First General Synthesis of (*p*-Nitroaryl)diarylmethanes *via* Vicarious Nucleophilic Substitution of Hydrogen

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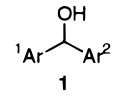
A general regiospecific method for the synthesis of (*p*-nitroaryl)diarylmethanes has been developed starting from diarylmethanols and 2- and/or 3-substituted nitrobenzenes. This utilizes the quantitative condensation between benzotriazole and diarylmethanols under acidic catalysis and in the presence of perfluorocarbon fluids, followed by vicarious nucleophilic substitution of the resulting diarylmethylbenzotriazoles upon nitrobenzenes in moderate to high yield. Oxidative nucleophilic substitution of hydrogen is observed as a side process. These vicarious nucleophilic substitutions complement Friedel−Crafts reactions for the synthesis of triarylmethanes.

Introduction

Substituted triarylmethanes are of considerable interest as leuco dyes,[1] photochromic agents,[2] and substrates for theoretical studies.[3] While many methods are available for the preparation of symmetrical triarylmethanes,[4−7] syntheses of unsymmetrical triarylmethanes are less developed. General methods include (i) condensation of unsymmetrical benzhydrols with phenols under acidic[8] or basic conditions[9] or with *N*,*N*-dimethylaniline or alkoxybenzenes under acidic conditions[10,11] and (ii) displacement of benzotriazole in (benzotriazol-1-yl)diphenylmethanes either by an electron-rich arene catalyzed by $ZnCl_2$[11] or by [4-(*N*,*N*-dimethyamino)phenyl]magnesium bromide.[1] Unsymmetrical diarylmethylindoles, -pyrroles, and -pyridines were synthesized by condensation of the corresponding heterocycle with diarylmethanols[1] or by Lewis acid-catalyzed displacement of benzotriazole in (benzotriazol-1-yl)diphenylmethanes.[11] However, to the best of our knowledge, unsymmetrical nitro-substituted triarylmethanes have not been previously synthesized: such compounds could be of significant versatility due to the easy reduction of the nitro group and subsequent transformations of the resulting amino derivatives.

Vicarious nucleophilic substitution of hydrogen (VNS) using carbon nucleophiles, developed by Makosza *et al.*,[12ab] has become a useful tool for introducing C-linked substituents into electrophilic arenes. While VNS has been used for syntheses of (nitroaryl)arylmethanes,[12b,c] no such syntheses of (nitroaryl)diarylmethanes have appeared.

Table 1. Diarylmethanols for the Synthesis of (*p*-Nitroaryl)diarylmethanes



1

1	Ar^1	Ar^2	yield (%)
a	phenyl	phenyl	
b	phenyl	2-methylphenyl	
c	phenyl	4-chlorophenyl	
d	phenyl	4-biphenylyl	
e	phenyl	4-methoxyphenyl	
f	4-methylphenyl	phenyl	
g	4-(*N*,*N*-dimethylamino)phenyl	phenyl	98
h	4-methylphenyl	2-methoxyphenyl	88
i	4-(*N*,*N*-dimethylamino)phenyl	4-*n*-hexyloxyphenyl	56
j	4-(*N*,*N*-dimethylamino)phenyl	3,4,5-trimethoxyphenyl	73
k	4-methoxyphenyl	5-methylthien-2-yl	47

Reactions of tris(benzotriazol-1-yl)methane with nitroarenes[13] in our laboratory showed that benzotriazole derivatives readily undergo VNS with benzotriazolate anion acting as a leaving group. We now demonstrate that nitroarenes undergo VNS when treated with benzotriazolyldiarylmethanes in THF in the presence of potassium *tert*-butoxide, that condensation of benzotriazole with diarylmethanols in the presence of catalytic amounts of *p*-toluenesulfonic acid[14] is a useful *umpolung* in building triarylmethanes, and that oxidative nucleophilic substitution of hydrogen in nitroarenes[15ab] is a common side process in benzotriazole-mediated VNS chemistry.

Results and Discussion

A series of diarymethanols **1** were used as substrates for this study (Table 1). While compounds **1a**−**f** were commercially available materials, we carried out the synthesis of compounds **1g**−**k**. Compound **1g** was obtained in 98% yield by reduction of the corresponding

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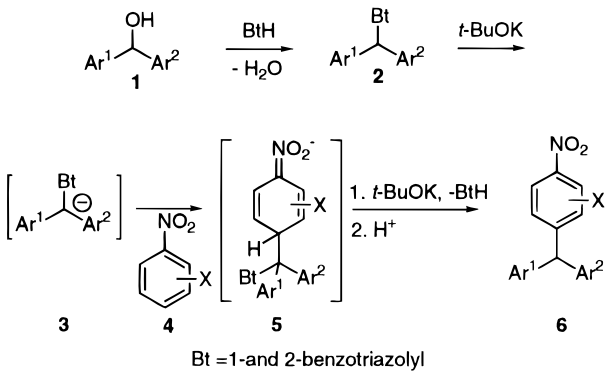
Scheme 1[a]



[a] For designation of Ar^1, Ar^2, and X see Table 2.

