Enantioselective Cyclizations of Silyloxyenynes Catalyzed by Cationic Metal Phosphine Complexes

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Supporting Information (Part A)

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I. General Information.

Unless otherwise noted, all reagents were obtained commercially and used without further purification. Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF) was ordered from Strem Chemicals. Tetrahydrofuran (THF), diethyl ether (Et_2O), and dichloromethane (CH_2Cl_2) were dried by passing commercially available predried, oxygen-free formulations through activated alumina columns.[1] Triethylamine (Et_3N) was distilled from CaH_2. Unless otherwise noted, all reaction mixtures were stirred with a magnetic stir bar in flame-dried glassware under a positive pressure of dry nitrogen. The gold(I)-catalyzed reactions were performed in screw-cap vials under air without exlusion of moisture. Racemic samples were obtained using DTBM-SEGPHOS$(AuCl)_2$ and NaBARF as catalyst. Chiral gold(I) catalysts were prepared according to a procedure previously described by our group.[2,3]

Chromatography. Analytical thin layer chromatography (TLC) was performed on Merck precoated glass-backed TLC plates (silica gel 60 F_{254}) and visualized by UV lamp (254 nm) and potassium permanganate ($KMnO_4$) stain. Chromatography on silica gel was carried out using ICN SiliTech 32-63 D 60 Å silica gel. Technical grade solvents were employed, which were distilled prior to use. Concentration under reduced pressure was performed by rotary evaporation at 40 °C at the appropriate pressure. Purified compounds were further dried under high vacuum (0.3 Torr). Yields refer to chromatographically purified and spectroscopically pure compounds, unless stated otherwise.

Nuclear magnetic resonance spectra. ^1H and ^{13}C spectra were recorded on a Bruker AV-300, AVQ-400, AVB-400 or AV-600 spectrometer. Chemical shifts (δ) are reported in ppm. ^1H NMR spectra were referenced to $CDCl_3$ (7.26 ppm) and ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 ppm). All ^{13}C spectra were measured with complete proton decoupling. Peak multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; and *J*, coupling constant in Hz.

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[1] Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Ed.* **2001**, *78*, 64.
[2] Johansson, M. J.; Gorin, D. J.; Stabe, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 18002.
[3] Melhado, A. D.; Luparia, M.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 12638.

HPLC analyses: Chiral high performance liquid chromatography (HPLC) was performed on Shimadzu VP and Shimadzu prominence series instruments using 4.6 x 25 cm Daicel Chiralcel OD-H and Chiralpak IB columns.

Mass spectroscopy. Mass spectral data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

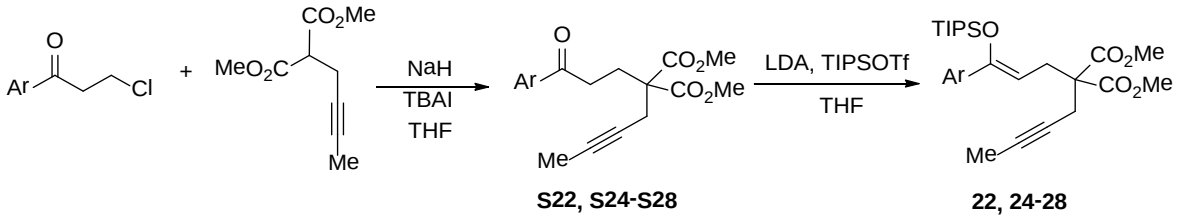
II. Palladium-catalyzed cyclizations

For more details on procedure and analytical data for compounds **1**–**21**, see reference Corkey, B. K.; Toste, F. D. *J. Am. Chem. Soc*. **2007***, 129*, 2764.

General Procedure for Palladium-catalyzed cyclizations of Silyloxy-1,6-enynes: A solution of substrate (0.02 mmol), acetic acid (2 drops, 10 μL) and (R)-DTBMSegphosPd$(OTf)_2$ (10 mol%) or BinaphanePd$(OTf)_2$ in diethyl ether (1 mL) was stirred until the reaction was complete as determined by TLC. The solvent was removed and the residue was purified on silica gel to give the desired products.

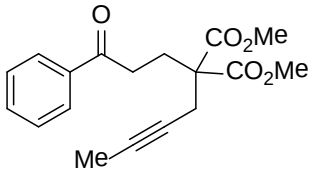
III. Synthesis of Silyloxy-1,6-enynes

*a) Synthesis of Silyloxy-1,6-enynes **22, 24-28***



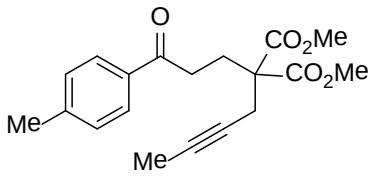
S22, S24-S28 **22, 24-28**

General Procedure A - Preparation of Aryl ketones: The alkyne (1.0 equiv.) was dissolved in THF (0.4 M) and cooled to 0 ^oC. Then, NaH (60 % in oil, 1.1 equiv.) was added in one portion. The reaction mixture was stirred for 30 min. at this temperature. The corresponding 3-chloroketone (1.0 equiv.) was dissolved in THF (0.5 M) and transferred slowly to the reaction mixture. Tetrabutylammonium iodide (TBAI, 0.1 equiv.) was added in one portion. The reaction was warmed to room temperature and then stirred at reflux for 5 h. The reaction mixture was quenched by the addition of an equal volume of sat. aq. NH_4Cl. The mixture was extracted with Et_2O (3 ×), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to provide analytically pure compound.



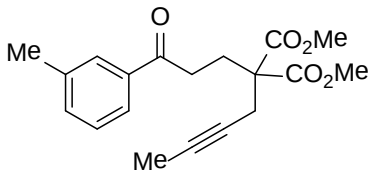
S22

Dimethyl-2-(but-2-yn-1-yl)-2-(3-oxo-3-phenylpropyl)malonate (S22): According to the general procedure A, the corresponding 3-chloroketone (342 mg, 2.0 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S22** (462 mg, 71%) as a white powder: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.63 – 7.53 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 3.76 (s, 6H), 3.16 – 2.94 (m, 2H), 2.95 – 2.77 (d, *J* = 2.7 Hz, 2H), 2.60 – 2.38 (m, 2H), 1.77 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.8, 170.80 136.7, 133.1, 128.6, 128.1, 79.4, 73.1, 56.6, 52.8, 33.8, 27.1, 24.3, 3.5; **HRMS** (ESI) calc for $[C_{18}H_{21}O_5]^+$ ($[M+H]^+$): *m/z* 317.1384, found 317.1388.



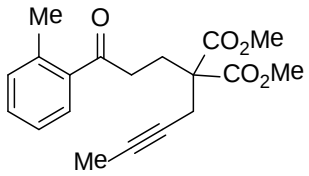
S24

Dimethyl-2-(but-2-yn-1-yl)-2-(3-oxo-3-(p-tolyl)propyl)malonate (S24): According to the general procedure A, the corresponding 3-chloroketone (547 mg, 3.0 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S24** (721 mg, 74%) as a viscous oil: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 3.75 (s, 6H), 3.02 (dd, *J* = 8.8, 7.1 Hz, 2H), 2.84 (s, 2H), 2.57 – 2.44 (m, 2H), 2.41 (s, 3H), 1.73 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.5, 170.8, 143.9, 134.2, 129.3, 128.2, 79.3, 73.1, 56.6, 52.8, 33.6, 27.2, 24.2, 21.6, 3.5; **HRMS** (ESI) calc for $[C_{19}H_{23}O_5]^+$ ($[M+H]^+$): *m/z* 331.1540, found 331.1544.



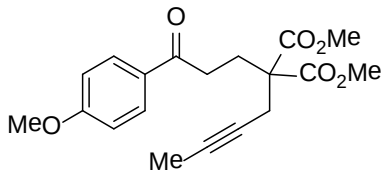
S25

Dimethyl-2-(but-2-ynyl)-2-(3-oxo-3-(m-tolyl)propyl)malonate (S25): According to the general procedure A, the corresponding 3-chloroketone (366 mg, 2.0 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S25** (401 mg, 59%) as an off-white solid: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.45 – 7.26 (m, 3H), 3.74 (s, 6H), 3.08 – 2.91 (m, 2H), 2.85 (d, *J* = 2.6 Hz, 1H), 2.54 – 2.44 (m, 1H), 2.41(s, 2H), 1.74 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.9, 170.7, 138.3, 136.6, 133.8, 128.5, 128.4, 125.3, 79.3, 73.0, 56.5, 52.7, 33.71, 27.0, 24.1, 21.3, 3.45; **HRMS** (ESI) calc for $[C_{19}H_{22}O_5Na]^+$ ($[M+Na]^+$): *m/z* 353.1359, found: 353.1361.



S26

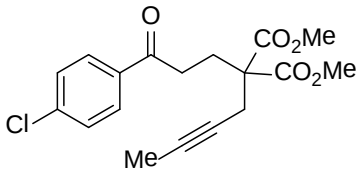
Dimethyl 2-(but-2-ynyl)-2-(3-oxo-3-o-tolylpropyl)malonate (S26): According to the general procedure A, the corresponding 3-chloroketone (366 mg, 2.0 mmol) was reacted under the standard conditions. The product was purified twice by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S26** (318 mg, 48%) as a viscous oil: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.23 (m, 2H), 3.74 (s, 6H), 2.95 (t, *J* = 7.8 Hz, 2H), 2.82 (q, *J* = 2.4 Hz, 2H), 2.50 (s, 3H), 2.48 – 2.43 (m, 2H), 1.79 – 1.70 (t, *J* = 2.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.6, 170.7, 138.2, 137.4, 131.9, 131.3, 128.5, 125.6, 79.2, 73.0, 56.5, 52.7, 36.4, 27.1, 24.1, 21.3, 3.4; **HRMS** (ESI) calc for $[C_{19}H_{22}O_5Na]^+$ ($[M+Na]^+$): *m/z* 353.1359, found: 353.1363.



S27

Dimethyl-2-(but-2-yn-1-yl)-2-(3-(4-methoxyphenyl)-3-oxopropyl)malonate (S27):

According to the general procedure A, the corresponding 3-chloroketone (393 mg, 2.0 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to give **S27** (541 mg, 78%) as an off-white solid: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 3.77 (s, 6H), 3.03 – 2.95 (m, 1H), 2.87 (s, 2H), 2.55 – 2.44 (m, 2H), 1.77 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.4, 170.8, 163.5, 130.4, 129.8, 113.7, 79.3, 73.1, 56.6, 55.5, 52.8, 33.4, 27.3, 24.2, 3.6; **HRMS** (ESI) calc for $[C_{19}H_{23}O_6]^+$ ($[M+H]^+$): *m/z* 347.1489, found: 347.1493.

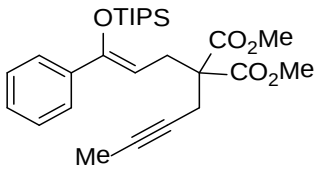


S28

Dimethyl-2-(but-2-yn-1-yl)-2-(3-(4-chlorophenyl)-3-oxopropyl)malonate (S28): According to the general procedure A, the corresponding 3-chloroketone (330 mg, 1.6 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S28** (391 mg, 70%) as an off-white solid: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 3.72 (s, 6H), 2.99 (t, *J* = 7.8 Hz, 2H), 2.81 (d, *J* = 2.5 Hz, 2H), 2.47 (t, *J* = 7.8 Hz, 2H), 1.72 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.6, 170.7, 139.5, 134.9, 129.5, 128.9, 79.4, 73.0, 56.5, 52.8, 33.8, 27.1, 24.3, 3.5; **HRMS** (ESI) calc for $[C_{18}H_{20}O_5Cl]^+$ ($[M+Na]^+$): *m/z* 351.0994, found: 351.1000.

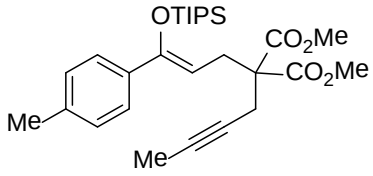
General Procedure B - Preparation of enolsilanes: A solution of diisopropylamine (1.1 equiv) in THF (0.5 M) was cooled to -78 ^{o}C and n-butyllithium (1.6 M solution of in n-hexane, 1.05 equiv.) was added slowly by a syringe. This mixture was stirred for 20 min at -78 ^{o}C and a solution (0.5 M) of the corresponding ketone (1.0 equiv) was added. The mixture was stirred for an additionnal 30 min and TIPSOTf (1.2 equiv) was added. The solution was stirred for 1.5 h at -78 ^{o}C and subsequently allowed to warm up to room temperature. The

reaction was quenched by the addition of an equal volume of sat. aq. NH_4Cl. The mixture was extracted with EtOAc (3 ×), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to provide analytically pure compound.



22

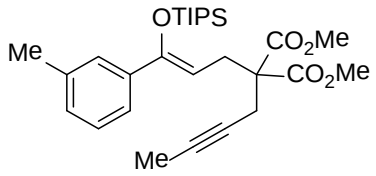
(Z)-dimethyl 2-(but-2-ynyl)-2-(3-phenyl-3-(triisopropylsilyloxy)allyl)malonate (22):
According to the general procedure B, ketone **S22** (158 mg, 0.5 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give **22** (180 mg, 76%) as a pale yellow viscous oil: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.3, 2.3 Hz, 2H), 7.32 – 7.15 (m, 3H), 4.76 (t, *J* = 7.1 Hz, 1H), 3.72 (s, 6H), 2.99 (d, *J* = 7.1 Hz, 2H), 2.77 (q, *J* = 2.6 Hz, 2H), 1.74 (t, *J* = 2.5 Hz, 3H), 1.13 – 0.90 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 153.4, 127.9, 127.8, 126.2, 103.7, 78.6, 73.7, 57.4, 52.6, 29.4, 23.6, 18.0, 13.5, 12.5, 3.6; **HRMS** (ESI) calc for $[C_{27}H_{41}O_5Si]^+$ ($[M+H]^+$): *m/z* 473.2718, found 473.2728.



24

(Z)-dimethyl 2-(but-2-ynyl)-2-(3-p-tolyl-3-(triisopropylsilyloxy)allyl)malonate (24):
According to the general procedure B, ketone **S24** (316 mg, 1.0 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give **24** (303 mg, 64%) as a pale yellow viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 4.73 (t, *J* = 7.0 Hz, 2H), 3.73 (s, 6H), 2.99 (d, *J* = 7.0 Hz, 2H), 2.78 (q, *J* = 2.7 Hz, 2H), 2.34 (s, 3H), 1.75 (s, 3H), 1.15 – 0.95 (m, 21H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.8, 153.3, 137. 5, 137.1, 128.5, 128.2,

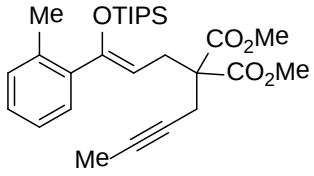
126.1, 102.9, 78.5, 73.7, 57.5, 52.5, 29.4, 23.5, 21.1, 17.9, 17.65, 13.43, 12.5, 3.5; **HRMS** (ESI) calc for $[C_{28}H_{43}O_5Si]^+$ ($[M+Na]^+$): *m/z* 487.2874, found 487.2884.



25

(Z)-dimethyl 2-(but-2-ynyl)-2-(3-m-tolyl-3-(triisopropylsilyloxy)allyl)malonate (25):

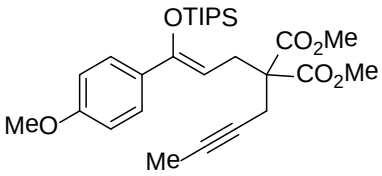
According to the general procedure B, ketone **S25** (168 mg, 0.5 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give **25** (182 mg, 77%) as a pale yellow viscous oil: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 – 7.11 (m, 3H), 7.06 (d, *J* = 7.4 Hz, 1H), 4.75 (t, *J* = 7.0 Hz, 1H), 3.73 (s, 6H), 3.00 (d, *J* = 6.9 Hz, 2H), 2.78 (q, *J* = 2.5 Hz, 2H), 2.32 (s, 3H), 1.75 (s, 3H), 1.20 – 0.97 (m, 21H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.8, 153.4, 139.8, 137.3, 128.4, 127.7, 126.9, 123.4, 103.4, 78.5, 73.7, 57.4, 52.5, 29.4, 23.5, 21.4, 17.8, 13.4, 3.5; **HRMS** (ESI) calc for $[C_{28}H_{43}O_5Si]^+$ ($[M+Na]^+$): *m/z* 487.2874, found 487.2882.



26

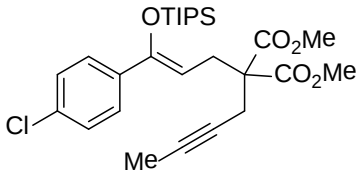
(Z)-dimethyl 2-(but-2-ynyl)-2-(3-o-tolyl-3-(triisopropylsilyloxy)allyl)malonate (26):

According to the general procedure B, ketone **S26** (168 mg, 0.5mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give **26** (191 mg, 81%) as a pale yellow viscous oil: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.07 (m, 4H), 4.48 (t, *J* = 7.0 Hz, 1H), 3.76 (s, 6H), 3.05 (d, *J* = 7.2 Hz, 2H), 2.80 (s, 2H), 2.37 (s, 3H), 1.78 (s, 3H), 1.16 – 0.95 (m, 21H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.0, 153.4, 140.3, 136.7, 130.1, 128.9, 128.1, 125.4, 105.2, 78.7, 73.9, 57.5, 52.8, 29.0, 23.5, 20.0, 17.9, 13.3, 3.8; **HRMS** (ESI) calc for $[C_{28}H_{43}O_5Si]^+$ ($[M+Na]^+$): *m/z* 487.2874, found 487.2883.



27

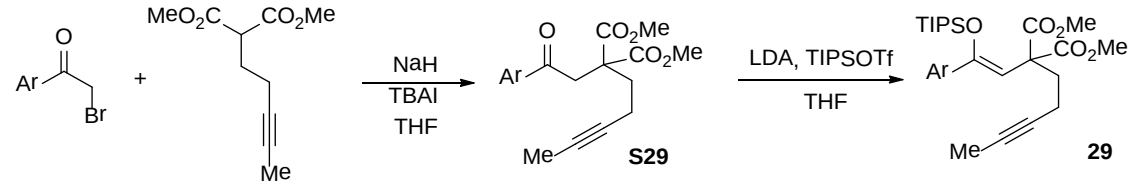
(Z)-dimethyl-2-(but-2-ynyl)-2-(3-(4-methoxyphenyl)-3-(triisopropylsilyloxy)allyl)malonate (27): According to the general procedure B, ketone **S27** (200 mg, 0.58 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give **27** (213 mg, 78%) as an off-white solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.67 (t, *J* = 7.0 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 6H), 2.98 (d, *J* = 6.9 Hz, 2H), 2.78 (q, *J* = 2.5 Hz, 2H), 1.75 (s, 3H), 1.19 – 0.94 (m, 21H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.6, 171.8, 170.99, 163.6, 138.2, 130.8, 129.4, 120.0, 113.8, 59.4, 55.5, 52.8, 52.7, 46.7, 42.5, 39.1, 15.0; **HRMS** (ESI) calc for $[C_{28}H_{43}O_6Si]^+$ ($[M+H]^+$): *m/z* 503.2823, found 503.2833.

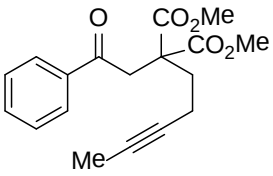


28

(Z)-dimethyl-2-(but-2-ynyl)-2-(3-(4-chlorophenyl)-3-(triisopropylsilyloxy)allyl)malonate (28): According to the general procedure B, ketone **S28** (289 mg, 0.82 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give **28** (269 mg, 65%) as an off-white solid: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.78 (t, *J* = 7.0 Hz, 1H), 3.72 (s, 6H), 2.98 (d, *J* = 7.0 Hz, 2H), 2.77 (q, *J* = 2.6 Hz, 2H), 1.74 (s, 3H), 1.18 – 0.97 (m, 21H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 152.2, 138.4, 133.4, 128.1, 127.4, 104.4, 78.6, 73.5, 57.3, 52.6, 29.5, 23.6, 17.8, 13.4, 3.5; **HRMS** (ESI) calc for $[C_{27}H_{40}O_5SiCl]^+$ ($[M+H]^+$): *m/z* 507.2328, found 507.2338.

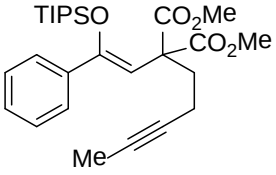
b) Synthesis of Silyloxy-1,6-enynes 29





S29

Dimethyl-2-(2-oxo-2-phenylethyl)-2-(pent-3-ynyl)malonate (S29): Alkyne (360 mg, 1.8 mmol) was dissolved in THF (0.4 M) and cooled to 0 ^{o}C. Then, NaH (60 % in oil, 88 mg, 2.1 mmol) was added in one portion. The reaction mixture was stirred for 30 min. at this temperature. The corresponding 3-chloroketone was dissolved in THF (0.5 M) and transferred slowly to the reaction mixture. The reaction was warmed to room temperature and then stirred at reflux for 5 h. The reaction mixture was quenched by the addition of an equal volume of sat. aq. NH_4Cl. The mixture was extracted with Et_2O (3 ×), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S29** (379 mg, 66%) as a pale yellow viscous oil: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.83 (s, 3H), 3.74 (s, 6H), 2.36 (t, *J* = 7.3 Hz, 2H), 2.18 – 2.10 (m, 2H), 1.67 – 1.28 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.4, 171.1, 136.4, 133.4, 128.6, 128.1, 77.9, 54.9, 52.9, 41.4, 31.8, 14.7, 3.2; **HRMS** (ESI) calc for $[C_{18}H_{21}O_5]^+$ ($[M+H]^+$): *m/z* 317.1384, found 317.1388.

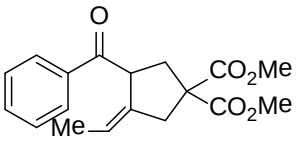


29

(Z)-dimethyl-2-(pent-3-yn-10-yl)-2-(2-phenyl-2-((triisopropylsilyl)oxy)vinyl)malonate (29): According to the general procedure B, 2-bromoketone **S29** (252 mg, 0.8 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give **29** (264 mg, 70%) as a pale yellow viscous oil: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 – 7.21 (m, 5H), 5.59 (s, 1H), 3.72 (s, 6H), 2.54 (t, *J* = 8.0 Hz, 2H), 2.25 – 2.09 (m, 2H), 1.83 – 1.65 (s, 3H), 1.17 – 0.80 (m, 21H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.8, 153.2, 140.1, 128.4, 127.9, 127.8, 104.9, 78.3, 75.8, 56.7, 52.7, 33.2, 17.8, 17.7, 14.7, 13.9, 3.5; **HRMS** (ESI) calc for $[C_{27}H_{40}O_5SiNa]^+$ ($[M+Na]^+$): *m/z* 495.2537, found 495.2541.

