PALLADIUM-CATALYZED α-ARYLATION OF ARYL NITROMETHANES

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Supporting Information

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**General Methods:**

All reactions were run in flame-dried glassware, and under an argon atmosphere. Unless otherwise noted, all reagents were reagent grade and used without further purification. Cyclopentyl methyl ether (CPME) was distilled over CaH₂ and stored under argon. Aryl nitromethanes were obtained via a previously reported method.¹ Flash column chromatography was performed using EM Reagents Silica Gel 60 (230-400). Analytical thin-layer chromatography (TLC) was performed using EM Reagents 0.25 mm silica gel 254-F plates. Visualization was accomplished with UV light and/or potassium permanganate stain.

¹H NMR and ¹³C NMR spectra were recorded on AV-II 500, AM 500, DMX 360, and DMX 300 Fourier transform NMR spectrometers. ³¹P NMR spectra were recorded on DMX 360 and DMX 300 Fourier transform NMR spectrometers, and are proton decoupled. Chemical shifts are reported relative to the solvent resonance peak δ 7.27 (CDCl₃) for ¹H and δ 77.23 (CDCl₃) for ¹³C. For ³¹P spectra, chemical shifts are reported relative to a capillary internal standard δ 0 (H₃PO₄). Peaks are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, m = multiplet), coupling constants, and number of protons. High resolution mass spectra were obtained using a VG Autospec using an ESI or CI ionization mode. Infrared spectra are reported in cm⁻¹ and recorded using a Perkin-Elmer spectrometer, model Spectrum BX. All yields refer to isolated yields, and product purity was determined by ¹H NMR spectroscopy.
Parallel Microscale Experimentation Data:

In a glovebox, the ligands (2 µmol phosphine) were dosed into the 1-mL vials of either the 96-well or 24-well reactor either as solutions in benzene or in advance of the screen. For pre-dosing the ligands, the solvent was removed after dosing by evacuation by a JKem-blow-down block, and the plates were then stored in a glovebox. The palladium source (0.1 µmol Pd) was then dosed as a solution in benzene. Depending on the solubility of the palladium source in benzene, a slurry was sometimes used. The solvent was removed via a JKem-blow-down block. The base (12 µmol) was dosed as a slurry in THF. The plate was again evacuated to dryness via a JKem-blow-down block. A parylene stir-bar was added to each vial. Finally, a solution of aryl halide (11 µmol) and aryl nitromethane starting material (10 µmol) in the reaction solvent was dosed to each vial, to afford a total volume of 100 µL in each vial of the reactor (0.1 M in aryl nitromethane). The reactor block was sealed and removed from the glovebox before heating. The 96-well reactor was heated and stirred on a VP 710 Series tumble stirrer (500 rpm). The 24-well reactor was heated on an IKA heating plate with vigorous stirring.

Upon cooling to room temperature, the reactions were quenched by the addition 500 µL of a 10% solution of glacial acetic acid in acetonitrile, containing an internal standard (1 µmol biphenyl, 10 mol%). The vials were stirred for 60 minutes. Into a 96-well plate LC block (Analytical Sales and Services, part # 17P687) was added 50 µL aliquots from each reaction vial, and 750 µL of acetonitrile. The 96-well plate LC block was then sealed with a polypropylene 1 mL cap mat (Analytical Sales and Services, part # 96057). The reactions were analyzed using an Agilent Technologies 1200 series HPLC with a 96-well plate auto-sampler. Assay conditions: Supelco Ascentis Express C18 100 mm x 4.6 mm; MeCN with H2O + 0.1 % H3PO4; 1.8 mL/min; 10 % in MeCN to 95 % MeCN in 6 minutes, hold for 2 minutes; Post time 2 minutes; Column at 40 °C; 210 nm, 230 nm, and 254 nm.

The initial 24-well screen followed the above procedure using 5 mol% Pd2(dba)3, 20 mol% phosphine ligands (10 mol% for bidentate phosphine ligands), 1.2 equivalents K3PO4, 1.1 equivalents 4-bromoanisole, 1.0 equivalents phenyl nitromethane,1 and 0.1 M of various solvents. Conditions tested: 12 ligands, 2 solvents. The plate was heated at 80°C for 18 h.

Ligand Set:
Solvent Set: toluene, 1,4-dioxane

Top Results based on assay yield (relative to internal standard):

| Ligand          | Solvent         | Assay Yield (%) |
|-----------------|-----------------|-----------------|
| BrettPhos       | Toluene         | 65.0310         |
| t-BuXPhos       | 1,4-dioxane     | 60.7561         |
| t-BuXPhos       | Toluene         | 57.9590         |
| t-BuBrettPhos   | 1,4-dioxane     | 52.5740         |
| BrettPhos       | 1,4-dioxane     | 43.4403         |
| t-BuBrettPhos   | Toluene         | 34.7629         |
| Ligand          | Solvent       | Yield (%) |
|-----------------|---------------|-----------|
| JohnPhos        | Toluene       | 15.2857   |
| XPhos           | 1,4-dioxane   | 14.1585   |
| (t-Bu)_3P HBF_4 | Toluene       | 13.8627   |
| (t-Bu)_3P HBF_4 | 1,4-dioxane   | 13.6496   |
| SPhos           | 1,4-dioxane   | 7.5738    |
| XPhos           | Toluene       | 5.9274    |
| QPhos           | Toluene       | 4.4360    |
| QPhos           | 1,4-dioxane   | 3.4622    |
| CataXClum A     | 1,4-dioxane   | 2.4985    |
| DPPF            | Toluene       | 0         |
| CataXClum A     | Toluene       | 0         |
| Cy_3P HBF_4     | Toluene       | 0         |
| DTBPF           | Toluene       | 0         |
| SPhos           | Toluene       | 0         |
| DPPF            | 1,4-dioxane   | 0         |
| Cy_3P HBF_4     | 1,4-dioxane   | 0         |
| JohnPhos        | 1,4-dioxane   | 0         |
| DTBPF           | 1,4-dioxane   | 0         |

A second, broader 96-well screen was performed following the above general procedure using 5 mol% Pd_2(dba)_3, 20 mol% phosphine ligands, 1.2 equivalents K_3PO_4, 1.1 equivalents 4-bromoanisole, 1.0 equivalents phenyl nitromethane and 0.1 M in solvent. Conditions tested: 12 ligands, 8 solvents.

