Copper-Catalyzed Hydroalkylation of Alkynes: Addition of sp^3 C–H Bonds Across Carbon–Carbon Triple Bonds

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Abstract: The regioselective copper-catalyzed addition of sp^3 C–H bonds adjacent to an oxygen atom to various alkynes has been accomplished under mild reactions conditions in the presence of *tert*-butyl hydroperoxide to give the corresponding alkenylated products.

Key words: C–H activation, copper, addition reactions, alkynes, *tert*-butyl hydroperoxide

Considerable effort has been devoted to selective C–H bond activation,[1] and important progress has been achieved in transition metal catalyzed activation of sp^2 C–H bonds which has provided promising economical alternatives to traditional organic chemistry.[2] Activation of an sp^3 C–H bond, however, is expected to be more difficult since cleavage of an sp^3 C–H bond is kinetically and thermodynamically unfavorable. Recent studies established that sp^3 C–H bonds adjacent to a heteroatom such as nitrogen, oxygen or sulfur were more reactive than those next to carbon atoms, and some promising catalytic systems have been reported for sp^3 C–H bond cleavage.[3] For example, Murai and co-workers pioneered the ruthenium-catalyzed addition of sp^3 C–H bonds adjacent to a nitrogen atom in alkylamines to alkenes.[4] The intramolecular catalytic cyclization of alkene–amide substrates in the presence of iridium complexes via cross-coupling of an sp^3 C–H bond adjacent to a nitrogen atom with an alkene moiety was reported by Sames and co-workers.[5] On the other hand, direct conversions of sp^3 C–H bonds adjacent to heteroatoms into C–C bonds using activated methylene compounds, alkenes or alkynes via cross-dehydrogenative coupling (CDC) have been developed by Li and others.[6] Oxygen-containing compounds are of significant interest in industrial and academic research. However, in contrast to cleavage of C–H bonds adjacent to nitrogen, examples of activation of C–H bonds next to oxygen atoms are limited because of its higher oxidation potential. Although cleavage of the benzylic C–H bond of benzyl ethers has been reported by Li and Zhang,[7] activation of a C–H bond adjacent to oxygen in an alkoxy group, which is less active, is not common.[8] Herein, we report the copper-catalyzed addition of sp^3 C–H bonds adjacent to the oxygen atom of tetrahydrofuran with various alkynes in the presence of *tert*-butyl hydroperoxide (TBHP) under mild reaction conditions. This transformation represents the first example of the transition metal mediated hydroalkylation of an alkyne with an sp^3 C–H bond.

Hydroalkylation is an important transformation in organic synthesis. Moreover, metal-mediated addition of sp^3 C–H bonds to alkynes remains a difficult task. Our studies started with the coupling of tetrahydrofuran and ethynylbenzene as shown in Table 1. It was found that the additive played an important role in the reaction. Benzoyl peroxide, which proved to be an efficient additive for activation of C–H bonds in phenylpyridines in our previous studies,[9] was completely inactive (Table 1, entry 1). However, a small amount of hydroalkylation product was obtained using *m*-chloroperoxybenzoic acid (MCPBA) (Table 1, entry 2), and the reaction yield was further improved using other peroxides (Table 1, entries 3 and 4). The optimal result was obtained using *tert*-butyl hydroperoxide as additive which afforded a 62% yield of product (Table 1, entry 5). A trace amount of the desired product was detected using the radical initiator 2,2′-azobis(isobutyronitrile) (AIBN). No reaction was observed when 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and *N*-bromosuccinimide (NBS) were employed as additives (Table 1, entries 6–8). A number of catalysts including salts of copper, silver and gold were able to promote this transformation in the presence of *tert*-butyl hydroperoxide as additive (Table 1, entries 9–20); copper(I) bromide demonstrated the best activity in comparison with the other metals tested (Table 1, entry 5). An increased loading of copper(I) bromide did not improve the reaction yield further and higher loadings (>30 mol%) led to the formation of the corresponding homocoupling product of ethynylbenzene. Chloro(triphenylphosphine)gold(I) (PPh_3AuCl) proved to be an efficient additive giving a 56% yield of product, however, the use of sodium tetrachloroaurate(III) dihydrate ($NaAuCl_4{\cdot}2H_2O$) (10 mol%) delivered a mixture of cross-coupling (25% yield) and homocoupling products whilst hydrogen tetrachloroaurate(III) tetrahydrate ($HAuCl_4{\cdot}4H_2O$) was inactive (Table 1, entries 18–20). Copper(I) bromide, being the more efficient and cheaper catalyst, was employed in subsequent experiments. Previous investigations on copper(I) bromide catalyzed reactions of alkynes with sp^3 C–H bonds adjacent to a nitrogen atom demonstrated that alkynylation occurred via a cross-dehydrogenative coupling process in the presence of *tert*-butyl hydroperoxide to give the corresponding propargylamines as the major products.[10] Thus it is apparent that the reactivity of a C–H bond

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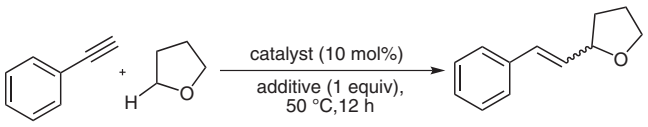
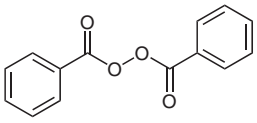
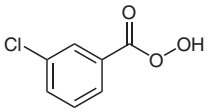
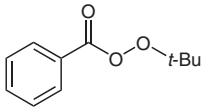
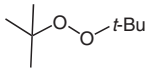
Table 1 The Effect of Various Metal Salts and Additives on the Hydroalkylation Reaction[a]



