Supporting Information

Cobalt-Catalyzed Carbonylative Cycloaddition of Substituted Diynes to Access Complexed Polycyclic Compounds

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1. General experimental information

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. All commercially available reagents were used without further purification. All of the solvents were treated according to known methods. Column chromatography was performed on silica gel (200-400 mesh). $^1$H NMR (400 MHz) chemical shifts were reported in ppm ($\delta$) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. $^{13}$C NMR (100 MHz) chemical shifts were reported in ppm ($\delta$) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz) and integration. HRMS measurements were obtained on a TOF analyzer. IR spectra were obtained using a thermo scientific spectrum Nicolet 5700-IR Spectrometer.
2. Preparation of benzene-1,3,5-triyl triformate (TFBen)¹

Formic acid (8.4 mL, 222.8 mmol, 5.0 equiv) was added to acetic anhydride (16.8 mL, 178.2 mmol, 4.0 equiv) at rt. The mixture was stirred at 60 °C for 1 h and cooled to rt. The resulting solution was poured into a flask containing 1,3,5-trihydroxybenzene (5.62 g, 44.6 mmol, 1.0 equiv) and AcONa (1.83 g, 22.3 mmol, 0.5 equiv). The mixture was stirred for 4 h in a water bath and then diluted with toluene (100.0 mL), washed with H₂O (50.0 mL) twice. Keep the organic phase in fridge (2-8 °C) for overnight. Then filtered and dried in vacuo to afford the desired product benzene-1,3,5-triyl triformate (TFBen) as a white solid (5.1 g, 55%).
3. General procedure for the synthesis of diynes (1a–t)

The diynes 1a-o and 1s were prepared according to a general procedure reported by Hajela and Snyder.

\[
\begin{align*}
R^1 & \quad \text{OH} \\
\text{Pd(PPh}_3)_2\text{Cl}_2 (1 \text{ mol}) & \quad \text{Br} \\
\text{CuI (2 mol)} & \quad \text{OH} \\
\text{NETs, rt, 4 h} & \quad \text{OH} \\
\end{align*}
\]

To a solution of Et\textsubscript{3}N (10.0 mL), Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (1.0 mol %), CuI (2.0 mol %) and an aryl iodide (6.0 mmol, 1.0 equiv) was added 2-methyl-3-butyne-2-ol (7.2 mmol, 1.2 equiv) under N\textsubscript{2} atmosphere. The mixture was allowed to stir at room temperature for 4 h. After completion of the reaction, it was filtered and the filtrate quenched with saturated NH\textsubscript{4}Cl solution and extracted with EtOAc (3 × 15.0 mL). The combined organic layers were washed with brine (10.0 mL), dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated. The mixture was purified by silica gel column chromatography (petroleum ether / ethyl acetate = 10:1) to give a propargyl alcohol.

To an oven dried round bottom flask was added NaH (60% in mineral oil, 1.2 equiv), which was then purged with argon. Anhydrous DMF (10.0 mL) was then added and the suspension cooled to 0 °C. A propargyl alcohol (4.0 mmol, 1.0 equiv) was added dropwise with stirring, and stirring continued at 0 °C for 1 h, followed by the addition of 1-bromobut-2-yne (4.8 mmol, 1.2 equiv). The solution was stirred at 0 °C for another 30 min, then allowed to warm to rt. After 14 h, the reaction was quenched by the addition of water (20.0 mL), and the mixture poured into a separatory funnel containing brine (50.0 mL). The organic layer was separated, and the aqueous layer extracted with DCM (2 × 15.0 mL). The combined organic layers were dried over Na\textsubscript{2}SO\textsubscript{4}, filtered, and the solvent was removed in vacuo. The mixture was purified by silica gel column chromatography (petroleum ether / ethyl acetate = 10:1) to give a diyne.

The diynes 1p-r were prepared according to a general procedure reported by Wu and Snyder.

\[
\begin{align*}
\text{R}^1 & \quad \text{OH} \\
\text{DMF, NaH, rt} & \quad \text{Br} \\
\text{NaH, DMF} & \quad \text{OH} \\
\end{align*}
\]

To a 50 mL round-bottom flask was added an alkyne (6 mmol, 1.0 equiv) in DMF (10.0 mL).
The mixture was cooled to 0 °C and stirred for 10 min. Then sodium hydride (60% in mineral oil, 1.2 equiv) was added and the reaction continued at 0 °C for 4 h. A ketone (7.2 mmol, 1.2 equiv) was added and the system was warmed to room temperature for 10 h. After the reaction was completed, the reaction mixture was diluted with saturated sodium bicarbonate solution (30.0 mL) and extracted with ethyl acetate (20.0 mL) three times. The combined organic layers were dried over Na₂SO₄, filtered, and the solvent removed in vacuo. The mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to obtain a propargyl alcohol.

To an oven-dried round-bottom flask was added NaH (60% in mineral oil, 1.2 equiv), which was then purged with argon. Anhydrous DMF (10.0 mL) was then added and the suspension cooled to 0 °C. A propargyl alcohol (4.0 mmol) was added dropwise with stirring, and stirring continued at 0 °C for 1 h, followed by the addition of 1-bromobut-2-yn-1-ol (4.8 mmol, 1.2 equiv). The solution was stirred at 0 °C for another 30 min, then allowed to warm to rt. After 14 h, the reaction was quenched by the addition of water (20.0 mL), and the mixture poured into a separatory funnel containing brine (50.0 mL). The organic layer was separated, and the aqueous layer extracted with DCM (2 × 15.0 mL). The combined organic layers were dried over Na₂SO₄, filtered, and the solvent was removed in vacuo. The mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to give a diyne.

The diyne was prepared according to a general procedure reported by Denes and Snyder:

![Chemical structure](image)

To a solution of ethynylcyclopropane (6.0 mmol, 1.0 equiv) in THF (20.0 mL) at −78 °C, was added n-BuLi (3.0 mL, 2.4 M/hexanes). The solution was warmed to -15 °C and stirred for 1 h and then, after it was recooled to -78 °C, a solution of ketone (7.2 mmol, 1.2 equiv) was added via cannula at -78 °C. After completion of the reaction (TLC monitoring), the solution was allowed to reach -30 °C and quenched with a saturated aqueous solution of NH₄Cl. The mixture was diluted with Et₂O and the aqueous layer was extracted with Et₂O. The organic phase was dried over Na₂SO₄, filtered and concentrated in vacuo. The mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to obtain a propargyl alcohol.

