

Synthesis of β -Hydroxy-1,4-disubstituted-1,2,3-triazoles catalysed by Copper ferrite nano particles in tap water using Click Chemistry

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General Information:

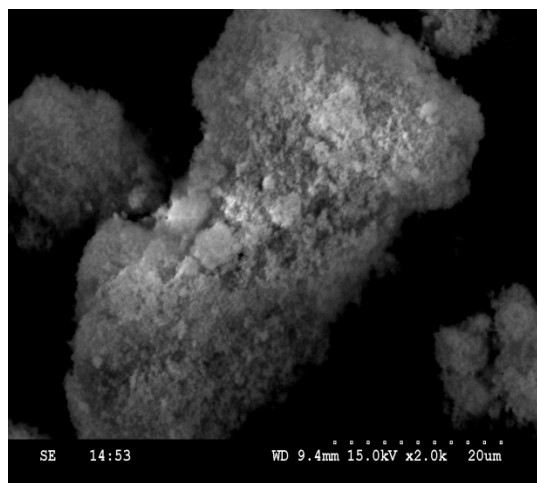
Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F₂₅₄ pre-coated plates. Visualization was accomplished with UV lamp or I₂ stain. All products were characterized by their NMR and MS spectra. ¹H and ¹³C NMR were recorded on 300 and 75 MHz in CDCl₃ using TMS as the internal standard, Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane.

General Procedure for the Synthesis of 1,4-Disubstituted 1, 2, 3-triazoles:

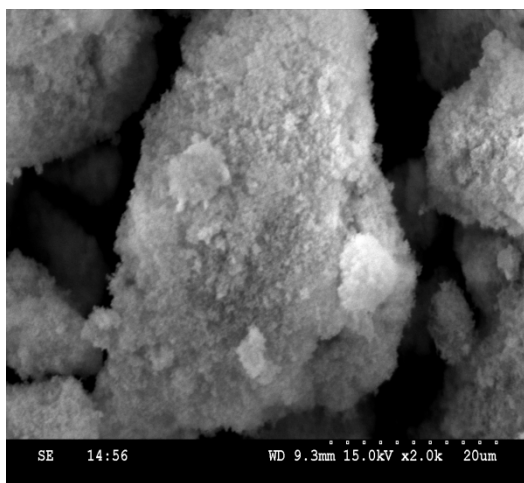
Styrene Oxide (1 mmol), phenyl acetylene (1 mmol) and NaN₃ (72 mg, 1.1 mmol) were placed in a 25 ml round-bottomed flask in H₂O (10 mL). Sequentially CuFe₂O₄ (5 mol%) (Purchase from Aldrich CAS No. 12018-79-0) was added. The reaction mixture was warmed to 60 °C and monitored by TLC until total conversion of the starting materials. After completion of the reaction, the reaction mixture was magnetically concentrated with the aid of a magnet to separate the catalyst. Catalyst was separated and washed several times with acetone, dried under vacuum. Water (30 mL) was added to the resulting reaction mixture followed by extraction with EtOAc (4x10 mL). The collected organic phases were dried with Na₂SO₄ and the solvent was removed under vacuum to give the corresponding triazole.

Characterization of the CuFe₂O₄ Nano Catalyst:

From SEM studies, it is revealed that the CuFe₂O₄ nanoparticles remained in the same state, even after four cycles.

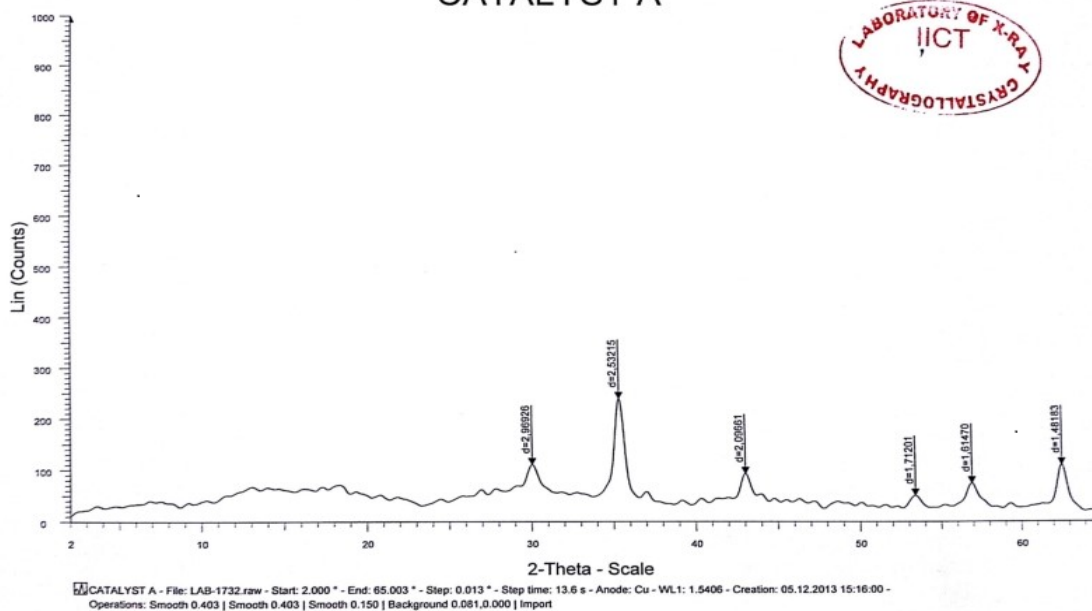


a. SEM-analysis of native CuFe₂O₄ catalyst

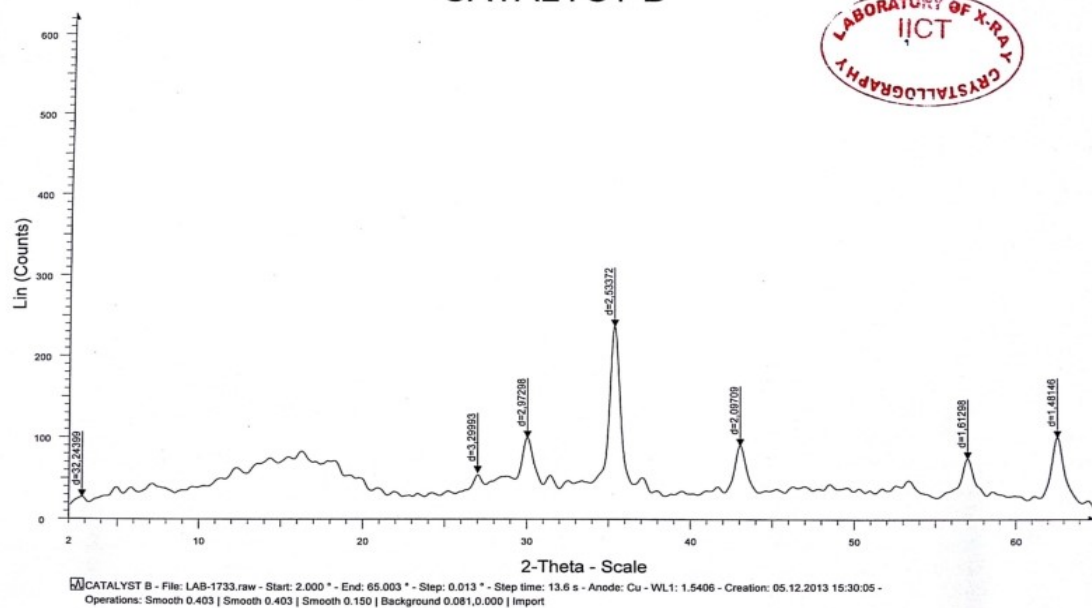


b. SEM-analysis of reused CuFe₂O₄ catalyst after 4 th cycle

CATALYST A

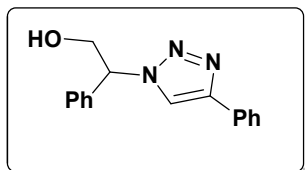


CATALYST B

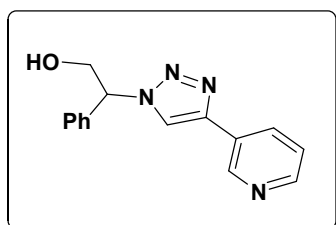


XRD spectra of CuFe_2O_4 catalyst (a) native and (b) after the 4th cycle.

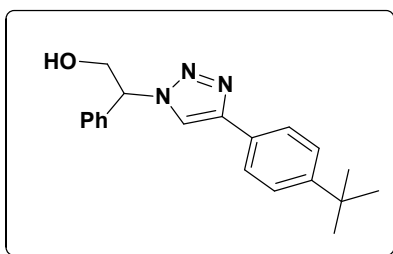
Supporting data



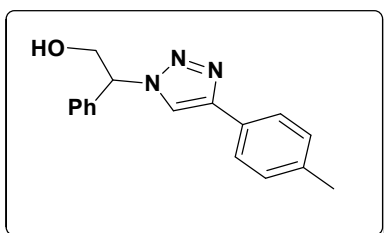
2-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethanol (Table 1, entry 1) ^1H NMR (300 MHz, CDCl_3): δ 4.24 (1H, dd, $J = 3.97, 11.93$ Hz), 4.64 (1H, dd, $J = 7.95, 12.93$ Hz), 5.68 (1H, dd, $J = 3.97, 7.95$ Hz), 7.20-7.47 (8H, m), 7.70 (1H, s), 7.77 (2H, d, $J = 7.95$ Hz); ESI-MS: m/z 266 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 266.1287 found 266.1282. $\text{C}_{16}\text{H}_{16}\text{ON}_3$



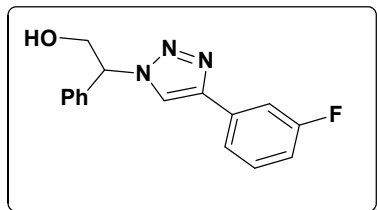
2-phenyl-2-(4-(pyridin-3-yl)-1H-1,2,3-triazol-1-yl)ethanol (Table 1, entry 2) ^1H NMR (300 MHz, CDCl_3): δ 4.15-4.32 (1H, m), 4.55-4.73 (1H, m), 5.60-5.80 (1H, m), 7.17-7.47 (6H, m), 7.78 (1H, t, $J = 7.36$ Hz) 8.03-8.38 (2H, m), 8.52 (1H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 64.86, 67.33, 122.95, 127.19, 128.91, 129.05, 135.77, 137.11, 147.96, 148.99. ESI-MS: m/z 267 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 267.1240 found 267.1235. $\text{C}_{15}\text{H}_{15}\text{ON}_4$



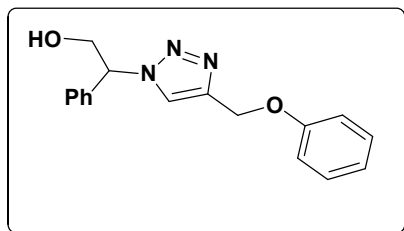
2-(4-(4-(tert-butyl)phenyl)-1H-1,2,3-triazol-1-yl)-2-phenylethanol (Table 1, entry 3) ^1H NMR (300 MHz, CDCl_3): δ 1.32 (9H, s), 4.20 (1H, dd, $J = 3.77, 12.08$ Hz), 4.61 (1H, dd, $J = 8.30, 12.08$ Hz), 5.66 (1H, dd, $J = 3.77, 8.30$ Hz), 7.13-7.47 (7H, m), 7.66 (3H, d, $J = 6.79$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 31.22, 34.61, 65.01, 67.38, 120.28, 125.34, 125.67, 127.07, 127.29, 128.86, 129.05, 136.10, 147.59, 151.34. ESI-MS: m/z 322 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 322.1913 found 322.1908. $\text{C}_{20}\text{H}_{24}\text{ON}_3$



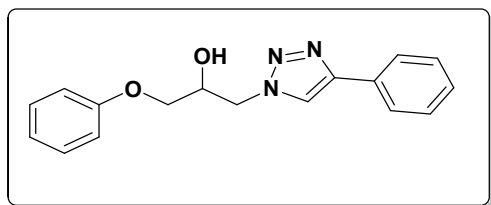
2-phenyl-2-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)ethanol (Table 1, entry 4) ^1H NMR (300 MHz, CDCl_3): δ 2.36 (3H, s), 3.52 (1H, s), 4.21 (1H, d, $J = 11.33$ Hz), 4.51-4.75 (1H, m), 5.59-5.73 (1H, m), 7.05-7.54 (8H, m), 7.65 (2H, t, $J = 3.60$ Hz); ESI-MS: m/z 280 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 280.1444 found 280.1439. $\text{C}_{17}\text{H}_{18}\text{ON}_3$



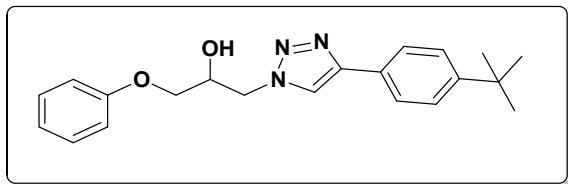
2-(4-(3-fluorophenyl)-1H-1,2,3-triazol-1-yl)-2-phenylethanol (Table 1, entry 5) ^1H NMR (300 MHz, CDCl_3): δ 3.30 (1H, dd, $J = 5.28, 8.30$ Hz), 4.10-4.34 (1H, m), 4.51-4.76 (1H, m), 5.67 (1H, dd, $J = 3.77, 8.30$ Hz), 6.90-7.10 (1H, m), 7.18-7.62 (8H, m), 7.71 (1H, s); ESI-MS: m/z 284 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 284.1194 found 284.1189. $\text{C}_{16}\text{H}_{15}\text{ON}_3\text{F}$



