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Divergent Roles of Urea and Phosphoric Acid Derived Catalysts in Reactions of Diazo Compounds

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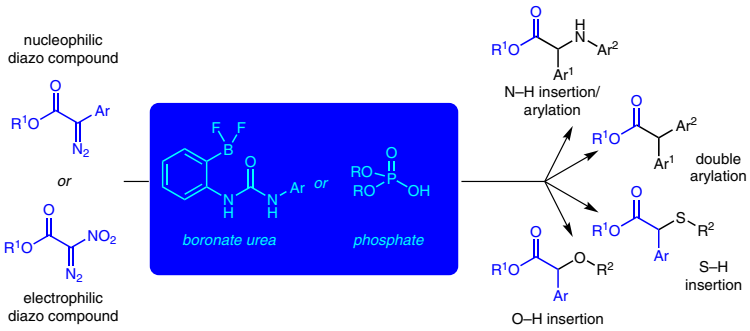

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Abstract Hydrogen-bond-donor catalysts enable a variety of formal insertion reactions of diazo compounds. The role of the catalyst in the reaction system may vary depending on several factors, including the nucleophilicity of the diazo compound and the acidity of the insertion partner. Ureas and phosphoric acid derivatives can offer complementary reactivity patterns when selected as catalysts for selected O–H and S–H insertion reactions of aryl- and diazo-substituted esters.

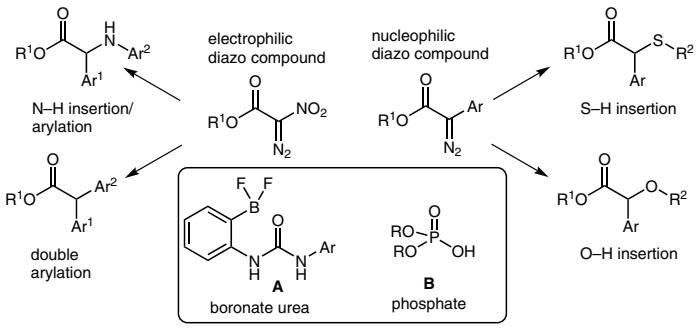
Key words diazo compounds, substituent effects, homogeneous catalysis, insertion reactions, urea catalysts, phosphate catalysts

Diazo compounds participate in a variety of attractive bond-forming reactions.[1] Conventionally, the useful reactivity patterns of diazo compounds are often accessed with the aid of transition metal catalysis.[2] Recent advances in hydrogen-bond-donor catalysis have demonstrated the potential to develop new and useful reactivity patterns that are difficult and/or inaccessible with transition metal catalysis.[3] To this end, we have been interested in the divergent abilities of ureas (e.g., **A**) and phosphates (e.g., **B**) to catalyze formal insertion reactions and multicomponent coupling reactions of both electrophilic and nucleophilic diazo compounds (Scheme 1).

Urea-Catalyzed Multicomponent Coupling Reactions of α-Nitro-α-diazo Esters

Early on, our investigations led us to the unanticipated finding that difluoroboronate urea **1** enabled the N–H insertion/arylation of α-nitro-α-diazo esters **2**, giving rise to glycines **3** in good to excellent yields (53–91%, Scheme 2).[4]

The well-documented observation that ureas can hydrogen bond and co-crystallize with a number of functional groups, including the nitro group, was the inspiration of our initial attempt to control reactions of nitrodiazo compounds with urea catalysis.[5] In the context of α-nitro-α-diazo ester **2**, it was initially hypothesized that hydrogen bonding of the urea functionality to the nitro group would lead to activation of the diazo compound through intermediate **4** (Figure 1). Further investigations, both experimental



Scheme 1

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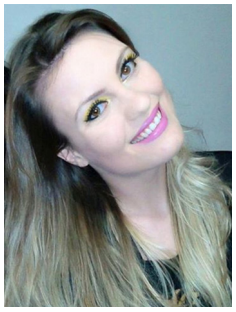
Biographical Sketches

Antonio C. B. Burtoloso graduated with a technological degree in chemistry at the Federal University of Rio de Janeiro (2001). He performed his M.Sc. in natural products chemistry at the Federal University of Rio de Janeiro (2002) and his Ph.D. in Chemistry at the State University of Campinas (2006). In 2007, he was a postdoctoral fellow at the Scripps Research Institute under the supervision of Prof. K. C. Nicolaou. Since 2008, he has been Professor at the Institute of Chemistry of São Carlos, University of São Paulo (IQSC - USP).



Barbara Bernardim was born in Guarapuava-PR, Brazil, in 1989. She received her degree in chemistry from Midwest State University (UNICENTRO) in 2010. In 2011, she moved to Sao Carlos-SP to start her M.Sc. in organic chemistry in the group of Prof. Dr. Antonio Burtoloso at the University of Sao Paulo. In 2013, she started her Ph.D in the same group working on the chemistry of α,β-unsaturated diazo ketones.

Anita Mattson received her B.Sc. degree from Northern Michigan University in 2002, where she studied polarity reversal catalysis in the context of radical reactions with Professor Frankie Ann McCormick. As a graduate student at Northwestern University, she joined the group of Professor Karl Scheidt and developed new thiazolium-based strategies for acyl anion addition reactions. In 2007, she completed her Ph.D. and became a National Institutes of Health postdoctoral fellow in Professor Michael Crimmins's group at the University of North Carolina at Chapel Hill, where she investigated a highly convergent approach toward hemibrevetoxin B. Mattson joined the faculty in the Department of Chemistry and Biochemistry at The Ohio State University in 2009. Her current research program centers on the design of new families of organic catalysts, the development of metal-free methodologies, and the synthesis of naturally occurring molecules.

Erica Couch received her B.Sc. degree from Butler University in 2012, where she worked with Professor LuAnne McNulty in the development of new strategies towards the synthesis of dihydropyran-containing natural products by tandem reactions of cyclic boronic half acids. Upon graduation, she joined Professor Anita Mattson's group at The Ohio State University, where she investigated boronate ureas as catalysts for metal-free diazo insertion chemistry. Graduating with her M.Sc in 2014, she is currently working at PPG in Texas.