Entry	Catalyst	Additive	Yield (%)[b]
1	CuBr		–
2	CuBr		<5
3	CuBr		32
4	CuBr		29
5	CuBr	TBHP	62
6	CuBr	AIBN	<5
7	CuBr	DDQ	–
8	CuBr	NBS	–
9	CuCl	TBHP	48
10	CuI	TBHP	50
11	Cu_2O	TBHP	47
12	$CuBr_2$	TBHP	–
13	CuO	TBHP	31
14	$Cu(OAc)_2$	TBHP	29
15	$Cu(OTf)_2$	TBHP	–
16	AgOAc	TBHP	–
17	$AgNO_3$	TBHP	22
18	$NaAuCl_4 \cdot 2H_2O$	TBHP	25
19	$HAuCl_4 \cdot 4H_2O$	TBHP	–
20	PPh_3AuCl	TBHP	56

[a] Ethynylbenzene (51 mg, 0.5 mmol), catalyst (0.05 mmol), additive (1 equiv), TBHP (1–1.2 equiv, 0.10 mL, 5–6 M in decane), THF (10 mL), 50 °C, 12 h.
[b] Yield of isolated product.

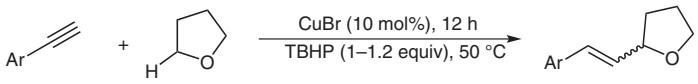
adjacent to a nitrogen atom is very different from that of a C–H bond next to an oxygen atom.

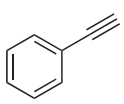
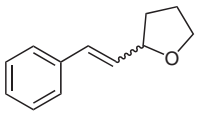
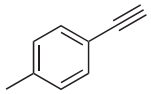
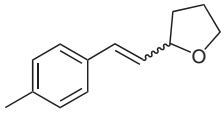
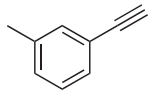
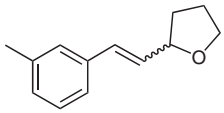
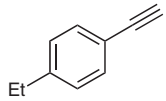
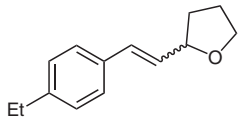
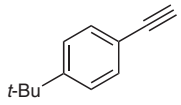
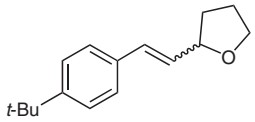
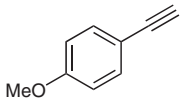
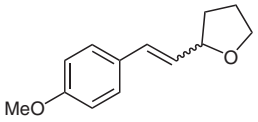
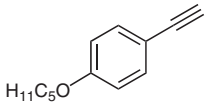
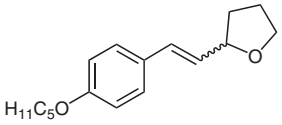
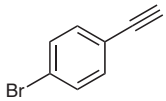
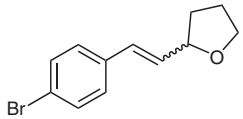
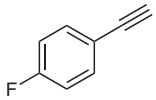
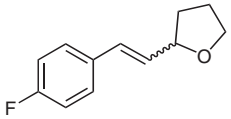
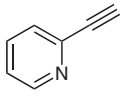
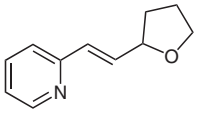
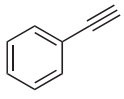
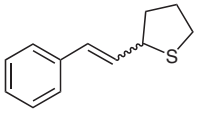
Terminal arylalkynes possessing electron-donating or electron-withdrawing substitutents on the aryl ring gave the corresponding hydroalkylated products in good yields (Table 2, entries 2–8). The reaction conditions also tolerated halide substituents which are useful for further functionalization. The regioselectivity of these reactions was different from those of metal-catalyzed hydroarylations of terminal arylalkynes in which α-aryl substituted alkenes were formed.[11] The present hydroalkylation reaction afforded exclusively β-alkylated alkenes, and only monoalkenylated tetrahydrofurans were observed. Both *cis* and *trans* alkenylated products were isolated with the *cis* isomers predominating. 2-Ethynylpyridine proved to be less reactive affording the *trans* stereoisomer as the sole hydroalkylation product (Table 2, entry 10). The reaction with tetrahydrothiophene afforded a 30% yield of product whilst pyrrolidine failed to give the desired adduct under the same reaction conditions. Six-membered cyclic ethers such as tetrahydro-2*H*-pyran and 1,4-dioxane gave the desired products in low yields, and these were difficult to purify.

We also studied the hydroalkylation reaction with 1,3-dioxolane, a substrate in which there are two different C–H bond environments next to oxygen. Under the conditions described above, reactions with various phenyl acetylenes occurred selectively via C–H bond activation at C-2 of 1,3-dioxolane to afford 2-alkenylated 1,3-dioxolanes **1a**–**5a** as the major products (Scheme 1). The observed byproducts **1b**–**5b** (>5%) were identified as the adducts resulting from reaction at C-4 of 1,3-dioxolane. Again, C–C bond formation occurred at the least-substituted carbon of the alkyne, and both *cis* and *trans* stereoisomers were obtained. This reaction represents a useful method to achieve formylation and aldehyde protection in a single step.

