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New light on an old reaction: phase-transfer-catalyzed intramolecular cyclization of propargyl compounds for synthesis of indene derivatives and disubstituted benzo[*b*]furans

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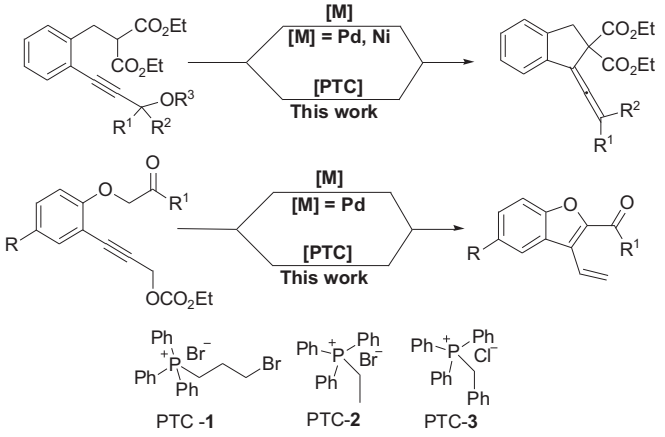
ABSTRACT

A variety of indene derivatives and disubstituted benzo[*b*]furans are readily prepared under the mild reaction condition from propargylic compounds by phase-transfer catalysis (PTC) instead of metal catalysis.

1. Introduction

Allenes, an important class of unsaturated hydrocarbons, have received considerable attention in recent years.[1–3,12] As a result, a number of routes leading to differently substituted allenes have been described in the literature.[4–12] Among our efforts in the area of allene chemistry,[13–15] we have demonstrated an efficient synthetic route to allenyl indene derivatives via the Palladium or Nickel-catalyzed reaction of propargylic carbonates with carbon nucleophiles (Scheme 1). Compared with metal-catalyzed methods, phase-transfer catalysis has long been recognized as a versatile methodology for organic synthesis in both industrial and academic laboratories, featuring its simple reaction procedure, safe, inexpensive, environmentally friendly reagents, absence of anhydrous solvents, ease of scale-up, and metal-free conditions.[16] Recently, we have reported the addition of carbon nucleophiles to alkynes by phase-transfer catalysis.[17] In this test, we report a new mild synthesis of allenyl indene derivatives and disubstituted benzo[*b*]furans by PTC. To the best of our knowledge, this is the first report about the synthesis of allenyl indene derivatives under metal-free condition.



Scheme 1. Transition metal-catalyzed or phase-transfer-catalyzed intramolecular cyclization of propargylic compounds.

2. Results and discussion

Initially, we focused on the reaction of 0.20 mmol of 3-(2-(2,2-di(ethoxycarbonyl)ethyl)phenyl)prop-2-ynyl methyl carbonate (**1a**), 5 mol % of PTC-1, and 2 equiv of K_2CO_3 in DMF at 60 °C in air. To our delight, the desired product **2a** was formed in 66% yield with high regioselectivity after 1.2 h (Table 1, entry 1). Encouraged by this result, we further optimized the reaction conditions. Other common

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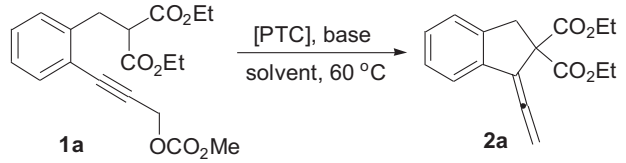
Table 1
Optimization of the phase-transfer-catalyzed intramolecular cyclization of **1a**[a]



