Electronic Supplementary Information

Gold(I) catalysed sequential dehydrative cyclisation/ intermolecular [4+2] cycloaddition of alkynylidenols onto activated alkynes/ alkenes; A facile route to substituted norbornadienes/ norbornenes

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<table>
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<tbody>
<tr>
<td>1</td>
<td>Copies of $^1$H/$^{13}$C NMR spectra of all new compounds (Figures S1-S90)</td>
<td>S2-S47</td>
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<td>S48</td>
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Figure S1. $^1$H NMR spectrum of compound 4aa

Figure S2. $^{13}$C NMR spectrum of compound 4aa
Figure S3. $^1$H NMR spectrum of compound 4ab

Figure S4. $^{13}$C NMR spectrum of compound 4ab
Figure S5. $^1$H NMR spectrum of compound 4ac

Figure S6. $^{13}$C NMR spectrum of compound 4ac
Figure S7. $^1$H NMR spectrum of compound 4ad

Figure S8. $^{13}$C NMR spectrum of compound 4ad
Figure S9. $^1$H NMR spectrum of compound 4ba

Figure S10. $^{13}$C NMR spectrum of compound 4ba
Figure S11. \(^1\)H NMR spectrum of compound 4bb

Figure S12. \(^{13}\)C NMR spectrum of compound 4bb
Figure S13. $^1$H NMR spectrum of compound 4ca

Figure S14. $^{13}$C NMR spectrum of compound 4ca
Figure S15. $^1$H NMR spectrum of compound 4cb

Figure S16. $^{13}$C NMR spectrum of compound 4cb
Figure S17. $^1$H NMR spectrum of compound 4da

Figure S18. $^{13}$C NMR spectrum of compound 4da
Figure S19. $^1$H NMR spectrum of compound 4aac

Figure S20. $^{13}$C NMR spectrum of compound 4aac
Figure S21. $^1$H NMR spectrum of compound 5aa

Figure S22. $^{13}$C NMR spectrum of compound 5aa
Figure S23. $^1$H NMR spectrum of compound 5ab

Figure S24. $^{13}$C NMR spectrum of compound 5ab
Figure S25. $^1$H NMR spectrum of compound 5ac

Figure S26. $^{13}$C NMR spectrum of compound 5ac
Figure S27. $^1$H NMR spectrum of compound 5ad

Figure S28. $^{13}$C NMR spectrum of compound 5ad
Figure S29. $^1$H NMR spectrum of compound 5ba

Figure S30. $^{13}$C NMR spectrum of compound 5ba
Figure S31. $^1$H NMR spectrum of compound 5bb

Figure S32. $^{13}$C NMR spectrum of compound 5bb
Figure S33. $^1$H NMR spectrum of compound 5ca

Figure S34. $^{13}$C NMR spectrum of compound 5ca
Figure S35. $^1$H NMR spectrum of compound 5cb

Figure S36. $^{13}$C NMR spectrum of compound 5cb
Figure S37. $^1$H NMR spectrum of compound 5da

Figure S38. $^{13}$C NMR spectrum of compound 5da
Figure S39. $^1$H NMR spectrum of compound 5aac

Figure S40. $^{13}$C NMR spectrum of compound 5aac
Figure S41. $^1$H NMR spectrum of compound 8

Figure S42. $^{13}$C NMR spectrum of compound 8
Figure S43. $^1$H NMR spectrum of compound 9

Figure S44. $^{13}$C NMR spectrum of compound 9
Figure S45. $^1$H NMR spectrum of compound 10

Figure S46. $^{13}$C NMR spectrum of compound 10
Figure S47. $^1$H NMR spectrum of compound 11

Figure S48. $^{13}$C NMR spectrum of compound 11
Figure S49. $^1$H NMR spectrum of compound 12

Figure S50. $^{13}$C NMR spectrum of compound 12
Figure S51. $^1$H NMR spectrum of compound 13

Figure S52. $^{13}$C NMR spectrum of compound 13
Figure S53. $^1\text{H}$ NMR spectrum of compound 14

Figure S54. $^{13}\text{C}$ NMR spectrum of compound 14
Figure S55. $^1$H NMR spectrum of compound 15

