Supporting Information

Super Electron Donor-mediated Reductive Transformation of Nitrobenzenes:
A Novel Strategy to Synthesize Azobenzenes and Phenazines

Kanako Nozawa-Kumada, Erina Abe, Shungo Ito, Masanori Shigeno and Yoshinori Kondo*
Graduate School of Pharmaceutical Sciences, Tohoku University, 6-3, Aoba, Aramaki, Aoba-ku,
Sendai 980-8578, Japan
*E-mail: ykondo@m.tohoku.ac.jp

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1. General Comments
Melting points (mp) were determined with a Yazawa micro melting point apparatus and uncorrected. Infrared (IR) data were recorded on SensIR ATR (Attenuated Total Reflectance) FT-IR. Absorbance frequencies are reported in reciprocal centimeters (cm$^{-1}$). NMR data were recorded on a JEOL AL400 spectrometer or a JEOL ECA600 spectrometer. Chemical shifts are expressed in δ (parts per million, ppm) values and coupling constants are expressed in hertz (Hz). $^1$H NMR spectra were referenced to tetramethylsilane as an internal standard or to a solvent signal (CDCl$_3$: 7.26 ppm, DMSO-$d_6$: 2.49 ppm). $^{13}$C NMR spectra were referenced to a solvent signal (CDCl$_3$: 77.0 ppm, DMSO-$d_6$: 39.5 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet. Low and high resolution mass spectra (LRMS and HRMS) were obtained from Mass Spectrometry Resource, Graduate School of Pharmaceutical Sciences, Tohoku University, on a JEOL JMS-DX 303 and JMS-700/JMS-T 100 GC spectrometer.

2. Materials
Nitrobenzenes and other commercially available materials were purchased from Tokyo Kasei Co., Aldrich Inc. and other commercial suppliers and were used as received. Flash column chromatography was performed with Kanto silica gel 60 N (spherical, neutral, 70–230 mesh).

3. Preparation of Starting Materials
Preparation of 1,3-bis(3-methyl-3H-benzimidazolium)propane diiodide (1')

\[
\begin{align*}
\text{N} & \quad \text{N} & \quad \text{I} & \quad \text{I} \\
\text{I} & \quad \text{I} & \quad \text{N} & \quad \text{N} \\
\end{align*}
\]

Under an Ar atmosphere, 1,3-diiodopropane (39 mmol, 8.7 g) was added to a solution of 1-methyl-1H-benzimidazole (90 mmol, 12 g) in acetonitrile (400 mL). The mixture was heated under reflux for 2 days. After cooling, diethyl ether (200 mL) was added to the mixture. The resulting precipitates were filtered and washed with diethyl ether (100 mL × 3). Recrystallization from CH$_2$Cl$_2$/ethanol to give 1' (85%, 14 g) as colorless prisms. mp 268–273 °C; IR (neat, cm$^{-1}$): 2361, 2344, 1570, 1487, 1351, 1201, 1126, 1008, 857, 762; $^1$H NMR (400 MHz, DMSO-$d_6$) δ (ppm): 9.73 (2H, s), 8.09–8.02 (4H, m), 7.73–7.67 (4H, m), 4.68 (4H, t, $J = 7.3$ Hz), 4.07 (6H, s), 2.59 (2H, quint, $J = 7.3$ Hz); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ (ppm): 142.8, 131.8, 130.8, 126.6, 126.5, 113.6, 113.5, 43.8, 33.4, 28.1; LRMS (FAB) m/z: 433 (M–I)$^+$; HRMS (FAB-EB) m/z: (M–I)$^+$ Caled. for C$_{19}$H$_{22}$IN$_4$:$^+$ 433.0884, found: 433.0894.
Preparation of 1,3-bis(N,N-dimethyl-4-aminopyridinium)propane diiodide (2')

Under an Ar atmosphere, 1,3-diiodopropane (30 mmol, 8.9 g) was added to a solution of 4-dimethylaminopyridine (75 mmol, 8.4 g) in acetonitrile (300 mL). The mixture was heated under reflux overnight. After cooling, diethyl ether (100 mL) was added to the mixture. The resulting precipitates were filtered and washed with diethyl ether (30 mL × 3). Recrystallization from CH$_2$Cl$_2$/ethanol to gave 2' (77%, 12 g) as colorless prisms. mp 303–308 °C (dec.); IR (neat, cm$^{-1}$): 1645, 1570, 1539, 1404, 1374, 1236, 1202, 1174, 1036, 946, 830, 743, 738; $^1$H NMR (400 MHz, DMSO-$d_6$) δ (ppm): 8.29 (4H, d, $J = 7.3$ Hz), 7.04 (4H, d, $J = 7.3$ Hz), 4.27–4.23 (4H, m), 3.18 (12H, s), 2.36–2.32 (2H, m); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ (ppm): 155.9, 141.9, 107.8, 53.8, 39.8, 31.0; LRMS (FAB) $m/z$: 413 (M–I)$^+$; HRMS (FAB-EB) $m/z$: (M–I)$^+$ Calcd. for C$_{17}$H$_{26}$IN$_4$$^+$: 413.1197, found: 413.1212.

