# Diels-Alder Approach for the Construction of Halogenated, *ortho*-Nitro Biaryl Templates and Application to the Total Synthesis of anti-HIV Agent Siamenol.

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**Electronic Supplementary Information: Experimental**

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**General.** Infrared spectra were recorded neat unless otherwise indicated and are reported in $cm^{-1}$. $^1H$ NMR spectra were recorded in deuterated solvents and are reported in ppm relative to tetramethylsilane and referenced internally to the residually protonated solvent. $^{13}C$ NMR spectra were recorded in deuterated solvents and are reported in ppm relative to tetramethylsilane and referenced internally to the residually protonated solvent.

Routine monitoring of reactions was performed using EM Science DC-Alufolien silica gel, aluminum-backed TLC plates. Flash chromatography was performed with the indicated eluents on EM Science Gedurian 230-400 mesh silica gel.

Air and/or moisture sensitive reactions were performed under usual inert atmosphere conditions. Reactions requiring anhydrous conditions were performed under a blanket of argon, in glassware dried in an oven at 120°C or by flame, then cooled under argon. Dry DMF, THF, DCM, and PhMe were obtained via a solvent purification system. All other solvents and commercially available reagents were either purified via literature procedures or used without further purification.

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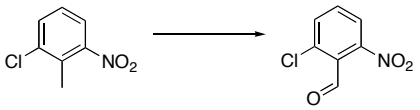
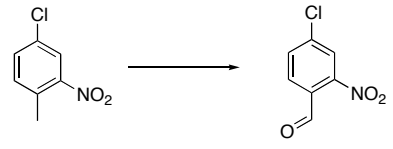



**1** **4**

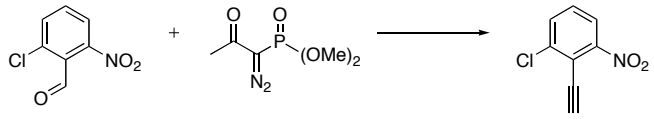
**Aldehyde 4:** To a stirred solution of **1** (18.53 g, 108.0 mmol) in dry DMF (240 mL) was added *N*,*N*-dimethylformamide dimethyl acetal (DMF•DMA) (39.5 g, 44.0 mL, 331 mmol). After heating at 140°C for 16 h, the dark red solution was cooled to 0°C and added slowly, over 1 h via cannula, to a rapidly stirred solution of $NaIO_4$ (83.0 g, 388.0 mmol) in $H_2O$ (291 mL) and DMF (77 mL) at 0°C. The reaction flask was washed with DMF (20 mL) at 0°C and added to $NaIO_4$ mixture. The reaction was stirred at 0°C for 2 h then allowed to warm to rt. After an additional 6 h, the orange solution was filtered and rinsed with PhMe/EtOAc (1:1, 200 mL). The filtrate was then washed with $H_2O$ (3 x 150 mL) and sat. aq. NaCl (3 x 150 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* to a dark red oil, and hexanes (40 mL) were added. Solids were isolated and recrystalized in PhMe to give the known aldehyde **4**[1] (17.23 g, 92.88 mmol, 86%). $^1H$ NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 8.01 (dd, $J$ = 1.0, 8.2 Hz, 1H), 7.79 (dd, $J$ = 1.0, 8.1 Hz, 1H), 7.65 (t, $J$ = 8.1 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 188.6, 148.4, 138.6, 132.9, 132.4, 123.4, 121.9.




**2** **5**

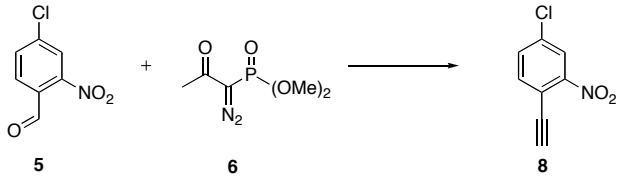
**Aldehyde 5:**[2] To a stirred solution of **2** (5.248 g, 30.59 mmol) in dry DMF (172 mL) was added *N*,*N*-dimethylformamide dimethyl acetal (DMF•DMA) (13.7 g, 12.0 mL, 88.5 mmol). After heating at 140°C for 16 h, the dark red solution was cooled to 0°C and added slowly, over 20 min via cannula, to a rapidly stirred solution of $NaIO_4$ (18.7 g, 87.4 mmol) in $H_2O$ (69 mL) and DMF (23 mL) at 0°C. The reaction flask was washed with DMF (20 mL) at 0°C and added to $NaIO_4$ mixture. The reaction was stirred at 0°C for 30 min then allowed to warm to rt. After an additional 4 h, the orange solution was filtered and rinsed with PhMe (200 mL). The filtrate was then washed with $H_2O$ (2 x 200 mL) and sat. aq. NaCl (2 x 100 mL). The dried ($MgSO_4$) extract was filtered, concentrated *in vacuo* to a dark red oil, and purified by flash chromatography over silica gel, eluting with 20-50% EtOAc / Hexanes to give known aldehyde **5**[3] (4.737 g, 25.53 mmol, 84%). $^1H$ NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 8.13 (d, $J$ = 2.0 Hz, 1H), 7.97

(dd, $J$ = 8.3 Hz, 1H), 7.78 (dd, $J$ = 2.0, 8.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.9, 150.1, 140.2, 134.2, 130.9, 129.3, 124.8.



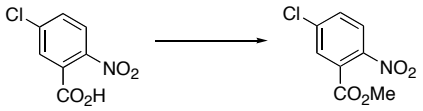
**4** **6** **7**

**Acetylene 7:** To a stirred solution of **4** (16.64 g, 89.67 mmol), $K_2CO_3$ (25.14 g, 181.9 mmol), and MeOH (1.34 L) was added diazophosphonate **6**[4] (24.33 g, 208.7 mmol) at rt. After 4 h, the solution was quenched with sat. aq. $NaHCO_3$ (500 mL) and concentrated *in vacuo* to remove the MeOH. The solution was diluted with EtOAc (700 mL) and washed with $H_2O$ (3 x 200 mL), and sat. aq. NaCl (2 x 150 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 1% EtOAc / Hexanes, to give **7** (13.84 g, 76.22 mmol, 85%) as a pale yellow solid. MP 94-95°C; IR (thin film) 3286, 1521, 1351, 808, 756, 736, 681 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, $J$ = 8.2, 1.1 Hz, 1H), 7.74 (dd, $J$ = 8.2, 1.1 Hz, 1H), 7.47 (t, $J$ = 8.2, 1H), 3.86 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.8, 134.0, 129.6, 123.1, 117.6, 109.9, 91.7, 75.3; HRMS (CI+) calcd. for $C_8H_5NO_2Cl$ (M+H) 182.0009, found 182.0005.



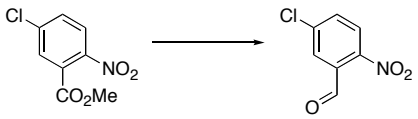
**5** **6** **8**

**Acetylene 8:** To a stirred solution of **5** (3.667 g, 19.76 mmol), $K_2CO_3$ (5.510 g, 39.87 mmol), and MeOH (330 mL) was added diazophosphonate **6**[4] (5.168 g, 26.90 mmol) at rt. After 4 h, the solution was quenched with sat. aq. $NaHCO_3$ (200 mL) and concentrated *in vacuo* to remove the MeOH. The solution was diluted with EtOAc (200 mL) and washed with $H_2O$ (3 x 50 mL), and sat. aq. NaCl (2 x 50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 1% EtOAc / Hexanes, to give **8** (2.870 g, 15.81 mmol, 81%) as a pale yellow solid. MP 68-70°C; IR (thin film) 3285, 1555, 1528, 1345, 891, 840, 791, 761 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, $J$ = 2.0 Hz, 1H), 7.67 (dd, $J$ = 8.4 Hz, 1H), 7.60 (dd, $J$ = 8.4, 2.0, 1H), 3.59 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 150.5, 136.4, 135.3, 133.1, 124.9, 115.9, 86.3, 77.6; HRMS (CI+) calcd. for $C_8H_5NO_2{}^{37}Cl$ (M+H) 183.9979, found 183.9980.



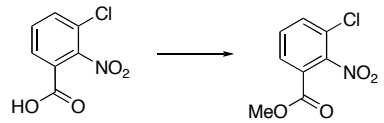
**9** **80**

**Methyl ester 80:** To a stirred solution of **9** (9.393 g, 46.60 mmol) in dry DMF (155 mL) at 0°C was added $K_2CO_3$ (13.23 g, 95.72 mmol) and MeI (19.38 g, 8.5 mL, 136.5 mmol) and warmed to 40°C. After 1 h, the solution was cooled to rt and diluted with EtOAc (115 mL). The solution was washed with $H_2O$ (3 x 100 mL), and sat. aq. NaCl (3 x 100 mL). The dried ($Na_2SO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica gel, eluting with 40-60% EtOAc / Hexanes, to give the known methyl ester **80**[5] (9.244 g, 42.87 mmol, 92%) as a pale yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, $J$ =8.7 Hz, 1H), 7.73 (d, $J$ = 2.3 Hz, 1H), 7.63 (dd, $J$ = 8.7, 2.3 Hz, 1H), 3.98 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.7, 146.1, 139.7, 131.6, 129.8, 129.4, 125.5, 53.6.



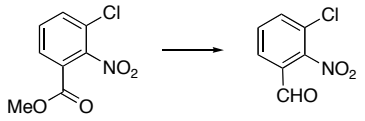

**80** **11**

**Aldehyde 11:** To a stirred solution of **80** (8.20 g, 38.0 mmol) and dry $CH_2Cl_2$ (205 mL) was added DIBAL-H (48.0 mL, 48.0 mmol, 1.0 M in $CH_2Cl_2$) at -78°C. After 45 min, MeOH (20 mL) was added and the solution was allowed to warm to rt. Next, aq. sodium tartrate (200 mL, 10% w/v) was added and the suspension was left to stir vigorously until a bilayer was distinct. The solution was diluted with $CH_2Cl_2$ (100 mL) and washed with $H_2O$ (2 x 100 mL), sat. aq. NaCl (2 x 100 mL). The dried ($Na_2SO_4$) extract was purified via flash chromatography over silica gel, eluting with 20-50% EtOAc / Hexanes to give the known aldehyde **13**[6] (6.80 g, 36.7 mmol, 97%). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 8.15 (d, $J$ = 8.7 Hz, 1H), 7.94 (d, $J$ = 2.3 Hz, 1H), 7.74 (dd, $J$ = 2.4, 8.7 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 187.0, 147.5, 141.0, 133.5, 132.7, 129.4, 126.2.



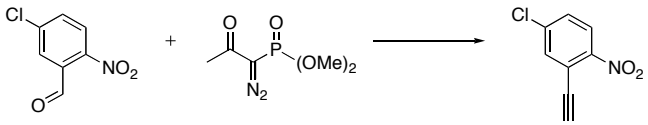

**10** **81**

**Methyl ester 81:** To a stirred solution of **10** (5.01 g, 24.9 mmol), $K_2CO_3$ (10.3 g, 74.7 mmol), and DMF (25 mL) was added MeI (3.10 mL, 7.07 g, 49.8 mmol). The reaction mixture was heated to 40˚C. After 1 h, the reaction was quenched with $H_2O$ (30 mL), diluted with EtOAc (50 mL), and washed with $H_2O$ (20 mL) and sat. aq. NaCl (20 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* to give known ester **81**[7] (5.31 g, 24.6 mmol, 99%) as a white crystalline solid. MP 101-103˚C; $^1$H NMR (300 MHz, $CDCl_3$) δ 8.01 (dd $J$ = 1.2, 7.8 Hz, 1H), 7.74 (dd, $J$ = 1.2, 8.1 Hz, 1H), 7.55 (dd, $J$ = 7.8, 8.1 Hz, 1H), 3.94 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.6, 148.4, 134.8, 130.7, 129.7, 126.4, 124.5, 53.4.




**81** **12**

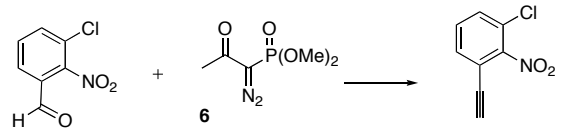
**Aldehyde 12:** To a stirred solution of **81** (2.91 g, 13.5 mmol) and $CH_2Cl_2$ (134 mL) at -78˚C was added DIBAL-H (16.0 mL, 16.0 mmol, 1.0 M in $CH_2Cl_2$) over 15 min. After an additional 10 min, the reaction was quenched with MeOH (1.0 mL) and warmed to rt. Next, a solution of aq. sodium potassium tartrate (190 mL, 10% w/v) was added and vigorously stirred. After 4 h, the reaction mixture was diluted with $CH_2Cl_2$ (50 mL) and washed with $H_2O$ (3 x 100 mL) and sat. aq. NaCl (100 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by recrystallization with EtOAc / Hexanes (1:3) to give known aldehyde **12**[8] (2.32 g, 12.7 mmol, 94%) as a white crystalline solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.92 (dd, $J$ = 1.4, 7.7 Hz, 1H), 7.80 (dd, $J$ = 1.4, 8.1 Hz, 1H), 7.67 (dd, $J$ = 7.7, 8.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.0, 148.1 136.0, 131.7, 130.1, 128.5, 126.6.



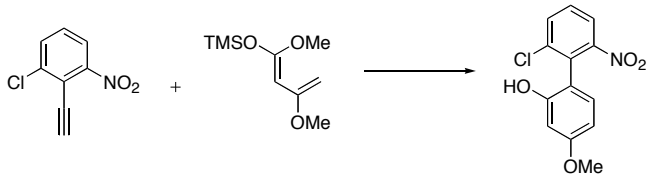

**11** **6** **13**

**Acetylene 13:** To a stirred solution of **11** (3.694 g, 19.90 mmol), $K_2CO_3$ (5.528 g, 40.00 mmol), and dry MeOH (350 mL) was added diazophosphonate **6**[4] (5.088 g, 26.48 mmol) at rt. After 4 h, the

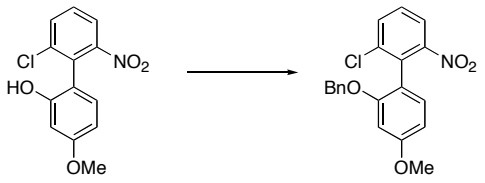
solution was quenched with sat. aq. $NaHCO_3$ (200 mL) and concentrated *in vacuo* to remove the MeOH. The solution was diluted with EtOAc (300 mL) and washed with $H_2O$ (3 x 100 mL), and sat. aq. NaCl (2 x 100 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 1% EtOAc / Hexanes, to give **13** (2.891 g, 15.92 mmol, 80%) as a pale yellow solid. MP 70-73°C; IR (thin film) 3286, 2112, 1599, 1559, 1516, 883, 834, 753 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 2.3 Hz, 1H), 7.49 (dd, *J* = 8.7, 2.3 Hz, 1H), 3.60 (s, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 148.5, 139.5, 135.2, 129.6, 126.0, 119.2, 86.6, 77.5; HRMS (CI+) calcd. for $C_8H_5NO_2{}^{37}Cl$ (M+H) 183.9979, found 183.9977.




