Electronic Supplementary Information for

Bis(bipyridine) Ruthenium(II) Bis(phosphido) Metalloligand: Synthesis of Heterometallic Complexes and Application to Catalytic Alkyne Semi-hydrogenation

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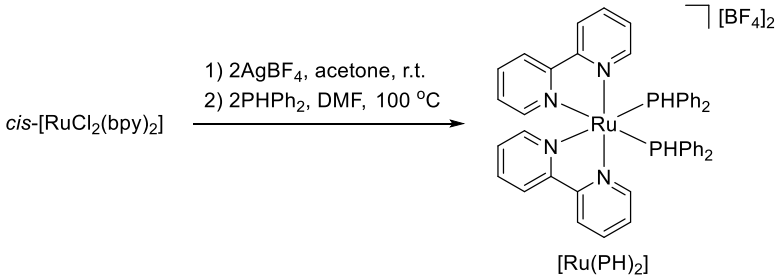
General Considerations

All operations were performed under a nitrogen atmosphere using standard Schlenk techniques, employing dry solvents and glassware unless otherwise noted. The compounds *cis*-$[RuCl_2(bpy)_2]\cdot 2H_2O$[1] and $[M(cod)_2][BF_4]$ (M = Rh, Ir)[2] were prepared by the literature methods. Deuterated solvents were degassed by freeze-pump-thaw cycles and stored over molecular sieves which had been dried at 300 °C under vacuum overnight. Other reagents were used as received from commercial venders. NMR spectra were obtained on JEOL JMN-AL400 or ECS 400 spectrometers. ^1H NMR chemical shifts are reported in parts per million (ppm) relative to residual solvent peaks (7.26 ppm for $CDCl_3$, 1.93 ppm for CD_3CN, 5.31 ppm for CD_2Cl_2, and 2.50 ppm for DMSO-d_6). $^{13}C\{^1H\}$ NMR chemical shifts were also reported relative to the solvent peak (39.52 ppm for DMSO-d_6, 53.84 ppm for CH_2Cl_2, and 1.32 ppm for CD_3CN). $^{31}P\{^1H\}$ NMR chemical shifts were reported relative to H_3PO_4. Elemental analyses were performed on a Perkin Elmer 2400 Series II analyzer. UV-vis and FT-IR spectra were recorded on JASCO V-630 and FT/IR-4100 spectrometers, respectively.

Synthetic Procedure

Synthesis of *cis*-$[(bpy)_2Ru(PHPh_2)_2][BF_4]_2$ ($[Ru(PH)_2]$)



A stirred slurry of *cis*-$[RuCl_2(bpy)_2]\cdot 2H_2O$ (973.5 mg, 1.871 mmol) in acetone (3 mL) was treated with $AgBF_4$ (910.5 mg, 2.5 equiv) dissolved in acetone (4 mL). The mixture was stirred in the dark for 2 h and then filtered. The deep red filtrate was evaporated to dryness, and the residue dissolved in DMF (10 mL). Diphenylphosphine (1.30 mL, 4 equiv) was added to the solution, and it was stirred at 100 °C for 12 h. After removal of DMF in vacuo, the residue was washed with several portions of methanol (total 50 mL) to leave a yellow solid, which was further washed with diethyl ether (30 mL) and finally dried in vacuo. Yield 1.188 g (1.238 mmol, 66%). Anal. Calcd for $C_{47}H_{46}B_2F_8N_4P_2Ru$: C, 55.08; H, 3.99; N, 5.84. Found: C, 55.08; H, 3.81; N, 5.80. ^1H NMR (400 MHz, DMSO-d_6): δ 8.79 (d, J = 5.6 Hz, 2H), 8.62 (d, J = 8.0 Hz, 2H), 8.50 (d, J = 8.2 Hz, 2H), 8.27 (dt, J = 7.3, 1.2 Hz, 2H), 8.04 (dt, J = 6.6, 1.3

Hz, 2H), 7.65 (m, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.34 (t, J = 6.6 Hz, 2H), 7.29 (t, J = 7.7 Hz, 2H), 7.20 (t, J = 7.0 Hz, 4H), 7.15-7.00 (m, 14H), 7.60-6.67 (2H, PH, AA'XX' pattern, J_{AX} = 368 Hz, $J_{A'X}$ = 8 Hz, $J_{AA'}$ = 4 Hz, $J_{XX'}$ = 16 Hz). $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6): δ 36.3 (s). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ 156.56, 154.58, 154.29, 148.83, 139.44, 139.25, 131.26 (t, J_{CP} = 4.0 Hz), 130.92 (t, J_{CP} = 3.9 Hz), 130.52, 130.31, 129.18 (t, J_{CP} = 4.5 Hz), 129.05 (t, J_{CP} = 4.0 Hz), 128.30, 128.10, 125.38, 124.37.

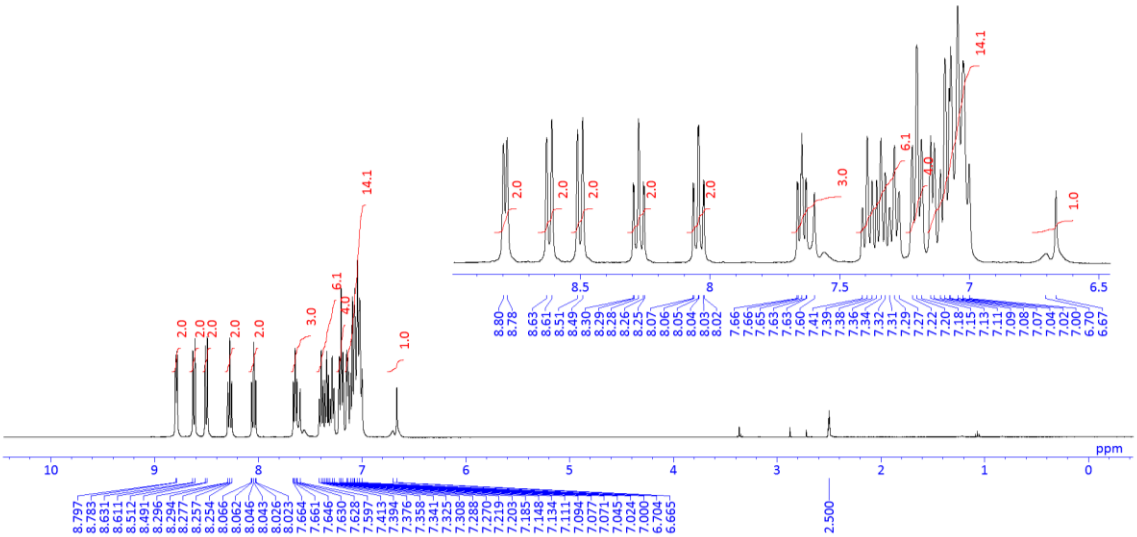


Fig. S1 ^{1}H NMR spectrum of [Ru(PH)$_2$] (400 MHz, DMSO-d_6).

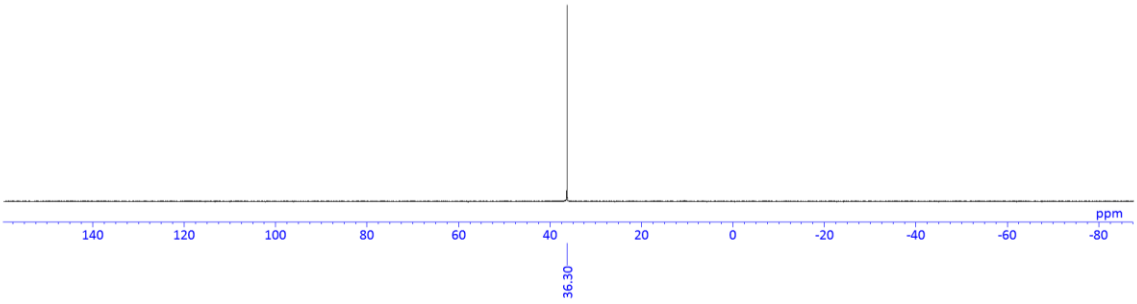


Fig. S2 $^{31}P\{^{1}H\}$ NMR spectrum of [Ru(PH)$_2$] (162 MHz, DMSO-d_6).

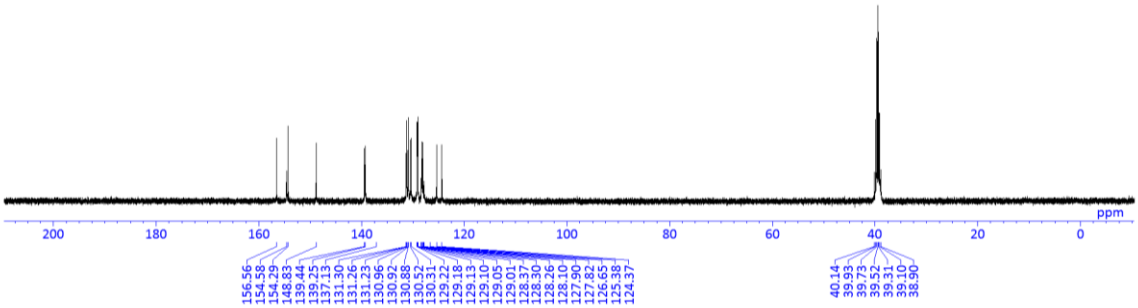


Fig. S3 $^{13}C\{^{1}H\}$ NMR spectrum of [Ru(PH)$_2$] (100 MHz, DMSO-d_6).

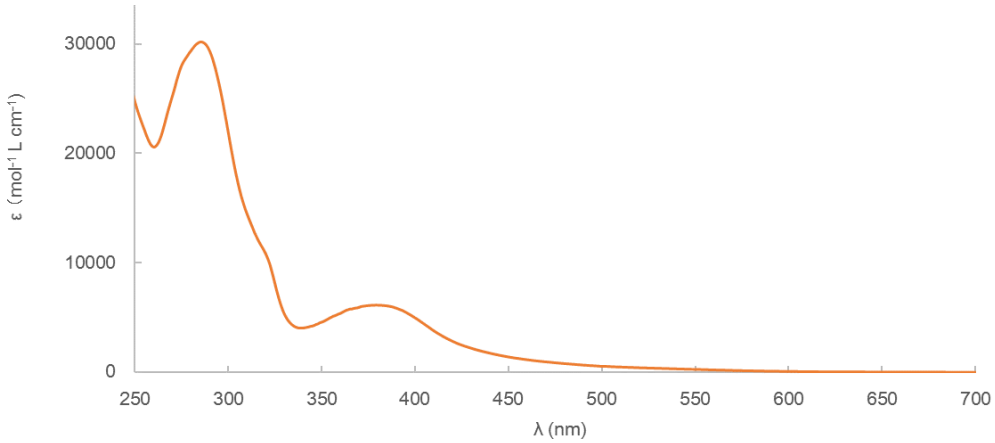
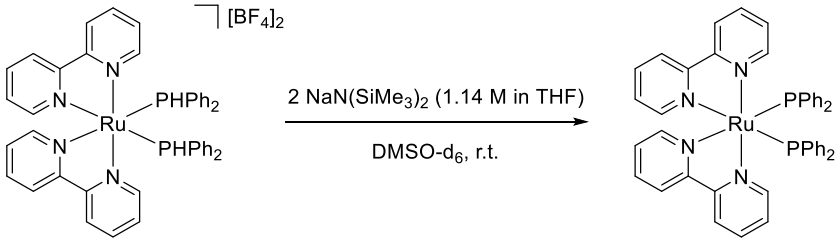


Fig. S4 UV-vis spectrum of $[Ru(PH)_2]$ (DMF).

Generation of *cis*-$[(bpy)_2Ru(PPh_2)_2]$ ($[RuP_2]$)



To a stirred solution of $[Ru(PH)_2]$ (50.6 mg, 0.0527 mmol) in DMSO-d_6 (0.8 mL) was added $NaN(SiMe_3)_2$ (1.14 M in THF, 0.10 mL, 2.2 equiv) at room temperature to form a dark green solution. THF was removed under reduced pressure, and the resulting DMSO-d_6 solution was analyzed by NMR spectroscopy, which showed the formation of $[RuP_2]$ as a major product. A separate run in the presence of $Ph_3P{=}O$ as an internal standard indicated 73% NMR yield of $[RuP_2]$. ^1H NMR (400 MHz, DMSO-d_6): δ 10.25 (m, 2H), 8.29 (d, J = 8.0 Hz, 2H), 8.06 (d, J = 8.0 Hz, 2H), 7.73 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 6.4 Hz, 2H), 7.14 (m, 8H), 6.64 (m, 12H), 6.53 (t, J = 6.0 Hz, 2H), 6.46 (d, J = 5.2 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6): δ 31.4 (s). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 157.78, 154.95, 154.48, 154.08, 150.69, 150.35, 147.32, 133.10, 132.76, 132.66, 132.56, 126.10, 124.56, 123.94, 122.55, 122.29, 121.74.

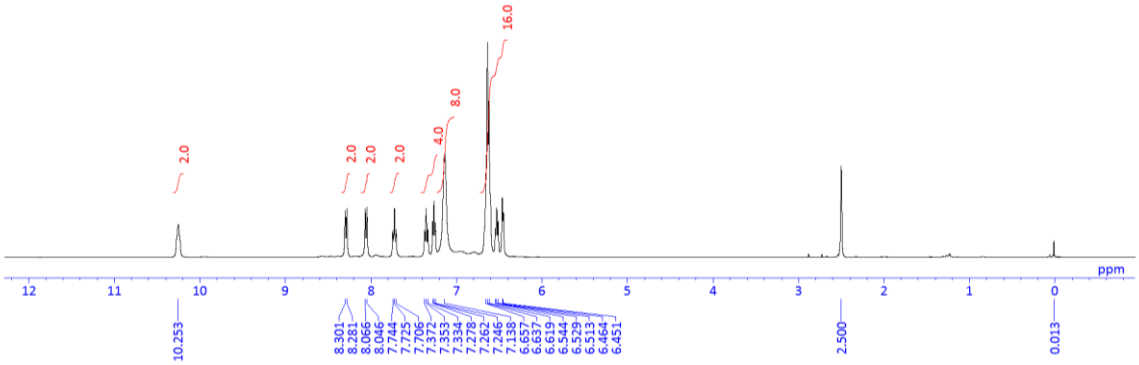


Fig. S5 ^{1}H NMR spectrum of [RuP_2] (400 MHz, DMSO-d_6).

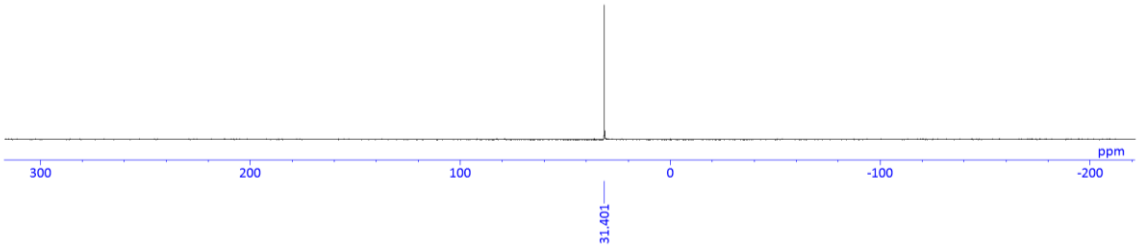


Fig. S6 $^{31}P\{^{1}H\}$ NMR spectrum of [RuP_2] (162 MHz, DMSO-d_6).

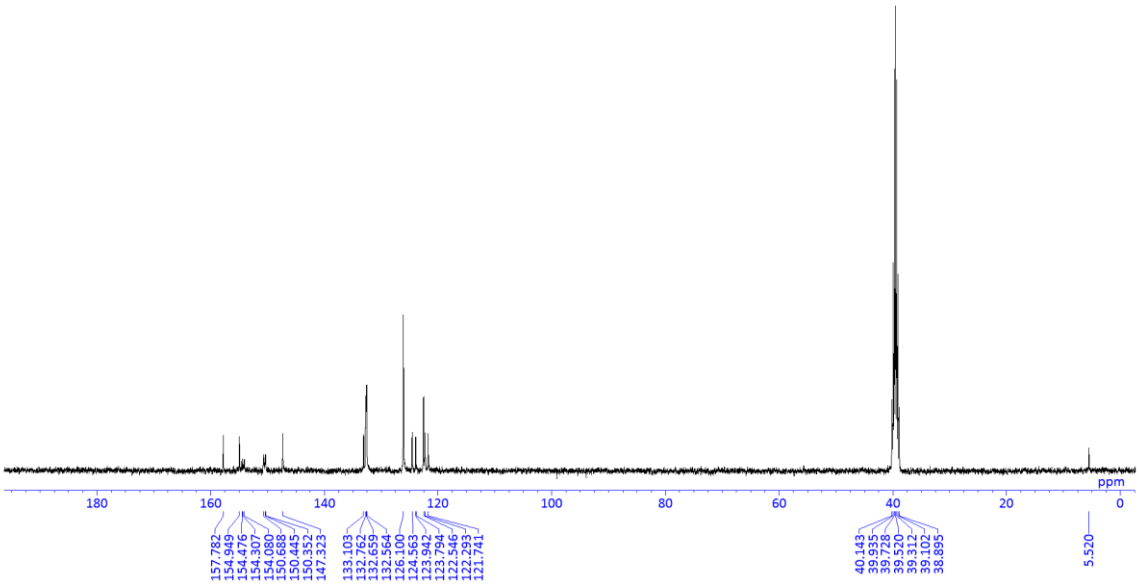
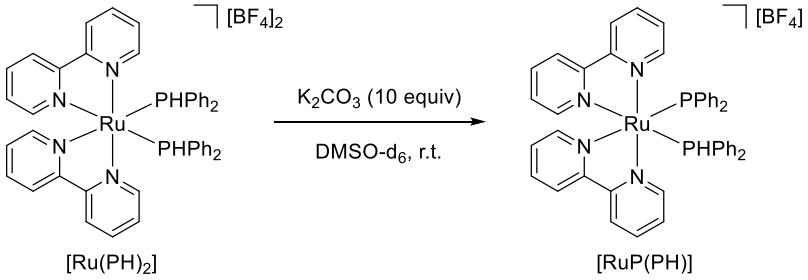


Fig. S7 $^{13}C\{^{1}H\}$ NMR spectrum of [RuP_2] (100 MHz, DMSO-d_6).

