Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Highly Selective Direct Azidation of Alcohols over Heterogeneous Povidone – Phosphotungstic Solid Acid Catalyst

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Supporting Information for New Journal OF Chemistry

Contents

Experimental procedure for the synthesis of alcohols

To the ice cold solution of ketone (10 mmol) in methanol (20 mL), sodium borohydride (5 mmol) was slowly added under stirring. Then, the mixture was further stirred for 1 h at 0 ^{o}C followed by 1 h at room temperature. After completion of the reaction monitored by TLC, mixture was extracted with ethyl acetate and washed with water. Evaporation of the ethyl acetate gave alcohol up to 95-99% yields.

XRD of fresh and recovered PVP-PWA (3:1)

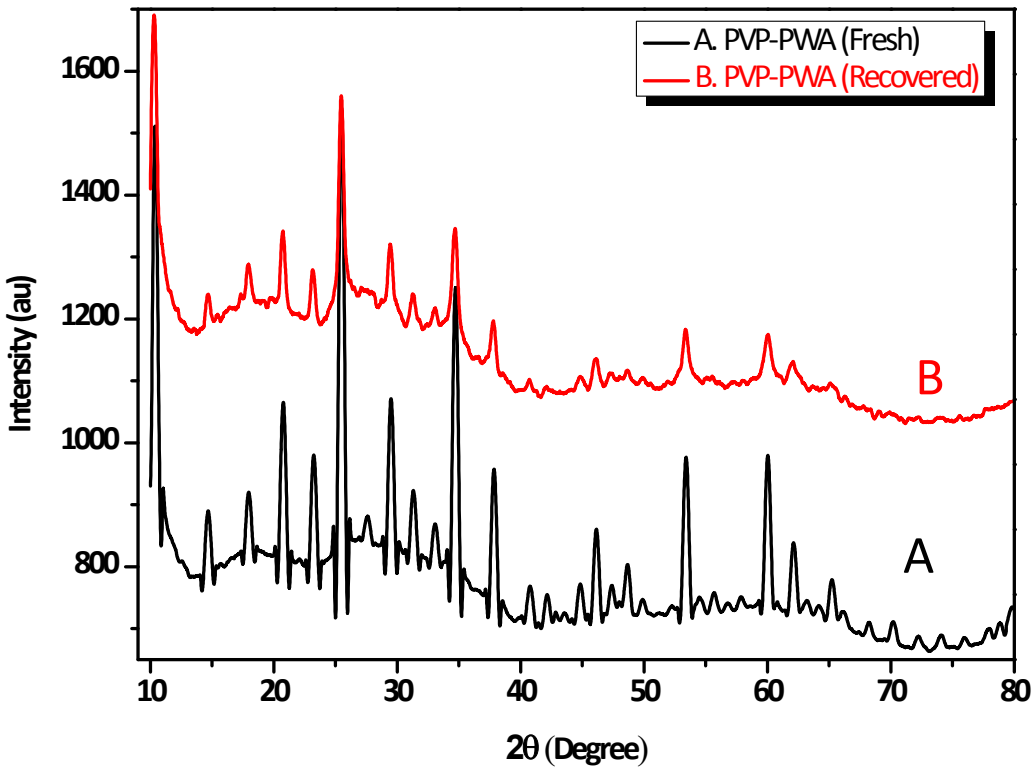
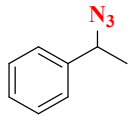


Fig. S1 XRD of A. Fresh and B. Recovered PVP-PWA (3:1)

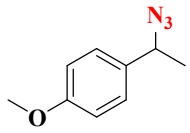
Spectroscopic data of all the compounds

All the compounds were confirmed using reported literature.[11-15, 21-24]



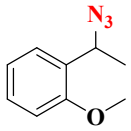
(1-azidoethyl)benzene, Table 3, Entry 1.

FT-IR (υ max**):** 2926, 2103, 1727, 1601, 1494, 1452, 1372, 1243, 1066, 1066, 762, 737, 700 $cm^{-1.}$ **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 7.28 - 7.44 (m, 5 H), 5.89 (q, *J*=6.6 Hz, 1 H), 1.55 ppm (d, *J*=6.6 Hz, 3 H).**^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 141.6, 128.5, 127.8, 126.1, 72.3, 22.2 ppm.



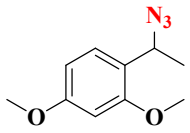
1-(1-azidoethyl)-4-methoxybenzene, Table 3, Entry 2.

FT-IR (υ max): 2978, 2935, 2837, 2098, 1611, 1585, 1513, 1463, 1376, 1340, 1304, 1285, 1243, 1176, 1120, 1061, 1032, 991, 830, 810, 747, 650, 628 cm^{-1}. **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 7.27 (d, *J*=8.7 Hz, 2 H), 6.92 (d, *J*=8.8 Hz, 2 H), 4.58 (q, *J*=6.9 Hz, 1 H), 3.83 (s, 3 H), 1.52 ppm (d, *J*=6.8 Hz, 3 H). **^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 159.4, 132.9, 127.7, 114.1, 77.7, 76.4, 60.7, 55.3, 21.5 ppm.



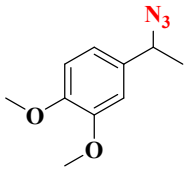
1-(1-azidoethyl)-2-methoxybenzene, Table 3, Entry 3.

FT-IR (υ max): 2092, 1492, 1463, 1438, 1286, 1242, 1061, 1047, 1028, 751 cm^{-1}. **^{1}HNMR** (CHLOROFORM-d, 200MHz): δ = 7.24 - 7.41 (m, 2 H), 6.88 - 7.06 (m, 2 H), 5.08 (q, *J*=6.8 Hz, 1 H), 3.87 (s, 3 H), 1.51 ppm (d, *J*=6.8 Hz, 3 H). **^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 156.4, 129.1, 128.9, 126.5, 120.7, 110.5, 55.3, 54.9, 20.1 ppm.



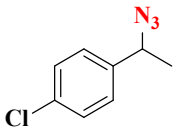
1-(1-azidoethyl)-2,4-dimethoxybenzene, Table 3, Entry 4.

FT-IR (υ max): 2930, 2790, 2089, 1589, 1512, 1461, 1420, 1350, 1299, 1245, 1220, 1159, 1135, 1100, 1050, 1012, 920, 860, 802, 699 cm^{-1}. **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 6.86 (s, 3 H), 4.57 (q, *J*=6.8 Hz, 1 H), 3.88 (s, 3 H), 3.91 (s, 3 H), 1.52 ppm (d, *J*=6.8 Hz, 3 H).**^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 149.1, 148.8, 133.2, 118.6, 110.9, 109.3, 60.9, 55.8, 21.5 ppm.



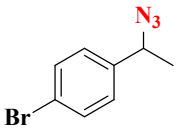
4-(1-azidoethyl)-1,2-dimethoxybenzene, Table 3, Entry 5.

FT-IR (υ max): 2936, 2836, 2105, 1605, 1592, 1515, 1463, 1419, 1375, 1353, 1310, 1256, 1235, 1162, 1141, 1102, 1065, 1025, 914, 855, 808, 765 cm^{-1}. **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 6.87 (s, 3 H), 4.58 (d, *J*=6.8 Hz, 1 H), 3.89 (s, 3 H), 3.92 (s, 3 H), 1.53 ppm (d, *J*=6.8 Hz, 3 H). **^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 149.1, 148.8, 133.2, 118.6, 110.9, 109.3, 60.9, 55.8, 21.5 ppm.



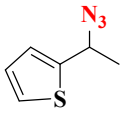
1-(1-azidoethyl)-4-chlorobenzene, Table 3, Entry 6.

IR (υ max**):** 2946, 2099, 1497, 1451, 1369, 1230, 1045, 1059, 752 cm^{-1}. **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 7.45 - 7.58 (m, *J*=8.5 Hz, 2 H), 7.12 - 7.26 (m, *J*=8.5 Hz, 2 H), 4.60 (q, *J*=6.9 Hz, 1 H), 1.52 ppm (d, *J*=6.8 Hz, 3 H).**^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 139.4, 133.8, 128.9, 127.7, 60.3, 21.6 ppm.



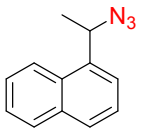
1-(1-azidoethyl)-4-bromobenzene, Table 3, Entry 7.

IR (υ max**):** 2936, 2101, 1605, 1489, 1377, 1222, 1052, 761, 730 cm^{-1}. **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 7.23 - 7.41 (m, 5 H), 4.61 (q, *J*=6.7 Hz, 1 H), 1.52 ppm (d, *J*=6.8 Hz, 3 H).**^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 139.6, 134.1, 129.2, 128.0, 77.9, 76.6, 60.6, 21.8 ppm.



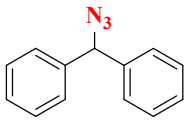
2-(1-azidoethyl)thiophene, Table 3, Entry 8.

IR (υ max): 2977, 2104, 1453, 1377, 1264, 1235, 1044, 895, 850, 808, 734, 702 cm^{-1}. **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 7.30 (dd, *J*=4.9, 1.5 Hz, 1 H), 6.98 - 7.07 (m, 2 H), 4.84 (q, *J*=6.8 Hz, 1 H), 1.64 ppm (d, *J*=6.8 Hz, 3 H). **^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 143.8, 126.7, 125.2, 124.8, 56.4, 21.7 ppm.



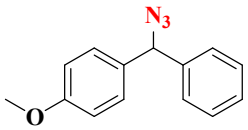
1-(1-azidoethyl)naphthalene, Table 3, Entry 9.

FT-IR (υ max): 3056, 2978, 2097, 1601, 1508, 1449, 1377, 1305, 1242, 1176, 1143, 1127, 1058, 1018, 988, 950, 894, 817, 770, 672, 619 cm^{-1}. **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 7.73 - 8.00 (m, 4 H), 7.40 - 7.60 (m, 3 H), 4.81 (q, *J*=6.8 Hz, 1 H), 1.64 ppm (d, *J*=6.8 Hz, 3 H). **^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 138.2, 133.2, 133.1, 128.7, 128.0, 127.7, 126.4, 126.2, 125.3, 124.2, 61.3, 21.5 ppm.



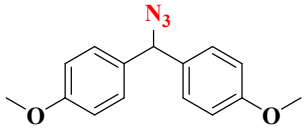
(Azidomethylene) dibenzene, Table 3, Entry 10.