Andrea Hardman-Baldwin was born in 1989 in Harrison, Arkansas. She received her B.Sc. degree in chemistry from Harding University in 2011 while working under the mentorship of Professor Carl B. Hollandsworth. In June of 2011, she moved to The Ohio State University to begin graduate studies with Professor Anita E. Mattson. Her graduate research is centered on the synthesis and functionalization of heterocycles by utilizing new classes of hydrogen-bond-donor organocatalysts.

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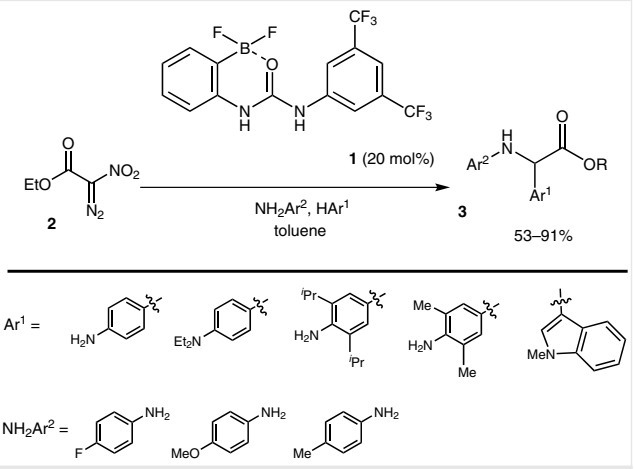


Scheme 2

and computational, were conducted and supported the likelihood of the urea activating the diazo compound through hydrogen bonding.[6] More specifically, ^{1}H NMR spectroscopic studies detected an observable binding interaction between boronate urea **1** and the α-nitro-α-diazo ester **2**. DFT calculations also supported the likelihood of this interaction.

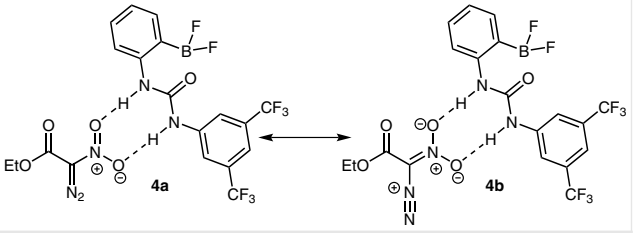
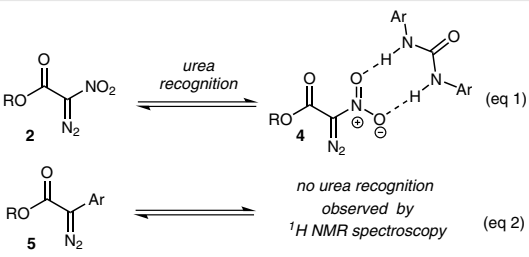


Figure 1

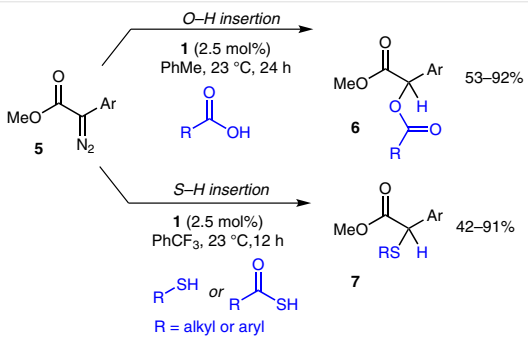
Urea-Catalyzed Formal Insertion Reactions of α-Aryl-α-diazo Esters

Whereas good evidence supporting urea recognition of the nitro group exists (Scheme 3, eq. 1), it was not obvious if or how a urea catalyst would interact with and/or activate an α-aryl-α-diazo ester. Indeed, our efforts to observe any binding between these two species by NMR spectroscopy were fruitless (Scheme 3, eq. 2).

Despite the unclear mode of action of urea catalysis in the context of α-aryl-α-diazo ester activation, excellent yields of both O–H and S–H insertion products were frequently isolated when α-aryl-α-diazo esters were treated with appropriate insertion partners in the presence of just 2.5 mol% of boronate urea catalyst **1** (Scheme 4).[7] Importantly, no reaction was observed if the boronate urea catalyst was omitted while otherwise keeping the reaction conditions identical. In our initial study, a variety of carboxylic acids were found to operate as insertion partners with electron-rich α-aryl-α-diazo esters **5** to afford **6** in high yields. The substrate scope was even more broad with respect to the S–H insertion: arenethiols, alkanethiols, and thioacids all reacted well with electron-rich α-aryl-α-diazo esters **5**.

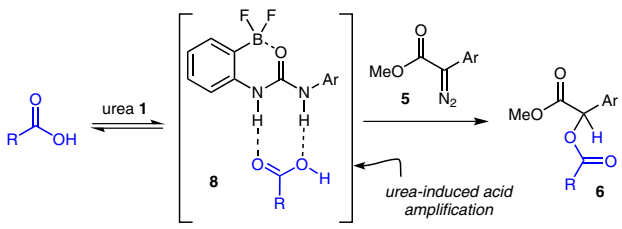


Scheme 3



Scheme 4

As mentioned above, the experiments in our laboratory suggested that direct urea activation of the α-aryl-α-diazo ester **5** was unlikely, and prompted us to consider a reaction pathway in which the urea was activating the insertion partner, the thiol or carboxylic acid, as opposed to the diazo compound (Scheme 5, intermediate **8**). Indeed several recent reports by Jacobsen, Seidel, and others describe the potential involvement of urea–Brønsted acid co-catalytic systems.[8] Moreover, a recent report by Cheng and co-workers provided support that the acidity of Brønsted acids could be enhanced up to 9 pK_a units in the presence of a urea.[9] Adding further support to the urea acid activation was Smith's evidence demonstrating the excellent molecular recognition of boronate ureas for acetate ions.[10]



