

TEMPO Catalyzed Oxidative Dehydrogenation of Hydrazobenzenes to Azobenzenes

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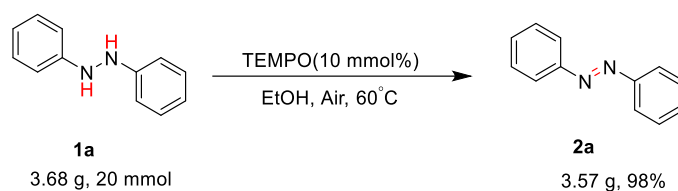
1. General Information

All commercially available reagents were obtained from commercial suppliers and used without further purification. All catalytic experiments were carried out using standard techniques. Chromatography was carried out over silica gel (Innochem 200–300 mesh) and TLC was performed using silica gel 60 F254 (Merck) plates. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker NMR spectrometer in CDCl_3 using TMS as an internal reference with chemical shift values reported in ppm. Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique. The diphenyl hydrazine derivatives (except for commercially available **1a**) were prepared by the literature procedures.^{1,2}

2. Procedure for the direct oxidative dehydrogenation of hydrazobenzenes

To a solution of 1,2-Diphenyl hydrazine **1a** (0.3 mmol) in EtOH (2 mL) TEMPO (10 mol%) was added. The reaction mixture was open to air and stirred at 60 °C for 12 h. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **2a** (54.2 mg, 99%).

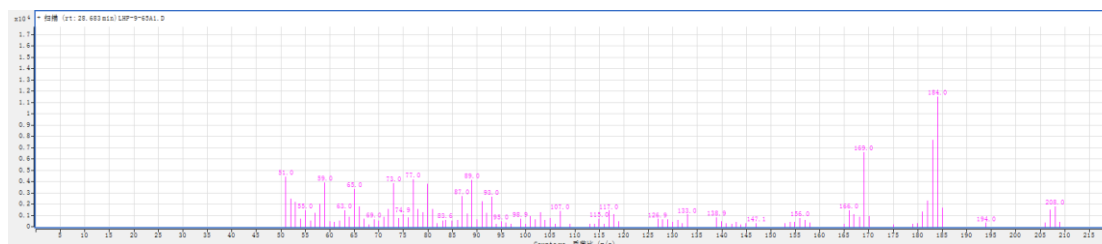
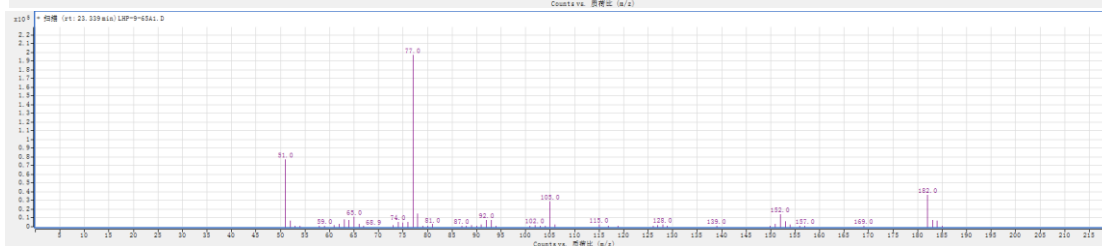
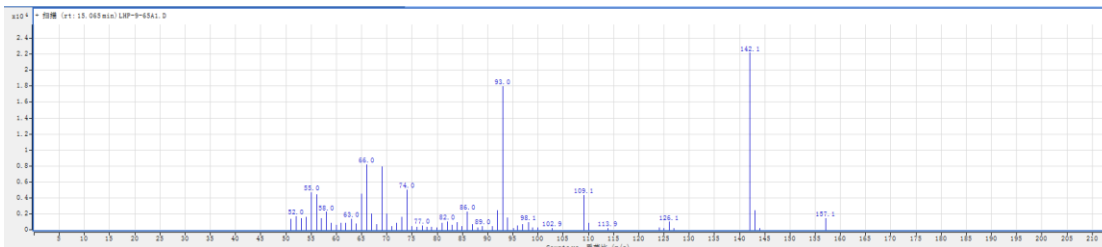
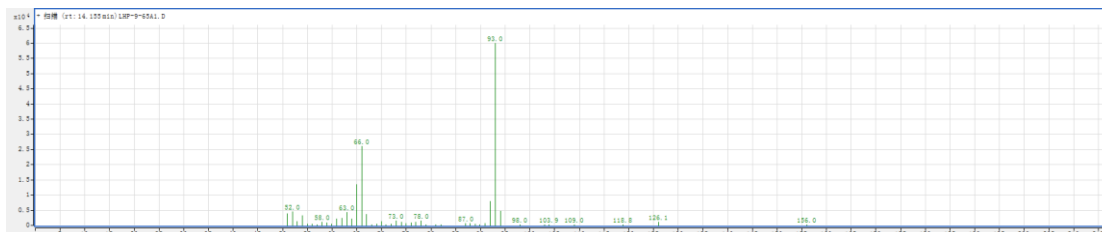
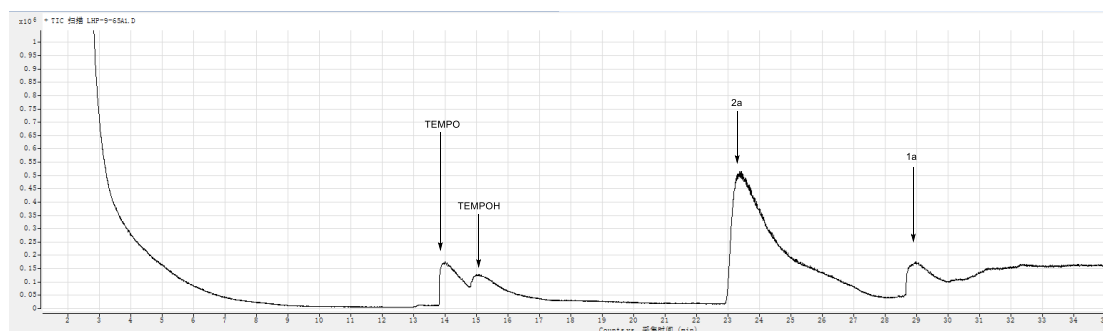
3. The gram scale reaction



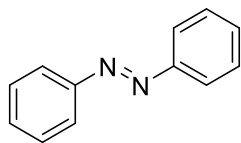
To a solution of 1,2-Diphenyl hydrazine **1a** (20.0 mmol) in EtOH (60 mL) was added TEMPO (10 mol%). The reaction mixture was open to air and stirred at 60 °C for 18 h. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **2a** in 98% yield (3.57 g).

4. Mechanistic Investigation

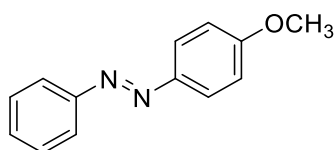
To a solution of 1,2-Diphenyl hydrazine **1a** (0.3 mmol, 1 equiv.) in EtOH (2 mL) was added TEMPO (10 mol%) under air atmosphere, and the reaction mixture was stirred at ambient temperature for 1 hour., the solution was detected using GC-MS [(TEMPO: 156.0 (14.155 min); TEMPOH: 157.1 (15.065 min); **2a**: 182.0(23.339 min) ; **1a**: 184.0(28.683 min)].



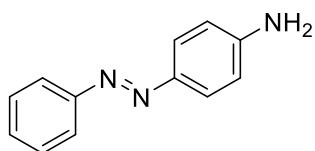
5. Characterization data for the products



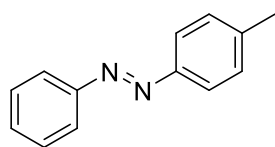
1,2-diphenyldiazene (2a)¹: Orange solid; m.p. 65-66 °C; 99% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.98–7.96 (m, 4H), 7.57–7.48 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 152.8, 131.1, 129.2, 123.0; IR (KBr) : 3433, 3061, 1955, 1897, 1624, 1580, 1479, 1450, 1399, 1297, 1218, 1152, 1069, 1017, 924, 775, 688, 545, 519 cm⁻¹; HRMS-ESI (m/z) [M + H]⁺ calcd for C₁₂H₁₁N₂ 183.0917, found 183.0915.



1-(4-methoxyphenyl)-2-phenyldiazene (2b)²: Red solid; m.p. 52-53 °C; 96% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.97–7.91 (m, 4H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.48-7.44 (m, 1H), 7.03 (d, *J* = 9.0 Hz, 2H), 3.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.2, 152.9, 147.1, 130.5, 129.1, 124.9, 122.7, 114.3, 55.7; IR (KBr) : 3433, 3060, 2958, 2838, 1889, 1656, 1601, 1582, 1498, 1441, 1411, 1230, 1249, 1179, 1145, 1104, 1070, 1027, 922, 838, 764, 720, 686, 553, 534, 516 cm⁻¹; HRMS-ESI (m/z) [M + H]⁺ calcd for C₁₃H₁₃N₂O 213.1022, found 213.1018.

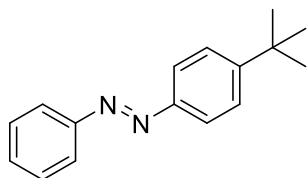


4-(phenyldiazenyl)aniline (2c): Red solid; m.p. 123-124 °C; 95% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.97–7.94 (m, 2H), 7.91–7.89 (m, 2H), 7.57–7.53 (m, 2H), 7.48–7.44 (m, 1H), 6.73–6.71 (m, 2H), 4.06 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 151.8, 148.6, 144.2, 128.7, 127.9, 124.0, 121.2, 113.4; IR (KBr) : 2945, 1717, 1595, 1490, 1438, 1405, 1280, 1216, 1193, 1145, 1107, 1005, 961, 931, 864, 780, 696, 547, 475 cm⁻¹; HRMS-ESI (m/z) [M + H]⁺ calcd for C₁₂H₁₂N₃ 198.1026, found 198.1024.

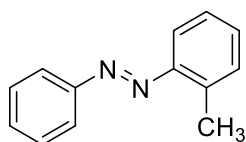


1-phenyl-2-(p-tolyl)diazene (2d)²: Orange solid; m.p. 66-67 °C; 98% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 7.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.9, 150.9, 141.7, 130.8, 129.9, 129.2,

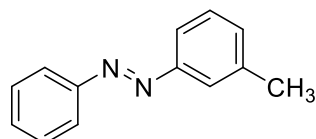
123.0, 122.9, 21.6; IR (KBr) : 3434, 3033, 2920, 2361, 2338, 1890, 1756, 1650, 1599, 1580, 1500, 1483, 1441, 1405, 1297, 1212, 1148, 1105, 1067, 1036, 1014, 917, 840, 820, 763, 705, 681, 544, 523, 488 cm⁻¹; HRMS-ESI (m/z) [M + H]⁺ calcd for C₁₃H₁₃N₂ 197.1073, found 197.1070.



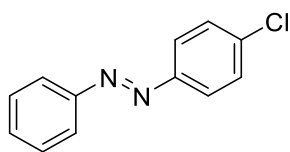
1-(4-(*tert*-butyl)phenyl)-2-phenyldiazene (2e)³: Orange solid; m.p. 51-52 °C; 95% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.96–7.94 (m, 2H), 7.92–7.90 (m, 2H), 7.58–7.46 (m, 5H), 1.41 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 154.7, 153.0, 150.8, 130.8, 129.2, 126.1, 122.9, 122.7, 35.1, 31.4; IR (KBr): 3065, 2963, 2906, 2868, 1952, 1915, 1798, 1670, 1600, 1501, 1467, 1444, 1396, 1364, 1302, 1267, 1228, 1201, 1158, 1107, 1070, 1017, 952, 824, 843, 768, 740, 688, 609, 569, 533, 511 cm⁻¹; HRMS-ESI (m/z) [M + H]⁺ calcd for C₁₆H₁₉N₂ 239.1543, found 239.1540.



