d, *J* 8.0, 2H, Ar-H), 7.28 (d, 1H, *J* 8.0, 1H, Bt-H); 7.43-7.50 (m, 4H, 2Ar-H and 2Bt-H*), 7.87 (d, 1H, *J* 8.0, Bt-H); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 55.4, 72.8, 109.5, 119.5, 124.4, 127.6, 127.7, 131.9, 133.8, 134.5, 139.3, 145.0; IR (KBr) ν/cm^{-1} 3393, 3059, 2941, 2895, 1494, 1493, 1450, 1407, 1245, 1327, 1231, 1158, 1066, 1007, 875, 858, 820, 756, 735, 538, 510. HRMS (FTMS + pEI) *m/z* calcd. for $C_{14}H_{13}BrN_3O$ $[M]^+$ 318.0236, found 318.0246; *Bt-H: benzotriazole hydrogens.

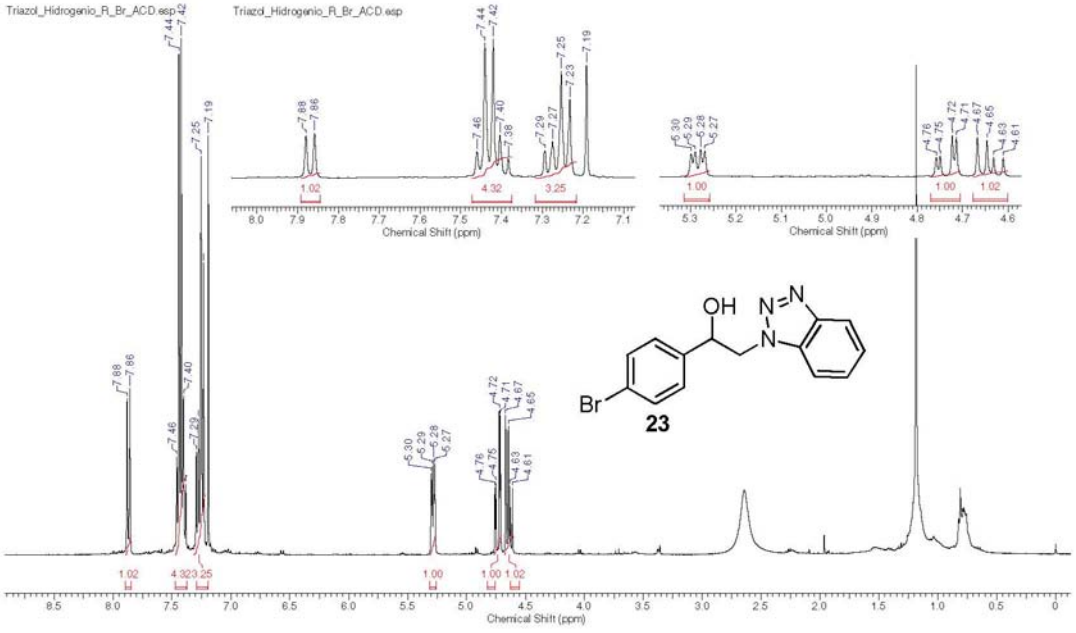

Figure S54. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-bromophenyl)ethanol (**23**).

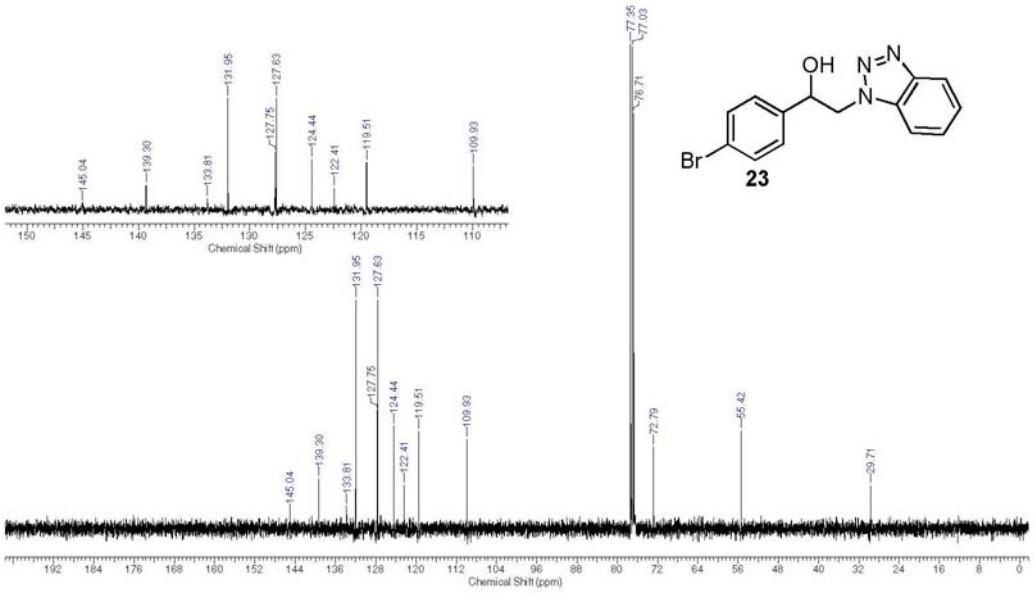

Figure S55. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-bromophenyl)ethanol (**23**).