tert-Butyl 4-nitrobenzoate (4o)

To a slurry of 4-nitrobenzoic acid (10 mmol, 1.8 g) in pyridine (20 mL), tosyl chloride (20 mmol, 3.8 g) was added with stirring. Once the solid was completely dissolved, the solution was cooled to 0 °C, and t-buty1 alcohol (2 mL) was added. After stirring at 0 °C for 2 h, the reaction mixture was allowed to warm to rt. After an additional 2 h of stirring, another portion of t-buty1 alcohol (2 mL) was added. The reaction mixture was stirred for additional 14 h. The solvent was evaporated, and the residue was partitioned between ethyl acetate (30 mL), and sat. NaHCO$_3$ (30 mL). The organic layer was washed with sat. NaHCO$_3$ (30 mL × 3), and the pooled aqueous layer was washed with ethyl acetate (30 mL). The organic layer was pooled and washed with brine (30 mL), sat. NaHSO$_4$ (30 mL × 4), and brine (30 mL), and then dried over MgSO$_4$. The solvent was removed under reduced pressure and the residue was recrystallized from CH$_2$Cl$_2$/hexane to give 4o (43%, 0.97 g) as colorless prisms. mp 122–123 °C (lit.$^4$ 114–116 °C); IR (neat, cm$^{-1}$): 2980, 1711, 1608, 1521, 1461, 1396, 1373, 1365, 1345, 1324, 1298, 1254, 1156, 1123, 1103, 1010, 874, 841, 786, 716, 707; $^1$H NMR (400 MHz, CDCl$_3$/TMS) δ (ppm): 8.26 (2H, d, $J = 8.8$ Hz), 8.15 (2H, d, $J = 8.8$ Hz), 1.62 (9H, s); $^{13}$C NMR (100 MHz, CDCl$_3$/TMS) δ (ppm): 163.7, 150.3, 137.4 130.5, 123.3, 82.6, 28.1; LRMS (EI) $m/z$: 223 (M$^+$); HRMS (EI-TOF) $m/z$: (M$^+$) Calcd. for C$_{11}$H$_8$NO$_4$: 223.0845, found: 223.0817.
4. General Procedure for the Synthesis of Azobenzenes

Method in a glove box
In a glove box, a mixture of \( 2' \) (0.40 mmol, 0.22 g) and NaH (paraffin oil free, 1.0 mmol, 25 mg) in DMF (2.9 mL) was stirred at rt for 1 h. After the SED generated, nitrobenzene 4 (0.20 mmol) was added to the mixture and stirred at rt for 15 min. The reaction mixture was quenched with saturated NH\(_4\)Cl aq. and extracted with ethyl acetate (10 mL \( \times \) 3). The combined organic layer was washed by water (30 mL \( \times \) 3) and brine (30 mL), and then dried over Na\(_2\)SO\(_4\). The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to give the azobenzene 6.

Method using a manifold
Under an Ar atmosphere, a mixture of \( 2' \) (0.42 mmol, 0.23 g) and NaH (60% dispersion in paraffin oil, 0.82 mmol, 33 mg) in DMF (2.9 mL) was stirred at rt for 1 h. After the SED generated, nitrobenzene (0.20 mmol) was added to the mixture and stirred at rt for 15 min. The reaction mixture was quenched with H\(_2\)O at 0 °C and extracted with ethyl acetate (10 mL \( \times \) 3). The combined organic layer was washed by water (30 mL \( \times \) 3) and brine (30 mL), and then dried over Na\(_2\)SO\(_4\). The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to give the azobenzene 6.

Azoxybenzene (5a)

Obtained as yellow oil; IR (neat, cm\(^{-1}\)): 3063, 3027, 2946, 2871, 1600, 1586, 1496, 1468, 1244, 1171, 1038, 750; \(^1\)H NMR (400 MHz, CDCl\(_3\)/TMS) \( \delta \) (ppm): 8.32–8.30 (2H, m), 8.16 (2H, dd, \( J = 1.5, 8.8 \) Hz), 7.58–7.47 (5H, m), 7.39 (1H, t, \( J = 7.3 \) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)/TMS) \( \delta \) (ppm): 148.4, 144.0, 131.6, 129.6, 128.8, 128.7, 125.5, 122.4; LRMS (EI) \( m/z \): 198 (M\(^+\)); HRMS (EI-EB) \( m/z \): Calcd. for C\(_{12}\)H\(_{10}\)N\(_2\)O: 198.0793, found: 198.0795.