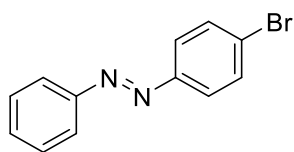
1-phenyl-2-(*o*-tolyl)diazene (2f)³: Red oil; 97% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.96–7.93 (m, 2H), 7.66–7.64 (m, 1H), 7.55–7.46 (m, 3H), 7.40–7.27 (m, 3H), 2.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.2, 150.9, 138.3, 131.4, 131.1, 130.9, 129.2, 126.6, 123.1, 115.6, 17.7; IR (KBr) : 3060, 2955, 2924, 2856, 1953, 1598, 1481, 1454, 1377, 1302, 1280, 1216, 1197, 1152, 1106, 1070, 1040, 1020, 949, 923, 772, 714, 688, 569, 553, 494, 446 cm⁻¹; HRMS-ESI (m/z) [M + H]⁺ calcd for C₁₃H₁₃N₂ 197.1073, found 197.1072.



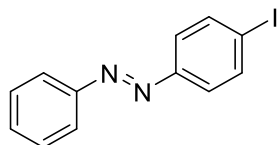
1-phenyl-2-(*m*-tolyl)diazene (2g)¹: Red oil; 99% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.97–7.94 (m, 2H), 7.78–7.77 (m, 2H), 7.57–7.42 (m, 4H), 7.32 (d, *J* = 7.4 Hz, 1H), 2.49 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.9, 152.9, 139.1, 131.9, 131.0, 129.2, 129.0, 123.0, 122.9, 120.7, 21.5; IR (KBr) : 3060, 2921, 2861, 1798, 1603, 1470, 1378, 1304, 1245, 1151, 1085, 1041, 1021, 1000, 920, 882, 790, 766, 691, 576, 523, 492, 439 cm⁻¹; HRMS-ESI (m/z) [M + H]⁺ calcd for C₁₃H₁₃N₂ 197.1073, found 197.1074.



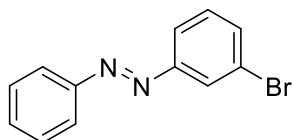
1-(4-chlorophenyl)-2-phenyldiazene (2h)²: Yellow solid; m.p. 83-84 °C; 99% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.56–7.49 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 152.6, 151.1, 137.0, 131.4, 129.4, 129.2, 124.3, 123.1; IR (KBr): 3434, 3057, 1916, 1758, 1669, 1571, 1477, 1438, 1397, 1296, 1211, 1146, 1084, 1021, 1001, 915, 840, 765, 704, 680, 629, 543, 521, 426 cm⁻¹; HRMS-ESI (*m/z*) [*M* + *H*]⁺ calcd for C₁₂H₁₀ClN₂ 217.0527, found 217.0532.



1-(4-bromophenyl)-2-phenyldiazene (2i)¹: Orange solid; m.p. 90-91 °C; 95% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.94–7.92 (m, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.55–7.49 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.6, 151.5, 132.5, 131.5, 129.3, 125.5, 124.5, 123.1; IR (KBr): 3429, 3056, 2383, 1895, 1757, 1661, 1568, 1474, 1439, 1392, 1294, 1216, 1147, 1096, 1064, 1021, 999, 915, 837, 766, 701, 682, 627, 542, 521, 481 cm⁻¹; HRMS-ESI (*m/z*) [*M* + *H*]⁺ calcd for C₁₂H₁₀BrN₂ 261.0022, found 261.0017.

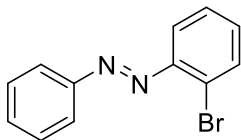


1-(4-iodophenyl)-2-phenyldiazene (2j)³: Orange solid; m.p. 90-91 °C; 93% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.93–7.90 (m, 2H), 7.89–7.85 (m, 2H), 7.68–7.64 (m, 2H), 7.55–7.49 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.6, 152.1, 138.5, 131.5, 129.3, 124.6, 123.1, 97.8; IR (KBr): 3429, 3055, 2365, 1915, 1657, 1563, 1489, 1442, 1390, 1297, 1275, 1217, 1181, 1151, 1094, 1069, 1047, 998, 927, 833, 764, 704, 685, 542, 521, 480 cm⁻¹; HRMS-ESI (*m/z*) [*M* + *H*]⁺ calcd for C₁₂H₁₀IN₂ 308.9883, found 308.9888.

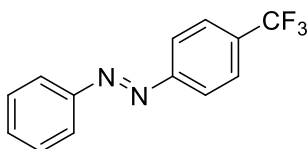


1-(3-bromophenyl)-2-phenyldiazene (2k)¹: Orange solid; m.p. 64-65 °C; 96% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.08–8.07 (m, 1H), 7.95–7.88 (m, 3H), 7.62–7.49 (m, 4H), 7.40 (t, *J* = 8.0 Hz, 1H); ¹³C NMR

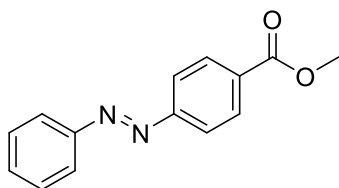
(100 MHz, CDCl₃) δ 153.6, 152.5, 133.7, 131.7, 130.6, 129.3, 124.8, 123.3, 123.2, 123.1; IR (KBr): 3430, 3055, 2362, 1959, 1758, 1694, 1563, 1443, 1405, 1300, 1205, 1166, 1145, 1053, 1015, 990, 926, 877, 838, 789, 765, 684, 648, 521, 496, 435 cm⁻¹; HRMS-ESI (m/z) [M + H]⁺ calcd for C₁₂H₁₀BrN₂ 261.0022, found 261.0021.



1-(2-bromophenyl)-2-phenyldiazene (2l)³: Red oil; 92% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.01–7.99 (m, 2H), 7.78–7.76 (m, 1H), 7.70–7.68 (m, 1H), 7.56–7.49 (m, 3H), 7.42–7.30 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 152.8, 149.8, 133.9, 132.0, 131.7, 129.3, 128.1, 125.9, 123.6, 117.9; IR (KBr) : 3449, 3059, 2955, 2924, 2855, 2313, 1953, 1806, 1756, 1598, 1481, 1454, 1377, 1302, 1280, 1217, 1197, 1152, 1106, 1070, 1040, 1020, 949, 923, 864, 837, 772, 714, 688, 569, 552, 495, 447 cm⁻¹; HRMS-ESI (m/z) [M + H]⁺ calcd for C₁₂H₁₀BrN₂ 261.0022, found 261.0018.

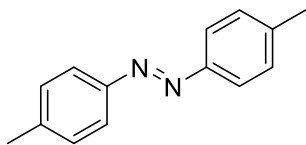


1-phenyl-2-(4-(trifluoromethyl)phenyl)diazene (2m)¹: Orange solid; m.p. 83-84 °C; 99% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.02–7.96 (m, 4H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.58–7.52 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 154.6, 152.6, 132.4 (q, ²*J*_{CF} = 32.4 Hz), 132.0, 129.3, 126.4 (q, ³*J*_{CF} = 3.7 Hz), 124.1 (q, ¹*J*_{CF} = 270.5 Hz), 123.3, 123.2; IR (KBr) : 3428, 3065, 2362, 1693, 1608, 1585, 1484, 1446, 1411, 1326, 1220, 1169, 1126, 1150, 1104, 1065, 1007, 924, 850, 769, 739, 684, 599, 539, 522 cm⁻¹; HRMS-ESI (m/z) [M + H]⁺ calcd for C₁₃H₁₀F₃N₂ 251.0791, found 251.0790.

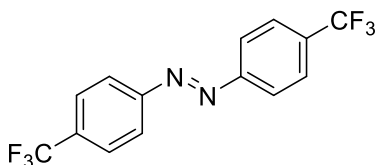


methyl-4-(phenyldiazenyl)benzoate (2n): Red solid; m.p. 129-130 °C; 92% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.20–8.17 (m, 2H), 7.96–7.93 (m, 4H), 7.55–7.49 (m, 3H), 3.94 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 155.1, 152.5, 131.8, 131.7, 130.6, 129.2, 123.2, 122.7, 52.3; IR (KBr) : 3475, 3380, 3204, 1692, 1619, 1595, 1501, 1460, 1413, 1303, 1229, 1138, 1067, 1017, 945, 920, 833, 769,

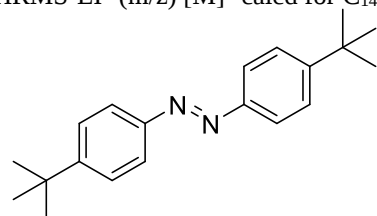
721, 687, 545, 525, 489 cm^{-1} ; HRMS-ESI (m/z) [$M + H$] $^{+}$ calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_2$ 241.0972, found 241.0978.



1,2-di-*p*-tolyl diazene (2o)²: Orange solid; m.p. 143-144 $^{\circ}\text{C}$; 98% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.4$ Hz, 4H), 7.32 (d, $J = 8.0$ Hz, 4H), 2.44 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.0, 141.3, 129.8, 122.9, 21.6; IR (KBr) : 3434, 3021, 2975, 2918, 2854, 2363, 1918, 1632, 1597, 1497, 1410, 1295, 1206, 1150, 1109, 1033, 1008, 950, 844, 822, 711, 639, 544, 525, 462 cm^{-1} ; HRMS-ESI (m/z) [$M + H$] $^{+}$ calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2$ 211.1230, found 211.1228.

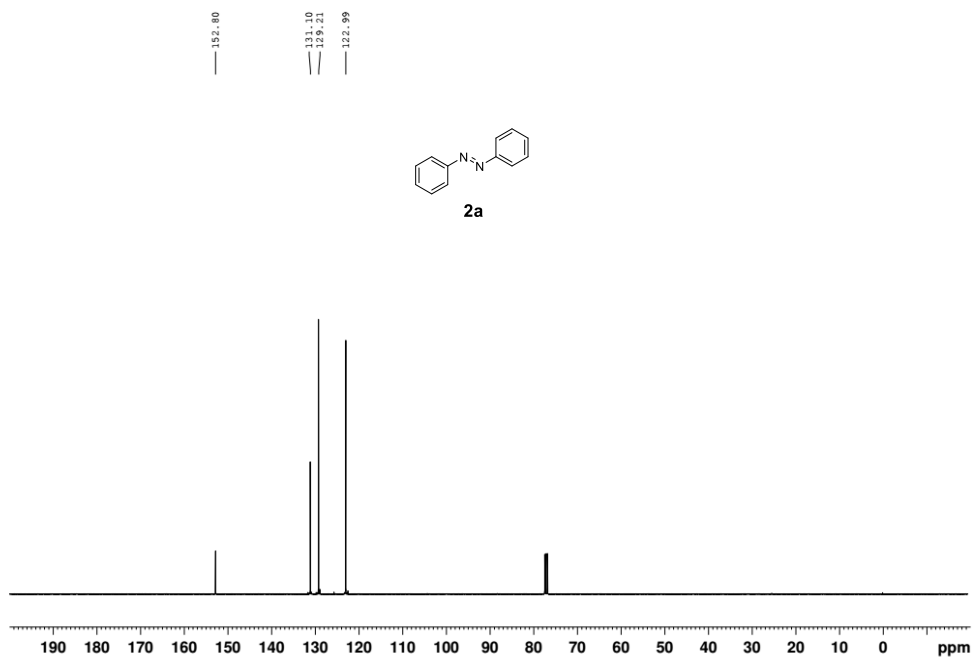
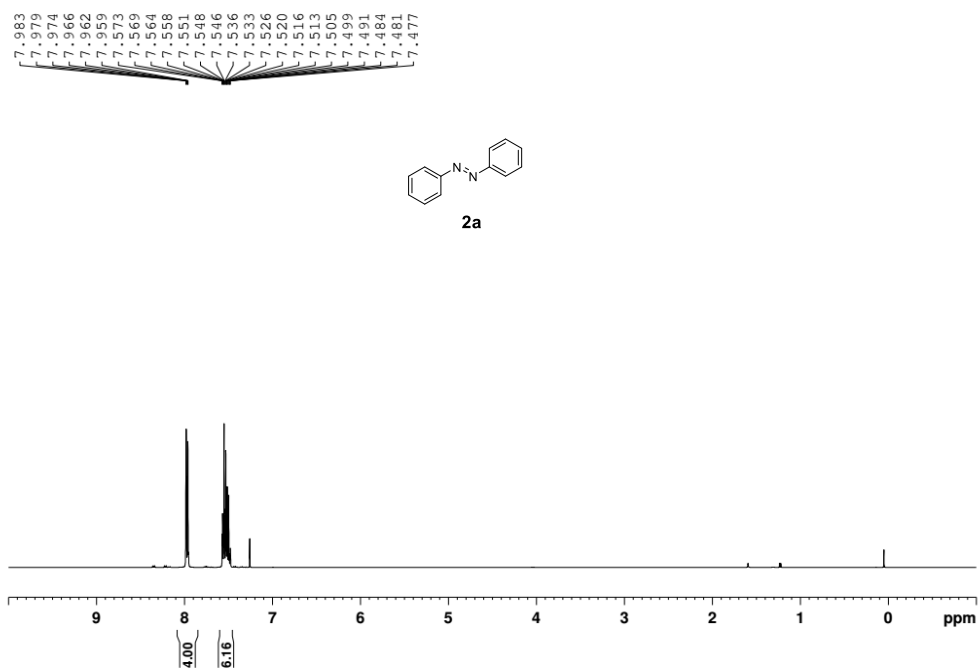


