

Advanced
**Synthesis &
Catalysis**

Supporting Information

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Copper (II) triflate Catalyzed Nucleophilic Substitution of Propargylic Acetates with Enoxysilanes. A Straightforward Synthetic Route to Polysubstituted Furans

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General methods and materials. Melting points are uncorrected. NMR spectra were in CDCl₃ (¹H at 400 MHz and ¹³C at 100 MHz). Column chromatography was performed on silica gel (300-400 mesh). Unless otherwise noted, all reagents were obtained commercially and used without further purification. Acetonitrile and toluene were distilled over Phosphorus pentoxide.

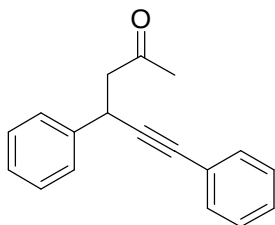
General procedure for synthesis of α -Alkynyl ketones. To a 5-mL flask, propargylic acetate **1** (0.5 mmol), enoxysilane **2** (1.5 mmol), CH₃CN (1.0 mL), and Cu(OTf)₂ (0.005 mmol) were successively added, the reaction mixture was stirred at room temperature, and monitored periodically by TLC. Upon completion, the solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified by silica gel column chromatography (EtOAc/hexane) to afford corresponding α -alkynyl ketones **3** and allenyl isomers **4**.

General procedure for synthesis of substituted furans. To a 10-mL flask, propargylic acetate **1** (0.5 mmol), enoxysilane **2** (1.5 mmol), CH₃CN (1.0 mL) and Cu(OTf)₂ (0.005 mmol) were successively added, the reaction mixture was stirred at room temperature, and monitored periodically by TLC. Upon completion, the solvent was removed under reduced pressure by an aspirator, followed by the addition of toluene (6.0 mL) and a stoichiometric amount of 4-methylbenzenesulfonic acid (0.5 mmol). The reaction was heated to reflux and monitored by TLC. When completed, toluene was concentrated under reduced pressure by an aspirator, and then the residue was purified by silica gel column chromatography (hexane) to afford corresponding furans **6**.

Procedure for synthesis of substituted furan 6bf. To a 10-mL flask, propargylic acetate **1b** (1.5 mmol, 0.345 g), enoxysilane **2f** (0.5 mmol, 0.153 g), CH₃CN (1.0 mL) and Cu(OTf)₂ (0.005 mmol, 0.002 g) were successively added, the reaction mixture was stirred at room temperature, and monitored periodically by TLC. Upon reaction completion, the solvent CH₃CN was removed under reduced pressure by an aspirator, followed by the addition of toluene (6.0 mL) and 4-methylbenzenesulfonic acid (1.0 mmol, 0.172 g). The reaction was heated to reflux and monitored by TLC. When completed, toluene was

concentrated under reduced pressure by an aspirator, and then the residue was purified by silica gel column chromatography (hexane) to afford corresponding substituted furan **6bf** (0.166 g, 66 % yield).

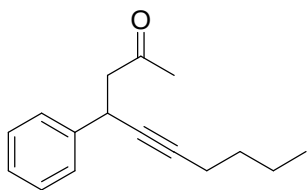
4,6-Diphenylhex-5-yn-2-one (3aa) ^[1]:



Yield 87%. A yellow oil. ¹H NMR (CDCl₃, 400 MHz): d 2.21 (s, 3H), 2.94 (dd, 1H, *J* = 16.4 and 6.4 Hz), 3.06 (dd, 1H, *J* = 16.4 and 8.4 Hz), d 4.41 (dd, 1H, *J* = 8 and 6.4 Hz), 7.22-7.30 (m, 4H), 7.31-7.37 (m, 2H), 7.39-7.47 (m, 4H) ppm; ¹³C NMR (CDCl₃, 100 MHz): d 30.1, 33.6, 51.9, 83.3, 90.4, 123.3, 127.2, 127.5, 128.0, 128.2, 128.7, 131.7, 141.0, 205.8 ppm; IR (film): 3055, 3024, 1715, 1594, 1487, 1452 cm⁻¹; ESI-MS: *m/z* (%) = 271(100) [M+Na⁺], 287(89) [M+K⁺].

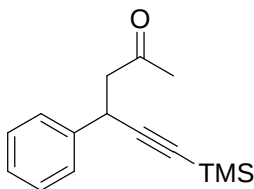
Data are in accordance with previously reported results. ^[1]

4-Phenyldec-5-yn-2-one (3ba) ^[2]:



Yield 81% . A yellow oil. ¹H NMR (CDCl₃, 400 MHz): d 0.90 (t, 3H, *J* = 7.2 Hz), 1.34-1.53 (m, 4H), 2.14 (s, 3H), 2.20 (td, 2H, *J* = 7.2 and 2 Hz), d 2.75 (dd, 1H, *J* = 16 and 6 Hz), d 2.91 (dd, 1H, *J* = 16 and 8.8 Hz), 4.15 (ddt, 1H, *J* = 8.6, 6.4 and 2 Hz), 7.22 (tt, 1H, *J* = 7.2, and 1.2 Hz), 7.28-7.34 (m, 2H), 7.35-7.40 (m, 2H) ppm; ¹³C NMR (CDCl₃, 100 MHz): d 13.6, 18.5, 21.9, 30.7, 31.0, 33.2, 52.4, 80.6, 83.6, 126.9, 127.3, 128.6, 141.6, 206.2 ppm; IR (film): 3058, 3025, 1715, 1594, 1495, 1450 cm⁻¹; ESI-MS: *m/z* (%) = 251(72) [M+Na⁺], 267(100) [M+K⁺].

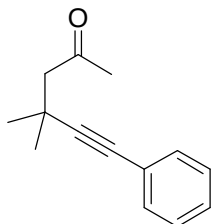
4-Phenyl-6-(trimethylsilyl)hex-5-yn-2-one (3ca):



Yield 88%. A colorless oil. ¹H NMR (CDCl₃, 400 MHz): d 0.16 (s, 9H), 2.14 (s, 3H), 2.87 (dd, 1H, *J* = 16.4 and 6.4 Hz), 2.96 (dd, 1H, *J* = 16 and 8 Hz), 4.21 (dd, apparent t, 1H, *J* = 7.2 Hz), 7.20-7.26 (m, 1H), 7.32 (dd, apparent t, 2H, *J* = 7.6 Hz), 7.37 (apparent d, 2H, *J* = 7.6 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz): d 0.0, 30.7, 33.9, 52.0, 87.5, 107.0, 127.0, 127.4, 128.6, 140.6, 205.8 ppm; IR (film): 3063,

3030, 2173, 1721, 1603, 1494, 1455 cm^{-1} ; **ESI-MS**: m/z (%) = 267(100) $[\text{M}+\text{Na}^+]$, 283(4) $[\text{M}+\text{K}^+]$; **Anal** calcd for $\text{C}_{15}\text{H}_{20}\text{OSi}$: C, 73.71; H, 8.25. Found: C, 73.65; H, 8.00.

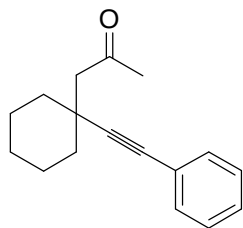
4,4-Dimethyl-6-phenylhex-5-yn-2-one (3da)^[1]:



Yield 91%. A colorless oil. **^1H NMR** (CDCl_3 , 400 MHz): δ 1.39 (s, 6H), 2.29 (s, 3H), 2.61 (s, 2H), 7.18-7.29 (m, 3H), 7.31-7.40 (m, 2H) ppm; **^{13}C NMR** (CDCl_3 , 100 MHz): δ 29.5, 30.1, 31.8, 55.5, 81.2, 95.7, 123.5, 127.8, 128.2, 131.5, 207.4 ppm; **IR** (film): 3058, 3027, 2229, 1714, 1594, 1487, 1451 cm^{-1} ; **ESI-MS**: m/z (%) = 201(17) $[\text{M}+\text{H}^+]$, 223(100) $[\text{M}+\text{Na}^+]$, 239(9) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[1]

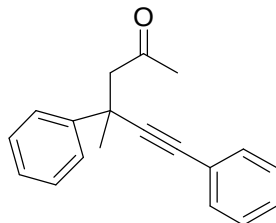
1-(1-(2-Phenylethynyl)cyclohexyl)propan-2-one (3ea)^[1]:



