Supporting Information

**Regioselective [5,5]-sigmatropic rearrangement reactions of
aryl hydrazides**

Hong-Min Kang, Young-Kwan Lim, In-Ji Shin, Hee-Yeon Kim and Cheon-Gyu Cho*

Department of Chemistry, Hanyang University, Seoul, Korea 133-791.

Materials and Methods. Reactions were carried out in oven or flame-dried glassware under an argon atmosphere, unless otherwise noted. All solvents were reagent grade. Diethyl ether (Et₂O) and tetrahydrofuran (THF) were freshly distilled from sodium/benzophenone under argon. *n*-Butyllithium and *t*-butyllithium were purchased from Aldrich. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) with 0.25 mm E. Merck pre-coated silica gel plates. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. Infrared spectra were recorded on a Jasco Model FT/IR-480 Plus spectrometer. Proton and carbon-13 NMR spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts are reported relative to chloroform ($\delta = 7.26$) or TMS ($\delta = 0.00$) for ¹H NMR and chloroform ($\delta = 77.0$) for ¹³C NMR. High resolution mass spectra were measured at the Korean Basic Research Center, Seoul, Korea.

Experimental Procedures

***N*-Phenyl-hydrazinecarboxylic acid *tert*-butyl ester (4a)**

¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.08 - 7.04 (m, 1H), 4.43 (bs, 2H), 1.48 (s, 9H); Lim, Y.-K.; Choi, S.; Park, K.-B.; Cho, C.-G. *J. Org. Chem.* **2004**, 69, 2603.

***N*-o-Tolyl-hydrazinecarboxylic acid *tert*-butyl ester (4b)**

¹H NMR (400 MHz, CDCl₃) 7.19 – 7.16 (m, 4H), 4.46 (bs, 2H), 2.25 (s, 3H), 1.39 (s, 9H); Wolter, M.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2001**, 3, 3803.

N-(2-Methoxy-phenyl)-hydrazinecarboxylic acid *tert*-butyl ester (4c)

^1H NMR (400 MHz, CDCl_3) δ 7.24-7.18 (m, 2H), 6.92 - 6.88 (m, 2H), 4.48 (s, 2H), 3.83 (s, 3H), 1.40 (s, 9H); Lim, Y.-K.; Choi, S.; Park, K.-B.; Cho, C.-G. *J. Org. Chem.* **2004**, 69, 2603.

N-[3-(*N-tert*-Butoxycarbonyl-hydrazino)-phenyl]-hydrazinecarboxylic acid *tert*-butyl ester (8)

To a sealed tube were charged 2.00 g (6.06 mmol) of 1,3-diiodobenzene, 1.15 g (6.06 mmol) of CuI, 1.09 g (6.06 mmol) of 1,10-phenanthroline, 5.92 g (18.18 mmol) of Cs_2CO_3 , 2.40 g (18.18 mmol) of *tert*-butyl hydrazate, and 5 mL anhydrous DMF at rt. The reaction mixture was degassed, charged with Ar gas and heated to 80 °C. After 6 h, The resulting mixture was directly purified by column chromatography (hexane:EtOAc = 5:1) to afford 1.67 g of product in 82% yields. ^1H NMR (400 MHz, CDCl_3) δ 7.67 (s, 1H), 7.21 (bs, 3H), 4.43 (bs, 4H), 1.51 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.0, 143.0, 127.5, 119.5, 118.2, 81.8, 28.3; FT-IR (CHCl_3) 3339, 2977, 2930, 1771, 1699, 1602, 1488, 1368 cm^{-1} ; HRMS Calcd for $\text{C}_{16}\text{H}_{26}\text{N}_4\text{NaO}_4$ ($\text{M} + \text{Na}^+$): 361.1852, found 361.1862.