FT-IR (υ max): 3063, 3030, 2094, 1953, 1809, 1601, 1493, 1452, 1237, 1181, 1157, 1078, 1030, 1002, 940, 909, 870, 758, 741, 695, 673, 640, 617 cm^{-1}.**^{1}H NMR** (200 MHz, CHLOROFORM-*d*) δ = ppm 5.73 (s, 1 H) 7.28 - 7.40 (m, 10 H). **^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 139.5, 128.7, 128.0, 127.4, 68.5 ppm.



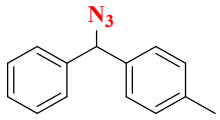
1-(azido (phenyl) methyl)-4-methoxybenzene, Table 3, Entry 11.

FT-IR (υ max): 2976, 2838, 2091, 1601, 1588, 1492, 1464, 1438, 1372, 1346, 1286, 1242, 1194, 1173, 1162, 1121, 1062, 1047, 1028, 993, 935, 842, 803, 751, 691, 647 cm^{-1}.**^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 7.34 (d, *J*=2.4 Hz, 5 H), 7.24 (d, *J*=8.8 Hz, 2 H), 6.90 (d, *J*=8.7 Hz, 2 H), 5.69 (s, 1 H), 3.82 ppm (s, 3 H).**^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 128.8, 128.7, 128.0, 127.3, 114.1, 68.1, 55.3 ppm.



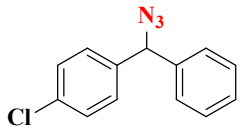
4,4'-(azidomethylene)bis(methoxybenzene, Table 3, Entry12.

FT-IR (υ max): 3001, 2956, 2836, 2094, 1609, 1584, 1509, 1462, 1441, 1421, 1303, 1242, 1172, 1111, 1031, 943, 881, 826, 810, 778, 729, 706, 664, 625 cm^{-1}. **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 7.23 (d, *J*=8.6 Hz, 4 H), 6.86 - 6.94 (m, 4 H), 5.65 (s, 1 H), 3.81 ppm (s, 6 H).**^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 159.2, 131.9, 128.5, 113.9, 67.5, 55.2 ppm.



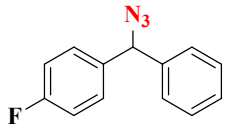
1-(azido(phenyl)methyl)-4-methylbenzene, Table 3, Entry 13.

FT-IR (υ max): 3027, 2922, 2096, 1512, 1493, 1451, 1241, 1176, 1111, 1079, 1057, 1029, 1020, 915, 875, 842, 797, 779, 731, 719, 696, 667, 640, 622 cm^{-1}. **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 7.28 - 7.45 (m, 5 H), 7.12 - 7.26 (m, 4 H), 5.70 (s, 1 H), 2.36 ppm (s, 3 H). **^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 142.5, 139.8, 139.3, 129.4, 129.0, 128.6, 128.3, 127.9, 127.3, 127.3, 68.3, 21.1 ppm.



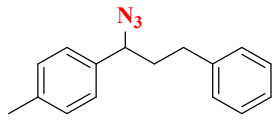
1-(azido(phenyl)methyl)-4-chlorobenzene, Table 3, Entry14.

FT-IR (υ max): 3030, 2096, 1599, 1490, 1453, 1407, 1239, 1179, 1090, 1030, 1015, 949, 913, 872, 794, 752, 717, 698, 657, 630 cm^{-1}**^{1}H NMR** (CHLOROFORM-d, 400MHz): δ = 7.27 - 7.41 (m, 8 H), 7.24 - 7.27 (m, 1 H), 5.70 ppm (s, 1 H).**^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 165.0, 160.1, 139.6, 135.7, 129.4, 129.2, 129.0, 128.7, 128.4, 127.5, 116.0, 115.6, 68.0 ppm



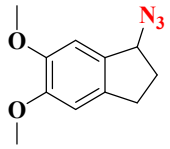
1-(azido(phenyl)methyl)-4-fluorobenzene, Table 3, Entry 15.

FT-IR (υ max): 2096, 1603, 1507, 1494, 1453, 1280, 1223, 1181, 1157, 1097, 1077, 1057, 1028, 1015, 876, 849, 813, 792, 737, 720, 696, 669, 638, 616 cm^{-1}.**^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 7.28 - 7.44 (m, 6 H), 7.23 - 7.26 (m, 1 H), 7.04 (t, *J*=8.7 Hz, 2 H), 5.70 ppm (s, 1 H).**^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 164.8, 159.9, 139.4, 129.2, 129.0, 128.8, 128.2, 127.3, 115.8, 115.4, 67.8 ppm.



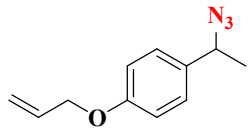
1-(1-azido-3-phenylpropyl)-4-methylbenzene, Table 3, Entry 16.

FT-IR (υ max): 3026, 2923, 2092, 1603, 1514, 1496, 1454, 1306, 1242, 1182, 1113, 1082, 1030, 1019, 908, 882, 815, 772, 748, 721, 698, 637 cm^{-1}. **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 7.14 - 7.36 (m, 9 H), 4.37 (t, *J*=7.2 Hz, 1 H), 2.61 - 2.76 (m, 2 H), 2.37 (s, 3 H), 2.00 - 2.27 ppm (m, 3 H).**^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 140.9, 138.1, 136.3, 129.5, 128.4, 126.9, 126.0, 65.2, 37.5, 32.3, 21.1 ppm.



1-azido-5,6-dimethoxy-2,3-dihydro-1H-indene, Table 3, Entry 17.

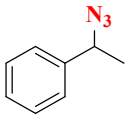
FT-IR (υ max): 2937, 2086, 1606, 1503, 1464, 1454, 1413, 1338, 1308, 1257, 1220, 1187, 1167, 1089, 1036, 1008, 980, 923, 890, 850, 801, 773, 759, 654 cm^{-1}. **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 6.90 (s, 1 H), 6.80 (s, 1 H), 4.82 (dd, *J*=7.1, 4.3 Hz, 1 H), 3.89 (s, 3 H), 3.90 (s, 3 H), 2.72 - 3.16 (m, 2 H), 2.38 - 2.61 (m, 1 H), 2.06 - 2.28 ppm (m, 1 H).**^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 150.0, 148.5, 135.8, 132.2, 107.5, 107.2, 77.8, 77.1, 76.5, 66.5, 56.1, 56.0, 32.9, 30.5 ppm.



1-(allyloxy)-4-(1-azidoethyl)benzene, Table 3, Entry 18.

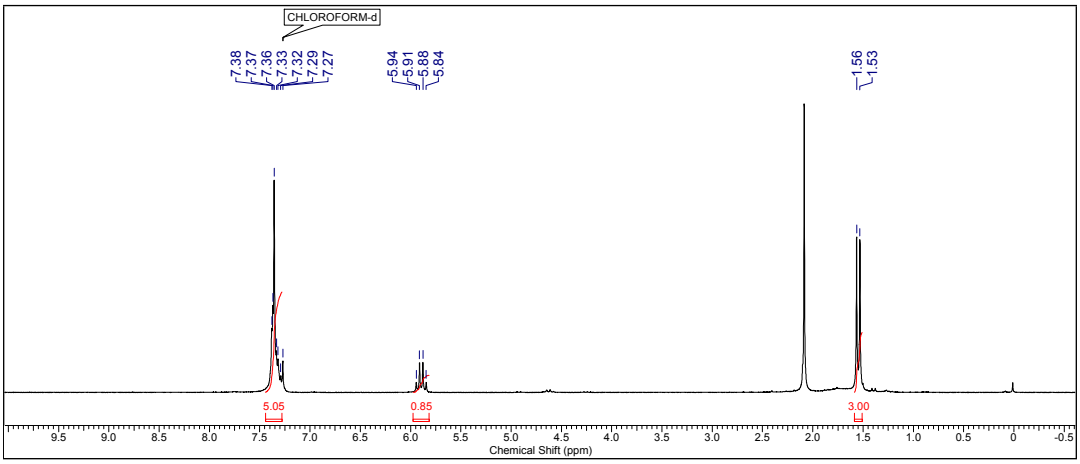
FT-IR (υ max): 2967, 2925, 2102, 1609, 1510, 1455, 1373, 1237, 1175, 1104, 1022, 996, 928, 831, 732, 700 cm^{-1}. **^{1}H NMR** (CHLOROFORM-d, 200MHz): δ = 7.21 - 7.30 (m, 2 H), 6.85 - 6.99 (m, 2 H), 5.96 - 6.18 (m, 1 H), 5.23 - 5.51 (m, 2 H), 4.47 - 4.65 (m, 3 H), 1.52 ppm (d, *J*=6.8 Hz, 3 H). **^{13}C NMR** (CHLOROFORM-d, 50MHz): δ = 158.4, 133.1, 133.0, 127.6, 117.7, 114.8, 68.8, 60.6, 21.4 ppm.

^{1}H and ^{13}C NMR data of the compounds

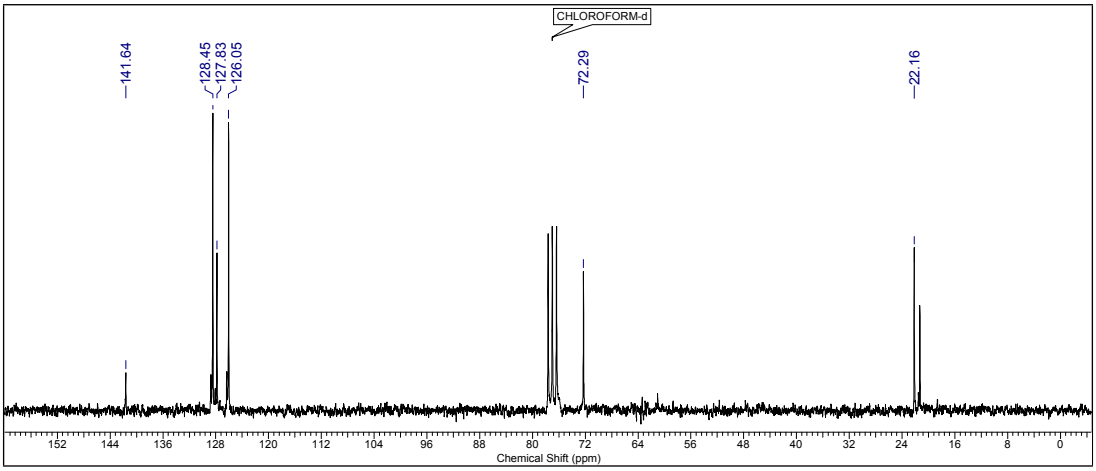


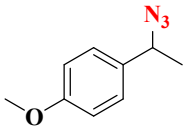
(1-azidoethyl)benzene, Table3, Entry 1.