Scheme 5

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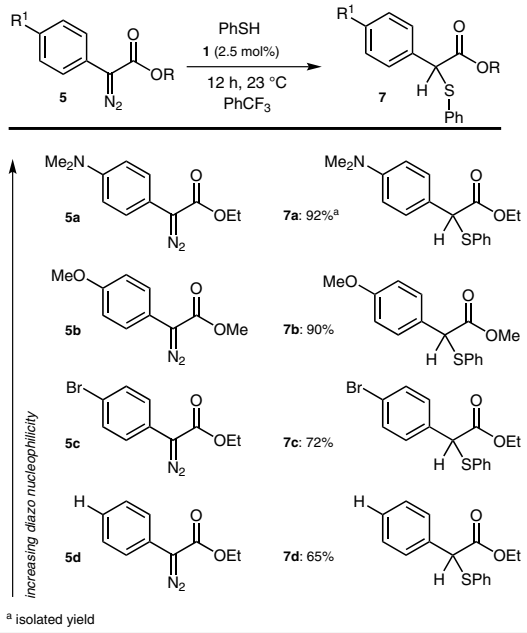
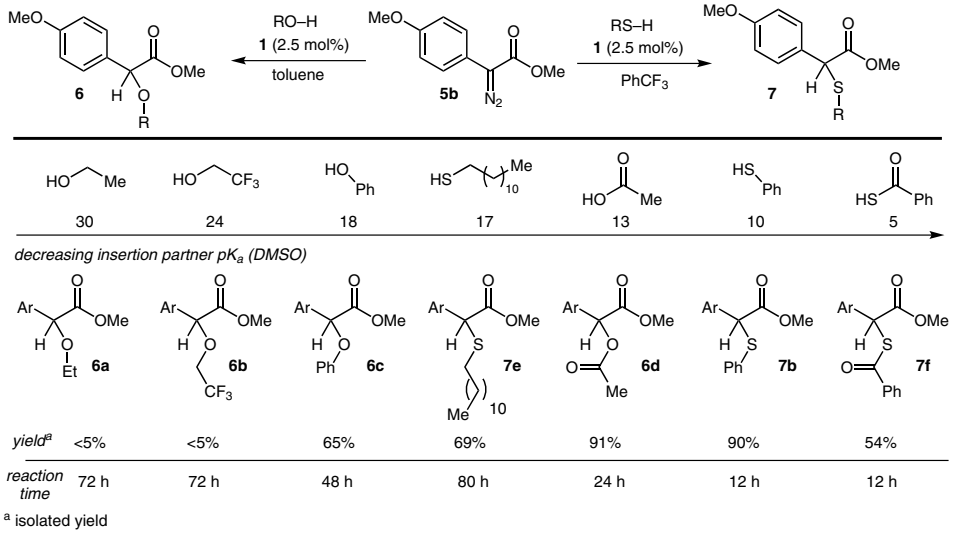


Scheme 6

In addition to the literature precedent, a variety of experiments suggested urea activation of the insertion partner as the proposed mode of action. First, no reaction was observed when base was added to the reaction mixture [Et_3N (1 equiv) in addition to the optimized reaction conditions]. Moreover, removal of the acidic X–H bond from the reaction, for instance, sodium acetate used in place of acetic acid, resulted in no reaction. These data provided us with two theories: (a) the X–H bond is essential for the reaction to occur, and (b) nucleophilic attack is likely not occurring in the first step of the reaction system. Control experiments also ruled out the direct protonation of the diazo compound with the boronate urea.

With the hypothesis that the reaction is proceeding with urea activation of the insertion partner, we set out to first explore the tolerance of the reaction to the nucleophilicity of the α-aryl-α-diazo ester **5** (Scheme 6). Several diazo compounds were prepared and subjected to an insertion reaction with thiophenol catalyzed by **1**. As a general trend, the more nucleophilic diazo compounds afforded higher yields of product. The most electron-rich dimethylamino-substituted diazo ester **5a** gave the highest yield of insertion product **7a** (92%). The methoxy-subsituted diazo ester **5b** also operated well in the formal S–H insertion event, giving rise to **7b** in 90% yield. The less electron-rich diazo compounds **5c** and **5d** also participated in the desired bond-forming reactions, although the yields of isolated products **7c** and **7d** were somewhat lower (72% and 65%, respectively).

The investigations next turned to probe the effect of insertion partner acidity on the outcome of the reaction (Scheme 7). Several alcohols and thiols, with pK_a values in dimethyl sulfoxide ranging from 5 to 30, were selected as reactants with methoxy-substituted diazo ester **5b**. The most reactive partner for this reaction turned out to be thiophenol [pK_a ~10 (DMSO)] giving rise to product **7b** in 90% yield after 12 hours at 23 °C. Acetic acid also gave rise to high yields of product, although a longer reaction time was required (**6d**, 91% after 24 h). The less acidic dodecanethiol and phenol also participated in the insertion event, giving, however, lower yields of product after extended reaction times.[11] The two alcohols ethanol and trifluoroethanol afforded minimal amounts of desired products **6a** and **6b**. The most acidic species tested in this study, thio-



Scheme 7

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benzoic acid, was tolerated and gave rise to a modest yield of **7f** after a reaction time of 12 hours (54%).

At the conclusion of this short study, it appeared that boronate urea **1** was most successful facilitating the coupling of more nucleophilic diazo compounds (**5a** and **5b**) with O–H and S–H partners having a pK_a (DMSO) between 10 and 13.

Phosphate-Catalyzed Formal Insertion Reactions of α-Aryl-α-diazo Esters

While urea **1** was only an effective catalyst with moderately acidic insertion partners, we were curious to know if less acidic alcohols would insert into diazo compounds with a different type of hydrogen bond donor. Specifically, we were interested in analyzing phosphates as catalysts in diazo insertion reactions. Our studies were inspired by the recent success of phosphoric acid-derived catalysts in a variety of reaction platforms.[12,13]