Azobenzene (6a)

Obtained in 98% yield (13.4 mg, 0.15 mmol scale); Recrystallized from hexane, orange plates, mp 66–70 °C (lit.\(^6\) 65–66 °C); IR (neat, cm\(^{-1}\)): 3061, 2956, 2924, 2855, 2358, 2323, 1483, 1452, 1299, 1222, 1151, 1071, 1019, 926, 773; \(^1\)H NMR (400 MHz, CDCl\(_3\)/TMS) \( \delta \) (ppm): 7.94–7.91 (4H, m),
7.54–7.45 (6H, m); $^{13}$C NMR (100 MHz, CDCl$_3$/TMS) $\delta$ (ppm): 152.7, 131.0, 129.1, 122.8; LRMS (EI) $m/z$: 182 (M$^+$); HRMS (EI-TOF) $m/z$: (M$^+$) Calcd. for C$_{12}$H$_{10}$N$_2$: 182.0844, found: 182.0847.

4,4´-Dimethylazobenzene (6b)

Obtained in 70% yield (14.6 mg); Recrystallized from methanol/hexane, orange plates, mp 146–147 °C (lit.5 145–146 °C); IR (neat, cm$^{-1}$): 3023, 2922, 1598, 1580, 1503, 1412, 1296, 1209, 1153, 1110, 1037, 1011, 840; $^1$H NMR (400 MHz, CDCl$_3$/TMS) $\delta$ (ppm): 7.81 (4H, d, $J = 8.3$ Hz), 7.30 (4H, d, $J = 8.3$ Hz), 2.43 (6H, s); $^{13}$C NMR (100 MHz, CDCl$_3$/TMS) $\delta$ (ppm): 150.8, 141.2, 129.7, 122.7, 21.5; LRMS (EI) $m/z$: 210 (M$^+$); HRMS (EI-TOF) $m/z$: (M$^+$) Calcd. for C$_{14}$H$_{14}$N$_2$: 210.1157, found: 210.1180.

3,3´-Dimethylazobenzene (6c)

Obtained as orange oil in 98% yield (20.6 mg); IR (neat, cm$^{-1}$): 2919, 1607, 1599, 1481, 1457, 1378, 1306, 1250, 1144, 1084, 1041, 999, 914, 881, 790; $^1$H NMR (400 MHz, CDCl$_3$/TMS) $\delta$ (ppm): 7.76–7.69 (4H, m), 7.39 (2H, t, $J = 7.8$ Hz), 7.27 (2H, d, $J = 7.8$ Hz), 2.45 (6H, s); $^{13}$C NMR (100 MHz, CDCl$_3$/TMS) $\delta$ (ppm): 152.9, 139.0, 131.6, 128.9, 122.9, 120.4, 21.3; LRMS (EI) $m/z$: 210 (M$^+$); HRMS (EI-EB) $m/z$: (M$^+$) Calcd. for C$_{14}$H$_{14}$N$_2$: 210.1157, found: 210.1157.

2,2´-Dimethylazobenzene (6d)

Obtained in 38% yield (8.0 mg); Recrystallized from methanol/hexane, orange plates, mp 55–57 °C (lit.6 53–54 °C); IR (neat, cm$^{-1}$): 2926, 1597, 1479, 1456, 1376, 1303, 1278, 1218, 1194, 1150, 1120, 1041, 950, 865, 769, 717; $^1$H NMR (400 MHz, CDCl$_3$/TMS) $\delta$ (ppm): 7.62 (2H, d, $J = 8.3$ Hz), 7.35–7.33 (4H, m), 7.28–7.25 (2H, m), 2.74 (6H, s); $^{13}$C NMR (100 MHz, CDCl$_3$/TMS) $\delta$ (ppm): 151.1, 138.0, 131.3, 130.7, 126.3, 115.9, 17.6; LRMS (EI) $m/z$: 210 (M$^+$); HRMS (EI-TOF) $m/z$: (M$^+$) Calcd. for C$_{14}$H$_{14}$N$_2$: 210.1157, found: 210.1176.
4,4´-Di-tert-butylazobenzene (6e)