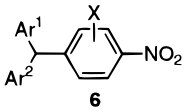
benzophenone with sodium borohydride. Compound **1h** was obtained by the reaction of (4-methylphenyl)magnesium bromide with *o*-anisaldehyde in 88% yield. Compounds **1i** and **1j** were synthesized by the reaction of the corresponding aldehyde with [4-(*N*,*N*-dimethylamino)-phenyl]magnesium bromide in 56 and 73% yield, respectively by means of our previously reported procedure.[1] In an effort to test a heterocyclic substrate, compound **1k** was synthesized by α-lithiation of 2-methylthiophene[16] and subsequent reaction with *p*-anisaldehyde in 47% yield. New compounds **1h**−**k** were fully characterized.

(Diarylmethyl)benzotriazoles of type **2** (Scheme 1) were previously prepared in our group from benzotriazole and diarylmethanols in the presence of a catalytic amount of *p*-toluenesulfonic acid (PTSA) in benzene with azeotropic removal of water.[14] We now find that the use of perfluorocarbon fluids for water removal,[17] diarylmethanols, benzotriazole in 1.3 molar excess, and a catalytic amount of PTSA (or even without catalyst in case of **1e**,**g**−**k**) gives the 1- and 2-(diarylmethyl)benzotriazole mixtures **2a**−**k** in almost quantitative yields with respect to the diarylmethanols **1a**−**k** (Scheme 1). These mixtures were used as such after removal of excess benzotriazole.

The (diarylmethyl)benzotriazoles **2** were reacted with a series of *o*- and *m*-substituted nitrobenzenes **4**. An equimolar mixture of **2** and **4** was added to a solution of potassium *tert*-butoxide in dry THF to give a deep red reaction mixture. Upon quenching with saturated ammonium chloride solution, (nitroaryl)diarylmethanes **6** were obtained (Scheme 1 and Table 2). Reaction times were limited to 4 h since longer reaction times lower the observed yields of the desired product **6**. The temperature needs to be carefully controlled: studies showed that carbanions of types **3** generated from the corresponding 1-(diarylmethyl)benzotriazoles **2** with *ca.* 5 equiv of potassium *tert*-butoxide in dry THF are stable at −20 °C. However higher temperatures cause triazole ring fragmentation as evidenced by detection of benzophenones in the GCMS spectra of the reaction mixture, probably through a pathway previously described.[18]

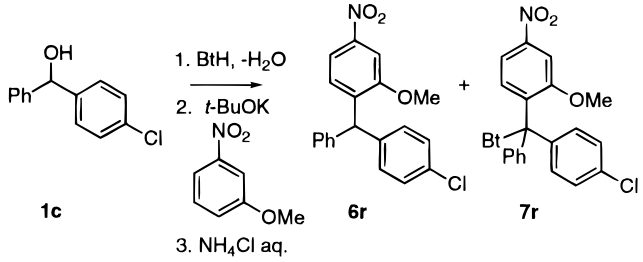
The addition step of anions **3** to nitroarenes **4** to form σ^H-adducts of type **5** (Scheme 1) is fast, as evidenced by a reaction between 3-nitroanisole and **2c** that was quenched at −20 °C after 10 min with a nondegassed aqueous acidic solution to give compound **7r** as the only product observed (Scheme 2). Compounds of type **7** are

Table 2. *o*- and/or *m*-Substituted (*p*-Diarylmethyl)nitrobenzenes



6	X	Ar^1	Ar^2	yield (%)
a	H	phenyl	phenyl	82
b	2-F	phenyl	phenyl	87
c	2-Cl	2-methoxyphenyl	4-methylphenyl	86
d	2-Cl	4-(*N*,*N*-dimethylamino)-phenyl	phenyl	79
e	2-Cl	4-(*N*,*N*-dimethylamino)-phenyl	3,4,5-trimethoxy-phenyl	68
f	2-Br	4-methylphenyl	phenyl	52
g	2-Br	4-biphenylyl	phenyl	38
h	2-MeO	phenyl	phenyl	68
i	2-MeO	4-chlorophenyl	phenyl	76
j	2-MeO	2-methylphenyl	phenyl	31
k	2-MeO	5-methylthien-2-yl	4-methoxyphenyl	28
l	2-MeO	4-(*N*,*N*-dimethylamino)-phenyl	4-(*n*-hexyloxy)-phenyl	48
m	2-Ph	4-biphenylyl	phenyl	91
n	2-*t*-Bu	4-methoxyphenyl	phenyl	33
o	2-CF_3	4-(*N*,*N*-dimethylamino)-phenyl	phenyl	50
p	2,3-$(CH)_4$	4-chlorophenyl	phenyl	94
q	3-F	4-methoxyphenyl	phenyl	56
r	3-MeO	4-chlorophenyl	phenyl	52

Scheme 2



products of oxidative nucleophilic substitution (ONSH),[15a] and their formation indicates a high concentration of adduct **5** in the early stages of the reaction.[19]