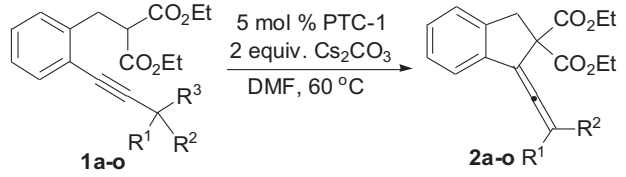
Entry	[PTC]	Base	Solvent	Time (h)	Yield (%)
1	PTC-1	K_2CO_3	DMF	1.2	70
2	PTC-1	Na_2CO_3	DMF	1.5	73
3	PTC-1	Cs_2CO_3	DMF	0.8	93
4	PTC-1	Cs_2CO_3	CH_3CN	0.8	92
5	PTC-1	Cs_2CO_3	THF	5.5	58
6	PTC-2	Cs_2CO_3	DMF	0.8	87
7	PTC-3	Cs_2CO_3	DMF	0.8	84
8	TBAB	Cs_2CO_3	DMF	1	86
9	TBAC	Cs_2CO_3	DMF	1	87
10	TEAI	Cs_2CO_3	DMF	1	90
11	TEAI	Cs_2CO_3	DMF	1	80

[a] Reactions were carried out on a 0.2 mmol scale in 2.0 mL of solvent in air at 60 °C with 1.0 equiv of **1a**, 2.0 equiv of base, and 5 mol % equiv of PTC.

bases, such as Na_2CO_3, Cs_2CO_3 were also tested; Cs_2CO_3 gave the better yield of 93% (entries 2 and 3). The effect of the solvent was also investigated. Changing the solvent to THF, CH_3CN failed to improve the yield of the product **2a** (entries 4 and 5). When different PTCs were examined, the results showed that PTC-2 and PTC-3 could also promote this cyclization, but the desired product **2a** was only obtained with 87% and 84% yield, respectively (entries 6 and 7). Tetraalkyl ammonium salts, such as Et_4NI, Bu_4NBr, Bu_4NCl, and Bu_4NF have also been applied to this process, and the yields were not better than PTC-1 (entries 8–11). Thus, we chose the following reaction conditions as optimum for all subsequent cyclization: 0.20 mmol of **1a**, 5 mol % PTC-1, and 0.40 mmol Cs_2CO_3 in DMF at 60 °C in air.

With the optimized conditions in hand, the breadth and scope of this reaction was then investigated, and the results are summarized in Table 2. The reactions of different substituted primary propargylic compounds were investigated first. All of the propargylic substrates, such as propargylic carbonates, acetate, benzoate, and phosphate gave the desired products in excellent yields (Table 2, entries 1–5), while the propargylic bromide gave the poor yield (entry 6). This indicated that the activity of the reaction has a great dependence on the leaving group. Next the reaction of substituted secondary and tertiary propargyl substrates were investigated. Secondary carbonates possessing various substituents (aryl- substituted and heterocyclic-) at the propargylic position also worked well, and afforded the corresponding products in moderate yields (entries 7–13). Functional groups, such as methyl, methoxyl, chloro, bromo were well tolerated in the reaction. The secondary carbonate, having methyl substituent, produced high yield of the indene derivative (entry 14). Meanwhile, the reaction of tertiary propargylic acetate has also been studied in our system and the expected product has been obtained although the result was not very good (entry 15).

Table 2
Synthesis of allenyl indene derivatives catalyzed by PTC-1[a]

