**Supplemental Data:**

Proton NMR spectra for the intermediate piperidines **56**-**60** and acetylenes **63**-**81** and **85**, **86**.

**2-Propylpiperidine (56)*.**

**3-Butylpiperidine (57).**

$^1$NMR ($CDCl_3$) δ 0.87 (t, 3H), 1.13-1.49 (m, 9H), 1.56(m, 2H), 1.76 (br d, 1H), 2.30 (dd, 1H), 2.49 (t, 0.5H), 2.51 (t, 0.5H), 2.98 (m, 2H).

**3-Phenylpiperidine (58).**

$^1$NMR ($CDCl_3$) δ 1.62 (m, 3H), 1.87 (br d, 1H), 2.01 (m, 1H), 2.64 (m, 3H), 3.13 (m, 2H), 7.25 (m, 5H).

**2,3-Dimethylpiperidine (59)*.**

**2,5-Dimethylpiperidine (60)***

**3-Ethynylbenzonitrile (63).**

$^1$H NMR ($CDCl_3$) δ 3.18 (s, 1H, CH), 7.43 (m, 1H, aromatic H ), 7.68 (m, 3H, aromatic Hs).

**4-Chlorophenylacetylene (64)**

$^1$H NMR ($CDCl_3$) δ 3.10 (s, 1H, CH), 7.29 (d, 2H, aromatic Hs), 7.42 (d, 2H, aromatic Hs).

**3-Chlorophenylacetylene (65).**

$^1$H NMR ($CDCl_3$) δ 3.12 (s, 1H, CH), 7.31 (m, 3H, aromatic Hs), 7.48 (s, 1H, aromatic H).

**2-Chlorophenylacetylene (66).**

$^1$H NMR ($CDCl_3$) δ 3.37 (s, 1H, CH), 7.26 (m, 2H, aromatic Hs), 7.41 (d, 1H, aromatic H), 7.53 (d, 1H, aromatic H).

**2,3-Dichlorophenylacetylene (67).**

$^1$H NMR ($CDCl_3$) δ 3.42 (s, 1H, CH), 7.16 (m, 1H, aromatic H), 7.45 (d, 2H, aromatic Hs).

**2,6-Dichlorophenylacetylene (68).**

$^1$H NMR ($CDCl_3$) δ 3.69 (s, 1H, CH), 7.22 (m, 1H, aromatic H), 7.35 (d, 2H, aromatic Hs).

**3,4-Dichlorophenylacetylene (69).**

$^1$H NMR ($CDCl_3$) δ 3.15 (s, 1H, CH), 7.29 (dd, 1H, aromatic H), 7.38 (d, 1H, aromatic H), 7.56 (d, 1H, aromatic H).

**3,5-Dichlorophenylacetylene (70).**

$^1$H NMR ($CDCl_3$) δ 3.16 (s, 1H, CH), 7.36 (s, 3H, aromatic Hs).

**4-Chloro-3-trifluoromethylphenylacetylene (71).**

$^1$H NMR ($CDCl_3$) δ 3.18 (s, 1H, CH), 7.52 (m, 2H, aromatic Hs), 7.80 (d, 1H, aromatic H).

**4-Fluorophenylacetylene (72).**

$^1$H NMR ($CDCl_3$) δ 3.05 (s, 1H, CH), 7.03 (t, 2H, aromatic Hs), 7.49 (m, 2H, aromatic Hs).

**3,5-Difluorophenylacetylene (73).**

$^1$H NMR ($CDCl_3$) δ 3.15 (s, 1H, CH), 6.83 (m, 1H, aromatic H), 7.00 (m, 2H, aromatic Hs).

**4-Trifluoromethylphenylacetylene (74).**

$^1$H NMR ($CDCl_3$) δ 3.20 (s, 1H, CH), 7.59 (s, 4H, aromatic Hs).

**3-Methylphenylacetylene (75).**

$^1$H NMR ($CDCl_3$) δ 3.05 (s, 1H, acetylenic proton).

**3-Methoxyphenylacetylene (76).**

$^1$H NMR ($CDCl_3$) δ 3.09 (s, 1H, acetylenic proton).

**4-Ethynylbenzenesulfonamide (77).**

$^1$H NMR ($CDCl_3$) δ 3.16 (s, 1H, CH), 6.36 (s, 2H, $NH_2$), 7.45 (d, 2H, aromatic Hs), 7.76 (d, 2H, aromatic Hs).

**3-Ethynylthiophene (78).**

$^1$H NMR ($CDCl_3$) δ 3.05 (s, 1H, CH), 7.16 (d, 1H, aromatic H), 7.26 (m, 1H, aromatic H), 7.52 (d, 1H, aromatic H).

**2-Naphthylacetylene (79).**

$^1$H NMR ($CDCl_3$) δ 3.18 (s, 1H, CH), 7.53 (m, 3H, aromatic Hs), 7.82 (m, 3H, aromatic Hs), 8.06 (s, 1H, aromatic H)..

**3-Ethynylpyridine (80).**

$^1$H NMR ($CDCl_3$) δ 3.22 (s, 1H, CH), 7.26 (m, 1H, aromatic H), 7.77 (d t, 1H, aromatic H), 8.57 (dd, 1H, aromatic H), 8.72 (t, 1H, aromatic H).

**5-Ethynylpyrimidine (81).**

$^1$H NMR ($CDCl_3$) δ 3.40 (s, 1H, CH), 8.77 (s, 2H, aromatic Hs), 9.11 (s, 1H, aromatic H).

**2,4-Dichlorophenylacetylene (85).**

$^1$H NMR ($CDCl_3$) δ 3.40 (s, 1H, CH), 7.33 (m, 1H, aromatic H), 7.45 (m, 2H, aromatic Hs).

**3-Chloro-5-methoxyphenylacetylene (86).**

$^1$H NMR ($CDCl_3$) δ 3.09 (s, 1H, CH), 3.80 (s, 3H, $OCH_3$), 6.90 (d, 2H, aromatic Hs), 7.08 (t, 1H, aromatic H).

*See Eliel, E. L.; Kandasamy, D.; Yen, C-Y; Hargrave, K. D. Conformational Analysis 39. $^{13}$C NMR Spectra of Saturated Heterocycles 9. Piperidine and N-Methylpiperidine. *J. Am. Chem. Soc.*, **1980**, *102(11)*, 3698-3707.