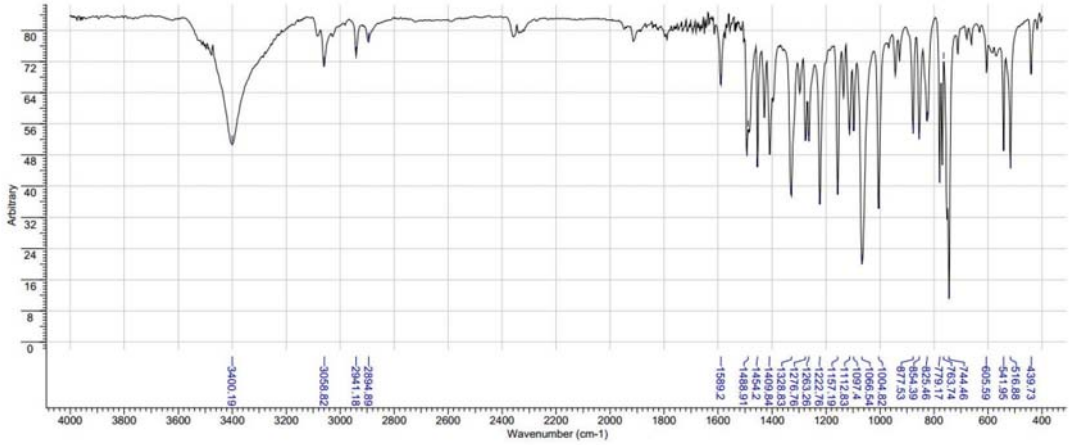

Figure S56. IR spectrum (KBr) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-bromophenyl)ethanol (**23**).

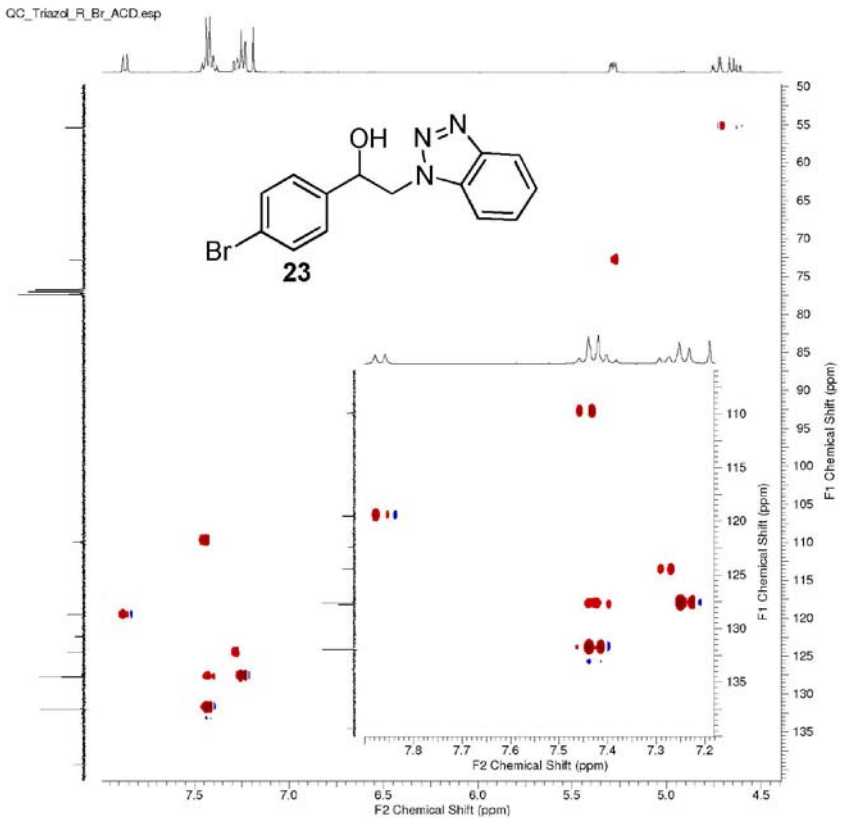

Figure S57. 2D RMN HSQC spectra of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-bromophenyl)ethanol (**23**).