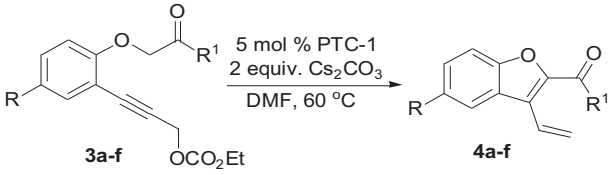


Entry	Substrate **1**	Product **2**	Time (h)	Yield[b] (%)
1	R^1=R^2=H, R^3=OCO_2CH_3 **1a**	**2a**	0.8	93
2	R^1=R^2=H, R^3=OCO_2Et **1b**	**2a**	0.8	90
3	R^1=R^2=H, R^3=OAc **1c**	**2a**	0.8	80
4	R^1=R^2=H, R^3=OCOPh **1d**	**2a**	0.8	93
5	R^1=R^2=H, R^3=$PO(OEt)_2$ **1e**	**2a**	0.8	83
6	R^1=R^2=H, R^3=Br **1f**	**2a**	1.2	38
7	R^1=H, R^2=Ph, R^3=OCO_2Et **1g**	**2g**	1	70
8	R^1=H, R^2=*p*-$CH_3C_6H_4$, R^3=OCO_2Et **1h**	**2h**	1	72
9	R^1=H, R^2=*p*-ClC_6H_4, R^3=OCO_2Et **1i**	**2i**	1.5	65
10	R^1=H, R^2=*p*-BrC_6H_4, R^3=OCO_2Et **1j**	**2j**	2	60
11	R^1=H, R^2=*m*-$CH_3C_6H_4$, R^3=OCO_2Et **1k**	**2k**	2	62
12	R^1=H, R^2=*o*-$OCH_3C_6H_4$, R^3=OCO_2Et **1l**	**2l**	2	65
13	R^1=H, R^2=2-furyl, R^3=OCO_2Et **1m**	**2m**	2	60
14	R^1=H, R^2=CH_3, R^3=OCO_2Et **1n**	**2n**	1.5	93
15	R^1=R^2=Ph, R^3=OAc **1o**	**2o**	5	46

[a] Reactions were carried out on a 0.2 mmol scale in 2.0 mL of DMF in air at 60 °C with 1.0 equiv of **1**, 2.0 equiv of Cs_2CO_3, and 5 mol % equiv of PTC-**1**.
[b] Isolated yields.

Very recently, we have reported a convenient approach to the synthesis of a variety of 2-aroyl(acyl, or carboxyl)-3-vinyl benzo[*b*]furans via Pd/C-catalyzed carboannulation of propargylic compounds. We expected to investigate these substrates using our PTC instead of the palladium. Fortunately, the cyclization/isomerization products were obtained and the yields were comparable with the latter under the optimized conditions (Table 3, entries 1–7). It is noteworthy that Cs_2CO_3 alone did not cyclize the reaction, only the combination of base and PTC could take place.

Table 3
Synthesis of 2-aroyl-3-vinyl benzo[*b*]furans catalyzed by PTC-1[a]



Entry	Substrate **3**	Product **4**	Time (h)	Yield[b] (%)
1	R=H, R^1=Ph, **3a**	**4a**	1	82
2	R=CH_3, R^1=Ph, **3b**	**4b**	1	84
3	R=*t*-Bu, R^1=Ph, **3c**	**4c**	1	86
4	R=Cl, R^1=Ph, **3d**	**4d**	1	80
5	R=H, R^1=CH_3, **3e**	**4e**	3	94
6	R=*t*-Bu, R^1=CH_3, **3f**	**4f**	3	90
7	R=Cl, R^1=OEt, **3g**	**4g**	6	60

[a] Reactions were carried out on a 0.2 mmol scale in 2.0 mL of DMF in air at 60 °C with 1.0 equiv of **3**, 2.0 equiv of Cs_2CO_3, and 5 mol % equiv of PTC-**1**.
[b] Isolated yields.

3. Conclusion

In conclusion, we have demonstrated for the first time that phase-transfer-catalyzed cyclization of propargylic compounds is a novel and efficient method for synthesis of allenyl indene derivatives and disubstituted benzo[*b*]furans. These reactions are run under mild conditions, tolerate various functional groups, and generally provide the desired products in moderated to good yields. Compared to the expensive transitionmetal-catalyzed reaction, the process showed considerable synthetic advantages in terms of mild reaction condition, environmentally friendly, and low cost. The scope, mechanism, and synthetic applications of this reaction are currently under investigation.

