

*Supporting Information for:*

**Intramolecular [4+2] Cycloadditions of 1,3-Enynes or Arylalkynes with Alkenes with Highly Reactive Cationic Phosphine Au(I) Complexes**

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**Synthesis of [Au(L)Cl] complexes:**

These complexes were prepared following a literature procedure:<sup>1</sup> Sodium tetrachloroaurate(III) dihydrate<sup>2</sup> (1 mmol) was dissolved in water, and the orange solution was cooled in ice. To this solution 2,2'-thiodiethanol (3 mmol) was slowly added (ca. 45 min) with stirring. A solution of the phosphine ligand (1 mmol) in EtOH was added dropwise to give a white solid. The solid was filtered off, washed with MeOH, and dried in vacuo.

**[Au(PPh<sub>3</sub>)Cl]**

Yield 84%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.03-1.93 (m, 9H), 1.89-1.85 (m, 6H), 1.75-1.72 (m, 3H), 1.52-1.41 (m, 6H), 1.35-1.21 (m, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 33.28 (d, <sup>1</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 31 Hz), 30.75, 26.96 (d, <sup>2</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 12.2 Hz), 25.80 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 1.5 Hz); <sup>31</sup>P NMR (161.98 MHz, CDCl<sub>3</sub>) δ 57.12. HRMS-ESI Cald. for C<sub>20</sub>H<sub>36</sub>AuNP (M<sup>+</sup>+MeCN-Cl): 518.2251. Found: 518.2241.

**[Au{P(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}Cl]**

Yield 82 %; <sup>31</sup>P NMR (161.98 MHz, CDCl<sub>3</sub>) δ 57.08.

**[Au{P(*o*-Tol)<sub>3</sub>}Cl]**

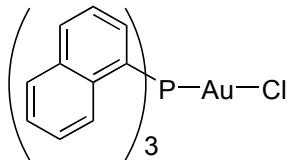
Yield 49%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 (tt, *J* = 7.5, 1.5 Hz, 3H), 7.35 (m, 3H), 7.19 (t, *J* = 7.7 Hz, 3H), 6.92 (ddd, *J* = 13.3, 7.8, 1.1 Hz, 3H), 2.67 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.0 (d, <sup>2</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 12 Hz), 133.49 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 9.6 Hz), 132.42 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 9.1 Hz), 131.97 (d, <sup>4</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 2.6 Hz), 126.69 (d, <sup>2</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 10.5 Hz), 125.00 (d, <sup>1</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 61.3 Hz), 23.31 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 11.3 Hz); <sup>31</sup>P NMR (161.98 MHz, CDCl<sub>3</sub>) δ 11.50. HRMS-ESI Cald. for C<sub>23</sub>H<sub>24</sub>AuNP (M<sup>+</sup>+MeCN-Cl): 542.1312. Found: 542.1318.

(1) Al-Sa'Ady, A. K.; McAuliffe, C. A.; Parish, R. V.; Sandeank, J. A. *Inorg. Synt.* **1985**, 191-194.

(2) Tetrachloroauric acid can also be used as the starting salt.

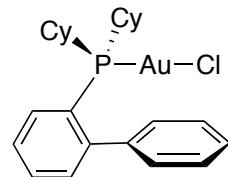
**[Au(AsPh<sub>3</sub>)Cl]**

Yield 88%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55-7.50 (m, 15H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 133.23, 131.44, 131.05, 129.62. HRMS-ESI Cald. for C<sub>20</sub>H<sub>18</sub>AuNAs (M<sup>+</sup>+MeCN-Cl): 544.0321. Found: 544.0306.



This compound was prepared according to the described procedure.<sup>3</sup> Yield 80%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.82 (d, *J* = 8.5 Hz, 3H), 8.09 (d, *J* = 8.0 Hz, 3H), 8.00 (d, *J* = 8.2 Hz, 3H), 7.61 (dd, *J* = 7.9, 7.1 Hz, 3H), 7.51 (dd, *J* = 8.1, 7.5 Hz, 3H) 7.33 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.04 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 8.1 Hz), 134.14 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 8.1 Hz), 133.94 (d, <sup>2</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 11.8 Hz), 133.51, 129.26 (d, <sup>4</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 1.3 Hz), 127.79, 126.97, 126.50 (d, <sup>2</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 14.4 Hz), 125.13 (d, <sup>2</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 12.0 Hz), 122.53 (d, <sup>1</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 62.7 Hz); <sup>31</sup>P NMR (161.98 MHz, CDCl<sub>3</sub>) δ 9.59. HRMS-ESI Cald. for C<sub>32</sub>H<sub>24</sub>AuNP (M<sup>+</sup>+MeCN-Cl): 650.1312. Found: 650.1335.

**Complex 1a**

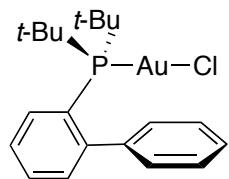


Yield 69%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76-7.71 (m, 1H), 7.57-7.44 (m, 5H), 7.33-7.28 (m, 1H), 7.18 (d, *J* = Hz, 3H), 2.08-1.94 (m, 4H) 1.83-1.74 (m, 4H), 1.68-1.43 (m, 6H) 1.33-1.18 (m, 8H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.09, 134.29, 132.48 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 7.4 Hz), 130.71, 129.24, 128.64, 128.35, 127.43 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 8.4 Hz), 124.43, 36.58 (d, <sup>1</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 33.3 Hz), 31.16 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 4.5 Hz), 29.42, 26.54 (d, <sup>2</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 10 Hz), 24.43 (d, <sup>2</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 14 Hz), 25.58; <sup>31</sup>P NMR (161.98 MHz, CDCl<sub>3</sub>) δ 47.15. HRMS-ESI Cald. for C<sub>26</sub>H<sub>34</sub>AuNP (M<sup>+</sup>+MeCN-Cl): 588.2094. Found: 588.2075.

