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Organogold(I) Phosphanes in Palladium-Catalyzed Cross-Coupling Reactions in Aqueous Media

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Dedicated to Professor Julio Delgado Martín on the occasion of his 70th birthday

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Cross-coupling reaction of organogold(I) phosphanes with organic electrophiles in aqueous media has been investigated. Reactions between isolated aryl-, alkenyl-, or alkynylgold(I) phosphanes and aryl halides or triflates, alkenyl halides, and allyl acetates proceed under palladium catalysis conditions at room temperature or 80 °C in water with THF as a co-solvent. The coupling reactions give good yields and are highly versatile and chemoselective, allowing the presence of free amino or hydroxy groups in the electrophile. This methodology was applied to the preparation of substituted phenylalanine esters in a demonstration that gold(I) organometallics are suitable reagents for metal-catalyzed cross-coupling reactions under protic conditions.

Introduction

Water is a unique green solvent because it is inexpensive, safe, and environmentally friendly.[1] Research into organic reactions in (or on) water is important for understanding and reproduction of the chemical transformations that occur in biological systems. However, the development of synthetic methodologies under aqueous conditions has significant limitations associated either with the low solubilities of organic compounds or with their hydrolysis. A key strategy for overcoming these problems involves the use of solubilizing agents, phase-transfer catalysts, or water-tolerant reagents, in what is a research area of current interest.[2]

Transition-metal-catalyzed cross-coupling reactions are among the most important chemical reactions in contemporary chemistry,[3] a fact recognized with the 2010 Nobel Prize in Chemistry.[4] However, despite their high selectivity and functional group compatibility, most cross-coupling reactions are performed in organic solvents; this is mainly due to better solubilities of the organometallic reagents or to prevent their hydrolysis.[5] In this field, the higher stabilities of organoboron reagents have allowed the establishment of a protocol for Suzuki–Miyaura coupling in aqueous media,[6] but the use of other organometallics is limited to particular reaction conditions.[7]

In recent years, the use of gold(I) complexes in organic synthesis has increased considerably, due to their particular Lewis acid character and their ability to catalyze nucleophilic additions to unsaturated carbon-carbon bonds.[8] Carbon–gold(I) species have been postulated as intermediates in these transformations, and in some cases they have even been isolated.[9] These findings have stimulated research into gold(I) organometallics in metal-catalyzed reactions, and cross-coupling reactions under palladium and nickel catalysis conditions have been developed.[10] In this research area, we have reported that organogold(I) phosphanes ($RAuPPh_3$) react efficiently with aryl, benzyl, benzoyl, alkenyl, and allyl electrophiles under palladium catalysis conditions.[11] The main features of gold(I) organometallics in palladium-catalyzed cross-coupling reactions are their high reactivity and efficiency under mild conditions, as well as their versatility and stability in air. Although the mechanisms of palladium-catalyzed cross-coupling reactions with organogold reagents have not been fully established, transmetallation from the Au^{I} reagent to a Pd^{II} complex (formed by oxidative addition of the electrophile to Pd^{0}) followed by reductive elimination has been proposed.[12] On the other hand, the preparation of water-soluble gold(I) complexes and organometallics has allowed their use in catalysis.[13] Here we report palladium-catalyzed cross-coupling reactions between organogold(I) phosphanes and organic electrophiles in aqueous media.

Results and Discussion

Our study started with the preparation of a variety of gold(I) organometallics from the corresponding organo-

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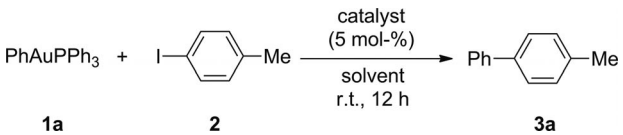
lithium compounds, Grignard reagents, or boronic acids and the commercially available (triphenylphosphane)gold(I) chloride (Ph_3PAuCl).[14] In the light of our previous results, the feasibility of palladium-catalyzed cross-coupling reactions in aqueous media was assessed in the reaction between phenyl(triphenylphosphane)gold(I) ($PhAuPPh_3$, **1a**, Table 1) and 4-iodotoluene (**2**) in the presence of different palladium catalysts and under different reaction conditions. Organogold(I) reagents are insoluble in alcohols and water but are generally soluble in most common organic solvents, so we envisaged carrying out the coupling reactions in water with THF as co-solvent to dissolve the organogold phosphane. Interestingly, the addition of $PdCl_2(PPh_3)_2$ (5 mol-%) to a homogeneous H_2O/THF (9 mL, 2:1) solution of previously isolated $PhAuPPh_3$ (110 mol-%) and 4-iodotoluene (100 mol-%), afforded the cross-coupling product **3a** in 91% yield in 1 h at room temperature (Table 1, Entry 1). This result is identical to that obtained with pure THF as solvent (Table 1, Entry 2)[11a] and shows the high stability of the organogold(I) phosphane in aqueous media (protodeauration was not detected). It is interesting to note that is not necessary to use degassed solvents and that the reaction can be carried out with water taken directly from the tap.

Table 1. Cross-coupling reaction between phenyl(triphenylphosphane)gold(I) (**1a**) and 4-iodotoluene (**2**).



1a **2** **3a**

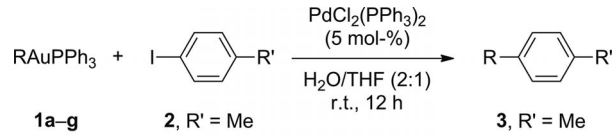
Entry	Catalyst	Solvent	Yield [%][a,b]
1	$PdCl_2(PPh_3)_2$	H_2O/THF[c]	91
2	$PdCl_2(PPh_3)_2$	THF	92
3	$PdCl_2(PPh_3)_2$	H_2O	92
4	$PdCl_2(PPh_3)_2$	neat	70
5	Pd_2dba_3	H_2O/THF[c]	93
6	$Pd(PPh_3)_4$	H_2O/THF[c]	90
7	Pd/C	H_2O/THF[c]	84
8	$PdCl_2$	H_2O/THF[c]	90
9	$Pd(OAc)_2$	H_2O/THF[c]	88

[a] Isolated yields. [b] All the reactions were performed with isolated $PhAuPPh_3$. [c] H_2O/THF (2:1).

The observed high reactivity led us to try the reaction in neat water. In this case, even though the reagents are insoluble in water, the reaction proceeded smoothly over 12 h at room temperature and the coupling product **3a** was isolated in 92% yield (Table 1, Entry 3). To our delight, simple mixing of the reaction components in air at room temperature, in the absence of solvent, provided **3a** in good yield after 24 h stirring (70%, Table 1, Entry 4). This is a good example of a sustainable transformation and suggests that the coupling takes place *on water*.[15] Other palladium complexes such as $Pd(PPh_3)_4$ or Pd_2dba_3 also proved to be efficient (Table 1, Entries 5 and 6) and the reaction also proceeded under ligand-free conditions [Pd/C, $PdCl_2$, or $Pd(OAc)_2$, 5 mol-%] at room temperature, to give the cross-coupling product **3a** in high yield (Table 1, Entries 7–9). It should be noted that these conditions avoid the use of phosphane ligands and that this makes the reaction environmentally desirable.[16] These successful coupling reactions with either Pd^{II} or Pd^0 complexes seem to indicate that the catalytic cycle starts with a oxidative addition to Pd^0, followed by transmetallation (Au^I/Pd^{II}) and reductive elimination. The high reactivities and stabilities of gold(I) organometallics in aqueous media are remarkable, which gives further evidence of the potential for performing tandem gold-catalyzed transformations/cross-coupling reactions under aqueous conditions.[17]

Encouraged by these results, we studied the aqueous coupling with a variety of organogold(I) phosphanes and functionalized organic electrophiles. Gold(I) reagents bearing aryl, heteroaryl, alkynyl, and alkenyl groups (**1a**–**g**, Table 2) were employed, whereas the electrophiles were aryl halides functionalized with amino or hydroxy groups, such as 4-iodoaniline (**4**) and 4-iodophenol (**5**). As in our first screening, the reactions were performed in water with THF as co-solvent in order to obtain homogeneous reaction mixtures.[18] For practical reasons we also decided to use the commercially available $PdCl_2(PPh_3)_2$ as catalyst.

Table 2. Cross-coupling reaction of organogold(I) phosphanes with aryl iodides in aqueous media.