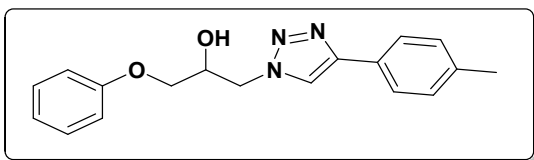
2-(4-(phoxymethyl)-1H-1,2,3-triazol-1-yl)-2-phenylethanol (Table 1, entry 6) ^1H NMR (300 MHz, CDCl_3): δ 3.4 (1H, s), 4.04-4.29 (1H, m), 4.48-4.69 (1H, m), 5.17 (2H, s), 5.63 (1H, dd, $J = 3.77, 8.20$ Hz), 6.90-7.04 (3H, m), 7.12-7.46 (7H, m), 7.59 (1H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 61.73, 64.79, 67.18, 114.64, 121.22, 123.58, 127.05, 128.35, 128.89, 129.03, 129.46, 135.80, 143.99, 158.04. ESI-MS: m/z 296 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 296.1393 found 296.1385. $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_3$



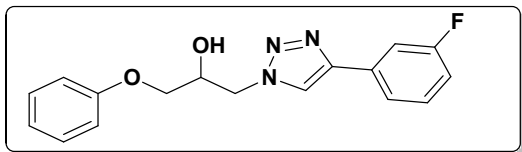
1-phenoxy-3-(4-phenyl-1H-1,2,3-triazol-1-yl)propan-2-ol (Table 1, entry 7) ^1H NMR (300 MHz, CDCl_3): δ 3.96-4.12 (2H, m), 4.43-4.62 (2H, m), 4.64-4.80 (1H, m), 6.78-7.06 (3H, m), 7.14-7.44 (5H, m), 7.54-7.73 (2H, m), 7.83 (1H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 53.36, 68.70, 68.81, 114.44, 121.38, 121.42, 125.44, 128.10, 128.74, 129.74, 129.95, 147.27, 158.07. ESI-MS: m/z 296 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 296.1393 found 296.1389. $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_3$



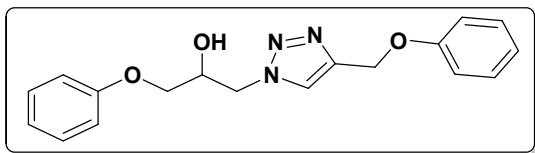
1-(4-(4-(tert-butyl)phenyl)-1H-1,2,3-triazol-1-yl)-3-phenoxypropan-2-ol (Table 1, entry 8) ^1H NMR (300 MHz, CDCl_3): δ 1.34 (9H, s), 3.55 (1H, s), 3.96-4.14 (2H, m), 4.47-4.62 (2H, m), 4.71 (1H, dd, $J = 2.44, 13.27$ Hz), 6.85-7.04 (3H, m), 7.21-7.49 (4H, m), 7.61-7.73 (2H, m), 7.84 (1H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 31.25, 34.61, 53.29, 68.80, 114.47, 121.10, 125.66, 127.19, 129.58, 147.29, 151.21, 158.09. ESI-MS: m/z 352 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 352.2019 found 352.2012. $\text{C}_{21}\text{H}_{26}\text{O}_2\text{N}_3$



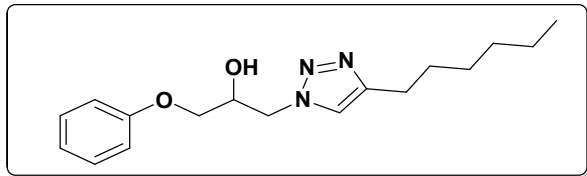
1-phenoxy-3-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)propan-2-ol (Table 1, entry 9) ^1H NMR (300 MHz, CDCl_3): δ 2.36 (3H, s), 4.02 (2H, dd, $J = 2.26, 4.72$ Hz), 4.44-4.61 (2H, m), 4.64-4.77 (1H, m), 6.78-7.05 (3H, m), 7.12-7.37 (4H, m), 7.60 (2H, d, $J = 8.12$ Hz), 7.81 (1H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 21.18, 53.32, 68.61, 68.81, 114.41, 120.99, 121.11, 121.27, 125.35, 127.12, 129.35, 129.48, 137.91, 147.28, 158.08. ESI-MS: m/z 310 ($\text{M}+\text{H}$) $^+$, 332 ($\text{M}+\text{Na}$). HRMS calcd. For 310.1550 found 310.1546. $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_3$



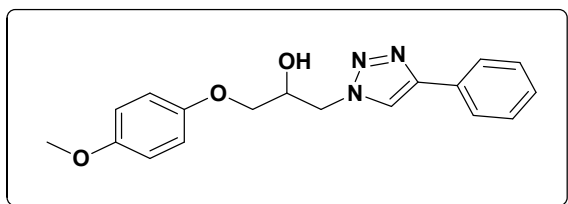
1-(4-(3-fluorophenyl)-1H-1,2,3-triazol-1-yl)-3-phenoxypropan-2-ol (Table 1, entry 10) ^1H NMR (300 MHz, CDCl_3): δ 3.96-4.13 (2H, m), 4.46-4.63 (2H, m), 4.65-4.80 (1H, m), 6.79-7.08 (4H, m), 7.17-7.55 (5H, m), 7.86-7.90 (1H, m); ^{13}C NMR (75 MHz, CDCl_3): δ 53.36, 63.58, 68.72, 112.20, 112.50, 114.42, 114.83, 115.11, 121.04, 121.47, 121.83, 130.30, 130.41, 146.25, 158.01, 161.36, 164.61. ESI-MS: m/z 314 ($\text{M}+\text{H}$) $^+$.



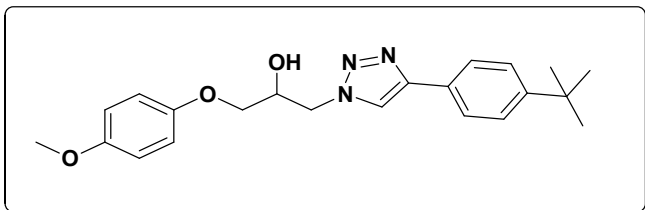
1-phenoxy-3-(4-(phoxymethyl)-1H-1,2,3-triazol-1-yl)propan-2-ol (Table 1, entry 11) ^1H NMR (300 MHz, CDCl_3): δ 3.84-4.14 (2H, m), 4.38-4.76 (3H, m), 5.15 (2H, t, $J = 19.87$ Hz), 6.76-7.07 (6H, m), 7.18-7.40 (4H, m), 7.75 (1H, t, $J = 19.98$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 53.00, 61.60, 68.63, 68.67, 114.42, 114.64, 121.20, 121.40, 124.42, 129.45, 129.50, 143.84, 157.95, 158.01. ESI-MS: m/z 326 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 326.1499 found 326.1494. $\text{C}_{18}\text{H}_{20}\text{O}_3\text{N}_3$



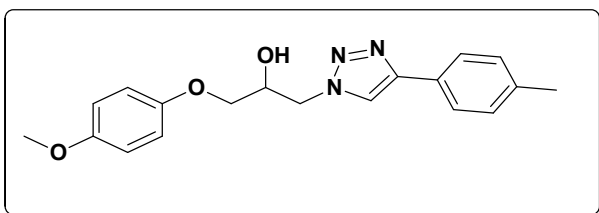
1-(4-hexyl-1H-1,2,3-triazol-1-yl)-3-phenoxypropan-2-ol (Table 1, entry 12) ^1H NMR (300 MHz, CDCl_3): δ 0.86 (3H, s), 1.27 (6H, s), 1.60 (2H, s), 2.63 (2H, s), 3.95 (2H, s), 4.30-4.77 (3H, m), 6.71-7.04 (3H, m), 7.12-7.49 (3H, m); ^{13}C NMR (75 MHz, CDCl_3): δ 13.88, 22.34, 25.27, 28.71, 29.06, 31.33, 52.82, 68.33, 68.63, 114.25, 121.06, 122.36, 129.31, 147.77, 158.00. ESI-MS: m/z 304 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 304.2019 found 304.2013. $\text{C}_{17}\text{H}_{26}\text{O}_2\text{N}_3$



1-(4-methoxyphenoxy)-3-(4-phenyl-1H-1,2,3-triazol-1-yl)propan-2-ol (Table 1, entry 13) ^1H NMR (300 MHz, CDCl_3): δ 3.52 (1H, d, $J = 4.72$ Hz), 3.76 (3H, s), 3.91-4.10 (2H, m), 4.40-4.63 (2H, m), 4.70 (1H, dd, $J = 2.83, 13.40$ Hz), 6.85 (4H, s), 7.21-7.47 (3H, m), 7.76 (2H, d, $J = 6.98$ Hz), 7.87 (1H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 53.01, 53.70, 68.98, 69.56, 114.74, 115.56, 121.27, 125.61, 128.17, 128.80, 130.23, 147.61, 152.18, 154.38. ESI-MS: m/z 326 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 326.1499 found 326.1492. $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_3$

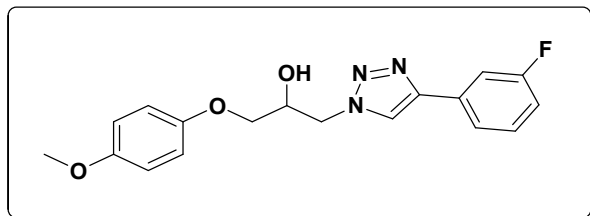


1-(4-(4-(tert-butyl)phenyl)-1H-1,2,3-triazol-1-yl)-3-(4-methoxyphenoxy)propan-2-ol (Table 1, entry 14) ^1H NMR (300 MHz, CDCl_3): δ 1.33 (9H, s), 3.76 (3H, s), 3.91-4.07 (2H, m), 4.43-4.59 (2H, m), 4.62-4.78 (1H, m), 6.83 (4H, dd, $J = 5.85, 7.17$ Hz), 7.41 (2H, d, $J = 8.30$ Hz), 7.62 (2H, d, $J = 8.30$ Hz), 7.82 (1H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 31.25, 34.60, 53.26, 55.67, 68.86, 69.66, 114.69, 115.53, 121.07, 125.23, 125.64, 127.25, 147.35, 151.18, 152.28, 154.28. ESI-MS: m/z 382 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 382.2125 found 382.2123. $\text{C}_{22}\text{H}_{28}\text{O}_3\text{N}_3$

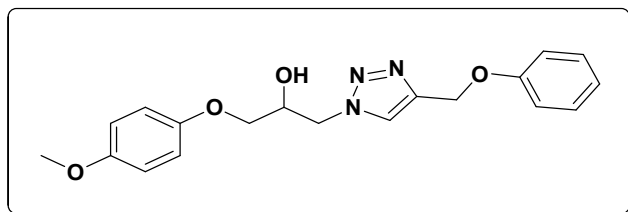


1-(4-methoxyphenoxy)-3-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)propan-2-ol (Table 1, entry 15) ^1H NMR (300 MHz, CDCl_3): δ 2.36 (3H, s), 3.76 (4H, s), 3.90-4.03 (2H, m), 4.42-4.61 (2H, m), 4.68 (1H, dd, $J = 2.74, 13.58$ Hz), 6.79-6.85 (4H, m), 7.19 (2H, d, $J = 7.78$ Hz), 7.61 (2H, d, $J = 7.78$ Hz), 7.82 (1H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 21.22, 53.17, 55.66, 68.83, 69.64, 114.67, 115.52,

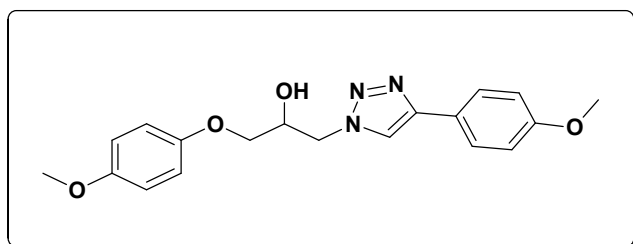
121.02, 125.45, 127.30, 129.41, 137.96, 147.47. ESI-MS: m/z 340 (M+H)⁺, 362 (M+Na). HRMS calcd. For 340.1655 found 340.1653. C₂₂H₂₈O₃N₃



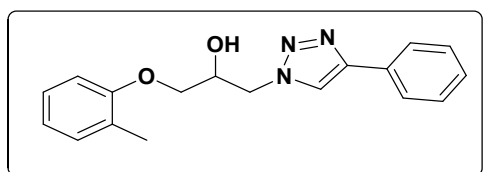
1-(4-(3-fluorophenyl)-1H-1,2,3-triazol-1-yl)-3-(4-methoxyphenoxy)propan-2-ol (Table 1, entry 16)
¹H NMR (300 MHz, CDCl₃): δ 3.76 (3H, s), 3.91-4.06 (2H, m), 4.42-4.60 (2H, m), 4.70 (1H, dd, J = 2.74, 13.42 Hz), 6.76-6.91 (4H, m), 6.94-7.01 (1H, m), 7.30-7.36 (1H, m), 7.42-7.44 (1H, m), 7.47-7.51 (1H, m), 7.88 (1H, s); ¹³C NMR (75 MHz, CDCl₃): δ 53.32, 55.65, 68.81, 69.58, 112.21, 112.52, 114.67, 115.10, 115.47, 121.06, 121.79, 130.30, 132.11, 146.28, 152.17, 154.28, 161.37, 164.63. ESI-MS: m/z 344 (M+H)⁺. HRMS calcd. For 344.1405 found 344.1400. C₁₈H₁₉O₃N₃F



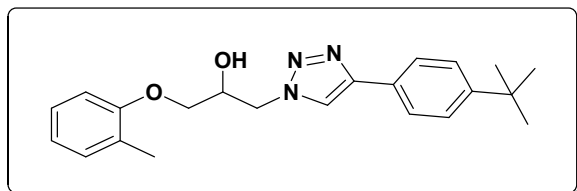
1-(4-methoxyphenoxy)-3-(4-(phoxymethyl)-1H-1,2,3-triazol-1-yl)propan-2-ol (Table 1, entry 17)
¹H NMR (300 MHz, CDCl₃): δ 3.76 (3H, s), 3.83-4.02 (2H, m), 4.35-4.59 (2H, m), 4.67 (1H, dd, J = 3.58, 13.97 Hz), 5.20 (2H, s), 6.82 (4H, s), 6.91-7.02 (3H, m), 7.22-7.33 (2H, m), 7.76 (1H, s); ¹³C NMR (75 MHz, CDCl₃): δ 52.98, 55.50, 68.53, 69.47, 114.55, 115.39, 121.13, 124.48, 129.37, 143.59, 152.08, 154.06, 157.94. ESI-MS: m/z 356 (M+H)⁺. HRMS calcd. For 356.1604 found 356.1602. C₁₉H₂₂O₄N₃