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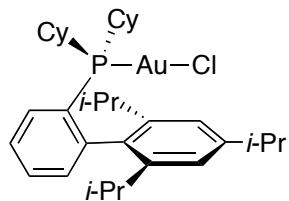
(3) Müller, T. E.; Green, J. C.; Mingos, D. M. P.; McPartlin, C. M.; Whittingham, C.; Williams, D. J.; Woodroffe, T. M. *J. Organomet. Chem.* **1998**, *551*, 313-330.

### Complex 1b



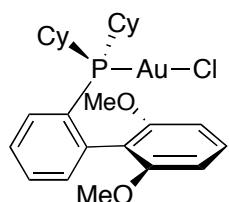
Yield 43%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (td,  $J = 7.7, 1.7$  Hz, 1H), 7.51 (m, 5H), 7.31 (m, 1H), 7.13 (dd,  $J = 8.0, 1.0$  Hz, 2H), 1.41 (d,  $J = 15.6$ , 18H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.16 (d,  $^2J(\text{C}-\text{P}) = 13.5$  Hz), 142.10 (d,  $^3J(\text{C}-\text{P}) = 6.3$  Hz), 133.46 (d,  $^4J(\text{C}-\text{P}) = 3.0$  Hz), 133.22 (d,  $^3J(\text{C}-\text{P}) = 7.5$  Hz), 129.19, 128.67, 128.22, 126.67 (d,  $^3J(\text{C}-\text{P}) = 6.8$ ), 126.06 (d,  $^1J(\text{C}-\text{P}) = 45.3$  Hz), 37.75 (d,  $^1J(\text{C}-\text{P}) = 25.7$  Hz), 30.84 (d,  $^2J(\text{C}-\text{P}) = 6.7$  Hz);  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{CDCl}_3$ )  $\delta$  63.11. HRMS-ESI Cald. for  $\text{C}_{22}\text{H}_{30}\text{AuNP} (\text{M}^+ + \text{MeCN-Cl})$ : 536.1781. Found: 536.1779.

### Complex 1c



Yield 61%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.55 (m, 1H), 7.47-7.45 (m, 2H), 7.23 (m, 1H), 7.05 (s, 2H), 2.95 (hept,  $J = 7.0$  Hz, 1H), 2.21 (hept,  $J = 6.7$  Hz, 2H) 2.05-2.01 (m, 4H), 1.83-1.71 (m, 6H), 1.67-1.61 (m, 2H), 1.53-1.42 (m, 3H), 1.35 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H), 1.23-1.13 (m, 7H), 0.92 (s, 3H), 0.91 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.06, 145.48, 133.82 (d,  $^3J(\text{C}-\text{P}) = 8.1$  Hz), 132.04 (d,  $^1J(\text{C}-\text{P}) = 3.2$  Hz), 130.35 (d,  $^1J(\text{C}-\text{P}) = 1.8$  Hz), 127.08 (d,  $^1J(\text{C}-\text{P}) = 7.1$  Hz), 121.70, 37.23 (d,  $^1J(\text{C}-\text{P}) = 33.5$  Hz), 34.30, 30.93, 30.81, 27.01 (d,  $^1J(\text{C}-\text{P}) = 13.5$  Hz), 26.69 (d,  $^1J(\text{C}-\text{P}) = 12.9$  Hz), 24.36, 23.12;  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{CDCl}_3$ )  $\delta$  38.48. HRMS-ESI Cald. for  $\text{C}_{33}\text{H}_{49}\text{AuPNa} (\text{M}^+ + \text{Na})$ : 731.2823. Found: 731.2789.

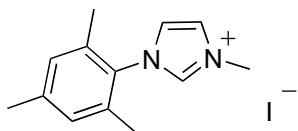
### Complex 1d



Yield 51%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66-7.42 (m, 4H), 7.23-7.20 (m, 1H), 6.66 (d,  $J = 8.4$  Hz, 2H), 3.70 (s, 6H), 2.18-2.13 (m, 2H), 1.98-1.93 (m, 2H) 1.83-1.64 (m, 8H), 1.48-1.36 (m, 4H),

1.33-1.15 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  176.44, 152.44 (d,  $^1\text{J}(\text{C}-\text{P}) = 7.9$  Hz), 151.08 (d,  $^1\text{J}(\text{C}-\text{P}) = 3.9$  Hz), 150.19 (d,  $^1\text{J}(\text{C}-\text{P}) = 2.4$  Hz), 149.25, 146.27 (d,  $^1\text{J}(\text{C}-\text{P}) = 3.3$  Hz), 146.16 (d,  $^1\text{J}(\text{C}-\text{P}) = 2.9$  Hz), 123.60, 74.54, 55.58 (d,  $^1\text{J}(\text{C}-\text{P}) = 34.20$  Hz), 49.52 (d,  $^1\text{J}(\text{C}-\text{P}) = 3.8$  Hz), 48.45, 45.94 (d,  $^1\text{J}(\text{C}-\text{P}) = 12.8$  Hz), 45.80 (d,  $^1\text{J}(\text{C}-\text{P}) = 14.3$  Hz), 44.94 (d,  $^1\text{J}(\text{C}-\text{P}) = 1.6$  Hz);  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{CDCl}_3$ )  $\delta$  41.79. HRMS-ESI Cald. for  $\text{C}_{28}\text{H}_{38}\text{AuPNO}_2$  ( $\text{M}^+ + \text{MeCN-Cl}$ ): 648.2306. Found: 648.2286.