1a–g **2**, R' = Me; **4**, R' = NH_2; **5**, R' = OH → **3**, R' = Me; **6**, R' = NH_2; **7**, R' = OH

Entry	R	Electrophile	Product	Yield [%][a]
1	Ph (**1a**)	**2**	**3a**	91
2	*o*-$MeOC_6H_4$ (**1b**)		**3b**	95
3	*m*-$O_2NC_6H_4$ (**1c**)		**3c**	89
4	*p*-$F_3CC_6H_4$ (**1d**)		**3d**	93
5	2-furyl (**1e**)		**3e**	89
6	PhC≡C (**1f**)		**3f**	98
7	(*E*)-hept-1-enyl (**1g**)[b]		**3g**[c]	96
8	Ph (**1a**)	**4**	**6a**	91
9	*o*-$MeOC_6H_4$ (**1b**)		**6b**	91
10	*m*-$O_2NC_6H_4$ (**1c**)		**6c**	99
11	*p*-$F_3CC_6H_4$ (**1d**)		**6d**	94
12	2-furyl (**1e**)		**6e**	92
13	PhC≡C (**1f**)		**6f**	88
14	(*E*)-hept-1-enyl (**1g**)[b]		**6g**[d]	89
15	Ph (**1a**)	**5**	**7a**	93

[a] Isolated yields. [b] As an *E*/*Z* (82:18) mixture by ^1H NMR spectroscopy. [c] As an *E*/*Z* (82:18) mixture by ^1H NMR spectroscopy. [d] As an *E*/*Z* (86:14) mixture by ^1H NMR spectroscopy.

The reactions between 4-iodotoluene and the isolated arylgold(I) phosphanes bearing either electron-donating groups (such as *o*-methoxy, **1b**) or electron-withdrawing groups (such as *m*-nitro, **1c**), under palladium catalysis conditions at room temperature, gave the corresponding cross-coupling products (such as **3b** and **3c**) in excellent yields (89–95%, Table 2, Entries 2 and 3). Analogously, the reaction with 4-trifluoromethylphenylgold(I) reagent **1d** at room

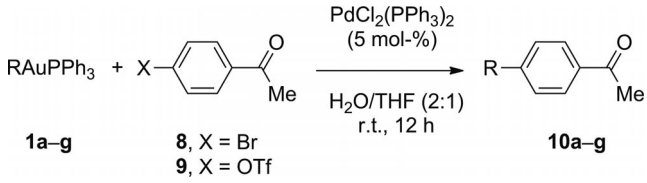
temperature afforded the biaryl compound **3d** in 93% yield, whereas the coupling reaction with the 2-furylgold(I) reagent **1e** gave the coupling product **3e** in high yield (89%, Table 2, Entries 4 and 5). The reactivity of alkynyl and alkenylgold(I) phosphanes in cross-coupling reactions in aqueous media was also investigated. Under the previously developed conditions, the reaction between the isolated phenylethynyl(triphenylphosphane)gold(I) (**1f**) and 4-iodotoluene in the presence of $PdCl_2(PPh_3)_2$ (5 mol-%) at room temperature in H_2O/THF (2:1) solution gave the arylalkyne **3f** in quantitative yield (98%, Table 2, Entry 6). Similarly, the reaction with the stereodefined (*E*)-hept-1-enyl(triphenylphosphane)gold(I) (**1g**) afforded the coupling product **3g** in 96% yield with retention of the double bond configuration (Table 2, Entry 7). In comparison with other organometallic reagents, it is interesting to highlight that all reactions proceed at room temperature without any additive or base, attractive features for the development of tandem and stereoselective transformations.

Once we had demonstrated the efficiency of this process with functionalized aryl-, heteroaryl-, alkynyl-, and alkenylgold(I) phosphanes, our next step was to test the functional group tolerance by using 4-iodoaniline (**4**) as the electrophile. Gratifyingly, we found that the reactions between arylgold(I) reagents **1a**–**e** and **4** gave the corresponding coupling products **6a**–**e** in excellent yields at room temperature (91–99%, Table 2, Entries 8–12). Analogously, the reaction with the alkynylgold(I) reagent **1f** provided **6f** in 88% yield and the reaction with the (*E*)-alkenylgold(I) **1g** gave the coupling product **6g** in 89% yield without isomerization of the double bond (Table 2, Entries 13 and 14).

Furthermore, this protocol was also assessed with 4-iodophenol (**5**) as electrophile. In this case, the reaction with phenyl(triphenylphosphane)gold(I) (**1a**) proceeded at room temperature, affording 1,1′-biphenyl-4-ol (**7a**) in 93% yield (Table 2, Entry 15). From these results it can be concluded that the cross-coupling reaction of organogold(I) phosphanes with aryl iodides in aqueous media at room temperature shows high reactivity, versatility, and chemoselectivity, tolerating organogold(I) reagents of different natures and electrophiles substituted with amino and hydroxy groups without any observed protodeauration.

As a continuation of this work, and to demonstrate that the aqueous palladium-catalyzed cross-coupling reaction of gold(I) organometallics is not limited to aryl iodides, other electrophiles were also tested. In this research, the coupling of arylgold(I) phosphanes **1a** and **1d** with 4-bromoacetophenone (**8**) under $PdCl_2(PPh_3)_2$ (5 mol-%) catalysis conditions in the homogeneous H_2O/THF mixture at room temperature afforded the coupling products only in low yields. However, when the mixtures were heated at 80 °C for 12 h the coupling products **10a** and **10d** were obtained in 90% and 80% yields, respectively (Table 3, Entries 1 and 2). Analogously, cross-coupling reaction with the 2-furyl- (reagent **1e**), alkynyl- (reagent **1f**), and alkenylgold(I) (reagent **1g**) phosphanes at 80 °C provided the cross-coupling products **10e**–**10g** in high yields (81–93%, Table 3, Entries 3–5).

Table 3. Cross-coupling reaction of organogold(I) phosphanes with aryl bromides and triflates in aqueous media.

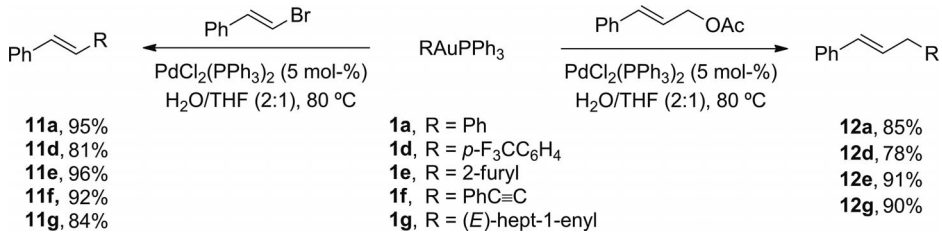


Entry	R	R–X	Product	Yield [%][a]
1	Ph (**1a**)	**8**	**10a**	90
2	*p*-$F_3CC_6H_4$ (**1d**)		**10d**	80
3	2-furyl (**1e**)		**10e**	92
4	PhC≡C (**1f**)		**10f**	93
5	(*E*)-hept-1-enyl (**1g**)[b]		**10g**[c]	81
6	Ph (**1a**)	**9**	**10a**	80 (99)[d,e]
7	PhC≡C (**1f**)		**10f**	77 (97)[d,e]

[a] Isolated yields. [b] As an *E*/*Z* (82:18) mixture by ^{1}H NMR spectroscopy. [c] As an *E*/*Z* (80:20) mixture by ^{1}H NMR spectroscopy. [d] Reactions performed with isolated $RAuPPh_3$ and LiCl (100 mol-%). [e] Yields based on recovered starting material in parentheses.

With the aim of assessing the influence of the leaving group, the aqueous cross-coupling reaction was studied with aryl triflate **9**. In this case, treatment of the isolated phenylgold(I) reagent **1a** with **9** in H_2O/THF (2:1) in the presence of $PdCl_2(PPh_3)_2$ (5 mol-%) as catalyst at 80 °C gave the coupling product **10a** in only 23% yield, along with significant amounts of biphenyl from dimerization of the gold organometallic and recovery of some starting material. Interestingly, a similar result was also reported by Gagné for the palladium-catalyzed cross-coupling reactions between isolated vinyl- or arylgold(I) reagents and tolyl triflate.[19] In our previous work,[11a] we reported that when the organogold reagent was generated in situ, the cross-coupling reaction between **1a** and **9** produced **10a** in 93% yield, which suggests that the lithium chloride generated during the formation of the organogold(I) phosphane could play a crucial role in the coupling. The LiCl effect in palladium-catalyzed cross-coupling reactions was discovered by Stille when using organotin reagents,[20] and can be attributed to stabilization of the palladium species after the oxidative addition.

To confirm the above hypothesis, we carried out the reaction between isolated organogold **1a** and the aryl triflate **9** in the presence of lithium chloride (100 mol-%). Under these conditions, the cross-coupling product **10a** was obtained in 80% yield after 12 h at 80 °C [99% yield based on recovered starting material (brsm), Table 3, Entry 6]. In this study, we also performed the reaction with the isolated phenylethynyl(triphenylphosphane)gold(I) (**1f**) in the absence of LiCl, which gave rise to the coupling product **10f** in 25% yield. The corresponding reaction with the organogold prepared in situ gave a 72% yield, and with the isolated **1f** and 100 mol-% of lithium chloride the coupling product was obtained in 77% yield (97% brsm, Table 3, Entry 7). These results confirm the key role of lithium chloride in the cross-coupling reactions with aryl triflates.