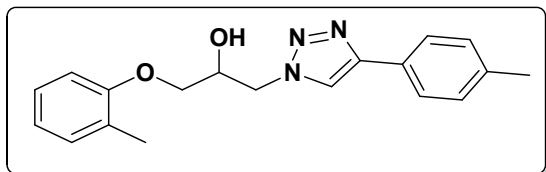
1-(4-methoxyphenoxy)-3-(4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)propan-2-ol (Table 1, entry 18)
¹H NMR (300 MHz, CDCl₃): δ 3.76 (3H, s), 3.91-4.04 (2H, m), 4.45-4.58 (2H, m), 4.63-4.75 (1H, m), 6.73-6.98 (6H, m), 7.60-7.67 (2H, m), 7.77 (1H, s); ESI-MS: m/z 356 (M+H)⁺. HRMS calcd. For 356.1604 found 356.1599. C₁₉H₂₂O₄N₃



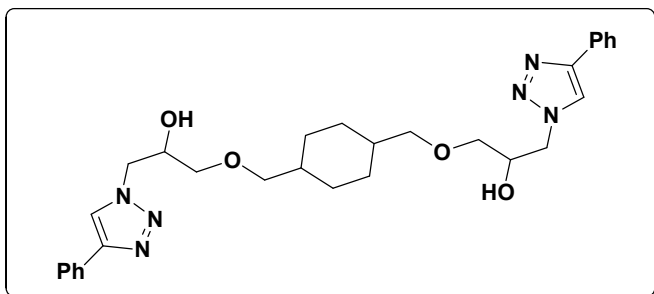
1-(4-phenyl-1H-1,2,3-triazol-1-yl)-3-(o-tolyloxy)propan-2-ol (Table 1, entry 19) ^1H NMR (300 MHz, CDCl_3): δ 2.25 (3H, s), 4.05 (2H, d, $J = 5.49$ Hz), 4.48-4.57 (2H, m), 4.72 (1H, dd, $J = 1.83, 13.73$ Hz), 6.80 (1H, d, $J = 8.39$ Hz), 6.89 (1H, t, $J = 7.32$ Hz), 7.14 (2H, t, $J = 7.32$ Hz), 7.27-7.36 (3H, m), 7.59-7.72 (2H, m), 7.83 (1H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 16.23, 53.58, 68.75, 68.96, 111.04, 121.03, 121.42, 125.39, 126.55, 126.87, 128.06, 128.71, 129.91, 130.74, 147.17, 156.14. ESI-MS: m/z 310 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 310.1550 found 310.1543. $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_3$



1-(4-(4-(tert-butyl)phenyl)-1H-1,2,3-triazol-1-yl)-3-(o-tolyloxy)propan-2-ol (Table 1, entry 20) ^1H NMR (300 MHz, CDCl_3): δ 1.33 (9H, s), 2.16 (3H, s), 4.04 (2H, d, $J = 5.09$ Hz), 4.44-4.62 (2H, m), 4.72 (1H, d, $J = 10.95$ Hz), 6.72-6.96 (2H, m), 7.04-7.21 (2H, m), 7.37 (2H, d, $J = 8.30$ Hz), 7.55-7.72 (2H, m), 7.82 (1H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 16.25, 31.19, 34.54, 53.58, 68.75, 68.99, 111.04, 120.98, 121.14, 126.87, 130.73, 147.16, 151.09, 156.17. ESI-MS: m/z 366 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 366.2176 found 366.2169. $\text{C}_{22}\text{H}_{28}\text{O}_2\text{N}_3$

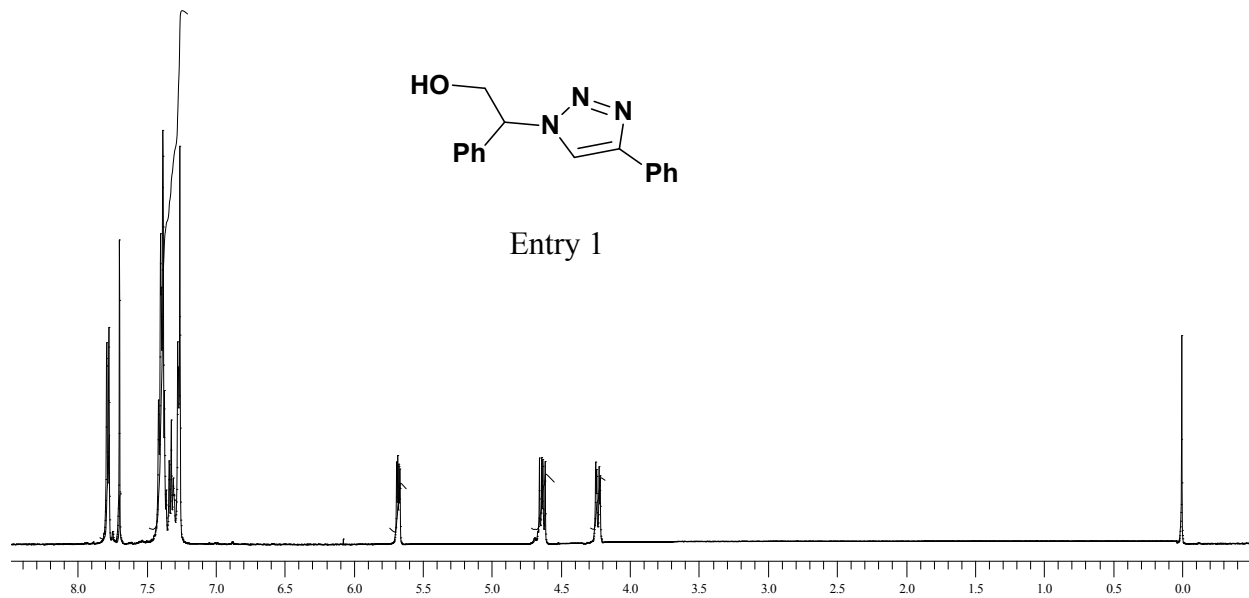


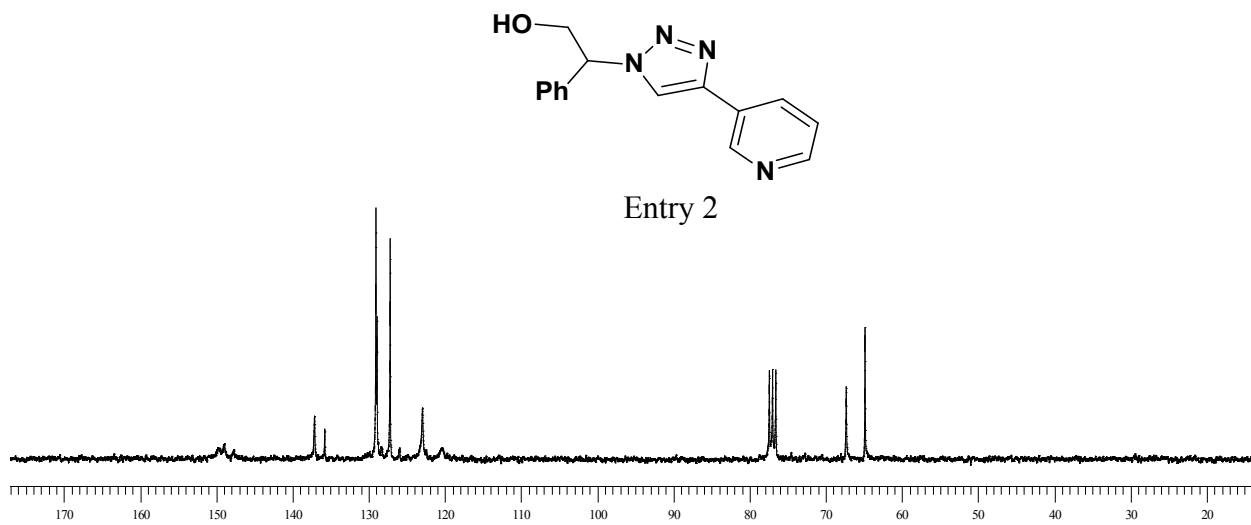
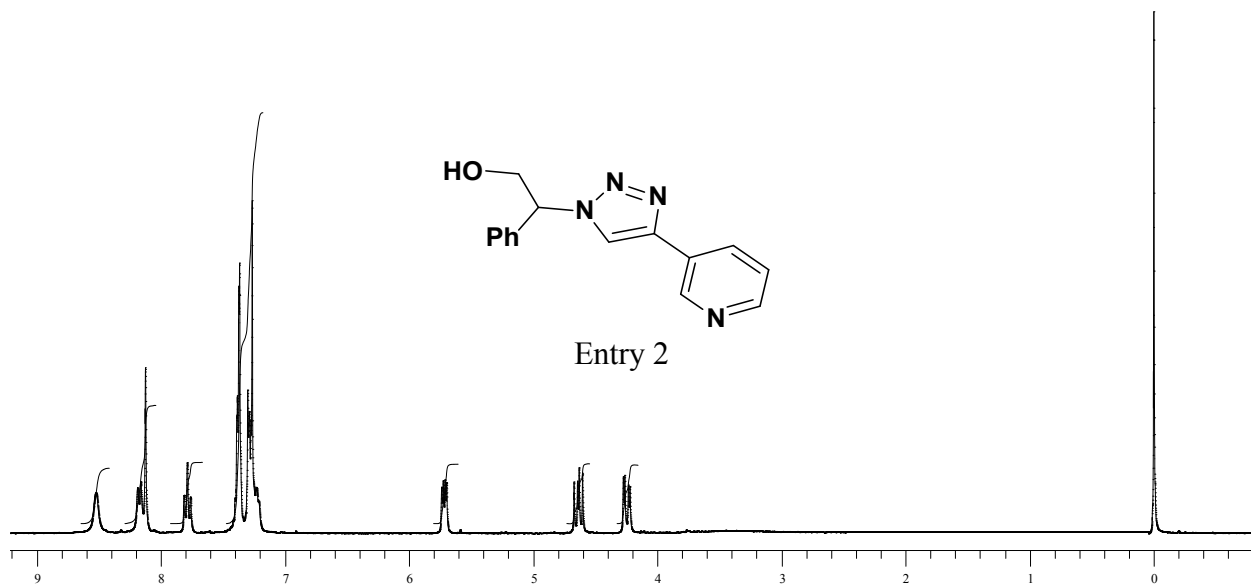
1-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)-3-(o-tolyloxy)propan-2-ol (Table 1, entry 21) ^1H NMR (300 MHz, CDCl_3): δ 2.25 (3H, s), 2.36, (3H, s), 4.02 (2H, d, $J = 5.18$ Hz), 4.44-4.62 (2H, m), 4.65-4.80 (1H, m), 6.80 (1H, d, $J = 8.24$ Hz), 6.90 (1H, t, $J = 7.47$ Hz), 7.09-7.24 (4H, m), 7.51-7.67 (2H, m), 7.73-7.87 (1H, m); ^{13}C NMR (75 MHz, CDCl_3): δ 16.23, 21.22, 53.32, 68.93, 111.18, 121.00, 121.15, 125.48, 126.60, 126.93, 127.32, 129.41, 130.80, 137.98, 147.53, 156.14. ESI-MS: m/z 324 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 324.1706 found 324.1701. $\text{C}_{19}\text{H}_{22}\text{O}_2\text{N}_3$