**Ligand Set:**
Solvent Set:

- t-BuOH
- CPME
- trifluorotoluene
- dichlorobenzene
- THF
- toluene
- benzene
- 1,4-dioxane

Top Results based on product / internal standard (IS):

| Ligand       | Solvent | Product / IS | Benzophenone / IS | Sum of Products / IS | Validation (Isolated Yield) |
|--------------|---------|--------------|-------------------|----------------------|-----------------------------|
| t-BuXPhos    | CPME    | 3.6597       | 4.8404            | 8.5001               | 80%                         |
| t-BuXPhos    | dioxane | 4.5728       | 3.8121            | 8.3849               | 38%                         |
| Catalyst       | Solvent       | $k$ (L/mol·s) | $t_{1/2}$ (h) | $T_d$ (°C) | Yield (%) |
|---------------|---------------|---------------|---------------|------------|-----------|
| CataCXium POMetB | CPME          | 2.2054        | 5.6431        | 7.8484     | 75%       |
| BrettPhos     | CPME          | 3.3759        | 4.2318        | 7.6077     | 49%       |
| t-BuXPhos     | benzene       | 1.8533        | 5.2585        | 7.1118     | 42%       |
| BrettPhos     | benzene       | 1.9910        | 4.6181        | 6.6092     | 41%       |
| t-BuXPhos     | THF           | 1.6656        | 4.0443        | 5.7100     | -         |
| t-BuBrettPhos | benzene       | 0.2566        | 5.2508        | 5.5075     | -         |
| CataCXium POMetB | THF           | 2.0863        | 3.3966        | 5.4829     | -         |
| BrettPhos     | trifluorotoluene | 0.9600        | 4.0791        | 5.0391     | -         |
| BrettPhos     | THF           | 0.4069        | 4.5695        | 4.9764     | -         |
| t-BuXPhos     | trifluorotoluene | 0.4755        | 4.2906        | 4.7661     | -         |
| JohnPhos      | CPME          | 2.7890        | 1.9277        | 4.7168     | -         |
| BrettPhos     | dioxane       | 1.7608        | 2.7982        | 4.5591     | -         |
| JohnPhos      | dioxane       | 3.2512        | 1.2053        | 4.4565     | -         |
| CataCXium POMetB | trifluorotoluene | 0.5818        | 3.7341        | 4.3159     | -         |
| JohnPhos      | THF           | 2.1985        | 1.4055        | 3.6040     | -         |
| BrettPhos     | tBuOH         | 0.3682        | 3.2211        | 3.5893     | -         |
| CataCXium POMetB | tBuOH         | 0.3140        | 2.8638        | 3.1778     | -         |
| JohnPhos      | tBuOH         | 1.9581        | 1.0805        | 3.0386     | -         |
| t-BuXPhos     | tBuOH         | 0.1416        | 2.6495        | 2.7911     | -         |
| CataCXium POMetB | dioxane       | 0.0000        | 2.6767        | 2.6767     | -         |
| JohnPhos      | trifluorotoluene | 1.0616        | 0.9515        | 2.0131     | -         |
| BrettPhos     | toluene       | 1.9501        | 0.0000        | 1.9501     | -         |
| CataCXium POMetB | benzene       | 0.3188        | 1.6206        | 1.9395     | -         |
| t-BuBrettPhos | trifluorotoluene | 0.1676        | 1.5367        | 1.7043     | -         |
| Ligand         | Solvent       | 1.6941 | 0.0000 | 1.6941 | -  |
|----------------|---------------|--------|--------|--------|---|
| JohnPhos      | toluene       |        |        |        |    |
| CataCXium     | POMetB        | 0.0000 | 1.5178 | 1.5178 | -  |
| t-BuBrettPhos | dichlorobenzene | 0.0000 | 1.4935 |        |    |
| t-BuXPhos     | dioxane       | 0.3708 | 1.2667 | 1.2667 | -  |
| JohnPhos      | benzene       | 0.7288 | 0.5316 | 1.2604 | -  |
| t-BuBrettPhos | tBuOH         | 0.0000 | 1.0488 | 1.0488 | -  |
| (t-Bu)$_3$P HBF$_4$ | dioxane    | 0.5813 | 1.4935 |        |    |
| (t-Bu)$_3$P HBF$_4$ | benzene     | 1.0020 | 0.0000 | 1.0020 | -  |
| XantPhos      | tBuOH         | 0.9788 | 0.9788 |        |    |
| XPhos          | benzene       | 0.0000 | 0.8813 | 0.8813 | -  |
| XPhos          | CPME          | 0.1335 | 0.7636 |        |    |
| t-BuXPhos     | toluene       | 0.6706 | 0.6706 |        |    |
| BrettPhos     | dichlorobenzene | 0.0000 | 0.6558 | 0.6558 | -  |
| QPhos          | CPME          | 0.0000 | 0.5683 | 0.5683 | -  |
| t-BuBrettPhos | dichlorobenzene | 0.0000 | 0.5650 | 0.5650 | -  |
| (t-Bu)$_3$P HBF$_4$ | tBuOH    | 0.0000 | 0.5619 | 0.5619 | -  |