The elimination of the benzotriazole from adducts of type **5** (Scheme 1) works well for unsubstituted and *o*-chloro-, *o*-fluoro-, and *o*-phenyl-substituted nitrobenzenes **4** to give **6a**−**e**,**m** in good to excellent yields regardless of the structure of compound **1** (Table 2) but is slow with *o*-bromonitrobenzene (**4**, X = 2-Br) (affording **6f** and **6g** in only 52 and 38% yields, respectively) and does not work at all for *o*-iodonitrobenzene (**4**, X = 2-I). The reactions of *o*-methoxynitrobenzene (**4**, X = 2-MeO) show how the structure of the diarylmethanol **1** influences the outcome of the reaction: the electron-rich **1i** and **1k** and the sterically hindered **1b** gave low yields of the VNS product. A comparison between the reaction of **1a** with unsubstituted nitobenzene (**4**, X = H) and *o*-methoxynitrobenzene (**4**, X = 2-MeO) suggests that the more electron-rich adduct **5h** eliminates benzotriazole more slowly than **5a**. *o*-*tert*-Butylnitrobenzene (**4**, X = 2-*t*-Bu) and *o*-(trifluoromethyl)nitrobenzene (**4**, X = 2-CF_3) underwent VNS to give only 33% and 50% yields, respectively, of the corresponding nitroaryldiarylmethanes. *m*-Substituted nitrobenzenes **4** show the same slow elimination rate to give the VNS products: *m*-fluoro- and *m*-methoxynitrobenzenes **4** gave the VNS products in

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moderate yields. In case of the latter, compound **7r** was isolated and fully characterized in 8% yield. Surprisingly, 1-nitronaphthalene reacts cleanly and gives the VNS product in 94% yield.

Most likely, the bimolecular[12a] elimination step **5** → **6,** which needs elevated temperatures and high base concentration to achieve a reasonable rate, is rate controlling. Process **5** → **6** probably requires a high degree of order in the transition state, in which case steric effects should be important. Further study is needed to support these postulates.

The regiochemistry of the reaction is always *para* with respect to the nitro group with both 2- and 3-substituted nitrobenzenes. This preference is probably due to the bulkiness of the anion. Despite the fact that our base and solvent are the ones held responsible for the "*ortho* effect" in VNS, *i.e.*, *t*-BuOK/THF,[12a] no *ortho* substitution was observed.

Oxidative nucleophilic substitution of hydrogen has previously been observed by Bernard with σ^H-adducts derived from benzotriazole-stabilized anions and nitroarenes.[20] No systematic study of the factors that influence this process has been published so far. Attempts to measure the ratio of the VNS and ONSH products by GCMS were unsuccesful due to decomposition of the ONSH product. However, ^{1}H NMR allows quantitative evaluation of the ratio of the two products: the C_{sp^3}–H bond in compound **6** gives a signal at 5.5−5.8 ppm, while C_{sp^2}–H in position 7 of the benzotriazolyl ring in compound **7** gives a signal at 6.5 ppm. By this means, the ratios of the VNS and ONSH products could be quantified. When the quenching solution was degassed prior to its addition to the reaction mixture, only traces of ONSH product were observed. A study of the ONSH of benzotriazole bearing anionic σ-adducts is under way in our laboratory.

In conclusion, a general regiospecific method for synthesis of (*p*-nitroaryl)diarylmethanes was developed starting from diarylmethanols and 2- and 3-substituted nitrobenzenes, making use of the quantitative reaction between benzotriazole and diarylmethanols under acidic catalysis and in the presence of perfluorocarbon fluids. In the presence of Brönsted or Lewis acids, diarylmethanols are highly electrophilic, reacting with electron-rich arenes in Friedel−Crafts fashion. In contrast, (diarylmethyl)benzotriazoles in the presence of strong bases are highly nucleophilic, allowing reactions with electron poor arenes. Hence, our present VNS procedure complements Friedel−Crafts approaches to similar compounds, as pointed out by Makosza.[19]

Experimental Section

General Methods. Melting points were determined on a capillary melting point apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^{1}H (300 MHz) or solvent as the internal standard for ^{13}C (75 MHz). Tetrahydrofuran was distilled under nitrogen immediately prior to use from sodium benzophenone ketyl. Potassium *tert*-butoxide was reagent grade purchased from Acros Organics and was handled in a drybox under nitrogen. All reactions involving potassium *tert*-butoxide and Grignard reagents were carried out under argon atmosphere. Column chromatography was conducted with silica gel 230−400 mesh. Compounds **1a**−**f** were reagent-grade commercially available materials. Perfluorocarbon fluid (bp 104 °C) was purchased from 3M Co. [4-(*N*,*N*-Dimethylamino)phenyl]magnesium bromide 1 M solution in THF was prepared according to literature procedure.[1]

Preparation of 4-(*N*,*N*-Dimethylamino)-α-phenylbenzenemethanol (1g). Sodium borohydride was added (0.83 g, 22 mmol) to a solution of 4-(*N*,*N*-dimethylamino)benzophenone (4.51 g, 20 mmol) in ethanol (50 mL). The mixture was stirred at rt for 6 h, solvent was distilled off under reduced pressure, and water (20 mL) and methylene chloride (30 mL) were added to the residue. The organic layer was separated, washed with water (20 mL) and brine (20 mL), and dried ($MgSO_4$). After solvent removal, 4.50 g (98%) of product was obtained as a light green solid: mp 68−69 °C (lit.[21] mp 69−70 °C); ^{1}H NMR 2.42 (br s, 1H), 2.87(s, 6H), 5.68 (br s, 1H), 6.65 (d, J = 8.6 Hz, 2H), 7.15−7.22 (m, 3H), 7.26−7.35 (m, 4H); ^{13}C NMR 40.5 (2C), 75.8, 112.5 (2C), 126.3 (2C), 127.0, 127.7 (2C), 128.2 (2C), 132.1, 144.3, 150.0.

