Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

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

Jonathan P. Reeds,[a] Adrian C. Whitwood,[a] Mark P. Healy[b] and Ian J. S. Fairlamb*[a]

[a] *Department of Chemistry, University of York, Heslington, York, YO10 5DD, United Kingdom. Fax: +44 (0)1904 434091; Tel: +44 (0)1904 432516; E-mail: ijsf1@york.ac.uk*

[b] *GlaxoSmithKline, New Frontiers Science Park, Third Avenue, Harlow, Essex, CM19 5AW, United Kingdom.*

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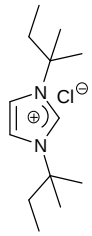
1.0 General Details

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

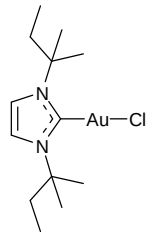
2.1 I^{t}Pe.HCl



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 *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_2CH), 7.48 (d, *J* = 2 Hz, 2H, imidazole C*H*), 2.04 (q, *J* = 7.5 Hz, 4H, ^{t}Pe CH_2CH_3), 1.75 (s, 12H, ^{t}Pe $C(CH_3)_2$), 0.75 (t, *J* = 7.5 Hz, 6H, ^{t}Pe CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3 (N_2CH), 119.7 (imidazole *C*H), 63.5 (^{t}Pe quaternary *C*), 35.3 (^{t}Pe CH_2CH_3), 27.4 ($C(CH_3)_2$), 8.1 (^{t}Pe CH_2CH_3). IR (CH_2Cl_2, cm^{-1}) υ_{max} 3657 (w), 3338 (w), 3165 (w), 3041 (w), 2972 (s), 2358 (w), 1534 (w), 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.

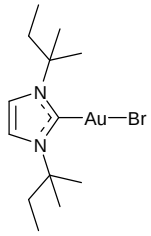
2.2 (I^{t}Pe)AuCl



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 $(Me_2S)AuCl$ (435 mg, 1.47 mmol, 1 equiv.) was added. The solution was stirred overnight at room temperature and filtered through Celite™. 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*H*), 2.48 (q, *J* = 7.5 Hz, 4H, ^{t}Pe CH_2CH_3), 1.79 (s, 12H, ^{t}Pe CH_3), 0.64 (t, *J* = 7.5 Hz, 6H, ^{t}Pe CH_2CH_3). ^{13}C NMR (400 MHz, $CDCl_3$) δ 168.1 (carbene Au-*C*), 117.3 (imidazole *C*), 61.7 (^{t}Pe quaternary *C*), 36.3 (^{t}Pe CH_2CH_3), 29.3 (^{t}Pe CH_2CH_3), 7.8 (^{t}Pe

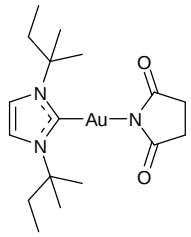
C(CH_3)$_2$). IR (CH_2Cl_2, cm^{-1}) υ_{max} 3680 (w), 3196 (w), 3172 (w), 3046 (m), 2972 (s), 2929 (m), 2880 (m), 2360 (w), 1604 (w), 1567 (w), 1460 (m), 1407 (m), 1393 (s), 1377 (s), 1339 (w), 1309 (m), 1228 (m), 1190 (s), 1152 (w). ESI-MS *m/z* 463.1 (100%, $[MNa]^+$), 226.9 (5%). ESI-HRMS calcd. for $C_{13}H_{24}AuClN_2Na$ ($[MNa]^+$) 463.1186; found 463.1186.

2.3 (I^tPe)AuBr (1e)



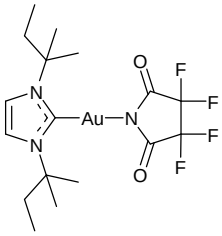
A protocol similar to that reported by de Frémont *et al* was used.[6] (I^tPe)AuCl (83.6 mg, 190 μmol, 1 equiv.) and LiBr (141 mg, 1.62 mmol, 8.5 equiv.) were dissolved in acetone (2 ml). The solution was stirred at room temperature for 24 hours to give a clear solution. The solution was then reduced 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 μmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 2H, imidazole C*H*), 2.48 (q, *J* = 7.5 Hz, 4H, ^{t}Pe CH_2CH_3), 1.81 (s, 12H, ^{t}Pe C(CH_3)$_2$), 0.65 (t, *J* = 7.5 Hz, 6H, ^{t}Pe CH_2CH_3). ^{13}C NMR (400 MHz, $CDCl_3$) δ 172.3 (carbene Au-*C*), 117.2 (imidazole *C*H), 61.8 (^{t}Pe quaternary *C*), 36.3 (^{t}Pe *C*H_2CH$_3$), 29.3 (^{t}Pe C(*C*H_3)$_2$), 7.9 (^{t}Pe CH_2*C*H_3). IR (CH_2Cl_2, cm^{-1}) υ_{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 (I^{t}Pe)Au(*N*-succ)



(I^{t}Pe)AuCl (120 mg, 269 μmol, 1 equiv.) and silver succinimidate (55.4 mg, 269 μmol, 1 equiv.) were dissolved in dichloromethane (10 ml) and stirred at room temperature for 1 hour. The suspension was filtered through Celite^{TM} and the filtrate reduced to dryness *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 μmol, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 2H, imidazole C*H*), 2.62 (s, 4H, succ CH_2), 2.48 (q, *J* = 7.5 Hz, 4H, ^{t}Pe CH_2), 1.82 (s, 12H, ^{t}Pe C(CH_3)$_2$), 0.66 (t, *J* = 7.5 Hz, 6H, ^{t}Pe CH_2CH_3). ^{13}C NMR (400 MHz, $CDCl_3$) δ 188.7 (succ *C*=O), 170.8 (carbene Au-*C*), 117.3 (imidazole *C*H), 61.9 (^{t}Pe quaternary *C*), 36.3 (^{t}Pe *C*H_2CH$_3$), 31.6 (succ *C*H_2), 29.3 (^{t}Pe C(*C*H$_3$)$_2$), 7.9 (^{t}Pe CH_2*C*H$_3$). IR (CH_2Cl_2, cm^{-1}) υ_{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]$^+$), 433.2 (21%), 363.1 (6%), 292.0 (4%), 209.2 (4%). ESI-HRMS calcd. for $C_{17}H_{29}AuN_3O_2$ ([MH]$^+$) 504.1920; found 504.1916.

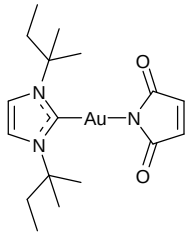
2.5 (I^{t}Pe)Au(*N*-tfs)



(I^{t}Pe)AuCl (100 mg, 228 μmol, 1 equiv.), silver(I) oxide (31.7 mg, 137 μmol, 0.6 equiv.), and tetrafluorosuccinimide (42.9 mg, 251 μmol, 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 C*H*), 2.48 (q, *J* = 7.5 Hz, 4H, ^{t}Pe CH_2CH$_3$), 1.83 (s, 12H, ^{t}Pe C(*C*H$_3$)$_2$), 0.69 (t, *J* = 7.5 Hz, 6H, ^{t}Pe CH$_2$C*H*$_3$). ^{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),[7] 167.5 (carbene Au-*C*), 117.8 (imidazole *C*H), 107.4 (tt, *J* = 267 and 22 Hz, tfs *C*F$_2$), 62.1 (^{t}Pe quaternary *C*), 36.6 (^{t}Pe *C*H$_2$CH$_3$), 29.4 (^{t}Pe C(*C*H$_3$)$_2$), 7.9 (^{t}Pe CH$_2$*C*H$_3$). IR (CH_2Cl_2, cm^{-1}) υ_{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), 1271 (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 $C_{17}H_{24}AuF_4N_3NaO_2$ ([MNa]$^{+}$) 598.1362; found 598.1380.

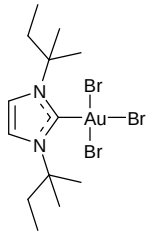
2.6 (I^{t}Pe)Au(*N*-mal)



A protocol similar to that used for (I^{t}Pe)Au(*N*-succ) gave the title compound as a white solid (using 117 mg, 267 μmol, of (I^{t}Pe)AuCl) (128 mg, 256 μmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 2H, imidazole C*H*), 6.54 (s, 2H, mal C*H*), 2.50 (q, *J* = 7.5 Hz, 4H, ^{t}Pe CH_2CH$_3$), 1.82 (s, 12H, ^{t}Pe C(C*H*$_3$)$_2$), 0.67 (t, *J* = 7.5 Hz, 6H, ^{t}Pe CH$_2$C*H*$_3$). ^{13}C NMR (400 MHz, $CDCl_3$) δ 182.3 (mal *C*=O), 170.7 (carbene Au-*C*), 135.9 (mal *C*H), 117.3 (imidazole *C*H), 61.8 (^{t}Pe quaternary *C*), 36.3 (^{t}Pe *C*H$_2$CH$_3$), 29.3 (^{t}Pe C(*C*H$_3$)$_2$), 7.9 (^{t}Pe CH$_2$*C*H$_3$). IR (CH_2Cl_2, cm^{-1}) υ_{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

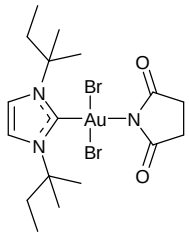
(100%, $[MH]^+$), 433.2 (46%), 363.1 (16%), 293.0 (8%), 272.8 (2%). ESI-HRMS calcd. for $C_{17}H_{27}AuN_3O_2$ ($[MH]^+$) 502.1763; found 502.1760.