N, N'-Diphenyl-hydrazinecarboxylic acid *tert*-butyl ester (6a)

To a round flask were charged 329 mg (1.58 mmol) of *N*-phenyl-hydrazine carboxylic acid *tert*-butyl ester, 267 mg (1.32 mmol) of iodobenzene, 5 mol% of $\text{Pd}(\text{OAc})_2$, 5 mol% of $\text{P}(t\text{-Bu})_3\cdot\text{BF}_4$, 602 mg (1.85 mmol) of Cs_2CO_3 , and 5 mL of anhydrous toluene at rt. The reaction mixture was

stirred for 30 min and refluxed for 2 h. The resulting mixture was directly purified by column chromatography (hexane:EtOAc = 20:1) to afford 360 mg of product in 96% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, J = 7.6 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.27 – 7.21 (m, 2H), 7.13 – 7.10 (m, 1H), 6.93 – 6.88 (m, 1H), 6.81 (d, J = 7.2 Hz, 2H), 6.38 (bs, 1H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.9, 148.3, 142.8, 129.1, 128.4, 124.4, 121.5, 120.9, 112.9, 82.2, 28.0; FT-IR (CHCl_3) 3354, 3055, 2983, 2933, 1710, 1601, 1496, 1369, 1265 cm^{-1} ; HRMS Calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2$ (M^+): 284.1525, found 284.1529.

***N*-Phenyl-*N*-*o*-tolyl-hydrazinecarboxylic acid *tert*-butyl ester (6b)**

^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.39 (m, 1H), 7.26 – 7.16 (m, 5H), 6.94 – 6.88 (m, 3H), 6.40 (bs, 1H), 2.35 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.8, 148.7, 142.2, 135.2, 131.6, 129.8, 127.9, 127.4, 127.1, 121.7, 114.3, 82.4, 28.8, 19.1; FT-IR (CHCl_3) 3325, 3057, 2978, 2928, 1701, 1601, 1497, 1369, 1333, 1240, 1154 cm^{-1} ; HRMS Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2$ (M^+): 298.1681, found 298.1693.

***N,N'*-Di-*o*-tolyl-hydrazinecarboxylic acid *tert*-butyl ester (6c)**

^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.42 (m, 1H), 7.23 – 7.13 (m, 4H), 7.08 – 7.05 (d, J = 8.8 Hz, 2H), 6.84 – 6.80 (td, J = 7.3, 1.1 Hz, 1H), 6.34 (bs, 1H), 2.38 (s, 3H), 2.22 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.7, 146.3, 142.1, 135.2, 131.6, 131.1, 127.8, 127.5, 127.4, 127.0, 123.2, 121.3, 112.8, 82.4, 28.7, 19.3, 17.7; FT-IR (CHCl_3) 3301, 3022, 2977, 2930, 1702, 1607, 1590, 1482, 1457, 1368, 1332, 1247, 1155; HRMS Calcd for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2$ (M^+): 312.1838, found 312.1831.

***N'*-(2,6-Dimethyl-phenyl)-*N*-*o*-tolyl-hydrazinecarboxylic acid *tert*-butyl ester (6d)**

^1H NMR (400 MHz, CDCl_3) δ 7.71 – 7.10 (m, 2H), 6.99 – 6.95 (m, 1H), 6.91 – 6.83 (m, 3H), 6.67 (dd, J = 1.2 Hz, 1H), 5.76 (s, 1H), 2.24 (s, 3H), 2.12 (s, 6H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 141.8, 141.0, 135.1, 131.1, 130.7, 128.8, 128.0, 127.9, 126.3, 124.0, 80.8, 28.2, 17.9, 17.4; FT-IR (CHCl_3) 3257, 2976, 2927, 2568, 1716, 1684, 1521, 1507 cm^{-1} ; HRMS Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{NaO}_2$ ($\text{M} + \text{Na}^+$): 349.1892, found 349.1879.