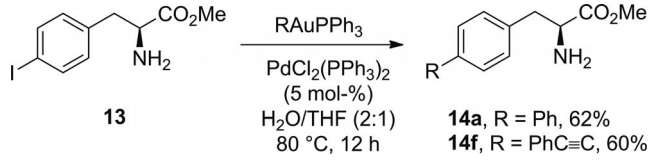


Scheme 1. Cross-coupling reaction of organogold(I) phosphanes with β-(*E*)-bromostyrene and (*E*)-cinnamyl acetate in aqueous media.

To expand the scope of this methodology, we studied the reactivity of the gold(I) organometallics with alkenyl and allylic electrophiles. The cross-coupling reaction of phenyl-, *p*-trifluoromethylphenyl-, furyl-, alkynyl-, and heptenylgold(I) phosphanes (**1a**–**g**) with the stereodefined alkenyl halide β-bromostyrene (*E*/*Z* = 90:10) in the presence of $PdCl_2(PPh_3)_2$ (5 mol-%) as catalyst in H_2O/THF (2:1) mixtures took place effectively at 80 °C to produce the corresponding alkenes **11a**–**11g** in excellent yields (81–96%, Scheme 1). It is worth noting that the aqueous cross-coupling reaction proceeds stereospecifically without isomerization of the double bonds either in the electrophile or in the gold(I) reagent.

The suitability of allylic substrates in the aqueous cross-coupling reaction was also analyzed. Recently, we reported that aryl- and alkenylgold(I) organometallics react regioselectively with allylic electrophiles such as cinnamyl and geranyl halides (bromide, chloride) and acetates under palladium catalysis conditions in dry THF at 80 °C to afford the α-substitution products with moderate to high yields.[11b] Here, we found that the palladium-catalyzed reactions between the phenylgold(I) phosphane **1a** and cinnamyl bromide or chloride in H_2O/THF (2:1) as solvent at 80 °C only led to hydrolysis of the allyl halides. However, when the corresponding reaction was performed with cinnamyl acetate, the α-substituted coupling product **12a** was obtained in 85% yield with retention of the double bond configuration (Scheme 1). Analogously, treatment of cinnamyl acetate (100 mol-%) with *p*-trifluoromethylphenylgold(I) (reagent **1d**) and 2-furylgold(I) (reagent **1e**) phosphanes (110 mol-%) under palladium catalysis conditions also provided the α-substituted products **12d** and **12e** stereoselectively in high yields (Scheme 1). The cross-coupling reaction with the stereodefined hept-1-enylgold(I) phosphane **1g** (*E*/*Z* = 82:18) proceeded effectively to give the (1*E*,4*E*)-diene **12g** in 90% yield with retention of configuration in both reagents (4*E*/4*Z* 83:17, Scheme 1).

The high chemoselectivity exhibited by the organogold(I) phosphanes led us to apply our methodology to the synthesis of functionalized α-amino acids. Metal-catalyzed cross-coupling reactions have been used to prepare non-natural aromatic α-amino acids, but most procedures require the use of protecting groups at the amino and the carboxylic acid functionalities.[21] By our methodology, the coupling of $PhAuPPh_3$ (**1a**) with the methyl ester of *p*-iodophenylalanine (**13**, Scheme 2) in the presence of $PdCl_2(PPh_3)_2$ in H_2O/THF at room temperature afforded the coupling product **14a** in 51% yield with recovery of some of the starting iodide and organometallic reagent. Alternatively, when the reaction was performed at 80 °C the coupling product was isolated in higher yield (62%). Analogously, the reaction between phenylethynyl(triphenylphosphane)gold(I) (**1f**) and **13** at 80 °C provided the coupling product **14f** in 60% yield. These examples show the utility of organogold(I) phosphanes in the synthesis of phenylalanine analogues.



Scheme 2. Synthesis of 4-substituted phenylalanines.

Conclusions

In summary, we have shown that isolated aryl-, heteroaryl-, alkynyl- and alkenylgold(I) organometallics react with aryl and alkenyl halides, aryl triflates, and allyl acetates in aqueous media under palladium catalysis conditions. The reactions take place under mild conditions and in short reaction times to afford the corresponding cross-coupling products in excellent yields. The stability of the organogold reagents under aqueous conditions is remarkable, as is their versatility and chemoselectivity, with amino and hydroxy groups being tolerated in the electrophile. Our reactions support the classical mechanism for palladium-catalyzed cross-coupling reactions and suggest the use of the transient gold(I) organometallics in aqueous gold-catalyzed processes. Further studies to confirm the mechanism and to develop dual gold/palladium-catalyzed cross-coupling reactions are currently underway in our laboratories.

Experimental Section

General Methods: Reaction temperatures refer to external bath temperatures. Anhydrous THF was obtained by distillation from sodium/benzophenone. All other commercially available reagents were used as received. Organic extracts were dried with anhydrous $MgSO_4$, filtered, and concentrated with a rotary evaporator at aspirator pressure (20–30 Torr). TLC was carried out on silica gel 60 F_{254} (layer thickness 0.2 mm) and components were located by observation under UV light and/or by treating the plates with a phosphomolybdic acid or *p*-anisaldehyde reagent followed by heat-

ing. Column chromatography was performed on silica gel (230–400 mesh).[22] NMR spectra were obtained with a Bruker Avance 300 spectrometer with use of the residual solvent signal as internal standard. DEPT was used to assign carbon types. The low-resolution electron-impact mass spectra were measured with a Thermo Finnigan Trace MS spectrometer at 70 eV. The high-resolution mass spectra were measured with a Thermo Finnigan MAT 95XP spectrometer. Infrared spectra were obtained with a Bruker Vector 22 instrument and with ATR ("attenuated total reflectance").

General Procedure for the Preparation of Organogold Compounds:[11a] A 25 mL round-bottomed flask containing a stirrer bar was charged with Ph_3PAuCl (75 mg, 0.152 mmol) and a positive argon pressure was established. Dry THF (3 mL) was added, and the resulting solution was cooled to –20 °C. A solution of RLi or RMgBr (0.182 mmol) was added dropwise, the mixture was stirred for 20 min, the cooling bath was removed, and the reaction mixture was stirred for 1 h at room temp. The solvent was evaporated under reduced pressure and toluene (5 mL) was added. The mixture was filtered through Celite, concentrated to dryness in vacuo, washed with pentane, and dried. The solid was re-extracted with the minimum possible quantity of toluene, filtered, washed with pentane, and dried under high vacuum.

Phenyl(triphenylphosphane)gold (1a):[10c] The General Procedure afforded **1a** as a white powder (74.8 mg, 0.139 mmol, 92%), m.p. 160–161 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 6.88–6.97 (m, 9 H), 7.26 (t, J = 7.4 Hz, 1 H), 7.37–7.44 (m, 6 H), 7.52 (t, J = 7.5 Hz, 2 H), 8.11 (d, J = 7.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 125.9 (s, 2× CH), 127.5 (s, 3× C), 127.7 (s, C), 127.7 (br. s, 2× CH), 128.7 [d, J(C,P) = 10.5 Hz, 6× CH], 130.6 (br. s, CH), 134.2 [d, J(C,P) = 13.9 Hz, 6× CH], 140.0 (s, 3× CH) ppm. ^{31}P NMR (121.5 MHz, C_6D_6): δ = 43.99 (s) ppm. IR (ATR): $\tilde{\nu}$ = 3051, 3006, 2922, 2851, 1571, 1478, 1434 cm^{-1}. MS (EI): m/z (%) = 536 (71) $[M]^+$, 459 (100) $[M - C_6H_5]^+$. HRMS (EI): calcd. for $C_{24}H_{20}PAu$ $[M]^+$ 536.0963; found 536.0944.

2-Methoxyphenyl(triphenylphosphane)gold (1b):[11b] The General Procedure afforded **1b** as a white powder (69.3 mg, 0.122 mmol, 81%), m.p. 140–142 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 3.65 (s, 3 H), 6.89–7.00 (m, 10 H), 7.22–7.33 (m, 2 H), 7.44–7.51 (m, 6 H), 8.09 [dt, J(C,P) = 1.9, 6.5 Hz, 1 H] ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 55.0 (s, CH_3), 110.0 [d, J(C,P) = 4.3 Hz, CH], 120.9 [d, J(C,P) = 6.0 Hz, CH], 126.6 (s, CH), 128.7 [d, J(C,P) = 10.6 Hz, 6× CH], 130.5 [d, J(C,P) = 2.1 Hz, 3× CH], 131.6 [d, J(C,P) = 48.8 Hz, 3× C], 134.3 [d, J(C,P) = 13.8 Hz, 6× CH], 140.2 (s, CH), 160.5 [d, J(C,P) = 112.8 Hz, C], 166.1 [d, J(C,P) = 0.9 Hz, C] ppm. ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): δ = 44.25 (s) ppm. IR (ATR): $\tilde{\nu}$ = 3054, 2944, 2828, 1566, 1479 cm^{-1}. MS (EI): m/z (%) = 566 (1) $[M]^+$, 459 (2) $[M - C_7H_7O]^+$, 262 (100) $[M - C_7H_7OAu]^+$. HRMS (EI): calcd. for $C_{25}H_{22}OPAu$ $[M]^+$ 566.1068; found 566.1063.