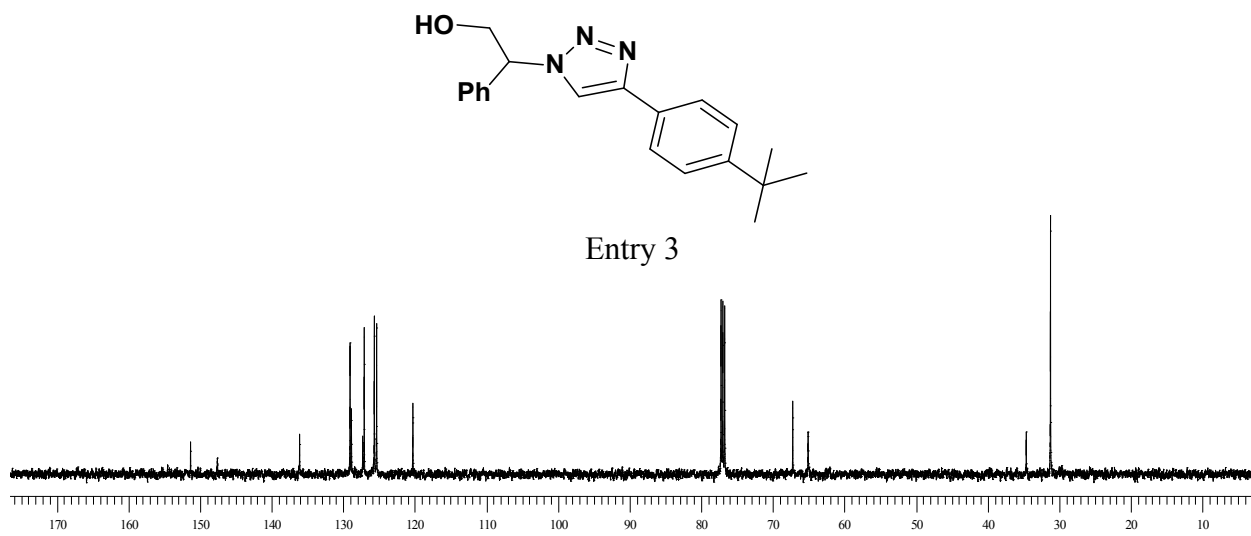
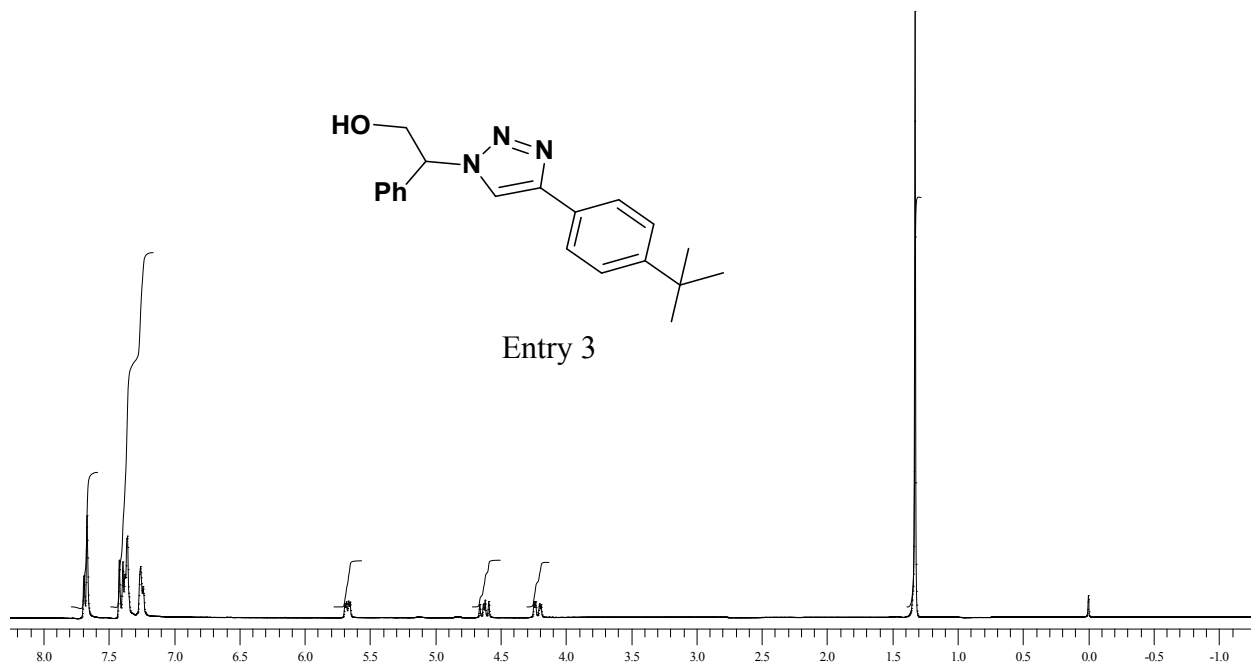


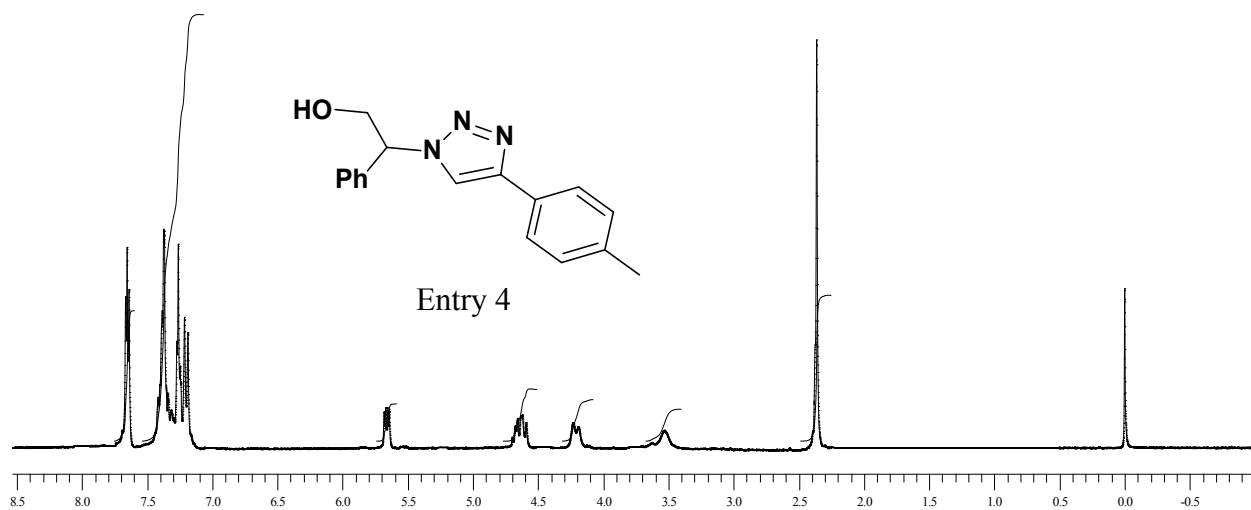
3,3'-((cyclohexane-1,4-diylbis(methylene))bis(oxy))bis(1-(4-phenyl-1H-1,2,3-triazol-1-yl)propan-2-ol) (Table 1, entry 22) ^1H NMR (300 MHz, CDCl_3): δ 0.75-1.06 (4H, m), 1.78 (4H, m), 1.99-2.12 (2H, m), 3.09-3.95 (12H, m), 4.10 (1H, dd, $J = 6.86, 14.03$ Hz), 4.25 (1H, s), 4.35-4.45 (1H, m), 4.59 (1H, d, $J = 14.03$ Hz), 7.17-7.52 (6H, m), 7.64-8.00 (6H, m); ESI-MS: m/z 547 ($\text{M}+\text{H}$) $^+$. HRMS calcd. For 547.3027 found 547.3016. $\text{C}_{30}\text{H}_{39}\text{O}_4\text{N}_6$

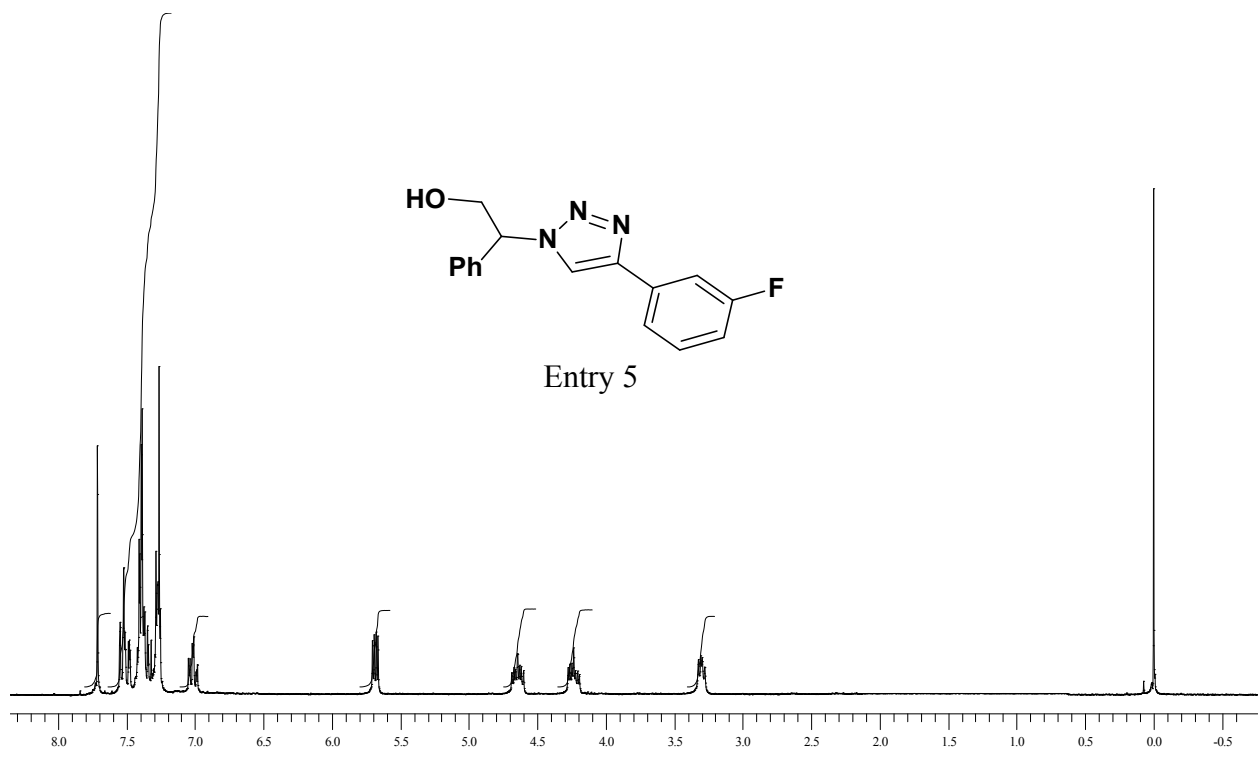
Copies of ^1H & ^{13}C NMR spectra:

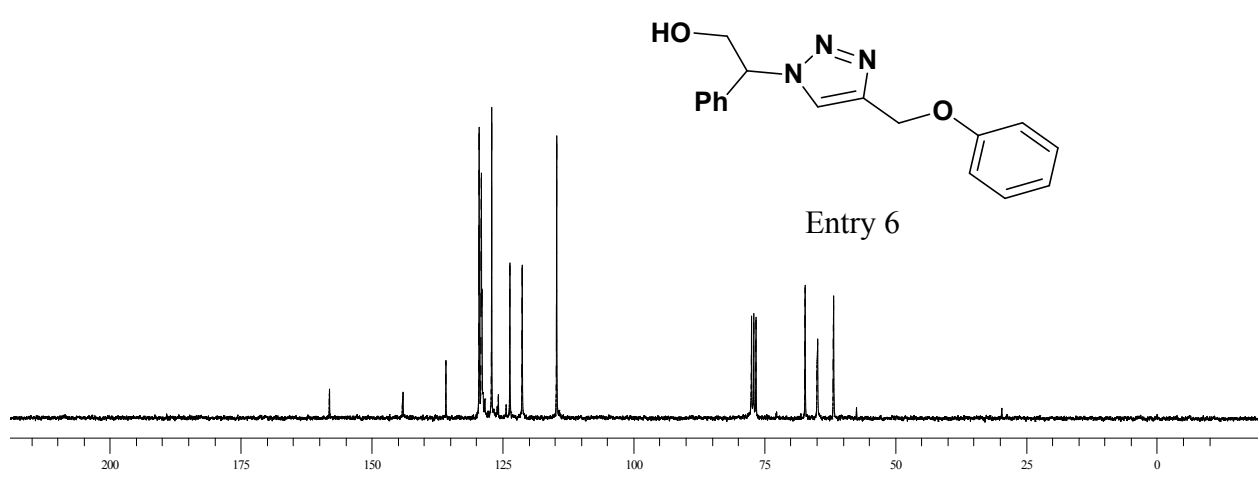
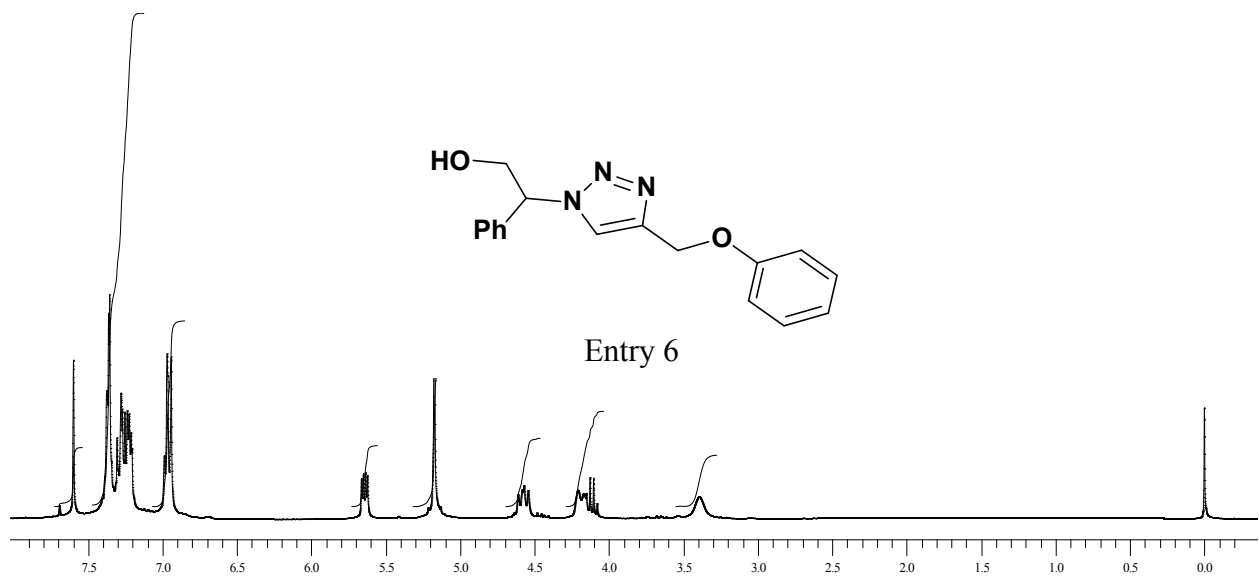