Generation of *cis*-[(bpy)$_2$Ru(PPh$_2$)(PHPh$_2$)][BF$_4$] ([RuP(PH)])



A stirred solution of [Ru(PH)$_2$] (50.9 mg, 0.053 mmol) in DMSO-d$_6$ (0.8 mL) was treated with K_2CO_3 (73 mg, 10 equiv) at room temperature. The resulting dark green slurry was filtered, and the filtrate was analyzed by NMR spectroscopy, which showed the formation of [RuP(PH)]. A separate run in the presence of $Ph_3P{=}O$ as an internal standard indicated 95% NMR yield of [RuP(PH)]. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.46 (dd, J = 8.0, 4.4 Hz, 1H), 7.36 (t, J = 6.4 Hz, 2H), 7.27 (d, J = 4.4 Hz, 1H), 7.22 (d, J = 6.4 Hz, 1H), 7.06 (d, J = 6.8 Hz, 1H), 6.98 (t, J = 6.0 Hz, 1H), 6.86 (m, 2H), 6.66 (t, J = 6.4 Hz, 1H), 6.54 (t, J = 5.2 Hz, 1H), 6.33-5.92 (m, 25.5H, aryl + a half of P-H), 5.34 (d, J = 6.0 Hz, 0.5 H, a half of P-H). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d$_6$): δ 44.63 (d, $^2J_{PP}$ = 9.7 Hz), 25.37 (d, $^2J_{PP}$ = 9.7 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ 157.45, 156.78, 154.95, 154.16, 154.04, 153.97, 153.77, 153.38, 148.61, 147.81, 145.48, 145.13, 137.37, 137.04, 136.48, 135.37, 133.45, 131.58, 131.51, 130.78, 130.72, 129.60, 128.95, 128.82, 128.74, 128.12, 128.04, 126.99, 126.76, 126.71, 126.26, 124.75, 124.01, 123.66, 123.61, 122.63.

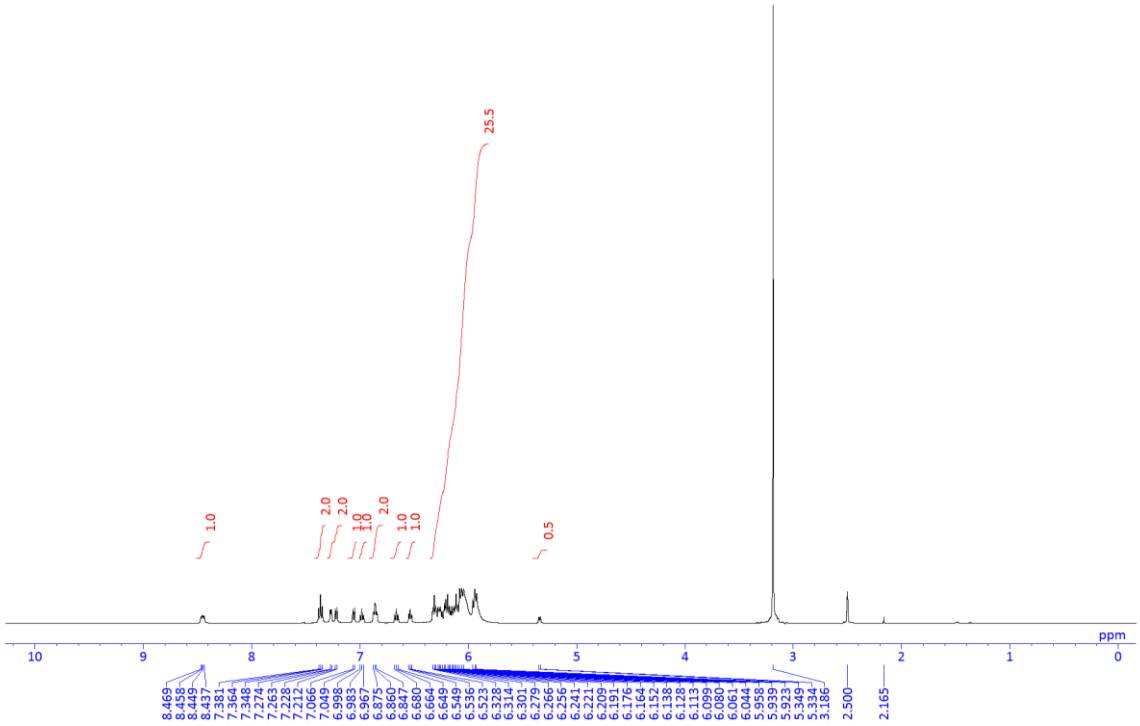


Fig. S8 ^{1}H NMR spectrum of [RuP(PH)] (400 MHz, DMSO-d$_6$). The signal at 3.19 ppm is due to H_2O contaminated from K_2CO_3.

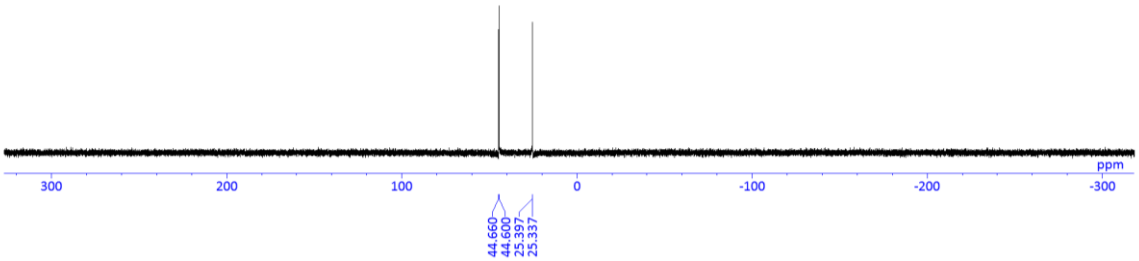


Fig. S9 $^{31}P\{^{1}H\}$ NMR spectrum of [RuP(PH)] (162 MHz, DMSO-d_6).

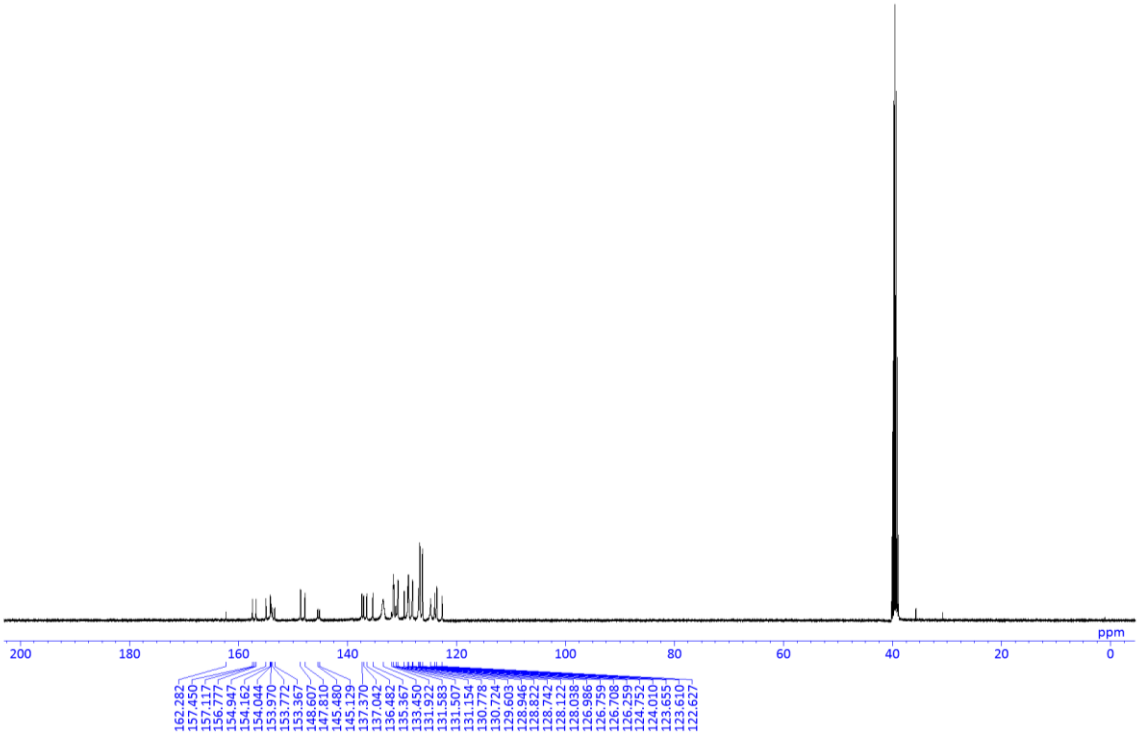
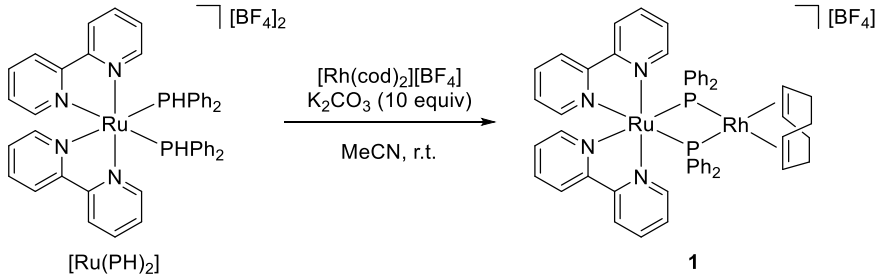


Fig. S10 $^{13}C\{^{1}H\}$ NMR spectrum of [RuP(PH)] (100 MHz, DMSO-d_6).

Synthesis of [([RuP$_2$])Rh(cod)][BF$_4$] (1)



In a Schlenk tube [Ru(PH)$_2$] (27.9 mg, 0.030 mmol) and [Rh(cod)$_2$][BF$_4$] (12.2 mg, 0.030 mmol) were dissolved in MeCN (2 mL), and the yellow solution was treated with K_2CO_3 (42.0 mg, 0.30 mmol). The resulting red slurry was stirred for 1 h and filtered. The filtrate was evaporated to dryness, and the residue was extracted with CH_2Cl_2 (15 mL). Dilution of the

extract with diethyl ether (35 mL) caused precipitation of a reddish brown solid, which was collected by filtration, washed three times with diethyl ether (3 mL), and dried in vacuo. Yield 30.1 mg (0.0278 mmol, 93%). Anal. Calcd. for $C_{52}H_{48}N_4P_2RuRhBF_4$: C, 57.74; H, 4.47; N, 5.18. Found: C, 57.72; H, 4.45; N, 5.21. ^{1}H NMR (400 MHz, CD_3CN): δ 9.18 (d, J = 5.2 Hz, 2H), 8.16 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 7.87 (t, J = 7.6 Hz, 2H), 7.60-7.55 (m, 8H), 7.22 (m, 6H), 7.09 (t, J = 2.0 Hz, 2H), 6.93 (t, J = 6.4 Hz, 2H), 6.86 (m, 6H), 6.56 (t, J = 7.6 Hz, 4H), 4.32 (m, 4H, cod olefinic), 2.46 (m, 2H, cod CH_2), 2.28 (m, 2H, cod CH_2), 2.13 (m, 2H, cod CH_2), 1.95 (m, 2H, cod CH_2). ^{31}P {^{1}H} NMR (162 MHz, CD_3CN): δ -52.5 (d, J_{RhP} = 107.4 Hz). ^{13}C {^{1}H} NMR (100 MHz, CD_3CN): δ 158.63, 158.43 (t, J = 3.3 Hz), 150.617, 142.38 (t, J = 6.1 Hz), 141.770 (t, J = 4.1 Hz), 136.81 (t, J = 4.0 Hz), 136.77, 136.71, 134.78 (t, J = 4.0 Hz), 129.49, 128.63, 128.46 (t, J = 4.0 Hz), 127.63 (t, J = 4.2 Hz), 127.10, 126.60, 126.12, 124.29, 123.33, 92.13 (dt, J = 7.6, 4.0 Hz), 91.51 (dt, J = 7.6 Hz, 4.0 Hz), 31.713, 30.358.

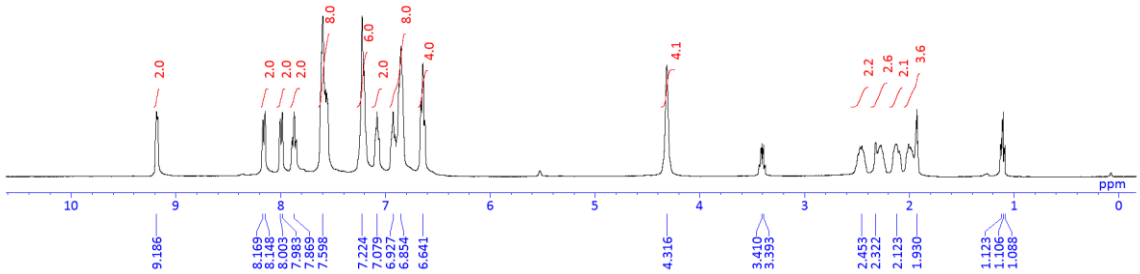


Fig. S11 ^{1}H NMR spectrum of [([RuP_2])Rh(cod)][BF_4] (**1**) (400 MHz, CD_3CN).

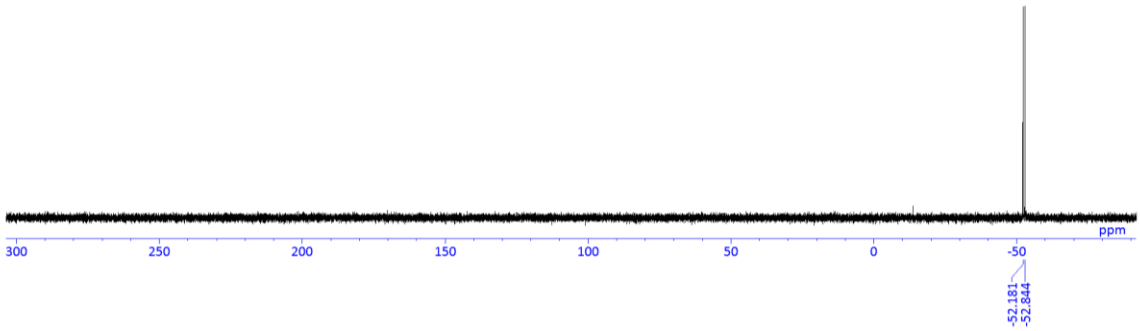


Fig. S12 ^{31}P{^{1}H} NMR spectrum of [([RuP_2])Rh(cod)][BF_4] (**1**) (162 MHz, CD_3CN).

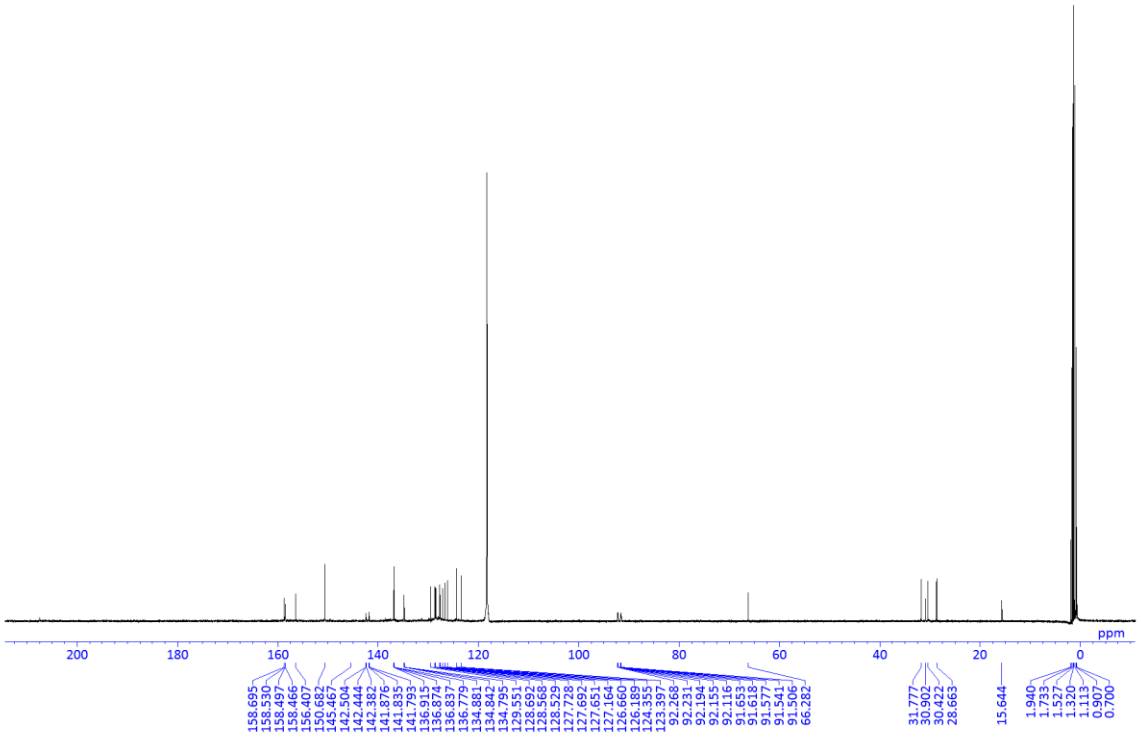


Fig. S13 $^{13}C\{^{1}H\}$ NMR spectrum of [([RuP_2])Rh(cod)][BF_4] (**1**) (100 MHz, CD_3CN).