***N'*-(2,6-Dimethyl-phenyl)-*N*-(2-methoxy-phenyl)-hydrazinecarboxylic acid *tert*-butyl ester (6e)** ^1H NMR (400 MHz, CDCl_3) δ 7.20 – 7.16 (m, 1H), 6.91 – 6.86 (m, 3H), 6.80 – 6.70 (m, 3H), 6.30 (bs, 1H), 3.92 (s, 3H), 2.18 (s, 6H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.0, 155.0, 143.0, 131.7, 130.2, 129.8, 129.5, 129.4, 123.4, 121.0, 111.8, 81.4, 56.1, 28.9, 18.6; FT-IR (CHCl_3) 3278, 2975, 2930, 1730, 1700, 1533, 1493, 1458, 1248 cm^{-1} ; HRMS Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{NaO}_3$ ($\text{M} + \text{Na}^+$): 365.1841, found 365.1837.

2-(*N'*-*tert*-Butoxycarbonyl-*N'*-*o*-tolyl-hydrazino)-benzoic acid methyl ester (6f)

^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.91 (dd, J = 8.1, 1.5 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.25 – 7.14 (m, 4H), 6.81 – 6.77 (td, J_1 = 7.3 Hz, J_2 = 1.1 Hz, 1H), 3.87 (s, 3H), 2.41 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.1, 155.5, 151.8, 141.9, 135.4, 135.1, 132.0, 131.8, 128.0, 127.3, 127.1, 118.8, 113.3, 112.1, 82.3, 52.5, 28.7, 19.1; FT-IR (CHCl_3) 3328, 2977, 2929, 1718, 1693, 1606, 1586, 1498, 1457, 1438, 1368, 1331, 1256, 1160; HRMS Calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{NaO}_4$ ($\text{M} + \text{Na}^+$): 379.1634, found 379.1628.

***N'*-(1,3-Dimethyl-buta-1,3-dienyl)-*N*-phenyl-hydrazinecarboxylic acid *tert*-butyl ester (13a)**

^1H NMR (400 MHz, CDCl_3) δ 7.60 – 7.58 (m, 2H), 7.33 – 7.29 (m, 2H), 7.12 – 7.08 (m, 2H), 6.72 – 6.70 (d, J = 7.3 Hz, 1H), 6.62 – 6.60 (m, 2H), 6.34 (bs, 1H), 2.27 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.6, 149.0, 143.6, 139.7, 129.7, 129.1, 125.1, 122.5, 122.2, 114.2, 110.8, 82.9, 28.7, 22.2; FT-IR (CHCl_3) 3338, 3042, 2978, 2929, 1714, 1611, 1596, 1494, 1455, 1392, 1368, 1335, 1307, 1251, 1156; HRMS Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2$ (M^+): 298.1681, found 298.1687.

Di-*tert*-butyl 1-(3-bromophenyl)-2-phenylhydrazine-1,2-dicarboxylate (13b)

^1H NMR (400 MHz, CDCl_3) δ 7.66 (bs, 1H), 7.37 – 7.26 – 7.40 (m, 6H), 7.18 – 7.14 (t, J = 8.1 Hz, 2H), 1.52 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) 153.6, 153.4, 143.1, 141.5, 135.0, 130.5, 129.3, 129.0, 126.4, 122.9 (bs), 122.7, 121.1 (bs), 83.5, 83.3, 28.8, 28.8; FT-IR (CHCl_3) 2979, 2932, 1726, 1590, 1573, 1494, 1477, 1456, 1369, 1341, 1320, 1255, 1153; HRMS Calcd for $\text{C}_{22}\text{H}_{27}\text{BrN}_2\text{O}_4$ (M^+): 462.1154, found 462.1148.

Di-*tert*-butyl 1,1'-(1,3-phenylene)bis(2-phenylhydrazinecarboxylate) (9a)

^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.38 – 7.36 (m, 2H), 7.28 – 7.20 (m, 5H), 6.91 – 6.88 (t, J = 7.3 Hz, 2H), 6.81 – 6.79 (d, J = 7.7 Hz, 4H), 6.37 (bs, 2H), 1.35 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.6, 148.0, 143.0, 129.0, 128.1, 120.9, 117.8, 115.2, 113.0, 82.3, 28.1; FT-IR (CHCl_3) 3336, 2982, 2928, 2857, 1709, 1601, 1497, 1455, 1369, 1322, 1304, 1254, 1151; HRMS Calcd for $\text{C}_{28}\text{H}_{34}\text{N}_4\text{NaO}_4$ ($\text{M} + \text{Na}^+$): 513.2478, found 513.2487.