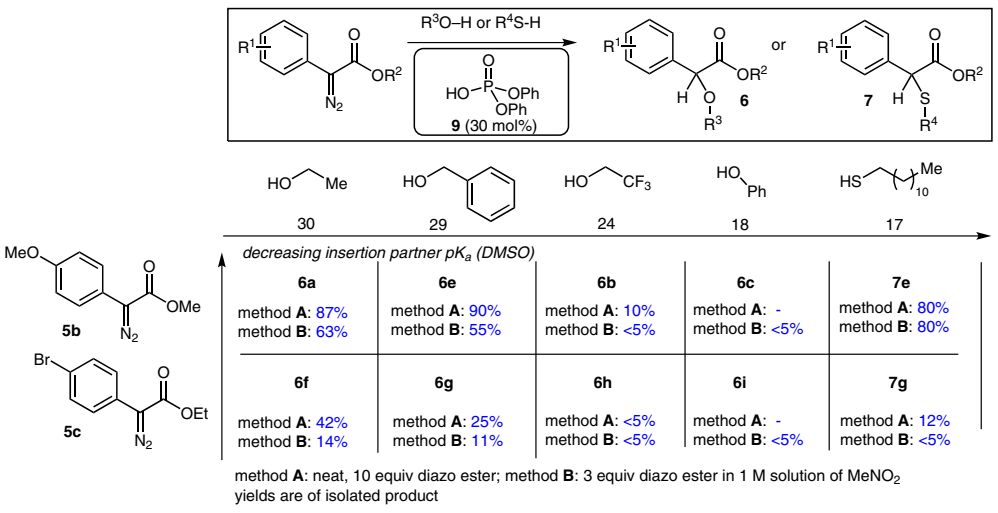
Early on in our studies, we were delighted to find that diphenyl phosphate **9** proved to be a suitable catalyst for insertion reactions of the less acidic alcohols [pK_a ~30 (DMSO), Scheme 8]. Under the best conditions found to effect these formal insertions, namely neat alcohol or thiol (10 equiv) with diphenyl phosphate **9** (30 mol%; method A), excellent yields of products **6a** and **6e** were obtained by insertion reactions of ethanol and benzyl alcohol into diazo ester **5b** (87% and 90%, respectively). Importantly, if no catalyst was included, the yields dropped to between 2–6%. The reaction system also tolerated moderately acidic, strongly nucleophilic species, like alkanethiols. For example, **7e** was prepared in 80% yield by the phosphate-catalyzed insertion reaction. As an alternative for expensive or solid alcohols/thiols, the reaction can also be performed with minimal background reactions (7–10%) by using nitromethane as the solvent and three equivalents of the insertion partner (Scheme 8, method B).

Divergent Roles of Ureas and Phosphates in Reactions of Diazo Compounds

The role of urea and phosphate catalysts in reactions of diazo compounds may vary depending upon the nature of the diazo substrate and the insertion partner. Several modes of action by which the catalysts may be operating are considered in Scheme 9. Plausible catalytic cycles are also described.

Select electrophilic diazo compounds, such as α-nitro-α-diazo esters, may experience direct activation by a hydrogen-bond-donor catalyst. For example, in the case of urea-catalyzed reactions of α-nitro-α-diazo compounds, the initial hydrogen bonding of the urea catalyst to the nitro group is proposed to prime the α-nitro-α-diazo ester for reaction with aniline (**4**, Scheme 9). Our investigations into the mechanism suggest that the α-nitro-α-diazo ester operates as an electrophile while aniline undergoes addition to eventually give rise to the N–H insertion product **11**. The subsequent formation of an iminium ion from **11** yields a species that reacts in a Friedel–Crafts-type process to give rise to glycine **3**, which is isolable if the reaction is conducted under mild temperatures (23 °C or lower).

The role of the urea catalyst is likely significantly different in the reaction of α-aryl-α-diazo esters and O–H or S–H insertion partners. In this case, the proposed reaction pathway begins with urea coordination to the insertion partner to yield hydrogen-bonded complex **12** (Scheme 9). It is thought that this interaction serves to acidify the insertion partner to enable its deprotonation by the diazo-substitut-



method **A**: neat, 10 equiv diazo ester; method **B**: 3 equiv diazo ester in 1 M solution of $MeNO_2$
yields are of isolated product

Scheme 8

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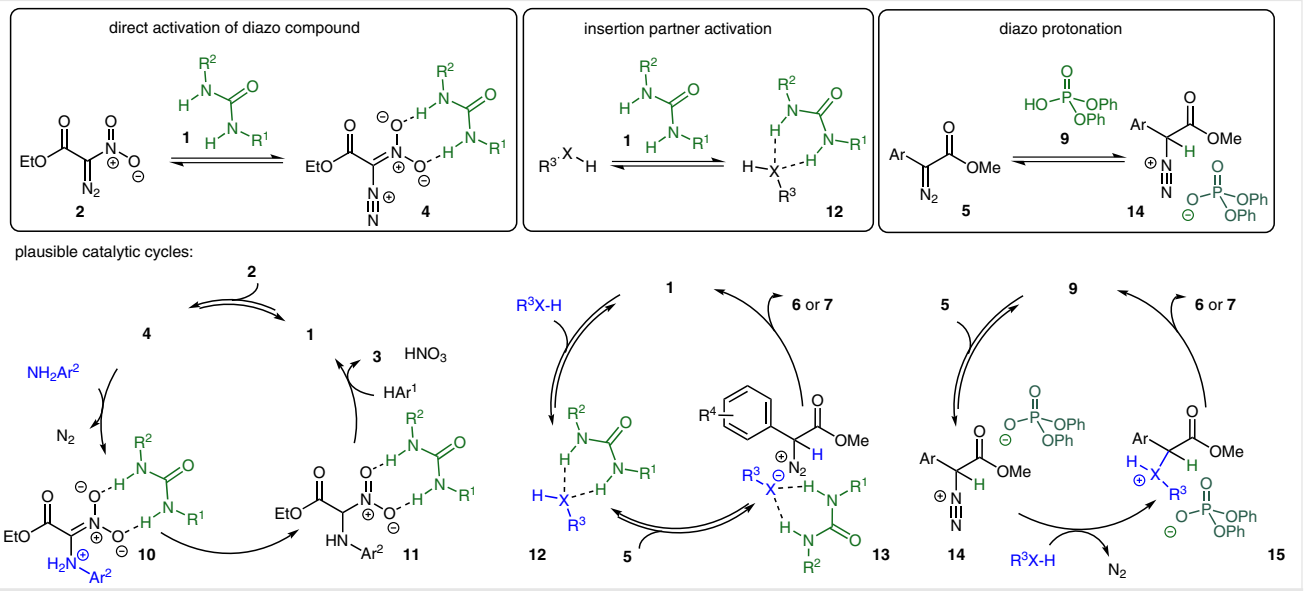

Scheme 9

ed ester to generate ion pair **13**. The addition of the conjugate base produced in the deprotonation event completes the formal insertion reaction and reintroduces the urea back in the catalytic cycle.

