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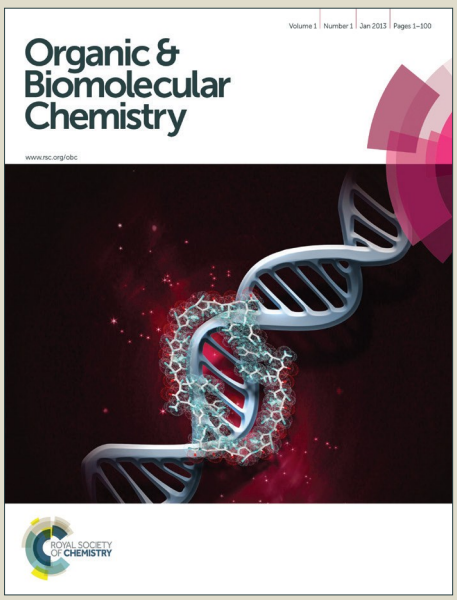

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ARTICLE

Metal-free yne-addition/1,4-aryl migration/decarboxylation cascade reaction of alkynoates with C_{sp3}-H centers

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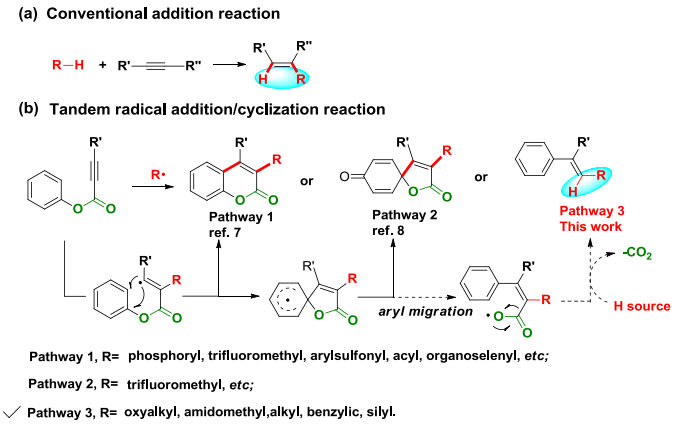
A metal-free cascade reaction of aryl alkynoates with five different types of radical precursors (R-H) through yne-addition/1,4-aryl migration/decarboxylation process was reported, which allowed facile and convenient access to functionalized vinyl products with "R" and proton located at the identical carbon of the formed double bond.

Introduction

During the past few years, radical chemistry has played an important role in the development of modern organic chemistry. The synthetic methodologies based on radical species and radical cascade reaction have been extensively investigated[1] and applied in the construction of highly complex and polycyclic molecular frameworks.[2] In particular, radical mediated sp^3 C–H[3] and Si–H[4] activation have been demonstrated to be powerful tools for C-C and C-Si bond formations due to the high atom-economy and low environmental costs. The intermolecular addition of carbon- and heteroatom-center radicals to mono- and disubstituted alkynes and related triple bond systems also represent an extremely attractive synthetic method.[5] The fascination comes from the highly reactive vinyl radicals generated in this step, which can be trapped by fast cyclization or addition onto other π-systems subsequently. Although radical addition reactions of alkynes have been well established in the past decades, new reactions against the general principle of addition reactions [Scheme 1, eq. (a)], that the broken two parts separately attach to different carbon atoms of the formed double bond, are still highly desirable.

Cascade radical reactions with alkynes can show more artistic features.[6] In the case of aryl alkynoates, which are elegant radical acceptors, two radical cascade pathways have been observed so far [Scheme 1, eq. (b), pathway 1 and 2].[7,8] Under transition-metal catalysed conditions, reactions of aryl alkynoates with various types of radicals (phosphoryl, trifluoromethyl, arylsulfonyl, acyl, organoselenyl, etc.) would provide the products of cumarin derivatives though a cascade cyclized process.[7] Very recently, Li[8a] and Liang[8b] described a Cu(I)-catalyzed functionalization of phenyl alkynoate which afforded the dearomatic and spriocyclic products. While, both two pathways formally gave double bonds by adding two groups to each carbon of the tripe bonds. In the case of alkyl alkynoate, the reaction with sp^3 carbon radical under either photo-promotion or transition-metal catalysis would afford vinyl products in the mode of eq. (a).[9] Inspired by recently well developed migration/desulfonylation reactions,[2] we envisioned whether the presence of ester unit in alkynoate would trigger an aryl migration/decarboxylation-process to give trisubstituted olefins products by employing appropriate 'R-H' substrates as radical precursors and hydrogen donors without the needs of extra hydrogen sources [Scheme 1, eq. (b), pathway 3]. In this assumed pathway, the process would afford the functionalized single-site-addition vinyl products. It is worthy to note that radical aryl-migration reactions[10] and decarboxylation of vinyl carboxyl group[11] have been exploited extensively, but there are very few reports on the combination of aryl-migration with decarboxylation *via ipso*-cyclized intermediate in a one pot process.



Scheme 1. The addition reactions of alkynes and alkynoates.

During the preparation of our manuscript, Han *et al*. reported the oxidative difunctionalization of alkynoates with cycloalkanes as substrates.[12] Herein, we would like to report the successful execution of our hypothesis by employing different types of 'R-H' substrates as radical precursors and hydrogen donors, such as ethers, amides, benzylic compounds *etc.,* to react with alkynoates *via* yne-

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addition/1,4-aryl migration/decarboxylation cascade process under metal-free conditions [Scheme 1, Eq. (b), pathway 3]. It was particularly interesting and rare that the carbon atom, which R· radical initially attacked, was also involved in the final hydrogen abstraction step in a cascade process.

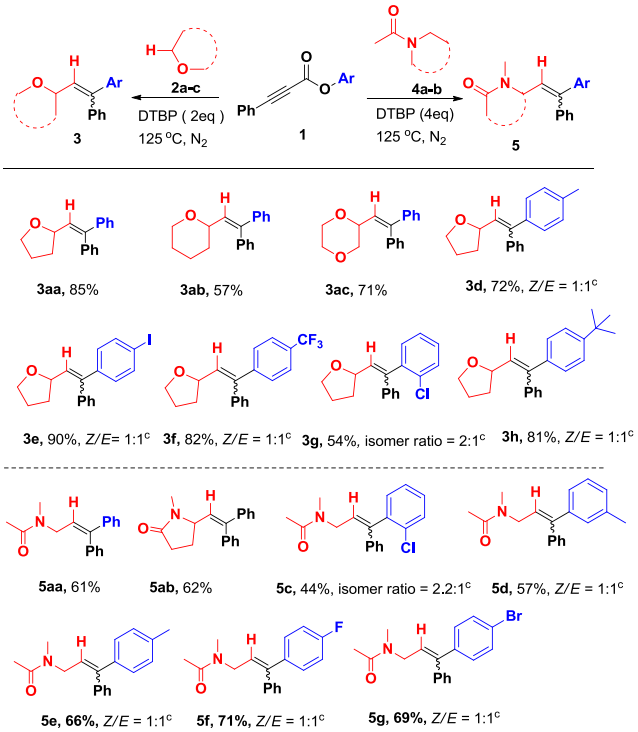
Results and discussion

sp^3 Carbon radicals species were commonly generated by radical initiators, thermolysis, photolysis or oxidants[13]. It was known that the sp^3 C–H bonds adjacent to oxygen atom could be activated generating sp^3 carbon radicals. In an initial experiment, phenyl 3-phenylalkynoate (**1a**) and THF (**2a**) were chosen to react along with DTBP (2equiv.) as the oxidant at 125 °C (sealed tube) for 5 h in a nitrogen atmosphere. Pleasingly, the aryl allyl cyclic ether **3aa** could be obtained in 85% yield in the condition. It was assumed by the structural analysis of the product **3aa** that the reaction should undergo a radical yne-addition/1,4-aryl-migration/decarboxylation cascade process.