2.7 (I^tPe)$AuBr_3$ (1d)



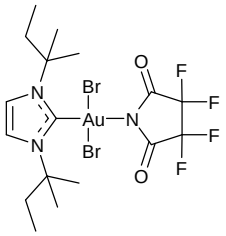
A protocol similar to that reported by de Frémont *et al.* was used.[6] (I^tPe)AuBr (40.7 mg, 89.1 μmol, 1 equiv.) was dissolved in dichloromethane (2 ml), bromine (16.2 mg, 101 μmol, 1.1 equiv.) was added. The orange solution was stirred at room temperature for 1 hour. The solution was reduced under 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 mg, 86.1 μmol, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 2H, imidazole C*H*), 2.02 (q, *J* = 7.5 Hz, 4H, ^{t}Pe CH_2CH$_3$), 2.01 (s, 12H, ^{t}Pe C(CH_3)$_2$), 0.86 (t, *J* = 7.5 Hz, 6H, ^{t}Pe CH$_2$CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6 (carbene Au-*C*), 122.2 (imidazole *C*H), 65.5 (^{t}Pe quaternary *C*), 36.7 (^{t}Pe *C*H$_2$CH$_3$), 29.6 (^{t}Pe C(*C*H$_3$)$_2$), 8.6 (^{t}Pe CH$_2$*C*H$_3$). IR (CH_2Cl_2, cm^{-1}) υ_{max} 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 *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; found 666.9066.

2.8 (I^tPe)$AuBr_2$(*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^tPe)Au(*N*-succ)) (127 mg, 192 μmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 2H, imidazole C*H*), 2.74 (s, 4H, succ CH_2), 2.04 (s, 12H, ^{t}Pe C(CH_3)$_2$), 2.03 (q, *J* = 7.5 Hz, 4H, ^{t}Pe CH_2CH$_3$), 0.84 (t, *J* = 7.5 Hz, 6H, ^{t}Pe 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 *C*H), 65.4 (^{t}Pe quaternary *C*), 36.8 (^{t}Pe *C*H$_2$CH$_3$), 31.4 (succ *C*H$_2$), 29.8 (^{t}Pe C(*C*H$_3$)$_2$), 8.5 (^{t}Pe CH$_2$*C*H$_3$). IR (CH_2Cl_2, cm^{-1}) υ_{max} 3686 (w), 3052 (m), 2979 (m), 2940 (w), 2882 (w), 1663 (s, C=O), 1540 (w), 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 $C_{17}H_{29}AuBr_2N_3O_2$ ([MH]$^+$) 662.0287; found 662.0313.

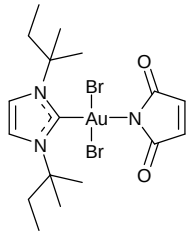
2.9 (I^tPe)$AuBr_2$(*N*-tfs) (1b)



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^tPe)Au(*N*-tfs)) (60.0 mg, 81.6 μmol, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 2H, imidazole C*H*), 2.05 (s, 12H, ^{t}Pe C(CH_3)$_2$), 2.04 (q, *J* = 7.5 Hz, 4H, ^{t}Pe CH_2CH$_3$), 0.86 (t, *J* = 7.5 Hz, 6H, ^{t}Pe 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 *C*H), 107.0 (tt, *J* = 269 and 23 Hz, CF_2), 65.8 (^{t}Pe quaternary *C*), 36.8 (^{t}Pe *C*H$_2$CH$_3$), 29.7 (^{t}Pe C(*C*H$_3$)$_2$), 8.5 (^{t}Pe *C*H$_2$*C*H$_3$). IR (CH_2Cl_2, cm^{-1})

υ_{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 $C_{17}H_{24}AuBr_2F_4N_3NaO_2$ ($[MNa]^+$) 757.9714; found 757.9703.

2.10 (I^tPe)$AuBr_2$(*N*-mal) (1c)



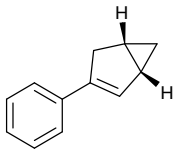
(I^tPe)Au(*N*-mal) (30.1 mg, 60.1 μmol, 1 equiv.) was dissolved in dichloromethane (1 ml), bromine (9.6 mg, 60.1 μmol, 1 equiv.) was added and the brown solution stirred for 1 hour at -78 ˚C and warmed to room temperature. The solution was reduced *in vacuo* to < 0.5 ml and pentane (5 ml) added which 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 μmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H, imidazole C*H*), 6.64 (s, 2H, mal C*H*), 2.07 (s, 12H, ^{t}Pe C(CH_3)$_2$), 2.03 (q, *J* = 7.5 Hz, 4H, ^{t}Pe CH_2CH_3), 0.86 (t, *J* = 7.5 Hz, 6H, ^{t}Pe CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3 (mal *C*=O), 136.8 (mal *C*H), 132.0 (carbene Au-*C*), 122.2 (imidazole *C*H), 65.4 (^{t}Pe quaternary *C*), 36.9 (^{t}Pe CH_2CH_3), 29.8 (^{t}Pe C(CH_3)$_2$), 8.6 (^{t}Pe CH_2CH_3). IR (CH_2Cl_2, cm^{-1}) υ_{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 $C_{17}H_{26}AuBr_2N_3NaO_2$ 683.9935; found 683.9901.

2.11 General procedure for the cycloisomerisation of 3-phenylhex-5-en-1-yne

2 **3a**

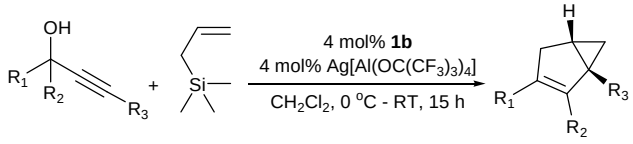
To a solution of 3-phenylhex-5-en-1-yne (**2**) (50.0 mg, 0.321 mmol, 1 equiv.) in dichloromethane (0.64 mL, 0.50 M) AgOTf (0.8 mg, 3.1 μmol, 0.01 equiv.) and gold complex (3.2 μmol, 0.01 equiv.) were added. The solution was stirred at 25 ˚C for 3 h and filtered through a plug of silica which was washed with dichloromethane (2 mL). The solution was reduced *in vacuo* and conversion was analyzed by ^{1}H 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)



^{1}H NMR (400 MHz, $CDCl_3$) 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), 0.17 (dd, *J* = 7 and 4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{12}H_{12}$ ($[M]^{+}$) 156.0939; found 156.0934. Data in accordance with literature.[8]

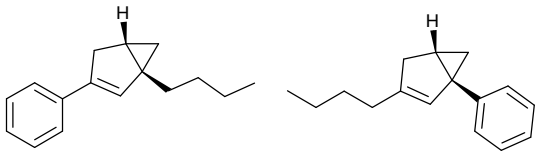
2.13 General procedure for the tandem nucleophillic substitution-cycloisomerisation of propargyl alcohols



4 **5a** **3**

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^tPe)$AuBr_2$(*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 ^{1}H 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)



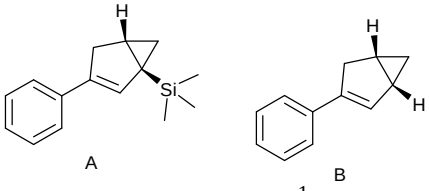
A B

Ratio of isomers A:B 94:6 (By ^{1}H NMR)

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%):** ^{1}H 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). ^{13}C 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. {**Isomer B (6%):** Selected Peaks, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (s, 1H), 2.77 (dd, *J* = 17 and 6.5 Hz, 1H), 2.32 (d, *J* = 17 Hz, 1H), 2.09 (at, *J* = 7.5 Hz, 2H), 0.63 (m, 1H), 0.12 (m, 1H) (other peaks overlapping with isomer A). ^{13}C NMR (101 MHz, $CDCl_3$) δ (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.} Data in accordance with literature (Isomer A).[9]

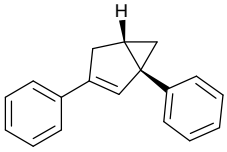
2.15 1-Trimethylsilyl-3-phenylbicyclo[3.1.0]hex-2-ene (3d)



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

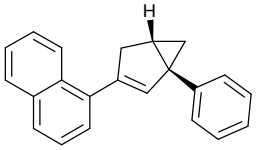
Preparation by the general procedure gave the title compound as a colourless oil (from 76.9 mg, 377 μmol, of 1-phenyl-3-trimethylsilyl-2-propyn-1-ol (**4d**)) (57.6 mg, 281 μmol, 75% (51% A, 24% B)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H, A and B), 7.33-7.27 (m, 2H, A and B), 7.24-7.18 (m, 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, 1 H, B), 1.75 (m, 1H, b), 1.69 (tdd, *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). ^{13}C NMR (101 MHz, $CDCl_3$) δ 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). MS-EI$^+$ 228 (30%, [M(A)]$^+$), 213 (10%), 154 (100%), 135 (19%), 128 (8%), 115 (10%), 73 (48%), 59 (15%), 45 (11%). EI$^+$-HRMS calcd. for $C_{15}H_{20}Si$ 228.1334 ([M]$^+$) ; found 228.1325.

2.16 1,3-Diphenylbicyclo[3.1.0]hex-2-ene (3e)

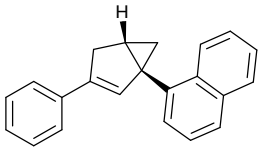


Preparation by the general procedure gave the title compound as a white powder (from 78.6 mg, 378 μmol, of 1,3-diphenyl-2-propyn-1-ol) (80.2 mg, 346 μmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8 Hz, 2H), 7.40-7.22 (m, 8H), 6.67 (s, 1H), 3.27 (dd, *J* = 17 and 7 Hz, 1H), 2.88 (d, *J* = 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-Napthyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3f)



A



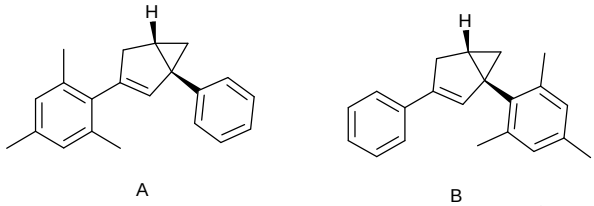
B

Ratio of isomers A:B 56:44 (Crude 83:17) (By ^{1}H NMR)

Preparation by the general procedure gave the title compound as a white powder (from 48.7 mg, 189 μmol, of 1-napthyl-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, 133.5, 132.6, 131.9, 131.7, 130.9, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 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**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 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)

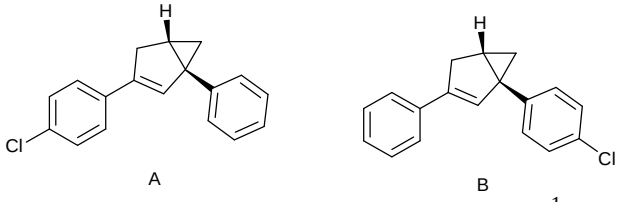


Ratio of isomers A:B 35:65 (Crude 97:3) (By ^{1}H NMR)