IV. Gold(I) cyclizations for Silyloxy-1,6-enynes

General Procedure C - Gold(I) cyclizations: (*R*)-MeO-DTBM-BIPHEP$(AuCl)_2$ (0.05 equiv.) and NaBARF (0.1 equiv.) was dissolved in dichloroethane (DCE, 0.1 M) and stir for 15 minutes at room temperature. The mixture was cooled at -30 ^oC and a solution of the corresponding substrate (1.0 equiv.) in DCE (0.1 M) was transferred to the catalyst mixture. The solution was stirred at the specified temperature until consumption of the starting material as indicated by TLC (12-36 hours). The solution was concentrated and purified on silica gel.

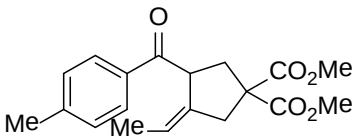


23

(Z)-dimethyl 3-benzoyl-4-ethylidenecyclopentane-1,1-dicarboxylate (23): According to the general procedure C, enolsilane **22** (16.5 mg, 35 μmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **23**[4] (9.3 mg, 84%) as a pale yellow viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 2H), 5.60 (q, *J* = 6.3 Hz, 1H), 4.57 (t, *J* = 8.5 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 3.28 – 3.11 (m,

[4] The gold-catalyzed hydration of 1,6-diynes furnished product **23** in less than 5% yield, see: Sperger, C.; Fiksdahl, A. *Org. Lett.* **2009**, *11*, 2449.

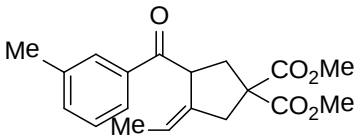
1H), 3.05 – 2.83 (m, 2H), 2.26 (dd, *J* = 13.2, 8.1 Hz, 1H), 1.40 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.0, 171.8, 171.0, 137.9 136.5, 133.3, 128.8, 128.6, 120.4, 59.4, 53.0, 52.8, 47.1, 42.4, 39.0, 15.2; **HRMS** (ESI) calc for $[C_{18}H_{21}O_5]^+$ ($[M+H]^+$): *m/z* 317.1384, found 317.1386; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IB column (99:1 hexanes : iPrOH, 1.0 ml/min, 204 nm); major enantiomer tr = 26.5 min, minor enantiomer tr = 21.6 min; 93% ee.



30

(Z)-dimethyl-3-ethylidene-4-(4-methylbenzoyl)cyclopentane-1,1-dicarboxylate (30):

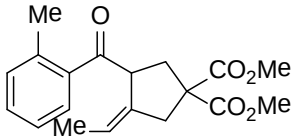
According to the general procedure C, enolsilane **24** (17.0 mg, 35 μmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **30** (9.6 mg, 83%) as a pale yellow viscous oil: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 5.57 (q, *J* = 6.8 Hz, 1H), 4.54 (t, *J* = 8.7 Hz, 1H), 3.76 (s, 3H), 3.70 (s, 3H), 3.18 (dt, *J* = 15.5, 2.5 Hz, 1H), 2.95 (m, 2H), 2.42 (s, 3H), 2.23 (dd, *J* = 13.2, 8.3 Hz, 2H), 1.38 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.6, 171.8, 171.0, 144.0, 138.1, 134.0, 129.4, 128.6, 120.1, 59.4, 52.8, 52.7, 47.0, 42.5, 39.0, 21.6, 15.0; **HRMS** (ESI) calc for $[C_{19}H_{23}O_5]^+$ ($[M+H]^+$): *m/z* 331.1546, found 331.1546; **HPLC**: enantiomeric excess determined by HPLC Chiralpak IB column (99:1 hexanes : iPrOH, 1.0 ml/min, 204 nm); major enantiomer tr = 29.0 min, minor enantiomer tr = 24.6 min; 86% ee.



31

(Z)-dimethyl-3-ethylidene-4-(3-methylbenzoyl)cyclopentane-1,1-dicarboxylate (31):

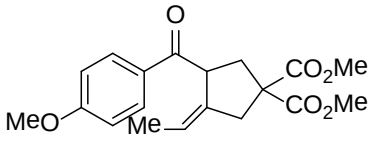
According to the general procedure C, enolsilane **25** (17.0 mg, 35 μmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **31** (10.3 mg, 86%) as a pale yellow viscous oil: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.44 – 7.34 (m, 3H), 5.61 – 5.56 (q, *J* = 6.6 Hz, 1H), 4.55 (t, *J* = 8.5 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.17(ddd, *J* = 15.4, 5.0, 2.6 Hz, 1H), 3.02 – 2.87 (m, 2H), 2.43 (s, 3H), 2.24 (dd, *J* = 13.2, 8.1 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.2, 171.9, 171.0, 138.6, 138.0, 136.6, 134.0, 129.0, 128.6, 125.8, 120.2, 59.4, 52.9, 52.8, 47.2, 42.5, 39.0, 21.4, 15.1; **HRMS** (ESI) calc for $[C_{19}H_{22}O_5Na]^+$ ($[M+Na]^+$): *m/z* 353.1359, found 353.1362; **HPLC**: enantiomeric excess determined by HPLC Chiralpak IB column (99:1 hexanes : iPrOH, 1.0 ml/min, 204 nm); major enantiomer tr = 26.8 min, minor enantiomer tr = 19.8 min; 90% ee.



32

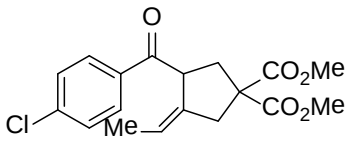
(Z)-dimethyl-3-ethylidene-4-(2-methylbenzoyl)cyclopentane-1,1-dicarboxylate (32):

According to the general procedure C, enolsilane **26** (17.0 mg, 35 μmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **32** (8.3 mg, 70%) as a pale yellow viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.32 – 7.21 (m, 2H), 5.54 (q, *J* = 6.9 Hz, 1H), 4.45 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.13 (dd, *J* = 15.4, 2.5 Hz, 1H), 2.98 – 2.79 (m, 2H), 2.48 – 2.40 (m, 4H), 1.30 (dd, *J* = 6.8, 2.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.4, 171.9, 171.2, 138.3, 138.1, 137.6, 131.8, 131.2, 128.1, 125.7, 120.6, 59.2, 52.9, 52.9, 50.2, 42.1, 37.5, 20.8, 14.9; **HRMS** (ESI) calc for $[C_{19}H_{22}O_5Na]^+$ ($[M+Na]^+$): *m/z* 353.1359, found 353.1363; **HPLC**: enantiomeric excess determined by HPLC Chiralpak IB column (99.2:0.8 hexanes : iPrOH, 0.8 ml/min, 205 nm); major enantiomer tr = 36.7 min, minor enantiomer tr = 35.4 min; 91% ee.



33

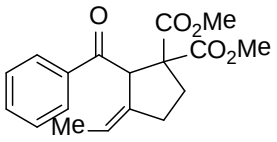
(Z)-dimethyl-3-ethylidene-4-(4-methoxybenzoyl)cyclopentane-1,1-dicarboxylate (**33)**: According to the general procedure C, enolsilane **26** (17.5 mg, 35 μmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **33** (9.8 mg, 81%) as a pale yellow viscous oil: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.59 (q, *J* = 6.5 Hz, 1H), 4.55 (t, *J* = 8.6 Hz, 1H), 3.91 (s, 3H), 3.78 (s, 3H), 3.73 (s, 3H), 3.25 – 3.17 (m, 1H), 3.04 – 2.93 (m, 2H), 2.25 (dd, *J* = 13.1, 8.4 Hz, 1H), 1.42 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.6, 171.8, 171.0, 163.6, 138.2, 130.8, 129.4, 120.0, 113.9, 59.4, 55.5, 52.8, 52.7, 46.7, 42.5, 39.1, 15.0; **HRMS** (ESI) calc for $[C_{19}H_{23}O_6]^+$ ($[M+H]^+$): *m/z* 347.1489, found 347.1488. **HPLC**: enantiomeric excess determined by HPLC Chiralpak IB column (98:2 hexanes : iPrOH, 1.0 ml/min, 244 nm); major enantiomer tr = 21.8 min, minor enantiomer tr = 19.7 min; 79% ee.



34

(Z)-dimethyl-3-(4-chlorobenzoyl)-4-ethylidenecyclopentane-1,1-dicarboxylate (**34)**: According to the general procedure C, enolsilane **28** (17.1 mg, 35 μmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S1a** (8.6 mg, 73%) as a pale yellow viscous oil: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 5.59 (q, *J* = 6.7 Hz, 1H), 4.50 (t, *J* = 8.6 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.16 (dq, *J* = 15.9, 2.6 Hz, 1H), 3.00 – 2.89 (m, 2H), 2.23 (dd, *J* = 13.3, 8.1 Hz, 1H), 1.42 – 1.35 (dd, *J* = 6.9, 2.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.8, 171.7, 170.9, 139.7, 137.7, 134.8, 129.9, 129.0, 120.4, 59.3, 52.9, 52.7, 47.1, 42.3, 38.8, 31.9, 31.8, 15.1; **HRMS** (ESI) calc for $[C_{18}H_{19}O_5ClNa]^+$ ($[M+Na]^+$): *m/z* 373.0813, found 373.0816. **HPLC**: enantiomeric excess determined by HPLC Chiralpak

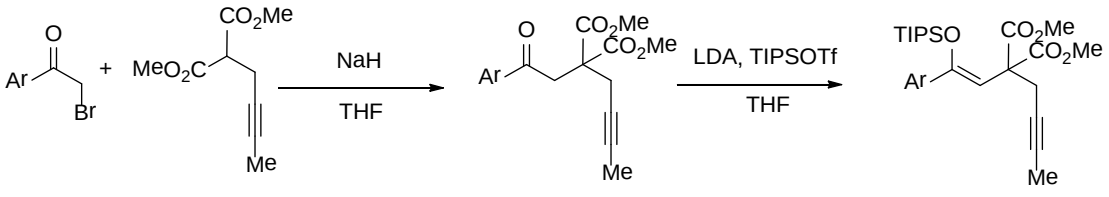
IB column (99:1 hexanes : iPrOH, 1.0 ml/min, 210 nm); major enantiomer tr = 28.9 min, minor enantiomer tr = 20.2 min; 70% ee.



35

(Z)-dimethyl-2-benzoyl-3-ethylidenecyclopentane-1,1-dicarboxylate (35): According to the general procedure C, enolsilane **29** (16.6 mg, 35 μmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **35** (8.8 mg, 79%) as a pale yellow viscous oil: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 5.45 – 5.40 (m, 1H), 5.40 (s, 1H), 3.81 (s, 3H), 3.44 (s, 3H), 2.86 (ddd, *J* = 13.1, 9.8, 8.0 Hz, 1H), 2.77 – 2.68 (m, 1H), 2.48 – 2.41 (m, 1H), 2.31 (ddd, *J* = 13.0, 8.2, 4.7 Hz, 1H), 1.40 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 132.9, 128.6, 128.6, 119.6, 65.2, 53.3, 53.2, 52.4, 32.1, 31.2, 15.4; **HRMS** (ESI) calc for $[C_{18}H_{21}O_5]^+$ ($[M+H]^+$): *m/z* 317.1384, found 317.1388; **HPLC**: enantiomeric excess determined by HPLC Chiralpak IB column (99:1 hexanes : iPrOH, 1.0 ml/min, 244 nm); major enantiomer tr = 13.0 min, minor enantiomer tr = 11.0 min; 50% ee.

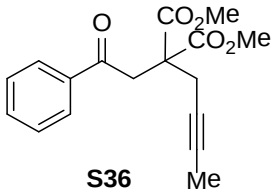
V. Synthesis of Silyloxy-1,5-enynes



S36, S38-S44 **36, 38-44**

General Procedure D - Preparation of Aryl ketones: The alkyne was dissolved in THF (0.4 M) and cooled to 0 ^{o}C. Then, NaH (60 % in oil, 1.1 equiv.) was added in one portion. The reaction mixture was stirred for 30 min. at this temperature. The corresponding 2-bromoketone was dissolved in THF (0.5 M) and transferred slowly to the reaction mixture.

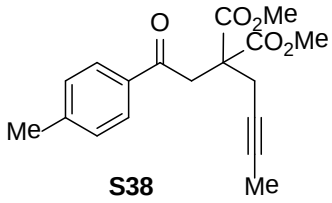
The reaction was warmed to room temperature and quenched by the addition of an equal volume of sat. aq. NH_4Cl. The mixture was extracted with Et_2O (3×), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to provide analytically pure compounds.



S36

Dimethyl-2-(but-2-ynyl)-2-(2-oxo-2-phenylethyl)malonate (S36):

According to the general procedure D, the corresponding 2-bromoketone (0.94 g, 4.7 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S36** (0.99 g, 70%) as a pale yellow viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 5.34 (s, 3H), 3.94 (s, 2H), 3.80 (s, 6H), 3.09 (q, *J* = 2.5 Hz, 2H), 1.76 (t, *J* = 2.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.8, 170.1, 136.4, 133.4, 128.6, 128.1, 79.3, 73.7, 54.9, 53.0, 41.1, 23.8, 3.5; **HRMS** (ESI) calc for $[[C_{17}H_{18}O_5Na]^+$ ($[M+Na]^+$): *m/z* 325.1046, found 325.1043.

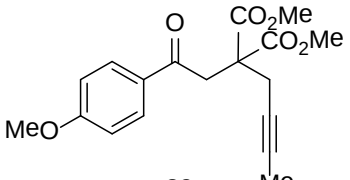


S38

Dimethyl-2-(but-2-ynyl)-2-(2-oxo-2-p-tolylethyl)malonate (S38):

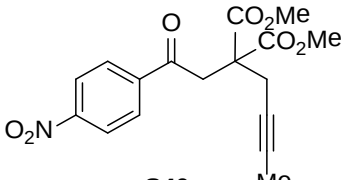
According to the general procedure D, the corresponding 2-bromoketone (0.60 g, 2.8 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S38** (0.69 g, 78%) as an off-white solid: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.89 (s, 2H), 3.78 (s, 6H), 3.06 (s, 2H), 2.45 (s, 3H), 1.74 (s, 3H); **^{13}C NMR** (151 MHz,

$CDCl_3$) δ 196.4, 170.2, 144.3, 134.1, 129.3, 128.3, 79.3, 73.8, 55.0, 53.0, 41.0, 23.8, 21.7, 3.5; **HRMS** (ESI) calc for $[C_{18}H_{20}O_5Na]^+$ ($[M+Na]^+$): *m/z* 339.1203, found 339.1202.



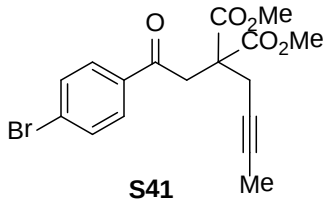
S39

Dimethyl-2-(but-2-ynyl)-2-(2-(4-methoxyphenyl)-2-oxoethyl)malonate (S39): According to the general procedure D, the corresponding 2-bromoketone (0.41 g, 1.8 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to give **S39** (0.47 g, 78%) as an off-white solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H), 3.86 (s, 2H), 3.78 (s, 6H), 3.05 (d, *J* = 2.5 Hz, 2H), 1.73 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.3, 170.2, 163.8, 130.5, 129.6, 113.8, 79.2, 73.9, 55.5, 55.0, 53.0, 40.7, 23.8, 3.5; **HRMS** (ESI) calc for $[C_{18}H_{20}O_6Na]^+$ ($[M+Na]^+$): *m/z* 355.1152, found 355.1151.



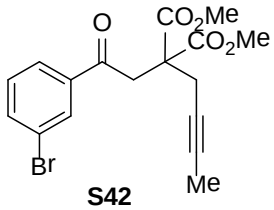
S40

Dimethyl-2-(but-2-ynyl)-2-(2-(4-nitrophenyl)-2-oxoethyl)malonate (S40): According to the general procedure D, the corresponding 2-bromoketone (0.45 g, 1.8 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to give **S40** (0.43 g, 69%) as a pale yellow solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H), 5.34 (s, 3H), 3.94 (s, 2H), 3.82 (s, 6H), 3.08 (d, *J* = 2.6 Hz, 2H), 1.76 (t, *J* = 2.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 195.5, 169.8, 150.6, 140.9, 129.2, 123.9, 79.8, 73.5, 55.1, 53.2, 41.7, 23.9, 3.5**; HRMS** (ESI) calc for $[C_{17}H_{17}O_7NNa]^+$ ($[M+Na]^+$): *m/z* 370.0897, found 370.0900.



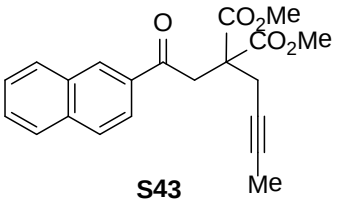
S41

Dimethyl-2-(2-(4-bromophenyl)-2-oxoethyl)-2-(but-2-ynyl)malonate (**S41)**: According to the general procedure D, the corresponding 2-bromoketone (0.50 g, 1.8 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S41** (0.51 g, 75%) as an off-white solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 2H), 3.77 (s, 6H), 3.04 (d, *J* = 2.5 Hz, 2H), 1.72 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.9, 169.9, 135.2, 131.9, 129.7, 128.7, 79.5, 73.6, 54.9, 53.1, 41.0, 23.8, 3.5; **HRMS** (ESI) calc for $[C_{17}H_{17}O_5BrNa]^+$ ($[M+Na]^+$): *m/z* 403.0152, found 403.0152.



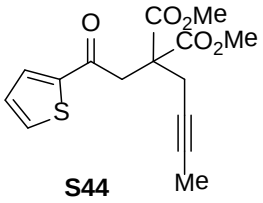
S42

D**imethyl-2-(2-(3-bromophenyl)-2-oxoethyl)-2-(but-2-ynyl)malonate (S42)**: According to the general procedure D, the corresponding 2-bromoketone (0.30 g, 1.1 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S42** (0.27 g, 65%) as a yellow solid: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.16 (t, *J* = 1.7 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.77 – 7.69 (m, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 3.87 (s, 2H), 3.78 (s, 6H), 3.05 (q, *J* = 2.5 Hz, 2H), 1.75 (t, *J* = 2.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 195.6, 167.0, 138.2, 136.3, 131.3, 130.3, 126.7, 123.0, 79.6, 73.6, 54.9, 53.1, 41.2, 23.8, 3.6; **HRMS** (ESI) calc for $[C_{17}H_{17}O_5BrNa]^+$ ($[M+Na]^+$): *m/z* 403.0152, found 403.0151.



S43

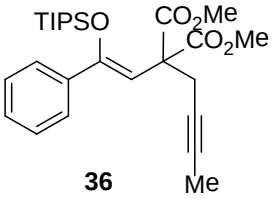
Dimethyl-2-(but-2-ynyl)-2-(2-(naphthalen-2-yl)-2-oxoethyl)malonate (S43): According to the general procedure D, the corresponding 2-bromoketone (0.37 g, 1.5 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S43** (0.42 g, 80%) as an off-white solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.07 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.92 (dd, *J* = 12.5, 8.4 Hz, 2H), 7.67 – 7.62 (m, 1H), 7.61 – 7.59 (m, 1H), 4.07 (s, 2H), 3.81 (s, 6H), 3.12 (d, *J* = 2.5 Hz, 2H), 1.74 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.8, 170.2, 135.8, 132.5, 130.1, 129.6, 128.7, 128.5, 127.8, 126.9, 123.7, 79.4, 73.8, 55.5, 55.1, 53.1, 41.2, 23.8, 3.6; **HRMS** (ESI) calc for $[C_{21}H_{20}O_5Na]^+$ ($[M+Na]^+$): *m/z* 375.1203, found 375.1201.



S44

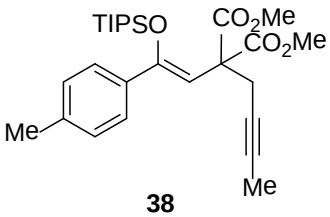
Dimethyl-2-(but-2-ynyl)-2-(2-oxo-2-(thiophen-2-yl)ethyl)malonate (S44): According to the general procedure D, the corresponding 2-bromoketone (0.23 g, 1.1 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (25% EtOAc in hexanes) to give **S44** (0.26 g, 78%) as a light brown solid: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 3.1 Hz, 1H), 7.69 (d, *J* = 4.9 Hz, 1H), 7.20 – 7.15 (m, 1H), 3.85 (s, 2H), 3.79 (s, 6H), 3.04 (d, *J* = 2.5 Hz, 2H), 1.75 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 189.7, 169.9, 143.7, 134.1, 132.4, 128.2, 79.5, 73.7, 55.0, 53.1, 41.5, 23.8, 3.5; **HRMS** (ESI) calc for $[C_{15}H_{16}O_5SNa]^+$ ($[M+Na]^+$): *m/z* 331.0611, found 331.0609.

General Procedure E - Preparation of enolsilanes: A solution of diisopropylamine (1.1 equiv) in THF (0.5 M) was cooled to -78 ^{o}C and n-butyllithium (1.6 M solution of in n-hexane, 1.05 equiv.) was added slowly by a syringe. This mixture was stirred for 20 min at -78 ^{o}C and a solution (0.5 M) of the corresponding ketone (1.0 equiv) was added. The mixture was stirred for an additionnal 30 min and TIPSOTf (1.2 equiv) was added. The solution was stirred for 1.5 h at -78 ^{o}C and subsequently allowed to warm up to room temperature. The reaction was quenched by the addition of an equal volume of sat. aq. NH_4Cl. The mixture was extracted with EtOAc (3 ×), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to provide analytically pure compounds.



36

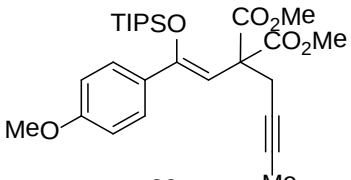
(Z)-dimethyl-2-(but-2-ynyl)-2-(2-phenyl-2-(triisopropylsilyloxy)vinyl)malonate (36):
According to the general procedure E, ketone **S36** (0.22 g, 0.72 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (12% EtOAc in hexanes) to give **36** (0.24 g, 74%) as a pale yellow solid: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.32 – 7.27 (m, 3H), 5.34 (s, 1H), 3.75 (d, *J* = 7.8 Hz, 6H), 3.16 (d, *J* = 2.2 Hz, 2H), 1.75 (s, 3H), 1.05 (s, 3H), 0.97 (d, *J* = 6.2 Hz, 18H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.1, 153.1, 140.0, 128.3, 128.0, 127.8, 105.7, 77.8, 74.4, 56.7, 52.8, 25.1, 17.8, 17.7, 13.9, 12.3, 3.5; **HRMS** (ESI) calc for $[C_{26}H_{39}O_5Si]^+$ ($[M+H]^+$): *m/z* 459.2561, found 459.2569.