Using the applicable condition, the scopes of alkynoates and other cyclic ethers were subsequently investigated. As shown in table 1, six-membered cyclic ethers, such as tetrahydropyran (**2b**) and 1,4-dioxane (**2c**), which represented excellent resources of α-oxy radical, were employed to react with **1a** and the corresponding products **3ab** and **3ac** were obtained in 57% and 71% yields, respectively. Reaction with both electron-neutral and electron-deficient aryl-substituted alkynoates smoothly afforded the desired products **3d-3f** in high yield with 1:1 ratio of Z/E and **3g** in 54% yield with 2:1 ratio of isomers. In addition, larger *tert*-butyl group on the *para* position of the phenyl ring had no significant effect on the reaction (**3h**).

It was revealed that sp^3 C–H bonds adjacent to nitrogen atom could also be activated for the generation of sp^3 carbon radicals. Thus, we then explored the direct synthesis of aryl allylamines compounds by employing amides as the radical donors in this cascade reaction. As well known, aryl allylamines motifs were frequently incorporated as an integral part of many pharmaceutically important molecules and natural products, such as abmine-SG, abmine and naftifine, which exhibited a wide range of biological properties.[14] Current biological research[15] clearly evidenced that aryl allylamines possessed high sigma (σ) receptor affinity and good σ1/σ2 selectivity. However, arylallylamines were generally synthesized by mono or di Heck arylation of allylamines derivatives[16] or by the nucleophilic addition of the appropriate aromatic anion to β-aminoketones, followed by dehydration. In this section, *N,N*-dimetylacetamide (DMA, **4a**) was applied for the generation of sp^3 carbon radical adjacent to the nitrogen and the reactions of which with aryl alkynoates in the presence of DTBP (4 equiv.) at 125 °C for 12 h proceeded smoothly, affording the arylallylamines products in 44-71% yields (Table 1, **5c-5g**). Both electron-deficient and electron-rich aryl groups as well as the substitution patterns (*ortho*, *meta* and *para*) on the phenyl rings of the ester of phenylynoates tolerated well in the tandem reaction. Additionally, under the same conditions, cyclic amide, 1-methyl-2-pyrrolidinone (**4b**) was applicable for the reaction with **1a**, providing the desired product **5ab** in 62% yield.

Table 1. The cascade radical addition reactions of alkynoates with ethers and amides.[a,b]



[a] Reaction conditions, for ethers: **1** (0.2 mmol), ether (2 mL), DTBP (0.4 mmol), sealed tube, 125 °C, 5h. For amides: **1** (0.2 mmol), amide (2 mL), DTBP (0.8 mmol), 125 °C, 12h. [b] Isolated yield. [c] Determined by the integral area of ^{1}HNMR.

To display the usefulness of the reaction further, more radical precursors were investigated afterwards (Table 2). Gratifyingly, benzylic substrates were proven to be suitable for this domino process *via* generating the benzylic primary sp^3 carbon radicals. The reactions of **6a-6e** with **1a** afforded the corresponding products **7aa-7ae** in good yield (63-80%). Next, several cycloalkanes were also employed to react with phenyl 3-phenylpropiolat **1a**. As a result, these radical reactions afforded the corresponding 1,1-hydroalkylation-products **9** bearing five- (**9ab**), six- (**9ab**) and seven membered (**9ac**) rings with moderate to excellent yield (40% - 95%). However, the yield decreased dramatically when more steric bulk cyclooctane was used as the substrate, and only a trace amount of the desired product (**9ad**) was detected. It is noteworthy that in addition to substituted-phenyl 3-phenylpropiolates, we also tried the reaction of phenyl but-2-ynoate **1b** with **8b** and the product **9bb** of the tandem reaction was obtained in 55% yield.

Hydrosilylation of alkynes was the most straightforward method to access vinylsilanes. However, the direct synthesis of β,β-disubstituted alkenylsilane *via* Si-H activation has never been reported before. To our delight, β,β-disubstituted alkenylsilanes could also be synthesised by this method. We employed representative triethylsilane as the radical precursor and the reactions of which with aryl alkynoates smoothly afforded vinylsilanes **10a** and **10b** in good yield.

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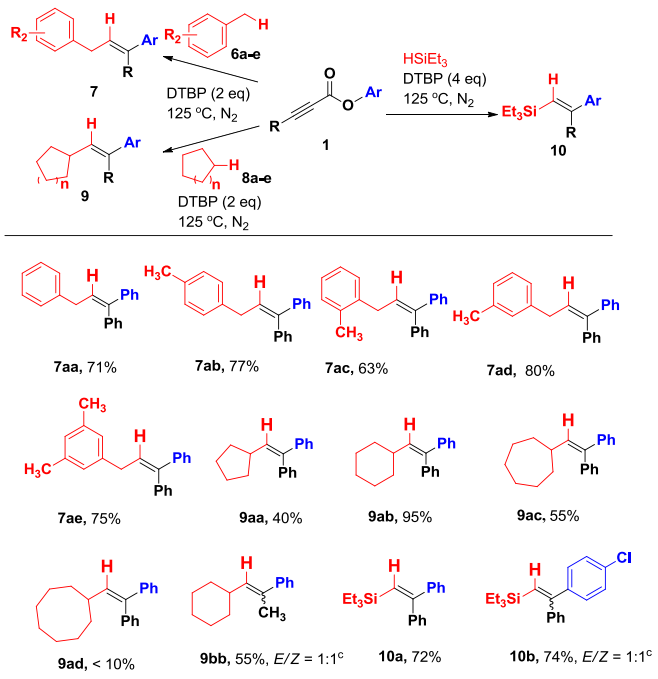
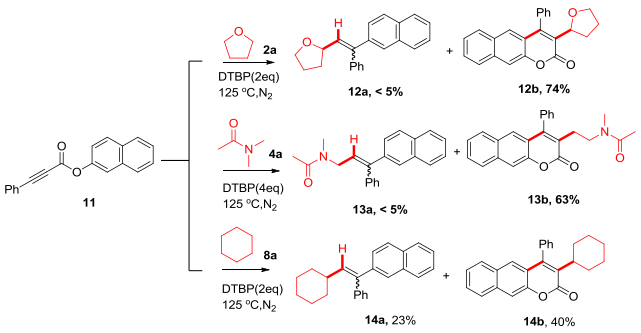
Table 2. The cascade radical addition reactions of alkynoates with cycloalkanes, benzylic substrates, and silanes.[a,b]



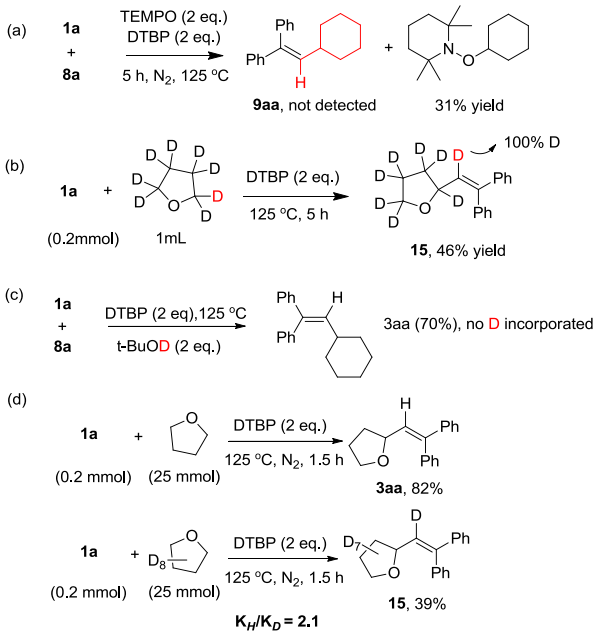
[a]Reaction condition: **1** (0.2 mmol), solvent (2 mL), DTBP (0.4 mmol), sealed tube, 125 °C, 5h. For benzylic substrates and $SiEt_3$ the reaction time is 12 h. [b]Isolated yield. [c]Determined by the integral area of ^{1}HNMR.