^{1}H NMR



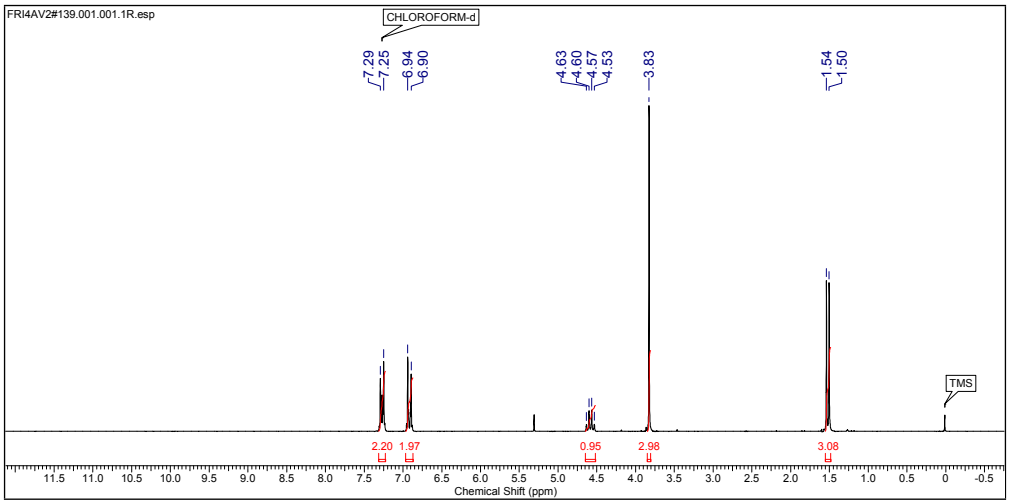
^{13}C NMR



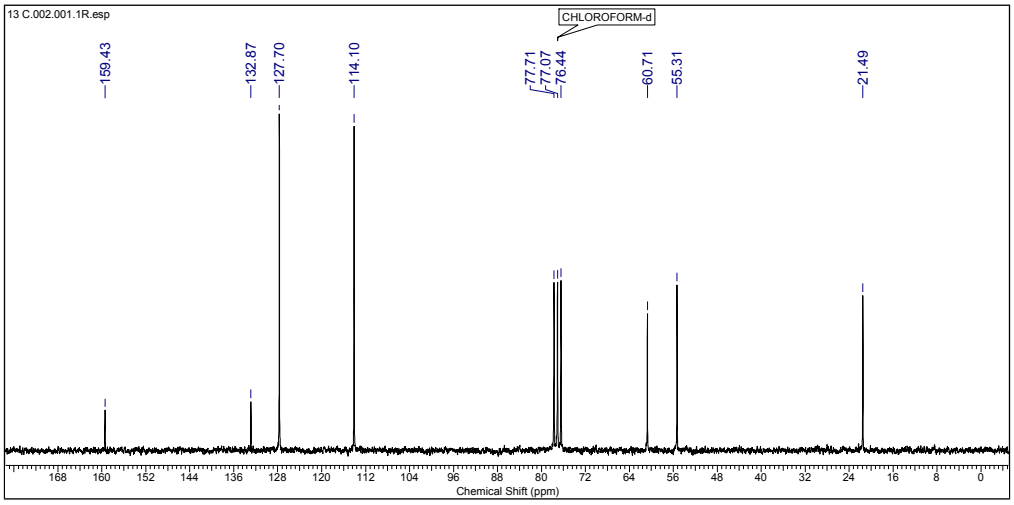


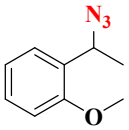
1-(1-azidoethyl)-4-methoxybenzene Table 3, Entry 2.

^{1}H NMR



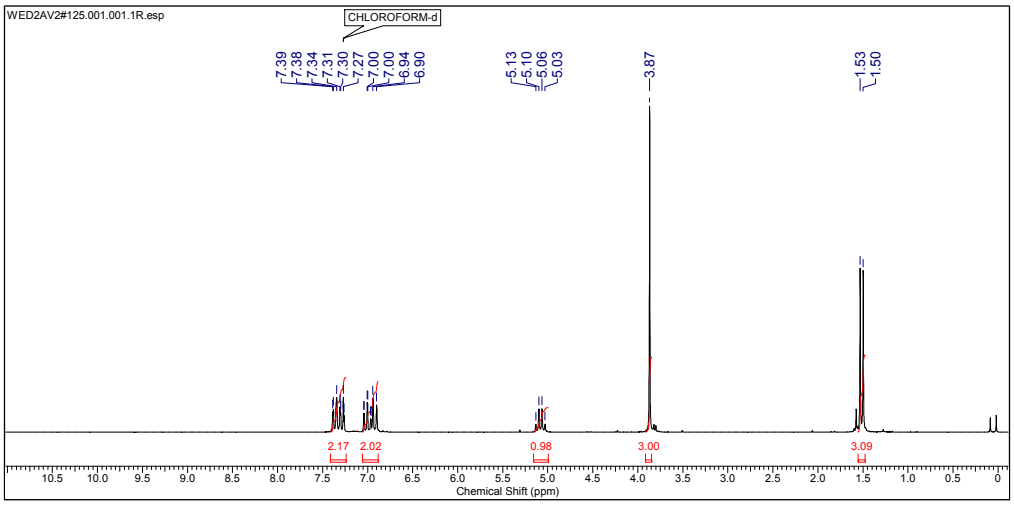
^{13}C NMR



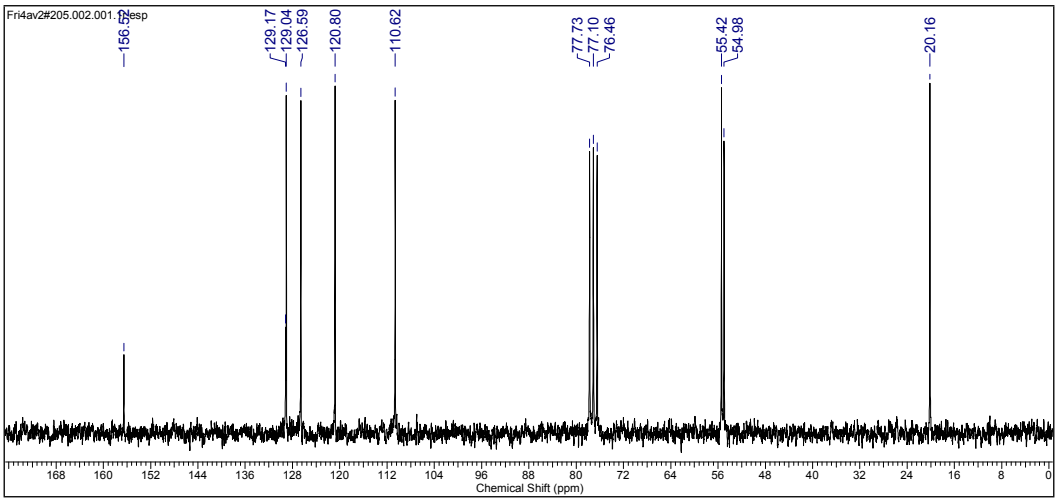


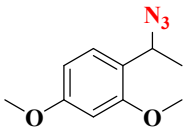
1-(1-azidoethyl)-2-methoxybenzene, Table 3, Entry 3.