<image of the molecule>

Obtained in 95% yield (27.9 mg); Recrystallized from methanol/hexane, orange prisms, mp 188–192 °C; IR (neat, cm⁻¹): 2959, 2904, 2867, 1602, 1458, 1404, 1362, 1268, 1161, 1107, 1010, 845; ¹H NMR (400 MHz, CDCl₃/TMS) δ (ppm): 7.84 (4H, d, J = 8.6 Hz), 7.52 (4H, d, J = 8.6 Hz) 1.37 (18H, s); ¹³C NMR (100 MHz, CDCl₃/TMS) δ (ppm): 154.2, 150.8, 126.0, 122.4, 35.0, 31.3; LRMS (EI, m/z): 294 (M⁺); HRMS (EI-TOF) m/z: (M⁺) Calcd. for C₂₀H₂₆N₂: 294.2096, found: 294.2091.

4,4´-Dimethoxyazobenzene (6f)

<image of the molecule>

Obtained in 79% yield (18.8 mg); Recrystallized from ethanol/hexane, orange prisms, mp 169–171 °C (lit. 7 166.5–167 °C); IR (neat, cm⁻¹): 2970, 2840, 1578, 1496, 1456, 1439, 1421, 1317, 1293, 1242, 1178, 1143, 1023, 839, 823, 745, 733; ¹H NMR (400 MHz, CDCl₃/TMS) δ (ppm): 7.89–7.85 (4H, m), 7.01–6.98 (4H, m), 3.88 (6H, s); ¹³C NMR (100 MHz, CDCl₃/TMS) δ (ppm): 161.5, 147.1, 124.3, 114.1, 55.5; LRMS (EI) m/z: 242 (M⁺); HRMS (EI-TOF) m/z: (M⁺) Calcd. for C₁₄H₁₄N₂O₂: 242.1055, found: 242.1045.

4,4´-Difluoroazobenzene (6g)

<image of the molecule>

Obtained in 51% yield (11.3 mg); Orange plates, mp 102–104 °C (lit. 8 97–100 °C); IR (neat, cm⁻¹): 3112, 3062, 2924, 1896, 1592, 1496, 1415, 1289, 1229, 1201, 1140, 1094, 1008, 892, 839, 801, 754, 720; ¹H NMR (400 MHz, CDCl₃/TMS) δ (ppm): 7.94–7.91 (4H, m), 7.22–7.18 (4H, m); ¹³C NMR (150 MHz, CDCl₃/TMS) δ (ppm): 164.4 (d, J_FC = 252.4 Hz), 149.0, 124.8 (d, J_FC = 8.6 Hz), 116.1 (d, J_FC = 21.5 Hz); LRMS (EI) m/z: 218 (M⁺); HRMS (EI-TOF) m/z: (M⁺) Calcd. for C₁₂H₇F₂N₂: 218.0656, found: 218.0615.
3,3'-Difluoroazobenzene (6h)

![Chemical Structure]

Obtained in 65% yield (14.2 mg) as a orange plates; mp 66–74 °C (lit.9 77–79 °C); IR (neat, cm⁻¹): 3080, 2924, 2854, 2364, 2323, 1582, 1479, 1465, 1315, 1240, 1111, 951, 887, 798, 743; ¹H NMR (400 MHz, CDCl₃/TMS) δ (ppm): 7.78–7.76 (2H, m), 7.61 (2H, dt, J = 2.4, 9.8 Hz), 7.54–7.48 (2H, m), 7.23–7.18 (2H, m); ¹³C NMR (100 MHz, CDCl₃/TMS) δ (ppm): 163.3 (d, J_FC = 249.4 Hz), 153.8 (d, J_FC = 7.4 Hz), 130.3 (d, J_FC = 9.1 Hz), 120.8 (d, J_FC = 3.3 Hz), 118.2 (d, J_FC = 22.2 Hz), 108.1 (d, J_FC = 23.0 Hz); LRMS (EI) m/z: 218 (M⁺); HRMS (EI-TOF) m/z: (M⁺) Calcd. for C₁₂H₈F₂N₂: 218.0656, found: 218.0665.

4,4'-Dichloroazobenzene (6i)

![Chemical Structure]

Obtained in 80% yield (20.2 mg); Recrystallized from ethyl acetate/hexane, orange prisms, mp 186–190 °C (lit.5 184.5–185.5 °C); IR (neat, cm⁻¹): 3086, 2360, 2343, 1923, 1585, 1570, 1479, 1404, 1295, 1209, 1145, 1105, 1082, 1004, 846, 823, 717; ¹H NMR (400 MHz, CDCl₃/TMS) δ (ppm): 7.88–7.84 (4H, m), 7.51–7.47 (4H, m); ¹³C NMR (100 MHz, CDCl₃/TMS) δ (ppm):150.8, 137.2, 129.4, 124.2; LRMS (EI) m/z: 250 (M⁺); HRMS (EI-TOF) m/z: (M⁺) Calcd. for C₁₂H₈Cl₂N₂: 250.0065, found: 250.0045.

