Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Synthesis of polyfunctional secondary amines by the addition of functionalized zinc reagents to nitroso-arenes†

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Table of Contents

General All reactions were carried out under an argon atmosphere in flame-dried glassware. Syringes, which were used to transfer anhydrous solvents or reagents, were purged with argon prior to use. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be >95% pure as determined by ^{1}H-NMR (25 °C) and capillary GC. Chemical shifts are reported as δ-values in ppm relative to the solvent peak. NMR spectra were recorded in a solution of $CDCl_3$ (residual chloroform: δ 7.25 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR). For the characterization of the observed signal multiplicities the following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of a doublet), ddd (doublet of a doublet of a doublet), dt (doublet of triplet), tt (triplet of triplet) and m (multiplet). Column chromatographic purification was performed using SiO_2 (0.040 – 0.063 mm, 230 – 400 mesh ASTM) from Merck if not indicated. All reagents were obtained from commercial sources.

Preparation of $ZnCl_2$ (1 M solution in THF):

A dry and argon flushed 250 mL Schlenk-flask equipped with a magnetic stirring bar and a septum was charged with $ZnCl_2$ (13.6 g, 100 mmol). The salt was heated to 140 °C under high vacuum for 10 h. After cooling to 25 °C, dry THF (100 mL) was added and stirring was continued until the salt was dissolved completely (4 h).

Preparation of adamantylzinc reagent[1]: LiCl-mediated magnesium insertion in the presence of zinc chloride in adamantyl bromides:

A dry, argon flushed Schlenk-flask equipped with a magnetic stirring bar and a septum was charged with LiCl (1.1 equiv) and heated to 450 °C under high vacuum for 5 min. After cooling to room temperature, magnesium turnings (2 equiv) were added followed by THF (1.4 mL/mmol). The magnesium was activated using 1,2-dibromoethane (5 mol%) and trimethylsilyl chloride (5 mol%). The suspension was cooled to 0 °C, $ZnCl_2$-solution (1.1 equiv, 1 M in THF) was added followed by the adamantyl bromide (1 equiv). The reaction mixture was stirred at 25 °C until GC-analysis of hydrolyzed reaction aliquot showed full consumption of the starting material. The solids were allowed to settle or the reaction mixture was centrifuged (10 min, 2000 rpm). The yield of the insertion reaction was determined by iodometric titration of the supernatant solution.

Preparation of functionalized aryl and heteroarylzinc reagents[2] via LiCl-mediated magnesium insertion in the presence of zinc chloride in aryl and heteroaryl halides:

A dry, argon flushed Schlenk-flask equipped with a magnetic stirring bar and a septum was charged with LiCl (1.3 equiv) and heated to 450 °C under high vacuum for 5 min. After cooling to room temperature magnesium turnings (2.5 equiv) were added, followed by THF (2 mL/mmol). The magnesium was activated using 1,2-dibromoethane (5 mol%) and trimethylsilyl chloride (5 mol%). The suspension was cooled to 0 °C, $ZnCl_2$-solution (1.1 equiv, 1 M in THF) was added followed by the aryl or heteroaryl halide (1.0 equiv). The reaction mixture was stirred until GC-analysis of hydrolyzed reaction aliquot showed full consumption of the starting material. The solids were allowed to settle or the reaction mixture was centrifuged (10 min, 2000 rpm). The yield of the insertion reaction was determined by iodometric titration[3] of the supernatant solution.

Preparation of nitroso arenes[4] by oxidation of arylamine with H_2O_2 catalysed by PhSeSePh:

To a stirred solution of PhSeSePh (5 mol%) and arylamine (1 equiv) in $CHCl_3$, 35% aqueous H_2O_2 (2.2 equiv) was added at room temperature. The reaction mixture was stirred vigorously for 1-2 h until GC-analysis of a reaction aliquot showed full convertion to the corresponding arylnitroso compound. After quenching with H_2O, the reaction mixture was extracted with $CHCl_3$. The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue obtained was purified by flash-column chromatography to give the analytically pure nitroso product.

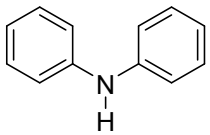
Typical Experimental Procedure 1 (TP1): Preparation of secondary amines by the reaction of functionalized zinc reagents with various nitroso electrophiles:

A dry, argon flushed Schlenk-flask equipped with a magnetic stirring bar and a septum was charged with freshly prepared zinc reagent (1.1 mmol. 1.1 equiv) in dry THF (2 mL) and cooled to 0 °C. The nitroso substrate (1.0 mmol, 1.0 equiv) was added and the reaction mixture was stirred at 0 to 25 °C for 2-3 h until GC analysis of reaction aliquot showed full consumption of the starting material. Ethanol (1.0 mL), $FeCl_2$ (2.0 mmol, 2.0 equiv) and $NaBH_4$ (1.0 mmol, 1.0 equiv) were added and the reaction mixture was stirred at room temperature for 15 h. After quenching with sat. NH_4Cl solution (10 mL), the mixture was neutralized with 2 M sat. NaOH solution and extracted with EtOAc (6x25 mL). The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue

obtained was purified by flash-column chromatography to give the analytically pure amine product.

Synthesis of secondary amines by the reaction of functionalized zinc reagents with various nitroso electrophiles:

Preparation of diphenylamine (5a)



The amination reaction of freshly prepared arylzinc reagent **2a** (0.65 mL, 1.1 mmol, 1.68 M in THF) with nitrosobenzene **3a**[4] (108 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 87:13) furnished **5a** as a colorless solid (144 mg, 85 %).

m.p.: 51.4-52.2 °C (Lit. m.p.: 51-53 °C).[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.23-7.40 (m, 4 H), 7. 06-7.20 (m, 4 H), 6.98 (t, J = 7.3 Hz, 2 H), 5.68 (bs, 1 H).

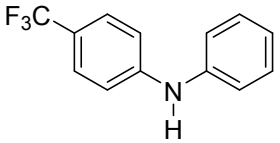
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 143.2, 129.4, 121.0, 117.9.

MS (ESI), *m/z* (%) = 170 ([M+H]$^+$, 100), 133 (2), 85 (6).

HRMS (ESI), *m/z* calc. for **$C_{12}H_{12}N$** (170.0970 ([M+H])): 170.0964 ([M+H]).

IR (ATR) υ (cm^{-1}) = 3407, 3383, 3041, 2923, 2853, 1593, 1513, 1493, 1458, 1418, 1315, 1307, 1242, 1220, 1172, 1158, 1148, 1084, 1074, 1023, 993, 976, 875, 846, 838, 820, 742, 700, 688.

Preparation of *N*-phenyl-4-(trifluoromethyl)aniline (5b)



The amination reaction of freshly prepared arylzinc reagent **2b** (3.92 mL, 1.1 mmol, 0.28 M in THF) with nitrosobenzene **3a** (108 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 80:20) furnished **5b** as a pale yellow solid (164 mg, 69 %).

m.p.: 61.6-63.3 °C (Lit. m.p.: 61-62 °C).[6]

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.48 (d, J = 8.6 Hz, 2 H), 7.29-7.39 (m, 2 H), 7.12-7.21 (m, 2 H), 7.11-7.00 (m, 3 H), 5.92 (bs, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 146.8(q, J = 1.2 Hz), 141.1, 129.5, 126.7 (q, J = 3.7 Hz), 124.6 (q, J = 269.3 Hz), 122.9, 121.7 (q, J = 32.5 Hz), 120.1, 115.3.

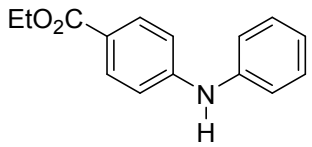
^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -61.49 (s, 3 F).

MS (EI), *m/z* (%) = 237 (M^+, 100), 236 (17), 216 (13), 168 (13), 167 (33), 77 (8).

HRMS (EI), *m/z* calc. for **$C_{13}H_{10}F_3N$** (237.0765) : 237.0772.

IR (ATR) υ (cm^{-1}) = 3399, 2923, 2852, 1616, 1595, 1522, 1500, 1495, 1449, 1403, 1362, 1320, 1309, 1245, 1224, 1170, 1152, 1098, 1082, 1061, 1027, 1009, 969, 948, 890, 878, 845, 822, 806, 762, 744, 730, 692, 662.

Preparation of ethyl-4-(phenylamino)benzoate (5c)



The amination reaction of freshly prepared arylzinc reagent **2c** (4.58 mL, 1.1 mmol, 0.24 M in THF) with nitrosobenzene **3a** (108 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 65:35) furnished **5c** as a pale yellow solid (183 mg, 76 %).

m.p.: 108.4-109.3 °C (Lit. m.p.: 111 °C).[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.86-7.99 (m, 2 H), 7.28-7.39 (m, 2 H), 7.13-7.23 (m, 2 H), 7.11-6.95 (m, 3 H), 6.12 (bs, 1 H), 4.35 (q, J = 7.2 Hz, 2 H), 1.38 (t, J = 7.2 Hz, 3 H).

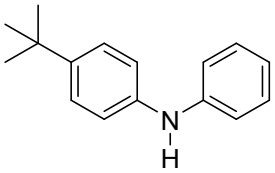
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 166.5, 148.0, 141.0, 131.4, 129.5, 123.0, 121.5, 120.3, 114.6, 60.4, 14.4.

MS (ESI), *m/z* (%) = 242 ($[M+H]^+$, 100), 214 (24), 196 (7).

HRMS (ESI), *m/z* calc. for **$C_{15}H_{16}NO_2$** (242.1181 ([M+H])): 242.1176 ([M+H]).

IR (ATR) υ (cm^{-1}) = 3359, 3335, 2982, 2925, 2854, 1688, 1676, 1588, 1528, 1496, 1475, 1447, 1412, 1398, 1365, 1335, 1277, 1249, 1174, 1153, 1110, 1077, 1019, 1006, 982, 968, 962, 906, 900, 875, 845, 838, 817, 807, 768, 750, 704, 693, 662.

Preparation of 4-(*tert*-butyl)-*N*-phenylaniline (5d)



The amination reaction of freshly prepared arylzinc reagent **2d** (3.57 mL, 1.0 mmol, 0.28 M in THF) with nitrosobenzene **3a** (96.4 mg, 0.9 mmol), ethanol (0.9 mL), $FeCl_2$ (229 mg, 1.8 mmol) and $NaBH_4$ (34 mg, 0.9 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 93:7) furnished **5d** as a pale yellow solid (195 mg, 96 %).

m.p.: 64.0-65.4 °C (Lit. m.p.: 66-67 °C).[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.23-7.37 (m, 4 H), 7.06 (d, J = 8.0 Hz, 4 H), 6.92 (t, J = 7.0 Hz, 1 H), 5.65 (bs, 1 H), 1.35 (s, 9 H).

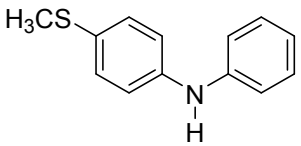
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 144.2, 143.7, 140.3, 129.3, 126.1, 120.4, 118.2, 117.1, 34.2, 31.5.

MS (EI), *m/z* (%) = 225 (M^+, 34), 211 (19), 210 (100), 195 (9), 92 (7), 91 (8), 90 (8).

HRMS (EI), *m/z* calc. for **$C_{16}H_{19}N$** (225.1517): 225.1518.

IR (ATR) υ (cm^{-1}) = 3387, 2960, 2864, 1593, 1514, 1496, 1437, 1392, 1378, 1362, 1313, 1304, 1290, 1265, 1247, 1202, 1174, 1153, 1110, 1078, 1026, 1016, 993, 878, 851, 839, 819, 807, 739, 688.

Preparation of 4-(methylthio)-*N*-phenylaniline (5e)[9]



The amination reaction of freshly prepared arylzinc reagent **2e** (4.40 mL, 1.1 mmol, 0.25 M in THF) with nitrosobenzene **3a** (108 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 65:35) furnished **5e** as a colorless solid (150 mg, 70 %).

m.p.: 80.4-81.4 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.20-7.34 (m, 4 H), 6.88-7.13 (m, 5 H), 5.73 (bs, 1 H), 2.47 (s, 3 H).

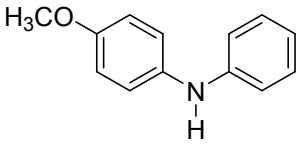
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 143.0, 141.3, 129.9, 129.4, 129.1, 121.2, 118.6, 117.8, 17.9.

MS (ESI), *m/z* (%) = 216 ($[M+H]^+$, 100), 215 (4).

HRMS (ESI), *m/z* calc. for **$C_{13}H_{14}NS$** (216.0847 ([M+H]): 216.0840 ([M+H]).

IR (ATR) υ (cm^{-1}) = 3392, 3051, 3034, 2959, 2918, 1604, 1588, 1505, 1496, 1484, 1440, 1422, 1392, 1316, 1303, 1280, 1235, 1222, 1195, 1182, 1174, 1159, 1112, 1092, 1076, 1028, 1009, 992, 967, 953, 934, 907, 876, 854, 819, 798, 758, 745, 711, 693, 672.

Preparation of 4-methoxy-*N*-phenylaniline (5f)



The amination reaction of freshly prepared arylzinc reagent **2f** (2.0 mL, 1.1 mmol, 0.55 M in THF) with nitrosobenzene **3a** (108 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 70:30) furnished **5f** as a pale yellow solid (155 mg, 78 %).

m.p.: 103.9-104.9 °C (Lit. m.p.: 104-106 °C).[10]

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.24 (t, *J* = 8.0 Hz, 2 H), 7.03-7.15 (m, 2 H), 6.80-6.99 (m, 5 H), 5.54 (bs, 1 H), 3.82 (s, 3 H).

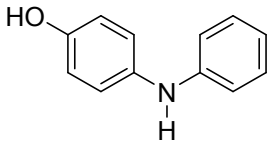
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 155.3, 145.2, 135.7, 129.3, 122.2, 119.6, 115.7, 114.7, 55.6.

MS (ESI), *m/z* (%) = 200 ($[M+H]^+$, 100), 123 (3).

HRMS (ESI), *m/z* calc. for **$C_{13}H_{14}NO$** (200.1075 ([M+H])): 200.1070 ([M+H]).

IR (ATR) υ (cm^{-1}) = 3387, 3008, 2958, 2930, 2837, 1610, 1595, 1511, 1500, 1489, 1462, 1456, 1442, 1401, 1316, 1297, 1248, 1236, 1181, 1169, 1152, 1106, 1079, 1033, 993, 978, 876, 844, 824, 811, 770, 749, 710, 694.

Preparation of 4-(phenylamino)phenol (5g)



The amination reaction of freshly prepared arylzinc reagent **2g** (6.11 mL, 1.1 mmol, 0.18 M in THF) with nitrosobenzene **3a** (108 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 30:70) furnished **5g** as a colorless solid (165 mg, 89 %).

m.p.: 67.2-68.1 °C (Lit. m.p.: 70 °C).[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.14-7.36 (m, 2 H), 7.02 (d, J = 8.8 Hz, 2 H), 6.64-6.97 (m, 5 H), 5.48 (bs, 1 H), 5.01 (bs, 1 H).

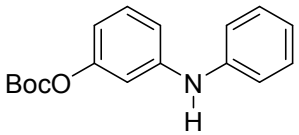
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 151.0, 145.1, 135.8, 129.4, 122.4, 119.7, 116.2, 115.8.

MS (EI), *m/z* (%) = 185 (M^+, 100), 184 (15), 183 (7), 156 (5), 154 (5), 77 (7).

HRMS (EI), *m/z* calc. for **$C_{12}H_{11}NO$** (185.0841): 185.0838.

IR (ATR) υ (cm^{-1}) = 3407, 3371, 3282, 1597, 1504, 1492, 1450, 1414, 1368, 1315, 1251, 1227, 1184, 1169, 1158, 1148, 1103, 1080, 1012, 994, 838, 820, 780, 749, 742, 712, 692.

Preparation of *tert*-butyl(3-(phenylamino)phenyl)carbonate (5h)



The amination reaction of freshly prepared arylzinc reagent **2h** (4.78 mL, 1.1 mmol, 0.23 M in THF) with nitrosobenzene **3a** (108 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 75:25) furnished **5h** as a colorless solid (205 mg, 72 %).

m.p.: 115.4-116.6 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 7.17-7.33 (m, 3 H), 7.08 (d, J = 8.2 Hz, 2 H), 6.96 (t, J = 7.4 Hz, 1 H), 6.81-6.92 (m, 2 H), 6.71 (d, J = 8.2 Hz, 1 H), 5.76 (bs, 1 H), 1.55 (s, 9 H).

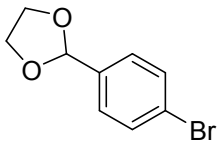
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) = 152.0, 151.8, 144.6, 142.2, 129.9, 129.4, 121.7, 118.6, 114.4, 113.3, 109.9, 83.4, 27.7.

MS (EI), *m/z* (%) = 285 (M^+, 2), 186 (14), 185 (100), 184 (27), 183 (7), 166 (9), 57 (9), 44 (10).

HRMS (EI), *m/z* calc. for **$C_{17}H_{19}NO_3$** (285.1365): 285.1348.

IR (ATR) υ (cm^{-1}) = 3369, 2972, 1737, 1605, 1593, 1532, 1500, 1483, 1457, 1426, 1396, 1369, 1337, 1289, 1273, 1260, 1251, 1243, 1181, 1155, 1135, 1079, 1051, 1028, 1000, 980, 960,, 924, 892, 868, 846, 822, 784, 754, 740, 728, 698, 682.

Preparation of 2-(4-bromophenyl)-1,3-dioxolane (1i)



To a solution of 4-bromobenzaldehyde (6 g, 32.42 mmol) in dry toluene (200 mL), *p*-toluenesulfonic acid (616 mg, 3.24 mmol), ethane-1,2-diol (12.08 g, 194.57 mmol) were added and refluxed in Dean-Stark apparatus for 24 h. Removal of solvent followed by quenching with H_2O (100 mL), the reaction mixture was extracted with EtOAc (4x40 mL). The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue obtained was purified by Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 66:33) furnished 2-(4-bromophenyl)-1,3-dioxolane **1i** as a colorless solid (6.3 g, 85 %).

m.p.: 34.1-35.3 °C.

^{1}H NMR (800 MHz, DMSO-d_6) δ (ppm) = 7.60 (d, J = 8.3 Hz, 2 H), 7.39 (d, J = 8.3 Hz, 2 H) 5.73 (s, 1 H), 4.00 - 4.07 (m, 2 H), 3.90 - 3.98 (m, 2 H).

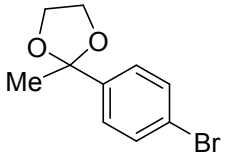
^{13}C NMR (200 MHz, DMSO-d_6) δ (ppm) = 138.0, 131.7, 129.3, 122.8, 102.5, 65.4.

MS (EI), *m/z* (%) = 229 ([M-H]$^+$, 10), 227 ([M-H]$^+$, 10), 183 (40), 149 (38), 119 (14), 89 (37), 73 (41), 44 (46).

HRMS (EI), *m/z* calc. for **$C_9H_8BrO_2$** (226.9708 ([M-H])): 226.9683 ([M-H]).

IR (ATR) υ (cm^{-1}) = 2946, 2879, 2826, 2782, 1907, 1793, 1650, 1593, 1481, 1422, 1379, 1349, 1292, 1280, 1218, 1172, 1136, 1104, 1066, 1023, 1007, 968, 939, 875, 855, 816, 721, 709, 679.

Preparation of 2-(4-bromophenyl)-2-methyl-1,3-dioxolane (1j)



To a solution of 1-(4-bromophenyl)ethan-1-one (6 g, 30.14 mmol) in dry toluene (200 mL), *p*-toluenesulfonic acid (573 mg, 3.01 mmol), ethane-1,2-diol (11.22 g, 180.76 mmol) were added and refluxed in Dean-Stark apparatus for 24 h. Removal of solvent followed by

quenching with H_2O (100 mL), the reaction mixture was extracted with EtOAc (4x40 mL). The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue obtained was purified by Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 66:33) furnished 2-(4-bromophenyl)-2-methyl-1,3-dioxolane **1j** as a colorless solid (6.5 g, 89 %).

m.p.: 42.4-43.8 °C.

^{1}H NMR (800 MHz, DMSO-d_6) = 7.54 (d, J = 8.3 Hz, 2 H), 7.36 (d, J = 8.3 Hz, 2 H), 3.92-4.04 (m, 2 H), 3.60-3.74 (m, 2 H), 1.54 (s, 3 H).

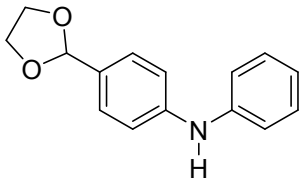
^{13}C NMR (200 MHz, DMSO-d_6) δ (ppm) = 143.2, 131.6, 127.9, 121.5, 108.2, 64.6, 27.6.

MS (EI), *m/z* (%) = 229 ([M-CH_3]$^+$, 40), 227 ([M-CH_3]$^+$, 42), 185 (16), 183 (18), 87 (9), 61 (14), 45 (13), 44 (55), 43 (100).

HRMS (EI), *m/z* calc. for **$C_9H_8BrO_2$** (226.9708 ([M-CH_3])): 226.9702 ([M-CH_3]).

IR (ATR) υ (cm^{-1}) = 2982, 2891, 1915, 1588, 1480, 1443, 1392, 1370, 1244, 1221, 1194, 1143, 1117, 1091, 1078, 1066, 1025, 1008, 943, 891, 868, 827, 765, 721, 690.

Preparation of 4-(1,3-dioxolan-2-yl)-*N*-phenylaniline



The amination reaction of freshly prepared arylzinc reagent **2i**[2] (12.69 mL, 3.3 mmol, 0.26 M in THF) with nitrosobenzene **3a** (324 mg, 3.0 mmol), ethanol (3.0 mL), $FeCl_2$ (762 mg, 6.0 mmol) and $NaBH_4$ (114 mg, 3.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 66:33) furnished 4-(1,3-dioxolan-2-yl)-*N*-phenylaniline as a yellow solid (480 mg, 66 %).

m.p.: 75.9-77.2 °C.

^{1}H NMR (800 MHz, DMSO-d_6) δ (ppm) = 8.30 (s, 1 H), 7.20-7.33 (m, 4 H), 7.01-7.15 (m, 4 H), 6.85 (t, J = 7.1 Hz, 1 H), 5.62 (s, 1 H), 3.99-4.09 (m, 2 H) 3.84-3.97 (m, 2 H).

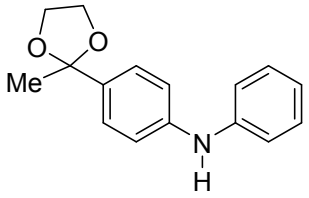
^{13}C NMR (200 MHz, DMSO-d_6) δ (ppm) = 144.8, 143.4, 129.7, 129.2, 128.3, 120.6, 117.7, 116.2, 103.6, 65.1.

MS (EI), *m/z* (%) = 241 (M^+, 100), 240 (83), 197 (48), 196 (69), 183 (15), 182 (72), 180 (21), 169 (72), 168 (30), 167 (54), 83 (13), 77 (18), 51 (11).

HRMS (EI), *m/z* calc. for **$C_{15}H_{15}NO_2$** (241.1103): 241.1100.

IR (ATR) υ (cm^{-1}) = 3357, 3033, 2924, 2885, 2745, 2544, 1930, 1667, 1585, 1518, 1493, 1449, 1421, 1390, 1301, 1246, 1223, 1173, 1161, 1112, 1059, 1028, 1013, 994, 970, 959, 936, 878, 827, 797, 747, 714, 694.

Preparation of 4-(2-methyl-1,3-dioxolan-2-yl)-*N*-phenylaniline



The amination reaction of freshly prepared arylzinc reagent **2j**[2] (11.78 mL, 3.3 mmol, 0.28 M in THF) with nitrosobenzene **3a** (324 mg, 3.0 mmol), ethanol (3.0 mL), $FeCl_2$ (762 mg, 6.0 mmol) and $NaBH_4$ (114 mg, 3.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 66:33) furnished 4-(2-methyl-1,3-dioxolan-2-yl)-*N*-phenylaniline as a yellow solid (590 mg, 77 %).

m.p.: 67.6-68.5 °C.

^{1}H NMR (800 MHz, DMSO-d_6) δ (ppm) = 8.20 (s, 1 H), 7.17-7.33 (m, 4 H), 6.98-7.13 (m, 4 H), 6.82 (t, J = 7.2 Hz, 1 H), 3.89-4.01 (m, 2 H), 3.63-3.76 (m, 2 H), 1.54 (s, 3 H).

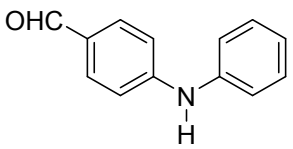
^{13}C NMR (200 MHz, DMSO-d_6) δ (ppm) = 143.7, 143.5, 134.7, 129.6, 126.5, 120.2, 117.3, 116.5, 108.6, 64.4, 27.8.

MS (EI), *m/z* (%) = 255 (M^+, 18), 241 (18), 240 (100), 196 (41), 168 (9), 167 (25), 98 (13), 83(11), 43 (10).

HRMS (EI), *m/z* calc. for **$C_{16}H_{17}NO_2$** (255.1259): 255.1251.

IR (ATR) υ (cm^{-1}) = 3362, 3038, 2978, 2964, 2926, 2897, 1896, 1656, 1598, 1518, 1497, 1483, 1473, 1446, 1398, 1373, 1339, 1319, 1303, 1245, 1230, 1213, 1191, 1172, 1138, 1096, 1081, 1028, 1009, 947, 893, 879, 862, 840, 804, 742, 691, 662.

Preparation of 4-(phenylamino)benzaldehyde (5i)



To a stirred solution of 4-(1,3-dioxolan-2-yl)-*N*-phenylaniline (100 mg, 0.41 mmol) in dry DCM (4 mL), trifluoroacetic acid (946 mg, 8.29 mmol) was added slowly at room temperature and the reaction mixture was stirred at 25 °C for 5 h. After quenching with H_2O (20 mL), the mixture was neutralized with 2 M sat. NaOH solution and extracted with EtOAc (4x20 mL). The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue obtained was purified by Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 66:33) furnished **5i** as a yellow solid (78 mg, 97 %).

m.p.: 93.5-94.2 °C.

^{1}H NMR (800 MHz, $CDCl_3$) δ (ppm) = 9.81 (s, 1 H), 7.76 (d, J = 8.6 Hz, 2 H) 7.38 (t, J = 7.8 Hz, 2 H) 7.23 (d, J = 7.8 Hz, 2 H), 7.14 (t, J = 7.3 Hz, 1 H), 7.06 (d, J = 8.6 Hz, 2 H), 6.46 (bs, 1 H).

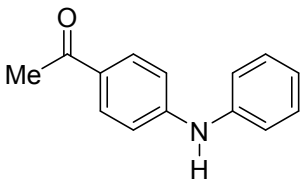
^{13}C NMR (200 MHz, $CDCl_3$) δ (ppm) = 190.5, 150.0, 140.1, 132.2, 129.6, 128.5, 123.9, 121.4, 114.5.

MS (EI), *m/z* (%) = 197 (M^+, 100), 196 (64), 182 (30), 168 (27), 166 (11), 83 (13), 77 (12), 43 (35).

HRMS (EI), *m/z* calc. for **$C_{13}H_{11}NO$** (197.0841): 197.0832.

IR (ATR) υ (cm^{-1}) = 3252, 3162, 3118, 3093, 3071, 3022, 2924, 2832, 2756, 1903, 1662, 1581, 1573, 1525, 1491, 1449, 1399, 1346, 1305, 1262, 1227, 1162, 1148, 1114, 1071, 1026, 1000, 945, 907, 878, 855, 841, 820, 812, 800, 741, 716, 691, 664.

Preparation of 1-(4-(phenylamino)phenyl)ethan-1-one (5j)



To a stirred solution of 4-(2-methyl-1,3-dioxolan-2-yl)-*N*-phenylaniline (100 mg, 0.39 mmol) in dry DCM (4 mL), trifluoroacetic acid (894 mg, 7.84 mmol) was added slowly at room temperature and the reaction mixture was stirred at 25 °C for 8 h. After quenching with H_2O (20 mL), the mixture was neutralized with 2 M sat. NaOH solution and extracted with EtOAc (4x20 mL). The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue obtained was purified by Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 66:33) furnished **5j** as a yellow solid (81 mg, 98 %).

m.p.: 93.3-94.1 °C.

^{1}H NMR (800 MHz, $CDCl_3$) δ (ppm) = 7.89 (d, J = 8.6 Hz, 2 H), 7.37 (t, J = 7.7 Hz, 2 H) 7.21 (d, J = 7.8 Hz, 2 H), 7.11 (t, J = 7.3 Hz, 1 H), 7.02 (d, J = 8.56 Hz, 2 H), 6.29 (bs, 1 H), 2.56 (s, 3 H).

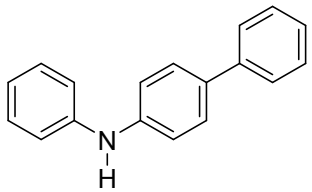
^{13}C NMR (200 MHz, $CDCl_3$) δ (ppm) = 196.6, 148.5, 140.6, 130.7, 129.6, 128.9, 123.4, 120.7, 114.4, 26.2.

MS (EI), *m/z* (%) = 211 (M^+, 64), 197 (17), 196 (100), 168 (21), 167 (44), 83 (9), 44 (13), 43 (37).

HRMS (EI), *m/z* calc. for **$C_{14}H_{13}NO$** (211.0997): 211.0995.

IR (ATR) υ (cm^{-1}) = 3317, 3030, 1648, 1583, 1568, 1523, 1494, 1449, 1414, 1356, 1323, 1276, 1250, 1175, 1154, 1125, 1072, 1025, 954, 898, 882, 841, 810, 753, 730, 709, 692.

Preparation of *N*-phenyl-[1,1'-biphenyl]-4-amine (5k)



The amination reaction of freshly prepared arylzinc reagent **2a** (0.69 mL, 1.1 mmol, 1.60 M in THF) with 4-nitroso-1,1'-biphenyl **3b**[12] (184 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 70:30) furnished **5k** as a colorless solid (193 mg, 79 %).

m.p.: 109.6-110.9 °C (Lit. m.p.: 112 °C).[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.58-7.65 (m, 2 H), 7.52-7.58 (m, 2 H), 7.41-7.50 (m, 2 H), 7.26-7.40 (m, 3 H), 7.16 (t, J = 7.6 Hz, 4 H), 7.00 (t, J = 7.3 Hz, 1 H), 5.85 (bs, 1 H).

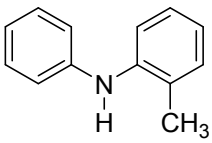
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 142.8, 142.5, 140.8, 133.8, 129.4, 128.8, 128.0, 126.6, 126.6, 121.3, 118.1, 117.8.

MS (EI), *m/z* (%) = 245 (M^+, 100), 244 (8), 168 (10), 167 (24), 115 (9), 78 (17), 77 (24).

HRMS (EI), *m/z* calc. for **$C_{18}H_{15}N$** (245.1204): 245.1197.

IR (ATR) υ (cm^{-1}) = 3407, 3371, 3026, 2924, 1595, 1522, 1504, 1495, 1482, 1452, 1434, 1399, 1321, 1308, 1270, 1238, 1224, 1180, 1157, 1148, 1116, 1079, 1038, 1030, 1018, 1004, 993, 980, 968, 910, 879, 846, 833, 820, 759, 744, 737, 714, 691.

Preparation of 2-methyl-*N*-phenylaniline (5l)[14]



The amination reaction of freshly prepared arylzinc reagent **2a** (0.65 mL, 1.1 mmol, 1.68 M in THF) with 1-methyl-2-nitrosobenzene **3c**[4] (122 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 94:6) furnished **5l** as a yellow oil (141 mg, 77 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.14-7.39 (m, 5 H), 6.83-7.11 (m, 4 H), 5.45 (bs, 1 H), 2.31 (s, 3 H).

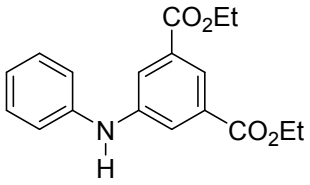
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 144.0, 141.2, 131.0, 129.4, 128.3, 126.8, 122.0, 120.5, 118.8, 117.5, 18.0.

MS (EI), *m/z* (%) = 183 (M^+, 100), 182 (50), 180 (21), 168 (17), 167 (25), 106 (10), 91 (9).

HRMS (EI), *m/z* calc. for **$C_{13}H_{13}N$** (183.1048): 183.1045.

IR (ATR) υ (cm^{-1}) = 3389, 3046, 2973, 2926, 2855, 1636, 1593, 1582, 1494, 1481, 1464, 1442, 1418, 1379, 1308, 1292, 1251, 1227, 1175, 1154, 1112, 1078, 1047, 1028, 994, 986, 935, 879, 741, 715, 692.