Preparation by the general procedure gave the title compound as a white powder (from 47.3 mg, 189 μmol, of 1-mesityl-3-phenyl-2-propyn-1-ol (**4g**)) (37.5 mg, 137 μmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) (Mixture of isomers A and B, all data quoted) δ 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:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 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).}

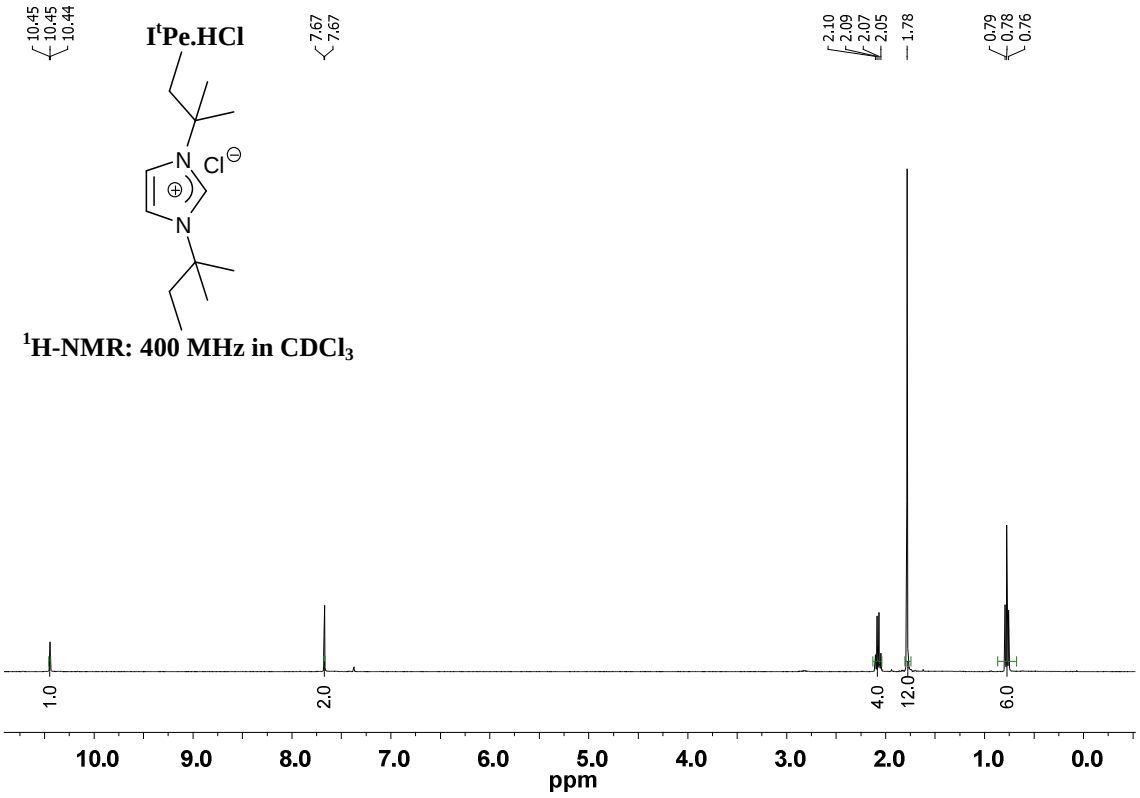
2.19 3-(4-Chlorophenyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3h)



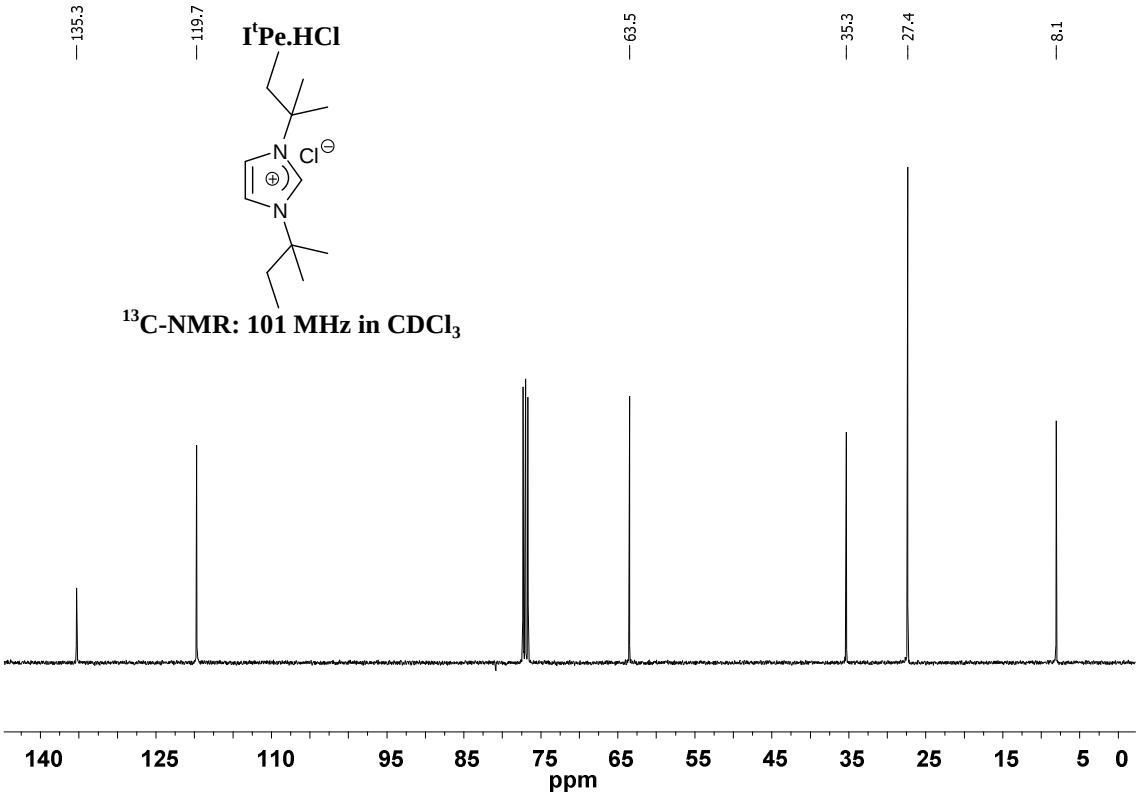
Ratio of isomers A:B 59:41 (Crude 88:12) (By ^{1}H NMR)

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

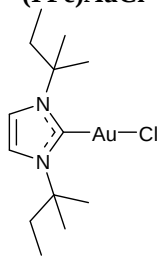


^{1}H-NMR: 400 MHz in $CDCl_3$



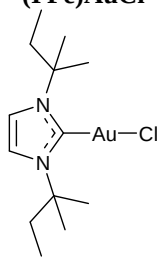
^{13}C-NMR: 101 MHz in $CDCl_3$

(I^tPe)AuCl



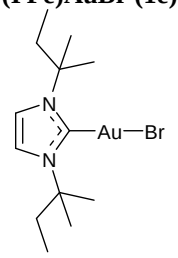
^{1}H-NMR: 400 MHz in $CDCl_3$

(I^tPe)AuCl



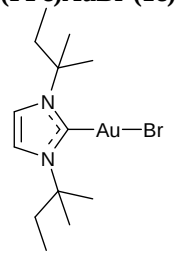
^{13}C-NMR: 101 MHz in $CDCl_3$

(I^tPe)AuBr (1e)



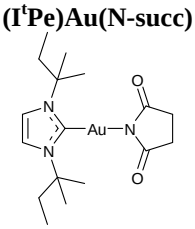
^{1}H-NMR: 400 MHz in $CDCl_3$

(I^tPe)AuBr (1e)



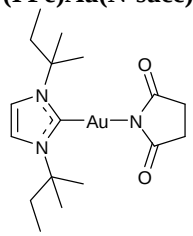
^{13}C-NMR: 101 MHz in $CDCl_3$

(I^tPe)Au(N-succ)



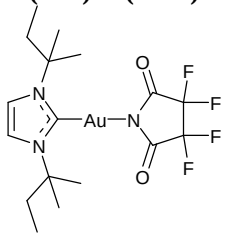
^{1}H-NMR: 400 MHz in $CDCl_3$

(I^tPe)Au(N-succ)



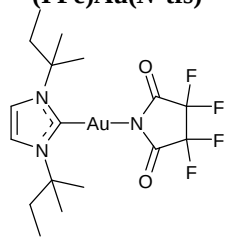
^{13}C-NMR: 101 MHz in $CDCl_3$

(I^tPe)Au(*N*-tfs)



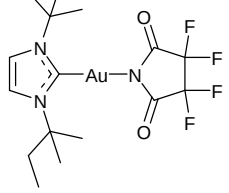
^{1}H-NMR: 400 MHz in $CDCl_3$

(I^tPe)Au(*N*-tfs)



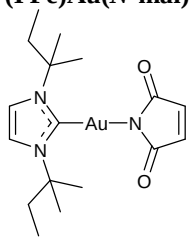
^{19}F-NMR: 376MHz in $CDCl_3$

(I^{t}Pe)Au(*N*-tfs)