To an oven-dried round-bottom flask was added NaH (60% in mineral oil, 1.2 equiv), which
was then purged with argon. Anhydrous DMF (10.0 mL) was then added and the suspension cooled to 0 °C. A propargyl alcohol (4.0 mmol, 1.0 equiv) was added dropwise with stirring, and stirring continued at 0 °C for 1 h, followed by the addition of 1-bromobut-2-yne (4.8 mmol, 1.2 equiv). The solution was stirred at 0 °C for another 30 min, then allowed to warm to rt. After 14 h, the reaction was quenched by the addition of water (20.0 mL), and the mixture poured into a separatory funnel containing brine (50.0 mL). The organic layer was separated, and the aqueous layer extracted with DCM (2 × 15.0 mL). The combined organic layers were dried over Na₂SO₄, filtered, and the solvent was removed in vacuo. The mixture was purified by silica gel column chromatography (petroleum ether / ethyl acetate = 10:1) to give a diyne.
4. General procedure for the synthesis of tetracyclic products (2a-p) and Pauson-Khand products (2q–t)

Diyne 1 (0.5 mmol, 1.0 equiv), Co$_2$(CO)$_8$ (51.3 mg, 0.15 mmol, 30 mol%), NMO (35.1 mg, 0.3 mmol, 60 mol%) and a 1.5 mL vial containing TFBen (315.2 mg, 1.5 mmol, 3.0 equiv) were added to an oven-dried tube (15.0 mL) which was then placed under vacuum and refilled with nitrogen three times. Then DCE (2.0 mL) were added into the tube via syringe. The tube was sealed and stirred at 90 °C for 24 h. Upon the reaction was completed, the resulting mixture was concentrated under vacuum and purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 20:1) to obtain the product 2.
5. Characterization data of compounds 1a-t

(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)benzene (1a). Yellow oil in 80% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 – 7.41 (m, 2H), 7.31 – 7.29 (m, 3H), 4.31 (q, $J$ = 2.3 Hz, 2H), 1.85 (t, $J$ = 2.4 Hz, 3H), 1.58 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 131.8, 128.3, 122.7, 90.5, 85.0, 81.9, 76.1, 71.3, 53.2, 28.9, 3.9.

1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-methylbenzene (1b). Yellow oil in 82% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 (d, $J$ = 8.1 Hz, 2H), 7.06 (d, $J$ = 8.0 Hz, 2H), 4.27 (q, $J$ = 2.3 Hz, 2H), 2.29 (s, 3H), 1.81 (t, $J$ = 2.4 Hz, 3H), 1.55 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.1, 131.4, 128.8, 119.4, 89.5, 84.8, 81.4, 76.0, 71.0, 52.8, 28.7, 21.2, 3.5.

1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-ethylbenzene (1c). Yellow oil in 88% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 (d, $J$ = 8.2 Hz, 2H), 7.11 (d, $J$ = 8.2 Hz, 2H), 4.30 (q, $J$ = 2.3 Hz, 2H), 2.61 (q, $J$ = 7.6 Hz, 2H), 1.83 (t, $J$ = 2.4 Hz, 3H), 1.57 (s, 6H), 1.20 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.6, 131.6, 127.7, 119.7, 89.6, 85.0, 81.6, 76.0, 71.1, 52.9, 28.8, 28.7, 15.3, 3.7.

1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-propylbenzene (1d). Yellow oil in 85% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J$ = 8.1 Hz, 2H), 7.10 (d, $J$ = 8.1 Hz, 2H), 4.29 (q, $J$ = 2.3 Hz, 2H), 2.58 – 2.54 (m, 2H), 1.84 (t, $J$ = 2.3 Hz, 3H), 1.61 (dd, $J$ = 15.1, 7.5 Hz, 2H), 1.57
(s, 6H), 0.91 (t, J = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.3, 131.7, 128.5, 119.9, 89.8, 85.1, 81.8, 76.1, 71.4, 53.1, 38.0, 29.0, 24.5, 13.8, 3.9.

1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-(tert-butyl)benzene (1e). Yellow oil in 79% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 4.26 (q, $J = 2.2$ Hz, 2H), 1.79 (t, $J = 2.3$ Hz, 3H), 1.54 (s, 6H), 1.25 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 151.2, 131.2, 124.9, 119.4, 89.5, 84.7, 81.2, 75.9, 70.9, 52.7, 34.4, 30.9, 28.7, 3.4.

1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-fluorobenzene (1f). Yellow oil in 81% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 – 7.27 (m, 2H), 6.91 – 6.87 (m, 2H), 4.18 (q, $J = 2.3$ Hz, 2H), 1.74 (t, $J = 2.4$ Hz, 3H), 1.47 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.2 (d, $J = 249.5$ Hz, 1C), 133.3 (d, $J = 8.3$ Hz, 1C), 118.5 (d, $J = 3.4$ Hz, 1C), 115.3 (d, $J = 22.1$ Hz, 1C), 90.0, 83.5, 81.4, 75.8, 70.9, 52.8, 28.5, 3.4.

1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-chlorobenzene (1g). Yellow oil in 77% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (d, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 4.25 (q, $J = 2.2$ Hz, 2H), 1.81 (t, $J = 2.3$ Hz, 3H), 1.53 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.3, 132.9, 128.5, 121.1, 91.5, 83.7, 81.7, 75.9, 71.1, 53.1, 28.7, 3.7.

1-bromo-4-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)benzene (1h). Yellow solid in 73% yield, mp 41.0 – 42.2 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (d, $J = 8.5$ Hz, 2H), 7.32 (d, $J = 8.6$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 4.25 (q, $J = 2.2$ Hz, 2H), 1.81 (t, $J = 2.3$ Hz, 3H), 1.53 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.3, 132.9, 128.5, 121.1, 91.5, 83.7, 81.7, 75.9, 71.1, 53.1, 28.7, 3.7.
Hz, 2H), 4.32 (q, J = 2.3 Hz, 2H), 1.90 (t, J = 2.4 Hz, 3H), 1.61 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 133.3, 131.6, 122.7, 121.7, 91.8, 83.9, 82.1, 75.9, 71.3, 53.2, 28.8, 3.9.