Preparation of diethyl-5-(phenylamino)isophthalate (5m)



The amination reaction of freshly prepared arylzinc reagent **2a** (0.65 mL, 1.1 mmol, 1.68 M in THF) with diethyl-5-nitrosoisophthalate **3d**[15] (252 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 85:15) furnished **5m** as a pale yellow solid (260 mg, 83 %).

m.p.: 170.7-171.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.17 (t, *J* = 1.5 Hz, 1 H), 7.89 (d, *J* = 1.6 Hz, 2 H), 7.28-7.36 (m, 2 H), 7.08-7.16 (m, 2 H), 7.02 (t, *J* = 7.4 Hz, 1 H), 6.00 (s, 1 H), 4.38 (q, *J* = 7.0 Hz, 4 H), 1.39 (t, *J* = 7.1 Hz, 6 H).

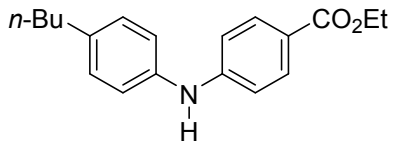
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 165.9, 144.0, 141.7, 131.9, 129.6, 122.3, 122.2, 121.4, 118.8, 61.3, 14.3.

MS (EI), *m/z* (%) = 313 (M^+, 100), 285 (16), 268 (14), 257 (16), 168 (26), 167 (26), 166 (17), 44 (10), 43(40).

HRMS (EI), *m/z* calc. for **$C_{18}H_{19}NO_4$** (313.1314): 313.1317.

IR (ATR) υ (cm^{-1}) = 3363, 2984, 1713, 1698, 1606, 1589, 1535, 1497, 1475, 1456, 1391, 1372, 1346, 1317, 1270, 1244, 1210, 1174, 1130, 1115, 1103, 1079, 1027, 1002, 961, 937, 896, 879, 873, 846, 828, 750, 718, 700, 670, 656.

Preparation of ethyl-4-((4-butylphenyl)amino)benzoate (5n)



The amination reaction of freshly prepared arylzinc reagent **2k** (4.78 mL, 1.1 mmol, 0.23 M in THF) with ethyl-4-nitrosobenzoate **3e**[16] (180 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 75:25) furnished **5n** as a pale yellow oil (287 mg, 97 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.80-8.01 (m, 2 H), 7.01-7.24 (m, 4 H), 6.86-6.99 (m, 2 H), 5.99 (s, 1 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 2.52-2.66 (m, 2 H), 1.52-1.70 (m, 2 H), 1.24-1.48 (m, 5 H), 0.85-1.04 (m, 3 H).

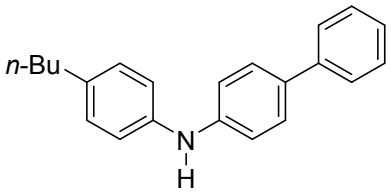
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 166.6, 148.6, 138.3, 138.1, 131.4, 129.3, 121.0, 120.9, 114.0, 60.4, 35.0, 33.7, 22.3, 14.4, 13.9.

MS (ESI), *m/z* (%) = 298 ($[M+H]^+$, 100), 283 (35), 268 (6), 222 (2), 132 (2), 59 (6).

HRMS (ESI), *m/z* calc. for **$C_{19}H_{24}NO_2$** (298.1807 ([M+H])): 298.1798 ([M+H]).

IR (ATR) υ (cm^{-1}) = 3349, 2956, 2928, 2871, 2857, 1705, 1684, 1597, 1513, 1476, 1464, 1446, 1430, 1366, 1333, 1309, 1270, 1171, 1103, 1018, 877, 833, 767, 698, 668.

Preparation of *N*-(4-butylphenyl)-[1,1'-biphenyl]-4-amine (5o)



The amination reaction of freshly prepared arylzinc reagent **2k** (4.78 mL, 1.1 mmol, 0.23 M in THF) with 4-nitroso-1,1'-biphenyl **3b** (184 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 85:15) furnished **5o** as a pale yellow solid (270 mg, 90 %).

m.p.: 84.7-86.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.38-7.64 (m, 6 H), 7.31 (t, J = 7.3 Hz, 1 H), 7.00-7.20 (m, 6 H), 5.69 (s, 1 H), 2.60 (t, J = 7.7 Hz, 2 H), 1.63 (dq, J = 7.6, 7.4 Hz, 2 H), 1.32-1.48 (m, 2 H), 0.97 (t, J = 7.3 Hz, 3 H).

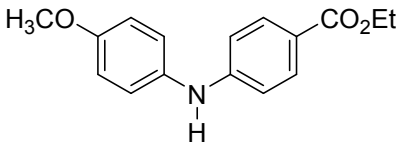
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 143.3, 140.9, 140.2, 136.3, 133.1, 129.3, 128.7, 127.9, 126.5, 126.5, 119.0, 117.0, 35.0, 33.8, 22.4, 14.0.

MS (ESI), *m/z* (%) = 302 ([M+H]$^+$, 100), 283 (4), 268 (2), 186 (8), 89 (6).

HRMS (ESI), *m/z* calc. for **$C_{22}H_{24}N$** (302.1909 ([M+H])): 302.1899 ([M+H]).

IR (ATR) υ (cm^{-1}) = 3417, 3025, 2958, 2919, 2873, 2855, 1607, 1583, 1526, 1514, 1489, 1464, 1448, 1417, 1392, 1377, 1342, 1312, 1272, 1231, 1201, 1192, 1181, 1158, 1128, 1075, 1039, 1014, 1002, 954, 922, 907, 900, 879, 854, 823, 774, 755, 736, 709, 686.

Preparation of ethyl-4-((4-methoxyphenyl)amino)benzoate (5p)



The amination reaction of freshly prepared arylzinc reagent **2f** (2.0 mL, 1.1 mmol, 0.55 M in THF) with ethyl-4-nitrosobenzoate **3e** (180 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 50:50) furnished **5p** as a pale yellow solid (219 mg, 81 %).

m.p.: 84.4-85.3 °C (Lit. m.p.: 76-78 °C).[17]

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.79-7.97 (m, 2 H), 7.04-7.22 (m, 2 H), 6.75-6.98 (m, 4 H), 5.92 (s, 1 H), 4.32 (q, J = 7.2 Hz, 2 H), 3.81 (s, 3 H), 1.36 (t, J = 7.2 Hz, 3 H).

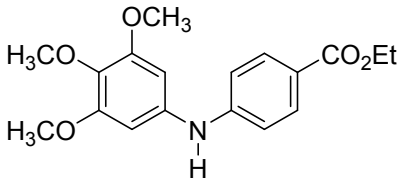
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 166.6, 156.5, 149.7, 133.5, 131.4, 124.3, 120.4, 114.8, 113.3, 60.3, 55.5, 14.4.

MS (ESI), *m/z* (%) = 272 ([M+H]$^+$, 100), 244 (7), 226 (2).

HRMS (ESI), *m/z* calc. for **$C_{16}H_{18}NO_3$** (272.1287 ([M+H])): 272.1280 ([M+H]).

IR (ATR) υ (cm^{-1}) = 3356, 2974, 2929, 2903, 2841, 1695, 1685, 1614, 1594, 1574, 1528, 1512, 1498, 1478, 1464, 1445, 1434, 1366, 1343, 1312, 1303, 1271, 1253, 1241, 1176, 1165, 1118, 1102, 1029, 1005, 964, 950, 882, 858, 843, 831, 816, 803, 770, 759, 711, 696, 664.

Preparation of ethyl-4-((3,4,5-trimethoxyphenyl)amino)benzoate (5q)



The amination reaction of freshly prepared arylzinc reagent **2l** (3.57 mL, 1.0 mmol, 0.28 M in THF) with ethyl-4-nitrosobenzoate **3e** (161 mg, 0.9 mmol), ethanol (0.9 mL), $FeCl_2$ (229 mg, 1.8 mmol) and $NaBH_4$ (34 mg, 0.9 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 40:60) furnished **5q** as a pale yellow oil (289 mg, 97 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.91 (d, *J* = 8.8 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 6.41 (s, 2 H), 6.02 (s, 1 H), 4.33 (q, *J* = 7.2 Hz, 2 H), 3.83 (s, 3 H) 3.81 (s, 6 H) 1.36 (t, *J* = 7.1 Hz, 3 H).

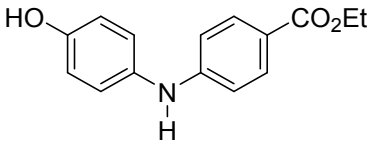
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.5, 153.8, 148.4, 136.9, 134.2, 131.5, 121.2, 114.4, 98.7, 61.0, 60.5, 56.1, 14.4.

MS (EI), *m/z* (%) = 331 (M$^+$, 61), 317 (23), 316 (100), 288 (15), 243 (8), 121 (5), 42 (8).

HRMS (EI), *m/z* calc. for **$C_{18}H_{21}NO_5$** (331.1420): 331.1415.

IR (ATR) υ (cm^{-1}) = 3345, 2978, 2936, 2841, 1702, 1685, 1654, 1591, 1522, 1502, 1452, 1428, 1397, 1366, 1311, 1271, 1255, 1228, 1194, 1170, 1122, 1100, 1043, 1002, 926, 862, 829, 812, 782, 768, 716, 696, 656.

Preparation of ethyl-4-((4-hydroxyphenyl)amino)benzoate (5r)



The amination reaction of freshly prepared arylzinc reagent **2g** (6.11 mL, 1.1 mmol, 0.18 M in THF) with ethyl-4-nitrosobenzoate **3e** (180 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 50:50) furnished **5r** as a pale yellow solid (249 mg, 97 %).

m.p.: 131.9-133.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.75-7.95 (m, 2 H), 6.97-7.10 (m, 2 H), 6.71-6.94 (m, 4 H), 6.39 (bs, 1 H), 5.90 (s, 1 H), 4.33 (q, J = 7.0 Hz, 2 H), 1.36 (t, J = 7.2 Hz, 3 H).

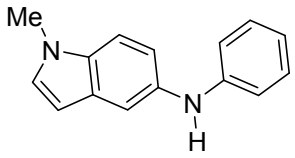
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 167.4, 153.0, 150.1, 133.0, 131.6, 124.8, 119.7, 116.3, 113.1, 60.7, 14.4.

MS (EI), *m/z* (%) = 257 (M^+, 100), 229 (45), 212 (48), 184 (9), 183 (13), 154(7).

HRMS (EI), *m/z* calc. for **$C_{15}H_{15}NO_3$** (257.1052): 257.1046.

IR (ATR) υ (cm^{-1}) = 3404, 3354, 1665, 1602, 1578, 1511, 1472, 1441, 1394, 1366, 1342, 1313, 1284, 1243, 1224, 1173, 1124, 1107, 1099, 1018, 949, 933, 875, 832, 768, 711, 698, 670.

Preparation of 1-methyl-*N*-phenyl-1*H*-indol-5-amine (5s)



The amination reaction of freshly prepared heteroarylzinc reagent **2m** (4.54 mL, 1.0 mmol, 0.22 M in THF) with nitrosobenzene **3a** (96.4 mg, 0.9 mmol), ethanol (0.9 mL), $FeCl_2$ (229 mg, 1.8 mmol) and $NaBH_4$ (34 mg, 0.9 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 85:15) furnished **5s** as a pale yellow solid (125 mg, 63 %).

m.p.: 167.9-168.8 °C (Lit. m.p.: 163-165 °C).[18]

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.44 (d, J = 1.7 Hz, 1 H), 7.18-7.33 (m, 3 H), 7.02-7.16 (m, 2 H), 6.90-7.01 (m, 2 H), 6.83 (t, J = 7.3 Hz, 1 H), 6.43 (d, J = 3.0 Hz, 1 H), 5.80 (bs, 1 H), 3.80 (s, 3 H).

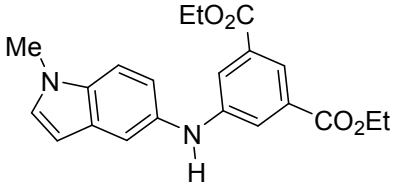
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 146.3, 134.6, 133.9, 129.5, 129.2, 129.1, 119.1, 118.0, 115.3, 113.6, 109.8, 100.6, 33.0.

MS (EI), *m/z* (%) = 222 (M^+, 100), 221 (14), 207 (100), 206 (28), 180 (7), 103 (7).

HRMS (EI), *m/z* calc. for **$C_{15}H_{14}N_2$** (222.1157): 222.1156.

IR (ATR) υ (cm^{-1}) = 3380, 3097, 2923, 1598, 1573, 1508, 1495, 1480, 1452, 1422, 1377, 1360, 1334, 1300, 1249, 1240, 1175, 1150, 1102, 1079, 1026, 992, 886, 854, 813, 754, 728, 708, 694.

Preparation of diethyl-5-((1-methyl-1*H*-indol-5-yl)amino)isophthalate (5t)



The amination reaction of freshly prepared heteroarylzinc reagent **2m** (5.23 mL, 1.1 mmol, 0.21 M in THF) with diethyl-5-nitrosoisophthalate **3d** (252 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 55:45) furnished **5t** as a pae yellow solid (201 mg, 55%).

m.p.: 146.5-147.9 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.06 (t, *J* = 1.5 Hz, 1 H), 7.71 (d, *J* = 1.4 Hz, 2 H), 7.40 (d, *J* = 1.9 Hz, 1 H), 7.29 (d, *J* = 8.6 Hz, 1 H), 7.10-7.01 (m, 2 H), 6.42 (d, *J* = 3.0 Hz, 1 H), 5.88 (s, 1 H), 4.35 (q, *J* = 7.0 Hz, 4 H), 3.78 (s, 3 H), 1.36 (t, *J* = 7.0 Hz, 6 H).

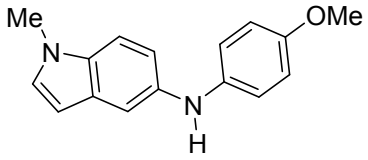
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 166.2, 147.0, 134.3, 133.3, 131.8, 129.7, 129.2, 120.5, 119.2, 118.2, 114.6, 110.1, 100.7, 61.1, 33.0, 14.3.

MS (EI), *m/z* (%) = 366 (M^+, 100), 338 (17), 321 (5), 319 (5), 310 (16), 291 (6), 220 (9), 219 (8).

HRMS (EI), *m/z* calc. for **$C_{21}H_{22}N_2O_4$** (366.1580): 366.1557.

IR (ATR) υ (cm^{-1}) = 3366, 1713, 1694, 1605, 1526, 1509, 1487, 1460, 1444, 1423, 1397, 1374, 1336, 1315, 1294, 1280, 1263, 1238, 1227, 1170, 1151, 1133, 1102, 1094, 1085, 1022, 995, 978, 890, 879, 862, 834, 801, 757, 737, 722, 713, 674, 654.

Preparation of *N*-(4-methoxyphenyl)-1-methyl-1*H*-indol-5-amine (5u)



The amination reaction of freshly prepared heteroarylzinc reagent **2m** (5.23 mL, 1.1 mmol, 0.21 M in THF) with 1-methoxy-4-nitrosobenzene **3f**[4] (138 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 67:33) furnished **5u** as a pale yellow solid (152 mg, 60 %).

m.p.: 102.1-103.8 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.21-7.32 (m, 2 H), 6.92-7.07 (m, 4 H), 6.77-6.89 (m, 2 H), 6.38 (d, J = 2.2 Hz, 1 H), 5.40 (bs, 1 H), 3.79 (s, 3 H), 3.77 (s, 3 H).

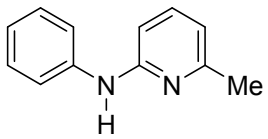
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 153.8, 139.5, 136.8, 133.2, 129.4, 129.1, 118.6, 116.3, 114.7, 110.7, 109.8, 100.3, 55.7, 32.9.

MS (EI), *m/z* (%) = 252 (M^+, 95), 238 (21), 237 (100), 219 (11), 207 (7), 131 (7).

HRMS (EI), *m/z* calc. for **$C_{16}H_{16}N_2O$** (252.1263): 252.1251.

IR (ATR) υ (cm^{-1}) = 3418, 3105, 2997, 2958, 2913, 2836, 2821, 1614, 1508, 1465, 1441, 1423, 1375, 1361, 1336, 1309, 1296, 1250, 1240, 1229, 1183, 1154, 1109, 1080, 1036, 1014, 950, 938, 927, 863, 835, 812, 803, 774, 759, 733, 715, 701.

Preparation of 6-methyl-*N*-phenylpyridin-2-amine (5v)[19]



The amination reaction of freshly prepared arylzinc reagent **2a** (0.4 mL, 0.67 mmol, 1.68 M in THF) with 2-methyl-6-nitrosopyridine **3g**[20] (75 mg, 0.61 mmol), ethanol (0.6 mL), $FeCl_2$ (154.6 mg, 1.22 mmol) and $NaBH_4$ (23.2 mg, 0.61 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 60:40) furnished **5v** as a colorless liquid (75 mg, 67 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 7.35-7.40 (m, 1 H), 7.25-7.34 (m, 4 H), 6.98-7.07 (m, 1 H), 6.71 (d, J = 8.2 Hz, 1 H), 6.64 (bs, 1 H), 6.59 (d, J = 7.4 Hz, 1 H), 2.43 (s, 3 H).

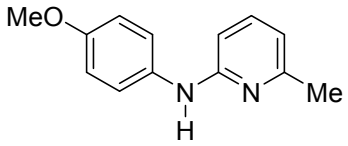
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) = 157.3, 155.4, 140.7, 138.0, 129.2, 122.6, 120.2, 114.4, 104.8, 24.3.

MS (EI), *m/z* (%) = 184 (M^+, 40), 183 (100), 182 (8), 80 (8), 77 (7), 65 (7), 43 (13).

HRMS (EI), *m/z* calc. for $\mathbf{C_{12}H_{11}N_2}$ (183.0922 ([M-H])): 183.0920 ([M-H]).

IR (ATR) υ (cm^{-1}) = 3400, 3219, 3034, 2958, 2921, 2854, 1603, 1587, 1574, 1520, 1495, 1456, 1447, 1411, 1375, 1324, 1262, 1236, 1215, 1177, 1157, 1092, 1076, 1030, 989, 892, 829, 775, 744, 731, 691.

Preparation of *N*-(4-methoxyphenyl)-6-methylpyridin-2-amine (5w)



The amination reaction of freshly prepared arylzinc reagent **2f** (5.23 mL, 1.1 mmol, 0.21 M in THF) with 2-methyl-6-nitrosopyridine **3g** (123 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 40:60) furnished **5w** as a pale yellow solid (205 mg, 96 %).

m.p.: 62.4-63.6 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.26-7.38 (m, 1 H), 7.13-7.24 (m, 2 H), 6.78-6.96 (m, 2 H), 6.36-6.61 (m, 3 H), 3.79 (s, 3 H), 2.39 (s, 3 H).

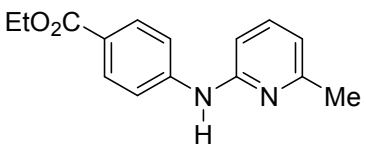
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 157.2, 156.9, 156.2, 137.9, 133.5, 124.1, 114.6, 113.6, 103.7, 55.5, 24.2.

MS (EI), *m/z* (%) = 214 (M^+, 81), 213 (24), 200 (12), 199 (100), 171 (11), 92 (23), 65 (15).

HRMS (EI), *m/z* calc. for $\mathbf{C_{13}H_{14}N_2O}$ (214.1106): 214.1100.

IR (ATR) υ (cm^{-1}) = 3197, 3093, 3039, 2992, 2959, 2933, 2909, 2836, 1608, 1592, 1579, 1525, 1505, 1451, 1438, 1384, 1338, 1288, 1264, 1228, 1178, 1165, 1152, 1102, 1089, 1035, 1008, 990, 958, 939, 858, 845, 830, 780, 757, 738, 716, 680.

Preparation of ethyl-4((6-methylpyridin-2-yl)amino)benzoate (5x)



The amination reaction of freshly prepared arylzinc reagent **2c** (7.14 mL, 1.0 mmol, 0.14 M in THF) with 2-methyl-6-nitrosopyridine **3g** (110 mg, 0.9 mmol), ethanol (0.9 mL), $FeCl_2$ (229

mg, 1.8 mmol) and $NaBH_4$ (34 mg, 0.9 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 20:80) furnished **5x** as a pale yellow solid (191 mg, 83 %).

m.p.: 112.7-114.6 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.82-8.12 (m, 2 H), 7.29-7.58 (m, 3 H), 6.52-6.97 (m, 3 H), 4.34 (q, J = 7.0 Hz, 2 H), 2.46 (s, 3 H), 1.37 (t, J = 7.0 Hz, 3 H).

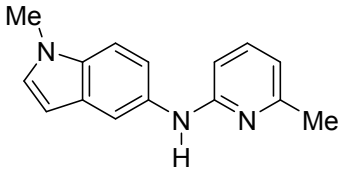
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 166.4, 157.5, 153.8, 145.2, 138.1, 131.1, 123.0, 117.0, 115.7, 106.8, 60.5, 24.3, 14.4.

MS (EI), *m/z* (%) = 256 (M^+, 100), 255 (90), 228 (14), 227 (67), 211 (45), 183 (32), 182 (17), 181 (15), 105 (16), 92 (22), 91 (13), 80 (15), 65 (25).

HRMS (EI), *m/z* calc. for **$C_{15}H_{16}N_2O_2$** (256.1212): 256.1211.

IR (ATR) υ (cm^{-1}) = 3331, 3214, 3126, 2987, 2977, 2937, 2920, 2906, 1686, 1649, 1606, 1579, 1525, 1513, 1473, 1454, 1437, 1397, 1372, 1362, 1339, 1310, 1300, 1274, 1253, 1244, 1216, 1175, 1158, 1130, 1124, 1111, 1019, 991, 977, 969, 961, 946, 880, 866, 848, 823, 812, 785, 766, 746, 730, 698, 680.

Preparation of 1-methyl-*N*-(6-methylpyridin-2-yl)-1*H*-indol-5-amine (5y)



The amination reaction of freshly prepared heteroarylzinc reagent **2m** (6.11 mL, 1.1 mmol, 0.18 M in THF) with 2-methyl-6-nitrosopyridine **3g** (123 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 30:70) furnished **5y** as a yellow solid (166 mg, 70 %).

m.p.: 132.9-133.9 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.52 (d, J = 1.7 Hz, 1 H), 7.23-7.35 (m, 2 H), 6.99-7.18 (m, 2 H), 6.33-6.66 (m, 4 H), 3.78 (s, 3 H), 2.42 (s, 3 H).

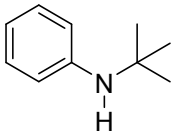
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 157.9, 157.1, 137.9, 134.4, 132.4, 129.6, 129.0, 119.1, 115.7, 113.2, 109.8, 103.3, 100.7, 32.9, 24.3.

MS (EI), *m/z* (%) = 237 (M^+, 98), 236 (100), 222 (5), 221 (13), 220 (5), 118 (6), 111 (5), 77 (6).

HRMS (EI), *m/z* calc. for **$C_{15}H_{14}N_3$** (236.1188 ([M-H])): 236.1183([M-H]).

IR (ATR) υ (cm^{-1}) = 3200, 3010, 2955, 1596, 1584, 1510, 1493, 1453, 1422, 1388, 1372, 1325, 1276, 1260, 1234, 1150, 1104, 1093, 1081, 1032, 1026, 1013, 990, 958, 894, 834, 774, 754, 733, 702, 653.

Preparation of *N*-(*tert*-butyl)aniline (7a)[21]



The amination reaction of freshly prepared *tert*-butylzinc reagent **6a** (0.93 mL, 1.1 mmol, 1.18 M in THF) with nitrosobenzene **3a** (108 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 75:25) furnished **7a** as a yellow liquid (75 mg, 50 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.05-7.25 (m, 2 H), 6.48-6.93 (m, 3 H), 3.44 (bs, 1 H), 1.36 (s, 9 H).

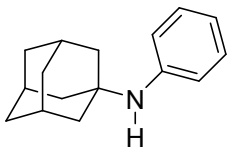
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 146.8, 128.9, 118.4, 117.5, 51.5, 30.1.

MS (ESI), *m/z* (%) = 150 ($[M+H]^+$, 100), 135 (29).

HRMS (ESI), *m/z* calc. for **$C_{10}H_{16}N$** (150.1283 ([M+H])): 150.1277 ([M+H]).

IR (ATR) υ (cm^{-1}) = 3406, 2958, 2924, 2855, 1616, 1602, 1518, 1506, 1484, 1474, 1466, 1459, 1439, 1392, 1363, 1320, 1305, 1272, 1259, 1248, 1221, 1210, 1189, 1161, 1081, 1025, 965, 928, 907, 894, 847, 819, 789, 763, 746, 721, 685.

Preparation of (3s,5s,7s)-*N*-phenyladamantan-1-amine (7b)[22]



The amination reaction of freshly prepared adamantylzinc reagent **6b**[1] (3.92 mL, 1.1 mmol, 0.28 M in THF) with nitrosobenzene **3a** (108 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-

column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 90:10) furnished **7b** as a pale yellow solid (203 mg, 89 %).

m.p.: 80.6-82.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.16 (dd, J = 8.7, 7.3 Hz, 2 H), 6.60-6.92 (m, 3 H), 3.25 (s, 1 H), 2.04-2.21 (m, 3 H), 1.81-2.01 (m, 6 H), 1.57-1.79 (m, 6 H).

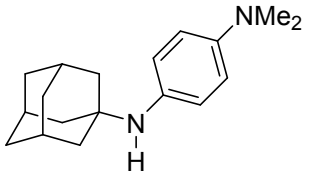
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 146.0, 128.7, 119.2, 119.1, 52.2, 43.5, 36.5, 29.8.

MS (ESI), *m/z* (%) = 228 ([M+H]$^+$, 100), 135 (37), 114 (1).

HRMS (ESI), *m/z* calc. for **$C_{16}H_{22}N$** (228.1752 ([M+H])): 228.1746 ([M+H]).

IR (ATR) υ (cm^{-1}) = 3408, 3048, 3013, 2954, 2904, 2847, 2668, 2591, 1598, 1502, 1494, 1472, 1448, 1432, 1366, 1356, 1345, 1323, 1305, 1286, 1271, 1236, 1178, 1152, 1130, 1106, 1096, 1081, 1038, 1027, 992, 978, 938, 906, 862, 837, 819, 741, 690.

Preparation of *N*^{1}-((3s,5s,7s)-adamantan-1-yl)-N^4,N^4-dimethylbenzene-1,4-diamine (7c)



The amination reaction of freshly prepared adamantylzinc reagent **6b** (3.92 mL, 1.1 mmol, 0.28 M in THF) with *N*,*N*-dimethyl-4-nitrosoaniline **3h**[23] (151 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 50:50) furnished **7c** as a pale yellow solid (193 mg, 71 %).

m.p.: 103.0-104.1 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 6.83 (d, J = 8.3 Hz, 2 H), 6.66 (d, J = 8.3 Hz, 2 H), 2.89 (s, 6 H), 2.80 (bs, 1 H), 1.97-2.16 (m, 3 H), 1.50-1.85 (m, 12 H).

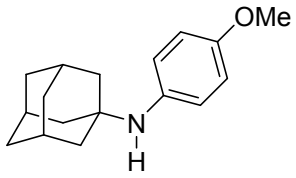
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 146.6, 135.1, 125.0, 113.5, 52.6, 43.8, 41.3, 36.5, 29.8.

MS (EI), *m/z* (%) = 270 (M$^+$, 100), 269 (5), 213 (14), 136 (13), 135 (34), 121 (12), 93 (7), 79 (6).

HRMS (EI), *m/z* calc. for **$C_{18}H_{26}N_2$** (270.2096): 270.2090.

IR (ATR) υ (cm^{-1}) = 3295, 2901, 2842, 2790, 1616, 1511, 1479, 1443, 1416, 1402, 1362, 1354, 1340, 1326, 1309, 1282, 1243, 1213, 1185, 1176, 1162, 1124, 1107, 1100, 1094, 1054, 1040, 1010, 991, 975, 944, 934, 922, 882, 862, 819, 806, 788, 773, 722, 700, 689.

Preparation of (3s,5s,7s)-*N*-(4-methoxyphenyl)adamantan-1-amine (7d)



The amination reaction of freshly prepared adamantylzinc reagent **6b** (5.0 mL, 1.1 mmol, 0.22 M in THF) with 1-methoxy-4-nitrosobenzene **3f** (138 mg, 1.0 mmol), ethanol (1.0 mL), $FeCl_2$ (254 mg, 2.0 mmol) and $NaBH_4$ (38 mg, 1.0 mmol) was performed according to **TP1**. Flash-column chromatography (silica gel (pre-neutralized with triethylamine), *i*-hexane/ethyl acetate 55:45) furnished **7d** as a pale yellow solid (144 mg, 56 %).

m.p.: 68.6-70.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 6.81 (d, J = 8.5 Hz, 2 H), 6.67-6.77 (m, 2 H), 3.75 (s, 3 H), 2.72 (s, 1 H), 2.11-2.01 (m, 3 H), 1.71-1.75 (m, 6 H), 1.55-1.67 (m, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) = 154.8, 138.3, 124.2, 113.8, 55.4, 52.6, 43.7, 36.5, 29.7.

MS (EI), *m/z* (%) = 257 (M^+, 97), 201 (18), 200 (91), 135 (100), 122 (16), 93 (32), 79 (35), 77 (23), 67 (16), 45 (33), 42 (31), 40 (21).

HRMS (EI), *m/z* calc. for **$C_{17}H_{23}NO$** (257.1780): 257.1770.

IR (ATR) υ (cm^{-1}) = 3300, 2990, 2901, 2848, 1593, 1508, 1481, 1465, 1450, 1438, 1412, 1355, 1348, 1343, 1311, 1299, 1286, 1252, 1231, 1189, 1179, 1174, 1154, 1122, 1110, 1102, 1092, 1038, 1024, 992, 976, 935, 910, 885, 835, 819, 796, 776, 745, 700, 668.