Interestingly, replacing phenyl with β-naphthyl on the ester unit, less aryl migration/decarboxylation product were obtained in the reactions of β-naphthyl 3-phenylpropenyoate with THF (**2a**), DMA (**4a**), and cyclohexane (**8a**) under the standard conditions. Instead, the reactions afforded more cyclized products. (Scheme 2).



Scheme 2. The reactions of β-naphthyl 3-phenylpropenyoate with sp^3 C radicals.

To elucidate the mechanism, TEMPO was employed as a radical scavenger in the reaction of **8a** with **1a** at 125 °C. As a result, the formation of desired product **9aa** was suppressed and the TEMPO-Cy adduct was obtained, which provided an evidence of the generation of cyclohexyl radical species in the reaction (Scheme 3a). Subsequently, deuterium-labelling experiment was conducted by using fully deuterated THF in the reaction with **1a**. It suggested that the exclusive hydrogen source in the formed double bond was from THF (Scheme 3b). The addition of ^{t}BuOD (2 equiv.) to the reaction mixtures of **1a** with **8a** did not lead to any deuterium-containing products at all, thus practically ruling out the possibility that the terminal hydrogen abstraction step of the tandem reaction might be involved by ^{t}BuOH formed from homo-cleavage of DTBP (Scheme 3c). In addition, two parallel reactions were carried out with THF and THF-d8 as the substrates respectively to determine the kinetic isotopic effect (KIE) (Scheme 3d). As a result, a k_H/k_D = 2.1 was obtained.



Scheme 3. Mechanistic studies.

On the bases of the above results and literatures,[4,17] the cascade reactions were supposed to be through the attack of a sp^3 C free radical generated from hydrogen abstraction by a *tert*-butoxy radical of DTBP homolysis to alkynoates, leading to yne-addition/1,4-aryl migration/decarboxylation process. [12]

Conclusions

In conclusion, we have developed an unprecedented radical cascade reaction of alkynoates with ethers, amides, benzylic compounds *etc.*, which proceeds through yne-addition/1,4-aryl migration/decarboxylation cascade process and allows facile and convenient access to interesting single-site-addition vinyl products. In this cascade reaction, sp^3 C-H substrates act as both radical precursors and hydrogen donors without the addition of extra hydrogen sources. This synthetic approach represents a strategy of direct decarboxylation of esters *via ipso*-cyclized intermediate, which is especially different with the common migration/desulfonylation reactions.

Experimental section

General procedure for the synthesis of 3: A mixture of alkynoate (0.20 mmol), cyclic ethers (2 mL) and DTBP (0.4 mmol) was sealed in

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a teflon septum screw-capped tube under N_2. The mixture was stirred in an oil bath at 125 °C for 5 h. After completion of the reaction, the products were obtained by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent.

2-(2,2-diphenylvinyl)tetrahydrofuran (3aa)[18]: Colorless oil, 43 mg, yield 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 3H), 7.27 - 7.20 (m, 7H), 6.06 (d, *J* = 9.0 Hz, 1H), 4.33 – 4.25 (m, 1H), 3.98 – 3.91 (m, 1H), 3.77 – 3.67 (m, 1H), 2.04 – 1.97 (m, 2H), 1.91 – 1.81 (m, 1H), 1.72 – 1.67 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 142.0, 139.4, 130.0, 129.7, 128.1, 127.6, 127.4, 127.3, 76.6, 68.1, 33.1, 26.4. HRMS (APCI): calculated $C_{18}H_{19}O^+$ ([M+H]$^+$): 251.1430, found: 251.1430. IR (KBr, cm^{-1}) 3056, 3023, 2969, 2867, 1599, 1492, 1444, 1205, 1151, 1049, 764, 700.

2-(2,2-diphenylvinyl)tetrahydro-2H-pyran (3ab)[19]: White solid, 30 mg, yield 57%, m.p. 51~52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 3H), 7.29 – 7.20 (m, 7H), 6.04 (d, *J* = 8.9 Hz, 1H), 4.02 – 3.93 (m, 1H), 3.87 – 3.78 (m, 1H), 3.36 (m, 1H), 1.80 (m, 1H), 1.68 – 1.35 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 142.1, 139.6, 129.8, 129.8, 128.1, 128.0(8), 127.6, 127.4, 127.3, 75.7, 67.9, 32.3, 25.7, 23.1. HRMS (APCI): calculated $C_{19}H_{21}O^+$ ([M+H]$^+$): 265.1587, found: 265.1586. IR (KBr, cm^{-1}) 3056, 3023, 2933, 2851, 1726, 1493, 1448, 1444, 1202, 1082, 1032, 775, 763, 702.

2-(2,2-diphenylvinyl)-1,4-dioxane (3ac)[19]: White solid, 38 mg, yield 71%, m.p. 89~92 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.32 (m, 3H), 7.31 – 7.15 (m, 7H), 5.94 (d, *J* = 8.9 Hz, 1H), 4.13 (m, 1H), 3.84 – 3.60 (m, 5H), 3.55 – 3.44 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 141.4, 139.1, 129.5, 128.3, 128.2, 127.9, 127.7, 127.5, 124.1, 73.7, 70.3, 66.1, 66.1. HRMS (APCI): calculated $C_{18}H_{19}O_2^+$ ([M+H]$^+$): 267.1379, found: 267.1379. IR (KBr, cm^{-1}) 3055, 3025, 2959, 2850, 1725, 1493, 1445, 1117, 1090, 1050, 907, 875, 764, 701.

2-(2-phenyl-2-(p-tolyl)vinyl)tetrahydrofuran (3d): Pale yellow solid, 38 mg, yield 72%, m.p. 46~48 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.06 (m, 9H), 6.03 (d, *J* = 9.0 Hz, 1H), 4.35 – 4.24 (m, 1H), 3.98 – 3.90 (m, 1H), 3.76 – 3.69 (m, 1H), 2.38(s, 1.5H), 2.32 (s, 1.5H), 2.04 – 1.97 (m, 2H), 1.90 – 1.85 (m, 1H), 1.77 – 1.68 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 143.6, 142.3, 139.6, 139.2, 137.2, 137.0, 136.5, 130.0, 129.9, 129.5, 128.9, 128.8(7), 128.8(2), 128.0, 127.7, 127.5, 127.4, 127.3, 76.7, 68.1, 33.1, 26.4, 21.3, 21.1. HRMS (APCI) calculated $C_{19}H_{21}O^+$ ([M+H]$^+$): 265.1587 found: 265.1586. IR (KBr, cm^{-1}) 3052, 3022, 2970, 2921, 1653, 1633, 1511, 1444, 1050,818, 765, 700.

2-(2-(4-iodophenyl)-2-phenylvinyl)tetrahydrofuran (3e): Colorless oil, 62 mg, yield 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.17 (m, 5H), 7.07 – 6.92 (m, 2H), 6.05 (dd, *J* = 8.5, 4.7 Hz, 1H), 4.25 (M, 1H), 3.94 M, 1H), 3.76-3.72 (m, 1H), 2.05 -1.98 (m, 2H), 1.95 – 1.83 (m, 1H), 1.79 – 1.68 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 140.5, 140.4, 137.9, 137.7, 136.2, 136.2, 130.9, 129.3, 129.2, 128.9, 128.4, 127.3, 127.2, 126.6, 126.5, 92.1, 92.1, 75.5, 75.4, 67.1, 32.0, 32.0, 25.4. HRMS (APCI): calculated $C_{18}H_{18}IO^+$ ([M+H]$^+$): 377.0396, found: 377.0395. IR (KBr, cm^{-1}) 3056, 3022, 2965, 2868, 1725, 1493, 1049, 1006, 1014, 821, 745, 701.