Preparation of 2-Methoxy-α-(4-methylphenyl)benzenemethanol (1h). To a suspension of Mg (0.48 g, 0.02 mol) in THF (10 mL) was added 4-bromotoluene (2.07 g, 0.012 mol). After 3 h reflux, 10 mL of the resulting cold solution was added to 2-methoxybenzaldehyde in THF (30 mL) at 0 °C and stirred under reflux for 5 h. The resulting mixture was treated with saturated ammonium chloride solution (40 mL) and extracted with methylene chloride (3 × 30 mL). The organic extract was dried ($MgSO_4$), the solvent was removed to yield an oil that was dissolved in ethanol (10 mL), sodium borohydride (0.019 g, 0.005 mol) was added, and the mixture was stirred at rt for 5 h. The solvent was removed under reduced pressure, and water (20 mL) was added and extracted with methylene chloride (2 × 20 mL). The organic extract was washed with water (2 × 20 mL) and brine (10 mL) and the solvent removed to yield an oil that was subjected to column chromatography with hexanes:ethyl ether (3:1) to give 2.02 g (88%) of a colorless oil: ^{1}H NMR δ 2.30 (s, 3H), 3.09 (s, 1H), 3.73 (s, 3H), 5.98 (s, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.19−7.25 (m, 4H); ^{13}C NMR δ 21.0, 55.2, 71.8, 110.6, 120.6, 126.4 (2C), 127.6, 128.4, 128.7 (2C), 132.1, 136.6, 140.3, 156.6. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.32; H, 7.26.

General Procedure for the Preparation of Compounds 1i and 1j. To a solution of the appropriate aldehyde (20 mmol) in dry THF (30 mL) was added a solution of [4-(*N*,*N*-dimethylamino)phenyl]magnesium bromide in THF (1 M, 20 mL, 20 mmol) with stirring and cooling at 0 °C. After 10 h reflux, the solution was treated with saturated ammonium chloride solution (40 mL) and extracted with methylene chloride (2 × 50 mL), and the combined organic layer was washed with NaOH 5% (2 × 20 mL) and brine (20 mL) and dried ($MgSO_4$). The solvent was removed to give an oil that was dissolved in ethanol (20 mL), $NaBH_4$ (0.38 g, 10 mmol) was added, and the mixture was stirred at rt for 1 h. The solvent was removed, the remaining oil was treated with water (50 mL), extracted with methylene chloride (3 × 50 mL), and dried ($MgSO_4$), and the solvent was removed to give an oil that was recrystallized from the appropriate solvent.

4-(*N*,*N*-Dimethylamino)-α-(4-*n*-hexyloxyphenyl)benzenemethanol (1i): 3.55 g (56%) of white needles; mp 62−64 °C (hexanes:methylene chloride); ^{1}H NMR δ 0.87−0.92 (t, J = 6.4 Hz, 3H), 1.31−1.45 (m, 6H), 1.69−1.76 (m, 2H), 2.46 (d, J = 2.4 Hz, 1H), 2.87 (s, 6H), 3.89 (t, J = 6.5 Hz, 2H), 5.63 (s, 1H), 6.65 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H); ^{13}C NMR δ 14.0, 22.5, 25.6, 29.2, 31.5, 40.5 (2C), 67.9, 75.3, 112.4 (2C), 114.1 (2C), 127.5 (2C), 127.5 (2C), 132.4, 136.4, 149.9, 158.1. Anal. Calcd for $C_{21}H_{29}NO_2$: C, 77.03; H, 8.93; N, 4.28. Found: C, 77.02; H, 9.06; N, 4.18.

4-(*N*,*N*-Dimethylamino)-α-(3,4,5-trimethoxyphenyl)-benzenemethanol (1j): 4.64 g (73%) of a white solid; mp 139−141 °C (methanol); ^{1}H NMR δ 2.32 (br s, 1H), 2.92 (s, 6H), 3.82 (s, 9H), 5.67 (s, 1H), 6.62 (s, 2H), 6.68 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H); ^{13}C NMR δ 40.4 (2C), 55.9 (2C), 60.6, 75.7, 103.3 (2C), 112.4 (2C), 127.5 (2C), 131.8, 136.7,

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140.0, 150.0, 152.9 (2C). Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.30; N, 4.41. Found: C, 68.05; H, 7.50; N, 4.33.