1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-(trifluoromethyl)benzene (1i). Yellow oil in 80% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (q, J = 8.4 Hz, 4H), 4.28 (q, J = 2.3 Hz, 2H), 1.84 (t, J = 2.4 Hz, 3H), 1.58 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 132.0, 130.2 (q, J = 32.7 Hz, 1C), 126.5, 125.3 (q, J = 3.7 Hz, 1C), 121.3 (q, J = 272.3 Hz, 1C), 93.1, 83.6, 82.1, 75.8, 71.2, 53.3, 28.7, 3.8.

1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-4-(trifluoromethoxy)benzene (1j). Yellow oil in 72% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 4.27 (q, J = 2.3 Hz, 2H), 1.83 (t, J = 2.4 Hz, 3H), 1.56 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.0, 133.3, 121.5, 120.9, 120.4 (q, J = 257.7 Hz, 1C), 91.4, 83.5, 82.0, 75.9, 71.2, 53.2, 28.8, 3.8.

4-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-1,1'-biphenyl (1k). Yellow solid in 77% yield, mp 69.7 – 70.8 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.61 – 7.59 (m, 2H), 7.53 (dd, J = 19.8, 8.4 Hz, 4H), 7.45 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 4.35 (dd, J = 4.6, 2.2 Hz, 2H), 1.88 (t, J = 2.3 Hz, 3H), 1.62 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.1, 140.3, 132.2, 128.9, 127.7, 127.1, 127.0, 121.6, 91.1, 84.8, 81.9, 76.0, 71.4, 57.0, 53.2, 28.9, 3.9.

1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-3-methylbenzene (1l). Yellow oil in 81% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 (s, 1H), 7.22 (d, J = 7.7 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.11
(d, $J = 7.4$ Hz, 1H), 4.30 (q, $J = 2.3$ Hz, 2H), 2.31 (s, 3H), 1.85 (t, $J = 2.4$ Hz, 3H), 1.58 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.9, 132.3, 129.2, 128.7, 128.2, 122.4, 90.0, 85.1, 81.7, 76.0, 71.2, 53.0, 28.8, 21.2, 3.8.

1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-3-methoxybenzene (1m). Yellow oil in 83% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17 (t, $J = 8.0$ Hz, 1H), 6.99 (d, $J = 7.6$ Hz, 1H), 6.92 (dd, $J = 2.4$, 1.4 Hz, 1H), 6.83 (ddd, $J = 8.3$, 2.6, 0.7 Hz, 1H), 4.27 (q, $J = 2.3$ Hz, 2H), 3.75 (s, 3H), 1.82 (t, $J = 2.4$ Hz, 3H), 1.55 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.2, 129.3, 124.2, 123.5, 116.4, 114.9, 90.2, 84.8, 81.7, 75.9, 71.2, 55.2, 53.0, 28.8, 3.7.

1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-2-methylbenzene (1n). Yellow oil in 70% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J = 7.5$ Hz, 1H), 7.24 – 7.17 (m, 2H), 7.14 – 7.11 (m, 1H), 4.33 (d, $J = 2.3$ Hz, 2H), 2.42 (s, 3H), 1.86 (dd, $J = 2.9$, 1.7 Hz, 3H), 1.609 (s, 3H), 1.606 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.2, 132.0, 129.5, 128.4, 125.6, 122.5, 94.6, 83.9, 81.9, 76.0, 71.5, 53.2, 29.1, 20.8, 3.9.

1-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)-2-fluorobenzene (1o). Yellow oil in 72% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (td, $J = 7.3$, 1.7 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.09 – 7.02 (m, 2H), 4.31 (q, $J = 2.3$ Hz, 2H), 1.84 (t, $J = 2.4$ Hz, 3H), 1.58 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.8 (d, $J = 251.6$ Hz, 1C), 133.5, 130.1 (d, $J = 7.9$ Hz, 1C), 123.9 (d, $J = 3.7$ Hz, 1C), 115.5 (d, $J = 20.9$ Hz, 1C), 111.2 (d, $J = 15.8$ Hz, 1C), 95.8 (d, $J = 3.3$ Hz, 1C), 81.9, 78.4, 75.9, 71.3, 53.2, 28.8, 3.8.
(3-(but-2-yn-1-yloxy)-3-ethylpent-1-yn-1-yl)benzene (1p). Yellow oil in 54% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 – 7.40 (m, 2H), 7.31 – 7.28 (m, 3H), 4.28 (q, $J = 2.3$ Hz, 2H), 1.84 (t, $J = 2.4$ Hz, 3H), 1.80 (q, $J = 7.4$ Hz, 2H), 1.02 (t, $J = 7.5$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 131.7, 128.2, 122.8, 89.2, 86.9, 81.4, 78.3, 76.2, 52.8, 30.6, 8.38, 8.36, 3.8.

((1-(but-2-yn-1-yloxy)cyclobutyl)ethynyl)benzene (1q). Yellow oil in 49% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.44 (m, 2H), 7.32 – 7.30 (m, 3H), 4.21 (d, $J = 1.5$ Hz, 2H), 2.46 – 2.37 (m, 4H), 1.97 – 1.88 (m, 2H), 1.85 (d, $J = 0.5$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 131.9, 128.43, 128.37, 122.8, 89.8, 85.7, 82.1, 75.6, 73.5, 57.1, 53.3, 36.2, 13.5, 3.9.

((1-(but-2-yn-1-yloxy)cyclopentyl)ethynyl)benzene (1r). Yellow oil in 50% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 – 7.41 (m, 2H), 7.31 – 7.29 (m, 3H), 4.28 (q, $J = 2.2$ Hz, 2H), 2.17 – 2.10 (m, 2H), 2.03 – 1.97 (m, 2H), 1.85 (t, $J = 2.3$ Hz, 3H), 1.84 – 1.81 (m, 2H), 1.79 – 1.73 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 131.8, 128.4, 122.9, 90.1, 85.6, 81.8, 81.4, 76.1, 53.7, 39.8, 23.5, 3.9.