In the phosphate-catalyzed reaction, it is proposed that diphenyl phosphate initially protonates diazo-substituted ester **5**, leading to the diazonium **14**. Nucleophilic displacement of molecular nitrogen by the alcohol or thiol, followed by hydrogen abstraction by the conjugate base of the catalyst, leads to the product and regenerates the catalyst. Although less probable due to the presence of an ester, formation of the benzylic carbocation from **14** when nucleophilic diazo-substituted esters are employed (R^1 = OMe, NR_2) may compete with the S_N2 mechanism. Investigations are ongoing to learn more about the reaction pathway.

Conclusion

Useful formal insertion and multicomponent coupling reactions are accessible when diazo compounds are subjected to the influence of hydrogen-bond-donor catalysis. Urea and phosphate catalysts can provide complementary reactivity of diazo compound insertion reactions with alcohols and thiols. The difference in reactivity is plausibly due to their divergent roles in the presence of the diazo compound and insertion partner. Studies that more fully relate the boundaries of the substrate scope to the type of hydrogen-bond donor or Brønsted acid catalyst are current topics of interest.

CH_2Cl_2, THF, DMF, and MeCN were purified by passage through a bed of activated alumina.[14] Purification of reaction products was carried out by flash chromatography over Aldrich 60 Å (40–63 μm) silica gel. Analytical TLC was performed on EMD Chemicals 0.25 μm silica gel 60-F_{254} plates. Visualization was accomplished with UV light and ceric ammonium molybdate stains followed by heating. Melting points were obtained on a Thermo Scientific Mel-temp apparatus and are uncorrected. IR spectra were obtained on a Perkin Elmer Spectrum 100R spectrophotometer; liquid products were prepared as thin films on a NaCl disk and solid products were prepared as NaBr pellets. ^{1}H NMR spectra of samples in deuterated solvents were recorded on a Bruker Avance AVIII 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm relative to the solvent as internal standard ($CHCl_3$, δ = 7.26 and DMSO, δ = 2.50). Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker Avance AVIII 400 (100 MHz) spectrometer and are reported in ppm relative to the solvent as internal standard ($CHCl_3$, δ = 77.16; DMSO, δ = 39.52). Proton-decoupled ^{19}F NMR spectra were recorded on a Bruker Avance AVIII 400 (376 MHz) spectrometer and are reported in ppm relative to $CF_3C_6H_5$ as an external standard (δ = –63.72). ^{11}B NMR spectra were recorded on a Bruker Avance DPX 500 (160 MHz) or Bruker Avance AVIII 400 (128 MHz) spectrometer and are reported in ppm relative to $BF_3{\cdot}OEt_2$ as an external standard (δ = 0.00). Electrospray mass spectra (ESI-MS) were obtained by using a Bruker MicrOTOF mass spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were purchased and used without further purification. **CAUTION**: While we have not experienced any problems handling α-nitro-α-diazo esters, aryldiazoacetates, or 4-acetamidobenzenesulfonyl azide (*p*-ABSA), appropriate care should be exercised when handling any diazo compound or azide.

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Preparation of Boronate Urea Catalyst 1[15]

1-[3,5-Bis(trifluoromethyl)phenyl]-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]urea

A flame-dried round-bottom flask under N_2 was charged with 2-aminophenylboronic acid pinacol ester (600 mg, 2.74 mmol). Freshly distilled MeCN (30 mL) was added to create a colorless solution. Last, 3,5-bis-trifluoromethylphenyl isocyanate (473 µL, 2.74 mmol) was introduced to the reaction flask dropwise by syringe. Shortly after addition of the isocyanate, a white precipitate began to form. The reaction mixture was allowed to stir at 23 °C for 4 h. The pure boronate urea pinacol ester was isolated as a white solid after vacuum filtration followed by washing with hexanes. The solid was dried under vacuum.

Yield: 1.08 g (83%); R_f = 0.94 (EtOAc–hexanes–MeOH, 4:4:1); mp 215.2–216.9 °C.

IR (NaBr): 3415, 3132, 2985, 1640, 1600, 1581, 1476, 1184, 1129 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 9.93 (br s, 1 H), 9.19 (br s, 1 H), 8.16 (s, 2 H), 7.69 (s, 1 H), 7.52–7.50 (m, 1 H), 7.42–7.34 (m, 2 H), 7.08–7.04 (m, 1 H), 1.24 (s, 12 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 154.0, 142.2, 141.7, 134.7, 131.2 (q, J = 33 Hz, CCF_3), 130.8, 123.8 (q, J = 271 Hz, CF_3), 123.4, 119.7, 119.4, 115.6, 83.0, 25.5. The carbon bonded to boron was not seen due to broadening.[16]

^{11}B NMR (160 MHz, DMSO-d_6): δ = 26.0 (br s).

HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{21}H_{21}BF_6N_2O_3$: 475.1622; found: 475.1614.

1-[3,5-Bis(trifluoromethyl)phenyl]-3-[2-(difluoroboryl)phenyl]urea (1)

A flame-dried round-bottom flask under N_2 was charged with the above-described boronate urea pinacol ester (2.18 g, 4.6 mmol) and freshly distilled MeOH (30 mL). A 4.5 M solution of KHF_2 in H_2O (4 mL, 18.4 mmol) was introduced to the reaction flask dropwise by syringe, resulting in a white heterogeneous mixture, and the reaction mixture was heated to 50 °C. Shortly after heating, the reaction mixture became a colorless solution. After 2 h at 50 °C, the reaction mixture was cooled to 23 °C and concentrated. The white solid was filtered and washed several times with H_2O to afford the potassium trifluoroboryl urea salt (92%). The urea salt (1.95 g, 4.29 mmol) was dissolved in EtOAc (15 mL) and extracted with H_2O (2 × 5 mL). The organic layer was dried and concentrated in a 500 mL round-bottom flask. To the flask was added CH_2Cl_2 (250 mL) and the mixture was allowed to stir rapidly at r.t. for 1 h, after which the solid was filtered and washed with CH_2Cl_2 to afford difluoroboryl urea **1** as a white powder.

Yield: 1.55 g (3.11 mmol, 85%); mp 205.3–205.9 °C.

IR (NaBr): 3628, 3345, 2986, 1741, 1671, 1585, 1479, 1187, 1128 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 11.27 (br s, 1 H), 10.65 (br s, 1 H), 8.11 (s, 2 H), 7.96 (s, 1 H), 7.42–7.40 (m, 1 H), 7.32–7.28 (m, 1 H), 7.15–7.10 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 154.4, 138.1, 137.5, 131.0 (q, J = 33 Hz, CCF_3), 130.6, 128.2, 124.6, 123.0, 123.0 (q, J = 271 Hz, CF_3), 118.4, 115.4, (the carbon bonded to boron was not seen due to broadening).[16]

^{11}B NMR (160 MHz, DMSO-d_6): δ = 3.63 (br s).