4. Experimental

4.1. General methods

All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel GF254 plates. The silica gel

(200–300 mesh) is used for column chromatography, and the distillation range of petroleum is 60–90 °C. ^{1}H and ^{13}C NMR spectra were recorded on the Varian Mercury-300 MHz or Varian Mercury-400 MHz instruments, using $CDCl_3$ as a solvent. IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in cm^{-1}. All new compounds were further characterized by element analysis; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Commercially available reagents and solvents were used without further purification.

4.2. Typical procedure for the preparation of 2

To a solution of **1** (0.20 mmol) in 2.0 mL of DMF was added Cs_2CO_3 (130.3 mg, 0.40 mmol) in the reaction vessel. The mixture was allowed to stir at room temperature for 1 min and PTC (3.15 mg, 5 mol %) was added. The vessel was sealed and the resulting mixture was then heated at 60 °C. When the reaction was considered complete as determined by TLC analysis, the reaction was allowed to cool to room temperature and quenched with a saturated aqueous solution of ammonium chloride, and the mixture was extracted with EtOAc. The combined organic extracts were washed with water and saturated brine. The organic layers were dried over Na_2SO_4, filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford **2**.

*4.2.1. Diethyl 1-vinylidene-1H-indene-2,2(3H)-dicarboxylate (**2a**).* Oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.18 (m, 4H), 5.38 (s, 2H), 4.27–4.19 (q, J=6.9 Hz, 4H), 3.70 (s, 2H), 1.28–1.24 (t, J=7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 169.9, 139.4, 136.5, 128.0, 127.4, 124.5, 122.4, 82.5, 62.3, 61.9, 39.6, 14.0; IR (neat, cm^{-1}) 1736, 1245, 1178, 1057, 862, 765. Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.48; H, 6.62.

*4.2.2. Diethyl 1-(2-phenylvinylidene)-1H-indene-2,2(3H)-dicarboxylate (**2g**).* Oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.23 (m, 9H), 6.84 (s, 1H), 4.33–4.05 (m, 4H), 3.90–3.75 (q, J=17.1 Hz, 2H), 1.32–1.27 (t, J=7.2 Hz, 3H), 1.13–1.09 (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.2, 169.8, 169.8, 140.1, 136.3, 133.3, 128.6, 128.4, 127.5, 127.4, 127.4, 124.7, 122.6, 111.3, 101.9, 62.8, 62.2, 61.9, 39.7, 14.1, 13.7; IR (neat, cm^{-1}) 1734, 1247, 1183, 1057, 764, 694. Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.41; H, 6.26.

*4.2.3. Diethyl 1-(2-p-tolylvinylidene)-1H-indene-2,2(3H)-dicarboxylate (**2h**).* Oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.18 (m, 6H), 7.11–7.09 (d, J=7.5 Hz, 2H), 6.76 (s, 1H), 4.28–4.03 (m, 4H), 3.86–3.71 (q, J=17.1 Hz, 2H), 2.32 (s, 3H), 1.26–1.20 (m, 3H), 1.12–1.06 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.8, 170.0, 170.0, 140.0, 137.4, 136.5, 130.3, 129.3, 128.2, 127.4, 127.3, 124.7, 122.6, 111.2, 101.6, 62.8, 62.1, 61.8, 39.6, 21.2, 14.1, 13.8; IR (neat, cm^{-1}) 1736, 1248, 1183, 1059, 852, 758. Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43. Found: C, 76.39; H, 6.36.

*4.2.4. Diethyl 1-(2-(4-chlorophenyl)vinylidene)-1H-indene-2,2(3H)-dicarboxylate (**2i**).* Oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.18 (m, 8H), 6.75 (s, 1H), 4.29–4.04 (m, 4H), 3.78 (s, 2H), 1.27–1.21 (m, 3H), 1.14–1.09 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.5, 169.9, 169.8, 140.2, 136.1, 133.1, 132.1, 128.8, 128.7, 128.6, 127.5, 124.8, 122.7, 111.7, 100.9, 62.8, 62.1, 62.0, 39.7, 14.2, 13.9; IR (neat, cm^{-1}) 1731, 1248, 1176, 1089, 1054, 853, 758. Anal. Calcd for $C_{23}H_{21}ClO_4$: C, 69.61; H, 5.33. Found: C, 69.76; H, 5.27.