2-(2-phenyl-2-(4-(trifluoromethyl)phenyl)vinyl)tetrahydrofuran (3f): Colorless oil, 52 mg, yield 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.32 (m, 4H), 7.31 – 7.25 (m, 2H), 7.23 – 7.17 (m, 2H), 6.12 (m, 1H), 4.33-3.30 (m, 1H), 4.26 – 4.19 (m, 1H), 3.96-3.92 (m, 1H), 3.79 – 3.71 (m, 1H), 2.10 – 1.96 (m, 2H), 1.93 – 1.84 (m, 1H), 1.80 – 1.70 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 143.2, 142.5(7), 142.5(2), 141.2, 138.6, 131.8, 130.8, 130.3, 129.9, 129.7, 129.5, 129.4, 129.2, 128.3(2), 128.3, 127.8, 127.8, 127.7, 127.5, 125.3, 125.1(6), 125.1(3), 125.1, 125.0(7), 125.0(4), 76.4, 76.3(9), 68.2(4), 68.2(1), 33.0(7), 33.0(6), 26.4(6), 26.4(4). HRMS (APCI): calculated $C_{19}H_{18}F_3O^+$ ([M+H]$^+$): 319.1304, found: 319.1302. IR (KBr, cm^{-1}) 2928, 2869, 1616, 1494, 1444, 1324, 1165, 1124, 1066, 1051, 838, 765, 701.

2-(2-(2-chlorophenyl)-2-phenylvinyl)tetrahydrofuran (3g) : Colorless oil, 31 mg, yield 54%.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 6.6 Hz, 1H), 7.28 – 7.12 (m, 13.4H), 6.18 (dd, *J* = 14.5, 8.9 Hz, 1H), 5.70 (d, *J* = 9.1 Hz, 1H), 4.46 (dt, *J* = 9.0, 7.4 Hz, 0.6H), 4.07 – 3.99 (m, 1H), 3.86 (m, 1.6H), 3.70 (m, 0.6H), 3.63 (m, 1H), 2.14 – 2.04 (m, 0.6H), 2.03 – 1.82 (m, 3H), 1.80 – 1.59 (m, 2.8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 140.7, 139.3, 138.6, 137.7, 137.1, 132.9, 132.5, 132.2, 130.9, 130.5, 130.5, 130.2, 129.7, 128.9, 128.8, 128.4, 128.3, 127.8, 127.5, 127.2, 126.8, 126.5, 126.3, 125.9, 125.4, 125.4, 125.3, 75.9, 74.9, 67.1, 67.0, 32.0, 31.1, 25.4, 25.2. HRMS (APCI): calculated $C_{18}H_{18}ClO^+$ ([M+H]$^+$): 285.1040, found: 285.1039. IR (KBr, cm^{-1}) 3056, 3023, 2971, 2926, 2868, 1725, 1494, 1470, 1445, 1050, 761, 749, 696.

2-(2-(4-(tert-butyl)phenyl)-2-phenylvinyl)tetrahydrofuran (3h): Colorless oil, 50 mg, yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.16 (m, 6H), 7.16 – 7.03 (m, 3H), 5.98 (d, *J* = 9.0 Hz, 1H), 5.94 (d, *J* = 9.1 Hz, 1H), 4.30 -4.24 (m, 0.5H), 4.22 -4.16 (m, 0.5H), 3.89 – 3.83 (m, 1H), 3.70 – 3.61 (m, 1H), 2.03 – 1.86 (m, 2H), 1.86 – 1.73 (m, 1H), 1.73 – 1.59 (m, 1H), 1.32 – 1.21 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 149.1, 142.7, 142.2, 141.3, 138.5, 137.9, 135.2, 128.9, 128.6, 128.5, 127.9, 127.0, 126.7, 126.3, 126.2, 126.1, 124.0, 123.8, 75.6, 67.0, 67.0, 33.5, 33.4, 32.1, 32.0(8), 30.3, 30.2, 25.5, 25.4. HRMS (APCI): calculated $C_{22}H_{27}O^+$ ([M+H]$^+$): 307.2056, found: 307.2055. IR (KBr, cm^{-1}) 3055, 3027, 2963, 2867, 1734, 1512, 1493, 1444, 1363, 1268, 1050, 831, 760, 703.

General procedure for the synthesis of 5: A mixture of alkynoate (0.20 mmol), amide (2 mL) and DTBP (0.8 mmol) was sealed in a teflon septum screw-capped tube under N_2. The mixture was stirred in an oil bath at 125 °C for 12 h. After completion of the reaction, the products were obtained by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent.

N-(3,3-diphenylallyl)-N-methylacetamide (5aa): Pale yellow oil, 32 mg, yield 61%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.14(m, 10H), 6.03 (q, *J* = 6.8 Hz, 1H), 4.09 (d, *J* = 6.9 Hz, 1H), 3.96 (d, *J* = 6.6 Hz, 1H), 2.90 (m, 3H), 2.13 – 1.96 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 145.3, 144.9, 141., 141.1, 139.0, 138.6, 129.7, 129.6, 128.5, 128.3(7), 128.3(3), 128.2, 127.9, 127.5, 127.4, 127.3, 127.2, 124.3, 123.1, 49.8, 46.1, 35.5, 33.2, 21.8, 21.4. HRMS (ESI): calculated $C_{18}H_{19}ONNa^+$ ([M+Na]$^+$): 288.1358, found: 288.1355. IR (KBr, cm^{-1}) 3055, 3023, 2922, 2851, 1647, 1493, 1444, 1139, 1018, 763, 702.

5-(2,2-diphenylvinyl)-1-methylpyrrolidin-2-one (5ab): Colorless oil, 34 mg, yield 62%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.13 (m, 10H), 5.93 (d, *J* = 9.8 Hz, 1H), 4.09 (m, 1H), 2.75 (s, 3H), 2.45 (m, 1H), 2.33 (m, 1H), 2.21 (m, 1H), 1.87 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 145.6, 141.0, 138.8, 129.5, 128.5, 128.4, 128.3, 128.0, 127.7, 127.3, 58.9, 30.2, 27.9, 25.8. HRMS (ESI): calculated $C_{19}H_{19}ONNa^+$ ([M+Na]$^+$): 300.1358, found: 300.1356**.** IR (KBr, cm^{-1}) 3055, 2921, 2686, 1492, 1444, 1393, 1266, 1113, 1074, 1029, 766, 702.

N-(3-(2-chlorophenyl)-3-phenylallyl)-N-methylacetamide (5c): Pale yellow oil, 28 mg, yield 44%.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54– 7.12 (m, 13H), 6.19 (m, 1H), 5.71 (m, 0.5H), 4.30 (d, *J* = 6.6 Hz, 0.5H), 4.22

Organic & Biomolecular Chemistry Accepted Manuscript

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– 4.10 (m, 1H), 3.87 (m, 0.5H), 3.82 – 3.68 (m, 1H), 2.96 – 2.90 (m, 4.5H), 2.05 (dd, *J* = 39.8, 13.5 Hz, 4.5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 143.1, 142.6, 142.0, 141.8, 141.7, 141.2, 139.4, 139.1, 138.4, 138.0, 137.6, 137.2, 133.7, 133.6, 133.0, 131.6, 131.3, 131.2, 131.1, 130.0(5), 130.0, 129.8(7), 129.8(5), 129.5, 129.4, 129.3, 129.1(2), 129.1, 129.0, 128.9, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 127.4, 127.0, 126.9, 126.6, 126.5, 126.4, 126.3, 125.6, 124.7, 115.4, 49.9, 49.4, 46.3, 45.5, 35.8, 35.5, 33.4, 33.5, 21.8, 21.7, 21.4, 21.3. HRMS (ESI): calculated $C_{18}H_{18}ONClNa^+$ ([M+Na]$^+$): 322.0969, found: 322.0965. IR (KBr, cm^{-1}) 3055, 3022, 2922, 2851, 1724, 1651, 1494, 1401, 1261, 1140, 1033, 759, 696.