Yield 80%. A colorless oil. **^1H NMR** (CDCl_3 , 400 MHz): δ 1.11-1.27 (m, 1H), 1.36 (td, 2H, J = 12.8 and 3.6 Hz), 1.56-1.82 (m, 5H), 1.90 (apparent d, 2H, J = 12.8 Hz), 2.32 (s, 3H), 2.60 (s, 2H), 7.27-7.31 (m, 3H), 7.39-7.44 (m, 2H) ppm; **^{13}C NMR** (CDCl_3 , 100 MHz): δ 22.9, 25.8, 32.2, 35.5, 38.0, 55.8, 84.2, 93.8, 123.6, 127.8, 128.2, 131.5, 207.6 ppm; **IR** (film): 3054, 3081, 2225, 1707, 1599, 1490, 1443 cm^{-1} ; **ESI-MS**: m/z (%) = 263(88) $[\text{M}+\text{Na}^+]$, 279(100) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[1]

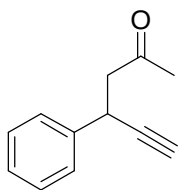
4-Methyl-4,6-diphenylhex-5-yn-2-one (3fa)^[1]:



Yield 81%. A colorless oil. **^1H NMR** (CDCl_3 , 400 MHz): δ 1.76 (s, 3H), 2.11 (s, 3H), 2.94 (d, 1H, J = 14 Hz), 3.07 (d, 1H, J = 14 Hz), 7.23-7.29 (m, 1H), 7.29-7.40 (m, 5H), 7.45-7.51 (m, 2H), 7.59-7.65 (m, 2H) ppm; **^{13}C NMR** (CDCl_3 , 100 MHz): δ 31.1, 31.5, 38.7, 56.6, 84.6, 93.5, 123.2, 125.8, 126.9, 128.1, 128.3, 128.5, 131.6, 144.4, 205.4 ppm; **IR** (film): 3055, 3023, 1725, 1596, 1491, 1444 cm^{-1} ; **ESI-MS**: m/z (%) = 263(4) $[\text{M}+\text{H}^+]$, 285(100) $[\text{M}+\text{Na}^+]$, 301(49) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[1]

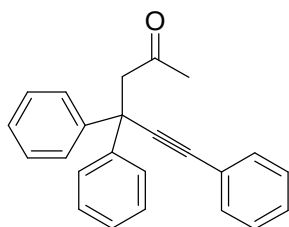
4-Phenylhex-5-yn-2-one (3ga)^[3]:



Yield 82%. A yellow oil. ¹H NMR (CDCl₃, 400 MHz): d 2.14 (s, 3H), 2.26 (d, 1H, *J* = 2.4 Hz), 2.82 (dd, 1H, *J* = 16.8 and 6 Hz), d 3.00 (dd, 1H, *J* = 16.8 and 8.4 Hz), 4.20 (ddd, 1H, *J* = 8.4, 6 and 2.4 Hz), 7.20-7.27 (m, 1H), 7.28-7.35 (m, 2H), 7.36-7.41 (m, 2H) ppm; ¹³C NMR (CDCl₃, 100 MHz): d 30.6, 32.6, 51.6, 71.1, 85.0, 127.2, 127.4, 128.8, 140.3, 205.5 ppm; IR (film): 3289, 3062, 3030, 2116, 1719, 1598, 1494, 1451 cm⁻¹; ESI-MS: *m/z* (%) = 173(15) [M+H⁺], 195(100) [M+Na⁺], 211(37) [M+K⁺].

Data are in accordance with previously reported results.^[3]

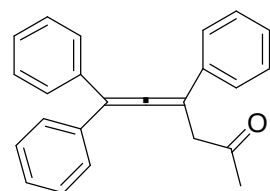
4,4,6-Triphenylhex-5-yn-2-one (3ha)^[1]:



Yield 53%. A pale yellow solid. (m.p. 91-94°C). ¹H NMR (CDCl₃, 400 MHz): d 2.12 (s, 3H), 3.50 (s, 2H), 7.20-7.26 (m, 2H), 7.29-7.36 (m, 7H), 7.47-7.55 (m, 6H) ppm; ¹³C NMR (CDCl₃, 100 MHz): d 31.3, 47.2, 55.3, 86.7, 92.7, 123.1, 127.0, 127.1, 128.3, 128.3, 128.5, 131.7, 144.3, 205.6 ppm; IR (film): 3059, 3029, 1723, 1594, 1491, 1445 cm⁻¹; ESI-MS: *m/z* (%) = 347(100) [M+Na⁺], 363(3) [M+K⁺].

Data are in accordance with previously reported results.^[1]

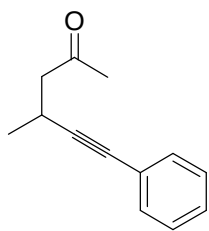
4,6,6-Triphenylhexa-4,5-dien-2-one (4ha)^[1]:



Yield 37%. A pale yellow solid. (m.p. 72-73°C). ¹H NMR (CDCl₃, 400 MHz): d 2.12 (s, 3H), 3.68 (s, 2H), 7.20-7.26 (m, 1H), 7.27-7.38 (m, 8H), 7.39-7.46 (m, 6H) ppm; ¹³C NMR (CDCl₃, 100 MHz): d 29.1, 46.5, 103.1, 113.3, 125.9, 127.6, 127.8, 128.5, 128.6, 128.9, 134.9, 136.0, 206.7, 208.4 ppm; IR (film): 3054, 3025, 1952, 1713, 1594, 1492, 1441 cm⁻¹; ESI-MS: *m/z* (%) = 325(2) [M+H⁺], 347(100) [M+Na⁺], 363(2) [M+K⁺].

Data are in accordance with previously reported results.^[1]

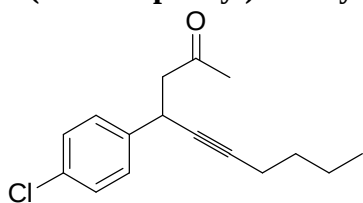
4-Methyl-6-phenylhex-5-yn-2-one (3ia)^[1]:



Yield 36%. A pale yellow oil. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): d 1.28 (d, 3H, $J = 6.8$ Hz), 2.21 (s, 3H), 2.59 (dd, 1H, $J = 16.4$ and 6.8 Hz), 2.78 (dd, 1H, $J = 16.4$ and 7.2 Hz), 3.18 (ddq, apparent sextet, 1H, $J = 6.8$, 6.8 and 6.8 Hz), 7.25-7.31 (m, 3H), 7.35-7.40 (m, 2H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): d 20.9, 22.2, 30.5, 50.3, 80.9, 93.0, 123.5, 127.7, 128.2, 131.5, 206.7 ppm; **IR** (film): 3054, 2233, 1717, 1598, 1489, 1443 cm^{-1} ; **ESI-MS**: m/z (%) = 209(100) $[\text{M}+\text{Na}^+]$.

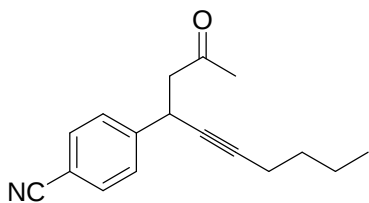
Data are in accordance with previously reported results.^[1]

4-(4-chlorophenyl)dec-5-yn-2-one (3ka):



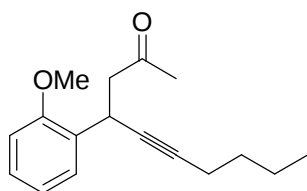
Yield 85% . A yellow oil. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): d 0.92 (t, 3H, $J = 7.2$ Hz), 1.37-1.45 (m, 2H), 1.45-1.54 (m, 2H), 2.15 (s, 3H), 2.21 (td, 2H, $J = 7.2$ and 2.4 Hz), 2.75 (dd, 1H, $J = 16.4$ and 6.4 Hz), 2.91 (dd, 1H, $J = 16.4$ and 8.0 Hz), 4.15 (ddt, 1H, $J = 8.2$, 6.4 and 2.4 Hz), 7.24-7.37 (m, 4H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): d 13.6, 18.4, 21.9, 30.6, 30.9, 32.5, 52.1, 80.1, 83.8, 128.6, 128.8, 132.6, 140.2, 205.8 ppm; **IR** (film): 3076, 1716, 1585, 1482, 1085 cm^{-1} ; **ESI-MS**: m/z (%) = 263(17) $[\text{M}+\text{H}^+]$, 285(100) $[\text{M}+\text{Na}^+]$. **Anal** calcd for $\text{C}_{16}\text{H}_{19}\text{ClO}$: C, 73.13; H, 7.29. Found: C, 73.21; H, 7.17.