| (t-Bu)$_3$P HBF$_4$ | THF        | 0.0000 | 0.5443 | 0.5443 | -  |
| XPhos          | tBuOH         | 0.0632 | 0.5074 |        |    |
| XPhos          | THF           | 0.2231 | 0.4982 |        |    |
| QPhos          | dichlorobenzene | 0.2328 | 0.4829 |        |    |
| (t-Bu)$_3$P HBF$_4$ | CPME    | 0.0000 | 0.4791 | 0.4791 | -  |
| dppf           | THF           | 0.0000 | 0.4041 | 0.4041 | -  |
| QPhos          | dioxane       | 0.1719 | 0.3688 |        |    |
| QPhos          | benzene       | 0.0000 | 0.3234 | 0.3234 | -  |
| XPhos          | dioxane       | 0.0000 | 0.3121 | 0.3121 | -  |
| XPhos          | trifluorotoluene | 0.1533 | 0.3069 |        |    |
| QPhos          | THF           | 0.0000 | 0.2905 | 0.2905 | -  |
| Phosphine    | Solvent            | Yield         | MSY | Ratio  |
|--------------|--------------------|---------------|-----|--------|
| QPhos        | trifluorotoluene   | 0.0000        | 0.2747 | 0.2747 |
| t-BuBrettPhos| toluene            | 0.2409        | 0.0000 | 0.2409 |
| (t-Bu)_3P HBF_4| toluene            | 0.2235        | 0.0000 | 0.2235 |
| CataCXium POMetB | toluene            | 0.2155        | 0.0000 | 0.2155 |
| (t-Bu)_3P HBF_4| trifluorotoluene   | 0.0000        | 0.1925 | 0.1925 |
| dpff         | trifluorotoluene   | 0.0000        | 0.1432 | 0.1432 |
| SPhos        | THF                | 0.1322        | 0.0000 | 0.1322 |
| XPhos        | toluene            | 0.1191        | 0.0000 | 0.1191 |
| QPhos        | tBuOH              | 0.0000        | 0.0813 | 0.0813 |
| SPhos        | tBuOH              | 0.0645        | 0.0000 | 0.0645 |
| (t-Bu)_3P HBF_4| dichlorobenzene    | 0.0000        | 0.0000 | 0.0000 |
| CataCXium A  | dioxane            | 0.0000        | 0.0000 | 0.0000 |
| CataCXium A  | benzene            | 0.0000        | 0.0000 | 0.0000 |
| CataCXium A  | toluene            | 0.0000        | 0.0000 | 0.0000 |
| CataCXium A  | THF                | 0.0000        | 0.0000 | 0.0000 |
| CataCXium A  | dichlorobenzene    | 0.0000        | 0.0000 | 0.0000 |
| CataCXium A  | trifluorotoluene   | 0.0000        | 0.0000 | 0.0000 |
| CataCXium A  | CPME               | 0.0000        | 0.0000 | 0.0000 |
| CataCXium A  | tBuOH              | 0.0000        | 0.0000 | 0.0000 |
| dpff         | dioxane            | 0.0000        | 0.0000 | 0.0000 |
| dpff         | benzene            | 0.0000        | 0.0000 | 0.0000 |
| dpff         | toluene            | 0.0000        | 0.0000 | 0.0000 |
| dpff         | dichlorobenzene    | 0.0000        | 0.0000 | 0.0000 |
| dpff         | CPME               | 0.0000        | 0.0000 | 0.0000 |
| dpff         | tBuOH              | 0.0000        | 0.0000 | 0.0000 |
| JohnPhos     | dichlorobenzene    | 0.0000        | 0.0000 | 0.0000 |
| QPhos        | toluene            | 0.0000        | 0.0000 | 0.0000 |
| Phosphine | Solvent     | Yield 1 | Yield 2 | Yield 3 | Yield 4 | Result |
|-----------|-------------|---------|---------|---------|---------|--------|
| SPhos     | dioxane     | 0.0000  | 0.0000  | 0.0000  | 0.0000  | -      |
| SPhos     | benzene     | 0.0000  | 0.0000  | 0.0000  | 0.0000  | -      |
| SPhos     | toluene     | 0.0000  | 0.0000  | 0.0000  | 0.0000  | -      |
| SPhos     | dichlorobenzene | 0.0000 | 0.0000 | 0.0000 | 0.0000 | -      |
| SPhos     | trifluorotoluene | 0.0000 | 0.0000 | 0.0000 | 0.0000 | -      |
| SPhos     | CPME        | 0.0000  | 0.0000  | 0.0000  | 0.0000  | -      |
| t-BuBrettPhos | THF  | 0.0000  | 0.0000  | 0.0000  | 0.0000  | -      |
| t-BuBrettPhos | CPME    | 0.0000  | 0.0000  | 0.0000  | 0.0000  | -      |
| XantPhos  | dioxane     | 0.0000  | 0.0000  | 0.0000  | 0.0000  | -      |
| XantPhos  | benzene     | 0.0000  | 0.0000  | 0.0000  | 0.0000  | -      |
| XantPhos  | toluene     | 0.0000  | 0.0000  | 0.0000  | 0.0000  | -      |
| XantPhos  | THF         | 0.0000  | 0.0000  | 0.0000  | 0.0000  | -      |
| XantPhos  | dichlorobenzene | 0.0000 | 0.0000 | 0.0000 | 0.0000 | -      |
| XantPhos  | trifluorotoluene | 0.0000 | 0.0000 | 0.0000 | 0.0000 | -      |
| XantPhos  | CPME        | 0.0000  | 0.0000  | 0.0000  | 0.0000  | -      |
| XPhos     | dichlorobenzene | 0.0000 | 0.0000 | 0.0000 | 0.0000 | -      |

