Supporting Information for:

Remarkable anion effects uncovered in the development of a Au(III)-catalyzed tandem nucleophilic substitution-1,5-enyne cycloisomerisation process

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Table of Contents

1.0 General Details .......................................................................................................................... 3
2.0 Experimental ............................................................................................................................ 3
2.1 1'Pe.HCl ................................................................................................................................ 3
2.2 (1'Pe)AuCl .............................................................................................................................. 4
2.3 (1'Pe)AuBr (1e) ....................................................................................................................... 5
2.4 (1'Pe)Au(N-succ) .................................................................................................................... 6
2.5 (1'Pe)Au(N-tfs) ....................................................................................................................... 6
2.6 (1'Pe)Au(N-mal) ..................................................................................................................... 7
2.7 (1'Pe)AuBr₃ (1d) ..................................................................................................................... 8
2.8 (1'Pe)AuBr₂(N-succ) (1a) ......................................................................................................... 9
2.9 (1'Pe)AuBr₂(N-tfs) (1b) .......................................................................................................... 9
2.10 (1'Pe)AuBr₂(N-mal) (1c) ....................................................................................................... 10
2.11 General procedure for the cycloisomerisation of 3-phenylhex-5-en-1-yne.......................... 11
2.12 3-Phenylbicyclo[3.1.0]hex-2-ene (3a) .................................................................................... 11
2.13 General procedure for the tandem nucleophillic substitution-cycloisomerisation of propargyl alcohols .......... 12
2.14 1-Butyl-3-phenylbicyclo[3.1.0]hex-2-ene (3c) ........................................................................ 12
2.15 1-Trimethylsilyl-3-phenylbicyclo[3.1.0]hex-2-ene (3d) ............................................................ 13
2.16 1,3-Diphenylbicyclo[3.1.0]hex-2-ene (3e) ............................................................................. 14
2.17 3-(2-Napthyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3f) .............................................................. 14
2.18 3-Mesityl-1-phenylbicyclo[3.1.0]hex-2-ene (3g) .................................................................... 15
2.19 3-(4-Chlorophenyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3h) .................................................... 16
3.0 NMR spectra of key compounds ............................................................................................ 17
4.0 X-Ray crystallography ............................................................................................................. 36
4.1 Selected X-ray diffraction data ............................................................................................... 37
5.0 References .............................................................................................................................. 38
1.0 General Details

All reactions involving silver salts were carried out in the absence of light. Preparation of gold complexes was carried out under an inert atmosphere unless otherwise stated. Dichloromethane was dried by passing through a column of activated alumina, tetrahydrofuran was distilled from sodium benzophenone ketyl. Infrared spectra were recorded on a Unicam Research Series FT-IR. Mass spectrometry was carried out using a Fisons Analytical (VG) Autospec instrument. $^1$H, $^{13}$C and $^{19}$F spectra were collected on a JEOL ECX400 spectrometer operating at 400, 101 and 376 MHz respectively. All column chromatography was performed using silica gel (mesh 220-440) purchased from Fluka Chemicals with the solvent systems specified within the text. 1-Phenyl-2-propyn-1-ol, allyltrimethylsilane, and silver(I)triflate were purchased from Alfa Aesar. All other chemicals were purchased from Sigma Aldrich Inc. and used without further purification unless otherwise stated. Tetrafluorosuccinimide,$^1$ 4-phenyl-1-hexen-5-yne$^2$ and propargyl alcohols$^3$ were prepared according to literature procedures.

2.0 Experimental

2.1 $^{1}$Pe.HCl

A protocol similar to that reported by Jafarpour et al. was used.$^4$ tert-Pentylamine (5.18 g, 59.4 mmol, 2 equiv.) and glyoxal (3.35 ml, 29.8 mmol, 1 equiv., 40% in water) were dissolved in ethanol (50 ml). Formic acid (4 drops) was added and the solution was stirred at room temperature for 2 days. The resulting yellow solution was reduced $\text{in vacuo}$ to give a yellow oil and redissolved in toluene (60 ml). Paraformaldehyde (0.612 g, 20.4 µmol, 0.7 equiv.) was added and the suspension stirred at 100 °C
until a clear solution formed. HCl (5.10 ml, 20.4 µmol, 0.7 equiv., 4 M in dioxane) was added at 40 °C and the solution was then stirred at 70 °C overnight. The resulting white precipitate was separated by filtration and washed with acetone to give the title product as a white powder (2.50 g, 10.2 mmol, 34%). 

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.45 (t, $J = 2$ Hz, 1H, N$_2$C), 7.48 (d, $J = 2$ Hz, 2H, imidazole C), 2.04 (q, $J = 7.5$ Hz, 4H, tPe CH$_2$CH$_3$), 1.75 (s, 12H, tPe C(CH$_3$)$_2$), 0.75 (t, $J = 7.5$ Hz, 6H, tPe CH$_2$CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 135.3 (N$_2$C), 119.7 (imidazole C), 63.5 (tPe quaternary C), 35.3 (tPe CH$_2$CH$_3$), 27.4 (C(CH$_3$)$_2$), 8.1 (tPe CH$_2$CH$_3$). IR (CH$_2$Cl$_2$, cm$^{-1}$) $\nu_{\text{max}}$ 3657 (w), 3338 (w), 3165 (w), 3041 (w), 2972 (s), 2358 (w), 1534 (m), 1463 (m), 1386 (m), 1274 (m), 1184 (m), 1126 (m).

ESI-MS $m/z$ 209.2 (100%, [MH]$^+$), 139.1 (4%). ESI-HRMS calcd. for C$_{13}$H$_{26}$ClN$_2$ ([MH]$^+$) 209.2012; found 209.2014.

