Supprting Information for:

(π-Allyl)palladium Complexes Bearing Diphosphinidenecyclobutene Ligands: A Highly Active Catalyst for Hydroamination of 1,3-Dienes**

Tatsuya Minami, Hideyuki Okamoto, Shintaro Ikeda, Rika Tanaka, Fumiyuki Ozawa,* and Masaaki Yoshifuji†

Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558-8585 (Japan)

†Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578 (Japan)

[E-mail: ozawa@a-chem.eng.osaka-cu.ac.jp; Fax: (+81) 6-6605-2978]

Experimental Section

General Procedure. All manipulations were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was dried by passing through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts are reported in δ (ppm), referred to ^1H (of residual protons) and ^{13}C signals of the deuterated solvents or to the ^{31}P signal of an external 85% H_3PO_4 standard. GLC analysis was performed on a Shimadzu GC-14B instrument equipped with a FID detector and a capillary column (CBP-1, 25 m ∞ 0.25 mm). Mass spectra were measured with a Shimadzu QP-5000 GC-mass spectrometer (EI, 70 eV). Flash column chromatography was performed using Merck silica gel 60 (230–400 mesh). Toluene, benzene, THF, and Et_2O were dried over sodium benzophenone ketyl and distilled prior to use. CH_2Cl_2 was dried over CaH_2 and distilled prior to use.

Preparation of Diphosphinidenecyclobutene Ligands. The syntheses basically follow the procedure reported for 1,2-diphenyl-3,4-bis[(2,4,6-triisopropylphenyl)phosphinidene]cyclobutene.[1]

1,2-Bis(4-methoxyphenyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene. Bis(dimethylamino)chlorophosphine[2] (1.85 g, 12.0 mmol) was added at –78 °C to a solution of (4-methoxyphenyl)ethynyllithium, which was prepared in situ from 4-methoxyethynylbenzene (1.60 g, 12.1 mmol) and *n*-butyllithium (7.50 mL, 1.60 M in hexane, 12.0 mmol) in Et_2O (20 mL) at –78 °C. The mixture was stirred for 12 h at room temperature. Hydrogen chloride gas (*ca*. 240 mmol) was passed through the reaction mixture at –78 °C for 15 min, and the resulting precipitate of dimethylammonium chloride was removed by filtration through a celite pad. The solvent was evaporated, and the remaining pale yellow oil was distilled under reduced pressure (0.05 mmHg) to give [(4-methoxyphenyl)ethynyl]phosphorous dichloride (1.6 g, *ca* 60%), which was highly moisture-sensitive. The product was dissolved in THF (20 mL) and used immediately for the next reaction.

The THF solution thus prepared was added at –78 °C to a solution of 2,4,6-tri-*t*-butylphenyllithium,[3] which was prepared from 2,4,6-tri-*t*-buthylphenylbromide (2.40 g, 7.4 mmol) and *n*-butyllithium (4.5 mL, 1.60 M in hexane, 7.2 mmol) in THF at –78 °C. The mixture was warmed to room temperature with stirring to give a solution of (2,4,6-tri-*t*-butylphenyl)[(4-methoxyphenyl)ethynyl]phosphinous chloride. Zinc powder (970 mg, 14.8 mmol) was added in one portion to the solution, and the mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO_2, hexane) to give the title compound as a yellow crystalline solid (980 mg, 32% yield based on 2,4,6-tri-*t*-buthylphenylbromide). ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 1.39 (s, 18H, *p*-*t*-Bu), 1.55 (s, 36H, *o*-*t*-Bu), 3.67 (s, 6H, OMe), 6.31 (d, *J* = 9.0 Hz, 4H, *o*-Ph), 6.43 (d, *J* = 9.0 Hz, 4H, *m*-Ph), 7.37 (s, 4H, PPh); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 31.7 (s, *p*-C*Me*$_3$), 33.2 (s, *o*-C*Me*$_3$), 35.1 (s, *p*-*C*Me$_3$), 38.4 (s, *o*-*C*Me$_3$), 55.0 (s, O*C*H$_3$), 113.0 (s), 129.7 (s), 121.7 (s), 124.4 (s), 129.5 (d,

J = 27 Hz), 149.8 (s), 154.7 (s), 158.9 (s), 159.9 (dd, *J* = 52, 28 Hz, P=C), 176.5 (dd, *J* = 17, 10 Hz, P=C–*C*); $^{31}P\{^{1}H\}$ NMR (121.5 Hz, $CDCl_3$, 20 °C): δ = 162.2 (s).