3-(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)thiophene (1s). Yellow oil in 83% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.23 (dd, $J = 5.2$, 1.1 Hz, 1H), 7.17 (dd, $J = 3.6$, 1.1 Hz, 1H), 6.95 (dd, $J = 5.2$, 3.6 Hz, 1H), 4.26 (q, $J = 2.3$ Hz, 2H), 1.84 (t, $J = 2.4$ Hz, 3H), 1.56 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 132.2, 127.2, 126.9, 122.5, 94.3, 81.9, 78.2, 75.9, 71.4, 57.0, 53.2, 28.7, 3.8.
(3-(but-2-yn-1-yloxy)-3-methylbut-1-yn-1-yl)cyclopropane (1t). Yellow oil in 68% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.17 (q, $J = 2.4$ Hz, 2H), 1.83 (t, $J = 2.4$ Hz, 3H), 1.42 (s, 6H), 1.26 – 1.19 (m, 1H), 0.77 – 0.72 (m, 2H), 0.66 – 0.62 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 88.7, 81.7, 76.7, 76.2, 71.1, 52.8, 29.2, 29.1, 8.4, 3.9, -0.6.
6. Characterization data of products 2a–p, 2q–t and 3a

**Compound 2a.** Yellow solid, 91.7 mg, 81% yield, mp 205.1 – 205.9 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 (d, \(J = 7.7\) Hz, 1H), 7.41 – 7.34 (m, 4H), 7.30 – 7.28 (m, 2H), 7.19 (dd, \(J = 7.9, 1.5\) Hz, 2H), 7.03 – 7.01 (m, 1H), 4.53 (dd, \(J = 12.9, 0.9\) Hz, 1H), 4.37 (dd, \(J = 12.9, 1.3\) Hz, 1H), 4.05 (q, \(J = 9.7\) Hz, 2H), 2.02 (s, 3H), 1.83 (s, 3H), 1.12 (s, 6H), 1.07 (s, 3H), 0.97 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 214.4, 187.0, 140.4, 137.8, 135.5, 132.5, 131.3, 131.2, 130.9, 130.4, 129.2, 128.6, 128.5, 127.9, 127.2, 127.1, 83.9, 80.7, 69.4, 66.5, 65.5, 63.1, 28.1, 27.4, 26.7, 26.4, 23.1, 18.4; HRMS (ESI-TOF) Calcd. for C\(_{31}\)H\(_{33}\)O\(_3\)\(^{+}\)[M+H]\(^+\): 453.2424; found: 453.2419. IR \(\nu\) max cm\(^{-1}\): 2971, 1713, 1594, 1360, 1141, 1120, 1054, 1025, 773, 743, 705, 669 cm\(^{-1}\).

**Compound 2b.** Yellow oil, 90.1 mg, 75% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (dd, \(J = 7.8, 1.5\) Hz, 1H), 7.20 – 7.17 (m, 3H), 7.10 – 7.06 (m, 3H), 6.90 (dd, \(J = 7.7, 1.5\) Hz, 1H), 4.52 (d, \(J = 12.8\) Hz, 1H), 4.35 (dd, \(J = 12.8, 1.0\) Hz, 1H), 4.03 (q, \(J = 9.7\) Hz, 2H), 2.37 (s, 3H), 2.36 (s, 3H), 2.00 (s, 3H), 1.83 (s, 3H), 1.11 (s, 3H), 1.10 (s, 3H), 1.07 (s, 3H), 0.97 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 214.6, 186.3, 140.3, 138.5, 136.6, 135.4, 134.7, 132.4, 131.0, 130.8, 130.3, 129.2, 129.0, 128.6, 128.3, 127.7, 84.0, 80.7, 69.5, 66.5, 65.4, 63.0, 28.1, 27.4, 26.7, 26.4, 23.2, 21.5, 21.4, 18.4; HRMS (ESI-TOF) Calcd. for C\(_{33}\)H\(_{37}\)O\(_3\)\(^{+}\)[M+H]\(^+\): 481.2737; found: 481.2743. IR \(\nu\) max cm\(^{-1}\): 2976, 2818, 2360, 1711, 1600, 1511, 1457, 1381, 1352, 1144, 1021, 736, 669 cm\(^{-1}\).
**Compound 2c.** Yellow solid, 80.1 mg, 63% yield. mp 136.9 – 137.8 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (dd, $J = 7.9$, 1.7 Hz, 1H), 7.22 – 7.19 (m, 3H), 7.10 (d, $J = 8.1$ Hz, 3H), 6.91 (dd, $J = 7.7$, 1.7 Hz, 1H), 4.52 (dd, $J = 12.8$, 0.9 Hz, 1H), 4.35 (dd, $J = 12.8$, 1.3 Hz, 1H), 4.03 (q, $J = 9.6$ Hz, 2H), 2.70 – 2.63 (m, 4H), 2.01 (s, 3H), 1.84 (s, 3H), 1.26 (t, $J = 6.0$ Hz, 3H), 1.23 (t, $J = 6.0$ Hz, 3H), 1.12 (s, 3H), 1.11 (s, 3H), 1.06 (s, 3H), 0.97 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 214.7, 186.3, 144.8, 143.0, 140.2, 135.5, 134.9, 132.4, 131.1, 130.8, 130.3, 129.3, 129.1, 128.5, 128.0, 127.3, 126.4, 84.0, 80.7, 69.5, 66.5, 65.4, 63.1, 28.8, 28.7, 28.1, 27.4, 26.7, 26.4, 23.2, 18.5, 15.64, 15.59; HRMS (ESI-TOF) Calcd. for C$_{33}$H$_{41}$O$_3$ $[M+H]^+$: 509.3050; found: 509.3055. IR $\nu$ max cm$^{-1}$: 2961, 2930, 2891, 1709, 1660, 1593, 1509, 1461, 1361, 1146, 1040, 1013, 836, 817 cm$^{-1}$.

