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Rhodium-Catalyzed Decarboxylative Cycloaddition Route to Substituted Anilines

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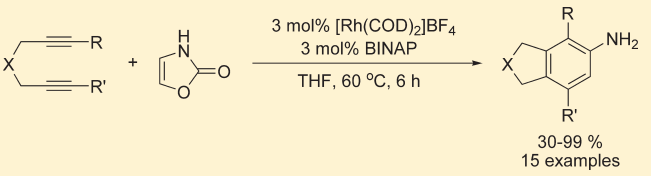
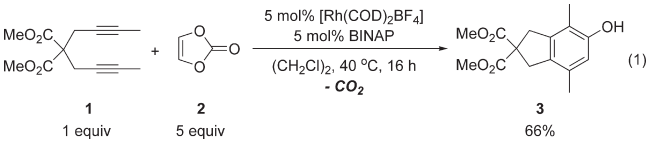
Supporting Information

ABSTRACT: A convenient method for preparing substituted anilines via a Rh-catalyzed [2 + 2 + 2] cycloaddition reaction of diynes and 2-oxazolone was discovered. The initial cycloaddition adducts undergo facile decarboxylation of carbon dioxide to afford aniline products. Reaction conditions are mild, and only 3 mol % Rh catalyst is required. High regioselectivity was observed when an unsymmetrical diyne was used as a starting material.



Substituted anilines are important structural motifs that are found in a variety of natural products, biologically active compounds, and agrochemicals.[1] As such, efficient methods for the synthesis of substituted anilines are highly desirable. Although a variety of procedures that generate substituted anilines exist,[2] [2 + 2 + 2] cycloaddition routes are rare.[3] The lack of cycloaddition routes could be due to the lack of suitable nitrogen-containing starting materials that can undergo cycloaddition chemistry.[4] One such starting material is the ynamide.[5] For example, both the Hsung group[6] and the Tanaka group[7] have reported the use of ynamides in the enantioselective preparation of axially chiral anilides through a rhodium-catalyzed [2 + 2 + 2] cycloaddition. We have been interested in expanding the repertoire of cycloaddition chemistry[8] to include other readily available nitrogen-containing starting materials. Herein we report our findings that demonstrate that 2-oxazolones can be used as substrates in [2 + 2 + 2] cycloaddition chemistry. These cycloadditions afford substituted anilines through spontaneous decarboxylation of the initial cycloaddition product.



Tanaka and co-workers reported the Rh(I)/BINAP-catalyzed [2 + 2 + 2] cycloaddition of diyne **1** and vinylene carbonate **2** to synthesize a phenol derivative **3** through elimination of carbon dioxide (eq 1).[9] Inspired by Tanaka's work,[10] we investigated whether 2-oxazolones could be used instead of vinylene carbonates. Thus, the [2 + 2 + 2] cycloaddition of 1,6-diyne **1** and 2-oxazolone **4**[11] (5 equiv) was examined in the presence of 10 mol % cationic rhodium(I)/BINAP at 60 °C (eq 2, Table 1). Gratifyingly, the desired aniline product was obtained in excellent yield (as determined by GC). Other bidentate phosphines were also evaluated. Although good yields of aniline were formed when either (*S*)-H_8-BINAP or dppf were used as the

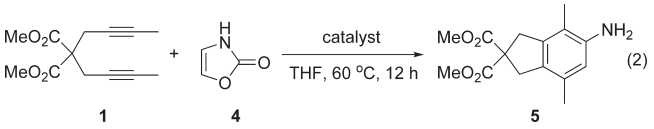


Table 1. Rh-Catalyzed Cycloadditions of Diyne and 2-Oxazolone[a]

entry	metal source	ligands	conversion[b] (%)	yield[b] (%)
1	$[Rh(COD)_2]BF_4$	BINAP	>99	>99
2	$[Rh(COD)_2]BF_4$	(*S*)-H_8-BINAP	>99	80
3	$[Rh(COD)_2]BF_4$	dppf	79	83
4	$[Rh(COD)_2]BF_4$	dppe	69	0
5[c]	$Ni(COD)_2$	IMes	12	0
6[c]	$Ni(COD)_2$	IPr	21	0

[a] 10 mol % $[Rh(COD)_2]BF_4$ (0.01 M), 10 mol % ligand (0.01 M), **1** (0.1 M), **4** (0.5 M) in THF at 60 °C. [b] Conversions of diyne **1** and yields of **5** were determined by GC with naphthalene as an internal standard. [c] 10 mol % $Ni(COD)_2$ (0.01 M), 20 mol % ligand (0.02 M) in THF at 60 °C.

ligand, these systems still gave substantially lower product yields than the parent BINAP system (entries 2 and 3). Interestingly, no product was observed when a slightly different bidentate phosphine (i.e., dppe) was used (entry 4). Our group has had success employing a combination of Ni(0) and *N*-heterocyclic carbene ligands as catalysts for a variety of [2 + 2 + 2] cycloadditions.[8] However, the Ni/NHC system was not an effective catalyst system for either the [2 + 2 + 2] cycloaddition of diyne **1** and either vinylene carbonate **2** or 2-oxazolone **4** (entries 5 and 6).