Validation was performed at 0.2 mmol scale, using 4-bromotoluene and 5 mol% Pd\textsubscript{2}(dba)\textsubscript{3}, following the general procedure as described on S13. Isolated yield refers to the isolated yield after Nef reaction. The Nef reaction was performed as per the general procedure described on S17.

Average yield of two trials.

Next, a 24-well screen followed the above procedure using 5 mol% Pd\textsubscript{2}(dba)\textsubscript{3}, 20 mol% phosphine ligands (10 mol% for bidentate phosphine ligands), 1.2 equivalents base, 1.1 equivalents 4-bromotoluene, 1.0 equivalents phenyl nitromethane, and 0.2 M in CPME (50 µL total solvent). Conditions tested: 12 bases, 2 solvents. The plate was heated at 80°C for 18 h.

**Base Set:**

| Base | Name   | Formulary | Formulary | Formulary | Formulary |
|------|--------|-----------|-----------|-----------|-----------|
|      | K\textsubscript{3}PO\textsubscript{4} | NaOMe | KHCO\textsubscript{3} | KOAc | KOH | KHMD | K\textsubscript{2}CO\textsubscript{3} |
| KOt-Bu | | | | | | | |
| Cs\textsubscript{2}CO\textsubscript{3} | Na\textsubscript{2}CO\textsubscript{3} | DIPEA | DBU |
**Ligand Set:** CataCXium POMetB, t-BuXPhos

**Top Results based on assay yield (relative to internal standard):**

| Ligand            | Solvent     | Product / IS | Benzophenone / IS | Sum of Products / IS | Validation (Isolated Yield)$^a$ |
|-------------------|-------------|--------------|-------------------|----------------------|---------------------------------|
| t-BuXPhos         | $K_2CO_3$   | 0.228        | 0.000             | 1.046                | 94%                             |
| t-BuXPhos         | $KHCO_3$    | 0.083        | 0.000             | 1.014                | 70%$^b$                         |
| t-BuXPhos         | $K_3PO_4$   | 0.116        | 0.000             | 1.003                | 70%$^c$                         |
| t-BuXPhos         | $Cs_2CO_3$  | 0.261        | 0.000             | 0.988                | 61%                             |
| t-BuXPhos         | KOH         | 0.000        | 0.000             | 0.955                | 71%                             |
| CataCXium POMetB  | $K_3PO_4$   | 0.173        | 0.000             | 0.919                | -                               |
| CataCXium POMetB  | $Cs_2CO_3$  | 0.274        | 0.000             | 0.833                | -                               |
| t-BuXPhos         | KOAc        | 0.060        | 0.000             | 0.799                | -                               |
| t-BuXPhos         | KOt-Bu      | 0.257        | 0.509             | 0.766                | -                               |
| t-BuXPhos         | Na$_2CO_3$  | 0.020        | 0.000             | 0.715                | -                               |
| t-BuXPhos         | DIPEA       | 0.000        | 0.000             | 0.696                | -                               |
| t-BuXPhos         | KHMDS       | 0.211        | 0.439             | 0.650                | -                               |
| CataCXium POMetB  | DIPEA       | 0.000        | 0.000             | 0.637                | -                               |
| CataCXium POMetB  | KOt-Bu      | 0.145        | 0.473             | 0.618                | -                               |
| CataCXium POMetB  | $K_2CO_3$   | 0.094        | 0.395             | 0.489                | -                               |
| CataCXium POMetB  | KOH         | 0.032        | 0.389             | 0.422                | -                               |
| CataCXium POMetB  | KHMDS       | 0.253        | 0.000             | 0.253                | -                               |
| CataCXium KOAc    | KOAc        | 0.058        | 0.000             | 0.058                | -                               |

$^a$Validation (Isolated Yield)
|                 | Reagent    | Yield 1 | Yield 2 | Yield 3 | Reaction | 
|----------------|------------|---------|---------|---------|----------|
| POMetB         | KHCO₃      | 0.044   | 0.000   | 0.044   |          |
| CataCXium POMetB | NaOMe     | 0.000   | 0.000   | 0.000   |          |
| POMetB         | Na₂CO₃     | 0.000   | 0.000   | 0.000   |          |
| POMetB         | DBU        | 0.000   | 0.000   | 0.000   |          |
| t-BuXPhos      | NaOMe     | 0.000   | 0.000   | 0.000   |          |
| t-BuXPhos      | DBU        | 0.000   | 0.000   | 0.000   |          |

*a* Validation was performed at 0.2 mmol scale, with 5 mol% Pd₂(dba)₃, following the general procedure as described on S13. Isolated yield refers to the isolated yield after Nef reaction. The Nef reaction was performed as per the general procedure described on S17.

*b* Reaction time for cross-coupling was 10 h

*c* Average yield of two trials.
Synthesis of Diaryl Nitromethanes 3aa – 3ge:

**General Method 1:** In a glovebox, a flame-dried microwave vial containing a magnetic stir-bar was charged with K$_2$CO$_3$ (46.7 mg, 0.34 mmol), Pd$_2$(dba)$_3$ (12.9 mg, 0.014 mmol), t-BuXPhos (24.0 mg, 0.056 mmol), the aryl nitromethane$^1$ (if a solid) (0.28 mmol), and the aryl halide (if a solid) (0.31 mmol). The vial was capped and brought out of the glovebox. CPME (1.4 mL) was added via syringe, followed by the aryl halide (if a liquid) (0.31 mmol) and the aryl nitromethane$^1$ (if a liquid) (0.28 mmol). The vial was heated to 80 °C in an oil bath with vigorous stirring. Upon consumption of the aryl nitromethane, as monitored by TLC or $^1$H NMR, the reaction mixture was allowed to cool to room temperature, then quenched with 1.0 mL of 1.0 M HCl. This mixture was diluted with H$_2$O and extracted with CH$_2$Cl$_2$ (3 x 20 mL). The combined organic layers were dried over MgSO$_4$ and concentrated in vacuo. The resulting residue chromatographed to afford the pure diaryl nitromethanes 3ab-3kb.

1-Methoxy-3-(nitro(p-tolyl)methyl)benzene (3ab). The general method 1 was followed with a reaction time of 18 hours, using 1-methyl-4-(nitromethyl)benzene$^2$ and 3-bromoanisole. Purification by chromatography (30% CH$_2$Cl$_2$/hexanes) provided the title compound as a pale yellow oil (62.3 mg, 86%).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.33 (dd, J = 8.0 Hz, 8.0 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 6.953 (d, J = 8.0 Hz, 1H), 6.949 (d, J = 8.0 Hz, 1H), 6.90 (dd, J = 2.0 Hz, 2.0 Hz, 1H), 6.75 (s, 1H), 3.81 (s, 3H), 2.39 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 160.1, 139.8, 136.1, 131.5, 130.2, 129.8, 128.7, 120.7, 114.9, 114.3, 94.5, 55.6, 21.4; IR (neat) 2922, 1553, 1357, 1265, 738 cm$^{-1}$; HRMS (ESI) calculated for C$_{15}$H$_{15}$O[M-NO$_2$]$^+$, m/z = 211.1123; found 211.1118.