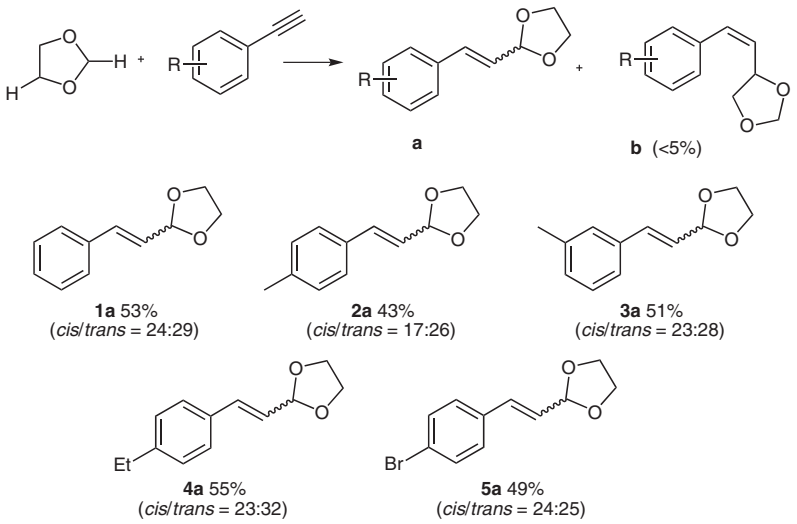
The exact mechanism of this addition reaction is not clear at present. Since peroxides are the most common source of spontaneously induced free radicals and transition metals such as copper(I) usually promote the generation of such free radicals, it was assumed, initially, that a free-radical process might be involved in this addition reaction. We therefore envisaged that the addition of a free-radical scavenger would suppress the hydroalkylation reaction. To our surprise, the reaction was virtually unaffected by the addition of one equivalent of the free-radical scavenger, 2,6-di-*tert*-butyl-4-methylphenol (BHT). This result highlights the unique activity of the copper catalyst in mediating this reaction. A similar phenomenon was also observed by Li and Zhao using the copper(I) bromide/*tert*-butyl hydroperoxide catalytic system,[6c] thus indicating that a radical pathway is unlikely. On the other hand, *tert*-butyl hydroperoxide is crucial to the success of the reaction. Copper(I) bromide alone did not catalyze this reaction under the same conditions, however, *tert*-butyl hydroperoxide without the copper catalyst gave the desired products, albeit in lower yields (Table 2, entries 1–11). Interestingly, the reaction with *tert*-butyl hydroperoxide alone was almost completely suppressed by the addition of 2,6-di-*tert*-butyl-4-methylphenol implicating the possible involvement of free radical intermediates in the absence of metals.[12] Hence it appears that reactions with and without metal catalysts proceed via different path-

Table 2 Scope of the Addition Reaction[a]



Entry	Alkyne	Product	Yield (%)[b] (*cis*/*trans*)[c]	Yield (%)[d] (*cis*/*trans*)[c]
1			51 (60:40)	62 (60:40)
2			36 (58:42)	61 (58:42)
3			33 (59:41)	65 (59:41)
4			49 (59:41)	68 (59:41)
5			59 (59:41)	64 (59:41)
6			33 (61:39)	57 (59:41)
7			40 (54:46)	50 (54:46)
8			43 (73:27)	61 (73:27)
9			35 (55:45)	63 (56:44)
10			22 (0:100)	26 (0:100)
11[e]			trace	30 (60:40)

[a] Alkyne (51 mg, 0.5 mmol), CuBr (7 mg, 0.05 mmol), TBHP (0.10 mL, 5–6 M in decane), THF (10 mL), 50 °C (oil-bath temp), 12 h.
[b] Yield of isolated product in the absence of CuBr.
[c] *cis*/*trans* Ratios were determined by ^{1}H NMR spectroscopy. The stereoisomers were isolated by silica gel column chromatography.
[d] Yield of isolated product in the presence of CuBr.
[e] Tetrahydrothiophone was used as the substrate.



Scheme 1 Reaction of 1,3-dioxolane with various alkynes and the structures of the major products obtained. *Reagents and conditions*: alkyne (51 mg, 0.5 mmol), CuBr (7 mg, 0.05 mmol), TBHP (0.10 mL, 5–6 M in decane), 1,3-dioxolane (10 mL), 50 °C, 12 h. *E*:*Z* ratio in parentheses as determined by ^{1}H NMR spectroscopy.

ways. Furthermore, the use of copper(I) bromide (10 mol%) and 2,6-di-*tert*-butyl-4-methylphenol (1 equiv) led to the formation of the desired adducts in ca. 8% isolated yields, thus revealing that *tert*-butyl hydroperoxide was not absolutely essential for the copper-catalyzed reaction. The metal-free reaction conditions are a highly desirable advantage, however, the efficiency remains to be improved.

In conclusion, a promising protocol for the addition of sp^3 C–H bonds to alkynes has been established under mild conditions in the presence, or absence, of metal catalysts. The C–H bond adjacent to an oxygen atom in an alkyl group is selectively cleaved to give the corresponding alkyne adduct. The use of *tert*-butyl hydroperoxide as an additive is crucial to the success of this coupling reaction. Further studies on the mechanism and scope of this process are currently in progress.