N-methyl-N-(3-phenyl-3-(m-tolyl)allyl)acetamide (5d): Pale yellow oil, 32 mg, yield 57%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 6.95 (m, 9H), 6.08 – 5.95 (m, 1H), 4.15 – 4.02 (m, 1H), 3.95 (dd, *J* = 6.5, 4.5 Hz, 1H), 2.96 – 2.84 (m, 3H), 2.36 - 2.31 (m, 3H), 2.08 - 1.98 (d, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 170.4, 145.4, 145.0, 144.9, 141.6, 141.5, 141.2, 141.1, 139.1, 138.9, 138.7, 138.6, 138.2, 137.9, 137.7, 130.9, 130.4, 130.1, 129.7, 129.6, 128.8, 128.6, 128.5, 128.4, 128.3, 128.3(4), 128.3(1), 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.4, 127.3, 127.2, 126.8, 126.7, 124.7, 124.5, 124.3, 124.2, 123.1, 49.8(4), 49.8(0), 46.1, 46.0, 35.5, 33.2, 33.2, 29.7, 22.7, 21.8, 21.4(4), 21.4(2), 21.3. HRMS (ESI): calculated $C_{19}H_{21}ONNa^+$ ([M+Na]$^+$): 302.1515, found: 302.1511. IR (KBr, cm^{-1}) 3022, 2924, 2854, 1734, 1651, 1601, 1492, 1444, 1401, 1258, 1137, 1020, 787, 765, 701.

N-methyl-N-(3-phenyl-3-(p-tolyl)allyl)acetamide (5e): Pale yellow oil, 36 mg, yield 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.03 (m, 9H), 6.04 – 5.95 (m, 1H), 4.08 (m, 1H), 3.95 (m, 1H), 2.90 - 2.87 (m, 3H), 2.40 - 2.32 (m, 3H), 2.08 - 1.98 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 145.2, 145.1, 144.8, 144.7, 141.7, 141.4, 139.2, 138.7, 138.3, 137., 137.6, 137.3, 137.1, 136.0, 135.6, 129.8, 129.7, 129.6, 129.5, 129.2, 129.0, 128.9, 128.5, 128.3, 128.2, 128.1, 127.8, 127.4, 127.3(8), 127.3, 127.2, 127.1, 124.2, 123.4, 123.0, 122.3, 49.8, 49.7(8), 46.1, 46.0, 35.5, 33.2(6), 33.2, 21.8, 21.4, 21.3, 21.1. HRMS (ESI): calculated $C_{19}H_{21}ONNa^+$ ([M+Na]$^+$): 302.1515, found: 302.1511. IR (KBr, cm^{-1}) 3023, 2921, 2851, 1651, 1510, 1491, 1137, 1019, 818, 765, 701.

N-(3-(4-fluorophenyl)-3-phenylallyl)-N-methylacetamide (5f): Colorless oil, 40 mg, yield 71%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.27 (m, 3H), 7.24 – 7.05 (m, 5H), 7.01 – 6.92 (m, 1H), 6.07 – 5.93 (m, 1H), 4.12 – 4.04 (m, 1H), 3.95 (dd, *J* = 6.6, 3.6 Hz, 1H), 2.90 (m, 3H), 2.11 - 2.00 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 163.5, 163.3, 163.1, 161.6, 161.3, 161.2, 144.4, 143.9, 141.3, 140.9, 138.8, 138.4, 137.6, 137.5, 137.2(4), 137.2(1), 134.8, 134.4, 131.5, 131.4, 131.3(5), 131.3, 129.6, 129.5(6), 129.5(1), 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.7, 127.6, 127.4, 127.2, 124.5, 123.9, 123.4, 122.8, 120.3, 115.7, 115.5, 115.4(7), 115.4, 115.3, 115.1(4), 115.1(1), 114.9, 49.8, 46.3, 46.2, 35.6, 33.4, 33.3, 21.8, 21.3(6), 21.3(4). HRMS (ESI): calculated $C_{18}H_{18}ONFNa^+$ ([M+Na]$^+$):306.1264, found: 306.1260. IR (KBr, cm^{-1}) 3055, 2920, 2850, 1644, 1601, 1507, 1402, 1223, 1159, 1016, 836, 765, 700.

N-(3-(4-bromophenyl)-3-phenylallyl)-N-methylacetamide (5g): Pale yellow oil, 44 mg, yield 69%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (m, 1H), 7.47 – 7.24 (m, 4H), 7.23 – 7.01 (m, 4H), 6.09 – 5.96 (m, 1H), 4.07 (dd, *J* = 6.8, 2.4 Hz, 1H), 3.95 (d, *J* = 6.6 Hz, 1H), 2.89 (m, 3H), 2.11 - 2.00 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 144.4, 144.3, 143.9, 143.8, 140.9, 140.6, 140.4, 140.0, 138.4, 138.0, 137.9, 137.5, 131.8, 131.6, 131.5, 131.3, 129.7, 129.5, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.1, 127.7, 127.7, 127.3, 127.2, 124.7, 123.6, 123.5, 122.1, 122.0, 121.7, 121.6, 49.8, 46.3, 46.2, 35.6, 33.4, 29.71, 21.78, 21.4, 21.3. HRMS (ESI): calculated $C_{18}H_{19}ONBr^+$ ([M+H]$^+$): 344.0644, found: 344.0640. IR (KBr, cm^{-1}) 3024, 2923, 2852, 1734, 1644, 1485, 1399, 1366, 1260, 1071, 1010, 823, 767, 703.

General procedure for the synthesis of 7 and 9: A mixture of phenyl alkynoate (1a, 0.20 mmol), alkanes (2a, 4 mL) and DTBP (0.4 mmol) was sealed in a teflon septum screw-capped tube under N_2. The mixture was stirred in an oil bath at 125 °C. After completion of the reaction, the desired products were obtained by flash column chromatography on silica gel with petroleum ether as eluent.

prop-1-ene-1,1,3-triyltribenzene (7aa)[18]: Colorless oil, 40 mg, yield 77%. ^{1}H NMR (500 MHz, $CDCl_3$) δ7.40 - 7.19(m, 15H), 6.26 (t, *J* = 7.6 Hz, 1H), 3.46 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 142.5, 141.0, 139.8, 129.9, 128.5, 128.4, 128.3, 128.1, 127.8, 127.4, 127.2, 127.1, 126.0, 35.9. HRMS (APCI): calculated $C_{21}H_{19}^+$ ([M+H]$^+$): 271.1481, found: 271.1482. IR (KBr, cm^{-1}) 3080, 3053, 3020, 2921, 2852, 2246, 1598, 1513, 1494, 1443, 1073, 1030, 910, 763, 700.

(3-(o-tolyl)prop-1-ene-1,1-diyl)dibenzene (7ab)[20]: Colorless oil, 34 mg, yield 63%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.11 (m, 14H), 6.19 (t, *J* = 7.4 Hz, 1H), 3.43 (d, *J* = 7.4 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 139.9, 139.3, 136.3, 130.1, 129.9, 128.6, 128.3, 128.1, 127.4, 127.2, 127.0, 126.2, 126.0, 33.8, 19.5. HRMS (APCI): calculated $C_{22}H_{21}^+$ ([M+H]$^+$): 285.1637, found: 285.1639. IR (KBr, cm^{-1}) 3055, 3020, 2920, 2850, 1494, 1443, 1030, 741, 700.

(3-(*m*-tolyl)prop-1-ene-1,1-diyl)dibenzene (7ac)[18]: Colorless oil, 45 mg, yield 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.28 – 7.20 (m, 7H), 7.18 (dd, *J* = 10.2, 5.2 Hz, 1H), 7.00 (t, *J* = 7.0 Hz, 3H), 6.26 (t, *J* = 7.6 Hz, 1H), 3.43 (d, *J* = 7.6 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 141.3, 139.8, 138.8, 137.0, 128.9, 128.2, 127.3, 127.2, 127.1, 126.9, 126.3, 126.1, 126.0, 125.7, 124.4, 34.8, 20.4. HRMS (APCI): calculated $C_{22}H_{21}^+$ ([M+H]$^+$): 285.1637, found: 285.1639. IR (KBr, cm^{-1}) 3055, 3021, 2922, 2850, 1600, 1494, 1443, 1030, 771, 700.