#### N-Methyl-N’-(2,4,6-trimethylphenyl)imidazolium Iodide<sup>4</sup>



Over a solution of the 1-(2,4,6-trimethyl)imidazole<sup>5</sup> (500 mg, 2.7 mmol) in THF (2 ml), MeI (1916.2 mg, 13.5 mmol) was added dropwise. The mixture was refluxed while the white product precipitated. After 48 h, the reaction mixture was filtered to give a white solid (1.98 mmol, 73%). The solid was used without any further purification. $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.91 (s, 1H), 7.86 (t,  $J = 1.8$  Hz, 1H), 7.18 (t,  $J = 1.8$  Hz, 1H), 6.99 (s, 2H), 4.36 (s, 3H), 2.33 (s, 3H), 2.08 (s, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  141.39, 137.66, 134.25, 130.46, 129.85, 124.69, 123.07, 37.96, 21.06, 17.91. HRMS-EI Cald. for  $\text{C}_{13}\text{H}_{16}\text{N}_2\text{I}$  ( $\text{M}^+ - \text{H}$ ): 327.0358. Found: 327.0359.

#### General Procedure for NHC Au(I) complexes 2a-c<sup>6</sup>

$\text{Ag}_2\text{O}$  (0.5 mmol) was added to a solution of the imidazolium ligand (1mmol)<sup>7</sup> in  $\text{CH}_2\text{Cl}_2$ . The suspension became clear after stirring 3 h at room temperature. Then a solution of  $\text{Me}_2\text{SAuCl}$  (1mmol) in  $\text{CH}_2\text{Cl}_2$  was added drop wise. The reaction mixture was stirred for another 4 h. Then the solution was filtered through Celite and the solvent was partially evaporated. Addition of hexane led to the precipitation of the methiodides.

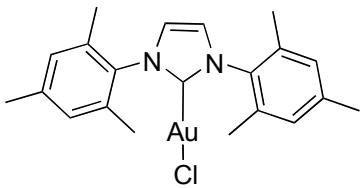
(4) Bohm, V. P. W.; Weskamp, T.; Gstottmayr, C. W. K.; Herrmann, W. A. *Angew. Chem. Int. Ed.* **2000**, *39*, 1602-1604.

(5) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239-247.

(6) (a)Wang, H. M. J.; Lin, I. J. B. *Organomet.* **1998**, *17*, 972-975. (b) Wang, H. M. J.; Chen, C. Y. L.; Lin, I. J. B. *Organomet.* **1999**, *18*, 1216-1223.

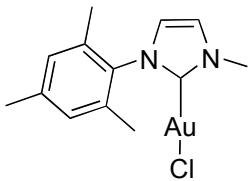
(7) Synthesis of *N,N'*-dimethylimidazolium iodide: Overberger, C. G.; Salamone, J. C.; Yaroslavsky, S. *J. Org. Chem.* **1965**, *30*, 3580.

### Complex 2a



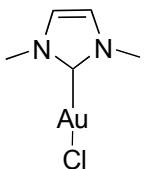
Yield 49%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.08 (s, 2H), 6.97 (bs, 4H), 2.33 (s, 6H), 2.09 (s, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.79, 134.68, 129.49, 122.12, 21.13, 17.75 (one signal is missing). HRMS-FAB Cald. for  $\text{C}_{21}\text{H}_{25}\text{AuN}_2\text{Cl} (\text{M}^++\text{H})$ : 537.1372. Found: 537.1361.

### Complex 2b



Yield 60%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14 (d,  $J = 2.0$  Hz, 1H), 6.95 (bs, 2H), 6.88 (d,  $J = 2.0$  Hz, 1H), 3.95 (s, 3H), 2.32 (s, 3H), 2.00 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.69, 139.71, 134.80, 134.69, 129.45, 122.18, 121.69, 38.37, 21.12, 17.85. HRMS-ESI Cald. for  $\text{C}_{13}\text{H}_{17}\text{AuN}_2\text{Cl} (\text{M}^++\text{H})$ : 433.0746. Found: 433.0739.

### Complex 2c



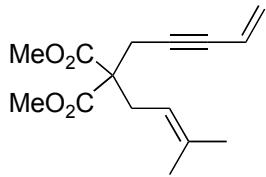
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.92 (bs, 2H), 3.82 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.32, 121.72, 38.19.

### General procedure for the synthesis of substituted alkynes.<sup>8</sup>

CuI (0.1 mmol) and  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$  (0.05 mmol) were suspended in  $i\text{-Pr}_2\text{NH}$ , and the resulting mixture was stirred for 5 min. The corresponding alkenyl- or arylbromide (1.3 mmol) and the alkyne 1,6-enyne (1 mmol) in  $i\text{-Pr}_2\text{NH}$  were added sequentially. The reaction was stirred at room temperature until TLC showed total conversion. The crude mixture was diluted with  $\text{Et}_2\text{O}$ , filtered through Celite, and purified by chromatography.

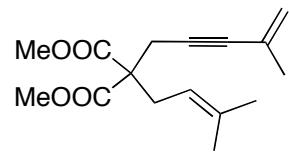
(8) Forsyth, C. J.; Clardy, J. *J. Am. Chem. Soc.* **1990**, *112*, 3497-3505.