Di-*tert*-butyl 1,1'-(1,3-phenylene)bis(2-*o*-tolylhydrazinecarboxylate) (9b)

^1H NMR (400 MHz, CDCl_3) δ 7.90 (s, 1H), 7.38 – 7.35 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.8$ Hz, 2H), 7.23 – 7.21 (m, 1H), 7.07 – 7.04 (m, 4H), 6.82 – 6.75 (m, 4H), 6.35 (bs, 2H), 2.23 (s, 6H), 1.33 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.5, 145.7, 142.9, 130.1, 128.1, 126.9, 122.0, 120.5, 117.7, 115.5, 111.5, 82.2, 28.1, 17.1; FT-IR (CHCl_3) 3354, 2978, 2928, 2853, 1712, 1598, 1480, 1455, 1365, 1329, 1301, 1251, 1154; HRMS Calcd for $\text{C}_{30}\text{H}_{38}\text{N}_4\text{NaO}_4$ ($\text{M} + \text{Na}^+$): 541.2791, found 541.2801.

Di-*tert*-butyl 1,1'-(1,3-phenylene)bis(2-(2,6-dimethylphenyl)hydrazinecarboxylate) (9c)

^1H NMR (400 MHz, CDCl_3) δ 7.90 (t, $J = 2.4$ Hz, 1H), 7.40 (dd, $J = 2.0$ Hz, 2H), 7.22 (t, $J = 4.0$ Hz, 1H), 6.88 (d, $J = 7.2$ Hz, 4H), 7.74 (t, $J = 3.6$ Hz, 2H), 6.16 (s, 2H), 2.17 (s, 12 H), 1.31 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.3, 143.4, 143.3, 129.2, 128.1, 125.8, 121.6, 118.4, 115.7, 82.0, 28.1, 19.9; FT-IR (CHCl_3) 3357, 2976, 2930, 2592, 1920, 1717, 1701, 1598, 1475 cm^{-1} ; HRMS Calcd for $\text{C}_{32}\text{H}_{42}\text{N}_4\text{NaO}_4$ ($\text{M} + \text{Na}^+$): 569.3104, found 569.3113.

Di-*tert*-butyl 1,1'-(1,3-phenylene)bis(2-(2-(methoxycarbonyl)phenyl)hydrazinecarboxylate) (9d)

^1H NMR (400 MHz, CDCl_3) δ 9.62 (s, 2H), 7.95 – 7.91 (m, 3H), 7.38 – 7.33 (m, 4H), 7.27 (t, $J = 3.2$ Hz, 1H), 6.89 (d, $J = 8.4$ Hz, 2H), 6.84 – 6.80 (m, 2H), 3.90 (s, 6H), 1.34 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.2, 153.4, 151.4, 143.0, 134.5, 131.2, 128.5, 118.6, 117.5, 114.9, 112.7, 112.0, 82.2, 51.8, 27.9; FT-IR (CHCl_3) 3327, 2977, 1718, 1698, 1589, 1500, 1325, 1257 cm^{-1} ;

HRMS Calcd for $C_{32}H_{38}N_4NaO_8$ ($M + Na^+$): 629.2587, found 629.2572.