(3-(p-tolyl)prop-1-ene-1,1-diyl)dibenzene (7ad)[18]: Colorless oil, 39 mg, yield 71%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.27 – 7.19 (m, 7H), 7.12 – 7.06 (m, 4H), 6.25 (t, *J* = 7.8 Hz, 1H), 3.43 (d, *J* = 7.6 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 142.3, 139.9, 137.9, 135.5, 130.0, 129.2, 128.3, 128.3, 128.1, 128.1, 127.34, 127.1, 127.0, 35.5, 21.0. HRMS (APCI): calculated $C_{22}H_{21}^+$ ([M+H]$^+$): 285.1637, found: 285.1639. IR (KBr, cm^{-1}) 3058, 3025, 2920, 2850, 1494, 1452, 1443, 1073, 1030, 760, 697.

(3-(3,5-dimethylphenyl)prop-1-ene-1,1-diyl)dibenzene (7ae)[18]: Colorless oil, 42 mg, yield 75%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.16 (dt, *J* = 16.5, 4.4 Hz, 7H), 6.80 – 6.70 (m, 3H), 6.18 (t, *J* = 7.6 Hz, 1H), 3.32 (d, *J* = 7.6 Hz, 2H), 2.21 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 142.2, 140.9, 139.9, 138.0, 130.0, 128.3, 128.1(2), 128.1, 127.7, 127.4, 127.1, 127.0, 126.2, 35.8, 21.3. HRMS (APCI): calculated $C_{23}H_{23}^+$ ([M+H]$^+$): 299.1795, found: 299.1795. IR (KBr, cm^{-1}) 3054, 3019, 2918, 2851, 1602, 1494, 1443, 1073, 1030, 845, 760, 700.

(2-cyclopentylethene-1,1-diyl)dibenzene (9aa)[18]: Colorless oil, 20 mg, yield 40%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 -7.21 (m, 3H), 7.20 – 7.10 (m, 7H), 5.90 (d, *J* = 10.0 Hz, 1H), 2.50 – 2.40 (m, 1H), 1.76 – 1.66 (m, 2H), 1.64 -1.57(m, 2H), 1.48 – 1.39 (m, 2H), 1.35 -1.28 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 139.5, 138.9, 134.4, 128.9, 127.0(3), 127.0, 126.2, 125.74, 125.6, 39.4, 33.2, 24.5. HRMS (APCI):

Organic & Biomolecular Chemistry Accepted Manuscript

calculated $C_{19}H_{21}^+$ ([M+H]$^+$): 249.1637; found: 249.1639. IR (KBr, cm^{-1}) 3055, 3021, 2952, 2860, 1598, 1494, 1444, 1073, 1030, 801, 762, 699.

2-cyclohexylethene-1,1-diyl)dibenzene (9ab)[3c]: Colorless oil, 50 mg, yield 95%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.29 (m, 3H), 7.23-7.16 (m, 7H), 5.90 (d, *J* = 9.9 Hz, 1H), 2.25-2.04 (m, 1H), 1.55-1.70 (m, 5H), 1.20-1.22 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 140.6, 139.6, 136.0, 130.0, 128.1, 128.0, 127.2, 126.8, 126.7, 38.4, 33.4, 26.0, 25.6; HRMS (APCI): calculated $C_{20}H_{23}^+$ ([M+H]$^+$): 263.1794; found: 263.1798. IR (KBr, cm^{-1}) 3080, 3056, 3021, 2922, 2850, 1632, 1579, 1495, 1445, 1073, 969, 898, 761, 700.

(2,2-diphenylvinyl)cycloheptane (9ac): Colorless oil, 30 mg, yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 7.21 (m, 7H), 6.01 (d, *J* = 10.3 Hz, 1H), 2.31 (m, *J* = 13.4, 8.9, 4.5 Hz, 1H), 1.80 – 1.67 (m, 2H), 1.68 – 1.57 (m, 2H), 1.53 – 1.32 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 140.6, 138.1, 136.6, 129.8, 128.1, 128.0, 127.2, 126.7, 126.6, 45.6, 35.0, 28.6, 26.2. HRMS (APCI): calculated $C_{21}H_{25}^+$ ([M+H]$^+$): 277.1950; found: 277.1951. IR (KBr, cm^{-1}) 3079, 3055, 3021, 2922, 2851, 1597, 1494, 1457, 1443, 1072, 761, 700.

(1-cyclohexylprop-1-en-2-yl)benzene (9bb)[21]: Colorless oil, 22 mg, yield 56%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.14 (m, 5H), 5.63 (dd, *J* = 9.0, 1.1 Hz, 0.5H), 5.27 (dd, *J* = 10.0, 1.2 Hz, 0.5H), 2.45 – 2.17 (m, 1H), 2.03 (dd, *J* = 14.7, 1.3 Hz, 3H), 1.87 1.03 (m, 11H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 142.6, 134.6, 134.2, 134.0, 132.7, 128.9, 128.1, 128.0, 127.9, 127.8, 126.4, 126.3, 125.6, 122.9, 37.7, 37.3, 33.6, 33.0, 31.9, 29.7, 26.7, 26.1, 26.0, 25.8, 25.7, 15.8. HRMS (EI): calculated $C_{15}H_{20}$: 200.1565; found: 200.1561. IR (KBr, cm^{-1}) 3056, 3022, 2922, 2850, 1659, 1633, 1447, 1260, 1025, 802, 756, 699.

General procedure for the synthesis of 10: A mixture of alkynoate (0.10 mmol), silane (2 mL) and DTBP (0.4 mmol) was sealed in a teflon septum screw-capped tube under N_2. The mixture was stirred in an oil bath at 125 °C for 12 h. After completion of the reaction, the products were obtained by flash column chromatography on silica gel with petroleum as eluent.

(2,2-diphenylvinyl)triethylsilane (10a)[22]: Colorless oil, 22 mg, yield 72%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.19 (m, 10H), 6.23 (s, 1H), 0.85 (t, *J* = 7.8, 9H), 0.76 (q, *J* = 7.8, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 143.6, 142.8, 129.5, 128.0, 127.7, 127.5, 127.3, 127.2, 126.7, 7.5, 4.4. IR (KBr, cm^{-1}) 3056, 3023, 2952, 2873, 1486, 1457, 1584, 1334, 1261, 1090, 1014, 819, 719.

(2-(4-chlorophenyl)-2-phenylvinyl)triethylsilane (10b)： Colorless oil, 24 mg, yield 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.13 (m, 9H), 6.25-6.21 (d, 1H), 0.88-0.83 (m, 9H), 0.41-0.32 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ156.8, 156.7, 143.2, 142.3, 142.1, 141.3, 133.4, 133.3, 130.9, 129.4, 128.5, 128.1(1), 128.1(0), 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.2, 7.5, 4.5, 4.4. HRMS (EI): calculated $C_{20}H_{25}SiCl$: 328.1414, found: 328.1415. IR (KBr, cm^{-1}) 2952, 2873, 1486, 1457, 1584, 1334, 1261, 1090, 1014, 819, 719, 700.

4-phenyl-3-(tetrahydrofuran-2-yl)-2H-benzo[g]chromen-2-one (12b): Pale yellow oil, 50 mg, yield 74%. ^{1}H NMR (500 MHz, CDCl3) δ 8.57 – 8.51 (m, 1H), 7.74 (dd, *J* = 6.7, 2.4 Hz, 1H), 7.56 (m, 2H), 7.50 – 7.41 (m, 4H), 7.32 – 7.27 (m, 1H), 7.18 – 7.14 (m, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 4.67 – 4.58 (m, 1H), 4.04 – 3.97 (m, 1H), 3.74 (m, 1H), 2.35 (m, 1H), 2.16 – 2.06 (m, 1H), 1.95 – 1.88 (m, 1H), 1.82 – 1.75 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 152.3, 149.0, 133.6, 133.4, 127.8, 127.7, 127.6(7), 127.6, 127.5, 127.2, 126.5, 126.0, 124.2, 122.6, 122.1, 121.8, 121.6, 114.5, 75.5, 68.6, 29.1, 26.5. HRMS (ESI): calculated $C_{23}H_{19}O_3^+$ ([M+H]$^+$): 343.1328, found: 343.1321**.** IR (KBr, cm^{-1}) 2949, 1724, 1588, 1556, 1468, 1347, 1101, 1055, 1020, 932, 818, 774, 703.