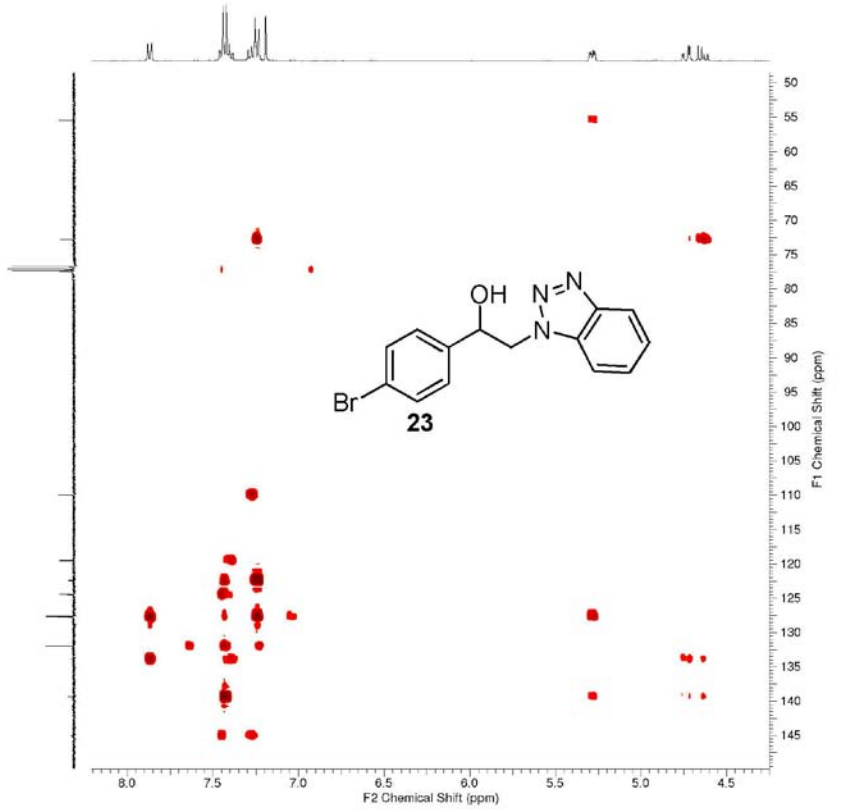

Figure S58. 2D RMN HMBC of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-bromophenyl)ethanol (**23**).