***N'*-[3-(*tert*-Butoxycarbonyl-*N'*-phenyl-hydrazino)-5-methyl-phenyl]-*N*-phenyl-hydrazinecarboxylic acid *tert*-butyl ester (9e)**

1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.6 Hz, 4H), 7.30 – 7.26 (m, 4H), 7.11 – 7.07 (m, 2H), 6.31 (s, 2H), 6.18 (d, J = 2.0 Hz, 2H), 6.07 (t, J = 1.6 Hz, 1H), 2.19 (s, 3H), 1.36 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 149.3, 142.7, 140.1, 128.4, 124.4, 121.7, 106.7, 95.0, 82.1, 28.0, 21.7; FT-IR ($CHCl_3$) 3340, 2977, 2929, 2256, 1715, 1608, 1495, 1368, 1338 cm^{-1} ; HRMS Calcd for $C_{29}H_{36}N_4NaO_4$ ($M + Na^+$): 527.2634, found 527.2622.

***N'*-[3-(*tert*-Butoxycarbonyl-*N'*-phenyl-hydrazino)-5-methyl-phenyl]-*N*-*o*-tolyl-hydrazinecarboxylic acid *tert*-butyl ester (9f)**

1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.34 (m, 2H), 7.21 – 7.11 (m, 6H), 6.38 (s, 1H), 6.32 (bs, 2H), 6.27 (s, 2H), 2.31 (s, 6H), 2.22 (s, 3H), 1.36 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 149.1, 141.5, 139.7, 134.3, 130.8, 127.0, 126.6, 126.3, 107.4, 96.0, 81.5, 28.0, 21.7, 18.4; FT-IR ($CHCl_3$) 3336, 2976, 2928, 2583, 2135, 1715, 1702, 1520, 1507, 1456, 1367, 1158 cm^{-1} ; HRMS Calcd for $C_{31}H_{40}N_4NaO_4$ ($M + Na^+$): 555.2947, found 555.2944.

***N'*-[3-[*N'*-*tert*-Butoxycarbonyl-*N'*-(2-methoxy-phenyl)-hydrazino]-5-methyl-phenyl]-*N*-(2-methoxy-phenyl)-hydrazinecarboxylic acid *tert*-butyl ester (9g)**

^1H NMR (400 MHz, CDCl_3) δ 7.38 (dd, $J_1 = 0.8$ Hz, $J_2 = 1.6$ Hz, 2H), 7.24 – 7.19 (m, 2H), 6.91 – 6.87 (m, 4H), 6.43 (s, 3H), 6.22 (s, 2H), 3.87 (s, 6H), 2.20 (s, 3H), 1.38 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.1, 154.4, 148.8, 139.5, 128.7, 128.44, 128.40, 120.4, 111.5, 106.7, 95.5, 81.1, 55.5, 28.1, 21.8; FT-IR (CHCl_3) 3350, 2976, 2929, 2594, 1730, 1718, 1526, 1505, 1458, 1158 cm^{-1} ; HRMS Calcd for $\text{C}_{31}\text{H}_{40}\text{N}_4\text{NaO}_6$ ($\text{M} + \text{Na}^+$): 587.2846, found 587.2855.

***N'*-[3,5-Bis-(*N'*-*tert*-butoxycarbonyl-*N'*-phenyl-hydrazino)-phenyl]-*N*-phenyl-hydrazinecarboxylic acid *tert*-butyl ester (11a)**

^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, $J = 8.0$ Hz, 6H), 7.21 (t, $J = 8.8$ Hz, 6H), 7.03 (t, $J = 7.2$ Hz, 3H), 6.43 (bs, 3H), 5.81 (s, 3H), 1.32 (s, 27H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.6, 150.1, 142.5, 128.1, 124.2, 121.8, 90.7, 82.0, 28.1; FT-IR (CHCl_3) 3344, 2978, 2931, 1711, 1616, 1495, 1339, 1156 cm^{-1} ; HRMS Calcd for $\text{C}_{39}\text{H}_{49}\text{N}_6\text{O}_6$ (M^+): 697.3714, found 697.3687.