2.2 (tPe)AuCl

![A protocol similar to that reported by Baker et al was used.](image)

A protocol similar to that reported by Baker et al was used.$^5$ 1,3-Di-tert-pentylimidazolium chloride (390 mg, 1.60 mmol, 1.1 equiv.) and silver(I) oxide (219 mg, 946 µmol, 0.64 equiv.) in dichloromethane (60 ml) were stirred under a N$_2$ atmosphere. The suspension was stirred at room temperature overnight, filtered by cannula, and (Me$_2$S)AuCl (435 mg, 1.47 mmol, 1 equiv.) was added. The solution was stirred overnight at room temperature and filtered through Celite$^{\text{TM}}$. The solvent was removed in vacuo and the residue precipitated from dichloromethane/pentane. The resultant solid was washed with diethyl ether to give the title compound as a white powder (0.642 g, 1.46 mmol, 99%).$^1$H NMR (400 MHz, CDCl$_3$) δ 7.04 (s, 2H, imidazole C), 2.48 (q, $J = 7.5$ Hz, 4H, tPe CH$_2$CH$_3$), 1.79 (s, 12H, tPe CH$_3$), 0.64 (t, $J = 7.5$ Hz, 6H, tPe CH$_2$CH$_3$).$^{13}$C NMR (400 MHz, CDCl$_3$) δ 168.1 (carbene Au-C), 117.3 (imidazole C), 61.7 (tPe quaternary C), 36.3 (tPe CH$_2$CH$_3$), 29.3 (tPe CH$_2$CH$_3$), 7.8 (tPe
$C(CH_3)_2$. IR (CH$_2$Cl$_2$, cm$^{-1}$) $v_{\text{max}}$ 3680 (w), 3196 (w), 3172 (w), 3046 (m), 2972 (s), 2929 (m), 2880 (m), 2360 (w), 1604 (w), 1567 (w), 1460 (m), 1407 (m), 1393 (s), 1377 (s), 1339 (w), 1228 (m), 1190 (s), 1152 (w). ESI-MS m/z 463.1 (100%, [MNa$^+$]), 226.9 (5%). ESI-HRMS calcd. for $C_{13}H_{24}AuClN_2Na$ ([MNa$^+$]) 463.1186; found 463.1186.

2.3 (I$^\text{I}$Pe)AuBr (1e)

A protocol similar to that reported by de Frémont et al was used.$^6$ (I$^\text{I}$Pe)AuCl (83.6 mg, 190 $\mu$mol, 1 equiv.) and LiBr (141 mg, 1.62 mmol, 8.5 equiv.) were dissolved in acetone (2 ml). The solution was stirred at room temperature for 24 hours to give a clear solution. The solution was then reduced to dryness in vacuo and redissolved in dichloromethane (2 ml), dried over MgSO$_4$, and filtered through a plug of silica-gel. The solution was reduced to $< 0.5$ ml and 5 ml of pentane was added resulting in a white precipitate. This was removed by filtration, washed with cold pentane, and dried in vacuo to give the title compound as a white powder (87.9 mg, 180 $\mu$mol, 95%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.05 (s, 2H, imidazole CH), 2.48 (q, $J = 7.5$ Hz, 4H, I$^\text{I}$Pe CH$_2$CH$_3$), 1.81 (s, 12H, I$^\text{I}$Pe C(CH$_3$)$_2$), 0.65 (t, $J = 7.5$ Hz, 6H, I$^\text{I}$Pe CH$_2$CH$_3$). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 172.3 (carbene Au-C), 117.2 (imidazole CH), 61.8 (I$^\text{I}$Pe quaternary C), 36.3 (I$^\text{I}$Pe CH$_2$CH$_3$), 29.3 (I$^\text{I}$Pe C(CH$_3$)$_2$), 7.9 (I$^\text{I}$Pe CH$_2$CH$_3$). IR (CH$_2$Cl$_2$, cm$^{-1}$) $v_{\text{max}}$ 3196 (w), 3172 (w), 3047 (m), 2972 (s), 2930 (m), 2880 (w), 1704 (w), 1566 (w), 1558 (w), 1461 (m), 1406 (w), 1266 (m), 1260 (m), 1229 (m), 1271 (s), 1227 (m), 1191 (s), 1064 (w), 1037 (w), 1005 (w). ESI-MS m/z 507.1 (6%, [MNa$^+$]), 433.2 (15%), 413.3 (2%), 363.1 (19%), 293.0 (100%), 266.0 (2%). ESI-HRMS calcd. for $C_{13}H_{24}AuBrN_2Na$ ([MNa$^+$]) 507.0681; found 507.0675.
2.4 (\textsuperscript{1}Pe)Au(N-succ)

(\textsuperscript{1}Pe)AuCl (120 mg, 269 \textmu mol, 1 equiv.) and silver succinimdate (55.4 mg, 269 \textmu mol, 1 equiv.) were dissolved in dichloromethane (10 ml) and stirred at room temperature for 1 hour. The suspension was filtered through Celite\textsuperscript{TM} and the filtrate reduced to dryness \textit{in vacuo}. The resulting white powder was precipitated from dichloromethane/pentane and washed with diethyl ether to give the title compound as a white powder (126 mg, 251 \textmu mol, 93%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.05 (s, 2H, imidazole CH), 2.62 (s, 4H, succ CH\textsubscript{2}), 2.48 (q, \(J = 7.5\) Hz, 4H, \textsuperscript{1}Pe CH\textsubscript{2}), 1.82 (s, 12H, \textsuperscript{1}Pe C(CH\textsubscript{3})\textsubscript{2}), 0.66 (t, \(J = 7.5\) Hz, 6H, \textsuperscript{1}Pe CH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 188.7 (succ C=O), 170.8 (carbene Au-C), 117.3 (imidazole CH), 61.9 (\textsuperscript{1}Pe quaternary C), 36.3 (\textsuperscript{1}Pe CH\textsubscript{2}CH\textsubscript{3}), 31.6 (succ CH\textsubscript{2}), 29.3 (\textsuperscript{1}Pe C(CH\textsubscript{3})\textsubscript{2}), 7.9 (\textsuperscript{1}Pe CH\textsubscript{2}CH\textsubscript{3}). IR (CHCl\textsubscript{2}, cm\textsuperscript{-1}) \(\nu_{\text{max}}\) 3670 (w), 3172 (w), 3052 (m), 2970 (m), 2936 (m), 2880 (m), 2360 (w), 1644 (s, C=O), 1461 (m), 1435 (w), 1407 (m), 1393 (m), 1379 (m), 1352 (s), 1310 (w), 1285 (m), 1230 (s), 1191 (m). ESI-MS \(m/z\) 504.2 (100\%, [MH]\textsuperscript{+}), 433.2 (21\%), 363.1 (6\%), 292.0 (4\%), 209.2 (4\%). ESI-HRMS calcd. for C\textsubscript{17}H\textsubscript{29}AuN\textsubscript{3}O\textsubscript{2} ([MH]\textsuperscript{+}) 504.1920; found 504.1916.