^{19}F NMR (376 MHz, DMSO-d_6): δ = –61.7 (s, 6 F), –132.8 (s, 1 F), –132.9 (s, 1 F)

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{21}H_{20}BF_6N_2O_3Na$: 419.0572; found: 419.0580.

Synthesis of Reagent 5a

Ethyl 2-[4-(Dimethylamino)phenyl]-2-oxoacetate

A modified version of a previously reported procedure was used.[17] A flame-dried 100 mL round-bottom flask was charged with 4-bromo-*N*,*N*-dimethylaniline (3.00 g, 15.0 mmol), dissolved in THF (25 mL), and placed under an atmosphere of N_2. The reaction mixture was cooled to –78 °C and 1.3 M *n*-BuLi in hexanes (11.65 mL, 15.15 mmol) was added dropwise over 15 min. The reaction mixture was stirred at –78 °C for an additional 15 min. The resulting suspension was then transferred dropwise via cannula at –78 °C to a separate 250 mL flame-dried round-bottom flask containing a solution of diethyl oxalate (3.26 mL, 24 mmol) in THF (25 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 20 min and then allowed to warm to 0 °C. H_2O (40 mL) was slowly added to quench the reaction. The reaction mixture was then extracted with Et_2O (3 × 75 mL), washed with H_2O (3 × 75 mL), dried ($MgSO_4$), and concentrated to afford a viscous yellow oil. The residue was recrystallized from benzene to afford ethyl 2-[4-(dimethylamino)phenyl]-2-oxoacetate as bright yellow flakes; yield: 2.23 g (67%).

IR (film): 3056, 2986, 2917, 1729, 1650, 1591, 1549, 1443, 1375, 1229 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.90 (app d, J = 9.2 Hz, 2 H), 6.66 (app d, J = 9.2 Hz, 2 H), 4.41 (q, J = 7.2 Hz, 2 H), 3.09 (s, 6 H), 1.40 (t, J = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.0, 165.1, 154.6, 132.6, 120.4, 111.0, 61.9, 40.1, 14.3.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{12}H_{15}NNaO_3$: 244.0944; found: 244.0945.

Ethyl 2-Diazo-2-[4-(dimethylamino)phenyl]acetate (5a)

A solution of hydrazine hydrate (5.77 mL, 117.52 mmol, 52 equiv) in an AcOH–H_2O mixture (1:1; 18 mL) was added to ethyl 2-[4-(dimethylamino)phenyl]-2-oxoacetate (500 mg, 2.26 mmol, 1 equiv) in MeOH (31 mL) at r.t. The reaction mixture was stirred for 72 h and then the solvent was removed under reduced pressure. CH_2Cl_2 (25 mL) was added and the mixture was washed with H_2O (25 mL), 10% aq HCl (25 mL), and sat. aq $NaHCO_3$ (25 mL). The organic layer was dried with Na_2SO_4 and concentrated to provide the hydrazone as a yellow solid; yield: 505.2 mg (95%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.21 (app d, J = 14.4 Hz, 2 H), 6.78 (app d, J = 14.4 Hz, 2 H), 6.16 (br s, 2 H), 4.31 (q, J = 11.6 Hz, 2 H), 3.00 (s, 6 H), 1.35 (t, J = 11.2 Hz, 3 H).

The hydrazone (387 mg, 1.528 mmol, 1 equiv) was dissolved in CH_2Cl_2 (55 mL) and MnO_2 (1.5 g, 17.3 mmol, 11 equiv) was added in one portion. After stirring at r.t. for 2 h, the mixture was filtered through Celite, concentrated, and purified by chromatography (silica gel, EtOAc–hexanes, 5:95 to 10:90) to afford pure **5a**.

Yield: 256 mg (67%); R_f = 0.72 (EtOAc–hexanes, 30:70).

IR (film): 2980, 2802, 2076, 1703, 1613, 1520, 1338, 1253, 1152, 1049 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.31 (app d, J = 8.8 Hz, 2 H), 6.77 (app d, J = 8.8 Hz, 2 H), 4.31 (q, J = 7.2 Hz, 2 H), 2.95 (s, 6 H), 1.33 (t, J = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 149.1, 126.1, 113.1, 111.7, 60.8, 40.5, 14.5.

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HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{16}N_3O_2$: 234.1237; found: 234.1238.

O–H Insertion Catalyzed by 1a; General Procedure

A dry, screw-capped reaction vial, equipped with a magnetic stir bar, was charged with **5** (0.364 mmol) and catalyst (0.0091 mmol, 2.5 mol%), and placed under a N_2 atmosphere. Toluene (1.45 mL) was added and the reaction mixture was degassed by bubbling N_2 through the solution for 5 min at 23 °C. The appropriate insertion partner (0.437 mmol, 1.2 equiv) was added in one portion and the reaction mixture was allowed to stir for the appropriate amount of time at 23 °C and then immediately purified by flash column chromatography (silica gel) to afford **6**.

Methyl 2-(4-Methoxyphenyl)-2-phenoxyacetate (6c)

The compound was isolated after 48 h at 23 °C as a white solid by flash column chromatography (silica gel, EtOAc–hexanes, 5:95 to 20:80).

Yield: 43 mg (65%); R_f = 0.4 (EtOAc–hexanes, 20:80).

IR (film): 2953, 2838, 1756, 1610, 1588, 1513, 1494, 1458, 1437, 1304, 1235, 1175, 1062, 1031 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.47 (app d, *J* = 8.4 Hz, 2 H), 7.29–7.23 (2 H), 7.00–6.90 (5 H), 5.59 (s, 1 H), 3.81 (s, 3 H), 3.74 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8, 160.3, 157.5, 129.7, 128.7, 127.7, 121.9, 115.6, 114.4, 78.4, 55.5, 52.7.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{16}O_4Na$: 295.0941; found: 295.0940.

Methyl 2-Acetoxy-2-(4-methoxyphenyl)acetate (6d)

The compound was isolated as a clear solid by flash column chromatography (silica gel, EtOAc–hexanes, 5:95 to 20:80).