### Dienyne 5a



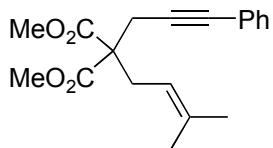
Yield 83%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.71 (ddt,  $J = 17.5, 11.0, 2.1$  Hz, 1H), 5.53 (ddt,  $J = 17.5, 2.2, 0.6$  Hz, 1H), 5.39 (dd,  $J = 11.0, 2.3$  Hz, 1H), 4.91 (bt,  $J = 7.7$  Hz, 1H), 3.73 (s, 6H), 2.88 (d,  $J = 2.1$  Hz, 2H), 2.76 (d,  $J = 7.7$  Hz, 2H), 1.70 (d,  $J = 1.1$  Hz, 3H), 1.65 (d,  $J = 1.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.58, 136.74, 126.49, 117.08, 117.06, 85.30, 81.99, 57.36, 52.62, 30.91, 26.03, 23.40, 17.87. HRMS-Cl Cald. for  $\text{C}_{15}\text{H}_{21}\text{O}_4$  ( $\text{M}^++\text{H}$ ): 265.1440. Found: 265.1441.

### Dienyne 5b

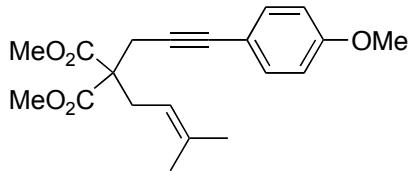


$^1\text{H}$  RMN (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.21 (s, 1H), 5.17 (s, 1H), 4.93 (t,  $J = 7.7$  Hz, 1H), 3.75 (s, 6H), 2.89 (s, 2H), 2.79 (d,  $J = 7.7$  Hz, 2H), 1.85 (s, 3H), 1.72 (s, 3H), 1.68 (s, 3H);  $^{13}\text{C}$  RMN (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 136.7, 126.7, 121.2, 117.2, 84.6, 83.7, 57.5, 52.6, 30.9, 26.1, 23.5, 23.3, 17.9; HRMS-Cl Cald. for  $\text{C}_{16}\text{H}_{23}\text{O}_4$  ( $\text{M}^++\text{H}$ ): 279.1596. Found: 279.1696.

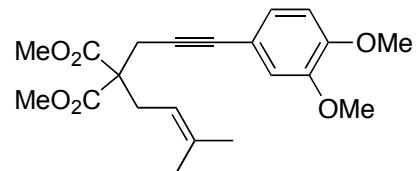
### Enyne 9a



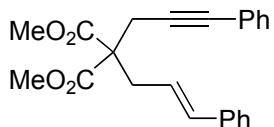
Yield 81%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.33 (m, 2H), 7.29-7.23 (m, 3H), 4.96 (t,  $J = 7.7$  Hz, 1H), 3.75 (s, 6H), 2.99 (s, 2H), 2.84 (d,  $J = 7.7$  Hz, 2H), 1.71 (s, 3H), 1.67 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.11, 170.65, 136.82, 131.62, 128.18, 127.91, 123.31, 117.17, 84.76, 83.34, 57.53, 52.67, 30.80, 26.07, 23.48, 17.97. HRMS-Cl Cald. for  $\text{C}_{19}\text{H}_{22}\text{O}_4$  ( $\text{M}^++\text{H}$ ): 315.1596. Found: 315.1596.

**Enyne 9b**

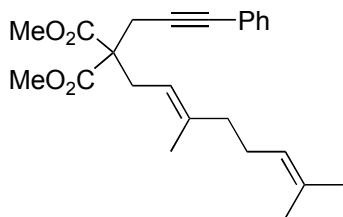
Yield 20%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 8.8$  Hz, 2H), 6.81 (d,  $J = 8.8$  Hz, 3H), 4.97 (t,  $J = 7.7$  Hz, 1H), 3.80 (s, 3H), 3.76 (s, 6H), 2.98 (s, 2H), 2.85 (d,  $J = 7.7$  Hz, 2H), 1.73 (s, 3H), 1.69 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.71, 159.34, 136.74, 132.98, 117.23, 115, 47, 113.82, 83.12, 60.37, 57.56, 55.25, 52.64, 30.96, 26.07, 23.48, 17.96. HRMS-Cl Cald. for  $\text{C}_{20}\text{H}_{25}\text{O}_5$  ( $\text{M}^++\text{H}$ ): 345.1702. Found: 345.1697.

**Enyne 9c**

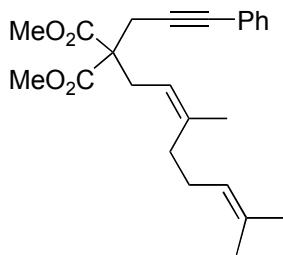
Yield 35%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.95 (dt,  $J = 8.1, 1.6$  Hz, 1H), 6.85 (t,  $J = 1.5$  Hz, 1H), 6.75 (dd,  $J = 8.1, 1.4$  Hz, 1H), 4.94 (m, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.74 (s, 6H), 2.94 (s, 2H), 2.83 (d,  $J = 8.1$  Hz, 2H), 1.71 (s, 3H), 1.67 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.22, 149.25, 136.62, 127.21, 117.11, 115.50, 114.35, 110.91, 107.92, 83.35, 83.07, 57.53, 55.91, 52.67, 31.03, 26.10, 23.52, 18.00. HRMS-Cl Cald. for  $\text{C}_{21}\text{H}_{27}\text{O}_6$  ( $\text{M}^++\text{H}$ ): 375.1808. Found: 375.1794.