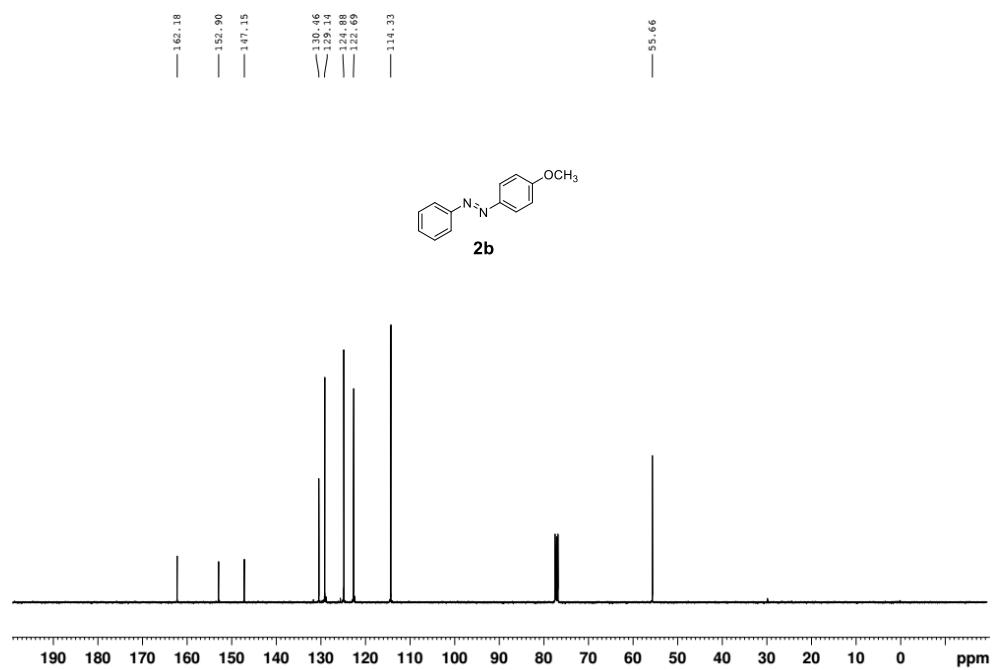
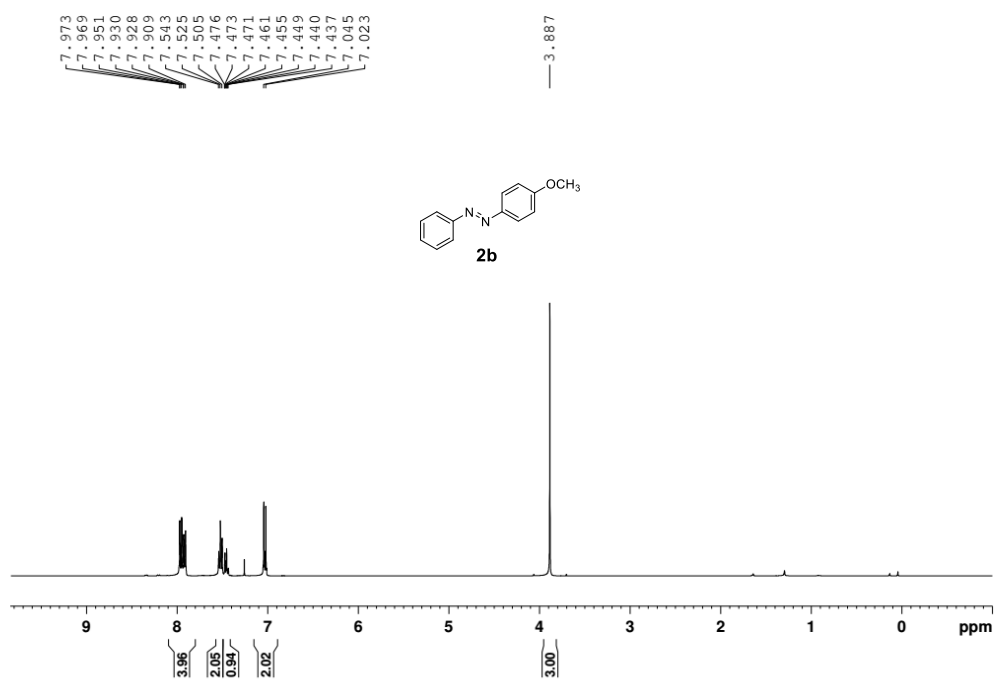
1,2-bis(4-(trifluoromethyl)phenyl)diazene (2p)²: Red solid; m.p. 110-111 $^{\circ}\text{C}$; 95% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.4$ Hz, 4H), 7.81 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.3, 133.2 (q, $^2J_{\text{CF}} = 32.3$ Hz), 126.6 (q, $^3J_{\text{CF}} = 3.7$ Hz), 124.0 (q, $^1J_{\text{CF}} = 270.9$ Hz), 123.5; IR (KBr) : 3424, 1932, 1803, 1611, 1415, 1321, 1219, 1175, 1133, 1102, 1062, 1010, 853, 747, 637, 601, 525 cm^{-1} ; HRMS-EI $^{+}$ (m/z) [M] $^{+}$ calcd for $\text{C}_{14}\text{H}_8\text{F}_6\text{N}_2$ 318.0593, found 318.0592.

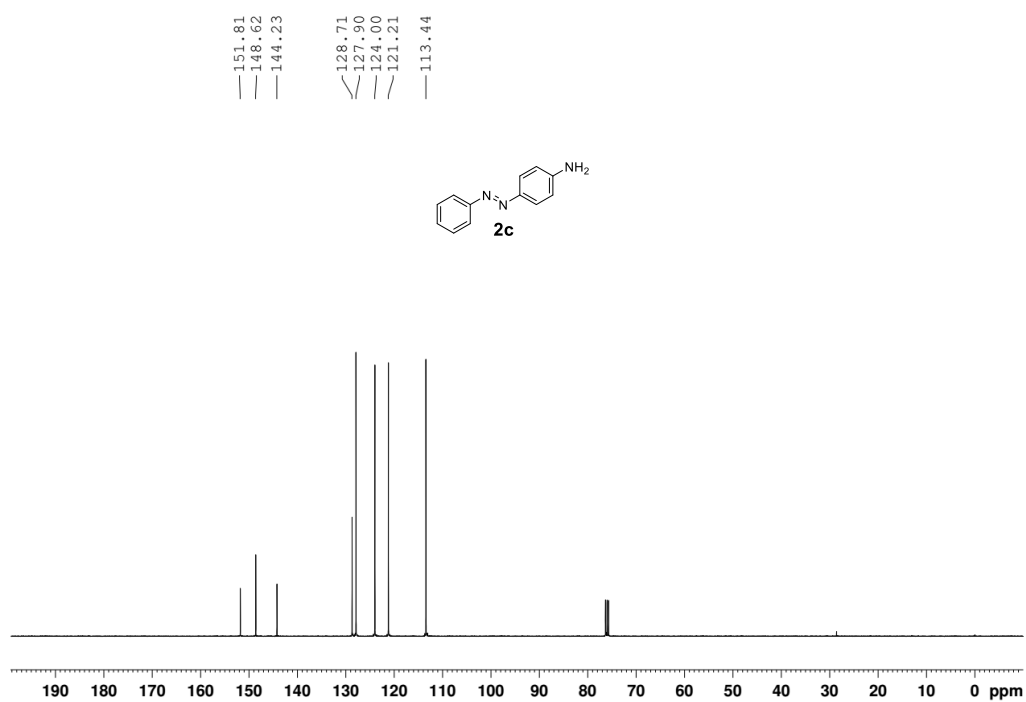
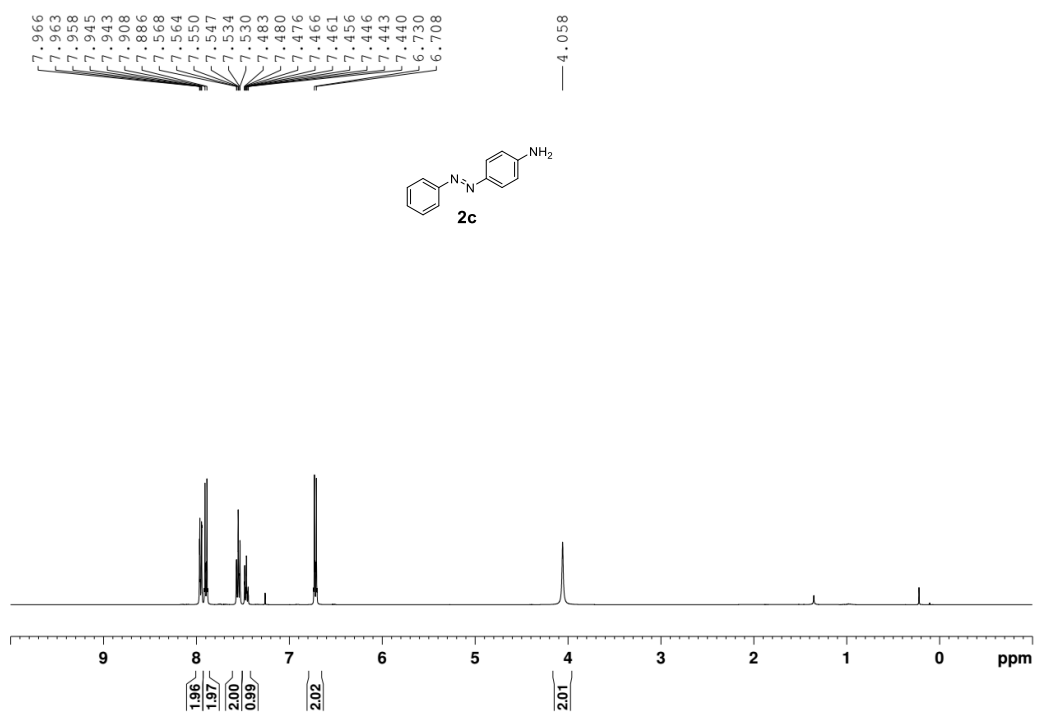