**Acetylene 14:** To a stirred solution of **12** (1.02 g, 5.59 mmol), $K_2CO_3$ (1.54 g, 11.1 mmol), and MeOH (56.0 mL) was added diazophosphonate reagent **6**[4] (1.39 g, 1.07 mL, 7.26 mmol) at rt. After 2 h, the reaction was quenched with aq. $NaHCO_3$ (60 mL, 5% w/v), and the MeOH was removed *in vacuo*. The reaction mixture was diluted with EtOAc (30 mL) and washed with aq. $NaHCO_3$ (25 mL, 5% w/v), $H_2O$ (25 mL), and sat. aq. NaCl (20 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 5 – 20% EtOAc / Hexanes, to give **14** (1.01 g, 4.94 mmol, 88%) as a pale yellow solid. MP 42-43˚C; IR (neat) 3289, 3072, 1549 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 1.4, 7.9 Hz, 1H), 7.54 (dd, *J* = 1.4, 7.9 Hz, 1H), 7.44 (dd, *J* = 7.9, 7.9 Hz, 1H), 3.35 (s, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 151.6, 132.0, 131.0, 130.7, 125.4, 117.1, 85.1, 75.8; HRMS (CI+) calcd. for $C_8H_4NO_2Cl$ (M+H) 182.0009, found 182.0001.

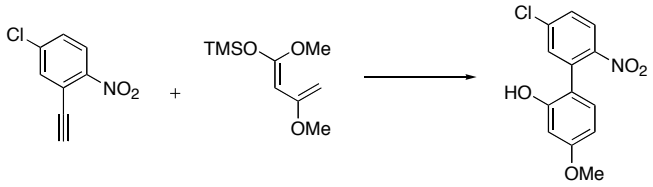



**Phenol 82:** To a pressure vessel containing **7** (1.739 g, 9.578 mmol) and PhMe (20 mL) was added diene **15**[9] (8.423 g, 41.63 mmol) at rt. The mixture was heated at 80°C. After 24 h, the reaction was cooled to 0°C and DABCO (4.414 g, 39.35 mmol) was added and gradually warmed to 40°C over 30 min. After 1h at 40°C, the brown mixture was cooled to rt and quenched with aq. HCl (1 M) until pH = 2, diluted with EtOAc (100 mL), washed with $H_2O$ (50 mL), and sat. aq. NaCl (2 x 50 mL). The dried ($Na_2SO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica, eluting with 0-20% EtOAc / Hexanes to give **82** (1.795 g, 6.417 mmol, 67%) as a yellow solid. MP 134-135°C; IR (thin film) 3423, 1620, 1529, 1444, 1356 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.73 (dd, *J* = 8.1, 1.0, Hz, 1H), 7.46 (t, *J* = 8.1, 1H), 7.00 (d, 8.5 Hz, 1H), 6.58 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.49 (d, *J* = 2.4 Hz, 1H), 5.05 (s, 1H), 3.82 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.8, 154.2, 152.2, 137.6, 134.0, 131.3, 131.2, 129.6, 122.6, 114.2, 107.1, 102.5, 55.8; HRMS (CI+) calcd. for $C_{13}H_{10}NO_4Cl$ (M+) 279.0298, found 279.0304.



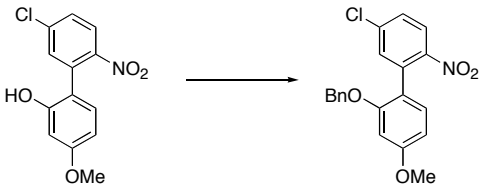

**82** **16**

**Chloride 16:** To a stirred solution of **82** (1.245 g, 4.500 mmol) and dry DMF (22.0 mL) was added NaH (397.2 mg, 9.93 mmol, 60% dispersion in mineral oil) at 0°C. To this dark red solution was added BnBr (7.76 g, 5.40 mL, 45.4 mmol). After 10 min, the yellow solution was quenched with sat. aq. $NH_4Cl$ (100 mL), diluted with EtOAc (150 mL), washed with $H_2O$ (50 mL), and sat. aq. NaCl (2 x 100 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 0-10% $Et_2O$ / Hexanes to give **16** (1.582 g, 4.277 mmol, 95%) as a bright yellow crystalline solid. MP 99-100°C; IR (thin film) 2936, 1612, 1583, 1529, 1441 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.73 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.443 (t, *J* = 8.1 Hz, 1H), 7.36-7.23 (m, 5H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.63 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.60 (d, *J* = 2.3 Hz, 1H), 5.05 (s, 2H), 3.85 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.4, 156.6, 151.4, 136.8, 136.7, 133.4, 132.0, 130.7, 128.6, 128.4, 127.7, 126.8, 122.2, 116.2, 105.1, 100.3, 70.3, 55.3; HRMS (FAB+) calcd. for $C_{20}H_{16}NO_4Cl$ (M+) 369.0768, found 369.0759.




**13** **15** **83**

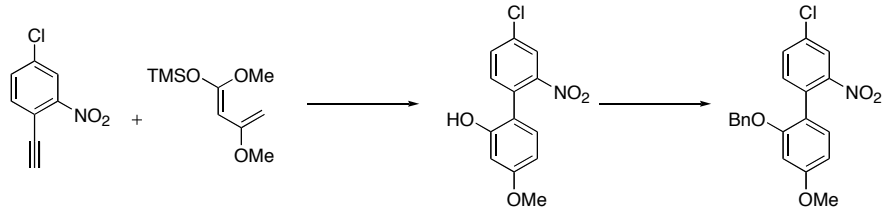
**Phenol 83:** To a pressure vessel containing **13** (189.3 mg, 1.043 mmol) and PhMe (2.0 mL) was added diene **15**[9] (872.8 mg, 4.313 mmol) at rt. The mixture was heated at 80°C. After 24 h, the reaction was cooled to 0°C and DABCO (670.8 mg, 5.980 mmol) was added and gradually warmed to 40°C over 30 min. After 30 min at 40°C, the brown mixture was cooled to rt and quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (25 mL), washed with $H_2O$ (10 mL), and sat. aq. NaCl (2 x 20 mL). The dried ($Na_2SO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica, eluting with 0-20% EtOAc / Hexanes to give **83** (178.9 mg, 646.6 μmol, 62%) as a yellow oil. IR (thin film) 3389, 2933, 1622, 1600, 1561, 1518, 865, 830, 727 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 1H), 7.46 (dd, *J* = 8.5, 2.3, Hz, 1H), 7.43 (d, *J* = 2.3, 1H), 7.17 (d, 8.5 Hz, 1H), 6.63 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.41 (d, *J* = 2.4 Hz, 1H), 4.94 (s, 1H), 3.84 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.4, 153.4, 147.9, 138.8, 134.4, 132.6, 130.5, 127.9, 125.6, 116.6, 106.9, 102.0, 55.4; HRMS (EI+) calcd. for $C_{13}H_{10}NO_4Cl$ (M+) 279.0298, found 279.0290.




**83** **17**

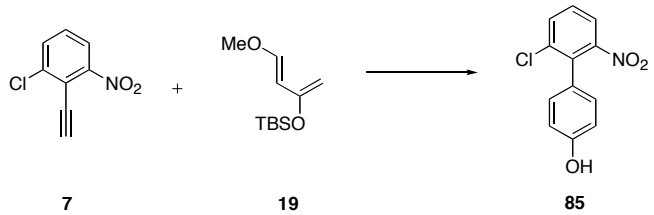
**Chloride 17:** To a stirred solution of **83** (100 mg, 361.4 μmol) and dry DMF (1.8 mL) was added NaH (30.8 mg, 0.77 mmol, 60% dispersion in mineral oil) at 0°C. To this dark red solution was added BnBr (7.19 mg, 500 μL, 4.20 mmol). After 10 min, the yellow solution was quenched with sat. aq. $NH_4Cl$

(15 mL), diluted with EtOAc (20 mL), washed with $H_2O$ (15 mL), and sat. aq. NaCl (2 x 25 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 0-10% $Et_2O$ / Hexanes to give **17** (124.3 mg, 336.2 μmol, 93%) as a bright yellow crystalline solid. MP 121-124°C; IR (thin film) 2925, 2851, 1617, 1595, 1531, 1268, 1049 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 0.3, 8.6 Hz, 1H), 7.45-7.39 (m, 2H), 7.37-7.33 (m, 3H), 7.27-7.22 (m, 3H), 6.65 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 5.00 (s, 2H), 3.85 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.5, 156.2, 147.9, 138.6, 136.3, 135.1, 132.6, 130.2, 128.5, 127.9, 127.6, 127.2, 125.5, 119.2, 105.6, 100.3, 70.7, 55.4; HRMS (EI+) calcd. for $C_{20}H_{16}NO_4Cl$ (M+) 369.0768, found 369.0776.



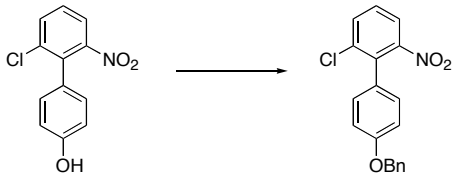

**Phenol 83:** To a pressure vessel containing **8** (185.2 mg, 1.020 mmol) and PhMe (2.0 mL) was added diene **15**[9] (834.1 mg, 4.102 mmol) at rt. The mixture was heated at 80°C. After 24 h, the reaction was cooled to 0°C and DABCO (493.6 mg, 4.401 mmol) was added and gradually warmed to 40°C over 30 min. After 1h, the brown mixture was cooled to rt and quenched with sat. aq. $NH_4Cl$ (15 mL), diluted with EtOAc (20 mL), washed with $H_2O$ (20 mL), and sat. aq. NaCl (2 x 15 mL). The dried ($Na_2SO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica, eluting with 0-20% EtOAc / Hexanes to give impure **84** (363.0 mg) as a yellow oil and used without further purification.

**Chloride 18:** To a stirred solution of **84** (363.0 mg) and dry DMF (3.6 mL) was added NaH (93.2 mg, 2.33 mmol, 60% dispersion in mineral oil) at 0°C. To this dark red solution was added BnBr (1.22 g, 0.85 mL, 7.15 mmol). After 10 min, the yellow solution was quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (30 mL), washed with $H_2O$ (10 mL), and sat. aq. NaCl (2 x 10 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 0-10% $Et_2O$ / Hexanes to give **18** (233.9 mg, 0.632 mmol, 62% over 2 steps) as a bright yellow crystalline solid. MP 126-128°C; IR (thin film) 3032, 2925, 1608, 1527, 1260, 1050 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.2 Hz, 1H), 7.58 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.44-7.20 (m, 7H), 6.63 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 5.00 (s, 2H), 3.84 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.4, 156.1, 149.7, 136.3, 133.8, 133.3, 132.6, 131.7, 130.2, 128.5, 127.9, 127.1, 124.2, 119.2, 105.6, 100.3, 70.6, 55.4; HRMS (EI+) calcd. for $C_{20}H_{16}NO_4Cl$ (M+) 369.0768, found 369.0766.



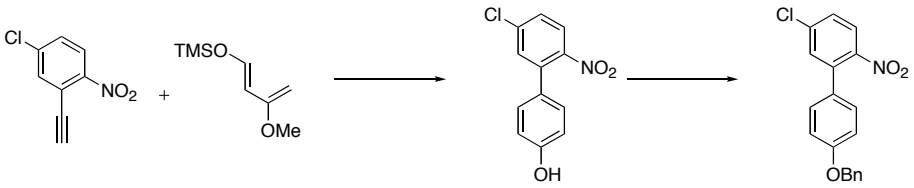

**Phenol 85:** To a pressure vessel containing **7** (147.1 mg, 810.2 μmol) and PhMe (1.3 mL) was added diene **19** (630 mg, 700 μL, 2.94 mmol) at rt. The mixture was heated at 120°C. After 24 h, the reaction was cooled to 0°C and TBAF (3.0 mL, 3.0 mmol, 1.0 M in THF) was added. After 15 min, the brown mixture was quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (20 mL), washed with $H_2O$ (10 mL), and sat. aq. NaCl (2 x 10 mL). The dried ($Na_2SO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica, eluting with 0-20% EtOAc / Hexanes to give **85** (161.0 mg, 644.9 μmol, 80%) as a yellow solid. MP 83-84°C; IR (thin film) 3423, 1614, 1529, 1361, 1201 $cm^{-1}$; $^1H$ NMR

(400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.5, 2H), 6.94 (d, 8.5 Hz, 2H), 5.00 (s, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 156.3, 151.9, 136.5, 134.7, 133.5, 130.7, 129.1, 126.5, 122.2, 115.9; HRMS (CI+) calcd. for $C_{12}H_9NO_3Cl$ (M+H) 250.0271, found 250.0277.




**85** **20**

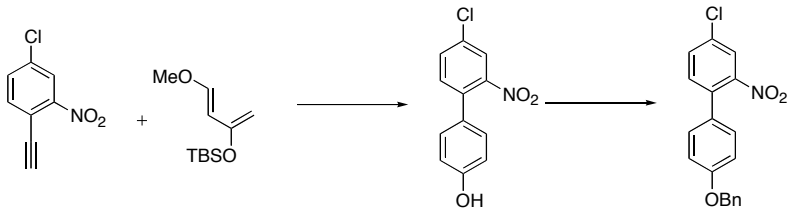
**Chloride 20:** To a stirred solution of **85** (111.4 mg, 446.2 μmol) and dry DMF (2.0 mL) was added NaH (48.1 mg, 1.20 mmol, 60% dispersion in mineral oil) at 0°C. To this dark red solution was added BnBr (790.9 mg, 550 μL, 4.624 mmol). After 10 min, the yellow solution was quenched with sat. aq. $NH_4Cl$ (20 mL), diluted with EtOAc (20 mL), washed with $H_2O$ (10 mL), and sat. aq. NaCl (2 x 10 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 0-10% $Et_2O$ / Hexanes to give **20** (137.2 mg, 403.8 mmol, 90%) as a bright yellow crystalline solid. MP 85-89°C; IR (thin film) 3088, 2873, 1610, 1531, 1244, 1027 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.55-7.35 (m, 6H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 5.14 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 159.2, 151.6, 136.7, 136.1, 134.4, 133.2, 130.2, 128.7, 128.7, 128.1, 127.7, 126.2, 121.9, 114.8, 70.1; HRMS (FAB+) calcd. for $C_{19}H_{14}NO_3Cl$ 339.0662, found 339.0669.




**13** **19** **86** **21**

**Phenol 86:** To a pressure vessel containing **13** (116.8 mg, 643.3 μmol) and PhMe (1 mL) was added diene **19** (495 mg, 550 μL, 2.32 mmol) at rt. The mixture was heated at 120°C. After 24 h, the reaction was cooled to 0°C and THF (3.6 mL, 3.6 mmol, 1.0 M in THF) was added. After 15 min, the brown mixture was quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (30 mL), washed with $H_2O$ (15 mL), and sat. aq. NaCl (2 x 10 mL). The dried ($Na_2SO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica, eluting with 0-20% EtOAc / Hexanes to give impure **86** (171.3 mg) as a yellow oil, and was used without further purification.