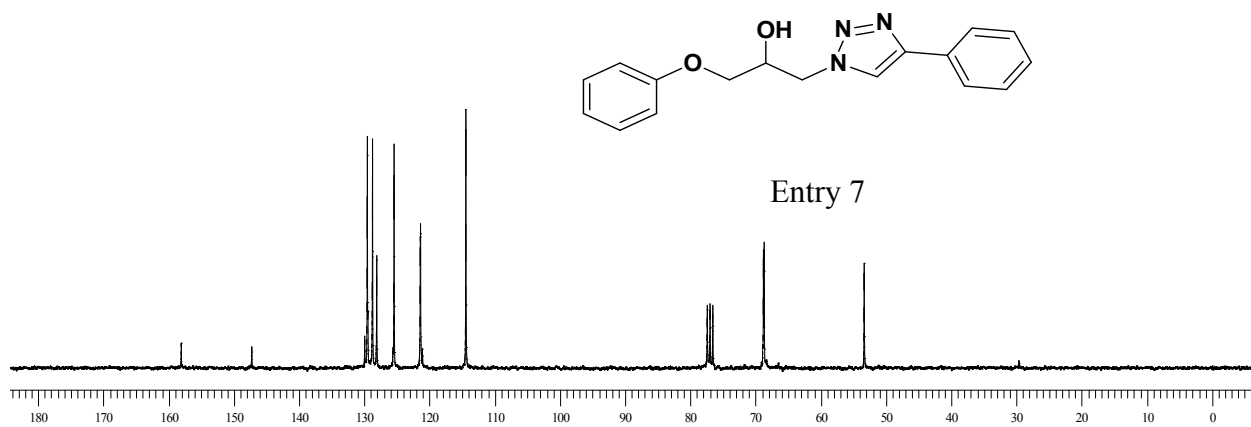
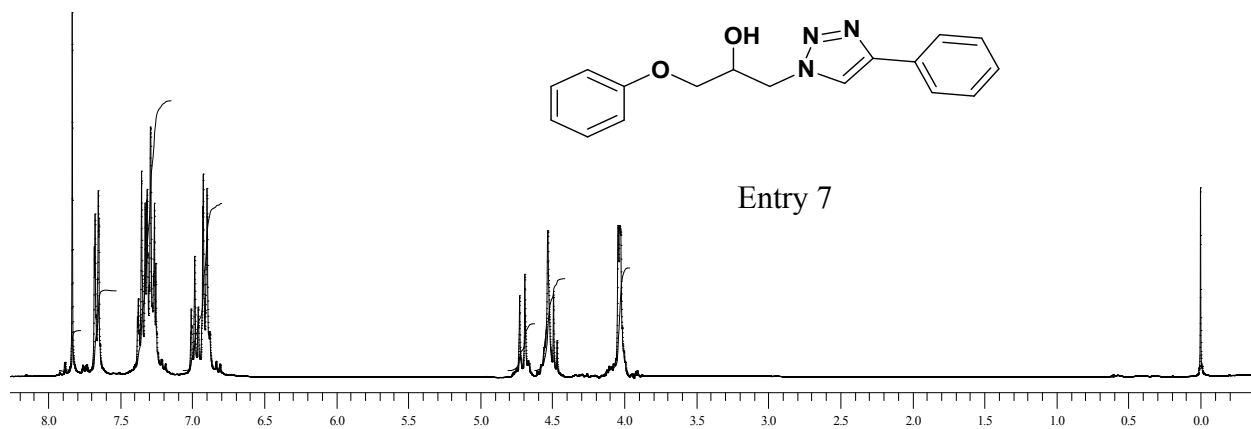


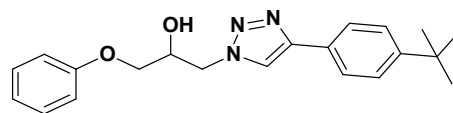




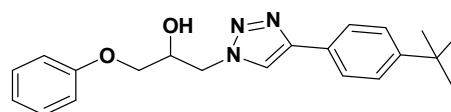
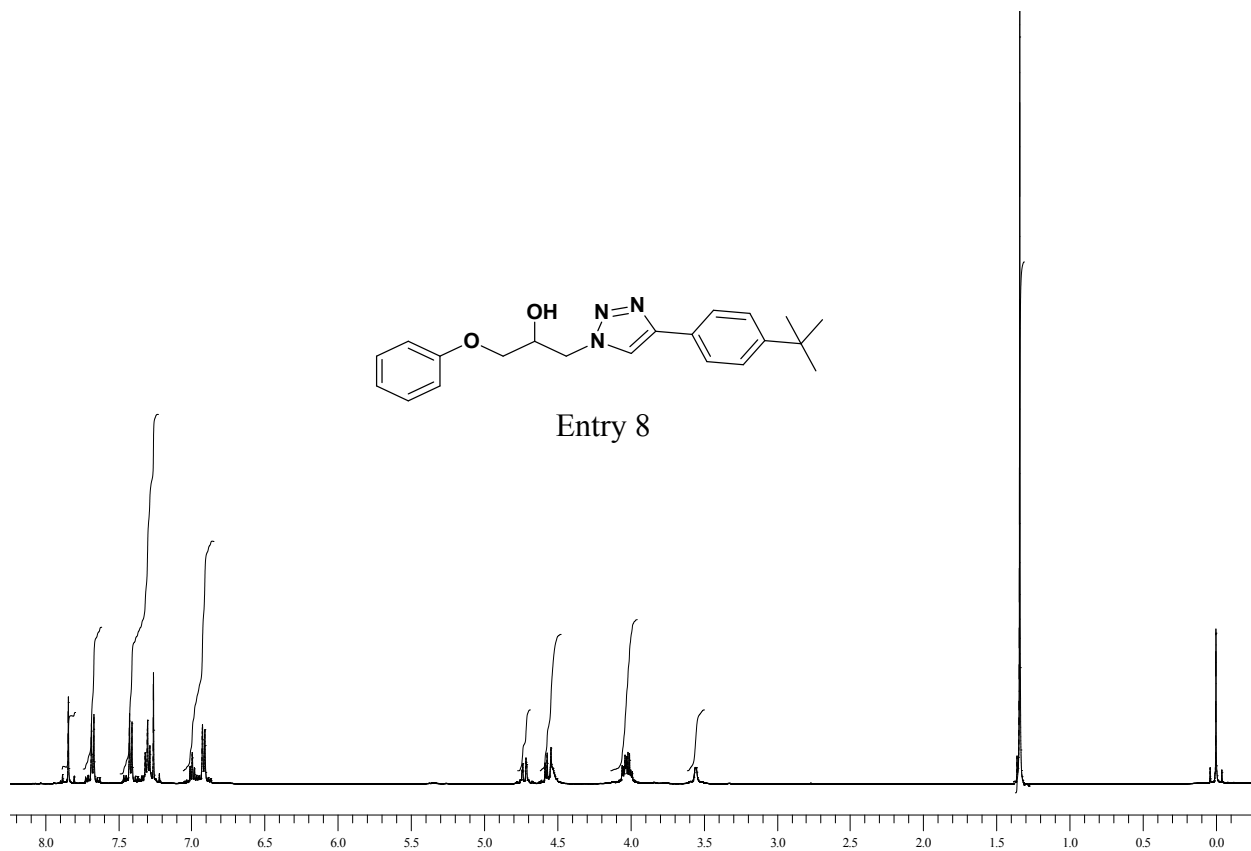




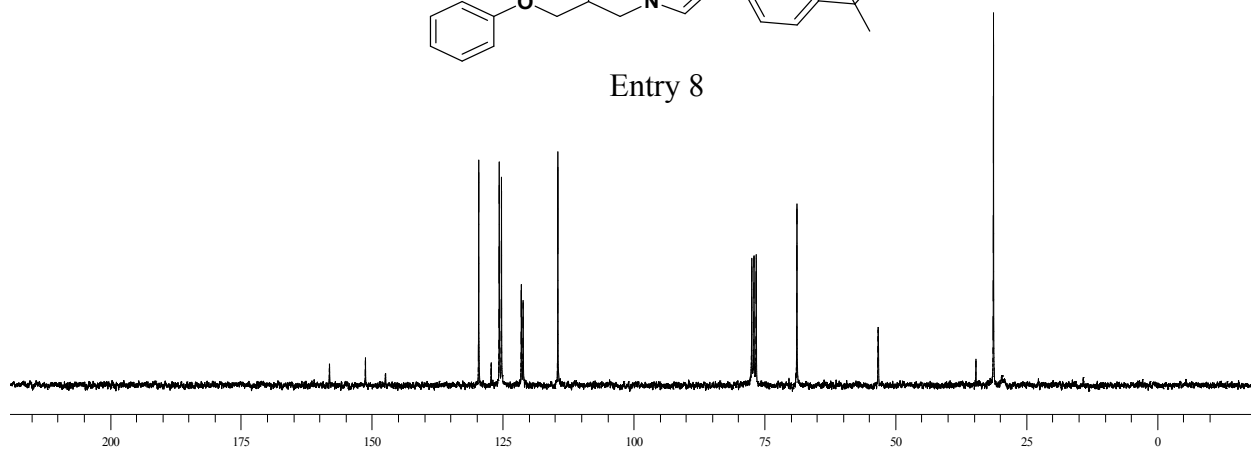


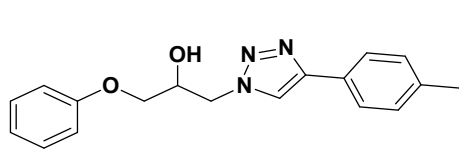


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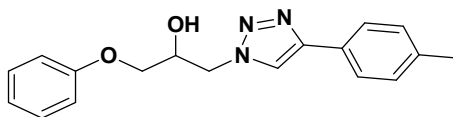
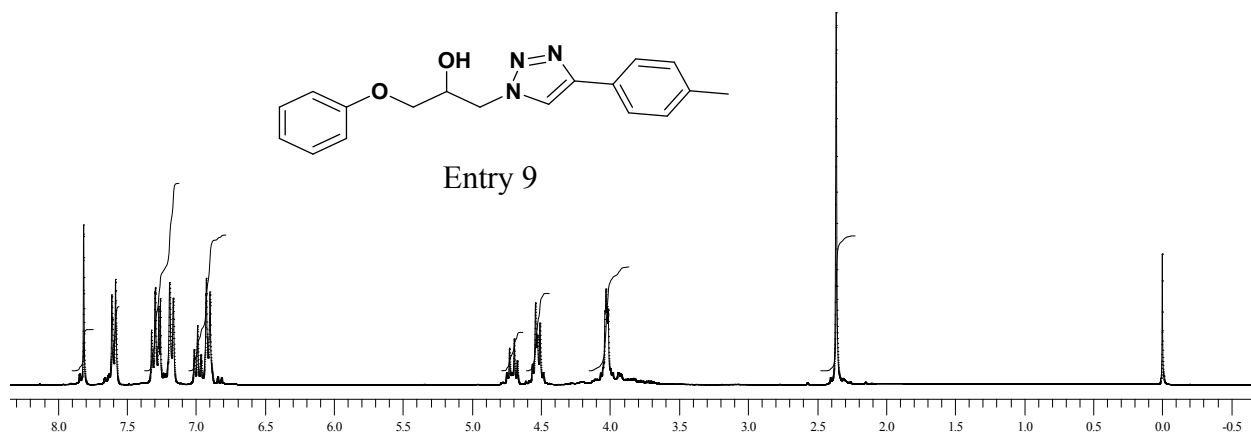


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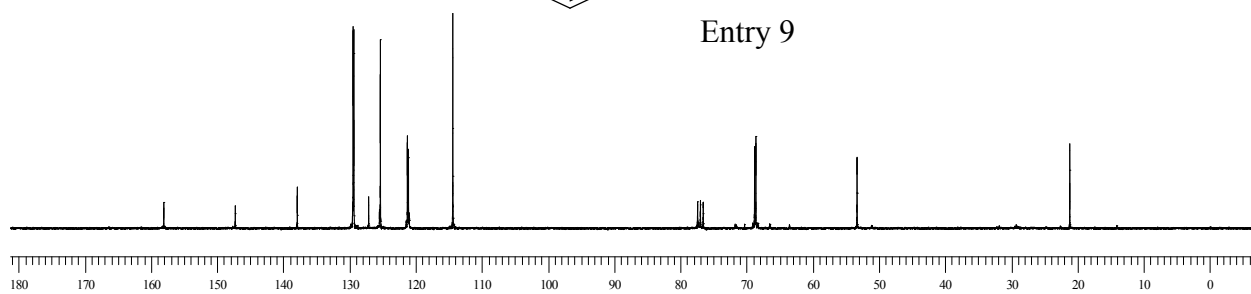


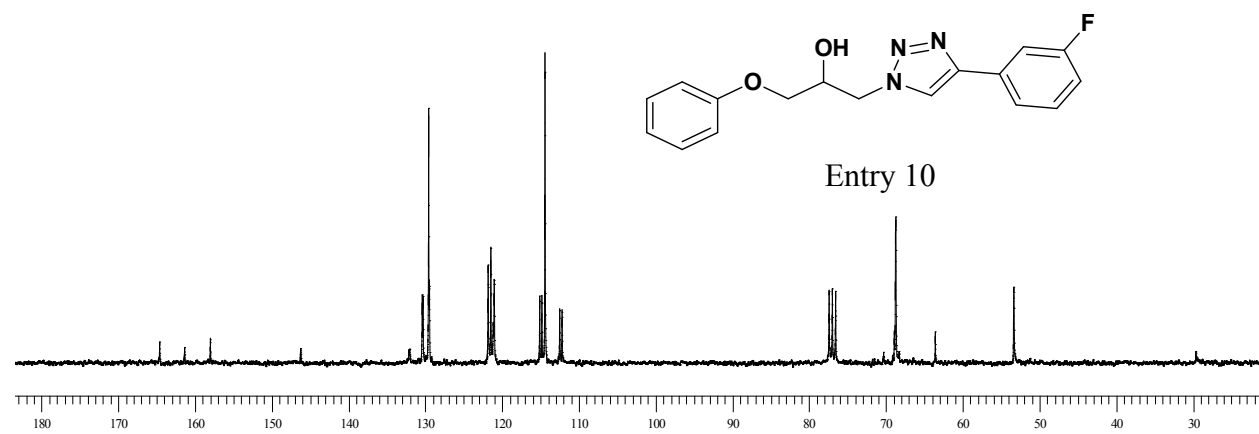
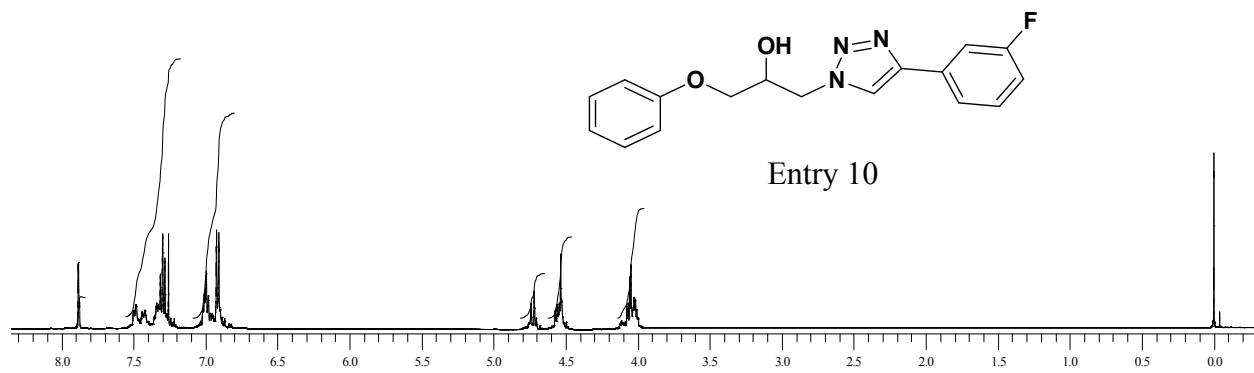


