Supporting Information

Photocatalytic Annulation-Alkynyl Migration Strategy for Multiple Functionalization of Dual Unactivated Alkenes

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General Information

$^1$H NMR ($^{13}$C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl$_3$ (DMSO-$d_6$) with chemical shift ($\delta$) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (APCI and ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

General Procedure for the Synthesis of Compounds 1a-1z with aryl moiety linked by quaternary carbon$^1$

A mixture of Pd(PPh$_3$)$_2$Cl$_2$ (2 mol %, 0.2 mmol), CuI (4 mol %, 0.4 mmol), Et$_3$N (1.5 equiv, 15 mmol) and acyl chloride II (1.2 equiv, 12 mmol), dissolving in 20 mL anhydrous tetrahydrofuran (THF), were stirred for 10 minutes at room temperature under argon conditions. Then, terminal alkyne (1.0 equiv, 10 mmol) was added to the reaction vial by dropwise and stirred for overnight. The reaction process was determined by TLC until the starting material consumed completely. The resulting mixture was extracted with 50 mL H$_2$O and 20 mL ethyl acetate for three times. The organic phase was concentrated to a bottle and was dried over MgSO$_4$. Then, the mixture was filtrated and the colature was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (100:1) as the eluent to afford compound III. Then, III was dissolved in 10 mL THF and added to a flame-dried flask equipped with a magnetic stir bar. After that, 20 mL (0.5 mol/L) isopropenylmagnesium bromide solution was added to the flask by dropwise at -10 °C and stirred for 10 mins. Then, the mixture was moved to room temperature for another 6 hours. The resulting mixture was stirred until TLC indicated complete consumption of the starting material III. Subsequently, the mixture was quenched by saturated ammonium chloride solution at -10 °C and extracted with 20 mL ethyl acetate for three times at room temperature. The organic phase was concentrated and evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (50:1) as the eluent to afford compound 1.
General Procedure for the Synthesis of Compounds 1aa-1cc with alkyl moiety linked by quaternary carbon

A flame-dried Schlenk tube was subjected to evacuation/flushing with argon three times and then 3-phenylpropionaldehyde IV (1.0 equiv) was dissolved in 15 mL anhydrous THF and the mixture was loaded in the tube under argon atmosphere. Subsequently, the mixture was cooled to 0 °C and 6 mL (1.0 mol/L) alkylmagnesium bromide (1.2 equiv) was added to the Schlenk tube by dropwise. The mixture was stirred at room temperature until 3-phenylpropionaldehyde consumed completely. Then the mixture was quenched by saturated ammonium chloride solution at -10 °C and extracted with 20 mL ethyl acetate for three times at room temperature. The organic phase was concentrated and evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (50:1) as the eluent to afford compound V. The compound V was dissolved in 10 mL DCM and Dess-Martin periodinane (1.2 equiv) was loaded in the mixture at 0 °C. Then the mixture was stirred at room temperature until TLC indicated complete consumption of V. The resulting mixture was extracted with saturated sodium bicarbonate solution and DCM for three times. The organic phase was concentrated to a bottle and was dried over Na₂SO₄. Then, the mixture was filtrated and the colature was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (100:1) as the eluent to afford compound VI. VI was dissolved in 10 mL THF and added to a flame-dried flask equipped with a magnetic stir bar. After that, 20 mL (0.5 mol/L) isopropenylmagnesium bromide solution was added to the flask by dropwise at -10 °C and stirred for 10 mins. Then, the mixture was moved to room temperature for another 6 hours. The resulting mixture was stirred until TLC indicated complete consumption of the starting material VI. Subsequently, the mixture was quenched by saturated ammonium chloride solution at -10 °C and extracted with 20 mL ethyl acetate for three times at room temperature. The organic phase was concentrated and evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (50:1) as the eluent to afford compounds 1aa-1cc.

General Procedure for the Synthesis of Compounds 1hh²⁻⁶
Step 1: To a solution of estrone VII (1.0 equiv) in 20 mL benzene was added ethylene glycol VIII (6.0 equiv) and PPTS (30 mol %). The reaction mixture was stirred and heated at reflux with a Dean-Stark apparatus in oil bath for 24 h. The resulting mixture was cooled to room temperature and extracted with saturated sodium bicarbonate solution and ethyl acetate for three times. The organic phase was concentrated and evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford compound IX.

Step 2: IX (1.0 equiv) was dissolved in 20 mL DCM and the mixture was loaded in an oven-dried flask equipped with a magnetic stir bar. Then, pyridine (2.0 equiv) was added to the flask and the mixture was cooled to 0 °C. Subsequently, Tf₂O (1.2 equiv) was added dropwise to the mixture at 0 °C and the mixture was stirred under room temperature overnight. The mixture was then quenched with HCl (10%) and extracted with DCM, washed with saturated NaHCO₃ and saturated brine. The organic layer was dried over anhydrous MgSO₄ and filtered. The colature was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as the eluent to afford compound X.

Step 3: A mixture of X (1.0 equiv), ethynyltrimethylsilane (1.4 equiv), triethylamine (4.0 mL), and Pd(PPh₃)₂Cl₂ (3 mol %) in 20 mL DMF was stirred for 4 h in oil bath at 90 °C under argon atmosphere. The resulting mixture was extracted with 50 mL H₂O and 20 mL ethyl acetate for three times. The organic phase was concentrated to a bottle and was dried over MgSO₄. Then, the mixture
was filtrated and the colature was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as the eluent to afford compound XI.

**Step 4:** XI (1.0 equiv) was dissolved in 10 mL MeOH and K₂CO₃ (1.5 equiv) was loaded in the mixture, which was stirred at room temperature. The reaction process was determined by TLC until the starting material XI consumed completely. The mixture was quenched by saturated ammonium chloride solution and extracted with ethyl acetate for three times. The organic phase was concentrated and evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as the eluent to afford compound XII.

**Step 5-6:** The two steps are similar to the synthesis of 1,4-enynes 1a.

**General Procedure for the Synthesis of Compounds 1ii ⁷,⁸**

Isopulegol XIV (1.0 equiv) was dissolved in 10 mL DCM and Dess-Martin periodinane (1.2 equiv) was loaded in the mixture at 0 °C. Then the mixture was stirred at room temperature until TLC indicated complete consumption of XIV. The resulting mixture was extracted with saturated sodium bicarbonate solution and DCM for three times. The organic phase was concentrated to a bottle and was dried over Na₂SO₄. Then, the mixture was filtrated and the colature was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (50:1) to afford compound XV. A hexane solution of nBuLi (1.1 equiv) was added to a THF (dry) solution of corresponding alkynes (1.1 equiv) at -78 °C under Ar conditions and the mixture was stirred for 1 h at -78 °C. Then the ketones XV (1.0 equiv) was loaded in reaction vial at -78 °C under argon atmosphere, then the mixture was warmed to room temperature and stirred until the ketones XV consumed completely by TLC determination. The resulting mixture was quenched by saturated ammonium chloride solution and extracted with ethyl acetate for three times. The organic phase was concentrated and dried over MgSO₄, then the mixture was filtrated and the colature was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (50:1) as the eluent to afford compound 1ii.
General Procedure for the Synthesis of Compounds 1jj 9-12

Step 1: D-α-tocopherol XVI was purchased from TCI. 4-(Bromomethyl)benzaldehyde XVII was purchased from J&K. D-α-tocopherol XVI (1.5 equiv) and K₂CO₃ (2.0 equiv) were dissolved in acetone. Then the 4-(bromomethyl)benzaldehyde XVII (1.0 equiv) was added to the reaction vial and the reaction was refluxed overnight. The resulting mixture was cooled to room temperature and filtered. Then the filtrate was extracted with ethyl acetate and saturated aqueous sodium chloride. The organic phase was concentrated, dried by MgSO₄ and filtered. The filtrate was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (50:1) to afford compound XVIII.

Step 2: A hexane solution of nBuLi (1.1 equiv) was added to a THF (dry) solution of corresponding alkynes (1.1 equiv) at -78 °C under Ar conditions and the mixture was stirred for 1 h at -78 °C. Then the aldehyde XVIII (1.0 equiv) was loaded in reaction vial at -78 °C under argon atmosphere, then the mixture was warmed to room temperature and stirred until the aldehyde XVIII consumed completely by TLC determination. The resulting mixture was quenched by saturated ammonium chloride solution and extracted with ethyl acetate for three times. The organic phase was concentrated and dried over MgSO₄, then the mixture was filtrated and the colature was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (50:1) to afford the alcohol intermediate, which is further oxidized by Dess-Martin periodinane (1.2 equiv) to produce desired compound XIX (purified with petroleum ether/ethyl acetate (50:1)).

