**Palladium(0)-Catalyzed Regioselective and Multi-Component Synthesis of
1,2,3-Trisubstituted Indenes**

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Supplementary Material

General Techniques. Reactions were carried out in clean, dry glassware under argon atmosphere using high quality solvents. Anhydrous solutions of reaction mixtures were transferred *via* an oven-dried cannula. Anhydrous dichloromethane (CH_2Cl_2), *N,N*-dimethylformamide (DMF), methanol (MeOH) and toluene were obtained by distillation from phosphorus (V) oxide, calcium hydride, magnesium and sodium benzophenone ketyl, respectively. Yields refer to chromatographically and spectroscopically homogenous materials. Reagents were purchased at the highest commercial quality and used without further purification. Reactions were monitored by thin layer chromatography separations carried out on 0.2 mm E. Merck silica gel plates (60 F254) using UV light as a visualizing agent and phosphomolybdic acid, *p*-anisaldehyde, or potassium permanganate solutions and heat as developing agents. Flash chromatographies were performed with Kanto silica gel 60 N (spherical, neutral, 63-210 μm grade). Purifications of 1*H*-indenols and indenamines were performed on 0.75 mm Wakogel[®] B-5F PLC plates. Infrared (IR) data were recorded on SensIR technologies' TravelIR[™]. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). ^1H and ^{13}C nuclear magnetic resonance (NMR) were recorded on JEOL AL 400 (400 and 100 MHz respectively). Chemical shifts are reported in delta (δ) units, in parts per million ppm) relative to the singlet at 7.25 ppm for chloroform-*d*. Splitting pattern are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. Coupling constants (*J*) are reported in Hertz (Hz). Low and high resolution mass spectral (LRMS and HRMS) were obtained from Mass Spectrometry Resource, Graduate School of Pharmaceutical Sciences, Tohoku University, on a JEOL JMS-DX303 and JMS-700 spectrometer respectively.

Preparation of Substrates.

Substrates **5a**¹, **5b**², **5c**², **5e**³, **5l**⁴ were prepared according to the literature procedure.

Substrates **5d** and **5j** were prepared by Sonogashira coupling of **5a** with commercially available 4-ethynyl-*N,N*-dimethylaniline and 1-phenyl-1,3-butadiyne⁵.

Substrates **5f-i** were prepared by Sonogashira coupling of **5a** with commercially available 4'-iodoacetophenone, 1-iodo-4-nitrobenzene, 2-bromothiophene, and *cis*-1-bromo-1-propene.

Substrate **5k** was prepared from 6-ethynyl-1, 3-benzodioxole-5-carboxaldehyde⁶ by 1,2-addition of methylmagnesium bromide, Sonogashira coupling with 4'-iodoacetophenone, and Swern oxidation.

Substrates **5m-5o** were prepared from **5c** by condensation with benzylamine⁷, aniline, and *p*-toluenesulfonamide under reflux in toluene with a Dean-Stark water separator.

General Procedure for the Pd⁰-Catalyzed Synthesis of 1*H*-Indenols 1.

General procedure for the arylation cyclization of **5a-o** (Table 1, entries 1-15, 17-21):

To a test tube containing **5a-o** (1 eq., see Table 1S), arylboronic acid **6A-E** (1.5 eq.), Pd source (A: Pd₂dba₃ B: (η^3 -allyl)(η^5 -cyclopentadienyl)Pd, 5 mol%), and PCy₃ (20 mol%) was added anhydrous solvent (MeOH for **5a-l** or *t*BuOH for **5m-o**, 0.24 M) under argon. The resulting mixture was sealed with a screw cap and agitated at 80 °C for **5a-g-j** and 100 °C for **5h-i-k-o** for the time described in Table 1. The mixture was cooled down to room temperature, and then *N,N*-diethanolaminomethyl polystyrene⁸ (PS-DEAMTM, 1.8 mmol/g, 3 eq., X g) and THF (10 x X mL) were added to remove an excess of **6A-E**. The mixture was agitated at room temperature for 2 h. The mixture was filtered and thoroughly washed with CHCl₃. The filtrate was concentrated *in vacuo* and the residue was purified by preparative TLC.