***N'*-[3,5-Bis-(*N'*-*tert*-butoxycarbonyl-*N'*-*o*-tolyl-hydrazino)-phenyl]-*N*-*o*-tolyl-hydrazinecarboxylic acid *tert*-butyl ester (11b)**

^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 7.2$ Hz, 3H), 7.19 – 7.08 (m, 9H), 6.30 (bs, 3H), 6.08 (s, 3H), 2.29 (s, 9H), 1.36 (s, 27H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.8, 150.1, 141.4, 134.3, 130.8,

127.0, 126.7, 126.3, 92.1, 81.5, 28.0, 18.4; FT-IR (CHCl₃) 3337, 2977, 2930, 2580, 2124, 1716, 1616, 1519, 1300, 1158 cm⁻¹; HRMS Calcd for C₄₂H₅₄N₆NaO₆ (M + Na⁺): 761.4003, found 761.4000.

***N'*-[3,5-Bis-(*N'*-*tert*-butoxycarbonyl-*N'*-(2-methoxy-phenyl)-hydrazino)-phenyl]-*N*-(2-methoxy-phenyl)-hydrazinecarboxylic acid *tert*-butyl ester (11c)**

¹H NMR (400 MHz, CDCl₃) δ 7.35 - 7.32 (m, 3H), 7.19 - 7.15 (m, 3H), 6.87 - 6.81 (m, 6H), 6.36 (bs, 3H), 6.03 (s, 3H), 3.84 (s 9H), 1.35 (s, 27H); ¹³C NMR (100 MHz, CDCl₃) δ 155.7, 154.1, 149.5, 131.4, 128.7, 129.2, 120.3, 111.3, 91.2, 81.0, 55.5, 28.2; FT-IR (CHCl₃) 3340, 2977, 1715, 1613, 1500, 1340, 1159 cm⁻¹; HRMS Calcd for C₄₂H₅₅N₆O₉ (M + Na⁺): 787.4031, found 787.4033.

3-Methylbiphenyl-4,4'-diamine (7b)

¹H NMR (400 MHz, CDCl₃) 7.35 – 7.33 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.20 (m, 2H), 6.74 – 6.69 (m, 3H), 3.64 (bs, 4H), 2.21 (s, 3H). Eggertsen, F. T.; Weiss, F. T. *Anal. Chem.* **1956**, 28, 1008.

3,3'-Dimethylbiphenyl-4,4'-diamine (7c)

^1H NMR (400 MHz, CDCl_3) 7.24 – 7.20 (m, 4H), 6.70 – 6.68 (d, J = 8.0 Hz, 2H), 3.56 (bs, 4H), 2.20 (s, 6H); Gupta, P. N.; Raina, A. *J. Indian Chem Soc.* **1989**, 66, 865.

3, 5, 3'-Trimethyl-biphenyl-4, 4'-diamine (7d)

^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.19 (m, 2H), 7.13 (s, 2H), 6.66 (d, J = 8.0 Hz, 1H), 3.52 (bs, 4H), 2.20 (s, 6H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.0, 141.3, 132.1, 131.2, 128.5, 126.3, 124.9, 122.4, 121.9, 115.2, 17.7, 17.4; FT-IR (CHCl_3) 3458, 3374, 2906, 1625, 1483, 1267 cm^{-1} ; HRMS Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2$ (M^+): 226.1470, found 226.1474.

3'-Methoxy-3, 5-dimethyl-biphenyl-4, 4'-diamine (7e)

^1H NMR (400 MHz, CDCl_3) δ 7.13 (s, 2H), 6.98 – 6.96 (m, 2H), 6.72 (d, J = 8.4 Hz, 1H), 3.89 (s, 3H), 3.66 (bs, 4H), 2.22 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.4, 141.4, 134.5, 132.4, 131.5, 126.4, 121.9, 119.0, 115.1, 109.0, 55.4, 17.7; FT-IR (CHCl_3) 3466, 3364, 3052, 2982, 1622, 1467, 1266 cm^{-1} ; HRMS Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}$ (M^+): 242.1419, found 242.1424.