^{1}H NMR



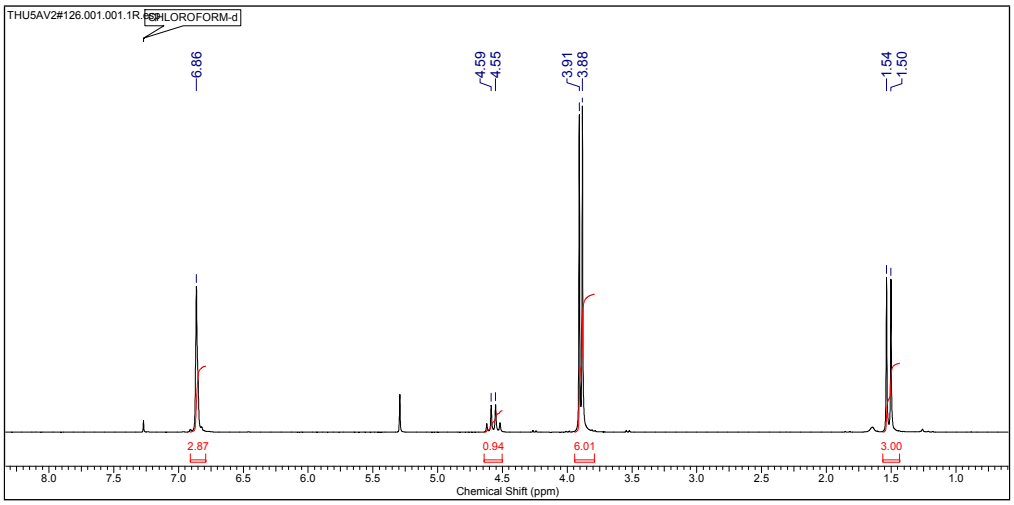
^{13}C NMR



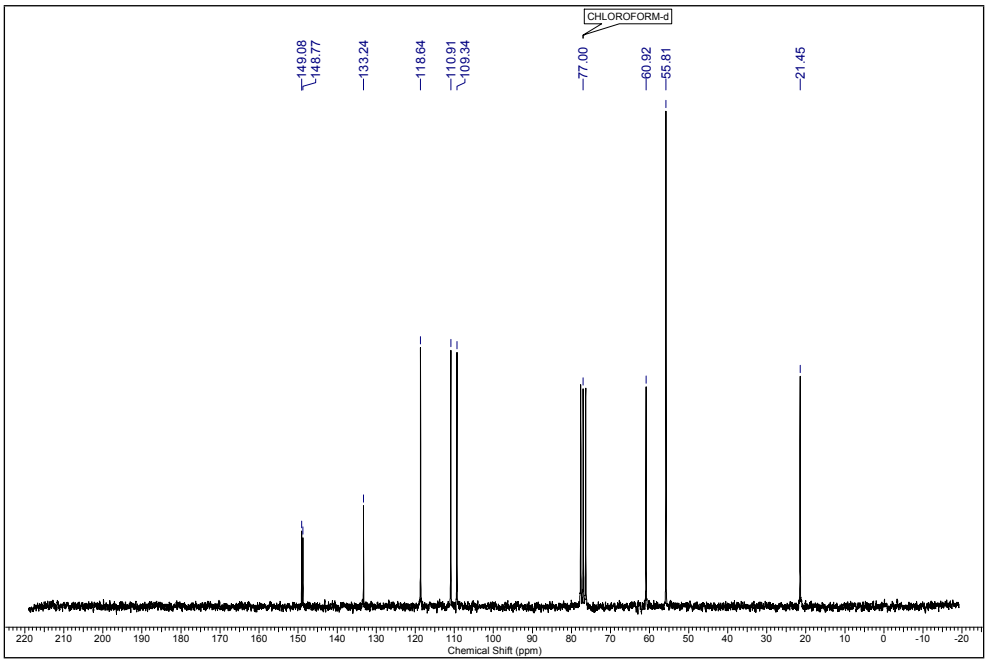


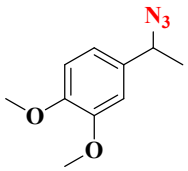
1-(1-azidoethyl)-2,4-dimethoxybenzene, Table 3, Entry 4.

^{1}H NMR



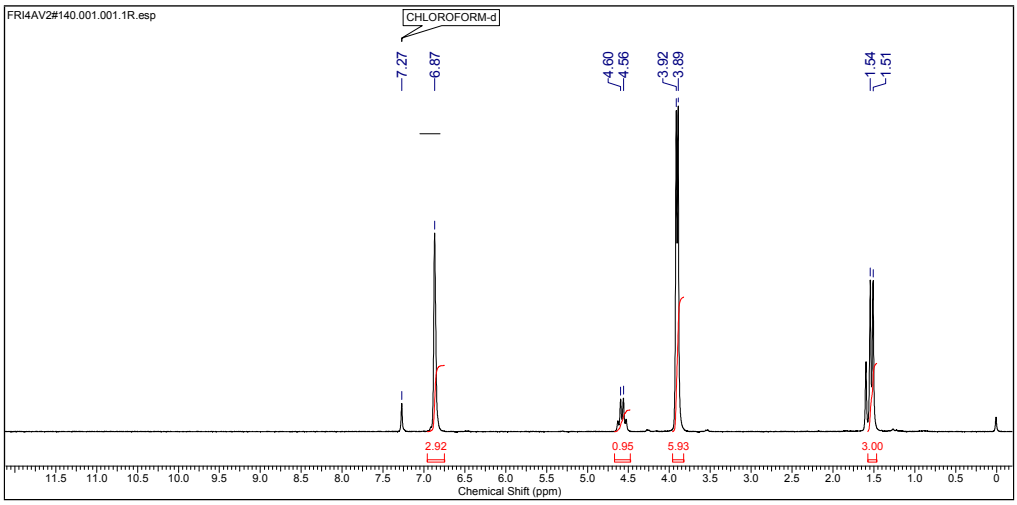
^{13}C NMR



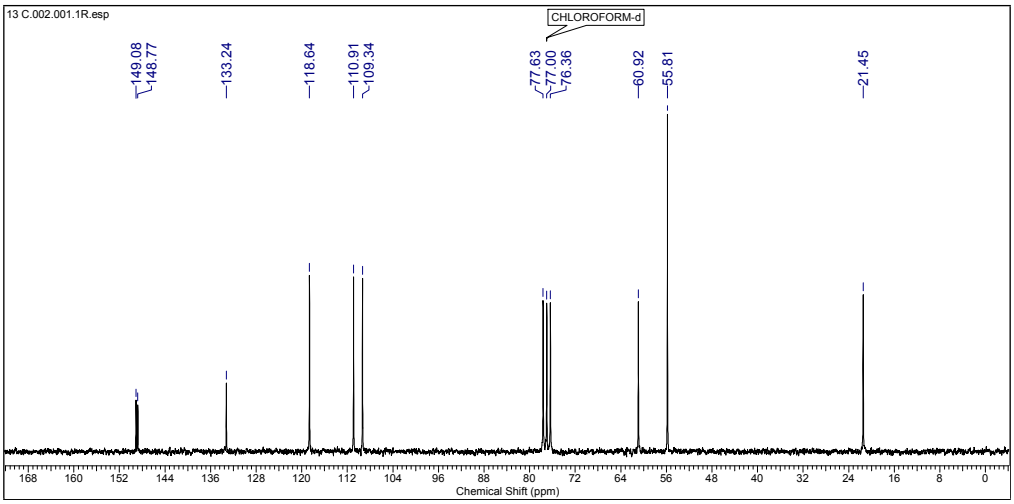


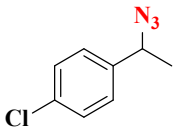
4-(1-azidoethyl)-1,2-dimethoxybenzene, Table 3, Entry 5.

^{1}H NMR



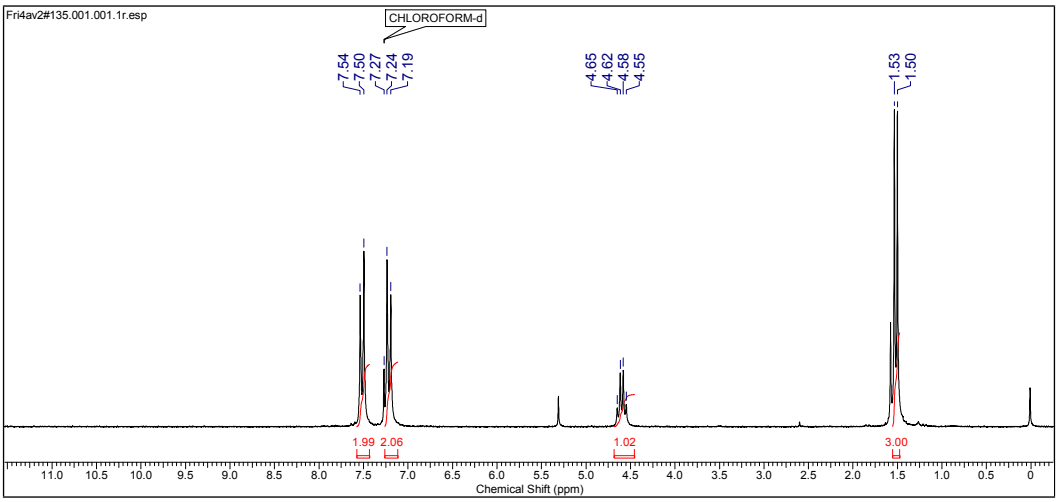
^{13}C NMR



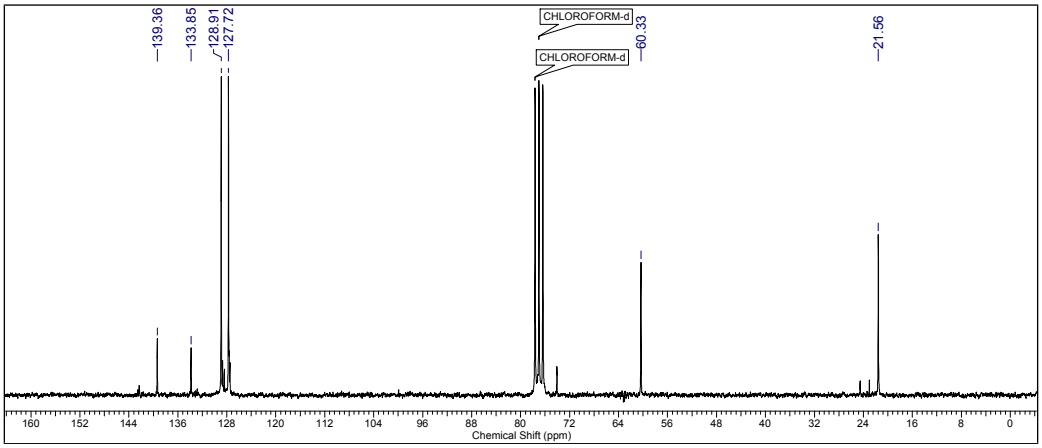


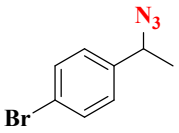
1-(1-azidoethyl)-4-chlorobenzene, Table 3, Entry 6.

^{1}H NMR



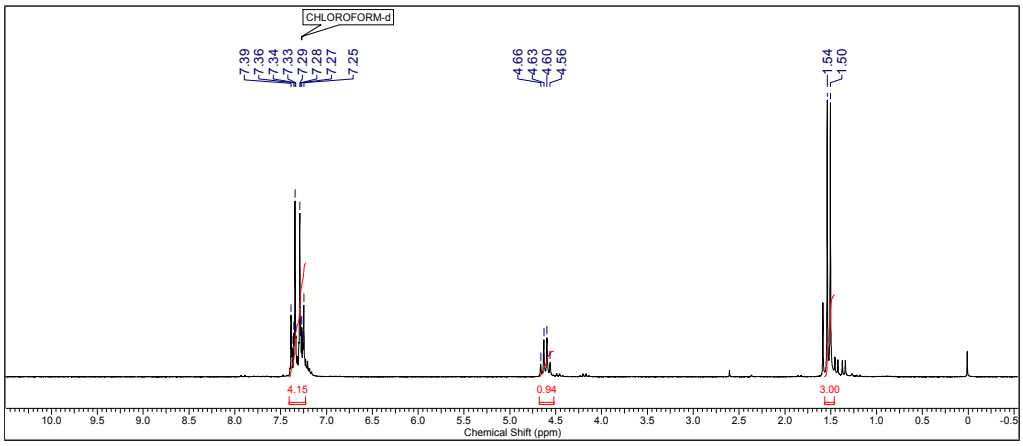
^{13}C NMR



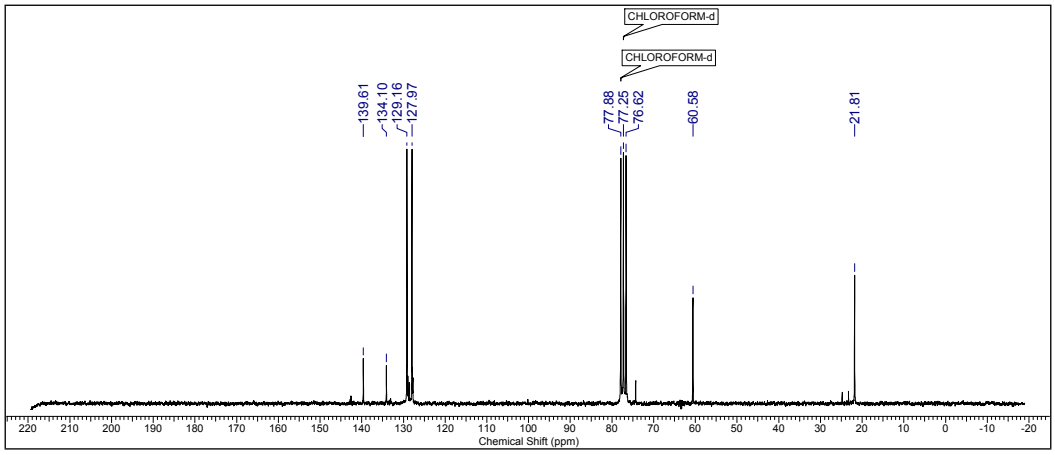


1-(1-azidoethyl)-4-bromobenzene, Table 3, Entry 7.