Table 1S

5 (mg, mmol)	6 (mg, mmol)	[Pd] (mg, μ mol)	PCy ₃ (mg, μ mol)	product (mg, mmol, %)
5a ; 15.4, 0.118	6A ; 24.7, 0.182	A: 2.9, 3.2	7.2, 26	1aA ; 0, 0, 0
5b ; 24.7, 0.118	6A ; 24.8, 0.182	A: 2.8, 3.1	7.0, 25	1bA ; 0, 0, 0
5c ; 24.7, 0.120	6A ; 24.6, 0.181	A: 2.8, 3.1	7.0, 25	1cA ; 30.4, 0.102, 85
5d ; 29.4, 0.118	6A ; 24.5, 0.180	A: 3.0, 3.3	7.2, 26	1dA ; 32.8, 0.0944, 80
5e ; 28.4, 0.120	6A ; 24.7, 0.182	A: 2.9, 3.2	7.1, 25	1eA ; 34.3, 0.104, 87
5f ; 29.7, 0.119	6A ; 24.5, 0.180	A: 3.1, 3.4	7.2, 26	1fA ; 30.2, 0.0881, 74
5g ; 30.2, 0.120	6A ; 24.5, 0.180	A: 3.2, 3.5	7.0, 25	1gA ; 28.1, 0.0816, 68
5h ; 25.5, 0.119	6A ; 24.6, 0.181	A: 2.9, 3.2	7.0, 25	1hA ; 34.8, 0.119, 100
5i ; 20.4, 0.120	6A ; 24.8, 0.182	A: 3.0, 3.3	6.9, 25	1iA ; 20.3, 0.0816, 68
5i ; 20.2, 0.119	6A ; 24.8, 0.182	B: 1.3, 6.1	7.0, 25	1iA ; 26.3, 0.105, 88
5j ; 27.4, 0.119	6A ; 24.6, 0.181	B: 1.5, 7.0	6.9, 25	1jA ; 29.6, 0.0952, 80
5c ; 24.5, 0.119	6B ; 27.4, 0.180	A: 2.8, 3.1	7.2, 26	1cB ; 32.8, 0.104, 87
5c ; 24.8, 0.120	6C ; 22.5, 0.184	A: 2.9, 3.2	7.0, 25	1cC ; 25.9, 0.0912, 76
5c ; 24.7, 0.120	6D ; 29.7, 0.181	A: 3.0, 3.3	7.1, 25	1cD ; 29.0, 0.0888, 74
5c ; 24.6, 0.119	6E ; 15.4, 0.179	A: 2.8, 3.1	7.2, 26	1cE ; 21.2, 0.0845, 71
5k ; 36.9, 0.120	6B ; 27.2, 0.179	B: 1.4, 6.6	6.8, 24	1kB ; 48.2, 0.116, 97
5l ; 35.6, 0.126	6A ; 24.6, 0.181	A: 2.9, 3.2	7.0, 25	1lA ; 34.6, 0.0970, 77
5m ; 37.8, 0.128	6A ; 24.3, 0.179	B: 1.2, 5.6	6.7, 24	2mA ; 0, 0, 0
5n ; 36.7, 0.121	6A ; 24.2, 0.170	B: 1.3, 6.1	6.7, 24	2nA ; 0, 0, 0
5o ; 43.1, 0.120	6A ; 24.5, 0.180	B: 1.3, 6.1	6.8, 24	2oA ; 39.6, 0.0876, 73

Procedure for the ethylative cyclization of **5c** (Table 1, entry 16):

To a test tube containing **5c** (24.8 mg, 0.120 mmol), (η^3 -allyl)(η^5 -cyclopentadienyl)Pd (1.9 mg, 8.1 μ mol), and PCy₃ (7.2 mg, 26 μ mol) were added anhydrous MeOH (0.26 mL) and a 1.0 M solution of triethylborane (**6F**) in THF (0.24 mL, 0.24 mmol) under argon. The resulting mixture was sealed with a screw cap and agitated at 80 °C for 1.5 h. The mixture was cooled down to room temperature, and then partitioned between EtOAc and saturated aqueous NaHCO₃. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by preparative TLC eluting with 10% EtOAc/hexane to yield 23.0 mg (0.0972 mmol, 81%) of **1cF** as a yellow oil.

3-(4-Methylphenyl)-2-phenyl-1*H*-inden-1-ol (**1cA**) was isolated by preparative TLC

eluting with 5% EtOAc/hexane.

Pale yellow amorphous mass. IR (neat): 3510-3120 (br), 791, 717 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.55-7.15 (m, 11 H), 7.10 (d, J = 7.5 Hz, 2H), 5.66 (s, 1H), 2.34 (s, 3H), 1.86 (br-s, 1H). ^{13}C NMR (100 M Hz, CDCl_3): δ 140.0, 139.5, 139.2, 138.5, 137.2, 136.3, 135.4, 132.3, 130.2, 129.9, 128.7, 128.6, 122.3, 121.4, 121.3, 115.0, 78.1, 21.4. LRMS (EI) m/z (relative intensity) 298 $[\text{M}]^+$ (100), 91 (34). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{22}\text{H}_{18}\text{O}$, 298.1358; found, 298.1360.

2-[4-(Dimethylamino)phenyl]-3-(4-methylphenyl)-1*H*-inden-1-ol (**1dA**) was isolated by preparative TLC eluting with 10% EtOAc/hexane.

Pale yellow amorphous mass. IR (neat): 3530-3110 (br), 1310, 1012, 917 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.42-7.15 (m, 8 H), 7.06 (d, J = 7.6 Hz, 2H), 6.59 (d, J = 7.8 Hz, 2H), 5.67 (s, 1H), 2.97 (s, 6H), 2.37 (s, 3H) 1.86 (br-s, 1H). ^{13}C NMR (100 M Hz, CDCl_3): δ 143.7, 138.6, 136.9, 133.7, 132.0, 131.9, 129.6, 129.1, 129.0, 128.2, 128.1, 127.3, 127.1, 127.0, 126.1, 113.0, 77.2, 43.6, 21.0. LRMS (EI) m/z (relative intensity) 341 $[\text{M}]^+$ (100), 91 (45). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{24}\text{H}_{23}\text{NO}$, 341.1780; found, 341.1772.