Preparation of α-(4-Methoxyphenyl)-5-methyl-2-thiophenemethanol (1k). To a solution of 2-methylthiophene (1.96 g, 20 mmol) in THF (80 mL) at −40 °C was added, *n*-BuLi (2 M, 10.5 mL, 21 mmol). After 30 min of stirring, the temperature was lowered to −78 °C, and *p*-anisaldehyde (2.72 g, 20 mmol) in THF (20 mL) was added. The mixture was allowed to warm to rt, treated with saturated ammonium chloride solution (90 mL), and extracted with methylene chloride (2 × 50 mL). The organic layer was washed with NaOH solution (5%, 2 × 50 mL), brine (2 × 50 mL), and water (2 × 50 mL) and dried ($MgSO_4$), and solvent was removed to give an oil that was recrystallized from ether−hexanes to yield 2.21 g (47%) of a white solid: mp 67.5−68 °C; ^{1}H NMR δ 2.40 (s, 3H), 2.68 (s, 1H), 3.76 (s, 3H), 5.83 (s, 1H), 6.54 (d, J = 3.0 Hz, 1H), 6.61 (d, J = 3.3 Hz, 1H), 6.84 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 15.2, 55.1, 71.2, 113.7 (2C), 124.5, 124.5, 127.4 (2C), 135.5, 139.8, 146.0, 159.1. Anal. Calcd for $C_{13}H_{14}OS$: C, 66.64; H, 6.02. Found: C, 66.73; H, 6.25.

General Procedure for Preparation of Compounds 6a−o and 7r. The mixture of corresponding diphenylmethanol (2 mmol), benzotriazole (0.31 g, 2.6 mmol), *p*-toluenesulfonic acid monohydrate (0.042 g, 0.2 mmol) (no catalyst was used for the preparation of compounds **2e**,**g**−**k**), and perfluorocarbon fluid (bp 104 °C) (20 mL) was refluxed overnight. The perfluorocarbon fluid was removed on cooling, the remaining oil was dissolved in methylene chloride (20 mL), and the solution was washed with NaOH solution (5%, 2 × 20 mL), brine (20 mL), and water (20 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a solid that was mixed with the appropriate nitroarene (2 mmol) (air replaced with argon) and dissolved in THF (10 mL). The solution was added dropwise *via* a cannula (over 40 min) to a solution of potassium *tert*-butoxide (1.12 g, 10 mmol) in THF (10 mL) at −20 °C with stirring. After an additional 4 h of stirring at −20 °C, saturated ammonium chloride solution (30 mL) was added, and when the deep red color disappeared the reaction mixture was extracted with methylene chloride (3 × 20 mL). The organic layer was dried ($MgSO_4$) and solvent removed under reduced pressure. The remaining oil was dissolved in methylene chloride (40 mL), washed with NaOH solution (5%, 20 mL), brine (2 × 20 mL), and water (20 mL), and dried ($MgSO_4$), solvent was removed under reduced pressure, and the remaining oil was subjected to column chromatography.

4-(Diphenylmethyl)nitrobenzene (6a). Hexanes:diethyl ether (3:1) was used as the eluent to give yellow plates: mp 95−97 °C (hexanes) (lit.[6] mp 93 °C); ^{1}H NMR δ 5.63 (s, 1H), 7.09 (d, J = 6.9 Hz, 4H), 7.25−7.34 (m, 8H), 8.14 (d, J = 8.5 Hz, 2H); ^{13}C NMR δ 56.6, 123.5, 126.9, 128.6, 129.3, 130.2, 142.3, 145.5, 151.6.

4-(Diphenylmethyl)-2-fluoronitrobenzene (6b). Hexanes:diethyl ether (3:1) was used as the eluent to give yellow plates: mp 59−60 °C (hexanes); ^{1}H NMR δ 5.58 (s, 1H), 6.99−7.10 (m, 6H), 7.25−7.36 (m, 6H), 7.99 (t, J = 7.8 Hz, 1H); ^{13}C NMR δ 56.5, 119.0 (d, J = 21.2 Hz, 1C), 125.5 (d, J = 37.6 Hz, 1C), 127.2 (2C), 128.8 (4C), 129.2 (4C), 141.6 (2C), 153.7 (d, J = 18.4 Hz, 1C), 155.4 (d, J = 275.0 Hz, 1C). Anal. Calcd for $C_{19}H_{14}FNO_2$: C, 74.26; H, 4.59; N, 4.56. Found: C, 74.36; H, 4.73; N, 4.66.

2-Chloro-4-[(2-methoxyphenyl)(4′-methyldiphenyl)-methyl]nitrobenzene (6c). Hexanes:diethyl ether (3:1) was used as the eluent to give a yellow oil: ^{1}H NMR δ 2.33 (s, 3H), 3.72 (s, 3H), 5.86 (s, 1H), 6.80 (d, J = 6.4 Hz, 1H), 6.86−6.95 (m, 4H), 7.08−7.12 (m, 3H), 7.22−7.28 (m, 2H), 7.77 (d, J = 8.5 Hz, 1H); ^{13}C NMR δ 21.0, 49.0, 55.4, 110.7, 120.5, 125.4, 127.0, 128.3, 128.4, 129.3 (4C), 130.0, 130.5, 132.3, 136.5, 138.5, 145.8, 151.3, 156.8. Anal. Calcd for $C_{21}H_{18}NO_3Cl$: C, 68.57; H, 4.93; N, 3.81. Found: C, 68.38; H, 5.07; N, 3.87.