38

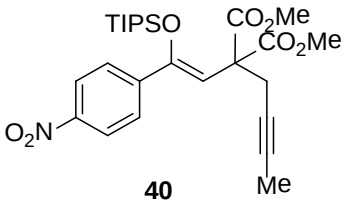
(Z)-dimethyl-2-(but-2-ynyl)-2-(2-p-tolyl-2-(triisopropylsilyloxy)vinyl)malonate (38):

According to the general procedure E, ketone **S38** (0.20 g, 0.63 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (12% EtOAc in hexanes) to give **38** (0.21 g, 70%) as a yellow viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 9.7 Hz, 4H), 7.14 (d, *J* = 7.9 Hz, 2H), 5.35 (s, 1H), 3.78 (s, 6H), 3.20 (d, *J* = 2.5 Hz, 2H), 2.39 (s, 3H), 1.79 (t, *J* = 2.5 Hz, 3H), 1.02 (d, *J* = 5.3 Hz, 18H), 0.98 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.1, 153.1, 138.1, 137.2, 128.5, 127.9, 105.3, 77.7, 74.5, 56.7, 25.1, 21.3, 17.9, 17.7, 13.9, 12.3; **HRMS** (ESI) calc for $[C_{27}H_{40}O_5SiNa]^+$ ($[M+Na]^+$): *m/z* 495.2537, found 495.2540.



39

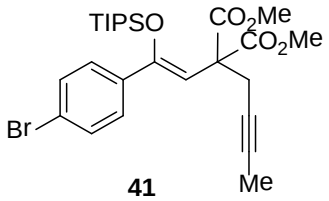
(Z)-dimethyl-2-(but-2-ynyl)-2-(2-(4-methoxyphenyl)-2-(triisopropylsilyloxy)vinyl)malonate (39): According to the general procedure E, ketone **S39** (0.098 g, 0.29 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (12% EtOAc in hexanes) to give **39** (0.10 g, 71%) as a yellow viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.32 (s, 1H), 3.86 (s, 3H), 3.78 (s, 6H), 3.19 (d, *J* = 2.5 Hz, 2H), 1.79 (t, *J* = 2.5 Hz, 3H), 1.09 (s, 3H), 1.03 (d, *J* = 5.5 Hz, 18H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.2, 159.7, 152.8, 132.7, 129.4, 113.1, 105.1, 77.7, 74.5, 56.76, 55.3, 52.8, 25.1, 17.9, 13.9, 3. 6; **HRMS** (ESI) calc for $[C_{27}H_{41}O_6Si]^+$ ($[M+H]^+$): *m/z* 489.2667, found 489.2668.



40

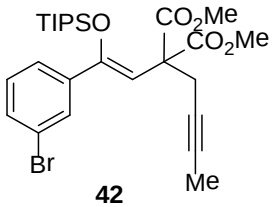
(Z)-dimethyl-2-(but-2-ynyl)-2-(2-(4-nitrophenyl)-2-(triisopropylsilyloxy)vinyl)malonate (40): According to the general procedure E, ketone **S40**(0.18 g, 0.52 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica

gel (15% EtOAc in hexanes) to give **40** (0.17 g, 68%) as a brown viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 5.55 (s, 1H), 3.80 (s, 6H), 3.21 (d, *J* = 2.5 Hz, 2H), 1.79 (t, *J* = 2.5 Hz, 3H), 1.09 (s, 3H), 1.04 (d, *J* = 6.2 Hz, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 150.9, 147.6, 146.6, 128.4, 123.4, 108.7, 78.2, 73.9, 56.7, 53.0, 25.0, 17.8, 14.0, 3.6; **HRMS** (ESI) calc for $[C_{26}H_{37}O_7NSiNa]^+$ ($[M+Na]^+$): *m/z* 526.2232, found 526.2240.



41

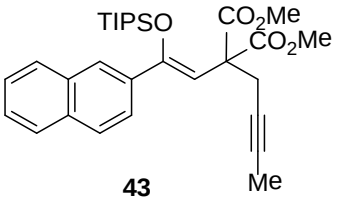
(Z)-dimethyl-2-(2-(4-bromophenyl)-2-(triisopropylsilyloxy)vinyl)-2-(but-2-ynyl)malonate (41): According to the general procedure E, ketone **S41** (0.18 g, 0.46 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (12% EtOAc in hexanes) to give **41** (0.18 g, 73%) as a pale yellow solid: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 2H), 5.34 (s, 1H), 3.74 (s, 6H), 3.14 (q, *J* = 2.4 Hz, 2H), 1.74 (t, *J* = 2.5 Hz, 3H), 0.98 (d, *J* = 5.2 Hz, 18H), 0.92 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.9, 151.9, 139.1, 131.1, 129.6, 122.4, 106.4, 77.9, 74.3, 56.7, 52.9, 25.0, 17.9, 17.7, 13.9, 3.6; **HRMS** (ESI) calc for $[C_{26}H_{37}O_5BrSiNa]^+$ ($[M+Na]^+$): *m/z* 559.1486, found 559.1487.



42

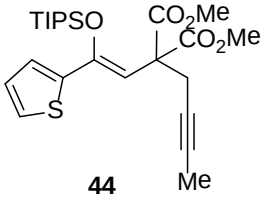
(Z)-dimethyl-2-(2-(3-bromophenyl)-2-(triisopropylsilyloxy)vinyl)-2-(but-2-ynyl)malonate (42): According to the general procedure E, ketone **S42** (0.18 g, 0.46 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (12% EtOAc in hexanes) to give **42** (0.17 g, 70%) as a yellow solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 5.40 (s, 1H), 3.77 (s, 7H), 3.17 (d, *J* = 2.4 Hz, 2H), 1.77 (t, *J* = 2.3 Hz, 3H), 1.01 (d, *J* =

6.6 Hz, 18H), 0.98 – 0.94 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.9, 151.5, 142.1, 131.3, 130.9, 129.6, 126.5, 121.9, 106.7, 78.0, 74.2, 56.6, 52.9, 25.0, 17.8, 17.7, 13.9, 12.3, 3. 6; **HRMS** (ESI) calc for $[C_{26}H_{38}O_5BrSi]^+$ ($[M+H]^+$): *m/z* 537.1666, found 537.1675.



43

(Z)-dimethyl-2-(but-2-ynyl)-2-(2-(naphthalen-2-yl)-2-(triisopropylsilyloxy)vinyl)malonate (43): According to the general procedure E, ketone **S43** (0.16 g, 0.50 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give **43** (0.22 g, 85%) as a off-white solid: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.85 (dd, *J* = 9.1, 6.6 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.55 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.55 – 7.50 (m, 2H), 5.51 (s, 1H), 3.80 (s, 6H), 3.24 (d, *J* = 2.4 Hz, 2H), 1.81 (t, *J* = 2.3 Hz, 3H), 1.02 (d, *J* = 6.0 Hz, 18H), 1.00 – 0.95 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.1, 153.1, 137.5, 133.1, 132.8, 128.2, 127.7, 127.5, 126.8, 126.3, 126.2, 125.9, 106.4, 77.9, 74.5, 56.9, 52.9, 25.2, 17.9, 14.0, 3.6; **HRMS** (ESI) calc for $[C_{30}H_{41}O_5Si]^+$ ($[M+H]^+$): *m/z* 509.2718, found 509.2726.

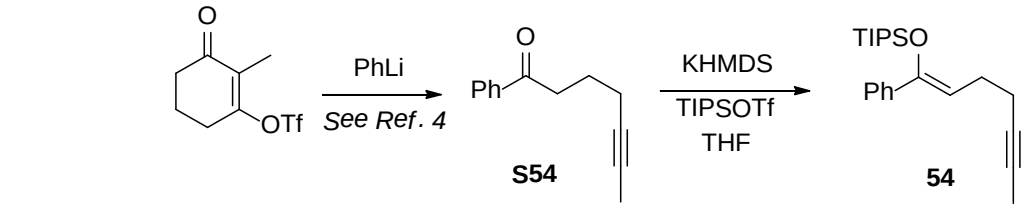


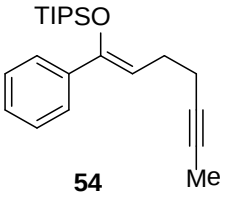
44

(Z)-dimethyl-2-(but-2-ynyl)-2-(2-(thiophen-2-yl)-2-(triisopropylsilyloxy)vinyl)malonate (44): According to the general procedure E, ketone **S44** (0.23 g, 0.75 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give **44** (0.26 g, 75%) as a brown viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 5.1 Hz, 1H), 7.11 (d, *J* = 3.4 Hz, 1H), 6.98 – 6.94 (m, 1H), 5.57 (s, 1H), 3.77 (s, 6H), 3.16 (d, *J* = 2.2 Hz, 2H), 1.77 (s, 3H), 1.12 (s, 3H), 1.11 – 1.01 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 145.6, 141.4, 126.7, 126.5, 125.3, 107.6, 78.0, 74.2,

56.8, 25.0, 17.9, 17.7, 14.1, 12.3, 3.6; **HRMS** (ESI) calc for $[C_{24}H_{37}O_5SSi]^+$ ($[M+H]^+$): *m/z* 465.2126, found 465.2130.

*Synthesis of substrate **54***



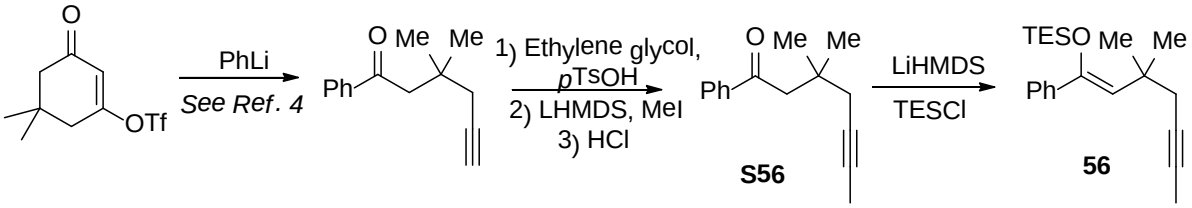


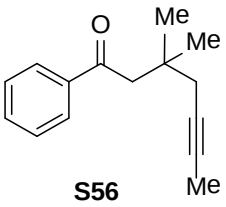
54

(Z)-triisopropyl(1-phenylhept-1-en-5-ynyloxy)silane (54): A solution of diisopropylamine (104 μl) in THF (0.5 M) was cooled to -78 ^oC and n-butyllithium (287 μl, 1.6 M solution of in n-hexane, 1.05 equiv.) was added slowly by a syringe. This mixture was stirred for 20 min at -78 ^oC and a solution (0.5 M) of ketone **S54**[5] (0.12 g, 0.67 mmol 1.0 equiv) was added. The mixture was stirred for an additionnal 30 min and TIPSOTf (336 μl, 1.2 equiv) was added. The solution was stirred for 1.5 h at -78 ^oC and subsequently allowed to warm up to room temperature. The reaction was quenched by the addition of an equal volume of sat. aq. NH_4Cl. The mixture was extracted with EtOAc (3 ×), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (1% EtOAc in hexanes) to give **54** (0.16 g, 71%) as a colorless viscous oil: **^{1}H NMR** (300 MHz, CD_2Cl_2) δ 7.52 – 7.43 (m, 2H), 7.37 – 7.27 (m, 3H), 5.09 (t, *J* = 6.9 Hz, 1H), 2.49 – 2.37 (m, 2H), 2.29 – 2.22 (m, 2H), 1.80 (t, *J* = 2.5 Hz, 3H), 1.08 (d, *J* = 4.3 Hz, 18H), 1.03 (m, 3H); **^{13}C NMR** (151 MHz, CD_2Cl_2) δ 150.9, 140.1, 127.8, 127.5, 126.0, 109.5, 78.7, 75.4, 25.9, 18.9, 17.6, 13.5, 3.1; **HRMS** (EI) calc for $[C_{22}H_{34}OSi]^+$ ($[M]^+$): *m/z* 342.2379, found 342.2377.

[5] Kamijo, S.; Dudley, G. B. *J. Am. Chem. Soc.* **2006**, *128*, 6499.

*Synthesis of substrate **56***



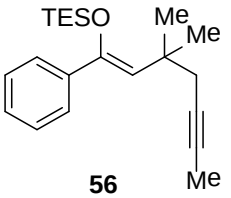


3,3-dimethyl-1-phenylhept-5-yn-1-one (S56): To a stirred solution of ketone[5] (1.20 g, 7.5 mmol) in dry benzene (50 mL) were added ethylene glycol (0.63 mL, 11.3 mmol, 1.5 equiv.) and a catalytic amount of *p*TsOH. The mixture was refluxed overnight using a Dean-Stark apparatus. Then, the reaction cooled to rt and poured into a sat. solution of $NaHCO_3$. The mixture was extracted with Et_2O (3×), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum.

The crude acetal (7.5 mmol, 1 equiv.) was dissolved in THF (15 mL, 0.5 M) and cooled to -78 ^oC. A solution of LiHDMS (7.5 mL, 1.0 M in THF, 1 equiv.) was slowly added. The resulting solution was stirred for 1 h and methyl iodide (0.60 mL, 9.4 mmol, 1.25 equiv.) was slowly added, then the solution was stirred overnight with temperature rising to rt. The reaction mixture was quenched with a sat. solution of NH_4Cl and extracted with Et_2O (3×). The organic layer was collected, washed with brine, dried with $MgSO_4$ and concentrated under vacuum.

The crude alkylated product (7.5 mmol, 1 equiv.) was dissolved in THF (15 mL) and a solution of HCl (5 %, 10 mL) was slowly added. The resulting solution was stirred for 4 h and the reaction mixture was quenched with a sat. solution of $NaHCO_3$ and extracted with EtOAc (3×). The organic layer was collected, washed with brine, dried with $MgSO_4$ and concentrated under vacuum.The product was purified by flash column chromatography on silica gel (7% EtOAc in hexanes) to give **S56** (1.09 g, 68% over three steps) as a pale yellow viscous oil: **^1H NMR (**400 MHz, CDCl3) δ 8.01 – 7.95 (m, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.01 (s, 2H), 2.29 (dd, *J* = 4.9, 2.4 Hz, 2H), 1.80 (t, *J* = 2.5 Hz, 3H), 1.14 (s, 6H); **^{13}C**

NMR (151 MHz, CDCl3) δ 200.0, 138.5, 132.7, 128.5, 128.1, 77.7, 63.7, 47.1, 34.2, 32.5, 27.4, 3.5; **HRMS** (EI) calc for $[C_{15}H_{18}O]$+ ([M]+): m/z 214.1358, found 214.1348.

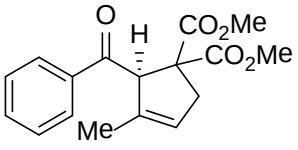


56

(Z)-(3,3-dimethyl-1-phenylhept-1-en-5-ynyloxy)triethylsilane (56): A solution of KHMDS (1.5 equiv.) in THF (0.5 M) was cooled to -78 °C and stirred for 10 min. Ketone **S56** (1 equiv.) in THF (0.5 M) was slowly added. The resulting solution was stirred for 2 h. TESCl (1.2 equiv.) in THF (0.5 M) was slowly added, then the solution was stirred overnight with temperature raising to rt, quenched with sat. NH_4Cl, extracted with Et_2O. The organic layer was collected, washed with brine, dried with $MgSO_4$, concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (1% Et_3N in pentane) to give **56** (0.041 g, 71%) as a colorless viscous oil: **^{1}H NMR** (300 MHz, CD_2Cl_2) δ 7.43 – 7.22 (m, 5H), 4.73 (s, 1H), 2.31 (q, *J* = 2.4 Hz, 2H), 1.79 (t, *J* = 2.5 Hz, 3H), 1.26 (s, 6H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.9 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.1, 141.4, 127.8, 127.5, 127.1, 118.5, 77.7, 76.6, 35.0, 33.0, 27.6, 6.7, 5.6, 3.6; **HRMS** (EI) calc for $[C_{21}H_{32}OSi]$+ ([M]+): m/z 328.2222, found 328.2213.

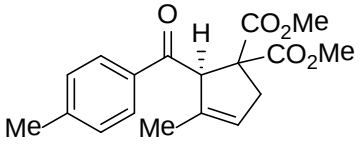
VI. Gold(I) cyclizations for Silyloxy-1,5-enynes

General Procedure F - Gold(I) cyclizations: (*R*)-DTBM-SEGPHOS$(AuCl)_2$ (2.9 mg, 3.5 μmol) and NaBARF (3.1 mg, 7.0 μmol) was dissolved in CH_2Cl_2 and stir for 15 minutes at room temperature. The mixture was cooled at -50 °C and a solution of the corresponding enolsilane (35 μmol) in CD_2Cl_2 was transferred to the catalyst mixture. The solution was stirred at the specified temperature until consumption of the starting material as indicated by TLC (1 to 14 hours). The solution was concentrated and purified on silica gel.



37

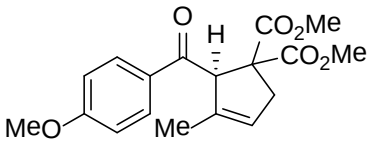
(R)-dimethyl-2-benzoyl-3-methylcyclopent-3-ene-1,1-dicarboxylate (37): According to the general procedure F, enolsilane **36** (16 mg, 0.035 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (11% EtOAc in hexanes) to give **37**(8.0 mg, 75%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 8.04 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 5.54 (d, *J* = 0.9 Hz, 1H), 5.34 (s, 1H), 3.82 (s, 3H), 3.58 (ddd, *J* = 16.9, 4.6, 2.3 Hz, 1H), 3.50 (s, 3H), 2.89 (dt, *J* = 16.9, 1.9 Hz, 1H), 1.69 – 1.58 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.4, 172.0, 169.7, 138.0, 137.6, 133.4, 128.71, 128.70, 125.9, 64.7, 61.0, 53.3, 52.4, 40.1, 16.2; **HRMS** (ESI) calc for $[C_{17}H_{18}O_5Na]^+$ ($[M+Na]^+$): *m/z* 325.1046, found 325.1046; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99:1 hexanes : Butanol, 0.8 ml/min, 237 nm); major enantiomer t_r = 14.1 min, minor enantiomer t_r = 16.9 min; 94% ee; absolute configuration was assigned by analogy to the x-ray analysis of **47**.



45

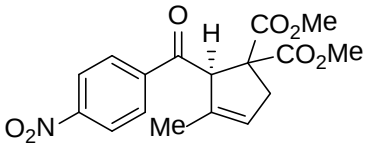
(R)-dimethyl-3-methyl-2-(4-methylbenzoyl)cyclopent-3-ene-1,1-dicarboxylate (45): According to the general procedure F, enolsilane **38** (17 mg, 0.035 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give **45** (8.9 mg, 81%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 5.52 (s, 1H), 5.30 (s, 1H), 3.80 (s, 3H), 3.57 (d, *J* = 16.9 Hz, 1H), 3.49 (s, 3H), 2.86 (d, *J* = 16.7 Hz, 1H), 2.46 (s, 3H), 1.62 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.8, 172.1, 169.7, 144.3, 138.1, 135.1, 129.4, 128.9, 125.7, 64.7, 60.9, 53.2, 52.4, 40.1, 21.7, 16.2; **HRMS** (ESI) calc for $[C_{18}H_{21}O_5]^+$ ($[M+H]^+$): *m/z* 317.1384, found 317.1386; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99:1 hexanes : Butanol, 0.8 ml/min, 210 nm); major enantiomer

t_r = 14.0 min, minor enantiomer t_r = 18.2 min; 91% ee; absolute configuration was assigned by analogy to the x-ray analysis of **47**.



39

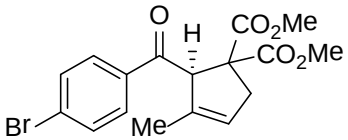
(R)-dimethyl 2-(4-methoxybenzoyl)-3-methylcyclopent-3-ene-1,1-dicarboxylate (46): According to the general procedure F, enolsilane **39** (17.1 mg, 0.035 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **46** (10.7 mg, 92%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 2H), 7.03 – 6.97 (m, 2H), 5.52 (m, 1H), 5.30 (s, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.58 (ddd, *J* = 16.9, 4.7, 2.4 Hz, 1H), 3.50 (s, 3H), 2.87 (dt, *J* = 16.9, 1.9 Hz, 1H), 1.69 – 1.61 (m, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.5, 172.1, 170.0, 163.8, 138.1, 131.1, 130.6, 125.6, 113.8, 64.6, 60.7, 55.5, 53.2, 52.3, 40.1, 16.1; **HRMS** (ESI) calc for $[C_{18}H_{20}O_6Na]^+$ ($[M+Na]^+$): *m/z* 355.1152, found 355.1152. **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99:1 hexanes : Butanol, 0.8 ml/min, 210 nm); major enantiomer t_r = 14.9 min, minor enantiomer t_r = 19.4 min; 94% ee; absolute configuration was assigned by analogy to the x-ray analysis of **47**.



47

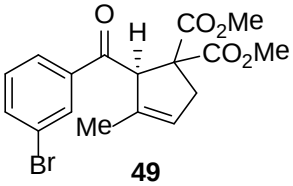
(R)-dimethyl-3-methyl-2-(4-nitrobenzoyl)cyclopent-3-ene-1,1-dicarboxylate (47): According to the general procedure F, enolsilane **40** (18.1 mg, 0.035 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **47** (9.2 mg, 71%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 – 8.35 (m, 2H), 8.27 – 8.20 (m, 2H), 5.60 (s, 1H), 5.32 (s, 1H), 3.84 (s, 3H), 3.53 (m, 1H), 3.52 (s, 3H), 2.94 (m, 1H), 1.64 (d, *J* = 1.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.5, 171.6, 169.8, 137.2, 129.6, 129.2, 126.8, 123.9, 123.9, 65.1, 61.3, 53.2,

41.7, 23.9, 16.1; **HRMS** (ESI) calc for $[C_{17}H_{17}O_7NNa]^+$ ($[M+Na]^+$): *m/z* 370.0897, found 370.0905; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99:1 hexanes : Butanol, 0.8 ml/min, 260 nm); major enantiomer t_r = 18.1 min, minor enantiomer t_r =26.4 min; 94% ee; absolute configuration was assigned by analogy to the x-ray analysis.