2.5 (\textsuperscript{1}Pe)Au(N-tfs)

(\textsuperscript{1}Pe)AuCl (100 mg, 228 \textmu mol, 1 equiv.), silver(I) oxide (31.7 mg, 137 \textmu mol, 0.6 equiv.), and tetrafluorosuccinimide (42.9 mg, 251 \textmu mol, 1.1 equiv.) were mixed in dichloromethane (5 ml) under an inert atmosphere and stirred at room temperature for 2 hours. The suspension was filtered through...
Celite™ and the filtrate reduced to dryness in vacuo. The resulting white powder was precipitated from dichloromethane/pentane, washed with diethyl ether and dried in vacuo to give the title compound as a white powder (122 mg, 212 µmol, 93%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.11 (s, 2H, imidazole CH), 2.48 (q, J = 7.5 Hz, 4H, $^1$Pe CH$_2$CH$_3$), 1.83 (s, 12H, $^1$Pe C(CH$_3$)$_2$), 0.69 (t, J = 7.5 Hz, 6H, $^1$Pe CH$_2$CH$_3$). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -127.5 (s, CF$_2$). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.4 (m, C=O), 167.5 (carbene Au-C), 117.8 (imidazole CH), 107.4 (tt, J = 267 and 22 Hz, tfs CF$_2$), 62.1 ($^1$Pe quaternary C), 36.6 ($^1$Pe CH$_2$CH$_3$), 29.4 ($^1$Pe C(CH$_3$)$_2$), 7.9 ($^1$Pe CH$_2$CH$_3$). IR (CH$_2$Cl$_2$, cm$^{-1}$) $\nu_{max}$ 3173 (w), 2971 (s), 2930 (m), 2880 (m), 1784 (w), 1704 (s, C=O), 1559 (w), 1540 (w), 1461 (m), 1394 (m), 1380 (m), 1305 (s), 1279 (s), 1260 (s), 1193 (s), 1150 (s), 1067 (s), 1016 (s). ESI-MS m/z 598.1 (95%, [MNa]$^+$), 463.1 (23%), 422.2 (100%), 239.2 (6%). ESI-HRMS calcd. for C$_{17}$H$_{24}$AuF$_4$N$_3$NaO$_2$ ([MNa]$^+$) 598.1362; found 598.1380.

2.6 (I$^1$Pe)Au(N-mal)

A protocol similar to that used for (I$^1$Pe)Au(N-succ) gave the title compound as a white solid (using 117 mg, 267 µmol, of (I$^1$Pe)AuCl) (128 mg, 256 µmol, 96%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.05 (s, 15 H, 2H, imidazole CH), 6.54 (s, 2H, mal CH), 2.50 (q, J = 7.5 Hz, 4H, $^1$Pe CH$_2$CH$_3$), 1.82 (s, 12H, $^1$Pe C(CH$_3$)$_2$), 0.67 (t, J = 7.5 Hz, 6H, $^1$Pe CH$_2$CH$_3$). $^{13}$C NMR (400 MHz, CDCl$_3$) δ 182.3 (mal C=O), 170.7 (carbene Au-C), 135.9 (mal CH), 117.3 (imidazole CH), 61.8 ($^1$Pe quaternary C), 36.3 ($^1$Pe CH$_2$CH$_3$), 29.3 ($^1$Pe C(CH$_3$)$_2$), 7.9 ($^1$Pe CH$_2$CH$_3$). IR (CH$_2$Cl$_2$, cm$^{-1}$) $\nu_{max}$ 3680 (w), 3195 (w), 3172 (w), 3062 (w), 2971 (s), 2933 (m), 2880 (w), 1660 (s, C=O), 1608 (w), 1567 (w), 1460 (m), 1407 (w), 1393 (m), 1380 (m), 1347 (s), 1310 (w), 1228 (m), 1179 (m). ESI-MS m/z 524.2 (3%, [MNa]$^+$), 502.2
A protocol similar to that reported by de Frémont et al. was used.\(^6\) (\(^{1}\text{Pe})\text{AuBr} (40.7 \text{ mg, 89.1 } \mu\text{mol, 1 equiv.}) was dissolved in dichloromethane (2 ml), bromine (16.2 \text{ mg, 101 } \mu\text{mol, 1.1 equiv.}) was added. The orange solution was stirred at room temperature for 1 hour. The solution was reduced under vacuum to < 0.5 ml and pentane (5 ml) added to give an orange precipitate. This was separated by filtration, washed with pentane, and dried in vacuo to give the title compound as an orange powder (53.1 \text{ mg, 86.1 } \mu\text{mol, 97%}).\(^5\) \(^1\text{H NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 7.39 (s, 2H, imidazole CH)}, 2.02 (q, J = 7.5 Hz, 4H, \(^1\text{Pe CH}_2\text{CH}_3\)), 2.01 (s, 12H, \(^1\text{Pe C(CH}_3\text{)}_2\)), 0.86 (t, J = 7.5 Hz, 6H, \(^1\text{Pe CH}_2\text{CH}_3\)). \(^{13}\text{C NMR (101 MHz, CDCl}_3\text{) } \delta \text{ 135.6 (carbene Au-C), 122.2 (imidazole CH), 65.5 (}\(^1\text{Pe quaternary C}), 36.7 (}\(^1\text{Pe CH}_2\text{CH}_3\)), 29.6 (}\(^1\text{Pe C(CH}_3\text{)}_2\)), 8.6 (}\(^1\text{Pe CH}_2\text{CH}_3\)). \text{IR (CH}_2\text{Cl}_2\text{, cm}^{-1} \text{) } \nu_{\text{max}} \text{ 3200 (m), 3165 (m), 3050 (m), 2979 (s), 2941 (m), 2883 (m), 1585 (w), 1465 (m), 1413 (m), 1382 (m), 1281 (w), 1260 (s), 1199 (m), 1175 (s), 1161 (m), 1067 (w), 1033 (w), 1006 (w). ESI-MS } \text{ m/z 666.9 (100%, [MNa]^+), 507.1 (54%), 463.1 (8%), 289 (37%). ESI-HRMS calcd. for } C_{13}H_{24}AuBr_3N_2Na ([MNa]^+) 666.9027; \text{ found 666.9066.}
2.8 (I^5Pe)AuBr$_2$(N-succ) (1a)