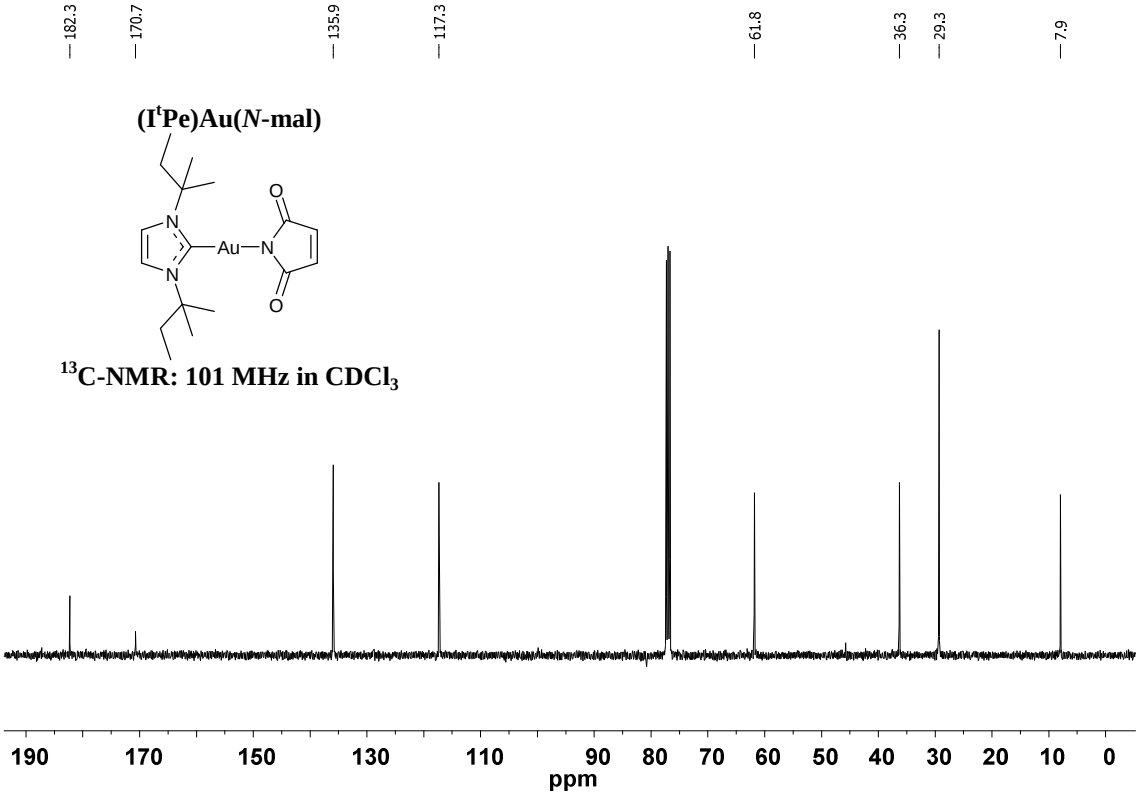


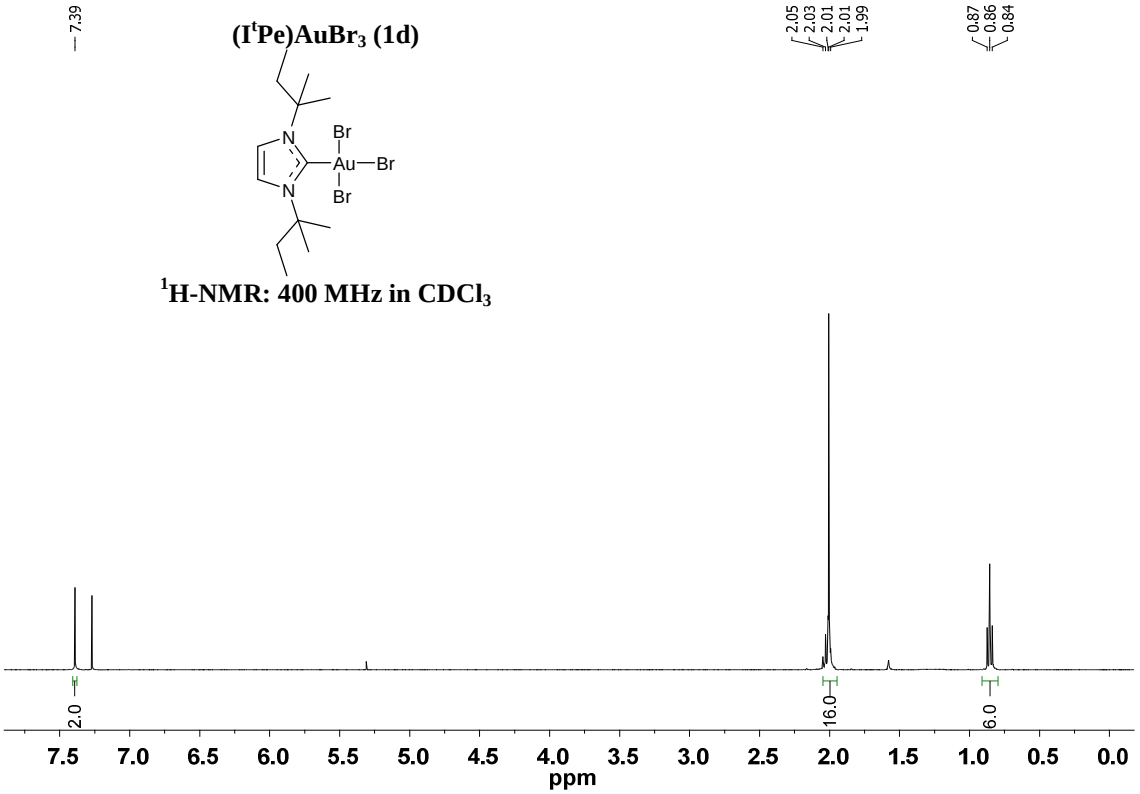
^{13}C-NMR: 101 MHz in $CDCl_3$

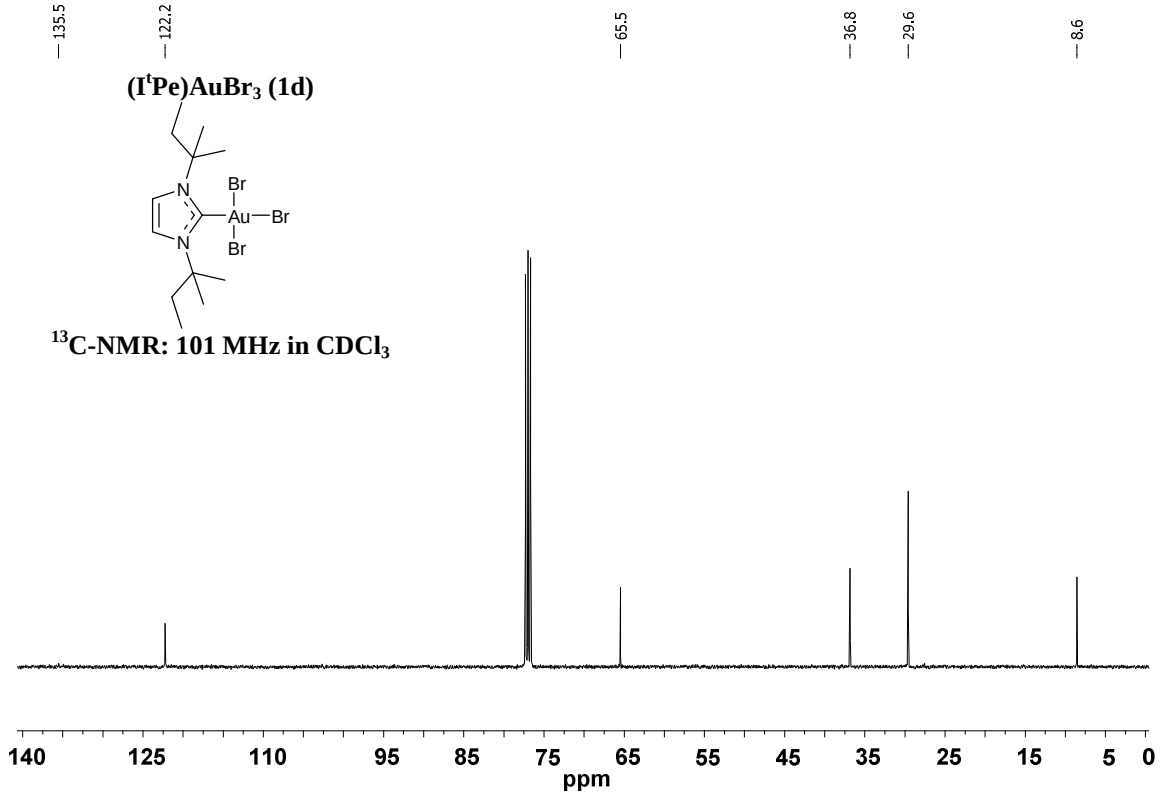
(I^{t}Pe)Au(*N*-mal)

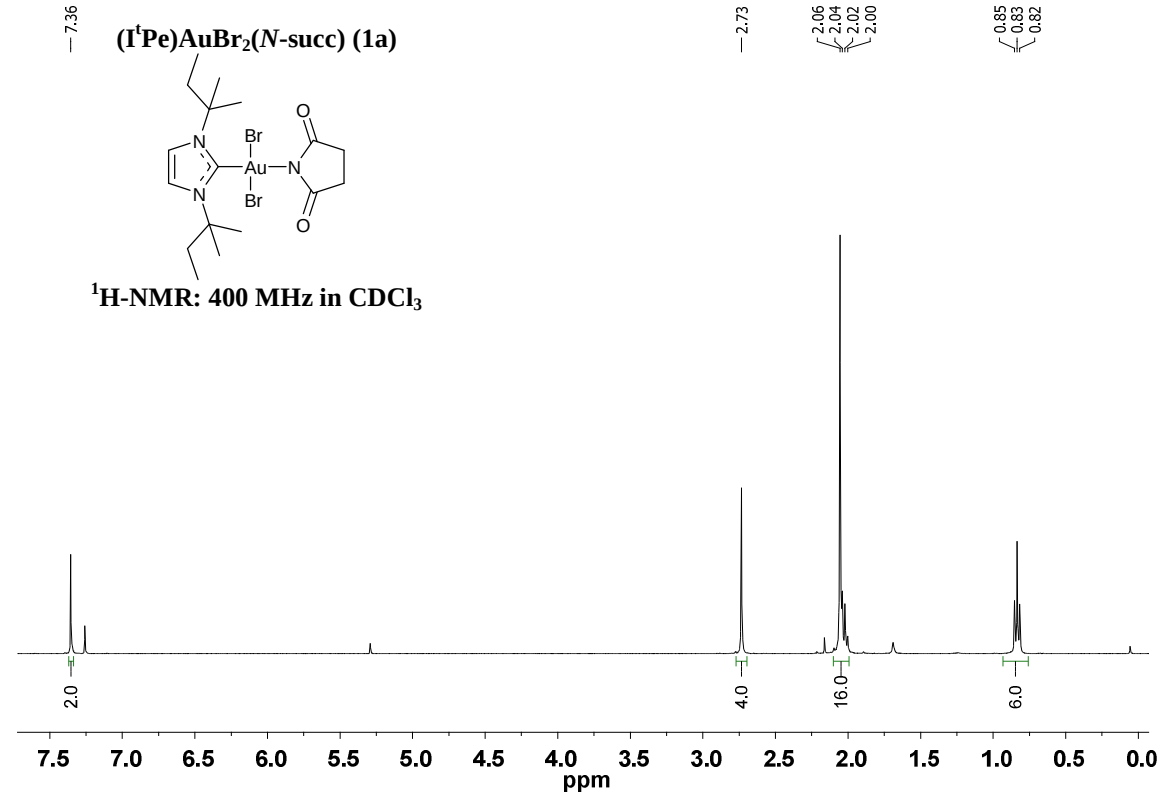


^{1}H-NMR: 400 MHz in $CDCl_3$

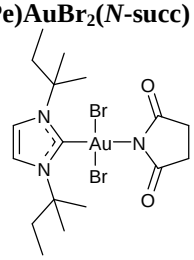

182.3
170.7
135.9
117.3
61.8
36.3
29.3
7.9
(I^{t}Pe)Au(*N*-mal)
^{13}C-NMR: 101 MHz in CDCl$_3$
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm


7.39
2.05
2.03
2.01
2.01
1.99
0.87
0.86
0.84
(I^{t}Pe)AuBr$_3$ (1d)
^{1}H-NMR: 400 MHz in CDCl$_3$
2.0
16.0
6.0
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
ppm


135.5
122.2
65.5
36.8
29.6
8.6
(I^tPe)AuBr3 (1d)
Br
Au
Br
Br
N
N
13C-NMR: 101 MHz in CDCl3
140
125
110
95
85
75
65
55
45
35
25
15
5
0
ppm

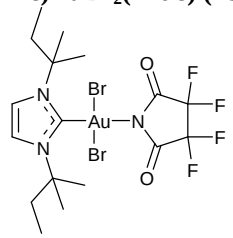

7.36
2.73
2.06
2.04
2.02
2.00
0.85
0.83
0.82
(I^tPe)AuBr2(N-succ) (1a)
Br
Au
N
Br
O
O
N
N
1H-NMR: 400 MHz in CDCl3
2.0
4.0
16.0
6.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

(I^tPe)$AuBr_2$(*N*-succ) (1a)



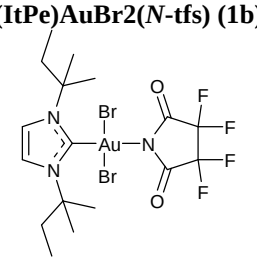
^{13}C-NMR: 101 MHz in $CDCl_3$

(I^tPe)$AuBr_2$(*N*-tfs) (1b)



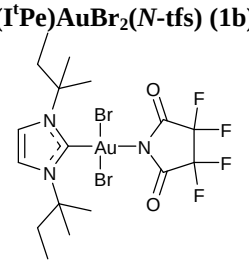
^{1}H-NMR: 400 MHz in $CDCl_3$

(ItPe)AuBr2(*N*-tfs) (1b)



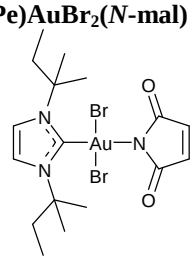
^{19}F-NMR: 376MHz in $CDCl_3$

(I^tPe)$AuBr_2$(*N*-tfs) (1b)



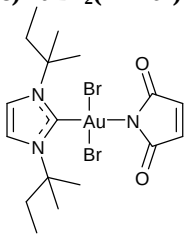
^{13}C-NMR: 101 MHz in $CDCl_3$

(I^tPe)$AuBr_2$(*N*-mal) (1c)



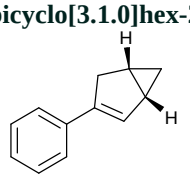
^{1}H-NMR: 400 MHz in $CDCl_3$

(I^tPe)$AuBr_2$(*N*-mal) (1c)



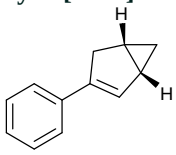
^{13}C-NMR: 101 MHz in $CDCl_3$

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

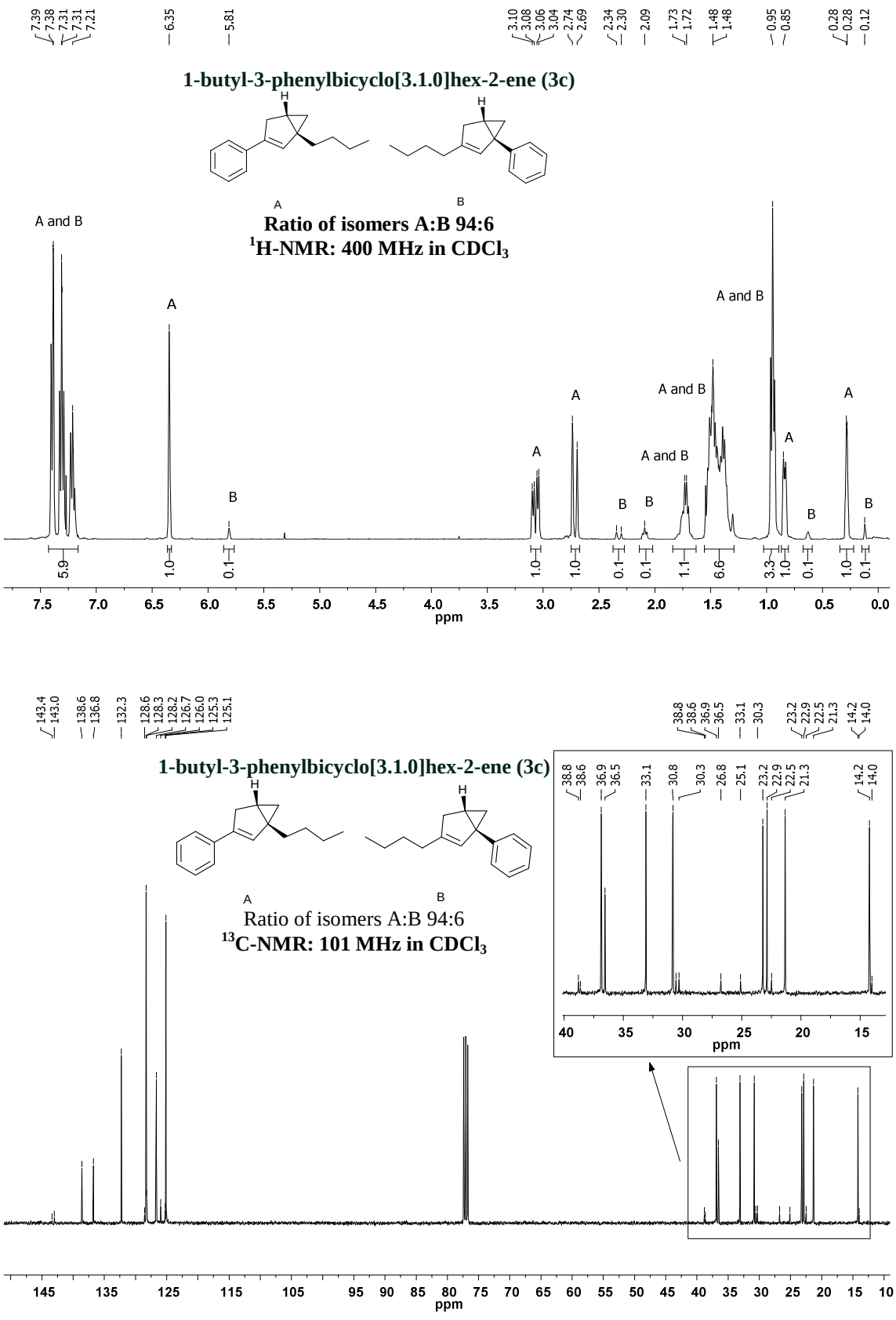


^{1}H-NMR: 400 MHz in $CDCl_3$

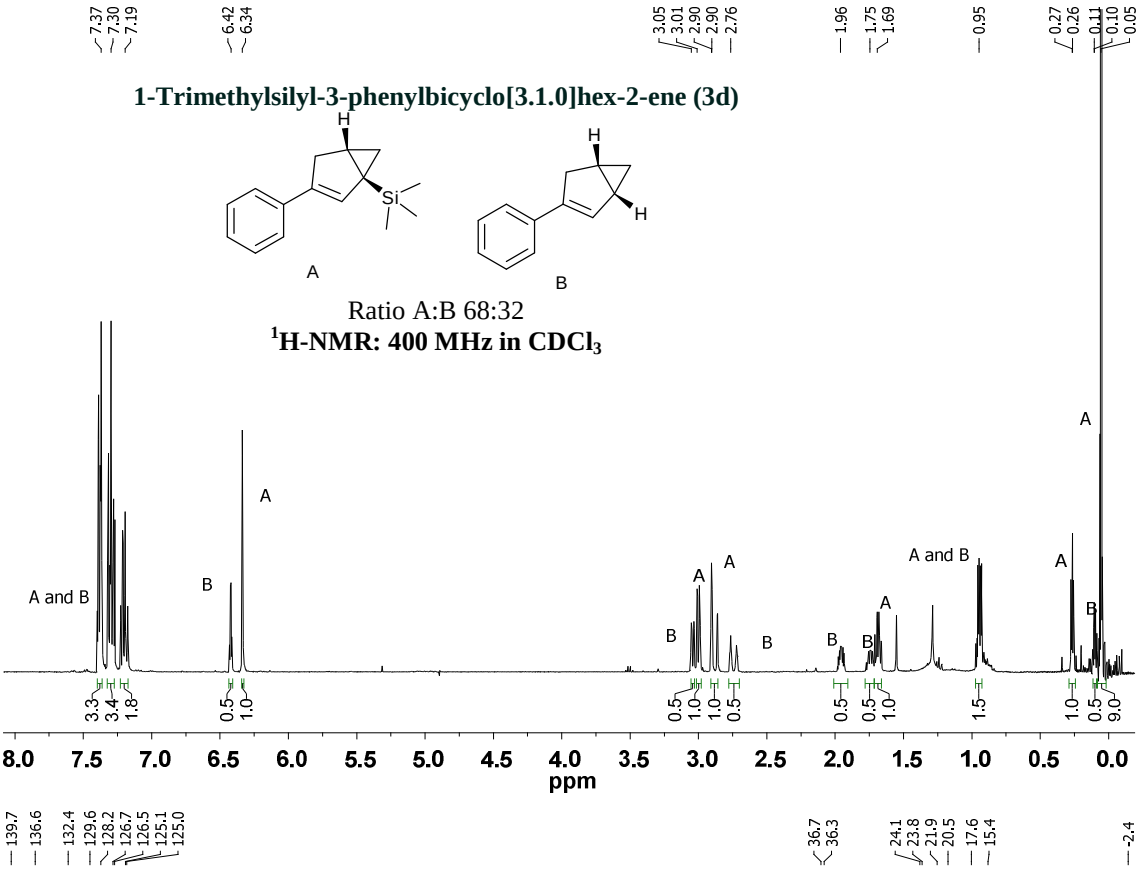
3-phenylbicyclo[3.1.0]hex-2-ene (3a)