Similarly, 1,2-diphenyl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene and 1,2-bis(4-trifluoromethylphenyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene were prepared in 41 and 54% yields, respectively, using ethynylbenzene and 4-trifluoromethyl-ethynylbenzene in place of 4-methoxyethynylbenzene. The former is a known compound.[4] The NMR data for the latter compound are as follows. ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 1.36 (s, 18H, *p*-*t*-Bu), 1.54 (s, 36H, *o*-*t*-Bu), 6.57 (d, *J* = 8.1 Hz, 4H, *o*-Ph), 7.06 (d, *J* = 8.1 Hz, 4H, *m*-Ph), 7.43 (s, 4H, PPh); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 31.6 (s, *p*-C*Me*$_3$), 33.3 (s, *o*-C*Me*$_3$), 35.1 (s, *p*-*C*Me$_3$), 38.4 (s, *o*-*C*Me$_3$), 121.9 (s), 128.1 (s), 123.7 (q, *J* = 275 Hz, CF_3), 124.6 (d, *J* = 4 Hz), 128.3 (d, *J* = 27 Hz), 129.3 (q, *J* = 32 Hz), 134.7 (s), 150.7 (s), 154.8 (s), 134.5 (dd, *J* = 49, 28 Hz, P=C), 174.5 (dd, *J* = 18, 10 Hz, P=C–*C*); $^{31}P\{^{1}H\}$ NMR (121.5 Hz, $CDCl_3$, 20 °C): δ = 181.0 (s).

Preparation of Complex 1. To a solution of $[Pd(\pi\text{-allyl})Cl]_2$ (110 mg, 0.30 mmol) and 1,2-diphenyl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (500 mg, 0.66 mmol) in dichloromethane (15 mL) was added AgOTf (155 mg, 0.60 mmol) at 0 °C in one portion. After stirring for 2 h at room temperature, the white precipitate of AgCl was removed by filtration through a celite pad. The filtrate was concentrated under reduced pressure and layered with Et_2O, giving a yellowish orange solid of **1** (608 mg, 96%). ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 1.44 (s, 18H, *p*-*t*-Bu), 1.51 (s, 18H, *o*-*t*-Bu), 1.61 (s, 18H, *o*-*t*-Bu), 3.73 (dt, *J* = 13.5, 6.9 Hz, 2H, allyl H^{anti}), 4.99 (dt, *J* = 6.9, 3.3 Hz, 2H, allyl H^{syn}), 5.94 (tt, *J* = 13.5, 6.9 Hz, 1H, allyl $H^{central}$), 6.76 (d, *J* = 7.8 Hz, 4H, *o*-Ph), 6.96 (t, *J* = 7.8 Hz, 4H, *m*-Ph), 7.25 (t, *J* = 7.8 Hz, 2H, *p*-Ph), 7.60 (d, *J* = 1.5 Hz, 2H, PPh), 7.63 (d, *J* = 1.5 Hz, 2H, PPh); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 31.3 (s, *p*-C*Me*$_3$), 33.6 (s, *o*-C*Me*$_3$), 33.8 (s, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 38.7 (s, *o*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 76.8 (t, *J* = 19 Hz, allyl $C^{1,3}$), 120.9 (q, *J* = 321 Hz, CF_3SO_3), 122.2 (t, *J* = 8 Hz, allyl C^{2}), 123.4 (t, *J* = 5 Hz), 123.5 (t, *J* = 4 Hz), 125.7 (t, *J* = 2 Hz), 128.1 (s), 128.7 (s), 129.0 (s), 131.4 (s), 154.0 (m, *J* = 68, 47 Hz, P=C), 155.2 (s), 156.9 (s), 157.1 (s), 173.8 (dd, *J* = 32, 29 Hz, P=C–*C*); $^{31}P\{^{1}H\}$

NMR (121.5 MHz, $CDCl_3$, 20 °C): δ = 144.3 (s); elementary analysis calcd for $C_{56}H_{73}O_3P_2SF_3Pd$: C 63.96; H 7.00; found: C 63.81; H 7.04.