3-Nitrophenyl(triphenylphosphane)gold (1c):[14] Cs_2CO_3 (236.9 mg, 0.727 mmol) and Ph_3PAuCl (180 mg, 0.363 mmol) were added successively to a solution of 3-nitrophenylboronic acid (121.4 mg, 0.727 mmol) in dry isopropyl alcohol (5 mL). The resulting white suspension was stirred at 50 °C for 24 h and taken to dryness by rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated to dryness in vacuo, washed with pentane, and dried. The solid was re-extracted with a minimum of benzene, filtered, washed with pentane, and dried under high vacuum, to give the organogold phosphane **1c** as a white powder (192.5 mg, 0.331 mmol, 91%), m.p. 170–171 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.41 (dd, J = 7.3, 8.1 Hz, 1 H), 7.46–7.64 (m, 15 H), 7.87–7.94 (m, 2 H), 8.45 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 120.5 (s, CH), 127.5 (s, CH), 129.2 [d, J(C,P) = 10.8 Hz, 6× CH], 130.2 (s, C), 130.9 (s, C), 131.3 [d, J(C,P) = 2.2 Hz, CH], 133.5 (s, CH), 134.3 [d, J(C,P) = 13.8 Hz, 6× CH], 146.0 (s, 3× CH), 147.5 (s, 3× C) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 43.36 (s) ppm. IR (ATR): $\tilde{\nu}$ = 3052, 2923, 2852, 1509, 1479, 1435 cm^{-1}. MS (EI): m/z (%) = 581 (3) $[M]^+$, 459 (12) $[M - C_6H_4NO_2]^+$, 262 (100) $[M - C_7H_4F_3Au]^+$. HRMS (EI): calcd. for $C_{24}H_{19}NO_2PAu$ $[M]^+$ 581.0813; found 581.0823.

[4-(Trifluoromethyl)phenyl](triphenylphosphane)gold (1d):[10c] The General Procedure afforded **1d** as a brown powder (72.6 mg, 0.120 mmol, 79%), m.p. 155–157 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 6.91–6.99 (m, 9 H), 7.33–7.41 (m, 6 H), 7.66 (d, J = 7.7 Hz, 2 H), 7.95 (t, J = 6.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 123.6 (m, 2× CH), 127.6 (s, 3× C), 128.9 [d, J(C,P) = 10.9 Hz, 6× CH], 130.5 (s, C), 130.8 [d, J(C,P) = 2.1 Hz, 2× CH], 131.2 (s, C), 134.2 [d, J(C,P) = 13.7 Hz, 6× CH], 139.9 (s, 3× CH), 178.3 [d, J(C,P) = 116.8 Hz, C] ppm. ^{31}P NMR (121.5 MHz, C_6D_6): δ = 43.62 (s) ppm. IR (ATR): $\tilde{\nu}$ = 3057, 1591, 1556, 1479, 1322 cm^{-1}. MS (EI): m/z (%) = 604 (1) $[M]^+$, 459 (3) $[M - C_7H_4F_3]^+$, 262 (100) $[M - C_7H_4F_3Au]^+$. HRMS (EI): calcd. for $C_{25}H_{19}F_3PAu$ $[M]^+$ 604.0837; found 604.0808.

2-Furyl(triphenylphosphane)gold (1e):[23] The General Procedure afforded **1e** as a white powder (74.2 mg, 0.141 mmol, 93%), m.p. 157–159 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 6.68 (dd, J = 1.6, 3.0 Hz, 1 H), 6.83–7.00 (m, 10 H), 7.25–7.33 (m, 6 H), 7.90 (d, J = 1.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 108.4 (s, CH), 118.9 (br. s, CH), 127.6 (s, 3× C), 128.8 [d, J(C,P) = 10.8 Hz, 6× CH], 130.6 [d, J(C,P) = 2.3, 51.5 Hz, C], 130.8 [d, J(C,P) = 2.3 Hz, CH], 134.2 [d, J(C,P) = 13.8 Hz, 6× CH], 144.2 (s, 3× CH) ppm. ^{31}P NMR (121.5 MHz, C_6D_6): δ = 43.90 (s) ppm. IR (ATR): $\tilde{\nu}$ = 3062, 1478, 1433, 1350 cm^{-1}. MS (EI): m/z (%) = 526 (1) $[M]^+$, 459 (2) $[M - C_4H_3O]^+$, 262 (100) $[M - C_4H_3OAu]^+$. HRMS (EI): calcd. for $C_{22}H_{18}OPAu$ $[M]^+$ 526.0755; found 526.0740.

2-Phenylethynyl(triphenylphosphane)gold (1f):[24] The General Procedure afforded **1f** as a white powder (84.3 mg, 0.150 mmol, 99%), m.p. 161–162 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 6.84–6.98 (m, 9 H), 7.02–7.08 (m, 3 H), 7.19–7.26 (m, 6 H), 7.84 (d, J = 7.9 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 126.1 (s, CH), 127.5 (s, C), 127.8 (s, C), 128.1 [d, J(C,P) = 12.2 Hz, CH], 128.8 [d, J(C,P) = 11.2 Hz, CH], 129.9 (s, C), 130.6 (s, C), 130.8 [d, J(C,P) = 2.2 Hz, CH], 132.4 (s, CH), 134.1 [d, J(C,P) = 13.9 Hz, CH] ppm. ^{31}P NMR (121.5 MHz, C_6D_6): δ = 41.98 (s) ppm. IR (ATR): $\tilde{\nu}$ = 3053, 2923, 2357, 1595, 1483, 1435, 1331 cm^{-1}. MS (EI): m/z (%) = 560 (18) $[M]^+$, 459 (1) $[M - C_8H_5]^+$, 404 (100). HRMS (EI): calcd. for $C_{26}H_{20}PAu$ $[M]^+$ 560.0963; found 560.0985.

(*E*)-Hept-1-enyl(triphenylphosphane)gold (1g):[11a] A solution of (*E*)-hept-1-enyllithium, prepared from (*E*)-1-iodohept-1-ene (40.8 mg, 0.182 mmol, *E*/*Z* = 82:18) and *t*BuLi (0.215 mL, 1.7 M in pentane, 0.364 mmol), was added to a solution of Ph_3PAuCl (90 mg, 0.182 mmol) in THF (3 mL) as described in the General Procedure, and the resulting organogold phosphane **1g** was used directly in the palladium-catalyzed cross-coupling reaction. Alternatively, **1g** can be prepared from (*E*)-hept-1-enylboronic acid: Cs_2CO_3 (105.4 mg, 0.323 mmol) and Ph_3PAuCl (80 mg, 0.161 mmol) were added successively to a solution of (*E*)-hept-1-enylboronic acid (45.9 mg, 0.323 mmol) in dry isopropyl alcohol (5 mL). The resultant white suspension was stirred at 50 °C for 24 h and taken to dryness by rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated in vacuo to dryness, washed with pentane, and dried. The solid was re-extracted with a

minimum of benzene, filtered, washed with pentane, and dried under high vacuum, to give the organogold phosphane **1g** as a pale brown solid (80.7 mg, 0.145 mmol, 90%), m.p. 91–93 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.87 (t, J = 7.2 Hz, 3 H), 1.26–1.49 (m, 4 H), 1.61–1.71 (m, 2 H), 2.56 (q, J = 6.9 Hz, 2 H), 6.43–6.56 (m, 1 H), 6.85–6.97 (m, 9 H), 7.35–7.43 (m, 6 H), 7.53 (dd, J = 18.4, 5.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 14.0 (s, CH_3), 22.8 (s, 2× CH_2), 30.2 (s, CH_2), 31.7 (s, CH_2), 128.7 [d, J(C,P) = 10.5 Hz, 6× CH], 130.5 (s, CH), 131.7 [d, J(C,P) = 47.2 Hz, 3× C], 134.2 [d, J(C,P) = 13.8 Hz, 6× CH], 144.4 (s, CH), 146.4 (s, 3× CH) ppm. ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): δ = 45.41 (s) ppm. IR (ATR): $\tilde{\nu}$ = 3053, 2952, 2916, 2849, 1583, 1479 cm^{-1}. MS (EI): m/z (%) = 556 (1) $[M]^+$, 459 (2) $[M - C_7H_{13}]^+$, 262 (100) $[M - C_7H_{13}Au]^+$.

General Procedure for the Palladium-Catalyzed Cross-Coupling Reactions: A solution of isolated $RAuPPh_3$ (1.1 equiv.) in H_2O/THF (2:1, 9 mL) was added to a mixture of the electrophile (1.0 equiv.) and palladium catalyst (5 mol-%). The resulting homogeneous solution was stirred either at room temp. or at 80 °C until the starting material had been consumed (TLC). The reaction mixture was diluted with Et_2O (20 mL), and the ethereal phase was washed with brine (10 mL), dried with $MgSO_4$, filtered, and concentrated to a reduced volume under vacuum. The residue was purified by flash chromatography to afford, after concentration and high-vacuum drying, the corresponding cross-coupling product in the reported yield.