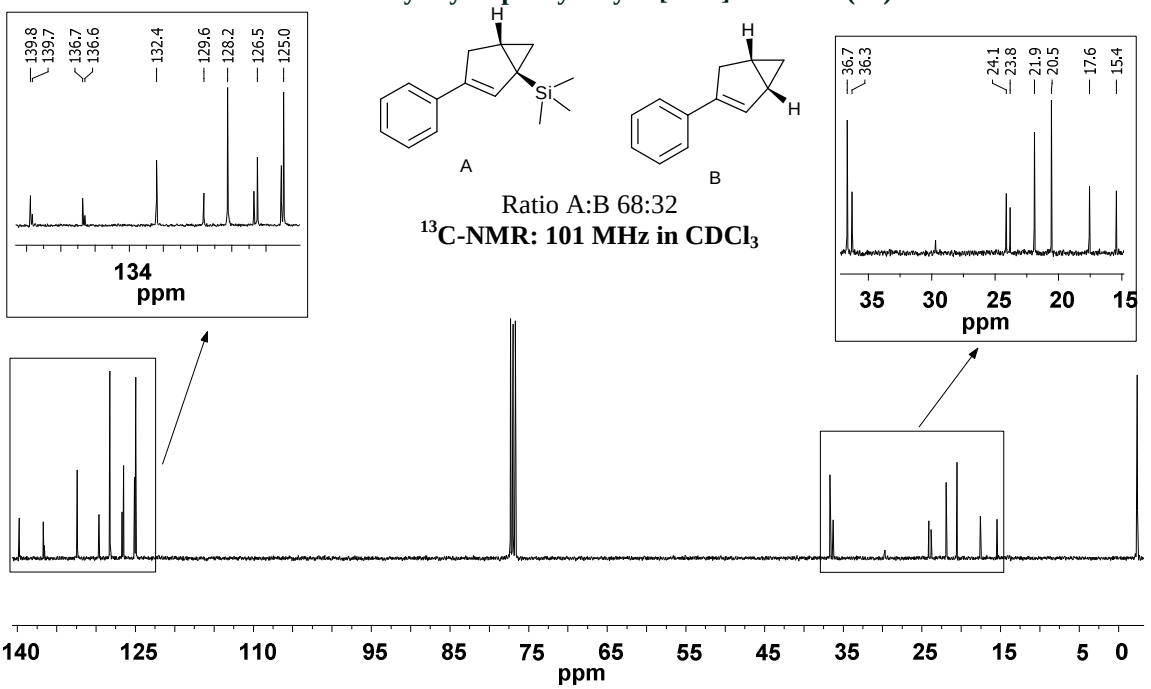
^{13}C-NMR: 101 MHz in $CDCl_3$


1-butyl-3-phenylbicyclo[3.1.0]hex-2-ene (3c)
A
B
Ratio of isomers A:B 94:6
1H-NMR: 400 MHz in CDCl3
A and B
ppm
1-butyl-3-phenylbicyclo[3.1.0]hex-2-ene (3c)
Ratio of isomers A:B 94:6
13C-NMR: 101 MHz in CDCl3
ppm

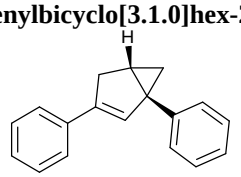
1-Trimethylsilyl-3-phenylbicyclo[3.1.0]hex-2-ene (3d)



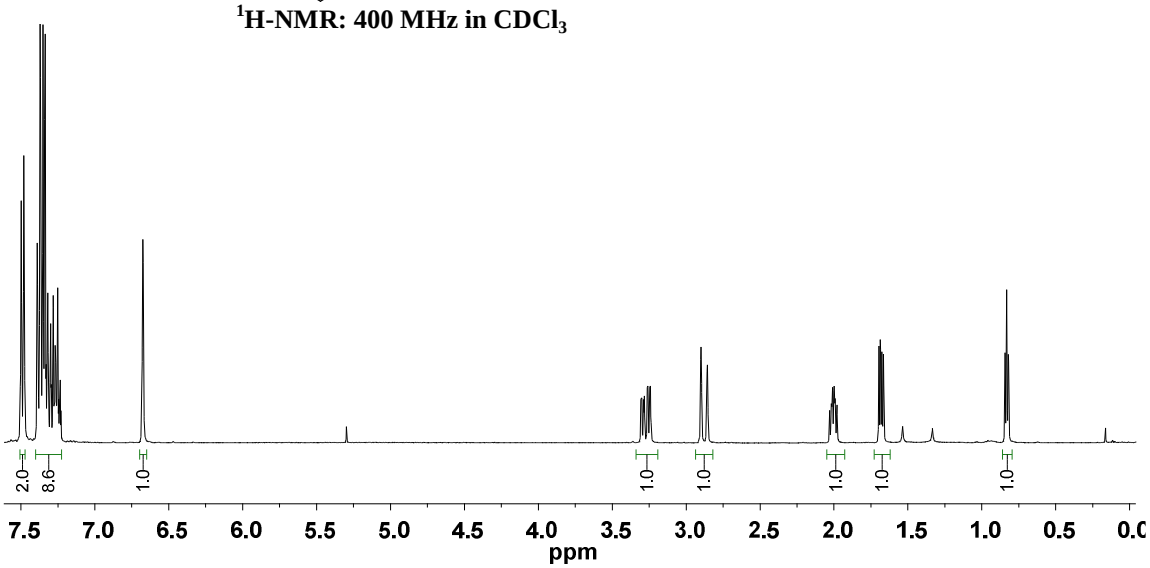
1-Trimethylsilyl-3-phenylbicyclo[3.1.0]hex-2-ene (3d)



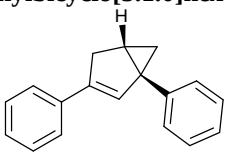
1,3-Diphenylbicyclo[3.1.0]hex-2-ene (3e)



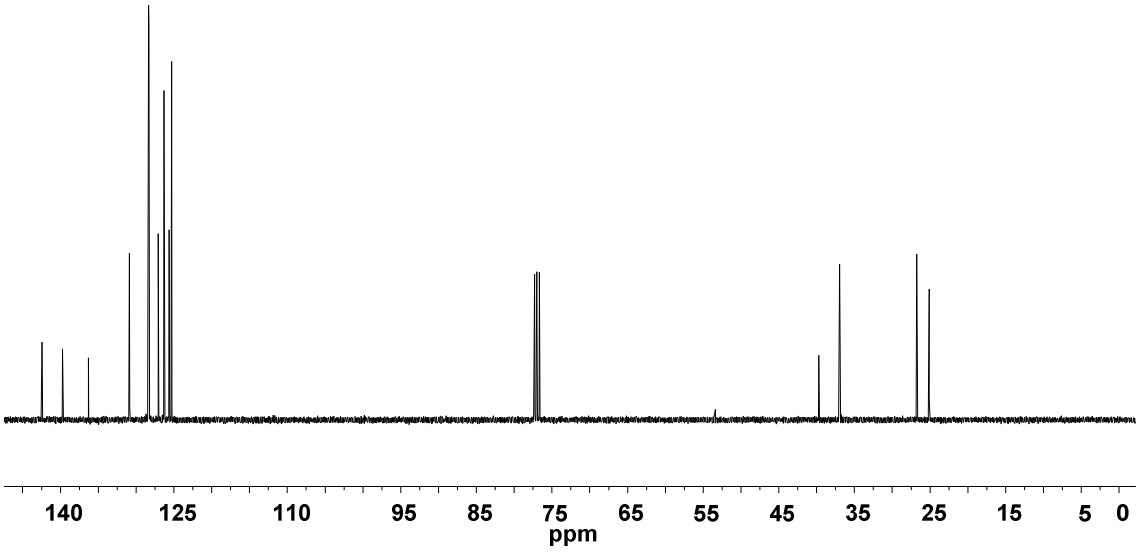
^{1}H-NMR: 400 MHz in $CDCl_3$



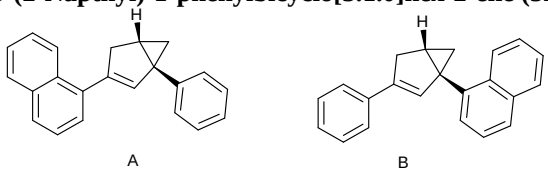
1,3-Diphenylbicyclo[3.1.0]hex-2-ene (3e)