Yield: 79 mg (91%); R_f = 0.42 (EtOAc–hexanes, 20:80).

IR (film): 3057, 2957, 2840, 1751, 1612, 1515, 1458, 1438, 1428, 1374, 1235, 1179, 1034 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (app d, *J* = 8.4 Hz, 2 H), 6.91 (app d, *J* = 8.8 Hz, 2 H), 5.88 (s, 1 H), 3.81 (s, 3 H), 3.719 (s, 3 H), 2.18 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 169.7, 160.5 129.3, 126.0, 114.4, 74.3, 55.5, 52.7, 20.9.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{14}NaO_5$: 261.0733; found: 261.0726.

S–H Insertion Catalyzed by 1a; General Procedure

A dry, screw-capped reaction vial, equipped with a magnetic stir bar, was charged with **5** (0.485 mmol) and catalyst (0.012 mmol, 2.5 mol%), and placed under a N_2 atmosphere. $PhCF_3$ (0.97 mL) was added and the reaction mixture was degassed by bubbling N_2 through the solution for 5 min at 23 °C. The appropriate thiol (0.533 mmol, 1.1 equiv) was added in one portion and the reaction mixture was allowed to stir for the appropriate amount of time at 23 °C and then immediately purified by flash column chromatography (silica gel) to afford **7**.

Ethyl 2-[4-(Dimethylamino)phenyl]-2-(phenylsulfanyl)acetate (7a)

The compound was isolated as a yellow oil by flash column chromatography (silica gel, Et_2O–hexanes, 5:95 to 20:80).

Yield: 140.5 mg (92%); R_f = 0.20 (Et_2O–hexanes, 5:95).

IR (film): 3051, 2984, 2925, 2805, 1735, 1610, 1522, 1477, 1356, 1144, 1026 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.38 (m, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.30–7.21 (m, 3 H), 6.68 (app d, *J* = 8.4 Hz, 2 H), 4.88 (s, 1 H), 4.11 (AB dq, J_{ab} = 10.8, 7.2 Hz, Δδ = 0.02, 2 H), 2.96 (s, 6 H), 1.16 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 150.6, 134.7, 132.4, 129.4, 129.0, 127.7, 122.7, 112.5, 61.6, 55.9, 40.6, 14.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{22}SNO_2$: 316.1366; found: 316.1362.

Methyl 2-(4-Methoxyphenyl)-2-(phenylsulfanyl)acetate (7b)

The compound was isolated as a white solid by flash column chromatography (silica gel, Et_2O–hexanes, 5:95 to 15:85).

Yield: 125.7 mg (90%); R_f = 0.15 (EtOAc–hexanes, 5:95).

IR (film): 3003, 2951, 2838, 1737, 1607, 1509, 1443, 1251, 1154, 1027 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.33 (m, 4 H), 7.29–7.24 (m, 3 H), 6.85 (app d, *J* = 8.8 Hz, 2 H), 4.88 (s, 1 H), 3.80 (s, 3 H), 3.67 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 159.8, 134.0, 132.7, 129.9, 129.1, 128.1, 127.7, 114.2, 55.8, 55.4, 52.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{16}SNaO_3$: 311.0712; found: 311.0714.

Ethyl 2-(4-Bromophenyl)-2-(phenylsulfanyl)acetate (7c)

The compound was isolated as a colorless oil by flash column chromatography (silica gel, Et_2O–hexanes, 5:95).

Yield: 123.4 mg (72%); R_f = 0.24 (EtOAc–hexanes, 5:95).

IR (film): 3058, 2980, 2935, 1738, 1585, 1487, 1439, 1271, 1148, 1072 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (app d, *J* = 8.4 Hz, 2 H), 7.40–7.34 (m, 2 H), 7.31 (app d, *J* = 8.4 Hz, 2 H), 7.27 (app d, *J* = 2.8 Hz, 2 H), 4.83 (s, 1 H), 4.13 (AB dq, J_{ab} = 10.8, 7.2 Hz, Δδ = 0.02, 2 H), 1.17 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 135.0, 133.4, 133.1, 131.9, 130.4, 129.2, 128.4, 122.5, 62.0, 56.0, 14.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{15}NaBrSO_2$: 372.9868; found: 372.9866.

Ethyl 2-Phenyl-2-(phenylsulfanyl)acetate (7d)

The compound was isolated as a colorless oil by flash column chromatography (silica gel, Et_2O–hexanes, 5:95 to 10:90).

Yield: 86.4 mg (65%); R_f = 0.26 (EtOAc–hexanes, 5:95).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.43 (m, 2 H), 7.40–7.36 (m, 2 H), 7.34–7.28 (m, 3 H), 7.28–7.25 (m, 3 H), 4.90 (s, 1 H), 4.12 (m, 2 H), 1.17 (t, *J* = 7.1 Hz, 3 H). All spectral data match those previously reported.[18]

Methyl 2-(4-Methoxyphenyl)-2-(dodecanylsulfanyl)acetate (7e)

The compound was isolated after 80 h at 23 °C as a colorless oil by flash column chromatography (silica gel, EtOAc–hexanes, 5:95 to 10:90).

Yield: 64 mg (69%); R_f = 0.7 (EtOAc–hexanes, 20:80).

IR (film): 2918, 1747, 1732, 1614, 1584, 1504, 1470, 1434 1336, 1248, 1148, 1035 cm^{-1}.

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^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (app d, *J* = 8.8 Hz, 2 H), 6.87 (app d, *J* = 8.8 Hz, 2 H), 4.55 (s, 1 H), 3.80 (s, 3 H), 3.73 (s, 3 H), 2.49 (m, 2 H), 1.56 (m, 2 H), 1.35–1.20 (m, 18 H), 0.88 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.8, 159.6, 129.8, 128.3, 114.2, 55.4, 52.7, 51.7, 32.11, 32.06, 29.78, 29.77, 29.72, 29.6, 29.5, 29.3, 29.1, 29.0, 22.8, 14.3.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{36}NaO_3S$: 403.2277; found: 403.2274.

Methyl 2-(Benzoylsulfanyl)-2-(4-methoxyphenyl)acetate (7f)

The compound was isolated as a colorless oil by flash column chromatography (silica gel, Et_2O–hexanes, 5:95 to 15:85).