Step 3: The alkynyl ketones XIX (1.0 equiv) was dissolved in THF and added to a flame-dried flask equipped with a magnetic stir bar. After that, isopropenylmagnesium bromide solution (1.2 equiv, 1 mol/L) was added to the flask by dropwise at -10 °C and stirred for 10 mins. Then, the mixture was moved to room temperature and stirred until TLC indicated complete consumption of the
starting material XIX. Subsequently, the mixture was quenched by saturated ammonium chloride solution at -10 °C and extracted with ethyl acetate for three times at room temperature. The organic phase was concentrated and evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (50:1) as the eluent to afford compound 1jj.

General Procedure for the Synthesis of Products 3

Example for the synthesis of 3a:
K₂HPO₄ (2.0 equiv, 0.2 mmol, 34.8 mg) and Ir(dFppy)₃ (1 mol %, 0.8 mg) was added to a flame-dried reaction tube with a magnetic stir bar. Then, the reaction tube was linked to the photo-reactor and the tube was subjected to evacuation/flushing with argon three times. Then the 1,4-enyne 1a (1.0 equiv, 0.1 mmol, 24.8 mg) was dissolved in 1.0 mL HFIP and added to the tube. Subsequently, α-allyl-α-bromomalonate 2a (1.5 equiv, 0.15 mmol, 46.1 mg) was dissolved in 0.5 mL HFIP and added to the mixture. Then the mixture was stirred in photocatalytic parallel reactor at 30 °C under blue light (blue LEDs) irradiation until complete consumption of 1a as monitored by TLC analysis. After the reaction was finished, the reaction mixture was filtered and the filtrate was concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 75:1) to afford the desired product 3a as a colorless oil in 63% yield.

Amplification Reaction for the Synthesis of 3k

Synthetic Details: K₂HPO₄ (2.0 equiv, 2.0 mmol, 348 mg) and Ir(dFppy)₃ (1 mol %, 7.6 mg) was added to a flame-dried reaction tube with a magnetic stir bar. Then, the reaction tube was linked to the photo-reactor and the tube was subjected to evacuation/flushing with argon three times. Then the 1,4-enyne 1k (1.0 equiv, 1.0 mmol, 327 mg) was dissolved in 2.5 mL HFIP and added to the
tube. Subsequently, α-allyl-α-bromomalonate 2a (1.5 equiv, 1.5 mmol, 461 mg) was dissolved in 2.5 mL HFIP and added to the mixture. Then the mixture was stirred in photocatalytic parallel reactor at 30 °C under blue light (blue LEDs) irradiation until complete consumption of 1k as monitored by TLC analysis. After the reaction was finished, the reaction mixture was filtered and the filtrate was concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 75:1) to afford the desired product 3k as a colorless oil (287 mg) in 52% yield.

**Mechanistic Investigations**

**Control Experiment with TEMPO**

K₂HPO₄ (2.0 equiv, 0.2 mmol, 34.8 mg), Ir(dFppy)₃ (1 mol %, 0.8 mg) and TEMPO (2.0 equiv, 0.2 mmol, 31.2 mg) was added to a flame-dried reaction tube with a magnetic stir bar. Then, the reaction tube was linked to the photo-reactor and the tube was subjected to evacuation/flushing with argon three times. Then the 1,4-enyne 1a (1.0 equiv, 0.1 mmol, 24.8 mg) was dissolved in 1.0 mL HFIP and added to the tube. Subsequently, α-allyl-α-bromomalonate 2a (1.5 equiv, 0.15 mmol, 46.1 mg) was dissolved in 0.5 mL HFIP and added to the mixture. Then the mixture was stirred at 30 °C under blue light (blue LEDs) irradiation. The corresponding intermolecular alkynyl migration product was not detected according to TLC analysis. The product (E)-diethyl 2-(3-methylbut-1-en-1-yl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)malonate was detected by ESI-HRMS.

**Luminescence Quenching Experiment**

The luminescence quenching experiment was taken using a F-4600 Spectrophotometer (Hitachi, Japan). The excitation wavelength was 387 nm. The emission intensity was collected at 506 nm. The samples were prepared by mixing Ir(dFppy)₃ (1.0×10⁻⁴ mol/L) and different amount of
quenchers (1,4-enynes 1a and α-allyl-α-bromomalonate 2a) in HFIP (total volume = 2.0 mL) in a light path quartzfluorescence cuvette. The concentration of 1a and 2a stock solution both are $1.0 \times 10^{-4}$ mol/L in HFIP. For each quenching experiment, each volume of quenchers (1a and 2a) stock solution was titrated to a mixed solution of Ir(dFppy)$_3$ (20, 20, 20, 20, 20, 20, 20×10$^{-3}$ mL, in a total volume = 2.0 mL). Then the emission intensity was collected and the results were presented in Figure 1.

![Luminescence quenching of Ir(dFppy)$_3$ with 1a](image1)

![Luminescence quenching of Ir(dFppy)$_3$ with 2a](image2)

**Figure 1 Luminescence Quenching Experiment**

**Distortionless Enhancement by Polarization Transfer and 2D-NMR of 1a**
DEPT 135
$^1$H-$^1$C HSQC
\(^1\text{H}-^1\text{H} \text{ COSY}

References:

Diethyl 3-benzoyl-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3a)

30 mg, 63%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.67-7.63 (m, 2H), 7.37-7.32 (m, 1H), 7.29-7.27 (m, 2H), 7.25-7.18 (m, 5H), 4.27-4.19 (m, 4H), 3.11 (d, $J$ = 14.4 Hz, 1H), 3.05-2.98 (m, 1H), 2.59-2.54 (m, 1H), 2.29-2.23 (m, 2H), 1.65 (s, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.29-1.25 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 210.2, 173.6, 171.6, 140.8, 131.4, 130.3, 128.1, 127.9, 127.8, 127.6, 123.8, 96.9, 83.1, 61.9(3), 61.9(6), 61.6, 57.6, 56.3, 49.7, 37.4, 33.1, 31.9, 29.0, 28.6, 14.2, 14.1. IR (film, ν, cm$^{-1}$) 2977, 2935, 1731, 1682, 1598, 1444, 1365, 1254, 1194, 1071, 966, 757, 693. HR-MS (ESI) m/z calcd for C$_{30}$H$_{34}$NaO$_5$ [M+Na]$^+$ 497.2304, found 497.2305.

Diethyl 3-benzoyl-3-methyl-4-(2-methyl-4-(p-tolyl)but-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3b)

26 mg, 53%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.68-7.64 (m, 2H), 7.37-7.33 (m, 1H), 7.30-7.28 (m, 2H), 7.15-7.12 (m, 2H), 7.01 (d, $J$ = 7.6 Hz, 2H), 4.27-4.18 (m, 4H), 3.10 (d, $J$ = 14.4 Hz, 1H), 3.04-2.97 (m, 1H), 2.58-2.52 (m, 1H), 2.30 (s, 3H), 2.28-2.23 (m, 2H), 1.65 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.29-1.25 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 210.3, 173.7, 171.6, 140.9, 137.6, 131.3, 130.3, 128.9, 127.9, 127.8, 120.7, 96.1, 83.1, 61.9(3), 61.9(5), 61.6, 57.6, 56.3, 49.8, 37.4, 33.0, 32.0, 28.8, 28.6, 21.5, 14.2, 14.1. IR (film, ν, cm$^{-1}$) 2977, 2931, 1731, 1684, 1510, 1444, 1386, 1254, 1193, 1072, 966, 817, 701. HR-MS (ESI) m/z calcd for C$_{31}$H$_{36}$NaO$_5$ [M+Na]$^+$ 511.2460, found 511.2497.
Diethyl 3-benzoyl-3-methyl-4-(2-methyl-4-(m-tolyl)but-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3c)

\( (>19:1 \text{ dr}) \)

25 mg, 51%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.69-7.65 (m, 2H), 7.38-7.34 (m, 1H), 7.31-7.26 (m, 2H), 7.12-7.07 (m, 1H), 7.06-6.99 (m, 3H), 4.27-4.19 (m, 4H), 3.11 (d, \(J = 14.0\ \text{Hz}, 1\text{H}), 3.03-2.97 (m, 1\text{H}), 2.59-2.54 (m, 1\text{H}), 2.30-2.23 (m, 2H), 2.24 (s, 3H), 1.66 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.29-1.25 (m, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 210.1, 173.6, 171.6, 140.8, 137.7, 132.0, 130.3, 128.5(0), 128.5(7), 128.0, 127.8, 123.5, 96.5, 83.2, 61.9(3), 61.9(5), 61.6, 57.6, 56.3, 49.6, 37.4, 33.0, 32.0, 28.9, 28.7, 21.3, 14.2, 14.1. IR (film, \(\nu\), cm\(^{-1}\)) 2977, 2934, 1732, 1683, 1598, 1445, 1255, 1188, 966, 784, 693. HR-MS (ESI) m/z calcd for C\(_{31}\)H\(_{36}\)NaO\(_5\) [M+Na\(^+\)] 511.2460, found 511.2491.