3,3'-Dichloroazobenzene (6j)

![Chemical Structure]

Obtained in 71% yield (18.0 mg); Recrystallized from methanol/hexane, orange plates, mp 104–105 °C (lit.8 100–102 °C); IR (neat, cm⁻¹): 3079, 3072, 2356, 2325, 1955, 1889, 1820, 1704, 1585, 1568, 1462, 1416, 1303, 1196, 1154, 1066, 996, 885, 791; ¹H NMR (400 MHz, CDCl₃/TMS) δ (ppm): 7.90 (2H, s), 7.85–7.82 (2H, m), 7.48–7.46 (4H, m); ¹³C NMR (100 MHz, CDCl₃/TMS) δ (ppm):
153.1, 135.2, 131.2, 130.2, 122.6, 121.9; LRMS (EI) m/z: 250 (M⁺); HRMS (EI-TOF) m/z: Calcd. for C₁₂H₈³⁵Cl₂N₂: 250.0065, found: 250.0093.

2,2'-Dichloroazobenzene (6k)

![结构式]

Obtained in 74% yield (18.5 mg); Recrystallized from ethanol (orange prisms); mp 133–134 °C (lit.⁵ 137–139 °C); IR (neat, cm⁻¹): 2923, 1723, 1582, 1574, 1465, 1443, 1433, 1288, 1220, 1159, 1129, 1059, 1032, 952, 942, 833, 763, 725, 747; ¹H NMR (400 MHz, CDCl₃/TMS) δ (ppm): 7.77 (2H, dd, J = 2.0, 7.8 Hz), 7.57 (2H, dd, J = 1.5, 7.8 Hz), 7.42 (2H, td, J = 2.0, 7.8 Hz), 7.36 (2H, td, J = 1.5, 7.8 Hz); ¹³C NMR (100 MHz, CDCl₃/TMS) δ (ppm): 148.8, 135.8, 132.2, 130.8, 127.4, 118.1; LRMS (EI) m/z: 250 (M⁺); HRMS (EI-TOF) m/z: (M⁺) Calcd. for C₁₂H₈³⁵Cl₂N₂: 250.0065, found: 250.0070.

4,4'-Dibromoazobenzene (6l)

![结构式]

Obtained in 68% yield (23.2 mg); Recrystallized from chloroform/hexane, orange plates, mp 208–210 °C (lit.⁵ 203–204.5 °C); IR (neat, cm⁻¹): 3088, 1907, 1773, 1646, 1570, 1473, 1398, 1282, 1218, 1154, 1098, 1065, 1006, 833, 816, 711; ¹H NMR (400 MHz, CDCl₃/TMS) δ (ppm): 7.79 (4H, d, J = 8.8 Hz), 7.65 (4H, d, J = 8.8 Hz); ¹³C NMR (100 MHz, CDCl₃/TMS) δ (ppm): 151.2, 132.4, 125.8, 124.4; LRMS (EI) m/z: 338 (M⁺); HRMS (EI-TOF) m/z: (M⁺) Calcd. for C₁₂H₈⁷⁹Br₂N₂: 337.9054, found: 337.9064.

3,3’-Dibromoazobenzene (6m)

![结构式]

Obtained in 71% yield (24.1 mg); Recrystallized from methanol/chloroform, orange needles, mp 129–130 °C (lit.¹⁰ 139–141 °C); IR (neat, cm⁻¹): 3065, 1759, 1564, 1458, 1411, 1300, 1207, 1197, 1147, 1058, 995, 882, 867, 859, 794; ¹H NMR (400 MHz, CDCl₃/TMS) δ (ppm): 8.05 (2H, s), 7.88 (2H, d, J = 8.0 Hz), 7.62 (2H, d, J = 8.0 Hz), 7.41 (2H, t, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃/TMS) δ
(ppm): 153.2, 134.1, 130.5, 124.8, 123.2 (2C); LRMS (EI) m/z: 338 (M⁺); HRMS (EI-TOF) m/z: (M⁺) Calcd. for C₁₂H₮Br₂N₂: 337.9054, found: 337.9027.