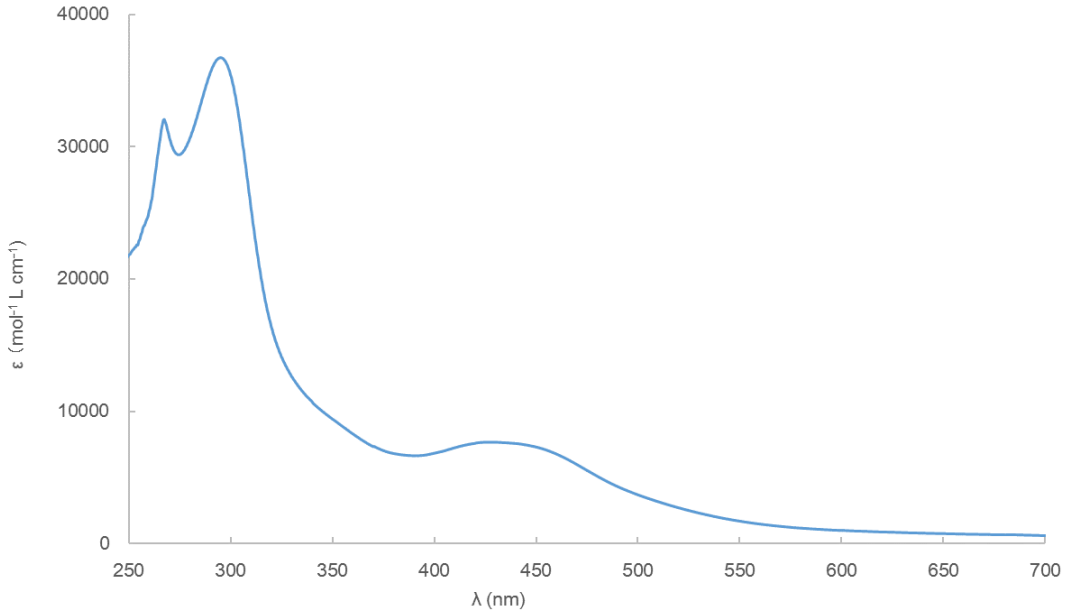
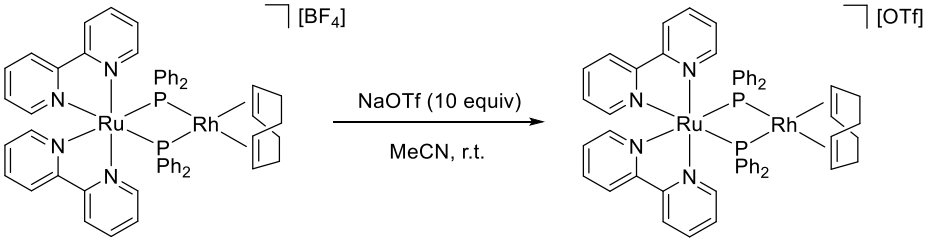


Fig. S14 UV-vis spectrum of [([RuP_2])Rh(cod)][BF_4] (**1**) in DMF.

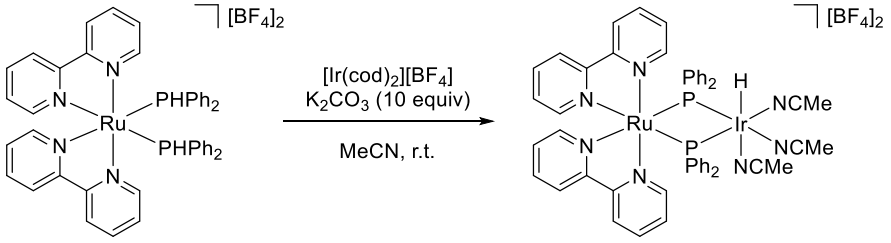
Synthesis of [([RuP$_2$])Rh(cod)][OTf] (1')



1 **1'**

Complex **1** (63 mg, 0.058 mmol) and NaOTf (107 mg, 0.62 mmol) were dissolved in MeCN (5 mL). The solution was stirred for 2 h. The solvent was removed in vacuo, and the residue extracted with CH_2Cl_2 (20 mL). The extract was filtered, concentrated to ca. 2.5 mL, and then layered with hexane (10 mL). After the diffusion of the solvents was complete, the dark red needle-like crystals were collected by filtration and dried in vacuo. Yield 51 mg (0.045 mmol, 76%). The analytical data for the crystals matched the composition **1'**·CH_2Cl_2. Anal. Calcd for $C_{53}H_{48}F_3N_4O_3P_2RhRuS{\cdot}CH_2Cl_2$: C, 52.78; H, 4.10; N, 4.56. Found: C, 52.76; H, 4.18; N, 4.59. ^{1}H and ^{31}P{^{1}H} NMR data for **1'** are essentially the same as those of **1**.

Synthesis of [([RuP$_2$])IrH(MeCN)$_3$][BF$_4$]$_2$ (2)



[Ru(PH)$_2$] **2**

In a Schlenk tube [Ru(PH)$_2$] (104 mg, 0.108 mmol) and [Ir(cod)$_2$][BF$_4$] (59.1 mg, 0.119 mmol) were dissolved in MeCN (2 mL), and the solution was treated with K_2CO_3 (142 mg, 1.03 mmol). The resulting red slurry was stirred for 2 h, and then filtered. The filtrate was evaporated to dryness, and the residue was extracted with dichloromethane (10 mL). Dilution of the filtrate with diethyl ether (20 mL) afforded a reddish brown solid, which was collected by filtration and dried in vacuo. Yield 102 mg (0.080 mmol, 74%). Anal. Calcd. for $C_{50}H_{46}B_2F_8IrN_7P_2Ru$: C, 47.17; H, 3.64; N, 7.70. Found: C, 46.98; H, 3.00; N, 7.44. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.67 (d, J = 4.0 Hz, 1H), 8.40 (m, 2H), 8.35 (d, J = 8.0 Hz, 1H), 7.88 (dt, J = 8.0, 1.2 Hz), 7.78 (m, 6H), 7.60 (t, J = 8.4 Hz, 2H), 7.49 (m, 2H), 7.44 (d, J = 5.6 Hz, 1H), 7.25 (m, 8H), 7.15 (m, 1H), 6.88 (m, 3H), 6.78 (m, 2H), 6.59 (m, 6H), 2.53, 2.42, 2.09 (s, 3H each, MeCN), -18.44 (dd, $^2J_{PH}$ = 16.8, 11.6 Hz, 1H, Ir-H). ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2): δ -71.86 (d, J_{PP} = 99 Hz), -80.49 (d, J_{PP} = 99 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 158.60, 158.30, 157.67, 156.06, 155.72, 154.41, 150.11, 149.43, 140.51, 140.30,

137.57, 137.36, 137.14, 136.38, 135.35 (d, J = 6.1 Hz), 134.74 (m), 134.53 (m), 134.34 (d, J = 9.1 Hz), 132.85 (d, 9.2 Hz), 132.30 (d, J = 7.6 Hz), 129.37, 128.71, 128.24 (d, J = 6.1 Hz), 127.95 (d, J = 9.1 Hz), 127.69, 127.51, 127.35, 126.58, 126.46, 129.19, 124.73, 124.48, 123.72, 123.33, 123.09, 122.88 (d, J = 12.9 Hz), 121.81 (d, J = 12.9 Hz), 121.55, 3.75, 3.03, 3.05.

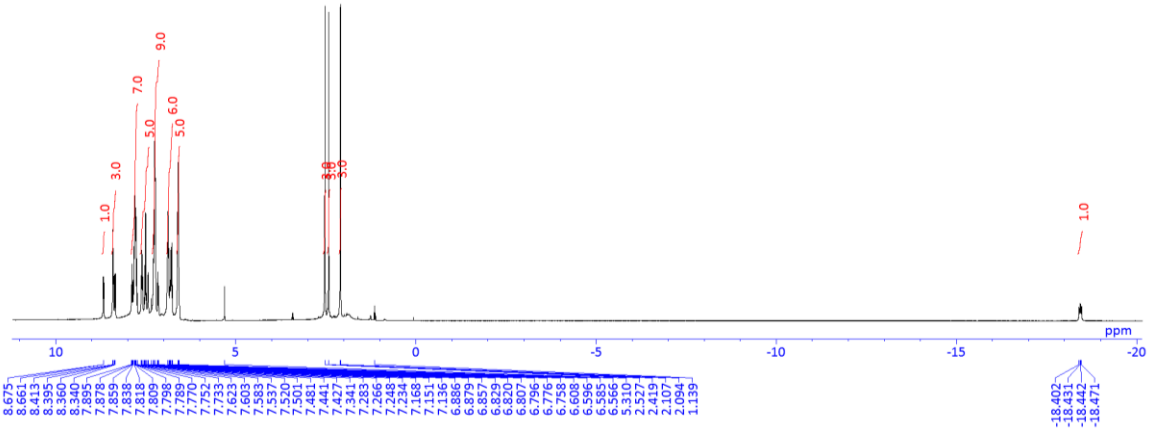


Fig. S15 ^{1}H NMR spectrum of [([RuP$_2$])IrH(MeCN)$_3$][BF$_4$]$_2$ (**2**) (400 MHz, CD$_2$Cl$_2$).

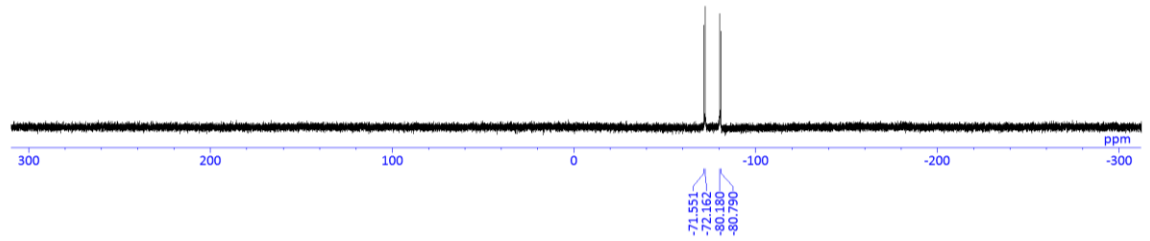


Fig. S16 ^{31}P{^{1}H} NMR spectrum of [([RuP$_2$])IrH(MeCN)$_3$][BF$_4$]$_2$ (**2**) (162 MHz, CD$_2$Cl$_2$).

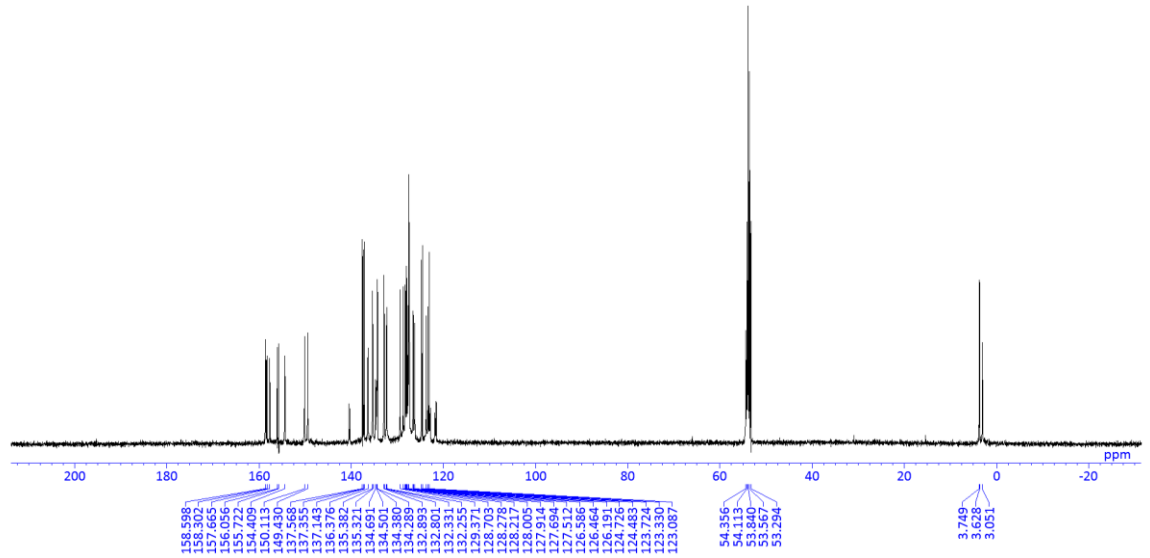


Fig. S17 ^{13}C{^{1}H} NMR spectrum of [([RuP$_2$])IrH(MeCN)$_3$][BF$_4$]$_2$ (**2**) (100 MHz, CD$_2$Cl$_2$).

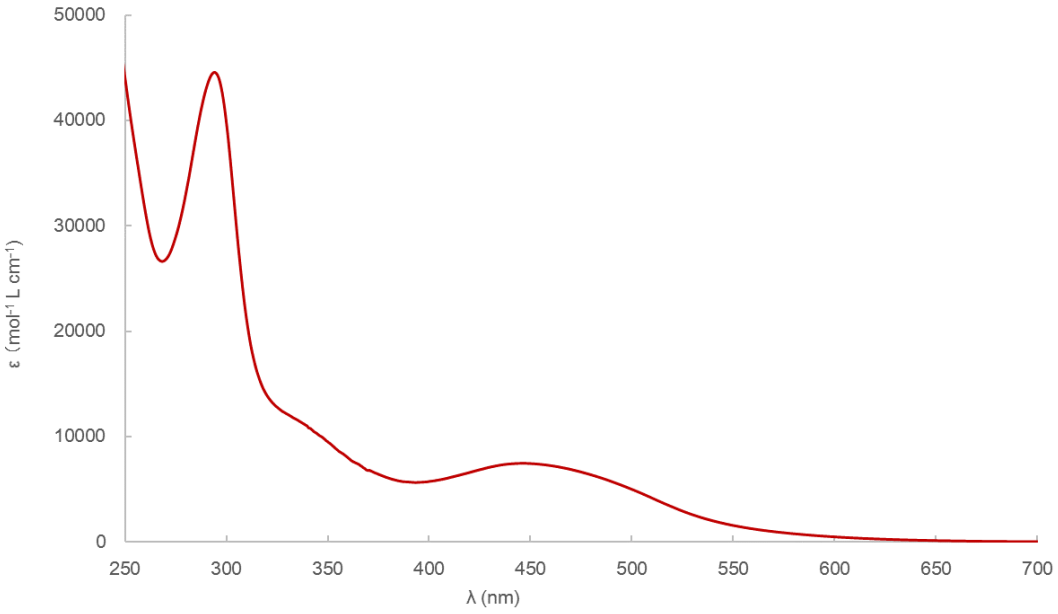
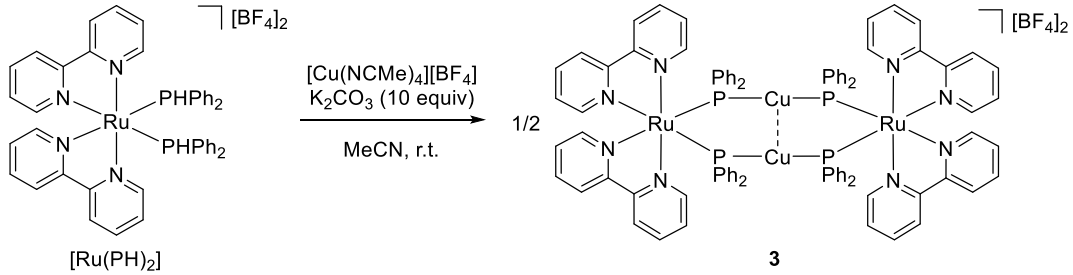


Fig. S18 UV-vis spectrum of [([RuP_2])IrH($MeCN)_3$][BF_4]$_2$ (**2**) in MeCN.

Synthesis of [Cu_2([RuP_2])$_2$][BF_4]$_2$ (3)



[$Ru(PH)_2$] (101 mg, 0.105 mmol) and [$Cu(MeCN)_4$][BF_4] (33.8 mg, 0.107 mmol) were dissolved in MeCN (2 mL), and the solution was treated with K_2CO_3 (140 mg, 1.01 mmol). The resulting mixture was stirred for 2 h, and then filtered. The solvent was removed in vacuo, and the residue was extracted with CH_2Cl_2. The extract was concentrated to ca. 2 mL under reduced pressure, and then layered with THF (7 mL). After the diffusion of the solvents was complete, the dark brown crystals that deposited were collected by filtration and dried in vacuo. Yield 92.6 mg (0.0496 mmol, 94%). Anal. Calcd. for $C_{88}H_{72}N_8P_4B_2F_8Ru_2Cu_2$: C, 56.57; H, 3.88; N, 6.00. Found: C, 56.55; H, 4.01; N, 6.02. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.65 (d, J = 5.6 Hz, 4H), 8.10 (d, J = 8.4 Hz, 4H), 7.98 (d, J = 8.4 Hz, 4H), 7.73 (m, 12H), 7.65 (t, J = 7.6 Hz, 4H), 7.33 (d, J = 5.2 Hz, 4H), 7.29 (t, J = 7.6 Hz, 4H), 7.12 (t, J = 6.4 Hz, 4H), 6.96 (m, 4H), 6.91 (t, J = 7.8 Hz, 8H), 6.62 (m, 16H), 6.11 (t, J = 6.6 Hz, 4H). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6): δ 10.2 (s). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 157.10, 155.22, 155.05,

149.11, 139.32, 137.84, 136.41, 135.75, 134.87, 132.56, 128.03, 127.67, 126.97, 126.30, 125.95, 124.79, 123.49, 123.04.

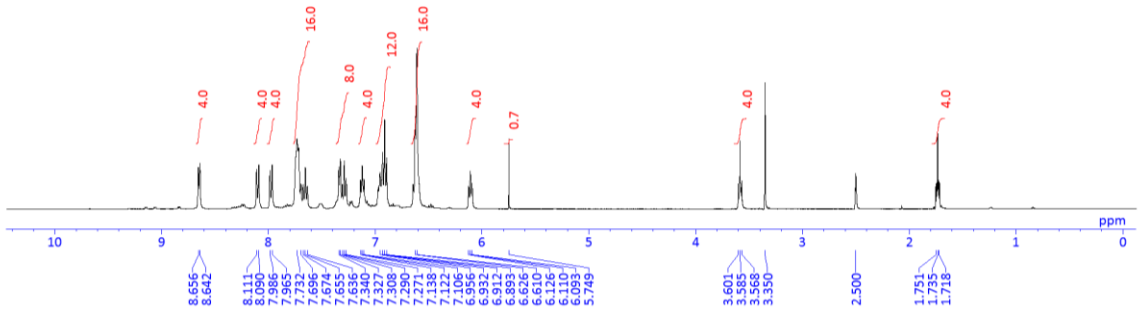


Fig. S19 ^{1}H NMR spectrum of $[Cu_2([RuP_2])_2][BF_4]_2$ (**3**) (400 MHz, DMSO-d_6).