1-Methyl-4-(nitro(4-(trifluoromethyl)phenyl)methyl)benzene (3ac). The general method 1 was followed with a reaction time of 21 hours, using 1-methyl-4-(nitromethyl)benzene$^2$ and 4-bromobenzotrifluoride. Purification by chromatography (20% CH$_2$Cl$_2$/hexanes) provided the title compound as a pale oil (48.2 mg, 58%).

$^1$H NMR (360 MHz, acetone-D$_6$) δ 7.83 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 7.9 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.23 (s, 1H), 2.37 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.4, 138.4, 131.8 (q, J = 33.0 Hz), 130.9, 130.1, 128.9, 128.6, 126.1 (q, J = 3.6 Hz), 123.9 (q, J = 272.5 Hz), 93.9, 21.4; IR (neat) 3050, 2921, 1557, 1326, 739 cm$^{-1}$; HRMS (ESI) calculated for C$_{15}$H$_{11}$NO$_2$F$_3$[M-H]$^-$, m/z = 294.0742; found 294.0748.
1-(5-(Nitro(p-tolyl)methyl)-1H-indol-1-yl)ethan-1-one (3ah). The general method 1 was followed with a reaction time of 18 hours, using 1-methyl-4-(nitromethyl)benzene and 1-(5-bromo-1H-indol-1-yl)ethan-1-one. Purification by chromatography (50% CH$_2$Cl$_2$/hexanes) provided the title compound as a yellow oil (49.9 mg, 57%). $^1$H NMR (500 MHz, acetone-D$_6$) δ 8.45 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 3.5 Hz, 1H), 7.69 (d, J = 1.5 Hz, 1H), 7.43 (dd, J = 1.5 Hz, 8.7 Hz, 1H), 7.37 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.17 (s, 1H), 6.75 (d, J = 3.5 Hz, 1H), 2.69 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (126 MHz, acetone-D$_6$) δ 170.5, 140.6, 137.1, 134.0, 132.3, 131.7, 130.9, 129.8, 129.2, 126.4, 122.5, 117.8, 109.6, 95.4, 24.5, 21.7; IR (thin film) 3029, 2957, 2924, 1714, 1515, 1366, 755, 723 cm$^{-1}$; HRMS (ESI) calculated for C$_{18}$H$_{15}$N$_2$O$_3$ [M-H]$, m/z$ = 307.1083; found 307.1089.

![Chemical structure of 1-(5-(Nitro(p-tolyl)methyl)-1H-indol-1-yl)ethan-1-one (3ah).](image)

Ethyl 4-(nitro(p-tolyl)methyl)benzoate (3ai). The general method 1 was followed with a reaction time of 21 hours, using 1-methyl-4-(nitromethyl)benzene and ethyl 4-bromobenzoate. Purification by chromatography (45% CH$_2$Cl$_2$/hexanes) provided the title compound as a pale oil (51.0 mg, 60%). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.09 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.24 (m, 4H), 6.81 (s, 1H), 4.40 (q, J = 7.2 Hz, 2H), 2.39 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (90 MHz, CD$_2$Cl$_2$) δ 166.2, 140.7, 139.5, 132.2, 131.6, 130.5, 130.3, 129.1, 128.8, 94.5, 61.8, 21.5, 14.7; IR (neat) 3056, 1718, 1556, 1278, 1108, 739 cm$^{-1}$; HRMS (CI) calculated for C$_{17}$H$_{17}$O$_3$ [M-NO$_2$]$^+$, $m/z$ = 269.1178; found 269.1180.

![Chemical structure of Ethyl 4-(nitro(p-tolyl)methyl)benzoate (3ai).](image)

1-Methoxy-3-(nitro(p-tolyl)methyl)benzene (3ba, ArBr). The general method 1 was followed, with a reaction time of 17 hours, using 1-methoxy-3-(nitromethyl)benzene and 4-bromotoluene. Purification by chromatography (25% CH$_2$Cl$_2$/hexanes) provided the title compound as a pale yellow oil (64.4 mg, 89%). All spectra were in agreement with that of 3ab (see above).
1-Methoxy-3-(nitro(p-tolyl)methyl)benzene (3ba, ArCl). The general method 1 was followed, with a reaction time of 17 hours, using 1-methoxy-3-(nitromethyl)benzene\(^3\) and 4-chlorotoluene. Purification by chromatography (25% CH\(_2\)Cl\(_2\)/hexanes) provided the title compound as a pale yellow oil (55.7 mg, 76%). All spectra were in agreement with that of 3ab (see above).

1-Methyl-4-(nitro(4-(trifluoromethyl)phenyl)methyl)benzene (3ca). The general method 1 was followed with a reaction time of 20 hours, using 1-(nitromethyl)-4-(trifluoromethyl)benzene\(^4\) and 4-bromotoluene. Purification by chromatography (25% CH\(_2\)Cl\(_2\)/hexanes) provided the title compound as a yellow oil (60.6 mg, 73%). All spectra were in agreement with that of 3ac (see above).

1-Methoxy-4-(nitro(4-(trifluoromethyl)phenyl)methyl)benzene (3dc). The general method 1 was followed with a reaction time of 20.5 hours, using 4-methoxy-1-(nitromethyl)benzene\(^3\) and 4-bromobenzo trifluoride. Purification by chromatography (40% CH\(_2\)Cl\(_2\)/hexanes) provided the title compound as a pale yellow oil (48.9 mg, 56%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.69 (d, \(J = 8.3\) Hz, 2H), 7.48 (d, \(J = 8.3\) Hz, 2H), 7.30 (d, \(J, J = 9.0\) Hz, 2H), 6.95 (d, \(J = 9.0\) Hz, 2H), 6.80 (s, 1H), 3.84 (s, 3H); \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 161.0, 138.6, 131.7 (q, \(J = 32.7\) Hz), 130.4, 128.7, 126.2 (q, \(J = 4.2\) Hz), 125.8, 123.9 (q, \(J = 272.9\) Hz), 114.7, 93.7, 55.6; IR (thin film) 2962, 2936, 1557, 1327, 836, 822 cm\(^{-1}\); HRMS (CI) calculated for C\(_{15}\)H\(_{13}\)NO\(_3\)F\(_3\) [M+H]\(^+\), \(m/z\) = 312.0848; found 312.0844.