4,4’-Dicyanoazobenzene (6n)

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\begin{align*}
&\text{NC}^- \quad \text{N} \\
&\text{N} \quad \text{N} \quad \text{CN} \\
&\text{Obtained in 72\% yield (16.8 mg); Recrystallized from ethyl acetate/hexane, red needles; IR (neat, cm}^{-1} \text{: 3092, 2358, 2228, 1931, 1801, 1598, 1491, 1408, 1306, 1296, 1219, 1163, 1099, 1011; \text{¹H NMR (600 MHz, CDCl}_3/TMS) \delta (ppm): 8.04 (4H, d, J = 8.8 Hz), 7.85 (4H, d, J = 8.8 Hz); \text{¹³C NMR (150 MHz, CDCl}_3/TMS) \delta (ppm): 154.0, 133.4, 123.7, 118.1, 115.2; LRMS (EI) m/z: 232 (M⁺); HRMS (EI-EB) m/z: (M⁺) Calcd. for C₁₄H₈N₄: 232.0749, found: 232.0747.}
\end{align*}
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Di-tert-buthylazobenzene-4,4’-dicarboxylate (6o)

\[
\begin{align*}
&\text{t-BuO}_2\text{C} \quad \text{CO}_2\text{t-Bu} \\
&\text{Obtained in 57\% yield (21.9 mg); Recrystallized from hexane, orange needles; mp 186–188 °C; IR (neat, cm}^{-1} \text{: 2979, 1705, 1367, 1288, 1256, 1170, 1118, 1098, 1010, 870, 850, 781, 700; \text{¹H NMR (400 MHz, CDCl}_3/TMS) \delta (ppm): 8.14 (4H, d, J = 8.3 Hz), 7.96 (4H, d, J = 8.3 Hz); \text{¹³C NMR (100 MHz, CDCl}_3/TMS) \delta (ppm): 165.1, 154.7, 134.3, 130.4, 122.7, 81.6, 28.2; LRMS (EI) m/z: 382 (M⁺); HRMS (EI-EB) m/z: (M⁺) Calcd. for C₂₂H₂₆N₂O₄: 382.1893, found: 382.1888.}
\end{align*}
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Hydrazobenzene (7a)

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\begin{align*}
&\text{Colorless solid; mp 127–129 °C (lit.¹¹ 124–125 °C); IR (neat, cm}^{-1} \text{: 3327, 2925, 1598, 1586, 1478, 1304, 1246, 1073, 888, 750; \text{¹H NMR (400 MHz, CDCl}_3/TMS) \delta (ppm): 7.22–7.19 (4H, m), 6.86–6.82 (4H, m), 5.59 (2H, br.s); \text{¹³C NMR (100 MHz, CDCl}_3/TMS) \delta (ppm): 148.8, 129.3, 119.9, 112.3; LRMS (EI) m/z: 184 (M⁺); HRMS (EI-EB) m/z: (M⁺) Calcd. for C₁₂H₁₂N₂: 184.1000, found: 183.0993.}
\end{align*}
\]
3-Phenyl-2-oxa-3-azabicyclo[2.2.2]oct-5-ene (9)

Obtained in 9% yield (3.4 mg); IR (neat, cm\(^{-1}\)): 2960, 2930, 2853, 1595, 1489, 1450, 1369, 1237, 1228, 1179, 1164, 1151, 1085, 1060, 1026, 956, 950, 937, 900, 874, 821, 806, 762, 719; \(^1\)H NMR (600 MHz, CDCl\(_3\)/TMS) \(\delta\) (ppm): 7.21 (2H, t, \(J = 7.4\) Hz), 7.01 (2H, d, \(J = 2.8, 8.3\) Hz), 6.92 (1H, t, \(J = 7.9\) Hz), 6.59–6.57 (1H, m), 6.15 (1H, t, \(J = 2.8\) Hz), 4.70 (1H, t, \(J = 7.9\) Hz), 4.44–4.42 (1H, m), 2.32–2.27 (1H, m), 2.25–2.21 (1H, m), 1.60–1.57 (1H, m), 1.37 (1H, td, \(J = 3.7, 11.9\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)/TMS) \(\delta\) (ppm): 152.3, 131.6, 130.0, 128.3, 122.0, 117.4, 69.1, 56.5, 24.0, 21.4; LRMS (EI) \(m/z\): 187 (M\(^+\)); HRMS (EI-EB) \(m/z\): (M\(^+\)) Calcd. for C\(_{12}\)H\(_{13}\)NO: 187.0997, found: 187.0990.

5. General Procedure for the Synthesis of Phenazines

Under an Ar atmosphere, a mixture of \(2^*\) (0.40 mmol, 0.23 g) and NaH (60% dispersion in paraffin oil, 0.80 mmol, 33 mg) in DMF (2.9 mL) was stirred at rt for 1 h. After the SED generated, 2-fluoronitrobenzene (0.20 mmol) was added to the mixture and stirred at rt for 15 min. The reaction mixture was quenched with H\(_2\)O at 0 °C and extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed by water (30 mL × 3) and brine (30 mL), and then dried over Na\(_2\)SO\(_4\). The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to give the phnazine 11.