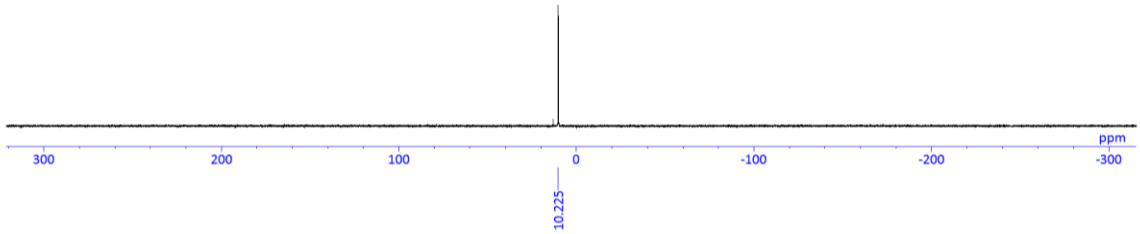


Fig. S20 $^{31}P\{^{1}H\}$ NMR spectrum of $[Cu_2([RuP_2])_2][BF_4]_2$ (**3**) (162 MHz, DMSO-d_6).

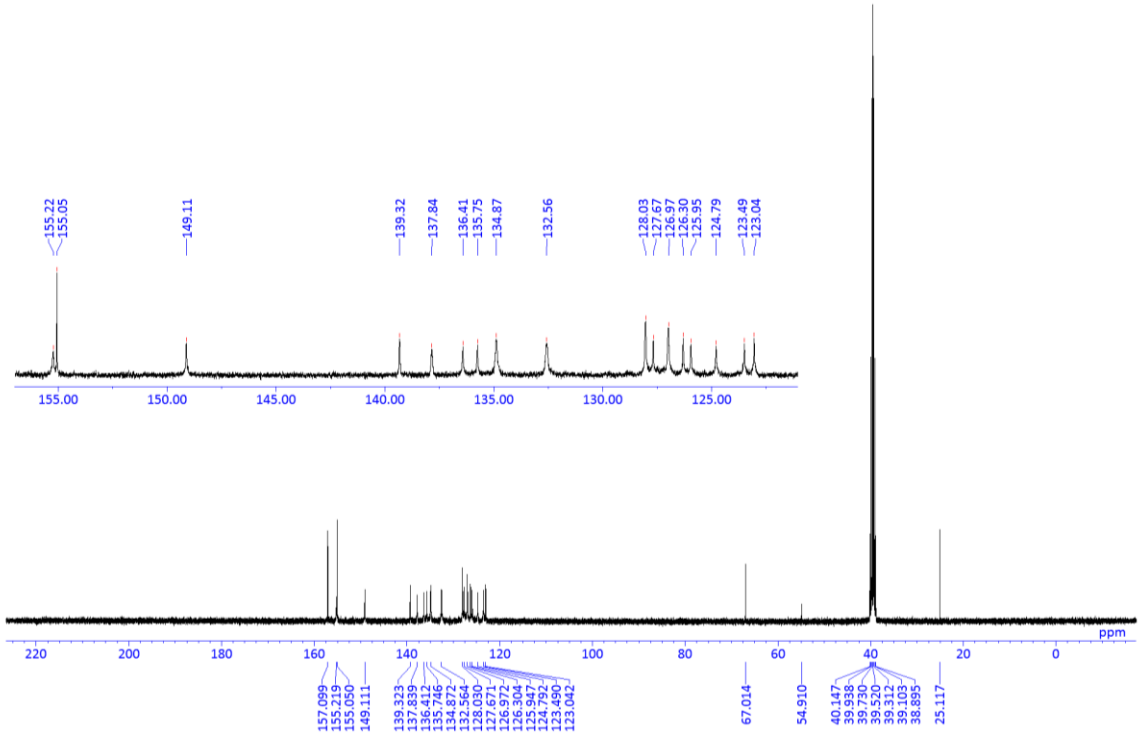


Fig. S21 $^{13}C\{^{1}H\}$ NMR spectrum of $[Cu_2([RuP_2])_2][BF_4]_2$ (**3**) (100 MHz, DMSO-d_6).

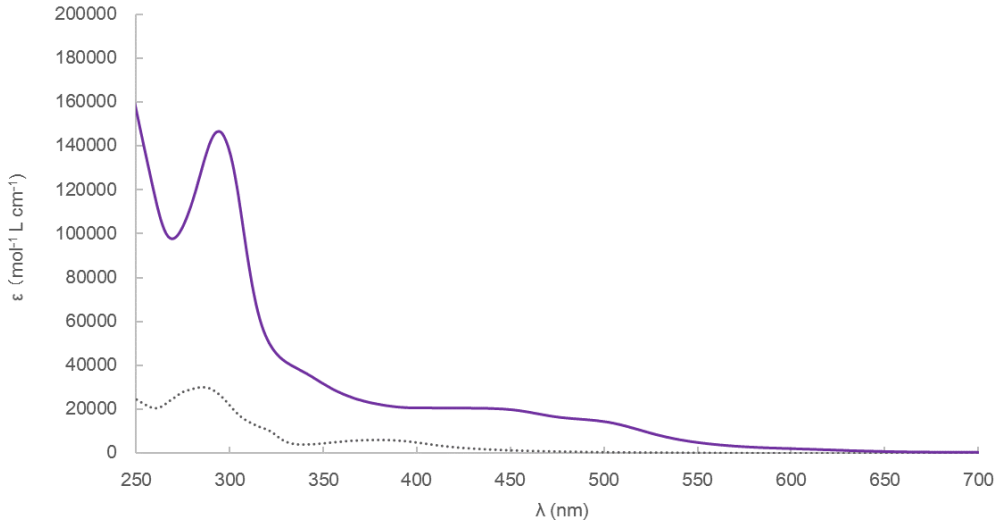
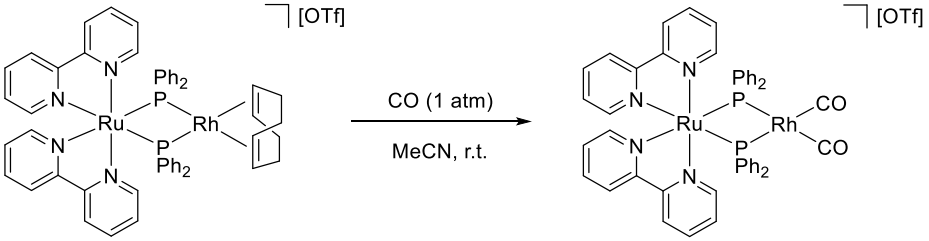


Fig. S22 UV-vis spectrum of $[Cu_2([RuP_2])_2][BF_4]_2$ (**3**, solid line) in DMF co-plotted with that of $[Ru(PH)_2]$ (dotted line) for comparison of molar absorptivity.

Synthesis of $[([RuP_2])Rh(CO)_2][OTf]$ (4)



1' **4**

Complex **1'** (0.080 mmol) was dissolved in MeCN (2 mL), and the solution was stirred under CO atmosphere (1 atm) for 1 h. Dilution with diethyl ether (30 mL) caused precipitation of a reddish brown solid, which was collected by filtration, washed with diethyl ether, and dried in vacuo. Yield 61.5 mg (0.0563 mmol, 70%). Anal. Calcd. for $C_{47}H_{36}F_3N_4O_5P_2RhRuS$: C, 51.70; H, 3.32; N, 5.13. Found: C, 51.69; H, 3.50; N, 5.35. ^{1}H NMR (400 MHz, CD_3CN): δ 8.81 (d, J = 5.6 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.70-7.62 (m, 8H), 7.53 (d, J = 5.6 Hz, 2H), 7.23-7.17 (m, 6H), 7.09 (m, 2H), 6.93 (m, 4H), 6.82 (m, 4H), 6.55 (t, J = 7.6 Hz, 4H). ^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ -67.8 (d, J_{Rh-P} = 88.1 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN): δ 189.9 (m, CO), 158.27, 157.82, 156.63, 151.02, 140.81 (t, J = 10.0 Hz), 139.81 (t, J = 6.1 Hz), 137.66, 137.30, 137.17, 137.11, 134.56, 129.86, 129.16, 128.34, 128.13, 127.26, 124.57, 124.21. IR (KBr pellet, cm^{-1}): 2045 (vs), 1986 (vs), 1601 (w), 1467 (w), 1433 (m), 1263 (vs), 1234 (w), 1158 (s), 1032 (s), 763 (m), 699 (m), 638 (m), 517 (m).

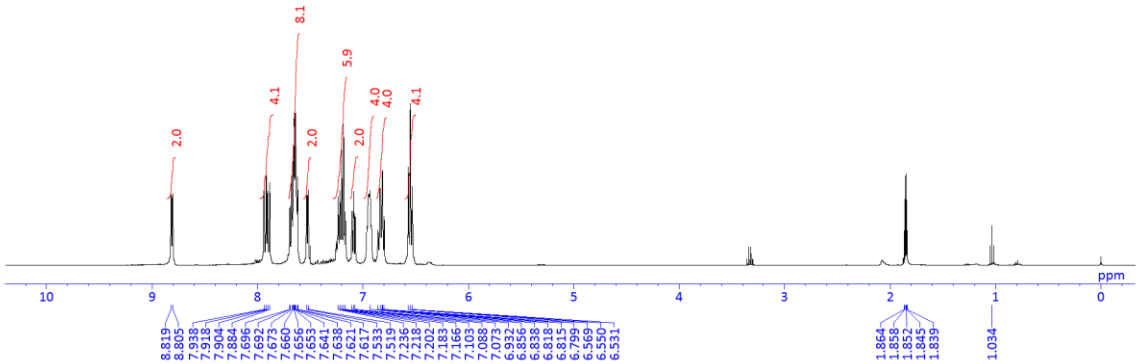


Fig. S23 ^{1}H NMR spectrum of [([RuP$_2$])Rh(CO)$_2$][OTf] (**4**) (400 MHz, CD$_3$CN).

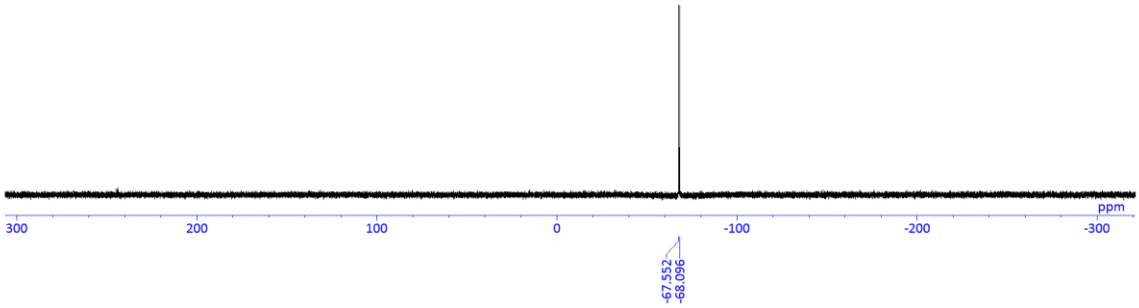


Fig. S24 $^{31}P\{^{1}H\}$ NMR spectrum of [([RuP$_2$])Rh(CO)$_2$][OTf] (**4**) (162 MHz, CD$_3$CN).

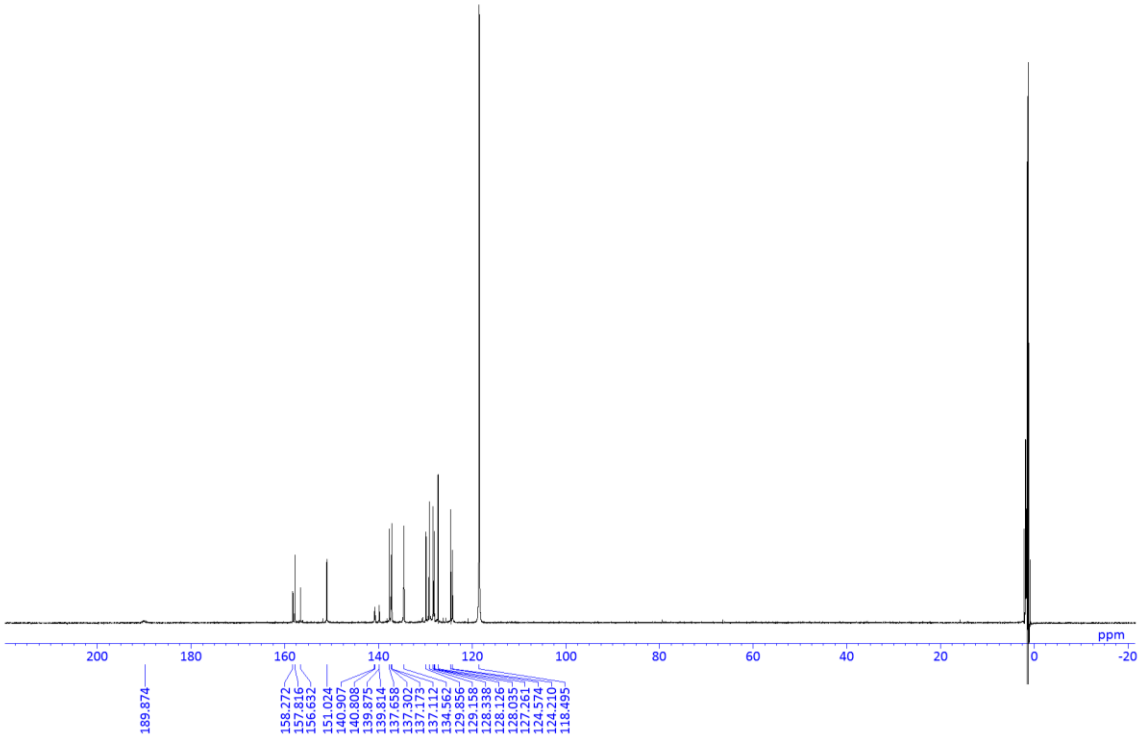


Fig. S25 $^{13}C\{^{1}H\}$ NMR spectrum of [([RuP$_2$])Rh(CO)$_2$][OTf] (**4**) (100 MHz, CD$_3$CN).

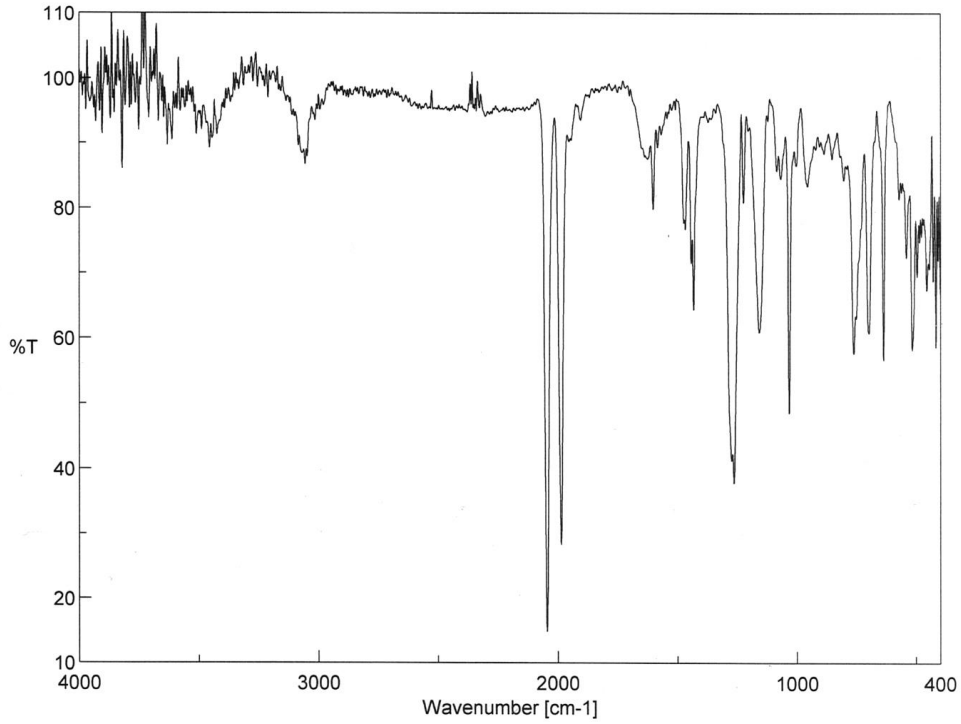
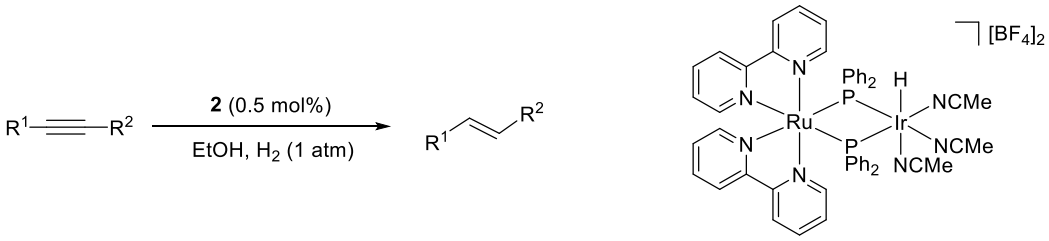


Fig. S26 IR spectrum of [([RuP_2])$Rh(CO)_2$][OTf] (**4**) (KBr pellet).

Standard procedure for alkyne semi-hydrogenation



2

A 50-mL Schlenk tube was charged with catalyst **2** (0.010 mmol, 0.5 mol%), alkyne (2.0 mmol), and EtOH (20 mL) under nitrogen. After the nitrogen was pumped off under vacuum, the Schlenk tube was connected to a balloon filled with H_2 gas and then placed in an oil bath maintained at specified temperature. After stirring for the specified time, the reaction tube was disconnected from the H_2 balloon and cooled to room temperature. Phenanthrene was added as an internal standard, and a 3 mL portion of the reaction solution was taken and evaporated to dryness. The crude mixture was analyzed by ^{1}H NMR spectroscopy. Diphenylacetylene, 1-phenyl-1-hexyne, 1-phenyl-2-trimethylsilylacetylene, 4-octyne and *p*-bromodiphenylacetylene were purchased from TCI or Sigma Aldrich. The remainder of the alkyne substrates were prepared according to literature procedures.[3] The reaction of 4-octyne was done in MeOH-d_4 and analyzed directly by ^{1}H NMR.

Spectroscopic data for the product alkenes

(*E*)-Stilbene:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58-7.53 (m, 4H, Ph), 7.43-7.38 (m, 4H, Ph), 7.31 (dt, J = 7.2, 2.0 Hz, 2H, Ph), 7.16 (s, 2H, olefinic).

(*E*)-1-Phenyl-1-hexene:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, J = 7.2 Hz, 2H, Ph), 7.34 (t, J = 7.2 Hz, 2H, Ph), 7.24 (t, J = 7.2 Hz, 1H, Ph), 6.43 (d, J = 16.0 Hz, 1H, olefinic), 6.28 (dt, J = 16.0, 6.8 Hz, 1H, olefinic), 2.26 (q, J = 6.4 Hz, 2H, CHC*H*$_2$), 1.53-1.40 (m, 4H, CH_2CH_2), 0.99 (t, J = 7.2 Hz, 3H, CH_3).