4-(2-oxodec-5-yn-4-yl)benzonitrile (3la):



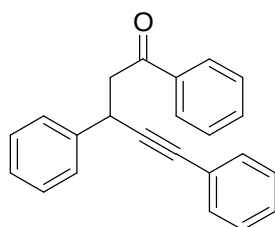
Yield 78% . A pale yellow oil. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): d 0.91 (t, 3H, $J = 7.2$ Hz), 1.35-1.53 (m, 4H), 2.15 (s, 3H), 2.20 (td, 2H, $J = 6.8$ and 2.2 Hz), 2.77 (dd, 1H, $J = 16.8$ and 6.4 Hz), 2.91 (dd, 1H, $J = 16.8$ and 7.6 Hz), 4.22 (dd, apparent t, 1H, $J = 7.2$ Hz), 7.50 (d, 2H, $J = 8.4$ Hz), 7.60 (d, 2H, $J = 8.4$ Hz) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): d 13.6, 18.3, 21.9, 30.5, 30.8, 32.9, 51.6, 79.3, 84.5, 110.8, 118.7, 128.3, 132.3, 147.1, 205.1 ppm; **IR** (film): 3055, 2216, 1716, 1607, 1497, 1463 cm^{-1} ; **ESI-MS**: m/z (%) = 276(100) $[\text{M}+\text{Na}^+]$. **Anal** calcd for $\text{C}_{17}\text{H}_{19}\text{NO}$: C, 80.60; H, 7.56, N, 5.53. Found: C, 80.72; H, 7.44, N, 5.65.

4-(2-methoxyphenyl)dec-5-yn-2-one (3ma):



Yield 89% . A pale yellow oil. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 0.91 (t, 3H, $J = 7.2$ Hz), 1.35-1.45 (m, 2H), 1.45-1.54 (m, 2H), 2.19 (s, 3H), 2.21 (td, 2H, $J = 7$ and 2.4 Hz), 2.70 (dd, 1H, $J = 15.6$ and 9.6 Hz), 2.78 (dd, 1H, $J = 15.2$ and 4.8 Hz), 3.82 (s, 3H), 4.50 (ddt, 1H, $J = 7.2$, 4.8 and 2.4 Hz), 6.84 (d, 1H, $J = 8$ Hz), 6.96 (t, 1H, $J = 7.6$ Hz), 7.22 (td, 1H, $J = 8$ and 1.2 Hz), 7.57 (dd, 1H, $J = 7.2$ and 1.6 Hz) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 13.6, 18.5, 21.9, 27.6, 30.2, 31.1, 50.6, 55.3, 80.3, 83.4, 110.3, 120.6, 128.0, 128.5, 129.4, 156.0, 206.9 ppm; **IR** (film): 3070, 3005, 1713, 1601, 1494, 1451 cm^{-1} ; **ESI-MS**: m/z (%) = 281(100) $[\text{M}+\text{Na}^+]$. **Anal** calcd for $\text{C}_{17}\text{H}_{22}\text{O}_2$: C, 79.03; H, 8.58. Found: C, 79.21; H, 8.45.

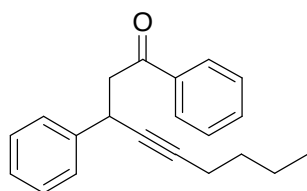
1,3,5-Triphenylpent-4-yn-1-one (3ab) ^[4]:



Yield 88%. A white solid. (m.p. 89-90°C). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 3.50 (dd, 1H, $J = 16.8$ and 6.4 Hz), 3.75 (dd, 1H, $J = 16.4$ and 8.0 Hz), 4.74 (dd, apparent t, 1H, $J = 6.8$ and 6.8 Hz), 7.32-7.37 (m, 4H), 7.41-7.47 (m, 4H), 7.53 (apparent t, 2H, $J = 8.0$ Hz), 7.60-7.66 (m, 3H), 8.05 (apparent d, 2H, $J = 8.0$ Hz) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 33.8, 47.3, 83.4, 90.8, 123.4, 127.2, 127.7, 127.9, 128.2, 128.3, 128.7, 128.8, 131.7, 133.3, 136.9, 141.3, 197.1 ppm; **IR** (film): 3061, 3030, 2229, 1687, 1597, 1490, 1449 cm^{-1} ; **ESI-MS**: m/z (%) = 311(6) $[\text{M}+\text{H}^+]$, 333(100) $[\text{M}+\text{Na}^+]$, 349(5) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results. ^[4]

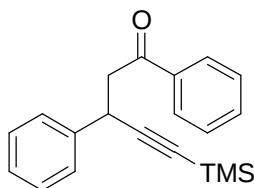
1,3-Diphenylnon-4-yn-1-one (3bb) ^[5]:



Yield 93%. A pale yellow oil. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 0.85 (t, 3H, $J = 7.2$ Hz), 1.29-1.45 (m, 4H), 2.15 (td, 2H, $J = 6.0$ and 1.2 Hz), 3.25 (dd, 1H, $J = 16.4$ and 6 Hz), 3.52 (dd, 1H, $J = 16.4$ and 8.0 Hz), 4.39 (dd, apparent t, 1H, $J = 6.2$ and 6.2 Hz), 7.19-7.25 (m, 1H), 7.32 (apparent t, 2H, $J = 7.2$ Hz), 7.44 (apparent t, 4H, $J = 7.2$ Hz), 7.55 (apparent t, 1H, $J = 7.2$ Hz), 7.93 (apparent d, 2H, $J = 7.2$ Hz) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 13.6, 18.5, 21.9, 31.0, 33.4, 47.7, 80.9, 83.6, 126.9, 127.5, 128.2, 128.5, 128.6, 133.1, 137.0, 142.0, 197.5 ppm; **IR** (film): 3061, 3028, 1687, 1597, 1493, 1448 cm^{-1} ; **ESI-MS**: m/z (%) = 291 (5) $[\text{M}+\text{H}^+]$, 313 (100) $[\text{M}+\text{Na}^+]$, 329 (7) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[5]

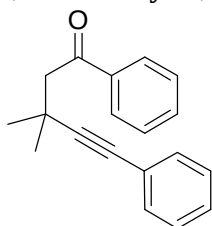
1,3-Diphenyl-5-(trimethylsilyl)pent-4-yn-1-one (3cb)^[6]:



Yield 92%. A colorless oil. ¹H NMR (CDCl₃, 400 MHz): δ 0.9 (s, 9H), 3.21 (dd, 1H, *J* = 16.4 and 6.4 Hz), 3.46 (dd, 1H, *J* = 16.4 and 7.6 Hz), 4.37 (dd, apparent t, 1H, *J* = 7.2 and 7.2 Hz), 7.13 (tt, 1H, *J* = 7.6 and 2.4 Hz), 7.20-7.26 (m, 1H), 7.30-7.38 (m, 4H), 7.44 (tt, 2H, *J* = 7.6 and 1.2 Hz), 7.81-7.86 (m, 2H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ 0.1, 34.2, 47.4, 87.5, 107.4, 127.1, 127.6, 128.3, 128.6, 128.7, 133.2, 137.0, 141.0, 197.2 ppm; IR (film): 3062, 3029, 2173, 1688, 1598, 1494, 1449, 840 cm⁻¹; ESI-MS: *m/z* (%) = 329(100) [M+Na⁺].

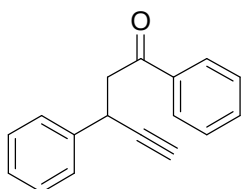
Data are in accordance with previously reported results.^[6]

3,3-Dimethyl-1,5-diphenylpent-4-yn-1-one (3db):



Yield 96%. A pale yellow solid. (m.p. 39-41°C). ¹H NMR (CDCl₃, 400 MHz): δ 1.49 (s, 6H), 3.18 (s, 2H), 7.13-7.17 (m, 2H), 7.18-7.22 (m, 3H), 7.42-7.47 (m, 2H), 7.54 (tt, 1H, *J* = 7.2 and 1.6 Hz), 8.00-8.04 (m, 2H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ 29.7, 30.7, 49.5, 81.3, 96.1, 123.5, 127.6, 128.0, 128.5, 128.6, 131.5, 132.9, 138.0, 198.5 ppm; IR (film): 3059, 2235, 1685, 1598, 1489, 1448 cm⁻¹; ESI-MS: *m/z* (%) = 263(4) [M+H⁺], 285(100) [M+Na⁺], 301(4) [M+K⁺]. Anal calcd for C₁₉H₁₈O: C, 86.99; H, 6.92. Found: C, 86.72; H, 7.17.