All reactions were carried out under a nitrogen atmosphere in oven-dried flasks. THF was distilled over Na using benzophenone as the indicator. Reagents and substrates were purchased from commercial sources and were used without additional purification. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz or 500 MHz and 100 MHz or 125 MHz, respectively, using Bruker Avance DMX 400 and DMX 500 spectrometers, respectively, and TMS as the internal standard. The NMR solvent is specified in each case. High resolution EI mass spectra were measured with a Micromass GCT-MS spectrometer. Column chromatographic purification was carried out on silica gel (300–400 mesh) purchased from Yinlong Company.

Copper-catalyzed Hydroalkylation of Alkynes; General Procedure

To a mixture of alkyne (51 mg, 0.5 mmol), CuBr (7 mg, 0.05 mmol) and THF (10 mL), *tert*-butyl hydroperoxide (0.10 mL, 5–6 M in decane) was added dropwise under an N_2 atm at r.t. The resulting mixture was stirred at 50 °C for 12 h. On completion, the reaction mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. The residue was purified on a silica gel column to afford the desired product.

2-[(*Z*)-2-Phenylethenyl]tetrahydrofuran (Table 2, Entry 1)[12a]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.23 (m, 5 H), 6.59 (d, *J* = 11.6 Hz, 1 H), 5.71 (dd, *J* = 11.4, 9.0 Hz, 1 H), 4.67 (q, *J* = 7.7 Hz, 1 H), 3.96 (q, *J* = 7.3 Hz, 1 H), 3.79 (dt, *J* = 7.8, 6.4 Hz, 1 H), 2.18–2.10 (m, 1 H), 2.06–1.87 (m, 2 H), 1.74–1.67 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 132.8, 131.4, 128.8, 128.1, 127.1, 75.0, 68.0, 32.9, 26.3.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{14}O$: 174.1045; found: 174.1053.

2-[(*E*)-2-Phenylethenyl]tetrahydrofuran (Table 2, Entry 1)[12a]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7.6 Hz, 2 H), 7.31 (t, *J* = 7.4 Hz, 2 H), 7.22 (t, *J* = 7.4 Hz, 1 H), 6.58 (d, *J* = 15.6 Hz, 1 H), 6.21 (dd, *J* = 15.6, 6.8 Hz, 1 H), 4.48 (q, *J* = 7.2 Hz, 1 H), 3.98 (q, *J* = 7.2 Hz, 1 H), 3.85 (q, *J* = 7.3 Hz, 1 H), 2.17–2.10 (m, 1 H), 2.05–1.90 (m, 2 H), 1.76–1.67 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 130.4, 130.3, 128.4, 127.4, 126.3, 79.5, 68.0, 32.3, 25.8.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{14}O$: 174.1045; found: 174.1037.

2-[(*Z*)-2-(4-Methylphenyl)ethenyl]tetrahydrofuran (Table 2, Entry 2)[12a]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.4 Hz, 2 H), 6.57 (d, *J* = 11.6 Hz, 1 H), 5.67 (dd, *J* = 11.6, 8.8 Hz, 1 H), 4.68 (q, *J* = 7.6 Hz, 1 H), 3.97 (q, *J* = 7.2 Hz, 1 H), 3.79 (dt, *J* = 7.8, 6.0 Hz, 1 H), 2.35 (s, 3 H), 2.18–2.11 (m, 1 H), 2.06–1.88 (m, 2 H), 1.73–1.65 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 133.7, 132.0, 131.3, 128.7, 128.6, 75.0, 67.9, 32.8, 26.2, 21.0.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{16}O$: 188.1201; found: 188.1193.

2-[(*E*)-2-(4-Methylphenyl)ethenyl]tetrahydrofuran (Table 2, Entry 2)[12a]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 6.58 (d, *J* = 16.0 Hz, 1 H), 6.18 (dd, *J* = 16.0, 6.8 Hz, 1 H), 4.48 (q, *J* = 6.7 Hz, 1 H), 3.99 (q, *J* = 7.3 Hz, 1 H), 3.86 (dt, *J* = 8.0, 6.0 Hz, 1 H), 2.35 (s, 3 H), 2.18–2.10 (m, 1 H), 2.06–1.91 (m, 2 H), 1.77–1.69 (m, 1 H).

^{13}C NMR (100 MHz, CDC l_3): δ = 137.1, 133.9, 130.3, 129.3, 129.0, 126.2, 79.7, 68.0, 32.2, 25.8, 21.0.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{16}O$: 188.1201; found: 188.1202.

2-[(*Z*)-2-(3-Methylphenyl)ethenyl]tetrahydrofuran (Table 2, Entry 3)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (t, *J* = 8.2 Hz, 1 H), 7.15–7.09 (m, 3 H), 6.59 (d, *J* = 12.0 Hz, 1 H), 5.71 (dd, *J* = 12.0, 8.8 Hz, 1 H), 4.70 (q, *J* = 7.5 Hz, 1 H), 3.99 (q, *J* = 7.3 Hz, 1 H), 3.81 (dt, *J* = 8.0, 6.0 Hz, 1 H), 2.38 (s, 3 H), 2.22–2.12 (m, 1 H), 2.08–1.90 (m, 2 H), 1.76–1.67 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.6, 136.6, 132.7, 131.5, 129.5, 128.0, 127.8, 125.8, 75.0, 68.0, 32.9, 26.3, 21.4.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{16}O$: 188.1201; found: 188.1198.