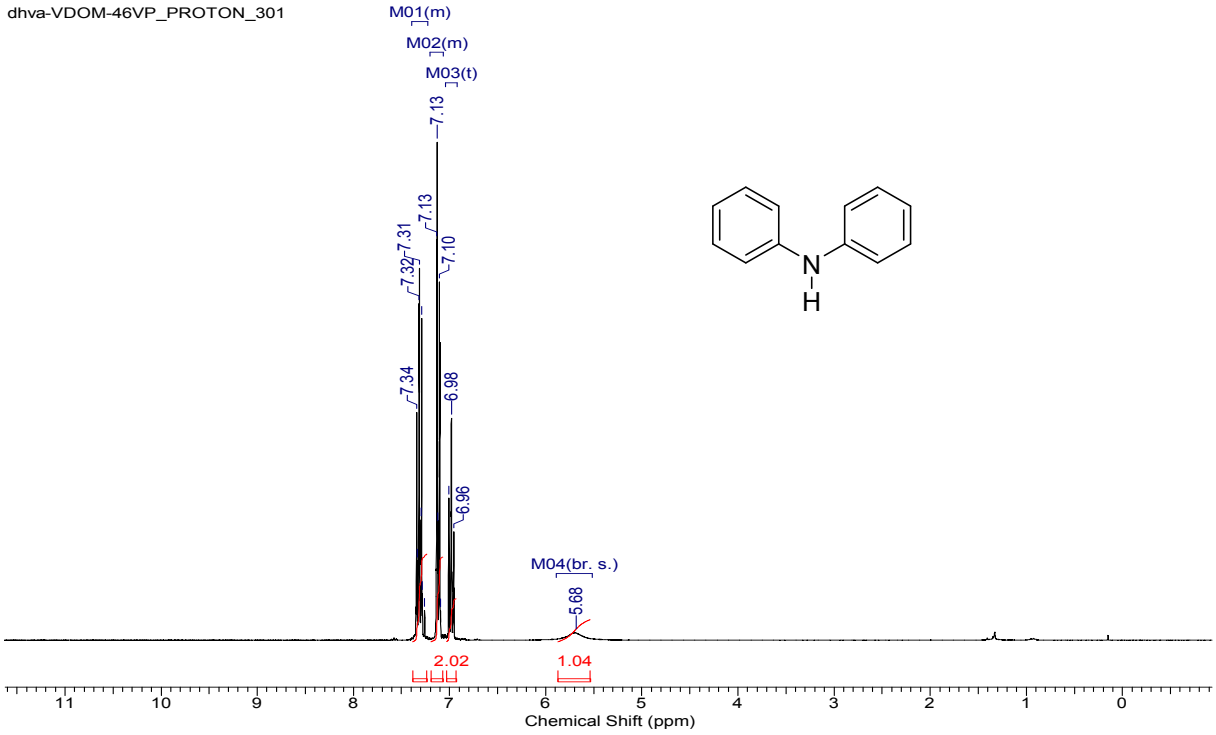
References

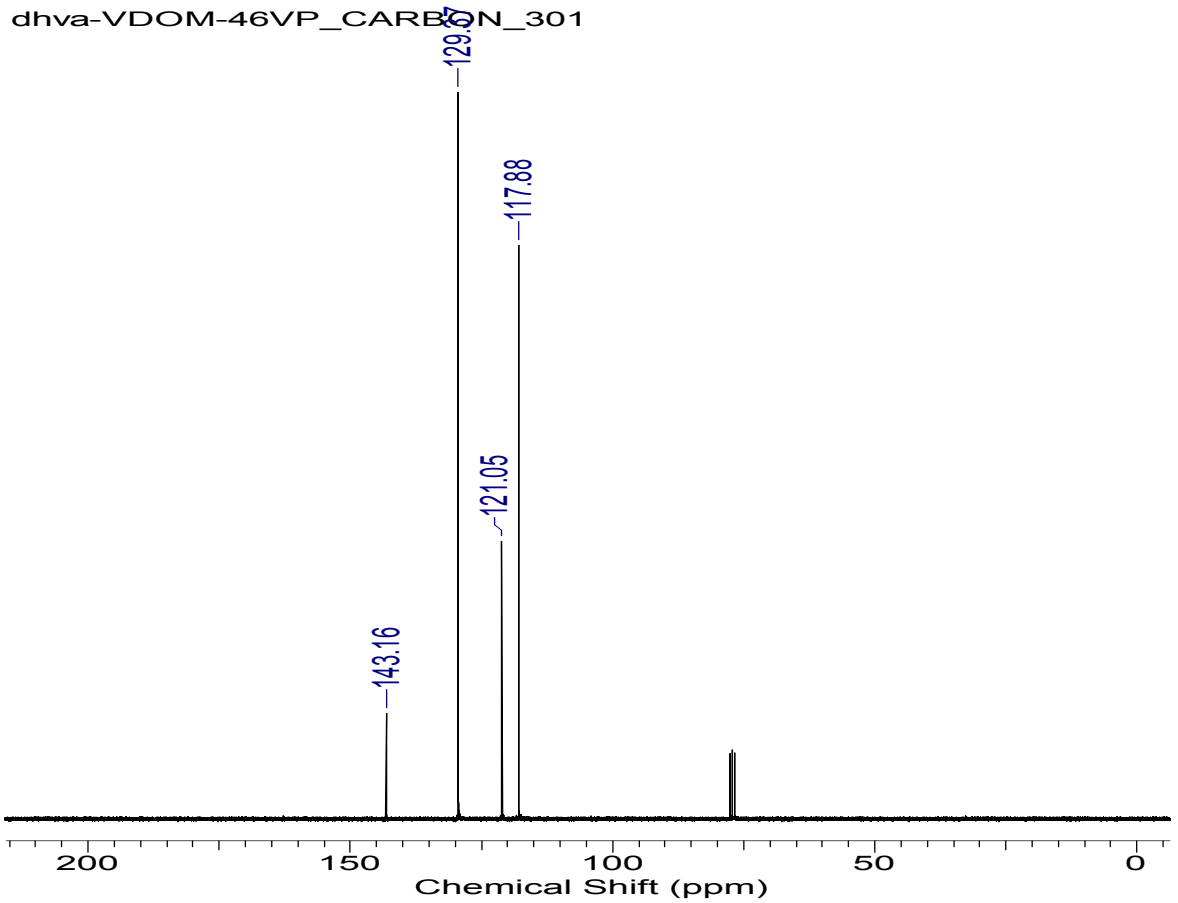
1. C. Sämann, V. Dhayalan, P. R. Schreiner, P. Knochel, *Org. Lett.* **2014**, *16*, 2418.
2. (a) F. M. Piller, P. Appukkuttan, A. Gavryushin, M. Helm, P. Knochel, *Angew. Chem. Int. Ed.* **2008**, *47*, 6802; (b) F. M. Piller, A. Metzger, M. A. Schade, B. A. Haag, A. Gavryushin, P. Knochel, *Chem. Eur. J.* **2009**, *15*, 7192.
3. A. Krasovskiy, P. Knochel, *Synthesis* **2006**, 890.
4. D. Zhao, M. Johansson, J-E. Bäckvall, *Eur. J. Org. Chem.* **2007**, 4431.

5. N. G. Gaylord, *J. Org. Chem*. **1960**, *25*, 1874.
6. Y. Yu, J. Srogl, L. S. Liebeskind, *Org. Lett.* **2004**, *6*, 2631.
7. L. Ackermann, R. Sandmann, W. Song, *Org. Lett.* **2011**, *13*, 1784.
8. D. Craig, *J. Am. Chem. Soc.* **1935**, *57*, 195.
9. H. Takeuchi, S. Hirayama, M. Mitani, K. Koyama, *J. Chem. Soc. Perkin Trans. 1*, **1988**, 521.
10. M. A. Carroll, R. A. Wood, *Tetrahedron* **2007**, *63*, 11349.
11. D. Maiti, S. L. Buchwald, *J. Am. Chem. Soc.* **2009**, *131*, 17423.
12. W. A. Lees, A. Burawoy, *Tetrahedron* **1963**, *19*, 419.
13. J. Piccard, *J. Am. Chem. Soc.* **1926**, *48*, 2878.
14. J. Li, M. Cui, A. Yu, Y. Wu, *J. Organomet. Chem.* **2007**, *692*, 3732.
15. S. Wang, X. Wang, L. Li, R. C. Advincula, *J. Org. Chem*. **2004**, *69*, 9073.
16. O. A. Blackburn, B. J. Coe, M. Helliwell, *Organometallics* **2011**, *30*, 4910.
17. I. Sapountzis, P. Knochel, *J. Am. Chem. Soc.* **2002**, *124*, 9390.
18. R. E. Tundel, K. W. Anderson, S. L. Buchwald, *J. Org. Chem.* **2006***, 71*, 430.
19. M. Kim, S. Chang, *Org. Lett.* **2010**, *12*, 1640.
20. E. C. Taylor, C-P. Tseng, J. B. Rampal, *J. Org. Chem*. **1982**, *47*, 552.
21. T. Arnauld, D. H. R. Barton, E. Doris, *Tetrahedron* **1997**, *53*, 4137.
22. T. D. Quach, R. A. Batey, *Org. Lett.* **2003,** *5,* 4397.
23. *Sigma-Aldrich, CAS Number 138-89-6* (*N*,*N*-dimethyl-4-nitrosoaniline).

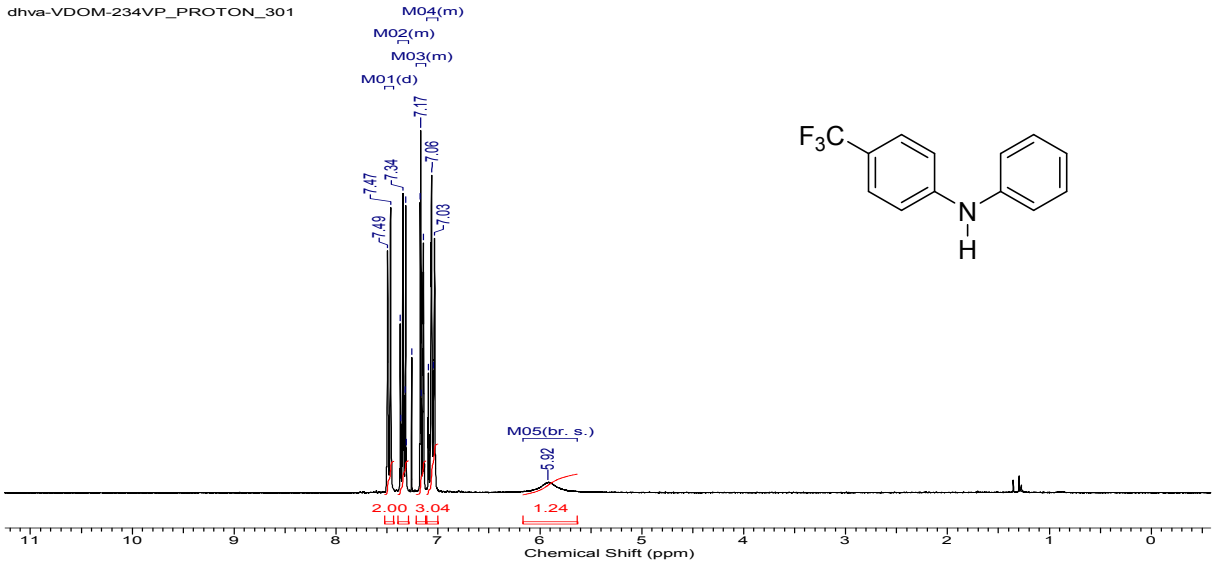
NMR-SPECTRA

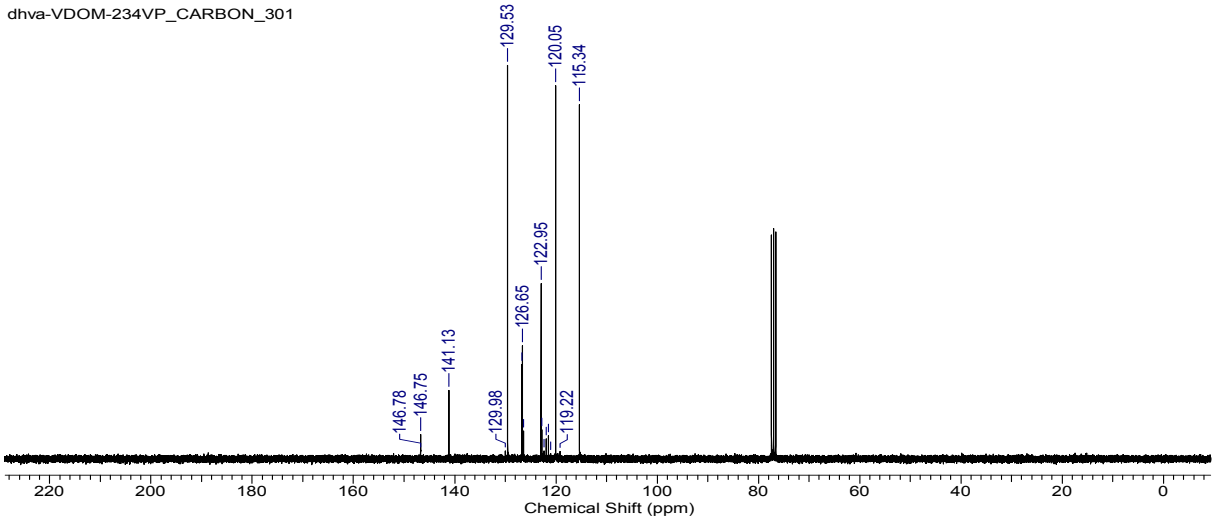
Diphenylamine (5a)

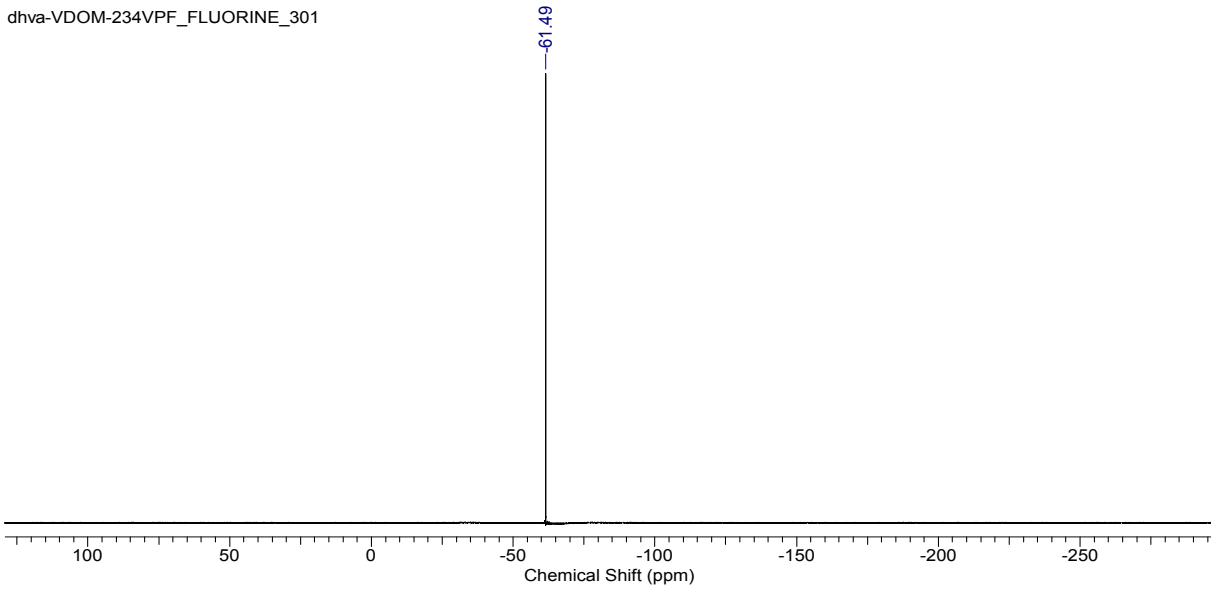




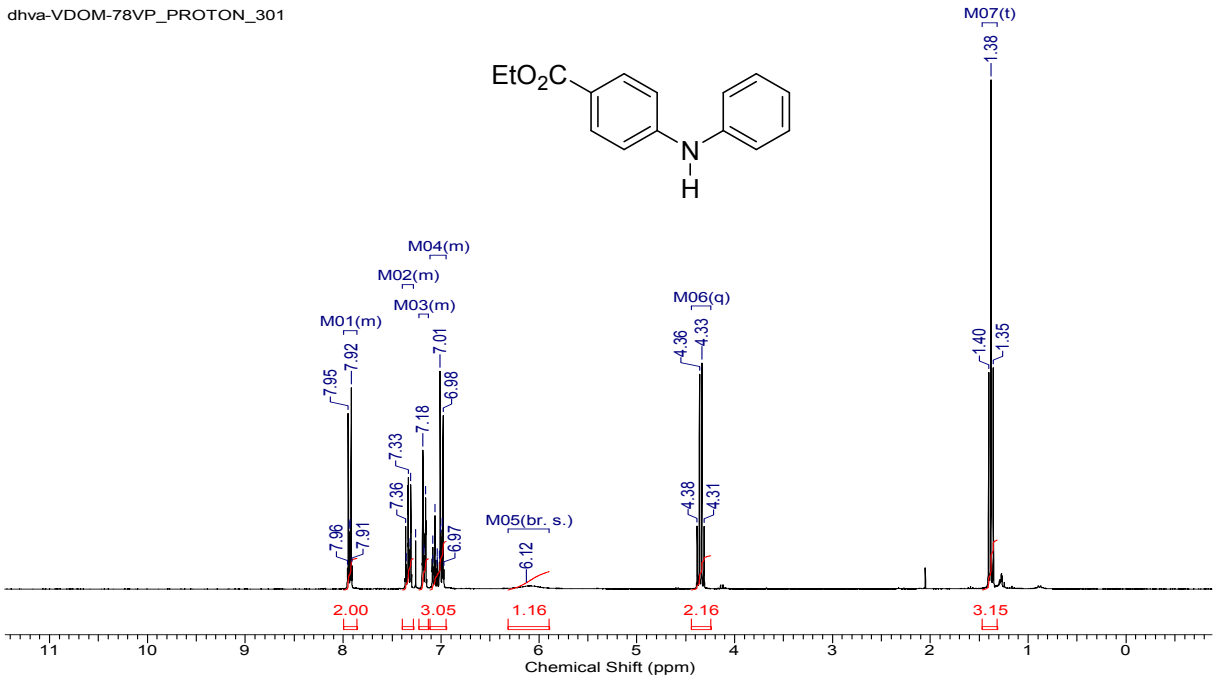
N-Phenyl-4-(trifluoromethyl)aniline (5b)

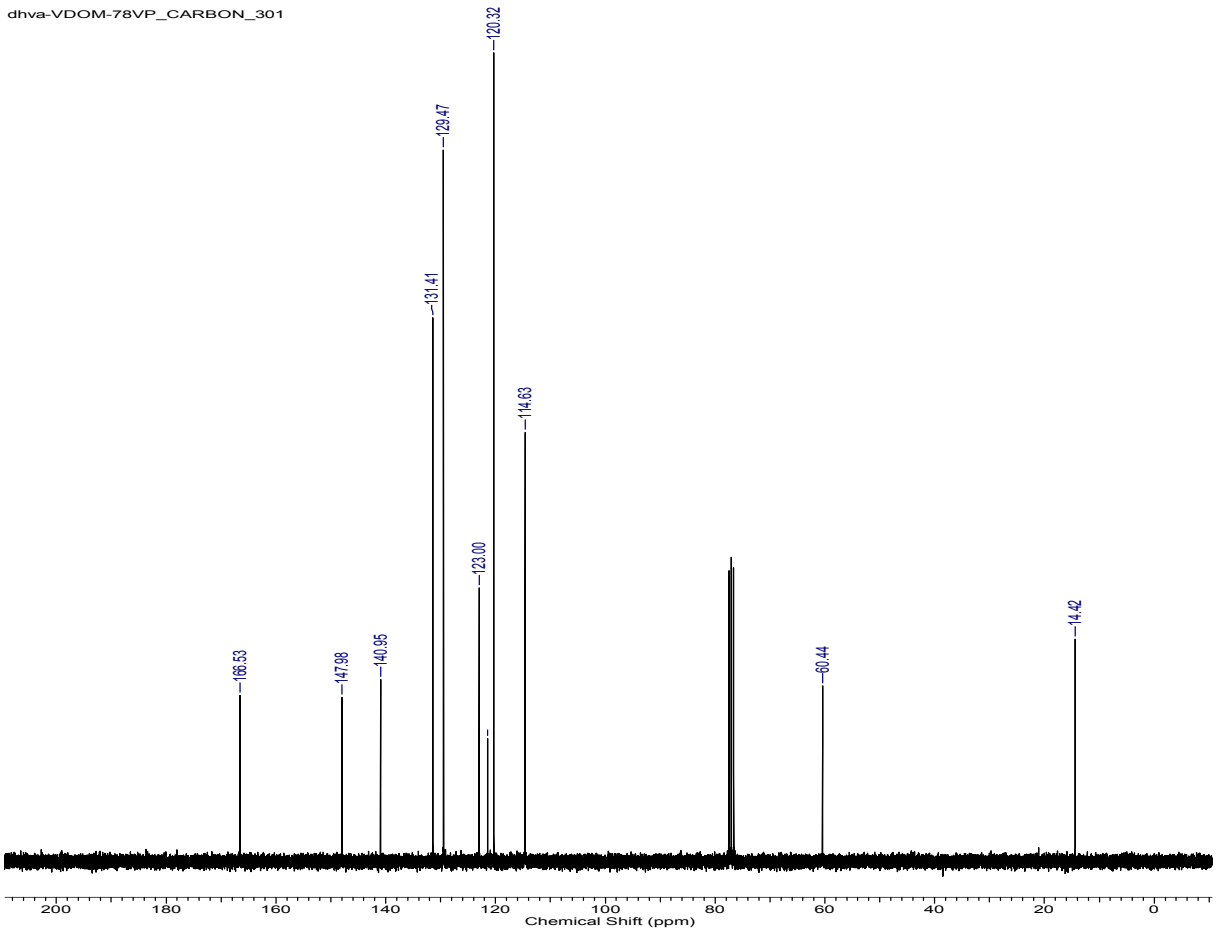




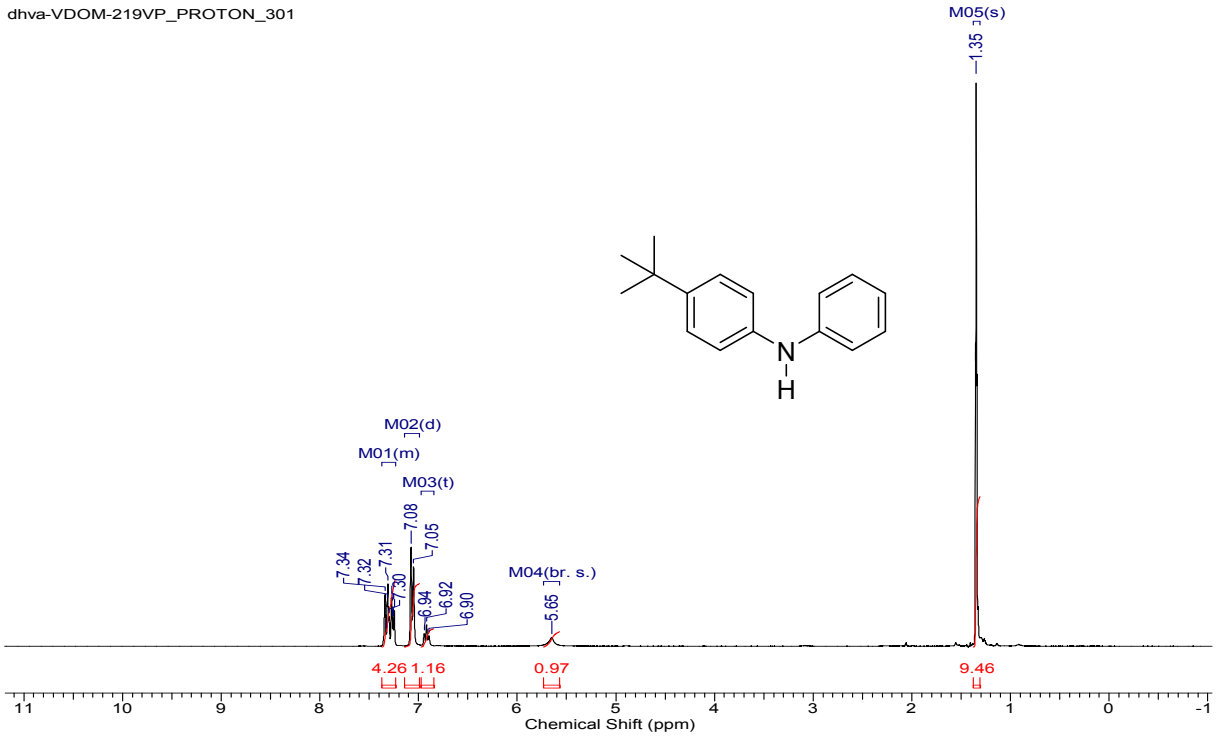


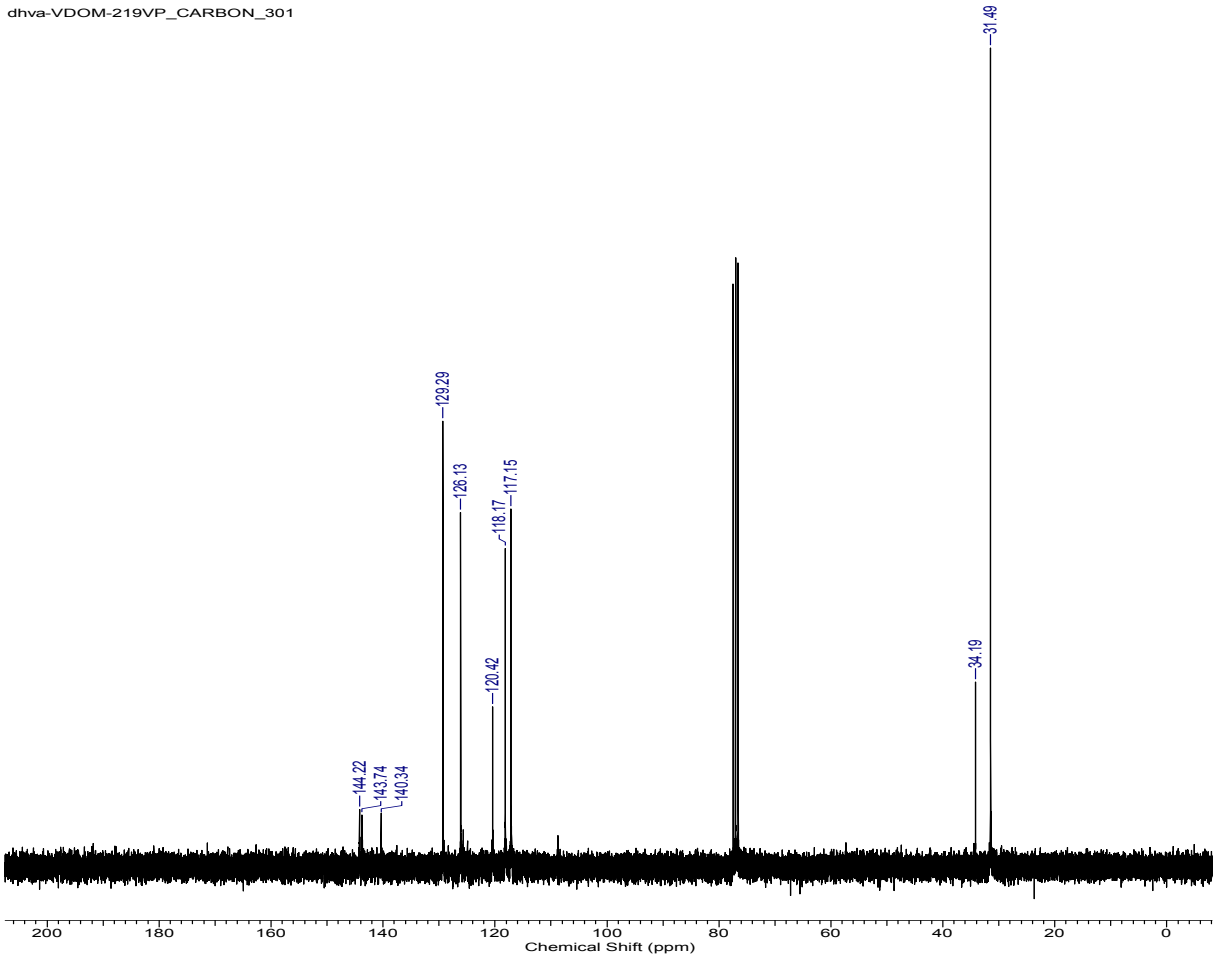
Ethyl-4-(phenylamino)benzoate (5c)



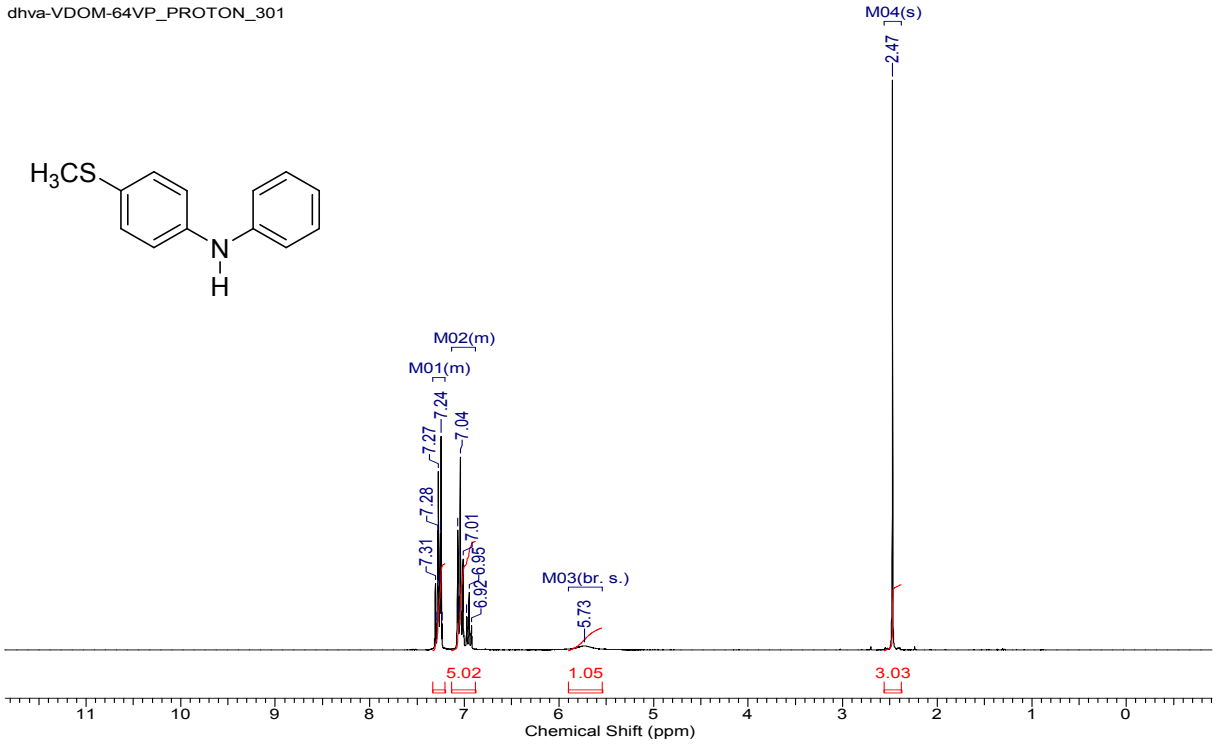


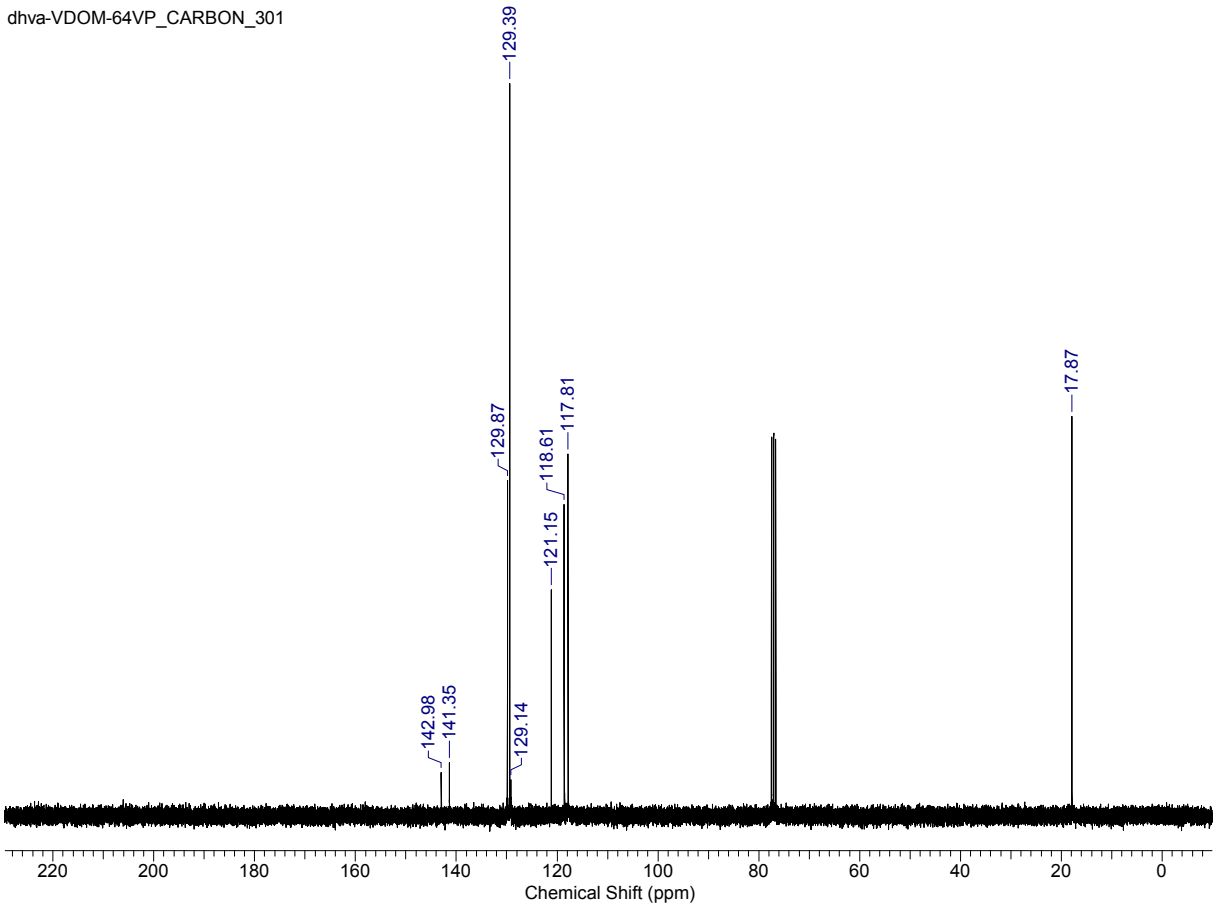
4-(*tert*-Butyl)-*N*-phenylaniline (5d)