N-methyl-N-((2-oxo-4-phenyl-2H-benzo[g]chromen-3-yl) methyl) acetamide (13b): Pale yellow oil, 48 mg, yield 63%. ^{1}H NMR (500 MHz, CDCl3) δ 8.61 (m, 1H), 7.84 (m, 1H), 7.71 – 7.49 (m, 6H), 7.39 – 7.32 (m, 1H), 7.29 – 7.27 (m, 1H), 6.98 (m, 1H), 4.40 (d, 2H), 2.99 - 2.74 (m, 3H), 1.89 (m, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 170.9, 170.4, 161.4, 161.2, 155.9, 154.4, 150.4, 149.9, 134.8, 134.5, 134.1, 133.8, 129.4, 129.3, 129.1, 128.9, 128.7, 128.6, 128.3, 128.1, 127.7, 127.6, 127.4, 127.1, 124.2, 123.9, 123.0, 122.9(2), 122.9, 122.8, 122.6, 122.5, 121.1, 120.0, 115.7, 115.4, 46.6, 45.6, 37.1, 31.3, 21.7, 21.1. HRMS (ESI): calculated $C_{23}H_{20}O_3N^+$ ([M+H]$^+$): 358.1437, found: 358.1430**.** IR (KBr, cm^{-1}) 3051, 2926, 2853, 1720, 1643, 1590, 1559, 1468, 1399, 1352, 1102, 1072, 1021, 819, 799, 755, 705.

3-cyclohexyl-4-phenyl-2H-benzo[g]chromen-2-one (14b): White solid. Yield 40%, m.p. 186~189 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.1 Hz, 1H), 7.81 – 7.79 (m, 1H), 7.66 – 7.45 (m, 6H), 7.24 (dd, *J* = 7.8, 1.4 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 1H), 2.47 – 2.35 (m, 1H), 2.20 (m, 2H), 1.72 (d, 2H), 1.55 – 1.49 (m, 2H), 1.28 (m, 2H), 1.08 – 0.99 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 151.3, 149.3, 135.8, 134.0, 130.52, 128.8, 128.4, 128.2, 128.0, 127.5, 126.9, 123.4, 123.3, 122.9, 122.4, 116.0, 41.2, 29.2, 26.5, 25.5. HRMS (ESI): calculated $C_{25}H_{23}O_2^+$ ([M+H]$^+$): 355.1692, found: 355.1685**.** IR (KBr, cm^{-1}) 2922, 2851, 1718, 1632, 1588, 1553, 1504, 1469, 1449, 1351, 1101, 1067,966, 817,791, 774, 743, 714, 701.

2-(2-cyclohexyl-1-phenylvinyl)naphthalene (14a): Colorless oil. Yield 23%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.65 (m, 3H), 7.52 – 7.32 (m, 4H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.25 – 7.18 (m, 3H), 6.02 (dd, *J* = 24.9, 10.0 Hz, 1H), 2.25 – 2.16 (m, 1H), 1.69 (m, 4H), 1.27 – 1.06 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 140.5, 140.3, 139.6, 139.5, 138.1, 136.6, 136.4, 133.3, 132.4, 132.4, 129.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.5, 127.5, 127.3, 126.8, 126.8, 126.2, 125.9, 125.9, 125.7, 125.5, 125.4, 38.4, 38.3, 33.3, 26.0, 25.9, 25.6, 25.5 $C_{24}H_{25}^+$ ([M+H]$^+$): 312.1956, found: 312.1960. IR (KBr, cm^{-1}) 3054, 2922, 2849, 1654, 1632, 1492, 1445, 1264, 1073, 896, 816, 761, 746.

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Notes and references

1 (a) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.* 2013, **113**, 5322; (b) B. Zhang and A. Studer, *Chem. Soc. Rev.* 2015, **44**, 3505;(c) S. Tang, K. Liu, C. Liu and A. Lei, *Chem. Soc. Rev.* 2015, **44**, 1070;(d) J.-R. Chen, X.-Y. Yu and W.-J. Xiao, *Synthesis* 2015, **45**, 604; (e) C. Liu, D. Liu and A. Lei, *Acc. Chem. Res.* 2014, **47**, 3459;(f) H. Togo, *Advanced free radical reactions for organic synthesis*. Elsevier: UK, 2004.

2 (a) N. Fuentes, W.-Q. Kong, L. Fernández-Sánchez, E. Merino and C. Nevado, *J. Am. Chem. Soc.* 2015, **137**, 964; (b) W.-Q. Kong, N. Fuentes, A. García-Domínguez, E. Merino and C.

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Nevado, *Angew. Chem., Int. Ed.* 2015, **54**, 2487;(c) W.-Q. Kong, E. Merino and C. Nevado, *Angew. Chem., Int. Ed.* 2014, **53**, 5078; (d) W.-Q. Kong, M. Casimiro, N. Fuentes, E. Merino and C. Nevado, *Angew. Chem., Int. Ed.* 2013, **52**, 13086; (e) W.-Q. Kong, M. Casimiro, E. b. Merino and C. Nevado, *J. Am. Chem. Soc.* 2013, **135**, 14480; (f) P. Gao, Y.-W. Shen, R. Fang, X.-H. Hao, Z.-H. Qiu, F. Yang, X.-B.Yan, Q.Wang, X.-J. Gong, X.-Y. Liu and Y.-M. Liang, *Angew. Chem., Int. Ed.* 2014, **53**, 7629. (g) W. Thaharn, D.Soorukram, C. Kuhakarn, P. Tuchinda, V. Reutrakul, M. Pohmakotr, *Angew. Chem., Int. Ed.*2014, **53**, 2212. (h) A. Gheorghe, B. Quiclet-Sire, X. Vila and S. Z. Zard, *Org. Lett.*, 2005, **7**, 1653.

3 A reviews on CDC reaction involved by sp^3C radical, see: (a) "*From C-H to C-C Bonds*", Ed. by C.-J. Li, RSC, 2015. Another recent selected examples, see (b) J. Li, J. Zhang, H. Tan and D.-Z. Wang, *Org. Lett*. 2015, **17**, 2522; (c) Y. Zhu and Y. Wei, *Chem. Sci*. 2014, **5**, 2379; (d) Z. Li., Y. Zhang, L. Zhang and Z.-Q. Liu, *Org. Lett*. 2014, **16**, 382; (e) L. Chen, J. Yang, L. Li, Z. Weng and Q. Kang, *Tetrahedron Lett*. 2014, **55**, 6096; (f) F. Punner and G. Hilt, *Chem. Commun*. 2014, **50**, 7310; (g) W.-T. Wei, M.-B. Zhou, J.-H. Fan, W. Liu, R.-J. Song, Y. Liu, M. Hu, P. Xie and J.-H. Li, *Angew. Chem. Int. Ed*. 2013, **52**, 3638; (h) Z.-Q. Liu, L. Sun, J.-G Wang, J. Han, Y.-K Zhao and B. Zhou, *Org. Lett*. 2009, **11**, 1437.

4 For selected examples on silyl radicals, see: (a) C. Chatgilialoglu, *Chem. Rev.* 1995, **95**, 1229; (b) C. Chatgilialoglu and V. I. Timokhin, *Adv. Organomet. Chem*. 2008, **57**, 117; (c) L.-Z. Zhang, D. Liu and Z.-Q. Liu, *Org. Lett*. 2015, **17**, 2534; (d) L. Wang, H. Zhu, S.-J. Guo, J. Cheng and J.-T.Yu, *Chem. Comm.* 2014, **50**, 10864; (e) D. Leifert and A. Studer, *Org. Lett*. 2015, **17**, 386; (f) L.-Z, Zhang, Z.-J. Hang and Z.-Q. Liu, *Angew. Chem. Int. Ed.* 2015, DOI: 10.1002/anie.201509537.