2-Chloro-4-[[4-(*N*,*N*-Dimethylamino)phenyl]phenylmethyl]nitrobenzene (6d). Hexanes:diethyl ether (3:1) was used as the eluent to give an orange oil: ^{1}H NMR δ 2.93 (s, 6H), 5.46 (s, 1H), 6.67 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 7.07−7.15 (m, 3H), 7.22−7.33 (m, 4H), 7.78 (d, J = 8.5 Hz, 1H); ^{13}C NMR δ 40.4 (2C), 55.4, 112.5 (2C), 125.5, 126.8, 127.1, 128.4, 128.6 (2C), 129.1 (2C), 129.3, 129.8 (2C), 132.5, 142.4, 145.8, 149.4, 151.6. Anal. Calcd for $C_{21}H_{19}ClNO_2$: C, 68.76; H, 5.22; N, 7.64. Found: C, 68.91; H, 5.45; N, 7.62.

2-Chloro-4-[[4-(*N*,*N*-dimethylamino)phenyl]-3,4,5-trimethoxyphenyl]methyl]nitrobenzene (6e). Hexanes:diethyl ether (3:1) was used as the eluent to give orange prisms: mp 58−60 °C; ^{1}H NMR δ 2.95 (s, 6H), 3.75 (s, 6H), 3.84 (s, 3H), 5.40 (s, 1H), 6.30 (s, 2H), 6.68 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.5 Hz, 2H), 7.15−7.17 (m, 1H), 7.31 (s, 1H), 7.81 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 40.4 (2C), 55.6, 56.1 (2C), 60.8, 106.4 (2C), 112.5 (2C), 125.5, 127.1, 128.3, 129.1, 129.7 (2C), 132.4, 136.8, 138.0, 145.8, 149.5, 151.5, 153.3 (2C). Anal. Calcd for $C_{24}H_{25}N_2O_5Cl$: C, 63.09; H, 5.51; N, 6.13. Found: C, 63.06; H, 5.51; N, 6.00.

2-Bromo-4-[(4-methylphenyl)phenylmethyl]nitrobenzene (6f). Hexanes:diethyl ether (3:1) was used as the eluent to give an orange oil: ^{1}H NMR δ 2.31 (s, 3H), 5.51 (s, 1H), 6.95 (d, J = 8.0 Hz, 2H), 7.05−7.32 (m, 8H), 7.48 (d, J = 1.5 Hz, 1H), 7.73 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 20.9, 55.7, 114.5, 125.5, 127.0, 128.7 (2C), 129.0 (3C), 129.1 (2C), 129.4 (2C), 135.6, 136.7, 138.7, 141.9, 147.8, 150.7. Anal. Calcd for $C_{20}H_{16}BrNO_2$: C, 62.84; H, 4.22; N, 3.66. Found: C, 62.45; H, 4.30; N, 3.80.

2-Bromo-4-[(4-biphenylyl)phenylmethyl]nitrobenzene (6g). Hexanes:diethyl ether (3:1) was used as the eluent to give orange prisms: mp 59−61 °C; ^{1}H NMR δ 5.57 (s, 1H), 7.09−7.43 (m, 11H), 7.52−7.57 (m, 5H), 7.75 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 55.8, 114.7, 125.6, 127.0 (2C), 127.2, 127.4 (3C), 128.8 (4C), 129.1, 129.2 (2C), 129.6 (2C), 135.7, 140.0, 140.3, 140.7, 141.6, 147.9, 150.4. Anal. Calcd for $C_{25}H_{18}BrNO_2$: N, 3.15. Found: N, 3.21.

4-(Diphenylmethyl)-2-methoxynitrobenzene (6h). Hexanes:diethyl ether (3:1) was used as the eluent to give orange prisms: mp 142−144 °C (methanol); ^{1}H NMR δ 3.80 (s, 3H), 5.58 (s, 1H), 6.75 (dd, J_1 = 8.4 Hz, J_2 = 1.0 Hz, 1H), 6.83 (s, 1H), 7.09 (d, J = 6.8 Hz, 4H), 7.22−7.36 (m, 6H), 7.78 (d, J = 8.5 Hz, 1H); ^{13}C NMR δ 56.2, 56.7, 114.6, 121.2, 125.6, 126.8 (2C), 128.5 (4C), 129.2 (4C), 137.7, 142.2 (2C), 151.4, 153.0. Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39. Found: C, 75.17; H, 5.30; N, 4.23.

4-[(4-Chlorophenyl)phenylmethyl]-2-methoxynitrobenzene (6i). Hexanes:diethyl ether (3:1) was used as the eluent to give an orange oil: ^{1}H NMR δ 3.80 (s, 3H), 5.55 (s, 1H), 6.72 (dd, J = 8.5 Hz, 1.4 Hz, 1H), 6.82 (d, J = 1.4 Hz, 1H), 7.03 (d, J = 8.3 Hz, 2H), 7.06−7.09 (m, 2H), 7.25−7.34 (m, 5H), 7.77 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 56.1, 56.3, 114.5, 121.1, 125.8, 127.1, 128.7 (4C), 129.1 (2C), 130.6 (2C), 132.7, 137.9, 140.8, 141.7, 150.8, 153.1. Anal. Calcd for $C_{20}H_{16}ClNO_3$: C, 67.90; H, 4.56; N, 3.96. Found: C, 67.52; H, 4.60; N, 4.11.