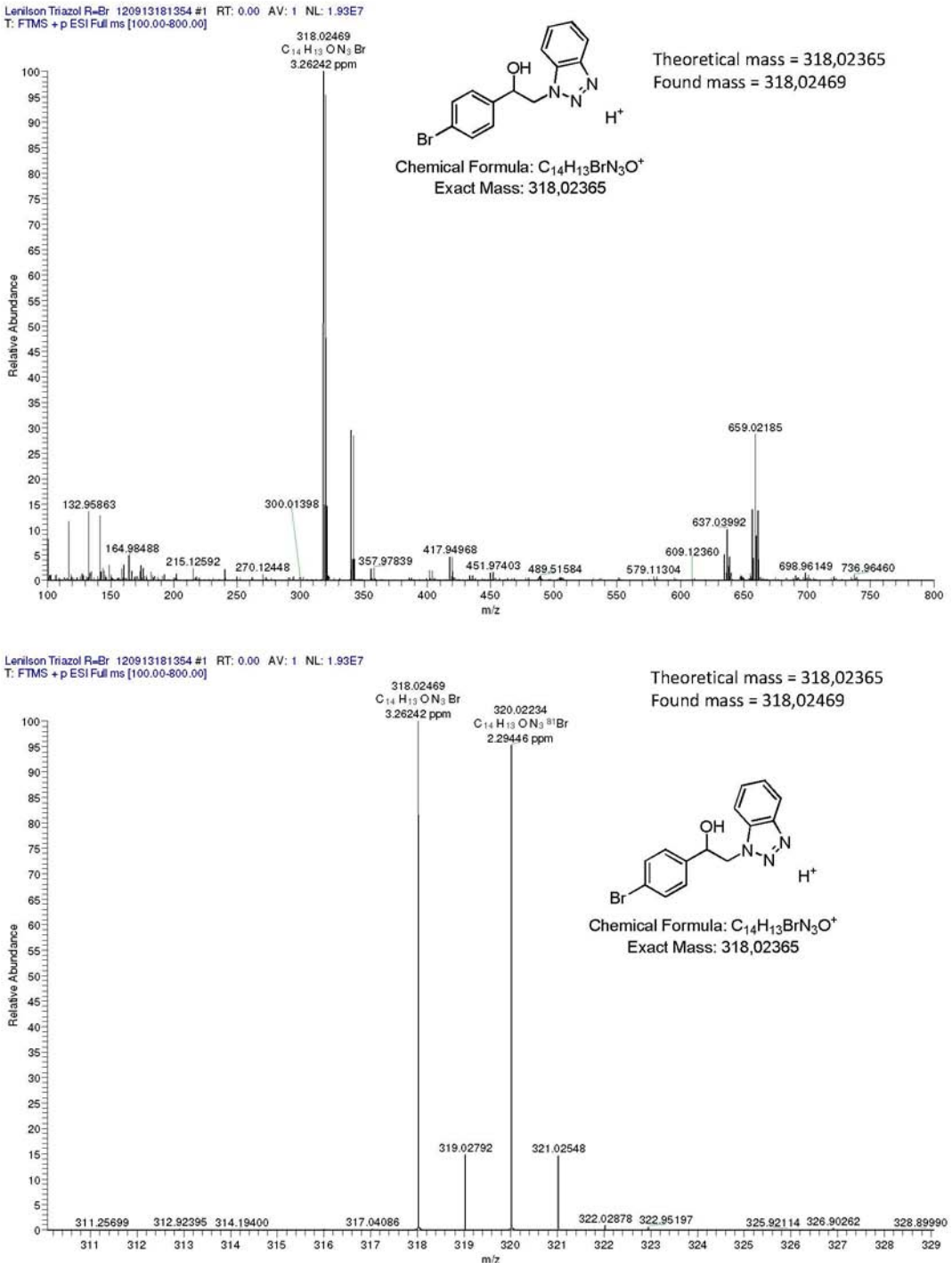

Figure S59. HRMS spectrum of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-bromophenyl)ethanol (**23**).

(–)-(*R*)-2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-(4-chlorophenyl)ethanol (**24**): $[\alpha]_D^{25}$ −34.8 (*c* 1.00, $CHCl_3$, > 99% ee) mp 157-158 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 4.68 (dd, *J* 16.0, 8.0, 1H, CH_2), 4.82 (dd, *J* 16.0, 4.0, 1H, CH_2), 5.41 (dd, *J* 8.0, 4.0. 1H, CHOH), 7.30 (td, *J* 8.3, 1.0, 1H, Bt-H*), 7.36 (d, *J* 8.0, 2H, Ar-H), 7.41 (d, *J* 8.0, 2H, Ar-H), 7.47 (td, *J* 8.3, 1.0, 1H, Bt-H), 7.53 (dt, *J* 8.3, 1.0, 1H, Bt-H), 7.88 (dt, *J* 8.3, 1.0, 1H, Bt-H); ^{13}C NMR (100,62 MHz, $CDCl_3$) δ 55.7, 72.7, 109.5, 119.5, 124.1, 127.2, 127.4, 129.2, 134.5, 138.7, 138.9, 145.5; IR (KBr) ν/cm^{-1} 3394, 3058, 2948, 2923, 1492, 1454, 1421, 1307, 1222, 1143, 1062, 744, 541, 516. HRMS (FTMS + pESI) *m/z* calcd. for $C_{14}H_{13}ClN_3O$ $[M]^+$ 274.0741, found 274.0749; *Bt-H: benzotriazole hydrogens.

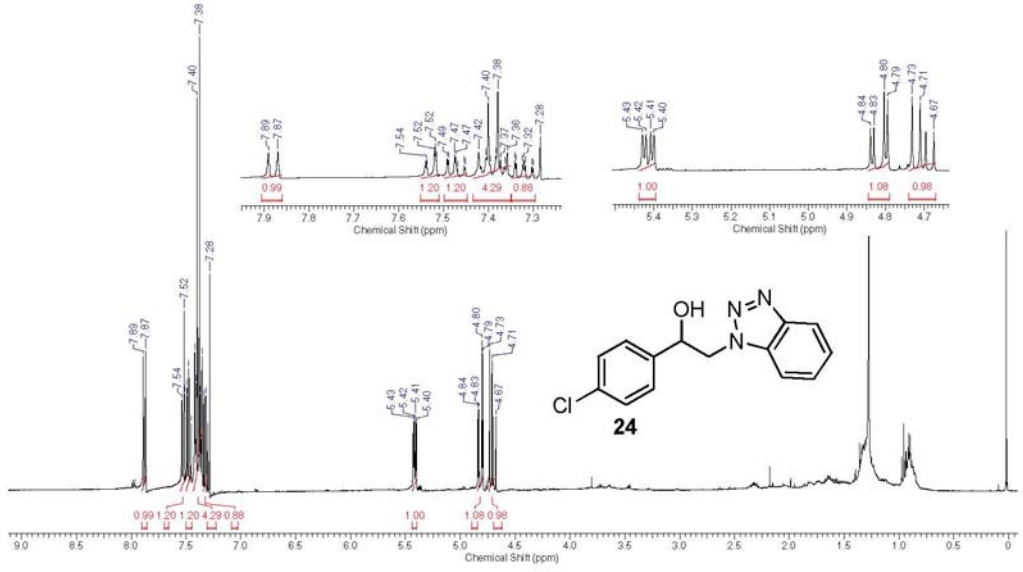

Figure S60. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-chlorophenyl)ethanol (**24**).