48

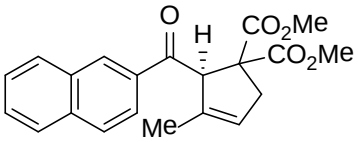
(R)-dimethyl-2-(4-bromobenzoyl)-3-methylcyclopent-3-ene-1,1-dicarboxylate (48): According to the general procedure F, enolsilane **41** (19.1 mg, 0.035 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give **48** (8.9 mg, 67%) as a pale yellow viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 5.55 (s, 1H), 5.27 (s, 1H), 3.82 (s, 3H), 3.60 – 3.53 (m, 1H), 3.51 (s, 3H), 2.95 – 2.84 (m, 1H), 1.63 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.4, 171.8, 169.8, 137.7, 136.3, 132.0, 130.2, 128.7, 126.2, 64.8, 60.9, 53.3, 52.5, 40.1, 16.1; **HRMS** (ESI) calc for $[C_{17}H_{17}O_5BrNa]^+$ ($[M+Na]^+$): *m/z* 403.0152, found 403.0161; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99:1 hexanes : Butanol, 0.8 ml/min, 260 nm); major enantiomer t_r = 13.8 min, minor enantiomer t_r = 19.6 min; 92% ee; absolute configuration was assigned by analogy to the x-ray analysis of **47**.



49

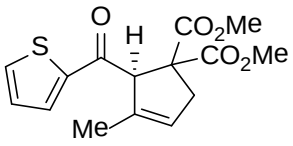
(R)-dimethyl-2-(3-bromobenzoyl)-3-methylcyclopent-3-ene-1,1-dicarboxylate (49): According to the general procedure F, enolsilane **42** (19.2 mg, 0.035 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give **49** (9.7 mg, 72%) as a pale yellow viscous oil: **^{1}H NMR**

(400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 5.54 (s, 1H), 5.24 (s, 1H), 3.81 (s, 3H), 3.53 (d, *J* = 16.9 Hz, 1H), 3.52 (s, 3H), 2.89 (d, *J* = 16.9 Hz, 1H), 1.63 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.1, 171. 8, 169.8, 139.3, 137.6, 136.2, 131.6, 130.3, 127.3, 126.7, 123.1, 64.8, 61.0, 53.4, 52.5, 40.1, 16.1; **HRMS** (ESI) calc for $[C_{17}H_{17}O_5BrNa]^+$ ($[M+Na]^+$): *m/z* 403.0152, found 403.0159; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99:1 hexanes : Butanol, 0.8 ml/min, 260 nm); major enantiomer t_r = 11.9 min, minor enantiomer t_r = 14.9 min; 93% ee; absolute configuration was assigned by analogy to the x-ray analysis of **47**.



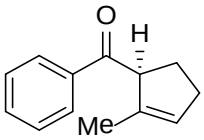
50

(R)-dimethyl-2-(2-naphthoyl)-3-methylcyclopent-3-ene-1,1-dicarboxylate (50): According to the general procedure F, enolsilane **43** (18.5 mg, 0.035 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (8% EtOAc in hexanes) to give **50** (10.1 mg, 82%) as a off-white solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.09 (dt, *J* = 9.5, 4.8 Hz, 2H), 7.95 (t, *J* = 8.7 Hz, 2H), 7.71 – 7.58 (m, 2H), 5.57 (s, 1H), 5.52 (s, 1H), 3.85 (s, 3H), 3.64 (ddd, *J* = 17.0, 4.7, 2.4 Hz, 1H), 3.49 (s, 3H), 2.92 (d, *J* = 16.9 Hz, 1H), 1.67 (d, *J* = 1.4 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.2, 172.1, 167.0, 138.1, 135.7, 134.9, 132.6, 130.7, 129.8, 128.7, 128.6, 127.8, 126.9, 125.9, 124.2, 64.8, 61.1, 53.3, 52.4, 40.2, 16.2; **HRMS** (ESI) calc for $[C_{21}H_{20}O_5Na]^+$ ($[M+Na]^+$): *m/z* 375.1203, found 375.1202; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99.5:0.5 hexanes : Butanol, 0.8 ml/min, 237 nm); major enantiomer t_r = 14.1 min, minor enantiomer t_r = 18.2 min; 89% ee; absolute configuration was assigned by analogy to the x-ray analysis of **47**.



51

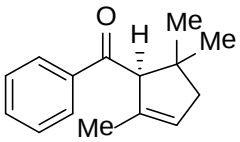
(R)-dimethyl-3-methyl-2-(thiophene-2-carbonyl)cyclopent-3-ene-1,1-dicarboxylate (51): According to the general procedure F, enolsilane **44** (16.3 mg, 0.035 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (12% EtOAc in hexanes) to give **51** (10.1 mg, 94%) as a brown solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 3.8, 0.9 Hz, 1H), 7.74 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.22 (dd, *J* = 4.9, 3.9 Hz, 1H), 5.56 (s, 1H), 5.12 (s, 1H), 3.81 (s, 3H), 3.62 – 3.57 (m, 1H), 3.55 (s, 3H), 2.93 – 2.80 (m, 1H), 1.71 (d, *J* = 1.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.4, 171.9, 169.7, 144.8, 137.6, 134.8, 133.2, 128.4, 126.1, 64.6, 62.6, 53.3, 52.5, 40.2, 16.1; **HRMS** (ESI) calc for $[C_{15}H_{16}O_5SNa]^+$ ($[M+Na]^+$): *m/z* 331.0611, found 331.0611; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (98:2 hexanes : Butanol, 0.8 ml/min, 237 nm); major enantiomer t_r = 14.1 min, minor enantiomer t_r = 16.9 min; 90% ee; absolute configuration was assigned by analogy to the x-ray analysis of **47**.



57

(S)-(2-methylcyclopent-2-enyl)(phenyl)methanone (57): According to the general procedure F, enolsilane **54** (17.1 mg, 0.05 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give **57** (7.2 mg, 77%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 – 8.04 (m, 2H), 7.65 – 7.57 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 5.70 – 5.63 (m, 1H), 4.44 – 4.39 (m, 1H), 2.57 – 2.46 (m, 1H), 2.45 – 2.34 (m, 2H), 2.20 – 2.06 (m, 1H), 1.74 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.5, 164.5, 140.6, 135.5, 134.3, 129.2, 129.1, 33.9, 29.7, 28.2, 9.6; **HRMS** (EI) calc for $[C_{13}H_{14}O]^+$ ($[M]^+$): *m/z* 186.1045, found 186.1040; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99.9:0.1 hexanes : Butanol, 0.8

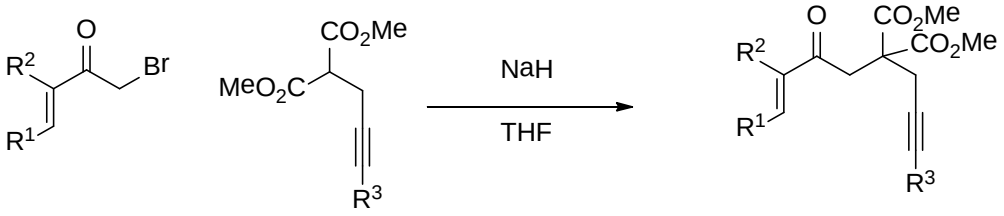
ml/min, 237 nm); major enantiomer t_r = 8.6 min, minor enantiomer t_r = 9.9 min; 55% ee; absolute configuration was assigned by analogy to the x-ray analysis of **47**.



59

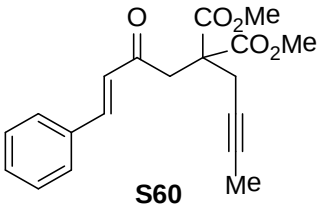
(S)-phenyl(2,5,5-trimethylcyclopent-2-enyl)methanone (59): According to the general procedure F, enolsilane **56** (11.5 mg, 0.035 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (1% EtOAc in hexanes) to give **59** (6.1 mg, 81%) as a colorless viscous oil: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (d, J = 7.4 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 5.60 (s, 1H), 4.12 (s, 1H), 2.39 (ddd, *J* = 15.8, 4.2, 2.1 Hz, 1H), 2.18 (d, *J* = 15.8 Hz, 1H), 1.68 (s, 3H), 1.30 (s, 3H), 0.92 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.5, 138.3, 132.8, 128.6, 128.5, 127.2, 65.6, 48.2, 43.7, 31.6, 25.8, 16.3; **HRMS** (EI) calc for $[C_{15}H_{18}O]$+ ([M]+): m/z 214.1358, found 214.1358; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99.9:0.1 hexanes : Butanol, 0.8 ml/min, 210 nm); major enantiomer t_r = 7.9 min, minor enantiomer t_r = 11.1 min; 90% ee; absolute configuration was assigned by analogy to the x-ray analysis of **47**.

VII. Synthesis of Silyloxy-1,3-dien-7-ynes



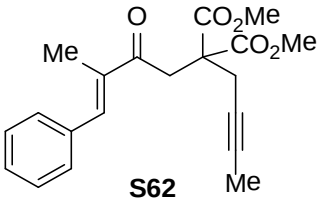
General Procedure G - Preparation of α,β-unsaturated ketones: The appropriate alkyne (the ethyl substituted alkyne was used for **63**) was dissolved in THF (0.4 M) and cooled to 0 ^{o}C. Then, NaH (60 % in oil, 1.1 equiv.) was added in one portion. The reaction mixture was stirred for 30 min. at this temperature. The corresponding 2-bromo-α,β-unsaturated ketone

was dissolved in THF (0.5 M) and transferred slowly to the reaction mixture. The reaction was warmed to room temperature and quenched by the addition of an equal volume of sat. aq. NH_4Cl. The mixture was extracted with EtOAc (3 ×), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to provide analytically pure compound.



S60

(E)-dimethyl-2-(but-2-ynyl)-2-(2-oxo-4-phenylbut-3-enyl)malonate (S60): According to the general procedure G, the corresponding 2-bromo-α,β-unsaturated ketone (1.13 g, 5 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S60** (971 mg, 63%) as a white powder: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16.3 Hz, 1H), 7.58- 7.54 (m, 2H), 7.42-7.40 (m, 3H), 6.74 (d, *J* = 16.2 Hz, 1H), 3.76 (s, 6H), 3.59 (s, 2H), 2.99 (d, *J* = 2.5 Hz, 2H), 1.75 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 170.0, 143.3, 134.3, 130.6, 129.0, 128.3, 125.8, 79.2, 73.7, 54.9, 53.0, 42.9, 23.8, 3.5; **HRMS** (ESI) calc for $[C_{19}H_{21}O_5]^+$ ($[M+H]^+$): *m/z* 329.1384, found 329.1382. The spectral data was in accordance with the literature.[6]

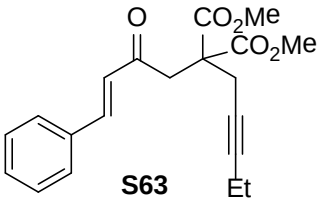


S62

(E)-dimethyl-2-(but-2-ynyl)-2-(3-methyl-2-oxo-4-phenylbut-3-enyl)malonate (S62): According to the general procedure G, the corresponding 2-bromo-α,β-unsaturated ketone (1.23 g, 5.1 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S62** (995 mg,

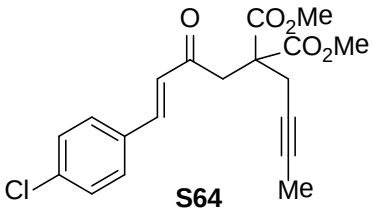
[6] Kusama, H.; Yamabe, H.; Onizawa, Y.; Hoshino, T.; Iwasawa, N. *Angew. Chem. Int. Ed.* **2005**, *44*, 468.

57%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.50-7.40 (m, 5H), 3.81 (s, 6H), 3.78 (s, 2H), 3.03 (q, *J* = 2.5 Hz, 2H), 2.10 (s, 3H), 1.79 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.9, 170.3, 139.5, 137.0, 135.8, 129.8, 128.7, 128.5, 79.3, 13.9, 55.2, 53.0, 40.3, 23.8, 13.0, 3.6; **HRMS** (ESI) calc for $[C_{20}H_{23}O_5]^+$ ($[M+H]^+$): *m/z* 343.1540, found 343.1536.



S63

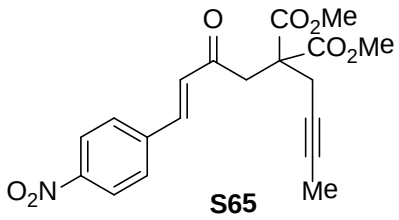
(E)-dimethyl-2-(2-oxo-4-phenylbut-3-enyl)-2-(pent-2-ynyl)malonate (S63): According to the general procedure G, the corresponding 2-bromo-α,β-unsaturated ketone (788 mg, 3.5 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give **S63** (622 g, 52%) as a colorless viscous oil: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16.2 Hz, 1H), 7.59-7.57 (m, 2H), 7.44-7.42 (m, 3H), 6.77 (d, *J* = 16.2 Hz, 1H), 3.79 (s, 6H), 3.62 (s, 2H), 3.03 (s, 2H), 2.15 (q, *J* = 7.4 Hz, 2H), 1.10 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 170.0, 143.3, 134.3, 130.6, 129.0, 128.3, 125.9, 85.4, 74.0, 55.0, 52.9, 42.8, 23.8, 14.1, 12.3; **HRMS** (ESI) calc for $[C_{20}H_{23}O_5]^+$ ($[M+H]^+$): *m/z* 343.1540, found 343.1540.



S64

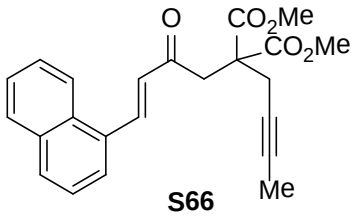
(E)-dimethyl-2-(but-2-ynyl)-2-(4-(4-chlorophenyl)-2-oxobut-3-enyl)malonate (S64): According to the general procedure G, the corresponding 2-bromo-α,β-unsaturated ketone (464 mg, 1.79 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (15% EtOAc in hexanes) to give **S64** (381 mg, 61%) as a white powder: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 16.2 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 1H), 6.74 (d, *J* = 16.2 Hz, 1H), 3.79 (s, 6H), 3.60 (s, 2H),

3.02 (s, 2H), 1.78 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) 196.4, 170.0, 141.8, 136.6, 132.8, 129.5, 129.3, 126.2, 79.3, 73.7, 54.9, 53.0, 43.1, 23.8, 3.5; **HRMS** (ESI) calc for $[C_{19}H_{20}O_5Cl]^+$ ($[M+H]^+$): *m/z* 363.0994, found 363.0999.



S65

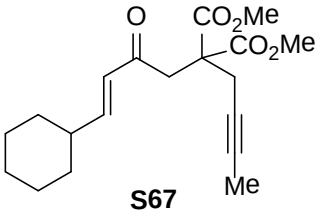
(E)-dimethyl-2-(but-2-ynyl)-2-(4-(4-nitrophenyl)-2-oxobut-3-enyl)malonate (S65): According to the general procedure G, the corresponding 2-bromo-α,β-unsaturated ketone (245 mg, 0.91 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (20% EtOAc in hexanes) to give **S65** (167 mg, 49%) as a white powder: **^{1}H NMR (**400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 16.2 Hz, 1H), 6.87 (d, *J* = 16.2 Hz, 1H), 3.79 (s, 6H), 3.61 (s, 2H), 3.02 (q, *J* = 2.5 Hz, 2H), 1.77 (t, *J* = 2.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.2, 169.9, 148.7, 140.5, 140.0, 129.2, 128.9, 124.2, 79.5, 73.6, 54.9, 53.1, 43.6, 23.9, 3.5; **HRMS** (ESI) calc for $[C_{19}H_{19}NO_7Na]^+$ ($[M+Na]^+$): *m/z* 396.1054, found 396.1052.



S66

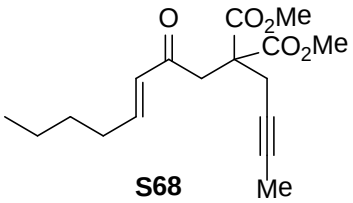
(E)-dimethyl-2-(but-2-ynyl)-2-(4-(naphthalen-1-yl)-2-oxobut-3-enyl)malonate (S66): According to the general procedure G, the corresponding 2-bromo-α,β-unsaturated ketone (825 mg, 3 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give **S66**(765 mg, 68%) as a white powder: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.51 (d, *J* = 15.8 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.1 Hz, 1H), 7.67 – 7.50 (m, 3H), 6.89 (d, *J* = 15.9 Hz, 1H), 3.82 (s, 6H), 3.69 (s, 2H), 3.06 (s, 2H), 1.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.5, 170.1, 140.0, 133.7, 131.6, 131.5, 130.9, 128.8,

128.1, 127.0, 126.3, 125.5, 125.2, 123.2, 79.4, 73.9, 55.0, 53.1, 43.4, 23.9, 3.6; **HRMS** (ESI) calc for $[C_{23}H_{23}O_5]^+$ ($[M+H]^+$): *m/z* 379.1540, found 379.1543.



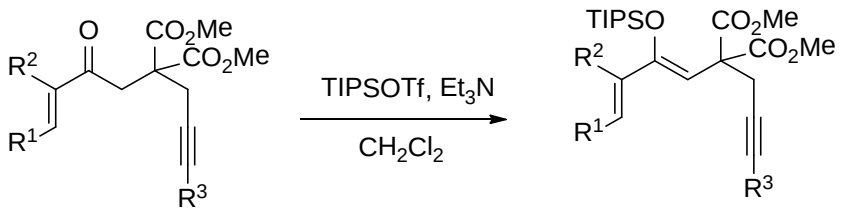
S67

(E)-dimethyl-2-(but-2-ynyl)-2-(4-cyclohexyl-2-oxobut-3-enyl)malonate (S67): According to the general procedure G, the corresponding 2-bromo-α,β-unsaturated ketone (1.0 g, 4.3 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (8/1/1 hexanes/$CHCl_3$/Et_2O) to give **S67** (661 mg, 46%) as a colorless viscous oil: **^{1}H NMR** δ 6.89 (dd, *J* = 16.1, 6.8 Hz, 1H), 6.08 (dd, *J* = 16.1, 1.3 Hz, 1H), 3.78 (s, 6H), 3.49 (s, 2H), 2.98 (d, *J* = 2.5 Hz, 2H), 2.27 – 2.09 (m, 1H), 1.85 – 1.73 (m, 2H), 1.42 – 1.08 (m, 8H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.3, 170.1, 170.0, 153.4, 149.6, 128.7, 127.6, 82.7, 79.1, 73.8, 54.9, 52.9, 42.7, 42.2, 40.7, 32.6, 31.7, 25.9, 25.7, 25.3, 23.7, 21.4, 3.5; **HRMS** (ESI) calc for $[C_{19}H_{27}O_5Na]^+$ ($[M+H]^+$): *m/z* 335.1583, found 335.1581.

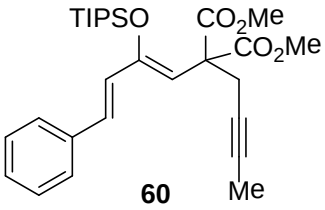


S68

(E)-dimethyl-2-(but-2-ynyl)-2-(2-oxooct-3-enyl)malonate (S68): According to the general procedure G, the corresponding 2-bromo-α,β-unsaturated ketone (762 mg, 3.72 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (10% EtOAc in hexanes) to give **S68** (698 mg, 61%) as a colorless oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 (dt, *J* = 15.7, 6.9 Hz, 1H), 6.09 (t, *J* = 14.0 Hz, 1H), 3.75 (s, 6H), 3.46 (s, 2H), 2.93 (s, 2H), 2.25 (q, *J* = 6.8 Hz, 2H) , 1.76 (s, 3H), 1.55 – 1.42 (m, 2H), 1.42 – 1.31 (m, 2H), 0.90 (dt, *J* = 8.6, 6.7 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.8, 170.1, 148.7, 129.9, 79.1, 73.7, 54.7, 53.0, 42.2, 32.2, 30.1, 23.7, 22.3, 13.8, 3.5; **HRMS** (ESI) calc for $[C_{17}H_{25}O_5]^+$ ($[M+H]^+$): *m/z* 309.1697, found 309.1696.

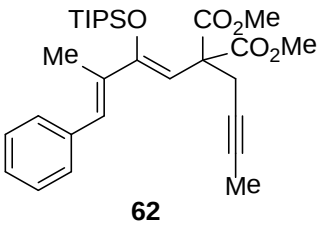


General Procedure H - Preparation of the enolsilanes: The appropriate ketone (1.0 equiv) was dissolved in CH_2Cl_2 (0.2 M) and Et_3N (2.0 equiv) was added at room temperature. TIPSOTf (1.25 equiv) was added and the reaction mixture was stirred overnight. Then, the reaction was quenched with brine and extracted with ethyl acetate (3x). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to provide analytically pure compound.



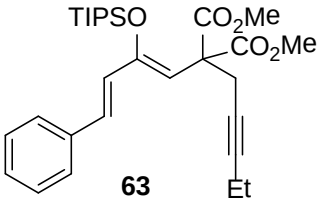
60

Dimethyl-2-(but-2-ynyl)-2-((1Z,3E)-4-phenyl-2-(triisopropylsilyloxy)buta-1,3-dienyl)malonate (60): According to the general procedure H, ketone **S60** (0.93 g, 2.93 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give **60** (1.10 g, 77%) as a white powder: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.27 (m, 5H), 6.97 (d, *J* = 15.8 Hz, 1H), 6.49 (d, *J* = 15.7 Hz, 1H), 5.70 (s, 1H), 3.79 (s, 6H), 3.15 (d, *J* = 2.5 Hz, 2H), 1.79 (t, *J* = 2.4 Hz, 2H), 1.24-1.09 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 151.3, 136.5, 131.8, 128.7, 128.0, 126.6, 125.8, 102.7, 77.2, 74.4, 56.7, 52.8, 25.1, 18.0, 13.8, 3.6; **HRMS** (ESI) calc for $[C_{28}H_{41}O_5Si]^+$ ($[M+H]^+$): *m/z* 485.2718, found 485.2706. The spectral data was in accordance with the literature.[5]



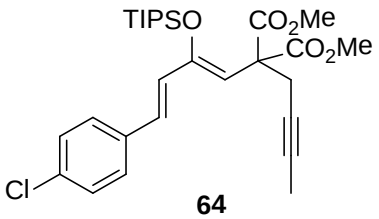
62

Dimethyl-2-(but-2-ynyl)-2-((1Z,3E)-3-methyl-4-phenyl-2-(triisopropylsilyloxy)buta-1,3-dienyl)malonate (62): According to the general procedure H, ketone **S62** (400 mg, 1.17 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give **62** (305 mg, 52%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.26 (m, 5H), 6.68 (s, 1H), 5.45 (s, 1H), 3.77 (s, 6H), 3.14 (q, *J* = 2.4 Hz, 2H), 2.08 (s, 3H), 1.76 (m, *J* = 2.4 Hz, 3H), 1.20-1.05 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 156.1, 137.3, 136.5, 129.2, 129.0, 128.7, 128.3, 126.8, 103.9, 77.8, 74.4, 56.5, 52.8, 26.2, 18.1, 17.7, 14.2, 3.5; **HRMS** (ESI) calc for $[C_{30}H_{43}O_5Si]^+$ ($[M+H]^+$): *m/z* 499.2874, found 499.2870.