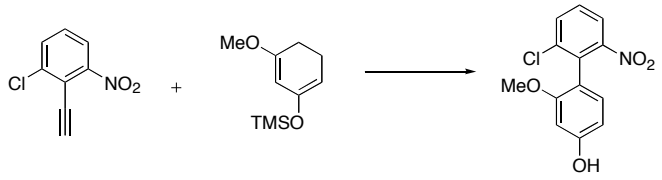
**Chloride 21:** To a stirred solution of **86** (171.3 mg) and dry DMF (3.2 mL) was added NaH (101.5 mg, 2.538 mmol, 60% dispersion in mineral oil) at 0°C. To this dark red solution was added BnBr (1.44 g, 1.00 mL, 8.41 mmol). After 10 min, the yellow solution was quenched with sat. aq. $NH_4Cl$ (15 mL), diluted with EtOAc (30 mL), washed with $H_2O$ (15 mL), and sat. aq. NaCl (2 x 10 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 0-10% $Et_2O$ / Hexanes to give **21** (170.6 mg, 502.0 μmol, 78% over 2 steps) as a bright yellow crystalline solid. MP 144-147°C; IR (thin film) 3087, 2888, 1609, 1653, 1249, 1028 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.2 Hz, 1H), 7.60 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.53-7.36 (m, 6H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 5.14 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 159.2, 149.5, 136.7, 134.3, 133.5, 133.0, 132.3, 129.2, 128.7, 128.6, 128.2, 127.6, 124.2, 115.3, 70.1; HRMS (EI+) calcd. for $C_{19}H_{14}NO_3Cl$ (M+) 339.0662, found 339.0660.




**8** **19** **87** **22**

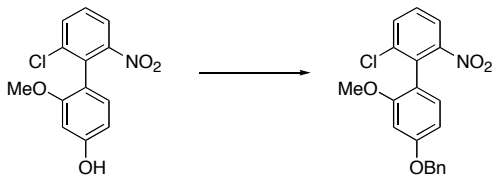
**Phenol 87:** To a pressure vessel containing **8** (123.7 mg, 681.3 μmol) and PhMe (1 mL) was added diene **19** (495 mg, 550 μL, 2.203 mmol) at rt. The mixture was heated at 120°C. After 24 h, the reaction was cooled to 0°C and TBAF (3.7 mL, 3.7 mmol, 1.0 M in THF) was added. After 10 min, the brown mixture was quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (30 mL), washed with $H_2O$ (15 mL), and sat. aq. NaCl (2 x 10 mL). The dried ($Na_2SO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica, eluting with 0-20% EtOAc / Hexanes to give **87** (169.4 mg) as a yellow oil, with minor impurities, and used without further purification.

**Chloride 22:** To a stirred solution of **87** (169.4 mg) and dry DMF (3.0 mL) was added NaH (155.6 mg, 3.89 mmol, 60% dispersion in mineral oil) at 0°C. To this dark red solution was added BnBr (1.44 g, 1.0 mL, 8.41 mmol). After 10 min, the yellow solution was quenched with sat. aq. $NH_4Cl$ (15 mL), diluted with EtOAc (20 mL), washed with $H_2O$ (15 mL), and sat. aq. NaCl (2 x 10 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 0-10% $Et_2O$ / Hexanes to give **22** (175.9 mg, 517.6 μmol, 76% over 2 steps) as a bright yellow crystalline solid. MP 147-148°C; IR (thin film) 3067, 1609, 1531, 1249, 1028 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.0 Hz, 1H), 7.60 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.55-7.35 (m, 6H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 5.14 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 159.2, 149.5, 136.7, 134.3, 133.5, 133.0, 132.3, 129.2, 128.7, 128.6, 128.2, 127.6, 124.2, 115.3, 70.1; HRMS (EI+) calcd. for $C_{19}H_{14}NO_3Cl$ (M+) 339.0662, found 339.0652.



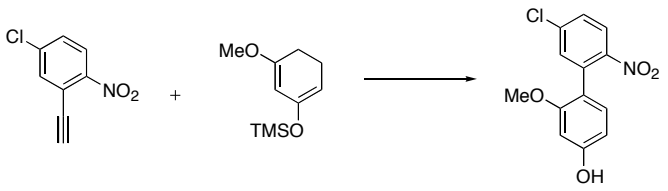

**7** **23** **88**

**Phenol 88:** To a pressure vessel containing **7** (52.6 mg, 289.7 μmol) was added diene **23** (269.9 mg, 1.361 mmol) at rt. The mixture was heated at 140°C. After 24 h, the reaction was cooled to 0°C and TBAF (1.4 mL, 1.4 mmol, 1M in THF) was added. After 10 min, the brown mixture was quenched with sat. aq. $NH_4Cl$ (20 mL), diluted with EtOAc (30 mL), washed with $H_2O$ (20 mL), and sat. aq. NaCl (2 x 20 mL). The dried ($Na_2SO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica, eluting with 0-20% EtOAc / Hexanes to give **88** (53.6 mg, 191.6 μmol, 66%) as a bright yellow solid. MP 136-138°C; IR (thin film) 3432, 3080, 2929, 1613, 1587, 1531, 1355, 1303 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.73 (dd, *J* = 8.1, 1.2, Hz, 1H), 7.44 (t, *J* = 8.1, 1H), 7.05 (d, 8.8 Hz, 1H), 6.56-6.50 (m, 2H), 3.74 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 157.8, 157.6, 151.5, 136.7, 133.5, 131.8, 130.9, 128.5, 122.1, 115.3, 107.4, 99.4, 55.6; HRMS (EI+) calcd. for $C_{13}H_{10}NO_4Cl$ (M+H) 279.0298, found 279.0293.



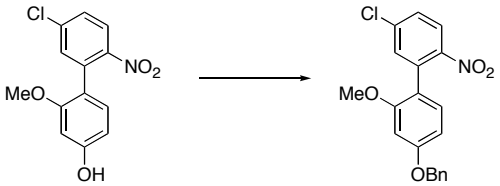

**88** **24**

**Chloride 24:** To a stirred solution of **88** (26.4 mg, 94.4 μmol) and dry DMF (50 μL) was added NaH (8.2 mg, 0.205 mmol, 60% dispersion in mineral oil) at 0°C. To this dark red solution was added BnBr (187 mg, 130 μL, 1.07 mmol). After 10 min, the yellow solution was quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (20 mL), washed with $H_2O$ (10 mL), and sat. aq. NaCl (2 x 10 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 0-10% $Et_2O$ / Hexanes to give **24** (18.1 mg, 48.9 μmol, 96%) as a bright yellow crystalline solid. MP 104-106°C; IR (thin film) 2959, 1614, 1583, 1530, 1245, 1037 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.72 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.53-7.34 (m, 6H), 7.12 (d, *J* = 8.3 Hz, 1H), 6.69 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.65 (d, *J* = 2.3 Hz, 1H), 5.11 (s, 2H), 3.73 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ160.9, 157.5, 151.5, 136.7, 136.7, 133.5, 131.8, 130.8, 128.7, 128.5, 128.2, 127.8, 122.2, 115.9, 105.4, 99.6, 70.3, 55.6; HRMS (EI+) calcd. for $C_{20}H_{16}NO_4Cl$ (M+) 369.0768, found 369.0760.




**13** **23** **89**

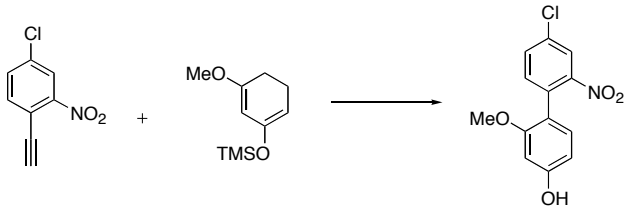
**Phenol 89:** To a pressure vessel containing **7** (106.8 mg, 588.2 μmol) was added diene **23** (364.7 mg, 1.839 mmol) at rt. The mixture was heated at 140°C. After 24 h, the reaction was cooled to 0°C and TBAF (1.8 mL, 1.8 mmol, 1M in THF) was added. After 10 min, the brown mixture was quenched with sat. aq. $NH_4Cl$ (20 mL), diluted with EtOAc (30 mL), washed with $H_2O$ (20 mL), and sat. aq. NaCl (2 x 20 mL). The dried ($Na_2SO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica, eluting with 0-20% EtOAc / Hexanes to give **89** (124.6 mg, 445.5 μmol, 76%) as a bright yellow solid. MP 178-181°C; IR (thin film) 3458, 1613, 1596, 1523, 1350, 1037 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$) δ 9.83 (s, 1H), 7.95 (dd, *J* = 8.4, Hz, 1H), 7.61 (dd, *J* = 8.4, 2.4, 1H), 7.51 (d, 2.4 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.50 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.45 (d, *J* = 2.0, 1H), 3.58 (s, 3H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) δ 160.2, 157.1, 148.3, 137.8, 134.8, 132.3, 130.9, 128.1, 126.2, 116.1, 108.4, 99.5, 55.4; HRMS (EI+) calcd. for $C_{13}H_{10}NO_4Cl$ (M+) 279.0298, found 279.0303.




**89** **25**

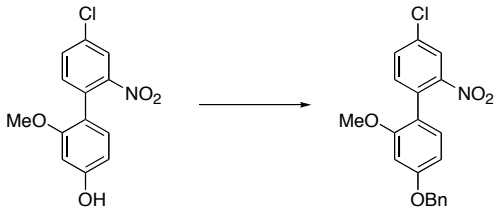
**Chloride 25:** To a stirred solution of **89** (28.9 mg, 103.3 μmol) and dry DMF (50 μL) was added NaH (12.0 mg, 300 μmol, 60% dispersion in mineral oil) at 0°C. To this dark red solution was added BnBr (186.9 mg, 130 μL, 1.07 mmol). After 10 min, the yellow solution was quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (30 mL), washed with $H_2O$ (10 mL), and sat. aq. NaCl (2 x 10 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting

with 0-10% $Et_2O$ / Hexanes to give **25** (36.1 mg, 97.6 μmol, 94%) as a bright yellow crystalline solid. MP 98-99°C; IR (thin film) 3062, 2941, 1612, 1582, 1526, 1273, 1040 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.58-7.34 (m, 7H), 7.25 (d, *J* = 8.4 Hz, 1H), 6.72 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.60 (d, *J* = 2.3 Hz, 1H), 5.14 (s, 2H), 3.70 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 160.93, 157.0, 148.0, 138.6, 136.6, 134.7, 132.4, 130.1, 128.7, 128.2, 127.7, 127.6, 125.4, 118.8, 106.0, 99.5, 70.3, 55.2; HRMS (EI+) calcd. for $C_{20}H_{16}NO_4Cl$ (M+) 369.0768, found 369.0762.



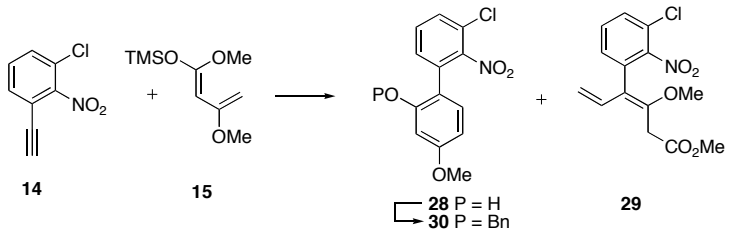

**8** **23** **90**

**Phenol 90:** To a pressure vessel containing **7** (103.0 mg, 567.3 μmol) was added diene **23** (353.4 mg, 1.782 mmol) at rt. The mixture was heated at 140°C. After 24 h, the reaction was cooled to 0°C and TBAF (1.8 mL, 1.8 mmol, 1M in THF) was added. After 10 min, the brown mixture was quenched with sat. aq. $NH_4Cl$ (20 mL), diluted with EtOAc (30 mL), washed with $H_2O$ (20 mL), and sat. aq. NaCl (2 x 20 mL). The dried ($Na_2SO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica, eluting with 0-20% EtOAc / Hexanes to give **90** (115.8 mg, 414.0 μmol, 73%) as a bright yellow solid. MP 90-92°C; IR (thin film) 3385, 1617, 1531, 1359, 1265, 1037 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$) δ 9.81 (s, 1H), 8.04 (d, *J* = 2.0 Hz, 1H), 7.81 (dd, *J* = 8.4, 2.0, 1H), 7.47 (d, 8.4 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.51 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 3.58 (s, 3H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) δ 160.1, 157.0, 150.1, 134.4, 133.2, 132.2, 131.5, 130.8, 124.1, 116.2, 108.4, 99.5, 55.3; HRMS (EI+) calcd. for $C_{13}H_{10}NO_4Cl$ (M) 279.0298, found 279.0293.



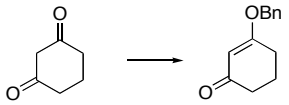

**90** **26**

**Chloride 26:** To a stirred solution of **90** (26.4 mg, 94.4 μmol) and dry DMF (50 μL) was added NaH (15.0 mg, 0.375 mmol, 60% dispersion in mineral oil) at 0°C. To this dark red solution was added BnBr (187 mg, 130 μL, 1.07 mmol). After 10 min, the yellow solution was quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (30 mL), washed with $H_2O$ (10 mL), and sat. aq. NaCl (2 x 10 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 0-10% $Et_2O$ / Hexanes to give **26** (32.2 mg, 87.1 μmol, 92%) as a bright yellow crystalline solid. MP 94-97°C; IR (thin film) 2933, 1613, 1532, 1357, 1261, 1036 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.2 Hz, 1H), 7.61 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.52-7.32 (m, 6H), 7.23 (d, *J* = 8.4 Hz, 1H), 6.72 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.60 (d, *J* = 2.3 Hz, 1H), 5.14 (s, 2H), 3.70 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 160.8, 156.9, 149.8, 136.6, 133.6, 133.3, 132.6, 131.3, 130.2, 128.7, 128.2, 127.7, 124.2, 118.8, 106.0, 99.5, 70.31, 55.2; HRMS (CI+) calcd. for $C_{20}H_{16}NO_4Cl$ (M+) 369.0768, found 369.0756.




**Enol Ether 29:** To a pressure vessel containing **14** (144 mg, 0.790 mmol) was added diene **15**[9] (642 mg, 3.17 mmol) and heated to 110˚C. After 24 h, the reaction was cooled to 0˚C, diluted with toluene (0.79 mL) and DABCO (357 mg, 3.17 mmol) was added. After 2 h, the reaction mixture was quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (25 mL), and washed with $H_2O$ (10 mL) and sat. aq. NaCl (10 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 15-35% EtOAc / Hexanes, to sequentially give impure **28** (40.0 mg) and impure **29** (44.5 mg) as a yellow oil. **29** was further purified by chromatography over silica gel containing silver nitrate, eluting with 10 – 20% EtOAc / Hexanes. **29**: IR (neat) 2915, 1735, 1537, 1027 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 1.2, 8.1 Hz, 1H), 7.48 (dd, *J* = 7.7, 8.1 Hz, 1H), 7.30 (dd, *J* = 1.2, 7.7 Hz, 1H), 7.01 (ddd, *J* = 6.8, 10.8, 17.6 Hz, 1H), 5.09 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 17.6 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.26 (d, *J* = 16.7 Hz, 1H), 3.03 (d, *J* = 16.7 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.7, 150.2, 149.8, 131.6, 131.4, 131.3, 130.9, 130.0, 125.1, 119.8, 115.8, 57.3, 52.3, 35.4; HRMS (EI+) calcd. for $C_{14}H_{14}NO_5Cl$ (M+H) 311.0560, found 311.0567.