4-Methylbiphenyl (3a):[25] The General Procedure afforded **3a** as a white solid (22.9 mg, 0.136 mmol, 91%), m.p. 46–48 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.42 (s, 3 H), 7.24–7.63 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.1 (CH_3), 126.9 (2× CH), 127.0 (2× CH), 127.2 (CH), 128.7 (2× CH), 129.5 (2× CH), 137.0 (C), 138.4 (C), 140.2 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3027, 2922, 2857, 2360, 1739, 1601, 1518, 1486 cm^{-1}. MS (EI): m/z (%) = 168 (100) $[M]^+$, 167 (76) $[M - 1]^+$, 153 (19) $[M - CH_3]^+$. HRMS (EI): calcd. for $C_{13}H_{12}$ $[M]^+$ 168.0934; found 168.0935.

2-Methoxy-4′-methylbiphenyl (3b):[26] The General Procedure afforded **3b** as a white solid (20.7 mg, 0.104 mmol, 95%), m.p. 77–79 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.41 (s, 3 H), 3.83 (s, 3 H), 7.02 (dd, J = 7.4 Hz, 2 H), 7.25 (d, J = 7.9 Hz, 2 H), 7.30–7.36 (m, 2 H), 7.45 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH_3), 55.5 (CH_3), 111.2 (CH), 120.8 (CH), 128.4 (CH), 128.7 (2× CH), 129.4 (2× CH), 130.7 (C), 130.8 (C), 135.6 (C), 136.6 (C), 156.5 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3025, 2922, 2835, 1904, 1598, 1584 cm^{-1}. MS (EI): m/z (%) = 198 (100) $[M]^+$, 183 (37) $[M - CH_3]^+$. HRMS (EI): calcd. for $C_{14}H_{14}O$ $[M]^+$ 198.1039; found 198.1046.

4-Methyl-3-nitrobiphenyl (3c):[27] The General Procedure afforded **3c** as a colorless oil (28.0 mg, 0.131 mmol, 89%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.42 (s, 3 H), 7.30 (d, J = 7.9 Hz, 2 H), 7.53 (d, J = 8.1 Hz, 2 H), 7.59 (t, J = 7.9 Hz, 1 H), 7.90 (dq, J = 1.0, 7.9 Hz, 1 H), 8.17 (dq, J = 1.0, 8.1 Hz, 1 H), 8.44 (t, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.1 (CH_3), 121.6 (CH), 121.7 (CH), 126.9 (2× CH), 129.6 (CH), 129.8 (2× CH), 132.8 (CH), 135.7 (C), 138.6 (C), 142.8 (C), 148.7 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3089, 3027, 2921, 2852, 2361, 1914, 1614, 1529 cm^{-1}. MS (EI): m/z (%) = 213 (100) $[M]^+$, 167 (24) $[M - NO_2]^+$, 152 (43) $[M - CH_3NO_2]^+$. HRMS (EI): calcd. for $C_{13}H_{11}O_2N$ $[M]^+$ 213.0784; found 213.0787.

4-Methyl-4′-(trifluoromethyl)biphenyl (3d):[28] The General Procedure afforded **3d** as a white solid (32.5 mg, 0.137 mmol, 93%), m.p. 131–132 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.43 (s, 3 H), 7.30 (d, J = 7.9 Hz, 2 H), 7.52 (d, J = 8.1 Hz, 2 H), 7.68–7.77 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.1 (CH_3), 125.6 (q, J = 3.8 Hz, CH), 127.1 (2× CH), 127.2 (2× CH), 127.6 (CH), 128.8 (C), 129.2 (C), 129.7 (2× CH), 136.9 (C), 138.1 (C), 144.6 (C) ppm. IR (ATR): $\tilde{\nu}$ = 2922, 2852, 2361, 2340, 1615, 1329 cm^{-1}. MS (EI): m/z (%) = 236 (100) $[M]^+$, 235 (21) $[M - 1]^+$, 167 (25) $[M - CF_3]^+$. HRMS (EI): calcd. for $C_{14}H_{11}F_3$ $[M]^+$ 236.0807; found 236.0808.

2-(*p*-Tolyl)furan (3e):[29] The General Procedure afforded **3e** as a yellow oil (19.4 mg, 0.123 mmol, 89%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.37 (s, 3 H), 6.46 (dd, J = 1.8, 3.3 Hz, 1 H), 6.60 (dd, J = 0.6, 3.3 Hz, 1 H), 7.19 (d, J = 7.9 Hz, 2 H), 7.45 (dd, J = 0.8, 1.8 Hz, 1 H), 7.57 (d, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 20.0 (CH_3), 103.0 (CH), 110.3 (CH), 122.6 (2× CH), 127.0 (C), 128.1 (2× CH), 135.9 (C), 140.5 (CH), 153.0 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3115, 3029, 2923, 2855, 1517, 1485 cm^{-1}. MS (EI): m/z (%) = 158 (100) $[M]^+$, 129 (51). HRMS (EI): calcd. for $C_{11}H_{10}O$ $[M]^+$ 158.0726; found 158.0727.

1-Methyl-4-(2-phenylethynyl)benzene (3f):[30] The General Procedure afforded **3f** as a colorless oil (22.4 mg, 0.116 mmol, 98%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.39 (s, 3 H), 7.17 (d, J = 7.7 Hz, 2 H), 7.33–7.39 (m, 3 H), 7.45 (d, J = 8.1 Hz, 2 H), 7.52–7.57 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (CH_3), 88.7 (C), 89.5 (C), 120.2 (C), 123.5 (C), 128.1 (CH), 128.3 (2× CH), 129.1 (2× CH), 131.5 (2× CH), 131.6 (2× CH), 138.4 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3030, 2919, 2852, 2216, 1661, 1595, 1509, 1485 cm^{-1}. MS (EI): m/z (%) = 192 (100) $[M]^+$, 191 (46) $[M - 1]^+$. HRMS (EI): calcd. for $C_{15}H_{12}$ $[M]^+$ 192.0934; found 192.0930.

(*E*)-1-(Hept-1-enyl)-4-methylbenzene (3g):[31] The General Procedure afforded **3g** as a colorless oil (24.0 mg, 0.127 mmol, 96%, *E*/*Z* = 82:18). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.91 (t, J = 6.9 Hz, 3 H), 1.27–1.52 (m, 6 H), 2.20 (q, J = 6.8 Hz, 2 H), 2.33 (s, 3 H), 6.18 (dt, J = 6.8, 15.8 Hz, 1 H), 6.35 (d, J = 15.8 Hz, 1 H), 7.11 (d, J = 8.0 Hz, 2 H), 7.25 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 21.1 (CH_3), 22.5 (CH_2), 29.1 (CH_2), 31.4 (CH_2), 33.0 (CH_2), 125.8 (2× CH), 129.1 (2× CH), 129.5 (CH), 130.2 (CH), 135.2 (C), 136.4 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3021, 2955, 2923, 2855, 1512, 1458 cm^{-1}. MS (EI): m/z (%) = 188 (44) $[M]^+$, 131 (100) $[M - C_4H_9]^+$, 91 (13) $[M - C_7H_{13}]^+$. HRMS (EI): calcd. for $C_{14}H_{20}$ $[M]^+$ 188.1560; found 188.1553.

Biphenyl-4-amine (6a):[32] The General Procedure afforded **6a** as a yellow solid (18.3 mg, 0.108 mmol, 91%), m.p. 52–54 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.73 (br. s, 2 H), 6.75–6.80 (m, 2 H), 7.25–7.32 (m, 1 H), 7.38–7.46 (m, 4 H), 7.53–7.58 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.4 (2× CH), 126.2 (CH), 126.4 (2× CH), 128.0 (2× CH), 128.7 (2× CH), 131.6 (C), 141.2 (C), 145.8 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3426, 3393, 3309, 3207, 3059, 3032, 2925, 2854, 2359 cm^{-1}. MS (EI): m/z (%) = 169 (100) $[M]^+$, 168 (10) $[M - 1]^+$. HRMS (EI): calcd. for $C_{12}H_{11}N$ $[M]^+$ 169.0886; found 169.0879.

2′-Methoxybiphenyl-4-amine (6b):[33] The General Procedure afforded **6b** as a brown oil (19.1 mg, 0.096 mmol, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.71 (br. s, 2 H), 3.82 (s, 3 H), 6.75 (d, J = 8.6 Hz, 2 H), 6.96–7.04 (m, 2 H), 7.25–7.32 (m, 2 H), 7.37 (d, J = 8.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.5 (CH_3), 111.2 (CH), 114.8 (CH), 120.8 (CH), 127.8 (CH), 128.7 (C), 130.4 (2× CH), 130.5 (2× CH), 130.7 (C), 145.4 (C), 156.5 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3445, 3372, 3218, 3026, 2925, 2851, 2834, 1728, 1620 cm^{-1}. MS (EI): m/z (%) = 199 (100) $[M]^+$, 183 (48) $[M - NH_2]^+$. HRMS (EI): calcd. for $C_{13}H_{13}ON$ $[M]^+$ 199.0992; found 199.0983.