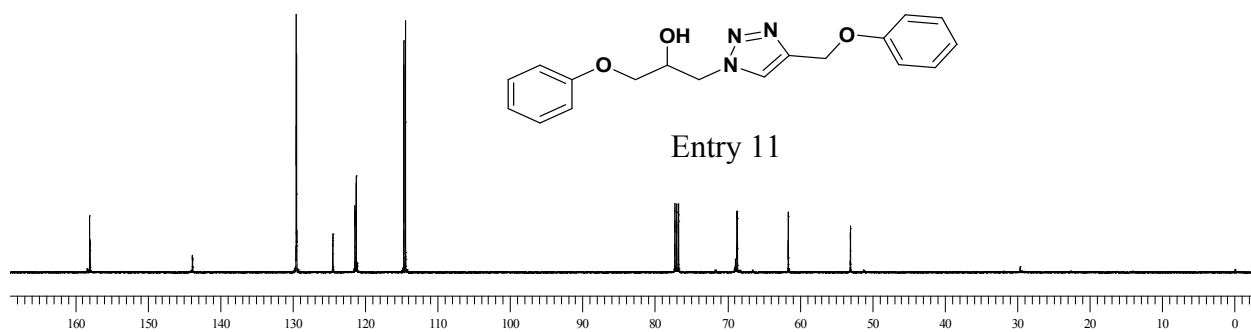
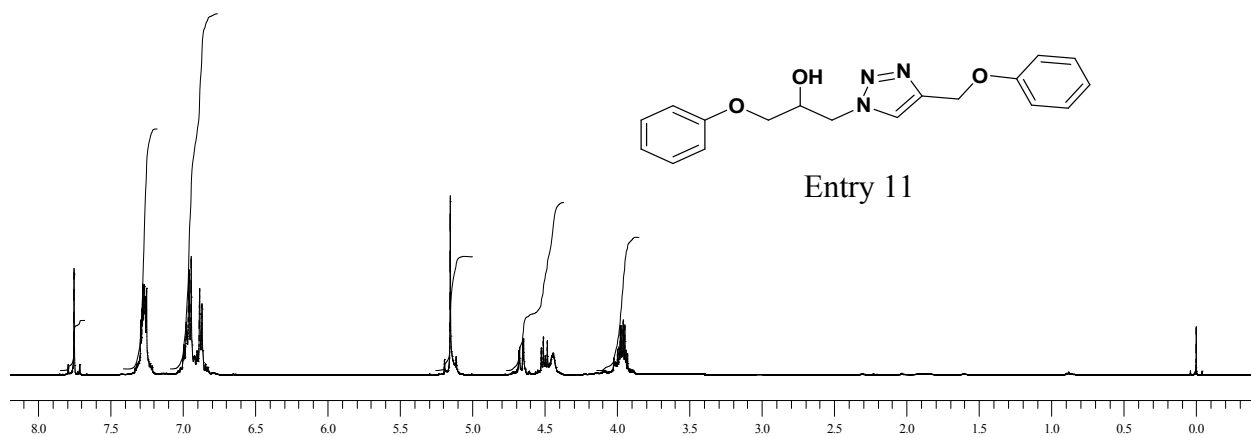
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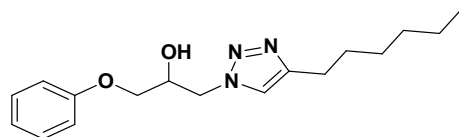


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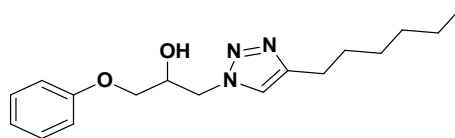
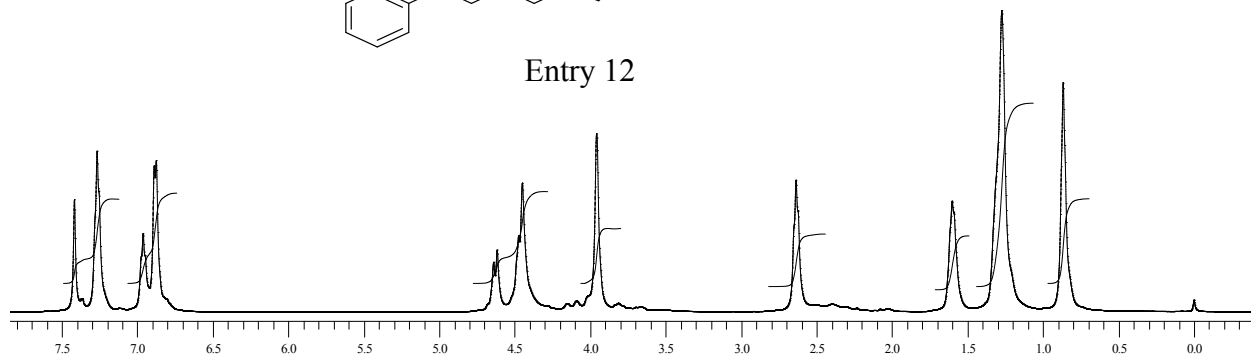




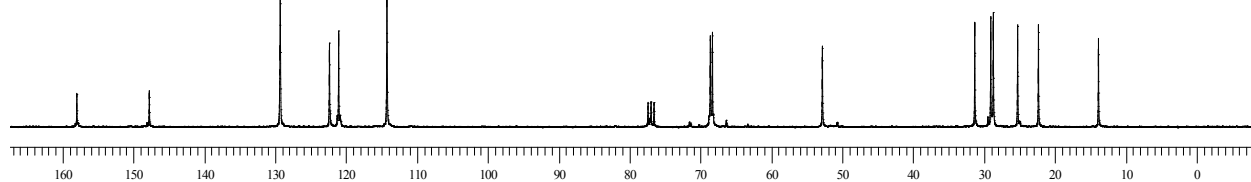


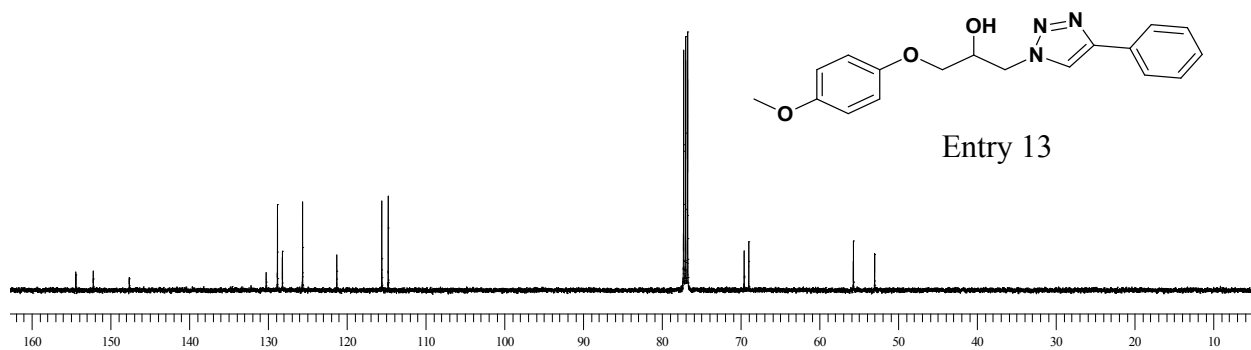
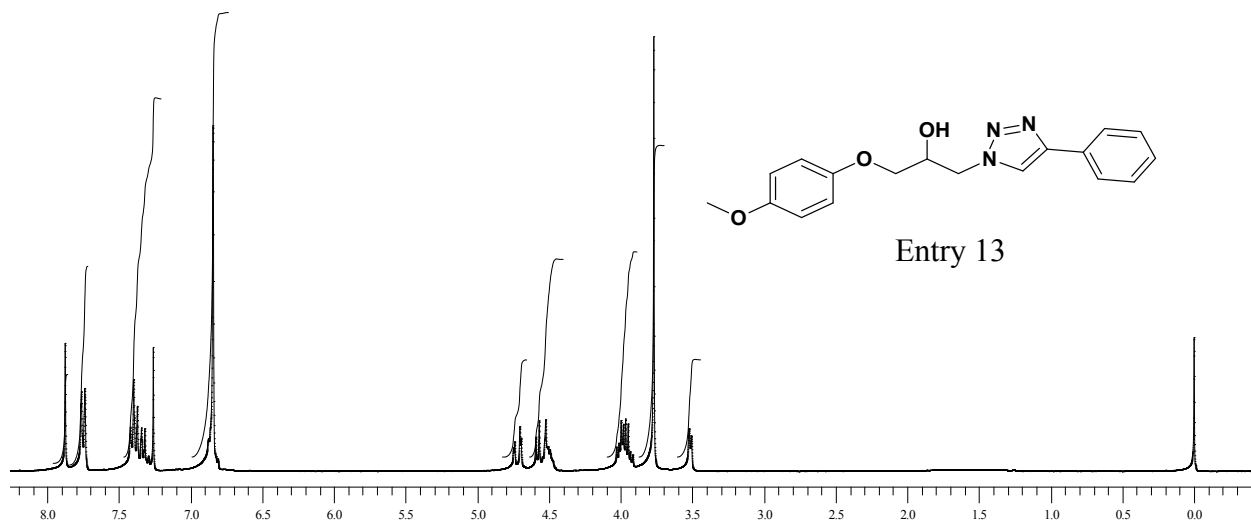


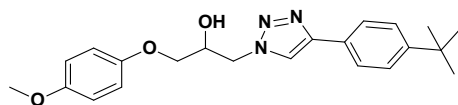
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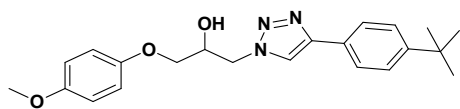
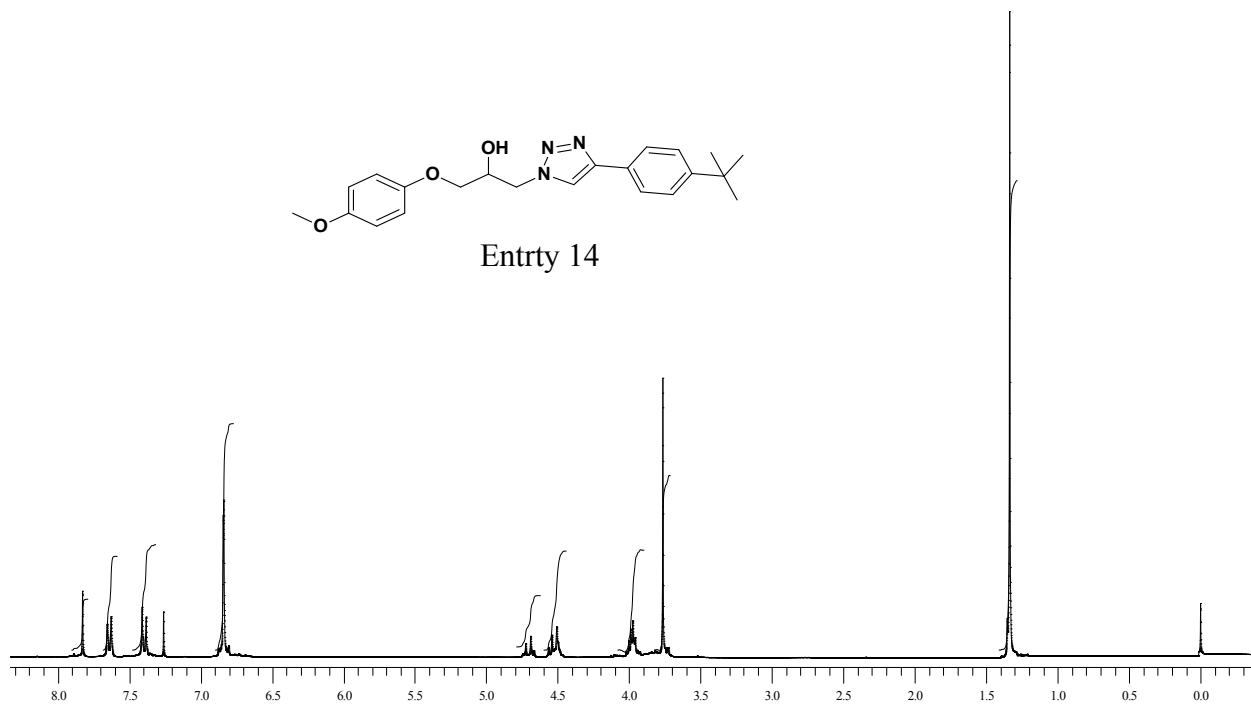
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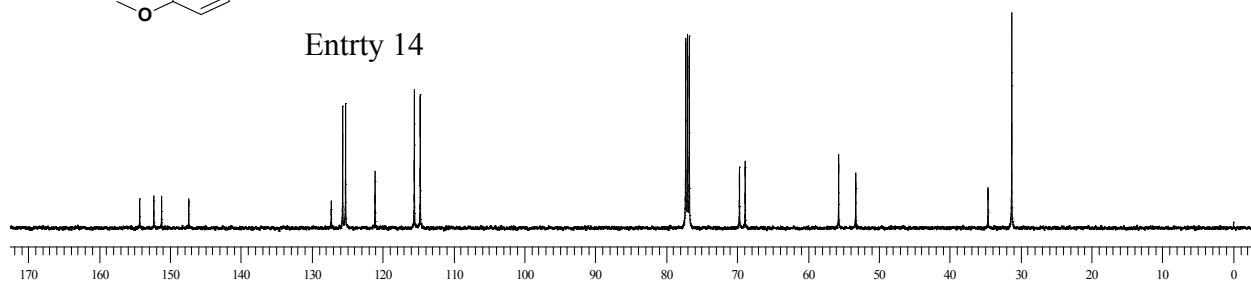