2-[(*E*)-2-(3-Methylphenyl)ethenyl]tetrahydrofuran (Table 2, Entry 3)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.18 (m, 3 H), 7.05 (d, *J* = 7.6 Hz, 1 H), 6.56 (d, *J* = 16.0 Hz, 1 H), 6.20 (dd, *J* = 15.6, 6.8 Hz, 1 H), 4.47 (q, *J* = 6.8 Hz, 1 H), 3.98 (q, *J* = 7.5 Hz, 1 H), 3.85 (q, *J* = 7.3 Hz, 1 H), 2.34 (s, 3 H), 2.18–2.09 (m, 1 H), 2.05–1.89 (m, 2 H), 1.76–1.66 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 136.7, 130.5, 130.3, 128.3, 128.2, 127.1, 123.6, 79.7, 68.1, 32.4, 25.9, 21.3.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{16}O$: 188.1201; found: 188.1194.

2-[(*Z*)-2-(4-Ethylphenyl)ethenyl]tetrahydrofuran (Table 2, Entry 4)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.0 Hz, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 6.59 (d, *J* = 12.0 Hz, 1 H), 5.69 (dd, *J* = 11.0, 8.5 Hz, 1 H), 4.71 (q, *J* = 7.7 Hz, 1 H), 3.98 (q, *J* = 7.3 Hz, 1 H), 3.81 (dt, *J* = 8.0, 6.0 Hz, 1 H), 2.67 (q, *J* = 7.8 Hz, 2 H), 2.19–2.13 (m, 1 H), 2.07–1.90 (m, 2 H), 1.74–1.67 (m, 1 H), 1.26 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.5, 134.3, 132.4, 131.7, 129.1, 127.9, 75.4, 68.2, 33.1, 28.8, 26.6, 15.7.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{18}O$: 202.1358; found: 202.1353.

2-[(*E*)-2-(4-Ethylphenyl)ethenyl]tetrahydrofuran (Table 2, Entry 4)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 6.57 (d, *J* = 15.5 Hz, 1 H), 6.17 (dd, *J* = 15.5, 6.5 Hz, 1 H), 4.47 (q, *J* = 7.0 Hz, 1 H), 3.98 (q, *J* = 7.5 Hz, 1 H), 3.85 (dt, *J* = 8.0, 6.0 Hz, 1 H), 2.64 (q, *J* = 7.7 Hz, 2 H), 2.16–2.10 (m, 1 H), 2.04–1.91 (m, 2 H), 1.75–1.68 (m, 1 H), 1.24 (t, *J* = 7.8 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.9, 134.6, 130.7, 129.8, 128.2, 126.7, 80.0, 68.4, 32.7, 28.8, 26.1, 15.8.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{18}O$: 202.1358; found: 202.1355.

2-[(*Z*)-2-(4-*tert*-Butylphenyl)ethenyl]tetrahydrofuran (Table 2, Entry 5)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 6.59 (d, *J* = 11.2 Hz, 1 H), 5.69 (dd, *J* = 12.0, 8.8 Hz, 1 H), 4.72 (q, *J* = 8.0 Hz, 1 H), 3.99 (q, *J* = 7.3 Hz, 1 H), 3.81 (dt, *J* = 8.0, 6.0 Hz, 1 H), 2.21–2.13 (m, 1 H), 2.08–1.90 (m, 2 H), 1.76–1.67 (m, 1 H), 1.35 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 133.8, 132.3, 131.3, 128.6, 125.1, 75.1, 68.0, 34.5, 32.9, 31.3, 26.4.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{22}O$: 230.1671; found: 230.1667.

2-[(*E*)-2-(4-*tert*-Butylphenyl)ethenyl]tetrahydrofuran (Table 2, Entry 5)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (s, 4 H), 6.58 (d, *J* = 16.0 Hz, 1 H), 6.18 (dd, *J* = 16.0, 6.8 Hz, 1 H), 4.48 (q, *J* = 6.8 Hz, 1 H), 3.98 (q, *J* = 7.5 Hz, 1 H), 3.85 (q, *J* = 7.3 Hz, 1 H), 2.17–2.09 (m, 1 H), 2.04–1.92 (m, 2 H), 1.76–1.69 (m, 1 H), 1.32 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5, 134.1, 130.2, 129.7, 126.1, 125.4, 79.7, 68.1, 34.5, 32.4, 31.3, 25.9.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{22}O$: 230.1671; found: 230.1667.

2-[(*Z*)-2-(4-Methoxyphenyl)ethenyl]tetrahydrofuran (Table 2, Entry 6)[12a]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8.8 Hz, 2 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 6.55 (d, *J* = 11.2 Hz, 1 H), 5.64 (dd, *J* = 11.6, 8.8 Hz, 1 H), 4.68 (q, *J* = 7.7 Hz, 1 H), 3.98 (q, *J* = 7.3 Hz, 1 H), 3.83–3.78 (m, 4 H), 2.20–2.12 (m, 1 H), 2.08–1.89 (m, 2 H), 1.74–1.65 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 131.2, 131.0, 130.0, 129.2, 113.5, 75.0, 67.9, 55.1, 32.8, 26.3.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1144.