2 (66% yield): ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 1.45 (s, 18H, *p*-*t*-Bu), 1.52 (s, 18H, *o*-*t*-Bu), 1.61 (s, 18H, *o*-*t*-Bu), 3.64 (dt, *J* = 13.2, 7.0 Hz, 2H, allyl H^{anti}), 3.74 (s, 6H, OMe), 4.92 (dt, *J* = 7.3, 3.3 Hz, 2H, allyl H^{syn}), 5.86 (tt, *J* = 13.2, 7.3 Hz, 1H, allyl $H^{central}$), 6.46 (d, *J* = 8.9 Hz, 4H, Ph) (d, *J* = 8.9 Hz, 4H, Ph), 7.62 (d, *J* = 1.2 Hz, 2H, PPh), 7.64 (d, *J* = 1.2 Hz, 2H, PPh); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 31.3 (s, *p*-C*Me*$_3$), 33.5 (s, *o*-C*Me*$_3$), 33.7 (s, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 38.7 (s, *o*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 55.4 (s, OMe), 76.0 (t, *J* = 19 Hz, allyl $C^{1,3}$), 114.2 (s), 120.9 (q, *J* = 321 Hz, CF_3SO_3), 121.4 (s), 121.6 (t, *J* = 7 Hz, allyl C^2), 123.3 (t, *J* = 3 Hz), 123.4 (t, *J* = 4 Hz), 126.2 (t, *J* = 1 Hz), 130.1 (s), 152.9 (m, *J* = 70, 49 Hz, P=C), 155.0 (s), 157.0 (s), 157.2 (s), 161.9 (s), 174.3 (dd, *J* = 32, 29 Hz, P=C–*C*); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): δ = 135.2 (s); elementary analysis calcd for $C_{58}H_{77}O_5P_2SF_3Pd$: C 62.67; H 6.98; found: C 62.55; H 7.02.

3 (93% yield): ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 1.44 (s, 18H, *p*-*t*-Bu), 1.52 (s, 18H, *o*-*t*-Bu), 1.62 (s, 18H, *o*-*t*-Bu), 3.91 (dt, *J* = 13.2, 7.0 Hz, 2H, allyl H^{anti}), 5.11 (dt, *J* = 7.1, 3.3 Hz, 2H, allyl H^{syn}), 6.06 (tt, *J* = 13.2, 7.1 Hz, 1H, allyl $H^{central}$), 6.83 (d, *J* = 8.2 Hz, 4H, Ph), 7.23 (d, *J* = 8.2 Hz, 4H, Ph), 7.61 (d, *J* = 1.0 Hz, 2H, PPh), 7.64 (d, *J* = 1.0 Hz, 2H, PPh); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 31.2 (s, *p*-C*Me*$_3$), 33.7 (s, *o*-C*Me*$_3$), 33.9 (s, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 38.7 (s, *o*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 78.3 (t, *J* = 18 Hz, allyl $C^{1,3}$), 120.8 (q, *J* = 321 Hz, CF_3SO_3), 123.2 (q, *J* = 273 Hz, CF_3), 123.2 (t, *J* = 8 Hz, allyl C^2), 123.6 (t, *J* = 3 Hz), 123.7 (t, *J* = 3 Hz), 125.1 (t, *J* = 3 Hz), 125.7 (q, *J* = 4 Hz), 128.2 (s), 132.2 (s), 132.5 (q, *J* = 33 Hz), 152.2 (m, *J* = 66, 45 Hz, P=C), 155.7 (s), 157.1 (s), 157.4 (s), 172.2 (dd, *J* = 32, 29 Hz, P=C–*C*); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): δ = 155.1 (s); elementary analysis calcd for $C_{57}H_{72}O_3P_2SF_6Pd$: C 61.15; H 6.48; found: C 61.02; H 6.35.

Catalytic Hydroamination. A typical procedure (entry 1 in Table 1) is as follows. To a solution of **1** (21.0 mg, 0.020 mmol) and 1,3-cyclohexadiene (0.10 mL, 1.05 mmol) in toluene (2 mL) was added aniline (0.18 mL, 1.98 mmol) under a nitrogen atmosphere. The mixture was stirred at room temperature for 5 h. GLC analysis revealed complete

consumption of the diene. The reaction mixture was concentrated to dryness by pumping and purified by column chromatography (SiO_2, hexane/AcOEt = 100/1) to give 162 mg (89% yield) of 3-(*N*-phenylamino)cyclohexene.