1-Nitro-3-(nitro(p-tolyl)methyl)benzene (3fa). The general method 1 was followed with a reaction time of 18 hours, using 3-nitro-1-(nitromethyl)benzene\(^2\) and 4-bromotoluene. Purification by chromatography (50% CH\(_2\)Cl\(_2\)/hexanes) provided the title compound as a yellow oil (44.9 mg, 58%). \(^1\)H NMR (360 MHz,
acetone-$d_6$ δ 8.34-8.31 (m, 2H), 7.95 (d, J = 7.6 Hz, 1H), 7.80 (ddd, J = 11.5 Hz, 3.8 Hz, 3.8 Hz, 1H), 7.40 (d, J = 8.3 Hz, 2H), 7.33 (m, 2H), 7.31 (s, 1H), 2.37 (s, 3H); $^{13}$C NMR (90 MHz, acetone-$D_6$) δ 140.8, 138.0, 135.9, 132.4, 131.4, 130.8, 130.3, 129.2, 125.1, 124.5, 93.3, 21.2; IR (neat) 2923, 1555, 1531, 1351, 726 cm$^{-1}$; HRMS (ESI) calculated for C$_{14}$H$_{11}$N$_2$O$_4$ [M-H]$^-$, m/z = 271.0719; found 271.0726.

![Chemical Structure](image)

(4-(Nitro(p-tolyl)methyl)phenyl)(phenyl)methanone (3ja). The general method 1 was followed with a reaction time of 28 hours, using (4-(nitromethyl)phenyl)(phenyl)methanone$^4$ and 4-bromotoluene. Purification by chromatography (60% CH$_2$Cl$_2$/hexanes) provided the title compound as a pale yellow oil (53.6 mg, 57%). $^1$H NMR (500 MHz, CDCl$_3$) 7.85 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.64-7.61 (m, 1H), 7.52-7.48 (m, 4H), 7.30-7.25 (m, 4H), 6.84 (s, 1H), 2.40 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) 196.0, 140.3, 138.64, 138.59, 137.3, 133.0, 131.0, 130.7, 130.3, 130.0, 128.7, 128.6, 128.4, 94.2, 21.4; IR (thin film) 3062, 2957, 2921, 1660, 1553, 1527, 796, 783 cm$^{-1}$; HRMS (ESI) calculated for C$_{21}$H$_{18}$NO$_3$ [M+H]$^+$, m/z = 332.1287; found 332.1285.

1-Methoxy-3-(nitro(m-tolyl)methyl)benzene (3kb). The general method 1 was followed with a reaction time of 17 hours, using 3-methyl-1-(nitromethyl)benzene$^5$ and 3-bromoanisole. Purification by chromatography (25% CH$_2$Cl$_2$/hexanes) provided the title compound as an pale oil (57.1 mg, 79%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.34 (dd, J = 8.0 Hz, 8.0 Hz, 1H), 7.31 (dd, J = 6.9 Hz, 6.9 Hz, 1H), 7.24-7.17 (m, 3H), 6.96-6.95 (m, 2H), 6.91 (dd, J = 2.0 Hz, 2.0 Hz, 1H), 6.75 (s, 1H), 3.81 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 160.1, 139.0, 135.9, 134.3, 130.5, 130.2, 129.2, 129.0, 125.7, 120.9, 114.9, 114.5, 94.7, 55.6, 21.6; IR (thin film) 3006, 2960, 2937, 2924, 1556, 1537, 1164, 767, 740 cm$^{-1}$; HRMS (ESI) calculated for C$_{15}$H$_{16}$O [M-NO$_3$]$^+$, m/z = 211.1123; found 211.1121.
Synthesis of Benzophenones 4aa – 4bf:

**General Method 2:** The general method 1 was followed to generate the crude diaryl nitromethane (3). The crude diaryl nitromethane (3) (0.28 mmol) was charged to a 25 mL round-bottom flask containing a magnetic stir-bar. The residue was dissolved in MeOH (1.7 mL). A slurry of Na$_2$HPO$_4$ (160.1 mg, 1.13 mmol) in 1.0 M aqueous NaOH (2.0 mL) was charged, and the reaction mixture was stirred for 1 hour. Next, a solution of oxone (173.4 mg, 0.28 mmol) in deionized H$_2$O (0.9 mL) was charged and the reaction mixtures was stirred for 1 hour further. Finally, 5.0 M aqueous HCl (6.0 mL) was charged and the reaction mixture was stirred for an additional 30 minutes. The reaction mixture was diluted with H$_2$O and extracted with CH$_2$Cl$_2$ (2 x 25 mL). The combined organic layers were washed with saturated brine (2 x 30 mL). The organic layers were then dried over MgSO$_4$ and concentrated in vacuo. The resulting residue was purified by flash column chromatography to afford the pure benzophenones 4aa – 4bf.\(^6\)

Di-p-tolymethanone (4aa). The general method 1 was followed, using 1-methyl-4-((nitromethyl)benzene\(^2\) and 4-bromotoluene. The crude reaction product 3aa was taken forward, where general method 2 was followed. Purification by chromatography (50% CH$_2$Cl$_2$/hexanes) provided the title compound as a white solid (36.6 mg, 62%). All spectra were in agreement with the published literature values.\(^7,8\)