1,3-Diphenylpent-4-yn-1-one (3gb)^[3]:

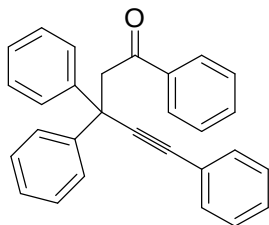


Yield 84%. A pale yellow solid. (m.p. 86-88°C). ¹H NMR (CDCl₃, 400 MHz): δ 2.25 (d, 1H, *J* = 2.4 Hz), 3.35 (dd, 1H, *J* = 17.0 and 5.2 Hz), 3.60 (dd, 1H, *J* = 17.0 and 8.0 Hz), 4.44 (ddd, 1H, *J* = 8.2, 6.0 and 2.4 Hz), 7.21-7.39 (m, 3H), 7.41-7.62 (m, 5H), 7.91-7.96 (m, 2H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ 32.6, 47.1, 71.0, 85.3, 127.2, 127.5, 128.1, 128.6, 128.7, 133.3, 136.6, 140.6, 196.7 ppm; IR (film): 3288, 3061,

3027, 2116, 1688, 1597, 1495, 1449 cm^{-1} ; **ESI-MS**: m/z (%) = 235(7) $[\text{M}+\text{H}^+]$, 257(100) $[\text{M}+\text{Na}^+]$, 273(8) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[3]

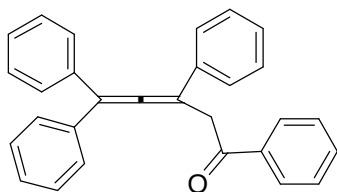
1,3,3,5-Tetraphenylpent-4-yn-1-one (3hb)^[1]:



Yield 38%. A white solid. (m.p. 91-92°C). **¹H NMR** (CDCl_3 , 400 MHz): δ 4.01 (s, 2H), 7.14-7.21 (m, 5H), 7.21-7.29 (m, 6H), 7.33 (t, 2H, $J = 7.2$ Hz), 7.41-7.49 (m, 5H), 7.81-7.89 (m, 2H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 47.6, 49.1, 86.3, 93.1, 123.3, 126.8, 127.2, 128.0, 128.1, 128.3, 128.4, 128.5, 131.7, 132.9, 137.7, 144.7, 195.8 ppm; **IR** (film): 3058, 3028, 2221, 1665, 1597, 1489, 1448 cm^{-1} ; **ESI-MS**: m/z (%) = 409(100) $[\text{M}+\text{Na}^+]$.

Data are in accordance with previously reported results.^[1]

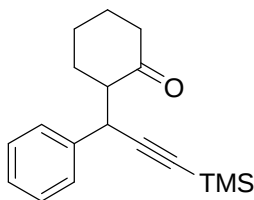
1,3,5,5-Tetraphenylpenta-3,4-dien-1-one (4hb)^[1]:



Yield 52%. A white solid. (m.p. 126-127°C). **¹H NMR** (CDCl_3 , 400 MHz): δ 4.13 (s, 2H), 7.04-7.16 (m, 14H), 7.19-7.28 (m, 2H), 7.37 (d, 2H, $J = 7.6$ Hz), 7.75 (d, 2H, $J = 7.6$ Hz) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 41.3, 103.9, 114.0, 125.8, 127.4, 127.5, 128.3, 128.4, 128.5, 128.7, 132.9, 135.1, 135.7, 136.1, 197.5, 208.5 ppm; **IR** (film): 3054, 3024, 1932, 1682, 1596, 1491, 1446 cm^{-1} ; **ESI-MS**: m/z (%) = 387(11) $[\text{M}+\text{H}^+]$, 409(100) $[\text{M}+\text{Na}^+]$, 425(18) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[1]

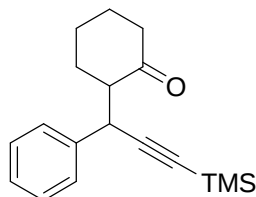
2-(1-Phenyl-3-(trimethylsilyl)prop-2-ynyl)cyclohexanone (3cc-1, one of the two diastereomers):



Yield 33%. A pale yellow oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 0.18 (s, 9H), 1.53-1.92 (m, 4H), 1.98-2.12 (m, 2H), 2.25 (dt, 1H, $J = 14.0$ and 6.0 Hz), 2.42-2.55 (m, 2H), 4.45 (d, 1H, $J = 4.8$ Hz), 7.22 (tt, 1H, $J = 7.2$ and 1.6 Hz), 7.28-7.33 (m, 2H), 7.34-7.38 (m, 2H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 0.2, 24.8, 27.3, 29.1, 37.4, 42.1, 56.8, 89.2, 105.7, 126.7, 128.1, 128.3, 140.4, 209.8 ppm; **IR** (film): 3058, 3027,

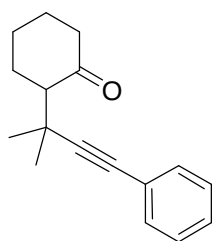
2172, 1713, 1601, 1494, 1452, 844 cm^{-1} ; **ESI-MS**: m/z (%) = 285(5) $[\text{M}+\text{H}^+]$, 307(100) $[\text{M}+\text{Na}^+]$, 323(3) $[\text{M}+\text{K}^+]$; **Anal** calcd for $\text{C}_{19}\text{H}_{18}\text{O}$: C, 76.00; H, 8.50. Found: C, 76.25; H, 8.55.

2-(1-Phenyl-3-(trimethylsilyl)prop-2-ynyl)cyclohexanone (3cc-2, one of the two diastereomers):



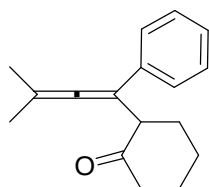
Yield 60%. A white solid. (m.p. 48-50°C). ^1H NMR (CDCl_3 , 400 MHz): δ 0.18 (s, 9H), 1.16-1.25 (m, 1H), 1.57-1.62 (m, 2H), 1.78-2.02 (m, 3H), 2.28-2.47 (m, 2H), 2.73-2.81 (m, 1H), 4.26 (d, 1H, J = 6.4 Hz), 7.22 (tt, 1H, J = 7.2 and 1.2 Hz), 7.25-7.32 (m, 2H), 7.35-7.40 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz): δ 0.1, 24.6, 27.5, 30.5, 37.2, 42.0, 57.2, 86.6, 108.0, 126.9, 128.1, 129.0, 138.7, 209.9 ppm; **IR** (film): 3059, 3029, 2171, 1713, 1601, 1494, 1451, 841 cm^{-1} ; **ESI-MS**: m/z (%) = 285(4) $[\text{M}+\text{H}^+]$, 307(100) $[\text{M}+\text{Na}^+]$, 323(51) $[\text{M}+\text{K}^+]$; **Anal** calcd for $\text{C}_{19}\text{H}_{18}\text{O}$: C, 76.00; H, 8.50. Found: C, 75.76; H, 8.37.

2-(2-Methyl-4-phenylbut-3-yn-2-yl)cyclohexanone (3dc):



Yield 55%. A colorless oil. ^1H NMR (CDCl_3 , 400 MHz): δ 1.40 (s, 3H), 1.43 (s, 3H), 1.66-1.79 (m, 3H), 1.95-2.10 (m, 2H), 2.29-2.45 (m, 4H), 7.23-7.30 (m, 3H), 7.35-7.40 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz): δ 25.4, 25.7, 28.1, 28.3, 30.7, 33.1, 43.7, 59.2, 80.9, 96.9, 124.0, 127.5, 128.1, 131.6, 211.0 ppm; **IR** (film): 3079, 3050, 2225, 1711, 1598, 1490, 1460 cm^{-1} ; **ESI-MS**: m/z (%) = 263(100) $[\text{M}+\text{Na}^+]$; **Anal** calcd for $\text{C}_{17}\text{H}_{20}\text{O}$: C, 84.96; H, 8.39. Found: C, 84.69; H, 8.36.

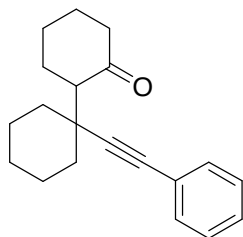
2-(3-Methyl-1-phenylbuta-1,2-dienyl)cyclohexanone (4dc):



Yield 33%. A white solid. (m.p. 41-42°C). ^1H NMR (CDCl_3 , 400 MHz): δ 1.69-1.78 (m, 1H), 1.81 (s, 3H), 1.82 (s, 3H), 1.85-2.04 (m, 4H), 2.05-2.16 (m, 1H), 2.38-2.44 (m, 1H), 2.49-2.55 (m, 1H), 3.54 (dd, 1H, J = 8.8 and 5.6 Hz), 7.10-7.21 (m, 1H), 7.22-7.35 (m, 4H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz): δ 20.1, 20.4, 24.0, 28.0, 33.1, 41.7, 52.0, 100.0, 103.0, 126.3, 128.2, 137.5, 202.8, 211.1 ppm; **IR** (film): 3046,

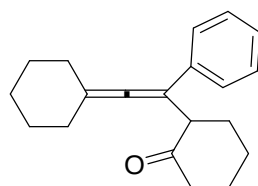
3025, 1951, 1711, 1597, 1494, 1446 cm^{-1} ; **ESI-MS**: m/z (%) = 263(100) $[\text{M}+\text{Na}^+]$; **Anal** calcd for $\text{C}_{17}\text{H}_{20}\text{O}$: C, 84.96; H, 8.39. Found: C, 84.77; H, 8.23.