Diethyl 3-benzoyl-4-(4-(4-ethylphenyl)-2-methylbut-3-yn-2-yl)-3-methylcyclopentane-1,1-dicarboxylate (3d)

\( (>19:1 \text{ dr}) \)

22 mg, 44%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.68-7.65 (m, 2H), 7.38-7.33 (m, 1H), 7.31-7.26 (m, 2H), 7.18-7.14 (m, 2H), 7.04 (d, \(J = 8.0\ \text{Hz}, 2\text{H}), 4.27-4.19 (m, 4H), 3.10 (d, \(J = 14.4\ \text{Hz}, 1\text{H}), 3.04-2.97 (m, 1\text{H}), 2.63-2.52 (m, 3H), 2.28-2.23 (m, 2H), 1.65 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.29-1.25 (m, 6H), 1.21-1.18 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 210.3, 173.7, 171.6, 144.0, 140.9, 131.4, 130.3, 127.9, 127.8, 127.7, 120.9, 96.1, 83.1, 61.9(3), 61.9(5), 61.6, 57.5, 56.3, 49.8, 37.4, 33.0, 32.0, 28.8(2), 28.8(5), 28.6, 15.5, 14.2, 14.1. IR (film, \(\nu\), cm\(^{-1}\)) 2969, 2934, 2873, 1732, 1683, 1510, 1445, 1366, 1254, 1189, 1072, 966, 835, 701. HR-MS (ESI) m/z calcd for C\(_{32}\)H\(_{38}\)NaO\(_5\) [M+Na\(^+\)] 525.2617, found 525.2637.
Diethyl 3-benzoyl-4-(4-(4-\text{tert-butyl})phenyl)-2-methylbut-3-yn-2-yl)-3-methylcyclopentane-1,1-dicarboxylate (3e)

18 mg, 34%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.69-7.65 (m, 2H), 7.38-7.34 (m, 1H), 7.31-7.27 (m, 2H), 7.25-7.22 (m, 2H), 7.20-7.17 (m, 2H), 4.27-4.18 (m, 4H), 3.09 (d, $J = 14.0$ Hz, 1H), 3.04-2.97 (m, 1H), 2.57-2.52 (m, 1H), 2.28-2.23 (m, 2H), 1.65 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.29-1.25 (m, 15H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 210.3, 173.7, 171.6, 150.8, 140.9, 131.1, 130.3, 127.9, 127.8, 125.1, 120.8, 96.2, 83.1, 61.9(1), 61.9(5), 61.6, 57.5, 56.3, 49.8, 37.3, 34.7, 33.0, 32.0, 31.3, 28.7, 28.5, 14.2, 14.1. IR (film, ν, cm$^{-1}$) 2967, 2871, 1684, 1507, 1458, 1365, 1254, 1189, 1072, 966, 835, 701. HR-MS (ESI) m/z calcd for C$_{34}$H$_{42}$NaO$_5$ [M+Na]$^+$ 553.2930, found 553.2954.

Diethyl 3-benzoyl-4-(4-(4-methoxyphenyl)-2-methylbut-3-yn-2-yl)-3-methylcyclopentane-1,1-dicarboxylate (3f)

27 mg, 54%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 50/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.67-7.64 (m, 2H), 7.37-7.33 (m, 1H), 7.28 (d, $J = 7.6$ Hz, 2H), 7.18-7.14 (m, 2H), 6.75-6.71 (m, 2H), 4.27-4.18 (m, 4H), 3.77 (s, 3H), 3.10 (d, $J = 14.4$ Hz, 1H), 3.04-2.97 (m, 1H), 2.58-2.53 (m, 1H), 2.28-2.22 (m, 2H), 1.64 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.28-1.25 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 210.3, 173.7, 171.6, 159.1, 140.9, 132.8, 130.3, 127.9, 127.8, 116.0, 113.7, 95.3, 82.9, 62.1, 61.9, 61.6, 57.6, 56.3, 55.3, 49.7, 37.4, 33.0, 31.9, 29.0, 28.6, 14.2, 14.1. IR (film, ν, cm$^{-1}$) 2976, 1732, 1684, 1508, 1457, 1247, 1181, 1031, 832. HR-MS (ESI) m/z calcd for C$_{31}$H$_{36}$NaO$_6$ [M+Na]$^+$ 527.2410, found 527.2409.
Diethyl 3-benzoyl-4-(4-(4-fluorophenyl)-2-methylbut-3-yn-2-yl)-3-methylcyclopentane-1,1-dicarboxylate (3g)

![Chemical Structure](image)

(13:1 dr)

28 mg, 57%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.64-7.59 (m, 2H), 7.36-7.32 (M, 1H), 7.28-7.24 (m, 2H), 7.20-7.14 (m, 2H), 6.90-6.84 (m, 2H), 4.26-4.18 (m, 4H), 3.12 (d, $J = 14.4$ Hz, 1H), 3.04-2.98 (m, 1H), 2.60-2.55 (m, 1H), 2.27 (d, $J = 14.4$ Hz, 1H), 2.25-2.20 (m, 1H), 1.62 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.28-1.24 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 210.0, 173.6, 171.6, 162.2 ($^1$J$_{CF}$ = 246.9 Hz), 140.8, 133.3 ($^2$J$_{CF}$ = 8.2 Hz), 130.3, 127.9, 127.8, 119.8 ($^3$J$_{CF}$ = 3.5 Hz), 115.4 ($^2$J$_{CF}$ = 21.6 Hz), 115.2, 96.3, 82.2, 62.1, 61.9, 61.6, 57.6, 56.3, 49.5, 37.6, 33.1, 31.6, 29.5, 28.7, 14.2, 14.1. IR (film, ν, cm$^{-1}$) 2978, 1732, 1684, 1490, 1366, 1253, 1193, 1090, 966, 869, 736. HR-MS (ESI) m/z calcd for C$_{30}$H$_{33}$FNaO$_5$ [M+Na]$^+$ 540.2210, found 540.2243.

Diethyl 3-benzoyl-4-(4-(4-chlorophenyl)-2-methylbut-3-yn-2-yl)-3-methylcyclopentane-1,1-dicarboxylate (3h)

![Chemical Structure](image)

(13:1 dr)

32 mg, 63%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.63-7.59 (m, 2H), 7.37-7.33 (m, 1H), 7.29-7.27 (m, 2H), 7.17-7.10 (m, 4H), 4.26-4.19 (m, 4H), 3.12 (d, $J = 14.4$ Hz, 1H), 3.04-2.97 (m, 1H), 2.60-2.55 (m, 1H), 2.27 (d, $J = 14.4$ Hz, 1H), 2.24-2.19 (m, 1H), 1.62 (s, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.28-1.24 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 209.9, 173.6, 171.6, 140.7, 133.5, 132.7, 130.4, 128.4, 127.9, 127.8, 122.2, 97.7, 82.2, 62.0, 61.9, 61.6, 57.6, 56.3, 49.4, 37.6, 33.2, 31.5, 29.5, 28.7, 14.2, 14.1. IR (film, ν, cm$^{-1}$) 2978, 2934, 1732, 1684, 1490, 1366, 1253, 1193, 1090, 966, 869, 701. HR-MS (ESI) m/z calcd for C$_{30}$H$_{33}$ClNaO$_5$ [M+Na]$^+$ 531.1914, found 531.1915.
Diethyl 3-benzoyl-4-(4-(3-chlorophenyl)-2-methylbut-3-yn-2-yl)-3-methylcyclopentane-1,1-dicarboxylate (3i)

\[
\begin{align*}
\text{EtO}_2\text{C} & \quad \text{EtO}_2\text{C} \\
\text{Cl} & \\
\end{align*}
\]

(13:1 dr)

31 mg, 61%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) (δ, ppm) 7.64-7.61 (m, 2H), 7.38-7.34 (m, 1H), 7.31-7.26 (m, 2H), 7.19-7.16 (m, 1H), 7.13-7.06 (m, 3H), 4.26-4.19 (m, 4H), 3.13 (d, \(J = 14.4\) Hz, 1H), 3.03-2.96 (m, 1H), 2.60-2.55 (m, 1H), 2.28 (d, \(J = 14.0\) Hz, 1H), 2.25-2.20 (m, 1H), 1.63 (s, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.28-1.24 (m, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (δ, ppm) 209.6, 173.4, 171.5, 140.5, 133.8, 131.2, 130.4, 129.5, 129.2, 127.9, 127.8(3), 127.8(7), 125.4, 98.1, 82.0, 61.9, 61.8, 61.6, 57.6, 56.3, 49.3, 37.5, 33.1, 31.5, 29.3, 28.7, 14.1(3), 14.1(7). IR (film, ν, cm\(^{-1}\)) 2978, 1730, 1683, 1592, 1444, 1385, 1257, 1192, 1075, 966, 860, 784, 683. HR-MS (ESI) m/z calcd for C\(_{30}\)H\(_{33}\)ClNaO\(_5\) [M+Na\(^+\)] 531.1914, found 531.1918.