The reaction conditions were further optimized (Table 2). The catalyst loading could be reduced from 5 to 3 mol % with little effect on the GC yields (Table 2, entries 1−3). Importantly,

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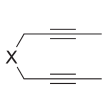
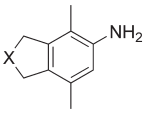
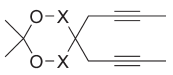
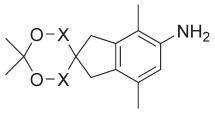
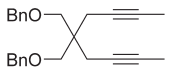
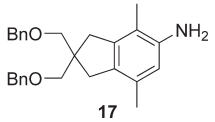
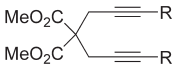
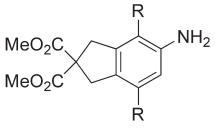
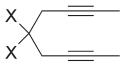
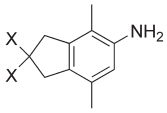
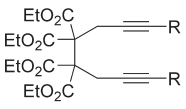
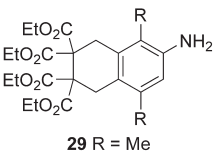
Table 2. Various Rh-Catalyzed Cycloaddition Conditions[a]

entry	$[Rh(COD)_2]BF_4$ (mol %)	BINAP (mol %)	**4** (M)	T (°C)	yield[b] (%)
1	5	5	0.5	60	>99
2	3	3	0.5	60	95
3	1	1	0.5	60	25
4	3	3	0.3	60	>99
5	3	3	0.15	60	>99
6	3	3	0.1	60	>99
7	3	3	0.1	40	83
8	3	3	0.1	rt	73

[a] **1** (0.1 M) in THF at 60 °C. [b] Determined by GC with naphthalene as an internal standard.

Table 3. Decarboxylative Rh-Catalyzed [2 + 2 + 2] Cycloadditions with 2-Oxazolone 4[a]

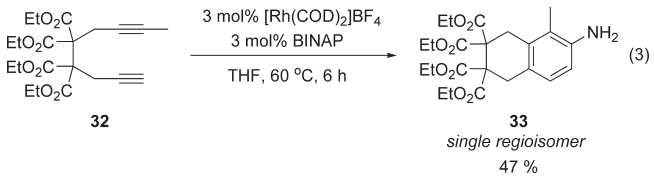
entry	diynes	product	yields[b]
			
1	**1** X = $C(CO_2Me)_2$	**5** X = $C(CO_2Me)_2$	85 %
2	**6** X = $CH(CO_2Me)$	**7** X = $CH(CO_2Me)$	78 %
3	**8** X = O	**9** X = O	67 %
4	**10** X = NTs	**11** X = NTs	87 %
			
5	**12** X = CH_2	**13** X = CH_2	83 %
6	**14** X = C(O)	**15** X = C(O)	72 %
7	 **16**	 **17**	72 %
			
8	**18** R = H	**19** R = H	30 %
9	**20** R = Ph	**21** R = Ph	84 %
10	**22** R = *i*Pr	**23** R = *i*Pr	39 %
			38 %
11	**24** X = CN	**25** X = CN	38 %
12	**26** X = SO_2Ph	**27** X = SO_2Ph	99 %
			
13	**28** R = Me	**29** R = Me	79 %
14	**30** R = H	**31** R = H	41 %

[a] 3 mol % $[Rh(COD)_2]BF_4$ (0.003 M), 3 mol % BINAP (0.003 M), diyne (0.1 M), and 2-oxazolone (0.1 M) in THF at 60 °C for 6 h. [b] Isolated yields (average of two runs).

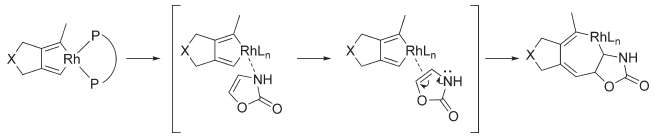
the concentration of 2-oxazolone **4** could be substantially reduced to only 1 equiv without compromising product yield (entries 2, 4−6). Although the reaction proceeds at lower temperatures, lower product yields were observed (entries 7 and 8). Thus, our optimized reaction conditions utilized 3 mol % $[Rh(COD)_2]BF_4$, 3 mol % BINAP, 0.1 M diyne, and 0.1 M 2-oxazolone in THF at 60 °C.

A variety of diynes were subjected to the optimized Rh-catalyzed [2 + 2 + 2] cycloaddition reactions described above (Table 3). In addition to the standard diyne (**1**), more flexible diynes such as diyne **6**, ether diyne **8**, and *N*-sulfonamide diyne **10** were converted to their respective anilines (**7**, **9**, and **11**) in good yields (entries 1−4). Similarly, highly oxygenated diynes such as **12** and **14** afforded good yields of cyclotrimerized products (entries 5−7). Interestingly, diynes prone to homodimerization[12] (i.e., terminal diynes **18**[13] and **30** as well as phenyl-substituted diyne **20**) could also be used as cycloaddition substrates (entries 8, 9, and 14), although some homodimerization was still observed. However, the phenyl-substituted diyne afforded the aniline product in substantially higher yield than its terminal diyne analogue. The cycloaddition was somewhat tolerant to steric hindrance on the diyne. For example, diyne **22** that possesses *i*-Pr groups was converted aniline **13**, albeit in lower yield (entry 10). A similar yield was obtained when cyano groups were present on the diyne (**24**, entry 11). Despite the low aniline yield, no pyridine products were observed in this reaction.[14] Diyne **26** bearing two phenyl sulfones was converted to aniline product **27** inexcellent 99% yield (entry 12). In addition, a diyne possessing a four atom linker instead of a three atom linker (diynes **28** and **30**) were effectively converted to their respective anilines **29** and **31** in good yield (entries 13 and 14).