^{13}C-NMR: 101 MHz in $CDCl_3$

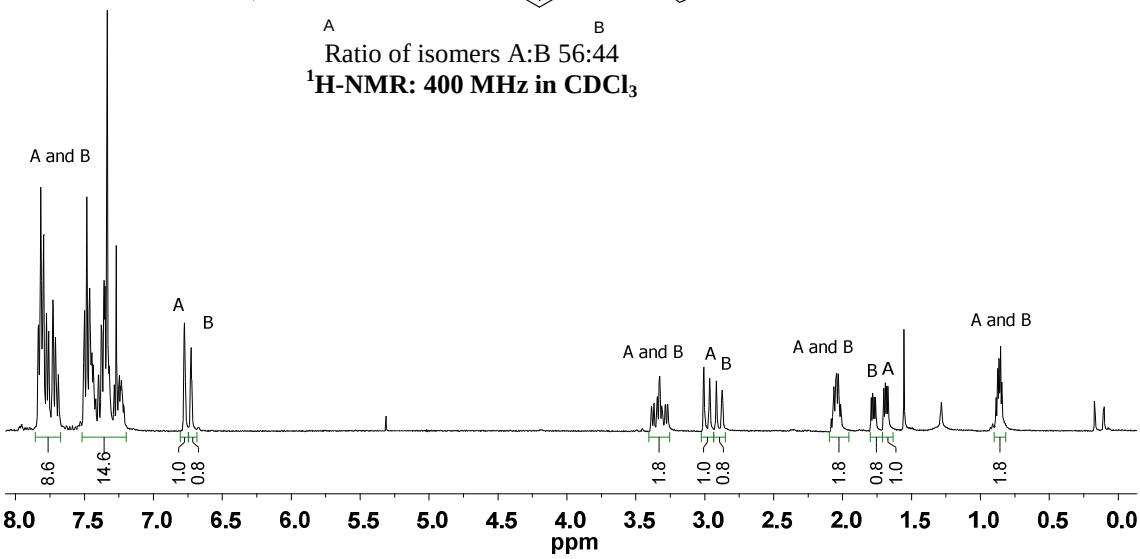


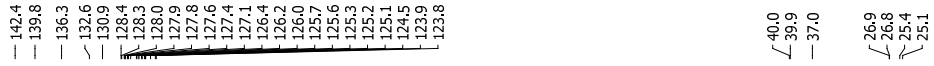
3-(2-Napthyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3f)



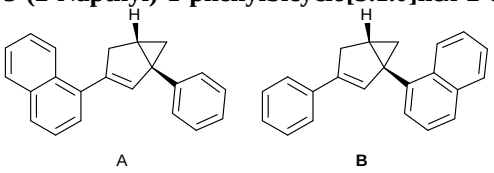
Ratio of isomers A:B 56:44

^{1}H-NMR: 400 MHz in $CDCl_3$





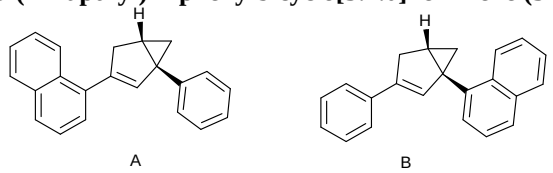
3-(2-Napthyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3f)



Ratio of isomers A:B 56:44

^{13}C-NMR: 101 MHz in $CDCl_3$

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

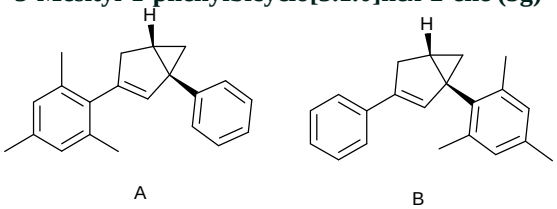


A B

Crude ratio of isomers A:B 83:17

Crude ^{1}H-NMR: 400 MHz in $CDCl_3$

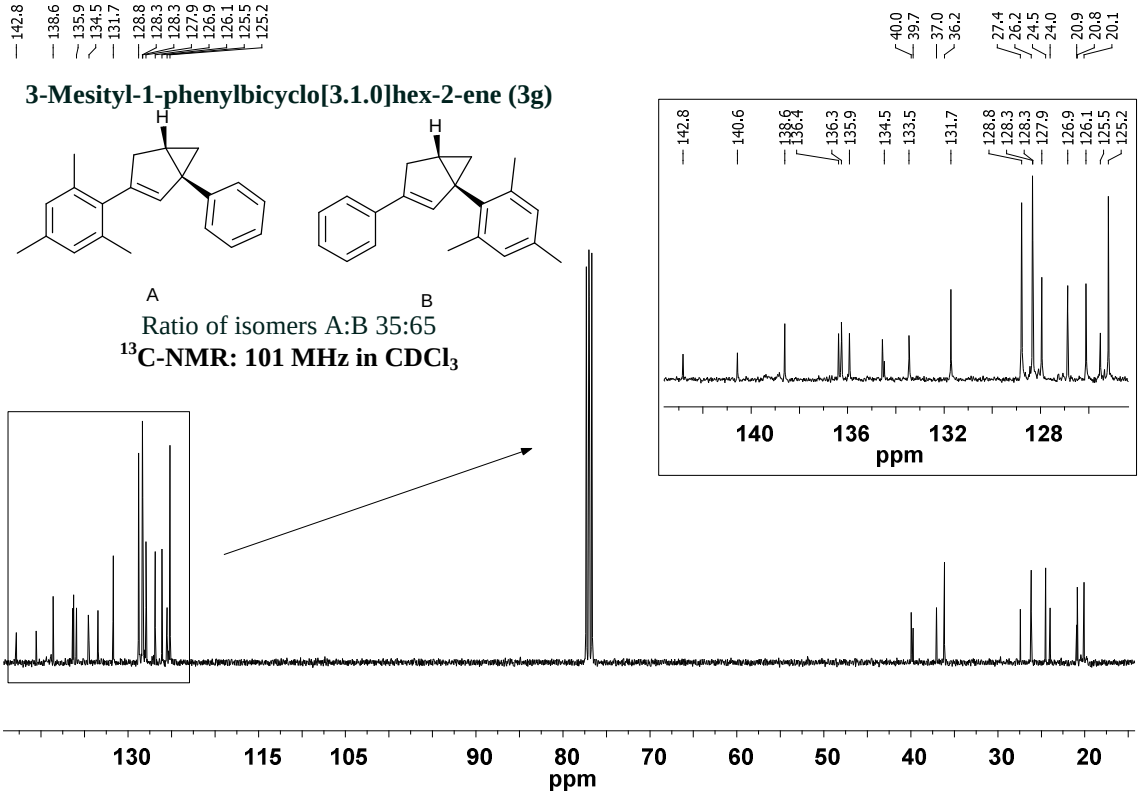
3-Mesityl-1-phenylbicyclo[3.1.0]hex-2-ene (3g)