Diethyl 3-benzoyl-4-(4-(2-chlorophenyl)-2-methylbut-3-yn-2-yl)-3-methylcyclopentane-1,1-dicarboxylate (3j)

\[
\begin{align*}
\text{EtO}_2\text{C} & \quad \text{EtO}_2\text{C} \\
\text{Cl} & \\
\end{align*}
\]

(8:1 dr)

28 mg, 55%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) (δ, ppm) 7.66-7.63 (m, 2H), 7.35-7.31 (m, 2H), 7.29-7.27 (m, 2H), 7.21-7.19 (m, 1H), 7.17-7.13 (m, 1H), 7.09-7.05 (m, 1H), 4.26-4.19 (m, 4H), 3.12 (d, \(J = 14.4\) Hz, 1H), 3.06-3.00 (m, 1H), 2.62-2.57 (m, 1H), 2.31-2.24 (m, 2H), 1.65 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H), 1.29-1.25 (m, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (δ, ppm) 209.9, 173.5, 171.5, 140.6, 135.7, 133.1, 130.3, 129.0, 128.6, 127.9, 127.7, 126.2, 123.5, 102.3, 80.1, 61.8, 61.7, 61.6, 57.5, 56.3, 49.5, 37.4, 33.4, 31.5, 28.8, 28.6, 14.1(3), 14.1(7). IR (film, ν, cm\(^{-1}\)) 2978, 2936, 1731, 1683, 1473, 1386, 1258, 1195, 1059, 967, 756. HR-MS (ESI) m/z calcd for C\(_{30}\)H\(_{33}\)ClNaO\(_5\) [M+Na\(^+\)] 531.1914, found 531.1923.
Diethyl 3-benzoyl-4-(4-(4-bromophenyl)-2-methylbut-3-yn-2-yl)-3-methylcyclopentane-1,1-dicarboxylate (3k)

33 mg, 60%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.63-7.59 (m, 2H), 7.37-7.33 (m, 1H), 7.33-7.26 (m, 4H), 7.07-7.03 (m, 2H), 4.26-4.18 (m, 4H), 3.11 (d, $J = 14.4$ Hz, 1H), 3.03-2.97 (m, 1H), 2.60-2.54 (m, 1H), 2.27 (d, $J = 14.0$ Hz, 1H), 2.24-2.19 (m, 1H), 1.62 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.28-1.24 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 209.8, 173.5, 171.5, 140.7, 132.9, 131.3, 130.3, 127.8(8), 127.8(6), 122.7, 121.7, 97.9, 82.2, 62.0, 61.8, 61.6, 57.6, 56.3, 49.4, 37.5, 33.2, 31.5, 29.4, 28.7, 14.1(3), 14.1(7). IR (film, v, cm$^{-1}$) 2978, 2935, 1731, 1684, 1559, 1457, 1255, 1194, 1071, 756, 692. HR-MS (ESI) m/z calcd for C$_{30}$H$_{33}$BrNaO$_5$ [M+Na]$^+$ 575.1409 found 575.1428.

Diethyl 3-benzoyl-3-methyl-4-(2,5,5-trimethylhex-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3l)

9 mg, 20%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.74-7.71 (m, 2H), 7.42-7.33 (m, 3H), 4.30-4.17 (m, 4H), 2.99-2.89 (m, 2H), 2.45-2.40 (m, 1H), 2.22-2.15 (m, 2H), 1.60 (s, 3H), 1.31-1.24 (m, 9H), 1.17 (s, 3H), 1.11 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 211.1, 174.0, 171.8, 141.1, 130.4, 128.0, 127.7, 90.8, 85.5, 61.8, 61.7, 61.5, 57.3, 56.1, 50.7, 37.1, 32.5, 32.3, 31.1, 28.3, 28.2, 27.4, 14.2, 14.1. IR (film, v, cm$^{-1}$) 2969, 2932, 2870, 1732, 1684, 1457, 1256, 1185, 1074, 967, 740. HR-MS (ESI) m/z calcd for C$_{28}$H$_{38}$NaO$_5$ [M+Na]$^+$ 477.2617, found 477.2632.

Diethyl 3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)-3-(4-methylbenzoyl)cyclopentane-1,1-dicarboxylate (3m)
24 mg, 49%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) (δ, ppm) 7.60 (d, \(J = 8.0\) Hz, 2H), 7.24-7.20 (m, 5H), 7.07 (d, \(J = 7.6\) Hz, 2H), 4.26-4.18 (m, 4H), 3.11 (d, \(J = 14.4\) Hz, 1H), 3.01-2.95 (m, 1H), 2.57-2.52 (m, 1H), 2.31 (s, 3H), 2.28-2.24 (m, 2H), 1.67 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.28-1.24 (m, 6H).

\(^1\)C NMR (100 MHz, CDCl\(_3\)) (δ, ppm) 209.5, 173.7, 171.7, 140.9, 137.9, 131.5, 128.4(1), 128.4(8), 128.1, 127.6, 123.8, 97.0, 83.0, 61.9, 61.8, 61.6, 57.6, 56.4, 49.7, 37.3, 33.1, 31.8, 28.7(0), 28.7(9), 21.5, 14.2, 14.1. IR (film, \(ν\), cm\(^{-1}\)) 2978, 2935, 1731, 1677, 1444, 1386, 1255, 1187, 968, 757, 692. HR-MS (ESI) m/z calc'd for C\(_{31}\)H\(_{36}\)NaO\(_5\) [M+Na]\(^+\) 511.2460, found 511.2465.

Diethyl 3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)-3-(3-methylbenzoyl)cyclopentane-1,1-dicarboxylate (3n)

25 mg, 51%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) (δ, ppm) 7.47-7.44 (m, 1H), 7.40 (s, 1H), 7.25-7.18 (m, 5H), 7.18-7.12 (m, 2H), 4.26-4.19 (m, 4H), 3.10 (d, \(J = 14.0\) Hz, 1H), 3.04-2.97 (m, 1H), 2.58-2.53 (m, 1H), 2.28-2.22 (m, 2H), 2.20 (s, 3H), 1.65 (s, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.29-1.25 (m, 6H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) (δ, ppm) 210.4, 173.6, 171.6, 140.8, 137.6, 131.5, 131.0, 128.6, 128.1, 127.6(2), 127.6(5), 124.8, 123.8, 97.0, 83.0, 61.9, 61.6, 57.6, 56.3, 49.6, 37.4, 33.0, 32.0, 28.8, 28.7, 21.3, 14.2, 14.1. IR (film, \(ν\), cm\(^{-1}\)) 2978, 2933, 1731, 1684, 1444, 1366, 1254, 1193, 1071, 978, 861, 757, 693. HR-MS (ESI) m/z calc'd for C\(_{31}\)H\(_{36}\)NaO\(_5\) [M+Na]\(^+\) 511.2460, found 511.2459.

Diethyl 3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)-3-(2-methylbenzoyl)cyclopentane-1,1-dicarboxylate (3o)
Diethyl 3-(4-(tert-butyl)benzoyl)-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3p)

28 mg, 57%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.69 (d, $J = 7.6$ Hz, 1H), 7.34-7.31 (m, 2H), 7.23-7.21 (m, 3H), 7.19-7.15 (m, 2H), 7.10-7.05 (m, 1H), 4.27-4.17 (m, 4H), 3.17-3.07 (m, 2H), 2.62-2.57 (m, 1H), 2.30 (s, 3H), 2.23-2.18 (m, 1H), 2.15 (d, $J = 14.4$ Hz, 1H), 1.52 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H), 1.29-1.25 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 213.6, 173.8, 171.5, 142.0, 134.1, 131.5, 130.9, 128.6, 128.2, 127.7, 124.9(3), 124.9(0), 123.7, 96.2, 83.5, 62.0, 61.9, 61.6, 57.3, 56.2, 49.7, 37.7, 33.4, 31.7, 29.2, 27.6, 20.2, 14.2, 14.1. IR (film, ν, cm$^{-1}$) 2923, 2852, 1732, 1683, 1457, 1385, 1254, 1196, 1071, 964, 756, 668. HR-MS (ESI) m/z calcd for C$_{31}$H$_{36}$NaO$_5$ [M+Na]$^+$ 511.2460, found 511.2458.