Unsymmetrical diyne **32** was also evaluated under these reaction conditions (eq 3). Surprisingly, high regioselectivity was observed in the cycloaddition reaction, and aniline derivative **33** was the only observed product.[15] Selective insertion of the oxazolone, possibly due to initial binding of the nitrogen or the polarized nature of the double bond, may account for the regioselectivity observed (Scheme 1).



Scheme 1. Possible Mechanism for Regioselective Oxazolone Insertion



N-Acetyl-2-oxazolone **34** was also examined as a potential substrate in the Rh-catalyzed cycloaddition reactions. The reaction of **34** with diyne **1** afforded a mixture of three products (eq 4). Diyne dimerization product **35** was the major product. Only trace amounts of the corresponding acetyl-protected

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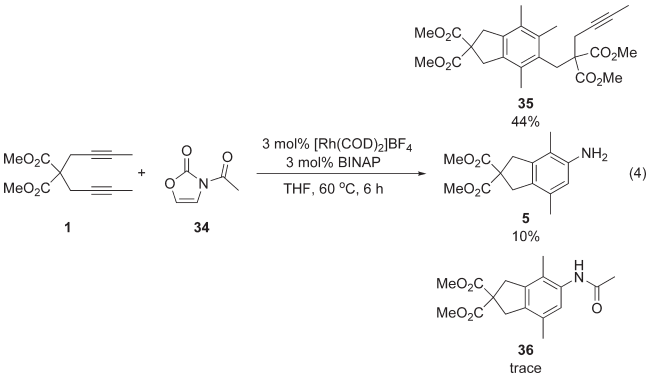
aniline **36** was detected by GC−MS. Aniline **5** was isolated in 10% yield from this reaction.

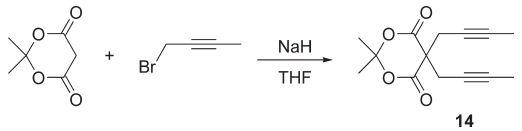


In summary, we have developed a new method to synthesize highly functionalized bicyclic aniline derivatives via $[Rh(COD)_2]BF_4$/BINAP-catalyzed [2 + 2 + 2] cycloaddition reactions of diynes and 2-oxazolone. When unsymmetrical diynes were used, high regioselectivities were observed. Further exploration of this methodology is underway.

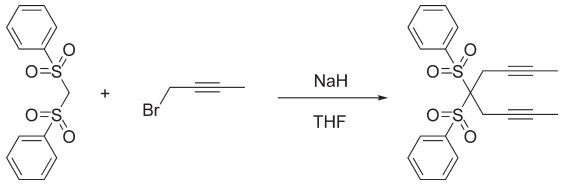
EXPERIMENTAL SECTION

Dimethyl 2,2-di(but-2-yn-1-yl)malonate (**1**),[16] methyl 2-(but-2-yn-1-yl)hex-4-ynoate (**6**),[17] 5,5-di(but-2-yn-1-yl)-2,2-dimethyl-1,3-dioxane (**12**),[18] 1-(but-2-yn-1-yloxy)but-2-yne (**8**),[8c] (((2,2-di(but-2-yn-1-yl)-propane-1,3-diyl)bis(oxy))bis(methylene)]dibenzene (**16**),[8c] dimethyl 2,2-di(prop-2-yn-1-yl)malonate (**18**),[19] dimethyl 2,2-bis(3-phenylprop-2-yn-1-yl)malonate (**20**),[20] dimethyl 2,2-bis(4-methylpent-2-yn-1-yl)malonate (**22**),[8c] 2,2-di(but-2-yn-1-yl)malononitrile (**24**),[21] (nona-2,7-diyne-5,5-diyldisulfonyl)dibenzene (**26**),[22] tetraethyl deca-2,8-diyne-5,5,6,6-tetracarboxylate (**28**),[8a] and tetraethyl octa-1,7-diyne-4,4,5,5-tetracarboxylate (**30**)[23] were prepared according to literature procedures. 2-Oxazolone (**4**) and *N*-acetyl-2-oxazolone were prepared according to literature procedures.[24]