(*E*)-Styryltrimethylsilane:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, J = 7.2 Hz, 2H, Ph), 7.34 (t, J = 7.2 Hz, 2H, Ph), 7.28 (t, J = 7.2 Hz, 1H, Ph), 6.94 (d, J = 19.2 Hz, 1H, olefinic), 6.53 (d, J = 19.2 Hz, 1H, olefinic), 0.22 (s, 9H, $SiMe_3$).

(*E*)-4-ocetene: ^{1}H NMR (CD_3OD, 400 MHz): δ 5.38 (tt, J = 4.0, 0.4 Hz, 2H, olefinic), 1.95 (m, 4H, CHC*H*$_2$), 1.36 (sext, 4H, CH_2), 0.89 (t, J = 7.6 Hz, 6H, CH_3). These data matched those of commercial authentic sample.

(*E*)-4-Methoxystilbene:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 7.2 Hz, 2H, Ph), 7.81 (d, J = 8.8 Hz, 2H, C_6H_4), 7.73 (t, J = 7.2 Hz, 2H, Ph), 7.62 (t, J = 7.2 Hz, 1H, Ph), 7.45 (d, J = 16.4 Hz, 1H, olefinic), 7.35 (d, J = 16.4 Hz, 1H, olefinic), 7.25 (d, J = 8.8 Hz, 2H, C_6H_4), 4.13 (s, 3H, OMe).

(*E*)-4-Styrylphenylmethanol:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 (m, 4H), 7.22 (m, 4H), 7.12 (m, 1H), 6.98 (s, 2H), 4.53 (s, 2H).

(*E*)-4-Aminostilbene:[4] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 7.2 Hz, 2H, Ph), 7.40 (t, J = 7.2 Hz, 2H, Ph), 7.38 (d, J = 8.8 Hz, 2H, C_6H_4), 7.28 (t, J = 7.2 Hz, 1H, Ph), 7.10 (d, J = 16.4 Hz, 1H, olefinic), 6.99 (d, J = 16.4 Hz, 1H, olefinic), 6.65 (d, J = 8.8 Hz, 2H, C_6H_4), 3.64 (br s, 2H, NH_2).

(*E*)-4-Bromostilbene:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, J = 7.2 Hz, 2H, Ph), 7.49 (d, J = 8.4 Hz, 2H, C_6H_4), 7.36 (m, 1H, Ph), 7.32 (d, J = 8.4 Hz, 2H, C_6H_4), 7.08 (d, J = 16.4 Hz, 1H, olefinic), 7.01 (d, J = 16.4 Hz, 1H, olefinic).

(*E*)-4-Acetylstilbene:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (2H, overlapped with internal standard peak), 7.56 (m, 4H), 7.43 (m, 3H), 7.35 (m, 1H), 7.17 (d, J = 16.4 Hz, 1H, olefinic), 7.07 (d, J = 16.4 Hz, 1H, olefinic), 2.54 (s, 3H, Me).

(*Z*)-4-Acetylstilbene:[5] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, J = 8.4 Hz, 2H, C_6H_4), 7.35 (d, J = 8.4 Hz, 2H, C_6H_4), 7.29 (m, 5H), 6.69 (d, J = 12.4 Hz, 1H, olefinic), 6.56 (d, J = 12.4 Hz, 1H, olefinic), 2.50 (s, 3H, Me).

(*E*)-4-Nitrostilbene:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, J = 8.8 Hz, 2H, C_6H_4), 7.62 (d, J = 8.8 Hz, 2H, C_6H_4), 7.59 (m, 2H, Ph), 7.44 (m, 2H, Ph), 7.38 (m, 1H, Ph), 7.29 (d, J = 16.4 Hz, 1H, olefinic), 7.15 (d, J = 16.4 Hz, 1H, olefinic).

(*Z*)-4-Nitrostilbene:[6] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (d, J = 8.8 Hz, 2H, C_6H_4), 7.39 (d, J = 8.8 Hz, 2H, C_6H_4), 7.32-7.22 (m, 5H, Ph), 6.85 (d, J = 12.0 Hz, 1H, olefinic), 6.63 (d, J = 12.0 Hz, 1H, olefinic).

(*E*)-4-Cyanostilbene:[3] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.51 (m, 5H), 7.43-7.35 (m, 4H), 7.17 (d, J = 16.4 Hz, 1H, olefinic), 7.03 (d, J = 16.4 Hz, 1H, olefinic).

(*Z*)-4-Cyanostilbene.[7] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, J = 8.8 Hz, 2H), 7.32-7.12 (m, 7H), 6.85 (d, J = 12.0 Hz, 1H, olefinic), 6.63 (d, J = 12.0 Hz, 1H, olefinic).

Time course of semi-hydrogenation of diphenylacetylene

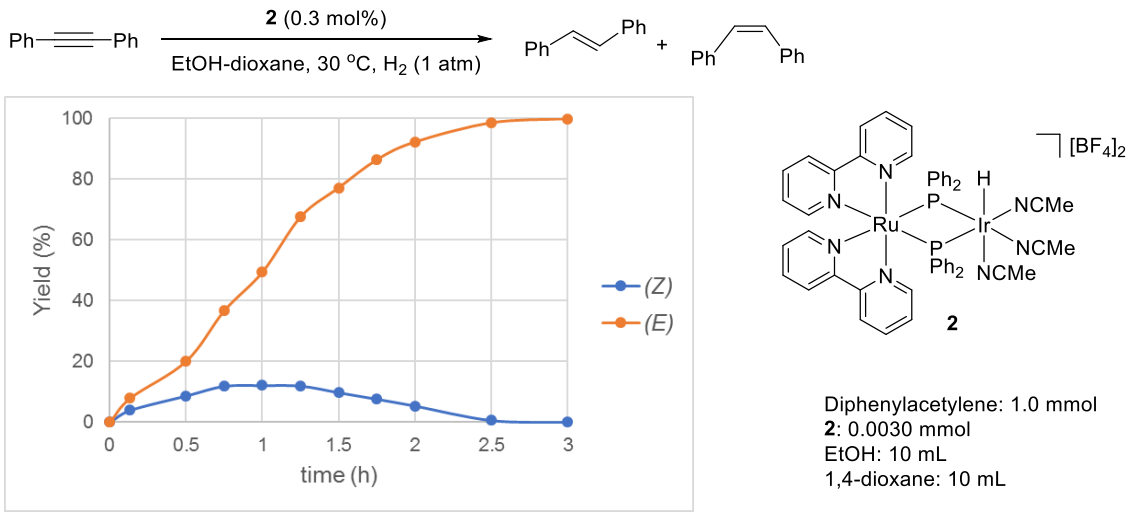
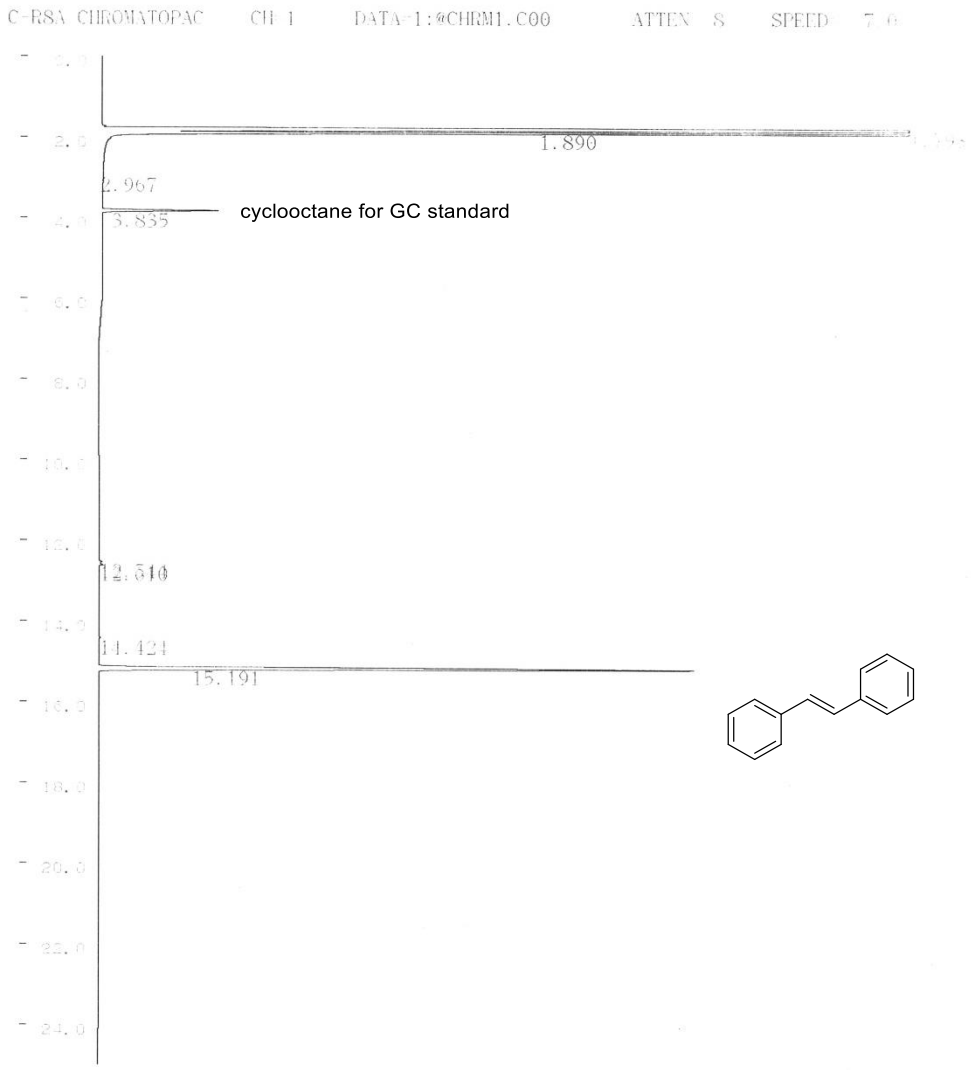


Fig. S27 Time course of catalytic semi-hydrogenation of diphenylacetylene.

GC chromatograms



C-RSA CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00 17/12/01 16:15:00

** CALCULATION REPORT **

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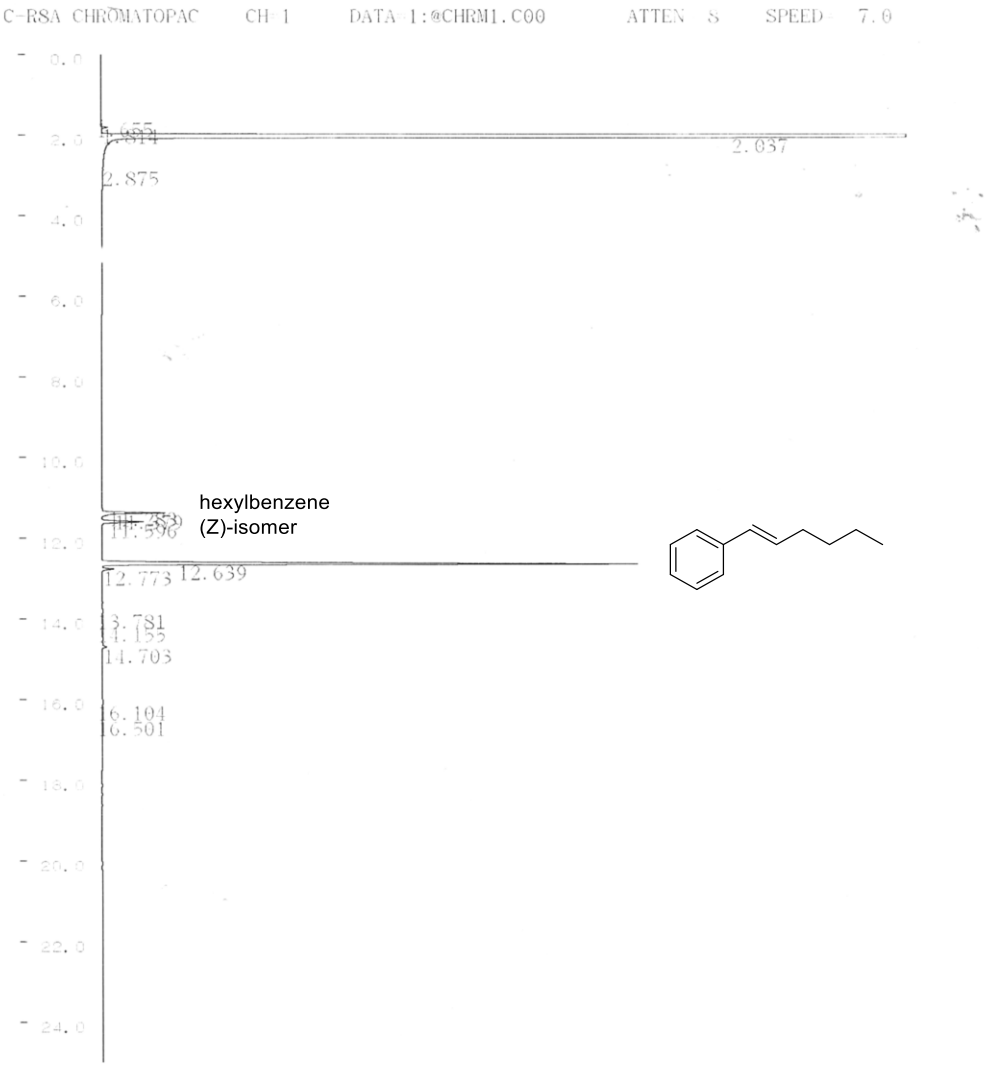
1	1	1.793	6302835	2817152			75.3128	
	2	1.89	1368873	644700	V		16.3567	
	4	3.835	81201	36868			0.9703	
	8	15.191	615965	188881			7.3602	
		TOTAL	8368874	3687601			100	

Fig. S28 GC for catalytic semi-hydrogenation of diphenylacetylene (0.5 mol% **2**, 30 °C, 1 h, H_2 1 atm).

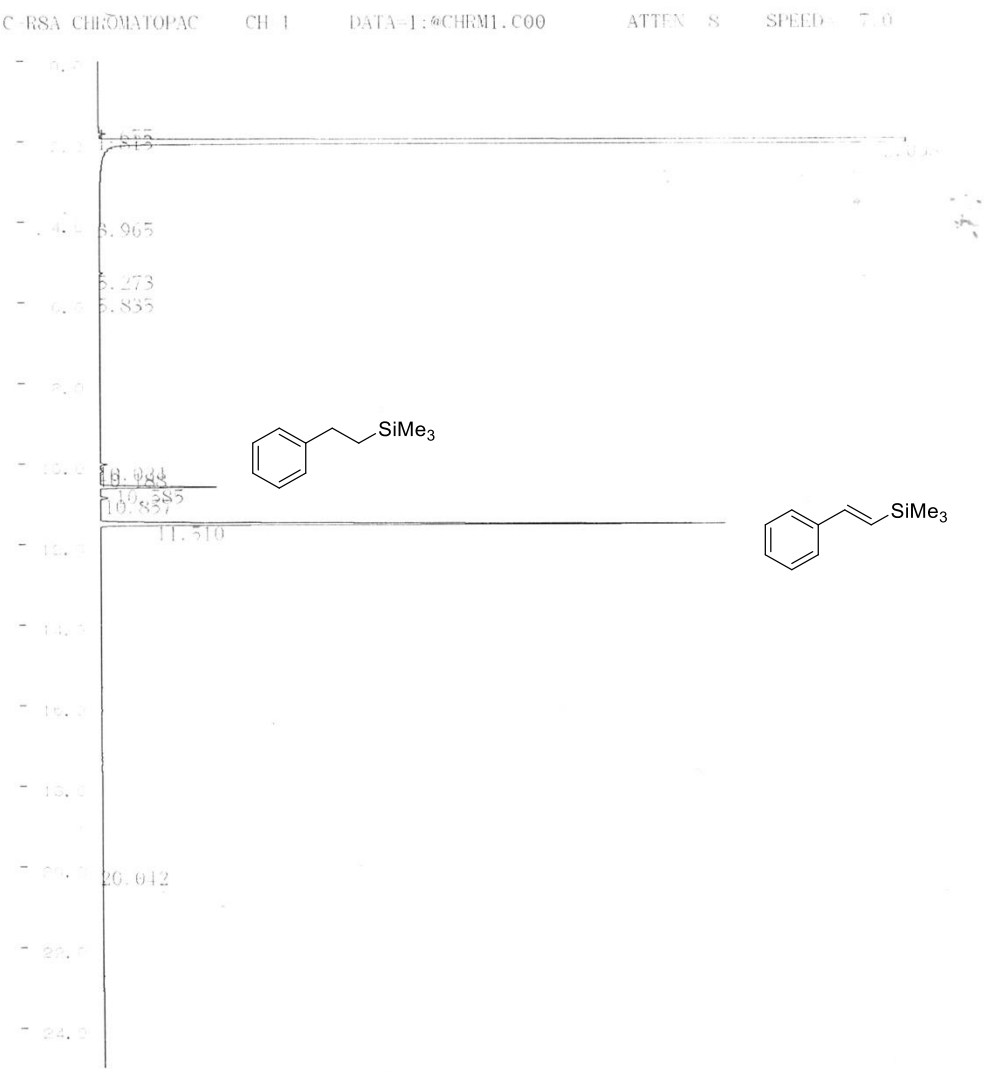


C-RSA CHROMATOPAC CH=1 Report No.=5 DATA=1:@CHRM1.C00 18/03/08 17:22:26

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	1.814	5069	2221	V		0.0437	
	3	2.037	11003330	3527119	SV		94.8465	
	6	11.379	57590	20174	V		0.4964	
	7	11.596	35129	13123	V		0.3028	
	8	12.639	490129	170138			4.2248	
	9	12.773	9954	3807	V		0.0858	
		TOTAL	11601199	3736581			100	

Fig. S29 GC for catalytic semi-hydrogenation of 1-phenyl-1-hexyne (0.5 mol% **2**, 30 ºC, 10 h, H_2 1 atm).