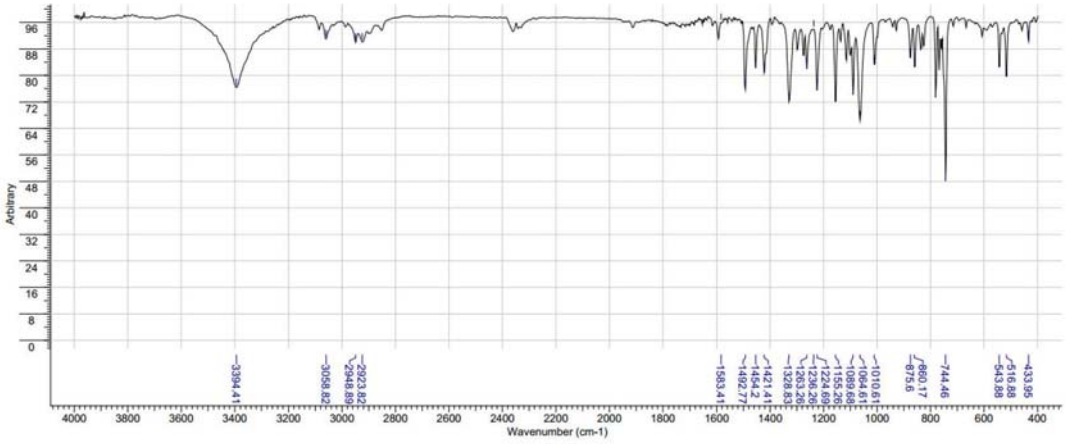

Figure S61. IR spectrum (KBr) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-chlorophenyl)ethanol (**24**).

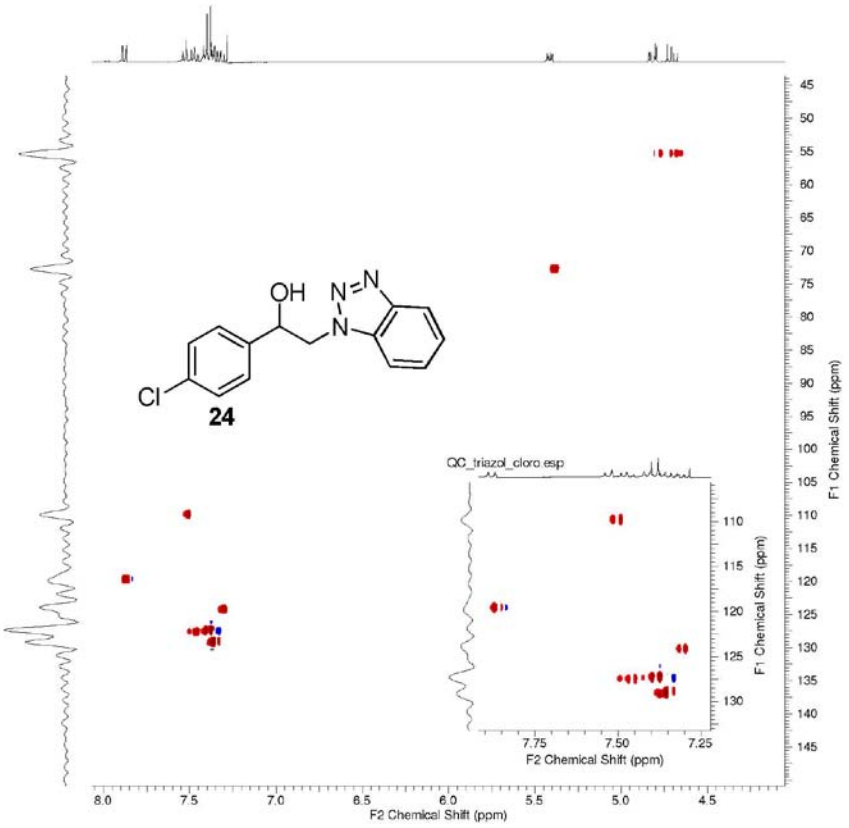

Figure S62. 2D RMN HSQC spectra of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-chlorophenyl)ethanol (**24**).