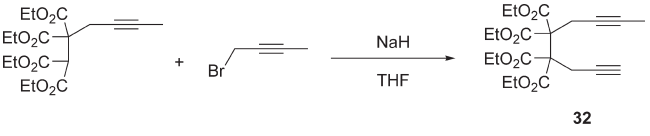
5,5-Di(but-2-yn-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione (14). To a suspended solution of sodium hydride (366 mg, 15.3 mmol, 0.1 M) in THF (153 mL) was added 2,2-dimethyl-1,3-dioxane-4,6-dione (1.000 g, 6.940 mmol) dropwise via a disposable syringe at 0 °C. The reaction mixture was stirred for 30 min until it became clear, and then 1-bromo-but-2-yne (2.030 g, 15.30 mmol) was added dropwise via a disposable syringe. The reaction was refluxed for 40 h and then quenched by cold saturated ammonium chloride solution. The aqueous layer was extracted 3 × 50 mL with diethyl ether. The organic layer was combined, dried over sodium sulfate, and concentrated under vacuum to give crude product **14**. Purification by flash column chromatography (20% diethyl ether/pentane) yielded pure product **14** (1.24 g, 72%) as a white powder. R_f = 0.45 (20% diethyl ether/pentane). Mp: 153−154 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.76 (q, J = 2 Hz, 4H), 1.81 (s, 6H), 1.73 (t, J = 1.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 168.2, 106.9, 81.1, 73.0, 54.8, 30.1, 28.7, 3.8. IR (CH_2Cl_2, cm^{-1}): 3486, 2923, 1773, 1740, 1359, 1268, 1112, 1053, 958. HRMS (ESI) calcd for $C_{14}H_{16}O_4Na$ $[M + Na]^+$: 271.0946, found 271.0953.



(Nona-2,7-diyne-5,5-diyldisulfonyl)dibenzene (26). To a suspended solution of sodium hydride (366 mg, 15.3 mmol, 0.1 M) in THF (153 mL) was added bis(phenylsulfonyl)methane (2.780 g, 6.940 mmol) dropwise via a disposable syringe at 0 °C. The reaction mixture was stirred for 30 min until it became clear, and then 1-bromo-but-2-yne (2.03 g, 15.3 mmol) was added dropwise via a disposable syringe. The reaction was refluxed for 40 h and then quenched by cold saturated ammonium chloride solution. The aqueous layer was extracted 3 × 50 mL with diethyl ether. The organic layer was combined, dried over sodium sulfate, and concentrated under vacuum to give crude product **26**. Purification by flash column chromatography (20% diethyl ether/pentane) yielded pure product **26** (1.84 g, 49%) as a yellow powder. R_f = 0.30 (20% diethyl ether/pentane). Mp: 140−142 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.20 (d, J = 7.5 Hz, 4H), 7.70 (t, J = 7.2 Hz, 2H), 7.58 (t, J = 7.8 Hz, 4H), 3.16 (d, J = 2.7 Hz, 4H), 1.76 (t, J = 1.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 137.1, 135.0, 131.9, 128.7, 88.2, 82.2, 70.8, 21.6, 4.2. IR (CH_2Cl_2, cm^{-1}): 3067, 2920, 2254, 1448, 1335, 1314, 1149, 1078, 912. HRMS (ESI) calcd for $C_{21}H_{20}O_4S_2Na$ $[M + Na]^+$: 423.0701, found 423.0706.



2-But-2-ynyl-2,3-bis-ethoxycarbonyl-3-prop-2-ynyl-succinic Acid Diethyl Ester (32). To a suspended solution of sodium hydride (366 mg, 15.3 mmol, 0.1 M) in THF (153 mL) was added monoalkyne[8d] (5.15 g, 13.9 mmol) dropwise via a disposable syringe at 0 °C. The reaction mixture was stirred for 30 min until it became clear, and then propargyl bromide (2.03 g, 15.3 mmol) was added dropwise via a disposable syringe. The reaction was refluxed for 40 h and then quenched by cold saturated ammonium chloride solution. The aqueous layer was extracted 3 × 50 mL with diethyl ether. The organic layer was combined, dried over sodium sulfate, and concentrated under vacuum to give crude product **32**. Purification by flash column chromatography (20% diethyl ether/pentane) yielded pure product **32** (4.88 g, 86%) as a white powder. R_f = 0.40 (20% diethyl ether/pentane). Mp: 55−56 °C. ^{1}H NMR (500 MHz, CDCl3, ppm): δ 4.17−4.31 (m, 8H), 3.19 (d, J = 3 Hz, 2H), 3.04 (d, J = 2.5 Hz, 2H), 2.01 (s, 1H), 1.74 (t, J = 2.5 Hz, 3H), 1.29 (t, J = 7 Hz, 12H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 169.0, 168.8, 80.4, 78.8, 74.7, 70.9, 62.3, 62.2, 61.9, 61.8, 23.2, 22.7, 14.2, 4.0. IR (CH_2Cl_2, cm^{-1}): 3276, 2985, 1736, 1446, 1368, 1208, 1096, 1038, 864. HRMS (ESI) calcd for $C_{21}H_{28}O_8Na$ $[M + Na]^+$: 431.1682, found 431.1681.



General Procedure for Rh-Catalyzed Cycloaddition Reaction. In a glovebox, diyne (1 equiv) and 2-oxazolone (1 equiv) were directly weighed into a scintillation vial equipped with a stir bar. A catalyst stock solution was prepared by dissolution of $[Rh(COD)_2]BF_4$ (5.0 mg, 0.012 mmol, 0.0030 M) and BINAP (7.7 mg, 0.012 mmol, 0.0030 M) in THF (4.1 mL). To the scintillation vial containing diyne and 2-oxazolone was added an aliquot of catalyst stock solution. The scintillation vial was sealed, brought out of the box, and heated for 6 h at 60 °C. The solvent was removed under vacuum,

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and the crude product was purified by flash column chromatography on silica gel.