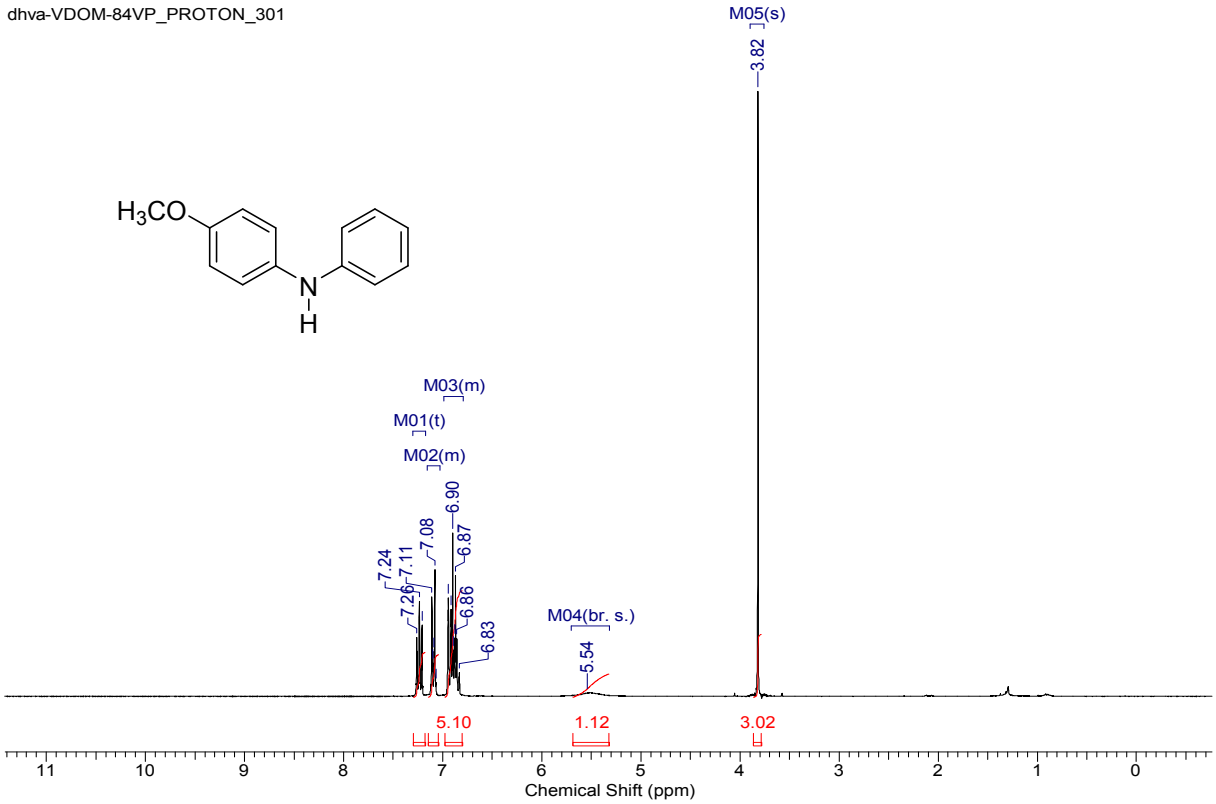


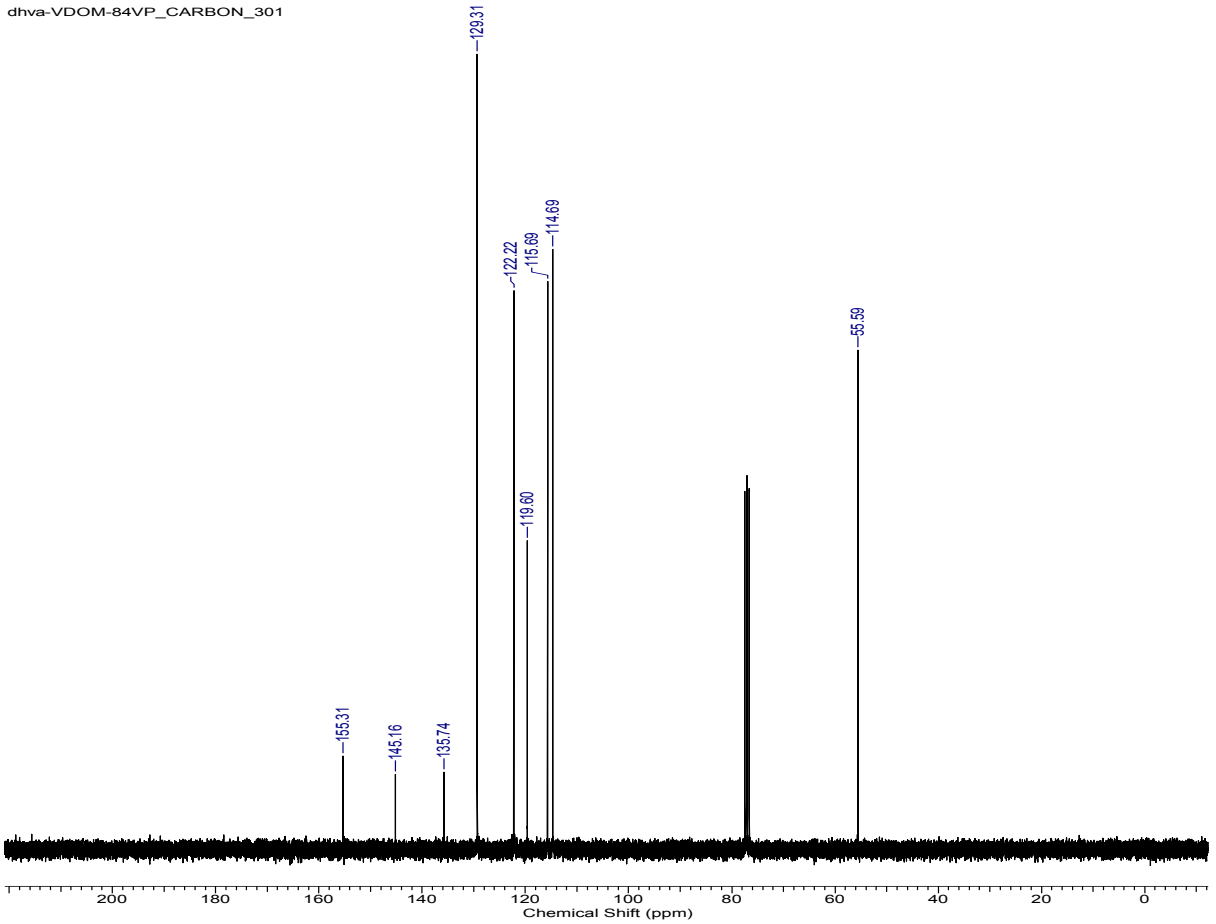
4-(Methylthio)-*N*-phenylaniline (5e)



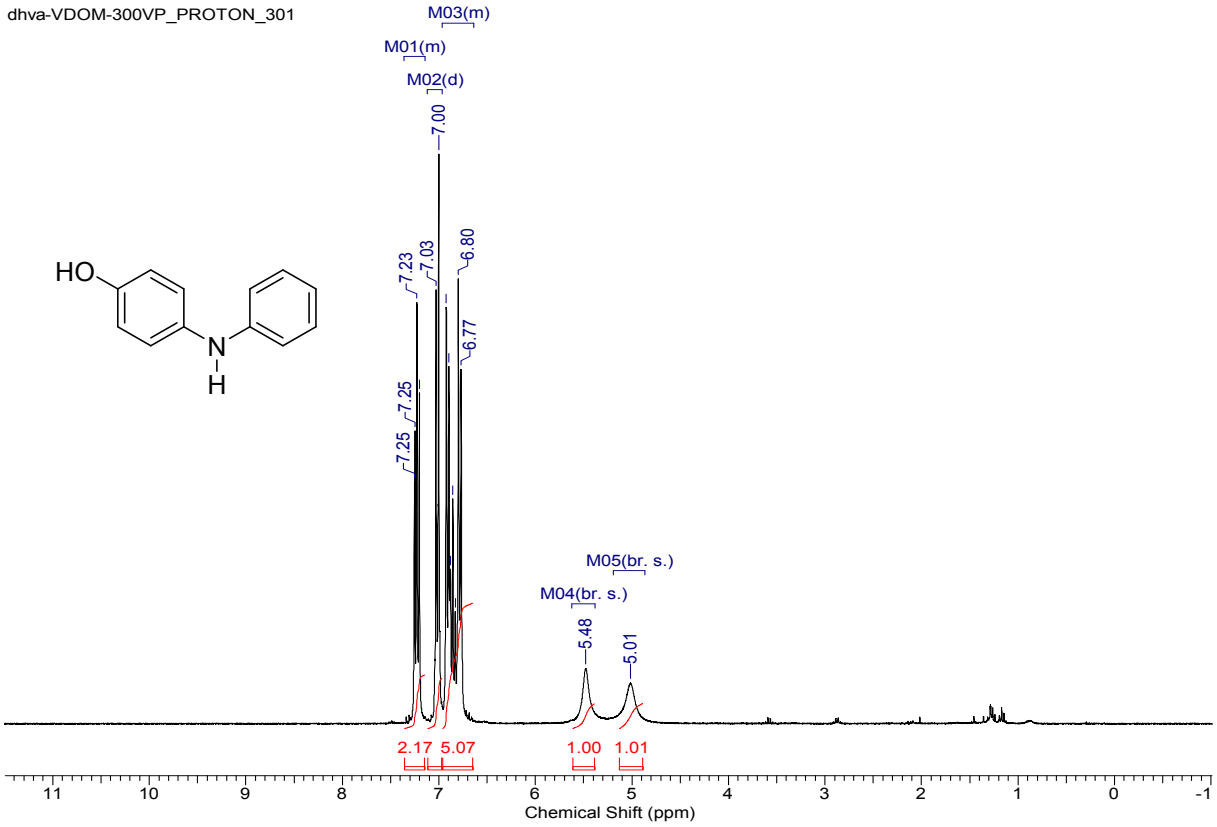


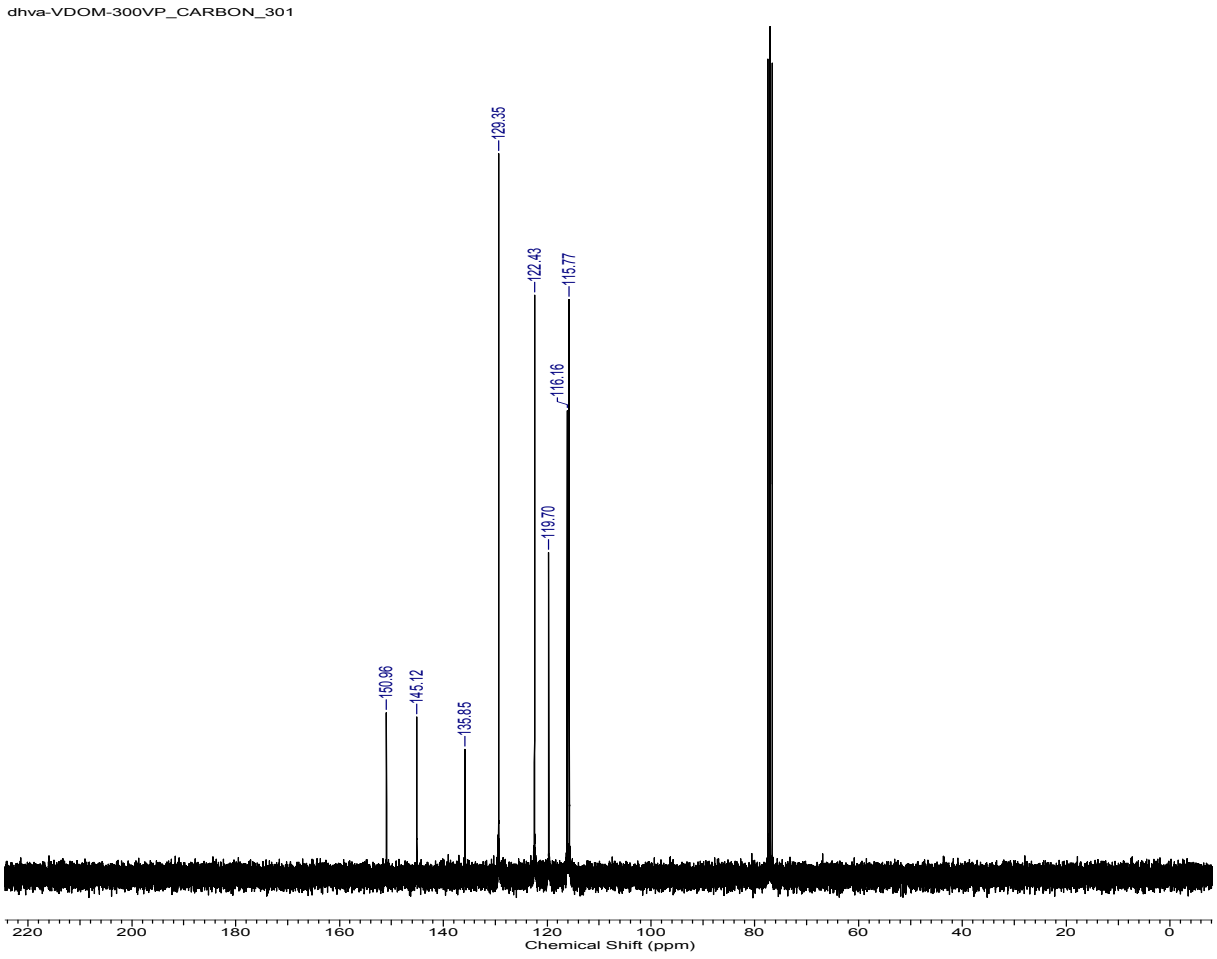
4-Methoxy-*N*-phenylaniline (5f)



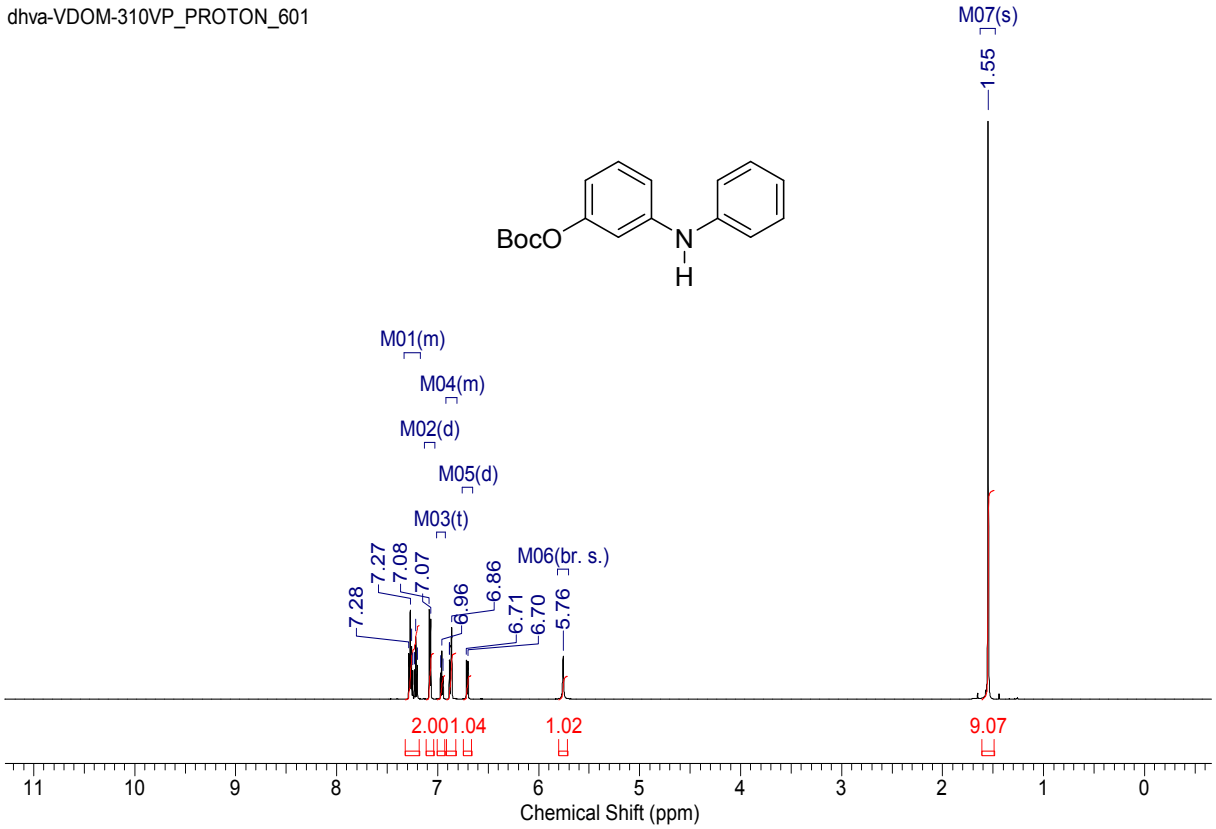


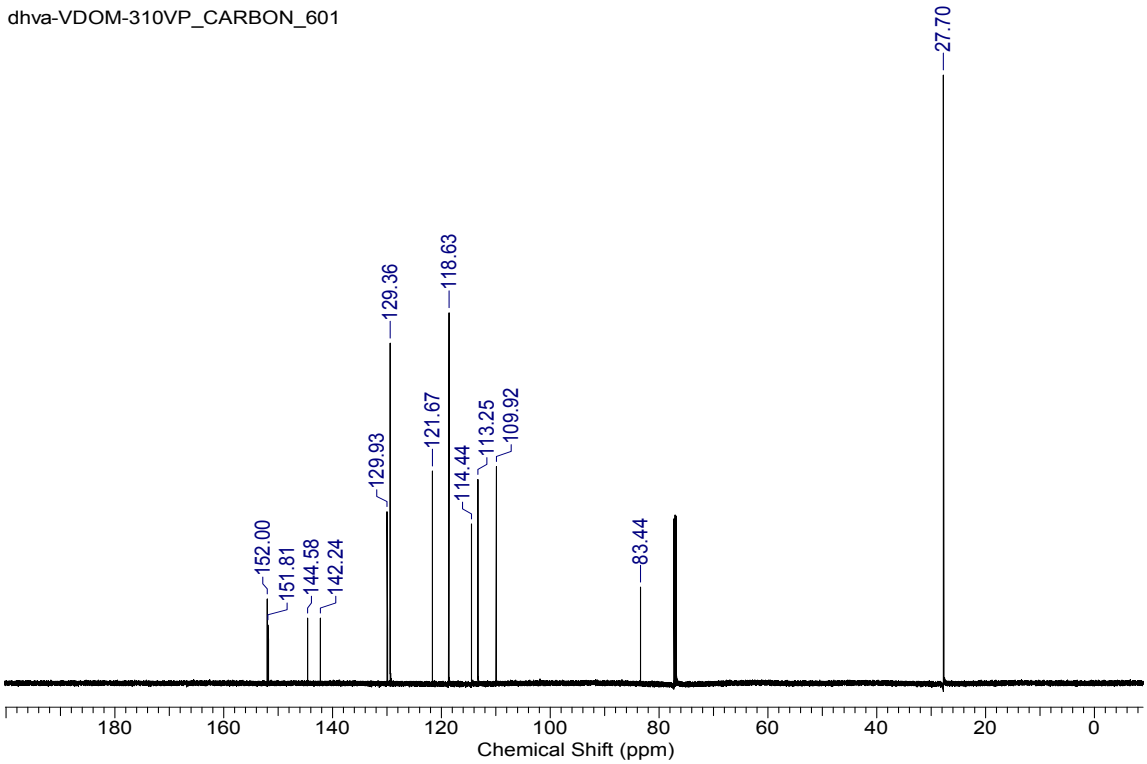
4-(Phenylamino)phenol (5g)



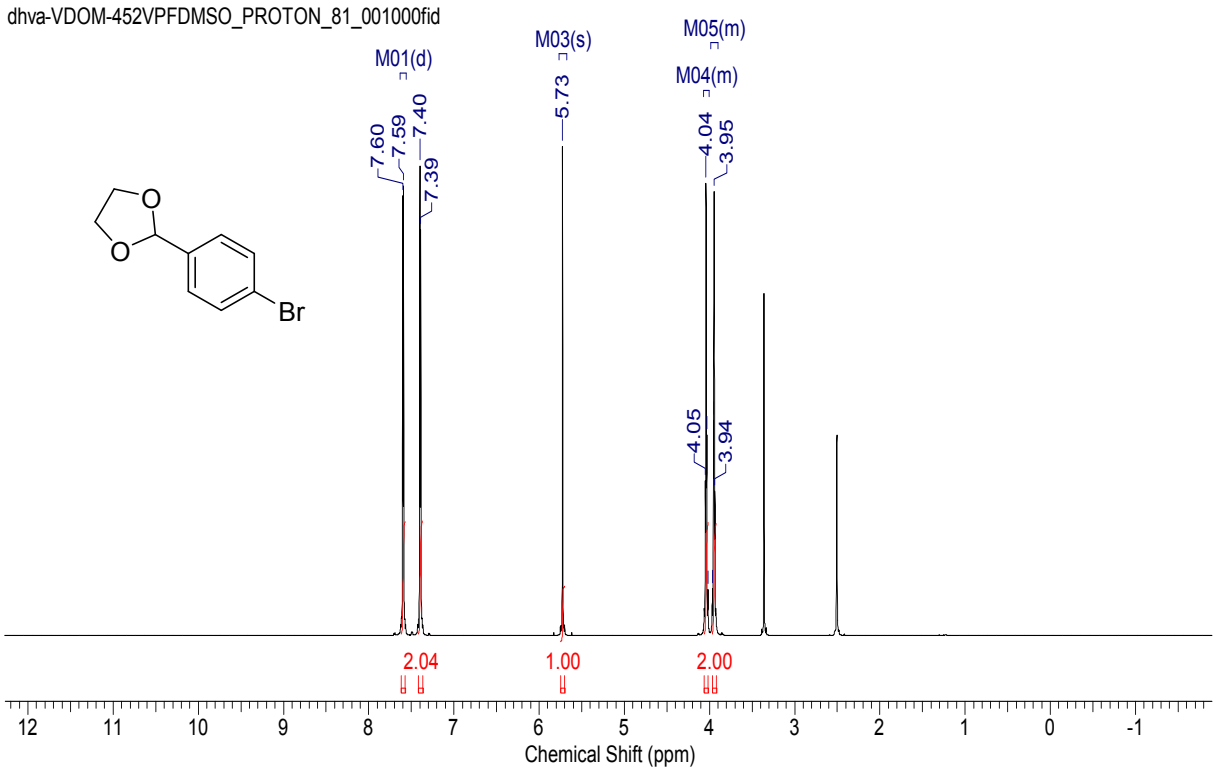


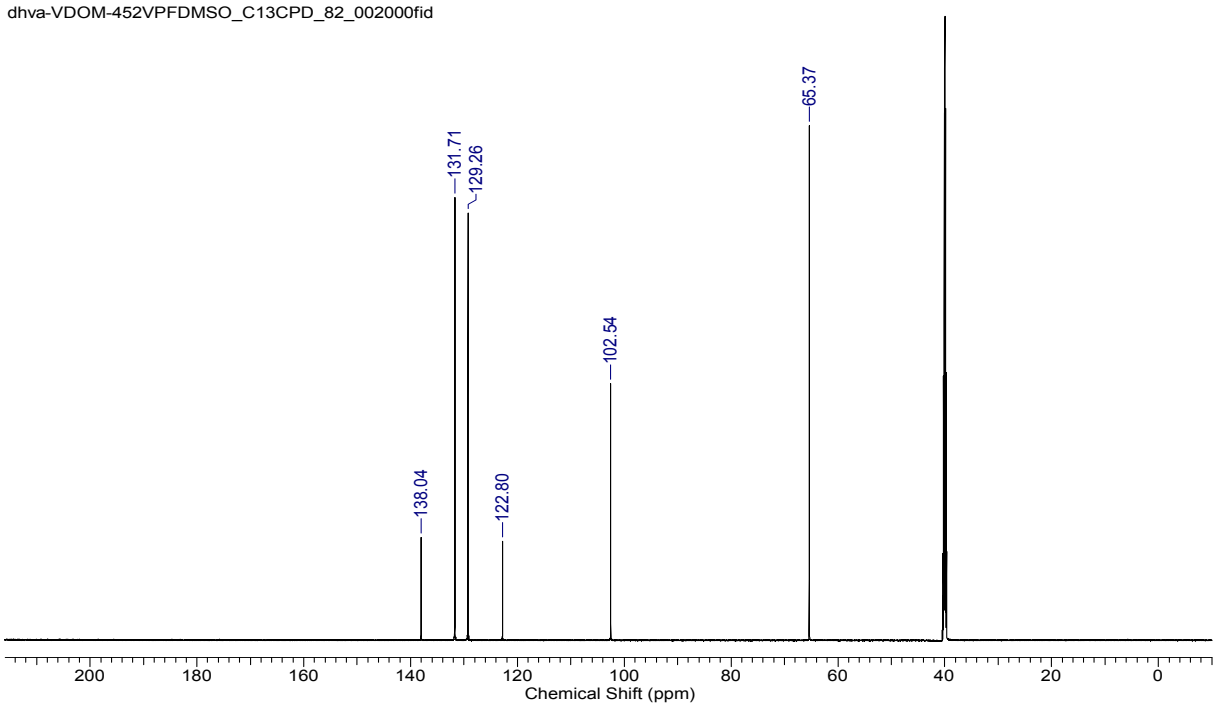
tert-Butyl(3-(phenylamino)phenyl)carbonate (5h)



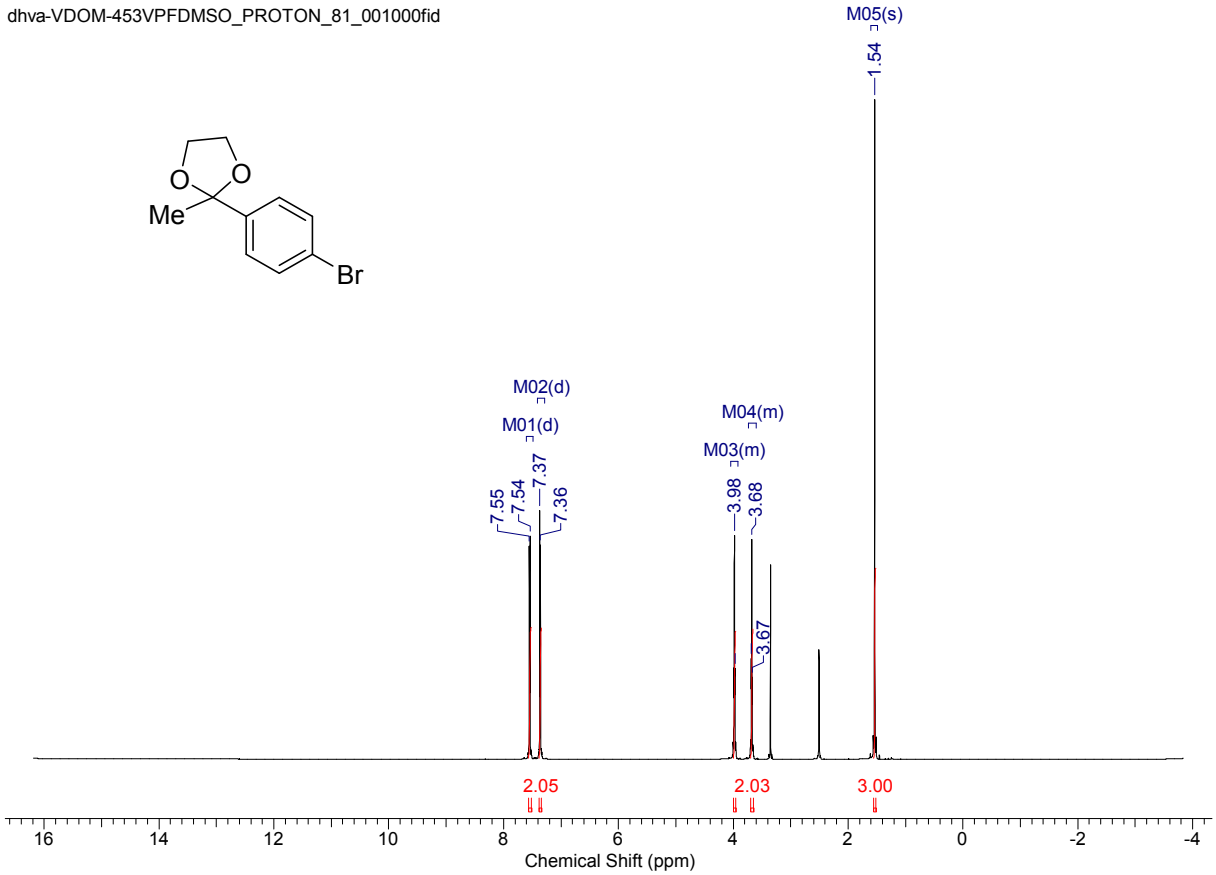


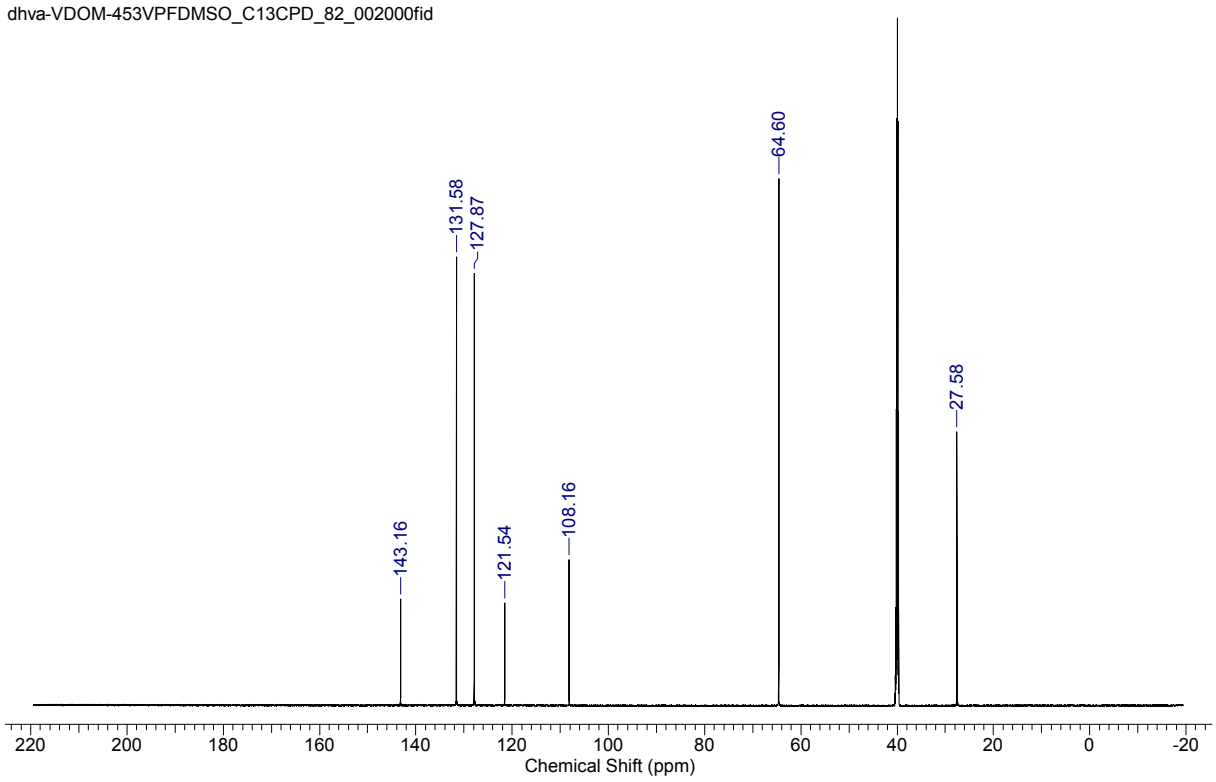
2-(4-Bromophenyl)-1,3-dioxolane (1i)