**Compound 2d.** Yellow oil, 68.4 mg, 51% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (dd, $J = 7.9$, 1.6 Hz, 1H), 7.19 – 7.17 (m, 3H), 7.11 – 7.07 (m, 3H), 6.91 (dd, $J = 7.7$, 1.6 Hz, 1H), 4.51 (d, $J = 12.0$ Hz, 1H), 4.35 (dd, $J = 12.8$, 1.2 Hz, 1H), 4.03 (q, $J = 9.6$ Hz, 2H), 2.59 (dd, $J = 14.6$, 6.4 Hz, 4H), 2.00 (s, 3H), 1.84 (s, 3H), 1.69 – 1.65 (m, 2H), 1.63 – 1.60 (m, 2H), 1.12 (s, 3H), 1.11 (s, 3H), 1.05 (s, 3H), 0.96 (s, 3H), 0.93 (td, $J = 7.4$, 5.4 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 214.8, 186.3, 143.3, 141.4, 140.2, 135.5, 134.9, 132.4, 131.0, 130.7, 130.2, 129.3, 129.0, 128.7, 128.5, 127.9, 127.1, 84.0, 80.7, 69.5, 66.5, 65.4, 63.1, 38.0, 37.9, 28.2, 27.4, 26.7, 26.4, 24.61, 24.56, 23.2, 18.4, 13.9; HRMS (ESI-TOF) Calcd. for C$_{37}$H$_{45}$O$_3$ $[M+H]^+$: 537.3363; found: 537.3369. IR $\nu$ max cm$^{-1}$: 1590, 1384, 1353, 773, 620 cm$^{-1}$. 
**Compound 2e.** Yellow solid, 70.6 mg, 50% yield, mp 245.6 – 247.8 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.85 (m, 1H), 7.38 (d, $J = 2.8$ Hz, 4H), 7.13 (d, $J = 3.2$ Hz, 2H), 6.93 – 6.91 (m, 1H), 4.52 (d, $J = 11.7$ Hz, 1H), 4.35 (d, $J = 11.5$ Hz, 1H), 4.04 (d, $J = 7.5$ Hz, 2H), 2.01 (s, 3H), 1.85 (s, 3H), 1.34 (s, 9H), 1.31 (s, 9H), 1.14 (s, 3H), 1.12 (s, 3H), 1.05 (s, 3H), 0.96 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 214.8, 186.3, 151.6, 150.0, 140.2, 134.6, 132.4, 130.7, 130.5, 130.2, 129.4, 128.9, 128.2, 125.5, 124.7, 123.7, 84.0, 80.7, 69.5, 66.5, 65.4, 63.1, 34.8, 34.6, 31.6, 31.4, 28.2, 27.3, 26.7, 26.5, 23.2, 18.5; HRMS (ESI-TOF) Calcd. for C$_{39}$H$_{49}$O$_3$ $^+$ [M+H]$^+$: 565.3676; found: 565.3673. IR ν max cm$^{-1}$: 2968, 1716, 1593, 1378, 1353, 1020, 838, 759, 725, 704, 687, 598, 559 cm$^{-1}$.

**Compound 2f.** Yellow solid, 95.3 mg, 78% yield, mp 210.5 – 211.6 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 – 7.93 (m, 1H), 7.19 – 7.16 (m, 2H), 7.08 (t, $J = 8.5$ Hz, 3H), 6.99 (d, $J = 6.7$ Hz, 2H), 4.51 (d, $J = 12.9$ Hz, 1H), 4.35 (d, $J = 12.9$ Hz, 1H), 4.03 (q, $J = 9.8$ Hz, 2H), 2.01 (s, 3H), 1.82 (s, 3H), 1.12 (s, 3H), 1.09 (d, $J = 4.4$ Hz, 3H), 1.06 (s, 3H), 0.96 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 214.5, 187.5, 163.0 (d, $J = 248.7$ Hz, 1C), 162.1 (d, $J = 246.1$ Hz, 1C), 141.1, 134.5, 133.4 (d, $J = 3.3$ Hz, 1C), 133.0 (d, $J = 7.8$ Hz, 1C), 132.44, 132.35 (d, $J = 7.8$ Hz, 1C), 131.0 (d, $J = 8.2$ Hz, 1C), 130.7, 128.0, 127.2, 84.0, 80.7, 69.5, 66.5, 65.6, 62.8, 28.1, 27.4, 26.7, 26.4, 23.2, 18.5; HRMS (ESI-TOF) Calcd. for C$_{31}$H$_{31}$F$_2$O$_3$ $^+$ [M+H]$^+$: 489.2236; found: 489.2229. IR ν max cm$^{-1}$: 2831, 1593, 1353, 1090, 776, 743, 619 cm$^{-1}$.
**Compound 2g.** Yellow solid, 97.8 mg, 75% yield, mp 105.6 – 107.1 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92 (dd, \(J = 8.3, 2.1\) Hz, 1H), 7.39 – 7.35 (m, 3H), 7.28 (dd, \(J = 8.1, 2.2\) Hz, 1H), 7.14 – 7.12 (m, 2H), 6.97 (dd, \(J = 8.1, 2.1\) Hz, 1H), 4.51 (dd, \(J = 12.9, 1.0\) Hz, 1H), 4.36 (dd, \(J = 12.9, 1.3\) Hz, 1H), 4.05 – 4.00 (m, 2H), 2.00 (s, 3H), 1.82 (s, 3H), 1.12 (s, 3H), 1.08 (s, 3H), 1.07 (s, 3H), 0.96 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 214.1, 188.0, 141.1, 136.1, 134.8, 134.3, 133.3, 132.7, 132.5, 132.2, 130.8, 130.5, 129.6, 128.2, 127.4, 83.8, 80.7, 69.4, 66.5, 65.6, 62.8, 28.0, 27.4, 26.7, 26.4, 23.1, 18.5; HRMS (ESI-TOF) Calcd. for C\(_{31}\)H\(_{31}\)O\(_3\)[M+H]\(^{+}\): 521.1645; found: 521.1666. IR \(\nu\) max cm\(^{-1}\): 1593, 1508, 1383, 1352, 844, 822, 770, 557, 525 cm\(^{-1}\).