2-[(*E*)-2-(4-Methoxyphenyl)ethenyl]tetrahydrofuran (Table 2, Entry 6)[12a]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.8 Hz, 2 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 6.55 (d, *J* = 15.2 Hz, 1 H), 6.09 (dd, *J* = 16.0, 7.2 Hz, 1 H), 4.46 (q, *J* = 6.8 Hz, 1 H), 3.98 (q, *J* = 7.5 Hz, 1 H), 3.87–3.82 (m, 4 H), 2.17–2.10 (m, 1 H), 2.06–1.90 (m, 2 H), 1.76–1.68 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 130.2, 129.5, 128.1, 127.5, 113.8, 79.8, 68.0, 55.1, 32.3, 25.8.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1144.

2-[(*Z*)-2-(4-Pentyloxyphenyl)ethenyl]tetrahydrofuran (Table 2, Entry 7)

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.21 (d, *J* = 8.4 Hz, 2 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 6.44 (d, *J* = 11.6 Hz, 1 H), 5.54 (dd, *J* = 11.6, 8.8 Hz, 1 H), 4.52 (q, *J* = 7.6 Hz, 1 H), 3.93 (t, *J* = 6.6 Hz, 2 H), 3.80 (q, *J* = 7.2 Hz, 1 H), 3.63 (dt, *J* = 8.0, 6.4 Hz, 1 H), 2.15–2.07 (m, 1 H), 1.96–1.80 (m, 2 H), 1.69 (quin, *J* = 6.8 Hz, 2 H), 1.61–1.52 (m, 1 H), 1.40–1.27 (m, 4 H), 0.87 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.3, 131.8, 130.5, 130.3, 128.9, 114.6, 74.9, 67.7, 67.5, 32.8, 28.7, 28.1, 26.2, 22.3, 14.3.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{24}O_2$: 260.1776; found: 260.1769.

2-[(*E*)-2-(4-Pentyloxyphenyl)ethenyl]tetrahydrofuran (Table 2, Entry 7)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.4 Hz, 2 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 6.53 (d, *J* = 15.6 Hz, 1 H), 6.07 (dd, *J* = 15.6, 6.4 Hz, 1 H), 4.45 (q, *J* = 7.1 Hz, 1 H), 4.00–3.93 (m, 3 H), 3.84 (dt, *J* = 8.0, 6.4 Hz, 1 H), 2.16–2.08 (m, 1 H), 2.05–1.89 (m, 2 H), 1.79 (quin, *J* = 7.0 Hz, 2 H), 1.73–1.66 (m, 1 H), 1.48–1.34 (m, 4 H), 0.94 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.7, 130.2, 129.4, 128.0, 127.6, 114.4, 79.9, 68.0, 67.9, 32.4, 28.9, 28.2, 26.0, 22.5, 14.0.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{17}H_{24}O_2$: 260.1776; found: 260.1769.

2-[(*Z*)-2-(4-Bromophenyl)ethenyl]tetrahydrofuran (Table 2, Entry 8)[12a]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.5 Hz, 2 H), 7.17 (d, *J* = 8.5 Hz, 2 H), 6.51 (d, *J* = 11.5 Hz, 1 H), 5.73 (dd, *J* = 11.5, 8.5 Hz, 1 H), 4.59 (q, *J* = 7.7 Hz, 1 H), 3.95 (q, *J* = 7.3 Hz, 1 H), 3.78 (dt, *J* = 8.0, 6.5 Hz, 1 H), 2.15–2.09 (m, 1 H), 2.05–1.89 (m, 2 H), 1.71–1.64 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.0, 133.1, 130.8, 129.9, 120.7, 74.3, 67.6, 32.4, 25.9.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{13}BrO$: 252.0150; found: 252.0144.

2-[(*E*)-2-(4-Bromophenyl)ethenyl]tetrahydrofuran (Table 2, Entry 8)[12a]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.8 Hz, 2 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 6.52 (d, *J* = 16.0 Hz, 1 H), 6.20 (dd, *J* = 16.0, 6.4 Hz, 1 H), 4.45 (q, *J* = 6.8 Hz, 1 H), 3.96 (q, *J* = 7.3 Hz, 1 H), 3.84 (q, *J* = 7.3 Hz, 1 H), 2.17–2.09 (m, 1 H), 2.04–1.90 (m, 2 H), 1.74–1.65 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.3, 131.1, 130.9, 128.7, 127.5, 120.7, 79.0, 67.7, 31.8, 25.4.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{13}BrO$: 252.0150; found: 252.0144.

2-[(*Z*)-2-(4-Fluorophenyl)ethenyl]tetrahydrofuran (Table 2, Entry 9)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (dd, *J* = 8.4, 5.6 Hz, 2 H), 6.99 (t, *J* = 8.4 Hz, 2 H), 6.51 (d, *J* = 11.6 Hz, 1 H), 5.66 (dd, *J* = 11.6, 8.8 Hz, 1 H), 4.57 (q, *J* = 7.6 Hz, 1 H), 3.93 (q, *J* = 7.3 Hz, 1 H), 3.76 (dt, *J* = 8.0, 6.0 Hz, 1 H), 2.13–2.06 (m, 1 H), 2.03–1.85 (m, 2 H), 1.70–1.61 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8 (d, *J* = 244.9 Hz, 1 C), 132.5 (d, *J* = 4.3 Hz, 1 C), 130.4, 130.3, 130.2, 114.9 (d, *J* = 20.5 Hz, 1 C), 74.7, 67.9, 32.7, 26.2.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{13}FO$: 192.0950; found: 192.0945.