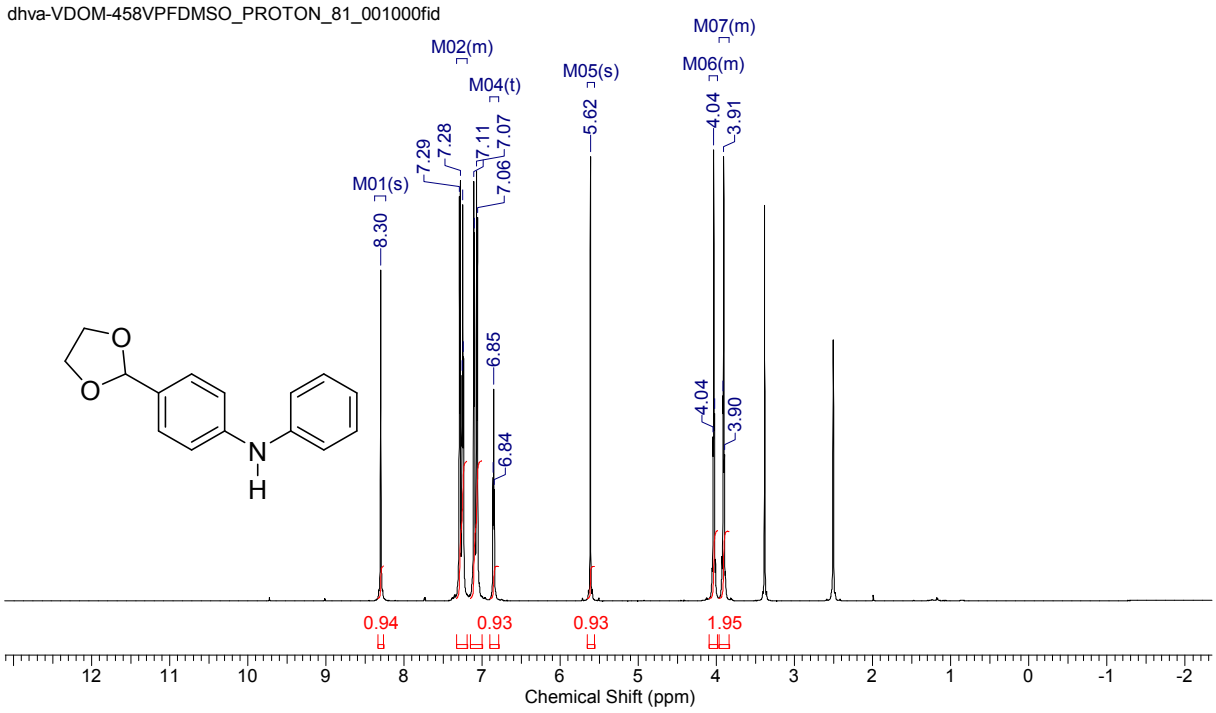


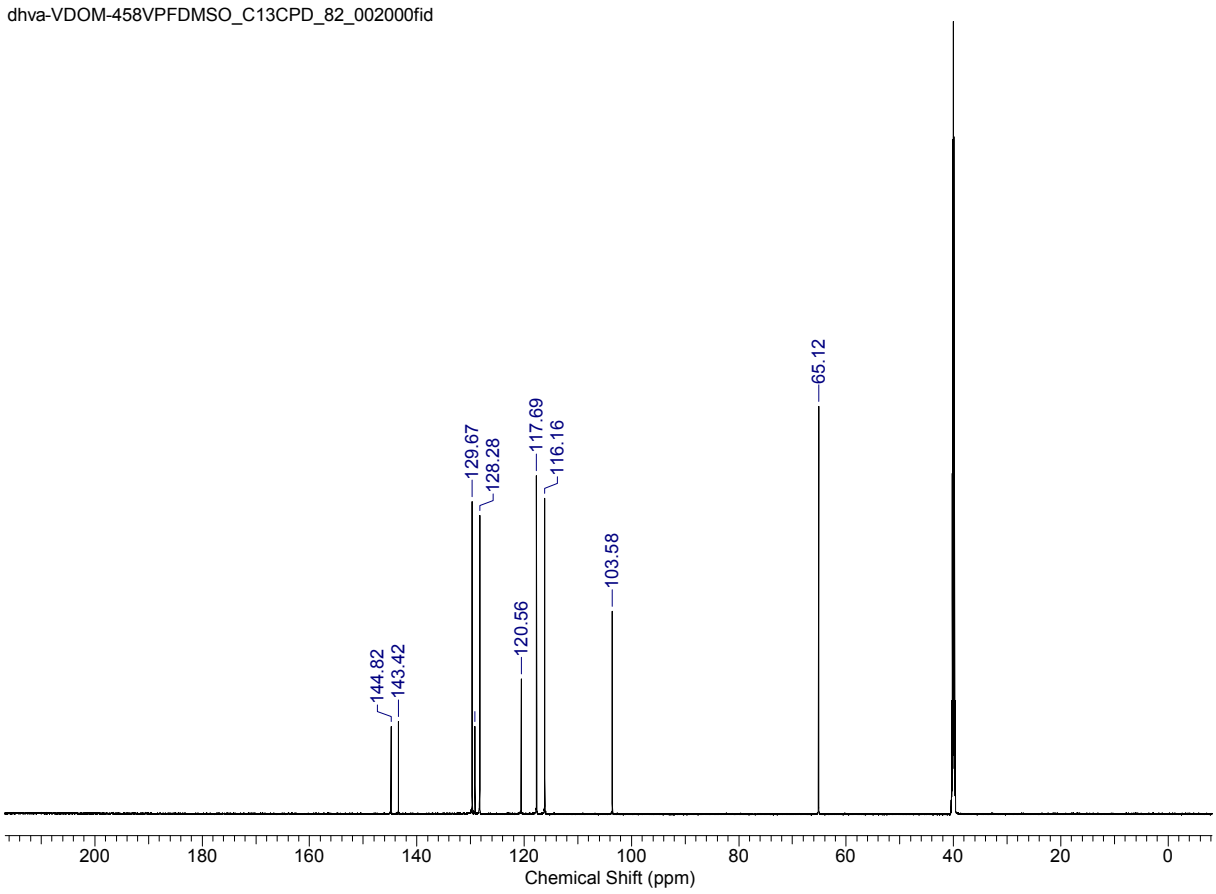
2-(4-Bromophenyl)-2-methyl-1,3-dioxolane (1j)



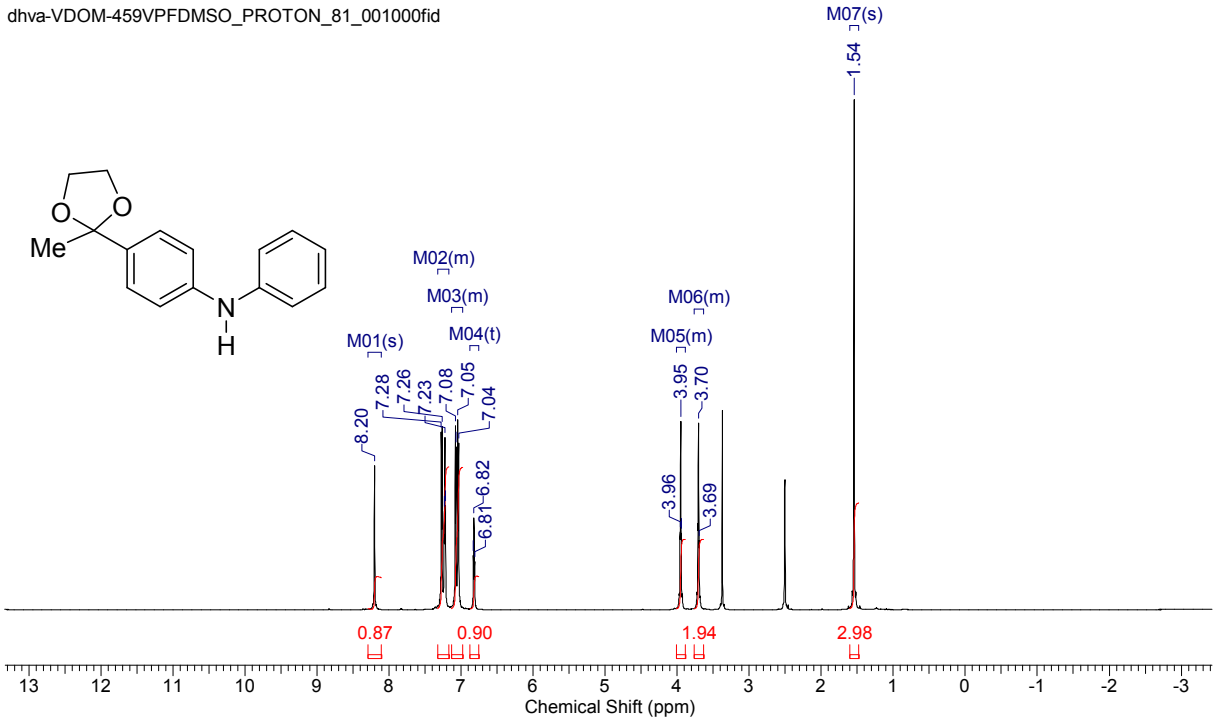


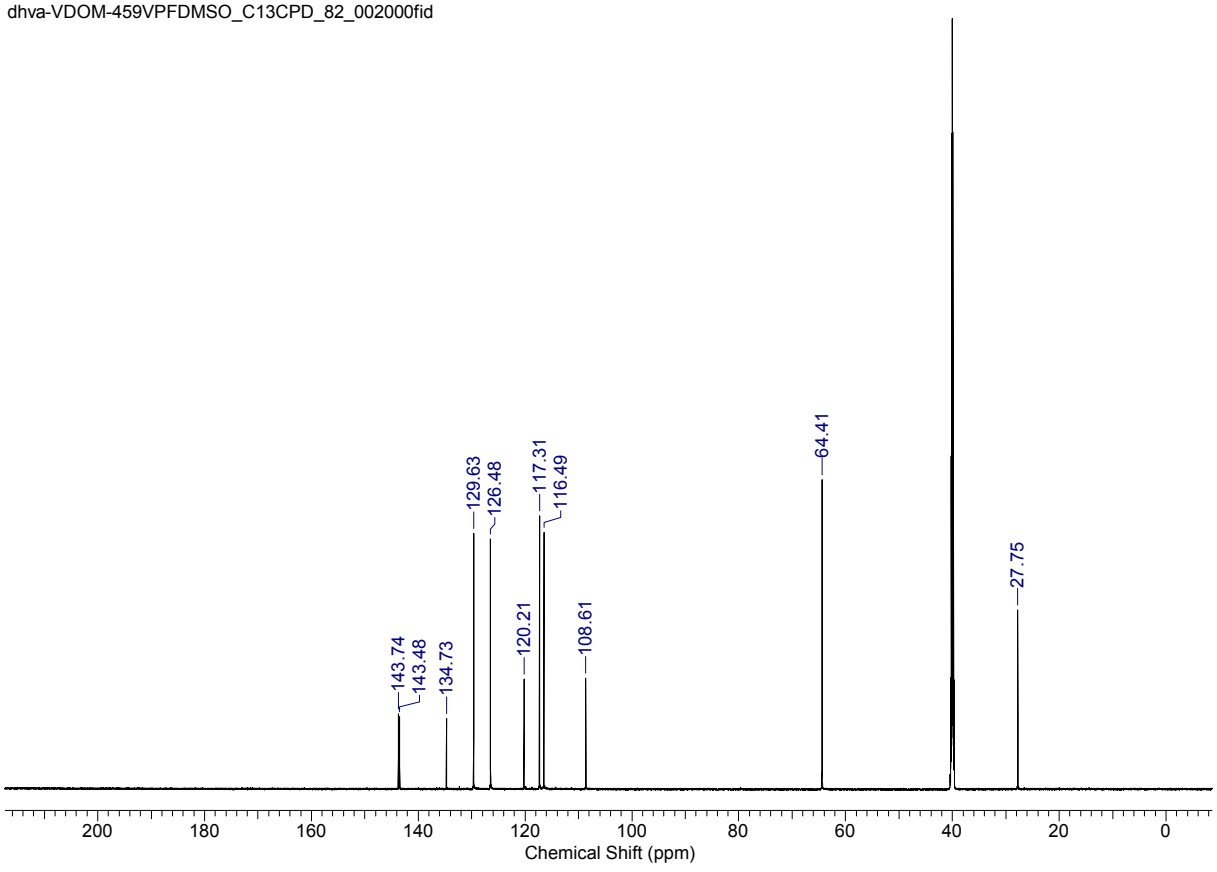
4-(1,3-Dioxolan-2-yl)-*N*-phenylaniline



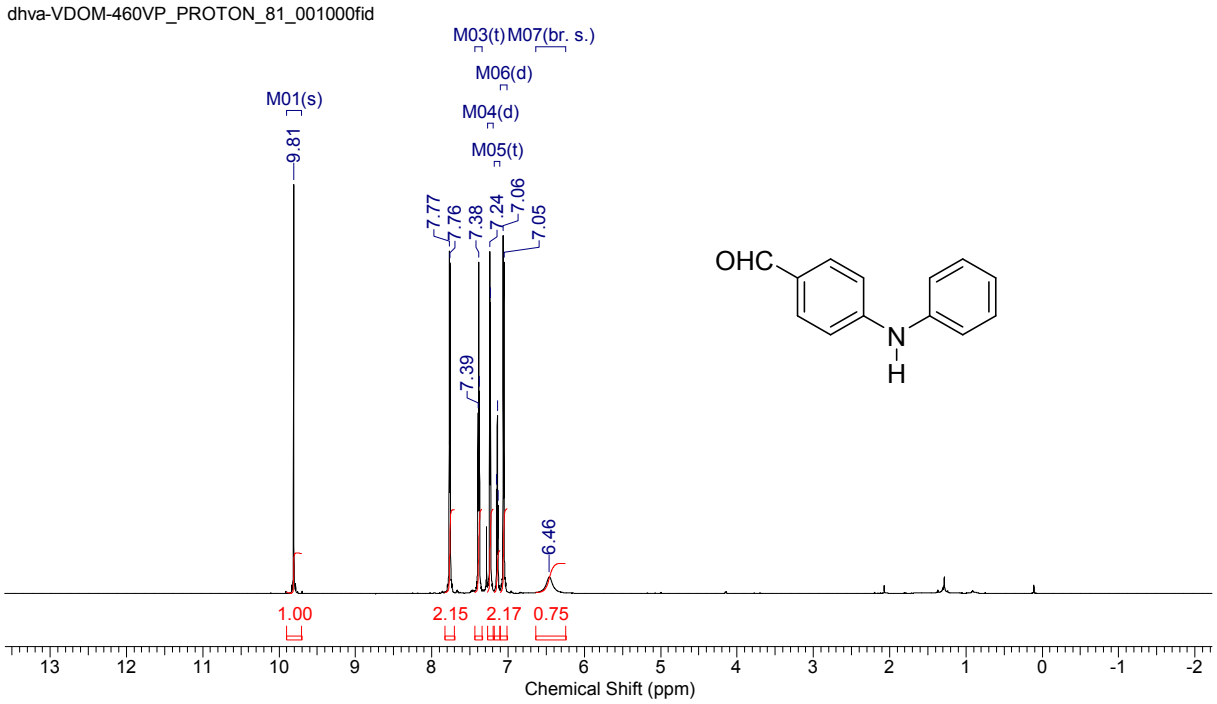


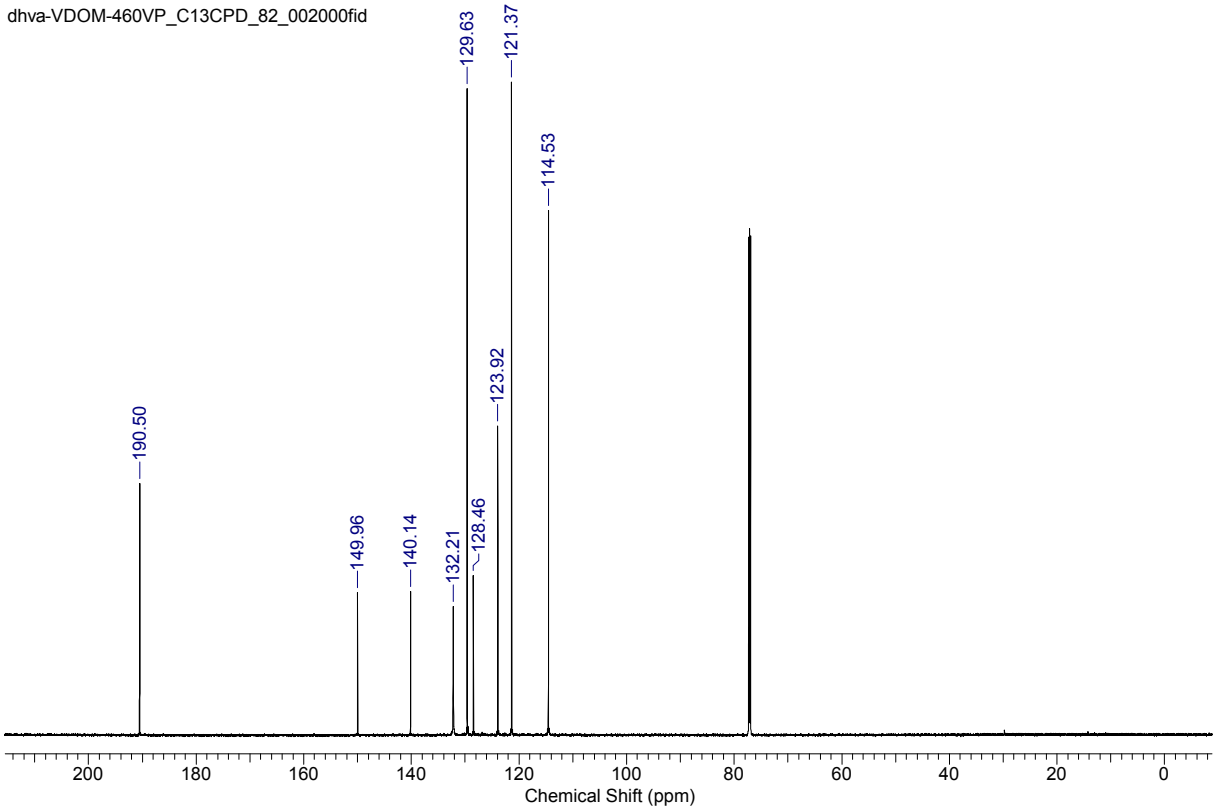
4-(2-Methyl-1,3-dioxolan-2-yl)-*N*-phenylaniline



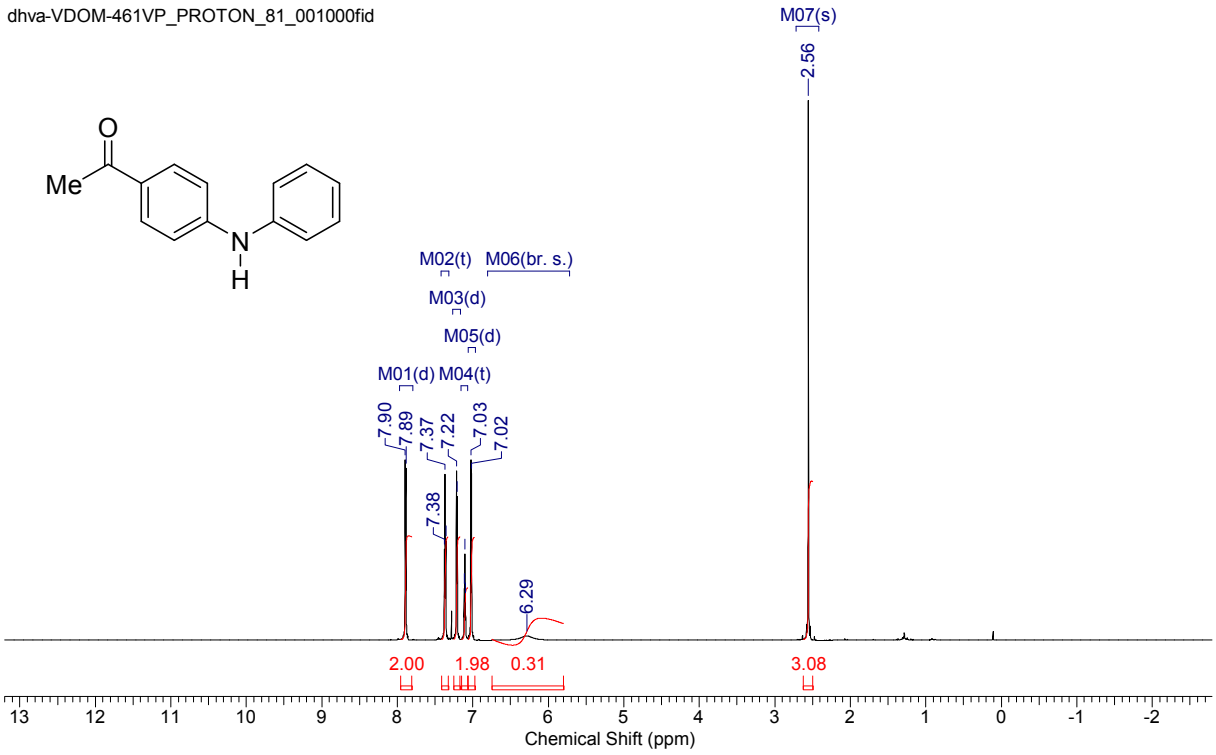


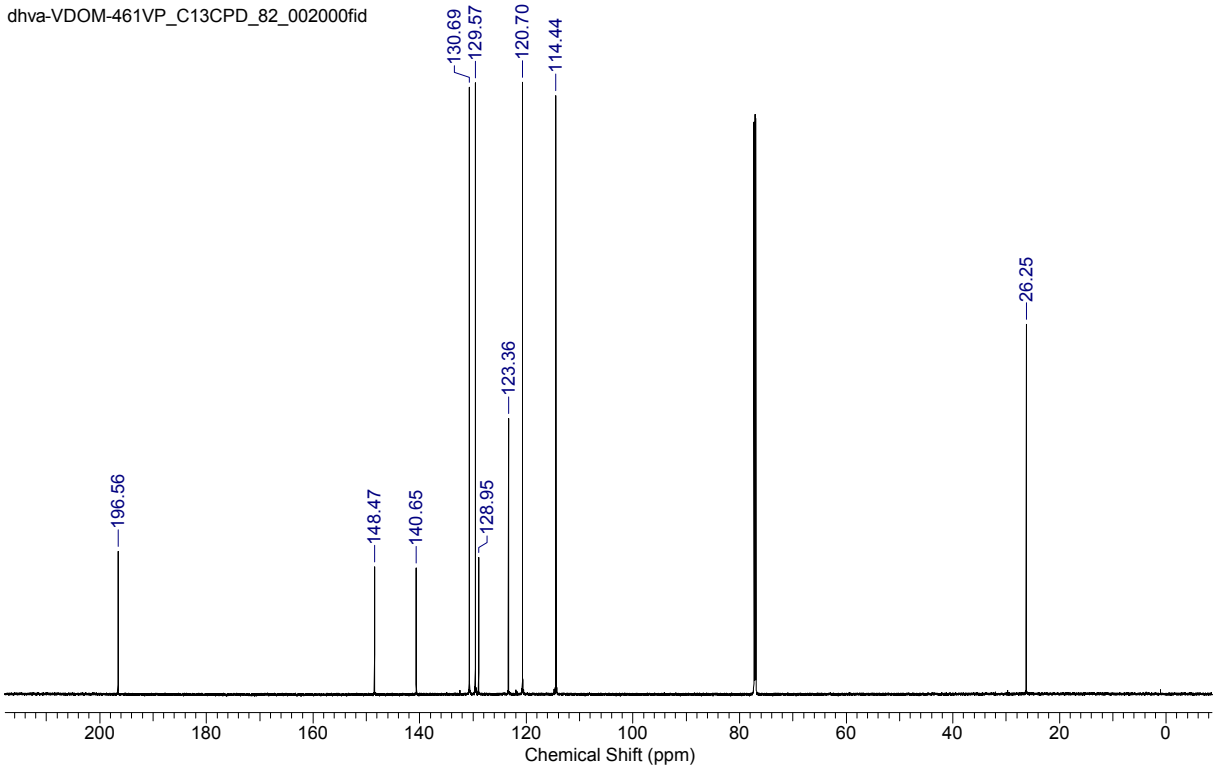
4-(Phenylamino)benzaldehyde (5i)



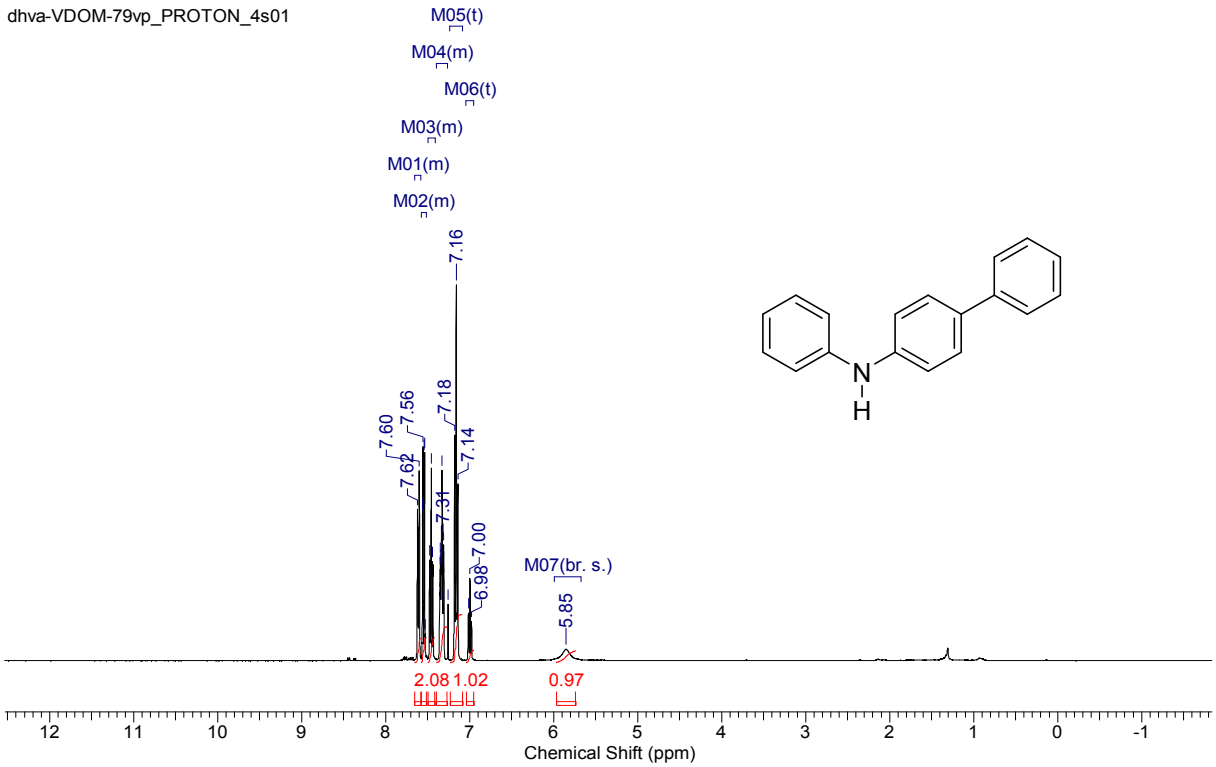


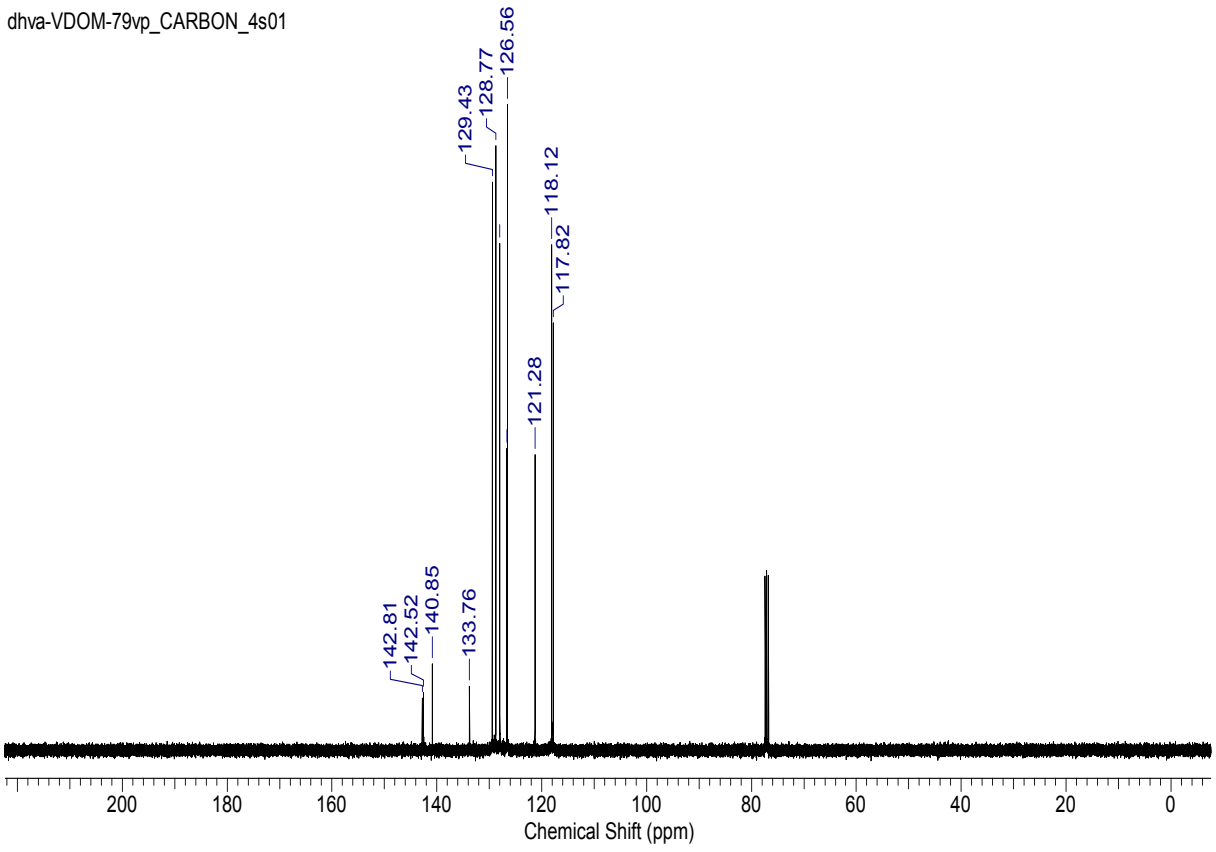
1-(4-(Phenylamino)phenyl)ethan-1-one (5j)



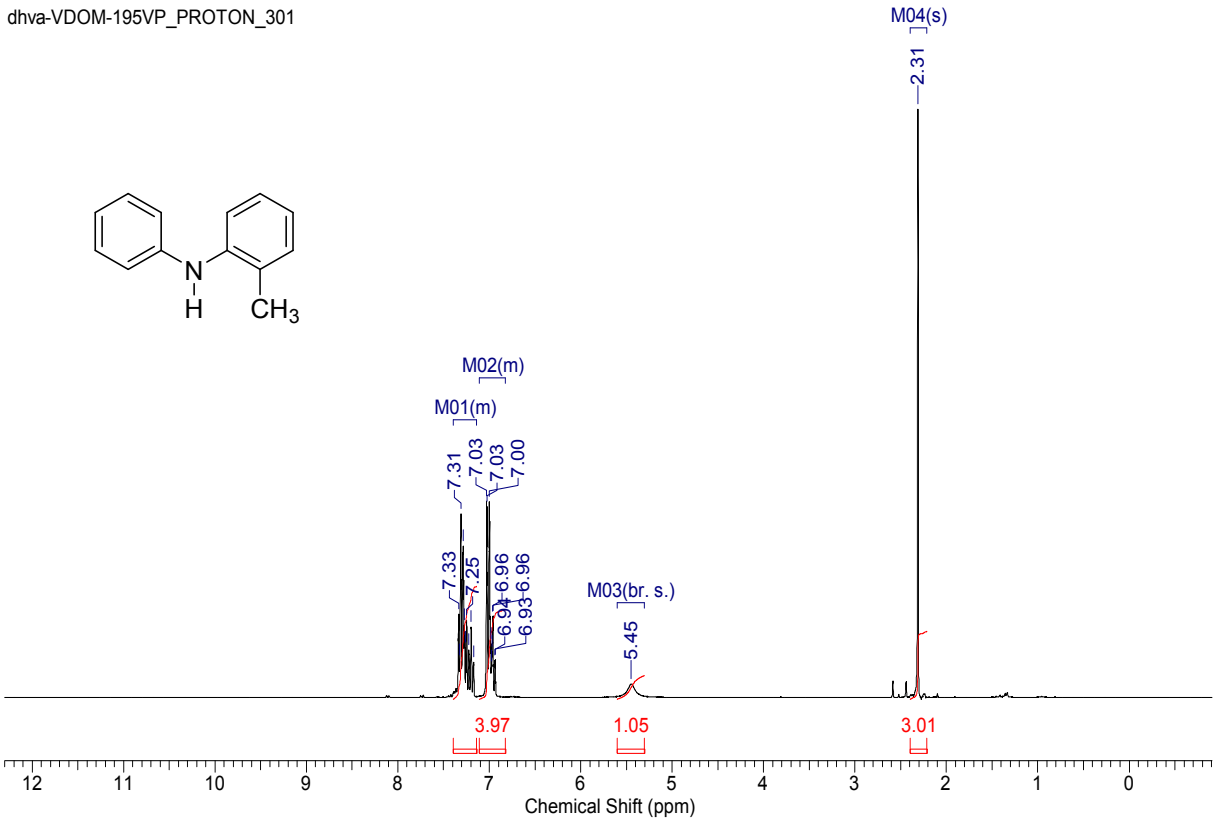


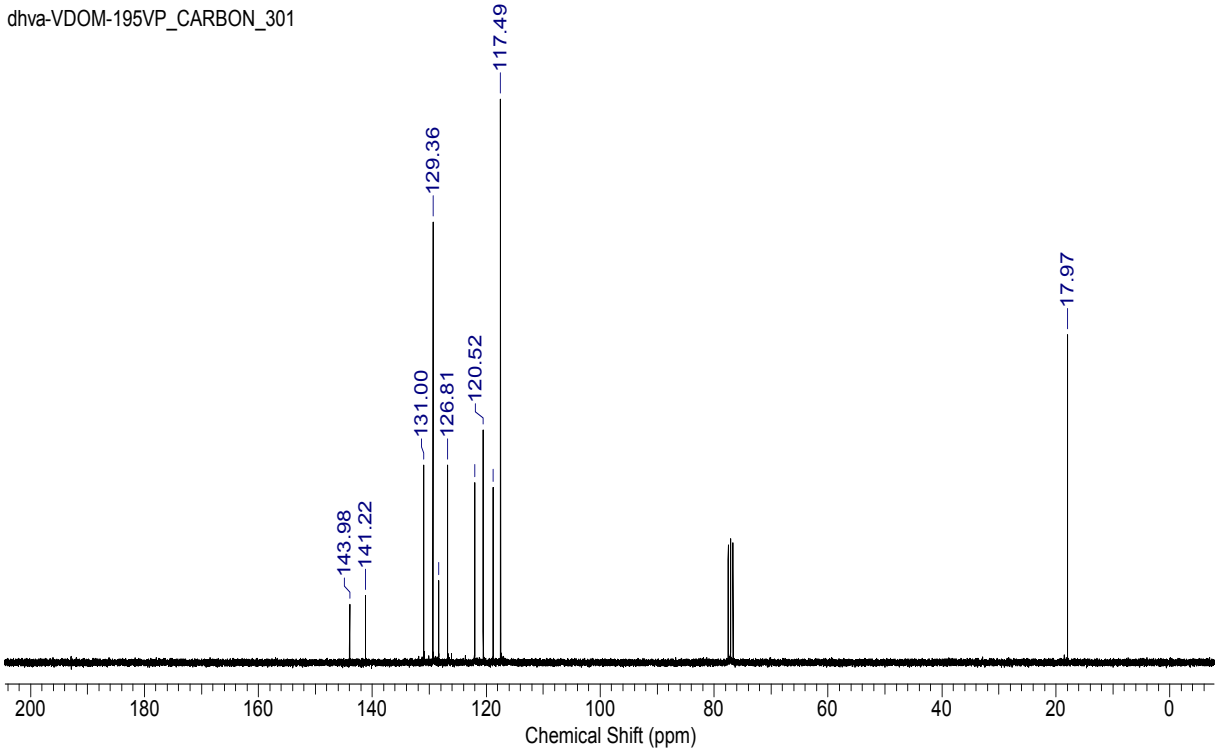
N-Phenyl-[1,1'-biphenyl]-4-amine (5k)