**Compound 2h.** Yellow solid, 117.5 mg, 77% yield, mp 198.5 – 199.5 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 (dd, \(J = 8.3, 2.1\) Hz, 1H), 7.54 – 7.51 (m, 3H), 7.44 (dd, \(J = 8.1, 2.1\) Hz, 1H), 7.08 – 7.04 (m, 2H), 6.91 (dd, \(J = 8.1, 2.1\) Hz, 1H), 4.53 – 4.50 (m, 1H), 4.36 (dd, \(J = 12.9, 1.3\) Hz, 1H), 4.05 – 3.99 (m, 2H), 2.00 (s, 3H), 1.82 (s, 3H), 1.12 (s, 3H), 1.08 (s, 3H), 1.07 (s, 3H), 0.96 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 214.0, 188.1, 141.1, 136.6, 134.6, 134.3, 133.1, 132.5, 131.9, 131.2, 130.8, 130.7, 130.4, 130.1, 127.7, 123.0, 121.5, 83.8, 80.7, 69.4, 66.5, 65.6, 62.8, 28.0, 27.4, 26.7, 26.5, 23.1, 18.5; HRMS (ESI-TOF) Calcd. for C\(_{31}\)H\(_{31}\)Br\(_2\)O\(_3\)[M+H]\(^{+}\): 611.0614; found: 611.0609. IR \(\nu\) max cm\(^{-1}\): 2980, 1710, 1590, 1488, 1380, 1352, 836, 818, 773, 737, 707, 680, 563, 509 cm\(^{-1}\).
**Compound 2i.** Yellow solid, 76.5 mg, 52% yield, mp 147.6 – 148.8 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (d, $J = 8.0$ Hz, 1H), 7.68 – 7.64 (m, 3H), 7.58 (d, $J = 7.8$ Hz, 1H), 7.31 (d, $J = 7.8$ Hz, 2H), 7.17 (d, $J = 7.8$ Hz, 1H), 4.54 (d, $J = 12.8$ Hz, 1H), 4.38 (d, $J = 12.9$ Hz, 1H), 4.06 (s, 2H), 2.04 (s, 3H), 1.84 (s, 3H), 1.12 (s, 3H), 1.10 (s, 3H), 1.06 (s, 3H), 0.95 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 213.6, 189.3, 141.5 (q, $J = 17.7$ Hz, 1C), 134.9, 134.2, 132.6, 131.8, 131.2, 131.0, 130.8 (q, $J = 32.7$ Hz, 1C), 129.6 (q, $J = 32.3$ Hz, 1C), 129.5, 128.9, 125.6 (q, $J = 3.6$ Hz, 1C), 124.9 (q, $J = 3.6$ Hz, 1C), 124.3 (q, $J = 3.7$ Hz, 1C), 83.7, 80.7, 69.4, 66.5, 65.8, 62.9, 29.9, 28.0, 27.3, 26.7, 23.1, 18.5; HRMS (ESI-TOF) Calcd. for C$_{33}$H$_{30}$F$_6$O$_3$Na$^+$ [M+Na]$^+$: 611.1991; found: 611.1985. IR $\nu$ max cm$^{-1}$: 2829, 1593, 1354, 1122, 1067, 765, 619 cm$^{-1}$.

**Compound 2j.** Yellow solid, 94.6 mg, 61% yield, mp 186.0 – 187.5 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.02 (dd, $J = 8.5$, 1.7 Hz, 1H), 7.27 (s, 1H), 7.24 (s, 4H), 7.16 (d, $J = 8.3$ Hz, 1H), 7.06 (dd, $J = 8.3$, 1.7 Hz, 1H), 4.53 (d, $J = 12.8$ Hz, 1H), 4.37 (d, $J = 12.6$ Hz, 1H), 4.08 – 4.02 (m, 2H), 2.02 (s, 3H), 1.84 (s, 3H), 1.14 (s, 3H), 1.10 (s, 3H), 1.07 (s, 3H), 0.96 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 214.2, 188.4, 149.5, 148.6, 141.3, 136.2, 134.1, 132.9, 132.5, 132.2, 130.9, 130.7, 129.8, 127.6, 121.9 (q, $J = 8.1$ Hz, 1C), 121.1, 120.4, 119.6, 119.3 (d, $J = 8.9$ Hz, 1C), 83.8, 80.7, 69.4, 66.5, 65.7, 62.8, 28.0, 27.3, 26.7, 26.5, 23.2, 18.5; HRMS (ESI-TOF) Calcd. for C$_{33}$H$_{31}$F$_6$O$_5$ [M+H]$^+$: 621.2070; found: 621.2078. IR $\nu$ max cm$^{-1}$: 2989, 1712, 1593, 1383, 1352, 1279, 1206, 1169, 1142, 668 cm$^{-1}$.
Compound 2k. Yellow solid, 90.7 mg, 60% yield, mp 112.0 – 113.2 °C; 1H NMR (400 MHz, CDCl3) δ 8.06 (dd, J = 8.1, 1.6 Hz, 1H), 7.68 – 7.65 (m, 3H), 7.63 – 7.60 (m, 4H), 7.56 (dd, J = 7.9, 1.9 Hz, 1H), 7.46 (td, J = 7.6, 2.4 Hz, 4H), 7.39 – 7.34 (m, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.11 (dd, J = 7.9, 1.6 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.40 (dd, J = 12.9, 1.2 Hz, 1H), 4.09 (q, J = 9.7 Hz, 2H), 2.06 (s, 3H), 1.90 (s, 3H), 1.20 (s, 3H), 1.19 (s, 3H), 1.13 (s, 3H), 1.03 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 214.6, 187.2, 141.4, 140.8, 140.63, 140.58, 139.8, 136.8, 135.1, 132.5, 131.7, 131.3, 130.5, 130.2, 129.6, 129.0, 128.98, 127.7, 127.4, 127.3, 127.2, 127.1, 126.5, 125.7, 84.0, 80.8, 69.5, 66.5, 65.6, 63.1, 28.2, 27.5, 26.8, 26.5, 23.3, 18.6; HRMS (ESI-TOF) Calcd. for C43H41O3+ [M+H]+: 605.3050; found: 605.3055. IR ν max cm⁻¹: 2816, 1600, 1488, 1354, 766, 697, 619 cm⁻¹.

Compound 2l. Yellow oil, 94.9 mg, 79% yield; 1H NMR (400 MHz, CDCl3) δ 7.76 (s, 1H), 7.29 – 7.26 (m, 1H), 7.24 (d, J = 2.8 Hz, 1H), 7.15 (dd, J = 7.3, 5.2 Hz, 2H), 7.10 (d, J = 7.3 Hz, 1H), 6.98 (d, J = 5.3 Hz, 2H), 6.83 – 6.79 (m, 1H), 4.52 (dd, J = 12.8, 0.9 Hz, 1H), 4.36 (d, J = 12.9 Hz, 1H), 4.08 – 4.00 (m, 2H), 2.36 (d, J = 18.9 Hz, 3H), 2.35 (s, 3H), 2.02 (s, 3H), 1.82 (d, J = 3.1 Hz, 3H), 1.12 (s, 6H), 1.06 (d, J = 12.4 Hz, 3H), 0.97 (d, J = 8.1 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 214.4, 186.7, 140.1, 138.1, 137.7, 137.3, 136.5, 135.6, 132.5, 131.7, 131.2, 130.3, 129.7, 129.4, 128.4, 128.2, 128.1, 127.8, 126.9, 126.3, 84.0, 80.7, 69.4, 66.5, 65.4, 63.1, 28.1, 27.3, 26.7, 26.5, 23.1, 21.6, 21.5, 18.4; HRMS (ESI-TOF) Calcd. for C33H37O3+ [M+H]+: 481.2737; found: 481.2739. IR ν max cm⁻¹: 2976, 1597, 1382, 1352, 765, 724, 620 cm⁻¹.
**Compound 2m.** Yellow oil, 59.0 mg, 46% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 – 7.56 (m, 1H), 7.33 – 7.28 (m, 1H), 7.19 (t, $J = 7.9$ Hz, 1H), 6.90 – 6.84 (m, 2H), 6.77 (d, $J = 7.5$ Hz, 1H), 6.71 (s, 1H), 6.61 – 6.56 (m, 1H), 4.52 (d, $J = 12.9$ Hz, 1H), 4.37 (d, $J = 12.9$ Hz, 1H), 4.07 – 4.00 (m, 2H), 3.83 (d, $J = 15.9$ Hz, 3H), 3.80 (s, 3H), 2.01 (s, 3H), 1.83 (d, $J = 3.4$ Hz, 3H), 1.13 (d, $J = 3.6$ Hz, 6H), 1.10 (d, $J = 11.3$ Hz, 3H), 0.99 (d, $J = 6.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 214.1, 187.0, 159.6, 159.1, 158.6, 140.2, 139.1, 135.4, 132.6, 129.6, 128.9, 128.1, 123.8, 123.5, 121.7, 117.2, 116.0, 115.0, 113.9, 113.5, 112.0, 84.0, 80.7, 69.4, 66.5, 65.4, 63.1, 55.4, 27.9, 27.3, 26.8, 26.5, 22.9, 18.4; HRMS (ESI-TOF) Calcd. for C$_{33}$H$_{37}$O$_5$ $^+ [M+H]^+$: 513.2636; found: 513.2637. IR $\nu$ max cm$^{-1}$: 1594, 1384, 1354, 765, 620 cm$^{-1}$.