2-[(*E*)-2-(4-Fluorophenyl)ethenyl]tetrahydrofuran (Table 2, Entry 9)[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (dd, *J* = 8.4, 5.6 Hz, 2 H), 6.96 (t, *J* = 8.6 Hz, 2 H), 6.51 (d, *J* = 16.0 Hz, 1 H), 6.09 (dd, *J* = 16.0, 6.4 Hz, 1 H), 4.42 (q, *J* = 6.8 Hz, 1 H), 3.93 (q, *J* = 7.3 Hz, 1 H), 3.80 (q, *J* = 7.3 Hz, 1 H), 2.13–2.05 (m, 1 H), 2.01–1.86 (m, 2 H), 1.71–1.63 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1 (d, *J* = 245.5 Hz, 1 C), 132.8 (d, *J* = 3.4 Hz, 1 C), 130.1 (d, *J* = 1.9 Hz, 1 C), 129.1, 127.8 (d, *J* = 7.6 Hz, 1 C), 115.2 (d, *J* = 21.6 Hz, 1 C), 79.4, 68.0, 32.2, 25.7.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{13}FO$: 192.0950; found: 192.0942.

2-[(*E*)-2-(Tetrahydrofuran-2-yl)ethenyl)pyridine (Table 2, Entry 10)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 4.8 Hz, 1 H), 7.62 (dt, *J* = 7.6, 2.0 Hz, 1 H), 7.28 (d, *J* = 7.6 Hz, 1 H), 7.12 (dd, *J* = 7.6, 5.6 Hz, 1 H), 6.74 (dd, *J* = 15.2, 5.6 Hz, 1 H), 6.67 (d, *J* = 15.6 Hz, 1 H), 4.57 (q, *J* = 6.4 Hz, 1 H), 3.98 (q, *J* = 7.2 Hz, 1 H), 3.86 (q, *J* = 7.3 Hz, 1 H), 2.19–2.11 (m, 1 H), 2.04–1.89 (m, 2 H), 1.81–1.73 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 149.3, 136.5, 135.3, 129.3, 122.0, 121.7, 78.9, 68.2, 32.1, 25.7.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{11}H_{13}NO$: 175.0997; found: 175.0999.

2-[(*Z*)-2-Phenylethenyl]tetrahydrothiophene (Table 2, Entry 11)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.23 (m, 5 H), 6.44 (d, *J* = 11.2 Hz, 1 H), 5.68 (t, *J* = 10.8 Hz, 1 H), 4.38 (dt, *J* = 8.8, 6.0 Hz, 1 H), 3.07–3.01 (m, 1 H), 2.96–2.90 (m, 1 H), 2.25–2.15 (m, 2 H), 1.96–1.85 (m, 1 H), 1.73–1.64 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 133.5, 129.2, 128.7, 128.2, 126.9, 45.8, 38.7, 33.3, 31.1.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{14}S$: 190.0816; found: 190.0811.

2-[(*E*)-2-Phenylethenyl]tetrahydrothiophene (Table 2, Entry 11)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 7.6 Hz, 2 H), 7.30 (t, *J* = 7.4 Hz, 2 H), 7.21 (t, *J* = 7.4 Hz, 1 H), 6.46 (d, *J* = 16.0 Hz, 1 H), 6.17 (dd, *J* = 15.6, 8.8 Hz, 1 H), 4.12 (dt, *J* = 8.2, 6.0 Hz, 1 H), 3.05–2.99 (m, 1 H), 2.95–2.90 (m, 1 H), 2.26–2.15 (m, 2 H), 2.03–1.92 (m, 1 H), 1.82–1.74 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.8, 131.6, 129.7, 128.4, 127.3, 126.2, 51.2, 38.2, 33.2, 30.9.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{14}S$: 190.0816; found: 190.0811.

2-[(*Z*)-2-Phenylethenyl]-1,3-dioxolane [(*Z*)-1a][14]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.30 (m, 5 H), 6.84 (d, *J* = 11.2 Hz, 1 H), 5.73 (dd, *J* = 12.0, 7.2 Hz, 1 H), 5.54 (d, *J* = 7.2 Hz, 1 H), 4.09 (t, *J* = 6.8 Hz, 2 H), 3.94 (t, *J* = 6.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.2, 128.5, 127.7, 127.3, 127.1, 126.1, 99.2, 64.7.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{11}H_{12}O_2$: 176.0837; found: 176.0835.

2-[(*E*)-2-Phenylethenyl]-1,3-dioxolane [(*E*)-1a][14]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 7.2 Hz, 2 H), 7.29 (t, *J* = 7.2 Hz, 1 H), 6.79 (d, *J* = 16.0 Hz, 1 H), 6.18 (dd, *J* = 16.0, 5.6 Hz, 1 H), 5.45 (d, *J* = 6.0 Hz, 1 H), 4.08 (t, *J* = 7.0 Hz, 2 H), 3.97 (t, *J* = 6.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.3, 134.4, 128.1, 127.9, 126.4, 124.6, 103.4, 64.6.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{11}H_{12}O_2$: 176.0837; found: 176.0835.