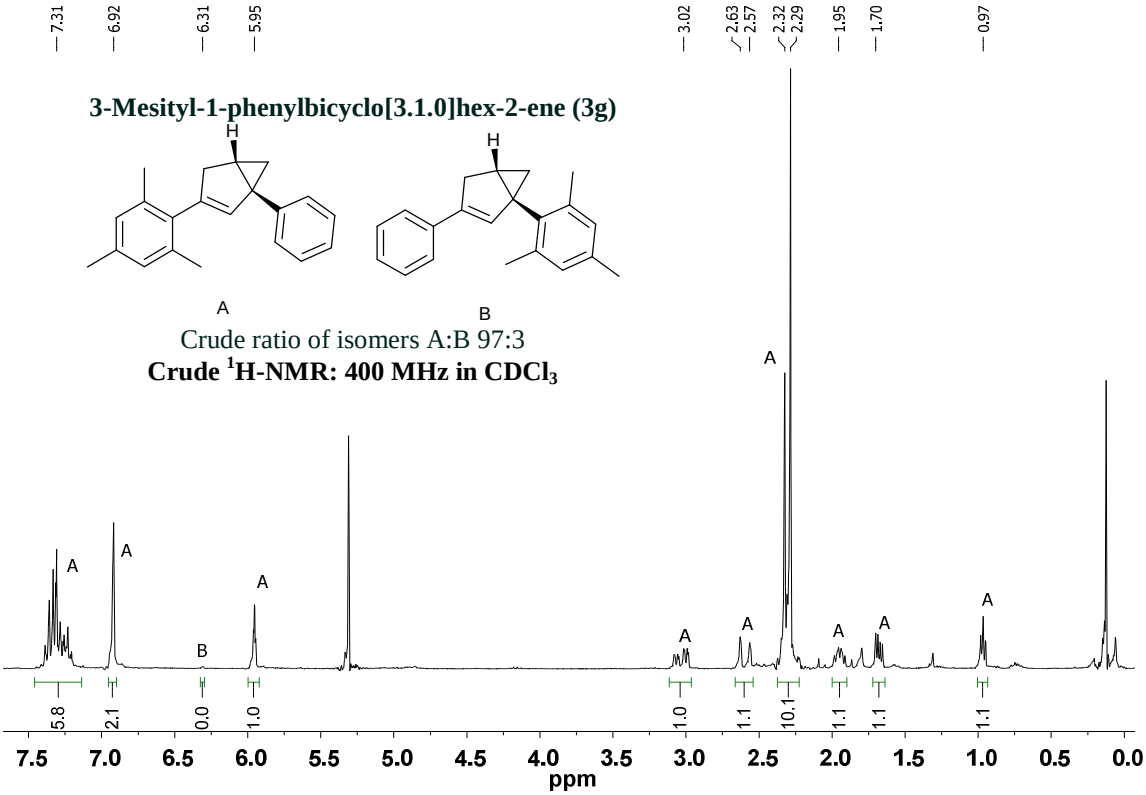


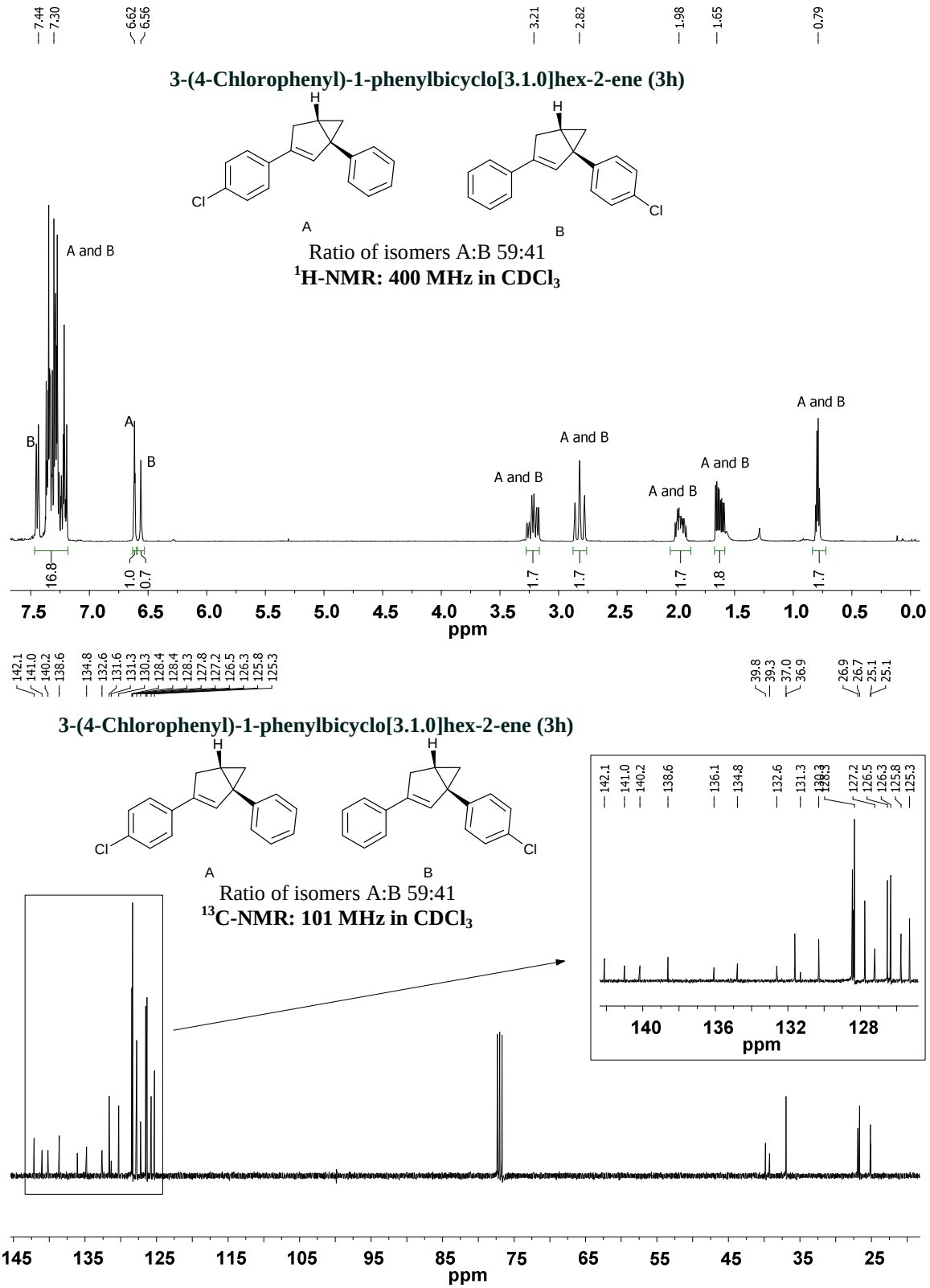
A B

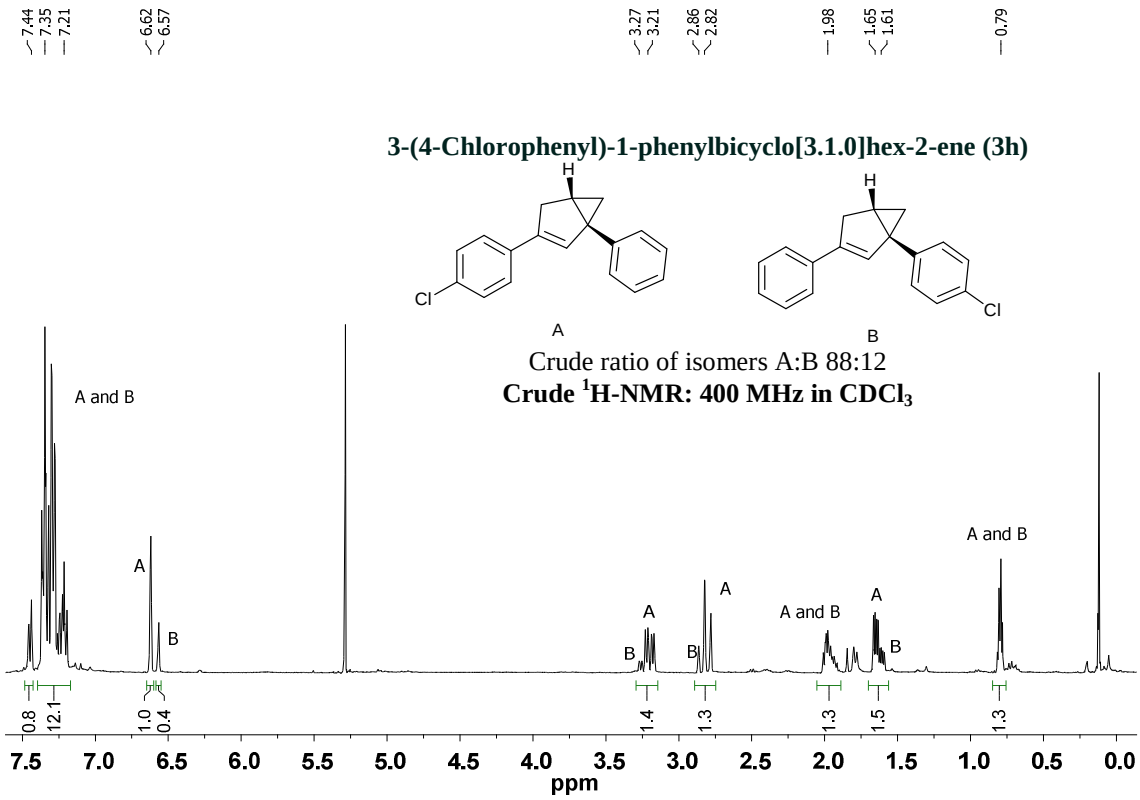
Ratio of isomers A:B 35:65

^{1}H-NMR: 400 MHz in $CDCl_3$


142.8
138.6
135.9
134.5
131.7
128.8
128.3
128.3
127.9
126.9
126.1
125.5
125.2
40.0
39.7
37.0
36.2
27.4
26.2
24.5
24.0
20.9
20.8
20.1
3-Mesityl-1-phenylbicyclo[3.1.0]hex-2-ene (3g)
H
H
A
B
Ratio of isomers A:B 35:65
13C-NMR: 101 MHz in CDCl3
142.8
140.6
138.6
136.4
136.3
135.9
134.5
133.5
131.7
128.8
128.3
128.3
127.9
126.9
126.1
125.5
125.2
140
136
132
128
ppm
130
115
105
90
80
70
60
50
40
30
20
ppm


7.31
6.92
6.31
5.95
3.02
2.63
2.57
2.32
2.29
1.95
1.70
0.97
3-Mesityl-1-phenylbicyclo[3.1.0]hex-2-ene (3g)
H
H
A
B
Crude ratio of isomers A:B 97:3
Crude 1H-NMR: 400 MHz in CDCl3
A
A
A
B
A
A
A
A
A
5.8
2.1
0.0
1.0
1.0
1.1
10.1
1.1
1.1
1.1
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
ppm


7.44
7.30
6.62
6.56
3.21
2.82
1.98
1.65
0.79
3-(4-Chlorophenyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3h)
H
Cl
A
B
Ratio of isomers A:B 59:41
1H-NMR: 400 MHz in CDCl3
A and B
A
B
16.8
1.0
0.7
1.7
1.7
1.7
1.8
1.7
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
ppm
142.1
141.0
140.2
138.6
134.8
132.6
131.6
131.3
130.3
128.4
128.4
128.3
127.8
127.2
126.5
126.3
125.8
125.3
39.8
39.3
37.0
36.9
26.9
26.7
25.1
25.1
3-(4-Chlorophenyl)-1-phenylbicyclo[3.1.0]hex-2-ene (3h)
Ratio of isomers A:B 59:41
13C-NMR: 101 MHz in CDCl3
142.1
141.0
140.2
138.6
136.1
134.8
132.6
131.3
127.2
126.5
126.3
125.8
125.3
140 136 132 128
ppm
145 135 125 115 105 95 85 75 65 55 45 35 25
ppm



4.0 X-Ray crystallography

Diffraction data were collected at 110 K on a Bruker Smart Apex diffractometer with Mo-K_α radiation (λ = 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 (I^tPe)$AuBr_2$(*N*-tfs) (**1b)** (CCDC deposition 753414).

formula	$C_{17}H_{24}AuBr_2F_4N_3O_2$	
M_r	735.18	
cryst syst	Orthorhombic	
space group	Pbca	
crystal size/mm	0.44 x 0.33 x 0.13	
cell constants	a = 13.5158(18) Å	α = 90˚
	b = 18.242(2) Å	β = 90˚
	c = 18.874(2) Å	γ = 90˚
V(Å^3)	4653.7(10)	
Z	8	
λ(Å)	0.71073	
ρ(calcd)(g/cm^3)	2.099	
μ(mm^{-1})	9.806	
F(000)	2784	
T(K)	110(2)	
$2\theta_{max}$ (deg)	60.12	
no. of rflns measd	66257	
no. of indep rflns	6784	
R_{int}	0.0403	
no. of data/restraints/params	6784 / 91 / 332	
Goodness-of-fit on F^2	1.439	
R indices (all data)	R_1 = 0.0502, ωR_2 = 0.1011	
Final R indices [I>2sigma(I)]	R_1 = 0.0430, ωR_2 = 0.0989	
max, min $\Delta\rho$ (e Å^{-3})	+1.345, -1.236	

5.0 References

1. A. L. Henne and W. F. Zimmer, *J. Am. Chem. Soc.*, 1951, **73**, 1103-1104.
2. T. Schwier, M. Rubin and V. Gevorgyan, *Org. Lett.*, 2004, **6**, 1999-2000.
3. R. Sanz, A. Martínez, J. M. Álvarez-Gutiérrez and F. Rodríguez, *Eur. J. Org. Chem.*, 2006, 1381-1386.
4. L. Jafarpour, E. D. Stevens and S. P. Nolan, *J. Organomet. Chem.*, 2000, **606**, 49.
5. M. V. Baker, P. J. Barnard, S. K. Brayshaw, J. L. Hickey, B. W. Skelton and A. H. White, *Dalton Trans.*, 2005, 37-43.
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7. Unresolved multiplet due to C-F coupling.
8. M. R. Luzung, J. P. Markham and F. D. Toste, *J. Am. Chem. Soc.*, 2004, **126**, 10858-10859.
9. R. Sanz, A. Martinez, D. Miguel, J. M. Alvarez-Gutierrez and F. Rodriguez, *Synthesis*, 2007, **20**, 3252-3256.