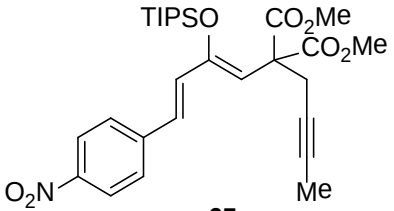
63

Dimethyl-2-(pent-2-ynyl)-2-((1Z,3E)-4-phenyl-2-(triisopropylsilyloxy)buta-1,3-dienyl)malonate (63): According to the general procedure H, ketone **S63** (303 mg, 0.88 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (4% EtOAc in hexanes) to give **63** (316mg, 72%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.30 (m, 5H), 6.97 (d, *J* = 15.8 Hz, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 5.75 (s, 1H), 3.79 (s, 6H), 3.17 (t, *J* = 2.3 Hz, 2H), 2.16 (qd, *J* = 7.5, 5.2 Hz, 2H), 1.22-1.09 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 151.3, 136.5, 131.8, 128.7, 128.1, 126.6, 125.8, 102.9, 84.0, 74.8, 56.8, 52.8, 25.2, 18.0, 13.9, 12.4; **HRMS** (ESI) calc for $[C_{29}H_{43}O_5Si]^+$ ($[M+H]^+$): *m/z* 499.2885, found 499.2873.



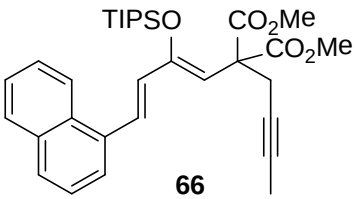
64

D**imethyl-2-(but-2-ynyl)-2-((1Z,3E)-4-(4-chlorophenyl)-2-(triisopropylsilyloxy)buta-1,3-dienyl)malonate (64)**: According to the general procedure H, ketone **S64**(204 mg, 0.58 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give **64** (232 mg, 77%) as a white powder: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (s, 4H), 6.89 (d, *J* = 15.7 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 5.71 (s, 1H), 3.76 (s, 6H), 3.12 (q, *J* = 2.5 Hz, 2H), 1.76 (t, *J* = 2.4 Hz, 3H), 1.19-1.07 (m, 21H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.0, 151.1 135.0, 133.8, 130.5, 128.9, 128.1, 127.8, 126.5, 103.2, 77.8, 74.4, 56.7, 52.8, 25.1, 18.0, 17.7, 13.8, 12.7, 12.3, 3.6; **HRMS** (ESI) calc for $[C_{28}H_{40}O_5Si]^+$ ($[M+H]^+$): *m/z* 519.2328, found 519.2326.



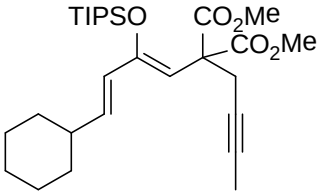
65

Dimethyl-2-(but-2-ynyl)-2-((1Z,3E)-4-(4-nitrophenyl)-2-(triisopropylsilyloxy)buta-1,3-dienyl)malonate (65): According to the general procedure H, ketone **S65** (80 mg, 0.21 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (8% EtOAc in hexanes) to give **65** (84 mg, 76%) as a white powder: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 15.8 Hz, 1H), 6.63 (d, *J* = 15.8 Hz, 1H), 5.82 (s, 1H), 3.77 (6H), 3.14 (s, 2H), 1.76 (s, 3H), 1.19-1.07 (m, 21H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.5, 149.8, 147.1, 143.3, 129.2, 127.4, 125.2, 124.1, 110.3, 79.2, 73.3, 56.9, 53.2, 28.5, 18.0, 12.7, 3.4; **HRMS** (ESI) calc for $[C_{20}H_{40}NO_7Si]^+$ ($[M+H]^+$): *m/z* 530.2580, found 530.2582.



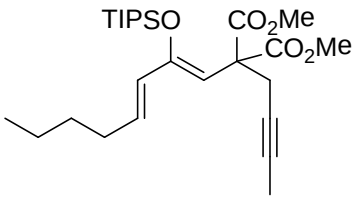
66

Dimethyl-2-(but-2-ynyl)-2-((1Z,3E)-4-(naphthalen-1-yl)-2-(triisopropylsilyloxy)buta-1,3-dienyl)malonate (66): According to the general procedure H, ketone **S66** (475 mg, 1.25 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (4% EtOAc in hexanes) to give **66** (600 mg, 89%) as a white powder: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.9 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 15.4 Hz, 1H), 7.62-7.49 (m, 4H), 6.55 (d, *J* = 15.4 Hz, 1H) 5.85 (s, 1H), 3.82 (s, 6H), 3.20 (s, 2H) 1.83 (s, 3H), 1.27-1.10 (m, 21H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.1, 151.7, 134.1, 133.7, 131.4, 129.1, 128.9, 128.6, 128.5, 126.3, 125.9, 125.6, 123.7, 103.3, 77.8, 74.5, 56.8, 52.8, 25.3, 18.0, 17.7, 13.9, 12.3, 3.6; **HRM**S (ESI) calc for $[C_{32}H_{43}O_5Si]^+$ ($[M+H]^+$): *m/z* 535.2874, found 535.2875.



67

Dimethyl-2-(but-2-ynyl)-2-((1Z,3E)-4-cyclohexyl-2-(triisopropylsilyloxy)buta-1,3-dienyl)malonate (67): According to the general procedure H, ketone **S67** (435 mg, 1.3 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (4% EtOAc in hexanes) to give **67** (477 mg, 75%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.02 (dd, *J* = 15.4, 6.6 Hz, 1H), 5.72 (d, *J* = 15.4 Hz, 1H), 5.42 (s, 1H), 3.74 (s, 6H), 3.07 (d, *J* = 2.5 Hz, 2H), 2.03-1.96 (m, 1H), 1.76-1.73 (m, 7H), 1.32-1.08 (m, 27H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 152.0, 140.4, 124.9, 101.2, 77.5, 74.6, 56.7, 52.7, 40.6, 32.3, 26.1, 26.0, 25.2, 17.9, 13.9, 3.6; **HRMS** (ESI) calc for $[C_{28}H_{47}O_5Si]^+$ ($[M+H]^+$): *m/z* 491.3198, found 491.3186.

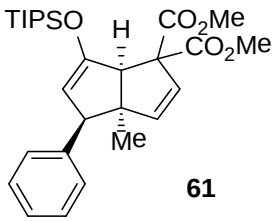


68

Dimethyl-2-(but-2-ynyl)-2-((1Z,3E)-2-(triisopropylsilyloxy)octa-1,3-dienyl)malonate (68): According to the general procedure H, ketone **S68** (306 mg, 1 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (2% EtOAc in hexanes) to give **68** (217 mg, 47%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.17 – 6.03 (m, 1H), 5.79 (d, *J* = 15.2 Hz, 1H), 5.46 (s, 1H), 3.76 (s, 6H), 3.09 (d, *J* = 2.3 Hz, 2H), 2.12 (q, *J* = 7.1 Hz, 3H), 1.77 (s, 3H), 1.48 – 1.23 (m, 6H), 1.22 – 1.02 (m, 21H), 0.95 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 151.7, 135.1, 127.3, 101.8, 101.3, 98.2, 77.5, 74.6, 56.6, 52. 8, 32.3, 30.9, 25.2, 22.3, 17.9, 17.7, 13.9, 13.8, 3.6; **HRMS** (ESI) calc for $[C_{25}H_{42}O_5Si]^+$ ($[M+H]^+$): *m/z* 450.2796, found 450.2796.

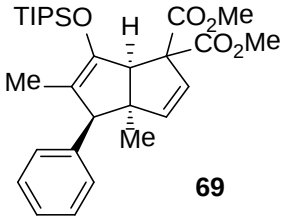
VIII. Gold cyclization with dienol silyl ether

General Procedure I - Gold(I) cyclizations: The (*R*)-DTBM-SEGPHOS$(AuCl)_2$ (5 mol %) and NaBARF (10 mol %) was dissolved in CH_2Cl_2. Dried molecular sieves were added and the mixture was stirred for 15 minutes at room temperature. A solution of the α,β-unsaturated enolsilane (1 equiv.) in CH_2Cl_2 was transferred to the catalyst mixture. The solution was stirred at this temperature until consumption of the starting material as indicated by TLC (1 to 14 hours). The solution was diluted in CH_2Cl_2 and filtered on Celite before being concentrated and purified on silica gel.



61

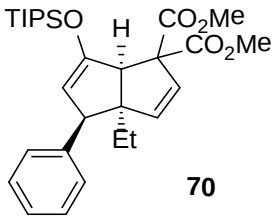
(3aS,4R,6aR)-dimethyl-3a-methyl-4-phenyl-6-(triisopropylsilyloxy)-3a,4-dihydropentalene-1,1(6aH)-dicarboxylate (61): According to the general procedure I, dienol silyl ether **60** (24.1 mg, 0.05 mmol) was reacted under the standard conditions (1,2-dichloroethane was used as solvent). The product was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give **61** (22 mg, 91%) as a white powder: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 5H), 5.47 (d, J = 5.7 Hz, 1H), 4.83 (d, *J* = 5.7 Hz, 1H), 4.69 (s, 1H), 3.91 (s, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.65 (s, 1H), 1.32 (s, 3H), 1.26 – 1.18 (m, 3H), 1.12 (t, *J* = 7.6 Hz, 18H); The spectral data was in accordance with the literature[5]; **HRMS** (ESI) calc for $[C_{28}H_{41}O_5Si]^+$ ($[M+H]^+$): *m/z* 485.2718, found 485.2719; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99.9: 0.1 hexanes : Butanol, 0.8 ml/min, 218 nm); major enantiomer t_r = 16.7 min, minor enantiomer t_r = 19.3 min; 99% ee; absolute configuration was assigned by x-ray analysis of **76**.



69

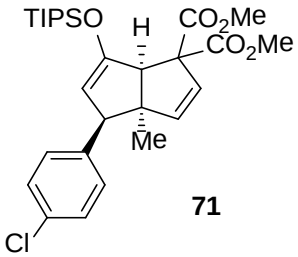
(3aS,4R,6aR)-dimethyl-3a,5-dimethyl-4-phenyl-6-(triisopropylsilyloxy)-3a,4-dihydropentalene-1,1(6aH)-dicarboxylate (69): According to the general procedure I, dienol silyl ether **62** (24.9 mg, 0.05 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (4% EtOAc in hexanes) to give **69** (18.9 mg, 76%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H), 7.27-7.23 (m, 1H), 7.17 (d, *J* = 7.0 Hz, 2H), 5.45 (d, *J* = 5.6 Hz, 1H), 4.81 (d, *J* = 5.6 Hz, 1H), 3.97 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.43 (s, 1H), 1.35 (s, 3H), 1.26 (s, 3H), 1.24-1.17 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 170.7, 145.9, 142.1, 141.0, 129.6, 127.9, 126.3, 126.1, 115.6, 69.7, 62.7, 62.3, 57.1, 52.5, 28.2, 18.1, 17.9, 13.4, 11.6; **HRMS** (ESI) calc for $[C_{29}H_{43}O_5Si]^+$ ($[M+H]^+$): *m/z* 499.2885, found 499.2883;

HPLC: enantiomeric excess determined by HPLC with a Chiralpak IC column (99.9:0.1 hexanes : Butanol, 0.8 ml/min, 220 nm); major enantiomer t_r = 10.3 min, minor enantiomer t_r = 12.1 min; 96% ee; absolute configuration was assigned by analogy with **76**.



70

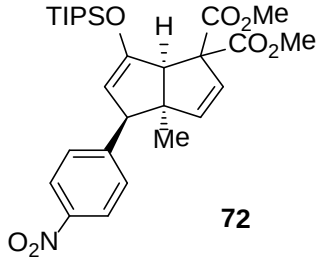
(3aS,4R,6aR)-dimethyl-3a-ethyl-4-phenyl-6-(triisopropylsilyloxy)-3a,4-dihydropentalene-1,1(6aH)-dicarboxylate (70): According to the general procedure I, dienol silyl ether **63** (21 mg, 0.042 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (4% EtOAc in hexanes) to give **70** (12.8 g, 61%) as a colorless viscous oil: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.19 (m, 5H), 5.52 (d, *J* = 5.6 Hz, 1H), 4.85 (d, *J* = 5.6 Hz, 1H), 4.69 (s, 1H), 3.95 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.72 (s, 1H), 1.68 (q, *J* = 7.4 Hz, 2H), 1.28 – 1.18 (m, 3H), 1.14 (t, *J* = 7.8 Hz, 18H), 0.90 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 170.7, 152.5, 142.6, 140.4, 129.1, 127.8, 126.9, 126.3, 107.48, 69.3, 63.0, 59.2, 55.5, 52.6, 52.5, 33.0, 18.0, 17.9, 12.5, 12.4, 9.2; **HRMS** (ESI) calc for $[C_{29}H_{43}O_5Si]^+$ ($[M+H]^+$): *m/z* 499.2885, found 499.2877; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99.9:0.1 hexanes : Butanol, 0.8 ml/min, 220 nm); major enantiomer t_r = 10.3 min, minor enantiomer t_r = 12.1 min; 96% ee; absolute configuration was assigned by analogy with **76**.



71

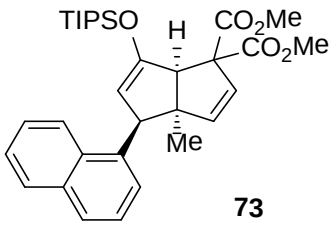
(3aS,4R,6aR)-dimethyl-4-(4-chlorophenyl)-3a-methyl-6-(triisopropylsilyloxy)-3a,4-dihydropentalene-1,1(6aH)-dicarboxylate (71): According to the general procedure I, dienol silyl ether **64** (25.9 mg, 0.05 mmol) was reacted under the standard conditions. The product

was purified by flash column chromatography on silica gel (5% EtOAc in hexanes) to give **71** (16.6 mg, 64%) as a white powder: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.50 (d, *J* = 5.5 Hz, 1H), 4.84 (d, *J* = 5.5 Hz, 1H), 4.65 (s, 1H), 3.92 (s, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.63 (s, 1H), 1.34 (s, 3H),1.25-1.21 (m, 3H), 1.15-1.12 (m, 18H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.2, 170.5, 152.9, 141.2, 140.8, 132.2, 129.9, 128.1, 126.5, 106.6, 68.96, 61.6, 58.4, 57.0, 52.7, 52.5, 27.4, 18.0, 17.9, 12.5; **HRMS** (ESI) calc for $[C_{28}H_{40}ClO_5Si]^+$ ($[M+H]^+$): *m/z* 519.2340, found 519.2328; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99.9:0.1 hexanes : Butanol, 0.8 ml/min, 212 nm); major enantiomer t_r = 9.4 min, minor enantiomer t_r = 10.7 min; 98% ee; absolute configuration was assigned by analogy with **76**.



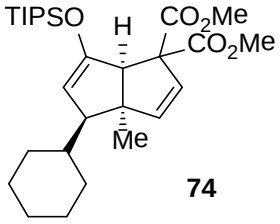
72

(3aS,4R,6aR)-dimethyl-3a-methyl-4-(4-nitrophenyl)-6-(triisopropylsilyloxy)-3a,4-dihydropentalene-1,1(6aH)-dicarboxylate (72): According to the general procedure I, dienol silyl ether **65** (15 mg, 0.028 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (7% EtOAc in hexanes) to give **72** (12.1 mg, 81%) as a white powder: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 5.54 (d, *J* = 5.6 Hz, 1H), 4.78 (d, *J* = 5.6 Hz, 1H), 4.72 – 4.61 (m, 1H), 3.96 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 1.40 (s, 3H), 1.32 – 1.20 (m, 3H), 1.20 – 1.11 (m, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 170.3, 153.8, 150.4, 146.9, 140.4, 129.4, 127.3, 123.3, 105.7, 68.9, 61.8, 58.6, 57.6, 52.7, 52.6, 27.8, 17.9, 17.8, 17.7, 12.5; **HRMS** (ESI) calc for $[C_{28}H_{40}NO_7Si]^+$ ($[M+H]^+$): *m/z* 530.2580, found 530.2569; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99.9:0.1 hexanes : Butanol, 0.8 ml/min, 270 nm); major enantiomer t_r = 9.2 min, minor enantiomer t_r = 9.9 min; 89% ee; absolute configuration was assigned by analogy with **76**.



73

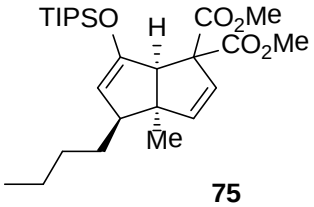
(3aS,4S,6aR)-dimethyl-3a-methyl-4-(naphthalen-1-yl)-6-(triisopropylsilyloxy)-3a,4-dihydropentalene-1,1(6aH)-dicarboxylate (73): According to the general procedure, dienol silyl ether **66** (26.7 mg, 0.05 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexanes) to give **73** (24.2 mg, 91%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.36 (m, 4H), 6.26 (d, *J* = 5.4 Hz, 1H), 5.83 (d, *J* = 5.5 Hz, 1H), 4.89 – 4.74 (m, 2H), 3.90 (s, 1H), 3.79 (s, 6H), 1.47 – 1.26 (m, 3H), 1.27 – 1.10 (m, 18H), 0.59 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 170.5, 152.5, 143.8, 139.1, 133. 8, 132.9, 128.9, 127.0, 127.0, 125.9, 125.7, 125.4, 125.2, 123.6, 107.2, 68.7, 63.3, 58.8, 52.7, 52.6, 23.4, 18.1, 17.9, 12.6; **HRMS** (ESI) calc for $[C_{32}H_{43}O_5Si]^+$ ($[M+H]^+$): *m/z* 535.2874, found 535.2877; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99.9:0.1 hexanes : Butanol, 0.8 ml/min, 230 nm); major enantiomer t_r = 16.1 min, minor enantiomer t_r = 18.6 min; 91% ee; absolute configuration was assigned by analogy with **76**.



74

(3aS,4S,6aR)-dimethyl-4-cyclohexyl-3a-methyl-6-(triisopropylsilyloxy)-3a,4-dihydropentalene-1,1(6aH)-dicarboxylate (74): According to the general procedure I, dienol silyl ether **67** (17.1 g, 0.035 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexanes) to give **74** (12.9 mg, 76%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.92 (d, *J* = 5.6 Hz, 1H), 5.69 (d, *J* = 5.6 Hz, 1H), 4.70 (d, *J* = 1.6 Hz, 1H), 3.79 – 3.71 (m, 4H), 3.70 (s, 3H), 2.10

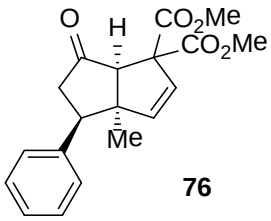
(dd, *J* = 8.5, 1.8 Hz, 1H), 1.96 – 1.82 (m, 1H), 1.81 – 1.66 (m, 5H), 1.39 – 1.00 (m, 27H); **HRMS** (ESI) calc for $[C_{28}H_{47}O_5Si]^+$ ($[M+H]^+$): *m/z* 491.3198, found 491.3196; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99.9:0.1 hexanes : Butanol, 0.8 ml/min, 210 nm); major enantiomer tr = 14.0 min, minor enantiomer tr = 15.8 min; 80% ee; absolute configuration was assigned by analogy with **76**.



75

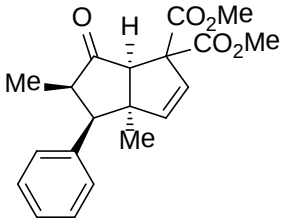
(3aS,4S,6aR)-dimethyl-4-cyclohexyl-3a-methyl-6-(triisopropylsilyloxy)-3a,4-dihydropentalene-1,1(6aH)-dicarboxylate (75): According to the general procedure I, dienol silyl ether **68** (29.3 g, 0.062 mmol) was reacted under the standard conditions. The product was purified by flash column chromatography on silica gel (4% EtOAc in hexanes) to give **75** (24.0 mg, 82%) as a colorless viscous oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.81 (d, *J* = 5.6 Hz, 1H), 5.68 (d, *J* = 5.6 Hz, 1H), 4.67 (s, 1H), 3.83 – 3.75 (m, 4H), 3.71 (s, 3H), 1.53 – 1.40 (m, 1H), 1.40 – 1.15 (m, 12H), 1.12 (t, *J* = 7.1 Hz, 18H), 0.94 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 170.6, 150.6, 140.9, 127.1, 107.7, 68. 9, 62.3, 57.1, 52.6, 52.5, 51.6, 32.3, 31.2, 27.4, 23.1, 18.0, 17.9, 14.2, 12.5; HRMS (ESI) calc for $[C_{25}H_{42}O_5Si]^+$ ($[M+H]^+$): *m/z* 450.2796, found 450.2796; **HPLC**: enantiomeric excess determined by HPLC with a Chiralpak IC column (99.9:0.1 hexanes : Butanol, 0.8 ml/min, 210 nm); major enantiomer t_r = 11.8 min, minor enantiomer t_r = 13.4 min; 73% ee; absolute configuration was assigned by analogy with **76**.

IX. Synthesis of 76, 77 and 78



76

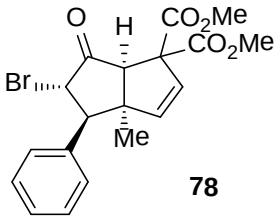
(3aS,4R,6aR)-dimethyl-3a-methyl-6-oxo-4-phenyl-4,5,6,6a-tetrahydropentalene-1,1(3aH)-dicarboxylate (76): To a cold (0 ^{o}C) solution of enolsilane **61** (13.1 mg, 0.027 mmol) in CH_2Cl_2 (2 ml) was added with a few drops of TfOH and the reaction mixture was stirred for 2 h. Then, the reaction was quenched with sat. sol. of $NaHCO_3$ and extracted with ethyl acetate (3x). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (15% EtOAc in hexanes) to provide **76** (7.4 mg, 83%) as a colorless powder. The ketone **76** was recrystallized from hexanes to give colorless crystals: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.34-7.32 (m, 1H), 7.29-7.26 (m, 2H), 5.86 (d, *J* = 5.5 Hz, 1H), 5.51 (d, *J* = 5.5 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.43 (s, 1H), 3.25 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.78 (dd, *J* = 17.2, 14.3 Hz, 1H), 2.56 (ddd, *J* = 17.2, 6.8, 1.5 Hz, 1H), 1.30 (s, 3H); **HRMS** (ESI) calc for $[C_{19}H_{20}O_5Na]^+$ ($[M+Na]^+$): *m/z* 351.1203, found 351.1196.