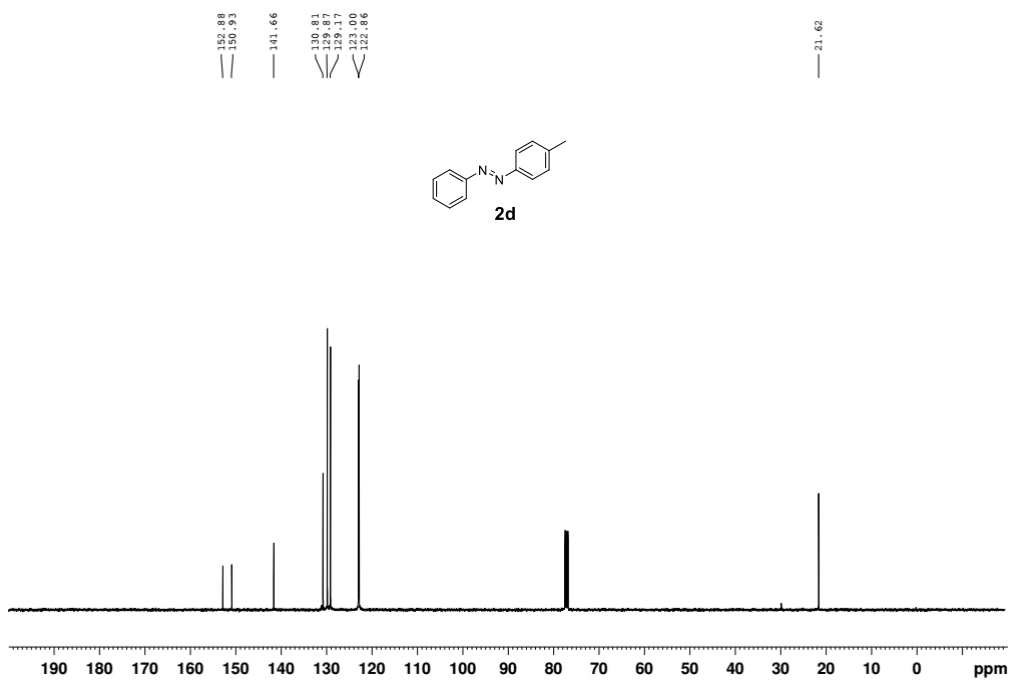
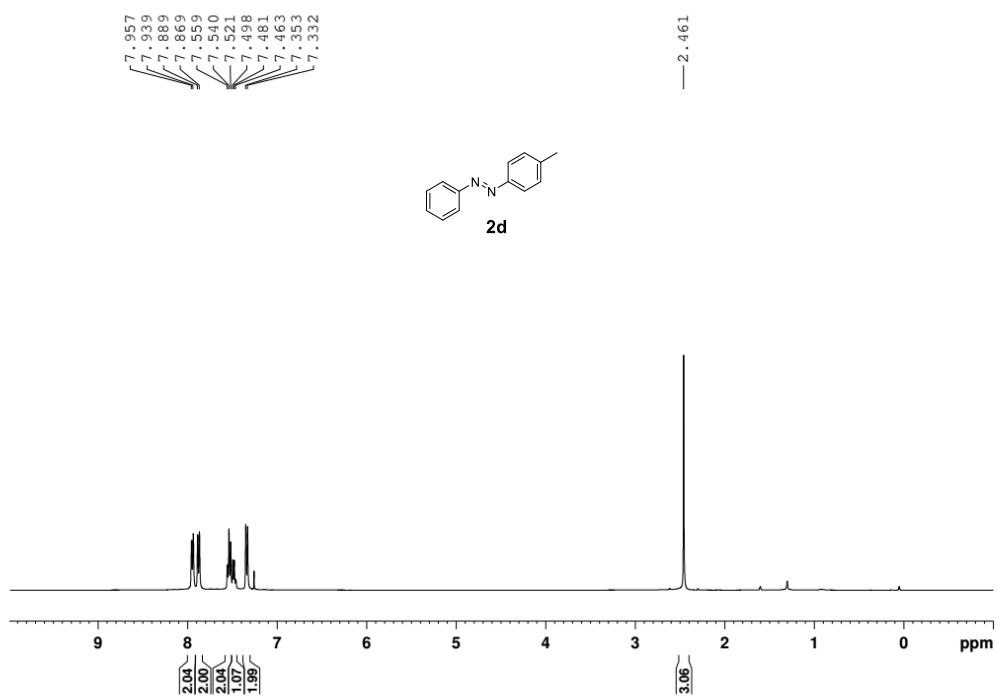
1,2-bis(4-(*tert*-butyl)phenyl)diazene (2q)³: Orange solid; m.p. 178-180 $^{\circ}\text{C}$; 96% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.7$ Hz, 4H), 7.55 (d, $J = 8.7$ Hz, 4H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.4, 150.9, 126.1, 122.6, 35.1, 31.4; IR (KBr) : 2959, 2865, 1598, 1495, 1462, 1402, 1362, 1265, 1231, 1201, 1160, 1106, 1008, 845, 665, 643, 574, 531 cm^{-1} ; HRMS-ESI (m/z) [$M + H$] $^{+}$ calcd for $\text{C}_{20}\text{H}_{27}\text{N}_2$ 295.2169, found 295.2168.

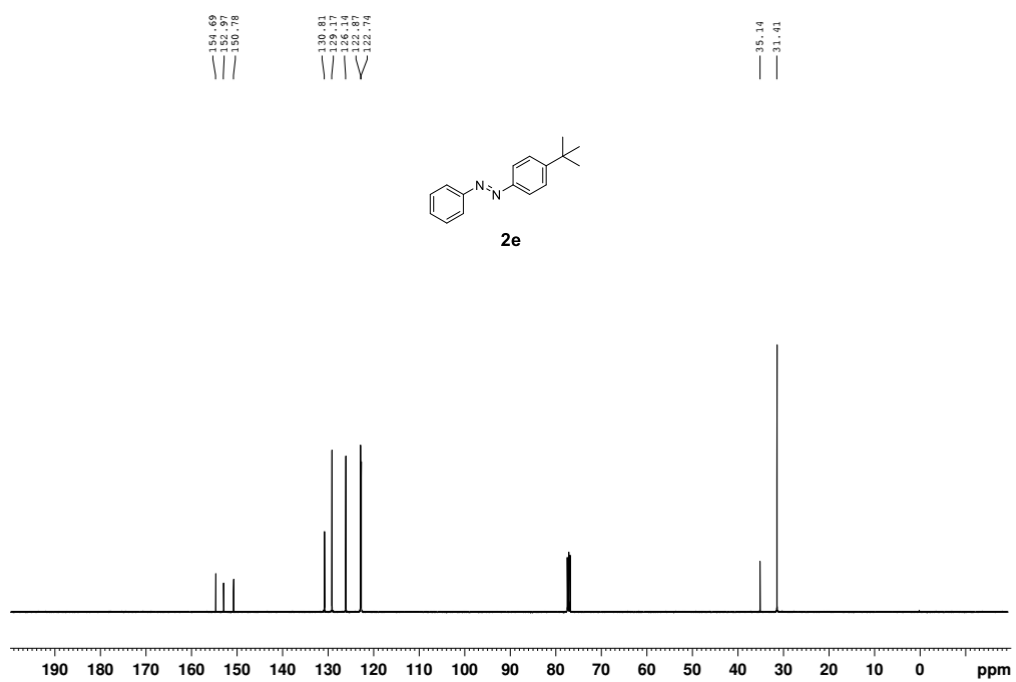
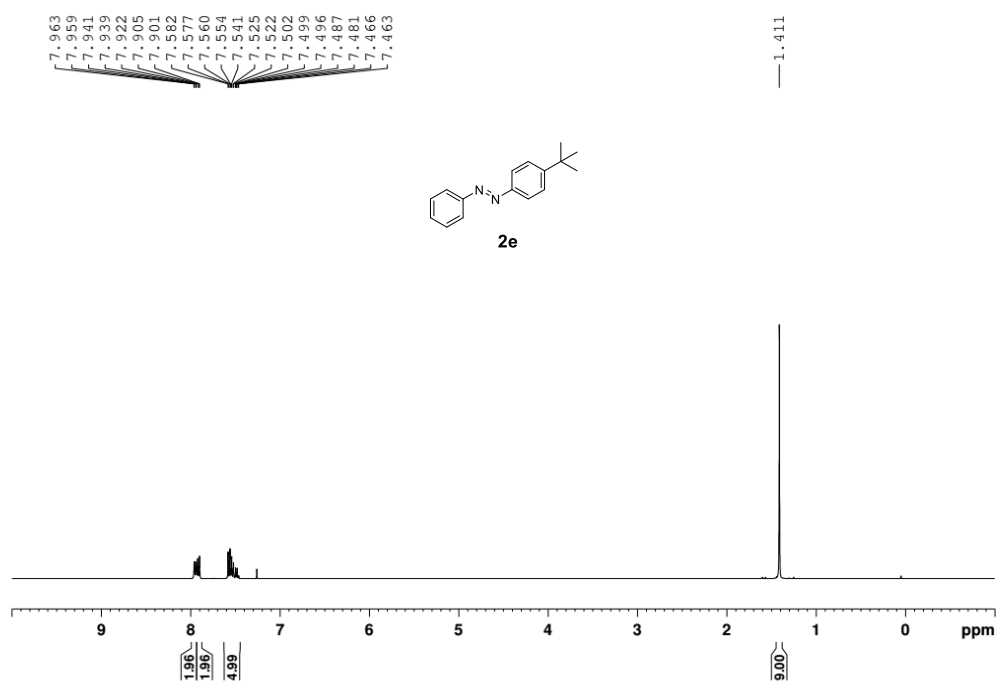
6. NMR spectra for the products