*4.2.5. Diethyl 1-(2-(4-bromophenyl)vinylidene)-1H-indene-2,2(3H)-dicarboxylate (**2j**).* Solid: mp 99–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.43 (d, J=8.4 Hz, 2H), 7.32–7.20 (m, 6H), 6.75 (s, 1H), 4.28–4.04 (m, 4H), 3.79 (m, 2H), 1.28–1.24 (t, J=7.2 Hz, 3H), 1.14–1.09 (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.4, 169.8, 169.7, 140.2, 135.9, 132.6, 131.7, 128.9, 128.8, 127.5, 124.8, 122.7, 121.3, 111.7, 101.1, 62.8, 62.2, 62.0, 39.7, 14.2, 13.9; IR (KBr, cm^{-1}) 1735, 1247, 1176, 1054, 1006, 852, 757. Anal. Calcd for $C_{23}H_{21}BrO_4$: C, 62.60; H, 4.80. Found: C, 62.68; H, 4.96.

*4.2.6. Diethyl 1-(2-m-tolylvinylidene)-1H-indene-2,2(3H)-dicarboxylate (**2k**).* Oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.09 (m, 7H), 6.95–6.94 (m, 1H), 6.68 (s, 1H), 4.17–3.94 (m, 4H), 3.78–3.61 (q, J=17.1 Hz, 2H), 2.22 (s, 3H), 1.19–1.10 (m, 3H), 1.03–0.98 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.4, 169.9, 140.2, 138.3, 136.4, 133.4, 128.6, 128.4, 128.2, 127.5, 124.6, 124.6, 122.7, 111.2, 101.9, 62.7, 62.1, 61.9, 39.8, 21.3, 14.2, 13.9; IR (neat, cm^{-1}) 1732, 1250, 1184, 1056, 908, 734. Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43. Found: C, 76.46; H, 6.35.

*4.2.7. Diethyl 1-(2-(2-methoxyphenyl)vinylidene)-1H-indene-2,2(3H)-dicarboxylate (**2l**).* Oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 1H), 7.30–7.18 (m, 6H), 6.90–6.86 (m, 2H), 4.27–4.15 (m, 3H), 4.08–4.03 (m, 1H), 3.84–3.72 (m, 5H), 1.27–1.23 (m, 3H), 1.11–1.08 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.5, 170.1, 156.3, 139.7, 136.6, 128.6, 128.5, 128.1, 127.5, 124.7, 122.6, 121.7, 120.6, 110.9, 110.6, 96.0, 62.8, 62.0, 61.8, 55.6, 39.8, 14.2, 13.9; IR (neat, cm^{-1}) 1730, 1250, 1176, 1055, 857, 758. Anal. Calcd for $C_{24}H_{24}O_5$: C, 73.45; H, 6.16. Found: C, 73.39; H, 6.25.

*4.2.8. Diethyl 1-(2-(furan-2-yl)vinylidene)-1H-indene-2,2(3H)-dicarboxylate (**2m**).* Oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.20 (m, 5H), 6.77 (s, 1H), 6.40–6.35 (m, 2H), 4.28–4.08 (m, 4H), 3.91–3.63 (q, J=17.1 Hz, 2H), 1.28–1.23 (t, J=7.2 Hz, 3H), 1.13–1.08 (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.8, 169.9, 169.7, 147.3, 142.4, 140.3, 136.2, 128.6, 127.5, 124.6, 123.0, 111.6, 108.6, 92.2, 62.8, 62.1, 61.9, 39.6, 14.1, 13.7; IR (neat, cm^{-1}) 1729, 1245, 1178, 1056, 1013, 759, 737. Anal. Calcd for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.51; H, 5.74.