**Enyne 9d**

Yield 80%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.18 (m, 10H), 6.51 (d,  $J = 15.7$  Hz, 1H), 6.02 (dt,  $J = 15.5, 7.6$  Hz, 1H), 3.78 (s, 6H), 3.07 (s, 2H), 3.02 (dd,  $J = 7.6, 1.2$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.33, 137.03, 134.61, 131.66, 128.48, 128.21, 128.01, 127.48, 126.30, 123.34, 84.27, 83.77, 57.66, 52.82, 36.21, 23.96 (one signal is missing due to overlapping). HRMS-Cl Cald. for  $\text{C}_{23}\text{H}_{23}\text{O}_4$  ( $\text{M}^++\text{H}$ ): 363.1596. Found: 363.1597.

**Enyne 9e**

Yield 79%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.33 (m, 2H), 7.28-7.24 (m, 3H), 5.05 (m, 1H), 4.95 (m, 1H), 3.75 (s, 6H), 2.99 (s, 2H), 2.85 (d,  $J = 7.7$  Hz, 2H), 2.11-1.98 (m, 4H), 1.68 (s, 3H), 1.66 (s, 3H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.64, 140.36, 131.61, 131.58, 128.17, 127.89, 124.01, 123.39, 117.24, 84.85, 83.29, 57.55, 52.66, 39.99, 30.86, 26.50, 25.66, 23.40, 17.69, 16.20. HRMS-Cl Cald. for  $\text{C}_{24}\text{H}_{31}\text{O}_4$  ( $\text{M}^++\text{H}$ ): 383.2222. Found: 383.2223.

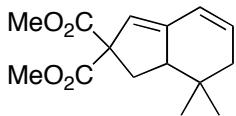
**Enyne 9f**

Yield 74%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.34 (m, 2H), 7.29-7.26 (m, 3H), 5.09 (m, 1H), 4.95 (t,  $J = 7.8$  Hz, 1H), 3.77 (s, 6H), 3.01 (s, 2H), 2.87 (d,  $J = 7.3$  Hz, 2H), 2.37-1.88 (m, 4H), 1.73 (s, 3H), 1.65 (s, 3H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.63, 140.63, 131.67, 128.51, 127.91, 124.122, 117.63, 117.26, 109.83, 84.73, 83.44, 57.48, 52.69, 39.99, 32.02, 30.60, 25.63, 23.47, 17.62, 16.20. HRMS-Cl Cald. for  $\text{C}_{24}\text{H}_{31}\text{O}_4$  ( $\text{M}^++\text{H}$ ): 383.2222. Found: 383.2226.

**General Procedure for the Cyclization of Scheme 3 and Table 1**

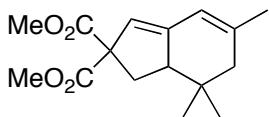
To a solution of Au(I) complex (0.002 mmol) and  $\text{AgSbF}_6$  (0.002 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (0.5 mL), the enyne was added dissolved in dry  $\text{CH}_2\text{Cl}_2$  (0.5 mL). The reaction was stirred at the stated conditions for 1-48 h. The resulting mixture was filtered through Celite and purified by chromatography.

**Dimethyl 4,4-Dimethyl-3a,4-dihydro-1*H*-indene-2,2(6*H*)dicarboxylate (6a)**



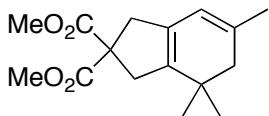
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.24 (dd, *J* = 9.7, 2.9 Hz, 1H), 5.84 (ddd, *J* = 9.6, 5.9, 2.1 Hz, 1H), 5.56 (d, *J* = 2.4 Hz, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 2.76 (td, *J* = 9.5, 2.2 Hz, 1H), 2.62 (dd, *J* = 13.2, 7.6 Hz, 1H), 2.07 (t, *J* = 18.2 Hz, 1H), 1.99 (dd, *J* = 13.2, 9.3 Hz, 1H), 1.94 (td, *J* = 18.1, 5.9 Hz, 1H), 0.97 (s, 3H), 0.70 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.24, 171.51, 145.79, 132.55, 122.70, 120.91, 65.38, 52.65, 52.63, 52.12, 42.03, 33.16, 32.50, 28.72, 19.42. HRMS-Cl Cald. for C<sub>18</sub>H<sub>21</sub>O<sub>4</sub> (M<sup>+</sup>+H): 265.1440. Found: 265.1441. The structure was confirmed by COSY, HMQC and HMBC experiments.

**Dimethyl 4,4,6-Trimethyl-3a,4-dihydro-1*H*-indene-2,2(6*H*)dicarboxylate (6b)**



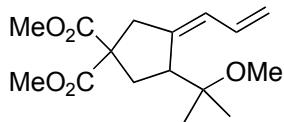
<sup>1</sup>H-RMN (500 MHz, CDCl<sub>3</sub>) δ 6.01 (s, 1H), 5.43 (s, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 2.69 (td, *J* = 9.4, 2.9 Hz, 1H), 2.59 (dd, *J* = 13.1, 7.6 Hz, 1H), 2.11 (d, *J* = 17.4 Hz, 1H), 1.95 (dd, *J* = 13.1, 9.3 Hz, 1H), 1.75 (s, 3H) overlap 1.77 (t, *J* = 8.7 Hz, 1H), 0.96 (s, 3H), 0.68 (s, 3H); <sup>13</sup>C-RMN (125 MHz, CDCl<sub>3</sub>) δ 172.4, 171.7, 146.7, 141.9, 118.4, 118.1, 65.5, 52.5, 51.7, 47.3, 32.9, 32.4, 28.6, 23.8, 19.3; HRMS-Cl Cald. for C<sub>16</sub>H<sub>23</sub>O<sub>4</sub> (M<sup>+</sup>+H) 279.1596. Found: 279.1606. The structure was confirmed by COSY, HMQC and HMBC experiments.