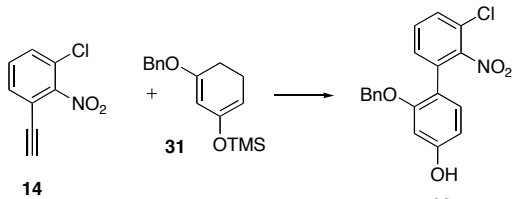
**Biaryl 30:** To a stirred solution of **28** (40.0 mg, 0.143 mmol) and DMF (0.900 mL) at 0˚C was added NaH (10.6 mg, 0.265 mmol, 60% in mineral oil). After bubbling ceased, BnBr (376 mg, 0.263 mL, 2.20 mmol) was added dropwise to the deep red solution. After 15 min, the reaction was warmed to rt. After 1 h, the reaction was quenched with sat. aq. $NH_4Cl$ (5 mL), diluted with EtOAc (15 mL), washed with $H_2O$ (15 mL) and sat. aq. NaCl (15 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 3-10% EtOAc / Hexanes, to give **30** (41.2 mg, 0.11 mmol, 14% over two steps) as a yellow solid. MP 110-111˚C; IR (neat) 2921, 1530 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 1.8, 8.0 Hz, 1H), 7.43 (dd, *J* = 7.6, 8.0 Hz, 1H), 7.36 (dd, *J* = 1.8, 7.6 Hz, 1H), 7.33-7.27 (m, 5H), 7.14 (dd, *J* = 1.7, 7.5 Hz, 1H), 6.56 (dd, *J* = 2.4, 7.5 Hz, 1H), 6.54 (dd, *J* = 1.7 Hz, 1H), 5.05 (s, 2H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.5, 156.7, 149.6, 136.6, 133.4, 131.0, 130.8, 130.2, 129.1, 128.5, 127.8, 126.8, 125.1, 117.4, 105.3, 100.7, 70.5, 55.4; HRMS (CI+) calcd. for $C_{20}H_{16}NO_4Cl$ (M+H) 370.0846, found 370.0849.




**Enone 92:** To a stirred solution of **91** (1.07 g, 9.53 mmol) and PhMe (48.0 mL) was added BnOH (1.96 mL, 2.06 g, 19.1 mmol), and *p*-TSA (45.4 mg, 0.238 mmol). The reaction flask was equipped with a Dean Stark trap and heated at 140˚C. After 12 h, the reaction was cooled to rt, concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 20 – 50% EtOAc / Hexanes to give known enone **92**[10] (1.65 g, 8.16 mmol, 86%) as a yellow crystalline solid. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.44-7.28 (m, 5H), 5.50 (s, 1H), 4.91 (s, 2H), 2.50 (t, *J* = 6.3 Hz, 2H), 2.39 (t, *J* = 6.3 Hz, 2H), 2.03 (q, *J* = 6.3 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 199.7, 177.5, 135.2, 128.7, 128.6, 127.9, 103.4, 70.5, 36.8, 29.1, 21.2.

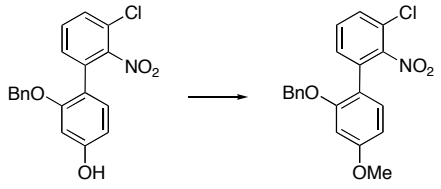

**92** **31**

**Diene 31:** To a flask containing LDA[11] (15.7 mL, 13.4 mmol, 0.86 M in THF / hexanes) was added a solution of **92** (2.56 g, 12.8 mmol) in THF (6.7 mL) at -78˚C. After 10 min, TMSCl (1.67 g, 1.95 mL, 15.3 mmol) was added. After 1 h, the reaction was warmed to rt, poured into a cold solution of aq. $NaHCO_3$ (50 mL, 5% w/v), extracted with $Et_2O$ (100 mL), and washed with $H_2O$ (75 mL) and sat. aq. NaCl (75 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* to give **31** (3.51 g, 12.8 mmol, 99%) as a pale yellow oil. IR (neat) 2943, 1605, 1361 $cm^{-1}$, $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.42-7.31 (m, 5H), 4.88 (s, 1H), 4.81 (s, 2H), 4.61-4.59 (m, 1H), 2.31-2.25 (m, 4H), 0.23 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 160.1, 149.0, 136.6, 128.5, 128.0, 127.7, 96.0, 94.7, 69.4, 27.4, 21.8, 0.21; HRMS (CI+) calcd. for $C_{16}H_{22}O_2Si$ (M+H) 275.1467, found, 275.1477.




**14** **93**

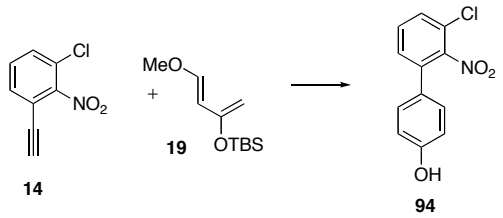
**Phenol 93:** To a pressure vessel containing **14** (1.88 g, 13.4 mmol) was added diene **31** (8.02 g, 29.2 mmol) and heated to 140˚C. After 5 h, the reaction was cooled to -30˚C, diluted with THF (20 mL) and TBAF (31.1 mL, 31.1 mmol, 1.0 M in THF) was added. After 15 min, the reaction was quenched with sat. aq. $NH_4Cl$ (30 mL), diluted with EtOAc (50 mL), and washed with $H_2O$ (30 mL) and sat. aq. NaCl (30 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 15-50% EtOAc / Hexanes, to give **93** (2.90 g, 8.16 mmol, 79%) as an orange oil. MP 98-100˚C; IR (neat) 3443, 1614, 1537 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.48 (dd, $J$ = 1.5, 8.0 Hz, 1H), 7.44 (dd, $J$ = 7.7, 8.0 Hz, 1H), 7.34 (dd, $J$ = 1.6, 7.7 Hz, 1H), 7.26-7.33 (m, 5H), 7.04 (d, $J$ = 8.2 Hz, 1H), 6.48 (d, $J$ = 2.3 Hz, 1H), 6.43 (dd, $J$ = 2.3, 8.2 Hz, 1H), 5.58 (s, 1H), 4.99 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 157.7, 156.8, 149.5, 136.5, 133.4, 131.1, 131.0, 130.4, 129.2, 128.5, 127.8, 126.8, 125.1, 117.1, 108.0, 101.1, 70.4; HRMS (CI+) calcd. for $C_{19}H_{14}NO_4Cl$ (M+H) 355.0611, found 355.0624.



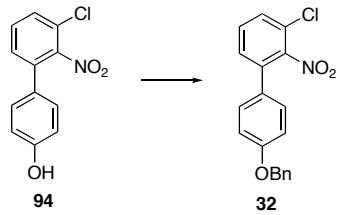

**93** **30**

**Chloride 30:** To a stirred solution of **93** (2.23 g, 6.27 mmol) and DMF (31.0 mL) at 0˚C, was added NaH (300 mg, 7.5 mmol, 60% in mineral oil). After bubbling ceased, MeI (0.780 mL, 12.5 mmol) was added dropwise to the deep red solution. After 30 min, the reaction mixture was warmed to rt. After an additional 20 min, the reaction was quenched with sat. aq. $NH_4Cl$ (20 mL), diluted with EtOAc (50 mL), and washed with $H_2O$ (20 mL) and sat. aq. NaCl (20 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by recrystallization with $Et_2O$ / Hexanes (2:1) to give **30** (1.68 g, 4.55 mmol, 73%) as a yellow solid. MP 110-111.5˚C; IR (neat) 2921, 1530 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, $J$ = 1.8, 8.0 Hz, 1H), 7.43 (dd, $J$ = 7.6, 8.0 Hz, 1H), 7.36 (dd, $J$ = 1.8, 7.6 Hz, 1H), 7.33-7.27 (m, 5H), 7.14 (dd, $J$ = 1.7, 7.5 Hz, 1H), 6.56 (dd, $J$ = 2.4, 7.5 Hz, 1H), 6.54 (dd, $J$ = 1.7 Hz, 1H), 5.05 (s, 2H), 3.80 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.5, 156.7, 149.6, 136.6, 133.4, 131.0, 130.8, 130.2, 129.1, 128.5, 127.8,

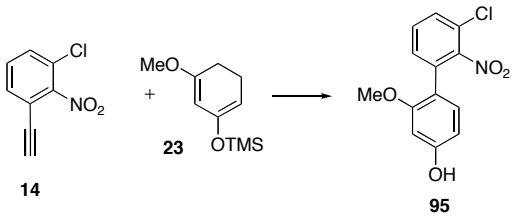
126.8, 125.1, 117.4, 105.3, 100.7, 70.5, 55.4; HRMS (CI+) calcd. for $C_{20}H_{16}NO_4Cl$ (M+H) 370.0846, found 370.0849.




**Phenol 94**: To a pressure vessel containing **14** (59.2 mg, 0.325 mmol) and PhMe (0.650 mL) was added diene **19** (277 mg, 0.308 mL, 1.30 mmol) and heated to 115°C. After 14 h, the reaction was cooled to $0^{°C}$ and TBAF (1.95 mL, 1.95 mmol, 1.0 M in THF) was added. After 15 min, the reaction was quenched with sat. aq. $NH_4Cl$ (8 mL), diluted with $Et_2O$ (15 mL), and washed with $H_2O$ (10 mL) and sat. aq. NaCl (10 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 20-50% EtOAc / Hexanes, to yield **94** (64.2 mg, 0.258 mmol, 78%) as a white crystalline solid. MP 132-134°C; IR (neat) 3518, 1610, 1534, 1459, 1369, 1199 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 2.1, 8.1 Hz, 1H), 7.48 (t, *J* = 8.1 Hz, 1H), 7.37 (dd, *J* = 2.1, 7.0 Hz, 1H), 7.27 (dt, *J* = 2.2, 8.8 Hz, 2H), 6.90 (dt, *J* = 2.2, 8.8 Hz, 2H), 5.19 (s, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 156.8, 149.4, 136.2, 131.1, 129.9, 129.9, 129.4, 128.2, 125.6, 116.3; HRMS (CI+) calcd. for $C_{12}H_8NO_3Cl$ (M+H) 250.0271, found 250.0269.

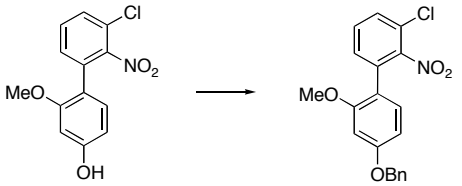



**Chloride 32:** To a stirred solution of **94** (34.0 mg, 0.140 mmol) and DMF (0.70 mL) at 0˚C, was added NaH (6.72 mg, 0.168 mmol, 60% in mineral oil). After bubbling ceased, BnBr (0.170 mL, 1.40 mmol) was added dropwise to the deep red solution. After 30 min, the reaction mixture was warmed to rt and stirred for 20 min. The reaction was quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (20 mL), and washed with $H_2O$ (10 mL) and sat. aq. NaCl (10 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 3-10% EtOAc / Hexanes to give **32** (46.3 mg, 0.136 mmol, 97%) as a white crystalline solid. MP 125-127˚C; IR (neat) 2927, 1537, 1249 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.49-7.42 (m, 5H), 7.39 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.37 (dd, *J* = 2.0, 6.8 Hz, 1H), 7.33 (dt, *J* = 2.0, 8.8 Hz, 2H), 7.06 (dt, *J* = 2.0, 8.8 Hz, 2H), 5.13 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 159.5, 149.1, 136.6, 135.8, 130.6, 129.5, 129.3, 128.9, 128.7, 128.2, 127.9, 127.6, 125.2, 115.3, 70.1; HRMS (EI+) calcd. for $C_{19}H_{14}NO_3Cl$ (M+H) 339.0662, found 339.0670.



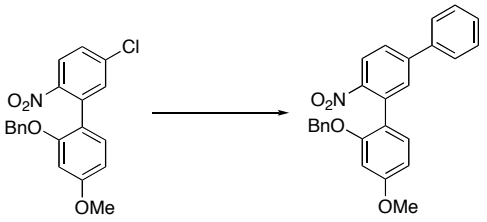

**Phenol 95:** To a pressure vessel containing **14** (87.1 mg, 0.480 mmol) was added diene **23**[12,13] (286 mg, 1.44 mmol) and heated to 140˚C. After 3.5 h, the reaction was cooled to rt and the crude oil was

purified by chromatography over silica gel, eluting with 5-40% EtOAc / Hexanes, to give **95** (103 mg, 0.370 mmol, 76%) as an orange solid. IR (neat) 3385, 2924, 1534 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 1.6, 8.2 Hz, 1H), 7.46 (dd, *J* = 7.5, 8.2 Hz, 1H), 7.33 (dd, *J* = 1.6, 7.5 Hz, 1H), 7.08 (dd, *J* = 2.4, 6.5 Hz, 1H), 6.49 (s, 1H), 6.48 (dd, *J* = 2.4, 6.5 Hz, 1H) 4.94 (s, 2H), 3.79 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 157.7, 150.9, 133.6, 131.1, 130.8, 130.5, 129.2, 125.3, 124.9, 115.5, 107.5, 99.3, 55.4; HRMS (EI+) calcd. For $C_{13}H_{10}ClNO_4$ (M+H) 279.0298, found 279.0288.



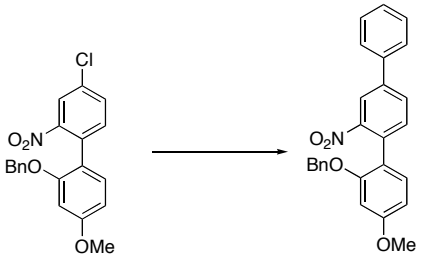

**95** **33**

**Chloride 33:** To a stirred solution of **95** (54.0 mg, 0.190 mmol) and DMF (0.97 mL) at 0˚C, was added NaH (9.26 mg, 0.232 mmol, 60% in mineral oil). After bubbling ceased, BnBr (0.230 mL, 1.93 mmol) was added dropwise to the deep red solution. After 30 min, the reaction mixture was warmed to rt and stirred for 1 h. The reaction was quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (20 mL), and washed with $H_2O$ (10 mL) and sat. aq. NaCl (10 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 3-10% EtOAc / Hexanes to give **33** (71.3 mg, 0.190 mmol, 99%) as a yellow solid. MP 126-127˚C; IR (neat) 1611, 1534, 1200 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 1.5, 8.1 Hz, 1H), 7.48-7.37 (m, 6H), 7.34 (dd, *J* = 1.5, 7.6 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.65 (dd, *J* = 2.2, 8.4 Hz, 1H), 6.62 (d, *J* = 2.2 Hz, 1H), 5.11 (s, 2H), 3.74 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 160.9, 157.5, 149.4, 136.6, 133.6, 130.9, 130.8, 130.5, 129.2, 128.7, 128.2, 127.7, 125.4, 117.4, 105.7, 99.7, 70.3, 55.4; HRMS (EI+) calcd. for $C_{20}H_{16}NO_4Cl$ (M+H) 369.0768, found 369.0771.