Dimethyl 5-Amino-4,7-dimethyl-1*H*-indene-2,2(3*H*)-dicarboxylate (5). The general cycloaddition procedure was used with diyne **1** (20.0 mg, 0.085 mmol, 0.1 M), 2-oxazolone **4** (7.2 mg, 0.85 mmol, 0.1 M), and a 0.85 mL aliquot of the $[Rh(COD)_2]BF_4$/BINAP-catalyst stock solution in THF (0.85 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (50% diethyl ether/pentane) to afford **5** (20.9 mg, 89% first run, 19.0 mg, 81% second run) as a light yellow solid. R_f = 0.45 (50% diethyl ether/pentane). Mp: 96−98 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.39 (s, 1H), 3.76 (s, 6H), 3.53 (s, 2H), 3.47 (brs, 2H), 3.46 (s, 2H), 2.14 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 172.8, 144.1, 139.7, 131.7, 129.0, 115.8, 60.1, 53.2, 40.4, 39.6, 19.0, 13.5. IR (CH_2Cl_2, cm^{-1}): 3377, 2954, 1733, 1627, 1434, 1263, 1198, 1163. HRMS (ESI) calcd for $C_{15}H_{20}NO_4$ $[M + H]^+$: 278.1389, found 278.1392.

Methyl 5-Amino-4,7-dimethyl-2,3-dihydro-1*H*-indene-2-carboxylate (7). The general cycloaddition procedure was used with diyne **6** (25.0 mg, 0.140 mmol, 0.1 M), 2-oxazolone **4** (11.9 mg, 0.140 mmol, 0.1 M), and a 1.4 mL aliquot of the $[Rh(COD)_2]BF_4$/BINAP-catalyst stock solution in THF (1.4 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (60% diethyl ether/pentane) to afford **7** (23.7 mg, 77% first run, 24.3 mg, 79% second run) as a yellow solid. R_f = 0.52 (60% diethyl ether/pentane). Mp: 86−88 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.40 (s, 1H), 3.74 (s, 3H), 3.48 (s, 2H), 3.32 (dd, J = 17.3 Hz, 8.7 Hz, 1H), 3.07−3.17 (m, 4H), 2.15 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 176.5, 143.8, 141.4, 131.8, 130.6, 115.9, 115.3, 52.2, 43.3, 35.8, 35.0, 19.1, 13.5. IR (CH_2Cl_2, cm^{-1}): 3382, 2947, 2851, 1724, 1626, 1500, 1435, 1362, 1266, 1206, 1165. HRMS (ESI) calcd for $C_{13}H_{18}NO_2$ $[M + H]^+$: 220.1338, found 220.1332.

4,7-Dimethyl-1,3-dihydroisobenzofuran-5-amine (9). The general cycloaddition procedure was used with diyne **8** (25.0 mg, 0.21 mmol, 0.1 M), 2-oxazolone **4** (17.4 mg, 0.21 mmol, 0.1 M), and a 2.1 mL aliquot of the $[Rh(COD)_2]BF_4$/BINAP-catalyst stock solution in THF (2.1 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (75% diethyl ether/pentane) to afford **9** (21.0 mg, 63% first run, 23.7 mg, 71% second run) as a yellow solid. R_f = 0.32 (75% diethyl ether/pentane). Mp: 120−122 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.44 (s, 1H), 5.08 (s, 2H), 5.04 (s, 2H), 3.56 (s, 2H), 2.13 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 144.4, 139.2, 129.4, 128.2, 115.8, 113.0, 74.0, 73.9, 18.8, 13.6. IR (CH_2Cl_2, cm^{-1}): 3466, 3360, 3232, 2846, 1635, 1503, 1370, 1303, 1048, 896, 852. HRMS (ESI) calcd for $C_{10}H_{14}NO$ $[M + H]^+$: 164.1075, found 164.1054.

4,7-Dimethyl-2-tosylisoindolin-5-amine (11). The general cycloaddition procedure was used with diyne **10** (20.0 mg, 0.073 mmol, 0.1 M), 2-oxazolone **4** (6.2 mg, 0.073 mmol, 0.1 M), and a 0.73 mL aliquot of the $[Rh(COD)_2]BF_4$/BINAP-catalyst stock solution in THF (0.73 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (80% diethyl ether/pentane) to afford **11** (19.3 mg, 84% first run, 20.7 mg, 90% second run) as a white solid. R_f = 0.40 (80% diethyl ether/pentane). Mp: 198−200 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.78 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.40 (s, 1H), 4.54 (s, 2H), 4.49 (s, 2H), 3.55 (s, 2H), 2.42 (s, 3H), 2.08 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 144.7, 143.8, 136.1, 134.1, 130.8, 130.1, 127.9, 125.1, 116.0, 114.1, 54.0, 53.6, 21.8, 18.7, 13.4. IR (CH_2Cl_2, cm^{-1}): 3378, 2922, 2853, 1631, 1506, 1462, 1339, 1162, 1099, 666. HRMS (ESI) calcd for $C_{17}H_{20}N_2O_2SNa$ $[M + Na]^+$: 339.1143, found 339.1151.