Phenazine (11a)

Obtained in 68% yield (12.1 mg); Recrystallized from CH\(_2\)Cl\(_2\)/hexane, yellow prisms, mp 177–179 °C (lit.\(^9\) 172–175 °C); IR (neat, cm\(^{-1}\)): 3060, 1627, 1513, 1472, 1431, 1361, 1210, 1147, 1109, 997, 957, 903, 858, 820, 741; \(^1\)H NMR (600 MHz, CDCl\(_3\)/TMS) \(\delta\) (ppm): 8.28–8.25 (4H, m), 7.87–7.84 (4H, m); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)/TMS) \(\delta\) (ppm): 143.6, 130.5, 129.7; LRMS (EI) \(m/z\): 180 (M\(^+\)); HRMS (EI-TOF) \(m/z\): (M\(^+\)) Calcd. for C\(_{12}\)H\(_8\)N\(_2\): 180.0687, found: 180.0702.

2,7-Dimethylphenazine (11b)

Obtained as orange solid (10b: 30% yield, 6.3 mg, 10b*: 22% yield, 4.6 mg); mp 169–170 °C (lit.\(^9\) 161–163 °C); IR (neat, cm\(^{-1}\)): 2970, 2944, 2910, 1639, 1515, 1507, 1481, 1449, 1418, 1379, 1356,
1133, 1037, 1009, 881, 874, 863, 801, 768, 749; \( ^1\)H NMR (400 MHz, CDCl\(_3\)/TMS) \( \delta \) (ppm): 8.12 (2H, d, \( J = 8.8 \) Hz), 7.97 (2H, s), 7.67–7.65 (2H, m), 2.65 (6H, s); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)/TMS) \( \delta \) (ppm): 143.2, 142.3, 140.5, 133.3, 129.0, 127.7, 22.2; LRMS (EI) \( m/z \): 208 (M\(^+\)); HRMS (EI-TOF) \( m/z \): (M\(^+\)) Calcd. for C\(_{14}\)H\(_{12}\)N\(_2\): 208.1000, found: 208.1000.

2,7-Dichlorophenazine (11c)

\[ \text{Cl} \]
\[ \text{N} \]
\[ \text{Cl} \]

10c: 43% yield, 10.7 mg, 10c': 45% yield, 11.2 mg; Recrystallized from methanol/hexane, yellow prisms; IR (neat, cm\(^{-1}\)): 3054, 1924, 1773, 1618, 1506, 1458, 1412, 1399, 1373, 1351, 1320, 1285, 1258, 1180, 1166, 1127, 1067, 1049, 951, 935, 921, 884, 855, 846, 809, 740, 730; \( ^1\)H NMR (400 MHz, CDCl\(_3\)/TMS) \( \delta \) (ppm): 8.24 (2H, d, \( J = 2.2 \) Hz), 8.18 (2H, d, \( J = 9.3 \) Hz), 7.80 (2H, dd, \( J = 2.2, 9.3 \) Hz); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)/TMS) \( \delta \) (ppm): 143.3, 142.3, 136.9, 132.6, 130.9, 128.1; LRMS (EI) \( m/z \): 248 (M\(^+\)); HRMS (EI-TOF) \( m/z \): (M\(^+\)) Calcd. for C\(_{12}\)H\(_{6}\)Cl\(_2\)N\(_2\): 247.9908, found: 247.9920.

2,7-Bis(trifluoromethyl)phenazine (11d)

\[ \text{F}_3\text{C} \]
\[ \text{N} \]
\[ \text{Cl} \]

Obtained in 28% yield as yellow solid (8.6 mg); mp 119–122 °C; IR (neat, cm\(^{-1}\)): 3031, 1517, 1487, 1428, 1326, 1288, 1256, 1206, 1162, 1139, 1130, 1046, 984, 935, 915, 892, 856, 836, 807, 771, 755; \( ^1\)H NMR (600 MHz, CDCl\(_3\)/TMS) \( \delta \) (ppm): 8.63 (2H, s), 8.43 (2H, d, \( J = 8.9 \) Hz), 8.04 (2H, dd, \( J = 1.4, 8.9 \) Hz); \( ^{13}\)C NMR (150 MHz, CDCl\(_3\)/TMS) \( \delta \) (ppm): 144.4, 143.1, 133.1 (q, \( J_{FC} = 33.0 \) Hz), 131.5, 128.2 (q, \( J_{FC} = 5.7 \) Hz), 126.5, 123.4 (q, \( J_{FC} = 272.5 \) Hz); LRMS (EI) \( m/z \): 316 (M\(^+\)); HRMS (EI-EB) \( m/z \): (M\(^+\)) Calcd. for C\(_{14}\)H\(_6\)F\(_6\)N\(_2\): 316.0435, found: 316.0433.