Diethyl 3-(4-methoxybenzoyl)-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3q)

22 mg, 41%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.64-7.61 (m, 2H), 7.30-7.26 (m, 2H), 7.20-7.15 (m, 5H), 4.26-4.19 (m, 4H), 3.12 (d, $J = 14.4$ Hz, 1H), 3.02-2.96 (m, 1H), 2.59-2.53 (m, 1H), 2.29-2.23 (m, 2H), 1.68 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H), 1.28-1.27 (m, 3H), 1.26 (s, 9H), 1.26-1.24 (m 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 209.4, 173.6, 171.7, 153.8, 137.7, 131.4, 128.3, 128.1, 127.5, 124.6, 123.8, 96.9, 83.0, 62.0, 61.9, 61.6, 57.7, 56.4, 49.5, 37.4, 34.9, 33.1, 31.8, 31.2(2), 31.2(0), 31.2(5), 29.0, 28.9, 14.2, 14.1. IR (film, ν, cm$^{-1}$) 2978, 2933, 1731, 1684, 1490, 1254, 1193, 1071, 757, 861, 693. HR-MS (ESI) m/z calcd for C$_{34}$H$_{42}$NaO$_5$ [M+Na]$^+$ 553.2930, found 553.2954.
Diethyl 3-(3-methoxybenzoyl)-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3r)

22 mg, 43%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 50/1); ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.34-7.26 (m, 4.6H), 7.26-7.17 (m, 9H), 7.15-7.14 (m, 1H), 7.10-7.09 (m, 0.8H), 7.00-6.98 (m, 0.8H), 6.90-6.87 (m, 1H), 4.27-4.19 (m, 7.2H), 3.79 (s, 2.4H), 3.60 (s, 3H), 3.15-3.09 (m, 1.8H), 3.05-2.98 (m, 1H), 2.80 (d, J = 14.0 Hz, 0.8H), 2.76-2.71 (m, 0.8H), 2.67-2.60 (m, 1.6H), 2.58-2.53 (m, 1H), 2.29-2.21 (m, 2H), 1.66 (s, 3H), 1.54 (s, 2.4H), 1.43 (s, 3H), 1.38 (s, 2.4H), 1.37 (s, 3H), 1.29-1.24 (m, 10.8H), 1.20 (s, 2.4H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 209.9, 173.6, 171.6, 159.1, 142.1, 131.5, 128.7, 128.1, 127.7, 123.8, 120.0, 116.7, 112.8, 96.8, 83.2, 62.0, 61.9, 61.6, 57.6, 56.3, 55.2, 49.7, 37.5, 33.1, 31.8, 29.2, 28.6, 14.2, 14.1. IR (film, v, cm⁻¹) 2979, 2934, 1731, 1684, 1458, 1257, 1194, 913, 749, 693. HR-MS (ESI) m/z calcd for C₃₁H₃₆NaO₆ [M+Na]⁺ 527.2410, found 527.2410.

Diethyl 3-(4-fluorobenzoyl)-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3s)

18 mg, 36%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 50/1); ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.74 (d, J = 8.8 Hz, 2H), 7.21 (s, 5H), 6.75 (d, J = 8.4 Hz, 2H), 4.26-4.19 (m, 4H), 3.77 (s, 3H), 3.12 (d, J = 14.4 Hz, 1H), 2.98-2.92 (m, 1H), 2.57-2.52 (m, 1H), 2.30-2.24 (m, 2H), 1.71 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H), 1.28-1.24 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 207.6, 173.5, 171.6, 161.4, 132.8, 131.4, 130.8, 128.0, 127.5, 123.7, 112.8, 97.0, 82.9, 61.7(3), 61.7(8), 61.5, 57.6, 56.5, 55.3, 49.6, 37.2, 33.0, 31.7, 28.8, 28.5, 14.1, 14.0. IR (film, v, cm⁻¹) 2977, 2933, 1731, 1601, 1507, 1385, 1254, 1177, 1031, 757, 692, 669. HR-MS (ESI) m/z calcd for C₃₁H₃₆NaO₆ [M+Na]⁺ 527.2410, found 527.2418.
Diethyl 3-(4-chlorobenzoyl)-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3t)

29 mg, 59%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.73-7.68 (m, 2H), 7.24-7.18 (m, 5H), 6.96-6.90 (m, 2H), 4.27-4.19 (m, 4H), 3.09 (d, $J = 14.4$ Hz, 1H), 2.99-2.93 (m, 1H), 2.58-2.53 (m, 1H), 2.29-2.23 (m, 1H), 1.66 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.29-1.25 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 208.2, 173.5, 171.5, 163.9 ($^1$J$_{CF}$ = 250.0 Hz), 136.6 ($^4$J$_{CF}$ = 3.3 Hz), 131.3, 130.7 ($^3$J$_{CF}$ = 8.6 Hz), 128.1, 127.7, 123.6, 114.7 ($^2$J$_{CF}$ = 21.5 Hz), 96.8, 83.2, 61.9(9), 61.9(5), 61.6, 57.5, 56.5, 49.5, 37.3, 33.0, 31.8, 28.9, 28.7, 14.1(3), 14.1(7). IR (film, $\nu$, cm$^{-1}$) 2978, 2933, 1731, 1684, 1599, 1457, 1256, 1194, 1071, 969, 844, 757, 692. HR-MS (ESI) m/z calcd for C$_{30}$H$_{33}$FNaO$_5$ [M+Na]$^+$ 515.2210, found 515.2231.

Diethyl 3-(3-chlorobenzoyl)-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3u)

26 mg, 51%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.64-7.60 (m, 2H), 7.24-7.19 (m, 7H), 4.27-4.19 (m, 4H), 3.08 (d, $J = 14.4$ Hz, 1H), 2.99-2.92 (m, 1H), 2.59-2.54 (m, 1H), 2.28-2.22 (m, 2H), 1.64 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.28-1.25 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 208.6, 173.4, 171.5, 138.8, 136.6, 131.3, 129.6, 128.1, 128.0, 127.7, 123.5, 96.7, 83.3, 62.0, 61.9, 61.6, 57.5, 56.5, 49.5, 37.3, 33.0, 31.8, 29.0, 28.6, 14.1(3), 14.1(7). IR (film, $\nu$, cm$^{-1}$) 2977, 2932, 1731, 1684, 1489, 1457, 1255, 1194, 1092, 968, 757, 692. HR-MS (ESI) m/z calcd for C$_{30}$H$_{33}$ClNaO$_5$ [M+Na]$^+$ 531.1914, found 531.1921.
27 mg, 53%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.56-7.52 (m, 2H), 7.40-7.37 (m, 2H), 7.25-7.19 (m, 5H), 4.27-4.19 (m, 4H), 3.08 (d, \(J = 14.4\) Hz, 1H), 2.99-2.92 (m, 1H), 2.59-2.54 (m, 1H), 2.29-2.22 (m, 2H), 1.64 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.28-1.25 (m, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 208.8, 173.5, 171.6, 139.3, 131.4, 131.0, 129.8, 128.2, 127.8, 125.1, 123.5, 96.7, 83.4, 62.0, 61.9, 61.7, 57.5, 56.5, 49.5, 37.4, 33.1, 31.8, 29.0, 28.6, 14.2, 14.1. IR (film, \(\nu\), cm\(^{-1}\)) 2977, 2932, 1731, 1684, 1457, 1365, 1255, 1193, 1071, 967, 756, 692. HR-MS (ESI) m/z calcd for C\(_{30}\)H\(_{33}\)ClNaO\(_5\) [M+Na]\(^+\) 531.1914, found 531.1928.

Diethyl 3-(2-chlorobenzoyl)-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3v)

25 mg, 50%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.74-7.71 (m, 1H), 7.35-7.31 (m, 4H), 7.24-7.20 (m, 4H), 4.25-4.17 (m, 6H), 3.35 (d, \(J = 14.4\) Hz, 1H), 3.15-3.08 (m, 1H), 2.62-2.57 (m, 1H), 2.20 (d, \(J = 14.8\) Hz, 1H), 2.16-2.11 (m, 1H), 1.49 (s, 3H), 1.47 (s, 3H), 1.42 (s, 3H), 1.38 (s, 1.5H), 1.28-1.24 (m, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 210.5, 173.8, 171.4, 142.2, 131.6, 129.6(3), 129.6(9), 129.1, 128.2, 127.8, 126.6, 126.5, 123.6, 95.5, 84.0, 62.5, 61.9, 61.6, 57.2, 56.4, 49.4, 38.1, 33.7, 31.0, 30.8, 26.5, 14.2, 14.1. IR (film, \(\nu\), cm\(^{-1}\)) 2978, 2934, 1732, 1697, 1457, 1386, 1254, 1194, 1071, 965, 757, 692. HR-MS (ESI) m/z calcd for C\(_{30}\)H\(_{33}\)ClNaO\(_5\) [M+Na]\(^+\) 531.1914, found 531.1925.