^{1}H NMR

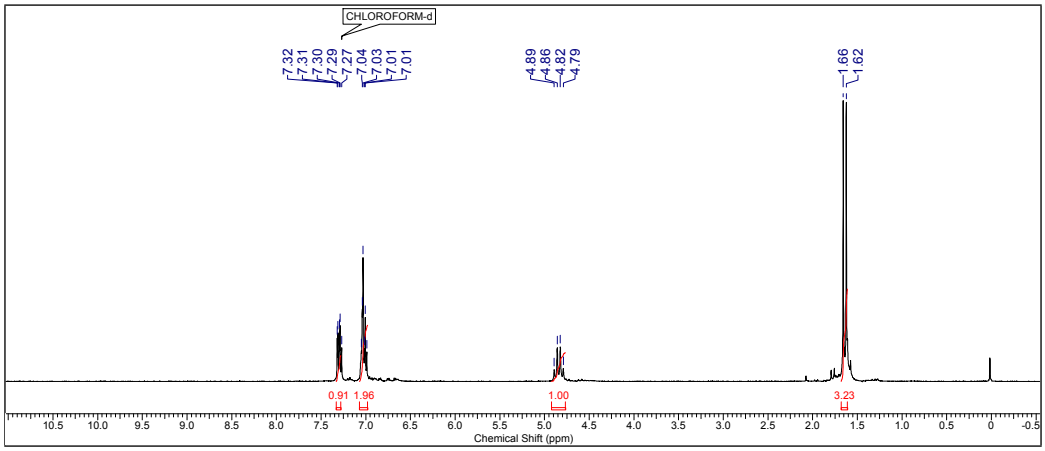


^{13}C NMR

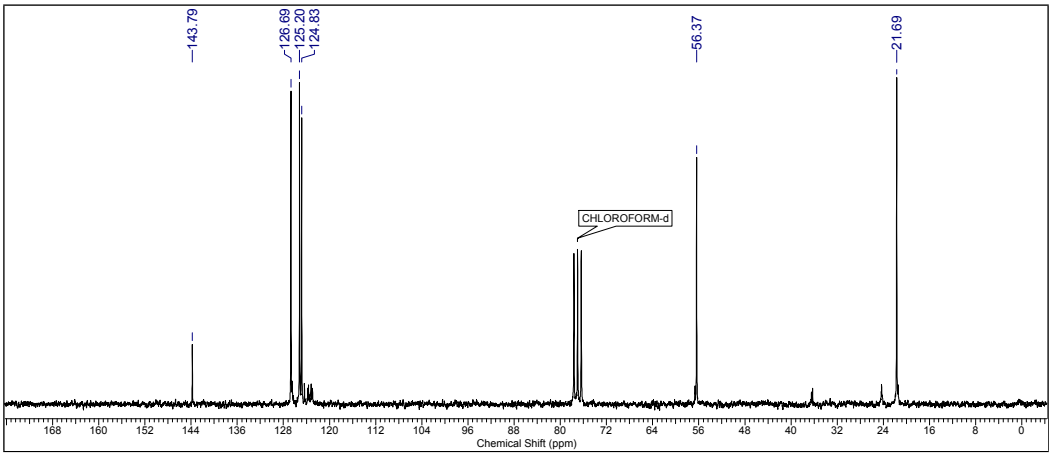


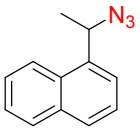
2-(1-azidoethyl)thiophene, Table 3, Entry 8.

^{1}H NMR



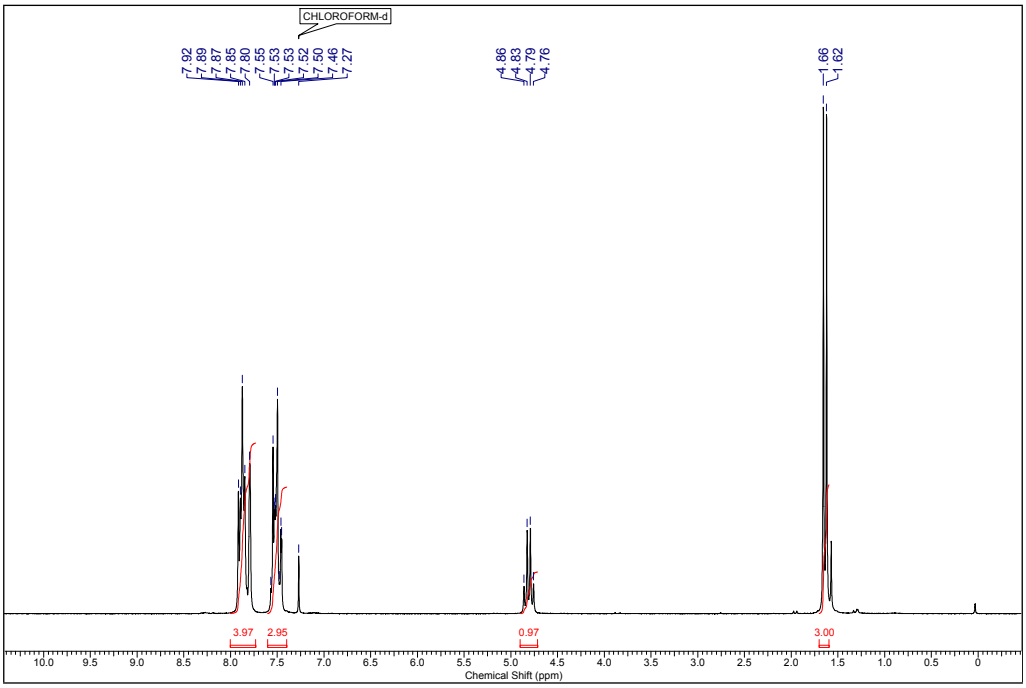
^{13}C NMR



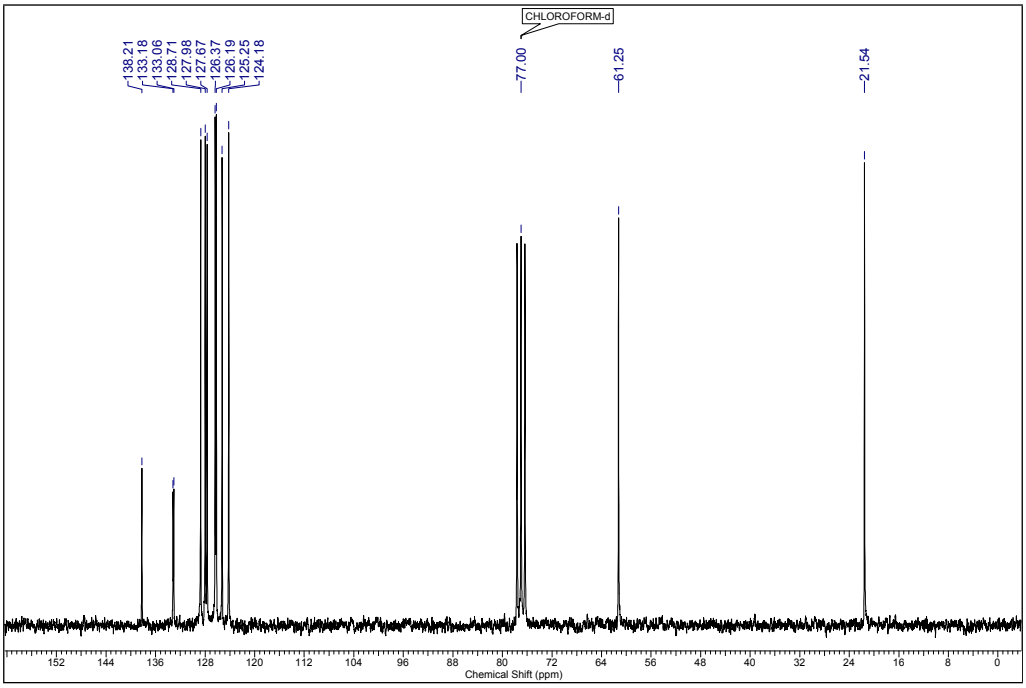


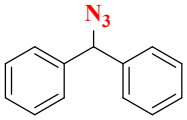
1-(1-azidoethyl)naphthalene, Table 3, Entry 9.