3-(*N*-Phenylamino)cyclohexene[5] (Table 1). ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 1.56–1.82 (m, 3H, CH_2), 1.82–2.01 (m, 1H, CH_2), 2.01–2.16 (m, 2H, CH_2), 3.66 (br, 1H, NH), 4.02 (br, 1H, CHN), 5.78 (ddt, *J* = 10.1, 2.9, 2.0 Hz, 1H, NCHC*H*=CH), 5.88 (dtd, *J* = 10.1, 3.5, 1.5 Hz, 1H, CH_2C*H*=CH), 6.65 (m, 2H, *o*-Ph), 6.71 (tt, *J* = 7.3, 1.1 Hz, 2H, *m*-Ph), 7.20 (m, 1H, *p*-Ph); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 19.6 ($CH_2CH_2CH_2$), 25.1 (CH_2CHN), 28.8 (C=CHCH_2), 47.8 (CHN), 113.2 (*o*-Ph), 117.1 (*p*-Ph), 128.5 (NCH*C*H=CH), 129.3 (*m*-Ph), 130.1 (CH_2*C*H=CH), 147.1 (*ipso*-Ph); IR (neat): ν = 3404, 3020, 2924, 2858, 1915, 1820, 1601, 1503, 1309, 1244, 1103, 864, 748, 725 cm^{-1}; MS, m/z (relative intensity): 173 (M^+, 44), 154 (10), 145 (51), 130 (14), 93 (100), 77 (46), 65 (21).

A mixture of 2-(*N*-phenylamino)-3-decene and 4-(*N*-phenylamino)-2-decene (80 : 10 ; entry 1 in Table 2). ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 0.84–0.95 (m, 3H, CH_3), 1.19–1.59 (m, 13H), 3.59 (brs, 0.8H, NH), 3.70 (brs, 0.2H, NH), 3.73 (dt, *J* = 6.6, 6.6 Hz, 0.2H, NCH), 3.94 (dq, *J* = 6.3, 6.3 Hz, 0.8H, NCH), 5.33 (ddq, *J* = 15.4, 6.6, 1.6 Hz, 0.2H, CH=C*H*CHN), 5.40 (ddt, *J* = 15.4, 6.3, 1.3 Hz, 0.8H, CH=C*H*CHN), 5.63 (dtd, *J* = 15.4, 6.4, 1.0 Hz, 0.8H, CH=C*H*CH_2), 5.56–5.72 (m, 0.2H, CH=C*H*CH_2), 6.57–6.71 (m, 3H, *o*- and *p*-Ph), 7.12–7.18 (m, 2H, *m*-Ph); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): major isomer, δ = 14.1 (CH_2CH_3), 22.1 (CH_2), 22.6 (CH_2), 28.7 (CH(NHPh)CH_3), 29.2 (CH_2), 31.7 (CH_2), 32.2 (CH=CHCH_2), 50.5 (*C*HNPh), 113.4 (*o*-Ph), 117.0 (*p*-Ph), 129.0 (*m*-Ph), 130.7 (CH_2*C*H), 132.9 (CH=*C*HCHNPh), 147.5 (*ipso*-Ph); minor isomer, δ = 17.7 (CH_2CH_3), 22.6 (CH_2), 25.9 (CH_2), 29.2 (CH_2), 31.8 (CH_2), 32.2 (CH_2), 36.2 (CH=CHCH_3), 55.3 (*C*HNPh), 113.2 (*o*-Ph), 116.8 (*p*-Ph), 125.9 (CH_2*C*H=CH), 129.0 (*m*-Ph), 133.2 (CH=*C*HCHNPh), 147.8 (*ipso*-Ph); IR (neat): ν = 3408, 3051, 3019, 2957, 2926, 2855, 1912, 1817, 1601, 1504, 1318, 1255, 967, 747, 691 cm^{-1}; MS, m/z (relative intensity): major isomer, 231 (M^+, 16), 216 (35), 146 (45), 132 (23), 118 (13), 93 (100), 77 (Ph); minor isomer, 231 (M^+, 6), 216 (2), 146 (100), 118 (7), 93 (25), 77 (13).