2-Methoxy-4-[(2-methylphenyl)phenylmethyl]nitrobenzene (6j). Hexanes:diethyl ether (3:1) was used as the eluent to give yellow prisms: mp 126−127 °C; ^{1}H NMR δ 2.21 (s, 3H), 3.76 (s, 3H), 5.70 (s, 1H), 6.69 (dd, J_1 = 8.5 Hz, J_2 = 1.7 Hz, 1H), 6.76 (d, J = 1.1 Hz, 1H), 6.79 (s, 1H), 7.03 (d, J = 6.7 Hz, 2H), 7.13−7.29 (m, 6H), 7.75 (d, J = 8.4 Hz, 1H); ^{13}C NMR δ 19.8, 53.5, 56.2, 114.6, 121.4, 125.6, 125.9, 126.8, 126.9, 128.5 (2C), 129.0, 129.3 (2C), 130.6, 136.5, 137.7, 140.7, 141.7, 151.1, 153.0. Anal. Calcd for $C_{21}H_{19}NO_3$: C, 75.66; H, 5.74; N, 4.20. Found: C, 75.63; H, 5.89; N, 4.14.

2-Methoxy-4-[(2-methoxyphenyl)(5-methylthien-2-yl)-methyl]nitrobenzene (6k). Hexanes:diethyl ether (3:1) was used as the eluent to give a yellow oil; ^{1}H NMR δ 2.44 (s, 3H), 3.81 (s, 3H), 3.87 (s, 3H), 5.59 (s, 1H), 6.49 (d, J = 3.3 Hz, 1H), 6.61 (d, J = 2.5 Hz, 1H), 6.88 (d, J = 8.5 Hz, 3H), 6.96 (s, 1H), 7.13 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 15.2, 51.4, 55.2, 56.3, 113.9 (3C), 120.6, 124.7, 125.8, 126.4, 129.6 (2C), 134.4, 137.8, 139.6, 143.8, 151.5, 153.1, 158.6. Anal. Calcd for $C_{20}H_{19}NO_4S$: C, 65.02; H, 5.18; N, 3.79. Found: C, 65.37; H, 5.26; N, 3.70.

4-[[4-(*N*,*N*-Dimethylamino)phenyl][4′-(*n*-hexyloxy)-phenyl]methyl]-2-methoxynitrobenzene (6l). Hexanes:diethyl ether (4:1) was used as the eluent to give an yellow oil: ^{1}H NMR δ 0.85−0.91 (t, J = 6.6 Hz, 3H), 1.27−1.47 (m, 6H), 1.71−1.78 (m, 2H), 2.90 (s, 6H), 3.79 (s, 3H), 3.91 (t, J =

6.4 Hz, 2H), 5.41 (s, 1H), 6.65 (d, J = 8.7 Hz, 2H), 6.75 (d, J = 8.3 Hz, 1H), 6.81 (d, J = 8.5 Hz, 2H), 6.85 (s, 1H), 6.93 (d, J = 8.5 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 13.9, 22.5, 25.6, 29.2, 31.5, 40.4 (2C), 55.2, 56.2, 67.9, 112.4 (2C), 114.3 (2C), 114.4, 121.2, 125.5, 129.7 (2C), 130.0 (2C), 130.3, 134.9, 137.5, 149.2, 152.8, 153.0, 157.8. Anal. Calcd for $C_{28}H_{34}N_2O_4$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.73; H, 7.64; N, 6.23.

4-[(4-Biphenylyl)phenylmethyl]-2-phenylnitrobenzene (6m). Hexanes:diethyl ether (5:1) was used as the eluent to give yellow prisms: mp 55−57 °C; ^{1}H NMR δ 5.65 (s, 1H), 7.14−7.43 (m, 18H), 7.55 (t, J = 7.5 Hz, 3H), 7.78 (d, J = 8.4 Hz, 1H); ^{13}C NMR δ 56.2, 124.3, 127.0 (2C), 127.3 (2C), 127.9 (2C), 128.1, 128.6 (2C), 128.7 (2C), 128.8 (2C), 129.0, 129.3 (2C), 129.7 (2C), 131.9, 132.2 (2C), 132.9, 136.4, 137.4, 139.7, 140.5, 141.4, 147.5, 149.0. Anal. Calcd for $C_{31}H_{23}NO_2$: C, 84.33; H, 5.25; N, 3.17. Found: C, 83.95; H, 5.50; N, 3.35.

2-*tert*-Butyl-4-[(4-methoxyphenyl)methyl]nitrobenzene (6n). Hexanes:diethyl ether (3:1) was used as the eluent to give a yellow oil: ^{1}H NMR δ 1.32 (s, 9H), 3.79 (s, 3H), 5.51 (s, 1H), 6.84 (d, J = 8.6 Hz, 2H), 6.98−7.01 (m, 3H), 7.07 (d, J = 7.4 Hz, 2H), 7.22−7.33 (m, 5H); ^{13}C NMR δ 30.6 (3C), 35.6, 55.2, 55.8, 113.9 (2C), 123.9, 126.6, 127.6, 128.5 (2C), 129.2 (2C), 129.7, 130.2 (2C), 134.9, 141.3, 143.2, 147.2, 149.5, 158.3. Anal. Calcd for $C_{24}H_{25}NO_3$: C, 76.77; H, 6.71; N, 3.73. Found: C, 76.78; H, 6.82; N, 3.81.