A protocol similar to that used for 1d gave the title compound as a yellow powder (from 98.8 mg, 196 µmol, of (I^5Pe)Au(N-succ)) (127 mg, 192 µmol, 98%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 (s, 2H, imidazole CH), 2.74 (s, 4H, succ CH$_2$), 2.04 (s, 12H, I^5Pe C(CH$_3$)$_2$), 2.03 (q, $J = 7.5$ Hz, 4H, I^5Pe CH$_2$CH$_3$), 0.84 (t, $J = 7.5$ Hz, 6H, I^5Pe CH$_2$CH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 183.9 (succ C=O), 132.6 (carbene Au-C), 122.1 (imidazole CH), 65.4 (I^5Pe quaternary C), 36.8 (I^5Pe CH$_2$CH$_3$), 29.8 (I^5Pe C(CH$_3$)$_2$), 8.5 (I^5Pe CH$_2$CH$_3$). IR (CH$_2$Cl$_2$, cm$^{-1}$) $\nu_{max}$ 3686 (w), 3052 (m), 2979 (m), 2940 (w), 2882 (w), 1663 (s, C=O), 1465 (m), 1434 (w), 1414 (w), 1387 (m), 1352 (m), 1284 (m), 1230 (m), 1176 (w). MS-ESI m/z 664.0 (100%, [MH]$^+$), 593.9 (72%), 523.9 (86%), 472.9 (21%), 433.2 (34%), 414.3 (93%), 391.3 (99%), 289.1 (58%), 217.0 (42%), 149.0 (58%), 127.3 (23%).

ESI-HRMS calcd. for C$_{17}$H$_{29}$AuBr$_2$N$_3$O$_2$ ([MH]$^+$) 662.0287; found 662.0313.

2.9 (I^5Pe)AuBr$_2$(N-tfs) (1b)

A protocol similar to that used for 1d gave the title compound as a yellow powder (from 50.5 mg, 87.8 µmol, of (I^5Pe)Au(N-tfs)) (60.0 mg, 81.6 µmol, 93%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 (s, 2H, imidazole CH), 2.05 (s, 12H, I^5Pe C(CH$_3$)$_2$), 2.04 (q, $J = 7.5$ Hz, 4H, I^5Pe CH$_2$CH$_3$), 0.86 (t, $J = 7.5$ Hz, 6H, I^5Pe CH$_2$CH$_3$). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -127.1 (s, CF$_2$). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.0 (m, C=O)$^7$, 126.0 (carbene Au-C), 122.8 (imidazole CH), 107.0 (tt, $J = 269$ and 23 Hz, CF$_2$), 65.8 (I^5Pe quaternary C), 36.8 (I^5Pe CH$_2$CH$_3$), 29.7 (I^5Pe C(CH$_3$)$_2$), 8.5 (I^5Pe CH$_2$CH$_3$). IR (CH$_2$Cl$_2$, cm$^{-1}$)
\[ \nu_{\text{max}} \] 3490 (w), 3200 (w), 3166 (w), 2979 (m), 2941 (w), 2884 (w), 1819 (w), 1789 (w), 1720 (m), 1716 (s, C=O), 1586 (w), 1480 (w), 1465 (w), 1417 (w), 1387 (m), 1322 (m), 1305 (m), 1195 (s), 1156 (m), 1065 (m), 1017 (m). ESI-MS \[ m/z \] 799.0 (6%, [MNa+MeCN]+), 758.0 (100%, [MNa]+), 598.1 (3%), 463.1 (4%). ESI-HRMS calcd. for \( \text{C}_{17}\text{H}_{24}\text{AuBr}_2\text{F}_4\text{N}_3\text{NaO}_2 \) ([MNa]+) 757.9714; found 757.9703.

2.10 (I^\text{15}Pe)AuBr_2(N-mal) (1c)

\[(\text{I}^\text{15}\text{Pe})\text{Au(N-mal)}\ (30.1 \text{ mg, } 60.1 \mu \text{mol, 1 equiv.}) \text{ was dissolved in dichloromethane (1 ml), bromine (9.6 mg, 60.1 } \mu \text{mol, 1 equiv.) was added and the brown solution stirred for 1 hour at -78 \degree \text{C and warmed to room temperature. The solution was reduced } \text{in vacuo} \text{ to } < 0.5 \text{ ml and pentane (5 ml) added which produced a yellow precipitate. This was separated by filtration and washed (pentane, diethyl ether) to give the title compound as a yellow powder (34.7 mg, 52.5 } \mu \text{mol, 87%).} \]

\[ ^1\text{H NMR (400 MHz, CDCl}_3 \] \( \delta \)
7.38 (s, 2H, imidazole CH), 6.64 (s, 2H, mal CH), 2.07 (s, 12H, \( ^1\text{Pe C(CH}_3\text{)}_2 \)), 2.03 (q, \( J = 7.5 \text{ Hz, 4H, } \text{Pe CH}_2\text{CH}_3 \)), 0.86 (t, \( J = 7.5 \text{ Hz, 6H, } ^1\text{Pe CH}_2\text{CH}_3 \)). \[ ^1\text{C NMR (101 MHz, CDCl}_3 \] \( \delta \)
177.3 (mal C=O), 136.8 (mal CH), 132.0 (carbene Au-C), 122.2 (imidazole CH), 65.4 (\( ^1\text{Pe quaternary C} \)), 36.9 (\( ^1\text{Pe CH}_2\text{CH}_3 \)), 29.8 (\( ^1\text{Pe C(CH}_3\text{)}_2 \)), 8.6 (\( ^1\text{Pe CH}_2\text{CH}_3 \)). IR (\( \text{CH}_2\text{Cl}_2 \), cm\(^{-1} \)) \( \nu_{\text{max}} \) 3054 (m), 2979 (m), 2940 (w), 2883 (w), 2360 (m), 2342 (m), 1734 (m), 1676 (s, C=O), 1437 (m), 1419 (m), 1348 (s), 1269 (s), 1180 (m). ESI-MS \( m/z \) 684.0 (100%, [MNa]+), 649.2 (33%), 619.0 (9%), 524.2 (12%). ESI-HRMS calcd. for \( \text{C}_{17}\text{H}_{26}\text{AuBr}_2\text{N}_3\text{NaO}_2 \) 683.9935; found 683.9901.
2.11 General procedure for the cycloisomerisation of 3-phenylhex-5-en-1-yne