2-(4-Methoxyphenyl)-3-(4-methylphenyl)-1*H*-inden-1-ol (**1eA**) was isolated by preparative TLC eluting with 10% EtOAc/hexane.

Pale yellow amorphous mass. IR (neat): 3560-3120 (br), 1379, 1240, 791, 717 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.63 (d, J = 6.8 Hz, 1H), 7.31-7.21 (m, 8 H), 7.14 (d, J = 7.3 Hz, 1H), 6.80 (d, J = 9.0 Hz, 2H), 5.64 (d, J = 8.7 Hz, 1H), 3.79 (s, 3H), 2.41 (s, 3H), 1.75 (d, J = 8.7 Hz, 1H). ^{13}C NMR (100 M Hz, CDCl_3): δ 143.5, 138.4, 136.3, 133.3, 131.7, 130.6, 130.4, 129.4, 129.2, 128.6, 127.6, 127.2, 127.1, 127.0, 126.1, 113.8, 77.9, 56.3, 21.4. LRMS (EI) m/z (relative intensity) 328 $[\text{M}]^+$ (100), 91 (56). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{23}\text{H}_{20}\text{O}_2$, 328.1463; found, 328.1453.

2-(4-Acetylphenyl)-3-(4-methylphenyl)-1*H*-inden-1-ol (**1fA**) was isolated by preparative TLC eluting with 10% EtOAc/hexane.

Yellow amorphous mass. IR (neat): 3540-3110 (br), 1693, 914, 717 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.86 (d, J = 8.0 Hz, 2H), 7.55-7.20 (m, 8 H), 7.13 (d, J = 7.6 Hz, 2H), 5.65 (s, 1H), 2.53 (s, 3H), 2.35 (s, 3H), 1.86 (br-s, 1H). ^{13}C NMR (100 M Hz, CDCl_3): δ 197.0, 142.0, 139.5, 138.6, 137.2, 136.8, 135.7, 132.4, 131.5, 130.0, 129.7, 122.8, 126.4, 125.4, 121.7, 121.5, 115.0, 78.3, 23.0, 21.5. LRMS (EI) m/z (relative intensity) 340 $[\text{M}]^+$ (89), 297 (100), 91 (34). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{24}\text{H}_{20}\text{O}_2$, 340.1463; found,

340.1465.

3-(4-Methylphenyl)-2-(4-nitrophenyl)-1*H*-inden-1-ol (**1gA**) was isolated by preparative TLC eluting with 20% EtOAc/hexane.

Brown amorphous mass. IR (neat): 3540-3110 (br), 1534, 1345, 914, 845, 717 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 8.13 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.55-7.20 (m, 6 H), 7.17 (d, J = 7.8 Hz, 2H), 5.67 (s, 1H), 2.35 (s, 3H), 1.92 (br-s, 1H). ^{13}C NMR (100 M Hz, CDCl_3): δ 148.0, 141.0, 137.1, 136.4, 135.3, 133.8, 133.7, 132.5, 131.2, 131.0, 129.9, 124.5, 123.4, 122.3, 121.1, 115.7, 77.3, 21.4. LRMS (EI) m/z (relative intensity) 343 $[\text{M}]^+$ (100), 91 (56). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{22}\text{H}_{17}\text{NO}_3$, 343.1208; found, 343.1220.

3-(4-Methylphenyl)-2-(2-thienyl)-1*H*-inden-1-ol (**1hA**) was isolated by preparative TLC eluting with 10% EtOAc/hexane.

Pale yellow amorphous mass. IR (neat): 3560-3120 (br), 1240, 974, 911, 845, 811, 723 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.43-7.12 (m, 7 H), 7.10 (d, J = 7.6 Hz, 2H), 7.01 (dd, J = 3.6, 1.4 Hz, 1H), 7.00 (dd, J = 4.9, 3.6 Hz, 1H), 5.57 (s, 1H), 2.34 (s, 3H), 1.87 (br-s, 1H). ^{13}C NMR (100 M Hz, CDCl_3): δ 143.3, 138.5, 136.2, 133.1, 131.3, 130.4, 130.3, 129.1, 129.0, 128.4, 127.4, 127.1, 127.0, 126.9, 126.0, 113.9, 77.5, 21.5. LRMS (EI) m/z (relative intensity) 290 $[\text{M}]^+$ (100), 91 (56), 83 (12). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{19}\text{H}_{14}\text{OS}$, 290.0765; found, 290.0758.

3-(4-Methylphenyl)-2-[(*Z*)-1-propenyl]-1*H*-inden-1-ol (**1iA**) was isolated by preparative TLC eluting with 10% EtOAc/hexane.