Figure S56. $^{13}$C NMR spectrum of compound 15
Figure S57. $^1$H NMR spectrum of compound 16

Figure S58. $^{13}$C NMR spectrum of compound 16
Figure S59. $^1$H NMR spectrum of compound 17

Figure S60. $^{13}$C NMR spectrum of compound 17
Figure S61. $^1$H NMR spectrum of compound 18 (cf. main text for details)

Figure S62. $^{13}$C NMR spectrum of compound 18 (cf. main text for details)
Figure S63. $^1$H NMR spectrum of compound 19

Figure S64. $^{13}$C NMR spectrum of compound 19
Figure S65. $^1$H NMR spectrum of compound 20

Figure S66. $^{13}$C NMR spectrum of compound 20
Figure S67. $^1$H NMR spectrum of compound 21

Figure S68. $^{13}$C NMR spectrum of compound 21
Figure S69. $^1$H NMR spectrum of compound 22

Figure S70. $^{13}$C NMR spectrum of compound 22
Figure S71. $^1$H NMR spectrum of compound 23

Figure S72. $^{13}$C NMR spectrum of compound 23
Figure S73. $^1$H NMR spectrum of compound 24

Figure S74. $^{13}$C NMR spectrum of compound 24
Figure S75. $^1$H NMR spectrum of compound 25

Figure S76. $^{13}$C NMR spectrum of compound 25
Figure S77. $^1$H NMR spectrum of compound 26

Figure S78. $^{13}$C NMR spectrum of compound 26
Figure S79. NOESY spectrum of compound 26
Figure S80. NOESY expansion of compound 26
Figure S81. $^1$H NMR spectrum of compound 27

Figure S82. $^{13}$C NMR spectrum of compound 27
Figure S83. $^1$H NMR spectrum of compound 28

Figure S84. $^{13}$C NMR spectrum of compound 28
Figure S85. $^1$H NMR spectrum of compound 29

Figure S86. $^{13}$C NMR spectrum of compound 29
Figure S87. $^1$H NMR spectrum of compound 30

Figure S88. $^{13}$C NMR spectrum of compound 30
Figure S89. $^1$H NMR spectrum of compound 31

Figure S90. $^{13}$C NMR spectrum of compound 31
Figure S91. HRMS for the blank reaction mixture using 5bb + AuCl (i.e., without DMAD)
Detector A (254nm)

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Totals              | 24256270   | 100.000 | 1013146 | 100.000 |

Figure S92. HPLC of compound 27 (isopropanol/hexane; 5:95; chiralpack AS-H column; 0.5 mL/min flow rate; peak at ~ 7 min is due to solvent)

Detector A (254nm)

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Totals              | 29132932   | 100.000 | 515696  | 100.000 |

Figure S93. HPLC of compound 28 (isopropanol/hexane; 5:95; chiralpack AS-H column; 0.5 mL/min flow rate; peak at ~ 7 min is due to solvent)
Figure S94. HPLC of compound 29 (isopropanol/hexane; 5:95; chiralpack AS-H column; 0.5 mL/min flow rate; peak at ~7 min is due to solvent)
Fig. S95. ORTEP (probability level 50%) of compound 5aa. Only one molecule (of the four) is shown. Selected bond lengths [Å] with esds in parentheses: O(1)-C(25) 1.408(3), C(7)-C(8) 1.490(2), C(8)-C(9) 1.436(3), C(9)-C(10) 1.194(3), C(10)-C(11) 1.438(3), C(8)-C(17) 1.351(2), C(24)-C(25) 1.486(3).

Figure S96. Molecular pictures of compound 25 (ORTEP probability level 50%). Selected bond lengths [Å] with esds in parentheses: C(1)-C(2) 1.345(6), C(1)-C(6) 1.559(6), C(1)-C(8) 1.418(6), C(2)-C(3) 1.532(5), C(3)-C(4) 1.550(6), C(3)-C(7) 1.502(6), C(4)-C(5) 1.533(6), C(5)-C(6) 1.592(5), C(8)-C(9) 1.191(5). The data quality was only moderate for this structure, and there appears to be some residual electron density close to C19. The exo-stereochemistry is clarified in the lower drawing.