To a solution of 3-phenylhex-5-en-1-yne (2) (50.0 mg, 0.321 mmol, 1 equiv.) in dichloromethane (0.64 mL, 0.50 M) AgOTf (0.8 mg, 3.1 µmol, 0.01 equiv.) and gold complex (3.2 µmol, 0.01 equiv.) were added. The solution was stirred at 25 °C for 3 h and filtered through a plug of silica which was washed with dichloromethane (2 mL). The solution was reduced in vacuo and conversion was analyzed by ¹H NMR spectroscopy. For characterization purposes the product can be purified by column chromatography on silica-gel using petroleum ether (40-60 °C) as eluent (R.F. 0.76). Fractions containing the product were combined and reduced in vacuo to give the title compound as a white powder.

2.12 3-Phenylbicyclo[3.1.0]hex-2-ene (3a)

¹H NMR (400 MHz, CDCl₃) δ 7.45-7.2 (m, 2H), 7.38-7.33 (m, 2H), 7.26 (m, 1H), 6.48 (q, J = 2 Hz, 1H), 3.08 (ddd, J = 17, 7.5 and 2 Hz, 1H), 2.80 (ad, J = 17 Hz, 1H), 2.01 (m, 1H), 1.79 (m, 1H), 1.00 (td, J = 7.5 and 4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 139.7, 136.6, 129.6, 128.2, 126.7, 125.1, 36.3, 23.8, 17.6, 15.4. MS-EI⁺ 156 (100%, [M]+), 141 (56%), 128 (39%), 115 (43%), 102 (7%), 91 (18%), 77 (12%), 63 (5%), 51 (6%). EI⁺-HRMS calcd. for C₁₂H₁₂ ([M]+) 156.0939; found 156.0934. Data in accordance with literature.⁸
2.13 General procedure for the tandem nucleophillic substitution-cycloisomerisation of propargyl alcohols

Propargyl alcohol (4) (0.378 mmol, 1 equiv.) was dissolved in dichloromethane (2 ml, 0.2 M), allyltrimethylsilane (5) (180 µl, 1.13 mmol, 3 equiv.) was added, followed by Ag[Al(OC(CF_3)_3)_4] (16 mg, 15 µmol, 0.04 equiv.) followed by (I^9Pe)AuBr_2(N-tfs) (1b) (11 mg, 15 µmol, 0.04 equiv.). The solution was stirred in the dark at 0 °C and allowed to warm to room temperature and stirred for 15 h. The solution was filtered through a plug of silica-gel which was washed with dichloromethane (2 mL). The solution was reduced in vacuo and conversion was analyzed by ^1H NMR spectroscopy. For characterization purposes the products can be purified by column chromatography on silica-gel using petroleum ether (40-60 °C) as eluent. Fractions containing the products were combined and reduced in vacuo to give the title compounds.

2.14 1-Butyl-3-phenylbicyclo[3.1.0]hex-2-ene (3c)

Preparation by the general procedure gave the title compound as a colourless oil (from 71.1 mg, 378 µmol, of 1-phenyl-2-heptyn-1-ol (4c)) (61.1 mg, 288 µmol, 76%, 94:6 ratio of isomers). Isomer A (94%): ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.36 (m, 2H), 7.34-7.28 (at, J = 7.5 Hz, 2H), 7.21 (m, 1H), 6.35 (br s, 1H), 3.07 (ddd, J = 17, 7 and 2 Hz, 1H), 2.72 (d, J = 17 Hz, 1H), 1.74 (m, 1H), 1.56-1.33 (m, 6H), 0.97-0.91 (m, 3H), 0.84 (m, 1H), 0.28 (m, 1H). ^13C NMR (101 MHz, CDCl_3) δ 138.6, 137.7, 132.2, 128.2, 126.6, 125.1, 36.8, 36.5, 33.1, 30.8, 23.2, 22.8, 21.3, 14.2. MS-EI^+ 212 (19%, [M]^+), 170 (53%), 155 (100%), 141 (21%), 128 (14%), 115 (14%), 91 (12%), 77 (6%). EI^+HRMS calcd. for
C_{16}H_{20} ([M]^+) 212.1561; found 212.1565. \{\text{Isomer B (6\%):} \text{ Selected Peaks,} \ H^1 \text{ NMR (400 MHz, CDCl}_3\} \delta 5.81 (s, 1H), 2.77 (dd, \ J = 17 \text{ and } 6.5 \text{ Hz, } 1H), 2.32 (d, \ J = 17 \text{ Hz, } 1H), 2.09 (at, \ J = 7.5 \text{ Hz, } 2H), 0.63 (m, 1H), 0.12 (m, 1H) (other peaks overlapping with isomer A). \ C_{15} \text{ NMR (101 MHz, CDCl}_3\} \delta (\text{selected peaks}) 143.0, 128.5, 128.2, 125.9, 125.2, 38.8, 38.6, 30.5, 30.3, 26.7, 25.1, 22.4, 14.0.\} \text{ Data in accordance with literature (Isomer A).}\n
\textbf{2.15 1-Trimethylsilyl-3-phenylbicyclo[3.1.0]hex-2-ene (3d)}

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {A};
\node (b) at (1,0) {B};
\draw (a) -- (b);
\end{tikzpicture}
\end{center}