Yield: 83.6 mg (54%); R_f = 0.15 (Et_2O–hexanes, 5:95).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.92 (m, 2 H), 7.60–7.54 (m, 1 H), 7.47–7.38 (m, 4 H), 6.89 (app d, *J* = 8.8 Hz, 2 H), 5.45 (s, 1 H), 3.80 (s, 3 H), 3.78 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.5, 170.9, 159.9, 136.2, 133.9, 129.9, 128.8, 127.5, 126.7, 114.5, 55.4, 53.2, 50.7. All spectral data match those previously reported.

Insertion Reactions Catalyzed by 9; General Procedure

Method A: To a dry screw-capped reaction vial charged with **5** (0.186 mmol) under a N_2 atmosphere was added the appropriate alcohol or thiol (1.860 mmol, 10 equiv). The catalyst (0.0558 mmol, 30 mol%) was then added in one portion and the reaction mixture was allowed to stir at r.t. for 24 h (for larger scales, adding a needle to the cap to vent the nitrogen gas formed during the reaction is recommended). After this period, the reaction mixture was purified by flash column chromatography (silica gel) to afford **6** or **7**.

Method B: To a 1.0 M solution of **5** (0.186 mmol) in $MeNO_2$ under a N_2 atmosphere was added the appropriate alcohol or thiol (0.558 mmol, 3.0 equiv). Catalyst (0.058 mmol, 30 mol%) was then added in one portion. The reaction mixture was allowed to stir for 24 h at r.t. and then purified by flash column chromatography on silica gel to afford **6** or **7** (for larger scales, adding a needle to the cap to vent the nitrogen gas formed during the reaction is recommended).

Methyl 2-Ethoxy-2-(4-methoxyphenyl)acetate (6a)

The compound was isolated as a pale yellow oil by flash column chromatography (silica gel, EtOAc–hexanes, 5:95 to 20:80).

Yield: 36 mg (0.162 mmol, 87%); R_f = 0.20 (EtOAc–hexanes, 10:90).

IR (film): 3063, 3032, 2953, 2837, 1751, 1611, 1585, 1512, 1437, 1248, 1173, 1097, 1030 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.34 (m, 2 H), 6.91–6.86 (m, 2 H), 4.83 (s, 1 H), 3.79 (s, 3 H), 3.70 (s, 3 H), 3.60–3.45 (m, 2 H), 1.26 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.7, 159.8, 128.6, 128.5, 114.0, 80.4, 65.0, 55.2, 52.1, 15.1

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{16}NaO_4$: 247.0940; found: 247.0934.

Methyl 2-(Benzyloxy)-2-(4-methoxyphenyl)acetate (6e)

The compound was isolated as a pale yellow oil by flash column chromatography (silica gel, EtOAc–hexanes, 5:95 to 20:80).

Yield: 48 mg (0.167 mmol, 90%); R_f = 0.17 (EtOAc–hexanes, 10:90).

IR (film): 3003, 2953, 2837, 1751, 1611, 1512, 1248, 1173, 1097, 1030 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 7 H), 6.93–6.88 (m, 2 H), 4.88 (s, 1 H), 4.56 (q, *J* = 12.0 Hz, 2 H), 3.81 (s, 3 H), 3.71 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.6, 160.1, 137.3, 128.9, 128.6, 128.5, 128.2, 128.0, 114.2, 79.2, 71.0, 55.4, 52.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{18}NaO_4$: 309.1097; found: 309.1087.

Ethyl 2-(4-Bromophenyl)-2-ethoxyacetate (6f)

The compound was isolated as a pale yellow oil by flash column chromatography (silica gel, EtOAc–hexanes, 5:95 to 20:80).

Yield: 26 mg (0.089 mmol, 42%); R_f = 0.34 (EtOAc–hexanes, 10:90).

IR (film): 2980, 2899, 1751, 1487, 1400, 1206, 1179, 1113, 1013 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$); δ = 7.50–7.46 (m, 2 H), 7.36–7.32 (m, 2 H), 4.81 (s, 1 H), 4.25–4.10 (m, 2 H), 3.64–3.45 (m, 2 H), 1.27 (t, *J* = 7.0 Hz, 3 H), 1.21 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.7, 136.0, 131.8, 128.9, 122.7, 80.4, 65.6, 61.5, 15.2, 14.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{15}BrNaO_3$: 309.0097; found: 309.0085.

Ethyl 2-(Benzyloxy)-2-(4-bromophenyl)acetate (6g)

The compound was isolated as a pale yellow oil by flash column chromatography (silica gel, EtOAc–hexanes, 5:95 to 20:80).

Yield: 16 mg (0.0465 mmol, 25%); R_f = 0.30 (EtOAc–hexanes, 10:90).

IR (film): 2980, 2928, 1748, 1487, 1206, 1179, 1096 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.47 (m, 2 H), 7.37–7.28 (m, 7 H), 4.87 (s, 1 H), 4.59 (d, *J* = 1.3 Hz, 2 H), 4.24–4.11 (m, 2 H), 1.21 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 137.1, 135.6, 131.9, 129.1, 128.7, 128.2, 128.2, 122.9, 79.2, 71.5, 61.6, 14.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{17}BrNaO_3$: 371.0253; found: 371.0244.

Ethyl 2-(4-Bromophenyl)-2-(dodecylsulfanyl)acetate (7g)

The compound was isolated as a pale yellow oil by flash column chromatography (silica gel, EtOAc–hexanes, 5:95 to 20:80).

Yield: 12%; R_f = 0.60 (EtOAc–hexanes, 10:90).

IR (film): 2955, 2926, 2855, 1738, 1487, 1271, 1146, 1013 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.44 (m, 2 H), 7.39–7.32 (m, 2 H), 4.50 (s, 1 H), 4.30–4.08 (m, 2 H), 2.65–2.35 (m, 2 H), 1.67–1.44 (m, 3 H), 1.44–1.16 (m, 20 H), 0.88 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 135.6, 131.9, 130.3, 122.2, 61.9, 51.8, 32.2, 32.0, 29.7, 29.7, 29.6, 29.4, 29.9, 29.2, 29.1, 28.9, 22.8, 14.3, 14.2.

HRMS (ESI): *m*/*z* [M – 28 + Na]$^+$ calcd for $C_{20}H_{31}BrNaO_2S$: 437.1126; found: 437.1117.

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Supporting Information

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