^{1}H NMR



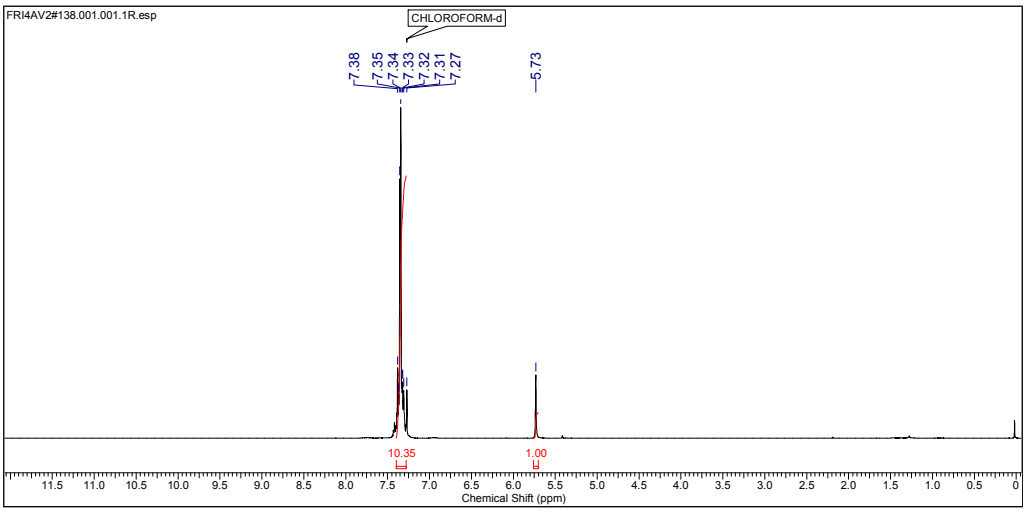
^{13}C NMR



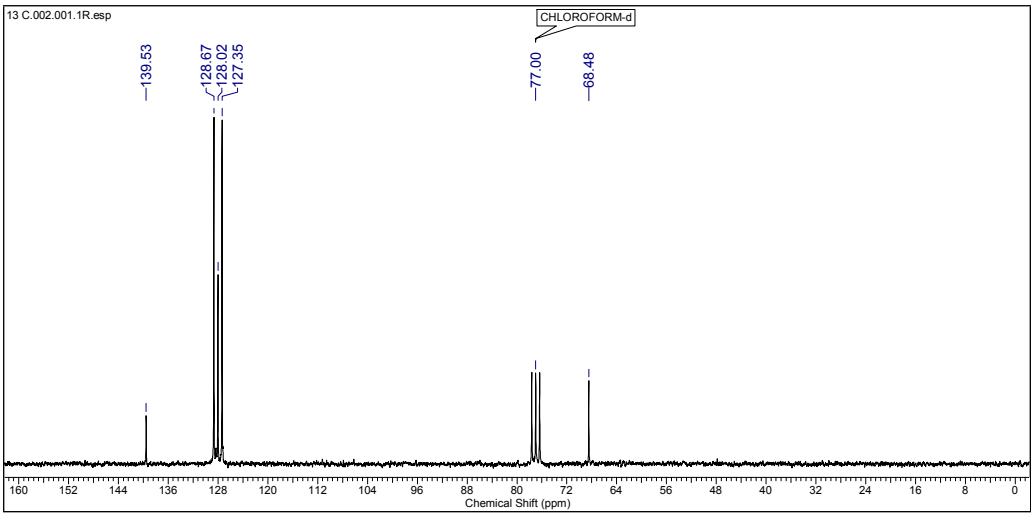


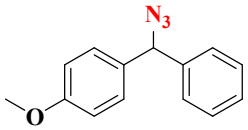
(Azidomethylene) dibenzene, Table 3, Entry 10.

^{1}H NMR



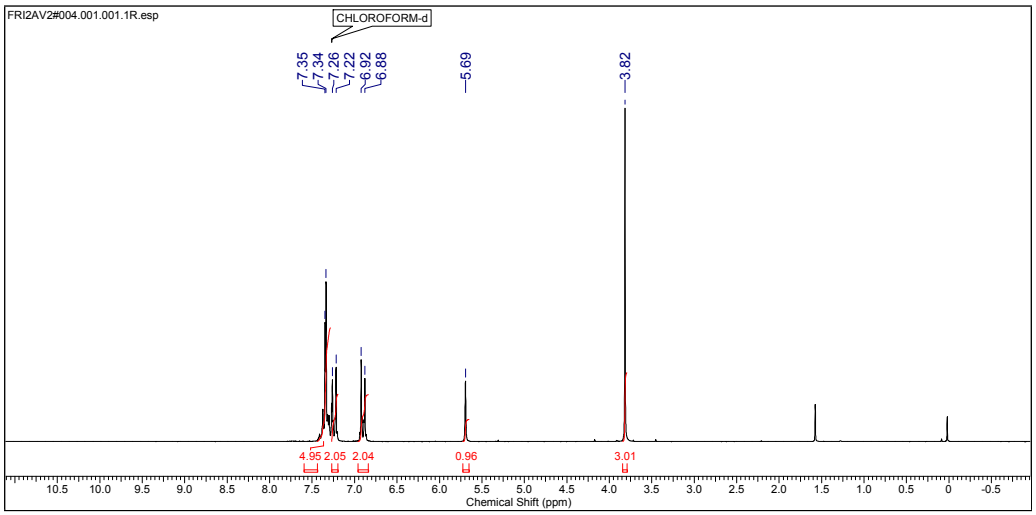
^{13}C NMR



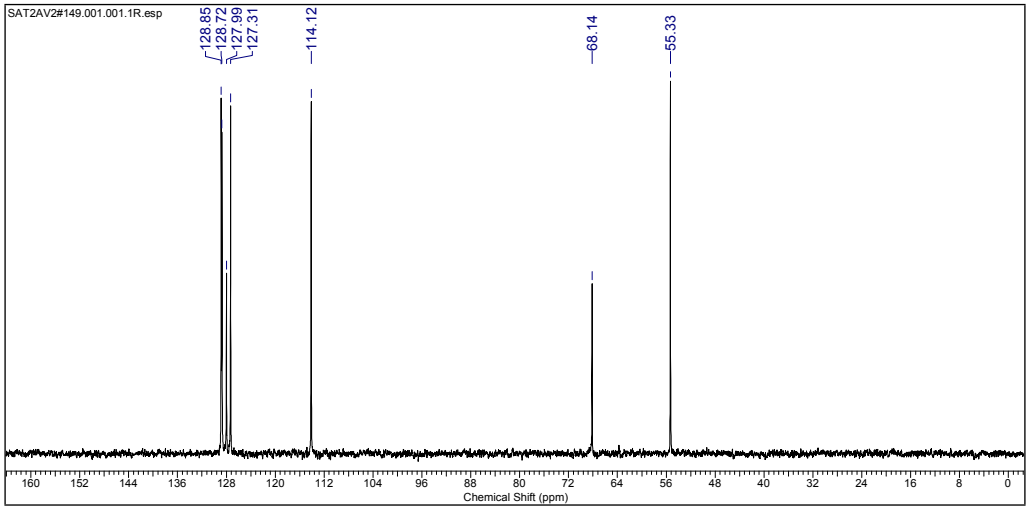


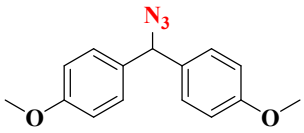
1-(azido (phenyl) methyl)-4-methoxybenzene, Table 3, Entry 11.

^{1}H NMR



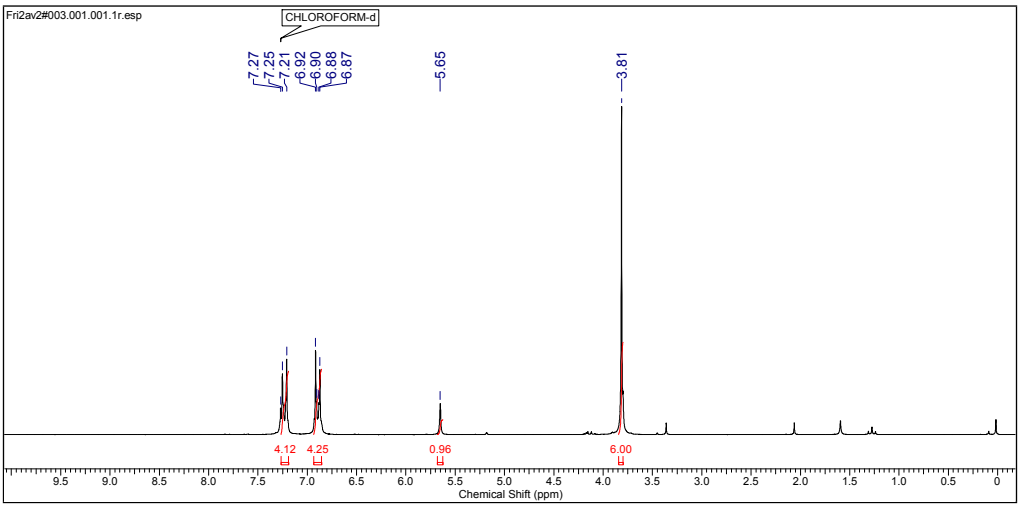
^{13}C NMR



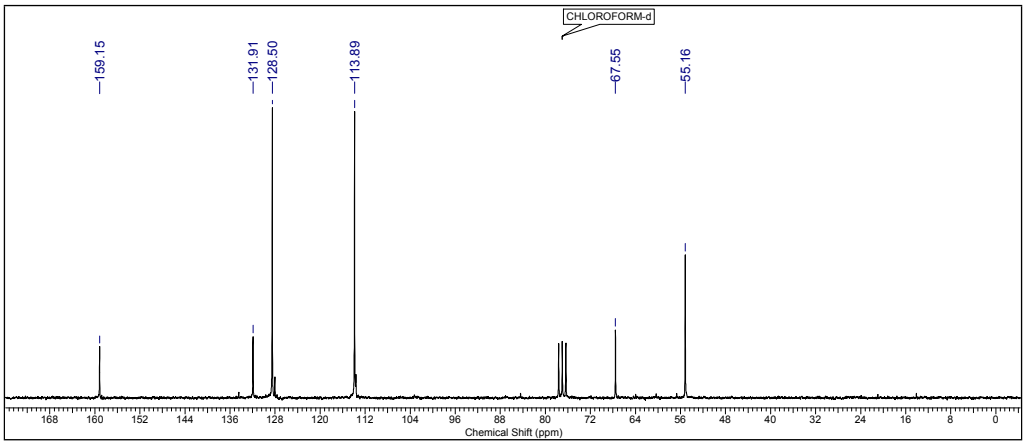


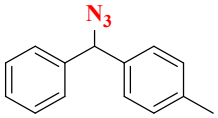
4,4'-(azidomethylene)bis(methoxybenzene , Table 3, Entry12.