1-Phenyl-3-(*N*-phenylamino)-1-butene[6] (entry 2 in Table 2). ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 1.47 (dd, *J* = 6.6, 1.8 Hz, 3H, CH_3), 3.78 (br, 1H, NH), 4.21 (m, 1H, CHN), 6.28 (ddd, *J* = 15.9, 5.8, 1.9 Hz, 1H, PhCH=C*H*), 6.65 (d, *J* = 15.9 Hz, 1H, PhC*H*=CH), 6,70–6.79 (m, 3H, *p*- and *o*-NPh), 7.15–7.45 (m, 7H, Ph and *m*-NPh); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 22.1 (CH_3), 50.8 (*C*HNPh), 113.3 (*o*-NPh), 117.3 (*p*-NPh), 126.3 (*Ph*), 127.3 (*Ph*), 128.5 (*Ph*), 129.2 (PhCH=*C*H), 129.2 (*m*-NPh), 133.2 (Ph*C*H=CH), 136.9 (*ipso*-Ph), 147.4 (*ipso*-NPh); IR (neat): ν = 3407, 3051, 3023, 2968, 2924, 1945, 1878, 1815, 1719, 1600, 1503, 1318, 1256, 1178, 1073, 967, 747, 692 cm^{-1}; MS, m/z (relative intensity): 223 (M^+, 21), 208 (11), 131 (100), 115 (19), 91 (51), 77 (25), 51 (21).

A mixture of 3-methyl-1-(*N*-phenylamino)-2-butene[7] **and 2-methyl-1-(*N*-phenylamino)-2-butene** (88 : 12, entry 3 in Table 2). ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 1.65 (dq, *J* = 6.8, 1.1 Hz, 0.36H, C*H*$_3$CH=C), 1.69 (t, *J* = 1.1 Hz, 0.36H, CH=C(C*H*$_3$)), 1.74 (br, 2.64H, (C*H*$_3$)$_2$C=C), 1.77 (br, 2.64H, (C*H*$_3$)$_2$C=C), 3.60 (br, 1H, NH), 3.66 (br, 0.24H, C*H*$_2$NPh), 3.71 (d, *J* = 6.6 Hz, 1.76H, C*H*$_2$NPh), 5.36 (t of septet, *J* = 6.8, 1.5 Hz, 0.88H, C=C*H*), 5.52 (qq, *J* = 6.8, 1.3 Hz, 0.12H, CH$_3$C*H*=C), 6.59–6.67 (m, 2H, *o*-Ph), 6.73 (tt, *J* = 7.3, 1.1 Hz, 1H, *p*-Ph), 7.13–7.25 (m, 2H, *m*-Ph); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): major isomer, δ = 18.0 (*C*H$_3$), 25.7 (*C*H$_3$), 41.9 (*C*H$_2$NPh), 112.8 (*o*-Ph), 117.2 (*p*-Ph), 121.6 ((CH$_3$)$_2$C=*C*H), 129.2 (*m*-Ph), 135.5 ((CH$_3$)$_2$*C*=CH), 148.4 (*ipso*-Ph); minor isomer, δ = 13.2 (*C*H$_3$), 14.4 (*C*H$_3$), 51.7 (*C*H$_2$NPh), 113.2 (*o*-Ph), 117.1 (*p*-Ph), 120.4 (CH$_3$*C*H=C), 129.1 (*m*-Ph), 132.4 (CH=*C*(CH$_3$)CH$_2$), 146.9 (*ipso*-Ph); IR (neat): ν = 3401, 3050, 3019, 2969, 2912, 2857, 1914, 1819, 1601, 1505, 1428, 1376, 1316, 1252, 1179, 1093, 1063, 750, 691 cm^{-1}; MS, m/z (relative intensity): major isomer, 161 (M^+, 22), 146 (13), 93 (100), 69 (27), 41 (90); minor isomer, 161 (M^+, 34), 146 (28), 106 (53), 93 (78), 77 (34), 41 (100).