(4-Methoxyphenyl)(p-tolyl)methanone (4ad). The general method 1 was followed, using 1-methyl-4-((nitromethyl)benzene\(^2\) and 4-bromoanisole. The crude reaction product 3ad was taken forward, where the general method 2 was followed. Purification by chromatography (65% CH$_2$Cl$_2$/hexanes) provided the title compound as a yellow solid (47.7 mg, 75%). All spectra were in agreement with the published literature values.\(^9,10\)

(3,5-Dimethylphenyl)(p-tolyl)methanone (4ae). The general method 1 was followed, using 1-methyl-4-((nitromethyl)benzene\(^2\) and 1-bromo-3,5-dimethylbenzene. The crude reaction product 3ae was taken
forward, where the general method 2 was followed. Purification by chromatography (50% CH$_2$Cl$_2$/hexanes) provided the title compound as a white solid (45.3 mg, 72%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.39 (s, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.22 (s, 1H), 2.45 (s, 3H), 2.38 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 197.1, 143.2, 138.3, 138.1, 135.4, 134.0, 130.5, 129.1, 127.9, 29.9, 21.4; IR (thin film) 3054, 2986, 2926, 1655, 1265, 739 cm$^{-1}$; HRMS (Cl) calculated for C$_{16}$H$_{17}$O [M+H]$^+$, m/z = 225.1279; found 225.1278.$^{11}$

![Structure Image](image)

**(3-Nitrophenyl)(p-tolyl)methanone (4af).** The general method 1 was followed, using 1-methyl-4-(nitromethyl)benzene$^2$ and 1-bromo-3-nitrobenzene. The crude reaction product 3af was taken forward, where the general method 2 was followed. Purification by chromatography (40% CH$_2$Cl$_2$/hexanes) provided the title compound as a yellow powder (29.7 mg, 58%). IR (neat) 3057, 1662, 1534, 1265, 736 cm$^{-1}$; HRMS (Cl) calculated for C$_{14}$H$_{11}$NO$_3$ [M]$^+$, m/z = 241.0739; found 241.0735. All spectra were in agreement with the published literature values.$^{12,13}$

![Structure Image](image)

**Naphthalen-2-yl(p-tolyl)methanone (4ag).** The general method 1 was followed, using 1-methyl-4-(nitromethyl)benzene$^2$ and 2-bromonaphthalene. The crude reaction product 3ag was taken forward, where the general method 2 was followed. Purification by chromatography (25% CH$_2$Cl$_2$/hexanes) provided the title compound as a yellow solid (40.6 mg, 58%). All spectra were in agreement with the published literature values.$^{14,15}$

![Structure Image](image)

**Benzofuran-5-yl(p-tolyl)methanone (4al).** The general method 1 was followed, using 1-methyl-4-(nitromethyl)benzene$^2$ and 5-bromobenzofuran. The crude reaction product 3al was taken forward, where the general method 2 was followed. Purification by chromatography (55% CH$_2$Cl$_2$/hexanes) provided the title compound as a beige solid (27.7 mg, 42%). mp: 81.5-83 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.08 (d, J = 1.5 Hz, 1H), 7.83 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 2.0 Hz, 1H), 7.59 (d, J = 9.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 6.86 (dd, J = 2.3 Hz, 1.0 Hz, 1H), 2.47 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 196.6, 157.3, 146.5, 143.1, 135.7, 133.4, 130.5, 129.1, 127.4, 126.9, 124.5, 111.5, 107.4,
21.9; IR (thin film) 3114, 2921, 2851, 1651, 1439, 1295 cm\(^{-1}\); HRMS (ESI) calculated for C\(_{16}\)H\(_{13}\)O\(_2\) [M+H]\(^+\), m/z = 237.0916; found 237.0916.

\[ \text{p-Tolyl(3-(trifluoromethyl)phenyl)methanone (4am).} \]
The general method 1 was followed, using 1-methyl-4-(nitromethyl)benzene\(^2\) and 3-bromobenzotrifluoride. The crude reaction product 3am was taken forward, where the general method 2 was followed. Purification by chromatography (40% CH\(_2\)Cl\(_2\)/hexanes) provided the title compound as a white powder (35.1 mg, 47%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.05 (s, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.63 (dd, J = 7.9 Hz, 7.9 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 195.2, 144.2, 138.9, 134.3, 133.2, 131.1 (q, J = 34.0 Hz), 130.5, 129.5, 129.1, 128.1 (q, J = 3.4 Hz), 126.8 (q, J = 3.8 Hz), 123.9 (q, J = 27.25 Hz), 21.9; IR (thin film) 2926, 1609, 1510, 1264, 810, 704 cm\(^{-1}\); HRMS (CI) calculated for C\(_{15}\)H\(_{12}\)F\(_3\)O [M]\(^+\), m/z = 265.0840; found 265.0832.\(^{16}\)

\[ \text{(3-Methoxyphenyl)(3-nitrophenyl)methanone (4bf).} \]
The general method 1 was followed, using 3-methoxy-1-(nitromethyl)benzene\(^2\) and 1-bromo-3-nitrobenzene. The crude reaction product 3bf was taken forward, where the general method 2 was followed. Purification by chromatography (50% CH\(_2\)Cl\(_2\)/hexanes) provided the title compound as a beige semi-solid (42.8 mg, 60%). IR (neat) 2926, 1609, 1510, 1264, 810, 704 cm\(^{-1}\); HRMS (CI) calculated for C\(_{14}\)H\(_{11}\)NO\(_4\) [M]\(^+\), m/z = 257.0688; found 257.0686. All spectra were in agreement with the published literature values.\(^{17}\)
Synthesis of Diarylmethanamines 5aa – 5ag:

**General Method 3:** The general method 1 was followed to generate the crude diaryl nitromethane (3). The unpurified diaryl nitromethane (3) (0.28 mmol) was charged to a 25 mL round-bottom flask containing a magnetic stir-bar. The residue was dissolved in glacial AcOH (2.0 mL). To this solution was added purified zinc dust (4 x 6 equivalents, in 30 minute intervals) at room temperature. The reaction mixture was stirred for 16 h. The reaction was quenched with saturated aqueous K$_2$CO$_3$ and extracted with EtOAc (3 x 15mL), dried with MgSO$_4$, and concentrated in vacuo. The resulting residue was purified by flash column chromatography to afford the pure diarylmethanamines 5aa – 5ag.