**Compound 2n.** Yellow oil, 54.1 mg, 45% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 – 7.79 (m, 1H), 7.24 – 7.18 (m, 6H), 7.02 – 7.00 (m, 1H), 4.56 (d, $J = 12.8$ Hz, 1H), 4.40 – 4.34 (m, 1H), 4.06 (s, 2H), 2.15 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.69 (s, 3H), 1.17 (s, 3H), 1.15 (s, 3H), 1.07 (s, 3H), 0.95 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 213.1, 187.7, 140.1, 137.0, 136.7, 136.6, 132.4, 131.5, 131.4, 130.7, 129.5, 128.9, 128.7, 128.4, 127.8, 127.4, 125.8, 125.7, 125.3, 83.9, 80.4, 68.9, 66.7, 64.8, 64.0, 29.8, 27.1, 26.9, 26.3, 25.1, 21.9, 20.8, 18.5; HRMS (ESI-TOF) Calcd. for C$_{33}$H$_{37}$O$_5^+$ $[M+H]^+$: 481.2737; found: 481.2722. IR $\nu$ max cm$^{-1}$: 2828, 1594, 1354, 765, 750, 620 cm$^{-1}$.
**Compound 2o.** Yellow solid, 81.8 mg, 67% yield, mp 180.8 – 182.2 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 (td, \(J = 7.6, 1.8\) Hz, 1H), 7.38 – 7.32 (m, 1H), 7.32 – 7.27 (m, 1H), 7.19 – 7.15 (m, 2H), 7.11 – 7.07 (m, 2H), 7.06 – 7.01 (m, 1H), 4.55 (dd, \(J = 12.8, 1.0\) Hz, 1H), 4.37 (dd, \(J = 12.8, 1.4\) Hz, 1H), 4.09 (q, \(J = 9.8\) Hz, 2H), 2.02 (s, 3H), 1.71 (s, 3H), 1.21 (s, 3H), 1.16 (s, 3H), 1.04 (s, 3H), 1.03 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 213.3, 189.6, 160.3 (d, \(J = 242.0\) Hz, 1C), 160.0 (d, \(J = 248.1\) Hz, 1C), 142.2, 133.8 (d, \(J = 1.8\) Hz, 1C), 132.3, 131.5 (d, \(J = 2.9\) Hz, 1C), 130.9 (d, \(J = 33.1\) Hz, 1C), 130.5 (d, \(J = 32.5\) Hz, 1C), 129.5, 129.4, 125.1 (d, \(J = 17.2\) Hz, 1C), 124.2 (d, \(J = 3.5\) Hz, 1C), 123.7 (d, \(J = 3.2\) Hz, 1C), 122.1, 119.2 (d, \(J = 16.1\) Hz, 1C), 116.0 (d, \(J = 21.6\) Hz, 1C), 114.9 (d, \(J = 23.0\) Hz, 1C), 83.8, 80.5, 69.4, 66.6, 65.3, 63.5, 26.8, 26.5, 25.6, 21.5, 18.5; HRMS (ESI-TOF) Calcd. for C\(_{31}\)H\(_{31}\)F\(_2\)O\(_3\)\([M+H]^+\): 489.2236; found: 489.2238. IR \(\nu\) max cm\(^{-1}\): 2819, 1593, 1492, 1383, 1352, 1105, 760, 620 cm\(^{-1}\).

**Compound 2p.** Yellow oil, 63.6 mg, 50% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.02 (d, \(J = 7.7\) Hz, 1H), 7.39 – 7.33 (m, 4H), 7.29 – 7.27 (m, 2H), 7.21 – 7.19 (m, 2H), 7.00 – 6.98 (m, 1H), 4.62 (d, \(J = 12.2\) Hz, 1H), 4.46 (dd, \(J = 12.9, 1.1\) Hz, 1H), 4.03 (d, \(J = 9.6\) Hz, 1H), 3.94 (d, \(J = 9.6\) Hz, 1H), 2.42 (dq, \(J = 15.1, 7.6\) Hz, 1H), 2.09 (dq, \(J = 14.4, 7.3\) Hz, 1H), 1.98 (s, 3H), 1.63 – 1.57 (m, 1H), 1.55 – 1.51 (m, 1H), 1.41 (dd, \(J = 14.2, 7.3\) Hz, 1H), 1.36 – 1.29 (m, 2H), 1.10 (s, 3H), 1.06 (t, \(J = 7.5\) Hz, 3H), 0.99 (dd, \(J = 14.2, 7.2\) Hz, 1H), 0.84 (t, \(J = 7.3\) Hz, 3H), 0.76 (t, \(J = 7.2\) Hz, 3H), 0.65 (t, \(J = 7.5\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 215.0, 187.1, 137.8, 136.6, 135.1, 134.4, 132.4, 130.3, 130.2, 130.0, 129.5, 128.4, 127.9, 127.2, 127.1, 91.1, 85.3, 69.8, 68.8, 65.8, 63.3, 33.7, 32.0, 29.9, 29.8, 23.2, 18.2, 9.1, 8.8, 8.5, 8.2; HRMS (ESI-TOF) Calcd. for C\(_{35}\)H\(_{41}\)O\(_3\)\([M+H]^+\): 509.3050; found: 509.3056. IR \(\nu\) max cm\(^{-1}\): 2816, 1594, 1353, 774, 620 cm\(^{-1}\).
4'-methyl-6'-phenylspiro[cyclobutane-1,1'-cyclopenta[c]furan]-5'(3'H)-one (2q). Yellow solid, 79.5 mg, 63% yield, mp 120.3 – 121.6 °C; 1H NMR (400 MHz, CDCl₃) δ 7.51 – 7.42 (m, 5H), 3.99 (d, J = 9.4 Hz, 1H), 3.56 (d, J = 9.4 Hz, 1H), 2.93 – 2.78 (m, 2H), 2.14 (t, J = 8.2 Hz, 2H), 2.00 – 1.89 (m, 1H), 1.69 – 1.65 (m, 1H), 1.08 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 207.6, 181.8, 137.7, 130.8, 129.4, 129.2, 128.6, 83.5, 68.8, 65.6, 53.1, 35.6, 34.2, 13.7, 13.2; HRMS (ESI-TOF) Calcd. for C₁₇H₁₇O₂ [M+H]⁺: 253.1223; found: 253.1226.