\text{Ratio A:B 68:32 (By } H^1 \text{ NMR)}

Preparation by the general procedure gave the title compound as a colourless oil (from 76.9 mg, 377 \mu \text{mol, of 1-phenyl-3-trimethylsilyl-2-propyn-1-ol (4d)}) (57.6 mg, 281 \mu \text{mol, 75\% (51\% A, 24\% B)).} \ H^1 \text{ NMR (400 MHz, CDCl}_3\} \delta 7.40-7.36 (m, 2H, A and B), 7.33-7.27 (m, 2H, A and B), 7.24-7.18 (m, 1H, A and B), 6.42 (q, \ J = 2 Hz, 1H, B), 6.34 (t, \ J = 2 Hz, 1H, A), 3.02 (apparent ddd, \ J = 17, 7 and 1.5 Hz, 1H, A and B), 2.89 (apparent ddd, \ J = 17, 2 and 1 Hz, 1H, A), 2.75 (apparent ddd, \ J = 17, 3.5 and 1.5 Hz, 1H, B), 1.96 (m, 1H, B), 1.75 (m, 1H, b), 1.69 (ddd, \ J = 7, 4 and 1 Hz, 1H, A), 0.98-0.93 (m, 1H, A and B), 0.28 (dd, \ J = 4 and 3.5 Hz, 1H, A), 0.11 (q, \ J = 4 Hz, 1H, B), 0.05 (s, 9H, A). \ C_{15} \text{ NMR (101 MHz, CDCl}_3\} \delta 139.8 (A), 139.7 (B), 136.7 (A), 136.6 (B), 132.4 (A), 129.6 (B), 128.2 (A and B), 126.7 (B), 126.5 (A), 125.1 (B), 125.0 (A), 36.7 (A), 36.3 (B), 24.1 (A), 23.8 (B), 21.9 (A), 20.5 (A), 17.6 (B), 15.4 (B), -2.4(A). \text{MS-El}^+ 228 (30\%, [M(A)]^+), 213 (10\%), 154 (100\%), 135 (19\%), 128 (8\%), 115 (10\%), 73 (48\%), 59 (15\%), 45 (11\%). \text{EI}^+/HRMS \text{ calcd. for C}_{15}H_{20}Si 228.1334 \text{ ([M]^+); found 228.1325.}
2.16 1,3-Diphenylbicyclo[3.1.0]hex-2-ene (3e)

Preparation by the general procedure gave the title compound as a white powder (from 78.6 mg, 378 µmol, of 1,3-diphenyl-2-propyn-1-ol) (80.2 mg, 346 µmol, 91%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48, (d, $J = 8$ Hz, 2H), 7.40-7.22 (m, 8H), 6.67 (s, 1H), 3.27 (dd, $J = 17$ and 7 Hz, 1H), 2.88 (d, $J = 17$ Hz, 1H), 2.00 (m, 1H), 1.68 (dd, $J = 8$ and 4 Hz, 1H), 0.82 (apparent t, $J = 4$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.4, 139.7, 136.3, 130.9, 128.4, 128.3, 127.1, 126.3, 125.7, 125.3, 39.7, 37.0, 26.7, 25.1. EI$^+$-MS m/z 232 (100%, [M]$^+$), 217 (44%), 202 (22%), 191 (6%), 153 (13%), 141 (13%), 128 (11%), 115 (14%), 91 (12%), 69 (6%). EI$^+$-HRMS calcd. for C$_{18}$H$_{16}$ ([M]$^+$) 232.1252; found 232.1243.

Data in accordance with literature.$^8$

2.17 3-(2-Naphthyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3f)

Preparation by the general procedure gave the title compound as a white powder (from 48.7 mg, 189 µmol, of 1-naphthyl-3-phenyl-2-propyn-1-ol (4f)) (36.2 mg, 128 µmol, 68%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85-7.68 (m, 5H, A and B), 7.52-7.21 (m, 7H, A and B), 6.77 (s, 1H, A), 6.73 (s, 1H, B), 3.40-3.26 (m, 1H, A and B), 2.99 (d, $J = 17$ Hz, 1H, A), 2.89 (d, $J = 17$ Hz, 1H, B), 2.09-2.00 (m, 1H, A and B), 1.78 (dd, $J = 8$ and 4 Hz, 1H, B), 1.69 (dd, $J = 8$ and 4 Hz, 1H, A), 0.89-0.83 (m, 1H, A and B). $^{13}$C NMR (101 MHz, CDCl$_3$) (Mixture of isomers A and B, all data quoted) δ 142.4, 140.0, 139.9, 139.8, 136.3, 133.7, 133.5, 132.6, 131.9, 131.7, 130.9, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 127.4, 127.1, 126.4, 126.2, 126.1, 125.7, 125.6, 125.3, 125.2, 125.2, 124.5, 123.9, 123.8, 40.0.
39.9, 37.0 (2 peaks), 26.9, 26.8, 25.5, 25.1. MS-EI+ 282 (100%, [M]+), 267 (39%), 265 (29%), 252 (19%), 239 (5%), 203 (5%), 191 (16%), 178 (6%), 165 (6%), 141 (25%). EI+HRMS calcd. for C_{22}H_{18} ([M]+) 282.1409; found 282.1418. \{Isomer A from analysis of crude product: \^H NMR (400 MHz, CDCl3) \(\delta\) 7.85-7.76 (m, 3H), 7.74-7.68 (m, 2H), 7.52-7.43 (m, 2H), 7.39-7.32 (m, 4H), 7.25 (m, 1H), 6.77 (t, \(J = 2\) Hz, 1H), 3.36 (ddd, \(J = 17, 7\) and 2 Hz, 1H), 2.99 (d, \(J = 17\) Hz, 1H), 2.05 (m, 1H), 1.69 (dd, \(J = 8\) and 4 Hz, 1H), 0.86 (t, \(J = 4\) Hz, 1H).\}

2.18 3-Mesityl-1-phenylbicyclo[3.1.0]hex-2-ene (3g)