2-(1-(2-Phenylethynyl)cyclohexyl)cyclohexanone (3ec):



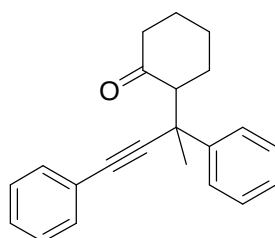
Yield 46%. A white solid. (m.p. 76-77°C). ^1H NMR (CDCl_3 , 400 MHz): δ 1.14-1.28 (m, 1H), 1.51 (dt, 2H, J = 12.4 and 3.6 Hz), 1.57-1.90 (m, 9H), 1.94-2.07 (m, 3H), 2.28-2.41 (m, 3H), 2.45-2.52 (m, 1H), 7.24-7.31 (m, 3H), 7.39-7.43 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 23.1, 23.2, 25.0, 26.0, 28.1, 29.6, 34.2, 35.6, 38.6, 43.6, 59.7, 84.5, 94.2, 124.2, 127.5, 128.2, 131.5, 211.5 ppm; **IR** (film): 3052, 3029, 2217, 1712, 1597, 1488, 1446 cm^{-1} ; **ESI-MS**: m/z (%) = 303(100) $[\text{M}+\text{Na}^+]$; **Anal** calcd for $\text{C}_{20}\text{H}_{24}\text{O}$: C, 85.67; H, 8.63. Found: C, 85.51; H, 8.51.

2-(2-Cyclohexylidene-1-phenylvinyl)cyclohexanone (4ec):



Yield 41%. A white solid. (m.p. 103-107°C). ^1H NMR (CDCl_3 , 400 MHz): δ 1.52-2.28 (m, 16H), 2.37-2.46 (m, 1H), 2.49-2.58 (m, 1H), 3.56 (ddd, 1H, J = 8.4, 5.6 and 0.8 Hz), 7.11-7.17 (m, 1H), 7.27 (d, 4H, J = 4.4 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz): δ 24.0, 26.1, 27.6, 27.7, 28.1, 31.1, 31.5, 33.1, 41.7, 51.9, 102.8, 107.2, 126.2, 128.2, 137.6, 199.1, 211.2 ppm; **IR** (film): 3054, 3023, 1951, 1699, 1594, 1487, 1445 cm^{-1} ; **ESI-MS**: m/z (%) = 281(10) $[\text{M}+\text{H}^+]$, 303(100) $[\text{M}+\text{Na}^+]$, 319(10) $[\text{M}+\text{K}^+]$; **Anal** calcd for $\text{C}_{20}\text{H}_{24}\text{O}$: C, 85.67; H, 8.63. Found: C, 85.39; H, 8.59.

2-(2,4-Diphenylbut-3-yn-2-yl)cyclohexanone (3fc-1, one of the two diastereomers) ^[1]:

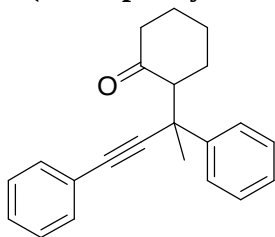


Yield 45%. A white solid. (m.p. 83-85°C). ^1H NMR (CDCl_3 , 400 MHz): δ 1.39-1.51 (m, 1H), 1.68-1.74 (m, 2H), 1.75 (s, 3H), 1.81-2.01 (m, 3H), 2.11-2.22 (m, 1H), 2.45 (dt, 1H, J = 12.8 and 4.8 Hz), 2.72 (dd, 1H, J = 11 and 5.2 Hz), 7.10-7.16 (m, 1H), 7.20-7.32 (m, 5H), 7.37-7.42 (m, 2H), 7.52-7.55 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 24.7, 27.5, 27.9, 30.9, 42.2, 43.3, 60.4, 85.4, 93.2, 123.7, 126.5, 126.6, 127.8,

128.2, 131.6, 144.8, 210.4 ppm; **IR** (film): 3057, 3022, 2229, 1712, 1597, 1490, 1444 cm^{-1} ; **ESI-MS**: m/z (%) = 303(2) $[\text{M}+\text{H}^+]$, 325(100) $[\text{M}+\text{Na}^+]$, 341(5) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[1]

2-(2,4-Diphenylbut-3-yn-2-yl)cyclohexanone (3fc-2, one of the two diastereomers)^[1]:

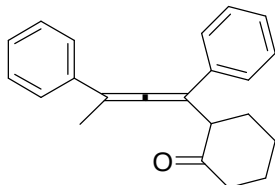


Read out from the spectrum of a mixture containing **3fc**.

Yield 30%. A white solid. **¹H NMR** (CDCl_3 , 400 MHz): δ 1.51-1.67 (m, 4H), 1.64 (s, 3H), 1.76-1.82 (m, 1H), 2.20-2.32 (m, 3H), 2.91 (dd, 1H, J = 12.4 and 5.2 Hz), 7.16-7.20 (m, 1H), 7.20-7.32 (m, 5H), 7.38-7.43 (m, 2H), 7.55-7.57 (m, 2H); **¹³C NMR** (CDCl_3 , 100 MHz): δ 25.5, 27.7, 28.0, 30.4, 41.5, 43.4, 60.4, 84.2, 94.0, 123.9, 126.3, 126.6, 127.7, 127.9, 128.1, 131.6, 145.1, 208.9 ppm; **IR** (film): 3057, 3022, 2229, 1712, 1597, 1490, 1444 cm^{-1} ; **ESI-MS**: m/z (%) = 303(2) $[\text{M}+\text{H}^+]$, 325(100) $[\text{M}+\text{Na}^+]$, 341(5) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[1]

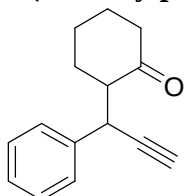
2-(1,3-Diphenylbuta-1,2-dienyl)cyclohexanone (4fc)^[1]:



Yield 15%. A white solid. **¹H NMR** (CDCl_3 , 400 MHz): δ 1.69-2.19 (m, 6H), 2.13-2.28 (m, 1H), 2.21 (s, 3H), 2.33-2.55 (m, 1H), 3.66-3.74 (m, 1H), 7.17-7.37 (m, 8H), 7.42-7.51 (m, 2H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 16.6, 24.5, 28.1, 33.1, 41.9, 52.6, 105.1, 107.3, 125.5, 126.2, 126.8, 126.9, 128.4, 128.5, 136.1, 136.4, 206.3, 210.3 ppm; **IR** (film): 3055, 3023, 1960, 1689, 1598, 1497, 1445 cm^{-1} ; **ESI-MS**: m/z (%) = 325(100) $[\text{M}+\text{Na}^+]$.

Data are in accordance with previously reported results.^[1]

2-(1-Phenylprop-2-ynyl)cyclohexanone (3gc-1, one of the two diastereomers)^[3]:

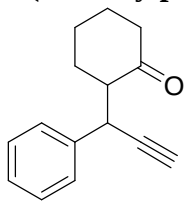


Yield 53%. A colorless oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 1.18-1.31 (m, 1H), 1.55-2.10 (m, 4H), 2.25 (d, 1H, J = 2.4 Hz), 2.32-2.51 (m, 3H), 2.78-2.89 (m, 1H), 4.12 (dd, 1H, J = 7.6 and 2.4 Hz), 7.24-7.29 (m, 1H), 7.30-7.35 (m, 2H), 7.36-7.41 (m, 2H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 24.7, 27.9, 31.3, 36.4,

42.2, 57.0, 70.4, 85.7, 127.1, 128.3, 128.6, 138.5, 210.4 ppm; **IR** (film): 3288, 3058, 3027, 2114, 1712, 1599, 1494, 1451 cm^{-1} ; **ESI-MS**: m/z (%) = 235(100) $[\text{M}+\text{Na}^+]$, 251(14) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[3]

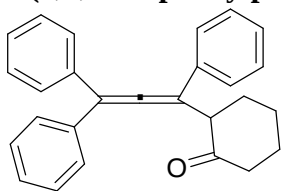
2-(1-Phenylprop-2-ynyl)cyclohexanone (3gc-2, one of the two diastereomers)^[3]:



Yield 36%. A colorless oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 1.53 (tt, 1H, J = 12.8 and 3.6 Hz), 1.68 (tt, 1H, J = 13.2 and 4.0 Hz), 1.76-1.85 (m, 1H), 1.86-1.94 (m, 1H), 2.01-2.11 (m, 2H), 2.18-2.32 (m, 2H), 2.42-2.57 (m, 2H), 4.46 (dd, 1H, J = 7.8 and 2.8 Hz), 7.20-7.27 (m, 1H), 7.32 (apparent t, 2H, J = 7.2 Hz), 7.37 (apparent d, 2H, J = 8.0 Hz) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 24.8, 27.2, 28.7, 36.2, 42.1, 56.5, 72.7, 83.2, 126.9, 128.0, 128.4, 139.8, 209.9 ppm; **IR** (film): 3288, 3058, 3024, 1709, 1597, 1494, 1450 cm^{-1} ; **ESI-MS**: m/z (%) = 235(100) $[\text{M}+\text{Na}^+]$, 251(14) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[3]

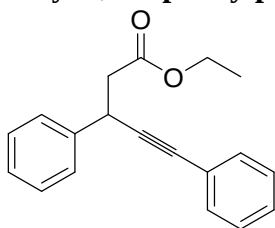
2-(1,3,3-Triphenylpropa-1,2-dienyl)cyclohexanone (4hc)^[1]:



Yield 87%. A white solid. (m.p. 172-174°C). **¹H NMR** (CDCl_3 , 400 MHz): δ 1.71-1.89 (m, 2H), 1.90-2.14 (m, 3H), 2.20-2.29 (m, 1H), 2.47-2.62 (m, 2H), 3.81 (dd, 1H, J = 10.8 and 5.2 Hz), 7.22-7.29 (m, 1H), 7.31-7.51 (m, 14H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 24.7, 28.2, 33.3, 42.3, 52.4, 108.8, 114.2, 126.2, 127.2, 127.5, 127.6, 128.2, 128.4, 128.5, 128.6, 128.7, 135.6, 135.9, 136.5, 207.4, 210.2 ppm; **IR** (film): 3056, 3028, 1952, 1715, 1597, 1495, 1446 cm^{-1} ; **ESI-MS**: m/z (%) = 365(5) $[\text{M}+\text{H}^+]$, 387(100) $[\text{M}+\text{Na}^+]$, 403(27) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[1]

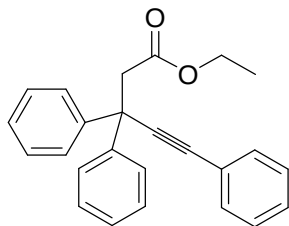
Ethyl 3,5-diphenylpent-4-ynoate (3ad):



Yield 57% . A pale yellow oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 1.22 (t, 3H, J = 6.8 Hz), 2.80 (dd, 1H, J = 15.6 and 7.2 Hz), 2.90 (dd, 1H, J = 15.2 and 8.4 Hz), 4.15 (quartet, 2H, J = 6.8 Hz), 4.38 (dd, 1H, J = 8.4 and 7.2 Hz), 7.24-7.30 (m, 4H), 7.32-7.44 (m, 4H), 7.45-7.51 (m, 2H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 14.2, 34.9, 43.4, 60.7, 83.5, 89.9, 123.3, 125.9, 127.3, 127.5, 128.0, 128.3, 131.7, 144.5, 170.9

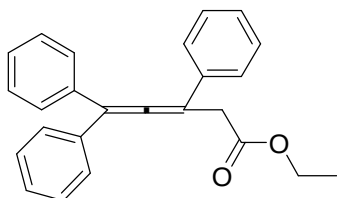
ppm. **IR** (film): 3055, 1736, 1598, 1491, 1446 cm^{-1} ; **ESI-MS**: **ESI-MS**: m/z (%) = 279(5) $[\text{M}+\text{H}^+]$, 301(100) $[\text{M}+\text{Na}^+]$, 317(16) $[\text{M}+\text{K}^+]$.

Ethyl 3,3,5-triphenylpent-4-ynoate (3hd):



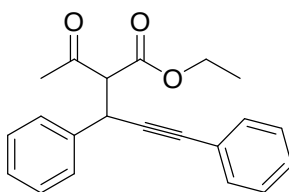
Yield 43% . A yellow oil. ^1H **NMR** (CDCl_3 , 400 MHz): d 1.06 (t, 3H, $J = 7.2$ Hz), 3.41 (s, 2H), 4.09 (quartet, 2H, $J = 7.2$ Hz), 7.19-7.25 (m, 2H), 7.28-7.36 (m, 7H) , 7.48-7.54 (m, 6H) ppm; ^{13}C **NMR** (CDCl_3 , 100 MHz): d 14.0, 46.4, 47.6, 60.4, 86.2, 92.4, 123.4, 126.8, 127.2, 128.0, 128.2, 128.3, 131.7, 144.3, 169.8 ppm; **IR** (film): 3059, 1735, 1599, 1491, 1447 cm^{-1} ; **ESI-MS**: m/z (%) = 377(100) $[\text{M}+\text{Na}^+]$, 393(3) $[\text{M}+\text{K}^+]$; **Anal** calcd for $\text{C}_{25}\text{H}_{22}\text{O}_2$: C, 84.72; H, 6.26. Found: C, 84.65; H, 6.52.

Ethyl 3,5,5-triphenylpenta-3,4-dienoate (4hd):



Yield 46% . A colorless oil. ^1H **NMR** (CDCl_3 , 400 MHz): d 1.12 (t, 3H, $J = 7.2$ Hz), 3.63 (s, 2H), 4.09 (quartet, 2H, $J = 7.2$ Hz), 7.20-7.38 (m, 9H), 7.42-7.50 (m, 6H) ppm; ^{13}C **NMR** (CDCl_3 , 100 MHz): d 14.0, 37.4, 61.0, 103.0, 113.4, 125.8, 127.4, 127.6, 128.4, 128.5, 128.7, 135.0, 136.0, 171.0, 208.1 ppm; **IR** (film): 3054, 1949, 1734, 1599, 1492, 1445 cm^{-1} ; **ESI-MS**: m/z (%) = 355(18) $[\text{M}+\text{H}^+]$, 377(100) $[\text{M}+\text{Na}^+]$, 393(10) $[\text{M}+\text{K}^+]$; **Anal** calcd for $\text{C}_{25}\text{H}_{22}\text{O}_2$: C, 84.72; H, 6.26. Found: C, 84.63; H, 6.28.

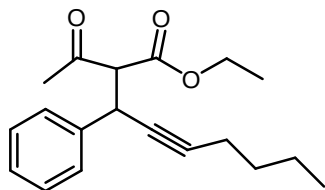
Ethyl 2-acetyl-3,5-diphenylpent-4-ynoate (3ae):



Yield 85% . A yellow oil. Two diastereomers with the ratio of 62 : 38. ^1H **NMR** (CDCl_3 , 400 MHz): d 1.04 and 1.28 (t each, 3H, $J = 7.2$ Hz), 2.00 and 2.42 (s each, 3H), 3.98 and 4.25 (quartet each, 2H, $J = 7.2$ Hz, 7.2 Hz), 4.00 and 4.06 (d each, 1H, $J = 10.8$ Hz), 4.16 and 4.64 (d each, 1H, $J = 10.8$ Hz), 7.23-7.46 (m, 10H) ppm; ^{13}C **NMR** (CDCl_3 , 100 MHz): d 13.8 and 14.2, 29.9 and 30.7, 37.8 and 37.9, 61.6 and 61.9, 66.6 and 66.8, 84.1 and 84.7, 88.2 and 88.5, 122.8 and 123.1, 127.6 and 127.7, 128.1 and 128.2, 128.2 and 128.3, 128.3 and 128.4, 128.7 and 128.8, 131.6 and 131.7, 138.2 and 138.3, 166.8 and 167.1,

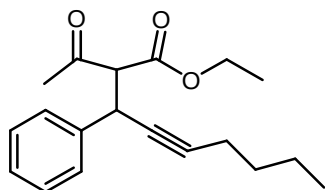
200.4 and 200.8 ppm; **IR** (film): 3061, 3031, 1746, 1599, 1491, 1449 cm^{-1} ; **ESI-MS**: m/z (%) = 343(100) $[\text{M}+\text{Na}^+]$; **Anal** calcd for $\text{C}_{21}\text{H}_{20}\text{O}_3$: C, 78.73; H, 6.29. Found: C, 78.62; H, 6.51.