77

(3aS,4R,5R,6aR)-dimethyl 3a,5-dimethyl-6-oxo-4-phenyl-4,5,6,6a-tetrahydropentalene-1,1(3aH)-dicarboxylate (77): To a cold (0 ^{o}C) solution of enolsilane **69** (18.3 mg, 0.038 mmol) in CH_2Cl_2 (2 ml) was added with a few drops of TfOH and the reaction mixture was stirred for 2 h. Then, the reaction was quenched with sat. sol. of $NaHCO_3$ and extracted with ethyl acetate (3x). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (15%

EtOAc in hexanes) to provide **77** (12.1 mg, 93%) as a sticky oil: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 3H), 7.25 – 7.18 (m, 2H), 5.81 (d, *J* = 5.5 Hz, 1H), 5.51 (d, *J* = 5.5 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.41 (s, 1H), 2.78 – 2.67 (m, 2H), 1.25 (s, 3H), 0.94 (d, *J* = 5.5 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 216.6, 169.9, 169.6, 139.8, 137.0, 128.7, 128.6, 128.5, 127.3, 70.2, 61.3, 57.7, 57.1, 53.2, 52.9, 47.9, 24.3, 11.2; **HRMS** (ESI) calc for $[C_{20}H_{22}O_5Na]^+$ ($[M+Na]^+$): *m/z* 365.1359, found 365.1362.

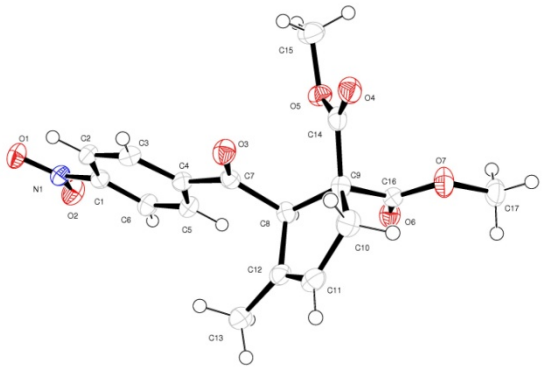


78

(3aR,4R,5S,6aR)-dimethyl-5-bromo-3a-methyl-6-oxo-4-phenyl-4,5,6,6a-tetrahydropentalene-1,1(3aH)-dicarboxylate (78): To a cold (-78 ^{o}C) solution of enolsilane **61** (13.9 mg, 0.025 mmol) in THF (2 ml) was added N-bromoosuccinimide and the reaction mixture was stirred at this temperature for 2 h. Then, the reaction was slowly warmed to r.t., quenched with sat. sol. of $NaHCO_3$ and extracted with ethyl acetate (3x). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (20% EtOAc in hexanes) to provide **78** (7.5 mg, 74%) as a white powder: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 2H), 7.39 – 7.31 (m, 1H), 7.24 – 7.19 (dd, *J* = 6.8, 1.7 Hz, 2H), 5.86 (d, *J* = 5.4 Hz, 1H), 5.53 (d, *J* = 5.6 Hz, 1H), 4.82 (d, *J* = 13.7 Hz, 1H), 3.76 (s, 6H), 3.57 (s, 1H), 3.30 (d, *J* = 13.6 Hz, 1H), 1.29 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.8, 169.2, 168.9, 138.7, 134.5, 129.3, 128.6, 128.4, 127.9, 70.3, 59.5, 58.7, 58.0, 54.5, 53.3, 53.2, 24.8; **HRMS** (ESI) calc for $[C_{19}H_{19}O_5Br]^+$ ($[M+Na]^+$): *m/z* 429.0308, found 429.0314.

X. Crystal structures

A) Crystallograpic data for **47**

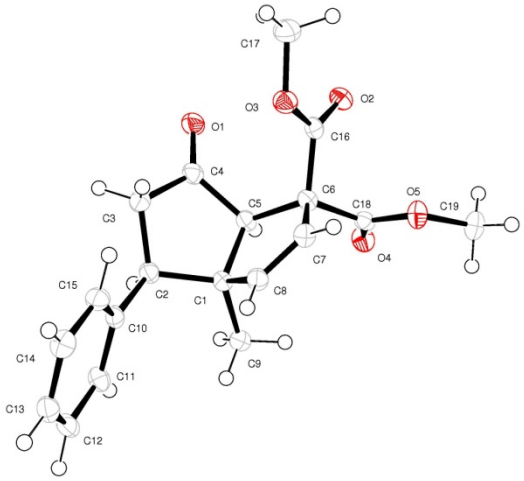


A colorless plate 0.10 x 0.08 x 0.04 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 1.0°. Data collection was 98.8% complete to 67.00° in θ. A total of 12448 reflections were collected covering the indices, -11<=*h*<=11, -7<=*k*<=8, -15<=*l*<=15. 2707 reflections were found to be symmetry independent, with an R_{int} of 0.0147. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P2(1) (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-2008) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. Absolute stereochemistry was unambiguously determined to be *R* at C8.

Table 1. Crystal data and structure refinement for toste40.

X-ray ID	toste40	
Sample/notebook ID	JFB-03-045	
Empirical formula	C17 H17 N O7	
Formula weight	347.32	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 9.3322(8) Å	α= 90°.
	b = 7.1038(6) Å	β= 107.090(3)°.
	c = 12.7222(11) Å	γ = 90°.
Volume	806.17(12) $Å^3$	
Z	2	
Density (calculated)	1.431 Mg/m^3	
Absorption coefficient	0.953 mm^{-1}	
F(000)	364	
Crystal size	0.10 x 0.08 x 0.04 mm^3	
Crystal color/habit	colorless plate	
Theta range for data collection	3.63 to 67.87°.	
Index ranges	-11<=h<=11, -7<=k<=8, -15<=l<=15	
Reflections collected	12448	
Independent reflections	2707 [R(int) = 0.0147]	
Completeness to theta = 67.00°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9629 and 0.9107	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2707 / 1 / 229	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0302, wR2 = 0.0830	
R indices (all data)	R1 = 0.0304, wR2 = 0.0832	
Absolute structure parameter	0.04(14)	
Largest diff. peak and hole	0.216 and -0.160 $e.Å^{-3}$	

B) Crystallographic data for **76**



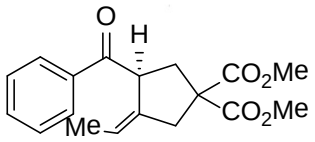
A colorless prism 0.15 x 0.10 x 0.10 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 1.0°. Data collection was 99.8% complete to 67.00° in θ. A total of 23485 reflections were collected covering the indices, -8<=*h*<=12, -14<=*k*<=14, -16<=*l*<=16. 3050 reflections were found to be symmetry independent, with an R_{int} of 0.0161. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be P2(1)2(1)2(1) (No. 19). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-2008) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. Absolute stereochemistry was unambiguously determined to be *R* at C(1), C(2), and C(5), respectively.

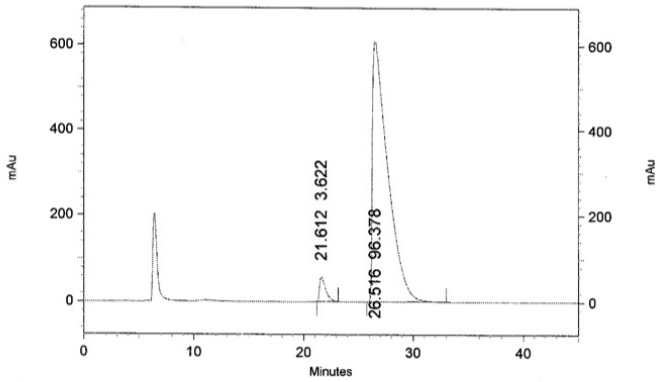
Table 1. Crystal data and structure refinement for toste33.

X-ray ID	toste33	
Sample/notebook ID	JFB-02-104	
Empirical formula	C19 H20 O5	
Formula weight	328.35	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.1287(9) Å	α= 90°.
	b = 11.8446(12) Å	β= 90°.
	c = 14.0140(14) Å	γ = 90°.
Volume	1681.3(3) $Å^3$	
Z	4	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.771 mm^{-1}	
F(000)	696	
Crystal size	0.15 x 0.10 x 0.10 mm^3	
Crystal color/habit	colorless prism	
Theta range for data collection	4.89 to 68.34°.	
Index ranges	-8<=h<=12, -14<=k<=14, -16<=l<=16	
Reflections collected	23485	
Independent reflections	3050 [R(int) = 0.0161]	
Completeness to theta = 67.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9269 and 0.8931	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3050 / 0 / 220	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0261, wR2 = 0.0697	
R indices (all data)	R1 = 0.0263, wR2 = 0.0699	
Absolute structure parameter	-0.04(13)	

XI. HPLC traces

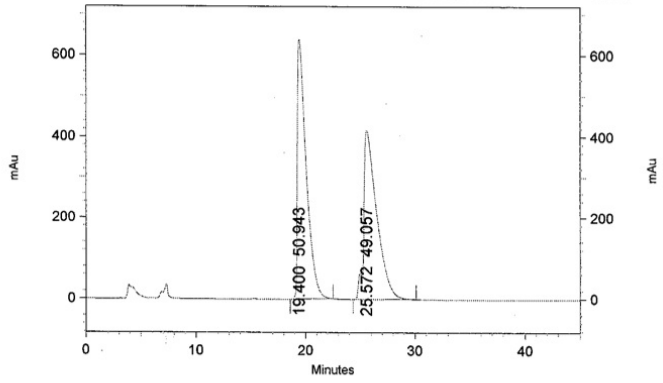
Table 4, Entry 10





1: 244 nm,
4 nm Results

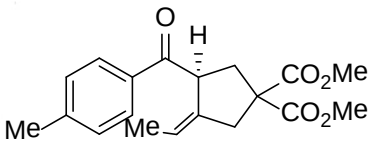
Pk #	Retention Time	Area Percent	Lambda Max
1	21.612	3.622	203
2	26.516	96.378	204

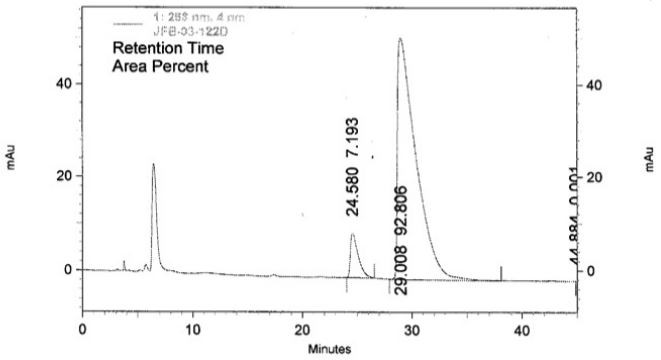


1: 243 nm,
4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	19.400	50.943	204
2	25.572	49.057	203

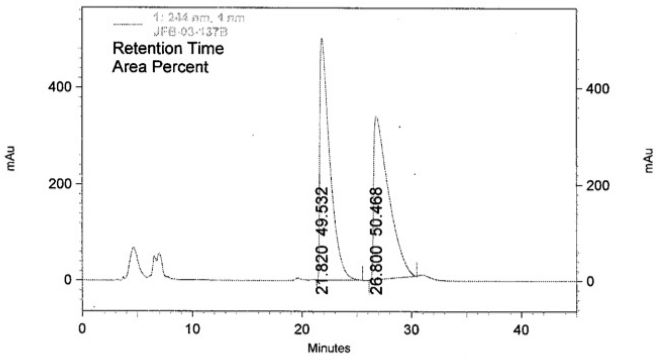
Table 5, Entry 1





1: 268 nm,
4 nm Results

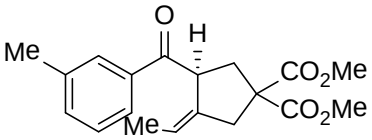
Pk #	Retention Time	Area Percent	Lambda Max
1	24.580	7.193	204
2	29.008	92.806	204
3	44.884	0.001	483

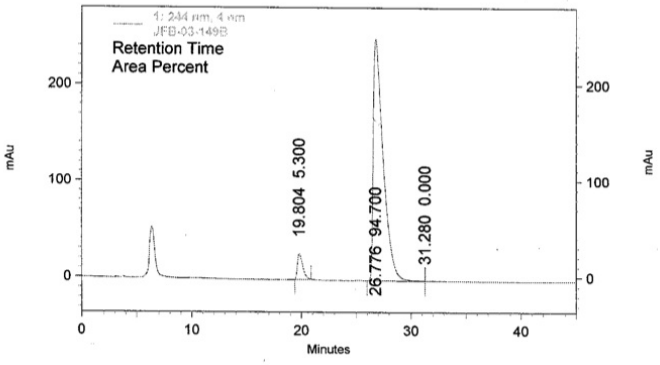


1: 244 nm,
4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	21.820	49.532	204
2	26.800	50.468	204

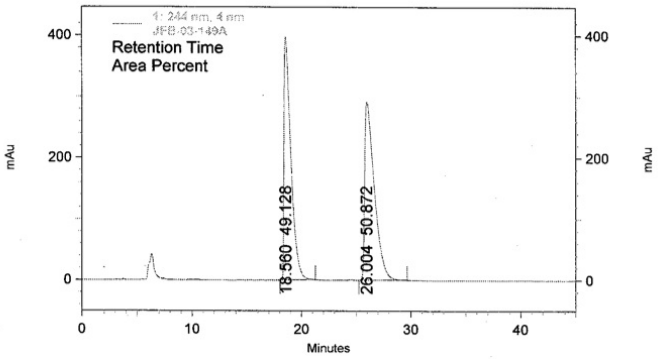
Table 5, Entry 2





1: 244 nm,
4 nm Results

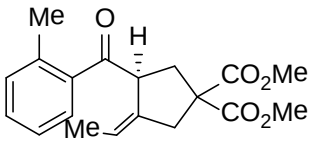
Pk #	Retention Time	Area Percent	Lambda Max
1	19.804	5.300	205
2	26.776	94.700	205
3	31.280	0.000	483

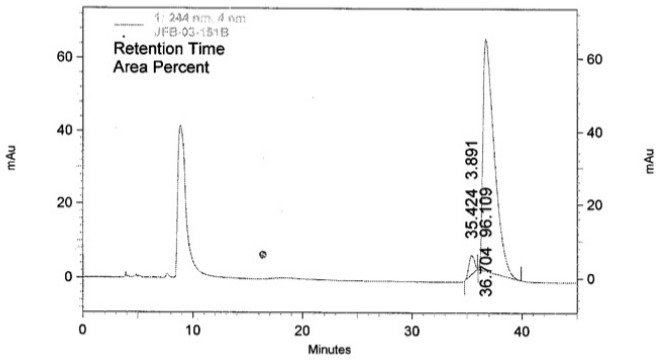


1: 244 nm,
4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	18.560	49.128	205
2	26.004	50.872	205

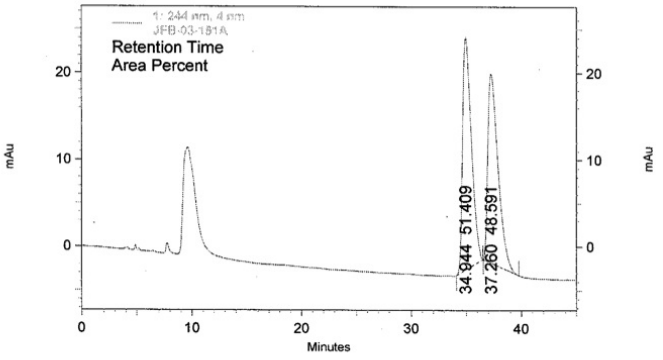
Table 5, Entry 3





1: 244 nm,
4 nm Results

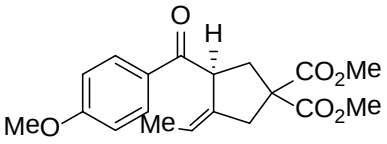
Pk #	Retention Time	Area Percent	Lambda Max
1	35.424	3.891	211
2	36.704	96.109	206

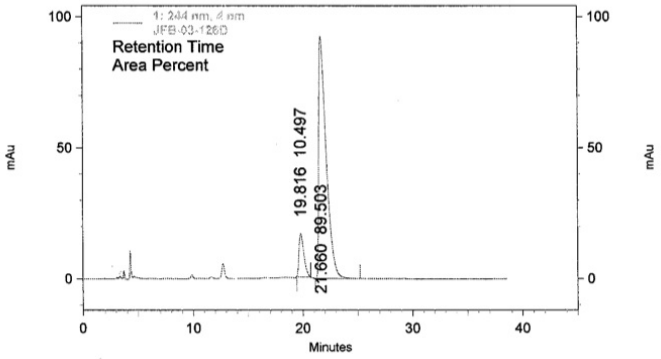


1: 244 nm,
4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	34.944	51.409	207
2	37.260	48.591	207

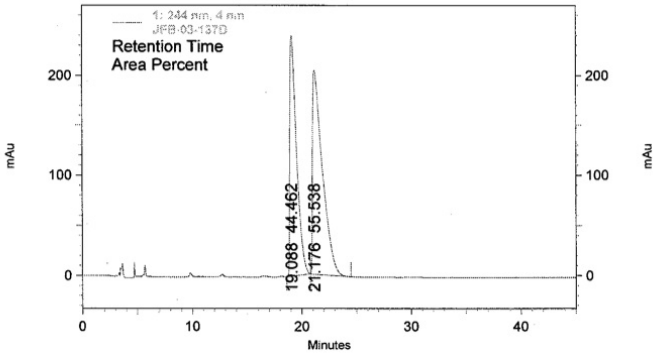
Table 5, Entry 4





1: 244 nm,
4 nm Results

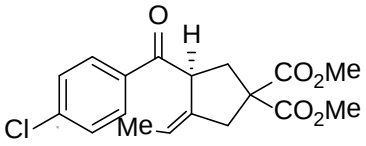
Pk #	Retention Time	Area Percent	Lambda Max
1	19.816	10.497	202
2	21.660	89.503	200

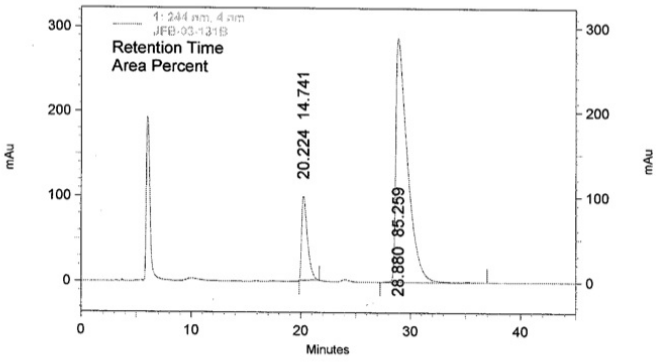


1: 244 nm,
4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	19.088	44.462	191
2	21.176	55.538	267

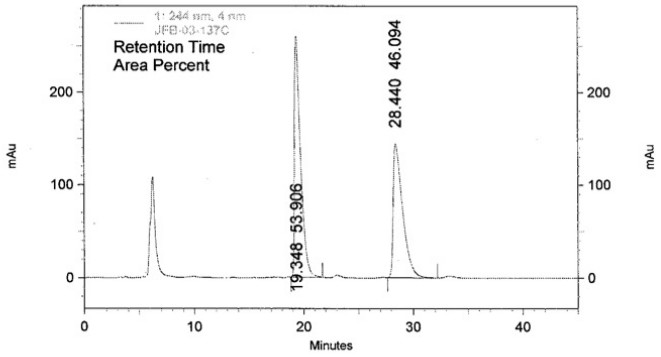
Table 5, Entry 5





1: 244 nm,
4 nm Results

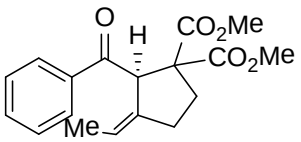
Pk #	Retention Time	Area Percent	Lambda Max
1	20.224	14.741	203
2	28.880	85.259	204

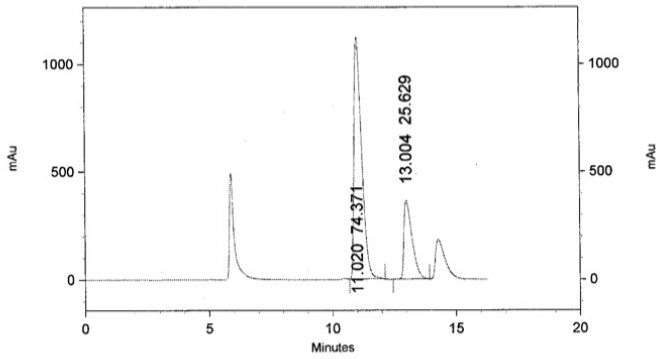


1: 244 nm,
4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	19.348	53.906	205
2	28.440	46.094	205

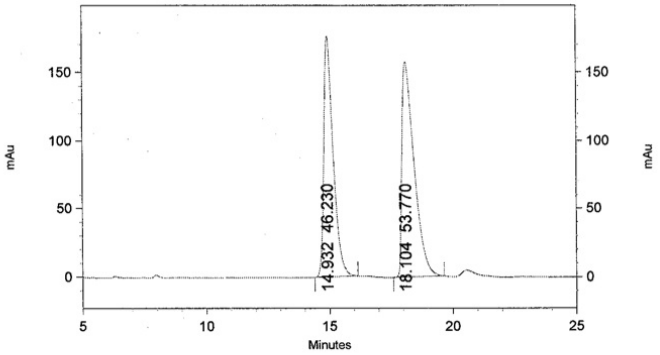
Table 5, Entry 6





1: 244 nm,
4 nm Results

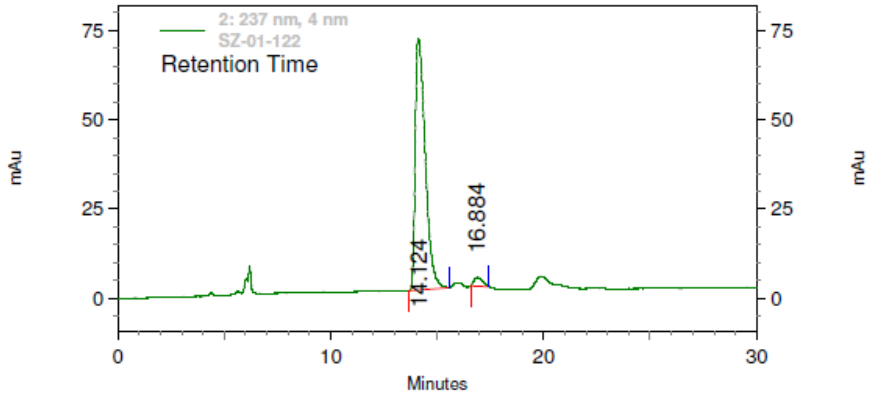
Pk #	Retention Time	Area Percent	Lambda Max
1	11.020	74.371	193
2	13.004	25.629	204