2,2,4′,7′-Tetramethyl-1′,3′-dihydrospiro[[1,3]dioxane-5,2′-inden]-5′-amine (13). The general cycloaddition procedure was used with diyne **12** (25.0 mg, 0.11 mmol, 0.1 M), 2-oxazolone **4** (9.7 mg, 0.11 mmol, 0.1 M), and a 1.1 mL aliquot of the $[Rh(COD)_2]BF_4$/BINAP-catalyst stock solution in THF (1.1 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (60% diethyl ether/pentane) to afford **13** (23.7 mg, 80% first run, 25.5 mg, 86% second run) as a white solid. R_f = 0.30 (60% diethyl ether/pentane). Mp: 147−148 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.40 (s, 1H), 3.78 (d, J = 11.1 Hz, 2H), 3.75 (d, J = 11.0 Hz, 2H), 3.47 (s, 2H), 2.83 (s, 2H), 2.73 (s, 3H), 2.14 (s, 3H), 2.04 (s, 3H), 1.49 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 143.7, 141.2, 132.4, 130.4, 116.4, 115.3, 105.3, 98.2, 69.7, 41.5, 40.0, 38.9, 24.6, 23.9, 19.1, 13.5. IR (CH_2Cl_2, cm^{-1}): 3452, 3362, 2991, 2936, 2856, 1625, 1499, 1453, 1381, 1246, 1198, 1154, 1096, 831. HRMS (ESI) calcd for $C_{16}H_{24}NO_2$ $[M + H]^+$: 262.1807, found 262.1798.

5′-Amino-2,2,4′,7′-tetramethyl-1′,3′-dihydrospiro[[1,3]dioxane-5,2′-indene]-4,6-dione (15). The general cycloaddition procedure was used with diyne **14** (25.0 mg, 0.10 mmol, 0.1 M), 2-oxazolone **4** (8.8 mg, 0.10 mmol, 0.1 M), and a 1.0 mL aliquot of the $[Rh(COD)_2]BF_4$/BINAP-catalyst stock solution in THF (1.0 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (80% diethyl ether/pentane) to afford **15** (21.3 mg, 73% first run, 20.7 mg, 71% second run) as a light yellow solid. R_f = 0.38 (20% diethyl ether/pentane). Mp: 177−178 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.42 (s, 1H), 3.64 (s, 2H), 3.54 (s, 2H), 3.51 (s, 2H), 2.12 (s, 3H), 2.02 (s, 3H), 1.83 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 171.3, 144.7, 139.0, 131.5, 127.7, 116.4, 115.4, 105.3, 52.4, 45.3, 29.3, 19.1, 13.6. IR (CH_2Cl_2, cm^{-1}): 3386, 2932, 1765, 1732, 1628, 1385, 1284, 1202, 1045, 949, 734. HRMS (ESI) calcd for $C_{16}H_{19}NO_4Na$ $[M + Na]^+$: 312.1212, found 312.1218.

2,2-Bis((benzyloxy)methyl)-4,7-dimethyl-2,3-dihydro-1*H*-inden-5-amine (17). The general cycloaddition procedure was used with diyne **16** (25.0 mg, 0.069 mmol, 0.1 M), 2-oxazolone **4** (5.9 mg, 0.069 mmol, 0.1 M), and a 0.69 mL aliquot of the $[Rh(COD)_2]BF_4$/BINAP-catalyst stock solution in THF (0.69 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (60% diethyl ether/pentane) to afford **17** (20.1 mg, 72% first run, 20.1 mg, 72% second run) as a white solid. R_f = 0.40 (60% diethyl ether/pentane). Mp: 120−122 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.28−7.33 (m, 10H), 6.38 (s, 1H), 4.54 (s, 4H), 3.53 (s, 4H), 3.44 (s, 2H), 2.79 (s, 2H), 2.72 (s, 2H), 2.11 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 143.4, 141.9, 139.2, 132.2, 131.3, 128.6, 127.8, 127.7, 116.4, 115.1, 74.2, 73.5, 47.8, 39.0, 38.1, 19.1, 16.4, 13.5. IR (CH_2Cl_2, cm^{-1}): 3366, 2858, 1621, 1498, 1361, 1104, 731. HRMS (ESI) calcd for $C_{27}H_{31}NO_2Na$ $[M + Na]^+$: 424.2252, found 424.2254.

Dimethyl 5-Amino-1*H*-indene-2,2(3*H*)-dicarboxylate (19). The general cycloaddition procedure was used with diyne **18** (25.0 mg, 0.120 mmol, 0.1 M), 2-oxazolone **4** (10.2 mg, 0.120 mmol, 0.1 M), and a 1.2 mL aliquot of the $[Rh(COD)_2]BF_4$/BINAP-catalyst stock solution in THF (1.2 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (75% diethyl ether/pentane) to afford **19** (8.6 mg, 29% first run, 9.3 mg, 31% second run) as a white solid. R_f = 0.30 (75% diethyl ether/pentane). Mp: 84−86 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.96 (d, J = 7.8 Hz, 2H), 6.54 (s, 1H), 6.51 (d, J = 8.4 Hz, 2H), 3.73 (s, 6H), 3.55 (br, 2H), 3.50 (s, 2H), 3.48 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 172.6, 145.9, 141.5, 130.1, 125.1, 114.5, 111.3, 61.0, 53.3, 40.9, 40.2. IR (CH_2Cl_2, cm^{-1}): 3376, 2955, 1732, 1626, 1499, 1435, 1253, 1200, 1067. HRMS (ESI) calcd for $C_{13}H_{16}NO_4$ $[M + H]^+$: 250.1079, found 250.1071.