Yellow oil. IR (neat): 3540-3160 (br), 1621, 1334, 1218, 721, 720 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.45-7.11 (m, 6 H), 7.01 (d, J = 7.6 Hz, 2H), 5.64 (d, J =11.5 Hz, 1H), 5.63 (dq, J = 11.5, 5.2 Hz, 1H), 5.57 (s, 1H), 2.34 (s, 3H), 1.88 (br-s, 1H), 1.76 (d, J =5.2 Hz, 3H). ^{13}C NMR (100 M Hz, CDCl_3): δ 143.1, 138.1, 136.3, 130.2, 130.0, 129.6, 129.3, 128.2, 127.8, 127.4, 127.0, 126.5, 126.3, 115.4, 77.4, 21.5, 18.5. LRMS (EI) m/z (relative intensity) 262 $[\text{M}]^+$ (100), 91 (75). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{19}\text{H}_{18}\text{O}$, 262.1358; found, 262.1365.

3-(4-Methylphenyl)-2-(phenylethynyl)-1*H*-inden-1-ol (**1jA**) was isolated by preparative TLC eluting with 5% EtOAc/hexane.

Pale yellow amorphous mass. IR (neat): 3500-3120 (br), 2176, 791, 717 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.55-7.15 (m, 11 H), 7.12 (d, J = 7.8 Hz, 2H), 5.64 (s, 1H), 2.33 (s,

3H), 1.83 (br-s, 1H). ^{13}C NMR (100 M Hz, CDCl_3): δ 140.1, 139.3, 139.0, 138.4, 137.1, 136.2, 135.3, 132.1, 130.1, 129.5, 128.3, 128.1, 122.2, 121.6, 121.5, 115.0, 91.5, 89.4, 78.1, 21.4. LRMS (EI) m/z (relative intensity) 322 $[\text{M}]^+$ (100), 91 (22). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{24}\text{H}_{18}\text{O}$, 322.1358; found, 322.1369.

3-(4-Methoxyphenyl)-2-phenyl-1*H*-inden-1-ol (**1cB**) was isolated by preparative TLC eluting with 10% EtOAc/hexane. The ^1H , ^{13}C NMR and HRMS spectra were agreed with the reported value.⁹

Pale yellow amorphous mass. IR (neat): 3560-3120 (br), 1369, 1232, 792, 718 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.63 (d, J = 6.8 Hz, 1H), 7.42-7.21 (m, 9H), 7.13 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 2H), 5.64 (s, 1H), 3.77 (s, 3H), 1.82 (br-s, 1H). ^{13}C NMR (100 M Hz, CDCl_3): δ 144.1, 144.0, 143.1, 137.8, 134.9, 130.4, 128.9, 128.8, 128.7, 128.6, 127.6, 126.2, 125.9, 123.6, 120.2, 113.7, 77.3, 55.1. LRMS (EI) m/z (relative intensity) 314 $[\text{M}]^+$ (100), 223 (40). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{22}\text{H}_{18}\text{O}_2$, 314.1307; found, 314.1325.

2,3-Diphenyl-1*H*-inden-1-ol (**1cC**) was isolated by preparative TLC eluting with 5% EtOAc/hexane. The ^1H , ^{13}C NMR and HRMS spectra were agreed with the reported value.⁹

Pale yellow amorphous mass. IR (neat): 3540-3120 (br), 1221, 796, 711 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.65 (dd, J = 6.8, 0.8 Hz, 1H), 7.42-7.12 (m, 13 H), 5.68 (s, 1H), 1.81 (br-s, 1H). ^{13}C NMR (100 M Hz, CDCl_3): δ 144.2, 143.8, 143.7, 139.6, 134.6, 133.9, 123.5, 129.2, 128.9, 128.7, 128.6, 128.1, 127.6, 127.2, 126.2, 120.6, 77.3. LRMS (EI) m/z (relative intensity) 284 $[\text{M}]^+$ (100), 91 (56). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{21}\text{H}_{26}\text{O}$, 284.1201; found, 284.1215.

3-(4-Acetylphenyl)-3-phenyl-1*H*-inden-1-ol (**1cD**) was isolated by preparative TLC eluting with 10% EtOAc/hexane.

Yellow amorphous mass. IR (neat): 3530-3120 (br), 1697, 915, 710 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.84 (d, J = 8.2 Hz, 2H), 7.57-7.21 (m, 11 H), 5.68 (s, 1H), 2.54 (s, 3H), 1.91 (br-s, 1H). ^{13}C NMR (100 M Hz, CDCl_3): δ 197.0, 140.5, 139.5, 139.2, 138.5, 137.2, 136.2, 135.4, 132.3, 130.1, 129.9, 128.6, 128.4, 122.3, 121.4, 121.1, 115.1, 78.3, 23.0. LRMS (EI) m/z (relative intensity) 326 $[\text{M}]^+$ (86), 235 (100), 91 (56). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{23}\text{H}_{18}\text{O}_2$, 326.1307; found, 326.1295.

2-Phenyl-3-[(*Z*)-1-propenyl]-1*H*-inden-1-ol (**1cE**) was isolated by preparative TLC

eluting with 10% EtOAc/hexane.