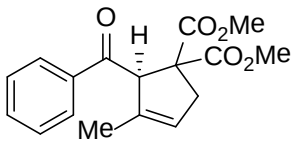


1: 244 nm,
4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	14.932	46.230	204
2	18.104	53.770	204

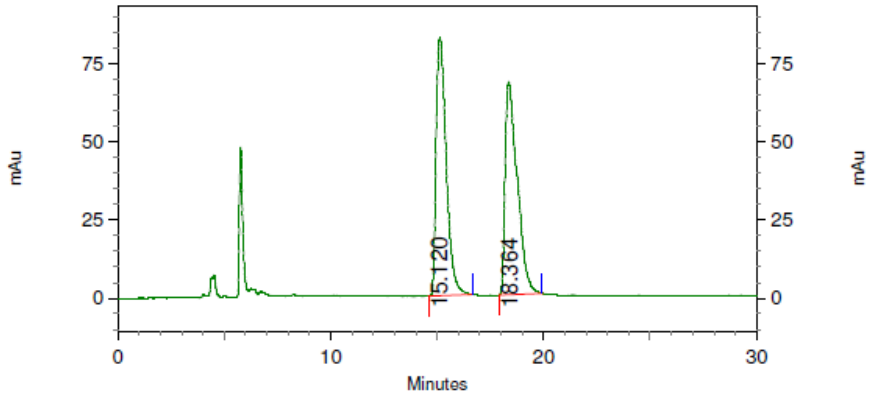
Table 6, Entry 9





2: 237 nm, 4 nm Results

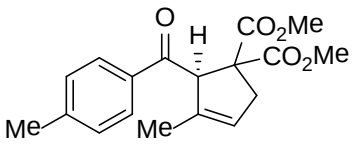
Retention Time	Area	Area Percent	Lambda Max
14.124	2304225	97.082	205
16.884	69261	2.918	204

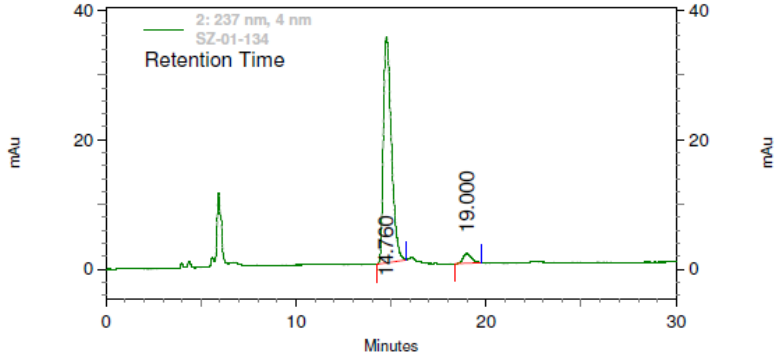


2: 237 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
15.120	2732760	50.309	204
18.364	2699192	49.691	204

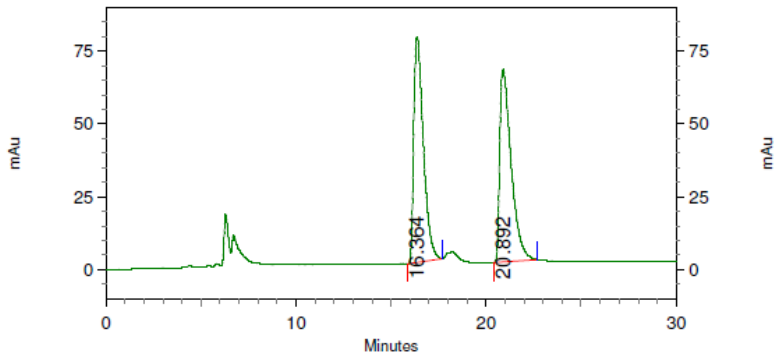
Table 7, Entry 1





2: 237 nm, 4 nm Results

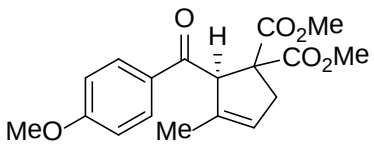
Retention Time	Area	Area Percent	Lambda Max
14.760	1018387	95.733	206
19.000	45388	4.267	209

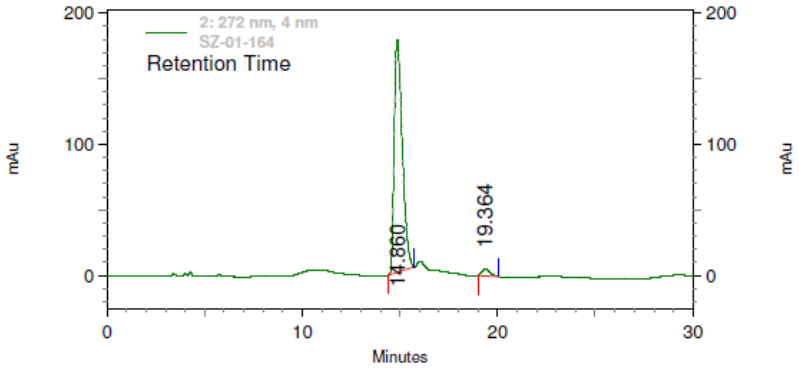


2: 237 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
16.364	2701430	49.564	206
20.892	2748968	50.436	206

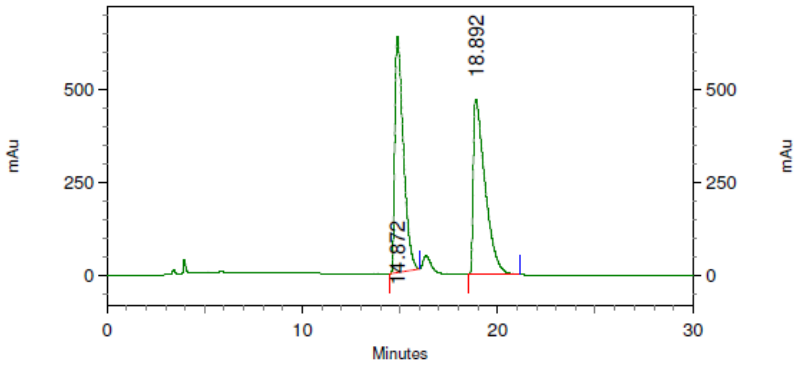
Table 7, Entry 2





2: 272 nm, 4 nm Results

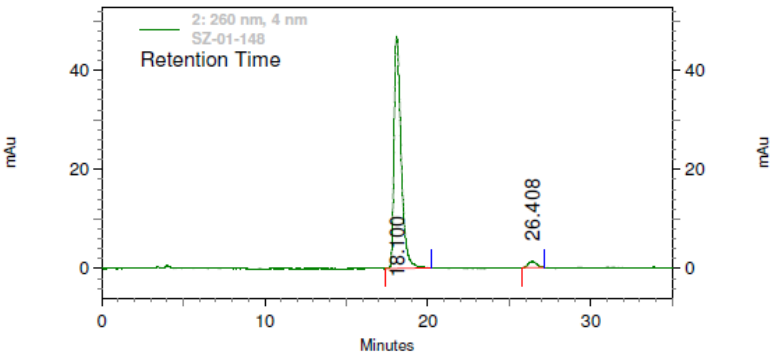
Retention Time	Area	Area Percent	Lambda Max
14.860	5070748	96.970	271
19.364	158454	3.030	224

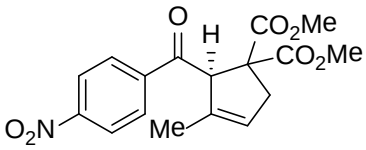


2: 272 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
14.872	19198107	49.197	271
18.892	19824472	50.803	271

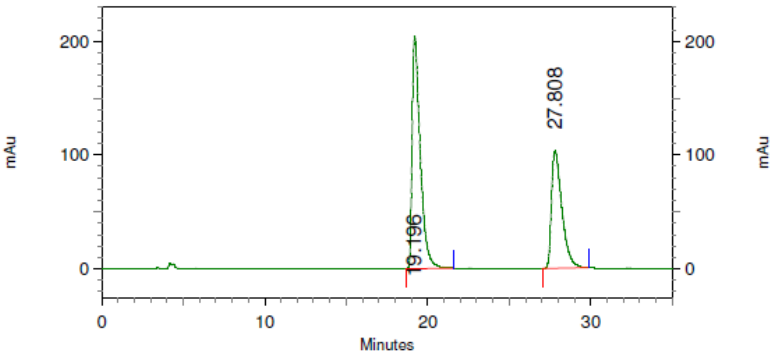
Table 7, Entry 3





2: 260 nm, 4 nm Results

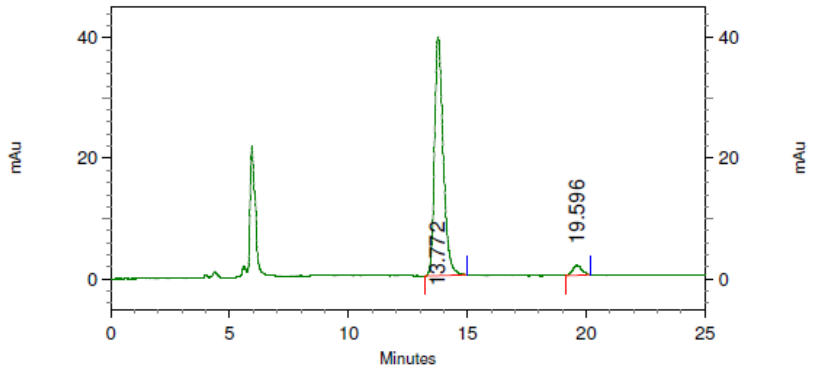
Retention Time	Area	Area Percent	Lambda Max
18.100	1413574	96.947	260
26.408	44522	3.053	252

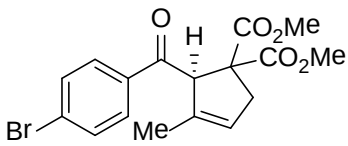


2: 260 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
19.196	7053065	60.690	260
27.808	4568330	39.310	260

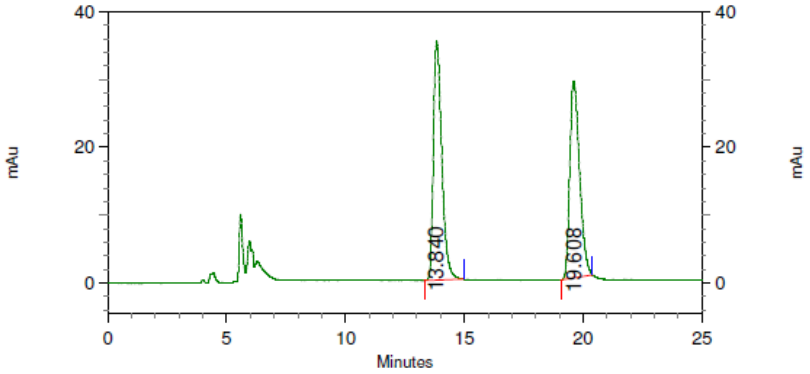
Table 7, Entry 4





2: 237 nm, 4 nm Results

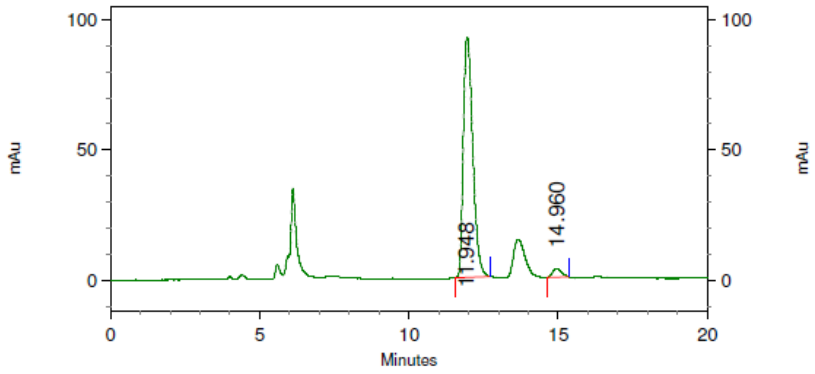
Retention Time	Area	Area Percent	Lambda Max
13.772	1005672	95.822	205
19.596	43846	4.178	205

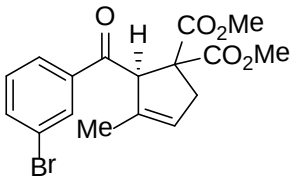


1: 237 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
13.840	862909	51.036	205
19.608	827892	48.964	205

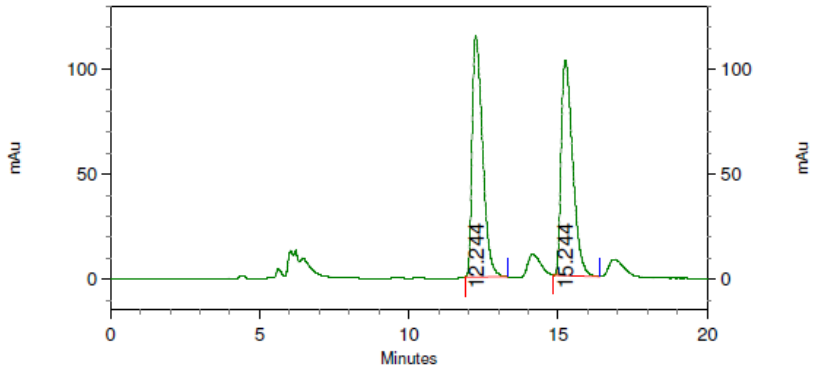
Table 7, Entry 5





2: 237 nm, 4 nm Results

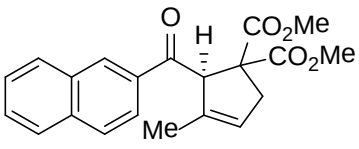
Retention Time	Area	Area Percent	Lambda Max
11.948	2014624	96.647	211
14.960	69897	3.353	205

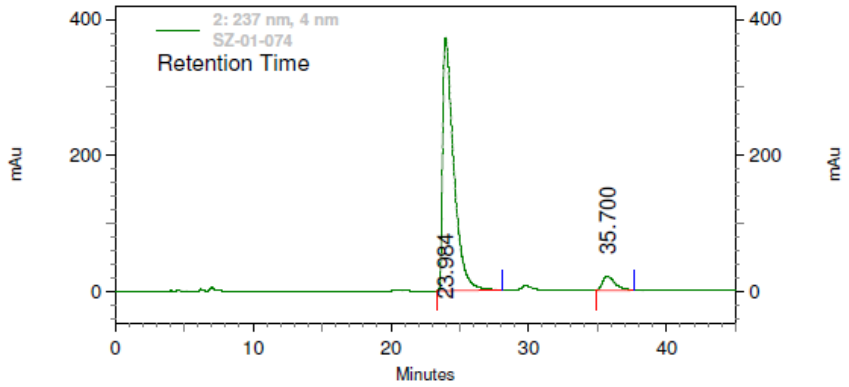


1: 237 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
12.244	2814579	50.429	211
15.244	2766664	49.571	211

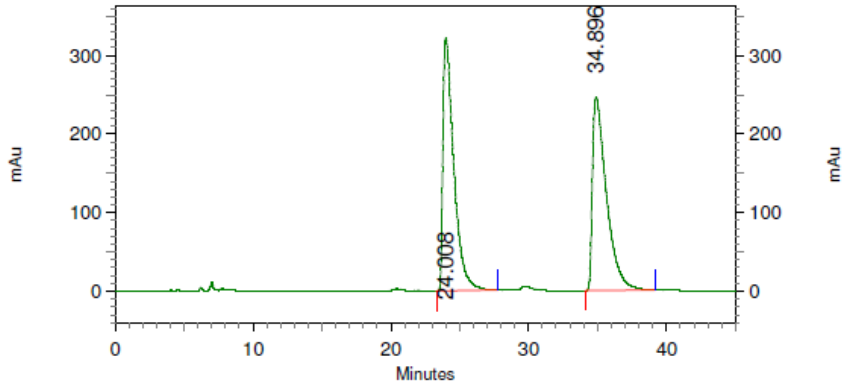
Table 7, Entry 6





2: 237 nm, 4 nm Results

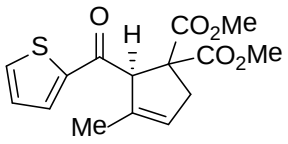
Retention Time	Area	Area Percent	Lambda Max
14.072	2789661	94.347	207
18.212	167147	5.653	496

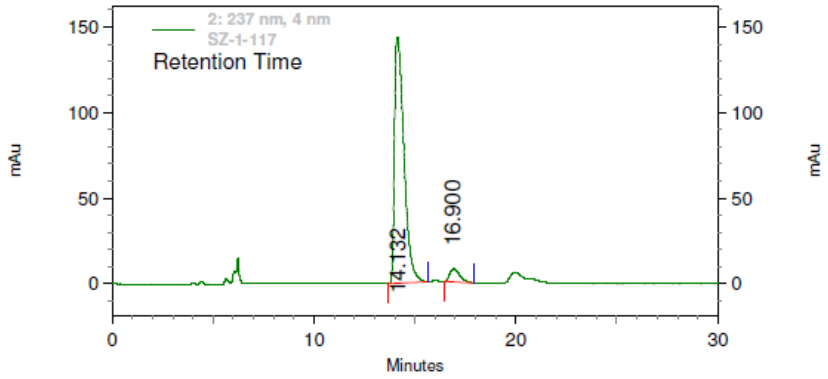


5: 237 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
24.008	17497231	50.035	247
34.896	17472718	49.965	248

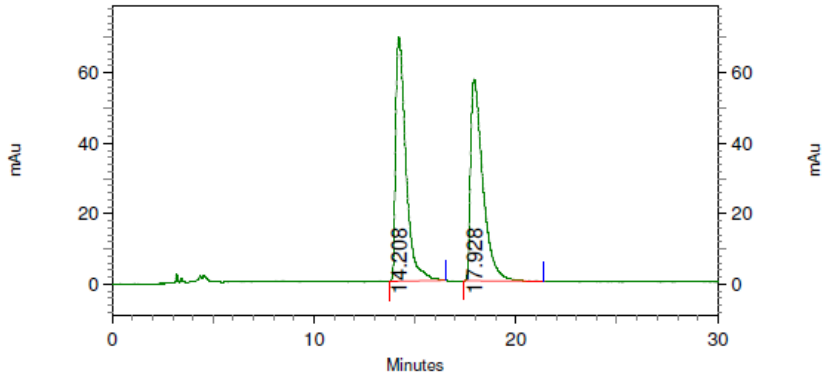
Table 7, Entry 7





2: 237 nm, 4 nm Results

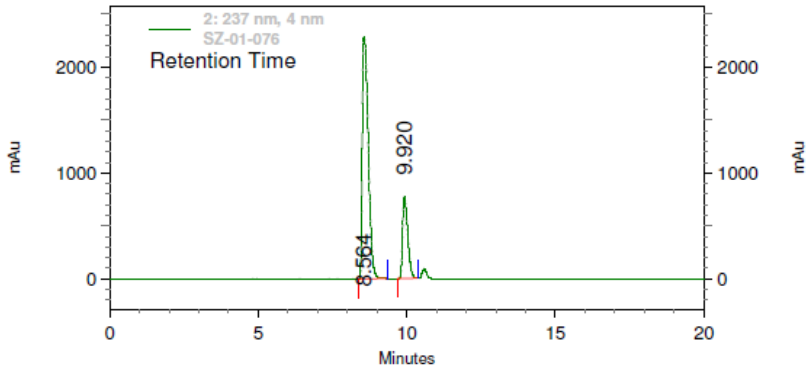
Retention Time	Area	Area Percent	Lambda Max
14.132	4722157	94.714	205
16.900	263544	5.286	207

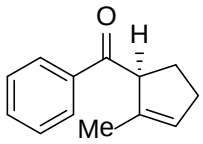


2: 257 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
14.208	2452185	50.391	260
17.928	2414137	49.609	260

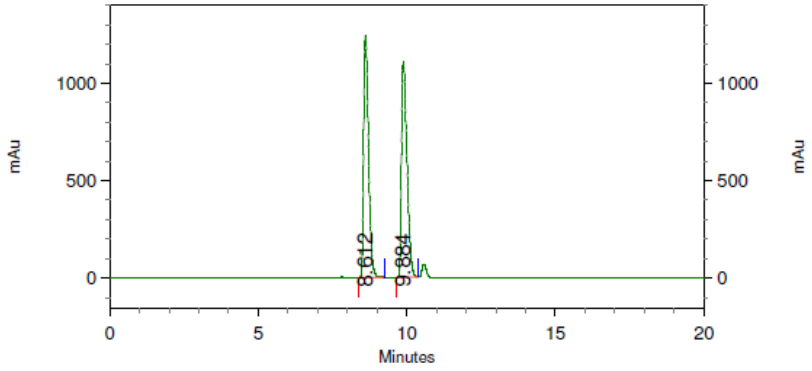
Table 8, Entry 4





2: 237 nm, 4 nm Results

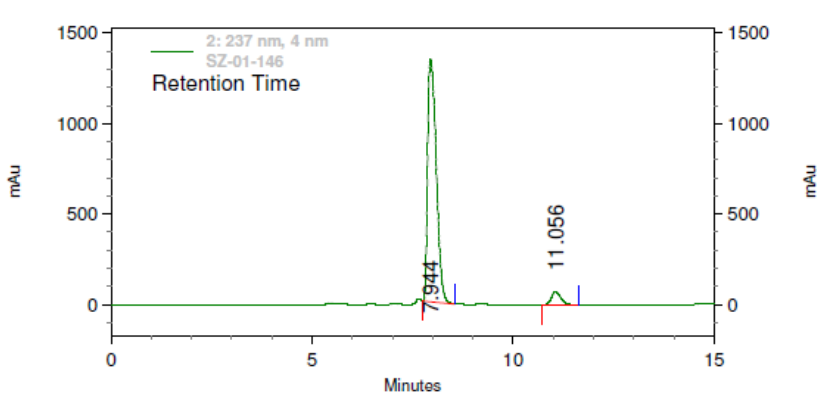
Retention Time	Area	Area Percent	Lambda Max
8.564	32268288	77.535	234
9.920	9349316	22.465	204