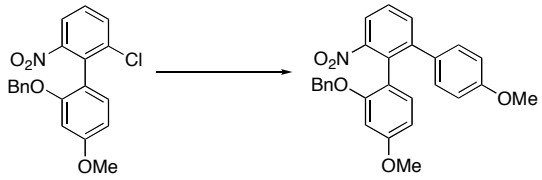

**17** **35**

**Triaryl 35:** To a pressure vessel was added **17** (36.7 mg, 99.2 μmol), $PhB(OH)_2$ (53.0 mg, 435 μmol), $Cs_2CO_3$ (82.9 mg, 254 μmol), $Pd_2(dba)_3$ (3.4 mg, 3.8 μmol), $PCy_3$ (8.1 mg, 29 μmol), and dry dioxane (300 μL). The solution was sealed under Ar and heated to 80°C. After 24 h, the mixture was filtered over a pad of Celite-®, eluting with $Et_2O$ (60 mL) and concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 10% $Et_2O$/hexanes, to give **35** (37.3 mg, 96.1 μmol, 84%) as a bright yellow crystalline solid. MP 127-131°C; IR (thin film) 3067, 2932, 1611, 1586, 1519, 1348, 1050 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.75-7.57 (m, 4H), 7.57-7.4 (m, 3H), 7.4-7.2(m, 6H), 6.67 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.60 (d, *J* = 2.0, 1H), 5.05(s, 2H), 3.86 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.2, 156.3, 148.4, 145.6, 139.0, 136.5, 133.8, 131.4, 130.3, 129.1, 128.6, 128.5, 127.8, 127.4, 127.1, 126.1, 124.8, 120.6, 105.5, 100.4, 70.7, 55.4; HRMS (EI+) calcd. for $C_{26}H_{21}NO_4$ (M+) 411.1471, found 411.1475.



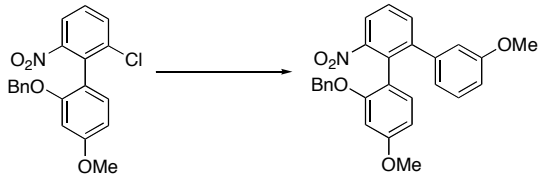

**18** **36**

**Triaryl 36:** To a pressure vessel was added **18** (13.2 mg, 35.7 μmol), $PhB(OH)_2$ (17.6 mg, 144 μmol), $Cs_2CO_3$ (24.8 mg, 76.1 μmol), $Pd_2(dba)_3$ (0.1 mg, 1.2 μmol), $PCy_3$ (1.1 mg, 3.9 μmol), and dry dioxane (60 μL). The solution was sealed under Ar and heated to 80°C. After 24 h, the mixture was filtered over a pad of Celite-®, eluting with $Et_2O$ (40 mL) and concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 0-10% $Et_2O$/hexanes, to give **36** (12.2 mg, 31.5 μmol, 88%) as a bright yellow crystalline solid. MP 130-2°C; IR (thin film) 3054, 2925, 1610, 1520, 1356, 1091, 1024 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 1.9 Hz, 1H), 7.86 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.74-7.63 (m, 2H), 7.58-7.42 (m, 4H), 7.38-7.23 (m, 6H), 6.67 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.58 (d, *J* = 2.3 Hz, 1H), 5.04 (s, 2H), 3.85, (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.1, 156.3, 149.9, 140.9, 138.6, 136.5, 133.2, 131.8, 130.8, 130.3, 129.1, 128.5, 128.3, 127.8, 127.1, 127.0, 122.5, 120.1, 105.5, 100.4, 70.7, 55.4; HRMS (EI+) calcd. for $C_{26}H_{21}NO_4$ (M+) 411.1471, found 411.1455.



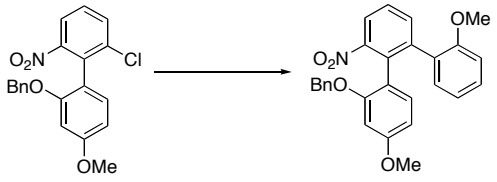

**16** **38**

**Triaryl 38:** To a pressure vessel was added **16** (43.8 mg, 118 μmol), *p*-MeO-$C_6H_4$-$B(OH)_2$ (68.9 mg, 453 μmol), $Cs_2CO_3$ (69.6 mg, 214 μmol), $Pd_2(dba)_3$ (2.3 mg, 2.5 μmol), $PCy_3$ (4.3 mg, 15 μmol), and dry dioxane (250 μL). The solution was sealed under Ar and heated to 80°C. After 24 h, the mixture was filtered over a pad of Celite-®, eluting with $Et_2O$ (60 mL) and concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 10% $Et_2O$/hexanes, to give **38** (47.0 mg, 107 μmol, 90%) as a bright yellow crystalline solid. MP 131-133°C; IR (thin film) 2957, 2923, 2853, 1610, 1581, 1527, 1514, 1356, 1246 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.61 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.40-7.24 (m, 3H), 7.18 (d, *J* = 6.3 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.73 (d, *J* = 8.9 Hz, 2H), 6.41 (d, *J* = 2.3 Hz, 1H), 6.39 (dd, *J* = 8.3, 2.4 Hz, 1H), 4.98 (d, *J* = 12.6 Hz, 1H), 4.88 (d, *J* = 12.5 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 160.6, 158.6, 156.8, 151.3, 144.3, 137.0, 133.9, 132.5, 131.5, 130.9, 130.4, 128.4, 127.7, 127.6, 126.7, 122.2, 117.7, 113.3, 104.9, 99.9, 70.0, 55.2, 55.2; HRMS (CI+) calcd. for $C_{27}H_{24}NO_5$ (M+H) 442.1654, found 442.1668.



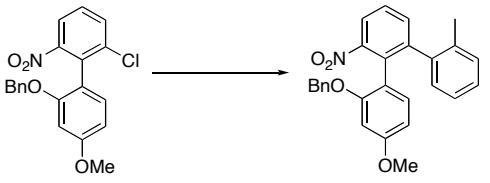

**16** **39**

**Triaryl 39:** To a pressure vessel was added **16** (47.3 mg, 128 μmol), *m*-MeO-$C_6H_4$-$B(OH)_2$ (65.5 mg, 431 μmol), $Cs_2CO_3$ (92.0 mg, 282 μmol), $Pd_2(dba)_3$ (2.9 mg, 3.2 μmol), $PCy_3$ (1.8 mg, 6.4 μmol), and dry dioxane (300 μL). The solution was sealed under Ar and heated to 80°C. After 24 h, the mixture was filtered over a pad of Celite-®, eluting with $Et_2O$ (60 mL) and concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 10% $Et_2O$/hexanes, to give **39** (51.4 mg, 116 μmol, 91%) as a crystalline yellow, 1:1 mixture of atropisomers. MP 127-129°C; IR (thin film) 2929, 1612, 1583, 1528, 1512, 1360, 1227, 1042, 753 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.91-7.85 (m, 1H), 7.69-7.63 (m, 1H), 7.57-7.50 (m, 1H), 7.39-7.19 (m, 5H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.89-6.84 (m, 1H), 6.80-6.76 (m, 1H), 7.64-6.68 (m, 1H), 6.63-6.58 (m, 1H), 6.47-6.38 (m, 2H), 4.99 (d, *J* = 12.4 Hz, 1H), 4.87 (d, *J* = 12.4 Hz, 1H), 3.75 (s, 3H), 3.60 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 160.8, 158.9, 156.8, 151.2, 144.4, 141.4, 137.0, 133.8, 131.4, 131.0, 128.8, 128.4, 127.8, 127.6, 126.7, 122.6, 121.8, 117.6, 114.4, 113.4, 104.9, 99.9, 70.1, 55.3, 55.0; HRMS (CI+) calcd. for $C_{27}H_{23}NO_5$ 441.1576, found 441.1577.




**16** **40**

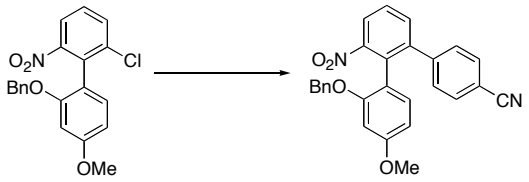
**Triaryl 40:** To a pressure vessel was added **16** (42.3 mg, 114 μmol), *o*-MeO-$C_6H_4$-$B(OH)_2$ (64.4 mg, 432 μmol), $Cs_2CO_3$ (74.3 mg, 228 μmol), $Pd_2(dba)_3$ (2.5 mg, 2.7 μmol), $PCy_3$ (3.3 mg, 12 μmol), and dry dioxane (230 μL). The solution was sealed under Ar and heated to 80°C. After 24 h, the mixture was filtered over a pad of Celite-®, eluting with $Et_2O$ (60 mL) and concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 10% $Et_2O$/hexanes, to give **40** (40.4 mg, 91.5 μmol, 80%) as a bright yellow crystalline solid. MP 123-124°C; IR (thin film) 3003, 2954, 1613, 1582, 1527, 1512, 1358, 1274, 1242, 1039, 1026, 755 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.63-7.55 (br, 1H), 7.50, (t, *J* = 8.0 Hz, 1H), 7.39-7.16 (m, 6H), 7.04-6.59 (br, 4H), 6.48-6.21 (br, 2H), 4.98, (d, *J* = 12.4 Hz, 1H), 4.92 (d, *J* = 12.4 Hz, 1H), 3.719 (s, 3H), 3.5-3.2 (br, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 160.4, 156.5, 156.1, 150.7, 141.7, 137.0, 134.8, 132.3, 131.0, 130.9, 128.9, 128.4, 127.8, 127.6, 127.3, 126.7, 122.7, 120.0, 118.1, 110.3, 104.2, 99.5, 70.0, 55.2, 55.0; HRMS (FAB+) calcd. for $C_{27}H_{23}NO_5$ 441.1576, found 441.1595.




**16** **41**

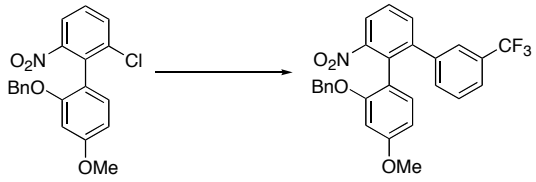
**Triaryl 41:** To a pressure vessel was added **16** (39.0 mg, 105 μmol), *o*-Me-$C_6H_4$-$B(OH)_2$ (69.5 mg, 511 μmol), $Cs_2CO_3$ (112.3 mg, 344.7 μmol), $Pd_2(dba)_3$ (2.4 mg, 2.6 μmol) and dry dioxane (300 μL). The solution was sealed under Ar and heated to 80°C. After 24 h, the mixture was filtered over a pad of

Celite-®, eluting with $Et_2O$ (60 mL) and concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 10% $Et_2O$/hexanes, to give **41** (40.0 mg, 93.9 μmol, 89%) as a crystalline yellow, *1:1 mixture of atropisomers*. MP 72-75°C; IR (thin film) 3062, 2924, 1613, 1578, 1528, 1512, 1269, 1049, 757 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.95-7.87 (m, 1H), 7.57-7.45 (m, 2H), 7.39-7.10 (m, 8H), 7.06-6.89 (m, 1H), 6.83-6.72 (m, 1H), 6.37 (dd, *J* = 10.0, 2.4 Hz, 1H), 6.28 (dt, *J* = 8.5, 2.3 Hz, 1H), 5.05-4.85 (m, 2H), 3.71 (s, 3H), 2.19 (s, 1.3 H), 1.80 (s, 1.7 H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 160.5, 160.4, 156.6, 156.3, 151.2, 151.1, 144.4, 144.4, 139.5, 139.4, 137.0, 136.8, 136.1, 135.1, 134.5, 134.3, 132.2, 131.8, 131.5, 130.4, 130.1, 129.7, 129.6, 128.5, 128.4, 127.7, 127.6, 127.4, 127.4, 127.3, 126.8, 126.7, 125.1, 125.0, 122.7, 122.6, 117.8, 117.0, 104.6, 104.4, 99.5, 70.1, 70.0, 55.1, 20.4, 19.3; HRMS (EI+) calcd. for $C_{27}H_{23}NO_4$ 425.1627, found 425.1612.




**16** **42**

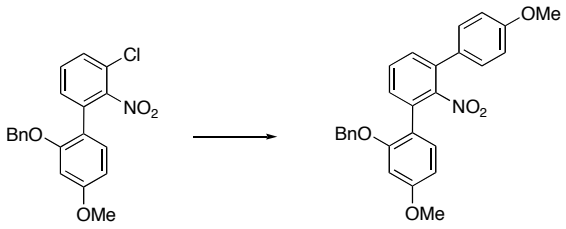
**Triaryl 42:** To a pressure vessel was added **16** (41.0 mg, 111 μmol), *p*-CN-$C_6H_4$-$B(OH)_2$ (64.2 mg, 437 μmol), KF (58.4 mg, 1.00 mmol), Pd[$^t$Bu$_3$P]$_2$ (4.0 mg, 7.8 μmol) and NMP (300 μL). The solution was sealed under Ar and heated to 80°C. After 24 h, the mixture was filtered over a pad of Celite-®, eluting with $Et_2O$ (60 mL) and concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 10% $Et_2O$/hexanes, to give **42** (40.0 mg, 91.5 μmol, 80%) as a bright yellow crystalline solid. MP 142-144°C; IR (thin film) 2950, 2918, 2228, 1610, 1582 1531, 1513, 1272, 1242, 1048, 737 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.93 (t, *J* = 4.8 Hz, 1H), 7.85-7.78 (m, 1H), 7.75-7.70 (m, 1H), 7.60-7.54 (m, 2H), 7.50-7.45 (m, 2H), 7.37-7.28 (m, 1H), 7.19-7.10 (m, 4H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.42 (d, *J* = 2.3 Hz, 1H), 6.39 (dd, *J* = 8.4, 2.3 Hz, 1H), 4.96 (d, *J* = 12.4 Hz, 1H), 4.84 (d, *J* = 12.4 Hz, 1H), 3.77 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.1, 156.6, 151.2, 144.9, 142.7, 136.6, 133.3, 132.9, 131.6, 131.3, 130.0, 128.5, 128.2, 127.8, 126.8, 123.5, 118.7, 116.6, 110.9, 105.1, 100.0, 70.1, 55.3; HRMS (CI+) calcd. for $C_{27}H_{20}N_2O_4$ 436.2423, found 436.1426.




**16** **45**

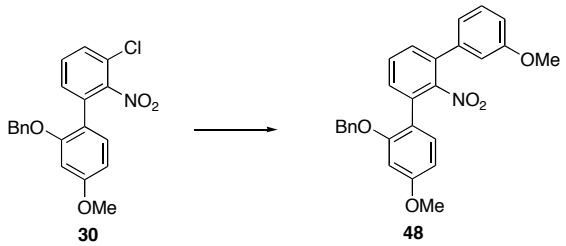
**Triaryl 45:** To a pressure vessel was added **16** (110.3 mg, 298.2 μmol), *m*-$CF_3$-$C_6H_4$-$B(OH)_2$ (235.8 mg, 1.241 mmol), KF (155.5 mg, 2.676 mmol), Pd[$^t$Bu$_3$P]$_2$ (9.0 mg, 18 μmol) and NMP (600 μL). The solution was sealed under Ar and heated to 80°C. After 48 h, the mixture was filtered over a pad of Celite-®, eluting with $Et_2O$ (60 mL) and concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 50-75% PhMe/hexanes, to give **45** (100.2 mg, 229.6 μmol, 77%) as a bright yellow crystalline solid. MP 121-124°C; IR (thin film) 3067, 2938, 1613, 1582, 1531, 1513, 1359, 1335, 1271, 1061, 756 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.93, (dd, *J* = 8.0, 1.4 Hz, 1H), 7.63 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.57 (t, *J* = 7.8, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.36-7.20 (m, 8H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.42 (d, *J* = 2.2 Hz, 1H), 6.39 (dd, *J* = 8.3, 2.2 Hz, 1H), 4.97 (d, *J* = 12.4 Hz, 1H), 4.86 (d, *J* = 12.4 Hz, 1H), 3.74 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.1, 156.7, 151.2, 143.1, 140.7, 136.7, 133.5, 132.5, 131.4, 131.3, 130.0 (q, $J_{(C-F)}$= 32 Hz), 128.4, 128.2, 128.1, 127.7, 126.7, 126.1 (q, $J_{(C-F)}$= 4

Hz), 123.9 (q, $J_{(C\text{-}F)}$= 273 Hz), 123.9 (q, $J_{(C\text{-}F)}$= 4 Hz), 123.2, 122.6, 119.9, 116.9, 105.1, 99.9, 70.1, 55.3; HRMS (EI+) calcd. for $C_{27}H_{20}F_3NO_4$ 479.1344, found 479.1334.