**Dimethyl 4,4,6-Trimethyl-4,5-dihydro-1*H*-indene-2,2(3*H*)dicarboxylate (7)**



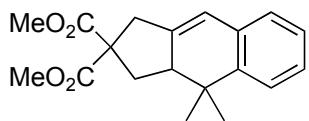
<sup>1</sup>H-RMN (500 MHz, CDCl<sub>3</sub>) δ 5.58 (s, 1H), 3.73 (s, 6H), 3.02 (s, 4H), 1.97 (s, 2H), 1.77 (s, 3H), 0.95 (s, 6H); <sup>13</sup>C-RMN (125 MHz, CDCl<sub>3</sub>) δ 172.7, 137.3, 135.5, 129.2, 116.8, 58.5, 52.7, 45.3, 41.6, 39.2, 32.5, 25.9, 23.3. HRMS-Cl Cald. for C<sub>16</sub>H<sub>23</sub>O<sub>4</sub> (M<sup>+</sup>+H) 279.1596. Found: 279.1600. The structure was confirmed by COSY, HMQC and HMBC experiments.

**(Z)-Dimethyl 3-Allylidene-4-(2-methoxypropan-2-yl)cyclopentane-1,1-dicarboxylate (8)**



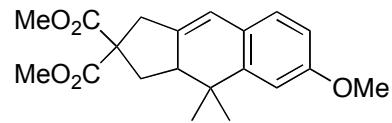
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.47 (dt, *J* = 16.9, 10.6 Hz, 1H), 6.06 (d, *J* = 11.0 Hz, 1H), 5.11 (d, *J* = 16.8 Hz, 1H), 5.03 (d, *J* = 10.2 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.19 (d, *J* = 15.0 Hz, 1H), 3.15 (s, 3H), 3.01 (m, 1H), 2.71 (d, *J* = 14.9 Hz, 1H), 2.61 (dd, *J* = 13.9, 9.1 Hz, 1H), 2.35 (dd, *J* = 14.1, 5.2 Hz, 1H), 1.19 (s, 3H), 1.11 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.49, 172.10, 143.20, 134.41, 126.27, 115.99, 77.71, 58.41, 52.72, 52.62, 49.01, 48.41, 44.15, 34.99, 23.04. HRMS-Cl Cald. for C<sub>15</sub>H<sub>21</sub>O<sub>4</sub> (M<sup>+</sup>-OMe): 265.1434. Found: 265.1431. The structure was confirmed by COSY, HMQC and HMBC experiments.

**Dimethyl 4,4-Dimethyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)dicarboxylate (10a)**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29-7.27 (m, 1H), 7.13 (m, 2H), 7.01 (m, 1H), 6.34 (bs, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 3.27 (dd, *J* = 18.0, 1.3 Hz, 1H), 2.97 (dt, *J* = 18.0, 3.0 Hz, 1H), 2.69-2.63 (m, 1H), 2.57 (ddd, *J* = 12.3, 7.6, 1.1 Hz, 1H), 2.13 (t, *J* = 12.3 Hz, 1H), 1.42 (s, 3H), 0.92 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.09, 171.19, 143.99, 142.85, 133.87, 126.87, 123.23, 126.20, 123.42, 119.32, 58.86, 52.83, 52.81, 48.40, 39.15, 36.58, 34.76, 25.59, 21.98. HRMS-Cl Cald. for C<sub>19</sub>H<sub>22</sub>O<sub>4</sub> (M<sup>+</sup>): 314.1518. Found: 314.1511. The structure was confirmed by COSY, HMQC and HMBC experiments.

**Dimethyl 6-Methoxy-4,4-dimethyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)dicarboxylate (10b)**

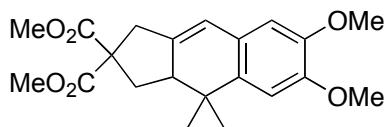


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.96 (d, *J* = 8.3 Hz, 1H), 6.88 (d, *J* = 2.5 Hz, 1H), 6.67 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.31 (bs, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.73 (s, ·H), 3.28 (dd, *J* = 17.9, 1.5 Hz, 1H), 2.98 (dt, *J* = 17.8, 3.0 Hz, 1H), 2.69-2.63 (m, 1H), 2.59 (ddd, *J* = 13.6, 7.5, 1.3 Hz, 1H), 2.14 (t, *J* = 12.3 Hz, 1H), 1.41 (s, 3H), 0.90 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.19, 172.02, 158.74, 146.00, 140.16, 127.13, 118.71, 110.81, 110.02, 100.03, 59.00, 55.30, 52.87, 52.84, 48.22, 39.08,

36.96, 34.85, 25.59, 21.94. HRMS-CI Cald. for C<sub>20</sub>H<sub>25</sub>O<sub>5</sub> (M<sup>+</sup>+H): 345.1702. Found: 345.1692.

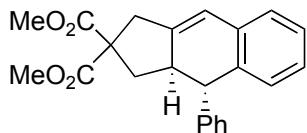
The structure was confirmed by COSY, HMQC and HMBC experiments.