2,3-Dimethyl-1-(*N*-phenylamino)-2-butene[8] (entry 4 in Table 2). ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 1.70 (s, 3H, CH_3), 1.75 (s, 6H, CH_3), 3.51 (br, 1H, NH), 3.67 (s, 2H, CH_2N), 6.56–6.63 (m, 2H, *o*-Ph), 6.65–6.73 (m, 1H, *p*-Ph), 7.21–7.13 (m, 2H, *m*-Ph); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 17.5 (C=C*C*H$_3$), 20.2 ((*C*H$_3$)$_2$C=C), 20.8 ((*C*H$_3$)$_2$C=C), 47.1 (CH_2N), 112.6 (*o*-Ph), 117.0 (*p*-Ph), 125.2 (*C*=C), 128.8 (s, C=*C*), 129.1

(*m*-NPh), 148.8 (*ipso*-NPh); IR (neat): ν = 3417, 3049, 2989, 2913, 2859, 1914, 1603, 1603, 1505, 1427, 1317, 1250, 1093, 748, 691 cm^{-1}; MS, m/z (relative intensity): 175 (M^+, 16), 160 (8), 106 (16), 93 (100), 77 (22), 55 (59).

A mixture of 1-[1-(*N*-phenylamino)ethyl]-3,4-dihydronaphthalene[9] **and 1-ethylidenyl-2-(*N*-phenylamino)-1,2,3,4-tetrahydronaphthalene** (93 : 7, entry 5 in Table 2). ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 1.49 (d, *J* = 6.5 Hz, 2.79H, C*H*$_3$), 1.91 (d, *J* = 7.0 Hz, 0.21H, C*H*$_3$), 2.23–2.33 (m, 2H, C*H*$_2$CH=C), 2.77 (t, *J* = 8.1 Hz, 2H, ArC*H*$_2$-), 3.89 (br, 1H, NH), 4.56 (q, *J* = 6.5 Hz, 0.93H, C*H*NPh), 4.78 (t, *J* = 3.3 Hz, 0.07H, C*H*NPh), 6.19 (td, *J* = 4.7, 1.2 Hz, 0.93H, C=C*H*), 6.31 (q, *J* = 7.0 Hz, 0.07H, CH_3C*H*=C), 6.56–6.62 (m, 2H, *o*-Ph), 6.67–6.75 (m, 1H, *p*-Ph), 7.14–7.30 (m, 5H, *m*-Ph and Ar), 7.35 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): major isomer, δ = 21.6 (CH_3), 22.9 (*C*H$_2$C=C), 28.3 (Ar*C*H$_2$), 48.9 (*C*HNPh), 112.9 (*o*-Ph), 117.0 (*p*-Ph), 122.0 (Ar), 123.8 (Ar), 126.4 (Ar), 126.7 (C=*C*H), 127.8 (Ar), 129.1 (*m*-Ph), 133.9 (Ar), 137,1 (Ar), 137.7 (*C*=CH), 147.2 (*ipso*-Ph); IR (neat): ν = 3417, 3051, 3018, 2966, 2931, 2884, 2830, 1914, 1817, 1601, 1504, 1427, 1317, 1264, 1179, 737, 692 cm^{-1}; MS, m/z (relative intensity): 249 (M^+, 38), 234 (43), 156 (52), 141 (100), 129 (52), 115 (52), 93 (97), 77 (35).

1-Methyl-3-(*N*-phenylamino)cyclohexene[10] (entry 6 in Table 2). ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 1.32–1.90 (m, 4H, CH_2CH_2), 1.70 (s, 3H, CH_3), 1.92–2.00 (m, 2H, C*H*$_2$C=C), 3.62 (br, 1H, NH), 3.98 (br, 1H, CHNPh), 5.46–5.54 (m, 1H, C=C*H*CHNPh), 6.60–6.65 (m, 2H, *o*-Ph), 6.66–6.71 (m, 2H, *p*-Ph), 7.14–7.21 (m, 2H, *m*-Ph); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 19.8 (CH_2), 23.7 (CH_2), 28.5 (CH_3), 30.1 (*C*H$_2$C=C), 48.2 (*C*HNPh), 113.2 (*o*-Ph), 116.9 (*p*-Ph), 122.8 (*C*H=C), 129.3 (*m*-Ph), 137.8 (CH=*C*), 147.3 (*ipso*-Ph); IR (neat): ν = 3405, 3048, 3017, 2928, 2858, 1914, 1820, 1600, 1503, 1428, 1311, 1245, 1180, 1101, 747, 691 cm^{-1}; MS, m/z (relative intensity): 187 (M^+, 18), 172 (6), 144 (5), 93 (100), 77 (25), 67 (28).

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