5 Wille, U., *Chem. Rev.* 2013, **113**, 813.

6 For selected examples, see: (a) J. Marco-Contelles, *Chem. Commun*. 1996, 2629; (b) H.-Y. Lee and B. G. Kim, *Org. Lett.* 2000, **2**, 1951; (c) I. V. Alabugin, K. Gilmore, S. Patil, M. Manoharan, S. V. Kovalenko, R. J. Clark and I. Ghiviriga, *J. Am. Chem. Soc*. 2008, **130**, 11535.

7 Recent examples for the pathway 1, see: (a) W.-J. Fu, M. Zhu, G.-L. Zou, C. Xu, Z.-Q. Wang and B.-M. Ji, *J. Org. Chem.* 2015, **80**, 4766; (b) K. Yan, D.-S. Yang, W. Wei, F. Wang, Y.-Y. Shuai, Q.-N. Li and H. Wang, *J. Org. Chem.* 2015, **80**, 1550; (c) X. Mi, C.-Y. Wang, M.-M. Huang, Y.-S. Wu and Y.-J. Wu, *J. Org. Chem.* 2015, **80**, 148; (d) X. Mi, C.-Y. Wang, M.-M. Huang, J.-Y. Zhang, Y.-S. Wu and Y.-J. Wu, *Org. Lett.* 2014, **16**, 3356; (e) Y.-W. Li, Y. Lu, G. Qiu and Q.-P. Ding, *Org. Lett.* 2014, **16**, 4240; (f) W. Wei, J.-W. Wen, D.-S. Yang, M.-Y. Guo, Y.-Y. Wang, J.-M. You and H. Wang, *Chem. Commun.* 2015, *51*, 768; (g) A. C. Mantovani, T. A. Goulart, D. F. Back, P. H. Menezes and G. Zeni, *J. Org. Chem.* 2014, **79**, 10526; (h) W.-C. Yang, S. Yang, P.-H. Li, and L. Wang, *Chem. Commun*. 2015, ***51***, 7520; (i) T. Liu, Q.-P. Ding, Q.-S. Zong and G. Qiu, *Org. Chem. Front*. 2015, ***2***, 670.

8 Selected examples for the pathway 2, see: (a) W.-T. Wei, R.-J. Song, X.-H. Ouyang, Y. Li, H.-B. Li, and J.-H. Li, *Org. Chem. Front.* 2014, **1**, 484; (b) H.-L. Hua, Y.-T. He, Y.-F. Qiu, Y.-X. Li, B. Song, P. Gao, X.-R. Song, D.-H. Guo, X.-Y. Liu and Y.-M. Liang, *Chem. - Eur. J.* 2015, **21**, 1468.

9 (a) J. Li, J. Zhang, H. Tan and D.-Z. Wang, *Org. Lett.*, 2015, ***17***, 2522; (b) L. Chen, J.-J. Yang, L. Li and Z.-Q. Weng, *Tetrahedron Lett.* 2014, **55**, 6096; (c) F. Punner and G. Hilt, *Chem. Commun*. 2014, ***50***, 7310; (d) R.-A. Doohan, J.-J. Hannan and N. W. A. Geraghty, *Org. Biomol. Chem*, 2006, **4**, 942.

10 For reviews on aryl-migration, see: (a) A. Studer and M Bossart, *Tetrahedron* 2001, **57**, 9649; (b) Z.-M. Chen, X.-M. Zhang and Y.-Q. Tu, *Chem. Soc. Rev.* 2015, **44**, 5220.

11 (a) Z. Cong, T. Miki, O.Urakawa and H. Nishino, *J. Org. Chem.* 2009, **74**, 3978; (b) W. R. Bowman, E. Mann and J. Parr, *J. Chem. Soc., PerkinTrans. 1*, 2000, 2991

12 S.-Y. Ni, Y. Zhang, C. Xie, H.-B. Mei, J.-L, Han and Y. Pan,*Org. Lett.*, 2015, **17**, 5524.

13 For references on generation of sp^3 carbon-centered radical through homolytic cleavage initiated by peroxides, see: (a) D. Liu, C. Liu, H. Li and A.-W. Lei, *Angew. Chem., Int. Ed.* 2013, **52**, 4453; (b) L.-L. Zhou, S. Tang, X.-T. Qi, C.-T. Lin, K. Liu, C. Liu, Y. Lan and A.-W. Lei, *Org. Lett.*, 2014, **16**, 3404; (c) D. Liu, Y.-X. Li, X.-T. Qi, C. Liu, Y. Lan and A.-W. Lei, *Org. Lett*., 2015, **17**, 998. (d) Z. Cui, X. Shang, X.-F. Shao and Z.-Q. Liu, *Chem. Sci.* 2012, **3**, 2853; (e) Z. Li, Z. Cui and Z.-Q. Liu, *Org. Lett.* 2013, **15**, 406; (f) Z. Li, F. Fan, J. Yang and Z.-Q. Liu, *Org. Lett.* 2014, **16**, 3396; (g) L. Zhang, Z. Li and Z.-Q. Liu, *Org. Lett.* 2014, **16**, 3688; (h) Y. Tian and Z.-Q. Liu, *RSC Adv.* 2014, **4**, 64855; (i) Z. Li, Y. Xiao and Z.-Q. Liu, *Chem. Commun.* 2015, **51**, 9969.

14 (a) A. Stuetz, A. Georgopoulos, W. Granitzer, G. Petranyi, and D. Berney, *J. Med. Chem*. 1986, **29**, 112; (b) P. Prediger, L. F. Barbosa, Y. Genisson, and C. R. D. Correia, *J. Org. Chem.* 2011, **76**, 7737; (c) J. Limberger, T. S. Claudino, and A. L. Monteiro, *RSC Adv.* 2014, **4**, 45558; (d) Prediger, P.; da Silva, A. R.; Correia, C. R. D. *Tetrahedron*, 2014, **70**, 3333.

15 D. Rossi, A. Pedrali, M. Urbano, R. Gaggeri, M. Serra, L. Fernández, M. Fernández, J. Caballero, S. Ronsisvalle, O. Prezzavento, D. Schepmann, B. Wuensch, M.Peviani, D. Curti, O. Azzolina and S. Collina, *Bioorg. Med. Chem.* 2011, **19**, 6210.

16 (a) Z. Jiang, L.-J. Zhang, C-N. Dong, B.-D. Ma, W.-J. Tang, L.-J. Xu, Q-H. Fan, J.-L. Xiao, *Tetrahedron*. 2012, **68**, 4919; (b) Z.-S. Ye, T. F. Brust, V. J. Watts, and M. Dai, *Org. Lett.* 2015, **17**, 892.

17 (a) T. P. Goumans, M. K. van Alem and G. Lodder, *Eur. J. Org. Chem.* 2008, 435; (b) P. R. Jenkins, M. C. Symons, S. E. Booth and C. J. Swain, *Tetrahedron Lett.* 1992, **33**, 3543;(c) D. P. Curran, N. A. Porter and B. Giese, *Stereochemistry of radical reactions: concepts, guidelines, and synthetic applications*. Germany: Wiley-VCH Verlag: Weinheim, 1996.

18 H.-D. Gu, C.-Y. Wang, *Org. Biomol. Chem.* 2015, ***13***, 5880.

19 D. Liu, C. Liu, H. Li and A.-W. Lei, *Chem. Commun*. 2014, **50**, 3623.

20 C. L. Ricardo, X. Mo, J. A. McCubbin and D. G. Hall, *Chem. - Eur. J*. 2015, **21**, 4218.

21 A. Krasovskiy, C. Duplais and B. H. Lipshutz, *Org. Lett.* 2010, **12**, 4742.

22 W. Kong, C. Che, J.-L. Wu, L.-A. Ma and G.-G. Zhu, *J. Org. Chem.* 2014, **79**, 5799.

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