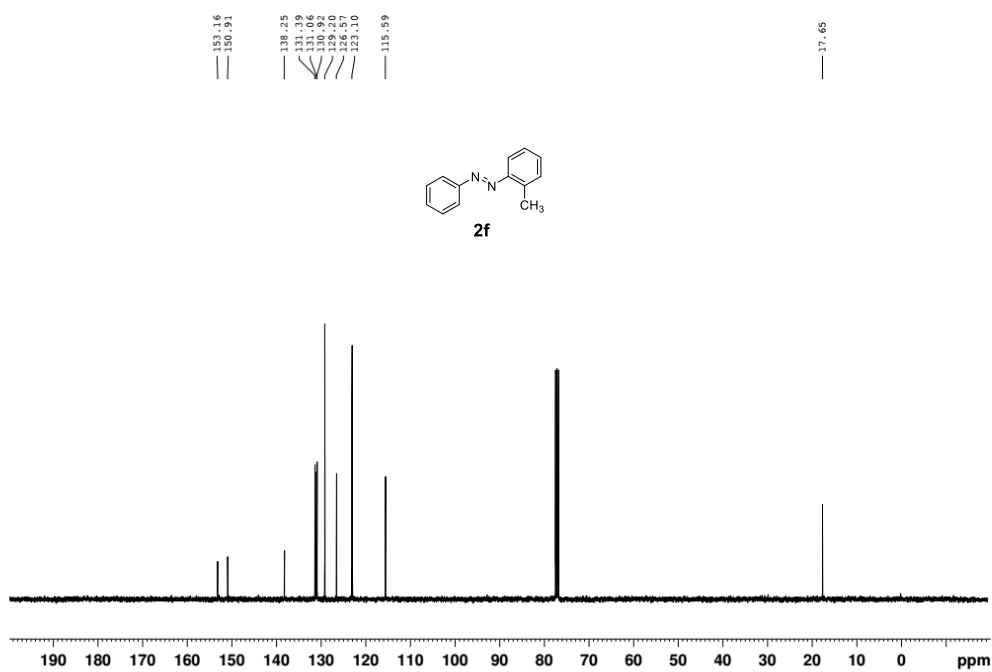
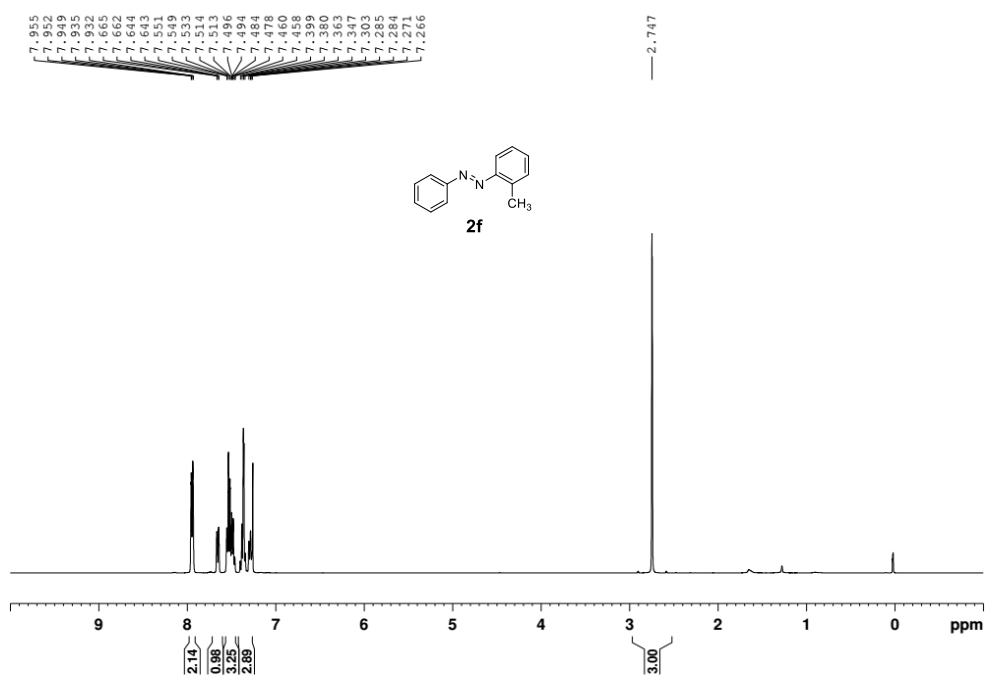


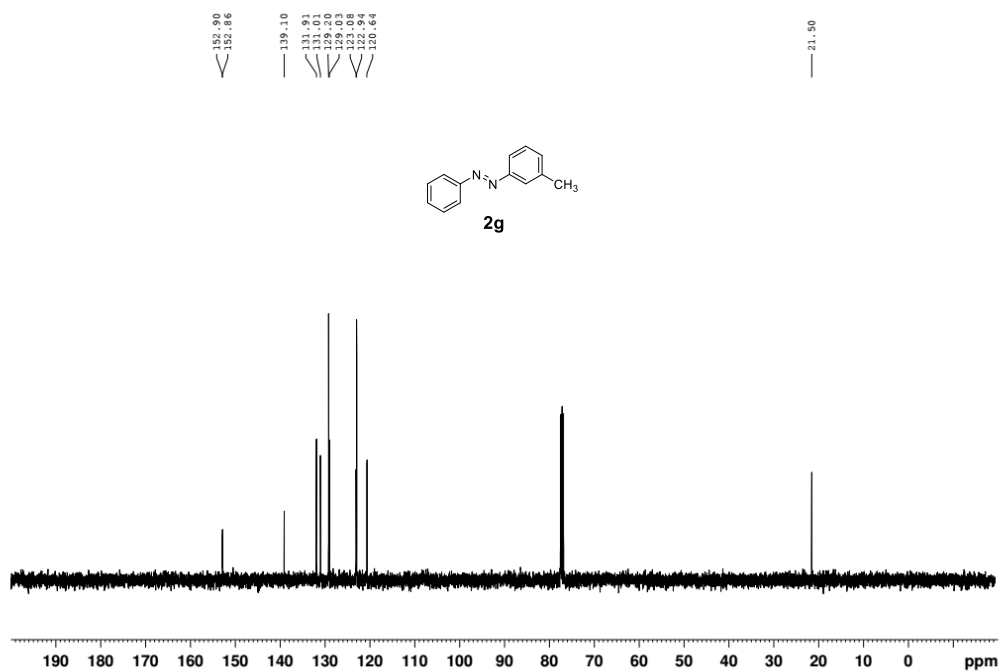
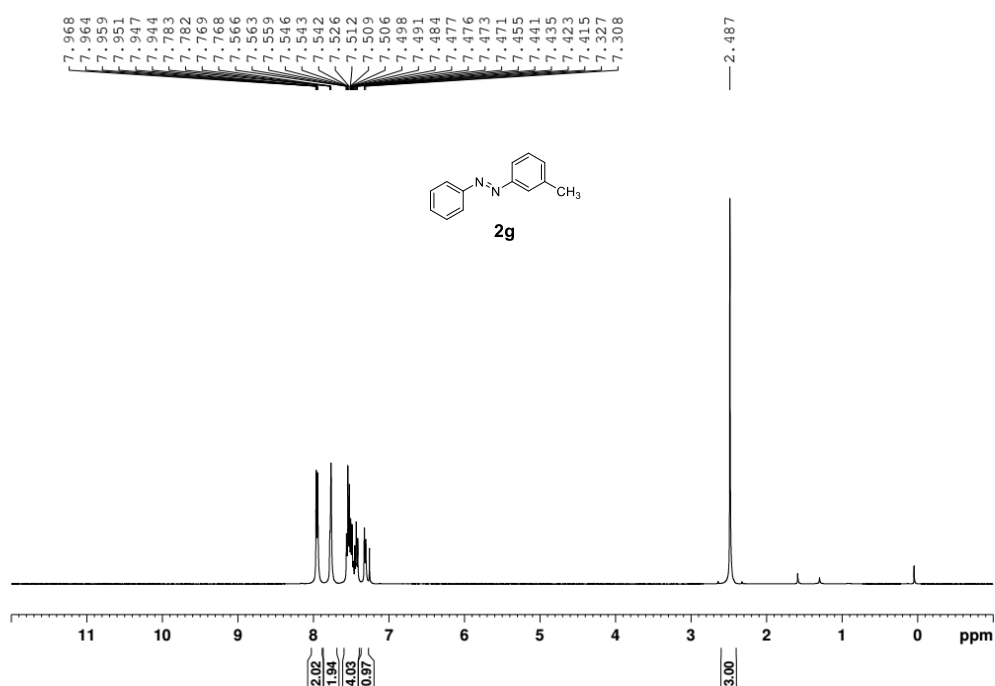


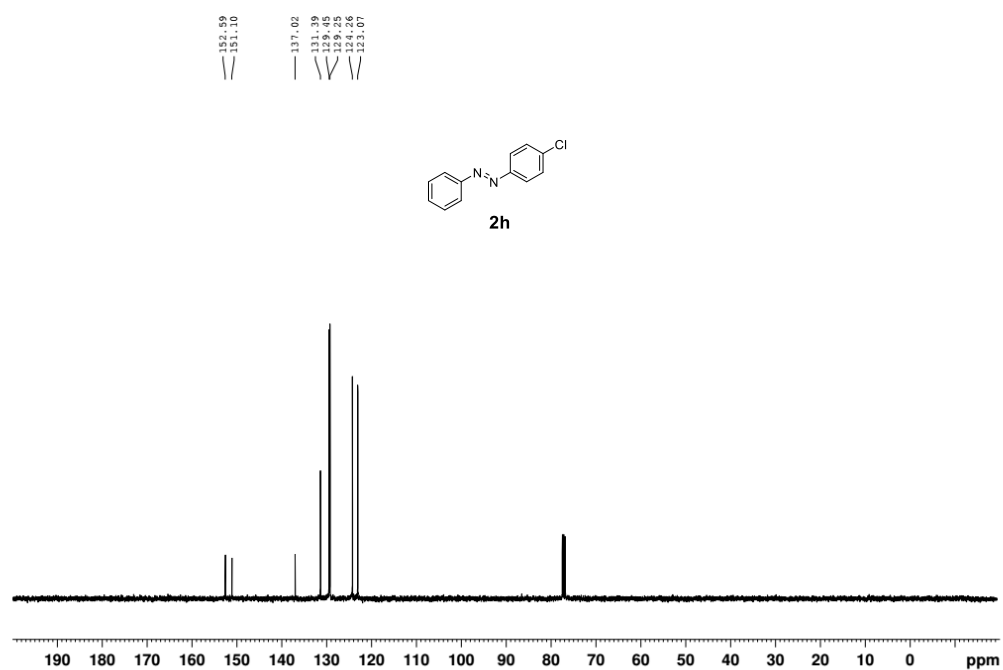
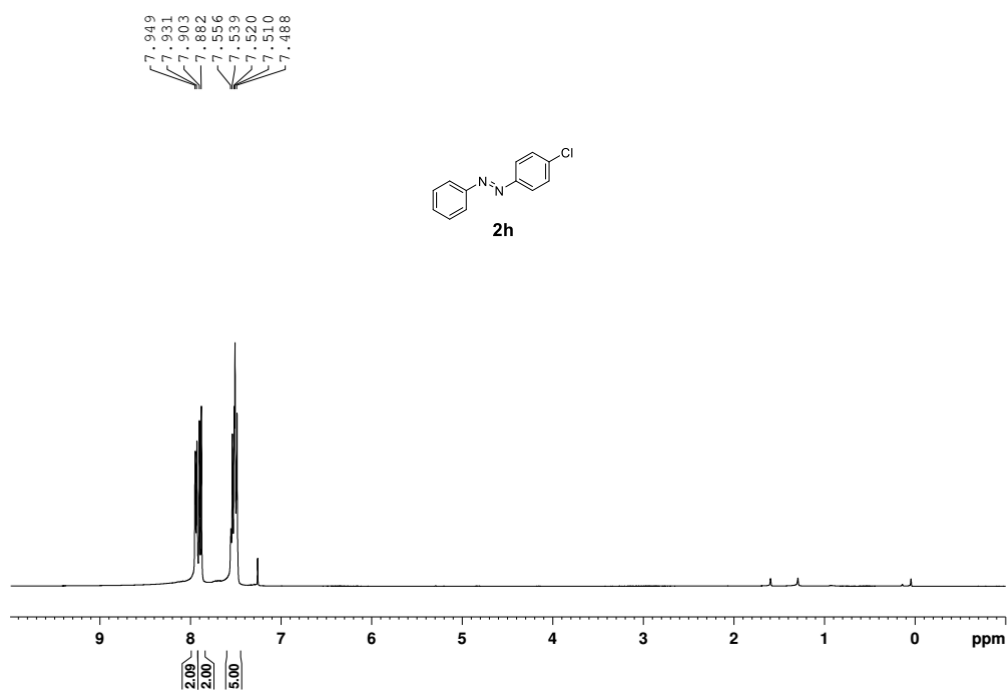