^{1}H NMR



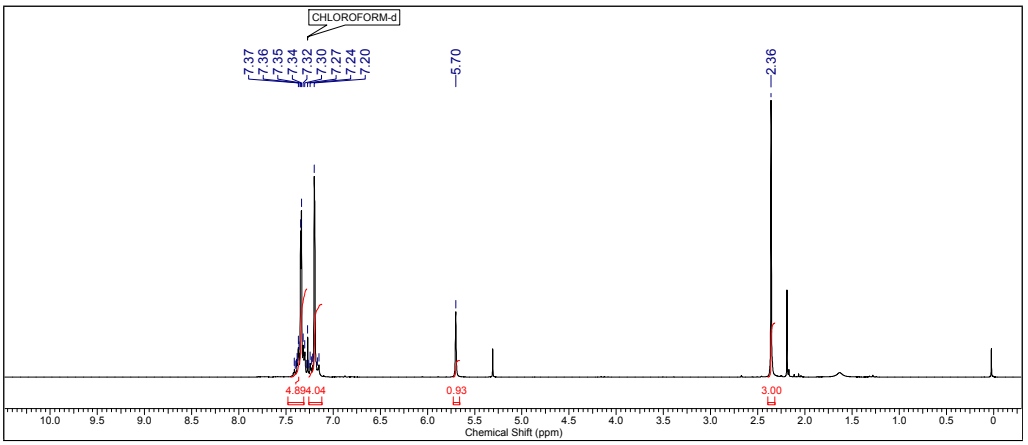
^{13}C NMR



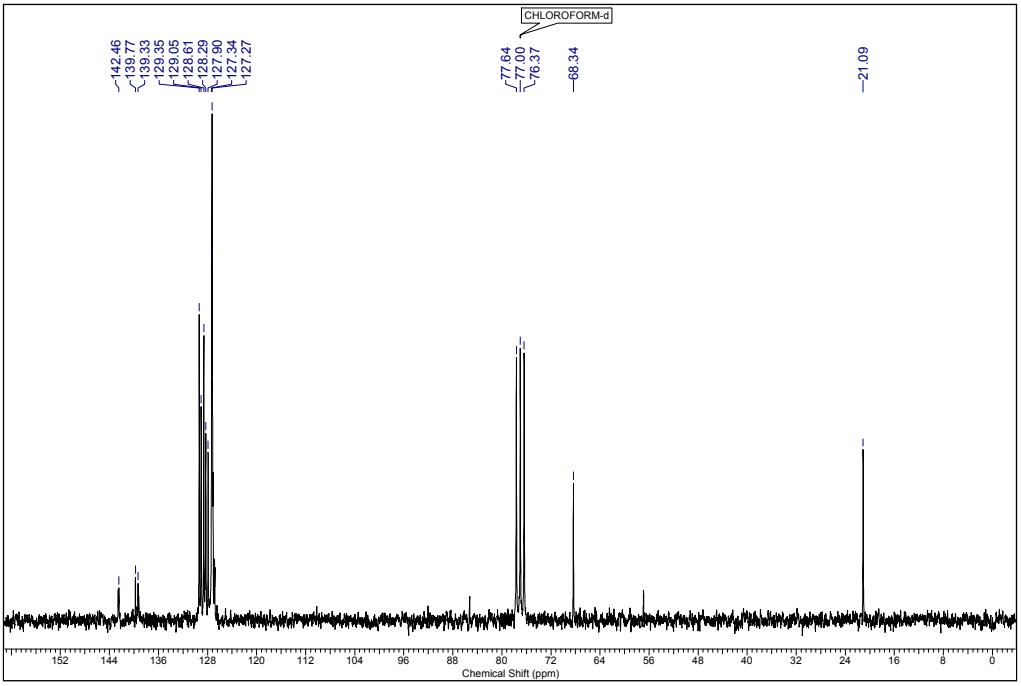


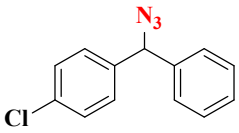
1-(azido(phenyl)methyl)-4-methylbenzene, Table 3, Entry 13.

^{1}H NMR



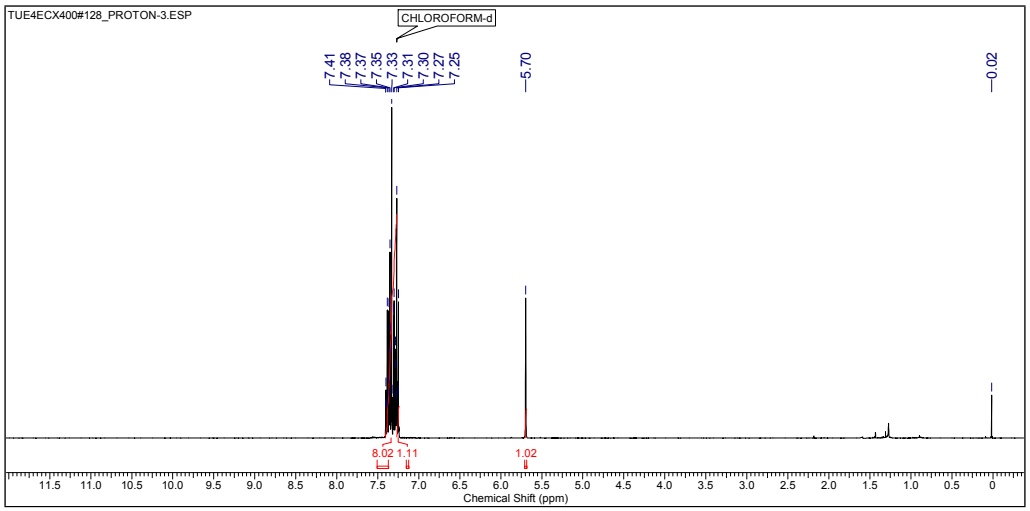
^{13}C NMR



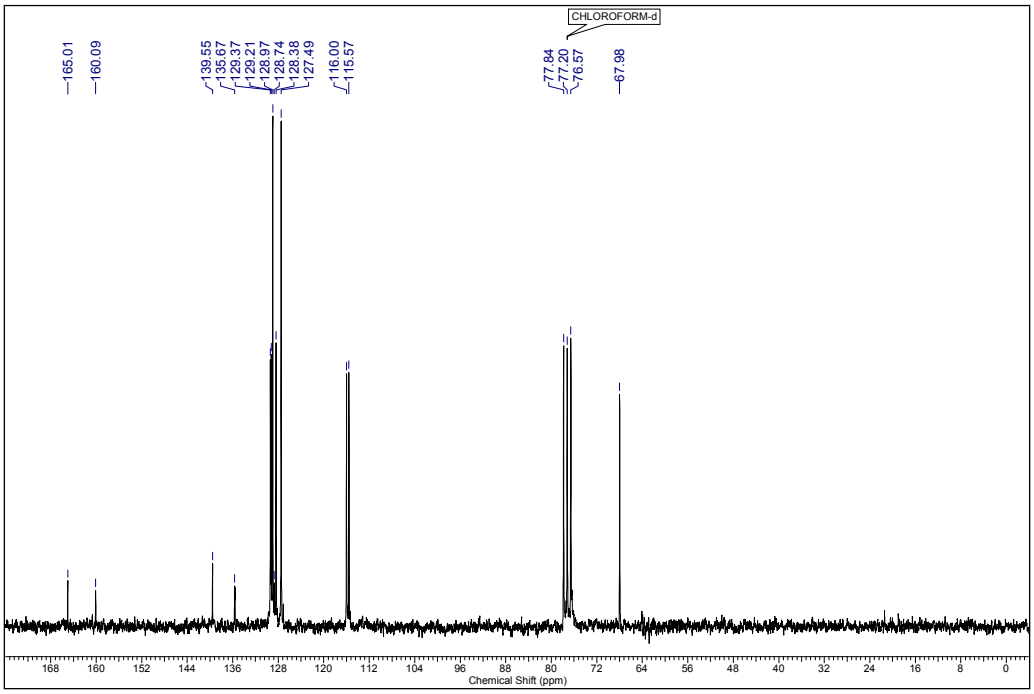


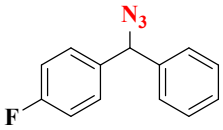
1-(azido(phenyl)methyl)-4-chlorobenzene, Table 3, Entry14.

^{1}H NMR



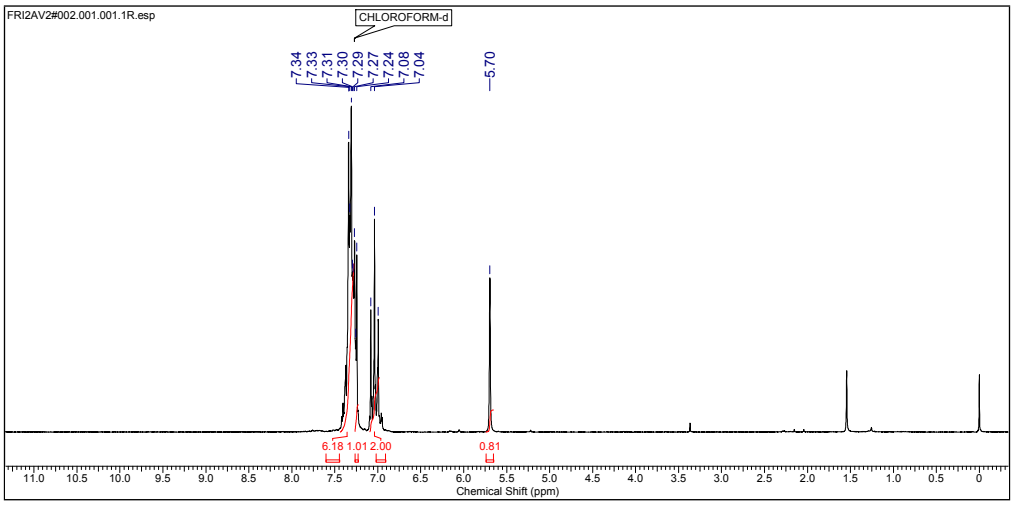
^{13}C NMR



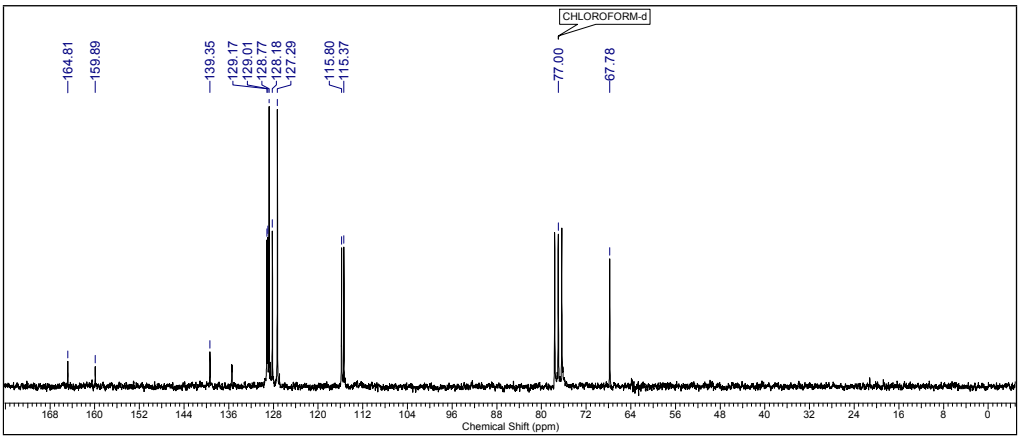


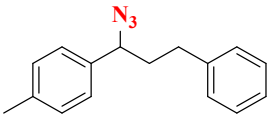
1-(azido(phenyl)methyl)-4-fluorobenzene, Table 3, Entry 15.