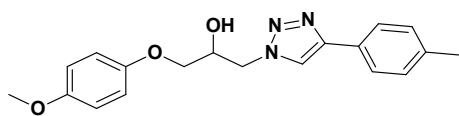


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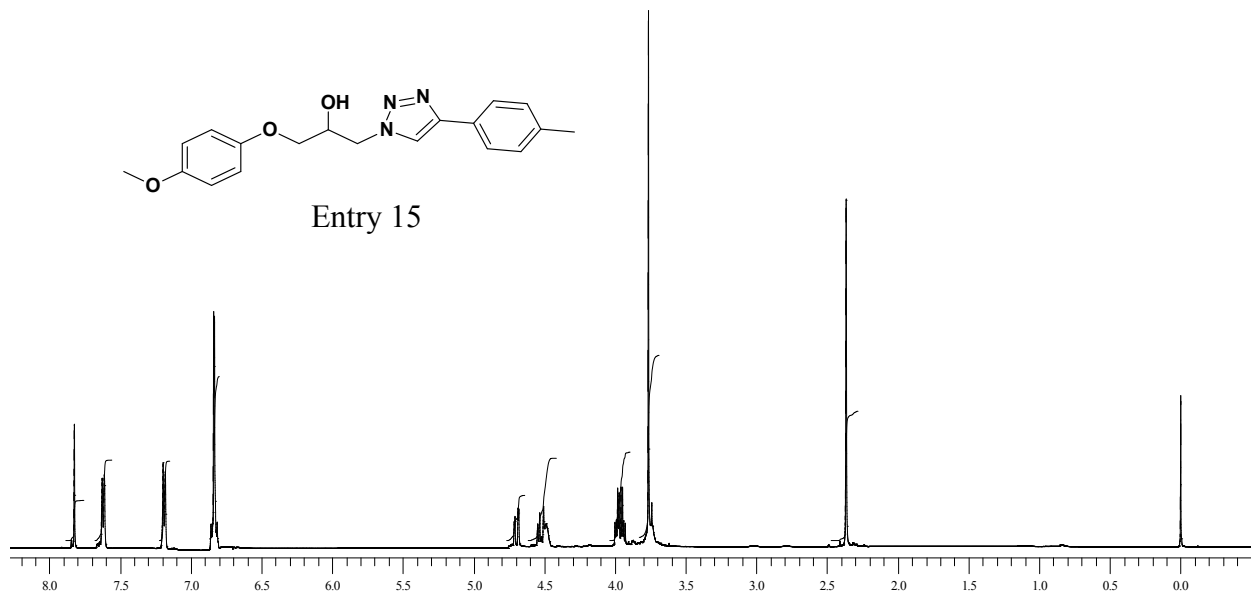


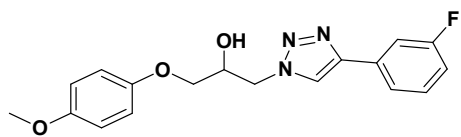
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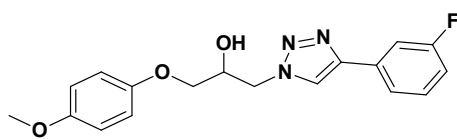
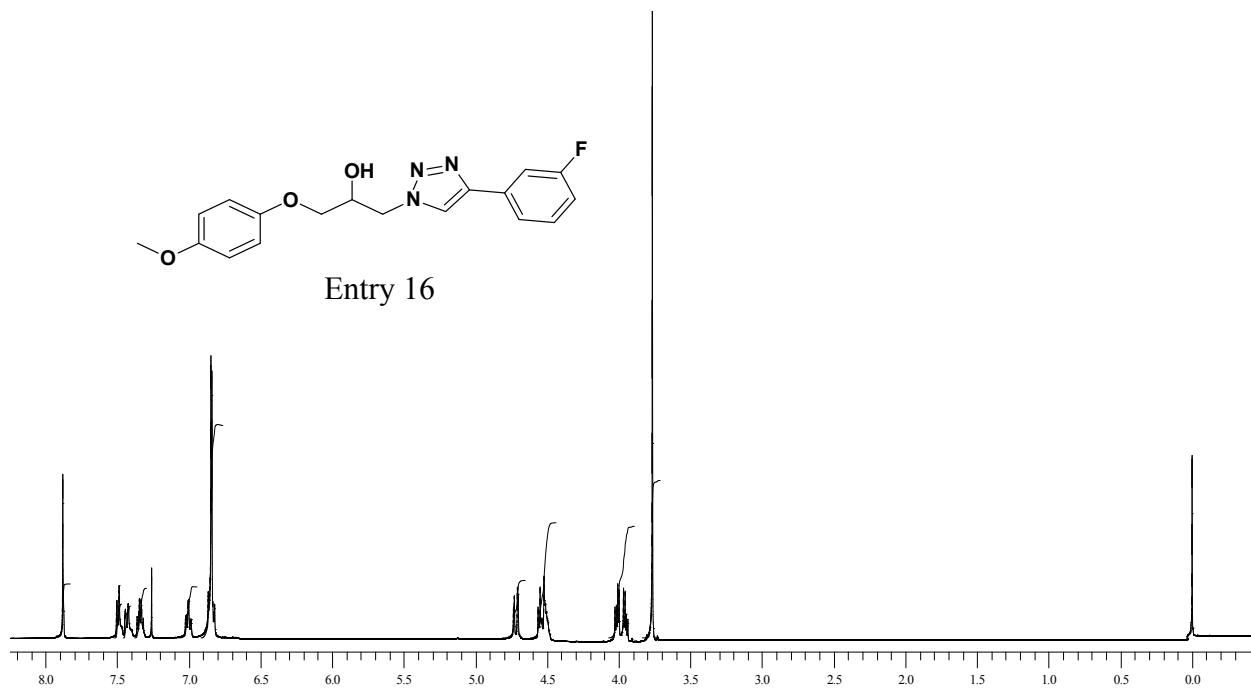


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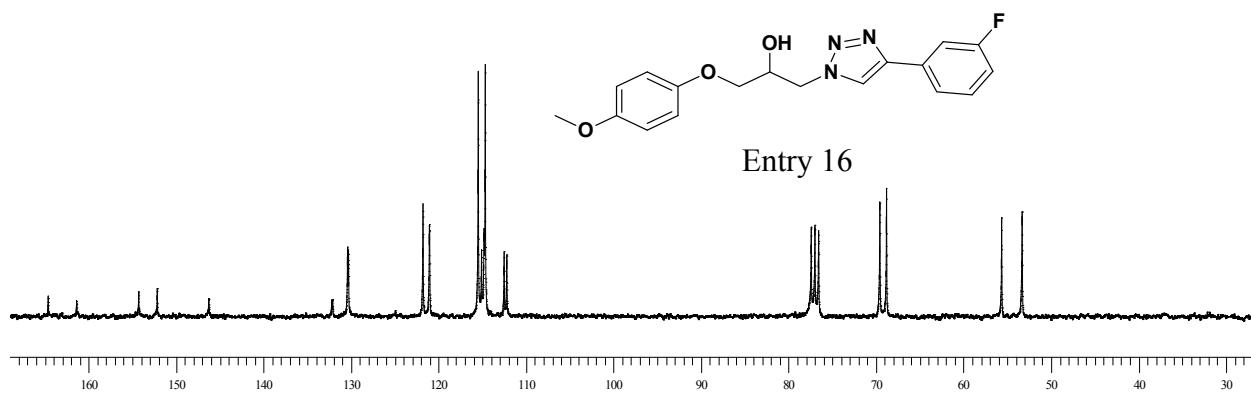


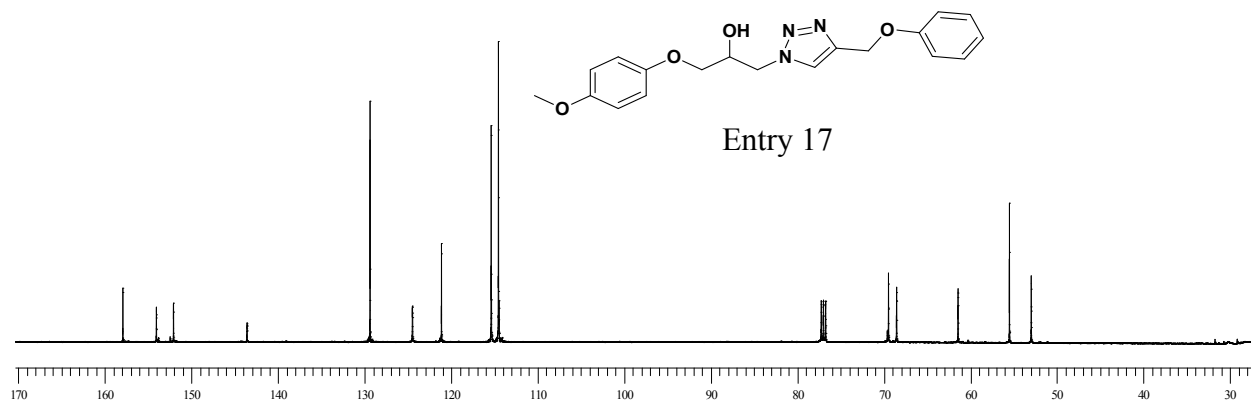
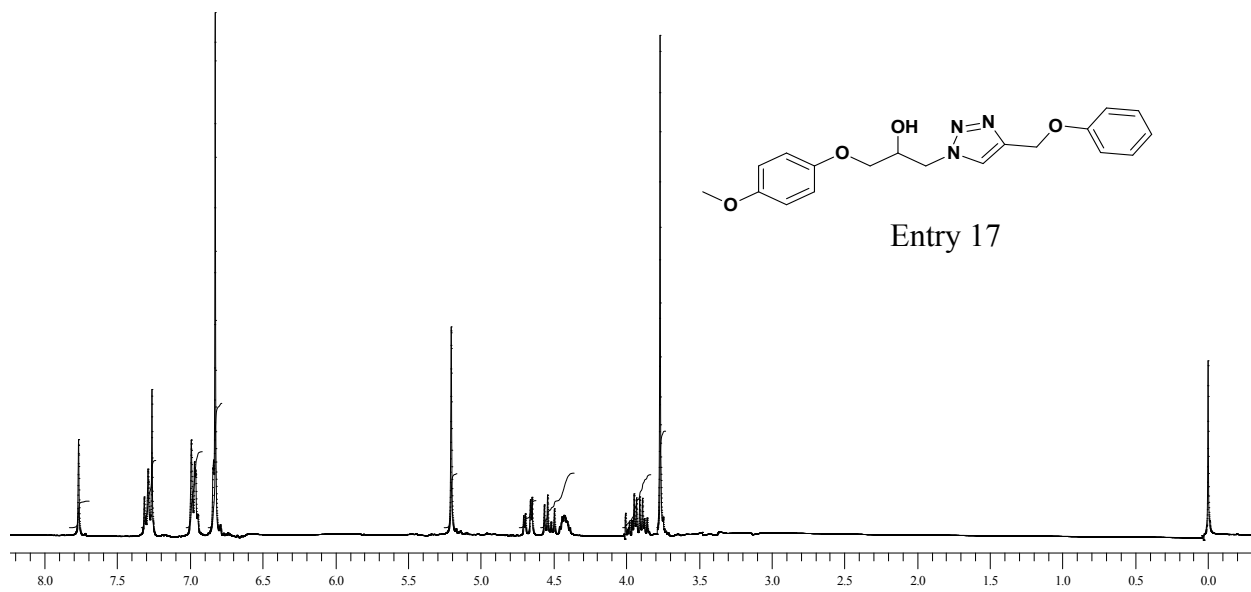


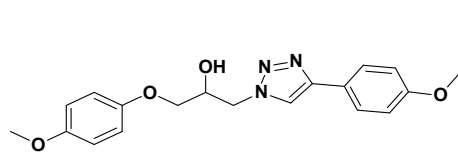
Entry 16



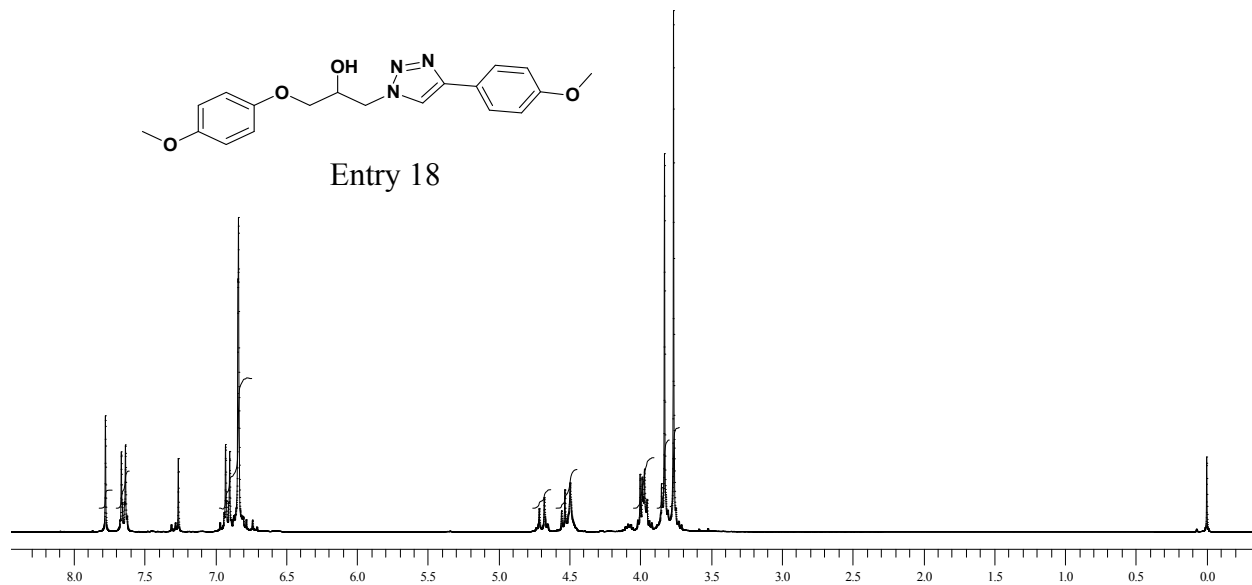
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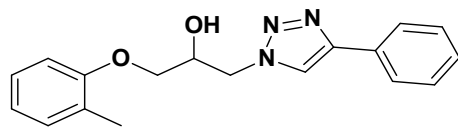