**Dimethyl 6,7-Dimetoxy-4,4-dimethyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)dicarboxylate (10c)**

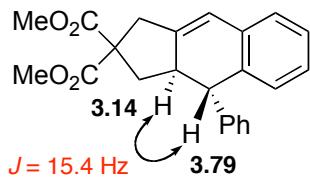


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.77 (s, 1H), 6.51 (s, 1H), 6.19 (bs, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 3.21 (d, *J* = 17.8 Hz, 1H), 2.90 (dt, *J* = 17.8, 2.8 Hz, 1H), 2.63-2.46 (m, 2H), 2.05 (t, *J* = 12.0 Hz, 1H), 1.34 (s, 3H), 0.83 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.14, 171.96, 147.65, 147.14, 141.03, 136.72, 127.17, 118.75, 109.95, 107.97, 58.97, 56.20, 55.92, 52.82, 48.57, 39.12, 36.44, 38.84, 25.88, 21.90. HRMS-CI Cald. for C<sub>21</sub>H<sub>27</sub>O<sub>6</sub> (M<sup>+</sup>+H): 375.1808. Found: 375.1796. The structure was confirmed by COSY, HMQC and HMBC experiments.

**(3a*R*<sup>\*</sup>,4*S*<sup>\*</sup>)-Dimethyl 4-Phenyl-3a,4-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (10d)**



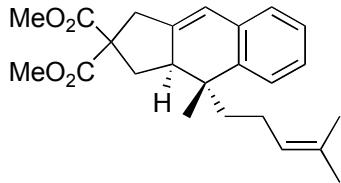
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.38 (t, *J* = 6.9 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 3H), 7.12 (td, *J* = 7.3, 1.1 Hz, 1H), 7.06 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.97 (td, *J* = 7.5, 1.4 Hz, 1H), 6.55 (d, *J* = 7.7 Hz, 1H), 6.41 (bs, 1H), 3.79 (d, *J* = 15.4 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.33 (d, *J* = 18.5 Hz, 1H), 3.16 (dt, *J* = 17.7, 2.4 Hz, 1H), 3.14 (m, 1H), 2.34 (dd, *J* = 13.0, 7.4 Hz, 1H), 1.95 (dd, *J* = 13.1, 11.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.07, 144.40, 141.78, 137.99, 135.21, 128.74, 128.26, 126.92, 126.91, 126.62, 126.47, 125.58, 119.42, 59.08, 52.82, 52.22, 45.07, 39.75, 38.81. HRMS-CI Cald. for C<sub>23</sub>H<sub>23</sub>O<sub>4</sub> (M<sup>+</sup>+H): 363.1596. Found: 363.1598. The structure was confirmed by COSY, HMQC and HMBC experiments. The configuration was assigned on the basis of the observed <sup>3</sup>J:



**(3a*R*<sup>\*</sup>,4*S*<sup>\*</sup>)-Dimethyl**

**4-Methyl-4-(4-methylpent-3-enyl)-3a,4-dihydro-1*H*-**

**cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (10e)**

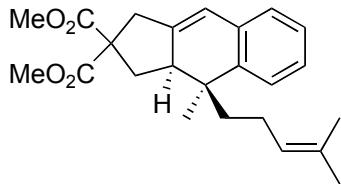


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22-7.10 (m, 3H), 7.04-7.01 (m, 1H), 6.31 (bs, 1H), 5.19 (m, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.30 (dd,  $J = 17.8, 1.0$  Hz, 1H), 3.02 (dt,  $J = 21.1, 2.9$  Hz, 1H) 2.94 (m, 1H) 2.56 (dd,  $J = 11.4, 7.4$  Hz, 1H), 2.11-1.98 (m, 5H), 1.71 (s, 3H), 1.60 (s, 3H), 0.99 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.09, 171.89, 142.78, 141.47, 134.84, 131.50, 126.82, 126.80, 126.10, 124.56, 123.97, 118.23, 58.92, 52.84, 43.78, 40.29, 39.27, 36.88, 34.31, 25.72, 23.28, 23.05, 17.63. HRMS-Cl Cald. for  $\text{C}_{24}\text{H}_{31}\text{O}_4$  ( $\text{M}^++\text{H}$ ): 383.2222. Found: 383.2220. The structure was confirmed by COSY, NOESY, HMQC and HMBC experiments.

**(3a*R*<sup>\*</sup>,4*R*<sup>\*</sup>)-Dimethyl**

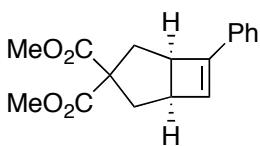
**4-Methyl-4-(4-methylpent-3-enyl)-3a,4-dihydro-1*H*-**

**cyclopenta[*b*]naphthalene-2,2(3*H*)-dicarboxylate (10f)**



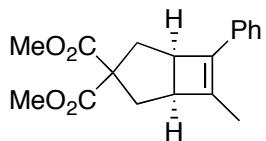
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24-7.18 (m, 1H), 7.15-7.11 (m, 2H), 6.98-6.95 (m, 1H), 6.33 (bs, 1H), 4.92 (dd,  $J = 7.2, 6.9$  Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.30 (d,  $J = 18.0$  Hz, 1H), 2.96 (dt,  $J = 18.0, 2.9$  Hz, 1H) 2.79-2.72 (m, 1H), 2.60-2.56 (m, 1H), 2.24 (t,  $J = 12.6$  Hz, 1H), 1.88-1.68 (m, 4H), 1.60 (s, 3H), 1.40 (s, 3H), 1.30 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.15, 142.77, 140.82, 134.52, 131.23, 126.31, 126.21, 126.04, 125.58, 124.72, 119.53, 58.82, 52.86, 52.78, 49.58, 39.18, 34.37, 32.60, 25.59, 23.41, 23.21, 17.35 (one signal is missing due to overlapping). HRMS-Cl Cald. for  $\text{C}_{24}\text{H}_{31}\text{O}_4$  ( $\text{M}^++\text{H}$ ): 383.2222. Found: 383.2206. The structure was confirmed by COSY, NOESY, HMQC and HMBC experiments.