4,4'-Diamino-3'-methyl-biphenyl-3-carboxylic acid methyl ester (7f)

^1H NMR (400 MHz, CDCl_3) δ 8.04 – 8.03 (d, J = 2.2 Hz, 1H), 7.49 – 7.46 (dd, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1H), 7.24 – 7.21 (m, 2H), 6.72 – 6.70 (d, J = 8.0 Hz, 1H), 6.70 – 6.68 (d, J = 8.4 Hz, 1H), 3.89 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 149.6, 144.1, 133.1, 131.7, 130.4, 129.2, 129.0, 125.5, 123.3, 117.8, 116.0, 111.6, 52.2, 18.2; FT-IR (CHCl_3) 3476, 3370, 2949, 1689, 1624, 1586, 1491, 1437, 1299, 1239cm^{-1} ; HRMS Calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2$ (M^+): 256.1212, found 256.1210.

2-methylbiphenyl-4,4'-diamine (14a)

^1H NMR (400 MHz, CDCl_3) 7.10 – 7.08 (d, J = 8.4 Hz, 2H), 7.02 – 7.00 (d, J = 8.0 Hz, 1H), 6.72 – 6.70 (d, J = 8.4 Hz, 2H), 6.60 – 6.59 (d, J = 2.4 Hz, 1H), 6.57 – 6.54 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H), 3.64 (bs, 4H), 2.21 (s, 3H); Badger, G. M.; Drewer, R. J.; Lewis, G. E. *Australian J. Chem.* **1963**, 16, 1042.

2-bromobiphenyl-4,4'-diamine (14b)

^1H NMR (400 MHz, CDCl_3) 7.20 – 7.17 (d, J = 8.6 Hz, 2H), 7.09 – 7.07 (d, J = 8.2 Hz, 1H), 6.98 – 6.97 (d, J = 2.8 Hz, 1H), 6.72 – 6.69 (d, J = 8.6 Hz, 2H), 6.65 – 6.21 (dd, J_1 = 8.2 Hz, J_2 = 2.8 Hz, 1H), 3.70 (bs, 4H); Kimura, M.; Kuwano, S.; Sawaki, Y.; Fujikawa, H. *J. Materials Chem.* **2005**, 15, 2393.

3,3''-Dimethyl-[1,1';3',1'']terphenyl-4,4',6',4''-tetraamine (10b)

^1H NMR (400 MHz, CDCl_3) δ 7.14 – 7.12 (m, 4H), 6.90 (s, 1H), 6.73 – 6.71 (d, J = 7.7 Hz, 2H), 6.18 (s, 1H), 3.67 (s, 8H), 2.19 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.0, 143.8, 133.1, 132.0, 130.5, 128.4, 123.3, 120.2, 115.8, 102.8, 18.1; FT-IR (CHCl_3) 3437, 3352, 2921, 2850, 1619, 1493, 1280, 1262 cm^{-1} ; HRMS Calcd for $\text{C}_{20}\text{H}_{22}\text{N}_4$ (M^+): 318.1844, found 318.1839.

3, 5, 3'', 5''-Tetramethyl-[1, 1'; 3', 1'']terphenyl-4, 4', 6', 4''-tetraamine (10c)

^1H NMR (400 MHz, CDCl_3) δ 7.05 (s, 4H), 6.91 (s, 1H), 6.19 (s, 1H), 3.72 (bs, 4H), 3.60 (bs, 4H), 2.20 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.0, 141.2, 132.3, 129.1, 128.9, 121.8, 119.6, 102.1, 17.8; FT-IR (CHCl_3) 3054, 2987, 2686, 1621, 1558, 1422 cm^{-1} ; HRMS Calcd for $\text{C}_{22}\text{H}_{26}\text{N}_4$ (M^+): 346.2157, found 346.2147.