Dimethyl 5-Amino-4,7-diphenyl-1*H*-indene-2,2(3*H*)-dicarboxylate (21). The general cycloaddition procedure was used with diyne **20** (25.0 mg, 0.063 mmol, 0.1 M), 2-oxazolone **4**

(5.9 mg, 0.063 mmol, 0.1 M), and a 0.66 mL aliquot of the $[Rh(COD)_2]$-BF_4/BINAP-catalyst stock solution in THF (0.66 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (60% diethyl ether/pentane) to afford **21** (22.6 mg, 81% first run, 24.2 mg, 87% second run) as a white solid. R_f = 0.60 (60% diethyl ether/pentane). Mp: 56−58 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.34−7.49 (m, 10H), 6.69 (s, 1H), 3.68 (s, 6H), 3.62 (s, 2H), 3.60 (brs, 2H), 3.36 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 172.5, 143.7, 141.1, 140.6, 138.4, 137.4, 129.9, 129.5, 128.7, 127.8, 127.6, 127.4, 123.8, 115.3, 60.7, 53.2, 40.7, 40.4. IR (CH_2Cl_2, cm^{-1}): 3381, 2953, 1734, 1650, 1475, 1435, 1249, 1201, 1164, 1072. HRMS (ESI) calcd for $C_{25}H_{24}NO_4$ $[M + H]^+$: 402.1705, found 402.1700.

Dimethyl 5-Amino-4,7-diisopropyl-1*H*-indene-2,2(3*H*)-dicarboxylate (23). The general cycloaddition procedure was used with diyne **22** (25.0 mg, 0.086 mmol, 0.1 M), 2-oxazolone **4** (7.3 mg, 0.086 mmol, 0.1 M), and a 0.86 mL aliquot of the $[Rh(COD)_2]BF_4$/BINAP-catalyst stock solution in THF (0.86 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (50% diethyl ether/pentane) to afford **23** (11.7 mg, 41% first run, 10.5 mg, 37% second run) as a light yellow oil. R_f = 0.55 (50% diethyl ether/pentane). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.47 (s, 1H), 3.74 (s, 6H), 3.59 (s, 2H), 3.56 (brs, 2H), 3.46 (s, 2H). 3.10 (dt, J = 14.4 Hz, 7.2 Hz, 1H), 2.84 (dt, J = 13.8 Hz, 6.9 Hz, 1H), 1.32 (d, 7.2 Hz, 6H), 1.18 (d, 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 172.7, 143.6, 142.6, 138.9, 128.9, 126.1, 113.2, 60.6, 53.2, 40.8, 38.3, 30.9, 28.6, 23.1, 21.0. IR (CH_2Cl_2, cm^{-1}): 2959, 1735, 1626, 1431, 1250, 1201, 1167. HRMS (ESI) calcd for $C_{19}H_{28}NO_4$ $[M + H]^+$: 334.2018, found 334.2013.

5-Amino-4,7-dimethyl-1*H*-indene-2,2(3*H*)-dicarbonitrile (25). The general cycloaddition procedure was used with diyne **24** (30.0 mg, 0.18 mmol, 0.1 M), 2-oxazolone **4** (15.0 mg, 0.18 mmol, 0.1 M), and a 1.8 mL aliquot of the $[Rh(COD)_2]BF_4$/BINAP-catalyst stock solution in THF (1.8 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (70% diethyl ether/pentane) to afford **25** (15.3 mg, 41% first run, 13.0 mg, 35% second run) as a white solid. R_f = 0.45 (70% diethyl ether/pentane). Mp: 176−178 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.46 (s, 1H), 3.64 (s, 2H), 3.62 (s, 2H), 3.59 (s, 2H), 2.16 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 145.4, 136.2, 132.5, 125.0, 117.2, 116.7, 116.0, 44.5, 43.7, 33.5, 19.1, 13.7. IR (CH_2Cl_2, cm^{-1}): 3481, 3390, 3370, 2921, 1626, 1502, 1441, 1346, 1061, 1018, 855. HRMS (ESI) calcd for $C_{13}H_{14}N_3$ $[M + H]^+$: 212.1188, found 212.1187.

4,7-Dimethyl-2,2-bis(phenylsulfonyl)-2,3-dihydro-1*H*-inden-5-amine (27). The general cycloaddition procedure was used with diyne **26** (25.0 mg, 0.062 mmol, 0.1 M), 2-oxazolone **4** (5.4 mg, 0.062 mmol, 0.1 M), and a 0.62 mL aliquot of the $[Rh(COD)_2]$-BF_4/BINAP-catalyst stock solution in THF (0.62 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (50% diethyl ether/pentane) to afford **27** (27.0 mg, 98% first run, 27.6 mg, 100% second run) as a yellow solid. R_f = 0.50 (50% diethyl ether/pentane). Mp: dec >200 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.91 (d, J = 8.5 Hz, 4H), 7.58 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 8.0 Hz, 4H), 6.19 (s, 1H), 4.00 (brs, 2H), 3.81 (s, 2H), 3.74 (s, 2H), 1.93 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 143.1, 137.8, 137.3, 134.7, 131.3, 130.8, 130.6, 129.0, 128.8, 127.7, 116.5, 116.0, 115.7, 92.8, 38.2, 37.5, 18.8, 13.4. IR (CH_2Cl_2, cm^{-1}): 3380, 2920, 1754, 1626, 1447, 1327, 1149, 1079. HRMS (ESI) calcd for $C_{23}H_{23}NO_4S_2Na$ $[M + Na]^+$: 464.0966, found 464.0969.