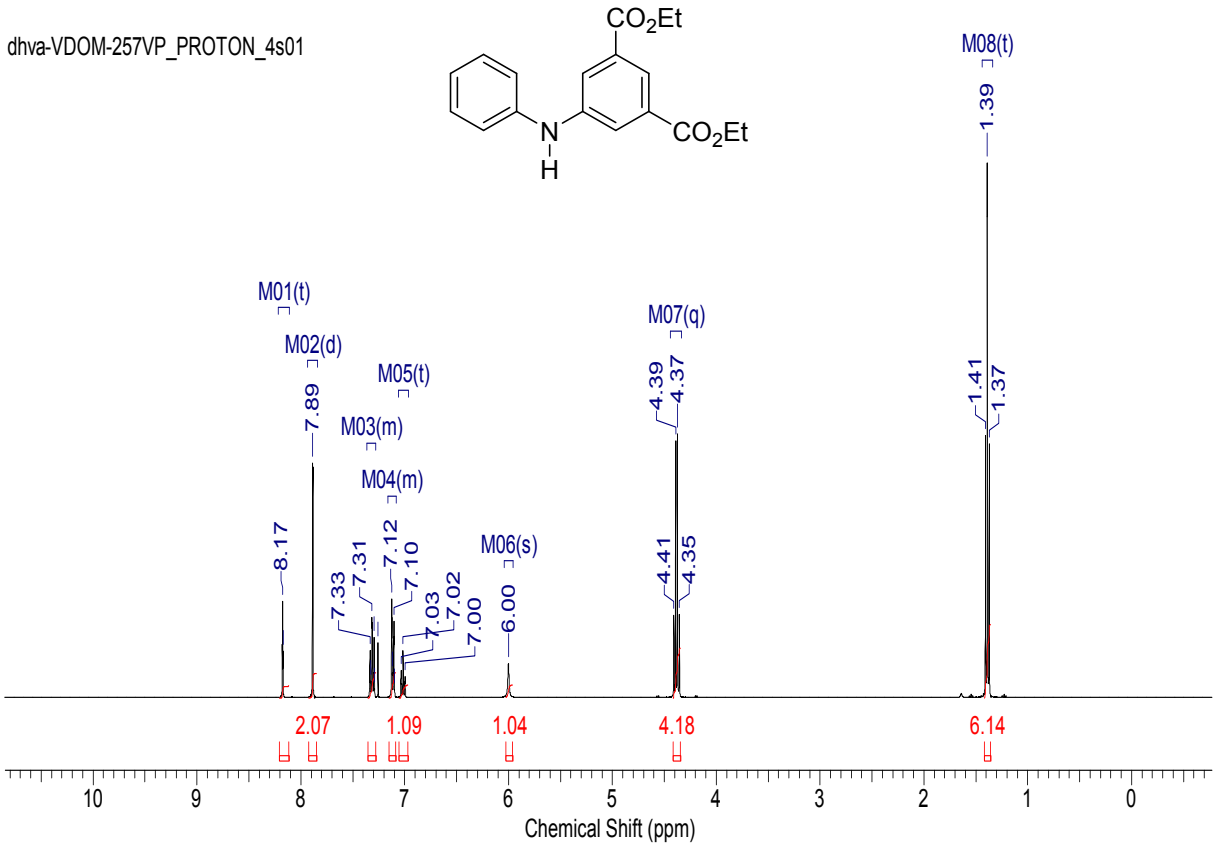


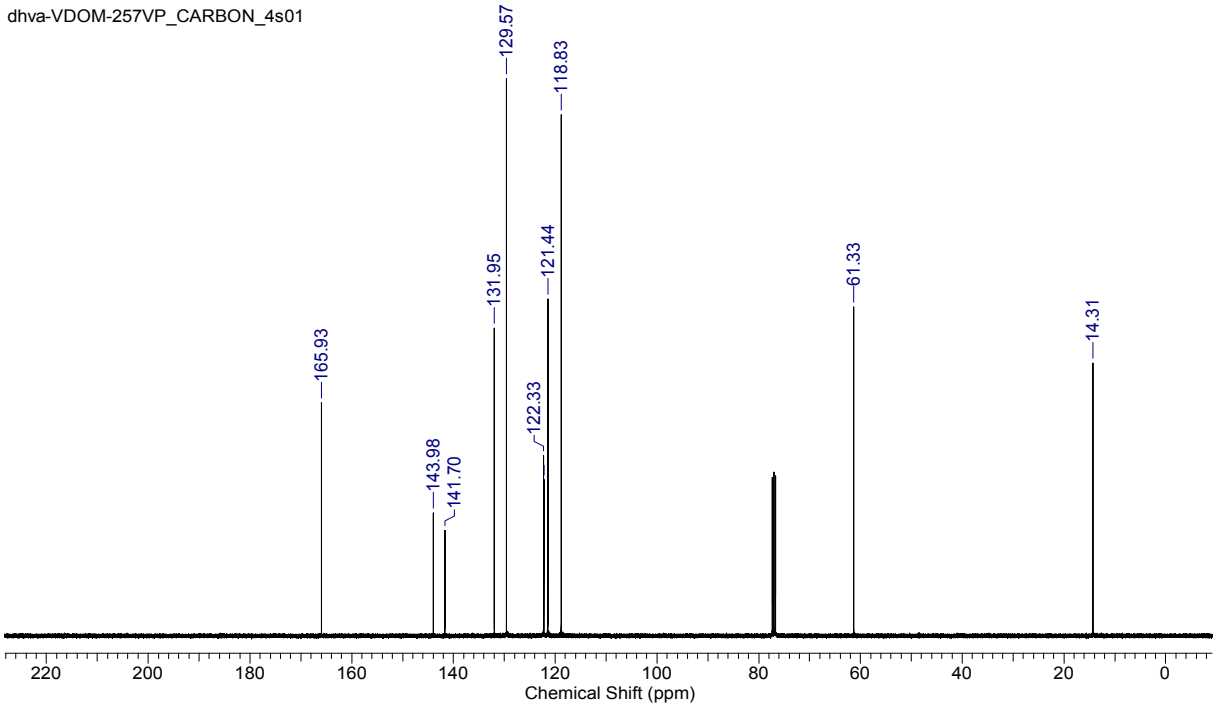
2-Methyl-*N*-phenylaniline (5l)





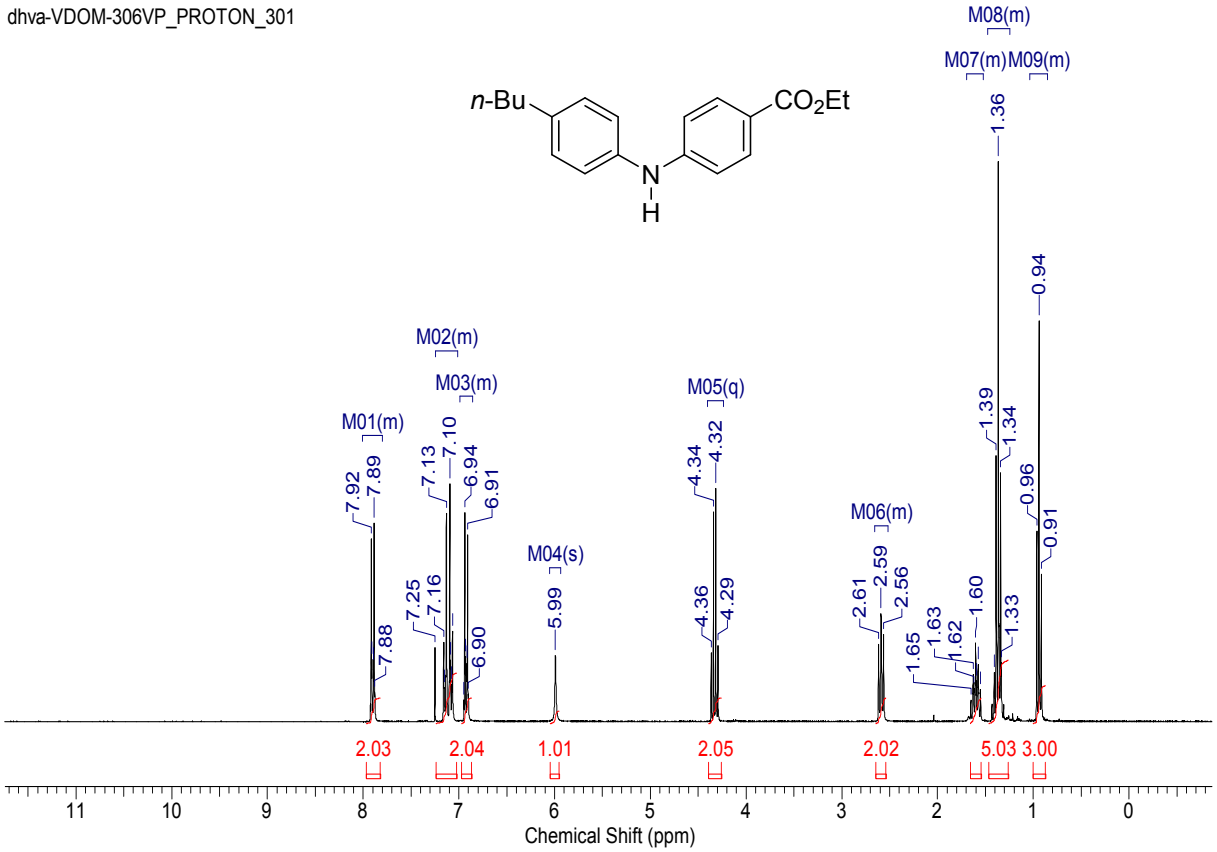
Diethyl-5-(phenylamino)isophthalate (5m)



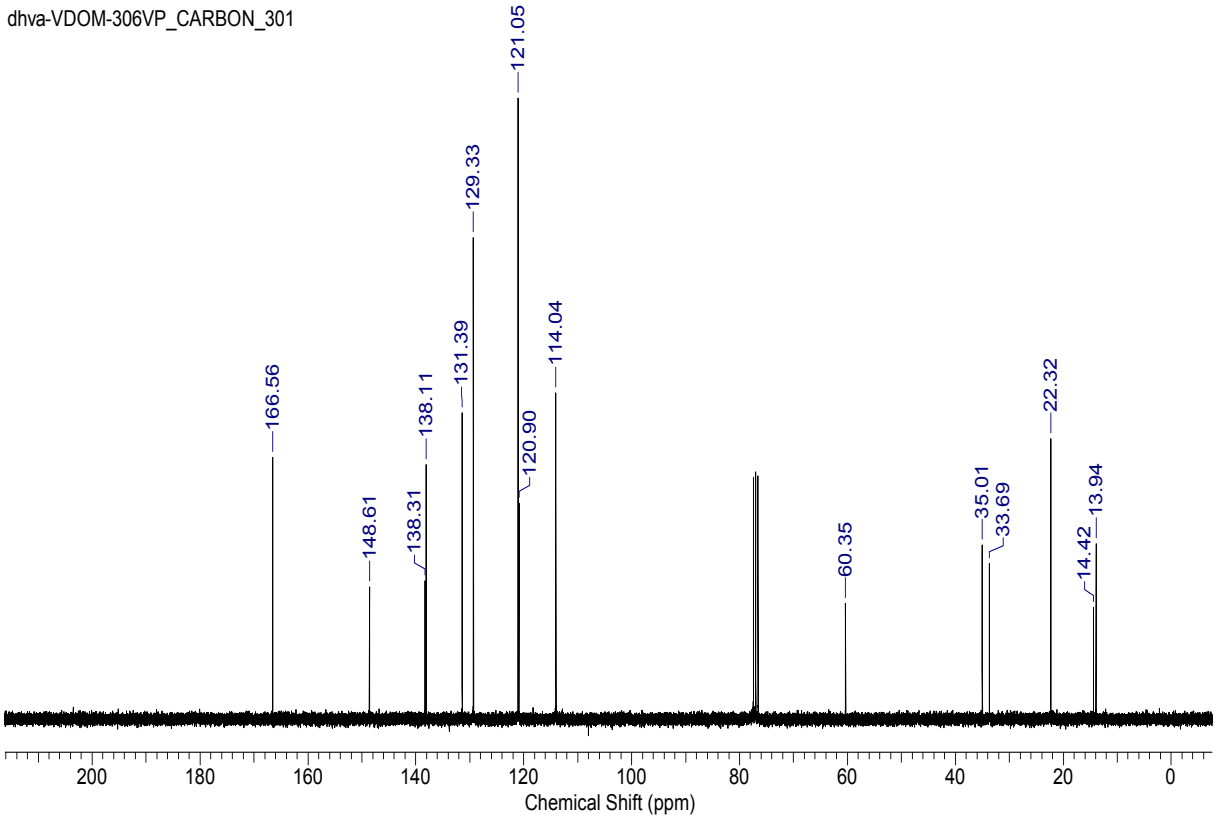


Ethyl-4-((4-butylphenyl)amino)benzoate (5n)

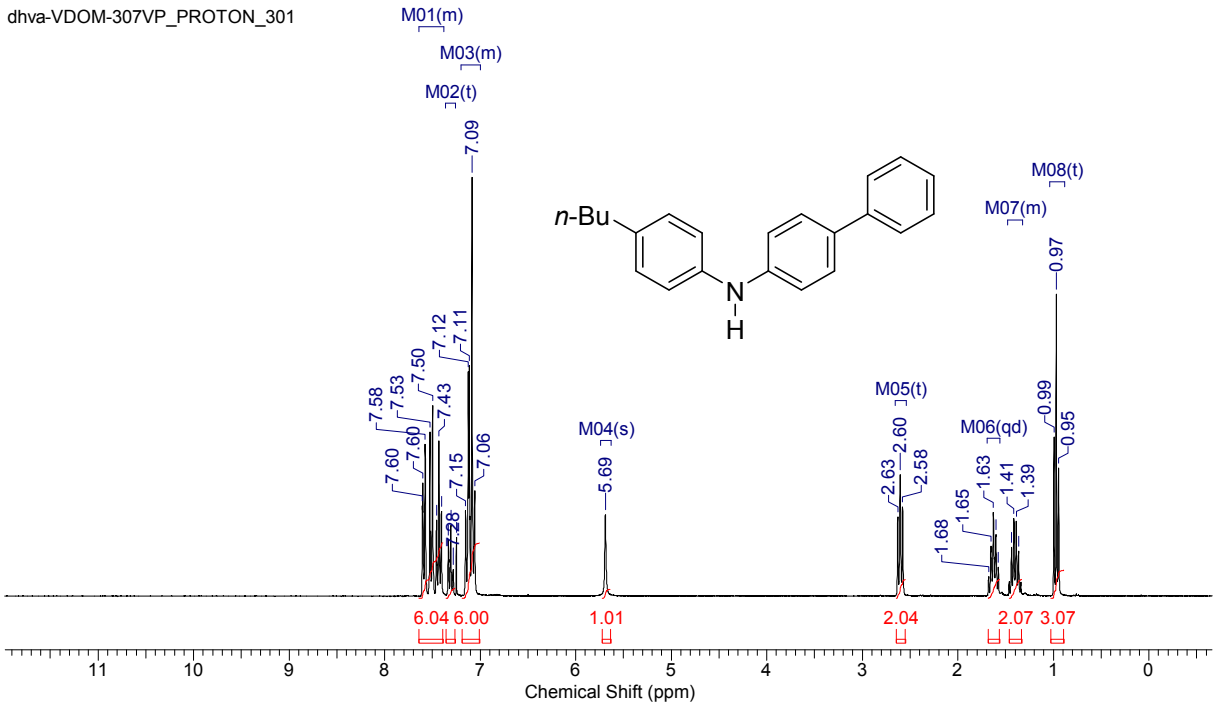
dhva-VDOM-306VP_PROTON_301

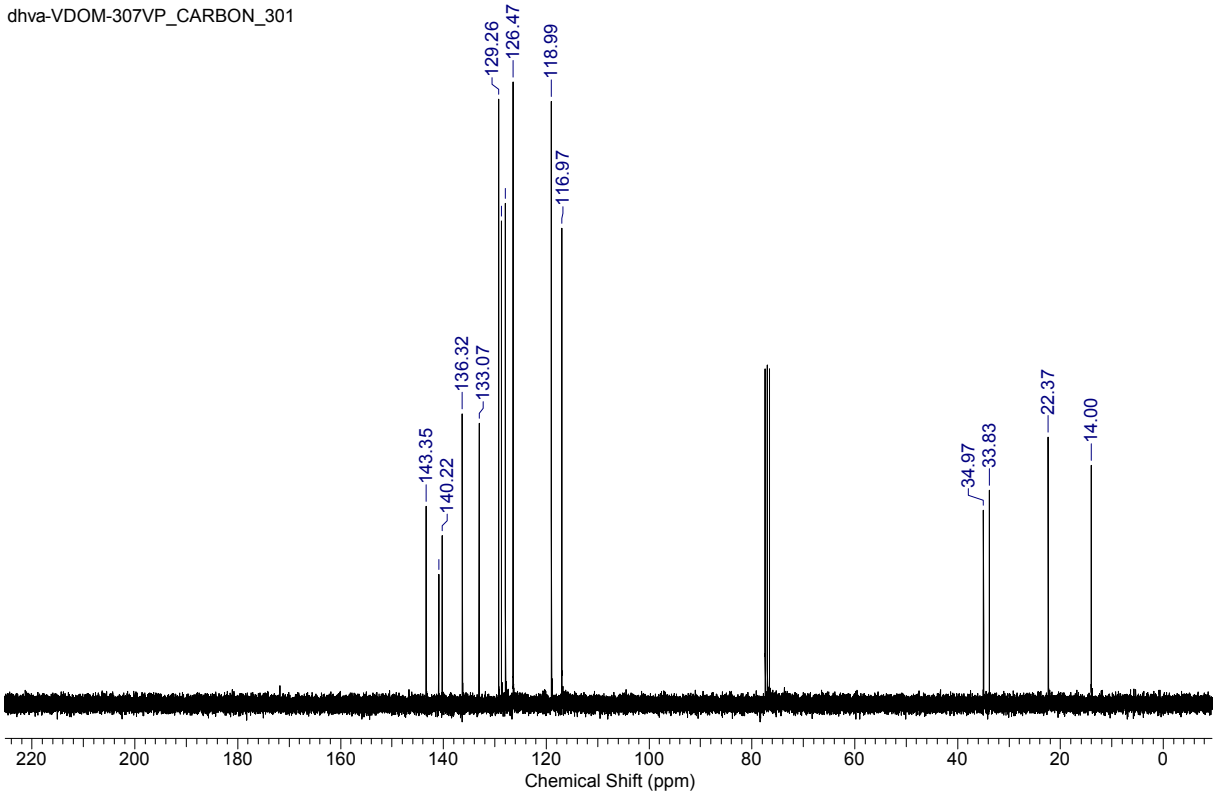


dhva-VDOM-306VP_CARBON_301

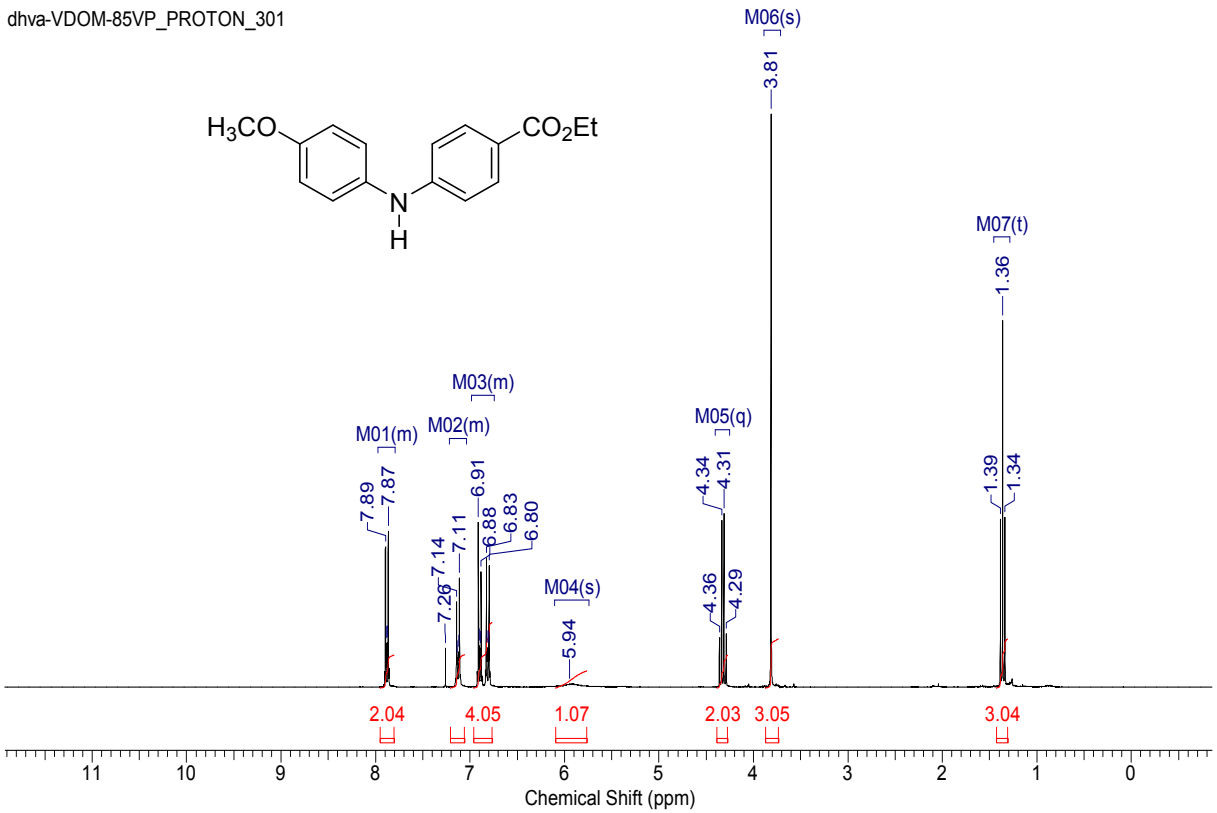


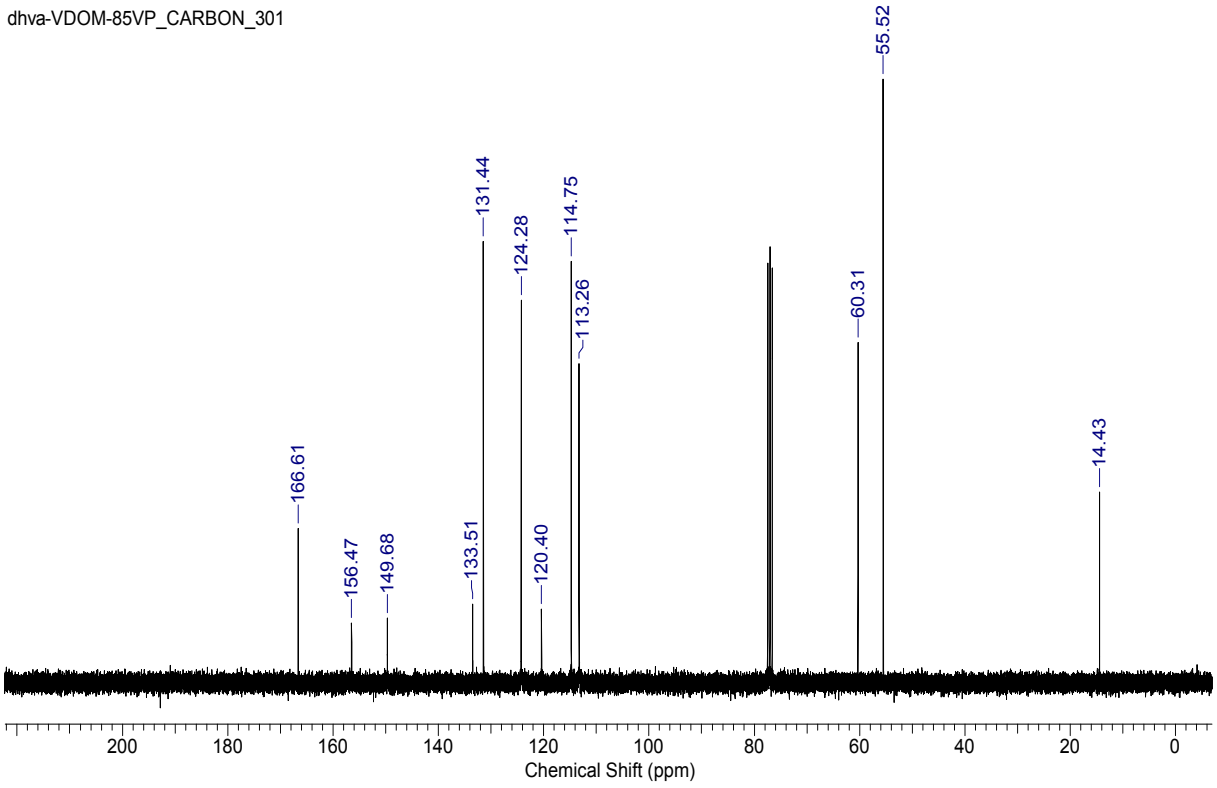
N-(4-Butylphenyl)-[1,1'-biphenyl]-4-amine (5o)



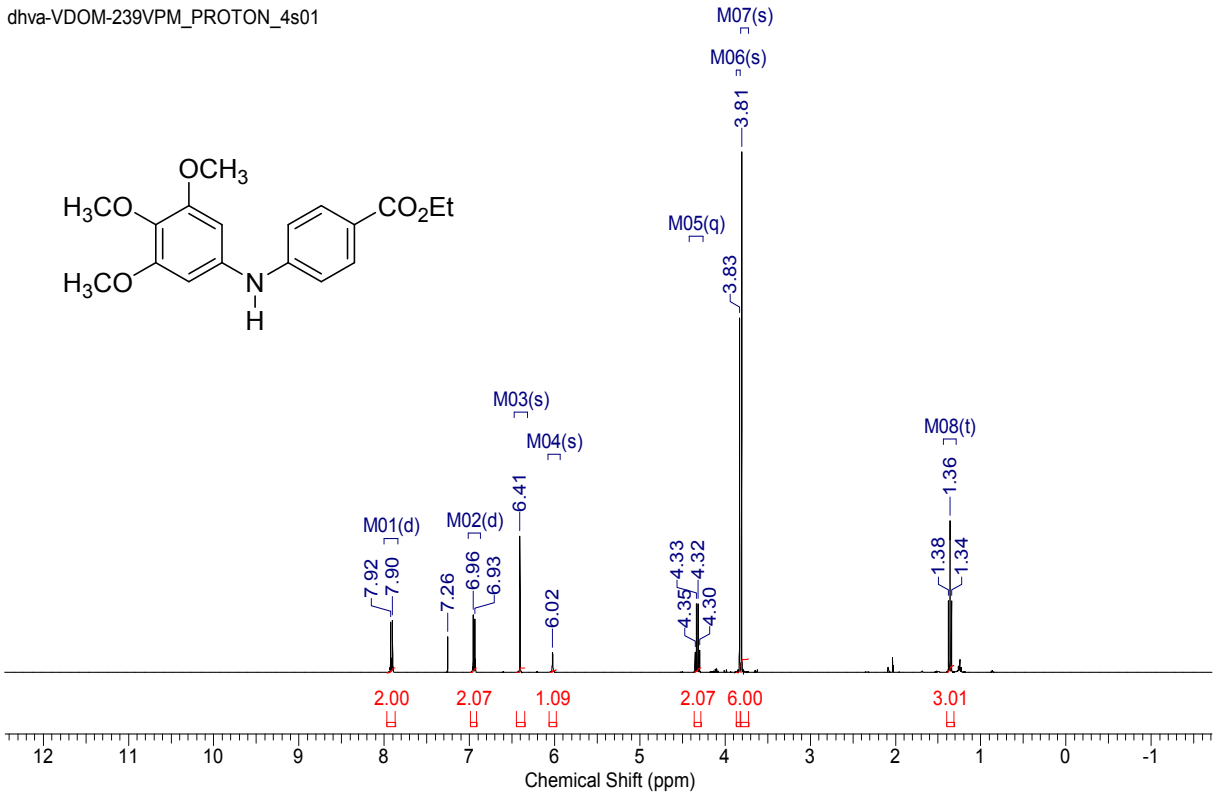


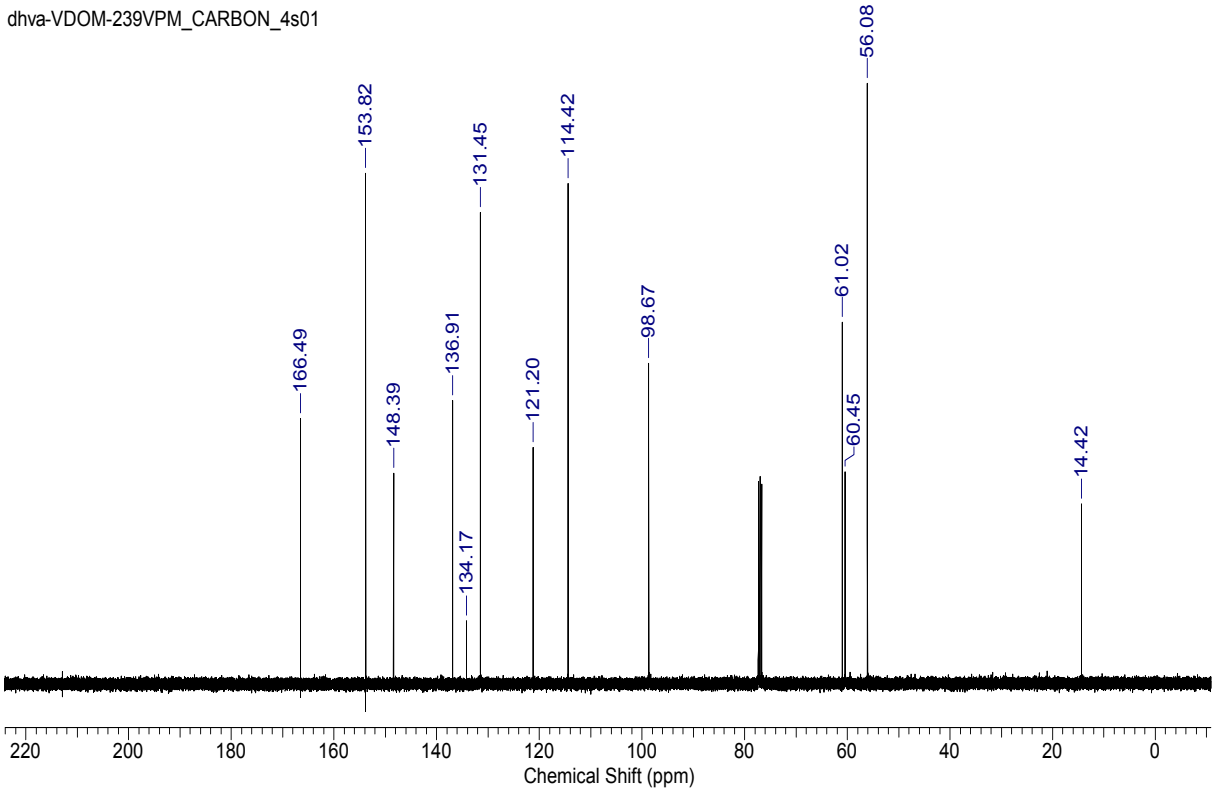
Ethyl-4-((4-methoxyphenyl)amino)benzoate (5p)