*4.2.9. Diethyl 1-(prop-1-enylidene)-1H-indene-2,2(3H)-dicarboxylate (**2n**).* Oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–7.16 (m, 4H), 5.82–5.75 (q, J=7.5 Hz, 1H), 4.28–4.16 (m, 4H), 3.77–3.63 (q, J=17.1 Hz, 2H), 1.85–1.83 (d, J=7.2 Hz, 3H), 1.31–1.23 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.0, 170.1, 139.4, 137.2, 127.7, 127.2, 124.4, 122.2, 107.2, 93.5, 62.3, 61.7, 61.6, 39.5, 14.1, 14.0, 13.9; IR (neat, cm^{-1}) 1736, 1247, 1182, 1057, 756. Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.11; H, 6.75.

*4.2.10. Diethyl 1-(2,2-diphenylvinylidene)-1H-indene-2,2(3H)-dicarboxylate (**2o**).* Solid: mp 102–104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.48 (m, 4H), 7.41–7.20 (m, 10H), 4.15–3.97 (m, 4H), 3.79 (s, 2H), 1.05–1.01 (t, J=6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.9, 170.0, 140.2, 136.6, 136.1, 128.6, 128.5, 128.4, 127.6, 127.5, 124.8, 122.5, 117.2, 110.4, 63.0, 61.9, 39.7, 13.5; IR (KBr, cm^{-1}) 1733, 1235, 1178, 1056, 765, 698. Anal. Calcd for $C_{29}H_{26}O_4$: C, 79.43; H, 5.98. Found: C, 79.38; H, 6.15.

4.3. Typical procedure for the preparation of 4

To a solution of 3 (0.20 mmol) in 2.0 mL of DMF was added Cs_2CO_3 (130.3 mg, 0.40 mmol) in the reaction vessel. The mixture was allowed to stir at room temperature for 1 min and PTC (3.15 mg, 5 mol %) was added. The vessel was sealed and the resulting mixture was then heated at 60 °C. When the reaction was considered complete as determined by TLC analysis, the reaction was allowed to cool to room temperature and quenched with a saturated aqueous solution of ammonium chloride, and the mixture was extracted with EtOAc. The combined organic extracts were washed with water and saturated brine. The organic layers

were dried over Na_2SO_4, filtered. Solvents were evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford **4**.

*4.3.1. Ethyl 3-(2-(2-oxo-2-phenylethoxy)phenyl)prop-2-ynyl carbonate (**4a**).* Yellow solid: mp 58–60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.09 (d, J=7.6 Hz, 2H), 8.02–8.00 (d, J=8.0 Hz, 1H), 7.64–7.49 (m, 6H), 7.39–7.35 (t, J=7.6 Hz, 1H), 6.18–6.13 (dd, J=0.8, 18.0 Hz, 1H), 5.72–5.69 (dd, J=1.2, 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6, 154.5, 147.9, 137.5, 132.6, 129.7, 128.2, 128.0, 127.9, 126.5, 125.9, 123.9, 122.8, 120.5, 112.3; IR (neat, cm^{-1}) 1649, 1530, 963, 729. Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.35; H, 4.78.

*4.3.2. Ethyl 3-(5-methyl-2-(2-oxo-2-phenylethoxy)phenyl)prop-2-ynyl carbonate (**4b**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–8.03 (d, J=8.0 Hz, 2H), 7.75 (s, 1H), 7.60–7.40 (m, 5H), 7.30–7.28 (d, J=8.0 Hz, 1H), 6.14–6.09 (dd, J=1.2, 18.0 Hz, 1H), 5.68–5.64 (dd, J=1.2, 11.6 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.7, 153.1, 148.1, 137.7, 133.6, 132.6, 129.8, 129.6, 128.2, 128.1, 126.4, 126.1, 122.4, 120.4, 111.9, 21.5; IR (neat, cm^{-1}) 1640, 1531, 1262, 1050, 802, 695. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.62; H, 5.26.