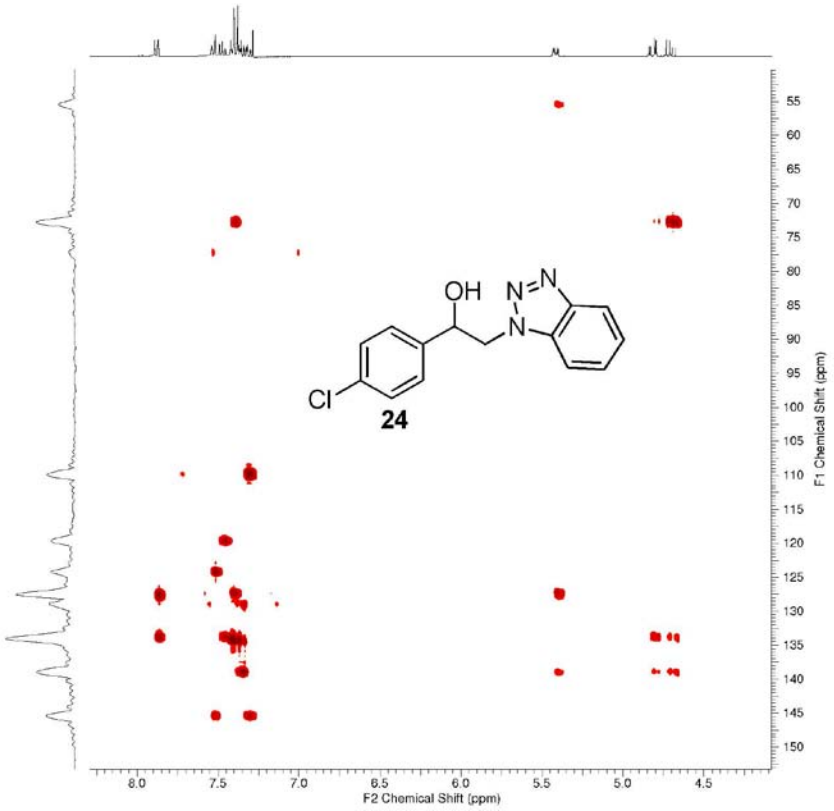

Figure S63. 2D RMN HMBC of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-chlorophenyl)ethanol (**24**).

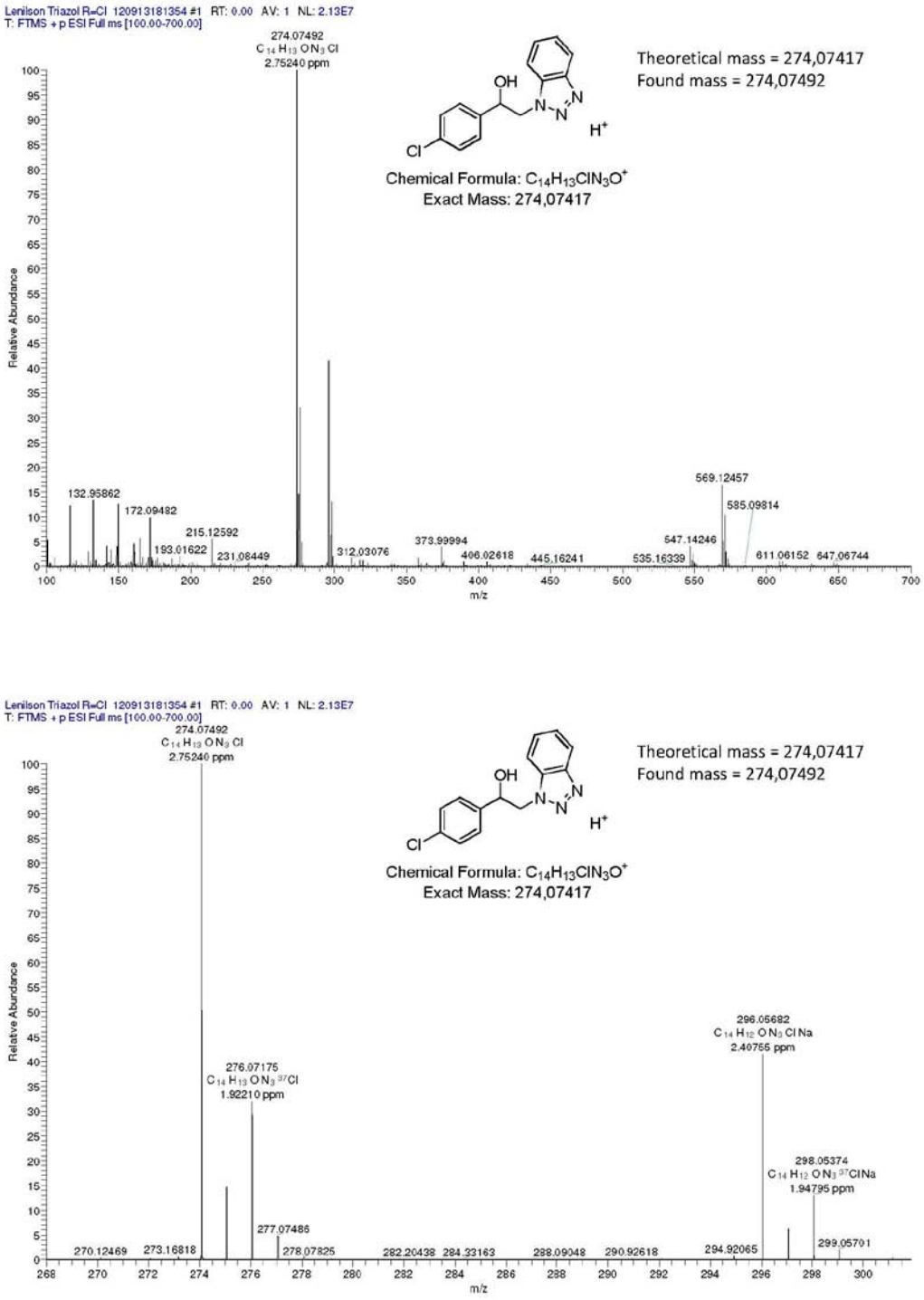

Figure S64. HRMS spectrum of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-chlorophenyl)ethanol (**24**).