2'-Methyl-[1, 1'; 3', 1'']terphenyl-4, 4', 6', 4''-tetraamine (10e)

^1H NMR (400 MHz, CDCl_3) δ 7.05 (d, J = 8.4 Hz, 4H), 6.79 (d, J = 8.4 Hz, 4H), 6.11 (s, 1H), 3.56 (bs, 8H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.0, 144.1, 136.7, 131.6, 128.9, 119.3, 115.6, 98.9, 18.9; FT-IR (CHCl_3) 3055, 2987, 2686, 2524, 1612, 1514, 1425, 1566 cm^{-1} ; HRMS Calcd for $\text{C}_{19}\text{H}_{20}\text{N}_4$ (M^+): 304.1688, found 304.1673.

3, 2', 3''-Trimethyl-[1, 1'; 3', 1'']terphenyl-4, 4', 6', 4''-tetraamine (10f)

^1H NMR (400 MHz, CDCl_3) δ 6.95 – 6.91 (m, 4H), 6.73 (d, J = 8.0 Hz, 2H), 6.10 (s, 1H), 3.52 (bs, 8H), 2.18 (s, 6H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.0, 143.1, 136.5, 132.7, 129.1, 129.0, 122.7, 119.5, 115.4, 99.0, 18.9, 17.4; FT-IR (CHCl_3) 3054, 2986, 2927, 2686, 1610, 1460, 1426, 1266 cm^{-1} ; HRMS Calcd for $\text{C}_{21}\text{H}_{24}\text{N}_4$ (M^+): 332.2001, found 332.2000.

3, 3''-Dimethoxy-2'-methyl-[1, 1'; 3', 1'']terphenyl-4, 4', 6', 4''-tetraamine (10g)

^1H NMR (400 MHz, CDCl_3) δ 6.77 (d, J = 3.6 Hz, 2H), 6.72 – 6.68 (m, 4H), 6.12 (s, 1H), 3.83 (s, 6H), 3.66 (bs, 8H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.6, 144.2, 136.6, 134.6, 128.9, 123.0, 119.5, 115.3, 112.8, 98.8, 55.5, 18.8; FT-IR (CHCl_3) 3054, 2987, 2685, 1610, 1518, 1421, 1263 cm^{-1} ; HRMS Calcd for $\text{C}_{21}\text{H}_{24}\text{N}_4\text{O}_2$ (M^+): 364.1899, found 364.1877.

12a: ^1H NMR (400 MHz, CD_3OD) δ 7.06 (d, J = 8.4 Hz, 6H), 6.83 (d, J = 8.4 Hz, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ 148.5, 143.1, 133.3, 127.1, 117.9, 109.1; FT-IR (CHCl_3) 3054, 2986, 2931, 1715, 1605, 1514, 1447, 1422, 1266 cm^{-1} ; HRMS Calcd for $\text{C}_{24}\text{H}_{24}\text{N}_6$ (M^+): 396.2062, found 396.2061.

12b: ^1H NMR (400 MHz, CDCl_3) δ 7.13 (s, 3H), 7.09 (dd, $J_1 = 1.6$ Hz, $J_2 = 2.0$ Hz, 3H), 6.76 (d, $J = 7.6$ Hz, 3H), 3.62 (bs, 6H), 3.31 (bs, 6H), 2.18 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 142.1, 133.4, 129.9, 126.5, 123.4, 115.9, 105.1, 17.4; FT-IR (CHCl_3) 3054, 2987, 2830, 1611, 1517, 1422, 1266 cm^{-1} ; HRMS Calcd for $\text{C}_{27}\text{H}_{30}\text{N}_6$ (M^+): 438.2532, found 438.2522.

12c: ^1H NMR (400 MHz, CDCl_3) δ 6.88 – 6.80 (m, 9H), 3.84 (s, 15H), 3.39 (bs, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.0, 142.5, 135.1, 126.3, 123.8, 115.8, 113.3, 104.8, 55.5; FT-IR (CHCl_3) 3054, 2987, 2835, 1733, 1603, 1517, 1440, 1422, 1265 cm^{-1} ; HRMS Calcd for $\text{C}_{27}\text{H}_{30}\text{N}_6\text{O}_3$ (M^+): 486.2379, found 486.2366.

7