Preparation by the general procedure gave the title compound as a white powder (from 47.3 mg, 189 \(\mu\)mol, of 1-mesityl-3-phenyl-2-propyn-1-ol (4g)) (37.5 mg, 137 \(\mu\)mol, 72%). \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 7.45-7.21 (m, 5H, A and B), 6.97-6.85 (m, 2H, A and B), 6.31 (t, \(J = 1.5\) Hz, 1H, B), 5.95 (t, \(J = 2\) Hz, 1H, A), 3.25 (ddd, \(J = 17, 7\) and 1.5 Hz, 1H, B), 3.03 (ddd, \(J = 17.5\) 7 and 2 Hz, 1H, A), 2.96 (dd, \(J = 17\) and 1 Hz, 1H, B), 2.59 (d, \(J = 17.5\) Hz, 1H, A), 2.52 (br s, 3H, B), 2.30 (m, 9H A and 6H B), 2.02-1.92 (m, 1H, A and B), 1.68 (dd, \(J = 8.5\) and 4 Hz, 1H, A), 1.24 (dd, \(J = 8.5\) and 4 Hz, 1H, B), 0.96 (t, \(J = 4\) Hz, 1H, A), 0.87 (t, \(J = 4\) Hz, 1H, B). \(^{13}\)C NMR (101 MHz, CDCl3) (Mixture of isomers A and B, all data quoted) \(\delta\) 142.8, 140.6, 138.6, 136.4, 136.3, 136.3, 135.9, 134.6, 134.5, 133.5, 131.7, 128.8, 128.3, 128.0, 126.9, 126.1, 15.5, 125.2, 40.0, 39.7, 37.0, 36.2, 27.4, 26.2, 24.5, 24.0, 20.9, 20.9, 20.1. EI+-MS m/z 274 (100%, [M]+), 259 (73%), 244 (27%), 229 (30%), 215 (15%), 202 (11%), 197 (7%), 183 (11 %), 170 (21%), 157 (17%), 141 (9 %), 133 (15%), 128 (12 %), 115 (12 %), 103 (5 %), 91 (8 %), 77 (6 %). EI+-HRMS calcd. for C_{21}H_{22} ([M]+) 274.1722; found 274.1725. \{Isomer A from analysis of crude product: \^H NMR (400 MHz, CDCl3) \(\delta\) 7.45-7.22 (m, 5H), 6.94
(s, 2H), 5.95 (t, $J = 2$ Hz, 1H), 3.03 (ddd, $J = 17.5$, 7 and 2 Hz, 1H), 2.59 (d, $J = 17.5$ Hz, 1H), 2.32 (s, 3H), 2.29 (s, 6H), 1.97 (m, 1 H), 1.68 (dd, $J = 8.5$ and 4 Hz, 1H), 0.96 (t, $J = 4$ Hz, 1H).

**2.19 3-(4-Chlorophenyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3h)**

Ratio of isomers A:B 59:41 (Crude 88:12) (By $^1$H NMR) Preparation by the general procedure gave the title compound as a white powder (from 91.7 mg, 378 µmol, of 1-(4-chlorophenyl)-3-phenyl-2-propyn-1-ol (4h)) (90.6 mg, 340 µmol, 90%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (m, 1H, B), 7.39-7.19 (m, 9H A and 8H B), 6.62 (t, $J = 1.5$ Hz, 1H, A), 6.56 (t, $J = 1.5$ Hz, 1H, B), 3.28-3.16 (m, 1H, A and B), 2.87-2.77 (m, 1H, A and B), 2.02-1.91 (m, 1H, A and B), 1.67-1.58 (m, 1H, A and B), 0.82-0.77 (m, 1H, A and B). $^{13}$C NMR (101 MHz, CDCl$_3$) (Mixture of isomers A and B, all data quoted) δ 142.1, 141.0, 140.2, 138.6, 136.1, 134.8, 132.6, 131.6, 131.3, 130.3, 128.5, 128.4, 128.3, 127.8, 127.2, 126.5, 126.3, 125.8, 123.3, 39.8, 39.3, 37.0, 36.9, 26.9, 26.7, 25.2, 25.1. MS-EI $^+$ 266 (100%, $^{35}$Cl[M]$^+$), 251 (18%), 231 (35%), 229 (11%), 215 (49%), 202 (7%), 189 (6%), 153 (11%), 141 (10%), 125 (10%), 115 (8%), 101 (6%), 91 (14%). EI$^+$-HRMS calcd. for C$_{18}$H$_{15}$Cl ([M]+$^+$) 266.0862; found 266.0865. **Isomer A from analysis of crude product: $^1$H NMR** (400 MHz, CDCl$_3$) δ 7.39-7.19 (m, 9H, ArH), 6.62 (t, $J = 1.5$ Hz, 1H), 3.21 (ddd, $J = 17$, 7 and 2 Hz, 1H), 2.81 (dd, $J = 17$, 1 Hz, 1H), 1.99 (m, 1H), 1.65 (dd, $J = 8$ and 4 Hz, 1H), 0.79 (t, $J = 4$ Hz, 1H).
3.0 NMR spectra of key compounds

\[ \text{Pe.HCl} \]

\[^1H\text{-NMR: 400 MHz in CDCl}_3\]

\[^{13}C\text{-NMR: 101 MHz in CDCl}_3\]
**(I^2Pe)AuCl**

$^1$H-NMR: 400 MHz in CDCl$_3$

$^{13}$C-NMR: 101 MHz in CDCl$_3$
$^1\text{H-NMR: 400 MHz in CDCl}_3$

$^{13}\text{C-NMR: 101 MHz in CDCl}_3$
\[ \text{(I}^\text{Pe})\text{Au(N-succ)} \]

\text{\( ^1H\)-NMR: 400 MHz in CDCl}_3

\[ \text{(I}^\text{Pe})\text{Au(N-succ)} \]

\text{\( ^{13}C\)-NMR: 101 MHz in CDCl}_3
({\textit{I}'Pe})Au(N-tfs)

$^1$H-NMR: 400 MHz in CDCl$_3$

$^{19}$F-NMR: 376 MHz in CDCl$_3$

Supplementary Material (ESI) for Chemical Communications
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(I^t)Pe)Au(N-tfs)

13C-NMR: 101 MHz in CDCl$_3$

(I^t)Pe)Au(N-mal)

1H-NMR: 400 MHz in CDCl$_3$
(I^1^Pe)Au(N-mal)

\[ \text{N} \quad \text{Au} \quad \text{N} \]