Diethyl 3-(2,3-dichlorobenzoyl)-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3w)
Diethyl 3-(2,4-dichlorobenzoyl)-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3x)

25 mg, 46%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^{1}$H NMR (400 MHz, CDCl$_3$) ($\delta$, ppm) 7.68 (d, $J = 8.4$ Hz, 1H), 7.43 (d, $J = 1.6$ Hz, 0.5H), 7.37-7.32 (m, 4.5H), 7.31-7.32 (m, 1H), 7.25-7.22 (m, 4H), 7.14-7.11 (m, 1H), 4.25-4.17 (m, 6H), 3.30 (d, $J = 14.8$ Hz, 1H), 3.11-3.04 (m, 1H), 3.01-2.96 (m, 0.5H), 2.75-2.57 (m, 3.5H), 2.20 (d, $J = 14.4$ Hz, 1H), 2.15-2.10 (m, 1H), 1.48 (s, 3H), 1.46 (s, 3H), 1.45 (s, 1.5H), 1.41 (s, 4.5H), 1.35 (s, 1.5H), 1.28-1.24 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) ($\delta$, ppm) 209.6, 173.7, 171.4, 140.6, 134.9, 131.5, 130.2, 129.5, 128.3, 127.9, 127.5, 127.0, 123.4, 95.3, 84.2, 62.6, 61.9, 61.6, 57.2, 56.4, 49.3, 38.1, 33.7, 31.1, 30.8, 26.5, 14.2, 14.1. IR (film, $v$, cm$^{-1}$) 2979, 2928, 1732, 1699, 1585, 1464, 1366, 1254, 1195, 1071, 966, 864, 757, 692. HR-MS (ESI) m/z calcd for C$_{30}$H$_{32}$Cl$_{2}$NaO$_{5}$ [M+Na]$^+$ 565.1524, found 565.1531.
Diethyl 3-(3,5-dichlorobenzoyl)-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3y)

33 mg, 61%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 8.20 (d, $J = 1.6$ Hz, 1H), 7.49 (d, $J = 2.0$ Hz, 2H), 7.40-7.37 (m, 1H), 7.28-7.27 (m, 1H), 7.24-7.22 (m, 3H), 4.28-4.20 (m, 4H), 3.67-3.64 (m, 0.6H), 3.06 (d, $J = 14.4$ Hz, 1H), 2.97-2.90 (m, 1H), 2.62-2.57 (m, 1H), 2.28-2.22 (m, 2H), 1.66 (s, 1.8H), 1.62 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H), 1.29-1.25 (m, 6H), 1.25-1.14 (m, 7.2H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 207.1, 173.2, 171.3, 142.9, 134.6, 131.4, 130.1, 128.1, 127.8, 126.3, 123.2, 96.5, 83.8, 62.1, 61.9, 61.7, 57.5, 56.6, 49.2, 37.3, 32.9, 29.0, 28.4, 26.6, 14.1(4), 14.1(7). IR (film, ν, cm$^{-1}$) 2980, 2936, 1732, 1694, 1563, 1444, 1367, 1253, 1196, 1071, 865, 757, 692. HR-MS (ESI) m/z calcd for C$_{30}$H$_{32}$Cl$_2$NaO$_5$ [M+Na]$^+$ 565.1524, found 565.1533.

Diethyl 3-(4-bromobenzoyl)-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3z)

29 mg, 52%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.62-7.61 (m, 1H), 7.53-7.51 (m, 1H), 7.31-7.28 (m, 1H), 7.26-7.17 (m, 6H), 4.27-4.19 (m, 4H), 3.08 (d, $J = 14.4$ Hz, 1H), 3.00-2.94 (m, 1H), 2.60-2.55 (m, 1H), 2.28-2.22 (m, 2H), 1.63 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.29-1.25 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 208.7, 173.5, 171.5, 142.2, 134.0, 131.5, 130.3, 129.1, 128.2, 128.1, 127.8, 125.9, 123.5, 96.7, 83.5, 62.0, 61.9, 61.7, 57.5, 56.5, 49.5, 37.4, 33.0, 32.0, 29.0, 28.5, 14.2, 14.1. IR (film, ν, cm$^{-1}$) 2977, 2934, 1732, 1684, 1559, 1457, 1255, 1194, 1071, 756, 692. HR-MS (ESI) m/z calcd for C$_{30}$H$_{33}$BrNaO$_5$ [M+Na]$^+$ 575.1409, found 575.1410.
Diethyl 3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)-3-propionycyclopentane-1,1-dicarboxylate (3aa)

24 mg, 56%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.39-7.35 (m, 2H), 7.31-7.26 (m, 3H), 4.32-4.24 (m, 2H), 4.22-4.16 (m, 2H), 2.97-2.88 (m, 1H), 2.80-2.69 (m, 2H), 2.57-2.47 (m, 1H), 2.38-2.33 (m, 1H), 2.13 (d, J = 14.4 Hz, 1H), 2.08-2.03 (m, 1H), 1.58 (s, 3H), 1.43 (s, 3H), 1.30-1.23 (m, 9H), 0.91-0.87 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 215.7, 173.9, 171.8, 131.6, 128.3, 127.8, 123.7, 95.3, 83.1, 61.8, 61.5, 60.8, 57.0, 56.4, 48.1, 36.9, 35.3, 33.0, 30.9, 29.5, 26.1, 14.2, 14.1, 8.0. IR (film, ν, cm⁻¹) 2978, 2937, 1731, 1699, 1559, 1457, 1364, 1255, 1190, 1073, 974, 756, 693. HR-MS (ESI) m/z calcd for C₂₆H₃₄NaO₅ [M+Na]⁺ 449.2304, found 449.2332.

Diethyl 3-heptanoyl-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3bb)

22 mg, 46%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.39-7.34 (m, 2H), 7.29-7.26 (m, 2H), 7.26-7.25 (m, 1H), 4.31-4.23 (m, 2H), 4.21-4.16 (m, 2H), 2.87-2.69 (m, 3H), 2.53-2.45 (m, 1H), 2.38-2.33 (m, 1H), 2.13 (d, J = 14.4 Hz, 1H), 2.07-2.02 (m, 1H), 1.57 (s, 3H), 1.47-1.32 (m, 5H), 1.30-1.23 (m, 9H), 1.18-1.06 (m, 6H), 0.80-0.77 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 215.3, 173.9, 171.7, 131.5, 128.3, 127.8, 123.7, 95.4, 83.1, 61.8, 61.5, 60.8, 57.0, 56.4, 47.9, 42.4, 37.0, 33.0, 31.7, 30.9, 29.7, 28.9, 26.2, 23.7, 22.6, 14.2, 14.1. IR (film, ν, cm⁻¹) 2958, 2931, 2871, 1731, 1697, 1457, 1385, 1254, 1191, 1076, 756, 692. HR-MS (ESI) m/z calcd for C₃₀H₄₂NaO₅ [M+Na]⁺ 505.2930, found 505.2942.

Diethyl 3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)-3-tridecanoylcyclopentane-1,1-dicarboxylate (3cc)
Diethyl 3-(4-fluorobenzoyl)-4-(4-(4-methoxyphenyl)-2-methylbut-3-yn-2-yl)-3-methylcyclopentane-1,1-dicarboxylate (3dd)

25 mg, 48%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 50/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.74-7.69 (m, 2H), 7.15-7.12 (m, 2H), 6.96-6.91 (m, 2H), 6.76-6.72 (m, 2H), 4.27-4.19 (m, 4H), 4.16-4.08 (m, 0.7H), 3.80 (s, 0.5H), 3.78 (s, 3H), 3.70 (d, $J = 14.4$ Hz, 1H), 2.98-2.92 (m, 1H), 2.57-2.52 (m, 1H), 2.28-2.22 (m, 2H), 1.65 (s, 3H), 1.65 (s, 0.5H), 1.43 (s, 0.5H), 1.41 (s, 3H), 1.36 (s, 0.5H), 1.32 (s, 3H), 1.28-1.25 (m, 7H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 208.5, 173.6, 171.6, 163.9 ($^1$J$_{CF} = 250.0$ Hz), 159.2, 136.8 ($^4$J$_{CF} = 3.6$ Hz), 132.7, 130.8 ($^1$J$_{CF} = 8.6$ Hz), 115.8, 114.8 ($^2$J$_{CF} = 21.6$ Hz), 113.8, 95.2, 83.1, 62.1, 61.9, 61.6, 57.6, 56.5, 55.3, 49.7, 37.3, 33.0, 31.9, 28.9, 28.7, 14.2, 14.1. IR (film, ν, cm$^{-1}$) 2978, 1733, 1700, 1569, 1457, 1385, 1249, 1182, 1072, 968, 749, 668. HR-MS (ESI) m/z calcd for C$_{31}$H$_{35}$FNaO$_6$ [M+Na]$^+$ 545.2315, found 545.2338.
Diethyl 4-(4-(4-chlorophenyl)-2-methylbut-3-yn-2-yl)-3-methyl-3-(4-methylbenzoyl)cyclopentane-1,1-dicarboxylate (3ee)

\[
\begin{align*}
\text{EtO}_2\text{C} & \quad \text{Cl} \\
\text{EtO}_2\text{C} & \quad \text{EtO}_2\text{C}
\end{align*}
\]

(>19:1 dr)

26 mg, 50%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.56 (d, \(J = 8.4\) Hz, 2H), 7.17-7.14 (m, 2H), 7.12-7.09 (m, 2H), 7.07 (d, \(J = 8.0\) Hz, 2H), 4.25-4.18 (m, 4H), 3.12 (d, \(J = 14.4\) Hz, 1H), 3.00-2.94 (m, 1H), 2.58-2.53 (m, 1H), 2.31 (s, 3H), 2.27 (d, \(J = 14.4\) Hz, 1H), 2.25-2.20 (m, 1H), 1.64 (s, 3H), 1.41 (s, 3H), 1.34 (s, 3H), 1.28-1.23 (m, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 209.1, 173.6, 171.6, 140.9, 137.7, 133.5, 132.7, 128.4(0), 128.4(6), 128.3, 122.3, 97.8, 82.1, 62.0, 61.9, 61.6, 57.7, 56.4, 49.4, 37.5, 33.2, 31.5, 29.3, 28.9, 21.4, 14.2, 14.1. IR (film, \(\nu\), cm\(^{-1}\)) 2978, 2934, 1731, 1684, 1559, 1457, 1365, 1254, 1187, 1072, 967, 828, 749, 669. HR-MS (ESI) m/z calcd for C\(_{31}\)H\(_{35}\)ClNaO\(_5\) [M+Na]\(^+\) 545.2071, found 545.2105.