C-RSA CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00 18/02/19 16:21:56

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	1.813	6646	2467	V		0.0528	
	3	2.038	11886287	3559843	V		94.3687	
	7	10.024	5729	2057			0.0455	
	9	10.585	100824	36868			0.8005	
	10	10.857	6568	2366	V		0.0521	
	11	11.51	589522	198200			4.6804	
		TOTAL	12595573	3801801			100	

Fig. S30 GC for catalytic semi-hydrogenation of 1-phenyl-2-trimethylsilylacetylene (0.5 mol% **2**, 30 ^{o}C, 1 h, H_2 1 atm).

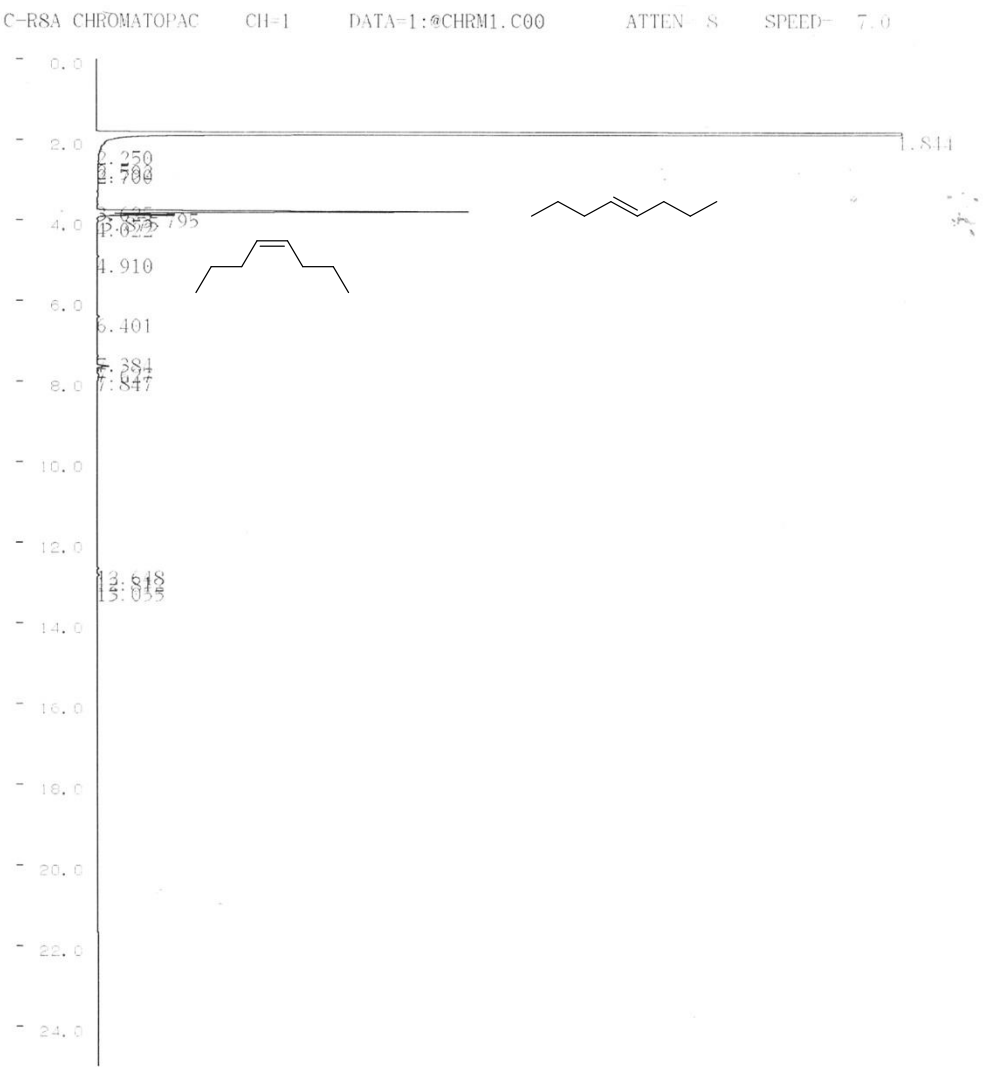
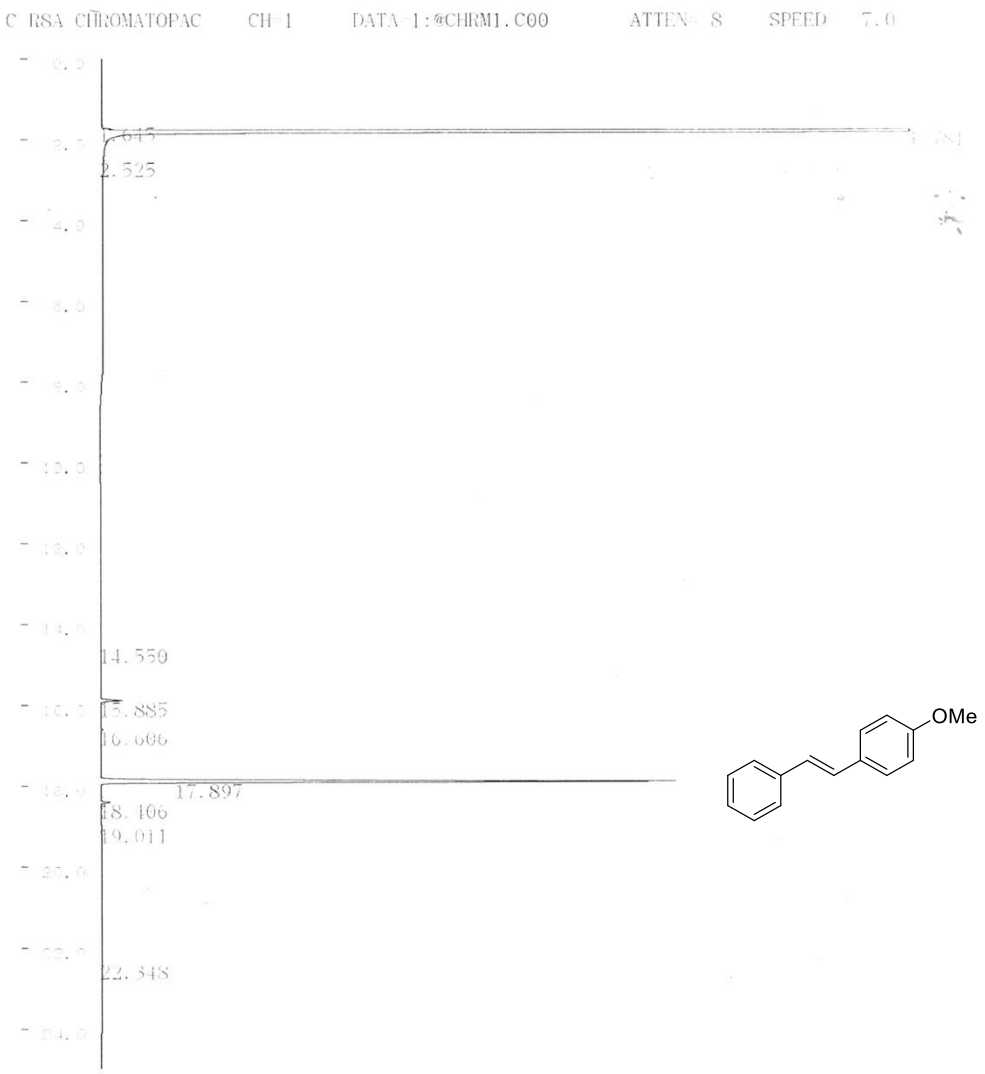


Fig. S31 GC for catalytic semi-hydrogenation of 4-octyne (0.5 mol% **2**, 30 ºC, 2 h, H_2 1 atm).

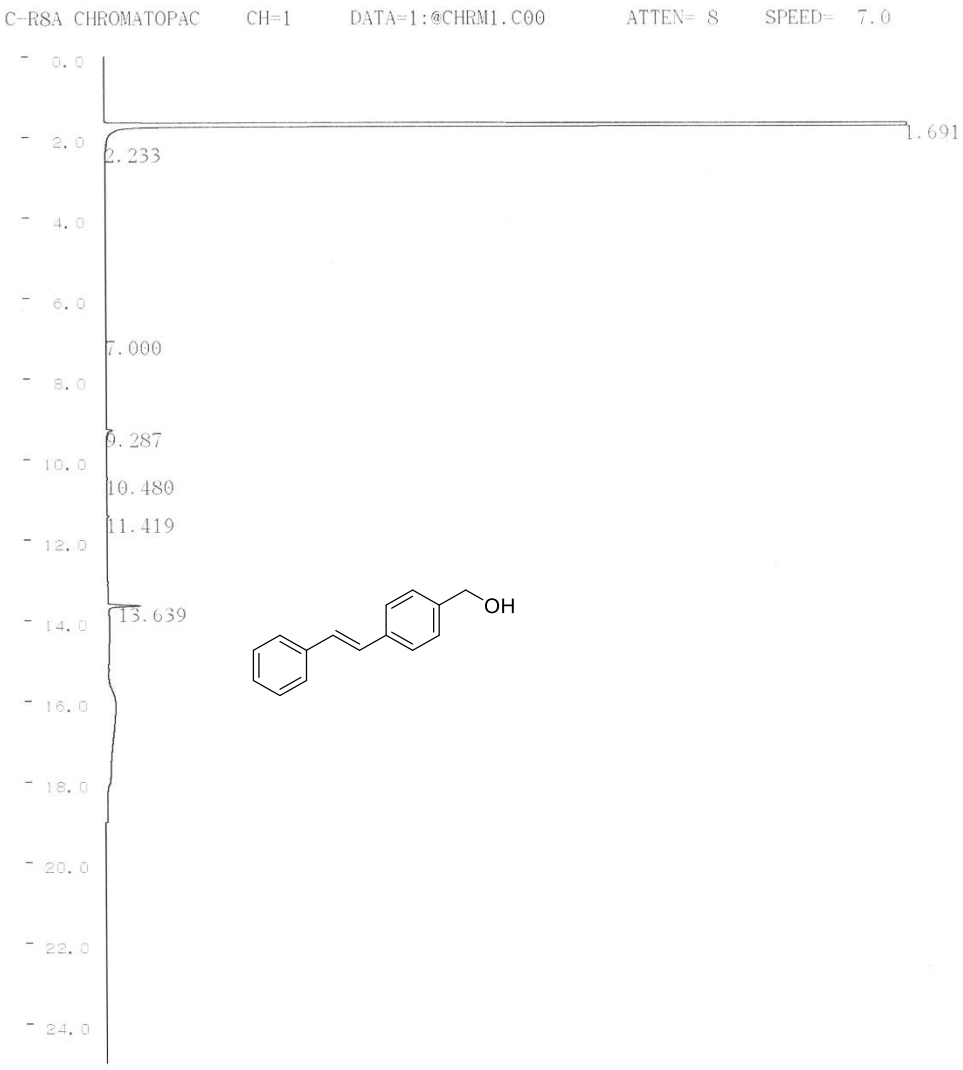


C-RSA CHROMATOPAC CH=1 Report No.=5 DATA=1:@CHRM1.C00 18/02/02 15:08:08

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	1.781	9706459	3651588	SV		93.7389	
	5	15.885	19349	6905			0.1869	
	7	17.897	620707	182462			5.9944	
	8	18.406	8268	2967			0.0798	
		TOTAL	10354780	3843921			100	

Fig. S32 GC for catalytic semi-hydrogenation of *p*-methoxydiphenylacetylene (0.5 mol% **2**, 30 ^{o}C, 2 h, H_2 1 atm).



C-R8A CHROMATOPAC CH=1 Report No.=39 DATA=1:@CHRM1.C00 18/11/09 14:07:40

** CALCULATION REPORT **

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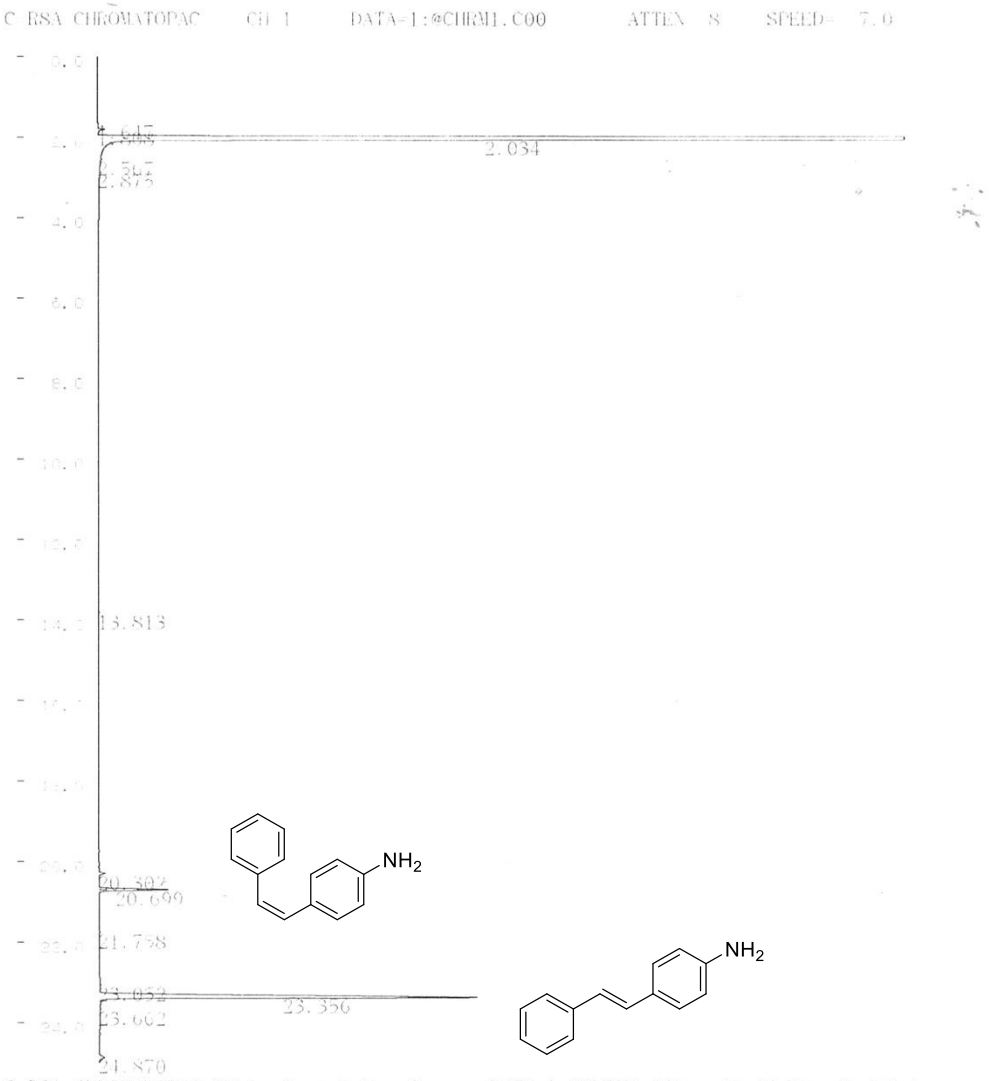
1	1	1.691	8754008	3565347	S		99.4693	
	4	9.287	9215	2130			0.1047	
	5	10.48	1097	333			0.0125	
	6	11.419	2074	719			0.0236	
	7	13.639	34317	10495			0.3899	
		TOTAL	8800709	3579025			100	

Fig. S33 GC for catalytic semi-hydrogenation of (*p*-hydroxymethyl)diphenylacetylene (0.5 mol% **2**, 30 ^{o}C, 2 h, H_2 1 atm).

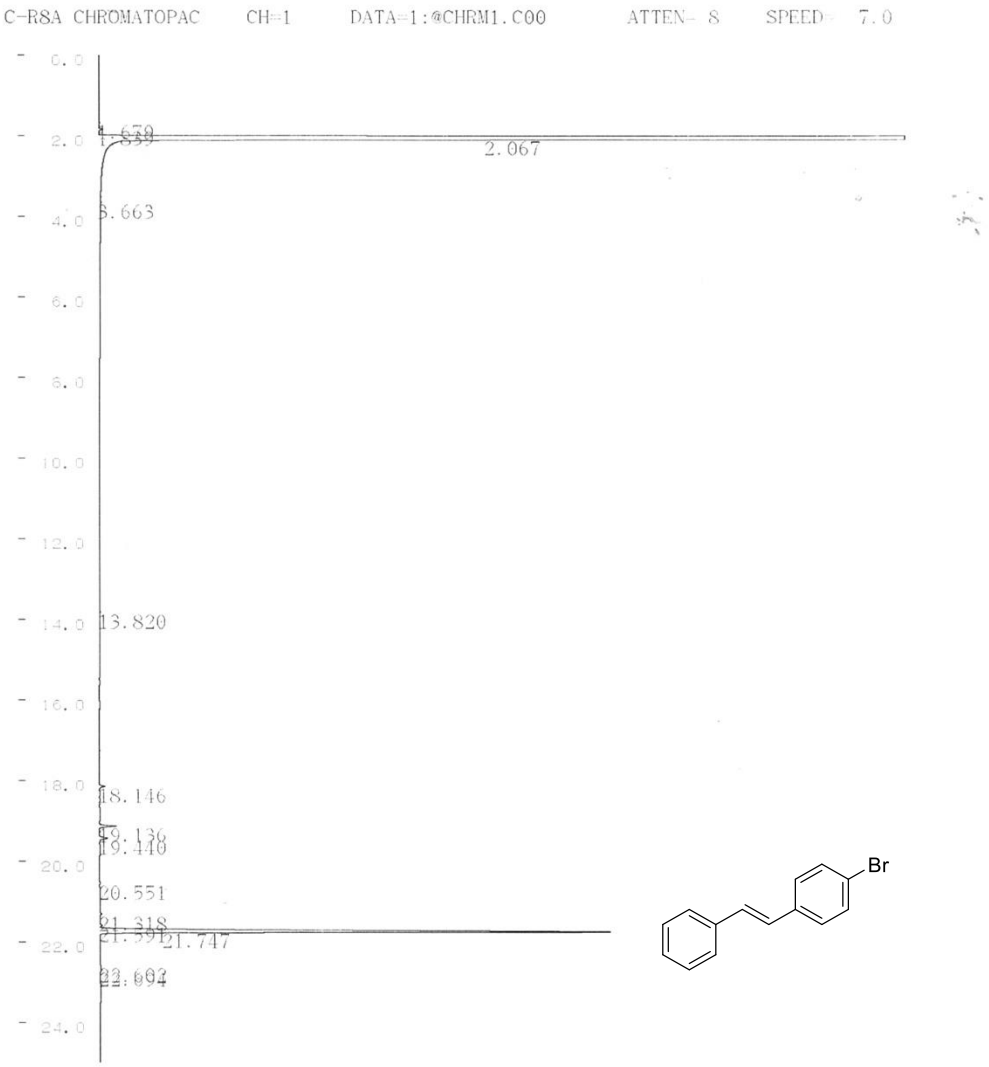


C-RSA CHROMATOPAC CH 1 Report No. =2 DATA=1:@CHRM1.C00 18 02/26 11:23:36

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	1.808	6363	2281	V		0.0562	
	3	2.034	10740642	3406748	SV		94.889	
	7	20.302	6225	1988			0.055	
	8	20.699	63295	22010			0.5592	
	11	23.356	495961	119928	V		4.3816	
	13	24.87	6682	1629			0.059	
		TOTAL	11319163	3554583			100	

Fig. S34 GC for catalytic semi-hydrogenation of *p*-aminodiphenylacetylene (0.5 mol% **2**, 70 ^{o}C, 15 h, H_2 1 atm).