(*R*)-2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-(4-nitrophenyl)ethanol (**25**): mp 201-203 °C; ^{1}H NMR (200.13 MHz, DMSO-d_6) δ 4.92-4.98 (m, 2H, CH_2), 5.28-5.34 (m, 1H, CH_2), 7.37 (t, *J* 8.0, 1H, Bt-H*), 7.51 (t, 1H, *J* 8.0, Bt-H), 7.67 (d, 2H, *J* 8.5, Ar-H), 7.86 (d, *J* 8.2, 1H, Bt-H), 8.00 (d, *J* 8.2, 1H, Bt-H), δ 8.19 (d, *J* 8.5, 2H, Ar-H); ^{13}C NMR (50.32 MHz, DMSO-d_6) δ 59.8, 70.9, 111.4, 118.9, 123.3, 123.8, 127.0, 127.6, 133.7, 138.5, 146.9, 149.8; IR (KBr) ν/cm^{-1} 3388, 3107, 3062, 2960, 2921, 2850, 1932, 1801, 1606, 1529, 1344, 1261, 1224, 1159, 1114, 1105, 1068, 869, 802, 773, 740, 694, 538, 509, 439. HRMS (FTMS + pESI) *m/z* calcd. for $C_{14}H_{13}ClN_4O_3$ $[M]^+$ 285.0982, found 285.0987; *Bt-H: benzotriazole hydrogens.

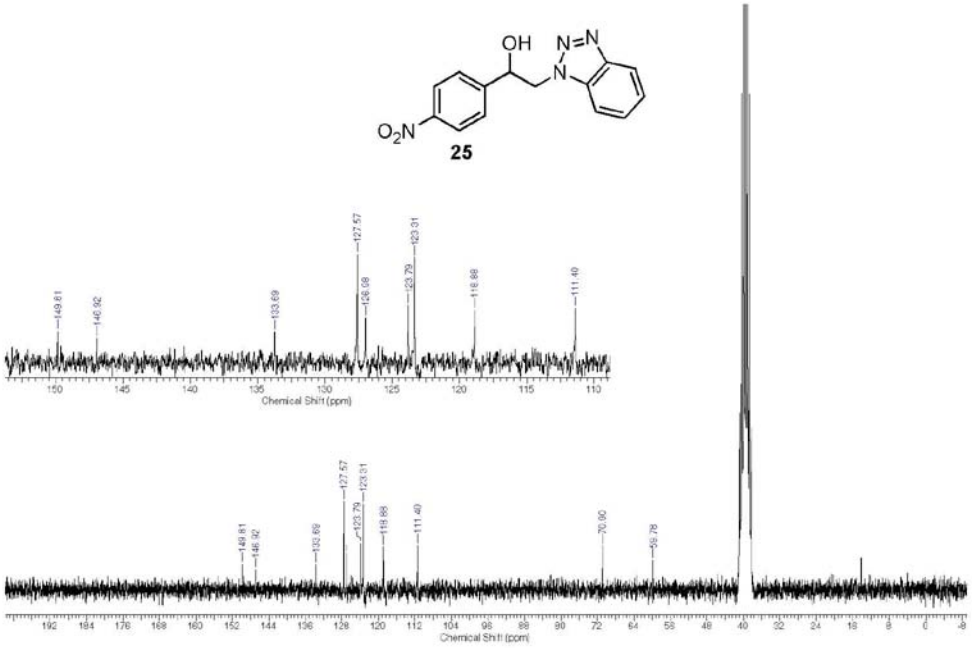

Figure S65. ^{1}H NMR spectrum (200 MHz, DMSO) 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-nitrophenyl)ethanol (**25**).