3′-Nitrobiphenyl-4-amine (6c): The General Procedure afforded **6c** as an orange solid (23.2 mg, 0.109 mmol, 99%), m.p. 128–130 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (br. s, 2 H), 6.80 (d, J = 8.6 Hz, 2 H), 7.47 (d, J = 8.6 Hz, 2 H), 7.55 (t, J = 8.0 Hz, 1 H), 7.85 (dq, J = 1.0, 7.7 Hz, 1 H), 8.11 (dq, J = 1.0, 8.2 Hz, 1 H), 8.40 (t, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.4 (2× CH), 120.8 (CH), 120.9 (CH), 128.1 (2× CH), 128.7 (C), 129.5 (CH), 132.1 (CH), 142.8 (C), 146.9 (C), 148.8 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3482, 3382, 2922, 2852, 2361, 2341, 1620, 1606 cm^{-1}. MS (EI): m/z (%) = 214 (100) $[M]^+$, 168 (46) $[M - NO_2]^+$. HRMS (EI): calcd. for $C_{12}H_{10}O_2N_2$ $[M]^+$ 214.0737; found 214.0736.

4′-(Trifluoromethyl)biphenyl-4-amine (6d):[34] The General Procedure afforded **6d** as a pale brown solid (26.5 mg, 0.112 mmol, 94%), m.p. 149–151 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (br. s, 2 H), 6.78 (d, J = 8.4 Hz, 2 H), 7.44 (d, J = 8.6 Hz, 2 H), 7.64 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.4 (2× CH), 119.0 (C), 122.6 (C), 125.6 (q, J = 3.8 Hz, 2× CH), 126.4 (2× CH), 128.2 (2× CH), 129.8 (C), 144.6 (C), 146.7 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3436, 3310, 3212, 3041, 2921, 2852, 1637, 1594 cm^{-1}. MS (EI): m/z (%) = 237 (100) $[M]^+$, 236 (5) $[M - 1]^+$. HRMS (EI): calcd. for $C_{13}H_{10}NF_3$ $[M]^+$ 237.0760; found 237.0763.

4-(Furan-2-yl)aniline (6e):[35] The General Procedure afforded **6e** as a pale brown solid (20.3 mg, 0.127 mmol, 92%), m.p. 57–59 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74 (br. s, 2 H), 6.42–6.46 (m, 2 H), 6.71 (d, J = 8.6 Hz, 2 H), 7.40 (t, J = 1.2 Hz, 1 H), 7.49 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 102.4 (CH), 11.4 (CH), 115.1 (2× CH), 122.0 (C), 125.2 (2× CH), 140.9 (CH), 145.6 (C), 154.6 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3460, 3371, 3204, 3140, 3115, 3038, 2923, 2852, 1618, 1518 cm^{-1}. MS (EI): m/z (%) = 159 (100) $[M]^+$, 130 (83) $[M - CHO]^+$. HRMS (EI): calcd. for $C_{10}H_9ON$ $[M]^+$ 159.0679; found 159.0681.

4-(Phenylethynyl)aniline (6f):[36] The General Procedure afforded **6f** as a yellow solid (20.2 mg, 0.104 mmol, 88%), m.p. 127–129 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (br. s, 2 H), 6.62–6.67 (m, 2 H), 7.29–7.37 (m, 5 H), 7.48–7.52 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 87.3 (C), 90.1 (C), 112.7 (C), 114.7 (2× CH), 123.9 (C), 127.6 (CH), 128.2 (2× CH), 131.3 (2× CH), 132.9 (2× CH), 146.6 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3476, 3381, 3200, 3037, 2923, 2853, 2212, 1617, 1592, 1515 cm^{-1}. MS (EI): m/z (%) = 193 (100) $[M]^+$, 165 (13). HRMS (EI): calcd. for $C_{14}H_{11}N$ $[M]^+$ 193.0886; found 193.0890.

(*E*)-4-(Hept-1-en-1-yl)aniline (6g): The General Procedure afforded **6g** as a brown oil (22.6 mg, 0.120 mmol, 89%, E/Z = 86:14). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 6.9 Hz, 3 H), 1.27–1.51 (m, 6 H), 2.17 (dq, J = 1.3, 6.9 Hz, 2 H), 3.75 (br. s, 2 H), 6.05 (dt, J = 6.9, 15.8 Hz, 1 H), 6.29 (d, J = 15.8 Hz, 1 H), 6.68 (d, J = 8.4 Hz, 2 H), 7.18 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6 (CH_2), 29.3 (CH_2), 31.5 (CH_2), 33.0 (CH_2), 115.6 (2× CH), 126.9 (2× CH), 128.0 (CH), 129.3 (CH), 129.4 (C), 144.2 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3362, 3025, 2956, 2924, 2854, 2361, 1619 cm^{-1}. MS (EI): m/z (%) = 189 (38) $[M]^+$, 132 (100) $[M - C_4H_9]^+$. HRMS (EI): calcd. for $C_{13}H_{19}N$ $[M]^+$ 189.1512; found 189.1511.

Biphenyl-4-ol (7a):[37] The General Procedure afforded **7a** as a white solid (23.3 mg, 0.137 mmol, 93%), m.p. 158–160 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.89 (br. s, 1 H), 6.90–6.93 (m, 2 H), 7.31 (tt, J = 1.7, 7.3 Hz, 1 H), 7.42 (tt, J = 1.7, 7.6 Hz, 2 H), 7.47–7.50 (m, 2 H), 7.53–7.56 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.6 (2× CH), 126.7 (CH), 126.7 (2× CH), 128.4 (2× CH), 128.7 (2× CH), 134.0 (C), 140.7 (C), 155.0 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3413, 3061, 3036, 2921, 2851, 1608, 1596 cm^{-1}. MS (EI): m/z (%) = 170 (100) $[M]^+$, 141 (19). HRMS (EI): calcd. for $C_{12}H_{10}O$ $[M]^+$ 170.0726; found 170.0726.

4′-Phenylacetophenone (10a):[38] The General Procedure afforded **10a** as a white solid (21.1 mg, 0.107 mmol, 90% from 4-bromoacetophenone and 21.9 mg, 0.111 mmol, 80% from aryl triflate), m.p. 118–120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.65 (s, 3 H), 7.38–7.51 (m, 3 H), 7.63–7.72 (m, 4 H), 8.05 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.7 (CH_3), 127.2 (2× CH), 127.3 (2× CH), 128.2 (CH), 128.9 (2× CH), 129.0 (2× CH), 135.9 (C), 139.9 (C), 145.8 (C), 197.8 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3076, 3000, 2920, 1677, 1602, 1561, 1519 cm^{-1}. MS (EI): m/z (%) = 196 (69) $[M]^+$, 181 (100) $[M - CH_3]^+$, 152 (49) $[M - C_2H_3O]^+$. HRMS (EI): calcd. for $C_{14}H_{12}O$ $[M]^+$ 196.0883; found 196.0882.

1-[4′-(Trifluoromethyl)biphenyl-4-yl]ethanone (10d):[39] The General Procedure afforded **10d** as a white solid (27.0 mg, 0.102 mmol, 80%), m.p. 124–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.66 (s, 3 H), 7.70 (d, J = 8.5 Hz, 2 H), 7.72–7.74 (m, 4 H), 8.07 (d, J = 8.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.7 (CH_3), 125.9 (q, J = 3.8 Hz, 2× CH), 127.4 (2× CH), 127.6 (2× CH), 129.0 (2× CH), 130.0 (C), 130.4 (C), 136.6 (C), 143.4 (C), 144.2 (C), 197.5 (C) ppm. IR (ATR): $\tilde{\nu}$ = 2359, 1684, 1605, 1420, 1355 cm^{-1}. MS (EI): m/z (%) = 264 (49) $[M]^+$, 249 (100) $[M - CH_3]^+$, 221 (8) $[M - C_2H_3O]^+$. HRMS (EI): calcd. for $C_{15}H_{11}OF_3$ $[M]^+$ 264.0757; found 264.0747.

1-[4-(Furan-2-yl)phenyl]ethanone (10e):[40] The General Procedure afforded **10e** as a white solid (23.3 mg, 0.125 mmol, 92%), m.p. 105–107 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.62 (s, 3 H), 6.52 (dd, J = 1.8, 3.5 Hz, 1 H), 6.80 (dd, J = 0.6, 3.5 Hz, 1 H), 7.54 (dd, J = 0.6, 1.8 Hz, 1 H), 7.75 (d, J = 8.7 Hz, 2 H), 7.98 (d, J = 8.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.5 (CH_3), 107.5 (CH), 112.0 (CH), 123.5 (2× CH), 128.9 (2× CH), 134.8 (C), 135.5 (C), 143.3 (CH), 152.8 (C), 197.4 (C) ppm. IR (ATR): $\tilde{\nu}$ = 2956, 2920, 2851, 2357, 1714, 1667 cm^{-1}. MS (EI): m/z (%) = 186 (62) $[M]^+$, 171 (100) $[M - CH_3]^+$, 143 (23) $[M - C_2H_3O]^+$. HRMS (EI): calcd. for $C_{12}H_{10}O_2$ $[M]^+$ 186.0675; found 186.0676.