2-[(*Z*)-2-(4-Methylphenyl)ethenyl]-1,3-dioxolane [(*Z*)-2a][14]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.0 Hz, 2 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 6.80 (d, *J* = 11.6 Hz, 1 H), 5.69 (dd, *J* = 11.6, 7.6 Hz, 1 H), 5.55 (d, *J* = 7.2 Hz, 1 H), 4.08 (t, *J* = 6.8 Hz, 2 H), 3.98 (t, *J* = 6.8 Hz, 2 H), 2.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 135.5, 132.7, 128.8, 126.7, 125.0, 99.6, 65.0, 21.1.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{14}O_2$: 190.0994; found: 190.0989.

2-[(*E*)-2-(4-Methylphenyl)ethenyl]-1,3-dioxolane [(*E*)-2a][14]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.4 Hz, 2 H), 7.14 (d, *J* = 7.6 Hz, 2 H), 6.76 (d, *J* = 16.4 Hz, 1 H), 6.13 (dd, *J* = 16.0, 6.0 Hz, 1 H), 5.43 (d, *J* = 6.4 Hz, 1 H), 4.07 (t, *J* = 6.4 Hz, 2 H), 3.96 (t, *J* = 6.4 Hz, 2 H), 2.35 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 134.8, 132.8, 129.1, 126.7, 123.8, 103.9, 64.9, 21.1.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_{14}O_2$: 190.0994; found: 190.0989.

2-[(*Z*)-2-(3-Methylphenyl)ethenyl]-1,3-dioxolane [(*Z*)-3a]
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.17 (m, 3 H), 7.11 (d, *J* = 7.2 Hz, 1 H), 6.80 (d, *J* = 11.6 Hz, 1 H), 5.70 (dd, *J* = 11.6, 7.2 Hz, 1 H), 5.53 (d, *J* = 7.6 Hz, 1 H), 4.07 (t, *J* = 6.8 Hz, 2 H), 3.92 (t, *J* = 6.8 Hz, 2 H), 2.36 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 135.6, 134.8, 129.0, 128.3, 127.5, 124.7, 123.9, 103.8, 64.9, 21.2.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_{14}O_2$: 190.0994; found: 190.0988.

2-[(*E*)-2-(3-Methylphenyl)ethenyl]-1,3-dioxolane [(*E*)-3a]
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.23 (m, 4 H), 6.76 (d, *J* = 16.0 Hz, 1 H), 6.17 (dd, *J* = 16.0, 6.0 Hz, 1 H), 5.45 (d, *J* = 6.0 Hz, 1 H), 4.08 (t, *J* = 6.8 Hz, 2 H), 3.97 (t, *J* = 6.8 Hz, 2 H), 2.36 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7, 135.7, 135.5, 129.5, 128.4, 128.0, 127.3, 125.9, 99.6, 65.0, 21.3.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_{14}O_2$: 190.0994; found: 190.0988.

2-[(*Z*)-2-(4-Ethylphenyl)ethenyl]-1,3-dioxolane [(*Z*)-4a]
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 6.82 (d, *J* = 11.6 Hz, 1 H), 5.70 (dd, *J* = 11.6, 7.2 Hz, 1 H), 5.56 (d, *J* = 7.6 Hz, 1 H), 4.09 (t, *J* = 6.8 Hz, 2 H), 3.94 (t, *J* = 7.2 Hz, 2 H), 2.68 (q, *J* = 7.6 Hz, 2 H), 1.26 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 134.8, 133.1, 127.9, 126.8, 123.9, 103.9, 64.9, 28.5, 15.3.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1148.

2-[(*E*)-2-(4-Ethylphenyl)ethenyl]-1,3-dioxolane [(*E*)-4a]
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 6.75 (d, *J* = 15.6 Hz, 1 H), 6.12 (dd, *J* = 16.0, 6.0 Hz, 1 H), 5.42 (d, *J* = 6.4 Hz, 1 H), 4.06 (t, *J* = 6.8 Hz, 2 H), 3.95 (t, *J* = 6.8 Hz, 2 H), 2.64 (q, *J* = 7.2 Hz, 2 H), 1.23 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 135.5, 133.0, 128.9, 127.6, 126.7, 99.7, 65.0, 28.5, 15.3.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1148.

2-[(*Z*)-2-(4-Bromophenyl)ethenyl]-1,3-dioxolane [(*Z*)-5a]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.4 Hz, 2 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 6.73 (d, *J* = 12.0 Hz, 1 H), 5.75 (dd, *J* = 11.6, 7.2 Hz, 1 H), 5.45 (d, *J* = 7.2 Hz, 1 H), 4.07 (t, *J* = 7.2 Hz, 2 H), 3.92 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.1, 133.9, 130.9, 130.1, 128.0, 121.5, 99.0, 64.7.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{11}H_{11}BrO_2$: 253.9942; found: 253.9944.

2-[(*E*)-2-(4-Bromophenyl)ethenyl]-1,3-dioxolane [(*E*)-5a][15]
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 7.6 Hz, 2 H), 6.75 (d, *J* = 15.6 Hz, 1 H), 6.12 (dd, *J* = 16.0, 6.4 Hz, 1 H), 5.42 (d, *J* = 6.0 Hz, 1 H), 4.07 (t, *J* = 6.8 Hz, 2 H), 3.95 (t, *J* = 6.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 134.5, 134.4, 131.3, 130.5, 128.4, 121.9, 99.4, 65.2.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{11}H_{11}BrO_2$: 253.9942; found: 253.9944.

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