*4.3.3. 3-(5-tert-Butyl-2-(2-oxo-2-phenylethoxy)phenyl)prop-2-ynyl ethyl carbonate (**4c**).* White thick oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–8.04 (d, J=8.0 Hz, 2H), 7.96 (s, 1H), 7.61–7.47 (m, 6H), 6.16–6.11 (dd, J=0.8, 18.0 Hz, 1H), 5.71–5.68 (dd, J=1.2, 11.6 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 153.0, 148.3, 147.2, 137.8, 132.6, 129.8, 128.3, 128.2, 126.8, 126.5, 125.7, 120.5, 118.5, 111.8, 34.9, 31.7; IR (neat, cm^{-1}) 1673, 1540, 1361, 1114, 812. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.73; H, 6.84.

*4.3.4. 3-(5-Chloro-2-(2-oxo-2-phenylethoxy)phenyl)prop-2-ynyl ethyl carbonate (**4d**).* White solid: mp 93–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–8.04 (d, J=8.4 Hz, 2H), 7.92 (s, 1H), 7.63–7.41 (m, 6H), 6.06–6.01 (dd, J=1.2, 18.4 Hz, 1H), 5.69–5.67 (d, J=8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.3, 152.7, 148.8, 137.2, 132.9, 129.7, 129.7, 128.3, 128.3, 127.4, 127.1, 125.7, 122.3, 120.8, 113.4; IR (neat, cm^{-1}) 1649, 1535, 1266, 968, 693. Anal. Calcd for $C_{17}H_{11}ClO_2$: C, 72.22; H, 3.92. Found: C, 72.34; H, 3.83.

*4.3.5. Ethyl 3-(2-(2-oxopropoxy)phenyl)prop-2-ynyl carbonate (**4e**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.92 (d, J=8.0 Hz, 1H), 7.59–7.46 (m, 3H), 7.34–7.30 (m, 1H), 6.12–6.07 (dd, J=1.2, 18.0 Hz, 1H), 5.67–5.64 (dd, J=1.2, 11.6 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 154.3, 147.5, 128.1, 127.8, 126.2, 124.1, 123.9, 123.0, 120.9, 112.3, 27.9; IR (neat, cm^{-1}) 1675, 1545, 1131, 746. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.31; H, 5.58.

*4.3.6. 3-(5-tert-Butyl-2-(2-oxopropoxy)phenyl)prop-2-ynyl ethyl carbonate (**4f**).* Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81–7.80 (d, J=1.8 Hz, 1H), 7.51–7.33 (m, 3H), 6.04–5.97 (dd, J=1.8, 18.3 Hz, 1H), 5.59–5.55 (dd, J=1.8, 11.7 Hz, 1H), 2.51 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1, 152.6, 147.8, 147.0, 127.9, 126.5, 125.8, 124.3, 120.7, 118.6, 111.6, 34.8, 31.6, 27.9; IR (neat, cm^{-1}) 1649, 1536, 1271, 1053, 811, 697. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.24; H, 7.62.

*4.3.7. Ethyl 2-(4-chloro-2-(3-(ethoxycarbonyloxy)prop-1-ynyl)phenoxy)acetate (**4g**).* White solid: mp 66–68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.44–7.34 (m, 3H), 5.98–5.91 (dd, J=1.2, 18.3 Hz, 1H), 5.63–5.59 (d, J=10.5 Hz, 1H), 4.46–4.39 (dd, J=1.2, 14.7 Hz, 2H), 1.43–1.39 (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 152.9, 142.0, 129.5, 127.9, 127.1, 126.8, 124.9, 122.0, 120.4, 113.4, 61.5, 14.3; IR (neat, cm^{-1}) 1713, 1554, 1273, 907, 802. Anal. Calcd for $C_{13}H_{11}ClO_3$: C, 62.29; H, 4.42. Found: C, 62.44; H, 4.27.

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