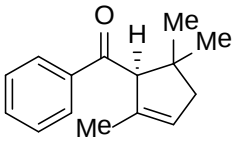


5: 237 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
8.612	14247847	50.067	205
9.884	14209891	49.933	205

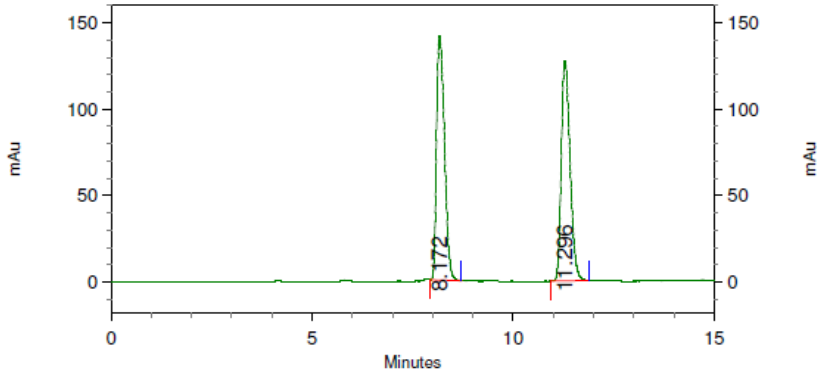
Table 8, Entry 6





2: 237 nm, 4 nm Results

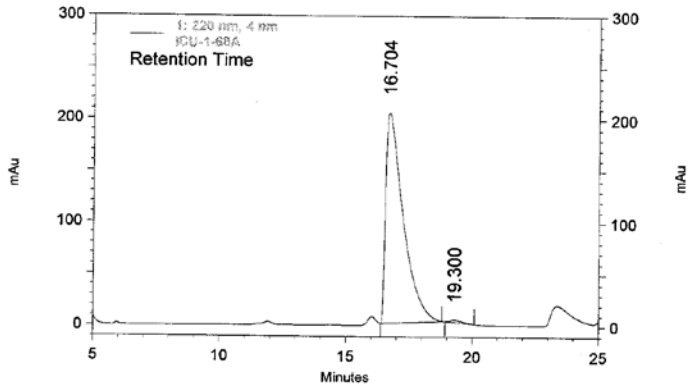
Retention Time	Area	Area Percent	Lambda Max
7.944	19824686	94.713	205
11.056	1106587	5.287	205

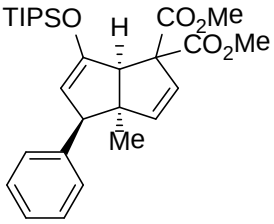


2: 237 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
8.172	1933862	50.021	202
11.296	1932246	49.979	202

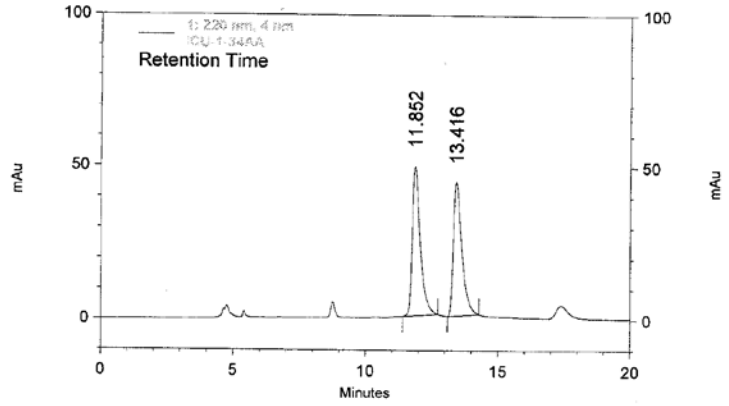
Table 9, Entry 2





1: 220 nm, 4 nm Results

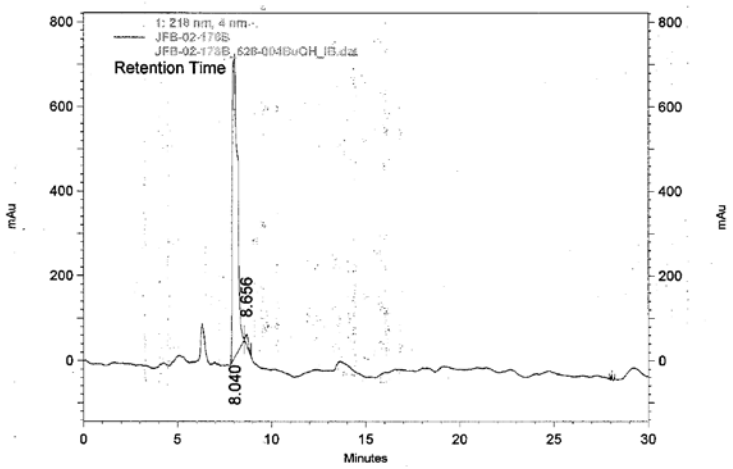
Retention Time	Area	Area Percent	Lamb
16.704	9784492	99.222	
19.300	76740	0.778	

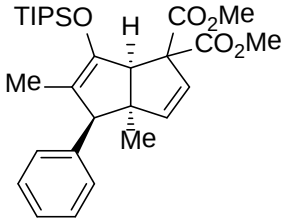


1: 220 nm, 4 nm Results

Retention Time	Area	Area Percent	Lam
11.852	1027361	51.231	
13.416	977994	48.769	

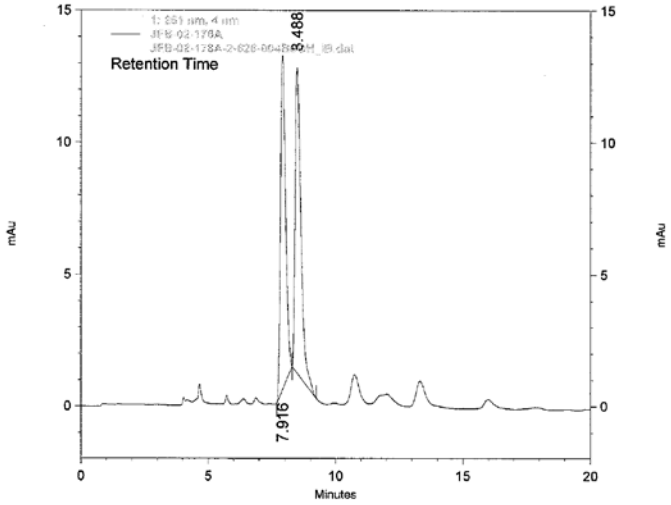
Table 10, Entry 1





1: 218 nm, 4 nm Results

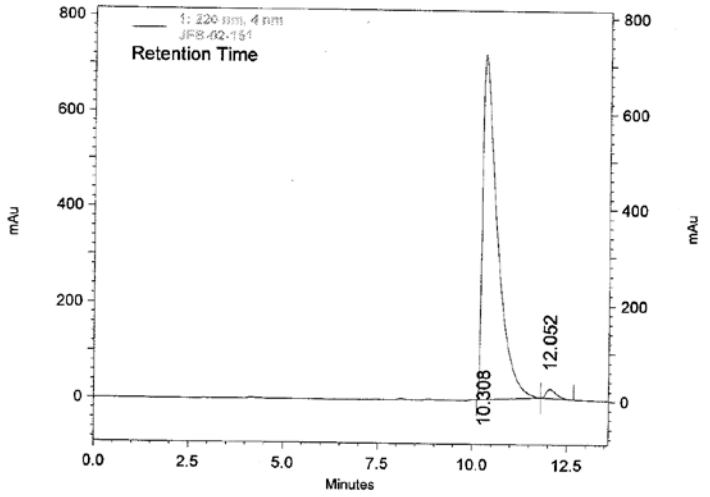
Retention Time	Area	Area Percent	Lambda Max
8.040	13186301	97.777	221
8.656	299833	2.223	221

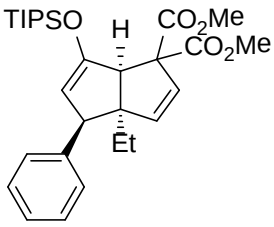


1: 261 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
7.916	176141	48.981	219
8.488	183468	51.019	219

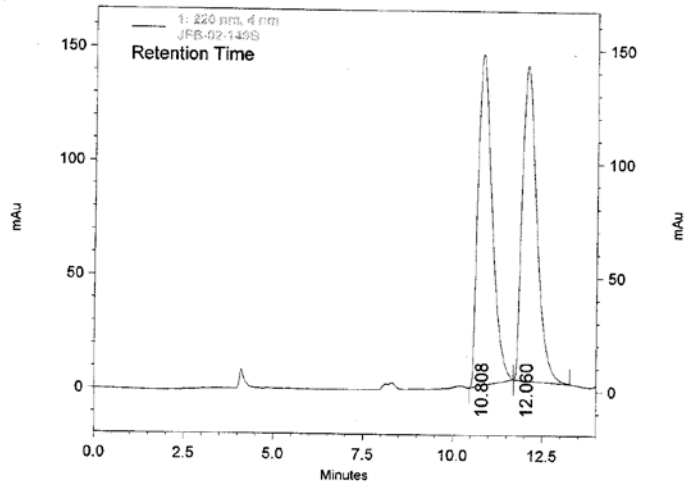
Table 10, Entry 2





1: 220 nm, 4 nm Results

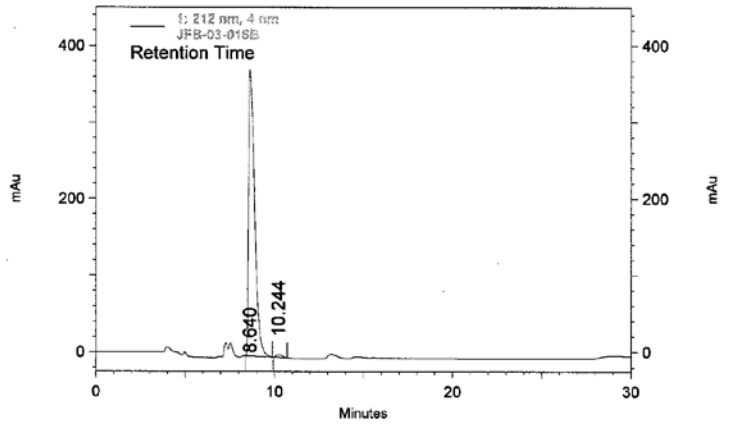
Retention Time	Area	Area Percent	Lamb
10.308	19540283	98.140	
12.052	370325	1.860	



1: 220 nm, 4 nm Results

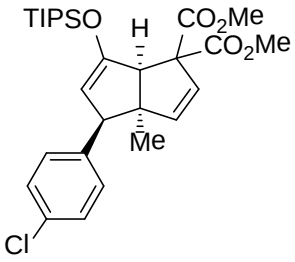
Retention Time	Area	Area Percent	Lamb
10.808	3975347	50.354	
12.060	3919375	49.646	

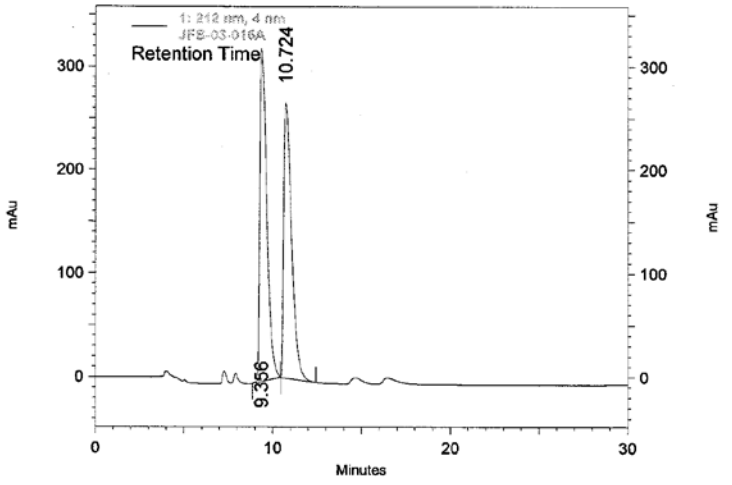
Table 10, Entry 3



1: 212 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambd
8.640	8842660	99.048	
10.244	84999	0.952	

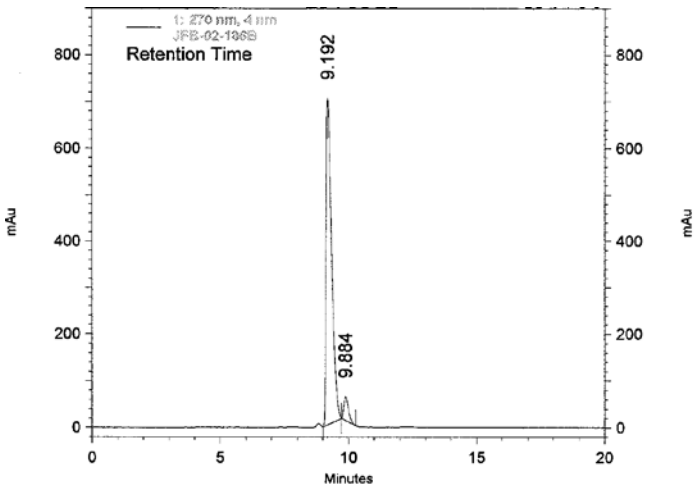


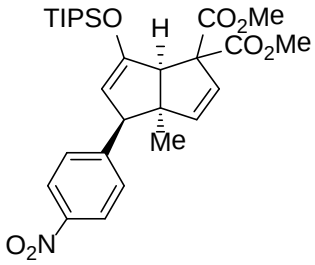


1: 212 nm, 4 nm Results

Retention Time	Area	Area Percent	Lamb
9.356	8808118	51.612	
10.724	8257904	48.388	

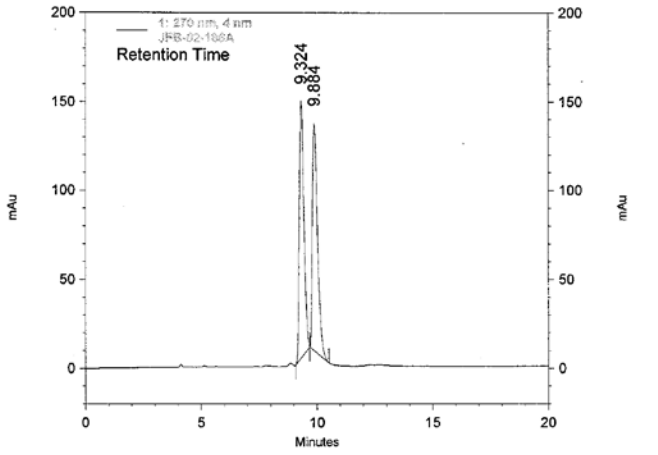
Table 10, Entry 4





1: 270 nm, 4
nm Results

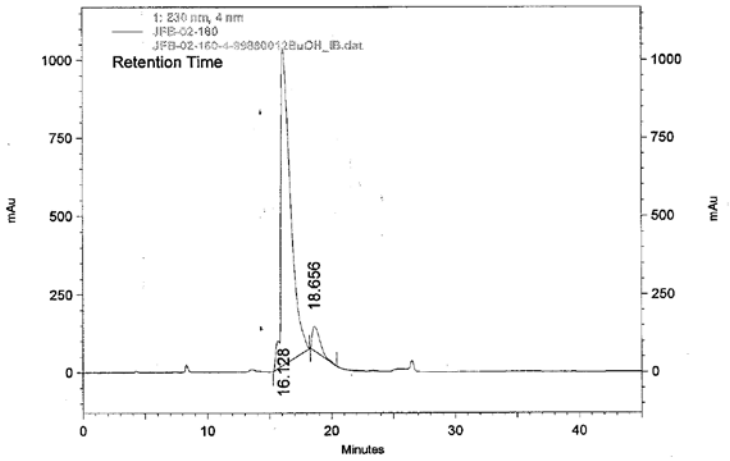
Retention Time	Area	Area Percent	Lam
9.192	10598415	94.243	
9.884	647438	5.757	

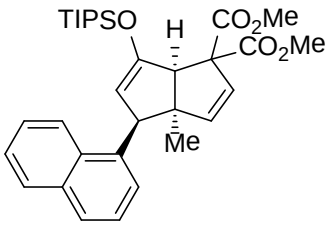


1: 270 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambd
9.324	1987724	50.212	
9.884	1970915	49.788	

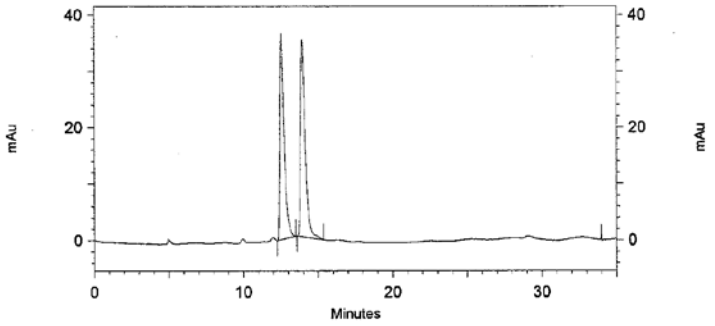
Table 10, Entry 5





1: 230 nm, 4 nm Results

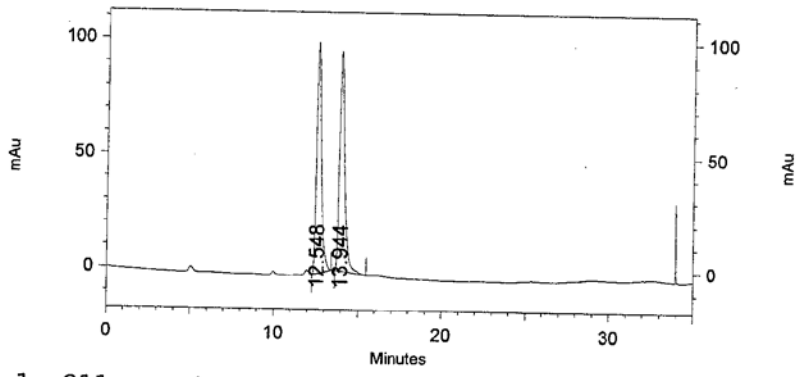
Retention Time	Area	Area Percent	Lambda Max
16.128	55493849	94.107	222
18.656	3474743	5.893	224

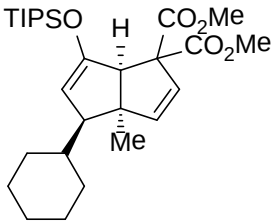


1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent	Lamb
12.548	730461	49.312	
13.944	750851	50.688	

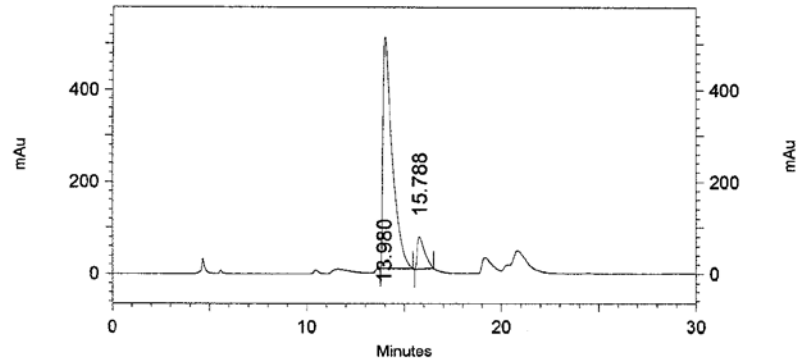
Table 10, Entry 6





1: 211 nm, 4 nm Results

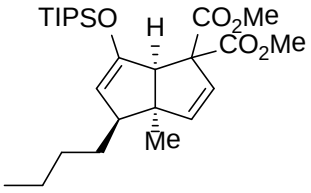
Retention Time	Area	Area Percent	Lambda Max
12.548	2014209	49.484	212
13.944	2056214	50.516	212

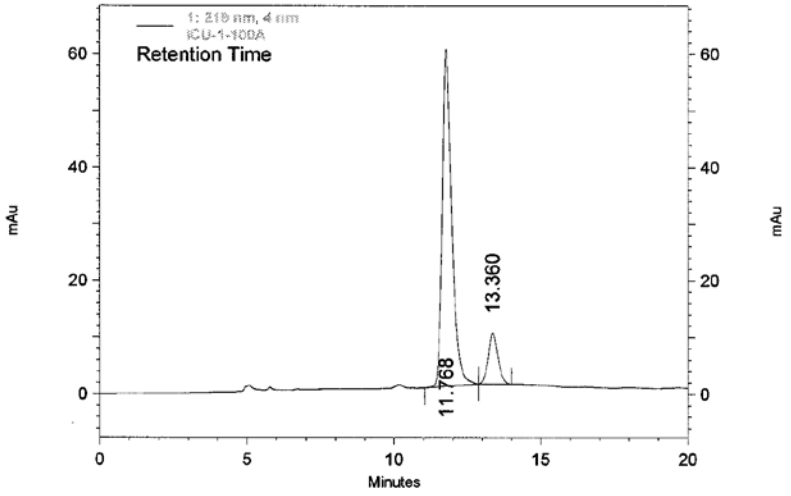


1: 211 nm, 4 nm Results

Retention Time	Area	Area Percent	Lam
13.980	17032659	90.142	
15.788	1862619	9.858	

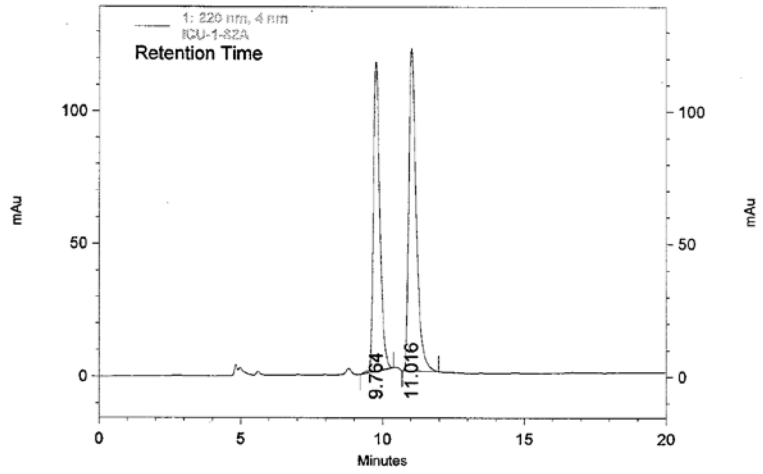
Table 10, Entry 7





1: 219 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda
11.768	1337582	86.559	
13.360	207708	13.441	



1: 220 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda
9.764	1840727	45.311	
11.016	2221676	54.689	