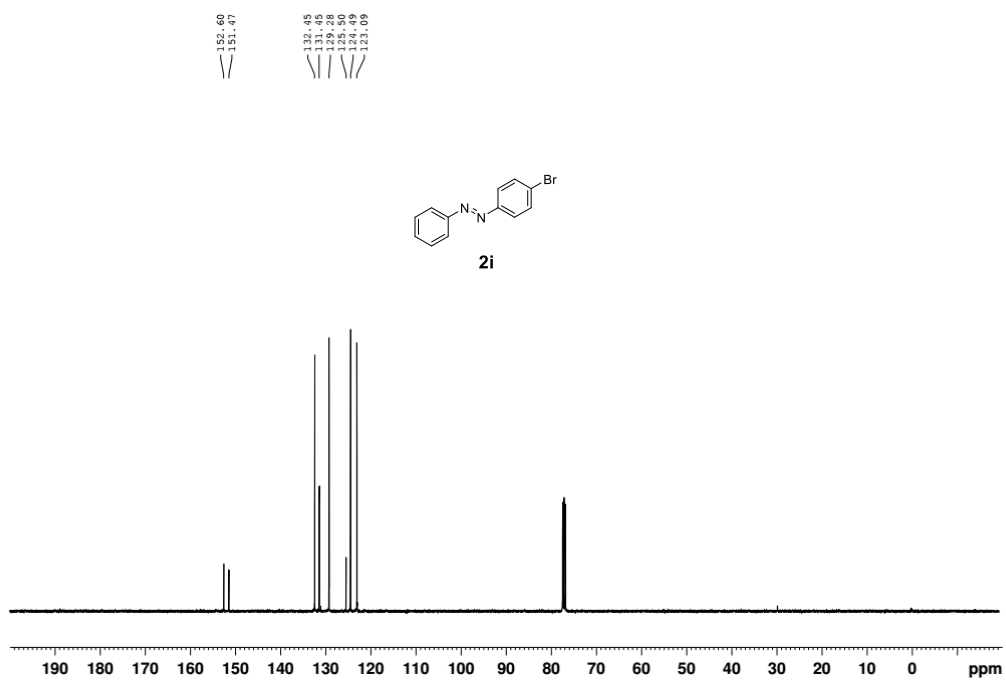
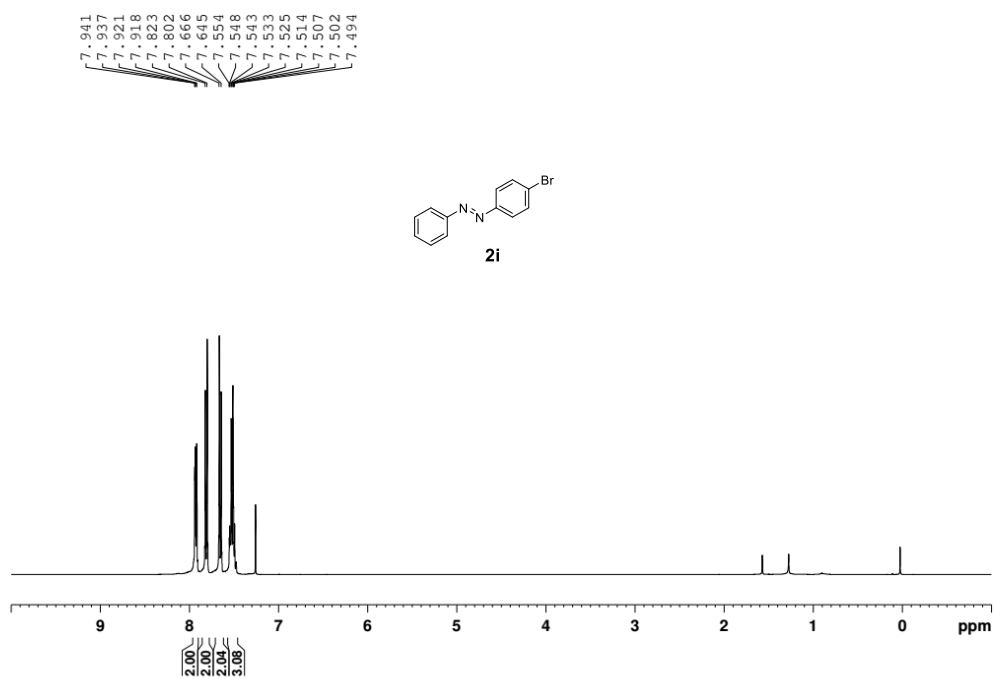


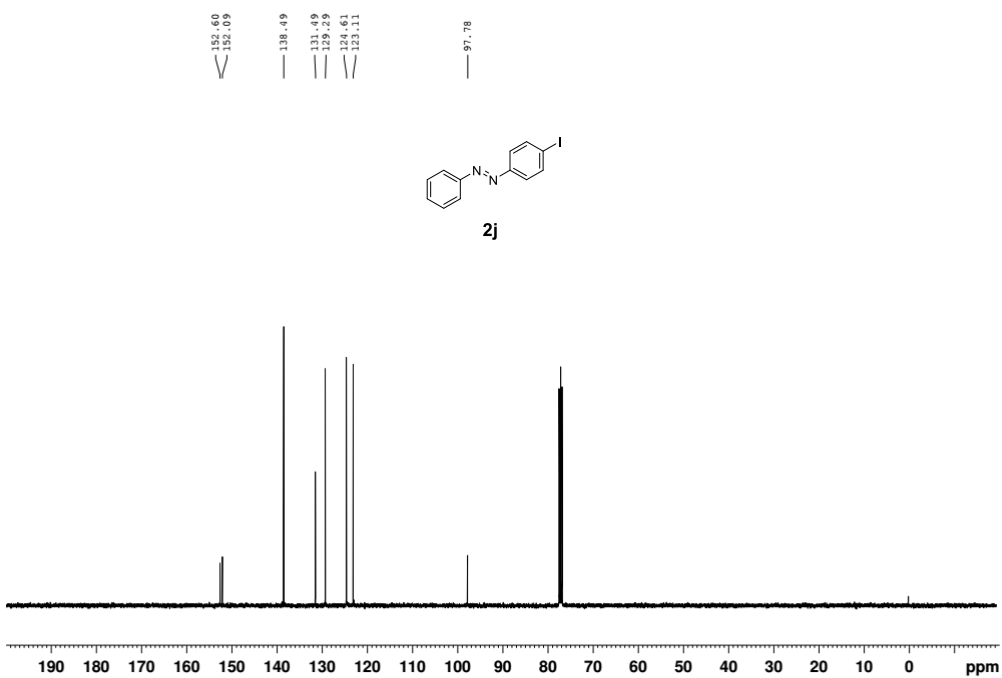
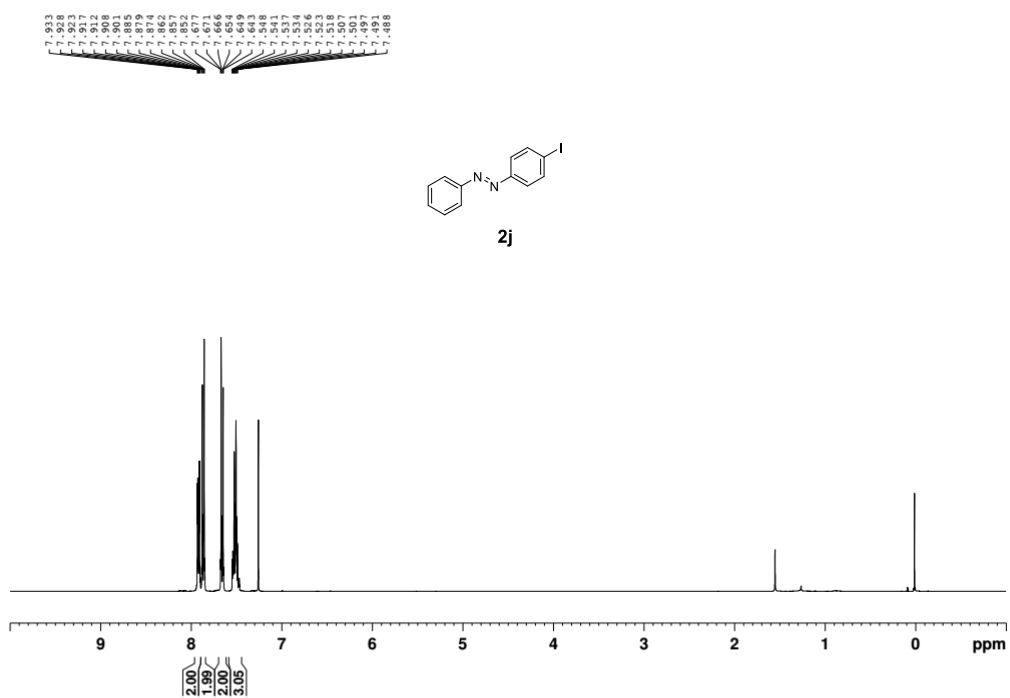


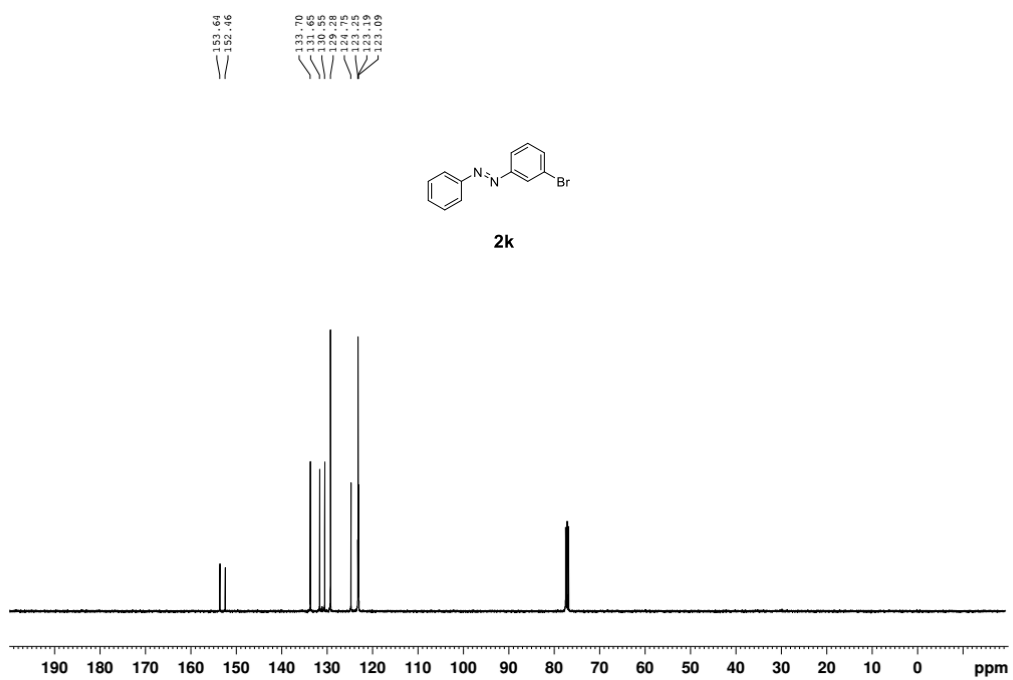
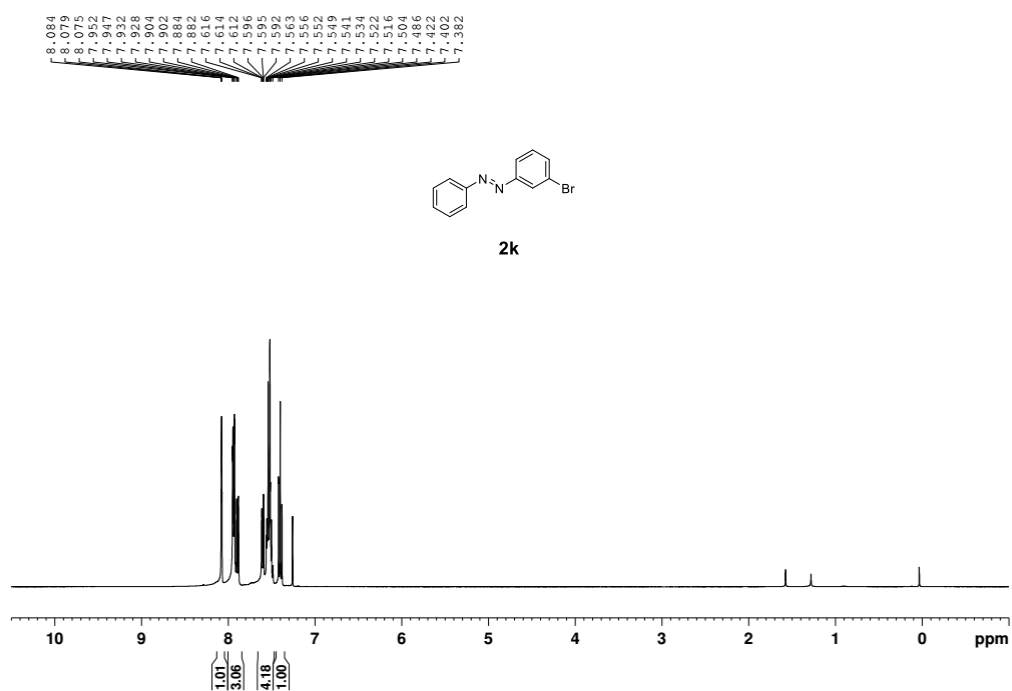


