## Supporting Information

## Cascade and lodo-Selective Base-Promoted Homolytic Aromatic Substitution

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Figure 1: BHAS Reactions with arenes (solids at room temperature)
(Delayed Reaction Initiation by Arene-Melt)


- KOtBu
- 1,4-Dimethoxy Benzene
- Bis(haloaryl)acetal
- 1,4-Dimethoxy Benzene
- 1,10-Phenanthroline
- Stirring bar
${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}-$ NMR Spectra of Compounds




${ }^{13}$ CAR NMR $(101 \mathrm{MHz}, \mathrm{CHLOROFORM}-\mathrm{d}) ~ \delta=156.8,153.2,138.4,133.6,128.5,124.0,118.8,116.7,113.1,91.4,85.3$ This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/


[^0]


${ }^{13 C}$ CMR ( 101 MHz, CHLOROFORM-d) $\delta=156.7,155.5,139.6,138.4,129.5,124.4,118.8,115.2,91.2,87.2,85.3$




$\begin{aligned} & \text { 13C NMR }(101 \mathrm{MHz}, \mathrm{CHLOROFORM-d}) ~ \\ & \text { CARBON_cdcl3 }\end{aligned}=155.7,139.6,129.7,124.4,115.5,91.7,87.1$


 $\underset{\text { PROTON_Cdcl3_01 }}{5.20(\mathrm{~s}, 2 \mathrm{H}), 2.28(\mathrm{~s}, 3 \mathrm{H})}$
















$\underset{\text { PROTON_cdcl3_02 }}{\text { H. }} 7.03(\mathrm{t}, ~ J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.76(\mathrm{~s}, 2 \mathrm{H})$




[^1]

 blpunodmos $\underset{\text { PROTON_ddcl_ _01 }}{\text { H. }} 6.81 \mathrm{~m}, ~, 6.81-6.79(\mathrm{~m}, 1 \mathrm{H}), 6.80(\mathrm{t}, J=2.2 \mathrm{~Hz}, 4 \mathrm{H}), 6.70(\mathrm{qd}, J=0.9,8.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.74(\mathrm{~s}, 2 \mathrm{H}), 1.36(\mathrm{~s}, 9 \mathrm{H})$



CARBON_ddCl_-01









$\underset{\text { PROTON_cdcl3_01 }}{1 \mathrm{H})} \mathbf{7 . 1 8 - 7 . 1 2 ( \mathrm { m } , 4 \mathrm { H } ) , 6 . 9 4 - 6 . 9 0 ( \mathrm { m } , 3 \mathrm { H } ) , 6 . 8 5 ( \mathrm { dd } , J = 3 . 1 , 9 . 0 \mathrm { Hz } , 2 \mathrm { H } ) , 5 . 6 3 ( \mathrm { s } , 2 \mathrm { H } ) , 3 . 8 0 ( \mathrm { s } , 3 \mathrm { H } ) , 3 . 7 6 ( \mathrm { s } , 3 \mathrm { H } )}$



CARBON_Cdcli_01
Ci












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 ${ }^{13} \mathrm{C}$ NMR ( 101 MHz, ,CHLOROFORM-d) $\delta=155.6,154.5,139.5,136.9,133.8,131.7,130.5,130.4,129.6,129.6,129.0,128.9,128.7,128.6,128.5,128.3$,






























5ROTON_CdCl3_01
PR




 ${ }^{13} \mathrm{C}$ NMR ( 101 MHz, CHLOROFORM-d) $\delta=154.0,152.2,136.1,133.5,133.4,132.4,131.8,131.3,130.9,129.1,129.0,128.3,128.1,127.9,127.1,126.2$,





(td, $J=5.1,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.31(\mathrm{~d}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.26(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.18(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.66(\mathrm{~d}, J=0.8 \mathrm{~Hz}, 2 \mathrm{H})$









$(\mathrm{m}, 3 \mathrm{H}), 6.86(\mathrm{ddd}, J=7.8,6.3,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.66-6.69(\mathrm{~m}, 1 \mathrm{H}), 5.64-5.66(\mathrm{~m}, 2 \mathrm{H})$



 CARBON_docis_01



 ${ }_{\text {PROTON_cdcl3_01 }}^{1 \mathrm{H}}, 7.27(\mathrm{dd}, J=3.52,4.70 \mathrm{~Hz}, 2 \mathrm{H}), 7.22(\mathrm{~d}, J=8.61 \mathrm{~Hz}, 2 \mathrm{H}), 6.89-6.96(\mathrm{~m}, 1 \mathrm{H}), 5.81(\mathrm{~s}, 2 \mathrm{H})$




$J=7.8,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.25-7.32(\mathrm{~m}, 4 \mathrm{H}), 6.90-6.97(\mathrm{~m}, 1 \mathrm{H}), 5.84(\mathrm{~s}, 2 \mathrm{H})$
PROTON_cdli_01









112.5, 91.5, 56.3, 55.8




4H), $7.30-7.36(\mathrm{~m}, 2 \mathrm{H}), 7.29(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.95(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.87$ (s, 2H)



 $\underset{\text { CARBON_Cdci3_01 }}{\text { 125.4. }} 123.116 .7,116.3,116.3,113.1,91.6$ ${ }^{13} \mathrm{C}$ NMR (CHLOROFORM-d ,101MHz): $\delta(\mathrm{ppm}) 156.3,153.5,139.6,135.1,133.8,133.6,131.7,131.3,128.6,128.3,127.5,127.0,126.0,126.0,125.8$,














[^0]:    $\underset{\text { PROTON_cdcl3_02 }}{\mathrm{Hz}, 3 \mathrm{H})} 6.95 \mathrm{~m}, 6 \mathrm{H}), 6.78(\mathrm{dt}, J=1.4,7.5 \mathrm{~Hz}, 3 \mathrm{H}), 5.72(\mathrm{~s}, 6 \mathrm{H})$ ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CHLOROFORM}-\mathrm{d}$ ) $\delta=7.76(\mathrm{dd}, J=1.6,7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.61-7.56(\mathrm{~m}, 6 \mathrm{H}), 7.29(\mathrm{ddd}, J=1.6,7.2,8.4 \mathrm{~Hz}, 3 \mathrm{H}), 7.13(\mathrm{dd}, J=1.2,8.2$

[^1]:    $\underset{\text { PROTON_Cdcli_02 }}{(\mathrm{m}, 1 \mathrm{H}), 7.32-7.22(\mathrm{~m}, 2 \mathrm{H}), 7.05-6.97(\mathrm{~m}, 2 \mathrm{H}), 5.25(\mathrm{~s}, 1 \mathrm{H})(1)}$
    