Yellow oil. IR (neat): 3520-3140 (br), 1614, 1322, 1221, 734, 708 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.43-7.14 (m, 9 H), 5.64 (d, J = 10.7 Hz, 1H), 5.62 (dq, J = 10.7, 6.8 Hz, 1H), 5.61 (s, 1H), 1.73 (d, J = 6.8 Hz, 3H), 1.86 (br-s, 1H). ^{13}C NMR (100 M Hz, CDCl_3): δ 143.0, 138.0, 135.6, 130.8, 130.2, 129.9, 129.4, 128.2, 127.8, 127.3, 127.1, 126.7, 126.4, 115.2, 77.1, 18.7. LRMS (EI) m/z (relative intensity) 248 $[\text{M}]^+$ (100), 207 (42). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{18}\text{H}_{16}\text{O}$, 248.1201; found, 248.1222.

3-Ethyl-2-phenyl-1*H*-inden-1-ol (**1cF**): IR (neat): 3540-3310 (br), 961, 734, 708 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.45-7.13 (m, 8H) 7.06 (dd, J = 7.8, 7.8 Hz, 1H), 5.62 (s, 1H), 2.13 (q, J = 7.3 Hz, 2H), 1.84 (br-s, 1H), 1.04 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 M Hz, CDCl_3): δ 143.1, 137.9, 135.3, 130.4, 130.1, 129.7, 129.5, 128.1, 127.8, 127.4, 126.2, 115.1, 77.4, 26.3, 11.7. LRMS (EI) m/z (relative intensity) 236 $[\text{M}]^+$ (100), 207 (23). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{17}\text{H}_{16}\text{O}$, 236.1201; found, 236.1196.

6-(4-Acetylphenyl)-7-(4-methoxyphenyl)-5-methyl-5*H*-indeno[5,6-*d*]-1,3-dioxol-5-ol (**1kB**) was isolated by preparative TLC eluting with 10% EtOAc/hexane.

Yellow oil. IR (neat): 3530-3100 (br), 1682, 920, 711 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.82 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.43 (s, 1H), 7.24 (s, 1H), 7.12 (d, J = 7.9 Hz, 2H), 6.82 (d, J = 7.9 Hz, 2H), 6.10 (d, J = 13.8 Hz, 1H), 5.92 (d, J = 13.8 Hz, 1H), 3.76 (s, 3H), 2.57 (s, 3H), 1.81 (br-s, 1H), 1.60 (s, 3H). ^{13}C NMR (100 M Hz, CDCl_3): δ 197.1, 142.0, 139.4, 138.2, 137.7, 136.4, 135.2, 132.3, 131.0, 130.6, 129.3, 129.2, 126.3, 125.4, 121.2, 121.0, 115.4, 91.3, 81.2, 55.3, 27.4, 21.1. LRMS (EI) m/z (relative intensity) 414 $[\text{M}]^+$ (23), 386 (100). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{26}\text{H}_{22}\text{O}_5$, 414.1467; found, 414.1488.

3-(4-Methylphenyl)-1,2-diphenyl-1*H*-inden-1-ol (**1IA**) was isolated by preparative TLC eluting with 5% EtOAc/hexane.

Pale yellow amorphous mass. IR (neat): 3560-3130 (br), 1225, 776, 715 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.43-7.12 (m, 16 H), 7.08 (d, J = 7.8 Hz, 2H), 2.35 (s, 3H), 1.92

(br-s, 1H). ^{13}C NMR (100 M Hz, CDCl_3): δ 143.2, 138.7, 138.2, 137.6, 136.4, 133.1, 132.3, 131.1, 130.8, 130.5, 130.0, 129.9, 129.3, 128.5, 127.3, 127.2, 127.1, 126.8, 126.2, 113.9, 92.0, 21.5. LRMS (EI) m/z (relative intensity) 374 $[\text{M}]^+$ (27), 359 (100), 91 (89). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{26}\text{H}_{22}\text{O}$, 374.1671; found, 374.1664.

1-[*N*-(4-Methylbenzenesulfonyl)amino]-3-(4-methylphenyl)-2-phenyl-1*H*-indene (**2oA**) was isolated by preparative TLC eluting with 20% EtOAc/hexane.

Yellow amorphous mass. IR (neat): 1341, 1221, 1142, 796, 711 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.73 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 7.8 Hz, 1H), 7.34-7.15 (m, 12 H), 7.10 (d, J = 7.9 Hz, 2H), 5.01 (d, J = 3.6 Hz, 1H), 4.52 (d, J = 3.6 Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 M Hz, CDCl_3): δ 143.4, 139.2, 138.2, 136.8, 136.4, 133.1, 132.5, 131.1, 130.8, 130.5, 129.9, 129.3, 128.5, 128.2, 127.3, 127.2, 127.1, 126.8, 126.2, 113.9, 50.4, 21.5, 21.3. LRMS (EI) m/z (relative intensity) 451 $[\text{M}]^+$ (89), 281 (100), 91 (51). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{29}\text{H}_{25}\text{NO}_2\text{S}$, 451.1606; found, 451.1623.