4'-methyl-6'-phenylspiro[cyclopentane-1,1'-cyclopenta[c]furan]-5'(3'H)-one (2r). Yellow solid, 93.2 mg, 70% yield, mp 115.1 – 116.7 °C; 1H NMR (400 MHz, CDCl₃) δ 7.46 – 7.35 (m, 5H), 4.14 (d, J = 9.6 Hz, 1H), 3.50 (d, J = 9.7 Hz, 1H), 2.64 – 2.58 (m, 1H), 2.40 – 2.33 (m, 1H), 1.96 – 1.89 (m, 1H), 1.75 – 1.65 (m, 2H), 1.55 – 1.45 (m, 3H), 1.11 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 207.7, 184.1, 137.4, 131.0, 129.4, 129.0, 128.6, 90.9, 67.7, 66.1, 53.2, 40.2, 37.5, 25.5, 25.1, 13.7; HRMS (ESI-TOF) Calcd. for C₁₈H₁₉O₂S [M+H]⁺: 267.1380; found: 267.1378.

1,1,4-trimethyl-6-(thiophen-3-yl)-1H-cyclopenta[c]furan-5(3H)-one (2s). Yellow oil, 50.5 mg, 41% yield; 1H NMR (400 MHz, CDCl₃) δ 7.55 – 7.54 (m, 1H), 7.49 (dd, J = 5.0, 0.7 Hz, 1H), 7.16 (dd, J = 5.0, 3.8 Hz, 1H), 4.04 (d, J = 10.0 Hz, 1H), 3.56 (d, J = 10.0 Hz, 1H), 1.96 (s, 3H), 1.39 (s, 3H), 1.09 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 207.2, 181.6, 131.1, 130.0, 129.1, 128.1, 127.5, 81.5, 68.1, 67.2, 52.8, 26.2, 24.3, 13.6; HRMS (ESI-TOF) Calcd. for C₁₄H₁₅O₂S [M+H]⁺: 247.0787; found: 247.0787. 
6-cyclopropyl-1,1,4-trimethyl-1H-cyclopenta[c]furan-5(3H)-one (2t). Yellow solid, 48.0 mg, 47% yield, mp 135.6 – 137.2 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.83 (d, \(J = 9.7\) Hz, 1H), 3.42 (d, \(J = 9.7\) Hz, 1H), 1.66 (s, 3H), 1.49 (s, 3H), 1.46 – 1.40 (m, 2H), 1.02 – 0.96 (m, 1H), 0.88 (s, 3H), 0.85 – 0.76 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 209.0, 182.8, 136.8, 80.4, 67.1, 66.2, 52.8, 26.5, 24.3, 13.3, 8.2, 6.1, 5.0; HRMS (ESI-TOF) Calcd. for C\(_{13}\)H\(_{17}\)O\(_2\)\([\text{M+H}]^+\): 205.1223; found: 205.1232.

1,1,4-trimethyl-6-phenyl-1H-cyclopenta[c]furan-5(3H)-one (3a). Yellow oil, 32.4 mg, 27% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47 – 7.41 (m, 3H), 7.37 (d, \(J = 6.8\) Hz, 2H), 4.15 (d, \(J = 10.0\) Hz, 1H), 3.62 (d, \(J = 10.0\) Hz, 1H), 1.86 (s, 3H), 1.11 (s, 3H), 1.10 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 207.9, 184.3, 138.1, 130.7, 129.2, 129.1, 128.6, 81.2, 67.3, 66.8, 53.5, 29.7, 27.2, 25.4, 13.4.
7. References


8. X-ray crystal data for compound 2a (CCDC: 2057915)

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<td>c/Å</td>
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<td>γ/°</td>
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<td>2Θ range for data collection/°</td>
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<td>Index ranges</td>
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<td>Goodness-of-fit on $F^2$</td>
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<td>Largest diff. peak/hole / e Å$^{-3}$</td>
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9. $^1$H, $^{13}$C spectra of 1a–t, 2a–p, 2q–t and 3a
400 MHz in CDCl₃

100 MHz in CDCl₃
$\text{1g}$

400 MHz in CDCl$_3$

$\text{1g}$

100 MHz in CDCl$_3$
400 MHz in CDCl₃

100 MHz in CDCl₃
400 MHz in CDCl₃

100 MHz in CDCl₃
$1m$ 

$400 \text{ MHz in CDCl}_3$ 

$100 \text{ MHz in CDCl}_3$
$^1$F

$^{400}$ MHz in CDCl$_3$

$^1$F

$^{100}$ MHz in CDCl$_3$
$^1p$

400 MHz in CDCl$_3$

$^1p$

100 MHz in CDCl$_3$
1t

400 MHz in CDCl₃

1t

100 MHz in CDCl₃
10. IR spectra of 2a–p
$\text{H}_2\text{O}$

$\text{F}_3\text{CO}$

$\text{OCF}_3$

$\text{2j}$

$\text{Ph}$

$\text{2k}$

$\text{Me}$

$\text{2l}$

$\text{H}_2\text{O}$