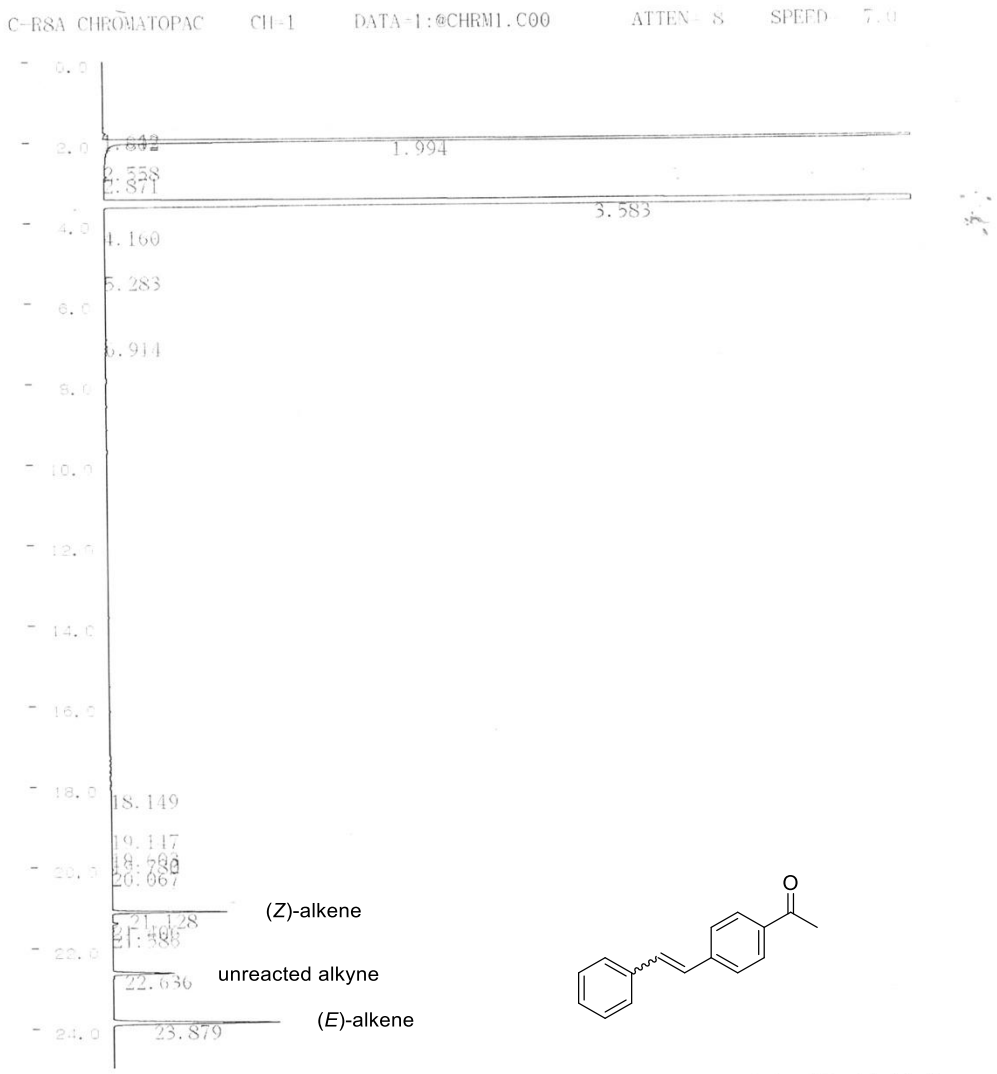


C-RSA CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00 18/11/01 14:12:36

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	3	2.067	12486943	3695484			95.5053	
	6	18.146	5482	1938			0.0419	
	7	19.136	16356	5803			0.1251	
	8	19.44	7684	2604			0.0588	
	12	21.747	558147	162325	V		4.2689	
		TOTAL	13074609	3868152			100	

Fig. S35 GC for catalytic semi-hydrogenation of *p*-bromodiphenylacetylene (0.5 mol% **2**, 70 ^{o}C, 3 h, H_2 1 atm).

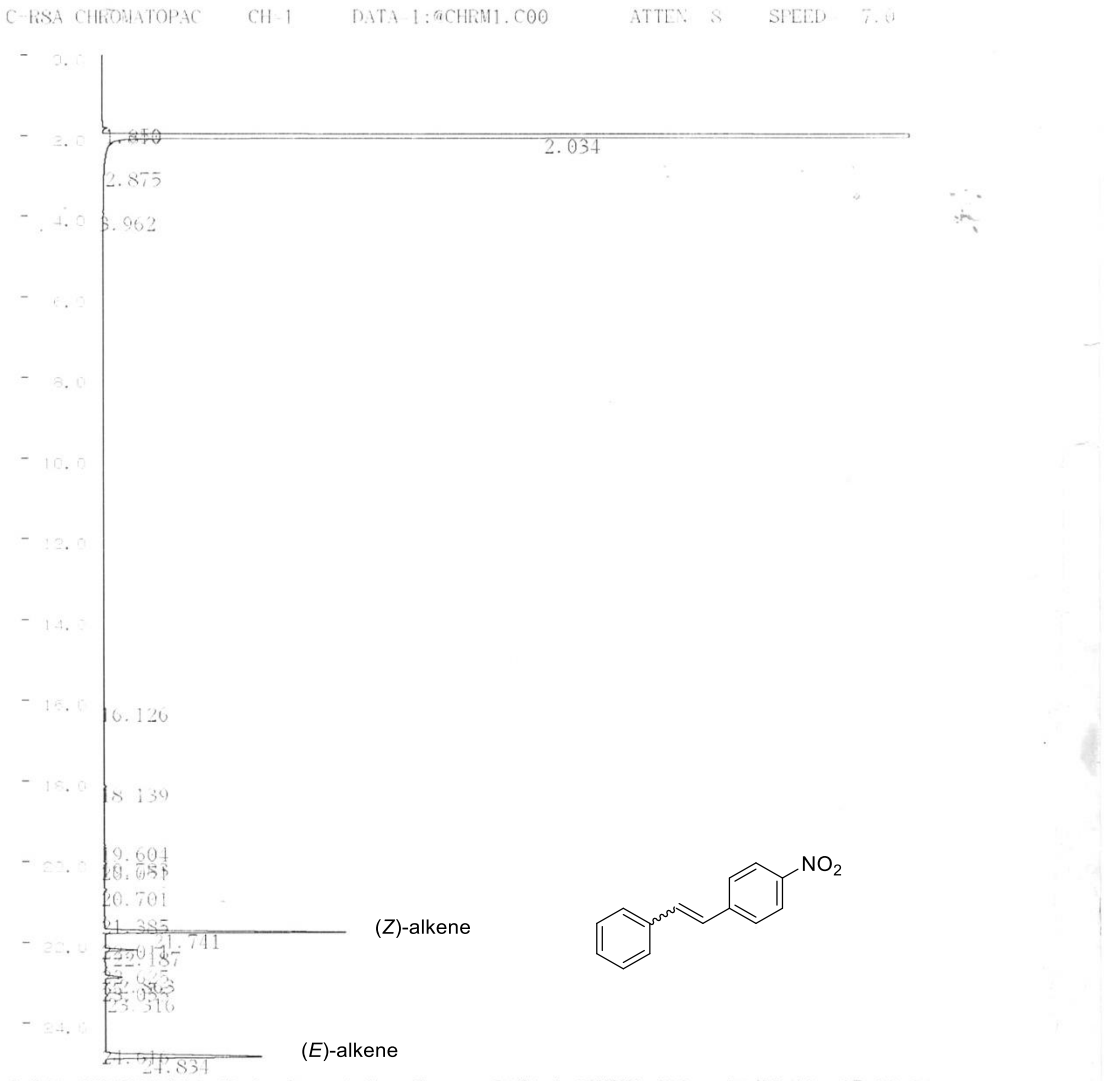


C-R8A CHROMATOPAC CH-1 Report No.-2 DATA=1:@CHRM1.C00 18/03/17 14:11:42

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	3	1.994	3303013	1661469	SV		30.1246	
	6	3.583	7296853	1490666			66.5499	
	15	21.128	101310	36399			0.924	
	16	21.406	5170	1826	V		0.0472	
	18	22.636	62219	19538			0.5675	
	19	23.879	195924	52660			1.7869	
		TOTAL	10964488	3262557			100	

Fig. S36 GC for catalytic semi-hydrogenation of *p*-acetyldiphenylacetylene (0.5 mol% **2**, 70 ^{o}C, 89 h, H_2 1 atm).

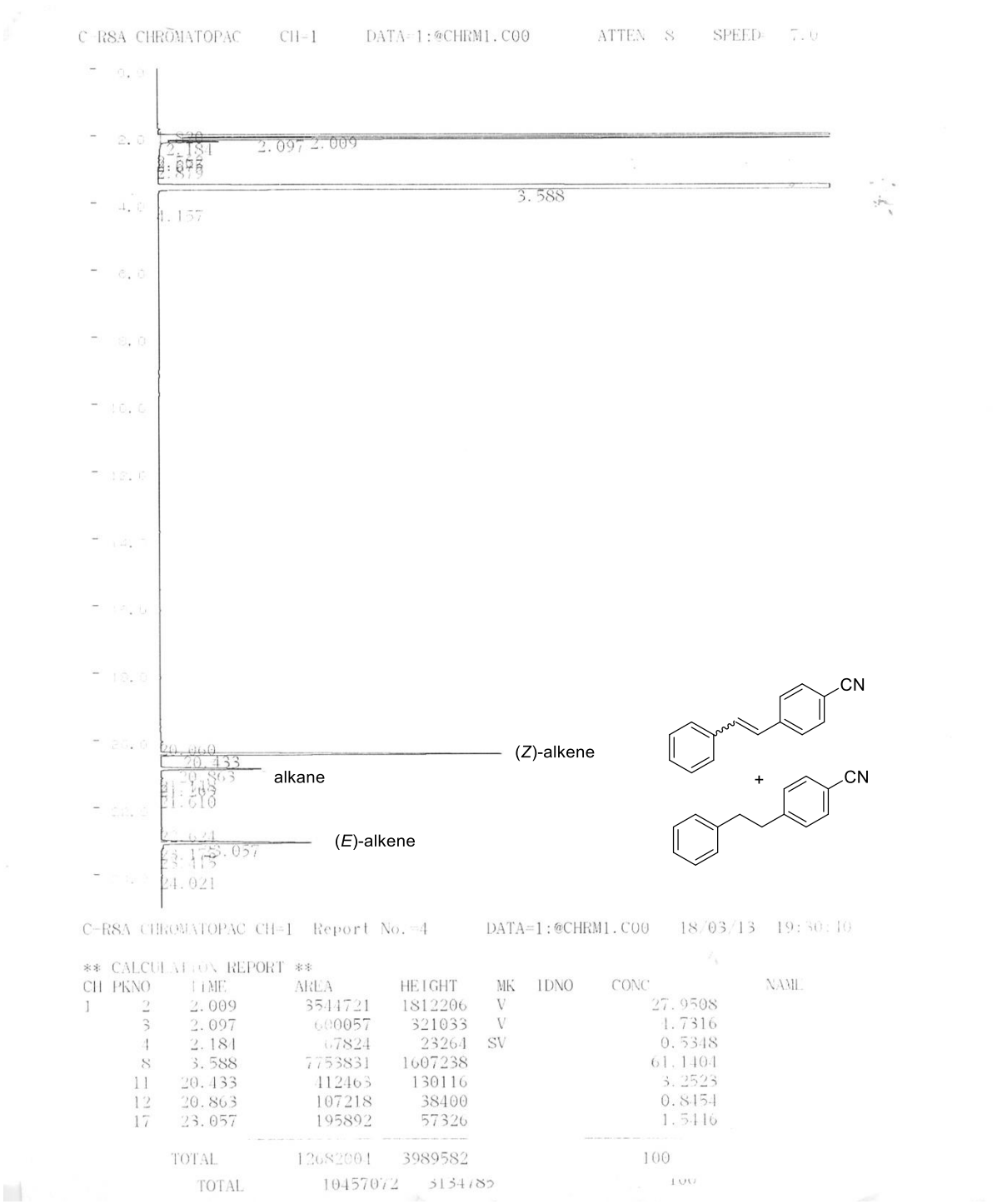


C-RSA CHROMATOPAC CH=1 Report No.=5 DATA=1:@CHRM1.C00 18/03/01 17:12:16

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	1.81	5183	1625	V		0.0426	
	3	2.034	11653607	3619034	SV		95.875	
	13	21.741	228730	76690			1.8818	
	15	22.187	29176	10106	V		0.21	
	17	22.863	18056	5687	V		0.1485	
	21	24.834	220253	49766	V		1.812	
		TOTAL	12155004	3762908			100	

Fig. S37 GC for catalytic semi-hydrogenation of *p*-nitrodiphenylacetylene (0.5 mol% **2**, 70 ^{o}C, 39 h, H_2 1 atm).



C-RSA CHROMATOPAC CH=1 Report No.=4 DATA=1:@CHRM1.C00 18/03/13 19:30:10

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	2.009	3544721	1812206	V		27.9508	
	3	2.097	680057	321033	V		1.7316	
	4	2.181	67824	23264	SV		0.5348	
	8	3.588	7753831	1607238			61.1404	
	11	20.433	412463	130116			3.2523	
	12	20.863	107218	38400			0.8454	
	17	23.057	195892	57326			1.5446	
		TOTAL	12682001	3989582			100	
		TOTAL	10457072	3134782			100	

Fig. S38 GC for catalytic semi-hydrogenation of *p*-cyanodiphenylacetylene (0.5 mol% **2**, 70 ^{o}C, 73 h, H_2 1 atm).

^{1}H NMR spectra for the alkyne semi-hydrogenation reactions

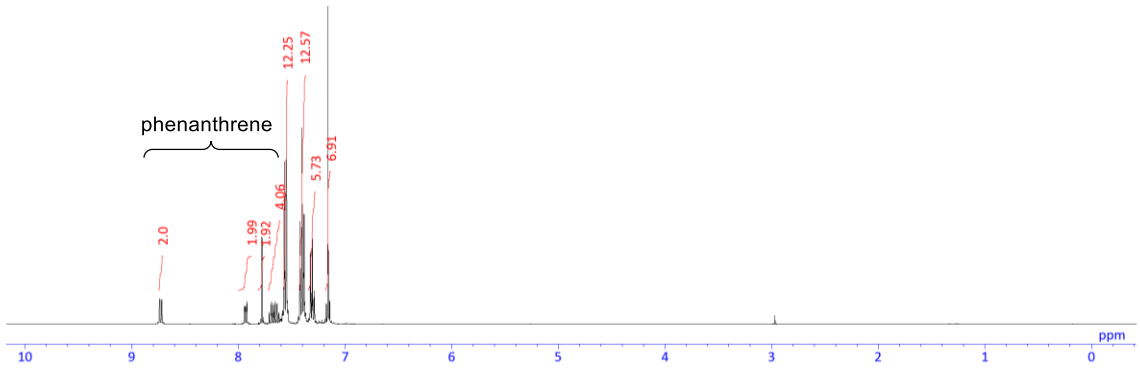


Fig. S39 ^{1}H NMR spectrum ($CDCl_3$) for catalytic semi-hydrogenation of diphenylacetylene (0.5 mol% **2**, 30 °C, 1 h, H_2 1 atm).

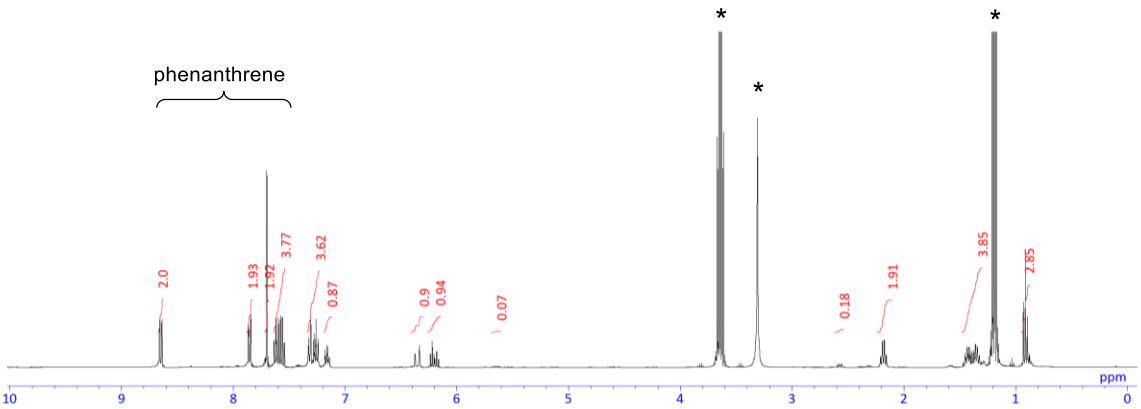


Fig. S40 ^{1}H NMR spectrum ($CDCl_3$) for catalytic semi-hydrogenation of 1-phenyl-1-hexyne (0.5 mol% **2**, 30 °C, 10 h, H_2 1 atm; *residual ethanol).