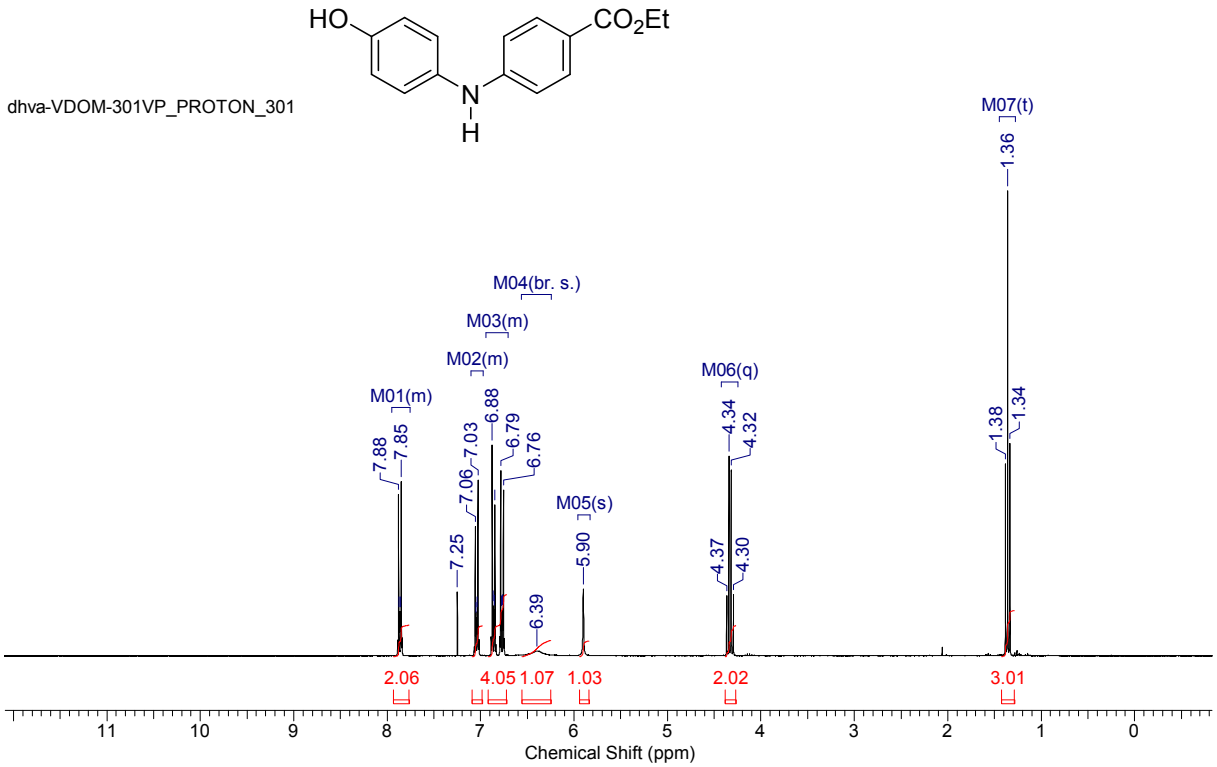


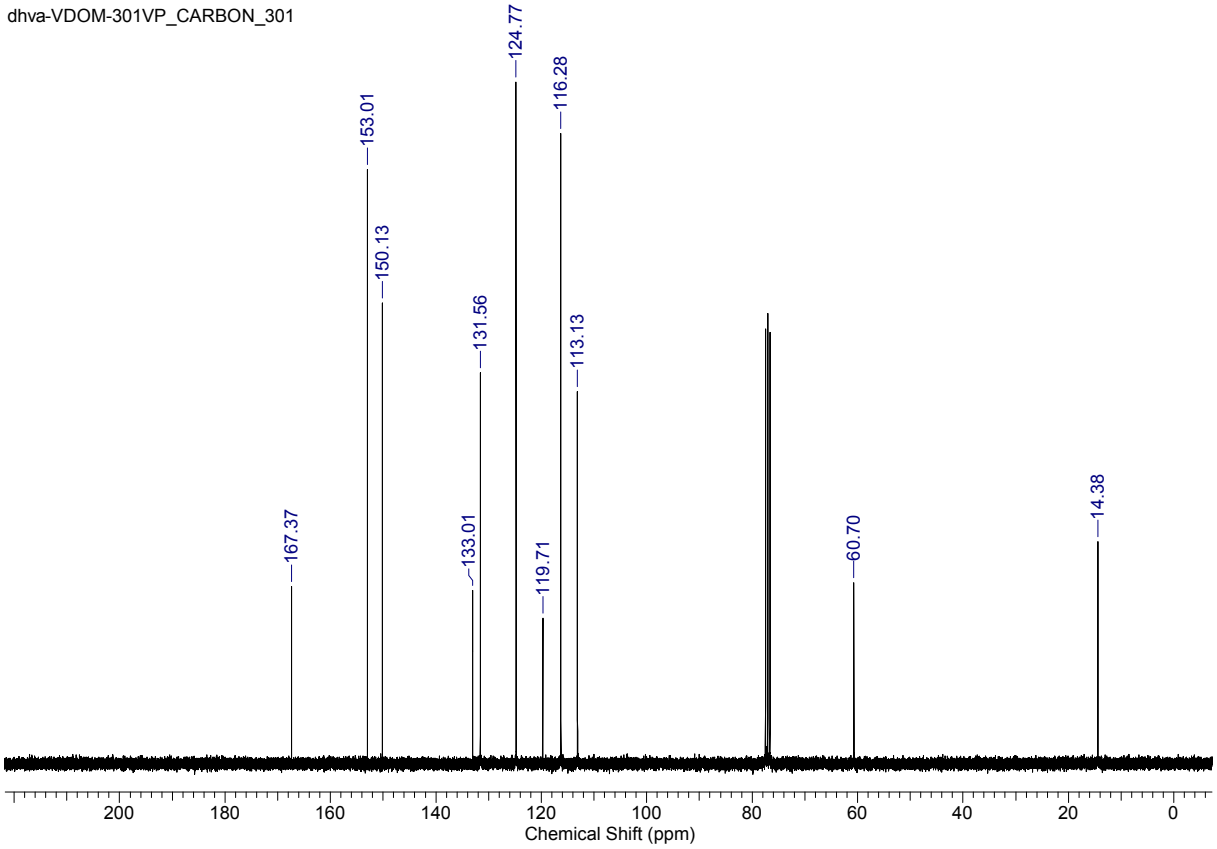
Ethyl-4-((3,4,5-trimethoxyphenyl)amino)benzoate (5q)



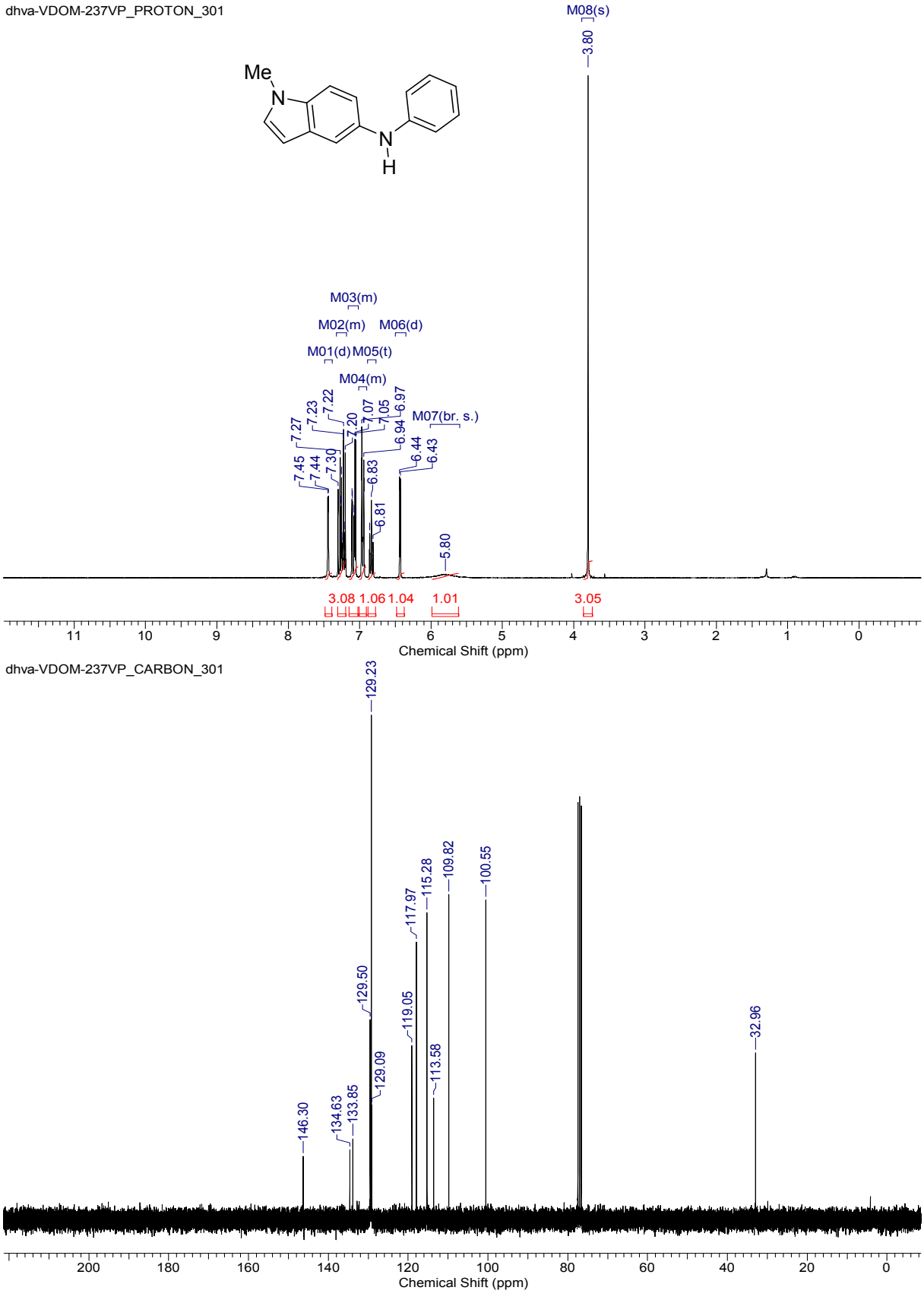


Ethyl-4-((4-hydroxyphenyl)amino)benzoate (5r)

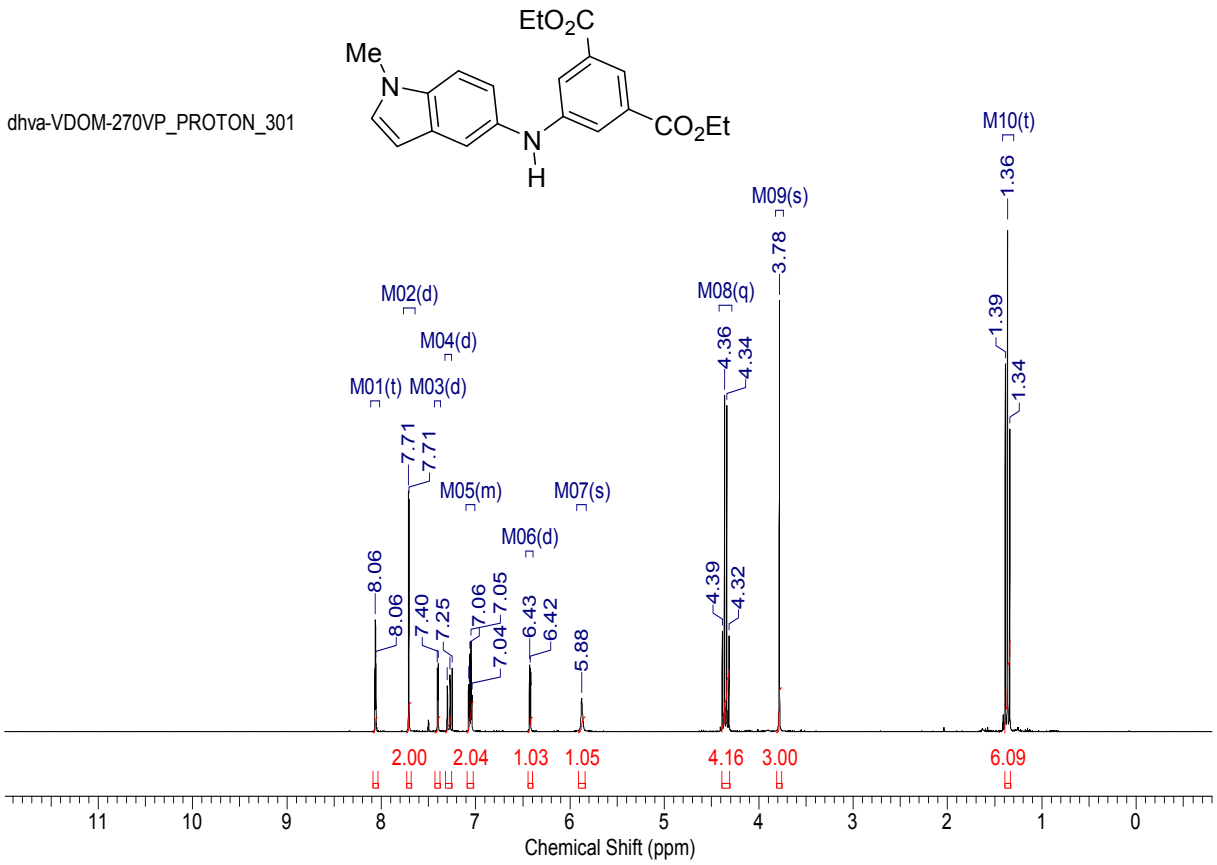


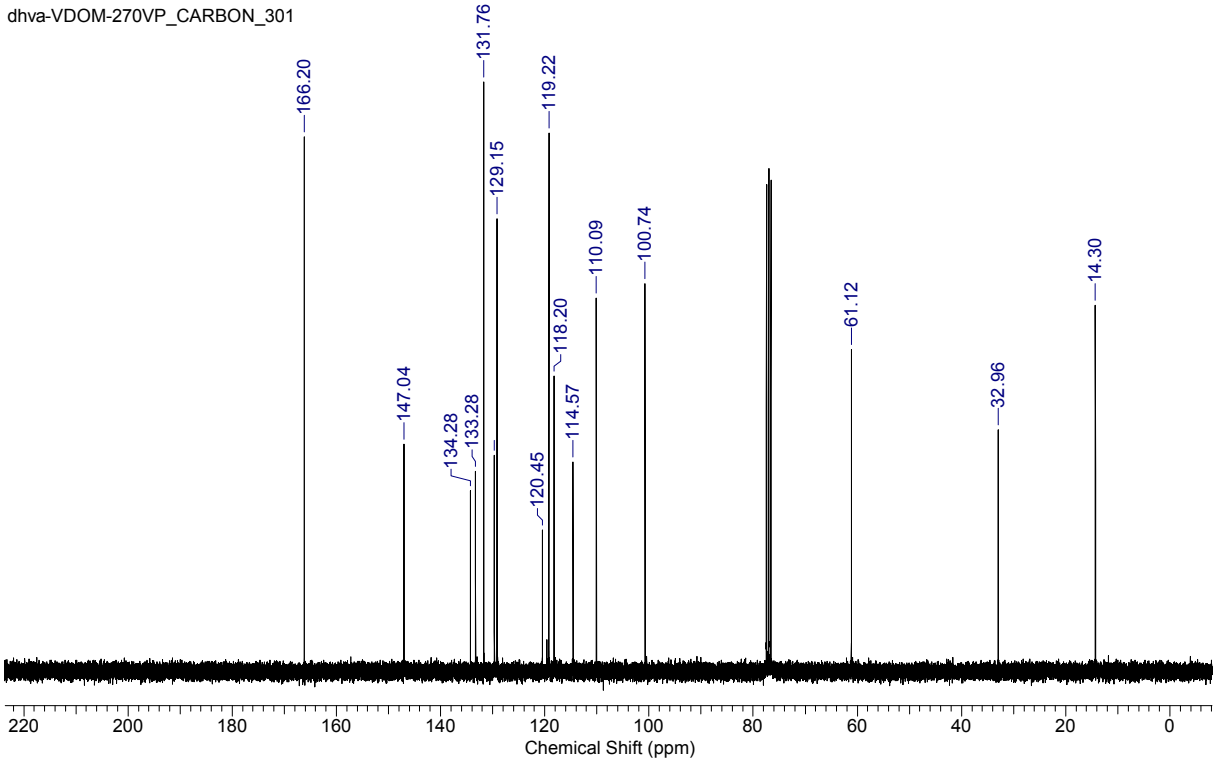


1-Methyl-*N*-phenyl-1*H*-indol-5-amine (5s)

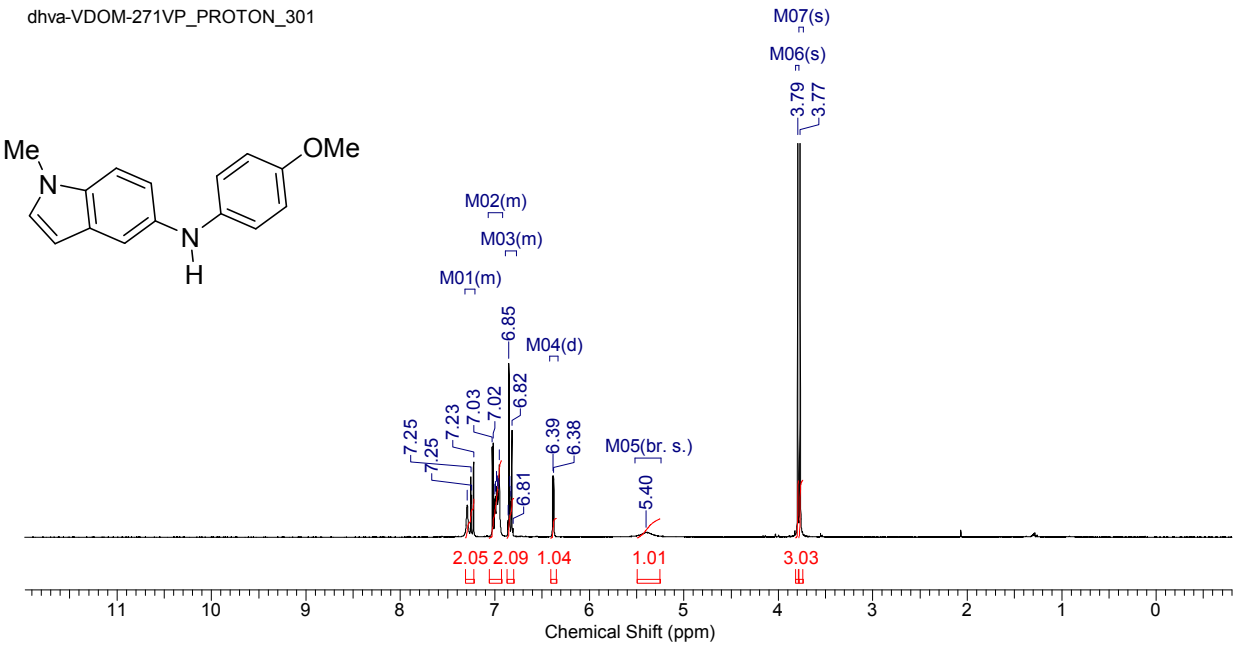


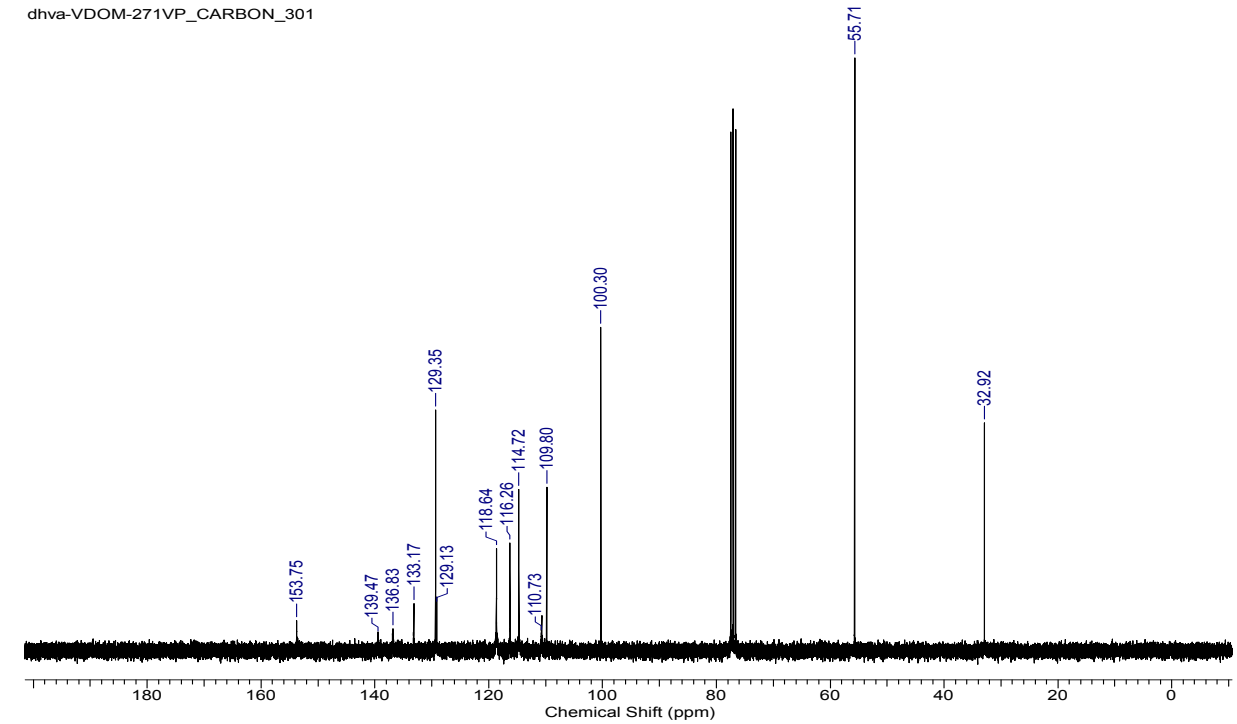
Diethyl-5-((1-methyl-1*H*-indol-5-yl)amino)isophthalate (5t)



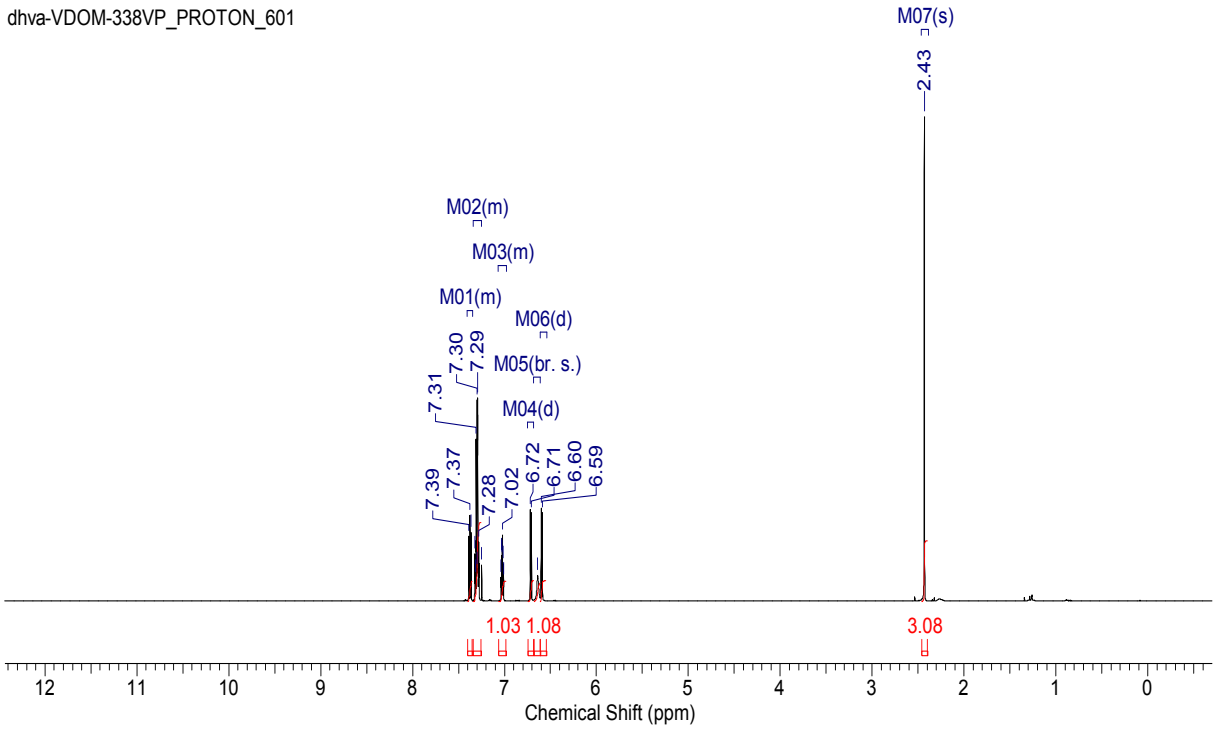


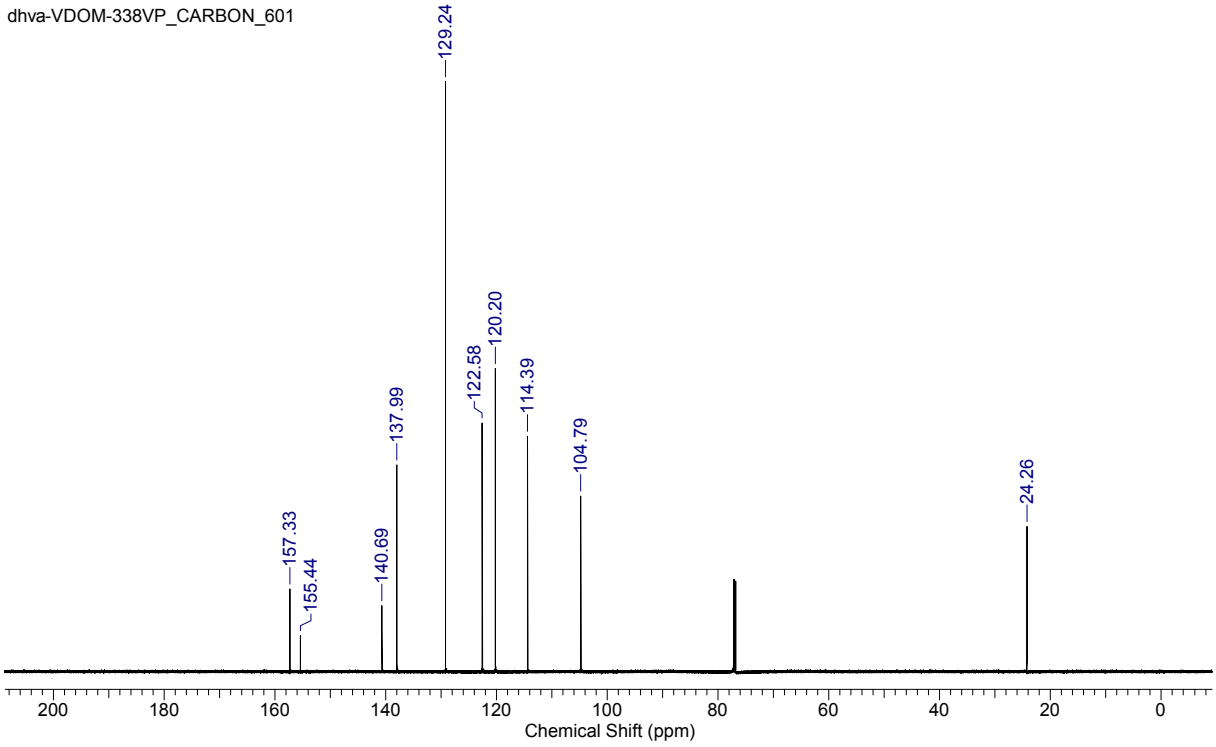
N-(4-Methoxyphenyl)-1-methyl-1*H*-indol-5-amine (5u)



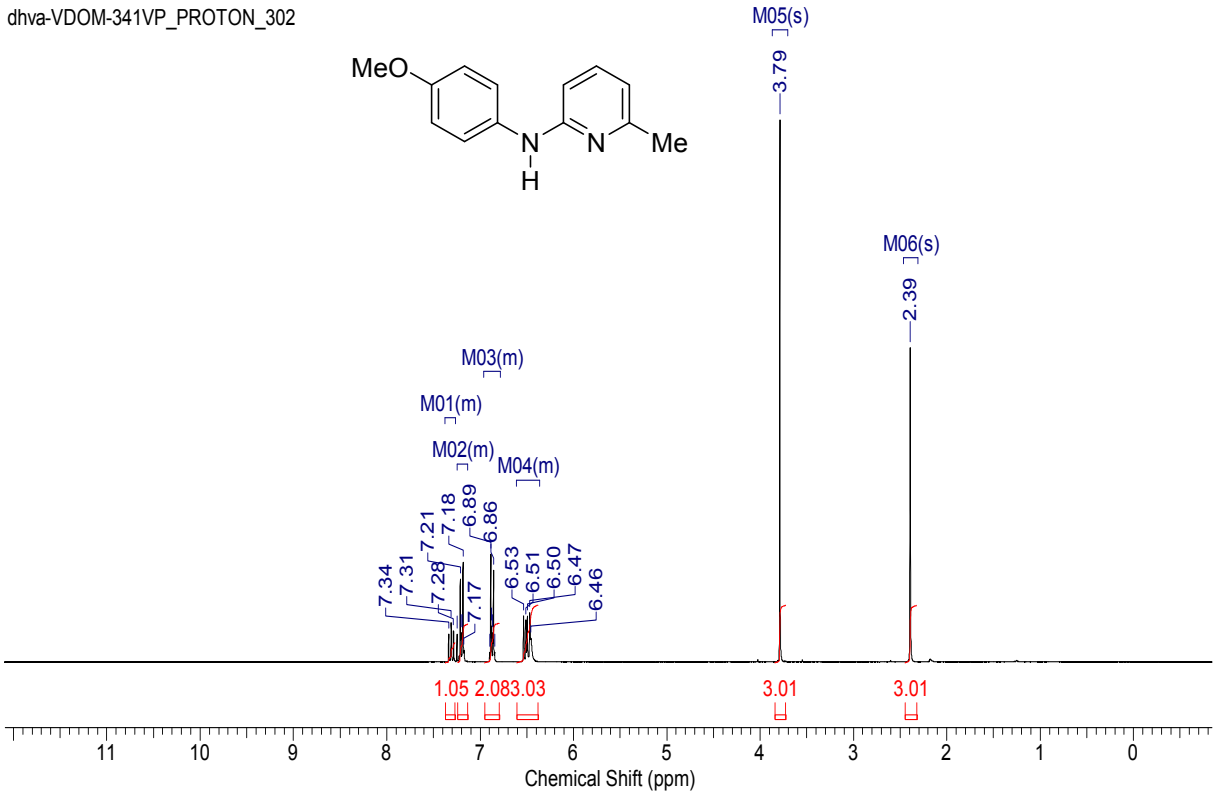


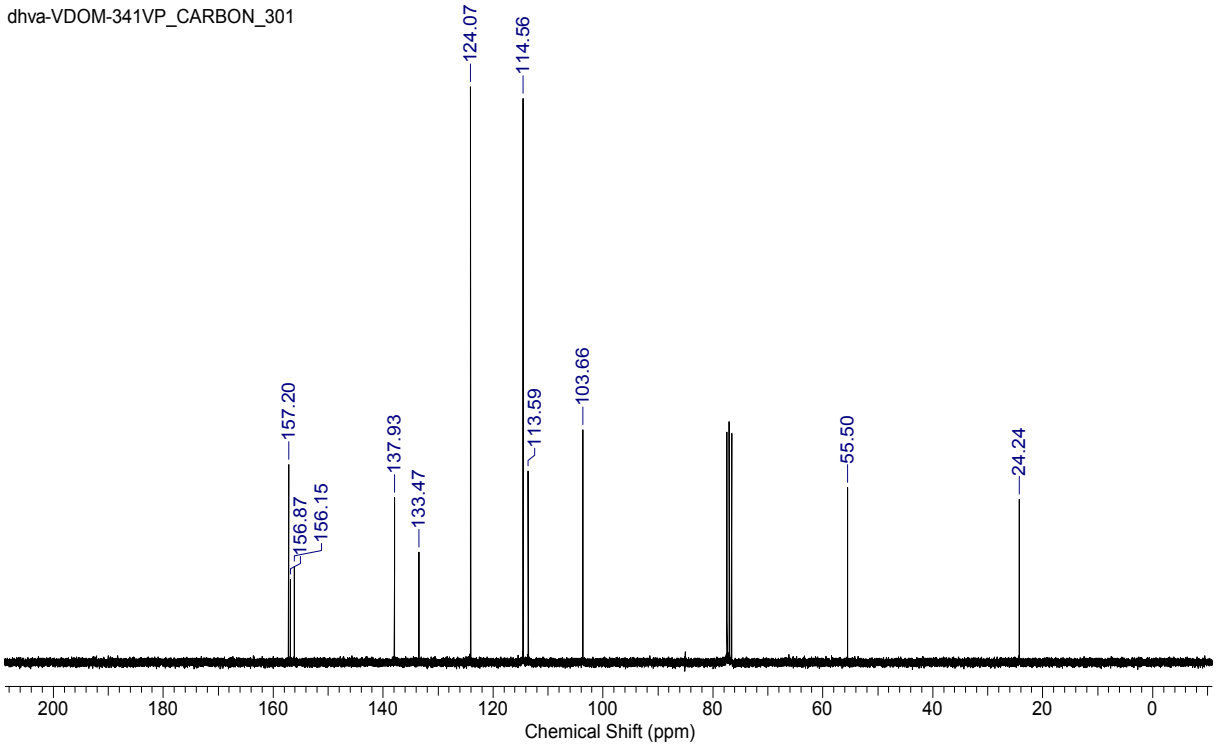
6-Methyl-*N*-phenylpyridin-2-amine (5v)