4′-(2-Phenylethynyl)acetophenone (10f):[41] The General Procedure afforded **10f** as a white solid (30.0 mg, 0.136 mmol, 93% from 4-bromoacetophenone and 22.0 mg, 0.099 mmol, 77% from aryl triflate), m.p. 84–86 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.63 (s, 3 H), 7.36–7.40 (m, 3 H), 7.55–7.58 (m, 2 H), 7.62 (d, J = 8.6 Hz, 2 H), 7.95 (d, J = 8.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 26.6 (CH_3), 88.6 (C), 92.7 (C), 122.6 (C), 128.2 (C), 128.3 (2× CH), 128.4 (2× CH), 128.8 (CH), 131.7 (2× CH), 131.7 (2× CH), 136.2 (C), 197.3 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3339, 3064, 2999, 2919, 2850, 2219, 1896, 1676, 1601 cm^{-1}. MS (EI): m/z (%) = 220 (73) $[M]^+$, 205 (100) $[M - CH_3]^+$, 177 (14) $[M - C_2H_3O]^+$. HRMS (EI): calcd. for $C_{16}H_{12}O$ $[M]^+$ 220.0883; found 220.0885.

(*E*)-1-[(4-Acetyl)phenyl]hept-1-ene (10g):[42] The General Procedure afforded **10g** as a colorless oil (23.5 mg, 0.109 mmol, 81%, E/Z = 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, J = 6.9 Hz, 3 H), 1.27–1.53 (m, 6 H), 2.21–2.28 (m, 2 H), 2.59 (s, 3 H), 6.33–6.46 (m, 2 H), 7.41 (d, J = 8.3 Hz, 2 H), 7.89 (d, J = 8.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.5 (CH_2), 26.5 (CH_3), 28.8 (CH_2), 31.4 (CH_2), 33.1 (CH_2), 125.9 (2× CH), 128.7 (2× CH), 128.9 (CH), 134.6 (CH), 135.4 (C), 142.7 (C), 197.6 (C) ppm. IR (ATR): $\tilde{\nu}$ = 2956, 2925, 2855, 1679, 1648, 1601 cm^{-1}. MS (EI): m/z (%) = 216 (100) $[M]^+$, 201 (99) $[M - CH_3]^+$, 131 (73) $[M - C_4H_9]^+$. HRMS (EI): calcd. for $C_{15}H_{20}O$ $[M]^+$ 216.1509; found 216.1509.

(*E*)-Stilbene (11a): The General Procedure afforded **11a** as a white solid (24.3 mg, 0.135 mmol, 95%), m.p. 120–122 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.14 (s, 2 H), 7.26–7.31 (m, 2 H), 7.38 (t, J = 7.7 Hz, 4 H), 7.53–7.56 (m, 4 H) ppm. ^{13}C NMR

(75 MHz, $CDCl_3$, 25 °C): δ = 126.5 (4× CH), 127.6 (2× CH), 128.6 (4× CH), 128.7 (2× CH), 137.3 (2× C) ppm. IR (ATR): $\tilde{\nu}$ = 3077, 3058, 3021, 2925, 1598, 1577, 1495, 1451 cm^{-1}. MS (EI): *m/z* (%) = 180 (100) $[M]^+$, 103 (33) $[M - C_6H_5]^+$. HRMS (EI): calcd. for $C_{14}H_{12}$ $[M]^+$ 180.0937; found 180.0933.

(*E*)-1-Styryl-4-(trifluoromethyl)benzene (11d):[43] The General Procedure afforded **11d** as a white solid (30.1 mg, 0.121 mmol, 81%, *E*/*Z* = 92:8), m.p. 134–136 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.13 (d, *J* = 16.3 Hz, 1 H), 7.21 (d, *J* = 16.3 Hz, 1 H), 7.28–7.34 (m, 1 H), 7.36–7.43 (m, 2 H), 7.55 (d, *J* = 7.1 Hz, 2 H), 7.61–7.63 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 125.6 (q, *J* = 3.8 Hz, 2× CH), 126.6 (2× CH), 126.8 (2× CH), 127.1 (CH), 128.3 (CH), 128.8 (2× CH), 129.0 (C), 129.5 (C), 131.2 (CH), 136.6 (C), 140.8 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3025, 2928, 1615, 1580, 1323 cm^{-1}. MS (EI): *m/z* (%) = 248 (100) $[M]^+$, 179 (44) $[M - CF_3]^+$. HRMS (EI): calcd. for $C_{15}H_{11}F_3$ $[M]^+$ 248.0807; found 248.0800.

(*E*)-2-Styrylfuran (11e):[44] The General Procedure afforded **11e** as a white solid (21.9 mg, 0.129 mmol, 96%, *E*/*Z* = 93:7), m.p. 51–53 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.37 (d, *J* = 3.3 Hz, 1 H), 6.44 (dd, *J* = 1.6, 3.3 Hz, 1 H), 6.91 (d, *J* = 16.3 Hz, 1 H), 7.06 (d, *J* = 16.3 Hz, 1 H), 7.25–7.28 (m, 1 H), 7.33–7.39 (m, 2 H), 7.42 (d, *J* = 1.8 Hz, 1 H), 7.45–7.50 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 108.5 (CH), 111.6 (CH), 116.5 (CH), 126.3 (2× CH), 127.1 (CH), 127.6 (CH), 128.7 (2× CH), 137.0 (C), 142.1 (CH), 153.3 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3025, 2922, 2850, 2361, 1597, 1498, 1483, 1446 cm^{-1}. MS (EI): *m/z* (%) = 170 (100) $[M]^+$, 169 (26) $[M - 1]^+$. HRMS (EI): calcd. for $C_{12}H_{10}O$ $[M]^+$ 170.0726; found 170.0729.

(*E*)-1,4-Diphenylbut-1-en-3-yne (11f):[45] The General Procedure afforded **11f** as a white solid (24.2 mg, 0.118 mmol, 92%, *E*/*Z* = 90:10), m.p. 92–94 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.40 (d, *J* = 16.2 Hz, 1 H), 7.06 (d, *J* = 16.2 Hz, 1 H), 7.30–7.56 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 88.9 (C), 91.7 (C), 108.1 (CH), 123.4 (C), 126.3 (2× CH), 128.2 (CH), 128.3 (2× CH), 128.6 (CH), 128.7 (2× CH), 131.5 (2× CH), 136.3 (C), 141.2 (CH) ppm. IR (ATR): $\tilde{\nu}$ = 3080, 3032, 2923, 1973, 1900, 1810, 1748, 1678 cm^{-1}. MS (EI): *m/z* (%) = 204 (100) $[M]^+$, 101 (22) $[M - C_8H_7]^+$. HRMS (EI): calcd. for $C_{16}H_{12}$ $[M]^+$ 204.0939; found 204.0943.

(1*E*,3*E*)-Nona-1,3-dienylbenzene (11g):[46] The General Procedure afforded **11g** as a colorless oil (21.8 mg, 0.109 mmol, 84%, 1*E*,3*E*/1*E*,3*Z* 85:15). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.91 (t, *J* = 6.9 Hz, 3 H), 1.27–1.49 (m, 6 H), 2.15 (q, *J* = 6.9 Hz, 2 H), 5.85 (dt, *J* = 15.1, 7.0 Hz, 1 H), 6.22 (dd, *J* = 15.1, 10.4 Hz, 1 H), 6.45 (d, *J* = 15.7 Hz, 1 H), 6.77 (dd, *J* = 15.7, 10.4 Hz, 1 H), 7.17–7.44 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.0 (CH_3), 22.5 (CH_2), 29.0 (CH_2), 31.4 (CH_2), 32.8 (CH_2), 126.1 (2× CH), 127.0 (CH), 128.5 (2× CH), 129.5 (CH), 129.9 (CH), 130.4 (CH), 136.0 (CH), 137.7 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3079, 3059, 3021, 2955, 2924, 2854, 1643, 1596 cm^{-1}. MS (EI): *m/z* (%) = 200 (100) $[M]^+$, 199 (37) $[M - 1]^+$. HRMS (EI): calcd. for $C_{15}H_{20}$ $[M]^+$ 200.1565; found 200.1560.

(*E*)-1,3-Diphenylpropene (12a):[47] The General Procedure afforded **12a** as a colorless oil (24.2 mg, 0.124 mmol, 85%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.58 (d, *J* = 6.3 Hz, 2 H), 6.39 (dt, *J* = 6.3, 15.7 Hz, 1 H), 6.49 (d, *J* = 15.8 Hz, 1 H), 7.20–7.41 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 39.4 (CH_2), 126.1 (2× CH), 126.2 (CH), 127.1 (CH), 128.5 (4× CH), 128.7 (2× CH), 129.2 (CH), 131.1 (CH), 137.5 (C), 140.2 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3059, 3025, 2897, 1600, 1494, 1451 cm^{-1}. MS (EI): *m/z* (%) = 194 (64) $[M]^+$, 117 (50) $[M - C_6H_5]^+$. HRMS (EI): calcd. for $C_{15}H_{14}$ $[M]^+$ 194.1090; found 194.1092.