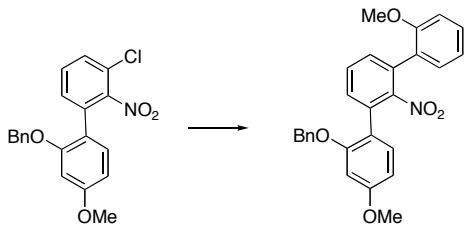

**30** **47**

**Triaryl 47:** To a pressure vessel containing **30** (41.9 mg, 0.110 mmol), was sequentially added KF (57.4 mg, 0.990 mmol), *p*-OMe-$C_6H_4$-$B(OH)_2$ (68.9 mg, 0.450 mmol), ($t$-$Bu_3P)_2Pd$ (2.8 mg, 0.0060 mmol), and NMP (1.10 mL). The solution was sealed under Ar and heated to 80˚C. After 48 h, the reaction was quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (25 mL), and washed with $H_2O$ (20 mL) and sat. aq. NaCl (20 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 5-20% EtOAc / Hexanes to give **47** (42.0 mg, 0.0950 mmol, 86%) as a yellow crystalline solid. MP 102-103˚C; IR (neat) 2927, 1608, 1530, 1246 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.54 (t, $J$ = 7.6 Hz, 1H), 7.41 (d, $J$ = 7.6 Hz, 2H), 7.36 (dt, $J$ = 2.0, 3.2, 8.4 Hz, 2H), 7.36-7.27 (m, 5H), 7.20 (d, $J$ = 8.4 Hz, 1H), 6.98 (dt, $J$ = 1.6, 3.2, 8.4 Hz, 2H), 6.57 (dd, $J$ = 2.4, 8.4 Hz, 1H), 6.56 (d, $J$ = 2.4 Hz, 1H), 5.08 (s, 2H), 3.87 (s, 3H), 3.81 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.2, 159.7, 156.8, 150.4, 137.0, 134.2, 131.7, 131.1, 130.9, 130.0, 129.5, 129.4, 129.3, 128.4, 127.6, 126.8, 118.6, 114.2, 105.2, 100.8, 70.5, 55.4, 55.3; HRMS (TOF-MS/ES+) calcd. for $C_{27}H_{23}NO_5$ (M+Na) 464.1474, found 464.1460.



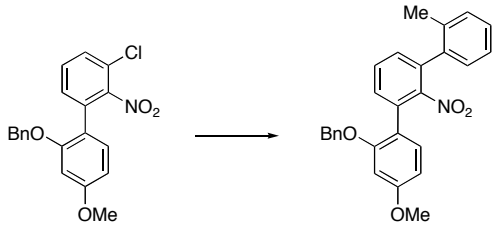

**30** **48**

**Triaryl 48:** To a pressure vessel containing **30** (23.4 mg, 0.0630 mmol), was sequentially added KF (32.9 mg, 0.570 mmol), *m*-OMe-$C_6H_4$-$B(OH)_2$ (38.3 mg, 0.250 mmol), ($t$-$Bu_3P)_2Pd$ (1.6 mg, 0.0030 mmol), and NMP (0.63 mL). The solution was sealed under Ar and heated to 80˚C. After 48 h, the reaction was quenched with sat. aq. $NH_4Cl$ (10 mL), diluted with EtOAc (25 mL), and washed with $H_2O$ (20 mL) and sat. aq. NaCl (20 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 5-20% EtOAc / Hexanes to give **48** (17.9 mg, 0.0410 mmol, 64%) as a yellow crystalline solid. MP 107-108˚C; IR (neat) 3063, 2930, 1608, 1534 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, $J$ = 7.6, 7.7 Hz, 1H), 7.45 (dd, $J$ = 1.4, 5.2 Hz, 1H), 7.43 (dd, $J$ = 1.4, 5.2 Hz, 1H), 7.38-7.27 (m, 6H), 7.21 (d, $J$ = 8.4 Hz, 1H), 7.00 (d, $J$ = 7.6 Hz, 1H), 6.97 (dd, $J$ = 2.0, 4.0 Hz, 2H), 6.58 (dd, $J$ = 2.4, 8.4 Hz, 1H), 6.56 (d, $J$ = 2.4 Hz, 1H), 5.07 (s, 2H), 3.85 (s, 3H), 3.82 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.2, 159.6, 156.8, 150.3, 138.4, 136.9, 134.4, 131.7, 131.6, 130.9, 129.8, 129.7, 129.6, 128.4, 127.6, 126.8, 120.5, 118.6, 114.2, 113.6, 105.2, 100.8, 70.5, 55.4, 55.3; HRMS (EI+) calcd. for $C_{27}H_{23}NO_5$ (M+H) 441.1576, found 441.1569.



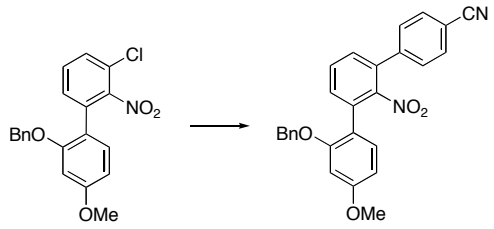

**30** **49**

**Triaryl 49:** To a pressure vessel containing **30** (36.2 mg, 0.0980 mmol) was sequentially added KF (51.2 mg, 0.880 mmol), *o*-OMe-$C_6H_4$-$B(OH)_2$ (62.3 mg, 0.390 mmol), and ($t$-$Bu_3P)_2Pd$ (2.5 mg, 0.0050 mmol), and NMP (0.98 mL). The solution was sealed under Ar and heated to 80˚C. After 24 h, the reaction was quenched with sat. aq. $NH_4Cl$ (5 mL), diluted with EtOAc (15 mL), and washed with $H_2O$ (5 mL) and sat. aq. NaCl (5 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 3-10% EtOAc / Hexanes to give **49** (19.1 mg, 0.0430 mmol, 44%) as a pale yellow solid. MP 156-157˚C; IR (neat) 2924, 1610, 1530 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, $J$ = 7.6, 8.0 Hz, 1H), 7.41 (dd, $J$ = 7.6, 8.0 Hz, 3H), 7.34-7.25 (m, 7H), 7.08 (t, $J$ = 7.6 Hz, 1H), 6.96 (d, $J$ = 8.4 Hz, 1H), 6.61 (dd, $J$ = 2.0, 8.4 Hz, 1H), 6.53 (d, $J$ = 2.0 Hz, 1H), 5.04 (s, 2H), 3.81 (s, 3H), 3.72 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.0, 156.7, 156.4, 150.4, 137.0, 132.3, 132.2, 131.5, 130.9, 130.8, 130.7, 130.4, 130.1, 129.7, 128.4, 127.5, 126.7, 120.9, 119.8, 111.0, 105.4, 100.7, 70.5, 55.4, 55.3; HRMS (FAB+) calcd. for $C_{27}H_{23}NO_5$ (M+H) 441.1576, found 441.1613.



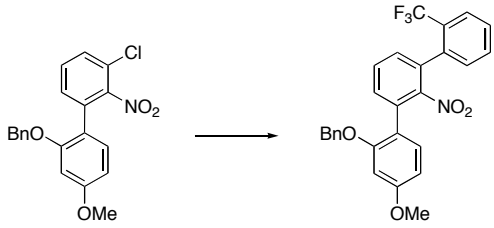

**30** **50**

**Triaryl 50:** To a pressure vessel containing **30** (59.5 mg, 0.160 mmol) was sequentially added KF (83.5 mg, 1.44 mmol), *o*-Me-$C_6H_4$-$B(OH)_2$ (87.0 mg, 0.640 mmol), ($t$-$Bu_3P)_2Pd$ (4.1 mg, 0.0080 mmol), and NMP (1.60 mL). The solution was sealed under Ar and heated to 80˚C. After 48 h, the reaction was quenched with sat. aq. $NH_4Cl$ (5 mL), diluted with EtOAc (20 mL), and washed with $H_2O$ (10 mL) and sat. aq. NaCl (10 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 3-10% EtOAc / Hexanes followed by recrystallization with $Et_2O$ / Hexanes (1:2) to give **50** (22.8 mg, 0.0540 mmol, 34%) as a pale yellow solid. MP 126-127˚C; IR (neat) 3062, 2860, 1617, 1531 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.53 (t, $J$ = 7.6 Hz, 1H), 7.42 (dd, $J$ = 1.6, 8.0 Hz, 1H), 7.32-7.26 (m, 8H), 7.24 (d, $J$ = 8.0 Hz, 1H), 7.19 (dd, $J$ = 2.0, 6.8 Hz, 1H), 7.16 (dd, $J$ = 1.6, 8.0 Hz, 1H), 6.58 (dd, $J$ = 2.4, 8.4 Hz, 1H), 6.56 (d, $J$ = 2.4 Hz, 1H), 5.02 (s, 2H), 3.82 (s, 3H), 2.16 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.2, 156.6, 150.6, 136.8, 136.5, 134.5, 131.7, 131.4, 131.0, 130.0, 129.8, 129.5, 128.8, 128.5, 128.4, 128.3, 127.7, 127.0, 125.5, 118.9, 105.3, 100.5, 70.4, 55.4, 20.1; HRMS (TOF/ES+) calcd. for $C_{27}H_{23}NO_4$ (M+Na) 448.1525, found 448.1512.



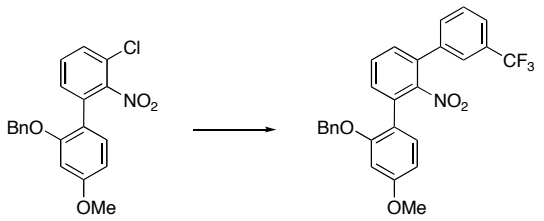

**30** **51**

**Triaryl 51:** To a pressure vessel containing **30** (48.6 mg, 0.130 mmol), was sequentially added KF (68.4 mg, 1.18 mmol), *p*-CN-$C_6H_4$-$B(OH)_2$ (76.1 mg, 0.520 mmol), ($t$-$Bu_3P)_2Pd$ (3.4 mg, 0.0070 mmol), and NMP (1.30 mL). The solution was sealed under Ar and heated to 80˚C. After 24 h, the reaction was quenched with sat. aq. $NH_4Cl$ (5 mL), diluted with EtOAc (15 mL), and washed with $H_2O$ (5 mL) and sat. aq. NaCl (5 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 5-20% EtOAc / Hexanes to give **51** (34.8 mg, 0.0800 mmol, 61%) as a pale yellow solid. MP 178-179.5˚C; IR (neat) 2921, 2223, 1610, 1530 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.75 (d, $J$ = 8.0 Hz, 2H), 7.61 (dd, $J$ = 8.0, 7.6 Hz, 1H), 7.52 (d, $J$ = 8.0 Hz, 2H), 7.51 (d, $J$ = 7.6 Hz, 1H), 7.38 (dd, $J$ = 1.2, 7.6 Hz, 1H), 7.34-7.28 (m, 5H), 7.20 (d, $J$ = 8.4 Hz, 1H), 6.60 (dd, $J$ = 2.4, 8.4 Hz, 1H), 6.57 (d, $J$ = 2.4 Hz, 1H), 5.06 (s, 2H), 3.82 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.4, 156.6, 149.9, 141.9, 136.8, 132.9, 132.7, 132.5, 132.4, 130.8, 130.1, 129.4, 128.9, 128.5, 127.7, 126.8, 118.5, 118.1, 112.4, 105.4, 100.6, 70.4, 55.4; HRMS (FAB+) calcd. for $C_{27}H_{20}N_2O_4$ (M+) 436.1423, found 436.1440.



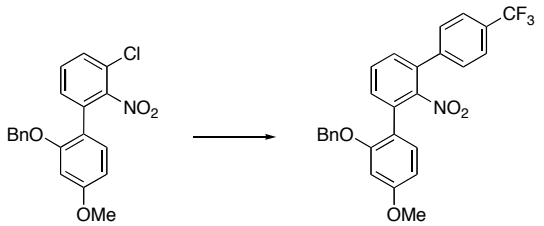

**30** **53**

**Triaryl 53:** To a pressure vessel containing **30** (36.2 mg, 0.0980 mmol), was sequentially added KF (51.2 mg, 0.880 mmol), *o*-$CF_3$-$C_6H_4$-$B(OH)_2$ (74.5 mg, 0.390 mmol), ($t$-$Bu_3P)_2Pd$ (2.5 mg, 0.0050 mmol), and NMP (0.98 mL). The solution was sealed under Ar and heated to 80˚C. After 24 h, the reaction was quenched with sat. aq. $NH_4Cl$ (5 mL), diluted with EtOAc (15 mL), and washed with $H_2O$ (10 mL) and sat. aq. NaCl (10 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 3-5% EtOAc / Hexanes followed by recrystallization with $Et_2O$ / Hexanes (2:1) to give **55** (10.1 mg, 0.0210 mmol, 22%) as a yellow crystalline solid. MP 102-104˚C; IR (neat) 3063, 2933, 1530 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.78 (dd, $J$ = 2.4, 7.2 Hz, 1H), 7.57-7.52 (m, 2H), 7.47 (dd, $J$ = 1.8, 7.8 Hz, 1H), 7.34-7.28 (m, 5H), 7.24 (d, $J$ = 8.4 Hz, 1H), 6.59 (dd, $J$ = 2.4, 8.4 Hz, 1H), 6.55 (d, $J$ = 2.4 Hz, 1H), 5.01 (s, 2H), 3.82 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.2, 156.6, 150.1, 136.7, 135.4, 132.3, 132.1, 131.3, 131.2, 131.1, 130.9, 129.9, 129.8, 129.3, 128.5, 128.4, 127.6, 126.9, 126.4, 126.3, 119.0, 105.4, 100.5, 70.5, 55.4; HRMS (EI+) calcd. for $C_{27}H_{20}F_3NO_4$ (M+) 479.1344, found 479.1323.