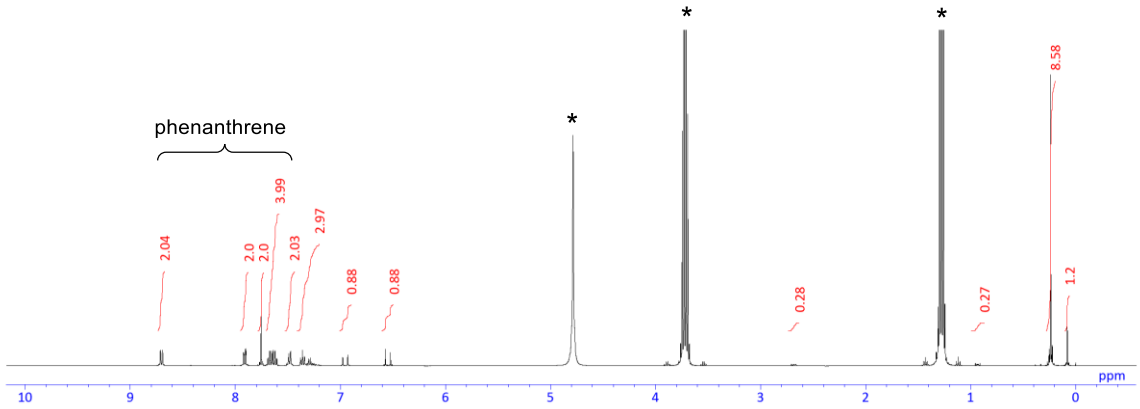


Fig. S41 ^{1}H NMR spectrum ($CDCl_3$) for catalytic semi-hydrogenation of 1-phenyl-2-trimethylsilyl acetylene (0.5 mol% **2**, 30 °C, 1 h, H_2 1 atm; *residual ethanol).

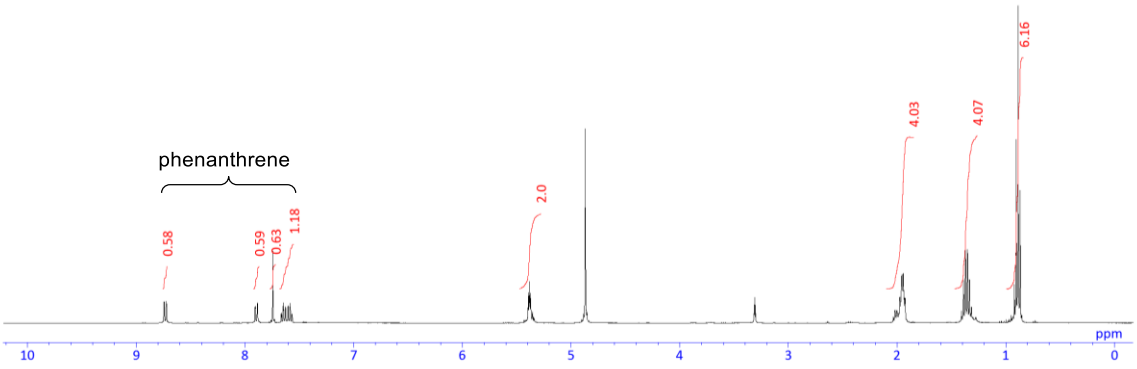


Fig. S42 ^{1}H NMR spectrum (CD_3OD) for catalytic semi-hydrogenation of 4-octyne (0.5 mol% **2**, 30 °C, 2 h, H_2 1 atm).

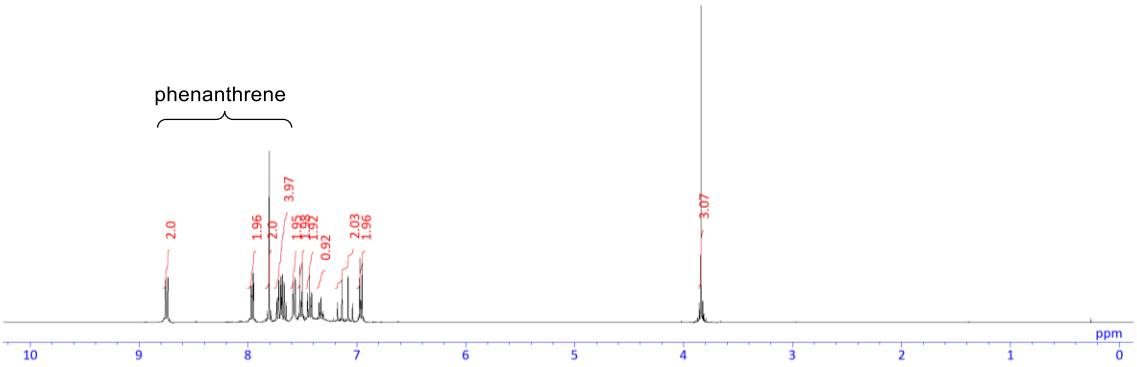


Fig. S43 ^{1}H NMR spectrum ($CDCl_3$) for catalytic semi-hydrogenation of *p*-methoxydiphenylacetylene (0.5 mol% **2**, 30 °C, 2 h, H_2 1 atm).

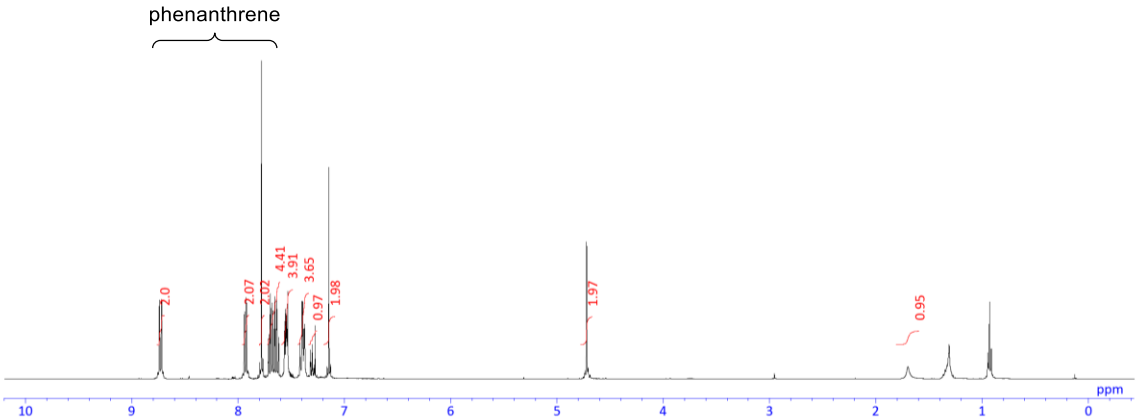


Fig. S44 ^{1}H NMR spectrum ($CDCl_3$) for catalytic semi-hydrogenation of (*p*-hydroxymethyl) diphenylacetylene (0.5 mol% **2**, 30 °C, 2 h, H_2 1 atm).

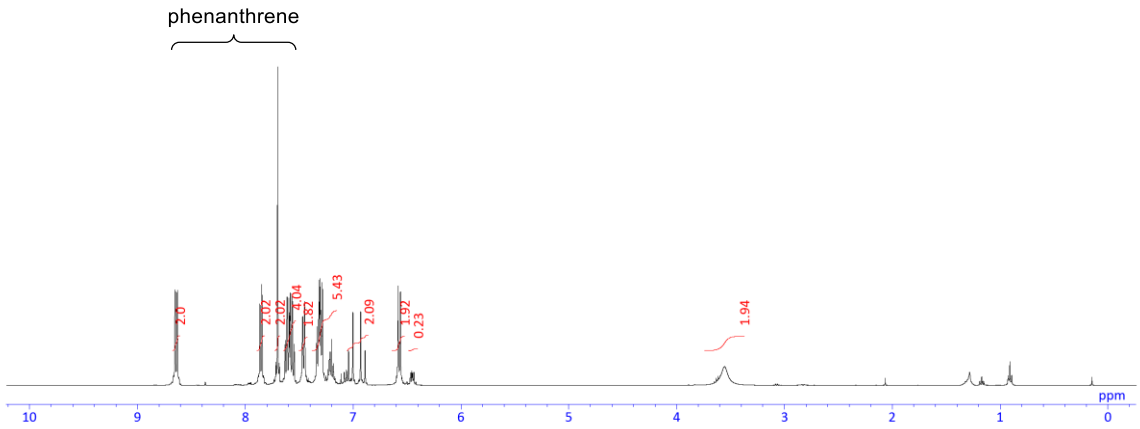


Fig. S45 ^{1}H NMR spectrum ($CDCl_3$) for catalytic semi-hydrogenation of *p*-amino diphenylacetylene (0.5 mol% **2**, 70 °C, 15 h, H_2 1 atm).

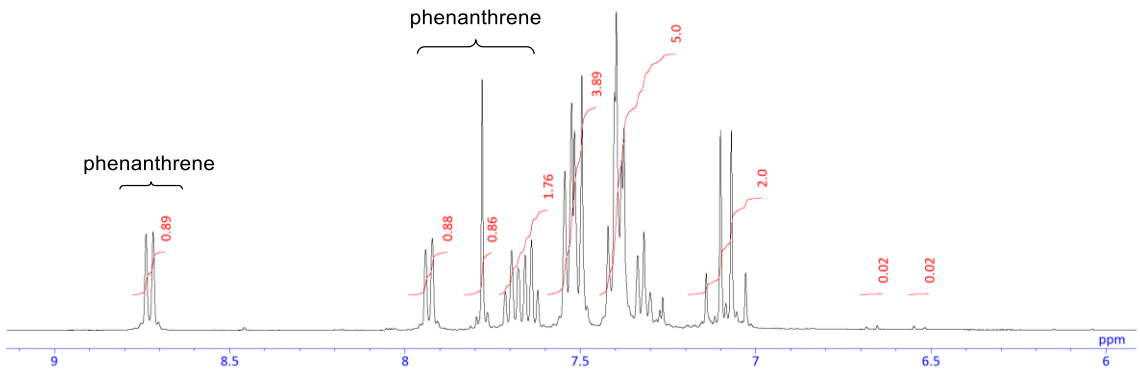


Fig. S46 ^{1}H NMR spectrum ($CDCl_3$) for catalytic semi-hydrogenation of *p*-bromo diphenylacetylene (0.5 mol% **2**, 70 °C, 3 h, H_2 1 atm).

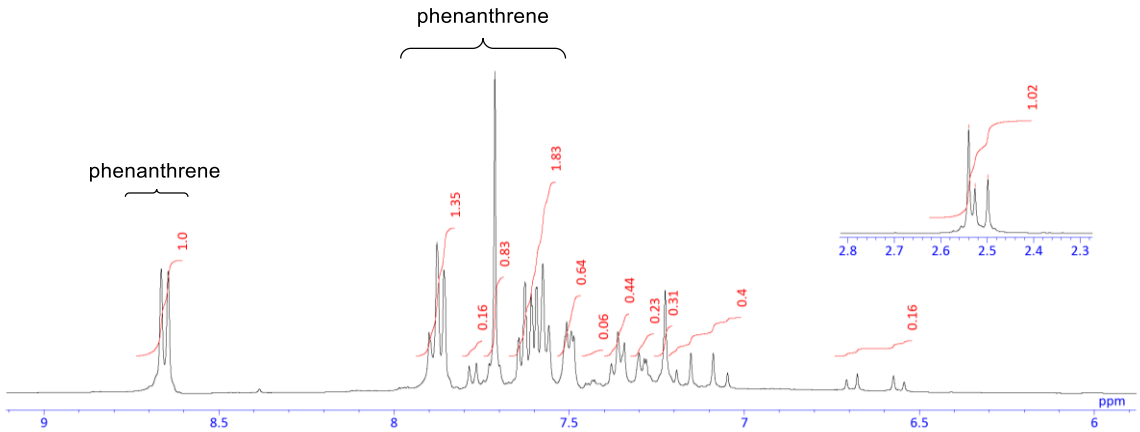


Fig. S47 ^{1}H NMR spectrum for catalytic semi-hydrogenation of *p*-acetyldiphenylacetylene (0.5 mol% **2**, 70 °C, 89 h, H_2 1 atm).

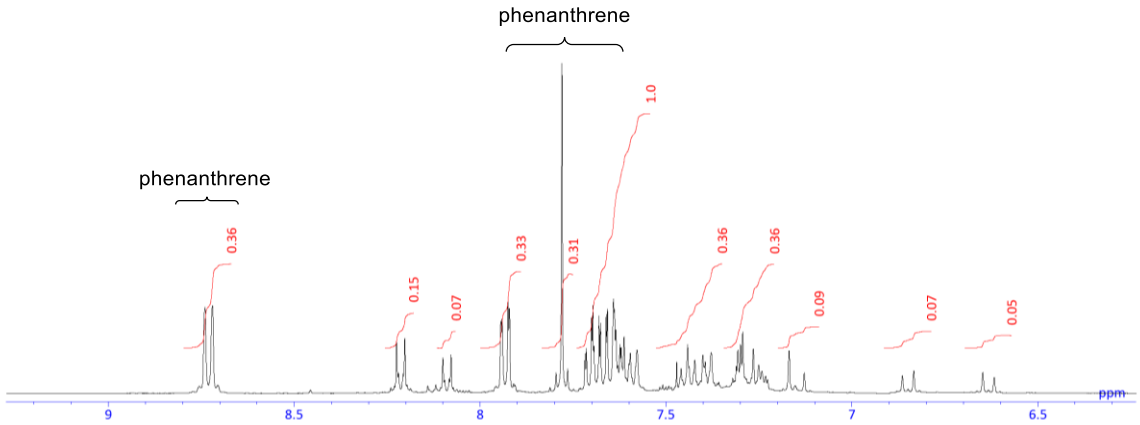


Fig. S48 ^{1}H NMR spectrum for catalytic semi-hydrogenation of *p*-nitrodiphenylacetylene (0.5 mol% **2**, 70 °C, 39 h, H_2 1 atm).

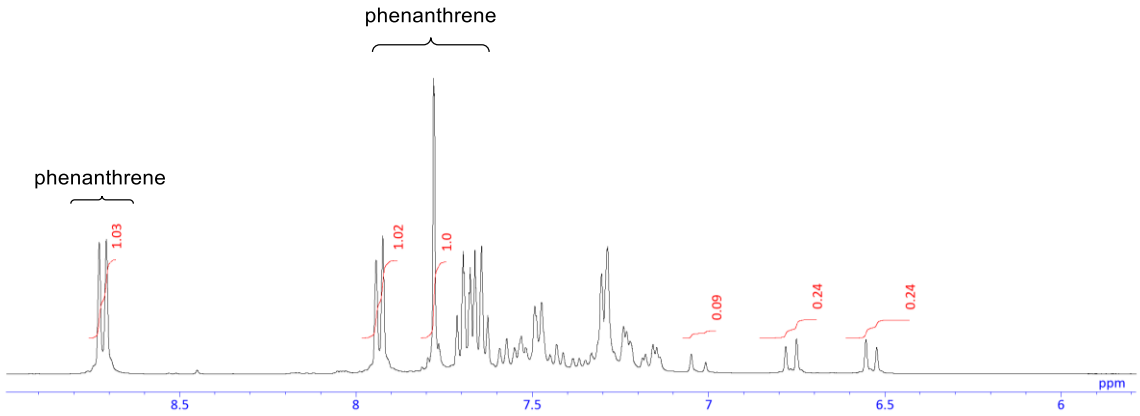


Fig. S49 ^{1}H NMR spectrum for catalytic semi-hydrogenation of *p*-cyanodiphenylacetylene (0.5 mol% **2**, 70 °C, 73 h, H_2 1 atm).

X-ray crystallography

Single crystals of each compound were prepared as described in the synthetic procedures. All measurements were performed on a Rigaku R-AXIS Rapid imaging plate detector with graphite monochromated Mo Kα radiation (λ = 0.71069 Å) at 173 K. The frame data were processed using Rigaku PROCESS-AUTO,[8] and the reflection data were corrected for absorption with ABSCOR.[9] The structures were solved by SHELXS-97 and refined by SHELXL-97.[10] All non-hydrogen atoms were refined with anisotropic displacement parameters unless otherwise mentioned. Hydrogen atoms were placed at calculated positions and treated as riding models unless otherwise mentioned. Complex **1'** crystallized as the dichloromethane solvate **1'**·$(CH_2Cl_2)_2$. One of the CH_2Cl_2 molecules was found in two different orientations which share the carbon (C55) and one of the chlorine atoms (Cl5). This CH_2Cl_2 molecule was thus treated as a split occupancy model (occ. = 0.60 for Cl5-C55-Cl4 and 0.40 for Cl5-C55-Cl3). Hydrogen atoms on this CH_2Cl_2 molecule were not included in the refinement of the structure. Selected crystallographic data are summarized in Table S1. Further details are provided in the crystallographic information file (CIF).

Table S1 Selected Crystallographic data for **1'**·$(CH_2Cl_2)_2$ and **3**·$(CH_2Cl_2)_2(THF)_4$.

	1'·$(CH_2Cl_2)_2$	**3**·$(CH_2Cl_2)_2(THF)_4$
formula	$C_{55}H_{52}N_4O_3F_3P_2SCl_4RuRh$	$C_{106}H_{108}B_2N_8O_4F_8P_4Cl_4Cu_2Ru_2$
M	1313.83	2326.62
T/K	173(2)	173 (2)
size (mm)	0.40 × 0.10 × 0.01	0.40 × 0.20 × 0.10
crystal system	triclinic	monoclinic
space group	*P*-1	*C*2/*c*
Z	2	4
a (Å)	10.7935(6)	33.050(3)
b (Å)	15.5987(9)	16.3313(11)
c (Å)	17.0524(11)	22.7509(16)
α (deg)	82.036(6)	90.0000
β (deg)	88.284(6)	123.565(9)
γ (deg)	74.438(5)	90.0000
V (Å^3)	2739.0(3)	10232.2(16)
D_{calc} (g/cm^3)	1.593	1.510
μ (mm^{-1})	0.926	0.938

reflns collected	26334	76424
unique reflns	12104	11617
GOF on F^2	1.022	1.043
R1 [$I > 2\sigma(I)$][a]	0.0578	0.0489
wR2 (all data)[b]	0.1489	0.1427

[a] $R1 = (\Sigma \, ||Fo| - |Fc|| \,) / \Sigma \, |Fo|$, [b] $wR2 = [\{\Sigma \, (w(Fo^2 - Fc^2)^2 \,)\} / \Sigma \, w(Fo^2)^2]^{1/2}$

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