^{1}H NMR



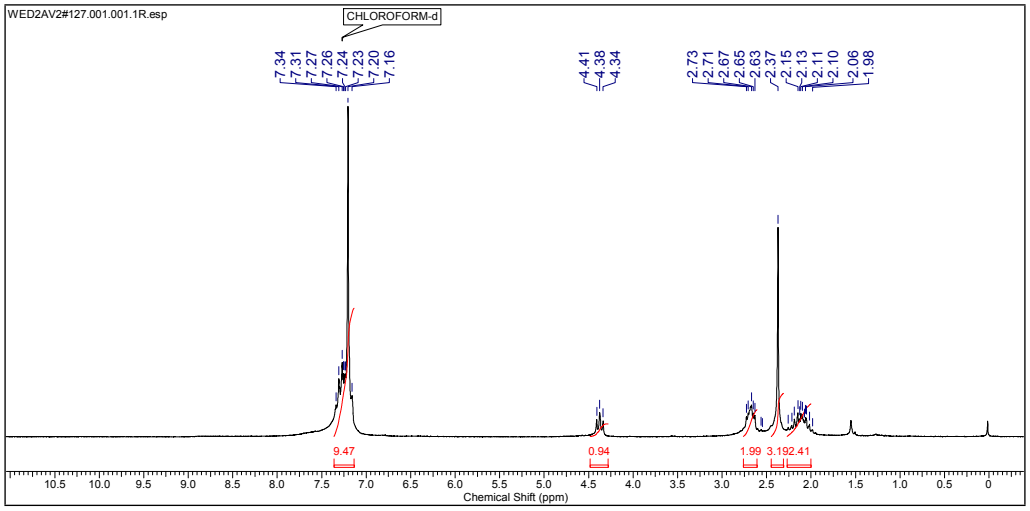
^{13}C NMR



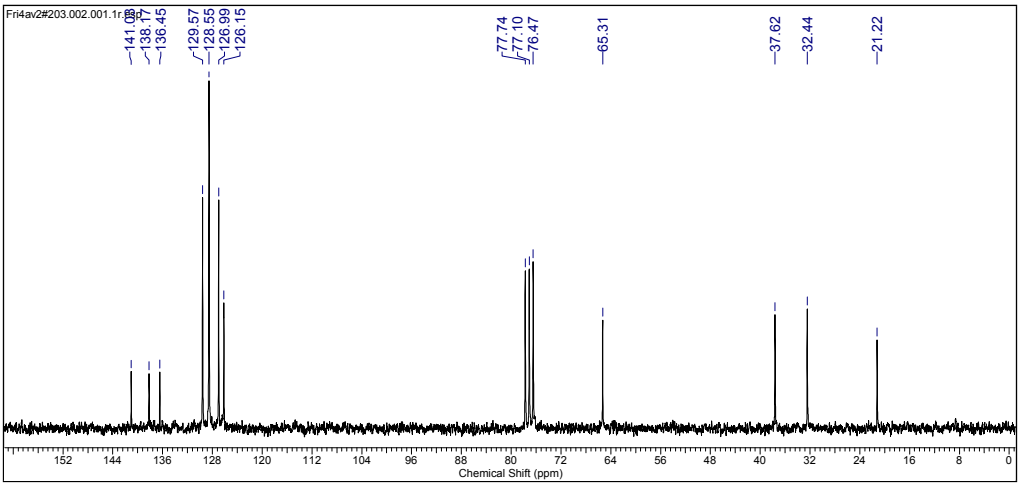


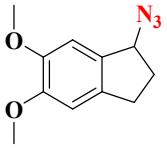
1-(1-azido-3-phenylpropyl)-4-methylbenzene, Table 3, Entry 16.

^{1}H NMR



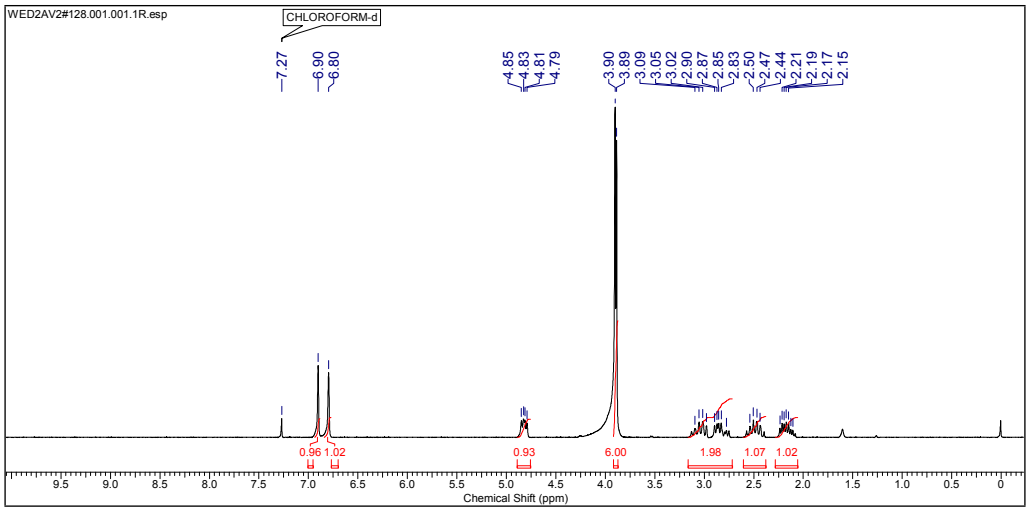
^{13}C NMR



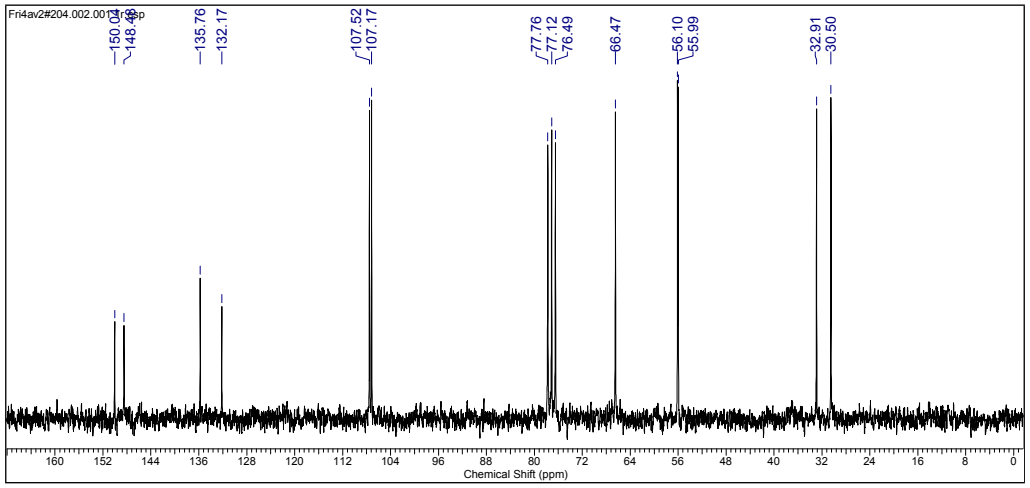


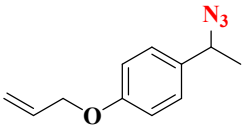
1-azido-5,6-dimethoxy-2,3-dihydro-1H-indene, Table 3, Entry 17.

^{1}H NMR



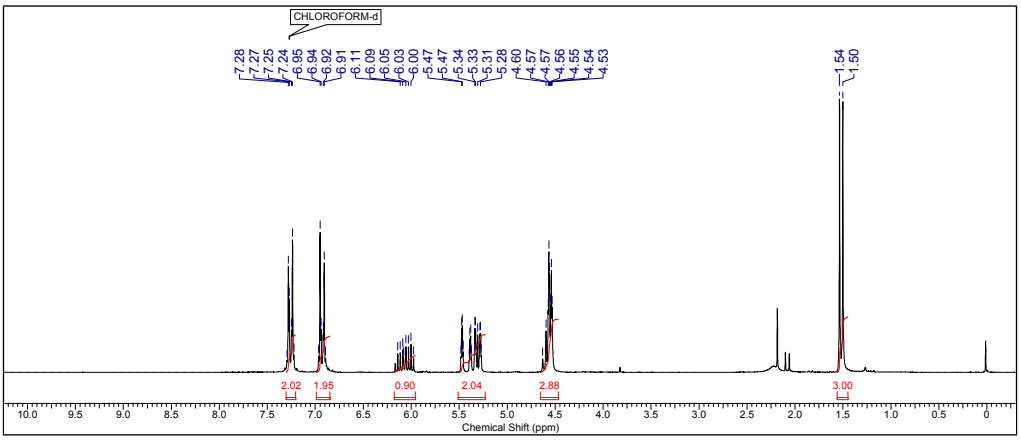
^{13}C NMR





1-(allyloxy)-4-(1-azidoethyl)benzene, Table 3, Entry 18.

^{1}H NMR



^{13}C NMR