Chemoselective Hydrogenation of **1iA**

A solution of **1iA** (26.0 mg, 99.2 μmol) and tris(triphenylphosphine)rhodium chloride (13.8 mg, 14.9 μmol) in toluene (1 ml) was stirred at room temperature for 6 h under hydrogen atmosphere. The resulting mixture was concentrated *in vacuo* and the residue was purified by preparative TLC eluting with 10% EtOAc/hexane to yield 23.3 mg (0.0883 mmol, 89%) of 3-(4-methylphenyl)-2-propyl-1*H*-inden-1-ol (**15**) as a yellow oil.

IR (neat): 3530-3150 (br), 1336, 1213, 745, 731 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.48-7.12 (m, 6 H), 7.02 (d, J = 7.5 Hz, 2H), 5.24 (s, 1H), 2.34 (s, 3H), 1.96 (t, J = 7.6 Hz, 2H), 1.73 (br-s, 1H), 1.35 (tq, J = 7.6, 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 M Hz, CDCl_3): δ 143.1, 138.1, 136.3, 130.0, 129.6, 128.2, 128.1, 128.0, 127.8, 127.0, 126.3, 115.4, 77.4, 29.6, 21.5, 21.2, 13.9. LRMS (EI) m/z (relative intensity) 264 $[\text{M}]^+$ (100), 91 (54). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{19}\text{H}_{20}\text{O}$, 264.1514; found, 264.1501.

General Procedure for the Pd⁰-Catalyzed Synthesis of 1*H*-Indenamines 17 and 18.

General procedure for the *p*-methylphenylative cyclization of **5c** with dibenzylamine (**6A**) (Table 2, entries 1-4):

To a test tube containing **5c** (1 eq., see Table 2S-1), *p*-methylphenylboronic acid (**2c**) (2 eq.), dibenzylamine (**16A**) (6 eq.), (η^3 -allyl)(η^5 -cyclopentadienyl)Pd (5 mol%), and PCy₃ (15 mol%) was added anhydrous solvent (MeOH, toluene, THF, or DMF, 0.24 M) under argon. The resulting mixture was sealed with a screw cap and agitated at 80 °C for the time described in Table 2. The mixture was cooled down to room temperature, and then partitioned between EtOAc and saturated aqueous Na₂CO₃. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with water and brine, dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by preparative TLC eluting with 5% EtOAc/hexane to yield **18cAA**.

Table 2S-1

solvent	5c (mg, mmol)	6A (mg, mmol)	16A (μ l, mmol)	[Pd] (mg, μ mol)	PCy ₃ (mg, μ mol)	18cAA (mg, mmol, %)
MeOH	24.5, 0.119	32.7, 0.240	138, 0.720	1.3, 6.1	5.6, 20	18.3, 0.0381, 32
toluene	24.4, 0.118	32.5, 0.238	138, 0.720	1.2, 5.6	5.6, 20	34.4, 0.0708, 60
THF	24.5, 0.119	35.6, 0.239	138, 0.720	1.4, 6.6	5.4, 19	32.1, 0.0666, 56
DMF	24.7, 0.120	32.5, 0.238	138, 0.720	1.3, 6.1	5.8, 20	49.3, 0.103, 86

General procedure for the arylative cyclization of **5c-f-I** with secondary amines **16A-F** (Table 2, entries 5-11, 13):

To a test tube containing **5c-f-I** (1 eq., see Table 2S-2), arylboronic acid **6A-B-D** (1.5 eq.), secondary amine **16A-F** (2 eq.), (η^3 -allyl)(η^5 -cyclopentadienyl)Pd (5 mol%), and PCy₃ (15 mol%) was added anhydrous DMF (0.24 M) under argon. The resulting mixture was sealed with a screw cap and agitated at 80 °C for the time described in Table 2. The mixture was cooled down to room temperature, and then PS-DEAMTM (1.8 mmol/g, 3 eq., X g) and THF (10 x X mL) were added to remove an excess of **6A-B-D**. The mixture was agitated at room temperature for 2 h. The mixture was filtered and thoroughly washed with CHCl₃. The filtrate was concentrated *in vacuo* under azeotropic distillation with toluene and the residue was purified by preparative TLC.