Ethyl 2-acetyl-3-phenylnon-4-ynoate (3be-1, one of the two diastereomers):



Yield 43%. A pale oil. ^1H NMR (CDCl_3 , 400 MHz): δ 0.88 (t, 3H, $J = 7.2$ Hz), 1.02 (t, 3H, $J = 7.2$ Hz), 1.31-1.51 (m, 4H), 2.12-2.19 (m, 2H), 2.38 (s, 3H), 3.84 (d, 1H, $J = 10.8$ Hz), 3.95 (q, 2H, $J = 7.2$ Hz), 4.36 (dt, 1H, $J = 10.8$ and 2.4 Hz), 7.20-7.26 (m, 1H), 7.27-7.32 (m, 2H), 7.33-7.38 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz): δ 13.4, 13.8, 18.3, 21.8, 29.6, 30.7, 37.5, 61.4, 67.2, 78.6, 84.3, 127.4, 128.1, 128.4, 138.8, 167.0, 201.1 ppm; **IR** (film): 3033, 2960, 1747, 1719, 1602, 1498, 1460, 1030 cm^{-1} ; **ESI-MS**: m/z (%) = 323(100) $[\text{M}+\text{Na}^+]$, 339(3) $[\text{M}+\text{K}^+]$. **Anal** calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3$: C, 75.97; H, 8.05. Found: C, 76.10; H, 7.93.

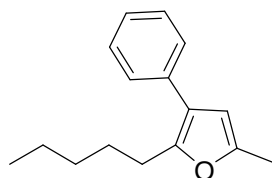
Ethyl 2-acetyl-3-phenylnon-4-ynoate (3be-2, one of the two diastereomers):



Read out from the spectrum of a mixture containing **3be**.

Yield 29%. A pale oil. ^1H NMR (CDCl_3 , 400 MHz): δ 0.89 (t, 3H, $J = 7.2$ Hz), 1.29 (t, 3H, $J = 7.2$ Hz), 1.31-1.50 (m, 4H), 1.95 (s, 3H), 2.12-2.19 (m, 2H), 3.93 (d, 1H, $J = 10.8$ Hz), 4.23 (q, 2H, $J = 7.2$ Hz), 4.36 (dt, 1H, $J = 10.8$ and 2.4 Hz), 7.20-7.26 (m, 1H), 7.27-7.32 (m, 2H), 7.33-7.38 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz): δ 13.5, 14.1, 18.4, 21.7, 30.6, 30.8, 37.4, 61.6, 66.9, 78.9, 85.2, 127.3, 128.2, 128.5, 138.9, 167.2, 200.7 ppm; **IR** (film): 3033, 2960, 1747, 1719, 1602, 1498, 1460, 1030 cm^{-1} ; **ESI-MS**: m/z (%) = 323(100) $[\text{M}+\text{Na}^+]$, 339(3) $[\text{M}+\text{K}^+]$. **Anal** calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3$: C, 75.97; H, 8.05. Found: C, 76.28; H, 7.90.

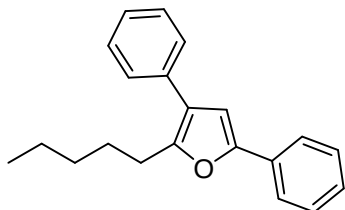
5-Methyl-2-pentyl-3-phenylfuran (6ba):



Yield 77%. A colorless oil. ^1H NMR (CDCl_3 , 400 MHz): δ 0.88 (t, 3H, $J = 7.2$ Hz), 1.28-1.36 (m, 4H), 1.68 (apparent quintet, 2H, $J = 7.6$ Hz), 2.29 (s, 3H), 2.71 (t, 2H, $J = 7.6$ Hz), 6.08 (s, 1H), 7.21-7.26 (m, 1H), 7.32-7.39 (m, 4H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz): δ 13.5, 14.0, 22.5, 27.0, 28.5, 31.6, 107.1,

121.3, 126.1, 127.6, 128.5, 134.7, 149.8, 150.2 ppm; **IR** (film): 3055, 1599, 1494, 1447, 1007 cm^{-1} ; **ESI-MS**: m/z (%) = 267 (100) $[\text{M}+\text{K}^+]$. **Anal** calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: C, 84.16; H, 8.83. Found: C, 84.20; H, 9.12.

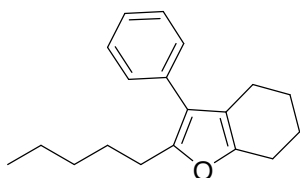
2-Pentyl-3,5-diphenylfuran (6bb)^[6]:



Yield 80%. A pale yellow oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 0.79 (t, 3H, $J = 7.2$ Hz), 1.20-1.32 (m, 4H), 1.67 (apparent quintet, 2H, $J = 7.2$ Hz), 2.73 (t, 2H, $J = 7.6$ Hz), 6.66 (s, 1H), 7.11-7.21 (m, 2H), 7.25-7.34 (m, 6H), 7.58 (apparent d, 2H, $J = 8.4$ Hz) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 14.0, 22.4, 27.0, 28.3, 31.5, 106.5, 122.9, 123.4, 126.5, 127.0, 127.7, 128.5, 128.6, 130.9, 134.2, 151.5, 151.9 ppm; **IR** (film): 3061, 1594, 1490, 1451, 1015 cm^{-1} ; **ESI-MS**: m/z (%) = 329 (100) $[\text{M}+\text{K}^+]$.

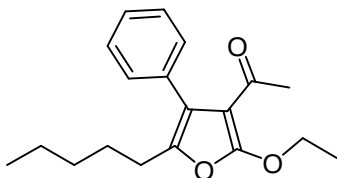
Data are in accordance with previously reported results.^[6]

2-Pentyl-3-phenyl-4,5,6,7-tetrahydrobenzofuran (6bc):



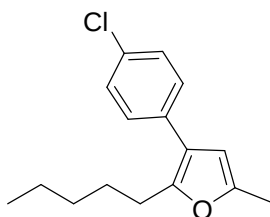
Yield 81%. A pale yellow oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 0.79 (t, 3H, $J = 7.0$ Hz), 1.17-1.27 (m, 4H), 1.54-1.68 (m, 4H), 1.75-1.82 (m, 2H), 2.30-2.36 (m, 2H), 2.51-2.60 (m, 4H), 7.16-7.23 (m, 3H), 7.27-7.33 (m, 2H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 14.0, 21.8, 22.4, 23.0, 23.1, 23.2, 26.6, 28.7, 31.6, 116.9, 120.7, 126.1, 128.3, 128.7, 134.2, 148.6, 150.1 ppm; **IR** (film): 3054, 1598, 1497, 1442, 1166 cm^{-1} ; **ESI-MS**: m/z (%) = 269 (100) $[\text{M}+\text{H}^+]$, 307 (53) $[\text{M}+\text{K}^+]$. **Anal** calcd for $\text{C}_{19}\text{H}_{24}\text{O}$: C, 85.03; H, 9.01. Found: C, 84.95; H, 9.24.

1-(2-ethoxy-5-pentyl-4-phenylfuran-3-yl)ethanone (6be):



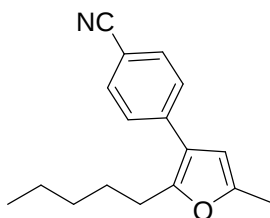
Yield 65%. Yellow oil. **¹H NMR** (CDCl_3 , 400 MHz): δ 0.84 (t, 3H, $J = 6.8$ Hz), 1.07 (t, 3H, $J = 7.2$ Hz), 1.18-1.27 (m, 4H), 1.53-1.62 (m, 2H), 2.49 (t, 2H, $J = 7.6$ Hz), 2.58 (s, 3H), 4.09 (q, 2H, $J = 7.2$ Hz), 7.21-7.25 (m, 2H), 7.26-7.31 (m, 1H), 7.31-7.37 (m, 2H) ppm; **¹³C NMR** (CDCl_3 , 100 MHz): δ 13.88, 13.92, 14.1, 22.3, 25.8, 28.2, 31.2, 59.7, 113.5, 121.2, 126.7, 127.5, 130.0, 133.4, 151.3, 157.4, 164.4 ppm; **IR** (film): 3053, 2957, 1712, 1606, 1587, 1447, 1077 cm^{-1} ; **ESI-MS**: m/z (%) = 323(100) $[\text{M}+\text{Na}^+]$, 339(12) $[\text{M}+\text{K}^+]$. **Anal** calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3$: C, 75.97; H, 8.05. Found: C, 75.90; H, 8.23.

3-(4-chlorophenyl)-5-methyl-2-pentylfuran (6ka):



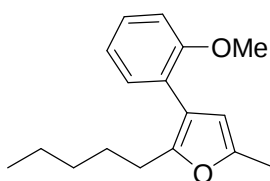
Yield 75%. A pale yellow oil. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): d 0.88 (t, 3H, $J = 7.6$ Hz), 1.27-1.36 (m, 4H), 1.66 (apparent quintet, 2H, $J = 7.6$ Hz), 2.28 (s, 3H), 2.68 (t, 2H, $J = 7.6$ Hz), 6.03 (s, 1H), 7.24-7.26 (m, 2H), 7.32-7.39 (m, 2H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): d 13.4, 13.9, 22.4, 26.9, 28.3, 31.5, 106.8, 120.3, 128.6, 128.8, 131.8, 133.2, 149.9, 150.4 ppm; **IR** (film): 3033, 1561, 1494, 1457, 1098, 1012, 829 cm^{-1} ; **ESI-MS**: m/z (%) = 301 (100) [$\text{M}+\text{K}^+$]. **Anal** calcd for $\text{C}_{16}\text{H}_{19}\text{ClO}$: C, 73.13; H, 7.29. Found: C, 73.06; H, 7.41.