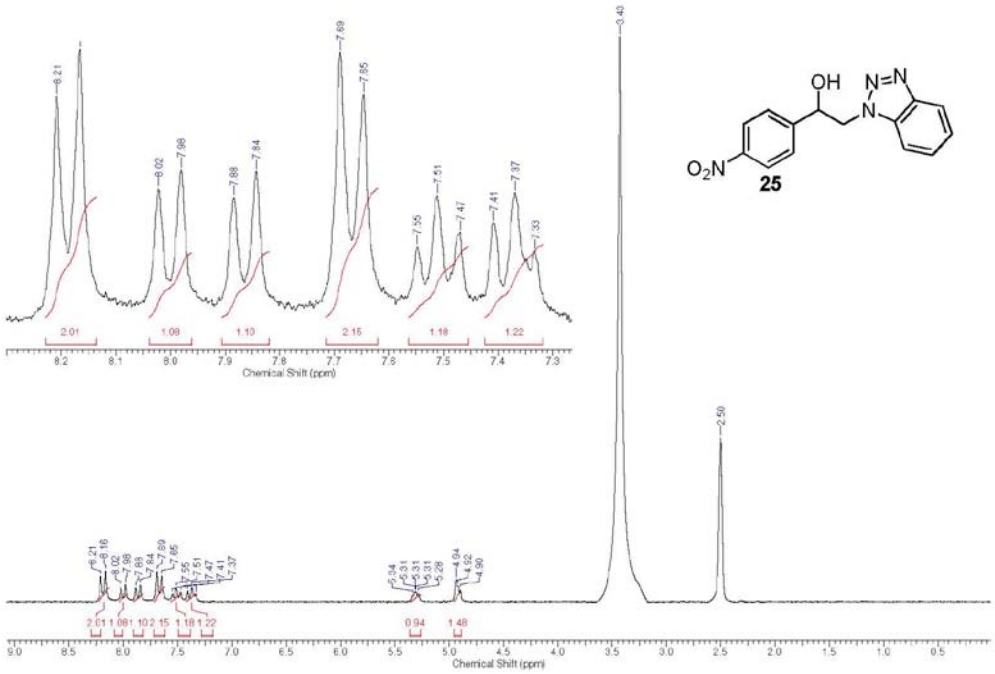

Figure S66. ^{13}C NMR spectrum (50 MHz, DMSO) 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-nitrophenyl)ethanol (**25**).

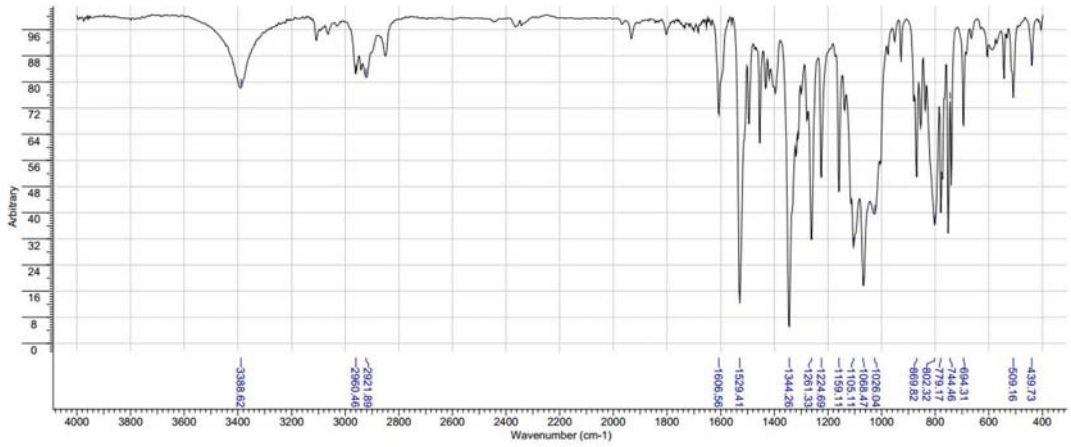

Figure S67. IR spectrum (KBr) of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-nitrophenyl)ethanol (**25**).

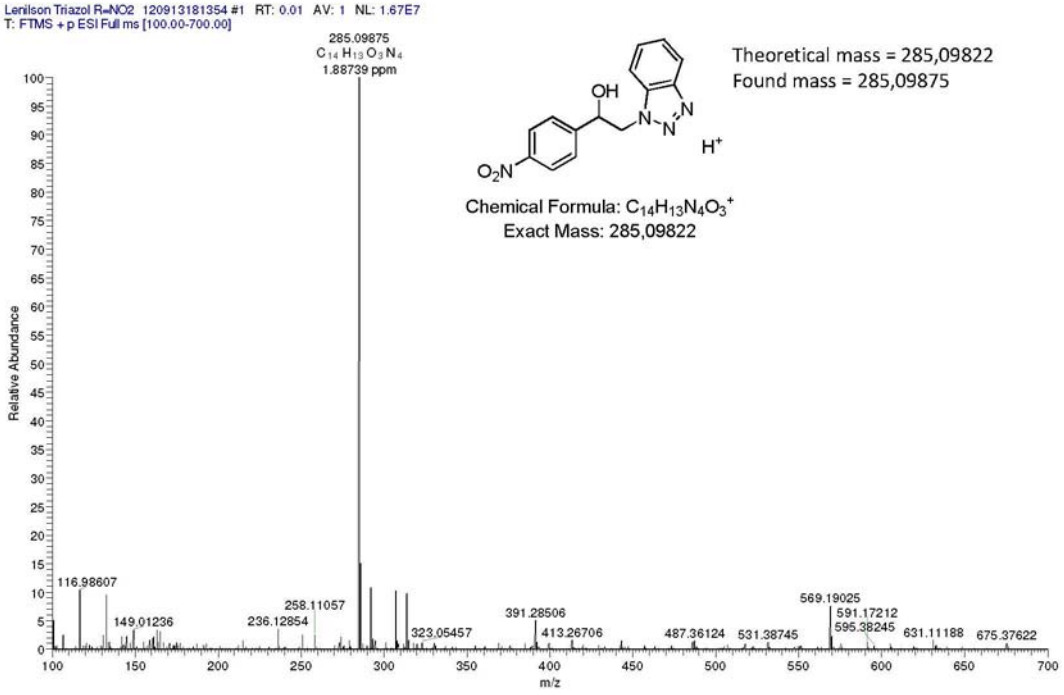

Figure S68. HRMS spectrum of 2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-1-(4-nitrophenyl)ethanol (**25**).