Diethyl 4-(4-(4-chlorophenyl)-2-methylbut-3-yn-2-yl)-3-(4-fluorobenzoyl)-3-methylcyclopentane-1,1-dicarboxylate (3ff)

\[
\begin{align*}
\text{F} & \quad \text{Cl} \\
\text{EtO}_2\text{C} & \quad \text{EtO}_2\text{C}
\end{align*}
\]

(>19:1 dr)

28 mg, 53%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) (\(\delta\), ppm) 7.69-7.64 (m, 2H), 7.19-7.16 (m, 2H), 7.12-7.09 (m, 2H), 6.97-6.91 (m, 2H), 4.26-4.19 (m, 4H), 3.09 (d, \(J = 14.4\) Hz, 1H), 2.99-2.92 (m, 1H), 2.59-2.54 (m, 1H), 2.29-2.20 (m, 2H), 1.63 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.28-1.24 (m, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) (\(\delta\), ppm) 208.0, 173.5, 171.6, 164.0 (\(^3\)J\(_\text{CF} = 250.4\) Hz), 136.6 (\(^4\)J\(_\text{CF} = 3.5\) Hz), 133.7, 132.6, 130.7 (\(^2\)J\(_\text{CF} = 8.6\) Hz), 128.5, 122.1, 114.8 (\(^2\)J\(_\text{CF} = 21.5\) Hz), 97.7, 82.3, 62.0, 61.9, 61.7, 57.6, 56.5, 49.4, 37.5, 33.2, 31.5, 29.4, 28.8, 14.2, 14.1. IR (film, \(\nu\), cm\(^{-1}\)) 2979, 2934, 1731, 1684, 1599, 1457, 1255, 1194, 1073, 969, 830, 744, 669. HR-MS (ESI) m/z calcd for C\(_{30}\)H\(_{32}\)ClFNaO\(_5\) [M+Na]\(^+\) 549.1820, found 549.1828.
Diethyl 3-(4-chlorobenzoyl)-4-(4-(4-chlorophenyl)-2-methylbut-3-yn-2-yl)-3-methylcyclopentane-1,1-dicarboxylate (3gg)

(Scheme 1)

22 mg, 40%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.60-7.56 (m, 2H), 7.25-7.22 (m, 2H), 7.19-7.16 (m, 2H), 7.12-7.09 (m, 2H), 4.26-4.19 (m, 4H), 3.09 (d, $J = 14.4$ Hz, 1H), 2.98-2.92 (m, 1H), 2.60-2.55 (m, 1H), 2.27 (d, $J = 14.4$ Hz, 1H), 2.24-2.19 (m, 1H), 1.61 (s, 3H), 1.41 (s, 3H), 1.34 (s, 3H), 1.28-1.24 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 208.4, 173.4, 171.5, 138.8, 136.7, 133.7, 132.6, 129.6, 128.5, 128.1, 122.0, 97.6, 82.4, 62.1, 61.9, 61.7, 57.6, 56.5, 49.3, 37.5, 33.2, 31.5, 29.5, 28.7, 14.2, 14.1. IR (film, ν, cm$^{-1}$) 2978, 2935, 1732, 1684, 1559, 1457, 1365, 1255, 1194, 1073, 968, 830, 743. HR-MS (ESI) m/z calcd for C$_{30}$H$_{32}$Cl$_2$NaO$_5$ [M+Na]$^+$ 565.1524, found 565.1547.

Diethyl 3-benzoyl-3-methyl-4-(3-phenylprop-2-yn-1-yl)cyclopentane-1,1-dicarboxylate (3hh)

(Scheme 2)

23 mg, 52%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); $^1$H NMR (400 MHz, CDCl$_3$) (δ, ppm) 7.92-7.88 (m, 2H), 7.53-7.45 (m, 3H), 7.37-7.33 (m, 2H), 7.31-7.28 (m, 3H), 4.31-4.20 (m, 5.3H), 3.38 (d, $J = 14.8$ Hz, 1H), 3.15-2.93 (m, 2H), 2.85-2.77 (m, 1H), 2.76-2.72 (m, 1H), 2.49-2.40 (m, 3H), 2.28-2.21 (m, 0.7H), 1.53 (s, 3H), 1.44 (s, 1H), 1.34-1.28 (m, 6H), 1.27-1.25 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 204.6, 172.9, 172.5, 137.4, 132.2, 131.6, 128.6, 128.5, 128.2, 127.7, 123.7, 88.6, 81.9, 61.9, 58.4, 57.4, 49.6, 43.4, 37.8, 25.9, 21.2, 14.1(3), 14.1(6). IR (film, ν, cm$^{-1}$) 2981, 2934, 2931, 1731, 1671, 1559, 1457, 1364, 1251, 1182, 975, 757, 693. HR-MS (ESI) m/z calcd for C$_{28}$H$_{32}$NaO$_5$ [M+Na]$^+$ 469.1991, found 469.1995.

Ethyl 1-acetyl-3-benzoyl-3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentancarboxylate (3ii)

(Scheme 3)
18 mg, 41%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); 1H NMR (400 MHz, CDCl3) (δ, ppm) 7.67-7.58 (m, 3H), 7.30-7.27 (m, 2H), 7.24-7.20 (m, 5H), 4.25-4.18 (m, 2.5H), 3.11 (d, J = 14.4 Hz, 1H), 2.98-2.92 (m, 1H), 2.65-2.60 (m, 1H), 2.50-2.45 (m, 0.3H), 2.30 (s, 3H), 2.26-2.23 (m, 1H), 2.23-2.22 (m, 0.8H), 2.22-2.19 (m, 1H), 1.64 (s, 3H), 1.62 (s, 0.8H), 1.43 (s, 3H), 1.41 (s, 0.8H), 1.37 (s, 3H), 1.35 (s, 0.8H), 1.29-1.25 (m, 3.8H).

13C NMR (100 MHz, CDCl3) (δ, ppm) 210.3, 203.5, 173.7, 140.7, 131.4, 130.4, 128.2, 127.8(2), 127.8(9), 127.7, 123.7, 96.6, 83.2, 63.8, 61.9(2), 61.9(6), 56.2, 48.2, 36.7, 33.1, 31.8, 29.3, 28.6, 26.9, 14.1. IR (film, ν, cm⁻¹) 2972, 2924, 1715, 1683, 1443, 1362, 1237, 1187, 1071, 966, 757, 693. HR-MS (ESI) m/z calcd for C29H32NaO4 [M+Na]+ 467.2198, found 467.2223.

Diethyl 3-benzoyl-3-methyl-4-(2-methyl-4-((8R,9S,13S,14S)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2′-[1,3]dioxolan]-3-yl)but-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3jj)

31 mg, 45%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); 1H NMR (400 MHz, CDCl3) (δ, ppm) 7.69-7.67 (m, 2H), 7.39-7.35 (m, 2H), 7.32-7.28 (m, 2H), 7.14 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.91 (s, 1H), 4.27-4.18 (m, 4H), 3.98-3.89 (m, 4H), 3.09 (d, J = 14.0 Hz, 1H), 3.02-2.95 (m, 1H), 2.77-2.71 (m, 2H), 2.56-2.51 (m, 1H), 2.33-2.21 (m, 4H), 2.06-1.99 (m, 1H), 1.89-1.72 (m, 4H), 1.65 (s, 3H), 1.63-1.45 (m, 4H), 1.42 (s, 3H), 1.40-1.35 (m, 2H), 1.34 (s, 3H), 1.29-1.25 (m, 6H), 0.87 (s, 3H). 13C NMR (100 MHz, CDCl3) (δ, ppm) 210.3, 173.7, 171.6, 140.8, 140.2, 136.6, 131.8, 130.4, 128.6, 128.0, 127.8, 125.2, 120.8, 119.5, 96.0, 83.1, 65.4, 64.7, 61.9(8), 61.9(5), 61.6, 57.5, 56.3, 49.5, 46.2, 44.1, 38.8(6), 38.8(5), 37.3, 34.3, 33.0, 32.1, 30.8, 29.3(1), 29.3(9), 28.6(6), 28.6(5), 26.9, 25.9, 22.4, 14.4, 14.2,
14.1. IR (film, ν, cm⁻¹) 2972, 2936, 1732, 1684, 1457, 1366, 1256, 1181, 1073, 967, 701. HR-MS (ESI) m/z calcd for C₄₄H₅₄NaO₇ [M+Na]⁺ 717.3767, found 717.3786.