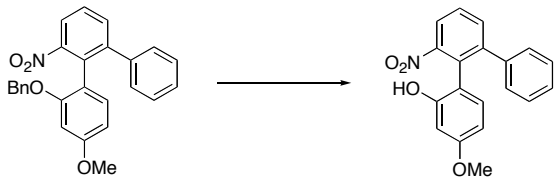

**30** **54**

**Triaryl 54:** To a pressure vessel containing **30** (39.4 mg, 0.107 mmol), was sequentially added KF (55.9 mg, 0.960 mmol), *m*-$CF_3$-$C_6H_4$-$B(OH)_2$ (81.3 mg, 0.430 mmol), (*t*-$Bu_3P)_2Pd$ (2.7 mg, 0.0050 mmol), and NMP (1.07 mL). The solution was sealed under Ar and heated to 80˚C. After 48 h, the reaction was quenched with sat. aq. $NH_4Cl$ (5 mL), diluted with EtOAc (15 mL), and washed with $H_2O$ (5 mL) and sat. aq. NaCl (5 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 3-5% EtOAc / Hexanes to give **54** (36.3 mg, 0.0800 mmol, 71%) as a pale yellow oil. IR (neat) 2921, 1527, 1339 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.69-7.67 (m, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 5.7 Hz, 1H), 7.48 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.39 (dd, *J* = 1.2, 7.5 Hz, 1H), 7.35-7.25 (m, 6H), 7.20 (d, *J* = 8.4 Hz, 1H), 6.58 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 5.05 (s, 2H), 3.81 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 161.3, 156.8, 150.2, 137.9, 136.8, 133.2, 132.3, 132.2, 131.4, 131.3, 130.9, 130.2, 129.9, 129.8, 129.1, 128.4, 127.7, 126.9, 125.3, 125.2 (q, *J* = 3.8 Hz, 1C), 118.3, 105.3, 100.6, 70.5, 55.4; HRMS (EI+) calcd. for $C_{27}H_{20}F_3NO_4$ (M+) 479.1344, found 479.1324.



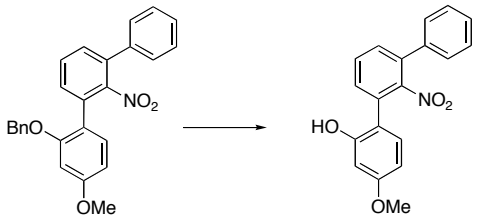

**30** **55**

**Triaryl 55:** To a pressure vessel containing **30** (48.5 mg, 0.130 mmol), was sequentially added KF (68.4 mg, 1.18 mmol), *p*-$CF_3$-$C_6H_4$-$B(OH)_2$ (99.5 mg, 0.520 mmol), (*t*-$Bu_3P)_2Pd$ (3.4 mg, 0.0070 mmol), and NMP (1.31 mL). The solution was sealed under Ar and heated to 80˚C. After 24 h, the reaction was quenched with sat. aq. $NH_4Cl$ (5 mL), diluted with EtOAc (15 mL), and washed with $H_2O$ (5 mL) and sat. aq. NaCl (5 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 5-20% EtOAc / Hexanes to give **55** (37.5 mg, 0.0780 mmol, 60%) as a yellow crystalline solid. MP 113-114˚C; IR (neat) 2918, 1527, 1323 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.49 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.39 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.33-7.27 (m, 5H), 7.20 (d, *J* = 8.3 Hz, 1H), 6.58 (dd, *J* = 2.4, 8.3 Hz, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 5.06 (s, 2H), 3.81 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.3, 156.7, 150.2, 140.8, 136.8, 133.3, 132.4, 132.2, 130.8, 130.3, 129.9, 129.6, 128.6, 128.5, 127.7, 126.8, 125.7, 125.6, 118.3, 105.3, 100.7, 70.5, 55.4; HRMS (EI+) calcd. for $C_{27}H_{20}NO_4F_3$ (M+) 479.1344, found 479.1353.



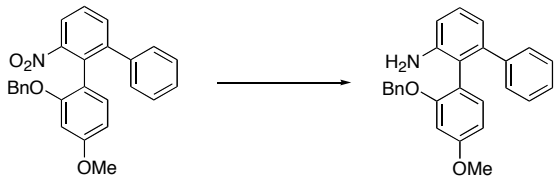

**34** **56**

**Phenol 56:** To a stirred solution of **34** (45.3 mg, 110 μmol) in $CH_2Cl_2$ (98 μL) was added $BCl_3$ (600 μL, 600 μmol, 1.0 M in heptane) at 0˚C. After 4 h, the reaction was quenched with MeOH (2.0 mL), concentrated *in vacuo,* and purified via flash chromatography over silica gel, eluting with 10-30% EtOAc / hexanes to give **56** (32.9 mg, 102 μmol, 92%) as a bright yellow oil. IR (neat) 3522, 1620, 1592, 1526, 1360, 1264, 1040, 877, 764 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.68 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.28-7.21 (m, 3H), 7.19-7.12 (m, 2H), 6.77(d, *J* = 8.0 Hz, 1H), 6.41-6.32 (m, 2H), 4.95 (br, 1H), 3.65 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 160.8, 154.0, 151.7, 145.2, 139.5, 134.1, 131.5, 129.7, 129.1, 128.5, 128.0, 127.4, 122.6, 115.0, 106.7, 101.7, 55.2; HRMS (EI+) calcd. for $C_{19}H_{15}NO_4$ 321.1001, found 321.0999.




**37** **57**

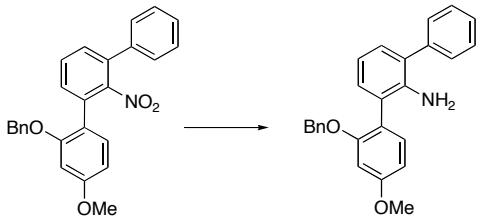
**Phenol 57**: To a stirred solution of **37** (45.2 mg, 0.110 mmol) in $CH_2Cl_2$ (1.10 mL) was added $BCl_3$ (0.660 mL, 0.660 mmol, 1.0 M in hexanes) at 0˚C. After 4 h, the reaction was quenched with MeOH (2.0 mL), concentrated *in vacuo,* and purified via recrystallization with $CH_2Cl_2$ to yield **57** (29.0 mg, 0.0900 mmol, 82%) as a yellow crystalline solid. MP 166-167˚C; IR (neat) 3409, 2921, 1617, 1530 $cm^{-1}$; $^1H$ NMR (400 MHz, MeOD) δ 7.62 (t, *J* = 7.7 Hz, 1H), 7.46-7.38 (m, 7H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.50-6.47 (m, 2H), 3.81 (s, 3H); $^{13}C$ NMR (100 MHz, MeOD) δ 161.3, 155.6, 152.8, 150.5, 137.4, 134.4, 132.0, 131.5, 130.5, 129.5, 128.2, 127.9, 127.8, 116.6, 104.7, 101.0, 54.3; HRMS (EI+) calcd. for $C_{19}H_{15}NO_4$ (M+H) 321.1001, found 321.1004.




**34** **58**

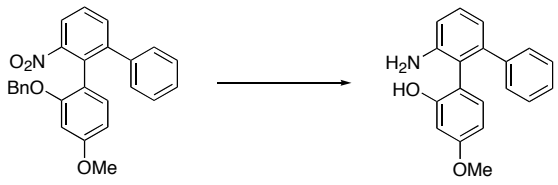
**Aniline 58:** To a stirred solution of **34** (44.6 mg, 101 μmol) in glacial HOAc (410 μL) was added Zn dust (41.0 mg, 627 μmol) at rt. After 20 h, the mixture was quenched with sat. aq. $NaHCO_3$ (15 mL), diluted with EtOAc (20 mL) and washed with $H_2O$ (20 mL) and sat. aq. NaCl (20 mL). The dried extract ($Na_2SO_4$) was concentrated *in vacuo* and purified via flash chromatography over silica gel, eluting with 15-25% EtOAc / Hexanes to give **58** (34.2 mg, 90.9 μmol, 90%) as a colorless oil. IR (neat) 3471, 3379, 3058, 2835, 1609, 1580, 1266, 1044 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.38-7.13 (m, 11H), 7.01 (d, *J* = 9.0 Hz, 1H), 6.87 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.83 (dd, *J* = 8.0, 1.1 H, 1H), 6.54-6.41 (m, 2H), 5.02 (d, *J* = 12.8 Hz, 1H), 4.92 (d, *J* = 12.8 Hz, 1H), 3.76 (s, 3H), 3.52 (br, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 160.2, 157.2,

145.0, 143.2, 142.4, 137.4, 132.9, 129.3, 128.4, 128.1, 127.5, 127.4, 126.6, 126.0, 122.9, 120.2, 119.4, 114.3, 105.4, 100.6, 69.9, 55.3; HRMS (EI+) calcd. for $C_{26}H_{23}NO_2$ 381.1729, found 381.1721.



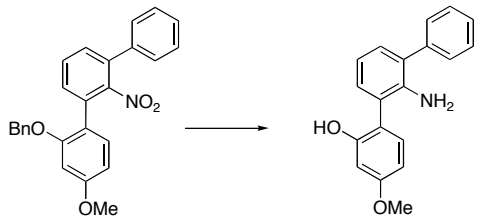

**37** **59**

**Aniline 59:** To a stirred solution of **37** (54.4 mg, 0.132 mmol) in glacial HOAc (0.55 mL) was added Zn dust (43.2 mg, 0.660 mmol) at rt. After 20 h, the mixture was quenched with sat. aq. $NaHCO_3$ (15 mL), diluted with EtOAc (20 mL) and washed with $H_2O$ (20 mL) and sat. aq. NaCl (20 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 15-25% EtOAc / Hexanes to give **59** (49.0 mg, 0.128 mmol, 97%) as a yellow oil. IR (neat) 3471, 3385, 3057, 2933, 1611, 1503, 1163 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.56-7.48 (m, 4H), 7.41 (dt, *J* = 1.5, 1.5, 7.2 Hz, 1H), 7.38-7.32 (m, 6H), 7.20 (dd, *J* = 1.2, 7.2 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.71-6.67 (m, 2H), 5.12 (s, 2H), 3.88 (s, 3H), 3.85 (broad s, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 160.5, 156.9, 142.0, 140.2, 137.2, 132.4, 130.7, 129.5, 129.4, 128.8, 128.5, 127.8, 127.7, 127.1, 126.9, 125.0, 122.0, 117.9, 106.0, 101.3, 70.7, 55.5; HRMS (EI+) calcd. for $C_{26}H_{23}NO_2$ (M+H) 382.1729, found 381.1728.




**34** **60**

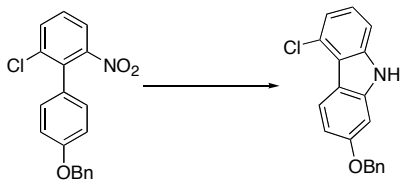
**Phenol 60:** To a stirred solution of **34** (54.7 mg, 132.3 μmol) and EtOH (460 μL, absolute) was added Pd/C (62.3 mg, 10% Pd). After stirring under an atmosphere of $H_2$ for 21 h, the mixture was filtered over a pad of Celite-® with EtOAc (50 mL) and concentrated *in vacuo*. The product was purified via flash chromatography over silica gel, eluting with 15-20% EtOAc / Hexanes to give **60** (26.1 mg, 89.6 μmol, 67%) as a colorless oil; IR (neat) 3472, 3382, 3187, 3057, 2959, 1621, 1573, 1265, 1161, 1039 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.9 Hz, 1H), 7.25-7.10 (m, 5H), 6.95 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 6.54 (d, *J* = 2.5 Hz, 1H), 6.38 (dd, 8.5, 2.5 Hz, 1H), 3.78 (s, 3H), 4.70-3.40 (br, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 160.7, 154.7, 144.7, 144.0, 141.3, 132.6, 129.1, 129.1, 127.7, 126.5, 121.4, 120.6, 115.9, 114.9, 107.3, 101.6, 55.2; HRMS (EI+) calcd. for $C_{19}H_{17}NO_2$ 291.1259, found 291.1251.




**37** **61**

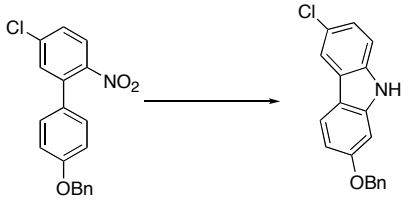
**Phenol 61:** To a stirred solution of **37** (25.6 mg, 0.0620 mmol) and EtOH (0.31 mL) was added Pd/C (29.9 mg, 10% Pd). After stirring under an atmosphere of $H_2$ for 21 h, the mixture was filtered over a

pad of celite-® with EtOAc (50 mL) and concentrated *in vacuo*. The product was purified by chromatography over silica gel, eluting with 15-20% EtOAc / Hexanes to give **61** (15.3 mg, 0.0530 mmol, 85%) as a white solid. MP 87-89˚C; IR (neat) 3394, 3301, 2921, 1731, 1617, 1160 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.55-7.50 (m, 4H), 7.45 (m, 1H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.26 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.23 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.69 (m, 2H), 3.87 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 161.1, 154.9, 139.0, 138.9, 131.9, 131.1, 129.9, 129.8, 129.3, 129.1, 127.7, 126.3, 120.6, 118.8, 107.9, 103.1 55.4; HRMS (EI+) calcd. for $C_{19}H_{17}NO_2$ (M+H) 291.1259, found 291.126.



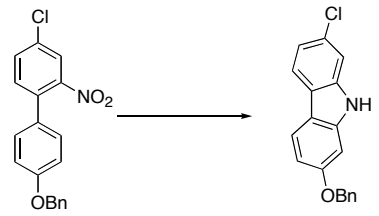

**20** **62**

**Carbazole 62**: To a pressure vessel containing **20** (38.7 mg, 114 µmol) and *o*-$C_6H_4Cl_2$ (230 µL) was added $PPh_3$ (75.5 mg, 289 µmol) at rt. The mixture was heated to 180°C. After 24 h, the reaction was cooled to rt and purified via flash chromatography over silica gel, eluting with 10-30% EtOAc / Hexanes to give impure **62** (40.2 mg) as a brown solid. Recrystallization from $CHCl_3$ / Pentane afforded **61** (26.3 mg, 85.5 µmol, 75%) as an off-white solid. MP 158-160°C; IR (thin film) 3387, 1177 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.7 Hz, 1H), 8.02 (br s, 1H), 7.52 (d, *J*= 7.2 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.33-7.18 (m, 3 H), 7.03 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.97 (d, *J*= 0.9 Hz, 1H), 5.19 (s, 2H) ; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 158.5, 140.8, 140.6, 137.0, 128.7, 128.0, 127.8, 127.5, 125.0, 123.9, 120.9, 120.3, 116.4, 109.3, 108.6, 95.7, 70.4; HRMS (EI+) calcd. for $C_{19}H_{14}NOCl$ (M+) 307.0764, found 307.0775.



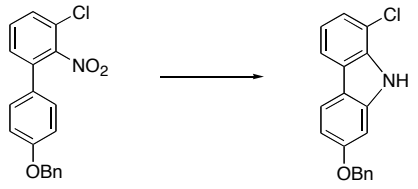

**21** **63**

**Carbazole 63:** To a pressure vessel containing **21** (49.9 mg, 147 µmol) and *o*-$C_6H_4Cl_2$ (300 µL) was added $PPh_3$ (119.4 mg, 455 µmol) at rt. The mixture was heated to 180°C. After 24 h, the reaction was cooled to rt and purified via flash chromatography over silica gel, eluting with 10-30% EtOAc / Hexanes to give impure **63** (50.4 mg) as a brown solid. Recrystallization from $CHCl_3$ / Pentane afforded **63** (43.7 mg, 142 µmol, 89%) as an off-white solid. MP 222-224˚C; IR (KBr) 3390, 2916, 1624, 1225, 1176, 1027, 816, 728 $cm^{-1}$; $^1H$ NMR (400 MHz, $d_6$-DMSO) δ11.30 (s, 1H), 8.11 (s, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.68-7.19 (m, 7H), 7.08 (s, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.22 (s, 2H); $^{13}C$ NMR (100 MHz, $d_6$-DMSO) δ158.5, 142.2, 138.7, 137.7, 128.9, 128.3, 128.2, 124.5, 124.3, 123.4, 122.0, 119.4, 116.0, 112.5, 109.4, 96.2, 70.0; HRMS (EI+) calcd. for $C_{19}H_{14}NOCl$ (M+) 307.0764, found 307.0764.