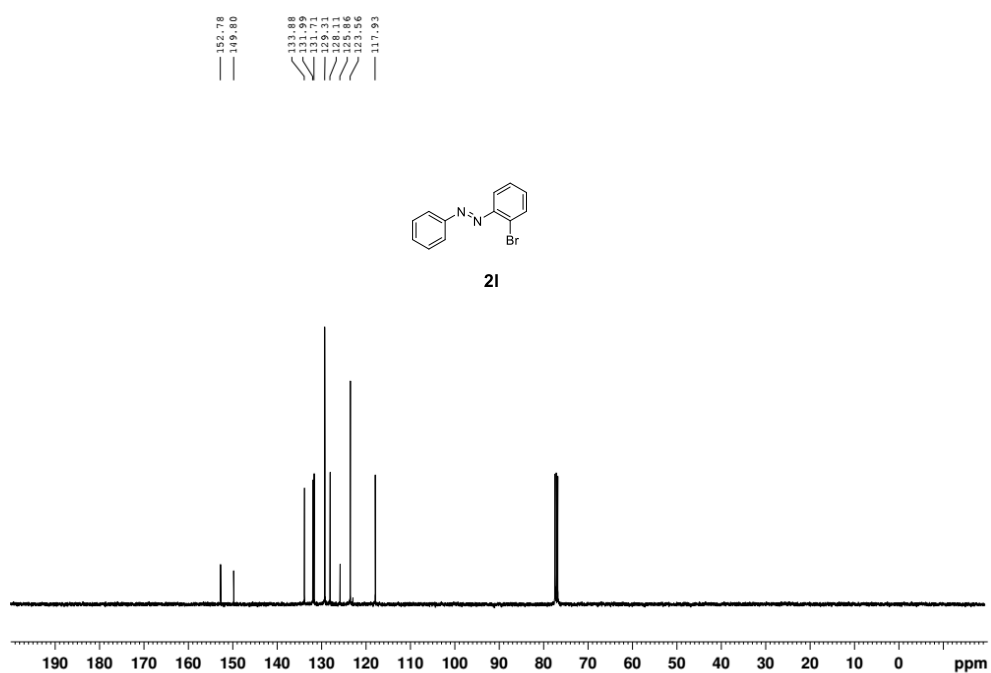
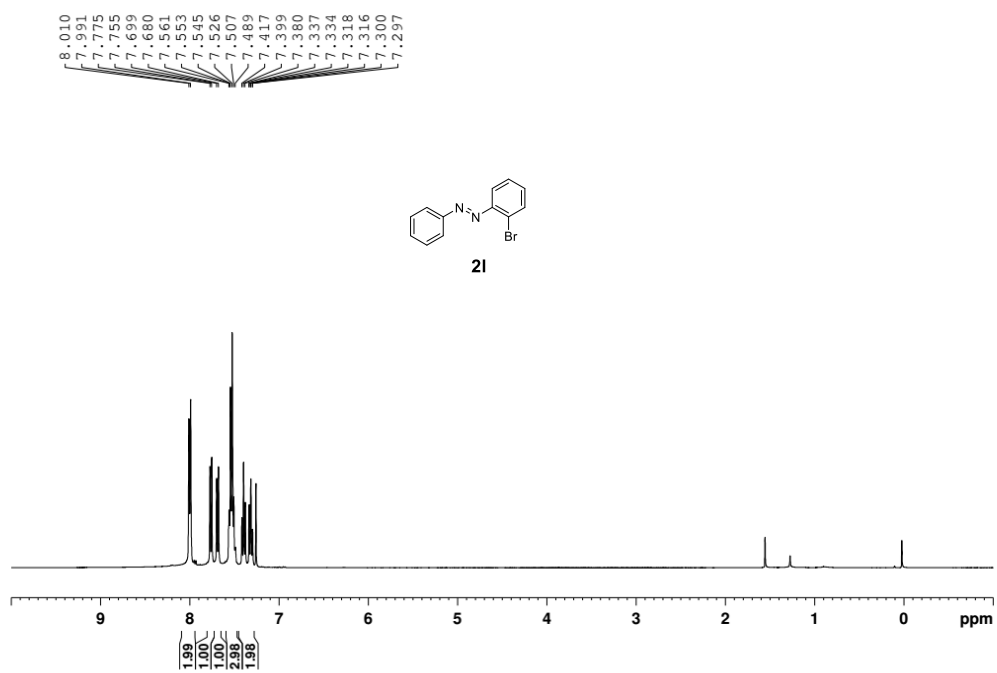


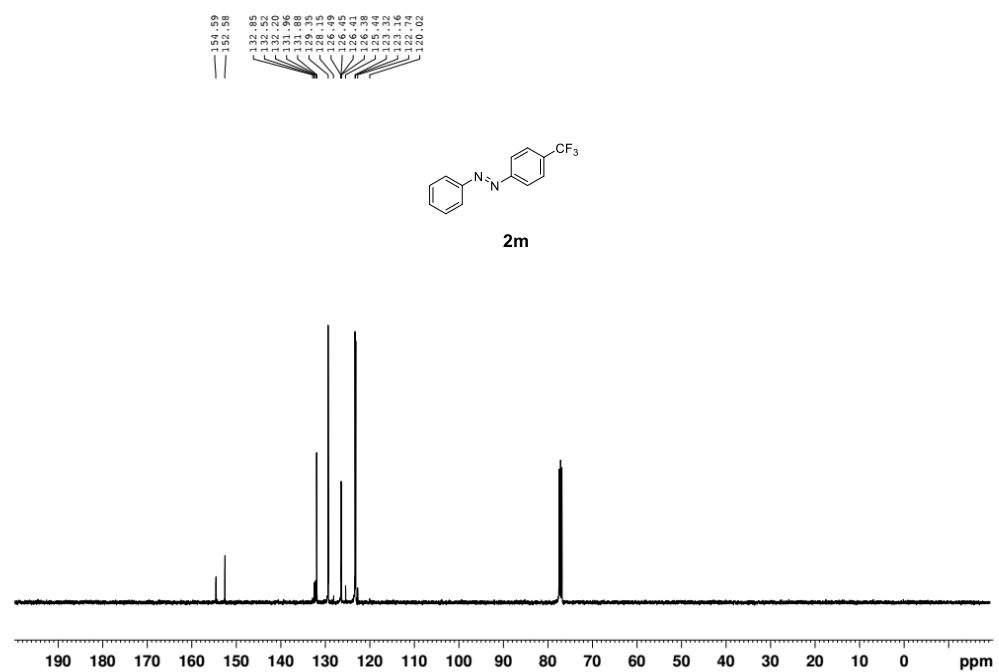
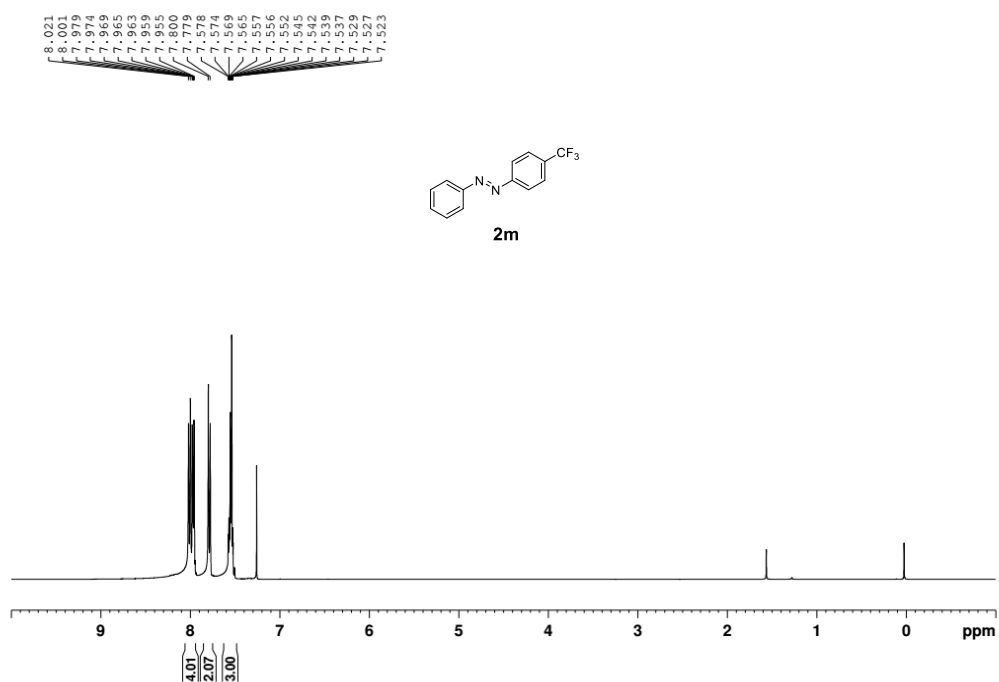