4-(5-methyl-2-pentylfuran-3-yl)benzonitrile(6la):



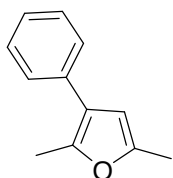
Yield 70%. A pale yellow oil. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): d 0.89 (t, 3H, $J = 7.2$ Hz), 1.28-1.37 (m, 4H), 1.68 (apparent quintet, 2H, $J = 7.6$ Hz), 2.30 (s, 3H), 2.72 (t, 2H, $J = 7.6$ Hz), 6.09 (s, 1H), 7.43 (d, 2H, $J = 8.8$ Hz), 7.64 (d, 2H, $J = 8.8$ Hz) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): d 13.4, 14.0, 22.4, 27.1, 28.2, 31.5, 106.3, 109.4, 119.1, 120.1, 127.8, 132.3, 139.5, 150.6, 151.7 ppm; **IR** (film): 3073, 2235, 1610, 1503, 1466, 1018 cm^{-1} ; **ESI-MS**: m/z (%) = 254 (100) [$\text{M}+\text{H}^+$]. **Anal** calcd for $\text{C}_{17}\text{H}_{19}\text{NO}$: C, 80.60; H, 7.56, N, 5.53. Found: C, 80.38; H, 7.75, N, 5.62.

3-(2-methoxyphenyl)-5-methyl-2-pentylfuran (6ma):



Yield 85%. A pale yellow oil. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): d 0.86 (t, 3H, $J = 7.2$ Hz), 1.25-1.31 (m, 4H), 1.64 (apparent quintet, 2H, $J = 7.6$ Hz), 2.29 (s, 3H), 2.57 (t, 2H, $J = 8$ Hz), 3.82 (s, 3H), 6.06 (s, 1H), 6.91-6.98 (m, 2H), 7.20 (dd, 1H, $J = 7.6$ and 0.8 Hz), 7.26 (td, 1H, $J = 7.6$ and 0.8 Hz) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): d 13.5, 14.0, 22.4, 27.0, 28.3, 31.6, 55.4, 108.6, 110.8, 117.4, 120.4, 123.6, 127.9, 130.8, 149.1, 151.1, 156.8 ppm; **IR** (film): 3082, 1594, 1494, 1463, 1027 cm^{-1} ; **ESI-MS**: m/z (%) = 259 (100) [$\text{M}+\text{H}^+$]. **Anal** calcd for $\text{C}_{17}\text{H}_{22}\text{O}_2$: C, 79.03; H, 8.58. Found: C, 79.17; H, 8.43.

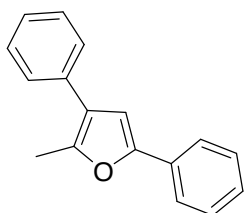
2,5-Dimethyl-3-phenylfuran (6ga)^[7]:



Yield 75%. A pale yellow oil. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): d 2.29 (s, 3H), 2.40 (s, 3H), 6.10 (s, 1H), 7.21-7.25 (m, 1H), 7.36-7.39 (m, 4H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): d 12.9, 13.4, 106.9, 121.4, 126.0, 127.3, 128.5, 134.5, 145.8, 149.7 ppm; **IR** (film): 3050, 1598, 1489, 1446, 1010 cm^{-1} ; **ESI-MS**: m/z (%) = 211(100) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[7]

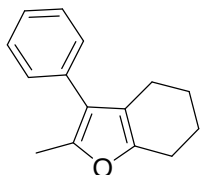
2-Methyl-3,5-diphenylfuran (6gb)^[8]:



Yield 78%. A brown oil. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): d 2.45 (s, 3H), 6.72 (s, 1H), 7.14-7.24 (m, 2H), 7.28-7.39 (m, 6H), 7.61 (apparent d, 2H, $J = 7.2$ Hz) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): d 13.2, 106.4, 123.0, 123.4, 126.4, 127.0, 127.5, 128.6, 128.7, 130.8, 134.0, 147.6, 151.6 ppm; **IR** (film): 3058, 1599, 1498, 1447, 1022 cm^{-1} ; **ESI-MS**: m/z (%) = 273 (100) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[8]

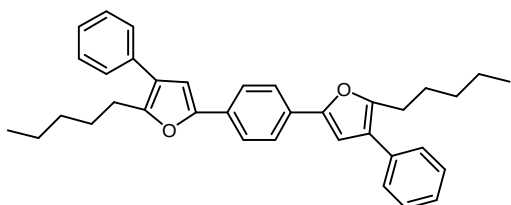
2-Methyl-3-phenyl-4,5,6,7-tetrahydrobenzofuran (6gc)^[9]:



Yield 76%. A yellow oil. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): d 1.68-1.75 (m, 2H), 1.81-1.89 (m, 2H), 2.34 (s, 3H), 2.42 (t, 2H, $J = 6.0$ Hz), 2.60 (t, 2H, $J = 6.0$ Hz), 7.23-7.31 (m, 3H), 7.35-7.41 (m, 2H) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): d 12.6, 12.9, 23.0, 23.2, 23.3, 117.1, 120.9, 126.1, 128.4, 128.6, 134.1, 145.8, 148.6 ppm; **IR** (film): 3054, 1609, 1493, 1446, 1193 cm^{-1} ; **ESI-MS**: m/z (%) = 213 (65) $[\text{M}+\text{H}^+]$, 351 (100) $[\text{M}+\text{K}^+]$.

Data are in accordance with previously reported results.^[9]

2-pentyl-5-(4-(5-pentyl-4-phenylfuran-2-yl)phenyl)-3-phenylfuran (6bf):



Yield 66%. A yellow solid. (m.p. 79-82 °C). **¹H NMR** (CDCl₃, 400 MHz): d 0.91 (t, 6H, *J* = 7.2 Hz), 1.32-1.44 (m, 8H), 1.79 (tt, apparent quin, 4H, *J* = 7.6 Hz), 2.84 (t, 4H, *J* = 7.2 Hz), 6.78 (s, 2H), 7.27-7.33 (m, 2H), 7.38-7.45 (m, 8H), 7.69 (s, 4H) ppm; **¹³C NMR** (CDCl₃, 100 MHz): d 14.0, 22.4, 27.1, 28.3, 31.6, 106.6, 123.1, 123.7, 126.5, 127.7, 128.6, 129.4, 134.2, 151.4, 152.0 ppm; **IR** (film): 3055, 3028, 1603, 1494, 1443, 1178 cm⁻¹; **ESI-MS**: *m/z* (%) = 525(100) [M+Na⁺]. **Anal** calcd for C₃₆H₃₈O₂: C, 86.02; H, 7.62. Found: C, 86.25; H, 7.43.

References:

- [1] I. Matsuda, K. Komori, K. Itoh, *J. Am. Chem. Soc.* **2002**, *124*, 9072 – 9073.
- [2] F. Hiroaki, T. Ei-ichi, H. Shoji, S. Akira, *Chem. Lett.* **1992**, *4*, 695– 698.
- [3] Y. Nishibayashi, I. Wakiji, Y. Ishii, S. Uemura, M. Hidai, *J. Am. Chem. Soc.* **2001**, *123*, 3393– 3394.
- [4] J. M. Chong, L.x. Shen, N. J. Taylor, *J. Am. Chem. Soc.* **2000**, *122*, 1822–1823.
- [5] S. Ikuya, K. Takeyoshi, K. Nobuaki, F. Shoji, B. Akio, *Angew. Chem. Int. Ed.* **2002**, *41*, 1389–1392.
- [6] D.I. MaGee, J.D. Leach, S. Setiadji, *Tetrahedron.* **1999**, *55*, 2847–2856.
- [7] I. Pri-bar, P. S. Pearlman, J. K. Stille, *J. Org. Chem.* **1983**, *48*, 4629–4634.
- [8] A. E. Mattson, A. R. Bharadwaj, A. M. Zuhl, K. A. Scheidt, *J. Org. Chem.* **2006**, *71*, 5715–5724.
- [9] Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. D. Milton, M. Hidai, S. Uemura, *Angew. Chem. Int. Ed.* **2003**, *42*, 2681–2684.