Tetraethyl 6-Amino-5,8-dimethylnaphthalene-2,2,3,3-(1*H*,4*H*)-tetracarboxylate (29). The general cycloaddition procedure was used with diyne **28** (25.0 mg, 0.059 mmol, 0.1 M), 2-oxazolone **4** (5.0 mg, 0.059 mmol, 0.1 M), and a 0.59 mL aliquot of the $[Rh(COD)_2]BF_4$/BINAP-catalyst stock solution in THF (0.59 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (70% diethyl ether/pentane) to afford **29** (20.8 mg, 76% first run, 22.5 mg, 82% second run) as a light yellow solid. R_f = 0.28 (70% diethyl ether/pentane). Mp: 92−94 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.42 (s, 1H), 4.10−4.28 (m, 8H), 3.42 (brs, 2H), 3.38 (s, 2H), 3.29 (s, 2H), 2.13 (s, 3H), 2.02 (s, 3H), 1.21 (t, J = 6.9 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 170.5, 142.2, 133.7, 131.7, 122.1, 117.5, 116.2, 61.9, 57.6, 57.3, 33.5, 32.4, 19.8, 14.0, 12.4. IR (CH_2Cl_2, cm^{-1}): 3379, 2983, 1734, 1627, 1478, 1444, 1389, 1263, 1204, 1095, 1051. HRMS (ESI) calcd for $C_{24}H_{33}NO_8Na$ $[M + Na]^+$: 486.2104, found 486.2104.

Tetraethyl 6-Aminonaphthalene-2,2,3,3(1*H*,4*H*)-tetracarboxylate (31). The general cycloaddition procedure was used with diyne **30** (30.0 mg, 0.076 mmol, 0.1 M), 2-oxazolone **4** (6.5 mg, 0.076 mmol, 0.1 M), and a 0.76 mL aliquot of the $[Rh(COD)_2]BF_4$/BINAP-catalyst stock solution in THF (0.76 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (30% diethyl ether/pentane) to afford **31** (12.6 mg, 38% first run, 14.6 mg, 44% second run) as a light yellow oil. R_f = 0.30 (30% diethyl ether/pentane). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.86 (d, J = 7.5 Hz, 1H), 6.47 (d, J = 7.5 Hz, 1H), 6.41 (s, 1H), 4.13−4.25 (m, 8H), 3.48 (brs, 2H), 3.42 (s, 2H), 3.40 (s, 2H), 1.22 (td, J = 7.1 Hz, 3.4 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 170.3, 144.7, 133.8, 129.4, 123.2, 114.7, 114.4, 62.1, 62.0, 58.0, 57.8, 35.8, 34.3, 14.1. IR (CH_2Cl_2, cm^{-1}): 3455, 3378, 2983, 1734, 1625, 1512, 1444, 1367, 1265, 1201, 1095, 1039. HRMS (ESI) calcd for $C_{22}H_{29}NO_8Na$ $[M + Na]^+$: 458.1791, found 458.1788.

Tetraethyl 6-Amino-5-methylnaphthalene-2,2,3,3(1*H*,4*H*)-tetracarboxylate (33). The general cycloaddition procedure was used with diyne **32** (25.0 mg, 0.061 mmol, 0.1 M), 2-oxazolone **4** (5.3 mg, 0.061 mmol, 0.1 M), and a 0.61 mL aliquot of the $[Rh(COD)_2]$-BF_4/BINAP-catalyst stock solution in THF (0.61 mL total volume) at 60 °C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel (70% diethyl ether/pentane) to afford **33** (12.1 mg, 44% first run, 13.8 mg, 50% second run) as a colorless oil. R_f = 0.20 (70% diethyl ether/pentane). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 6.76 (d, J = 8 Hz, 1H), 6.53 (d, J = 7.5 Hz, 1H), 4.13−4.26 (m, 8H), 3.47 (s, 2H), 3.43 (s, 2H), 3.39 (s, 2H), 2.04 (s, 3H), 1.23 (dt, J = 10.7 Hz, 7.1 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 170.6, 170.4, 142.8, 131.9, 126.6, 123.5, 120.0, 114.5, 62.1, 62.0, 58.1, 57.4, 34.9, 33.5, 14.1, 12.7. IR (CH_2Cl_2, cm^{-1}): 3453, 3379, 2983, 1734, 1627, 1491, 1444, 1367, 1266, 1204, 1096, 1047, 863. HRMS (ESI) calcd for $C_{23}H_{31}NO_8Na$ $[M + Na]^+$: 472.1947, found 472.1950.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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