(*E*)-1-Phenyl-3-(4-trifluoromethylphenyl)propene (12d):[48] The General Procedure afforded **12d** as a colorless oil (30.7 mg, 0.117 mmol, 78%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.62 (d, *J* = 6.7 Hz, 2 H), 6.34 (dt, *J* = 6.7, 15.8 Hz, 1 H), 6.50 (d, *J* = 15.8 Hz, 1 H), 7.21–7.40 (m, 7 H), 7.59 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 39.1 (CH_2), 125.4 (q, *J* = 3.8 Hz, CF_3), 125.4 (C), 126.2 (4× CH), 127.4 (CH), 127.9 (CH), 128.6 (2× CH), 128.9 (2× CH), 131.9 (CH), 137.1 (C), 144.3 (d, *J* = 1.3 Hz, C) ppm. IR (ATR): $\tilde{\nu}$ = 3029, 1620, 1601, 1497, 1323 cm^{-1}. MS (EI): *m/z* (%) = 262 (100) $[M]^+$, 193 (25) $[M - CF_3]^+$. HRMS (EI): calcd. for $C_{16}H_{13}F_3$ $[M]^+$ 262.0964; found 262.0957.

(*E*)-1-Phenyl-3-(furan-2-yl)propene (12e):[49] The General Procedure afforded **12e** as a colorless oil (21.7 mg, 0.117 mmol, 91%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.57 (d, *J* = 6.7 Hz, 2 H), 6.09 (dd, *J* = 0.8, 3.2 Hz, 1 H), 6.27–6.38 (m, 2 H), 6.51 (d, *J* = 15.8 Hz, 1 H), 7.20–7.40 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 31.8 (CH_2), 105.6 (CH), 110.3 (CH), 125.6 (CH), 126.2 (2× CH), 127.3 (CH), 128.5 (2× CH), 132.0 (CH), 137.2 (C), 141.4 (CH), 153.9 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3082, 3059, 3027, 1596, 1504, 1448 cm^{-1}. MS (EI): *m/z* (%) = 184 (100) $[M]^+$, 155 (31) $[M - CHO]^+$. HRMS (EI): calcd. for $C_{13}H_{12}O$ $[M]^+$ 184.0883; found 184.0874.

(1*E*,4*E*)-1-Phenyldeca-1,4-diene (12g): The General Procedure afforded **12g** as a colorless oil (25.9 mg, 0.121 mmol, 90%, 4*E*/4*Z* 83:17). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.91 (t, *J* = 6.8 Hz, 3 H), 1.25–1.44 (m, 6 H), 2.00–2.07 (m, 2 H), 2.90–2.94 (m, 2 H), 5.44–5.59 (m, 2 H), 6.24 (dt, *J* = 6.5, 15.8 Hz, 1 H), 6.41 (d, *J* = 15.8 Hz, 1 H), 7.18–7.39 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.1 (CH_3), 22.6 (CH_2), 29.2 (CH_2), 31.4 (CH_2), 32.6 (CH_2), 35.9 (CH_2), 126.0 (2× CH), 126.9 (CH), 127.5 (CH), 128.5 (2× CH), 129.4 (CH), 130.2 (CH), 132.1 (CH), 137.8 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3025, 2955, 2923, 2871, 2854, 1494, 1448 cm^{-1}. MS (EI): *m/z* (%) = 214 (47) $[M]^+$, 143 (100) $[M - C_5H_{11}]^+$, 130 (43) $[M - C_6H_{12}]^+$. HRMS (EI): calcd. for $C_{16}H_{22}$ $[M]^+$ 214.1716; found 214.1711.

Methyl (*S*)-2-Amino-3-(4-iodophenyl)propanoate (13): Et_3N (2 mL) was added at room temp. to a stirred suspension of 4-iodo-L-phenylalanine methyl ester hydrochloride[50] (0.839 g, 2.45 mmol) in CH_2Cl_2 (15 mL), and the mixture was stirred for a further 30 min. The solvent was removed under reduced pressure, EtOAc (15 mL) was added, and the mixture was filtered. The filtrate was washed with a saturated solution of $NaHCO_3$ (3× 15 mL) and water (3× 15 mL), dried with anhydrous $MgSO_4$, and filtered. The solution was concentrated under reduced pressure and the residue was purified by column chromatography (10% MeOH/CH_2Cl_2) to afford **13** (0.440 g, 1.44 mmol) as a slightly brown oil. ^1H NMR [500 MHz, $(CD_3)_2SO$, 25 °C]: δ = 1.75 (br. s, 2 H), 2.72 (dd, *J* = 7.5, 13.4 Hz, 1 H), 2.82 (dd, *J* = 6.1, 13.4 Hz, 1 H), 3.54 (t, *J* = 6.2 Hz, 1 H), 3.57 (s, 3 H), 7.00 (d, *J* = 8.3 Hz, 2 H), 7.62 (d, *J* = 8.3 Hz, 2 H) ppm. ^{13}C NMR [125 MHz, $(CD_3)_2SO$, 25 °C]: δ = 40.0 (CH_2), 51.4 (CH_3), 55.5 (CH), 92.1 (C), 131.7 (2× CH), 136.8 (2× CH), 137.9 (C), 175.3 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3379, 3312, 2948, 2925, 2853, 1732 cm^{-1}. MS (EI): *m/z* (%) = 305 (10) $[M]^+$, 246 (38) $[M - C_2H_3O_2]^+$, 88 (100). HRMS (EI) calcd. for $C_{10}H_{12}O_2NI$ $[M]^+$ 304.9907; found 304.9911.

Methyl (*S*)-2-Amino-3-(biphenyl-4-yl)propanoate (14a): The General Procedure afforded **14a** as a white solid (19.1 mg, 0.075 mmol, 62%), m.p. 47–49 °C. ^1H NMR [500 MHz, $(CD_3)_2SO$, 25 °C]: δ = 1.80 (br. s, 2 H), 2.80 (dd, *J* = 7.3, 13.4 Hz, 1 H), 2.91 (dd, *J* = 6.1, 13.4 Hz, 1 H), 3.58–3.62 (m, 4 H), 7.27 (d, *J* = 8.1 Hz, 2 H), 7.34

(t, J = 7.4 Hz, 1 H), 7.45 (t, J = 7.4 Hz, 2 H), 7.57 (d, J = 8.2 Hz, 2 H), 7.61–7.65 (m, 2 H) ppm. ^{13}C NMR [125 MHz, $(CD_3)_2SO$, 25 °C]: δ = 40.2 (CH_2), 51.3 (CH_3), 55.6 (CH), 126.3 (2× CH), 126.4 (2× CH), 127.1 (CH), 128.6 (2× CH), 129.7 (2× CH), 137.2 (C), 138.0 (C), 139.9 (C), 175.3 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3378, 3027, 2950, 2924, 2853, 1736 cm^{-1}. MS (EI): m/z (%) = 255 (7) $[M]^+$, 196 (24) $[M - C_2H_3O_2]^+$, 167 (100). HRMS (EI) calcd. for $C_{16}H_{17}O_2N$ $[M]^+$ 255.1254; found 255.1257.

(*S*)-Methyl 2-Amino-3-[4-(phenylethynyl)phenyl]propanoate (14f): The General Procedure afforded **14f** as a white solid (20.3 mg, 0.073 mmol, 60%). Mp 103–105 °C. ^{1}H NMR [500 MHz, $(CD_3)_2SO$, 25 °C]: δ = 1.79 (br. s, 2 H), 2.80 (dd, J = 7.4, 13.4 Hz, 1 H), 2.89 (dd, J = 6.2, 13.4 Hz, 1 H), 3.57–3.60 (m, 4 H), 7.24 (d, J = 8.1 Hz, 2 H), 7.41–7.44 (m, 2 H), 7.46 (d, J = 8.0 Hz, 2 H), 7.52–7.65 (m, 3 H) ppm. ^{13}C NMR [125 MHz, $(CD_3)_2SO$, 25 °C]: δ = 40.4 (CH_2), 51.3 (CH_3), 55.5 (CH), 88.9 (C), 89.3 (C), 120.0 (C), 122.3 (C), 128.6 (CH), 128.7 (2× CH), 129.6 (2× CH), 131.0 (2× CH), 131.2 (2× CH), 138.9 (C), 175.2 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3381, 3058, 3030, 2923, 2853, 1736 cm^{-1}. MS (EI): m/z (%) = 279 (50) $[M]^+$, 220 (15) $[M - C_2H_3O_2]^+$, 191 (100). HRMS (EI) calcd. for $C_{18}H_{17}O_2N$ $[M]^+$ 279.1254; found 279.1249.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra for all compounds prepared.

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