6. References
7. $^1$H- and $^{13}$C-NMR Spectra

$^1$H-NMR Spectra of 1'

[Image of NMR spectra with chemical shifts and proton assignments]
$^{13}$C-NMR Spectra of $1'$
'H-NMR Spectra of 2'

S15
$^{13}$C-NMR Spectra of 2'

![C-NMR Spectra Image]

Chemical structures and data points are shown in the image.
$^1$H-NMR Spectra of 4o
$^{13}$C-NMR Spectra of 4o

S18
$^1$H-NMR Spectra of 5a

![1H-NMR Spectra of 5a](image)
$^{13}$C-NMR Spectra of 5a
$^1$H-NMR Spectra of 6a
$^{13}$C-NMR Spectra of 6a
$^1$H-NMR Spectra of $6b$
$^{13}$C-NMR Spectra of 6b
$^1$H-NMR Spectra of 6c
$^{13}$C-NMR Spectra of 6c

![C-NMR Spectra of 6c](image-url)
$^1$H-NMR Spectra of 6d
$^{13}$C-NMR Spectra of 6d
$^1$H-NMR Spectra of 6e
13C-NMR Spectra of 6e
$^1$H-NMR Spectra of 6f
$^{13}$C-NMR Spectra of 6f
$^1$H-NMR Spectra of 6g
$^{13}$C-NMR Spectra of 6g

\[ \text{6g} \]

PPM

\[ \begin{align*}
165.2956 & \quad 163.5872 \\
148.9834 & \\
136.8082 & \quad 134.2880 \\
126.9847 & \quad 124.3874 \\
116.1879 & \quad 113.9941 \\
77.7911 & \quad 77.0900 \\
72.0999 & \quad -0.0166
\end{align*} \]
$^1$H-NMR Spectra of 6h

6h
\( ^{13}\text{C-NMR Spectra of 6h} \)
$^1$H-NMR Spectra of $6i$
$^{13}$C-NMR Spectra of 6i
$^1$H-NMR Spectra of 6j

![H-NMR Spectra of 6j](image)
$^{13}$C-NMR Spectra of 6j

![C-NMR Spectra of 6j](image)
$^1$H-NMR Spectra of 6k

6k

[Chemical Structure Image]
$^{13}$C-NMR Spectra of 6k

![13C-NMR Spectra of 6k](image)
$^1$H-NMR Spectra of 6l

![H-NMR Spectra of 6l](image_url)

**6l**
$^{13}$C-NMR Spectra of 6l
$^1$H-NMR Spectra of 6m
$^{13}$C-NMR Spectra of 6m

![13C-NMR Spectra of 6m](image)
$^{1}H$-NMR Spectra of 6n

\[
\text{\begin{center}
\includegraphics[width=\textwidth]{hnmr_spectra}
\end{center}}
\]
$^{13}$C-NMR Spectra of 6n

![Chemical structure of 6n](image)

- 152.9811
- 133.0952
- 123.7440
- 118.4269
- 77.2802
- 77.0090
- 76.7894

PPM

200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
$^1$H-NMR Spectra of 6o
$^{13}$C-NMR Spectra of 6o

![C-NMR Spectra of 6o with chemical structure and spectral data]
$^{13}$C-NMR Spectra of 7a
$^1$H-NMR Spectra of 9
$^{13}$C-NMR Spectra of 9

![C-NMR Spectrum of 9](image)
H-NMR Spectra of 11a

11a

N

N

Chemical Shifts:
- 8.2787
- 8.2702
- 8.2616
- 8.2531
- 7.8663
- 7.8577
- 7.8492
- 7.8407
- 7.2599
- 1.5654
- 0.0000
$^{13}$C-NMR Spectra of 11a
$^1$H-NMR Spectra of 11b

![NMR Spectra Image]

11b
$^{13}$C-NMR Spectra of 11b
$^1$H-NMR Spectra of 11c
$^{13}$C-NMR Spectra of 11c

11c

- Cl
- N
- Cl

11c
$^1$H-NMR Spectra of 11d

![NMR Spectra of 11d](image)
$^{13}$C-NMR Spectra of 11d

![C-NMR Spectra of 11d](image)