Table 2S-2

5 (mg, mmol)	6 (mg, mmol)	16 (μ l, mmol)	[Pd] (mg, μ mol)	PCy ₃ (mg, μ mol)	18 (mg, mmol, %)
5c ; 24.5, 0.119	6A ; 24.7, 0.182	16B ; 24.8, 0.240	1.4, 6.6	5.8, 21	18cAB ; 37.8, 0.106, 89
5c ; 24.6, 0.119	6A ; 24.8, 0.182	16C ; 20.0, 0.240	1.3, 6.1	5.6, 20	18cAC ; 23.6, 0.0666, 56
5c ; 24.5, 0.119	6A ; 24.6, 0.181	16D ; 21.0, 0.240	1.4, 6.6	5.7, 20	18cAD ; 44.1, 0.119, 100
5c ; 24.5, 0.119	6A ; 24.5, 0.180	16E ; 33.6, 0.240	1.4, 6.6	5.7, 20	18cAE ; 0, 0, 0
5c ; 24.7, 0.120	6A ; 24.3, 0.179	16F ; 26.0, 0.240	1.2, 5.6	5.8, 21	18cAF ; 0, 0, 0
5f ; 29.8, 0.120	6B ; 27.8, 0.183	16B ; 24.8, 0.240	1.3, 6.1	5.8, 21	18fBB ; 46.4, 0.113, 94
5c ; 247, 0.120	6D ; 29.6, 0.181	16B ; 24.8, 0.240	1.5, 7.1	5.5, 20	18cDB ; 40.3, 0.105, 88
5I ; 33.6, 0.119	6A ; 24.6, 0.181	16B ; 24.8, 0.240	1.2, 5.6	5.7, 20	18IAB ; 0, 0, 0

Procedure for the ethylative cyclization of **5c** with diethylamine (**16B**) (Table 2, entry 12):

To a test tube containing **5c** (24.8 mg, 0.120 mmol), diethylamine (**16B**) (24.8 μ l, 0.240 mmol), (η^3 -allyl)(η^5 -cyclopentadienyl)Pd (1.4 mg, 6.6 μ mol), and PCy₃ (5.8 mg, 21 μ mol) were added anhydrous DMF (0.26 mL) and a 1.0 M solution of triethylborane (**6F**) in THF (0.24 mL, 0.24 mmol) under argon. The resulting mixture was sealed with a screw cap and agitated at 80 °C for 1 h. The mixture was concentrated *in vacuo* under azeotropic distillation with toluene and the residue was purified by preparative TLC eluting with Et₃N-EtOAc-hexane (5:10:85) to yield with 25.5 mg (0.0876 mmol) of **17cFB** (73%) as yellow oil.

3-Dibenzylamino-1-(4-methylphenyl)-2-phenyl-1*H*-indene (**18cAA**):

Pale yellow amorphous mass. IR (neat): 1362, 1175, 930, 782, 711 cm⁻¹. ¹H NMR (400 M Hz, CDCl₃): δ 7.60 (d, *J*= 7.2 Hz, 1H), 7.42 (d, *J*= 7.7 Hz, 2H), 7.39-7.09 (m, 20H), 4.84 (s, 1H), 4.39-4.03 (m, 4H), 2.35 (s, 3H). ¹³C NMR (100 M Hz, CDCl₃): δ 141.2, 140.1, 140.0, 140.0, 136.4, 134.9, 134.9, 134.3, 134.1, 129.5, 128.4, 128.4, 128.2, 128.1, 128.1, 128.0, 127.4, 126.4, 126.1, 125.7, 57.8, 43.7, 21.0. LRMS (EI) *m/z* (relative

intensity) 477 [M]⁺ (51), 281 (65), 91 (100). HRMS (EI, [M]⁺): calcd for C₃₆H₃₁N, 477.2456; found, 477.2432.

3-Diethylamino-1-(4-methylphenyl)-2-phenyl-1*H*-indene (**18cAB**) was isolated by preparative TLC eluting with Et₃N-EtOAc-hexane (5:10:85).

Colorless oil. IR (neat): 1332, 1156, 910, 770, 716 cm⁻¹. ¹H NMR (400 M Hz, CDCl₃): δ 7.58 (d, *J* = 7.0 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.40-7.11 (m, 10H), 4.85 (s, 1H), 3.31-3.10 (m, 4H), 2.34 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (100 M Hz, CDCl₃): δ 141.5, 140.3, 140.3, 135.2, 134.8, 134.7, 134.6, 129.5, 128.5, 128.1, 128.1, 128.0, 127.5, 126.8, 126.1, 125.8, 44.2, 43.6, 21.0, 14.3. LRMS (EI) *m/z* (relative intensity) 353 [M]⁺ (100), 281 (86), 91 (56). HRMS (EI, [M]⁺): calcd for C₂₆H₂₇N, 353.2143; found, 353.2164.

1-(4-Methylphenyl)-2-phenyl-3-pyrrolidino-1*H*-indene (**18cAC**) was isolated by preparative TLC eluting with Et₃N-EtOAc-hexane (5:10:85).

Colorless oil. IR (neat): 1352, 1171, 938, 771, 709 cm⁻¹. ¹H NMR (400 M Hz, CDCl₃): δ 7.58 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.40-7.10 (m, 10H), 4.85 (s, 1H), 3.45-3.32 (m, 4H), 2.33 (s, 3H), 1.42-1.23 (m, 4H). ¹³C NMR (100 M Hz, CDCl₃): δ 142.4, 140.8, 140.3, 135.1, 134.7, 134.2, 134.0, 130.8, 128.9, 128.6, 128.5, 128.0, 127.2, 126.8, 126.4, 125.4, 45.6, 43.6, 25.5, 21.0. LRMS (EI) *m/z* (relative intensity) 351 [M]⁺ (80), 281 (100), 91 (49). HRMS (EI, [M]⁺): calcd for C₂₆H₂₅N, 351.1987; found, 351.2003.