**Diethyl 3-methyl-3-(4-methyl-2-oxocyclohexyl)-4-(2-methyl-4-phenylbut-3-yn-2-yl)cyclopentane-1,1-dicarboxylate (3kk)**

![Chemical structure](image)

(2.5:1 dr)

23 mg, 48%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.41-7.31 (m, 3H), 7.30-7.26 (m, 4H), 4.31-4.12 (m, 5.6H), 3.10 (d, J = 14.8 Hz, 0.4H), 2.96-2.92 (m, 1.4H), 2.90-2.85 (m, 1H), 2.80-2.66 (m, 2.4H), 2.52-2.43 (m, 0.8H), 2.34-2.27 (m, 2H), 2.21-2.14 (m, 2H), 2.05-1.77 (m, 5.4H), 1.42 (s, 1.2H), 1.35 (s, 1.2H), 1.32 (s, 3H), 1.30 (s, 3H), 1.29-1.20 (m, 12H), 1.18 (s, 3H), 0.93 (d, J = 5.6 Hz, 3H), 0.82 (d, J = 6.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) (δ, ppm) 212.7, 173.2, 172.8, 131.3, 128.3, 127.6, 124.2, 97.2, 82.8, 61.5(0), 61.5(6), 56.8, 56.2, 52.7, 50.3, 46.0, 43.6, 37.2, 35.7, 35.3, 33.2, 31.0, 30.5, 30.4, 22.4, 22.1, 14.2, 14.1. IR (film, ν, cm⁻¹) 2978, 2927, 1733, 1684, 1559, 1457, 1385, 1252, 1193, 757, 669. HR-MS (ESI) m/z calcd for C₃₀H₄₀NaO₅ [M+Na]⁺ 503.2773, found 503.2806.

**Diethyl 3-methyl-4-(2-methyl-4-phenylbut-3-yn-2-yl)-3-(4-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)benzoyl)cyclopentane-1,1-dicarboxylate (3ll)**

![Chemical structure](image)

(>19:1 dr)

34 mg, 37%; colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 75/1); ¹H NMR (400 MHz, CDCl₃) (δ, ppm) 7.71 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.25-7.19 (m, 5H), 4.66 (s, 2H), 4.28-4.20 (m, 4H), 3.14 (d, J = 14.0 Hz, 1H), 3.05-2.98 (m, 1H), 2.60-2.55 (m, 3H), 2.31-2.25 (m, 2H), 2.18 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 1.86-1.73 (m,
2H), 1.69 (s, 3H), 1.60-1.35 (m, 14H), 1.30-1.23 (m, 15H), 1.17-1.02 (m, 7H), 0.88-0.84 (m, 12H).

$^{13}$C NMR (100 MHz, CDCl$_3$) (δ, ppm) 209.6, 173.6, 171.6, 148.1, 148.0, 140.5, 140.0, 131.5, 128.3, 128.1, 127.9, 127.6, 126.7, 126.0, 123.8, 123.1, 117.7, 96.9, 83.2, 74.9, 74.1, 62.0, 61.9, 61.6, 57.6, 56.4, 49.6, 40.1, 39.5, 37.5(4), 37.5(0), 37.4, 33.1, 32.9, 32.8, 31.8, 31.4, 28.9, 28.7, 28.1, 24.9, 24.5, 24.0, 22.8, 22.7, 21.1, 20.8, 19.9, 19.8, 14.2, 14.1, 12.9, 12.1, 11.9. IR (film, ν, cm$^{-1}$) 2927, 2868, 1733, 1684, 1458, 1367, 1256, 1193, 1089, 969, 862, 756, 692. HR-MS (ESI) m/z calcd for C$_{60}$H$_{84}$NaO$_7$ [M+Na]$^+$ 939.6115, found 939.6118.
$^1$H NMR Spectrum of Compound 3a
$^{13}$C NMR Spectrum of Compound 3a
$^1$H NMR Spectrum of Compound 3b
$^{13}$C NMR Spectrum of Compound 3b
$^1$H NMR Spectrum of Compound 3c

S40
$^{13}$C NMR Spectrum of Compound 3c
$^1$H NMR Spectrum of Compound 3d
$^{13}$C NMR Spectrum of Compound 3d
The image shows a 1H NMR Spectrum of Compound 3e. The spectrum presents various peaks at different ppm values, indicating the chemical shifts of hydrogen atoms in the compound. The peaks are labeled with their respective ppm values, which are crucial for identifying the chemical structure of the compound. The spectrum is rendered on a graph with the x-axis representing ppm values and the y-axis showing the intensity of the signals. The molecular structure of Compound 3e is also depicted, providing a visual representation of the molecule's functional groups and their expected chemical shifts.
$^{13}$C NMR Spectrum of Compound 3e
S46

1H NMR Spectrum of Compound 3f
$^{13}$C NMR Spectrum of Compound 3f
$^1$H NMR Spectrum of Compound 3g
$^{13}$C NMR Spectrum of Compound 3g
$^1$H NMR Spectrum of Compound 3h

S50
$^{13}$C NMR Spectrum of Compound 3h
$^1$H NMR Spectrum of Compound 3i
$^{13}$C NMR Spectrum of Compound 3i


$^1$H NMR Spectrum of Compound 3j

S54
$^{13}$C NMR Spectrum of Compound 3j
$^1$H NMR Spectrum of Compound 3k

S56
$^{13}$C NMR Spectrum of Compound 3k
$^1$H NMR Spectrum of Compound 3l
$^{13}$C NMR Spectrum of Compound 3l

S59
\[ 1^H \text{NMR Spectrum of Compound 3m} \]
$^{13}$C NMR Spectrum of Compound 3m

S61
S62

1H NMR Spectrum of Compound 3n

S62
$^{13}$C NMR Spectrum of Compound 3n
$^1H$ NMR Spectrum of Compound 3o

$dr = 5:1$
$^{13}$C NMR Spectrum of Compound 3o

$\text{dr} = 5:1$
$^1$H NMR Spectrum of Compound 3p

866
$^{13}$C NMR Spectrum of Compound 3p
$^1$H NMR Spectrum of Compound 3q

S68
$^{13}$C NMR Spectrum of Compound 3q

869
$^1$H NMR Spectrum of Compound 3r

S70
$^{13}$C NMR Spectrum of Compound 3β
$^1$H NMR Spectrum of Compound 3s
$^{13}$C NMR Spectrum of Compound 3s
$^1$H NMR Spectrum of Compound 3t
$^{13}$C NMR Spectrum of Compound 3t
1H NMR Spectrum of Compound 3u

S76
$^{13}$C NMR Spectrum of Compound 3u
1H NMR Spectrum of Compound 3v
$^{13}$C NMR Spectrum of Compound 3v

S79
$\text{\textsuperscript{1}H NMR Spectrum of Compound 3w}$
$^{13}$C NMR Spectrum of Compound 3w
$^1$H NMR Spectrum of Compound 3x
$^{13}$C NMR Spectrum of Compound 3x
1H NMR Spectrum of Compound 3y

dr 1:7:1
$^{13}$C NMR Spectrum of Compound 3y

S85
$^1$H NMR Spectrum of Compound 3z
$^{13}$C NMR Spectrum of Compound 3z

S87
$^{1}H$ NMR Spectrum of Compound 3aa
$^{13}$C NMR Spectrum of Compound 3aa

S89
$^1$H NMR Spectrum of Compound 3bb

S90
$^{13}$C NMR Spectrum of Compound 3bb
$^{13}$C NMR Spectrum of Compound 3cc
1H NMR Spectrum of Compound 3dd
$^{13}$C NMR Spectrum of Compound 3dd

S95
1H NMR Spectrum of Compound 3ee
1H NMR Spectrum of Compound 3ff
$^{13}$C NMR Spectrum of Compound 3ff
$^1$H NMR Spectrum of Compound 3gg
$^{13}$C NMR Spectrum of Compound 3gg

S101
1H NMR Spectrum of Compound 3hh

S102
$^{13}$C NMR Spectrum of Compound 3hh
$^1$H NMR Spectrum of Compound 3ii

S104
$^{13}$C NMR Spectrum of Compound 3ii
$^1$H NMR Spectrum of Compound 3jj
$^{13}C$ NMR Spectrum of Compound 3jj
S107
1H NMR Spectrum of Compound 3kk

dr 2.5:1
$^{13}$C NMR Spectrum of Compound 3kk

S109
$^{13}$C NMR Spectrum of Compound 3ll

S111