4-[[4-(*N*,*N*-Dimethylamino)phenyl]phenylmethyl]-2-(trifluoromethyl)nitrobenzene (6o). Hexanes:diethyl ether (3:1) was used as the eluent to give orange prisms: mp 86−88 °C; ^{1}H NMR δ 2.90 (s, 6H), 5.55 (s, 1H), 6.67 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 7.07 (d, J = 7.3 Hz, 2H), 7.22−7.32 (m, 3H), 7.39 (d, J = 8.3 Hz, 1H), 7.62 (s, 1H), 7.74 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 40.3 (2C), 55.5, 112.5 (2C), 122.0 (q, J = 271.9 Hz, 1C), 123.4 (q, J = 33.5 Hz, 1C), 125.1, 126.9, 128.6 (3C), 129.1 (2C), 129.8 (2C), 133.5, 142.3, 146.1, 149.5, 150.9. Anal. Calcd for $C_{22}H_{19}F_3N_2O_2$: C, 65.99; H, 4.78; N, 7.00. Found: C, 66.23; H, 4.84; N, 7.05.

4-[(4-Chlorophenyl)phenylmethyl]-1-nitronaphthalene (6p). Hexanes:diethyl ether (3:1) was used as the eluent to give yellow plates: mp 70−74 °C; ^{1}H NMR δ 6.27 (s, 1H), 7.00−7.07 (m, 5H), 7.24−7.34 (m, 5H), 7.53 (t, J = 8.0 Hz, 1H), 7.66 (t, J = 7.4 Hz, 1H), 8.02−8.09 (m, 2H), 8.52 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 52.9, 56.3, 122.9, 123.7, 124.8, 125.4, 126.0, 127.2, 127.7, 128.8 (4C), 129.4 (2C), 130.8 (2C), 132.5, 132.9, 141.0, 141.9, 146.2, 146.5. Anal. Calcd for $C_{23}H_{16}ClNO_2$: C, 73.90; H, 4.31; N, 3.75. Found: C, 73.77; H, 3.96; N, 3.59.

3-Fluoro-4-[(4-methoxyphenyl)phenylmethyl]nitrobenzene (6q). Hexanes:diethyl ether (3:1) was used as the eluent to give a yellow oil: ^{1}H NMR δ 3.76 (s, 3H), 5.81 (s, 1H), 6.84 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 7.06−7.15 (m, 3H), 7.24−7.32 (m, 3H), 7.86−7.93 (m, 2H); ^{13}C NMR δ 48.8, 55.2, 111.2 (d, J = 27.6 Hz, 1C), 111.3, 114.0 (2C), 119.0, 127.0, 128.6 (2C), 129.0 (2C), 130.1 (2C), 131.3 (d, J = 3.5 Hz, 1C), 132.9, 139.4 (d, J = 14.2 Hz, 1C), 141.3, 147.3 (d, J = 8.6 Hz, 1C), 158.6, 159.9 (d, J = 250.4 Hz, 1C). Anal. Calcd for $C_{20}H_{16}FNO_3$: C, 71.21; H, 4.78; N, 4.15. Found: C, 71.14; H, 4.88; N, 4.14.

4-[(4-Chlorophenyl)phenylmethyl]-3-methoxynitrobenzene (6r). Hexanes:diethyl ether (3:1) was used as the eluent to give a yellow oil: ^{1}H NMR δ 3.80 (s, 3H), 5.90 (s, 1H), 6.96−7.05 (m, 5H), 7.22−7.30 (m, 5H), 7.71−7.75 (m, 2H); ^{13}C NMR δ 49.2, 56.0, 105.4, 115.5, 126.8, 128.5 (4C), 129.1 (2C), 130.3, 130.5 (3C), 132.3, 139.7, 140.8, 141.6, 147.6, 157.2. Anal. Calcd for $C_{20}H_{16}ClNO_3$: C, 67.90; H, 4.56; N, 3.96. Found: C, 67.99; H, 4.54; N, 3.95.

4-[(Benzotriazol-1-yl)(4-chlorophenyl)phenylmethyl]-3-methoxynitrobenzene (7r). Hexanes:diethyl ether (3:1) was used as the eluent to give yellow microcrystals: mp 124−126 °C; ^{1}H NMR δ 3.38 (s, 3H), 6.54 (d, J = 8.5 Hz, 1H), 7.06−7.19 (m, 6H), 7.25−7.31 (m, 6H), 7.72 (d, J = 1.7 Hz, 1H), 7.79 (dd, J = 1.9, 8.6 Hz, 1H), 8.05 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 55.8, 76.7, 107.5, 112.7, 115.0, 120.1, 123.7, 127.0, 127.9 (2C), 128.0 (2C), 128.3, 129.4 (2C), 129.8, 131.1 (2C), 133.5, 134.0, 137.6, 138.0, 139.0, 146.5, 149.3, 158.8. Anal. Calcd for $C_{26}H_{19}ClN_4O_3$: N, 11.90. Found: N, 11.77.

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