**(1*R*<sup>\*</sup>,5*S*<sup>\*</sup>)-Dimethyl 7-Phenylbicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (11a)**



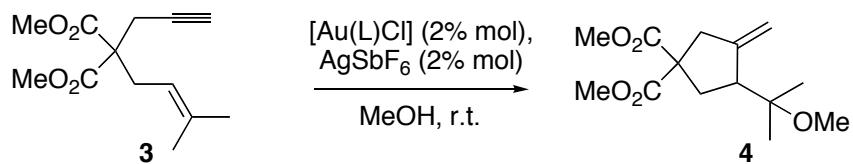
White solid: mp = 68-70°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25-7.15 (m, 5H), 6.01 (s, 1H); 3.63 (s, 3H), 3.56 (dd,  $J$  = 7.4, 3.5 Hz, 1H), 3.25 (dd,  $J$  = 7.5, 3.5 Hz, 1H), 3.15 (s, 3H), 2.76 (d,  $J$  = 13.5 Hz, 1H), 2.61 (d,  $J$  = 13.3 Hz, 1H) 1.95 (dd,  $J$  = 13.5, 7.5 Hz, 1H); 1.90 (dd,  $J$  = 13.3, 1.5 Hz, 1H);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  172.57, 171.93, 146.69, 133.32, 129.80, 128.26, 127.77, 124.61, 60.89, 52.93, 51.76, 45.75, 43.48, 35.36, 34.05. HRMS-CI Cald. for  $\text{C}_{17}\text{H}_{19}\text{O}_4$  ( $\text{M}^++\text{H}$ ): 287.1283. Found: 287.1274. The structure was confirmed by COSY, NOESY, HMQC and HMBC experiments.

**(1*R*,5*S*)-Dimethyl 6-Methyl-7-phenylbicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate (11b)**



$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.25 (m, 4H), 7.21-7.15 (m, 1H), 3.68 (s, 3H), 3.50-3.45 (m, 1H), 3.22 (s, 3H), 3.15-3.11 (m, 1H), 2.72 (dd,  $J$  = 28.8, 13.3 Hz, 1H), 2.02 (dd,  $J$  = 13.4, 7.2 Hz, 1H), 1.86 (dd,  $J$  = 13.2, 7.6 Hz, 1H), 1.85 (dd,  $J$  = 2.8, 1.4 Hz, 3H);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  172.65, 172.41, 140.89, 138.50, 134.61, 128.25, 126.73, 125.65, 60.58, 52.78, 51.83, 46.35, 43.57, 34.65, 33.56, 13.92. HRMS-CI Cald. for  $\text{C}_{28}\text{H}_{20}\text{O}_4$  ( $\text{M}^++\text{H}$ ): 301.1440. Found: 301.1437. The structure was confirmed by COSY, NOESY, HMQC and HMBC experiments.

**Table 3. Au(I)-catalyzed methoxycyclization of enyne **3**.<sup>9</sup>**

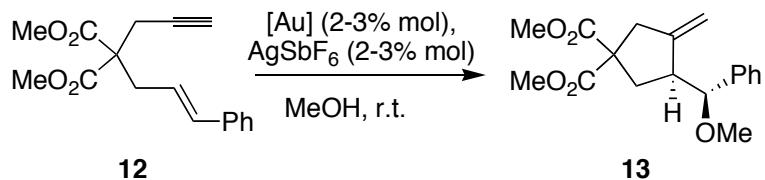


Entry	Complex	Time (h)	Conversion (%) <sup>a</sup>	Yield of <b>4</b> (%)
1	AuCl	24	32	10
2	[Au(Me <sub>2</sub> S)Cl]	24	<2	<2
3	[Au(Ph <sub>3</sub> P)Cl]	3	>98	84
4	[Au(Cy <sub>3</sub> P)Cl]	3.5	>98	77
5	[Au{(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> P}Cl]	5	>98	77
6	[Au{(o-Tol) <sub>3</sub> P}Cl]	24	>98	90
7	[Au(Ph <sub>3</sub> As)Cl]	4	>98	78
8	[Au{P(1-Naph) <sub>3</sub> }Cl]	12	>98	76
9	<b>1b</b>	0.25	>98	90
10	<b>1a</b>	0.5	>98	97
11	<b>1c</b>	0.25	>98	92
12	<b>1d</b>	0.25	>98	89
13	<b>2a</b>	1.5	>98	71
14	<b>2b</b>	5	>98	87
15	<b>2c</b>	24	>98	34

<sup>a</sup>Conversions were determined by GC.

(9) Méndez, M.; Muñoz, M. P.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 10511-10520.

**Table 4. Au(I)-catalyzed methoxycyclization of enyne 12.<sup>9</sup>**



Entry	Complex	Time (h)	Conversion (%) <sup>a</sup>	Yield of <b>13</b> (%)
1	AuCl	48	50	35
2	[Au(Me <sub>2</sub> S)Cl]	48	21	5
3	[Au(Ph <sub>3</sub> P)Cl]	18	93	70
4	[Au(Cy <sub>3</sub> P)Cl]	18	>98	83
5	[Au{(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> P}Cl]	48	66	44
6	[Au{(o-Tol) <sub>3</sub> P}Cl]	30	>98	79
7	[Au(Ph <sub>3</sub> As)Cl]	48	68	48
8	<b>1a</b>	18	>98	68
9	<b>1c</b>	18	>98	94
10	<b>2a</b>	20	>98	76
11	<b>2b</b>	24	73	51
12	<b>2c</b>	48	84	48

<sup>a</sup>Conversions were determined by GC.