1-(4-Methylphenyl)-3-morpholino-2-phenyl-1*H*-indene (**18cAD**) was isolated by preparative TLC eluting with Et₃N-EtOAc-hexane (5:10:85).

Yellow oil. IR (neat): 1312, 1110, 902, 793, 748 cm⁻¹. ¹H NMR (400 M Hz, CDCl₃): δ 7.52 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.42-7.10 (m, 10H), 4.82 (s, 1H), 3.83-3.66 (m, 4H), 3.51-3.30 (m, 4H), 2.33 (s, 3H). ¹³C NMR (100 M Hz, CDCl₃): δ 141.6, 140.2, 138.4, 136.7, 135.1, 134.9, 134.3, 129.5, 128.3, 128.1, 128.0, 127.5, 127.1, 126.9, 126.7, 125.8, 78.2, 59.0, 43.6, 21.0. LRMS (EI) *m/z* (relative intensity) 367 [M]⁺ (100), 281 (92), 91 (23). HRMS (EI, [M]⁺): calcd for C₂₆H₂₅NO, 367.1936; found, 367.1910.

2-(4-Acetylphenyl)-3-diethylamino-1-(4-methoxyphenyl)-1*H*-indene (**18fBB**) was isolated by preparative TLC eluting with Et₃N-EtOAc-hexane (5:20:75).

Colorless oil. IR (neat): 1643, 1489, 1345, 917, 759 cm⁻¹. ¹H NMR (400 M Hz, CDCl₃):

δ 8.19 (d, J = 7.5 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.43 (d, J = 7.2 Hz, 1H), 7.34-7.26 (m, 2H), 7.23 (d, J = 7.3 Hz, 1H), 7.12 (d, J = 7.6 Hz, 2H), 6.87 (d, J = 7.6 Hz, 2H), 4.83 (s, 1H), 3.79 (s, 3H), 3.19-2.94 (m, 4H), 2.55 (s, 3H), 2.35 (s, 3H), 1.12 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 M Hz, CDCl_3): δ 197.3, 141.9, 140.9, 140.5, 135.4, 134.1, 134.0, 133.9, 133.4, 133.2, 131.5, 129.9, 128.1, 127.7, 126.5, 126.2, 125.2, 45.2, 44.8, 43.2, 23.1, 14.3. LRMS (EI) m/z (relative intensity) 411 $[\text{M}]^+$ (100), 339 (21). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{28}\text{H}_{29}\text{NO}_2$, 411.2198; found, 411.2232.

1-(4-Acetylphenyl)-3-diethylamino-2-phenyl-1*H*-indene (**18cDB**) was isolated by preparative TLC eluting with Et_3N - EtOAc -hexane (5:20:75).

Colorless oil. IR (neat): 1684, 1321, 1141, 910, 771 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 8.12 (d, J = 7.4 Hz, 2H), 7.57 (d, J = 7.4 Hz, 2H), 7.53 (d, J = 7.0 Hz, 1H), 7.43 (d, J = 7.6 Hz, 2H), 7.30-7.11 (m, 6H), 4.86 (s, 1H), 3.37-3.16 (m, 4H), 2.56 (s, 3H), 1.12 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 M Hz, CDCl_3): δ 196.5, 144.5, 143.4, 142.8, 136.5, 134.9, 134.8, 134.6, 130.5, 128.9, 128.2, 128.1, 127.2, 127.0, 126.8, 126.4, 125.1, 44.9, 43.2, 23.6, 14.0. LRMS (EI) m/z (relative intensity) 381 $[\text{M}]^+$ (100), 338 (50), 309 (52). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{27}\text{H}_{27}\text{NO}$, 381.2093; found, 381.2072.

3-Ethyl-1-diethylamino-2-phenyl-1*H*-indene (**17cFB**): IR (neat): 2966, 1459, 1378, 1210, 1069, 760, 735, 695 cm^{-1} . ^1H NMR (400 M Hz, CDCl_3): δ 7.54 (d, J = 7.3 Hz, 1H), 7.38-7.25 (m, 6H), 7.17 (ddd, J = 7.3, 7.0, 1.7 Hz, 1H), 4.90 (s, 1H), 2.60 (q, J = 7.6 Hz, 2H), 2.46 (q, J = 7.1 Hz, 4H), 1.24 (t, J = 7.6 Hz, 3H), 1.05 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 M Hz, CDCl_3): δ 145.1, 144.3, 144.0, 140.8, 137.3, 128.9, 127.7, 127.1, 126.4, 124.5, 124.0, 119.3, 68.7, 44.9, 19.2, 14.7, 14.0. LRMS (EI) m/z (relative intensity) 291 $[\text{M}]^+$ (63), 276 (27), 262 (100), 219 (74), 204 (36). HRMS (EI, $[\text{M}]^+$): calcd for $\text{C}_{21}\text{H}_{25}\text{N}$, 291.1987; found, 291.1974.

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1dA

1hA

1cE

15

18cAA

18cDB

17cFB