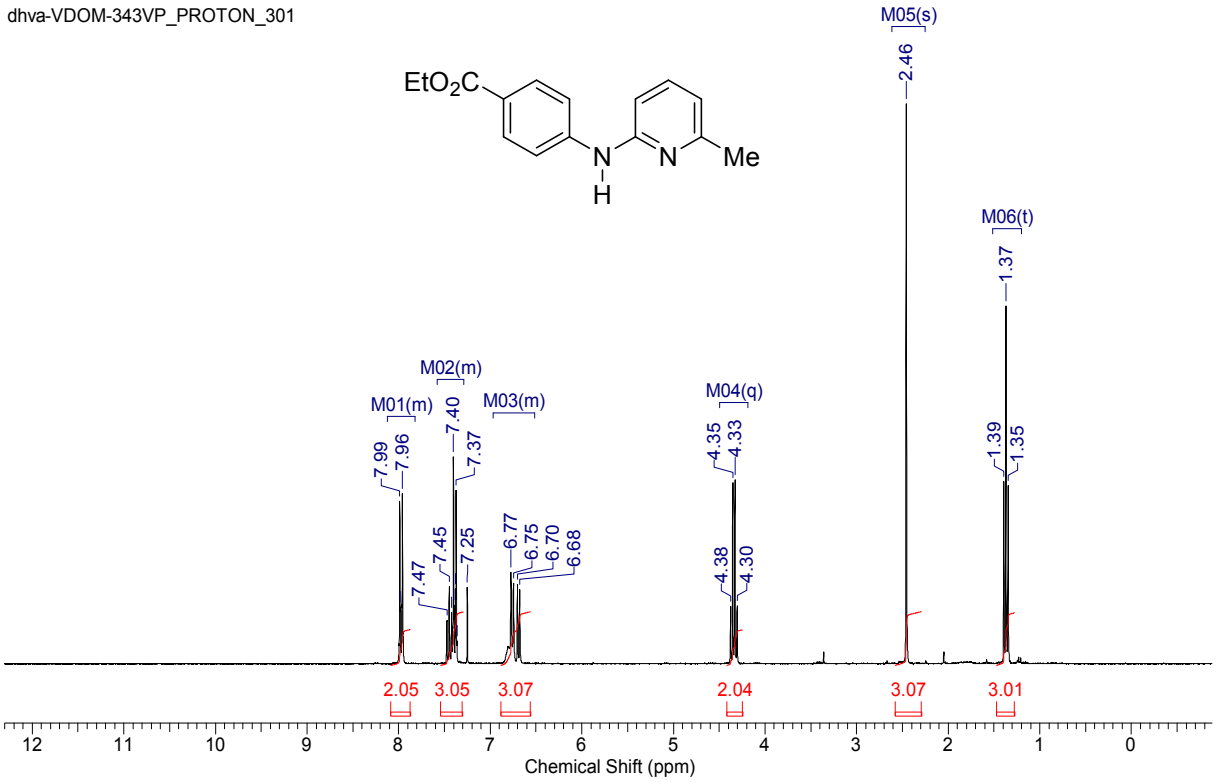


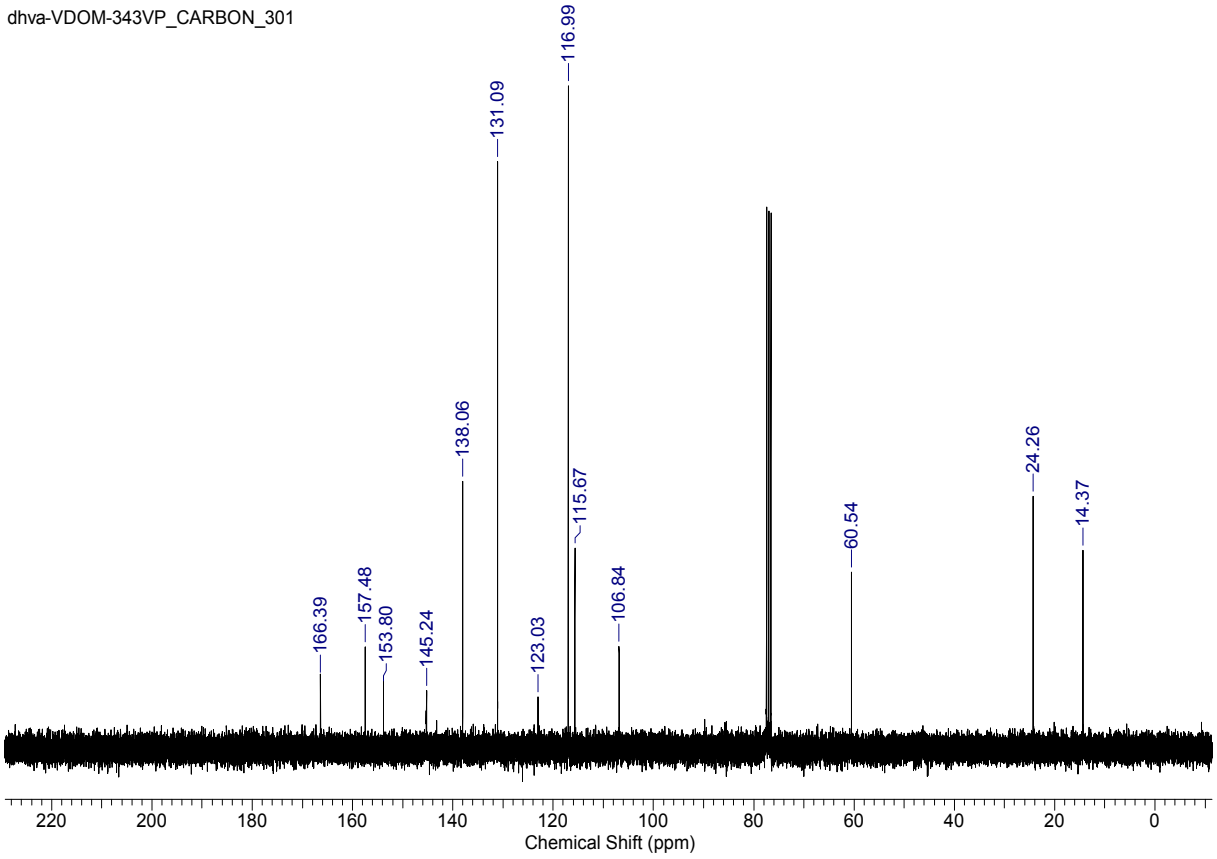
N-(4-Methoxyphenyl)-6-methylpyridin-2-amine (5w)



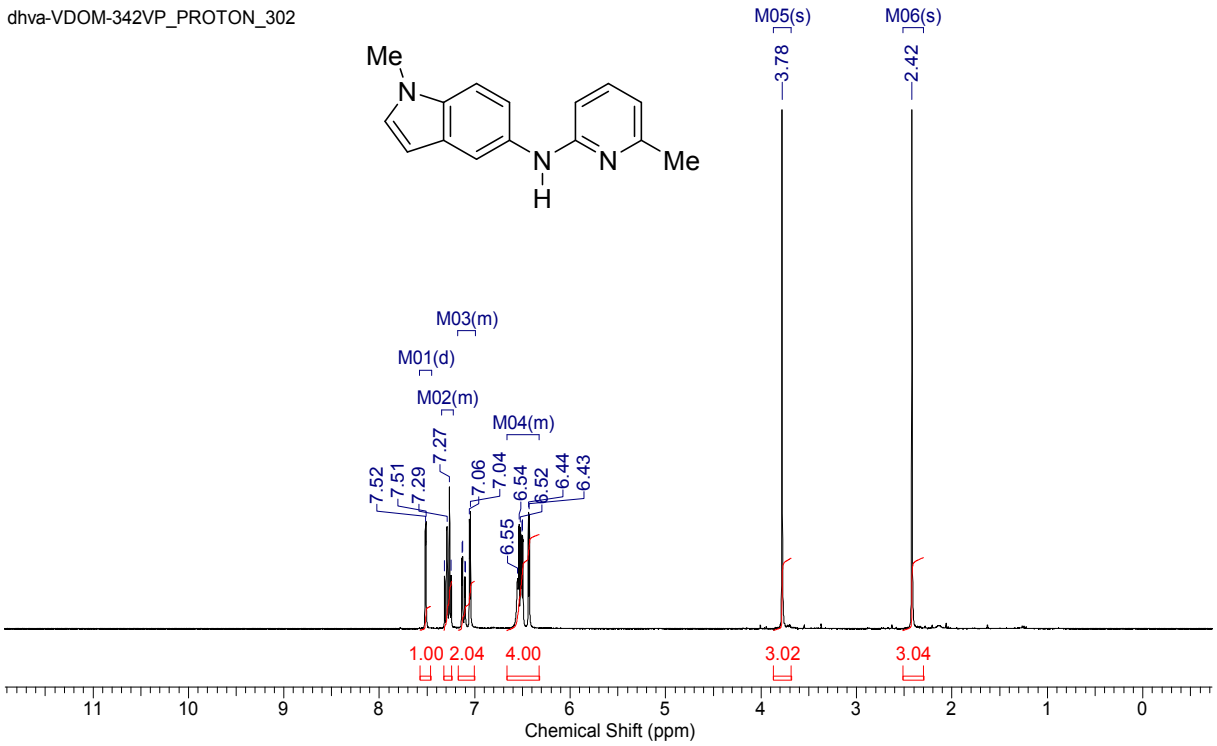


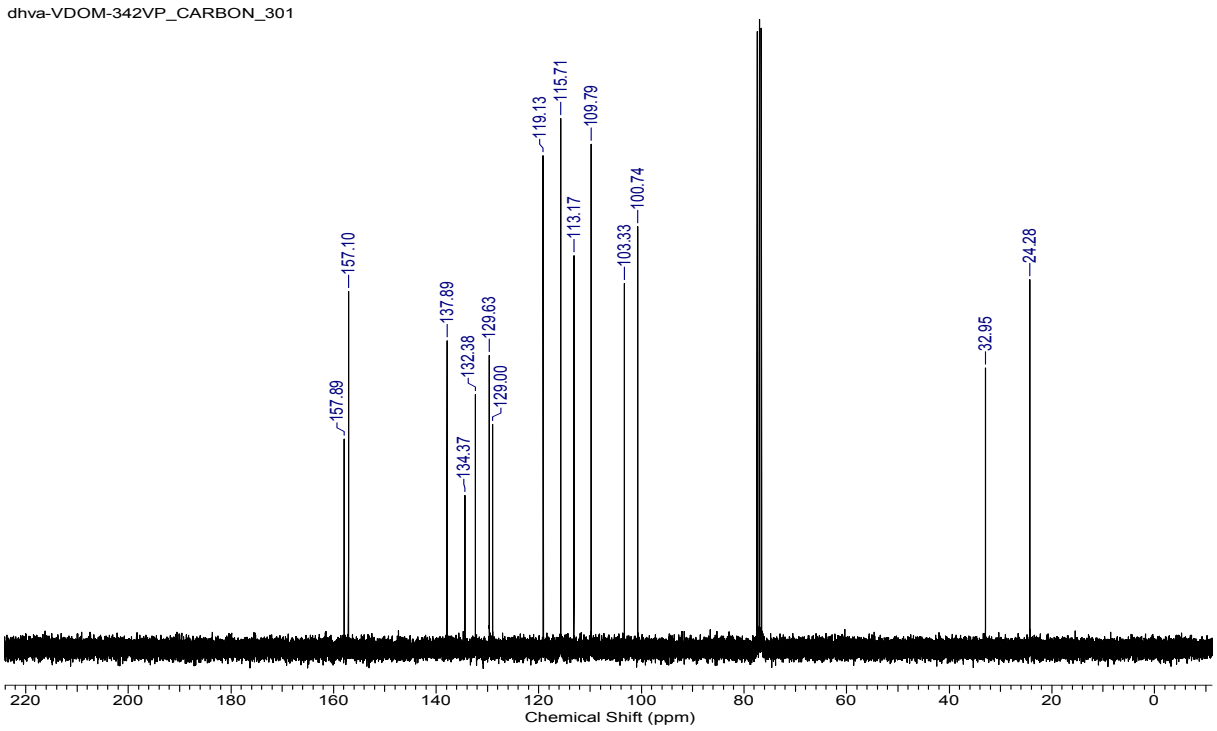
Ethyl-4((6-methylpyridin-2-yl)amino)benzoate (5x)



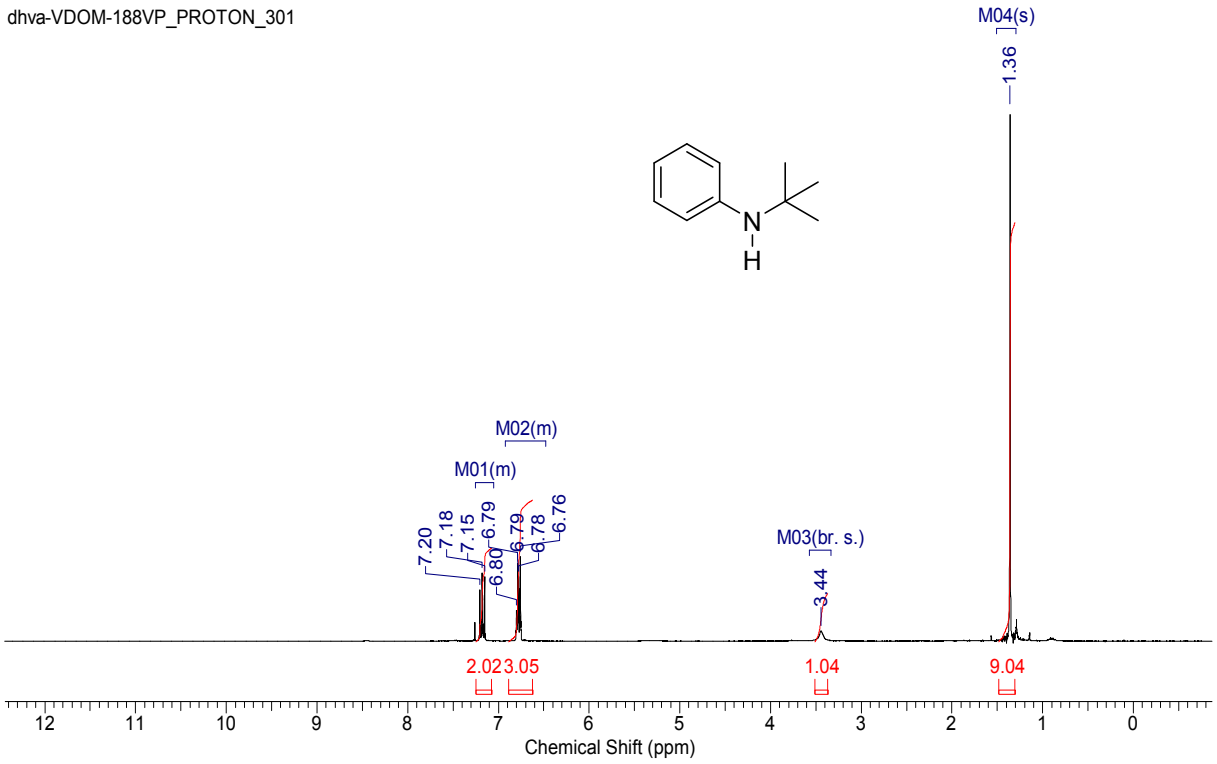


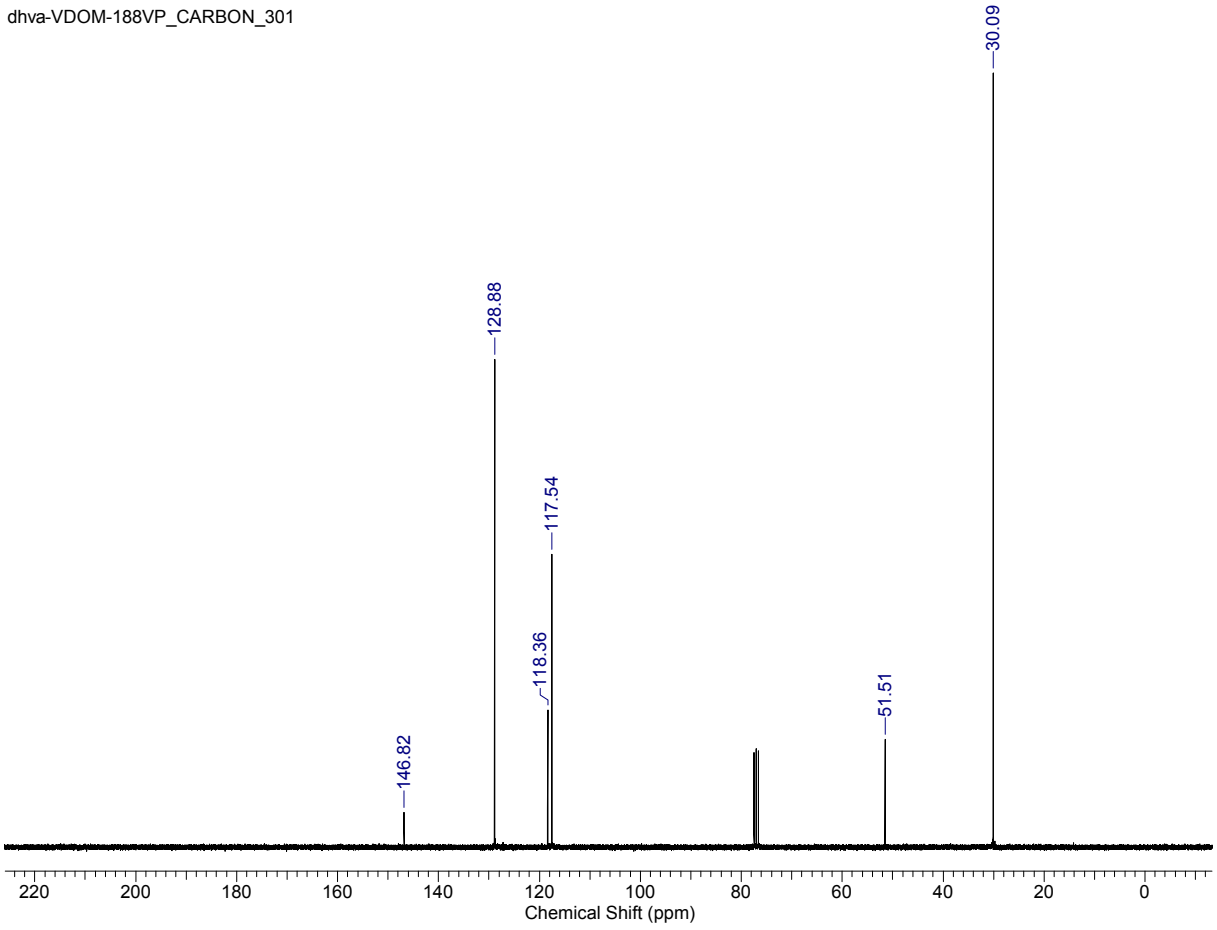
1-Methyl-*N*-(6-methylpyridin-2-yl)-1*H*-indol-5-amine (5y)



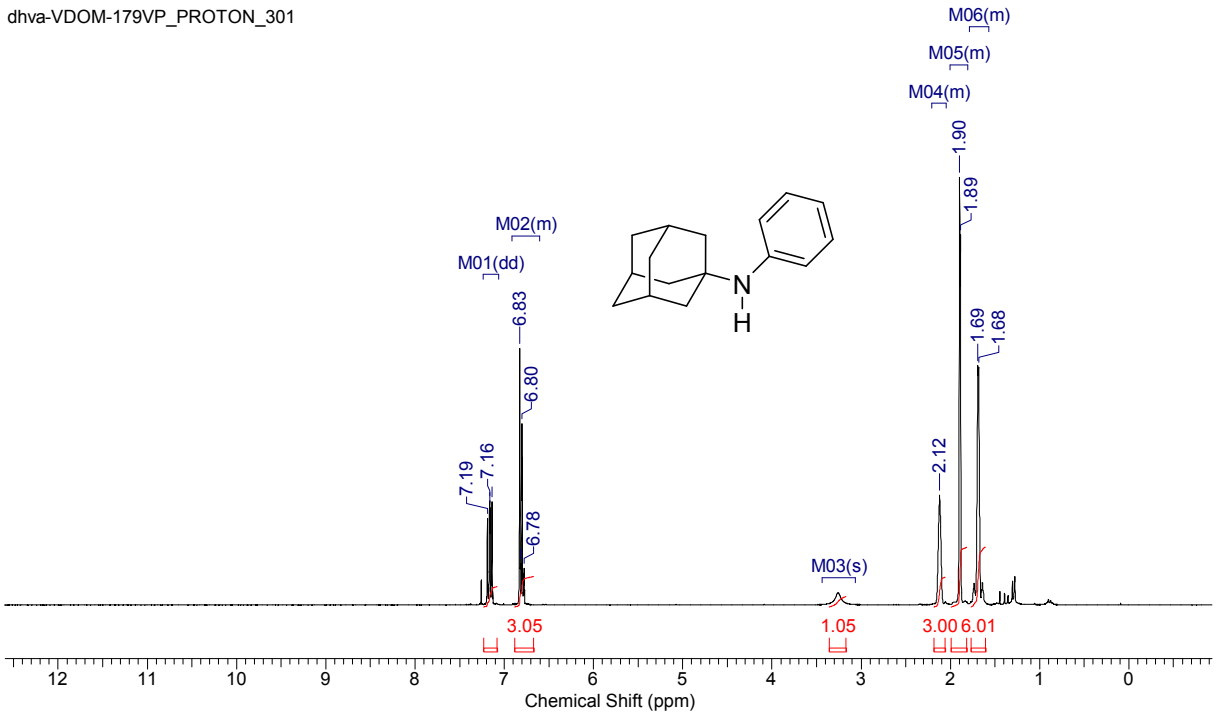


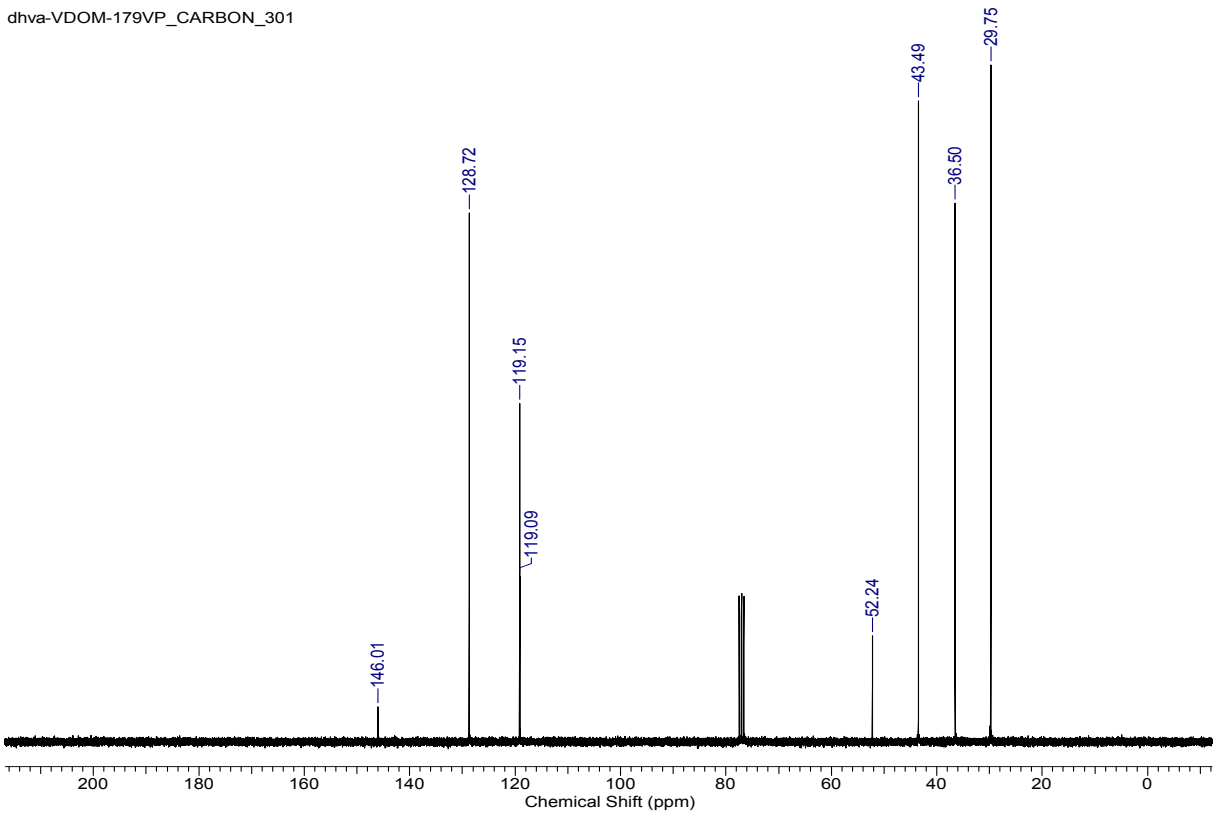
N-(*tert*-Butyl)aniline (7a)



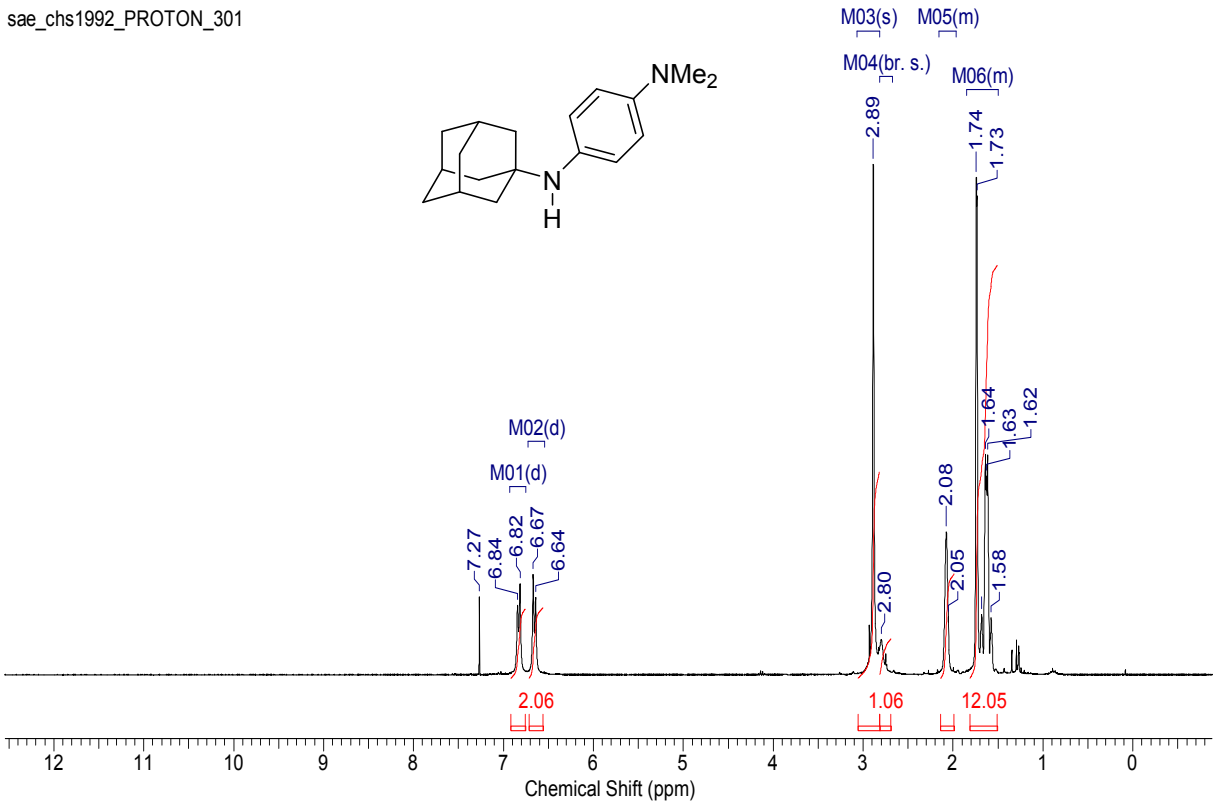


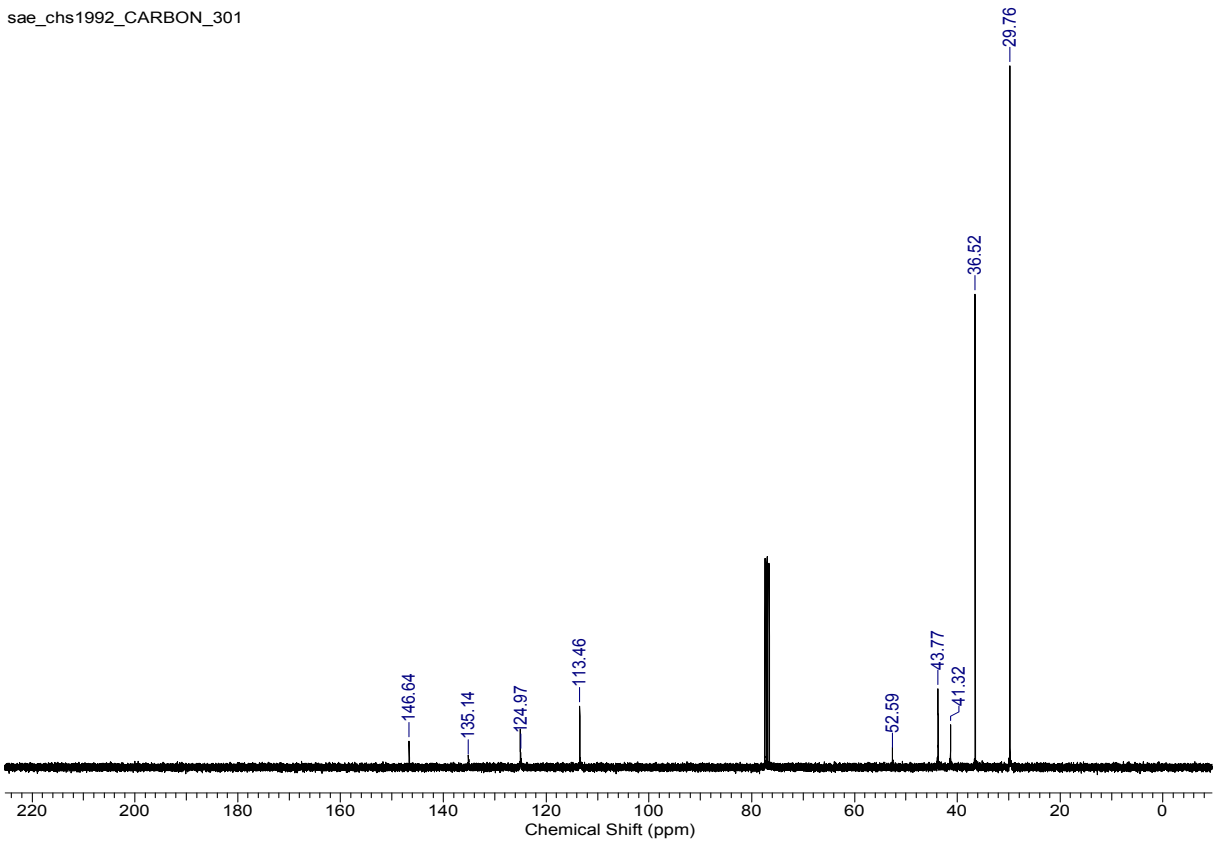
(3s,5s,7s)-*N*-Phenyladamantan-1-amine (7b)





N^1-((3s,5s,7s)-Adamantan-1-yl)-N^4,N^4-dimethylbenzene-1,4-diamine (7c)





(3s,5s,7s)-*N*-(4-Methoxyphenyl)adamantan-1-amine (7d)