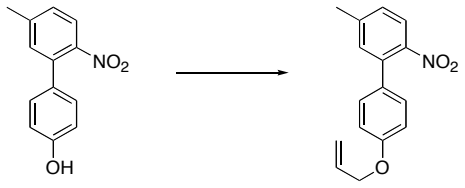

**22** **64**

**Carbazole 64:** To a pressure vessel containing **22** (18.7 mg, 55.0 mmol) and *o*-$C_6H_4Cl_2$ (150 µL) was added $PPh_3$ (44.1 mg, 168 µmol) at rt. The mixture was heated to 180°C. After 24 h, the reaction was cooled to rt and purified via flash chromatography over silica gel, eluting with 10-30% EtOAc / Hexanes to give impure **64** (17.6 mg) as a brown solid. Recrystallization from $CHCl_3$ / Pentane afforded **64** (14.2 mg, 46.1 µmol, 84%) as an off-white solid. MP 235-238°C; IR (KBr) 3396, 2923, 1605, 1016, 797 $cm^{-1}$; $^1H$ NMR (400 MHz, $d_6$-DMSO) 11.29 (s, 1H), 8.02 (d, *J* = 3.3 Hz, 1H), 8.00 (d, *J* = 3.7 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.14 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.09 (d, *J* = 2.3 Hz, 1H), 6.90 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.21 (s, 2H); $^{13}C$ NMR (100 MHz, $d_6$-DMSO) δ 158.3, 141.9, 140.9, 137.7, 129.0, 128.9, 128.3, 128.2, 122.0, 121.6, 121.1, 119.1, 116.2, 110.8, 109.4, 96.4, 70.0; HRMS (EI+) calcd. for $C_{19}H_{14}NOCl$ (M+) 307.0764, found 307.0772.




**32** **65**

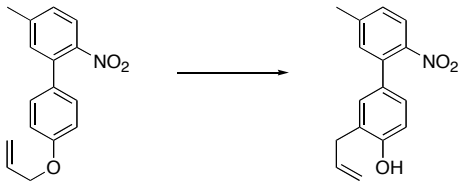
**Carbazole 65:** To a pressure vessel containing **32** (17.2 mg, 0.0510 mmol) and *o*-dichlorobenzene (100 µL) was added $PPh_3$ (66.4 mg, 0.254 mmol) at rt. The mixture was heated at 180˚C. After 48 h, the reaction was purified via flash chromatography over silica gel, eluting with 0-20% EtOAc / Hexanes to give **65** (10.2 mg, 0.033 mmol, 65%) as a white solid. MP 145-146˚C; IR 3419, 2911, 1419, 735 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.21 (bs, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.1, 7.6 Hz, 2H), 7.38 (t, *J* = 7.2, 7.8 Hz, 2 H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 2.0 Hz, 1H), 7.00 (dd, *J* = 2.2 Hz, 8.6 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 158.7, 140.5, 137.0, 136.7, 128.7, 128.1, 127.5, 125.0, 123.9, 121.6, 120.4, 117.9, 117.6, 115.8, 109.8, 96.2, 70.5; HRMS (FAB+) calcd. For $C_{19}H_{14}ClNO$ (M+H) 308.0842, found 308.0846.




**73** **96**

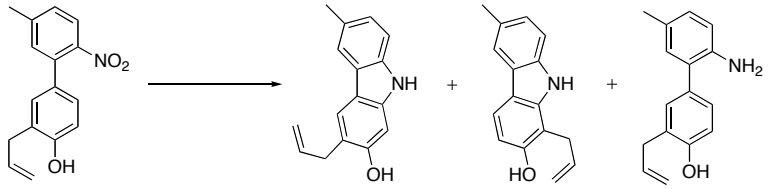
**Allyl ether 96:** To a stirred solution of **73** (843.0 mg, 3.677 mmol) and dry DMF (18.0 mL) was added NaH (320.9 mg, 8.022 mmol, 60% dispersion in mineral oil) at 0°C. To this dark red solution was added allyl iodide (3.12 g, 1.70 mL, 18.59 mmol). After 10 min, the yellow solution was quenched with sat. aq. $NH_4Cl$ (20 mL), diluted with EtOAc (100 mL), washed with $H_2O$ (10 mL), and sat. aq. NaCl (2 x 10 mL). The dried ($Na_2SO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with PhMe to give **96** (990 mg, 3.68 mmol, 99%) as a bright yellow oil. IR (neat) 1610, 1516, 1353, 734 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.782 (d, *J*= 8.9, 1H), 7.31-7.22 (m, 4H), 7.03-6.97 (m, 2H), 6.18-6.05 (m, 1H), 5.48 (dq, *J*= 17.2, *J*= 1.5 Hz, 1H), 5.34 (dq, *J*= 10.5, 1.3 Hz, 1H), 4.60 (dt, *J*= 5.3, 1.5 Hz, 2H), 2.47 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ158.6, 147.1, 143.3, 136.1, 133.2, 132.6,

130.1, 129.1, 128.3, 124.3, 117.8, 114.9, 68.9, 21.4; HRMS (EI+) calcd. for $C_{16}H_{15}NO_3$ (M+) 269.1052, found 269.1042.




**96** **68**

**Phenol 68**: To a stirred solution of **96** (990 mg, 3.68 mmol) in $CH_2Cl_2$ (37.0 mL) was added $BCl_3$ (11.1 mL, 11.1 mmol, 1.0 M in hexanes) at -78˚C. After 2 h, the reaction was quenched with MeOH (2.0 mL) at -78°C and warmed to rt. The solution was diluted with $CH_2Cl_2$ (45 mL) and washed with $H_2O$ (2 x 20 mL) and sat. aq. NaCl (2 x 20 mL). The dried ($Na_2SO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica gel, eluting with 10-30% $Et_2O$ / PhMe to give **68** (845.7 mg, 3.141 mmol, 85%) as a yellow crystalline solid. MP 82-83˚C; IR (thin film) 3486, 1609, 1520, 1351, 1215, 758 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.28-7.22 (m, 2H), 7.14-7.08 (m, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.06 (m, 1H), 5.24 (dq, *J*= 5.25, 1.5 Hz, 1H), 5.21 (t, *J* = 1.6 Hz, 2H), ; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ; HRMS (EI+) calcd. for $C_{19}H_{15}NO_4$ (M+) 269.1052, found 269.1053.



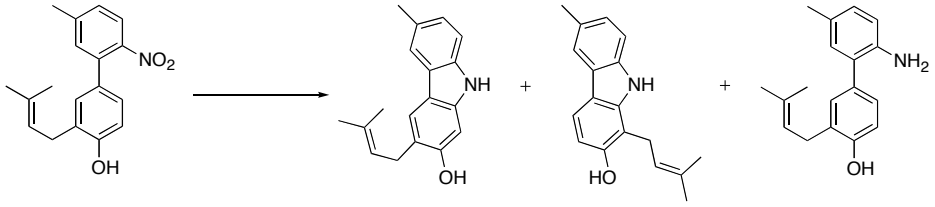

**68** **74** **75** **76**

**Carbazoles 74 and 75 and Aniline 76:** METHOD A - To a pressure vessel containing **68** (51.6 mg, 191.6 μmol) and *o*-$C_6H_4Cl_2$ (2.00 mL) was added $PPh_3$ (205 mg, 782 μmol) at rt. The mixture was heated at 180°C. After 30 h at 180°C, the reaction was cooled to rt and passes trough a silica plug. Purification via flash chromatography over silica gel, eluting with 10-15% EtOAc / Hexanes gave sequentially **75** (23.2 mg, 97.8 μmol, 51%), **76** (5.3 mg, 22.1 μmol, 11%), and **74** (14.5 mg, 61.1μmol, 32%) as off-white solids. METHOD B - To a pressure vessel containing **68** (26.6 mg, 98.8 μmol) and *o*-$C_6H_4Cl_2$ (1.00 mL) was added $P^nBu_3$ (81 mg, 100 μL, 400 μmol) at rt. The mixture was heated at 180°C. After 12 h at 180°C, the reaction was cooled to rt and purified via flash chromatography over silica gel, eluting with 10-25% EtOAc / Hexanes to give sequentially **75** (5.6 mg, 24 μmol, 23%), **76** (9.4 mg, 39 μmol, 38%), and **74** (6.5 mg, 27 μmol, 27%) as off-white solids.

**74**: MP 131-133°C; IR (thin film) 3412, 3212, 2920, 2851, 1639, 1615, 1211, 909, 802 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 4.9 Hz, 3H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.18 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.86 (s, 1H), 6.15 (ddt, *J*= 16.5, 10.1, 6.3 Hz, 1H), 5.26 (dq, *J*= 12.2, 1.6 Hz, 1H), 5.23 (dt, *J* = 4.9, 1.7 Hz, 1H), 5.19 (br s, 1H), 3.61 (d, *J* = 3.6 Hz, 2H), 2.54 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 153.4, 140.1, 137.8, 137.3, 128.7, 125.8, 123.7, 121.5, 119.5, 117.9, 117.4, 116.4, 110.0, 97.4, 35.7, 21.5; HRMS (EI+) calcd. for $C_{16}H_{15}NO$ 237.1154 (M+), found 237.1149.

**75**: MP 154-156°C; IR (thin film) 3459, 3356, 2918, 2850, 1614, 1211, 912, 804 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.91 (br s, 1H), 7.80 (d, *J*= 8.1 Hz, 1H), 7.79 (s, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.19 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.76 (d, *J*= 8.3 Hz, 1H), 6.13 (ddt, *J*= 16.0, 10.1, 6.0 Hz, 1H), 5.29-5.19 (m, 2H), 4.96 (br s, 1H), 3.72 (dt, *J* = 5.9, 1.6 Hz, 2H), 2.54 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 152.0, 140.8, 137.9, 135.6, 128.9, 125.9, 124.1, 119.5, 119.0, 117.5, 116.3, 110.2, 108.9, 106.5, 29.4, 21.5; HRMS (EI+) calcd. for $C_{16}H_{15}NO$ 237.1154 (M+), found 237.1149.

**76**: MP 136-138°C; IR (thin film) 3376, 3311, 1607, 1270 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.29-7.18 (m, 2H), 7.06-6.97 (m, 2H), 6.85 (d, *J*= 8.0 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.09 (m, 1H), 5.29-5.17 (m, 2H), 3.92 (br s, 1H), 3.49 (d, *J*= 6.4 Hz, 2), 2.34 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 153.4, 140.6, 136.4, 131.9, 131.1, 131.1, 128.7, 128.4, 128.4, 128.1, 126.1, 116.6, 116.1, 116.0, 35.1, 20.5. HRMS (EI+) calcd. for $C_{16}H_{17}NO$ 239.1310 (M+), found 239.1321.




**77** **66** **67** **78**

**Siamenol 66, Carbazole 67 and Amine 78:** To a pressure vessel containing **77** (50.4 mg, 169 μmol) and *o*-$C_6H_4Cl_2$ (400 μL) was added $P^nBu_3$ (138 mg, 170 μL, 681 μmol) at rt. The mixture was heated at 100°C. After 12 h at 100°C, the reaction was cooled to rt and purified via flash chromatography over silica gel, eluting with 10-25% EtOAc / Hexanes to give sequentially **67** (19.2 mg, 72.3 μmol, 43%), **78** (10.8 mg, 40.4 μmol, 24%), and **66** (12.4 mg, 46.7 μmol, 28%) as white solids.

**66**: MP 140-143°C; IR (thin film) 3406, 3252, 2920, 2852, 1636, 1617, 1465, 1319, 1210, 1014, 802 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.77 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J*=8.0 Hz, 1H), 6.86 (s, 1H), 5.44 (tt, *J* = 7.2, 1.2 H, 1H), 5.30 (s, 1H), 3.55 (d, *J* = 7.2 Hz, 2H), 2.54 (s, 3H), 1.88 (s, 3H), 1.85 (s, 3H); $^1H$ NMR (400 MHz, $d_4$-MeOD) δ 7.64 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.60 (s, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.79 (s, 1H), 5.43 (t-sept, *J* = 7.3, 1.4 Hz, 1H), 3.41 (d, *J* = 7.3 Hz, 2H), 2.45 (s, 3H), 1.78 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 153.7, 139.9, 137.7, 134.7, 128.6, 125.7, 123.7, 122.6, 120.8, 119.4, 117.2, 109.9, 97.2, 30.5, 25.8, 21.4, 17.9; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 154.16, 140.4, 138.5, 131.1, 127.3, 124.7, 124.0, 123.9, 120.5, 119.7, 118.5, 116.1, 109.7, 95.9, 28.5, 24.9, 20.4, 16.7 HRMS (EI+) calcd. for $C_{18}H_{19}NO$ 265.1467 (M+), found 265.1471.

**67**: MP 126-128°C; IR (thin film) 3524, 3424, 3261,2919, 2853, 1614, 1227, 1211, 1032, 802 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.85 (br s, 1H), 7.78 (d, *J* = 1.0 Hz, 1H), 7.76 (d, *J* = 3.6 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.18 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 5.41 (d-quint, *J* = 6.9, 1.4 Hz, 1H), 5.11 (br s, 1H), 3.64 (d, *J* = 6.9 Hz, 2H), 2.54 (s, 3H), 1.94 (s, 3H), 1.82 (d, *J* = 1.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 152.2, 140.4, 137.8, 134.9, 128.8, 125.8, 124.2, 121.5, 119.5, 118.6, 117.4, 110.1, 109.0, 108.3, 25.8, 24.4, 21.5, 18.1; HRMS (EI+) calcd. for $C_{16}H_{15}NO$ 237.1154 (M+), found 237.1155.

**78**: MP 126-132°C; IR (thin film) 3363, 3276, 2920, 1604, 1431, 1279, 1233 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 2.0 Hz, 1H), 7.21 (dd, *J* = 8.3, 2.1Hz, 1H), 7.00 (d, *J* = 9.1 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 5.40 (tt, *J* = 5.9, 1.3 Hz, 1H), 4.18 (br s, 1H), 3.44 (d, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.83 (s, 3H), 1.82 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 153.6, 140.9, 134.8, 131.9, 131.1, 130.7, 128.6, 128.1, 128.0, 128.0, 127.4, 121.7, 115.9, 115.9, 29.8, 25.9, 20.5, 17.9; HRMS (EI+) calcd. for $C_{18}H_{21}NO$ (M+) 267.1623, found 267.162

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11. To a stirred solution of i-$Pr_2NH$ (1.42 g, 1.97 mL, 14.1 mmol) in THF (7.78 mL) at -78°C was added dropwise *n*-BuLi (5.59 mL, 13.2 mmol, 2.4 M in hexanes). After 10 min a white precipitate appeared and the solution was warmed to 0°C. After 5 min, the solution was recooled to -78°C and ready for use.

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