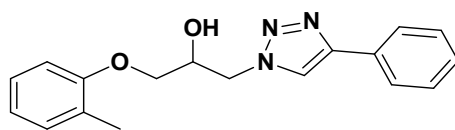
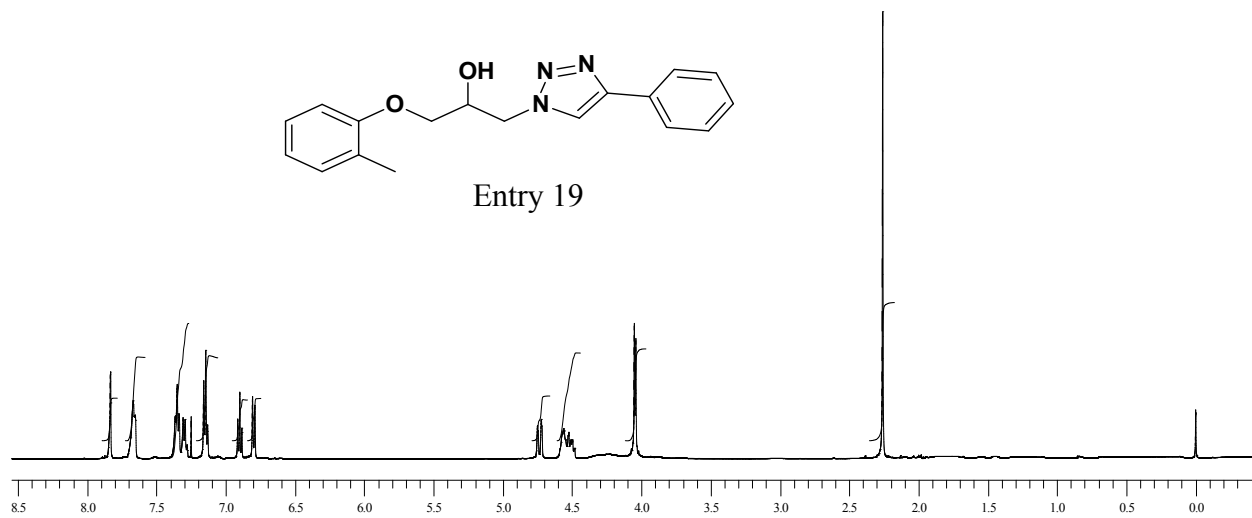


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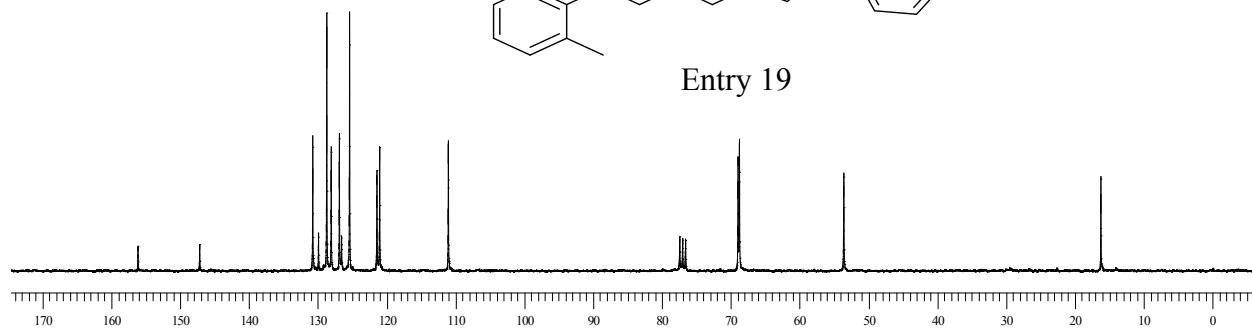


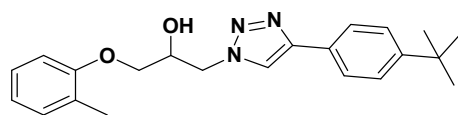


Entry 19

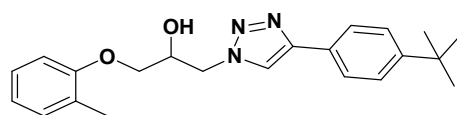
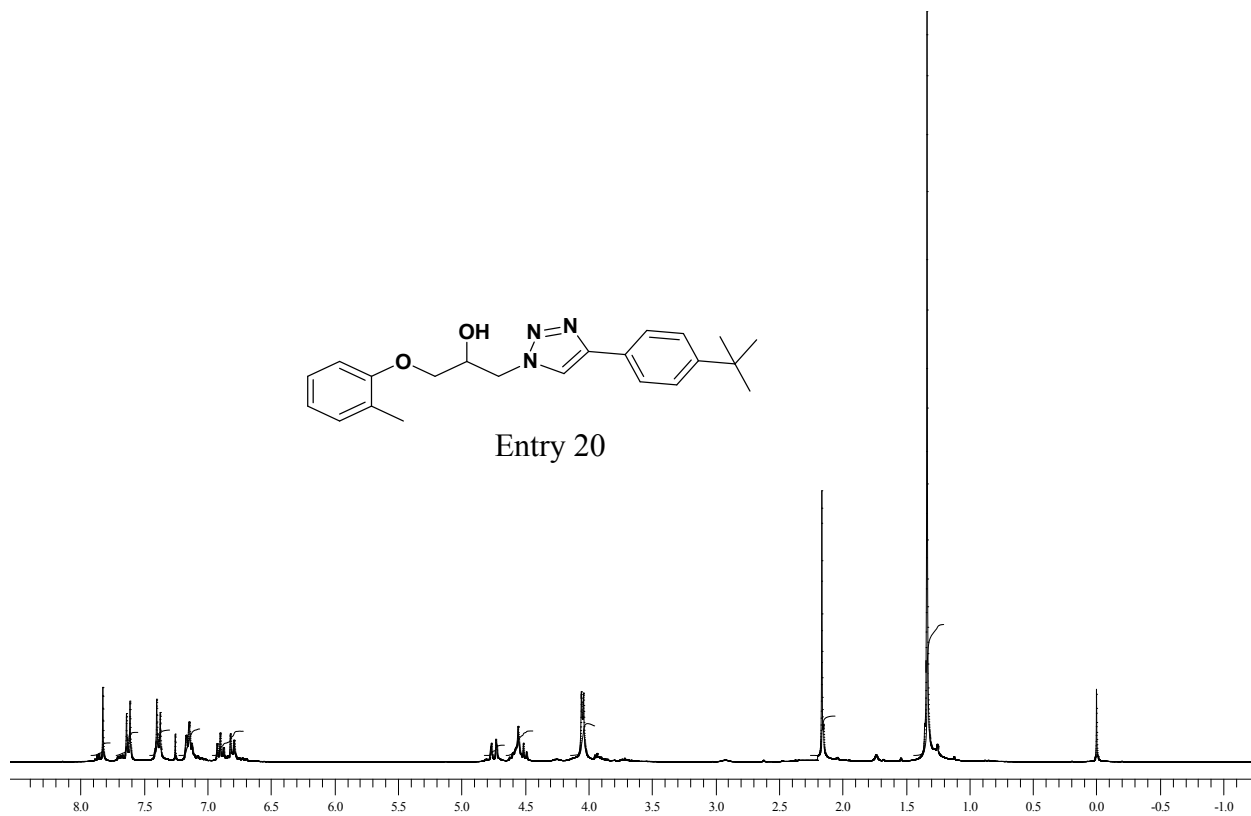


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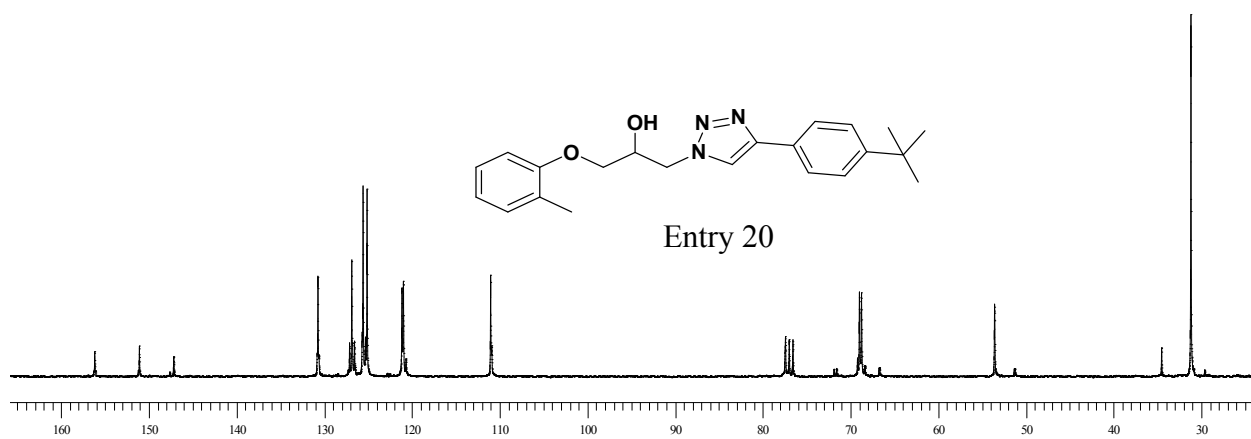


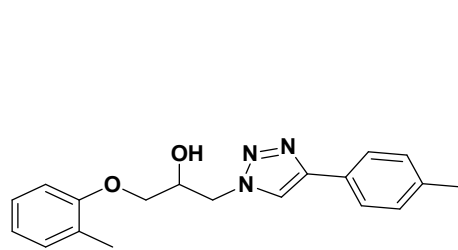


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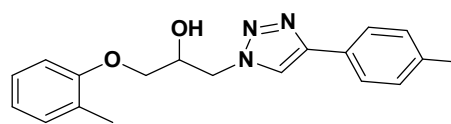
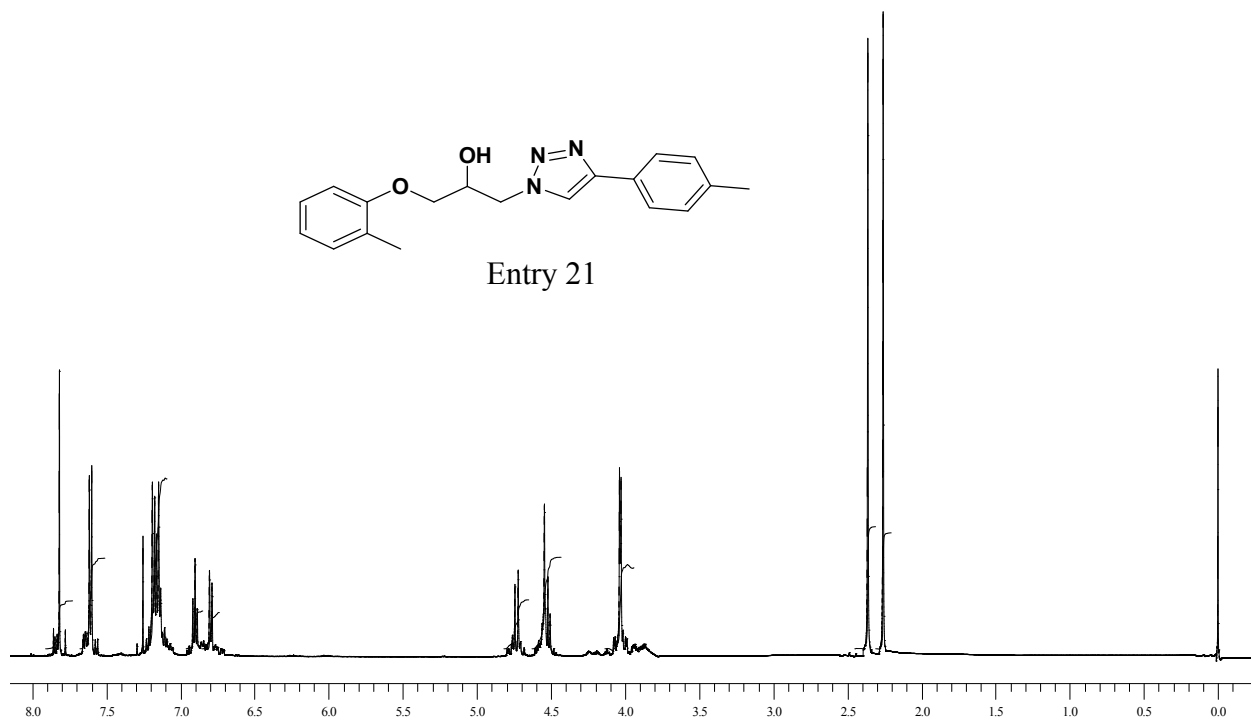


Entry 20





Entry 21



Entry 21