![Di-p-tolylmethanamine (5aa)](image)

**Di-p-tolylmethanamine (5aa).** The general method 1 was followed, using 1-methyl-4-(nitromethyl)benzene$^2$ and 4-bromotoluene. The crude reaction product 3aa was taken forward, where general method 3 was followed. Purification by chromatography (90% EtOAc/hexanes) provided the title compound as a light yellow solid (36.5 mg, 61%). All spectra were in agreement with the published literature values.$^{19-21}$

![4-Methoxyphenyl)(p-tolyl)methanamine (5ad)](image)

**4-Methoxyphenyl)(p-tolyl)methanamine (5ad).** The general method 1 was followed, using 1-methyl-4-(nitromethyl)benzene$^2$ and 4-bromoanisole. The crude reaction product 3ad was taken forward, where general method 3 was followed. Purification by chromatography (5% MeOH/CH$_2$Cl$_2$) provided the title compound as a light pink semi-solid (42.4 mg, 66%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.28 (d, J = 9.0 Hz, 2H), 7.24 (d, J = 7.7 Hz, 2H), 7.12 (d, J = 7.7 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 5.71 (br s, 2H), 5.20 (s, 1H), 3.78 (s, 3H), 2.32 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.1, 139.9, 137.3, 135.0, 129.5, 128.5, 127.1, 114.2, 58.5, 55.4, 21.3; IR (thin film) 3725, 3627, 3053, 2924, 2839, 1610, 1265, 808 cm$^{-1}$; HRMS (Cl) calculated for C$_{15}$H$_{16}$NO [M-H]$^-$, m/z = 226.1232; found 226.1234.

![3,5-Dimethylphenyl)(p-tolyl)methanamine (5ae)](image)

**3,5-Dimethylphenyl)(p-tolyl)methanamine (5ae).** The general method 1 was followed, using 1-methyl-4-(nitromethyl)benzene$^2$ and 1-bromo-3,5-dimethylbenzene. The crude reaction product 3ae was taken
forward, where general method 3 was followed. Purification by chromatography (5% MeOH/CH₂Cl₂) provided the title compound as a pale yellow oil (39.6 mg, 62%). ¹H NMR (500 MHz, CDCl₃) δ 7.26 (d, J = 7.8 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 6.98 (s, 2H), 6.89 (s, 1H), 5.16 (s, 1H), 3.57 (br s, 2H), 2.33 (s, 3H), 2.27 (s, 3H); ¹³C NMR (125.8 MHz, CDCl₃) δ 145.1, 142.2, 138.2, 136.8, 129.4, 128.9, 127.0, 124.8, 59.4, 21.6, 21.3; IR (thin film) 3380, 3017, 2919, 2859, 1606, 1455, 854, 820, 754 cm⁻¹; HRMS (CI) calculated for \( \text{C}_{16}\text{H}_{17}\) [M-NH₂]⁺, \( m/z = 209.1330 \); found 209.1325.

Naphthalen-2-yl(p-tolyl)methanamine (5ag). The general method 1 was followed, using 1-methyl-4-(nitromethyl)benzene² and 4-bromoanisole. The crude reaction product 3ag was taken forward, where general method 3 was followed. Purification by chromatography (5% MeOH/CH₂Cl₂) provided the title compound as a beige semi-solid (30.6 mg, 44%). ¹H NMR (500 MHz, CDCl₃) δ 7.89 (s, 1H), 7.84 – 7.79 (m, 2H), 7.76 (d, J = 8.5 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.40 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 7.28 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 5.38 (s, 1H), 4.29 (br s, 2H), 2.33 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 142.0, 141.4, 137.1, 133.6, 132.8, 129.5, 128.5, 128.2, 127.8, 127.2, 126.3, 126.0, 125.7, 125.3, 59.5, 21.3; IR (neat) 3287, 3053, 3022, 2922, 2855, 1603, 1404, 818, 765 cm⁻¹; HRMS (ESI) calculated for \( \text{C}_{18}\text{H}_{15}\) [M-NH₂]⁺, \( m/z = 231.1174 \); found 2321.1171.
One Pot Diarylation of Nitromethane:

**Step 1:** In a glovebox, a flame-dried microwave vial containing a magnetic stir-bar was charged with 4-bromotoluene (68.4 mg, 0.4 mmol), Pd$_2$(dba)$_3$ (9.2 mg, 0.01 mmol), XPhos (11.4 mg, 0.024 mmol), and K$_3$PO$_4$ (101.9 mg, 0.48 mmol). The vial was capped and brought out of the glovebox. 1,4-dioxane (2.0 mL) was added via syringe, followed by nitromethane (43.1 µL, 0.8 mmol). The vial was heated to 70 °C in an oil bath with vigorous stirring. Upon consumption of the aryl halide, as monitored by $^1$H NMR, the reaction mixture was allowed to cool to room temperature.

**Step 2:** In a glovebox, the vial was opened and charged with Pd$_2$(dba)$_3$ (18.3 mg, 0.02 mmol), t-BuXPhos (18.3 mg, 0.08 mmol), and K$_2$CO$_3$ (66.3 mg, 0.48 mmol). The vial was capped and brought out of the glovebox. 3-bromoanisole (55.7 µL, 0.44 mmol) was added via syringe. The vial was heated to 80 °C in an oil bath with vigorous stirring. Upon completion of the reaction, as monitored by TLC or $^1$H NMR, the reaction mixture was allowed to cool to room temperature, then quenched with 1.0 mL of 1.0 M HCl. This mixture was diluted with H$_2$O and extracted with CH$_2$Cl$_2$ (3 x 20 mL). The combined organic layers were dried over MgSO$_4$ and concentrated *in vacuo*. Purification by chromatography (60% CH$_2$Cl$_2$/hexanes) provided the title compound as a pale yellow oil (54.1 mg, 53%). All spectra were in agreement with that of 3ab (see above).
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