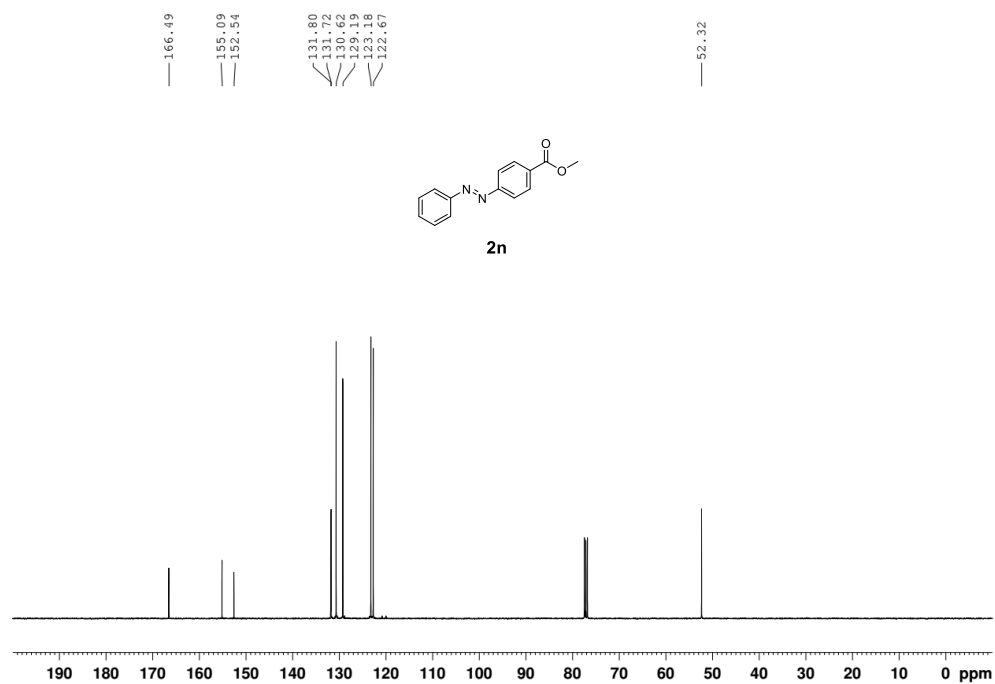
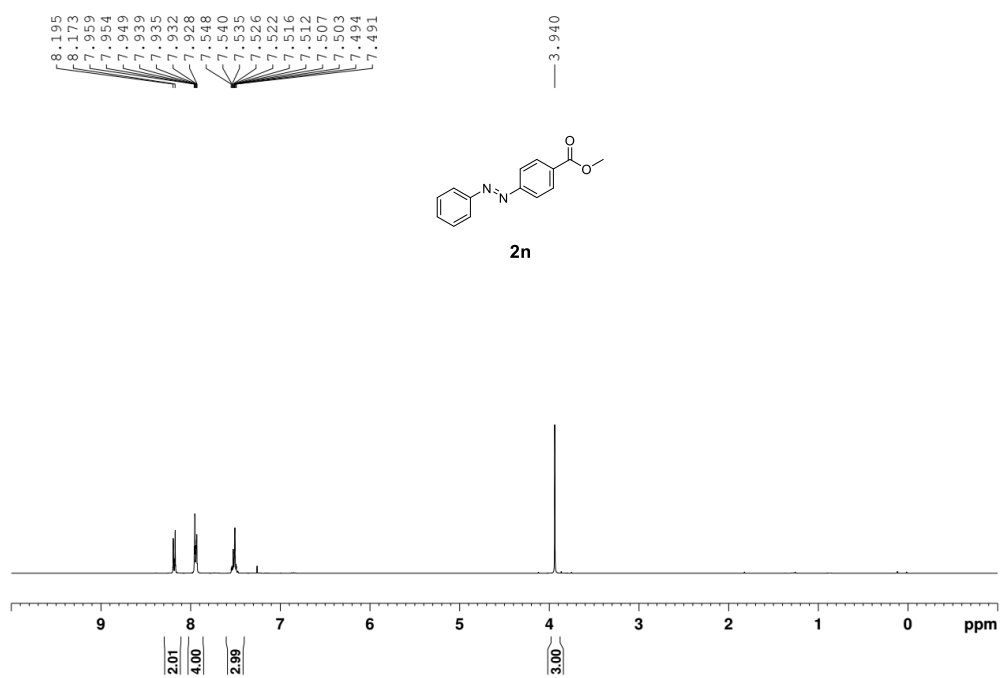


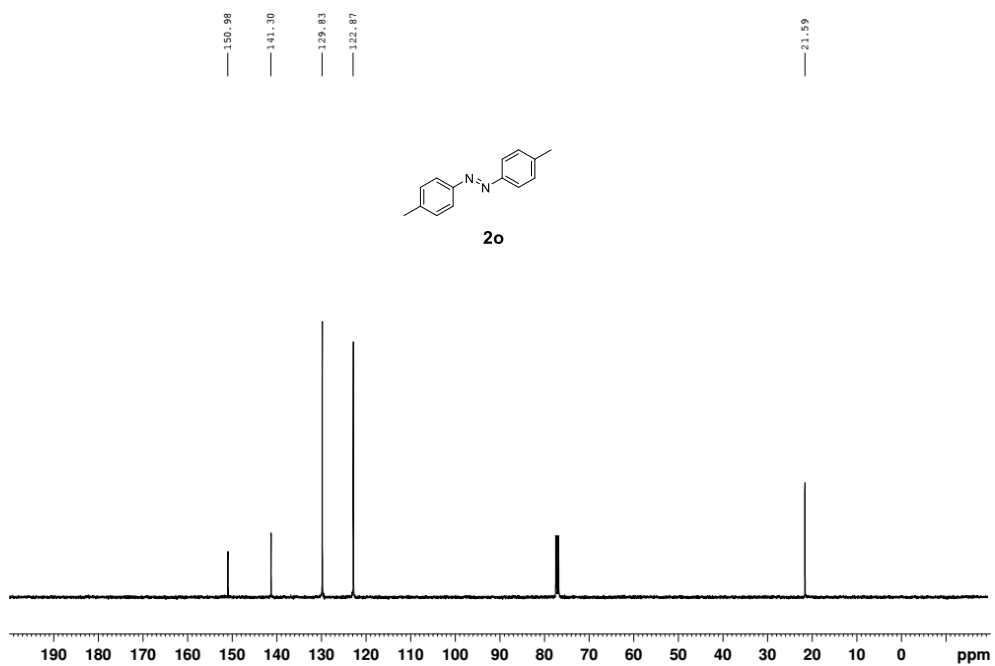
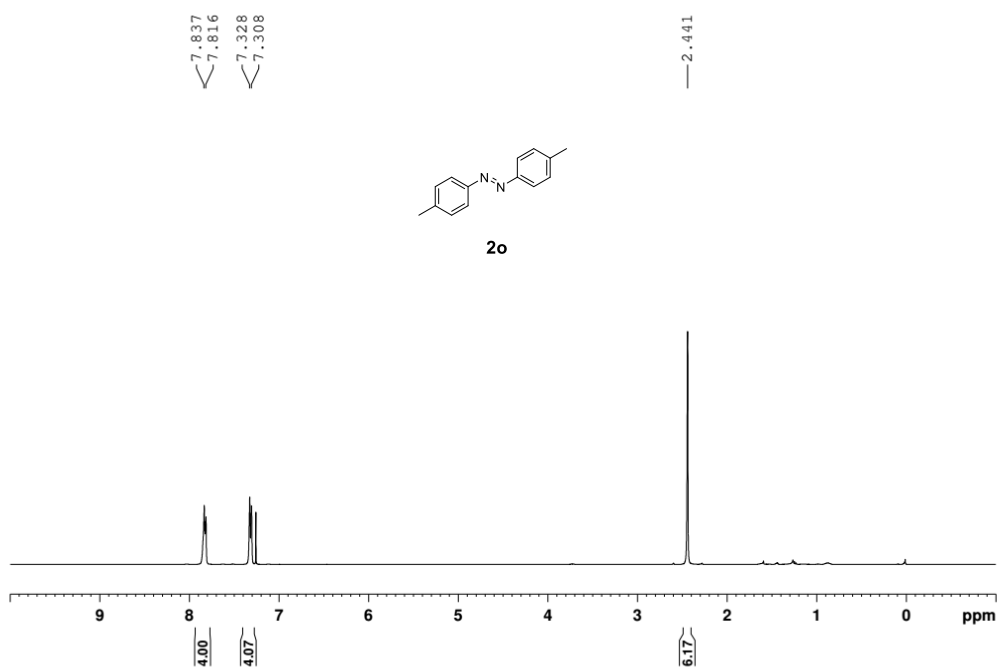


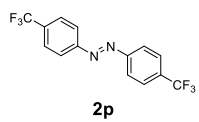
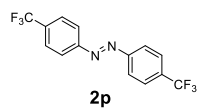


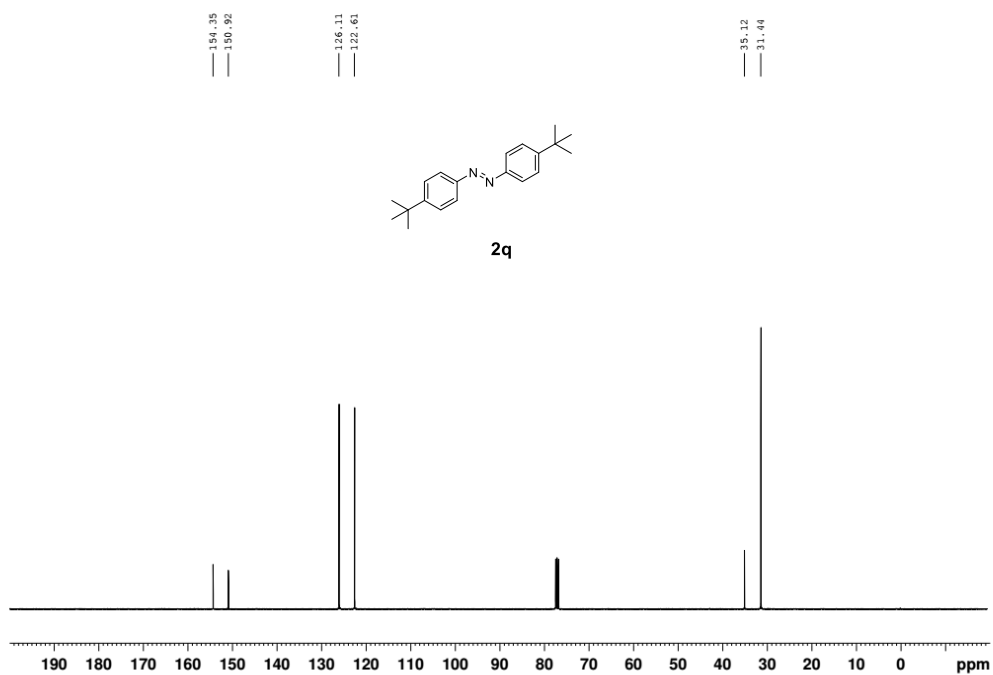
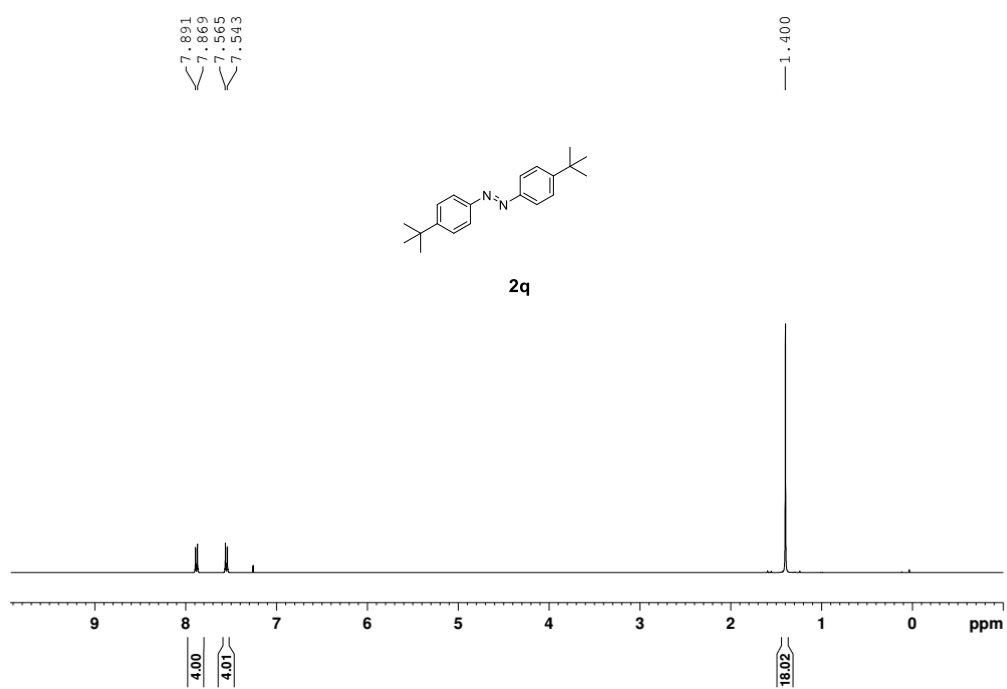












7. References

- (1) L. Wang, A. Ishida, Y. Hashidoko, M. Hashimoto. *Angew. Chem. Int. Ed.*, 2017, **56**, 870-873.
- (2) M. K. Sahoo, K. Saravanakumar, G Jaiswal, E Balaraman. *ACS Catal.*, 2018, **8**, 7727-7733.
- (3) H.-P. Lv, R. D. Laishram, J.-Y. Li, Y.-Y. Zhou, D.-D. Xu, S. More, Y.-Z. Dai, B.-M. Fan, *Green Chem.*, 2019, **21**, 4055-4061.