$^{13}$C-NMR: 101 MHz in CDCl$_3$

$I^1^Pe$AuBr$_3$ (1d)

\[ \text{N} \quad \text{Au} \quad \text{Br} \quad \text{Br} \quad \text{Br} \]

$^1$H-NMR: 400 MHz in CDCl$_3$
(I^3Pe)AuBr₃ (1d)

\[
\begin{array}{c}
\text{N} \\
\text{Au-Br} \\
\text{Br} \\
\end{array}
\]

\[1^3\text{C-NMR: 101 MHz in CDCl}_3\]

(II^3Pe)AuBr₂(N-succ) (1a)

\[
\begin{array}{c}
\text{N} \\
\text{Br} \\
\text{Au-N} \\
\text{Br} \\
\end{array}
\]

\[1^H\text{-NMR: 400 MHz in CDCl}_3\]
(IPe)AuBr$_2$(N-succ) (1a)

$^{13}$C-NMR: 101 MHz in CDCl$_3$

$^1$H-NMR: 400 MHz in CDCl$_3$

(IPe)AuBr$_2$(N-tfs) (1b)

$^1$H-NMR: 400 MHz in CDCl$_3$
(ItPe)AuBr2(N-tfs) (1b)

$^{19}$F-NMR: 376MHz in CDCl$_3$

(C)Pe)AuBr$_2$(N-tfs) (1b)

$^{13}$C-NMR: 101 MHz in CDCl$_3$
$^{1}$H-NMR: 400 MHz in CDCl$_3$

$^{13}$C-NMR: 101 MHz in CDCl$_3$
3-phenylbicyclo[3.1.0]hex-2-ene (3a)

$^1$H-NMR: 400 MHz in CDCl$_3$

3-phenylbicyclo[3.1.0]hex-2-ene (3a)

$^{13}$C-NMR: 101 MHz in CDCl$_3$
1-butyl-3-phenylbicyclo[3.1.0]hex-2-ene (3c)

Ratio of isomers A:B 94:6

$^1$H-NMR: 400 MHz in CDCl$_3$

13C-NMR: 101 MHz in CDCl$_3$
1-Trimethylsilyl-3-phenylbicyclo[3.1.0]hex-2-ene (3d)

Ratio A:B 68:32

$^1$H-NMR: 400 MHz in CDCl$_3$
1,3-Diphenylbicyclo[3.1.0]hex-2-ene (3e)

$^1$H-NMR: 400 MHz in CDCl$_3$

$^{13}$C-NMR: 101 MHz in CDCl$_3$
3-(2-Napthyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3f)

Ratio of isomers A:B 56:44

$^1$H-NMR: 400 MHz in CDCl$_3$

$^1$H-NMR spectra showing peaks at various ppm values for A and B isomers.

3-(2-Napthyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3f)

Ratio of isomers A:B 56:44

$^{13}$C-NMR: 101 MHz in CDCl$_3$

$^{13}$C-NMR spectra showing peaks at various ppm values.
3-Mesityl-1-phenylbicyclo[3.1.0]hex-2-ene (3g)

A and B

Ratio of isomers A:B 35:65

$^1$H-NMR: 400 MHz in CDCl$_3$

3-(2-Napthyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3f)

A and B

Crude ratio of isomers A:B 83:17

Crude $^1$H-NMR: 400 MHz in CDCl$_3$
3-Mesityl-1-phenylbicyclo[3.1.0]hex-2-ene (3g)

Ratio of isomers A:B 35:65

$^1$H-NMR: 400 MHz in CDCl$_3$

$^{13}$C-NMR: 101 MHz in CDCl$_3$
3-(4-Chlorophenyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3h)

\[
\begin{align*}
\text{A} & \quad \text{B} \\
\text{Cl} & \quad \text{Cl} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Ratio of isomers A:B 59:41

\(^1\)H-NMR: 400 MHz in CDCl\(_3\)

\[
\begin{align*}
\text{ppm} & : 7.5 & 7.0 & 6.5 & 6.0 & 5.5 & 5.0 & 4.5 & 4.0 & 3.5 & 3.0 & 2.5 & 2.0 & 1.5 & 1.0 & 0.5 & 0.0
\end{align*}
\]

3-(4-Chlorophenyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3h)

\[
\begin{align*}
\text{A} & \quad \text{B} \\
\text{Cl} & \quad \text{Cl} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Ratio of isomers A:B 59:41

\(^{13}\)C-NMR: 101 MHz in CDCl\(_3\)
4.0 X-Ray crystallography

Diffraction data were collected at 110 K on a Bruker Smart Apex diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) using a SMART CCD camera. Diffractometer control, data collection and initial unit cell determination was performed using “SMART” (v5.625 Bruker-AXS). Frame integration and unit-cell refinement software was carried out with “SAINT+” (v6.22, Bruker AXS). Absorption corrections were applied by SADABS (v2.03, Sheldrick). Structures were solved by direct methods using SHELXS-97 (Sheldrick, 1990) and refined by full-matrix least squares using SHELXL-97 (Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a “riding model” and included in the refinement at calculated positions.
4.1 Selected X-ray diffraction data

Table 1. Crystal data and structure refinement for complex (t^1Pe)AuBr$_2$(N-tfs) (1b) (CCDC deposition 753414).

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<thead>
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<th>Property</th>
<th>Value</th>
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<tbody>
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<td>C$<em>{17}$H$</em>{24}$AuBr$_2$F$_4$N$_3$O$_2$</td>
</tr>
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<td>Pbca</td>
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<tr>
<td>cell constants</td>
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<tr>
<td></td>
<td>$b = 18.242(2)$ Å, $\beta = 90^\circ$</td>
</tr>
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<td></td>
<td>$c = 18.874(2)$ Å, $\gamma = 90^\circ$</td>
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<tr>
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<tr>
<td>$Z$</td>
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<tr>
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<td>$\mu$(mm$^{-1}$)</td>
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<tr>
<td>$F$(000)</td>
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<td>Goodness-of-fit on $F^2$</td>
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<td>R indices (all data)</td>
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<td>Final R indices [I&gt;2sigma(I)]</td>
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<tr>
<td>max, min $\Delta \rho$ (e Å$^{-3}$)</td>
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</table>
5.0 References

7. Unresolved multiplet due to C-F coupling.